Electronic Supplementary Information

Easy access to amphiphilic nitrogenous block copolymers *via* switchable catalysis

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Materials

Unless otherwise stated, all chemicals were used without further purification. Acetonitrile (MeCN, 99.9%, Macklin) was refluxed with sodium and distilled under nitrogen before use. Allyl glycidyl ether (AGE, 99.0%, Aladdin), styrene oxide (SO, 98.0%, Macklin), cyclohexene oxide (CHO, 98%, Macklin), propylene oxide (PO, 98%, Macklin) and vinyl propylene oxide (VPO, 98%, Macklin) were distilled over CaH_2 under reduced pressure prior to use. Phthalic anhydride (PA, 99.0 %, Aladdin) was purified by sublimation before use. Triethylborane (TEB) [1 M in tetrahydrofuran (THF), Alfa], PPNCl ([PPN]: bis(triphenylphosphine) iminium, 98%, Alfa), Boc-Sarcosine (99%, Alfa), *N*-Boc-*N*-ethylglycine (97%, Alfa), phosphorus tribromide (98%, TCI), PCl_3 (98%, TCI) were used as received. High glucose DMEM, fetal bovine serum (FBS), trypsin-EDTA, and cell counting kit-8 (CCK-8) were obtained from Adamas life. Antibiotic-Antimycotic was purchased from Gibco.

Measurements

Nuclear magnetic resonance spectroscopy (NMR). ^1H, ^{13}C and 2D NMR spectra were recorded on a Bruker AV-400/500 spectrometer at room temperature. ^1H NMR chemical shifts were referenced as follows: 7.26 ppm for chloroform-*d* ($CDCl_3$), 2.50 ppm for dimethyl sulfoxide-d_6 (DMSO-d_6). ^{13}C NMR chemical shifts were referenced as follows: 77.16 ppm for $CDCl_3$, 39.52 ppm for DMSO-d_6.
Size exclusion chromatography (SEC). SEC analyses of copolymerization solutions and polymers were conducted by an Agilent differential refractive index (RI) detector (1200 Infinity Series from Agilent Technologies, USA) with two linear Styragel columns (8 × 300 mm，3μm). High performance liquid chromatography (HPLC) grade DMF (0.01 M LiBr) was used as eluent with a constant flow rate of 1 mL/min, 60 ºC, polystyrene (PS) standards.
***In-situ* attenuated total reflection infrared (*in-situ* ATR-IR) spectroscopy.** All in situ ATR-IR spectroscopic reactions were carried out with a Mettler-Toledo ReactIR 702L Reaction Analysis System fitted with a SiComp fiber probe. Data were acquired and analyzed using ReactIR software version 7.1.
Dynamic light scattering (DLS). DLS was used to determine the hydrodynamic diameter (D_h) and polydispersity of the nanostructures formed from block copolymers, in aqueous solution, using the ZETASIZER Nano series instrument (Malvern Instruments ZS 90) at a fixed scattering angle of 90°.
Zeta potential. Studies were performed on a Nano-ZS 90 Nanosizer (Malvern Instruments Ltd., Worcestershire, U.K.) at 25°C. Each reported measurement was conducted three times.
Transmission electron microscopy (TEM). The diluted particles solution (0.2 mg/mL, 10 μL) was dropped onto a carbon-coated copper grid. The samples were frozen at −80 °C using a refrigerator and then freeze-dried using a lyophilizer. Then the grids were dried in an ambient environment. Images were recorded on a JEOL JEM-2100F instrument at 200 kV equipped with a Gantan 894 Ultrascan 1k CCD camera.
Cytotoxicity assay. NCTC clone 929 (L929) cells were purchased from Haixing. L929 cells were cultured in high glucose DMEM culture medium supplemented with 10.0% FBS, 1.0% antibiotic-antimycotic. Cells were maintained at 37 °C in a 5% CO_2 water-saturated atmosphere. Cytotoxicity assay of the block copolymer P(SO-*alt*-PA)-*b*-PSar was conducted using

a cell counting kit-8 (CCK-8) assay. Firstly, L929 cells were added to DMEM, consisting of 20% FBS and 1.0% antibiotic-antimycotic. Secondly, a suspension of L929 (100 μL) was seeded in each 96-well plate, with a density of 5×10^4 cells/per well. Thirdly, the cells were cultured at 37 °C/ 5% CO_2 incubator for more than 24 h. After the cells were attached, 10 μL of various concentrations of the particle dispersion was added into each well, an equal amount of sterile water was added to the control group, and the wells were then cultured for 2 h. Finally, 10 μL of the CCK-8 dye was added to each well. The 96-well plate was then placed in an incubator for 3-4 h. the absorbance at 450 nm of each well was measured with a microplate reader. The above steps were repeated three times. The relative cell viability of the cells was determined by comparing the absorbance with the control group, and the relative cell viability (*Vc*) was calculated using the following equation:

$$Vc = \frac{A_{sample}}{A_{control}} \times 100\%$$

Where A_{sample} and A_{control} represent the mean absorbance of sample and control, respectively.

Adsorption experiment. Firstly, the calibration curve of BSA was created. BSA was dispersed in PBS buffer to form a solution of different concentrations, and the absorbance at 280 nm wavelength (characteristic absorbance of BSA protein) was measured by UV-vis spectrophotometer. Secondly, P(SO-*alt*-PA)-*b*-PSar nanoparticles were suspended in BSA solutions (0.375 mg/mL BSA in PBS). The samples were vibrated on a rocking table for 12 h at 37 °C, then the mixture was centrifuged. The supernatants were collected and the concentration of BSA in the supernatants was measured at 280 nm. The adsorption quantity of P(SO-*alt*-PA)-*b*-PSar nanoparticles for BSA was calculated by the following equation:

$$Adsorption\ quantity = \frac{C}{C_{PBS}} \times 100\%$$

Where C and C_{PBS} are the absorbance values of the supernatants of the samples and negative (PBS), respectively.

Hemolysis test. To assay hemolytic activity of the P(SO-*alt*-PA)-*b*-PSar nanoparticles, the erythrocytes were obtained by centrifuging (2000 rpm) the rabbit blood for 10 min and washed three times with PBS. The purified erythrocytes were diluted to a concentration of 2% (v/v). The P(SO-*alt*-PA)-*b*-PSar nanoparticles dispersion was diluted to 1.0/ 0.50/ 0.25/ 0.125/ 0.063/ 0.033/ 0.016 mg/mL by PBS. The P(SO-*alt*-PA)-*b*-PSar dispersion (0.5 mL) and the erythrocyte suspension (500 μL) were added into a 2.0 mL tube and mixed by gently pipetting. After incubated at 37 °C for 1 h, the samples were centrifuged (2000 rpm, 10.0 min) and the absorbance of the clear supernatant was measured at 545 nm using a microplate reader (Multiskan Go, Thermo Scientific, USA). Triton X-100 (0.1%) and PBS served as the positive and negative control, respectively. The tests were replicated three times for each sample. The hemolysis percentage of the nanoparticles was calculated using the equation:

$$Hemolysis\ ratio = \frac{A_h - A_p}{A_t - A_p} \times 100\%$$

Where A_{h}, A_{p}, and A_{t} are the absorbance values of the supernatant fraction of the samples, negative (PBS), and positive control (Triton X), respectively.

Experimental section

Sarcosine-NCA (Sar-NCA) was synthesized by following a precedent procedure with modifications.[1] Boc-Sarcosine (4.70 g, 25.0 mmol) was dissolved in anhydrous CH_2Cl_2 (150 mL) and then PCl_3 (6.80 g, 25.0 mmol) was added dropwise to the reaction flask under ice-water bath and N_2 protection. The reaction mixture was stirred under N_2 for 2 h. The reaction mixture was filtered and the filtrate was concentrated under vacuum. The crude NCA was recrystallized using dried CH_2Cl_2/hexane to afford a white crystal (1.82 g, 65% yield.). ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.06 (3H, s, CH_3–), 4.14 ppm (2H, s, –NCH_2–CO–).

General procedure for the synthesis of *N*-ethyl *N*-carboxyanhydride (Et-NNCA). Et-NNCA was synthesized by following a precedent procedure with modifications.[2] *N*-Boc-*N*-ethylglycine (8.40 g, 41.0 mmol) was dissolved in anhydrous CH_2Cl_2 (100 mL) and then PCl_3 (11.1 g, 41.0 mmol) was added dropwise to the reaction flask under ice-water bath and N_2 protection. The reaction mixture was stirred at 0°C for 1 h and was allowed to warm to room temperature for additional 2 h under N_2 protection. The reaction mixture was filtered and the solution was concentrated under vacuum to yield an oily residue. Inside the glovebox, the residue was extracted with anhydrous CH_2Cl_2 and filtered. The volatiles were removed under vacuum to afford a clear liquid (2.21 g, 30% yield). ^{1}H NMR (400 MHz; $CDCl_3$): δ = 1.25 (3H, t, CH_3CH_2–), 3.47 (2H, m, CH_3CH_2-), 4.15 ppm (2H, s, –NCH_2–CO–).

General procedures for ring-opening copolymerization of epoxides and cyclic anhydrides. A typical polymerization procedure was as follows: in a glovebox, the appropriate amount of cyclic anhydride (1.25 mmol, 50 equiv.), PPNCl (25.0 μmol, 1 equiv.) and TEB (1 M in THF, 76.0 μL, 3 equiv.) were added in an oven-dried tube equipped with a magnetic stir, followed by MeCN (0.60 mL) and epoxide (0.60 mL) as mixture solvent. The tube was removed from the glovebox and placed in a predetermined temperature oil bath. After the predetermined time, the reaction mixture was dropwise precipitated into anhydrous ethyl ether or hexene with vigorous stirring, the product was isolated by centrifuge and dried under vacuum for 24 h. All analyses and further chemical modification were performed on crude samples.

General procedures for ring-opening polymerization of NNCAs. A typical polymerization procedure was as follows: in a glovebox, the appropriate amount of NNCA (1.00 mmol, 40 equiv.), PPNCl (25.0 μmol, 1 equiv.) and TEB (1 M in THF, 76.0 μL, 3 equiv.) were added in an oven-dried tube equipped with a magnetic stir, followed by MeCN (0.60 mL) and epoxide (0.60 mL) as mixture solvent. The tube was removed from the glovebox and placed in a predetermined temperature oil bath. After the predetermined time, the reaction mixture was dropwise precipitated into anhydrous ethyl ether or hexene with vigorous stirring, the product was isolated by centrifuge and dried under vacuum for 24 h. All analyses and further chemical modification were performed on crude samples.

General procedures for switchable polymerization of epoxides, cyclic anhydrides and NNCAs. A typical polymerization procedure was as follows: in a glovebox, the appropriate amount of NNCA (1.00 mmol, 40 equiv.), cyclic anhydride (1.25 mmol, 50 equiv.), PPNCl (25.0 μmol, 1 equiv.) and TEB (1 M in THF, 76.0 μL, 3 equiv.) were added in an oven-dried tube equipped with a magnetic stir, followed by MeCN (0.60 mL) and epoxide (0.60 mL) as mixture solvent. The tube was removed from the glovebox and placed in a predetermined temperature oil bath. After the predetermined time, the reaction mixture was dropwise precipitated into anhydrous ethyl ether or hexene with vigorous stirring, the product was isolated by centrifuge and dried under vacuum for 24 h. All analyses were performed on crude samples.

Results

Synthesis of NNCA monomers

Sar-NCA and Et-NNCA monomers were successfully synthesized with yields of 65% and 30%, respectively. The ^{1}H NMR spectra were shown in Fig. S1.

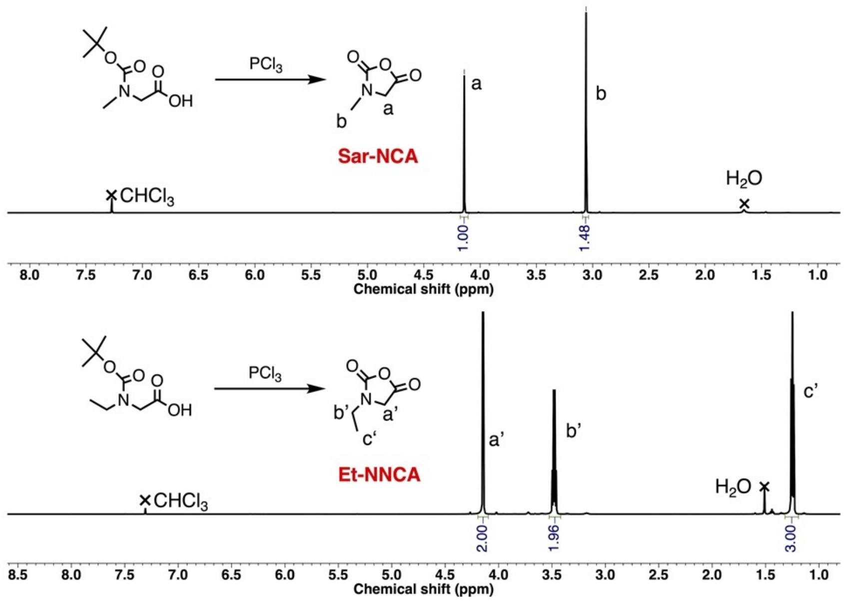

Fig. S1 ^{1}H NMR spectra of Sar-NCA and Et-NNCA in $CDCl_3$.

