10.1071/CH15401_AC

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Supplementary Material

for

Formation and Direct Detection of non-Conjugated Triplet 1,2-Biradical from β,γ-Vinylarylketone

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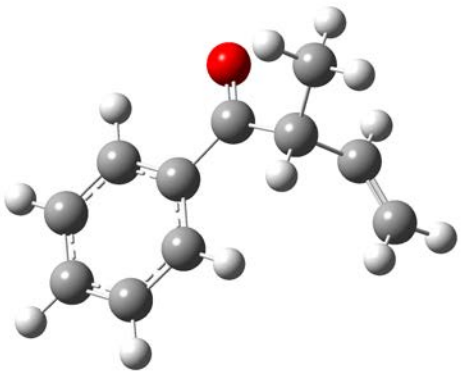
Table of Contents

1. Calculations

1.1 Optimized Geometries, Energies and TD-DFT calculations of 1



DFT/B3LYP/6-31+G(d) E: -501.61865608 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.371463	-1.451791	0.494964
2	6	0	-1.050092	-1.001662	0.450202
3	6	0	-0.754935	0.301386	0.015778
4	6	0	-1.813364	1.143375	-0.371672
5	6	0	-3.131533	0.697097	-0.319351
6	6	0	-3.414216	-0.603581	0.114286
7	1	0	-2.585003	-2.464575	0.826553
8	1	0	-0.255115	-1.679496	0.740784
9	1	0	-1.576502	2.146956	-0.710551
10	1	0	-3.940075	1.359929	-0.616691

11	1	0	-4.442643	-0.953806	0.153799
12	6	0	0.640678	0.849118	-0.066680
13	8	0	0.841924	1.947891	-0.568030
14	6	0	1.835562	0.024209	0.451221
15	1	0	1.495484	-0.691227	1.207186
16	6	0	2.423665	-0.745692	-0.713777
17	1	0	2.741867	-0.131971	-1.557719
18	6	0	2.588651	-2.070927	-0.758191
19	1	0	2.286386	-2.717636	0.064215
20	1	0	3.039348	-2.558578	-1.618841
21	6	0	2.888695	0.952113	1.088208
22	1	0	3.729626	0.357677	1.460738
23	1	0	3.262933	1.675359	0.358392
24	1	0	2.458416	1.512369	1.926432

TD-DFT calculations of 1

Gas Phase (S_{1K}, S_{2K}, …..)

TD-DFT/RB3LYP/6-31+G(d) E: -501.48694514 a.u.

```
Excited State   1:      Singlet-A      3.5840 eV  345.93 nm  f=0.0036
<S**2>=0.000
      40 -> 44        -0.16926
      43 -> 44         0.66885


 Excited State   2:      Singlet-A      4.6229 eV  268.20 nm  f=0.0124
<S**2>=0.000
      41 -> 44         0.54903
      41 -> 45        -0.12221
      42 -> 44        -0.36374
      42 -> 45        -0.19543

 Excited State   3:      Singlet-A      4.7982 eV  258.40 nm  f=0.0917
<S**2>=0.000
      40 -> 44         0.49014
      41 -> 44        -0.22019
      42 -> 44        -0.41025
      43 -> 44         0.17434

 Excited State   4:      Singlet-A      5.0816 eV  243.99 nm  f=0.1868
<S**2>=0.000
      40 -> 44         0.45586
      41 -> 44         0.28862
      42 -> 44         0.40708
      42 -> 45        -0.13221
```

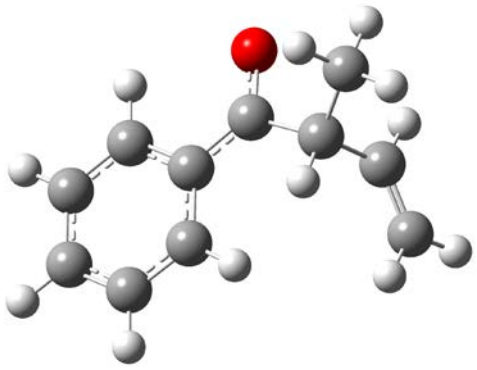
```
 Excited State   5:      Singlet-A      5.4067 eV  229.32 nm  f=0.0081
<S**2>=0.000
      43 -> 45         0.69683
```

Gas Phase (T_{1K}, T_{2K}, …..)

TD-DFT/RB3LYP/6-31+G(d) E: -501.50461258 a.u.

```
Excited State   1:      Triplet-A      3.1033 eV  399.53 nm  f=0.0000
<S**2>=2.000
      40 -> 44        -0.15638
      41 -> 44         0.12072
      43 -> 44         0.65181

 Excited State   2:      Triplet-A      3.3000 eV  375.71 nm  f=0.0000
<S**2>=2.000
      40 -> 44         0.12947
      41 -> 44         0.27886
      41 -> 45         0.21416
      42 -> 44         0.55069
      42 -> 45        -0.14204

 Excited State   3:      Triplet-A      3.9077 eV  317.28 nm  f=0.0000
<S**2>=2.000
      40 -> 44        -0.21649
      40 -> 46        -0.27260
      40 -> 47         0.10186
      41 -> 44         0.47413
      42 -> 44        -0.21328
      43 -> 46        -0.22558

 Excited State   4:      Triplet-A      3.9561 eV  313.40 nm  f=0.0000
<S**2>=2.000
      40 -> 44         0.32060
      40 -> 46         0.26071
      41 -> 44         0.35756
      41 -> 46        -0.11853
      42 -> 44        -0.27226
      43 -> 46         0.24874

 Excited State   5:      Triplet-A      4.3889 eV  282.49 nm  f=0.0000
<S**2>=2.000
      41 -> 44        -0.14545
      41 -> 45         0.48739
      42 -> 44        -0.21209
      42 -> 45        -0.39826
```

