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Theoretical investigation of the chemoselectivity and synchronously pyrazole ring formation mechanism from ethoxymethylenemalononitrile and hydrazine hydrate in the gas and solvent phases: DFT study and NBO analysis

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Supplementary Materials:

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Table 1(S). total and relative energies of the intermediates
and product in the gas phase at the B3LYP level.

Species	G+ZPE(a.u)	ΔG_{rel}(kcal.mol^{-1})
R1+ R2	-528.830156	0.0
Inter1(r1)	-528.824169	3.7
Inter2(r1)	-528.836878	-4.2
Inter3(r1)	-528.851200	-13.2
Inter4 (r1)	-528.840290	-6.4
Inter5(r1)	-528.850580	-12.8
Inter6 (r1)	-528.846665	-10.4
Inter7 (r1)	-528.849147	-12.0
Inter8 (r1)	-528.853725	-14.8
Inter9 (r1)	-528.889453	-37.2
Inter1(r2)	-528.836937	-4.3
Inter3(r2)	-528.845646	-9.7
P	-528.893283	-39.6

Table 2(S). Total energies, Gibbs free energy of activation and imaginary
vibrational frequencies of the TSs for two routes in the gas phase at B3LYP level.

Species	G+ZPVE(a.u)	$\Delta G^{\neq}$ (kcal.mol^{-1})	ν (icm^{-1})
TS1(r1)	-528.765749	40.4	1626.97
TS2(r1)	-528.731181	58.4	1828.36
TS3(r1)	-528.770874	33.5	1632.90
TS4(r1)	-528.750637	46.2	362.49
TS5(r1)	-528.735545	72.6	1899.13
TS6(r1)	-528.735065	66.1	1804.92
TS7(r1)	-528.762978	46.4	1235.94
TS8(r1)	-528.742807	59.0	1926.70
TS9(r1)	-528.758905	48.9	1929.37
TS10(r1)	-528.764993	45.1	1658.66
TS11(r1)	-528.759509	54.7	2061.02
TS12(r1)	-528.804212	31.1	235.23
TS13(r1)	-528.796419	33.2	1331.40
TS14(r1)	-528.793264	35.9	1887.33
TS15(r1)	-528.817730	45.0	1746.91
TS1(r2)	-528.742583	55.0	1734.26
TS2(r2)	-528.742321	59.4	1596.37
TS3(r2)	-528.773284	39.9	1872.20
TS8(r2)	-528.773592	45.2	1640.26

Table 3(S). ZPVE-corrected total energies and relative Gibbs free energies of the intermediates and product in methanol at the B3LYP level.

Species	G+ZPE(a.u)	ΔG_{rel}(kcal.mol^{-1})
R1+ R2	-528.860659	0.0
Inter1(r1)	-528.840037	12.9
Inter2(r1)	-528.852658	5.0
Inter3(r1)	-528.872398	-7.4
Inter4(r1)	-528.857016	2.3
Inter5 (r1)	-528.877371	-10.5
Inter6 (r1)	-528.87035	-6.1
Inter7 (r1)	-528.865562	-3.1
Inter8(r1)	-528.865219	-2.9
Inter9(r1)	-528.913203	-31.3
Inter1(r2)	-528.860508	0.1
Inter3(r2)	-528.863955	-2.1
P	-528.910477	-33.0

Table 4(S). Total energies and Gibbs free energies of activation of the TSs for two routes in methanol at the B3LYP level.

Species	G+ZPE(a.u)	$\Delta G^{\neq}$ (kcal.mol^{-1})
TS1(r1)	-528.790398	44.1
TS2(r1)	-528.752467	54.9
TS3(r1)	-528.790537	31.1
TS4(r1)	-528.771314	43.2
TS5(r1)	-528.766199	66.7
TS6(r1)	-528.757847	62.2
TS7(r1)	-528.782438	44.1
TS8(r1)	-528.763072	56.2
TS9(r1)	-528.774113	49.3
TS10(r1)	-528.860659	38.4
TS11(r1)	-528.78088	56.2
TS12(r1)	-528.833122	20.2
TS13(r1)	-528.817178	30.4
TS14(r1)	-528.809995	42.3
TS15(r1)	-528.832427	49.0
TS1(r2)	-528.770763	56.4
TS2(r2)	-528.774001	54.3
TS3(r2)	-528.791003	43.7
TS8(r2)	-528.793112	44.5

Table 5(S). Total energies and relative energy of intermediates and product in the gas phase at the MPWB95 level.

Species	E+ZPE(a.u)	ΔE_{rel}(kcal.mol^{-1})
R1+ R2	-528.6513091	0.0
Inter1(r1)	-528.6655019	-8.9
Inter2(r1)	-528.6891967	-23.8
Inter3(r1)	-528.6675917	-10.2
Inter4 (r1)	-528.661104	-6.1
Inter5(r1)	-528.6851823	-21.3
Inter6 (r1)	-528.6754903	-15.2
Inter7 (r1)	-528.7035616	-32.8
Inter8 (r1)	-528.6991209	-30.0
Inter9 (r1)	-528.7211358	-43.8
Inter1(r2)	-528.6772109	-16.2
Inter3(r2)	-528.845646	-20.1
P	-528.7302076	-49.5

Table 6(S). Total energies and relative energy of activation of the TSs for two main pathways in the gas phase at the MPWB95 level.

Species	E+ZPVE(a.u)	$\Delta E^{\neq}$ (kcal.mol^{-1})
TS1(r1)	-528.6027558	30.5
TS2(r1)	-528.5744847	57.1
TS3(r1)	-528.770874	42.9
TS4(r1)	-528.5744847	60.3
TS5(r1)	-528.5632684	65.4
TS6(r1)	-528.5613961	62.5
TS7(r1)	-528.592655	60.6
TS8(r1)	-528.5904419	62.0
TS9(r1)	-528.6049544	52.9
TS10(r1)	-528.5632684	79.0
TS11(r1)	-528.58878	54.4
TS12(r1)	-528.6404487	36.8
TS13(r1)	-528.6305036	45.9
TS14(r1)	-528.6235876	38.7
TS15(r1)	-528.6472131	46.4
TS1(r2)	-528.5731479	49.0
TS2(r2)	-528.5907889	54.2
TS3(r2)	-528.6057504	44.8
TS8(r2)	-528.6258462	36.1

Table 7(S). Total energies and relative energies of the intermediates and product in the solvent phase at the MPWB95 level.

Species	E+ZPE(a.u)	ΔE_{rel}(kcal.mol^{-1})
R1+ R2	-528.6721157	0.0
Inter1(r1)	-528.7013928	-18.4
Inter2(r1)	-528.7078207	-22.4
Inter3(r1)	-528.6911158	-11.9
Inter4(r1)	-528.6779319	-3.6
Inter5 (r1)	-528.7131069	-25.7
Inter6 (r1)	-528.699838	-17.4
Inter7 (r1)	-528.720666	-30.5
Inter8(r1)	-528.6991209	-29.8
Inter9(r1)	-528.746668	-46.8
Inter1(r2)	-528.7013928	-18.4
Inter3(r2)	-528.7032059	-19.5
P	-528.7489884	-48.2

Table 8(S). Total energies and relative energies of activation for two main pathways in the solvent phase at the MPWB95 level.

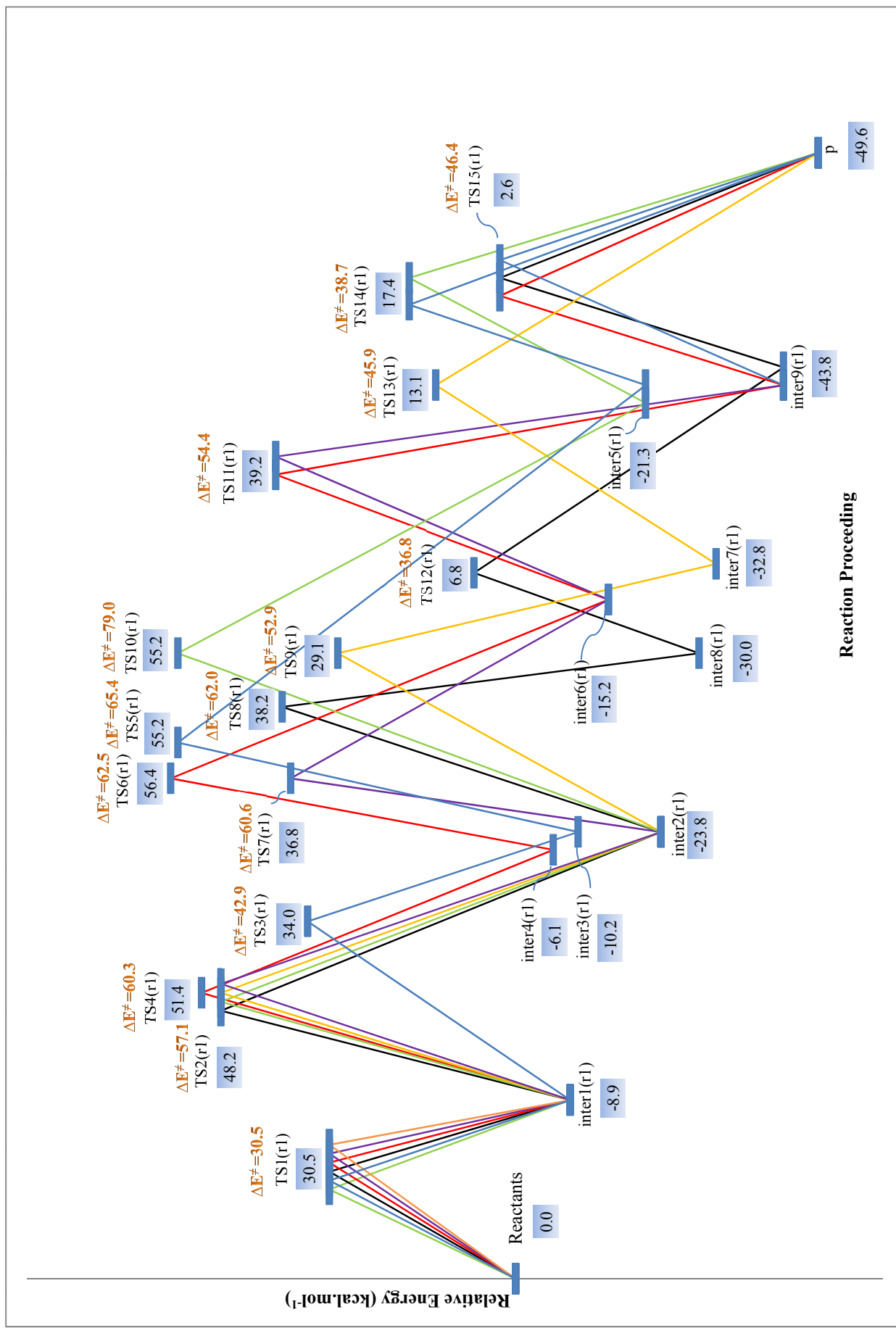| Species	E+ZPE(a.u)	$\Delta E^{\neq}$ (kcal.mol^{-1})
TS1(r1)	-528.6263138	28.7
TS2(r1)	-528.5963247	66.0
TS3(r1)	-528.6162498	53.5
TS4(r1)	-528.5963247	58.7
TS5(r1)	-528.5841472	67.1
TS6(r1)	-528.5820048	60.1
TS7(r1)	-528.6110032	60.7
TS8(r1)	-528.6106628	61.0
TS9(r1)	-528.6194729	55.4
TS10(r1)	-528.5841472	77.6
TS11(r1)	-528.6040534	60.1
TS12(r1)	-528.5963247	33.4
TS13(r1)	-528.649259	44.8
TS14(r1)	-528.6377286	47.3
TS15(r1)	-528.6472131	54.1
TS1(r2)	-528.6012682	44.5
TS2(r2)	-528.6249088	48.0
TS3(r2)	-528.6229073	49.3
TS8(r2)	-528.6460246	22.8

