Gold carbenes via 1,2-dialkoxycyclopropane ring-opening: a mass spectrometric and DFT study of the reaction pathways

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General Experimental

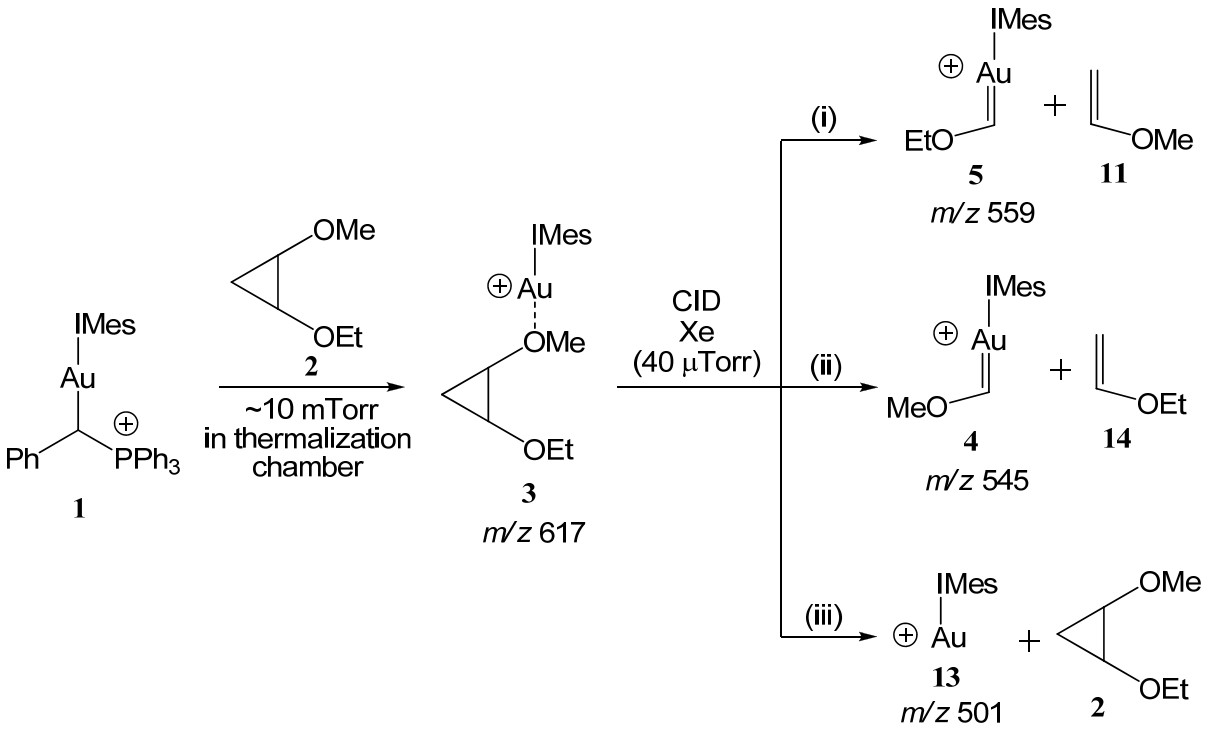
IMes-supported gold ylid complex **1**[1] and 1-ethoxy-2-methoxycyclopropane **2**[2] were prepared following literature procedures. NMR measurements were run on a Varian Mercury XL 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) spectrometer.

Mass Spectrometric Measurements

Mass spectrometric measurements were performed on a Finnigan MAT TSQ-700 instrument, in which the first transfer octopole has been replaced by a custom-made 24-pole ion guide.[3] Species of interest were mass selected in the first quadrupole and collided with xenon in the octopole collision cell to give characteristic fragmentation patterns that were analyzed in the second quadrupole. The resolution in parent-ion selection was always kept high enough to ensure that fragmentation in the daughter mode occurs only for the ions of interest.

The cation **1** was obtained from complex **1**-BF_4 by electrospray of its $1\cdot10^{-7}$ mol/L solution in dichloromethane. It was then reacted in the radiofrequency 24-pole ion guide with 1-ethoxy-2-methoxycyclopropane **2** (Scheme 1) under 10 millitorr pressure of the reactant gas to yield a cationic coordination complex **3**. Ions **3** (Scheme 1) were further mass selected and directed into the collision octopole for CID. The fragmentation behavior of these ions was studied at different pressures of xenon and collision offset voltages.

Scheme 1: Dissociation channels observed for mass spectrometric experiments with 1-ethoxy-2-methoxycyclopropane (only one regioisomer of **3** is shown)



Up to -15.0 V collision offset, only two daughter signals are observed at *m/z* 545 and *m/z* 559 (Figure 1). They correspond to the NHC-gold(I) Fischer carbenes **4** and **5** (Scheme 1, (i, ii)).

An increase of the parent ions' kinetic energy (collision offsets from −20.0 to −60.0 V, Figure 1) leads to the appearance of a third daughter channel at *m/z* 501. The latter corresponds to the NHC-gold(I) cation **13** and indicates that a rupture of the Au−O bond in **3** occurs at excess energies (Scheme 1 (iii)). This signal becomes the major dissociation pathway when collision offsets higher than −40.0 V are applied (Figure 1).

Figure 1: Finnigan MAT TSQ-700 daughter-ion mass spectra produced by mass selection of cation **3** and subsequent collision induced dissociation with 40 µTorr of xenon. Approximately up to -15.0 V collision offset (Lab frame), the formation of only two daughter ions **4** and **5** is observed.

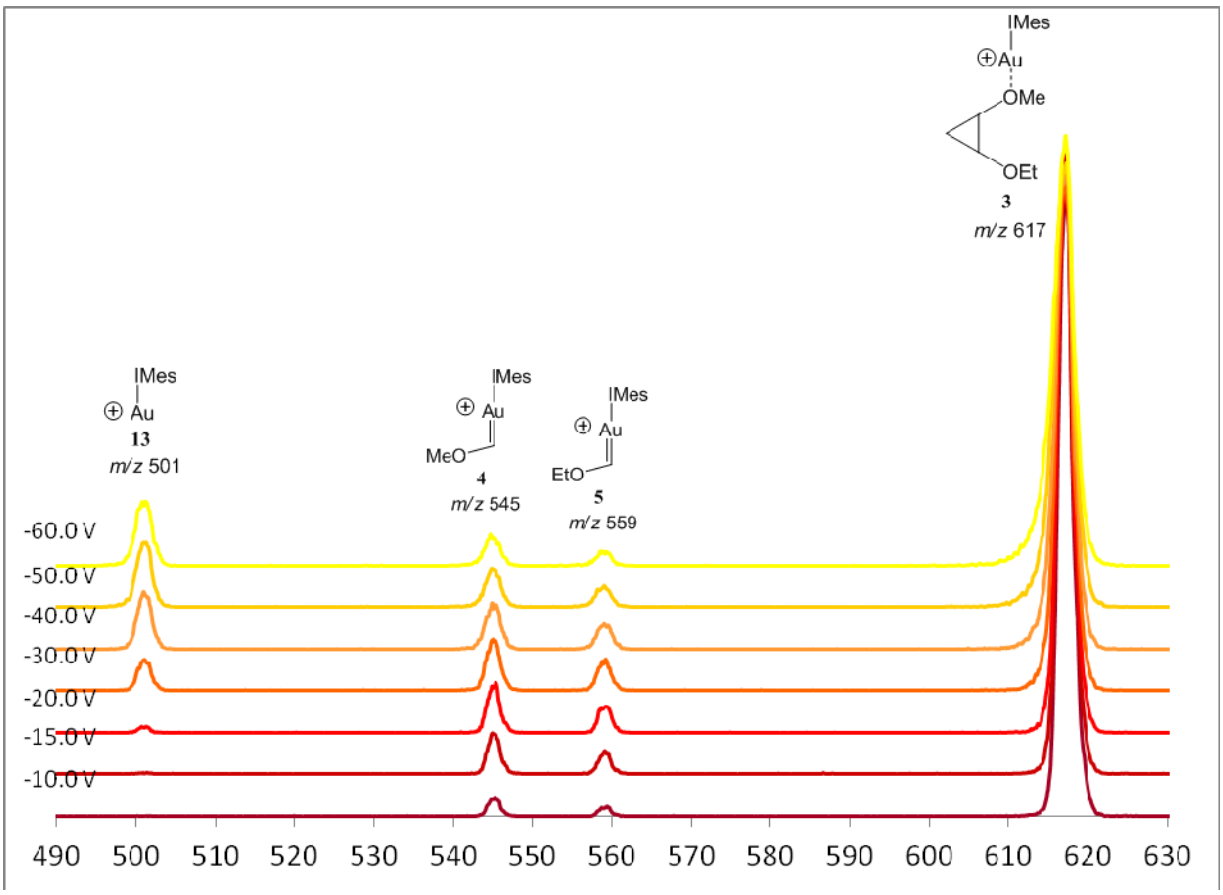
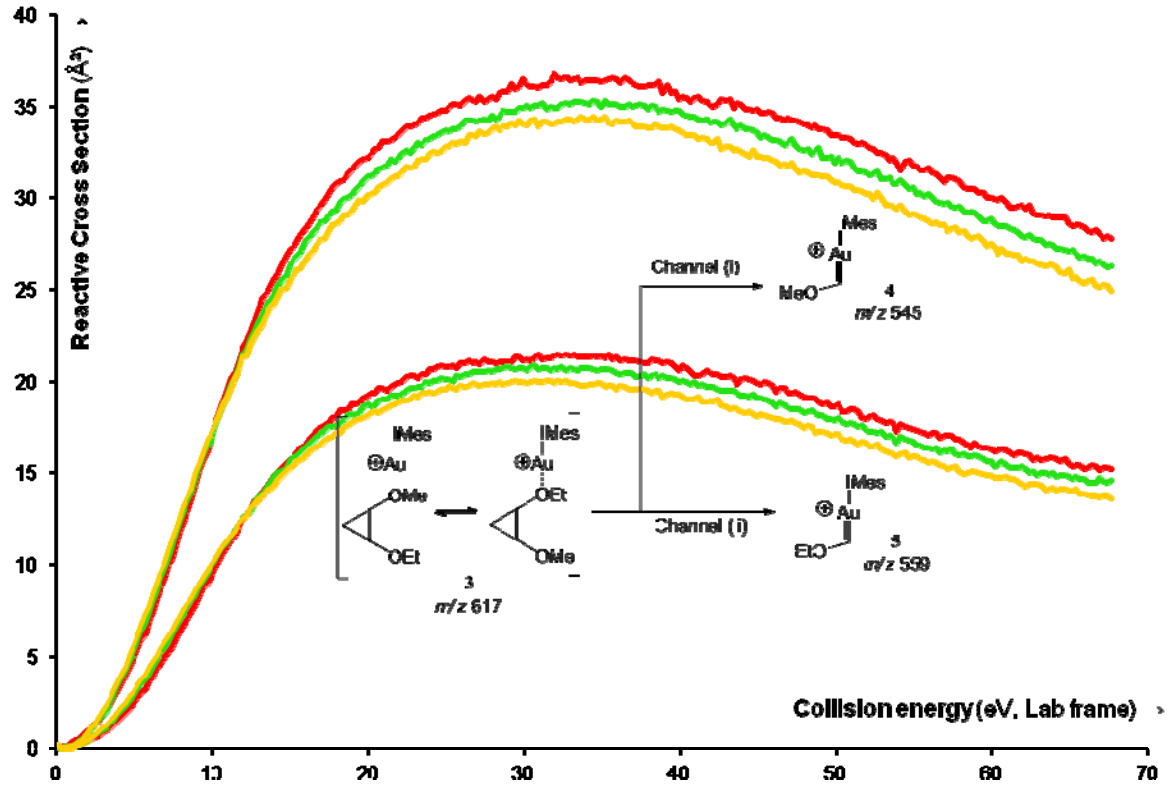


