Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

ELECTRONIC SUPPLEMENTARY INFORMATION

Exploring the mechanism of the reductive amination of acetophenones *via* Borch approach: the role of the acid catalyst

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SUMMARY

1. IRCs FOR THE ACETOPHENONE'S AMINATION

Figure S1. IRC plot for the nucleophilic attack for pathway a (A) without and (B) with ethanol assistance obtained with M06-2X/6-31+G(d,p) level of theory

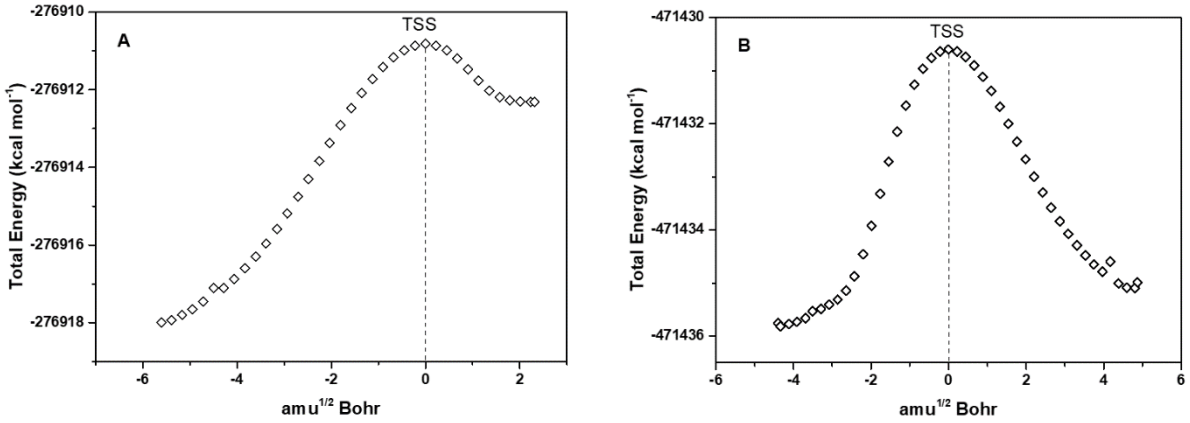


Figure S2. IRC plot for the intramolecular protonation of the zwitterionic intermediate in pathway a (A) without and (B) with ethanol assistance obtained with M06-2X/6-31+G(d,p) level of theory

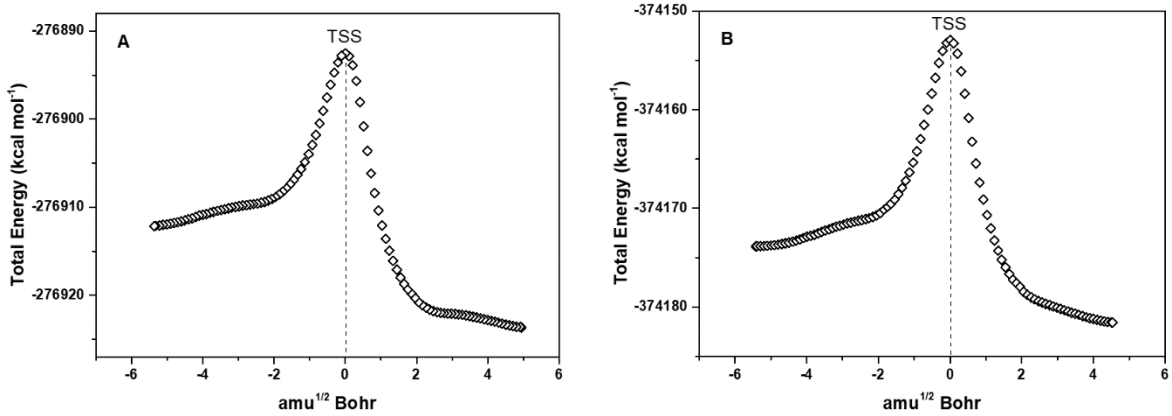


Figure S3. IRC plot for the prototropism in pathway b obtained with M06-2X/6-31+G(d,p) level of theory

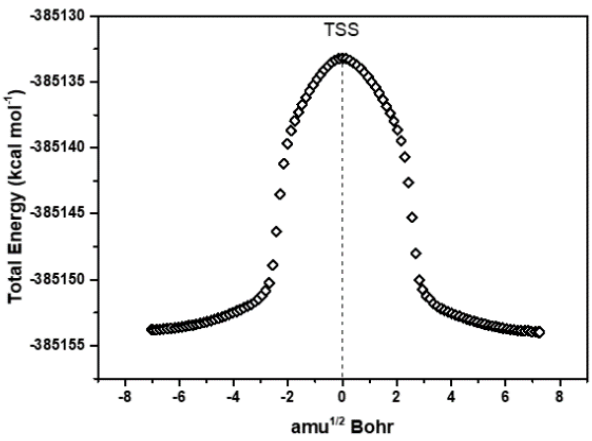


Figure S4. IRC plot for the nucleophilic attack for pathway c (A) without and (B) with ethanol assistance obtained with M06-2X/6-31+G(d,p) level of theory

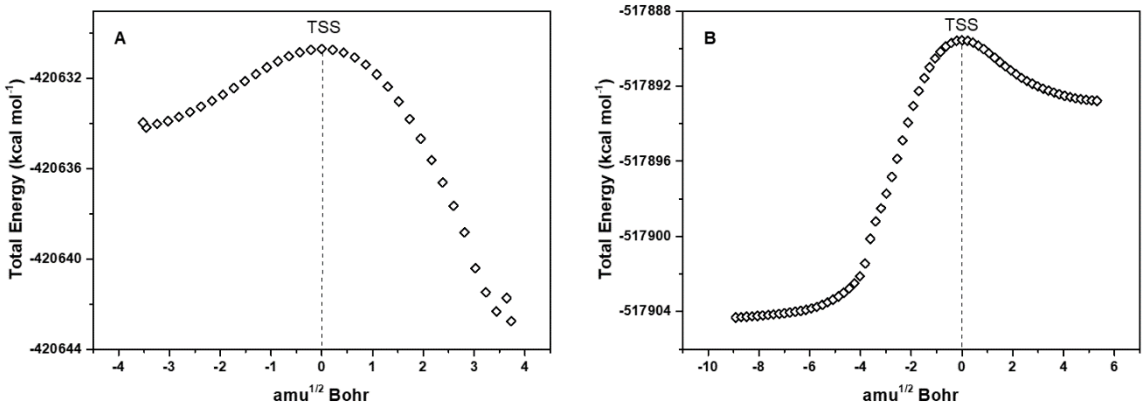


Figure S5. IRC plot for the nucleophilic attack for (A) pathway d and (B) pathway e obtained with M06-2X/6-31+G(d,p) level of theory

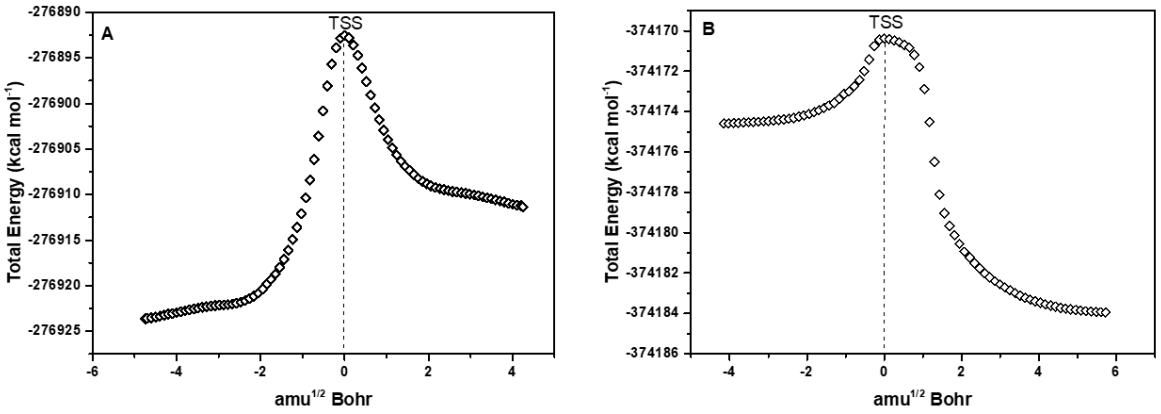
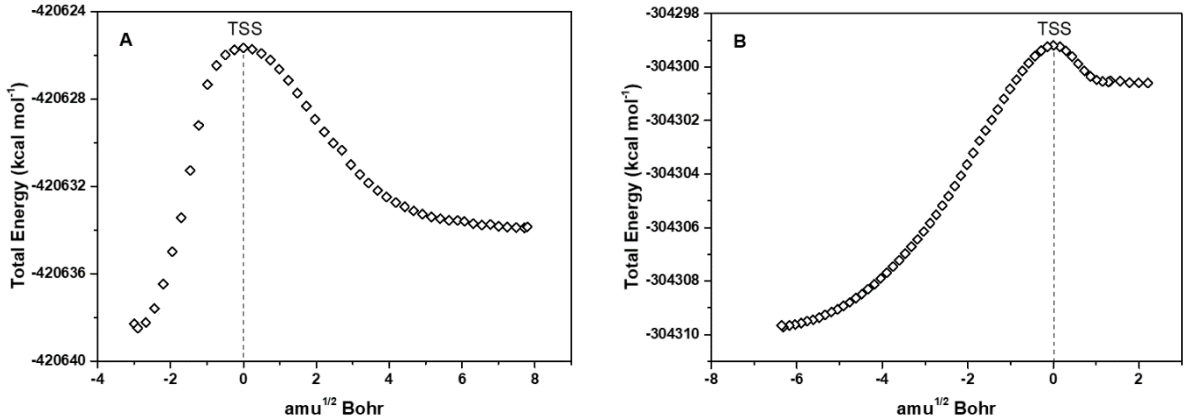


Figure S6. IRC plot for (A) the step ii (dehydration – TSS2 of highest energy) and (B) the step iii (reduction – TSS3) obtained with M06-2X/6-31+G(d,p) level of theory



2. IRCs FOR THE 4-NITROACETOPHENONE'S AMINATION

Figure S7. IRC plot for the nucleophilic attack for (A) pathway a and (B) pathway c obtained with M06-2X/6-31+G(d,p) level of theory

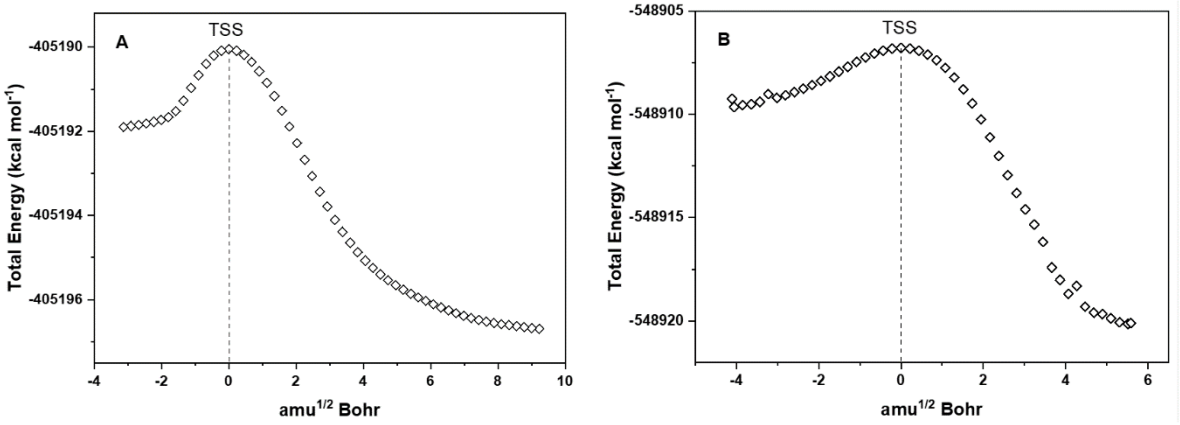


Figure S8. IRC plot for the step ii (dehydration) through (A) the TSS2 of lowest energy and (B) the TSS2 of highest energy obtained with M06-2X/6-31+G(d,p) level of theory

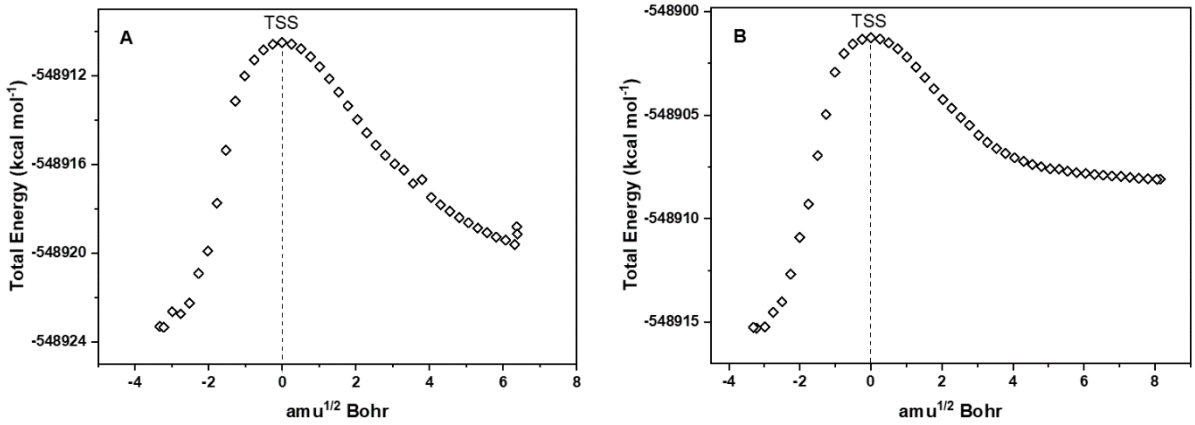
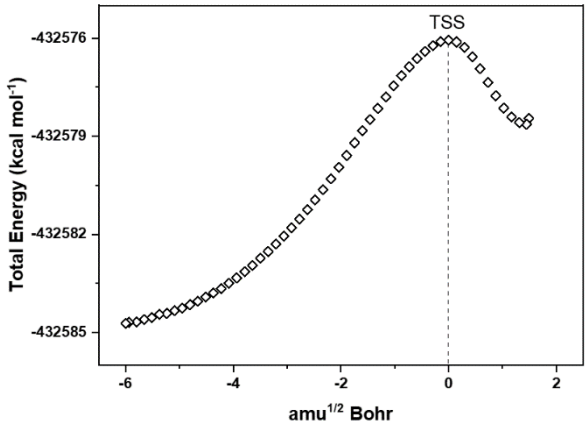


Figure S9. IRC plot for the step iii (reduction – TSS3) obtained with M06-2X/6-31+G(d,p) level of theory



3. IRCs FOR THE 4-(THIOMETHYL)ACETOPHENONE'S AMINATION

Figure S10. IRC plot for the nucleophilic attack for (A) pathway a and (B) pathway c obtained with M06-2X/6-31+G(d,p) level of theory

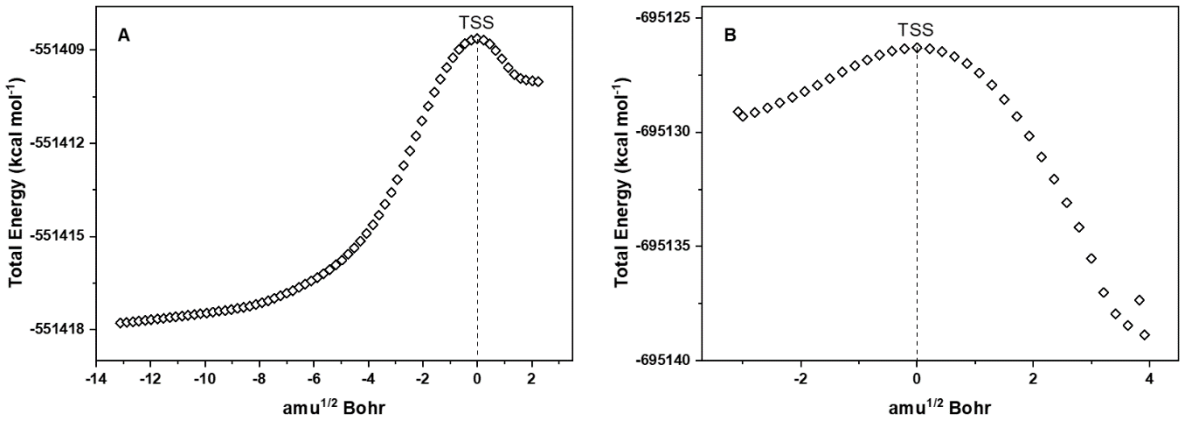


Figure S11. IRC plot for the step ii (dehydration) through (A) the TSS2 of lowest energy and (B) the TSS2 of highest energy obtained with M06-2X/6-31+G(d,p) level of theory

