

Supplementary Table S1. Cartesian coordinates for the stationary points involved in the I32CA reaction of (*E*)-*N*-((2-((methylbut-2-en-1-yl)thio)-1*H*-indol-3-yl)methylene)methanamine-oxide **1** together with the imaginary frequencies of transition states

1

C	4.81698700	0.12237800	0.17690400
C	4.91172000	-1.27376700	0.35098000
C	3.78849400	-2.08515500	0.26241000
C	2.56016900	-1.46358600	0.01136600
C	2.43284800	-0.05447900	-0.13707800
C	3.59595700	0.73492100	-0.06842000
N	1.30962300	-2.01148500	-0.16579400
C	0.39230400	-1.01096300	-0.42935300
C	1.03652400	0.22300400	-0.40798600
C	0.36438800	1.46798000	-0.73910700
S	-1.29268700	-1.40290100	-0.76140000
C	-2.15610300	-0.68320800	0.74439900
C	-3.59730000	-1.07923000	0.71835400
C	-4.62963900	-0.33532200	0.28468200
C	-6.03557300	-0.88045900	0.32579500
C	-4.51056900	1.06372900	-0.26329000
N	0.47441100	2.62999700	-0.12464500
O	-0.10654200	3.69303300	-0.52585100
C	1.24236800	2.80493500	1.12874600
H	5.71786800	0.72609900	0.22914700
H	5.88055100	-1.72309400	0.54649400
H	3.86056000	-3.16281400	0.37610500
H	3.54373200	1.80736300	-0.22419100
H	1.07102100	-2.98962900	-0.11994600
H	-0.33480900	1.49380300	-1.56861600
H	-1.64957700	-1.09112900	1.62213800
H	-2.00723200	0.39615100	0.72039500
H	-3.80619900	-2.08878200	1.06884000
H	-6.07080300	-1.89518300	0.73042300
H	-6.68481300	-0.24340400	0.94031900
H	-6.47769000	-0.89596800	-0.67871900
H	-3.48664900	1.43881500	-0.29490500
H	-4.90988000	1.10499700	-1.28431000
H	-5.11129900	1.76301500	0.33215500
H	1.61337000	1.85823600	1.51510100
H	2.06587100	3.49208000	0.92769500
H	0.55760500	3.27734500	1.83375400

TS-2n

Imaginary frequency= -408.1941 cm⁻¹

C	4.13854700	-1.84434100	-0.31279300
C	4.90588300	-0.66294200	-0.33976700
C	4.30945900	0.58730400	-0.21546900
C	2.91920900	0.62614400	-0.07746300
C	2.12612200	-0.55224700	-0.04597900
C	2.75799100	-1.80109900	-0.16099500

N	2.06293600	1.70440900	0.05386200
C	0.76324300	1.25285900	0.17387800
C	0.75563600	-0.13503100	0.14223700
S	-0.60843700	2.33460700	0.19175900
C	-1.68776400	1.54331800	-1.18925700
C	-1.94469200	0.06993200	-1.18647700
C	-0.45042800	-0.94749100	0.12643600
C	-3.11956000	-0.51650000	-0.65118600
O	-2.46204000	-1.58745800	0.86696600
N	-1.29078500	-1.07537900	1.17621800
C	-3.69868900	-1.71174900	-1.37330900
C	-4.13701700	0.32705300	0.08766100
C	-1.25321800	-0.25336500	2.38468200
H	4.63833300	-2.80371700	-0.40659200
H	5.98321600	-0.72904200	-0.45773500
H	4.90126600	1.49784500	-0.23242600
H	2.17573400	-2.71733200	-0.12672700
H	2.31741700	2.67737700	-0.00705600
H	-2.59563300	2.14166000	-1.07574200
H	-1.19532900	1.84500900	-2.11425400
H	-1.51635600	-0.43400900	-2.04859900
H	-0.47046300	-1.81812500	-0.52145000
H	-4.26829500	-2.34643400	-0.68858900
H	-4.37371800	-1.38426800	-2.17530800
H	-2.91107000	-2.32162400	-1.82451200
H	-4.76647100	-0.29990900	0.72334600
H	-3.66984500	1.08447900	0.72104100
H	-4.79545300	0.84652400	-0.62421900
H	-1.75708000	0.70587400	2.23633800
H	-0.21600500	-0.07224700	2.66961800
H	-1.76233000	-0.82038600	3.16523200

TS-2x

Imaginary frequency= -479.0103 cm⁻¹

C	3.41219100	-2.13583200	0.08873100
C	4.34427400	-1.16520600	0.50954400
C	4.01487900	0.18509500	0.55016200
C	2.72025400	0.54633100	0.16371200
C	1.77400500	-0.41793500	-0.29108500
C	2.13188100	-1.77639600	-0.31169800
N	2.11254500	1.78750100	0.13374900
C	0.82980000	1.64921600	-0.37530900
C	0.59281100	0.31263300	-0.65956600
S	-0.40912800	2.88389900	-0.37491500
C	-1.87755900	1.96263800	0.49806200
C	-1.57142900	0.53863400	0.81269900
C	-0.73664300	-0.04072700	-1.12100800
C	-2.44892800	-0.53529400	1.08027800
O	-1.49028200	-1.92246100	-0.07928000