The effect of the solvent on the ring-opening polymerization of NNCA

The solvent is crucial for switchable polymerization. On the one hand, the polarity of the solvent affects the interactions between Lewis acids, bases or monomers. On the other hand, it is essential for both blocks to have good solubility in the solvent. The ROP of Sar-NCA or Et-NNCA enables the synthesis of hydrophilic polypeptoids. As the alkyl chain length of the substituent increases, the hydrophilicity of the resulting polypeptoids gradually decreases.[3] Therefore, to successfully synthesize amphiphilic polyester-*b*-polypeptoid copolymers, various solvents for polymerization were screened.

The ^{1}H NMR results from different solvent systems are depicted in Fig. S2. It is evident that in the SO, CHO/MeCN, and SO/MeCN systems, the disappearance of peaks corresponding to the Sar-NCA monomer (4.10 and 3.10 ppm) and the appearance of characteristic peaks for PSar (4.00-4.30 ppm) were observed. These results indicate that the ROP of Sar-NCA to produce PSar proceeds smoothly in these solvent systems. However, no PSar was observed in pure MeCN, while poor solubility of PSar was observed in pure CHO. Finally, a mixed solvent system of epoxide/MeCN (v/v, 1/1) was prioritized as the polymerization solvent.

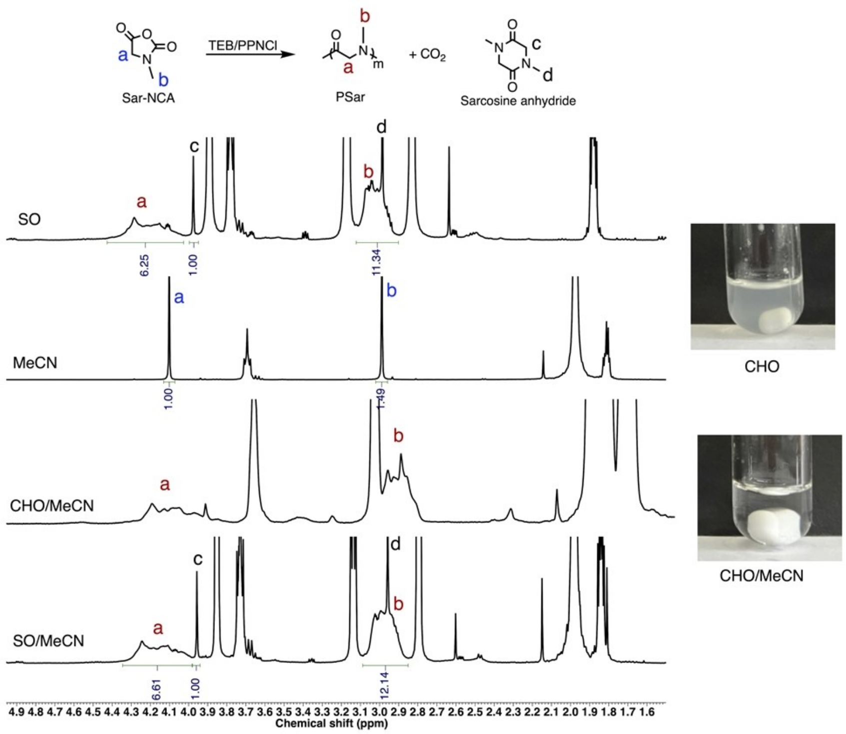

Fig. S2 ^{1}H NMR spectra of polymerization solution in SO, MeCN, CHO/MeCN or SO/MeCN. The reaction was performed in 1.2 mL SO, MeCN or epoxide/MeCN (1/1, v/v) at 50 °C with [Sar-NCA]/[TEB]/[PPNCl] = 40/3/1.

ROP of NNCA

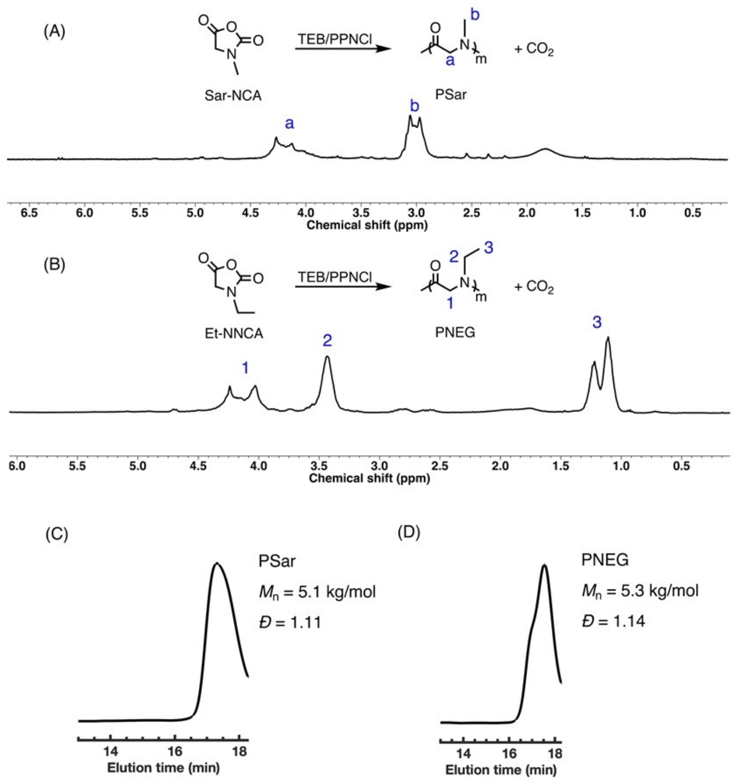

Fig. S3 The spectra of (A) PSar and (B) PNEG (in $CDCl_3$). The SEC traces of (C) PSar and (D) PNEG (Table 1 entries 1-2) in DMF. The presence of a shoulder peak on the left side of the main peak indicates the existence of impurities such as diol or water. These impurities acted as chain transfer agents, causing a decrease in the M_n of the polymer.

In accordance with previous reports, the TEB/PPNCl-catalyzed ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides involves TEB primarily activating the epoxide, while PPNCl functions as an initiator to commence the copolymerization process.[4, 5] However, the specific role of this catalytic system in the ring-opening polymerization (ROP) of Sar-NCA has remained elusive. To elucidate the initiation mechanism and assess the influence of the catalytic system components on the ROP of Sar-NCA, *in-situ* ATR-IR spectroscopy was employed to monitor the polymerization dynamics.

Initially, when employing a mixture of epoxide and acetonitrile (1/1, v/v) as solvents, it was found that TEB alone was incapable of mediating the ROP of Sar-NCA (Fig. S4). Conversely, while PPNCl solely could initiate polymerization, the process was uncontrolled, yielding products with poor solubility (Fig. S5). Notably, upon the addition of TEB/PPNCl at a molar ratio of 3/1 (Fig. S6), a gradual decrease in the carbonyl band of Sar-NCA at 1783 cm^{-1} was observed, concomitant with an increase in the intensity of the characteristic PSar peak at 1675 cm^{-1}. After approximately 109 min, the intensities of both the monomer and polymer bands remained constant, indicating the completion of the polymerization reaction. Therefore, it is concluded that the combined use of TEB/PPNCl, despite exhibiting an induction period, facilitated a more controlled polymerization process.

The above results indicate that both TEB and PPNCl play crucial roles in the ROP of Sar-NCA. PPNCl initiates the polymerization process, while TEB stabilizes the chain ends during polymerization. This stabilization by TEB allows the polymerization to proceed in a controlled manner and affects the solubility of the polymer product in the solvent.

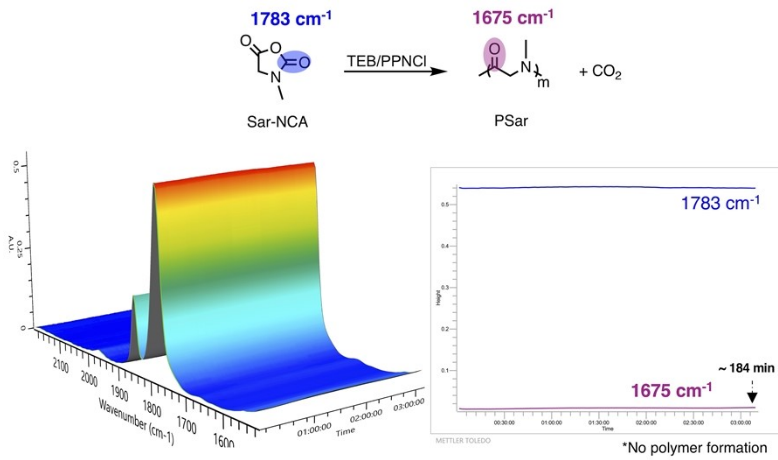

Fig. S4 *In-situ* ATR-IR spectroscopy monitoring ROP of Sar-NCA with TEB (38 μL, 1M in THF solution) as catalyst. The reaction was performed in 0.3 mL CHO, 0.3 mL MeCN at 25 °C with [Sar-NCA]: [TEB] = 40/3.

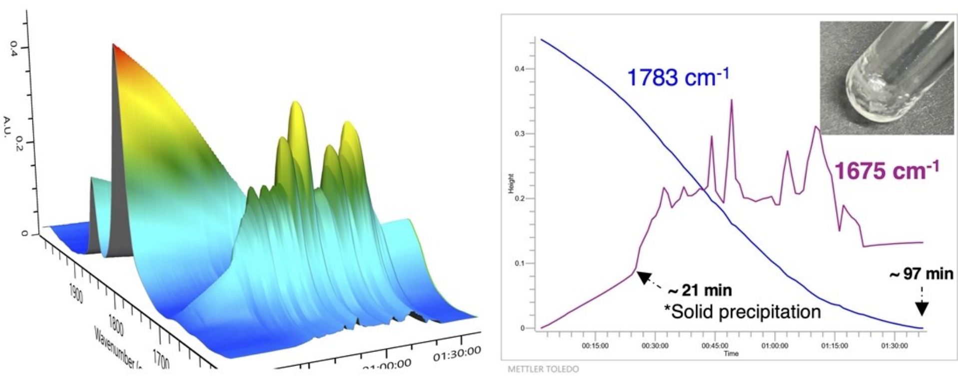

Fig. S5 *In-situ* ATR-IR spectroscopy monitoring ROP of Sar-NCA with PPNCl as catalyst. The reaction was performed in 0.3 mL CHO, 0.3 mL MeCN at 25 °C with [Sar-NCA]/[PPNCl] = 40/1.

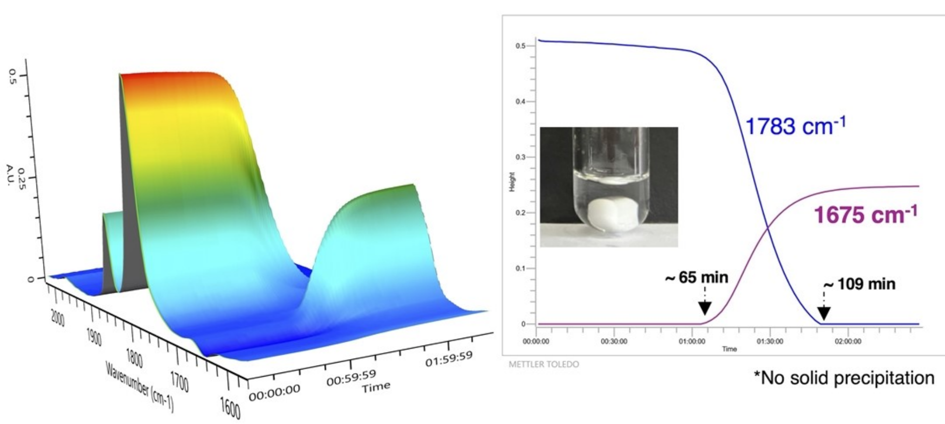

Fig. S6 *In-situ* ATR-IR spectroscopy monitoring ROP of Sar-NCA with PPNCl and TEB (38 μL, 1M in THF solution). The reaction was performed in 0.3 mL CHO, 0.3 mL MeCN at 25 °C with [Sar-NCA]/[TEB]/[PPNCl] = 40/3/1.

Secondly, in this study, TEB was dispersed in THF at a concentration of 1 M. To exclude the effect of THF on the polymerization process, an equal amount of anhydrous THF was added as a control experiment (Fig. S7). These results indicate that the THF introduced with TEB does not significantly affect the reaction rate and controllability of the copolymerization system. In addition, uncontrolled polymerization was observed.

