

**Deciphering the Exceptional Selectivity of Semipinacol
Rearrangements in Cis-Fused β -Lactam Diols Using High-
Level Quantum Chemical Methods**

Abdulkader Baroudi^{†,*} and Amir Karton^{‡,*}

[†] College of Engineering and Technology, American University of the Middle East, Kuwait.

[‡] School of Molecular Sciences, The University of Western Australia, Perth, WA 6009, Australia.

Supporting Information

(Figures S1–S5, Table S1–S2)

Total 25 Pages

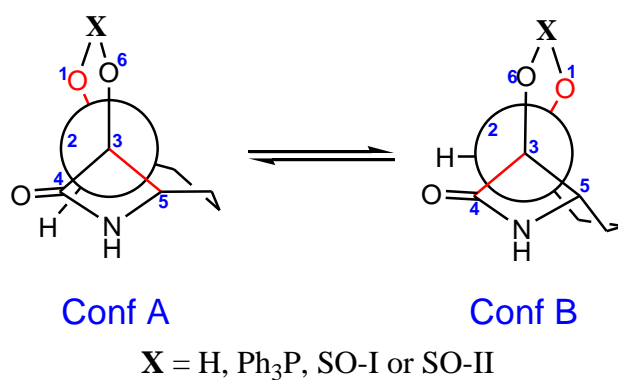


Figure S1. Different Conformers of the Cis-Fused β -Lactam Diol and its Phospharane and Sulfite Derivatives.

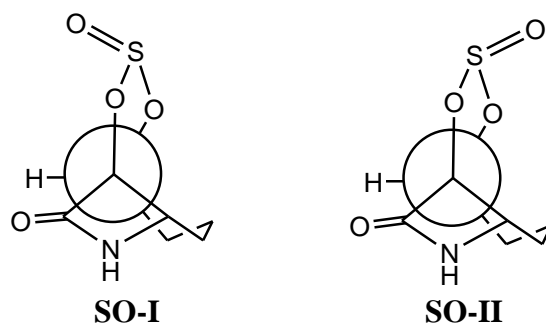


Figure S2. Diastereomers of Sulfites (Conf B).

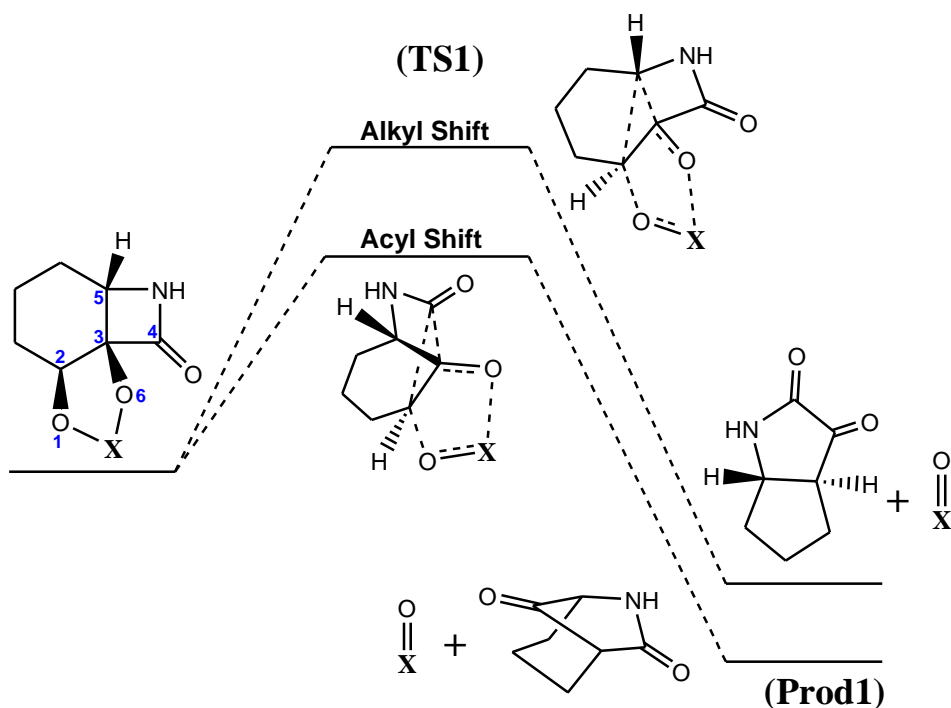


Figure S3. Reaction profile for the alkyl and acyl migration pathways in the concerted semipinacol rearrangement of Cis-Fused β -Lactam Diol Phospharane and Sulfite Derivatives. Dashed lines in the transition structures represent bonds being broken and formed.

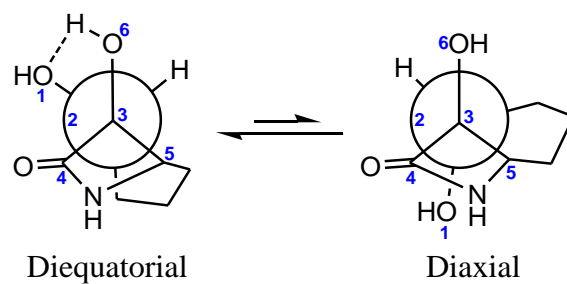


Figure S4. Staggered Conformers of Trans-Fused β -Lactam Diol.

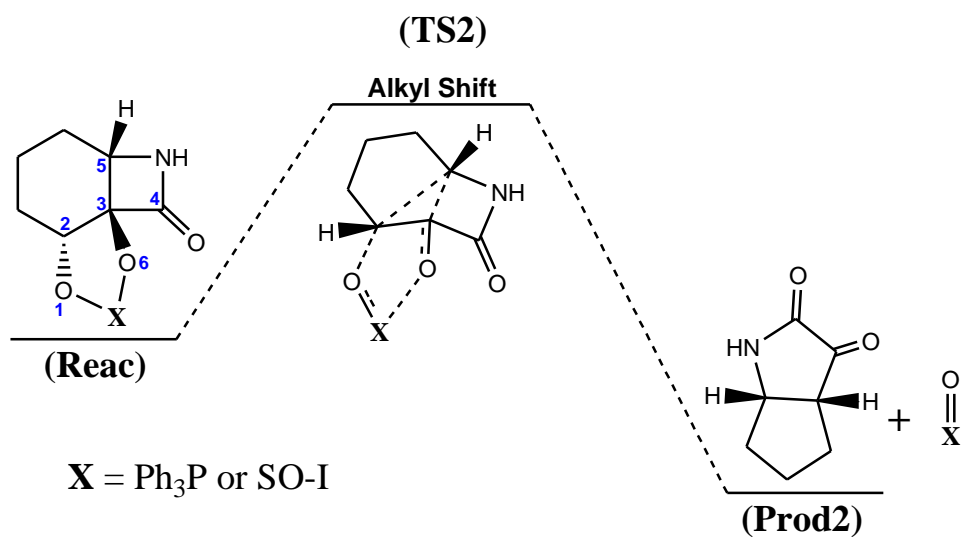


Figure S5. Reaction profile for the alkyl migration pathway in the concerted semipinacol rearrangement of Trans-Fused β -Lactam Diol Phospharane and Sulfite Derivatives. Dashed lines in the transition structures represent bonds being broken and formed.

