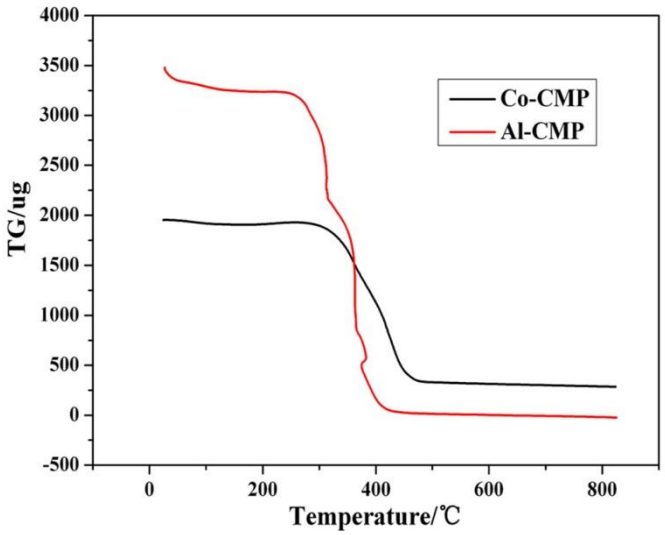
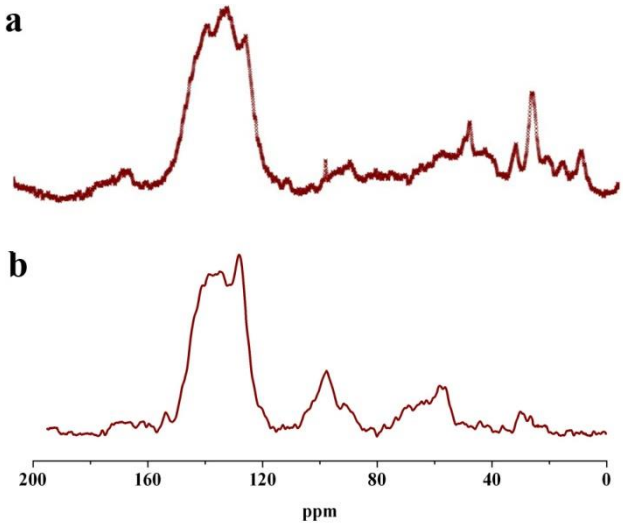
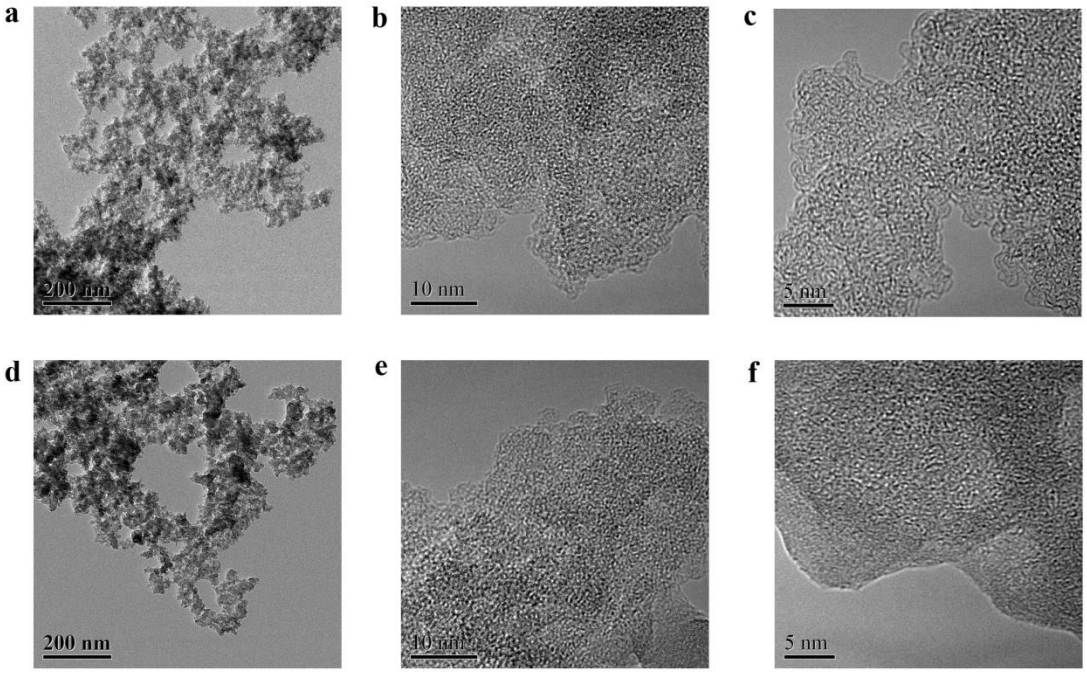


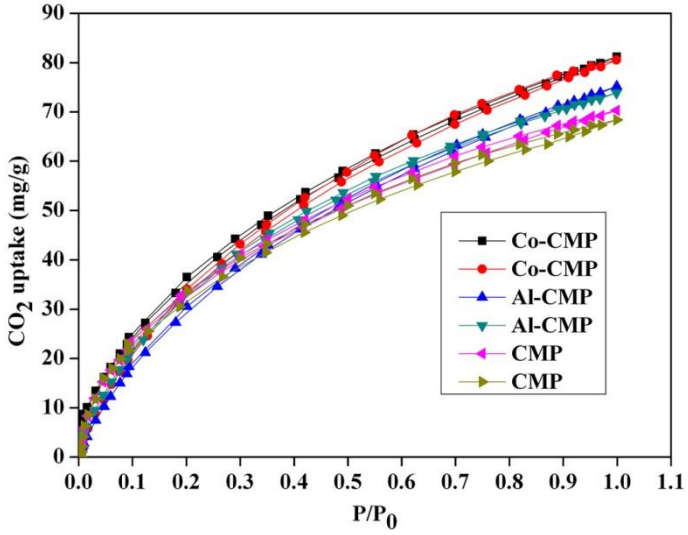
Supplementary Figure S1 | Thermogravimetric analysis of Co-CMP and Al-CMP. The samples were heated at a rate of 20°C /min up to 1000°C under a nitrogen atmosphere. Co-CMP and Al-CMP were found to possess good thermal stability and a high decomposition temperature of approximately 300°C in a nitrogen atmosphere.



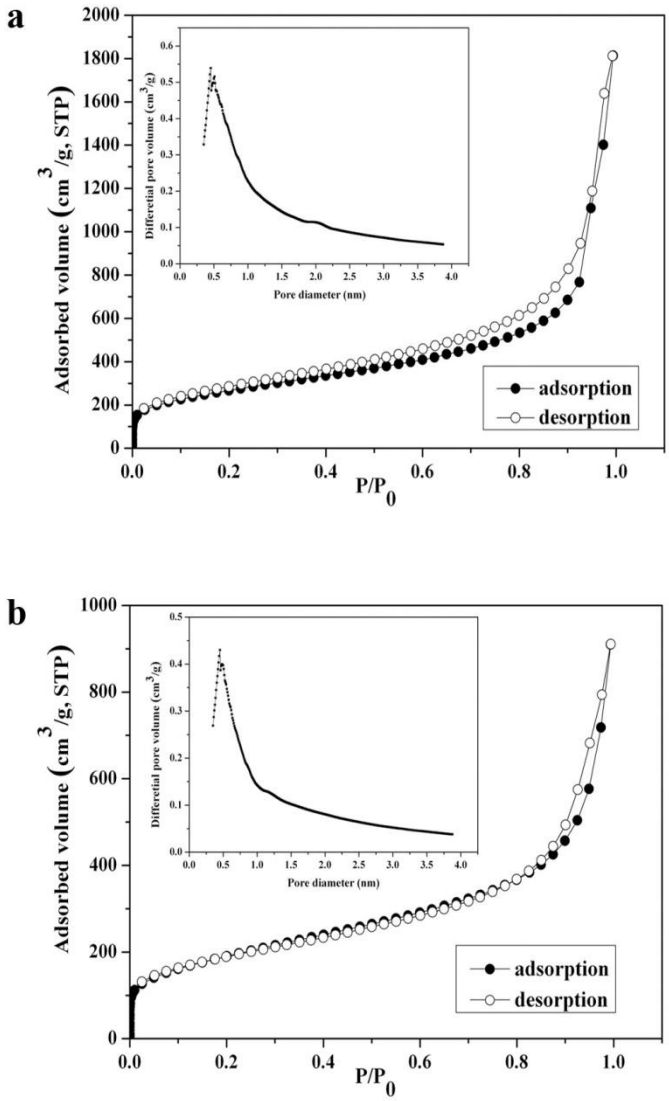
Supplementary Figure S2 | Solid-state ^{1}H-^{13}C CP/MAS NMR spectrum. (**a**) Al-CMP. (**b**) Co-CMP.