Figure 1(S). Potential energy diagram, according to the relative energy of the species involved in route1 in the gas phase
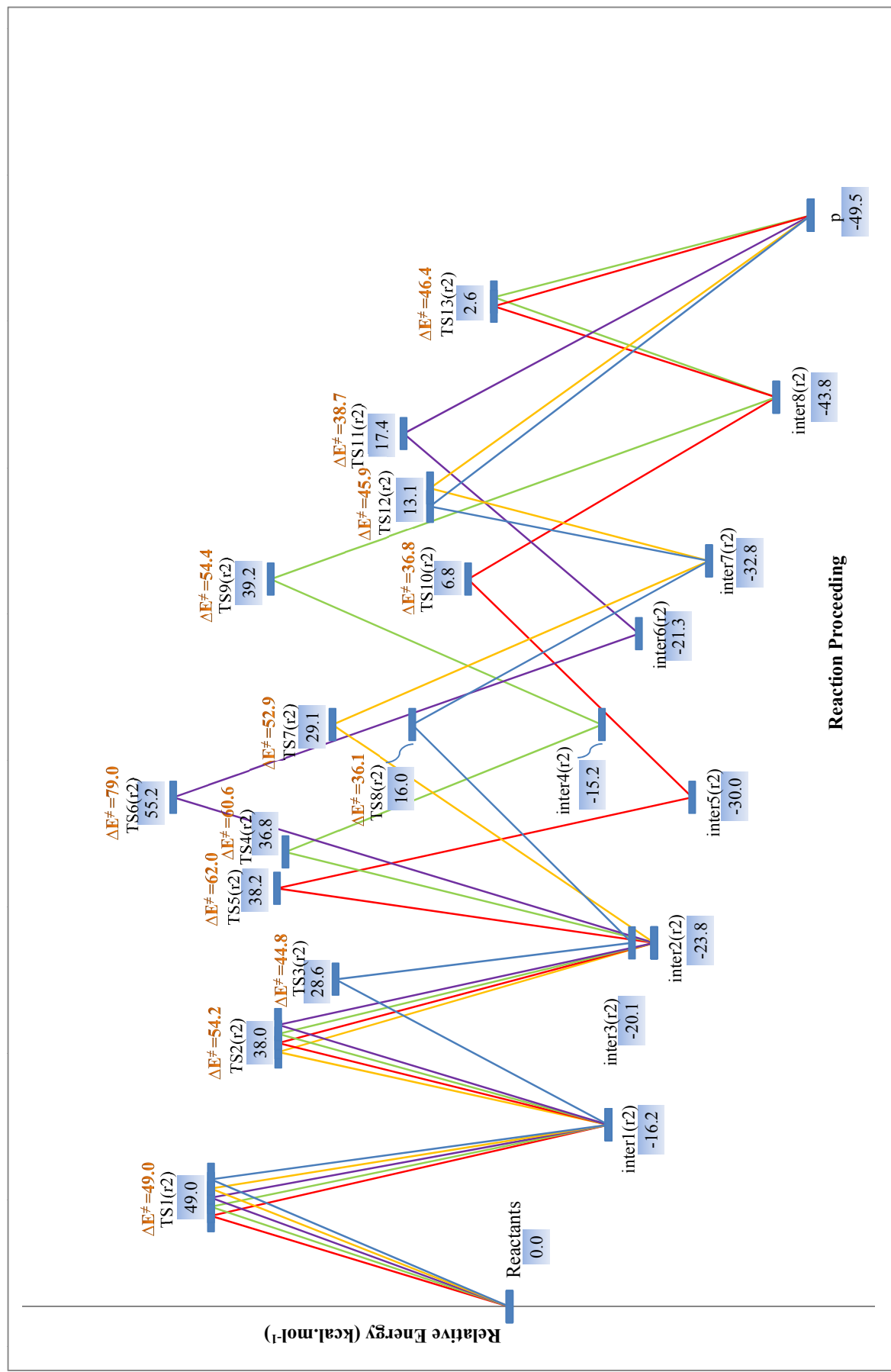
Figure 2(S). Potential energy diagram, according to the relative energy of the species involved in route 2 in the gas phase
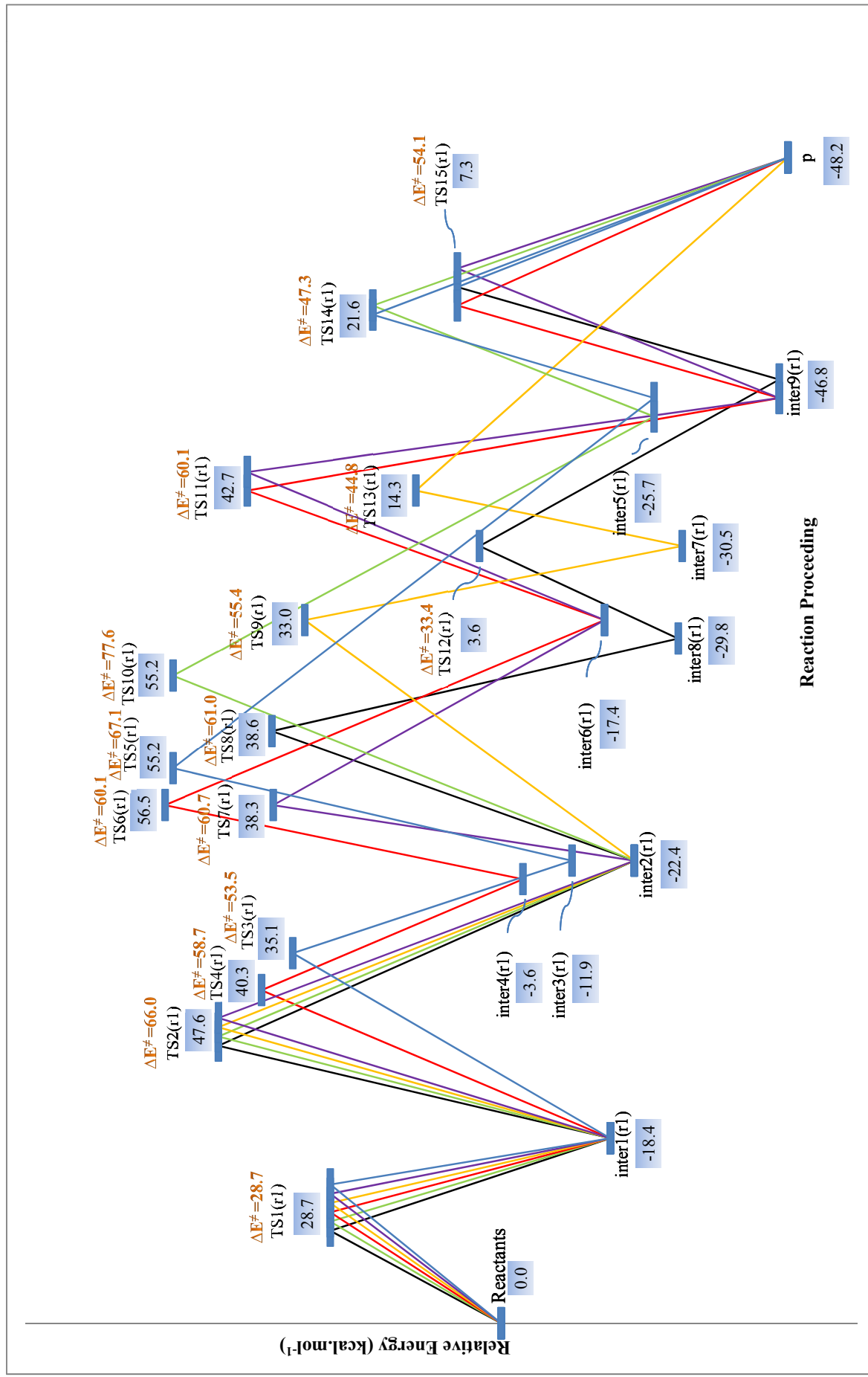
Figure 3(S). Potential energy diagram, according to the relative energy of the species involved in route 1 in the solvent phase
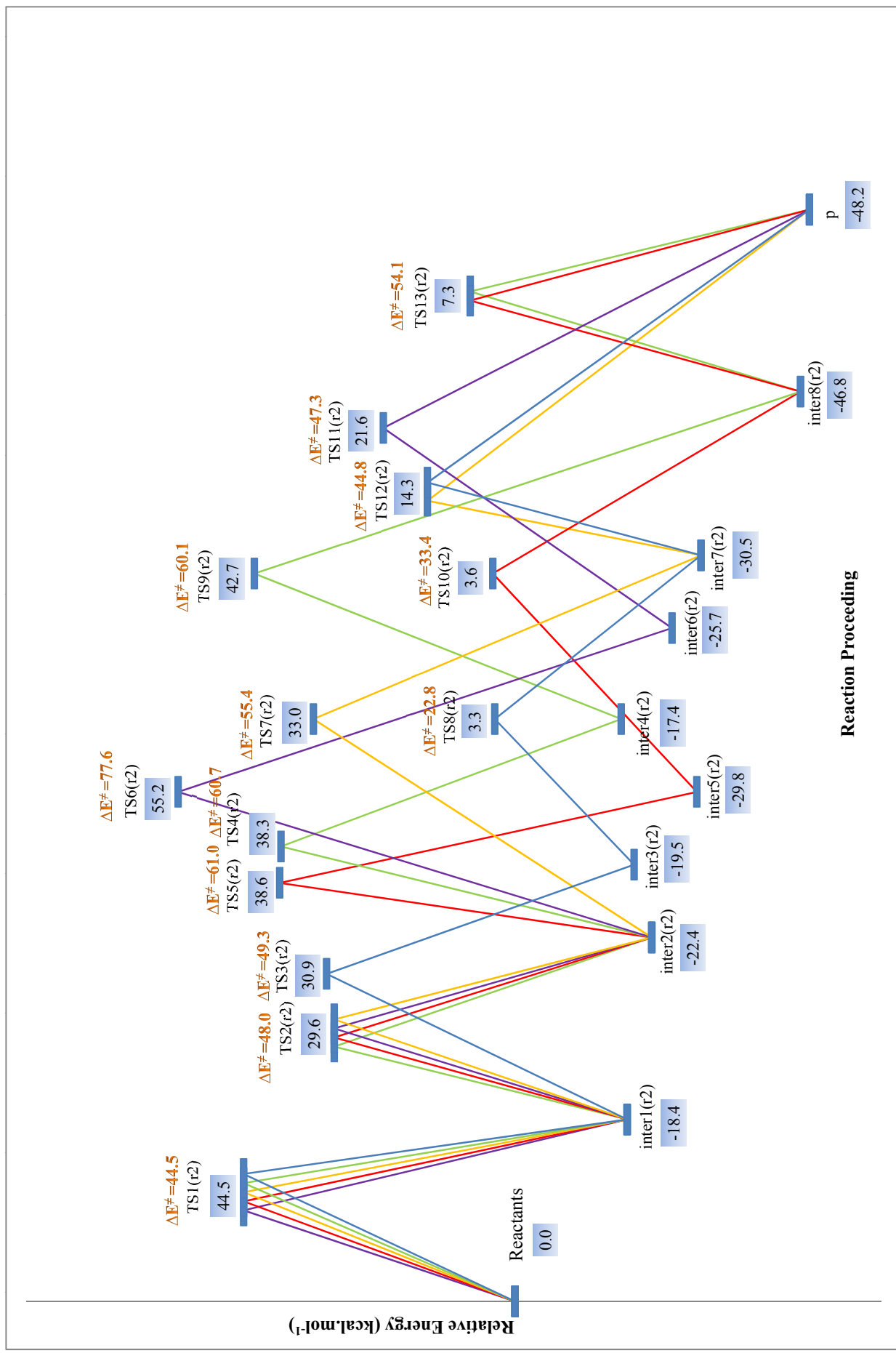
Figure 4(S). Potential energy diagram, according to the relative energy of the species involved in route 2 in the solvent phase.

