

Electronic Supporting Information (ESI)

for

Kinetics and Mechanism of the Barton-Kellogg Olefination: A Computational DFT Study
Using CTST Theory and Topological Approaches

Ahmad Seif ^{a,*} Temer S. Ahmadi ^b, Axel Klein ^{a,*}

^a University of Cologne, Faculty of Mathematics and Natural Sciences, Department of Chemistry, Institute for Inorganic Chemistry, Greinstrasse 6, 50939 Koeln, Germany.

Email: ahmaseif@yahoo.com; ORCID: 0000-0002-4172-6073 (A.S.).

Email: axel.klein@uni-koeln.de (A.K.); ORCID: 0000-0003-0093-9619; Tel.: +49-221-470-4006 (A.K.).

^b Department of Chemistry, Villanova University, Villanova, PA, 19085, USA; Email: temer.ahmadi@villanova.edu; ORCID: 0000-0002-3984-4695 (T.A.).

contents:

Table S1 Cartesian coordinates for all species at MN15-L/def2-TZVP level of theory in the solvent phase.

Table S2 Cartesian coordinates for all species at M0-62x/def2-TZVP level of theory in the solvent phase.

Table S1 Cartesian coordinates for all species at MN15-L/def2-TZVP level of theory in the solvent phase.

R1

S	1.81613900	-1.72334700	0.00000000
C	0.35494600	-1.00692200	0.00000000
C	-0.34186200	-0.57865900	1.27025500
C	-0.34186200	0.96925400	1.35051500
S	-1.27118100	1.71836400	0.00000000
C	-0.34186200	0.96925400	-1.35051500
C	-0.34186200	-0.57865900	-1.27025500
H	-1.39326100	-0.92358500	1.25748000
H	0.17977200	-1.00089400	2.14452500
H	-0.81079300	1.30484000	2.28987400
H	0.70212500	1.33670300	1.33789800

H	-0.81079300	1.30484000	-2.28987400
H	0.70212500	1.33670300	-1.33789800
H	0.17977200	-1.00089400	-2.14452500
H	-1.39326100	-0.92358500	-1.25748000

R2

C	0.33377000	-0.97843100	0.00000000
C	-0.22519000	-0.48483000	1.31319000
C	-0.22519000	1.05388400	1.35855100
S	-1.18661000	1.76204100	0.00000000
C	-0.22519000	1.05388400	-1.35855100
C	-0.22519000	-0.48483000	-1.31319000
H	-1.27141700	-0.83406700	1.43884400
H	0.36993500	-0.89160500	2.15013500
H	-0.68487600	1.42162200	2.29140600
H	0.81121600	1.43883800	1.30625900
H	-0.68487600	1.42162200	-2.29140600
H	0.81121600	1.43883800	-1.30625900
H	0.36993500	-0.89160500	-2.15013500
H	-1.27141700	-0.83406700	-1.43884400
N	1.28717900	-1.85537300	0.00000000
N	2.13253200	-2.63324200	0.00000000

TS1

C	1.61297300	0.00046800	0.81125900
S	0.28219100	0.00095400	1.82097500
N	0.50791200	-0.00030800	-1.20070900
N	-0.60433200	0.00001300	-0.86835800
C	-1.50143500	0.00026500	0.12669900
C	2.36274900	1.30742900	0.57624100
C	2.36253900	-1.30682300	0.57738800
C	-2.26427300	1.29766100	0.31136700
C	-2.26381900	-1.29726400	0.31235200
H	-2.57238200	1.33674800	1.37135400

H	-1.59048400	2.15156600	0.11577300
H	-2.57177800	-1.33571600	1.37240900
H	-1.58970500	-2.15105700	0.11734900
H	2.98614300	-1.49736000	1.47498800
H	1.62306400	-2.12853800	0.52257200
H	2.98614600	1.49889100	1.47378300
H	1.62335300	2.12915000	0.52039100
C	3.28448500	1.34049700	-0.65141700
C	3.28408700	-1.34119900	-0.65035600
C	-3.50654000	-1.35998400	-0.59487600
C	-3.50691300	1.35925800	-0.59602000
H	2.70710400	-1.27804700	-1.59007300
H	3.85079900	-2.28718100	-0.66831600
H	2.70755100	1.27683400	-1.59113100
H	3.85152500	2.28627000	-0.67009200
S	4.49533800	-0.00052300	-0.62433800
H	-3.20008300	-1.33395300	-1.65856100
H	-4.06575000	-2.29528900	-0.42458400
H	-4.06637000	2.29458200	-0.42663700
H	-3.20035000	1.33232100	-1.65965300
S	-4.65171400	-0.00036800	-0.26738200

P1

S	-0.35088900	0.29117100	1.08475300
C	1.24308900	0.13511200	0.17667200
N	0.91802400	0.20082900	-1.27224900
N	-0.27878000	0.19530800	-1.59394500
C	-1.28107700	0.12355600	-0.49251300
C	-1.97826900	-1.25367400	-0.63211500
C	-3.10537500	-1.44089100	0.39459600
S	-4.44303800	-0.22847000	0.17599900
C	-3.41572100	1.26433800	0.33055700
C	-2.27536300	1.28870500	-0.69856700
C	1.90834500	-1.24347100	0.43323400

C	3.24144000	-1.42798500	-0.31429800
S	4.48835800	-0.21838700	0.21927900
C	3.52731600	1.25881500	-0.22613800
C	2.17936300	1.32086600	0.51432500
H	-2.38747000	-1.32970000	-1.66130200
H	-1.21083900	-2.04649400	-0.49981000
H	-3.56447500	-2.44099100	0.28096100
H	-2.69914000	-1.37264500	1.42641700
H	-4.08968400	2.12815000	0.17759100
H	-3.00958200	1.33888700	1.36294700
H	-1.71360700	2.24260700	-0.62279200
H	-2.69265400	1.20310300	-1.72339700
H	2.07403200	-1.34090300	1.52527900
H	1.18635400	-2.03209300	0.12832700
H	3.65692600	-2.43157700	-0.10321300
H	3.08995400	-1.34496400	-1.40959600
H	4.14559300	2.13614800	0.04279500
H	3.36796600	1.27777800	-1.32321000
H	1.64495000	2.25948300	0.25740400
H	2.35357800	1.31902000	1.60993200

