10.1071/CH14399_AC

Australian Journal of Chemistry 2015, 68 (6), 931-938

Supplementary Material

Modelling of Transition State in Grignard Reaction of Rigid *N*-(Aryl)imino-Acenapthenone (Ar-BIAO): A Combined Experimental and Computational Study

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[B]Corresponding authors. Email: tpanda@iith.ac.in; bhabani@iith.ac.in

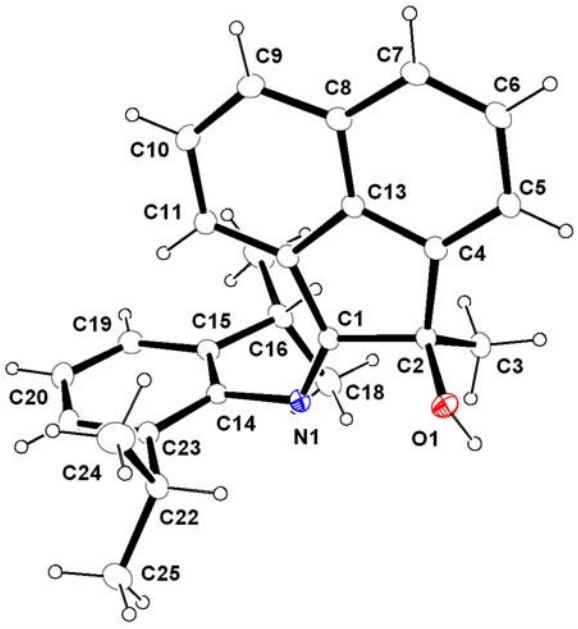


Fig S1. Solid-state structure of **1a** (*R*-isomer) showing the atom labelling scheme. Selected bond lengths in [Å]: O(1)-C(2) 1.4257(15), N(1)-C(1) 1.2742(16), N(1)-C(14) 1.4345(15), C(1)-C(12) 1.4837(17), C(1)-C(2) 1.5611(16), C(2)-C(4) 1.5158(18), C(2)-C(3) 1.5196(18); Selected bond angles in [°]: C(1)-N(1)-C(14) 118.08(10), N(1)-C(1)-C(12) 131.17(11), N(1)-C(1)-C(2) 120.17(11), C(12)-C(1)-C(2) 108.63(10), O(1)-C(2)-C(4) 108.97(10), O(1)-C(2)-C(3) 112.85(10), C(4)-C(2)-C(3) 111.96(10), O(1)-C(2)-C(1) 110.87(10), C(4)-C(2)-C(1) 102.15(10), C(3)-C(2)-C(1) 109.53(10), C(5)-C(4)-C(2) 131.41(12), C(13)-C(4)-C(2) 109.51(11).

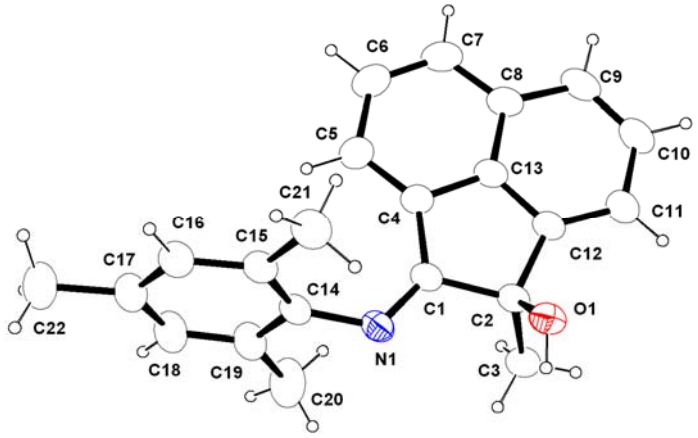


Fig S2. Solid state structure of compound **3a** (*R*-isomer) ellipsoids are drawn to encompass 30% probability. Selected bond lengths in [Å] and bond angles in [^{o}]: O(1)-C(2) 1.419(2), N(1)-C(1) 1.270(2), N(1)-C(14) 1.427(2), C(13)-C(12) 1.398(3), C(4)-C(1) 1.481(3), C(1)-C(2) 1.547(3), C(12)-C(2) 1.511(3), C(2)-C(3) 1.533(2), 109.5, C(1)-N(1)-C(14) 122.31(17), N(1)-C(1)-C(4) 131.86(19), N(1)-C(1)-C(2) 119.52(17), C(4)-C(1)-C(2) 108.62(15), C(11)-C(12)-C(2) 131.55(19), C(13)-C(12)-C(2) 109.00(16), O(1)-C(2)-C(12) 108.96(15), O(1)-C(2)-C(3) 111.73(16), C(12)-C(2)-C(3) 111.97(16), O(1)-C(2)-C(1) 111.32(15), C(12)-C(2)-C(1) 102.48(15), C(3)-C(2)-C(1) 110.03(16).