Cartesian coordinates of the structures

Reactants:

0 1
C	-0.20188300	-2.43203300	-1.75967900
N	-0.43794700	-1.83891100	-0.79603000
C	0.09975600	-3.15821900	-2.94791600
C	-0.96275400	-3.72228900	-3.71277200
N	-1.80866500	-4.19299600	-4.34384800
C	1.39809300	-3.31116600	-3.33299900
H	2.19621000	-2.87958700	-2.73279400
O	1.72975800	-3.98484300	-4.41286100
C	3.14417000	-4.04834600	-4.78215400
C	3.55058800	-2.82403600	-5.57924300
H	3.72953300	-4.16224300	-3.86504800
H	3.20818400	-4.96074000	-5.37453100
H	3.45870800	-1.90461900	-4.99457500
H	4.59520200	-2.92528800	-5.88610100
H	2.93835400	-2.72949700	-6.47822900
N	2.05607100	-6.75493100	-6.59243500
N	1.06677400	-6.99166800	-5.57878900
H	1.64376700	-6.59692500	-7.51024500
H	2.64104600	-7.58097700	-6.65365900
H	0.75841600	-6.09227700	-5.22702600
H	0.25312300	-7.48225500	-5.94166700

Inter1(r1):

0 1
C	1.35916200	-4.75450200	-2.12482800
N	0.59003300	-5.36240000	-1.52092700
C	2.32964700	-3.97649100	-2.90096500
C	2.57557100	-2.67441500	-2.27059900
N	2.77757500	-1.63276100	-1.82086800
C	1.85496700	-3.84192100	-4.38991400
H	0.85883600	-3.37225400	-4.40766000
O	1.77948800	-5.14667400	-4.87864700
C	0.64105700	-5.45878400	-5.70623800
C	0.72751900	-6.92590400	-6.07514600
H	-0.27827500	-5.25348300	-5.14322100
H	0.66081000	-4.82023600	-6.59333700
H	0.71787000	-7.55301700	-5.18105400
H	-0.12627000	-7.20136900	-6.70013200
H	1.64369300	-7.13025100	-6.63354000
N	2.41087200	-2.76124600	-6.42686900
N	2.85374800	-3.06653300	-5.10550300
H	3.19995800	-2.84595300	-7.05661900
H	2.03495600	-1.81836400	-6.49349800
H	3.27416900	-4.53155000	-2.93432000
H	3.11139000	-2.23037700	-4.58764900

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Inter2(r1):

0 1

C	1.12915200	1.66841600	-0.19489700
N	1.24162500	2.60129500	-0.86257900
C	0.99907100	0.47746200	0.64242600
C	1.93608200	-0.64608500	0.17972800
N	3.12086400	-0.78621400	0.60635400
C	-0.37631300	-0.22410400	0.47069500
H	-0.52887600	-0.89000000	1.33124400
O	-1.41636600	0.67494800	0.33306600
C	-2.73318300	0.20561000	0.68103200
C	-3.42255900	-0.55280600	-0.44406400
H	-2.66317300	-0.40931800	1.58708700
H	-3.28663300	1.11214300	0.93099600
H	-2.88926700	-1.47207600	-0.69344900
H	-4.43980400	-0.81572900	-0.13804200
H	-3.48806500	0.06865000	-1.34044500
N	-0.19071000	-1.08028400	-0.73238700
N	1.19935100	-1.42154500	-0.71791700
H	1.21750100	0.73873600	1.67791100
H	-0.34461500	-0.48260800	-1.54477400
H	3.58901000	-1.59529000	0.19463800
H	1.37343400	-2.41782800	-0.73352000

Inter3(r1):

0 1

C	1.28346400	-2.24413400	-0.78467700
N	0.95921400	-3.26442800	-1.22462400
C	1.66310600	-0.98434800	-0.24930100
C	2.82873200	-0.87530500	0.55555600
N	3.76081100	-0.70746200	1.22193000
C	0.89580500	0.13143000	-0.50671700
H	-0.00071900	0.02795600	-1.10632200
O	-2.25407000	0.91786000	0.35642900
C	-3.60845300	0.98692700	-0.12790200
C	-4.25693100	-0.38376200	-0.24312400
H	-4.19826600	1.64610400	0.51980500
H	-3.53530000	1.46474000	-1.10678800
H	-4.33882200	-0.86683800	0.73583900
H	-5.26789600	-0.29066700	-0.65033100
H	-3.67847600	-1.03659600	-0.90069800
N	0.27714400	2.46189400	-0.23671300
N	1.14522100	1.36842900	-0.06282400
H	-0.67818100	2.16651500	-0.03428300
H	0.34422500	2.80329900	-1.19104900
H	-2.25629100	0.48815500	1.21899800
H	1.92707000	1.53974800	0.55594300

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Inter4(r1):

