Supporting Information

for

Comparison of Photochemistry of 3-Phenyl-2-Methyl-2H-Azirine and 2-Phenyl-3-Methyl-2H-Azirine

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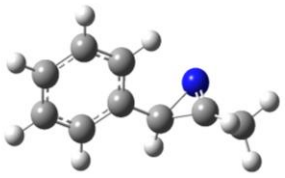
1. Calculations

1.1 1a



B3LYP 6-31+G(d) E = -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

1.1.1 TD-DFT of 1a in 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

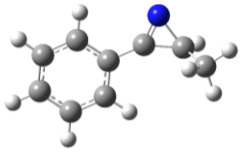
```
      35 -> 39         0.13947
 Excited State   4:   Singlet-A      5.6787 eV  218.33 nm  f=0.0068
      34 -> 36        -0.34136
      34 -> 37         0.11284
      34 -> 38        -0.11023
      35 -> 39         0.57397
Excited State   5:   Singlet-A      5.8010 eV  213.73 nm  f=0.1400
      34 -> 36         0.45714
      34 -> 38         0.25721
      35 -> 37         0.20213
      35 -> 39         0.32303
      35 -> 40        -0.19028
```

1.1.2 TD-DFT of 1a in Acetonitrile

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
```

1.2 1b



B3LYP 6-31+G(d) E = -403.08518317 a.u. C=N band: 1808 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.162692	-0.386293	-0.248790
2	6	0	-2.517975	0.103903	-0.447356
3	7	0	-2.004265	-1.333658	-0.224759

4	6	0	-3.342880	0.753381	0.642911
5	1	0	-2.942012	0.518128	1.635034
6	1	0	-3.355449	1.845598	0.528864
7	1	0	-4.382227	0.402274	0.603065
8	6	0	0.263535	-0.150557	-0.115329
9	6	0	0.778206	1.150660	-0.228863
10	6	0	1.135903	-1.228156	0.123997
11	6	0	2.150420	1.373841	-0.104573
12	1	0	0.097973	1.977799	-0.414404
13	6	0	2.504512	-1.000445	0.246783
14	1	0	0.727745	-2.231534	0.209902
15	6	0	3.013484	0.299890	0.132915
16	1	0	2.545947	2.382181	-0.192885
17	1	0	3.177826	-1.833475	0.431057
18	1	0	4.082123	0.473896	0.229427
19	1	0	-2.857155	0.303400	-1.466914

1.2.1 TD-DFT of 1b in Gas Phase

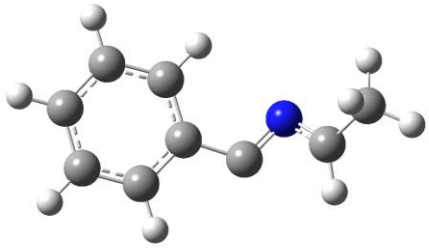
Excitation energies and oscillator strengths:

```
Excited State   1:   Singlet-A      4.2021 eV  295.05 nm  f=0.0008
      34 -> 36        0.67926
      35 -> 36       -0.10385
Excited State   2:   Singlet-A      4.8440 eV  255.95 nm  f=0.0100
      33 -> 36        0.58133
      35 -> 37        0.39720
Excited State   3:   Singlet-A      4.9890 eV  248.51 nm  f=0.3639
      33 -> 37       -0.12220
      35 -> 36        0.61847
Excited State   4:   Singlet-A      5.5930 eV  221.68 nm  f=0.0002
      34 -> 37        0.69596
      35 -> 37       -0.11533
```

1.2.2 TD-DFT of 1b in Acetonitrile

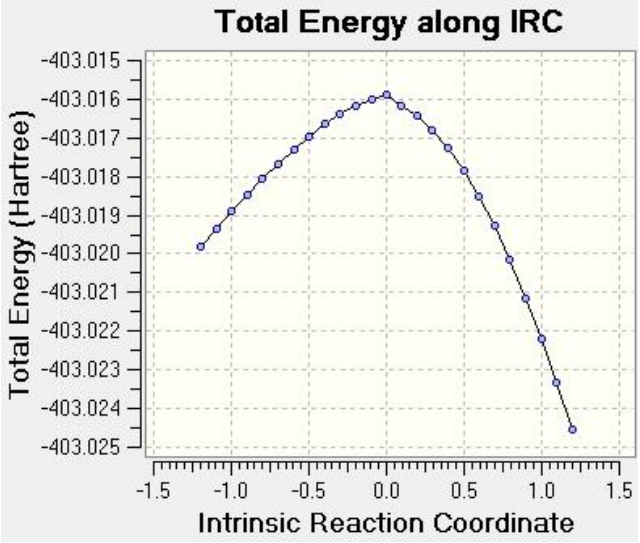
```
Excited State   1:   Singlet-A      4.3409 eV  285.62 nm  f=0.0015
      33 -> 36        0.66608
      34 -> 36       -0.16253
Excited State   2:   Singlet-A      4.7484 eV  261.11 nm  f=0.0249
      33 -> 36        0.13945
      34 -> 36        0.60045
      35 -> 37        0.32182
Excited State   3:   Singlet-A      4.8802 eV  254.05 nm  f=0.4681
      35 -> 36        0.62863
Excited State   4:   Singlet-A      5.9299 eV  209.08 nm  f=0.0380
      33 -> 37        0.59902
      34 -> 36        0.10733
      34 -> 37       -0.15268
      35 -> 37       -0.29093
```

1.3 TS for forming Ylide 8 from 1b & IRC calculations

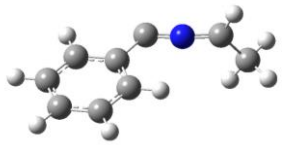


−403.01588685 a.u. Negative Frequency −453 cm^{-1}.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.122339	1.391376	-0.017458
2	6	0	-0.796641	1.042838	-0.263730
3	6	0	-0.395014	-0.310733	-0.222704
4	6	0	-1.352863	-1.296466	0.082490
5	6	0	-2.679715	-0.946536	0.334489
6	6	0	-3.063648	0.397450	0.283704
7	1	0	-2.428273	2.434153	-0.054939
8	1	0	-0.056006	1.801729	-0.497622
9	1	0	-1.032463	-2.334207	0.112107
10	1	0	-3.412883	-1.714489	0.566998
11	1	0	-4.097129	0.673369	0.479698
12	6	0	0.977158	-0.748037	-0.508464
13	6	0	2.848305	-0.410367	-0.064498
14	1	0	3.008712	-1.483882	-0.076844
15	6	0	3.749227	0.455573	0.756574
16	1	0	3.380485	0.550223	1.787923
17	1	0	4.758689	0.030061	0.812695
18	1	0	3.782315	1.464049	0.328405
19	7	0	1.872819	0.161201	-0.820120



1.4 Ylide 8



B3LYP 6-31+G(d) E = -403.07147213 a.u. C=N=C band: 1968 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.967355	1.478738	-0.086399
2	6	0	-0.689822	0.932714	-0.192476
3	6	0	-0.495714	-0.459070	-0.087771
4	6	0	-1.611143	-1.286019	0.124230
5	6	0	-2.891536	-0.739276	0.234387
6	6	0	-3.070850	0.642731	0.128727
7	1	0	-2.107898	2.553790	-0.169708
8	1	0	0.168129	1.579957	-0.359417
9	1	0	-1.453485	-2.358141	0.199958
10	1	0	-3.747171	-1.388862	0.399907
11	1	0	-4.067078	1.070174	0.212161
12	6	0	0.830036	-1.096686	-0.196025
13	6	0	3.028558	0.074053	-0.486501
14	1	0	3.392523	0.222784	-1.503619
15	6	0	3.910009	0.439233	0.678202
16	1	0	3.404081	0.236850	1.626966
17	1	0	4.846488	-0.136161	0.656824
18	1	0	4.183960	1.502473	0.651821
19	7	0	1.875337	-0.457338	-0.344734

1.4.1 TD-DFT of 8 in Gas Phase

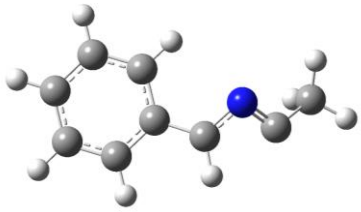
```
Excited State   1:   Singlet-A      2.7204 eV  455.75 nm  f=0.0017
      35 -> 36        0.68439
Excited State   2:   Singlet-A      4.0462 eV  306.42 nm  f=0.0002
      35 -> 37        0.70445
Excited State   3:   Singlet-A      4.5986 eV  269.61 nm  f=0.0636
      34 -> 36       -0.12532
      35 -> 38        0.50632
      35 -> 39       -0.35006
      35 -> 40        0.21021
 Excited State   4:   Singlet-A      4.8524 eV  255.51 nm  f=0.0088
      33 -> 36        0.59835
      34 -> 37       -0.34697
```

1.4.2 TD-DFT of 8 in Acetonitrile

```
Excited State   1:   Singlet-A      2.8773 eV  430.90 nm  f=0.0026
      35 -> 36        0.68536
Excited State   2:   Singlet-A      4.2848 eV  289.36 nm  f=0.0007
      35 -> 37        0.66159
      35 -> 38       -0.24536
Excited State   3:   Singlet-A      4.6246 eV  268.09 nm  f=0.1731
```

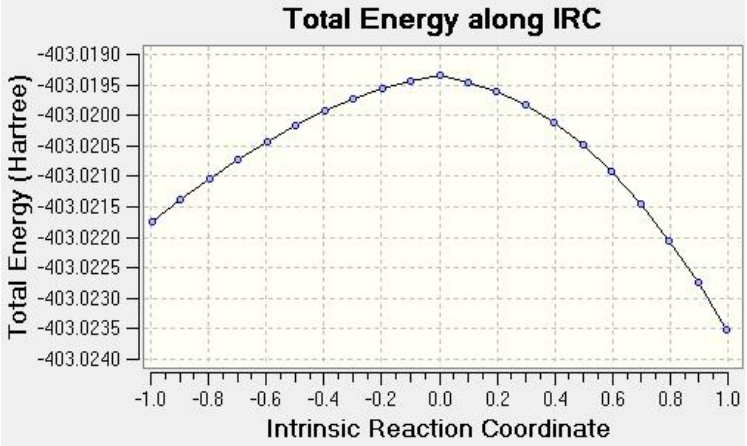
```
      34 -> 36         0.13552
      35 -> 37         0.20095
      35 -> 38         0.55898
      35 -> 39         0.18207
Excited State   4:   Singlet-A      4.8066 eV  257.94 nm  f=0.0370
      33 -> 36         0.61999
      34 -> 37        -0.30507
      34 -> 38         0.11809
```

1.5 TS for forming Ylide from 1a & IRC calculations

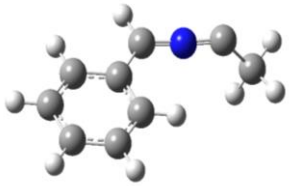


B3LYP 6-31+G(d) E = -403.01933864 a.u. Negative Frequency -381 cm^{-1}

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



1.6 Ylide from 1a



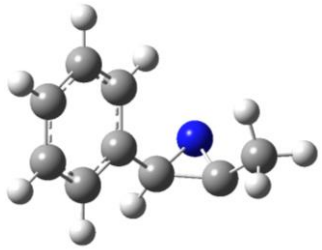
B3LYP 6-31+G(d) E = −403.07639701 a.u. C=N=C band: 2001 cm^{-1}

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

1.6.1 TD-DFT for the Ylide from 1a in Gas Phase

```
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
```

1.7 T_1 for 1a



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

1.7.1 TD-DFT of T_1 of 1a in Gas Phase

```
Excited State   1:  3.010-A      1.2753 eV  972.20 nm  f=0.0042  <S**2>=2.015
     32B -> 35B        0.44680
     34B -> 35B        0.88937

 Excited State   2:  3.018-A      2.4468 eV  506.73 nm  f=0.0008  <S**2>=2.028
     32B -> 35B       -0.18242
     33B -> 35B        0.97448

 Excited State   3:  3.023-A      2.5855 eV  479.53 nm  f=0.0012  <S**2>=2.034
     31B -> 35B        0.15432
     32B -> 35B        0.84528
     33B -> 35B        0.21867
     34B -> 35B       -0.43281

 Excited State   4:  3.008-A      3.1724 eV  390.82 nm  f=0.0011  <S**2>=2.011
     28B -> 35B       -0.10432
     29B -> 35B        0.21458
     31B -> 35B        0.93531
     32B -> 35B       -0.14802

 Excited State   5:  3.901-A      3.6303 eV  341.53 nm  f=0.0023  <S**2>=3.555
     34A -> 37A       -0.15811
     34A -> 38A       -0.34254
     35A -> 37A        0.37629
     35A -> 38A       -0.16194
     36A -> 37A        0.43126
     36A -> 38A       -0.18313
     32B -> 38B        0.14877
     33B -> 37B        0.36816
     34B -> 36B       -0.39917
     34B -> 38B       -0.33379

 Excited State   6:  3.150-A      4.0764 eV  304.15 nm  f=0.0189  <S**2>=2.231
     35A -> 37A        0.14594
     36A -> 37A       -0.21240
     36A -> 38A        0.86878
     32B -> 36B       -0.10893
     33B -> 37B        0.13052
     34B -> 36B       -0.28988
     34B -> 37B       -0.13227

 Excited State   7:  3.185-A      4.0909 eV  303.07 nm  f=0.0196  <S**2>=2.286
     34A -> 38A        0.15152
     35A -> 38A        0.15573
     36A -> 37A        0.83171
     36A -> 38A        0.33380
     33B -> 37B       -0.17585
     34B -> 36B        0.24347
     34B -> 37B       -0.11303

 Excited State   8:  3.299-A      4.2510 eV  291.66 nm  f=0.0030  <S**2>=2.471
     34A -> 37A       -0.14808
     34A -> 38A       -0.29228
     35A -> 37A        0.10466
     36A -> 37A       -0.16949
     36A -> 38A        0.15343
     32B -> 36B        0.35823
     33B -> 37B        0.31205
     34B -> 36B        0.70032
     34B -> 38B       -0.23266
```

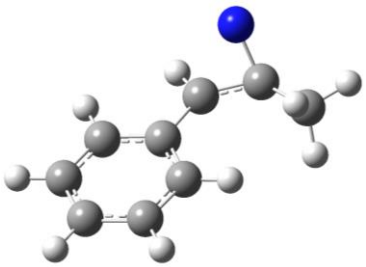
```
 Excited State   9:  3.950-A      4.6479 eV  266.75 nm  f=0.0009  <S**2>=3.650
     34A -> 37A        0.36920
     34A -> 38A       -0.23077
     35A -> 37A       -0.22434
     35A -> 38A       -0.41335
     36A -> 37A        0.11830
     36A -> 38A        0.23184
     32B -> 37B       -0.13362
     33B -> 36B       -0.35741
     33B -> 38B       -0.27469
     34B -> 37B        0.52534
```

1.7.2 TD-DFT of T_1 of 1a in Acetonitrile

```
Excited State   1:  3.010-A      1.2557 eV  987.34 nm  f=0.0052  <S**2>=2.015
     32B -> 35B       -0.44325
     34B -> 35B        0.89165
Excited State   2:  3.018-A      2.2861 eV  542.34 nm  f=0.0007  <S**2>=2.027
     33B -> 35B        0.99298

 Excited State   3:  3.018-A      2.4906 eV  497.81 nm  f=0.0013  <S**2>=2.028
     31B -> 35B        0.13705
     32B -> 35B        0.86482
     33B -> 35B        0.10917
     34B -> 35B        0.43979

 Excited State   4:  3.007-A      3.1473 eV  393.94 nm  f=0.0013  <S**2>=2.011
     28B -> 35B       -0.12515
     29B -> 35B        0.27256
     30B -> 35B       -0.12268
     31B -> 35B        0.91748
     32B -> 35B       -0.12671

 Excited State   5:  3.937-A      3.6572 eV  339.01 nm  f=0.0011  <S**2>=3.625
     34A -> 38A       -0.38081
     35A -> 37A        0.42149
     36A -> 37A        0.39661
     32B -> 38B        0.14211
     33B -> 37B        0.38190
     34B -> 36B        0.41734
     34B -> 38B        0.36514

 Excited State   6:  3.026-A      4.1469 eV  298.98 nm  f=0.0440  <S**2>=2.040
     36A -> 37A       -0.58353
     36A -> 38A        0.33299
     32B -> 36B       -0.29657
     34B -> 36B        0.62182
     34B -> 38B       -0.12102

 Excited State   7:  3.261-A      4.2264 eV  293.36 nm  f=0.0036  <S**2>=2.409
     35A -> 38A        0.19992
     36A -> 37A        0.33126
     36A -> 38A        0.85877
     33B -> 36B        0.12362
     33B -> 38B        0.11648
     34B -> 36B       -0.13536
     34B -> 37B        0.22227

