

## Torsional Steering as Friend and Foe: Development of a Synthetic Route to the Briarane Diterpenoid Stereotetrad

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## Complete reference 54

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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, Inc., Wallingford CT, 2013.

## Tabulated free energies for all calculated structures

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All energies are calculated for T = 298.15 K and 1 atm using SMD solvation for toluene.

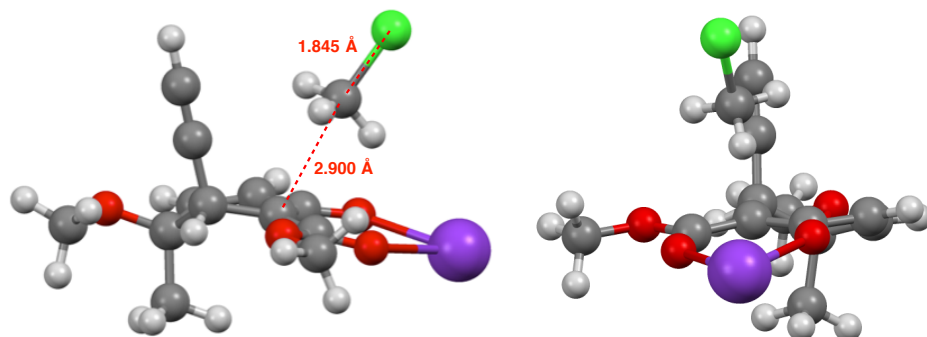
Compound	G <sub>calc</sub> (Hartrees)	G <sub>calc</sub> (kcal)
CH <sub>3</sub> Cl	-500.14185	-313843.5122
Conformer <b>22A</b>	-1365.98757	-857169.4941
Conformer <b>22B</b>	-1365.998106	-857176.1055
Transition structure <b>TS-1</b>	-1866.087099	-1170986.449
Transition structure <b>TS-2</b>	-1866.098817	-1170993.803
Transition structure <b>TS-3</b>	-1866.096641	-1170992.437
Transition structure <b>TS-4</b>	-1866.09753	-1170992.995

All energies are calculated for T = 298.15 K and 1 atm using SMD solvation as noted.

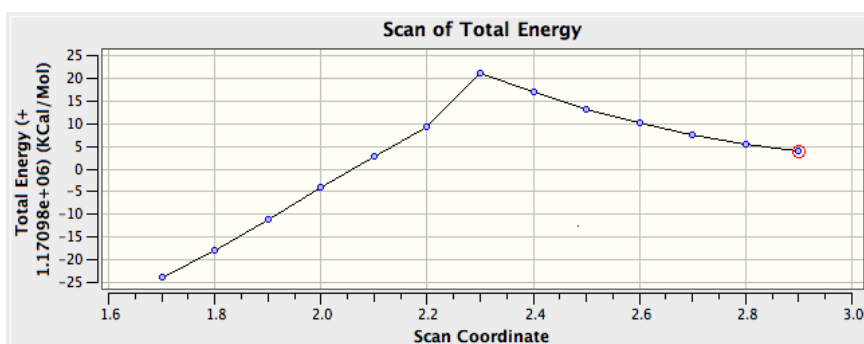
Compound	G <sub>calc</sub> (Hartrees)	G <sub>calc</sub> (kcal)
<b>20<sub>AX</sub></b> with SMD <sup>THF</sup>	-1100.034400	-690281.4863
<b>20<sub>EQ</sub></b> with SMD <sup>THF</sup>	-1100.029406	-690278.3525
<b>20<sub>AX</sub></b> with SMD <sup>MeOH</sup>	-1100.035426	-690282.1301
<b>20<sub>EQ</sub></b> with SMD <sup>MeOH</sup>	-1100.030730	-690279.1834

## Relaxed scan experiments to locate initial guess for TS-4

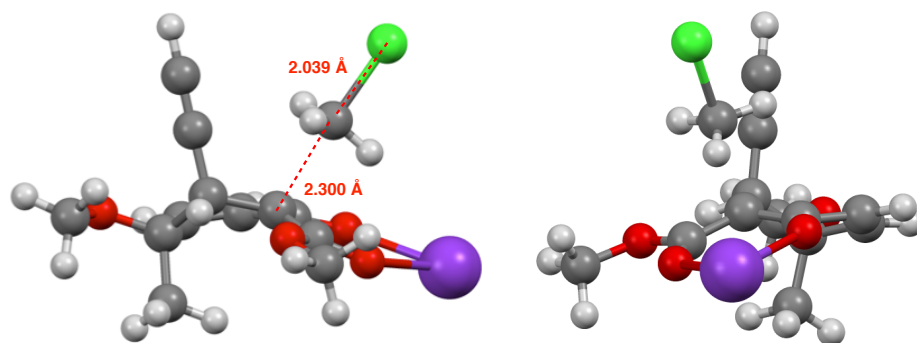
The relaxed scan was performed using B3LYPD3/6-31+G(d) at T = 298.15 K and 1 atm, and with SMD solvation for toluene.



**Figure S1.** Starting structure for relaxed scan of developing C–C bond. Left: side view. Right: end view.

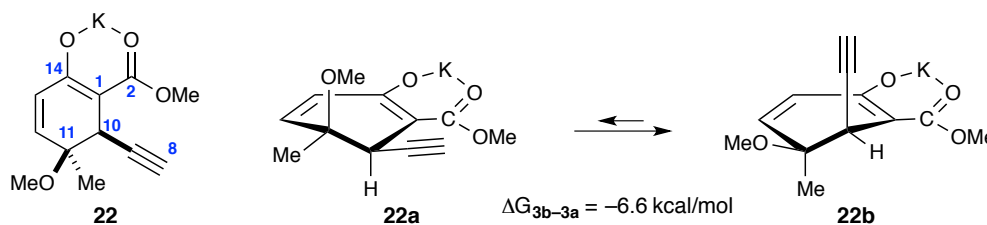


**Figure S2.** Plot of total energy as C–C bond is shortened from 2.900 Å to 1.700 Å.



**Figure S3.** Structure with maximum energy during relaxed scan of developing C–C bond. This was used as the starting structure for the transition state optimization. Left: side view. Right: end view.

## NBO analysis for conformers 22a and 22b



**Table S1.** Selected Donor–Acceptor Energies from Second Order Perturbation Analysis of 22a.

Hyperconjugation from axial OMe into extended $\pi$ -system		
Donor NBO	Acceptor NBO	Energy (kcal/mol)
C11–OMe ( $\sigma$ )	C12–C13 ( $\pi^*$ )	1.29
C12–C13 ( $\pi$ )	C14–C1 ( $\pi^*$ )	11.52
C14–C1 ( $\pi$ )	C2–O ( $\pi^*$ )	40.24
<i>Sum</i>		53.05

Hyperconjugation from extended $\pi$ -system into axial OMe		
Donor NBO	Acceptor NBO	Energy (kcal/mol)
C12–C13 ( $\pi$ )	C11–OCH <sub>3</sub> ( $\sigma^*$ )	7.35
C14–C1 ( $\pi$ )	C12–C13 ( $\pi^*$ )	8.47
C2–O ( $\pi$ )	C14–C1 ( $\pi^*$ )	2.10
<i>Sum</i>		17.92
<i>Sum of hyperconjugation effects</i>		70.97

Other selected donor–acceptor pairs		
C10–C9 ( $\sigma$ )	C8–C9 ( $\sigma^*$ )	9.04
C1–C10 ( $\sigma$ )	C11–Me(equatorial) ( $\sigma^*$ )	1.97

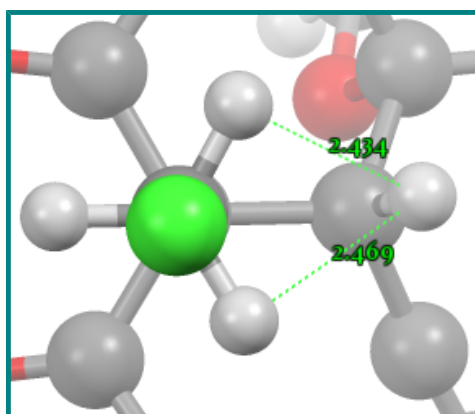
**Table S2.** Selected Donor–Acceptor Energies from Second Order Perturbation Analysis of 22b.

Hyperconjugation from axial Me into extended $\pi$ -system		
Donor NBO	Acceptor NBO	Energy (kcal/mol)
C11–Me ( $\sigma$ )	C12–C13 ( $\pi^*$ )	2.43
C12–C13 ( $\pi$ )	C14–C1 ( $\pi^*$ )	13.68
C14–C1 ( $\pi$ )	C2–O ( $\pi^*$ )	45.22
<i>Sum</i>		61.33

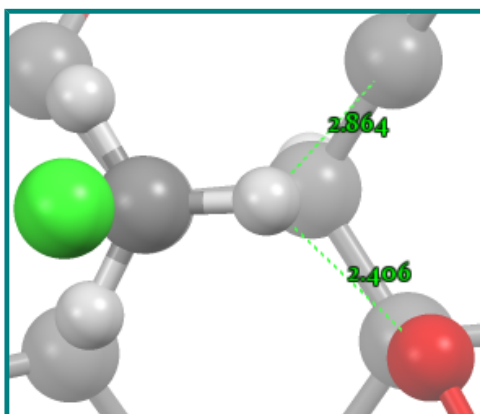
Hyperconjugation from extended $\pi$ -system into axial Me		
Donor NBO	Acceptor NBO	Energy (kcal/mol)
C12–C13 ( $\pi$ )	C11–Me ( $\sigma^*$ )	2.88
C14–C1 ( $\pi$ )	C12–C13 ( $\pi^*$ )	6.90
C2–O ( $\pi$ )	C14–C1 ( $\pi^*$ )	2.36
<i>Sum</i>		12.14
<i>Sum of hyperconjugation effects</i>		73.47

Other selected donor–acceptor pairs		
C10–C9 ( $\sigma$ )	C8–C9 ( $\sigma^*$ )	9.64
C1–C10 ( $\sigma$ )	C11–OMe(equatorial) ( $\sigma^*$ )	2.97

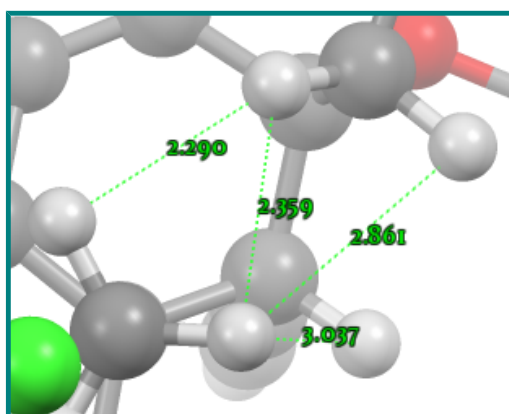
### Measurement of through-space interactions in TS-1–TS-4 (Figure S4)



