

SUPPORTING INFORMATION

**Reactions of Thiiuranium and Sulphonium Ions with
Alkenes in the Gas-Phase**

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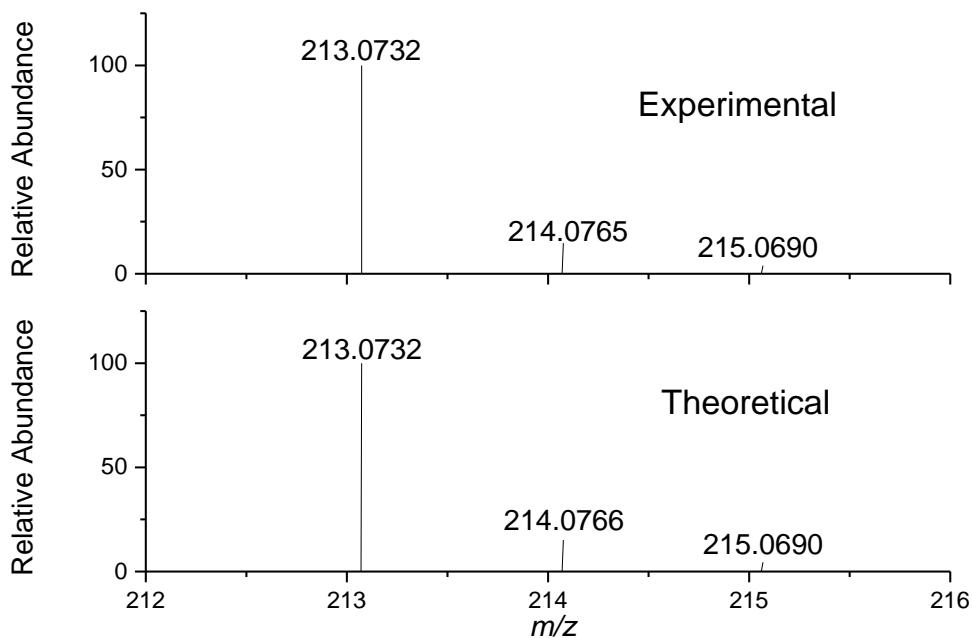


Figure S1. Experimental and theoretical high-resolution accurate mass measurements for the ions corresponding to thiiranium ion **11** [$\text{C}_{14}\text{H}_{13}\text{S}^+$] (m/z 213). The m/z used is represented on the most intense sulphur isotope (^{32}S). The full isotopic envelope is shown.

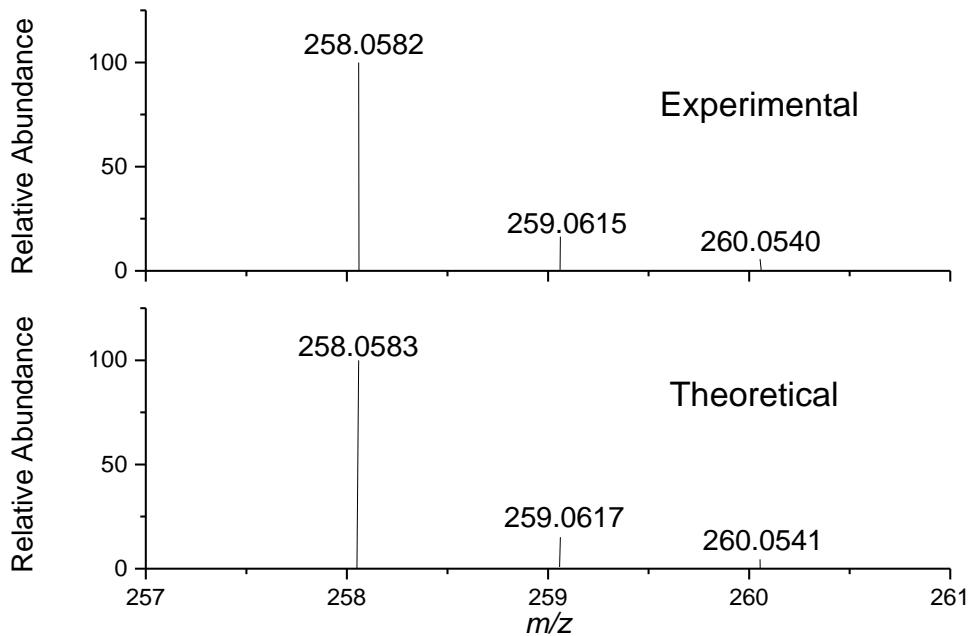


Figure S2. Experimental and theoretical high-resolution accurate mass measurements for the ions corresponding to thiiranium ion **18** [$\text{C}_{14}\text{H}_{12}\text{NO}_2\text{S}^+$] (m/z 258). The m/z used is represented on the most intense sulphur isotope (^{32}S). The full isotopic envelope is shown.

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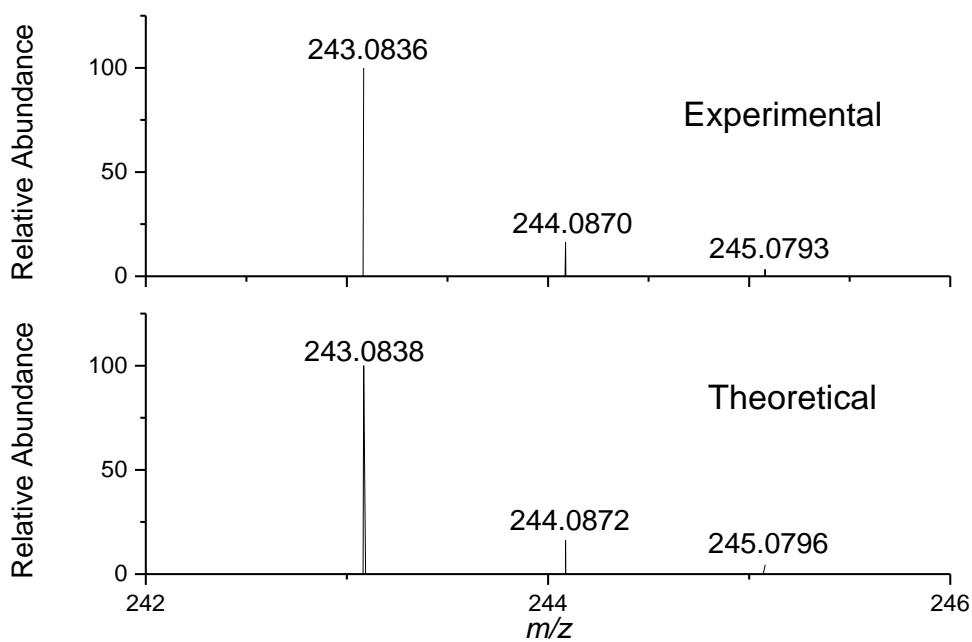


Figure S3. Experimental and theoretical high-resolution accurate mass measurements for the ions corresponding to thiiranium ion **19** [$\text{C}_{15}\text{H}_{15}\text{OS}^+$] (m/z 243). The m/z used is represented on the most intense sulphur isotope (^{32}S). The full isotopic envelope is shown.

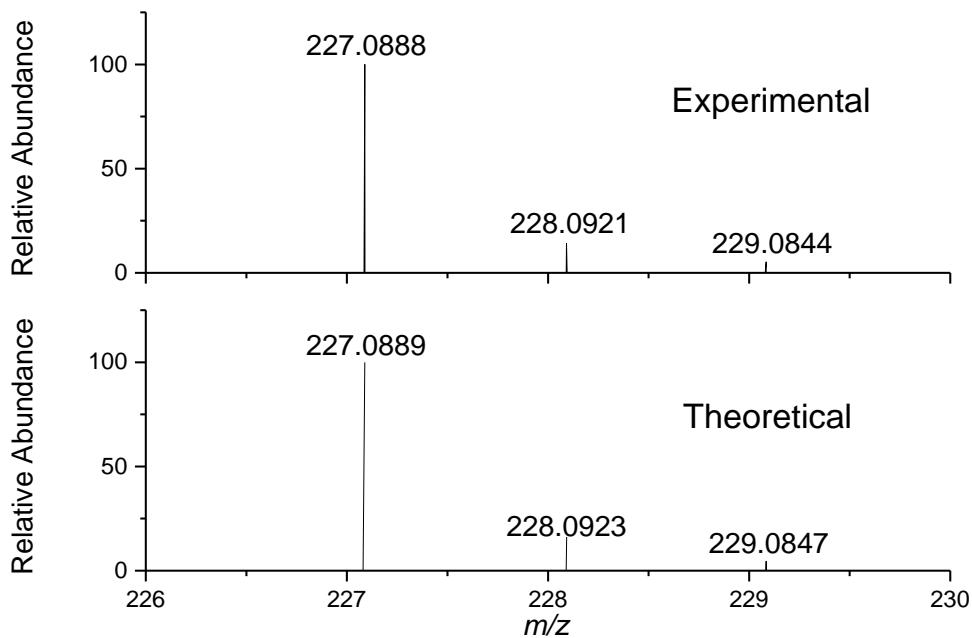


Figure S4. Experimental and theoretical high-resolution accurate mass measurements for the ions corresponding to thiiranium ion **20** [$\text{C}_{15}\text{H}_{15}\text{S}^+$] (m/z 227). The m/z used is represented on the most intense sulphur isotope (^{32}S). The full isotopic envelope is shown.

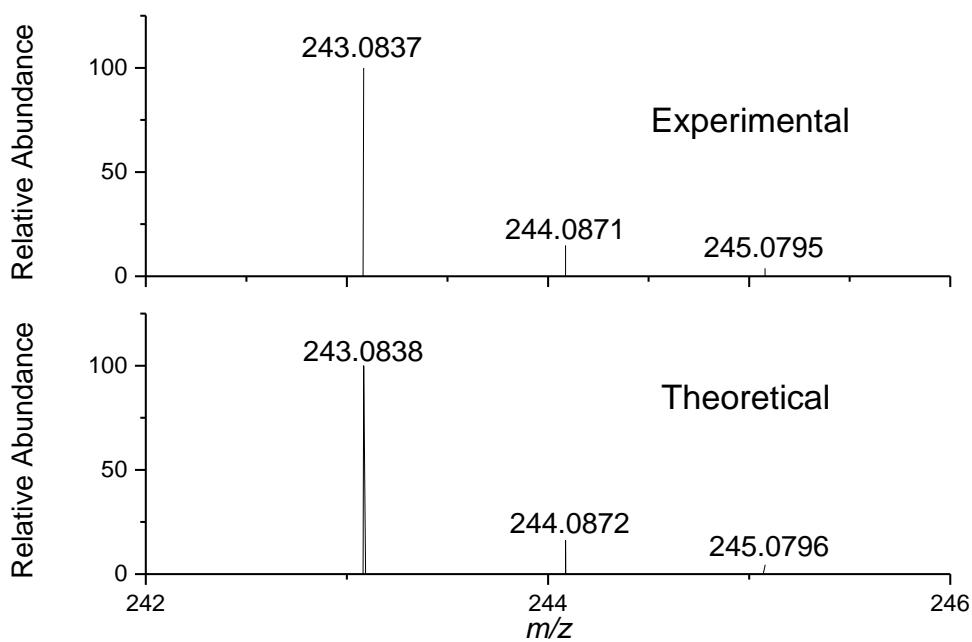


Figure S5. Experimental and theoretical high-resolution accurate mass measurements for the ions corresponding to thiiranium ion **21** $[\text{C}_{15}\text{H}_{15}\text{OS}]^+$ (m/z 243). The m/z used is represented on the most intense sulphur isotope (^{32}S). The full isotopic envelope is shown.

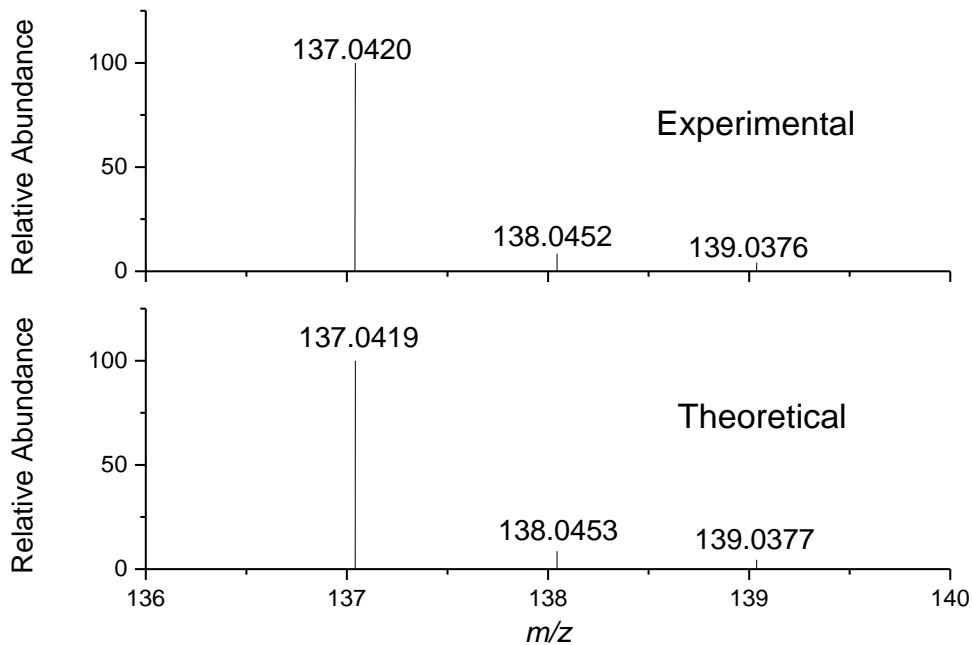


Figure S6. Experimental and theoretical high-resolution accurate mass measurements for the ions corresponding to thiiranium ion **25** $[\text{C}_8\text{H}_9\text{S}]^+$ (m/z 137). The m/z used is represented on the most intense sulphur isotope (^{32}S). The full isotopic envelope is shown.

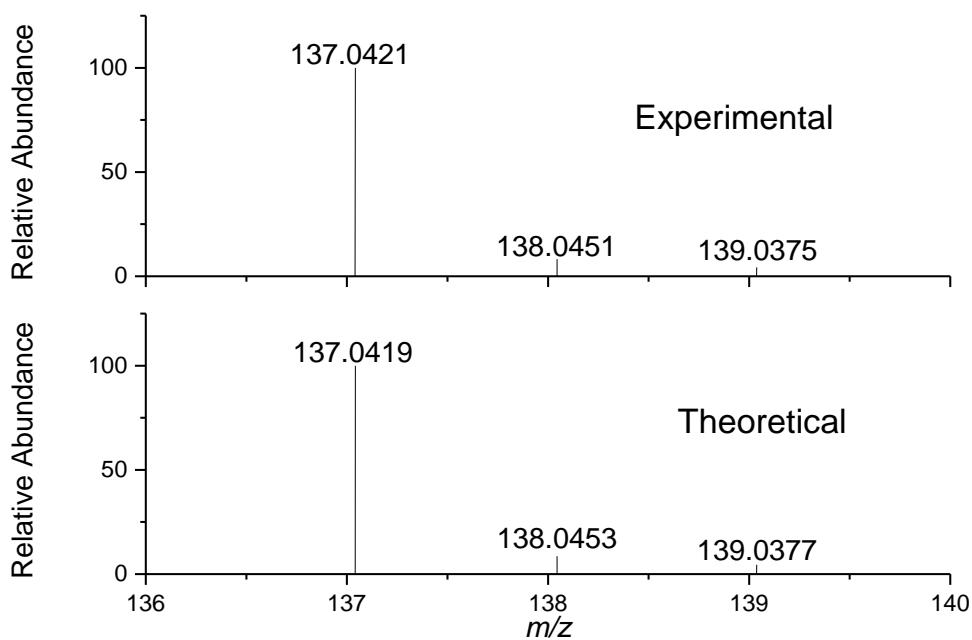


Figure S7. Experimental and theoretical high-resolution accurate mass measurements for the ions corresponding to sulphonium ion **27** $[C_8H_9S]^+$ (m/z 137). The m/z used is represented on the most intense sulphur isotope (^{32}S). The full isotopic envelope is shown.

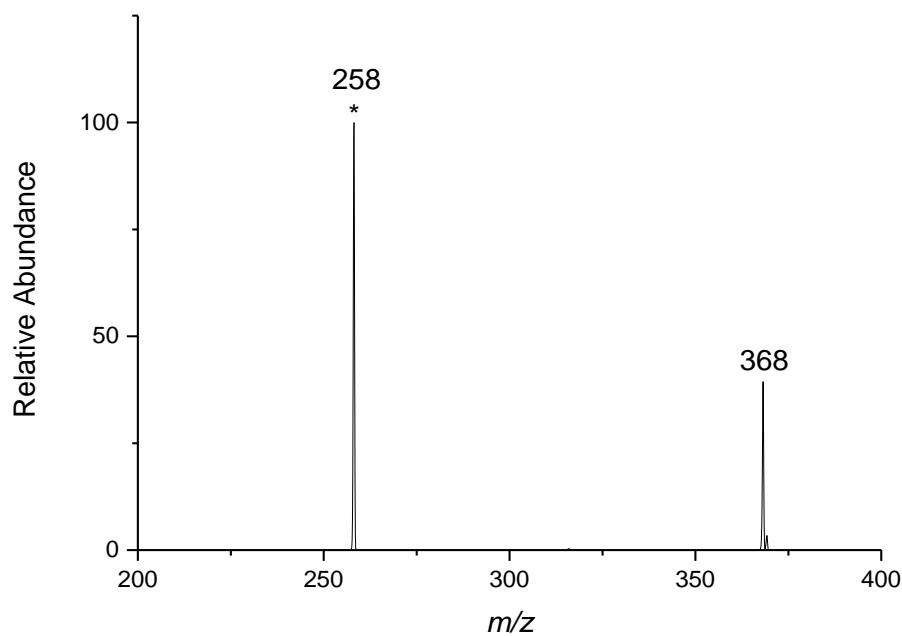


Figure S8. Ion-molecule reaction of thiiranium ion **18** (m/z 258) with *cis*-cyclooctene (conc. $ca\ 6.13 \times 10^{10}$ molecules cm^{-3}) for 1000 ms. Addition product observed at m/z 368. The mass selected ion is denoted by an asterisk (sulphur isotope ^{32}S was selected).

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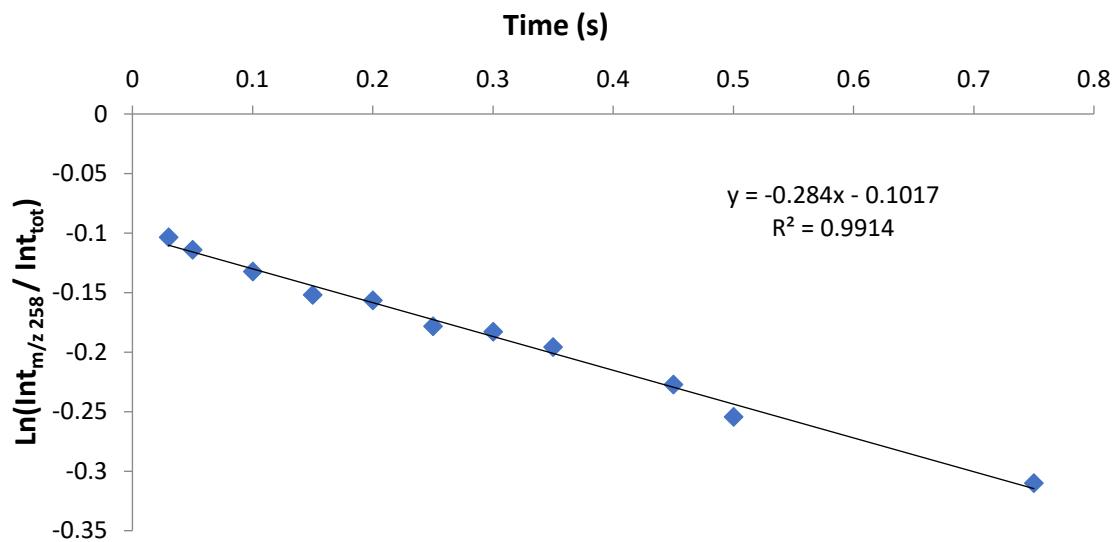


Figure S9. Early onset of the reaction of thiiranium ion **18** (m/z 258) with *cis*-cyclooctene (conc. $ca\ 6.13 \times 10^{10}$ molecules cm^{-3}) in the ion trap mass spectrometer in the formation of addition product m/z 368.

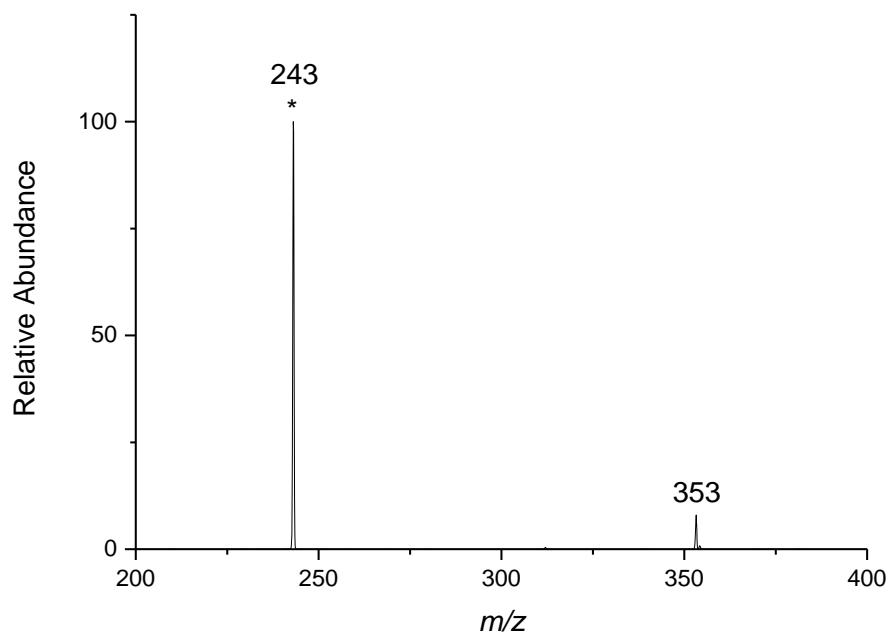


Figure S10. Ion-molecule reaction of thiiranium ion **19** (m/z 243) with *cis*-cyclooctene (conc. $ca\ 6.13 \times 10^{10}$ molecules cm^{-3}) for 3000 ms. Addition product observed at m/z 353. The mass selected ion is denoted by an asterisk (sulphur isotope ^{32}S was selected).

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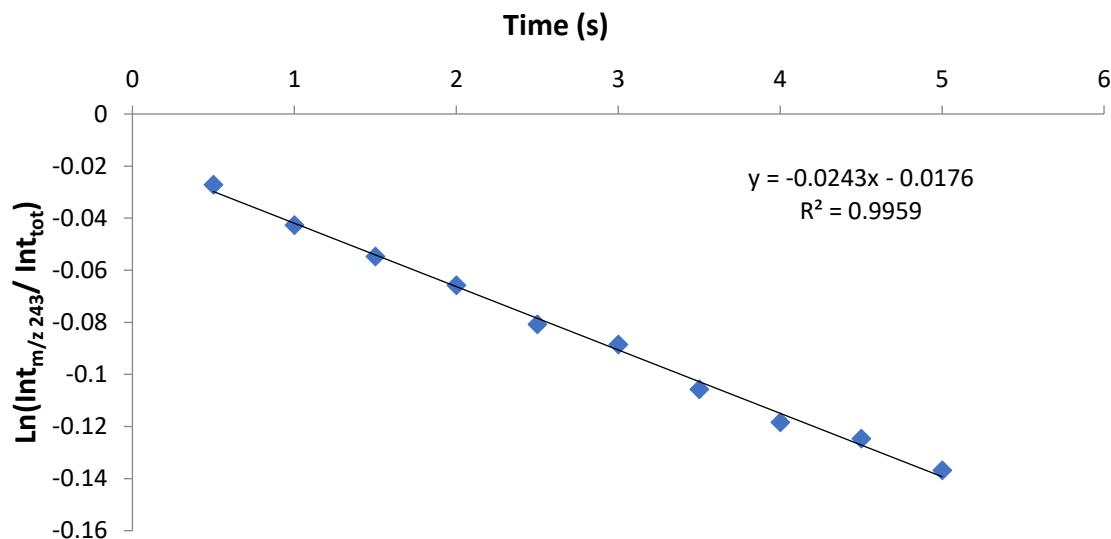


Figure S11. Early onset of the reaction of thiiranium ion **19** (m/z 243) with *cis*-cyclooctene (conc. *ca* 6.13×10^{10} molecules cm^{-3}) in the ion trap mass spectrometer in the formation of addition product m/z 353.

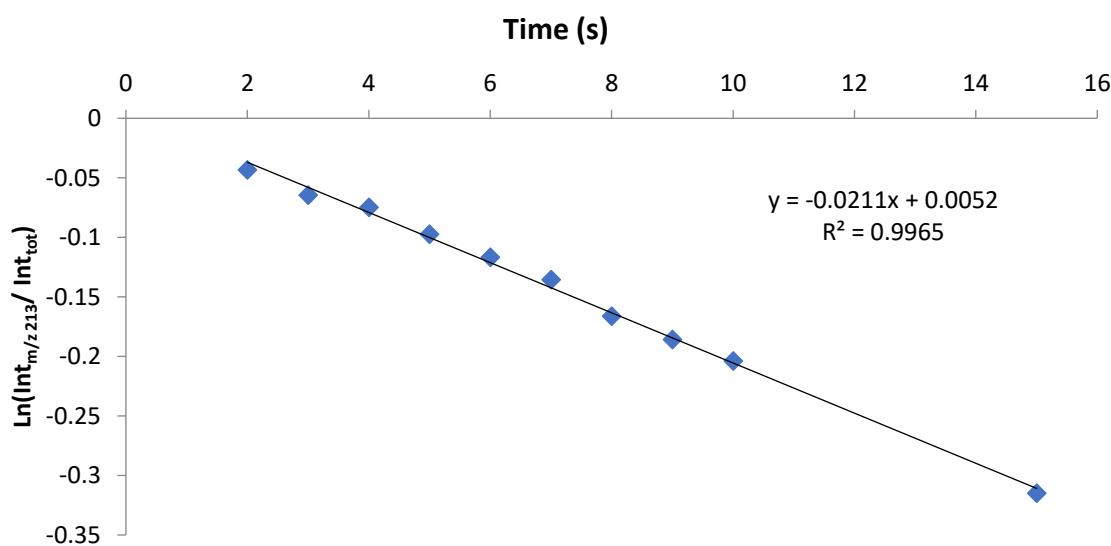


Figure S12. Early onset of the reaction of thiiranium ion **11** (m/z 213) with *cis*-cyclooctene (conc. *ca* 6.13×10^{10} molecules cm^{-3}) in the ion trap mass spectrometer in the formation of addition product **17b** m/z 323.

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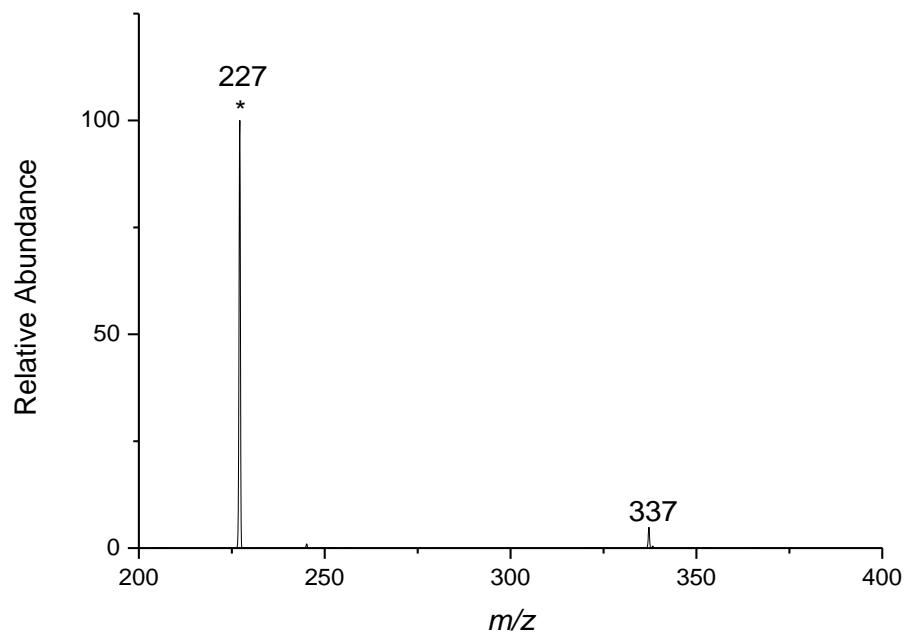


Figure S13. Ion-molecule reaction of thiiranium ion **20** (m/z 227) with *cis*-cyclooctene (conc. $ca 6.13 \times 10^{10}$ molecules cm^{-3}) for 4000 ms. Addition product observed at m/z 337. The mass selected ion is denoted by an asterisk (sulphur isotope ^{32}S was selected).

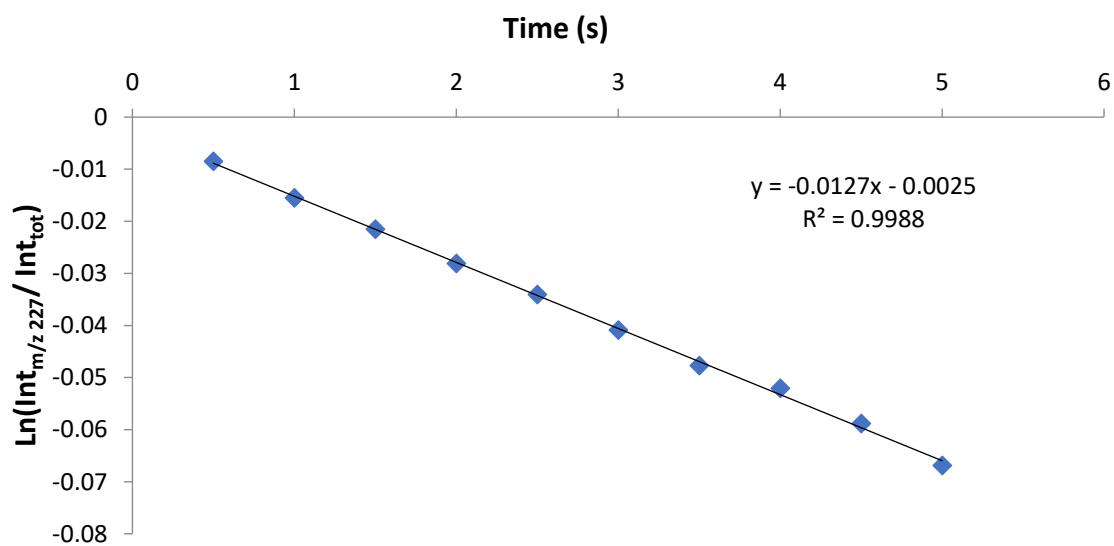


Figure S14. Early onset of the reaction of thiiranium ion **20** (m/z 227) with *cis*-cyclooctene (conc. $ca 6.13 \times 10^{10}$ molecules cm^{-3}) in the ion trap mass spectrometer in the formation of addition product m/z 337.