TS2

S	0.01015300	0.47661100	-0.85780800
C	-1.38087200	0.60117900	0.14927500
N	-0.57643500	2.02800600	1.41390400
N	0.57096600	2.06984000	1.39465900
C	1.40774300	0.65026200	0.13858300
C	1.83001000	-0.31343200	1.22940900
C	2.55190100	-1.54419400	0.64775500
S	4.09396500	-1.09338400	-0.17961900
C	3.40297300	0.09722800	-1.34875600
C	2.58387500	1.20088300	-0.64882400
C	-2.56323800	1.20590500	-0.58805100
C	-3.42728000	0.15757400	-1.31539000

S	-4.12443300	-1.05838500	-0.17659900
C	-2.56956500	-1.59149400	0.57135200
C	-1.78761900	-0.41799300	1.19484700
H	2.52840700	0.23221500	1.89301400
H	0.97924000	-0.63629700	1.84640700
H	2.82285000	-2.25276100	1.44904200
H	1.88595800	-2.07214100	-0.06303500
H	4.25732400	0.53189300	-1.89551800
H	2.76454500	-0.43156600	-2.08341600
H	2.23545200	1.92986600	-1.40236200
H	3.23615500	1.73156000	0.07154300
H	-3.18567300	1.71857700	0.17147800
H	-2.21502600	1.96267100	-1.31368600
H	-4.27945900	0.63872400	-1.82516200
H	-2.82135700	-0.36072800	-2.08442700
H	-2.83041900	-2.33637900	1.34253400
H	-1.94444600	-2.09626600	-0.19159500
H	-0.92057300	-0.81637300	1.74077200
H	-2.43723100	0.09910300	1.92768800

P2

S	0.00001600	-0.00008400	-1.50391000
C	-0.75668800	-0.00001600	0.17963400
C	0.75666200	-0.00003300	0.17956400
C	1.53428300	-1.27317000	0.54499400
C	2.89544900	-1.34672600	-0.16809200
S	4.01407900	0.00009700	0.31166100
C	2.89532400	1.34674100	-0.16825200
C	1.53423600	1.27310300	0.54500700
C	-1.53423300	1.27315300	0.54515500
C	-2.89534200	1.34683800	-0.16811500
S	-4.01410600	0.00006400	0.31149000
C	-2.89539800	-1.34680400	-0.16801800
C	-1.53425600	-1.27319200	0.54513700

H	1.69177800	-1.28589700	1.64605600
H	0.96190300	-2.17523400	0.26477300
H	3.40839100	-2.29502400	0.07961000
H	2.73526500	-1.32480500	-1.26825100
H	3.40823600	2.29510300	0.07928000
H	2.73502700	1.32467000	-1.26839600
H	0.96165300	2.17513600	0.26510100
H	1.69194100	1.28569200	1.64603600
H	-1.69198900	1.28574800	1.64617900
H	-0.96169300	2.17525700	0.26544300
H	-3.40840800	2.29509100	0.07955300
H	-2.73492100	1.32496700	-1.26823200
H	-3.40843800	-2.29504300	0.07974900
H	-2.73505500	-1.32500300	-1.26814200
H	-0.96191500	-2.17532200	0.26508500
H	-1.69182200	-1.28593300	1.64619100

N2

N	0.00000000	0.00000000	0.54995200
N	0.00000000	0.00000000	-0.54995200

TS3

S	0.00000000	1.94798300	-0.00001200
C	-1.23568300	0.75501200	0.03877100
C	1.23568200	0.75501100	-0.03878000
C	2.04282700	0.50044300	-1.28014200
C	3.53122000	0.23703600	-0.96513500
S	3.75140100	-1.19269000	0.11343300
C	2.73220200	-0.57865500	1.47127700
C	1.27833700	-0.30448100	1.02943300
C	-2.04282900	0.50046000	1.28013500
C	-3.53122200	0.23705300	0.96512800
S	-3.75140100	-1.19269100	-0.11341600
C	-2.73219900	-0.57868100	-1.47126900

C	-1.27833600	-0.30449500	-1.02942800
H	1.64825000	-0.40614200	-1.79860300
H	1.94882600	1.35042600	-1.98100900
H	4.08949900	0.03260500	-1.89404000
H	3.98060200	1.12648000	-0.48442800
H	2.75068400	-1.34724000	2.26245500
H	3.18932500	0.34353400	1.87806600
H	0.68974600	0.01940800	1.90674800
H	0.85488400	-1.27598300	0.67248500
H	-1.64825500	-0.40612100	1.79860500
H	-1.94882600	1.35045000	1.98099300
H	-4.08950600	0.03264100	1.89403400
H	-3.98059800	1.12648900	0.48440200
H	-2.75067700	-1.34728400	-2.26243000
H	-3.18932300	0.34349800	-1.87808000
H	-0.68974700	0.01938500	-1.90674800
H	-0.85487700	-1.27599100	-0.67246800

P3

S	-0.00092742	1.46617977	0.06941052
C	-1.44830021	0.44432115	-0.10189235
C	1.44666952	0.43429758	0.15140126
C	2.14610771	0.03447979	-1.18465295
C	3.67700966	-0.04293700	-1.04384214
S	4.09323102	-1.08666435	0.31366739
C	3.46031363	-0.13231819	1.65294035
C	1.92646893	-0.05655474	1.55215675
C	-2.17314520	-0.03491522	1.19413447
C	-3.70123911	-0.10099440	1.02096093
S	-4.09191540	-1.05898611	-0.40522450
C	-3.43372429	-0.02644446	-1.67235475
C	-1.90144429	0.04085856	-1.53887247
H	1.77021750	-0.92362714	-1.47488320
H	1.91859884	0.75775382	-1.93879668

