Surface-Doped Graphitic Carbon Nitride Sensitized Photooxidation of Olefins and Dienes: Chemical Evidence for Singlet Oxygen and Electron Transfer Mechanism

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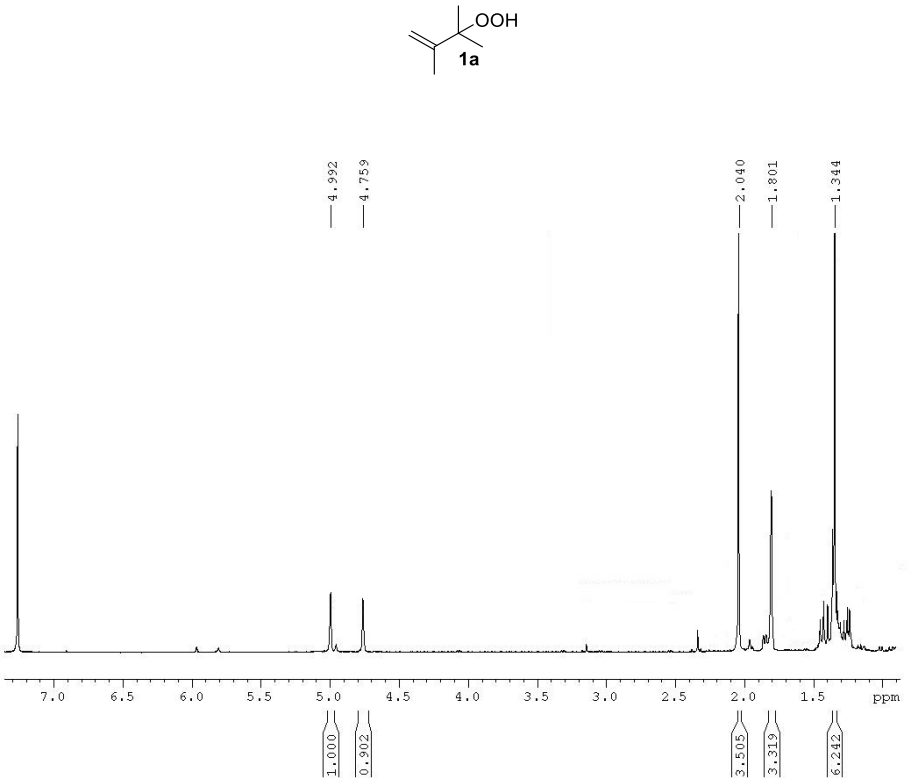