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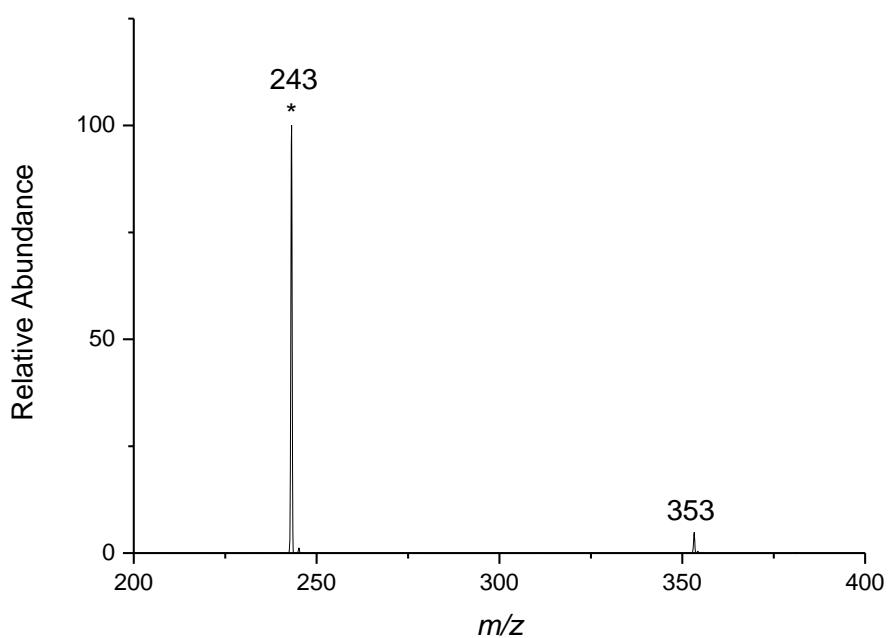


Figure S15. Ion-molecule reaction of thiiranium ion **21** (m/z 243) with *cis*-cyclooctene (conc. ca 6.13×10^{10} molecules cm^{-3}) for 10,000 ms. Addition product observed at m/z 353. The mass selected ion is denoted by an asterisk (sulphur isotope ^{32}S was selected).

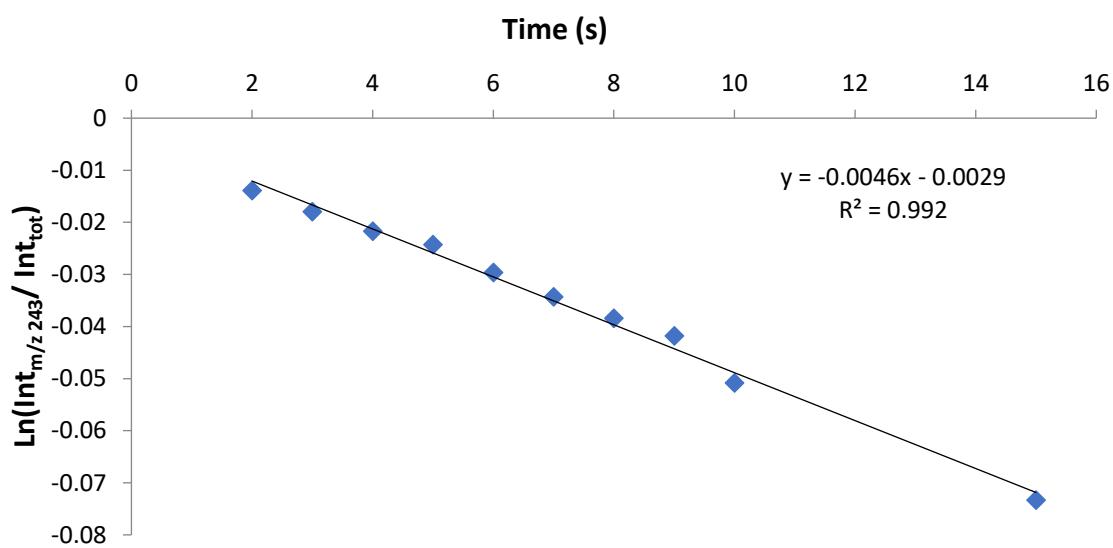


Figure S16. Early onset of the reaction of thiiranium ion **21** (m/z 243) with *cis*-cyclooctene (conc. ca 6.13×10^{10} molecules cm^{-3}) in the ion trap mass spectrometer in the formation of addition product m/z 353.

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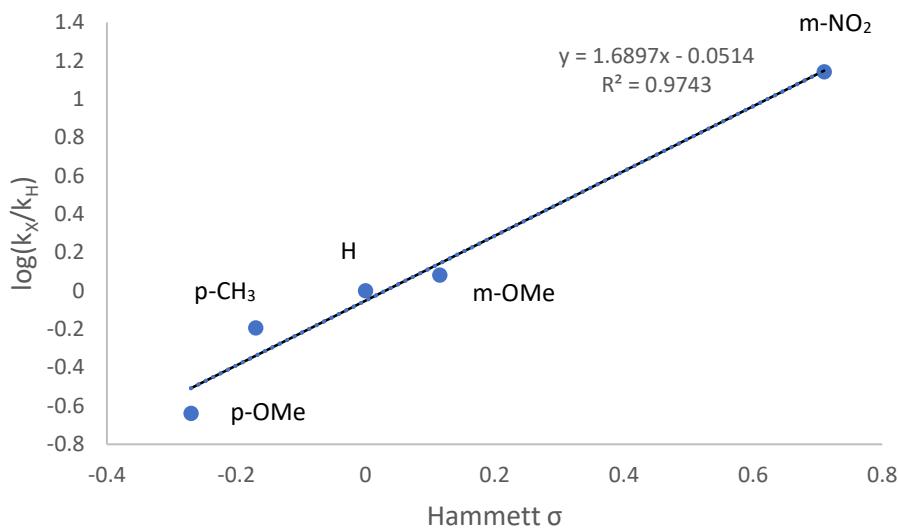


Figure S17. Hammett plot for addition of *cis*-cyclooctene to thiiranium ions **11** and **18-21** using σ constants. $\rho = +1.69$, $R^2 = 0.974$.

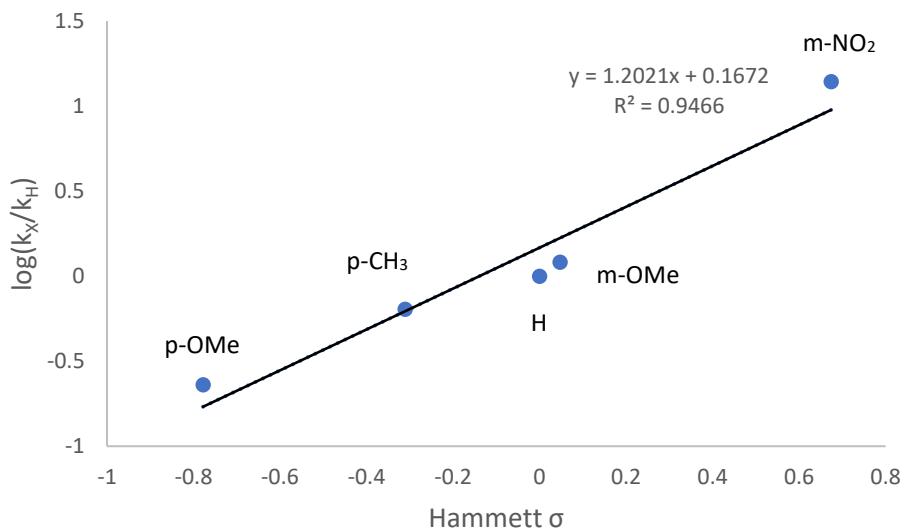


Figure S18. Hammett plot for addition of *cis*-cyclooctene to thiiranium ions **11** and **18-21** using σ^+ constants. $\rho = +1.20$, $R^2 = 0.947$

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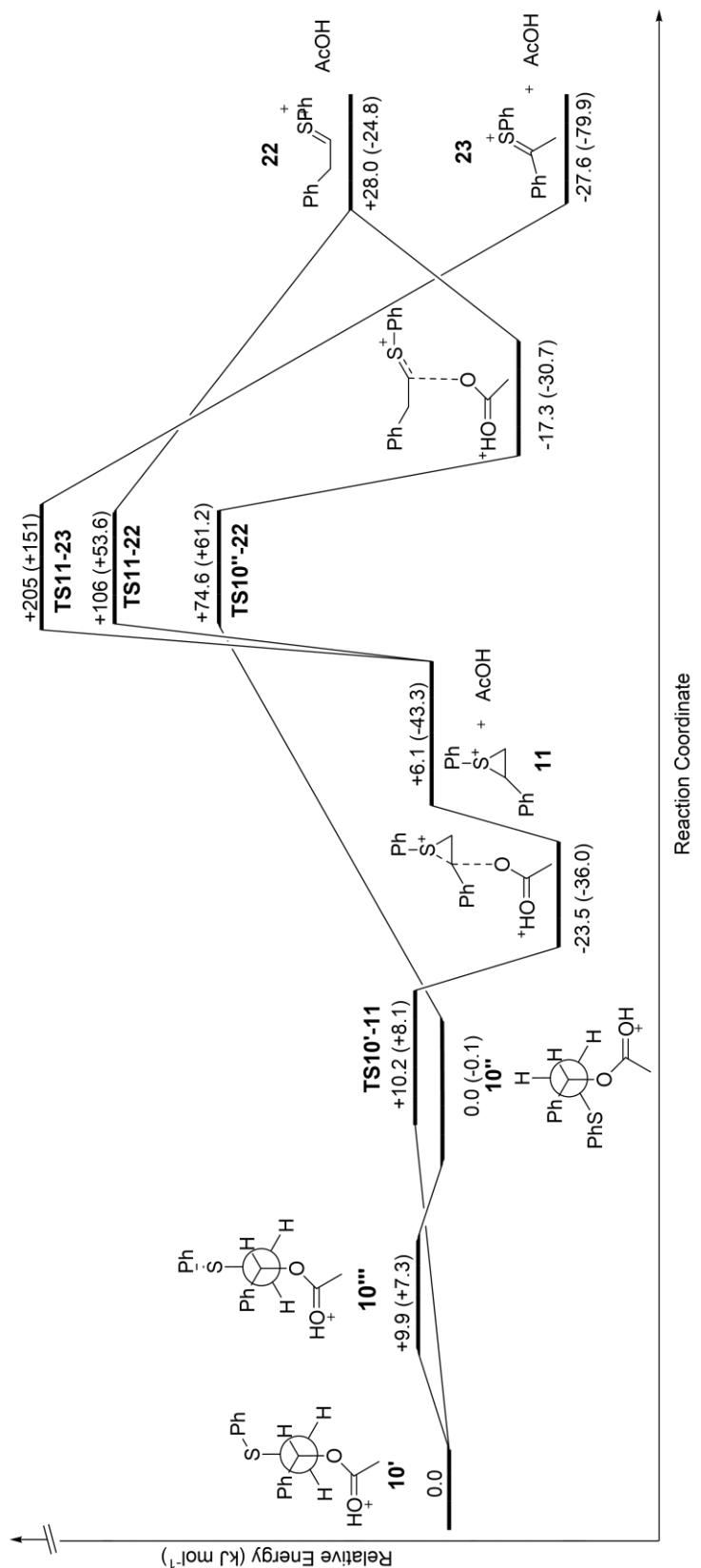


Figure S19. Full isomerisation pathway (expanded from **Figure 6**)

SUPPORTING INFORMATION

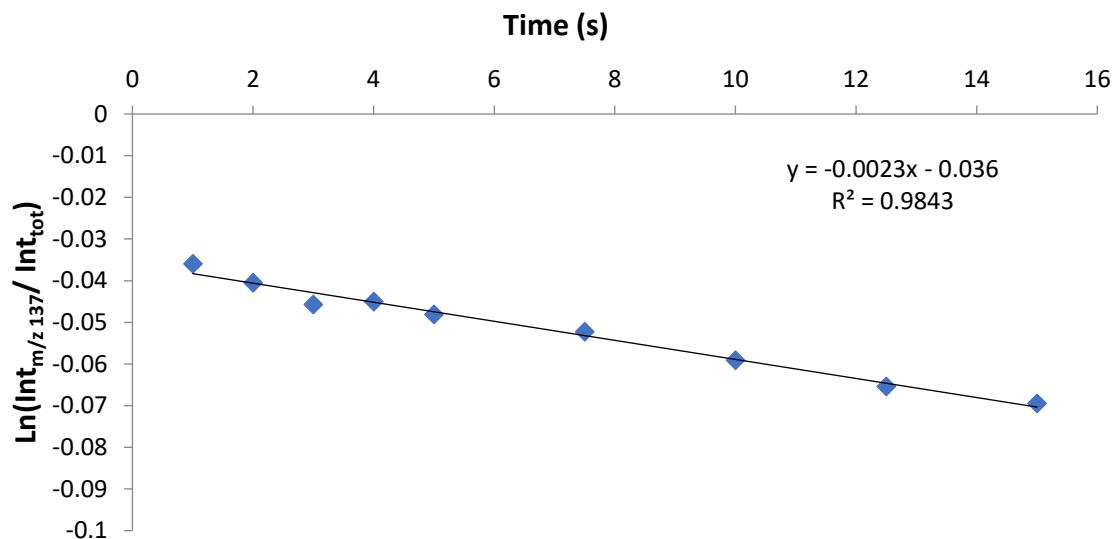


Figure S20. Early onset of the reaction of thiiranium ion **25** (m/z 137) with *cis*-cyclooctene (conc. *ca* 6.14×10^{10} molecules.cm $^{-3}$) in the ion trap mass spectrometer in the formation of addition product **30** (m/z 247).

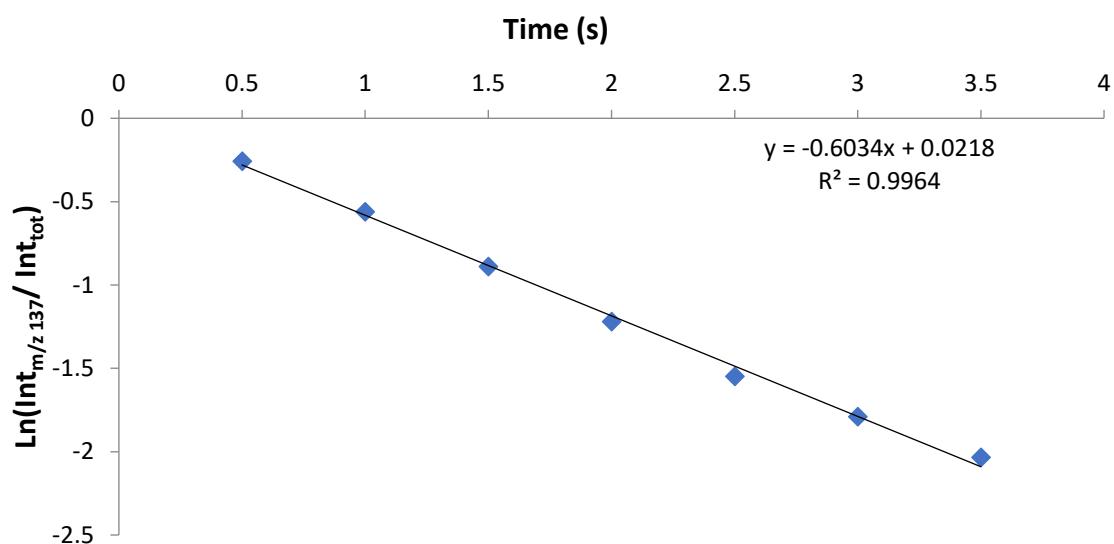


Figure S21. Early onset of the reaction of sulphonium ion **27** (m/z 137) with *cis*-cyclooctene (conc. *ca* 6.14×10^{10} molecules.cm $^{-3}$) in the ion trap mass spectrometer in the formation of addition product **32** (m/z 247).

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Table S1: Experimental and calculated vibrational frequencies (in cm^{-1}) of thiiranium ion **11** (m/z 213). Two sets of calculated intensities (in km mol^{-1}) are given in parentheses. The first column refers to the band number in Figure 7.

| Band # | Theory | Mode description | Exp. (-3dB) | Exp. |
|--------|------------|-----------------------------------|-------------|------|
| | 1058 (24) | Styrene CH ₂ twist | | |
| | 1063 (37) | S-C(Ph) st. | | |
| | 1087 (2) | | | |
| | 1088 (11) | | | |
| 1 | 1131 (20) | Styrene CH ₂ wag. | 1120 | 1130 |
| | 1184 (11) | | | |
| 2 | 1189 (36) | Styrene (Ph ip CH bend) | 1170 | 1180 |
| 3 | 1244 (78) | Styrene (CH bend) | 1240 | 1245 |
| 4 | 1328 (12) | | 1305 | 1310 |
| 5 | 1330 (66) | Styrene (Ph ip ring def.) | 1365 | 1375 |
| | 1345 (10) | | | |
| 6 | 1417 (124) | Styrene (Ph-CH st.) | 1405 | 1415 |
| | 1450 (6) | Ph(SPh) CH ip bend | | |
| | 1452 (24) | Styrene CH ₂ s-scis. | | |
| | 1475 (55) | Styrene (Ph ip CH bend + CH bend) | | |
| 7 | 1507 (90) | Styrene (Ph ip CH bend + CH bend) | | 1520 |
| 8 | 1584 (10) | | | |
| | 1601 (172) | Styrene Ph ip bend | 1585 | 1590 |

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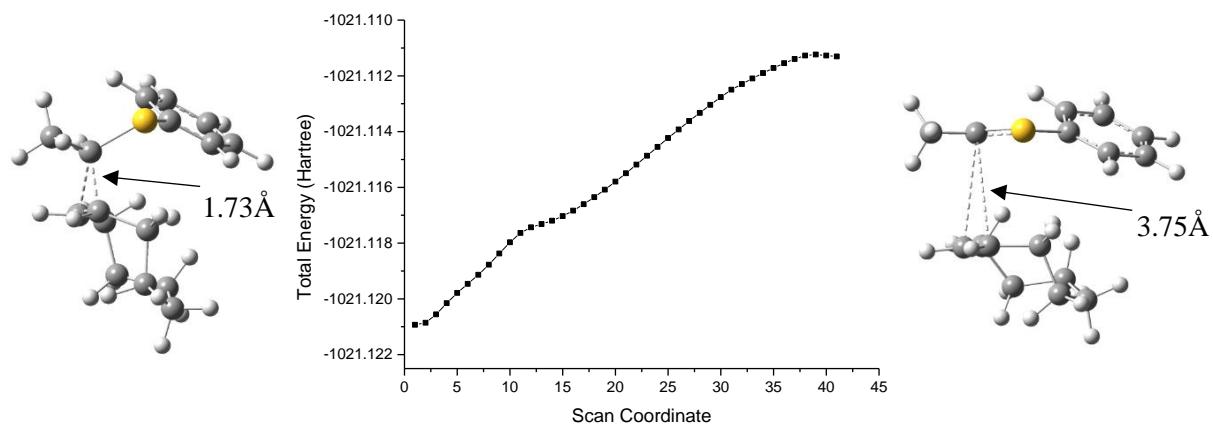


Figure S22. Scan of total energy upon lengthening of the midpoint of the C=C----C bond of **31'** (defined using general internal coordinates) at M06-2X/6-31+G(d). The slight dip at 15 steps corresponds to Association Complex **31**.

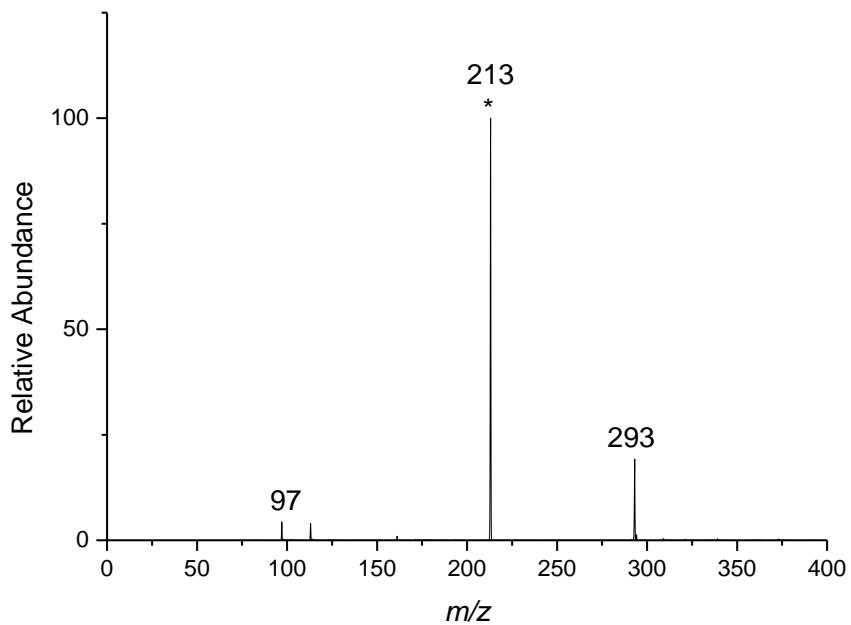


Figure S23. Ion-molecule reaction of thiiranium ion **11** (*m/z* 213) with 1,3-cyclohexadiene (conc. *ca* 10^{11} molecules cm^{-3}) for 1000 ms. Addition product observed at *m/z* 293. The mass selected ion is denoted by an asterisk (sulphur isotope ^{32}S was selected).

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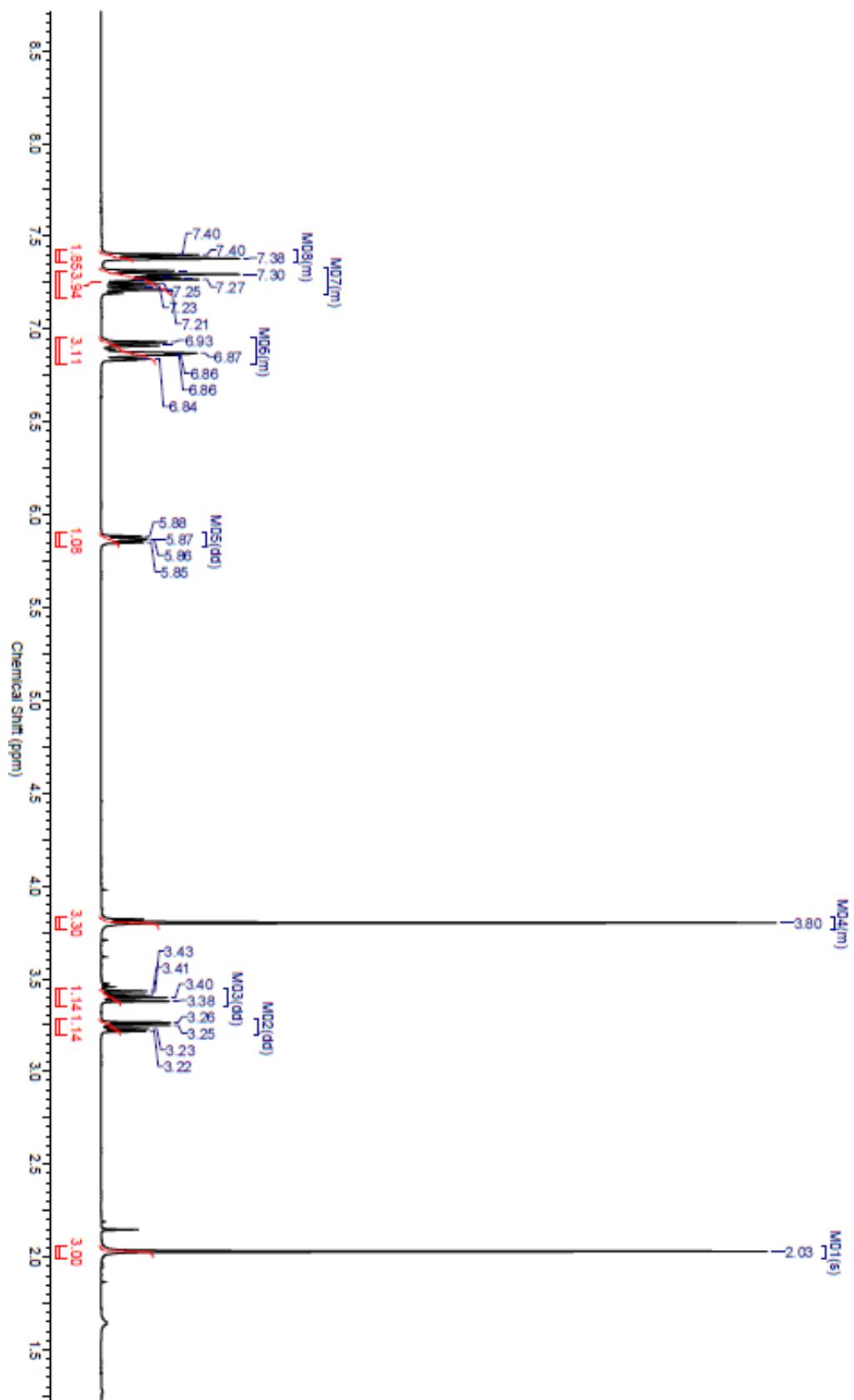


Figure S24: ¹H-NMR of 1-(3-Methoxyphenyl)-2-(phenylthiol)ethyl acetate **34** (CDCl₃, 400 MHz)

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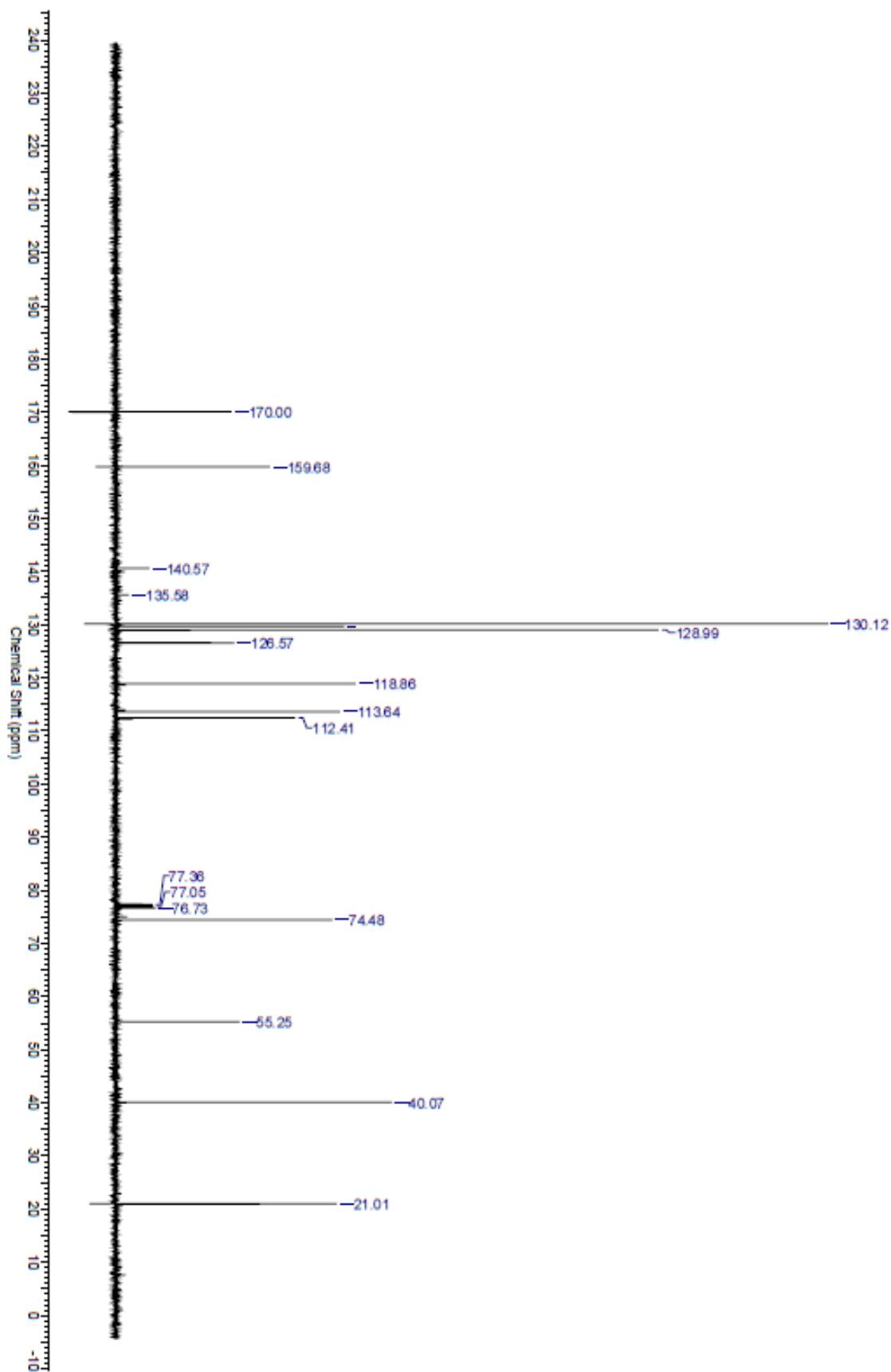


Figure S25: ¹³C-NMR of 1-(3-Methoxyphenyl)-2-(phenylthiol)ethyl acetate **34** (CDCl_3 , 400 MHz)

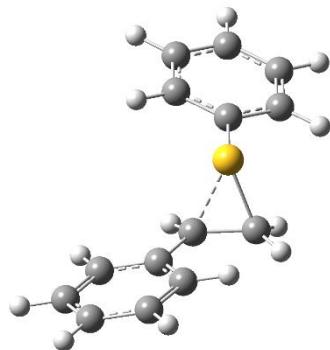
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Gaussian Cartesian Coordinates and Energies Calculated at M06-2X/def2-TZVP:

Energies given as sum of electronic and zero-point vibrational energies (E), sum of electronic and thermal enthalpies (H), sum of electronic and thermal Free energies (G), and zero-point vibrational energy (ZPVE) in Hartrees

Calculated energies and structures of species involved in Figure 4 (π -ligand exchange of cyclohexene with styrene at the sulphur of thiiranium ion **11**)

Thiiranium Ion **11**



E= -938.962390

H= -938.948717

G= -939.003707

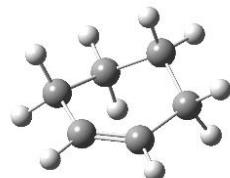
ZPVE= 0.229899

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 0.74702600 | -0.02208800 | 0.88469700 |
| H | 0.22680500 | 0.83839800 | 1.29074300 |
| C | 0.15748400 | -1.32242200 | 1.19446700 |
| H | -0.65422500 | -1.36357900 | 1.90848300 |
| H | 0.77454300 | -2.20932600 | 1.13485800 |
| S | -0.41210400 | -0.77816400 | -0.46007000 |
| C | -1.99886700 | -0.06129100 | -0.12693400 |
| C | -2.21967300 | 1.24984500 | -0.53221900 |
| C | -3.00559000 | -0.83835400 | 0.43444000 |
| C | -3.47923000 | 1.79893600 | -0.34678000 |
| H | -1.42548500 | 1.83061100 | -0.98474700 |
| C | -4.25809800 | -0.27305300 | 0.61332400 |
| H | -2.82206600 | -1.86726600 | 0.71806000 |
| C | -4.49200000 | 1.04050700 | 0.22547800 |
| H | -3.66794000 | 2.81901800 | -0.65219100 |
| H | -5.05293600 | -0.86227800 | 1.04986700 |
| H | -5.47293900 | 1.47420700 | 0.36625800 |
| C | 2.14399100 | 0.18939200 | 0.48245800 |
| C | 2.97461600 | -0.86075100 | 0.08851200 |
| C | 2.63892900 | 1.49323900 | 0.50666600 |
| C | 4.28489400 | -0.60439500 | -0.27396300 |
| H | 2.61132000 | -1.88079200 | 0.05566000 |
| C | 3.95433900 | 1.74356100 | 0.15336000 |

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| | | | |
|---|------------|-------------|-------------|
| H | 1.99572400 | 2.30895100 | 0.81465200 |
| C | 4.77583200 | 0.69590700 | -0.23898100 |
| H | 4.92731500 | -1.41874700 | -0.57978200 |
| H | 4.33785000 | 2.75420200 | 0.18413000 |
| H | 5.80295000 | 0.89062800 | -0.51722300 |

Cyclohexene



E= -234.466555

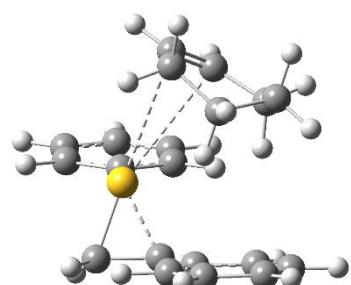
H= -234.460147

G= -234.495133

ZPVE= 0.147371

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 0.66136200 | 1.29625600 | 0.06006100 |
| C | -0.66136200 | 1.29625600 | -0.06006100 |
| C | -1.48917200 | 0.04202400 | -0.11162000 |
| C | -0.68856500 | -1.18126700 | 0.32844500 |
| C | 0.68856500 | -1.18126700 | -0.32844500 |
| C | 1.48917200 | 0.04202400 | 0.11162000 |
| H | -2.37473000 | 0.16382700 | 0.51698400 |
| H | -1.18890700 | 2.24244800 | -0.11903300 |
| H | 1.18890700 | 2.24244800 | 0.11903300 |
| H | -0.56334000 | -1.15602300 | 1.41533700 |
| H | -1.23343600 | -2.09593100 | 0.08968500 |
| H | 1.23343600 | -2.09593100 | -0.08968500 |
| H | 0.56334000 | -1.15602300 | -1.41533700 |
| H | 1.86459700 | -0.10225600 | 1.13116400 |
| H | 2.37473000 | 0.16382700 | -0.51698400 |
| H | -1.86459700 | -0.10225600 | -1.13116400 |

Association Complex 12a



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E= -1173.441239

H= -1173.420291

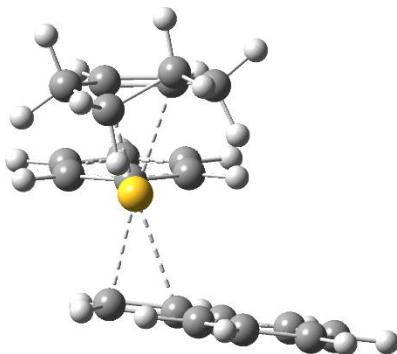
G= -1173.492416

ZPVE= 0.378280

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| S | 0.68435600 | -0.46374000 | -1.17637300 |
| C | 2.12636400 | -1.15416500 | -0.40229100 |
| C | 3.17411300 | -1.57449500 | -1.21259800 |
| C | 2.20838200 | -1.19328200 | 0.98355600 |
| C | 4.32522000 | -2.06176800 | -0.61279000 |
| H | 3.09630100 | -1.52089700 | -2.29146500 |
| C | 3.36466400 | -1.68702600 | 1.56769600 |
| H | 1.38941900 | -0.83550000 | 1.59525000 |
| C | 4.41783500 | -2.11923400 | 0.77172200 |
| H | 5.14940100 | -2.39435800 | -1.22893800 |
| H | 3.44345100 | -1.72945200 | 2.64549900 |
| H | 5.31828400 | -2.50102000 | 1.23389100 |
| C | -4.43838800 | 0.40591400 | -0.13026500 |
| C | -3.72036000 | -0.03504600 | 0.97429600 |
| C | -2.52768200 | -0.71418700 | 0.79421100 |
| C | -2.04511600 | -0.95596700 | -0.49229000 |
| C | -2.77599700 | -0.52274500 | -1.59757800 |
| C | -3.96933400 | 0.15622600 | -1.41350000 |
| H | -5.37045300 | 0.93725600 | 0.00874700 |
| H | -4.09201300 | 0.14728300 | 1.97356900 |
| H | -1.96634600 | -1.06120300 | 1.65410600 |
| H | -2.42848200 | -0.70606700 | -2.60611900 |
| H | -4.53544800 | 0.48930700 | -2.27263200 |
| C | -0.73786200 | -1.62000400 | -0.62361800 |
| H | -0.38388300 | -2.16256400 | 0.24603300 |
| C | -0.10109000 | -1.96574300 | -1.89227900 |
| H | -0.61140000 | -1.74542600 | -2.81989500 |
| H | 0.57459600 | -2.80984300 | -1.91650600 |
| C | 1.33542800 | 2.05179200 | 0.90007600 |
| C | 1.33508700 | 2.62481700 | -0.30108900 |
| H | 2.27781500 | 2.76802400 | -0.82046900 |
| H | 2.27697800 | 1.72598800 | 1.33057700 |
| C | 0.09505000 | 3.13431200 | -0.97949200 |
| H | 0.14857000 | 4.22722100 | -1.02229700 |
| H | 0.08493500 | 2.80500200 | -2.02311700 |
| C | 0.08919300 | 1.87947800 | 1.72629500 |
| H | -0.25404100 | 0.83510900 | 1.67389000 |
| H | 0.31806800 | 2.06462800 | 2.77776000 |
| C | -1.03216800 | 2.79729600 | 1.24683800 |
| H | -0.79037300 | 3.82751300 | 1.52154400 |
| H | -1.96905100 | 2.54177600 | 1.74434300 |
| C | -1.18477800 | 2.69743600 | -0.26720800 |
| H | -2.02853100 | 3.29549700 | -0.61331600 |
| H | -1.41568400 | 1.65798900 | -0.52464900 |

SUPPORTING INFORMATION

Transition State TS12a-13a



E= -1173.418168

H= -1173.397556

G= -1173.469245

ZPVE= 0.377228

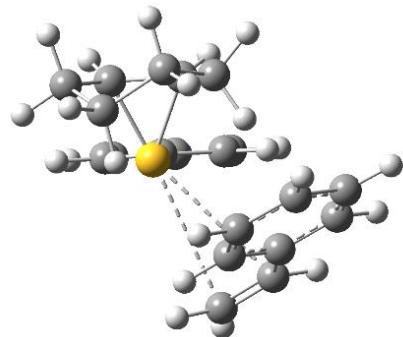
Imaginary Frequency = -280.4135 cm⁻¹

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| S | 0.52461900 | 0.09941500 | -0.54280800 |
| C | 1.96295500 | -0.82580400 | -0.07215200 |
| C | 3.02728300 | -0.95727500 | -0.96156900 |
| C | 2.01528100 | -1.42124700 | 1.18548700 |
| C | 4.14474900 | -1.68657900 | -0.58799200 |
| H | 2.97555200 | -0.49011500 | -1.93768100 |
| C | 3.13740700 | -2.14923900 | 1.55228200 |
| H | 1.18124400 | -1.31198800 | 1.86828800 |
| C | 4.19924800 | -2.28129100 | 0.66702400 |
| H | 4.97316200 | -1.79078400 | -1.27568000 |
| H | 3.18187600 | -2.61319200 | 2.52842800 |
| H | 5.07334500 | -2.84969300 | 0.95560700 |
| C | -4.75146000 | -0.62406500 | 0.56652300 |
| C | -4.02995800 | -1.55021500 | 1.30751900 |
| C | -2.78717400 | -1.96750500 | 0.86274100 |
| C | -2.25659000 | -1.47222900 | -0.33294100 |
| C | -2.99458100 | -0.53786500 | -1.07143500 |
| C | -4.23134400 | -0.11695300 | -0.62110500 |
| H | -5.72423800 | -0.29782900 | 0.91015900 |
| H | -4.43722800 | -1.94670800 | 2.22759000 |
| H | -2.22065400 | -2.69217500 | 1.43553100 |
| H | -2.60838000 | -0.14537300 | -2.00366100 |
| H | -4.80033600 | 0.59985600 | -1.19769000 |
| C | -0.94709000 | -1.93426100 | -0.74937200 |
| H | -0.45839100 | -2.63815100 | -0.08166800 |
| C | -0.26995800 | -1.56925900 | -1.88246500 |
| H | -0.73674700 | -0.97229300 | -2.65393700 |
| H | 0.64493800 | -2.07812700 | -2.15096600 |
| C | 1.03955800 | 1.94513900 | 0.94341000 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|------------|-------------|
| C | 1.64523300 | 2.19003700 | -0.25690300 |
| H | 2.65784700 | 1.83428800 | -0.41313900 |
| H | 1.57404100 | 1.36336200 | 1.68654600 |
| C | 1.05195000 | 3.09842700 | -1.29011200 |
| H | 1.62032400 | 4.03515400 | -1.25462100 |
| H | 1.22067700 | 2.68335900 | -2.28539400 |
| C | -0.27268000 | 2.55348300 | 1.33319700 |
| H | -1.04284100 | 1.77237100 | 1.30739000 |
| H | -0.20660500 | 2.86795200 | 2.37684200 |
| C | -0.66566200 | 3.72112600 | 0.42852800 |
| H | -0.06896500 | 4.59882600 | 0.69012900 |
| H | -1.70878200 | 3.98380500 | 0.60041600 |
| C | -0.42862700 | 3.37348800 | -1.03782100 |
| H | -0.76683900 | 4.18067800 | -1.68650800 |
| H | -1.01792600 | 2.48877700 | -1.30129300 |

Dissociation Complex 13a



E= -1173.441239

H= -1173.420291

G= -1173.492416

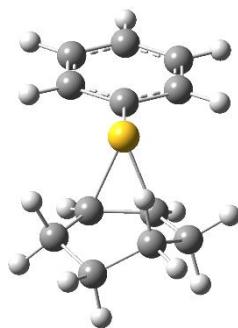
ZPVE= 0.378280

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| S | 0.68435600 | -0.46374000 | -1.17637300 |
| C | 2.12636400 | -1.15416500 | -0.40229100 |
| C | 3.17411300 | -1.57449500 | -1.21259800 |
| C | 2.20838200 | -1.19328200 | 0.98355600 |
| C | 4.32522000 | -2.06176800 | -0.61279000 |
| H | 3.09630100 | -1.52089700 | -2.29146500 |
| C | 3.36466400 | -1.68702600 | 1.56769600 |
| H | 1.38941900 | -0.83550000 | 1.59525000 |
| C | 4.41783500 | -2.11923400 | 0.77172200 |
| H | 5.14940100 | -2.39435800 | -1.22893800 |
| H | 3.44345100 | -1.72945200 | 2.64549900 |
| H | 5.31828400 | -2.50102000 | 1.23389100 |
| C | -4.43838800 | 0.40591400 | -0.13026500 |
| C | -3.72036000 | -0.03504600 | 0.97429600 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| C | -2.52768200 | -0.71418700 | 0.79421100 |
| C | -2.04511600 | -0.95596700 | -0.49229000 |
| C | -2.77599700 | -0.52274500 | -1.59757800 |
| C | -3.96933400 | 0.15622600 | -1.41350000 |
| H | -5.37045300 | 0.93725600 | 0.00874700 |
| H | -4.09201300 | 0.14728300 | 1.97356900 |
| H | -1.96634600 | -1.06120300 | 1.65410600 |
| H | -2.42848200 | -0.70606700 | -2.60611900 |
| H | -4.53544800 | 0.48930700 | -2.27263200 |
| C | -0.73786200 | -1.62000400 | -0.62361800 |
| H | -0.38388300 | -2.16256400 | 0.24603300 |
| C | -0.10109000 | -1.96574300 | -1.89227900 |
| H | -0.61140000 | -1.74542600 | -2.81989500 |
| H | 0.57459600 | -2.80984300 | -1.91650600 |
| C | 1.33542800 | 2.05179200 | 0.90007600 |
| C | 1.33508700 | 2.62481700 | -0.30108900 |
| H | 2.27781500 | 2.76802400 | -0.82046900 |
| H | 2.27697800 | 1.72598800 | 1.33057700 |
| C | 0.09505000 | 3.13431200 | -0.97949200 |
| H | 0.14857000 | 4.22722100 | -1.02229700 |
| H | 0.08493500 | 2.80500200 | -2.02311700 |
| C | 0.08919300 | 1.87947800 | 1.72629500 |
| H | -0.25404100 | 0.83510900 | 1.67389000 |
| H | 0.31806800 | 2.06462800 | 2.77776000 |
| C | -1.03216800 | 2.79729600 | 1.24683800 |
| H | -0.79037300 | 3.82751300 | 1.52154400 |
| H | -1.96905100 | 2.54177600 | 1.74434300 |
| C | -1.18477800 | 2.69743600 | -0.26720800 |
| H | -2.02853100 | 3.29549700 | -0.61331600 |
| H | -1.41568400 | 1.65798900 | -0.52464900 |

Product Ion 14a



E= -863.950979

H= -863.938542

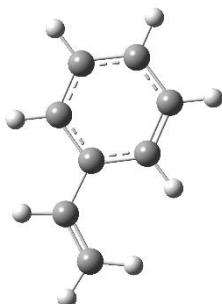
G= -863.989449

ZPVE= 0.242955

SUPPORTING INFORMATION

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| S | 0.25667500 | 0.02396400 | 0.82808800 |
| C | 1.16749300 | -0.76133400 | -0.60543100 |
| H | 0.43180200 | -1.27501800 | -1.21341300 |
| C | 1.15027000 | 0.70603900 | -0.66363400 |
| H | 0.41757700 | 1.16151000 | -1.32042000 |
| C | -1.44095500 | 0.00656000 | 0.31255000 |
| C | -2.09286700 | 1.21495400 | 0.09832100 |
| C | -2.10319200 | -1.21234900 | 0.22910900 |
| C | -3.43929300 | 1.19394200 | -0.23095500 |
| H | -1.56360700 | 2.15532100 | 0.19049600 |
| C | -3.44927700 | -1.21524700 | -0.10241100 |
| H | -1.58171500 | -2.14173000 | 0.42161500 |
| C | -4.11256500 | -0.01679200 | -0.33237000 |
| H | -3.96200700 | 2.12471600 | -0.40388700 |
| H | -3.97962700 | -2.15483100 | -0.17617100 |
| H | -5.16358700 | -0.02612900 | -0.58817900 |
| C | 2.43317500 | -1.52536500 | -0.25005600 |
| H | 2.30114100 | -2.01795900 | 0.71447600 |
| H | 2.54009000 | -2.32275500 | -0.98608700 |
| C | 3.68033900 | -0.63861100 | -0.23074500 |
| H | 4.01319700 | -0.45279600 | -1.25510100 |
| H | 4.48560400 | -1.17405700 | 0.26962800 |
| C | 3.41111900 | 0.69859100 | 0.45151100 |
| H | 3.04923500 | 0.53841600 | 1.47292600 |
| H | 4.32977100 | 1.27674100 | 0.53785200 |
| C | 2.39305400 | 1.50030400 | -0.35412900 |
| H | 2.82407600 | 1.76627600 | -1.32491000 |
| H | 2.12033900 | 2.43513700 | 0.13557900 |

Styrene



E= -309.482605

H= -309.475774

G= -309.512470

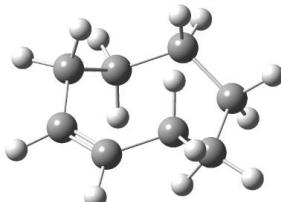
ZPVE= 0.134219

SUPPORTING INFORMATION

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 2.24915500 | 0.26465200 | 0.00014000 |
| C | 1.77288800 | -1.03720000 | 0.00018000 |
| C | 0.40599600 | -1.27507800 | 0.00001100 |
| C | -0.50947600 | -0.22294600 | -0.00017100 |
| C | -0.01449200 | 1.08355000 | -0.00024800 |
| C | 1.34812600 | 1.32399600 | -0.00008500 |
| H | 3.31414400 | 0.45624800 | 0.00025800 |
| H | 2.46471400 | -1.86952200 | 0.00033300 |
| H | 0.03638700 | -2.29381500 | 0.00004000 |
| H | -0.70007100 | 1.92084100 | -0.00049300 |
| H | 1.71276800 | 2.34314900 | -0.00016000 |
| C | -1.94802000 | -0.53277900 | -0.00028500 |
| H | -2.18340300 | -1.59295700 | -0.00093700 |
| C | -2.95227700 | 0.33645100 | 0.00038400 |
| H | -2.79618400 | 1.40758800 | 0.00114700 |
| H | -3.97826900 | -0.00479500 | 0.00022700 |

Calculated energies and structures of species involved in Figure 4 (π -ligand exchange of *cis*-cyclooctene with styrene at the sulphur of thiiranium ion **11**)

***cis*-Cyclooctene**



E= -313.004249

H= -312.995450

G= -313.036148

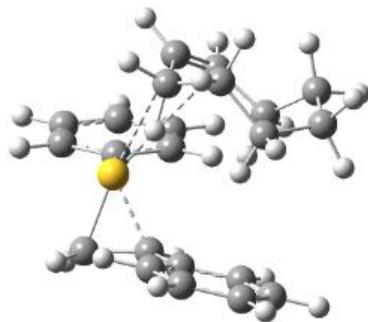
ZPVE= 0.205463

| Symbol | X | Y | Z |
|--------|------------|-------------|-------------|
| C | 0.61044500 | 0.18140500 | -0.09808000 |
| C | 2.10186300 | -0.04029900 | -0.07365700 |
| C | 1.18474500 | 3.38569100 | -0.05007100 |
| C | 2.95210200 | 0.97599000 | 0.72646600 |
| C | 2.70958300 | 3.49009600 | 0.03483300 |
| C | 3.48421300 | 2.17327200 | -0.07994500 |
| H | 2.48453900 | -0.07221600 | -1.09940100 |
| H | 2.38882100 | 1.32036500 | 1.59775800 |
| H | 0.79742600 | 3.02518500 | 0.90446400 |
| H | 2.96233200 | 3.97236000 | 0.98316800 |
| H | 0.00254200 | -0.60410000 | 0.33905600 |
| H | 2.28085900 | -1.03336400 | 0.33953300 |
| H | 0.77891600 | 4.39063800 | -0.17977100 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|------------|-------------|
| H | 3.81206800 | 0.43088000 | 1.11931700 |
| H | 3.07071400 | 4.15983500 | -0.75096900 |
| H | 4.51136600 | 2.37869700 | 0.22952100 |
| H | 3.55614400 | 1.87938000 | -1.13019500 |
| C | -0.01560700 | 1.23900900 | -0.60125300 |
| H | -1.09900700 | 1.27036500 | -0.54065200 |
| C | 0.66644600 | 2.45056900 | -1.17020700 |
| H | 1.49971600 | 2.14009400 | -1.80602800 |
| H | -0.02759100 | 2.98827200 | -1.81577500 |

Association Complex 12b



E= -1251.981105

H= -1251.957756

G= -1252.035022

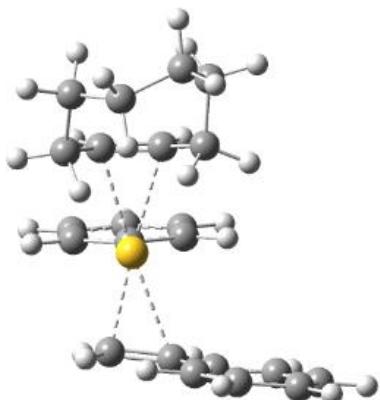
ZPVE= 0.436545

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -1.26869600 | 2.56550700 | -0.74785300 |
| H | -2.25747600 | 2.93098000 | -0.50632900 |
| S | -1.22276100 | 0.73680300 | -0.90919200 |
| H | -0.76999500 | 3.06086000 | -1.57016100 |
| C | -0.29787100 | -2.35056200 | -0.14321000 |
| H | -1.19158200 | -2.91447400 | 0.10849400 |
| C | 0.02027100 | -2.23592600 | -1.43210400 |
| H | -0.64606200 | -2.70547900 | -2.14923700 |
| C | -2.77374600 | 0.28237600 | -0.17216400 |
| C | -3.93925600 | 0.53214100 | -0.88675400 |
| C | -2.78733600 | -0.37418800 | 1.05061900 |
| C | -5.14955300 | 0.12478900 | -0.34738000 |
| H | -3.90517700 | 1.03164100 | -1.84711600 |
| C | -4.00667700 | -0.77092000 | 1.57837500 |
| H | -1.86284800 | -0.57689000 | 1.57564500 |
| C | -5.18183000 | -0.52229700 | 0.88125800 |
| H | -6.06630000 | 0.31183200 | -0.88968800 |
| H | -4.03665500 | -1.27857000 | 2.53288600 |
| H | -6.12951500 | -0.83752700 | 1.29680700 |
| C | 0.54432100 | -1.86802700 | 1.00431200 |
| H | 0.90868000 | -0.85433900 | 0.80150000 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | -0.06421400 | -1.81000500 | 1.90842500 |
| C | 1.23022100 | -1.54634700 | -2.01155900 |
| H | 1.15694000 | -1.61680300 | -3.09695100 |
| H | 1.19878300 | -0.47333000 | -1.78071600 |
| C | 2.62308500 | -2.06437900 | -1.58159200 |
| H | 3.29700700 | -1.88000100 | -2.41883600 |
| H | 2.59123100 | -3.14885200 | -1.45536400 |
| C | 1.75372400 | -2.80246100 | 1.26364200 |
| H | 1.64016000 | -3.69244800 | 0.64344100 |
| H | 1.73982400 | -3.15147800 | 2.29672100 |
| C | 3.21191300 | -1.38390900 | -0.33422200 |
| H | 2.74311000 | -0.40190100 | -0.22017300 |
| H | 4.26943300 | -1.17412600 | -0.50782500 |
| C | 3.11019500 | -2.15616000 | 0.98296900 |
| H | 3.36119200 | -1.46970300 | 1.79767800 |
| H | 3.86923600 | -2.94167200 | 1.00298600 |
| C | -0.46032500 | 1.97656600 | 0.32018000 |
| H | -0.96086400 | 1.83930800 | 1.27204800 |
| C | 1.01334500 | 2.02357500 | 0.36401400 |
| C | 1.64276400 | 1.73007100 | 1.57300600 |
| C | 1.78181600 | 2.36781100 | -0.74857000 |
| C | 3.02321400 | 1.79841700 | 1.67476100 |
| H | 1.04865200 | 1.45815300 | 2.43763800 |
| C | 3.16103600 | 2.42905600 | -0.64460800 |
| H | 1.31791300 | 2.58925500 | -1.70226700 |
| C | 3.78194300 | 2.15023200 | 0.56719400 |
| H | 3.50479400 | 1.58057800 | 2.61838500 |
| H | 3.75306200 | 2.69850100 | -1.50859300 |
| H | 4.85949800 | 2.20545300 | 0.64577200 |

Transition State TS12b-13b



E= -1251.958759

H= -1251.935645

G= -1252.013534

ZPVE= 0.435509

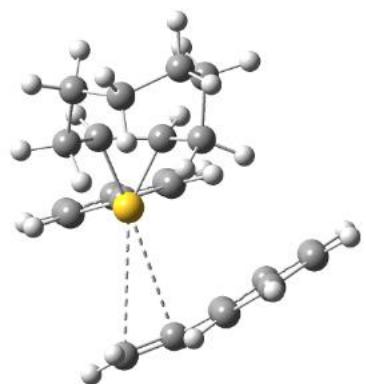
Imaginary Frequency = -277.2827 cm⁻¹

SUPPORTING INFORMATION

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 2.04751600 | 0.41411700 | -1.89244200 |
| H | 2.20607700 | 1.44949100 | -2.15838400 |
| S | 0.22481700 | 0.57518600 | -0.61570900 |
| H | 1.68634400 | -0.23578500 | -2.67773600 |
| C | -1.74919500 | 0.49991600 | 0.81083900 |
| H | -1.44256400 | 1.23725600 | 1.54635400 |
| C | -2.16901800 | 0.95495100 | -0.40383600 |
| H | -2.17376900 | 2.02923500 | -0.55780300 |
| C | 0.63029300 | 2.21287000 | -0.05981300 |
| C | 0.44269100 | 3.29995300 | -0.90946500 |
| C | 1.12946500 | 2.39943300 | 1.22637100 |
| C | 0.75869000 | 4.57567100 | -0.46842000 |
| H | 0.05051100 | 3.14375200 | -1.90719300 |
| C | 1.44332100 | 3.67862500 | 1.66056100 |
| H | 1.26656300 | 1.54565800 | 1.87934700 |
| C | 1.25849700 | 4.76424100 | 0.81418700 |
| H | 0.61325900 | 5.42251200 | -1.12553900 |
| H | 1.83148100 | 3.82739900 | 2.65923800 |
| H | 1.50383700 | 5.76112100 | 1.15531800 |
| C | -1.90287000 | -0.90684400 | 1.28034800 |
| H | -1.71570900 | -1.60391300 | 0.46074100 |
| H | -1.16881900 | -1.11867000 | 2.05638200 |
| C | -2.78804000 | 0.10183400 | -1.47102100 |
| H | -2.87586200 | 0.70612700 | -2.37305800 |
| H | -2.11565800 | -0.72511900 | -1.71899300 |
| C | -4.17613100 | -0.49134700 | -1.11204400 |
| H | -4.74746300 | -0.52090400 | -2.03956400 |
| H | -4.71713300 | 0.18982300 | -0.45035200 |
| C | -3.34868400 | -1.08991000 | 1.82056400 |
| H | -3.83728900 | -0.11395700 | 1.86480200 |
| H | -3.30829500 | -1.44545200 | 2.84995600 |
| C | -4.14238400 | -1.91241900 | -0.52445600 |
| H | -3.25297600 | -2.42471400 | -0.90122400 |
| H | -4.98434900 | -2.47409400 | -0.93190500 |
| C | -4.21523300 | -2.04838500 | 1.00017800 |
| H | -3.95237100 | -3.07775500 | 1.25523300 |
| H | -5.24976700 | -1.91194100 | 1.32268900 |
| C | 2.62039200 | -0.09293700 | -0.75089200 |
| H | 3.07310700 | 0.61822700 | -0.06608400 |
| C | 2.69686900 | -1.48468000 | -0.35828200 |
| C | 3.30081800 | -1.79472800 | 0.86522800 |
| C | 2.18709600 | -2.52162600 | -1.15059300 |
| C | 3.39925900 | -3.10859300 | 1.28829600 |
| H | 3.70118100 | -0.99523200 | 1.47747200 |
| C | 2.28120000 | -3.83182300 | -0.72282900 |
| H | 1.72603500 | -2.30791000 | -2.10627800 |
| C | 2.88771400 | -4.12693300 | 0.49506300 |
| H | 3.87548600 | -3.34043200 | 2.23117400 |
| H | 1.89182100 | -4.63032100 | -1.33981300 |
| H | 2.96565700 | -5.15569800 | 0.82129900 |