H	4.09548439	-0.42464691	-1.95074441
H	4.07011167	0.93388317	-0.85239293
H	3.73102513	-0.57527516	2.58826650
H	3.87299931	0.85268082	1.59182557
H	1.57815258	0.61670790	2.30655072
H	1.51396950	-1.03034142	1.71473757
H	-1.80442564	-1.01028050	1.43272692
H	-1.95809148	0.64124092	1.99442806
H	-4.13704096	-0.53721011	1.89532936
H	-4.08968422	0.88545792	0.88225889
H	-3.68714262	-0.41113005	-2.63784966
H	-3.84777663	0.95348508	-1.55876563
H	-1.53703215	0.75795143	-2.24396788
H	-1.48734477	-0.92163815	-1.75309270

PH3

P	0.87089312	0.35495753	-0.00675494
H	1.32087767	-0.91784014	-0.00675494
H	1.32090090	0.99134777	1.09551565
H	1.32090090	0.99134777	-1.10902553

TS4

S	0.98618100	1.58206900	1.19360700
C	0.85111800	0.07545300	0.16481300
C	-0.62539400	-0.21602700	0.04387200
C	-1.39426400	-0.53952200	1.29294500
C	-2.92282200	-0.45403700	1.21987800
S	-3.59120100	-1.52641800	-0.06768200
C	-2.71245000	-0.75240400	-1.43534000
C	-1.19092800	-0.70831700	-1.25719900
C	1.52508500	0.26487700	-1.21718500
C	3.03190600	0.51362100	-1.13562100
S	3.89662600	-0.93516900	-0.48268100
C	2.99731400	-1.01163800	1.08110900

C	1.48668300	-1.16449000	0.89446000
H	-1.14801400	-1.61403700	1.45994300
H	-0.98450200	0.03322300	2.13888800
H	-3.35144500	-0.79239800	2.17675000
H	-3.26250000	0.58498100	1.05538800
H	-2.95365100	-1.32851600	-2.34336800
H	-3.09927000	0.27244300	-1.58476600
H	-0.73878900	-0.17755500	-2.10824500
H	-0.78545000	-1.74970700	-1.29685600
H	1.37050400	-0.63760900	-1.84369600
H	1.03647300	1.12737200	-1.71572600
H	3.44117000	0.69812000	-2.14286800
H	3.24889300	1.39161800	-0.50311100
H	3.38922000	-1.88029500	1.63667300
H	3.20768300	-0.10203100	1.67175100
H	1.02493900	-1.26034000	1.89207100
H	1.27248000	-2.08361200	0.30609000
P	-1.56489300	2.41569700	-0.40110800
H	-2.70013100	3.02282700	-1.05150000
H	-0.60641400	3.36448600	-0.82553000
H	-1.83099100	2.92277200	0.89244300

P4

S	-1.05769500	1.87744700	-0.71250200
C	-0.81334700	0.16100500	-0.09618300
C	0.76737800	0.16315500	0.10143200
C	1.50397200	-0.06663300	-1.25038200
C	3.03697800	0.02897200	-1.16932900
S	3.72375100	-1.32525100	-0.17134800
C	2.82529800	-0.92302200	1.35295900
C	1.29527500	-0.82275000	1.17744800
C	-1.53052600	-0.03782100	1.26746200
C	-3.05861400	0.08750500	1.18015800
S	-3.77051900	-1.24759700	0.17321000

C	-2.82391300	-0.87213500	-1.33046300
C	-1.30102500	-0.89983500	-1.11089300
H	1.25925600	-1.09482500	-1.59043500
H	1.10339600	0.64595100	-2.00259700
H	3.47031800	-0.07408300	-2.18205800
H	3.37986900	1.00773900	-0.76790200
H	3.05122800	-1.73451500	2.07131900
H	3.23692600	0.01174500	1.78164100
H	0.86274900	-0.57075300	2.16852000
H	0.90048700	-1.82620100	0.89673300
H	-1.29160300	-1.04816900	1.66573600
H	-1.14914400	0.71245500	1.99759400
H	-3.50818500	0.00327800	2.18766300
H	-3.34182500	1.07210500	0.75507100
H	-3.11133600	-1.62875700	-2.08523400
H	-3.12450900	0.12436100	-1.71795400
H	-0.82259900	-0.71373000	-2.09237400
H	-0.99601000	-1.91204100	-0.75567000
P	0.95596300	1.98765600	0.51718400
H	2.22254300	1.86804100	1.24134300
H	0.30118900	2.55575200	1.63596500
H	1.48035200	3.00259800	-0.32811200

TS5

S	-1.15100600	2.17096000	-0.45775500
C	-0.68293100	-0.25281800	-0.01204600
C	0.75698200	-0.09333100	0.03591200
C	1.47150700	-0.34196200	-1.30577400
C	3.00351300	-0.22771600	-1.31701000
S	3.79642800	-1.26179400	-0.06824200
C	2.95824100	-0.46441800	1.31798900
C	1.44561500	-0.69664900	1.27482300
C	-1.40680300	-0.37022400	1.31236300
C	-2.93010800	-0.22605400	1.29300600

S	-3.71342600	-1.35173500	0.12191600
C	-2.88042700	-0.67599000	-1.32874000
C	-1.36054800	-0.81096600	-1.24442000
H	1.21458900	-1.35074500	-1.69042500
H	1.07960200	0.38592200	-2.04998200
H	3.38545000	-0.54546500	-2.30156000
H	3.35046100	0.80990800	-1.15997000
H	3.38167400	-0.87885500	2.24775500
H	3.20045800	0.61812600	1.29731700
H	1.01291600	-0.27122300	2.19972600
H	1.26616100	-1.79212200	1.31970900
H	-1.14617900	-1.37150600	1.72027000
H	-0.98424800	0.36870100	2.02029800
H	-3.33750200	-0.45262900	2.29180600
H	-3.21492300	0.81117200	1.03819500
H	-3.25532900	-1.22346100	-2.20897700
H	-3.16743100	0.38657400	-1.44605500
H	-0.90878700	-0.38595100	-2.15398500
H	-1.10355300	-1.89562600	-1.24051200
P	0.69676700	2.09354000	0.31111600
H	1.89523400	2.08975700	-0.45079100
H	0.93749900	1.80544800	1.68619600
H	0.78022500	3.53075600	0.52293400

