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SUPPLEMENTARY MATERIAL

Singlet Photoreactivity of 3-Methyl-2-phenyl-2*H*-azirine

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1. Calculations

1.1. Optimization of 1

B3LYP 6-31+G(d) Energy = -403.08423723 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.151081	-0.870548	-0.333687
2	6	0	2.332694	-0.076498	-0.006051
3	7	0	2.127351	-0.080548	-1.247205
4	6	0	3.242788	0.496346	1.012298
5	1	0	3.997351	1.133999	0.539920
6	1	0	2.671050	1.084648	1.739641
7	1	0	3.742207	-0.308059	1.565841
8	6	0	-0.242249	-0.375470	-0.155795
9	6	0	-1.258647	-1.284628	0.177311
10	6	0	-0.578429	0.979207	-0.312156
11	6	0	-2.574260	-0.853727	0.360544
12	1	0	-1.015357	-2.339345	0.291075
13	6	0	-1.894640	1.409955	-0.134716
14	1	0	0.190212	1.694522	-0.592482
15	6	0	-2.897997	0.497299	0.206041
16	1	0	-3.346722	-1.574141	0.618459
17	1	0	-2.138053	2.461493	-0.266670
18	1	0	-3.921854	0.834961	0.344609
19	1	0	1.247662	-1.955858	-0.392703

1.2. TD-DFT of 1

TD-DFT calculations for azirine 1 gas phase

Excitation energies and oscillator strengths:

```
Excited State   1:   Singlet-A      4.6077 eV  269.08 nm  f=0.0177
      33 -> 36         0.10093
      34 -> 37         0.11421
      35 -> 36         0.61692
      35 -> 37        -0.18464
      35 -> 38         0.18249
Excited State   2:   Singlet-A      5.1042 eV  242.91 nm  f=0.0452
```

```
      34 -> 36        -0.29843
      34 -> 37        -0.22852
      35 -> 37         0.43686
      35 -> 38         0.37053
Excited State   3:   Singlet-A      5.4223 eV  228.66 nm  f=0.1464
      34 -> 37        -0.29065
      35 -> 36        -0.18911
      35 -> 37        -0.38279
      35 -> 38         0.40914
      35 -> 39         0.13947
 Excited State   4:   Singlet-A      5.6787 eV  218.33 nm  f=0.0068
      34 -> 36        -0.34136
      34 -> 37         0.11284
      34 -> 38        -0.11023
      35 -> 39         0.57397
```

TD-DFT in Methanol (PCM)

```
Excitation energies and oscillator strengths:
Excited State   1:   Singlet-A      4.6042 eV  269.28 nm  f=0.0238
      34 -> 37         0.10863
      35 -> 36         0.63333
      35 -> 37        -0.15992
      35 -> 38         0.15997
 Excited State   2:   Singlet-A      5.1235 eV  241.99 nm  f=0.0605
      34 -> 36        -0.30090
      34 -> 37        -0.25012
      35 -> 37         0.43389
      35 -> 38         0.36515
Excited State   3:   Singlet-A      5.4350 eV  228.12 nm  f=0.1834
      34 -> 36        -0.10632
      34 -> 37         0.30508
      35 -> 36         0.16601
      35 -> 37         0.39259
      35 -> 38        -0.41005
Excited State   4:   Singlet-A      5.7004 eV  217.50 nm  f=0.1928
      34 -> 36         0.57757
      34 -> 37        -0.11447
      34 -> 38         0.24002
      35 -> 37         0.21997
      35 -> 39        -0.12657
Excited State   5:   Singlet-A      5.9560 eV  208.17 nm  f=0.0164
      35 -> 39         0.67192
      35 -> 40        -0.12632
```

TD-DFT in Acetonitrile (PCM)

```
Excitation energies and oscillator strengths:

Excited State   1:   Singlet-A      4.6036 eV  269.32 nm  f=0.0241
      34 -> 37         0.10830
      35 -> 36         0.63369
```

```
      35 -> 37        -0.15905
      35 -> 38         0.15969
Excited State   2:   Singlet-A      5.1230 eV  242.01 nm  f=0.0616
      34 -> 36        -0.30031
      34 -> 37        -0.25006
      35 -> 37         0.43521
      35 -> 38         0.36406
Excited State   3:   Singlet-A      5.4339 eV  228.17 nm  f=0.1854
      34 -> 36        -0.10435
      34 -> 37         0.30491
      35 -> 36         0.16549
      35 -> 37         0.39248
      35 -> 38        -0.41100
Excited State   4:   Singlet-A      5.6988 eV  217.56 nm  f=0.1941
      34 -> 36         0.57870
      34 -> 37        -0.11492
      34 -> 38         0.23860
      35 -> 37         0.21900
      35 -> 39        -0.12541
Excited State   5:   Singlet-A      5.9563 eV  208.16 nm  f=0.0164
      35 -> 39         0.67214
      35 -> 40        -0.12601
Excited State   6:   Singlet-A      6.2060 eV  199.78 nm  f=0.2697
      32 -> 36         0.15460
      33 -> 36         0.19465
      34 -> 37         0.42505
      34 -> 38        -0.12118
      34 -> 39        -0.10581
      35 -> 38         0.35164
```