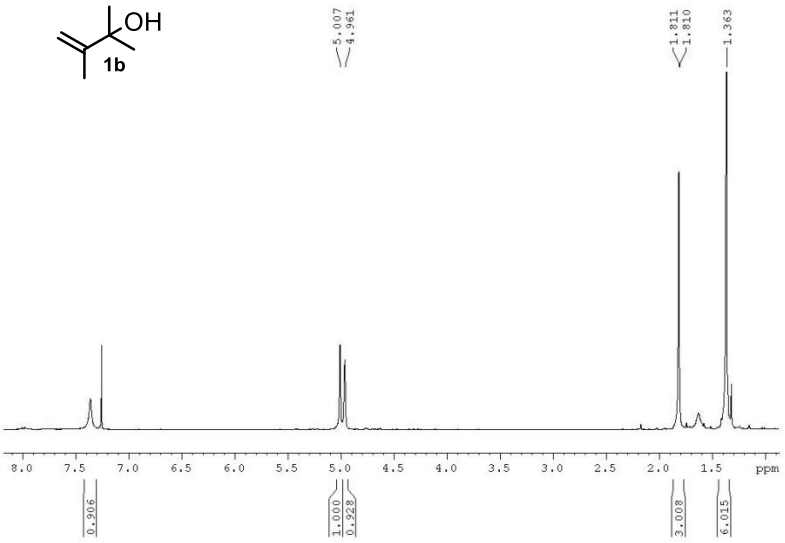
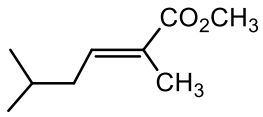
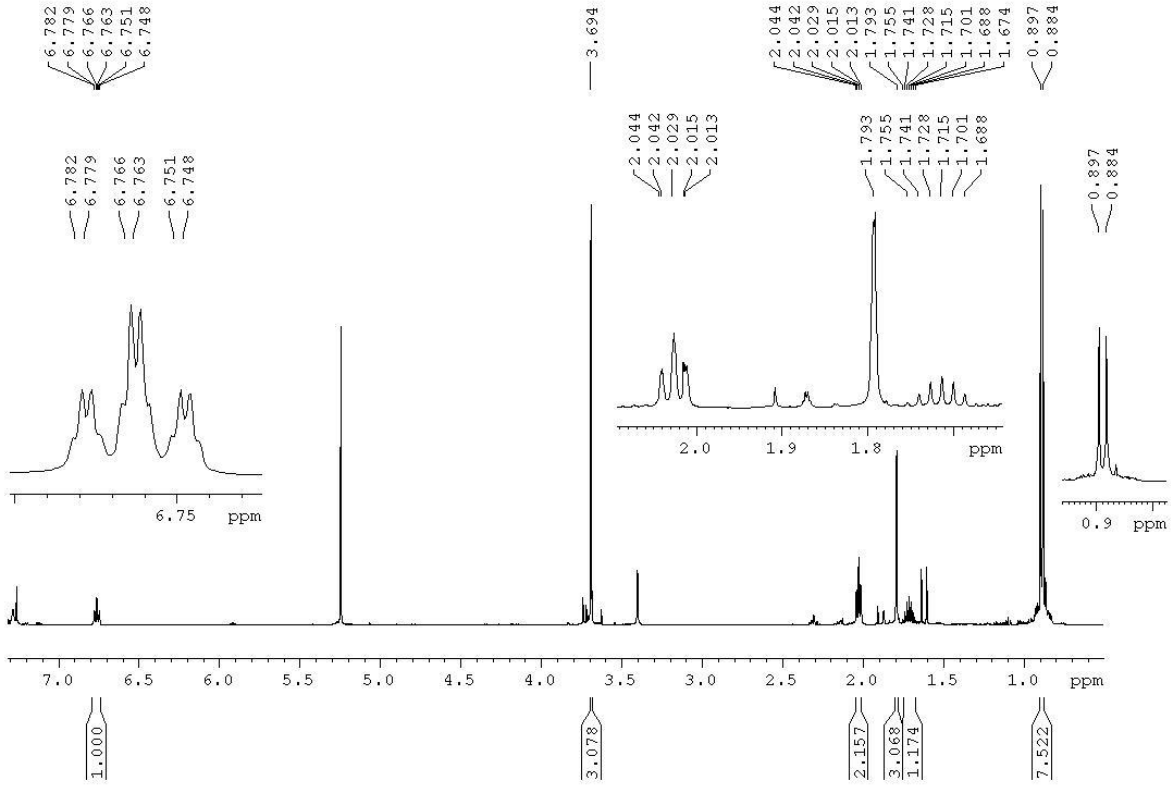
1.1 ^{1}H NMR spectra of 3-hydroperoxy-2,3-dimethylbut-1-ene (**1a**) and 2,3-dimethylbut-3-en-2-ol (**1b**)