TS6

S	0.00007100	1.25773600	-0.16978300
C	-0.69417600	-0.90765900	0.04144300
C	0.71512500	-0.91389600	0.04316600
C	1.51626800	-1.23163600	-1.21117000
C	2.86740700	-0.51315300	-1.32806000
S	3.97883600	-0.88590700	0.04282600
C	2.86526600	-0.26734900	1.31970200
C	1.51526100	-0.99749600	1.33475200
C	-1.48847600	-0.98157600	1.33829100

C	-2.85842500	-0.29130800	1.31480000
S	-3.95512100	-0.95415200	0.04616600
C	-2.85876900	-0.54333900	-1.32558200
C	-1.48914500	-1.22538900	-1.21761000
H	1.70496000	-2.32654900	-1.21458600
H	0.94197200	-0.99670800	-2.11856900
H	3.37637900	-0.82608600	-2.25484200
H	2.70755700	0.58016500	-1.37527300
H	3.37302400	-0.40271600	2.28913600
H	2.70381500	0.81580600	1.16339600
H	0.93999800	-0.60479100	2.18510000
H	1.70642100	-2.07334300	1.53577000
H	-1.64323700	-2.05546900	1.57648700
H	-0.91990100	-0.53919900	2.16901100
H	-3.36002600	-0.42783300	2.28720800
H	-2.72822700	0.79426700	1.14422800
H	-3.36054200	-0.86225900	-2.25415200
H	-2.72911800	0.55460300	-1.36423400
H	-0.92016400	-0.95117600	-2.11768000
H	-1.64488200	-2.32496500	-1.24554200
P	-0.05487900	3.67517500	-0.08842200
H	-1.15229200	4.13519500	0.68496000
H	0.97898700	4.20893800	0.72464300
H	-0.07412500	4.72846200	-1.05448100

PH3S

P	0.87089312	0.35495753	-0.00675494
H	1.32087730	-0.91784027	-0.00675494
H	1.32090103	0.99134804	1.09551544
H	1.32090103	0.99134804	-1.10902532
S	-1.18910688	0.35498313	-0.00675494

PMe₃

P	-0.00002400	-0.00001200	-0.60958100
---	-------------	-------------	-------------

C	1.25356700	-1.01293100	0.27805000
H	1.15416100	-2.07631300	0.00161900
H	2.27236100	-0.69212700	0.00198800
H	1.13997700	-0.92141900	1.37587900
C	-1.50414200	-0.57895800	0.27807500
H	-2.37523800	0.03899200	0.00167000
H	-1.73598100	-1.62158800	0.00195400
H	-1.36809700	-0.52632700	1.37590400
C	0.25060100	1.59193800	0.27808000
H	1.22176700	2.03679500	0.00234300
H	-0.53594200	2.31429000	0.00125800
H	0.22720000	1.44759100	1.37587300

PSMe₃

P	0.16880800	0.00012100	0.00008300
C	0.91225600	1.50910100	0.67420400
H	0.57927300	2.37533900	0.08055200
H	0.57479300	1.64890900	1.71355400
H	2.01413300	1.45127800	0.65097300
C	0.91368600	-0.17118800	-1.64313200
H	0.57763100	-1.11634700	-2.09840600
H	0.58030600	0.66126000	-2.28304800
H	2.01551000	-0.16649400	-1.58002000
C	0.91118100	-1.33851700	0.97023700
H	0.57505800	-1.25973000	2.01646000
H	0.57572900	-2.30813400	0.56896000
H	2.01305600	-1.28841300	0.93474800
S	-1.77877100	0.00025900	-0.00080500

[TS6]_{PM₃}

S	-0.10079000	0.58620800	0.16005800
C	1.66208500	-0.82599000	-0.03333900
C	0.42627900	-1.52043700	-0.04047900
C	-0.09369100	-2.25482100	1.19035700

C	-1.61973600	-2.25100800	1.34445400
S	-2.47464800	-3.02269400	-0.04627100
C	-1.74076400	-2.00985600	-1.34773600
C	-0.20662700	-2.02321200	-1.33374700
C	2.39906500	-0.48327500	-1.31762600
C	3.16107600	0.84906500	-1.29396900
S	4.41773600	0.90997800	-0.00109100
C	3.26227300	0.63877700	1.35761100
C	2.49477800	-0.68481000	1.23059600
H	0.24775200	-3.30912400	1.11360200
H	0.32846800	-1.83753500	2.11543200
H	-1.90693300	-2.82503000	2.24161800
H	-1.97526800	-1.21284600	1.47314800
H	-2.10962100	-2.41756200	-2.30411400
H	-2.10086000	-0.96776600	-1.25899600
H	0.12969700	-1.43359400	-2.19846300
H	0.13541800	-3.06881700	-1.48708000
H	3.13088800	-1.29591300	-1.51631900
H	1.70722200	-0.44789900	-2.17156400
H	3.67665400	1.00369000	-2.25657000
H	2.44919200	1.68252600	-1.14448700
H	3.85044700	0.64265500	2.29049800
H	2.54717100	1.48176900	1.39619900
H	1.86550700	-0.78098700	2.12730000
H	3.23245100	-1.51598000	1.24943500
P	-1.94506000	2.27059200	0.11347100
C	-2.32439700	3.94094100	0.77362000
C	-2.36727400	2.47152800	-1.65043800
C	-3.37807000	1.31323600	0.72093100
H	-1.63246600	3.12875400	-2.14439800
H	-2.32624600	1.48705400	-2.14726900
H	-3.37783100	2.90160400	-1.78164700
H	-1.60288700	4.67604400	0.38103300
H	-3.34663500	4.25757300	0.49033900

H	-2.24465800	3.94028700	1.87303300
H	-4.32792100	1.84107200	0.51385700
H	-3.40789600	0.32472700	0.23033500
H	-3.29251500	1.14972900	1.80846500

