Supplementary Information for:

Reaction dynamics of S(^{3}P) with 1,3-butadiene and isoprene: Crossed beam scattering, low temperature flow experiments, and high-level electronic structure calculations

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Low-energy pathways on the triplet PES for S + isoprene. All energies are at the CCSD(T)-F12a/cc-pVTZ-F12//ωB97X-D/6-311++G** level of theory. Only the relevant low-energy pathways are shown.

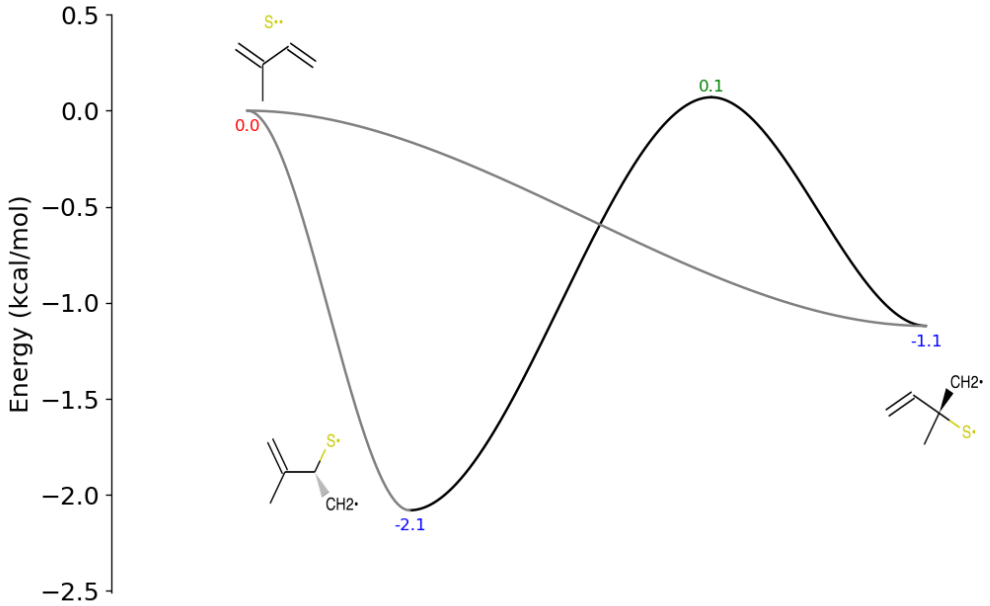


Figure S1. Addition to the central carbons.

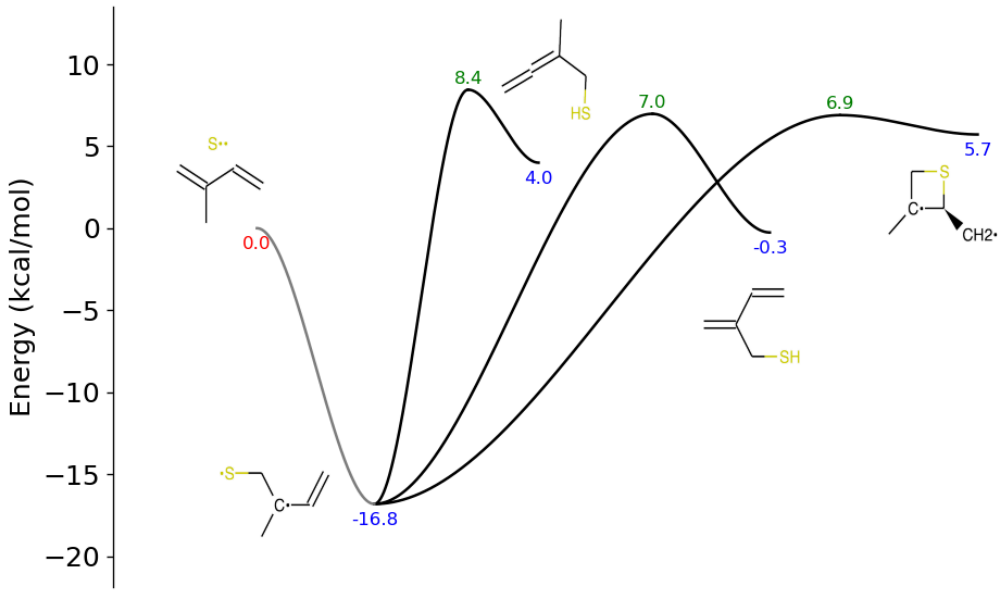


Figure S2. Addition to the terminal carbon producing 1-thyil-isoprene, and initial reaction pathways.