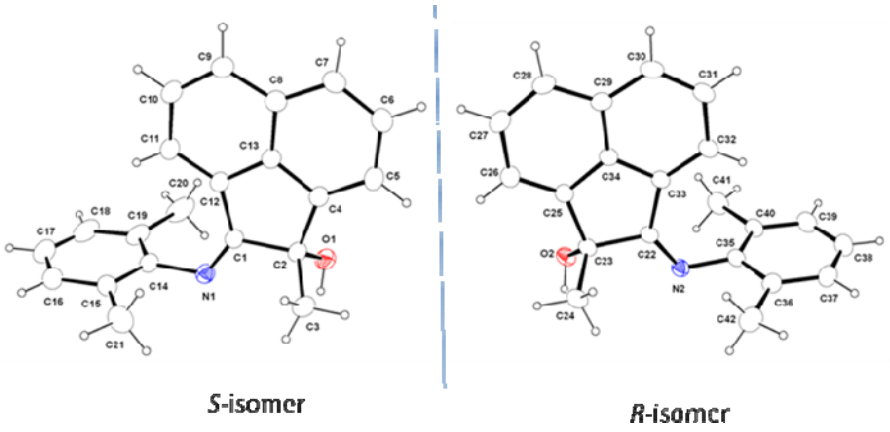


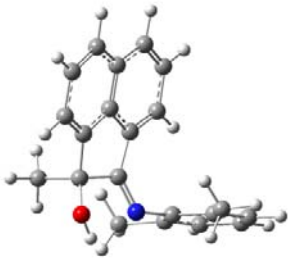
Fig S3. Solid state structure of compound **2a** (S- and R- isomers) ellipsoids are drawn to encompass 30% probability. Selected bond lengths in [Å] and bond angles in [^{o}]: S-isomer: O(1)-C(2) 1.422(2), O(1)-H(1) 0.8200, N(1)-C(1) 1.275(2), N(1)-C(14) 1.431(2), C(13)-C(8) 1.402(3), C(2)-C(4) 1.510(3), C(2)-C(3) 1.521(3), C(2)-C(1) 1.543(3), C(1)-C(12) 1.479(3), C(1)-N(1)-C(14) 121.11(16), O(1)-C(2)-C(4) 109.96(16), O(1)-C(2)-C(3) 111.30(17), C(4)-C(2)-C(3) 111.71(18), O(1)-C(2)-C(1) 111.36(16), C(4)-C(2)-C(1) 102.71(15), C(3)-C(2)-C(1) 109.51(16), C(5)-C(4)-C(2) 132.41(19), C(13)-C(4)-C(2) 108.88(16); R-isomer: O(2)-C(23) 1.419(2), N(2)-C(22) 1.275(2), N(2)-C(35) 1.431(2), C(23)-C(25) 1.514(2), C(23)-C(24) 1.527(3), C(23)-C(22) 1.550(2); C(22)-N(2)-C(35) 120.80(15), O(2)-C(23)-C(25) 110.59(15), O(2)-C(23)-C(24) 111.04(14), C(25)-C(23)-C(24) 111.19(16), O(2)-C(23)-C(22) 111.74(14), C(25)-C(23)-C(22) 102.28(14), C(24)-C(23)-C(22) 109.71(15), C(36)-C(35)-N(2) 117.52(17), C(40)-C(35)-N(2) 120.54(18), N(2)-C(22)-C(33) 130.86(16), N(2)-C(22)-C(23) 120.71(15).

Computational Information

Optimized Geometries:

Ligand **2a:**

HF/3-21G(d):



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C	-2.83316300	1.58148800	-0.14984500
C	-2.22628800	2.83509000	-0.42155700
C	-0.87581200	2.92560400	-0.60240200
H	1.03163700	1.91125700	-0.63035400
C	-2.42995800	-0.82553900	0.15168200
C	-4.20897600	1.33283300	0.10599100
H	-2.83671100	3.71552700	-0.47667800
H	-0.43364400	3.88106600	-0.80308500
C	-4.63181200	0.06826100	0.38645800
C	-3.73914800	-1.04129800	0.41095500
H	-4.90632400	2.14750900	0.08757400
H	-5.66919200	-0.10704800	0.59231300
H	-4.11159200	-2.02098000	0.63230700
C	-0.04676700	-0.78585000	-0.04397900
C	-1.24645700	-1.76202900	0.00965400
N	1.10932400	-1.22843900	0.14730600
O	-1.12526600	-2.68011200	1.09514100
C	-1.32165300	-2.51076300	-1.32903800
H	-0.41609100	-3.08980000	-1.46766700
H	-2.16907100	-3.18435000	-1.31362700
H	-1.43141900	-1.81795300	-2.15333900
C	2.29784100	-0.43898800	0.14503900
C	2.74297600	0.13395100	1.33399600
C	3.03379200	-0.31607700	-1.03099800
C	3.92841300	0.85198700	1.32457900
C	4.21426200	0.40983400	-1.00696100
C	4.66070100	0.99649500	0.16180700
H	4.27733000	1.29581500	2.23636200
H	4.78575200	0.50876200	-1.90907600
H	5.57661400	1.55322100	0.16848600
C	1.94184800	-0.03442400	2.60921300
H	1.00825500	0.51536700	2.55683200
H	1.70289900	-1.07820200	2.77416700

H	2.50231700	0.33039500	3.46034000
C	2.54779400	-0.97580700	-2.30592500
H	2.32038400	-2.02002300	-2.12828800
H	1.64627400	-0.49709600	-2.67448000
H	3.30317300	-0.91186500	-3.07859800
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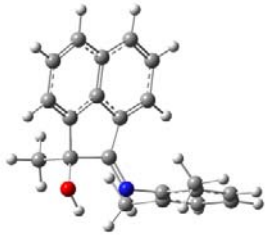

