Electronic Supplementary Material (ESI) for ChemComm.

α-Alkylation of a norbornene-derived tricyclic ketone: are steric factors really in control?

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SUPPORTING INFORMATION

Computational Methods. All calculations were performed using the *Gaussian* 09 suite[1] of electronic structure programs. All geometries were fully optimized at the M06-2X[2] level using the 6–31+G(d)[3] basis set. An ultrafine grid density was used for numerical integration.[4] Optimizations were performed with no frozen coordinates. In order to account for solvation effects, the SMD solvation model[5] for tetrahydrofuran was employed during geometry optimizations. Energy minima and transition states were identified through frequency analysis. The Gibbs energies for all relevant species can be found in Table S1.

Table S1: Tabulated free energies for all structures. All energies are calculated for T = 298.15 K and 1 atm using SMD solvation for THF.

compound	G_{calc} (Hartrees)	G_{calc} (kcal)
MeCl	-500.036536	-313777.6767
enolate conformer **7A**	-1024.869654	-643115.4441
enolate conformer **7B**	-1024.878413	-643120.9405
Transition state **TS7AN**	-1524.881091	-956877.371
Transition state **TS7AX**	-1524.878406	-956875.6861
Transition state **TS7BN**	-1524.884455	-956879.4819
Transition state **TS7BX**	-1524.887794	-956881.5772

(1) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09*, Rev C.01; Gaussian, Inc.: Wallingford, CT, 2010.
(2) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.
(3) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.
(4) Wheeler, S. E.; Houk, K. N. *J. Chem. Theory Comput.* **2010**, *6*, 395.
(5) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378.

Figure S1. Space filling model of conformer **7A**. Right: view from endo face. Left: view from exo face.

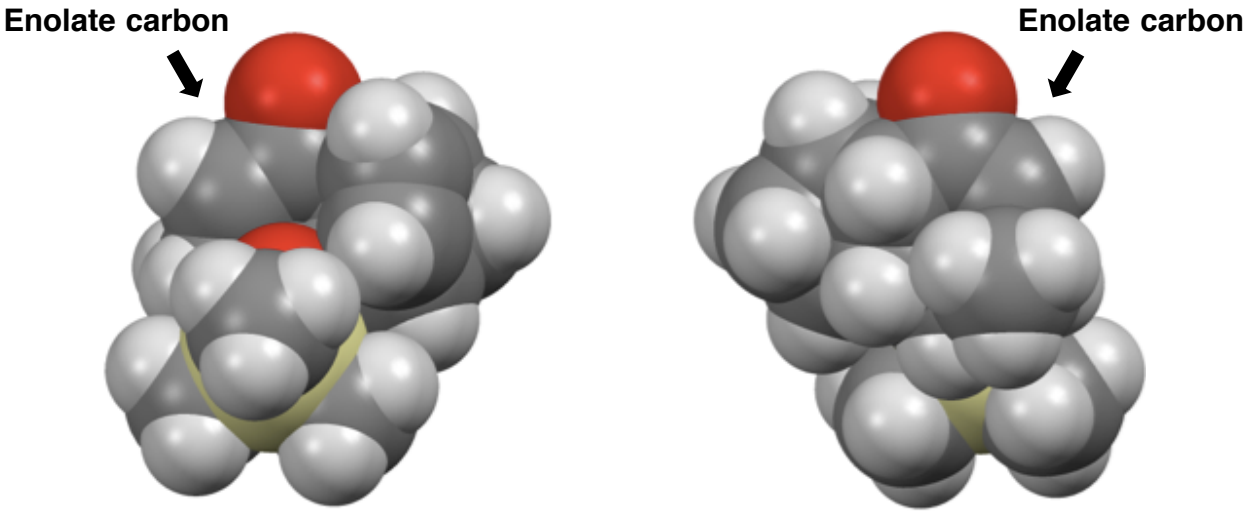


Figure S2. Space filling model of conformer **7B**. Right: view from endo face. Left: view from exo face.

