Supporting Information

Oxidative Evolution of *Z/E*-Diaminotetraphenylethylene

Xin Li,[a] Yongbing Zhuang,[b] Qichao Ran,[a*] Xiangyang Liu [a*]

[a] College of Polymer Science and Engineering, State Key Laboratory of Polymer Material and Engineering, Sichuan University, Chengdu 610065, P. R. China.

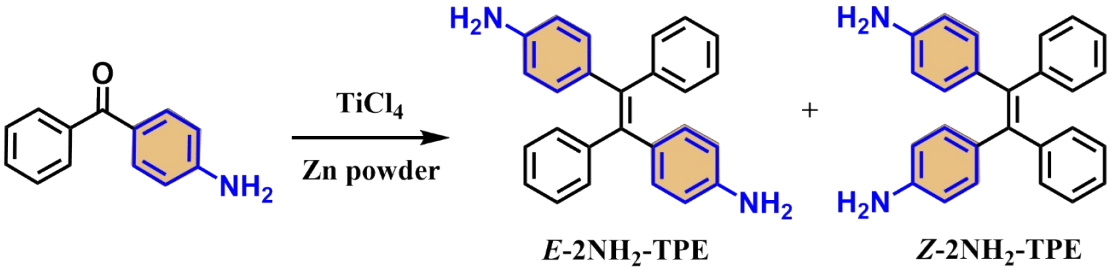
[b] State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, University of Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100190, P. R. China.

Materials and Methods

4-aminobenzophenone (98%), Titanium tetrachloride (99%), Tetrahydrofuran (THF, Extra Dry, 99.5%) and Zinc powder (AR) were purchased from Aladdin. Other organic solvents were purchased from Kelong Chemical Reagent Co, Ltd (Chengdu). All reagents were used without further purification unless otherwise stated.

The NMR spectra were recorded using an AV III HD 400 MHz NMR spectrometer (Bruker, Germany). High-resolution mass spectra (HRMS) were obtained on a LCMS-IT-TOF (ESI; Shimadzu, Japan). Absolute fluorescence quantum yields measurements were performed on an integrating sphere (Quanta-phi) of Fluorolog-3 (HORIBA, Japan). The crystallographic data collection was performed without any inert gas protection at room temperature on an Oxford Xcalibur EOS CCD area detector using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The data reduction and integration and global unit cell refinements were performed using the CrysAlis Pro program and the Olex2 software package, respectively.

Synthesis and Characterization



Scheme S1. Synthetic route of *E/Z*-2NH_2-TPE

The *Z/E*-2NH_2-TPE molecules were synthesized with McMurry coupling of 4-aminobenzophenone as reported. The mixture was separated by common column chromatography, and then further purified by recrystallization.

The *E*-2NH_2-TPE molecule: ^{1}H NMR (400 MHz, DMSO-*d6*) δ 7.13 – 7.07(m, 6H), 7.06-7.03 (d, J = 8.2 Hz, 4H), 6.98-6.96 (d, J = 8.2 Hz, 4H), 6.54-6.23 (d, J = 8.2 Hz, 4H), 4.96 (s, 4H). HRMS: calc. for [M+H$^+$] 363.1856, found 363.1848.

The *Z*-2NH_2-TPE molecule: ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.23 – 7.12 (m, 6H), 7.02 – 6.92 (m, 4H), 6.61 – 6.55 (m, 4H), 6.46 – 6.42 (m, 4H), 6.31 – 6.26 (m, 4H), 5.00 (s, 1H). HRMS: calc. for [M+H$^+$] 363.1856, found 363.1851.

The O-2NH_2-TPE molecule: ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62 – 7.60 (m, 2H), 7.37-7.34 (t, *J* = 7.3 Hz, 1H), 7.21 (dt, *J* = 12.4, 7.7 Hz, 4H), 7.15 – 6.99 (m, 3H), 6.83 – 6.75 (m, 4H), 6.47 – 6.40 (m, 4H), 5.06 (s, 4H). HRMS: calc. for [M+H$^+$] 379.1805, found 379.1834.

Theoretical calculations

All quantum-chemistry calculations were performed using density functional theory (DFT) via the Gaussian 16 suite of programs.

In the calculation of simulated ^{1}H NMR spectrums, the optimized ground state conformation of *Z/E*-2NH_2-TPE molecules were calculated in gas phase at B3LYP/6-31+G (d,p) level corrected with Grimme dispersion and BJ damping. ^{1}H NMR spectrums were determined in DMSO solvent at B3LYP/6-311+G (2d,p) level by the scaling method with the aid of Multiwfn package. Scaling method: the slope parameter was -1.0422 and intercept parameter was 31.7838.

The optimized conformation of cyclic intermediates, transition states, and ground

state were calculated with spin polarization and symmetry breaking in gas phase at M06-2X/6-311(d,p) level. The transition states gave an accurate vibration mode with a false frequency value of -1046. The intrinsic reaction coordinate path in the potential energy surface of ground state have been determined with the same level.

In the calculation of rearrangement reaction, the transition state was optimized with spin polarization and symmetry breaking in gas phase at M06-2X/6-311(d,p) level. The transition states gave an accurate vibration mode with a small false frequency value of -106. As for the nucleophilic rearrangement reaction, a small false frequency value of -33 was calculated at M06-2X/6-311(d,p) level, whereas -40 for B3LYP/6-31G(d) level corrected with Grimme dispersion and BJ damping. The intrinsic reaction coordinate paths were further determined at Figure S11-S12.

In the calculation of oxygen, the conformation was optimized with singlet, triplet and quintet quantum state. Atomic orbital binding energy of -150.2439371 Hartree, -150.3039478 Hartree and -150.105837 Hartree were calculated for singlet, triplet and quintet quantum state, correspondingly. Oxygen with triplet quantum state was employed.

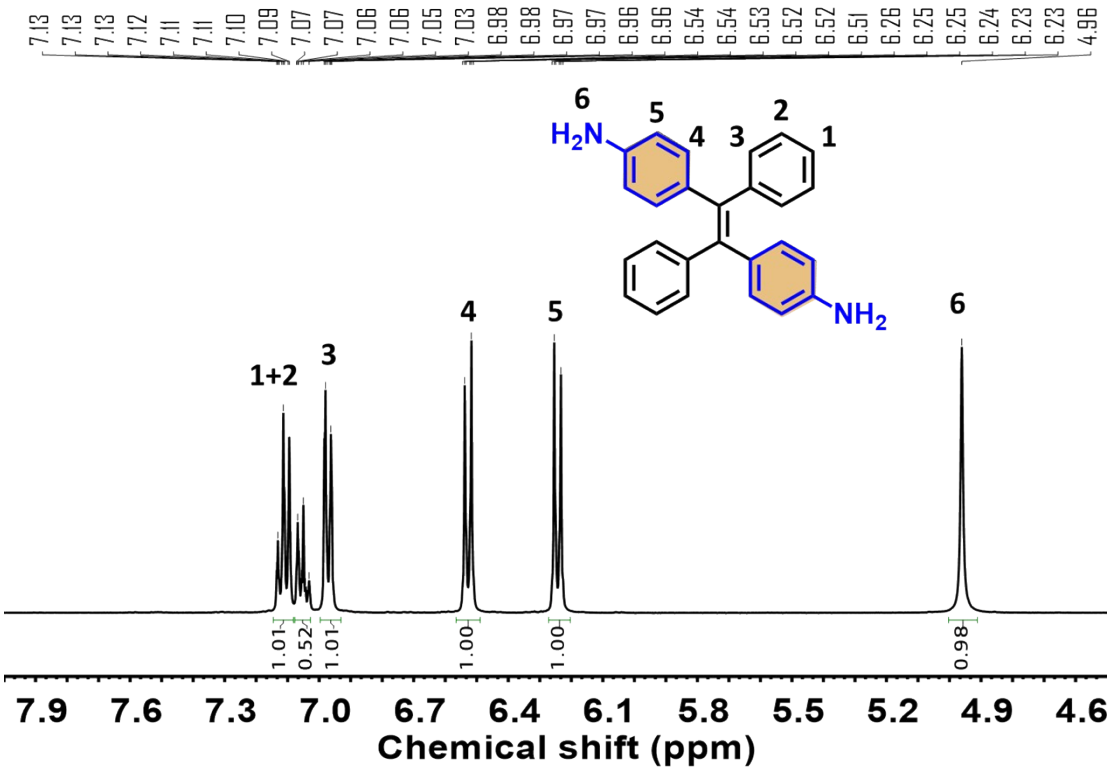


Figure S1. ^{1}H NMR spectrum of *E*-2NH$_2$-TPE in DMSO-d_6.

