

Electronic Supplementary Information

Origins of the ANRORC reactivity in nitroimidazole derivatives.

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1.- Cartesian coordinates for the all optimized structures for the model reaction.

Reactive complex

C	-0.05923300	-0.06840300	0.03253400
C	0.06448500	0.02191700	2.14161300
N	1.27309500	-0.01536700	0.40172300
H	-0.36977100	-0.11984900	-1.00129800
N	2.36057400	-0.01254600	-0.48730000
O	2.07715000	-0.06669000	-1.65912300
O	3.45382100	0.03925200	0.01476600
N	-0.39851000	0.08566000	3.49813700
O	-1.59823900	0.01780200	3.70270100
O	0.44692400	0.20868600	4.37334900
N	-0.80969600	-0.06054900	1.09344900
N	0.46140500	2.99254000	0.83719800
H	0.24291200	3.34519600	1.76175000
C	1.80458200	3.06767800	0.48089000
C	2.18666300	3.03239300	-0.87024600
C	2.80612600	3.09472100	1.46627400
C	3.53524500	3.03387600	-1.22130400
H	1.41735800	2.99846800	-1.63933500
C	4.15033200	3.09654600	1.10369300
H	2.51847500	3.11456700	2.51539100
C	4.52842300	3.06617400	-0.24100900
H	3.80857800	3.00540600	-2.27299500
H	4.90931400	3.12100200	1.88160400
H	5.57795900	3.06468700	-0.51865900
C	1.37404200	0.05529100	1.76566000
H	2.31102400	0.11328600	2.29989900
H	-0.18800800	3.33185900	0.13730100

TS-1b

C	0.07203700	0.03609300	-0.04206500
N	0.09831200	0.05400400	1.36367100
H	0.95678000	0.01470300	-0.65569300
N	1.12866300	-0.37761900	2.11601100
O	2.16844100	-0.64781900	1.52767600
O	0.95820400	-0.44825700	3.32725300
N	-1.30091000	1.90605700	2.25255700
H	-2.23395400	2.04701500	2.65338400
C	-0.25349100	2.33577400	3.14842900
C	0.97504100	2.70682900	2.60887300
C	-0.45495400	2.24170000	4.52275700
C	2.03427400	2.97517100	3.47398900
H	1.10091100	2.77555800	1.53030400

C	0.61049100	2.51621300	5.37596300
H	-1.42488600	1.94455600	4.91284100
C	1.85547900	2.87258500	4.85369300
H	2.99890500	3.26312800	3.06740300
H	0.46888500	2.44534000	6.45001000
H	2.68488700	3.07753800	5.52377700
C	-1.25598200	0.26762500	1.84564400
H	-1.46779100	-0.19958900	2.80596400
H	-1.26657000	2.40743000	1.35699000
N	-2.09957700	0.06457600	0.77681900
C	-1.26503300	0.06222900	-0.29090300
N	-1.79139900	0.03168400	-1.63694000
O	-3.00233400	-0.00110900	-1.77923100
O	-0.99407100	0.03530300	-2.56731800

TS-1a

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	2.13567100
N	1.34194700	0.00000000	0.44356800
H	-0.24631100	-0.00730000	-1.05193400
N	2.43826800	-0.23536200	-0.36227000
O	2.22249400	-0.25530800	-1.55565900
O	3.50256000	-0.40806700	0.18994800
N	-0.49052300	0.04358300	3.41033200
O	-1.71232000	-0.05301900	3.61663700
O	0.32739700	0.19137500	4.34468300
N	-0.80025800	-0.00031600	1.00683600
N	1.83965500	2.03250900	2.09878600
H	2.00301900	2.11162200	3.10376100
C	2.95564000	2.39508600	1.30322600
C	2.75566300	2.72153600	-0.04016100
C	4.24503600	2.27285500	1.82757600
C	3.86135500	2.89977600	-0.87013000
H	1.74480700	2.81961800	-0.43074100
C	5.33966200	2.46059400	0.99100600
H	4.37873000	2.01838000	2.87598400
C	5.15267700	2.76109900	-0.36135000
H	3.70900200	3.14364600	-1.91739300
H	6.34356100	2.36365700	1.39353900
H	6.01117400	2.89525400	-1.01236800
C	1.37735100	0.13492200	1.82808900
H	2.22464700	-0.23615900	2.39249100
H	0.98116400	2.52510800	1.84481100

TS-1c

C	-0.01857000	-0.01093300	-0.03968400
C	0.00459600	-0.00004700	2.11326200
N	1.34331200	-0.00934700	0.41373800
N	2.47740400	-0.24329700	-0.34384300
O	2.33787200	-0.24565400	-1.54728800

O	3.51019400	-0.42962400	0.26373200
N	-0.47785100	0.04230600	3.38587200
O	-1.70136600	-0.05324500	3.59993200
O	0.34369600	0.18851500	4.32143900
N	-0.79835500	-0.00268900	0.98604700
N	1.84134000	2.02679700	2.07441500
H	1.99406500	2.10230700	3.08128300
C	2.96548100	2.39511400	1.29371000
C	2.78093600	2.72440500	-0.05108200
C	4.24882300	2.28014700	1.83457400
C	3.89631000	2.91076800	-0.86633100
H	1.77449300	2.82068900	-0.45314200
C	5.35296000	2.47668600	1.01285800
H	4.37026400	2.02340900	2.88390800
C	5.18174600	2.77921500	-0.34114800
H	3.75624700	3.15692400	-1.91479200
H	6.35209400	2.38504500	1.42830600
H	6.04794200	2.92132000	-0.98019400
C	1.37642100	0.12913100	1.79926400
H	2.22262600	-0.24115800	2.36479800
H	0.98494500	2.51932500	1.81382100
C	-0.43124200	-0.02091800	-1.46409800
H	-0.02046300	0.83924200	-1.99919800
H	-0.09044000	-0.93000900	-1.96643100
H	-1.52106300	0.01911700	-1.48629300

TS-1d

C	1.59524100	1.06492500	0.12234900
N	0.48138300	0.49769800	0.75875900
N	-0.52306300	1.22843200	1.28028200
O	-0.44931500	2.44512500	1.13855500
O	-1.43005900	0.64209600	1.85873200
N	-0.29280100	-1.33327000	-0.74093200
H	-0.33119700	-2.35740800	-0.75868100
C	-1.60395500	-0.74556100	-0.86543500
C	-1.70626900	0.56074500	-1.33824000
C	-2.71971900	-1.45113000	-0.42073200
C	-2.95149800	1.18511200	-1.33034100
H	-0.81869400	1.08338100	-1.69055800
C	-3.95958900	-0.81910900	-0.42415900
H	-2.61081200	-2.47376800	-0.06953800
C	-4.07476900	0.50135700	-0.86472300
H	-3.04081400	2.20618600	-1.68685800
H	-4.83649400	-1.35718400	-0.07888300
H	-5.04223100	0.99304200	-0.85459400
C	0.60555900	-0.96877600	0.68569000
H	0.31953900	-1.02971500	-1.50534700
N	1.92356000	-1.21067700	0.37246800
C	2.39129500	-0.01796900	-0.06806100
N	3.70820400	0.09560800	-0.64727800
O	4.40073600	-0.90870800	-0.70243700

O	4.06959800	1.19702900	-1.04852200
H	1.69845700	2.11893900	-0.07117800
C	-0.02338500	-1.81547300	1.75669900
H	0.33536700	-1.47803000	2.73166500
H	-1.11139500	-1.77775600	1.74220300
H	0.31215300	-2.84128900	1.58976800

TS-1e

C	0.14322700	0.06448200	-0.01684800
C	0.02464700	0.05834100	2.11796800
N	1.45791300	-0.04865000	0.48784700
H	-0.05062400	0.09062100	-1.07903100
N	2.54844900	-0.26419200	-0.32674600
O	2.31937500	-0.28385800	-1.52002700
O	3.62871100	-0.42060800	0.19963000
N	-0.57750900	0.19543100	3.33105400
O	-1.82310600	0.16954500	3.41735300
O	0.13750400	0.36415900	4.34789800
N	-0.70478900	0.12106900	0.94306300
N	1.93851800	1.93617900	2.16954100
H	2.16784000	2.00329800	3.16396800
C	2.99430700	2.36324700	1.31610400
C	2.69645500	2.68710500	-0.00974500
C	4.31493500	2.32931800	1.76897100
C	3.73786100	2.94429400	-0.89860600
H	1.65997500	2.72100200	-0.34040400
C	5.34595900	2.59387000	0.87291900
H	4.52410400	2.08986800	2.80861000
C	5.06233800	2.88634000	-0.46353400
H	3.51142700	3.18569500	-1.93284500
H	6.37518700	2.56629300	1.21775400
H	5.87198800	3.08015300	-1.16050800
C	1.45106700	0.07828500	1.89853000
H	1.06451300	2.43632800	1.98994000
C	2.47524400	-0.62307700	2.74380700
H	2.51408200	-1.67129800	2.43142900
H	3.46841800	-0.19057100	2.62667500
H	2.16653500	-0.56768800	3.78588800