SUPPORTING INFORMATION

Dissociation Complex 13b



E= -1251.995585

H= -1251.972015

G= -1252.051115

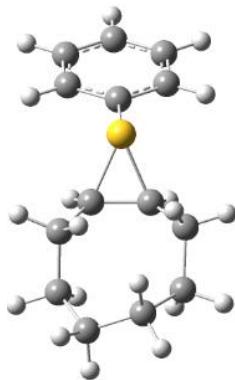
ZPVE= 0.436567

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 2.51866100 | -0.81894700 | -2.66530900 |
| H | 3.25977500 | -0.20788600 | -3.16230800 |
| S | 0.10897700 | 0.58251100 | -0.60452700 |
| H | 1.61252000 | -1.03251400 | -3.21984700 |
| C | -1.19024900 | 0.57296600 | 0.71409900 |
| H | -0.73048200 | 0.84355100 | 1.65850700 |
| C | -1.35625500 | 1.67958800 | -0.23686900 |
| H | -1.00756200 | 2.64797700 | 0.10585700 |
| C | 1.48203600 | 1.41957900 | 0.14894800 |
| C | 2.10868400 | 2.41636300 | -0.58911000 |
| C | 1.96084500 | 1.01405500 | 1.38690500 |
| C | 3.22974000 | 3.03453800 | -0.05810000 |
| H | 1.73134600 | 2.70116800 | -1.56338600 |
| C | 3.08408000 | 1.64247300 | 1.90492900 |
| H | 1.47826200 | 0.21194000 | 1.93071400 |
| C | 3.71448300 | 2.64875900 | 1.18542100 |
| H | 3.72535000 | 3.81594000 | -0.61789800 |
| H | 3.46730500 | 1.34166700 | 2.87064700 |
| H | 4.59062100 | 3.13375600 | 1.59452400 |
| C | -2.14549400 | -0.58447700 | 0.77845100 |
| H | -2.41871200 | -0.91541100 | -0.22428500 |
| H | -1.64957000 | -1.42448700 | 1.26277300 |
| C | -2.41577000 | 1.68982900 | -1.31288600 |
| H | -2.17503100 | 2.51188600 | -1.98679700 |
| H | -2.35578500 | 0.77684500 | -1.90881100 |
| C | -3.85799800 | 1.84781000 | -0.77828700 |
| H | -4.38608600 | 2.47300300 | -1.49729700 |
| H | -3.85905100 | 2.41197300 | 0.15876400 |
| C | -3.38675000 | -0.10688400 | 1.57032200 |
| H | -3.19909000 | 0.89979200 | 1.95571600 |
| H | -3.51683400 | -0.73405100 | 2.45182200 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| C | -4.63349700 | 0.52698500 | -0.62558700 |
| H | -4.23181200 | -0.19732100 | -1.33916300 |
| H | -5.66372800 | 0.69226800 | -0.94265400 |
| C | -4.69195400 | -0.09395900 | 0.77431300 |
| H | -5.06409100 | -1.11584100 | 0.67313100 |
| H | -5.43339700 | 0.44020700 | 1.37214200 |
| C | 2.73908700 | -1.30098200 | -1.44532300 |
| H | 3.66759400 | -1.04373200 | -0.94330400 |
| C | 1.81945100 | -2.14364800 | -0.66430900 |
| C | 2.05567000 | -2.31925800 | 0.70002200 |
| C | 0.70157700 | -2.76687900 | -1.22970100 |
| C | 1.19322300 | -3.07283300 | 1.48620700 |
| H | 2.93772300 | -1.87015600 | 1.14269300 |
| C | -0.15631300 | -3.52333900 | -0.44951100 |
| H | 0.51956000 | -2.68465700 | -2.29384600 |
| C | 0.08293200 | -3.67591500 | 0.91310900 |
| H | 1.40328400 | -3.21045100 | 2.53914200 |
| H | -1.00370300 | -4.01738300 | -0.90746000 |
| H | -0.57916900 | -4.28320700 | 1.51665300 |

Product Ion 14b



E= -942.498188

H= -942.483323

G= -942.539560

ZPVE= 0.301118

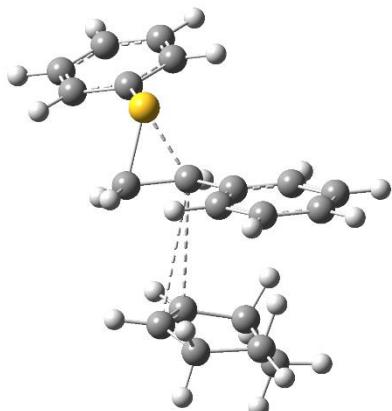
| Symbol | X | Y | Z |
|--------|------------|-------------|-------------|
| C | 0.60642600 | 0.75872900 | -0.23223100 |
| C | 1.73404300 | 1.65188500 | 0.22635500 |
| C | 2.79762900 | -1.58989700 | -0.67606100 |
| C | 3.03469300 | 1.49059700 | -0.59506000 |
| C | 4.13880900 | -0.88523100 | -0.47250600 |
| C | 4.08243700 | 0.55838300 | 0.03915200 |
| H | 1.95398100 | 1.47329100 | 1.28062000 |
| H | 2.80578500 | 1.18279000 | -1.61944100 |
| H | 2.33654200 | -1.21322100 | -1.59400000 |
| H | 4.66486300 | -0.90641300 | -1.42907100 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | 0.00861300 | 1.12522000 | -1.06030400 |
| H | 1.37285600 | 2.67785300 | 0.15795100 |
| H | 2.97604100 | -2.64945000 | -0.85592600 |
| H | 3.46856700 | 2.48621300 | -0.67861400 |
| H | 4.75017700 | -1.46489200 | 0.22233600 |
| H | 5.07051700 | 0.99055200 | -0.12190000 |
| H | 3.94577700 | 0.56654300 | 1.12382200 |
| C | 0.60692700 | -0.69551600 | -0.04746900 |
| H | -0.00686200 | -1.25258700 | -0.74836300 |
| C | 1.79710100 | -1.43061500 | 0.49639800 |
| H | 2.24777700 | -0.88113100 | 1.32307700 |
| H | 1.47992500 | -2.39684000 | 0.88464000 |
| S | -0.53705100 | 0.18925800 | 1.13307600 |
| C | -2.12623400 | 0.05170400 | 0.35544300 |
| C | -2.77672400 | 1.21099900 | -0.04925800 |
| C | -2.72269000 | -1.19941500 | 0.25616200 |
| C | -4.04947100 | 1.10509500 | -0.58844000 |
| H | -2.30208300 | 2.17860800 | 0.05653900 |
| C | -3.99618200 | -1.28735300 | -0.28445900 |
| H | -2.20677600 | -2.08837300 | 0.59732500 |
| C | -4.65485400 | -0.13941400 | -0.70592900 |
| H | -4.56881200 | 1.99677700 | -0.91204000 |
| H | -4.47447500 | -2.25335100 | -0.37166900 |
| H | -5.64927100 | -0.21477000 | -1.12492600 |

Calculated energies and structures of species involved in Figure 5 (addition of cyclohexene to thiiranium ion **11**)

Association Complex 15a



E= -1173.440596

H= -1173.419547

G= -1173.492916

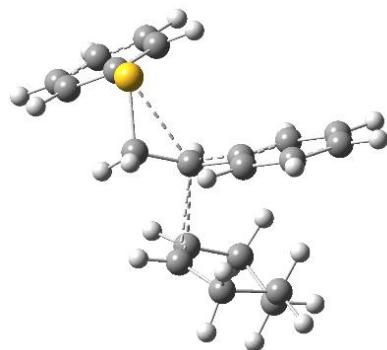
ZPVE= 0.378124

SUPPORTING INFORMATION

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -1.81712300 | -1.38918800 | 0.40007200 |
| H | -1.78235900 | -1.08826700 | 1.43838600 |
| C | -1.19501200 | -0.54631300 | -0.60886100 |
| H | -0.95076800 | -1.03689600 | -1.54510000 |
| C | -0.51748500 | 0.72882000 | -0.34170300 |
| C | -0.44572800 | 1.28315200 | 0.93573400 |
| C | 0.07913500 | 1.38905400 | -1.41696500 |
| C | 0.21686600 | 2.48341800 | 1.13130300 |
| H | -0.88866300 | 0.78375500 | 1.78801200 |
| C | 0.74270500 | 2.58729000 | -1.21757200 |
| H | 0.02737400 | 0.95610100 | -2.40933700 |
| C | 0.81034900 | 3.13524000 | 0.05719900 |
| H | 0.27652500 | 2.90851400 | 2.12402300 |
| H | 1.20920100 | 3.09189600 | -2.05260400 |
| H | 1.33049700 | 4.07051300 | 0.21560800 |
| C | 1.33148200 | -1.98253400 | 1.19981800 |
| C | 1.36538900 | -2.33642000 | -0.08261800 |
| C | 2.31750100 | -1.73475500 | -1.07936600 |
| C | 3.46917600 | -1.01290100 | -0.38403500 |
| C | 2.93951300 | -0.10697500 | 0.72321900 |
| C | 2.21503600 | -0.92190200 | 1.79285400 |
| H | 2.69662700 | -2.51927600 | -1.73744900 |
| H | 0.71264900 | -3.13235000 | -0.43296600 |
| H | 0.66638000 | -2.50896500 | 1.88005300 |
| H | 4.04676300 | -0.43915000 | -1.10928500 |
| H | 4.14434300 | -1.75631300 | 0.04855800 |
| H | 2.24604700 | 0.61739000 | 0.28563700 |
| H | 3.75037800 | 0.46415900 | 1.17620900 |
| H | 2.93962800 | -1.40605700 | 2.45648900 |
| H | 1.62304900 | -0.26449200 | 2.43678600 |
| H | 1.77966100 | -1.03204600 | -1.73050500 |
| S | -3.13658900 | -0.49669100 | -0.51795400 |
| H | -1.85002000 | -2.45612500 | 0.22499200 |
| C | -3.65484500 | -1.68524500 | -1.72725900 |
| C | -4.17049200 | -2.91002000 | -1.31939300 |
| C | -3.61415100 | -1.31568500 | -3.06661200 |
| C | -4.63443600 | -3.79083400 | -2.28351800 |
| H | -4.21973100 | -3.17000200 | -0.26928800 |
| C | -4.08351300 | -2.20807400 | -4.01831600 |
| H | -3.22528900 | -0.34874700 | -3.36099600 |
| C | -4.58908700 | -3.44085000 | -3.62729000 |
| H | -5.03771400 | -4.74824000 | -1.98301200 |
| H | -4.05545000 | -1.93749500 | -5.06498700 |
| H | -4.95509100 | -4.13238600 | -4.37424100 |

SUPPORTING INFORMATION

Transition State TS15a-16a



E= -1173.429188

H= -1173.409342

G= -1173.478580

ZPVE= 0.379072

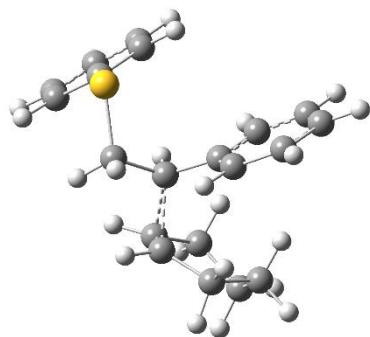
Imaginary Frequency= -64.9432 cm⁻¹

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -1.95957400 | -1.16358700 | 0.68069000 |
| H | -1.94050700 | -0.76212300 | 1.69068100 |
| C | -0.87984500 | -0.64869400 | -0.19529400 |
| H | -0.91461600 | -1.05996800 | -1.20018600 |
| C | -0.34909600 | 0.69240600 | -0.12319500 |
| C | -0.29954500 | 1.41731800 | 1.07542600 |
| C | 0.10298100 | 1.29279900 | -1.30765900 |
| C | 0.21350200 | 2.69977600 | 1.08877300 |
| H | -0.66282900 | 0.97837100 | 1.99604600 |
| C | 0.60945700 | 2.57888700 | -1.29189500 |
| H | 0.02710300 | 0.74987400 | -2.24233200 |
| C | 0.67356000 | 3.27723200 | -0.09177600 |
| H | 0.25167800 | 3.25780500 | 2.01435700 |
| H | 0.94714200 | 3.04144500 | -2.20914100 |
| H | 1.07194200 | 4.28330200 | -0.07602100 |
| C | 0.83884800 | -1.81923600 | 1.01161900 |
| C | 0.80264600 | -2.24901300 | -0.27487100 |
| C | 1.85155900 | -1.87028000 | -1.27483900 |
| C | 3.13770400 | -1.39665000 | -0.59607800 |
| C | 2.83609300 | -0.36005300 | 0.48148900 |
| C | 1.91207600 | -0.93810300 | 1.55229300 |
| H | 2.03956800 | -2.72636700 | -1.92452500 |
| H | 0.06746200 | -2.99634400 | -0.55791400 |
| H | 0.13415100 | -2.23281100 | 1.72553900 |
| H | 3.81724300 | -0.98676200 | -1.34219500 |
| H | 3.63965800 | -2.25703400 | -0.14605100 |
| H | 2.37026700 | 0.51715600 | 0.02652000 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | 3.75831200 | -0.01703600 | 0.94914700 |
| H | 2.47904700 | -1.56183600 | 2.25538900 |
| H | 1.47228800 | -0.14963100 | 2.16890300 |
| H | 1.46378600 | -1.08036100 | -1.92977100 |
| S | -3.47728700 | -0.52990000 | -0.11957400 |
| H | -2.00123200 | -2.24987800 | 0.71435100 |
| C | -3.57757000 | -1.64718900 | -1.49690900 |
| C | -3.87973400 | -2.99173600 | -1.29285300 |
| C | -3.39592200 | -1.15716500 | -2.78677400 |
| C | -3.97517400 | -3.84679300 | -2.37970200 |
| H | -4.06070000 | -3.35924300 | -0.28995000 |
| C | -3.50827100 | -2.01663700 | -3.87171600 |
| H | -3.18191300 | -0.10596300 | -2.93521600 |
| C | -3.79040400 | -3.35987700 | -3.66836000 |
| H | -4.21441200 | -4.89012900 | -2.22246300 |
| H | -3.37796600 | -1.63421400 | -4.87534400 |
| H | -3.87874800 | -4.02765200 | -4.51490000 |

Intermediate 16a



E= -1173.428582

H= -1173.408600

G= -1173.478051

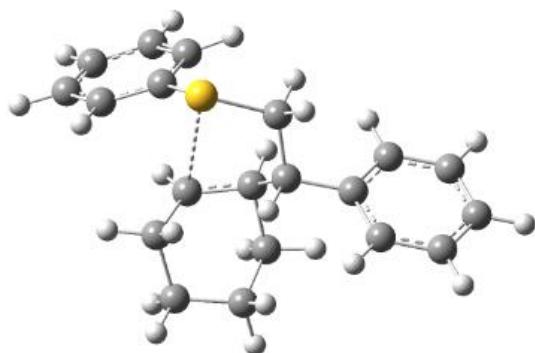
ZPVE= 0.380597

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -1.96564100 | -1.20778200 | 0.96313800 |
| H | -1.93244100 | -0.72606900 | 1.93964700 |
| C | -0.73926200 | -0.86461400 | 0.12657800 |
| H | -0.92864700 | -1.26630300 | -0.87569000 |
| C | -0.35917100 | 0.56721800 | -0.04046500 |
| C | -0.28945600 | 1.43139800 | 1.05080100 |
| C | -0.14431700 | 1.06818500 | -1.32363700 |
| C | 0.02092400 | 2.76772100 | 0.86281600 |
| H | -0.48923400 | 1.06713600 | 2.05173800 |
| C | 0.17298900 | 2.40492600 | -1.51115800 |
| H | -0.25002300 | 0.41421400 | -2.18218100 |
| C | 0.26323900 | 3.25324900 | -0.41694500 |
| H | 0.06672400 | 3.43434700 | 1.71338100 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | 0.33636600 | 2.78595200 | -2.51020900 |
| H | 0.50553200 | 4.29773300 | -0.56057000 |
| C | 0.61457000 | -1.69111300 | 1.07026100 |
| C | 0.52425400 | -2.37892300 | -0.13174700 |
| C | 1.51856300 | -2.20422400 | -1.23414300 |
| C | 2.87831700 | -1.73692900 | -0.70854900 |
| C | 2.72088500 | -0.53759900 | 0.21899500 |
| C | 1.83951200 | -0.88710900 | 1.41516200 |
| H | 1.58994900 | -3.15127300 | -1.77117900 |
| H | -0.22686000 | -3.15742900 | -0.23180700 |
| H | 0.05142400 | -2.07497000 | 1.91296700 |
| H | 3.52139300 | -1.49194700 | -1.55241800 |
| H | 3.35748200 | -2.55991800 | -0.17243200 |
| H | 2.29338300 | 0.30410600 | -0.32898100 |
| H | 3.69475900 | -0.21370500 | 0.58434600 |
| H | 2.39305300 | -1.53322600 | 2.10635400 |
| H | 1.56936300 | -0.00115200 | 1.98701200 |
| H | 1.12644200 | -1.48241600 | -1.95854600 |
| S | -3.47675200 | -0.61501500 | 0.15447500 |
| H | -2.03391200 | -2.28628000 | 1.11650400 |
| C | -3.33176700 | -1.53949700 | -1.35669500 |
| C | -3.42557200 | -2.93040000 | -1.35178100 |
| C | -3.11276900 | -0.86201000 | -2.55297000 |
| C | -3.27427100 | -3.63786100 | -2.53534200 |
| H | -3.64390400 | -3.45182200 | -0.42727700 |
| C | -2.98075800 | -1.57540200 | -3.73871600 |
| H | -3.05641600 | 0.21953600 | -2.54885800 |
| C | -3.05121900 | -2.96107000 | -3.72930900 |
| H | -3.35744200 | -4.71683600 | -2.53081600 |
| H | -2.82735100 | -1.04549200 | -4.66966700 |
| H | -2.95049300 | -3.51470100 | -4.65334200 |

Intermediate 16a'



E= -1173.436869

H= -1173.417426

G= -1173.483647

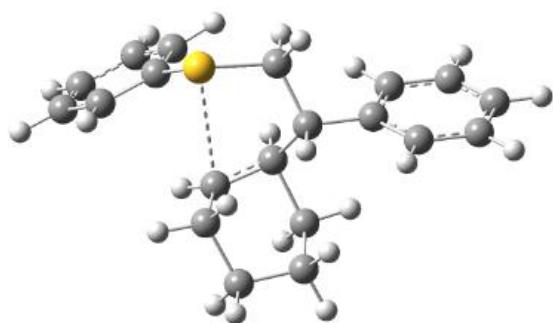
ZPVE= 0.381104

SUPPORTING INFORMATION

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 2.39470100 | -1.00287800 | 0.51674700 |
| C | 3.47245300 | -0.13716400 | 0.73629000 |
| C | 2.29688000 | -1.66114000 | -0.71531400 |
| C | 4.40878300 | 0.09270300 | -0.26306100 |
| H | 3.56937200 | 0.35111100 | 1.69880900 |
| C | 3.21645400 | -1.40554300 | -1.71719600 |
| H | 1.50865300 | -2.38238100 | -0.88687300 |
| C | 4.27280400 | -0.52349200 | -1.49834900 |
| H | 5.24211200 | 0.75643800 | -0.07353400 |
| H | 3.12671700 | -1.91588500 | -2.66724900 |
| H | 4.99555700 | -0.33880900 | -2.28163200 |
| C | -5.04350200 | -0.88336300 | -0.57239000 |
| C | -4.75612100 | -0.04098500 | 0.49062200 |
| C | -3.43636100 | 0.19328600 | 0.85501800 |
| C | -2.39219300 | -0.41146300 | 0.16364900 |
| C | -2.69128900 | -1.26226700 | -0.90013300 |
| C | -4.00780200 | -1.49529100 | -1.26711500 |
| H | -6.07052500 | -1.06797600 | -0.85716400 |
| H | -5.55803200 | 0.43322800 | 1.04063100 |
| H | -3.21955800 | 0.84528300 | 1.69397300 |
| H | -1.89618200 | -1.75423000 | -1.45029700 |
| H | -4.22678900 | -2.15917200 | -2.09286900 |
| C | -0.95807200 | -0.15290600 | 0.57378400 |
| H | -0.96887900 | 0.54772300 | 1.40986800 |
| C | -0.32140500 | -1.45836500 | 1.07097500 |
| H | -0.28378300 | -2.20754300 | 0.28041800 |
| H | -0.95666100 | -1.87240800 | 1.85473900 |
| C | -0.15350400 | 0.45497100 | -0.59466500 |
| C | -0.88532500 | 1.74255900 | -1.22880500 |
| C | -0.98181400 | 2.89030700 | -0.24358500 |
| H | -0.35782200 | 2.05418400 | -2.13274300 |
| H | -0.05286100 | -0.26573800 | -1.40545300 |
| H | -1.57201500 | 2.59960900 | 0.62739900 |
| H | -1.50972200 | 3.72019200 | -0.71719900 |
| H | -1.85671500 | 1.34928600 | -1.53260900 |
| S | 1.29395800 | -1.30137300 | 1.87403300 |
| C | 1.23855100 | 2.11274000 | 0.72043700 |
| H | 0.79746100 | 1.78730400 | 1.66123800 |
| H | 2.27094000 | 2.41645400 | 0.86618100 |
| C | 0.40946000 | 3.33858000 | 0.16716200 |
| H | 0.93820900 | 3.76415300 | -0.68766000 |
| H | 0.40080600 | 4.08837700 | 0.95684000 |
| C | 1.10432000 | 1.10702100 | -0.32341700 |
| H | 1.85427100 | 1.08890700 | -1.11327500 |

SUPPORTING INFORMATION

Transition State TS16a'-17a



E= -1173.435669

H= -1173.416800

G= -1173.482065

ZPVE= 0.380625

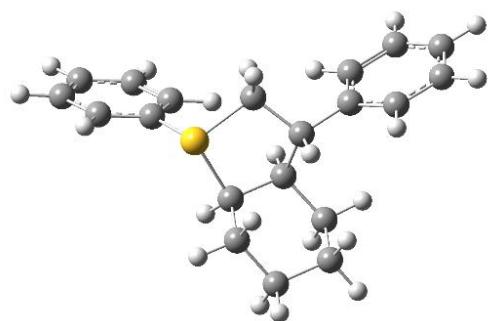
Imaginary frequency = -100.4468 cm⁻¹

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 2.50252200 | -0.85610400 | 0.59654200 |
| C | 3.63217000 | -0.03474000 | 0.59294600 |
| C | 2.33093000 | -1.78938600 | -0.42171100 |
| C | 4.56619200 | -0.13526800 | -0.42795600 |
| H | 3.77855200 | 0.67740600 | 1.39691700 |
| C | 3.25939900 | -1.86788400 | -1.45110400 |
| H | 1.49128400 | -2.47128600 | -0.41605400 |
| C | 4.37553200 | -1.04120300 | -1.46249900 |
| H | 5.44265500 | 0.49919400 | -0.41390800 |
| H | 3.11738200 | -2.59605900 | -2.23896800 |
| H | 5.09883000 | -1.11520600 | -2.26297400 |
| C | -4.92784600 | -1.34330900 | -0.52631100 |
| C | -4.79108300 | -0.31817900 | 0.39709400 |
| C | -3.52572200 | 0.11187800 | 0.77548400 |
| C | -2.38685400 | -0.47922700 | 0.23879900 |
| C | -2.53439900 | -1.51309100 | -0.68564300 |
| C | -3.79640900 | -1.94102800 | -1.06755600 |
| H | -5.91227800 | -1.68044100 | -0.82165900 |
| H | -5.66820900 | 0.14677500 | 0.82708500 |
| H | -3.42523700 | 0.90839300 | 1.50445500 |
| H | -1.66170200 | -1.99540400 | -1.11370400 |
| H | -3.89839000 | -2.74517500 | -1.78409900 |
| C | -1.01516400 | 0.00054100 | 0.65209100 |
| H | -1.14382000 | 0.81406600 | 1.36776100 |
| C | -0.23702500 | -1.12617000 | 1.35717800 |
| H | -0.16394800 | -2.00977300 | 0.72643500 |
| H | -0.78983500 | -1.42672000 | 2.24744700 |
| C | -0.20350800 | 0.50460400 | -0.55022400 |
| C | -0.99569500 | 1.61109700 | -1.42575600 |
| C | -1.20863400 | 2.90966900 | -0.67414200 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | -0.45303400 | 1.78643300 | -2.35605600 |
| H | 0.02205200 | -0.31189600 | -1.23581900 |
| H | -1.82551900 | 2.74445800 | 0.21173100 |
| H | -1.75821400 | 3.60069700 | -1.31643100 |
| H | -1.92517400 | 1.09445200 | -1.67216700 |
| S | 1.39422400 | -0.65187200 | 1.97562000 |
| C | 0.94859700 | 2.47056200 | 0.56779700 |
| H | 0.41665800 | 2.30390200 | 1.50004700 |
| H | 1.94888800 | 2.85271600 | 0.75624200 |
| C | 0.12983800 | 3.51828600 | -0.29253800 |
| H | 0.69927400 | 3.78464300 | -1.18485200 |
| H | 0.03705400 | 4.41299800 | 0.32138800 |
| C | 0.95824200 | 1.30762000 | -0.29947600 |
| H | 1.77864000 | 1.22377800 | -1.01084000 |

Addition Product 17a



E= -1173.494351

H= -1173.475670

G= -1173.541424

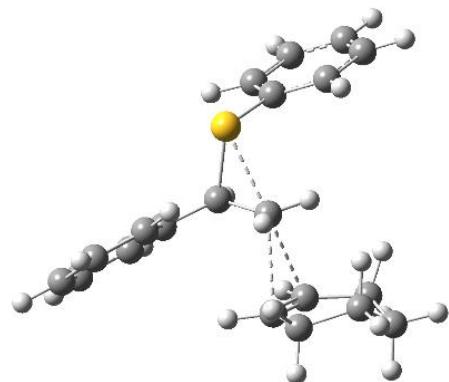
ZPVE= 0.383905

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -2.70204600 | -0.31402600 | -0.30829200 |
| C | -3.98769900 | -0.13188900 | -0.80371500 |
| C | -2.44409400 | -1.18329000 | 0.74756100 |
| C | -5.03610600 | -0.83464700 | -0.22629700 |
| H | -4.16632200 | 0.54494800 | -1.62926000 |
| C | -3.50018100 | -1.87614200 | 1.31330800 |
| H | -1.44057400 | -1.32596800 | 1.12545500 |
| C | -4.79215100 | -1.70179700 | 0.82753800 |
| H | -6.04035700 | -0.70362000 | -0.60527600 |
| H | -3.31543000 | -2.55545200 | 2.13433600 |
| H | -5.61087800 | -2.24986100 | 1.27424000 |
| C | 4.41605000 | -2.52621300 | 0.09545500 |
| C | 4.61362500 | -1.39581700 | -0.68217000 |
| C | 3.56028300 | -0.52242900 | -0.91970300 |
| C | 2.30194800 | -0.76953200 | -0.38280500 |
| C | 2.11301000 | -1.90820600 | 0.39809600 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| C | 3.16217500 | -2.78167100 | 0.63633700 |
| H | 5.23497200 | -3.20812000 | 0.28089000 |
| H | 5.58754300 | -1.19118200 | -1.10636200 |
| H | 3.72036400 | 0.36023100 | -1.52823300 |
| H | 1.14173800 | -2.12299500 | 0.83224200 |
| H | 3.00306400 | -3.66233500 | 1.24424800 |
| C | 1.17369600 | 0.20525700 | -0.62413400 |
| H | 1.55184000 | 1.00447100 | -1.26530500 |
| C | -0.01082800 | -0.46376800 | -1.33320800 |
| H | -0.27156100 | -1.42059000 | -0.88437600 |
| H | 0.12867400 | -0.59271900 | -2.40379100 |
| C | -0.62259900 | 1.64958000 | 0.23733300 |
| C | 0.59738800 | 0.82420200 | 0.66079500 |
| C | 1.59321200 | 1.65649900 | 1.47507100 |
| C | 1.92054800 | 3.00015600 | 0.83233200 |
| H | 1.16342600 | 1.83513700 | 2.46438000 |
| H | 0.25685600 | -0.00054100 | 1.29293100 |
| H | -1.35944700 | 1.74598600 | 1.03585800 |
| H | 2.46421600 | 2.85490400 | -0.10648700 |
| H | 2.58466900 | 3.56168000 | 1.48917000 |
| H | 2.49484300 | 1.06006500 | 1.62704400 |
| S | -1.44034100 | 0.65130100 | -1.09014200 |
| C | -0.28356900 | 3.01454800 | -0.36478300 |
| H | 0.21447300 | 2.88486000 | -1.33069600 |
| H | -1.20542500 | 3.56488500 | -0.55755600 |
| C | 0.64415100 | 3.79129300 | 0.56816000 |
| H | 0.13197700 | 3.98942700 | 1.51481100 |
| H | 0.86899700 | 4.75930400 | 0.12068300 |

Transition State – Attack by cyclohexene at methylene carbon of thiiranium ion 11



E= -1173.420362

H= -1173.400137

G= -1173.471150

ZPVE= 0.378148

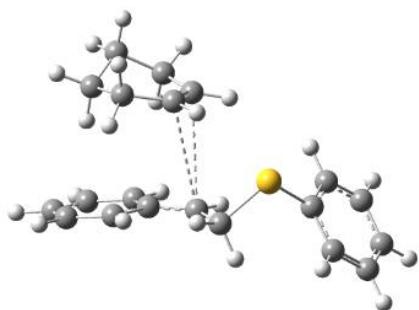
Imaginary Frequency= -349.1276 cm⁻¹

SUPPORTING INFORMATION

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -0.21378600 | -0.78869600 | 0.15763500 |
| H | 0.31809800 | -0.89844800 | 1.09803000 |
| C | -0.16443600 | 0.55466500 | -0.41095000 |
| H | 0.71933900 | 1.16083200 | -0.26641400 |
| H | -0.77342600 | 0.77670400 | -1.27731300 |
| C | -1.51356300 | -1.52252400 | 0.12287300 |
| C | -2.29037800 | -1.56324200 | -1.03374700 |
| C | -1.96549400 | -2.14908300 | 1.27833900 |
| C | -3.50959500 | -2.22061100 | -1.02803600 |
| H | -1.94066900 | -1.10025800 | -1.95093400 |
| C | -3.19112600 | -2.80170500 | 1.28357300 |
| H | -1.36063200 | -2.12752100 | 2.17730100 |
| C | -3.96326000 | -2.83680000 | 0.13253100 |
| H | -4.10483200 | -2.25826400 | -1.93044500 |
| H | -3.53823200 | -3.28553600 | 2.18657500 |
| H | -4.91591500 | -3.34910000 | 0.13478400 |
| S | 0.94497100 | -1.27991700 | -1.22069600 |
| C | -1.94144600 | 1.77016500 | 0.50059100 |
| C | -2.38015400 | 2.72046900 | -0.57035800 |
| C | -0.88166700 | 2.01187600 | 1.30534900 |
| C | -1.31110400 | 3.76417000 | -0.88542800 |
| H | -3.29685100 | 3.20817200 | -0.22087600 |
| H | -2.67517900 | 2.16089000 | -1.46261800 |
| C | -0.07867300 | 3.27728200 | 1.25375900 |
| H | -0.65389100 | 1.30182300 | 2.09500400 |
| C | -0.75078100 | 4.35587900 | 0.40450500 |
| H | -0.49895100 | 3.30313700 | -1.45836900 |
| H | -1.73131600 | 4.54485100 | -1.51805600 |
| H | 0.07142100 | 3.62467400 | 2.27824800 |
| H | 0.92910300 | 3.05954300 | 0.87824000 |
| H | -1.56855500 | 4.80273800 | 0.97552400 |
| H | -0.04123800 | 5.15377100 | 0.18956000 |
| H | -2.55213000 | 0.89020000 | 0.67932700 |
| C | 2.52450000 | -0.92918700 | -0.49787800 |
| C | 3.31367800 | 0.08235700 | -1.03674700 |
| C | 2.99076600 | -1.71301100 | 0.55477100 |
| C | 4.57441800 | 0.31731100 | -0.50681900 |
| H | 2.94891700 | 0.66916600 | -1.87058800 |
| C | 4.24689800 | -1.46274600 | 1.08338800 |
| H | 2.38194600 | -2.52027100 | 0.94324000 |
| C | 5.03703300 | -0.44971000 | 0.55345700 |
| H | 5.19539600 | 1.09749200 | -0.92604700 |
| H | 4.61542300 | -2.06893800 | 1.89995200 |
| H | 6.02085000 | -0.26447800 | 0.96344100 |