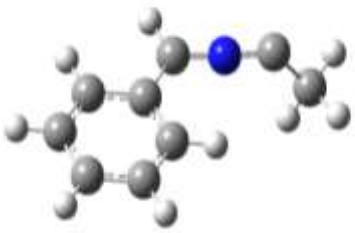
1.3. Optimized T_1 of 1

B3LYP/6-31+G(d)E = -402.96907528 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.290980	-0.745131	-0.640207
2	6	0	2.420091	-0.350782	0.200032
3	7	0	2.329880	0.183586	-1.164916
4	6	0	2.429465	0.541953	1.392134
5	1	0	3.450620	0.891448	1.586139
6	1	0	1.805851	1.438562	1.238235
7	1	0	2.059040	0.019071	2.281036
8	6	0	-0.121156	-0.340221	-0.336670

9	6	0	-1.033380	-1.302907	0.121549
10	6	0	-0.551519	0.983628	-0.508327
11	6	0	-2.351085	-0.945956	0.413058
12	1	0	-0.709554	-2.333414	0.250411
13	6	0	-1.871553	1.337354	-0.216324
14	1	0	0.142117	1.726593	-0.891388
15	6	0	-2.774308	0.376763	0.247178
16	1	0	-3.047969	-1.701851	0.766231
17	1	0	-2.195152	2.365268	-0.360004
18	1	0	-3.800957	0.654019	0.471640
19	1	0	1.361624	-1.673007	-1.222418

1.4. Optimization of Ylide 6



B3LYP 6-31+G(d) E = -403.07639701 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.859170	1.519812	-0.093807
2	6	0	-0.601436	0.922136	-0.147357
3	6	0	-0.467930	-0.477282	-0.040549
4	6	0	-1.634479	-1.251229	0.124531
5	6	0	-2.889896	-0.647835	0.181735
6	6	0	-3.010762	0.741459	0.072962
7	1	0	-1.942256	2.600479	-0.180882
8	1	0	0.285159	1.537253	-0.276130
9	1	0	-1.549403	-2.332962	0.205128
10	1	0	-3.776644	-1.263759	0.309906
11	1	0	-3.989204	1.212204	0.117731
12	6	0	0.823725	-1.150875	-0.105759
13	6	0	2.976426	0.059523	-0.527877
14	6	0	3.960647	0.608101	0.463385
15	1	0	4.944982	0.170499	0.263158
16	1	0	4.067402	1.685762	0.295936
17	1	0	3.686627	0.426219	1.512934
18	7	0	1.947589	-0.534432	-0.249999
19	1	0	0.857472	-2.237534	-0.061378

1.5. TD-DFT of the Ylide 6

TD-DFT in gas phase

Excitation energies and oscillator strengths:

```
Excited State   1:   Singlet-A      3.6611 eV  338.66 nm  f=0.0045
      35 -> 37         0.48484
      35 -> 38         0.46336
Excited State   2:   Singlet-A      3.7668 eV  329.15 nm  f=0.5010
      35 -> 36         0.59394
      35 -> 39        -0.11807
Excited State   3:   Singlet-A      4.1597 eV  298.06 nm  f=0.0400
      34 -> 36         0.22822
      35 -> 37        -0.44766
      35 -> 38         0.48043
Excited State   4:   Singlet-A      4.7527 eV  260.87 nm  f=0.0478
      35 -> 39         0.66575
      35 -> 41        -0.10669
Excited State   5:   Singlet-A      5.0065 eV  247.65 nm  f=0.0013
      33 -> 36         0.12367
      34 -> 36         0.10741
      35 -> 40         0.66530
Excited State   6:   Singlet-A      5.0669 eV  244.69 nm  f=0.0068
      33 -> 37         0.10945
      34 -> 36         0.37607
      35 -> 38        -0.11366
      35 -> 41         0.53641
      35 -> 44         0.10481
Excited State   7:   Singlet-A      5.1131 eV  242.48 nm  f=0.0427
      33 -> 37         0.12017
      33 -> 38        -0.13767
      34 -> 36         0.47118
      35 -> 37         0.12670
      35 -> 40        -0.12723
      35 -> 41        -0.40569
 Excited State   8:   Singlet-A      5.2695 eV  235.28 nm  f=0.0881
      33 -> 36         0.18186
      35 -> 40        -0.10003
      35 -> 42         0.64099
      35 -> 43        -0.10540
Excited State   9:   Singlet-A      5.4398 eV  227.92 nm  f=0.0286
      33 -> 36         0.15066
      35 -> 43         0.67025
Excited State  10:   Singlet-A      5.6042 eV  221.23 nm  f=0.0167
      33 -> 36         0.52099
      34 -> 37        -0.14666
      34 -> 38         0.12312
      35 -> 42        -0.13125
      35 -> 43        -0.12023
      35 -> 44         0.20900
      35 -> 45        -0.10424
      35 -> 46         0.22363
Excited State  11:   Singlet-A      5.6373 eV  219.94 nm  f=0.0224
      33 -> 36        -0.16606
      35 -> 41        -0.10212
      35 -> 44         0.65404
```

```
Excited State  12:   Singlet-A      5.9012 eV  210.10 nm  f=0.0040
      35 -> 45         0.62638
      35 -> 46        -0.17867
      35 -> 48         0.18180
```

