

Supporting Information

Insights into the temperature-driven Competitive Pericyclic Transformations of Allyloxy Furan

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1. Computational methods

1.1. Density Functional Theory Calculations:

All the geometry optimizations were done using the Gaussian 16 Revision A.03 software package¹. The Gauss view program was used for drawing and visualization of the structures. All the structures of the [3,3]-sigmatropic rearrangement reactions were optimized with the B3LYP functional^{2,3} in conjugation with 6-31G(d)⁴ basis set. Geometry optimization for the [4+2]-cycloaddition rearrangement was done by B3LYP/def2-SVP combination⁵, as 6-31g(d) basis set is not compatible with transition metal (Ru). The harmonic vibrational frequencies of normal modes were calculated using the respective level of theories for both [3,3]-sigmatropic rearrangement and [4+2]-cycloaddition reaction, which confirms the nature of all the stationary points. It was confirmed that all the intermediates are at a minimum with no imaginary frequencies, whereas all the transition states were accompanied by exactly one imaginary frequency, having first-order saddle points on the potential energy surface (PES), corresponding to the stretching of the bond involved in bond-breaking and bond-forming. Further, the transition states were confirmed by intrinsic reaction coordinates (IRC)^{6,7}. The effect of solvent on the reaction energies was considered through the implicit solvent model SMD⁸. The single point energy calculations for [3,3]-sigmatropic rearrangement reaction were carried out with B3LYP/6-311++G(d,p)/SMD (toluene) level of theory for all the atoms along with Grimme's dispersion⁹ and Becke–Johnson damping correction (GD3BJ)^{10,11,12}. Similarly, the single-point energy calculations for [4+2]-cycloaddition reaction were done with the B3LYP/def2-TZVPP/SMD (dichloroethane) level of theory. All the 3D structures were obtained by CYL view¹³.

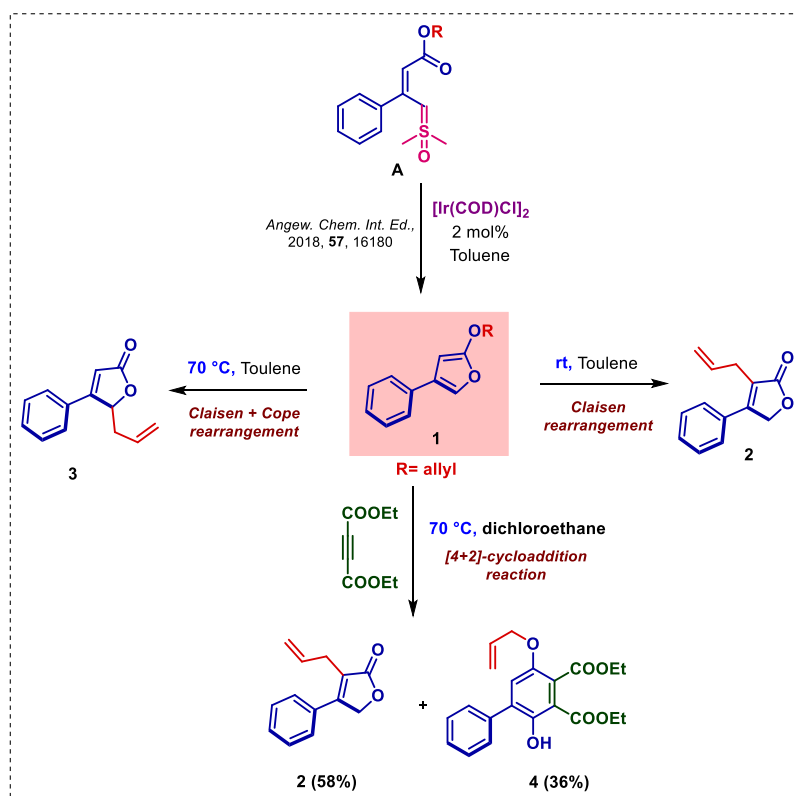
1.2. Energy decomposition Analysis (EDA):

Energy decomposition analysis calculations were performed using Psi4¹⁴ version 1.9.1. EDA was performed based on symmetry-adapted perturbation theory by using the SAPT(0) method. B3LYP/6-31G(d) was the level of theory used for the calculation.

1.3. Non-Covalent Interaction Analysis (NCI):

Noncovalent interaction analysis was carried out using NCIPLOT¹⁶ software and Mutiwnfn¹⁷ version 3.8 software package. The NCI images were visualized using VMD software¹⁸ and NCI plots were plotted through Mutiwnfn version 3.8 software package¹⁷.

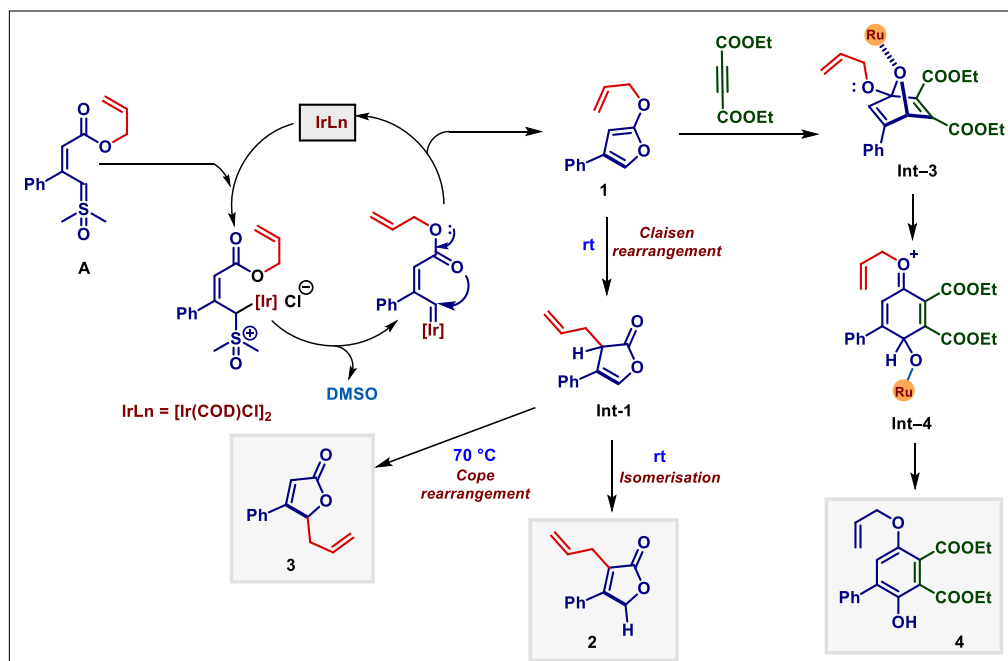
2. Reaction Scheme:



Scheme A: Diverse reactivity of vinyl sulfoxonium ylide-derived alkoxy furan

Vinyl sulfoxonium ylide (**A**) in the presence of a metal catalyst generates alkoxy furan (**1**), which was reported previously by Vaitla and coworkers (Scheme a).¹⁹ When the R group is allyl in vinyl sulfoxonium ylide, the allyloxy furan **1** constitutes a 1,5-diene system that is well-known to undergo [3,3]-sigmatropic rearrangement. However, such [3,3]-sigmatropic rearrangements are feasible at higher temperatures. In the present case, Gopalakrishnan et al. reported the Claisen rearrangement of allyloxy furan generated from vinyl sulfoxonium ylide at room temperature to yield α -allyl butenolide²⁰, **2**. Interestingly, the allyloxy furan (**1**) generated from vinyl sulfoxonium ylide is found to undergo Claisen followed by Cope rearrangement at 70 °C which leads to the formation of γ -allyl butenolide, **3**. Here, the in situ generated allyloxy furan is not isolated as the Claisen rearrangement is faster at room temperature. Thus, to prove the generation of allyloxy furan **1**, the authors carried out the competitive experiment of **1** with acetylene dicarboxylate as alkoxy furan can act as a good diene for the [4+2]-cycloaddition reaction. As per the previous report on benzannulation of vinyl sulfoxonium ylide, here also they observed the formation of arene product²¹ **4**. The formation of **4** confirms that the allyloxy furan is generated in situ which underwent [4+2]-cycloaddition followed by ring cleavage (Scheme B). In addition to the cycloaddition product **4**, butenolide **2** is also observed as a major product as intramolecular rearrangement is faster

than the intermolecular cycloaddition. Although this strategy accounts for the synthesis of diverse butenolides, the in-depth mechanistic investigations were not explored. Thus, we took the challenge of understanding the mechanism that can address the less energy demand for the [3,3]-sigmatropic rearrangement.