 Excited State   8:  3.394-A      4.2621 eV  290.90 nm  f=0.0038  <S**2>=2.629
     34A -> 38A        0.36970
     35A -> 37A       -0.15142
```

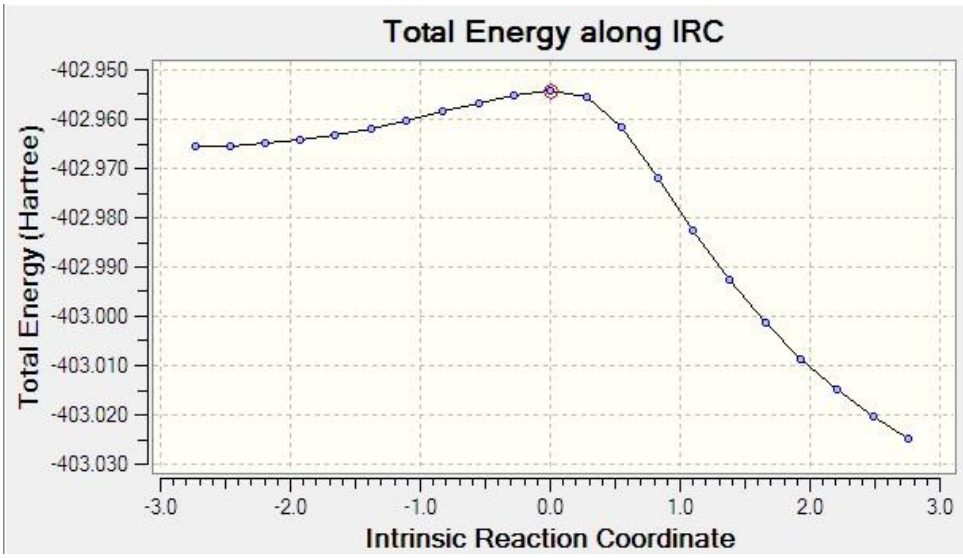
```
     36A -> 37A        0.57363
     36A -> 38A       -0.12917
     32B -> 36B       -0.25037
     33B -> 37B       -0.38015
     34B -> 36B        0.46732
     34B -> 38B       -0.17343
```

1.8 TS for forming Triplet Vinylnitrene 5 from T_1 of 1a & IRC Calculations

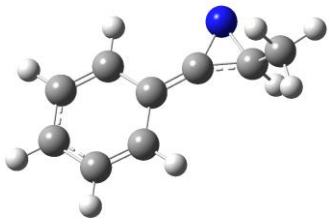


B3LYP 6-31+G(d) E = -402.95429468 a.u. 1 negative frequency -823cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.165826	-0.842466	-0.334855
2	6	0	-2.419012	-0.194214	-0.309859
3	7	0	-2.600857	-1.101803	0.789779
4	6	0	-2.751534	1.255100	-0.130893
5	1	0	-3.841006	1.374197	-0.102757
6	1	0	-2.360450	1.676301	0.812787
7	1	0	-2.366622	1.852528	-0.964649
8	6	0	0.204817	-0.342676	-0.161308
9	6	0	1.252741	-1.286422	-0.155889
10	6	0	0.529884	1.020618	-0.013468
11	6	0	2.578678	-0.887276	-0.003275
12	1	0	1.014971	-2.341794	-0.267214
13	6	0	1.856991	1.418753	0.140424
14	1	0	-0.251666	1.769684	-0.020482
15	6	0	2.884295	0.469131	0.146235
16	1	0	3.371609	-1.630386	0.000719
17	1	0	2.091564	2.473809	0.254190
18	1	0	3.917357	0.785336	0.265180
19	1	0	-1.195959	-1.910343	-0.568895



1.9 T_1 of 1b



B3LYP 6-31+G(d) E = -402.98643105 a.u.

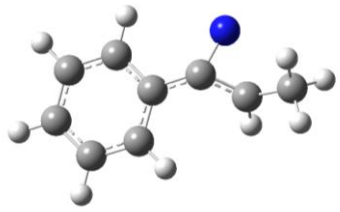
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.115374	-0.242000	-0.129056
2	6	0	-2.475267	0.096680	-0.442037
3	7	0	-2.064122	-1.318516	-0.214867
4	6	0	-3.477027	0.688470	0.544521
5	1	0	-3.226944	0.397433	1.568691
6	1	0	-3.462657	1.782787	0.478713
7	1	0	-4.487852	0.335019	0.312495
8	6	0	0.241253	-0.078012	-0.073199
9	6	0	0.866510	1.225972	-0.155398
10	6	0	1.107615	-1.227794	0.099176
11	6	0	2.234677	1.351934	-0.067046
12	1	0	0.234357	2.099743	-0.287828
13	6	0	2.475472	-1.067512	0.185181
14	1	0	0.651039	-2.210854	0.161750
15	6	0	3.060274	0.214231	0.105121
16	1	0	2.689149	2.337684	-0.131356
17	1	0	3.111249	-1.939974	0.315302
18	1	0	4.138016	0.329176	0.174066
19	1	0	-2.706295	0.326785	-1.491335

1.9.1 TD-DFT T_1 of 1b Gas Phase

```
Excited State   1:   ?Spin  -A      1.5869 eV  781.29 nm  f=0.0013
     32B -> 35B       -0.46475
     33B -> 35B        0.88935
     33B -> 36B       -0.11756

 Excited State   2:   ?Spin  -A      1.8768 eV  660.62 nm  f=0.0009
     36A -> 37A        0.30432
     34B -> 35B        0.98075

 Excited State   3:   ?Spin  -A      2.2103 eV  560.95 nm  f=0.0324
     36A -> 38A       -0.39843
     36A -> 39A       -0.30260
     36A -> 40A        0.26652
     36A -> 41A        0.10935
     32B -> 35B        0.81890
     33B -> 35B        0.41871

 Excited State   4:   ?Spin  -A      2.7738 eV  446.99 nm  f=0.0076
     36A -> 37A        0.95310
     34B -> 35B       -0.22461
     34B -> 36B        0.14328

 Excited State   5:   ?Spin  -A      2.9845 eV  415.43 nm  f=0.0029
     30B -> 35B       -0.15211
     31B -> 35B        0.97505
     31B -> 36B       -0.15504

 Excited State   6:   ?Spin  -A      3.6077 eV  343.67 nm  f=0.0692
     36A -> 38A        0.87046
     36A -> 39A       -0.38781
     36A -> 40A        0.11305
     32B -> 35B        0.15082

 Excited State   7:   ?Spin  -A      3.9029 eV  317.67 nm  f=0.2135
     36A -> 38A        0.23545
     36A -> 39A        0.85654
     36A -> 40A        0.11343
     32B -> 35B        0.22663
     32B -> 36B       -0.15994
     33B -> 35B        0.12058
     33B -> 36B       -0.12993

 Excited State   8:   ?Spin  -A      4.1093 eV  301.72 nm  f=0.0830
     36A -> 40A        0.92440
     36A -> 41A       -0.11432
     36A -> 42A        0.10243
     32B -> 35B       -0.14699
     32B -> 36B        0.18381
     33B -> 36B        0.13401

 Excited State   9:   ?Spin  -A      4.3066 eV  287.89 nm  f=0.0005
     35A -> 37A        0.13279
     36A -> 41A       -0.12069
     29B -> 35B       -0.11867
     30B -> 35B        0.89354
     31B -> 35B        0.14182
     32B -> 36B        0.12211
     33B -> 36B       -0.24113
     34B -> 37B       -0.15210

 Excited State  10:   ?Spin  -A      4.3161 eV  287.26 nm  f=0.0149
     34A -> 37A       -0.32156
```

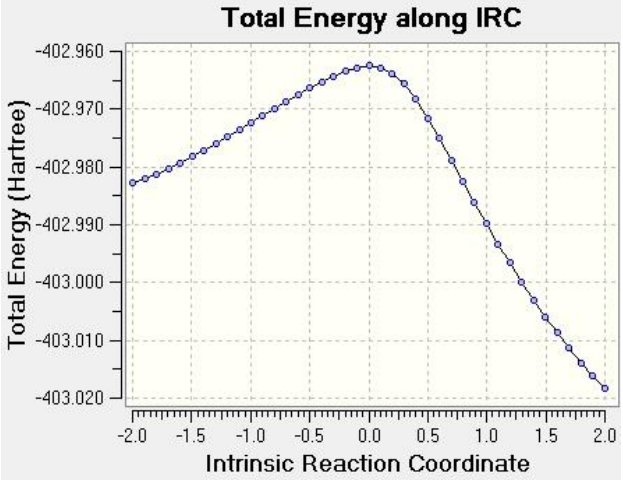
```
     35A -> 37A       -0.43348
     36A -> 41A        0.44964
     36A -> 42A        0.20973
     36A -> 57A       -0.11295
     29B -> 35B        0.40878
     30B -> 35B        0.25693
     34B -> 36B       -0.11757
     34B -> 37B        0.52676
```

1.10 TS for T_1 of 1b forming Triplet Vinylnitrene 10 & IRC Calculations

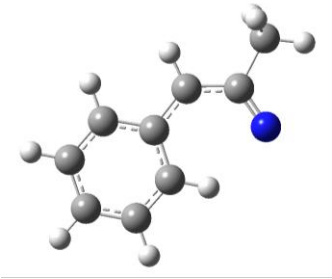


B3LYP 6-31+G(d) E = -402.96253310 a.u. Negative Frequency -1011 cm-1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.172240	0.280450	-0.204201
2	6	0	-2.242718	-0.440447	0.348162
3	7	0	-1.922266	1.418898	0.167508
4	6	0	-3.641650	-0.506836	-0.188975
5	1	0	-3.796119	0.175584	-1.027586
6	1	0	-3.819079	-1.534997	-0.542759
7	1	0	-4.380816	-0.302807	0.594576
8	6	0	0.235199	0.101218	-0.102302
9	6	0	0.810594	-1.199016	-0.068219
10	6	0	1.105671	1.225748	-0.065078
11	6	0	2.187480	-1.359460	0.006625
12	1	0	0.162017	-2.070228	-0.124684
13	6	0	2.482510	1.048570	0.004397
14	1	0	0.678382	2.224145	-0.094386
15	6	0	3.035390	-0.239743	0.043915
16	1	0	2.611705	-2.360427	0.027396
17	1	0	3.134529	1.918312	0.029902
18	1	0	4.112655	-0.372083	0.094414
19	1	0	-2.048821	-1.072685	1.224618



1.11 Triplet Vinylnitrene 5A



B3LYP 6-31+G(d) E = -403.05933111 a.u. C-N band: 1560 cm^{-1}

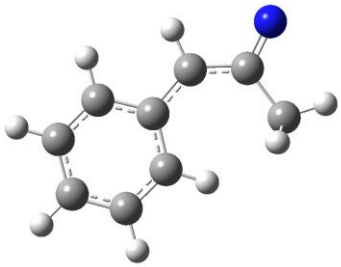
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.092471	1.319715	0.000151
2	6	0	-0.732136	1.030835	0.000350
3	6	0	-0.278096	-0.315087	0.000205
4	6	0	-1.259494	-1.343531	-0.000050
5	6	0	-2.616910	-1.045655	-0.000244
6	6	0	-3.042791	0.289342	-0.000170
7	1	0	-2.418320	2.356762	0.000278
8	1	0	-0.004099	1.836035	0.000747
9	1	0	-0.934125	-2.381641	-0.000132
10	1	0	-3.346954	-1.851018	-0.000460
11	1	0	-4.103885	0.524419	-0.000329
12	6	0	1.104326	-0.692602	0.000322
13	1	0	1.311053	-1.761531	0.000485
14	6	0	2.266958	0.156605	-0.000101
15	6	0	3.638791	-0.522576	0.000002
16	1	0	4.435526	0.224952	-0.000832
17	1	0	3.748363	-1.154011	0.889206
18	1	0	3.747940	-1.155629	-0.888088
19	7	0	2.233634	1.442771	-0.000524

1.11.1 TD-DFT Triplet Vinylnitrene 5A in the Gas Phase

```
Excited State   1:   Spin  -A      2.9519 eV  420.01 nm  f=0.0104
     34A -> 38A       -0.13379
     36A -> 37A       -0.30377
     36A -> 38A        0.28472
     33B -> 35B       -0.49616
     34B -> 35B        0.79105
Excited State   2:   Spin  -A      3.0646 eV  404.57 nm  f=0.0145
     34A -> 37A        0.10364
     36A -> 37A        0.44291
     33B -> 35B        0.72339
     34B -> 35B        0.56434
     34B -> 37B       -0.12563
Excited State   3:   Spin  -A      3.4972 eV  354.52 nm  f=0.0000
     32B -> 36B       -0.44764
     33B -> 36B        0.83813
     34B -> 36B       -0.33774
Excited State   4:   Spin  -A      4.0450 eV  306.51 nm  f=0.0533
     33A -> 37A        0.14408
     34A -> 38A        0.27705
     36A -> 37A        0.44392
     36A -> 38A        0.70691
     32B -> 35B        0.19873
     33B -> 35B       -0.21635
     33B -> 37B       -0.28346
     34B -> 35B       -0.15384
     34B -> 37B       -0.18514
Excited State   5:   Spin  -A      4.1163 eV  301.20 nm  f=0.0703
     33A -> 37A       -0.20552
     34A -> 37A       -0.13148
     34A -> 38A       -0.36231
     36A -> 37A       -0.23511
     36A -> 38A        0.56311
     36A -> 42A       -0.15609
     31B -> 36B        0.22374
     32B -> 35B       -0.40786
     33B -> 35B        0.22430
     33B -> 38B       -0.22129
     34B -> 35B       -0.13821
     34B -> 37B        0.25564
     34B -> 38B        0.23424
Excited State   6:   Spin  -A      4.1467 eV  298.99 nm  f=0.0000
     33B -> 36B        0.34639
     34B -> 36B        0.93581
Excited State   7:   Spin  -A      4.3030 eV  288.14 nm  f=0.0414
     33A -> 37A        0.14377
     36A -> 37A       -0.25727
     36A -> 42A        0.18604
     36A -> 46A       -0.13223
     29B -> 36B        0.10032
     31B -> 36B        0.69445
     32B -> 35B        0.57052
     33B -> 35B        0.15700
Excited State   8:   Spin  -A      4.3594 eV  284.41 nm  f=0.0211
     34A -> 37A        0.20292
```

34A -> 38A	0.44553
36A -> 42A	-0.16981
36A -> 46A	0.11014
31B -> 36B	0.54207
32B -> 35B	-0.50573
33B -> 35B	-0.12667
34B -> 37B	-0.40309
34B -> 38B	-0.16425

1.12 Triplet Vinylnitrene 5B



B3LYP 6-31+G(d) E = -403.05523119 a.u. C-N band: 1458 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.984267	1.369858	-0.000066
2	6	0	0.640393	1.008025	-0.000101
3	6	0	0.250648	-0.358955	-0.000042
4	6	0	1.294386	-1.327263	0.000042
5	6	0	2.633544	-0.958878	0.000079
6	6	0	2.990334	0.395925	0.000028
7	1	0	2.251240	2.423723	-0.000117
8	1	0	-0.106153	1.790890	-0.000196
9	1	0	1.027186	-2.381353	0.000083
10	1	0	3.403428	-1.726195	0.000147
11	1	0	4.036790	0.688566	0.000055
12	6	0	-1.097852	-0.855041	-0.000068
13	1	0	-1.188564	-1.939424	-0.000109
14	6	0	-2.365387	-0.185615	-0.000009
15	6	0	-2.575665	1.323309	0.000140
16	1	0	-2.130411	1.780572	0.890328
17	1	0	-2.130526	1.780753	-0.890011
18	1	0	-3.647185	1.540050	0.000228
19	7	0	-3.434830	-0.917967	-0.000061

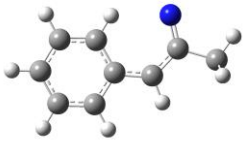
1.12.1 TD-DFT Triplet Vinylnitrene 5B in the Gas Phase

Excited State 1: Spin -A 3.1162 eV 397.87 nm f=0.0088

34A -> 37A	0.11968
34A -> 38A	-0.13126
36A -> 37A	-0.53449
36A -> 38A	-0.38643
32B -> 38B	0.11524
33B -> 35B	0.80389
34B -> 37B	-0.19209

```
Excited State   2:   Spin  -A      3.2275 eV  384.15 nm  f=0.0027
     36A -> 37A       -0.23805
     36A -> 38A        0.35059
     34B -> 35B        0.92502
Excited State   3:   Spin  -A      3.7233 eV  332.99 nm  f=0.0001
     32B -> 36B       -0.50002
     33B -> 36B        0.87039
Excited State   4:   Spin  -A      3.9440 eV  314.36 nm  f=0.0155
     34A -> 37A       -0.17319
     36A -> 37A       -0.55331
     36A -> 38A        0.68147
     33B -> 37B       -0.18673
     34B -> 35B       -0.34939
     34B -> 37B        0.11735
Excited State   5:   Spin  -A      4.2354 eV  292.73 nm  f=0.0546
     33A -> 37A        0.22568
     33A -> 38A        0.16271
     34A -> 37A       -0.32412
     34A -> 38A        0.45649
     36A -> 37A        0.17412
     36A -> 42A       -0.23132
     36A -> 46A       -0.14590
     32B -> 35B       -0.47324
     33B -> 35B        0.25252
     33B -> 38B       -0.26881
     34B -> 37B        0.53145
Excited State   6:   Spin  -A      4.3291 eV  286.40 nm  f=0.0058
     29B -> 36B        0.18356
     30B -> 36B       -0.14460
     31B -> 36B        0.95436
Excited State   7:   Spin  -A      4.3840 eV  282.81 nm  f=0.1346
     33A -> 37A       -0.11417
     34A -> 37A       -0.24383
     34A -> 38A        0.29914
     36A -> 37A        0.21708
     36A -> 38A        0.19400
     36A -> 42A        0.30648
     36A -> 46A        0.19521
     31B -> 36B        0.10261
     32B -> 35B        0.66160
     33B -> 35B        0.34478
     34B -> 37B        0.26548
Excited State   8:   Spin  -A      4.4350 eV  279.56 nm  f=0.0000
     34B -> 36B        0.99693
Excited State   9:   Spin  -A      4.4624 eV  277.84 nm  f=0.4011
     34A -> 37A        0.18743
     34A -> 38A       -0.24084
     36A -> 37A        0.48697
     36A -> 38A        0.42870
     36A -> 42A       -0.12094
     32B -> 35B       -0.22150
     33B -> 35B        0.35916
     34B -> 37B       -0.44347
```

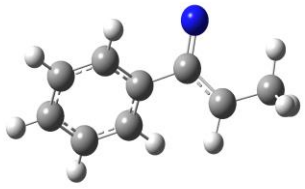
1.13 Singlet Vinylnitrene 5A



B3LYP 6-31+G(d) E = -403.04759813 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.104251	1.312373	0.000007
2	6	0	-0.740814	1.036985	0.000069
3	6	0	-0.276140	-0.302110	0.000005
4	6	0	-1.241953	-1.340878	-0.000126
5	6	0	-2.603813	-1.058390	-0.000185
6	6	0	-3.041988	0.271225	-0.000120
7	1	0	-2.441684	2.345583	0.000059
8	1	0	-0.013325	1.843415	0.000169
9	1	0	-0.905339	-2.375349	-0.000178
10	1	0	-3.325287	-1.871258	-0.000283
11	1	0	-4.105652	0.494915	-0.000167
12	6	0	1.115874	-0.671493	0.000067
13	1	0	1.311684	-1.744043	-0.000013
14	6	0	2.261165	0.152662	0.000191
15	6	0	3.638050	-0.532591	0.000053
16	1	0	4.429528	0.220068	-0.000877
17	1	0	3.754508	-1.161989	0.889996
18	1	0	3.753694	-1.163373	-0.889014
19	7	0	2.215013	1.457905	0.000076

1.14 Triplet Vinylnitrene 10A



B3LYP 6-31+G(d) E = -403.04759813 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.991815	-0.276890	0.096935
2	6	0	-2.144325	-1.342011	-0.221192

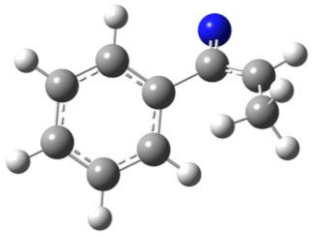
3	6	0	-0.764678	-1.140937	-0.303748
4	6	0	-0.216521	0.128114	-0.062883
5	6	0	-1.073832	1.195155	0.248263
6	6	0	-2.452500	0.991704	0.329850
7	1	0	-4.065457	-0.434200	0.160311
8	1	0	-2.556856	-2.329282	-0.413169
9	1	0	-0.114543	-1.969274	-0.573125
10	1	0	-0.653153	2.179251	0.432868
11	1	0	-3.105458	1.824623	0.577816
12	6	0	1.265970	0.361396	-0.159196
13	6	0	2.181454	-0.587788	0.353701
14	1	0	1.772671	-1.462282	0.855141
15	6	0	3.667017	-0.457066	0.268509
16	1	0	3.969354	0.465478	-0.233528
17	1	0	4.117614	-0.472335	1.271441
18	1	0	4.102214	-1.306885	-0.278012
19	7	0	1.672713	1.467834	-0.728740

1.14.1 TD-DFT of triplet Vinylnitrene 10A