Table S1. SMD-B3LYP-D3/6-31G(2df,p) optimized geometries (Å).

Conf A-H

Solvent: CH₃CN

C	1.93526700	0.57362800	-0.40955700
C	2.00919600	-0.93865100	-0.63786300
C	1.33482900	-1.67319200	0.52248000
C	-0.09057000	-1.20380200	0.76880300
C	-0.49348500	0.27615600	0.42015500
C	0.49723800	1.06881500	-0.50054400
H	1.33344000	-2.75679900	0.35892600
H	1.51909200	-1.19197300	-1.58611000
H	3.05232400	-1.25632600	-0.72227800
H	2.33666000	0.81006900	0.58662900
H	2.53713700	1.11660000	-1.14507800
H	-0.40732100	-1.43912600	1.78941600
H	0.15710000	0.95868900	-1.53508600
H	1.90961100	-1.49328500	1.43881400
O	-0.87911600	1.03176600	1.52571300
H	-0.71914700	1.95341600	1.26010700
O	0.38745500	2.46471100	-0.20336900
H	1.15015800	2.71128600	0.33560200
N	-1.10429000	-1.61708100	-0.22056300
H	-1.47519000	-2.53656500	-0.42284900
C	-1.64457100	-0.37929800	-0.40606000
O	-2.62724700	0.01622900	-0.99217400

Conf B-H

Solvent: CH₃CN

C	0.59869200	-1.04107300	0.55422300
C	1.39940100	0.04984500	1.26285200
C	2.05689700	0.97340900	0.23539500
C	1.02351500	1.78483300	-0.56177100
C	-0.25905100	1.00873500	-0.91123300
C	-0.48320400	-0.46568400	-0.36948300
H	2.75703100	1.65602500	0.72604300
H	0.73353500	0.61267900	1.92884000
H	2.15459800	-0.42803400	1.89563000
H	0.10009300	-1.69310800	1.28154300
H	0.72497200	2.66247500	0.02221400
H	1.48285300	2.16407700	-1.47936100
H	-0.48351900	1.05216300	-1.97930300
H	2.64432500	0.35004700	-0.44640400
C	-1.69498900	0.13672200	0.39524500
N	-1.43067700	1.37382300	-0.09079900
H	-1.87104600	2.26983400	0.07306600

O	-0.87688000	-1.40941800	-1.32209900
O	1.44650700	-1.83563000	-0.28957700
O	-2.54684200	-0.30877400	1.13160900
H	1.84627300	-2.52519900	0.25208100
H	-0.10422400	-1.98786400	-1.42957900

Conf A-Ph₃P

Solvent: CH₃CN

C	-4.15256700	-1.94858600	-0.15510200
C	-3.58870000	-0.73629900	0.57279500
C	-2.30618300	-0.02459400	0.00453100
C	-1.88413900	-0.39912300	-1.43575800
C	-2.31445200	-1.79749900	-1.85312400
C	-3.82471500	-1.95659900	-1.65098700
H	-3.44992100	-0.94782900	1.63700900
H	-3.71961700	-2.84465500	0.30530000
H	-5.23403900	-1.99934200	0.01472100
H	-2.27867500	0.33328700	-2.14638900
H	-2.02832600	-1.96155500	-2.89629900
H	-1.77728100	-2.53546800	-1.24322800
H	-4.35294200	-1.14155600	-2.16191500
H	-4.17207100	-2.89126900	-2.10010600
N	-4.27755000	0.55099600	0.36353800
H	-5.20379500	0.84590800	0.64422200
C	-3.16189800	1.27750700	0.06931600
O	-2.95974500	2.46103200	-0.08284200
O	-0.46482000	-0.27746600	-1.46691200
O	-1.17466700	-0.10917800	0.77996000
P	0.36668400	0.00966100	-0.07661800
C	1.94275700	-0.14485600	-1.11742000
C	2.11523000	-1.29561500	-1.90173300
C	3.00294900	0.76487300	-1.05586700
C	3.29406000	-1.52420800	-2.60308000
H	1.31439100	-2.02486600	-1.96201000
C	4.18915200	0.54051300	-1.75708400
H	2.91554400	1.66140800	-0.45478500
C	4.33995900	-0.60341100	-2.53356300
H	3.39921800	-2.42240800	-3.20350500
H	4.99382100	1.26625600	-1.69326900
H	5.26113500	-0.77879600	-3.07934900
C	1.02060400	-1.17155600	1.17137200
C	2.24868700	-0.93435100	1.79964400
C	0.33827400	-2.36141600	1.44271800
C	2.76810400	-1.85733700	2.70260100
H	2.79952300	-0.02519000	1.58962100
C	0.88030400	-3.30335400	2.31321900
H	-0.61893200	-2.54886800	0.97235100
C	2.09106400	-3.04948100	2.95350500

H	3.70832800	-1.64865400	3.20197000
H	0.34768400	-4.22984900	2.50064300
H	2.50537400	-3.77601400	3.64432000
C	0.52952200	1.75821000	0.38200800
C	0.67287500	2.15901900	1.71249700
C	0.45408700	2.72474900	-0.62452000
C	0.75769700	3.51183800	2.02934900
H	0.72096000	1.41641800	2.50049200
C	0.52242700	4.07741600	-0.30379500
H	0.34448900	2.41893900	-1.65935500
C	0.67929100	4.47307400	1.02291200
H	0.87897000	3.81508600	3.06393000
H	0.45629000	4.82147400	-1.09049700
H	0.73997300	5.52707700	1.27238700

Conf B-Ph₃P

Solvent: CH₃CN

C	2.16122800	-0.00474200	-1.01890900
C	3.29176900	0.88050400	-1.53158200
C	3.51214800	2.08501800	-0.61584300
C	4.06671700	1.63036300	0.73917500
C	3.18101300	0.56553700	1.40057000
C	2.23102100	-0.28774500	0.48971900
H	4.20809800	2.79302100	-1.07575700
H	4.21078700	0.28496000	-1.59622400
H	3.03471900	1.19315800	-2.54813800
H	2.15638800	-0.96616800	-1.55465000
H	5.06320800	1.20202900	0.58462000
H	4.18520800	2.48344800	1.41334500
H	2.62874100	0.96533300	2.25410700
H	2.55952900	2.61045500	-0.48054300
C	3.04168600	-1.51098200	0.97717200
N	3.84805800	-0.71423200	1.72154400
H	4.64833400	-0.92017500	2.30503500
O	0.90166000	-0.33652300	0.94875800
O	0.93043400	0.65027200	-1.17709600
O	2.97392900	-2.70589500	0.78992000
P	-0.31575100	0.08973900	-0.08695300
C	-0.79667800	-1.25325900	-1.22311100
C	-1.71878000	-1.08355500	-2.26024500
C	-0.20018900	-2.50678600	-1.03468500
C	-2.04434600	-2.15244300	-3.09144300
H	-2.19160100	-0.12195300	-2.41909500
C	-0.51966400	-3.56810300	-1.87812500
H	0.51978400	-2.65631400	-0.23719800
C	-1.44471500	-3.39623000	-2.90523200
H	-2.76696400	-2.00987200	-3.88807200
H	-0.04542900	-4.53224500	-1.72691700