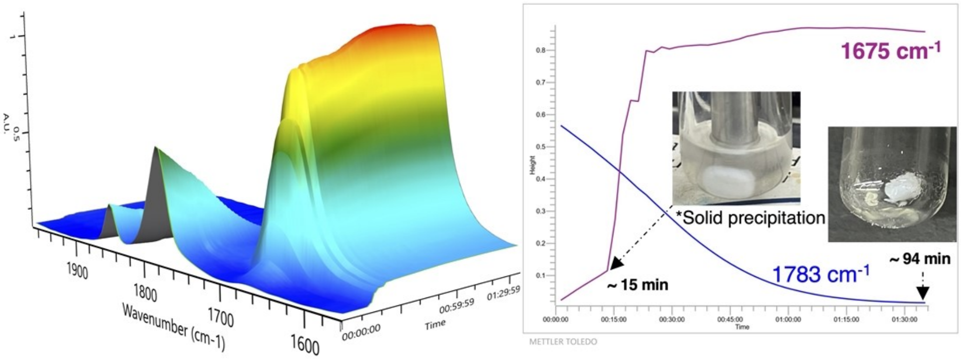

Fig. S7 *In-situ* ATR-IR spectroscopy monitoring ROP of Sar-NCA with PPNCl and 38 μL anhydrous THF. The reaction was performed in 0.3 mL CHO, 0.3 mL MeCN at 25 °C with [Sar-NCA]/[PPNCl] = 40/1.

The initiation mechanism of NNCAs ROP with TEB/PPNCl

Upon analyzing the prior experimental outcomes, it was evident that the utilization of pure acetonitrile (MeCN) as the solvent hindered the ability of the TEB/PPNCl catalytic system to effectuate the ring-opening polymerization (ROP) of Sar-NCA (Fig. S2). According to the integration of *in-situ* ATR-IR monitoring data (Fig. S4-S7) and existing literature reports,[4, 6] a hypothesis emerges: the direct activation of Sar-NCA's ring-opening by dissociated Cl^- ions from PPNCl is infeasible. Alternatively, the involvement of an epoxide monomer appears to be pivotal, as the Cl^- ion first induces the ring-opening of the epoxide, forming an alkoxide intermediate with α-Cl. With the presence of TEB, the alkoxide intermediate then further nucleophilically attacked the C5 carbonyl position of NNCA, effectively initiating the controlled ROP of NNCA.

To validate this hypothesis, a series of control experiments were conducted. Notably, in the absence of an epoxide monomer (CHO), minimal variation in the absorption intensity of Sar-NCA's carbonyl group was observed over a 4 h period (Fig. S8). Conversely, upon the introduction of CHO, a gradual decrease in the Sar-NCA carbonyl group's absorption intensity coincided with a concomitant increase in the PSar carbonyl group's intensity (Fig. S9). These observations reinforce our hypothesis, confirming that when epoxides and PPNCl are concurrently present, the initial ring-opening of the epoxide monomer is facilitated by the Cl^- ion, leading to the formation of alkoxide active species. Similar initiation mechanism has also been reported in the previous literature where TEB/PPNCl was used to catalyze the ROP of epoxides/cyclic anhydrides.[4, 5]

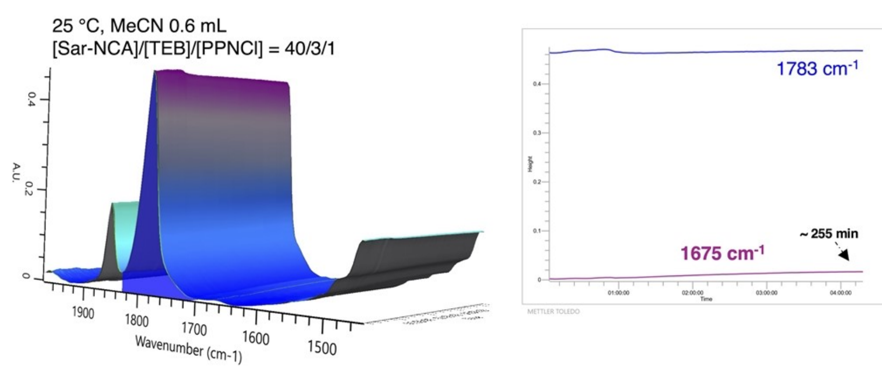

Fig. S8 *In-situ* ATR-IR spectroscopy monitoring ROP of Sar-NCA with TEB/PPNCl. The reaction was performed in 0.6 mL MeCN at 25 °C with [Sar-NCA]/[TEB]/[PPNCl] = 40/3/1.

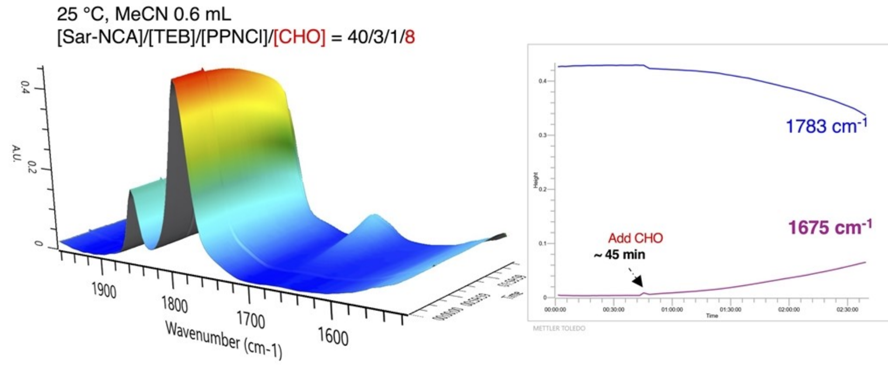

Fig. S9 *In-situ* ATR-IR spectroscopy monitoring ROP of Sar-NCA with TEB/PPNCl. The reaction was performed in 0.6 mL MeCN at 25 °C with [Sar-NCA]/[TEB]/[PPNCl] = 40/3/1. At about 45 minutes, 8 equiv. of CHO was added.

ROCOP of SO/PA

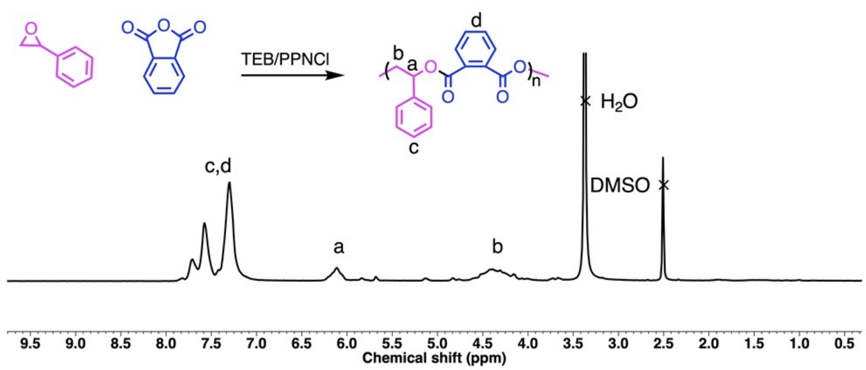

Fig. S10 The ^{1}H NMR spectrum of P(SO-*alt*-PA) in DMSO-d_6, (Table 1 entry 4). The reaction was performed in 1.2 mL SO/MeCN (1/1, v/v) at 50 °C with [SO]/[PA]/[TEB]/[PPNCl] = 210/50/3/1.

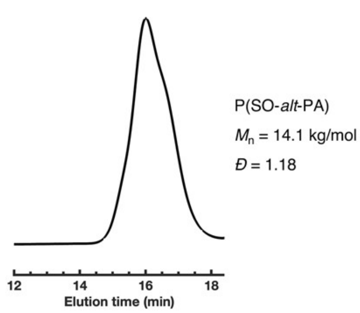

Fig S11. The SEC trace of P(SO-*alt*-PA) in DMF.

Switchable polymerization of SO/PA/Sar-NCA

The ^{1}H NMR results (Fig. 3A and Fig. S12) show that the spectra corresponding to the crude mixture and isolated polymer remain unchanged, indicating the formation of P(SO-*alt*-PA)-*b*-PSar copolymers. No signal peaks assigned to polyether (ca. 3.51 ppm), indicating that no homo-polymerization of epoxides occurred. Trace of signal peaks assigned to the cyclic carbonate was observed (ca. 5.48 ppm), but no polycarbonate (ca. 4.60 ppm), indicating that only trace amount of CO_2 and SO reacted with each other.

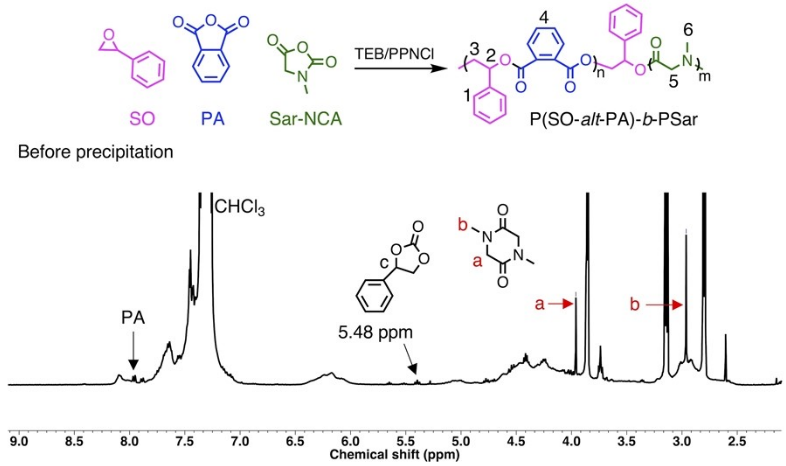

Fig. S12 ^{1}H NMR of the crude aliquot pipetted from polymerization mixture in $CDCl_3$ (Table 1 entry 5). The reaction was performed in 1.2 mL SO/MeCN (1/1, v/v) at 50 °C with [PA]/[Sar-NCA]/[TEB]/[PPNCl] = 50/40/3/1.

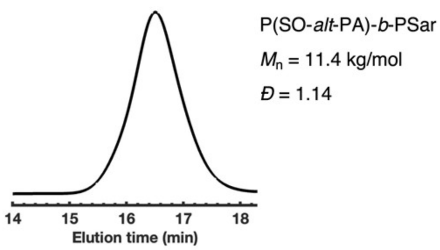

Fig. S13 The SEC trace of P(SO-*alt*-PA)-*b*-PSar in DMF.

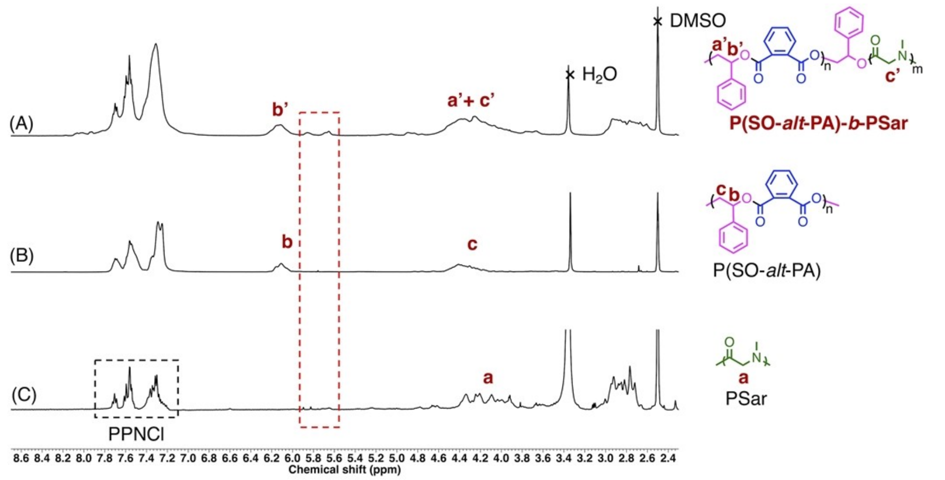

Fig. S14 The comparison of the ^{1}H NMR spectra of the P(SO-*alt*-PA)-*b*-PSar copolymers, P(SO-*alt*-PA), and PSar in DMSO-d_6, isolated from the reaction mixture by precipitation.

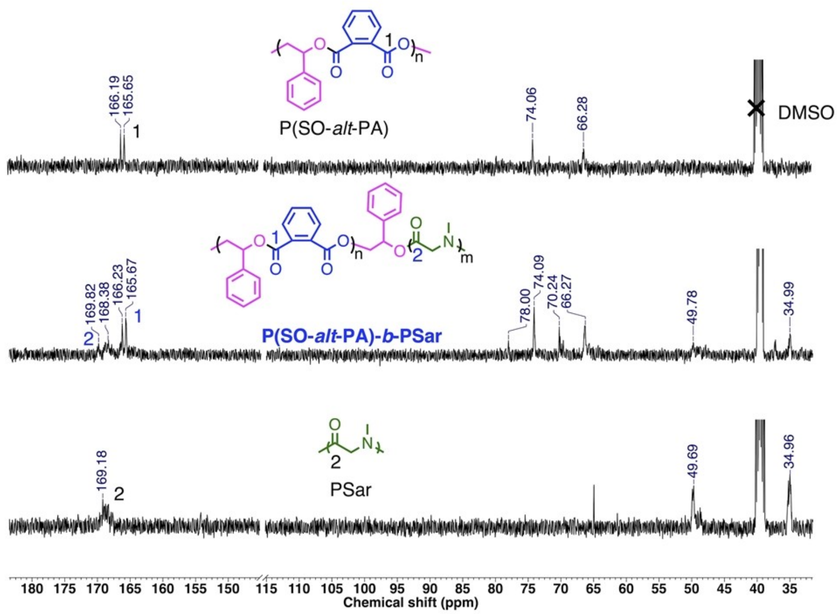

Fig. S15 The comparison of the ^{13}C NMR spectra of the P(SO-*alt*-PA), P(SO-*alt*-PA)-*b*-PSar copolymers and PSar in DMSO-d_6.