P(OEt)₃

P	0.07862000	-0.03822300	0.88605900
O	1.42321600	-0.91241000	0.86827000
O	-0.90441400	-1.10343000	0.13775100
O	0.28972000	0.97541000	-0.38195400
C	1.99214000	-1.39820100	-0.37001900
H	2.20952900	-2.46983700	-0.21595100
H	1.25334700	-1.31243200	-1.18664800
C	-2.22332800	-0.62521400	-0.15897800
H	-2.17092800	0.08358300	-1.01030500
C	0.34716400	2.38412400	-0.10703500
H	0.79611200	2.56297000	0.89088700
H	1.02238900	2.82270000	-0.86292900
H	-2.62570000	-0.06630200	0.71435300
C	-3.10160400	-1.81957900	-0.48826800
H	-3.15972900	-2.50879500	0.36962200
H	-4.12137100	-1.48472700	-0.73885200
H	-2.69450100	-2.37213400	-1.35088700
C	3.25557300	-0.61321200	-0.68385800
H	3.97751300	-0.68794800	0.14588100
H	3.73354600	-1.00587200	-1.59718000
H	3.01641200	0.45166500	-0.84383800
C	-1.04824200	2.98568400	-0.18804500
H	-1.49612300	2.78848800	-1.17682200
H	-1.70048500	2.53757700	0.58349000
H	-1.01771200	4.07622800	-0.02701200

PS(OEt)₃

P	0.07043800	-0.08151700	0.53167100
---	------------	-------------	------------

O	1.33241600	-0.98355500	0.82598100
O	-0.98457700	-1.16966000	0.05045000
O	0.37038100	0.63422800	-0.86461800
C	1.94466800	-1.74409400	-0.24422600
H	2.15573700	-2.74016000	0.17948700
H	1.22888800	-1.86656100	-1.07718400
C	-2.30864800	-0.71475300	-0.30119500
H	-2.22204900	0.15059100	-0.99010700
C	0.73960800	2.02644800	-0.96387400
H	1.18928900	2.36279600	-0.01243900
H	1.50595800	2.07437300	-1.75776000
H	-2.81421300	-0.37127300	0.62000100
C	-3.03655100	-1.87743600	-0.95261600
H	-3.09086800	-2.73330200	-0.26172000
H	-4.06235300	-1.57697000	-1.21829800
H	-2.51764600	-2.20033900	-1.86894100
C	3.21702200	-1.04359600	-0.69632500
H	3.90606000	-0.91068700	0.15231800
H	3.72585500	-1.63882700	-1.47199700
H	2.98211600	-0.05139400	-1.11579600
C	-0.49276000	2.84600900	-1.31474200
H	-0.94826900	2.47280500	-2.24717100
H	-1.23326500	2.77211500	-0.50122100
H	-0.22616100	3.90610200	-1.45435800
S	-0.42259000	1.04812000	1.98709300

[TS6]P(OEt)3

S	0.28923700	0.04678300	-0.33343400
C	2.21542000	1.13630300	-0.12315500
C	2.49207100	-0.25132900	-0.09318400
C	2.71942000	-0.99841900	1.21332500
C	2.20353300	-2.44315300	1.22564700
S	2.95354000	-3.48114500	-0.04485600
C	2.50446800	-2.44101400	-1.45030300

C	3.00864000	-0.99846400	-1.31379800
C	2.39608500	1.95432400	-1.39520000
C	1.46131100	3.16289600	-1.53416900
S	1.64505400	4.34694700	-0.18485900
C	1.20075900	3.16649200	1.10494900
C	2.14577200	1.95981600	1.15609200
H	3.81394300	-1.01288000	1.40332200
H	2.24381500	-0.47993400	2.05902400
H	2.43330600	-2.91535400	2.19575300
H	1.10668900	-2.43680000	1.09584900
H	2.94908000	-2.91033300	-2.34385900
H	1.40667400	-2.43670500	-1.57614700
H	2.75242500	-0.47233400	-2.24408000
H	4.11714600	-1.02201100	-1.24030100
H	3.44482400	2.32017100	-1.41570900
H	2.24607700	1.32568500	-2.28496600
H	1.68037400	3.69853700	-2.47264900
H	0.40926000	2.82072100	-1.57044200
H	1.22278400	3.70245100	2.06884500
H	0.16608900	2.82073600	0.92406900
H	1.83242700	1.33695800	2.00716600
H	3.17071100	2.32837300	1.37458700
P	-2.20527800	-0.45677700	-0.30134100
O	-3.24001000	-0.03047400	-1.44010700
O	-2.60705000	-2.00476500	-0.11898400
O	-2.84747700	0.09684400	1.08254500
C	-4.67154700	-0.19704500	-1.25926500
H	-5.03774200	-0.72000600	-2.15938000
H	-4.86809100	-0.83885500	-0.38208400
C	-1.88874600	-2.77319500	0.87152500
H	-2.64236200	-3.18793100	1.56455300
C	-2.48185700	1.42103400	1.52197900
H	-1.97818700	1.96849400	0.69840400
H	-3.42390600	1.95159300	1.75080200

H	-1.22289400	-2.10709800	1.45865200
C	-1.09820400	-3.86528300	0.17138000
H	-0.38497300	-3.41744000	-0.54160100
H	-0.52762100	-4.46418900	0.90164500
H	-1.77202500	-4.53666400	-0.38548600
C	-5.31316500	1.17032300	-1.10222300
H	-5.09619600	1.80672700	-1.97539700
H	-6.40724200	1.07039400	-1.00600100
H	-4.92985600	1.67545200	-0.19943500
C	-1.59014000	1.32663400	2.75009400
H	-2.10608600	0.78194800	3.55831300
H	-0.65651200	0.79269900	2.49972100
H	-1.33468700	2.33553500	3.11752400

Table S2 Cartesian coordinates for all species at M0-62x/def2-TZVP level of theory in the solvent phase.