H	-1.69760700	-4.22634500	-3.55601700
C	-1.10594400	1.72893500	-0.35069800
C	-1.54401000	2.46676300	0.75363100
C	-1.21837200	2.29414900	-1.62908700
C	-2.08212900	3.74072500	0.58818300
H	-1.46172300	2.04871500	1.74952000
C	-1.79472900	3.54892400	-1.79639700
H	-0.85169800	1.75376500	-2.49111600
C	-2.22261500	4.27859700	-0.68807200
H	-2.40037800	4.30573700	1.45774400
H	-1.89727200	3.96308300	-2.79385300
H	-2.66005400	5.26256300	-0.81970500
C	-1.55383600	-0.43914400	1.25365800
C	-1.22480000	-0.83754900	2.55340300
C	-2.91046000	-0.45466300	0.89334700
C	-2.21116100	-1.23593500	3.45785400
H	-0.19027900	-0.83648500	2.86751200
C	-3.89655000	-0.85557500	1.78728500
H	-3.20552700	-0.14735000	-0.10442400
C	-3.54939100	-1.24938300	3.07970000
H	-1.92588500	-1.53720700	4.46100900
H	-4.93649900	-0.85937000	1.47678300
H	-4.31548200	-1.56261000	3.78126800

Conf A-SO-I

Solvent: Ph₂O

C	-2.57908900	-0.58275600	0.77616800
C	-1.52532500	0.49474700	1.00059800
C	-0.15551200	0.33653500	0.25498300
C	0.05373100	-0.84446900	-0.72297400
C	-1.04974200	-1.89660500	-0.70950100
C	-2.43642700	-1.25581000	-0.59152700
H	-1.37444700	0.70424100	2.06261300
H	-2.47581400	-1.33938400	1.56264300
H	-3.57201700	-0.13556500	0.89575200
H	0.20001700	-0.44267400	-1.72931500
H	-0.96684700	-2.50933100	-1.61056100
H	-0.88207400	-2.55348300	0.15137600
H	-2.59023600	-0.52496400	-1.39499000
H	-3.20593500	-2.02327400	-0.70975800
N	-1.70504600	1.72176700	0.20527900
H	-2.44508800	2.41028400	0.21030500
C	-0.49744300	1.69951300	-0.42336200
O	0.05905000	2.43053400	-1.20005000
O	1.29101400	-1.47708900	-0.30746900
O	0.96700200	0.37365100	1.12702000
S	2.26646000	-0.45255700	0.50985100
O	2.94833900	0.40987400	-0.43686900

Conf B-SO-I

Solvent: Ph₂O

C	-0.17675000	-0.60468600	0.90307300
C	0.92187800	-1.59279200	1.25901200
C	1.66988600	-2.08009300	0.01705300
C	2.44078600	-0.92494600	-0.63150000
C	1.52958900	0.26361600	-0.97389900
C	0.21493300	0.44468600	-0.13883100
H	2.36563400	-2.87863100	0.28969800
H	1.61529900	-1.09588400	1.94797600
H	0.46581200	-2.42143900	1.80735800
H	-0.58234000	-0.11094400	1.79085600
H	3.20880800	-0.57782300	0.06858400
H	2.95899400	-1.26659300	-1.53166400
H	1.31274500	0.32151200	-2.04263600
H	0.95467700	-2.50890200	-0.69415000
C	0.84754000	1.77494400	0.36654300
N	1.94565700	1.56107600	-0.40802700
H	2.80599000	2.08281700	-0.50522800
O	-0.93173700	0.66640700	-0.95823900
O	-1.25605200	-1.34157800	0.26057200
O	0.50914500	2.64010500	1.13134800
S	-2.21605100	-0.32121900	-0.58087600
O	-3.06580400	0.40800200	0.34265600

Conf A-SO-II

Solvent: Ph₂O

C	-1.51977900	1.68291200	-0.93056600
C	-1.23055200	0.20131500	-1.12894900
C	-0.29610800	-0.51476600	-0.09004400
C	0.22454100	0.28153900	1.13262500
C	-0.01346700	1.78804700	1.06483000
C	-1.41706800	2.10212600	0.53837500
H	-0.91665300	-0.01930600	-2.15211300
H	-0.79374700	2.25501100	-1.51899700
H	-2.51037500	1.90901800	-1.34028400
H	-0.20925600	-0.14168500	2.04176800
H	0.14629500	2.21293600	2.05904500
H	0.73208000	2.22547200	0.39442500
H	-2.17598800	1.58494100	1.13890300
H	-1.61586400	3.17282100	0.63351200
N	-2.28401300	-0.71783700	-0.65937600
H	-3.24424700	-0.83338600	-0.95351400
C	-1.51283500	-1.44607000	0.19119600
O	-1.70204400	-2.40583400	0.89220100

O	1.64221300	-0.02475400	1.21876400
O	0.80954700	-1.22212600	-0.63760300
S	2.24147700	-0.50206400	-0.22300700
O	2.41326200	0.66789400	-1.07133700

Conf B-SO-II

Solvent: Ph₂O

C	0.17190700	0.13455200	1.28547100
C	-0.08373300	1.62641500	1.44884100
C	0.06968100	2.38158400	0.12849700
C	-1.02166800	1.95289300	-0.85908600
C	-1.01403100	0.43724600	-1.10417000
C	-0.45397300	-0.48537700	0.03433300
H	0.00329200	3.45864500	0.30533700
H	-1.10074900	1.75366700	1.84016000
H	0.60099800	2.00352200	2.21321400
H	-0.14276900	-0.42743500	2.16901100
H	-1.99926700	2.23253300	-0.45040600
H	-0.90783600	2.48007900	-1.81014800
H	-0.56096400	0.17939500	-2.06240000
H	1.05940700	2.18223900	-0.29601500
C	-1.89549500	-1.06453500	0.12548700
N	-2.30203300	-0.24834500	-0.88192700
H	-3.20986200	-0.11749200	-1.30695600
O	0.47271200	-1.47820200	-0.40814300
O	1.60647400	-0.10377700	1.15369400
O	-2.43208100	-1.89482000	0.81201500
S	2.01738100	-0.91406800	-0.20473300
O	2.28511300	0.06701000	-1.24616700