0 1
```
C         2.96816400   -0.33415300    0.79183500
N         3.61393600   -0.64226800    1.69473200
C         2.11397800    0.01868200   -0.35584400
C         2.03817000    1.48212400   -0.51337800
N         1.93526500    2.62110200   -0.65295100
C         0.72718600   -0.59448700   -0.23100000
H         0.11465600   -0.31160300    0.62594000
O        -2.65053500   -0.59270800    0.92905500
C        -3.53473600    0.54617900    0.89986300
C        -3.28124100    1.31817900   -0.37992900
H        -4.57562300    0.20499700    0.94386900
H        -3.34427600    1.17932300    1.77401400
H        -3.47913800    0.69578000   -1.25609000
H        -3.93796000    2.19066000   -0.42648600
H        -2.24756000    1.66818000   -0.42699400
N        -0.84452900   -2.00926200   -1.04383400
N         0.35852000   -1.40651800   -1.14228600
H        -1.15221300   -2.38809400   -1.92548000
H        -1.56047100   -1.56049900   -0.47062300
H         2.56917000   -0.39834300   -1.26088400
H        -2.81378100   -1.09926100    1.73139200
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Inter5(r1):

0 1
```
C         0.53597400    1.57526900    0.00800600
N        -0.05598300    2.56925200    0.00748500
C         1.18363800    0.32118400   -0.00332100
C         2.63171500    0.08019000   -0.01579600
N         3.56070100    0.94805900    0.04574300
C         0.55184000   -0.88354200    0.01437500
H        -0.51306500   -1.07207900   -0.02394300
O        -2.39295000    0.27883400   -0.11291500
C        -3.81641100    0.34749100    0.02846300
C        -4.36449200   -1.06723100    0.05101900
H        -4.07752100    0.87109100    0.95684500
H        -4.25043900    0.90946000   -0.80827500
H        -3.94642100   -1.62958700    0.88999800
H        -5.45266700   -1.05253800    0.15647400
H        -4.11695500   -1.59157300   -0.87563300
N         1.45793200   -1.90920400    0.08605700
N         2.75039800   -1.34206400   -0.11079200
H        -2.02832600    1.17323400   -0.11052800
H         1.28684000   -2.72266700   -0.49596900
H         4.48942400    0.53133100   -0.00498800
H         3.42780900   -1.74980400    0.52341500
```

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Inter6(r1):

0 1
C	-0.58271700	1.45480000	-0.05240700
N	-0.06790500	2.38147200	-0.50516500
C	-1.15099000	0.24052000	0.51533000
C	-2.64245200	0.01184200	0.20707900
N	-3.56058600	0.86526000	0.38800700
C	-0.53910800	-1.03673400	-0.04172000
H	0.52241400	-1.23310800	-0.09681100
O	2.39497100	0.32376700	-0.09536400
C	3.82670000	0.35391500	-0.12152600
C	4.34104900	-0.99724500	0.33908800
H	4.18079900	0.56871500	-1.13795600
H	4.19907700	1.14730500	0.53925800
H	3.98332900	-1.79152800	-0.32095400
H	5.43433800	-1.01100200	0.33200000
H	4.00095200	-1.21304400	1.35504400
N	-1.42372500	-1.86326500	-0.45129800
N	-2.67425700	-1.30462000	-0.23833800
H	2.05113900	1.17962900	-0.37872100
H	-1.02113300	0.27893000	1.60435900
H	-4.48398600	0.50806400	0.14224700
H	-3.45628400	-1.73861300	-0.70306600

Inter7(r1):

0 1
C	1.26459500	1.65141400	0.23696700
N	1.53850100	2.71113700	-0.12562800
C	0.99619300	0.30066400	0.70601200
C	1.62726500	-0.82204000	-0.11381100
N	2.92682400	-0.74748400	-0.56391200
C	-0.48905700	-0.14328100	0.66870800
H	-1.02123400	0.10397500	1.59187000
O	-1.12902400	0.45386600	-0.43716100
C	-2.49809800	0.83077200	-0.25190400
C	-3.46866500	-0.34422400	-0.29608300
H	-2.59952100	1.38316900	0.69172200
H	-2.70507500	1.52747500	-1.06568100
H	-3.31851800	-1.03144900	0.54207900
H	-4.49764500	0.02264700	-0.23652400
H	-3.35869100	-0.90083400	-1.22999300
N	-0.30627000	-1.59602700	0.56064200
N	0.87514100	-1.85049800	-0.19260600
H	1.36776800	0.21144000	1.73434400
H	-1.08430400	-2.05214100	0.09832800
H	3.21830300	0.15706300	-0.90995600
H	3.19834500	-1.51200000	-1.16771300

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Inter8(r1)

0 1
```
C         1.34879200    1.73215000    0.13485900
N         1.71952300    2.83172000    0.12869300
C         0.92766800    0.39318300    0.15473900
C         1.72718600   -0.68760300   -0.05612900
N         3.08298600   -0.75380300   -0.20129900
C        -0.48757900   -0.07537000    0.38225000
H        -0.88930300    0.21669700    1.36051700
O        -1.36693100    0.40406600   -0.62092100
C        -2.66916000    0.81312400   -0.18033400
C        -3.61040100   -0.35508000    0.08897100
H        -2.57107300    1.44742100    0.70943700
H        -3.05138000    1.43780700   -0.98949200
H        -3.24162500   -0.99193600    0.89813600
H        -4.59683000    0.01858400    0.38018600
H        -3.73052200   -0.96913600   -0.80747300
N        -0.36148500   -1.56250100    0.29640200
N         1.00763100   -1.88092600   -0.04613000
H         3.56399200    0.12818800   -0.30627500
H        -0.92132700   -1.83900400   -0.50526800
H         3.43776000   -1.49610100   -0.78691500
H         1.37614000   -2.54890100    0.62472900
```

Inter9(r1):

0 1
```
C         0.50502600    1.45057000   -0.03518200
N        -0.04946900    2.46824900   -0.05608000
C         1.16596700    0.20905600   -0.01534500
C         2.54559000   -0.00031500    0.04567400
N         3.58571200    0.89041700    0.18888800
C         0.59917400   -1.10028300   -0.08020800
H        -0.45157700   -1.34089100   -0.14213300
O        -2.48039500    0.28257200   -0.20479000
C        -3.87132600    0.38418700    0.11004800
C        -4.46578600   -1.01219300    0.10211900
H        -4.00498100    0.84704800    1.09697700
H        -4.38222100    1.01678500   -0.62810800
H        -3.97176800   -1.64488800    0.84381800
H        -5.53311400   -0.97407200    0.33738600
H        -4.34530100   -1.47579900   -0.88020600
N         1.52631600   -2.03152100   -0.06545200
N         2.70912600   -1.34148100    0.01187900
H        -2.08587900    1.16285300   -0.19104900
H         3.32790900    1.86024400    0.07079400
H         4.44686100    0.66015200   -0.28656700
H         3.56957500   -1.85779200    0.10011400
```

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Inter1(r2):

0 1
```
C         1.04196900    2.16323100    0.02952700
N         1.38661700    3.26303200    0.11160900
C         0.52282000    0.83406300   -0.07870100
C         1.50513700   -0.28122800    0.05266600
N         2.74230800    0.03495900    0.16893400
C        -0.81050200    0.75493200   -0.30113300
H        -1.39654400    1.66721900   -0.37328300
O        -1.48447000   -0.39335200   -0.47169200
C        -2.92983400   -0.30091900   -0.53855600
C        -3.55451100   -0.24607400    0.84403300
H        -3.19361800    0.57366800   -1.14163000
H        -3.23479200   -1.19548600   -1.08121800
H        -3.24492700    0.64962400    1.38815200
H        -4.64401100   -0.22653800    0.75270600
H        -3.27427200   -1.12294400    1.43135800
N         1.77340400   -2.70664700    0.01701600
N         0.97482200   -1.55864300    0.06561900
H         2.26096600   -2.83546800    0.89868300
H         2.45667400   -2.64777600   -0.73584500
H         3.33762600   -0.78721900    0.26081400
H         0.01812000   -1.70121400   -0.21546800
```

Inter3(r2):

0 1
```
C         0.96980400    2.09770300   -0.11284400
N         1.43377000    3.15740700   -0.05556900
C         0.44239100    0.77255700   -0.15816800
C         1.39393600   -0.34580000    0.02985800
N         2.59753100   -0.06311700    0.67460400
C        -0.90009600    0.68101200   -0.35607500
H        -1.47350700    1.59867900   -0.47615000
O        -1.58003200   -0.45376700   -0.42915500
C        -3.02136700   -0.34613000   -0.45549700
C        -3.59946400   -0.25375500    0.94631100
H        -3.30292200    0.51717500   -1.06831500
H        -3.35315100   -1.25094200   -0.96449100
H        -3.26596800    0.65377000    1.45620900
H        -4.69167300   -0.23221000    0.89520400
H        -3.29848300   -1.11679600    1.54364400
N         2.05586100   -2.50056000   -0.11188900
N         1.07030300   -1.52870100   -0.35850300
H         1.64966600   -3.40139100   -0.33074400
H         2.35233400   -2.50494800    0.86625900
H         2.84158600    0.91394700    0.75892600
H         3.36890600   -0.63587100    0.35069200
```

product:

```
0 1
C        -0.55581700    1.49990800   -0.00446000
N        -0.03580500    2.53532300   -0.01369400
C        -1.17173600    0.23355400   -0.00268700
C        -2.56971400   -0.07835400    0.02124300
N        -3.61655700    0.81272500    0.11866600
C        -0.53096300   -1.00082100   -0.03246000
H         0.52497200   -1.22288600   -0.05843800
O         2.42238400    0.27817300   -0.10437600
C         3.83995300    0.40397700    0.05003700
C         4.44687100   -0.98675900    0.04577000
H         4.25714900    1.00198500   -0.77044500
H         4.07317500    0.91703100    0.99198000
H         4.22810300   -1.49984000   -0.89424500
H         5.53266400   -0.92910500    0.16118100
H         4.04573200   -1.58484900    0.86808000
N        -1.50490300   -1.92022900   -0.02365200
N        -2.76207800   -1.38942300    0.00293700
H         2.02331500    1.15699300   -0.09762000
H        -1.40510900   -2.92193300   -0.03970700
H        -4.52014900    0.42750400   -0.11509300
H        -3.45509100    1.73191100   -0.26514500
```

Gas phase:

TS1(r1):