1.2. Optimized geometries, Energies and TD-DFT calculations of T_K of 1



DFT/UB3LYP/6-31+G(d) E: -501.51079249 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.397816	1.399888	0.555401
2	6	0	1.071863	0.986120	0.516691
3	6	0	0.730055	-0.308764	0.031849
4	6	0	1.792913	-1.147222	-0.425075
5	6	0	3.109954	-0.712699	-0.380403
6	6	0	3.431315	0.561791	0.110888
7	1	0	2.630180	2.392750	0.933513
8	1	0	0.299011	1.668658	0.853917
9	1	0	1.559045	-2.140205	-0.798827
10	1	0	3.899318	-1.373778	-0.730798
11	1	0	4.464226	0.896376	0.144035
12	6	0	-0.612872	-0.790427	-0.011693
13	8	0	-0.910041	-1.942583	-0.556104
14	6	0	-1.873316	-0.001186	0.444722
15	1	0	-1.509480	0.717986	1.186635
16	6	0	-2.436012	0.744528	-0.736666
17	1	0	-2.824655	0.124974	-1.545405
18	6	0	-2.480928	2.079332	-0.839095
19	1	0	-2.094414	2.729491	-0.056276
20	1	0	-2.911022	2.568536	-1.709136
21	6	0	-2.914011	-0.916006	1.117594
22	1	0	-3.730549	-0.304664	1.516902
23	1	0	-3.338855	-1.632580	0.407120
24	1	0	-2.463141	-1.479020	1.941868

TD-DFT calculations of T_K of 1

Gas Phase

TD-DFT/UB3LYP/6-31+G(d) E: -501.49133531 a.u.

```
Excited State   1:  3.016-A      0.5295 eV 2341.72 nm  f=0.0003
<S**2>=2.023
     32B -> 43B        0.10217
     34B -> 43B        0.10156
     38B -> 43B        0.29552
     40B -> 43B        0.15443
     41B -> 43B        0.85480
     42B -> 43B       -0.36823

 Excited State   2:  3.022-A      1.0248 eV 1209.82 nm  f=0.0001
<S**2>=2.034
     41B -> 43B        0.38521
     42B -> 43B        0.92212

 Excited State   3:  3.030-A      1.7011 eV  728.83 nm  f=0.0242
<S**2>=2.045
     38B -> 43B        0.13575
     40B -> 43B        0.95004
     41B -> 43B       -0.21180

 Excited State   4:  3.021-A      2.4502 eV  506.01 nm  f=0.0009
<S**2>=2.032
     32B -> 43B        0.25444
     33B -> 43B       -0.12251
     34B -> 43B        0.36617
     36B -> 43B        0.12482
     38B -> 43B        0.76357
     39B -> 43B        0.18351
     40B -> 43B       -0.22768
     41B -> 43B       -0.27544

 Excited State   5:  3.045-A      2.7882 eV  444.67 nm  f=0.0037
<S**2>=2.069
     44A -> 46A        0.96335
     42B -> 44B        0.21387

 Excited State   6:  3.049-A      2.9772 eV  416.45 nm  f=0.0657
<S**2>=2.074
     44A -> 45A        0.93918
     44A -> 51A        0.10211
     41B -> 44B       -0.21757

 Excited State   7:  3.025-A      3.1387 eV  395.01 nm  f=0.0026
<S**2>=2.038
     44A -> 45A        0.10213
```

```
     27B -> 43B        0.11742
     30B -> 43B        0.16853
     35B -> 43B       -0.35247
     38B -> 43B       -0.16073
     39B -> 43B        0.86903

 Excited State   8:  3.105-A      3.4043 eV  364.20 nm  f=0.0041
<S**2>=2.160
     43A -> 46A        0.11847
     44A -> 45A        0.24485
     44A -> 48A        0.44437
     44A -> 49A        0.41958
     44A -> 50A       -0.11906
     44A -> 51A       -0.40821
     41B -> 44B        0.52686
     42B -> 44B       -0.17157
     42B -> 46B        0.10558

 Excited State   9:  3.025-A      3.4945 eV  354.80 nm  f=0.0010
<S**2>=2.037
     44A -> 47A        0.98220

 Excited State  10:  3.032-A      3.6508 eV  339.61 nm  f=0.0033
<S**2>=2.048
     34B -> 43B       -0.14549
     35B -> 43B       -0.18872
     36B -> 43B        0.78160
     37B -> 43B        0.51309
     39B -> 43B       -0.17477
     41B -> 44B       -0.11110

 Excited State  11:  3.029-A      3.7731 eV  328.60 nm  f=0.0007
<S**2>=2.043
     35B -> 43B       -0.10468
     36B -> 43B       -0.59026
     37B -> 43B        0.75112
     39B -> 43B       -0.12157
     41B -> 44B       -0.11296

 Excited State  12:  3.028-A      3.8436 eV  322.57 nm  f=0.0100
<S**2>=2.042
     35B -> 43B        0.84175
     37B -> 43B        0.28690
     38B -> 43B       -0.17985
     39B -> 43B        0.33023

 Excited State  13:  3.038-A      3.9315 eV  315.36 nm  f=0.0113
<S**2>=2.057
     44A -> 48A        0.86603
     44A -> 49A       -0.26008
     44A -> 50A        0.15642
     44A -> 51A        0.31467
```

```
     41B -> 44B       -0.14534

 Excited State  14:  3.090-A      4.0217 eV  308.29 nm  f=0.0178
<S**2>=2.138
     44A -> 46A       -0.20400
     44A -> 49A        0.17270
     44A -> 50A        0.32998
     41B -> 44B        0.22485
     42B -> 44B        0.83846

 Excited State  15:  3.067-A      4.0481 eV  306.28 nm  f=0.0045
<S**2>=2.102
     44A -> 49A        0.63477
     44A -> 50A        0.58338
     44A -> 51A        0.29441
     40B -> 45B        0.10172
     41B -> 44B       -0.17654
     42B -> 44B       -0.25246

 Excited State  16:  3.710-A      4.1226 eV  300.74 nm  f=0.0171
<S**2>=3.191
     41A -> 45A        0.42205
     42A -> 45A        0.27634
     44A -> 45A       -0.11461
     44A -> 49A        0.11712
     44A -> 50A       -0.37657
     34B -> 43B        0.10469
     40B -> 44B        0.39015
     40B -> 45B        0.46212
     41B -> 44B       -0.14402
     41B -> 45B       -0.14971
     42B -> 44B        0.23703
```

Acetonitrile

TD-DFT/UB3LYP/6-31+G(d) E: -501.49507487 a.u.

