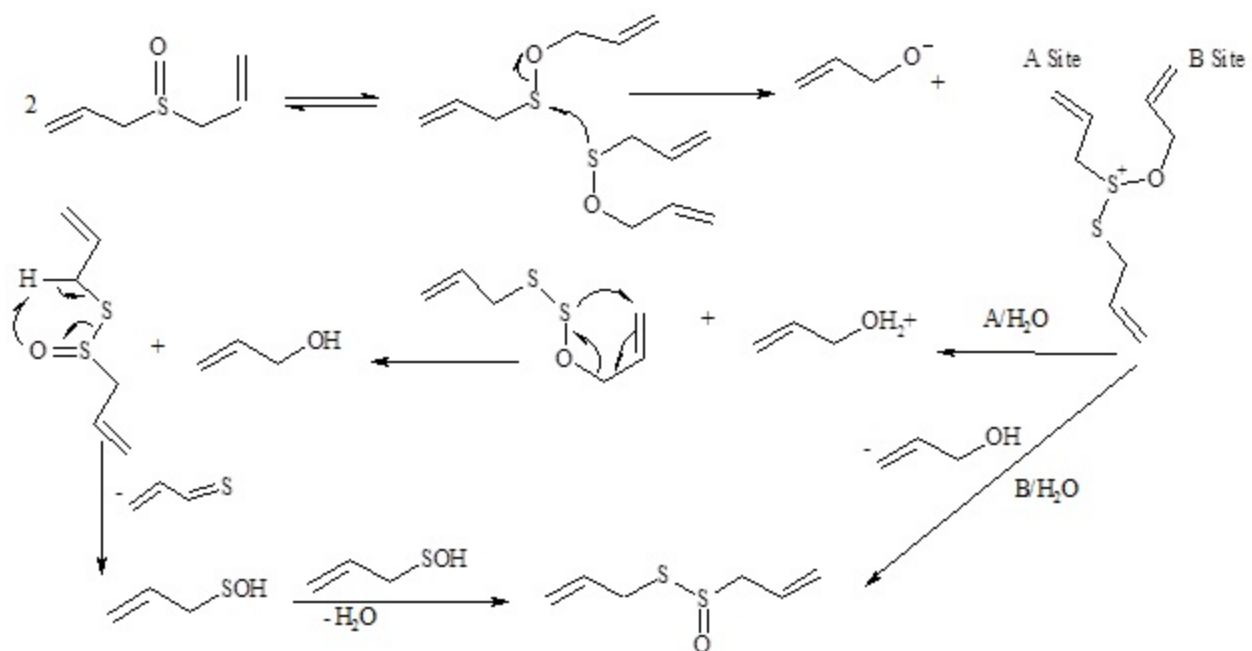
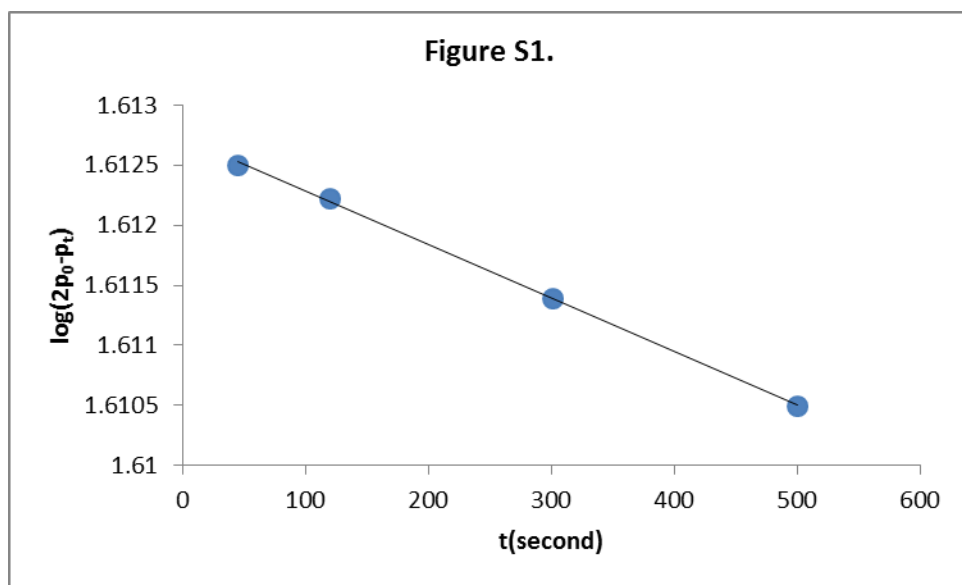