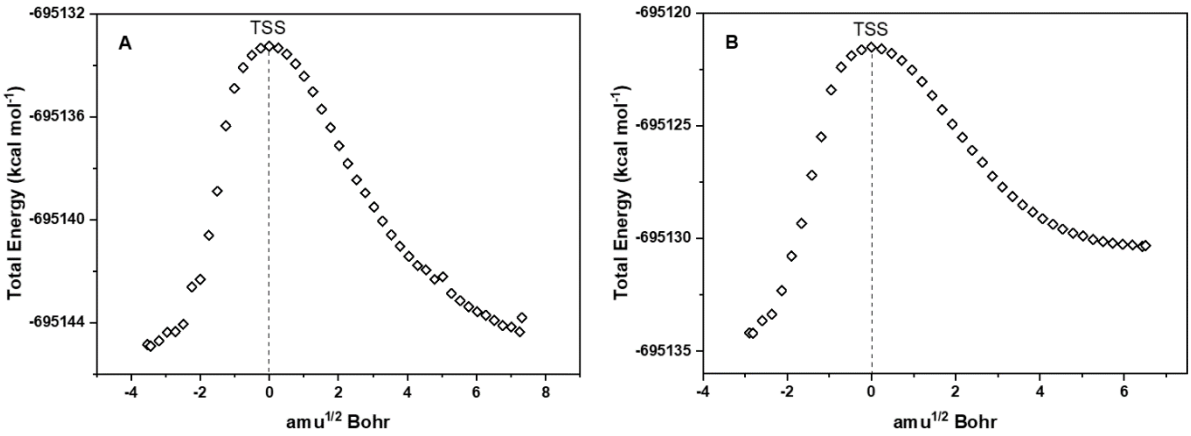
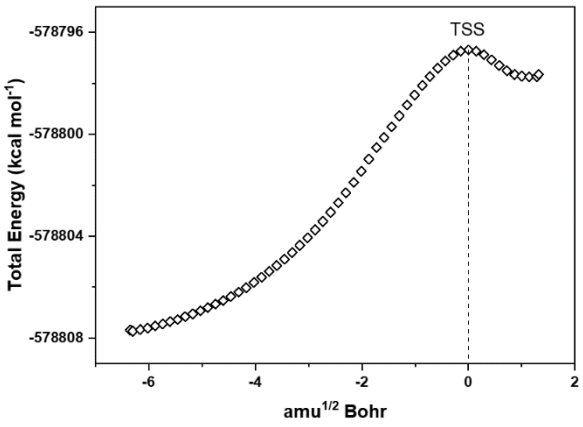


Figure S12. IRC plot for the step iii (reduction – TSS3) obtained with M06-2X/6-31+G(d,p) level of theory



4. IRCs FOR THE 4-HYDROXYACETOPHENONE'S AMINATION

Figure S13. IRC plot for the nucleophilic attack for (A) pathway a and (B) pathway c obtained with M06-2X/6-31+G(d,p) level of theory

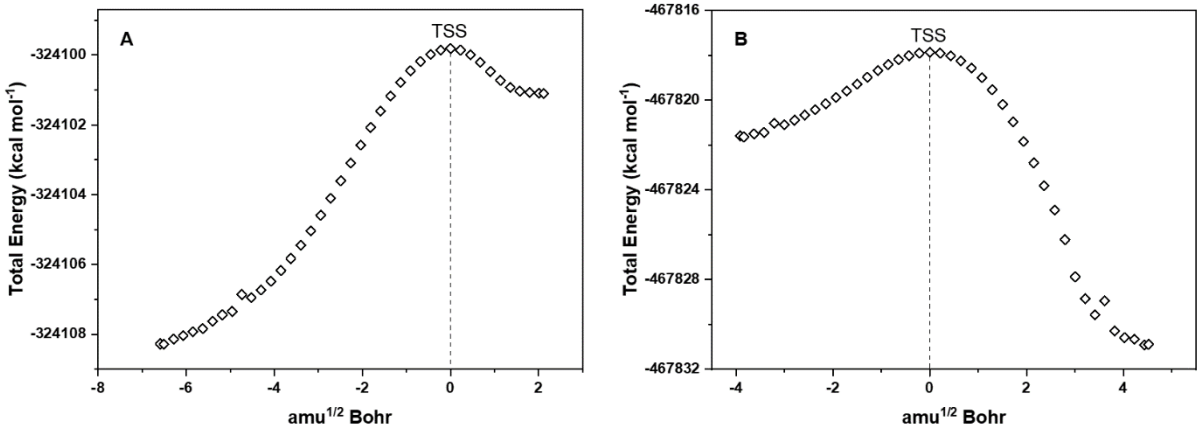


Figure S14. IRC plot for the step ii (dehydration) through (A) the TSS2 of lowest energy and (B) the TSS2 of highest energy obtained with M06-2X/6-31+G(d,p) level of theory

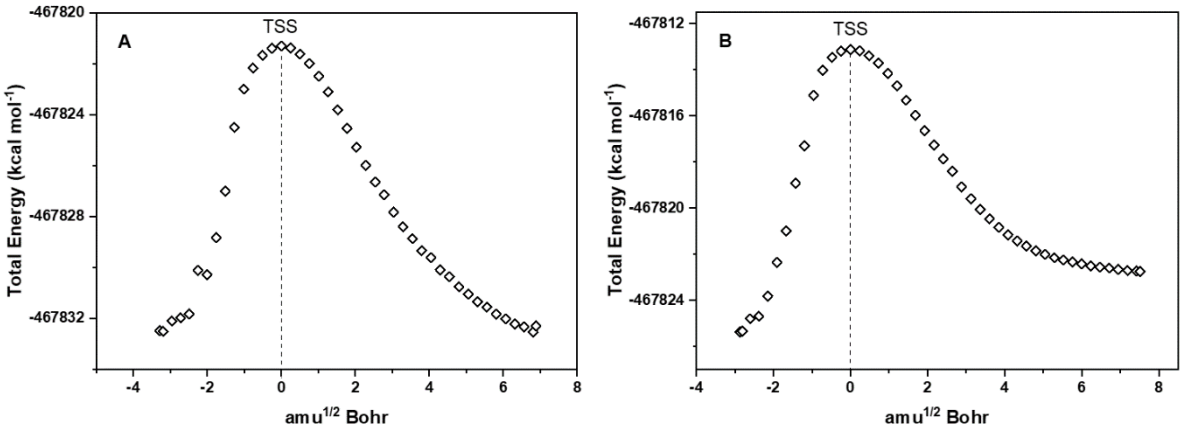
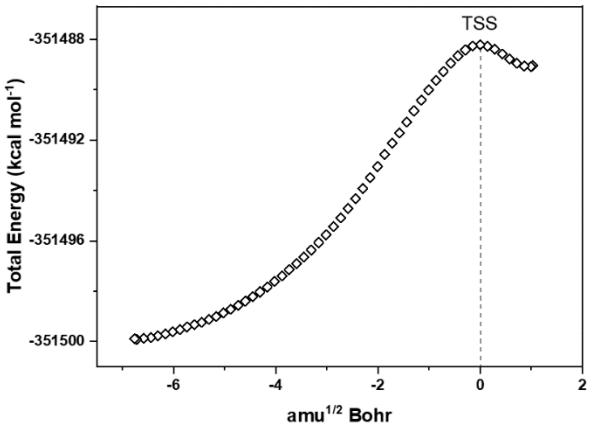


Figure S15. IRC plot for the step iii (reduction – TSS3) obtained with M06-2X/6-31+G(d,p) level of theory



5. IRCs FOR THE 4-(N-DIMETHYLAMINO)ACETOPHENONE'S AMINATION

Figure S16. IRC plot for (A) the step ii (dehydration – TSS2) and (B) the step iii (reduction – TSS3) obtained with M06-2X/6-31+G(d,p) level of theory

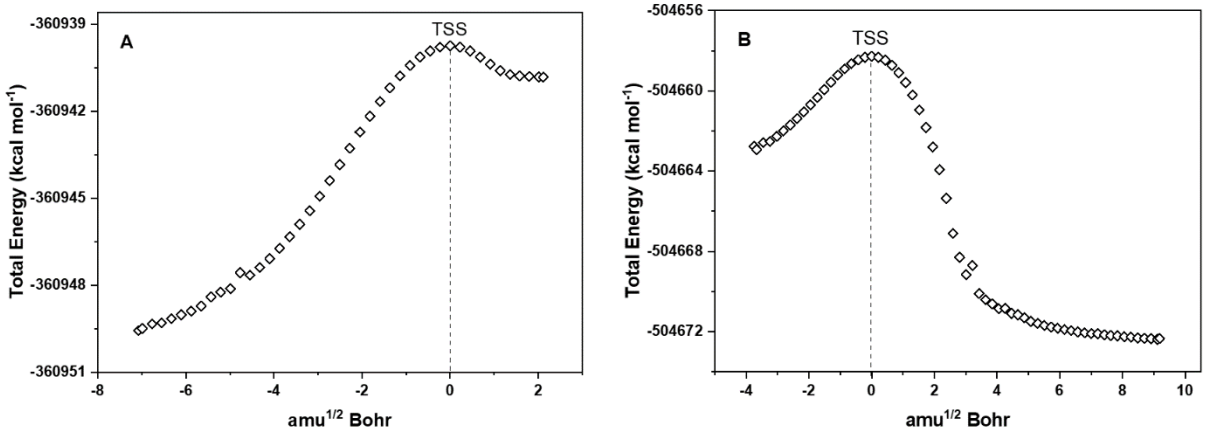


Figure S17. IRC plot for the step ii (dehydration) through (A) the TSS2 of lowest energy and (B) the TSS2 of highest energy obtained with M06-2X/6-31+G(d,p) level of theory

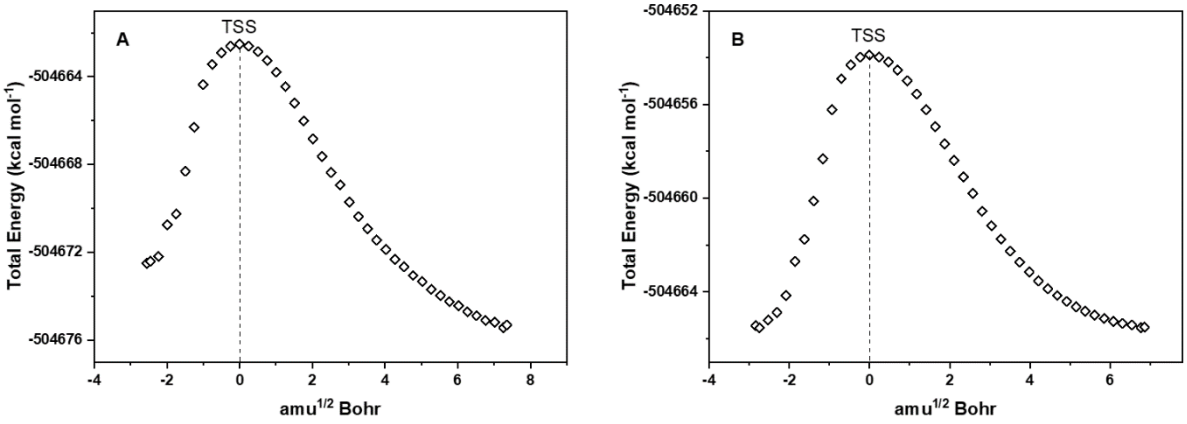
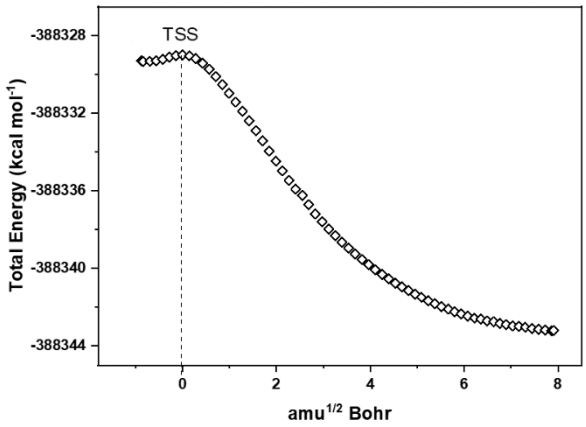


Figure S18. IRC plot for the step iii (reduction – TSS3) obtained with M06-2X/6-31+G(d,p) level of theory



6. OPTIMIZED GEOMETRIES FOR THE ACETOPHENONE'S AMINATION

6.1. Optimized Reactants

Table S1. Optimized structure of acetic acid in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -229.046833 Hartrees Number of imaginary frequencies = 0			
C	-0.74504900	0.35356200	0.00028300
C	-0.05780200	-0.97662500	0.00005800
H	-0.76965300	-1.80091800	0.00033200
H	0.58231400	-1.03473900	-0.88400500
H	0.58328000	-1.03472100	0.88339000
O	-2.07993700	0.26495800	-0.00257100
O	-0.16874400	1.42566400	0.00260200
H	-2.46257500	1.16084400	-0.00245300

Table S2. Optimized structure of ammonia in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -56.542159 Hartrees Number of imaginary frequencies = 0			
N	-0.74102900	0.55902300	0.12671100
H	-0.36073800	-0.38382400	0.12662200
H	-0.36070800	1.03059900	0.94315600
H	-0.36071100	1.03053400	-0.68979900

Table S3. Optimized structure of acetophenone in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -384.744721 Hartrees Number of imaginary frequencies = 0			
C	-4.45845800	0.22831100	-0.28459000
C	-3.58957900	1.19446500	-0.79784500
C	-2.22971800	1.12603500	-0.51428800
C	-1.72627000	0.09084500	0.28451600
C	-2.60120000	-0.87539900	0.79563400
C	-3.96390500	-0.80497800	0.51093500
H	-5.52054600	0.28180000	-0.50550800
H	-3.97441800	1.99861000	-1.41767700
H	-2.22772200	-1.68442400	1.41565400
H	-4.63827900	-1.55620800	0.91036700
C	-0.25780500	0.04724900	0.57119100
C	0.28740700	-1.06639600	1.42226900
H	-0.18285700	-1.05423100	2.41070100

H	0.06836600	-2.03606100	0.96385800
H	1.36577700	-0.94449800	1.52711800
O	0.48450600	0.90888700	0.11597300
H	-1.54592900	1.87165800	-0.90812900

Table S4. Optimized structure of cyanoborohydride in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -119.617184 Hartrees Number of imaginary frequencies = 0			
H	-1.70050100	0.58173700	-0.99835100
H	-1.70045700	-1.15539700	-0.00460100
H	-1.70084400	0.57379800	1.00290000
C	0.27343100	0.00002300	-0.00008300
N	1.43781400	0.00000400	0.00005800

Table S5. Optimized structure of ethanol in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -154.97405 Hartrees Number of imaginary frequencies = 0			
C	1.22227000	-0.22212200	0.00006600
H	1.29467800	-0.85663300	0.88910300
H	2.06939700	0.47029400	-0.00001100
H	1.29472000	-0.85685000	-0.88881400
C	-0.08018200	0.54734600	-0.00006300
H	-0.14669600	1.18814000	0.88827800
H	-0.14653400	1.18809500	-0.88845900
O	-1.15335500	-0.39621600	-0.00014100
H	-1.99124900	0.08533800	0.00100900

6.2. Optimized Minima Structures for Step i of the Mechanism (Hemiaminal Formation)

Table S6. Optimized structure of the hydroxy-ammonium ion in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -441.709049 Hartrees Number of imaginary frequencies = 0			
C	-4.31421100	0.22054600	-0.14585500
C	-3.52182300	1.36604000	-0.17157800
C	-2.13304600	1.26461800	-0.07658600
C	-1.53060300	0.01155800	0.04676900
C	-2.32845200	-1.13825700	0.07624600
C	-3.71362000	-1.03308300	-0.02291700
H	-5.39454900	0.30207400	-0.21862300

H	-3.98133500	2.34544400	-0.26447300
H	-1.87972300	-2.12379600	0.18002200
H	-4.32295300	-1.93136100	0.00097500
C	-0.01804900	-0.10654900	0.17384500
C	0.42962400	-0.84143000	1.42479500
H	0.06419800	-0.29532000	2.29707200
H	0.03408400	-1.85880400	1.45103400
H	1.52350900	-0.88635100	1.45894500
O	0.55629100	1.15380200	0.06499900
N	0.48957200	-0.89463900	-1.03600500
H	0.09560600	-1.84139600	-1.07848300
H	1.42159000	1.16453600	0.50185900
H	-1.52168400	2.15956400	-0.09254500
H	0.24400700	-0.40258400	-1.90284000
H	1.51205300	-0.98213100	-0.99672100

Table S7. Optimized structure of the hemiaminal in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -441.268746 Hartrees Number of imaginary frequencies = 0			
C	2.97266300	-2.03125800	-0.03217600
C	2.64923800	-1.33055000	-1.19537300
C	1.83360200	-0.20281800	-1.12853100
C	1.32927300	0.24376200	0.09944900
C	1.65833500	-0.46164800	1.25882500
C	2.47453800	-1.59313700	1.19314000
H	3.60625000	-2.91199500	-0.08193100
H	3.02997400	-1.66398800	-2.15656100
H	1.28253000	-0.13903100	2.22447300
H	2.71812500	-2.13161000	2.10453900
C	0.48389600	1.51522400	0.13022900
C	-0.30837600	1.70623900	1.41767900
H	-0.96085000	0.84818600	1.59807200
H	0.35086400	1.84838700	2.27647700
H	-0.93156500	2.60190900	1.31703200
O	-0.43963600	1.37652300	-0.96420100
N	1.37084000	2.65212000	-0.04147900
H	1.85525700	2.58462200	-0.93474000
H	0.82969100	3.51588500	-0.04800000
H	1.58067700	0.33345200	-2.03904400
H	-0.99529300	2.16960100	-0.98970700