TS-1f

C	-1.60895900	0.77002600	0.16389500
N	-0.34566300	0.53014100	-0.44383600
N	0.40668100	1.51009600	-1.01493200
O	0.02718900	2.66390700	-0.87703800
O	1.42586100	1.16541100	-1.59665700
N	0.58559500	-1.69223100	0.16573100
H	0.64789400	-2.64172600	-0.21365000
C	1.88675100	-1.12394700	0.41298600
C	2.01753600	-0.14778000	1.39687400
C	2.94515200	-1.46787900	-0.42343000

C	3.24126200	0.50445700	1.53910900
H	1.17315300	0.09521100	2.03721200
C	4.16277500	-0.81020200	-0.27089200
H	2.81056900	-2.23176000	-1.18416600
C	4.30951400	0.18007200	0.70263500
H	3.35653500	1.26737300	2.30209000
H	4.99655100	-1.06880200	-0.91544900
H	5.25995500	0.69194700	0.81439300
C	-0.33814500	-0.82958500	-0.96347700
H	0.26733800	-0.94979700	-1.85969700
H	0.00841700	-1.71568800	1.01342300
N	-1.62797900	-1.28944400	-0.94335100
C	-2.27777000	-0.37275300	-0.17085200
N	-3.63033500	-0.61805300	0.25743600
O	-4.08081900	-1.75099900	0.14465700
O	-4.27732700	0.32452900	0.70779800
C	-1.86964000	1.90789100	1.08754300
H	-0.93481700	2.23033100	1.55150900
H	-2.30754400	2.76420200	0.56575000
H	-2.56623500	1.59056500	1.86484200

Int-1a

C	-2.50738700	1.39736600	0.43786000
C	-2.03443300	-0.73134300	-0.01816600
N	-1.24689900	1.37012600	-0.06080200
H	-3.03190200	2.28569400	0.76825700
N	-0.47827600	2.49463600	-0.19069900
O	-0.96638700	3.54893600	0.16625500
O	0.62655900	2.32228700	-0.66158700
N	-2.34069700	-1.99032000	-0.24028100
O	-3.51283200	-2.41310200	0.02852600
O	-1.45837100	-2.77186200	-0.71891200
N	-2.97425800	0.18522600	0.45360600
N	0.31390400	-0.42460000	0.58734700
H	0.04990200	-0.55793400	1.55760000
C	1.68400100	-0.45823200	0.30066900
C	2.55982500	-0.72354600	1.36448000
C	2.21102700	-0.27215300	-0.98463700
C	3.93150400	-0.79962400	1.14789000
H	2.15332500	-0.86861300	2.36234900
C	3.58836100	-0.35325500	-1.18675000
H	1.56975900	-0.05581300	-1.83177800
C	4.45996600	-0.61471600	-0.13066900
H	4.58944200	-1.00491500	1.98781200
H	3.97908700	-0.20553400	-2.18973200
H	5.53055600	-0.67182500	-0.30037300
C	-0.71794300	-0.05387200	-0.28996700
H	-0.40932600	-0.13026300	-1.33406200
H	-3.90854700	-0.07009100	0.77720300

Int-1b

C	0.30628100	0.71467400	0.01597700
C	-0.05266000	-0.09179200	1.97062400
N	1.58660300	0.65290000	0.65051100
H	0.21852100	1.09780200	-0.99096000
N	2.71907800	0.39864200	-0.08278900
O	2.65829900	0.64249400	-1.27380800
O	3.69172700	-0.01297500	0.51869400
N	-0.69257200	-0.58441400	3.01453000
O	-1.94553600	-0.77586200	3.01641300
O	0.00499200	-0.85710300	4.05928400
N	-0.63526900	0.31083300	0.77995600
N	1.81217400	1.15592300	3.03957500
H	1.21601700	1.98713900	2.91194800
C	3.22667600	1.53716700	3.02750700
C	3.60067600	2.66468800	2.30867800
C	4.14567900	0.71069000	3.66096600
C	4.95778700	2.97004600	2.21664200
H	2.84981100	3.28938100	1.83168500
C	5.49737300	1.02970400	3.56063500
H	3.81114200	-0.16449300	4.21196400
C	5.90240900	2.15228700	2.83583900
H	5.27156400	3.84673500	1.65891000
H	6.23416700	0.39860000	4.04749300
H	6.95848500	2.39258700	2.75874400
C	1.42423600	0.11751300	1.98672800
H	2.04310400	-0.76318000	2.17972300
H	1.53980200	0.72853400	3.94217200

Int-1c

C	-0.05960000	-0.09085100	0.04507200
C	0.01937000	-0.02421600	2.18335100
N	1.28636800	-0.02245600	0.36548800
H	-0.39068600	-0.13908300	-0.98506300
N	2.29051500	0.03904100	-0.53559000
O	1.99210900	0.02180800	-1.71903500
O	3.41969100	0.10363300	-0.08028200
N	-0.41951200	-0.08349700	3.39879000
O	-1.76749900	-0.18981700	3.62426700
O	0.27800700	-0.05721800	4.44400400
N	-0.82243800	-0.09583600	1.08267300
N	2.02681100	1.37142000	2.24636100
H	1.44447700	2.18720900	2.09250600
C	3.33775500	1.60568400	2.67066800
C	3.70103400	2.93352800	2.94712400
C	4.28391900	0.58870900	2.85766000
C	4.98000000	3.23556400	3.40084000

H	2.96882900	3.72488300	2.80480200
C	5.56158900	0.90720500	3.31739700
H	4.04831300	-0.44781400	2.64331700
C	5.92396000	2.22469100	3.59203900
H	5.23732700	4.27078700	3.60748500
H	6.28192300	0.10562600	3.45594500
H	6.92274100	2.46060800	3.94572300
C	1.48776600	0.13293500	1.84931300
H	2.08250900	-0.70605800	2.21756700
H	-2.21433700	-0.19530300	2.75259400

TS-2a

C	-2.53159300	1.35806000	0.32106000
C	-1.97132600	-0.83079800	-0.10456100
N	-1.26674900	1.48725100	-0.07790200
H	-3.18513100	2.15548700	0.65945700
N	-0.65704600	2.69043000	0.01242200
O	-1.29587100	3.67575500	0.36374700
O	0.53013900	2.70362700	-0.28209700
N	-2.31876300	-2.09618600	-0.22881200
O	-3.51966400	-2.44685700	0.02068800
O	-1.45713300	-2.95821500	-0.60562800
N	-2.92770600	0.11261900	0.27364300
N	0.37178700	-0.70405200	0.42409000
H	0.09932500	-1.06215900	1.33872100
C	1.76894400	-0.57544800	0.20017000
C	2.61631200	-1.12420900	1.16471200
C	2.28946300	0.06097600	-0.92785200
C	3.99530100	-1.04217300	0.99533900
H	2.19357400	-1.61353200	2.03862300
C	3.67189900	0.13137500	-1.08579100
H	1.64314100	0.51272600	-1.67260500
C	4.52863200	-0.41634900	-0.13096300
H	4.65196900	-1.46963500	1.74693400
H	4.07814800	0.62633300	-1.96269900
H	5.60430800	-0.35240200	-0.26307000
C	-0.59492900	-0.34387000	-0.39548600
H	-0.32158100	-0.14375700	-1.42756600
H	-3.87039900	-0.18336200	0.52466600

TS-2b

C	0.02977400	0.00578400	-0.03083500
C	-0.05345900	0.01264000	2.17558800
N	1.37986200	-0.01617700	0.20018700
H	-0.36528500	-0.11327100	-1.03487400
N	2.19071200	-0.55591200	-0.73252100
O	1.77689300	-0.77940200	-1.86834900
O	3.35168000	-0.75888800	-0.38523800
N	-0.60765900	-0.80931600	3.17307800

O	-1.73526200	-1.28481700	3.01242900
O	0.04366000	-1.00455200	4.21146600
N	-0.76850100	0.14217100	0.98505200
N	1.87540600	1.58272300	1.98635900
H	1.26740500	2.13053000	1.36100500
C	2.04973500	2.28443300	3.27260100
C	3.30890700	2.29452700	3.85586600
C	0.93967700	2.87446100	3.86366800
C	3.46160900	2.93679500	5.08358300
H	4.14998000	1.81583300	3.36187100
C	1.10954000	3.51305800	5.08996300
H	-0.03051000	2.83769100	3.37516100
C	2.36570200	3.54287600	5.69740500
H	4.43821400	2.96276500	5.55634900
H	0.25853500	3.98647300	5.56899100
H	2.49058100	4.04106700	6.65400200
H	2.78221900	1.49193300	1.50468800
C	1.31330900	0.22733900	2.20893200
H	1.97234900	-0.35562500	2.84899000

TS-2c

C	-0.01742300	0.02409200	-0.00577000
C	-0.00246400	0.00916400	2.21375600
N	1.33097700	0.04109900	0.15403200
H	-0.47987100	0.05005900	-0.98857200
N	2.09657000	0.28288300	-0.91176800
O	1.60321100	0.43643000	-2.03498200
O	3.31279600	0.33449800	-0.71176000
N	-0.52362000	-0.37919100	3.34076400
O	-1.66440400	-0.87326200	3.54034300
O	0.27921800	-0.18417700	4.44241200
N	-0.75591800	-0.04118400	1.06130700
N	1.65557800	1.75350200	2.39064700
H	0.86398400	2.39740200	2.34497700
C	2.93741300	2.36272100	2.50734300
C	2.96995200	3.70426200	2.88781300
C	4.11040000	1.65537800	2.24701700
C	4.19861100	4.34426500	3.02109400
H	2.04112200	4.23529200	3.07927300
C	5.33234300	2.30853800	2.38993900
H	4.08717600	0.62069100	1.92241400
C	5.38233500	3.64800800	2.77609900
H	4.22714000	5.38816300	3.31762900
H	6.24947100	1.76454300	2.18598500
H	6.34025900	4.14839200	2.87951700
C	1.41612900	0.48252400	2.22762800
H	2.20798300	-0.23444300	2.42083700
H	-0.00690500	-0.86963700	5.07785400