Supplementary Figure S3 | Morphological structures of Co-CMP and Al-CMP. (**a**) Transmission electron microscope (TEM) image of Co-CMP. (**b**) (**c**) High-resolution transmission electron microscope (HR-TEM) images of Co-CMP at different magnifications. (**d**) Transmission electron microscope (TEM) image of Al-CMP. (**e**) (**f**) High-resolution transmission electron microscope (TEM) images of Al-CMP at different magnifications. The polymers used for the transmission electron microscope examination were ground, suspended in ethanol or acetone, and deposited on a copper specimen grid supported by a porous carbon film.

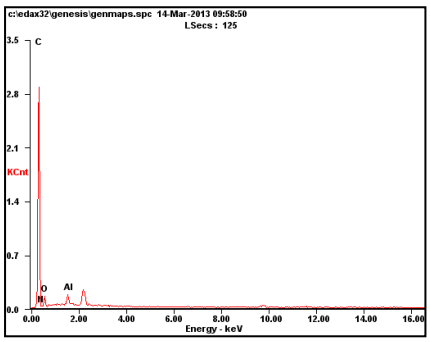


Supplementary Figure S4 | Gas uptake data for conjugated microprous polymers. CO_2 sorption and desorption isotherms for the polymers CMP (pink triangles and yellow triangles), Co-CMP (black squares and red circles) and Al-CMP (blue triangles and green triangles) at 298 K.

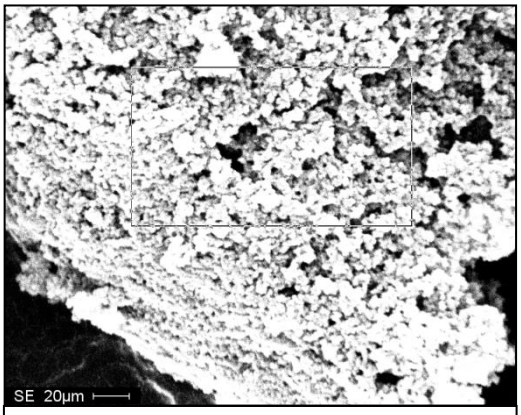


Supplementary Figure S5 | Gas uptake data for Co-CMP and Al-CMP. (**a**) N_2 adsorption and desorption isotherms for Co-CMP. (**b**) N_2 adsorption and desorption isotherms for Al-CMP. The solid and open circles represent adsorption and desorption points, respectively. The inset shows the size distributions calculated by NLDFT.

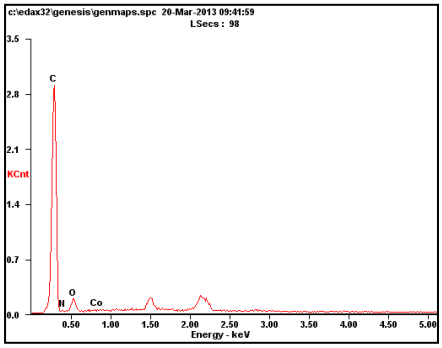
a



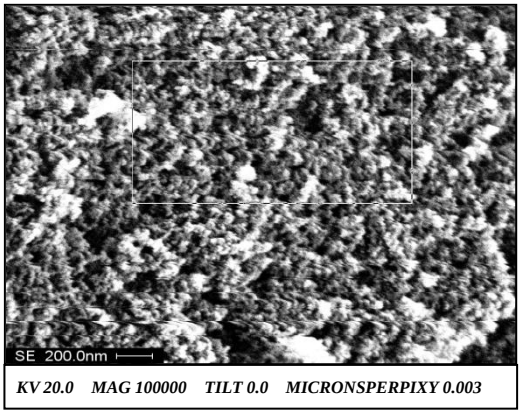
Element	*Wt%*	*At%*
CK	87.69	90.68
NK	01.82	01.61
OK	09.12	07.08
AlK	01.37	00.63
Matrix	Correction	ZAF



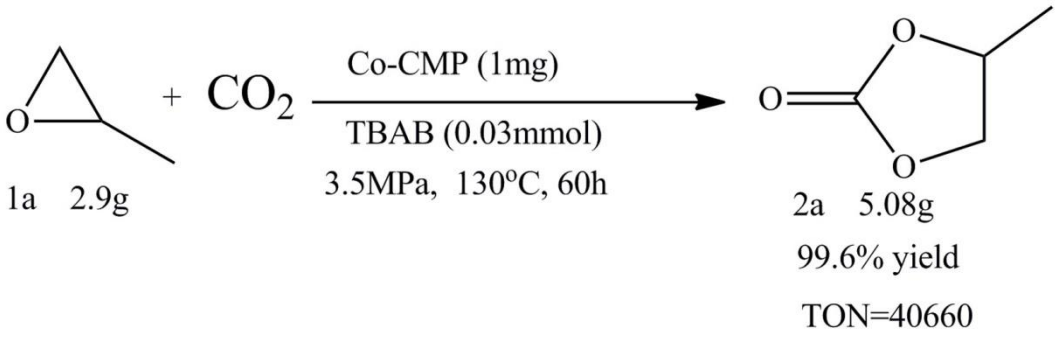
b



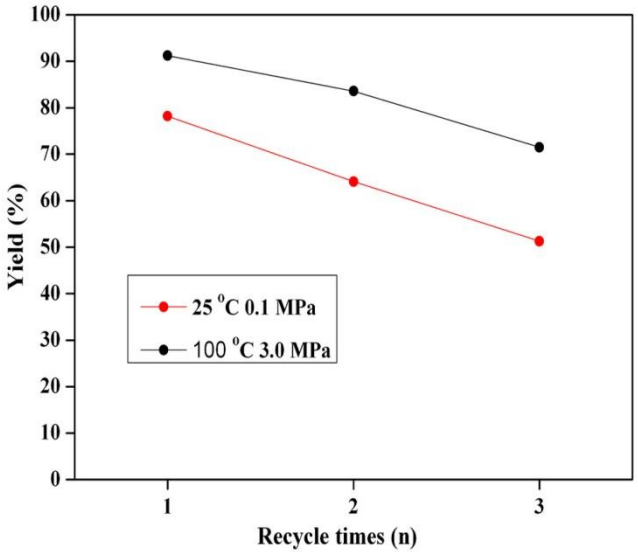
Element	*Wt%*	*At%*
CK	88.84	92.08
NK	01.23	01.09
OK	08.28	06.46
CoK	01.65	00.37
Matrix	Correction	ZAF



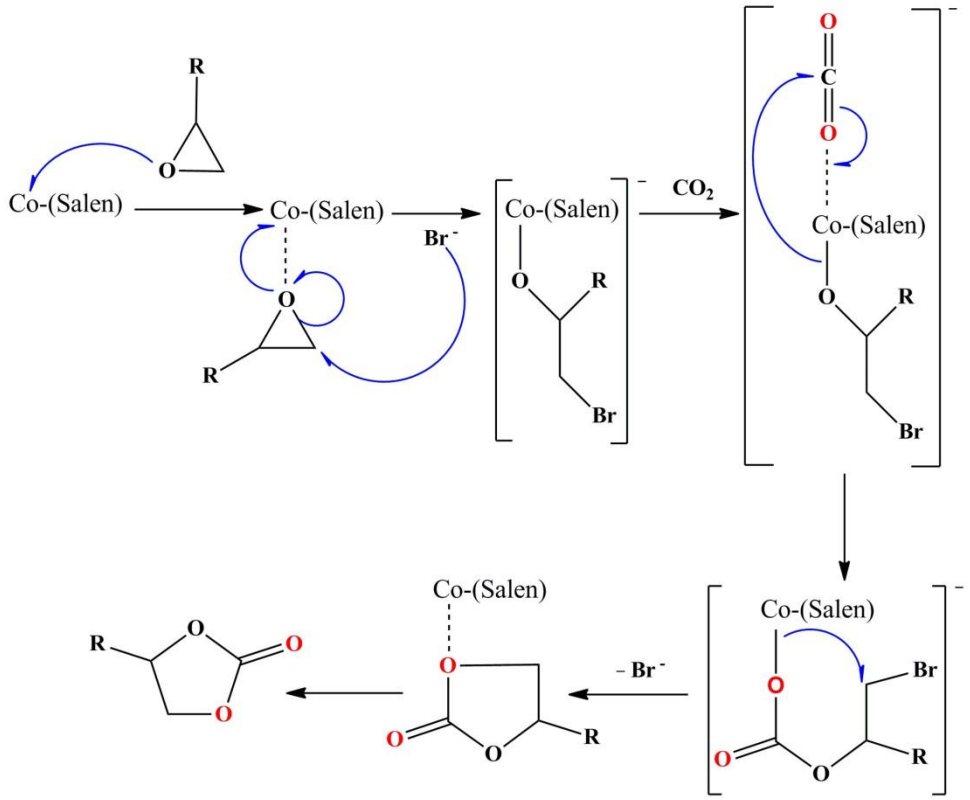
Supplementary Figure S6 | SEM-EDX analysis for conjugated microporous polymers. (**a**) Al-CMP. (**b**) Co-CMP. The squares in images were the areas for detection. The samples were deposited on a carbon holder and then were covered by a thin layer of Au.