Scheme S1



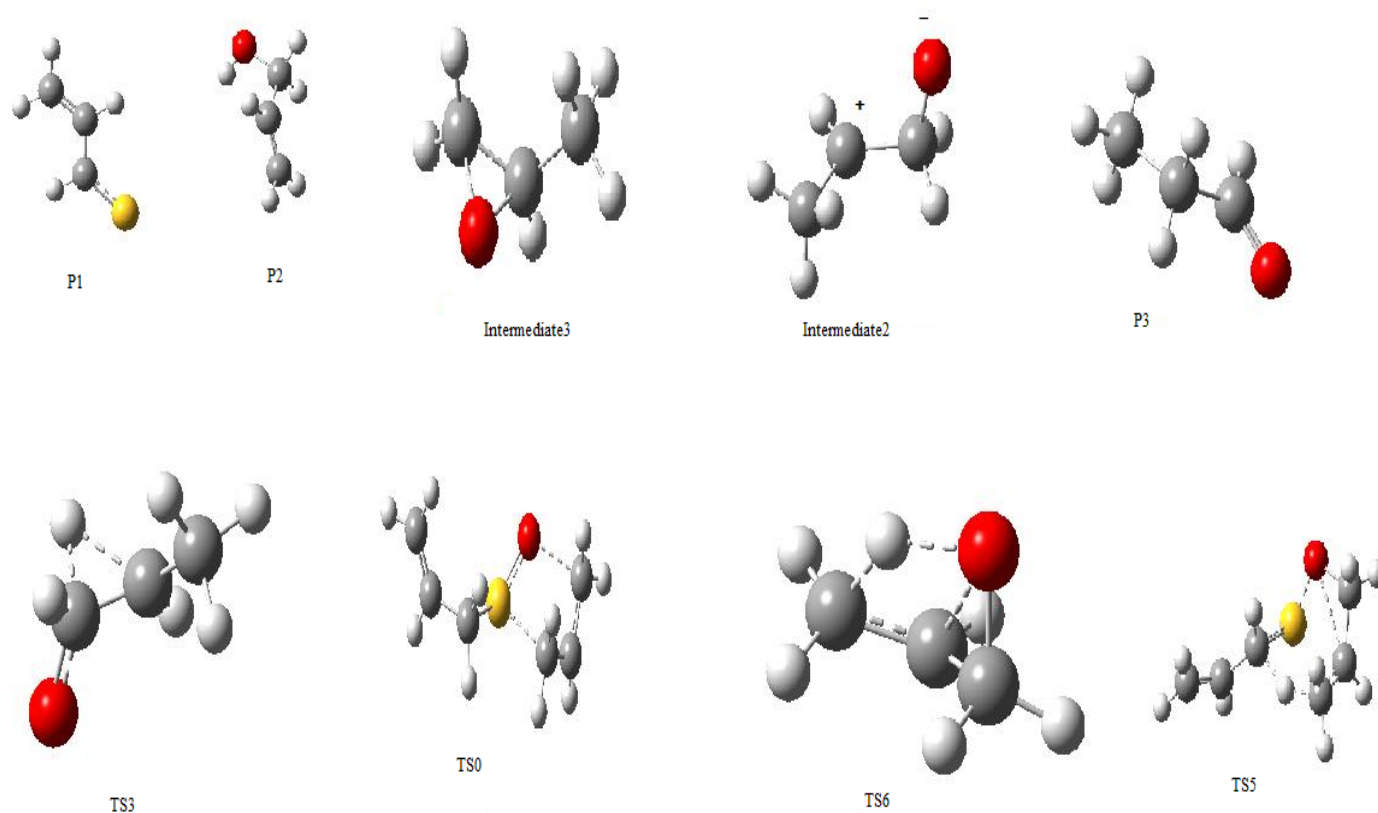


Figure S2.

Table S1.