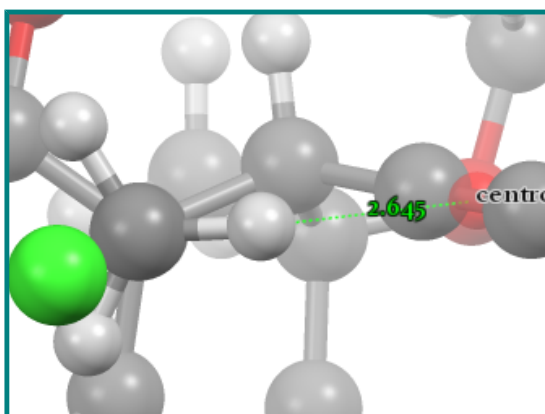
TS-1



TS-2



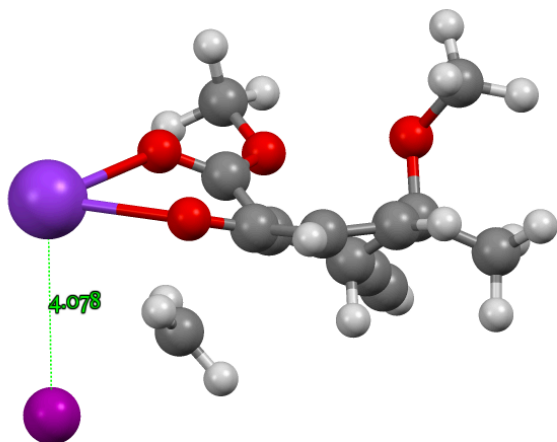
TS-3



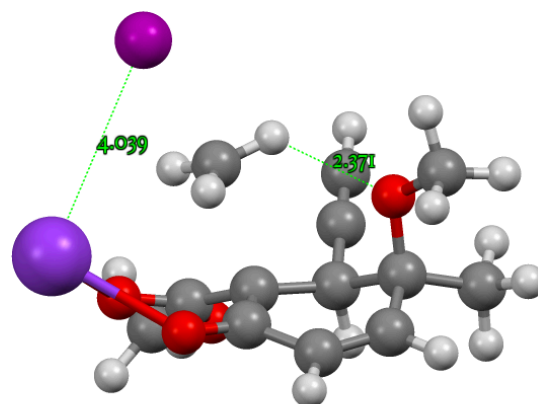
TS-4

## Transition state calculations using CH<sub>3</sub>I as electrophile

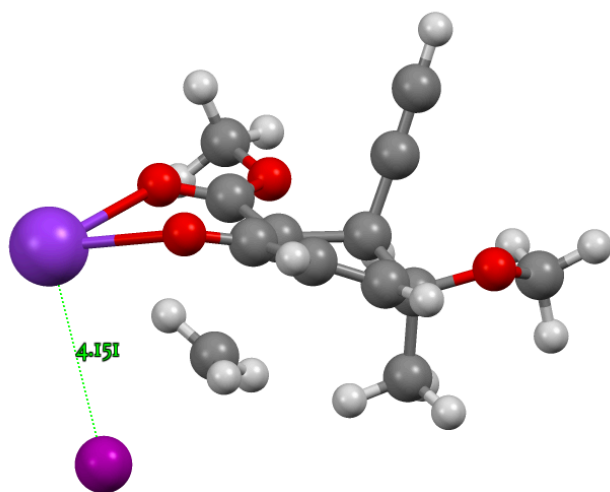
Calculations performed using B3LYPD3/6-31+G(d,p) (for C,H,O) and LANL2DZdp (for I),<sup>1</sup> SMD=Toluene.



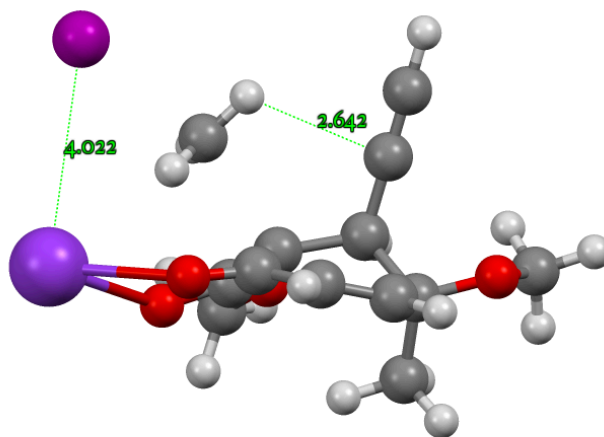
**TS-1-Mel**  
(5.2)



**TS-2-Mel**  
(0)



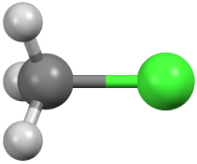
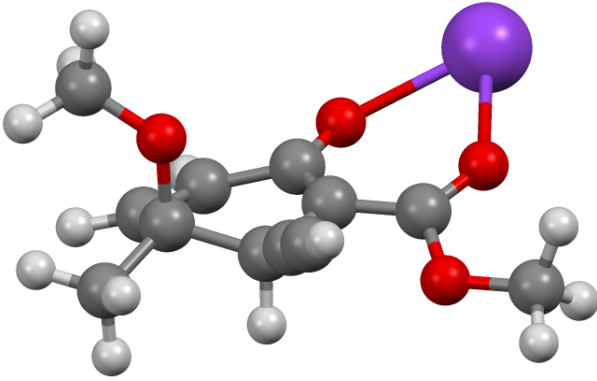
**TS-3-Mel**  
(0.9)



**TS-4-Mel**  
(0.3)

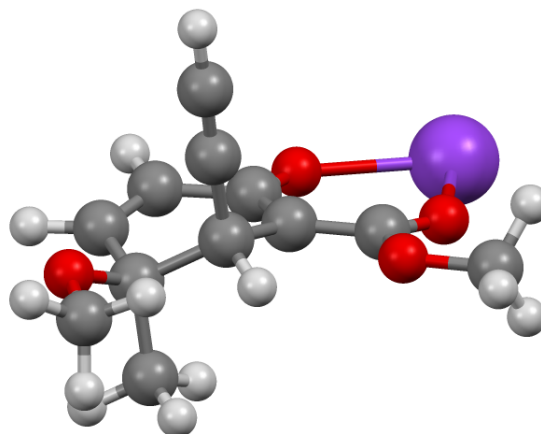
(1) C.E. Check, T.O. Faust, J.M. Bailey, B.J. Wright, T.M. Gilbert and L.S. Sunderlin, J. Phys. Chem. A, 105, 8111 (2001)

## Final coordinates and energies for all calculated structures

<p><b>CH<sub>3</sub>Cl</b> with SMD<sup>toluene</sup></p> <table border="1"> <tbody> <tr><td>C</td><td>0.000000</td><td>0.000000</td><td>-1.147000</td></tr> <tr><td>H</td><td>0.000000</td><td>1.034000</td><td>-1.488000</td></tr> <tr><td>H</td><td>-0.895000</td><td>-0.517000</td><td>-1.488000</td></tr> <tr><td>H</td><td>0.895000</td><td>-0.517000</td><td>-1.488000</td></tr> <tr><td>Cl</td><td>0.000000</td><td>0.000000</td><td>0.667000</td></tr> </tbody> </table>	C	0.000000	0.000000	-1.147000	H	0.000000	1.034000	-1.488000	H	-0.895000	-0.517000	-1.488000	H	0.895000	-0.517000	-1.488000	Cl	0.000000	0.000000	0.667000																																																																																																					
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<p><b>Conformer 22a</b> with SMD<sup>toluene</sup></p> <table border="1"> <tbody> <tr><td>C</td><td>2.018000</td><td>-1.533000</td><td>-1.040000</td></tr> <tr><td>C</td><td>0.771000</td><td>-1.996000</td><td>-1.115000</td></tr> <tr><td>H</td><td>2.853000</td><td>-2.103000</td><td>-1.438000</td></tr> <tr><td>H</td><td>0.546000</td><td>-2.953000</td><td>-1.577000</td></tr> <tr><td>C</td><td>-0.409000</td><td>-1.272000</td><td>-0.573000</td></tr> <tr><td>C</td><td>-0.249000</td><td>0.107000</td><td>-0.321000</td></tr> <tr><td>C</td><td>2.325000</td><td>-0.249000</td><td>-0.305000</td></tr> <tr><td>C</td><td>1.138000</td><td>0.755000</td><td>-0.483000</td></tr> <tr><td>H</td><td>1.232000</td><td>1.142000</td><td>-1.508000</td></tr> <tr><td>O</td><td>2.411000</td><td>-0.496000</td><td>1.119000</td></tr> <tr><td>C</td><td>3.634000</td><td>0.368000</td><td>-0.810000</td></tr> <tr><td>H</td><td>4.464000</td><td>-0.332000</td><td>-0.689000</td></tr> <tr><td>H</td><td>3.559000</td><td>0.610000</td><td>-1.874000</td></tr> <tr><td>H</td><td>3.865000</td><td>1.279000</td><td>-0.256000</td></tr> <tr><td>C</td><td>1.358000</td><td>1.896000</td><td>0.418000</td></tr> <tr><td>H</td><td>1.777000</td><td>3.654000</td><td>1.785000</td></tr> <tr><td>C</td><td>1.588000</td><td>2.830000</td><td>1.140000</td></tr> <tr><td>C</td><td>-1.404000</td><td>0.945000</td><td>-0.193000</td></tr> <tr><td>O</td><td>-2.552000</td><td>0.625000</td><td>0.161000</td></tr> <tr><td>O</td><td>-1.164000</td><td>2.237000</td><td>-0.564000</td></tr> <tr><td>C</td><td>-2.207000</td><td>3.186000</td><td>-0.329000</td></tr> <tr><td>H</td><td>-3.091000</td><td>2.964000</td><td>-0.931000</td></tr> <tr><td>H</td><td>-1.793000</td><td>4.152000</td><td>-0.619000</td></tr> <tr><td>H</td><td>-2.489000</td><td>3.206000</td><td>0.727000</td></tr> <tr><td>C</td><td>3.230000</td><td>-1.573000</td><td>1.543000</td></tr> <tr><td>H</td><td>4.269000</td><td>-1.480000</td><td>1.198000</td></tr> <tr><td>H</td><td>3.230000</td><td>-1.542000</td><td>2.634000</td></tr> <tr><td>H</td><td>2.837000</td><td>-2.546000</td><td>1.223000</td></tr> <tr><td>O</td><td>-1.477000</td><td>-1.954000</td><td>-0.464000</td></tr> <tr><td>K</td><td>-3.672000</td><td>-1.586000</td><td>0.616000</td></tr> </tbody> </table>	C	2.018000	-1.533000	-1.040000	C	0.771000	-1.996000	-1.115000	H	2.853000	-2.103000	-1.438000	H	0.546000	-2.953000	-1.577000	C	-0.409000	-1.272000	-0.573000	C	-0.249000	0.107000	-0.321000	C	2.325000	-0.249000	-0.305000	C	1.138000	0.755000	-0.483000	H	1.232000	1.142000	-1.508000	O	2.411000	-0.496000	1.119000	C	3.634000	0.368000	-0.810000	H	4.464000	-0.332000	-0.689000	H	3.559000	0.610000	-1.874000	H	3.865000	1.279000	-0.256000	C	1.358000	1.896000	0.418000	H	1.777000	3.654000	1.785000	C	1.588000	2.830000	1.140000	C	-1.404000	0.945000	-0.193000	O	-2.552000	0.625000	0.161000	O	-1.164000	2.237000	-0.564000	C	-2.207000	3.186000	-0.329000	H	-3.091000	2.964000	-0.931000	H	-1.793000	4.152000	-0.619000	H	-2.489000	3.206000	0.727000	C	3.230000	-1.573000	1.543000	H	4.269000	-1.480000	1.198000	H	3.230000	-1.542000	2.634000	H	2.837000	-2.546000	1.223000	O	-1.477000	-1.954000	-0.464000	K	-3.672000	-1.586000	0.616000	
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Sum of electronic and thermal Energies=	-1365.922498																																																																																																																								
Sum of electronic and thermal Enthalpies=	-1365.921554																																																																																																																								
Sum of electronic and thermal Free Energies=	-1365.987570																																																																																																																								

**Conformer 22b** with SMD<sup>toluene</sup>

C	0.501000	-2.301000	0.390000
C	1.769000	-2.018000	0.092000
H	0.205000	-3.286000	0.736000
H	2.564000	-2.751000	0.187000
C	-0.615000	-1.332000	0.203000
C	2.165000	-0.670000	-0.457000
C	2.062000	-0.690000	-1.992000
H	2.736000	-1.447000	-2.399000
H	2.325000	0.281000	-2.421000
H	1.042000	-0.926000	-2.299000
O	3.527000	-0.491000	-0.038000
C	1.217000	0.422000	0.131000
H	1.377000	1.333000	-0.449000
C	-0.260000	0.023000	-0.001000
C	-1.231000	1.048000	-0.196000
O	-0.678000	2.300000	-0.309000
C	-1.588000	3.386000	-0.500000
H	-0.968000	4.278000	-0.581000
H	-2.269000	3.486000	0.349000
H	-2.176000	3.256000	-1.413000
C	1.546000	0.743000	1.528000
C	1.784000	1.034000	2.672000
H	1.996000	1.277000	3.686000
O	-2.467000	0.935000	-0.279000
C	4.177000	0.714000	-0.418000
H	5.149000	0.701000	0.078000
H	4.341000	0.776000	-1.501000
H	3.638000	1.608000	-0.084000
O	-1.787000	-1.815000	0.228000
K	-4.099000	-0.957000	0.031000