TD-DFT in Acetonitrile (PCM)

```
Excited State   1:   Singlet-A      3.6632 eV  338.46 nm  f=0.6391
      35 -> 36         0.61767
Excited State   2:   Singlet-A      3.7569 eV  330.02 nm  f=0.0083
      35 -> 37         0.32656
      35 -> 38         0.59308
Excited State   3:   Singlet-A      4.2216 eV  293.69 nm  f=0.0314
      34 -> 36         0.24404
      35 -> 37         0.57437
      35 -> 38        -0.31918
Excited State   4:   Singlet-A      4.9141 eV  252.30 nm  f=0.0335
      33 -> 36        -0.10621
      35 -> 39         0.67151
Excited State   5:   Singlet-A      5.0615 eV  244.96 nm  f=0.0633
      33 -> 37         0.18910
      34 -> 36         0.61074
      35 -> 37        -0.17297
Excited State   6:   Singlet-A      5.1960 eV  238.61 nm  f=0.0481
      33 -> 36        -0.19307
      35 -> 40         0.63887
      35 -> 41         0.18297
Excited State   7:   Singlet-A      5.3742 eV  230.70 nm  f=0.0359
      33 -> 36        -0.10967
      35 -> 40        -0.18838
      35 -> 41         0.58462
      35 -> 42         0.29300
      35 -> 44         0.10482
Excited State   8:   Singlet-A      5.4190 eV  228.80 nm  f=0.0259
      33 -> 36        -0.11324
      35 -> 41        -0.29962
      35 -> 42         0.59607
      35 -> 43         0.11289
Excited State   9:   Singlet-A      5.5725 eV  222.49 nm  f=0.0624
      33 -> 36         0.54156
      34 -> 37        -0.16115
      35 -> 40         0.13974
      35 -> 42         0.16613
      35 -> 43        -0.25207
      35 -> 45         0.12882
Excited State  10:   Singlet-A      5.7272 eV  216.48 nm  f=0.0172
      33 -> 36         0.18567
      34 -> 37        -0.11365
      35 -> 43         0.62344
      35 -> 45         0.14998
Excited State  11:   Singlet-A      5.9443 eV  208.58 nm  f=0.0120
      35 -> 42        -0.11445
      35 -> 44         0.68002
Excited State  12:   Singlet-A      6.0338 eV  205.48 nm  f=0.0189
```

1.6. Calculated Transition State for azirine 1 forming ylide 6.

B3LYP/6-31G+(d)Energy = -403.01933864 a.u. Negative Frequency: 381 cm^{-1} (56)

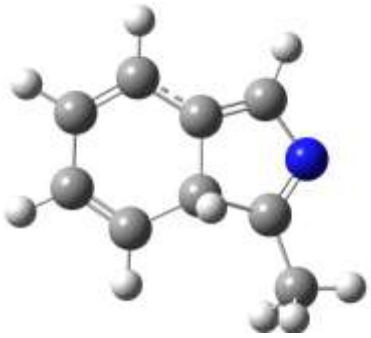
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.078750	1.418765	-0.041719
2	6	0	0.748696	1.040850	-0.206802
3	6	0	0.384821	-0.322189	-0.148850
4	6	0	1.383024	-1.284047	0.120666
5	6	0	2.708334	-0.898208	0.301536
6	6	0	3.061151	0.454334	0.216461
7	1	0	2.352291	2.469233	-0.098822
8	1	0	-0.023968	1.782445	-0.382799
9	1	0	1.108453	-2.335146	0.176871
10	1	0	3.468077	-1.647861	0.506551
11	1	0	4.095349	0.756261	0.360437
12	6	0	-0.967789	-0.764101	-0.418954
13	6	0	-2.896358	-0.434104	-0.086807
14	6	0	-3.835013	0.442935	0.682929
15	1	0	-4.811866	-0.029827	0.817743
16	1	0	-3.401839	0.578548	1.685440
17	1	0	-3.938898	1.438063	0.222586
18	7	0	-1.951541	0.127213	-0.775041
19	1	0	-1.180513	-1.827610	-0.373477

1.7 Calculated transition state for ylide 6 forming 9

B3LYP/6-31G+(d) Energy = -403.03997270 a.u. Negative Frequency -377 cm^{-1} (21)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.055298	-1.566009	0.071615
2	6	0	-0.046286	-0.597398	0.333941
3	6	0	-0.385928	0.798635	0.260381
4	6	0	-1.748237	1.174093	0.092656
5	6	0	-2.702346	0.208487	-0.149178
6	6	0	-2.350275	-1.168649	-0.191358
7	1	0	-0.808617	-2.623180	0.132398
8	1	0	0.743742	-0.904736	1.020796
9	1	0	-2.011377	2.229280	0.073374
10	1	0	-3.733106	0.501650	-0.332032
11	1	0	-3.119257	-1.911242	-0.388228
12	6	0	0.700652	1.680509	0.065267
13	6	0	1.972270	-0.157444	-0.424216
14	6	0	3.109344	-1.024784	0.021274
15	1	0	3.457744	-0.818792	1.043265
16	1	0	2.859800	-2.084683	-0.080439
17	1	0	3.945619	-0.824572	-0.662241
18	7	0	1.869582	1.084888	-0.180120
19	1	0	0.614999	2.757412	-0.028341