TS1-Alkyl-Ph₃P

Solvent: CH₃CN

C	-4.44836700	-1.65991800	-1.31694900
C	-4.30383200	-0.38222200	-0.52769000
C	-2.57549300	0.35419500	0.04706200
C	-2.05018300	-0.59313800	-0.94426600
C	-2.00531800	-2.07940800	-0.69221800
C	-3.44715500	-2.66686900	-0.71607000
H	-4.77419600	-0.43065000	0.45743600
H	-5.46316200	-2.07552400	-1.25601400
H	-4.23147400	-1.48288200	-2.37608300
H	-2.30176600	-0.33262300	-1.96521700
H	-1.39263300	-2.53393800	-1.47361500
H	-1.53264000	-2.28852900	0.26643100
H	-3.46853100	-3.61835200	-1.25538300
H	-3.75543800	-2.87814500	0.31358200

N	-4.36783000	0.90961100	-1.14838400
H	-5.15108600	1.33368400	-1.63140100
C	-3.28613800	1.56261700	-0.63468800
O	-3.01408100	2.74969100	-0.65415100
O	-0.29692700	-0.20057900	-1.20619800
O	-2.19177500	0.39379100	1.24816300
P	0.86064300	-0.01560900	-0.21812900
C	0.75821900	1.51037200	0.72097000
C	0.03252600	2.58107100	0.19201900
C	1.43759500	1.65422000	1.93616100
C	-0.01084000	3.79022000	0.87657800
H	-0.52561000	2.46105900	-0.72630900
C	1.39752200	2.87068200	2.61102600
H	1.98933200	0.82110300	2.35533500
C	0.67481300	3.93822600	2.08123400
H	-0.58878300	4.61381600	0.47276100
H	1.92406000	2.98111100	3.55261200
H	0.63926200	4.88352200	2.61229800
C	1.08764800	-1.35770400	0.96233800
C	2.15879200	-2.24849400	0.83614700
C	0.17080800	-1.50520100	2.01502400
C	2.31393200	-3.28192600	1.75650300
H	2.87115500	-2.13610300	0.02821400
C	0.33496600	-2.54115400	2.92727000
H	-0.67874600	-0.82859400	2.07066700
C	1.40531900	-3.42723400	2.80159900
H	3.14553800	-3.97056500	1.65609100
H	-0.37484100	-2.65875300	3.73908800
H	1.52982500	-4.23123800	3.51918900
C	2.35771700	0.06501800	-1.22260400
C	2.35144000	-0.52569300	-2.49053600
C	3.52007200	0.68011100	-0.74447400
C	3.50297100	-0.50416000	-3.27197900
H	1.44557400	-0.99175500	-2.85889400
C	4.66804500	0.69644200	-1.52943200
H	3.52802700	1.14659300	0.23366100
C	4.66074500	0.10426400	-2.79167400
H	3.49447600	-0.96122700	-4.25536400
H	5.56716500	1.17471100	-1.15685100
H	5.55710500	0.12101800	-3.40222900

TS1-Acyl-Ph₃P

Solvent: CH₃CN

C	-2.00404800	0.40158400	-1.40871500
C	-2.44480400	-0.59678800	-2.43850300
C	-2.43949200	-2.02719800	-1.87488100
C	-3.23272300	-2.19120000	-0.55909500
C	-3.49285800	-0.88274300	0.19447600

C	-2.54734800	0.36320000	-0.05405100
H	-2.82225100	-2.71425400	-2.63488600
H	-3.44465100	-0.31764000	-2.79002500
H	-1.78310000	-0.52309400	-3.30476100
H	-1.67997000	1.37938900	-1.74627400
H	-4.20627900	-2.65527800	-0.75554200
H	-2.69480200	-2.87589500	0.10277900
H	-3.56503200	-1.04523300	1.27196000
H	-1.39507000	-2.29483900	-1.70013200
C	-4.09779200	1.05735400	-0.58436600
N	-4.65493800	-0.13813000	-0.31380300
H	-5.63966400	-0.36270500	-0.21549600
O	-1.97411100	0.95368100	0.93323400
O	-0.16187700	-0.20192900	-1.28696800
O	-4.54249800	2.14524500	-0.84877100
P	0.88126700	0.03405300	-0.19994300
C	0.44772800	-0.66768300	1.39655200
C	-0.12855900	-1.94319400	1.40738200
C	0.72077600	-0.01421300	2.59903900
C	-0.45667600	-2.54550800	2.61633800
H	-0.32872300	-2.45419900	0.47246500
C	0.39888700	-0.62608200	3.80774400
H	1.16956100	0.97174600	2.59200300
C	-0.19478600	-1.88643800	3.81788200
H	-0.91369300	-3.52914500	2.62221900
H	0.60672900	-0.11440800	4.74126900
H	-0.44970800	-2.35834800	4.76074100
C	2.36596200	-0.86058600	-0.71693500
C	2.56753500	-1.10684900	-2.07872200
C	3.31096300	-1.29867100	0.21746500
C	3.70787000	-1.78336100	-2.50182800
H	1.82633200	-0.77552500	-2.79639200
C	4.45081400	-1.97181100	-0.21078500
H	3.15433300	-1.11576100	1.27441400
C	4.64951100	-2.21449600	-1.56924000
H	3.85972400	-1.97603800	-3.55830100
H	5.18053100	-2.31182200	0.51589200
H	5.53671900	-2.74362900	-1.90021200
C	1.36059800	1.76302200	0.00583600
C	2.67749300	2.17058500	-0.24109900
C	0.39396200	2.71104700	0.37739700
C	3.02670600	3.51246000	-0.11678100
H	3.43027600	1.44819300	-0.53006200
C	0.75526800	4.04905100	0.49653400
H	-0.62144800	2.36602600	0.57095100
C	2.06747200	4.45231000	0.25169200
H	4.04873000	3.82058100	-0.30885900
H	0.00824300	4.78163100	0.78428500
H	2.34192400	5.49764000	0.34775300

TS1-Alkyl-SO-I

Solvent: Ph₂O

C	-2.96081400	-0.34445200	-0.07664200
C	-1.94040100	0.61141000	0.49046600
C	-0.05143900	0.43974100	0.28685200
C	-0.44110400	-0.58697000	-0.63889200
C	-0.95042200	-1.92265400	-0.19529400
C	-2.46914700	-1.78865000	0.15783200
H	-1.93118000	0.63136000	1.58264800
H	-3.92769100	-0.20046400	0.41932300
H	-3.09945800	-0.14709200	-1.14341300
H	-0.75442200	-0.25844500	-1.62612500
H	-0.79559000	-2.64107900	-1.00087100
H	-0.38945100	-2.25878800	0.67638800
H	-3.07413400	-2.48856700	-0.42203500
H	-2.60030100	-2.04740500	1.21195600
N	-1.65179500	1.85795400	-0.14930200
H	-2.29593700	2.61699200	-0.32705600
C	-0.27977900	1.89815900	-0.16915300
O	0.48697700	2.79247700	-0.41290000
O	1.48239400	-1.19003600	-0.93820700
O	0.76099100	0.13728100	1.24642300
S	2.34011000	-0.79134300	0.23285200
O	3.21309000	0.33650300	-0.04310900