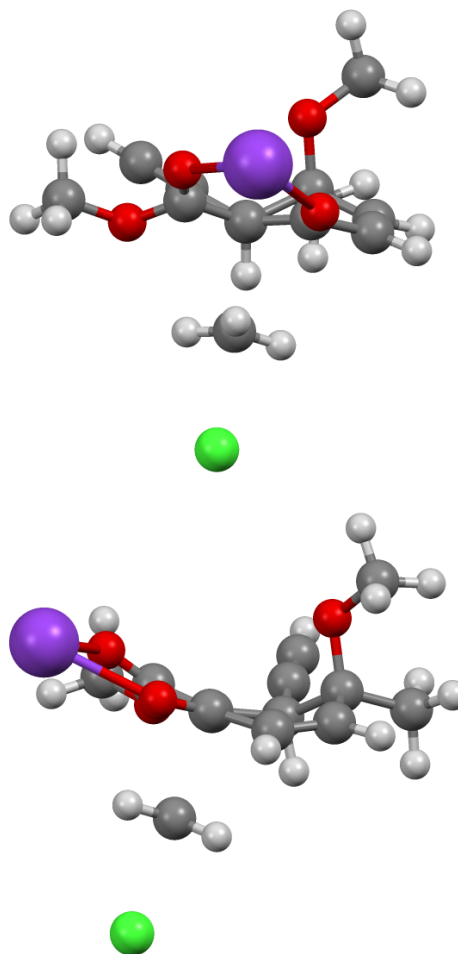
\*\*\* 0 imaginary frequencies \*\*\*

Sum of electronic and zero-point Energies=	-1365.951292
Sum of electronic and thermal Energies=	-1365.932965
Sum of electronic and thermal Enthalpies=	-1365.932020
Sum of electronic and thermal Free Energies=	-1365.998106



**Transition structure TS-1 with SMD<sup>toluene</sup>**

C	-2.091000	-0.209000	-1.953000
C	-0.896000	0.295000	-2.255000
H	-2.811000	-0.445000	-2.730000
H	-0.592000	0.499000	-3.276000
C	0.082000	0.673000	-1.208000
C	-0.000000	-0.029000	0.051000
C	-2.511000	-0.384000	-0.505000
C	-1.278000	-0.872000	0.328000
H	-1.096000	-1.901000	-0.010000
O	-2.857000	0.895000	0.063000
C	-3.670000	-1.379000	-0.401000
H	-4.494000	-1.083000	-1.054000
H	-3.344000	-2.374000	-0.716000
H	-4.037000	-1.437000	0.624000
C	-1.680000	-0.960000	1.735000
H	-2.425000	-1.158000	3.866000
C	-2.086000	-1.068000	2.861000
C	0.846000	0.413000	1.164000
O	1.478000	1.467000	1.243000
O	0.942000	-0.513000	2.134000
C	1.644000	-0.149000	3.333000
H	2.701000	0.026000	3.126000
H	1.528000	-0.998000	4.004000
H	1.206000	0.746000	3.780000
C	-3.921000	1.609000	-0.549000
H	-4.880000	1.085000	-0.464000
H	-3.998000	2.555000	-0.011000
H	-3.722000	1.827000	-1.606000
O	0.980000	1.483000	-1.532000
K	2.632000	3.013000	-0.426000
C	1.450000	-1.554000	-0.650000
H	0.837000	-1.836000	-1.488000
H	2.229000	-0.825000	-0.789000
H	1.349000	-2.073000	0.287000
Cl	3.051000	-3.224000	-1.319000

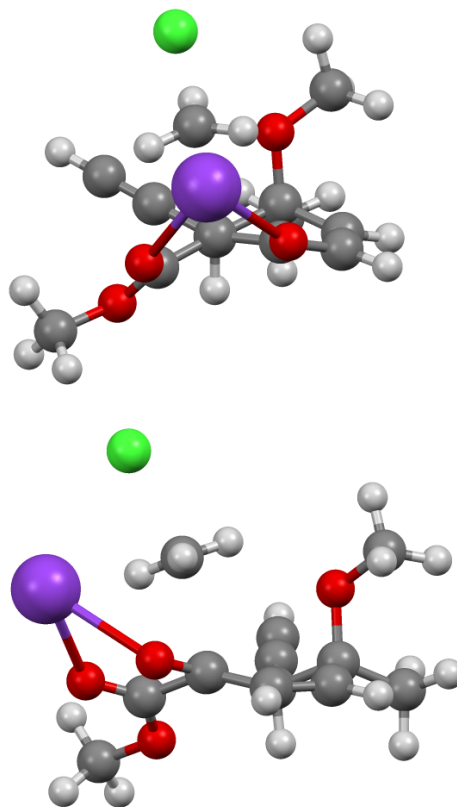


\*\*\* 1 imaginary frequency = -474.6927 \*\*\*

Sum of electronic and zero-point Energies=	-1866.034412
Sum of electronic and thermal Energies=	-1866.012196
Sum of electronic and thermal Enthalpies=	-1866.011251
Sum of electronic and thermal Free Energies=	-1866.087099

**Transition structure TS-2 with SMD<sup>toluene</sup>**

C	2.406000	-0.572000	-1.785000
C	1.205000	-0.539000	-2.366000
H	3.274000	-0.926000	-2.333000
H	1.055000	-0.865000	-3.390000
C	-0.020000	-0.104000	-1.659000
C	0.153000	0.642000	-0.429000
C	2.588000	-0.215000	-0.323000
C	1.589000	0.925000	0.046000
H	1.959000	1.823000	-0.467000
O	2.211000	-1.333000	0.507000
C	4.031000	0.216000	-0.044000
H	4.736000	-0.561000	-0.348000
H	4.274000	1.121000	-0.606000
H	4.169000	0.416000	1.020000
C	1.642000	1.194000	1.487000
H	1.730000	1.583000	3.718000
C	1.692000	1.401000	2.670000
C	-0.854000	1.674000	-0.177000
O	-2.072000	1.556000	-0.313000
O	-0.316000	2.839000	0.244000
C	-1.234000	3.873000	0.639000
H	-1.828000	4.211000	-0.213000
H	-0.613000	4.685000	1.012000
H	-1.901000	3.516000	1.427000
C	2.891000	-2.564000	0.302000
H	3.961000	-2.495000	0.531000
H	2.436000	-3.276000	0.993000
H	2.763000	-2.944000	-0.719000
O	-1.126000	-0.413000	-2.158000
K	-3.440000	-0.647000	-0.900000
C	-0.817000	-0.970000	0.915000
H	0.040000	-1.179000	1.533000
H	-1.490000	-0.186000	1.199000
H	-0.925000	-1.520000	0.002000
Cl	-2.323000	-2.475000	1.874000

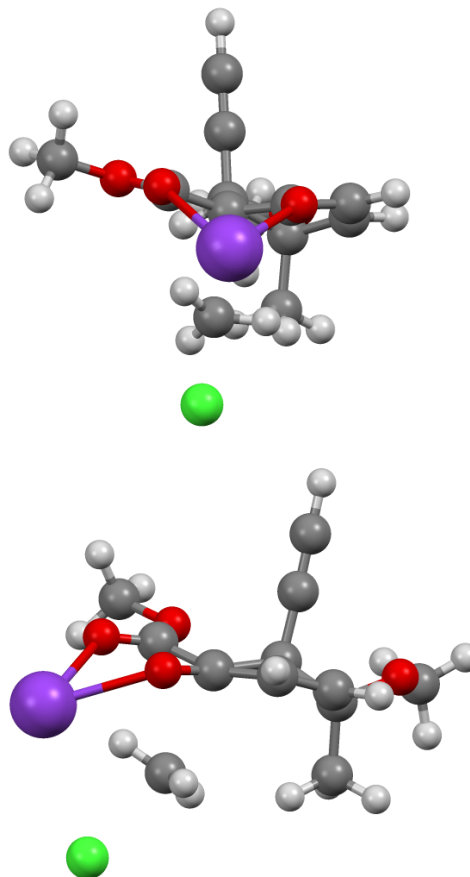


\*\*\* 1 imaginary frequency = -485.8644 \*\*\*

Sum of electronic and zero-point Energies=	-1866.047039
Sum of electronic and thermal Energies=	-1866.024751
Sum of electronic and thermal Enthalpies=	-1866.023807
Sum of electronic and thermal Free Energies=	-1866.098817

**Transition structure TS-3 with SMD<sup>toluene</sup>**

C	0.909000	-1.155000	2.075000
C	2.030000	-1.520000	1.449000
H	0.671000	-1.518000	3.069000
H	2.750000	-2.185000	1.916000
C	-0.132000	-0.300000	1.459000
C	2.351000	-1.091000	0.041000
C	1.890000	-2.181000	-0.943000
H	2.504000	-3.072000	-0.798000
H	1.991000	-1.853000	-1.980000
H	0.852000	-2.457000	-0.770000
O	3.780000	-0.977000	0.020000
C	1.670000	0.289000	-0.248000
H	1.713000	0.462000	-1.326000
C	0.191000	0.336000	0.191000
C	-0.566000	1.519000	-0.216000
O	0.082000	2.256000	-1.146000
C	-0.606000	3.419000	-1.640000
H	0.074000	3.874000	-2.358000
H	-0.819000	4.117000	-0.827000
H	-1.540000	3.138000	-2.130000
C	2.414000	1.376000	0.407000
C	2.992000	2.279000	0.951000
H	3.509000	3.072000	1.437000
O	-1.701000	1.830000	0.150000
C	4.392000	-0.640000	-1.220000
H	5.449000	-0.485000	-1.000000
H	4.305000	-1.445000	-1.959000
H	3.995000	0.288000	-1.647000
O	-1.243000	-0.241000	2.025000
K	-3.631000	0.243000	1.157000
C	-1.314000	-1.017000	-0.952000
H	-1.240000	-1.746000	-0.170000
H	-1.916000	-0.144000	-0.857000
H	-0.786000	-1.172000	-1.880000
Cl	-3.364000	-2.019000	-1.601000

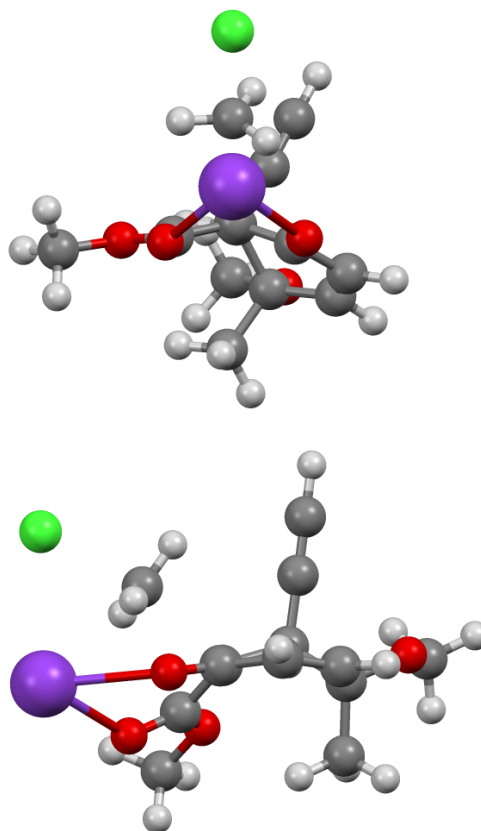


\*\*\* 1 imaginary frequency = -477.7543 \*\*\*

Sum of electronic and zero-point Energies=	-1866.045271
Sum of electronic and thermal Energies=	-1866.023201
Sum of electronic and thermal Enthalpies=	-1866.022257
Sum of electronic and thermal Free Energies=	-1866.096641