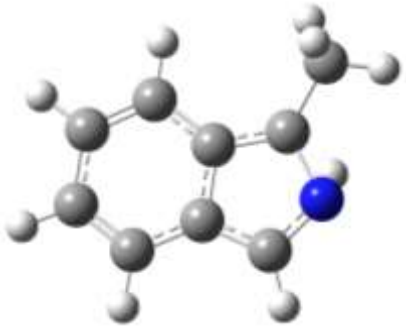
1.8. Optimized indole 9



B3LYP/6-31G+(d) Energy = -403.08563663 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.652108	-1.527916	-0.084308
2	6	0	0.201144	-0.380160	0.371044
3	6	0	-0.422551	0.973546	0.147561
4	6	0	-1.854319	1.098966	0.129786
5	6	0	-2.605439	-0.028079	-0.030900
6	6	0	-1.985801	-1.336683	-0.209122
7	1	0	-0.207759	-2.512953	-0.207682
8	1	0	0.302841	-0.507355	1.474692
9	1	0	-2.318399	2.082249	0.154802
10	1	0	-3.688199	0.042814	-0.093527
11	1	0	-2.629247	-2.175886	-0.464083
12	6	0	0.604190	1.819141	-0.148761
13	6	0	1.646200	-0.107886	-0.002533
14	6	0	2.735026	-1.130237	0.000908
15	1	0	2.779370	-1.674323	0.953835
16	1	0	2.564475	-1.880560	-0.784973
17	1	0	3.700745	-0.649837	-0.176848
18	7	0	1.847778	1.158148	-0.221877
19	1	0	0.563674	2.884665	-0.345136

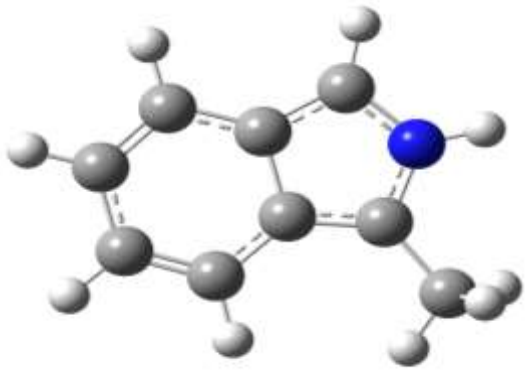
1.9. Calculated Transition State for 9 forming isoindole 10



B3LYP/6-31G+(d)Energy = -403.06532805 a.u. Negative frequency -1558 (202) cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.719221	-1.506449	-0.090667
2	6	0	-0.143981	-0.382418	-0.072279
3	6	0	0.394036	0.944697	0.024650
4	6	0	1.801107	1.135834	0.077668
5	6	0	2.618803	0.026093	0.052203
6	6	0	2.080973	-1.292675	-0.026873
7	1	0	0.317735	-2.515108	-0.150698
8	1	0	-2.035306	0.583818	-1.076250
9	1	0	2.220894	2.136920	0.138191
10	1	0	3.698171	0.150341	0.092690
11	1	0	2.762518	-2.139472	-0.035896
12	6	0	-0.701629	1.831886	0.024417
13	6	0	-1.556714	-0.252925	-0.110948
14	6	0	-2.615588	-1.276749	0.177143
15	1	0	-2.426387	-2.208670	-0.366574
16	1	0	-2.646734	-1.511057	1.250255
17	1	0	-3.604976	-0.904606	-0.107836
18	7	0	-1.881225	1.161379	-0.009403
19	1	0	-0.694708	2.914422	-0.009945

1.10. Optimized Isoindole 10



B3LYP/6-31G+(d) Energy = --403.13753684

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.719723	-1.510901	-0.004198
2	6	0	0.152984	-0.385571	-0.004436
3	6	0	-0.404363	0.956001	0.002018
4	6	0	-1.817313	1.134313	0.004229
5	6	0	-2.627547	0.023110	0.002444
6	6	0	-2.079050	-1.299959	-0.001623
7	1	0	-0.318313	-2.521960	-0.005537
8	1	0	-2.244542	2.134576	0.007552
9	1	0	-3.708194	0.142983	0.004390
10	1	0	-2.757401	-2.149618	-0.002100
11	6	0	0.670507	1.843272	0.002578
12	6	0	1.547594	-0.265997	-0.009732
13	6	0	2.630365	-1.296836	0.009928
14	1	0	3.109008	-1.389168	0.996089
15	1	0	2.218108	-2.278615	-0.242955
16	1	0	3.420542	-1.079781	-0.721897
17	7	0	1.814060	1.080976	-0.004529
18	1	0	0.713259	2.922688	-0.001734
19	1	0	2.748396	1.467472	-0.009351