SUPPORTING INFORMATION

Transition State – Attack by cyclohexene at benzylic carbocation of ring opened thiiranium ion 11



E= -1173.419417

H= -1173.398866

G= -1173.470252

ZPVE= 0.377087

Imaginary Frequency= -84.6131 cm⁻¹

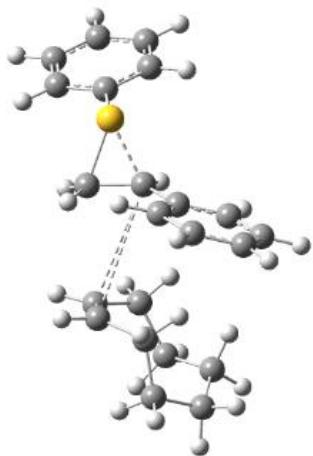
| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 2.28690900 | -1.04114300 | 1.02581500 |
| H | 1.84155100 | -0.98221800 | 2.01519600 |
| H | 2.96612100 | -1.89667000 | 0.99018200 |
| C | 1.31947100 | -1.12880600 | -0.06702300 |
| S | 3.28851600 | 0.46974500 | 0.73362100 |
| H | 1.74600300 | -1.01364900 | -1.06216800 |
| C | -0.04020000 | -1.43209600 | 0.00503400 |
| C | -0.70731600 | -1.68438600 | 1.23202700 |
| C | -0.73520600 | -1.62911400 | -1.21691700 |
| C | -2.00114600 | -2.14294600 | 1.22382600 |
| H | -0.19706000 | -1.52433600 | 2.17188900 |
| C | -2.02888600 | -2.09680900 | -1.21270600 |
| H | -0.22103300 | -1.43334800 | -2.14998400 |
| C | -2.65506300 | -2.35542300 | 0.00547800 |
| H | -2.51540000 | -2.34429500 | 2.15324900 |
| H | -2.55541500 | -2.26514800 | -2.14165500 |
| H | -3.67274100 | -2.72587700 | 0.01053800 |
| C | 0.06103600 | 1.87050700 | 0.76795800 |
| C | 0.24073300 | 1.95761500 | -0.54921300 |
| C | -0.89402100 | 2.01207500 | -1.53067700 |
| C | -2.21529100 | 2.35038100 | -0.84557200 |
| C | -2.39555000 | 1.48907800 | 0.39998300 |
| C | -1.28801000 | 1.76385200 | 1.41484800 |
| H | -0.66430700 | 2.73993200 | -2.31149100 |
| H | 1.25156500 | 2.03547000 | -0.93730300 |
| H | 0.92542900 | 1.90933800 | 1.42457500 |
| H | -3.04723900 | 2.21177500 | -1.53642100 |
| H | -2.20894400 | 3.40499700 | -0.55770700 |
| H | -2.36099400 | 0.43632100 | 0.10199900 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | -3.37225700 | 1.65763500 | 0.85454700 |
| H | -1.49318500 | 2.69217900 | 1.95893400 |
| H | -1.26788500 | 0.98177200 | 2.18254300 |
| H | -0.98192200 | 1.04508400 | -2.04702400 |
| C | 4.42923000 | -0.14827500 | -0.47260900 |
| C | 5.39483200 | -1.08982800 | -0.11823300 |
| C | 4.38646700 | 0.36024200 | -1.76770100 |
| C | 6.29963900 | -1.53381300 | -1.06739000 |
| H | 5.44772700 | -1.45450200 | 0.90065100 |
| C | 5.30597100 | -0.08032400 | -2.71053900 |
| H | 3.64592600 | 1.10599700 | -2.02833700 |
| C | 6.25595200 | -1.02894600 | -2.36276900 |
| H | 7.05172000 | -2.26151200 | -0.79337900 |
| H | 5.27889000 | 0.32024300 | -3.71503100 |
| H | 6.97151300 | -1.37129300 | -3.09837800 |

Calculated energies and structures of species involved in Figure 5 (addition of *cis*-cyclooctene to thiiranium ion **11**)

Association Complex 15b



$$E = -1251.980193$$

$$H = -1251.956718$$

$$G = -1252.035368$$

$$ZPVE = 0.436224$$

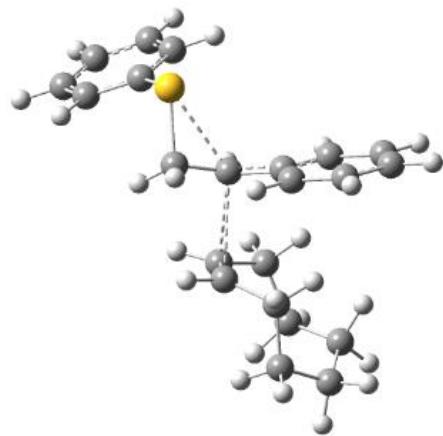
| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 1.17982400 | -0.03315500 | -1.31433700 |
| H | 0.66827200 | 0.34157400 | -2.19036900 |
| C | 0.75140200 | 0.42511800 | 0.00094700 |
| H | 1.00691400 | -0.22084000 | 0.83373400 |
| C | -0.34785400 | 1.37668800 | 0.22388400 |
| C | -0.83535800 | 2.20038700 | -0.79045500 |
| C | -0.92252200 | 1.42617700 | 1.49284100 |
| C | -1.88647500 | 3.06250900 | -0.53329600 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | -0.40346200 | 2.17831200 | -1.78408800 |
| C | -1.98806100 | 2.27706700 | 1.74136000 |
| H | -0.54507300 | 0.78535800 | 2.28136200 |
| C | -2.46758600 | 3.09693700 | 0.72933100 |
| H | -2.26101700 | 3.70308400 | -1.32021500 |
| H | -2.44003900 | 2.30202000 | 2.72362800 |
| H | -3.29561500 | 3.76573000 | 0.92292300 |
| C | -2.16091900 | -0.86798400 | -1.90169300 |
| C | -1.38164200 | -1.79397000 | -1.34655400 |
| H | -0.70571200 | -2.34095200 | -1.99895900 |
| H | -2.07743600 | -0.70810100 | -2.97363600 |
| S | 2.39627500 | 1.17999800 | -0.64829400 |
| H | 1.60637300 | -1.02306000 | -1.40359100 |
| C | 3.65533500 | 0.14708300 | 0.05297700 |
| C | 4.35528000 | -0.73598600 | -0.76080300 |
| C | 3.97364700 | 0.31948000 | 1.39495200 |
| C | 5.38499800 | -1.47843300 | -0.20476200 |
| H | 4.10969200 | -0.83723900 | -1.81064800 |
| C | 5.00664400 | -0.43116400 | 1.93517600 |
| H | 3.42709300 | 1.02695500 | 2.00608900 |
| C | 5.70714000 | -1.32698200 | 1.13816700 |
| H | 5.93932900 | -2.17087400 | -0.82345800 |
| H | 5.26474600 | -0.31261400 | 2.97865300 |
| H | 6.51349900 | -1.90821000 | 1.56492100 |
| C | -3.26546800 | -0.13629600 | -1.19627800 |
| H | -2.93459100 | 0.17944600 | -0.20248700 |
| H | -3.50784200 | 0.77420700 | -1.74373900 |
| C | -1.39202700 | -2.20799500 | 0.10300300 |
| H | -0.57016100 | -2.90949100 | 0.25829200 |
| H | -1.18296000 | -1.34048000 | 0.74083800 |
| C | -4.52171600 | -1.03494900 | -1.06866000 |
| H | -5.38450100 | -0.53503700 | -1.51030600 |
| H | -4.36470100 | -1.93896200 | -1.65935300 |
| C | -2.69499400 | -2.85691900 | 0.63433800 |
| H | -2.40224200 | -3.57102300 | 1.40494000 |
| H | -3.16229600 | -3.44337600 | -0.16003100 |
| C | -4.87224600 | -1.42579300 | 0.36876800 |
| H | -5.61717100 | -2.22402300 | 0.32761400 |
| H | -5.36076400 | -0.58200300 | 0.86370600 |
| C | -3.70476100 | -1.87472300 | 1.25304600 |
| H | -3.16007500 | -0.99739300 | 1.61637700 |
| H | -4.13622200 | -2.33204500 | 2.14530000 |

SUPPORTING INFORMATION

Transition State TS15b-16b



E= -1251.971540

H= -1251.948836

G= -1252.025307

ZPVE= 0.436485

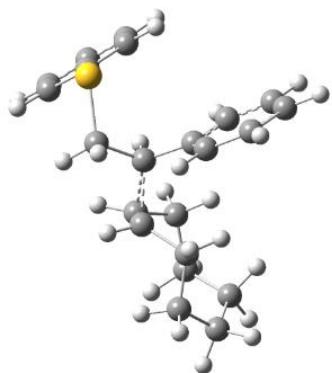
Imaginary Frequency= -132.0434 cm⁻¹

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 1.14850600 | 0.59465200 | -1.58013200 |
| H | 0.70561300 | 1.18467600 | -2.37635000 |
| C | 0.36851600 | 0.53272100 | -0.33913000 |
| H | 0.78177400 | -0.12048400 | 0.42303000 |
| C | -0.55049400 | 1.53350500 | 0.12040300 |
| C | -1.14610800 | 2.46314700 | -0.74773400 |
| C | -0.86076600 | 1.57546700 | 1.48902800 |
| C | -2.02374500 | 3.40581200 | -0.25478200 |
| H | -0.92662400 | 2.44227500 | -1.80739900 |
| C | -1.74572500 | 2.51861000 | 1.97767300 |
| H | -0.38039400 | 0.87723800 | 2.16395400 |
| C | -2.32626700 | 3.43165500 | 1.10550700 |
| H | -2.47848800 | 4.12401800 | -0.92322700 |
| H | -1.97569300 | 2.55286000 | 3.03370400 |
| H | -3.01567900 | 4.17403100 | 1.48610300 |
| C | -1.46659100 | -0.92668400 | -1.37531500 |
| C | -0.83410700 | -1.69253100 | -0.46327000 |
| H | 0.07572500 | -2.19878800 | -0.77490600 |
| H | -1.03941400 | -0.86682200 | -2.37299200 |
| S | 2.59056300 | 1.52234400 | -0.92358500 |
| H | 1.47483200 | -0.37219500 | -1.95103500 |
| C | 3.53397000 | 0.19712900 | -0.21686300 |
| C | 4.10975800 | -0.77239600 | -1.03501800 |
| C | 3.74328500 | 0.17422900 | 1.15857700 |
| C | 4.87607300 | -1.77801300 | -0.46826200 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | 3.97497900 | -0.72650200 | -2.10888500 |
| C | 4.52412400 | -0.82891000 | 1.71643200 |
| H | 3.30589300 | 0.94374900 | 1.78222200 |
| C | 5.08386900 | -1.80606100 | 0.90591400 |
| H | 5.32706600 | -2.53032900 | -1.10143600 |
| H | 4.69502600 | -0.84426500 | 2.78452200 |
| H | 5.69234200 | -2.58660800 | 1.34276800 |
| C | -2.81468100 | -0.32042000 | -1.17992600 |
| H | -2.90841800 | 0.07316600 | -0.16403300 |
| H | -2.94743600 | 0.51909400 | -1.86148500 |
| C | -1.33210500 | -1.98291600 | 0.91997600 |
| H | -0.54274600 | -2.50428100 | 1.46140000 |
| H | -1.50758200 | -1.03996400 | 1.44936900 |
| C | -3.90488600 | -1.40048500 | -1.43330800 |
| H | -4.58559200 | -1.05309900 | -2.21023800 |
| H | -3.42987500 | -2.29779200 | -1.83383900 |
| C | -2.63854600 | -2.81726900 | 1.00884700 |
| H | -2.55524800 | -3.42214600 | 1.91154900 |
| H | -2.68698800 | -3.52428200 | 0.17740000 |
| C | -4.71995700 | -1.77218200 | -0.19288500 |
| H | -5.28215100 | -2.67844600 | -0.42858500 |
| H | -5.46416000 | -0.99469200 | -0.00433400 |
| C | -3.93240100 | -1.99170400 | 1.10279100 |
| H | -3.69926400 | -1.02759300 | 1.56418100 |
| H | -4.60682600 | -2.48446000 | 1.80476000 |

Intermediate 16b



E= -1251.975362

H= -1251.953097

G= -1252.027175

ZPVE= 0.438882

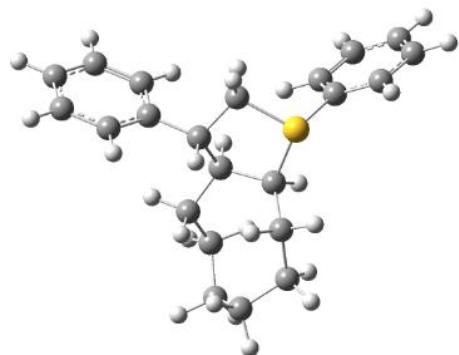
| Symbol | X | Y | Z |
|--------|------------|-------------|-------------|
| C | 0.89164500 | 0.63184500 | -1.96290600 |
| H | 0.37164600 | 1.28278200 | -2.66540300 |
| C | 0.00592200 | 0.31739700 | -0.75585500 |
| H | 0.67665600 | -0.21686000 | -0.05438700 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| C | -0.56427800 | 1.46275200 | 0.02951100 |
| C | -1.23733300 | 2.49536400 | -0.62000300 |
| C | -0.37189600 | 1.52981900 | 1.40592700 |
| C | -1.71950700 | 3.57387800 | 0.10188200 |
| H | -1.37568800 | 2.46787600 | -1.69444400 |
| C | -0.86623800 | 2.60593600 | 2.13072300 |
| H | 0.18788200 | 0.75045600 | 1.91184600 |
| C | -1.54175200 | 3.62662200 | 1.47949700 |
| H | -2.23155500 | 4.37742400 | -0.41013500 |
| H | -0.71075600 | 2.65188900 | 3.20022700 |
| H | -1.92051900 | 4.46994700 | 2.04116200 |
| C | -1.28626800 | -0.63572200 | -1.37644000 |
| C | -0.58502100 | -1.52402300 | -0.54817300 |
| H | 0.25700600 | -2.05655300 | -0.98561800 |
| H | -1.07129700 | -0.71996100 | -2.43727800 |
| S | 2.40503500 | 1.50249200 | -1.48115000 |
| H | 1.14844400 | -0.29145900 | -2.48591200 |
| C | 3.03705200 | 0.28365100 | -0.35298500 |
| C | 3.42787000 | -0.97494600 | -0.80892400 |
| C | 3.12354900 | 0.58770700 | 1.00279800 |
| C | 3.87694800 | -1.92924600 | 0.09208500 |
| H | 3.40503100 | -1.19342000 | -1.87012700 |
| C | 3.59254100 | -0.36634000 | 1.89874800 |
| H | 2.82882400 | 1.57144900 | 1.34646300 |
| C | 3.95914000 | -1.62584500 | 1.44690000 |
| H | 4.19006200 | -2.90137000 | -0.26596600 |
| H | 3.67404600 | -0.12099100 | 2.94959100 |
| H | 4.32667000 | -2.36618100 | 2.14501900 |
| C | -2.71214100 | -0.25161100 | -1.07468900 |
| H | -2.83242500 | 0.00996500 | -0.02380900 |
| H | -2.97499000 | 0.63561400 | -1.64690000 |
| C | -0.98571200 | -1.90265600 | 0.82907300 |
| H | -0.11667400 | -2.30361200 | 1.34927500 |
| H | -1.33436200 | -1.02461900 | 1.37417800 |
| C | -3.61224800 | -1.45001700 | -1.46272100 |
| H | -4.34557000 | -1.13097900 | -2.20263400 |
| H | -3.00803300 | -2.20999500 | -1.96576600 |
| C | -2.13467400 | -2.95869300 | 0.80821500 |
| H | -1.92975700 | -3.62908600 | 1.64151500 |
| H | -2.07686000 | -3.57856300 | -0.09083300 |
| C | -4.35432900 | -2.09845200 | -0.29148400 |
| H | -4.77508600 | -3.03939600 | -0.65194800 |
| H | -5.20576600 | -1.47335900 | -0.01463600 |
| C | -3.54189100 | -2.36556100 | 0.98006700 |
| H | -3.46538200 | -1.45231500 | 1.57541700 |
| H | -4.12500500 | -3.05497400 | 1.59216100 |

SUPPORTING INFORMATION

Addition Product 17b



E= -1252.037672

H= -1252.016511

G= -1252.087683

ZPVE= 0.441675

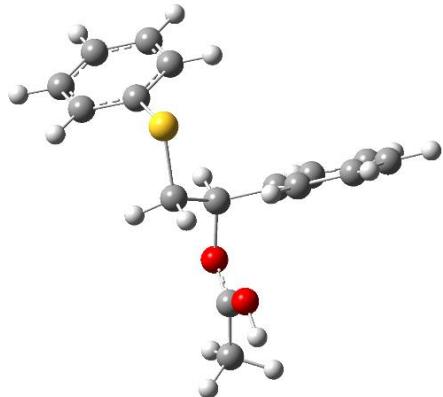
| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 0.76016900 | 1.00940500 | 1.18404500 |
| H | 1.02873900 | 1.57875500 | 2.07078100 |
| C | -0.73487000 | 1.01339900 | 0.86383200 |
| H | -1.29093200 | 0.83980100 | 1.79092800 |
| C | -1.17459400 | 2.34104300 | 0.29326900 |
| C | -0.63682300 | 2.81993600 | -0.89999600 |
| C | -2.14096900 | 3.09553700 | 0.94821400 |
| C | -1.05984400 | 4.02990600 | -1.42714100 |
| H | 0.11611000 | 2.24791300 | -1.43252300 |
| C | -2.56594100 | 4.30827500 | 0.42218500 |
| H | -2.56801800 | 2.73247100 | 1.87578100 |
| C | -2.02615600 | 4.77714000 | -0.76556300 |
| H | -0.63597700 | 4.39112300 | -2.35469000 |
| H | -3.31918700 | 4.88508000 | 0.94206100 |
| H | -2.35574600 | 5.72178100 | -1.17674500 |
| C | -0.97039300 | -0.18598700 | -0.06859300 |
| C | -0.33647900 | -1.42272400 | 0.59993800 |
| H | 0.09432300 | -2.11145800 | -0.12774700 |
| H | -0.41796800 | 0.00464000 | -0.99590100 |
| S | 1.14920300 | -0.74081400 | 1.49834000 |
| H | 1.36269400 | 1.33659400 | 0.33809100 |
| C | 2.56072900 | -1.12003500 | 0.50007000 |
| C | 2.59148600 | -0.85570400 | -0.86602300 |
| C | 3.63431700 | -1.71006600 | 1.15428200 |
| C | 3.72605100 | -1.19108400 | -1.58335500 |
| H | 1.74666400 | -0.39828500 | -1.36576300 |
| C | 4.76718100 | -2.03757800 | 0.42126600 |
| H | 3.58748100 | -1.90877800 | 2.21713700 |
| C | 4.81107000 | -1.77919100 | -0.93989200 |
| H | 3.76606800 | -0.99379700 | -2.64595300 |
| | 5.61179200 | -2.49483400 | 0.91813200 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | 5.69497900 | -2.03657400 | -1.50798500 |
| C | -2.43752200 | -0.37617900 | -0.42921800 |
| H | -3.01812200 | -0.45098400 | 0.49334700 |
| H | -2.77680600 | 0.53787800 | -0.91829900 |
| C | -1.16661000 | -2.20800400 | 1.62561600 |
| H | -0.46283700 | -2.67504200 | 2.31697100 |
| H | -1.76718300 | -1.51924600 | 2.22728200 |
| C | -2.67931700 | -1.60029600 | -1.32708600 |
| H | -2.98187100 | -1.27937100 | -2.32403300 |
| H | -1.74091100 | -2.14347900 | -1.47244700 |
| C | -2.05866400 | -3.33943100 | 1.06940100 |
| H | -2.10860800 | -4.08502400 | 1.86346200 |
| H | -1.55028900 | -3.83271300 | 0.23481700 |
| C | -3.72123600 | -2.56897000 | -0.77414300 |
| H | -3.72409000 | -3.46389800 | -1.40044300 |
| H | -4.71716800 | -2.12916600 | -0.86431600 |
| C | -3.49915900 | -2.97891200 | 0.68425900 |
| H | -3.85920100 | -2.20072000 | 1.36227200 |
| H | -4.13260600 | -3.84427400 | 0.88322900 |

Calculated energies and structures of species involved in Figure 6 and S19 (isomerisation pathways)

Protonated Acetate 10'



E= -1167.990807

H= -1167.971896

G= -1168.040555

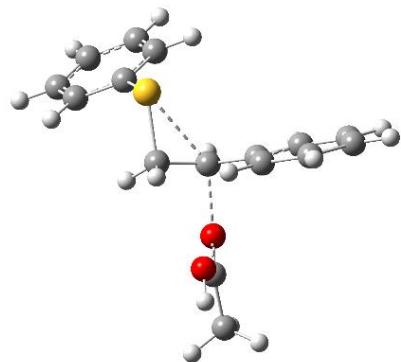
ZPVE= 0.296193

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -1.95294900 | 0.19867900 | -0.57278300 |
| C | -1.82570100 | -1.09888800 | -0.08491700 |
| C | -3.03607200 | 0.98636900 | -0.19141900 |
| C | -2.77887300 | -1.60291800 | 0.79023400 |
| H | -0.98784200 | -1.70824000 | -0.40067700 |
| C | -3.97794500 | 0.48124800 | 0.69222000 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | -3.14731900 | 1.98216600 | -0.60253800 |
| C | -3.85016700 | -0.81262600 | 1.18214300 |
| H | -2.68537300 | -2.61498700 | 1.16122700 |
| H | -4.82225600 | 1.09152700 | 0.98430300 |
| H | -4.59355600 | -1.20820600 | 1.86141500 |
| C | 0.16127600 | 1.95095600 | -0.61650200 |
| H | 0.87464400 | 2.47750200 | -1.24724800 |
| C | 0.83014600 | 1.16635300 | 0.48855200 |
| H | 0.07303100 | 0.64922700 | 1.07424200 |
| H | -0.52903700 | 2.67688600 | -0.18565600 |
| C | 1.96390500 | 0.24118800 | 0.16712800 |
| C | 2.29942400 | -0.72731800 | 1.11133800 |
| C | 2.67085700 | 0.30733500 | -1.02990600 |
| C | 3.34409800 | -1.60689100 | 0.87302700 |
| H | 1.73117200 | -0.79865000 | 2.03230600 |
| C | 3.70756300 | -0.57967300 | -1.27259600 |
| H | 2.40572900 | 1.03286900 | -1.78768200 |
| C | 4.04847000 | -1.53227300 | -0.32066600 |
| H | 3.59677500 | -2.35810500 | 1.60903800 |
| H | 4.24446400 | -0.53450300 | -2.21050700 |
| H | 4.85590200 | -2.22546500 | -0.51598800 |
| S | -0.74486600 | 0.82722700 | -1.71619600 |
| O | 1.29914000 | 2.15931900 | 1.58258600 |
| C | 2.23161900 | 2.97608000 | 1.43997300 |
| O | 2.80166500 | 3.08550300 | 0.28458100 |
| C | 2.67136000 | 3.79055700 | 2.59839900 |
| H | 2.71012500 | 4.84430800 | 2.31877800 |
| H | 1.99640000 | 3.64431000 | 3.43520000 |
| H | 3.67824100 | 3.47027900 | 2.87955600 |
| H | 3.52982300 | 3.72632200 | 0.27913000 |

Transition State TS10'-11



E= -1167.987210

H= -1167.967996

G= -1168.037461

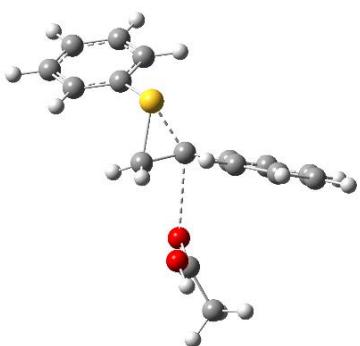
ZPVE= 0.293668

Imaginary Frequency= -237.6645 cm⁻¹

SUPPORTING INFORMATION

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -2.10237300 | 0.03130000 | -0.44123500 |
| C | -2.21215000 | -1.19053900 | 0.21521700 |
| C | -3.08094600 | 1.00909400 | -0.27973700 |
| C | -3.30045400 | -1.42882900 | 1.04358500 |
| H | -1.45431300 | -1.94981300 | 0.06794900 |
| C | -4.15679700 | 0.76854500 | 0.55976200 |
| H | -3.00770700 | 1.94352700 | -0.82259000 |
| C | -4.26713800 | -0.44947100 | 1.22006100 |
| H | -3.39135600 | -2.38066900 | 1.54956800 |
| H | -4.91925400 | 1.52561300 | 0.68555100 |
| H | -5.11418300 | -0.63732600 | 1.86627700 |
| C | 0.17426600 | 1.60860700 | -0.64998900 |
| H | 0.80090800 | 2.13156000 | -1.36450200 |
| C | 0.90293000 | 0.76851600 | 0.30988300 |
| H | 0.27603900 | 0.31600700 | 1.06957400 |
| H | -0.52587000 | 2.29084100 | -0.17670600 |
| C | 2.14342500 | 0.07895300 | 0.02735700 |
| C | 2.52179200 | -0.96129700 | 0.88420300 |
| C | 2.95822000 | 0.41017700 | -1.06199100 |
| C | 3.69269000 | -1.66076200 | 0.65809600 |
| H | 1.88714400 | -1.21461800 | 1.72513400 |
| C | 4.12329600 | -0.29600000 | -1.28914000 |
| H | 2.67919700 | 1.21061000 | -1.73385300 |
| C | 4.49050000 | -1.32820600 | -0.42982900 |
| H | 3.98128800 | -2.46645900 | 1.31894500 |
| H | 4.74811800 | -0.05046100 | -2.13695900 |
| H | 5.40362700 | -1.87899300 | -0.61457100 |
| S | -0.74147800 | 0.30009400 | -1.54913200 |
| O | 1.44197200 | 2.04864200 | 1.73050100 |
| C | 2.19214000 | 2.98923500 | 1.54411000 |
| O | 2.54874300 | 3.28650900 | 0.30386700 |
| C | 2.73207700 | 3.82617000 | 2.65723300 |
| H | 2.46834900 | 4.87227200 | 2.49384200 |
| H | 2.32621500 | 3.48516600 | 3.60352800 |
| H | 3.82079200 | 3.74484500 | 2.67211400 |
| H | 3.15196400 | 4.04142800 | 0.27017400 |

Dissociation Complex 10'-11 (Refer to Figure S19)



E= -1168.001129

SUPPORTING INFORMATION

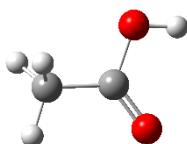
H= -1167.980851

G= -1168.054252

ZPVE= 0.292910

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -2.15873500 | -0.09415600 | -0.33295200 |
| C | -2.35731100 | -1.24961600 | 0.41292200 |
| C | -3.15153300 | 0.86788500 | -0.47488200 |
| C | -3.57665000 | -1.43064500 | 1.04761300 |
| H | -1.57497600 | -1.99349500 | 0.49750500 |
| C | -4.36425500 | 0.67179100 | 0.16650500 |
| H | -2.98578200 | 1.75107700 | -1.07906700 |
| C | -4.57430400 | -0.47253700 | 0.92558100 |
| H | -3.74570200 | -2.32186500 | 1.63638500 |
| H | -5.14661900 | 1.41197600 | 0.06854400 |
| H | -5.52377000 | -0.61980900 | 1.42249900 |
| C | 0.05136100 | 1.66051900 | -0.55589900 |
| H | 0.64604600 | 2.18490000 | -1.29187500 |
| C | 0.64486900 | 0.54081500 | 0.15796700 |
| H | 0.19422300 | 0.30340000 | 1.11341100 |
| H | -0.69570000 | 2.24933700 | -0.04116000 |
| C | 2.01880100 | 0.06004500 | -0.06139400 |
| C | 2.63394200 | -0.64962500 | 0.96711900 |
| C | 2.71646800 | 0.31493900 | -1.24163800 |
| C | 3.94025400 | -1.09142900 | 0.82159600 |
| H | 2.09392400 | -0.83728600 | 1.88722000 |
| C | 4.01483600 | -0.14031100 | -1.38937200 |
| H | 2.25172900 | 0.85942300 | -2.05570800 |
| C | 4.62884200 | -0.84065500 | -0.35664400 |
| H | 4.41696100 | -1.63610800 | 1.62530000 |
| H | 4.55049400 | 0.04927200 | -2.30969800 |
| H | 5.64477700 | -1.19343400 | -0.47469000 |
| S | -0.62947000 | 0.08352800 | -1.21370000 |
| O | 1.35578100 | 2.37008100 | 2.09618100 |
| C | 2.30667100 | 3.01065000 | 1.75032900 |
| O | 2.43671100 | 3.32377500 | 0.44076100 |
| C | 3.39676100 | 3.50273100 | 2.65668300 |
| H | 3.48353200 | 4.58794900 | 2.58612600 |
| H | 3.17113700 | 3.22009500 | 3.67939000 |
| H | 4.35032300 | 3.06464000 | 2.35633500 |
| H | 3.23803500 | 3.83641300 | 0.27900700 |