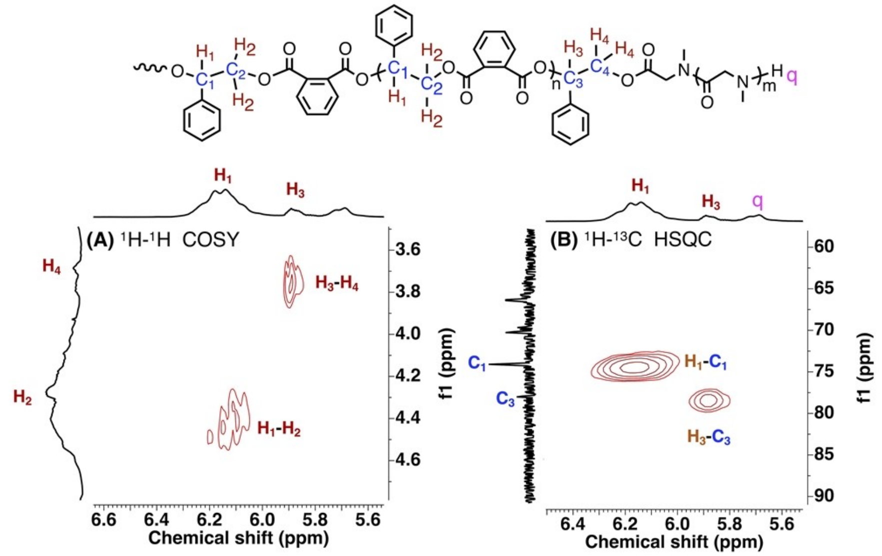

Fig. S16 Partial enlarged (A) ^1H COSY NMR spectra of P(SO-*alt*-PA)-*b*-PSar (in DMSO-d_6). (B) ^1H-^{13}C HSQC NMR spectra of P(SO-*alt*-PA)-*b*-PSar (in DMSO-d_6).

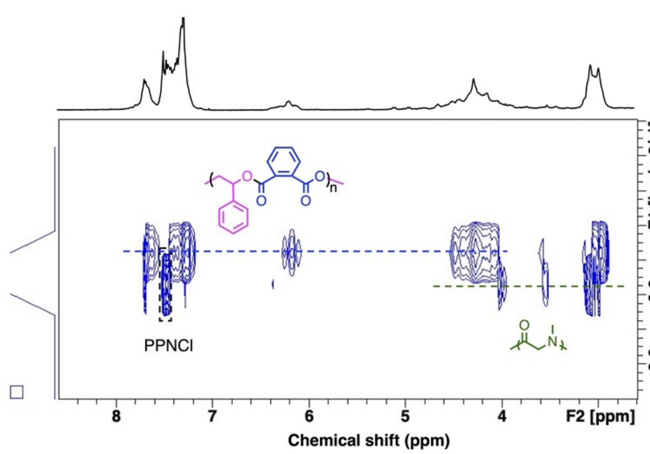

Fig. S17 The ^1H DOSY NMR of the blend of P(SO-*alt*-PA)-*b*-PSar in $CDCl_3$

***In-situ* ATR-IR spectroscopy monitoring of terpolymerization**

The ATR-IR spectra of Sar-NCA, PA, PSar, P(SO-*alt*-PA) and P(SO-*alt*-PA)-*b*-PSar copolymers are shown in Fig. S18. The ROP of Sar-NCA and the ROCOP of SO/PA were monitored separately. During the ROP of Sar-NCA (Fig. S19), the carbonyl absorption bands of the Sar-NCA monomer at 1852 cm^{-1} and 1784 cm^{-1} decrease in intensity with the progression of time. In contrast, the intensity of the PSar carbonyl group at 1676 cm^{-1} progressively increases. After ca. 110 min, the Sar-NCA is nearly depleted, as indicated by the stabilization of the PSar, signalling the termination of the ROP process. Additionally, the change in the absorption band at 981 cm^{-1} corresponds to the Sar-NCA consumption.

In the ROCOP of SO/PA (Fig. S19), the intensities of the PA monomer's carbonyl group absorption bands at 1852 cm^{-1} and 1779 cm^{-1} gradually diminish as the polymerization time increases. Concurrently, the intensity of the carbonyl group of the P(SO-*alt*-PA) at 1729 cm^{-1} steadily increases. Upon reaching 36 h, the PA is nearly entirely consumed, and the intensities of the relevant absorption bands remain constant, indicating the completion of the SO/PA copolymerization reaction.

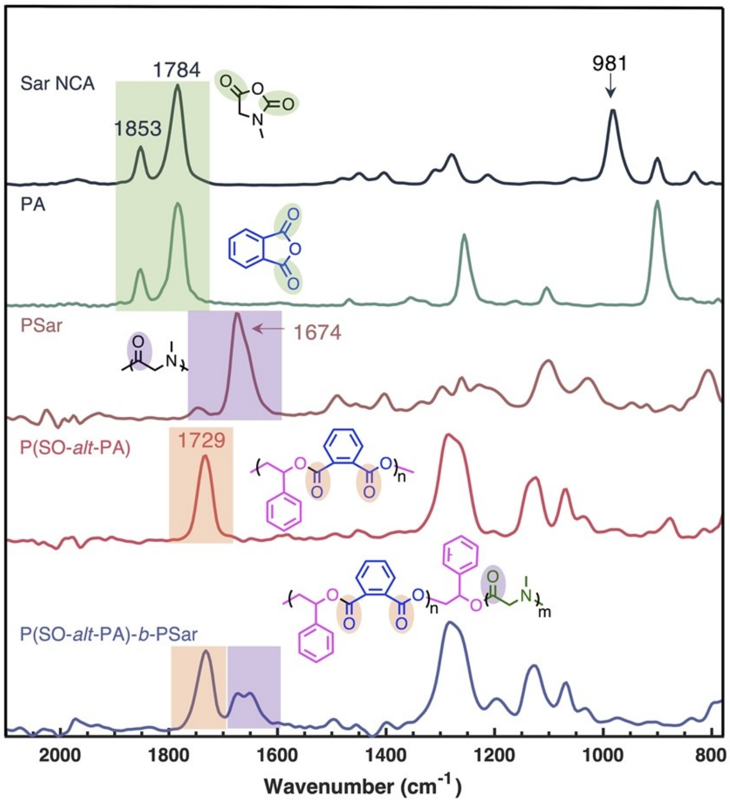

Fig. S18 Comparative ATR-IR spectra of Sar-NCA, PA, PSar, P(SO-*alt*-PA) and P(SO-*alt*-PA)-*b*-PSar copolymers, respectively.

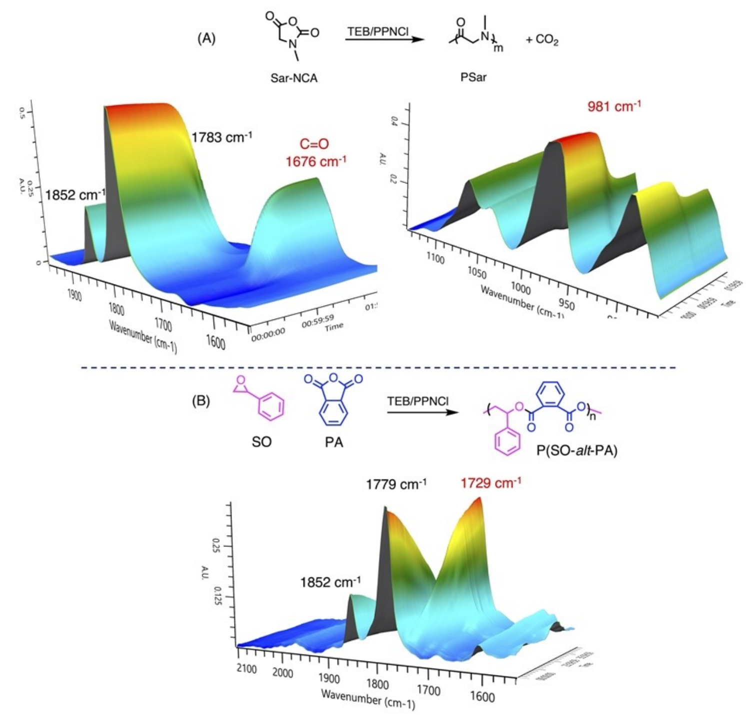

Fig. S19 *In-situ* ATR-IR spectroscopy monitoring: (A) ROP of Sar-NCA and (B) ROCOP of SO/PA.

^{1}H NMR monitoring of terpolymerization

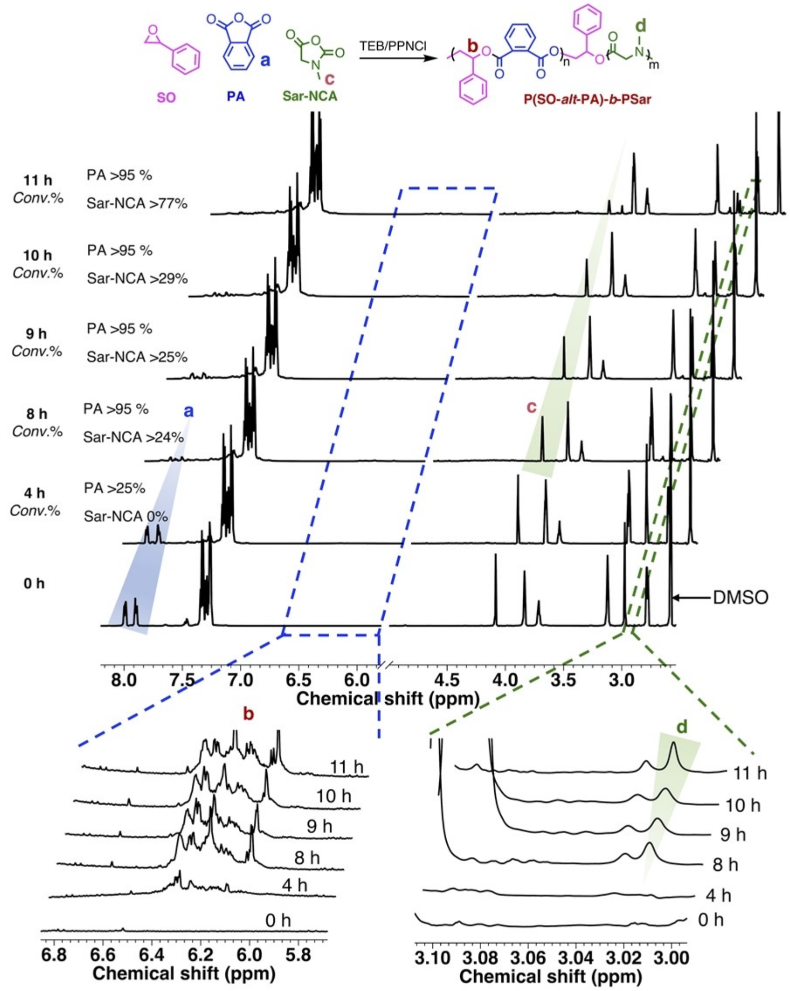

Fig. S20 Evolution of ^{1}H NMR spectra of the switchable copolymerization, the terpolymerization was performed in MeCN/SO (1/1, v/v) at 50 °C with a [SO]/[PA]/[Sar-NCA]/[TEB]/[PPNCl] feed ratio of 210/50/40/3/1. DMSO (2.6 ppm) was used as an internal standard to calculate monomer conversion.

Monomer adaptability

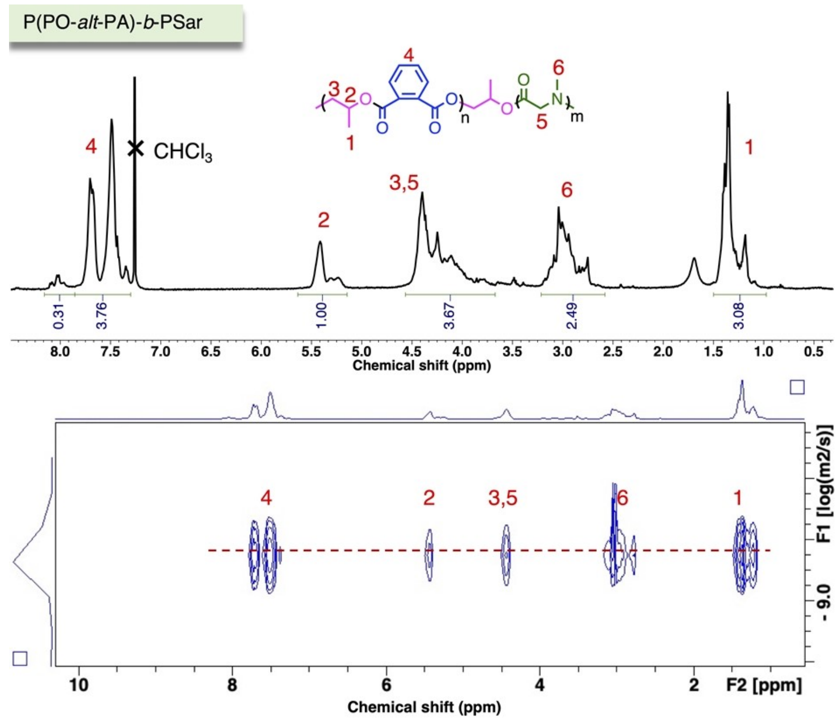

Fig. S21 ^{1}H NMR and ^{1}H DOSY NMR spectra of P(PO-*alt*-PA)-*b*-PSar in $CDCl_3$.