```
0 1
C        -0.96795000   -0.03192200    1.48703500
N        -0.72081400    0.05609000    2.61594000
C        -1.23504200   -0.04962300    0.08406400
C        -2.15572400   -1.02184400   -0.40635800
N        -2.90670700   -1.77368500   -0.86782600
C        -0.04518900    0.30674700   -0.83996600
H        -0.24263700   -0.08392000   -1.84611500
O         1.25365400    0.09237300   -0.42775800
C         1.63449800   -1.29893600   -0.33145200
C         3.06644100   -1.36124800    0.15612500
H         0.95624900   -1.80377500    0.36297300
H         1.52690300   -1.76177300   -1.32030000
H         3.15816500   -0.90321000    1.14290700
H         3.38186200   -2.40476200    0.23227000
H         3.73888900   -0.84895400   -0.53563300
N         0.46303200    2.66258500   -0.02343700
N        -0.29356200    1.82108600   -0.89737900
H         1.41780300    2.30638900    0.00207500
H         0.07970200    2.55270100    0.91266500
H        -1.37647100    1.38150600   -0.37653600
H        -0.24554300    2.20524100   -1.84001700
```

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TS2(r1):

0 1

C	1.28066900	1.88313800	-0.02582000
N	1.57363400	2.91092500	-0.46019400
C	0.88617000	0.57779500	0.48510100
C	1.98071700	-0.49130200	0.38496000
N	2.83237400	-1.07080300	1.06364100
C	-0.29986900	-0.04352800	-0.34682900
H	-0.39208200	0.48610500	-1.30308100
O	-1.47821900	0.00672200	0.37724700
C	-2.68946000	-0.04613000	-0.40837000
C	-3.86667600	0.03935200	0.54063800
H	-2.68563700	0.79560300	-1.11149600
H	-2.71015900	-0.97708100	-0.98445100
H	-3.83504700	0.96762700	1.11484100
H	-4.80122200	0.01462000	-0.02565500
H	-3.86532900	-0.80082000	1.23832900
N	1.50507600	-1.43912500	-0.74675500
N	0.06314400	-1.46755100	-0.66871800
H	1.79208900	-1.21010100	-1.70238700
H	2.33344800	-2.02891300	-0.02390200
H	0.57880200	0.67407300	1.52840600
H	-0.15800900	-2.02496600	0.15752900

TS3(r1):

0 1

C	-1.40829900	-1.65572200	-0.75200500
N	-1.64751400	-2.56730200	-1.42198600
C	-1.03982600	-0.54793200	0.08181100
C	-2.01819300	-0.08638700	1.02289000
N	-2.74676200	0.34066000	1.81391900
C	-0.20193700	0.51610500	-0.57833800
H	0.21519900	0.29630500	-1.55423200
O	1.19101300	0.01753500	0.44354800
C	2.36205700	-0.52385500	-0.18703600
C	3.31493100	-1.06412400	0.86794300
H	2.07482000	-1.31886200	-0.88846900
H	2.83330000	0.27986600	-0.76194200
H	2.84851200	-1.87141900	1.43748200
H	4.21601100	-1.45998900	0.39072500
H	3.60840300	-0.27525200	1.56379500
N	0.39797800	2.76178500	-0.90044800
N	-0.50427700	1.81378200	-0.37683100
H	1.05475000	3.05959500	-0.18278100
H	-0.12289300	3.56298200	-1.23925400
H	0.19535900	-0.72909400	0.67236800
H	-0.99993900	2.04460200	0.47976000

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TS4(r1):

0 1
C	0.75456200	-1.64360300	0.73272400
N	0.55934800	-2.52648500	1.44475000
C	1.02012800	-0.51982400	-0.17390500
C	2.41560900	-0.55139500	-0.65606600
N	3.49939400	-0.53468100	-1.04589900
C	0.74352400	0.80713800	0.50715000
H	1.07093200	0.96766600	1.52870100
O	-1.50452100	0.45643400	0.02376800
C	-2.74898500	-0.17427400	0.07166600
C	-2.93105400	-1.26179800	-0.99098700
H	-2.89089900	-0.62074500	1.07023800
H	-3.55472000	0.57458900	-0.03274900
H	-2.19169500	-2.05839800	-0.86285600
H	-3.92623000	-1.71510800	-0.92655300
H	-2.81502900	-0.84080600	-1.99504200
N	0.11321200	3.01701700	0.53364200
N	0.34900700	1.82646900	-0.19996200
H	-0.83393600	2.94604800	0.90800100
H	0.14435300	3.78977200	-0.12392700
H	0.33741100	-0.60328700	-1.02605500
H	-0.47343900	1.49508700	-0.80110900

TS5(r1):

0 1
C	-2.82753100	-1.09733600	-0.04382700
N	-3.64555200	-1.89524400	0.13486700
C	-1.84461800	-0.10850600	-0.26484900
C	-1.24424700	0.77743500	0.77009100
N	-0.78644700	0.80453800	1.91723400
C	-1.07242800	0.01729000	-1.37391300
H	-1.04109900	-0.64528100	-2.22834000
O	1.86379900	-0.21639400	0.37091300
C	3.15305800	-0.77505400	0.66721800
C	4.01144000	-0.68903400	-0.58033400
H	3.61930400	-0.22028100	1.49041300
H	3.04211800	-1.81945700	0.98251800
H	4.13460600	0.35047400	-0.89561000
H	5.00338100	-1.10587500	-0.38740600
H	3.55949400	-1.25165900	-1.40141400
N	-0.19616400	1.11797000	-1.36721700
N	-0.44442300	1.79006700	-0.11496000
H	1.30482300	-0.27519400	1.15758600
H	0.78837800	0.85782500	-1.43880900
H	0.06944100	1.70591200	1.02636700
H	-0.93678500	2.66459900	-0.30838700

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TS6(r1):

0 1

C	-0.56621900	1.62301900	0.26118100
N	0.03977800	2.55254400	-0.04983700
C	-1.25855100	0.41378600	0.67398800
C	-2.63691800	0.18086900	0.05203300
N	-3.45508800	0.64005100	-0.74440100
C	-0.57808600	-0.87958200	0.19605500
H	0.50015600	-0.96302400	0.09721900
O	2.36312400	0.35345700	0.01624300
C	3.76833800	0.25664200	-0.25099300
C	4.19858900	-1.18235000	-0.03706900
H	3.97633200	0.56704100	-1.28261000
H	4.32360000	0.92355800	0.42058800
H	3.66155200	-1.85148200	-0.71409800
H	5.26985100	-1.29060600	-0.22675700
H	3.99866400	-1.49608000	0.99063200
N	-1.35706200	-1.84714100	-0.12428900
N	-2.69928800	-1.36257100	0.01234200
H	-1.31895500	0.40081800	1.77011500
H	2.07003100	1.26144500	-0.12954200
H	-3.47673800	-0.88976300	-0.86416800
H	-3.17079300	-1.84405600	0.78080100

TS7(r1):

0 1

C	0.72197600	1.79160500	0.28565500
N	0.32984000	2.81889300	-0.05711600
C	1.21651900	0.50584200	0.76268200
C	2.04452700	-0.29971600	-0.25746000
N	3.09960400	0.14146800	-0.79970400
C	0.13187100	-0.47563200	1.12277400
H	-0.55481400	-0.35772700	1.94455600
O	-1.41033500	-0.48758500	-0.20794500
C	-2.53570000	0.14539100	-0.77631500
C	-3.82901700	-0.11753800	-0.00874000
H	-2.33312900	1.22385300	-0.82595300
H	-2.63479500	-0.19527000	-1.81769200
H	-3.75510100	0.25512900	1.01710000
H	-4.67552100	0.38285900	-0.49072800
H	-4.04393400	-1.18928100	0.03172000
N	0.34200800	-1.67515700	0.57263100
N	1.39461800	-1.52298200	-0.38001400
H	1.85028200	0.69353500	1.64009400
H	-0.69166100	-1.65572100	0.00357900
H	3.52099400	-0.52740500	-1.44429800
H	1.93681700	-2.36455900	-0.51697100

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TS8(r1):

0 1

C	1.23140000	1.63538400	-0.23038600
N	1.42669000	2.63897200	-0.77570100
C	1.02289400	0.42519700	0.50388400
C	1.82698300	-0.73148000	0.07225500
N	2.95382800	-0.72791900	0.72999100
C	-0.39437300	-0.18247000	0.43041400
H	-0.62921600	-0.74426800	1.34297000
O	-1.38447400	0.73302700	0.13438000
C	-2.70499500	0.44997900	0.62786700
C	-3.47801400	-0.53230800	-0.24130100
H	-2.63027300	0.08847400	1.66093900
H	-3.20135200	1.42144000	0.64804700
H	-2.99350300	-1.51067400	-0.26995100
H	-4.48904700	-0.66019900	0.15757900
H	-3.56145500	-0.15623300	-1.26399500
N	-0.26898000	-1.21733800	-0.69283100
N	1.12594100	-1.59057200	-0.68837200
H	2.30363000	0.24919800	1.34522300
H	-0.43005800	-0.70359200	-1.56018600
H	3.72340200	-1.36919500	0.54823800
H	1.29793900	-2.58698800	-0.67191400

TS9(r1):

0 1

C	1.14150500	1.75787100	-0.14468700
N	1.29057500	2.72132200	-0.75984500
C	0.97574000	0.54057800	0.64326400
C	1.86813700	-0.58877600	0.16540700
N	2.99764300	-1.19109100	0.49923300
C	-0.40428900	-0.19773400	0.41807100
H	-0.59979400	-0.78124400	1.32741600
O	-1.43345800	0.68702500	0.15717200
C	-2.75062300	0.29740700	0.59385800
C	-3.42659900	-0.69853200	-0.33684200
H	-2.68227900	-0.09987200	1.61439500
H	-3.30883900	1.23384100	0.63315400
H	-2.87828200	-1.64179100	-0.38232300
H	-4.43912000	-0.90579500	0.02251400
H	-3.50201500	-0.28974700	-1.34742700
N	-0.16881400	-1.17145900	-0.68781000
N	1.24981800	-1.36099400	-0.70671000
H	1.11822500	0.77414300	1.69908600
H	-0.42983200	-0.72889800	-1.56833200
H	3.82477600	-0.64273100	0.71757300
H	2.35705200	-2.06343500	-0.42193300

TS10(r1):

0 1
```
C       -1.65874900   1.67031100   0.10457100
N       -2.19703500   2.68962100   0.20754300
C       -0.95030900   0.44545000  -0.02995700
C       -1.62830400  -0.84032800  -0.29560800
N       -2.66514300  -1.02996100  -1.00341400
C        0.20397600   0.12838500   0.84596700
H        0.50887400   0.74977700   1.67859600
O        1.31969300   0.58153800  -0.34638800
C        2.48831600  -0.19888800  -0.68752300
C        3.74790700   0.44217000  -0.13044500
H        2.34152900  -1.21151200  -0.29623800
H        2.51579700  -0.25183500  -1.77806300
H        3.71756500   0.48740600   0.96105400
H        4.62479000  -0.14515400  -0.41927800
H        3.86971800   1.45694300  -0.51426900
N        0.24350800  -1.24921500   1.05565800
N       -0.86097100  -1.85758000   0.37080500
H        0.24318100   0.60317100  -0.88675500
H        0.24058100  -1.50514300   2.03580300
H       -2.94940800  -2.00919300  -1.00568200
H       -0.52970600  -2.57941600  -0.26023700
```

TS11(r1):

0 1
```
C       -0.60905900   1.43687600  -0.17495000
N       -0.01874200   2.34389300  -0.58688700
C       -1.25315100   0.30174800   0.40893700
C       -2.63231100  -0.04957400   0.02344800
N       -3.46895000   0.73217600   0.65533500
C       -0.58431200  -1.00860800   0.22226100
H        0.45389500  -1.23272600   0.42632300
O        2.38716200   0.29997700   0.06459200
C        3.79858000   0.34813200  -0.16121400
C        4.40366200  -0.95930400   0.31618100
H        4.00683200   0.49431800  -1.22931200
H        4.24087100   1.19166800   0.38503100
H        3.97692000  -1.80357800  -0.23127300
H        5.48589500  -0.95893600   0.15921100
H        4.21020700  -1.10616600   1.38178900
N       -1.34859400  -1.88164500  -0.34857900
N       -2.60637200  -1.24983200  -0.58120300
H        1.98651500   1.12612300  -0.23389000
H       -2.23848900   0.97585700   1.27346000
H       -4.46857600   0.75541900   0.47662500
H       -3.39321700  -1.86956300  -0.70332500
```

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TS12(r1):

0 1
C	-1.51825200	1.79627400	-0.21978900
N	-1.90903200	2.87740600	-0.08267700
C	-1.10476700	0.45629000	-0.35858600
C	-1.75813900	-0.64408800	0.21844700
N	-2.92837400	-0.67184900	0.90030800
C	0.02944400	-0.06653900	-1.00754200
H	0.71518400	0.44034400	-1.65969800
O	1.77707700	-0.46728900	0.20018100
C	2.82442900	0.12230000	0.89912900
C	3.98900800	0.56484400	0.00467000
H	2.46279700	0.99692000	1.47136600
H	3.21020400	-0.58353000	1.65821100
H	3.65533600	1.31280300	-0.72205400
H	4.80162100	1.00449100	0.59527800
H	4.38896400	-0.28990900	-0.54954800
N	-0.00679800	-1.44295800	-0.97132000
N	-1.05239300	-1.75664700	-0.07674900
H	0.94381200	-1.67312000	-0.53630800
H	-3.31187200	0.21913200	1.18086500
H	-3.10543400	-1.43525300	1.53499600
H	-1.47138200	-2.66971500	-0.17946200

TS13(r1):

0 1
C	-1.81685100	1.54605400	0.11106300
N	-2.57541100	2.41842600	0.10828900
C	-0.89576000	0.45204100	0.04711700
C	-1.38488900	-0.91916700	-0.27883700
N	-2.28442300	-1.17935100	-1.26541700
C	0.08209500	0.15998300	1.13174200
H	0.48363600	0.83841000	1.86557600
O	1.45644100	0.67124700	-0.25336700
C	2.52675500	-0.15919300	-0.62685800
C	3.88389700	0.47276700	-0.32270300
H	2.44273200	-1.13188800	-0.10436300
H	2.45559800	-0.39037800	-1.69958000
H	3.98195400	0.68217500	0.74644800
H	4.70186400	-0.19314800	-0.61884200
H	3.99227200	1.41677900	-0.86237000
N	0.03629700	-1.15307800	1.31330600
N	-0.78408300	-1.84680700	0.40677100
H	0.10980700	0.67037700	-0.67666600
H	0.63586900	-1.70171600	1.90865900
H	-2.66461600	-2.11304000	-1.30167700
H	-2.90878500	-0.43677500	-1.54004400

TS14(r1):