TS1-Acyl-SO-I

Solvent: Ph₂O

C	0.10129300	-0.09491100	0.97448700
C	1.02909800	-1.14557800	1.48435500
C	1.33367800	-2.17041400	0.37947900
C	1.92261200	-1.53545900	-0.89344300
C	1.43875100	-0.09909300	-1.14614000
C	0.18954400	0.38130500	-0.36003800
H	2.01001700	-2.93823700	0.76347800
H	1.94879000	-0.67683500	1.85988500
H	0.56133300	-1.62400900	2.34886600
H	-0.53784300	0.45204100	1.65584600
H	3.01646200	-1.50633300	-0.83864700
H	1.66859100	-2.15330400	-1.75838800
H	1.30965700	0.12019300	-2.20660400
H	0.38954400	-2.66141400	0.13068800
C	1.43806900	1.61371800	0.24921000
N	2.29088400	0.92068400	-0.50438600
H	3.22672500	1.21279000	-0.76454700
O	-0.85170900	0.88084300	-0.97020500
O	-1.71021000	-1.19426600	0.37211600

O	1.40554600	2.62123700	0.87108100
S	-2.46796300	-0.19054700	-0.43390500
O	-3.20116700	0.77739400	0.37140100

TS1-Alkyl-SO-II

Solvent: Ph₂O

C	2.47840400	-1.44165800	-0.02022800
C	1.96263100	-0.14127300	-0.58373800
C	0.23901100	0.61186900	-0.22088600
C	0.21636000	-0.44475200	0.75020600
C	-0.00009800	-1.89074700	0.41694400
C	1.34893900	-2.48863300	-0.10518000
H	1.84338300	-0.16125900	-1.66912900
H	3.34272900	-1.78574700	-0.59989300
H	2.80415800	-1.29619100	1.01378800
H	0.75138500	-0.24857000	1.67534500
H	-0.33091400	-2.40347000	1.32121800
H	-0.77879700	-1.99766700	-0.33535300
H	1.62464900	-3.38838800	0.44830700
H	1.21207600	-2.78216200	-1.14956200
N	2.35371600	1.12028600	-0.03331500
H	3.29193000	1.49170300	0.03329500
C	1.16976000	1.80249100	0.07769400
O	0.93211100	2.96332700	0.29153000
O	-1.71413100	0.06062000	1.25324100
O	-0.72653500	0.70999300	-1.07853700
S	-2.43699800	0.34660200	-0.03445500
O	-2.95827900	-0.84139800	-0.69653300

TS1-Acyl-SO-II

Solvent: Ph₂O

C	-0.32956100	-0.11395500	1.18262800
C	-0.74455900	1.27178400	1.54055400
C	-0.23283000	2.26031400	0.47942200
C	-0.73230300	1.93437400	-0.93830300
C	-0.92430800	0.43133500	-1.18930400
C	-0.29018600	-0.54771300	-0.16697200
H	-0.51519100	3.27991800	0.75387900
H	-1.83751600	1.32406100	1.64173000
H	-0.34168300	1.50533300	2.52986400
H	-0.19096800	-0.86717400	1.94710400
H	-1.69156800	2.42709600	-1.13213200
H	-0.02039800	2.32452400	-1.66884100
H	-0.63848100	0.13474300	-2.19816300
H	0.85852200	2.20346700	0.49011200
C	-2.07680600	-1.03309700	-0.00269900

N	-2.28572900	-0.04941700	-0.87332200
H	-3.14745100	0.11147300	-1.38402200
O	0.52551800	-1.49822800	-0.54429300
O	1.93229100	-0.16396600	1.24747600
O	-2.66069500	-1.92063200	0.51830500
S	2.34371300	-0.70492200	-0.07649700
O	2.45398000	0.32820000	-1.10577300

Prod1-Alkyl

Solvent: CH₃CN

C	1.90320700	-1.22883500	-0.14242500
C	0.54371900	-0.78206800	0.36922400
C	-1.04273500	0.90732000	-0.04385600
C	0.39652400	0.58822000	-0.30212400
C	1.69677400	1.29136700	0.05487000
C	2.72478000	0.10059400	-0.00198200
H	0.61523200	-0.63753300	1.45692700
H	2.34326300	-2.04930400	0.42799700
H	1.82749600	-1.53543600	-1.19059800
H	0.40272600	0.36855000	-1.38359100
H	1.95106800	2.09254800	-0.64058700
H	1.64922000	1.71918600	1.05985200
H	3.41461600	0.21392800	-0.84058500
H	3.32643200	0.08056200	0.90960900
N	-0.72400100	-1.42171600	0.04403000
H	-0.92478300	-2.39091500	0.25432000
C	-1.73442800	-0.50596800	-0.03999200
O	-2.92953100	-0.71009800	-0.09724600
O	-1.62850800	1.94342800	0.13176700

Prod1-Alkyl

Solvent: Ph₂O

C	1.90420400	-1.23015200	-0.13725000
C	0.54089600	-0.78361300	0.36691600
C	-1.04476600	0.91068100	-0.04601100
C	0.39642600	0.58577700	-0.30797100
C	1.69656000	1.28956800	0.04921500
C	2.72521900	0.09908000	0.00545400
H	0.60944900	-0.63623800	1.45562900
H	2.34370700	-2.05085100	0.43372300
H	1.83292500	-1.53945500	-1.18508200
H	0.40357000	0.36255700	-1.38854000
H	1.95328200	2.08704300	-0.64943500
H	1.64536000	1.72785600	1.04950700
H	3.42437200	0.20898900	-0.82585400
H	3.31993800	0.08162400	0.92176200

N	-0.72353400	-1.42239900	0.03326200
H	-0.93164400	-2.38671000	0.25505500
C	-1.74032100	-0.50284900	-0.04082900
O	-2.93075600	-0.71274500	-0.08943900
O	-1.61993500	1.94912300	0.13484600

Prod1-Acyl

Solvent: CH₃CN

C	-0.44853300	0.10577300	-1.03883100
C	0.25877400	-1.29729000	-1.08444100
C	1.50729600	-1.35038300	-0.17930700
C	1.32770000	-0.68233500	1.19981900
C	0.49318700	0.62330900	1.08516800
C	0.52879300	1.06539700	-0.38532000
H	1.82959100	-2.38798800	-0.05815100
H	-0.46949900	-2.06219100	-0.79855100
H	0.55619500	-1.50602700	-2.11427300
H	-0.82878700	0.41736000	-2.00910400
H	0.80951700	-1.34475600	1.90024600
H	2.31030900	-0.45886900	1.62363300
H	0.81993100	1.40008800	1.77545500
H	2.32141200	-0.83321700	-0.70021600
C	-1.54072600	0.02525100	0.03474600
N	-0.94272600	0.36487700	1.20954500
H	-1.38949800	0.20607400	2.10211100
O	1.18402400	1.94644000	-0.87642600
O	-2.69890400	-0.31180800	-0.12094600