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C	-2.83498300	1.61856100	-0.11129600
C	-2.20858400	2.87602300	-0.29654900
C	-0.83607100	2.96496800	-0.42105000
H	1.07671600	1.94793800	-0.44736800
C	-2.44222300	-0.81836500	0.09688800
C	-4.22060200	1.36246700	0.05239100
H	-2.81287400	3.77559400	-0.33765500
H	-0.38184500	3.93865500	-0.56149900
C	-4.66700500	0.07238700	0.23751600
C	-3.78417200	-1.03975900	0.25764900
H	-4.92611700	2.18545800	0.03704800
H	-5.72801200	-0.10501400	0.36906200
H	-4.17916800	-2.03757500	0.40623800
C	-0.04835800	-0.78477000	-0.04027300
C	-1.25819300	-1.76326800	0.02189900
N	1.12207200	-1.25302600	0.09294800
O	-1.18928200	-2.56812800	1.19537000
C	-1.29978400	-2.64877900	-1.22896400
H	-0.38800600	-3.24701300	-1.28413200
H	-2.16047500	-3.31721600	-1.17282600
H	-1.37902700	-2.05147300	-2.14008900
C	2.28787900	-0.45156500	0.09394200
C	2.77970100	0.05180100	1.31101100
C	2.99499300	-0.26927900	-1.10712400
C	3.97247000	0.77330400	1.29594900
C	4.18307400	0.45908000	-1.07427300
C	4.67176600	0.98541100	0.11467100
H	4.35763700	1.16830200	2.22972900
H	4.73294000	0.60754600	-1.99732000
H	5.59811700	1.54710500	0.12245000
C	2.03948200	-0.18940200	2.60093800
H	1.05989300	0.29579600	2.60781400

H	1.86264900	-1.25621200	2.76220500
H	2.60862200	0.19440300	3.44836500
C	2.48195500	-0.85367800	-2.39793200
H	2.28668800	-1.92432300	-2.29529300
H	1.54233100	-0.38955100	-2.71134200
H	3.20698500	-0.71143200	-3.20022100
H	-0.27547800	-2.88199300	1.25979500

Model System:

Pre-Complex (**R′**):

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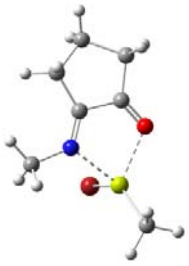

C	-2.83558900	-0.43969400	-1.43579300
C	-1.50130000	0.08883000	-0.99759700
C	-1.53449500	0.33196100	0.48825800
C	-2.88857300	-0.07964500	1.01494900
C	-3.45475400	-0.98785900	-0.12061300
H	-3.42011400	0.39457600	-1.81559600
H	-2.73418100	-1.17760300	-2.21752000
H	-2.82620100	-0.60056900	1.95921700
H	-3.51181100	0.80037500	1.14020900
H	-3.11940800	-2.00455900	0.03587500
H	-4.53313300	-0.97663300	-0.14543600
O	-0.49631900	0.31654500	-1.64907600
Mg	1.17686800	0.87554400	-0.46154700
Br	2.06261400	-1.28969300	0.10732100
C	1.85932400	2.85363200	-0.82849400
H	2.28486700	2.94172200	-1.83067700
H	1.05259900	3.58992000	-0.76242500
H	2.63539100	3.16455800	-0.12593700
N	-0.49145600	0.79050800	1.00480900
C	-0.31258100	1.06831100	2.43936500
H	0.48205700	0.42431800	2.79081600
H	0.00709300	2.09611700	2.53714700
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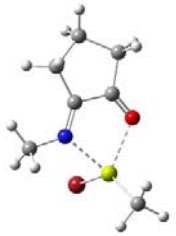

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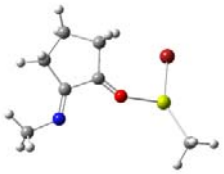
C	-1.58375000	0.13400000	-0.96818300
C	-1.60715400	0.10613900	0.53659300
C	-2.96463700	-0.36421000	0.99142700
C	-3.58411400	-1.00255500	-0.28037400
H	-3.48131100	0.63883200	-1.73446500
H	-2.85793900	-0.87064800	-2.39127400
H	-2.91603100	-1.05768800	1.83113500
H	-3.55395400	0.49946300	1.31957700
H	-3.32929800	-2.06333800	-0.31526900
H	-4.67003500	-0.92673300	-0.28827600
O	-0.58995000	0.44113100	-1.60218600
Mg	1.09336900	0.96984800	-0.32744900
Br	2.36691300	-1.11111600	-0.09500900
C	1.42017300	3.05885800	-0.37526700
H	2.02926800	3.35287500	-1.23759800
H	0.48925100	3.63588400	-0.43382900
H	1.95487600	3.40437800	0.51764000
N	-0.54169800	0.44989100	1.13421900
C	-0.42089800	0.44472000	2.57946000
H	0.42083600	-0.20071600	2.84117600
H	-0.16746400	1.45585700	2.90647800
H	-1.32238700	0.11018800	3.09594400