Int-2a

C	2.27413200	-0.19286500	0.89346000
C	0.73920600	1.27792800	-0.17046300
N	3.20691500	-1.09803200	1.10522500
H	1.95720100	0.31452600	1.80332300
N	3.68569000	-1.79835400	0.02734500
O	3.22094100	-1.65756400	-1.10414200
O	4.59604100	-2.57528400	0.27318900
N	1.26631400	2.58127800	-0.19403600
O	0.49384300	3.54756900	-0.19357900
O	2.49340500	2.72078700	-0.20274200
N	1.65815700	0.21298600	-0.21499900
N	-1.18489800	-0.10456900	-0.11968600
C	-0.62283500	1.09462800	-0.13589100
H	-1.26955900	1.96577100	-0.13007300
C	-2.57316100	-0.37518400	-0.03470300
C	-3.00793000	-1.64151700	-0.43184600
C	-3.48003000	0.56997500	0.44839600
C	-4.36173300	-1.95662200	-0.36091800
H	-2.28761100	-2.36745200	-0.79992300
C	-4.83351500	0.24462300	0.50279200
H	-3.14310600	1.53982300	0.79956400
C	-5.28098000	-1.01386600	0.10003700
H	-4.69648000	-2.94120300	-0.67331300
H	-5.53885600	0.97930400	0.87930700
H	-6.33708500	-1.25998400	0.15172900
H	-0.57932400	-0.92091700	-0.19104800
H	1.91680800	-0.18970300	-1.11349200

Int-2b

C	0.42662000	-0.64749400	0.14959800
C	-0.45373500	-0.06067700	2.28892300
N	0.98661400	-0.23616600	-1.06553000
H	0.32396700	-1.72929300	0.16024300
N	1.29179700	1.01248400	-1.46321200
O	1.10223700	1.95107000	-0.70780500
O	1.75667300	1.10999400	-2.59789500
N	-0.78853000	-1.32917900	2.78756800
O	-1.29288500	-1.44800500	3.91634100
O	-0.56742700	-2.31335700	2.06747200
N	0.10135200	0.17137700	1.06045600
N	-0.41061300	2.25963700	2.70332100
C	-0.70611500	1.03643800	3.10531700
H	-1.14049500	0.89716300	4.08831300
C	-0.63674600	3.46606500	3.40662300
C	0.06166300	4.59741100	2.97691700
C	-1.53349000	3.54787600	4.47452300
C	-0.12333400	5.81091600	3.63253800
H	0.74973000	4.51766900	2.13915500
C	-1.70209000	4.76729600	5.12649000
H	-2.11351000	2.68625800	4.78849700

C	-1.00126100	5.90058500	4.71299000
H	0.42409000	6.68694700	3.29778400
H	-2.40050200	4.83059800	5.95558100
H	-1.14451200	6.84781100	5.22364400
H	0.04286600	2.33875200	1.79107900
H	1.20321400	-0.93198200	-1.77537800

TS-3a

C	-0.00490400	-0.01601500	0.00722900
C	0.00691800	-0.00008400	2.27385400
N	0.60463900	-0.00125200	-1.18966800
H	-1.09011000	-0.04947300	-0.08250800
N	1.93101200	0.20374100	-1.17097400
O	2.50814700	0.62929700	-0.15658400
O	2.53500700	0.01230300	-2.22591500
N	-0.10349200	-0.72055300	3.52897700
O	-0.50451000	-0.10533900	4.50292400
O	0.22363600	-1.89326700	3.53164600
N	0.47096600	-0.68613500	1.14643900
N	-0.07045900	1.76605300	0.82903500
C	-0.32983700	1.28450900	2.15191000
H	-0.75538900	1.92201700	2.91962500
C	-1.03744300	2.60024300	0.18701900
C	-0.59574200	3.47612800	-0.80522700
C	-2.39384900	2.47126800	0.48387200
C	-1.52722700	4.24490800	-1.49700800
H	0.46672600	3.55224700	-1.02465200
C	-3.31519900	3.25021700	-0.21510100
H	-2.73057800	1.77662400	1.24900300
C	-2.88753600	4.13613800	-1.20324100
H	-1.18639200	4.93112500	-2.26633400
H	-4.37221000	3.15922900	0.01627200
H	-3.61087200	4.73942400	-1.74320700
H	0.87646800	2.16010100	0.76183500
H	1.48118000	-0.83718300	1.15814200

TS-3b

C	0.00921100	-0.07811400	0.04593200
C	-0.03521400	0.01420100	2.19042100
N	0.79918200	-0.19817100	-1.10519200
H	-1.04323200	-0.02155000	-0.25761400
N	2.12305400	0.10607600	-1.10531900
O	2.64408000	0.44618700	-0.05838300
O	2.69157500	0.02425000	-2.18337400
N	-0.06874800	-0.58573000	3.53193300
O	0.24029400	-1.75730900	3.63861200

O	-0.40664200	0.12316000	4.46711600
N	0.35292500	-0.75434900	1.16115800
N	-0.00491400	1.71432300	0.67090900
C	-0.22603200	1.34830200	2.04919900
H	-0.29916300	2.09725800	2.82519700
H	0.38842400	-0.14932000	-2.03577100
C	-1.00934000	2.43435800	-0.06426900
C	-0.61505200	3.07511300	-1.23997900
C	-2.34310000	2.42573400	0.33868900
C	-1.57162200	3.72389900	-2.01610400
H	0.43230700	3.06783300	-1.53443900
C	-3.29130500	3.07820800	-0.44939000
H	-2.63355400	1.92689000	1.25847300
C	-2.91145000	3.72702500	-1.62346300
H	-1.26773900	4.22946600	-2.92778700
H	-4.33121400	3.08059500	-0.13671300
H	-3.65493100	4.23687500	-2.22854700
H	0.89871600	2.19565900	0.57058000

Product-complex (4-nitro-1-phenyl-1H-imidazole + H₂O)

C	0.33856800	1.20437100	0.16043000
C	1.63166100	-0.44307700	-0.08808200
H	-0.07825200	2.18850500	0.32650700
O	4.06165400	2.46080400	0.46036900
N	2.85531300	-1.16359900	-0.20423400
O	2.79010000	-2.37701900	-0.36693700
O	3.90477300	-0.53956500	-0.13617900
N	1.61315000	0.90326000	0.11201900
N	-0.45084200	0.09434000	-0.00403900
C	0.37096600	-0.97958200	-0.16338100
H	0.01459000	-1.98585000	-0.32939700
C	-1.88224500	0.07229300	0.00495600
C	-2.54317600	-0.96218100	0.66412900
C	-2.58152700	1.08822100	-0.64271900
C	-3.93589800	-0.97851500	0.66528900
H	-1.97799300	-1.73319700	1.17939800
C	-3.97452600	1.06740500	-0.61934800
H	-2.04696200	1.87326500	-1.16887100
C	-4.65277100	0.03546400	0.02921100
H	-4.45880800	-1.78087700	1.17635100
H	-4.52690300	1.85527700	-1.12200600
H	-5.73841200	0.02100400	0.03856200
H	3.24301900	1.94017000	0.34387600
H	4.76783500	1.80353200	0.50842000

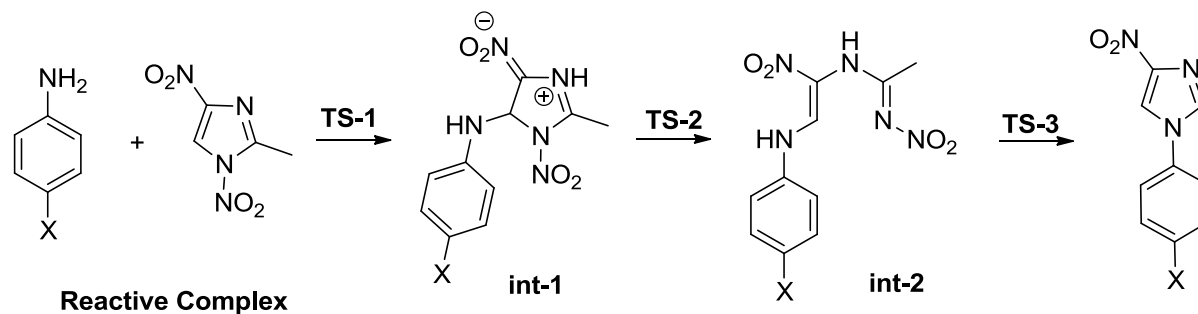
N₂O

N	0.07687500	0.00011200	0.00000000
O	-1.11368800	-0.00004700	0.00000000
N	1.19591200	-0.00005800	0.00000000

2.- Summary of the energies, thermal corrections to Gibbs free energy and number of imaginary frequencies (NIMAG) for the all optimized structures for the model reaction.