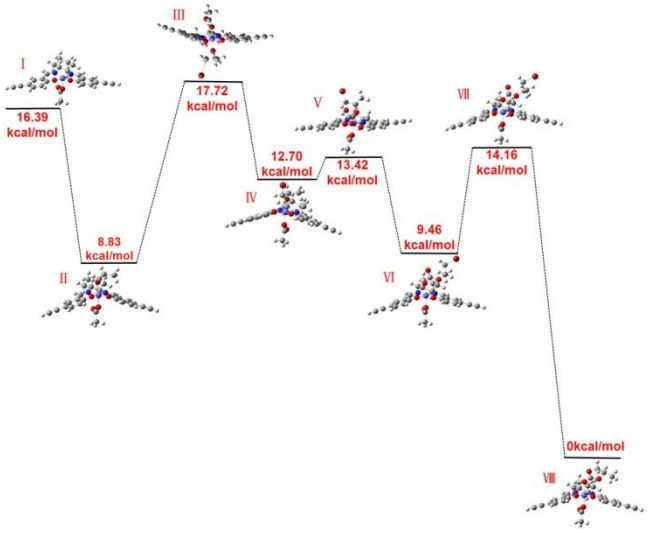
Supplementary Figure S7 | Conversion of CO_2 by Co-CMP under experimental conditions. The catalyst Co-CMP is applicable to large-scale synthesis, and the PO yields a TON value of 40660.



Supplementary Figure S8 | The recycling stability of Al-CMP at various experimental conditions. The recycling stability of Al-CMP at room temperature and atmospheric pressure (red circles). The recycling stability of Al-CMP under the higher CO_2 pressure and elevated temperature (black circles).

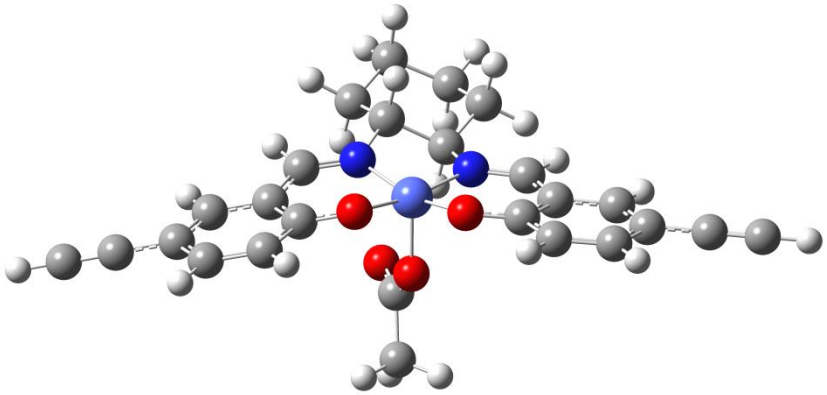


Supplementary Figure S9 | Mechanistic hypothesis for the catalytic reaction. Possible mechanism that could explain Co-CMP's catalytic activity.



Supplementary Figure S10 | Theoretical calculation for the catalytic reaction. Calculated energetics of the catalytic process, including intermediates and transition states with propylene carbonate as a solvent. The coordinates of geometries I-VIII are shown in Supplementary Table 1-8.

Supplementary Table S1 | Geometrical structure, energy and coordinates of intermediate I.

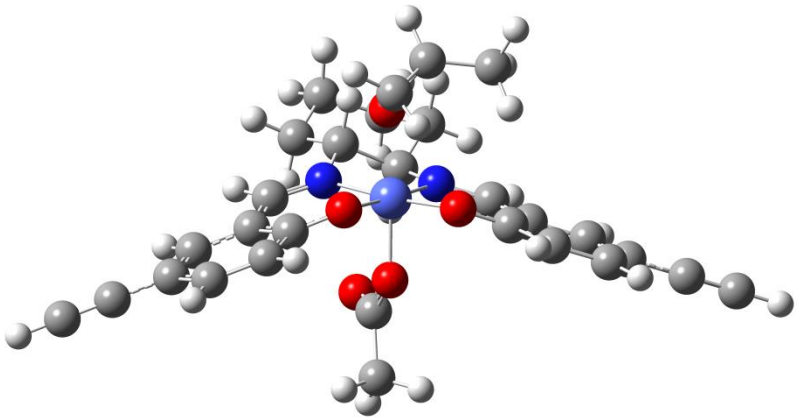


I E =-2797.235304 Hartree

C	1.43162000	3.64835500	-0.45749400
C	0.60908200	4.91785300	-0.74223600
C	-0.72900100	4.91855600	0.00881600
C	-1.55096000	3.64742200	-0.27258800
C	-0.71112600	2.40682800	0.05006100
C	0.59113100	2.40522000	-0.76568800
N	1.22550500	1.08695200	-0.55185500
N	-1.33897400	1.08493500	-0.18056200
O	1.18405700	-1.58793600	-0.90483300
C	2.46154800	-1.54508600	-0.66997900
C	3.18076400	-0.32813300	-0.42780000
C	2.51147900	0.93578700	-0.49249400
C	-2.62131200	0.91509700	-0.06627700
C	-3.31272400	-0.33077600	-0.18884800
C	-2.61875700	-1.53429300	-0.54356100
O	-1.34108900	-1.59063800	-0.76180300
C	3.21255400	-2.75255400	-0.71185700
C	4.57266500	-2.75531500	-0.50074700
C	5.28980400	-1.55188500	-0.24716700
C	4.57595500	-0.35784600	-0.22667300
C	-4.71108200	-0.35058800	0.00097600
C	-5.45181300	-1.51800900	-0.14625200
C	-4.75779100	-2.70801000	-0.50798800
C	-3.39604700	-2.71612600	-0.70316600
O	0.06603800	-0.73621300	1.39760300
H	1.74234700	3.61798300	0.59485500
H	2.34020400	3.66676500	-1.07066300
H	0.42068100	4.98943200	-1.82308900

H	1.19566300	5.80310100	-0.47010100
H	-1.31547400	5.80372800	-0.26430900
H	-0.53981000	4.98821100	1.08878900
H	-1.86678100	3.62194100	-1.32564000
H	-2.46154400	3.67386200	0.33646700
H	-0.42132400	2.41752700	1.10647300
H	0.31040200	2.43255300	-1.83150500
H	3.14697700	1.82084100	-0.51694600
H	-3.24562900	1.78768200	0.13029400
H	5.12285000	-3.69153200	-0.52487600
H	5.10513400	0.57531800	-0.05144000
H	-5.22079900	0.57168400	0.26826300
H	-5.32779800	-3.62490500	-0.62695300
H	-2.87048600	-3.62486700	-0.97755300
H	2.66972600	-3.67178800	-0.90601600
C	0.50799700	0.00774700	2.38669700
C	0.53061600	-0.78417000	3.69099500
H	1.27445000	-1.58479100	3.62069700
H	0.78597800	-0.11778100	4.51687000
H	-0.44007400	-1.25580300	3.87022200
O	0.87623100	1.17714400	2.33315700
Co	-0.05260100	-0.30195600	-0.38384200
C	6.70014100	-1.57579900	-0.03085600
C	7.89667400	-1.60629700	0.15075300
H	8.94991700	-1.63065600	0.31372100
C	-6.86475600	-1.52985900	0.05315300
C	-8.06376800	-1.55001200	0.21904000
H	-9.11936500	-1.56640500	0.36718400

Supplementary Table S2 | Geometrical structure, energy and coordinates of intermediate II.

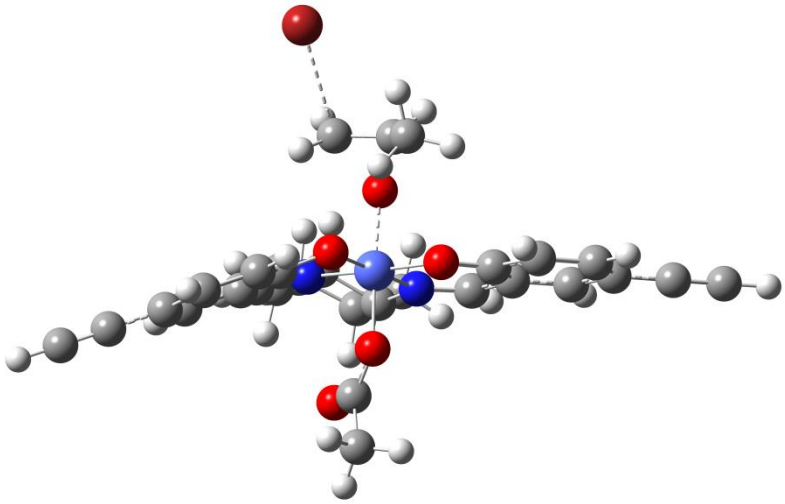


II E = -2990.239912 Hartree

C	-1.56264900	3.70922100	-0.43935900
C	-0.76488000	5.01659400	-0.26799900
C	0.64304000	4.92925600	-0.87773100
C	1.42690300	3.70943100	-0.35828600
C	0.60636400	2.43877900	-0.60933300
C	-0.74613900	2.53933100	0.11654900
N	-1.35290400	1.20195000	0.09744200
N	1.22458000	1.15741700	-0.19791700
O	-1.32701800	-1.35657800	1.06819500
C	-2.54966000	-1.41139600	0.63084300
C	-3.23643300	-0.30752600	0.02044300
C	-2.60673900	0.97819600	-0.10737300
C	2.43506400	0.86724100	-0.55259500
C	3.09762700	-0.38739000	-0.34073100
C	2.47092600	-1.46529700	0.37332600
O	1.28252700	-1.40297500	0.89060700
C	-3.29014700	-2.61355900	0.81102200
C	-4.60225500	-2.72059000	0.40705500
C	-5.28460100	-1.63154500	-0.20125000
C	-4.58258100	-0.44104600	-0.37248000
C	4.41249600	-0.53349100	-0.83026900
C	5.14327800	-1.70285600	-0.64453500
C	4.52197900	-2.76383900	0.07112300
C	3.24148100	-2.64834800	0.56326200
O	-0.16287400	-0.96320000	-1.23813400
H	-1.78326100	3.52844900	-1.49944700
H	-2.52077600	3.79981000	0.08630500
H	-0.68102000	5.24370700	0.80453700

