Modelling the Chemical Repair of Protein Carbon-Centered Radicals Formed via Oxidative Damaged with Dihydrolipoic Acid

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Supplementary Information

(21 pages)

Contents:

Table S1. $\langle S^2 \rangle$ values for the calculated transition states in the two solvents studied.

Radical	Solvent: water	Solvent: pentyl ethanoate
Repaired with S(1)		
α	0.759	0.759
β	0.759	0.759
γ	0.758	0.758
δ	0.759	0.759
Repaired with S(2)		
α	0.759	0.758
β	0.759	0.759
γ	0.758	0.758
δ	0.759	0.759

Table S2. Calculated rate constants (k and k_D in M^{-1} s^{-1}) for the repair reactions of N–formyl–leucinamide in two solvents at 298.15 K.[a]

	Solvent: water		Solvent: pentyl ethanoate	
Radical	k	k_D	k	k_D
Repaired with S(1)				
α	7.6×10^4	2.3×10^9	2.4×10^4	2.4×10^9
β	1.7×10^7	2.4×10^9	1.1×10^8	2.4×10^9
γ	1.5×10^7	2.3×10^9	1.5×10^6	2.5×10^9
δ	1.5×10^9	2.4×10^9	3.1×10^7	2.5×10^9
Repaired with S(2)				
α	3.1×10^5	2.3×10^9	8.4×10^5	2.5×10^9
β	6.8×10^{10}	2.4×10^9	2.5×10^6	2.4×10^9
γ	2.4×10^9	2.3×10^9	4.4×10^7	2.5×10^9
δ	1.8×10^9	2.4×10^9	1.1×10^9	2.5×10^9

[a] k is the non-corrected thermal rate constant and k_D is the diffusion-controlled rate constant.

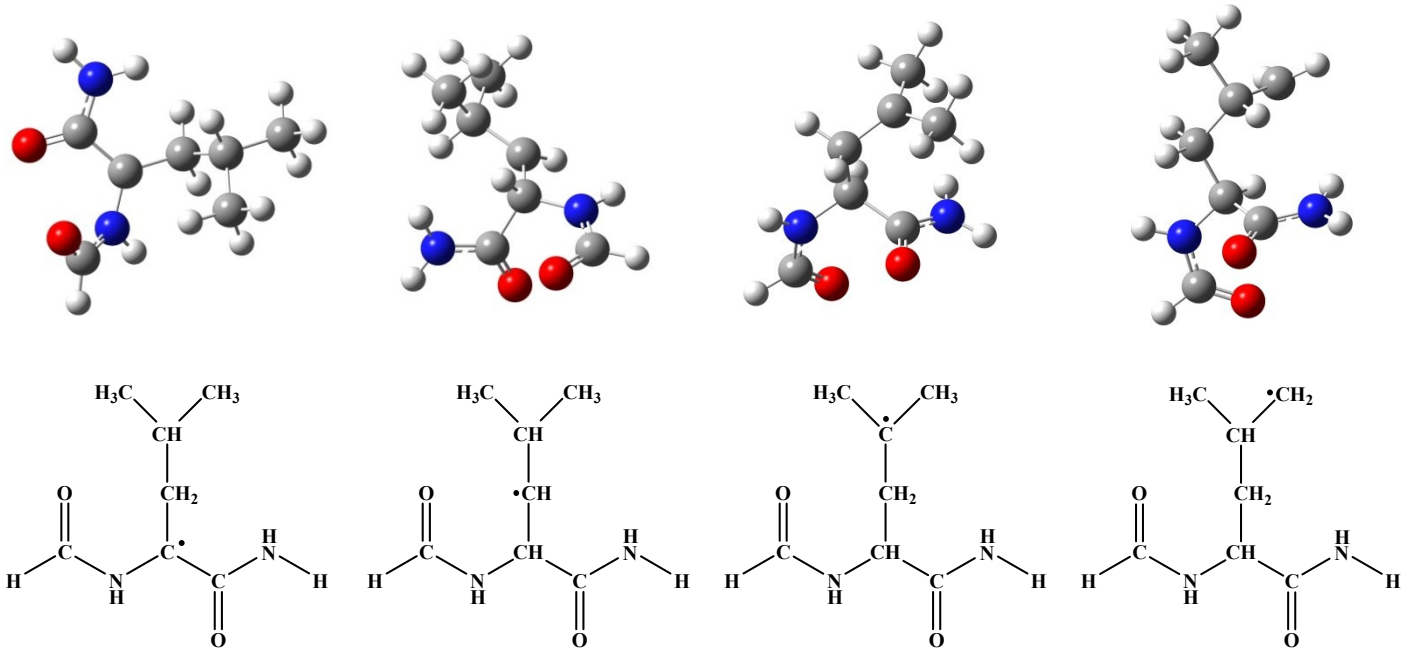
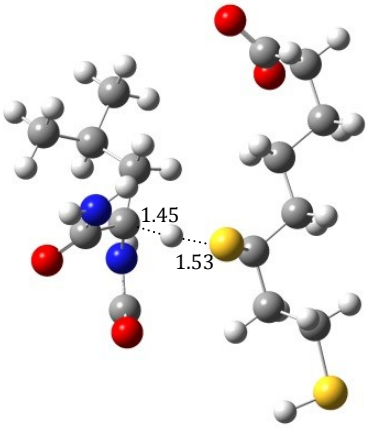
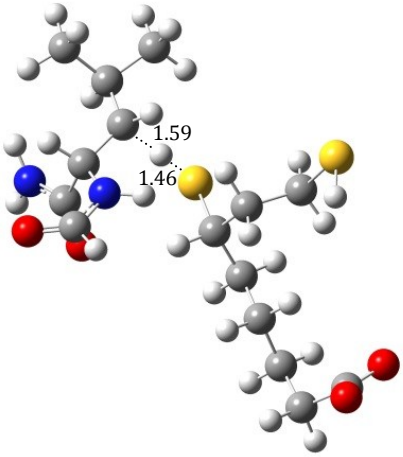