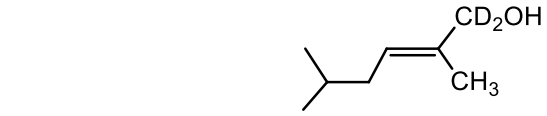


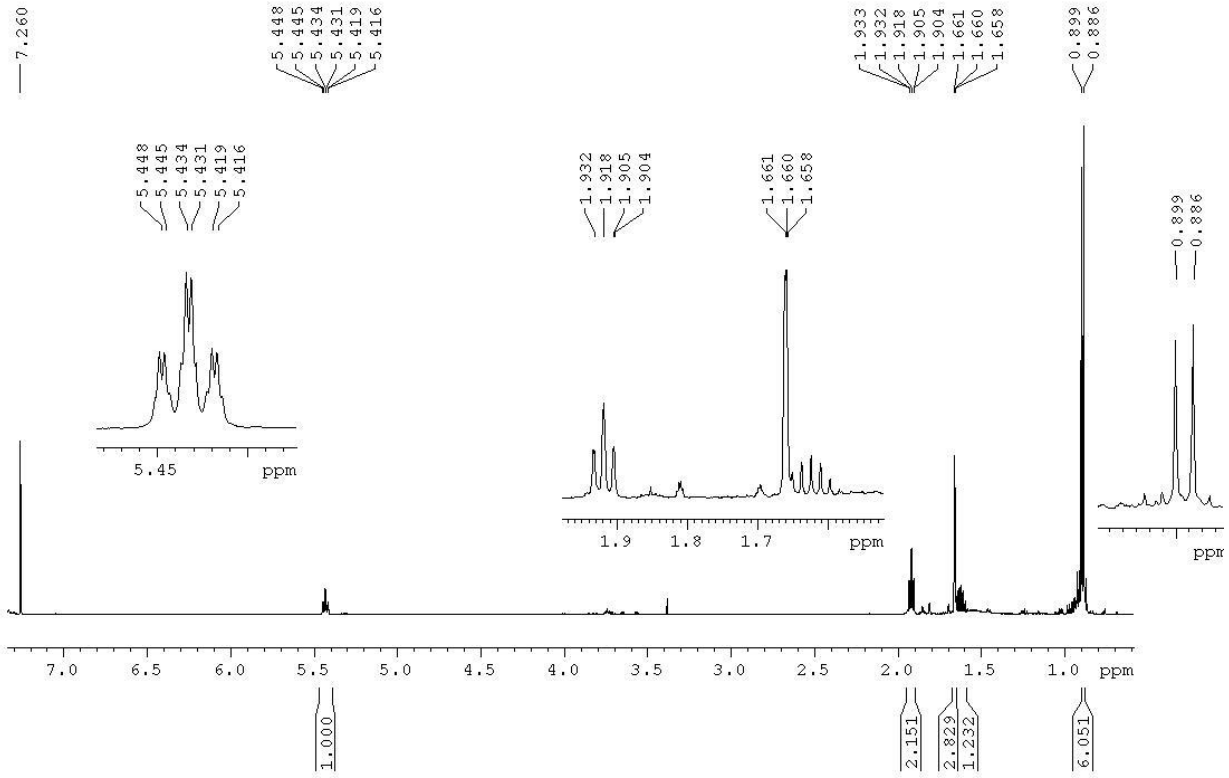
1.2 ^{1}H NMR spectrum of *E*-ester, precursor of alkene **2**



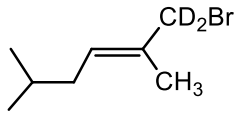


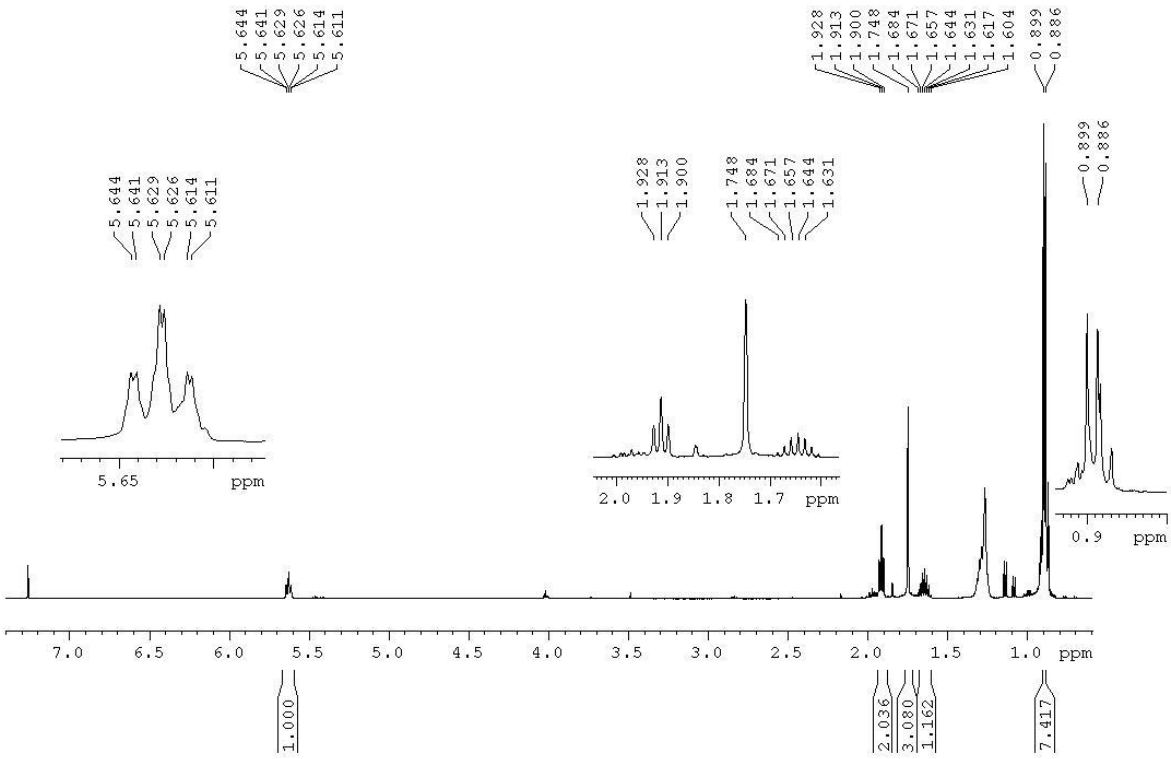
1.3 ^{1}H NMR of allylic alcohol-d_2,precursor of alkene **2**