**Transition structure TS-4 with SMD<sup>toluene</sup>**

C	-1.078000	-0.834000	2.241000
C	-2.343000	-0.689000	1.837000
H	-0.830000	-1.289000	3.194000
H	-3.177000	-1.028000	2.442000
C	0.060000	-0.283000	1.474000
C	-2.701000	-0.013000	0.534000
C	-2.878000	1.499000	0.763000
H	-3.697000	1.667000	1.466000
H	-3.105000	2.016000	-0.171000
H	-1.970000	1.938000	1.178000
O	-3.940000	-0.620000	0.149000
C	-1.557000	-0.291000	-0.498000
H	-1.742000	0.325000	-1.377000
C	-0.188000	0.112000	0.087000
C	0.436000	1.343000	-0.373000
O	-0.206000	1.916000	-1.424000
C	0.394000	3.103000	-1.972000
H	-0.243000	3.391000	-2.807000
H	1.407000	2.900000	-2.324000
H	0.423000	3.902000	-1.228000
C	-1.576000	-1.690000	-0.937000
C	-1.583000	-2.828000	-1.325000
H	-1.587000	-3.840000	-1.658000
O	1.469000	1.851000	0.070000
C	-4.509000	-0.225000	-1.093000
H	-4.772000	0.839000	-1.113000
H	-3.857000	-0.453000	-1.943000
H	-5.425000	-0.809000	-1.200000
O	1.163000	-0.176000	2.047000
K	3.551000	0.655000	1.185000
C	1.573000	-1.062000	-0.829000
H	1.788000	-0.251000	-1.499000
H	1.856000	-1.055000	0.200000
H	1.042000	-1.920000	-1.210000
Cl	3.778000	-1.847000	-1.215000

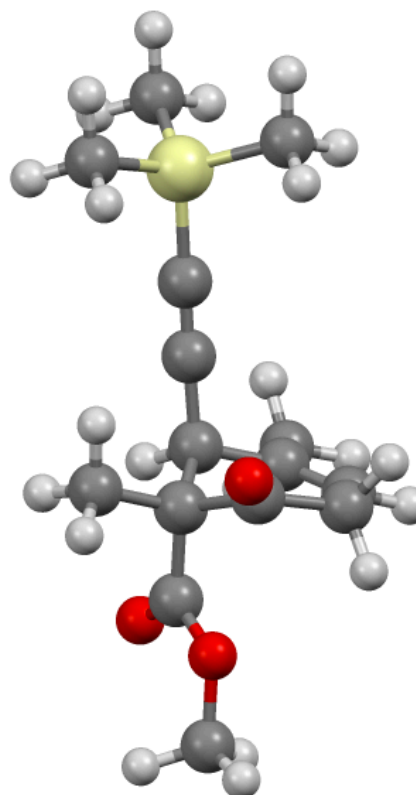


\*\*\* 1 imaginary frequency = -475.8786 \*\*\*

Sum of electronic and zero-point Energies=	-1866.046342
Sum of electronic and thermal Energies=	-1866.024276
Sum of electronic and thermal Enthalpies=	-1866.023332
Sum of electronic and thermal Free Energies=	-1866.097530

**20<sub>AX</sub>** with SMD<sup>THF</sup>

C	1.397000	-0.576000	-0.380000
C	1.581000	0.237000	2.073000
C	1.454000	1.611000	1.475000
C	0.970000	1.861000	0.257000
C	0.547000	0.707000	-0.655000
H	0.923000	0.123000	2.941000
H	1.758000	2.440000	2.109000
H	0.748000	0.992000	-1.692000
H	2.600000	0.076000	2.448000
C	0.791000	3.240000	-0.306000
H	1.067000	4.010000	0.418000
H	1.400000	3.374000	-1.207000
H	-0.252000	3.402000	-0.601000
C	-0.887000	0.447000	-0.517000
C	-2.068000	0.216000	-0.364000
Si	-3.850000	-0.193000	-0.090000
C	-4.180000	-0.128000	1.761000
H	-5.229000	-0.362000	1.974000
H	-3.557000	-0.850000	2.297000
H	-3.967000	0.867000	2.164000
C	-4.902000	1.074000	-0.997000
H	-4.700000	1.061000	-2.073000
H	-5.967000	0.862000	-0.851000
H	-4.707000	2.087000	-0.629000
C	-4.156000	-1.922000	-0.764000
H	-5.200000	-2.215000	-0.613000
H	-3.944000	-1.970000	-1.837000
H	-3.523000	-2.659000	-0.261000
C	0.966000	-1.762000	-1.255000
H	0.995000	-1.479000	-2.309000
H	1.624000	-2.618000	-1.100000
H	-0.049000	-2.066000	-0.999000
C	2.852000	-0.248000	-0.754000
O	3.178000	0.407000	-1.715000
O	3.717000	-0.842000	0.078000
C	5.125000	-0.675000	-0.214000
H	5.648000	-1.214000	0.573000
H	5.361000	-1.101000	-1.190000
H	5.393000	0.382000	-0.196000
C	1.285000	-0.904000	1.119000
O	0.958000	-2.002000	1.514000

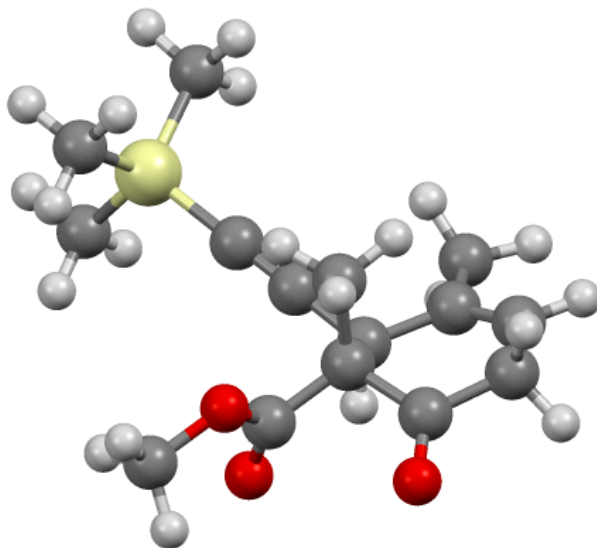


\*\*\* 0 imaginary frequencies \*\*\*

Sum of electronic and zero-point Energies=	-1099.980605
Sum of electronic and thermal Energies=	-1099.956932
Sum of electronic and thermal Enthalpies=	-1099.955988
Sum of electronic and thermal Free Energies=	-1100.034400

**20<sub>EQ</sub> with SMD<sup>THF</sup>**

C	-0.802000	-0.889000	-0.593000
C	-1.659000	0.145000	0.221000
C	-3.459000	-1.676000	0.517000
C	-2.371000	-2.662000	0.192000
C	-1.170000	-2.344000	-0.295000
H	-1.019000	-0.715000	-1.655000
H	-3.660000	-1.671000	1.599000
H	-4.402000	-1.953000	0.039000
H	-2.617000	-3.707000	0.358000
C	-1.278000	0.147000	1.719000
H	-0.271000	0.546000	1.847000
H	-1.968000	0.764000	2.295000
H	-1.297000	-0.869000	2.115000
C	0.621000	-0.606000	-0.401000
C	1.790000	-0.340000	-0.218000
Si	3.565000	0.072000	0.088000
C	4.414000	-1.466000	0.761000
H	5.469000	-1.262000	0.973000
H	3.941000	-1.803000	1.688000
H	4.367000	-2.287000	0.039000
C	4.341000	0.612000	-1.536000
H	3.832000	1.493000	-1.940000
H	5.397000	0.868000	-1.391000
H	4.288000	-0.183000	-2.287000
C	3.620000	1.471000	1.344000
H	4.656000	1.747000	1.569000
H	3.109000	2.362000	0.964000
H	3.138000	1.179000	2.282000
C	-3.141000	-0.253000	0.121000
O	-4.001000	0.533000	-0.215000
C	-0.146000	-3.386000	-0.653000
H	0.166000	-3.279000	-1.698000
H	0.757000	-3.281000	-0.045000
H	-0.545000	-4.393000	-0.514000
C	-1.505000	1.526000	-0.431000
O	-1.353000	1.698000	-1.619000
O	-1.577000	2.520000	0.459000
C	-1.490000	3.863000	-0.070000
H	-2.304000	4.048000	-0.772000
H	-1.576000	4.520000	0.793000
H	-0.530000	4.014000	-0.567000

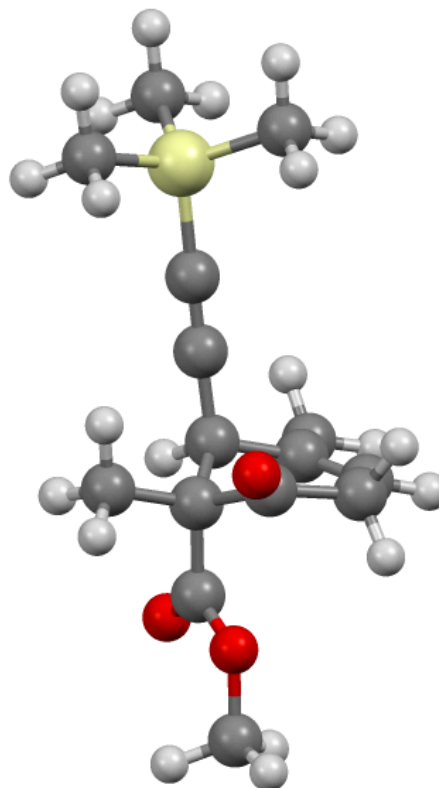


\*\*\* 0 imaginary frequencies \*\*\*

Sum of electronic and zero-point Energies=	-1099.976658
Sum of electronic and thermal Energies=	-1099.953356
Sum of electronic and thermal Enthalpies=	-1099.952412
Sum of electronic and thermal Free Energies=	-1100.029406

**20<sub>AX</sub>** with SMD<sup>MeOH</sup>

C	1.404000	-0.580000	-0.385000
C	1.573000	0.210000	2.075000
C	1.448000	1.588000	1.489000
C	0.964000	1.847000	0.272000
C	0.539000	0.697000	-0.644000
H	0.905000	0.080000	2.934000
H	1.756000	2.410000	2.129000
H	0.727000	0.990000	-1.682000
H	2.588000	0.050000	2.463000
C	0.795000	3.227000	-0.288000
H	1.070000	3.994000	0.439000
H	1.414000	3.356000	-1.185000
H	-0.244000	3.395000	-0.593000
C	-0.891000	0.427000	-0.499000
C	-2.074000	0.197000	-0.348000
Si	-3.865000	-0.189000	-0.089000
C	-4.209000	-0.118000	1.757000
H	-5.263000	-0.338000	1.959000
H	-3.600000	-0.847000	2.301000
H	-3.988000	0.876000	2.161000
C	-4.887000	1.094000	-1.008000
H	-4.674000	1.078000	-2.081000
H	-5.956000	0.896000	-0.872000
H	-4.682000	2.103000	-0.636000
C	-4.185000	-1.913000	-0.768000
H	-5.236000	-2.190000	-0.628000
H	-3.963000	-1.963000	-1.839000
H	-3.568000	-2.660000	-0.259000
C	0.989000	-1.762000	-1.273000
H	1.018000	-1.465000	-2.323000
H	1.660000	-2.610000	-1.126000
H	-0.025000	-2.079000	-1.023000
C	2.855000	-0.234000	-0.751000
O	3.173000	0.445000	-1.704000
O	3.724000	-0.829000	0.064000
C	5.135000	-0.638000	-0.220000
H	5.660000	-1.168000	0.572000
H	5.378000	-1.065000	-1.194000
H	5.378000	0.425000	-0.200000
C	1.303000	-0.920000	1.108000
O	1.002000	-2.034000	1.493000