Non-Chelated Pre-Complex (HF/3-21G*:)



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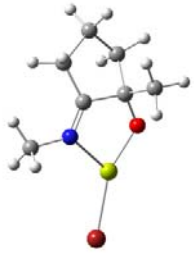
C	1.07887800	-0.08166800	0.38908600
C	2.51041300	0.13259800	-0.00256700
C	3.26517800	-1.15894400	0.26817700
C	2.14574500	-2.23512000	0.34599000
H	0.93854000	-1.44861500	1.98572900
H	-0.04414000	-1.88679900	0.59161100
H	3.99198800	-1.38422500	-0.49870200
H	3.78010200	-1.08679700	1.22142400
H	1.92693300	-2.60370500	-0.64776600

H	2.42625900	-3.06929700	0.96991900
O	0.20522800	0.77226300	0.30151600
N	2.86228900	1.24291100	-0.45626100
C	4.24061800	1.55883100	-0.84877800
H	4.22178000	1.87594900	-1.88273200
H	4.56232500	2.40110900	-0.25058100
H	4.93824700	0.73951900	-0.72811400
Mg	-1.72143400	1.20008200	0.17232000
Br	-2.62426600	-0.94164600	-0.40835200
C	-2.28212700	3.17956100	0.63083400
H	-1.80919700	3.88527200	-0.05498900
H	-3.35871200	3.33861400	0.57477500
H	-1.96252100	3.45406200	1.63845100

Post-Complex (**P′**):

HF/3-21G*:



C	2.85355800	-1.01597600	-0.95560100
C	1.73022900	-0.89290700	0.09218100
C	1.55409000	0.62898000	0.13564500
C	2.88962900	1.30672800	-0.09029000
C	3.81022700	0.16570800	-0.64093200
H	2.78774300	2.10710600	-0.81222700
H	3.27137200	1.73218400	0.83050600
H	4.35065100	0.49318900	-1.51751500
H	4.53247800	-0.12502300	0.10861200
H	2.40487300	-0.89584800	-1.93522300
H	3.34597400	-1.97716800	-0.91372500
O	0.52433100	-1.53090800	-0.22831800
C	2.21538800	-1.35237500	1.48376800
H	1.45261300	-1.13002200	2.22170500
H	2.34769000	-2.42630900	1.45117900
H	3.14443900	-0.88693100	1.78699200
Mg	-0.95125600	-0.45670800	-0.04155700
Br	-3.26424800	-0.12155900	-0.09914700
N	0.39214100	1.12074900	0.24009000
C	0.11547200	2.57016800	0.29803000
H	1.00487400	3.17023300	0.16086900
H	-0.60938500	2.81789800	-0.46493800
H	-0.32075700	2.79580900	1.26171100

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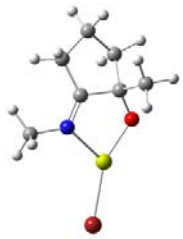

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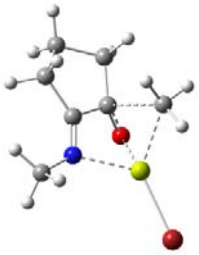
C	1.58612900	0.62765200	0.13822800
C	2.91604500	1.28301700	-0.13808600
C	3.82215000	0.12610400	-0.64231200
C	2.86123700	-1.04226200	-0.94215400
H	2.79201800	2.05946600	-0.89780400
H	3.31331500	1.78310200	0.74954100
H	4.40026800	0.42508500	-1.51696500
H	4.53992500	-0.15515900	0.12954400
H	2.42393300	-0.94474200	-1.93986700
H	3.34124200	-2.01974200	-0.88494100
C	2.20167600	-1.37583300	1.49068300
H	1.43662400	-1.16306300	2.24064500
H	2.33921700	-2.45717600	1.44289200
H	3.13926200	-0.91672300	1.81429000
O	0.54006000	-1.53464800	-0.23423300
Mg	-0.95940500	-0.42491500	-0.02804800
Br	-3.31423000	-0.11756800	-0.10450800
N	0.42737500	1.15205900	0.26574300
C	0.22771200	2.59806300	0.30979200
H	1.08422100	3.15950600	-0.06821900
H	-0.65788400	2.85817400	-0.27095600
H	0.04102000	2.90322200	1.34239500

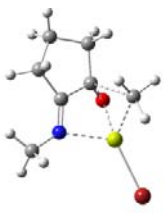
Transition State (**TS′)**

(Scan: HF/3-21G*):



C	2.86124600	-1.47969000	-0.16726900
C	1.52051500	-0.82265000	-0.39453500
C	1.65560000	0.66510000	-0.07959700
C	3.09920900	0.95737200	0.25042400
C	3.86610100	-0.29287900	-0.27797400
H	2.89365300	-1.91858300	0.81860000
H	3.02566400	-2.24465300	-0.91093700
H	3.45522400	1.87857100	-0.18824700
H	3.19223900	1.02541500	1.32998200
H	4.13071400	-0.13934100	-1.31618300
H	4.76879200	-0.47525600	0.28520200
O	0.61669400	-1.18700400	-1.21113700
Mg	-0.77254000	-0.36820300	-0.04070700
Br	-3.10149100	-0.08309800	-0.06865700
C	0.49467100	-1.20158500	1.70209000
H	0.64679300	-2.27857600	1.71146500
H	1.26942100	-0.72327100	2.29734600
H	-0.44971200	-1.01497900	2.23925800
N	0.61015800	1.35310000	-0.13747700
C	0.53656600	2.80140900	0.10015200
H	0.01925100	3.25338100	-0.73358900
H	-0.04945400	2.96988000	0.99404300
H	1.51196800	3.25615600	0.21622600