Prod1-Acyl

Solvent: Ph₂O

C	-0.44927400	0.10209700	-1.03956900
C	0.25705400	-1.30101200	-1.07950800
C	1.50683500	-1.35063700	-0.17545500
C	1.32934400	-0.67798200	1.20212700
C	0.49299500	0.62655200	1.08382100
C	0.52951400	1.06448000	-0.39034400
H	1.83147000	-2.38731300	-0.05174400
H	-0.47183700	-2.06471500	-0.79183000
H	0.55481400	-1.51601100	-2.10808900
H	-0.83005500	0.40981700	-2.01069500
H	0.81441900	-1.34027000	1.90554200
H	2.31313000	-0.45427900	1.62361900
H	0.82143500	1.40790800	1.76859300
H	2.31979200	-0.83422300	-0.69867100
C	-1.54403400	0.02555600	0.03310600
N	-0.94153100	0.36817800	1.20909700

H	-1.39615100	0.22326300	2.09899300
O	1.18680100	1.94123900	-0.88209900
O	-2.69941400	-0.31070800	-0.11845900

Ph₃PO

Solvent: CH₃CN

O	0.04984200	-0.12854800	2.42327700
P	0.01041200	-0.02177600	0.93391700
C	-0.45013000	1.61407100	0.31126200
C	-1.80310000	1.96904000	0.23307400
C	0.52834100	2.56891000	0.01174300
C	-2.16964000	3.25553600	-0.14841500
H	-2.56872100	1.23658100	0.46396900
C	0.15857600	3.85558800	-0.36967100
H	1.57818200	2.30622100	0.07285000
C	-1.18927300	4.19919100	-0.45192500
H	-3.21940800	3.52065300	-0.21167000
H	0.92310700	4.58821400	-0.60454100
H	-1.47631700	5.20106900	-0.75284700
C	1.61368000	-0.40980800	0.18380300
C	1.84409000	-0.30653700	-1.19326000
C	2.63733900	-0.85436900	1.02461100
C	3.08547900	-0.64716000	-1.71903800
H	1.05899700	0.04667700	-1.85211000
C	3.87994400	-1.19538700	0.49507600
H	2.44857400	-0.92737700	2.08960000
C	4.10384000	-1.09299700	-0.87565600
H	3.26078100	-0.56353200	-2.78616700
H	4.67128000	-1.53906600	1.15262500
H	5.07113000	-1.35856000	-1.28873400
C	-1.17220000	-1.17900500	0.19481200
C	-1.63083300	-2.23446300	0.98879600
C	-1.60265900	-1.07562600	-1.13338000
C	-2.50612500	-3.17983000	0.46020800
H	-1.30099500	-2.30123300	2.01942200
C	-2.47620400	-2.02199100	-1.65896200
H	-1.26653800	-0.25143300	-1.75217200
C	-2.92710800	-3.07542300	-0.86370500
H	-2.86041100	-3.99502500	1.08199500
H	-2.80891300	-1.93561600	-2.68773300
H	-3.60975400	-3.81097300	-1.27569400

SO₂

Solvent: Ph₂O

O	0.00000000	1.24185400	-0.36781800
S	0.00000000	0.00000000	0.36781800

O 0.00000000 -1.24185400 -0.36781800

Diequatorial-Trans-Diol

Solvent: CH₃CN

C	-0.13280300	1.30065200	0.20072900
C	0.92163200	1.30993100	-0.90502400
C	2.17156100	0.45091800	-0.56346700
C	2.02358700	-0.38477700	0.72155900
C	0.66169000	-1.05356300	0.82978400
C	-0.55497100	-0.11035100	0.58100500
H	2.37456000	-0.22277800	-1.40049600
H	0.44492500	0.94298400	-1.81972500
H	1.20861400	2.34823500	-1.09791700
H	0.27611800	1.76252700	1.11169700
H	2.81533400	-1.14032400	0.76638500
H	2.14721500	0.24708200	1.60906100
H	0.55466200	-1.62181300	1.75761900
H	3.05306300	1.08962700	-0.46126700
C	-0.89505200	-1.06716400	-0.61183200
N	0.21934100	-1.80719100	-0.35593600
H	0.60521100	-2.62589700	-0.80782100
O	-1.49955300	-0.09613500	1.61791800
O	-1.33433800	1.97172100	-0.17852200
O	-1.78214100	-1.16986200	-1.42815200
H	-1.15854500	2.91986400	-0.17595300
H	-2.10214800	0.63116000	1.40350200

Diaxial-Trans-Diol

Solvent: CH₃CN

C	0.43397300	0.28352700	-0.53779100
C	0.05683400	-1.22417600	-0.41052700
C	-1.21747000	-1.49398500	0.37736800
C	-2.33924600	-0.58844600	-0.16147600
C	-1.96394600	0.91971000	-0.17690700
C	-0.50975400	1.21562700	0.21980000
H	-1.50865600	-2.54543800	0.29114200
H	0.03486200	-1.70729400	-1.39186100
H	-2.58141900	-0.90716200	-1.18135400
H	-3.24492700	-0.74540800	0.43051300
H	-2.61577900	1.49043100	0.49396400
H	-2.11979500	1.33162500	-1.17813400
H	-0.26545000	2.25232200	-0.05883200
H	-1.03497200	-1.27814600	1.43181400
C	1.76605200	-0.11605700	0.16819600
N	1.34223300	-1.40418200	0.28439100
H	1.79920600	-2.23371900	0.63984200

O	2.79750000	0.44832800	0.45447000
O	0.57341100	0.67374500	-1.88420500
H	0.97916500	1.55095500	-1.89072900
O	-0.27351500	1.02340500	1.61229500
H	-0.97568800	1.48007300	2.09043800

Reac-Ph₃P

Solvent: CH₃CN

C	2.16123400	-0.37376500	0.70916700
C	3.40470600	-0.04562600	1.51246200
C	4.67970400	-0.27840000	0.63862700
C	4.40662500	-0.77855300	-0.79887100
C	3.34981500	0.05076200	-1.52802200
C	2.12451500	0.35022600	-0.61778200
H	5.24157700	0.65743800	0.57755600
H	3.35064700	0.99761500	1.83897200
H	3.43034300	-0.66436200	2.41317400
H	2.16477000	-1.45357100	0.47969100
H	5.34110100	-0.76212500	-1.36963400
H	4.06643900	-1.81987000	-0.78893000
H	3.11272700	-0.33653400	-2.52065400
H	5.33884300	-1.00002800	1.12757400
C	2.57837100	1.83308400	-0.67967900
N	3.60191600	1.50665700	-1.51305000
H	4.39965100	2.04110500	-1.83286600
O	0.81193100	0.16291300	-1.09121400
O	0.93515200	-0.01645200	1.28660800
O	2.18165800	2.88019100	-0.21584600
P	-0.34912600	-0.10052500	0.09118200
C	-0.63077400	-1.86249700	0.43970200
C	-1.09170600	-2.29688400	1.68544700
C	-0.30958000	-2.80482900	-0.54215700
C	-1.25144700	-3.65650300	1.93652600
H	-1.32803000	-1.57416400	2.45768200
C	-0.44857200	-4.16579800	-0.28045100
H	0.04806000	-2.47364500	-1.51091800
C	-0.92674200	-4.59307400	0.95617100
H	-1.62229700	-3.98488000	2.90168900
H	-0.18805900	-4.89031300	-1.04459300
H	-1.04480900	-5.65258700	1.15664000
C	-1.61330700	0.11035000	-1.30467400
C	-2.66213000	-0.78311900	-1.53948600
C	-1.57326200	1.28863200	-2.06584600
C	-3.63287500	-0.51751500	-2.50741400
H	-2.73545000	-1.69885300	-0.96575200
C	-2.53674500	1.55787400	-3.03151900
H	-0.77657000	2.00574300	-1.89748500
C	-3.57329000	0.65154200	-3.25832100