6.2.1. Optimized Structures for Pathway a

Table S8. Optimized TSS1 (nucleophilic attack) for pathway a in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -441.250992 Hartrees Number of imaginary frequencies = 1			
C	-2.86997600	0.14236300	0.03633600
C	-2.27882300	-1.11928600	0.08154700
C	-0.89042200	-1.24536700	0.01028400
C	-0.07900400	-0.11518600	-0.10861200
C	-0.67983600	1.14874800	-0.15673100
C	-2.06539100	1.27752200	-0.08217900
H	-3.95001700	0.24297600	0.09192700
H	-2.89738400	-2.00787100	0.17024600
H	-0.06859300	2.04330500	-0.24230600
H	-2.51757600	2.26456700	-0.11619300
C	1.43396900	-0.30453000	-0.20811300
C	2.13668200	0.59516300	-1.21537700
H	1.86209700	0.24589300	-2.21718900
H	1.86269200	1.64846100	-1.13002200
H	3.21815100	0.48975600	-1.09578800
O	1.89130400	-1.47409500	-0.05174700
N	1.92127200	0.64131800	1.38421700
H	1.65786400	1.62413700	1.45157200
H	2.93505200	0.56556700	1.46375200
H	-0.42573800	-2.22594700	0.04198600
H	1.50092700	0.13613000	2.16354600

Table S9. Optimized TSS1 (nucleophilic attack) with ethanol assistance for pathway a in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -751.177268 Hartrees Number of imaginary frequencies = 1			
C	-3.21117200	-1.82087100	-1.08496000
C	-2.20231700	-1.20401600	-1.83121600
C	-1.03362800	-0.78341000	-1.20556600
C	-0.85273900	-0.98589800	0.16795100
C	-1.85670600	-1.61309700	0.90809500
C	-3.03679700	-2.02329700	0.28231400
H	-4.12807100	-2.14180000	-1.57067800
H	-2.33278000	-1.04657500	-2.89789200
H	-1.73683600	-1.77057400	1.97579200
H	-3.81848900	-2.49901900	0.86717100
C	0.38749800	-0.43237200	0.82789800

C	0.66351400	-0.80424200	2.26618600
H	-0.02083200	-0.22743500	2.89999200
H	0.51929400	-1.86738600	2.46615200
H	1.68673200	-0.51577900	2.51838100
O	0.81472500	0.67959600	0.40613100
N	1.71065200	-1.79644400	0.02349300
H	1.56132000	-2.77351300	0.26922500
H	2.63671200	-1.50729300	0.34125900
H	-0.25266300	-0.28931300	-1.77859200
H	1.67788500	-1.71148200	-0.99100400
H	2.59609000	0.78825900	0.69341000
H	-0.43131000	1.80625100	-0.31675400
O	3.55239400	0.58944400	0.61722200
O	-1.14795900	2.43768600	-0.52587300
C	-2.27705700	2.11797500	0.28222200
H	-2.76500400	1.20576900	-0.09154800
H	-1.95580300	1.92547300	1.31560200
C	-3.24721500	3.28054200	0.24003900
H	-3.56245700	3.47708900	-0.78992700
H	-4.13759700	3.05568400	0.83495000
H	-2.78197900	4.18715500	0.63968300
C	3.92714900	0.79446900	-0.74316900
H	3.92241800	1.86773300	-0.97606800
H	3.20065400	0.30747400	-1.40921600
C	5.30904600	0.21489000	-0.95970000
H	5.63248400	0.37534400	-1.99248600
H	6.03398200	0.69291000	-0.29302800
H	5.31095100	-0.86170800	-0.75927500

Table S10. Optimized structure of the zwitterionic intermediate for pathway a in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -441.249041 Hartrees Number of imaginary frequencies = 0			
C	2.87751900	-0.09168300	0.01400600
C	2.24765300	1.15170700	0.00543600
C	0.85374700	1.23307800	-0.02171800
C	0.07283300	0.07666500	-0.04415400
C	0.71388500	-1.16948900	-0.04286300
C	2.10497000	-1.25435300	-0.00923100
H	3.96147400	-0.15681000	0.03737800
H	2.84060200	2.06195700	0.02030400
H	0.13259700	-2.08906800	-0.06633500
H	2.58545900	-2.22860100	-0.00346600
C	-1.46457100	0.21062900	-0.08806300

C	-2.06254700	-0.59426900	-1.25116500
H	-1.73450900	-0.12857300	-2.18492000
H	-1.75791300	-1.64512400	-1.26090800
H	-3.15477400	-0.53704500	-1.19953300
O	-1.92926600	1.43694900	0.02165300
N	-1.94821300	-0.59007400	1.22361700
H	-1.68705300	-1.57900000	1.25937200
H	-2.96811800	-0.51766300	1.26660400
H	0.35887000	2.19896000	-0.02735000
H	-1.56593800	-0.11781300	2.04682900

Table S11. Optimized structure of the zwitterionic intermediate with ethanol assistance for pathway a in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -751.17863 Hartrees Number of imaginary frequencies = 0			
C	-3.44278400	-1.55277100	-0.98360000
C	-2.41397000	-1.08012400	-1.80260600
C	-1.15775300	-0.82074300	-1.26239800
C	-0.90478800	-1.03720500	0.09806200
C	-1.93487200	-1.51723700	0.90874500
C	-3.19996500	-1.76958200	0.37056800
H	-4.42649400	-1.74770500	-1.40069000
H	-2.59468500	-0.90458600	-2.85915000
H	-1.76969600	-1.68818400	1.96772200
H	-3.99431200	-2.13395300	1.01557600
C	0.48029000	-0.67333100	0.64547500
C	0.64765000	-0.91984400	2.14325200
H	-0.02554900	-0.25328200	2.68859100
H	0.43894900	-1.95389900	2.43373500
H	1.67620000	-0.67143200	2.42267700
O	0.87720400	0.55707300	0.26270400
N	1.47114000	-1.69128200	-0.03086700
H	1.26956600	-2.66775400	0.20338000
H	2.42646100	-1.45533500	0.27280300
H	-0.37002100	-0.42554500	-1.89994800
H	1.43333800	-1.58289500	-1.04848400
H	2.46873500	0.63598600	0.48204000
H	-0.26351100	1.63236200	-0.21331400
O	3.45223800	0.43387200	0.53830400
O	-0.93211800	2.33322800	-0.45160300
C	-2.08473700	2.14858700	0.35626500
H	-2.67186700	1.28997700	-0.00507600
H	-1.78874600	1.93167100	1.39343300
C	-2.93145400	3.40535000	0.30957100

H	-3.22685200	3.62779300	-0.72126300
H	-3.83962000	3.27944900	0.90729900
H	-2.37362800	4.26187800	0.70162100
C	4.02433700	0.65709900	-0.74446400
H	3.98677800	1.72649000	-0.99424500
H	3.44761100	0.11969600	-1.51311000
C	5.45978200	0.17235100	-0.73905900
H	5.92609800	0.34156700	-1.71444800
H	6.04140600	0.70696100	0.01891800
H	5.50286200	-0.89896500	-0.51609800

Table S12. Optimized TSS for the intramolecular proton transfer in the zwitterionic intermediate for pathway a in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -441.221948 Hartrees Number of imaginary frequencies = 1			
C	-2.88643900	-0.04724600	-0.01720100
C	-2.22406100	1.17788100	0.03764400
C	-0.82802200	1.22252200	0.05051100
C	-0.08523600	0.04252200	0.01292300
C	-0.75505200	-1.18615900	-0.03680500
C	-2.14739700	-1.23180200	-0.05692000
H	-3.97193400	-0.08170400	-0.03024700
H	-2.79279900	2.10286200	0.06829900
H	-0.18561300	-2.11315300	-0.06537900
H	-2.65598400	-2.19047000	-0.10278100
C	1.43675200	0.09478200	0.07124500
C	1.96870500	-0.51344000	1.36408000
H	1.62972100	0.10001500	2.20366600
H	1.61417600	-1.53789300	1.51104400
H	3.06343400	-0.50698800	1.34641800
O	1.98489100	1.34375400	-0.21131300
N	2.04576800	-0.61461800	-1.13395100
H	2.71479200	-1.35266300	-0.91330800
H	2.43230500	0.53528200	-1.18580300
H	-0.30718000	2.17387700	0.08616600
H	1.38407400	-0.93123500	-1.84277000

6.2.2. Optimized Structures for Pathway b

Table S13. Optimized protonated ketone for pathway b in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -385.149764 Hartrees Number of imaginary frequencies = 0			
C	2.60852800	0.07327700	-0.00075300
C	1.96397300	-1.16730900	0.03441200
C	0.57957000	-1.22593800	0.03209200
C	-0.16808400	-0.03125000	0.00269300
C	0.48637200	1.21484700	-0.02752900
C	1.87322100	1.26035500	-0.03368700
H	3.69376100	0.11404300	-0.00185300
H	2.54507100	-2.08282600	0.06291200
H	-0.08176100	2.13875100	-0.05562400
H	2.38286300	2.21730900	-0.06353600
C	-1.61081200	-0.08716900	-0.00117100
C	-2.47672200	1.10921500	0.06165900
H	-2.20499400	1.70838100	0.93576600
H	-2.29425400	1.72043200	-0.82953700
H	-3.53112500	0.83456300	0.10748400
O	-2.12673100	-1.25968400	-0.06929500
H	0.07196100	-2.18407600	0.06052600
H	-3.10394900	-1.26526800	-0.06807200

6.2.3. Optimized Structures for Pathway c

Table S14. Optimized TSS1 for pathway c without ethanol assistance in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -670.294804 Hartrees Number of imaginary frequencies = 1			
C	-4.44460900	0.39153000	0.00320200
C	-3.55388200	1.46049200	-0.12110100
C	-2.18326600	1.24051700	-0.02209400
C	-1.68662700	-0.05056300	0.19188900
C	-2.58088100	-1.11759000	0.31580100
C	-3.95579200	-0.89476800	0.22471500
H	-5.51458600	0.56276100	-0.07043000
H	-3.92925600	2.46513400	-0.29230800
H	-2.21918400	-2.12573900	0.49105400
H	-4.64345500	-1.72879700	0.32860500
C	-0.19767700	-0.24362000	0.31123600
C	0.33798000	-1.61919400	0.62145200

H	0.14427500	-1.82301700	1.68170200
H	-0.12942600	-2.39973300	0.02134300
H	1.41737900	-1.63519100	0.45645400
O	0.49187800	0.76393200	0.61779700
N	0.15819200	-0.38901300	-1.79172600
H	-0.20931600	-1.17966400	-2.31678700
H	1.17728600	-0.38782500	-1.84481600
H	1.94534000	0.62672800	0.82076100
O	2.96564500	0.60172500	1.02314900
C	3.66194400	0.20837000	-0.02445100
C	5.14068200	0.14914400	0.22436800
H	5.49405200	1.13103500	0.55084700
H	5.34105200	-0.56179300	1.03111000
H	5.66508000	-0.15646000	-0.68010000
O	3.14275800	-0.08408200	-1.09789100
H	-1.48675600	2.06857800	-0.11349200
H	-0.18930300	0.46856600	-2.21640500

Table S15. Optimized TSS1 for pathway c with ethanol assistance in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -825.256291 Hartrees Number of imaginary frequencies = 1			
C	-3.94186900	-1.40117600	-0.33164900
C	-3.09726900	-1.05776900	-1.39176900
C	-1.74598800	-0.82929200	-1.15725300
C	-1.22283400	-0.95471600	0.13544100
C	-2.06564500	-1.30969800	1.19086000
C	-3.42532000	-1.52568100	0.95643500
H	-4.99907400	-1.57188800	-0.51260400
H	-3.49576700	-0.96413900	-2.39759000
H	-1.67716800	-1.40156400	2.20061300
H	-4.07842700	-1.78875800	1.78308500
C	0.21861600	-0.61039400	0.37098700
C	0.84202800	-0.90895500	1.70787700
H	0.50951200	-0.13596500	2.41202500
H	0.55203200	-1.88690700	2.09294300
H	1.92933100	-0.85389700	1.62387500
O	0.71860600	0.28831600	-0.35459700
N	1.03267200	-2.41162700	-0.57330700
H	0.88896200	-3.32502000	-0.14844300
H	2.03123700	-2.20421900	-0.59517100
H	-1.08574300	-0.55229800	-1.97492800
H	0.69112400	-2.44915900	-1.53138600
H	2.15470900	0.74086300	-0.12218100

H	-0.48781700	1.66491900	-0.90671200
O	3.09687400	1.12411500	0.01424600
O	-1.10395300	2.41852100	-0.92460700
C	-1.91724800	2.36504700	0.24559500
H	-2.67878400	1.57869000	0.14072100
H	-1.29915900	2.11885000	1.12015000
C	-2.58188700	3.71305500	0.43186100
H	-3.18996800	3.96315800	-0.44356200
H	-3.23431400	3.69697700	1.31008900
H	-1.83194800	4.49821600	0.56991800
C	4.02467300	0.19618600	-0.13874300
C	5.41995800	0.70903000	0.05935600
H	6.14208500	-0.09098800	-0.09785100
H	5.60820200	1.52916700	-0.63882200
H	5.51629700	1.10632000	1.07384600
O	3.75880800	-0.96905200	-0.41239800

6.2.4. Optimized Structures for Pathway d

Table S16. Optimized TSS1 for pathway d in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -441.221871 Hartrees Number of imaginary frequencies = 1			
N	2.04881400	-0.67520200	1.09676000
O	1.98391800	1.33066500	0.28312800
C	1.43621600	0.09839000	-0.06572000
C	-0.08515900	0.04262200	-0.00907200
H	2.71229300	-1.40479700	0.83533700
H	2.43875800	0.46896400	1.20790100
C	-0.75437600	-1.18660900	0.02420200
C	-2.14691100	-1.23290600	0.04290500
C	-2.88624400	-0.04835400	0.01634700
C	-2.22421800	1.17765600	-0.02518000
C	-0.82835800	1.22286900	-0.03556700
H	-0.18487000	-2.11394800	0.04170000
H	-2.65515300	-2.19220100	0.07807100
H	-3.97172000	-0.08324900	0.02918300
C	1.96613400	-0.43766200	-1.39094900
H	1.61063700	-1.45260600	-1.59252800
H	1.62536600	0.22051500	-2.19519900
H	3.06091700	-0.43243000	-1.37501700
H	1.38974600	-1.02296400	1.79327100
H	-0.30826000	2.17507100	-0.06015500

H	-2.79325500	2.10270400	-0.04670400
N	2.04881400	-0.67520200	1.09676000
O	1.98391800	1.33066500	0.28312800

6.2.5. Optimized Structures for Pathway e

Table S17. Optimized TSS1 for pathway e in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -596.208372 Hartrees Number of imaginary frequencies = 1			
N	0.81010700	0.87335300	-0.68665700
O	2.94147400	0.00992800	0.51527900
O	0.70728700	-0.79044300	0.93408100
C	0.04193500	0.34699300	0.53274600
C	-1.39237200	0.04949000	0.11610700
H	0.58400900	1.84322100	-0.91870800
H	1.84523300	0.76156800	-0.39318300
H	1.80075900	-0.52719500	0.86506100
C	-2.15867100	1.02612200	-0.53021900
C	-3.47855200	0.76342800	-0.89020600
C	-4.04942600	-0.47686300	-0.59840400
C	-3.29116000	-1.44971500	0.05049000
C	-1.96597400	-1.18902800	0.40516100
H	-1.72781300	1.99880500	-0.75819200
H	-4.06142500	1.52753900	-1.39604700
H	-5.07930300	-0.68152500	-0.87573600
C	0.10471300	1.45139200	1.58756100
H	-0.38814000	2.36760000	1.24935200
H	-0.39879600	1.09243900	2.48865400
H	1.14968900	1.67038600	1.83039900
H	0.63106900	0.28716000	-1.50652400
H	-1.37227000	-1.94585300	0.90640600
H	-3.72873600	-2.41670100	0.28123900
C	3.66457200	-0.86848900	-0.31518600
H	2.99544800	-1.33554200	-1.06244500
H	4.09003200	-1.69515200	0.27688500
C	4.78843600	-0.14430800	-1.04179700
H	5.48058400	0.30449500	-0.32099500
H	4.38388000	0.65674800	-1.67105300
H	5.35393800	-0.83147300	-1.68091300

6.3. Optimized Structures for Step ii (Dehydration) and iii (Reduction) of the Mechanism

Table S18. Optimized TSS2 (lowest energy) in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -670.28654 Hartrees Number of imaginary frequencies = 1			
C	-4.42639000	-0.31812800	-0.22272600
C	-3.57216400	-1.39565600	0.02369800
C	-2.21116300	-1.17746100	0.21120000
C	-1.69210200	0.12198400	0.15343600
C	-2.54610400	1.19669400	-0.10327500
C	-3.91193600	0.97479500	-0.28598400
H	-5.48867300	-0.48932900	-0.36944000
H	-3.96604200	-2.40662400	0.06302500
H	-2.15882700	2.20931300	-0.15300300
H	-4.57064500	1.81601300	-0.47884700
C	-0.23112500	0.35113200	0.39062000
C	0.36501300	1.69030800	0.05534100
H	0.08811300	2.00993900	-0.94989200
H	-0.00670200	2.42254500	0.77920000
H	1.45290100	1.64166200	0.14046300
O	0.43344000	-0.63006500	-1.06845000
N	0.29838900	-0.26610800	1.44964300
H	-0.14273200	-1.10711200	1.80191900
H	1.31160800	-0.18430300	1.57677400
H	0.12107400	-0.26102100	-1.91036500
O	2.89587900	-0.35204800	-1.08620400
C	3.61441500	-0.16947500	-0.04346400
C	5.10510500	-0.05120400	-0.28520800
H	5.29594900	0.78797200	-0.96072300
H	5.64707200	0.09904000	0.64891900
H	5.46509500	-0.95885700	-0.77838900
O	3.16566000	-0.08359300	1.12232900
H	-1.54781700	-2.02218900	0.37893800
H	1.48976800	-0.50656700	-1.03929800