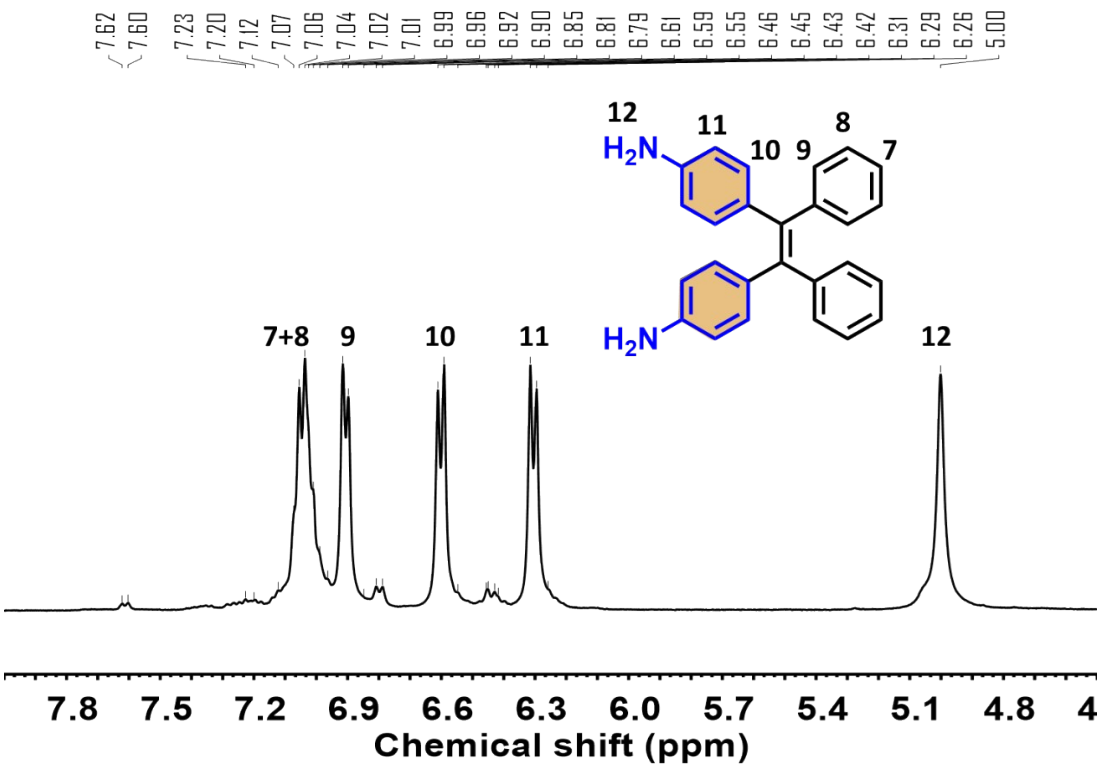


Figure S2. ^{1}H NMR spectrum of *Z*-2NH$_2$-TPE in DMSO-d_6.

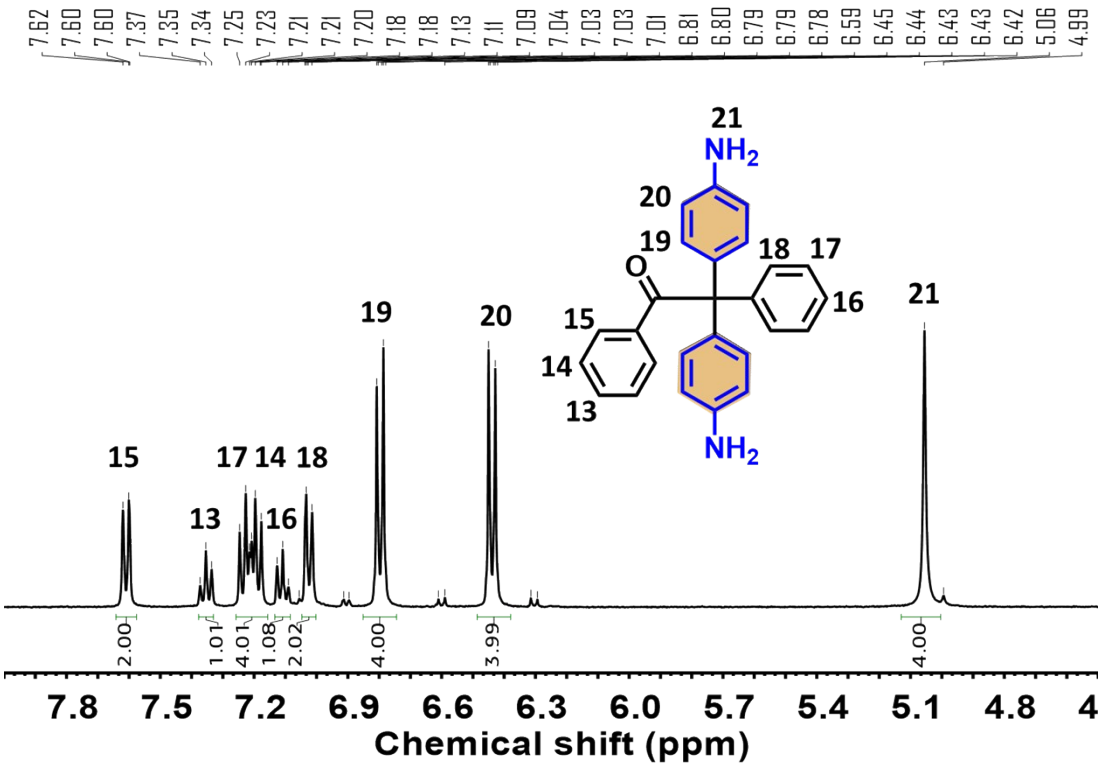


Figure S3 ^{1}H NMR spectrum of *O*-2NH$_2$-TPE in DMSO-d_6.

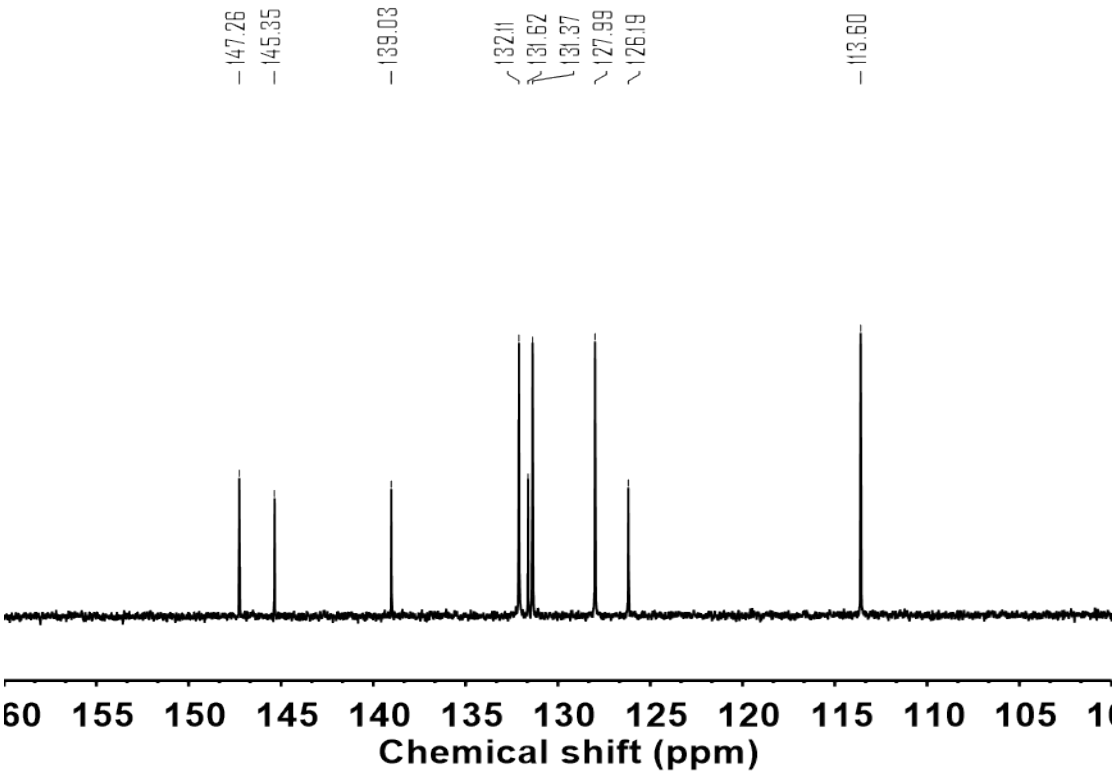


Figure S4. ^{13}C NMR spectrum of *E*-2NH$_2$-TPE in DMSO-d_6.