H	-4.43416900	-1.23106100	-2.67163700
H	-2.48075900	2.47546500	-3.60870600
H	-4.32627700	0.85855000	-4.01147300
C	-1.27770500	1.06629100	1.16444300
C	-0.68057700	2.25474000	1.59751000
C	-2.61505400	0.81263600	1.49086500
C	-1.41489100	3.17431900	2.34300000
H	0.34955400	2.46323700	1.33490600
C	-3.33177000	1.71548100	2.27057900
H	-3.09806700	-0.09298500	1.14317100
C	-2.73586900	2.90296400	2.69199100
H	-0.94802300	4.10115500	2.66018100
H	-4.35953900	1.49474800	2.53886800
H	-3.30015300	3.61396600	3.28616100

TS2-Ph₃P

Solvent: CH₃CN

C	2.03196400	-0.87463900	0.47513500
C	2.53966600	-1.31263700	1.82055800
C	3.92992000	-2.01678700	1.74936500
C	4.56623400	-1.88591100	0.35817600
C	4.24684300	-0.54520300	-0.25199000
C	2.52274700	0.29619700	-0.25483800
H	4.58052800	-1.55615300	2.49686700
H	2.59141400	-0.44367700	2.47997200
H	1.79669100	-1.99060700	2.24251100
H	1.69658500	-1.66856900	-0.18693600
H	5.65359300	-2.03794800	0.43328200
H	4.19347200	-2.66592400	-0.31552500
H	4.54104100	-0.43592900	-1.29811100
H	3.83736300	-3.07150100	2.02076400
C	3.36128000	1.28861400	0.59390500
N	4.53367800	0.60967300	0.56924000
H	5.40398100	0.84876300	1.03028200
O	1.98656400	0.68077100	-1.33904100
O	0.30866300	-0.38488300	1.04137600
O	3.08150900	2.36815200	1.08455000
P	-0.90704000	-0.06845100	0.16739700
C	-2.35122200	-0.16478600	1.24734000
C	-2.28735200	-0.99496300	2.37204700
C	-3.52371600	0.54777800	0.97341500
C	-3.39008800	-1.11338400	3.21232000
H	-1.37341600	-1.53604800	2.58583700
C	-4.62338200	0.42418100	1.81647000
H	-3.57766500	1.19875700	0.10911700
C	-4.55795100	-0.40561800	2.93460700
H	-3.33600600	-1.75568600	4.08442000
H	-5.52996400	0.97931400	1.60222400

H	-5.41595800	-0.49728700	3.59179800
C	-0.87216700	1.58335500	-0.53234700
C	-0.07028700	2.55878500	0.06809100
C	-1.66932100	1.90716700	-1.63466600
C	-0.08012500	3.85671200	-0.42980800
H	0.58834500	2.29718400	0.88625900
C	-1.67703600	3.21061800	-2.12441200
H	-2.27488700	1.14511700	-2.11226500
C	-0.88526700	4.18512000	-1.52042100
H	0.55143000	4.61106500	0.02691100
H	-2.29472900	3.46086300	-2.97991600
H	-0.88793500	5.19910600	-1.90620900
C	-1.16665500	-1.23976800	-1.17837400
C	-0.24472600	-1.27667300	-2.23677200
C	-2.25673000	-2.11731000	-1.16776900
C	-0.42227500	-2.19252000	-3.26807100
H	0.60819500	-0.59982400	-2.21437700
C	-2.42565900	-3.02693400	-2.20816200
H	-2.97272800	-2.09081200	-0.35564500
C	-1.51060800	-3.06480000	-3.25739600
H	0.29028700	-2.22507800	-4.08557200
H	-3.27268500	-3.70411300	-2.19744100
H	-1.64550600	-3.77383700	-4.06739600

Prod2

Solvent: CH₃CN

C	0.42534900	0.63777400	0.65783800
C	1.55664800	1.23855100	-0.21434100
C	2.59447400	0.10713900	-0.30419400
C	1.73240800	-1.15906700	-0.40276700
C	0.60233300	-0.90578300	0.61468100
C	-0.97342400	0.88044200	0.14668600
H	3.27816200	0.22462300	-1.14881300
H	1.17208300	1.47372200	-1.21233900
H	1.95413900	2.16120400	0.21175800
H	0.48119100	1.00882500	1.68469900
H	1.29259600	-1.23295700	-1.40372100
H	2.28117400	-2.08230400	-0.20289800
H	0.86988800	-1.30672900	1.59526100
H	3.19750100	0.07958300	0.61095300
C	-1.64950300	-0.49056800	-0.07583000
N	-0.70792900	-1.41110200	0.22106000
H	-0.89332800	-2.40135000	0.13514900
O	-1.50856000	1.93463600	-0.08784100
O	-2.79239200	-0.67186500	-0.45589800

Reac-SO-I

Solvent: Ph₂O

C	0.09385000	-1.16242600	0.07292000
C	1.13875200	-1.43059200	1.13484100
C	2.54647700	-1.03652700	0.57568800
C	2.55091400	-0.51540700	-0.87957900
C	1.51996700	0.59093700	-1.11933200
C	0.15171300	0.24823100	-0.46352600
H	2.97540200	-0.26653000	1.22155600
H	0.90018900	-0.84409800	2.02579300
H	1.10977100	-2.48437000	1.41942700
H	0.24540300	-1.84459400	-0.77445300
H	3.54998600	-0.13979100	-1.12410400
H	2.34900000	-1.32914400	-1.58530600
H	1.46530200	0.90389800	-2.16366200
H	3.21930700	-1.89513000	0.63225600
C	0.44578800	1.43358000	0.51279200
N	1.59827000	1.71136200	-0.16738700
H	2.36725500	2.32692700	0.06133700
O	-1.04327700	0.37697300	-1.22187400
O	-1.26506900	-1.30621900	0.52091400
O	-0.09394900	1.92588200	1.46785300
S	-2.30170000	-0.43443500	-0.44687000
O	-3.00108900	0.47555000	0.43385200