```
Excited State   1:  3.081-A      3.1366 eV  395.29 nm  f=0.0108  <S**2>=2.124
     35A -> 37A        0.11829
     36A -> 37A       -0.14249
     36A -> 44A       -0.10624
     31B -> 35B       -0.12012
     32B -> 35B        0.10668
     34B -> 35B        0.84715
     34B -> 36B       -0.40002

 Excited State   2:  3.036-A      3.2505 eV  381.43 nm  f=0.0013  <S**2>=2.054
     36A -> 37A       -0.20166
     31B -> 36B       -0.16983
     32B -> 36B        0.15703
     34B -> 35B        0.38941
     34B -> 36B        0.85367

 Excited State   3:  3.945-A      3.6658 eV  338.22 nm  f=0.0038  <S**2>=3.640
     33A -> 37A       -0.13253
     34A -> 37A        0.20799
     34A -> 38A        0.36274
     35A -> 37A        0.38872
     35A -> 38A       -0.15794
     36A -> 37A        0.26907
     33B -> 35B        0.21911
     33B -> 36B       -0.25995
     33B -> 38B        0.38048
     34B -> 36B        0.12458
     34B -> 37B        0.48222

 Excited State   4:  3.126-A      3.7496 eV  330.66 nm  f=0.0001  <S**2>=2.192
     35A -> 37A       -0.14207
     33B -> 35B        0.96088
     34B -> 37B       -0.13143

 Excited State   5:  3.154-A      4.0040 eV  309.65 nm  f=0.0008  <S**2>=2.237
     35A -> 37A        0.19142
     36A -> 37A        0.13605
     33B -> 35B        0.14256
     33B -> 36B        0.93584
     34B -> 37B        0.14070
```

```
 Excited State   6:  3.038-A      4.1356 eV  299.80 nm  f=0.0044  <S**2>=2.057
     36A -> 37A        0.23213
     27B -> 36B        0.13087
     29B -> 36B       -0.13959
     31B -> 35B       -0.26312
     31B -> 36B        0.54369
     32B -> 35B       -0.42536
     32B -> 36B        0.55203

 Excited State   7:  3.089-A      4.2376 eV  292.58 nm  f=0.0113  <S**2>=2.135
     34A -> 38A       -0.12938
     35A -> 37A       -0.14559
     36A -> 37A        0.68197
     36A -> 44A        0.11458
     31B -> 35B        0.10337
     31B -> 36B       -0.23696
     32B -> 35B       -0.36331
     32B -> 36B       -0.34186
     33B -> 36B       -0.11300
     33B -> 38B       -0.15417
     34B -> 35B        0.27696
```

1.15 Triplet Vinylnitrene 10B



B3LYP 6-31+G(d) E = -403.04538321 a.u.

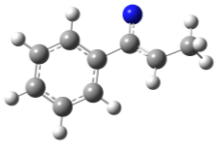
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.753202	-0.388462	0.099823
2	6	0	-1.885548	-1.205888	-0.630974
3	6	0	-0.535815	-0.866928	-0.750036
4	6	0	-0.039890	0.292643	-0.135500
5	6	0	-0.917634	1.115348	0.585914
6	6	0	-2.266284	0.772507	0.706945
7	1	0	-3.803397	-0.653255	0.191812
8	1	0	-2.259862	-2.105225	-1.113496
9	1	0	0.132191	-1.496983	-1.331645
10	1	0	-0.538118	2.020274	1.051795
11	1	0	-2.936526	1.414579	1.272669
12	6	0	1.403624	0.691501	-0.287237
13	6	0	2.483730	-0.132240	0.100930
14	1	0	3.476996	0.264353	-0.102120
15	6	0	2.396578	-1.460943	0.779298

```
    16          1           0        1.380195   -1.704393    1.098999
    17          1           0        2.747555   -2.268697    0.118160
    18          1           0        3.052690   -1.481245    1.660762
    19          7           0        1.633560    1.872196   -0.808846
 ---------------------------------------------------------------------
```

1.15.1 TD-DFT of 10B in Gas Phase

```
Excited State   1:  3.175-A      3.1162 eV  397.87 nm  f=0.0088  <S**2>=2.271
     36A -> 37A       -0.48573
     36A -> 38A       -0.34893
     33B -> 35B        0.75935
     34B -> 37B       -0.14647

 Excited State   2:  3.123-A      3.2275 eV  384.15 nm  f=0.0027  <S**2>=2.189
     36A -> 37A       -0.21982
     36A -> 38A        0.32163
     34B -> 35B        0.90643

 Excited State   3:  3.022-A      3.7233 eV  332.99 nm  f=0.0001  <S**2>=2.033
     32B -> 36B       -0.48696
     33B -> 36B        0.85882

 Excited State   4:  3.187-A      3.9440 eV  314.36 nm  f=0.0155  <S**2>=2.289
     34A -> 37A       -0.14309
     36A -> 37A       -0.56014
     36A -> 38A        0.68325
     33B -> 37B       -0.15510
     34B -> 35B       -0.37590
     34B -> 37B        0.10128

 Excited State   5:  3.709-A      4.2354 eV  292.73 nm  f=0.0546  <S**2>=3.190
     33A -> 37A        0.19186
     33A -> 38A        0.13531
     34A -> 37A       -0.28789
     34A -> 38A        0.40191
     36A -> 37A        0.17909
     36A -> 42A       -0.20939
     36A -> 46A       -0.12483
     32B -> 35B       -0.45227
     33B -> 35B        0.28419
     33B -> 38B       -0.23189
     34B -> 37B        0.47225

 Excited State   6:  3.040-A      4.3290 eV  286.40 nm  f=0.0058  <S**2>=2.061
     29B -> 36B        0.18175
     30B -> 36B       -0.14350
     31B -> 36B        0.94693

 Excited State   7:  3.265-A      4.3840 eV  282.81 nm  f=0.1346  <S**2>=2.415
     33A -> 37A       -0.10288
     34A -> 37A       -0.21989
     34A -> 38A        0.26914
     36A -> 37A        0.23345
     36A -> 38A        0.20615
     36A -> 42A        0.28368
     36A -> 46A        0.17333
     31B -> 36B        0.10240
     32B -> 35B        0.63670
     33B -> 35B        0.38459
     34B -> 37B        0.24582
```

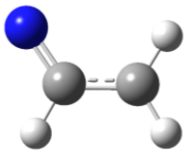
1.16 Singlet Vinylnitrene 10A



B3LYP 6-31+G(d) E = -403.02277554a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.994961	-0.268890	0.094893
2	6	0	-2.151755	-1.340596	-0.211668
3	6	0	-0.770792	-1.146606	-0.293167
4	6	0	-0.214712	0.120622	-0.059748
5	6	0	-1.069503	1.195072	0.233458
6	6	0	-2.449053	0.999411	0.315011
7	1	0	-4.069737	-0.419659	0.155020
8	1	0	-2.568590	-2.327130	-0.398614
9	1	0	-0.126226	-1.980765	-0.558891
10	1	0	-0.644807	2.180630	0.400907
11	1	0	-3.098383	1.838920	0.550312
12	6	0	1.269462	0.353156	-0.146694
13	6	0	2.171557	-0.589751	0.328949
14	1	0	1.767266	-1.488747	0.793155
15	6	0	3.655371	-0.468401	0.260424
16	1	0	3.967550	0.479196	-0.184241
17	1	0	4.094730	-0.557058	1.264551
18	1	0	4.080377	-1.293101	-0.331518
19	7	0	1.703447	1.491945	-0.688490

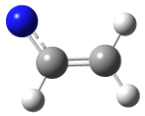
1.17 Triplet Vinylnitrene



B3LYP 6-31+G(d) E = -132.66232900 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.985224	-0.574513	0.000000
2	6	0	0.000000	0.424015	0.000000
3	7	0	1.281522	0.194536	0.000000
4	1	0	-0.706681	-1.623536	0.000000
5	1	0	-2.038270	-0.313823	0.000000
6	1	0	-0.314362	1.478593	0.000000

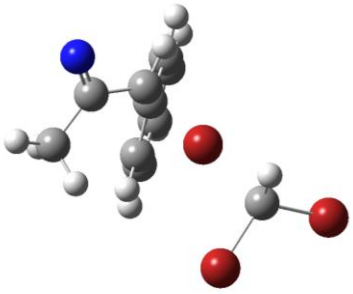
1.18 Singlet Vinylnitrene



B3LYP 6-31+G(d) E = -132.63612537 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.997324	-0.519582	0.000000
2	6	0	0.000000	0.424994	0.000000
3	7	0	1.294197	0.125913	0.000000
4	1	0	-0.757319	-1.578501	0.000000
5	1	0	-2.042683	-0.225555	0.000000
6	1	0	-0.275432	1.490194	0.000000

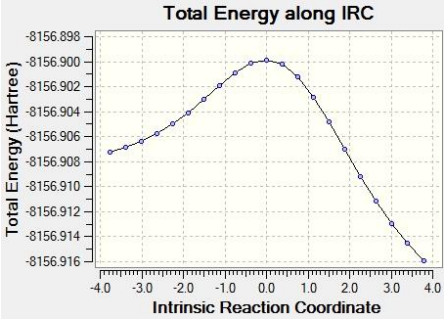
1.19 TS for Bromoform reacting with Triplet Vinylnitrene 5 & IRC



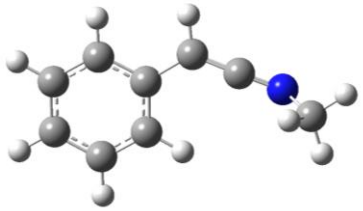
B3LYP 6-31+G(d) E = -8156.89984241 a.u. Negative Frequency -346 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.505970	-1.364099	1.906228
2	6	0	-2.730640	-0.426694	1.228197
3	6	0	-2.878078	-0.243623	-0.160407
4	6	0	-3.813059	-1.042666	-0.845171
5	6	0	-4.590593	-1.980936	-0.165310
6	6	0	-4.438816	-2.145191	1.213738
7	1	0	-3.372208	-1.497441	2.976532
8	1	0	-1.981794	0.138841	1.771675
9	1	0	-3.936231	-0.917124	-1.918293
10	1	0	-5.309745	-2.583976	-0.713192
11	1	0	-5.038428	-2.878756	1.746169
12	6	0	-2.243504	2.238400	-0.571238
13	6	0	-2.236856	2.725697	0.866297

14	1	0	-3.088900	2.314324	1.416777
15	1	0	-1.311496	2.411988	1.361961
16	1	0	-2.294804	3.816515	0.884018
17	7	0	-2.312502	3.082503	-1.515524
18	6	0	-2.154956	0.790052	-0.933060
19	1	0	-2.245727	0.662614	-2.009275
20	35	0	0.034474	0.377516	-0.696332
21	6	0	2.348229	0.039645	-0.518267
22	1	0	2.677222	0.484931	-1.451147
23	35	0	2.965758	1.019085	0.992750
24	35	0	2.701342	-1.827256	-0.455921



1.20 Ketene Imine 11



B3LYP 6-31+G(d) E = −403.09832663 a.u.

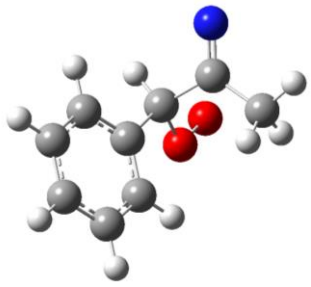
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.982698	-0.495751	-0.277086
2	6	0	0.818660	-1.118980	-0.147148
3	1	0	0.850525	-2.205677	-0.096776
4	7	0	3.041962	0.067935	-0.506545
5	6	0	-0.495946	-0.467144	-0.064229
6	6	0	-1.644917	-1.257917	0.123059
7	6	0	-0.660884	0.927771	-0.172694
8	6	0	-2.911870	-0.677482	0.202437
9	1	0	-1.540191	-2.337630	0.206003
10	6	0	-1.926820	1.505130	-0.093200
11	1	0	0.209521	1.561785	-0.325588
12	6	0	-3.061660	0.707693	0.096003
13	1	0	-3.783570	-1.311101	0.347407
14	1	0	-2.028990	2.584175	-0.180974
15	1	0	-4.047506	1.160773	0.157931

```
16        6           0        3.966194    0.548859    0.523083
17        1           0        4.110580    1.624438    0.382008
18        1           0        3.609511    0.354414    1.542380
19        1           0        4.933660    0.060194    0.372075
 ---------------------------------------------------------------------
```

1.20.1 TD-DFT of Ketene Imine 11 in gas phase