Table S19. Optimized TSS2 (highest energy) in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -670.285018 Hartrees Number of imaginary frequencies = 1			
C	1.19937200	2.61272300	0.18787500
C	0.31014400	2.53330900	-0.88589600
C	-0.71999400	1.59838500	-0.87096100
C	-0.86950000	0.73389300	0.22034700

C	0.01959200	0.81616700	1.29380400
C	1.05067600	1.75578800	1.27645000
H	2.00831400	3.33718300	0.17146100
H	0.42669600	3.19166900	-1.74127600
H	-0.07824100	0.14805200	2.14310700
H	1.73997600	1.81030500	2.11376900
C	-1.95340000	-0.29932700	0.21864900
C	-1.95809600	-1.36818800	1.27423000
H	-0.97720200	-1.83570400	1.36348100
H	-2.23289300	-0.90822700	2.22897500
H	-2.70697900	-2.12549200	1.02892100
O	-1.24492800	-1.32216600	-1.21499100
N	-3.15522100	0.10406900	-0.19236600
H	-3.25745000	0.90528600	-0.80222500
H	-3.93653400	-0.53943600	-0.15294000
H	-0.17061200	-1.29589500	-1.23993800
H	-1.38090400	1.51965200	-1.73056800
H	-1.51416000	-2.24750900	-1.10293700
O	1.20595600	-1.10495800	-1.31335500
C	1.82928400	-1.42824800	-0.23945900
O	1.35410400	-2.17002900	0.64573000
C	3.23693100	-0.88724400	-0.08945800
H	3.92882100	-1.59161200	-0.56494400
H	3.34076200	0.07961300	-0.58617100
H	3.50584600	-0.80268300	0.96529200

Table S20. Optimized structure of iminium in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -365.29033 Hartrees Number of imaginary frequencies = 0			
C	-4.34049300	-1.16237200	0.28114600
C	-3.91166700	-0.35323800	1.33263400
C	-2.60934700	0.13440800	1.34846000
C	-1.71907200	-0.20202000	0.31715900
C	-2.15951600	-1.01321500	-0.74264300
C	-3.46530600	-1.48646500	-0.75783400
H	-5.36000100	-1.53555000	0.26552700
H	-4.59076700	-0.09816000	2.13951800
H	-1.50684100	-1.25635900	-1.57606200
H	-3.80389500	-2.10232300	-1.58456700
C	-0.34528600	0.31519700	0.36553000
C	0.01609300	1.45834100	1.24726200
H	-0.69671600	2.27495600	1.11328800
H	-0.04284200	1.12857100	2.29023100

H	1.02893200	1.80837800	1.04529600
H	-2.28592000	0.76245300	2.17170600
N	0.58592900	-0.22401600	-0.35346700
H	0.42447200	-1.03830000	-0.94085600
H	1.53163000	0.15120700	-0.34154100

Table S21. Optimized TSS3 in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -484.880073 Hartrees
Number of imaginary frequencies = 1

C	-3.48116000	0.35562500	-0.41055300
C	-2.64261300	1.37281200	0.05265800
C	-1.30610900	1.10461200	0.32597300
C	-0.79328800	-0.18403100	0.13702400
C	-1.63458700	-1.20236000	-0.32104300
C	-2.97547000	-0.92879200	-0.59500700
H	-4.52448500	0.56658400	-0.62521700
H	-3.02960200	2.37711900	0.19484000
H	-1.25706300	-2.21289900	-0.44383900
H	-3.62260900	-1.72598200	-0.94781300
C	0.63279500	-0.49074900	0.49479000
C	1.07664900	-0.22264100	1.91031300
H	0.76236500	0.76825600	2.23839500
H	0.60575600	-0.97473100	2.55288700
H	2.16349500	-0.30979100	1.99219600
H	-0.64971100	1.90117500	0.66795800
H	1.19762300	0.73475100	-0.10113800
N	1.18837500	-1.55458300	-0.09198900
H	0.91462100	-1.82061800	-1.03131300
H	2.10366600	-1.86588800	0.21363700
H	1.64856900	1.92965300	-1.59885500
H	2.22450200	2.38584700	0.31474400
C	3.33003300	0.60031600	-0.69135200
N	4.21015100	-0.15341000	-0.78327700
B	2.08713900	1.55474400	-0.54328500

6.4. Optimized Products

Table S22. Optimized structure of ethyl-phenyl-amine in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -366.03688 Hartrees
Number of imaginary frequencies = 0

C	-3.55971600	0.21696200	-0.15033300

C	-2.72525400	1.33033200	-0.05776200
C	-1.34772000	1.16080200	0.09335500
C	-0.78592000	-0.11762100	0.15765600
C	-1.63159100	-1.22959800	0.06461900
C	-3.00755300	-1.06426700	-0.08937900
H	-4.63142600	0.34509400	-0.27221700
H	-3.14393300	2.33153600	-0.10858400
H	-1.20553900	-2.22809200	0.10913300
H	-3.65085300	-1.93689800	-0.16170300
C	0.70586000	-0.28532600	0.37775600
C	1.00125700	-0.62714900	1.83783700
H	0.63089300	0.15935600	2.50215800
H	0.51881900	-1.57201800	2.11095100
H	2.08077900	-0.72998900	1.99469200
H	-0.69943100	2.03206200	0.15933900
N	1.23283100	-1.35913200	-0.47377300
H	1.11855700	-1.11004500	-1.45439400
H	2.23423200	-1.44843700	-0.31353600
H	1.17836800	0.68315700	0.15463600

Table S23. Optimized structure of cyano-borane in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -118.85711 Hartrees Number of imaginary frequencies = 0			
B	-4.05753100	0.28344700	0.00000000
H	-4.61400100	1.32654500	0.00000000
H	-4.61400100	-0.75965100	0.00000000
C	-2.50738700	0.28344700	0.00000000
N	-1.34864500	0.28344700	0.00000000

Table S24. Optimized structure of acetate in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -228.595125 Hartrees Number of imaginary frequencies = 0			
O	-3.57060000	0.19449800	-1.34338600
C	-4.41114100	0.38447700	-0.42001200
O	-4.41102400	1.37511200	0.36460100
C	-5.53580300	-0.63401500	-0.26135600
H	-5.80740700	-0.75302800	0.79016900
H	-6.41693900	-0.25864200	-0.79400000
H	-5.26235700	-1.60061500	-0.68905500

Table S25. Optimized structure of water in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -76.435605 Hartrees Number of imaginary frequencies = 0			
O	-4.34004600	0.18975900	-1.10680300
H	-3.37497700	0.22781800	-1.10680300
H	-4.62627500	1.11213100	-1.10680300

6.5. Optimized Ion Pair Conformers

Table S26. Optimized structure of hydroxy-ammonium ion/acetate ion pair with lower energy in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -670.150309 Hartrees Number of imaginary frequencies = 0			
C	-4.45063800	-0.14092300	0.15115000
C	-3.68645000	-1.30142100	0.25344500
C	-2.29525600	-1.24085300	0.15118300
C	-1.65928000	-0.01593500	-0.05673400
C	-2.43056700	1.14751100	-0.16276100
C	-3.81807100	1.08589300	-0.05663700
H	-5.53253600	-0.18975400	0.23137100
H	-4.17059500	-2.26030900	0.41378900
H	-1.95473400	2.11162900	-0.32966600
H	-4.40451900	1.99610300	-0.13908300
C	-0.14270000	0.05838900	-0.18185500
C	0.30257200	0.65926500	-1.51121600
H	-0.06031900	0.01900500	-2.31876700
H	-0.09870900	1.66616600	-1.65058500
H	1.39526200	0.70258300	-1.55415300
O	0.41089100	-1.19186900	0.04046000
N	0.39194900	0.95609600	0.92191400
H	0.05848400	1.92076300	0.83981100
H	1.47086100	0.94610200	0.86576500
H	1.41103100	-1.15560800	-0.12257700
O	2.96770700	-1.10133600	-0.30592600
C	3.59163300	-0.09188500	0.13377300
C	5.09525900	-0.07696800	-0.03296000
H	5.51763600	-0.99868500	0.37598300
H	5.33134700	-0.05115900	-1.10133600
H	5.54264000	0.78752300	0.45825400
O	3.03580500	0.90174900	0.68902500
H	-1.70391000	-2.14602200	0.23119300
H	0.10017700	0.59218300	1.83380200

Table S27. Optimized structure of hydroxy-ammonium ion/acetate ion pair with higher energy in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -670.147195 Hartrees Number of imaginary frequencies = 0			
C	4.31890500	-0.73062800	-0.19757300
C	3.30690700	-1.64745600	0.09256000
C	1.99355600	-1.21179300	0.24850200
C	1.67780400	0.14619800	0.11988900
C	2.69193500	1.05955000	-0.17305700
C	4.00824400	0.62088600	-0.33005800
H	5.34366400	-1.06941800	-0.31778400
H	3.54028600	-2.70268400	0.19893900
H	2.47178500	2.11699600	-0.27662500
H	4.78961100	1.34109800	-0.55336600
C	0.22435400	0.57812500	0.26461800
C	0.01375900	2.07030700	0.45898300
H	0.57020800	2.40639300	1.33662200
H	0.33944700	2.63915000	-0.41508000
H	-1.05214100	2.26175700	0.61694200
O	-0.32883600	-0.16540200	1.31973300
N	-0.52299700	0.17441200	-0.98051400
H	-0.15132900	0.65915600	-1.80202700
H	-1.61602600	0.40395100	-0.85121200
H	-1.22619700	0.15307000	1.50856500
O	-3.00194400	0.69859300	-0.54748100
C	-3.61313300	-0.38263200	-0.21856800
C	-5.06029900	-0.22659600	0.20087200
H	-5.10995200	0.40866800	1.09060600
H	-5.61936100	0.27606100	-0.59356700
H	-5.51498100	-1.19383200	0.41740900
O	-3.07655000	-1.51007100	-0.22634900
H	1.20977300	-1.92870100	0.47715300
H	-0.42736800	-0.83327400	-1.13721000

Table S28. Optimized structure of iminium/acetate ion pair with lower energy in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -593.751923 Hartrees Number of imaginary frequencies = 0			
C	-4.36987600	-0.78972900	0.03653000
C	-3.31264900	-1.66347400	-0.22408200
C	-2.00630900	-1.18811200	-0.25211900
C	-1.74727300	0.17166800	-0.02253200
C	-2.81451700	1.04794700	0.21713000

C	-4.11941900	0.56439700	0.25613200
H	-5.38892300	-1.16395800	0.06018600
H	-3.50652300	-2.71445100	-0.41337500
H	-2.63035100	2.10331700	0.38939000
H	-4.93978800	1.24653300	0.45533000
C	-0.36393800	0.69120600	-0.04119400
C	-0.10691100	2.13679600	-0.30925700
H	-0.65703700	2.45932700	-1.19660500
H	-0.46593600	2.72737800	0.54033200
H	0.95953300	2.32311000	-0.43981600
N	0.64117100	-0.08174100	0.17715300
H	0.48404600	-1.06094700	0.40748000
H	1.69208200	0.26381100	0.12144600
H	-1.19817500	-1.87585100	-0.48458400
O	3.41181300	-1.52064800	0.19639900
C	3.84497700	-0.35551600	0.06180700
O	3.09372400	0.68332600	0.02717700
C	5.33365500	-0.10729200	-0.07652300
H	5.66233000	0.58646300	0.70269700
H	5.89843600	-1.03734600	-0.00338200
H	5.53136700	0.36603500	-1.04313100

Table S29. Optimized structure of iminium/acetate ion pair with higher energy in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -593.751018 Hartrees Number of imaginary frequencies = 0			
C	-3.15840700	-1.91541500	-0.06974900
C	-1.87714400	-2.02652300	0.47315900
C	-1.05027100	-0.91086000	0.54677700
C	-1.50440600	0.33126900	0.07690400
C	-2.79981600	0.44136100	-0.44798000
C	-3.61835700	-0.68137300	-0.52898900
H	-3.80061000	-2.78923400	-0.12706000
H	-1.52298800	-2.98259100	0.84540900
H	-3.16791500	1.39653600	-0.80741700
H	-4.61572800	-0.59083700	-0.94737600
C	-0.64021200	1.52604000	0.14282700
C	-1.24345500	2.89041000	0.10146000
H	-1.65647600	3.06921500	-0.89709600
H	-2.06332200	2.96426600	0.82003100
H	-0.49243800	3.65270800	0.31149100
N	0.63828800	1.39375400	0.22854700
H	1.20567000	0.45426800	0.16331200
H	1.20120500	2.24010000	0.29540200

H	-0.06303800	-1.00651500	0.98748800
O	2.10402700	-0.73036400	0.01964100
C	3.31190900	-0.32145400	-0.10833100
O	3.64375300	0.88418500	-0.07997000
C	4.36320300	-1.39569200	-0.30368700
H	4.33550400	-2.08955200	0.54171400
H	4.13101400	-1.96851100	-1.20654300
H	5.36059900	-0.96327900	-0.39090000

7. OPTIMIZED GEOMETRIES FOR THE 4-NITROACETOPHENONE'S AMINATION

Table S30. Optimized structure of 4-nitroacetophenone in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -589.237071 Hartrees Number of imaginary frequencies = 0			
C	1.41076600	0.00407800	-0.00007900
C	0.78397100	-1.23818900	0.00029700
C	-0.60378700	-1.26669100	0.00016100
C	-1.33824700	-0.07497400	-0.00024800
C	-0.67553200	1.15704400	-0.00061300
C	0.71469400	1.20592000	-0.00058200
H	1.36645200	-2.15168600	0.00067800
H	-1.23148900	2.08808400	-0.00098300
H	1.24298800	2.15160200	-0.00087600
C	-2.84171200	-0.15690700	-0.00018500
C	-3.63858100	1.11488300	0.00177900
H	-4.70156300	0.87347900	0.00234200
H	-3.39421100	1.71248600	0.88598600
H	-3.39566200	1.71423300	-0.88165300
O	-3.38486800	-1.25099300	-0.00162300
H	-1.12690400	-2.21679900	0.00044000
N	2.87963800	0.04757000	0.00011400
O	3.42427800	1.13967700	-0.00087300
O	3.48727400	-1.01060600	0.00125800

Table S31. Optimized TSS1 (nucleophilic attack) for pathway a in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -645.746119 Hartrees Number of imaginary frequencies = 1			
C	-1.74843000	-0.00738400	-0.03025800
C	-1.13716800	-1.25519100	0.00451900
C	0.25171800	-1.30674600	-0.05022400
C	1.00826500	-0.13568100	-0.13661000

C	0.35805600	1.10443500	-0.17083200
C	-1.02766500	1.18020200	-0.11671300
H	-1.73098600	-2.15938500	0.06965000
H	0.92831700	2.02591200	-0.23075900
H	-1.53873900	2.13529500	-0.13998400
C	2.53139700	-0.26213100	-0.21767600
C	3.22210600	0.72352900	-1.14644200
H	2.97527500	0.43691700	-2.17499700
H	2.92012000	1.76091900	-0.99318800
H	4.30308400	0.63652100	-1.01175600
O	3.02346500	-1.41581300	-0.10478400
N	2.92363700	0.62787600	1.46144500
H	2.61750400	1.59303900	1.58219200
H	3.93801300	0.59117800	1.55893900
H	0.76023600	-2.26434300	-0.03004600
H	2.51231400	0.05932500	2.20096200
N	-3.20970600	0.06200300	0.02612500
O	-3.73982700	1.16251300	-0.00669400
O	-3.83767900	-0.98304200	0.10415500

Table S32. Optimized TSS1 (nucleophilic attack) for pathway c in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -874.788601 Hartrees Number of imaginary frequencies = 1			
C	-3.33210700	-0.10053300	-0.06359700
C	-2.52735200	-1.23594900	-0.02885000
C	-1.15318400	-1.06487800	-0.11585100
C	-0.59999400	0.21631400	-0.22309800
C	-1.43596900	1.33567900	-0.25689400
C	-2.81719400	1.18411700	-0.18025800
H	-2.96701600	-2.22213500	0.06111000
H	-1.02606500	2.33518400	-0.34953200
H	-3.47665400	2.04331600	-0.21002900
C	0.90171600	0.34379000	-0.33285500
C	1.50756400	1.71172200	-0.50733300
H	1.33259500	2.02515400	-1.54387000
H	1.07606100	2.45379400	0.16406500
H	2.58484100	1.65370600	-0.33928300
O	1.53304100	-0.66835200	-0.71297400
N	1.20479600	0.29177200	1.81112300
H	0.87631700	1.05467400	2.39933200
H	2.22209100	0.23486500	1.86721300
H	3.03745300	-0.59765300	-0.88675500
O	4.05093800	-0.60720000	-1.05941500

