Supplementary Information

Directional glycolysis of waste PET by deep eutectic solvents for preparation of aromatic-based polyurethane elastomers

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1. Computational simulations of DES by density functional theory (DFT)

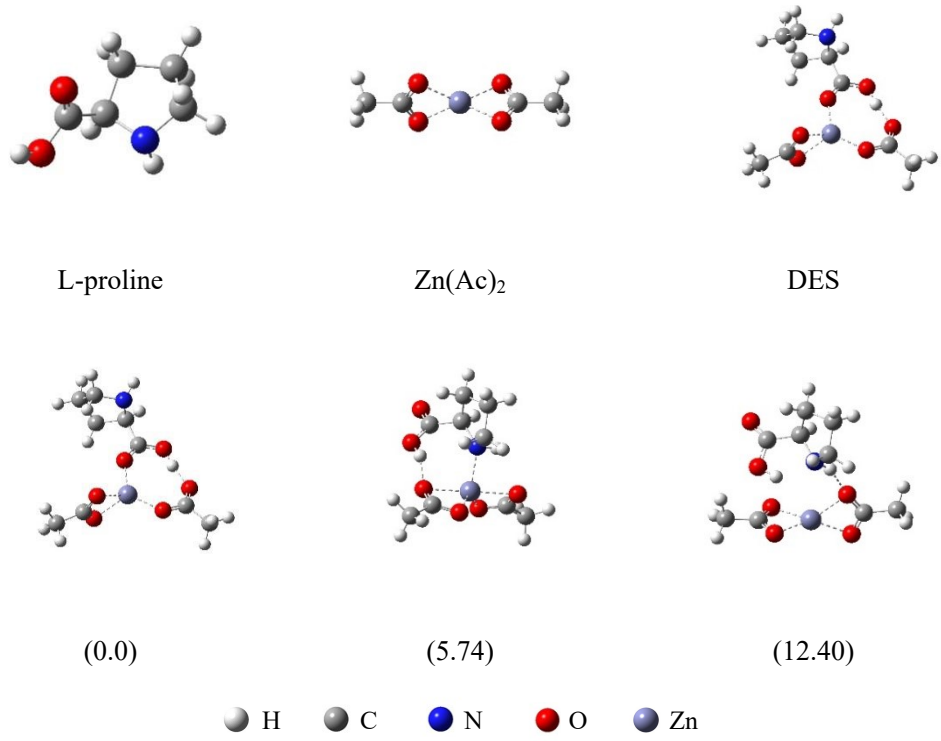

Figure S1. Optimized structures of Pro, $Zn(Ac)_2$ and DES with relative energies (kcal/mol).

2. TGA curve of DES

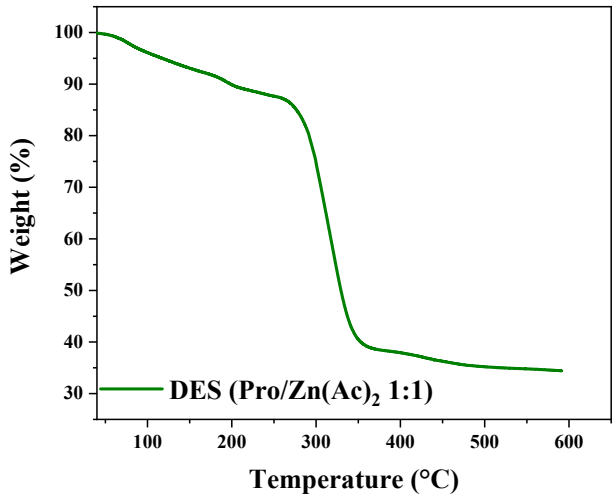

Figure S2. TGA curve of DES.

3. Characterization of PET and products

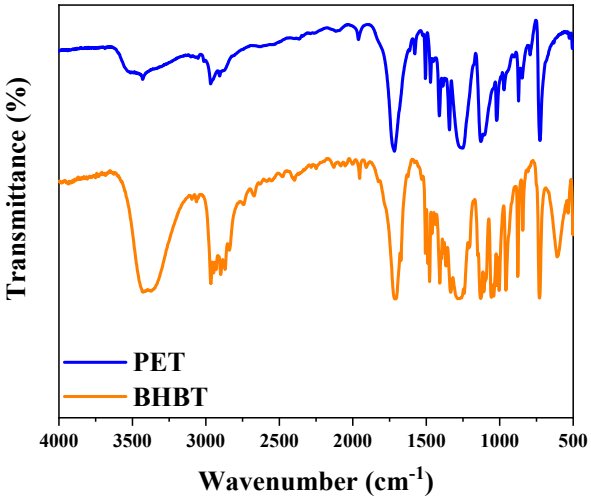

Figure S3. FT-IR spectra of raw PET and product.