Figure 2: Reactive cross sections measured for the formation of **4** and **5** from **3** at different Xe pressures (red: 38.3, green: 59.2 yellow: 80.0 μTorr)



By assigning signals at *m/z* 545 and *m/z* 559 to the carbenes **4** and **5**, we assume that they are produced by homologous processes. In order to prove this their reactive cross sections were measured at three Xe gas pressures, as shown in Figure 2. Within the studied collision energy range, the cross section for formation of **4** is about 1.7 times larger than that for formation of **5** but exhibit similar curvatures.

The rate-limiting transition states for homologous processes are expected to be very similar in character. Therefore the reaction barriers for channels (i) and (ii) and the related parameters were extracted from the cross sections using L-CID-fits.[4] Thus, activation energies for formation of **4**

and **5** were evaluated for Lab-frame collision energies up to 15 eV, where fragmentation of the parent species **3** affords no additional products (Figure 1). Over this range, the reactive cross sections were linearly extrapolated to zero pressure for fitting with L-CID.

In general the rate-limiting reaction step can be an internal rearrangement, which should be fitted with a tight transition-state model, or the fragmentation into products, which typically proceeds without a reverse barrier[5] and for which a loose transition-state model is appropriate. Given that the rate determining state of our mechanistic pathway is not clearly defined at this level of theory, we decided to perform L-CID fitting applying consecutively both tight and loose models. Such models should the same for homologous processes.

Our treatment is complicated by the fact that parent ion **3** may exist as MeO- and EtO-coordinated regioisomers (Figure 2). If interconversion is fast or when each regioisomer can afford both products, according to the Curtin–Hammett principle the ratio between the cross sections reflects the difference in overall reaction rate for formation of **4** vs **5**; in this case, a two-channel fit should be performed. Otherwise, if interconversion is slow and each regioisomer affords only one product, the ratio between the cross sections for formation of **4** and **5** reflect the ratio between the regioisomers of **3**; in this case, each cross section should be fitted separately by single channel fits.

Table 1: L-CID fitting results with tight and loose criteria assuming either double channel or two independent single reaction channels (E_0 in kcal·mol^{-1}, ν_{eff} and α' in cm^{-1}).

	Double-channel treatment		Single-channel treatment	
TS model	**4**	**5**	**4**	**5**

Tight	E_0	19	20	18	18
	$\nu_{\text{eff}}{}^a$	$[6.5\cdot10^2]$		$[6.3\cdot10^2]$	$[5.9\cdot10^2]$
	α'	$[3.0\cdot10^2]$	$[2.5\cdot10^2]$	$[3.3\cdot10^2]$	$[2.7\cdot10^2]$
Loose	E_0	33	34	31	33
	$\nu_{\text{eff}}{}^a$	$[5.9\cdot10^2]$		$[5.8\cdot10^2]$	$[5.5\cdot10^2]$
	α'	$[5.8\cdot10^3]$	$[5.4\cdot10^3]$	$[5.5\cdot10^3]$	$[5.5\cdot10^3]$

[a] In the two-channel treatment, a single effective frequency ν_{eff} is used.

L-CID furnished similar reaction parameters for formation of **4** and **5** (Table 1), supporting our homologous pathways assumption. Moreover separate single-channel fitting of the two reactive cross sections does not provide significantly different results, suggesting that the system follows Curtin–Hammett conditions.

For a reaction pathway such as that in Figures 2 and 3 of the main article, both "tight" rearrangement and "loose" product dissociation will contribute to the overall reaction kinetics. In this case, the reactive cross section is best fitted with a tight TS model, which will actually provide an upper bound to the dissociation barrier.[3] Indeed, the activation energies of ~19 kcal·mol^{-1} found with a tight TS model are in good agreement with the calculated barriers. The loose TS model affords too high barriers of ~33 kcal·mol^{-1}.

We conclude that species **4** and **5** are produced under Curtin–Hammett conditions via analogous pathways and therefore should be homologous. The close match of the calculated and experimental barriers with a tight TS model further corroborates our presented reaction profile. However, because of the 2.5:1 *trans:cis* diastereomeric mixture of **2** and, hence, species **3** in our

MS experiment, and because of the complicated overall reaction kinetics,[3] we limit ourselves here only to this semi-quantitative discussion.

Computational Details

Quantum-chemical calculations were performed with the Gaussian suite[6] employing the PW91 density functional in combination with the cc-pVDZ-PP small-core relativistic correlation consistent basis set[7] for gold and cc-pVDZ for the remaining elements. Geometry optimizations were performed with tight SCF and convergence criteria and an ultrafine integration grid, applying the geometry DIIS algorithm.[8] The nature of each stationary point was confirmed by a frequency analysis, which also afforded the zero-point energy (ZPE) correction (Table 2).

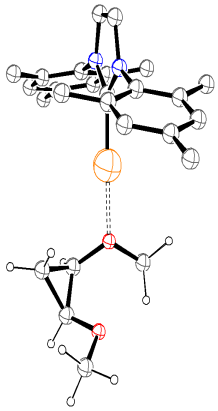
Table 2: Gaussian PW91/cc-pVDZ(-PP) absolute energies and zero-point energy corrected energies in Hartree and kcal/mol.