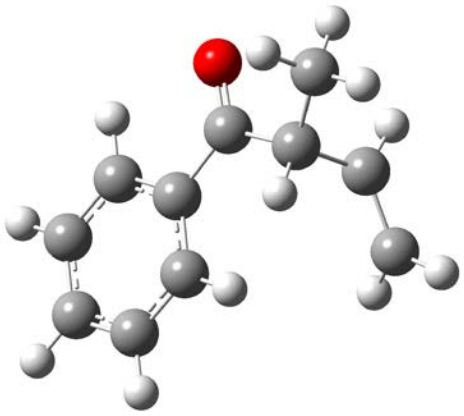
```
Excited State   1:  3.015-A      0.5826 eV 2128.17 nm  f=0.0003
<S**2>=2.023
     32B -> 43B       -0.11914
     37B -> 43B        0.19354
     38B -> 43B        0.20442
     40B -> 43B        0.22196
     41B -> 43B        0.85484
     42B -> 43B       -0.33520

 Excited State   2:  3.022-A      1.0609 eV 1168.62 nm  f=0.0003
<S**2>=2.033
     41B -> 43B        0.35450
     42B -> 43B        0.93438
```

```
 Excited State   3:  3.027-A      1.5262 eV  812.39 nm  f=0.0353
<S**2>=2.041
     40B -> 43B        0.94407
     41B -> 43B       -0.26764

 Excited State   4:  3.020-A      2.4453 eV  507.03 nm  f=0.0008
<S**2>=2.031
     32B -> 43B       -0.30993
     34B -> 43B        0.30192
     36B -> 43B        0.16276
     37B -> 43B        0.41201
     38B -> 43B        0.64684
     39B -> 43B       -0.23079
     40B -> 43B       -0.20791
     41B -> 43B       -0.26476

 Excited State   5:  3.043-A      2.7540 eV  450.20 nm  f=0.0050
<S**2>=2.065
     44A -> 45A        0.96845
     42B -> 44B        0.19966

 Excited State   6:  3.032-A      3.0422 eV  407.55 nm  f=0.0142
<S**2>=2.049
     44A -> 46A        0.43987
     30B -> 43B       -0.13973
     35B -> 43B        0.36644
     37B -> 43B        0.13639
     39B -> 43B        0.73264
     41B -> 44B       -0.17329

 Excited State   7:  3.049-A      3.0803 eV  402.50 nm  f=0.0659
<S**2>=2.074
     44A -> 46A        0.79888
     44A -> 48A       -0.16250
     35B -> 43B       -0.13042
     39B -> 43B       -0.45587
     41B -> 44B       -0.22255

 Excited State   8:  3.032-A      3.4343 eV  361.02 nm  f=0.0011
<S**2>=2.048
     44A -> 46A       -0.12980
     44A -> 48A       -0.30221
     44A -> 49A       -0.10533
     34B -> 43B        0.13679
     37B -> 43B        0.66217
     38B -> 43B       -0.59742
     39B -> 43B       -0.10740
     41B -> 44B       -0.14334

 Excited State   9:  3.091-A      3.4656 eV  357.76 nm  f=0.0132
<S**2>=2.138
     43A -> 45A        0.10288
```

```
     44A -> 46A        0.31619
     44A -> 47A        0.13196
     44A -> 48A        0.61245
     44A -> 49A        0.20607
     37B -> 43B        0.28462
     38B -> 43B       -0.23734
     40B -> 44B        0.14041
     41B -> 44B        0.45932
     42B -> 44B       -0.14856

 Excited State  10:  3.026-A      3.6737 eV  337.49 nm  f=0.0007
<S**2>=2.040
     44A -> 47A        0.96653
     44A -> 50A       -0.10805

 Excited State  11:  3.026-A      3.7071 eV  334.45 nm  f=0.0110
<S**2>=2.039
     35B -> 43B        0.60961
     36B -> 43B        0.66920
     37B -> 43B       -0.27596
     38B -> 43B       -0.13848
     39B -> 43B       -0.22612

 Excited State  12:  3.028-A      3.7173 eV  333.53 nm  f=0.0072
<S**2>=2.043
     26B -> 43B       -0.13784
     32B -> 43B       -0.11650
     35B -> 43B       -0.62232
     36B -> 43B        0.65327
     39B -> 43B        0.30473
     41B -> 44B       -0.10532

 Excited State  13:  3.118-A      4.0457 eV  306.46 nm  f=0.0226
<S**2>=2.180
     44A -> 45A       -0.19487
     41B -> 44B        0.22451
     42B -> 44B        0.90855

 Excited State  14:  3.462-A      4.1222 eV  300.77 nm  f=0.0598
<S**2>=2.747
     41A -> 46A        0.25077
     42A -> 46A        0.25170
     43A -> 45A       -0.14085
     44A -> 46A       -0.13902
     44A -> 48A        0.40677
     44A -> 49A       -0.33532
     44A -> 50A       -0.17505
     34B -> 43B        0.25084
     40B -> 44B        0.31278
     40B -> 46B        0.33878
     41B -> 44B       -0.33150
     41B -> 46B       -0.10958
```

```
42B -> 44B        0.13784
42B -> 45B       -0.18187
```

1.3 Optimized geometries, Energies and TD-DFT calculations of 2



DFT/UB3LYP/6-31+G(d) E: -501.51927154 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.352455	1.317309	0.628701
2	6	0	1.019730	0.900591	0.586137
3	6	0	0.681324	-0.354565	0.052631
4	6	0	1.709375	-1.183502	-0.432590
5	6	0	3.038110	-0.768723	-0.387741
6	6	0	3.363930	0.484685	0.143815
7	1	0	2.599018	2.291562	1.042825
8	1	0	0.251472	1.565501	0.966284
9	1	0	1.439998	-2.152371	-0.840990
10	1	0	3.821632	-1.420312	-0.766080
11	1	0	4.400867	0.809198	0.180360
12	6	0	-0.726105	-0.876845	-0.014011
13	8	0	-0.951505	-1.987961	-0.477012
14	6	0	-1.902496	0.012901	0.449836
15	1	0	-1.574489	0.649472	1.277804
16	6	0	-2.266204	0.886832	-0.732154
17	1	0	-2.721748	0.365149	-1.577984
18	6	0	-1.968502	2.305326	-0.837345
19	1	0	-1.047555	2.672577	-1.292891
20	1	0	-2.683432	3.062964	-0.512712
21	6	0	-3.088686	-0.848804	0.915700
22	1	0	-3.909698	-0.205087	1.249529
23	1	0	-3.448143	-1.487539	0.104322

```
     24          1           0       -2.793470   -1.498655    1.747751
 ---------------------------------------------------------------------
```