Structure	Energy (a.u)	G _{corr} (a.u)	NIMAG	ν (cm ⁻¹)
Reactive-complex	-922.480822	0.151885	0	-
TS-1a	-922.448740	0.154906	1	100i
TS-1b	-922.461893	0.155059	1	356i
Int-1a	-922.467272	0.154226	0	-
Int-1b	-922.474663	0.157942	0	-
Int-1c	-922.477222	0.155964	0	-
TS-2a	-922.457981	0.153024	1	135i
TS-2b	-922.412427	0.152393	1	427i
TS-2c	-922.456746	0.153352	1	132i
Int-2a	-922.493001	0.153568	0	-
Int-2b	-922.485808	0.151632	0	-
TS-3a	-922.445674	0.154832	1	281i
TS-3b	-922.426807	0.152763	1	350i
Product-Complex	-737.968126	0.138409	0	-
N ₂ O	-184.586286	-0.005796	0	-

3. Cartesian coordinates for the all optimized structures for the reaction between substituted anilines and 2-methyl-1,4-dinitro-1H-imidazole.



3.1 Cartesian coordinates for the reaction between 4-chloroaniline and 2-methyl-1,4-dinitro-1H-imidazole

Reactive complex-Cl

C	-0.03692400	-0.01079400	0.02650500
C	0.08280800	0.00423300	2.15439300
N	1.30937500	0.00050700	0.42264700
N	2.44120300	0.02931800	-0.40520300
O	2.23616500	0.02039500	-1.59465400
O	3.50704900	0.05853100	0.16035400
N	-0.39095400	0.02112300	3.50765400
O	-1.59353000	-0.03879500	3.69992300
O	0.44722500	0.09852800	4.39582000
N	-0.78118800	-0.02668500	1.09597900
N	0.48379200	3.01806800	0.69491900
H	0.12872300	3.34258500	1.58682300
C	1.86224700	3.08743700	0.54188800
C	2.44062200	3.10318600	-0.73791300
C	2.70970900	3.05606300	1.66273800
C	3.82346700	3.08223800	-0.89563400
H	1.80029000	3.12837800	-1.61629100
C	4.09181600	3.03818200	1.50982500
H	2.27754700	3.04087600	2.66064900
C	4.63989300	3.04759000	0.22998500

H	4.25632500	3.09002500	-1.89139300
H	4.73590600	3.01350700	2.38361700
C	1.39214300	0.02303600	1.79286600
H	2.32230100	0.03660200	2.34054400
H	-0.05730000	3.36945600	-0.08635100
C	-0.52547900	0.00398100	-1.37311500
H	-0.18031900	0.90178400	-1.89349300
H	-0.17039000	-0.86972600	-1.92496000
H	-1.61539500	-0.00143500	-1.33750100
Cl	6.38377400	3.01071600	0.03297700

TS-1-Cl

C	-0.01591700	-0.01053000	-0.03982500
C	0.00823900	-0.00388200	2.11382500
N	1.34736100	0.00296200	0.41250200
N	2.48174100	-0.23106200	-0.34414300
O	2.34325600	-0.23319800	-1.54754600
O	3.51524000	-0.41355200	0.26416200
N	-0.47272300	0.02971900	3.38539200
O	-1.69553700	-0.07841000	3.60132800
O	0.34884200	0.18135700	4.32135500
N	-0.79464800	-0.01093000	0.98616200
N	1.83269800	2.01808800	2.08362700
H	1.97506500	2.09213600	3.09269200
C	2.96189300	2.39447400	1.31505500
C	2.78629000	2.73754000	-0.02651900
C	4.24208400	2.27217300	1.85991700
C	3.89930900	2.93262400	-0.84026100
H	1.78480500	2.84077900	-0.43778800
C	5.35449200	2.47342000	1.05354200
H	4.36404500	2.00484900	2.90607700
C	5.16945600	2.78902600	-0.29174000
H	3.77400100	3.19086700	-1.88677600
H	6.35427000	2.37740200	1.46425400
C	1.38108200	0.13894400	1.79961000
H	2.22685600	-0.23921500	2.36132600
H	0.97855500	2.51188000	1.81634200
Cl	6.57285400	3.02507700	-1.31045700
C	-0.42862900	-0.01863500	-1.46400900
H	-0.02518900	0.84678300	-1.99613400
H	-0.08043100	-0.92308700	-1.96966300
H	-1.51875500	0.01257200	-1.48595100

Int-1-Cl

C	3.42896600	-0.37990300	0.14039400
C	1.99882800	1.32191100	-0.17215100

N	2.18343900	-0.90868600	-0.09674400
N	1.88980200	-2.24534900	-0.16455500
O	2.77115400	-3.03626400	0.10195300
O	0.75028400	-2.50999500	-0.48947000
N	1.65656200	2.57065800	-0.36466600
O	2.53360000	3.49766400	-0.29046900
O	0.43480500	2.84262100	-0.62489900
N	3.30831500	0.92040900	0.08899400
N	0.11220600	0.03897300	0.76845700
H	0.33306300	0.58874900	1.59321700
C	-1.25925300	-0.02680500	0.47899500
C	-2.15776000	0.52040900	1.40695400
C	-1.76446600	-0.64602800	-0.67137900
C	-3.52905500	0.45845600	1.19328500
H	-1.77481600	1.00186800	2.30322500
C	-3.13916200	-0.69522000	-0.89601000
H	-1.10443000	-1.10417400	-1.39898500
C	-4.01042000	-0.14579500	0.03597900
H	-4.21366000	0.88600600	1.91893400
H	-3.52120500	-1.17075800	-1.79400100
C	1.09697900	0.12875700	-0.25463300
H	0.64631300	0.01086100	-1.24371600
H	4.08405700	1.56695400	0.23847400
C	4.69380000	-1.09316500	0.40465000
H	4.59513500	-1.69702700	1.31028000
H	4.92429900	-1.76035400	-0.42992300
H	5.48574600	-0.35397000	0.52708100
Cl	-5.73978000	-0.21224000	-0.24814200

TS-2-Cl

C	-0.00138800	-0.03508900	0.00530600
C	0.00365800	-0.00231100	2.32998000
N	1.30707900	0.00803700	0.30650900
N	2.28839200	0.03672500	-0.61034700
O	2.03730200	-0.05225900	-1.80662900
O	3.42072800	0.14496300	-0.15098000
N	-0.66149400	0.29554700	3.43206400
O	-1.92527400	0.46936000	3.36217200
O	-0.06843400	0.38275700	4.55721400
N	-0.69976500	-0.07770900	1.12286000
N	2.27156000	0.61692700	2.85784600
H	1.88379400	1.51554500	3.13947300
C	3.64878000	0.42759800	3.12725200
C	4.29786100	1.43126100	3.84881300
C	4.35096900	-0.70391800	2.70774900
C	5.64723900	1.30835500	4.16106400
H	3.74796400	2.31239400	4.16901600
C	5.69989600	-0.83177400	3.02343200
H	3.87673400	-1.48762100	2.12769300

C	6.33476100	0.17357000	3.74577300
H	6.15151400	2.08995600	4.71960100
H	6.24980600	-1.70933800	2.69960700
C	1.46181000	-0.22405500	2.23913500
H	1.81833700	-1.24407200	2.11661200
H	-1.71822900	-0.07373100	1.13041900
C	-0.67430200	-0.01871100	-1.31722700
H	-0.35539200	0.86290500	-1.87855000
H	-0.38856900	-0.90535000	-1.88860000
H	-1.75409500	0.00125500	-1.16742300
Cl	8.03361700	0.00884300	4.13178100

Int-2-Cl

C	-0.07924000	-0.05700600	-0.03132200
C	-0.03426000	0.01865700	2.37555800
N	0.40742300	-0.04127100	-1.26666300
N	1.72780400	0.23542500	-1.47009600
O	2.47549500	0.63191600	-0.57233700
O	2.11679600	0.08918100	-2.62179500
N	-0.19103300	-1.27622200	2.90294700
O	-0.68583800	-1.41902000	4.02806100
O	0.15772000	-2.23761600	2.21138800
N	0.58154800	0.13821300	1.11758700
N	-0.32105100	2.34960300	2.67704600
C	-0.44356500	1.10303700	3.11346600
H	-0.87705400	0.94065800	4.09471100
C	-0.73391200	3.52029400	3.35554100
C	-0.15805400	4.72977500	2.96079500
C	-1.69428200	3.49317400	4.36812700
C	-0.52747300	5.91477700	3.58619900
H	0.58469300	4.74386600	2.16727100
C	-2.05844700	4.67701700	5.00266900
H	-2.18243400	2.56933900	4.66024700
C	-1.47168400	5.87456200	4.60693700
H	-0.08003400	6.85522200	3.28189800
H	-2.80633300	4.66170000	5.78919200
H	0.14255400	2.49884100	1.78204900
H	1.58101000	0.32916600	1.07722800
Cl	-1.94244500	7.36258600	5.39809100
C	-1.54110600	-0.35638800	0.04666700
H	-1.96719600	-0.35458500	-0.95505700
H	-1.68926400	-1.34384700	0.49794800
H	-2.04553300	0.38776900	0.66935200