Acetic Acid



E= -229.026320

H= -229.020858

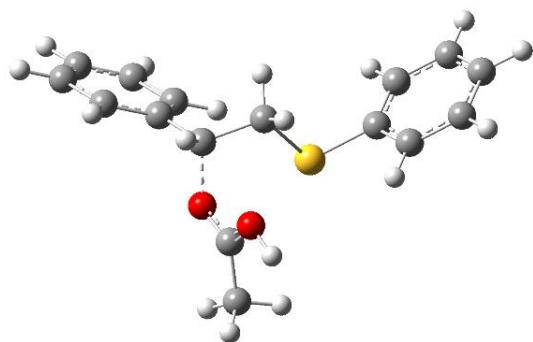
SUPPORTING INFORMATION

G= -229.053355

ZPVE= 0.062416

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -2.85225000 | -0.63389900 | -0.07902000 |
| H | -2.23493600 | -1.52236500 | -0.15921500 |
| H | -2.78656900 | -0.04105300 | -0.99081200 |
| H | -3.89740600 | -0.90860700 | 0.06036300 |
| C | -2.39349900 | 0.18959100 | 1.08655600 |
| O | -1.48993600 | -0.07774400 | 1.82603300 |
| O | -3.13162800 | 1.30912800 | 1.22523800 |
| H | -2.78133600 | 1.78705100 | 1.99071500 |

Protonated Acetate 10”



E= -1167.990796

H= -1167.971907

G= -1168.040603

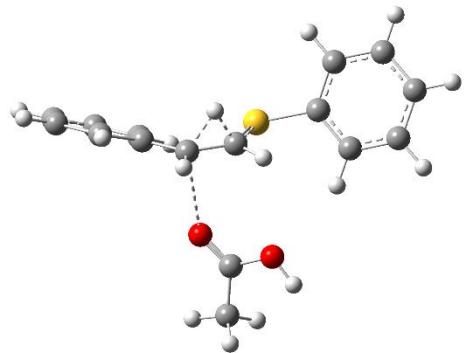
ZPVE= 0.296166

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 0.32261000 | 0.70745100 | 0.49327700 |
| C | 1.65812500 | 1.30886100 | 0.94737500 |
| H | 0.42821900 | -0.37619600 | 0.51267200 |
| C | -1.77908100 | 0.48474300 | -1.23541300 |
| C | -2.87189100 | 1.13515700 | -0.67063700 |
| C | -1.94049700 | -0.74640800 | -1.86106200 |
| C | -4.12536900 | 0.54540300 | -0.72115800 |
| H | -2.74001900 | 2.10197500 | -0.20053300 |
| C | -3.19910400 | -1.32880500 | -1.91376600 |
| H | -1.08644800 | -1.23926500 | -2.30700900 |
| C | -4.28834500 | -0.68586900 | -1.34309700 |
| H | -4.97645100 | 1.04981600 | -0.28344900 |
| H | -3.32716900 | -2.28500500 | -2.40309900 |
| H | -5.26832000 | -1.14202000 | -1.38682700 |
| H | -0.47581000 | 0.99073300 | 1.17613800 |
| C | 2.88864100 | 0.50617200 | 0.67705400 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| C | 3.88343000 | 0.45447900 | 1.64749300 |
| C | 3.05326200 | -0.18018700 | -0.52440900 |
| C | 5.03896000 | -0.27944300 | 1.42284100 |
| H | 3.75286300 | 0.98083700 | 2.58603900 |
| C | 4.21045000 | -0.90740500 | -0.74818300 |
| H | 2.28128400 | -0.14560600 | -1.28386300 |
| C | 5.20219000 | -0.95795200 | 0.22433900 |
| H | 5.80666200 | -0.32390300 | 2.18332200 |
| H | 4.33889400 | -1.43971600 | -1.68097300 |
| H | 6.10180200 | -1.53238000 | 0.04754800 |
| H | 1.60704800 | 1.58138500 | 2.00089800 |
| S | -0.16815500 | 1.23100700 | -1.18700200 |
| O | 1.87224800 | 2.62577900 | 0.22373100 |
| C | 1.07316700 | 3.58228200 | 0.34471800 |
| O | 0.17157200 | 3.51718400 | 1.26955900 |
| C | 1.19841700 | 4.74927100 | -0.55513200 |
| H | 1.08966500 | 5.67977100 | 0.00187400 |
| H | 2.15255200 | 4.71646900 | -1.07190800 |
| H | 0.39029200 | 4.67624700 | -1.28907000 |
| H | -0.40678400 | 4.29533100 | 1.28741200 |

Transition State TS10''-22



E= -1167.963718

H= -1167.943474

G= -1168.017242

ZPVE= 0.288944

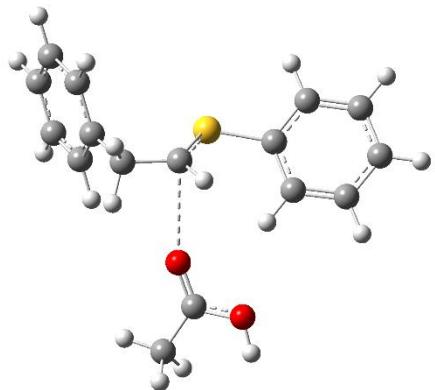
Imaginary Frequency= -702.2805 cm⁻¹

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 0.07766900 | 0.44782500 | 0.96452700 |
| C | 1.42278000 | 0.37593100 | 1.36721300 |
| H | 0.43898900 | -0.55295700 | 1.65858200 |
| C | -2.32436600 | 0.02963500 | -0.15649800 |
| C | -2.96111700 | 1.23694000 | 0.11085600 |
| C | -3.02790700 | -1.16797900 | -0.16569200 |
| C | -4.31692600 | 1.23535300 | 0.39973400 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | -2.39757500 | 2.16140100 | 0.08520800 |
| C | -4.38845500 | -1.15459600 | 0.10924700 |
| H | -2.51907900 | -2.09745500 | -0.38534700 |
| C | -5.02901400 | 0.04225800 | 0.39611600 |
| H | -4.82193200 | 2.16781100 | 0.61350700 |
| H | -4.94489800 | -2.08206400 | 0.10223300 |
| H | -6.08900800 | 0.04749300 | 0.61210000 |
| H | -0.59087700 | 0.98088500 | 1.63467900 |
| C | 2.56682200 | -0.17222300 | 0.67565700 |
| C | 3.65666300 | -0.58065000 | 1.45760900 |
| C | 2.63376000 | -0.27039300 | -0.71916600 |
| C | 4.77675800 | -1.12074800 | 0.85810400 |
| H | 3.61238900 | -0.47840300 | 2.53538700 |
| C | 3.76521900 | -0.79850600 | -1.31250800 |
| H | 1.83597400 | 0.11461700 | -1.33696100 |
| C | 4.82692200 | -1.23313800 | -0.52725200 |
| H | 5.61243200 | -1.44598600 | 1.46207100 |
| H | 3.82642300 | -0.86367400 | -2.39002800 |
| H | 5.70729300 | -1.64928700 | -0.99949900 |
| H | 1.59959500 | 0.77613800 | 2.36250600 |
| S | -0.59349600 | 0.00645300 | -0.56933400 |
| O | 1.55037900 | 2.70188600 | -0.17289400 |
| C | 0.90849500 | 3.71019200 | -0.10430300 |
| O | -0.25873000 | 3.69147600 | 0.58166000 |
| C | 1.28664000 | 5.02296100 | -0.72488100 |
| H | 1.36829300 | 5.79091200 | 0.04606900 |
| H | 2.23667000 | 4.91934800 | -1.23805300 |
| H | 0.51812200 | 5.33415200 | -1.43421400 |
| H | -0.67056600 | 4.56432700 | 0.59464000 |

Dissociation Complex 10''-22 (Refer to Figure S19)



E= -1167.998855

H= -1167.978474

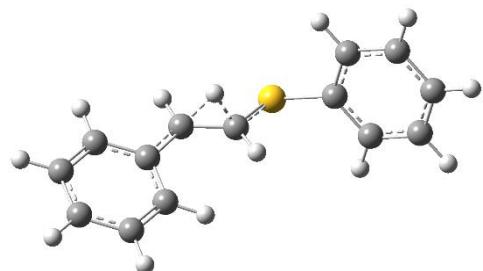
G= -1168.052240

ZPVE= 0.292519

SUPPORTING INFORMATION

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 0.42410600 | 0.54698400 | 1.37936200 |
| C | 1.86681900 | 0.68759300 | 1.66675400 |
| H | 1.99112100 | 0.47373100 | 2.73626100 |
| C | -1.88766200 | -0.22195700 | 0.23513400 |
| C | -2.45484100 | 1.04047500 | 0.37578700 |
| C | -2.66004700 | -1.35803800 | 0.01569700 |
| C | -3.83487000 | 1.15004300 | 0.33147800 |
| H | -1.83541000 | 1.92151500 | 0.48753400 |
| C | -4.03914600 | -1.22701700 | -0.02536100 |
| H | -2.19555200 | -2.32821500 | -0.10968400 |
| C | -4.62335900 | 0.02203600 | 0.13668100 |
| H | -4.29395500 | 2.12359700 | 0.43778000 |
| H | -4.65498900 | -2.10158600 | -0.18389700 |
| H | -5.70015700 | 0.11931200 | 0.10015200 |
| H | -0.28812900 | 1.13826000 | 1.94646500 |
| C | 2.77132200 | -0.15579200 | 0.81084000 |
| C | 3.18375100 | -1.41195100 | 1.24175600 |
| C | 3.16268800 | 0.30573200 | -0.44285500 |
| C | 3.98266300 | -2.20100400 | 0.42601600 |
| H | 2.89033300 | -1.77146100 | 2.22162100 |
| C | 3.96027200 | -0.48376900 | -1.25749400 |
| H | 2.84265400 | 1.28737000 | -0.77497300 |
| C | 4.36988000 | -1.73786400 | -0.82348400 |
| H | 4.30839500 | -3.17355700 | 0.76989000 |
| H | 4.26893500 | -0.11820800 | -2.22777900 |
| H | 4.99720800 | -2.35091800 | -1.45667000 |
| H | 2.07623500 | 1.75917000 | 1.55961800 |
| S | -0.13946500 | -0.46414400 | 0.24261300 |
| O | 0.43022100 | 3.00635200 | 0.22319800 |
| C | -0.00654200 | 4.08295400 | -0.09138000 |
| O | -1.29952800 | 4.34720100 | 0.14787500 |
| C | 0.79033600 | 5.17459300 | -0.74214200 |
| H | 0.77181700 | 6.06938400 | -0.11791600 |
| H | 1.81537700 | 4.84789800 | -0.88048700 |
| H | 0.35232800 | 5.42712200 | -1.70911500 |
| H | -1.54476800 | 5.23489000 | -0.14140300 |

Transition State TS11-22



E= -938.924335

H= -938.910554

SUPPORTING INFORMATION

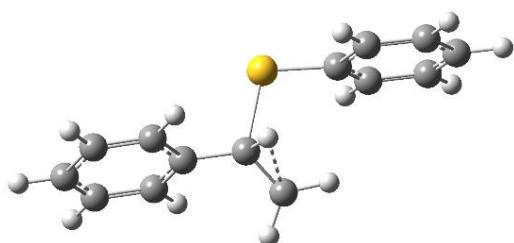
G= -938.966784

ZPVE= 0.225613

Imaginary Frequency= -696.2698 cm⁻¹

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -2.58371900 | -0.39586100 | -0.20580600 |
| C | -3.05001600 | -0.49203200 | 1.10085300 |
| C | -3.17458900 | 0.46812400 | -1.12086400 |
| C | -4.10876300 | 0.30920000 | 1.50031100 |
| H | -2.60005600 | -1.19375100 | 1.79162000 |
| C | -4.23593300 | 1.26179600 | -0.71015600 |
| H | -2.81412500 | 0.51209200 | -2.14033600 |
| C | -4.69837400 | 1.18398400 | 0.59651600 |
| H | -4.47931800 | 0.24226400 | 2.51425900 |
| H | -4.70417900 | 1.93610100 | -1.41438200 |
| H | -5.52896800 | 1.80185500 | 0.91068900 |
| C | 0.11138000 | -0.48669200 | -0.24266000 |
| H | -0.02524000 | 0.59009800 | -0.18727400 |
| C | 1.41458700 | -1.01345600 | -0.13687100 |
| H | 1.48598100 | -2.09997400 | -0.14365600 |
| C | 2.64316000 | -0.26727500 | -0.01338100 |
| C | 3.79226700 | -0.96642100 | 0.38134700 |
| C | 2.72012700 | 1.10469900 | -0.29466300 |
| C | 4.99550200 | -0.30006500 | 0.51392500 |
| H | 3.73186400 | -2.02891500 | 0.58414400 |
| C | 3.92510900 | 1.76241900 | -0.16028400 |
| H | 1.85171600 | 1.64814900 | -0.64371700 |
| C | 5.05883000 | 1.06220500 | 0.24740600 |
| H | 5.88241200 | -0.83761500 | 0.81930900 |
| H | 3.99264900 | 2.81796800 | -0.38455500 |
| H | 6.00182100 | 1.58412600 | 0.34536800 |
| H | 0.51822500 | -0.79921200 | 0.90661200 |
| S | -1.24950900 | -1.44240900 | -0.74378000 |

Transition State TS11-23



E= -938.887216

H= -938.872990

G= -938.929766

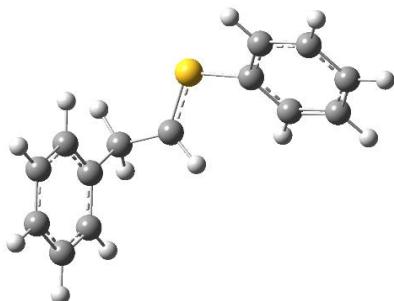
SUPPORTING INFORMATION

ZPVE= 0.224790

Imaginary Frequency= -350.1613 cm⁻¹

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -2.06256800 | -0.20844800 | -0.39672200 |
| C | -2.72645900 | 1.01143700 | -0.58180100 |
| C | -2.74564800 | -1.31213000 | 0.12626700 |
| C | -4.06101100 | 1.12223500 | -0.23882700 |
| H | -2.19430700 | 1.85172600 | -1.01155300 |
| C | -4.08102400 | -1.18970400 | 0.47090900 |
| H | -2.22946500 | -2.25689100 | 0.24097300 |
| C | -4.73438000 | 0.02349800 | 0.28930000 |
| H | -4.58248300 | 2.05761300 | -0.39008800 |
| H | -4.61520500 | -2.04065800 | 0.87098200 |
| H | -5.77966100 | 0.11385900 | 0.55454400 |
| C | 0.65650900 | 0.21085800 | 0.63022600 |
| C | 0.13641800 | 1.26982400 | 1.34865400 |
| H | -0.93824900 | 1.37703000 | 1.46749200 |
| H | 0.78284900 | 1.99242300 | 1.83949700 |
| H | 0.17512800 | -0.66825900 | 1.13076300 |
| C | 2.09639300 | 0.06690800 | 0.32843500 |
| C | 2.68837500 | -1.19368000 | 0.35522700 |
| C | 2.84957200 | 1.18982400 | -0.00640300 |
| C | 4.04020800 | -1.32287100 | 0.08307300 |
| H | 2.09526100 | -2.06948600 | 0.59253200 |
| C | 4.19996700 | 1.05459400 | -0.28121900 |
| H | 2.37899300 | 2.16469800 | -0.07470100 |
| C | 4.79471900 | -0.20005900 | -0.23160800 |
| H | 4.50452900 | -2.29902200 | 0.11311100 |
| H | 4.78635000 | 1.92423400 | -0.54456700 |
| H | 5.84887900 | -0.30417600 | -0.45098800 |
| S | -0.40783700 | -0.38437500 | -0.92090900 |

Sulphonium Ion 22



E= -938.954271

H= -938.940367

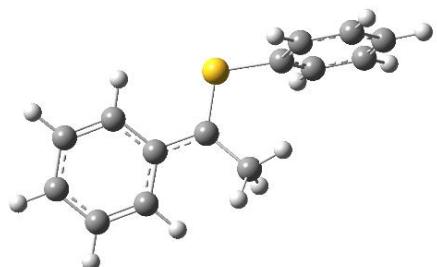
G= -938.996628

ZPVE= 0.229419

SUPPORTING INFORMATION

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -1.77222706 | 0.54441546 | 1.17374675 |
| C | -2.45439910 | 1.55472373 | 0.49263092 |
| C | -2.39909587 | -0.27934475 | 2.11318319 |
| C | -3.81505550 | 1.71653831 | 0.74058165 |
| H | -1.94063472 | 2.19504933 | -0.22567166 |
| C | -3.76038491 | -0.10185447 | 2.34290271 |
| H | -1.83395411 | -1.02659557 | 2.67366625 |
| C | -4.46439429 | 0.88947810 | 1.65756714 |
| H | -4.36837147 | 2.49252146 | 0.21225588 |
| H | -4.26855749 | -0.73184028 | 3.07264423 |
| H | -5.52890844 | 1.02568791 | 1.84862055 |
| C | 0.21580500 | -1.22729700 | 0.67590900 |
| H | -0.66530838 | -1.88124534 | 0.66388352 |
| C | 1.55688000 | -1.84204400 | 0.64738500 |
| H | 1.91805432 | -2.11728561 | 1.64578775 |
| C | 1.30692779 | -3.06777368 | -0.23661260 |
| C | 0.74508667 | -4.22005454 | 0.32446250 |
| C | 1.60241600 | -3.02293238 | -1.60337623 |
| C | 0.52181271 | -5.34017905 | -0.47148399 |
| H | 0.50229201 | -4.25171138 | 1.38978859 |
| C | 1.37150135 | -4.14408936 | -2.39597310 |
| H | 2.03991813 | -2.12388666 | -2.04239261 |
| C | 0.83246669 | -5.30107764 | -1.83143667 |
| H | 0.10624983 | -6.24565434 | -0.02940436 |
| H | 1.62189957 | -4.11748512 | -3.45650890 |
| H | 0.65593736 | -6.17807090 | -2.45447150 |
| H | 2.26998509 | -1.16281759 | 0.16044871 |
| S | -0.02326775 | 0.39000649 | 0.86602892 |

Sulphonium Ion 23



E= -938.975718

H= -938.961539

G= -939.017616

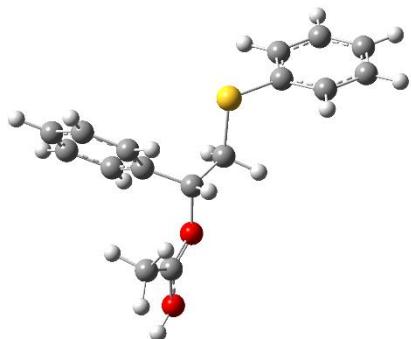
ZPVE= 0.229216

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -2.04090500 | -0.41494600 | -0.14394100 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| C | -2.64639100 | 0.32802500 | -1.15151100 |
| C | -2.74043900 | -0.82265400 | 0.98606400 |
| C | -3.97641600 | 0.69065900 | -1.00544000 |
| H | -2.09094200 | 0.61228400 | -2.03622500 |
| C | -4.07068800 | -0.45158100 | 1.11673400 |
| H | -2.25655000 | -1.41818900 | 1.74932000 |
| C | -4.68392300 | 0.30350100 | 0.12586300 |
| H | -4.46140000 | 1.26929200 | -1.77981900 |
| H | -4.62746000 | -0.75824700 | 1.99171700 |
| H | -5.72296700 | 0.58546300 | 0.23142800 |
| C | 0.59957700 | 0.33308600 | 0.13493600 |
| C | 0.01791700 | 1.63839400 | 0.54945700 |
| H | -1.01107800 | 1.53929300 | 0.88186900 |
| H | 0.02221100 | 2.31315100 | -0.31372500 |
| H | 0.62134800 | 2.08971900 | 1.33353200 |
| C | 2.02946600 | 0.14395000 | 0.09114700 |
| C | 2.87383100 | 1.27032900 | 0.09250600 |
| C | 2.60640000 | -1.14001500 | 0.02421000 |
| C | 4.24227200 | 1.11597800 | 0.00449400 |
| H | 2.45704800 | 2.26701400 | 0.13043300 |
| C | 3.97413100 | -1.28567500 | -0.04531400 |
| H | 1.98249900 | -2.02342700 | 0.06395500 |
| C | 4.79305600 | -0.15892100 | -0.06082400 |
| H | 4.88295900 | 1.98674900 | -0.01031300 |
| H | 4.41029000 | -2.27437700 | -0.07869500 |
| H | 5.86740200 | -0.27762300 | -0.11668600 |
| S | -0.36484300 | -0.94697600 | -0.34822900 |

Protonated Acetate 10''' (Refer to Figure S19)



E= -1167.986946

H= -1167.968113

G= -1168.037773

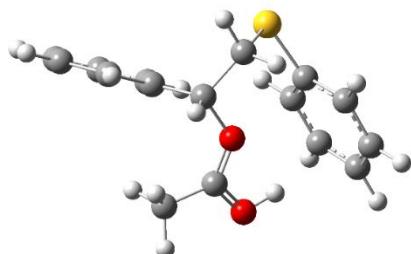
ZPVE= 0.296205

| Symbol | X | Y | Z |
|--------|-------------|------------|------------|
| C | -1.25321700 | 2.64814000 | 0.60448400 |
| C | -0.41910800 | 1.41262100 | 0.34624300 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| S | -1.95237200 | 2.48918100 | 2.27884700 |
| H | -0.62508100 | 3.53741200 | 0.56511000 |
| H | -2.04590100 | 2.72819600 | -0.14047000 |
| C | -2.32356700 | 4.20153200 | 2.58328800 |
| C | -1.36215900 | 5.03520800 | 3.14634000 |
| C | -3.59001100 | 4.69211700 | 2.28383900 |
| C | -1.66618700 | 6.36551100 | 3.39418100 |
| H | -0.38751700 | 4.63712000 | 3.39834900 |
| C | -3.88818800 | 6.02385700 | 2.53572300 |
| H | -4.33614200 | 4.02983200 | 1.86438200 |
| C | -2.92733700 | 6.85955100 | 3.08762200 |
| H | -0.92110200 | 7.01393800 | 3.83568900 |
| H | -4.87380500 | 6.40602500 | 2.30565300 |
| H | -3.16375200 | 7.89627600 | 3.28732600 |
| O | 0.17074100 | 1.65184800 | -1.01885600 |
| C | 1.00171000 | 0.87969000 | -1.55807400 |
| C | 1.56144400 | -0.34313900 | -0.93598900 |
| H | 0.79819800 | -1.12541200 | -0.99562600 |
| H | 2.46346500 | -0.66572200 | -1.45064100 |
| H | 1.76934400 | -0.17615500 | 0.11928200 |
| O | 1.33031500 | 1.24080800 | -2.75052300 |
| H | 1.98039300 | 0.65246200 | -3.16333900 |
| H | 0.42558900 | 1.38017400 | 1.03594500 |
| C | -1.18057200 | 0.12053900 | 0.34621500 |
| C | -0.97629900 | -0.79334700 | 1.37330700 |
| C | -2.11438400 | -0.14775900 | -0.65211300 |
| C | -1.70209400 | -1.97631100 | 1.40273300 |
| H | -0.26407800 | -0.57274700 | 2.16080900 |
| C | -2.82459400 | -1.33786000 | -0.62904000 |
| H | -2.29104000 | 0.57177300 | -1.44396400 |
| C | -2.61920000 | -2.25122800 | 0.39852200 |
| H | -1.55048500 | -2.68099500 | 2.20915800 |
| H | -3.54827200 | -1.54810000 | -1.40505200 |
| H | -3.18151600 | -3.17514200 | 0.41887000 |

Protonated Acetate 10* (lowest energy conformation, not involved in pathway)



E= -1168.001929

H= -1167.983656

G= -1168.048219

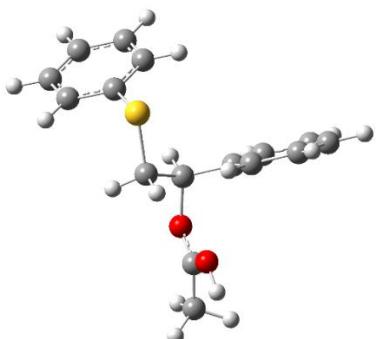
ZPVE= 0.296461

SUPPORTING INFORMATION

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 1.59422200 | -0.50841200 | -0.10559600 |
| C | 0.95034800 | -0.11546300 | 1.22263500 |
| H | 2.36164900 | -1.25228300 | 0.11244600 |
| C | 1.07158600 | 1.81738400 | -1.50761000 |
| C | 1.05532600 | 3.15683500 | -1.13115900 |
| C | -0.00283800 | 1.28743100 | -2.21835100 |
| C | -0.05381000 | 3.94848500 | -1.41453800 |
| H | 1.90633100 | 3.57875600 | -0.61093800 |
| C | -1.11820100 | 2.06909000 | -2.47806900 |
| H | 0.02888300 | 0.26081300 | -2.56110200 |
| C | -1.15477700 | 3.39959400 | -2.06469700 |
| H | -0.05764600 | 4.99175200 | -1.12587300 |
| H | -1.95419100 | 1.64885800 | -3.02175900 |
| H | -2.01966100 | 4.01267100 | -2.28171300 |
| H | 0.84748900 | -0.98128400 | -0.74294300 |
| C | 1.86721400 | 0.40156700 | 2.29142600 |
| C | 2.25767900 | -0.46888100 | 3.30348200 |
| C | 2.34057900 | 1.71125200 | 2.28197200 |
| C | 3.12676200 | -0.03827300 | 4.29579800 |
| H | 1.88472100 | -1.48710200 | 3.31824100 |
| C | 3.19599300 | 2.14312700 | 3.28470500 |
| H | 2.04543900 | 2.39166500 | 1.49251600 |
| C | 3.59277000 | 1.26869700 | 4.28841400 |
| H | 3.43141800 | -0.72082800 | 5.07754500 |
| H | 3.56194300 | 3.16105600 | 3.27724700 |
| H | 4.26427700 | 1.60775800 | 5.06573800 |
| H | 0.37855400 | -0.96886100 | 1.59572600 |
| S | 2.44905100 | 0.80379000 | -1.01840300 |
| O | -0.04693600 | 0.91079800 | 0.84218600 |
| C | -0.84675400 | 1.50017400 | 1.62377600 |
| O | -1.52944900 | 2.45794700 | 1.12156400 |
| C | -1.05102600 | 1.17725200 | 3.04911000 |
| H | -0.98496700 | 0.10317500 | 3.21306100 |
| H | -0.23950300 | 1.64773900 | 3.61318600 |
| H | -2.00589400 | 1.57509300 | 3.37991100 |
| H | -1.28580900 | 2.65774900 | 0.18354300 |

Calculated energies and structures of species involved in Figure 7 (Solution-phase)

Protonated Acetate 10'



SUPPORTING INFORMATION

E= -1168.066935

H= -1168.048260

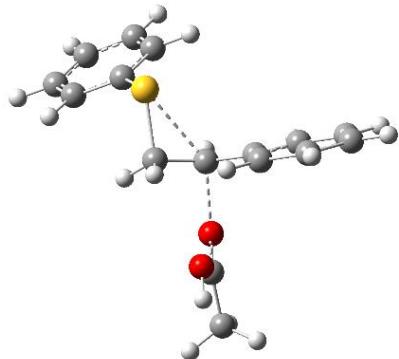
G= -1168.116265

ZPVE= 0.296804

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 2.53456100 | -0.20189700 | 0.61915700 |
| C | 2.73966900 | -1.28776800 | -0.22692100 |
| C | 3.35300000 | 0.92132300 | 0.52129800 |
| C | 3.76231900 | -1.24957100 | -1.16694500 |
| H | 2.09724500 | -2.15570000 | -0.14849300 |
| C | 4.36230700 | 0.96047000 | -0.42906200 |
| H | 3.20183400 | 1.75758000 | 1.19261800 |
| C | 4.57010600 | -0.12587200 | -1.27160300 |
| H | 3.92092000 | -2.09694600 | -1.82095700 |
| H | 4.99439900 | 1.83555300 | -0.50433700 |
| H | 5.36324300 | -0.09560700 | -2.00707600 |
| C | 0.09998600 | 0.96165400 | 1.18148500 |
| H | -0.65830400 | 1.10385100 | 1.94736500 |
| C | -0.47672800 | 0.49329700 | -0.14087500 |
| H | 0.34062200 | 0.31326800 | -0.83619700 |
| H | 0.62460200 | 1.90570700 | 1.03771000 |
| C | -1.40406900 | -0.69271400 | -0.14505300 |
| C | -1.55037800 | -1.39596200 | -1.33824300 |
| C | -2.10174600 | -1.10834100 | 0.98477500 |
| C | -2.39506000 | -2.49401000 | -1.40801900 |
| H | -0.99601000 | -1.08212700 | -2.21520800 |
| C | -2.93971000 | -2.21149400 | 0.91762700 |
| H | -1.99686000 | -0.58086400 | 1.92354000 |
| C | -3.09034900 | -2.90293200 | -0.27797200 |
| H | -2.50223600 | -3.03355500 | -2.33951300 |
| H | -3.47538300 | -2.53167600 | 1.80131400 |
| H | -3.74490400 | -3.76331000 | -0.32617100 |
| S | 1.24783000 | -0.27481000 | 1.84461600 |
| O | -1.13217700 | 1.65376800 | -0.84219800 |
| C | -2.16010600 | 2.24380000 | -0.41457200 |
| O | -2.66226800 | 1.86643300 | 0.70419100 |
| C | -2.74258500 | 3.33722400 | -1.21779700 |
| H | -2.77335600 | 4.24322500 | -0.61060000 |
| H | -2.15307000 | 3.49664200 | -2.11315900 |
| H | -3.76733500 | 3.06540200 | -1.47812400 |
| H | -3.45244000 | 2.37065800 | 0.96381500 |