C	4.72986300	-0.31957600	0.03626000
C	6.21624400	-0.32102500	-0.16424900
H	6.72329100	-0.06826200	0.76596600
H	6.53291800	-1.31006100	-0.50720400
H	6.47722600	0.40074800	-0.94318500
O	4.18705300	-0.07631800	1.10870300
H	-0.49799900	-1.92938500	-0.09735900
H	0.81304900	-0.57838200	2.16636200
N	-4.78547600	-0.26783100	0.02381500
O	-5.48715300	0.73086300	-0.01983300
O	-5.23148800	-1.39913400	0.13713800

Table S33. Optimized structure of the zwitterionic intermediate for pathway a in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -645.744108 Hartrees Number of imaginary frequencies = 0			
C	1.75358700	0.00483900	-0.01341600
C	1.12166200	1.24271200	-0.01709700
C	-0.26933800	1.27068600	-0.03345100
C	-1.01061400	0.08762800	-0.04777400
C	-0.33771000	-1.14243400	-0.05211500
C	1.05017700	-1.19590600	-0.03051000
H	1.70186500	2.15801500	-0.00570600
H	-0.88984000	-2.07833600	-0.07066500
H	1.57553800	-2.14355000	-0.02861200
C	-2.55384300	0.18597400	-0.08102100
C	-3.13343600	-0.63609500	-1.24118400
H	-2.81418000	-0.16880600	-2.17704000
H	-2.81204900	-1.68183800	-1.24493100
H	-4.22600200	-0.59593500	-1.18762400
O	-3.03518700	1.40280200	0.02543700
N	-3.00658600	-0.61928200	1.23554500
H	-2.73729000	-1.60638800	1.27011900
H	-4.02712000	-0.55737900	1.28628800
H	-0.79497000	2.21882300	-0.03509000
H	-2.62477900	-0.14267700	2.05689800
N	3.21601200	-0.03947800	0.00985200
O	3.76365300	-1.13211300	0.01731600
O	3.82902600	1.01743200	0.02199700

Table S34. Optimized structure of the hydroxi-ammonium ion in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -874.804899 Hartrees Number of imaginary frequencies = 0			
C	3.32541700	-0.05170900	-0.03513000
C	2.60824000	-1.23909200	-0.09665800
C	1.22022400	-1.17727100	-0.01756900
C	0.57328700	0.05260300	0.12011800
C	1.32764700	1.23104000	0.18188400
C	2.71311100	1.18955300	0.10292500
H	3.11958200	-2.18838800	-0.20389300
H	0.84267300	2.19686700	0.29516600
H	3.30384100	2.09657500	0.14885500
C	-0.94775400	0.11029800	0.22308300
C	-1.40911200	0.76646100	1.52067900
H	-1.03736200	0.17507800	2.36069700
H	-1.03287600	1.78855000	1.61039800
H	-2.50276600	0.78547000	1.55379000
O	-1.46879800	-1.16129200	0.05954700
N	-1.48523700	0.94151500	-0.92520600
H	-1.18463700	1.91959800	-0.87825400
H	-2.57480400	0.89718600	-0.88397900
H	-2.47237700	-1.14127800	0.21156200
O	-4.02633500	-1.10910100	0.37330400
C	-4.65647300	-0.15216000	-0.15904500
C	-6.16732200	-0.16825700	-0.11291900
H	-6.55328800	0.83915300	0.05603900
H	-6.53496200	-0.50959700	-1.08664400
H	-6.53084400	-0.84942200	0.65726900
O	-4.10215700	0.82033900	-0.75781400
H	0.63951200	-2.09040300	-0.06249600
H	-1.16820000	0.54889100	-1.81671400
N	4.78705300	-0.10774000	-0.11842000
O	5.41082600	0.93992600	-0.04684400
O	5.31773900	-1.19906100	-0.25577000

Table S35. Optimized structure of the hemiaminal in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -645.764001 Hartrees Number of imaginary frequencies = 0			
C	-1.74828600	0.00381400	-0.00328000
C	-1.09469300	1.22967800	-0.00306700
C	0.29706800	1.23817800	-0.01511100
C	1.01726600	0.03987100	-0.03394200

C	0.32300600	-1.17765900	-0.03094800
C	-1.06406600	-1.20874600	-0.01516500
H	-1.65855600	2.15505500	0.00721700
H	0.86923400	-2.11657400	-0.04367000
H	-1.60444500	-2.14787700	-0.01330700
C	2.54697200	0.02070200	-0.02329000
C	3.04702600	-0.44050700	1.34455900
H	2.66511400	0.22524700	2.12280400
H	2.71714200	-1.46102400	1.56026400
H	4.14148400	-0.41389600	1.35442100
O	2.96627300	1.35136700	-0.27572300
N	3.12650200	-0.83401700	-1.04983300
H	3.02870600	-1.81600300	-0.80368600
H	3.93393500	1.34067000	-0.31961300
H	0.82198100	2.18580300	-0.01250300
H	2.65404400	-0.68952300	-1.94034800
N	-3.21023300	-0.01486200	0.01028100
O	-3.77694800	-1.09789500	0.00918700
O	-3.80535900	1.05256600	0.02237900

Table S36. Optimized TSS2 (lowest energy) in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -874.77894 Hartrees Number of imaginary frequencies = 1			
C	-3.31665200	-0.06417600	-0.01321600
C	-2.52823300	-1.18510500	0.22790200
C	-1.15807900	-1.00580400	0.35191500
C	-0.59826800	0.27245400	0.23772900
C	-1.41560400	1.37657100	-0.01273400
C	-2.79251100	1.21474800	-0.13745000
H	-2.97430400	-2.16908000	0.30849400
H	-0.99318800	2.37102400	-0.10438500
H	-3.43938400	2.06298500	-0.32663200
C	0.88134800	0.45217000	0.40967700
C	1.51900300	1.74227700	-0.02011700
H	1.20559800	2.02656900	-1.02511600
H	1.21860400	2.52434800	0.68469500
H	2.60609000	1.64397400	0.01490300
O	1.42354700	-0.63157000	-1.05345700
N	1.42496700	-0.14830500	1.46285600
H	0.96336800	-0.94876300	1.87863900
H	2.44506300	-0.08803500	1.56206400
H	1.13632100	-0.26130100	-1.90372600
O	3.90481300	-0.53067600	-1.09116700
C	4.66397800	-0.28582600	-0.09227600

C	6.14967400	-0.25063100	-0.38536200
H	6.36103800	0.60429800	-1.03563000
H	6.73162100	-0.15843900	0.53219300
H	6.44266500	-1.15530100	-0.92463700
O	4.25918100	-0.06624100	1.07320800
H	-0.52379900	-1.87179900	0.51560000
H	2.48195600	-0.58319600	-1.03169700
N	-4.76714700	-0.24354000	-0.14685400
O	-5.45195100	0.74097300	-0.37397700
O	-5.22238100	-1.36929000	-0.02375400

Table S37. Optimized TSS2 (highest energy) in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -874.77728 Hartrees
Number of imaginary frequencies = 1

C	1.83105000	-0.78769700	-0.16634100
C	1.17723300	-1.42156000	0.88471500
C	-0.20598800	-1.51709000	0.83038200
C	-0.90837100	-0.99251700	-0.26078300
C	-0.22086900	-0.38175900	-1.31112200
C	1.16498500	-0.26929200	-1.26844000
H	1.73269800	-1.80354400	1.73280700
H	-0.75459400	0.03014100	-2.16000700
H	1.71029800	0.21740500	-2.06837900
C	-2.40769700	-1.03348800	-0.27425400
C	-3.15683900	-0.23194700	-1.29823600
H	-2.78553500	0.79216300	-1.34359600
H	-3.02460700	-0.71237000	-2.27335000
H	-4.22271900	-0.22897600	-1.05703200
O	-2.59677100	0.15951800	1.21211700
N	-2.97119300	-2.17566700	0.09800100
H	-2.47926800	-2.85277800	0.66826800
H	-3.97535600	-2.28728200	0.01963400
H	-1.79053900	0.86695000	1.27739000
H	-0.73225900	-1.95939000	1.67085800
H	-3.41996500	0.66190800	1.10572400
O	-0.63944300	1.65002900	1.39273500
C	-0.38881800	2.34896100	0.34597400
O	-1.23213800	2.60224700	-0.53921100
C	1.01688000	2.90496000	0.23180700
H	1.74898700	2.20039500	0.63447500
H	1.25543900	3.14604300	-0.80570400
H	1.07325900	3.82509300	0.82427000
N	3.28850600	-0.63706900	-0.09515400
O	3.83962300	0.04710100	-0.94280900

O	3.88292500	-1.19864800	0.81123000

Table S38. Optimized structure of iminium in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -569.77848 Hartrees Number of imaginary frequencies = 0			
C	1.45188200	0.00026300	-0.00518000
C	0.81369700	-1.22469100	0.14377800
C	-0.57426900	-1.24363900	0.13429400
C	-1.29245600	-0.04855800	-0.01499400
C	-0.61661800	1.17202700	-0.14333100
C	0.77208100	1.20198500	-0.15045000
H	1.38366500	-2.13706500	0.27052900
H	-1.16347800	2.10182600	-0.25178000
H	1.31030700	2.13561700	-0.25965400
C	-2.76985000	-0.05178100	-0.01273200
C	-3.53322600	1.15464500	0.39295200
H	-3.13056200	1.55763800	1.32484800
H	-3.41117700	1.91773000	-0.38447400
H	-4.59428400	0.92916000	0.50057500
N	-3.41037000	-1.11145400	-0.37396400
H	-2.94038500	-1.94558900	-0.72090700
H	-4.42825100	-1.13639500	-0.34420200
H	-1.08185900	-2.19205300	0.27927800
N	2.92469500	0.02703600	0.00371400
O	3.47837100	1.10078300	-0.15787100
O	3.51516600	-1.02596400	0.17181000

Table S39. Optimized TSS3 in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -689.371696 Hartrees Number of imaginary frequencies = 1			
C	-2.38618500	0.02654600	-0.05500200
C	-1.62204300	1.11497500	0.35551900
C	-0.25792800	0.93061600	0.52254500
C	0.32219300	-0.31990100	0.27959600
C	-0.47335300	-1.39654300	-0.12261900
C	-1.84377500	-1.22718000	-0.29708200
H	-2.08213700	2.07955300	0.53313000
H	-0.03788500	-2.37724300	-0.28260500
H	-2.47211600	-2.05304300	-0.60842200
C	1.78892400	-0.53493500	0.52549300
C	2.32420700	-0.24113400	1.90106000
H	1.96435000	0.72091500	2.26542400

H	1.96345200	-1.03104900	2.56937000
H	3.41722200	-0.24807700	1.89221900
H	0.36330700	1.76900800	0.82429500
H	2.21129400	0.79569100	-0.10427100
N	2.37476400	-1.52134200	-0.14006500
H	2.03344000	-1.80994000	-1.05089200
H	3.32371400	-1.79091300	0.09673200
H	2.46082500	2.04411500	-1.60896500
H	3.17413200	2.49504400	0.25536900
C	4.28504400	0.79807200	-0.88377900
N	5.19920000	0.10455300	-1.07108800
B	3.00191300	1.66736900	-0.60153000
N	-3.83021000	0.21332300	-0.23884900
O	-4.49420600	-0.74425900	-0.60200400
O	-4.30053800	1.31804200	-0.02026100

Table S40. Optimized structure of ethyl-4-nitrophenyl-amine in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -570.533294 Hartrees Number of imaginary frequencies = 0			
C	-1.47938000	0.00314200	-0.02251500
C	-0.88958800	1.24039400	-0.26581700
C	0.49546000	1.30036800	-0.34623600
C	1.27943100	0.15078000	-0.18416600
C	0.65020600	-1.07597700	0.05954100
C	-0.73479000	-1.16076800	0.14197500
H	-1.49928000	2.12704100	-0.39387300
H	1.25170600	-1.97019900	0.18235700
H	-1.22832700	-2.10715100	0.33018800
C	2.78988400	0.26977500	-0.21842700
C	3.31685100	0.55648100	1.18903200
H	2.88502800	1.47968500	1.58588200
H	3.06264100	-0.26946400	1.86198600
H	4.40621700	0.66724800	1.16639300
H	0.97740600	2.25476000	-0.54139000
N	3.39897700	-0.96728900	-0.71141900
H	3.14605400	-1.11596600	-1.68660600
H	4.41149600	-0.86773700	-0.68776700
H	3.03199900	1.13412500	-0.85438200
N	-2.93560100	-0.07657500	0.05946500
O	-3.58392800	0.94980200	-0.08712900
O	-3.44819900	-1.16610900	0.27219900

8. OPTIMIZED GEOMETRIES FOR THE 4-(THIOMETHYL)ACETOPHENONE'S AMINATION

Table S41. Optimized structure of 4-(thiomethyl)acetophenone in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -822.214597 Hartrees Number of imaginary frequencies = 0			
C	1.31514200	-0.29148800	-0.00046600
C	0.77096800	1.00023200	-0.00067700
C	-0.60872000	1.16950600	-0.00045500
C	-1.47223100	0.06879500	-0.00004900
C	-0.92138200	-1.22127600	0.00009400
C	0.45421700	-1.40096100	-0.00011900
H	1.41025000	1.87573900	-0.00104100
H	-1.56258500	-2.09739200	0.00038100
H	0.86472000	-2.40721200	0.00007800
C	-2.94530300	0.29812100	0.00014600
C	-3.86850000	-0.88982600	0.00090500
H	-3.68942200	-1.51076600	-0.88275900
H	-3.68790700	-1.51115700	0.88395500
H	-4.90193900	-0.54241600	0.00180900
O	-3.39522600	1.43929800	-0.00047400
H	-1.02552300	2.17211400	-0.00061200
S	3.04875600	-0.62815700	-0.00066900
C	3.78840700	1.02289100	0.00164800
H	3.51415100	1.57975700	0.89987000
H	4.86818500	0.85993100	0.00271500
H	3.51619700	1.58155900	-0.89606000

Table S42. Optimized TSS1 (nucleophilic attack) for pathway a in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -878.719349 Hartrees Number of imaginary frequencies = 1			
C	1.66032100	-0.27997100	-0.04673600
C	1.12248400	1.00913400	-0.03127900
C	-0.26216600	1.18750900	-0.07302800
C	-1.13198300	0.10102900	-0.13377900
C	-0.58360400	-1.18887900	-0.15553500
C	0.79070000	-1.38068300	-0.10945400
H	1.76435600	1.88238900	0.01060400
H	-1.22925400	-2.06238700	-0.19713600
H	1.19288400	-2.39075000	-0.12063500
C	-2.63442800	0.35740100	-0.19408000
C	-3.40935200	-0.54247200	-1.14710500

H	-3.14778800	-0.24481100	-2.16880000
H	-3.18454900	-1.60436200	-1.02853900
H	-4.48053900	-0.37959500	-1.00176100
O	-3.03060300	1.55459700	-0.07071400
N	-3.11550500	-0.49959900	1.43953700
H	-2.88078500	-1.48661400	1.54278000
H	-4.12435000	-0.38855700	1.53965700
H	-0.67263400	2.19264800	-0.06261300
H	-2.66043800	0.02456500	2.18623600
S	3.39710600	-0.63295600	0.00757000
C	4.14178000	1.01264000	0.10577000
H	5.22021200	0.84622900	0.15053900
H	3.91273700	1.60680300	-0.78128000
H	3.82729100	1.53789900	1.01013900

Table S43. Optimized TSS1 (nucleophilic attack) for pathway c in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -1107.764571 Hartrees Number of imaginary frequencies = 1			
C	-3.28644700	0.15480300	-0.05986400
C	-2.54526600	-1.02501200	0.05518900
C	-1.15527500	-0.98633500	-0.05067400
C	-0.48046500	0.21406200	-0.27313100
C	-1.22904500	1.39339500	-0.38763600
C	-2.61190200	1.36706600	-0.28077900
H	-3.03290700	-1.97881900	0.22315700
H	-0.73738800	2.34848400	-0.54508100
H	-3.17372200	2.29361100	-0.36745800
C	1.01679900	0.19570800	-0.40194000
C	1.68029300	1.23328100	-1.27345400
H	1.52147500	0.93021800	-2.31566600
H	1.27099200	2.23351900	-1.13665100
H	2.75414900	1.25202100	-1.07462800
O	1.60372800	-0.90144900	-0.21103400
N	1.41926900	1.22748700	1.43604700
H	1.16625700	2.20714400	1.54665500
H	2.43100100	1.12620000	1.52275200
H	3.05826500	-1.00191500	-0.42017200
O	4.07279000	-1.16074900	-0.58959300
C	4.82340400	-0.40195200	0.18371000
C	6.29594900	-0.59600400	-0.03072800
H	6.55279200	-1.64425300	0.14536700
H	6.54254200	-0.36309700	-1.07053700
H	6.86432900	0.04651500	0.64049700

O	4.35534800	0.38829000	0.99833200
H	-0.58694400	-1.90711300	0.03505100
H	0.97528400	0.69492700	2.18132300
S	-5.05117400	0.23198700	0.05489000
C	-5.51713000	-1.49240800	0.34053700
H	-6.60632600	-1.49361200	0.41957500
H	-5.22278500	-2.12745900	-0.49766500
H	-5.09353500	-1.86894100	1.27389200