TS-3-Cl

C	-0.00990100	0.01027900	0.00893400
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C	-0.00001500	-0.00694100	2.31542600
N	0.80222500	0.01479000	-1.08501000
N	2.09973900	0.21249400	-0.86812000
O	2.53061700	0.62139100	0.23037100
O	2.86121300	0.02782400	-1.82156500
N	-0.11753400	-0.70962300	3.58075900
O	-0.44035700	-0.06109700	4.56190000
O	0.13028600	-1.90156300	3.58257000
N	0.33729600	-0.74117100	1.17713200
N	0.04598400	1.74429900	0.86827400
C	-0.20861800	1.30331800	2.20788700
H	-0.52201500	1.98590900	2.98955900
C	-0.79697400	2.74240600	0.28157800
C	-0.30569500	3.42602100	-0.83071700
C	-2.08900100	2.96868400	0.75128800
C	-1.11342700	4.35064700	-1.48262000
H	0.70526700	3.23660700	-1.18349100
C	-2.89920200	3.89572800	0.10131800
H	-2.47452100	2.42937600	1.61205400
C	-2.40324400	4.57266400	-1.00778400
H	-0.74060400	4.89098900	-2.34664300
H	-3.90668100	4.08298400	0.45791100
H	1.03850500	2.00610000	0.78014000
H	1.31735500	-1.03061300	1.19244400
C	-1.45852800	-0.08728200	-0.36460300
H	-1.71120500	0.64738700	-1.13089200
H	-1.60814500	-1.09122600	-0.77337800
H	-2.10864400	0.03053100	0.50510800
Cl	-3.42362600	5.73750200	-1.82220200

Product-complex-Cl

C	1.17141100	1.05469000	0.08850900
C	2.41239600	-0.65975600	-0.10417100
O	4.79561300	2.32682400	0.35435100
N	3.61477900	-1.41631000	-0.17609300
O	3.52220300	-2.63160500	-0.31712500
O	4.68038700	-0.82017000	-0.09205300
N	2.43353900	0.69154200	0.05969700
N	0.35034400	-0.04787000	-0.05773900
C	1.13699500	-1.15441500	-0.17614900
H	0.74028500	-2.15057000	-0.30837000
C	-1.08101200	-0.05870400	-0.03869000
C	-1.73641300	-0.85926600	0.89311500
C	-1.78804400	0.71737700	-0.95300800
C	-3.12785500	-0.88735400	0.91186000
H	-1.16557000	-1.45107700	1.60272400
C	-3.17933900	0.70282400	-0.92814000
H	-1.26130400	1.31776400	-1.68824900
C	-3.82979200	-0.10119200	0.00310900

H	-3.65432300	-1.50560300	1.63145600
H	-3.74591400	1.30153300	-1.63347700
H	4.02346500	1.73509100	0.24870100
H	5.55336700	1.74007500	0.47330300
C	0.67162900	2.44151100	0.27815700
H	0.29282100	2.85773700	-0.65955200
H	-0.13417600	2.46571200	1.01747200
H	1.49885900	3.06195800	0.62671600
Cl	-5.57786000	-0.12581400	0.02936900

3.2 Cartesian coordinates for the reaction between aniline and 2-methyl-1,4-dinitro-1*H*-imidazole

Reactive-Complex-H

C	-0.03736500	-0.00723100	0.05327300
C	0.09213300	0.02076800	2.18021700
N	1.31005200	-0.01032100	0.44285400
N	2.43683300	-0.02522000	-0.39287000
O	2.22402800	-0.08573400	-1.57939800
O	3.50627500	0.01843300	0.16401700
N	-0.37662700	0.05419300	3.53463700
O	-1.57988300	0.02289700	3.73101000
O	0.46554700	0.11500400	4.42042500
N	-0.77678000	-0.00321600	1.12654800
N	0.54222000	3.00604900	0.85025400
H	0.31783900	3.35944200	1.77307200
C	1.88995500	3.06570400	0.50818500
C	2.28596000	3.02660900	-0.83869700
C	2.88167900	3.08375100	1.50385400
C	3.63816100	3.00941100	-1.17557800
H	1.52563400	3.00731200	-1.61714300
C	4.22946400	3.07068500	1.15540500
H	2.58340200	3.10770300	2.54990400
C	4.62137200	3.03200300	-0.18521100
H	3.92199100	2.97679900	-2.22437000
H	4.98047700	3.08842200	1.94119700
H	5.67366900	3.01794500	-0.45187400
C	1.40010400	0.02125900	1.81235800
H	2.33293000	0.02465000	2.35571000
H	-0.09618300	3.35359500	0.14410900
C	-0.53237900	-0.00197400	-1.34444300
H	-0.16630000	0.87757000	-1.88136900
H	-0.20278800	-0.89372200	-1.88321300
H	-1.62185200	0.02127200	-1.30386700

TS-1-H

C	-0.01857000	-0.01093300	-0.03968400
C	0.00459600	-0.00004700	2.11326200
N	1.34331200	-0.00934700	0.41373800
N	2.47740400	-0.24329700	-0.34384300
O	2.33787200	-0.24565400	-1.54728800
O	3.51019400	-0.42962400	0.26373200
N	-0.47785100	0.04230600	3.38587200
O	-1.70136600	-0.05324500	3.59993200
O	0.34369600	0.18851500	4.32143900
N	-0.79835500	-0.00268900	0.98604700
N	1.84134000	2.02679700	2.07441500
H	1.99406500	2.10230700	3.08128300
C	2.96548100	2.39511400	1.29371000
C	2.78093600	2.72440500	-0.05108200
C	4.24882300	2.28014700	1.83457400
C	3.89631000	2.91076800	-0.86633100
H	1.77449300	2.82068900	-0.45314200
C	5.35296000	2.47668600	1.01285800
H	4.37026400	2.02340900	2.88390800
C	5.18174600	2.77921500	-0.34114800
H	3.75624700	3.15692400	-1.91479200
H	6.35209400	2.38504500	1.42830600
H	6.04794200	2.92132000	-0.98019400
C	1.37642100	0.12913100	1.79926400
H	2.22262600	-0.24115800	2.36479800
H	0.98494500	2.51932500	1.81382100
C	-0.43124200	-0.02091800	-1.46409800
H	-0.02046300	0.83924200	-1.99919800
H	-0.09044000	-0.93000900	-1.96643100
H	-1.52106300	0.01911700	-1.48629300

Int-1-H

C	2.76801400	-0.27387300	0.19720300
C	1.27185100	1.35782800	-0.17608200
N	1.56264800	-0.86167500	-0.09911800
N	1.33591100	-2.21115900	-0.16974900
O	2.24390000	-2.95870800	0.13118800
O	0.22310800	-2.53188700	-0.53389100
N	0.87625000	2.59225000	-0.35707100
O	1.70411700	3.55833400	-0.23251200
O	-0.34738900	2.81309500	-0.65398800
N	2.58640400	1.01915500	0.14194700
N	-0.57450200	-0.01648000	0.71184700
H	-0.40299700	0.54665500	1.53936700
C	-1.93649100	-0.14393700	0.38521100
C	-2.88205600	0.36771800	1.28649800
C	-2.37944900	-0.79151600	-0.77548500
C	-4.24272300	0.23655200	1.02978900

H	-2.53901900	0.87155600	2.18724400
C	-3.74709800	-0.90165300	-1.02811800
H	-1.67351900	-1.22150400	-1.47760600
C	-4.68779400	-0.39480900	-0.13323800
H	-4.95803100	0.63981100	1.74119300
H	-4.07403400	-1.40235800	-1.93538800
H	-5.74978500	-0.49088700	-0.33693400
C	0.42957700	0.12339200	-0.28570500
H	0.01170400	-0.01620600	-1.28612500
H	3.32246000	1.70209600	0.32613500
C	4.05179600	-0.92455500	0.52437400
H	3.93848000	-1.52638300	1.42977700
H	4.35175000	-1.58603100	-0.29222000
H	4.80236000	-0.14895100	0.67651100

TS-2-H

C	0.04231300	0.17928600	-0.06253900
C	-0.10086700	0.08830400	2.25753300
N	1.30165700	0.43657000	0.32958800
N	2.31256000	0.69028500	-0.51725700
O	2.14551000	0.64679300	-1.73075800
O	3.38402600	0.95178000	0.01999400
N	-0.87151900	0.10571400	3.32873400
O	-2.13738800	-0.00148300	3.18192200
O	-0.37106700	0.20061200	4.49835700
N	-0.70321400	-0.03930000	1.00207600
N	1.95658200	1.13381700	2.95562700
H	1.38152200	1.93344500	3.21370300
C	3.32601500	1.22271300	3.31715600
C	3.71200600	2.35320000	4.04031700
C	4.26072600	0.23977700	2.98526300
C	5.03783500	2.49970000	4.43839300
H	2.97320100	3.11134000	4.28741600
C	5.58309100	0.39823700	3.39337200
H	3.98445500	-0.63654000	2.40896900
C	5.97930600	1.52264500	4.11829000
H	5.33050900	3.38098600	5.00108500
H	6.30893700	-0.36677500	3.13422200
H	7.01355100	1.63559200	4.42848700
C	1.37743200	0.16793500	2.26824100
H	1.94034800	-0.75449400	2.15209600
H	-1.70240200	-0.23050000	0.94153800
C	-0.54005000	0.12935400	-1.42686500
H	-0.36139800	1.07789900	-1.93889100
H	-0.05745700	-0.66302300	-2.00385000
H	-1.61081100	-0.06140300	-1.35075600