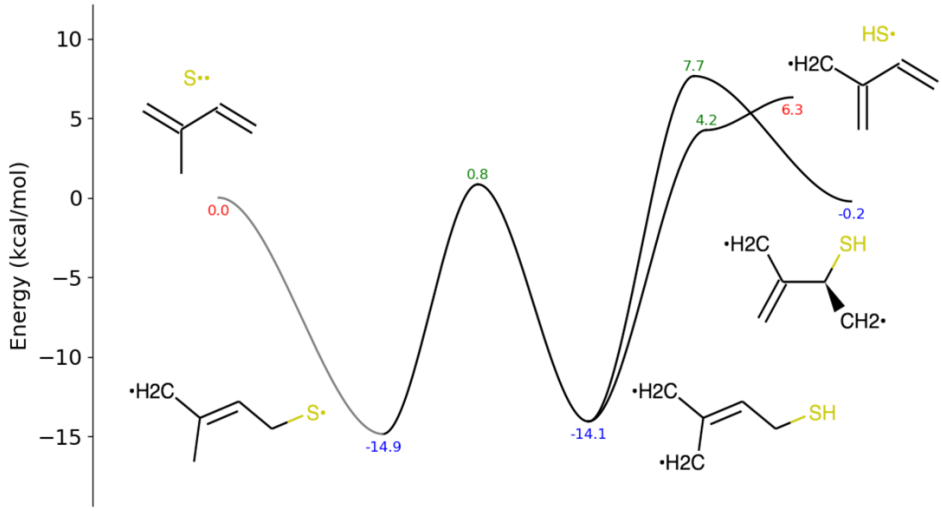
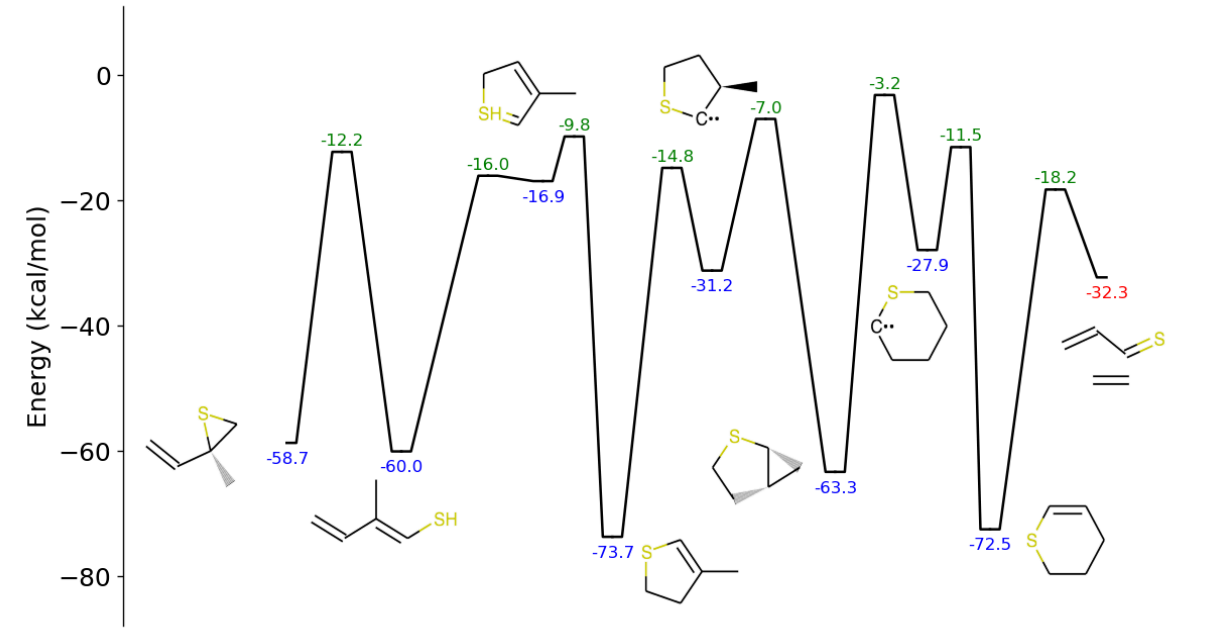