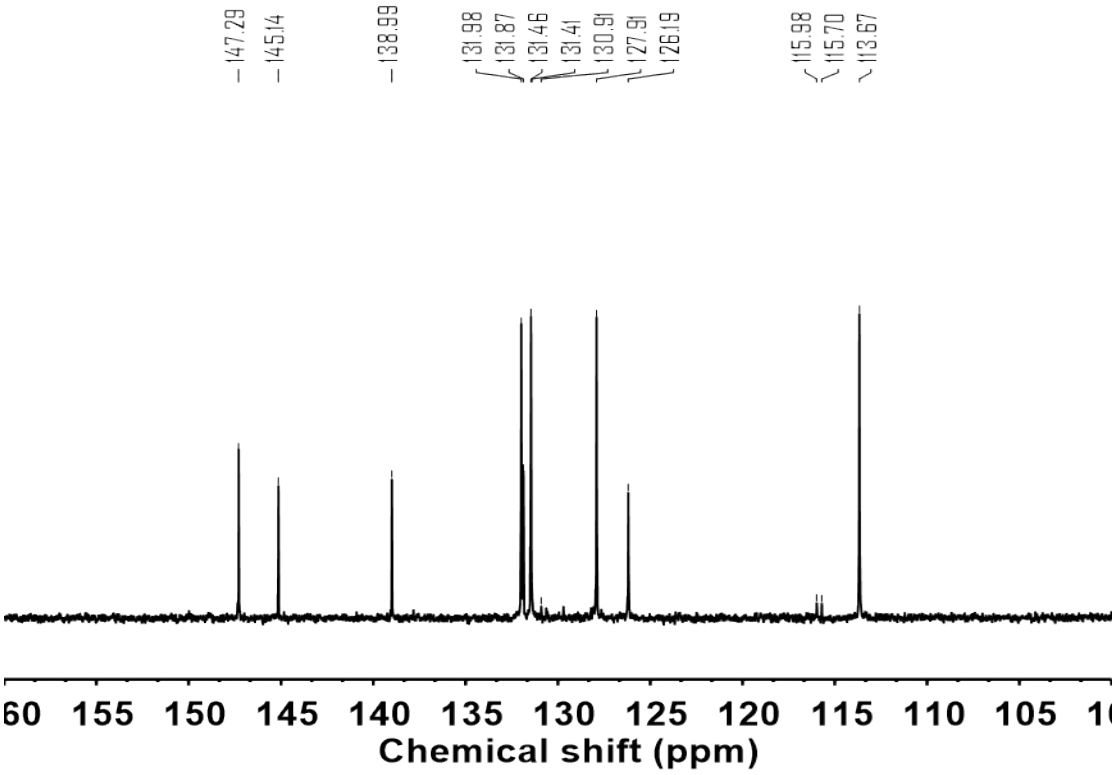


Figure S5. ^{13}C NMR spectrum of *Z*-2NH$_2$-TPE in DMSO-d_6.

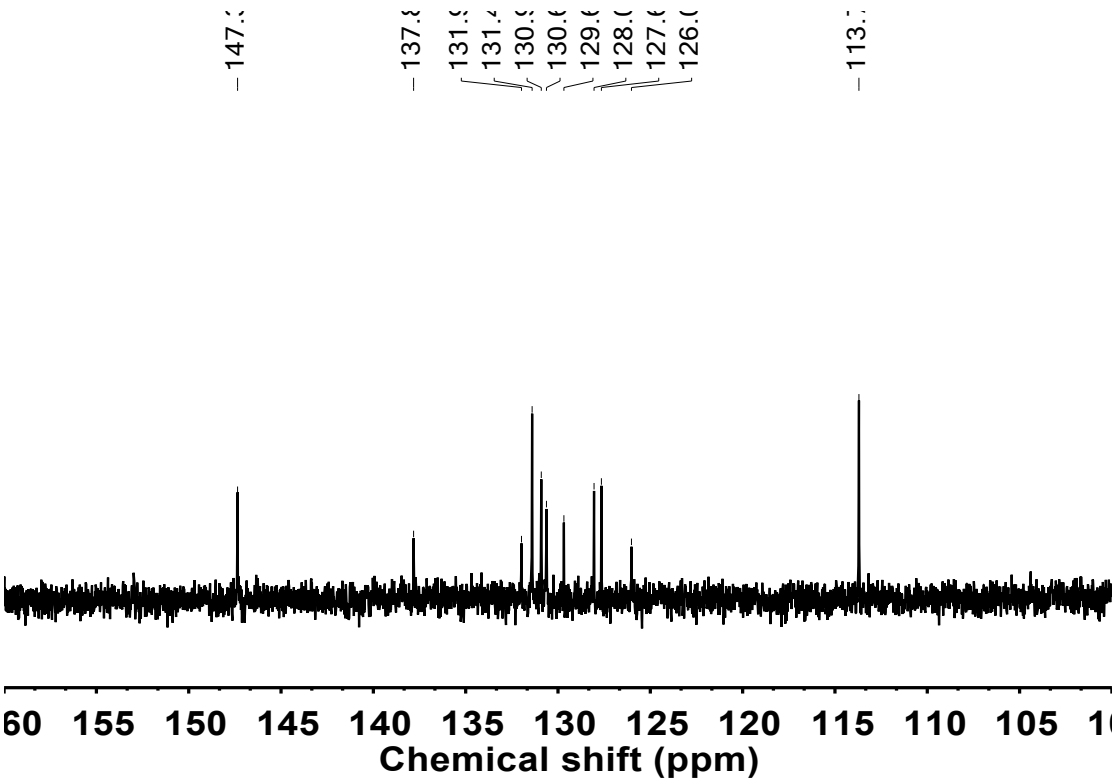


Figure S6. ^{13}C NMR spectrum of *O*-2NH$_2$-TPE in DMSO-d_6.

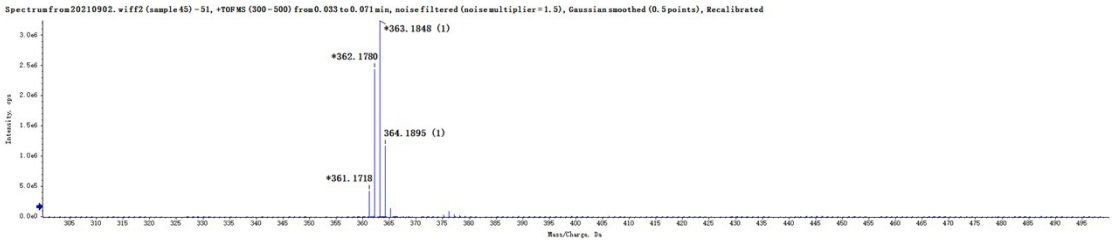


Figure S7. High-resolution mass spectrum of *E*-2NH$_2$-TPE.

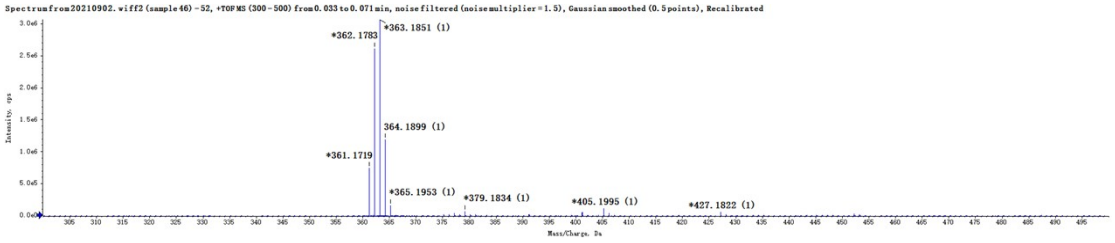


Figure S8. High-resolution mass spectrum of *Z*-2NH$_2$-TPE.

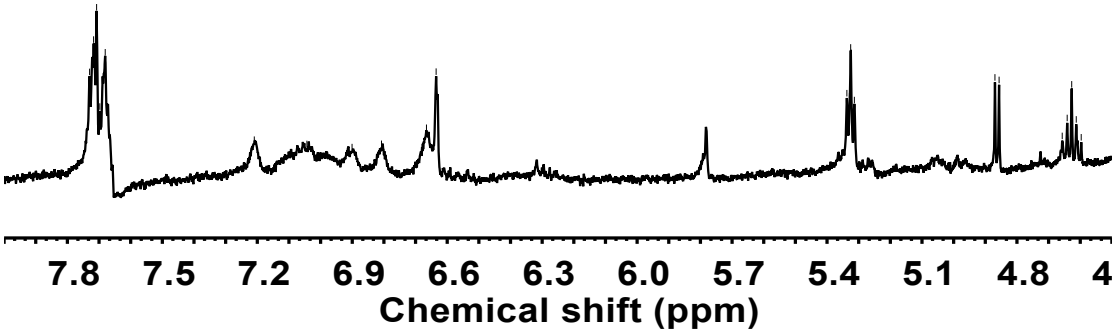


Figure S9 ^{1}H NMR spectrum of compounds then derived from *E*-2NH_2-TPE molecule.

As for *E*-2NH_2-TPE molecule, there were a new distinct dot during unfolding process detected by TLC. The derived dot was afterward collected and characterized with ^{1}H NMR spectrum as shown in Figure S9. Its peaks could not directly decipher the derivative structure. However, there existed some characteristic peaks. They belonged to neither the *E*-2NH_2-TPE molecule's peaks nor the *Z*-2NH_2-TPE molecule's peaks. In particular, the resonance at δ 7.68-7.73 ppm might result from phenyl proton connected with electron-withdrawing group. This is because the electron-withdrawing effect reduced the density of the electron cloud. The shielding effect was weakened, and the chemical shift moved to a low field.