```
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
```

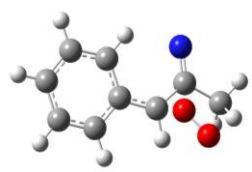
1.21 Triplet Peroxy-Biradical 13



B3LYP 6-31+G(d) E = -553.40058062 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.776159	0.921152	-0.609531
2	6	0	-1.408915	0.928863	-0.889695
3	6	0	-0.562670	-0.032962	-0.320335
4	6	0	-1.104181	-1.009508	0.527690
5	6	0	-2.475258	-1.020882	0.798090
6	6	0	-3.313133	-0.055440	0.234684
7	1	0	-3.421429	1.673001	-1.055930
8	1	0	-0.995340	1.689603	-1.547780
9	1	0	-0.463269	-1.771567	0.960250
10	1	0	-2.886752	-1.787713	1.449130
11	1	0	-4.378662	-0.065809	0.448315
12	6	0	1.700369	0.915787	0.366532
13	6	0	1.885464	0.447528	1.797420
14	1	0	0.911314	0.262668	2.263263
15	1	0	2.459366	-0.485304	1.815060
16	1	0	2.420394	1.207247	2.371405
17	7	0	2.135572	2.018019	-0.048786
18	8	0	1.439737	-1.345792	-0.580359
19	8	0	2.701325	-1.406642	-0.971900
20	6	0	0.917595	0.033641	-0.623048
21	1	0	1.098207	0.402134	-1.634989

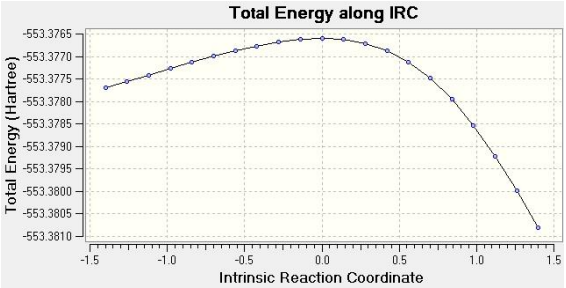
1.22 TS for Vinylnitrene 5 reacting with O_2 to form 13 & IRC



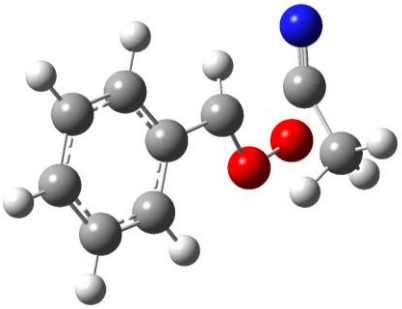
B3LYP 6-31+G(d) E = -553.37659727 a.u. Negative Frequency 253 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.628985	-1.022723	-0.720739
2	6	0	-1.254155	-1.036456	-0.505716
3	6	0	-0.645933	-0.051536	0.310498
4	6	0	-1.473936	0.943300	0.890397
5	6	0	-2.846465	0.949708	0.672065
6	6	0	-3.430562	-0.034763	-0.135524
7	1	0	-3.080377	-1.786532	-1.348250
8	1	0	-0.638893	-1.807036	-0.959090
9	1	0	-1.021430	1.710875	1.513954
10	1	0	-3.463797	1.718986	1.128124
11	1	0	-4.503788	-0.031828	-0.307058

12	6	0	0.769441	0.018973	0.555086
13	1	0	1.093693	0.762763	1.278330
14	6	0	1.773650	-1.024357	0.267510
15	6	0	3.185736	-0.773747	0.788842
16	1	0	3.857173	-1.575277	0.473540
17	1	0	3.558550	0.183690	0.408065
18	1	0	3.175290	-0.726981	1.884414
19	7	0	1.526993	-2.087695	-0.377167
20	8	0	1.385684	1.383960	-1.022652
21	8	0	2.319553	2.160392	-0.748145

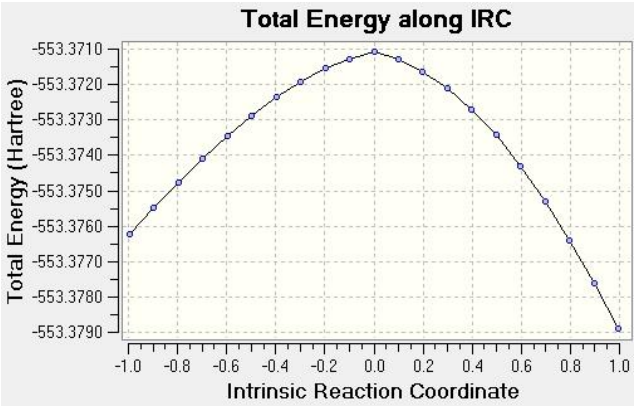


1.23 TS for Triplet Biradical forming 14 and Acetonitrile & IRC

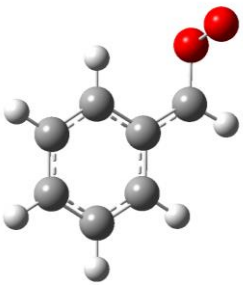


B3LYP 6-31+G(d) E = -553.37106515. Negative frequency = 576 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.712767	0.955820	-0.603742
2	6	0	-1.367670	0.848683	-0.936510
3	6	0	-0.570485	-0.178076	-0.377614
4	6	0	-1.165688	-1.087596	0.527154
5	6	0	-2.517065	-0.973359	0.849071
6	6	0	-3.295533	0.045445	0.289789
7	1	0	-3.313255	1.748809	-1.041331
8	1	0	-0.914087	1.562018	-1.619405
9	1	0	-0.572928	-1.889785	0.954832