SUPPORTING INFORMATION

Transition State TS10'-11



E= -1168.052411

H= -1168.033141

G= -1168.102569

ZPVE= 0.293410

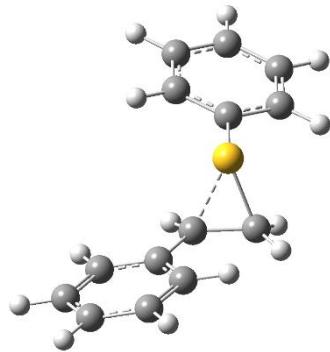
Imaginary Frequency= -294.3755 cm⁻¹

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -2.69537800 | -0.39629600 | -0.49542500 |
| C | -3.05526100 | -1.27177700 | 0.52422200 |
| C | -3.44991800 | 0.74809800 | -0.74253400 |
| C | -4.17358800 | -0.99820000 | 1.30054800 |
| H | -2.46030100 | -2.15698000 | 0.70861700 |
| C | -4.55597800 | 1.02154400 | 0.04703000 |
| H | -3.17683900 | 1.41526300 | -1.55055800 |
| C | -4.91989300 | 0.14827100 | 1.06603500 |
| H | -4.45451500 | -1.67875800 | 2.09320200 |
| H | -5.14068900 | 1.91222400 | -0.14076700 |
| H | -5.78751200 | 0.36279600 | 1.67588000 |
| C | -0.18039900 | 0.60561000 | -1.18865600 |
| H | 0.49801000 | 0.70074400 | -2.02829800 |
| C | 0.40033000 | 0.05269600 | 0.03369800 |
| H | -0.25111900 | 0.06317500 | 0.89867200 |
| H | -0.75057300 | 1.51550700 | -1.03432600 |
| C | 1.53219400 | -0.83234900 | 0.09837500 |
| C | 1.74805700 | -1.52553400 | 1.29715200 |
| C | 2.40940900 | -1.01476300 | -0.97965600 |
| C | 2.81863000 | -2.39143200 | 1.41667600 |
| H | 1.06689900 | -1.37625600 | 2.12593300 |
| C | 3.47465400 | -1.88439600 | -0.85606400 |
| H | 2.26232800 | -0.47626600 | -1.90560400 |
| C | 3.67864500 | -2.57057300 | 0.33905800 |
| H | 2.98383500 | -2.92768800 | 2.34078800 |
| H | 4.15185500 | -2.03064900 | -1.68614500 |
| H | 4.51642900 | -3.24982100 | 0.42877600 |
| S | -1.30782000 | -0.80379500 | -1.52354200 |
| O | 1.19560000 | 1.80465000 | 0.93634700 |

SUPPORTING INFORMATION

| | | | |
|---|------------|------------|-------------|
| C | 2.05085200 | 2.46681400 | 0.37922900 |
| O | 2.39206700 | 2.14886000 | -0.86042900 |
| C | 2.74038300 | 3.62627100 | 1.01969300 |
| H | 2.57598000 | 4.52123900 | 0.41855400 |
| H | 2.35647200 | 3.77385100 | 2.02289000 |
| H | 3.81285300 | 3.43149900 | 1.05366000 |
| H | 3.08423100 | 2.72884200 | -1.20821800 |

Thiiranium Ion 11



E= -939.029526

H= -939.015918

G= -939.071069

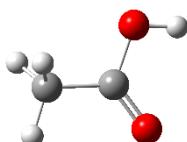
ZPVE= 0.230126

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 0.64276900 | -0.29898400 | 0.70562400 |
| H | 0.11735700 | 0.48051200 | 1.24480300 |
| C | 0.06925600 | -1.64018300 | 0.80834000 |
| H | -0.75215900 | -1.79564300 | 1.49391500 |
| H | 0.68799800 | -2.50449700 | 0.61022600 |
| S | -0.46589700 | -0.83188100 | -0.74294900 |
| C | -2.05576600 | -0.16479200 | -0.32414300 |
| C | -2.25799800 | 1.20045400 | -0.48305700 |
| C | -3.07641900 | -1.02093400 | 0.06934200 |
| C | -3.51683600 | 1.71950400 | -0.22043400 |
| H | -1.44842500 | 1.84565200 | -0.79840500 |
| C | -4.32874400 | -0.48494700 | 0.32745200 |
| H | -2.90068800 | -2.08387300 | 0.17150500 |
| C | -4.54663700 | 0.87969300 | 0.18395000 |
| H | -3.68974800 | 2.78111300 | -0.33133200 |
| H | -5.13349400 | -1.13640600 | 0.63928500 |
| H | -5.52614600 | 1.29104600 | 0.38770900 |
| C | 2.05033900 | -0.01336200 | 0.36451100 |
| C | 2.91999000 | -0.99559400 | -0.10706200 |
| C | 2.50735200 | 1.29319900 | 0.53093900 |
| C | 4.23270900 | -0.66885900 | -0.40779000 |
| H | 2.58837900 | -2.01675100 | -0.24387000 |
| C | 3.82267300 | 1.61407100 | 0.23560000 |

SUPPORTING INFORMATION

| | | | |
|---|------------|-------------|-------------|
| H | 1.83060700 | 2.05520000 | 0.89713800 |
| C | 4.68576300 | 0.63354200 | -0.23591200 |
| H | 4.90434700 | -1.43393900 | -0.77298700 |
| H | 4.17287000 | 2.62816100 | 0.37307400 |
| H | 5.71276000 | 0.88266900 | -0.46803000 |

Acetic Acid



E= -229.033900

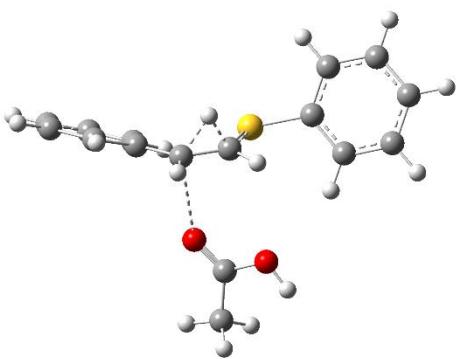
H= -229.028403

G= -229.061061

ZPVE= 0.062080

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 1.38768400 | -0.12225200 | 0.00012800 |
| H | 1.91712700 | 0.82451100 | -0.00151400 |
| H | 1.65763500 | -0.70762900 | -0.87828000 |
| H | 1.65682600 | -0.70385300 | 0.88133200 |
| C | -0.08885400 | 0.12119900 | -0.00091800 |
| O | -0.62521800 | 1.19907800 | 0.00022200 |
| O | -0.78649200 | -1.02425200 | 0.00007800 |
| H | -1.73089000 | -0.80532000 | 0.00080600 |

Transition State TS10''-22



E= -1168.029680

H= -1168.009588

G= -1168.082488

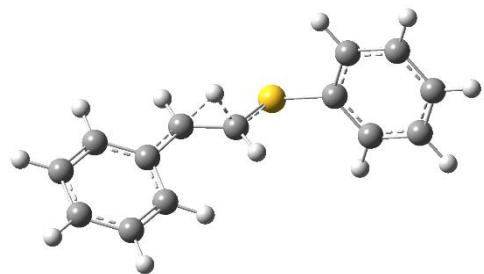
ZPVE= 0.289241

Imaginary Frequency= -680.3077 cm⁻¹

SUPPORTING INFORMATION

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -0.10851100 | -0.26918900 | 0.86128600 |
| C | 1.23230100 | -0.26421200 | 1.26781800 |
| H | 0.27504000 | -1.26801600 | 1.51010000 |
| C | -2.46402300 | -0.80184300 | -0.31548500 |
| C | -3.19712800 | 0.34911800 | -0.04632600 |
| C | -3.07378500 | -2.05029200 | -0.33576800 |
| C | -4.55237200 | 0.24086200 | 0.22865300 |
| H | -2.70861500 | 1.31504800 | -0.05426300 |
| C | -4.43397500 | -2.14596200 | -0.07371800 |
| H | -2.48962000 | -2.93542000 | -0.55005000 |
| C | -5.17008600 | -1.00402300 | 0.21228200 |
| H | -5.12771300 | 1.13102300 | 0.44528100 |
| H | -4.91469800 | -3.11495700 | -0.08781300 |
| H | -6.22899200 | -1.08288600 | 0.42007700 |
| H | -0.81238000 | 0.20059300 | 1.54056000 |
| C | 2.41137000 | -0.72624100 | 0.56826700 |
| C | 3.51497900 | -1.09373400 | 1.34943500 |
| C | 2.49492300 | -0.78687300 | -0.82756700 |
| C | 4.66960400 | -1.55488200 | 0.74614500 |
| H | 3.45235600 | -1.02332900 | 2.42810800 |
| C | 3.65899900 | -1.23605900 | -1.42446800 |
| H | 1.68087900 | -0.43736600 | -1.44486200 |
| C | 4.73842900 | -1.62910700 | -0.64070900 |
| H | 5.51653900 | -1.84851800 | 1.35060300 |
| H | 3.72999000 | -1.27236100 | -2.50274300 |
| H | 5.64441100 | -1.98287100 | -1.11521600 |
| H | 1.37651900 | 0.09349800 | 2.28365300 |
| S | -0.73234100 | -0.68571400 | -0.70831100 |
| O | 1.32842700 | 2.13526000 | -0.31189400 |
| C | 0.52901500 | 3.00286700 | -0.08173900 |
| O | -0.55151900 | 2.70541600 | 0.66348900 |
| C | 0.63076600 | 4.41858600 | -0.56490400 |
| H | 0.62627600 | 5.10092600 | 0.28572300 |
| H | 1.54547100 | 4.54352100 | -1.13425900 |
| H | -0.23044100 | 4.65429200 | -1.19108300 |
| H | -1.11587400 | 3.47873200 | 0.79719700 |

Transition State 11-22



E= -938.993140

H= -938.979367

SUPPORTING INFORMATION

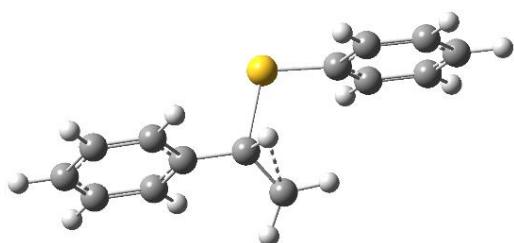
G= -939.035648

ZPVE= 0.225830

Imaginary Frequency= - 707.5079 cm⁻¹

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -2.58157200 | -0.43021800 | -0.13396600 |
| C | -2.91859400 | -0.21388900 | 1.19795800 |
| C | -3.29929700 | 0.17304500 | -1.16004100 |
| C | -3.97308200 | 0.63438900 | 1.50234500 |
| H | -2.36435300 | -0.70633700 | 1.98642100 |
| C | -4.36009200 | 1.01151600 | -0.84525300 |
| H | -3.02760000 | -0.00977400 | -2.19112600 |
| C | -4.69321000 | 1.24443200 | 0.48238300 |
| H | -4.23612900 | 0.81194200 | 2.53650000 |
| H | -4.92202200 | 1.48479800 | -1.63921400 |
| H | -5.51865700 | 1.90095600 | 0.72385600 |
| C | 0.11329000 | -0.51745600 | -0.18942100 |
| H | -0.02711900 | 0.55496800 | -0.28273400 |
| C | 1.40941500 | -1.02963300 | -0.03150900 |
| H | 1.48842700 | -2.10591700 | 0.10039200 |
| C | 2.63716100 | -0.26591100 | -0.00046700 |
| C | 3.78875300 | -0.91421400 | 0.46157800 |
| C | 2.70686600 | 1.06445100 | -0.43388700 |
| C | 4.99256300 | -0.23512000 | 0.50777500 |
| H | 3.72835500 | -1.94593300 | 0.78417900 |
| C | 3.91257900 | 1.73538900 | -0.38431100 |
| H | 1.83283900 | 1.56491500 | -0.82811300 |
| C | 5.05165300 | 1.08827200 | 0.08866900 |
| H | 5.88222000 | -0.73416900 | 0.86573100 |
| H | 3.97301400 | 2.76010800 | -0.72357300 |
| H | 5.99392200 | 1.61939600 | 0.12021200 |
| H | 0.51369300 | -0.67576800 | 0.98569900 |
| S | -1.25220000 | -1.53684300 | -0.55058400 |

Transition State 11-23



E= -938.958949

H= -938.945099

G= -939.000509

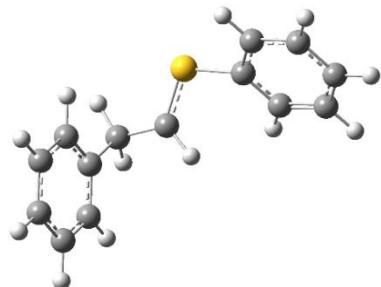
SUPPORTING INFORMATION

ZPVE= 0.225607

Imaginary Frequency= -497.7567 cm⁻¹

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -2.04481200 | -0.06717900 | -0.46217500 |
| C | -2.85977000 | 1.06446100 | -0.48782400 |
| C | -2.55126800 | -1.29228000 | -0.02601500 |
| C | -4.17878000 | 0.96948700 | -0.06858200 |
| H | -2.45937900 | 2.00704900 | -0.83927600 |
| C | -3.86772300 | -1.37651800 | 0.39711100 |
| H | -1.91614300 | -2.16904800 | -0.02742300 |
| C | -4.67947100 | -0.24750600 | 0.37545300 |
| H | -4.81319700 | 1.84522300 | -0.08896300 |
| H | -4.26295900 | -2.32419700 | 0.73722000 |
| H | -5.70794700 | -0.31859400 | 0.70399600 |
| C | 0.59167200 | 0.23160600 | 0.55314500 |
| C | 0.14500200 | 1.30320800 | 1.34654900 |
| H | -0.91856500 | 1.51716900 | 1.41461800 |
| H | 0.82508700 | 1.89981500 | 1.94951200 |
| H | 0.13944400 | -0.58743300 | 1.17566200 |
| C | 2.05185000 | 0.04325700 | 0.31218200 |
| C | 2.58997900 | -1.24034400 | 0.31177100 |
| C | 2.86130800 | 1.14294800 | 0.04490400 |
| C | 3.94295400 | -1.41830000 | 0.07148000 |
| H | 1.95143100 | -2.09453900 | 0.50208800 |
| C | 4.21472400 | 0.95969900 | -0.19772100 |
| H | 2.43782300 | 2.14049800 | 0.01189600 |
| C | 4.75527800 | -0.31903900 | -0.18152200 |
| H | 4.36347400 | -2.41476900 | 0.07952400 |
| H | 4.84356900 | 1.81483200 | -0.40533400 |
| H | 5.81050700 | -0.46089400 | -0.37366200 |
| S | -0.38242500 | 0.03899400 | -1.04827500 |

Sulphonium Ion 22



E= -939.022403

H= -939.008503

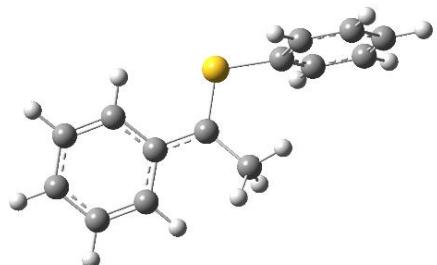
G= -939.064965

ZPVE= 0.229591

SUPPORTING INFORMATION

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 2.31985900 | -0.20273600 | -0.29049800 |
| C | 3.01879200 | 0.73793700 | -1.03873100 |
| C | 2.71716200 | -0.56898900 | 0.99120400 |
| C | 4.12452200 | 1.35078000 | -0.46955800 |
| H | 2.70001000 | 0.99476700 | -2.04072400 |
| C | 3.82314900 | 0.05517700 | 1.54346800 |
| H | 2.19334400 | -1.34041600 | 1.53998800 |
| C | 4.52150400 | 1.01345600 | 0.81747500 |
| H | 4.67314500 | 2.09177300 | -1.03420900 |
| H | 4.14697400 | -0.21837600 | 2.53820100 |
| H | 5.38727900 | 1.49180800 | 1.25528000 |
| C | -0.20059200 | -1.10582700 | 0.05174400 |
| H | -0.00602300 | -0.72648500 | 1.05128100 |
| C | -1.52642200 | -1.69221200 | -0.23759700 |
| H | -1.70084900 | -2.49693800 | 0.48038000 |
| C | -2.54782200 | -0.58276200 | -0.02905800 |
| C | -3.22720100 | -0.46308300 | 1.17855400 |
| C | -2.77787600 | 0.33564300 | -1.04861300 |
| C | -4.14651900 | 0.56098200 | 1.35798700 |
| H | -3.04457200 | -1.17606700 | 1.97341600 |
| C | -3.69969000 | 1.35705400 | -0.86826100 |
| H | -2.24326100 | 0.24510200 | -1.98742900 |
| C | -4.38387600 | 1.47100600 | 0.33549700 |
| H | -4.67997000 | 0.64527300 | 2.29558300 |
| H | -3.88296600 | 2.06310400 | -1.66733500 |
| H | -5.10235500 | 2.26774800 | 0.47634600 |
| H | -1.57374000 | -2.09681500 | -1.24678500 |
| S | 0.94019000 | -0.95894000 | -1.08723000 |

Sulphonium Ion 23



E= -939.038735

H= -939.024614

G= -939.080260

ZPVE= 0.229181

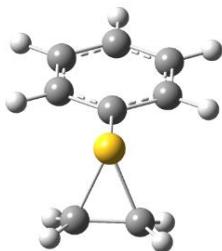
| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -2.03605100 | -0.39240300 | -0.21632200 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| C | -2.63034900 | 0.50673800 | -1.09417600 |
| C | -2.74446700 | -0.96971900 | 0.83053500 |
| C | -3.95968300 | 0.85004100 | -0.89949500 |
| H | -2.06369300 | 0.93162600 | -1.91219400 |
| C | -4.07396100 | -0.61640200 | 1.01156100 |
| H | -2.26452100 | -1.67672200 | 1.49400400 |
| C | -4.67752900 | 0.29113000 | 0.15070000 |
| H | -4.43375900 | 1.55234400 | -1.57148000 |
| H | -4.63615100 | -1.05286400 | 1.82577700 |
| H | -5.71495400 | 0.56123800 | 0.29603300 |
| C | 0.58958700 | 0.31459700 | 0.16962300 |
| C | 0.01033400 | 1.55475900 | 0.74277900 |
| H | -1.00544200 | 1.40342900 | 1.09517100 |
| H | -0.02309200 | 2.31470000 | -0.04602100 |
| H | 0.63527100 | 1.92771700 | 1.54963200 |
| C | 2.02397700 | 0.12886700 | 0.10973600 |
| C | 2.86301800 | 1.25221900 | 0.20134000 |
| C | 2.59800000 | -1.14413300 | -0.05858200 |
| C | 4.23276700 | 1.10601000 | 0.09973800 |
| H | 2.44212600 | 2.24053800 | 0.31920500 |
| C | 3.96753900 | -1.28255000 | -0.13944900 |
| H | 1.97310500 | -2.02694000 | -0.08629300 |
| C | 4.78553400 | -0.15836600 | -0.06672600 |
| H | 4.87119000 | 1.97669500 | 0.15353100 |
| H | 4.40315700 | -2.26563500 | -0.25021600 |
| H | 5.85969100 | -0.27108400 | -0.13219000 |
| S | -0.35845100 | -0.89123600 | -0.48640800 |

Calculated energies and structures of species involved in Figure 10A (addition of *cis*-cyclooctene to thiiranium ion **26**)

Thiiranium Ion 26



E= -707.993904

H= -707.984916

G= -708.027550

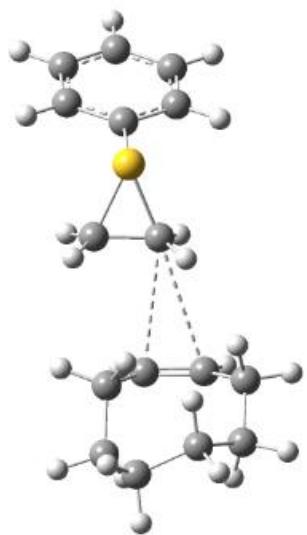
ZPVE= 0.148391

| Symbol | X | Y | Z |
|--------|------------|------------|------------|
| C | 2.11548500 | 1.12052300 | 0.54071100 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | 1.43253800 | 1.61267600 | 1.22023100 |
| C | 2.29666400 | -0.32977200 | 0.64286500 |
| H | 1.74322500 | -0.87546600 | 1.39541100 |
| H | 2.91279800 | 1.72522100 | 0.12854600 |
| C | -0.40909900 | 0.01744400 | -0.13008400 |
| C | -0.89610100 | -1.25450400 | 0.14447500 |
| C | -1.19948800 | 1.15572800 | -0.03025000 |
| C | -2.21229400 | -1.37912400 | 0.56125100 |
| H | -0.26806800 | -2.12992000 | 0.03490300 |
| C | -2.51304400 | 1.00977100 | 0.38795200 |
| H | -0.80476900 | 2.13429600 | -0.27397200 |
| C | -3.01444500 | -0.25159000 | 0.68342900 |
| H | -2.61034700 | -2.35911100 | 0.78620800 |
| H | -3.14437500 | 1.88305200 | 0.47849500 |
| H | -4.04107500 | -0.35729200 | 1.00752700 |
| H | 3.22472400 | -0.77191500 | 0.30462100 |
| S | 1.24014900 | 0.17911900 | -0.76621800 |

Association Complex 29



E= -1021.009374

H= -1020.990371

G= -1021.059882

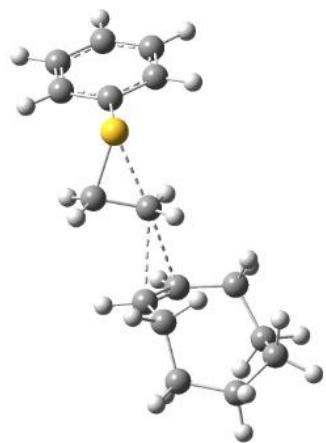
ZPVE= 0.354524

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 0.49612700 | 0.36106500 | -0.73264400 |
| H | 0.35016300 | -0.48808900 | -0.07824600 |
| C | 1.38899200 | 1.43518700 | -0.30987800 |
| H | 1.89407100 | 1.35606200 | 0.64245300 |
| H | 1.23684200 | 2.43270700 | -0.69961600 |
| S | 2.12317600 | 0.31441900 | -1.58629000 |
| C | -0.99601800 | 2.42813000 | 1.36730200 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| C | -0.16722400 | 3.42725700 | 1.66333800 |
| H | 0.40423300 | 3.35083900 | 2.58357100 |
| H | -1.06810400 | 1.59837800 | 2.06561500 |
| C | 3.06111600 | -0.84564400 | -0.62416000 |
| C | 4.18665600 | -0.39657700 | 0.05511900 |
| C | 2.70414900 | -2.18786700 | -0.66143400 |
| C | 4.95945800 | -1.32310000 | 0.73802400 |
| H | 4.45843900 | 0.65162500 | 0.05147200 |
| C | 3.48845700 | -3.09937600 | 0.02812100 |
| H | 1.83544200 | -2.51831200 | -1.21718200 |
| C | 4.60962300 | -2.66718800 | 0.72510700 |
| H | 5.83687400 | -0.99294800 | 1.27708000 |
| H | 3.22420900 | -4.14793700 | 0.01616800 |
| H | 5.21823000 | -3.38460700 | 1.25899200 |
| H | -0.30564800 | 0.58715600 | -1.42340500 |
| C | 0.01719900 | 4.69434600 | 0.86783900 |
| H | 0.82780300 | 5.25981300 | 1.32706400 |
| H | 0.35595500 | 4.46381600 | -0.15027500 |
| C | -1.95792800 | 2.42560200 | 0.21343000 |
| H | -1.47731400 | 2.83480000 | -0.68259000 |
| H | -2.25266900 | 1.40065300 | -0.02058800 |
| C | -1.21869800 | 5.62069900 | 0.74507100 |
| H | -0.84081400 | 6.64203900 | 0.69323900 |
| H | -1.81029600 | 5.56385600 | 1.66177700 |
| C | -3.21910000 | 3.26617400 | 0.54348400 |
| H | -4.11536800 | 2.65885200 | 0.41375700 |
| H | -3.18425700 | 3.53033800 | 1.60129900 |
| C | -3.36907200 | 4.53965300 | -0.29207700 |
| H | -3.75767300 | 4.28123300 | -1.28066200 |
| H | -4.13663600 | 5.15642300 | 0.18081700 |
| C | -2.10325100 | 5.37929400 | -0.48958900 |
| H | -2.42179500 | 6.34527900 | -0.88488100 |
| H | -1.48727500 | 4.94236900 | -1.28116500 |

Transition State TS29-30



E= -1020.996129

H= -1020.978008

SUPPORTING INFORMATION

G= -1021.043412

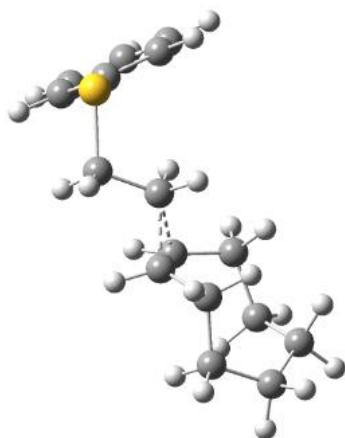
ZPVE= 0.354751

Imaginary frequency = -347.2729 cm⁻¹

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 0.05169300 | -0.31527800 | -0.29934600 |
| H | 0.26230200 | -0.83890900 | 0.62595500 |
| C | 0.48354300 | 1.07014800 | -0.39198300 |
| H | 1.38627200 | 1.36839500 | 0.12306700 |
| H | 0.13756200 | 1.69158100 | -1.20549000 |
| S | 1.34343300 | -0.64137800 | -1.56199900 |
| C | -1.34900300 | 2.08237500 | 0.76155200 |
| C | -0.25913900 | 2.71241400 | 1.24759500 |
| H | 0.21145600 | 2.28574100 | 2.12887000 |
| H | -1.69890400 | 1.20037500 | 1.29140900 |
| C | 2.74856800 | -1.01096800 | -0.54709900 |
| C | 3.86940800 | -0.19145500 | -0.62652600 |
| C | 2.74857200 | -2.15322400 | 0.24882800 |
| C | 4.99783900 | -0.51471000 | 0.11326300 |
| H | 3.86162700 | 0.68253100 | -1.26554300 |
| C | 3.87772500 | -2.45962800 | 0.99060100 |
| H | 1.88249400 | -2.80307600 | 0.27537400 |
| C | 4.99969000 | -1.64217100 | 0.92253600 |
| H | 5.87509500 | 0.11522700 | 0.05476000 |
| H | 3.88652100 | -3.34515000 | 1.61162800 |
| H | 5.88152300 | -1.89071000 | 1.49767800 |
| H | -0.92527900 | -0.54331600 | -0.71215900 |
| C | 0.29881900 | 4.00756500 | 0.73715400 |
| H | 1.25692500 | 4.17872800 | 1.22679400 |
| H | 0.50939700 | 3.93299400 | -0.33568100 |
| C | -2.24839900 | 2.62986000 | -0.29985600 |
| H | -1.66809400 | 3.12586300 | -1.08164500 |
| H | -2.80429600 | 1.82024300 | -0.77263600 |
| C | -0.60866000 | 5.24754600 | 0.96016600 |
| H | 0.06152100 | 6.09347700 | 1.11078400 |
| H | -1.16589600 | 5.13635600 | 1.89355200 |
| C | -3.22215600 | 3.65387900 | 0.34586200 |
| H | -4.25057200 | 3.36902100 | 0.12568900 |
| H | -3.12297700 | 3.59618100 | 1.43159700 |
| C | -3.00340500 | 5.10043500 | -0.10689000 |
| H | -3.46675500 | 5.24342000 | -1.08588000 |
| H | -3.55105700 | 5.74586200 | 0.58304900 |
| C | -1.55366400 | 5.58631400 | -0.20458400 |
| H | -1.59317000 | 6.67165800 | -0.30826900 |
| H | -1.10308400 | 5.23360100 | -1.13651900 |

SUPPORTING INFORMATION

Intermediate 30



E= -1021.014697

H= -1020.996802

G= -1021.061747

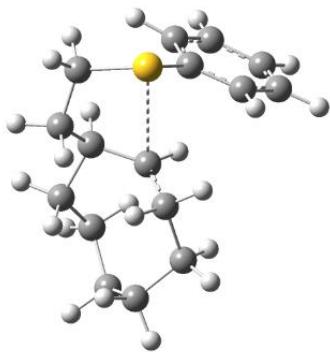
ZPVE= 0.356746

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -0.26258000 | -0.56172700 | -0.63985900 |
| H | -0.32706600 | -0.90893900 | 0.39292200 |
| C | -0.00369700 | 0.93692700 | -0.67500500 |
| H | 1.03300500 | 1.08448600 | -0.31444000 |
| H | -0.00933000 | 1.40714000 | -1.65698600 |
| S | 1.04104800 | -1.46061100 | -1.51686800 |
| C | -1.25943700 | 1.72602100 | 0.09882000 |
| C | -0.10941500 | 2.09830400 | 0.81004400 |
| H | 0.18964300 | 1.45633700 | 1.63543800 |
| H | -1.85686200 | 0.94360500 | 0.55739600 |
| C | 2.40357200 | -0.99431800 | -0.47456700 |
| C | 3.38888000 | -0.14324000 | -0.96836300 |
| C | 2.48900000 | -1.47464400 | 0.83152800 |
| C | 4.45278400 | 0.22974600 | -0.15523600 |
| H | 3.32681400 | 0.20977300 | -1.99020500 |
| C | 3.54426500 | -1.08614400 | 1.64282600 |
| H | 1.74435600 | -2.17095500 | 1.19828400 |
| C | 4.52659300 | -0.23407000 | 1.15013500 |
| H | 5.22562000 | 0.87786500 | -0.54697800 |
| H | 3.61415200 | -1.46821300 | 2.65281800 |
| H | 5.35759000 | 0.05337800 | 1.78047300 |
| H | -1.20085600 | -0.79926200 | -1.14068200 |
| C | 0.62780600 | 3.37841700 | 0.63459500 |
| H | 1.62066700 | 3.27286000 | 1.06862800 |
| H | 0.75088800 | 3.60568400 | -0.42544400 |
| C | -2.05165500 | 2.71034300 | -0.72198400 |
| H | -1.38760000 | 3.33925000 | -1.31603100 |
| H | -2.67942700 | 2.15994700 | -1.42186600 |
| C | -0.13724300 | 4.55510600 | 1.31210300 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|------------|-------------|
| H | 0.63109000 | 5.20326700 | 1.73064200 |
| H | -0.71801100 | 4.19614100 | 2.16663500 |
| C | -2.90196400 | 3.56700900 | 0.24412400 |
| H | -3.95345000 | 3.49643400 | -0.03138400 |
| H | -2.83728000 | 3.13980900 | 1.24886200 |
| C | -2.51237600 | 5.04734500 | 0.30259400 |
| H | -2.93079600 | 5.56222900 | -0.56463400 |
| H | -3.00502500 | 5.47983500 | 1.17563200 |
| C | -1.01655600 | 5.37760100 | 0.35551800 |
| H | -0.93537500 | 6.42644700 | 0.64372500 |
| H | -0.58489600 | 5.32803600 | -0.64735300 |

Intermediate 30'