Table S1. Crystal data and structure refinement

	E-2NH_2-TPE	*Z*-2NH_2-TPE	O-2NH_2-TPE
CCDC number	2120059	2120060	2120061
Formula	$C_{26}H_{22}N_2$	$C_{26}H_{22}N_2$	$C_{26}H_{22}N_2O$
Formula weight	362.45	365.45	378.45
Crystal system	triclinic	triclinic	tetragonal

Space group	P-1	P-1	$P4_32_12$
a /Å	6.1471(3)	9.1427(9)	10.1318(5)
b /Å	17.7972(9)	10.2655(10)	10.1318(5)
c /Å	20.5612(10)	11.2401(11)	39.042(4)
α /°	76.086(4)	76.016(8)	90
β /°	81.665(4)	84.388(8)	90
γ /°	86.606(4)	76.867(9)	90
Volume /$Å^3$	2159.65(18)	995.86(18)	4007.7(6)
Z	4	2	8
ρ_{calc} /$g*cm^{-3}$	1.115	1.209	1.254
μ /mm^{-1}	0.065	0.071	0.077
Temperature /K	293.15	293.15	293.15
2Θ range for data collection /°	6.076 to 52.74	5.78 to 52.732	5.686 to 52.742
Reflections collected R_1/ R_w	0.0546/0.1201	0.0611/0.1032	0.0564/0.0913
Reflections collected	17610	7741	8119
Rint	0.0218	0.0378	0.0351
F (000)	768.0	384.0	1600.0

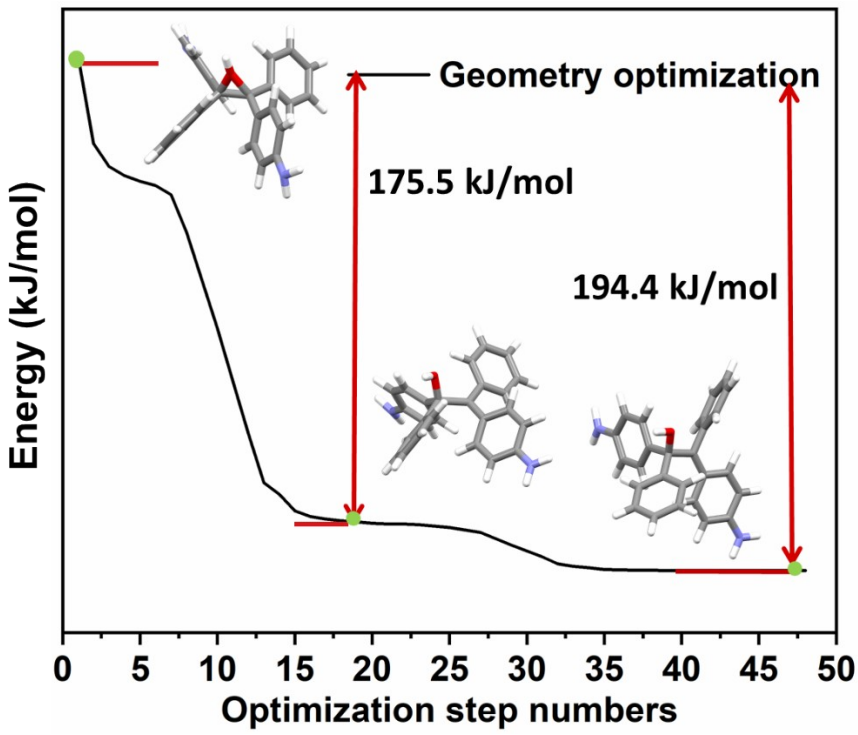


Figure S10 the geometry optimization curve of epoxy isomer added with hydrion.

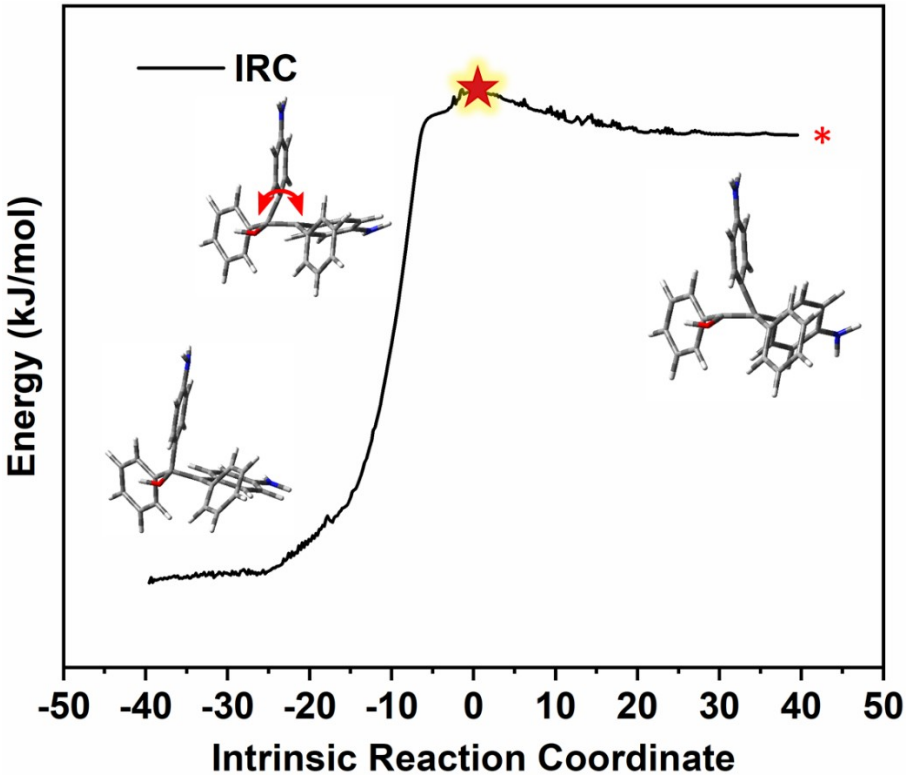


Figure S11 IRC curve of O-2NH_2-TPE was calculated in the S_0 at M06-2X/6-311G(d,p) level.

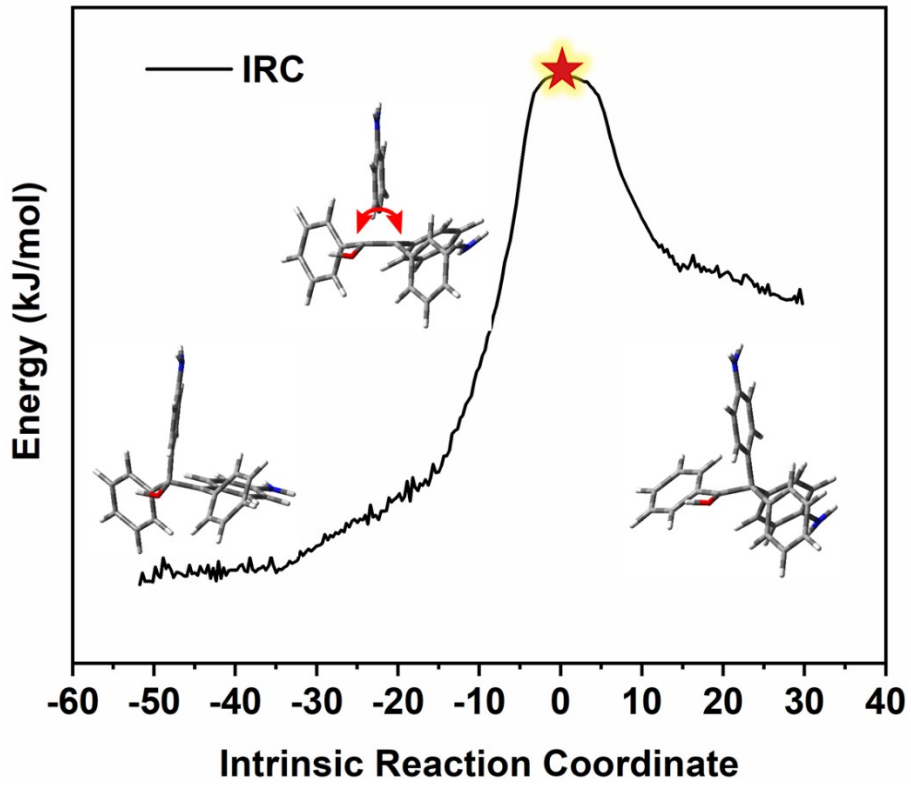


Figure S12 IRC curve of O-2NH_2-TPE was calculated in the S_0 at B3LYP/6-31G(d) level corrected with Grimme dispersion and BJ damping.

The optimized ground state and special points of *Z/E*-2NH_2-TPE molecular structure were in xyz format at M06-2X/6-311G (d,p) level unless otherwise stated.