Int-2-H

C	-0.05186200	-0.06126400	-0.04315000
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C	-0.09166700	0.02121500	2.36326000
N	0.47557100	-0.04214900	-1.26244300
N	1.80549200	0.21715900	-1.42155700
O	2.54558200	0.53349500	-0.48623000
O	2.21625200	0.12875600	-2.57169100
N	-0.26557300	-1.26933700	2.89008600
O	-0.80013300	-1.40912300	3.99826900
O	0.10933300	-2.23462900	2.21639300
N	0.56888200	0.13392900	1.12728800
N	-0.38368700	2.35486800	2.64959200
C	-0.52412200	1.11089100	3.08274100
H	-0.99271500	0.95164600	4.04819200
C	-0.82082000	3.52934400	3.31254100
C	-0.22015500	4.73580300	2.94526100
C	-1.82593000	3.50187600	4.28124900
C	-0.61458700	5.91758100	3.56563200
H	0.55556700	4.74180600	2.18318500
C	-2.20294900	4.69116400	4.90134100
H	-2.33015300	2.57703600	4.54227500
C	-1.60216900	5.90013100	4.55065400
H	-0.14263300	6.85262700	3.27905200
H	-2.98464200	4.66851600	5.65508100
H	0.11151600	2.50247400	1.77132500
H	1.57053700	0.31720000	1.12043400
H	-1.90740200	6.82210700	5.03588100
C	-1.51712000	-0.35444000	-0.01566200
H	-1.68808800	-1.32483300	0.46331500
H	-2.04408700	0.41328600	0.55815900
H	-1.90101400	-0.38593700	-1.03366300

TS-3-H

C	-0.04083200	-0.03176700	-0.06697100
C	-0.01750500	-0.01448500	2.24210200
N	0.76548300	0.00959900	-1.16036300
N	2.05442300	0.27133500	-0.94626300
O	2.46456000	0.71476900	0.14540000
O	2.82198100	0.11176700	-1.89864800
N	-0.10195500	-0.71280200	3.51220800
O	-0.42880300	-0.06752500	4.49451000
O	0.17307000	-1.89904900	3.51797900
N	0.34946300	-0.74288700	1.10892700
N	-0.07471800	1.73431200	0.78548100
C	-0.28756600	1.28423900	2.12690900
H	-0.63171200	1.95112800	2.90931500
C	-0.99125700	2.66974400	0.20580500
C	-0.56535300	3.37617100	-0.91983700
C	-2.28892700	2.80731200	0.69629700
C	-1.45488800	4.23433500	-1.55978600
H	0.45128800	3.24959500	-1.28478500
C	-3.16817200	3.67219700	0.04703400
H	-2.61504500	2.24479300	1.56705300

C	-2.75716700	4.38398900	-1.07957500
H	-1.12846600	4.78782500	-2.43500300
H	-4.17944800	3.78498800	0.42568200
H	-3.44774400	5.05557000	-1.58051400
H	0.89757700	2.05527200	0.67863400
H	1.34171400	-0.98644800	1.12194800
C	-1.48548200	-0.19759400	-0.42732000
H	-1.77810800	0.51687500	-1.19846800
H	-1.59392700	-1.21200600	-0.82353900
H	-2.13243700	-0.09885300	0.44711700

Product-complex-H

C	0.37290200	1.04773300	0.08598000
C	1.64969100	-0.63965600	-0.10663200
O	4.01171300	2.34567100	0.36156300
N	2.86676800	-1.37061700	-0.18389700
O	2.80001700	-2.58984300	-0.30654200
O	3.92021000	-0.75020000	-0.12294900
N	1.64317800	0.71270900	0.05092700
N	-0.42504600	-0.07208700	-0.05066600
C	0.38403800	-1.16136500	-0.16860300
H	0.00881600	-2.16660800	-0.29465700
C	-1.85828700	-0.11151900	-0.02735800
C	-2.49330000	-0.91277700	0.91845100
C	-2.58026800	0.64019000	-0.95112700
C	-3.88592100	-0.96039300	0.93516400
H	-1.90326100	-1.48185300	1.63144400
C	-3.97239400	0.59384600	-0.91522700
H	-2.05977200	1.23943800	-1.69224200
C	-4.62481700	-0.20529600	0.02402900
H	-4.39143500	-1.58182700	1.66795500
H	-4.54562400	1.17597500	-1.63020100
H	-5.70989600	-0.24083300	0.04501100
H	3.23226800	1.76504100	0.24876900
H	4.76420500	1.74689300	0.45063600
C	-0.15701200	2.42345200	0.27583800
H	-0.54256700	2.83309600	-0.66197700
H	-0.96520200	2.42855500	1.01288200
H	0.65484700	3.06177000	0.62817200

3.3 Cartesian coordinates for the reaction between 4-methoxyaniline and 2-methyl-1,4-dinitro-1H-imidazole

Reactive-complex-OCH₃

C	-2.00443400	1.52830200	-0.09247800
C	-2.65763500	-0.48427400	-0.34584900
N	-1.01746500	0.79478400	-0.76547200
N	0.22303900	1.25930000	-1.22720300

O	0.45714100	2.43108200	-1.05467600
O	0.92763900	0.43634100	-1.75821900
N	-3.52932600	-1.61773600	-0.24035400
O	-4.62711300	-1.45846400	0.26606100
O	-3.11464300	-2.68729600	-0.66667700
N	-3.01430000	0.73920600	0.14668400
N	-0.49522100	-0.07622100	2.19083000
H	-0.85590500	-0.95554000	2.54481900
C	0.77415100	-0.17634700	1.60546400
C	1.59887600	0.95471000	1.49500200
C	1.21879100	-1.37643200	1.04151800
C	2.82195300	0.88253800	0.84010500
H	1.27043000	1.89966200	1.92243700
C	2.45015000	-1.45855500	0.38651700
H	0.59441500	-2.26433800	1.11397700
C	3.25360900	-0.32291400	0.27886600
H	3.45460500	1.76188300	0.75305600
H	2.75943600	-2.40930400	-0.03367300
C	-1.42576800	-0.50648500	-0.91915400
H	-0.83644300	-1.26817900	-1.40722400
H	-0.56673000	0.65015000	2.89497900
C	-1.90748600	2.95882100	0.28518100
H	-1.05410800	3.12756500	0.94831100
H	-1.78279600	3.59132000	-0.59705800
H	-2.83003100	3.22357900	0.80270400
C	4.95575200	-1.50885300	-0.90509300
H	4.28129700	-1.88718600	-1.68148100
H	5.92339500	-1.27407100	-1.34954900
H	5.08723100	-2.26970600	-0.12742500
O	4.47202100	-0.29219300	-0.35345500

TS-1-OCH₃

C	1.50233400	-0.04109700	-0.30324300
C	0.21259100	0.80232300	1.19703500
N	1.86313900	-0.56384200	0.98156000
N	2.90266500	-1.41793700	1.27982700
O	3.48154900	-1.93739500	0.35126000
O	3.14650200	-1.56629600	2.46112500
N	-0.75705600	1.60667100	1.73025300
O	-1.50724000	2.26240800	0.98690700
O	-0.83930700	1.67422800	2.97676900
N	0.50793700	0.76308000	-0.15624300
N	2.39819200	1.35363000	2.83130800
H	3.13032900	0.80568600	3.28417600
C	2.85642700	2.20807400	1.80392400
C	2.08620700	3.31736900	1.43419600
C	3.97839900	1.85830100	1.05308300
C	2.43952300	4.06347000	0.31982300
H	1.21423400	3.59386600	2.02301400
C	4.33779900	2.60525900	-0.06837500
H	4.57944900	0.99839800	1.34373900

C	3.56028200	3.70597000	-0.44019700
H	1.85412700	4.92830600	0.02245600
H	5.21467500	2.31547500	-0.63523600
C	1.10729500	0.04715300	1.97900300
H	0.92265400	-0.45698400	2.91864400
H	1.81856100	1.81780600	3.53106300
O	3.82349600	4.49468700	-1.52089400
C	4.94962400	4.16268800	-2.32686000
H	4.83557400	3.16585400	-2.76637700
H	4.97772200	4.91061700	-3.11933900
H	5.87596500	4.21098100	-1.74464600
C	2.19749200	-0.37467200	-1.56942700
H	3.26194700	-0.12937500	-1.50723100
H	2.10434700	-1.43812100	-1.80355700
H	1.73257300	0.21629300	-2.35958600