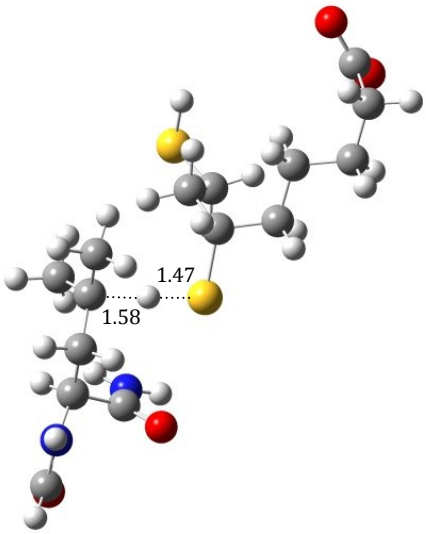
Figure S1. Optimized structures of the N–formyl–leucinamide radicals



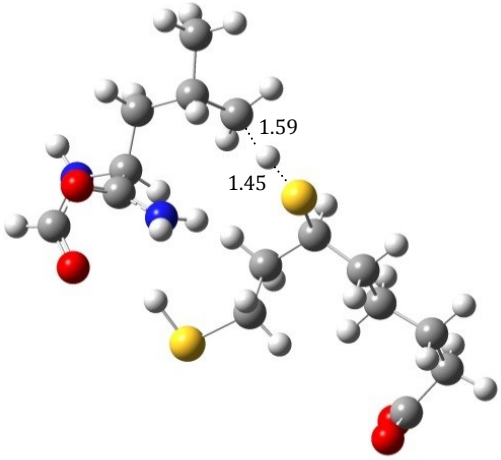
A. TS – α(1)



B. TS – β(1)

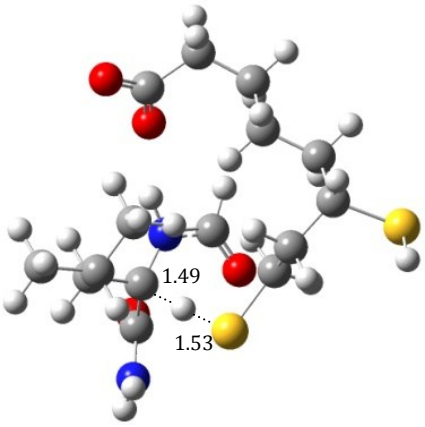


C. TS – γ(1)

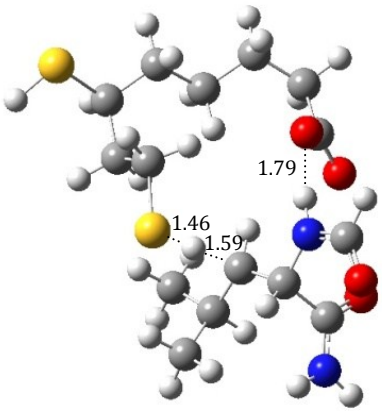


D. TS – δ(1)

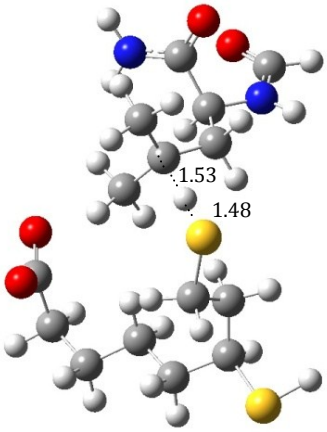
Figure S2. Optimized geometry of the TSs (repaired radicals with the S(1) site of DHL)



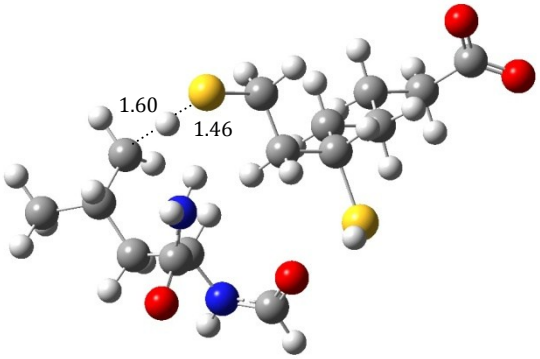
A. TS – α(2)



B. TS – β(2)



C. TS – γ(2)



D. TS – δ(2)

Figure S3. Optimized geometry of the TSs (repaired radicals with the S(2) site of DHL)