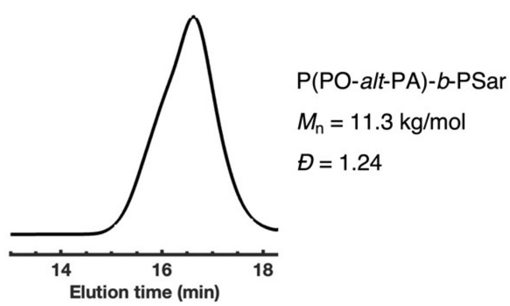

Fig. S22 SEC trace of P(PO-*alt*-PA)-*b*-PSar in DMF.

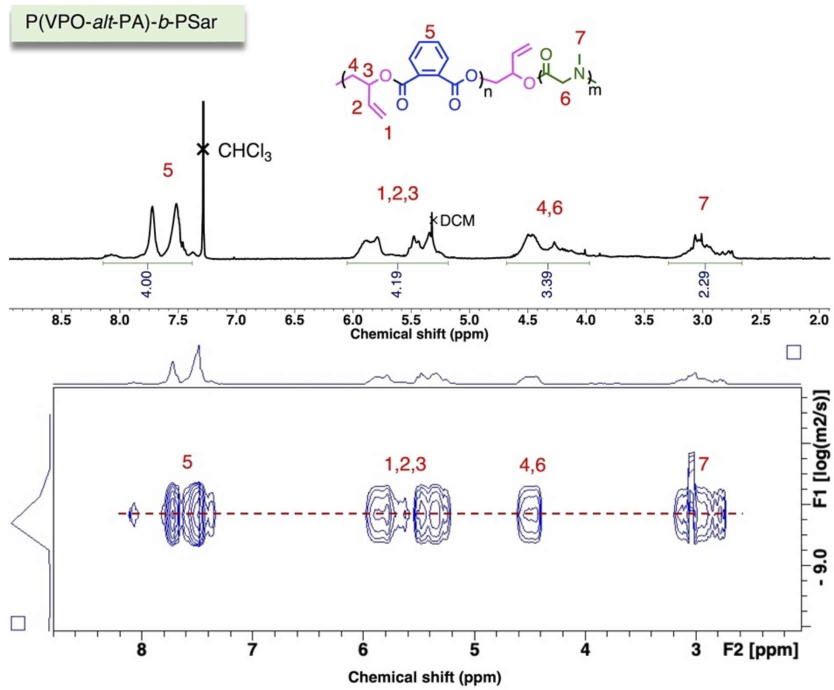

Fig. S23 [1]H NMR and [1]H DOSY NMR spectra of P(VPO-*alt*-PA)-*b*-PSar in $CDCl_3$.

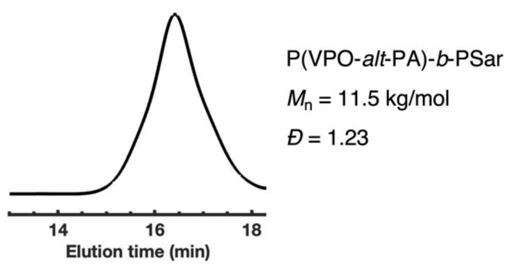

Fig. S24 SEC trace of P(VPO-*alt*-PA)-*b*-PSar in DMF.

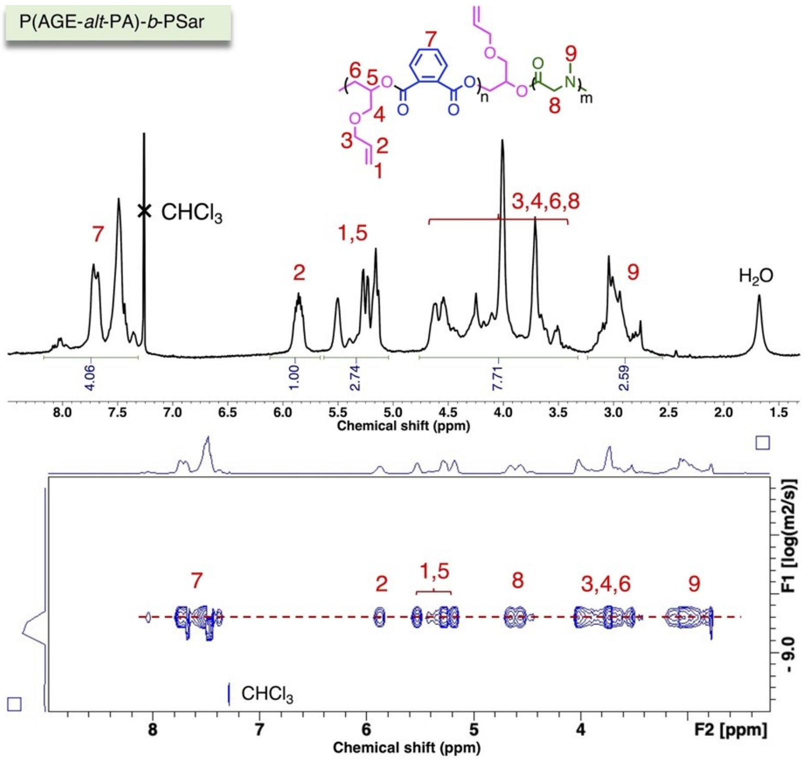

Fig. S25 ^{1}H NMR and ^{1}H DOSY NMR spectra of P(AGE-*alt*-PA)-*b*-PSar in $CDCl_3$.

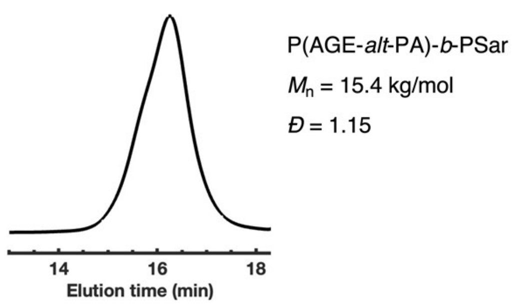

Fig. S26 SEC trace of P(AGE-*alt*-PA)-*b*-PSar in DMF.

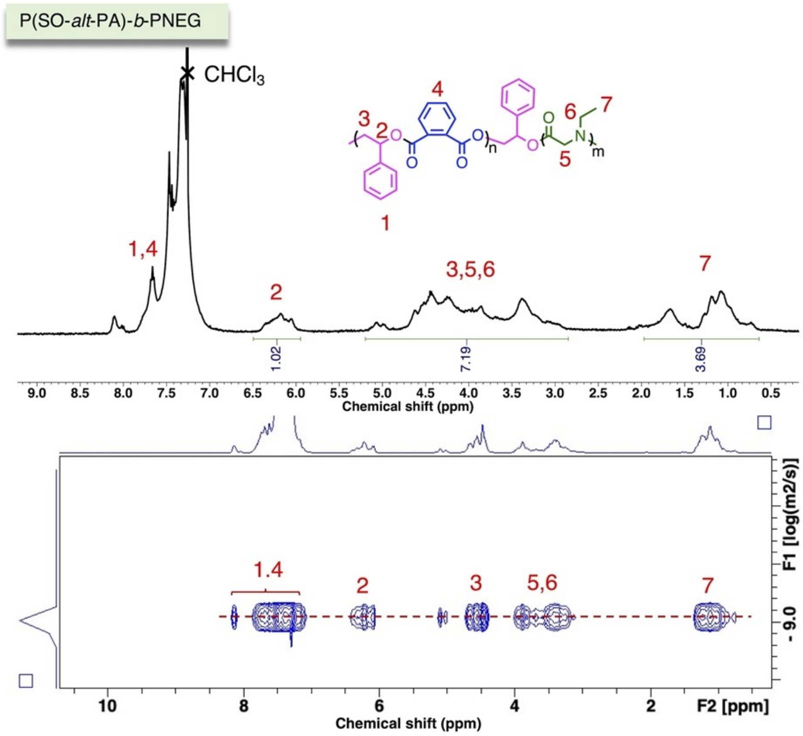

Fig. S27 [1]H NMR and [1]H DOSY NMR spectra of P(SO-*alt*-PA)-*b*-PNEG in $CDCl_3$.

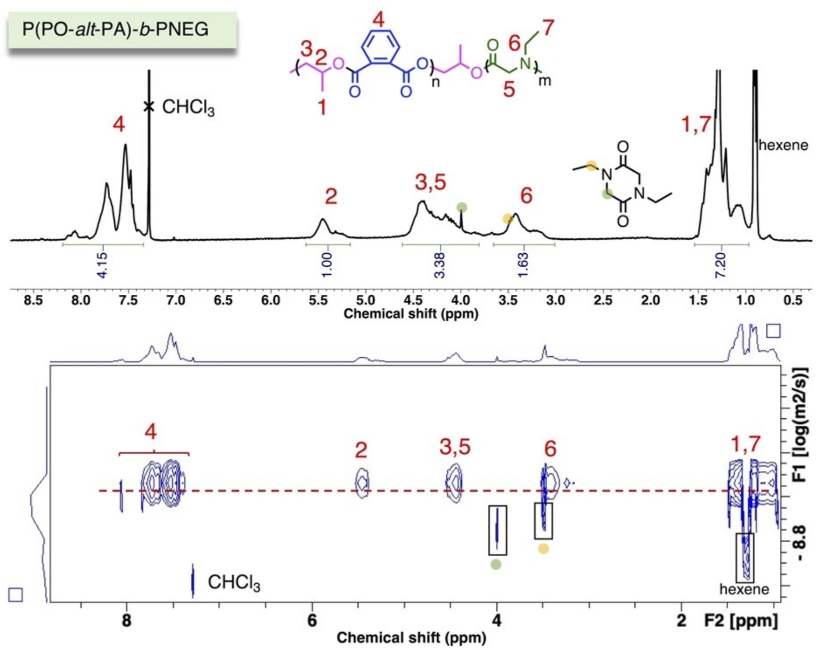

Fig. S28 [1]H NMR and [1]H DOSY NMR spectra of P(PO-*alt*-PA)-*b*-PNEG in $CDCl_3$.

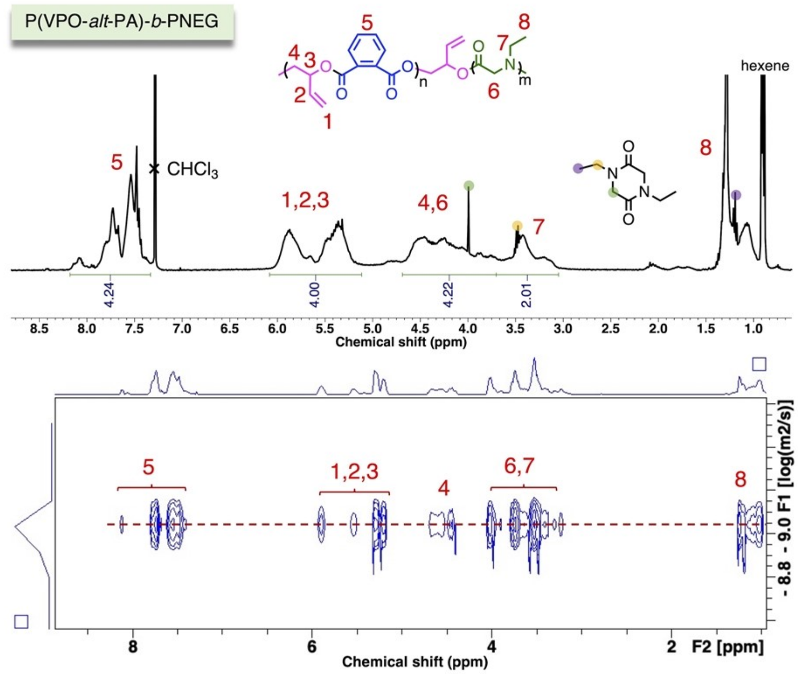

Fig. S29 ^{1}H NMR and ^{1}H DOSY NMR spectra of P(VPO-*alt*-PA)-*b*-PNEG in $CDCl_3$.