2. Irradiation of azirine 1 with 254 nm and above 300 nm light

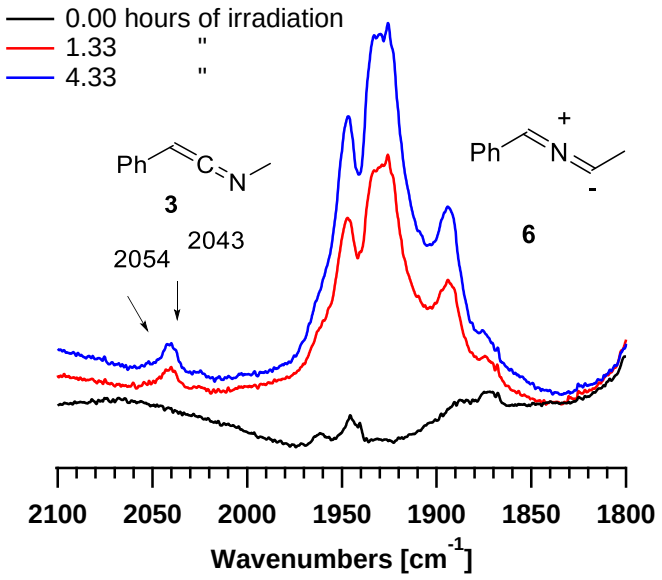


Figure S1. Irradiation of azirine 1 in argon matrix with light at 254 nm and above 300 nm