Int-1-OCH₃

C	3.48359000	-0.15062200	0.13082000
C	1.86701600	1.36912700	-0.21204300
N	2.30146800	-0.82254600	-0.06385000
N	2.16043500	-2.18597100	-0.08025600
O	3.11558900	-2.86254800	0.24278300
O	1.06763600	-2.59045500	-0.41969300
N	1.38170600	2.57443200	-0.36629500
O	2.15180400	3.59209600	-0.28234800
O	0.13173000	2.71611800	-0.59663300
N	3.21579700	1.12535000	0.03974600
N	0.13097200	-0.09946000	0.77698200
H	0.29108000	0.51721700	1.56883800
C	-1.24042600	-0.19401000	0.43263800
C	-2.18300700	0.50839900	1.18366200
C	-1.68637200	-1.00828500	-0.61731700
C	-3.54861300	0.40619000	0.91136000
H	-1.84911700	1.15064500	1.99547000
C	-3.04194200	-1.09547800	-0.90793900
H	-0.98182300	-1.58526300	-1.20718700
C	-3.98063600	-0.39477600	-0.14591400
H	-4.24947500	0.96537400	1.52079300
H	-3.38765700	-1.72219800	-1.72509000
C	1.10387500	0.07907200	-0.25273100
H	0.66792400	-0.12793400	-1.23497500
H	3.91503200	1.86166900	0.14368200
C	4.82888500	-0.70584700	0.38043100
H	4.83410200	-1.25716900	1.32392200
H	5.09908500	-1.39636500	-0.42248900
H	5.54068700	0.11933900	0.42160000
O	-5.29234800	-0.55586700	-0.50810600
C	-6.26999400	0.16945100	0.22678200
H	-6.10219800	1.24903400	0.14374600
H	-7.23110800	-0.08499200	-0.22071300
H	-6.26872200	-0.12606500	1.28160000

TS-2-OCH₃

C	-0.03995900	0.06210700	-0.00637100
C	-0.02650000	-0.05359400	2.32244000
N	1.25241900	-0.18265800	0.26705100
N	2.21190100	-0.22626400	-0.67224800
O	1.93532000	-0.16740500	-1.86551400
O	3.35479000	-0.34123600	-0.23991700
N	-0.69461800	0.00630400	3.45588200
O	-1.95730200	0.21221300	3.42947100
O	-0.09506200	-0.15326100	4.57362800
N	-0.72293000	0.09243300	1.12037800
N	2.25146500	0.55776200	2.78827500
H	1.87642100	1.48530200	2.98251200
C	3.63466800	0.38132300	3.06726400
C	4.29554800	1.43335900	3.70950700
C	4.32902100	-0.77999200	2.74158800
C	5.63938700	1.31959600	4.02687200
H	3.75153900	2.33966000	3.96377500
C	5.68092300	-0.89966400	3.06287300
H	3.84633000	-1.60422900	2.22858800
C	6.33934400	0.15061400	3.70683900
H	6.16121700	2.12938600	4.52735900
H	6.19991300	-1.81287800	2.79763600
C	1.43205500	-0.31873900	2.25114700
H	1.77463400	-1.34876900	2.19576800
H	-1.72539000	0.27428000	1.14754000
C	-0.71672200	0.29608900	-1.30704200
H	-0.26085900	1.15240600	-1.81025900
H	-0.59385100	-0.57714700	-1.95138000
H	-1.77558300	0.48692600	-1.12973900
O	7.65545000	0.12689800	4.05708700
C	8.40241100	-1.04676800	3.75061900
H	9.41362000	-0.85903800	4.11122900
H	7.98564700	-1.91935600	4.26465200
H	8.42507000	-1.22432100	2.67034600

Int-2-OCH₃

C	-0.07528800	0.06033000	-0.00745900
C	0.09406500	-0.03130500	2.39231400
N	0.34537700	0.08346500	-1.26726400
N	1.68140300	0.15550600	-1.53379000
O	2.53319900	0.32972600	-0.65823100
O	1.97884900	0.05616200	-2.71748000
N	-0.17639400	-1.32122700	2.86802700
O	-0.64456800	-1.46678900	4.00654500
O	0.04661700	-2.28458300	2.12468400
N	0.66221700	0.08196000	1.11050900
N	0.06082300	2.30196500	2.81395600

C	-0.16690000	1.05722500	3.19633700
H	-0.57380600	0.89388800	4.18902200
C	-0.22748700	3.46755800	3.57041900
C	0.51932800	4.62043200	3.30647100
C	-1.23037900	3.49106700	4.53468900
C	0.27629200	5.78054000	4.02271900
H	1.29346000	4.59974200	2.54341500
C	-1.46985200	4.65438800	5.26737500
H	-1.84890600	2.61761300	4.71751900
C	-0.71295400	5.80013200	5.01383700
H	0.84862700	6.68295800	3.83031200
H	-2.25536300	4.65187000	6.01441500
H	0.50170000	2.45465400	1.90802100
H	1.67574000	0.11367800	1.02304900
C	-1.56064300	-0.01533600	0.14023900
H	-2.02945300	0.05882100	-0.83919200
H	-1.83558700	-0.96954800	0.60270000
H	-1.91509300	0.79466500	0.78434600
C	-1.87372300	7.05668200	6.67960100
H	-1.82104500	8.07061600	7.07598800
H	-2.86806300	6.87925400	6.25636000
H	-1.67474800	6.33815300	7.48183200
O	-0.87202700	6.98252600	5.67042100

TS-3-OCH₃

C	-0.12043300	-0.00929100	-0.00241800
C	0.00153000	-0.01876000	2.30011600
N	0.59991500	-0.07733000	-1.15022600
N	1.92813100	-0.03713300	-1.04092100
O	2.49297800	0.30892500	0.01550900
O	2.57799400	-0.29905300	-2.05590700
N	-0.17310100	-0.71465500	3.56005900
O	-0.38362600	-0.04338300	4.55758000
O	-0.08602800	-1.92946800	3.54574100
N	0.22843500	-0.77765300	1.14642300
N	0.19949200	1.73759300	0.86842600
C	-0.06620300	1.30871800	2.20433600
H	-0.29455500	2.00768200	3.00147800
C	-0.51237200	2.84809900	0.31486500
C	0.03109000	3.45708200	-0.82058600
C	-1.73967900	3.26420600	0.81669100
C	-0.65287400	4.48827800	-1.44227800
H	0.98834900	3.11934900	-1.21092400
C	-2.42960200	4.30809900	0.19608500
H	-2.17706600	2.78530700	1.68841900
C	-1.88606300	4.91956000	-0.93503900
H	-0.24433500	4.97504200	-2.32264600
H	-3.38183800	4.62356800	0.60588500
H	1.21423600	1.84909600	0.73970000
H	1.18363900	-1.13944500	1.11421800

C	-1.59345800	0.08535800	-0.25913900
H	-1.80526200	0.85458000	-1.00339400
H	-1.90647400	-0.88596700	-0.65514300
H	-2.15340200	0.27982600	0.65830800
O	-2.48088900	5.94265500	-1.60938800
C	-3.72794700	6.42373600	-1.11779300
H	-3.62033800	6.81629500	-0.10101100
H	-4.02316500	7.22881100	-1.79040900
H	-4.48614200	5.63366000	-1.13565700