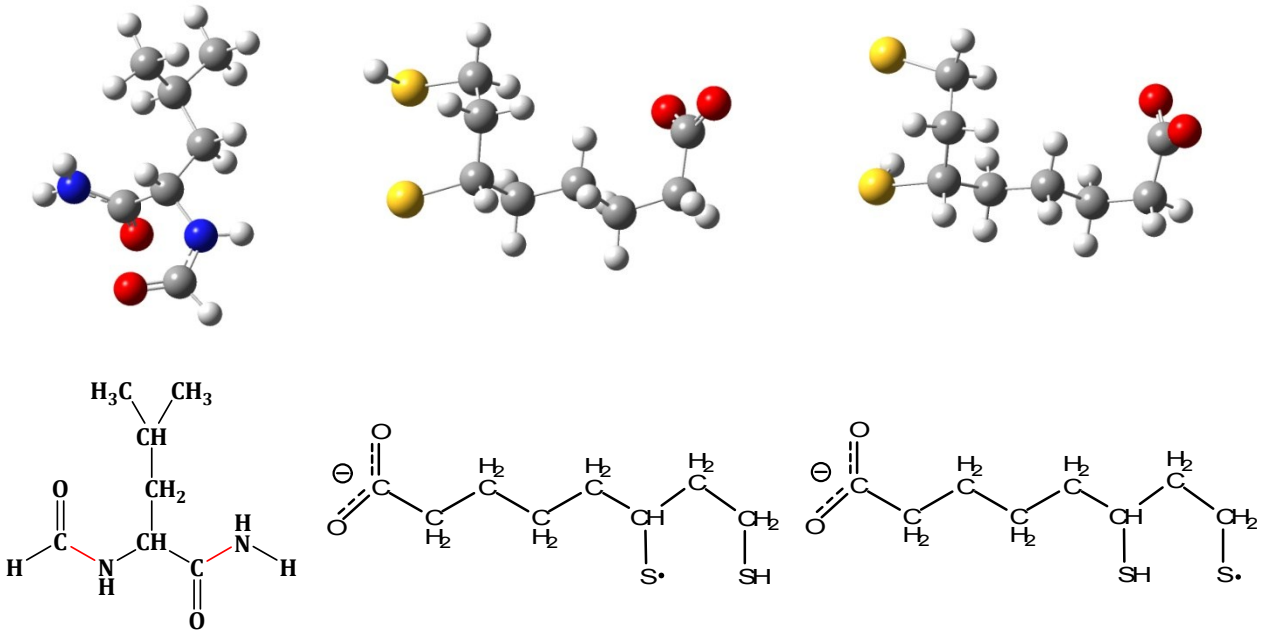


Figure S4. Optimized structures of the reaction products

M06-2X/6-31++G(d,p) Cartesian coordinates of the optimized geometries of the different reactants, products and TSs calculated in this study.

Radical α

Charge = 0 Multiplicity = 2

N	0.70588000	2.29624400	-0.59849600
H	-0.28288700	2.35050400	-0.79805000
H	1.31134700	3.02965700	-0.94173000
C	1.26949500	1.23606500	0.02109800
O	2.50469100	1.16030000	0.18449100
C	0.35608900	0.21591000	0.53932800
N	0.88952000	-1.00930000	0.90929600
H	0.44140400	-1.49283700	1.68432200
C	1.74404500	-1.76852000	0.16502400
O	2.15573700	-1.46731000	-0.95052900
H	2.02077800	-2.70557300	0.66439000
C	-1.08831400	0.45555600	0.82632200
H	-1.25512500	1.51175900	1.06252300
H	-1.36809000	-0.12423700	1.71715900
C	-2.03451500	0.03874300	-0.32831100
H	-1.79099500	0.65091500	-1.20696800
C	-3.47639600	0.32958800	0.08164600
H	-3.75541100	-0.27462900	0.95321500
H	-4.16642300	0.08710000	-0.73258600
H	-3.61257500	1.38421100	0.34188800
C	-1.85843900	-1.43104700	-0.70368700
H	-0.85494500	-1.63994000	-1.08887800
H	-2.57822100	-1.71245600	-1.47884900
H	-2.03187500	-2.07477300	0.16775000

Radical β

Charge = 0 Multiplicity = 2

N	-0.49537100	2.09344500	0.43689400
H	0.00164500	1.94057900	1.30465900
H	-0.70545900	3.04123800	0.14990100
C	-0.84634300	1.07072100	-0.35084400
O	-1.46292700	1.21206100	-1.41266800
C	-0.35101100	-0.31246000	0.12019200
H	-0.26305500	-0.28478500	1.21261800
N	-1.30560500	-1.33840900	-0.25463700
H	-1.02532500	-2.06501800	-0.90300300
C	-2.58038900	-1.27813400	0.14602700
O	-3.01840400	-0.39295600	0.89132500
H	-3.21282100	-2.09006900	-0.23489300
C	0.97567800	-0.57889100	-0.51982500

H	0.94587000	-0.97631300	-1.53309100
C	2.24423300	0.05132600	-0.03672100
H	2.21622600	1.12733800	-0.28508900
C	3.43968300	-0.56361700	-0.76840500
H	3.52609600	-1.62939800	-0.52785800
H	4.36946700	-0.07013400	-0.47090600
H	3.33165100	-0.46722400	-1.85310500
C	2.42385000	-0.06684000	1.48188100
H	1.64079000	0.45745800	2.03755400
H	3.38478600	0.36511000	1.77723500
H	2.41339800	-1.11950000	1.78709200

Radical γ

Charge = 0 Multiplicity = 2

N	0.00201100	1.68274500	1.00690700
H	0.25202100	1.21429300	1.86762500
H	0.11902800	2.68608100	0.93962100
C	-0.40295800	0.99222500	-0.06411700
O	-0.70916500	1.52837400	-1.13730600
C	-0.40510600	-0.52988700	0.09112500
H	-0.35862100	-0.77898300	1.15730700
N	-1.60999800	-1.09941700	-0.48302900
H	-1.52906900	-1.74937700	-1.25669300
C	-2.82995200	-0.72511000	-0.08274500
O	-3.02845000	0.10342100	0.81467000
H	-3.65231800	-1.21740600	-0.61752800
C	0.82266600	-1.12222600	-0.63763200
H	0.70147400	-0.92337100	-1.70941100
H	0.77497800	-2.20903900	-0.48550900
C	2.13139800	-0.58416800	-0.15073400
C	2.77098300	0.57015400	-0.85177600
H	3.86125900	0.54384100	-0.73895000
H	2.44036300	1.53824300	-0.43795200
H	2.53198400	0.57715500	-1.91994700
C	2.57090400	-0.90999900	1.23960600
H	2.20705400	-1.89229800	1.55952900
H	3.66383100	-0.89963400	1.32250500
H	2.19723600	-0.17309400	1.97097600

Radical δ

Charge = 0 Multiplicity = 2

N	0.37105300	2.06339700	-0.29274900
H	-0.01782400	1.96465400	-1.22185500
H	0.46067100	2.98827200	0.10904900
C	0.66399200	0.99055800	0.45030900