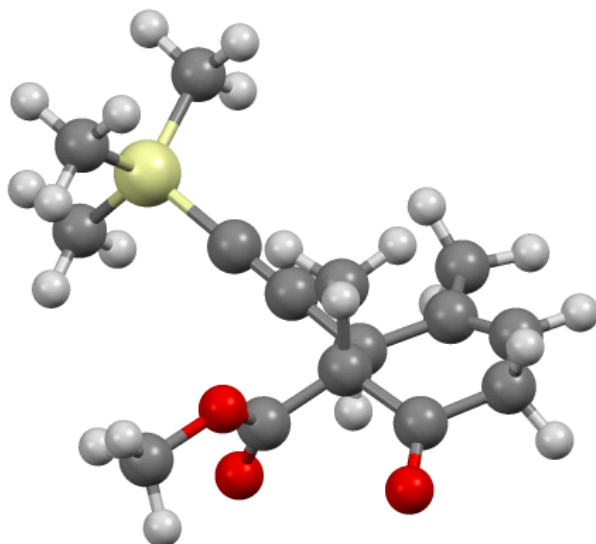


\*\*\* 1 imaginary frequency = -474.6927 \*\*\*

Sum of electronic and zero-point Energies=	-1099.981321
Sum of electronic and thermal Energies=	-1099.957646
Sum of electronic and thermal Enthalpies=	-1099.956701
Sum of electronic and thermal Free Energies=	-1100.035426

**20<sub>EQ</sub> with SMD<sup>MeOH</sup>**

C	-0.801000	-0.898000	-0.594000
C	-1.658000	0.138000	0.218000
C	-3.481000	-1.664000	0.459000
C	-2.387000	-2.657000	0.181000
C	-1.172000	-2.349000	-0.279000
H	-1.024000	-0.738000	-1.657000
H	-3.728000	-1.659000	1.531000
H	-4.406000	-1.932000	-0.061000
H	-2.640000	-3.698000	0.362000
C	-1.299000	0.128000	1.721000
H	-0.292000	0.524000	1.863000
H	-1.997000	0.741000	2.292000
H	-1.327000	-0.891000	2.109000
C	0.621000	-0.609000	-0.408000
C	1.789000	-0.337000	-0.229000
Si	3.566000	0.074000	0.082000
C	4.405000	-1.467000	0.757000
H	5.460000	-1.266000	0.972000
H	3.928000	-1.801000	1.684000
H	4.358000	-2.289000	0.035000
C	4.343000	0.609000	-1.543000
H	3.838000	1.492000	-1.947000
H	5.399000	0.862000	-1.395000
H	4.290000	-0.186000	-2.293000
C	3.616000	1.474000	1.334000
H	4.652000	1.747000	1.562000
H	3.108000	2.365000	0.952000
H	3.131000	1.184000	2.272000
C	-3.137000	-0.246000	0.090000
O	-3.983000	0.561000	-0.253000
C	-0.137000	-3.395000	-0.584000
H	0.210000	-3.309000	-1.620000
H	0.746000	-3.277000	0.053000
H	-0.539000	-4.400000	-0.437000
C	-1.488000	1.525000	-0.413000
O	-1.304000	1.708000	-1.600000
O	-1.592000	2.510000	0.474000
C	-1.491000	3.864000	-0.037000
H	-2.280000	4.047000	-0.767000
H	-1.615000	4.507000	0.831000
H	-0.511000	4.019000	-0.492000

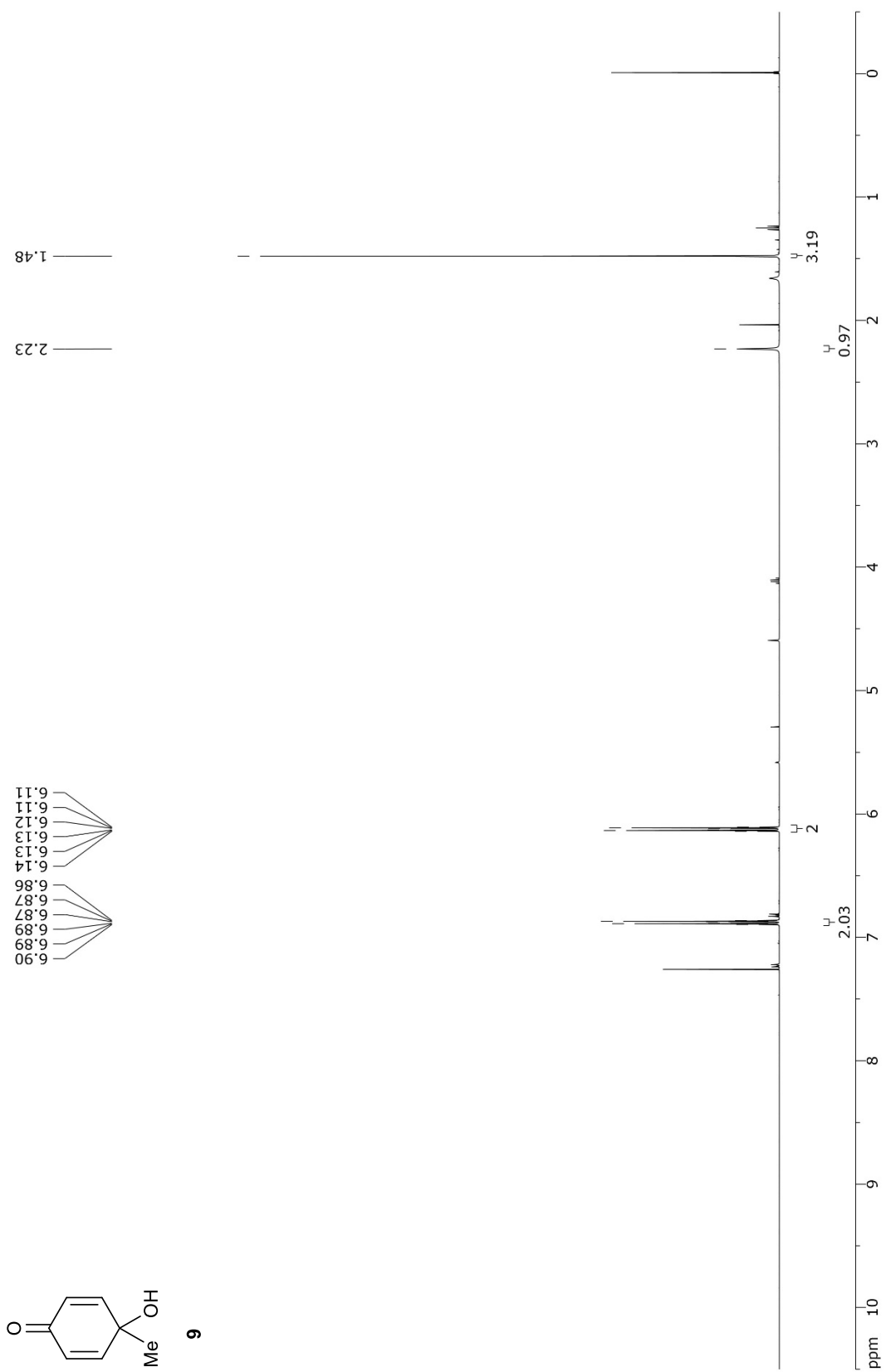


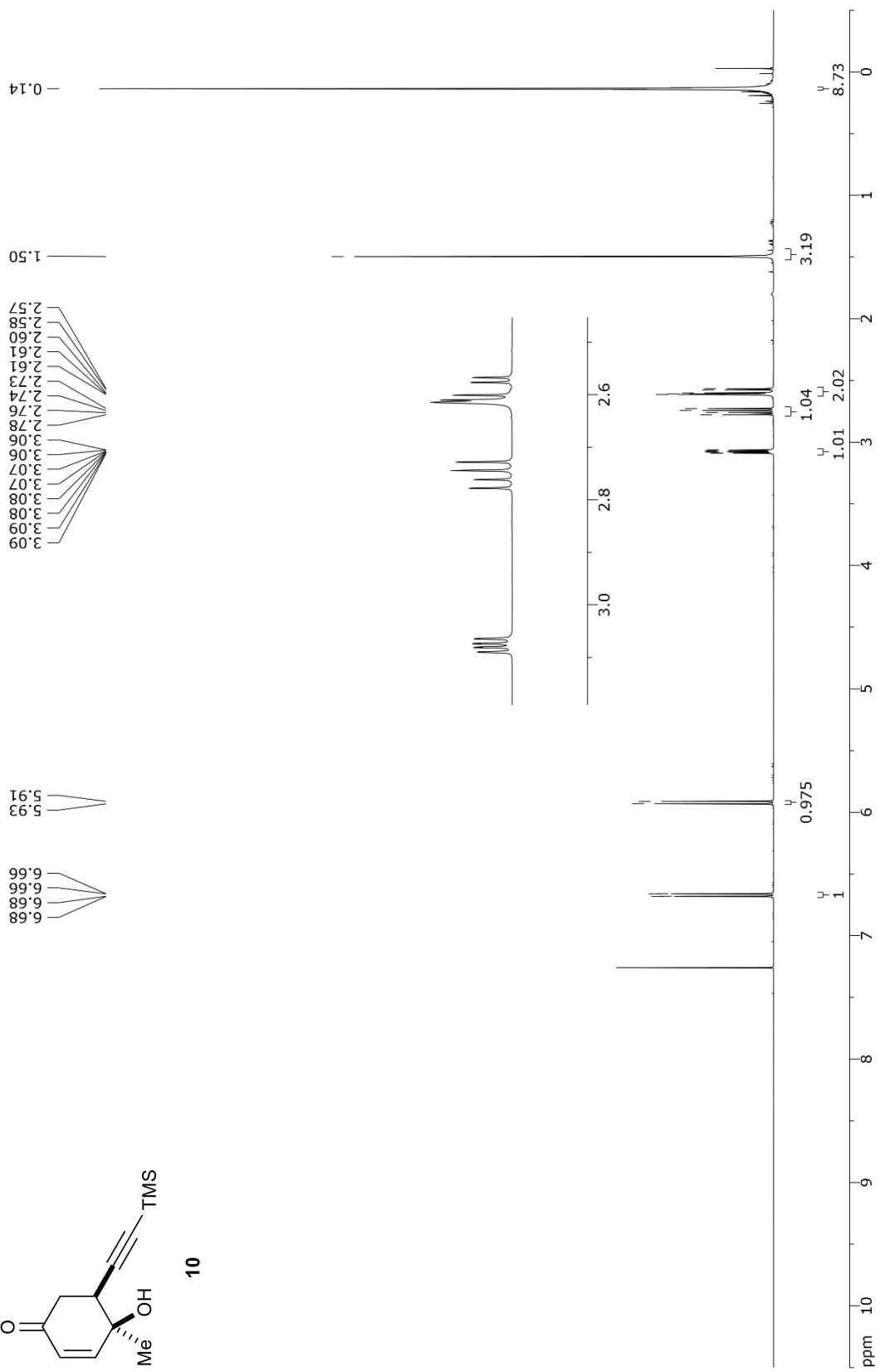
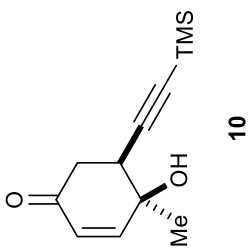
\*\*\* 1 imaginary frequency = -485.8644 \*\*\*