TS2-SO-I

Solvent: Ph₂O

C	-0.31679500	-0.95178700	0.03026700
C	-1.19705000	-1.29957100	-1.11670000
C	-2.70005300	-1.18833500	-0.67568600
C	-2.80198800	-0.67147500	0.76663900
C	-1.79327900	0.42415900	1.01957900
C	0.02399500	0.37625000	0.45525300
H	-3.20161500	-0.49705100	-1.35584300
H	-0.99429700	-0.64302000	-1.96411100
H	-0.96222800	-2.32121100	-1.42003600
H	-0.22563600	-1.69052700	0.81833000
H	-3.80866300	-0.27681900	0.96108500
H	-2.64091900	-1.47482500	1.49223700
H	-1.66495200	0.71010100	2.06377700
H	-3.20388100	-2.15216700	-0.76873900
C	-0.49618200	1.57873800	-0.35588400
N	-1.79071500	1.50271900	0.07239800
H	-2.59189000	2.02493500	-0.25739000
O	1.03636200	0.50409600	1.25976400
O	1.59853400	-1.44798200	-0.42964100
O	0.05879400	2.35537900	-1.08898800
S	2.54398800	-0.55311000	0.32921300

O 3.15798400 0.46893700 -0.50167500

Prod2

Solvent: Ph₂O

C	0.42689700	0.63426100	0.66202600
C	1.56416600	1.23608400	-0.20077900
C	2.59447100	0.09892100	-0.30683100
C	1.72439500	-1.16100400	-0.41220000
C	0.59948900	-0.91082400	0.61273000
C	-0.97234700	0.88469800	0.14332300
H	3.27539700	0.21932900	-1.15305500
H	1.18226400	1.49236600	-1.19450800
H	1.96912800	2.15011400	0.23657800
H	0.47695400	1.00077800	1.69087600
H	1.27881200	-1.22425300	-1.41151700
H	2.26959700	-2.08959100	-0.22640400
H	0.87487600	-1.31505300	1.59077700
H	3.20393400	0.05871300	0.60376700
C	-1.65633400	-0.48449600	-0.07509500
N	-0.71359800	-1.41042700	0.22611700
H	-0.90756000	-2.39785200	0.13944900
O	-1.49379000	1.94160900	-0.09720500
O	-2.79529000	-0.66753400	-0.45252300

Table S2. Absolute Energies (in Hartree) for All Structures Listed in Table S1.

Structure	Solvent	E_{DHDFT} dsdpbep86/def2tzvpp Gas	G298 B3LYP/6- 31G(2df,p) Solvent	E_e B3LYP/6- 31G(2df,p) Solvent	E_{sol} M05-2X/6- 31G(d) Solvent	E_{gas} M05-2X/6- 31G(d) Gas	$E_{\text{DHDFT}} + (G_{298} - E_e) +$ $(E_{\text{sol}} - E_{\text{gas}})$
Conf A-H	CH ₃ CN	-553.0429174	-553.7222860	-553.8695106	-553.7174657	-553.6941777	-552.9189808
Conf B-H	CH ₃ CN	-553.0426063	-553.7209890	-553.8683254	-553.7170138	-553.6948901	-552.9173936
Conf A-Ph ₃ P	CH ₃ CN	-1586.8079811	-1588.7673590	-1589.1479491	-1588.7753755	-1588.7358877	-1586.4668788
Conf B-Ph ₃ P	CH ₃ CN	-1586.8070656	-1588.7643590	-1589.1450185	-1588.7726735	-1588.7364288	-1586.4626508
TS1-Alkyl-Ph ₃ P	CH ₃ CN	-1586.7370345	-1588.7139720	-1589.0870645	-1588.7030903	-1588.6612163	-1586.4058160
TS1-Acyl-Ph ₃ P	CH ₃ CN	-1586.7382216	-1588.7195280	-1589.0911676	-1588.7035157	-1588.6605527	-1586.4095450
Diequatorial-Trans-Diol	CH ₃ CN	-553.0430589	-553.7211650	-553.8684615	-553.7179574	-553.6945702	-552.9191496
Di axial-Trans-Diol	CH ₃ CN	-553.0388622	-553.7175920	-553.8641273	-553.7128246	-553.6898030	-552.9153485
Reac-Ph ₃ P	CH ₃ CN	-1586.8011422	-1588.7594100	-1589.1396273	-1588.7691503	-1588.7311771	-1586.4588981
TS2-Ph ₃ P	CH ₃ CN	-1586.7381425	-1588.7197500	-1589.0906441	-1588.7061493	-1588.6629097	-1586.4104880
Prod1-Alkyl	CH ₃ CN	-476.6946080	-477.3117860	-477.4344245	-477.3092544	-477.2873670	-476.5938569
Prod1-Acyl	CH ₃ CN	-476.7133240	-477.3280180	-477.4515271	-477.3272472	-477.3072416	-476.6098205
Prod2	CH ₃ CN	-476.7148265	-477.3343220	-477.4563386	-477.3312390	-477.3083016	-476.6157473
Ph ₃ PO	CH ₃ CN	-1110.1228906	-1111.4971080	-1111.7306713	-1111.4853438	-1111.4557019	-1109.9189692
Conf A-SO-I	Ph ₂ O	-1024.8746112	-1025.9403290	-1026.0698653	-1025.8595570	-1025.8378207	-1024.7668112
Conf B-SO-I	Ph ₂ O	-1024.8746009	-1025.9396750	-1026.0691281	-1025.8591573	-1025.8378959	-1024.7664092
Conf A-SO-II	Ph ₂ O	-1024.8778530	-1025.9420660	-1026.0715070	-1025.8614658	-1025.8417367	-1024.7681411
Conf B-SO-II	Ph ₂ O	-1024.8776605	-1025.9418650	-1026.0714518	-1025.8610261	-1025.8420254	-1024.7670744
TS1-Alkyl-SO-I	Ph ₂ O	-1024.7885436	-1025.8701930	-1025.9938683	-1025.7685361	-1025.7409639	-1024.6924405

TS1-Acyl-SO-I	Ph ₂ O	-1024.8117990	-1025.8918570	-1026.0166200	-1025.7884959	-1025.7629617	-1024.7125702
TS1-Alkyl-SO-II	Ph ₂ O	-1024.7953529	-1025.8741850	-1025.9991376	-1025.7749464	-1025.7491992	-1024.6961475
TS1-Acyl-SO-II	Ph ₂ O	-1024.8120460	-1025.8914880	-1026.0159633	-1025.7876782	-1025.7638990	-1024.7113499
Reac-SO-I	Ph ₂ O	-1024.8628749	-1025.9284010	-1026.0587634	-1025.8491016	-1025.8266704	-1024.7549437
TS2-SO-I	Ph ₂ O	-1024.7927876	-1025.8745190	-1025.9989645	-1025.7736589	-1025.7451537	-1024.6968473
Prod1-Alkyl	Ph ₂ O	-476.6948279	-477.3095090	-477.4322892	-477.3066622	-477.2876079	-476.5911020
Prod1-Acyl	Ph ₂ O	-476.7133910	-477.3267490	-477.4503000	-477.3255175	-477.3073577	-476.6079998
Prod2	Ph ₂ O	-476.7148265	-477.3318250	-477.4538999	-477.3283084	-477.3085136	-476.6125464
SO₂	Ph ₂ O	-548.1786963	-548.6516840	-548.6344621	-548.5398147	-548.5329912	-548.2027417