O	1.11176400	1.06907200	1.60165700
C	0.36964500	-0.36508300	-0.19999100
H	0.33947000	-0.22818000	-1.28634300
N	1.42131200	-1.31130400	0.12448100
H	1.20579200	-2.11614700	0.70178600
C	2.69705500	-1.07651500	-0.20218900
O	3.06567100	-0.08146600	-0.83888700
H	3.40074000	-1.84793000	0.13564100
C	-0.97382400	-0.91564500	0.29331800
H	-0.89987800	-1.11077000	1.37010500
H	-1.13983700	-1.87730700	-0.20870800
C	-2.16961200	0.00477200	0.02004000
H	-2.03568900	0.93814200	0.58287900
C	-3.45602300	-0.66182200	0.54010900
H	-3.63504400	-1.60679500	0.01582800
H	-4.31973200	-0.01075200	0.37770400
H	-3.37734600	-0.87091300	1.61250400
C	-2.29815200	0.32906300	-1.43322700
H	-2.13323200	-0.44973000	-2.17315500
H	-2.81261200	1.22998800	-1.74993200

Dihydrolipoate

Charge = -1 Multiplicity = 1

C	3.39553800	-1.28183200	-0.00250900
H	4.18892700	-1.77661300	-0.57697700
H	3.55028100	-1.53960900	1.04983700
C	2.02826800	-1.76955900	-0.47796000
H	1.98507900	-2.86178100	-0.39021200
H	1.90351600	-1.53172200	-1.54112700
C	0.87950800	-1.15163000	0.31766600
H	0.96318400	-0.05750500	0.27512500
H	0.97115900	-1.43489200	1.37545400
C	-0.48561300	-1.58796800	-0.21251100
H	-0.52878700	-2.68397100	-0.23142200
C	-1.65226100	-1.06733500	0.63209800
C	-1.66782700	0.45465200	0.81996300
H	-0.81416500	0.72410800	1.45487400
H	-2.57030700	0.74056600	1.37166100
H	-1.59637900	-1.52796700	1.62299700
C	3.60538100	0.22474400	-0.17467900
O	3.18781400	0.76369400	-1.24069300
O	4.21138400	0.84471200	0.74829500
C	-1.59279700	1.24622900	-0.47946200
H	-0.67470700	1.02966600	-1.03048600
H	-2.43748400	1.00893700	-1.13224700

H	-0.59571400	-1.25063200	-1.25174600
S	-1.68967000	3.05277900	-0.21324200
H	-0.58961400	3.15409400	0.55228000
S	-3.20517600	-1.68401500	-0.14942600
H	-4.04952200	-1.19646700	0.77548900

TS – α(1)

Charge = -1 Multiplicity = 2

N	-0.10251000	-3.32230400	2.07062300
H	-0.43124300	-2.47453700	2.51356500
H	-0.02365800	-4.16293400	2.62854400
C	0.14016600	-3.39706300	0.75289000
O	0.51017500	-4.43931200	0.19921700
C	-0.07688800	-2.11828800	-0.02166700
N	0.52609400	-2.08756500	-1.28858100
H	0.01281700	-1.64709500	-2.04795900
C	1.84884700	-2.31731300	-1.51238600
O	2.64563000	-2.65626800	-0.64384600
H	2.14145500	-2.16386700	-2.55876600
C	-1.43780200	-1.45699400	0.02337900
H	-1.31267200	-0.43783100	-0.36082700
H	-1.76264300	-1.36326600	1.06671800
C	-2.55021900	-2.15120000	-0.78733600
H	-2.18662700	-2.31076800	-1.81137700
C	-3.75299500	-1.20944200	-0.84696400
H	-4.13372100	-1.01172700	0.16236800
H	-4.56497800	-1.64992800	-1.43397700
H	-3.48260500	-0.24932300	-1.29979200
C	-2.94523100	-3.50112600	-0.19084600
H	-2.11757000	-4.21715100	-0.19568100
H	-3.76643000	-3.94333500	-0.76374500
H	-3.28542900	-3.37630400	0.84436900
C	-3.01027200	3.49220400	0.88188200
H	-3.45364300	4.48445800	1.03657600
H	-3.17467400	2.92130500	1.80106500
C	-1.51485900	3.62736500	0.60087400
H	-1.04093500	4.13944200	1.44747600
H	-1.35908500	4.26146900	-0.28014400
C	-0.83908700	2.27480600	0.38423200
H	-1.27759100	1.79140100	-0.50010800
H	-1.05092800	1.62005700	1.24034700
C	0.66981200	2.38878000	0.19048600
H	1.11958500	2.87782200	1.06475500
C	1.36275700	1.04687500	-0.07366800
C	2.77204800	1.20369100	-0.65947000
H	2.68304900	1.69325900	-1.63734200

H	3.20122900	0.20905600	-0.82748400
H	0.76423700	0.49627400	-0.81078100
C	-3.80826000	2.83640100	-0.24754100
O	-3.49749600	3.11795900	-1.44166100
O	-4.76455000	2.07331100	0.07844400
C	3.70576600	2.02124600	0.22451900
H	3.37370000	3.06063900	0.29309100
H	3.74417300	1.61605800	1.23965500
H	0.87345600	3.03888000	-0.67250400
S	5.40833100	2.12066200	-0.43301500
H	5.66060700	0.80079000	-0.40450300
S	1.38267100	-0.00489500	1.44365200
H	0.69623000	-1.19121000	0.77445000

TS – β(1)