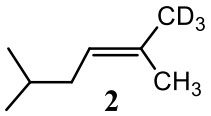


1.4 ^{1}H NMR spectrum of allylic bromide-d_2 precursor of alkene **2**

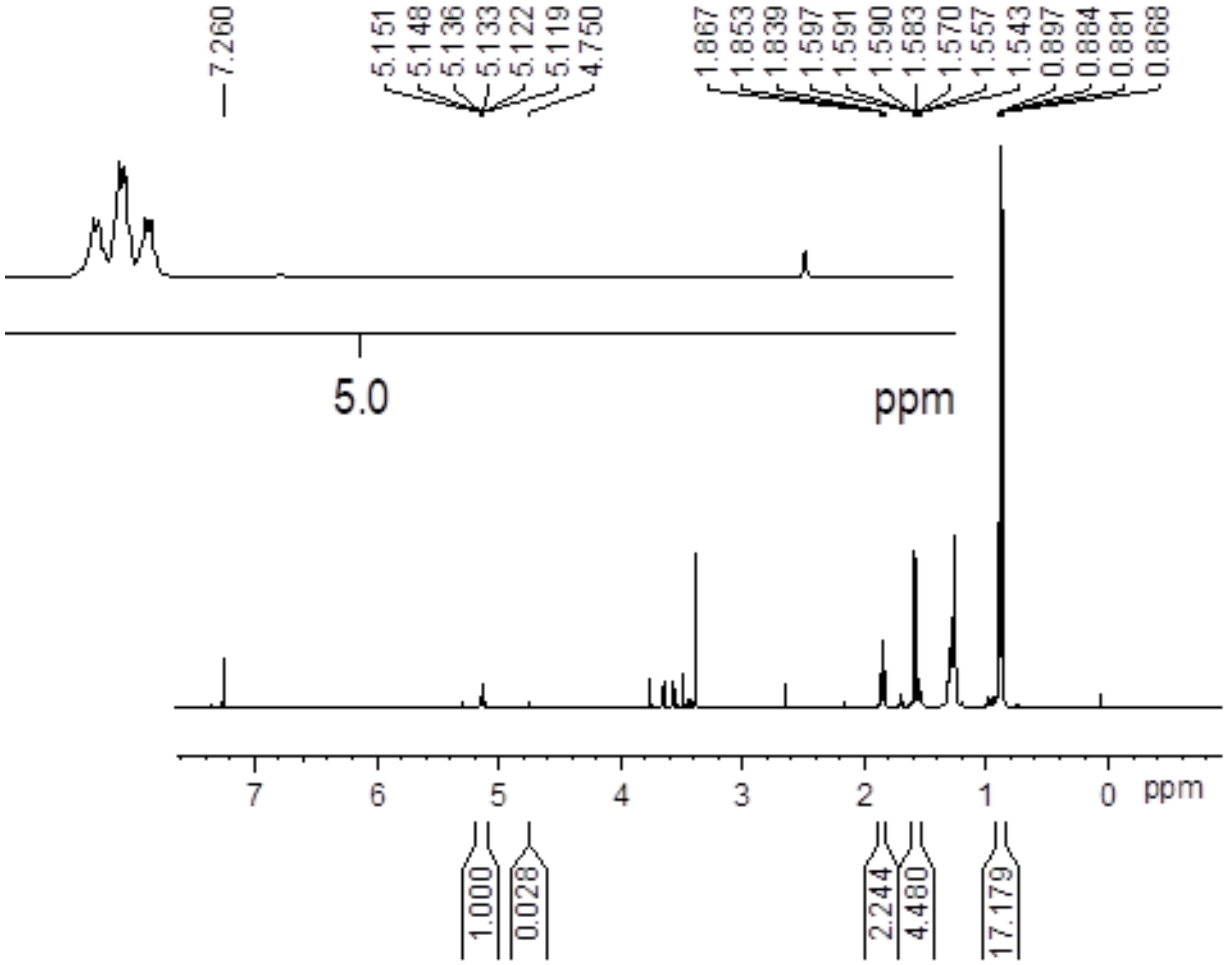




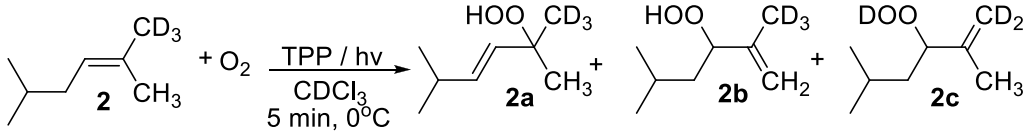