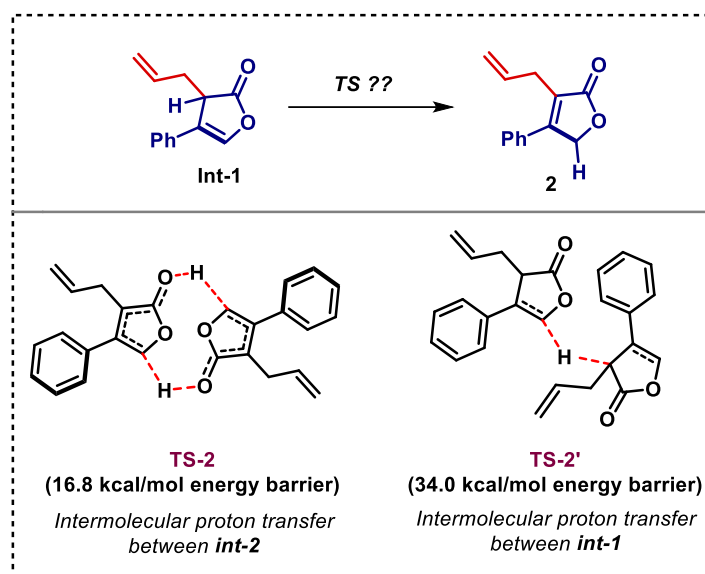


Scheme B: Reaction mechanism for rearrangement and cycloaddition reactions of allyloxy furan

The characterization data for both the starting materials and products are available in our previously published experimental paper.²⁰

3. Investigation of the transition state for isomerization:

Allyloxy furan **1** undergoes Claisen rearrangement to yield **int-1**. Experimental observations prove that the **int-1** undergoes isomerization at room temperature. To find out the respective transition state for the isomerization, we initially attempted for [1,3]-proton migration intramolecularly. But we were unsuccessful. Later, we tried intermolecular proton transfer between two molecules of **int-1** (via **TS-2'**) as shown in Scheme 3. Here, we observed a high energy barrier (34 kcal/mol) for the isomerization of **int-1**. This is not feasible as the experimental reaction goes at room temperature. Later, we proceeded for the tautomerization of **int-1** to form **int-2**, as we presumed that aromatization of **int-1** will be a driving force for the tautomerization. Now, the **int-2** can undergo intermolecular proton transfer to yield the allyl butenolide, **2**. This intermolecular proton transfer goes via **TS-2** with a comparatively less energy barrier 16.8 kcal/mol.



Scheme C: Investigation of transition states for isomerization

4. Results of EDA:

Furthermore, to gain deep insights into the energy values obtained from the DFT calculations Energy Decomposition Analysis (EDA) was carried out. EDA is a significant class of techniques for examining the interactions between various components in a chemical system. In this technique, the overall energy is decomposed into several physically comprehensible components which help in recognizing the roles of both primary and supporting factors present in the system. Understanding each energy component helps in comprehending the underlying reaction dynamics²² and stability of the system. In the present study, we have utilized symmetry-adapted perturbation theory (SAPT) to break down the overall energy into four physically meaningful components: electrostatics, induction, dispersion, and exchange-repulsion. Typically, the first three components are attractive, and the last one is repulsive. The induction component includes both the polarization from each monomer's response to the others electric field and occupied-vacant orbital interactions, also called charge transfer. The dispersion term measures induced dipole-induced dipole interactions present in the system. The exchange-repulsion (also known as closed-shell or Pauli repulsion) indicates the repulsive force due to the overlap of doubly occupied orbitals of interacting molecules.

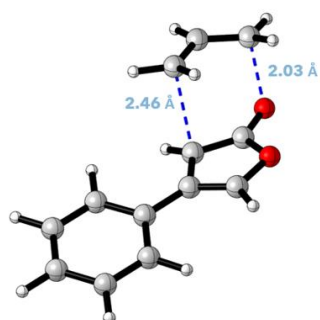
$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{ind}} + \Delta E_{\text{disp}}$$

In the present case, we have conducted the EDA for all the transition states (TS-1 to TS-3) and incorporated the contribution of each term in the table given below.

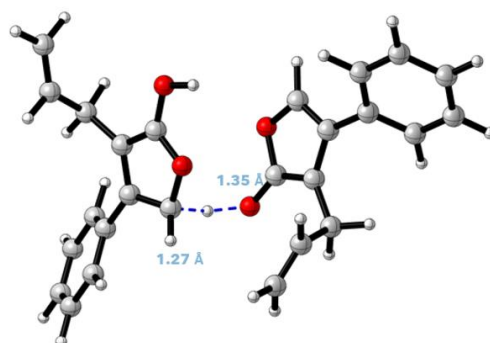
Table 1: Summary of EDA

	Electrostatic Energy	Exchange Energy	Induction Energy	Dispersion Energy	Total sSAPT0
TS-1	-154.61	91.79	-65.25	-16.04	-144.12
TS-2	-41.99	97.50	-69.55	-20.27	-34.32
TS-3	-194.94	171.27	-111.69	-29.73	-165.08

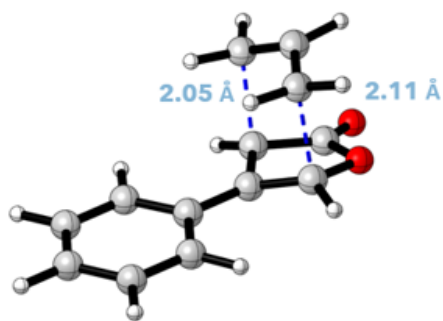
5. 3D structures of transition states:



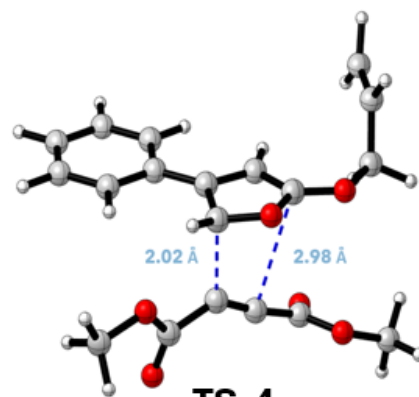
TS-1



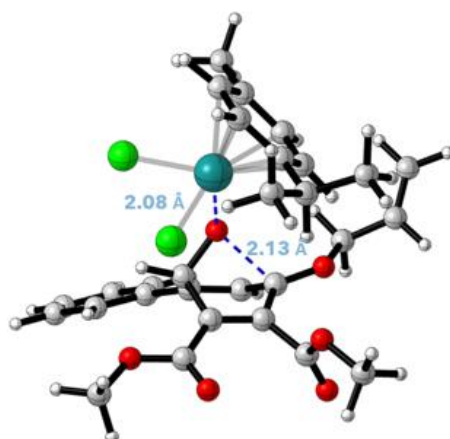
TS-2



TS-3



TS-4



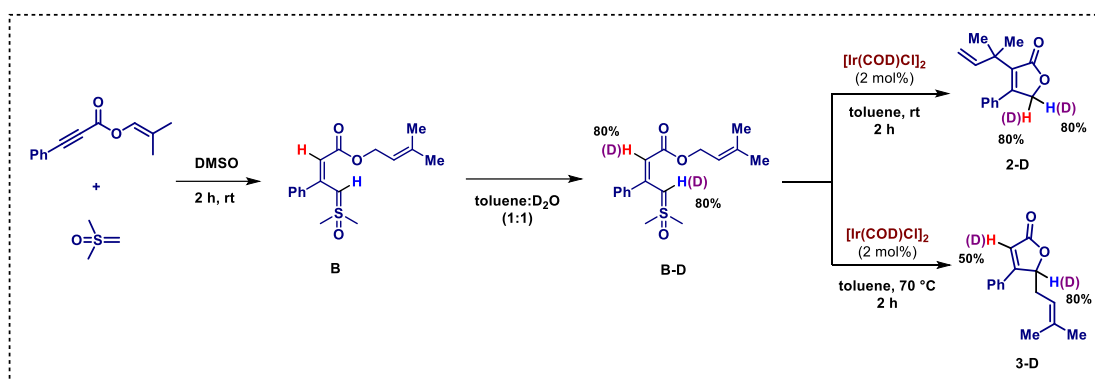
TS-5

Figure 1: 3D structures showing TS-1 to TS-5

6. Computed energy for all the stationary points:

Stationary points	SPE (Hartree)
1	-653.236114
TS-1	-653.212933
Int-1	-653.271659
Int-2	-653.251589
TS-2	-1306.492683
2	-1306.581126
TS-3	-653.229484
3	-653.284648
TS-4	-1186.553237
Int-3	-1186.595710
TS-5	-2591.759542
Int-4	-2591.787371
4	-1186.682853