Ground state of *E*-2NH_2-TPE molecular structure

C	-2.24652000	3.10648000	-1.32796200
C	-2.64187300	2.78560500	-0.07093700
C	-1.63031000	4.42435500	-1.65799900
C	-0.48642100	4.48503000	-2.45978200
C	-2.19882600	5.62164200	-1.21235700
C	0.09583800	5.70676800	-2.77530800
H	-0.05389100	3.56276500	-2.83220500
C	-1.62438900	6.84316500	-1.53743600
H	-3.09259500	5.58551000	-0.60008500
C	-0.47044000	6.89030000	-2.31383400
C	-2.28944600	3.60360100	1.12041600
C	-0.99521600	4.09350400	1.32253100
C	-3.24966800	3.88986300	2.09589300
C	-0.67834200	4.85810500	2.43248900
H	-0.22587900	3.87273100	0.59131900
C	-2.94613400	4.66326200	3.20495400

H	-4.25603200	3.50251500	1.97697200
C	-1.65221600	5.16217100	3.39087500
H	0.33295100	5.22815800	2.56397300
C	-2.39192800	2.17573400	-2.47937100
C	-2.86641800	2.63606700	-3.71171100
C	-2.04089300	0.82545400	-2.38420000
C	-3.02437000	1.78129600	-4.79088000
H	-3.12323400	3.68440500	-3.82122900
C	-2.18356900	-0.03484600	-3.45953600
H	-1.65358000	0.44451600	-1.44604500
C	-2.68948200	0.42726300	-4.68009600
H	-3.40154700	2.16186400	-5.73426700
C	-3.47039600	1.57852900	0.21612500
C	-3.13533100	0.72670800	1.27294900
C	-4.61563000	1.29427100	-0.53398000
C	-3.90118300	-0.40003800	1.54748300
H	-2.26321500	0.95389600	1.87651000
C	-5.38881000	0.17609000	-0.25169600
H	-4.88989900	1.95597500	-1.34758600
C	-5.03028100	-0.68010600	0.78506700
H	-3.61847300	-1.05748700	2.36133600
H	-2.07927500	7.76094900	-1.18403400
H	0.98998700	5.73448200	-3.38700600
H	-3.71429400	4.88643500	3.93790000
H	-1.89525100	-1.07612000	-3.36213400
H	-6.27476800	-0.02695800	-0.84176200
N	-2.78804300	-0.42438100	-5.77821200
H	-2.87912100	-1.40245700	-5.54786100
H	-3.45710600	-0.13824800	-6.47708400
H	-0.02064200	7.84374300	-2.56417900
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H	-1.95418000	5.86360300	5.27676500
H	-0.37846600	6.00435000	4.73492600
H	-5.63173800	-1.55471000	1.00282000

Ground state of *Z*-2NH_2-TPE molecular structure

C	-2.25208600	3.10509300	-1.33640500
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C	-0.50288900	4.49206700	-2.47351100
C	-2.20780500	5.62031200	-1.20861100
C	0.07879900	5.71536100	-2.78233700
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H	-3.09998600	5.58089400	-0.59417500
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C	-2.25652700	3.60258800	1.10787600
C	-0.94266600	4.03941300	1.30132400
C	-3.21763300	3.92718500	2.07058900
C	-0.60540400	4.80318100	2.41110700
H	-0.18702000	3.78031700	0.56855100
C	-2.88340500	4.70123400	3.17477500
H	-4.23383900	3.57039600	1.94233500
C	-1.57589000	5.14368200	3.34805600
H	0.41821600	5.13255900	2.54493200
C	-2.40885800	2.18197900	-2.49275100
C	-2.89253700	2.64982900	-3.71828500
C	-2.04995300	0.83266900	-2.41054000
C	-3.04908900	1.80390800	-4.80510900
H	-3.15593800	3.69754700	-3.81752300
C	-2.19034100	-0.01812900	-3.49356600
H	-1.65852900	0.44632200	-1.47629600
C	-2.70312500	0.45195300	-4.70860000
H	-3.43207500	2.19086900	-5.74354400
C	-3.45042100	1.57363000	0.23216900
C	-3.13052500	0.75153600	1.31682100
C	-4.58065500	1.24091600	-0.52152800
C	-3.87973500	-0.37556500	1.61639300
H	-2.27303100	0.99957100	1.93338100
C	-5.34328400	0.12465300	-0.22343100
H	-4.86022200	1.86913900	-1.35964500
C	-4.99876300	-0.71001200	0.84653100
H	-3.60677900	-1.00026600	2.46039400
H	-2.08604600	7.75964900	-1.16447900
H	0.97013900	5.74704200	-3.39791400
H	-3.64411700	4.95585100	3.90341700
H	-1.89341900	-1.05806300	-3.40752100
H	-6.22222000	-0.10507300	-0.81651100
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H	-6.33463900	-2.18298500	0.41725900
H	-5.32027700	-2.52819100	1.70093300
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H	-2.87855000	-1.37097900	-5.59491000
H	-3.46945500	-0.10211900	-6.51016700
H	-0.03400900	7.85092700	-2.55347400
H	-1.31322700	5.74263000	4.21193400

Transition state of isomerization

C	-1.22965300	1.24908600	-1.12157700
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C	-2.51113900	1.06717200	-3.18445200
C	-3.30627800	2.14783400	-2.81114100
C	-3.07995900	2.76623200	-1.58404500
C	-2.06272500	2.32735500	-0.75135800
H	-0.88723400	-0.22459900	-2.66080500
H	-2.68339700	0.57042500	-4.13215200
H	-3.71094100	3.58872400	-1.26728600
H	-1.92874500	2.79131400	0.21819900
C	-0.18932200	0.74173800	-0.24238800
C	0.18645300	-0.69285900	-0.35822500
C	1.24487200	-1.05082700	-1.28821400
C	1.29030800	-2.31267800	-1.91998600
C	2.22479600	-0.10473400	-1.65677600
C	2.28054800	-2.61782000	-2.84024000
H	0.51233700	-3.03714500	-1.71224200
C	3.21634700	-0.42120000	-2.57154500
H	2.20799500	0.87823300	-1.20137000
C	3.25710100	-1.67977300	-3.16623700
H	2.28231100	-3.59042200	-3.31872100
H	3.96418800	0.32131500	-2.82449800
C	-0.51989600	-1.65442000	0.45749000
C	-1.79001300	-1.35013300	0.99763700
C	0.04260800	-2.89594700	0.83278700
C	-2.46556200	-2.23666300	1.81165100
H	-2.25487500	-0.40270700	0.75126900
C	-0.62779100	-3.77994600	1.65471300
H	1.04289000	-3.14636700	0.50149700
C	-1.90137900	-3.47345000	2.15406700
H	-3.44910900	-1.97874400	2.19028400
H	-0.16090000	-4.71998000	1.93009200
C	0.49289000	1.55259500	0.74112200
C	1.15000600	0.95561300	1.84077100
C	0.62332700	2.95468800	0.61569400
C	1.84308300	1.70617400	2.76907800
H	1.09367000	-0.11898800	1.96829800
C	1.32393400	3.70586500	1.53830200
H	0.19868900	3.45125700	-0.24802200
C	1.93632500	3.09911600	2.64403400
H	2.32740600	1.21489700	3.60655200
H	1.42217200	4.77739200	1.39847500
N	2.67925000	3.84878100	3.54710700

H	2.43182000	4.82483600	3.60496500
H	2.80467800	3.42909700	4.45565700
N	-2.60407100	-4.38874100	2.92698100
H	-2.03959100	-5.07399900	3.40574800
H	-3.31796900	-3.99461200	3.52062500
H	4.03105900	-1.92203300	-3.88426200
H	-4.10007400	2.49487000	-3.46129400

Cyclic intermediates of *E*-2NH_2-TPE molecular structure

C	0.32065900	-0.64310700	0.03601100
C	-0.22849700	0.72313000	0.00905900
C	1.65651900	-0.84252100	-0.13759900
C	2.27917800	-2.14914300	-0.01835500
C	2.53844100	0.36070000	-0.45135900
C	3.61098700	-2.30596600	-0.06566400
H	1.64543900	-3.00393100	0.18062200
C	4.01506900	0.06947400	-0.40579400
H	2.29336200	0.67142400	-1.48563500
C	4.51155600	-1.16748600	-0.25997200
C	0.60941100	1.78627000	0.16677000
C	2.08293300	1.51378300	0.45191800
C	0.16011600	3.16504400	0.07726600
C	2.95382600	2.73916800	0.38686900
H	2.15274900	1.13689400	1.49132500
C	1.02354200	4.19525800	0.12826400
H	-0.89261800	3.34973300	-0.09381800
C	2.45777500	3.97332200	0.27364200
H	4.01949700	2.59345600	0.51840700
C	-0.62652300	-1.77371500	0.24785400
C	-0.76289700	-2.78526900	-0.70534800
C	-1.43718800	-1.81272000	1.38492300
C	-1.67944000	-3.81521500	-0.52414600
H	-0.15052400	-2.75048100	-1.60042200
C	-2.35135200	-2.84128700	1.56921800
H	-1.34921500	-1.02291600	2.12273000
C	-2.47646900	-3.84601100	0.61427900
H	-1.77521800	-4.58947500	-1.27635500
C	-1.69792000	0.88383700	-0.15978900
C	-2.47593100	1.53181800	0.80127500
C	-2.35671700	0.32794200	-1.25917100
C	-3.85336500	1.63220000	0.67100200
H	-1.99042400	1.95307700	1.67573000
C	-3.73071700	0.42340900	-1.40215100
H	-1.77827200	-0.19473100	-2.01336900

C	-4.50361300	1.07554200	-0.43452600
H	-4.43519400	2.14059400	1.43267100
H	4.69342200	0.89397100	-0.59577500
H	4.05377000	-3.28526600	0.08316200
H	0.66061000	5.21112400	0.02569200
H	-2.97029100	-2.85766800	2.45850300
H	-4.21754000	-0.01039700	-2.26914800
N	-5.88117600	1.21626100	-0.59929500
H	-6.30855400	0.50983700	-1.17954500
H	-6.39482800	1.35494500	0.25816900
N	5.87889600	-1.46524100	-0.19640500
H	6.12388700	-2.33819200	-0.64339700
H	6.47357600	-0.71597000	-0.52193400
H	-3.19368600	-4.64570300	0.75573300
H	3.11969300	4.83179100	0.27970700