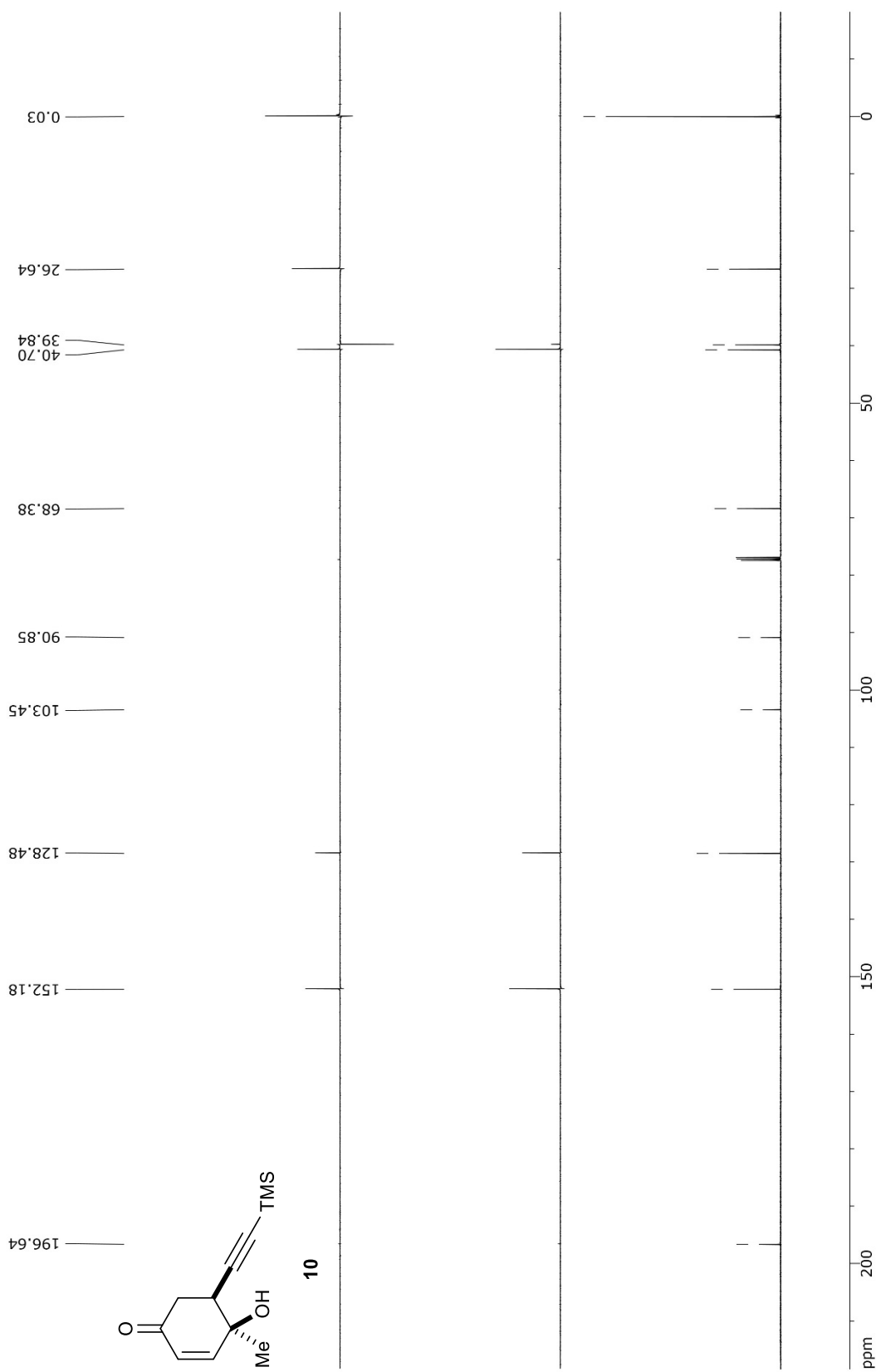
Sum of electronic and zero-point Energies=	-1099.977536
Sum of electronic and thermal Energies=	-1099.954207
Sum of electronic and thermal Enthalpies=	-1099.953263
Sum of electronic and thermal Free Energies=	-1100.030730