Table S44. Optimized structure of the zwitterionic intermediate for pathway a in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -878.71823 Hartrees Number of imaginary frequencies = 0			
C	1.66446700	-0.28511600	-0.01808300
C	1.10893600	0.99611300	-0.03483400
C	-0.27928000	1.15621200	-0.05182600
C	-1.13615600	0.05906400	-0.05680300
C	-0.56899900	-1.22310000	-0.04763200
C	0.80885700	-1.39774200	-0.02435900
H	1.73983400	1.87845300	-0.03461700
H	-1.20252700	-2.10755100	-0.05405500
H	1.22345200	-2.40283900	-0.01224900
C	-2.65955200	0.28780300	-0.08747200
C	-3.32754000	-0.51331000	-1.21385500
H	-2.98257800	-0.10404500	-2.16778700
H	-3.09609200	-1.58249300	-1.19026300
H	-4.41230700	-0.37937900	-1.15026600
O	-3.04188900	1.54338500	-0.00931100
N	-3.17276400	-0.44446900	1.25762600
H	-2.94889300	-1.44065500	1.32956500
H	-4.18881500	-0.33066200	1.30339500
H	-0.70476600	2.15473400	-0.06346700
H	-2.76592800	0.04286000	2.05993500
S	3.40791300	-0.61328200	0.01066100
C	4.13002200	1.04509700	0.03060300
H	5.21160800	0.89589900	0.05437500
H	3.87040900	1.60336700	-0.87124500
H	3.82993600	1.59889600	0.92276600

Table S45. Optimized structure of the hydroxi-ammonium ion in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -1107.779576 Hartrees Number of imaginary frequencies = 0			
C	-3.26745700	0.21870600	0.00324400
C	-2.57391200	-0.99261100	0.04261700
C	-1.17854700	-1.00540500	-0.02443600
C	-0.45491900	0.17928700	-0.13382300
C	-1.15598900	1.39187700	-0.17842400
C	-2.54161300	1.41519600	-0.10784700
H	-3.10033300	-1.93699400	0.12542000
H	-0.62342900	2.33620500	-0.26946400
H	-3.06346000	2.36806900	-0.14267700
C	1.06482500	0.16155100	-0.21350800
C	1.59482800	0.83756600	-1.47376300
H	1.22492600	0.28857600	-2.34290100
H	1.26037000	1.87586000	-1.54245900
H	2.68916700	0.81587100	-1.47701000
O	1.52535600	-1.13867000	-0.08201100
N	1.62299400	0.92654700	0.97630100
H	1.36207500	1.91674900	0.96111000
H	2.70003500	0.83758900	0.95493300
H	2.52892700	-1.15904000	-0.22007400
O	4.09174500	-1.20173500	-0.37184100
C	4.76633000	-0.29064100	0.18845400
C	6.27183100	-0.33212800	0.04772500
H	6.62194200	-1.35710700	-0.08432800
H	6.54508400	0.24218100	-0.84446200
H	6.75540400	0.12837300	0.91090100
O	4.25961300	0.67570300	0.83404100
H	-0.65544200	-1.95462300	0.00839900
H	1.26933300	0.51527600	1.84520300
S	-5.03260900	0.35733400	0.08518700
C	-5.56762200	-1.36587200	0.21104300
H	-6.65789900	-1.33316800	0.26286200
H	-5.27225400	-1.93856200	-0.67067400
H	-5.18389200	-1.83596100	1.11892500

Table S46. Optimized structure of the hemiaminal in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -878.737038 Hartrees Number of imaginary frequencies = 0			
C	-1.66355600	-0.29161100	-0.00488900
C	-1.08388800	0.97812400	-0.01500600

C	0.30738400	1.11573900	-0.02916400
C	1.14394400	0.00073800	-0.04122200
C	0.55251600	-1.26952700	-0.02672900
C	-0.82768400	-1.41902300	-0.00897700
H	-1.69717500	1.87268500	-0.01224100
H	1.17560900	-2.16077600	-0.03165100
H	-1.25968300	-2.41672400	-0.00040700
C	2.66713300	0.12488300	-0.02260900
C	3.20429700	-0.18887200	1.37319100
H	2.76150400	0.49565100	2.10144000
H	2.96053300	-1.21543000	1.66384100
H	4.29273300	-0.06818200	1.38287000
O	2.96774600	1.47081600	-0.36640500
N	3.34247000	-0.73758200	-0.98473000
H	3.34774900	-1.70235800	-0.66264200
H	3.93208000	1.53506900	-0.42998100
H	0.73499200	2.11263100	-0.03432900
H	2.85460700	-0.71639600	-1.87850600
S	-3.41340000	-0.58664900	0.01280700
C	-4.10288200	1.08564000	0.01878400
H	-5.18742000	0.95788900	0.02968200
H	-3.80287300	1.63667000	0.91269600
H	-3.82108300	1.63564900	-0.88160900

Table S47. Optimized TSS2 (lowest energy) in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -1107.755421 Hartrees Number of imaginary frequencies = 1			
C	-3.24566300	-0.29755100	0.00573600
C	-2.37601100	-1.39274500	0.14810700
C	-1.01327400	-1.19130300	0.29413000
C	-0.47934300	0.10560200	0.29871900
C	-1.34193500	1.18939000	0.14494700
C	-2.71736200	0.99545100	0.00602900
H	-2.76951800	-2.40574900	0.13606300
H	-0.95818800	2.20468200	0.14176400
H	-3.35831700	1.86315400	-0.10125100
C	0.98920700	0.31317800	0.48458100
C	1.57349100	1.67444300	0.22240300
H	1.25528600	2.06632600	-0.74429000
H	1.23423000	2.35187800	1.01252600
H	2.66391500	1.62074000	0.25782400
O	1.58886800	-0.56316400	-1.05796500
N	1.56619500	-0.37527500	1.47605100
H	1.14687000	-1.24588100	1.77968700

H	2.58499400	-0.30395100	1.55379800
H	1.23153900	-0.14890900	-1.86008600
O	4.04364600	-0.26995600	-1.18854700
C	4.80810000	-0.14562800	-0.16984600
C	6.28234400	0.02810800	-0.47038700
H	6.62464800	-0.78492500	-1.11648000
H	6.42602100	0.96576700	-1.01637500
H	6.87295000	0.04759100	0.44602300
O	4.41299500	-0.14901000	1.01798700
H	-0.35841300	-2.05463300	0.37732700
H	2.64719400	-0.43504300	-1.07628200
S	-4.96733900	-0.66430000	-0.17251200
C	-5.71504300	0.97261000	-0.35570500
H	-6.78520200	0.79476000	-0.48115900
H	-5.55985800	1.58243400	0.53666300
H	-5.33522300	1.48518600	-1.24199500

Table S48. Optimized TSS2 (highest energy) in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -1107.754923 Hartrees Number of imaginary frequencies = 1			
C	-1.87771800	-0.52734700	0.40311500
C	-1.33486100	-1.23967900	-0.67299000
C	0.03400300	-1.48419300	-0.72485500
C	0.88392700	-1.03081700	0.28702300
C	0.33836800	-0.32311500	1.36206400
C	-1.02738500	-0.07668600	1.42278300
H	-1.96117200	-1.59509100	-1.48333000
H	0.97333600	0.05054100	2.15863000
H	-1.43208500	0.47884700	2.26491300
C	2.35918300	-1.24515600	0.18681100
C	3.27003200	-0.56602500	1.17079700
H	3.04214800	0.49699100	1.25116400
H	3.13871500	-1.04252700	2.14760000
H	4.31027500	-0.69585200	0.86127800
O	2.62861000	-0.10801700	-1.29120100
N	2.75719900	-2.45585900	-0.21369800
H	2.15134200	-3.04641500	-0.76915300
H	3.74748100	-2.66567800	-0.24851100
H	1.91668200	0.70293400	-1.32044000
H	0.43467700	-1.99938500	-1.59439800
H	3.51555200	0.28193600	-1.23847600
O	0.89629200	1.63748400	-1.38716700
C	0.82124400	2.37949500	-0.34230100

O	1.75242700	2.52316600	0.47678900
C	-0.47760800	3.13482700	-0.14696700
H	-0.42027800	4.07182000	-0.71242100
H	-1.32470100	2.56024000	-0.52856600
H	-0.62802400	3.37715000	0.90677100
S	-3.59730200	-0.14395600	0.56589500
C	-4.31588500	-0.84859300	-0.93738200
H	-4.18155900	-1.93170300	-0.97240000
H	-5.38381800	-0.62634100	-0.88484100
H	-3.90056900	-0.38047800	-1.83219300

Table S49. Optimized structure of iminium in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -802.762522 Hartrees
Number of imaginary frequencies = 0

C	1.37208600	-0.29573800	-0.00014500
C	0.56176000	-1.44846500	0.00144700
C	-0.81373500	-1.33810500	0.00123000
C	-1.43306600	-0.07146800	-0.00036300
C	-0.61848700	1.07132000	-0.00202400
C	0.76577800	0.96699900	-0.00211800
H	1.01884200	-2.43367800	0.00307200
H	-1.05926700	2.06240300	-0.00344800
H	1.35887000	1.87372500	-0.00356000
C	-2.88352600	0.08439400	-0.00006100
C	-3.51667500	1.43355000	0.00365600
H	-3.19101600	1.98988700	0.88716400
H	-3.19759900	1.99117800	-0.88154200
H	-4.60319600	1.35131300	0.00758700
N	-3.67348500	-0.94575400	-0.00310000
H	-3.33904700	-1.90501700	-0.00641100
H	-4.68203500	-0.81752000	-0.00327000
H	-1.39282400	-2.25605500	0.00293400
S	3.10933200	-0.55059100	0.00072500
C	3.77331800	1.13201000	-0.00019700
H	4.85901800	1.01597000	0.00090900
H	3.47515300	1.67449800	-0.89955200
H	3.47346500	1.67605300	0.89766300

Table S50. Optimized TSS3 in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -922.349003 Hartrees
Number of imaginary frequencies = 1

C	2.30188400	-0.27424700	0.02555700
C	1.43250200	-1.33987200	0.31911400

C	0.07755100	-1.11241600	0.48850600
C	-0.45104100	0.18033800	0.36784900
C	0.41318300	1.23739100	0.08261500
C	1.78091500	1.01649600	-0.08773200
H	1.82046100	-2.35135600	0.40504900
H	0.03634000	2.25310800	0.00987300
H	2.42213200	1.86384400	-0.30253300
C	-1.91172100	0.42622100	0.59512200
C	-2.51140700	-0.02308900	1.90460100
H	-2.21273900	-1.04369600	2.14428600
H	-2.14096500	0.64776400	2.68733900
H	-3.60241100	0.03854300	1.86483800
N	-2.41542300	1.56361800	0.09695500
H	-2.04679800	1.94663300	-0.76613900
H	-3.37081700	1.81618100	0.32287700
H	-0.58331000	-1.95156600	0.69221000
H	-2.37730000	-0.69412700	-0.20629700
B	-3.18353900	-1.46177900	-0.86530200
H	-3.41848700	-2.38717900	-0.13529600
H	-2.58989100	-1.70217000	-1.88276700
C	-4.40857000	-0.49606200	-1.06840500
N	-5.27993200	0.26367800	-1.18881800
S	4.01299200	-0.67385600	-0.17637000
C	4.75248900	0.91772000	-0.61466500
H	5.81321800	0.71474600	-0.77677700
H	4.32219900	1.31276000	-1.53740100
H	4.65096100	1.64117000	0.19683400

Table S51. Optimized structure of ethyl-4-(tiomethyl)phenyl-amine in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -803.50554 Hartrees Number of imaginary frequencies = 0			
C	1.38044900	-0.26256700	-0.01337100
C	0.88434200	1.03373700	0.13723200
C	-0.49589600	1.24847000	0.19554700
C	-1.40276000	0.19428500	0.10316200
C	-0.89340700	-1.10292000	-0.04857400
C	0.47533000	-1.33216100	-0.10564900
H	1.55326000	1.88385600	0.21638900
H	-1.57876700	-1.94351200	-0.11750600
H	0.84630500	-2.34784100	-0.22187800
C	-2.89660900	0.44994800	0.12501300
C	-3.50339100	0.28172600	-1.26720500
H	-3.04167200	0.97461200	-1.97697400

H	-3.35114800	-0.74154900	-1.62745400
H	-4.58013600	0.48304300	-1.24088300
H	-0.86594500	2.26417100	0.31816200
N	-3.55655100	-0.48882900	1.04264300
H	-3.22116700	-0.33645500	1.99187200
H	-4.55598800	-0.29448900	1.05513600
H	-3.04295400	1.49568500	0.43487400
S	3.10866500	-0.66281800	-0.09271500
C	3.90470400	0.95445200	0.05686100
H	4.97871500	0.76091700	0.01466100
H	3.63146300	1.61112200	-0.77195100
H	3.66867900	1.42751000	1.01240000

9. OPTIMIZED GEOMETRIES FOR THE 4-HYDROXYACETOPHENONE'S AMINATION

Table S52. Optimized structure of 4-hydroxyacetophenone in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -459.975872 Hartrees Number of imaginary frequencies = 0			
C	2.13437200	0.06420200	0.00000600
C	1.49950000	-1.18344100	-0.00008600
C	0.11399900	-1.24240100	-0.00003600
C	-0.65784700	-0.07200100	0.00009400
C	-0.00414800	1.16916800	0.00018000
C	1.38211100	1.24241000	0.00014800
H	2.09729300	-2.09086500	-0.00019500
H	-0.57468000	2.09263400	0.00031200
H	1.89448700	2.19927100	0.00022100
C	-2.14155700	-0.18065100	0.00003500
C	-2.96598300	1.07889700	-0.00027800
H	-2.73763400	1.68364800	0.88311400
H	-2.73745000	1.68331600	-0.88384800
H	-4.02427200	0.81652800	-0.00033200
O	-2.68586600	-1.28105700	0.00018700
H	-0.38465100	-2.20674200	-0.00011300
O	3.48525000	0.18724700	-0.00010500
H	3.90916600	-0.68441300	-0.00018600

Table S53. Optimized TSS1 (nucleophilic attack) for pathway a in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -516.480197 Hartrees Number of imaginary frequencies = 1			
C	2.44921400	-0.03011300	0.00521200
C	1.81909100	1.21386900	0.04139400
C	0.43000200	1.28191500	-0.02176800
C	-0.34886400	0.12622100	-0.12333600
C	0.30205500	-1.11185400	-0.16076500
C	1.68999600	-1.19794000	-0.09550700
H	2.42269400	2.11372500	0.11513000
H	-0.27011100	-2.03297800	-0.23174000
H	2.18743200	-2.16406500	-0.12206400
C	-1.86566900	0.26040800	-0.20766900
C	-2.55169200	-0.70488200	-1.16600200
H	-2.29457800	-0.39749500	-2.18587400
H	-2.25162800	-1.74623500	-1.03297100
H	-3.63471900	-0.62196700	-1.04152200
O	-2.35837400	1.42573400	-0.10773800
N	-2.31056500	-0.60874600	1.41880400
H	-2.00073100	-1.57358800	1.53363300
H	-3.32631500	-0.57580800	1.50429000
H	-0.06350600	2.24847700	0.00226900
H	-1.90788100	-0.04465500	2.16645200
O	3.81232000	-0.05157300	0.07029500
H	4.13692100	-0.96322100	0.03096600

Table S54. Optimized TSS1 (nucleophilic attack) for pathway c in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = - -745.524675 Hartrees Number of imaginary frequencies = 1			
C	-4.04626500	-0.20796900	0.07312300
C	-3.23798700	-1.31722300	0.32652000
C	-1.85805700	-1.20611900	0.18591800
C	-1.26805300	-0.00160600	-0.20692700
C	-2.09506600	1.10165600	-0.45688400
C	-3.47353900	1.00613200	-0.31732100
H	-3.69154400	-2.25849700	0.62599800
H	-1.66757700	2.05627800	-0.74819900
H	-4.11637500	1.86051700	-0.50591500
C	0.22358700	0.05850500	-0.36634500
C	0.80253400	0.99019300	-1.40315300
H	0.65484500	0.51706400	-2.38171000
H	0.32296900	1.96832600	-1.41495500

H	1.87429000	1.11550500	-1.23296100
O	0.88641300	-0.96014000	-0.03049600
N	0.60120000	1.37343700	1.27573700
H	0.28918500	2.34186700	1.24732100
H	1.61886900	1.34589000	1.34630800
H	2.32646800	-1.00340500	-0.27717000
O	3.34716100	-1.12102400	-0.46419100
C	4.06786800	-0.21051100	0.15781400
C	5.54265700	-0.33656100	-0.09077900
H	5.87961800	-1.32879900	0.22186000
H	5.73692900	-0.24183100	-1.16296900
H	6.08629000	0.43277500	0.45610700
O	3.57348600	0.65874200	0.87070600
H	-1.22817400	-2.06883300	0.37778100
H	0.20626000	0.93265500	2.10397300
O	-5.40175000	-0.25289100	0.19227900
H	-5.68901800	-1.14004200	0.45618700