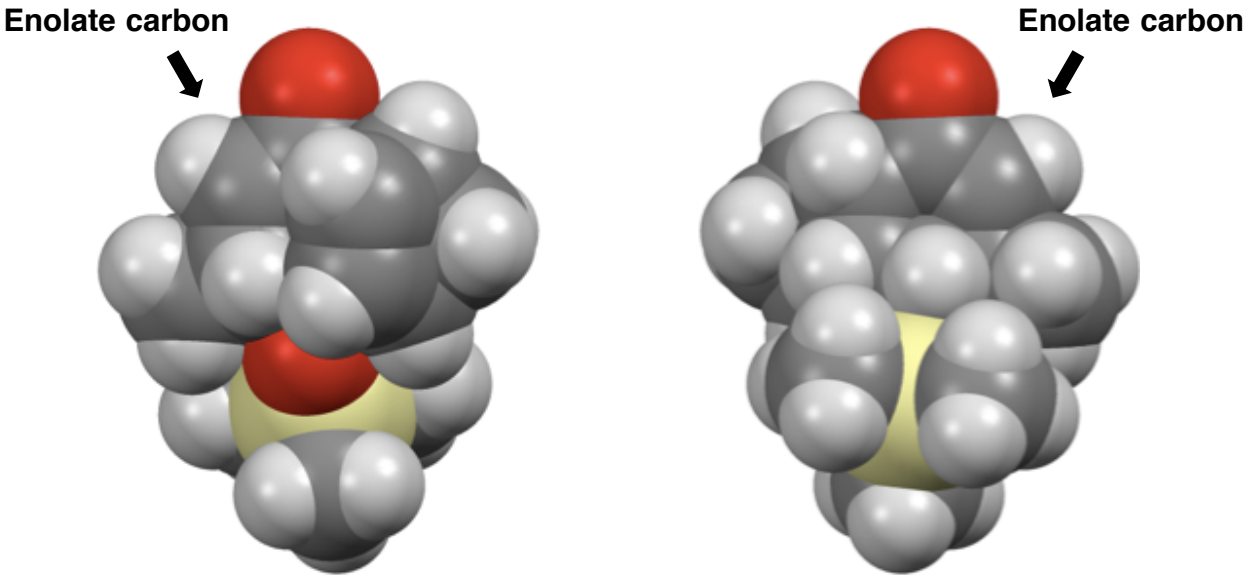
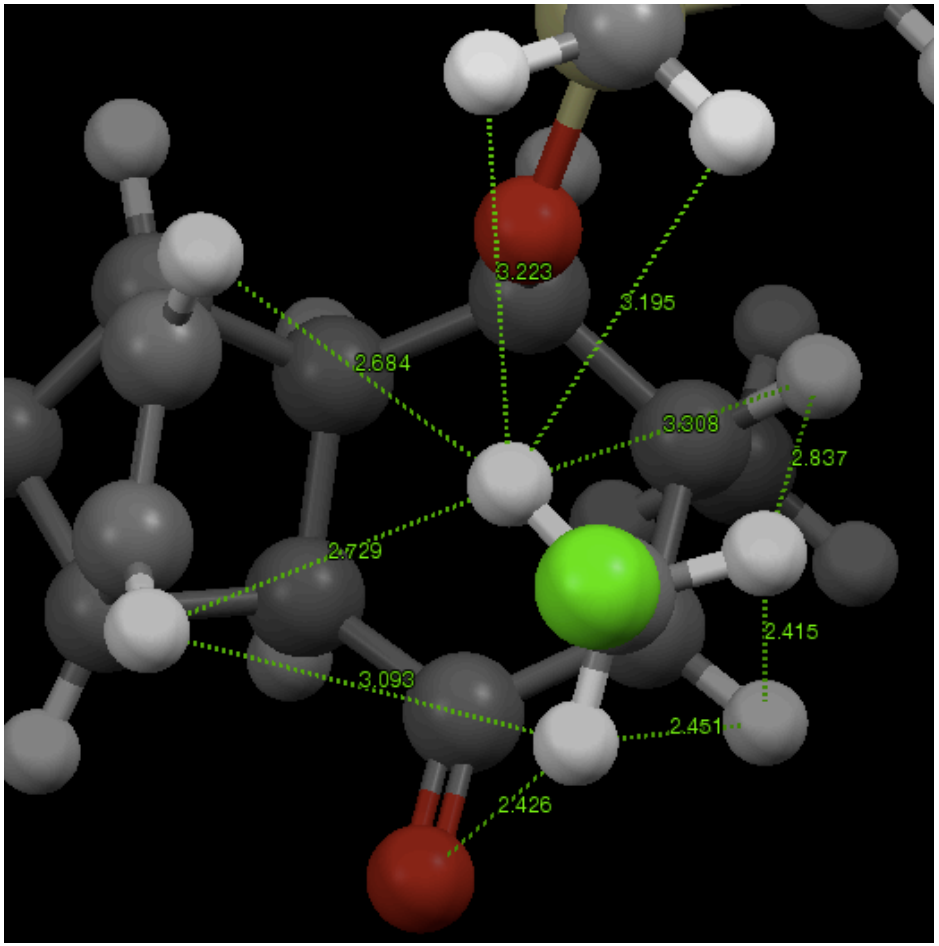