7. Deuterium Labelling Studies:

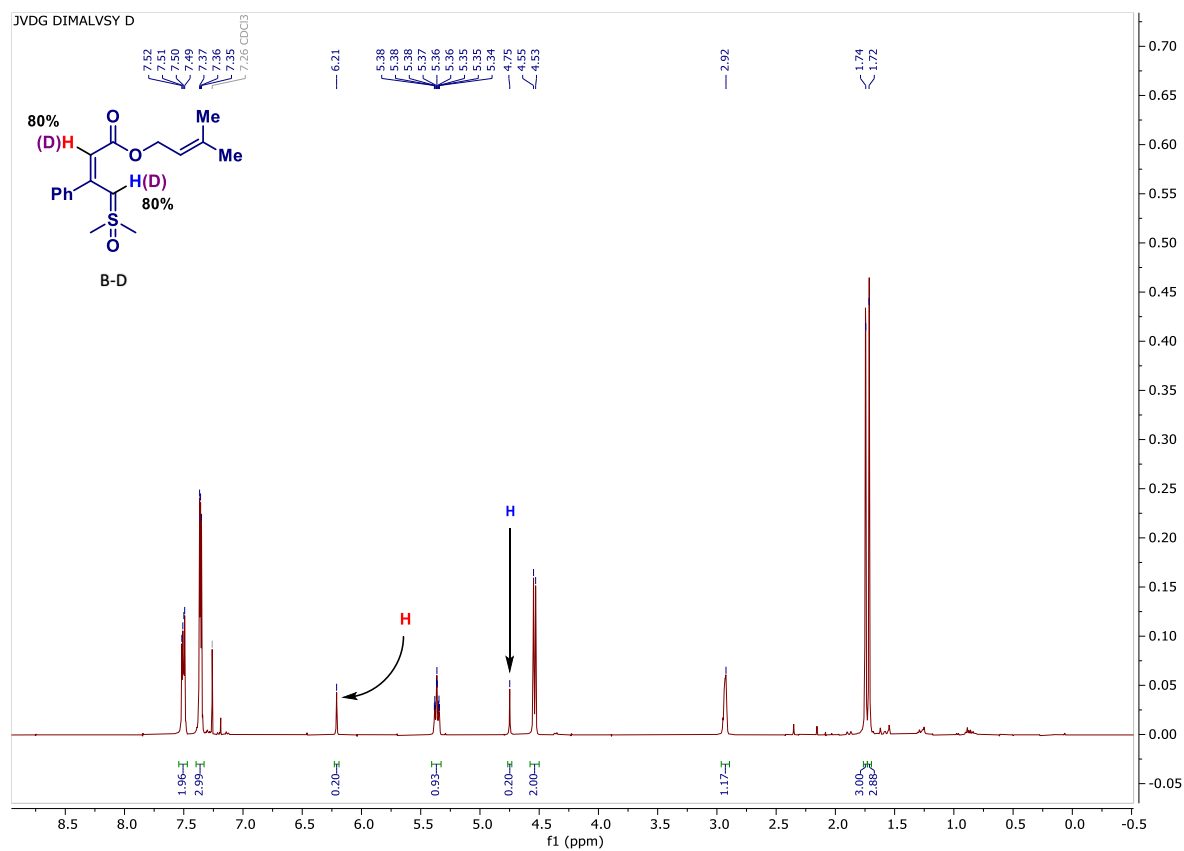
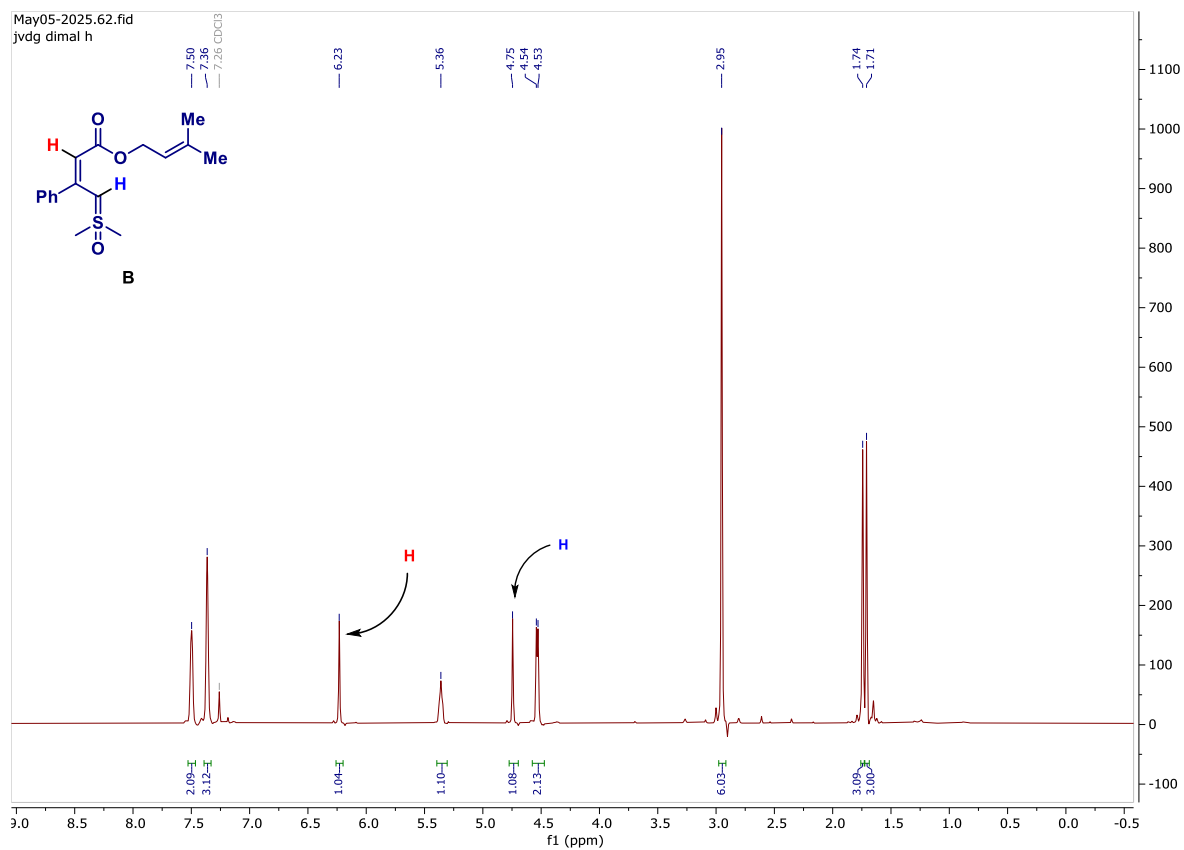