H	-1.31898700	5.84819300	-0.71896700
H	1.20138000	5.84892900	-0.66552400
H	0.56085900	4.85684000	-1.97092100
H	1.63077400	3.81477000	0.71736800
H	2.39777700	3.66050200	-0.86429500
H	0.38963300	2.33428600	-1.67716000
H	-0.53646600	2.74290700	1.17775700
H	-3.25324800	1.81378500	-0.37933400
H	3.02156200	1.63294800	-1.06650700
H	-5.13754000	-3.65521100	0.54919700
H	-5.08636500	0.41061100	-0.82295400
H	4.86695600	0.29407700	-1.36953400
H	5.07875300	-3.68422800	0.22288400
H	2.77202900	-3.46569700	1.10149400
H	-2.77516400	-3.45060900	1.27168700
C	-0.43001100	-0.45786500	-2.41694700
C	-0.51117100	-1.55241300	-3.47846100
H	-1.36947300	-2.20058400	-3.27167900
H	-0.62325300	-1.10029800	-4.46580900
H	0.38462100	-2.18006700	-3.44898400
O	-0.61445400	0.72359800	-2.70357100
Co	-0.04277000	-0.13444100	0.42105200
C	-6.64561300	-1.75752600	-0.61205700
C	-7.80114900	-1.87410600	-0.95512800
H	-8.81681100	-1.97510000	-1.26219500
C	6.47135500	-1.83697400	-1.14972400
C	7.59942900	-1.95775400	-1.57296200
H	8.59034200	-2.06338600	-1.95132700
O	-0.04648900	0.56978400	2.37400100
C	0.88119700	0.76120800	3.49328700
C	-0.05558100	-0.37283400	3.47358900
H	0.31561000	-1.35466400	3.19690100
H	-0.96985900	-0.34787600	4.06087300
H	0.58190600	1.63708200	4.06949800
C	2.36147300	0.61829700	3.27351400
H	2.86217400	0.62423700	4.24934400
H	2.60502000	-0.31091100	2.75927300
H	2.75432600	1.45959900	2.69291500

Supplementary Table S3 | Geometrical structure, energy, imaginary frequency and coordinates of transition state III.



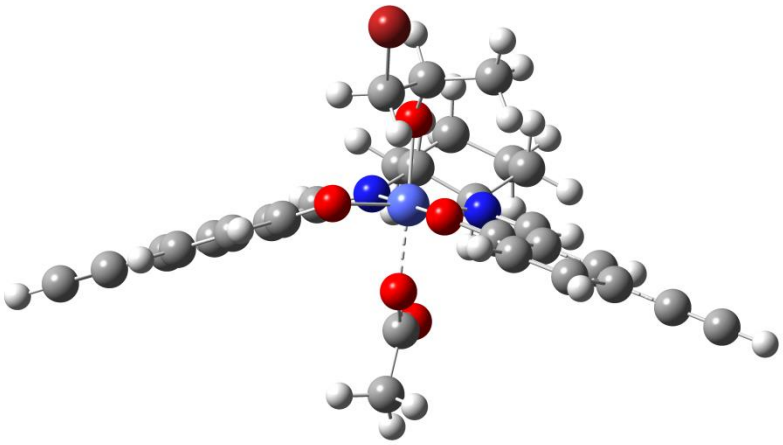
III E =-5564.559999 Hartree

Frequency= -378.0307 cm^{-1}

C	1.81954200	-2.79254500	2.81764200
C	1.03376400	-3.54539300	3.90506800
C	-0.18080000	-4.28357400	3.32524100
C	-1.09953700	-3.34308500	2.52488300
C	-0.29331000	-2.62490400	1.43701800
C	0.88289300	-1.84650000	2.06062100
N	1.46838200	-1.04147000	0.98184200
N	-1.02677700	-1.66822500	0.58494800
O	1.27270100	1.06742900	-0.76115000
C	2.54738300	0.91351500	-0.91131300
C	3.33357200	-0.05727200	-0.19925300
C	2.73592800	-0.91427000	0.78922000
C	-2.28100000	-1.81092600	0.31959800
C	-3.06059000	-0.97996200	-0.55528500
C	-2.48330900	0.13641600	-1.25618700
O	-1.25382500	0.50254200	-1.16795400
C	3.25004800	1.78474000	-1.79670000
C	4.61016200	1.68847200	-1.97838100
C	5.38778900	0.72099100	-1.28291100
C	4.72466700	-0.12476400	-0.39544700
C	-4.42442700	-1.28861200	-0.71865800
C	-5.26112300	-0.54669300	-1.54932400
C	-4.68848200	0.55634300	-2.24486200
C	-3.36092800	0.88250600	-2.10621800
O	0.57215100	-1.29356300	-1.66135700

H	2.26656900	-3.50263500	2.10884700
H	2.63841300	-2.23152500	3.28429200
H	0.69418800	-2.82642000	4.66448700
H	1.69664800	-4.25278000	4.41902100
H	-0.75195000	-4.76376800	4.12991700
H	0.16877200	-5.08809900	2.66297400
H	-1.56313200	-2.60353400	3.19349100
H	-1.91177800	-3.93370600	2.08526600
H	0.14998300	-3.35216000	0.74652700
H	0.46026000	-1.12103400	2.76946400
H	3.42498900	-1.47999300	1.41779800
H	-2.82303900	-2.63589800	0.78650500
H	5.11313600	2.36237800	-2.66682400
H	5.29844600	-0.86123300	0.16240900
H	-4.83697800	-2.13714100	-0.17700100
H	-5.32578300	1.14617500	-2.89854100
H	-2.92900800	1.72214900	-2.64158900
H	2.66323300	2.52737000	-2.32776000
C	1.10634400	-2.46645300	-1.82332900
C	1.39613900	-2.75251600	-3.29988200
H	2.13957800	-2.03946400	-3.67249800
H	1.77246800	-3.77132500	-3.41807300
H	0.48877300	-2.61490900	-3.89693100
O	1.38875100	-3.30628700	-0.96182900
Co	0.10871300	-0.28856100	-0.11677900
C	6.79734400	0.63020400	-1.48297700
C	7.99417200	0.55883900	-1.66162000
H	9.04711700	0.49744700	-1.81068100
C	-6.64029300	-0.87676500	-1.70157700
C	-7.81345200	-1.15074100	-1.83774700
H	-8.84480400	-1.39162600	-1.95173600
O	-0.44564800	0.76359900	1.43211900
C	-0.86305300	2.15605100	1.60146900
C	0.39552200	1.93008400	2.28685700
H	1.32065200	2.13350800	1.77023000
H	-1.74660500	2.19550300	2.24198700
C	-0.92776200	3.11027400	0.43715300
H	-0.84560600	4.11532000	0.86691400
H	-0.10129900	2.94294400	-0.25460300
H	-1.87149200	3.01473900	-0.10759300
H	0.42490800	1.60526000	3.31406400
Br	0.76929200	4.34829100	3.55004700

Supplementary Table S4 | Geometrical structure, energy and coordinates of intermediate IV.