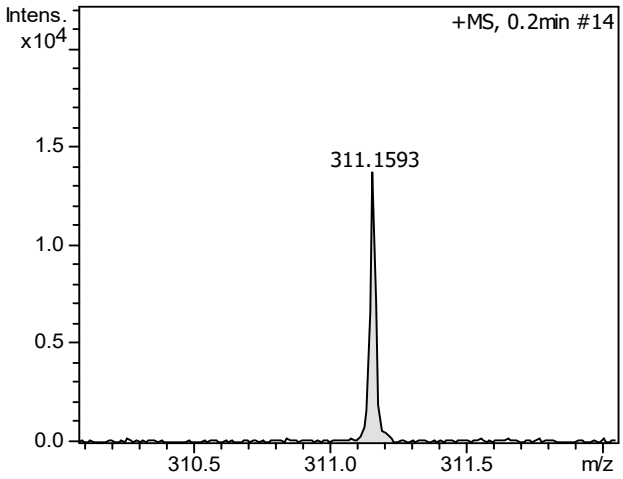

Figure S4. ESI-MS spectra of product glycolized by BDO.

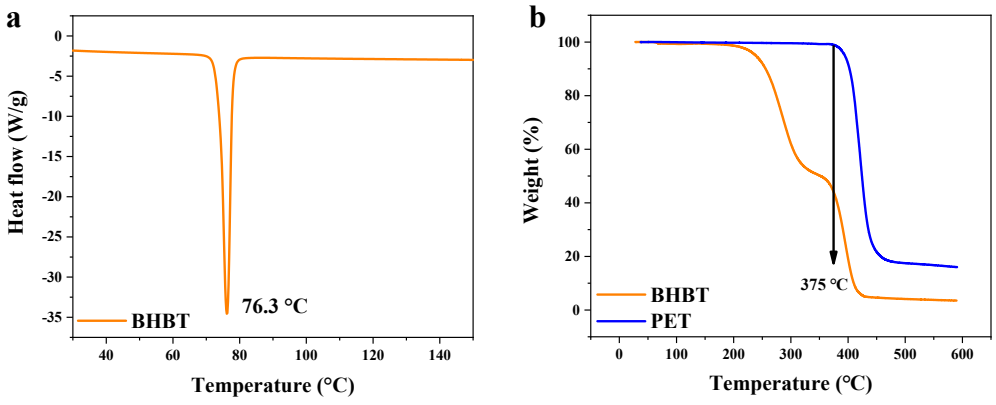

Figure S5. (a) DSC curve of product BHBT, (b) TGA curve of raw PET and product BHBT.

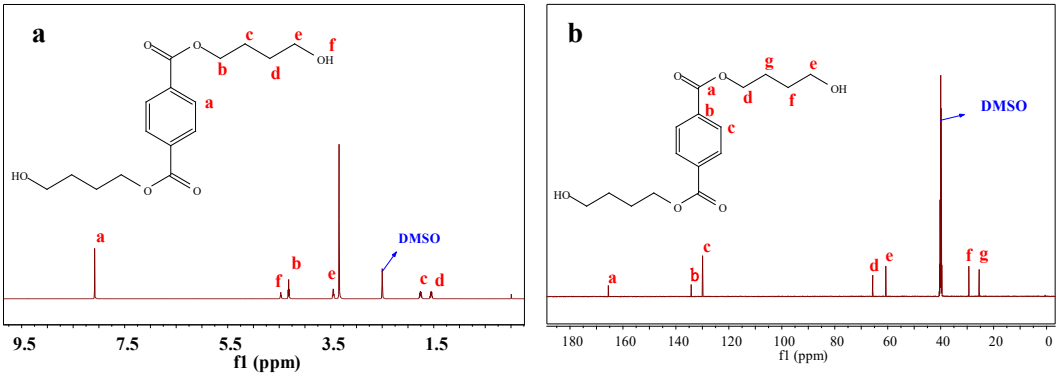

Figure S6. (a) the ^{1}H NMR spectra and (b) ^{13}C NMR spectra of purified product.