TD-DFT calculations of 2

Gas Phase

TD-DFT/UB3LYP/6-31+G(d) E: -501.41931789 a.u.

```
Excited State   1:  3.283-A      2.7199 eV  455.84 nm  f=0.0181
<S**2>=2.444
     41A -> 45A       -0.12611
     42A -> 45A       -0.18554
     44A -> 45A        0.90677
     42B -> 43B        0.30070

 Excited State   2:  3.442-A      3.2256 eV  384.37 nm  f=0.0125
<S**2>=2.711
     40A -> 45A        0.12780
     41A -> 45A       -0.16851
     43A -> 45A        0.11273
     44A -> 45A       -0.33253
     42B -> 43B        0.82266
     42B -> 44B        0.20421
     42B -> 45B       -0.22657
     42B -> 51B        0.13046

 Excited State   3:  3.958-A      3.3262 eV  372.75 nm  f=0.0057
<S**2>=3.666
     40A -> 45A       -0.36488
     40A -> 46A        0.16135
     41A -> 45A        0.33769
     41A -> 46A        0.14709
     42A -> 45A       -0.25488
     42A -> 46A       -0.10531
     44A -> 45A       -0.12157
     40B -> 43B        0.32199
     40B -> 45B       -0.19804
     40B -> 46B       -0.18466
     41B -> 43B        0.48929
     41B -> 44B        0.13903
     41B -> 45B       -0.27178
     41B -> 46B        0.16395
     42B -> 43B        0.19520

 Excited State   4:  3.038-A      3.6017 eV  344.24 nm  f=0.0036
<S**2>=2.057
```

```
     42A -> 45A       -0.16116
     43A -> 45A        0.97098
     42B -> 43B       -0.12255

 Excited State   5:  3.853-A      3.9028 eV  317.68 nm  f=0.0005
<S**2>=3.462
     40A -> 45A       -0.39318
     40A -> 46A        0.11357
     41A -> 45A       -0.26722
     42A -> 45A        0.18709
     44A -> 46A       -0.14536
     40B -> 43B        0.61084
     40B -> 44B        0.10678
     40B -> 45B       -0.24499
     41B -> 43B       -0.44955
     41B -> 45B        0.15098

 Excited State   6:  3.480-A      3.9958 eV  310.29 nm  f=0.0065
<S**2>=2.778
     41A -> 45A        0.50906
     42A -> 45A        0.72446
     42A -> 51A        0.13504
     43A -> 45A        0.17884
     44A -> 45A        0.16756
     42B -> 43B        0.17063
     42B -> 44B        0.21065
     42B -> 45B        0.17410

 Excited State   7:  3.039-A      4.0692 eV  304.69 nm  f=0.0006
<S**2>=2.059
     42A -> 45A       -0.13463
     42B -> 43B       -0.25734
     42B -> 44B        0.94534
```

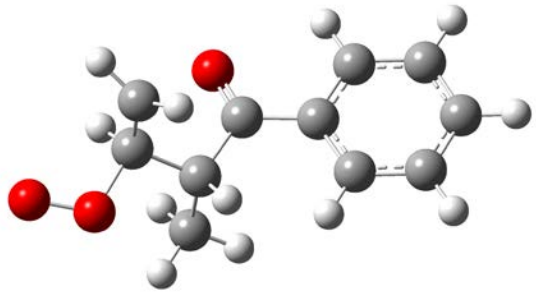
Acetonitrile

TD-DFT/UB3LYP/6-31+G(d) E: -501.42837156 a.u.

```
Excited State   1:  3.170-A      2.6577 eV  466.51 nm  f=0.0332
<S**2>=2.263
     40A -> 45A       -0.17667
     44A -> 45A        0.95300
     42B -> 43B        0.17585

 Excited State   2:  3.812-A      3.3024 eV  375.44 nm  f=0.0008
<S**2>=3.382
     41A -> 45A        0.39403
     42A -> 45A        0.24799
     42A -> 46A        0.17103
     43A -> 45A        0.29024
```

```
     44A -> 45A       -0.10936
     40B -> 43B       -0.24259
     40B -> 45B        0.16209
     40B -> 46B        0.10830
     41B -> 46B        0.16488
     42B -> 43B        0.65373
     42B -> 45B       -0.19468

 Excited State   3:  3.656-A      3.3615 eV  368.84 nm  f=0.0080
<S**2>=3.091
     40A -> 45A        0.14577
     41A -> 45A        0.28372
     42A -> 45A        0.21779
     42A -> 46A        0.14018
     43A -> 45A       -0.38361
     44A -> 45A        0.17566
     40B -> 43B       -0.41483
     40B -> 45B        0.17757
     41B -> 43B        0.45446
     41B -> 45B       -0.15987
     41B -> 46B        0.12844
     42B -> 43B       -0.38648
     42B -> 50B       -0.10062

 Excited State   4:  3.083-A      3.4268 eV  361.81 nm  f=0.0160
<S**2>=2.127
     43A -> 45A        0.86839
     44A -> 45A        0.10878
     40B -> 43B       -0.13940
     41B -> 43B        0.15998
     42B -> 43B       -0.40433

 Excited State   5:  3.868-A      3.8289 eV  323.81 nm  f=0.0007
<S**2>=3.491
     41A -> 45A       -0.29699
     41A -> 46A        0.10532
     42A -> 45A        0.42164
     44A -> 46A       -0.12292
     40B -> 43B        0.48483
     40B -> 45B       -0.16906
     41B -> 43B        0.60450
     41B -> 45B       -0.19239
     42B -> 43B        0.13370

 Excited State   6:  3.464-A      4.0767 eV  304.13 nm  f=0.0080
<S**2>=2.750
     40A -> 45A        0.92240
     40A -> 49A       -0.10143
     40A -> 50A       -0.13068
     44A -> 45A        0.13689
     42B -> 43B        0.21999
     42B -> 45B        0.10088
```