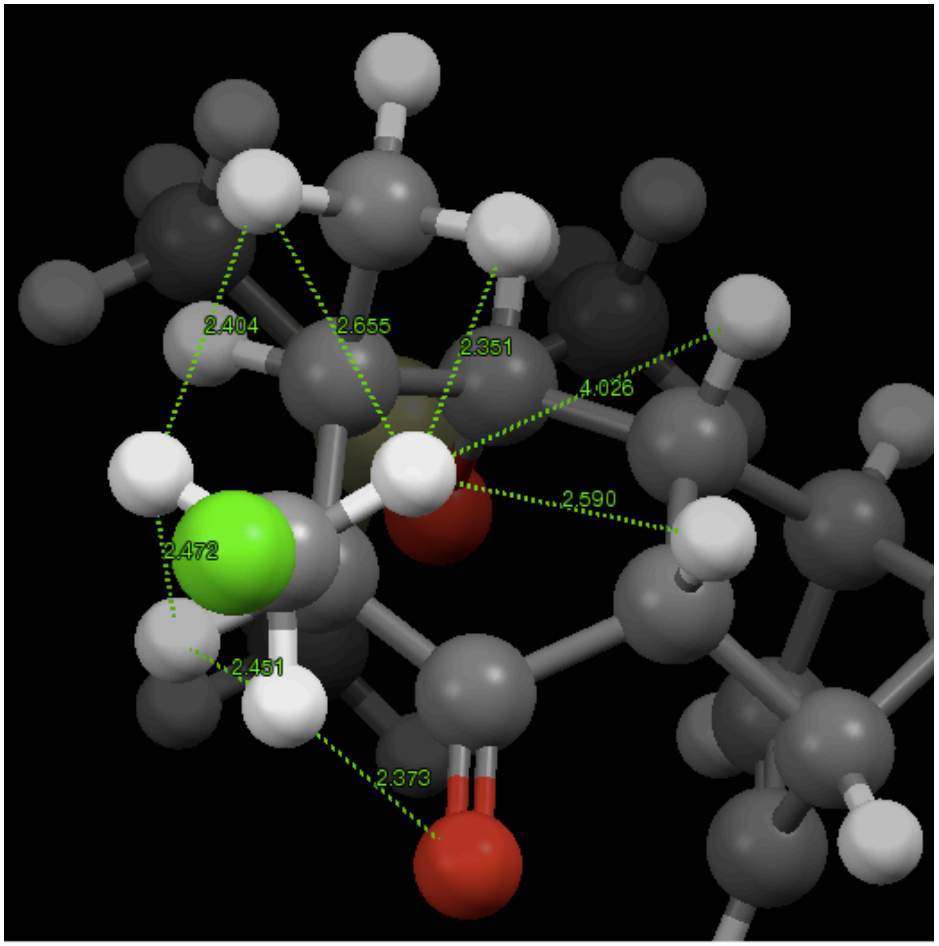