Table S55. Optimized structure of the zwitterionic intermediate for pathway a in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -516.477899 Hartrees Number of imaginary frequencies = 0			
C	2.45315000	-0.01419500	0.00034000
C	1.80079900	1.21800900	-0.00846400
C	0.40847100	1.25984500	-0.03295000
C	-0.35255200	0.08937100	-0.05316400
C	0.32214200	-1.13732800	-0.05019400
C	1.71333800	-1.19803400	-0.01937800
H	2.38953900	2.13069600	0.00382200
H	-0.23276300	-2.07299100	-0.06822700
H	2.22745600	-2.15588500	-0.01270300
C	-1.89014200	0.18864000	-0.09118700
C	-2.48492800	-0.65715500	-1.22634800
H	-2.17505300	-0.21036100	-2.17544600
H	-2.16126300	-1.70233600	-1.21195400
H	-3.57752900	-0.61922900	-1.16507000
O	-2.37993200	1.40753700	-0.00747800
N	-2.35015300	-0.59197700	1.24532000
H	-2.06704500	-1.57394100	1.29984300
H	-3.37090600	-0.54077900	1.29621400
H	-0.10255200	2.21728000	-0.03902900
H	-1.97024600	-0.09368300	2.05388100
O	3.81893000	-0.00923300	0.02826800
H	4.15777400	-0.91626800	0.02318100

Table S56. Optimized structure of the hydroxi-ammonium ion in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -745.540564 Hartrees Number of imaginary frequencies = 0			
C	-4.03634800	0.11126000	-0.10719300
C	-3.27798500	1.27720900	-0.20802400
C	-1.89105500	1.21145700	-0.10798100
C	-1.24484800	-0.01020900	0.09542300
C	-2.01941100	-1.17055300	0.19447900
C	-3.40630500	-1.11913200	0.09196400
H	-3.78152700	2.22671600	-0.36307200
H	-1.54795400	-2.13835600	0.35191600
H	-3.99933700	-2.02645800	0.16980000
C	0.27022100	-0.08064700	0.21387200
C	0.73236500	-0.72330100	1.51770400
H	0.37054900	-0.11544700	2.35036500
H	0.34234900	-1.73854600	1.62506800
H	1.82579700	-0.75791700	1.55023300
O	0.81315600	1.18256700	0.03276400
N	0.80900100	-0.93503100	-0.92277800
H	0.48050300	-1.90348600	-0.86897000
H	1.89021200	-0.91785900	-0.87391500
H	1.81128000	1.14788400	0.19123500
O	3.38215100	1.09489200	0.36327400
C	4.00525100	0.11552600	-0.13593900
C	5.51651200	0.11098600	-0.06610400
H	5.88390600	-0.89600000	0.14302700
H	5.90540700	0.41317400	-1.04446800
H	5.87907400	0.81134100	0.68720600
O	3.44608100	-0.86270600	-0.71884800
H	-1.30748600	2.12187600	-0.18600300
H	0.50583200	-0.54326300	-1.81910900
O	-5.39086000	0.23029500	-0.21071900
H	-5.81622400	-0.63440500	-0.11484100

Table S57. Optimized structure of the hemiaminal in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -516.497244 Hartrees Number of imaginary frequencies = 0			
C	-2.44841300	0.00896200	0.00822500
C	-1.76001600	1.22097800	-0.00451800
C	-0.36675200	1.22499400	-0.02803200
C	0.35899700	0.02988500	-0.04737100
C	-0.35058900	-1.17499200	-0.03006900

C	-1.74285800	-1.19524200	-0.00243900
H	-2.32094700	2.15095300	0.00377200
H	0.18369500	-2.12208100	-0.03877200
H	-2.28411500	-2.13790400	0.00886400
C	1.88758000	0.01353300	-0.02718600
C	2.39412400	-0.28509500	1.38334900
H	2.01334200	0.46747000	2.07888300
H	2.05819900	-1.27182200	1.71706300
H	3.48911400	-0.26230800	1.39441000
O	2.30921900	1.31151900	-0.42709500
N	2.48597600	-0.94709800	-0.94601600
H	2.40960700	-1.89236300	-0.57878200
H	3.27671300	1.29244400	-0.46976600
H	0.15826100	2.17419300	-0.03490700
H	2.00116900	-0.92652300	-1.84137500
O	-3.81395900	0.05591200	0.03143200
H	-4.18138100	-0.83995000	0.03627500

Table S58. Optimized TSS2 (lowest energy) in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -745.516057 Hartrees Number of imaginary frequencies = 1			
C	-4.02454000	-0.18872000	-0.13908600
C	-3.20340800	-1.29440800	0.10768500
C	-1.84044700	-1.10958200	0.28380900
C	-1.27367200	0.17123700	0.21569300
C	-2.10384900	1.26353100	-0.04361100
C	-3.47533200	1.09086500	-0.21526200
H	-3.64451700	-2.28533100	0.15110200
H	-1.69445900	2.26671900	-0.10470800
H	-4.11752600	1.94554100	-0.40898200
C	0.19194300	0.35808500	0.43326900
C	0.81024400	1.69526100	0.12618000
H	0.53610900	2.04313000	-0.87048300
H	0.45518200	2.41766000	0.86794400
H	1.89747900	1.62503600	0.20511200
O	0.82193300	-0.59892400	-1.04160500
N	0.72883600	-0.29000100	1.47563100
H	0.28639600	-1.13957100	1.80447200
H	1.74690100	-0.23871200	1.57227500
H	0.48915900	-0.21765500	-1.87018400
O	3.28157800	-0.34540600	-1.12903500
C	4.02380300	-0.20690500	-0.09551700
C	5.51009700	-0.09395900	-0.36398000

H	5.69502000	0.75476800	-1.02894600
H	6.07059700	0.03539800	0.56231800
H	5.85339400	-0.99618600	-0.87878300
O	3.59934900	-0.16051600	1.08104700
H	-1.21020500	-1.97918600	0.45168800
H	1.88346900	-0.48713700	-1.04131500
O	-5.35374200	-0.42404200	-0.30228000
H	-5.83082800	0.40421800	-0.46102200

Table S59. Optimized TSS2 (highest energy) in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -745.514905 Hartrees
Number of imaginary frequencies = 1

C	-2.21722200	-1.28236600	0.15473900
C	-1.44280200	-1.75769100	-0.90761700
C	-0.06265400	-1.60943500	-0.86783400
C	0.56121600	-0.99219900	0.22234900
C	-0.22575400	-0.52894800	1.28051900
C	-1.60818600	-0.67532400	1.25395200
H	-1.92554900	-2.22174000	-1.76339400
H	0.23089500	-0.04019900	2.13487600
H	-2.22357100	-0.31233700	2.07146600
C	2.03836700	-0.77798800	0.21952100
C	2.66113400	0.06302200	1.29878200
H	2.14088300	1.01521900	1.40614500
H	2.60780100	-0.49105800	2.24140700
H	3.71377900	0.24268900	1.06457700
O	2.07223400	0.46919300	-1.18222700
N	2.78626000	-1.80512800	-0.20101500
H	2.40409900	-2.49426300	-0.83600400
H	3.79503500	-1.71631800	-0.18733600
H	1.17216500	1.06528900	-1.22711600
H	0.52171100	-1.94535900	-1.72079000
H	2.82328600	1.07166700	-1.06088900
O	-0.05378400	1.69690900	-1.32616800
C	-0.38638300	2.31115300	-0.24850500
O	0.42424300	2.63873100	0.64223800
C	-1.85103200	2.67250500	-0.10619800
H	-2.02456700	3.62027200	-0.62827300
H	-2.48731400	1.91215100	-0.56479200
H	-2.11530600	2.80409900	0.94465200
O	-3.57359000	-1.38074200	0.16399500
H	-3.89009700	-1.80333000	-0.64838000

Table S60. Optimized structure of iminium in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -440.523793 Hartrees Number of imaginary frequencies = 0			
C	-2.18125300	-0.01147800	-0.00249000
C	-1.51404300	1.21948200	0.08364400
C	-0.13382400	1.25008400	0.08423800
C	0.61475900	0.05771000	0.00135100
C	-0.07389900	-1.16699800	-0.06963800
C	-1.45772200	-1.20713800	-0.07743200
H	-2.09504600	2.13281600	0.15665900
H	0.47233000	-2.10206900	-0.13216400
H	-1.98575900	-2.15394900	-0.14020600
C	2.07048000	0.05711400	-0.00472800
C	2.84228300	-1.20978900	0.14195600
H	2.51694800	-1.74542600	1.03702200
H	2.64772400	-1.84968300	-0.72431200
H	3.91221300	-1.00983800	0.20042200
N	2.74646700	1.15760700	-0.14638300
H	2.30798400	2.06107100	-0.29837800
H	3.76237800	1.14301400	-0.12416900
H	0.35050000	2.21746700	0.17734700
O	-3.52738100	0.01833100	-0.00178300
H	-3.89619000	-0.87722100	-0.05467800

Table S61. Optimized TSS3 in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -560.110014 Hartrees Number of imaginary frequencies = 1			
C	-3.08660400	0.19191800	-0.21529700
C	-2.27704100	1.22922300	0.26220000
C	-0.92591600	1.00258300	0.47144200
C	-0.35785000	-0.25125000	0.20821400
C	-1.17734100	-1.27824400	-0.26734700
C	-2.53665000	-1.06176000	-0.48036100
H	-2.71843400	2.20171000	0.45670700
H	-0.76915400	-2.26692800	-0.45321000
H	-3.17025400	-1.86586300	-0.84426000
C	1.09027200	-0.50373900	0.49578400
C	1.58497800	-0.25483700	1.89960200
H	1.24190600	0.71119200	2.27043100
H	1.17818700	-1.04489800	2.54015100
H	2.67743200	-0.29251700	1.93232400
H	-0.29672800	1.81628400	0.82466400

H	1.58408000	0.72686900	-0.08612300
N	1.65669200	-1.54614100	-0.13147900
H	1.36654300	-1.78641300	-1.07260300
H	2.60107100	-1.81353100	0.12220700
H	1.90220000	1.93713500	-1.60249400
H	2.53788700	2.43174800	0.28472500
C	3.69526300	0.70577700	-0.76953700
N	4.60925600	-0.00042600	-0.89915000
B	2.41307300	1.59552000	-0.56919700
O	-4.40528500	0.46605300	-0.40052000
H	-4.87411800	-0.31285600	-0.73616900

Table S62. Optimized structure of ethyl-4-hydroxyphenyl-amine in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -441.265812 Hartrees Number of imaginary frequencies = 0			
C	2.19748300	-0.05626200	-0.02137000
C	1.38697800	-1.18763600	-0.13834500
C	0.00226700	-1.05174300	-0.07552100
C	-0.59645200	0.19971400	0.10736500
C	0.23489700	1.31656200	0.22786500
C	1.62261800	1.20006500	0.16337400
H	1.84273900	-2.16470400	-0.27985200
H	-0.20809600	2.29911700	0.37549300
H	2.26435500	2.07112200	0.25829800
C	-2.10518000	0.34971100	0.12974200
C	-2.70096700	0.16016300	-1.26435600
H	-2.28703400	0.89175100	-1.96477700
H	-2.48029200	-0.84562600	-1.63835000
H	-3.78891400	0.28822100	-1.23662200
H	-0.62230200	-1.93642200	-0.16675000
O	3.56241400	-0.12648100	-0.07857800
H	3.84648500	-1.04174900	-0.21647200
N	-2.70102900	-0.64444900	1.03364800
H	-2.37403100	-0.48474400	1.98459600
H	-3.71101000	-0.51573200	1.05073200
H	-2.32387300	1.37831700	0.45427300

10. OPTIMIZED GEOMETRIES FOR THE 4-(N-DIMETHYLAMINO)ACETOPHENONE'S AMINATION

Table S63. Optimized structure of 4-(N-dimethylamino)acetophenone in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -518.631242 Hartrees Number of imaginary frequencies = 0			
C	1.36902000	0.00205600	-0.04209900
C	0.66766400	-1.23472500	-0.03063500
C	-0.71351700	-1.26175700	-0.01721400
C	-1.47574600	-0.08104900	-0.00860800
C	-0.78554100	1.14202000	-0.01245800
C	0.59785800	1.19385100	-0.02661200
H	1.21205600	-2.17115600	-0.03356200
H	-1.33358800	2.07972500	-0.00089600
H	1.08527600	2.16100100	-0.02303800
C	-2.94924300	-0.15714400	0.00997200
C	-3.74796600	1.12198300	0.02975700
H	-4.81159500	0.88153900	0.04247400
H	-3.49723100	1.71640600	0.91402800
H	-3.52129700	1.72894400	-0.85246800
O	-3.52908900	-1.24448800	0.01018600
H	-1.22580900	-2.21959700	-0.01002500
N	2.73047500	0.04012100	-0.06800700
C	3.42208100	1.31539700	0.02865900
H	3.13533900	1.98132100	-0.79195800
H	3.20993100	1.82353100	0.97882300
H	4.49485400	1.13966100	-0.03863700
C	3.49264300	-1.19198800	0.05931000
H	3.27664700	-1.70696300	1.00451700
H	3.27628400	-1.87806100	-0.76654100
H	4.55499500	-0.95315100	0.03142300

Table S64. Optimized TSS1 (nucleophilic attack) for pathway a in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -575.131475 Hartrees Number of imaginary frequencies = 1			
C	1.71607400	0.01324600	-0.14786500
C	1.02931800	1.24583400	-0.09792900
C	-0.36139400	1.29103500	-0.10562100
C	-1.13552500	0.13057500	-0.15239400
C	-0.45802200	-1.09340000	-0.18326600
C	0.93035000	-1.16170900	-0.17295800
H	1.57750600	2.17948100	-0.05981200
H	-1.01437100	-2.02754400	-0.19988400

H	1.39947300	-2.13808000	-0.18679900
C	-2.65359300	0.23967300	-0.17352100
C	-3.36196400	-0.76391700	-1.07660600
H	-3.15263600	-0.48124500	-2.11431300
H	-3.03664100	-1.79568500	-0.92752100
H	-4.44063700	-0.69712900	-0.91000700
O	-3.16217400	1.40408800	-0.09638900
N	-3.02480900	-0.57188200	1.48198400
H	-2.67853400	-1.52147400	1.61830000
H	-4.03776100	-0.56859100	1.60202700
H	-0.86038200	2.25524500	-0.07495400
H	-2.61503100	0.03168700	2.19409600
N	3.10152600	-0.04193400	-0.18735300
C	3.74151500	-1.31472800	0.10941300
H	3.49634900	-1.68283900	1.11772400
H	3.45050200	-2.07650500	-0.61830400
H	4.82208700	-1.18747900	0.03801200
C	3.83886700	1.14665700	0.21545600
H	3.62608600	1.98417200	-0.45383400
H	3.60408100	1.45512200	1.24588800
H	4.90652000	0.93527700	0.14982100

Table S65. Optimized TSS1 (nucleophilic attack) for pathway c in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -804.177312 Hartrees Number of imaginary frequencies = 1			
C	-3.30784900	-0.08863500	0.06544800
C	-2.47762200	-1.22870900	0.18072400
C	-1.09932000	-1.12153000	0.05527400
C	-0.47738800	0.10446000	-0.20418400
C	-1.29623500	1.23273300	-0.33556500
C	-2.67552200	1.14769700	-0.21072600
H	-2.90731500	-2.20580900	0.36561800
H	-0.86221000	2.20880300	-0.53187600
H	-3.26193500	2.05108700	-0.32586500
C	1.01010900	0.16327900	-0.34514700
C	1.61501600	1.25394500	-1.19769800
H	1.45554000	0.97490300	-2.24632700
H	1.16560600	2.23153700	-1.02621000
H	2.68970400	1.31686000	-1.01295300
O	1.65376900	-0.92029800	-0.21534900
N	1.42307200	1.11711700	1.48965700
H	1.12209000	2.07817700	1.63741300
H	2.44008700	1.06097600	1.55658800

H	3.06639100	-0.93375800	-0.45923800
O	4.09520800	-1.03659300	-0.66835900
C	4.84043700	-0.28779900	0.11502800
C	6.31248000	-0.40599000	-0.15632800
H	6.61998900	-1.44893200	-0.03978900
H	6.51304300	-0.11392700	-1.19108100
H	6.87659200	0.22845600	0.52621100
O	4.37241100	0.44236600	0.98610000
H	-0.48905300	-2.01491600	0.14753600
H	1.01461300	0.53449600	2.21748400
N	-4.67395700	-0.17396100	0.22472000
C	-5.29417500	-1.48996700	0.21976900
H	-5.12325900	-2.02741800	-0.72485700
H	-4.91362300	-2.10279200	1.04138300
H	-6.36821300	-1.37229900	0.36447600
C	-5.49660400	0.94363500	-0.21309500
H	-5.25585200	1.85020000	0.34878800
H	-5.37426600	1.15488000	-1.28575300
H	-6.54280200	0.70487000	-0.02231800

Table S66. Optimized structure of the zwitterionic intermediate for pathway a in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -575.129651 Hartrees Number of imaginary frequencies = 0			
C	1.71779000	0.00877200	-0.13955800
C	1.01932100	1.23392200	-0.10463300
C	-0.37299800	1.26618900	-0.07766000
C	-1.13642200	0.09931100	-0.07582100
C	-0.44529100	-1.11759500	-0.09603500
C	0.94424800	-1.17311900	-0.11719300
H	1.55800700	2.17395700	-0.10185800
H	-0.99048500	-2.05972100	-0.08548700
H	1.42214000	-2.14537000	-0.12073200
C	-2.67207300	0.18531100	-0.06031000
C	-3.29869600	-0.66783800	-1.17269800
H	-3.02873900	-0.21826000	-2.13266700
H	-2.96121000	-1.70881200	-1.16962100
H	-4.38889800	-0.64377900	-1.07248800
O	-3.17316700	1.39902200	0.04108600
N	-3.08256500	-0.60194600	1.29243200
H	-2.78089900	-1.57867000	1.33847500
H	-4.10192800	-0.56803300	1.37477700
H	-0.88150400	2.22536200	-0.05485100
H	-2.68533500	-0.09661100	2.08799100