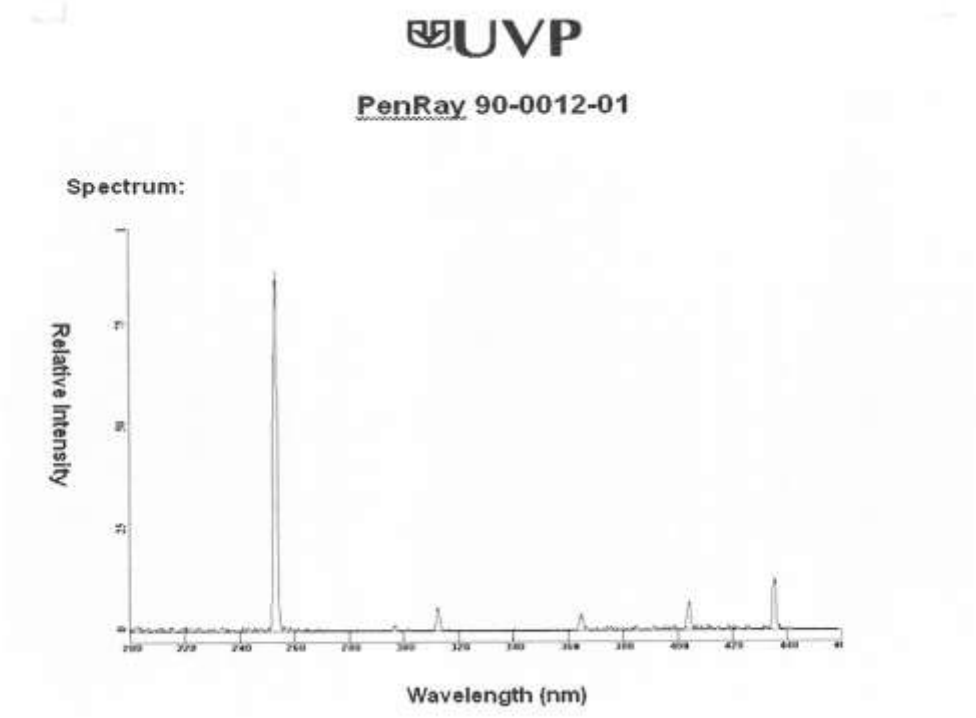
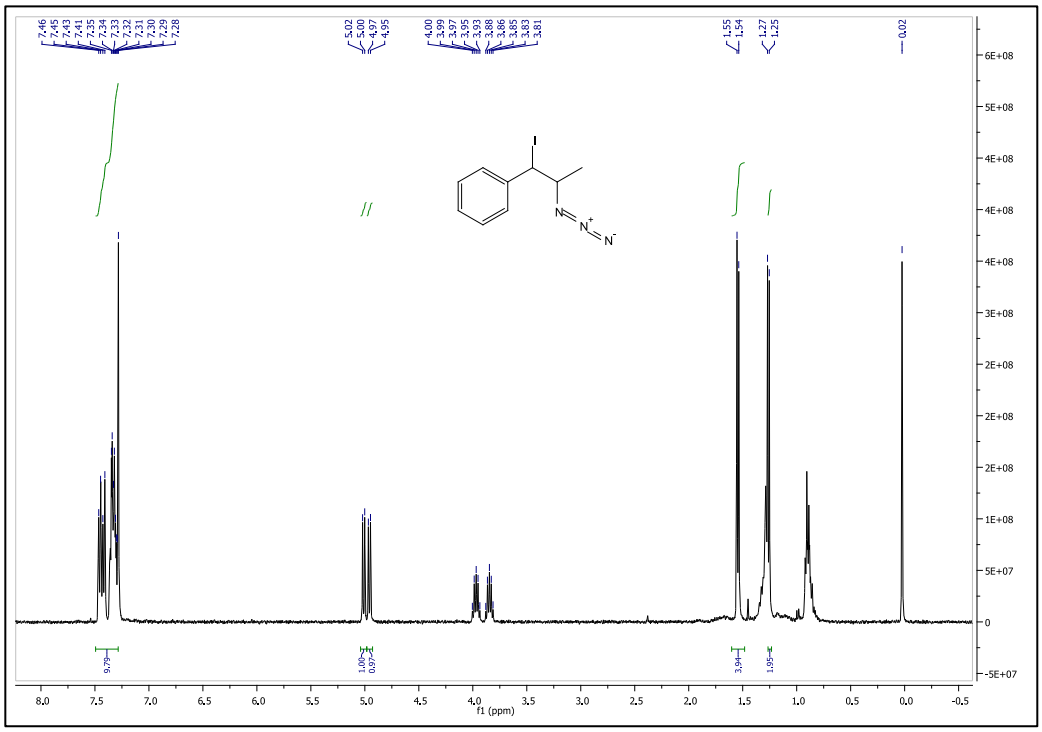
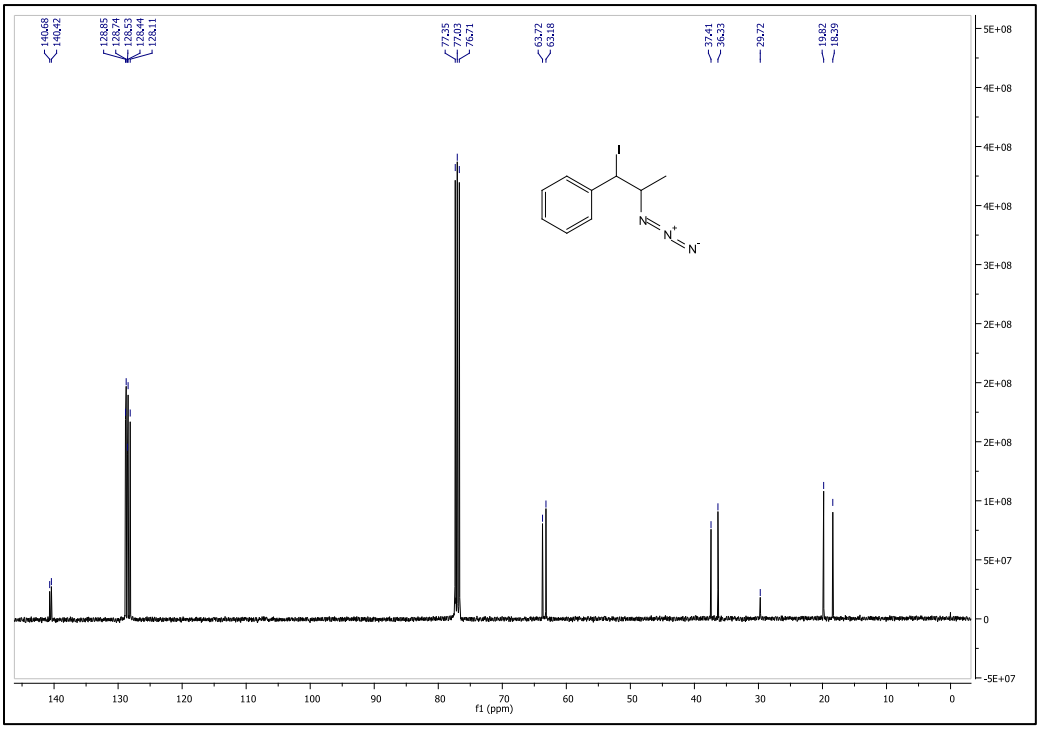