R1

S	-1.71116100	1.86559200	0.00000000
C	-0.34680800	0.99543400	0.00000000
C	0.31406400	0.53168900	1.26707800
C	0.31406400	-1.00005400	1.35622300
S	1.21557700	-1.77980000	0.00000000
C	0.31406400	-1.00005400	-1.35622300
C	0.31406400	0.53168900	-1.26707800
H	1.35066800	0.88161400	1.27331900
H	-0.20561400	0.94721300	2.12930800
H	0.80357800	-1.31881500	2.27601100
H	-0.71230000	-1.37246800	1.37404000
H	0.80357800	-1.31881500	-2.27601100
H	-0.71230000	-1.37246800	-1.37404000
H	-0.20561400	0.94721300	-2.12930800
H	1.35066800	0.88161400	-1.27331900

R2

C	-0.32050800	0.98669800	0.00000000
C	0.22965000	0.49180900	1.30922900
C	0.22965000	-1.03432000	1.36587800
S	1.15905000	-1.77576400	0.00000000
C	0.22965000	-1.03432000	-1.36587800
C	0.22965000	0.49180900	-1.30922900
H	1.25785300	0.84598700	1.43730100
H	-0.36508900	0.88941300	2.13371600
H	0.71024700	-1.38406300	2.27982700
H	-0.79234800	-1.41848700	1.34925500
H	0.71024700	-1.38406300	-2.27982700
H	-0.79234800	-1.41848700	-1.34925500
H	-0.36508900	0.88941300	-2.13371600
H	1.25785300	0.84598700	-1.43730100
N	-1.27597700	1.84383500	0.00000000
N	-2.11755100	2.60423100	0.00000000

TS1

C	1.59809200	-0.00000100	0.81659000
S	0.28427400	-0.00000200	1.83244600
N	0.53977700	-0.00000600	-1.15661600
N	-0.55366700	-0.00000400	-0.82658800
C	-1.49708800	0.00000000	0.09019200
C	2.36331600	1.29475300	0.60351400
C	2.36331300	-1.29475600	0.60350300
C	-2.24700100	1.29477400	0.27786700
C	-2.24700500	-1.29477000	0.27787600
H	-2.52754600	1.35208800	1.33111200
H	-1.58544300	2.13520800	0.06088900
H	-2.52755100	-1.35207500	1.33112200
H	-1.58545000	-2.13520800	0.06090500
H	2.99575600	-1.44516800	1.48514000
H	1.65098200	-2.12244200	0.57948500
H	2.99575700	1.44515500	1.48515400

H	1.65098700	2.12244100	0.57950000
C	3.25568100	1.34962200	-0.63194600
C	3.25567300	-1.34961600	-0.63196100
C	-3.50138400	-1.36411200	-0.59270500
C	-3.50138000	1.36411300	-0.59271600
H	2.66876000	-1.33013500	-1.55020500
H	3.83550800	-2.27274000	-0.62684700
H	2.66877100	1.33015700	-1.55019300
H	3.83552200	2.27274300	-0.62681800
S	4.45709500	0.00000000	-0.68282600
H	-3.23240200	-1.36648100	-1.65134900
H	-4.05523400	-2.27934800	-0.38366800
H	-4.05522700	2.27935100	-0.38368700
H	-3.23239900	1.36647000	-1.65136000
S	-4.64492300	0.00000300	-0.27012200

P1

S	-0.34691800	0.00001000	-1.08118300
C	1.24621300	0.00000400	-0.17364900
N	0.90065600	0.00001300	1.26001800
N	-0.27468000	0.00001000	1.57229100
C	-1.28482400	0.00000900	0.49187800
C	-2.12588300	1.26875400	0.66611600
C	-3.26076200	1.36262100	-0.34191600
S	-4.44179600	-0.00001300	-0.19016400
C	-3.26074200	-1.36263300	-0.34191100
C	-2.12586900	-1.26874500	0.66612100
C	2.04218900	1.27880700	-0.46810600
C	3.38294900	1.35165200	0.25282400
S	4.49244200	-0.00000800	-0.20508300
C	3.38294100	-1.35166000	0.25282600
C	2.04217900	-1.27880600	-0.46810200
H	-2.53248300	1.26715700	1.68034100
H	-1.47110900	2.13717500	0.56245800

H	-3.83306700	2.27539300	-0.17858500
H	-2.87187000	1.39533700	-1.36241000
H	-3.83303900	-2.27540900	-0.17857300
H	-2.87185200	-1.39534700	-1.36240500
H	-1.47108200	-2.13715600	0.56246800
H	-2.53246800	-1.26714700	1.68034700
H	2.20329900	1.33304700	-1.54657300
H	1.42718000	2.13579300	-0.18190400
H	3.89705800	2.27375800	-0.01788100
H	3.24505600	1.34891600	1.33464500
H	3.89704400	-2.27376800	-0.01788300
H	3.24505100	-1.34892600	1.33464800
H	1.42716300	-2.13578700	-0.18189800
H	2.20328800	-1.33305100	-1.54656800

TS2

S	0.01073100	0.55178100	-0.85008300
C	-1.36812500	0.56003900	0.16047400
N	-0.56727700	1.85432000	1.54453500
N	0.56465200	1.88823100	1.53239100
C	1.39076400	0.60188100	0.16158100
C	1.79398700	-0.46139300	1.15271200
C	2.57837100	-1.60058300	0.50009500
S	4.13565600	-1.03963900	-0.22730500
C	3.45970700	0.25891300	-1.28742900
C	2.57106900	1.24683800	-0.52893200
C	-2.55056000	1.24329300	-0.48927800
C	-3.47890800	0.30224500	-1.25751600
S	-4.16399400	-1.00606000	-0.21646400
C	-2.59917700	-1.63259600	0.43387800
C	-1.75821200	-0.54679900	1.10883900
H	2.42925600	0.02023300	1.90174600
H	0.93798500	-0.87183900	1.67966900
H	2.84991600	-2.34791700	1.24618300

H	1.97309900	-2.09216600	-0.26505400
H	4.31949600	0.77461000	-1.71602100
H	2.90077700	-0.19835300	-2.10695500
H	2.23003300	2.02156100	-1.21816200
H	3.16344700	1.73482400	0.25110200
H	-3.11672900	1.71937400	0.31759300
H	-2.20717000	2.03366900	-1.15933600
H	-4.33287000	0.85308700	-1.65260300
H	-2.95122600	-0.14776600	-2.10150700
H	-2.86240300	-2.40553400	1.15654100
H	-2.03397800	-2.10508700	-0.37288500
H	-0.88985000	-1.01780500	1.55959100
H	-2.34319600	-0.09711100	1.91669300