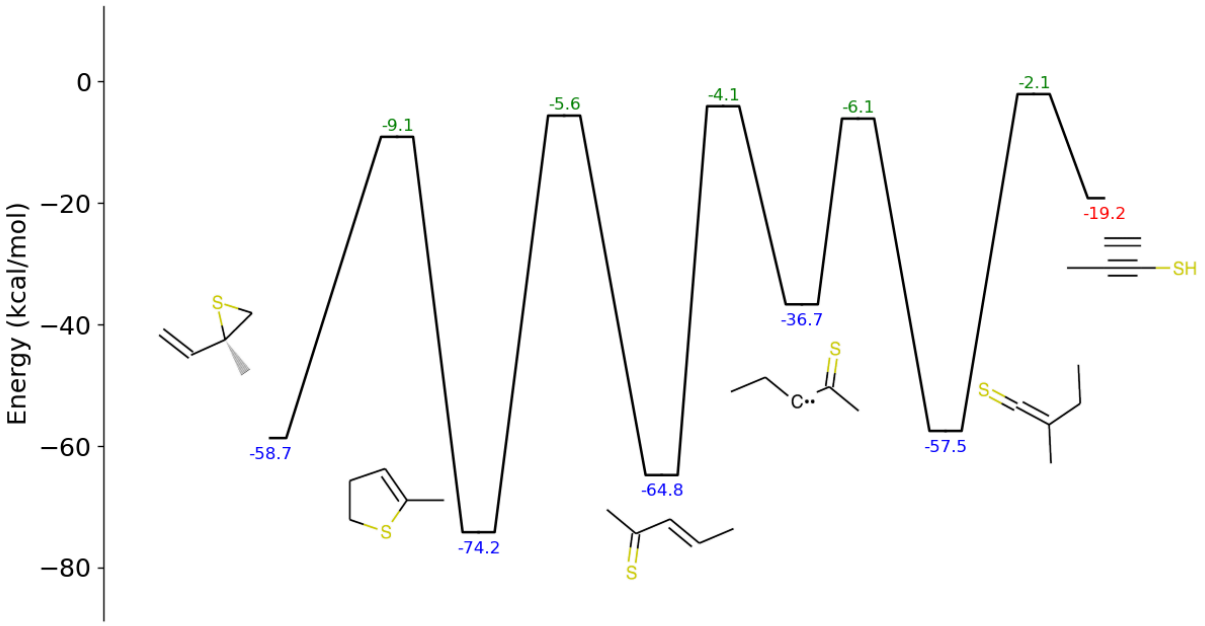