Figure S3. (left) Close contacts present in the endo transition structure leading from conformer **7A**. (right) Close contacts present in the exo transition structure leading from conformer **7A**.

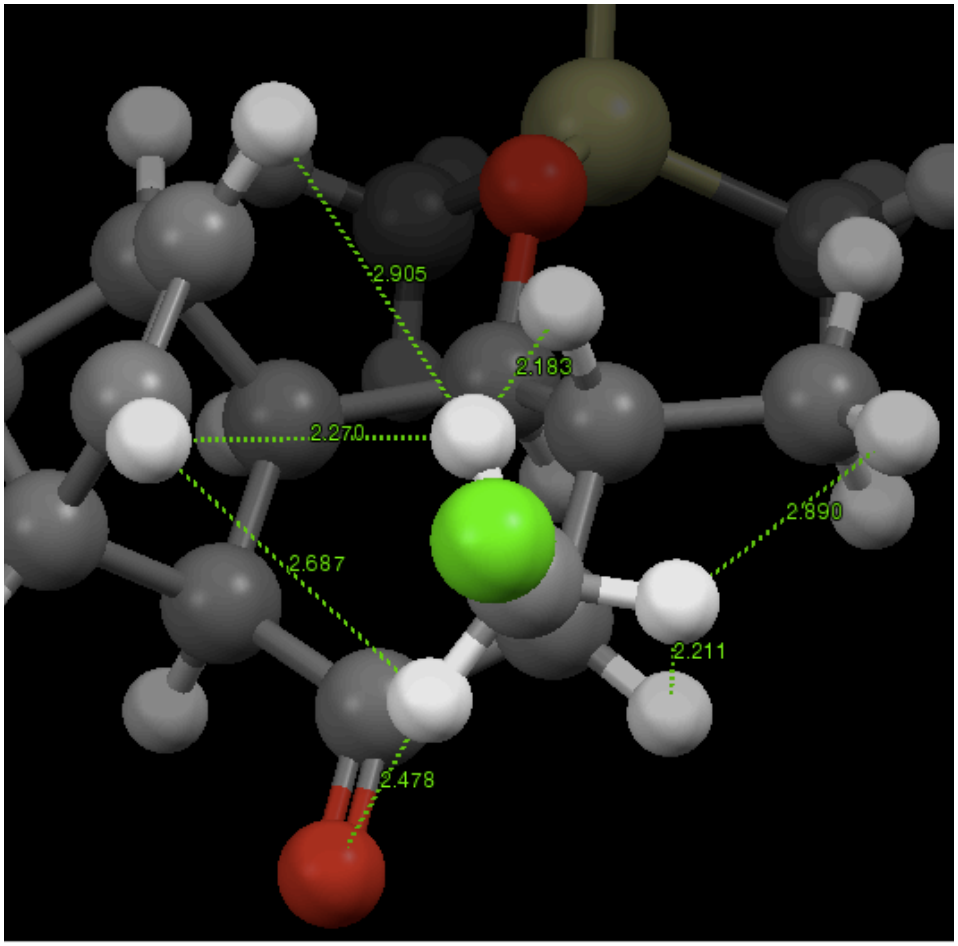


transition state **TS7AN**

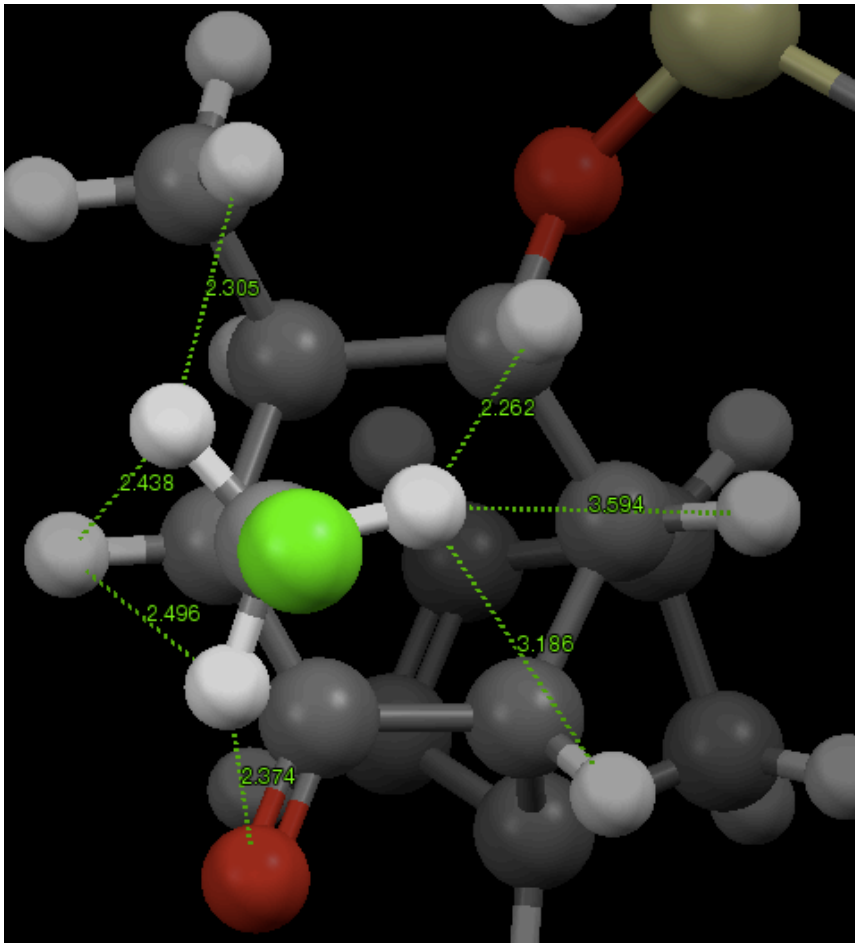


transition state **TS7AX**

Figure S4. (left) Close contacts present in the endo transition structure leading from conformer **7B**. (right) Close contacts present in the exo transition structure leading from conformer **7B**.



transition state **TS7BN**



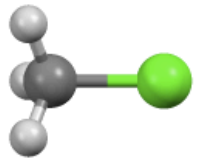
transition state **TS7BX**

Final coordinates and energies for calculated structures

The final optimized geometry of each species is given below, along with the following:
(i) Number of imaginary frequencies (frequency if present)
(ii) Returned energies (in Hartrees) at 298.15 K and 1 atm using SMD solvation for CH_3CN.

MeCl

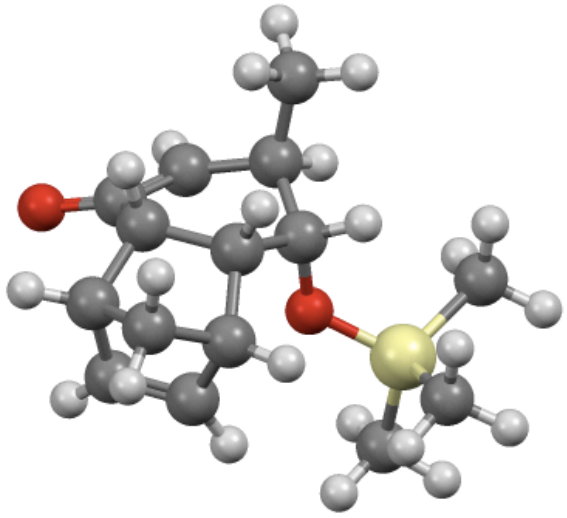
C	0.000000	0.000000	-1.135700
H	0.000000	1.034100	-1.476900
H	-0.895500	-0.517000	-1.476900
H	0.895500	-0.517000	-1.476900
Cl	0.000000	0.000000	0.661500