Charge = -1 Multiplicity = 2

N	-4.00979000	-1.96944000	-1.27798400
H	-4.89300800	-1.52358800	-1.06825000
H	-3.94668000	-2.57103000	-2.08983100
C	-2.93198700	-1.80421300	-0.50128500
O	-1.86288500	-2.38430000	-0.70201800
C	-3.11552800	-0.82463300	0.67862800
H	-4.11255800	-1.02271500	1.10025900
N	-2.13624300	-1.10021500	1.70883900
H	-1.32747200	-0.49383700	1.79676300
C	-2.10687200	-2.29183800	2.32261100
O	-2.96397800	-3.16636200	2.15475600
H	-1.26227800	-2.42345700	3.01095200
C	-3.04218300	0.62698100	0.25959400
H	-2.61257200	1.27524300	1.02758000
C	-4.14295900	1.25938300	-0.55771500
H	-4.23366600	0.73191400	-1.51701500
C	-3.81343400	2.72710800	-0.83661000
H	-3.73581500	3.28307300	0.10489600
H	-4.60163800	3.18624200	-1.43983700
H	-2.86649500	2.83588900	-1.37378900
C	-5.49325700	1.15850400	0.17491800
H	-5.82460800	0.12285000	0.29668900
H	-6.26031200	1.69217700	-0.39470400
H	-5.42253500	1.61555900	1.16820000
C	5.17647700	-1.86868400	-0.60202100
H	5.96884300	-2.26214000	-1.25049200
H	4.84479200	-2.68577900	0.04583900
C	4.01383900	-1.35767500	-1.45331800
H	3.65335800	-2.16848200	-2.09740900
H	4.37025200	-0.55937300	-2.11535800

C	2.85865400	-0.83436800	-0.60147100
H	3.23832300	-0.06369500	0.08353900
H	2.46921900	-1.64858400	0.02566900
C	1.72616500	-0.26058500	-1.45330400
H	1.42286700	-1.00678400	-2.19783000
C	0.49394500	0.12591100	-0.62860000
C	0.78752000	1.08674800	0.53154300
H	1.37529800	0.54611900	1.28524900
H	-0.15715500	1.36926700	1.01146800
H	0.06264200	-0.78970600	-0.21060600
C	5.80436600	-0.77297000	0.26127400
O	6.07993200	0.32870100	-0.29755200
O	6.02983000	-1.02985700	1.48052100
C	1.53691900	2.34836700	0.12309100
H	2.51727300	2.11635700	-0.29929600
H	0.97350100	2.90977500	-0.62764900
H	2.09538800	0.61035000	-2.01155400
S	1.77078400	3.51258900	1.51399000
H	2.47434200	2.67515000	2.29511200
S	-0.77724200	0.80714600	-1.77439900
H	-1.85691800	0.72737700	-0.79770400

TS – γ(1)

Charge = -1 Multiplicity = 2

N	-3.56847100	0.67698800	-1.72864000
H	-3.72171500	1.61543900	-1.38598300
H	-3.11352700	0.55007300	-2.62415200
C	-3.91933600	-0.39647200	-1.01425300
O	-3.78272300	-1.55417500	-1.42826900
C	-4.48556100	-0.12857200	0.38683100
H	-4.75341000	0.92974500	0.47565200
N	-5.68060400	-0.93299000	0.58486700
H	-5.67866300	-1.65684000	1.29430600
C	-6.75160800	-0.81468200	-0.20775100
O	-6.82596900	-0.00426700	-1.13925700
H	-7.57339800	-1.49892900	0.03884700
C	-3.47371100	-0.52116400	1.46968800
H	-3.19795700	-1.57476100	1.32894700
H	-4.00467700	-0.46331100	2.43446400
C	-2.22713900	0.32090300	1.60147800
C	-1.32320500	-0.14903400	2.70890600
H	-0.37101200	0.38928000	2.70916300
H	-1.12655500	-1.22440000	2.64267800
H	-1.80795400	0.03822900	3.67982500
C	-2.35806100	1.81137000	1.45717900
H	-3.05657100	2.19771300	2.21625100

H	-1.39424300	2.30409700	1.61273200
H	-2.74027800	2.11690600	0.47939200
C	5.94203100	-2.00033400	0.15107800
H	6.64441000	-2.68174600	-0.34428000
H	5.87115000	-2.30369900	1.20002300
C	4.57110300	-2.08746400	-0.52137600
H	4.21535100	-3.12385300	-0.47918900
H	4.66601200	-1.82585200	-1.58208900
C	3.54343800	-1.17109900	0.14045800
H	3.91480600	-0.13732900	0.11361000
H	3.44346400	-1.44257400	1.20091100
C	2.17433300	-1.24931500	-0.53535600
H	1.86346000	-2.29934700	-0.59456000
C	1.09156800	-0.46458000	0.21500400
C	1.44226600	1.01056700	0.45080100
H	2.27483900	1.05873000	1.16503000
H	0.59078300	1.50961600	0.92546400
H	0.95009200	-0.93692900	1.19282800
C	6.54732100	-0.59771200	0.07705200
O	6.56533700	-0.02725500	-1.05275800
O	7.01216900	-0.09069400	1.13977400
C	1.82498000	1.76677400	-0.81441600
H	2.72314100	1.35213200	-1.27792000
H	1.01748000	1.72407400	-1.55092300
H	2.25450700	-0.88658000	-1.56892900
S	2.10180500	3.54998200	-0.51680900
H	3.11979600	3.40535300	0.34861300
S	-0.49186300	-0.66161200	-0.70464800
H	-1.36590500	-0.12111400	0.35114000

TS – δ(1)

Charge = -1 Multiplicity = 2

N	2.55721200	0.36217700	1.70245700
H	1.72796000	-0.06180100	1.29893800
H	2.62910900	0.41611200	2.71148100
C	3.61513000	0.69330900	0.95328500
O	4.66547600	1.14087500	1.43016200
C	3.46838500	0.44759400	-0.55278400
H	2.40014000	0.39644900	-0.79592200
N	4.07340500	1.54213300	-1.29208000
H	4.83719400	1.34292900	-1.92814300
C	3.74743000	2.81938600	-1.06722000
O	2.87511900	3.17213000	-0.26421200
H	4.31710100	3.54185800	-1.66568900
C	4.17425500	-0.85392100	-0.95246900
H	5.20577800	-0.80969500	-0.58234000