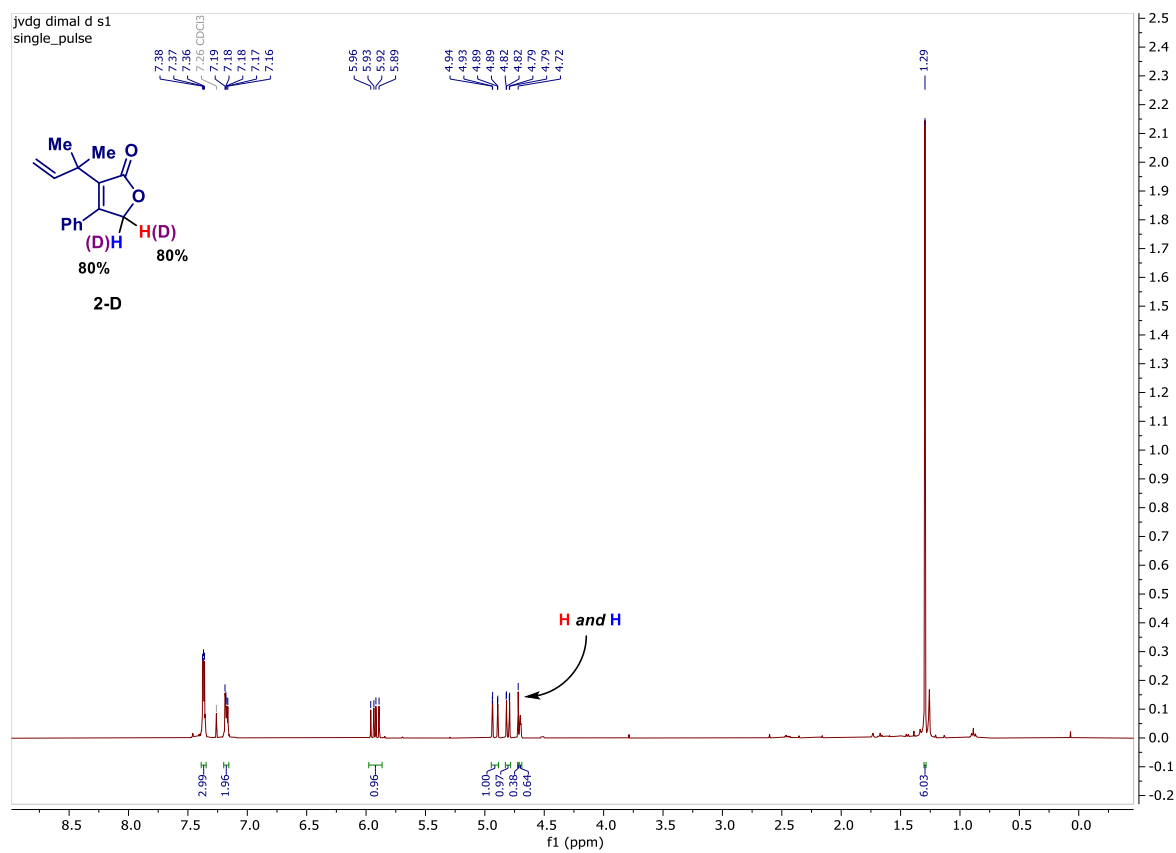
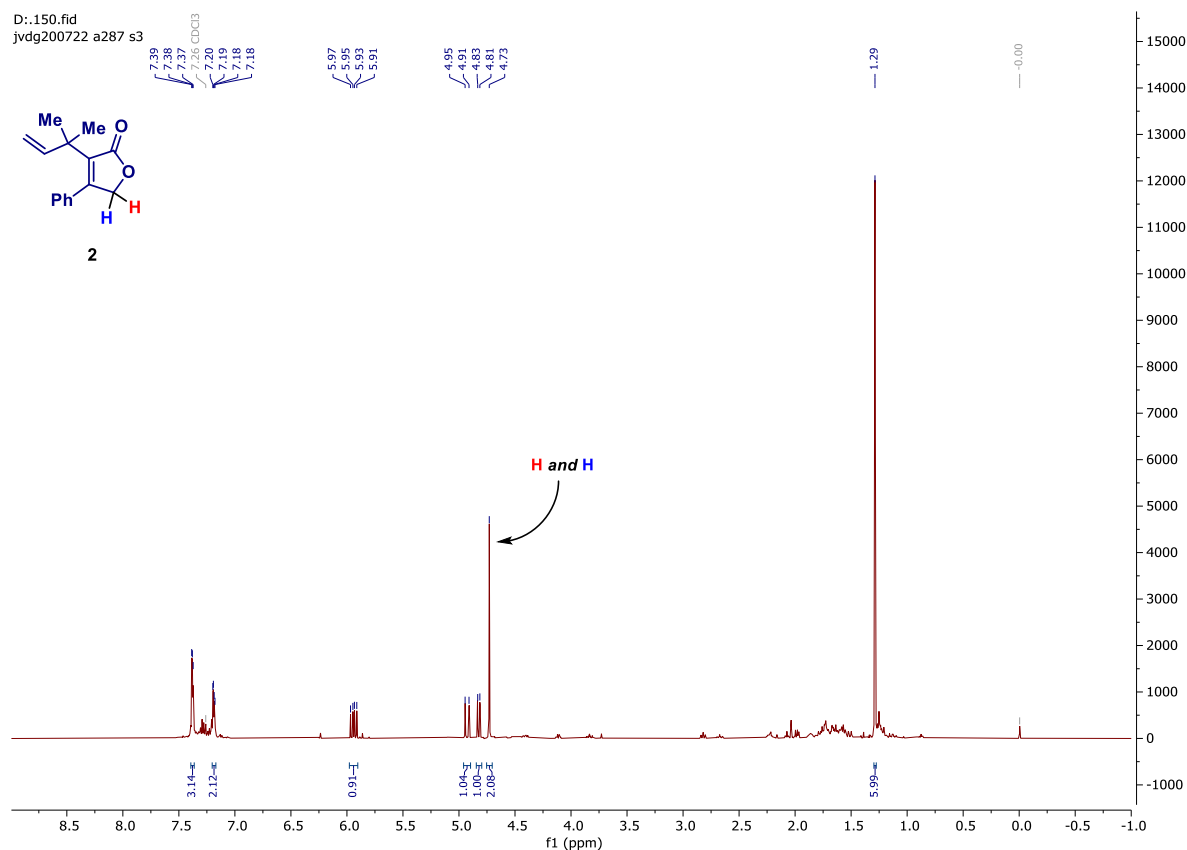
Allyl vinyl sulfoxonium ylide **B** is prepared from the propiolate as mentioned in the experimental paper.²⁰

Our computational studies found that **Int-2** is energetically less favorable, prompting us to conduct experimental investigations to verify its involvement in the mechanism. We therefore performed deuterium labeling studies using deuterated vinyl sulfoxonium ylide. First, the vinyl sulfoxonium ylide (**B**, 185 mg, 0.6 mmol) was dissolved in 2 mL of toluene: D₂O (1:1) and stirred at room temperature for 1 h. Later, hexane was added, and the precipitated deuterated vinyl sulfoxonium ylide (**B-D**) was filtered and dried. ¹H-NMR analysis of deuterated vinyl sulfoxonium ylide indicated the 80% deuteration at the α- and γ-positions.