N	3.10570000	-0.03519300	-0.21115900
C	3.83595200	1.16954000	0.15531300
H	3.59730400	1.99245300	-0.52302300
H	3.62073100	1.49298600	1.18574100
H	4.90477100	0.97092100	0.06853800
C	3.75918100	-1.28963700	0.13257900
H	3.52984500	-1.61519500	1.15933700
H	3.46572800	-2.08479000	-0.55727200
H	4.83778000	-1.15776500	0.04163400

Table S67. Optimized structure of the hydroxi-ammonium ion in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -804.192254 Hartrees Number of imaginary frequencies = 0			
C	-3.29996500	0.03597900	-0.13413500
C	-2.52234100	1.21338300	-0.16155300
C	-1.13461500	1.16220100	-0.06418500
C	-0.46006400	-0.05035400	0.07978200
C	-1.22614200	-1.21968800	0.13034900
C	-2.61104500	-1.18758300	0.02990100
H	-2.99462900	2.18318900	-0.26051400
H	-0.74439900	-2.18786100	0.25441700
H	-3.15365700	-2.12356900	0.08121400
C	1.05326900	-0.10408100	0.19870200
C	1.52485300	-0.79081500	1.47663900
H	1.15892200	-0.21840400	2.33226000
H	1.14269600	-1.81247600	1.54554100
H	2.61871500	-0.81821600	1.50715500
O	1.58146700	1.17184700	0.06580800
N	1.60723200	-0.90910600	-0.96896800
H	1.29021300	-1.88266900	-0.95066600
H	2.68473200	-0.87978100	-0.91882100
H	2.57903800	1.14321200	0.22538000
O	4.15220800	1.10497700	0.40793900
C	4.79230000	0.15225300	-0.12137500
C	6.30252200	0.16073000	-0.02808200
H	6.67988400	-0.85227600	0.12689700
H	6.70222200	0.52562200	-0.98042300
H	6.64478800	0.81975600	0.77071800
O	4.25204300	-0.80630100	-0.75188600
H	-0.57208000	2.08930200	-0.09290000
H	1.29864500	-0.48870500	-1.85026100
N	-4.67806300	0.07325700	-0.27548100
C	-5.34571900	1.35405400	-0.09649600

H	-5.17306400	1.78021600	0.90372900
H	-5.00890300	2.07660200	-0.84421900
H	-6.41789400	1.21211800	-0.23501300
C	-5.43639500	-1.10128400	0.13010400
H	-5.16848600	-1.96895800	-0.47817900
H	-5.27962200	-1.35501700	1.18968800
H	-6.49699500	-0.90409800	-0.02764900

Table S68. Optimized structure of the hemiaminal in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -575.149009 Hartrees Number of imaginary frequencies = 0			
C	-1.71376100	0.00266400	-0.13433800
C	-0.98979500	1.21173300	-0.09238900
C	0.40348900	1.21697800	-0.06309000
C	1.14100500	0.03161500	-0.07037900
C	0.42474500	-1.16901700	-0.08585700
C	-0.96536000	-1.19460100	-0.11134400
H	-1.50713600	2.16354000	-0.08435900
H	0.95614300	-2.11844500	-0.07401100
H	-1.46373300	-2.15648500	-0.11978100
C	2.66601200	0.01723100	0.00576400
C	3.12658000	-0.30046800	1.42795100
H	2.72216400	0.44205100	2.12096800
H	2.78022700	-1.29175200	1.73673600
H	4.22068700	-0.27811700	1.47672800
O	3.10092400	1.32122500	-0.36142000
N	3.29899800	-0.93069500	-0.90527300
H	3.20483600	-1.88094000	-0.55494100
H	4.06927100	1.30292600	-0.37046800
H	0.91898200	2.17162400	-0.03207800
H	2.84397300	-0.89637200	-1.81581200
N	-3.10338100	-0.01338500	-0.21315700
C	-3.80867700	1.21169100	0.13339000
H	-3.60409500	1.53715400	1.16555000
H	-3.53696900	2.02308300	-0.54625000
H	-4.88043700	1.03966900	0.02760400
C	-3.78119900	-1.24614200	0.16215800
H	-3.51324500	-2.06177200	-0.51399300
H	-3.54800600	-1.55576700	1.19295300
H	-4.85761000	-1.09173500	0.08033500

Table S69. Optimized TSS2 (lowest energy) in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -804.170169 Hartrees
Number of imaginary frequencies = 1

C	-3.29358700	-0.04475300	-0.11118900
C	-2.46896400	-1.18364500	0.06762800
C	-1.10148300	-1.05119400	0.24524700
C	-0.48282000	0.20633900	0.26171500
C	-1.29004200	1.33362800	0.08635400
C	-2.66444200	1.22103000	-0.08304200
H	-2.89540600	-2.17923900	0.05854700
H	-0.85442900	2.32813600	0.09912700
H	-3.24613800	2.12758000	-0.19510800
C	0.98506300	0.33103500	0.48069200
C	1.63574400	1.67469900	0.28303900
H	1.37118400	2.10994300	-0.68137200
H	1.29810900	2.34255400	1.08175300
H	2.72107900	1.57272400	0.35440100
O	1.59508900	-0.52169900	-1.04551500
N	1.51157500	-0.40576500	1.47629700
H	1.05304100	-1.27264000	1.72892800
H	2.53180100	-0.40038100	1.55137600
H	1.23983900	-0.09354400	-1.84125000
O	4.04799000	-0.26962100	-1.18687400
C	4.80353200	-0.24493500	-0.15288000
C	6.28508800	-0.08953100	-0.42518400
H	6.86290600	-0.12956500	0.49862500
H	6.61731600	-0.87893700	-1.10520200
H	6.45845600	0.86916200	-0.92366100
O	4.39252200	-0.33129900	1.02546800
H	-0.50593100	-1.95506900	0.35118200
H	2.66125800	-0.41357000	-1.06897800
N	-4.64759000	-0.16843100	-0.31853600
C	-5.47981000	1.02091600	-0.22408200
H	-6.51438500	0.74172100	-0.42249100
H	-5.42579200	1.48759700	0.77050500
H	-5.18620300	1.76301200	-0.97169900
C	-5.28376300	-1.45009800	-0.05396600
H	-6.34987600	-1.36145300	-0.26251300
H	-4.88126200	-2.22903200	-0.70761400
H	-5.15536900	-1.76963700	0.99047800

Table S70. Optimized TSS2 (highest energy) in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -804.168704 Hartrees
Number of imaginary frequencies = 1

C	-1.83595500	-0.85240200	0.20727300
C	-1.11119000	-1.44522600	-0.85571500
C	0.27162400	-1.52426500	-0.81799700
C	1.00355100	-1.01622800	0.26304900
C	0.29590200	-0.42276400	1.31073600
C	-1.09045700	-0.34106400	1.29373600
H	-1.62745500	-1.83133300	-1.72597200
H	0.82332800	0.00192100	2.15924400
H	-1.58779200	0.13805000	2.12811800
C	2.49218500	-1.02596000	0.24969600
C	3.23577400	-0.30042700	1.33864600
H	2.86938400	0.71938900	1.45686900
H	3.09615700	-0.84638000	2.27693200
H	4.30424200	-0.27923100	1.10842300
O	2.72716600	0.19153700	-1.13535400
N	3.08122000	-2.15864600	-0.17023600
H	2.60493800	-2.77105700	-0.81983200
H	4.09265300	-2.20683500	-0.17866700
H	1.90764200	0.89835200	-1.21522300
H	0.78168300	-1.94986400	-1.67933900
H	3.54706200	0.69277700	-1.00087500
O	0.78388800	1.66784300	-1.38380300
C	0.47304900	2.37757800	-0.36020600
O	1.26642700	2.65471500	0.56249200
C	-0.93973100	2.92627700	-0.33152000
H	-1.63565200	2.24022600	-0.82004700
H	-1.25630800	3.12310900	0.69452100
H	-0.95185200	3.87275500	-0.88400900
N	-3.21183500	-0.77843200	0.18163900
C	-3.87497000	0.08772600	1.14506200
H	-3.66826700	-0.23814200	2.16796700
H	-3.56443000	1.13838500	1.04392500
H	-4.95203800	0.02574400	0.98965600
C	-3.89260500	-0.98698600	-1.08844900
H	-3.56853200	-0.26750400	-1.85492500
H	-3.71777200	-1.99828900	-1.46493900
H	-4.96560200	-0.87283800	-0.93419100

Table S71. Optimized structure of iminium in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -499.182628 Hartrees Number of imaginary frequencies = 0			
C	1.41778500	-0.00037700	0.00636000
C	0.70224300	-1.23567900	0.03482900
C	-0.67158900	-1.25456500	0.03198900
C	-1.43194700	-0.06063200	0.00721200
C	-0.72106800	1.16132000	-0.00628300
C	0.65393600	1.20237700	-0.01009900
H	1.23804600	-2.17597800	0.06017700
H	-1.26033900	2.10276700	-0.02207600
H	1.14924300	2.16472200	-0.02528600
C	-2.86917900	-0.05456900	-0.00588600
C	-3.64279300	1.22280600	0.06212200
H	-3.35516300	1.78763500	0.95242600
H	-3.41811000	1.83641400	-0.81499500
H	-4.71462900	1.02599400	0.09183400
N	-3.56592200	-1.15970400	-0.08165400
H	-3.13869200	-2.07719300	-0.14947500
H	-4.57985100	-1.12787200	-0.07753800
H	-1.15485700	-2.22700000	0.06039800
N	2.76544500	0.02537000	-0.00244400
C	3.47519600	1.29790000	-0.04342900
H	3.20854800	1.86855600	-0.93971400
H	3.24991200	1.90477900	0.84049300
H	4.54553400	1.10193200	-0.06551600
C	3.52655900	-1.21767200	0.02182200
H	3.30103600	-1.80004100	0.92161100
H	3.30937000	-1.83117200	-0.85953100
H	4.58842800	-0.97865900	0.02406300

Table S72. Optimized TSS3 in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -618.764349 Hartrees Number of imaginary frequencies = 1			
C	-2.36329100	-0.01175300	0.04522500
C	-1.54661800	1.09807200	0.37908500
C	-0.17820300	0.95224400	0.53334800
C	0.45224600	-0.28516300	0.35315600
C	-0.34329100	-1.38070800	0.00397500
C	-1.71818400	-1.25388600	-0.15218800
H	-1.98062700	2.08132500	0.51234600
H	0.10398800	-2.36109500	-0.13255400
H	-2.28923100	-2.13432300	-0.41964400

C	1.92519200	-0.42588500	0.56338300
C	2.48889000	0.00787300	1.89712600
H	2.11456600	0.99214500	2.17964600
H	2.16913900	-0.72155300	2.64883500
H	3.58193900	0.03135900	1.86144600
H	0.41869900	1.83029800	0.77186700
H	2.31671100	0.69097900	-0.18218300
N	2.50290800	-1.53571000	0.04780200
H	2.18641400	-1.88016900	-0.85135700
H	3.48395700	-1.69476800	0.24687400
H	2.45067200	1.75754700	-1.82592200
H	3.20201200	2.46952100	-0.04953500
C	4.37039500	0.70172300	-1.02639000
N	5.30412600	0.02228800	-1.15636500
B	3.06771600	1.55543700	-0.81572100
N	-3.72812800	0.11362400	-0.07295600
C	-4.30788100	1.44687200	-0.12831600
H	-4.08738500	2.00592200	0.78521500
H	-3.94078300	2.02489600	-0.98907300
H	-5.39102200	1.35439400	-0.20725600
C	-4.47543300	-0.96394300	-0.70332000
H	-4.13994700	-1.15376100	-1.73340000
H	-4.38228000	-1.89168000	-0.13146100
H	-5.53066600	-0.69231200	-0.72511800

Table S73. Optimized structure of ethyl-4-(N-dimethylamino)phenyl-amine in cartesian coordinates (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -499.916825 Hartrees Number of imaginary frequencies = 0			
C	-1.44039900	0.00738600	-0.14288200
C	-0.79650400	1.26084100	-0.18428900
C	0.59455800	1.35100300	-0.17751300
C	1.40781000	0.21913200	-0.11210900
C	0.76975100	-1.02410400	-0.04909500
C	-0.61666000	-1.13739600	-0.05912900
H	-1.37363200	2.17647900	-0.23177400
H	1.36805600	-1.93006300	0.01063900
H	-1.05390300	-2.12735900	-0.00478600
C	2.91723000	0.33981000	-0.05842100
C	3.45187300	0.04746500	1.34291900
H	3.02438100	0.74207100	2.07232600
H	3.19500300	-0.97472200	1.64201000
H	4.54261700	0.15147700	1.36777500
H	1.05392500	2.33688700	-0.22016000

N	3.53623500	-0.60401800	-1.00126700
H	3.24537300	-0.38127500	-1.95127800
H	4.54752300	-0.48762200	-0.97454100
H	3.16767200	1.38324600	-0.30432000
N	-2.82890600	-0.09983500	-0.20414200
C	-3.60270900	1.09485500	0.10015500
H	-3.39834900	1.48190600	1.11103900
H	-3.39604500	1.88795100	-0.62257300
H	-4.66369900	0.85313800	0.02748500
C	-3.42330400	-1.34994600	0.24739800
H	-3.10384800	-2.18426500	-0.38174300
H	-3.16838800	-1.58302500	1.29325000
H	-4.50787100	-1.27213000	0.16230800

11. ACID-CATALYZED REDUCTION OF ACETOPHENONE

Scheme S1. Mechanism of the acid-catalyzed reduction of acetophenone

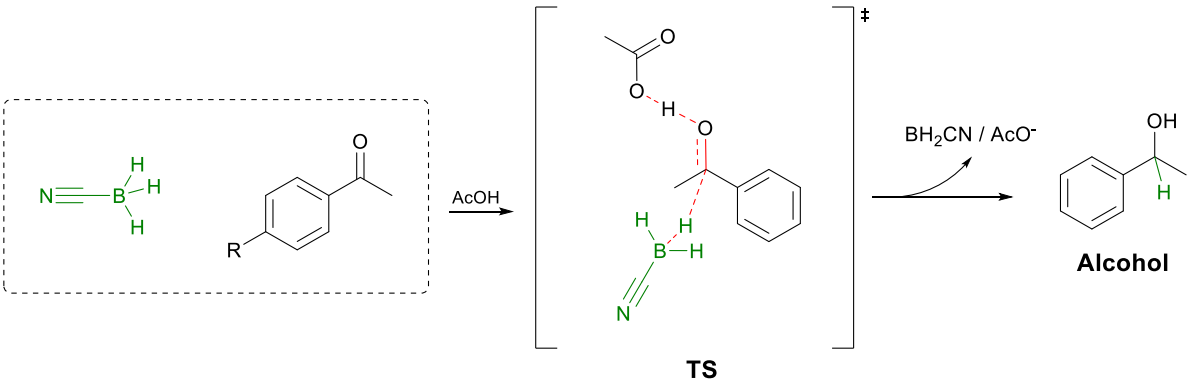


Table S74. Optimized TS for the acid-catalyzed reduction of the acetophenone (M06-2X/6-311++G(d,p)//M06-2X/6-31+G(d,p))

Sum of electronic and thermal Free Energies = -733.353250 Hartrees Number of imaginary frequencies = 1			
C	4.12903900	-1.15406100	-0.40821800
C	3.21301400	-1.01052300	-1.44846100
C	1.88764500	-0.66979400	-1.17381300
C	1.47129500	-0.48150200	0.14556400
C	2.39515200	-0.61889700	1.18792900
C	3.71754100	-0.95405300	0.91193200
H	5.16132500	-1.41512600	-0.62223000
H	3.52805100	-1.15876800	-2.47713400
H	2.08902100	-0.44346200	2.21603000
H	4.42942400	-1.05404000	1.72588500

C	0.02999800	-0.12682900	0.42286000
C	-0.66492500	-0.89222900	1.53463900
H	-0.81798500	-1.91791200	1.18095000
H	-0.06844600	-0.91651900	2.44768900
H	-1.63635400	-0.44047500	1.74936000
O	-0.67689500	0.14929600	-0.63872100
H	-1.83401000	0.30300500	-0.45263300
O	-3.01890500	0.55730500	-0.30018700
C	-3.78375900	-0.48987000	-0.30375100
C	-5.25027700	-0.20610500	-0.08319800
H	-5.38223600	0.27920300	0.88835500
H	-5.60608700	0.48795000	-0.84997600
H	-5.83365900	-1.12633500	-0.11770600
O	-3.36537700	-1.64449000	-0.47003900
H	1.17090100	-0.55132200	-1.97982500
H	0.24628900	1.00574300	1.14065600
B	0.22908500	2.31475400	1.22266700
H	-0.94317000	2.56765400	1.19165500
H	0.83458100	2.52954200	2.23649200
C	1.00618800	2.72424400	-0.08260300
N	1.58583800	3.00827400	-1.04808700