H	4.21801800	-0.88570000	-2.04839400
C	3.50411900	-2.14082200	-0.45605500
H	3.39954000	-2.08063000	0.63954500
C	4.40818300	-3.34324100	-0.75387800
H	4.57905300	-3.43533300	-1.83218700
H	3.94699100	-4.27002900	-0.40103700
H	5.37768400	-3.22982700	-0.25950700
C	2.14612900	-2.33978300	-1.08212800
H	1.73276100	-1.56119200	-1.72295800
H	1.85585300	-3.35585300	-1.34573000
C	-6.18358100	-0.76154800	-0.51504300
H	-7.15482300	-1.05601600	-0.09806700
H	-6.14679900	-1.12584500	-1.54630100
C	-5.05528900	-1.37765800	0.31110000
H	-5.18296600	-2.46625800	0.34306000
H	-5.12302500	-1.01740700	1.34472600
C	-3.67457800	-1.04564800	-0.25281400
H	-3.57616400	0.04456900	-0.34168700
H	-3.58699600	-1.45340100	-1.26954500
C	-2.54859600	-1.60128000	0.61932900
H	-2.71170800	-2.67415500	0.77661300
C	-1.15960300	-1.40500200	0.00455300
C	-0.82838300	0.05443700	-0.33326700
H	-1.45249300	0.37267700	-1.17710000
H	0.21204200	0.10785100	-0.67851100
H	-1.10335500	-1.99058100	-0.91984900
C	-6.15385200	0.76841400	-0.52800700
O	-5.95181800	1.36323200	0.57067100
O	-6.35694600	1.35654200	-1.63075700
C	-1.03284600	1.01728700	0.83066700
H	-2.09448300	1.12492500	1.07110000
H	-0.52659800	0.66430900	1.73361300
H	-2.58904400	-1.12868800	1.61023400
S	-0.46477000	2.71293500	0.45559500
H	0.83204500	2.41655400	0.24486900
S	0.09151300	-2.13631100	1.14715600
H	1.11891600	-2.23334100	0.12363300

TS – α(2)

Charge = -1 Multiplicity = 2

N	3.87254900	-2.25709100	0.45116200
H	3.67716100	-2.38007400	-0.53388000
H	4.62242500	-2.79494300	0.86676300
C	3.30661500	-1.27168300	1.16396300
O	3.59122200	-1.04974200	2.34648400
C	2.33361700	-0.39295500	0.40300500

N	1.38733000	0.26148800	1.20338700
H	1.11003600	1.22481900	0.97415100
C	0.64918300	-0.33826300	2.17288800
O	0.72868600	-1.52645600	2.47785300
H	-0.05267600	0.35211900	2.66078400
C	2.99734000	0.49392700	-0.64505100
H	4.01996000	0.13736200	-0.80068700
H	3.07239800	1.50490800	-0.21603200
C	2.30716200	0.59772200	-2.01566300
H	2.27099000	-0.40907800	-2.45033800
C	3.14741300	1.49101700	-2.92623000
H	3.21883300	2.50359700	-2.51135200
H	2.69501400	1.56595400	-3.92007400
H	4.16333000	1.09969300	-3.04306100
C	0.88413500	1.13352700	-1.89745500
H	0.26773700	0.50446100	-1.24833400
H	0.39978900	1.17064800	-2.87921500
H	0.88981100	2.14849000	-1.48062500
C	-2.04948100	3.61429000	0.69928300
H	-2.20602200	4.34553900	1.50295000
H	-2.52925100	4.02035200	-0.19693700
C	-2.67952500	2.27837700	1.08545800
H	-3.73321400	2.44497500	1.33989500
H	-2.19215100	1.88849700	1.98781200
C	-2.59105800	1.23700600	-0.03003000
H	-1.53431400	1.06083200	-0.27158100
H	-3.06235300	1.63487600	-0.93968700
C	-3.26730400	-0.07697700	0.36178100
H	-4.29025100	0.13765300	0.69459300
C	-3.33417700	-1.09495300	-0.78182000
C	-1.97033000	-1.46399100	-1.38257200
H	-1.60789600	-0.60914300	-1.96736400
H	-2.10023900	-2.29439100	-2.08578600
H	-3.96030400	-0.68206300	-1.57846200
C	-0.53988700	3.56834800	0.46085800
O	0.15347400	2.78661700	1.18043900
O	-0.05708500	4.34566600	-0.40858700
C	-0.93482600	-1.81784800	-0.32206300
H	-0.69949800	-0.92510900	0.26050500
H	-1.31933800	-2.57296300	0.36852500
H	-2.74164300	-0.51356100	1.22288500
S	0.63654700	-2.43169800	-1.02964400
H	1.54612200	-1.40875800	-0.34095200
S	-4.22168000	-2.57619000	-0.12998800
H	-4.26512500	-3.25319000	-1.28984800

TS – β(2)