Cyclic intermediates 1 of *Z*-2NH_2-TPE molecular structure

C	0.50961700	-0.73447700	-0.00173000
C	0.50965300	0.73452200	0.00163200
C	1.67595300	-1.43246000	-0.08220800
C	1.72174300	-2.88415300	-0.04521300
C	2.98887200	-0.70051500	-0.30772300
C	2.88436800	-3.54997900	0.09234700
H	0.78735100	-3.42978200	-0.06390700
C	4.18475200	-1.50343900	0.14386700
H	3.08149600	-0.57121200	-1.40599700
C	4.13700700	-2.83138700	0.27581200
C	1.67600800	1.43245000	0.08225100
C	2.98893900	0.70047600	0.30758300
C	1.72187800	2.88416800	0.04573000
C	4.18475500	1.50337100	-0.14429300
H	3.08178700	0.57131600	1.40585800
C	2.88452700	3.54996400	-0.09177100
H	0.78754200	3.42987500	0.06476700
C	4.13707200	2.83135700	-0.27584600
H	5.11489700	0.97816300	-0.32700800
C	-0.80779500	-1.43127500	0.05353200
C	-1.26760700	-2.19108500	-1.02230400
C	-1.64777300	-1.29712900	1.16035000
C	-2.51440700	-2.80010900	-0.99844900
H	-0.63696900	-2.29899900	-1.89911300
C	-2.89335700	-1.90213500	1.19761100
H	-1.31979900	-0.70045300	2.00440800
C	-3.34896900	-2.66187200	0.11426200

H	-2.84840000	-3.38782600	-1.84711400
C	-0.80775800	1.43134300	-0.05355300
C	-1.26784400	2.19066400	1.02250300
C	-1.64748500	1.29761800	-1.16061800
C	-2.51466800	2.79965200	0.99861800
H	-0.63743200	2.29820200	1.89952000
C	-2.89307300	1.90260600	-1.19791400
H	-1.31928900	0.70130400	-2.00484400
C	-3.34895600	2.66186500	-0.11434400
H	-2.84888700	3.38697400	1.84746800
H	5.11504000	-0.97829900	0.32603300
H	2.88615000	-4.63201100	0.14940200
H	2.88637200	4.63202100	-0.14837600
H	-3.52458800	-1.79035000	2.07287600
H	-3.52410400	1.79118000	-2.07337000
N	-4.58012400	3.31632300	-0.17029000
H	-5.25057200	2.89560300	-0.79620500
H	-4.98806900	3.52086100	0.72975000
N	-4.58011400	-3.31632800	0.17017500
H	-5.25066700	-2.89557200	0.79594400
H	-4.98791500	-3.52121600	-0.72984500
H	5.02250600	-3.38724000	0.56229200
H	5.02248800	3.38724000	-0.56252400

Cyclic intermediates 2 of *Z*-2NH_2-TPE molecular structure

C	-0.37247400	-0.73560500	0.02700000
C	-0.37250100	0.73557600	-0.02705800
C	0.79692800	-1.41514900	-0.12926500
C	0.89228200	-2.85784300	0.00985800
C	2.06212200	-0.62594500	-0.44411500
C	2.07362500	-3.49351600	-0.02139300
H	-0.01304000	-3.41668500	0.20996400
C	3.32644200	-1.43950000	-0.38026100
H	1.95857400	-0.26003800	-1.48415300
C	3.33196900	-2.77003900	-0.21713200
C	0.79688900	1.41515000	0.12918400
C	2.06207900	0.62597100	0.44410700
C	0.89223500	2.85782400	-0.01012300
C	3.32637700	1.43956500	0.38040300
H	1.95845700	0.26002100	1.48412200
C	2.07356100	3.49352200	0.02114000
H	-0.01308000	3.41661200	-0.21041600
C	3.33189300	2.77009400	0.21715600
H	4.25982100	0.92046100	0.56827000

C	-1.67388700	-1.42808100	0.24089300
C	-2.17063400	-2.33263300	-0.70021600
C	-2.44970800	-1.14015100	1.36635400
C	-3.40742600	-2.94114600	-0.51808500
H	-1.58233200	-2.54573400	-1.58669700
C	-3.68441200	-1.74784900	1.55115500
H	-2.07835600	-0.42835000	2.09545900
C	-4.16808200	-2.64992800	0.60852700
H	-3.78007800	-3.63656800	-1.26100100
C	-1.67392700	1.42802500	-0.24091500
C	-2.17060000	2.33261500	0.70020600
C	-2.44982900	1.14008700	-1.36631700
C	-3.40739300	2.94114000	0.51814600
H	-1.58223200	2.54572500	1.58664000
C	-3.68453700	1.74780000	-1.55104700
H	-2.07853900	0.42827400	-2.09544200
C	-4.16813200	2.64990500	-0.60840600
H	-3.77998300	3.63658600	1.26107100
H	4.25989600	-0.92033800	-0.56791500
H	2.12356800	-4.56519900	0.14126400
H	2.12352500	4.56517300	-0.14171500
H	-4.27277400	-1.51413700	2.43051300
H	-4.27295800	1.51407900	-2.43036300
N	4.49352800	3.55067200	0.13472600
H	4.40242900	4.45543000	0.57667800
H	5.32291200	3.07575000	0.46312800
N	4.49362500	-3.55059300	-0.13457100
H	4.40262200	-4.45531100	-0.57663500
H	5.32304500	-3.07561500	-0.46281400
H	-5.13432600	-3.11923600	0.74967900
H	-5.13437800	3.11922400	-0.74950500

TS of *E*-2NH_2-TPE molecular structure converting to cyclic intermediates

C	-2.24548000	3.06448400	-1.35020700
C	-2.65293200	2.74014300	-0.07405800
C	-1.58577800	4.34630200	-1.60378500
C	-0.65161900	4.49815900	-2.61679000
C	-1.76364900	5.42196300	-0.60683000
C	0.10330300	5.66538500	-2.75390700
H	-0.48653900	3.67397100	-3.30130700
C	-1.00834100	6.64684300	-0.84983900
H	-2.80447200	5.60928300	-0.33426600
C	-0.09124000	6.74014600	-1.85605900
C	-2.33849700	3.61398400	1.05354400

C	-1.26032800	4.60888600	0.89265900
C	-3.16766900	3.69727800	2.16421700
C	-1.06187700	5.53343900	2.00037200
H	-0.32372700	4.18546000	0.52375400
C	-2.99599300	4.66542900	3.14724000
H	-4.00031000	3.00832900	2.24880600
C	-1.92284200	5.59573800	3.06534700
H	-0.21427200	6.21021200	1.95233600
C	-2.41706300	2.13371400	-2.49269300
C	-2.97095800	2.57781100	-3.69767900
C	-2.04050000	0.78954600	-2.40975500
C	-3.16718900	1.71601300	-4.76498000
H	-3.26142500	3.61870200	-3.79242300
C	-2.22369500	-0.07818600	-3.47290200
H	-1.60077300	0.41934000	-1.49061000
C	-2.79980300	0.36921700	-4.66752000
H	-3.60516900	2.08409900	-5.68680200
C	-3.46574700	1.52517900	0.20257000
C	-3.08419700	0.63234900	1.20892100
C	-4.62895600	1.25521100	-0.52448700
C	-3.83110000	-0.51134500	1.46529100
H	-2.18944500	0.84047400	1.78567000
C	-5.38038200	0.11729200	-0.26302000
H	-4.93485500	1.94394800	-1.30360300
C	-4.98164900	-0.77339700	0.72901500
H	-3.51406200	-1.19836700	2.24117100
H	-1.18126400	7.48557400	-0.18472000
H	0.83156700	5.74726900	-3.55037600
H	-3.68647700	4.72451300	3.98063000
H	-1.91542000	-1.11457500	-3.38533500
H	-6.28052800	-0.07468700	-0.83497300
N	-2.94131600	-0.48910300	-5.75537400
H	-2.99719100	-1.46801700	-5.51748600
H	-3.65435900	-0.22084700	-6.41684700
H	0.47316700	7.65626700	-1.98908100
N	-1.80003700	6.56270800	4.06619000
H	-2.09609400	6.25137600	4.98004800
H	-0.89300300	7.00472900	4.10456000
H	-5.56642000	-1.66311400	0.93015500