Calculated energies (-Hartree) and energy barriers in kcal mol⁻¹ for some probable radicals and neutral compounds

Method	DASO	AllylS·	AllylO·	Intermediate1	AllylSSAllyl	Allyl·SOAllyl	$\Delta E^\ddagger$ ¹
HF	705.2622	514.0289	191.9741	705.4173	1028.1108	704.7620	367.58
MP2	706.4861	514.5639	191.9355	706.6149	1029.2407	705.9291	72.49
MP3	706.5344	514.6055	191.9721	706.6741	1029.3138	705.9876	60.55
MP4D	706.5667	514.6199	191.9859	706.7058	1029.3437	706.0185	62.75
MP4DQ	706.5385	514.6077	191.9741	706.6785	1029.3156	705.9915	60.66
MP4SDQ	706.5536	514.6132	191.9805	706.6916	1029.3263	706.0069	61.40
QCISD	706.5563	514.6179	191.9849	706.6937	1029.3288	706.0159	57.08
QCISD(T)	706.6092	514.6383	192.0065	706.7436	1029.3781	706.0671	62.01
S ² Value	0	0.84	0.78	0	0	0.76	-

¹ $\Delta E^\ddagger$ is equal to the energy difference between the obtained radicals and DASO in the rds.

All calculated energies in this table were obtained from the single point energy calculations at the QCISD(T) level not separated HF or MPn calculations.

C3H4S-P1

6	0.000000000	0.000000000	0.000000000
6	0.000000000	0.000000000	1.343000000
1	0.928000000	0.000000000	-0.564000000
1	-0.922000000	-0.000000000	-0.569000000
1	-0.931000000	-0.000000000	1.901000000
6	1.226000000	0.000000000	2.114000000
1	2.146000000	0.000000000	1.523000000
16	1.322000000	0.000000000	3.746000000

C6H10SO

6	3.407772000	-1.482131000	-0.220463000
6	3.053768000	-0.188629000	-0.147245000
1	4.441754000	-1.782298000	-0.343935000
1	2.667147000	-2.272541000	-0.154708000
1	3.796920000	0.600064000	-0.213187000
6	1.675882000	0.216734000	0.029628000
1	-3.786884000	0.579496000	0.984089000
1	0.941459000	-0.588749000	0.078222000
6	-3.376560000	0.905160000	-0.298518000
1	-2.680684000	1.663048000	0.058454000
1	-4.210816000	1.309045000	-0.865628000
6	-2.850618000	-0.337028000	-0.700995000
6	-2.098767000	-1.087017000	0.230532000
1	-3.423166000	-0.963208000	-1.384766000
1	-3.442451000	-0.042631000	1.694879000
1	-2.835643000	-0.859123000	1.313806000
16	1.167822000	1.770070000	0.154699000
8	-1.127706000	-1.765843000	0.374995000

C3H6O-P2

1	-0.312817000	0.164822000	0.316608000
8	-0.077715000	0.030272000	1.240939000
6	1.350247000	-0.016422000	1.333789000
1	1.558227000	-0.110388000	2.403035000
1	1.748660000	-0.909470000	0.834934000
6	1.996373000	1.219787000	0.779268000
6	2.895614000	1.218777000	-0.202821000
1	1.673625000	2.158520000	1.224610000
1	3.338670000	2.136285000	-0.573290000
1	3.228144000	0.294158000	-0.666152000

C3H5O.

6	-0.615872000	-0.408093000	0.182876000
6	0.663448000	0.383632000	0.249430000
1	0.531715000	1.420303000	-0.107300000
6	-1.786447000	0.113944000	-0.170448000
1	-2.690213000	-0.483565000	-0.203191000
1	-1.884037000	1.161261000	-0.441914000
1	-0.527193000	-1.460615000	0.439673000
1	0.972342000	0.502328000	1.314719000
8	1.753827000	-0.209576000	-0.321642000

C3H5S.