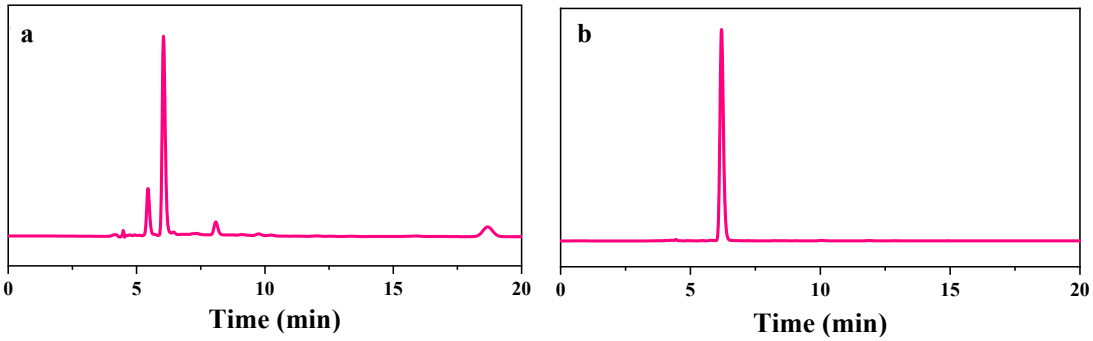

Figure S7. HPLC spectrum of product glycolized by BDO (a) before purification and (b) after purification.

3. Optimization of glycolysis reaction parameters

Table S1. Impact of reaction temperature on PET glycolysis

Entry	Reaction temperature (°C)	Conv. of PET (%)	Yield of BHET (%)
1	170	17.59	14.98
2	180	31.34	25.82
3	190	48.40	34.99
4	200	94.86	62.89
5	210	100.00	65.40
6	220	100.00	62.56

Reaction conditions: PET 5.0 g, BDO 25.0 g, Cat. 0.10 g, 30min

Table S2. Impact of reaction time on PET glycolysis

Entry	Reaction time (min)	Conv. of PET (%)	Yield of BHET (%)
1	5	16.24	12.06
2	10	98.10	57.12
3	15	100.00	67.11
4	20	100.00	66.36
5	25	100.00	66.26
6	30	100.00	65.55
7	60	100.00	62.13

Reaction conditions: PET 5.0 g, BDO 25.0 g, Cat. 0.10 g, 210°C

Table S3. Impact of catalyst ratio on PET glycolysis

Entry	Catalyst ratio (%)	Conv. of PET (%)	Yield of BHET (%)
1	0	0.14	0.02
2	0.5	97.61	55.46
3	1	100.00	61.64
4	1.5	100.00	64.30
5	2	100.00	67.11
6	2.5	100.00	66.65
7	3	100.00	64.84
8	3.5	100.00	64.61
9	4	100.00	64.52

Reaction conditions: PET 5.0 g, BDO 25.0 g, 210°C, 15 min

Table S4. Impact of BDO amount on PET glycolysis

Entry	BDO amount (g)	Conv. of PET (%)	Yield of BHET (%)
1	10	92.79	45.57
2	15	95.54	55.49
3	20	99.67	61.14
4	25	100.00	67.13
5	30	100.00	67.23

Reaction conditions: PET 5.0 g, Cat. 0.10 g, 210°C, 15 min

Table S5. The Influence of catalyst and single components on the glycolysis of PET

Entry	Catalysts	Conv. of PET (%)	Yield of BHET (%)
1	Pro	14.3	2.03
2	$Zn(Ac)_2$	98.41	54.94
3	$Pro/Zn(Ac)_2$	100	66.36

Reaction conditions: PET 1.0 g, BDO 5.0 g, Cat. 0.02 g,210°C, 20min

4. Reaction Kinetics

Table S6. Linear regressive result of kinetic data on PET glycolysis temperature

Temperature (°C)	Rate constant	Adj. R-Square
170	0.00255	0.9968
180	0.00784	0.9931
190	0.02161	0.9934
200	0.05590	0.9977
210	0.11273	0.9992