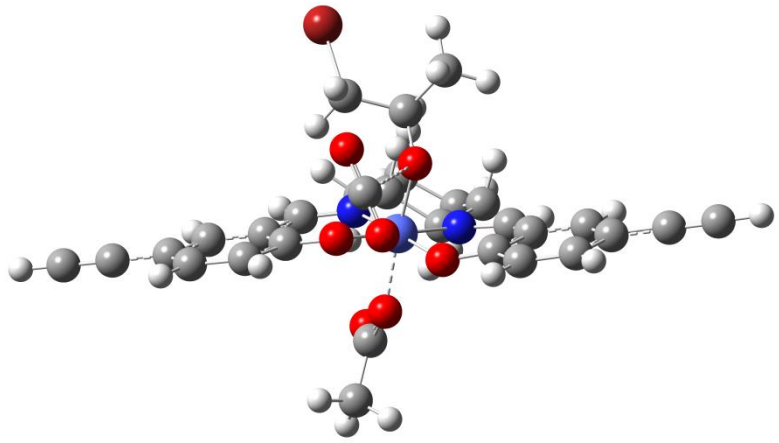


IV E = -5564.568003 Hartree

C	1.86427900	-2.76824700	2.81276000
C	1.09936700	-3.37327200	4.00431600
C	-0.23499500	-4.00469200	3.57696200
C	-1.10989700	-3.02349700	2.77548200
C	-0.31626700	-2.48689400	1.57765300
C	0.95793100	-1.78061000	2.07443600
N	1.51736900	-1.05299100	0.93500500
N	-1.02268900	-1.53763000	0.69310000
O	1.31166000	1.12372100	-0.75226500
C	2.56045400	0.90982500	-0.97514300
C	3.34207000	-0.12711500	-0.34750000
C	2.77030200	-0.98576500	0.65990000
C	-2.21512800	-1.78847700	0.27587900
C	-2.95608300	-1.01058000	-0.68247200
C	-2.42881800	0.20629100	-1.24510600
O	-1.28269800	0.71061400	-0.95239900
C	3.26008300	1.77606300	-1.87472200
C	4.59949400	1.62174300	-2.14387800
C	5.36762600	0.59381200	-1.52905700
C	4.71145500	-0.25158800	-0.63262600
C	-4.23729800	-1.46005500	-1.04754800
C	-5.04101500	-0.76916000	-1.95418300
C	-4.52178500	0.43534200	-2.50700200
C	-3.27502200	0.90259100	-2.16591000
O	0.40569200	-1.17194500	-1.63281500
H	2.18667700	-3.56128300	2.12398800
H	2.76752900	-2.26563800	3.18049700
H	0.90192900	-2.57899000	4.73848800

H	1.72477700	-4.11985300	4.51092100
H	-0.78285900	-4.35973300	4.45968400
H	-0.03318800	-4.88903400	2.95549800
H	-1.42490100	-2.18346800	3.41020000
H	-2.02140100	-3.53809400	2.44889100
H	0.00329400	-3.30890500	0.92686600
H	0.64130600	-0.98572700	2.76227600
H	3.47291400	-1.59697600	1.23060200
H	-2.72974100	-2.67334600	0.66111600
H	5.09349500	2.29422600	-2.84090000
H	5.28012100	-1.03485400	-0.13563500
H	-4.61337200	-2.38035500	-0.60541700
H	-5.13354000	0.98941400	-3.21446600
H	-2.88469100	1.82177600	-2.59177700
H	2.67951700	2.56215400	-2.34777000
C	0.76274300	-2.39725100	-1.84607800
C	0.94034200	-2.69207000	-3.34120500
H	1.75934800	-2.08338300	-3.74063700
H	1.16213100	-3.75113100	-3.49569700
H	0.03460300	-2.41432700	-3.89058300
O	0.97007300	-3.29270900	-1.01627400
Co	0.11929900	-0.16674600	-0.00320400
C	6.75675000	0.44275900	-1.81213300
C	7.93870700	0.32268200	-2.05757300
H	8.97528300	0.20958800	-2.27429500
C	-6.33635500	-1.24556800	-2.31240900
C	-7.43986100	-1.64254200	-2.62191600
H	-8.40798400	-1.99504700	-2.89178800
O	-0.06908400	0.82553700	1.61211900
C	-0.77836700	1.99833800	1.86187700
C	-0.40641900	3.07029800	0.82817100
H	-0.83862200	2.88498900	-0.15133900
H	-0.41836500	2.37473600	2.83817600
C	-2.29731300	1.80079500	2.00098700
H	-2.78793100	2.72476400	2.32793600
H	-2.74585800	1.48889300	1.05471600
H	-2.48864400	1.01935300	2.74567000
H	0.67147500	3.18458500	0.75300900
Br	-1.06954700	4.90290000	1.35893800

Supplementary Table S5 | Geometrical structure, energy, imaginary frequency and coordinates of transition state V.



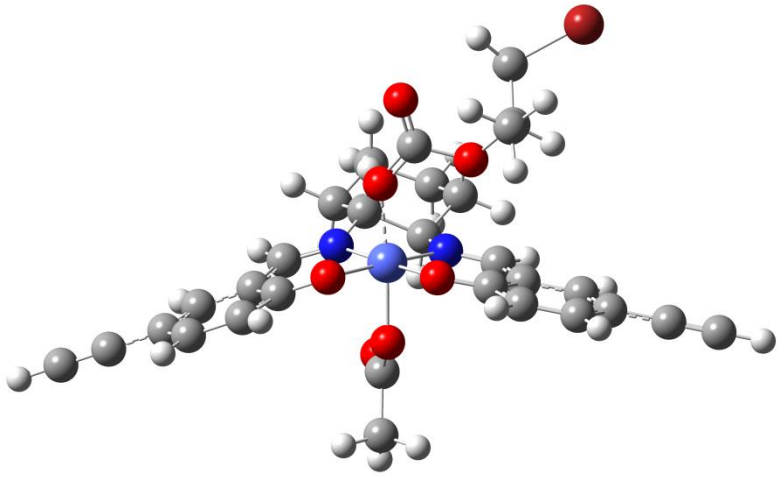
V E = -5753.184509 Hartree

Frequency= -15.6315 cm^{-1}

C	1.30535900	2.82081400	2.09745100
C	0.45719900	4.02407500	2.54761500
C	-0.80641500	3.59787200	3.30807000
C	-1.64993200	2.58943500	2.50690800
C	-0.78008400	1.39102100	2.11600000
C	0.43484600	1.85046200	1.29313900
N	1.08820100	0.63097000	0.77464700
N	-1.41844000	0.30584900	1.34980800
O	1.09370000	-1.80048500	-0.51426700
C	2.37611000	-1.66363100	-0.53247200
C	3.07162200	-0.51590000	-0.02152300
C	2.36076000	0.59386400	0.54429400
C	-2.70186700	0.12148100	1.33317400
C	-3.38117000	-0.97059500	0.71476900
C	-2.65722500	-2.03599900	0.07670100
O	-1.37541800	-2.11819600	0.02612900
C	3.16819300	-2.69176600	-1.12876400
C	4.53720900	-2.59491100	-1.19736500
C	5.23121200	-1.46172000	-0.68329200
C	4.47522400	-0.44095200	-0.11302400
C	-4.79088000	-1.00487400	0.77042800
C	-5.52245100	-2.04627800	0.21372900
C	-4.79981600	-3.09284700	-0.43725500
C	-3.43090300	-3.08917500	-0.50395700
O	0.28287700	-1.80531000	1.98990200
H	1.73254900	2.29248100	2.95866300

H	2.12800300	3.19188500	1.47689100
H	0.16732600	4.60318100	1.65927200
H	1.06503900	4.69222300	3.17085600
H	-1.41547300	4.47733200	3.55377700
H	-0.51809300	3.13773900	4.26376500
H	-2.06007500	3.06626400	1.60496500
H	-2.50142100	2.26921400	3.11953000
H	-0.38120300	0.92442400	3.02333200
H	0.06566400	2.39198000	0.41312100
H	2.96043600	1.47000700	0.78451600
H	-3.33549200	0.85074800	1.84093400
H	5.11482300	-3.39420900	-1.65400700
H	4.97956400	0.44181400	0.27228100
H	-5.31655200	-0.19209500	1.26694500
H	-5.36215100	-3.90263300	-0.89446400
H	-2.88396900	-3.86811300	-1.02240200
H	2.63968400	-3.55068100	-1.52905900
C	0.90468800	-1.50088200	3.09726300
C	1.16721000	-2.75862700	3.92927000
H	1.98894600	-3.32287600	3.47370500
H	1.44696400	-2.47454500	4.94630100
H	0.28917300	-3.41013900	3.93926500
O	1.27917200	-0.39662700	3.48983100
Co	-0.13522600	-0.80151400	0.48855900
C	6.65349500	-1.37818600	-0.75903900
C	7.86238200	-1.31882900	-0.82462600
H	8.92394700	-1.25678200	-0.88736200
C	-6.94673900	-2.07455600	0.28540600
C	-8.15713800	-2.11230800	0.34746200
H	-9.22115400	-2.13528900	0.38989900
O	-0.67429349	0.36835192	-1.33180360
C	-0.21586049	1.66886292	-1.66148260
C	1.25553351	1.66496992	-2.11644160
H	-0.27414749	2.22854192	-0.72491560
H	1.80728851	0.80982392	-1.74105060
H	1.40967751	1.78982992	-3.18178060
C	-0.69721549	-0.61185408	-2.52989660
O	-1.47866949	-1.52856908	-2.34100660
O	0.07286451	-0.26075208	-3.43643960
Br	2.22613851	3.27510492	-1.30120560
C	-1.12192649	2.39051892	-2.66607560
H	-2.14680949	2.43084492	-2.28163460
H	-0.76368749	3.41681792	-2.81921460
H	-1.11961549	1.86112792	-3.62108060

Supplementary Table S6 | Geometrical structure, energy and coordinates of intermediate VI.