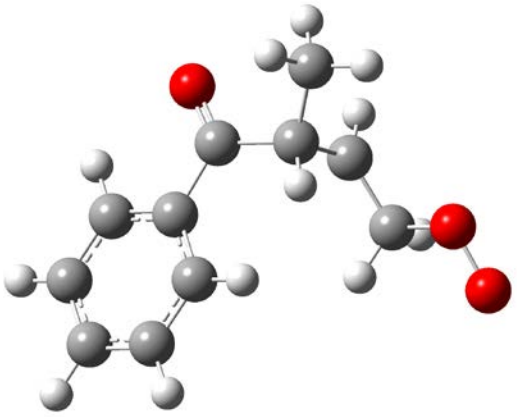
1.4 Optimized geometries, Energies of β substituted peroxy radical



DFT/UB3LYP/6-31+G(d) E: -651.89761141 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.163210	-1.434612	-0.617037
2	6	0	-1.830566	-1.105426	-0.359970
3	6	0	-1.488368	0.180017	0.093815
4	6	0	-2.510784	1.127886	0.283314
5	6	0	-3.838658	0.800753	0.021631
6	6	0	-4.168557	-0.482977	-0.429111
7	1	0	-3.414272	-2.433011	-0.965096
8	1	0	-1.067734	-1.861908	-0.512601
9	1	0	-2.238174	2.117408	0.636140
10	1	0	-4.618378	1.543379	0.169049
11	1	0	-5.205051	-0.739657	-0.632650
12	6	0	-0.081453	0.602569	0.397422
13	8	0	0.151625	1.729387	0.817376
14	6	0	1.073015	-0.399446	0.246906
15	1	0	0.836582	-1.135751	-0.529315
16	6	0	2.340033	0.347065	-0.198223
17	1	0	2.683200	1.046203	0.565499
18	6	0	2.252972	0.977381	-1.530819
19	1	0	2.844106	1.854355	-1.766730
20	1	0	1.685929	0.502630	-2.326848
21	6	0	1.260213	-1.132185	1.595473
22	1	0	2.052120	-1.882167	1.519881
23	1	0	1.529641	-0.418249	2.381764
24	1	0	0.335942	-1.636736	1.897427
25	8	0	3.412175	-0.736062	-0.232499
26	8	0	4.624735	-0.223656	-0.266993

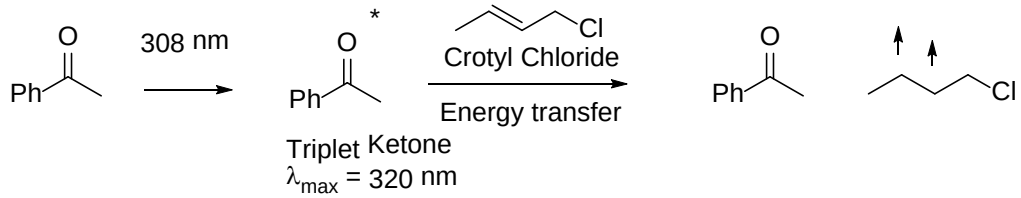
1.4. Optimized geometries, Energies of γ substituted peroxy radical



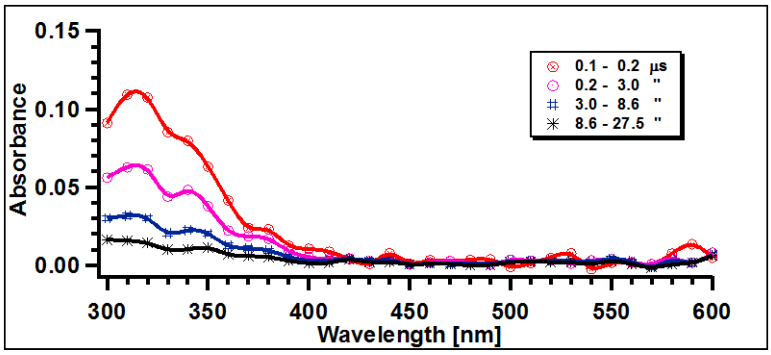
DFT/UB3LYP/6-31+G(d) E: -651.90249942 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.297464	-1.837963	0.793691
2	6	0	-1.274041	-0.887385	0.769652
3	6	0	-1.439164	0.322308	0.073049
4	6	0	-2.656252	0.559236	-0.593080
5	6	0	-3.673403	-0.391340	-0.574004
6	6	0	-3.496381	-1.594322	0.119983
7	1	0	-2.157075	-2.765833	1.341662
8	1	0	-0.358947	-1.096816	1.313555
9	1	0	-2.780669	1.498624	-1.122268
10	1	0	-4.605428	-0.197083	-1.098283
11	1	0	-4.290827	-2.335995	0.137460
12	6	0	-0.393929	1.398298	0.010229
13	8	0	-0.663287	2.499038	-0.448287
14	6	0	1.061437	1.096366	0.459228
15	1	0	1.056418	0.315802	1.226097
16	6	0	1.779573	0.584993	-0.755053
17	1	0	2.017186	1.304656	-1.534897
18	6	0	2.212070	-0.813912	-0.909968
19	1	0	2.543040	-1.058802	-1.921288
20	6	0	1.724215	2.361203	1.036547
21	1	0	2.751661	2.137837	1.341254
22	1	0	1.739183	3.163696	0.294247
23	1	0	1.170256	2.721285	1.910904
24	1	0	1.476151	-1.548291	-0.567580
25	8	0	3.415288	-1.047436	-0.021124
26	8	0	3.767886	-2.317098	-0.018403

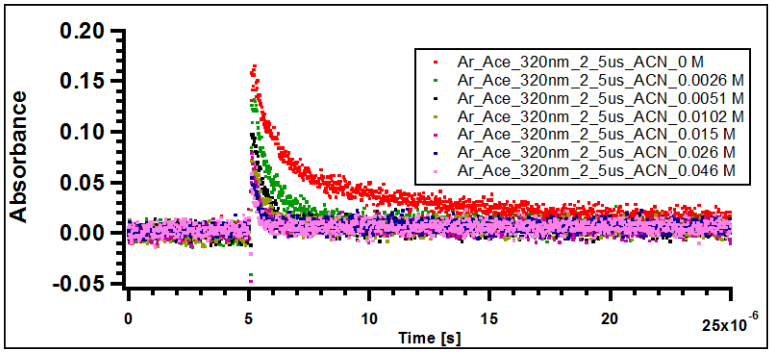
2. Laser flash photolysis of acetophenone.