Reaction conditions: PET 1.0 g, BDO 5.0 g, Cat. 0.02 g,210°C, 20min

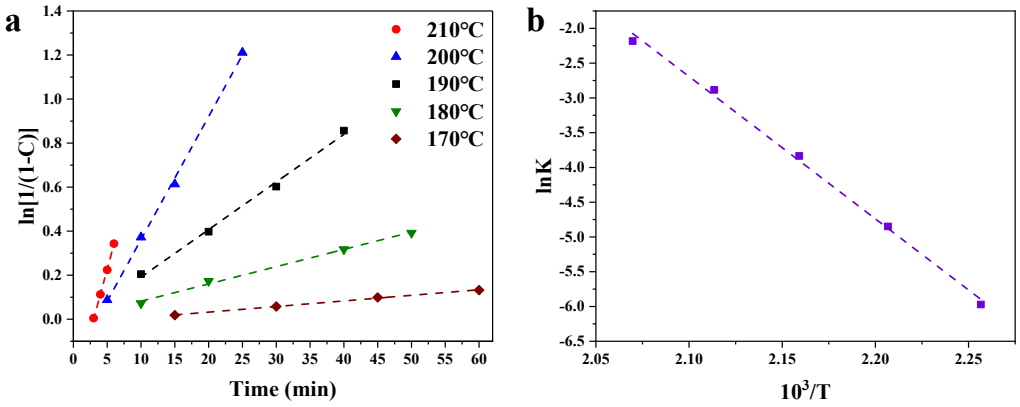

Figure S8. Kinetics of PET glycolysis on (a) temperature and (b) activation energy.

Reaction conditions: PET 5.0 g, BDO 25.0 g, Cat. (Pro/$Zn(Ac)_2$, 0.10 g)

5. Calculation of quantitative metrics

The reaction equation for the PET glycolysis from 1,4-butanediol is shown as Fig. S9.

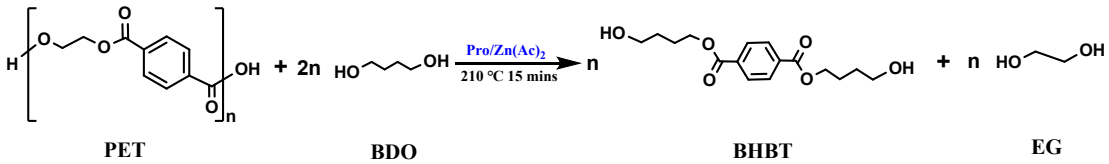

Figure S9. The reaction equation for the PET glycolysis from 1,4-butanediol.

Some quantitative typical metrics applied at First and Second Pass, such as Selectivity, atom economy (AE), reaction mass efficiency (RME), optimum efficiency (OE) and the total process mass intensity (PMI), were calculated according to the formula given in CHEM21 Metrics Toolkit, the calculation process is shown below:

(1) $Percentage\ selectivity = \frac{\%yield}{\%conversion} \times 100 = \frac{67.1\%}{100\%} \times 100 = 67.1\%$

(2) $AE = \frac{molecular\ weight\ of\ product}{total\ molecular\ weight\ of\ reactants} \times 100 = \frac{M_{BHBT}}{M_{PET} + 2M_{BDO}} \times 100 = 83.3\%$

(3) $RME = \frac{mass\ of\ isolated\ product}{total\ mass\ of\ reactants} \times 100 = \frac{m_{BHBT}}{m_{PET} + m_{reacted\ BDO}} \times 100 = 25.0\%$

(4) $OE = \frac{RME}{AE} \times 100 = \frac{25.0\%}{83.3\%} \times 100 = 30.0\%$

(5) $PMI = \frac{total\ mass\ in\ a\ process}{mass\ of\ product} = \frac{m_{PET} + m_{total\ BDO} + m_{Cat.}}{m_{BHBT}} = \frac{5 + 25 + 0.1}{5.2855} = 5.7$

Where m_{PET} is the initial weight of PET; $m_{total\ BDO}$ is the total mass of BDO as reactant and solvent; m_{BHBT} is the weight of BHBT, which are calculated by HPLC according to the peak area of BHBT. And M_{PET} =192 g·mol^{-1} (the molar mass of PET repeating unit), M_{BDO} =90.07 g·mol^{-1}, M_{BHBT} =310.14 g·mol^{-1}, M_{EG} =48.02 g·mol^{-1}.

56. DFT calculation

Computation details: The density functional theory (DFT) calculations were carried out to analysis the coordination and interaction. All calculations were carried out using the Gaussian 09 program. The B3LYP/6-311++G(d,p) method has been used for structure optimizations, and subsequent frequency calculations at the same level verify the optimized structures to be ground states without imaginary frequencies (NImag = 0).