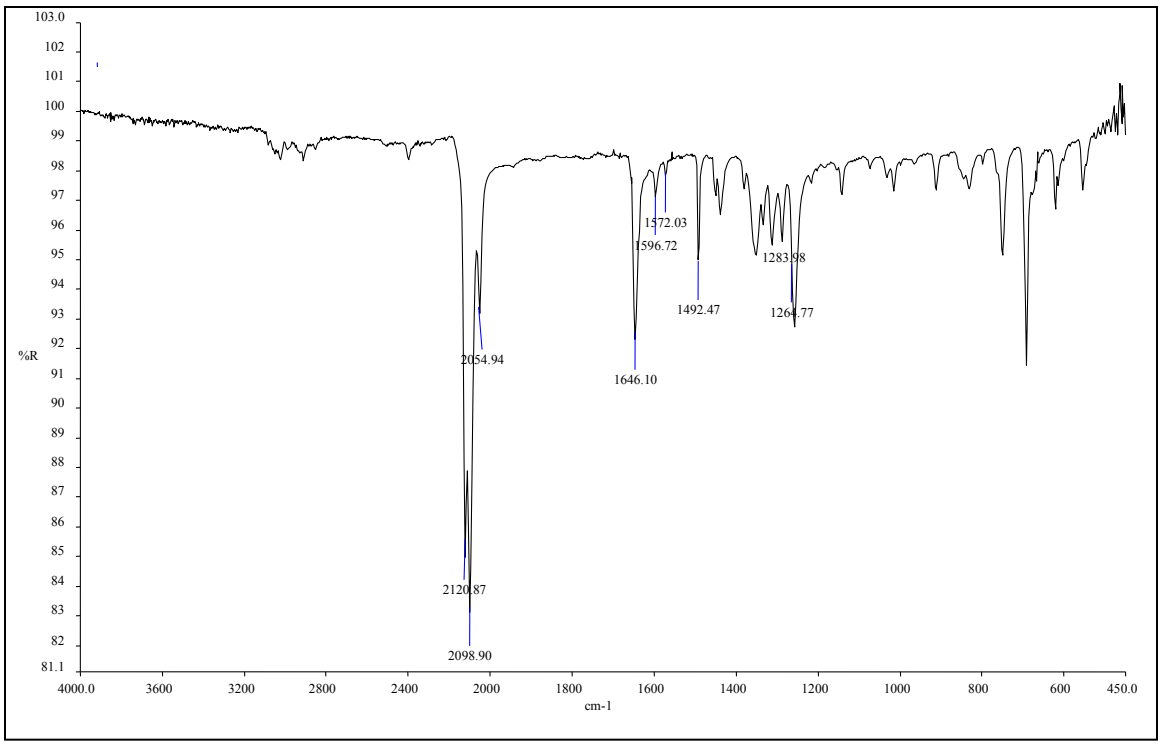
Figure S2. Light emission from the UV pen without filter that absorbs visible light