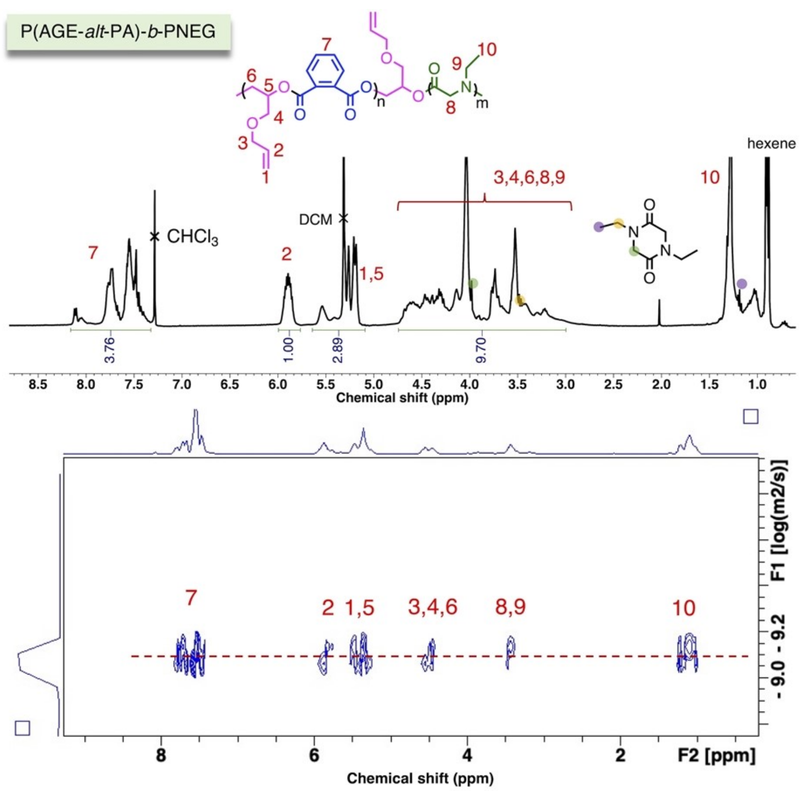

Fig. S30 ^{1}H NMR and ^{1}H DOSY NMR spectra of P(AGE-*alt*-PA)-*b*-PNEG in $CDCl_3$.

Density functional theory calculations (DFT)

All calculations were performed using the Gaussian 16 program package, with the computational methods adjusted according to the procedures outlined in reference.[6] Specifically, the following computational protocol was employed: initial geometry optimizations of all intermediates were conducted at 298.15 K and 1 atm using the B3LYPD3(BJ)/6-31G(d) level of theory, followed by transition state structure searches.[7-9] Vibrational analyses were performed at the same level of theory to ensure that all intermediates (IM) had no imaginary frequencies, and transition states (TS) exhibited only one imaginary frequency. Additionally, intrinsic reaction coordinate (IRC) calculations were carried out to ascertain the connectivity between transition states and intermediates.[10] The Gibbs free energy corrections for all structures at 323.15 K and 1 atm were obtained using the shermo program.[11]

Further, high-accuracy electronic energy calculations for optimized configurations of all intermediates were performed at 298.15 K and 1.013 × 10^5 Pa using the M06-2X/6-311G(d,p) level of theory.[12] Electronic energy calculations in solvent were conducted at the M05-2X/6-31G(d) level of theory, incorporating the SMD solvent model (acetonitrile).[13, 14] Finally, Gibbs free energies for all structures in solvent were computed and reported in the unit of kcal/mol, and bond lengths were displayed in Å. All structures were visualized using GaussView6.

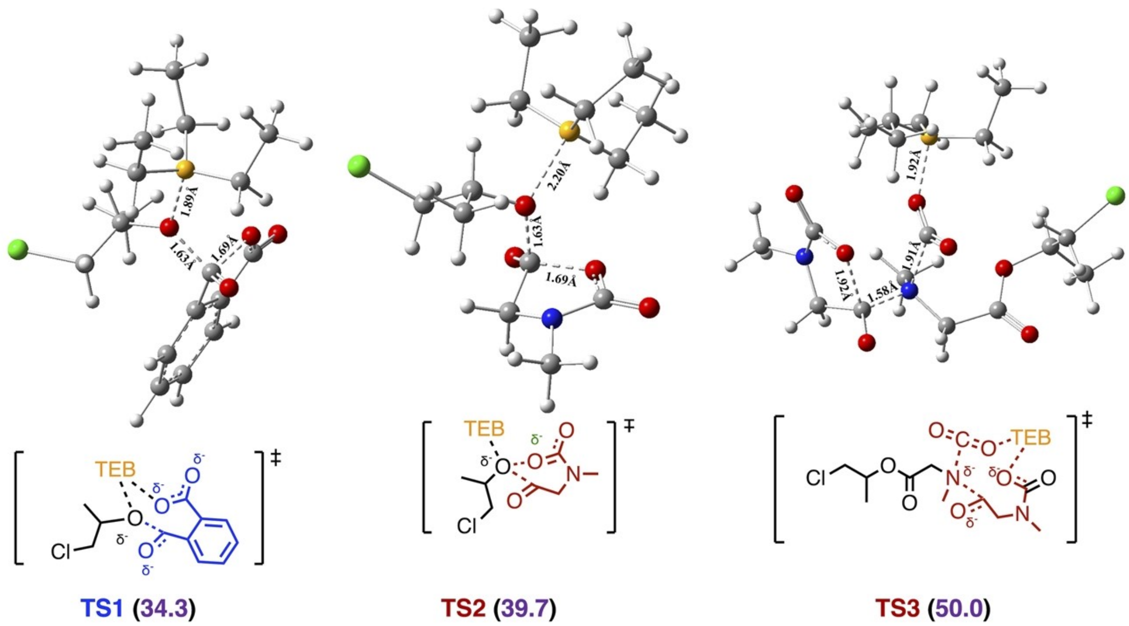

Fig. S31 The three-dimensional structures of optimized key transition states. Bond lengths are listed in Å. All energies are relative to the separated reactants in the unit of kcal/mol. In all cases, the following color-coding scheme applies: H = white, C = grey, O = red, B = blue, Cl = green.

References

1 Y. Wu, K. Chen, X. Wu, L. Liu, W. Zhang, Y. Ding, S. Liu, M. Zhou, N. Shao, Z. Ji, J. Chen, M. Zhu and R. Liu, *Angew. Chem. Int. Ed.*, 2021, **60**, 26063-26071.
2 S. H. Lahasky, X. Hu and D. Zhang, *ACS Macro Lett.*, 2012, **1**, 580-584.
3 C. Fetsch, A. Grossmann, L. Holz, J. F. Nawroth and R. Luxenhofer, *Macromolecules*, 2011, **44**, 6746-6758.
4 S. Ye, W. Wang, J. Liang, S. Wang, M. Xiao and Y. Meng, *ACS Sustainable Chem. Eng.*, 2020, **8**, 17860-17867.
5 J. Zhang, L. Wang, S. Liu, X. Kang and Z. Li, *Macromolecules*, 2021, **54**, 763-772.
6 J. Tang, M. Li, X. Wang and Y. Tao, *Angew. Chem. Int. Ed.*, 2022, **134**, e202115465.
7 T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51-57.
8 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456-1465.
9 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
10 K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363-368.
11 T. Lu and Q. Chen, *Comput. Theor. Chem.*, 2021, **1200**, 113249.
12 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2007, **120**, 215-241.
13 Y. Zhao, N. E. Schultz and D. G. Truhlar, *J. Chem. Theory Comput.*, 2006, **2**, 364-382.
14 M. A. V., C. C. J. and T. D. G., *J. Phys. Chem. B*, 2009, **113**, 6378-8396.

Cartesian Coordinates of Optimized Structures.

PO

E=-193.072007409 (a.u.)

C	0.15182000	-0.03933000	0.49059900
C	-1.04267400	0.61608400	-0.05962600
O	-0.82652000	-0.78887600	-0.24428900
H	0.15511200	-0.25934000	1.56078200
H	-0.95057800	1.22429000	-0.96036900
H	-1.87359100	0.88062600	0.59509100
C	1.50908800	0.10052000	-0.14874700
H	2.08624500	0.89644800	0.33670700
H	2.07617900	-0.83288700	-0.05875400
H	1.40938700	0.33823100	-1.21249400

PA

E=-532.883066397 (a.u.)

C	0.00000000	0.69574700	-0.17061700
C	0.00000000	-0.69574700	-0.17061700
C	0.00000000	-1.42627700	-1.35164600
C	0.00000000	-0.70153000	-2.54744800
C	0.00000000	0.70153000	-2.54744800
C	0.00000000	1.42627700	-1.35164600
C	0.00000000	1.14872700	1.24094800
C	0.00000000	-1.14872700	1.24094800
H	0.00000000	-2.51102900	-1.33841300
H	0.00000000	-1.23128000	-3.49518800
H	0.00000000	1.23128000	-3.49518800
H	0.00000000	2.51102900	-1.33841300
O	0.00000000	0.00000000	2.04190000
O	0.00000000	-2.25351100	1.70482200
O	0.00000000	2.25351100	1.70482200

Sar-NCA

E=-435.833048484 (a.u.)

O	0.78023800	1.08243200	0.00007400
C	0.46019500	-1.23573800	-0.00016600
H	0.59479800	-1.86655300	-0.88885200
H	0.59312500	-1.86531300	0.88970800
C	-0.60701900	0.83520400	-0.00032700
O	-1.42143300	1.71850400	0.00025000
C	1.47648200	-0.10130700	0.00010900
O	2.67083100	-0.17010000	0.00038200
N	-0.78906500	-0.51611000	-0.00178400
C	-2.09602700	-1.13770600	0.00071400
H	-2.22902700	-1.75984200	0.89373200
H	-2.84303600	-0.34305000	0.00075100
H	-2.23128600	-1.76188200	-0.89048200

TEB

E=-262.458441584 (a.u.)

B	-0.00046400	-0.00030800	-0.66120400
C	-1.58146900	-0.00521000	-0.63130300
C	-2.11537900	-0.62942000	0.67855700
H	-1.94555000	-0.61649000	-1.47247900
H	-2.01465100	0.99578400	-0.75984400
H	-3.21047600	-0.67573800	0.68529200
H	-1.73922400	-1.64946200	0.81685700
H	-1.80751700	-0.04474600	1.55374900
C	0.78584400	1.37139700	-0.63212700
C	0.51241100	2.14558400	0.67805500
H	0.43820800	1.99255400	-1.47297400
H	1.86930600	1.24618800	-0.76092100
H	1.01915200	3.11748800	0.68444800
H	-0.55910900	2.32908900	0.81701700
H	0.86582600	1.58697800	1.55306100
C	0.79437300	-1.36705200	-0.63092500
C	1.60431200	-1.51528300	0.67770500
H	1.50431800	-1.37790300	-1.47332300
H	0.14397000	-2.24297500	-0.75699000
H	2.19195900	-2.44050900	0.68485500
H	2.29986100	-0.67928600	0.81332300
H	0.94569500	-1.53952400	1.55416800

Cl^-

E=-460.266094636 (a.u.)

Cl	0.00000000	0.00000000	0.00000000

CO_2

E=-188.569240493 (a.u.)

C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.16912200
O	0.00000000	0.00000000	-1.16912200

IM1

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C	-2.32349000	-0.46989700	0.62593400
O	-0.27811800	0.56972200	0.79997600
H	-1.21917200	0.31596900	-1.03876300
H	-1.84015300	-1.44390900	0.58444400
H	-2.56776900	-0.21396200	1.65814100
C	-2.04995600	1.99370400	0.02688700
H	-1.34674700	2.70953300	-0.41006900
H	-2.99355200	2.03172100	-0.53005700
H	-2.23807800	2.29602000	1.06490500
B	1.07547700	0.11292600	0.21077400

C	1.45441000	1.15489000	-1.02338600
C	2.93665000	1.29798000	-1.40622400
H	1.09757700	2.15546300	-0.72437400
H	0.88805500	0.91070400	-1.94122600
H	3.10431300	2.02193500	-2.22162100
H	3.52972900	1.64019000	-0.54821500
H	3.37263200	0.34529300	-1.73101900
C	0.91460700	-1.45753700	-0.29559200
C	1.98507600	-2.02672700	-1.24134400
H	-0.05037900	-1.56800200	-0.82117900
H	0.83431500	-2.12154500	0.58449700
H	1.80497400	-3.08067400	-1.51223000
H	2.01831700	-1.45795200	-2.17975600
H	2.98987200	-1.97534500	-0.80507900
C	2.07585000	0.27261500	1.51297100
C	3.38662100	-0.52822100	1.53163300
H	1.49040000	-0.02253500	2.39953500
H	2.31429700	1.33939500	1.67318300
H	3.97962500	-0.36177100	2.44690400
H	3.18980100	-1.60686800	1.47204800
H	4.03571500	-0.27916800	0.68244300
Cl	-3.96008600	-0.69256000	-0.23449300

IM2

E=-1448.76803975 (a.u.)