```
0 1
C         0.50203800    1.61387000   -0.08185600
N        -0.07414600    2.61831800   -0.06791200
C         1.15929400    0.36833800   -0.11093900
C         2.56738800    0.07540400   -0.04604400
N         3.75571300    0.52590300    0.34462900
C         0.53444000   -0.87512800   -0.05817300
H        -0.52691200   -1.08394500   -0.05421000
O        -2.41823100    0.28466400   -0.07282200
C        -3.84403900    0.31855400    0.05907100
C        -4.35352500   -1.10960900    0.11410300
H        -4.12480100    0.85752400    0.97279000
H        -4.28812300    0.84744900   -0.79383400
H        -3.92638500   -1.63881600    0.96987100
H        -5.44240500   -1.12205700    0.21213600
H        -4.08533600   -1.65009700   -0.79738900
N         1.47399000   -1.83996200    0.00969700
N         2.72303400   -1.26604400   -0.17526400
H        -2.07755300    1.18790600   -0.08867100
H         1.33594800   -2.80960100   -0.23117900
H         4.06210400    1.45600400    0.08208700
H         3.87558900   -0.93775600    0.27595300
```

TS15(r1):

```
0 1
C         0.56113300    1.49709100   -0.04654500
N         0.06968100    2.54516100   -0.05337300
C         1.16107200    0.21848900   -0.03463400
C         2.54362500   -0.07054100    0.01438800
N         3.58506000    0.80191900    0.15746000
C         0.51654200   -1.02288300   -0.03960100
H        -0.55028700   -1.19862200   -0.01755500
O        -2.43589100    0.36952000    0.07824900
C        -3.86294800    0.38754900   -0.03808900
C        -4.36542000   -1.04168100    0.04727600
H        -4.29969300    0.99184500    0.76754200
H        -4.15871600    0.83773800   -0.99460800
H        -4.08330500   -1.49224100    1.00210300
H        -5.45524400   -1.06835700   -0.03758400
H        -3.94326700   -1.64735600   -0.75858900
N         1.39800300   -2.02335900   -0.11571700
N         2.74599500   -1.39800500   -0.08239400
H        -2.10039300    1.27283600    0.03960700
H         3.41623200    1.77362000   -0.05274100
H         4.49851700    0.45731900   -0.09541700
H         2.24808600   -2.17109800    0.76264900
```

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TS1(r2):

0 1
C   1.51292500   1.93227800   -0.23728400
N   2.08869800   2.91951100   -0.40778400
C   0.76625700   0.72791100   -0.04959500
C   1.50225200   -0.44021300   0.47533700
N   2.60302700   -0.59899700   1.03296200
C   -0.55372500   0.78326700   -0.34228100
H   -0.99914900   1.70614500   -0.70352500
O   -1.37799300   -0.27586200   -0.23030500
C   -2.79389800   -0.01218600   -0.40336500
C   -3.41913300   0.56516100   0.85424400
H   -2.92240900   0.65235700   -1.26398700
H   -3.22286200   -0.98257700   -0.65292400
H   -2.98514400   1.53505000   1.10893700
H   -4.49212100   0.70580400   0.69784500
H   -3.28182400   -0.10955600   1.70187200
N   0.61815300   -2.48675500   -0.93213800
N   0.88540300   -1.87240100   0.33897100
H   1.48518000   -2.44556800   -1.46248400
H   -0.07901900   -1.92615000   -1.41756400
H   0.07263900   -2.03477800   0.93568600
H   1.99361500   -1.96064000   0.89216300

TS2(r2):

0 1
C   1.06098800   1.89988000   0.27402800
N   1.13929000   3.05494000   0.24099300
C   0.92428800   0.49794200   0.38523400
C   1.75308700   -0.46423600   -0.34771600
N   2.76588200   -0.26498700   -1.08738000
C   -0.43189300   -0.15706900   0.55368800
H   -1.00290400   0.23420600   1.40094600
O   -1.19104000   -0.32985700   -0.57358600
C   -2.59138000   -0.61079800   -0.36829200
C   -3.41469500   0.66532200   -0.29626800
H   -2.88652900   -1.22016100   -1.22378100
H   -2.72152500   -1.22220000   0.53458900
H   -3.27733800   1.25521400   -1.20431500
H   -4.47624100   0.42075300   -0.19706300
H   -3.12957800   1.28438900   0.55839100
N   0.27527800   -1.43056800   1.08282300
N   1.17427000   -1.76228900   -0.00475100
H   0.95621500   -0.50975200   1.60051400
H   -0.29369000   -2.23243000   1.35969000
H   3.19161800   -1.13373000   -1.40934900
H   1.88289000   -2.40335000   0.34323100

TS3(r2):

0 1
C	1.65294700	1.71324300	0.36323300
N	2.33517900	2.59292100	0.67886200
C	0.80883900	0.63160300	-0.02778600
C	1.42922000	-0.68218600	-0.25095400
N	2.66913900	-0.92069400	-0.67054500
C	-0.50515300	0.91687800	-0.22963000
H	-0.86232500	1.92837800	-0.04085900
O	-1.38719900	0.05398800	-0.69956600
C	-2.77274800	0.47407100	-0.72381200
C	-3.44904500	0.23726500	0.61472300
H	-2.81709000	1.52685100	-1.02299000
H	-3.22392400	-0.12688600	-1.51296100
H	-2.99785600	0.84524000	1.40274600
H	-4.50727800	0.50357000	0.54271100
H	-3.37081900	-0.81181400	0.90437800
N	-0.06668400	-2.10633500	0.94973000
N	0.89928500	-1.89799500	-0.07042200
H	0.40966200	-2.39942200	1.80234700
H	-0.64842000	-2.88370100	0.65401600
H	3.11434100	-0.27069300	-1.31412200
H	2.15850200	-2.16393200	-0.50674800

TS8(r2):

0 1
C	1.86374300	1.44018000	0.24573600
N	2.53266500	2.37270400	0.08666300
C	1.06575600	0.29059800	0.45894300
C	1.31866800	-1.00026700	-0.17883600
N	2.42874500	-1.32075600	-0.90587700
C	-0.45555800	0.32505100	0.55972200
H	-0.82799200	0.94355300	1.38408600
O	-1.13059100	0.56333300	-0.61574900
C	-2.50127900	0.97874400	-0.50392000
C	-3.46412300	-0.16647000	-0.21870500
H	-2.57917600	1.76051600	0.26286200
H	-2.72690600	1.43384400	-1.46898900
H	-3.32921300	-0.57938400	0.78555200
H	-4.49484800	0.19378700	-0.28308300
H	-3.33459600	-0.96961400	-0.94747800
N	-0.39279800	-1.11535000	1.07137600
N	0.39138000	-1.87225400	0.14593200
H	0.61746400	-0.51109300	1.67749700
H	-1.24106200	-1.60766700	1.33701000
H	2.84479300	-0.58888500	-1.46159800
H	2.43307300	-2.23913600	-1.32416900

Solvent phase:

TS1(r1):


```
0 1
C       -1.01823100   -0.53684200    1.43761900
N       -0.82536100   -0.88892800    2.52488700
C       -1.25238700   -0.04477600    0.11925400
C       -2.28384500   -0.69936300   -0.61432600
N       -3.13666000   -1.18041400   -1.23521800
C       -0.00910100    0.45791500   -0.68685500
H       -0.14322100    0.26231800   -1.75502500
O        1.24052800    0.11380700   -0.22999100
C        1.70171500   -1.19170300   -0.65672600
C        3.10978200   -1.38573800   -0.13652700
H        1.02420700   -1.95493400   -0.26085000
H        1.66854600   -1.23122400   -1.75092400
H        3.13206300   -1.34210800    0.95452800
H        3.47980700   -2.36549700   -0.44801600
H        3.78153600   -0.62206200   -0.53460700
N        0.66105500    2.68962600    0.38183200
N       -0.24339200    1.96045800   -0.44362800
H        1.61358800    2.42829700    0.13150500
H        0.51457900    2.39632600    1.34384200
H       -1.31530100    1.39074100    0.10983600
H       -0.35712300    2.46554300   -1.32009900
```


TS2(r1):