TS 1 of *Z*-2NH_2-TPE molecular structure converting to cyclic intermediates

C	-2.25552800	3.07183500	-1.34151800
C	-2.65487700	2.74369400	-0.06440800
C	-1.59730300	4.35462200	-1.60400200

C	-0.66963200	4.50083600	-2.62335700
C	-1.76171700	5.43380000	-0.60922800
C	0.09208000	5.66337300	-2.76650100
H	-0.51411900	3.67570200	-3.30880900
C	-1.00243600	6.65441000	-0.85879600
H	-2.79897100	5.62516700	-0.32700900
C	-0.08966800	6.74061400	-1.86987600
C	-2.33815200	3.62708600	1.06086500
C	-1.25135600	4.61189100	0.88547000
C	-3.16014400	3.70861600	2.17403000
C	-1.04823400	5.54313700	1.99035000
H	-0.31961900	4.18483000	0.50907800
C	-2.96819100	4.67478400	3.16458800
H	-3.99208600	3.01905200	2.25877800
C	-1.89766900	5.59128000	3.05759600
H	-0.20518400	6.22250100	1.92956100
C	-2.43154700	2.14148800	-2.48489100
C	-2.99860700	2.58331300	-3.68407900
C	-2.04295300	0.80028900	-2.40767300
C	-3.19530900	1.72225100	-4.75249100
H	-3.29848100	3.62196900	-3.77454100
C	-2.22611400	-0.06610300	-3.47165800
H	-1.59628300	0.43136300	-1.49143500
C	-2.81507300	0.37897400	-4.66106000
H	-3.64312900	2.08884200	-5.67020300
C	-3.45350500	1.52480100	0.22092500
C	-3.07968400	0.64747800	1.24317900
C	-4.60096800	1.21126100	-0.51406100
C	-3.80278800	-0.50509300	1.50880600
H	-2.19965600	0.87310900	1.83612700
C	-5.33605400	0.06775400	-0.25118200
H	-4.91629400	1.87678600	-1.30963700
C	-4.94600800	-0.81364700	0.76392900
H	-3.48153200	-1.17803200	2.29690000
H	-1.16727600	7.49642500	-0.19562900
H	0.81568700	5.73922300	-3.56780000
H	-3.63629300	4.71641300	4.01511300
H	-1.90942700	-1.10028100	-3.38824700
H	-6.22213700	-0.15300100	-0.83700800
N	-2.95697900	-0.47883800	-5.74977600
H	-3.00370200	-1.45833000	-5.51205300
H	-3.67842000	-0.21590100	-6.40429100
H	0.47972600	7.65289000	-2.00747000
N	-5.64674800	-1.99747400	0.98858200

H	-5.54625500	-2.37765300	1.91787000
H	-6.61166100	-1.97839400	0.69400400
H	-1.73382400	6.31695100	3.84622300

TS 2 of *Z*-2NH_2-TPE molecular structure converting to cyclic intermediates

C	-2.24289000	3.05947500	-1.35791500
C	-2.66308300	2.74220100	-0.08328000
C	-1.57938900	4.33239400	-1.61878600
C	-0.63863300	4.47424500	-2.63040000
C	-1.73657800	5.41750700	-0.63009100
C	0.13510900	5.62110700	-2.76641500
H	-0.47669800	3.64849500	-3.31397100
C	-0.97532700	6.63379500	-0.88061900
H	-2.77608600	5.61953700	-0.36219900
C	-0.04142300	6.72041600	-1.88001800
C	-2.34558500	3.62070700	1.03722400
C	-1.25333400	4.60032100	0.87101700
C	-3.17558000	3.71972000	2.14634600
C	-1.04450800	5.52711800	1.97529600
H	-0.32127500	4.16108400	0.50839200
C	-2.99061100	4.68841600	3.12585000
H	-4.01820600	3.04301100	2.23161400
C	-1.90384900	5.60319800	3.04033300
H	-0.18922200	6.19375400	1.92318600
C	-2.41050600	2.11776600	-2.49614900
C	-2.98268100	2.55636700	-3.69475700
C	-2.00084100	0.78457500	-2.39969100
C	-3.16397100	1.68043100	-4.75793100
H	-3.29325700	3.59192400	-3.78166800
C	-2.17475500	-0.08941600	-3.46470800
H	-1.54992700	0.43640300	-1.47751000
C	-2.76185000	0.35343200	-4.64572900
H	-3.62074500	2.03407400	-5.67484300
C	-3.48620500	1.53493300	0.19229500
C	-3.12157000	0.64783600	1.21029500
C	-4.63965500	1.26355600	-0.54945500
C	-3.87517900	-0.49194500	1.46284100
H	-2.23422600	0.85703500	1.79793500
C	-5.39749400	0.12874400	-0.29237000
H	-4.93467200	1.94871800	-1.33589200
C	-5.01534900	-0.75614900	0.71090700
H	-3.57115600	-1.17513100	2.24723600
H	-1.14571000	7.48296000	-0.22602000
H	0.88663400	5.68302600	-3.54498300

H	-3.68042600	4.76076000	3.95874500
H	-1.85122600	-1.11937800	-3.37200100
H	-6.28878700	-0.06538800	-0.87716500
N	-1.76725500	6.57152600	4.03876000
H	-2.06816200	6.26578500	4.95301300
H	-0.85201600	6.99642900	4.07765500
H	-5.60454800	-1.64372100	0.90837000
N	0.76952300	7.84658200	-2.04502300
H	1.01978800	8.03668200	-3.00477100
H	0.42033800	8.67588600	-1.58671700
H	-2.90167400	-0.33023100	-5.47458000

Epoxy isomers

O	0.16689600	0.16067600	-1.68303900
N	-4.51334600	3.99466400	0.53809300
H	-5.21913900	3.58063800	1.12845200
H	-4.91482000	4.42210300	-0.28295500
N	4.46182300	-4.03385200	0.61573700
H	4.56830300	-4.83703000	0.01444900
H	4.58857300	-4.27246500	1.58777700
C	-0.00918400	-0.69725300	-0.56076400
C	0.10893900	0.79399100	-0.40911800
C	-1.36069400	-1.35183400	-0.47732900
C	-1.61894600	-2.31497300	0.49851600
H	-0.82611900	-2.62597600	1.16918900
C	-2.88361200	-2.88193600	0.60879900
H	-3.07380900	-3.62501600	1.37429300
C	-3.89691000	-2.50670100	-0.26616700
H	-4.88087500	-2.95285500	-0.18334600
C	-3.63714300	-1.56241600	-1.25397600
H	-4.41892200	-1.27122300	-1.94556800
C	-2.37797500	-0.98553900	-1.35869400
H	-2.17116300	-0.24125200	-2.11724500
C	-1.12239400	1.60876700	-0.15448600
C	-1.91858800	1.40171200	0.96864000
H	-1.66670600	0.60594800	1.66268600
C	-3.04530300	2.17757400	1.19579200
H	-3.65852800	2.00194500	2.07303700
C	-3.40910300	3.18095000	0.29113300
C	-2.60787000	3.38835300	-0.83792500
H	-2.87521600	4.16639600	-1.54504000
C	-1.47937900	2.61232700	-1.05090100
H	-0.86784600	2.77647100	-1.93179000
C	1.16372600	-1.56898600	-0.23019000

C	1.72844400	-1.58683100	1.04219200
H	1.33751400	-0.92595100	1.80957200
C	2.80149100	-2.41567800	1.33372400
H	3.24065900	-2.40782600	2.32542700
C	3.34273900	-3.24788400	0.34774100
C	2.77809100	-3.22450200	-0.93318900
H	3.19428000	-3.85681100	-1.71024900
C	1.70043800	-2.39851700	-1.21109300
H	1.27098500	-2.38587000	-2.20726200
C	1.40655300	1.39835600	0.05213500
C	2.58300900	1.17575100	-0.66366300
H	2.54262700	0.58263100	-1.56843800
C	3.78738600	1.70028000	-0.21261900
H	4.69477500	1.51949600	-0.77650700
C	3.83194300	2.44912700	0.95878100
H	4.77317300	2.85359700	1.31166700
C	2.66041500	2.68275100	1.66999700
H	2.68385100	3.27536500	2.57691800
C	1.45162600	2.16800200	1.21504200
H	0.53762000	2.37121600	1.76123800

Ground state of O-2NH$_2$-TPE molecule

O	0.58774600	-0.71637300	-2.56424800
N	-3.80916900	3.19889400	2.13579200
H	-4.66487500	2.68018700	2.26458200
H	-3.97866600	4.12221300	1.76600200
N	3.05377200	-3.61718400	3.06320700
H	3.31856000	-4.48214500	2.61824700
H	2.63646000	-3.76692300	3.96844400
C	-0.05607500	-0.55935700	-1.55983400
C	0.49477300	0.25889200	-0.34994400
C	-1.39430000	-1.24174800	-1.43053700
C	-1.46454400	-2.55467600	-0.97156800
H	-0.55736300	-3.07120500	-0.67912100
C	-2.70016600	-3.18739100	-0.87526700
H	-2.75553200	-4.20652900	-0.51222800
C	-3.85990400	-2.51621400	-1.24694400
H	-4.82064100	-3.01128500	-1.17131000
C	-3.78478600	-1.20988800	-1.72155500
H	-4.68593700	-0.68527400	-2.01499200
C	-2.55469500	-0.57151800	-1.81088100
H	-2.49382300	0.45612700	-2.15241800
C	-0.64000000	1.05620500	0.32190700
C	-1.67287400	0.40432800	1.01225500