Compound	PW91/cc pVDZ(PP) (Hartree)		PW91/cc pVDZ(PP) (kcal/mol)	
	non corrected	ZPE corrected	non corrected	ZPE corrected
6	−1406.394568	−1405.864185	−882526.6555	−882193.8347
TS6-7	−1406.367619	−1405.839556	−882509.7445	−882178.3798
7	−1406.379397	−1405.85085	−882517.1352	−882185.4669
TS7-8	−1406.367509	−1405.839637	−882509.6757	−882178.4306
8	−1406.367989	−1405.840116	−882509.9771	−882178.7312
TS8-9	−1406.367019	−-1405.839813	−-882509.3682	−882178.5411
9	−1406.383201	−1405.854498	−882519.5226	−882187.756
TS9-10	−1406.378566	−1405.851307	−882516.6136	−882185.7537
10	−1406.378956	−1405.851884	−882516.8588	−882186.1157

11	−1213.321030	−1212.877620	−761371.079479	−761092.835326
12	−193.037230	−192.955689	−121132.792199	−121081.624404
TS7-13	−1406.377133	−1405.849367	−882515.7148	−882184.5363
13	−1406.386068	−1405.856549	−882521.3216	−882189.0431
TS13-9	−1406.367916	−1405.840089	−882509.9309	−882178.7142

Cartesian coordinates (Å) of optimized structures at PW91/cc-pVDZ(-PP) level of theory obtained with Gaussian03

Intermediate **6**:



(N_{imag}=0)

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N	1.700264	-1.859577	0.279976
C	1.616856	-3.219409	0.536666
C	-1.848862	-2.301949	0.178814
Au	-0.012451	0.545868	-0.276213
O	-0.562907	2.546925	-0.728995
C	-0.588443	3.010699	-2.116678
C	2.937569	-1.126642	0.205942
C	-0.262006	3.596930	0.201351
C	-1.372756	4.574750	0.502061
O	-2.550400	4.385803	-0.214815
C	-3.692626	4.920684	0.466191
C	-0.964043	3.524774	1.532716
H	-0.213857	-4.502047	0.688843
H	2.502479	-3.835753	0.699435
H	0.408774	3.396800	-2.404629
H	-0.854577	2.134692	-2.731079
H	-1.364078	3.792972	-2.191086
H	0.779152	3.950230	0.130663
H	-1.674987	2.695220	1.655468
H	-0.404283	3.814994	2.431145
H	-1.083165	5.626018	0.686779
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H	-3.586728	6.014690	0.633381
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C	4.680995	0.165382	1.288135
C	5.343442	0.298508	0.061986
C	4.802952	-0.280940	-1.092185
C	3.600016	-0.993516	-1.020207
C	2.791953	-0.685075	2.630053
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C	6.589340	1.036533	-0.012563
H	5.318242	-0.177387	-2.045954
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H	2.110258	-2.101982	-1.965216
H	2.842327	-0.817192	-2.953065
H	3.747664	-2.312532	-2.626295
H	3.358377	-0.172534	3.406189
H	1.798428	-0.245452	2.555484
H	2.703765	-1.740792	2.882254
H	6.952882	1.032316	-1.039081
H	6.422756	2.063453	0.309317
H	7.328093	0.568113	0.636087
H	-2.347699	-2.901734	-3.095389

H	-1.003975	-1.952073	-2.420848
H	-1.118246	-3.694513	-2.084249
H	-0.882003	-1.921874	2.474546
H	-2.196210	-0.832075	2.972194
H	-2.310481	-2.574515	3.308793
H	-6.501826	-1.861589	0.878764
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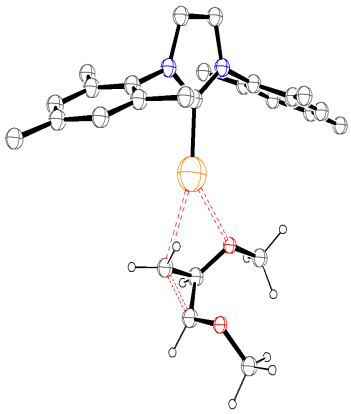
Transition State **$TS_{6\text{-}7}$**:



(N_{imag}=1: *-110.2350 cm^{-1}*)

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C	4.699954	-0.139618	1.231712
C	5.384255	-0.071173	0.003347
C	4.770512	-0.624846	-1.134033
N	1.576412	-1.937232	0.273491
C	0.369236	-1.314393	0.126939
N	-0.577635	-2.286286	0.293195
C	0.033900	-3.511442	0.541658
C	1.385942	-3.291853	0.529518
Au	0.039107	0.600501	-0.227614
O	-1.875081	2.300666	-0.451016
C	-3.292977	2.512993	-0.538998
C	-2.008266	-2.071969	0.219468
C	-2.699726	-1.713469	1.396014
C	-4.090218	-1.529373	1.295097
C	-4.780954	-1.696342	0.081167
C	-4.042508	-2.048318	-1.064625
C	-2.652766	-2.246382	-1.025133
C	-1.984777	-1.521366	2.709920
C	-6.278234	-1.533647	0.010246
C	-1.884592	-2.621827	-2.267550
C	2.724874	-0.799891	2.678867
C	6.750617	0.560184	-0.079015
C	2.873177	-1.826725	-2.313439
C	-1.098258	3.208766	-1.193518
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C	0.391268	3.087249	-0.910443
H	0.717319	2.571007	0.033290
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H	-0.189844	5.268487	-1.057498
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H	-2.488519	5.207891	0.927313
H	-1.198713	6.471963	0.845356
H	-0.548696	-4.419438	0.704182
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H	-2.705159	-1.329630	3.524410
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H	-1.109576	-1.866486	-2.510088
H	2.469419	-1.838161	2.971047
H	1.772785	-0.231101	2.650937

H	3.351831	-0.369304	3.479211
H	5.163016	0.290722	2.131455
H	7.523120	-0.120903	0.333350
H	7.034089	0.789835	-1.122081
H	6.801131	1.495745	0.510017
H	5.289035	-0.577860	-2.102402
H	1.908314	-1.331103	-2.545308
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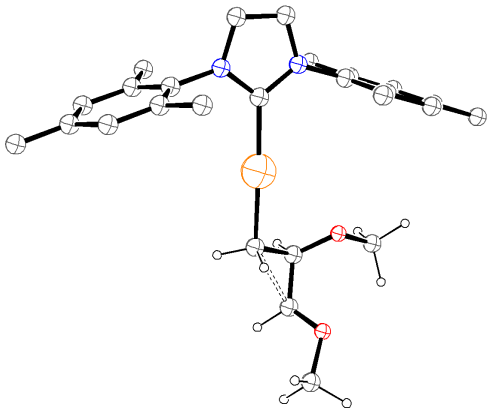
Intermediate **7**:



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C	2.081938	-3.051304	0.279045
C	0.785642	-3.490605	0.301266
Au	0.066208	0.661098	-0.117503
C	-0.575421	2.689627	-0.321459
C	-2.006117	2.669019	-0.931407
C	-2.140497	4.061975	-0.503822
O	-2.785490	4.352862	0.591331
C	-2.590479	5.673062	1.177121
C	3.197732	-0.823209	0.081296
C	-1.459550	-2.397621	0.161625
O	-2.846849	1.739232	-0.315055
C	-4.190475	1.788365	-0.821051
H	3.022885	-3.599460	0.347936
H	0.374374	-4.497128	0.393037
H	0.152784	3.210940	-0.968878
H	-0.531215	3.066745	0.720678
H	-1.945666	2.571321	-2.036329
H	-4.737706	0.970114	-0.322768
H	-4.213162	1.628449	-1.921160
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H	-2.364725	6.416800	0.389718
H	-3.533056	5.919503	1.691760
H	-1.762001	5.606932	1.906565
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C	4.872270	0.529209	1.197936
C	5.457607	0.825589	-0.038809
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C	3.783069	-0.526829	-1.155449
C	3.136091	-0.602155	2.538904
H	5.295892	0.939933	2.113235
C	6.627900	1.679431	-0.101007
H	5.368315	0.528111	-2.177513
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C	-4.258767	-2.455838	0.130139
C	-3.574942	-2.325642	1.344813
C	-2.175333	-2.296533	1.360555
C	-1.402028	-2.632515	-2.294799
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C	-5.708362	-2.485986	0.113835
H	-4.131719	-2.247010	2.277410
C	-1.467085	-2.161687	2.618610
H	-0.394097	-2.158406	2.432582
H	-1.755068	-1.227773	3.099017
H	-1.720172	-2.997609	3.269074
H	-2.098586	-2.726177	-3.126637
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H	3.965710	-1.686958	-2.876456
H	3.693340	-0.106372	3.332373
H	2.105046	-0.251698	2.545825
H	3.154577	-1.678936	2.700525
H	6.938125	1.795108	-1.138456
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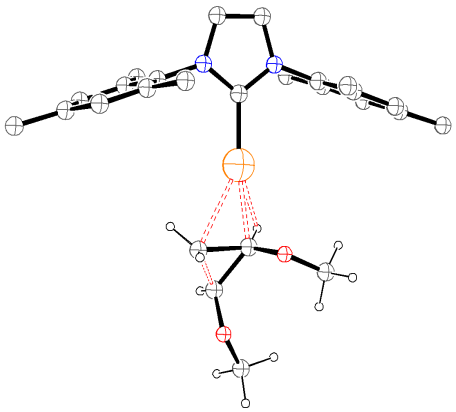
Transition State **$TS_{7\text{-}8}$**:



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C	5.231849	-0.640600	0.046613
C	4.581516	-1.012422	-1.143886
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C	0.131476	-1.421225	0.028670
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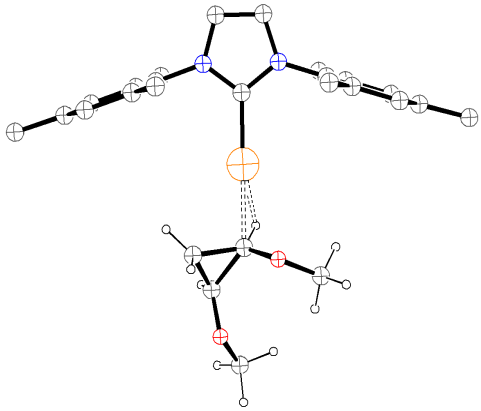
C	-0.424830	-3.603855	0.216441
C	0.942538	-3.521322	0.231034
Au	0.008616	0.550626	-0.127234
C	-0.406019	2.842311	-0.154217
O	-1.107427	2.992628	1.039218
C	-2.457394	3.438592	0.843543
C	-2.309588	-1.941484	0.029932
C	-2.978326	-1.616909	1.229425
C	-4.340232	-1.281490	1.136337
C	-5.025811	-1.268659	-0.091699
C	-4.310683	-1.595303	-1.259208
C	-2.949424	-1.939537	-1.229004
C	-2.267215	-1.612152	2.559542
C	-6.496592	-0.944080	-0.155479
C	-2.204851	-2.281257	-2.495435
C	2.494423	-1.412959	2.629854
C	6.651199	-0.133220	0.029705
C	2.597489	-1.911740	-2.444149
C	1.163339	2.982317	0.015262
C	0.437439	4.077008	-0.666248
O	0.311674	5.259161	0.032156
C	-0.475880	6.245607	-0.646535
H	-0.932234	2.308917	-0.995695
H	-2.894219	3.544272	1.851304
H	-2.493335	4.416740	0.321956
H	-3.045287	2.690251	0.267382
H	1.419478	3.168510	1.066975
H	1.875342	2.368787	-0.552581
H	0.533824	4.156969	-1.764082
H	-1.531016	5.921057	-0.777856
H	-0.450361	7.148402	-0.012910
H	-0.046411	6.485123	-1.643139
H	-1.096967	-4.460515	0.284692
H	1.711326	-4.291025	0.313606
H	-2.981743	-1.450234	3.385626
H	-1.736348	-2.565526	2.751601
H	-1.507062	-0.805175	2.608374
H	-4.882160	-1.026692	2.058491
H	-6.754166	-0.397681	-1.082151
H	-6.820653	-0.337703	0.710114
H	-7.102363	-1.873770	-0.149919
H	-4.828724	-1.586070	-2.229086
H	-1.787113	-3.307745	-2.466768
H	-2.871963	-2.215446	-3.372740
H	-1.351177	-1.593319	-2.663438

H	2.145434	-2.449674	2.808374
H	1.596454	-0.762445	2.665229
H	3.150258	-1.128775	3.471358
H	5.024266	-0.490519	2.201015
H	7.361954	-0.953037	0.261956
H	6.930005	0.272080	-0.960084
H	6.811049	0.655682	0.788560
H	5.110846	-0.908271	-2.101951
H	1.679479	-1.314924	-2.621557
H	2.290950	-2.977016	-2.445732
H	3.274463	-1.756146	-3.302385

Intermediate **8**:



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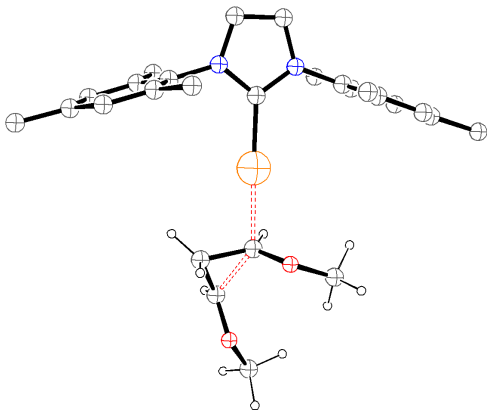
C	0.565738	-3.606531	0.193215
N	1.013010	-2.293012	0.088837
C	-0.051054	-1.439661	0.014956
N	-1.166890	-2.224196	0.075572
C	-0.803657	-3.563096	0.185232
Au	0.023709	0.542286	-0.121906
C	0.126173	2.865146	0.047602
C	1.594797	2.961228	0.517767
C	1.143015	4.006594	-0.427918
O	0.949470	5.270651	0.079306
C	0.445618	6.208787	-0.880829
C	2.402547	-1.883950	0.064060
C	-2.529936	-1.734561	0.027810
O	-0.816037	3.174085	1.015354
C	-2.022758	3.738251	0.479973
H	-2.676821	3.942418	1.344814
H	-1.822979	4.682856	-0.064407
H	-2.530933	3.017471	-0.198609
H	-0.251354	2.319465	-0.893760
H	2.339960	2.221392	0.200446
H	1.643123	3.265590	1.572147
H	0.395091	7.181682	-0.363204
H	1.127269	6.292389	-1.754162
H	-0.569530	5.931969	-1.239861
H	1.467248	3.938146	-1.481895
H	-1.551336	-4.355149	0.248158
H	1.261076	-4.444238	0.264435
C	-3.169669	-1.646216	-1.227881
C	-4.495067	-1.181648	-1.243792
C	-5.175427	-0.820505	-0.065919
C	-4.490941	-0.923393	1.158524
C	-3.164258	-1.380427	1.237732
C	-2.461368	-2.021767	-2.505476
H	-5.012398	-1.103018	-2.210875
C	-6.611274	-0.364004	-0.114577
H	-5.005332	-0.641936	2.088615
C	-2.452470	-1.471211	2.564479
H	-2.026247	-2.478820	2.740535
H	-1.610433	-0.750905	2.622485
H	-3.143305	-1.246496	3.395948
H	-3.126184	-1.887113	-3.376636
H	-1.557653	-1.399180	-2.667086
H	-2.125289	-3.078154	-2.498693
H	-6.868131	0.273045	0.751622
H	-6.829388	0.199581	-1.040914
H	-7.298826	-1.234819	-0.095920
C	3.038307	-1.576517	1.286543
C	4.388144	-1.189258	1.230601
C	5.094985	-1.111831	0.016479
C	4.413628	-1.426610	-1.173928
C	3.064852	-1.819791	-1.181305
C	2.304782	-1.648650	2.602688
H	4.903573	-0.944826	2.170577

C	6.553588	-0.732058	-0.006309
H	4.948873	-1.368309	-2.132637
C	2.357967	-2.149799	-2.472213
H	1.966989	-3.187064	-2.476631
H	1.490549	-1.480408	-2.644584
H	3.042788	-2.045839	-3.331995
H	2.986067	-1.430519	3.443703
H	1.469980	-0.919149	2.645080
H	1.862873	-2.650035	2.776651
H	6.825806	-0.210735	-0.942781
H	6.820840	-0.081945	0.847103
H	7.193133	-1.636528	0.059683

Transition State **$TS_{8\text{-}9}$**:

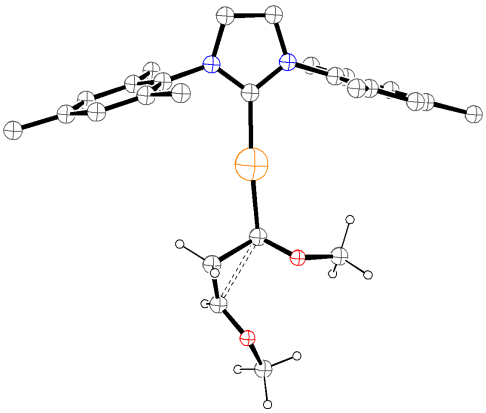


(N_{imag}=1: *-437.6530 cm^{-1}*)