6	-1.118678000	-0.143423000	0.444016000
6	0.075529000	0.711371000	0.149297000
1	-0.097826000	1.376498000	-0.700002000
16	1.606746000	-0.243879000	-0.126910000
6	-2.211650000	-0.178893000	-0.315134000
1	-3.053248000	-0.814466000	-0.065322000
1	-2.303390000	0.426858000	-1.211662000
1	-1.046855000	-0.770861000	1.328563000

1	0.322173000	1.349707000	1.009915000
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C6H10S2

6	-4.245212000	-0.507850000	-0.014357000
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6	-2.997743000	-0.811458000	0.340682000
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1	-4.568703000	0.521831000	-0.131628000
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1	-4.985729000	-1.278498000	-0.194938000
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1	-2.704586000	-1.854074000	0.437497000
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6	-1.929402000	0.201237000	0.602701000
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1	-1.390278000	-0.020424000	1.525411000
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1	-2.333863000	1.212044000	0.655898000
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6	1.946889000	0.003310000	0.833637000
---	-------------	-------------	-------------

1	2.607849000	0.599196000	1.468881000
---	-------------	-------------	-------------

1	1.279066000	-0.571086000	1.479637000
---	-------------	--------------	-------------

6	2.725152000	-0.881807000	-0.083866000
---	-------------	--------------	--------------

6	4.054833000	-0.931682000	-0.131435000
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1	2.135679000	-1.513714000	-0.743386000
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1	4.571878000	-1.593045000	-0.817050000
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1	4.673698000	-0.314189000	0.512755000
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16	-0.692901000	0.135126000	-0.791336000
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16	0.904644000	1.263715000	-0.050992000
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Intermediate 1

6	-4.022298000	-0.317956000	0.053132000
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6	-2.830710000	-0.290982000	0.648259000
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1	-4.271964000	0.367678000	-0.750737000
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1	-4.789131000	-1.022630000	0.353521000
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1	-2.607975000	-1.000681000	1.441068000
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6	-1.726579000	0.647990000	0.273334000
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1	-1.240013000	1.058333000	1.161202000
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1	-2.083479000	1.465003000	-0.354683000
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8	0.853813000	0.775374000	-0.602676000
6	1.796796000	0.589400000	0.479376000
1	2.332877000	1.539223000	0.545665000
1	1.247824000	0.431466000	1.415915000
6	2.747126000	-0.540650000	0.225681000
6	4.068681000	-0.400343000	0.165997000
1	2.294383000	-1.520995000	0.097134000
1	4.724186000	-1.247006000	-0.003631000
1	4.544147000	0.568347000	0.288756000
16	-0.448716000	-0.310405000	-0.652967000

Intermediate 3

1	0.294571000	1.688498000	-0.408478000
8	-1.268468000	-0.637998000	0.393599000
6	-2.548396000	-0.005579000	0.534889000
1	-3.387890000	-0.562620000	0.126192000
1	-2.724483000	0.466296000	1.498960000
6	-1.530374000	0.554594000	-0.362902000
6	-0.720327000	1.773294000	-0.009905000
1	-1.652230000	0.365273000	-1.429075000
1	-1.176574000	2.672722000	-0.435051000
1	-0.653697000	1.894398000	1.073550000

TS3

1	-3.786884000	0.579496000	0.984089000
6	-3.376560000	0.905160000	-0.298518000
1	-2.680684000	1.663048000	0.058454000
1	-4.210816000	1.309045000	-0.865628000
6	-2.850618000	-0.337028000	-0.700995000
6	-2.098767000	-1.087017000	0.230532000
1	-3.423166000	-0.963208000	-1.384766000

1	-3.442451000	-0.042631000	1.694879000
1	-2.835643000	-0.859123000	1.313806000
8	-1.127706000	-1.765843000	0.374995000

TS1

6	3.487922000	0.285182000	0.407523000
6	2.397258000	-0.079196000	-0.283248000
1	3.422753000	0.646566000	1.428654000
1	4.474496000	0.236877000	-0.036255000
1	2.522985000	-0.420267000	-1.309222000
6	1.031370000	0.003935000	0.213578000
1	0.261237000	1.352308000	-0.013475000
1	0.884162000	0.097440000	1.285636000
8	-1.324544000	-1.171389000	0.691606000
6	-2.333610000	-0.123917000	0.487704000
1	-3.246337000	-0.593964000	0.112742000
1	-2.530805000	0.296997000	1.478737000
6	-1.765199000	0.868889000	-0.488176000
6	-0.887748000	1.903521000	-0.060814000
1	-2.183952000	0.894670000	-1.486069000
1	-0.762184000	2.747032000	-0.737775000
1	-0.974018000	2.216691000	0.981672000
16	-0.178246000	-0.953358000	-0.556056000