Cartesian coordinates for the optimized structures in Fig. 7

BDO

C	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	1.09910000
H	1.04620000	0.00000000	-0.33670000
C	-0.71190000	-1.23910000	-0.51870000
H	-1.75700000	-1.19900000	-0.19200000
H	-0.72130000	-1.19880000	-1.61370000
C	-0.05430000	-2.53810000	-0.03990000
H	-0.04480000	-2.57830000	1.05510000
H	0.99080000	-2.57820000	-0.36660000
C	-0.76620000	-3.77710000	-0.55860000
H	-0.76650000	-3.77700000	-1.65770000
H	-1.81230000	-3.77730000	-0.22160000
O	-0.07750000	-4.92650000	-0.05730000
H	-0.51900000	-5.71850000	-0.37770000
O	-0.68840000	1.14930000	-0.50170000
H	-0.24820000	1.94140000	-0.17950000

BDO + Pro + Zn(Ac)$_2$

Zn	0.20780900	-0.63748500	0.54868600

C	0.95646200	-4.52590600	-1.28307200
H	1.97424400	-4.20186500	-1.49092600
H	0.97089100	-5.18249400	-0.40760200
H	0.54360700	-5.09195700	-2.11772400
C	0.08938200	-3.33946700	-0.96514200
O	-1.17996300	-3.54046800	-1.10503400
O	0.60650200	-2.27298800	-0.58720800
C	3.31112100	-0.25890500	3.18668000
H	2.91203400	0.41725900	3.94624300
H	3.35925300	-1.25431800	3.63432800
H	4.30846200	0.06219200	2.89167900
C	2.37692300	-0.28953300	1.99847300
O	2.75198100	0.02006200	0.85431800
O	1.16230300	-0.65628100	2.24075900
C	-3.53134200	0.55470000	-0.22793000
C	-2.80077400	2.74736300	0.48055600
C	-4.17965900	2.49498000	1.09536800
C	-4.27074200	0.96065800	1.07003600
H	-4.22665600	0.35538900	-1.04395900
H	-2.01546200	2.58316300	1.22327700
H	-2.66923400	3.74870400	0.06591300
H	-4.27691700	2.90639200	2.10230300
H	-4.96126900	2.94282900	0.47205100
H	-3.74683200	0.54181500	1.93154300
H	-5.29661700	0.58952400	1.07938700
N	-2.65776300	1.72894900	-0.59723800
H	-3.01508600	2.11873100	-1.46341100
C	-2.62794500	-0.67163800	-0.06898000
O	-1.75859200	-0.60726700	0.85924500
O	-2.76364500	-1.61387100	-0.87777500
H	-1.79321100	-2.70736900	-0.92773700
C	2.40934300	2.74804400	-1.09478800
H	2.07630200	2.39024800	-0.11763300
C	1.27957000	2.53258100	-2.11274300
H	1.65277600	2.67036800	-3.13656000
H	0.49613800	3.28618200	-1.97184100
C	0.64291000	1.14683300	-2.03406400
H	1.39184300	0.36031500	-2.12987900
H	2.61634100	3.81693900	-0.98502800
C	3.71035400	2.01691400	-1.46031200
H	4.26619500	2.58837200	-2.21027700
H	3.48246600	1.03884400	-1.90664900
O	4.57681500	1.85226200	-0.34998000
H	4.14911600	1.19740200	0.22793000