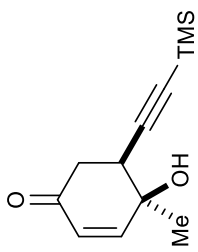


# NMR Spectra

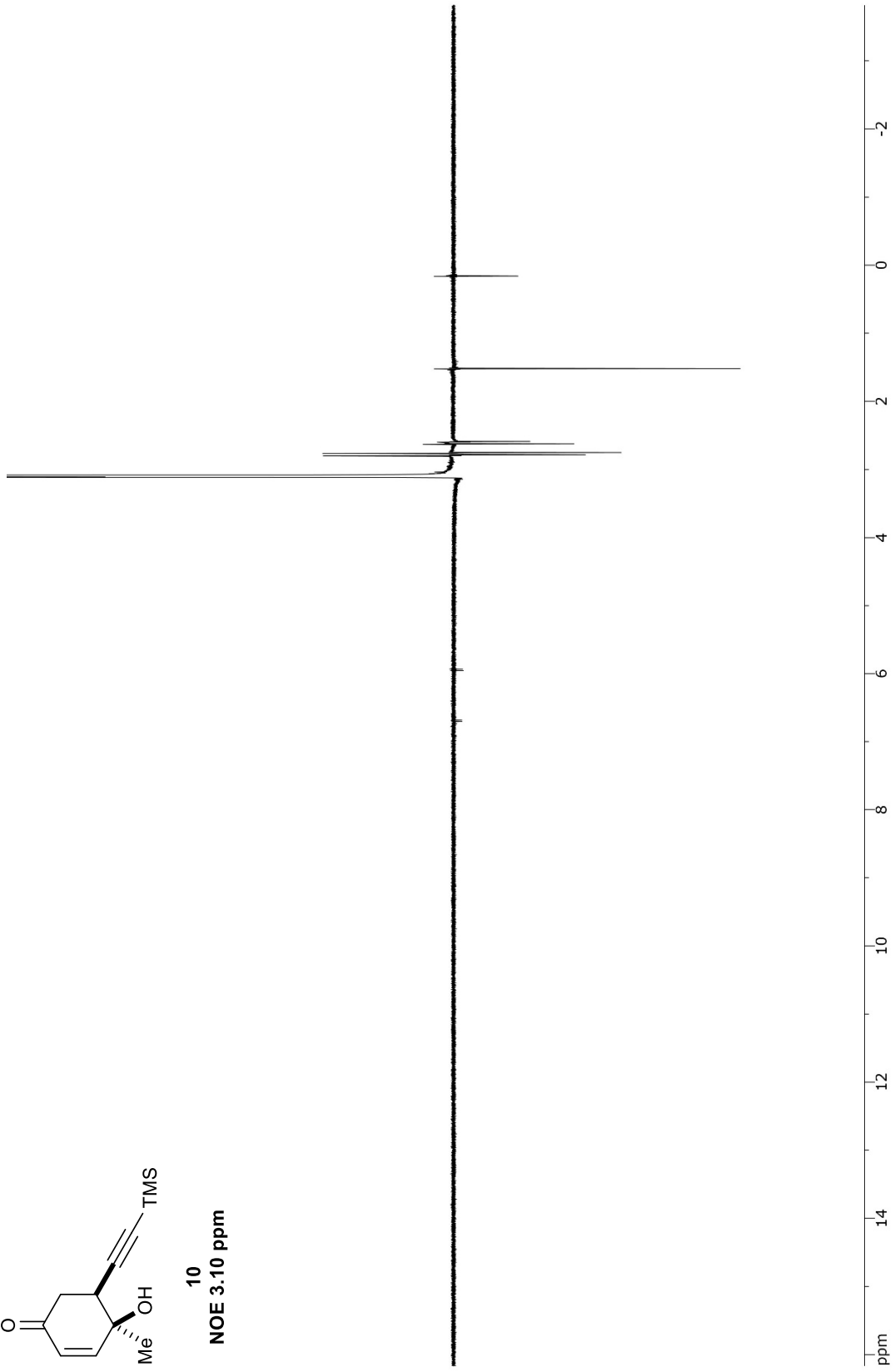


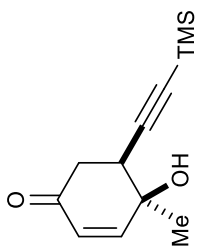




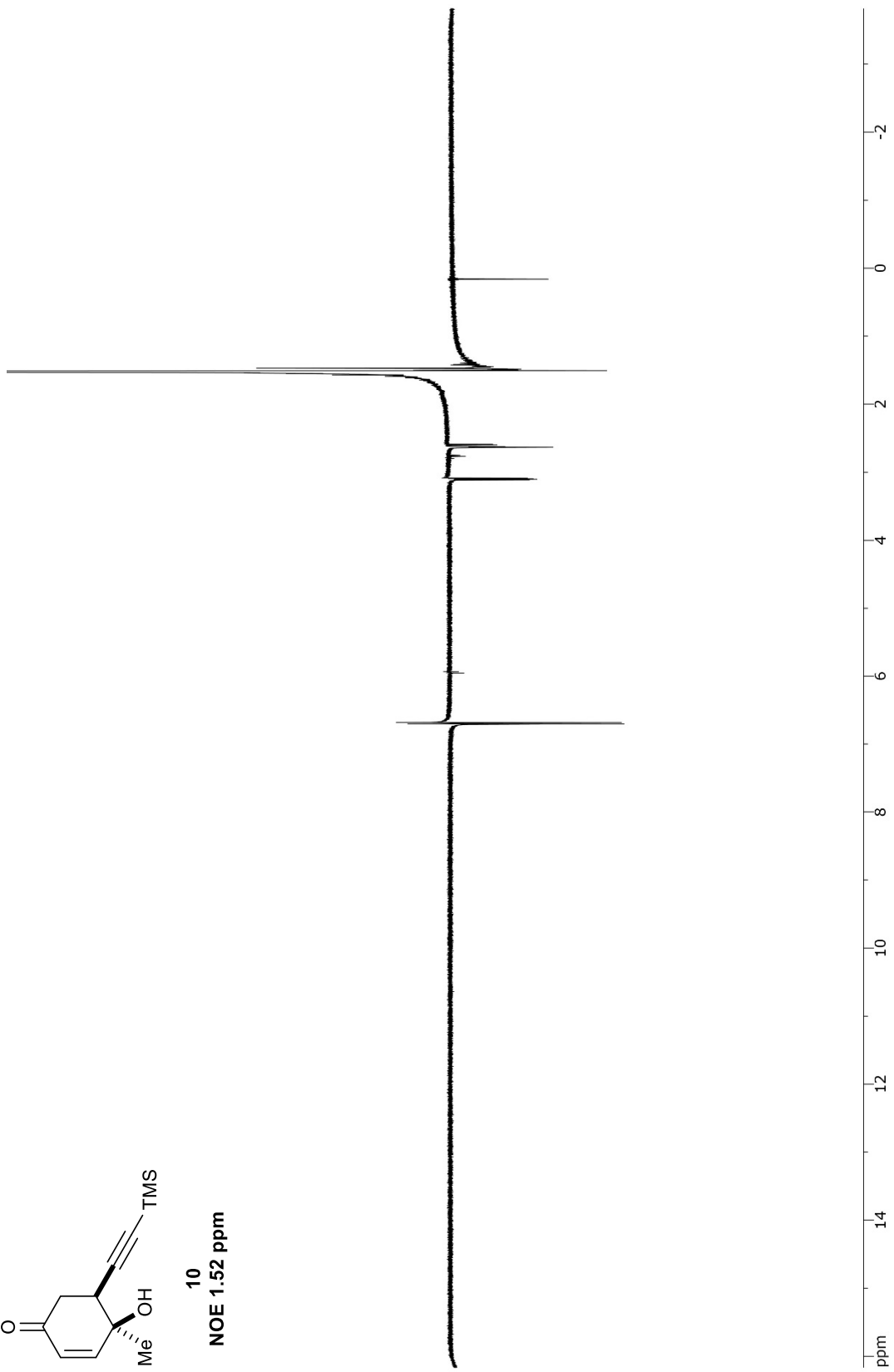


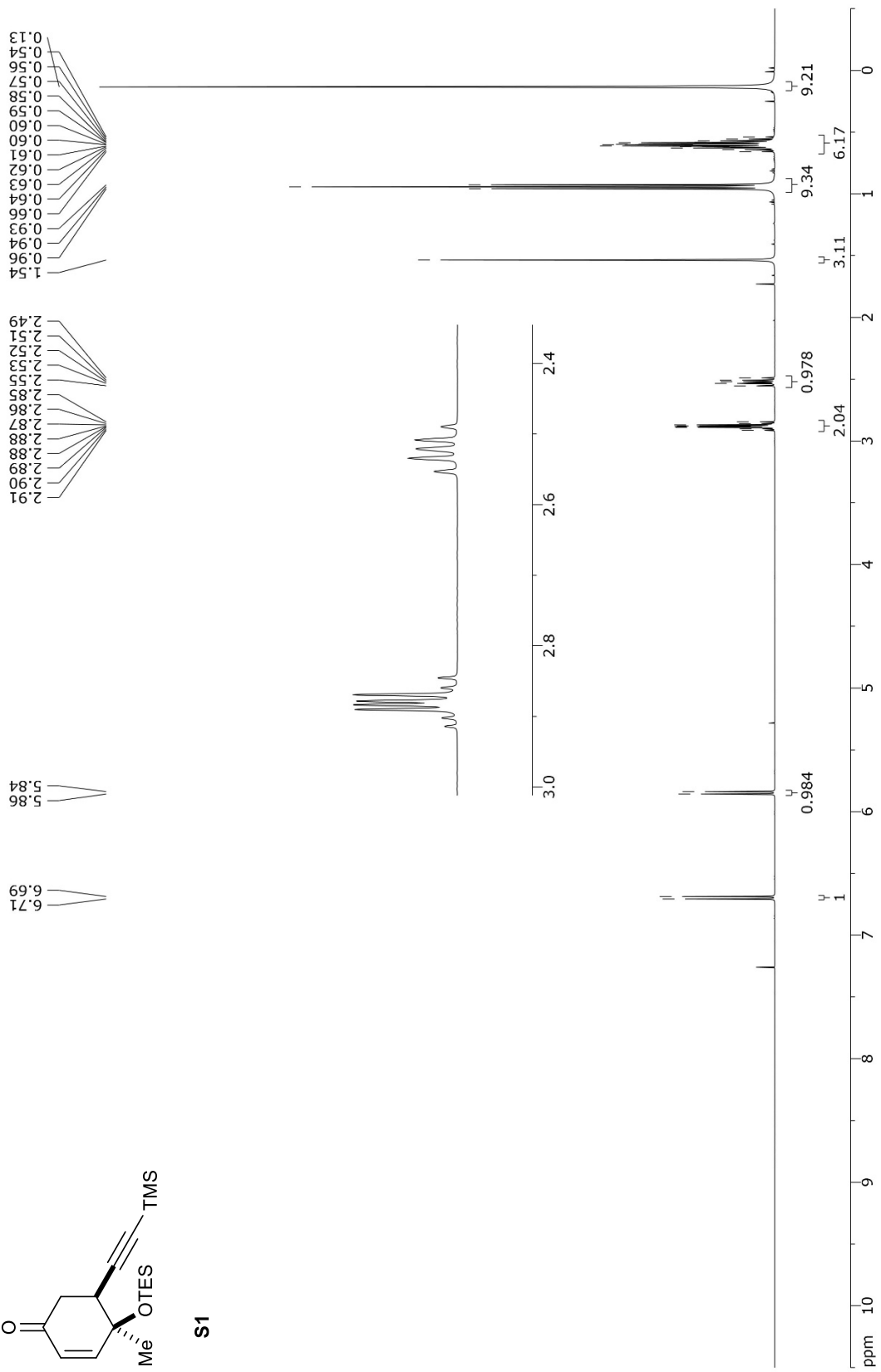
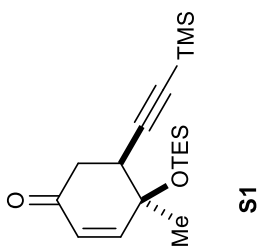
<sup>10</sup>  
NOE 3.10 ppm