Figure S3. Addition to the terminal carbon producing 4-thyil-isoprene, and initial reaction pathways. Note that the bimolecular product on the right had wavefunction convergence problems, signaling potentially significant uncertainty in its energy.


Energy (kcal/mol)
0
−20
−40
−60
−80
-58.7
-12.2
-60.0
-16.0
-16.9
-9.8
-73.7
-14.8
-31.2
-7.0
-63.3
-3.2
-27.9
-11.5
-72.5
-18.2
-32.3
SH
S
C


Energy (kcal/mol)
0
−20
−40
−60
−80
-58.7
-9.1
-74.2
-5.6
-64.8
-4.1
-36.7
-6.1
-57.5
-2.1
-19.2
SH
S
C

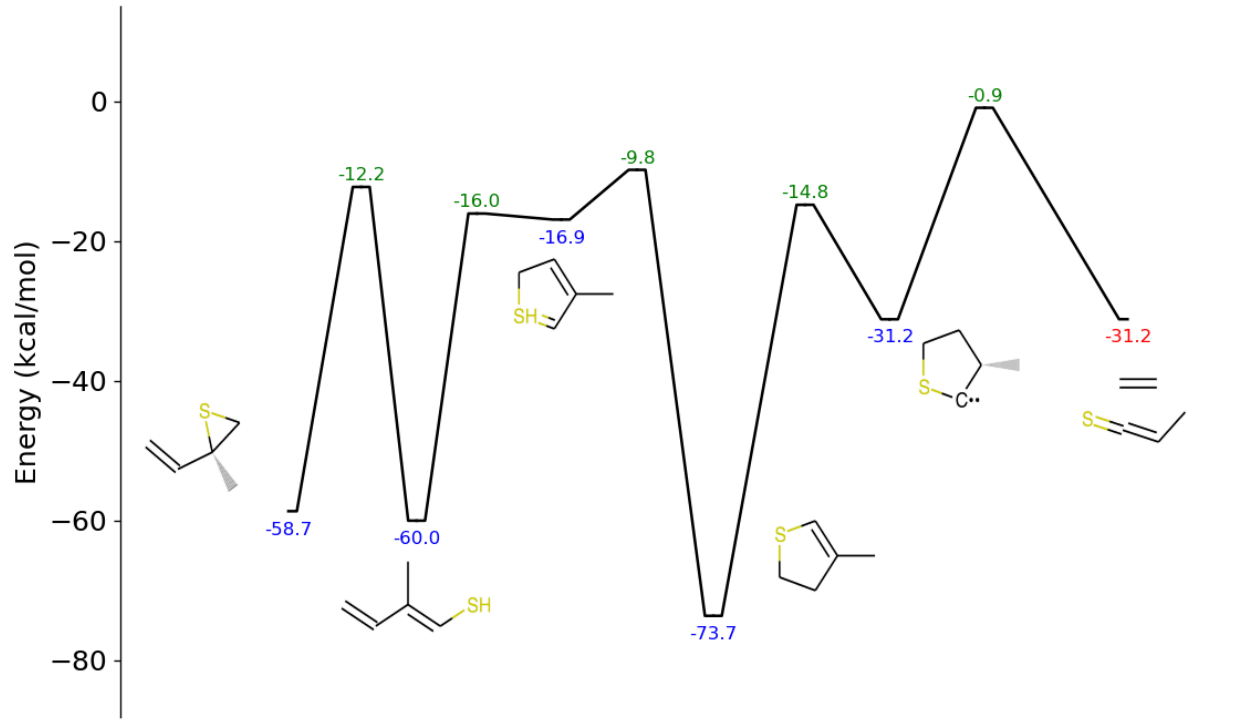


Figure S4. Pathways leading to ethene elimination and the detected 72 u coproduct.

The singlet PES can viewed in an interactive .html format, which can be viewed using popular browsers. The black nodes represent wells, while the blue ones represent bimolecular product pairs. Their energies are shown in kcal/mol under the nodes, relative to the triplet entrance. The black edges represent saddles, while the gray ones show reactions that are likely barrierless. The thickness of the lines show the barrier height the channels, thicker lines mean lower barriers. The values can be read by hovering over the nodes. Note that the graph can be arranged using the options at the bottom of that page. We recommend setting the solver to "forceAtlas2Based", "avoidOverlap to 1", and decrease "gravitationalConstant" and "springConstant". Once a desired arrangement is reached, disabling "physics" can be also helpful to look at the connections and structures in more detail. The graph can be panned and zoomed in and out, and the nodes can be moved manually, to further enhance viewing. Note that the structures are drawn automatically using RDKit,[1] which sometimes results in somewhat overlapping structures in the case of bimolecular structures (blue circles).

1. *Rdkit: Open-Source Cheminformatics*, http://www.rdkit.org, 2018.