P2

S	0.00001600	-0.00008400	-1.50391000
C	-0.75668800	-0.00001600	0.17963400
C	0.75666200	-0.00003300	0.17956400
C	1.53428300	-1.27317000	0.54499400
C	2.89544900	-1.34672600	-0.16809200
S	4.01407900	0.00009700	0.31166100
C	2.89532400	1.34674100	-0.16825200
C	1.53423600	1.27310300	0.54500700
C	-1.53423300	1.27315300	0.54515500
C	-2.89534200	1.34683800	-0.16811500
S	-4.01410600	0.00006400	0.31149000
C	-2.89539800	-1.34680400	-0.16801800
C	-1.53425600	-1.27319200	0.54513700
H	1.69177800	-1.28589700	1.64605600
H	0.96190300	-2.17523400	0.26477300
H	3.40839100	-2.29502400	0.07961000
H	2.73526500	-1.32480500	-1.26825100
H	3.40823600	2.29510300	0.07928000
H	2.73502700	1.32467000	-1.26839600

H	0.96165300	2.17513600	0.26510100
H	1.69194100	1.28569200	1.64603600
H	-1.69198900	1.28574800	1.64617900
H	-0.96169300	2.17525700	0.26544300
H	-3.40840800	2.29509100	0.07955300
H	-2.73492100	1.32496700	-1.26823200
H	-3.40843800	-2.29504300	0.07974900
H	-2.73505500	-1.32500300	-1.26814200
H	-0.96191500	-2.17532200	0.26508500
H	-1.69182200	-1.28593300	1.64619100

N2

N	0.00000000	0.00000000	0.54285800
N	0.00000000	0.00000000	-0.54285800

TS3

S	0.00000000	1.88407100	0.00000000
C	-1.18851900	0.67115400	0.06647000
C	1.18851900	0.67115400	-0.06647000
C	2.04283300	0.49987900	-1.28663700
C	3.52551400	0.31026400	-0.95122000
S	3.82420300	-1.11056300	0.12242400
C	2.72216900	-0.60076400	1.46005400
C	1.28017600	-0.39148000	0.98769700
C	-2.04283300	0.49987900	1.28663700
C	-3.52551400	0.31026400	0.95122000
S	-3.82420300	-1.11056300	-0.12242400
C	-2.72216900	-0.60076400	-1.46005400
C	-1.28017600	-0.39148000	-0.98769700
H	1.70878600	-0.38395800	-1.84989100
H	1.93192300	1.36380100	-1.94574800
H	4.09755000	0.13477600	-1.86242000
H	3.92151600	1.20709400	-0.47070400
H	2.75975300	-1.39358500	2.20764100

H	3.11230000	0.31286300	1.91358900
H	0.66633200	-0.11889600	1.84794400
H	0.91420400	-1.35996900	0.61133300
H	-1.70878600	-0.38395800	1.84989100
H	-1.93192300	1.36380100	1.94574800
H	-4.09755000	0.13477600	1.86242000
H	-3.92151600	1.20709400	0.47070400
H	-2.75975300	-1.39358500	-2.20764100
H	-3.11230000	0.31286300	-1.91358900
H	-0.66633200	-0.11889600	-1.84794400
H	-0.91420400	-1.35996900	-0.61133200

P3

S	-0.00002600	0.00001500	1.56251900
C	-0.74840800	0.00000700	-0.11072100
C	0.74841200	0.00000700	-0.11069600
C	1.50228800	1.26501200	-0.49417800
C	2.88861600	1.34742500	0.13028100
S	3.97899000	-0.00001000	-0.37701800
C	2.88860300	-1.34743100	0.13028700
C	1.50227500	-1.26500700	-0.49417200
C	-1.50225900	-1.26500700	-0.49422100
C	-2.88860700	-1.34743100	0.13019300
S	-3.97897700	-0.00001000	-0.37714700
C	-2.88862000	1.34742500	0.13018700
C	-1.50227100	1.26501200	-0.49422700
H	1.59402300	1.29283000	-1.58507800
H	0.95322100	2.14962300	-0.18138300
H	3.38274400	2.27081300	-0.17115400
H	2.80790900	1.35242700	1.22022600
H	3.38272100	-2.27082500	-0.17114400
H	2.80789600	-1.35242800	1.22023200
H	0.95319700	-2.14961000	-0.18137200
H	1.59401000	-1.29283200	-1.58507100

H	-1.59395900	-1.29283100	-1.58512400
H	-0.95319100	-2.14961000	-0.18140600
H	-3.38271600	-2.27082500	-0.17125500
H	-2.80793500	-1.35242900	1.22014000
H	-3.38273800	2.27081300	-0.17126300
H	-2.80794800	1.35242700	1.22013500
H	-0.95321500	2.14962300	-0.18141500
H	-1.59397200	1.29283000	-1.58513000

PH3

P	-0.00108400	-0.00000200	-0.12975000
H	0.58382100	-1.00361300	0.64513600
H	0.58776400	1.00135900	0.64509300
H	-1.15532300	0.00227800	0.65602100

TS4

S	0.96667800	1.63146700	1.09707300
C	0.85314500	0.06351800	0.13274200
C	-0.60653300	-0.21314700	0.03556100
C	-1.34891400	-0.55434600	1.28525700
C	-2.86797100	-0.49692200	1.24314900
S	-3.55985200	-1.53297500	-0.06181400
C	-2.68896500	-0.74658400	-1.42945000
C	-1.17947700	-0.68786400	-1.25751100
C	1.52003900	0.20560700	-1.24609000
C	3.01422900	0.47602500	-1.18155600
S	3.92102300	-0.89891400	-0.43429800
C	3.00113200	-0.93423900	1.12001400
C	1.50405100	-1.11112000	0.92814100
H	-1.07110600	-1.60574200	1.45849600
H	-0.95026200	0.02937600	2.11267900
H	-3.26486200	-0.87999300	2.18247700
H	-3.22636600	0.52705900	1.12964800
H	-2.92203400	-1.33013500	-2.31963100