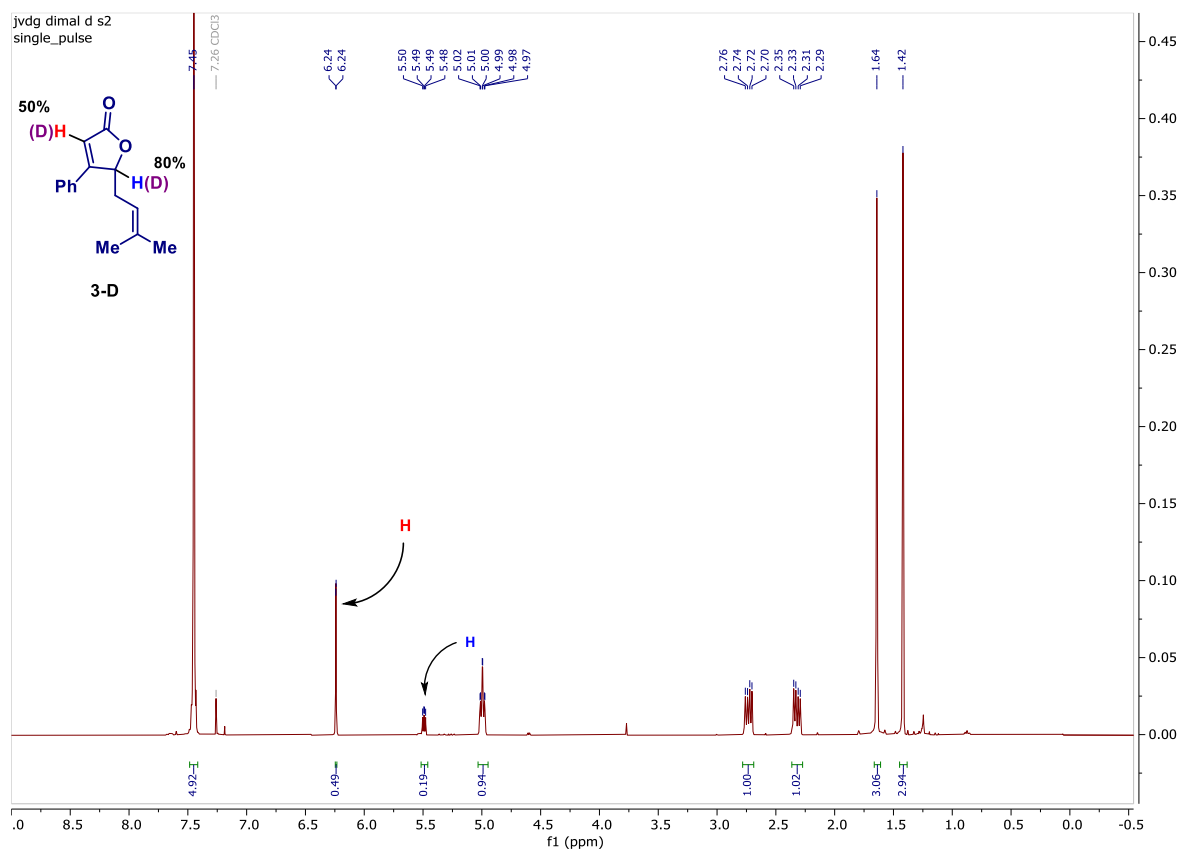
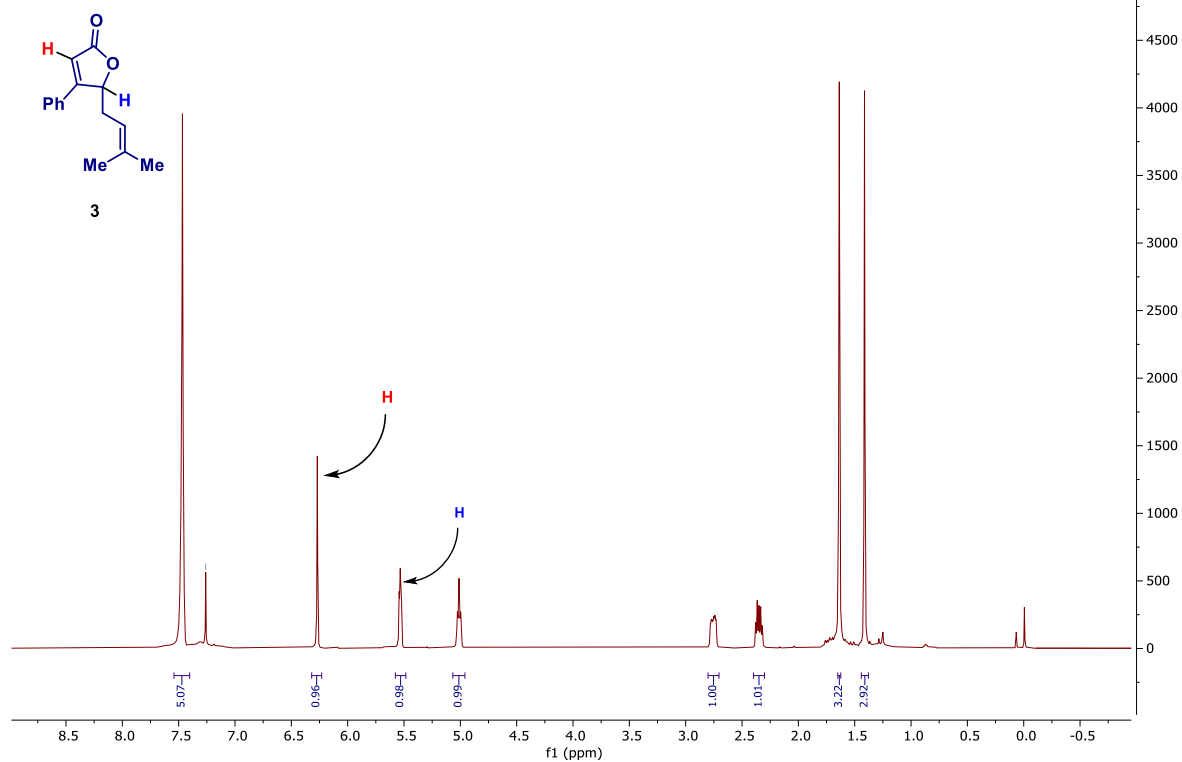
Further, the deuterated vinyl sulfoxonium ylide (**B-D**, 92 mg, 0.3 mmol) was dissolved in 2 mL of toluene. To the mixture, [Ir(COD)Cl]₂ (4 mg, 2 mol%) was added and stirred at room temperature for two hours. After the completion of the reaction, the reaction mixture is passed through Celite (eluted with DCM) and concentrated in *vacuo*. The crude mixture is purified using flash column chromatography to yield **2-D** (36 mg, 52% yield) as a colorless oil.

The deuterated vinyl sulfoxonium ylide (**B-D**, 92 mg, 0.3 mmol) was dissolved in 2 mL of toluene. To the mixture, [Ir(COD)Cl]₂ (4 mg, 2 mol%) was added and stirred at 70 °C for two hours. After the completion of the reaction, the reaction mixture is passed through Celite (eluted with DCM) and concentrated in *vacuo*. The crude mixture is purified using flash column chromatography to deliver butenolide **3-D** (46 mg, 67% yield) as a pale-yellow oil.





Proton/JVDG_300622 -A287 B2 S2
jvdg 300622 A243 B2 S2



8. Co-ordinates of intermediates and transition states:

1				C	-0.25782800	-0.61913200	-0.12624300
C	1.64881200	-0.36042300	-0.74151200	C	0.28813400	-1.74038900	0.43516900
C	0.47495400	0.29209200	-0.95335200	O	1.62433400	-1.84363900	0.19772000
C	-0.51706400	-0.39497900	-0.15644800	H	0.79215100	0.88224100	-1.45254400
C	0.15639400	-1.39608700	0.48602200	H	-0.14358800	-2.54216500	1.01777700
O	1.48130800	-1.39487100	0.13256200	C	-1.66361700	-0.19020600	-0.07920100
H	0.32788400	1.13375800	-1.61391300	C	-2.02116800	1.13648800	-0.37660600
H	-0.12715300	-2.13069200	1.22403700	C	-2.69053400	-1.08993400	0.26315900
C	-1.94832500	-0.07394300	-0.03799800	C	-3.35201900	1.55063100	-0.32532200
C	-2.42059700	1.22269200	-0.30392200	H	-1.25010900	1.85400100	-0.64280200
C	-2.88101800	-1.05415900	0.34685400	C	-4.01831500	-0.67410400	0.32019000
C	-3.77554500	1.52991700	-0.18375700	H	-2.44780400	-2.12879700	0.46993800
H	-1.71812500	1.99998000	-0.59144700	C	-4.35775300	0.64934000	0.02630400
C	-4.23331700	-0.74443100	0.47467000	H	-3.60159600	2.58260400	-0.55865800
H	-2.54334100	-2.07156700	0.52603700	H	-4.79287500	-1.38903200	0.58582200
C	-4.68856200	0.54946800	0.20872300	H	-5.39473300	0.97153400	0.06606200
H	-4.11709300	2.54050700	-0.39305200	O	3.18661100	-0.60985300	-0.94281300
H	-4.93575100	-1.51914800	0.77151800	C	4.05915700	0.63602700	0.40705100
H	-5.74447700	0.78896700	0.30185800	H	5.01737100	0.72389600	-0.09414200
O	2.85366600	-0.21131100	-1.30934400	H	4.00364400	-0.12564400	1.17804700
C	3.99629900	-0.17295700	-0.40610400	C	3.14676500	1.69256900	0.39442900
H	4.85352400	-0.20903200	-1.08523200	H	3.33319700	2.53213000	-0.27279500
H	4.00652200	-1.07362100	0.21574100	C	1.88945100	1.53455200	0.93935900
C	4.01092200	1.07253900	0.42704600	H	1.69662200	0.76639100	1.68293900
H	3.99997600	2.01252000	-0.12412100	H	1.13729700	2.31418000	0.86337500
C	4.04332000	1.07039200	1.75964000				
H	4.07384500	1.99351200	2.33318100	Int-1			
H	4.04677200	0.14354900	2.33047700	C	-2.15659800	1.14088400	-0.40225400
				O	-1.55174200	2.30960200	0.03010400
TS-1				C	-0.19606300	2.06020600	0.17265500
C	1.98627100	-0.75579800	-0.61243200	C	0.16970600	0.79899700	-0.10190600
C	0.85193400	0.06772200	-0.74623700	C	-1.09357900	0.04453600	-0.47143200