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -500.013909
Sum of electronic and thermal Energies= -500.010905
Sum of electronic and thermal Enthalpies= -500.009961
Sum of electronic and thermal Free Energies= -500.036536

enolate conformer 7A

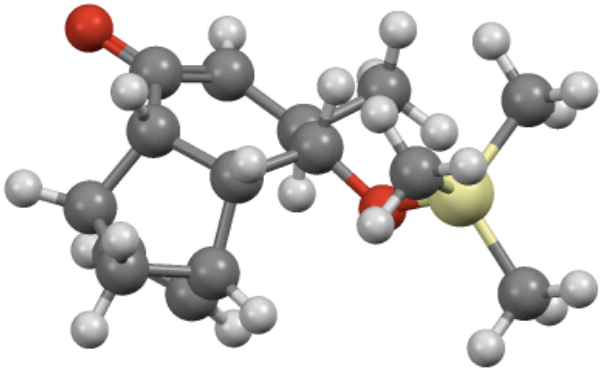
H	3.842500	-1.347700	0.195200
C	2.776200	-1.290600	-0.025300
C	0.659100	-2.066200	0.442800
C	0.925500	-0.096200	-1.085000
C	0.785100	-1.655200	-1.016600
C	2.276900	0.159200	-0.339200
C	1.845600	-1.854100	1.028500
H	-0.265500	-2.358600	0.928600
H	1.071800	0.156500	-2.143700
H	0.033900	-2.062900	-1.699100
H	2.990200	0.603300	-1.050600
H	2.076700	-1.923500	2.086600
C	2.259100	-2.039800	-1.271400
H	2.432000	-3.120500	-1.222800
H	2.652800	-1.641200	-2.214600
C	2.241800	1.089700	0.879900
C	1.219600	2.013300	0.924900
C	-0.285100	0.733100	-0.628000
C	0.152800	2.123800	-0.141300
O	-1.032200	0.087100	0.398100
O	3.204100	0.956700	1.719500
H	1.195600	2.722500	1.754200
H	-0.747500	2.586600	0.292300
C	0.567200	2.995400	-1.341700
H	-0.231400	3.072300	-2.095000
H	0.813300	4.008700	-1.004900
H	1.462100	2.591200	-1.831300
H	-0.940700	0.860700	-1.508100
Si	-2.658300	-0.231200	0.228400
C	-2.952500	-1.434000	-1.188000
H	-2.469300	-2.399900	-0.996400
H	-4.026700	-1.620900	-1.316500
H	-2.571000	-1.048300	-2.141600
C	-3.203900	-0.995200	1.846900
H	-3.007800	-0.319900	2.687900
H	-4.278900	-1.214400	1.833100
H	-2.673700	-1.934800	2.041700
C	-3.611400	1.353600	-0.114600
H	-4.678800	1.139500	-0.254900
H	-3.519300	2.064100	0.715400
H	-3.255700	1.852600	-1.025000



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -1024.823594
Sum of electronic and thermal Energies= -1024.804588
Sum of electronic and thermal Enthalpies= -1024.803644
Sum of electronic and thermal Free Energies= -1024.869654

enolate conformer 7B

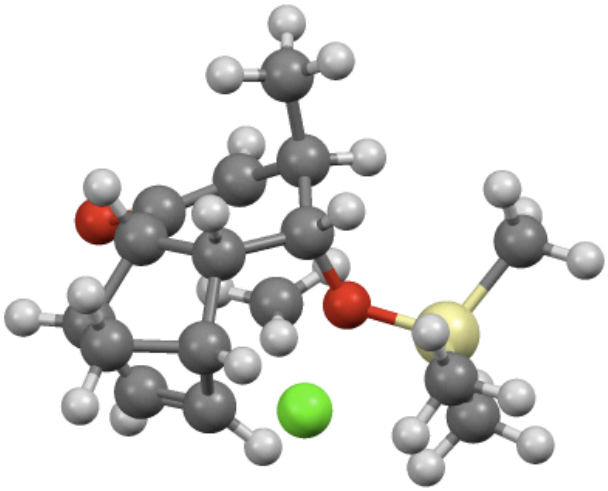
C	2.086100	-0.179700	-0.966600
C	2.994700	-1.206500	-0.194100
C	0.924000	-1.786900	0.472200
C	0.653300	-0.633400	-0.555500
H	2.240400	-0.342600	-2.041100
H	0.173400	-1.114900	-1.418100
C	2.109000	-2.466100	-0.248700
H	2.524000	-3.308600	0.315200
H	1.868500	-2.783500	-1.270800
C	2.877400	-0.862900	1.280500
H	3.619300	-0.312700	1.852100
C	1.644300	-1.210100	1.676600
H	1.183800	-1.013000	2.640200
H	4.007600	-1.276200	-0.593400
H	0.043900	-2.397600	0.683500
C	2.489600	1.272900	-0.682600
C	-0.280000	0.494300	-0.111900
O	-1.404100	-0.064100	0.580000
C	0.379200	1.572500	0.747400
C	1.658200	2.048100	0.101200
O	3.602700	1.636700	-1.207300
Si	-2.885900	-0.259900	-0.164100
C	-3.633000	1.405500	-0.609700
H	-4.606200	1.265700	-1.098400
H	-3.792400	2.027300	0.279000
H	-2.996200	1.966900	-1.304000
C	-3.958800	-1.148500	1.086000
H	-4.972200	-1.303000	0.696000
H	-3.540900	-2.130800	1.336400
H	-4.039800	-0.571300	2.014700
C	-2.717000	-1.277300	-1.735600
H	-2.270400	-2.259300	-1.537700
H	-3.704500	-1.444600	-2.185800
H	-2.098900	-0.768500	-2.485500
H	-0.630600	1.005600	-1.026800
H	0.553400	1.116400	1.738000
H	1.980000	3.068100	0.323400
C	-0.595500	2.733100	0.965000
H	-0.879400	3.184500	0.004200
H	-1.507200	2.403100	1.476000
H	-0.130500	3.517500	1.574500