C	2.67918400	0.42221200	-0.58133400
C	2.00182800	1.37494600	0.16823900
C	1.32279600	2.42481600	-0.43154200
C	1.33286500	2.47757000	-1.82675400
C	2.00600400	1.50736500	-2.58450300
C	2.69669200	0.46153300	-1.96854400
C	3.31114900	-0.53022300	0.35939600
C	2.18030500	1.03873800	1.59698500
H	0.79536800	3.15954000	0.16643100
H	0.79708800	3.27288800	-2.33671000
H	1.98051100	1.56891100	-3.66865700
H	3.21241800	-0.30243300	-2.54033700
O	2.97648700	-0.11239100	1.65402800
O	1.81043100	1.60454200	2.58834700
O	4.03810700	-1.46376900	0.15789900
C	-1.99001500	0.77445800	0.73393200
C	-1.74151900	1.49469100	2.06026100
O	-0.89031200	-0.01590600	0.40755700
H	-2.91631400	0.18632900	0.82217500
H	-1.62382200	0.74640800	2.85016900
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H	-2.35036500	1.18431700	-1.36393000
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C	-1.98953700	-2.81981000	-2.21877400
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C	-1.81295700	-2.25921700	1.31359200
C	-2.52011000	-3.60279700	1.07245900
H	-2.55931500	-1.59174000	1.77661600
H	-1.04853800	-2.40217500	2.09741500
H	-2.92345900	-4.04733700	1.99744100
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C	0.43401300	-2.02612700	-0.22238300
C	0.73875600	-3.52850000	-0.15714300
H	1.02774300	-1.54335000	0.56887600
H	0.82448400	-1.62910500	-1.17507900
H	1.81127500	-3.74357200	-0.28709800
H	0.44330600	-3.94676600	0.81328900
H	0.19799300	-4.09511800	-0.92556400
Cl	-3.63792300	2.87229900	-0.27047700
H	-2.56159400	2.17149300	2.32620000

TS1

E=-1448.73577064 (a.u.) -194.36 i cm^{-1}

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C	3.95978300	-1.14540000	0.56705700
C	4.72959700	-0.20493100	-0.12108700
C	4.15602200	0.56847400	-1.13989100
C	2.80389000	0.43202900	-1.46729200
C	0.58455400	-0.83289400	-0.98069800
C	1.60928400	-2.22599500	0.78995300
H	4.38160900	-1.78484100	1.33695800
H	5.78384300	-0.08419600	0.11593500
H	4.77366900	1.27484500	-1.68928800
H	2.36343500	0.99815600	-2.28278900
O	0.46534400	-2.07335700	0.15647300
O	1.84322100	-3.02865500	1.68455600
O	0.20532200	-1.10970400	-2.10071300
C	-0.11709000	1.27769900	0.58079000
C	0.83475100	0.99863400	1.74591400
O	-0.46941700	0.14861300	-0.22629000
H	-1.06348500	1.60276100	1.01216300
H	0.55190600	0.06194900	2.23183900

H	1.87895100	0.93142800	1.43741400
C	0.34057400	2.40636200	-0.34566800
H	1.35180400	2.26231100	-0.71785000
H	-0.35996000	2.51595000	-1.17157400
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C	-2.92703400	1.08055000	-0.72523100
C	-4.39350300	0.98348200	-1.18427100
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H	-2.85162400	1.92853600	-0.02424800
H	-4.76130300	1.93642800	-1.59299400
H	-4.50929700	0.22627800	-1.96792000
H	-5.06352900	0.70340800	-0.36296100
C	-2.47425300	-0.58227600	1.46945000
C	-3.90447500	-0.37974900	2.00551100
H	-1.82428700	0.06466800	2.07406500
H	-2.14234000	-1.60587900	1.69423400
H	-3.98141700	-0.61443800	3.07757000
H	-4.22987000	0.66101500	1.87828700
H	-4.63442200	-1.00897300	1.48406400
C	-2.49783400	-1.59919900	-1.06018300
C	-3.78409500	-2.39898400	-0.76869400
H	-1.65690100	-2.28196800	-0.91665000
H	-2.47741200	-1.33018200	-2.12513100
H	-3.88260900	-3.26186400	-1.44368800
H	-3.78319700	-2.79336400	0.25496700
H	-4.69601600	-1.79886100	-0.88073700
Cl	0.36542200	4.01782100	0.52826400
H	0.75156600	1.81017900	2.47599000

IM3

E=-1448.78332602 (a.u.)

C	1.41657900	1.22624100	0.71939200
C	0.60419300	1.90475300	-0.20197500
C	1.13931100	2.98904600	-0.90489500
C	2.45274600	3.40488700	-0.70456200
C	3.25125600	2.74394500	0.23026600
C	2.72727100	1.66803400	0.94489900
C	0.92132200	0.11478000	1.60722300
C	-0.83696000	1.51357300	-0.49642800
H	0.48109700	3.48738600	-1.60854300
H	2.85103100	4.24545600	-1.26738700
H	4.27320000	3.06764900	0.41089700
H	3.33510800	1.16804700	1.69488500
O	-1.18650400	0.42416000	0.10910200
O	-1.49417500	2.22736300	-1.25286400
O	0.47317500	0.34812800	2.70374600
C	1.71121400	-1.71536500	0.05539800
C	1.10964500	-1.22221700	-1.25275100

O	1.14763800	-1.18692000	1.27793800
H	1.48310500	-2.77989300	0.15684800
H	0.02234800	-1.22398300	-1.18825900
H	1.44374100	-0.21530000	-1.50927800
C	3.23129600	-1.55191900	0.14692300
H	3.54571600	-0.53787900	-0.09644100
H	3.58116900	-1.82431500	1.14337100
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C	-2.14834900	-1.81602600	0.72476600
C	-3.27931400	-2.70314900	1.27154100
H	-1.47137900	-1.59471700	1.56172800
H	-1.54911400	-2.42393100	0.02235400
H	-2.90456000	-3.64767200	1.69711700
H	-3.83168200	-2.18971900	2.06833000
H	-4.01308700	-2.96677700	0.49960400
C	-2.94935700	-0.53157000	-1.57647400
C	-4.20850700	-1.35801800	-1.88190300
H	-2.10301700	-0.98996300	-2.11963000
H	-3.06857100	0.46485000	-2.01920900
H	-5.07917300	-0.97180600	-1.33477700
H	-4.47159600	-1.35597900	-2.95180000
H	-4.08736700	-2.40735900	-1.58458100
C	-3.69814900	0.40215400	0.90532600
C	-4.26621000	1.71399000	0.34172700
H	-3.27720800	0.59459100	1.90647500
H	-4.54628400	-0.27993300	1.08220400
H	-5.01915600	2.16813800	1.00670900
H	-3.47873500	2.45240900	0.16643600
H	-4.75028100	1.54670100	-0.62962100
Cl	4.09124100	-2.65292900	-1.02337700
H	1.42578500	-1.90095500	-2.05111400

IM4

E=-1448.78369239 (a.u.)

C	1.76178000	1.31720400	0.66894400
C	0.53845000	1.40227000	-0.00999200
C	0.42057300	2.26956700	-1.10136400
C	1.49327600	3.06353100	-1.50050500
C	2.69856700	3.00900600	-0.79607400
C	2.82577600	2.14578600	0.28987900
C	1.99988200	0.41598100	1.85131100
C	-0.64641700	0.58709500	0.47084100
H	-0.53344800	2.30166400	-1.61554200
H	1.38747700	3.73315400	-2.35031600
H	3.53518900	3.63862900	-1.08821200
H	3.75704600	2.09963100	0.84786100
O	-1.60892100	0.56799400	-0.38546600
O	-0.55929400	0.03091900	1.56879000

O	2.14143400	0.86337000	2.96491700
C	2.38104900	-1.62507700	0.40940000
C	1.05380000	-1.94274000	-0.26696100
O	2.27677100	-0.90718000	1.66062500
H	2.82601400	-2.56465600	0.75001900
H	0.31660300	-2.25685700	0.47250600
H	0.64535900	-1.09167200	-0.81357200
C	3.40436500	-0.96401200	-0.52288400
H	2.97683600	-0.16928800	-1.12940400
H	4.25528500	-0.58352500	0.04304800
B	-3.08251000	-0.08164900	-0.29984600
C	-3.68680800	0.48711400	-1.72101900
C	-5.01098600	-0.10123900	-2.23161700
H	-2.92538000	0.32229600	-2.50273100
H	-3.79439500	1.58407600	-1.65416000
H	-5.32673800	0.33569600	-3.19259900
H	-4.93239400	-1.18545000	-2.38350600
H	-5.83251000	0.05770400	-1.52283200
C	-3.77099900	0.54246200	1.04427400
C	-5.23051600	0.13300800	1.29876800
H	-3.72318600	1.64439700	1.00441500
H	-3.17272900	0.25702100	1.92043600
H	-5.35089300	-0.95828500	1.27172500
H	-5.60470300	0.47542100	2.27655600
H	-5.90604100	0.54395100	0.53808500
C	-2.93813300	-1.71375500	-0.30845900
C	-2.62262500	-2.41313200	1.02430200
H	-2.17250400	-1.99630300	-1.05217600
H	-3.87451600	-2.14648300	-0.69818200
H	-2.47963500	-3.50017500	0.91046600
H	-1.72808400	-1.99170000	1.49086300
H	-3.44021700	-2.27190200	1.74360500
Cl	4.07478200	-2.19015000	-1.69696300
H	1.21267800	-2.75579900	-0.98274200

IM5

E=-1351.73527734 (a.u.)

O	3.73239500	-0.77944400	-0.91260200
C	1.77063600	-1.69115500	-0.03613800
H	0.78023800	-1.25713400	-0.25476700
H	1.64308000	-2.73214800	0.29013700
C	3.56871500	-0.28591700	0.40070800
O	4.33733400	0.51094200	0.88043100
C	2.69808900	-1.63062900	-1.22667100
O	2.62515900	-2.20476300	-2.27929500
N	2.47971200	-0.88719200	0.94026100
C	1.84964000	-0.41242400	2.15968100
H	1.75575200	-1.23178400	2.88345800

H	2.48087600	0.37127300	2.58038600
H	0.85851000	-0.01837700	1.92125000
C	-1.98090900	-0.84041500	0.63391600
C	-2.34081100	-1.77272000	-0.52753700
O	-0.83449900	-0.16234000	0.21538100
H	-2.82439900	-0.15356000	0.79354000
H	-2.49834600	-1.19685000	-1.43711100
H	-1.55831700	-2.51716500	-0.68849300
C	-1.71940200	-1.60035700	1.93649700
H	-2.59561700	-2.17411500	2.25731900
H	-0.87893300	-2.29489000	1.80794300
H	-1.45457200	-0.88792800	2.72380000
B	-0.89949700	1.37359500	-0.09966700
C	-1.29620400	2.12526300	1.32119100
C	-0.88097700	3.59668600	1.48281900
H	-0.82655300	1.56557500	2.14927400
H	-2.38200300	2.05398400	1.51475900
H	-1.17901600	4.02038900	2.45549800
H	0.20804400	3.70650800	1.40488000
H	-1.32010800	4.23456000	0.70680400
C	-2.02152800	1.60227500	-1.28987000
C	-2.54899500	3.03082600	-1.50408500
H	-2.90791300	0.97795600	-1.08339000
H	-1.62586600	1.22500800	-2.24979200
H	-3.28056300	3.09577400	-2.32539300
H	-3.04932500	3.40163500	-0.60025300
H	-1.74381900	3.73785500	-1.73381300
C	0.63962400	1.68498300	-0.60021500
C	0.88797700	2.95126200	-1.43444800
H	0.96564600	0.83074400	-1.21813800
H	1.33148500	1.70510100	0.25925500
H	1.94559700	3.06601100	-1.71645200
H	0.30666500	2.92943000	-2.36478300
H	0.59665900	3.86174600	-0.89720500
Cl	-3.89682000	-2.73167500	-0.25815400

TS2

E=-1351.68573521 (a.u.) -76.89 i cm^{-1}

O	-1.26386600	-1.72276900	-0.79879900
C	-2.59111300	0.22185500	-0.81442400
H	-2.69024500	1.25503200	-0.47861700
H	-3.17201400	0.11127000	-1.74499200
C	-2.27557100	-1.90822200	0.04162300
O	-2.55930100	-2.96016200	0.59637800
C	-1.13608600	-0.18232400	-1.15599600
O	-0.64391600	0.08670500	-2.25234900
N	-2.99339400	-0.72001100	0.19861100
C	-4.33406200	-0.74765300	0.72057200

H	-5.09437300	-0.82875400	-0.07652400
H	-4.41918300	-1.61865200	1.37297500
H	-4.54301400	0.16255100	1.29800300
C	-0.15821200	1.49543800	0.56725600
C	-0.20754600	2.51253200	-0.58148400
O	-0.19023900	0.16342700	0.07419800
H	0.82892700	1.60418900	1.02365300
H	0.48468100	2.22800100	-1.36878600
H	-1.19804500	2.64866400	-1.01041400
C	-1.17006500	1.73741800	1.69299700
H	-0.96708700	2.69732200	2.18000200
H	-2.20775400	1.74018300	1.35186900
H	-1.06332100	0.93616600	2.42921500
B	1.82332900	-0.71568100	0.08805600
C	1.80246000	-0.88331800	1.68612000
C	2.83060400	-1.91200300	2.19698900
H	0.80269500	-1.22880700	1.97813200
H	1.96948900	0.06895300	2.21537900
H	2.78747500	-2.03009600	3.28927900
H	2.64794900	-2.89795900	1.75425300
H	3.85927900	-1.62779400	1.94178000
C	2.68313000	0.47932700	-0.56212700
C	4.16828200	0.42210600	-0.14574900
H	2.31824500	1.46816100	-0.25950000
H	2.60959400	0.45279500	-1.65833900
H	4.75740900	1.22042700	-0.61922000
H	4.27658800	0.53877500	0.93989700
H	4.63680300	-0.53125600	-0.41525100
C	1.63384300	-2.02116200	-0.81159800
C	2.97027600	-2.62130800	-1.29685400
H	1.04500800	-1.75082600	-1.69393000
H	1.05706400	-2.79596600	-0.29245600
H	2.80811200	-3.52508700	-1.90112100
H	3.52566300	-1.91173500	-1.92294100
H	3.63124800	-2.90425800	-0.46660300
Cl	0.30052100	4.17902700	0.00731300

IM6

E=-1351.75041661 (a.u.)