E= -1021.021089

H= -1021.003761

G= -1021.064541

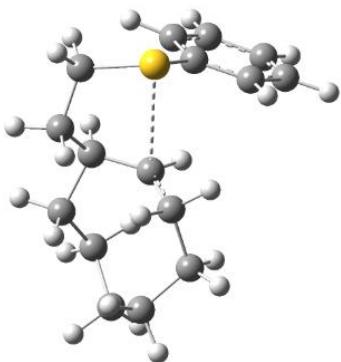
ZPVE= 0.357565

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 0.89064000 | 1.52444000 | 1.79274200 |
| H | 0.70041300 | 2.25610500 | 2.57875300 |
| C | -0.43549300 | 0.91479900 | 1.35691700 |
| H | -0.92677500 | 0.45165700 | 2.21419600 |
| C | -0.33713500 | -0.09199700 | 0.19937800 |
| C | 0.20118900 | -1.40111300 | 0.52641500 |
| H | 0.88194600 | -1.86667300 | -0.18497900 |
| H | 0.21902000 | 0.33303700 | -0.63607300 |
| S | 2.05585600 | 0.37409000 | 2.56363300 |
| H | 1.37360700 | 2.06670100 | 0.98114500 |
| C | 2.69803100 | -0.54582000 | 1.19024700 |
| C | 3.08876200 | -1.86656800 | 1.43781100 |
| C | 2.89318300 | -0.01253400 | -0.08619400 |
| C | 3.61596500 | -2.64832700 | 0.42192100 |
| H | 2.97722300 | -2.27452800 | 2.43603800 |
| C | 3.39670400 | -0.80737900 | -1.10536200 |
| H | 2.66312000 | 1.02413900 | -0.29094100 |
| C | 3.74993800 | -2.12934100 | -0.86054700 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | 3.91980300 | -3.66537700 | 0.63218100 |
| H | 3.53531900 | -0.38366000 | -2.09147400 |
| H | 4.15029400 | -2.74177500 | -1.65708600 |
| C | -1.79511900 | -0.43566200 | -0.30388700 |
| H | -2.41359800 | -0.62028400 | 0.57543600 |
| H | -2.14107200 | 0.50099400 | -0.74047300 |
| C | -0.26475800 | -2.26086900 | 1.59296700 |
| H | 0.62698100 | -2.64607100 | 2.09511900 |
| H | -0.89825900 | -1.75362600 | 2.31680900 |
| C | -1.90131400 | -1.59891000 | -1.30889300 |
| H | -2.34798900 | -1.23676300 | -2.23416400 |
| H | -0.90892400 | -1.94851500 | -1.60526100 |
| C | -0.99778100 | -3.51766900 | 0.98931600 |
| H | -0.94731900 | -4.26343600 | 1.78112500 |
| H | -0.42419100 | -3.91467400 | 0.14783400 |
| C | -2.73880900 | -2.78149000 | -0.80867500 |
| H | -2.60069900 | -3.60831200 | -1.50840100 |
| H | -3.79603200 | -2.51398400 | -0.86229300 |
| C | -2.45891000 | -3.27833700 | 0.61247200 |
| H | -2.90768900 | -2.61005700 | 1.35220400 |
| H | -2.98663300 | -4.22606500 | 0.73300500 |
| H | -1.09004700 | 1.71990800 | 1.01361700 |

Transition State TS30'-31



E= -1021.021116

H= -1021.004402

G= -1021.063815

ZPVE= 0.357075

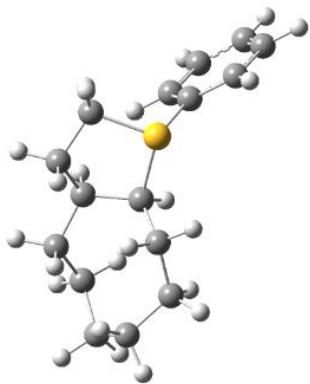
Imaginary frequency = -87.4598 cm⁻¹

| Symbol | X | Y | Z |
|--------|-------------|-------------|------------|
| C | 0.87931800 | 1.47351200 | 1.78086100 |
| H | 0.73235500 | 2.20020500 | 2.58030000 |
| C | -0.47598300 | 0.94286700 | 1.32664800 |
| H | -1.01815300 | 0.53331500 | 2.18082100 |
| C | -0.37476900 | -0.11154200 | 0.21711500 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| C | 0.12465200 | -1.41258400 | 0.62707200 |
| H | 0.84615400 | -1.90028500 | -0.02689500 |
| H | 0.22948300 | 0.26033800 | -0.61107800 |
| S | 1.95045100 | 0.21972800 | 2.51904600 |
| H | 1.40053000 | 1.99551100 | 0.98084300 |
| C | 2.75333700 | -0.57657000 | 1.14561400 |
| C | 3.19283400 | -1.88337200 | 1.37379400 |
| C | 2.98952300 | 0.01689300 | -0.09186000 |
| C | 3.83406700 | -2.59174200 | 0.36938800 |
| H | 3.03811000 | -2.33860000 | 2.34558800 |
| C | 3.61317800 | -0.70753000 | -1.09943700 |
| H | 2.70654100 | 1.04303700 | -0.28142300 |
| C | 4.03076800 | -2.01303800 | -0.87832200 |
| H | 4.17874800 | -3.59902300 | 0.56301400 |
| H | 3.78982100 | -0.23749800 | -2.05809300 |
| H | 4.52304600 | -2.56777000 | -1.66529500 |
| C | -1.81970900 | -0.43376700 | -0.33035500 |
| H | -2.47629500 | -0.57193200 | 0.52974100 |
| H | -2.12627900 | 0.49314400 | -0.81411400 |
| C | -0.38843700 | -2.24663700 | 1.68946500 |
| H | 0.48583300 | -2.64661700 | 2.21305500 |
| H | -1.02857100 | -1.71928400 | 2.39302900 |
| C | -1.91264900 | -1.63126300 | -1.29533000 |
| H | -2.30794700 | -1.29497300 | -2.25319200 |
| H | -0.91742300 | -2.01717800 | -1.53164300 |
| C | -1.13202900 | -3.49568900 | 1.07789100 |
| H | -1.11775400 | -4.23122700 | 1.88057800 |
| H | -0.54377600 | -3.91566100 | 0.25798900 |
| C | -2.80185800 | -2.77094000 | -0.78695500 |
| H | -2.66824900 | -3.62326200 | -1.45627900 |
| H | -3.84823500 | -2.47343000 | -0.88093400 |
| C | -2.57612000 | -3.22955900 | 0.65631600 |
| H | -3.02593000 | -2.52620800 | 1.36209300 |
| H | -3.13267600 | -4.15852300 | 0.79197200 |
| H | -1.07285800 | 1.77051000 | 0.93614800 |

Addition Product 31



E= -1021.077891

H= -1021.061421

SUPPORTING INFORMATION

G= -1021.120916

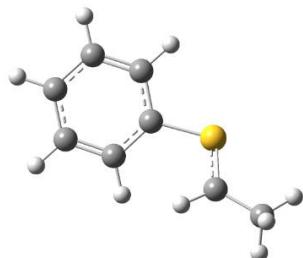
ZPVE= 0.360281

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 0.75934400 | 1.01064600 | 1.18146500 |
| H | 1.04239500 | 1.57192700 | 2.06847600 |
| C | -0.72996700 | 0.99720500 | 0.87208100 |
| H | -1.31165900 | 0.88282900 | 1.79028600 |
| C | -0.97588000 | -0.18451500 | -0.06387300 |
| C | -0.33604100 | -1.42664200 | 0.59624200 |
| H | 0.09240100 | -2.11127800 | -0.13658500 |
| H | -0.42674800 | 0.00671800 | -0.99270800 |
| S | 1.14911500 | -0.74417700 | 1.49180300 |
| H | 1.35968200 | 1.33151900 | 0.33165900 |
| C | 2.56404400 | -1.12105400 | 0.49839100 |
| C | 2.59667700 | -0.86239400 | -0.86883500 |
| C | 3.63801200 | -1.70429500 | 1.15831700 |
| C | 3.73444700 | -1.19617200 | -1.58162700 |
| H | 1.75183000 | -0.41042100 | -1.37314100 |
| C | 4.77397800 | -2.03024100 | 0.42946400 |
| H | 3.58916000 | -1.89904700 | 2.22181600 |
| C | 4.82014500 | -1.77715600 | -0.93263300 |
| H | 3.77648000 | -1.00300400 | -2.64489400 |
| H | 5.61914300 | -2.48212300 | 0.93026400 |
| H | 5.70657800 | -2.03325400 | -1.49738800 |
| C | -2.44550400 | -0.37352800 | -0.41794800 |
| H | -3.02070400 | -0.45783200 | 0.50637500 |
| H | -2.79205800 | 0.54190300 | -0.89989600 |
| C | -1.16372300 | -2.21531600 | 1.62126700 |
| H | -0.45869900 | -2.68566700 | 2.30894100 |
| H | -1.76166100 | -1.52804900 | 2.22746400 |
| C | -2.69066600 | -1.59151600 | -1.32324200 |
| H | -2.99735300 | -1.26532500 | -2.31713500 |
| H | -1.75145900 | -2.13148900 | -1.47488000 |
| C | -2.05797100 | -3.34382400 | 1.06218300 |
| H | -2.10487200 | -4.09344200 | 1.85254600 |
| H | -1.55257100 | -3.83287200 | 0.22331500 |
| C | -3.72866100 | -2.56484000 | -0.77103300 |
| H | -3.73184300 | -3.45624500 | -1.40220600 |
| H | -4.72586700 | -2.12683400 | -0.85535000 |
| C | -3.50016100 | -2.98202900 | 0.68437200 |
| H | -3.85874900 | -2.20838800 | 1.36837400 |
| H | -4.13208400 | -3.84898400 | 0.88088000 |
| H | -1.02479100 | 1.94094300 | 0.41334600 |

SUPPORTING INFORMATION

Calculated energies and structures of species involved in Figure 10B (addition of *cis*-cyclooctene to sulphonium ion 28)

***trans*-Sulphonium Ion 28**



E= -707.994682

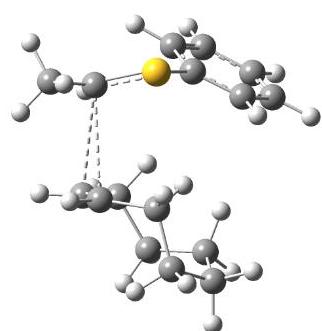
H= -707.985067

G= -708.028854

ZPVE= 0.146893

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -2.24707700 | 0.43268200 | 0.31460100 |
| H | -1.75768700 | 1.27088000 | 0.80480000 |
| S | -1.32331900 | -0.71774500 | -0.34918300 |
| C | -3.71794700 | 0.38279000 | 0.26929300 |
| H | -4.10325200 | -0.50655500 | -0.22274000 |
| H | -4.10010100 | 0.44609400 | 1.29293700 |
| H | -4.08174400 | 1.27907000 | -0.24468400 |
| C | 0.34823300 | -0.21971600 | -0.13796000 |
| C | 0.74982000 | 1.10772900 | -0.26566100 |
| C | 1.25501600 | -1.24752100 | 0.10681600 |
| C | 2.09009900 | 1.40842200 | -0.10198400 |
| H | 0.04334600 | 1.88715600 | -0.52094900 |
| C | 2.59287300 | -0.92489700 | 0.26874200 |
| H | 0.92373000 | -2.27577800 | 0.18238400 |
| C | 3.00588700 | 0.39676100 | 0.16929700 |
| H | 2.42416600 | 2.43191900 | -0.20345500 |
| H | 3.31047700 | -1.70809000 | 0.47057600 |
| H | 4.05274100 | 0.64173300 | 0.28918600 |

Association Complex 32



SUPPORTING INFORMATION

E= -1021.016645

H= -1020.997453

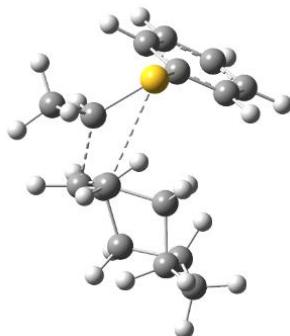
G= -1021.064433

ZPVE= 0.353723

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -2.87871300 | 0.50779000 | -1.17151300 |
| C | -2.20033400 | -0.61179700 | -0.89810000 |
| C | -1.03228200 | 1.97947600 | 1.39638800 |
| C | -1.42373200 | -0.84505900 | 0.35835100 |
| C | 0.14571400 | 1.00886100 | 1.25426200 |
| C | -0.03613400 | -0.15282400 | 0.27416300 |
| H | -1.97275300 | -0.43877300 | 1.21377800 |
| H | -1.78858600 | 1.55289400 | 2.06311200 |
| H | 0.37270300 | 0.61146600 | 2.24720500 |
| H | -3.30723100 | 0.60850000 | -2.16542100 |
| H | -2.10111900 | -1.35892100 | -1.68111700 |
| H | -0.65582100 | 2.85790000 | 1.92334600 |
| H | -1.30348400 | -1.91593200 | 0.52989100 |
| H | 1.03251100 | 1.56619200 | 0.94477300 |
| H | 0.75270100 | -0.88440400 | 0.44902100 |
| H | 0.10962300 | 0.20853400 | -0.74461500 |
| C | -3.03553300 | 1.68835800 | -0.24867700 |
| H | -3.50719500 | 1.37726200 | 0.69112800 |
| H | -3.72694500 | 2.38951600 | -0.71606500 |
| C | -1.72862200 | 2.44437200 | 0.10562500 |
| H | -1.03961200 | 2.40582200 | -0.74150300 |
| H | -1.99728100 | 3.49391600 | 0.22644600 |
| C | -4.84593100 | -1.44181700 | -0.15592300 |
| C | -4.90751900 | -2.42324400 | -1.25917700 |
| H | -4.37732200 | -3.34588400 | -1.03210400 |
| H | -5.96501300 | -2.66085600 | -1.42799700 |
| H | -4.52692000 | -1.97757400 | -2.17635800 |
| S | -4.50596200 | -1.89988100 | 1.37404900 |
| C | -4.79472300 | -0.46485000 | 2.36243000 |
| C | -3.86360900 | -0.19434200 | 3.35900000 |
| C | -5.91792500 | 0.33363900 | 2.17197700 |
| C | -4.04404700 | 0.92866000 | 4.15228800 |
| H | -3.00520000 | -0.83884400 | 3.50414300 |
| C | -6.07962000 | 1.45423700 | 2.96915800 |
| H | -6.66522800 | 0.07836900 | 1.43145000 |
| C | -5.14232400 | 1.75388300 | 3.95123800 |
| H | -3.32310000 | 1.15806000 | 4.92508400 |
| H | -6.94741600 | 2.08535300 | 2.83415300 |
| H | -5.27845800 | 2.62818000 | 4.57349000 |
| H | -5.17579500 | -0.42244000 | -0.32476700 |

SUPPORTING INFORMATION

Intermediate 32'



E= -1021.013456

H= -1020.995251

G= -1021.058501

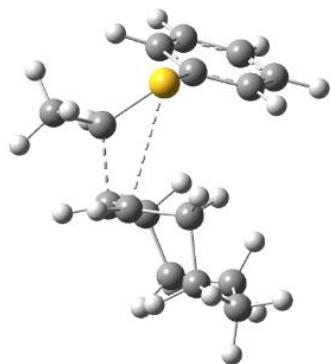
ZPVE= 0.356186

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -3.77548500 | 0.58410000 | -1.47464000 |
| C | -2.87965600 | -0.46587600 | -1.28462400 |
| C | -1.89266700 | 2.53098100 | 0.60180200 |
| C | -1.84168800 | -0.41579600 | -0.19823200 |
| C | -0.59424300 | 1.81662900 | 0.21154000 |
| C | -0.72722200 | 0.55891200 | -0.65214600 |
| H | -2.28403200 | -0.08558500 | 0.74088700 |
| H | -2.36195300 | 2.02593000 | 1.45066700 |
| H | -0.06699500 | 1.56414500 | 1.13397400 |
| H | -4.25947000 | 0.64962000 | -2.44726400 |
| H | -2.54444500 | -0.96138800 | -2.19059200 |
| H | -1.61318600 | 3.51684300 | 0.97649500 |
| H | -1.45255100 | -1.41789100 | -0.02947600 |
| H | 0.05215400 | 2.51543200 | -0.32327400 |
| H | 0.23033500 | 0.03945800 | -0.65829700 |
| H | -0.90080100 | 0.85518600 | -1.69014300 |
| C | -4.08284700 | 1.64712300 | -0.49484200 |
| H | -4.16472000 | 1.23760800 | 0.51290500 |
| H | -5.03401900 | 2.10873900 | -0.75243000 |
| C | -2.94906500 | 2.72772500 | -0.49618100 |
| H | -2.48232600 | 2.80305300 | -1.48229200 |
| H | -3.45834200 | 3.67691500 | -0.33671100 |
| C | -4.40919600 | -1.34071100 | -0.97496000 |
| C | -4.58236700 | -2.26746100 | -2.16576500 |
| H | -5.53320300 | -2.79018100 | -2.07220000 |
| H | -4.58554000 | -1.70711500 | -3.10147300 |
| H | -3.78267600 | -3.00641400 | -2.20424400 |
| S | -4.24337600 | -2.22028300 | 0.57666300 |
| C | -4.90522500 | -1.03567800 | 1.72368500 |
| C | -4.09018400 | -0.55914300 | 2.74497400 |
| C | -6.22401000 | -0.60172500 | 1.61459200 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| C | -4.58778800 | 0.38139500 | 3.63792700 |
| H | -3.07533600 | -0.92456200 | 2.84140900 |
| C | -6.70757800 | 0.35097300 | 2.49727200 |
| H | -6.87344300 | -1.01843400 | 0.85364100 |
| C | -5.88822900 | 0.84746700 | 3.50517400 |
| H | -3.95700800 | 0.74861200 | 4.43658300 |
| H | -7.73132600 | 0.69054100 | 2.41287500 |
| H | -6.27190700 | 1.58388100 | 4.19851000 |
| H | -5.28332900 | -0.69565900 | -0.87233700 |

Transition State TS32'-33



E= -1021.012804

H= -1020.995082

G= -1021.058822

ZPVE= 0.355328

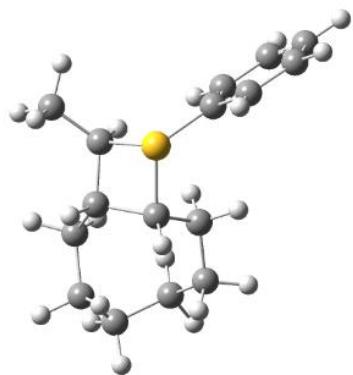
Imaginary frequency = -130.1118 cm⁻¹

| Symbol | X | Y | Z |
|--------|-------------|------------|-------------|
| C | -3.40817900 | 1.51395300 | -0.73541400 |
| C | -2.11356200 | 1.06317300 | -0.58716300 |
| C | -2.38462300 | 4.03108000 | 1.41773400 |
| C | -1.26326800 | 1.32264300 | 0.57529300 |
| C | -0.90368600 | 3.84650600 | 1.06954000 |
| C | -0.53972600 | 2.66122900 | 0.17356400 |
| H | -1.84869100 | 1.46859200 | 1.48100000 |
| H | -2.66108900 | 3.36472100 | 2.23997400 |
| H | -0.34646200 | 3.76664200 | 2.00521900 |
| H | -3.79446300 | 1.51201300 | -1.75093800 |
| H | -1.65865700 | 0.54893200 | -1.42916500 |
| H | -2.48445600 | 5.03712300 | 1.82690800 |
| H | -0.54549600 | 0.52150000 | 0.73597100 |
| H | -0.53666200 | 4.74596100 | 0.57096500 |
| H | 0.53456800 | 2.48661000 | 0.20148100 |
| H | -0.76595800 | 2.91575100 | -0.86577200 |
| C | -4.07567800 | 2.46524200 | 0.22259100 |
| H | -4.09360500 | 2.04032400 | 1.22675300 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | -5.11697600 | 2.56384000 | -0.08681300 |
| C | -3.41260300 | 3.86252100 | 0.28468800 |
| H | -2.97448400 | 4.12273500 | -0.68320700 |
| H | -4.21556100 | 4.58071800 | 0.44621400 |
| C | -3.87538900 | -0.27372300 | -0.30726800 |
| C | -3.52202500 | -1.22635700 | -1.42901500 |
| H | -2.54309900 | -1.68162700 | -1.28415300 |
| H | -4.26109100 | -2.02781000 | -1.43740200 |
| H | -3.54621300 | -0.72935600 | -2.39892500 |
| S | -3.54120700 | -0.92216600 | 1.29688800 |
| C | -4.81602600 | -0.20278400 | 2.30487500 |
| C | -4.44024700 | 0.48539600 | 3.45334800 |
| C | -6.15986900 | -0.37476100 | 1.99032300 |
| C | -5.41767600 | 1.02444200 | 4.27797300 |
| H | -3.39132500 | 0.59607700 | 3.69987800 |
| C | -7.12904100 | 0.18609700 | 2.80835300 |
| H | -6.45011800 | -0.96053700 | 1.12635700 |
| C | -6.75924400 | 0.88535400 | 3.95035600 |
| H | -5.12878100 | 1.55568200 | 5.17496300 |
| H | -8.17518000 | 0.05679800 | 2.56514900 |
| H | -7.51914100 | 1.31021600 | 4.59227900 |
| H | -4.90761400 | 0.06976300 | -0.35620000 |

Addition Product 33



E= -1021.060795

H= -1021.043681

G= -1021.104230

ZPVE= 0.358811

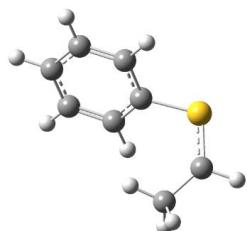
| Symbol | X | Y | Z |
|--------|------------|-------------|------------|
| C | 2.34534500 | -1.96509600 | 3.22498000 |
| C | 1.79210500 | -1.17883600 | 2.03926000 |
| C | 2.23092500 | 1.42156300 | 4.22065100 |
| C | 2.71943400 | -0.05324100 | 1.54354300 |
| C | 1.45227900 | 1.73854400 | 2.95812400 |
| C | 2.00592600 | 1.28353900 | 1.58052900 |
| H | 3.16403100 | -2.60621400 | 2.88994600 |

SUPPORTING INFORMATION

| | | | |
|---|------------|-------------|-------------|
| H | 0.82622400 | -0.74972300 | 2.32382900 |
| H | 3.62025900 | 0.00355300 | 2.15879800 |
| H | 3.30610500 | 1.51855200 | 4.04742100 |
| H | 1.55976200 | -2.63506300 | 3.58122200 |
| H | 1.57107100 | -1.86899700 | 1.22538800 |
| H | 1.96928500 | 2.18580500 | 4.95644000 |
| H | 3.05710800 | -0.24324000 | 0.52334700 |
| H | 0.38661500 | 1.57476900 | 3.10701400 |
| H | 1.17094800 | 1.26661100 | 0.87296500 |
| C | 2.84623300 | -1.11669800 | 4.39775500 |
| H | 3.84139500 | -0.71719000 | 4.18368000 |
| H | 2.98803000 | -1.78811200 | 5.24548000 |
| C | 1.93820600 | 0.03821700 | 4.84496400 |
| H | 0.88484400 | -0.22106000 | 4.70272500 |
| H | 2.06774700 | 0.16602800 | 5.91967700 |
| C | 2.85097800 | 2.54136600 | 1.29848400 |
| H | 3.79704700 | 2.48106800 | 1.83691600 |
| S | 1.68528700 | 3.49658300 | 2.35363900 |
| C | 3.02329400 | 3.03192200 | -0.11530400 |
| H | 3.54537000 | 3.98753100 | -0.14815900 |
| H | 3.62056600 | 2.30439200 | -0.66774800 |
| H | 2.06067900 | 3.13525500 | -0.61548400 |
| C | 2.51129400 | 4.52502200 | 3.52436400 |
| C | 1.73962200 | 5.56630600 | 4.03512500 |
| C | 3.83262000 | 4.34000400 | 3.92045800 |
| C | 2.29815100 | 6.42331100 | 4.97059200 |
| H | 0.71971700 | 5.70753500 | 3.70035800 |
| C | 4.38006500 | 5.21279100 | 4.84553600 |
| H | 4.43735700 | 3.54012900 | 3.51756800 |
| C | 3.61440200 | 6.24681700 | 5.37242300 |
| H | 1.70681800 | 7.23353900 | 5.37451000 |
| H | 5.40806700 | 5.08518000 | 5.15613800 |
| H | 4.05139700 | 6.92238600 | 6.09561600 |

Calculated energies and structures of species involved in Scheme 6 (*cis* vs *trans* isomer for sulphonium ion 28)

***cis*-Sulphonium Ion 28**



E= -707.993448

H= -707.983940

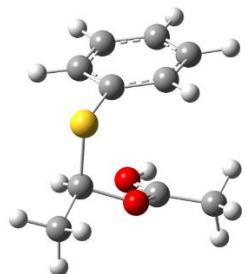
G= -708.027632

ZPVE= 0.147082

SUPPORTING INFORMATION

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | -2.51081600 | 0.07944200 | 0.12136400 |
| S | -1.45182100 | -0.98601900 | -0.49022800 |
| C | 0.16889400 | -0.36279800 | -0.20207100 |
| C | 0.54639500 | 0.89204900 | -0.67515400 |
| C | 1.07163700 | -1.22383900 | 0.41482800 |
| C | 1.85547600 | 1.30099000 | -0.48827300 |
| H | -0.16008100 | 1.52631800 | -1.19546600 |
| C | 2.37596500 | -0.79264900 | 0.59853000 |
| H | 0.76378100 | -2.20603500 | 0.75079600 |
| C | 2.76350400 | 0.46339800 | 0.15050700 |
| H | 2.17012200 | 2.26982200 | -0.85142500 |
| H | 3.08946500 | -1.44261100 | 1.08606800 |
| H | 3.78564500 | 0.78964100 | 0.28889500 |
| C | -2.28412200 | 1.32513200 | 0.86504700 |
| H | -1.25527700 | 1.45266600 | 1.18902100 |
| H | -2.57337000 | 2.16876700 | 0.22586700 |
| H | -2.97267800 | 1.34723100 | 1.71377500 |
| H | -3.54008100 | -0.21983400 | -0.07255900 |

Acetate Precursor to *trans*-Sulphonium Ion 28



E= -937.039443

H= -937.025226

G= -937.079558

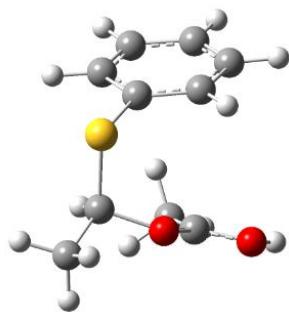
ZPVE= 0.214097

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 1.86396800 | 0.47306100 | 0.38574700 |
| H | 1.45660900 | 0.47631500 | 1.39276700 |
| C | 3.35559100 | 0.67164400 | 0.34055100 |
| H | 3.71987500 | 0.61493500 | -0.68403000 |
| H | 3.58665200 | 1.65646700 | 0.74425400 |
| H | 3.85809400 | -0.07998200 | 0.94734000 |
| C | -0.64741500 | 1.06451600 | -0.36717900 |
| C | -1.22591900 | 0.16389700 | -1.25903300 |
| C | -1.33158900 | 1.45506500 | 0.78035200 |
| C | -2.47779800 | -0.37407000 | -0.98079300 |
| H | -0.70100600 | -0.09812000 | -2.17028600 |
| C | -2.57762800 | 0.91162000 | 1.05498500 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | -0.88646700 | 2.17852200 | 1.45180700 |
| C | -3.14651300 | -0.00974400 | 0.18106500 |
| H | -2.93987500 | -1.05669900 | -1.68278900 |
| H | -3.11323300 | 1.21765100 | 1.94399300 |
| H | -4.12561000 | -0.41973400 | 0.39205100 |
| S | 1.00534100 | 1.63838600 | -0.67347500 |
| C | 0.69046500 | -1.65248600 | 0.25271700 |
| C | 0.36801700 | -2.89000500 | -0.49399100 |
| H | 0.88995700 | -2.89950000 | -1.44537600 |
| H | 0.67407800 | -3.75032500 | 0.10664300 |
| H | -0.71092500 | -2.94135900 | -0.65101700 |
| O | 1.60444700 | -0.90272600 | -0.17318800 |
| O | 0.09816300 | -1.35330300 | 1.35997900 |
| H | -0.64155400 | -1.94510200 | 1.56937900 |

Acetate Precursor to *trans*-Sulphonium Ion 28



E= -937.034998

H= -937.020925

G= -937.074848

ZPVE= 0.214447

| Symbol | X | Y | Z |
|--------|-------------|-------------|-------------|
| C | 1.77278500 | 0.59654300 | 0.38567900 |
| H | 1.31748400 | 0.51584100 | 1.37034600 |
| C | 3.23314600 | 0.96443000 | 0.43524300 |
| H | 3.64863200 | 1.00396800 | -0.57063200 |
| H | 3.33174900 | 1.94473300 | 0.89883300 |
| H | 3.78990400 | 0.23843000 | 1.02596700 |
| C | -0.76681500 | 1.02196800 | -0.36437000 |
| C | -1.24999400 | 0.04165800 | -1.22869400 |
| C | -1.51211600 | 1.40987100 | 0.74658100 |
| C | -2.46462400 | -0.57753600 | -0.95694900 |
| H | -0.67982700 | -0.22209500 | -2.11154700 |
| C | -2.72364300 | 0.78665500 | 1.01270400 |
| H | -1.14307800 | 2.19569900 | 1.39378200 |
| C | -3.19444600 | -0.21284200 | 0.16761200 |
| H | -2.84918600 | -1.32895000 | -1.63443400 |
| H | -3.30643900 | 1.08943300 | 1.87257000 |

SUPPORTING INFORMATION

| | | | |
|---|-------------|-------------|-------------|
| H | -4.14335900 | -0.69011100 | 0.37392300 |
| S | 0.84029000 | 1.72210000 | -0.65125000 |
| C | 0.94460700 | -1.68685500 | 0.13639500 |
| C | 0.17309000 | -1.71687000 | 1.40540100 |
| H | 0.82347500 | -1.45627900 | 2.24044900 |
| H | -0.63928600 | -0.98681800 | 1.35334500 |
| H | -0.24712500 | -2.70527000 | 1.57421200 |
| O | 1.70630700 | -0.75895300 | -0.24066000 |
| O | 0.92125200 | -2.67920600 | -0.68670700 |
| H | 0.36000000 | -3.40903500 | -0.38549400 |