Au	0.012693	0.554609	-0.096028
C	-0.024666	2.803664	0.021611
C	1.483766	3.117049	0.180763
C	0.837945	4.152527	-0.618299
H	-0.538080	2.444028	-0.912291
O	-0.798661	3.128687	1.128394
C	-2.146736	3.490360	0.806000
H	-2.629937	3.765125	1.759225
H	-2.185846	4.354449	0.110183
H	-2.692826	2.631573	0.356025
H	1.705849	3.384961	1.223038
H	2.215000	2.449752	-0.291430
H	0.920559	4.135513	-1.718325
O	0.555120	5.339110	-0.020764
C	-0.218539	6.246523	-0.823642
H	-1.237185	5.849868	-1.019160
H	-0.293484	7.180752	-0.242698
H	0.288037	6.450958	-1.789681
C	0.033075	-1.439940	0.008091
N	1.132928	-2.247934	0.079048
C	0.745555	-3.581867	0.168125
C	-0.624052	-3.600121	0.154237
N	-1.045637	-2.277141	0.056256
H	1.477634	-4.388095	0.234122
H	-1.335446	-4.425683	0.206062
C	2.503598	-1.780244	0.063233
C	3.167853	-1.679622	-1.178040
C	4.500606	-1.233508	-1.162152
C	5.164359	-0.902626	0.033113
C	4.455986	-1.017323	1.243795
C	3.122440	-1.456709	1.290662
C	2.479575	-2.025682	-2.474773
H	2.128072	-3.076871	-2.489322
H	3.163431	-1.888707	-3.330756
H	1.587796	-1.388430	-2.644635
H	5.037020	-1.146632	-2.118049
C	6.606983	-0.465080	0.023445
H	7.277957	-1.326825	0.219700
H	6.810673	0.286948	0.808655
H	6.899569	-0.038818	-0.953631
H	4.957465	-0.760177	2.188018
C	2.385088	-1.563736	2.602153
H	1.530514	-0.857529	2.646045
H	3.055669	-1.335108	3.448994
H	1.969706	-2.578469	2.763291
C	-2.428733	-1.849410	0.007579
C	-3.069792	-1.783624	-1.248879
C	-4.414660	-1.379078	-1.266112
C	-5.113166	-1.054069	-0.088266
C	-4.427164	-1.131347	1.137141
C	-3.081284	-1.529124	1.217098
C	-2.342190	-2.120838	-2.526267

H	-1.963940	-3.162872	-2.525490
H	-3.008360	-2.006488	-3.399332
H	-1.463195	-1.461738	-2.678446
H	-4.932981	-1.319656	-2.234089
C	-6.568268	-0.663003	-0.139005
H	-6.803742	-0.084147	-1.051744
H	-7.215085	-1.564553	-0.152408
H	-6.862445	-0.062945	0.741573
H	-4.955846	-0.878136	2.067400
H	-3.070522	-1.406922	3.376384
C	-2.368496	-1.593386	2.544767
H	-1.894536	-2.580336	2.715364
H	-1.561448	-0.834432	2.607199

Intermediate **9**:



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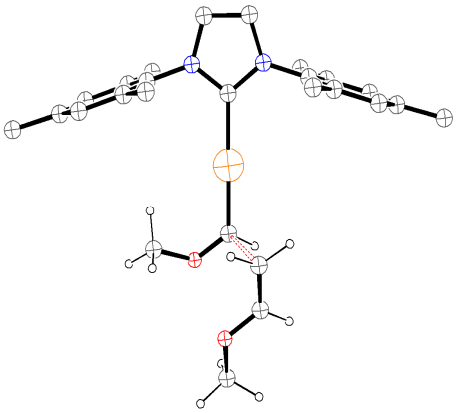
C	-0.255463	-3.673417	0.106773
N	-0.787863	-2.388034	0.040968
C	0.210637	-1.452899	0.006036
N	1.374627	-2.171040	0.051742
C	1.106629	-3.536721	0.113390
Au	-0.015080	0.558419	-0.075546
C	-0.389273	2.642193	-0.117469
C	0.944983	3.439858	0.227712
C	0.542651	4.685123	-0.393338
O	-0.237873	5.495586	0.272742
C	-0.938544	6.538766	-0.458431
C	-2.202429	-2.083093	0.012275
C	2.702550	-1.595936	0.038646
O	-1.365447	3.040225	0.804390
C	-2.696185	3.023971	0.287185
H	-3.355572	3.387132	1.094623
H	-2.792944	3.691002	-0.600953
H	-3.001155	1.996122	-0.004551
H	-0.720363	2.872653	-1.166949
H	1.818160	2.984383	-0.262201
H	1.060048	3.484054	1.323053
H	-0.991907	7.407693	0.217788
H	-0.396046	6.797157	-1.387358
H	-1.956665	6.172816	-0.687958
H	0.725527	4.897328	-1.463068
H	1.906235	-4.277696	0.156339
H	-0.892461	-4.558376	0.143293
C	-2.854661	-2.017981	-1.237945
C	-4.231049	-1.735719	-1.235815
C	-4.949482	-1.527814	-0.044017
C	-4.252133	-1.596172	1.175712
C	-2.875746	-1.874391	1.234891
C	-2.104995	-2.225887	-2.529870
H	-4.757775	-1.680437	-2.199592
C	-6.434962	-1.269798	-0.072745
H	-4.795513	-1.430825	2.117332
C	-2.150092	-1.926968	2.555787
H	-1.603659	-2.881258	2.692309
H	-1.399434	-1.113776	2.633477
H	-2.856954	-1.817648	3.397065
H	-2.787133	-2.158012	-3.395580
H	-1.308618	-1.464708	-2.659650
H	-1.608808	-3.216375	-2.566621
H	-6.765055	-0.679774	0.802341
H	-6.739368	-0.733919	-0.991185
H	-6.999011	-2.225313	-0.052824
C	3.312736	-1.272916	1.270015
C	4.610451	-0.736504	1.227269
C	5.293343	-0.526413	0.015082
C	4.639322	-0.858335	-1.184931
C	3.341739	-1.398125	-1.203624

C	2.599391	-1.480359	2.582434
H	5.103603	-0.478077	2.175655
C	6.701892	0.011940	0.007239
H	5.155254	-0.696575	-2.142508
C	2.659382	-1.737883	-2.504929
H	2.357391	-2.803454	-2.548837
H	1.736325	-1.138730	-2.643991
H	3.327068	-1.540934	-3.362154
H	3.248988	-1.202359	3.431001
H	1.677264	-0.866697	2.641345
H	2.290178	-2.535304	2.723888
H	6.946280	0.506398	-0.951001
H	6.866752	0.736622	0.826666
H	7.435793	-0.808307	0.148899

Transition State **$TS_{9\text{-}10}$**:

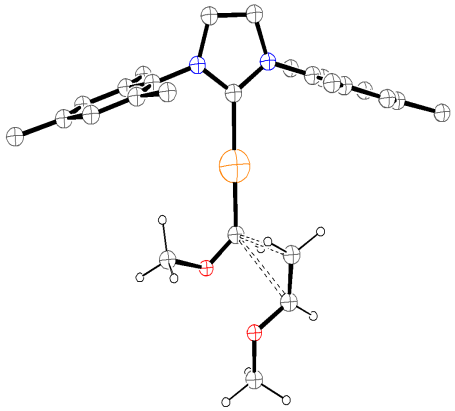


(N_{imag}=1: *-96.5680 cm^{-1}*)

Au	0.012336	0.564822	-0.276784
C	-0.539653	3.357369	1.157678
C	0.259419	2.520499	-0.794134
C	-0.435224	4.626049	0.646741
H	-0.505668	3.032325	-1.412269
O	1.410174	3.150845	-0.999062
C	2.596080	2.640610	-0.340594
H	2.565224	1.533778	-0.301024
H	2.646124	3.068763	0.678700
H	3.453159	2.994823	-0.938170
H	0.254917	2.957082	1.799853
H	-1.528365	2.886797	1.205426
H	-1.270172	5.118146	0.115720
O	0.726795	5.276671	0.683789
C	0.818892	6.485272	-0.106106
H	-0.087858	7.108025	0.021923
H	1.701312	7.029426	0.268468
H	0.962623	6.222739	-1.171706
C	-0.231332	-1.424994	0.083230
N	0.759504	-2.358496	0.229602
C	0.217706	-3.624284	0.431222
C	-1.144239	-3.478219	0.410237
N	-1.400600	-2.127244	0.195372
H	0.846761	-4.505118	0.568307
H	-1.949441	-4.205214	0.526418
C	2.175985	-2.063638	0.182724
C	2.832528	-2.085831	-1.067119
C	4.209457	-1.805340	-1.078996
C	4.924590	-1.516417	0.097974
C	4.223241	-1.500565	1.317435
C	2.846368	-1.773594	1.390613
C	2.089191	-2.382574	-2.345322
H	2.783654	-2.426231	-3.202681
H	1.548693	-3.348727	-2.296083
H	1.330708	-1.601840	-2.559963
H	4.739654	-1.818390	-2.042319
C	6.410296	-1.262475	0.055307
H	6.713165	-0.763509	-0.884257
H	6.744558	-0.640189	0.905946
H	6.971915	-2.218042	0.109462
H	4.764170	-1.272669	2.247340
C	2.117499	-1.742355	2.710769
H	1.635278	-2.713460	2.940969
H	2.811100	-1.507134	3.537173
H	1.312437	-0.979269	2.710821
C	-2.723392	-1.544727	0.111143
C	-3.337621	-1.438040	-1.155265
C	-4.628791	-0.886084	-1.202399
C	-5.300744	-0.454350	-0.044242
C	-4.642672	-0.576114	1.193008