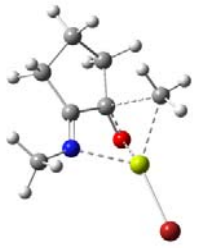
Scan- B3LYP/6-311+G(2d,p):



C	-2.58976600	-0.24471500	-1.49228200
C	-1.21123200	-0.22907000	-0.87363000
C	-1.36225100	0.12630800	0.60686300
C	-2.82768400	0.23893900	0.92640900
C	-3.54303700	-0.41179300	-0.28446100
H	-2.77080000	0.69746300	-2.01212900

H	-2.66231600	-1.04999100	-2.22253700
H	-3.09058700	-0.22426300	1.87811900
H	-3.08021700	1.30179300	1.00774300
H	-3.69740400	-1.47428400	-0.08522700
H	-4.52212100	0.03055500	-0.46404900
O	-0.22289600	-0.89561100	-1.26194300
Mg	0.96537000	0.58608300	-0.45465100
Br	3.32688000	0.92410400	-0.33683900
C	-0.51343800	2.08933500	-1.33493800
H	-0.59795000	2.02427000	-2.42199500
H	-1.42657700	2.52585100	-0.92864200
H	0.29907100	2.79846100	-1.09878600
N	-0.30436700	0.23774700	1.29856100
C	-0.30749400	0.52601600	2.72046600
H	0.38407600	-0.15413700	3.22007500
H	0.06694900	1.54087900	2.88105300
H	-1.29554400	0.43715800	3.17749700

QST2- HF/3-21G*:



C	-2.17212952	-0.12505548	-1.51898880
C	-0.87001388	-0.24799352	-0.77765377
C	-1.11763197	0.07693346	0.69370423
C	-2.60277316	0.25017434	0.89490174
C	-3.12870973	0.59654314	-0.53358631
H	-2.04653347	0.38870491	-2.45880526
H	-2.51286610	-1.13697602	-1.71984877
H	-3.02836233	-0.69063309	1.23187399
H	-2.83674091	1.01734140	1.61872223
H	-4.15227276	0.27903748	-0.66333757
H	-3.07258416	1.66359959	-0.68781876
O	0.14110014	-0.92566485	-1.09338346
Mg	1.33107329	0.43817981	-0.17744621
Br	3.62923281	0.57655466	0.29633799
C	-0.02651167	1.98231869	-1.13040249
H	-0.12764416	1.92038297	-2.21336502
H	-0.90838777	2.47369149	-0.72339534
H	0.79834111	2.69163401	-0.94782080
N	-0.11111299	0.13999755	1.43556097
C	-0.13803158	0.38404175	2.88465044
H	0.39109862	-0.42421167	3.36899305
H	0.39391848	1.30424292	3.08494725
H	-1.14405328	0.44919943	3.27858666

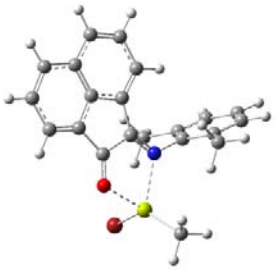
QST2- B3LYP/6-311+G(2d,p):

C	-2.36167623	0.26202274	-1.50839437
C	-1.04160552	-0.03887819	-0.84058745
C	-1.25781630	0.00311994	0.67425909
C	-2.72290572	0.21541155	0.94144454
C	-3.41282747	-0.05916041	-0.41891959
H	-2.39507125	1.31580041	-1.79089681
H	-2.46973749	-0.33316102	-2.41433379
H	-3.10238745	-0.41256526	1.74833316
H	-2.86724569	1.25635341	1.25102597
H	-3.68992647	-1.11373112	-0.47859406
H	-4.32497264	0.52412944	-0.53743719
O	-0.10591398	-0.71051109	-1.32469441
Mg	1.18230266	0.42082412	-0.14959254
Br	3.55047863	0.35719538	0.16800058
C	-0.03788748	2.23382973	-0.73481590
H	-0.06318948	2.40894793	-1.81344785
H	-0.93815349	2.65885507	-0.28768005
H	0.80621623	2.81428746	-0.32321901
N	-0.24621943	-0.16421567	1.42009483
C	-0.32060530	-0.19563823	2.86844204
H	0.26074996	-1.04399574	3.23267469
H	0.14505439	0.70892525	3.26947715
H	-1.34247348	-0.26640869	3.24760396

Real System:

Pre-complex (**R):**

HF/3-21G*:

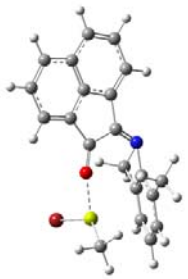


C	-1.85784000	2.17293400	-0.42132200
C	-1.67557500	0.87184900	-0.07624000
C	-2.79903400	0.01404900	0.00535100
C	-4.09211300	0.43095900	-0.25404200
C	-4.25831500	1.79585500	-0.61376200
C	-3.17851100	2.62522300	-0.69033600
H	-1.03599800	2.85368800	-0.49672700
C	-2.48888300	-1.31021400	0.37717200
C	-5.10833000	-0.55221200	-0.13168900
H	-5.24082800	2.16959400	-0.82526400
H	-3.31840700	3.65147200	-0.96265600
C	-4.80464000	-1.83740100	0.22607700
C	-3.47338000	-2.24031700	0.48977700
H	-6.12746700	-0.27922300	-0.32408500
H	-5.58882000	-2.56153000	0.31025500
H	-3.25571500	-3.25157200	0.76840500
C	-0.50572100	0.04487900	0.27173600
C	-1.04331300	-1.35961400	0.56886600
N	0.73090900	0.22074800	0.38540500
C	1.37754900	1.49677200	0.15314200
C	1.70116800	1.88090800	-1.14513400
C	1.68536400	2.28248300	1.25953700
C	2.34828000	3.09661900	-1.31670900
C	2.32933800	3.49081800	1.04401700
C	2.65962700	3.89611900	-0.23454300
H	2.61405600	3.40738900	-2.30730800
H	2.57580900	4.10799500	1.88477200
H	3.16455600	4.82919800	-0.38656100
C	1.37080400	1.00604500	-2.33981700
H	1.73945400	-0.00048900	-2.19750700
H	0.29839200	0.95681400	-2.50195900
H	1.82345000	1.41539700	-3.23337400
C	1.32114500	1.83265100	2.66082600
H	0.24390500	1.78444600	2.78584100
H	1.72932000	0.85262300	2.87007700
H	1.71181900	2.52926100	3.39057300

O	-0.29154800	-2.25882100	0.90700600
Mg	1.77218100	-1.73094600	0.90145100
C	2.60306800	-1.77663600	2.85773900
H	3.02706600	-2.76316300	3.05910300
H	1.85757000	-1.59146600	3.63687200
H	3.41011800	-1.05415900	2.99943200
Br	2.39021300	-2.48372000	-1.29671600

Non-chelated pre-complex:

HF/3-21G*:

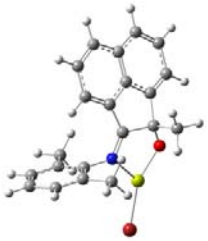


C	3.29868800	-2.27522100	-0.27861700
C	2.53289600	-1.18636500	-0.03361600
C	3.13607500	0.08122200	0.04345100
C	4.49243500	0.29393600	-0.12173400
C	5.28441500	-0.85991000	-0.37470800
C	4.70011000	-2.09097300	-0.44741200
H	2.86740100	-3.25309500	-0.34667500
C	2.22274100	1.11842700	0.29719200
C	4.92752200	1.64082700	-0.02363900
H	6.34302800	-0.75615500	-0.50986500
H	5.30823600	-2.95162200	-0.64004400
C	4.03686400	2.65344900	0.21893200
C	2.65365400	2.40557300	0.38475100
H	5.96901000	1.86698800	-0.14435700
H	4.39111600	3.66184100	0.28414000
H	1.97203500	3.21146300	0.56937500
C	1.07998000	-0.99897300	0.17556300
C	0.89914200	0.51572800	0.41754900
N	0.20696700	-1.89167400	0.11670400
C	-1.20499200	-1.74265600	0.26728900
C	-1.98565700	-2.00275500	-0.85754500
C	-1.78448000	-1.42816000	1.49847400
C	-3.36095200	-1.87891900	-0.75609900
C	-3.16897000	-1.29900000	1.55741800
C	-3.95255300	-1.50977400	0.43547900
H	-3.96418900	-2.04377900	-1.62562100
H	-3.62505100	-1.03245200	2.48947900
H	-5.01554000	-1.39180200	0.49674400
C	-1.32808200	-2.34275400	-2.17582700
H	-0.91952500	-1.44297700	-2.62421200

H	-0.52305000	-3.05167500	-2.03069200
H	-2.05050000	-2.76248800	-2.86311700
C	-0.95364000	-1.28916100	2.76338100
H	-0.19380900	-2.05986900	2.80577300
H	-0.47102700	-0.32221000	2.82696100
H	-1.59026600	-1.39126600	3.63152700
O	-0.15919300	1.07325600	0.67227200
Mg	-2.15873200	1.27251300	0.68293500
C	-2.88039100	2.06432600	2.51497300
H	-2.68913400	3.13801800	2.58007100
H	-2.40428600	1.60575000	3.38658500
H	-3.95806500	1.92669200	2.62898000
Br	-2.44530400	1.63488400	-1.66676800

Post-Complex (**P**):

HF/3-21G*:



C	-2.02394500	-2.08377900	0.19137900
C	-1.79385800	-0.74294900	0.26864700
C	-2.84266800	0.16479800	-0.00303700
C	-4.10888100	-0.24165100	-0.39341200
C	-4.33215000	-1.64097000	-0.44515000
C	-3.32710900	-2.52046800	-0.15166700
H	-1.25166300	-2.80150900	0.37250900
C	-2.45718000	1.51699400	0.09636800
C	-5.03321900	0.78724900	-0.72669900
H	-5.29916300	-2.00932600	-0.72813700
H	-3.51704800	-3.57378900	-0.20089800
C	-4.64829200	2.09202200	-0.66431800
C	-3.34250500	2.47981200	-0.24183600
H	-6.02541300	0.52641500	-1.03906100
H	-5.34611300	2.86031300	-0.93246400
H	-3.08095900	3.51750100	-0.19345700
C	-0.59449300	0.09310700	0.46179800
C	-1.05230000	1.56180000	0.69355400
N	0.64990300	-0.13804600	0.33144100
O	-0.11917800	2.46132700	0.17483300
C	-1.19906000	1.74252500	2.22511100
H	-0.23019000	1.62005700	2.69782300
H	-1.54315600	2.75133700	2.41198400
H	-1.90002700	1.03791300	2.65272900
Mg	1.56121400	1.71854800	-0.00714600
Br	3.84317200	2.00437800	-0.39902800

C	1.19639000	-1.45244000	0.10728300
C	1.37991600	-1.90027500	-1.19709700
C	1.58062800	-2.22014600	1.20145600
C	1.93084700	-3.15744000	-1.39211100
C	2.12831600	-3.47282000	0.97166200
C	2.29794700	-3.94263400	-0.31657800
H	2.07645200	-3.51572100	-2.39179600
H	2.42932800	-4.07447600	1.80625900
H	2.72514900	-4.91154700	-0.48167600
C	1.01205600	-1.02419700	-2.37918800
H	-0.01098500	-0.67510400	-2.31533100
H	1.66871000	-0.16021100	-2.43003600
H	1.12442500	-1.57332700	-3.30457800
C	1.42479800	-1.68445700	2.61124300
H	1.95503500	-0.74474400	2.71837900
H	0.38294000	-1.51247600	2.85776300
H	1.82977400	-2.38588200	3.32851300

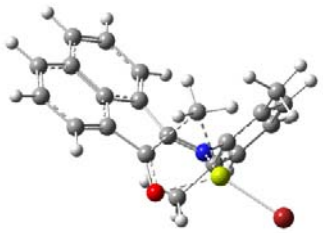
Transition State (**TS):**

Scan- HF/3-21G*:

C	-1.71432300	2.10705500	-0.07326300
C	-1.41783000	0.78428400	0.03029500
C	-2.46662800	-0.15407500	0.18207800
C	-3.80216600	0.20584500	0.22275600
C	-4.08804800	1.59261500	0.11211200
C	-3.07803800	2.49971200	-0.02956300
H	-0.94921100	2.84644700	-0.18679100
C	-2.03721500	-1.49289200	0.27403100
C	-4.73848800	-0.85279300	0.36459400
H	-5.10762500	1.92393700	0.13985900
H	-3.31127200	3.54182900	-0.11132400
C	-4.31853800	-2.15031300	0.44554700
C	-2.94315800	-2.49376500	0.39546000
H	-5.78576200	-0.62527800	0.40466900
H	-5.04108900	-2.93379100	0.55000700
H	-2.63513400	-3.51749100	0.46037800
C	-0.16641100	0.01283500	0.06228700
C	-0.57542800	-1.48165100	0.15748900
N	1.06345900	0.26889100	0.05757100
C	1.62002200	1.58085400	-0.14711900
C	1.76444500	2.04987400	-1.44978900
C	2.04189600	2.32279400	0.95071200
C	2.31786900	3.30668200	-1.63840100

C	2.58573800	3.57804000	0.72405600
C	2.71924900	4.07070500	-0.55943700
H	2.44060700	3.67969300	-2.63583400
H	2.91245600	4.16350500	1.56034300
H	3.14674300	5.04040400	-0.71918500
C	1.35110000	1.19557000	-2.63320700
H	1.75149300	0.19371600	-2.53714600
H	0.27101900	1.12159000	-2.70788700
H	1.72133800	1.62660800	-3.55386200
C	1.94598500	1.76068600	2.35497100
H	0.96839900	1.34447200	2.55772600
H	2.68394000	0.97609800	2.49406500
H	2.14569100	2.53452700	3.08469600
O	0.22251700	-2.37080300	-0.18657600
Mg	1.65625300	-1.59007800	1.09209200
C	-0.03422200	-1.43275600	2.52121400
H	-0.56766100	-2.37497700	2.65760600
H	-0.75403300	-0.62343800	2.64155700
H	0.63325400	-1.34871500	3.39519700
Br	3.90952800	-2.22114600	1.33369800

QST2- HF/3-21G*:



C	-1.70417855	2.12439141	-0.02472002
C	-1.41959961	0.79721626	0.05753935
C	-2.47503115	-0.13311121	0.21193056
C	-3.80638538	0.23906571	0.27478359
C	-4.07971571	1.62979039	0.18668764
C	-3.06289149	2.52939785	0.04355470
H	-0.93341712	2.85760400	-0.14037308
C	-2.05659596	-1.47720801	0.28005079
C	-4.75197335	-0.81233528	0.41210642
H	-5.09556608	1.97055706	0.23222448
H	-3.28734888	3.57465020	-0.02128737
C	-4.34303181	-2.11420999	0.46760506
C	-2.97103521	-2.47022790	0.39645793
H	-5.79640160	-0.57532052	0.46785349
H	-5.07157360	-2.89278707	0.56777100
H	-2.67291864	-3.49792454	0.44127799
C	-0.17552452	0.01359400	0.05815483
C	-0.59384728	-1.47768656	0.15094687
N	1.05822836	0.25790695	0.03178922
C	1.62483816	1.56488689	-0.17233131
C	1.74992332	2.04397435	-1.47342386