*** 0 imaginary frequencies ***
Sum of electronic and zero-point Energies= -1024.832323
Sum of electronic and thermal Energies= -1024.813312
Sum of electronic and thermal Enthalpies= -1024.812368
Sum of electronic and thermal Free Energies= -1024.878413

Transition state TS7AN

H	-3.918900	-0.211200	-1.307200
C	-2.867600	-0.498000	-1.273700
C	-0.742900	-0.172600	-2.102100
C	-1.058900	-1.664100	-0.110400
C	-0.952000	-1.617600	-1.673700
C	-2.354200	-0.832700	0.166000
C	-1.882900	0.490800	-1.865800
H	0.202400	0.249600	-2.425700
H	-1.272800	-2.706800	0.156500
H	-0.254600	-2.350000	-2.089800
H	-3.097900	-1.492200	0.638600
H	-2.044900	1.562400	-1.939500
C	-2.448100	-1.780800	-2.021300
H	-2.643400	-1.728100	-3.097500
H	-2.892700	-2.692900	-1.605000
C	-2.245100	0.376200	1.095700
C	-1.123200	0.453200	1.928600
C	0.206000	-1.284200	0.679900
C	-0.142300	-0.692700	2.054800
O	1.021100	-0.364500	-0.034800
O	-3.182500	1.226800	1.048600
H	-1.182200	1.143900	2.770600
H	0.804500	-0.311600	2.468500
C	-0.637200	-1.799900	3.001300
H	0.106100	-2.601400	3.119600
H	-0.847400	-1.385800	3.993600
H	-1.567800	-2.248400	2.631500
H	0.781000	-2.213500	0.836200
Si	2.664800	-0.567700	-0.239800
C	2.980400	-1.970000	-1.450600
H	2.546000	-1.750700	-2.433600
H	4.056300	-2.134600	-1.591600
H	2.547700	-2.913500	-1.094600
C	3.277100	1.067000	-0.907700
H	3.163000	1.859000	-0.158000
H	4.338600	1.013400	-1.179900
H	2.716300	1.370700	-1.799700
C	3.499000	-0.969900	1.396500
H	4.570500	-1.150200	1.239500
H	3.402800	-0.142900	2.110000
H	3.082100	-1.870500	1.864700
C	-0.222600	2.286300	0.685800
H	0.489400	2.335600	1.498200
H	-0.019900	1.589500	-0.110700
H	-1.229100	2.650600	0.838000
Cl	0.496300	4.049000	-0.335600



*** 1 imaginary frequency (-593.7389) ***
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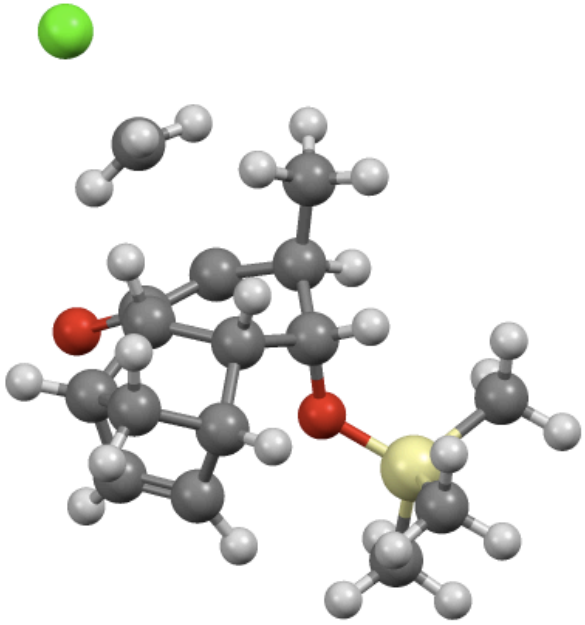
Sum of electronic and thermal Energies= -1524.807528
Sum of electronic and thermal Enthalpies= -1524.806584
Sum of electronic and thermal Free Energies= -1524.881091