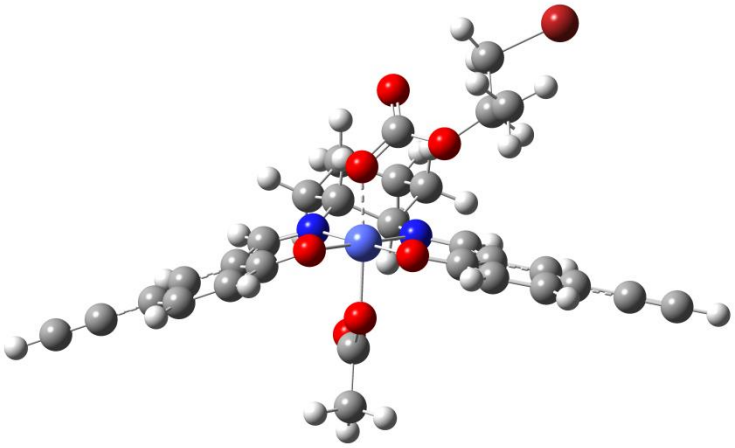


VI E = -5753.190827 Hartree

C	-2.00514100	-2.53072000	2.79615200
C	-0.98482000	-3.24951100	3.69873100
C	0.02339300	-2.27589400	4.32852900
C	0.71491500	-1.39480500	3.27284500
C	-0.34435300	-0.66961100	2.43379600
C	-1.26219100	-1.69758900	1.74788000
N	-2.05849200	-0.96786800	0.75799900
N	0.16107600	0.22803100	1.37645600
O	-2.13764500	0.36059500	-1.66385800
C	-3.39789200	0.11949500	-1.61311900
C	-4.05544200	-0.60634700	-0.55395800
C	-3.30398700	-1.19108600	0.52477200
C	1.13964000	1.03729100	1.60014400
C	1.65512700	2.01536300	0.68390100
C	1.12234700	2.16536900	-0.64704400
O	0.14726900	1.48550300	-1.12863700
C	-4.22813900	0.55840600	-2.69463400
C	-5.58165400	0.32417400	-2.71479300
C	-6.23144000	-0.38353300	-1.66329100
C	-5.44025500	-0.84139700	-0.61001600
C	2.72845000	2.81869200	1.11010800
C	3.31941600	3.77483000	0.28521200
C	2.80189500	3.91402500	-1.03438500
C	1.75577900	3.14302900	-1.48121300
O	-1.87685300	1.81827800	0.48023000
H	-2.65138300	-1.87356300	3.39374000
H	-2.64894700	-3.27656100	2.31416500
H	-0.44092800	-3.99182600	3.09715600

H	-1.51060000	-3.80843900	4.48357700
H	0.77535700	-2.83267600	4.90249700
H	-0.50101100	-1.62654200	5.04414700
H	1.34755400	-2.00595600	2.61406800
H	1.37611700	-0.68169900	3.77896700
H	-0.98338500	-0.05075900	3.07363700
H	-0.62526900	-2.36533200	1.15138000
H	-3.84538100	-1.88723400	1.16858600
H	1.64036300	0.99267000	2.57076100
H	-6.18140700	0.68215600	-3.54797600
H	-5.90900600	-1.40079700	0.19690000
H	3.11169600	2.68594300	2.11977300
H	3.25177600	4.65208400	-1.69371800
H	1.36178000	3.25712000	-2.48638100
H	-3.73754900	1.09664500	-3.49962700
C	-2.49260500	2.04997100	1.59890500
C	-3.16819400	3.42581200	1.59568600
H	-3.95187300	3.44835800	0.83037500
H	-3.60623800	3.63215600	2.57528000
H	-2.44156900	4.20301900	1.33717500
O	-2.58659700	1.31767900	2.59010400
Co	-0.95909100	0.28005600	-0.17022900
C	-7.63680600	-0.62155800	-1.69681700
C	-8.83297900	-0.81895800	-1.73605900
H	-9.88342800	-0.99238700	-1.76430200
C	4.40330900	4.58156100	0.74052600
C	5.32446500	5.27287800	1.12063100
H	6.13744600	5.87307800	1.45712800
O	-0.15699000	-1.27614400	-0.99164400
C	3.37322900	-0.94077600	-1.22402100
C	3.88735200	-2.36304100	-0.97199400
H	3.58555900	-2.72140900	0.01160300
H	3.59646200	-3.06657500	-1.74398100
C	1.02991900	-1.59100800	-1.35722700
O	1.33643900	-2.51611900	-2.10609200
O	2.01820900	-0.80668200	-0.76335400
Br	5.88810600	-2.38322500	-0.93443200
H	3.92004700	-0.26674600	-0.55725000
C	3.54904300	-0.46856900	-2.66545300
H	4.60564200	-0.52750400	-2.94831200
H	2.95897900	-1.09128900	-3.34160400
H	3.21795300	0.57047400	-2.75440300

Supplementary Table S7 | Geometrical structure, energy, imaginary frequency and coordinates of transition state VII.



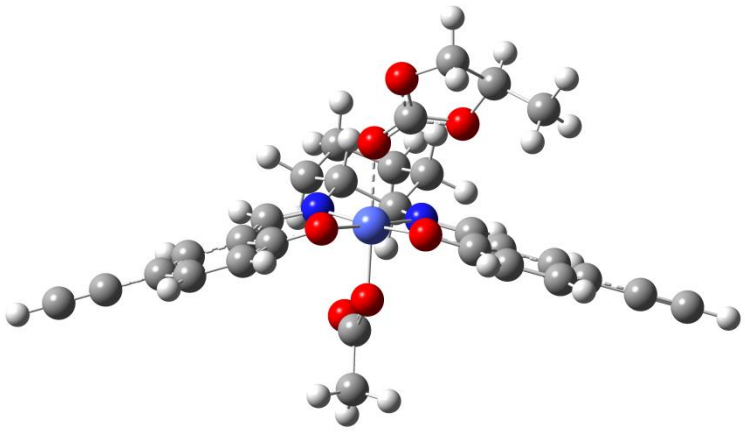
VII E =-5753.183336 Hartree

Frequency = -90.0576 cm^{-1}

C	-1.97783900	-2.59142800	2.64072200
C	-0.92626000	-3.36472200	3.45932200
C	0.12664900	-2.43532800	4.08382400
C	0.77650500	-1.51079400	3.03831300
C	-0.31784600	-0.72925300	2.29944400
C	-1.26776400	-1.72030400	1.60057700
N	-2.09440300	-0.94484600	0.67084000
N	0.14245000	0.23129300	1.27396400
O	-2.22907000	0.45119100	-1.70299700
C	-3.49170900	0.22129400	-1.62503400
C	-4.12497700	-0.53391900	-0.57270800
C	-3.34451800	-1.16170600	0.46238200
C	1.13533500	1.02524300	1.50066400
C	1.61962700	2.04718100	0.61716500
C	1.03011700	2.27303500	-0.68024900
O	0.02671600	1.63298400	-1.15171900
C	-4.34630400	0.69988600	-2.66882900
C	-5.70208900	0.47430600	-2.66043600
C	-6.32771900	-0.26346100	-1.61595300
C	-5.51135800	-0.76023800	-0.59919600
C	2.71829900	2.81952400	1.03944100
C	3.28111200	3.81476500	0.24294200
C	2.70848600	4.02842700	-1.04480400
C	1.63821200	3.29031000	-1.48754000
O	-1.96992100	1.83782600	0.49365400
H	-2.59030500	-1.95818900	3.29711000

H	-2.64983200	-3.30804200	2.15266100
H	-0.42365600	-4.08327600	2.79728000
H	-1.42251200	-3.95204200	4.24288800
H	0.89925700	-3.02988700	4.58824500
H	-0.35045600	-1.81708900	4.85781300
H	1.35469000	-2.09782500	2.31197800
H	1.47672000	-0.83540000	3.54433900
H	-0.92025200	-0.14620600	3.00496000
H	-0.65808500	-2.36846800	0.95663600
H	-3.86647900	-1.88785500	1.08887400
H	1.67415800	0.92553400	2.44648200
H	-6.32143700	0.86343800	-3.46483500
H	-5.96174300	-1.34418500	0.20075400
H	3.14256700	2.63008700	2.02333900
H	3.13729300	4.79784300	-1.68205300
H	1.20367000	3.45988900	-2.46776500
H	-3.87402100	1.26191000	-3.46856500
C	-2.53387200	2.01666400	1.64978800
C	-3.25342100	3.36807900	1.72049400
H	-4.07230600	3.38721100	0.99293000
H	-3.65124500	3.52958600	2.72530900
H	-2.56519200	4.17692500	1.45406200
O	-2.55085900	1.25432300	2.62121100
Co	-1.02965400	0.35424800	-0.23133300
C	-7.73495300	-0.49291000	-1.61937400
C	-8.93285000	-0.68318400	-1.63261900
H	-9.98476200	-0.84986100	-1.63730000
C	4.39039100	4.58917500	0.69291700
C	5.33278100	5.25412100	1.06801500
H	6.16477300	5.83005100	1.40043000
O	-0.16532800	-1.16608000	-1.07365200
C	3.40997400	-0.83059300	-1.21799600
C	3.88505400	-2.27285500	-0.99116100
H	3.54346300	-2.70343300	-0.06001700
H	3.67113300	-2.94362000	-1.81856000
C	1.03295500	-1.60673500	-0.97287400
O	1.35637300	-2.76723900	-0.70424800
O	1.98065000	-0.63491900	-1.23405400
Br	5.89385700	-2.27350600	-0.82084500
H	3.78459900	-0.22787300	-0.38111800
C	3.91388400	-0.23351300	-2.53209800
H	5.00638800	-0.21929000	-2.56606000
H	3.53791200	-0.82179800	-3.37752800
H	3.53699300	0.78798300	-2.63097100

Supplementary Table S8 | Geometrical structure, energy and coordinates of intermediate VIII.