A)



B)



C)

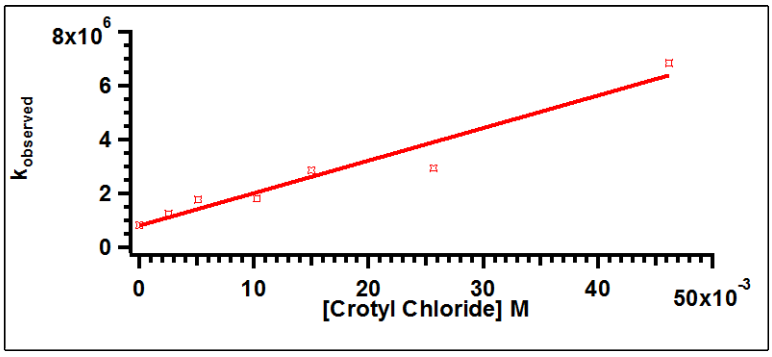
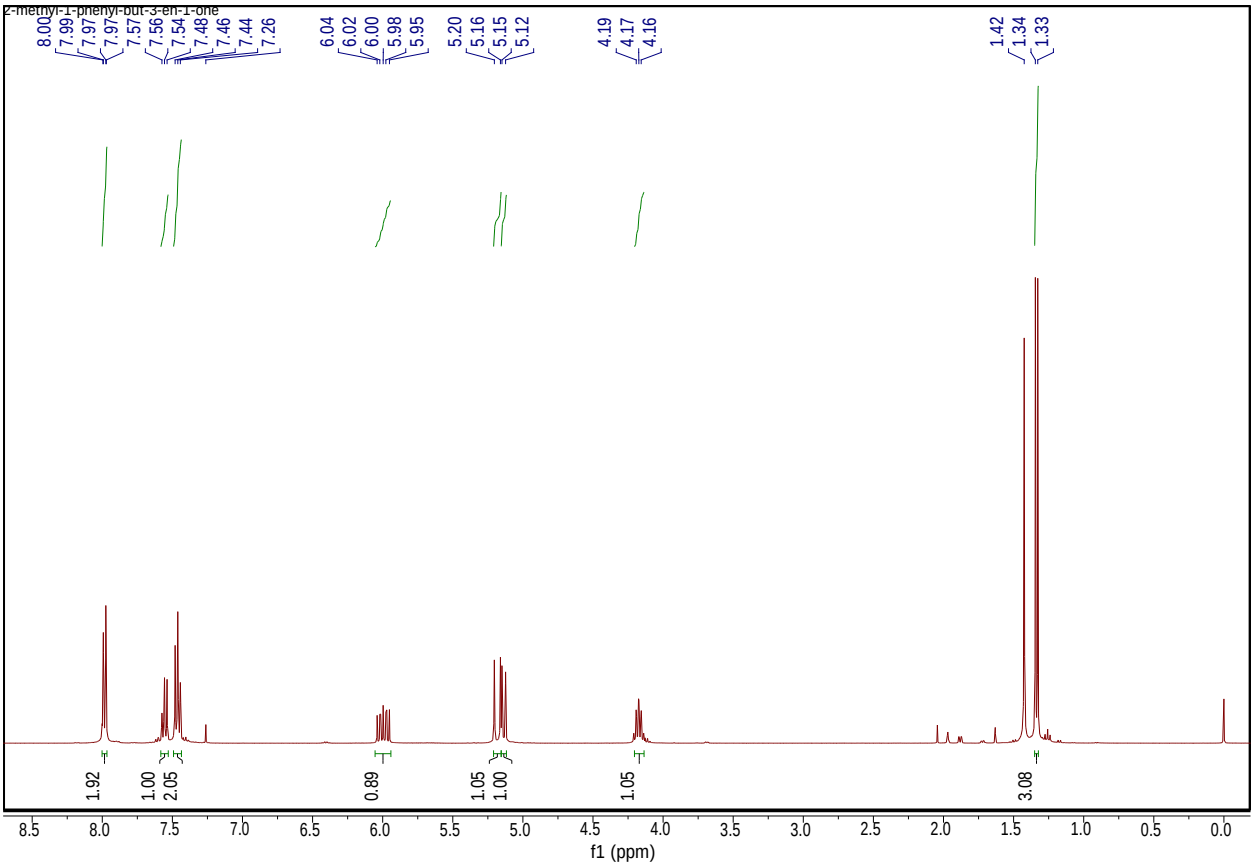