10	1	0	-2.965810	-1.685353	1.536785
11	1	0	-4.348359	0.130390	0.544902
12	6	0	1.805808	1.258972	0.403741
13	6	0	2.033835	0.629123	1.731696
14	1	0	1.092548	0.254383	2.145621
15	1	0	2.730569	-0.209372	1.643217
16	1	0	2.454624	1.376386	2.410805
17	7	0	1.921345	2.221876	-0.285909
18	8	0	1.447704	-1.478671	-0.354271
19	8	0	2.669369	-1.586967	-0.875935
20	6	0	0.834656	-0.234858	-0.723198
21	1	0	1.180154	0.099576	-1.694737



1.24 Triplet Peroxy-Biradical 14

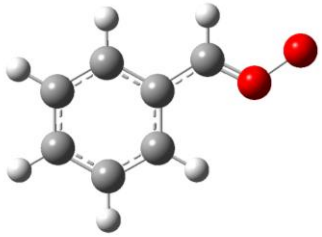


B3LYP 6-31+G(d) E = -420.63521639 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	2.278017	0.910731	0.165342
2	6	0	0.957514	1.319305	0.048202
3	6	0	-0.085817	0.363847	-0.127723
4	6	0	0.263900	-1.016523	-0.177892
5	6	0	1.590559	-1.406948	-0.058585
6	6	0	2.605975	-0.453210	0.113205
7	1	0	3.060896	1.652510	0.300136
8	1	0	0.706562	2.376480	0.090189
9	1	0	-0.516613	-1.758762	-0.309746
10	1	0	1.842727	-2.463487	-0.097888
11	1	0	3.641284	-0.769175	0.206025
12	6	0	-1.413922	0.814273	-0.256161
13	1	0	-1.726210	1.851570	-0.201261
14	8	0	-2.452888	-0.088992	-0.469086
15	8	0	-3.070362	-0.420756	0.690864

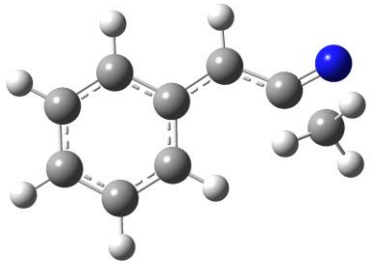
1.25 Ylide 15



B3LYP 6-31+G(d) E = -420.67329490 a.u.

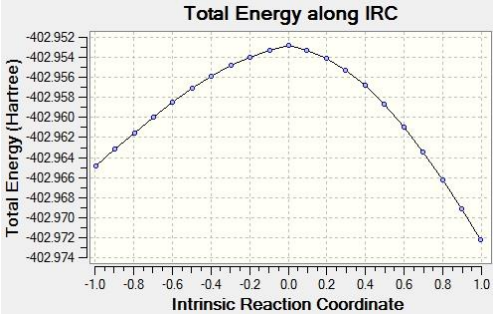
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.729705	-0.267677	0.000150
2	6	0	1.824948	-1.339152	-0.000002
3	6	0	0.455253	-1.102497	-0.000157
4	6	0	-0.028805	0.224620	-0.000175
5	6	0	0.887494	1.296696	-0.000116
6	6	0	2.258519	1.048785	0.000106
7	1	0	3.798965	-0.461238	0.000305
8	1	0	2.194379	-2.360875	0.000029
9	1	0	-0.248222	-1.929116	-0.000232
10	1	0	0.517802	2.319277	-0.000184
11	1	0	2.958301	1.879732	0.000214
12	6	0	-1.436811	0.534033	-0.000099
13	1	0	-1.815388	1.556098	-0.000044
14	8	0	-2.308382	-0.391806	0.000040
15	8	0	-3.635075	-0.029784	0.000167

1.26 TS for Vinylnitrene 5 forming T_1 of Ketene imine 11 & IRC

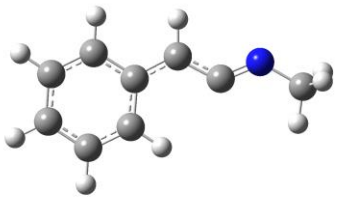


B3LYP 6-31+G(d) E = -402.95276562. Negative Frequency 917 cm^{-1}.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.913435	1.434059	-0.207270
2	6	0	0.619568	0.936513	-0.297216
3	6	0	0.356059	-0.448790	-0.106007
4	6	0	1.460358	-1.299312	0.176560
5	6	0	2.750893	-0.792719	0.265096
6	6	0	2.987162	0.576898	0.076613
7	1	0	2.094250	2.494676	-0.363058
8	1	0	-0.206679	1.599062	-0.538353
9	1	0	1.280759	-2.361627	0.324634
10	1	0	3.579842	-1.461884	0.481114
11	1	0	3.997256	0.971486	0.146522
12	6	0	-0.959875	-0.992263	-0.187874
13	1	0	-1.087735	-2.072972	-0.079203
14	6	0	-2.154956	-0.218116	-0.399120
15	6	0	-3.072992	0.973053	0.594240