Transition state TS7AX

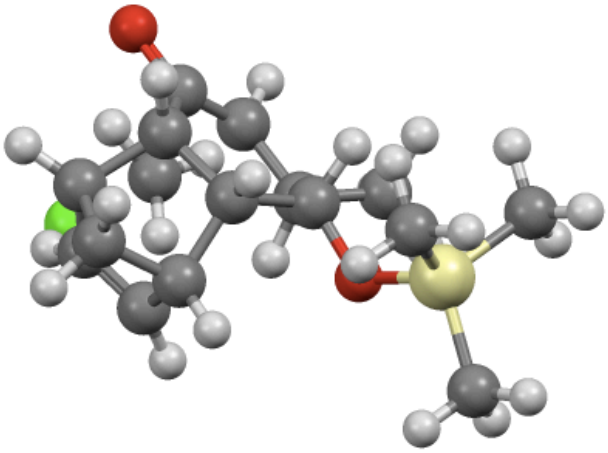
H	-1.344600	3.529300	0.311900
C	-0.520700	2.867100	0.043600
C	1.655700	2.226400	0.442100
C	0.256800	0.879200	-1.148800
C	1.289700	2.048500	-1.023400
C	-0.971300	1.422000	-0.345800
C	0.581500	2.717500	1.074000
H	2.584900	1.898500	0.895900
H	-0.023100	0.821100	-2.208500
H	2.126200	1.975600	-1.724300
H	-1.832200	1.503800	-1.027900
H	0.453700	2.854400	2.142400
C	0.319400	3.238600	-1.197100
H	0.815700	4.209800	-1.099600
H	-0.246800	3.200900	-2.135900
C	-1.426300	0.559600	0.834200
C	-1.315400	-0.827600	0.668700
C	0.724400	-0.529000	-0.767100
C	-0.489000	-1.426500	-0.459300
O	1.597900	-0.519100	0.354400
O	-1.972900	1.141100	1.817000
H	-1.473400	-1.438500	1.556500
H	-0.078000	-2.388500	-0.119500
C	-1.270000	-1.705800	-1.754900
H	-0.611800	-2.104100	-2.539600
H	-2.063600	-2.440400	-1.582200
H	-1.745100	-0.797500	-2.144700
H	1.260700	-0.948000	-1.637000
Si	3.115200	-1.208400	0.290500
C	4.190300	-0.320900	-0.972500
H	4.326900	0.736100	-0.713500
H	5.185900	-0.781800	-1.014900
H	3.765700	-0.370100	-1.982800
C	3.830000	-1.013700	2.007700
H	3.224100	-1.546700	2.749600
H	4.851600	-1.410000	2.057900
H	3.864800	0.041800	2.302400
C	2.990000	-3.022700	-0.186200
H	3.988700	-3.471600	-0.263400
H	2.424300	-3.593600	0.559600
H	2.496600	-3.154500	-1.157500
C	-3.685200	-0.959800	0.278000
H	-3.516800	-0.425900	-0.645100
H	-3.514000	-2.025000	0.289600
H	-3.667400	-0.403900	1.204800
Cl	-5.813300	-1.085100	0.089900



*** 1 imaginary frequency (-597.8861) ***
Sum of electronic and zero-point Energies= -1524.826620
Sum of electronic and thermal Energies= -1524.803926
Sum of electronic and thermal Enthalpies= -1524.802982
Sum of electronic and thermal Free Energies= -1524.878406