H	0.38478200	2.92686700	0.45815100	C	2.26785200	-0.64629800	-1.02260500
H	-1.06680400	-0.33291600	-1.50261900	C	3.23281500	0.90563100	1.08067800
O	-3.33138600	1.09724700	-0.64810300	H	1.27747200	0.68184700	1.94712700
C	1.52648200	0.23947100	-0.05632100	C	3.58886400	-0.19896200	-1.03452600
C	1.86576000	-0.89088400	-0.82178700	H	1.88534500	-1.23441300	-1.85249200
C	2.52726100	0.82199700	0.74537200	C	4.07576000	0.58242500	0.01521600
C	3.15957700	-1.41153600	-0.79661700	H	3.60463800	1.50611900	1.90697300
H	1.11655900	-1.35785300	-1.45505800	H	4.23552800	-0.45396200	-1.87028600
C	3.81985200	0.30547900	0.76332900	H	5.10301400	0.93692000	0.00324800
H	2.28150700	1.67465900	1.37255700	C	-1.42194600	1.35487500	0.61259100
C	4.14334400	-0.81524700	-0.00692000	H	-0.50745400	1.78388700	1.04002400
H	3.39816700	-2.28407200	-1.39910400	H	-2.21222100	1.49136400	1.36083500
H	4.57494600	0.77138700	1.39110600	C	-1.78317800	2.12159300	-0.63994200
H	5.15057200	-1.22214500	0.01453200	H	-1.05222600	2.07306500	-1.44811000
C	-1.42725600	-1.14008900	0.48195300	C	-2.90605300	2.81993700	-0.80967500
H	-1.54987000	-0.75981400	1.50288000	H	-3.11449100	3.35276100	-1.73465700
H	-0.54321700	-1.79195300	0.49205400	H	-3.66376200	2.88526700	-0.03037200
C	-2.63313600	-1.93773500	0.07118200				
H	-2.61900400	-2.33430400	-0.94548400	TS-2			
C	-3.67469900	-2.20215500	0.85948500	C	-1.02835200	-0.87843700	1.13644200
H	-4.51034600	-2.80766800	0.51742300	O	-1.05794400	0.42599200	1.63234800
H	-3.73617200	-1.82052000	1.87713600	C	-2.30645900	0.92395900	1.38399300
				C	-3.09586400	-0.01214300	0.76929100
Int-2				C	-2.26846400	-1.18597900	0.60083300
C	-2.19038700	-1.05371100	0.22899400	H	-2.52210200	1.90133800	1.79235200
O	-1.70479300	-2.27442600	-0.09905800	O	0.07628900	-1.53339300	1.22661300
C	-0.33814100	-2.12757600	-0.20781300	H	0.91865500	-1.14828100	0.24146100
C	0.02215800	-0.84012600	0.05894600	C	-4.50884400	0.19754200	0.39792500
C	-1.20733800	-0.11732600	0.35616300	C	-5.49064600	-0.77799200	0.65028100
H	0.21406700	-3.02800700	-0.42750600	C	-4.91773000	1.40453900	-0.19814800
O	-3.52295500	-0.93969900	0.37423300	C	-6.82597100	-0.55575900	0.31427000
H	-3.92787600	-1.81114000	0.22342600	H	-5.20784000	-1.70489200	1.14032100
C	1.40879000	-0.33040800	0.04429300	C	-6.25446000	1.63138100	-0.52425600
C	1.91412900	0.45149300	1.09774700	H	-4.17021800	2.16280600	-0.41702200

C	-7.21538000	0.64937200	-0.27439700	C	3.72035500	3.50286300	-0.73401200
H	-7.56642200	-1.32411300	0.52266100	H	4.22413600	3.09587000	-1.61139800
H	-6.54409200	2.57313400	-0.98419900	C	3.43360200	4.80309800	-0.68030800
H	-8.25634700	0.82119800	-0.53547600	H	3.69713200	5.47890300	-1.49028100
C	-2.54855000	-2.47233200	-0.13663500	H	2.92567400	5.24408500	0.17553800
H	-3.61989500	-2.70767800	-0.09663500				
H	-2.02221900	-3.29628000	0.35988600	2			
C	-2.12214500	-2.41812800	-1.58688300	C	1.30110400	-1.86791400	-1.53227200
H	-2.60052700	-1.64363700	-2.18874400	O	1.14378400	-0.75458600	-2.30993100
C	-1.22033400	-3.22215100	-2.15431000	C	2.13753100	0.21361800	-1.94945300
H	-0.95611600	-3.13568800	-3.20642700	C	2.96216100	-0.43626000	-0.86791800
H	-0.71809700	-4.00590200	-1.58911900	C	2.46957500	-1.67189600	-0.64177700
C	1.19032900	1.58100400	-0.57421900	H	2.73387000	0.45426700	-2.83845700
O	0.61741600	0.48833200	-1.03376400	O	0.55859600	-2.82331200	-1.61891400
C	1.51265700	-0.60045400	-0.73939400	H	-1.23743500	-1.51240800	-0.03022300
C	2.73747700	0.01905400	-0.28889000	C	4.07632700	0.28363200	-0.22470300
C	2.50121800	1.39103200	-0.11827500	C	5.34207300	-0.30867100	-0.07535700
H	1.49565100	-1.33055600	-1.54730200	C	3.88336400	1.59901500	0.23578500
O	0.49211600	2.70108200	-0.56369600	C	6.38642000	0.39392400	0.52441300
H	-0.43041400	2.50743400	-0.82216600	H	5.51168700	-1.31267300	-0.45343500
C	3.94660600	-0.75854500	0.01466800	C	4.92916000	2.29423100	0.84158400
C	4.67725200	-0.55173400	1.19933600	H	2.90323700	2.06061000	0.14966800
C	4.37683800	-1.75775900	-0.87859200	C	6.18292400	1.69622200	0.98601200
C	5.81158500	-1.31357600	1.47274700	H	7.36148000	-0.07509100	0.62619800
H	4.33105800	0.17689800	1.92524400	H	4.76221900	3.30536800	1.20307500
C	5.51625500	-2.51068200	-0.60530100	H	6.99746900	2.24220300	1.45439000
H	3.82827900	-1.92689900	-1.80078200	C	2.82050900	-2.71703400	0.38396900
C	6.23790900	-2.29001900	0.57007500	H	3.87380400	-2.61985600	0.66965700
H	6.35756400	-1.14967800	2.39760400	H	2.68569100	-3.70958900	-0.06023900
H	5.84091700	-3.27054400	-1.31063300	C	1.95639800	-2.59668700	1.62121700
H	7.12432400	-2.88056300	0.78459100	H	2.08706000	-1.67906800	2.19507200
C	3.40275200	2.50484600	0.35700700	C	1.07310500	-3.51008300	2.02510600
H	4.33714200	2.06605400	0.72219800	H	0.48651400	-3.37319400	2.93094600
H	2.94093900	3.02290400	1.20681000	H	0.90511600	-4.43091900	1.47010100

C	-0.70827500	1.44872800	0.00409900	H	-0.65459700	2.10800800	-1.04038200
O	-0.28301800	0.24318400	0.48624600	H	-0.92598500	-2.11336400	-0.31535200
C	-1.40693300	-0.63890100	0.60874600	O	-3.45670300	-1.12718900	-1.08780700
C	-2.60382400	0.17151400	0.17491500	C	1.26382300	-0.07637600	-0.33873300
C	-2.17799300	1.40744800	-0.17101700	C	1.88436200	-1.24160000	0.15309300
H	-1.46838600	-0.98086400	1.64846900	C	2.08145100	1.03583700	-0.62302400
O	0.06631900	2.35341500	-0.23641100	C	3.26247300	-1.29049900	0.35423000
H	1.63207600	1.12284100	-1.60715400	H	1.28501600	-2.11881900	0.37852900
C	-3.95465800	-0.41629000	0.16113700	C	3.45775400	0.98593100	-0.41767200
C	-4.83300600	-0.20794900	-0.91751700	H	1.63872700	1.94374600	-1.02255500
C	-4.37941900	-1.23374400	1.22427800	C	4.05668700	-0.17722800	0.07260200
C	-6.10228700	-0.78334100	-0.92126000	H	3.71654600	-2.20188700	0.73417300
H	-4.50574100	0.37872600	-1.77009100	H	4.06569400	1.85720100	-0.64685800
C	-5.65217900	-1.80182300	1.22110500	H	5.13108000	-0.21611800	0.22952300
H	-3.71741400	-1.40987700	2.06738500	C	-1.56216600	-0.76857200	1.69161700
C	-6.51857400	-1.57732900	0.14957600	H	-0.54075000	-0.98321400	1.99945100
H	-6.76390200	-0.61788200	-1.76718700	H	-2.26522900	-1.57417100	1.89547800
H	-5.96596800	-2.42201200	2.05635800	C	-2.02355400	0.56027700	1.73996700
H	-7.50893300	-2.02429000	0.14525800	H	-3.09890100	0.72419400	1.70433700
C	-2.91843800	2.65229000	-0.58427800	C	-1.18554900	1.61871600	1.38355900
H	-3.90624400	2.38813900	-0.97533800	H	-1.59773400	2.62517500	1.33747700
H	-2.36274300	3.14467100	-1.39039500	H	-0.12532900	1.58081800	1.62222000
C	-3.08245700	3.61294300	0.57444000				
H	-3.69883900	3.25133100	1.39829400	3			
C	-2.53246800	4.82473700	0.64284200	O	-2.70312700	0.04389200	0.46463300
H	-2.69047200	5.47418800	1.50071600	C	-2.70324000	-1.28437700	0.11295700
H	-1.90041200	5.21348100	-0.15301300	C	-1.30687600	-1.68961400	-0.09848500
				C	-0.49072300	-0.63908400	0.11475900
TS-3				H	-1.03398100	-2.71023100	-0.33257700
C	-2.42055000	-0.56068800	-0.84321500	C	0.97904700	-0.63548700	0.08985300
O	-2.27475700	0.80832400	-1.01782800	C	1.71989700	0.23940000	0.90542300
C	-0.96311100	1.14015600	-0.66541300	C	1.67699500	-1.54517300	-0.72696900
C	-0.18470400	-0.02320100	-0.54408400	C	3.11335000	0.19712500	0.91004200
C	-1.12972700	-1.04952800	-0.30141900	H	1.20611700	0.94686400	1.54874600