C	2.07542808	2.29385513	0.92306740
C	2.31529244	3.29550581	-1.66239243
C	2.63080931	3.54396079	0.69658830
C	2.74688657	4.04538380	-0.58529249
H	2.42313264	3.67556374	-2.65890704
H	2.97986642	4.11870941	1.53129028
H	3.18346956	5.01099413	-0.74529046
C	1.30065948	1.20663259	-2.65582781
H	1.68334359	0.19665602	-2.57484581
H	0.21822662	1.15277124	-2.71132374
H	1.66203685	1.63832049	-3.57972082
C	1.99377580	1.72334838	2.32471366
H	1.00607804	1.34139070	2.54652001
H	2.70577111	0.91184213	2.44116898
H	2.23696906	2.48360412	3.05546938
O	0.19339777	-2.36947883	-0.24812166
Mg	1.63153543	-1.63121585	0.99771544
C	-0.05521501	-1.44766554	2.49539483
H	-0.57291602	-2.38775049	2.68032873
H	-0.74242362	-0.63010126	2.69894600
H	0.73214665	-1.37509629	3.26448035
Br	3.85649832	-2.28414922	1.37512162

➢ Scan Plot for the Model System :

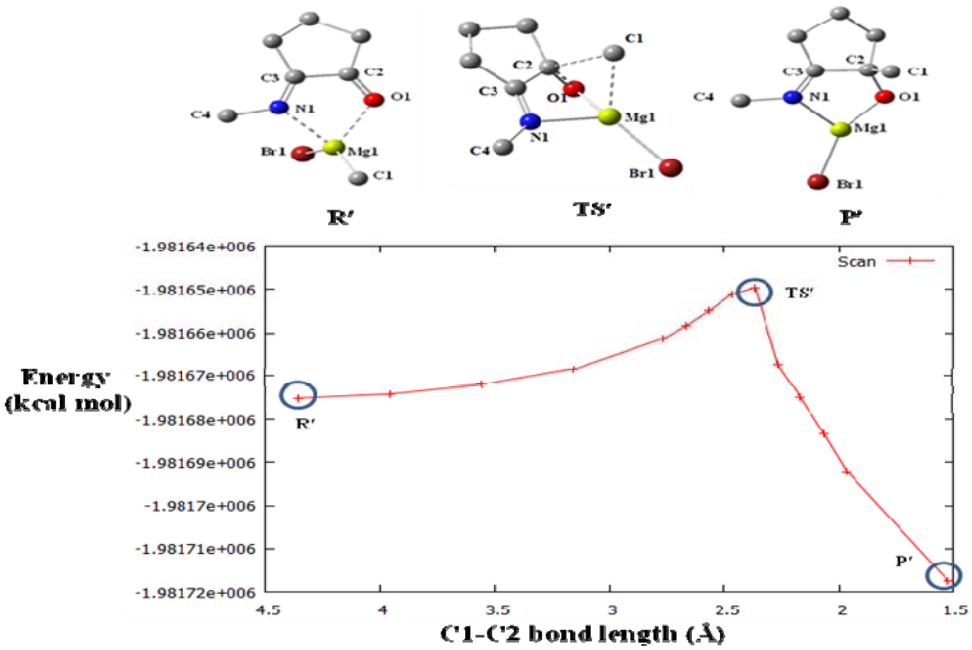


Figure S2: Plot of Energy (kcal/mol) vs C1-C2 bond length (Å) for model system.

- Comparison of Different Methodologies Model System:

Table TS1: Selected bond lengths (Å) and angles (°) for model system transition states obtained by different methodologies.

Bond Length(Å)/Angle (°)	Manual (HF/B3LYP) (TS=19.51 kcal/mol)	QST2 (HF/B3LYP) (TS=18.75 kcal/mol)	Manual (B3LYP/B3LYP) (TS=17.62 kcal/mol)	QST2 (B3LYP/B3LYP) (TS=17.62 kcal/mol)
C1-C2	2.36	2.41	2.46	2.49
Mg1-N1	2.17	2.18	2.19	2.20
C2-O1	1.27	1.26	1.25	1.25
C1-Mg1	2.31	2.27	2.28	2.26
Mg1-Br1	2.35	2.35	2.39	2.39
C2-C3	1.53	1.53	1.53	1.53
C3-N1	1.25	1.25	1.27	1.27
N1-C4	1.47	1.47	1.45	1.45
C2-C1-Mg1	60.75	61.16	59.49	59.75
C2-O1-Mg1	90.03	89.78	87.19	87.28
N1-Mg1-O1	81.84	81.62.	82.25	81.74
N1-Mg1-Br1	121.72	120.31	123.75	122.76
C2-C3-N1	116.86	116.83	117.75	117.76