N	-1.30404000	-1.27287600	-1.20909500
C	-2.20264600	-1.37472000	2.31389000
C	-3.89107700	-0.50395200	0.62589600
C	-2.32750900	-1.50249300	-2.23761600
H	3.70288600	-3.18203600	0.08180000
H	5.33799800	-1.47818100	0.81607400
H	4.73268200	0.92937200	0.88286100
H	1.40906800	-2.52381000	-0.62089100
H	2.53552800	2.66264200	0.39658700
H	-2.02057800	2.56103500	1.40254100
H	-2.73554000	2.10502200	-0.16249600
H	-0.65307800	0.45560900	1.38987500
H	-1.09744600	0.64121000	-1.89490100
H	-2.63350900	-2.37402800	2.20112700
H	-2.66364900	-0.90654500	3.19449800
H	-1.13291700	-1.48520200	2.50327000
H	-4.04821000	0.13248900	-0.24898400
H	-4.52807300	-0.11278700	1.43199100
H	-4.24812100	-1.51098600	0.39362200
H	-1.93816000	-1.21255500	-3.21594500
H	-2.54615500	-2.57009900	-2.23747700
H	-3.24977100	-0.94816700	-2.03339400

TS-3n

Imaginary frequency= -478.6035 cm⁻¹

C	-3.86816200	-1.72453300	0.14292600
C	-4.60522700	-0.52440100	0.17985600
C	-3.97257200	0.70807700	0.06390200
C	-2.58232900	0.70772300	-0.07905600
C	-1.81528100	-0.48572800	-0.11545100
C	-2.48679900	-1.71664000	-0.00626800
N	-1.69729800	1.75503600	-0.20641800
C	-0.40068400	1.27982700	-0.32570800
C	-0.42800000	-0.11191200	-0.29359500
C	0.64948000	-1.11021500	-0.37271500
S	0.85131300	2.51045600	-0.49002000
C	2.23568100	1.90818500	0.60721200
C	2.63862700	0.46403500	0.50558200
C	1.95706900	-0.56276600	1.20064100
C	2.75495100	-1.82646700	1.50843200
C	0.99189900	-0.23351200	2.33330000
N	1.57218400	-1.05489800	-1.37622000
O	2.18270600	0.09182100	-1.48163900
C	2.34556800	-2.22339600	-1.79374200
H	-4.39183100	-2.67196600	0.22891300
H	-5.68385300	-0.56224600	0.29812500
H	-4.53654800	1.63605700	0.08647000
H	-1.93999000	-2.65462200	-0.04254100
H	-1.92114900	2.73485300	-0.13291100

H	0.31302900	-2.12273500	-0.15760200
H	3.05882000	2.55803000	0.29982000
H	1.96385400	2.17653300	1.63131600
H	3.67073900	0.29435000	0.21937900
H	2.12204900	-2.72048000	1.54231100
H	3.22864000	-1.74079700	2.49611300
H	3.55378800	-2.00474000	0.78466100
H	1.55552500	-0.05187000	3.25895900
H	0.31383900	-1.07062700	2.53061000
H	0.37356500	0.64171900	2.13844900
H	2.51142500	-2.15199300	-2.87124500
H	3.31998100	-2.24068000	-1.29499300
H	1.79591500	-3.14125800	-1.57581300

CA2n

C	-4.04256700	-1.63305000	0.54002000
C	-4.81289600	-0.52284700	0.14375000
C	-4.20991300	0.68013200	-0.21029600
C	-2.81635700	0.74555300	-0.15102100
C	-2.01490900	-0.36254200	0.24549300
C	-2.65516400	-1.56540100	0.59201000
N	-1.95938800	1.79606100	-0.43398500
C	-0.66101200	1.38138700	-0.22221200
C	-0.63967800	0.06695900	0.18351400
S	0.73697600	2.43311200	-0.36531600
C	1.65357500	1.64672900	1.03974600
C	1.83444900	0.12163300	0.97359900
C	0.61504700	-0.70613300	0.43562300
C	3.04722100	-0.43998700	0.14613200
O	2.51452700	-1.65930200	-0.40067600
N	1.17045500	-1.27570700	-0.82040400
C	4.20769900	-0.85651700	1.04954300
C	3.53669900	0.45401300	-1.00071200
C	0.53097600	-2.50994600	-1.24324400
H	-4.54384000	-2.55833000	0.80814900
H	-5.89505000	-0.60578800	0.11323300
H	-4.80227700	1.53709600	-0.51803100
H	-2.07415900	-2.43074300	0.89739100
H	-2.23332000	2.74339000	-0.63965100
H	2.62011400	2.15562400	1.07738800
H	1.10223900	1.91186800	1.94503900
H	1.98852900	-0.18240500	2.01530300
H	0.41237100	-1.52377400	1.14728000
H	4.99419800	-1.33970300	0.46238800
H	4.64265400	0.01764900	1.54532800
H	3.86764800	-1.56026800	1.81471800
H	4.32771200	-0.07465400	-1.54131300
H	2.72506200	0.67113500	-1.69485100
H	3.95446100	1.39913100	-0.63838900
H	1.05596500	-2.89817100	-2.11889100
H	-0.49999000	-2.27938200	-1.52149900
H	0.53337300	-3.28043300	-0.45408100