C	3.06862400	-1.58043100	-0.72503900
H	1.12110700	-2.21255700	-1.37913700
C	3.79221900	-0.71083500	0.09552800
H	3.66854000	0.87482500	1.55270500
H	3.58971100	-2.28428100	-1.36820500
H	4.87843500	-0.73914300	0.09704800
O	-3.72343100	-1.92972700	0.03739900
C	-1.36050700	0.56830500	0.42890500
H	-1.14269000	0.97828700	1.42235600
C	-1.35773200	1.71489500	-0.61253000
H	-2.20883200	2.35596000	-0.35792900
H	-1.56838900	1.26760900	-1.59295900
C	-0.10249600	2.54343900	-0.67167700
H	0.77325900	2.07815700	-1.12023200
C	-0.01452300	3.79779900	-0.22485000
H	0.90978100	4.36601100	-0.29716100
H	-0.86481100	4.30939100	0.22360200

TS-4

C	0.58883000	0.98379900	-0.49384900
C	0.53694800	-0.14835100	-1.35602500
C	-1.52705000	0.48163400	-1.02799100
C	-0.75360500	1.31109000	-0.21638100
C	0.55657400	-1.66823200	-0.02055500
C	-0.52398700	-1.80036600	0.61031500
H	1.28261500	-0.47074300	-2.07688800
O	-0.76843700	-0.28053300	-1.81114600
H	-1.13529100	2.05483900	0.47562900
C	1.86302300	-2.36694900	-0.06659100
C	-1.77685500	-1.79531200	1.27919000
O	-2.81794700	0.35840500	-1.23491900
C	-3.73076600	1.19136500	-0.47659500
H	-4.69391300	0.66918800	-0.57693600
H	-3.44143600	1.18961800	0.58567500

C	-3.82550900	2.57846000	-1.03681200
H	-4.00731700	2.63965700	-2.11687800
C	-3.75325800	3.68826700	-0.29727000
H	-3.57790600	3.64862100	0.78371600
H	-3.88072200	4.67911600	-0.74377300
C	1.79202100	1.59546800	0.07928600
C	3.08219100	1.15719600	-0.28937700
C	1.68865300	2.65086000	1.01028200
C	4.22187500	1.75231400	0.25300000
H	3.19767100	0.34185600	-1.00502600
C	2.83015100	3.24544000	1.54850800
H	0.70566700	3.01254300	1.31769000
C	4.10248700	2.79958200	1.17329000
H	5.21093800	1.39626000	-0.04677200
H	2.72543300	4.06211500	2.26751100
H	4.99611800	3.26590600	1.59603400
O	-1.99816500	-1.25245400	2.35163400
O	2.25840400	-3.09325200	0.81683000
O	2.55556300	-2.14022100	-1.19426000
O	-2.71423700	-2.49614900	0.59712500
C	-4.00207100	-2.58856300	1.20622000
H	-4.61728700	-3.19271300	0.52655700
H	-3.94395300	-3.07919400	2.19052900
H	-4.45840900	-1.59466600	1.33510700
C	3.81589200	-2.81162700	-1.31717400
H	3.67801700	-3.90296100	-1.29239400
H	4.22901500	-2.50591300	-2.28641000
H	4.49605500	-2.51635000	-0.50430900

Int-3

C	1.15444200	0.73423300	0.06242700
C	0.39707300	0.08457500	-1.13496100
C	-1.11609600	1.11414400	-0.04654300
C	0.18693600	1.38066300	0.73991000

C	-0.49161500	-1.04880200	-0.55585400
C	-1.44869600	-0.40189500	0.12986300
H	0.97800800	-0.15573700	-2.03011300
O	-0.60243300	1.07588100	-1.38848600
H	0.23231600	1.88012400	1.70670200
C	-0.26496800	-2.50443500	-0.63177100
C	-2.49962600	-0.88785400	1.05961500
O	-2.21045200	1.90758800	0.12366000
C	-2.03420400	3.33275500	0.09884000
H	-2.94806800	3.72118000	0.57812200
H	-1.17513000	3.63158200	0.72251100
C	-1.91456800	3.89505900	-1.28885500
H	-2.63534500	3.50292300	-2.01711000
C	-1.04793000	4.84763500	-1.64245300
H	-0.31636600	5.25106400	-0.93286700
H	-1.03813500	5.26430400	-2.65437900
C	2.57577200	0.55001400	0.36273700
C	3.32990900	-0.44717900	-0.28898200
C	3.22623400	1.36388700	1.31627000
C	4.68370100	-0.62884900	0.00747200
H	2.85031100	-1.10103600	-1.02023900
C	4.57692700	1.18223500	1.60713500
H	2.66592500	2.15311300	1.82296700
C	5.31319400	0.18432600	0.95398100
H	5.24834600	-1.41192200	-0.50540100
H	5.06264800	1.82552500	2.34569600
H	6.37310000	0.04496500	1.18220600
O	-2.47265500	-0.64241400	2.24500000
O	-0.88124500	-3.33548400	0.00045500
O	0.71919800	-2.80299200	-1.49629500
O	-3.45909500	-1.57234500	0.44384000
C	-4.50376900	-2.10705500	1.26991300
H	-5.20536100	-2.60221500	0.58753900
H	-4.09396400	-2.83631800	1.98483700

H	-5.01441000	-1.30442000	1.82250000
C	1.03001600	-4.19176700	-1.66397800
H	0.15512400	-4.74266400	-2.04080300
H	1.84626800	-4.23508300	-2.39550600
H	1.35180000	-4.63739000	-0.71064100

TS-5

C	-2.60958700	-0.76221200	-0.77103600
C	-3.25882800	-0.59459000	0.47790600
C	-3.23221900	-1.70265000	1.39284400
C	-2.61121500	-2.92018900	1.04239800
C	-1.99524400	-3.11136500	-0.24480300
C	-1.99271800	-2.00578900	-1.12651900
H	-2.53846200	0.08402200	-1.45624500
H	-3.63432000	-1.59056300	2.39884900
H	-2.54353300	-3.71537600	1.78696000
H	-1.45185200	-2.08093300	-2.07161300
C	-1.32748000	-4.41096500	-0.58764100
H	-0.69835600	-4.75161300	0.24804200
H	-2.08604400	-5.18747500	-0.78593000
H	-0.69516900	-4.31141100	-1.48188300
C	-3.94637400	0.72914900	0.79100400
H	-3.22705700	1.52090300	0.52318200
C	-4.33049800	0.91450700	2.26166500
H	-3.45559500	0.80823500	2.91816200
H	-4.74837900	1.92310000	2.41054000
H	-5.10206900	0.19192000	2.57644300
C	-5.18330600	0.88751900	-0.11511200
H	-5.66395600	1.86275700	0.06508400
H	-4.92312000	0.83260600	-1.18374700
H	-5.92945800	0.10188600	0.09231300
Ru	-1.14464700	-1.32089500	0.77941500
Cl	-0.76524400	0.35696600	2.52805200
Cl	0.54563200	-2.70079800	1.91834200