C	-3.351934	-1.121226	1.301782
C	-2.635804	-1.882249	-2.414050
H	-2.300907	-2.936872	-2.352922
H	-1.731338	-1.269562	-2.607590
H	-3.302435	-1.788699	-3.289320
H	-5.125194	-0.794154	-2.179298
H	-7.448083	-0.724544	-0.081230
H	-6.922122	0.781166	0.714234
C	-6.702155	0.095920	-0.125169
H	-6.873908	0.638282	-1.073675
H	-5.150268	-0.239849	2.108745
C	-2.668319	-1.237751	2.641460
H	-1.716062	-0.669379	2.663015
H	-2.416798	-2.288896	2.888109
H	-3.315699	-0.849883	3.447634

Intermediate **10**:



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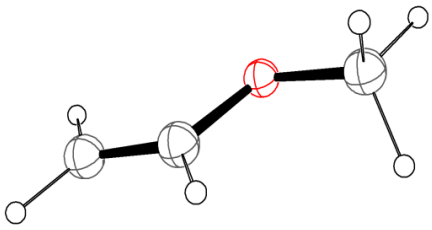
C	-0.774108	-3.509669	0.655541
N	-1.150779	-2.214741	0.314892
C	-0.049385	-1.423852	0.129031
N	1.021531	-2.245033	0.358580
C	0.595957	-3.529171	0.682259
C	-2.519756	-1.760451	0.185883
Au	-0.005055	0.544854	-0.406542
C	0.004089	2.455539	-1.044279
O	0.995719	3.306573	-1.115333
C	2.242612	2.997672	-0.430630
C	2.406051	-1.829588	0.276143
C	-1.219471	3.191298	1.183862
C	-1.134847	4.437044	0.645771
O	-0.009565	5.167846	0.749408
C	-0.021817	6.434578	0.060169
H	1.301742	-4.332622	0.898538
H	-1.510216	-4.292335	0.845317
H	3.049402	3.400807	-1.065976
H	2.218782	3.524252	0.540535
H	2.336516	1.902824	-0.294684
H	-0.842354	2.889831	-1.616554
H	-1.965088	4.887655	0.072999
H	0.920988	6.938963	0.329093
H	-0.061314	6.280995	-1.036672
H	-0.878529	7.054602	0.390725
H	-2.160809	2.634806	1.114532
H	-0.417147	2.799458	1.821793
C	-3.140023	-1.828392	-1.080665
C	-4.472792	-1.393970	-1.170890
C	-5.179709	-0.910505	-0.054331
C	-4.514901	-0.857495	1.183923
C	-3.182503	-1.279302	1.335180
C	-2.402392	-2.331708	-2.296010
H	-4.974547	-1.438881	-2.148357
C	-6.621762	-0.488906	-0.180019
H	-5.050301	-0.479968	2.067125
C	-2.493534	-1.207652	2.675370
C	3.040604	-1.357883	1.445363
C	4.388012	-0.971408	1.338980
C	5.094827	-1.050677	0.125263
C	4.415137	-1.522917	-1.012887
C	3.068798	-1.922135	-0.967268
C	2.305693	-1.258135	2.758925
H	4.901351	-0.601529	2.238375
C	6.551822	-0.670009	0.049976
H	4.949813	-1.587980	-1.971591
C	2.361974	-2.414907	-2.204998
H	-2.134480	-2.201200	3.011093
H	-1.605767	-0.543297	2.641585

H	-3.179470	-0.819673	3.448944
H	-3.073745	-2.378514	-3.171354
H	-1.551983	-1.667689	-2.554517
H	-1.980944	-3.344138	-2.136534
H	-6.922513	0.192155	0.637064
H	-6.816226	0.015702	-1.145184
H	-7.292996	-1.371406	-0.136594
H	2.972120	-0.880199	3.554181
H	1.435937	-0.573399	2.686569
H	1.910722	-2.240052	3.088309
H	1.913500	-3.417177	-2.055373
H	1.535295	-1.734065	-2.494628
H	3.061395	-2.480847	-3.056826
H	6.805617	-0.216113	-0.926374
H	6.832259	0.039967	0.849704
H	7.196404	-1.565692	0.166688

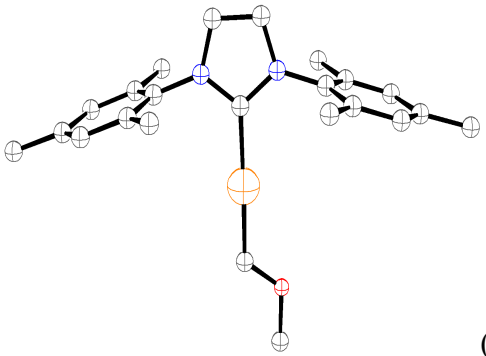
Methyl vinyl ether **11**:



(N_{imag}=0)

C	0.001170	0.000000	0.039254
C	-0.009510	0.000000	1.383109
H	0.942523	0.000000	-0.539222
O	-1.145764	0.000000	-0.701777
H	-0.953506	0.000000	1.942648
H	0.938028	0.000000	1.931758
C	-0.942778	0.000000	-2.111590
H	-1.945244	0.000000	-2.574399
H	-0.390859	0.904843	-2.448330
H	-0.390859	-0.904843	-2.448330

Intermediate **4**:

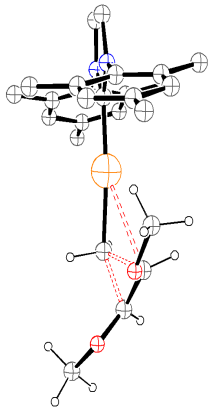


(N_{imag} =0)

C	2.997102	-1.263288	-1.239521
C	2.342470	-1.426253	0.000483
C	2.997601	-1.260527	1.239723
C	4.359962	-0.918528	1.207126
C	5.060313	-0.748704	-0.000898
C	4.359355	-0.921250	-1.208330
N	0.941660	-1.798058	0.001171
C	-0.102460	-0.912293	0.000893
N	-1.231242	-1.687394	0.001644
C	-0.897774	-3.034604	0.002381
C	0.472946	-3.104417	0.002083
Au	0.000609	1.125935	-0.000087
C	0.050688	3.109592	-0.000856
O	1.149431	3.790691	-0.001959
C	1.124035	5.255706	-0.002435
C	-2.586783	-1.174710	0.001718
C	-3.220979	-0.943314	1.240674
C	-4.541928	-0.463606	1.208598
C	-5.221427	-0.222954	0.001420
C	-4.542116	-0.466989	-1.206931
C	-3.222565	-0.946275	-1.238527
C	-2.516438	-1.189684	2.551423
C	-6.650040	0.258219	-0.004098
C	-2.517758	-1.196689	-2.548395
C	2.271493	-1.432608	2.550636
C	6.531597	-0.420419	-0.002051
C	2.270277	-1.438325	-2.549639
H	-1.659216	-3.816182	0.003119

H	1.151011	-3.959321	0.002488
H	-2.168821	-2.238022	2.645336
H	-1.620493	-0.544699	2.659781
H	-3.188113	-0.980920	3.402491
H	-5.055569	-0.275664	2.162384
H	-6.935326	0.706754	0.964840
H	-6.823860	1.006920	-0.800123
H	-7.346326	-0.583820	-0.196904
H	-5.056083	-0.281490	-2.161196
H	-1.620086	-0.554228	-2.657272
H	-2.172754	-2.246101	-2.640129
H	-3.188386	-0.987836	-3.400263
H	1.814308	-2.438111	2.643519
H	1.449550	-0.695842	2.661020
H	2.962240	-1.297734	3.401398
H	4.890087	-0.783302	2.160895
H	6.818040	0.169090	-0.892719
H	7.139299	-1.348858	-0.017037
H	6.824971	0.145550	0.901399
H	4.889011	-0.788150	-2.162674
H	1.447541	-0.702564	-2.660733
H	1.814025	-2.444442	-2.640469
H	2.960325	-1.304277	-3.401095
H	-0.859238	3.762936	-0.000352
H	0.077863	5.615893	-0.001714
H	1.666299	5.579541	-0.907656
H	1.667752	5.580157	0.901692

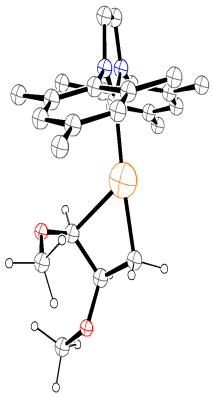
Transition State **$TS_{7\text{-}12}$**:



(N_{imag}=1: *-72.6890 cm^{-1}*)