```
0 1
C        1.21161100    1.90219300   -0.06848500
N        1.47479700    2.94765000   -0.47981000
C        0.87542700    0.58460100    0.44592800
C        2.00597000   -0.44673600    0.32421100
N        2.96726800   -0.90136900    0.96352000
C       -0.30679700   -0.10405900   -0.33797400
H       -0.39195600    0.33576800   -1.33801600
O       -1.48437200    0.01462800    0.37575800
C       -2.69645600   -0.18380400   -0.39425800
C       -3.87677800    0.11981900    0.50382400
H       -2.67132200    0.48720600   -1.25986400
H       -2.72856000   -1.21560600   -0.75558900
H       -3.84058200    1.15188700    0.85996100
H       -4.80578400   -0.01936300   -0.05449200
H       -3.89334400   -0.54960000    1.36696300
N        1.51446600   -1.48565300   -0.66116400
N        0.07750100   -1.54489000   -0.52501900
H        1.75439200   -1.31115800   -1.64051400
H        2.44746000   -1.98429300    0.04314800
H        0.59387100    0.67899900    1.49740300
H       -0.10528500   -2.03312400    0.35278200
```

TS3(r1):

0 1
C	-1.68411500	-1.41387800	-0.80276500
N	-2.11625200	-2.22904600	-1.50222100
C	-1.11064800	-0.44481400	0.07778200
C	-1.99684100	0.08841100	1.06468700
N	-2.67817000	0.51678000	1.89740800
C	-0.07911900	0.49762700	-0.52991200
H	0.24927700	0.23978300	-1.53157100
O	1.12902700	-0.17081500	0.42661700
C	2.31698200	-0.71408200	-0.20591700
C	3.19382800	-1.35944600	0.85034200
H	2.01872900	-1.43894600	-0.97039100
H	2.82821300	0.11822500	-0.69454700
H	2.67248800	-2.18426000	1.34186800
H	4.09631000	-1.75852500	0.37981700
H	3.49268800	-0.63100500	1.60709700
N	0.79330600	2.64720200	-0.90921900
N	-0.22936600	1.84089600	-0.34924500
H	1.49385400	2.86496300	-0.20359100
H	0.37417500	3.51799200	-1.21867800
H	0.10522400	-0.85392700	0.64208100
H	-0.59032100	2.13848200	0.55261000

TS4(r1):

0 1
C	-0.68172100	-1.59111400	-0.73310400
N	-0.43266300	-2.46432100	-1.44056200
C	-1.03659400	-0.50531100	0.18938600
C	-2.41082300	-0.68585300	0.70325900
N	-3.47713000	-0.79928000	1.12283900
C	-0.90816500	0.84701700	-0.48361900
H	-1.40112300	1.03351800	-1.43096600
O	1.49272400	0.30782200	-0.16531100
C	2.63785900	-0.47307200	-0.23224300
C	3.24732700	-0.77469200	1.14667700
H	2.42102900	-1.44494200	-0.72098900
H	3.42425400	-0.00025300	-0.85592700
H	2.52528900	-1.30234500	1.77858600
H	4.14579000	-1.39686900	1.05717100
H	3.52570700	0.15506900	1.65411300
N	-0.29026300	3.08810700	-0.50143300
N	-0.37343700	1.83738300	0.13475200
H	0.59440500	3.11404800	-1.00865800
H	-0.25411800	3.79649300	0.22679600
H	-0.32652000	-0.54242300	1.02140200
H	0.33065900	1.59005400	0.84964800

TS5(r1):

0 1
C	3.03365700	-1.22038300	0.01418100
N	3.98173900	-1.88692300	0.06426100
C	1.89863000	-0.39507000	-0.01239400
C	1.85905000	1.03743300	0.34305200
N	2.47279200	2.11718400	0.31224000
C	0.70105000	-0.67175200	-0.63227500
H	0.43780600	-1.56514500	-1.18165300
O	-2.96754400	0.15645700	-0.94025900
C	-3.96360900	-0.00699900	0.09741000
C	-3.52806900	-1.13284900	1.01363800
H	-4.06563500	0.93091900	0.65274000
H	-4.92564100	-0.23807400	-0.36947700
H	-2.56979800	-0.90641500	1.48824700
H	-4.27130600	-1.27478400	1.80215000
H	-3.43162400	-2.07038300	0.46054100
N	-0.18952800	0.35284300	-0.58072500
N	0.33327700	1.33846100	0.29769100
H	-3.27966700	0.81287300	-1.57395900
H	-1.21242400	0.26010800	-0.68547600
H	0.99090700	2.40640300	0.11955800
H	-0.12448300	1.27959700	1.21345900

TS6(r1):

0 1
C	-1.44100400	1.83201900	0.18141600
N	-1.40521800	2.92007600	-0.19676800
C	-1.49091300	0.46152200	0.66184500
C	-2.58067700	-0.40136900	0.02897800
N	-3.49835900	-0.37465200	-0.80049100
C	-0.28464000	-0.40664200	0.27106900
H	0.73506900	-0.03016700	0.21944600
O	2.70969200	0.88191700	0.16860600
C	3.90519300	0.32387500	-0.41078300
C	4.01914500	-1.12432400	0.02437100
H	3.85417700	0.39373600	-1.50341900
H	4.77809400	0.89474900	-0.07470500
H	3.15632100	-1.70292800	-0.31556200
H	4.92044100	-1.57276400	-0.40156300
H	4.08111100	-1.19938800	1.11317600
N	-0.54711300	-1.62906900	-0.01407900
N	-1.97163400	-1.78763800	0.06650400
H	-1.58216100	0.46945700	1.75518500
H	2.65220100	1.81049800	-0.08281900
H	-2.86607000	-1.74871700	-0.84997600
H	-2.21307400	-2.38131200	0.86385200

TS7(r1):

0 1
```
C        1.10810000    1.80256300    0.19938200
N        0.92117200    2.85196500   -0.23701100
C        1.36872600    0.48183700    0.75999900
C        2.11392500   -0.47193800   -0.19802700
N        3.23811100   -0.21698900   -0.71693000
C        0.12642800   -0.30319800    1.08002200
H       -0.66390900   -0.02613000    1.75250900
O       -1.68622400   -0.41271100   -0.34424600
C       -2.87988300    0.12705100   -0.81580000
C       -4.02953800    0.07669700    0.19861100
H       -2.73207300    1.17835600   -1.12722600
H       -3.20044300   -0.40163200   -1.73454600
H       -3.77369300    0.64280700    1.10026400
H       -4.94948000    0.50098700   -0.22055900
H       -4.23448800   -0.95752500    0.49438500
N        0.21430500   -1.50376800    0.56766900
N        1.29354500   -1.59288000   -0.33096900
H        1.96949300    0.61218500    1.67033200
H       -0.72550600   -1.80353900    0.19373300
H        3.57439500   -0.97459500   -1.31202100
H        1.70900800   -2.51559500   -0.38733500
```

TS8(r1):

0 1
```
C        1.22167000    1.64122800   -0.23729300
N        1.40354300    2.66395000   -0.75728500
C        1.02471700    0.43260300    0.48992500
C        1.83856400   -0.73419800    0.06421900
N        2.95478400   -0.72096800    0.73624600
C       -0.39024900   -0.18519900    0.41644200
H       -0.61887100   -0.74162800    1.33135400
O       -1.38361500    0.73371700    0.12208600
C       -2.70706600    0.44655900    0.62843600
C       -3.47705700   -0.54991200   -0.22402400
H       -2.62001700    0.09887400    1.66339700
H       -3.20903000    1.41494900    0.63797200
H       -2.99652900   -1.53034000   -0.22854600
H       -4.48746900   -0.66552500    0.17903500
H       -3.55939500   -0.19557900   -1.25462800
N       -0.25701800   -1.21785000   -0.70139900
N        1.13550000   -1.59047600   -0.68496100
H        2.25819000    0.23930600    1.35521800
H       -0.42011700   -0.71945900   -1.57716600
H        3.67384800   -1.43518700    0.64316000
H        1.32717700   -2.58422600   -0.70092200
```

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TS9(r1):

0 1

C	1.12621700	1.75869900	-0.11043300
N	1.26826200	2.73635700	-0.70537000
C	0.94712500	0.52566300	0.64684000
C	1.87491100	-0.57896800	0.18566000
N	3.00663400	-1.15771400	0.55109100
C	-0.42336500	-0.21434000	0.35000400
H	-0.68074400	-0.77063000	1.25655400
O	-1.43272500	0.66094800	-0.01138600
C	-2.75005300	0.38816600	0.52517900
C	-3.45055500	-0.76904900	-0.16764100
H	-2.66065900	0.21245600	1.60231600
H	-3.29669100	1.31984200	0.37749200
H	-2.91611300	-1.71029700	-0.01949500
H	-4.45681100	-0.88171000	0.24594600
H	-3.53998300	-0.58282500	-1.24065900
N	-0.12255400	-1.20673000	-0.72903900
N	1.30279800	-1.35269300	-0.71783400
H	1.04346600	0.74405900	1.71033300
H	-0.38244400	-0.79402900	-1.62401700
H	3.80634400	-0.58508800	0.80973300
H	2.41377700	-2.03493600	-0.39670300

TS10(r1):

0 1

C	-1.73663800	1.60359300	0.12144800
N	-2.36879500	2.57222600	0.21554900
C	-0.95469400	0.43709300	-0.03786200
C	-1.57545600	-0.88512600	-0.24588600
N	-2.64321000	-1.12948600	-0.90919500
C	0.29860700	0.19043100	0.75825600
H	0.58334900	0.81843000	1.59352500
O	1.25713700	0.62993200	-0.43466500
C	2.47761100	-0.09626400	-0.78454800
C	3.66015600	0.44169200	-0.00312600
H	2.30500900	-1.15644600	-0.59229300