3. Spectra of (2-azidoprop-1-en-1-yl)benzene and Azirine 1

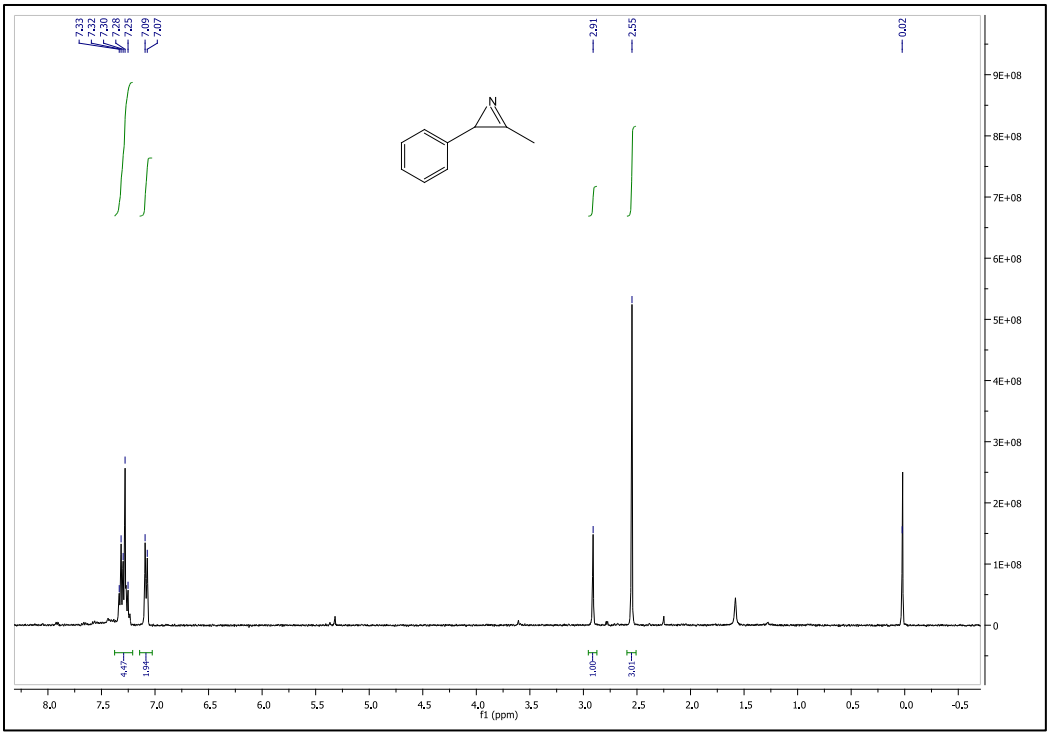


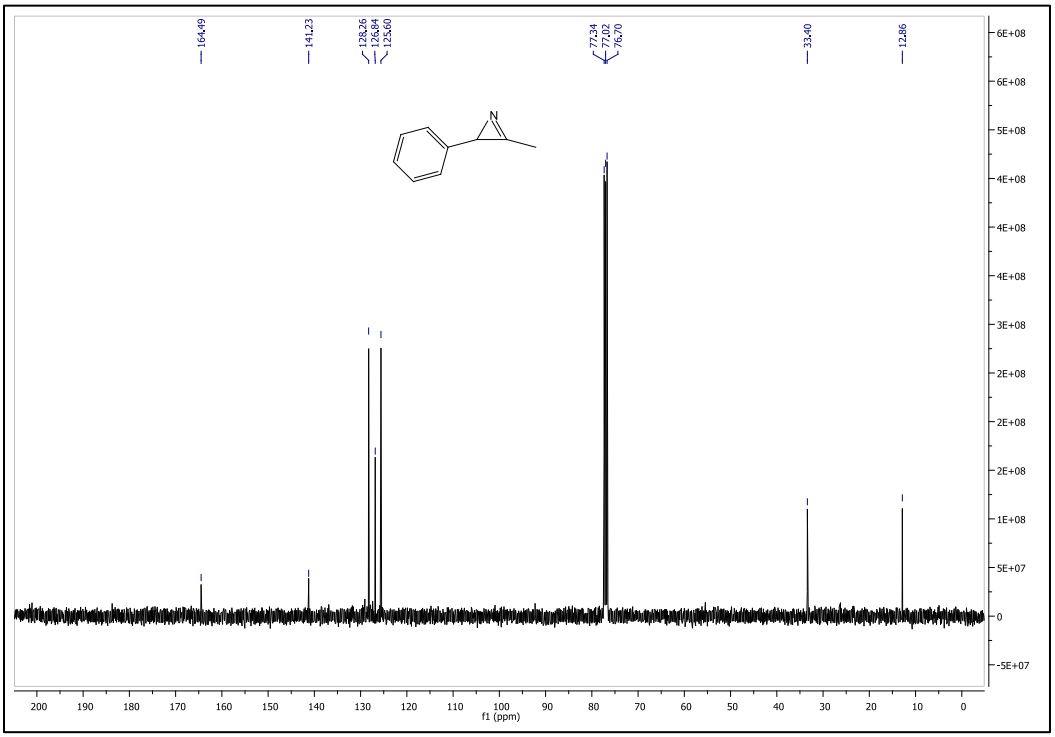


3.1. ^{1}H- and ^{13}C-NMR spectra of (2-azidoprop-1-en-1-yl)benzene

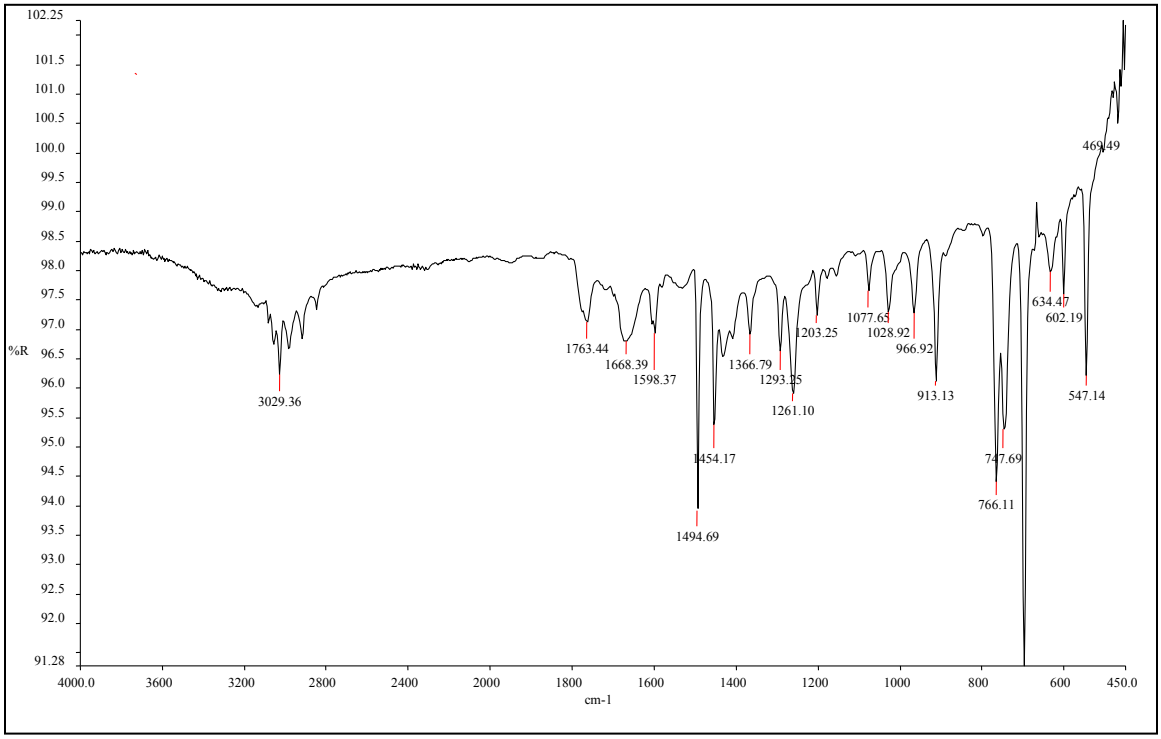


3.2. IR spectrum of (2-azidoprop-1-en-1-yl)benzene





3.3. ^{1}H- and ^{13}C-NMR of Azirine 1



3.4. IR Spectrum of Azirine 1