H	-3.08862800	0.25662900	-1.58218700
H	-0.73857700	-0.15431300	-2.09617100
H	-0.77163800	-1.71376800	-1.30861900
H	1.36982900	-0.70414400	-1.83674300
H	1.04228200	1.03822100	-1.77139000
H	3.41562400	0.59196000	-2.18830700
H	3.21386300	1.38849700	-0.62066300
H	3.39596800	-1.77463000	1.69152300
H	3.19860900	-0.01786500	1.67651700
H	1.04732400	-1.16423800	1.91550600
H	1.31482400	-2.05483700	0.40229200
P	-1.66490400	2.35084000	-0.35256700
H	-2.83712300	2.89310300	-0.95264300
H	-0.76479700	3.27002200	-0.90618600
H	-1.83939500	2.94337400	0.90498000

P4

S	-1.08499000	1.88387900	-0.70276300
C	-0.80974500	0.17384800	-0.09463900
C	0.75757100	0.16525200	0.08852400
C	1.48177900	-0.07265200	-1.25276200
C	3.00103100	0.00674300	-1.18719000
S	3.69598300	-1.30959300	-0.16207200
C	2.78599500	-0.91478900	1.34675700
C	1.27288900	-0.80977300	1.16356500
C	-1.51173500	-0.03228700	1.26061400
C	-3.02728400	0.07414900	1.19495400
S	-3.75160400	-1.22655500	0.16886100
C	-2.79700000	-0.87470100	-1.32504500
C	-1.29051300	-0.88123600	-1.09990100
H	1.22322100	-1.07662100	-1.59472000
H	1.10251800	0.63635500	-1.99271200
H	3.41839500	-0.13541100	-2.18382600
H	3.35545600	0.97521700	-0.82515900

H	3.00357200	-1.72327300	2.04527600
H	3.19792600	-0.00169000	1.77533900
H	0.84756600	-0.55236900	2.13603300
H	0.88407800	-1.79876300	0.89930600
H	-1.26166800	-1.02117800	1.65518100
H	-1.14571600	0.71045300	1.97717700
H	-3.45746000	-0.04953600	2.18885600
H	-3.32983700	1.04883400	0.81031600
H	-3.07009800	-1.64530800	-2.04614200
H	-3.11111500	0.08951800	-1.72885000
H	-0.82252700	-0.69926600	-2.06739300
H	-0.98348700	-1.87641300	-0.75696000
P	1.01031500	1.95275700	0.52172100
H	2.25199200	1.82833100	1.22275700
H	0.32612900	2.51497700	1.59661600
H	1.48817200	2.91378500	-0.37058200

TS5

S	-1.20754500	2.08363200	-0.33152800
C	-0.67665700	-0.19780800	-0.01016200
C	0.75835200	-0.09859900	0.02341300
C	1.46065100	-0.40110000	-1.30056400
C	2.98131700	-0.27058800	-1.31820500
S	3.79811400	-1.25057900	-0.04175400
C	2.94951000	-0.43858800	1.32856000
C	1.44132100	-0.64083500	1.27931700
C	-1.38494300	-0.43191400	1.30688200
C	-2.89765800	-0.28190400	1.31921400
S	-3.72629200	-1.31065300	0.09048500
C	-2.85586100	-0.62871700	-1.33549400
C	-1.34824200	-0.77709700	-1.23603800
H	1.21840300	-1.41557000	-1.63850100
H	1.07720300	0.27772500	-2.07274900
H	3.36445900	-0.61894000	-2.27737500

H	3.31155700	0.76320700	-1.19966600
H	3.35282000	-0.86364700	2.24760300
H	3.21613000	0.62229600	1.31368200
H	1.02651200	-0.16670000	2.17276300
H	1.24879400	-1.71564800	1.38746800
H	-1.12980800	-1.45354400	1.61722600
H	-0.97365900	0.23694300	2.06510400
H	-3.28658900	-0.58616600	2.29078200
H	-3.18172700	0.75955000	1.15840500
H	-3.22154300	-1.16761600	-2.20936300
H	-3.13423300	0.42115700	-1.45435300
H	-0.90099400	-0.36519900	-2.13855300
H	-1.10340900	-1.84857600	-1.22170900
P	0.73359800	2.14552800	0.20132900
H	1.79257900	2.09525500	-0.71298800
H	1.15576400	1.91620700	1.52000500
H	0.76859600	3.57083100	0.31551300

TS6

S	-0.00765500	1.24026200	-0.03514300
C	-0.68354900	-0.93812600	0.00942900
C	0.70631800	-0.92276900	0.00917500
C	1.50258400	-1.14630100	-1.26063500
C	2.83672500	-0.41400400	-1.33727400
S	3.96108100	-0.83749200	0.00885200
C	2.83547100	-0.35999300	1.33558000
C	1.50199500	-1.09576300	1.28711800
C	-1.47870300	-1.12925300	1.28497800
C	-2.81499800	-0.39830900	1.33798700
S	-3.93961900	-0.87323500	0.00904800
C	-2.81604200	-0.45578400	-1.34008000
C	-1.47922700	-1.18296300	-1.25662100
H	1.69232700	-2.22357400	-1.34318600
H	0.92917000	-0.85173200	-2.13515300

H	3.34830700	-0.67798000	-2.26278900
H	2.67059400	0.66456000	-1.33425900
H	3.34621100	-0.58579100	2.27158900
H	2.66862100	0.71750100	1.28852100
H	0.92780300	-0.76805300	2.14917500
H	1.69264500	-2.16883000	1.41174900
H	-1.66709000	-2.20443800	1.39380900
H	-0.90763500	-0.81418300	2.15360800
H	-3.32572300	-0.63177900	2.27216000
H	-2.65155900	0.67987800	1.29763700
H	-3.32736500	-0.72986700	-2.26283900
H	-2.65339300	0.62317700	-1.34664000
H	-0.90859400	-0.90504200	-2.13813700
H	-1.66705000	-2.26192200	-1.31945100
P	-0.05283000	3.65780800	-0.02061200
H	-1.24617900	4.27163500	0.39945700
H	0.82244500	4.34370100	0.84079000
H	0.16457400	4.44266600	-1.16891200

PH3S

P	-0.85774400	-0.00003700	0.00000100
S	1.08381900	-0.00003300	-0.00002700
H	-1.49227900	-0.07833200	-1.24833200
H	-1.49208000	-1.04179600	0.69250500
H	-1.49057200	1.12121100	0.55624200