16	1	0	-2.178079	1.237156	1.177927
17	1	0	-3.375152	1.780742	-0.065099
18	1	0	-3.851849	0.719948	1.325206
19	7	0	-3.378647	-0.560360	-0.271403



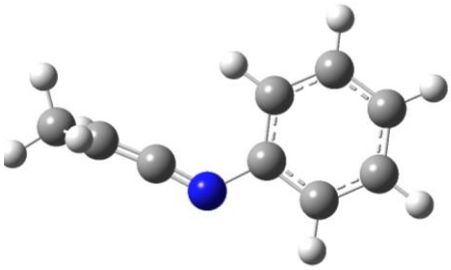
1.27 T_1 of Ketene Imine 11



B3LYP 6-31+G(d) E = -403.04027495 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.963380	-0.041421	0.000008
2	6	0	-0.804020	-0.857974	0.000007
3	1	0	-0.949583	-1.941683	0.000000
4	7	0	-3.173225	-0.379415	0.000002
5	6	0	0.537140	-0.363182	0.000001
6	6	0	1.626036	-1.275568	0.000000
7	6	0	0.835804	1.026649	0.000002
8	6	0	2.940260	-0.823154	-0.000006
9	1	0	1.418127	-2.343172	-0.000002
10	6	0	2.151798	1.470501	0.000001
11	1	0	0.013511	1.736265	0.000005
12	6	0	3.212785	0.552022	-0.000001
13	1	0	3.758136	-1.539220	-0.000011
14	1	0	2.359882	2.537589	0.000002
15	1	0	4.240662	0.904985	-0.000002
16	6	0	-4.322495	0.504247	-0.000008
17	1	0	-4.936591	0.292075	0.883366
18	1	0	-4.038509	1.564336	-0.000053
19	1	0	-4.936631	0.292009	-0.883338

1.28 Ketene Imine 12

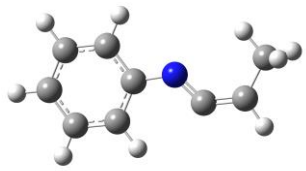


B3LYP 6-31+G(d) E = -403.09775555 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.064459	0.640180	0.132144

2	6	0	2.867372	-0.739639	0.233335
3	6	0	1.582496	-1.275413	0.121935
4	6	0	0.485584	-0.431440	-0.088705
5	6	0	0.682418	0.954606	-0.191718
6	6	0	1.967651	1.483845	-0.081590
7	1	0	4.064394	1.057375	0.217516
8	1	0	3.714021	-1.401121	0.397856
9	1	0	1.409599	-2.345065	0.195675
10	1	0	-0.170924	1.607010	-0.358953
11	1	0	2.115085	2.557989	-0.162769
12	6	0	-1.861049	-0.457033	-0.337319
13	6	0	-3.063057	0.057361	-0.488441
14	1	0	-3.415492	0.211693	-1.507951
15	6	0	-3.978619	0.441845	0.654195
16	1	0	-3.515707	0.234370	1.623872
17	1	0	-4.229636	1.509906	0.619212
18	1	0	-4.921081	-0.118761	0.602712
19	7	0	-0.790541	-1.051324	-0.192884

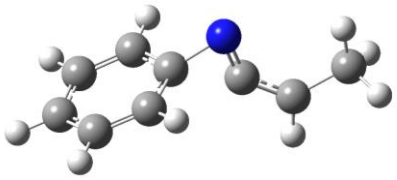
1.29 T_1 of Ketene Imine 12



B3LYP 6-31+G(d) E = -403.03752336 a.u.

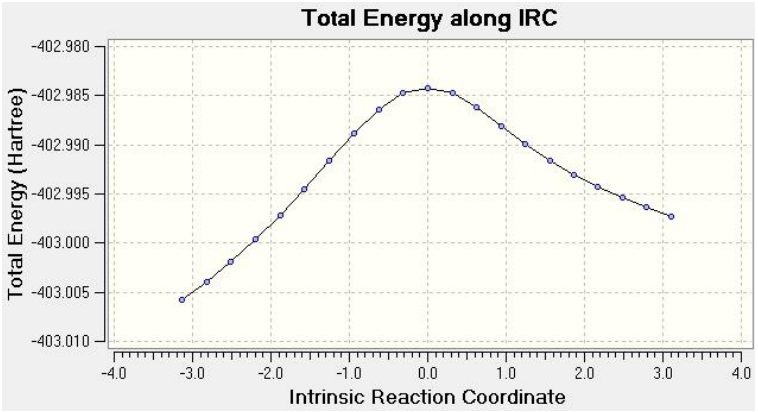
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.064459	0.640180	0.132144
2	6	0	2.867372	-0.739639	0.233335
3	6	0	1.582496	-1.275413	0.121935
4	6	0	0.485584	-0.431440	-0.088705
5	6	0	0.682418	0.954606	-0.191718
6	6	0	1.967651	1.483845	-0.081590
7	1	0	4.064394	1.057375	0.217516
8	1	0	3.714021	-1.401121	0.397856
9	1	0	1.409599	-2.345065	0.195675
10	1	0	-0.170924	1.607010	-0.358953
11	1	0	2.115085	2.557989	-0.162769
12	6	0	-1.861049	-0.457033	-0.337319
13	6	0	-3.063057	0.057361	-0.488441
14	1	0	-3.415492	0.211693	-1.507951
15	6	0	-3.978619	0.441845	0.654195
16	1	0	-3.515707	0.234370	1.623872