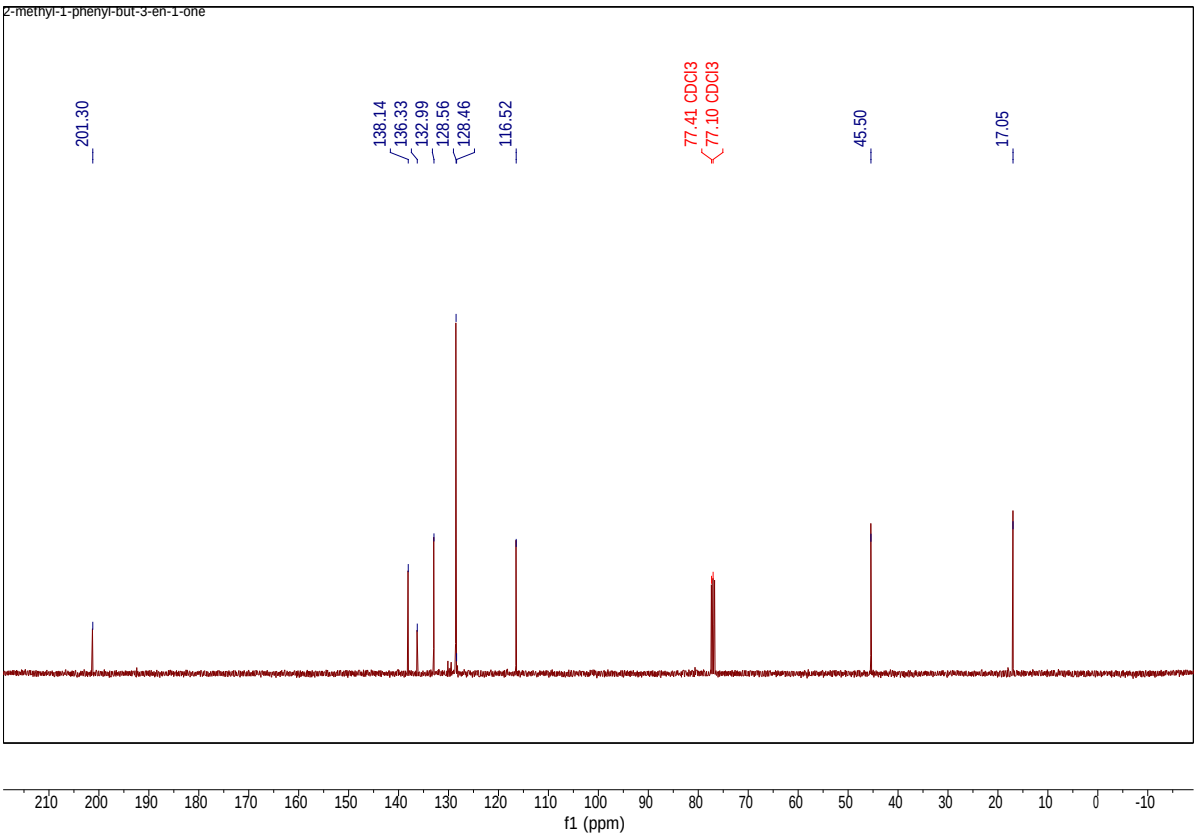
Figure S1. A) Laser flash photolysis of acetophenone in argon-saturated acetonitrile. B) Kinetic traces obtained at 320 nm at various concentration of crotyl chloride. C) The rate constant for the decay of T1K of acetophenone as a function of crotyl chloride concentration.

3. NMR and IR spectra of 1

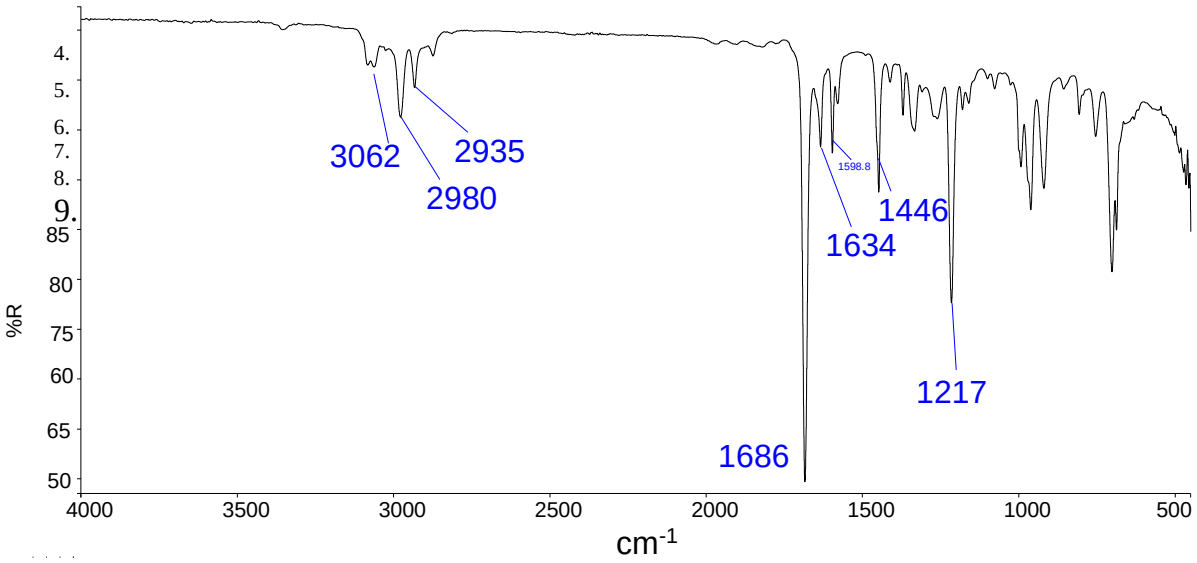
3.1 ^{1}H NMR spectrum of 2-methyl-1-phenyl-but-3-en-1-one (1)



3.2. ^{13}C NMR spectrum of 2-methyl-1-phenyl-but-3-en-1-one (1)



3.3. FTIR of spectrum 2-methyl-1-phenyl-but-3-en-1-one (1)



4. Synthesis of 1-d

4.1 Synthesis of racemic (Z)-1-Buten-3-ol-1D

(Z)-1Buten-3-ol-1D was synthesized by following the procedure reported by Tauchert et al.[1] In a flame dried three-necked flask (100 ml) equipped with a magnetic stirrer and a reflux condenser $LiAlH_4$ (2.0 g, 52 mmol, 1.3 eqiuv) was suspended with dry THF (50 mL). But-3-yn-2-ol (3.2 mL, 39 mmol, 1 equiv) was added by syringe and when an exothermic reaction commenced, reaction mixture was cooled in an ice bath. The ice bath was removed after the exothermic reaction stopped and reaction mixture was stirred for another 18 h at room temperature. The mixture was then cooled again in an ice bath and quenched with D_2O (5 mL). The formed slurry was filtered, the separated solid was extracted with THF (3 x 10 mL), and the resulting solution was dried over $MgSO_4$. The desired compound was isolated by Vigreux column distillation as a colorless liquid (0.99 g, 13.6 mmol, 35% yield). 30% over deuteration for the terminal E-hydogen ($H_{0.7}D_{1.3}C$=CH-CH(OD)CH_3) .^{1}H NMR data match the reported data in the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (d, 3H, J = 6.4 Hz), 4.3(m, 1H), 5.05 (dd, 0.7H, J = 10.4Hz, 1.2 Hz), 5.91 (m, 1 H) ppm.