O	-0.10625400	-0.66162100	1.54501200
C	1.11146500	-2.80505500	0.70025900
H	1.44858700	-3.75291800	0.26263700
H	1.12221100	-2.91884900	1.78702300
C	-0.72656800	-1.26303000	0.65624100
O	-1.81551200	-0.92724000	0.05115900
C	2.16532200	-1.73639700	0.40528900
O	3.20169300	-1.63077000	1.03034300
N	-0.21710400	-2.51135500	0.22333500

C	-0.57546800	-3.00968100	-1.09454200
H	-0.44645000	-4.09947800	-1.12598000
H	-1.61888700	-2.76528400	-1.28295100
H	0.03688500	-2.55995500	-1.89193900
C	2.48231100	0.30430100	-0.85717900
C	2.42892200	1.12841200	0.43104000
O	1.81356000	-0.96488100	-0.64249100
H	1.83013700	0.79039200	-1.58600300
H	1.43088200	1.07500200	0.86527900
H	3.17551100	0.80968500	1.15409200
C	3.87772600	0.11097500	-1.43687700
H	4.30603700	1.08328400	-1.69951800
H	4.52640800	-0.38502900	-0.71179100
H	3.82353400	-0.50176900	-2.34293500
B	-2.45344900	0.52474000	-0.14161200
C	-3.52110200	0.24644600	-1.35541500
C	-4.61731300	-0.78077900	-1.03749500
H	-2.97398500	-0.09019600	-2.25362400
H	-4.00486200	1.19395000	-1.64482200
H	-5.28152000	-0.99301300	-1.89128700
H	-4.17262800	-1.73254200	-0.71940400
H	-5.25269200	-0.43715400	-0.21058100
C	-1.24424000	1.51949900	-0.61821700
C	-1.70325400	2.91807100	-1.05532600
H	-0.69427400	1.05075500	-1.45427000
H	-0.51286200	1.63909400	0.19205500
H	-0.86625300	3.57800900	-1.33050900
H	-2.37806100	2.86677800	-1.91997100
H	-2.25855600	3.41776500	-0.24994600
C	-3.21554100	0.98842600	1.23226300
C	-2.34927600	1.57774300	2.35616100
H	-3.77644300	0.12985000	1.63726800
H	-3.99051400	1.72929200	0.96540200
H	-2.93127300	1.82601100	3.25914100
H	-1.55530700	0.87949100	2.63710100
H	-1.85514200	2.50314100	2.02969100
Cl	2.77827600	2.87658700	0.04948000

IM7

E=-1787.61949155 (a.u.)

O	-3.74620300	-1.96649000	-0.44573900
C	-3.51909900	0.24488200	0.27196000
H	-2.64187700	0.83638100	-0.01829000
H	-4.33936600	0.92620100	0.52742800
C	-3.24837000	-1.97850800	0.87389100
O	-2.94559500	-3.00784200	1.42803200
C	-3.91576900	-0.66727800	-0.86637400
O	-4.31314500	-0.38638600	-1.96366300

N	-3.22622500	-0.70227500	1.33005100
C	-2.53729400	-0.33728200	2.55947800
H	-3.05568400	0.50581400	3.02550500
H	-2.56780000	-1.19979700	3.22715200
H	-1.49614600	-0.06615200	2.36020300
O	0.41209300	-0.18649800	1.07348100
C	-0.01278200	-2.43365400	-0.19072400
H	-0.31882900	-3.25977100	-0.84200500
H	-0.38135800	-2.65957400	0.81079800
C	-0.20201900	-0.04958200	0.00447400
O	-0.60522300	1.04768300	-0.55344900
C	1.51055800	-2.42112400	-0.09106000
O	2.14311600	-3.12739200	0.66546900
N	-0.59338000	-1.20610700	-0.69652900
C	-0.84900500	-1.14000300	-2.13081600
H	-1.54889400	-1.93347900	-2.41355500
H	-1.29515200	-0.17569200	-2.36339500
H	0.07763300	-1.24963100	-2.71261200
C	3.44503200	-1.16860700	-0.84648400
C	3.66853500	-0.58111900	0.54823400
O	2.05385900	-1.55535900	-0.97626800
H	3.52844400	-0.35266400	-1.56862800
H	2.87248000	0.12140900	0.79166800
H	3.73640300	-1.35370400	1.31035400
C	4.39004200	-2.30088300	-1.22966300
H	5.41890000	-1.92896200	-1.25260500
H	4.31757900	-3.12056200	-0.51273700
H	4.13349500	-2.67663500	-2.22576200
B	-0.16381700	2.55686600	-0.22256500
C	-0.78701600	3.36405200	-1.50345700
C	-2.30871100	3.26162200	-1.69132000
H	-0.29803000	3.02371300	-2.43235300
H	-0.52435600	4.43016700	-1.40887300
H	-2.68188000	3.86000700	-2.53690800
H	-2.62084400	2.22573400	-1.87656900
H	-2.84381100	3.60488300	-0.79506300
C	1.46923800	2.58741700	-0.21367600
C	2.07860000	3.99707800	-0.18054400
H	1.85177800	2.06213000	-1.10641300
H	1.85349100	2.02695700	0.64951400
H	3.17749700	3.98591100	-0.12640400
H	1.80097500	4.57409400	-1.07196500
H	1.71680800	4.56391300	0.68828800
C	-0.86243900	3.03678700	1.18592400
C	-0.11662400	2.72322000	2.49271200
H	-1.88302600	2.62164500	1.25772900
H	-1.01999900	4.12804200	1.13562100
H	-0.68485900	3.01655900	3.39027200

H	0.11743200	1.65719100	2.56441400
H	0.84200200	3.25671700	2.53287900
Cl	5.24146000	0.33880400	0.58189700

TS3

E=-1787.54387433 (a.u.) -249.63 i cm^{-1}

O	-2.55822000	-0.35048400	1.35389300
C	-3.49287300	-1.98184600	-0.25207500
H	-3.37615400	-2.55021600	-1.18446000
H	-4.28999300	-2.46927700	0.33215400
C	-3.40696100	0.24164500	0.57182500
O	-3.87442200	1.37347800	0.67605900
C	-2.23739000	-2.09511300	0.62010000
O	-2.15884400	-2.92957400	1.50733100
N	-3.77277000	-0.59588300	-0.52581700
C	-4.97446900	-0.28029200	-1.26135100
H	-5.87900400	-0.72296400	-0.80606100
H	-5.08159200	0.80481100	-1.26182800
H	-4.90002700	-0.64475100	-2.29454400
O	0.37433000	-0.37311700	1.61646300
C	0.09522900	-2.78869300	0.24691100
H	-0.11589100	-3.71619500	-0.30295000
H	-0.05411400	-3.01339700	1.30163300
C	-0.20852000	-0.11901600	0.60580100
O	-0.47027900	0.72081700	-0.23348600
C	1.56881000	-2.48046200	0.06475900
O	2.42535400	-3.18105300	0.56378900
N	-0.88342200	-1.75016700	-0.11531500
C	-1.01919700	-1.58013700	-1.57611400
H	-1.28354000	-2.53539900	-2.04834100
H	-1.78937900	-0.83653400	-1.76753100
H	-0.07302100	-1.22585000	-1.97949900
C	3.17230100	-0.90610300	-0.85329300
C	3.70294800	-0.52047700	0.52784600
O	1.81544100	-1.41183800	-0.71633300
H	3.01528700	0.01311600	-1.42074100
H	2.95318200	0.05571700	1.06802300
H	4.00677900	-1.38951300	1.10617400
C	4.05480100	-1.86359400	-1.64284600
H	5.01741400	-1.38545800	-1.84697200
H	4.22207600	-2.78710700	-1.08593100
H	3.57810800	-2.10430500	-2.59866900
B	0.04001600	2.56936600	-0.27833700
C	-0.24955700	2.79059400	-1.84550400
C	-1.72161100	2.71928100	-2.27630700
H	0.33890900	2.06463700	-2.42946400
H	0.15968700	3.77784900	-2.12354200
H	-1.84788400	2.80370600	-3.36618200

H	-2.17712300	1.77658400	-1.95344600
H	-2.30972100	3.51985700	-1.81319600
C	1.59238600	2.47913000	0.13681300
C	2.23986900	3.87008900	0.25669900
H	2.16151600	1.89606800	-0.60388700
H	1.70815000	1.96132800	1.09854600
H	3.30475400	3.81175400	0.52056300
H	2.16538000	4.42786500	-0.68622500
H	1.73954700	4.47091000	1.02615800
C	-0.98081300	3.23544700	0.75785000
C	-0.79089100	2.91057000	2.24649400
H	-2.01368000	2.98791800	0.48856900
H	-0.88827000	4.32818800	0.61032600
H	-1.47667200	3.48941400	2.88067600
H	-0.99458300	1.85275300	2.43780900
H	0.23132000	3.12049900	2.58978800
Cl	5.16767900	0.54244300	0.34619300

IM8

E=-1599.03140320 (a.u.)

O	2.74976300	0.35281100	0.15614600
C	0.64107300	1.82750400	0.64315300
H	-0.01109800	2.63259400	1.00779300
H	0.87571300	1.18287500	1.48694600
C	2.97792200	1.61191800	-0.12909600
O	4.00627900	2.12023000	-0.57069500
C	-0.15589100	1.10150800	-0.44653800
O	-0.44716500	1.67897300	-1.49378300
N	1.85875600	2.42351600	0.15013100
C	1.78918900	3.74735100	-0.43319400
H	1.39053300	4.46599100	0.29835500
H	2.80467500	4.03405500	-0.70556200
H	1.14782500	3.76688400	-1.32401500
C	-1.37989300	-0.83318900	-1.19492200
H	-0.99393800	-1.82735700	-1.44384100
H	-1.34057100	-0.21337200	-2.09705700
C	-2.84264700	-0.99579600	-0.81619400
O	-3.59221200	-1.78814400	-1.35079200
N	-0.55783500	-0.18928200	-0.20245300
C	-0.26354700	-0.92796200	1.01970900
H	0.78190800	-0.79897900	1.29419500
H	-0.92255800	-0.62928100	1.84607200
H	-0.41663700	-1.99173800	0.82296000
C	-4.56390100	-0.17557100	0.67504300
C	-5.56382100	0.12885300	-0.44292100
O	-3.21116900	-0.13067700	0.15534400
H	-4.57345400	0.66545400	1.37292800
H	-5.21718300	0.97276500	-1.04066800

H	-5.74105000	-0.73327400	-1.08009800
C	-4.83389700	-1.47114600	1.42982100
H	-5.80930900	-1.41299600	1.92184200
H	-4.82688200	-2.32537700	0.75020000
H	-4.06603200	-1.61869000	2.19535700
B	3.88850200	-0.76404100	0.20408300
C	4.87078300	-0.38408600	1.45916600
C	4.16978600	-0.21528600	2.81551900
H	5.40568500	0.54814300	1.22371800
H	5.65053900	-1.15767900	1.56383200
H	4.85169100	0.08548200	3.62724200
H	3.38436300	0.55040300	2.75313200
H	3.68045800	-1.14602700	3.13484100
C	4.68650000	-0.79669700	-1.22537800
C	5.66377600	-1.97393500	-1.37333300
H	5.23637700	0.14179200	-1.36196200
H	3.96712300	-0.83521000	-2.06095600
H	6.21071400	-1.96263700	-2.32991200
H	6.41700700	-1.96687300	-0.57337200
H	5.14875300	-2.94270800	-1.30996300
C	3.05002900	-2.15106800	0.46877900
C	2.13614300	-2.58072600	-0.68927500
H	2.44795300	-2.07498000	1.38950200
H	3.76339700	-2.96626100	0.67389100
H	1.48780000	-3.44037600	-0.44790300
H	1.49154100	-1.74968300	-1.00115800
H	2.72577500	-2.86116800	-1.57075000

Cl	-7.16668600	0.61489600	0.27049800