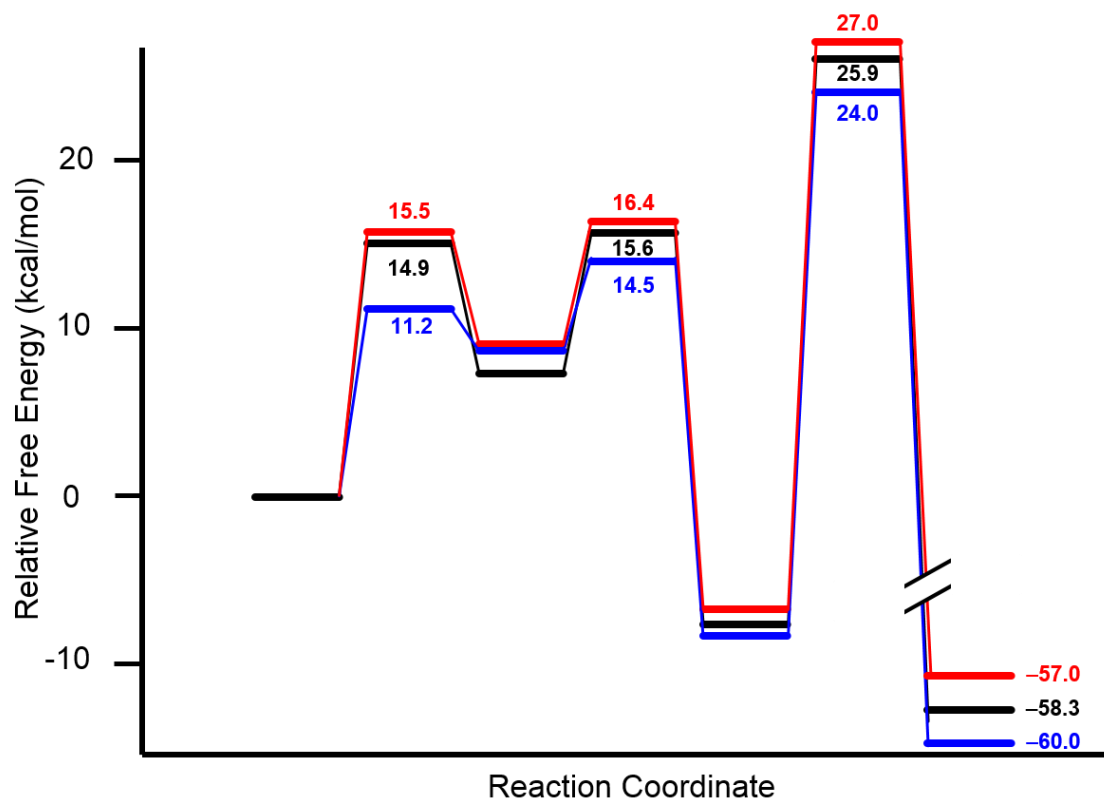
Product-complexOCH₃

C	1.20295700	1.07510000	0.08540800
C	2.40792700	-0.66372400	-0.10906200
O	4.91602900	2.14677400	0.55717800
N	3.58931900	-1.45159400	-0.16253400
O	3.46673700	-2.66107800	-0.33271900
O	4.66987300	-0.88980700	-0.03554400
N	2.45762000	0.68281100	0.08773900
N	0.36036000	-0.00093900	-0.11432200
C	1.12215700	-1.12248900	-0.23526900
H	0.70442600	-2.10442500	-0.40378100
C	-1.07208200	0.02655900	-0.13872200
C	-1.78045900	-0.73961800	0.77817100
C	-1.73732400	0.80684800	-1.08552400
C	-3.17497100	-0.73709600	0.76024900
H	-1.24705500	-1.33635600	1.51281300
C	-3.12299600	0.82347100	-1.09886700
H	-1.17368300	1.38670800	-1.81060100
C	-3.84531800	0.05199100	-0.17809200
H	-3.71451900	-1.34013100	1.48064400
H	-3.66595700	1.42175300	-1.82407300
H	4.09584000	1.63859500	0.39587700
H	5.61891700	1.48472200	0.58112800
C	0.72446100	2.46680200	0.29271100
H	0.34812100	2.89963600	-0.63854800
H	-0.08076600	2.49106200	1.03292500
H	1.55930900	3.07220500	0.64900400
O	-5.19870100	0.13449600	-0.27399500
C	-5.98114100	-0.60665000	0.65843100
H	-5.76467100	-0.29232900	1.68472600
H	-7.02012700	-0.38232200	0.41807700
H	-5.80170500	-1.68130200	0.54967300

4. Summary of the energies, thermal corrections to Gibbs free energy and number of imaginary frequencies (NIMAG) for the all optimized structures for the between substituted anilines and 2-methyl-1,4-dinitro-1*H*-imidazole.

Structure	Energy (a.u)	G _{corr} (a.u)	NIMAG	ν (cm ⁻¹)
Reactive-Cl	-1421.358716	0.165876	0	-
TS-1Cl	-1421.337299	0.169222	1	371i
Int-1Cl	-1421.348328	0.169948	0	-
TS-2Cl	-1421.334870	0.168190	1	160i
Int-2Cl	-1421.369925	0.166291	0	-
TS-3Cl	-1421.319219	0.169377	0	276i
Product-Cl	-1236.842825	0.151416	0	-
Reactive-H	-961.787884	0.177260	0	-
TS-1H	-961.768106	0.181146	1	361i
Int-1H	-961.778148	0.180920	0	-
TS-2H	-961.765725	0.179927	1	148i
Int-2H	-961.800812	0.177665	0	-
TS-3H	-961.750414	0.181119	1	278i
Product-H	-777.274036	0.163096	0	-
Reactive-OCH ₃	-1076.269599	0.207195	0	-
TS-1 OCH ₃	-1076.256309	0.211737	1	349i
Int-1 OCH ₃	-1076.260323	0.211718	0	-
TS-2 OCH ₃	-1076.249479	0.210218	1	129i
Int-2 OCH ₃	-1076.284385	0.208635	0	-
TS-3 OCH ₃	-1076.234205	0.210051	1	280i
Product- OCH ₃	-891.758837	0.193208	0	-

5. Reaction profile for the reaction of 4-chloroaniline (red pathway), aniline (black pathway) and 4-methoxyaniline (blue pathway) with 2-methyl-1,4-dinitro-1*H*-imidazole.



6.-Gas Phase IRC for an alternative ring opening mechanism for the model reaction

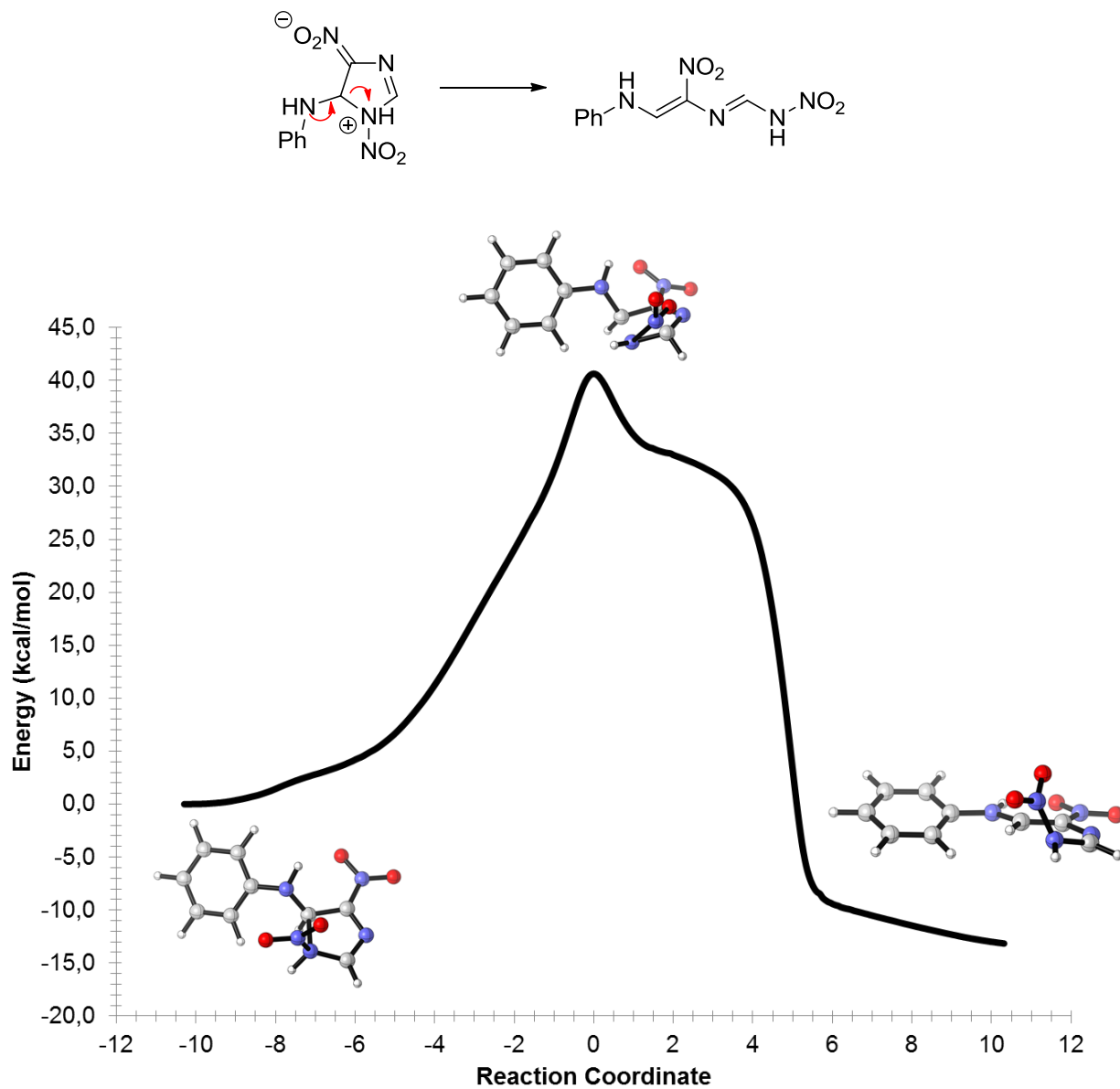
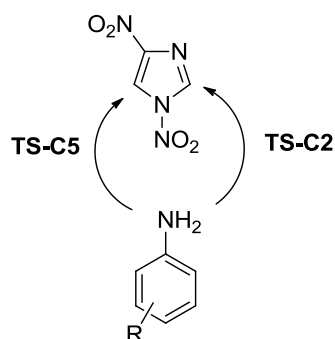


Figure S2. M06-2X/6-31+G(d,p) gas phase IRC for alternative ring-opening mechanism.

7. Table S1: Effects of substitution patterns at the aryl moiety onto the reaction selectivity.



Entry	Substituents	$\Delta G^\ddagger_{c2}$ (kcal/mol)	$\Delta G^\ddagger_{c5}$ (kcal/mol)
1	<i>o</i> -OCH ₃	25.3	13.3
2	<i>m</i> -OCH ₃	25.5	18.1
3	<i>p</i> -OCH ₃	24.1	15.4
4	<i>o</i> -CH ₃	26.2	19.0
5	<i>m</i> -CH ₃	24.8	17.7
6	<i>p</i> -CH ₃	24.3	16.4
7	<i>o</i> -Cl	28.3	20.5
8	<i>m</i> -Cl	27.6	19.5
9	<i>p</i> -Cl	26.1	18.0
10	<i>o</i> -NO ₂	33.7	24.8
11	<i>p</i> -NO ₂	33.4	25.3
12	<i>o</i> -CN	31.6	23.1
13	<i>p</i> -CN	29.7	22.4