H	2.59173700	0.05901200	-1.85714800
H	3.52919000	0.29083900	1.07087000
H	4.56547900	-0.08964100	-0.30973500
H	3.80484900	1.50698800	-0.19444300
N	0.37580100	-1.19376300	1.01134600
N	-0.74808000	-1.83547800	0.39225100
H	0.17834500	0.62083800	-0.97247500
H	0.38142700	-1.39483400	2.00508200
H	-2.86390600	-2.12509000	-0.89310700
H	-0.46010700	-2.61254600	-0.19230100

TS11(r1):

0 1
C	0.44615500	-0.33702100	-0.60099500
N	-0.70818100	-0.42597400	-0.61568400
C	1.86663400	-0.23738300	-0.65970100
C	2.54777800	0.83545700	0.10684700
N	2.45744600	1.95272900	-0.55384800
C	2.65373300	-1.41072200	-0.20899900
H	2.57219600	-2.43004300	-0.55974200
O	-3.63733100	-0.69210800	-0.40862300
C	-4.14089400	0.39631500	0.37316000
C	-5.64772800	0.25816300	0.49624000
H	-3.67982300	0.39111300	1.36951200
H	-3.88843300	1.35264400	-0.10340000
H	-5.91245400	-0.68250300	0.98691400
H	-6.05706200	1.08051600	1.08930400
H	-6.12108400	0.27836400	-0.48931400
N	3.45628700	-1.12517300	0.76340900
N	3.30554500	0.25713800	1.05577700
H	-2.67209100	-0.60306900	-0.47596900
H	2.03124700	0.97274800	-1.46663700
H	2.81981300	2.83748900	-0.20865500
H	4.07459100	0.69971400	1.54007800

TS12(r1):

0 1
C	1.68827200	1.75737000	0.15774400
N	2.10035800	2.83437300	0.05000000
C	1.20600200	0.44133900	0.27818700
C	1.84902500	-0.73279800	-0.21158000
N	3.03105900	-0.84717400	-0.81479700
C	0.01510800	0.01697100	0.86974300
H	-0.69555900	0.59410300	1.43187000
O	-1.89025000	-0.22416600	-0.39588500
C	-2.93187900	0.68301800	-0.32017200
C	-4.31509700	0.01355000	-0.25952900
H	-2.84290900	1.33289900	0.58178500
H	-2.94037700	1.38701100	-1.17992900
H	-4.38529800	-0.64182700	0.61514900
H	-5.11860600	0.75787100	-0.19712000
H	-4.48365200	-0.59714700	-1.15300200
N	-0.01174200	-1.34739700	0.89170600
N	1.04752500	-1.77360600	0.07894900
H	-0.93304900	-1.68546500	0.58171800
H	3.56952800	-0.02366900	-1.03315100
H	3.37104900	-1.73209400	-1.15872300
H	1.34189800	-2.73843600	0.15111600

TS13(r1):

0 1
C	-1.88645800	1.51399600	0.06370800
N	-2.65534100	2.37583300	0.04707700
C	-0.91776700	0.45327400	0.03324100
C	-1.35117500	-0.94785400	-0.30488900
N	-2.16830100	-1.25349300	-1.32554200
C	-0.04154300	0.19869800	1.21185400
H	0.36251800	0.90009900	1.92026500
O	1.52162800	0.77280600	-0.25640900
C	2.53363800	-0.13837300	-0.56445100
C	3.94085800	0.43046200	-0.35518500
H	2.42623800	-1.05096500	0.05810100
H	2.44209600	-0.48574300	-1.60871000
H	4.07858500	0.74169300	0.68511100
H	4.70812200	-0.31517900	-0.59358000
H	4.10152700	1.30356600	-0.99524200
N	-0.02859800	-1.09694100	1.38550700
N	-0.76621400	-1.83879800	0.45144400
H	0.02290700	0.70434000	-0.65277000
H	0.50662300	-1.60568000	2.07572000
H	-2.46924700	-2.20786100	-1.45215300
H	-2.68853300	-0.53415100	-1.80055100

TS14(r1):

0 1
C	1.57254200	1.88285300	-0.12012900
N	1.71702000	3.03252900	-0.13605900
C	1.41995100	0.48455400	-0.10577800
C	2.44907200	-0.51452100	-0.05431200
N	3.72630600	-0.76237200	0.27363900
C	0.21936500	-0.23042600	0.00344700
H	-0.80394400	0.12789100	0.02904700
O	-2.80630600	0.95017100	0.06768700
C	-4.06047100	0.29163200	0.33104200
C	-4.04475600	-1.06258200	-0.35113800
H	-4.19757900	0.17545000	1.41221400
H	-4.88478400	0.90378500	-0.05184100
H	-3.23254400	-1.68421900	0.03470900
H	-4.98859600	-1.58344900	-0.17024400
H	-3.91592500	-0.95258400	-1.43105200
N	0.50417500	-1.53692500	0.08428700
N	1.85638100	-1.72648600	-0.10584100
H	-2.82324200	1.81952900	0.48324400
H	-0.14390000	-2.30625400	-0.00638000
H	4.45437100	-0.18732400	-0.13953500
H	3.02520100	-2.07047600	0.26737000

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TS15(r1):

0 1

C	-1.50049900	1.76989000	0.04747600
N	-1.62659500	2.92009100	0.08450000
C	-1.37294400	0.36427000	0.00190500
C	-2.42951600	-0.58155000	0.03923800
N	-3.76820300	-0.34970500	0.03663700
C	-0.19765300	-0.37976000	-0.12882000
H	0.81710100	-0.01334200	-0.24176600
O	2.86827700	0.85706100	-0.48428900
C	4.01702300	0.44895500	0.28309300
C	4.16343800	-1.05586200	0.16453600
H	4.91319100	0.95190000	-0.09760000
H	3.88476700	0.74026400	1.33161400
H	4.30837600	-1.35111500	-0.87797000
H	5.02892400	-1.39433200	0.74008700
H	3.27635700	-1.56525600	0.54970800
N	-0.44776700	-1.69217800	-0.06384800
N	-1.92836700	-1.83375000	0.05081200
H	2.80151900	1.81766500	-0.44655500
H	-4.09654700	0.56356700	0.31317600
H	-4.36842800	-1.11658400	0.30241300
H	-1.19403800	-2.19612100	-0.90007500

TS1(r2):

0 1

C	1.65429500	1.84744600	-0.19770500
N	2.33981400	2.77325800	-0.31194800
C	0.82174000	0.70101700	-0.05527400
C	1.48680300	-0.52944100	0.41087700
N	2.62533400	-0.75901400	0.88351300
C	-0.50260400	0.85910300	-0.32754800
H	-0.88606400	1.82523400	-0.64483800
O	-1.37546800	-0.13382600	-0.23724100
C	-2.78975000	0.18636200	-0.43889800
C	-3.44534800	0.58830700	0.86660200
H	-2.85707800	0.97033500	-1.19615600
H	-3.21644900	-0.73029000	-0.84237300
H	-3.00650200	1.50439700	1.26911400
H	-4.50849500	0.77051000	0.68955000
H	-3.35232400	-0.20573400	1.61034200
N	0.36582200	-2.49183900	-0.87511200
N	0.77424100	-1.88825200	0.36003500
H	1.17269900	-2.47863200	-1.49427500
H	-0.36290500	-1.91544500	-1.29146000
H	0.00109900	-1.97176700	1.02187900
H	1.93246900	-2.05382200	0.83240500

TS2(r2):

0 1
C	1.18268200	1.85084900	0.26333500
N	1.39175100	2.98933100	0.18516300
C	0.93607900	0.46999500	0.39954300
C	1.72336700	-0.54431800	-0.31913800
N	2.76248800	-0.38457400	-1.04803500
C	-0.46311000	-0.11889100	0.54968400
H	-1.02486900	0.30097800	1.38589800
O	-1.19854500	-0.22461600	-0.60573900
C	-2.60873000	-0.52830800	-0.43407400
C	-3.43704300	0.72739500	-0.22108900
H	-2.89632400	-1.03614900	-1.35479300
H	-2.73236500	-1.23691100	0.39080400
H	-3.31957700	1.41348600	-1.06283500
H	-4.49373600	0.45745900	-0.14201400
H	-3.15637700	1.25024900	0.69677500
N	0.17620600	-1.40669800	1.07659200
N	1.07602100	-1.77862000	0.01063600
H	0.92467900	-0.45674900	1.58299500
H	-0.41841100	-2.18184900	1.36991500
H	3.15280600	-1.27914100	-1.34434300
H	1.70779500	-2.51085300	0.32346000

TS3(r2):

0 1
C	-1.64121300	-1.71839800	0.38251700
N	-2.33655900	-2.58573100	0.70901100
C	-0.79908900	-0.64109600	-0.00921500
C	-1.43311200	0.65553800	-0.27753600
N	-2.65604000	0.85966100	-0.77961100
C	0.52748300	-0.91729800	-0.18332800
H	0.89298900	-1.92239600	0.01735000
O	1.39723600	-0.04467200	-0.63206600
C	2.79396400	-0.46875700	-0.73060900
C	3.54034100	-0.18093100	0.55634200
H	2.81443200	-1.52910900	-0.99202700
H	3.18821900	0.10728500	-1.56596400
H	3.13527300	-0.75986300	1.38977300
H	4.58998600	-0.45781000	0.42831200
H	3.49210400	0.88065900	0.80608600
N	-0.05440200	2.12797300	1.00630500
N	-0.94792700	1.88347600	-0.07077700
H	-0.59580900	2.41305500	1.82178600
H	0.52042600	2.92363900	0.74664700
H	-3.00242000	0.21381900	-1.48728100
H	-2.17883500	2.11609600	-0.59166700

TS8(r2):

0 1

C	1.87578200	1.44053300	0.21794500
N	2.54354800	2.37673600	0.06601200
C	1.07711400	0.29713200	0.44026700
C	1.31696400	-1.00646600	-0.18453300
N	2.41189500	-1.34759600	-0.92840800
C	-0.44713300	0.33753800	0.57384000
H	-0.80214000	0.97234500	1.38982800
O	-1.13704200	0.54995800	-0.59815300
C	-2.51530900	0.97554800	-0.47743000
C	-3.48424700	-0.17699100	-0.26629800
H	-2.58847000	1.71065400	0.33143100
H	-2.72482700	1.48484100	-1.41848400
H	-3.34561300	-0.66083400	0.70370500
H	-4.50884300	0.20389900	-0.29891100
H	-3.37390600	-0.92695500	-1.05303300
N	-0.36884400	-1.08728200	1.11552000
N	0.39349700	-1.86332400	0.18842800
H	0.67864000	-0.44868800	1.66653100
H	-1.20650100	-1.56710800	1.43351400
H	2.77285500	-0.64411400	-1.55721000
H	2.39543900	-2.27720600	-1.32575500