4.2 Synthesis of racemic (Z)-3-chloro-1-butene-1D

Synthesized (Z)-1Buten-3-ol-1D (0.99g, 13.6 mmol, 1 eqiuv) was added to hexachloroacetone (4.89 mL, 26.5 mmol, 2 eqiuv)in a round bottom flask equipped with a magnetic stir bar and the mixture was cooled to 0°C. PPh_3 (3.74 g, 14 mmol, 1 eqiuv) was added slowly within 20 min, with the mixture never exceeding 10°C. The mixture color changed to very dark violet. The mixture was warmed to room temperature and stirred for another 30 min. Vacuum distillation was used to isolate the (Z)-3-chloro-1-butene-1D as a colorless liquid (0.84 g, 9 mmol). ^{1}H NMR data match the reported data in the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 (d, 3H, J = 6.4 Hz), 4.3 (m, 1H), 5.09 (dd, 0.7 H J = 10Hz, 0.8 Hz), 5.95 (m, 1 H) ppm.

4.3 Synthesis of 2-methyl-1-phenylbut-3-en-1-ol-4D and Oxidation to 2-methyl-1-phenylbut-3-en-1-ol-4D (1-d)

Synthesis of 2-methyl-1-phenylbut-3-en-1-ol-4D was carried out by using the same procedure described above for 2-methyl-1-phenylbut-3-en-1-ol. Benzaldehyde (0.817 g, 7 mmol) and (Z)-3-chloro-1-butene-1D (.84 g, 9 mmol, 1.2 eqiuv) resulted in crude 2-methyl-1-phenylbut-3-en-1-ol-4D in 1.86 g, 11.4 mmol. IR (neat): 3375 (br, OH). Without further purification the resulted 2-methyl-1-phenylbut-3-en-1-ol-4D (1.86 g, 11.4 mmol) was oxidized with Jones reagent as described above gave mixture of trans and cis 2-methyl-1-phenylbut-3-en-1-ol-4-D 0.82 g, (5 mmol, 44 % yield).

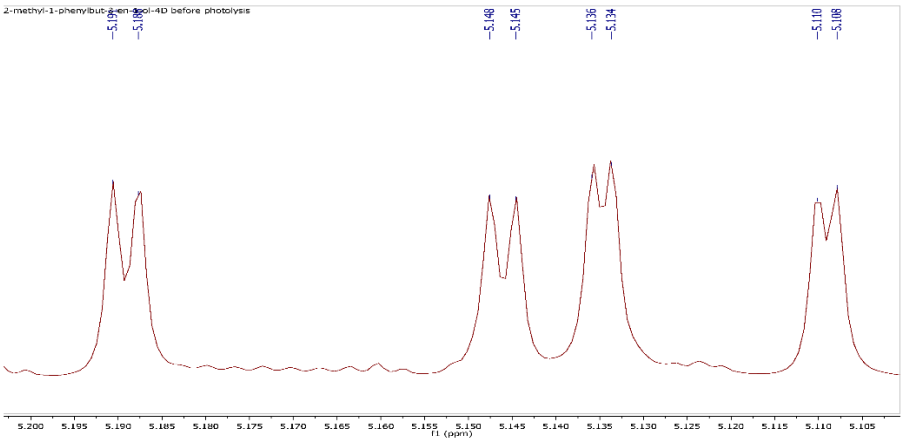
^{1}H NMR of cis-**1**d and trans-**1**-d ($CDCl_3$, 400 MHz): δ 1.33 (d, 6H, J = 6.8 Hz), 4.3 (m, 2H), 5.12 (dd, 0.72 H, J = 10.4 Hz, 0.8 Hz), 5.17 (dd, 0.76 H, J = 17.2 Hz, 1.2 Hz), 5.99 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 400 MHz): δ 201.2, 138, 137.9, 136.3, 132.9, 128.6, 128.5, 116.5, 45.4, 17.0 ppm. GC/MS (EI): *m/z*: 161 (M+)

4.4 References

1. M. E. Tauchert, D. C. M. Warth, S. M. Braun, I. Gruber, A. Ziesak, F. Rominger, et al. Highly Efficient Nickel-Catalyzed 2-Methyl-3-butenenitrile Isomerization: Applications and Mechanistic Studies Employing the TTP Ligand Family. *Organometallics*, **2011**, 30, 2790

5. ^{1}H-NMR spectra before and after irradiation of 1-d

A)



B)

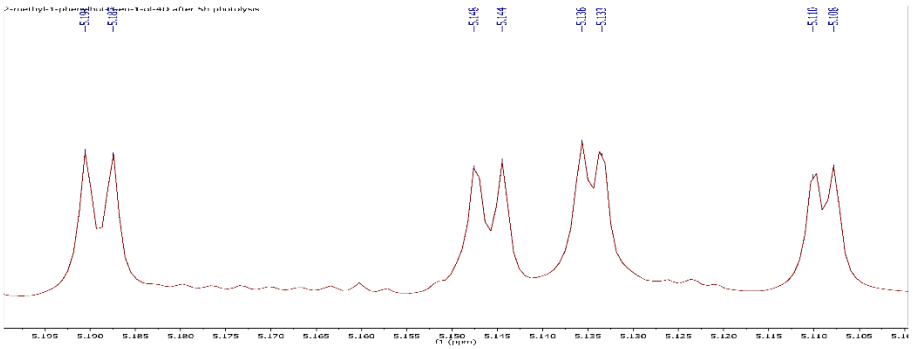


Figure S2. ^{1}H-NMR spectra of 1 A) Before (trans-cis ratio 47%) and B) after irradiation through Pyrex filter for 5 hours. The trans to cis ratio is (44%).