VIII E = -3178.871642 Hartree

C	-1.97007000	3.67611000	0.55485700
C	-1.17434100	4.92885000	0.96634600
C	0.11434000	5.09855600	0.14614500
C	0.98890900	3.83124900	0.16910300
C	0.15832400	2.63092200	-0.30003100
C	-1.06033800	2.44650300	0.62303500
N	-1.65147100	1.13865600	0.31394500
N	0.85110400	1.32426300	-0.36335600
O	-1.44696600	-1.58772400	0.44761800
C	-2.72721800	-1.57834900	0.25091900
C	-3.51714300	-0.38420800	0.12465300
C	-2.92197700	0.91338300	0.26857100
C	2.03393600	1.21944600	-0.87463000
C	2.75574100	-0.00265500	-1.09024700
C	2.22475400	-1.27784800	-0.69257600
O	1.08429500	-1.44474500	-0.10729300
C	-3.42449000	-2.82091000	0.20701000
C	-4.78818300	-2.87708000	0.03324600
C	-5.57225500	-1.69680300	-0.10037500
C	-4.91377800	-0.47193100	-0.04167900
C	4.03341400	0.07752200	-1.68014500
C	4.82017900	-1.05035700	-1.90057000
C	4.29015100	-2.31146100	-1.50901200
C	3.04711400	-2.42048200	-0.92751000
O	-0.67044500	-0.46575000	-1.77483500
H	-2.35848200	3.78327000	-0.46625800

H	-2.83033900	3.56076700	1.22482700
H	-0.91712100	4.85302000	2.03272400
H	-1.80657100	5.81853800	0.86192900
H	0.68900600	5.95397800	0.52140900
H	-0.14723900	5.32858700	-0.89585800
H	1.36863700	3.64502600	1.18417700
H	1.86142600	3.98525100	-0.47580100
H	-0.23008900	2.81020900	-1.30799000
H	-0.68143300	2.35481900	1.65272700
H	-3.60802100	1.75590300	0.36465300
H	2.55010600	2.13324900	-1.17840300
H	-5.28935000	-3.84026500	-0.00614100
H	-5.49209700	0.44495700	-0.12576200
H	4.41595800	1.05262500	-1.97265700
H	4.88613800	-3.20286800	-1.68479600
H	2.64229100	-3.38722200	-0.64407400
H	-2.83272600	-3.72510100	0.30733900
C	-1.15837400	0.33884200	-2.68628500
C	-1.39020100	-0.40214200	-4.00142300
H	-2.19682500	-1.13185700	-3.87206600
H	-1.66465500	0.31063800	-4.78155300
H	-0.49310400	-0.95667100	-4.29237300
O	-1.43032400	1.53225600	-2.57075200
Co	-0.30163300	-0.15747200	0.01639200
C	-6.98614300	-1.77286400	-0.27847100
C	-8.18579200	-1.84800000	-0.42759000
H	-9.24112300	-1.91046800	-0.56261800
C	6.11190000	-0.95056800	-2.49891600
C	7.21176300	-0.87467000	-3.00051400
H	8.17412000	-0.80587700	-3.45354800
O	0.08139200	-0.08325300	2.07278600
C	3.29684800	-0.58079700	3.25577700
C	2.42062000	-1.45677400	4.16836300
C	1.09567900	-0.41433300	2.65619700
O	1.07533100	-1.06296200	3.82821400
O	2.33865000	-0.14933900	2.24778100
H	3.62398700	0.32635400	3.77615100
C	4.46629500	-1.28284800	2.59627300
H	5.17345400	-1.62151700	3.36221300
H	4.12405600	-2.14619700	2.01825500
H	4.99179100	-0.60412400	1.91931000
H	2.57328000	-1.27475000	5.23306900
H	2.52814500	-2.52465400	3.95314000

Supplementary Methods

Materials

Tetrakis-(triphenylphosphine) palladium (0), 3-tert-butyl-2-hydroxybenzaldehyde, copper (I) iodide, (R,R)-1,2-diaminocyclohexane and other solvents were all purchased from Aldrich and used as received. 1,3,5-Triethynylbenzene was purchased from Alfa-Aesar and used as received. 5-bromo-3-tert-butyl-2-hydroxybenzaldehyde was synthesised by a modified method[30-31]. Cobalt (II) acetate, Aluminum triethoxide, Tetrabutylammonium bromide (TBAB) and Propylene oxide (PO) were purchased from Aladdin. Carbon dioxide (99.998% purity) was purchased from the Dalian Institute of Chemical Physics of Special Gases and used as received.

General Methods

All manipulations involving air- and/or moisture-sensitive compounds were carried out using a glove box or standard Schlenk line techniques under dry argon. The NMR spectra were recorded on a BRUKER MERCURY-PLUS 400-MHz type (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer. The chemical shifts were determined in ppm using TMS as an internal standard. The Solid-state NMR spectrum was measured on a Varian Infinity-400 spectrometer. The ^{1}H-^{13}C CP/MAS NMR spectra of Co-CMP and Al-CMP was recorded at a spinning speed of 10 kHz. The polymers' Brunauer-Emmett-Teller (BET) surface areas were screened by nitrogen adsorption and desorption at 77.3 K using a Quantachrome QUADRASORB SI Automated Surface Area & Pore Size Analyzer with a 6-point BET measurement between the pressure ranges of 0.05 to 0.30 P/P_0. The pore size distributions and volumes were derived from the adsorption branches of the isotherms using the nonlocal density functional theory (NL-DFT). The samples were degassed at 150 °C for

12 h under vacuum before analysis. Isotherm of carbon dioxide was measured at 298K using a Quantachrome AUTOSORB-1 volumetric adsorption analyser. TGA analysis was carried out using a DIAMONO TG-DTA analyser (DE Instruments) with an automated vertical overhead thermo balance. The samples were heated at the rate of 20 °C/min up to 1000 °C under a nitrogen atmosphere. High-resolution imaging of the polymer morphology was achieved using a Quanta 200 FEG (FEI Company) cold Field Emission Scanning Electron Microscope (FE-SEM). An Oxiford Instruments 7200 EDX was used to conduct elemental analysis of polymer composition. The sample was coated with a 2-nm layer of gold using a SCD050 automated sputter coater, and the morphology was studied with a high-resolution transmission electron microscope (HR-TEM, Tecnai G^2 F30, FEI, Japan). The samples used for the transmission electron microscope examination were ground, suspended in ethanol or acetone, and deposited on a copper specimen grid supported by a porous carbon film.

Computational methods

All calculations were performed with Becke's three-parameter B3LYP hybrid exchange-correlation function using the Gaussian 09 software package[32]. For the geometry optimisations and frequency calculations, we used the standard 6-31G* basis set, although single-point energy calculations were performed at each stationary point using the extended 6-31 G** basis set to obtain accurate energies. Because the experiment used ethylene oxide as a solvent, we also incorporated considerable solvent effects into the calculation. We estimated the solvation energies in terms of the PCM model with the ethylene oxide as a solvent.

Synthesis of 5-bromo-3-tert-butyl-2-hydroxybenzaldehyde

A solution of Br_2 (0.44 ml, 8.45 mmol) in CH_3COOH (2 ml) was added dropwise at room temperature over 30 min to a solution of 3-tert-butyl-2-hydroxybenzaldehyde (1.50 g, 8.41 mmol) in CH_3COOH (5 ml). After 2 hours, the reaction mixture was diluted with CH_2Cl_2 (50 ml) and washed with water (20 ml), saturated aqueous $Na_2S_2O_5$ (20 ml), saturated aqueous $NaHCO_3$ (10 ml), and saturated sodium chloride (20 ml). The organic phase was dried with anhydrous Na_2SO_4, and the solvents were evaporated, leaving the target compound as a yellow solid. The crude product was further purified through crystallisation from CH_3OH (10 ml) on an analytically pure sample (m.p. 64-65 ^oC). The product (yellow powder) was characterised by ^1H NMR (500 MHz, $CDCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 11.73 (s, 1H), 9.82 (s, 1H), 7.58 (d, J = 2.5 Hz, 1H), 7.51 (d, J = 2.5 Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.0, 160.2, 141.6, 137.3, 133.6, 124.5, 122.0, 35.6, 29.4.