Charge = -1 Multiplicity = 2

N	-4.77853700	-0.89624200	0.48343600
H	-4.73301200	-1.79103600	0.01533100
H	-5.60698400	-0.66224100	1.01671200
C	-3.81084500	0.01566400	0.34321800
O	-3.87584300	1.14930300	0.83024300
C	-2.55179200	-0.44353000	-0.42662500
H	-2.82056100	-1.32808000	-1.01889700
N	-2.11626500	0.61144200	-1.31938200
H	-1.32283000	1.22014400	-1.05547900
C	-2.91719700	1.03511100	-2.30040700
O	-4.00666200	0.51419800	-2.58393700
H	-2.52359700	1.89663400	-2.85659400
C	-1.45476700	-0.77545800	0.55850700
H	-0.80545000	0.06970800	0.80699000
C	-1.72011400	-1.75081900	1.67774100
H	-2.54304800	-1.32069300	2.27616300
C	-0.50001200	-1.87764100	2.58975200
H	0.32270300	-2.36962300	2.05875600
H	-0.74268400	-2.48333600	3.46792800
H	-0.15378900	-0.89713600	2.93255900
C	-2.16426800	-3.13763900	1.19620900
H	-3.00101300	-3.10190600	0.49347000
H	-2.47183500	-3.74624100	2.05151800
H	-1.33211000	-3.65024700	0.70132100
C	1.16402800	3.63746400	0.92361600
H	1.07333100	4.69167000	0.63230900
H	1.13507300	3.60663000	2.01764000
C	2.46880500	3.04988700	0.39516200
H	3.31536500	3.64801500	0.75165000
H	2.47176600	3.11375400	-0.69915400
C	2.64885300	1.59029200	0.81350500
H	1.69593800	1.06474100	0.66920000
H	2.87782300	1.53251300	1.88608500
C	3.74269100	0.89136600	0.00880000
H	4.69987600	1.40122200	0.17314600
C	3.89455800	-0.58914100	0.36630400
C	2.59191600	-1.39177400	0.24941300
H	1.93005200	-1.08564000	1.06872900
H	2.80804100	-2.45465200	0.40626800
H	4.25506100	-0.66973300	1.39621800
C	-0.08136900	2.92653300	0.39042100
O	-0.03276200	2.43491700	-0.77975100
O	-1.10192800	2.88516000	1.13100200
C	1.86083500	-1.21071000	-1.07668200

H	1.50309700	-0.18414300	-1.20563600
H	2.52356800	-1.43519300	-1.91853400
H	3.51362400	0.98826100	-1.06126500
S	0.43001900	-2.33255100	-1.26489500
H	-0.45011300	-1.59631500	-0.36408400
S	5.22560400	-1.27078200	-0.71391300
H	5.26497500	-2.49638200	-0.16387600

TS – γ(2)

Charge = -1 Multiplicity = 2

N	4.21301700	1.38846200	0.57335000
H	3.52043500	2.03726200	0.22345700
H	4.92093600	1.72229600	1.21569000
C	4.18959200	0.09757100	0.22760700
O	5.02490100	-0.72601800	0.62240300
C	3.01872400	-0.33303400	-0.65976900
H	2.53191300	0.55994300	-1.06713200
N	3.50189800	-1.15900700	-1.75284800
H	3.16780500	-2.11252000	-1.83481000
C	4.45285200	-0.73966400	-2.59524900
O	4.96986900	0.38240900	-2.53859200
H	4.73948900	-1.48015400	-3.35280300
C	2.00220100	-1.16277100	0.15050200
H	2.49828800	-2.08106900	0.48769700
H	1.20855100	-1.44577600	-0.55309400
C	1.39616100	-0.44358800	1.33038500
C	2.12165200	-0.50531700	2.64735900
H	1.45749700	-0.21494800	3.46826400
H	2.97339700	0.18994200	2.66287800
H	2.50757600	-1.51073700	2.84420500
C	0.62003200	0.81196100	1.04951800
H	0.11186300	0.76887700	0.08065600
H	-0.12304400	1.00195300	1.83297800
H	1.29147200	1.68437600	1.03390400
C	-2.56578200	3.65043800	-0.71437900
H	-3.10368900	4.59851800	-0.58714500
H	-2.06348700	3.69285100	-1.68592100
C	-3.54880300	2.48206100	-0.67365800
H	-4.31771100	2.63071900	-1.44132700
H	-4.06373400	2.46796200	0.29445800
C	-2.85538000	1.14011900	-0.90038500
H	-2.06178500	1.02104900	-0.15198700
H	-2.36501500	1.14357500	-1.88415700
C	-3.82228400	-0.03894000	-0.81308900
H	-4.67068500	0.14087700	-1.48503800
C	-3.17192300	-1.37223600	-1.19252800

C	-1.92336300	-1.72702000	-0.37361700
H	-1.11570900	-1.04458700	-0.66990700
H	-1.59381700	-2.73585000	-0.64662100
H	-2.88566300	-1.33120900	-2.24786300
C	-1.50234200	3.60158100	0.38583400
O	-1.86404700	3.25253500	1.54662200
O	-0.32226200	3.94427300	0.07961300
C	-2.12278600	-1.64484900	1.13564700
H	-2.25262600	-0.60934300	1.46438300
H	-3.01974000	-2.19778200	1.43399300
H	-4.23140400	-0.09915200	0.20450700
S	-0.76038600	-2.39450600	2.09631600
H	0.28657400	-1.43778700	1.67268900
S	-4.47840700	-2.66753900	-1.05101900
H	-3.73041100	-3.69621700	-1.48566200

TS – δ(2)

Charge = -1 Multiplicity = 2

N	-4.26147800	-0.30706600	1.69071700
H	-3.42968200	0.21354200	1.95273900
H	-4.99812700	-0.43998400	2.37293000
C	-4.35114400	-0.91194700	0.50164100
O	-5.30401800	-1.63302300	0.17812000
C	-3.21465600	-0.61423500	-0.48240100
H	-2.37540900	-0.18964900	0.07562100
N	-2.77131700	-1.84477000	-1.11438600
H	-2.83775700	-1.94034500	-2.12120900
C	-2.30063400	-2.87142600	-0.39818700
O	-2.21153700	-2.86009500	0.83615800
H	-1.99275000	-3.73780000	-0.99824500
C	-3.68270800	0.36874400	-1.56002600
H	-4.62673200	0.00082300	-1.97869700
H	-2.94033200	0.36181100	-2.36857000
C	-3.85202400	1.81290600	-1.07660300
H	-4.48531700	1.82908600	-0.17708900
C	-4.57552400	2.63323400	-2.15952800
H	-3.98938100	2.64450500	-3.08505300
H	-4.72166200	3.66611600	-1.83246800
H	-5.55529100	2.19617400	-2.37669100
C	-2.53333300	2.47022700	-0.76937800
H	-1.64331400	2.10208100	-1.28165000
H	-2.55165600	3.54403100	-0.58635200
C	6.17655300	0.47085800	-1.26984800
H	6.78119100	1.23140900	-1.78092600
H	6.17326700	-0.41352100	-1.91541700
C	4.75722900	0.98776200	-1.05634900