17	1	0	-4.229636	1.509906	0.619212
18	1	0	-4.921081	-0.118761	0.602712
19	7	0	-0.790541	-1.051324	-0.192884

1.30 TS for Triplet Vinylnitrene 10 forming T_1 of 12 & IRC

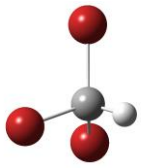


B3LYP 6-31+G(d) E = -402.98417826 a.u. Negative frequency -556 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.975586	0.000001	-0.443394
2	6	0	2.308634	1.213352	-0.196817
3	6	0	0.999391	1.229455	0.256838
4	6	0	0.281276	-0.000001	0.431637
5	6	0	0.999392	-1.229456	0.256837
6	6	0	2.308634	-1.213351	-0.196818
7	1	0	4.002741	0.000001	-0.796128
8	1	0	2.829583	2.156006	-0.348304
9	1	0	0.489301	2.164888	0.468125
10	1	0	0.489302	-2.164889	0.468123
11	1	0	2.829585	-2.156005	-0.348306
12	6	0	-1.391660	-0.000001	-0.071798
13	6	0	-2.573003	0.000000	-0.808163
14	1	0	-2.509989	0.000001	-1.893880
15	6	0	-3.929122	0.000001	-0.166581
16	1	0	-3.858866	0.000006	0.924635
17	1	0	-4.506362	0.881284	-0.482202
18	1	0	-4.506358	-0.881289	-0.482193
19	7	0	-1.019101	-0.000001	1.159954



1.31 Bromoform



B3LYP 6-31+G(d) E = -7753.85790665 a.u.

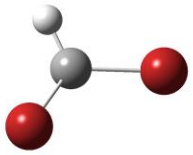
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000116	-0.000319	0.557658
2	1	0	-0.000042	-0.000309	1.641380
3	35	0	1.437532	-1.162639	-0.047505
4	35	0	0.288472	1.825871	-0.047480
5	35	0	-1.725983	-0.663169	-0.047509

1.32 Bromine

B3LYP 6-31+G(d) E = -2571.67167635 a.u.

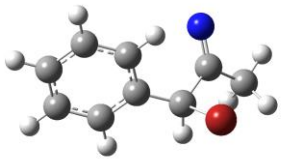
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	0.000000	0.000000	0.000000

1.33 Dibromomethyl radical



B3LYP 6-31+G(d) E = -5182.08186912 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.006662	0.838141	0.000000
2	1	0	-0.506335	1.792096	0.000000
3	35	0	0.006662	-0.097442	1.620740
4	35	0	0.006662	-0.097442	-1.620740

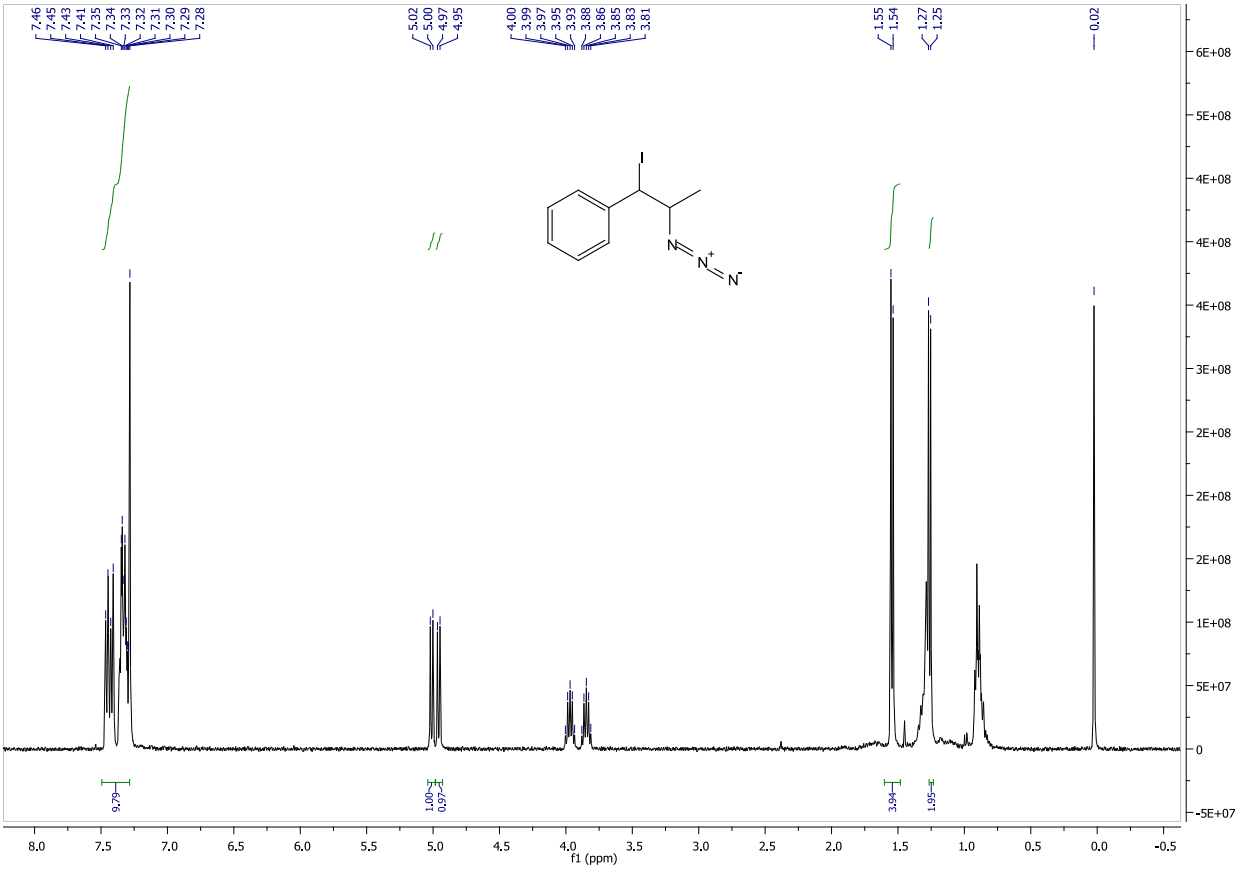


B3LYP 6-31+G(d) E = -2974.81871389 a.u.

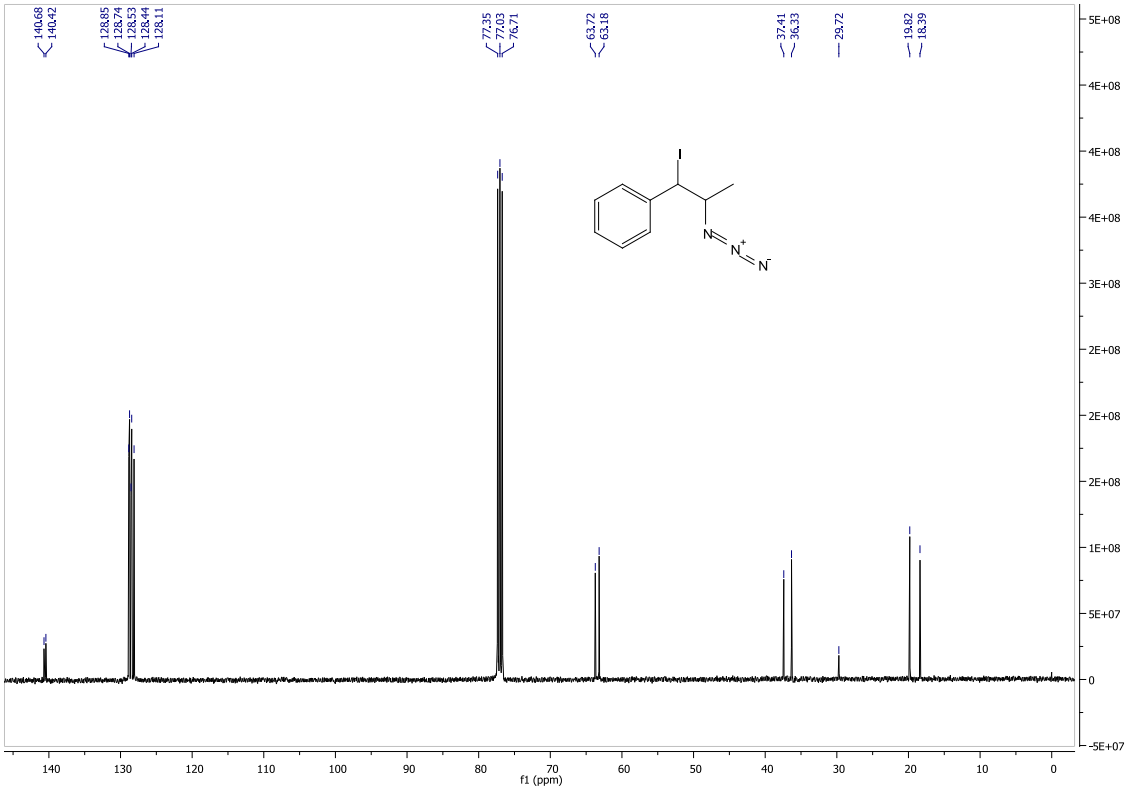
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.780280	-0.127117	-1.252317
2	6	0	1.407967	-0.029185	-1.034760
3	6	0	0.907329	0.127031	0.266457
4	6	0	1.803304	0.182806	1.341673
5	6	0	3.180664	0.078669	1.124163
6	6	0	3.671146	-0.076319	-0.173439
7	1	0	3.156948	-0.245090	-2.264837
8	1	0	0.720561	-0.076013	-1.873254
9	1	0	1.425740	0.308387	2.354370
10	1	0	3.864962	0.120718	1.967463
11	1	0	4.741342	-0.155803	-0.346082
12	6	0	-0.555164	0.325239	0.525524
13	6	0	-1.233160	1.501456	-0.182862
14	6	0	-2.451617	2.100607	0.502825
15	1	0	-2.899023	2.876535	-0.122082
16	1	0	-3.195066	1.319587	0.697371
17	1	0	-2.155155	2.542433	1.462200
18	7	0	-0.804073	1.972284	-1.265613