CA2x

C	3.77439100	-1.94186800	0.24336900
C	4.68106300	-0.86960800	0.34151400
C	4.23967700	0.44744200	0.26651500
C	2.87256900	0.66102000	0.08157600
C	1.93618700	-0.40517200	-0.04291400
C	2.41413100	-1.72469300	0.05843400
N	2.16778000	1.84872200	-0.00646300
C	0.82856600	1.56049300	-0.17972300
C	0.63827800	0.19658000	-0.22603400
S	-0.36295900	2.86328400	-0.24985900
C	-1.94076700	1.87258800	-0.25057000
C	-1.76241500	0.47944000	0.33482700
C	-0.74122100	-0.35676300	-0.45213800
C	-2.98535900	-0.46128300	0.37414500
O	-2.35561000	-1.74895700	0.55261600
N	-0.97696600	-1.73185700	0.02197200
C	-3.86400300	-0.24982400	1.60829700
C	-3.83757000	-0.45045500	-0.90561900
C	-0.95557200	-2.71892700	-1.05317200
H	4.14541700	-2.95945000	0.32328200
H	5.73782500	-1.07141500	0.48799800
H	4.93211600	1.27982700	0.35549400
H	1.72585000	-2.56071600	0.02282300
H	2.55732100	2.77203400	0.09145400
H	-2.64119600	2.46846000	0.34027000
H	-2.30177500	1.83326500	-1.28046400
H	-1.39014800	0.56935000	1.36112400
H	-0.98992100	-0.28513100	-1.52825100
H	-4.64488200	-1.01450800	1.65476800
H	-4.35220800	0.73000600	1.57717000
H	-3.26314500	-0.31863000	2.51841600
H	-3.22935700	-0.55424700	-1.80823900
H	-4.42025300	0.47364400	-0.99078100
H	-4.53733800	-1.29015200	-0.87590400
H	0.05887500	-2.75713800	-1.46077300
H	-1.20211000	-3.69912200	-0.63985800
H	-1.65628900	-2.48883900	-1.87133700

CA3n

C	3.89120700	-1.67090700	-0.00318700
C	4.62587500	-0.46940700	-0.05967600
C	3.98695100	0.76526800	-0.03029800
C	2.59177800	0.76897700	0.05175100
C	1.82640700	-0.43074700	0.10968400
C	2.50471400	-1.66309100	0.07964200
N	1.70119000	1.82215500	0.08832800

C	0.40939800	1.32834900	0.17576400
C	0.44213500	-0.04979400	0.20572100
C	-0.76673000	-0.93694300	0.28556800
S	-0.94800100	2.44365500	0.29944800
C	-2.23263800	1.68844300	-0.78340300
C	-2.66263100	0.22005800	-0.55463700
C	-1.68109600	-0.89811200	-0.98528900
C	-2.47514000	-2.21681100	-1.10469000
C	-0.94090600	-0.65272200	-2.30530700
N	-1.64591200	-0.47444700	1.40677500
O	-2.93617800	-0.08003800	0.80169900
C	-1.97622300	-1.49318500	2.39023300
H	4.42156500	-2.61834000	-0.02556000
H	5.70890000	-0.50792500	-0.12712200
H	4.55172600	1.69224100	-0.07223200
H	1.95414800	-2.59895600	0.12160300
H	1.93155700	2.79950600	0.00756000
H	-0.44402700	-1.96891500	0.46880200
H	-3.09777600	2.32536100	-0.57588200
H	-1.95847500	1.83588700	-1.83143800
H	-3.61900800	0.10657400	-1.08254900
H	-1.79609600	-3.06823400	-1.22004200
H	-3.12826200	-2.19338700	-1.98443200
H	-3.10166200	-2.38928500	-0.22713100
H	-1.65694900	-0.57427500	-3.13150700
H	-0.27529000	-1.49275800	-2.52952300
H	-0.32966300	0.25009200	-2.29084900
H	-2.67444800	-1.06449900	3.11304100
H	-2.42007000	-2.40852100	1.96688600
H	-1.05429100	-1.75294500	2.91864400