H	4.34607600	1.31507400	-2.01931100
H	4.78319500	1.86991900	-0.40578800
C	3.83171300	-0.06593400	-0.44942500
H	4.25022800	-0.42079900	0.50254200
H	3.79514900	-0.93371100	-1.12106500
C	2.42434800	0.47673900	-0.20644200
H	1.94802600	0.73309200	-1.16351500
C	1.50087000	-0.45582500	0.57655700
C	0.09580500	0.11950900	0.76885000
H	-0.52614700	-0.62025500	1.28743700
H	-0.35053700	0.29341900	-0.21910200
H	1.94729200	-0.66037900	1.55620000
C	6.92940400	0.12878900	0.01839200
O	6.66954100	0.79250900	1.06251000
O	7.80870500	-0.78139900	-0.04705800
C	0.08568500	1.41894200	1.57082300
H	0.65179600	1.30236300	2.50070100
H	0.53278700	2.24275800	1.01056900
H	2.50993400	1.40896300	0.36574600
S	-1.59246200	1.93830000	2.08985600
S	1.39205300	-2.06744700	-0.31908600
H	-2.09585900	2.15335300	0.73943700
H	0.38609100	-2.57685000	0.41429400

N–formyl–leucinamide

Charge = 0 Multiplicity = 1

N	-1.42379500	-1.33235000	-0.06455900
C	-0.39215700	-0.35427300	0.23811200
C	-0.71897200	0.97696400	-0.44445000
C	0.95089800	-0.88654000	-0.27705000
N	-0.53017100	2.07447000	0.29573700
O	-1.08589500	1.01621300	-1.62618100
C	2.16058600	0.02399700	-0.04309300
C	3.38608300	-0.59459600	-0.71622700
C	2.43448800	0.24970700	1.44452700
C	-2.71371600	-1.10594900	0.20441400
O	-3.12904900	-0.07315600	0.74514300
H	-1.16990500	-2.18392600	-0.55241900
H	-0.35946900	-0.19830300	1.32163100
H	0.84222000	-1.07754500	-1.35230300
H	1.13354600	-1.85279700	0.21143100
H	-0.25193300	2.01146500	1.26576500
H	-0.66328600	2.98756100	-0.12051800
H	1.96819900	0.99571300	-0.51887000
H	4.26328400	0.04835400	-0.59469500
H	3.21830500	-0.74538100	-1.78749800

H	3.61681200	-1.56893700	-0.26890200
H	3.34400500	0.84368600	1.57921900
H	2.57992400	-0.71150000	1.95257700
H	1.61919900	0.77671800	1.95011200
H	-3.38685800	-1.92027200	-0.09287000

Dihydrolipoate radical S(1)

Charge = -1 Multiplicity = 2

C	3.48597200	-0.97548700	-0.25336000
H	4.25092200	-1.27832100	-0.97873000
H	3.66863700	-1.53055100	0.67170700
C	2.09465300	-1.29547000	-0.80199100
H	2.03745300	-2.36358700	-1.04300500
H	1.93975000	-0.74913800	-1.74021600
C	0.98381000	-0.93867900	0.18508600
H	1.09771200	0.11020500	0.49131500
H	1.09641100	-1.54510900	1.09498700
C	-0.40831800	-1.15740300	-0.40796200
H	-0.46333100	-2.16432600	-0.83847100
C	-1.54051600	-1.01368000	0.61350400
C	-1.52442600	0.31822300	1.37660200
H	-0.62294700	0.35609000	2.00049200
H	-2.38413900	0.35873100	2.05333000
H	-1.43548100	-1.80884100	1.36612300
C	3.68300300	0.51807400	0.01165700
O	3.36764400	1.32163500	-0.91438900
O	4.16013900	0.87140500	1.12985100
C	-1.51311400	1.55463700	0.48574400
H	-1.51516300	2.45996700	1.09610500
H	-0.62184400	1.58646000	-0.14670900
H	-0.56940000	-0.45659000	-1.23827600
S	-2.91769100	1.64428800	-0.67937200
S	-3.17367600	-1.34571000	-0.12479200
H	-3.88755200	1.74105500	0.24679200

Dihydrolipoate radical S(2)

Charge = -1 Multiplicity = 2

C	3.52006700	-0.96826600	-0.19479100
H	4.28324300	-1.29267400	-0.91250100
H	3.70305600	-1.49690100	0.74546500
C	2.12798000	-1.30417400	-0.73182500
H	2.06538500	-2.38230800	-0.92142400
H	1.97675100	-0.80143400	-1.69462700
C	1.01946700	-0.89350900	0.23644300
H	1.11187100	0.17848700	0.45534300
H	1.15080700	-1.42446300	1.18949900

C	-0.37098200	-1.18488500	-0.32666000
H	-0.41707600	-2.23057700	-0.65394100
C	-1.49272300	-0.94643800	0.68652000
C	-1.50354900	0.45264600	1.31022500
H	-0.58324000	0.56748400	1.89520100
H	-2.33970700	0.53357800	2.01254400
H	-1.39220600	-1.67196400	1.49994300
C	3.71811400	0.53179400	0.02910000
O	3.40618200	1.31030400	-0.91909600
O	4.19176100	0.91418600	1.13907300
C	-1.57210200	1.59116900	0.29391400
H	-1.48072500	2.54157400	0.83081400
H	-0.74530400	1.52792500	-0.41827200
H	-0.53906600	-0.56717500	-1.21956800
S	-3.15779800	1.66500800	-0.59146000
S	-3.13176700	-1.32560500	-0.07432500
H	-2.72246600	-1.36536400	-1.35333800