C	2.65200200	0.00887100	-0.73853800	O	-1.30560100	3.39594400	-0.70580100
C	1.56816300	0.17251000	0.34375100	C	-1.96752100	4.63486700	-1.00068200
C	0.74957400	0.85993400	-1.83200000	H	-2.94608600	4.57953500	-0.50891800
C	2.11158200	0.32948300	-1.94357800	H	-1.38968700	5.47992700	-0.59753000
C	1.09199900	1.62470900	0.38065600	H	-2.09295000	4.76356400	-2.08593700
C	0.52789200	1.92932700	-0.80190700	C	2.34623300	2.94797800	3.56131300
H	1.84483300	-0.22216600	1.32534500	H	1.41413200	3.06156700	4.13577700
O	0.49319200	-0.55704100	-0.25213400	H	3.09967600	2.43100300	4.16822300
H	2.58754900	0.21277500	-2.91728100	H	2.71284400	3.94279800	3.26672700
C	1.26602300	2.58374600	1.49704300				
C	-0.09634600	3.22244200	-1.23459800	Int-4			
O	-0.12154300	0.82800800	-2.79571600	C	2.73779400	-1.45162900	1.29206000
C	0.09007300	-0.00761200	-3.97896700	C	2.11671200	-0.67737700	2.33582100
H	0.91657200	0.44898900	-4.54789200	C	2.66387400	0.59736300	2.60817200
H	0.38407100	-1.01679100	-3.65604700	C	3.80518500	1.08875700	1.89088100
C	-1.17273000	-0.00771500	-4.77629800	C	4.43165000	0.31443800	0.88678200
H	-1.57105900	0.97938900	-5.03954500	C	3.86437200	-0.97256100	0.58920200
C	-1.77562900	-1.12008500	-5.20425400	H	2.28841800	-2.40015300	0.99173300
H	-1.38806000	-2.11550900	-4.96118300	H	2.17388200	1.26132000	3.31952600
H	-2.67221100	-1.07484800	-5.82960100	H	4.15789700	2.10358600	2.08254700
C	3.99071300	-0.51719500	-0.47718700	H	4.26665200	-1.55600300	-0.24113600
C	4.54438200	-0.45148300	0.81985100	C	5.61039500	0.83019400	0.11370700
C	4.76961400	-1.08367500	-1.51214800	H	5.70127800	1.92196600	0.20728300
C	5.83332900	-0.92628700	1.06925500	H	6.53938200	0.37397500	0.49757700
H	3.97264000	-0.00138000	1.63282700	H	5.52073200	0.57751300	-0.95234200
C	6.05235600	-1.56199400	-1.25713000	C	0.88617800	-1.23088100	3.03333100
H	4.35578700	-1.16795000	-2.51914000	H	0.27567500	-1.68492500	2.23540000
C	6.59026700	-1.48460500	0.03489500	C	0.02583000	-0.17091700	3.72613900
H	6.24754400	-0.85920600	2.07835600	H	-0.26057200	0.63413200	3.03287300
H	6.63655700	-2.00535400	-2.06753700	H	-0.89873700	-0.63180300	4.10907400
H	7.59671400	-1.86237600	0.23290000	H	0.54414400	0.28284000	4.58709800
O	0.43231700	3.98514000	-2.01008300	C	1.29820500	-2.34327800	4.01507600
O	0.74904000	3.68031800	1.54375500	H	0.40590200	-2.80691200	4.46640500
O	2.12501100	2.12296900	2.41326200	H	1.87410300	-3.13907700	3.51607400

H	1.91912300	-1.94006500	4.83275800	H	2.11380700	-5.45729900	-3.09376800
Ru	2.24785400	0.51070800	0.44853000	O	-4.61812400	2.06768700	-1.23991300
Cl	1.21878600	2.73440900	0.52307200	O	-1.81231200	3.40392800	-1.06124300
Cl	2.69984300	0.89907400	-1.92685200	O	-0.31251000	2.47498300	-2.45819100
C	-0.97618300	-1.45992700	-1.21597800	O	-3.87028200	2.19218400	0.88157800
C	-0.43105500	-0.04698400	-1.16511300	C	-4.87434900	3.16573800	1.19810100
C	-3.08090100	-0.65398500	-0.31572600	H	-4.76106700	3.38240800	2.26748900
C	-2.23270800	-1.71024000	-0.66115400	H	-4.71861000	4.08199700	0.60911700
C	-1.50133300	1.02666800	-1.05752300	H	-5.88087900	2.76988700	0.99574800
C	-2.73125600	0.73884600	-0.56933100	C	0.11202100	3.76336300	-2.90738100
H	0.19629100	0.19188600	-2.03813900	H	0.55134800	4.32385400	-2.06978100
O	0.31282100	-0.16545300	0.02336800	H	0.87207100	3.58060000	-3.67651500
H	-2.58144800	-2.72665400	-0.49898400	H	-0.73211200	4.32953000	-3.33021300
C	-1.21402000	2.43775500	-1.48393700				
C	-3.83607600	1.75686400	-0.37477900	4			
O	-4.27672000	-0.80619300	0.20642000	C	-1.34143500	-0.28729100	-0.14606100
C	-4.85258800	-2.11665000	0.46164200	C	-0.39474300	-1.32142100	0.06817500
H	-4.87709500	-2.66332200	-0.49604100	C	0.47678100	1.34883300	-0.25435900
H	-4.20961200	-2.65832700	1.17196700	C	-0.88628800	1.02698000	-0.30110700
C	-6.23112000	-1.91374100	1.00197600	C	0.99214300	-1.00813200	0.11603300
H	-6.91067600	-1.33046700	0.36932300	C	1.41599400	0.33299400	-0.04255700
C	-6.65354300	-2.43153600	2.15784900	O	-0.87138000	-2.56771700	0.23674400
H	-5.98888800	-3.01740500	2.80240700	H	-1.62265900	1.80911800	-0.47729000
H	-7.68465900	-2.29630500	2.49783100	C	2.05051500	-2.03241300	0.33099200
C	-0.12386200	-2.55103700	-1.69865100	C	2.86305700	0.76027900	0.05024500
C	1.15828600	-2.29098600	-2.24141400	O	0.98376100	2.59933700	-0.43839000
C	-0.56966700	-3.89727800	-1.67901400	C	0.12742100	3.74200100	-0.49526000
C	1.95013000	-3.32686600	-2.73425500	H	0.79294900	4.54751100	-0.84628900
H	1.55591400	-1.27513100	-2.26645700	H	-0.66149700	3.61350900	-1.25661900
C	0.22473300	-4.92698600	-2.17463900	C	-0.44686300	4.11474500	0.84292300
H	-1.55243800	-4.15337700	-1.28345100	H	0.27028500	4.10874800	1.67364100
C	1.49076700	-4.64781300	-2.70454300	C	-1.71349000	4.48667800	1.04771600
H	2.93608700	-3.09702100	-3.14608400	H	-2.44755900	4.50183900	0.23383300
H	-0.14599000	-5.95455900	-2.15032000	H	-2.06268500	4.80275600	2.03558100

C	-2.80803500	-0.55949100	-0.18031900	O	3.23839000	-1.80452300	0.36840900
C	-3.69492300	0.28581200	0.51483100	O	1.56738600	-3.28991600	0.48917300
C	-3.35223500	-1.62306800	-0.92692500	O	3.46661600	0.71345700	-1.14054700
C	-5.07612800	0.07674900	0.46714500	C	4.84469700	1.09882400	-1.17261200
H	-3.29644500	1.10878800	1.11354800	H	5.44849600	0.43096100	-0.53936500
C	-4.73299800	-1.82767300	-0.97848900	H	5.16281800	1.01179800	-2.21935700
H	-2.68833800	-2.29017900	-1.47792900	H	4.97220500	2.13540100	-0.82525700
C	-5.60173800	-0.98108000	-0.28085600	C	2.52168200	-4.34535300	0.70374800
H	-5.74300600	0.74192800	1.02241900	H	3.09842200	-4.15783100	1.62045300
H	-5.13330800	-2.65488100	-1.57107000	H	1.93303600	-5.26493700	0.80462000
H	-6.68170000	-1.14676700	-0.31901100	H	3.20627700	-4.42109000	-0.15287100
O	3.37894000	1.17054900	1.06165600	H	-0.11747500	-3.17400100	0.38503400

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