1.5 ^{1}H NMR spectrum of 2-(1,1,1-trideuteromethyl)-5-methylhex-2-ene (**2**).

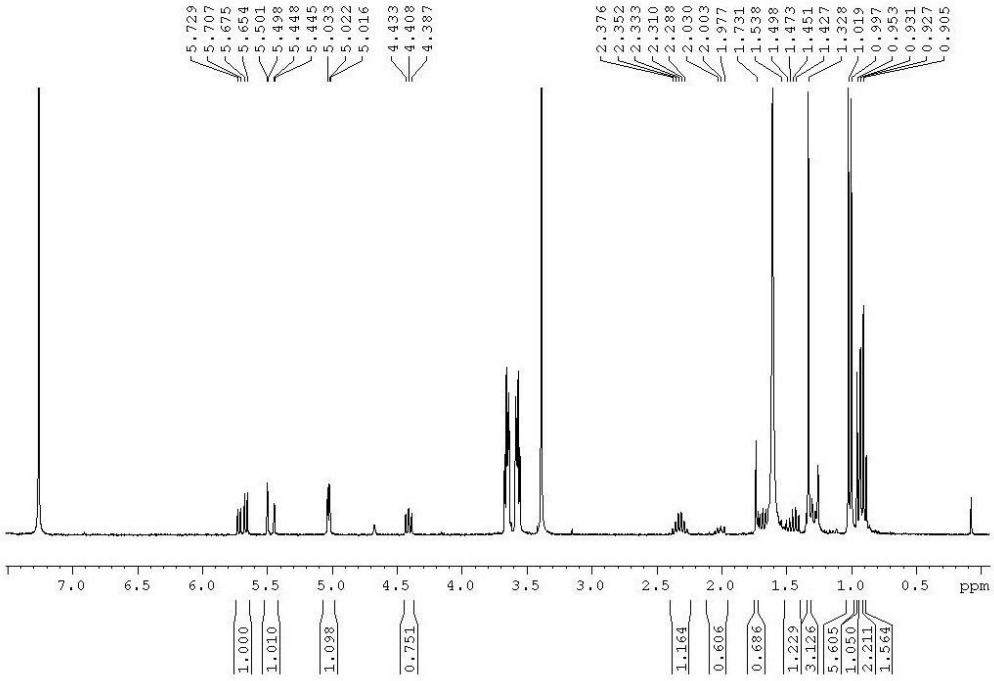


2



1.6 ^{1}H NMR spectrum of photooxidation products **2a, 2b and 2c** (TPP as the photosensitizer)