Synthesis of Salen

[*Salen = (R, R)-N,N'-bis(5-bromo-3-tert-butyl-salicylidene)-1,2-cyclohexanediamine*]

A solution of (R,R)-1,2-diaminocyclohexane (0.48 ml, 4 mmol) in ethanol (60 ml) was placed in a three-neck flask tube (250 ml) maintained under vacuum. The solution was stirred for 30 minutes under an argon atmosphere at ambient temperature. After the reaction solution was added to 80°C, the solution of 5-bromo-3-tert-butyl-salicylidene [(2.056 g, 8 mmol) 5-bromo-3-tert-butyl-salicylidene dissolved in 10 ml THF] was slowly added to the reaction solution over 30 minutes. The mixture solution was then stirred for 4-5 hours at 80°C, cooled to room temperature and combined with 60 ml of water, after which it was continually stirred at ambient temperature. The

insoluble precipitate was filtered and dissolved in ether, and this solution was washed 2-3 times with saturated sodium chloride solution and water to remove any unreacted residues. Removing the solvent yielded a yellow powder, which was dried in a vacuum for 24 hours at 50 °C (yield: 1.91 g, 80.2%). The Salen (yellow powder) was characterised by ^{1}H NMR (500 MHz, $CDCl_3$) as follows: δ 13.75 (s, 2H), 8.20 (s, 2H), 7.32 (d, ^{4}J = 2.0 Hz, 2H), 7.10 (d, ^{4}J = 2.0 Hz, 2H), 3.32 (br, 2H), 2.03 (br, 2H), 1.88 (br, 2H), 1.76 (m, 2H), 1.48 (m, 2H), 1.38 (s, 18H).

Synthesis of Salen-Co (II**)[23]**

A solution of $Co(OAc)_2$ (170 mg, 0.96 mmol) in CH_3OH (10 ml) was added to a solution of Salen (400 mg, 0.675 mol) in toluene (10 ml) under argon with a syringe, resulting in a dark red precipitate. The reaction mixture was heated to 80-85°C and stirred for 5-6 hours, then cooled down to room temperature and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (80 ml) and passed through a Celite pad to remove the excess $Co(OAc)_2$. Removing the solvent of the filtrate yielded a dark red power (yield: 390 mg, 89.1%).

Synthesis of Salen-Co-OAc[23]

Acetic acid (0.35 ml) was added to a solution of Salen-Co(II) (390 mg, 0.6 mmol) in toluene (6 ml) and CH_2Cl_2 (18 ml). The solution quickly changed from red to brown. After 5-6 hours, all solvents and excess acetic acid were removed, and the residue was dried in a vacuum for 24 hours at 70°C, yielding a brown powder. The Salen-Co-OAc (brown powder) was characterised by ^{1}H NMR (400 MHz, $CDCl_3$) as follows: δ 7.49 (s, 1H), 7.42 (br, 2H), 7.32 (d, ^{4}J = 2.4 Hz, 1H), 7.30 (d, ^{4}J = 2.4 Hz, 1H), 7.18 (s, 1H), 4.26 (m, 1H), 3.23 (m, 1H), 2.79 (m, 1H), 2.74 (m, 1H), 2.01 (m, 2H), 1.98 (br, 1H), 1.90 (br, 2H), 1.74 (m, 1H), 1.61 (s, 3H), 1.52 (s, 9H), 1.25 (s, 9H).

Synthesis of Co-CMP[15]

1,3,5-triethynylbenzene (180 mg, 1.2 mmol), Salen-Co-OAc (400 mg, 0.6 mmol), CuI (50 mg) and tetrakis-(triphenylphosphine)palladium(0) (100 mg) were dissolved in a mixture of toluene (15 ml) and triethylamine (6 ml). The reaction mixture was heated to 40 °C and stirred for 1 hour under an argon atmosphere (to exclude oxygen and prevent any homocoupling of the alkyne monomers). Next, the reaction mixture was heated to 80°C, stirred for 72 hours, then cooled to room temperature. The insoluble precipitated polymer was filtered and washed four times with dichloromethane, methanol, water, and acetone to remove any unreacted monomers or catalyst residues. Further purification of the polymer was carried out by Soxhlet extraction with methanol and dichloromethane (volume ratio = 1:1) for 48 hours. The product was dried in a vacuum for 24 hours at 70 °C and isolated as a brown powder (yield: 79.3%). The molecular-level structure of Co-CMP was assessed using ^{1}H-^{13}C CP/MAS solid-state NMR (Supplementary Fig. S2-b). The peaks at approximately 95.7 and 92.1 ppm were ascribed to sp-hybridised –C≡C– sites, and the shoulder at approximately 155.6 ppm was assigned to the –C=O groups in the carboxylate. The peaks at approximately 121.6, 124.4, 128.1, 131.9, 133.5 and 136.1 ppm corresponded to the C–C sites of the polymer's benzene rings. Furthermore, the peaks at approximately 138.7 ppm were ascribed to the –C=N groups in the polymer, and the peaks at approximately 56.1 ppm and 68.3 ppm were ascribed to sp^2-hybridised $–CH_2$ sites and sp-hybridised –CH sites in the cyclohexane. The lowest-intensity peak, at approximately 28.0 ppm, was ascribed to the $–CH_3$ groups.

Synthesis of CMP[15]

1,3,5-Triethynylbenzene (300 mg, 2 mmol), Salen (296 mg, 0.5 mmol), CuI (80 mg) and tetrakis (triphenylphosphine)palladium-(0) (120 mg) were dissolved in a mixture of toluene (10 mL) and

Et_3N (5 mL). The reaction mixture was heated to 40 °C and stirred for 1 hour under an argon atmosphere (to exclude oxygen and prevent any homocoupling of the alkyne monomers). Next, the reaction mixture was heated to 85°C, stirred for 72 hours, then cooled to room temperature. The insoluble precipitated polymer was filtered and washed four times with dichloromethane, methanol, water, and acetone to remove any unreacted monomers or catalyst residues. Further purification of the polymer was carried out by Soxhlet extraction with water, dichloromethane, acetone and methanol (volume ratio = 1:1:1:1) for 24 hours. The product was dried in a vacuum for 24 hours at 70 °C and isolated as a brown powder (yield: 41 mg, 80.8%).

Synthesis of Al-CMP

CMP (150 mg) was added to a solution of $Al(OEt)_3$ (300 mg) in 30 mL toluene, and the suspension was then refluxed for 24 hours. The mixture was cooled to room temperature, and the insoluble precipitated network polymer was filtered and washed four times with dichloromethane, water, methanol, and acetone to remove the unreacted aluminium complex. Further purification of the polymer was carried out using a Soxhlet extraction with water, acetone, dichloromethane and methanol (volume ratio = 1:1:1:1) for 24 hours. The product was dried in a vacuum for 24 hours at 70 °C and isolated as a brown powder (Al-CMP) (yield: 280 mg, 62.2%). The molecular-level structure of Al-CMP was assessed using ^{1}H-^{13}C CP/MAS solid-state NMR (Supplementary Fig. S2-a). With the exception of the carbonyl functional groups (–C=O) in Co-CMP, the assignment of the resonances for Al-CMP was similar to those observed in Co-CMP.

General procedure for the synthesis of propylene carbonate at ambient pressure and temperature

A mixture of Bu_4NBr (0.6-1.8 mmol, 200-600 mg) and Co-CMP (or Al-CMP) (50-100 mg) was

placed in a vacuum tube reaction. Propylene oxide (25 mmol, 1.75 ml) was added to the tube using a syringe, and CO_2 (at atmospheric pressure) was introduced. After being stirred for 12-72 hours at 25°C, the reaction mixture was dissolved with ethyl acetate (30 ml), and the insoluble solid material was filtered. Removing the solvent from the filtrate yielded a pale yellow oily substance. Further purification of the crude product was carried out by column chromatography (yield: 40%-81.5%). The propylene carbonate was assessed by ^{1}H NMR and ^{13}C NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.90-4.83 (m, 1H), 4.58 (dd, J=8.3 Hz, 1H), 4.05 (dd, J=8.3 Hz, 1H), 1.49 (d, J=6.2Hz, 3H); 13C NMR (100 MHz, $CDCl_3$): δ 155.0, 73.5, 70.7, 19.4.

General procedure for the synthesis of propylene carbonate at high temperatures and pressures

A pre-dried 50-ml autoclave was charged with Co-CMP (or Al-CMP) (50-100 mg) and propylene oxide (1.75-3.5 ml, 25-50 mmol) in the atmosphere. Next, the assembled autoclave was purged of air three times with CO_2. After the CO_2 (3.0-4.0 MPa) was introduced, the reaction mixture was stirred at 100-130°C for 1-3 hours. The autoclave was cooled to room temperature, and the CO_2 was released. The reaction mixture was then dissolved with ethyl acetate (30 ml), and the insoluble solid material was filtered. Removing the solvent of the filtrate yielded a pale yellow oil substance. Further purification of the crude product was carried out by column chromatography (yield: 90%-99.6%). The propylene carbonate was determined by ^{1}H NMR and ^{13}C NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.91-4.84 (m, 1H), 4.57 (dd, J=8.3 Hz, 1H), 4.04 (dd, J=8.3 Hz, 1H), 1.49 (d, J=6.2Hz, 3H); 13C NMR (100 MHz, $CDCl_3$): δ 155.4, 73.6, 70.9, 19.6.

Supplementary References

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