C	3.412326	-1.259495	-1.220534
C	2.809763	-1.427241	0.045356
C	3.443415	-1.051151	1.248744
C	4.727430	-0.487460	1.153030
C	5.373001	-0.302761	-0.082657
C	4.696053	-0.690688	-1.253973
N	1.495050	-2.030884	0.112101
C	0.313631	-1.341669	0.078476
N	-0.664292	-2.295265	0.164219
C	-0.099403	-3.565431	0.250055
C	1.258881	-3.398574	0.217256
Au	0.106241	0.651817	-0.029647
C	0.111008	2.840204	-0.003797
C	-1.176032	3.160276	-1.007587
O	-2.421629	2.978033	-0.495851
C	-3.026975	1.723187	-0.837933
C	-2.087757	-2.034403	0.157890
C	-2.732231	-1.751287	1.382647
C	-4.118402	-1.526662	1.346392
C	-4.855448	-1.584977	0.148275
C	-4.166427	-1.866551	-1.045379
C	-2.779606	-2.099232	-1.070655
C	-1.967400	-1.680616	2.680481
C	-6.348658	-1.375833	0.154139
C	-2.065533	-2.396150	-2.365715
C	2.772165	-1.232484	2.587117
C	6.766398	0.268580	-0.152375

C	2.707472	-1.664067	-2.491180
C	-0.458116	4.338912	-0.582684
O	-1.035829	5.155161	0.327474
C	-0.123275	6.077520	0.951073
H	-0.065401	2.979175	1.076143
H	1.163495	2.828107	-0.341736
H	-0.985271	2.788474	-2.029495
H	-3.086350	1.597264	-1.939745
H	-2.450759	0.875022	-0.399315
H	-4.042516	1.744370	-0.409498
H	0.290616	4.779699	-1.262341
H	0.593359	5.540019	1.606652
H	0.434913	6.660315	0.188678
H	-0.742250	6.758119	1.558513
H	-0.715131	-4.462594	0.328914
H	2.076158	-4.120001	0.260081
H	-1.382601	-2.603208	2.866957
H	-1.244742	-0.838814	2.677187
H	-2.653339	-1.535162	3.533382
H	-4.639114	-1.305063	2.289234
H	-6.641694	-0.550735	0.831043
H	-6.736283	-1.152806	-0.856538
H	-6.870020	-2.286230	0.514861
H	-4.725019	-1.914162	-1.991377
H	-1.260803	-1.659478	-2.564934
H	-1.585386	-3.395227	-2.353420
H	-2.768900	-2.373623	-3.216658
H	2.489090	-2.288480	2.769736
H	1.840090	-0.634903	2.656438
H	3.440062	-0.915973	3.407424
H	5.239397	-0.186606	2.078446
H	6.900725	0.907847	-1.045211
H	7.519548	-0.543474	-0.220622
H	7.009547	0.866327	0.745096
H	5.183283	-0.550250	-2.229761
H	1.757279	-1.107112	-2.623038
H	2.448904	-2.742024	-2.496512
H	3.342728	-1.466540	-3.372444



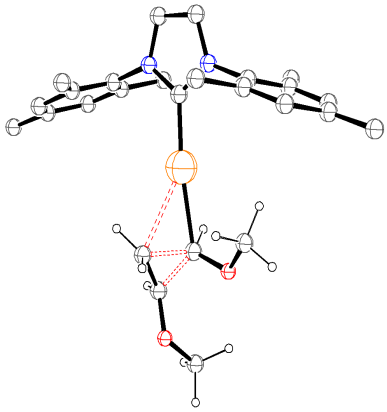
(N_{imag}=0)

N	1.248403	-2.019148	0.452098
C	0.130188	-1.287453	0.155905
N	-0.921809	-2.116390	0.437970
C	-0.468999	-3.346280	0.902506
C	0.900579	-3.284339	0.912384
Au	0.029935	0.626054	-0.641565
C	-0.128298	2.491135	-1.579635
C	0.336763	3.403982	-0.456981
O	-0.272593	4.676739	-0.452520
C	0.370773	5.626086	0.408526
C	-2.315274	-1.756253	0.276447
C	2.606530	-1.532946	0.323688
C	0.051627	2.496620	0.746116
O	-1.050563	2.502587	1.483402
C	-2.312381	2.943867	0.901194
H	-1.156472	-4.146950	1.179921
H	1.653047	-4.020955	1.198436
H	-2.978944	3.118813	1.761011
H	-2.162685	3.858965	0.302334
H	-2.704467	2.113545	0.280262
H	0.900755	2.137551	1.356115
H	1.448353	3.501985	-0.486412
H	-0.123470	6.596915	0.231354
H	0.262640	5.358156	1.482622
H	1.451891	5.716705	0.164743
H	0.484814	2.545811	-2.497092
H	-1.202435	2.637503	-1.802195
C	3.239093	-0.996123	1.465354

Intermediate **12**:

C	4.561031	-0.540679	1.318601
C	5.245313	-0.615332	0.092533
C	4.569257	-1.157849	-1.016420
C	3.248179	-1.626644	-0.931062
C	2.534058	-0.910752	2.796962
H	5.072163	-0.117505	2.195377
C	6.674115	-0.151181	-0.031660
H	5.087810	-1.223456	-1.983871
C	2.548611	-2.195942	-2.140194
H	2.087890	-3.181173	-1.929754
H	1.733105	-1.528217	-2.488551
H	3.255651	-2.322776	-2.978708
H	3.150189	-0.364348	3.532772
H	1.555259	-0.395808	2.715551
H	2.326427	-1.915084	3.219070
H	6.836278	0.417283	-0.967283
H	6.973875	0.486510	0.819616
H	7.366813	-1.017269	-0.058291
C	-2.941234	-2.013989	-0.964091
C	-4.295248	-1.664567	-1.089280
C	-5.020590	-1.086582	-0.029888
C	-4.351780	-0.850124	1.183967
C	-2.995511	-1.176190	1.367919
C	-2.189951	-2.634029	-2.115875
H	-4.800996	-1.857392	-2.046440
C	-6.482512	-0.756713	-0.193184
H	-4.903857	-0.404188	2.024074
C	-2.304026	-0.890939	2.678658
H	-1.713367	-1.755427	3.039014
H	-1.602668	-0.035931	2.585387
H	-3.040182	-0.634633	3.461261
H	-6.856857	-0.127044	0.634089
H	-6.674364	-0.228696	-1.147124
H	-7.094120	-1.681753	-0.211674
H	-2.858477	-2.793222	-2.979910
H	-1.352027	-1.988911	-2.450956
H	-1.749212	-3.613799	-1.843556

Transition State **$TS_{12\text{-}9}$**:

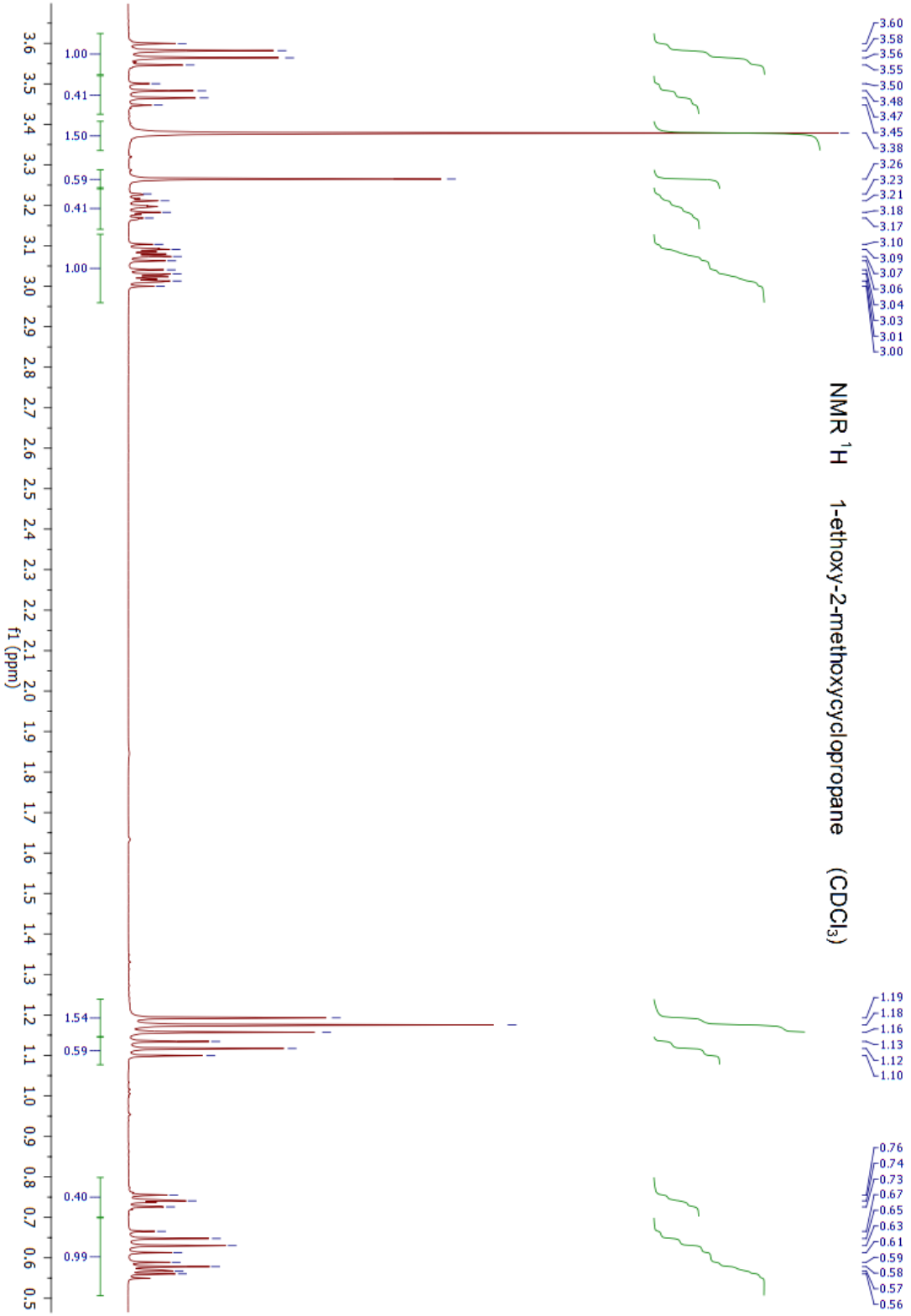


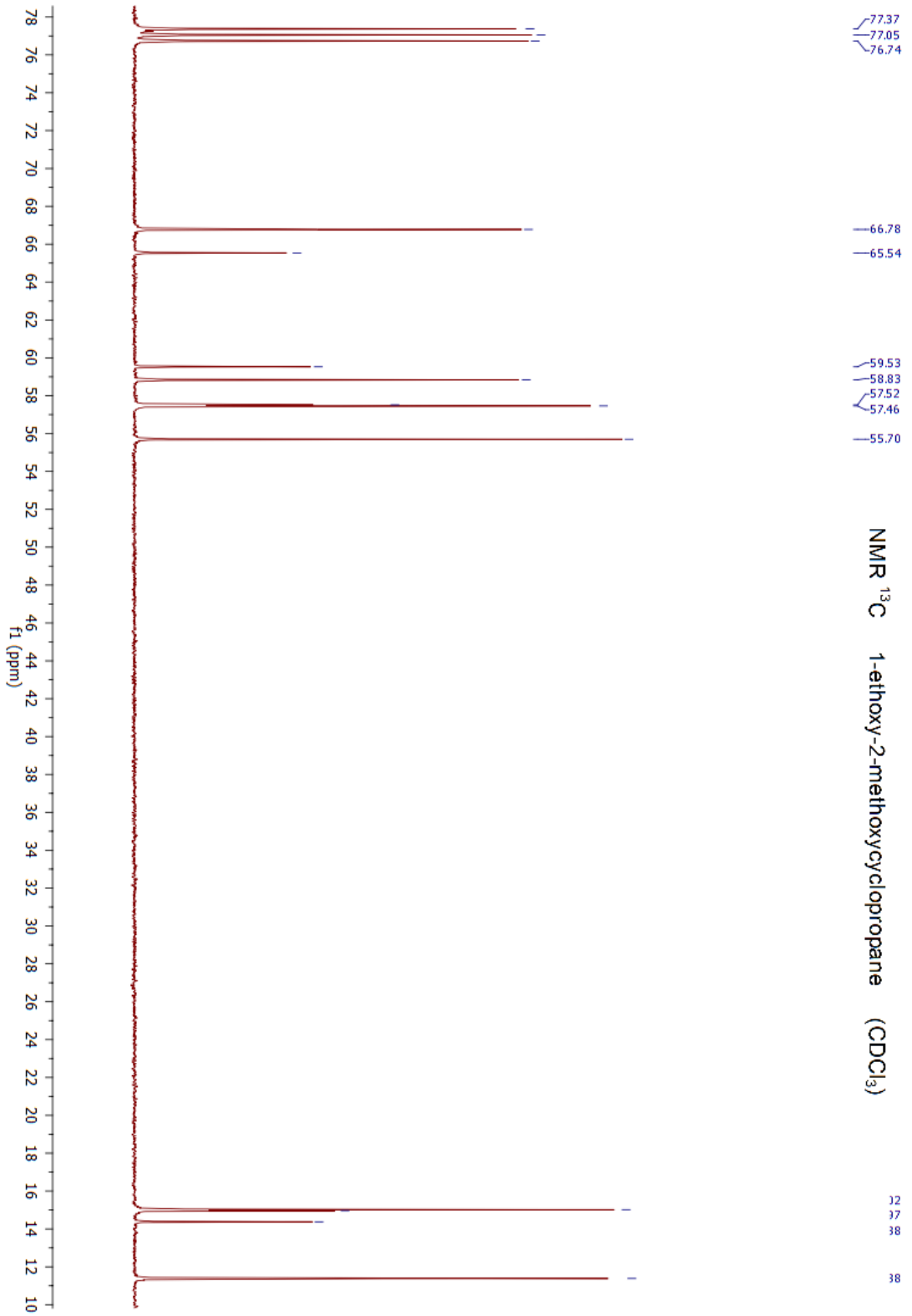
(N_{imag}=1: *-83.6230 cm^{-1}*)

C	3.301179	-1.340816	-1.247497
C	2.668284	-1.583251	-0.009764
C	3.291499	-1.329081	1.231928
C	4.595519	-0.808162	1.203393
C	5.272392	-0.550186	-0.003595
C	4.606293	-0.820032	-1.212549
N	1.326794	-2.129977	-0.011514
C	0.180821	-1.387234	-0.022851
N	-0.848428	-2.285443	-0.013079
C	-0.349534	-3.585328	0.004065
C	1.016468	-3.487524	0.004187
Au	0.017161	0.595799	-0.057472
C	-0.383470	2.890475	-0.279107
O	-1.708734	3.267029	-0.203388
C	-2.620503	2.345137	0.405730
C	-2.252130	-1.928282	-0.012835
C	-2.910432	-1.779432	1.227173
C	-4.272679	-1.434452	1.197069
C	-4.970668	-1.246961	-0.010252
C	-4.267363	-1.405467	-1.219163
C	-2.905537	-1.750255	-1.252092
C	-2.186708	-1.971488	2.536753
C	-6.441317	-0.916138	-0.011372
C	-2.176071	-1.909962	-2.562488
C	2.590449	-1.599284	2.540102
C	6.685895	-0.026713	0.003923
C	2.610512	-1.619222	-2.559199

C	0.514157	2.962288	1.065961
C	0.601477	4.060605	0.083704
O	0.038217	5.256915	0.454244
C	-0.331000	6.076567	-0.667831
H	-0.060780	2.388651	-1.235410
H	-2.707826	1.403135	-0.179859
H	-2.315881	2.103168	1.447568
H	-3.599694	2.855357	0.424374
H	1.391070	2.322804	1.243245
H	-0.121042	3.158700	1.939817
H	1.498584	4.110156	-0.561782
H	-1.147590	5.605068	-1.251213
H	-0.682088	7.033399	-0.245324
H	0.542607	6.267273	-1.328276
H	-1.011237	-4.452711	0.013470
H	1.794729	-4.252054	0.013196
H	-1.762181	-2.991306	2.629228
H	-2.870073	-1.814172	3.389659
H	-1.339990	-1.262748	2.642637
H	-4.804846	-1.312707	2.151513
H	-7.048731	-1.841817	-0.085975
H	-6.716318	-0.279154	-0.872641
H	-6.746254	-0.400577	0.917870
H	-4.795438	-1.260977	-2.172681
H	-1.698370	-2.905908	-2.652261
H	-2.868366	-1.789656	-3.414110
H	-1.369037	-1.156561	-2.671665
H	2.303794	-2.665199	2.643189
H	1.656662	-1.007851	2.633914
H	3.241560	-1.343178	3.394253
H	5.099636	-0.601875	2.158625
H	6.945411	0.466846	-0.950369
H	7.408430	-0.855438	0.153546
H	6.848985	0.694608	0.826704
H	5.118668	-0.623036	-2.165176
H	2.293855	-2.678051	-2.644260
H	1.696614	-1.001595	-2.677337
H	3.279818	-1.399113	-3.409280

^{1}H and ^{13}C NMR Spectra




77.37
77.05
76.74
66.78
65.54
59.53
58.83
57.52
57.46
55.70
f1 (ppm)
NMR ^{13}C 1-ethoxy-2-methoxycyclopropane ($CDCl_3$)

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[2] R. A. Olofson, K. D. Lotts, and G. N. Barber, *Tetrahedron Letters*, 1976, **42**, 3779-3782.

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