TS6

1	0.000000000	0.000000000	0.000000000
8	0.000000000	0.000000000	3.422869000
6	1.266666000	0.000000000	2.951663000
1	1.477148000	-1.583007000	2.574457000
1	2.100166000	0.188301000	3.595651000
6	1.412125000	-0.670655000	1.406538000

6	0.144739000	-0.686669000	0.807735000
1	2.163307000	-0.459272000	0.674456000
1	-0.191126000	-1.654304000	0.498255000
1	-0.458714000	-0.300595000	2.154578000

TS2

1	0.000000000	0.000000000	0.000000000
8	0.000000000	0.000000000	1.440939000
6	1.417026000	0.000000000	1.435345000
1	1.845257000	0.376140000	2.367422000
1	1.878678000	-0.954742000	1.156364000
6	1.299515000	0.980189000	0.331410000
6	0.889077000	0.447997000	-0.906052000
1	1.148328000	2.020388000	0.598252000
1	0.484672000	1.103267000	-1.667312000
1	1.379521000	-0.458088000	-1.256656000

TS7

6	3.421046000	0.782475000	0.574178000
6	2.216648000	0.559747000	0.021096000
1	3.855355000	1.774273000	0.601120000
1	4.005327000	-0.024005000	1.004840000
1	1.668270000	1.395423000	-0.402428000
6	1.623391000	-0.751719000	-0.091405000
1	-0.522975000	0.372074000	-0.981675000
1	2.187385000	-1.580550000	0.331787000
6	-1.298319000	1.533415000	-0.822306000
1	-0.554635000	2.095662000	-0.259658000
1	-1.504007000	1.900321000	-1.823526000
6	-2.299582000	0.892079000	-0.113385000
6	-2.026994000	0.190318000	1.172469000

1	-3.206537000	0.578505000	-0.621433000
1	-1.198888000	0.645577000	1.738873000
1	-2.897630000	0.106177000	1.835222000
16	0.125821000	-1.136326000	-0.657623000
8	-1.707743000	-1.040016000	0.581870000

TS4

1	-0.360000000	-0.174000000	0.547000000
8	-0.092000000	-0.035000000	3.059000000
6	0.986000000	-0.063000000	2.977000000
1	2.056000000	0.609000000	3.145000000
1	1.354000000	-1.072000000	2.678000000
6	0.889000000	0.898000000	1.843000000
6	0.915000000	0.487000000	0.343000000
1	0.379000000	1.828000000	2.087000000
1	1.078000000	1.347000000	-0.311000000
1	1.706000000	-0.261000000	0.225000000

Intermediate 2

1	0.000000000	0.000000000	0.000000000
8	0.000000000	0.000000000	4.002000000
6	1.231000000	0.000000000	3.274000000
1	1.934000000	0.642000000	3.763000000
1	1.623000000	-0.995000000	3.237000000
6	0.981000000	0.508000000	1.842000000
6	0.619000000	-0.487000000	0.725000000
1	1.059000000	1.553000000	1.624000000
1	1.514000000	-0.835000000	0.253000000
1	0.090000000	-1.318000000	1.144000000

TS5

6	0.262000000	-0.084000000	-0.201000000
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6	0.262000000	-0.084000000	1.155000000
1	1.189000000	-0.084000000	-0.736000000
1	-0.664000000	-0.084000000	-0.736000000
1	1.189000000	-0.084000000	1.690000000
6	-1.071000000	-0.084000000	1.925000000
1	-1.150000000	-0.414000000	3.370000000
1	-1.817000000	-0.589000000	1.346000000
6	-1.122000000	1.276000000	4.806000000
1	-0.840000000	0.488000000	4.138000000
1	-0.376000000	1.780000000	5.384000000
6	-2.312000000	1.629000000	5.078000000
6	-3.315000000	0.950000000	4.300000000
1	-2.594000000	2.416000000	5.745000000
1	-3.006000000	-0.059000000	4.121000000
1	-4.242000000	0.950000000	4.835000000
16	-1.585000000	1.594000000	2.221000000
8	-3.283000000	1.594000000	3.201000000