H	-0.09232100	1.00693400	-2.83351600
O	-0.01695200	0.92596300	-0.76511100
H	-0.95721600	1.27926800	-0.77004200

BDO + 2-pyrrolidone + $Zn(Ac)_2$

Zn	0.22438300	0.59289900	-0.17666500
C	-0.13154100	-1.90358700	-3.57221800
H	-0.95412700	-1.97955100	-4.28067200
H	0.77098900	-1.55888300	-4.08201400
H	0.08688800	-2.88863400	-3.15136300
C	-0.48238300	-0.94927400	-2.45128000
O	0.46082600	-0.75379000	-1.57855200
O	-1.59442100	-0.41140800	-2.39066400
C	0.97786100	4.77451500	-0.42255800
H	0.89472800	4.87700400	-1.50685700
H	0.04167400	5.13772000	0.00873500
H	1.81053600	5.36926500	-0.05148800
C	1.16041100	3.31433500	-0.06377200
O	2.14420400	2.96200500	0.61818400
O	0.24683600	2.52248900	-0.50705900
C	2.67284400	-2.42615200	1.79128300
H	1.78786500	-1.97492900	2.24996500
C	3.65625500	-1.33188500	1.34551800
H	4.55442300	-1.80288700	0.92391900
H	3.98678900	-0.76828300	2.22478200
C	3.14006900	-0.34242500	0.30957300
H	2.82801000	-0.84701400	-0.60851300
H	3.16718300	-3.00558400	2.57956400
C	2.20206600	-3.40707000	0.70185800
H	2.01246100	-4.38115600	1.15896900
H	2.99454200	-3.55590700	-0.04724600
O	0.97179600	-3.05842700	0.07372500
H	1.07419600	-2.30412900	-0.52523300
H	3.92902400	0.36595700	0.04077500
O	2.01296800	0.41007400	0.81634400
H	2.22477100	1.39786800	0.86013900
C	-4.53796600	-0.45078500	0.12832900
C	-4.65830200	-0.70813600	1.64849700
C	-3.39864400	-0.04923300	2.24055100
H	-5.09504200	0.43848200	-0.18544600
H	-4.87926600	-1.29390000	-0.47425200
H	-5.58607200	-0.31047100	2.05975900
H	-4.64062000	-1.78302800	1.84103100
H	-3.57528700	0.97834600	2.57579500

H	-2.95264000	-0.59162500	3.07428700
N	-3.10289200	-0.23560600	-0.05794200
H	-2.62697000	-0.23083600	-0.97409800
C	-2.44055300	0.00413600	1.06732700
O	-1.22046100	0.25753400	1.17506800

BDO + NEP+ $Zn(Ac)_2$

Zn	0.86459900	-0.68748200	0.47762800
C	0.46512700	2.36013200	2.99767200
H	-0.56770000	2.65106900	3.17932900
H	0.93822700	2.06894300	3.93833100
H	1.02933400	3.20769400	2.60154100
C	0.54209200	1.20963600	2.02874200
O	1.69399400	0.75985500	1.69592500
O	-0.49363800	0.68209900	1.54299400
C	1.64272100	-4.54947700	0.49021800
H	2.46521200	-4.80563300	-0.17575200
H	1.92368100	-4.82257200	1.51161300
H	0.74418700	-5.10974500	0.23101500
C	1.36847100	-3.06882200	0.45323500
O	0.23582000	-2.62687800	0.84034600
O	2.25709400	-2.25653900	0.06574800
C	2.48743500	2.19387600	-1.42202800
H	1.67734500	2.18930300	-0.68757300
C	2.01009200	1.47447600	-2.69249300
H	2.81127400	1.44379100	-3.44240200
H	1.19360200	2.05053000	-3.14107900
C	1.53774100	0.03509200	-2.48093900
H	2.35044000	-0.62472200	-2.17717200
H	2.68131400	3.24570700	-1.65388000
C	3.73946300	1.59854600	-0.76672000
H	4.62156100	1.81168500	-1.37822800
H	3.66193200	0.50626100	-0.68878900
O	3.99121700	2.16120900	0.51532000
H	3.34408100	1.77513300	1.12525900
H	1.10883100	-0.36552900	-3.40422300
O	0.54271200	-0.08154100	-1.43633600
H	-0.31365400	0.36719900	-1.66446100
C	-4.02679700	0.32516400	0.84461200
C	-4.36207600	1.81104500	0.61569500
C	-3.20037800	2.31406900	-0.25452400
H	-4.91648900	-0.30529200	0.89322300
H	-3.44001200	0.17118900	1.75752500
H	-5.30596100	1.89744800	0.07202400

H	-4.46557500	2.35453600	1.55510500
H	-3.48284400	3.04811300	-1.00994000
H	-2.38915500	2.74349400	0.34114400
N	-3.20747100	-0.02007000	-0.32136300
C	-2.65050900	1.05972900	-0.90953100
O	-1.80856500	1.04157900	-1.81738400
C	-2.80649400	-1.39726200	-0.60045900
H	-2.32975600	-1.81528900	0.29204300
C	-3.97116500	-2.27826200	-1.05471200
H	-4.74415200	-2.36548300	-0.28688200
H	-4.43103500	-1.88136100	-1.96317100
H	-3.60569600	-3.28590500	-1.26775500
H	-2.04808500	-1.35152100	-1.38166700