H	-1.66105900	-0.67528100	1.10675400
C	-2.71977600	1.09842200	1.59101200
H	-3.49693400	0.55580700	2.11893300
C	-2.78544300	2.49466300	1.50726600
C	-1.75611400	3.15673500	0.83869300
H	-1.76789100	4.23978100	0.77634300
C	-0.70735000	2.44875700	0.26345400
H	0.07290000	3.01046800	-0.23270100
C	1.09377400	-0.81462200	0.58591100
C	0.95134500	-0.77780000	1.97289600
H	0.35317000	-0.00254500	2.43505000
C	1.58130100	-1.70701200	2.78991300
H	1.45783400	-1.64629200	3.86623700
C	2.38302300	-2.71358600	2.24509200
C	2.54997200	-2.74170100	0.85548600
H	3.18999800	-3.49541200	0.40876700
C	1.92296300	-1.80572900	0.04981600
H	2.09697400	-1.83617600	-1.02021500
C	1.60784600	1.20287000	-0.82530000
C	1.47925100	1.91702900	-2.02064900
H	0.62146400	1.74956400	-2.65996300
C	2.43694800	2.84584300	-2.40406400
H	2.31722000	3.38310200	-3.33727700
C	3.54628900	3.08298800	-1.59812600
H	4.29541200	3.80580100	-1.89841000
C	3.68463700	2.38098000	-0.40908200
H	4.54360700	2.55350000	0.22854600
C	2.72461600	1.44752000	-0.02830100
H	2.85196900	0.90575600	0.90082600

TS of O-2NH_2-TPE molecule converting to epoxy isomers

O	0.58616900	-0.93058100	-2.30024900
N	-3.76125300	3.45554100	2.42315200
H	-4.59846500	2.99955200	2.74303900
H	-3.76221800	4.46091200	2.40673900
N	3.60483100	-2.98006900	2.88865900
H	4.32364400	-3.57817500	2.50967700
H	3.18742700	-3.37107400	3.71978800
C	0.02124900	-0.81376000	-1.12289500
C	0.09654100	0.61398300	-0.54292400
C	-1.38742800	-1.42104100	-1.16472200
C	-1.72376200	-2.63218600	-0.56931800
H	-0.98248300	-3.16916700	0.01065900
C	-3.00594000	-3.16166500	-0.71970100

H	-3.25327900	-4.10782100	-0.25158500
C	-3.96000300	-2.48819900	-1.47014600
H	-4.95681900	-2.89821500	-1.58262600
C	-3.61782600	-1.29046300	-2.09793000
H	-4.34851500	-0.76903200	-2.70584500
C	-2.34043400	-0.77182600	-1.95535900
H	-2.05918500	0.14636000	-2.46018800
C	-0.88636100	1.29433100	0.24956500
C	-2.00548500	0.65795200	0.85691400
H	-2.13679900	-0.40982600	0.77086200
C	-2.93552900	1.36188300	1.57825800
H	-3.76502600	0.84093700	2.04271200
C	-2.83957700	2.76298900	1.70878100
C	-1.76027800	3.42352600	1.08949900
H	-1.68656900	4.50308900	1.15499800
C	-0.81689700	2.70780000	0.39599300
H	-0.01635000	3.24661800	-0.09206700
C	0.90634500	-1.41058400	0.06494000
C	0.55779300	-1.50343600	1.41369500
H	-0.40818200	-1.15595000	1.76314300
C	1.43293400	-2.04447000	2.34482100
H	1.14358200	-2.11362600	3.38841900
C	2.69886900	-2.49257200	1.95016500
C	3.05549000	-2.38448300	0.59924200
H	4.03289200	-2.73215000	0.27957300
C	2.17408500	-1.84838400	-0.32232000
H	2.41115400	-1.76876600	-1.37717600
C	1.34275500	1.33395500	-0.84302700
C	1.82683500	1.45416300	-2.15218100
H	1.25722600	1.00859200	-2.95306200
C	3.02658300	2.12125800	-2.38165600
H	3.39144900	2.22372000	-3.39653900
C	3.76643000	2.63175700	-1.32289700
H	4.70982900	3.13127400	-1.51085300
C	3.30250200	2.49276100	-0.01545700
H	3.88829100	2.86766200	0.81496200
C	2.09207500	1.86385500	0.22161400
H	1.73503900	1.72832400	1.23690100

TS of nucleophilic rearrangement reaction at B3LYP/6-31G(d) level

N	1.57247900	-4.27998900	3.12210900
H	1.10899100	-4.42424300	4.00713100
H	2.55402600	-4.51546000	3.11051800
N	-1.56626400	4.31614000	2.82448200

H	-2.32590300	4.94731200	2.61197400
H	-1.09174100	4.44748400	3.70651500
C	0.33078200	0.68695800	-1.16226600
C	-0.46404000	-0.28350100	-0.40600400
C	1.82485800	0.82014900	-1.23270800
C	2.57651300	1.71084800	-0.46423900
H	2.09230300	2.33866600	0.27428500
C	3.95578200	1.81425500	-0.65701200
H	4.53009100	2.50793000	-0.05091400
C	4.58955000	1.04454600	-1.63000200
H	5.66186700	1.12659600	-1.77705900
C	3.83723700	0.17863400	-2.42873700
H	4.32088100	-0.41312100	-3.19963200
C	2.46289800	0.07505800	-2.24091200
H	1.87564000	-0.59276900	-2.86444200
C	0.14017000	-1.29534600	0.51885800
C	-0.63297100	-1.75594200	1.60117500
H	-1.62831600	-1.35336200	1.75722000
C	-0.15908700	-2.71595200	2.47525600
H	-0.78203900	-3.05358300	3.29904700
C	1.12127900	-3.28400400	2.29276900
C	1.89425600	-2.83361600	1.20701100
H	2.87653700	-3.26432500	1.03328900
C	1.41177000	-1.85889200	0.34315300
H	2.04033700	-1.55324000	-0.48084600
C	-0.46025700	1.26763100	0.18410700
C	0.20178000	1.44335800	1.44320100
H	0.96806500	0.73457800	1.73255800
C	-0.15284900	2.44210300	2.30676600
H	0.35033100	2.54392100	3.26364600
C	-1.20979900	3.33871200	1.97514400
C	-1.88372400	3.17893400	0.73115600
H	-2.68238000	3.86558000	0.46684900
C	-1.52010600	2.17948900	-0.12853700
H	-2.01554600	2.08453800	-1.08635100
C	-1.77592900	-0.73336800	-1.00365100
C	-1.72412500	-1.54165300	-2.14492400
H	-0.76552200	-1.75884700	-2.60603400
C	-2.89398300	-2.06835700	-2.68644700
H	-2.84252500	-2.68883700	-3.57584200
C	-4.12703200	-1.79932100	-2.08906100
H	-5.03847700	-2.21042300	-2.51175100
C	-4.18252700	-1.00168500	-0.94681300
H	-5.13672100	-0.79113700	-0.47335600

C	-3.01085500	-0.47169300	-0.40513500
H	-3.06241700	0.14827400	0.48476700
O	-0.27513400	1.07498600	-2.34202200
H	0.25254000	1.79745400	-2.72440900

TS of nucleophilic rearrangement reaction

N	-1.55552200	4.20806900	3.23629200
H	-0.94980600	4.56812900	3.95323000
H	-2.54306300	4.34505800	3.36456700
N	1.54367400	-4.20393900	2.89401600
H	2.31830100	-4.82109100	2.70749800
H	1.05961300	-4.31746000	3.77055300
C	-0.32684500	-0.68078900	-1.15853600
C	0.44142900	0.31195200	-0.40775900
C	-1.82056900	-0.80602700	-1.27581600
C	-2.56532700	-1.78280200	-0.62427400
H	-2.08570800	-2.47226500	0.05984700
C	-3.93408900	-1.88803000	-0.86275400
H	-4.51031100	-2.64773900	-0.34952300
C	-4.55447000	-1.03250800	-1.76242900
H	-5.61872500	-1.11568600	-1.94444800
C	-3.80330200	-0.07695000	-2.44499300
H	-4.28062800	0.58231600	-3.15928400
C	-2.44114600	0.02992600	-2.21145400
H	-1.85063000	0.77186300	-2.73852800
C	-0.14623500	1.32120300	0.52769600
C	0.71950900	1.98609800	1.41228700
H	1.78123300	1.77738600	1.38461300
C	0.26208300	2.91965700	2.31665600
H	0.96221100	3.41874200	2.97683800
C	-1.10339600	3.25299000	2.37615100
C	-1.97521000	2.59704600	1.49321700
H	-3.03057900	2.84441000	1.50414900
C	-1.50607900	1.65431900	0.59571800
H	-2.22873400	1.19060300	-0.05770400
C	0.40231200	-1.28111900	0.16038600
C	-0.27696300	-1.43880300	1.40888100
H	-1.07758000	-0.75360700	1.66247300
C	0.09048900	-2.39488000	2.30488000
H	-0.42381600	-2.48522000	3.25414300
C	1.17565200	-3.26977000	2.01453700
C	1.86262700	-3.13231400	0.77746200
H	2.67969700	-3.80528400	0.54636600
C	1.48654400	-2.17129300	-0.11178500

H	1.99531600	-2.08551000	-1.06354200
C	1.76915400	0.71927400	-0.99851600
C	1.73757300	1.50067400	-2.15272900
H	0.78580400	1.72897600	-2.61910900
C	2.91739700	1.98212700	-2.70318200
H	2.88361400	2.58404200	-3.60277000
C	4.13837600	1.69079000	-2.10314500
H	5.05823800	2.06638600	-2.53369600
C	4.17391100	0.91801100	-0.94904800
H	5.12068300	0.69250000	-0.47391400
C	2.99205500	0.43380700	-0.39735000
H	3.02363200	-0.16202600	0.50895700
O	0.30119000	-1.06581000	-2.32623300
H	-0.21427800	-1.77690000	-2.72501300