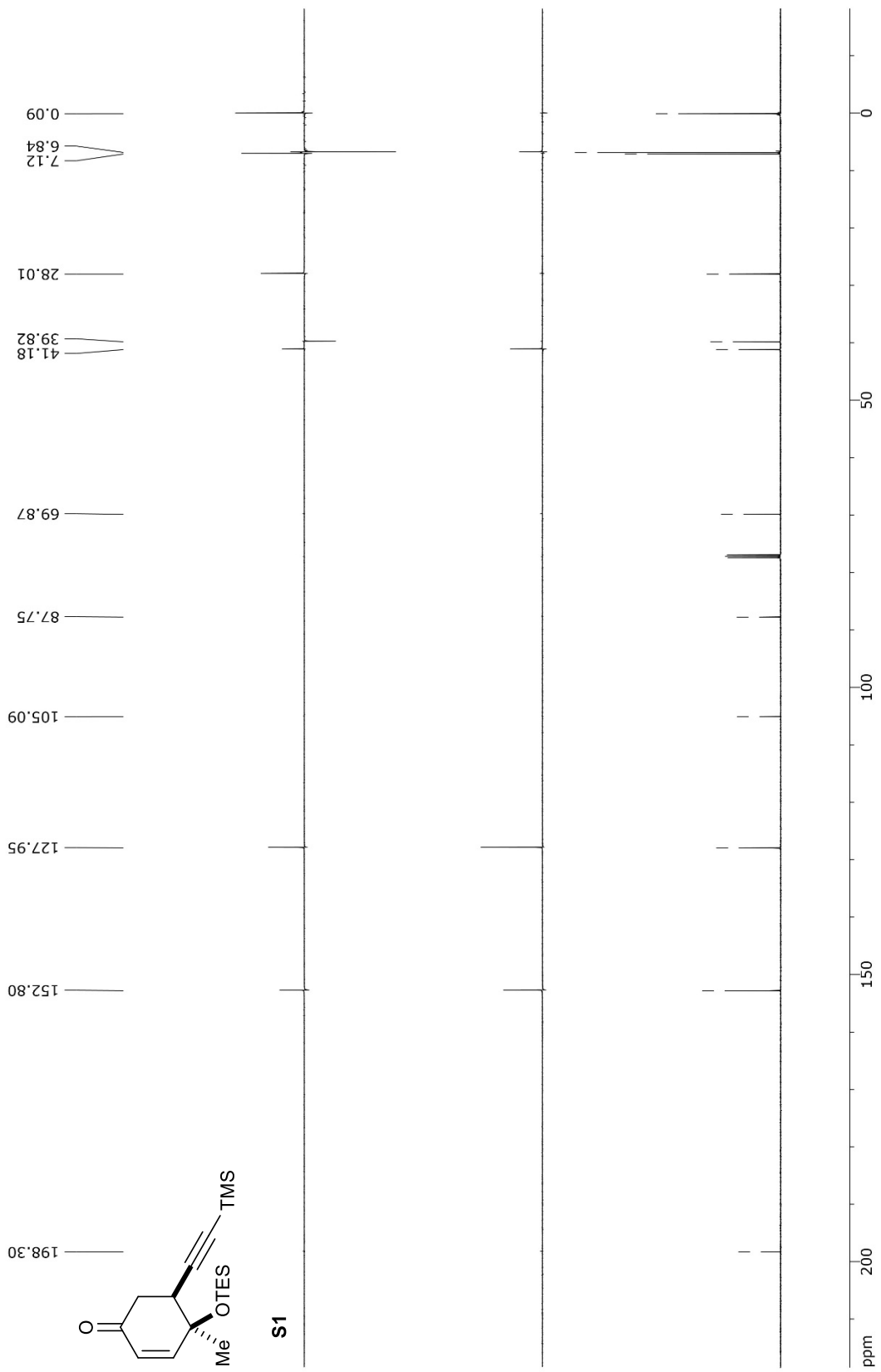


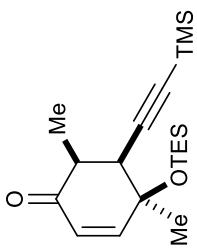


10  
NOE 1.52 ppm

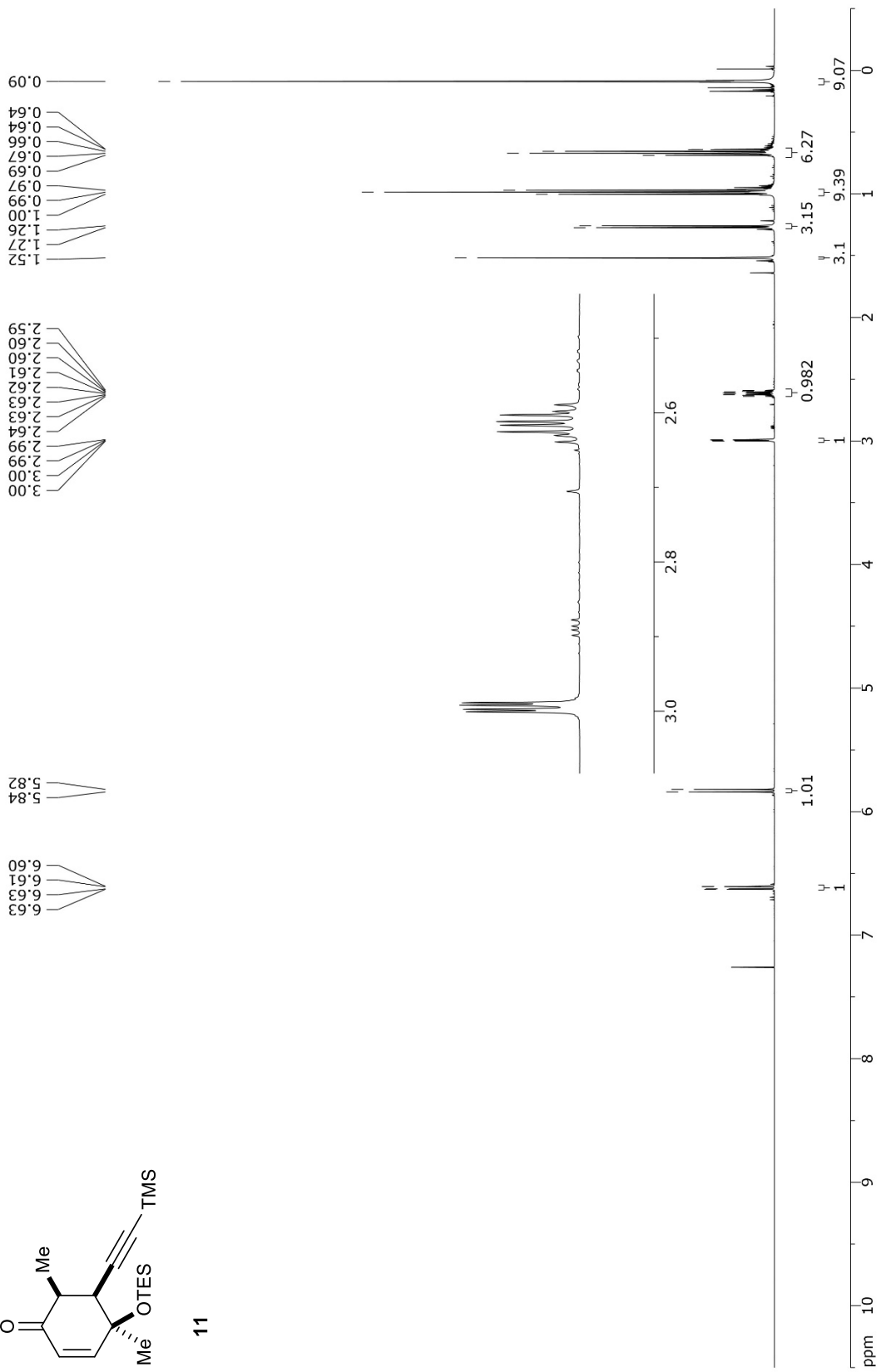




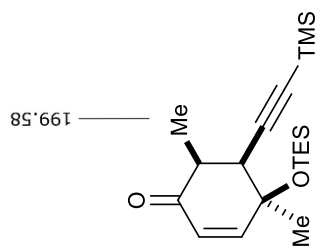




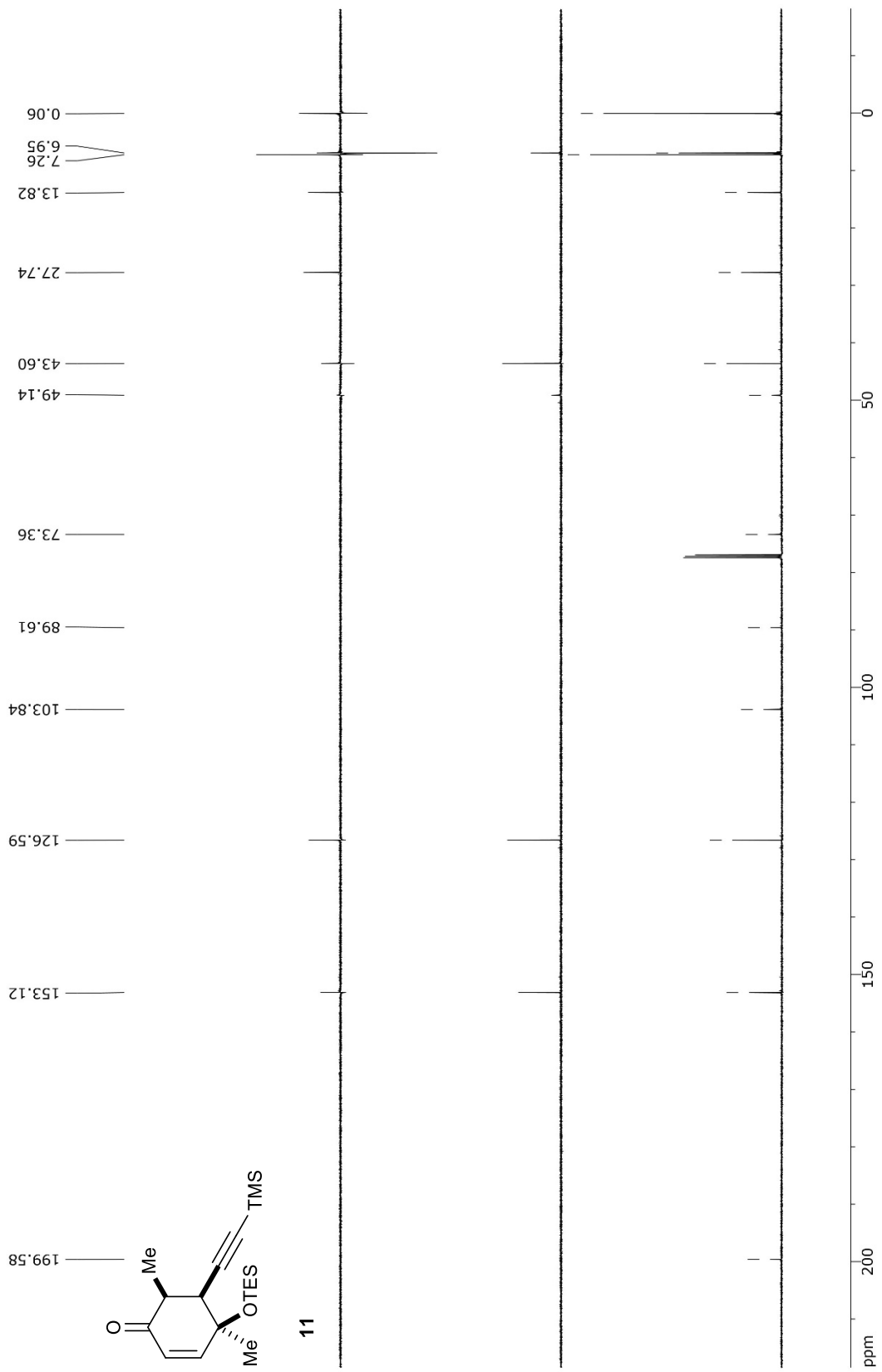
11

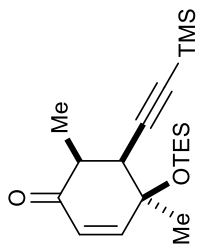




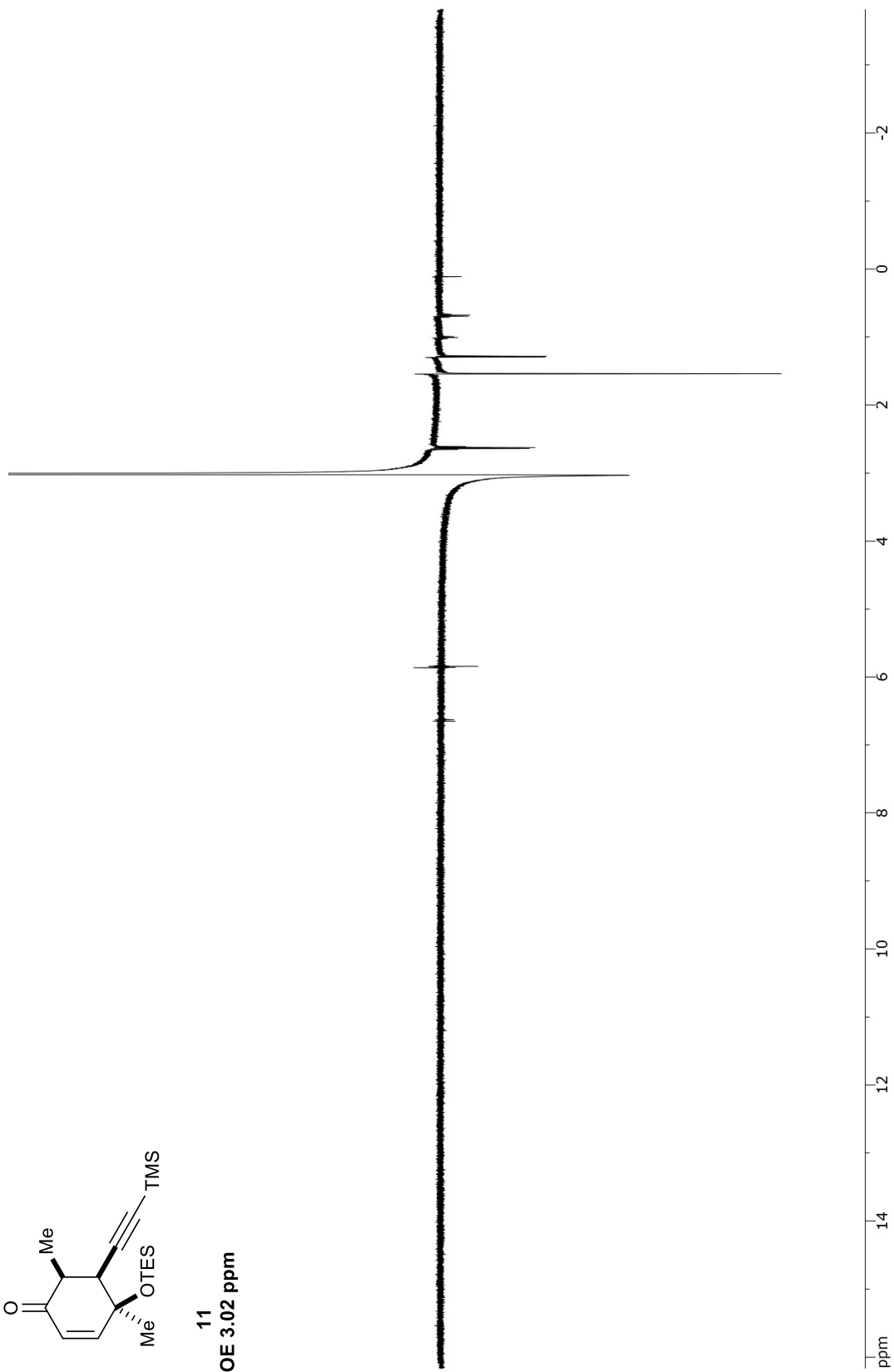


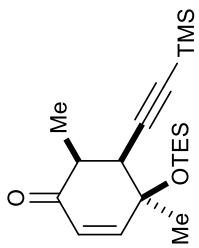
11



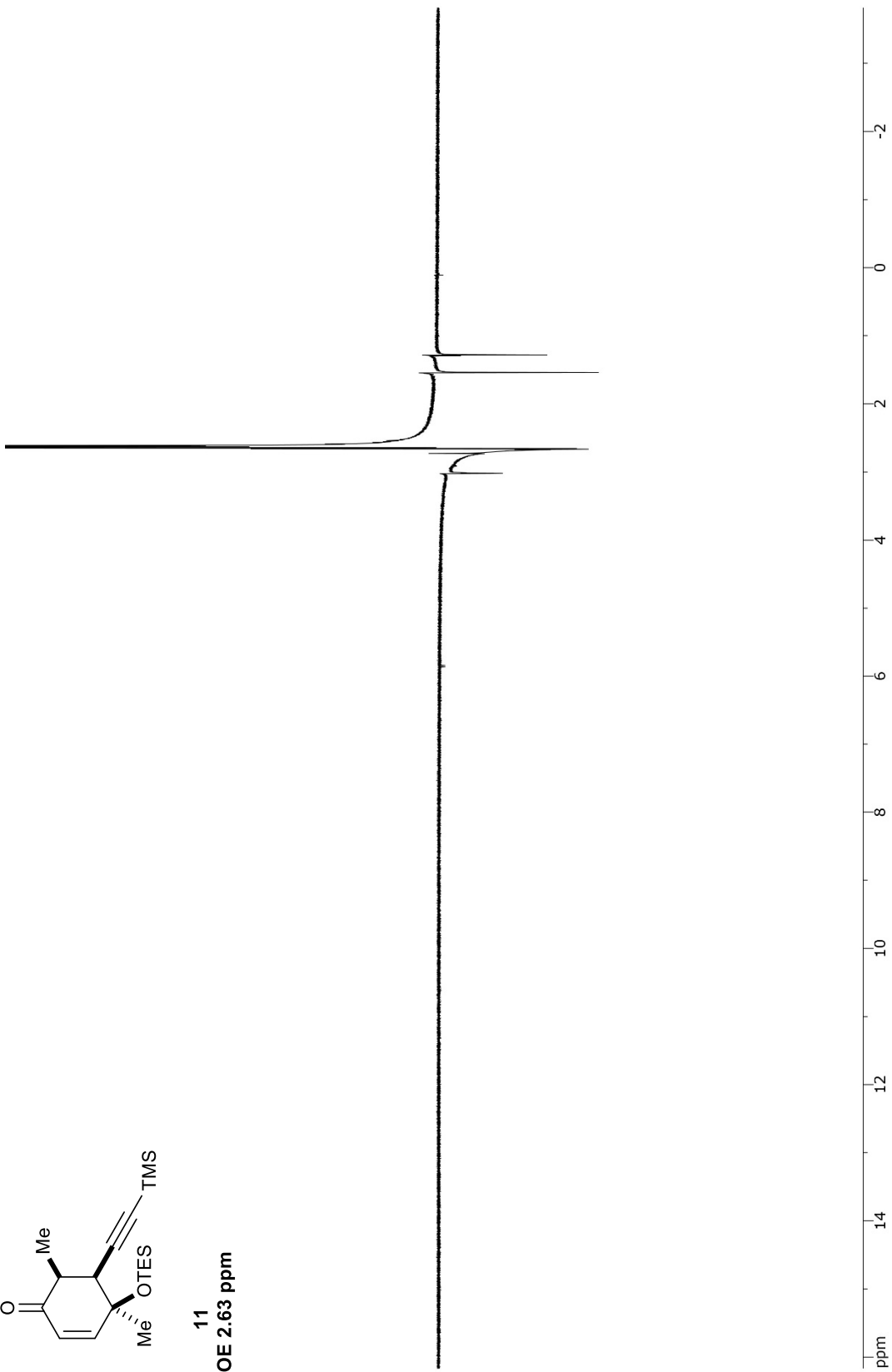


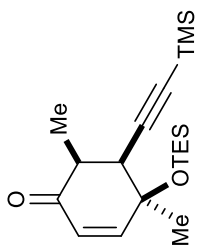
11  
NOE 3.02 ppm





11  
NOE 2.63 ppm





11  
NOE 1.29 ppm