19	1	0	-0.757477	0.395337	1.594716
20	35	0	-1.609680	-1.296892	-0.037548

2. NMR Spectra

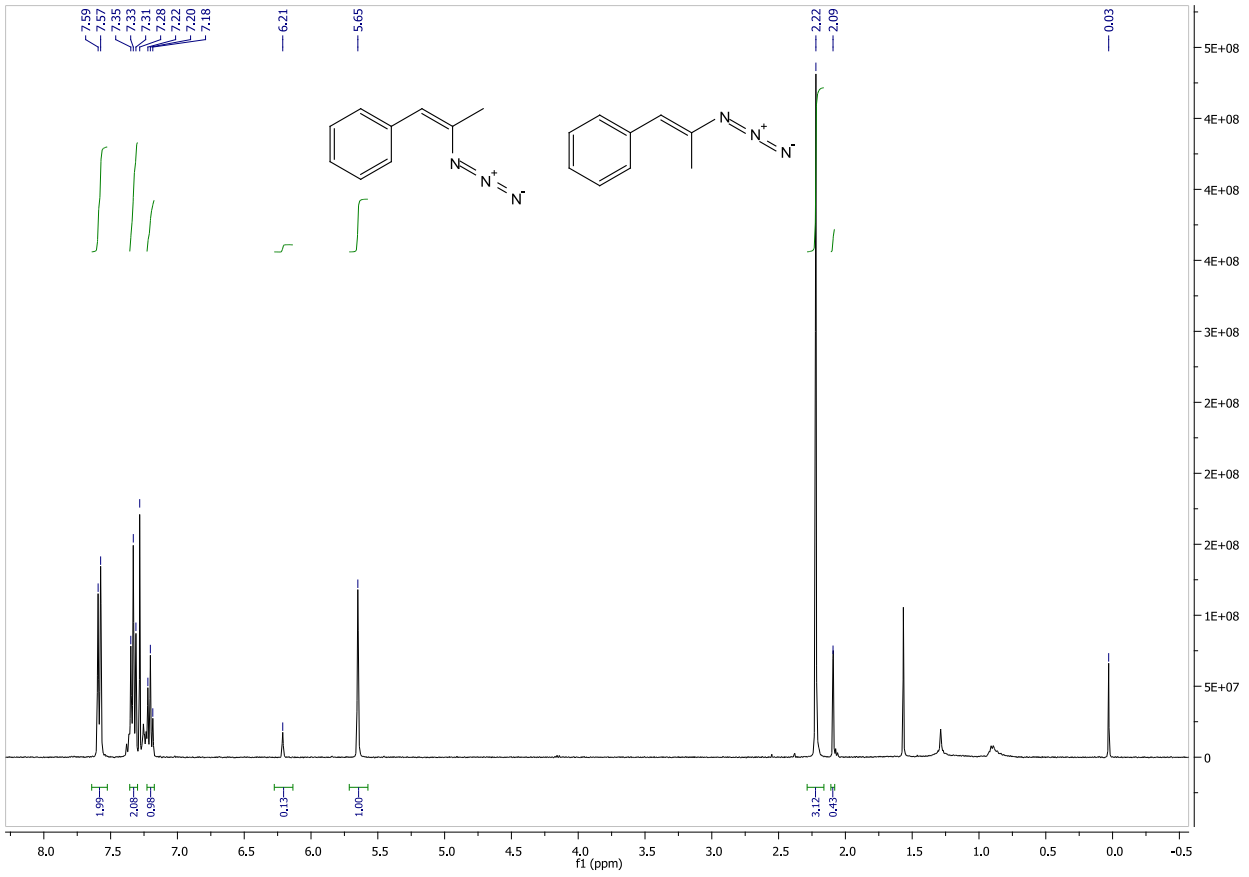
2.1 ^{1}H-NMR Spectrum of (2-azido-1-iodopropyl)benzene



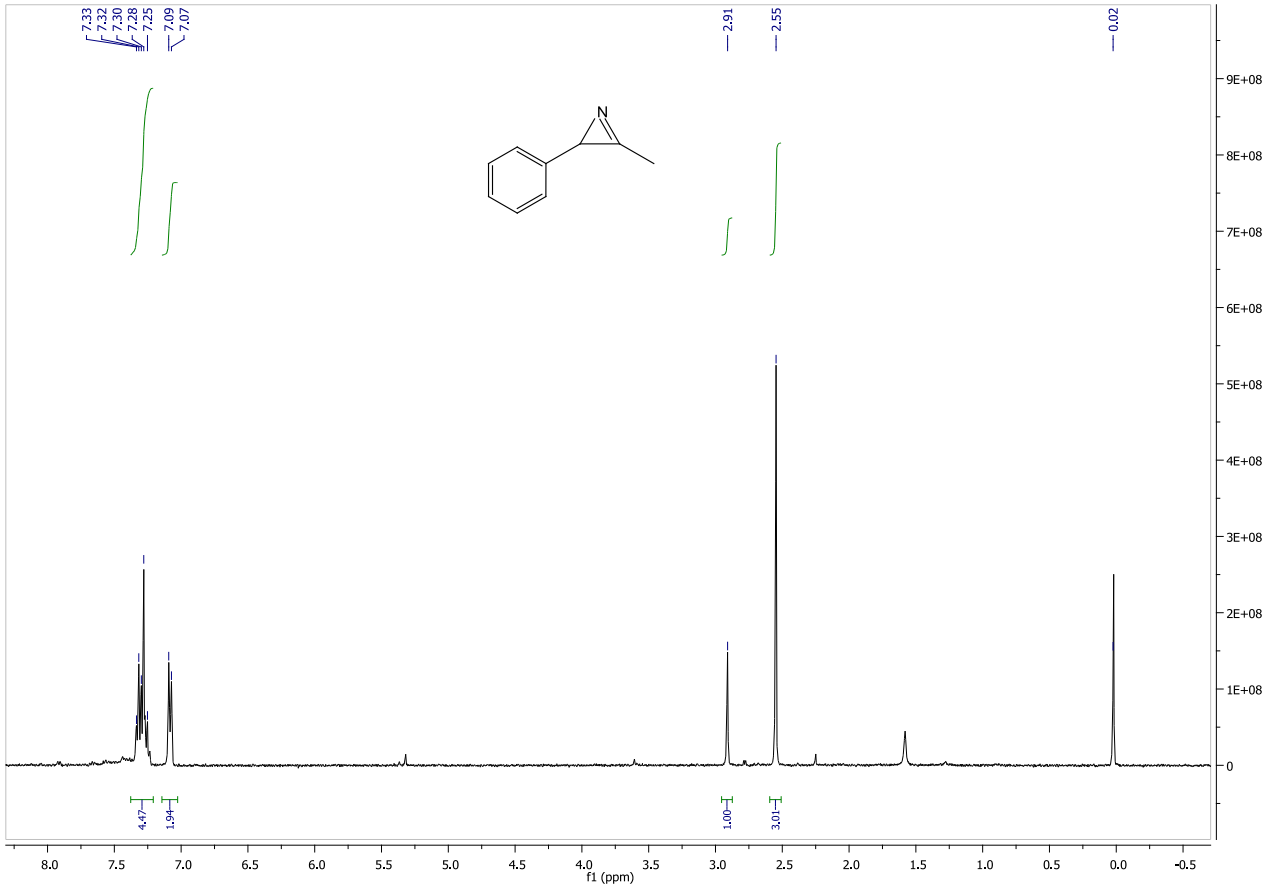
2.2 ^{13}C-NMR Spectrum of (2-azido-1-iodopropyl)benzene



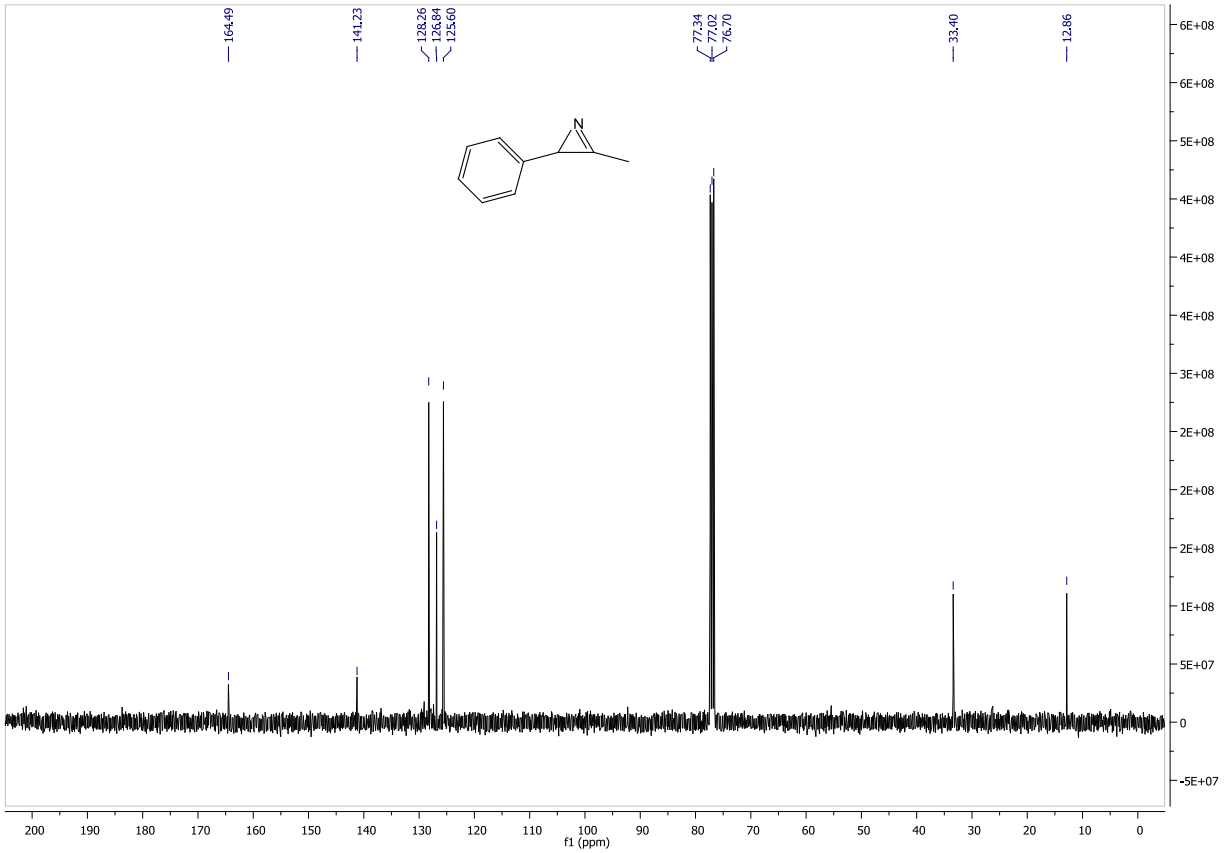
2.3 ^{1}H-NMR Spectrum of (2-azidoprop-1-en-1-yl)benzene



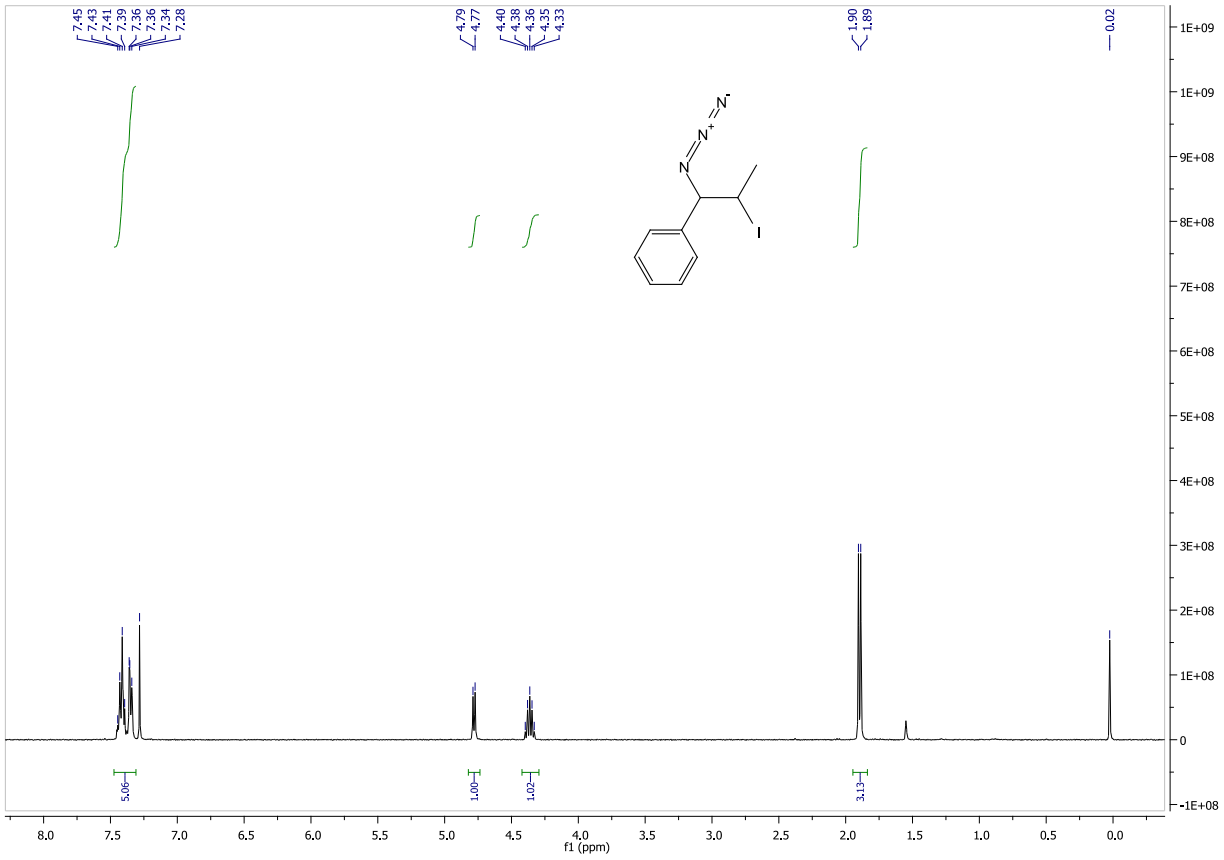
2.4 ^{1}H-NMR Spectrum of 3-methyl-2-phenyl-2H-azirine (1a)



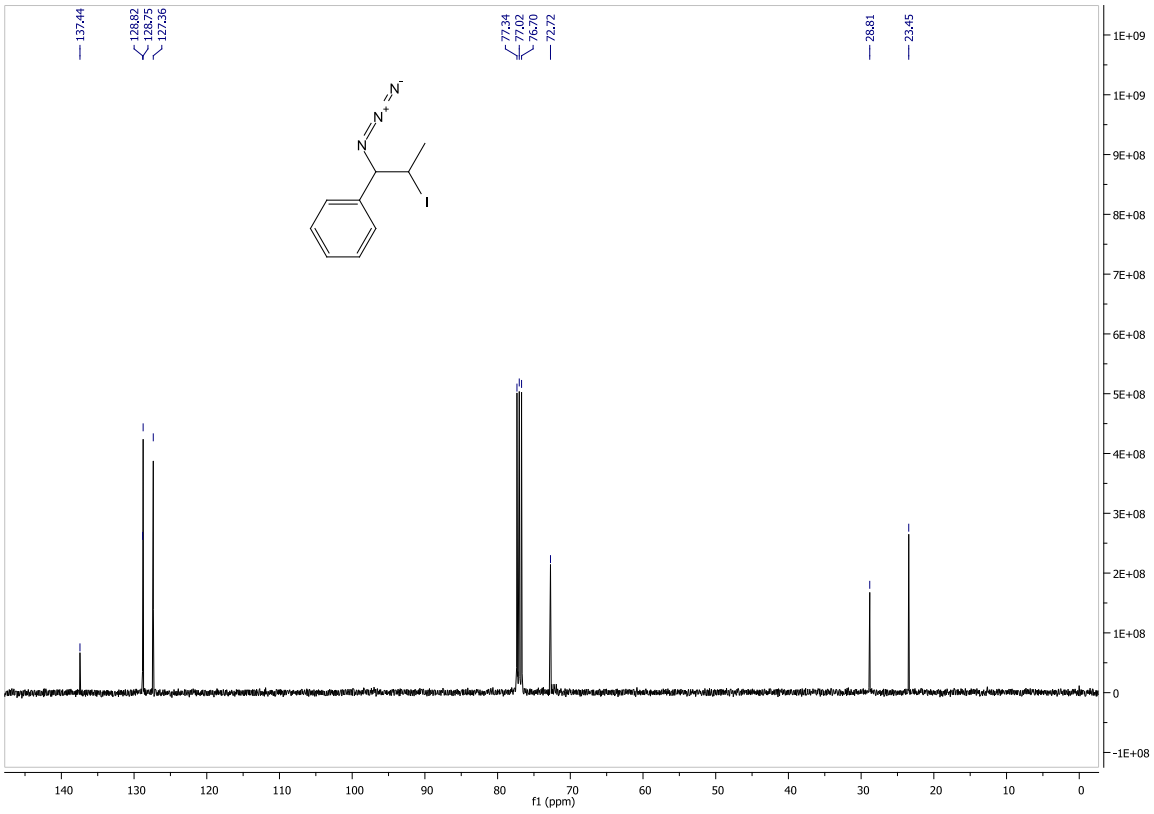
2.5 ^{13}C-NMR Spectrum of 3-methyl-2-phenyl-2H-azirine (1a)



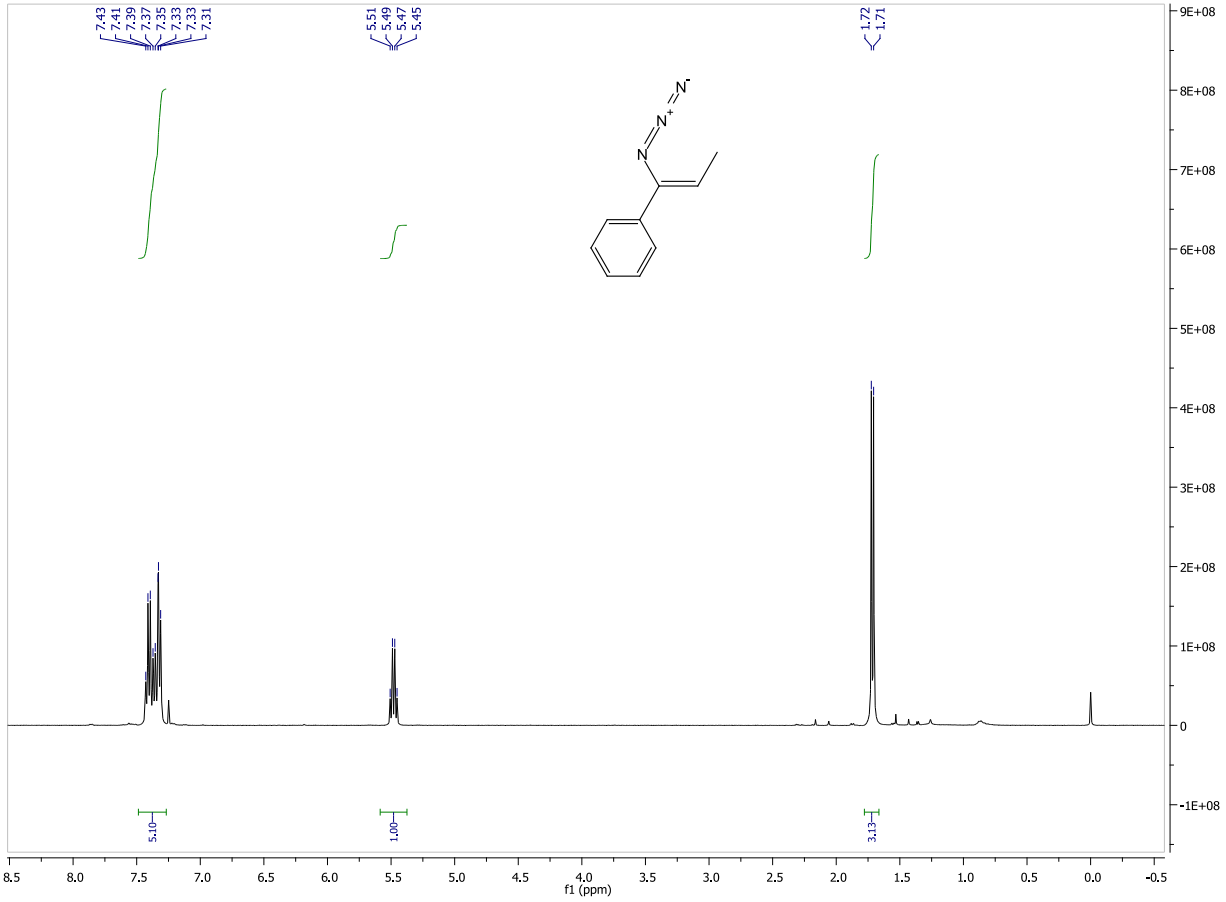
2.6 ^{1}H-NMR Spectrum of (1-azido-2-iodopropyl)benzene



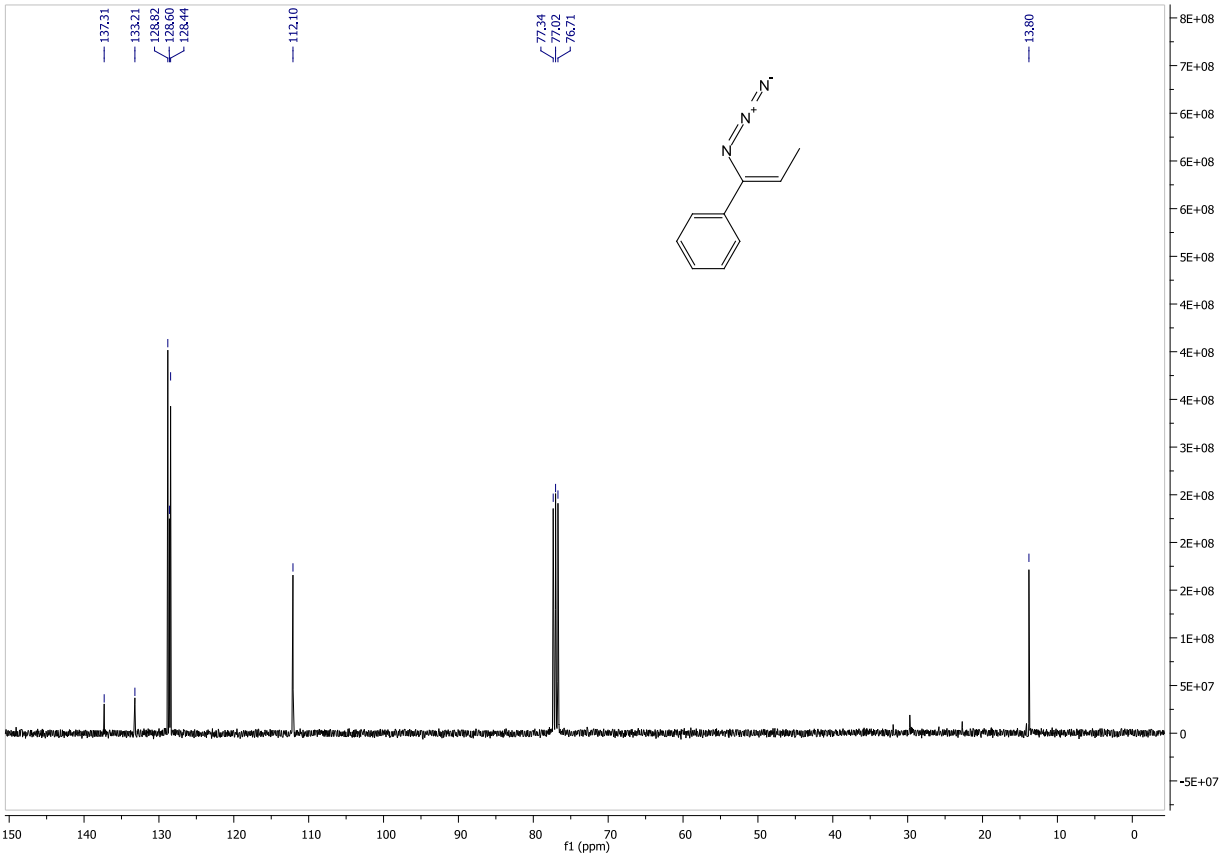
2.7 ^{13}C-NMR Spectrum of (1-azido-2-iodopropyl)benzene



2.8 ^{1}H-NMR Spectrum of (1-azidoprop-1-en-1-yl)benzene

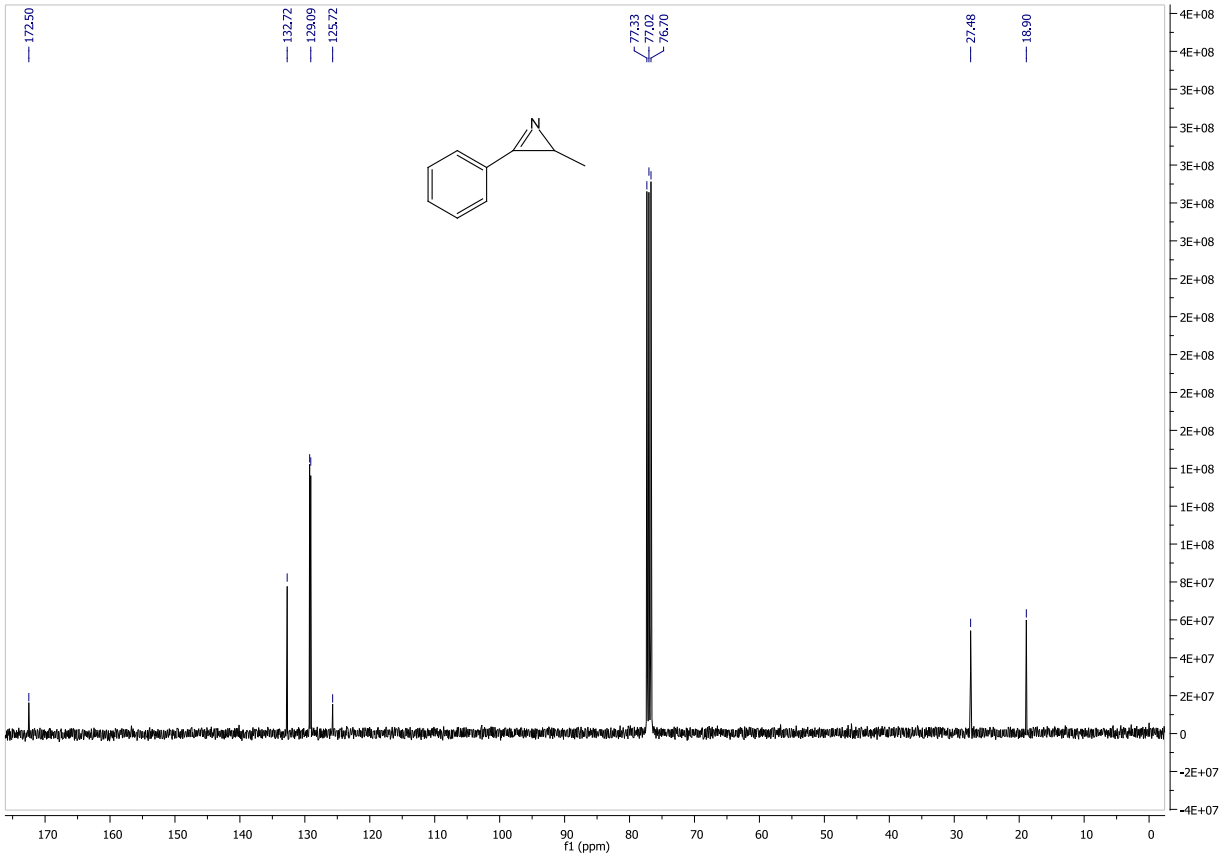


2.9 ^{13}C-NMR Spectrum of (1-azidoprop-1-en-1-yl)benzene

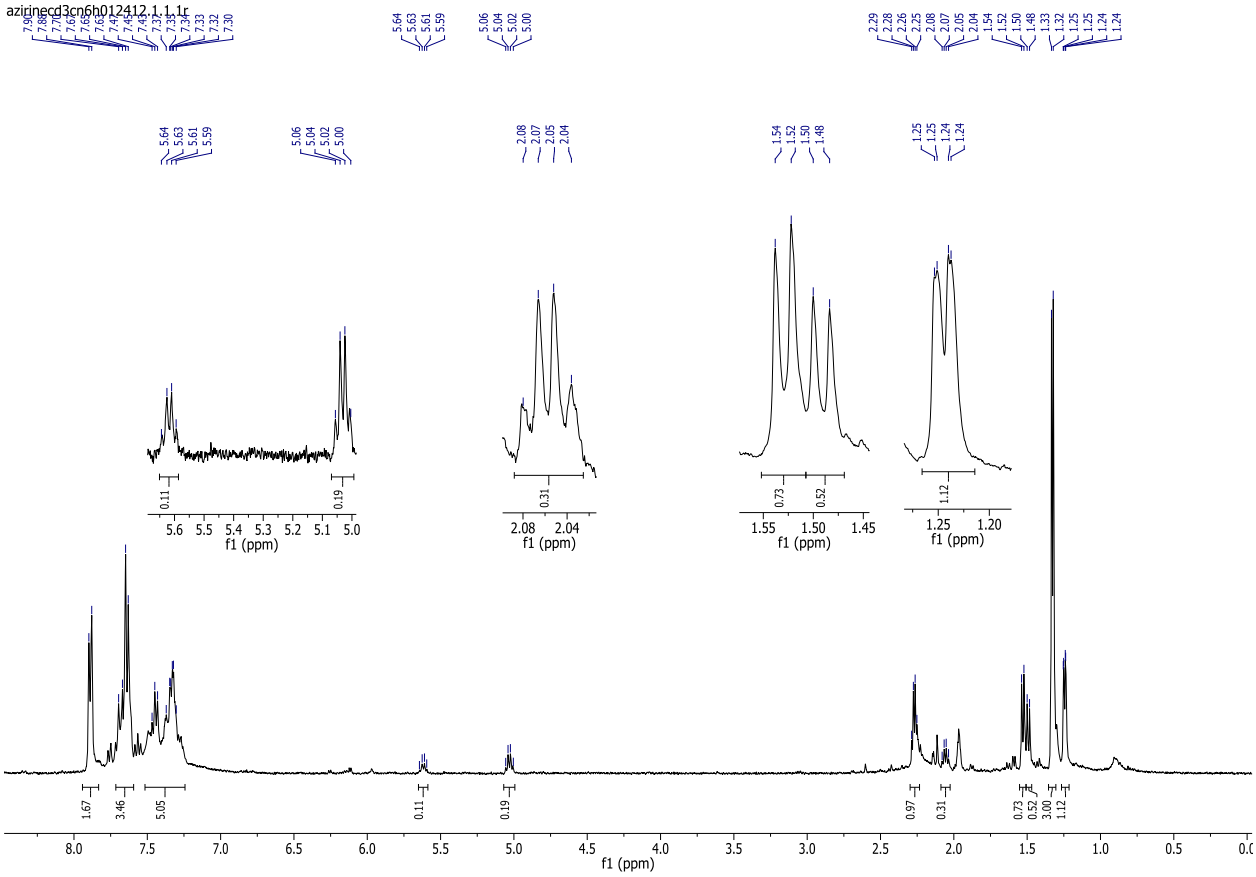


2.10 ^{1}H-NMR Spectrum of 2-methyl-3-phenyl-2H-azirine (1b)

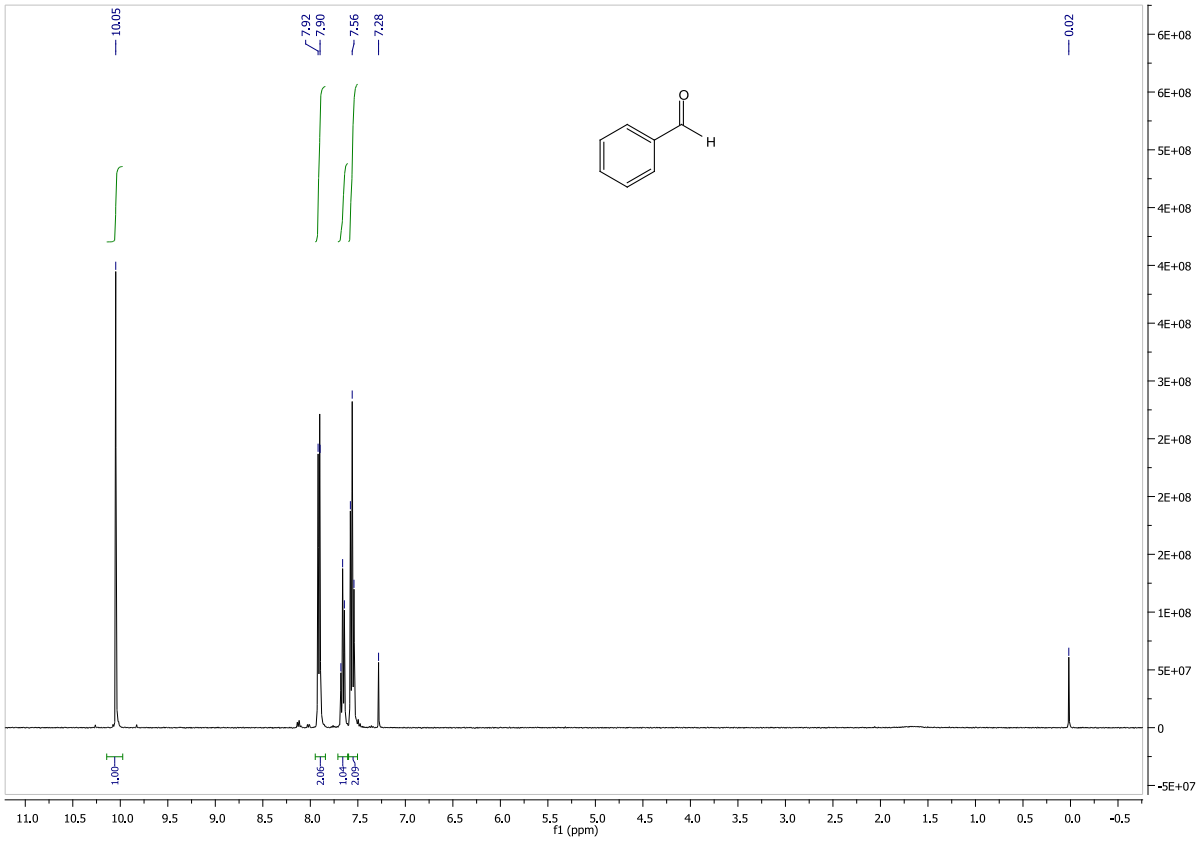
2.11 ^{13}C-NMR Spectrum of 2-methyl-3-phenyl-2H-azirine (1b)



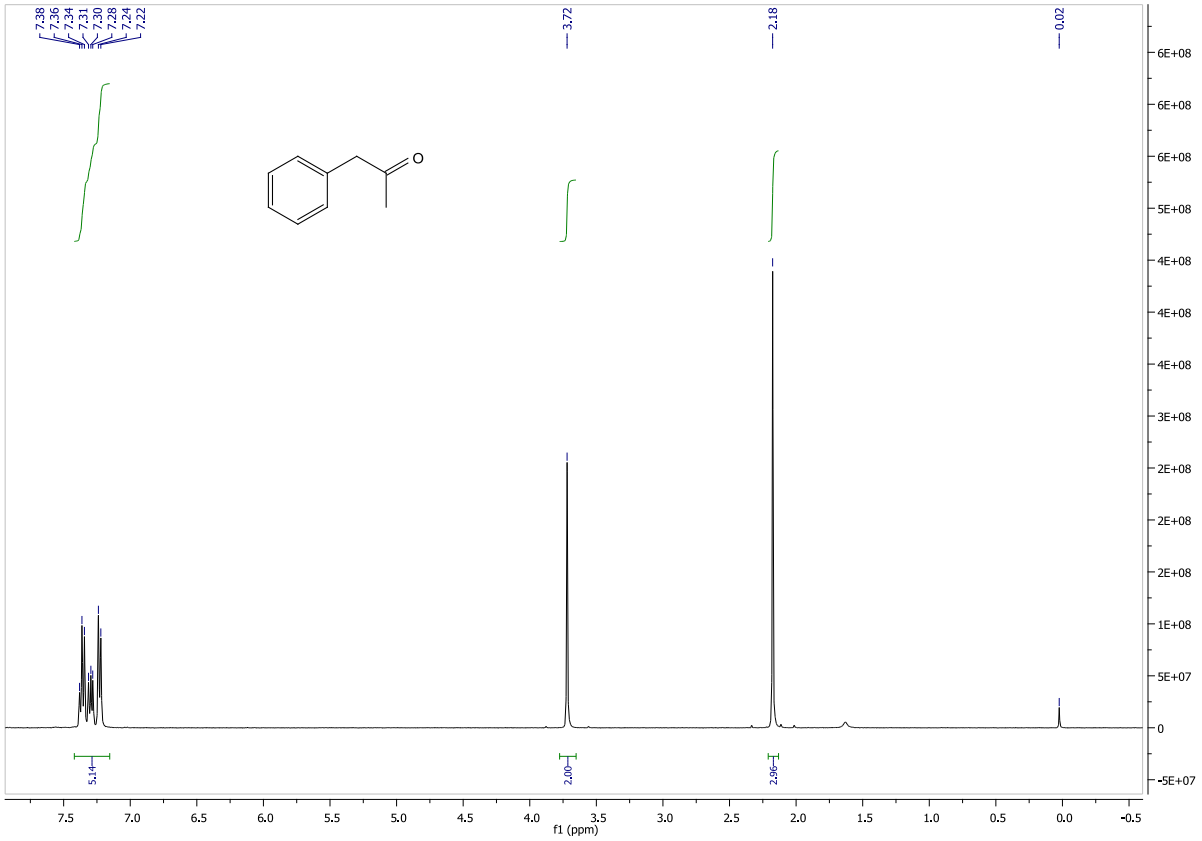
2.12 ^{1}H-NMR spectra of 6 and 7



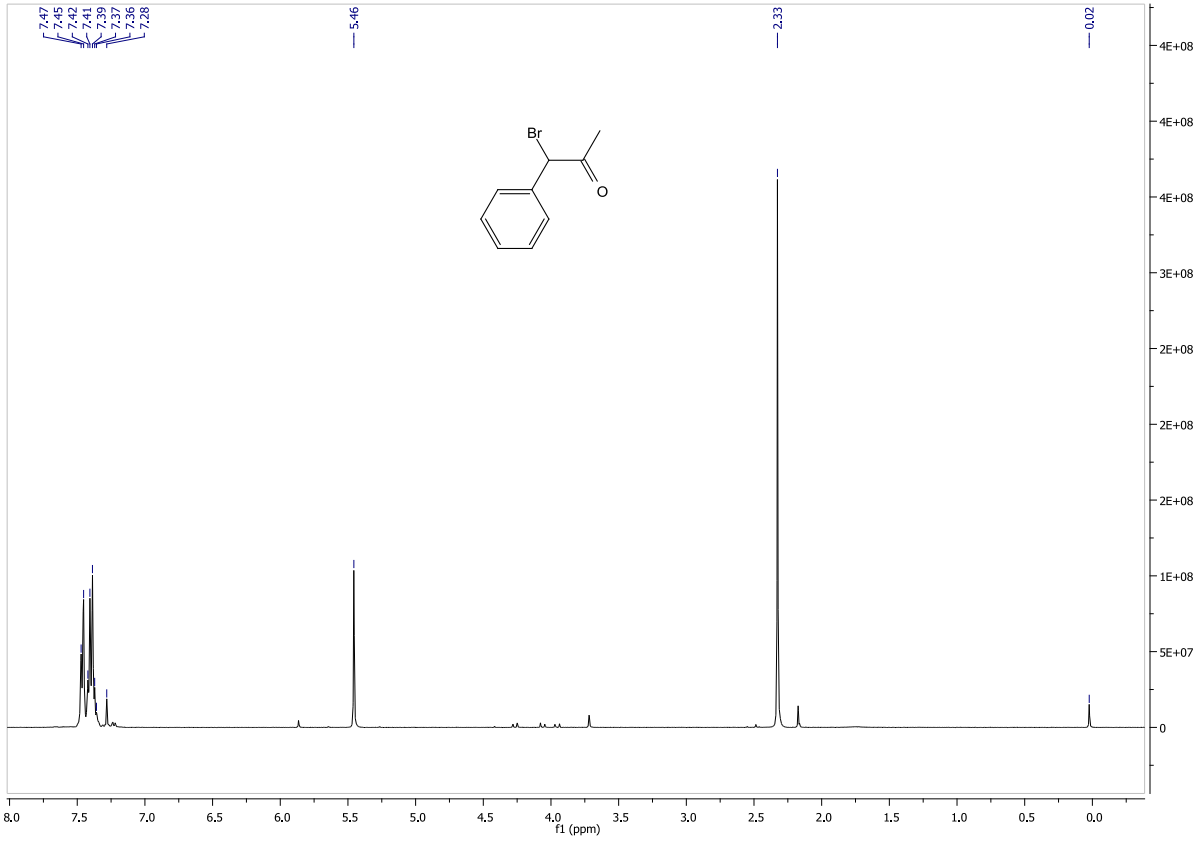
2.13 ^{1}H-NMR Spectrum of benzaldehyde (2)



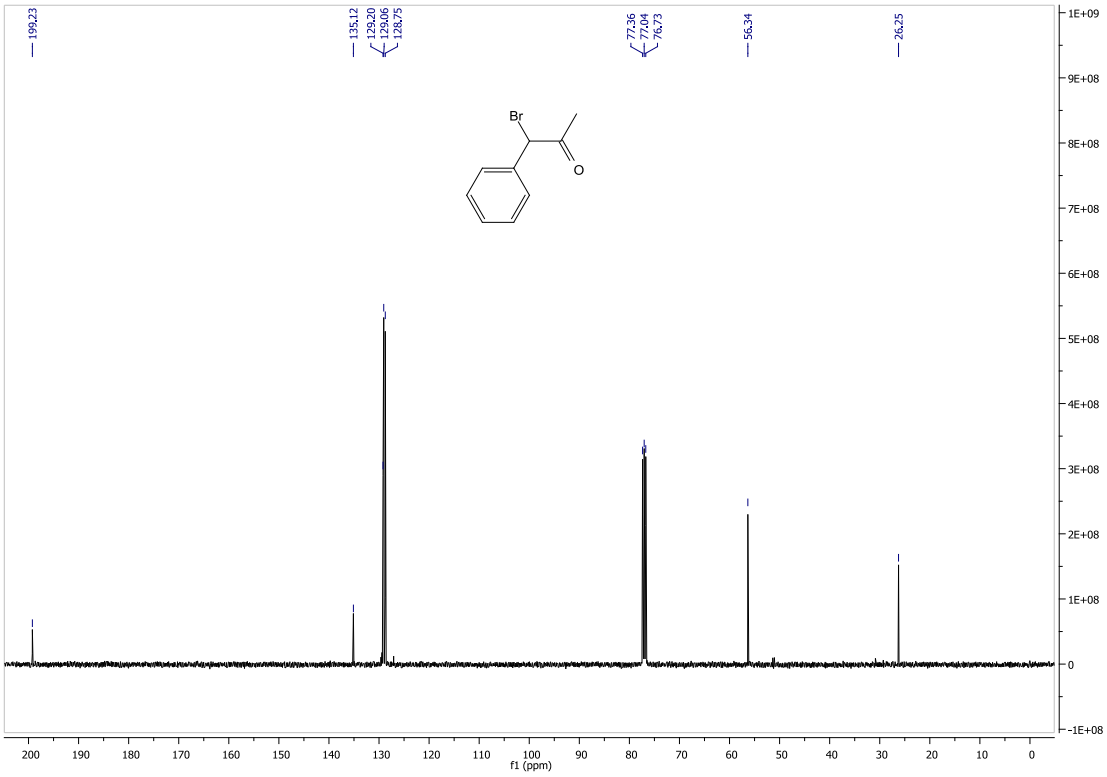
2.14 ^{1}H-NMR Spectrum of 1-phenylpropan-2-one (3)



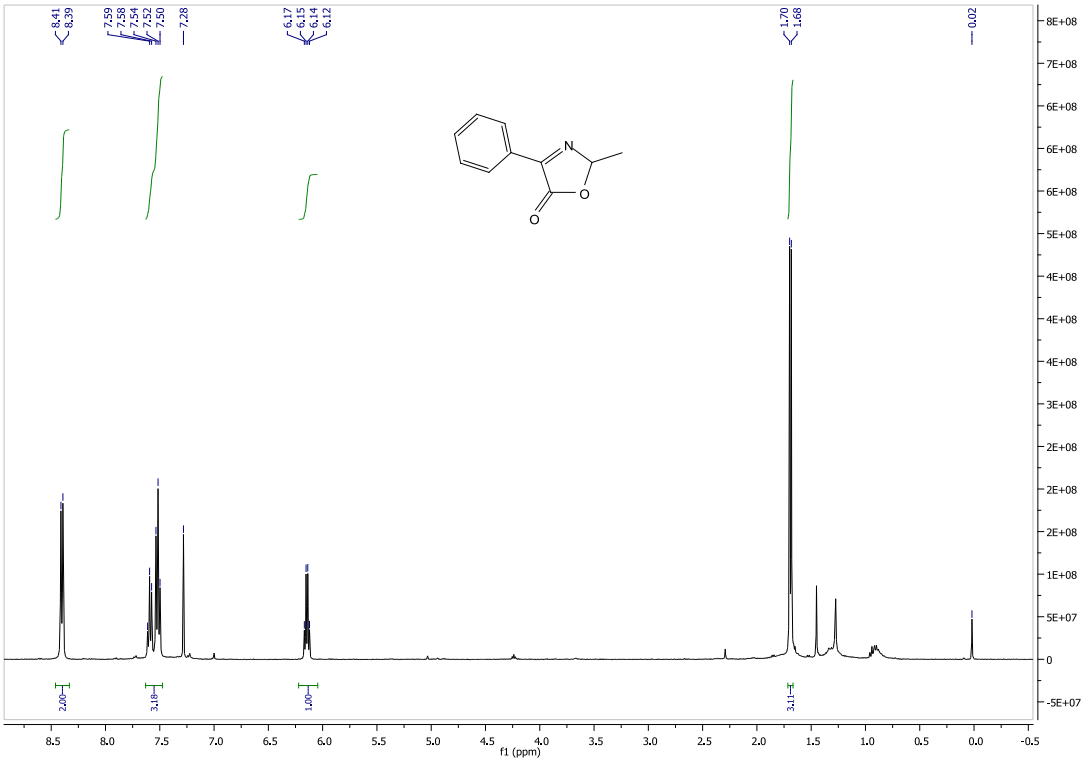
2.15 ^{1}H-NMR Spectrum of 1-bromo-1-phenylpropan-2-one (4)



2.16 ^{13}C-NMR Spectrum of 1-bromo-1-phenylpropan-2-one (4)

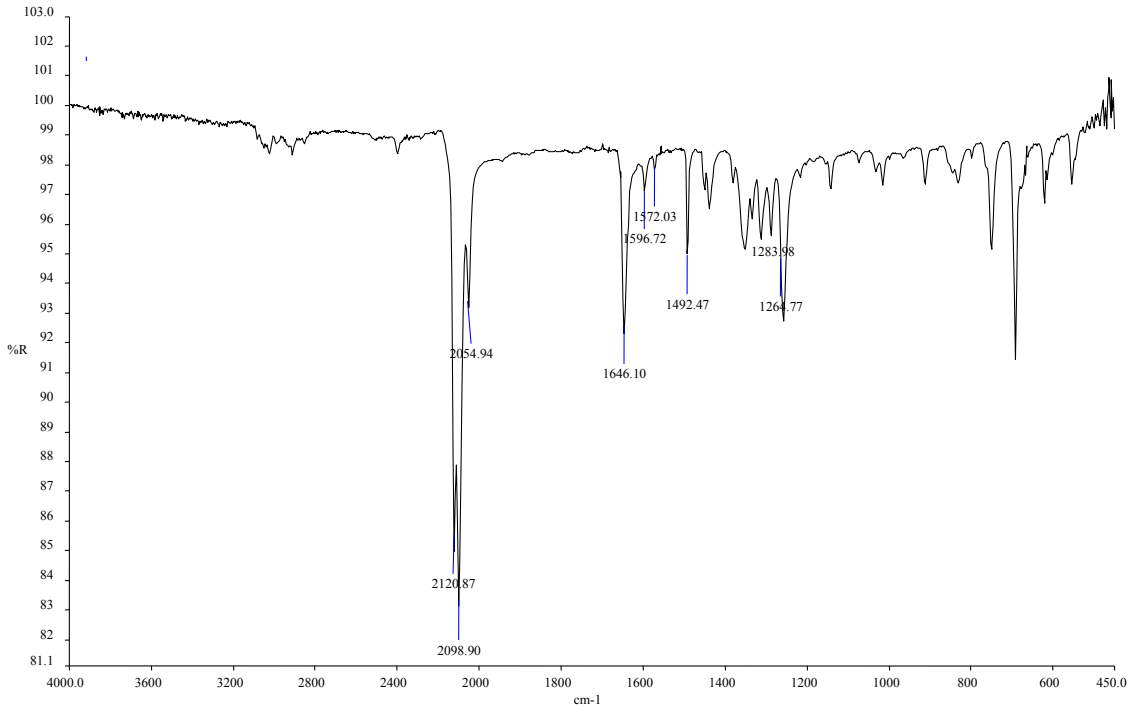


2.17 ^{1}H-NMR Spectrum of 2-methyl-4-phenyloxazol-5(2H)-one (9)

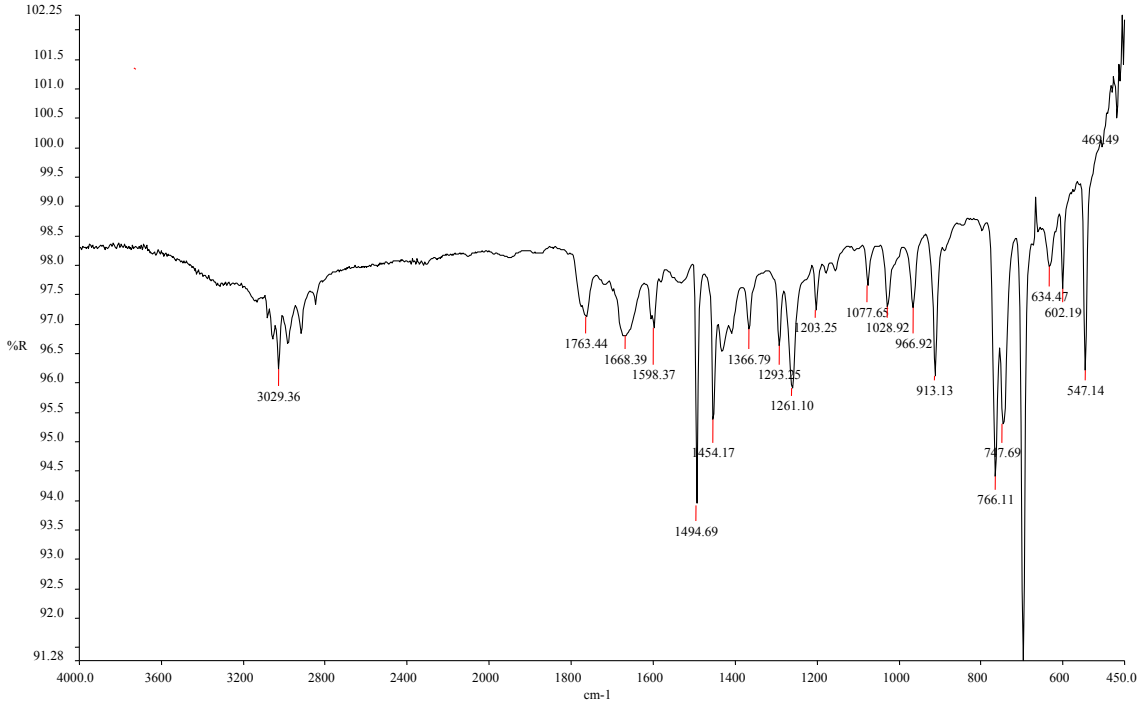


3. IR

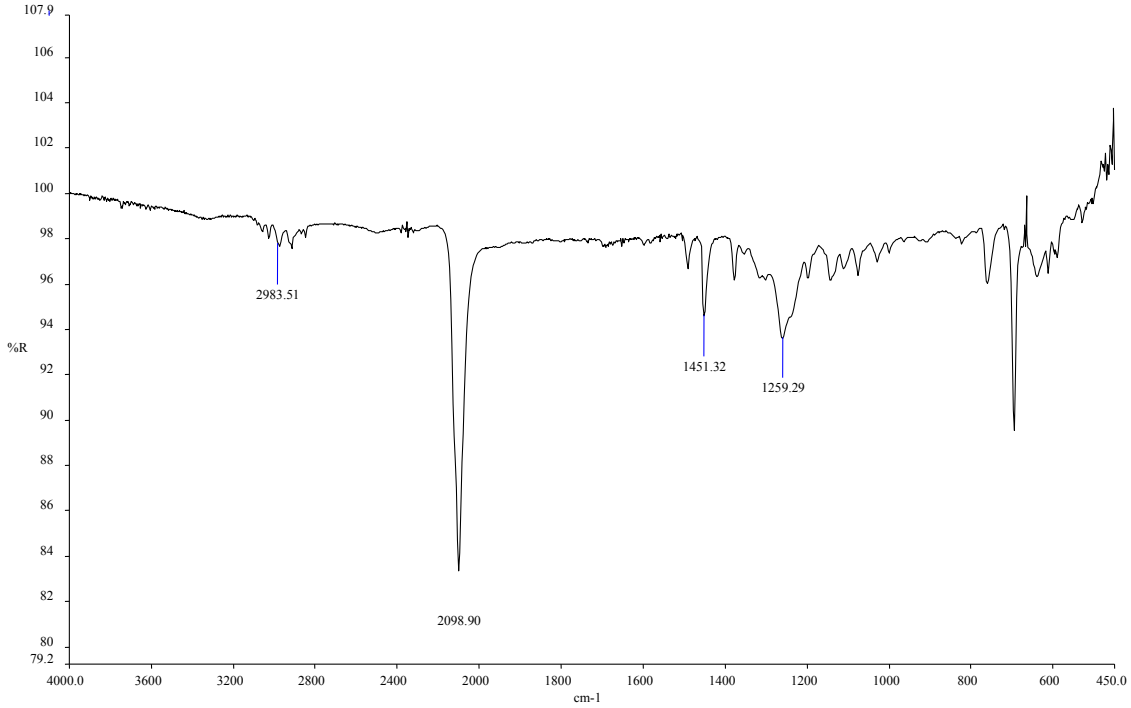
3.1 IR Spectrum of (2-azidoprop-1-en-1-yl)benzene



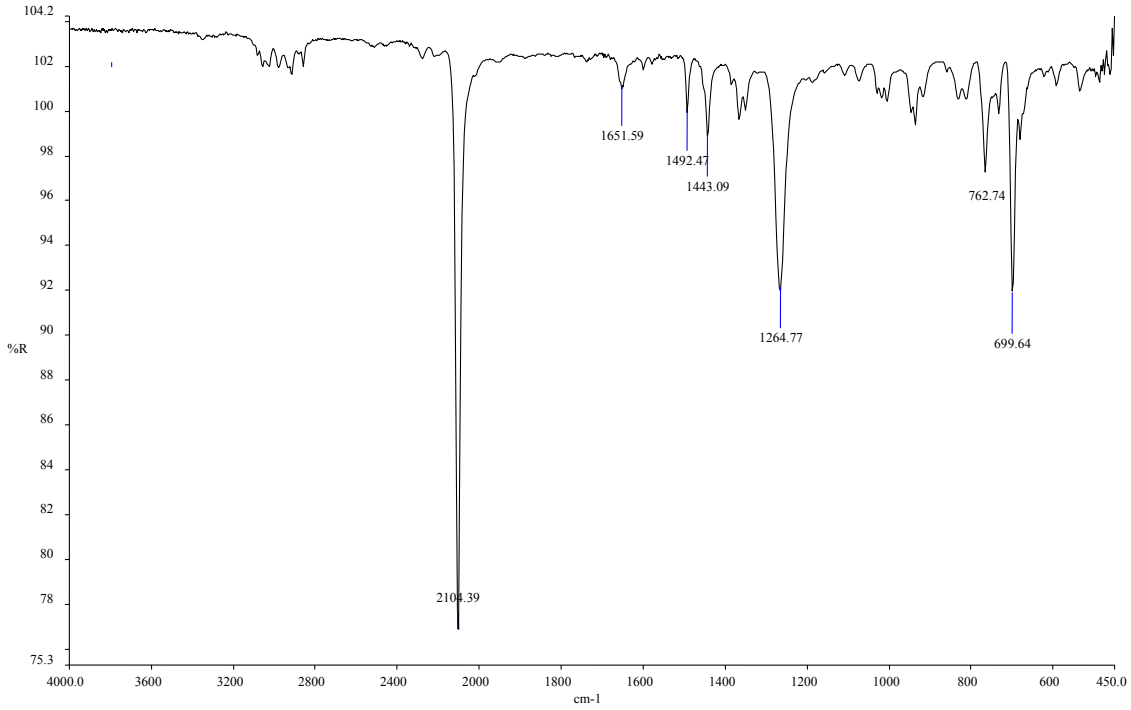
3.2 IR Spectrum of 3-methyl-2-phenyl-2H-azirine (1a)



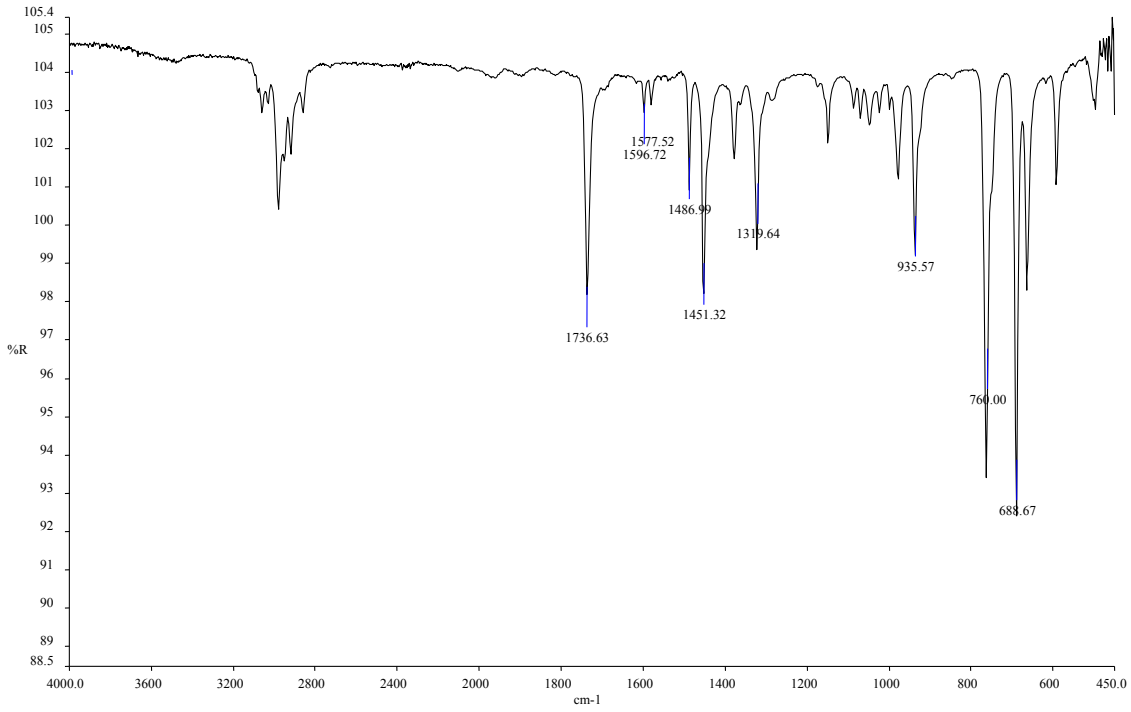
3.3 IR Spectrum of (1-azido-2-iodopropyl)benzene



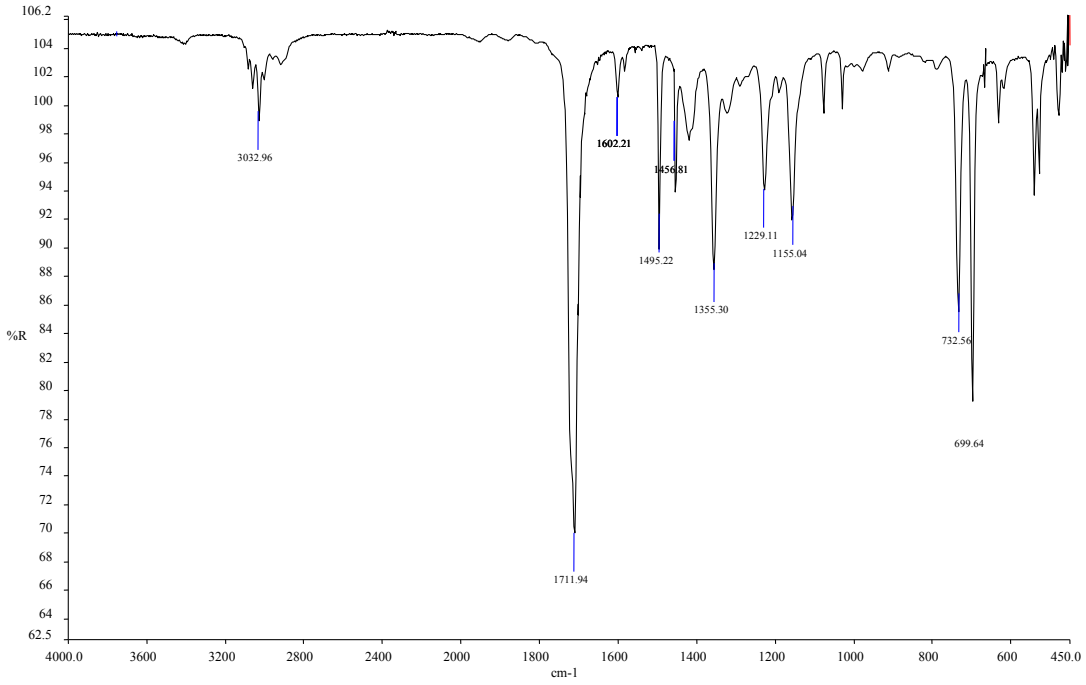
3.4 IR Spectrum of (1-azidoprop-1-en-1-yl)benzene



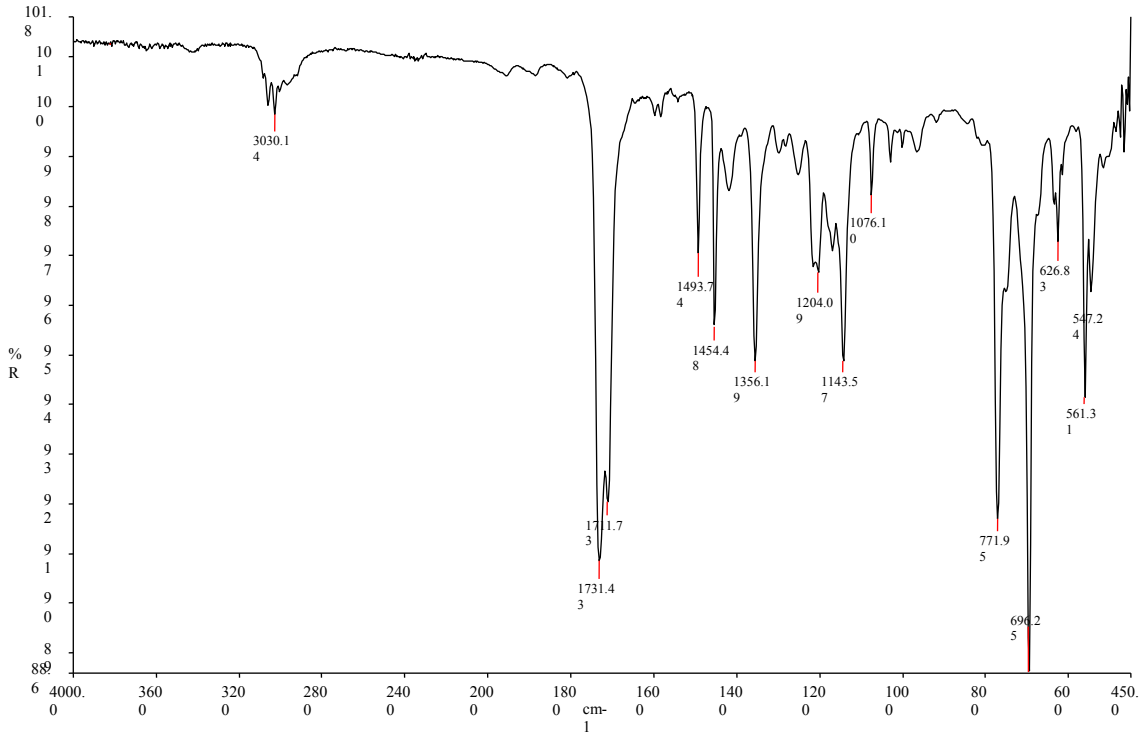
3.5 IR Spectrum of 2-methyl-3-phenyl-2H-azirine (1b)



3.6 IR Spectrum of 1-phenylpropan-2-one (3)

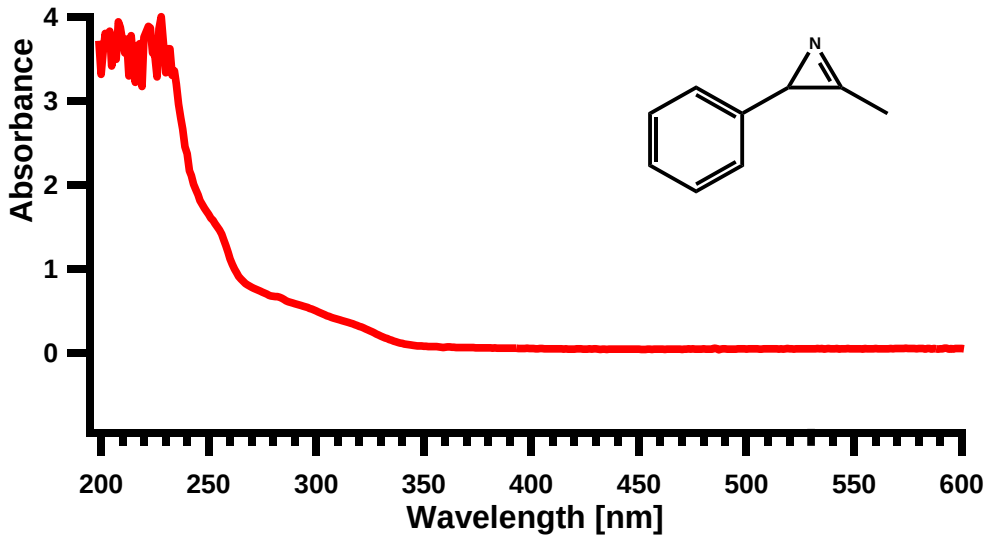


3.7 IR Spectrum of 1-bromo-1-phenylpropan-2-one (4)



4. UV-visible spectra

0.1mM 3-methyl-2-phenyl-2H-azirine (**1a**) acetonitrile solution



0.1mM 2-methyl-3-phenyl-2H-azirine (**1b**) acetonitrile solution