Transition state TS7BN

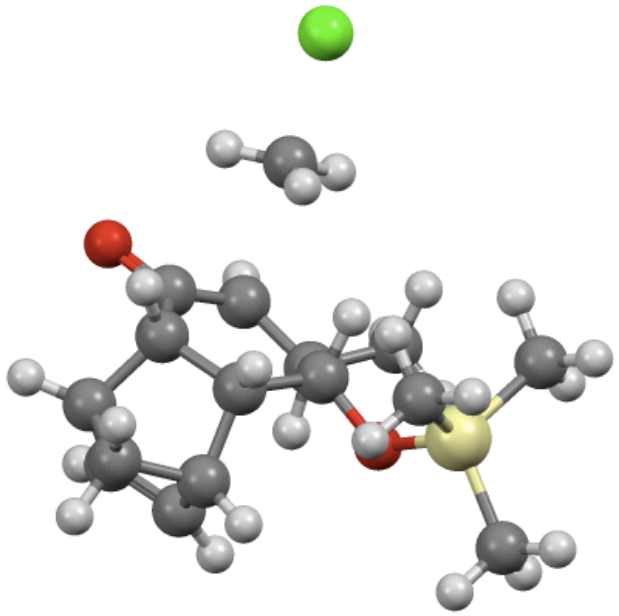
C	0.779000	1.582000	1.166400
C	1.546500	2.509200	0.152100
C	-0.296400	1.921000	-1.002000
C	-0.534300	1.254700	0.395500
H	0.553400	2.182000	2.056800
H	-1.356800	1.821000	0.851900
C	0.361500	3.233100	-0.517400
H	0.673000	3.883300	-1.341700
H	-0.262100	3.796000	0.187400
C	1.993900	1.624100	-0.995900
H	3.011200	1.276700	-1.149700
C	0.895700	1.264000	-1.675600
H	0.833300	0.557900	-2.498600
H	2.319900	3.120100	0.620300
H	-1.202900	2.003600	-1.604600
C	1.605700	0.398400	1.677400
C	-0.958800	-0.215400	0.422100
O	-1.940800	-0.444700	-0.592000
C	0.184900	-1.219400	0.269300
C	1.312700	-0.898000	1.223600
O	2.537800	0.675200	2.487600
Si	-3.573400	-0.521900	-0.240100
C	-3.936600	-1.979800	0.888100
H	-5.008400	-2.017300	1.123000
H	-3.664200	-2.932700	0.419600
H	-3.395800	-1.904300	1.839300
C	-4.428800	-0.727100	-1.891200
H	-4.203900	0.114400	-2.557500
H	-4.104700	-1.647400	-2.391300
H	-5.517400	-0.776600	-1.767000
C	-4.142400	1.052400	0.614000
H	-3.940100	1.940100	0.002400
H	-5.224200	1.014800	0.798100
H	-3.651200	1.188900	1.585300
H	-1.403400	-0.407400	1.416100
H	0.517100	-1.152300	-0.781800
H	1.695300	-1.711000	1.839800
C	-0.329600	-2.644000	0.482200
H	-0.745800	-2.758800	1.492500
H	-1.108400	-2.900400	-0.243900
H	0.486100	-3.369400	0.374200
C	3.276200	-1.283000	-0.008600
H	3.697300	-0.565700	0.682600
H	3.174100	-2.310200	0.308600
H	2.689800	-0.950300	-0.850400
Cl	5.083400	-1.603900	-1.142000



*** 1 imaginary frequency (-634.1905) ***
Sum of electronic and zero-point Energies= -1524.832164
Sum of electronic and thermal Energies= -1524.809497
Sum of electronic and thermal Enthalpies= -1524.808553
Sum of electronic and thermal Free Energies= -1524.884455

Transition state TS7BX

C	-1.207300	1.604500	-0.786300
C	-1.023000	3.161400	-0.642300
C	1.081900	2.393700	-0.428100
C	0.260700	1.087100	-0.709100
H	-1.634000	1.402400	-1.777600
H	0.567300	0.754100	-1.709300
C	0.321900	3.356200	-1.365800
H	0.691100	4.385700	-1.308600
H	0.306700	3.021500	-2.409900
C	-0.592700	3.407300	0.793800
H	-1.244400	3.765700	1.585300
C	0.661000	2.948500	0.920100
H	1.243200	2.869400	1.833300
H	-1.883300	3.732900	-0.993300
H	2.155300	2.275400	-0.586600
C	-2.211100	1.082200	0.242700
C	0.498900	-0.093300	0.238000
O	1.892400	-0.184300	0.544000
C	-0.308100	-0.054100	1.535900
C	-1.768900	0.207500	1.242700
O	-3.414700	1.440800	0.076800
Si	2.901400	-1.275900	-0.221400
C	2.450100	-3.038200	0.246000
H	3.133200	-3.745400	-0.242300
H	2.520200	-3.200100	1.328100
H	1.431800	-3.298000	-0.068200
C	4.622900	-0.850200	0.375000
H	5.368500	-1.534300	-0.048100
H	4.898500	0.170300	0.083500
H	4.688600	-0.915500	1.467400
C	2.781800	-1.099200	-2.088400
H	3.027700	-0.082600	-2.417800
H	3.485000	-1.786600	-2.576800
H	1.778200	-1.343700	-2.457800
H	0.184700	-1.008900	-0.294300
H	0.120000	0.755300	2.150800
H	-2.468900	0.014800	2.057400
C	-0.108100	-1.356000	2.317000
H	-0.742600	-1.373500	3.211500
H	-0.368700	-2.229400	1.705000
H	0.932600	-1.468200	2.639500
C	-2.758800	-1.636500	0.063600
H	-1.973600	-1.567600	-0.674500
H	-2.555300	-2.170100	0.979000
H	-3.572900	-0.926900	0.026700
Cl	-3.808100	-3.259500	-0.888000



*** 1 imaginary frequency (-596.9906) ***
Sum of electronic and zero-point Energies= -1524.834809
Sum of electronic and thermal Energies= -1524.811753
Sum of electronic and thermal Enthalpies= -1524.810809
Sum of electronic and thermal Free Energies= -1524.887794