Calculation of the conversion and selectivity (Table 1, Entry 1)

	δ ($CDCl_3$)
2a	5.69 (dd, 1H, J_1=16.0 Hz, J_2=6.5 Hz), 5.47 (d, 1H, J=16.0Hz) ppm
2b	5.03 (s, 1H), 5.02 (s, 1H) ppm
2c	1.73 (s, 3H) ppm

Total amount of compounds = 2a + 2b +2c = 0 + 2.01 + 1.10+ (0.69×2/3) = 3.57 (100%)

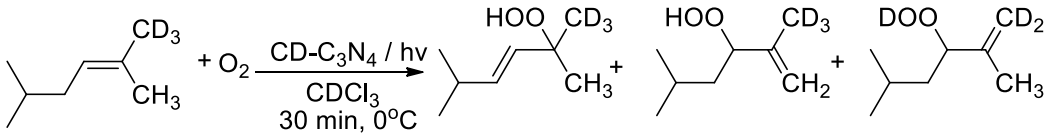
Selectivity: 2a+2b+2c= 3.57 (100%).

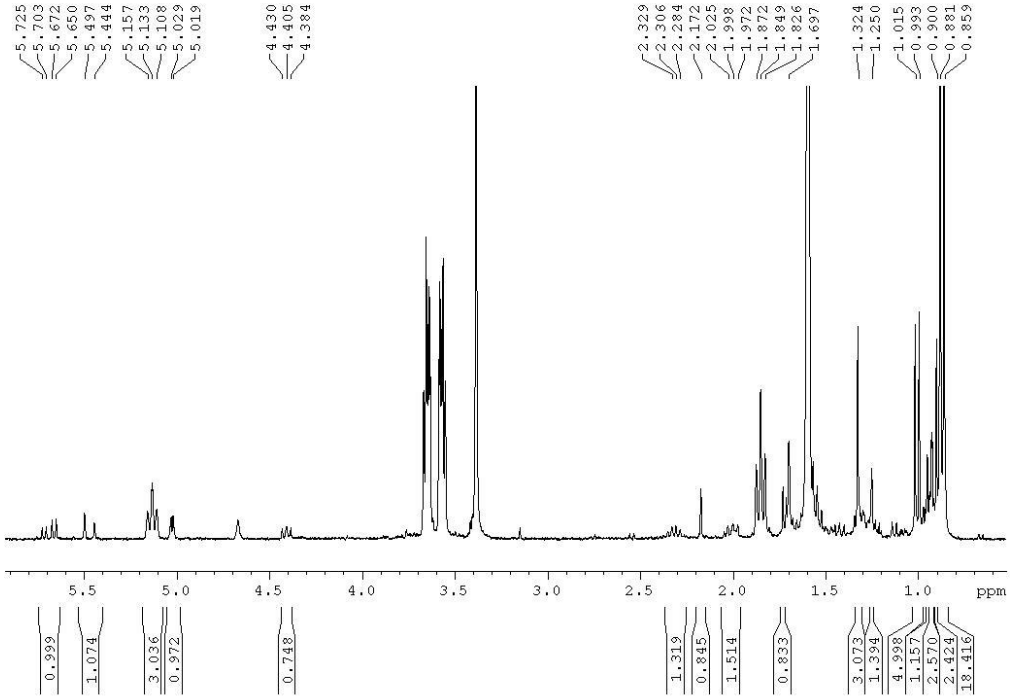
Selectivity of 2a = (2.01/3.57) ×100 = 56%

Selectivity of 2b = (1.10/3.57) ×100 = 31%

Selectivity of 2c = (0.69×2/3/3.33) ×100 = 13%

1.7 ^{1}H NMR spectrum of photooxidation products **2a, 2b, 2c** (CD-C_3N_4 as the photocatalyst)





Calculation of the conversion and selectivity (Table 1, Entry 2)

	δ ($CDCl_3$)
2a	5.69 (dd, 1H, J_1=16.0 Hz, J_2=6.5 Hz), 5.47 (d, 1H, J=16.0Hz) ppm
2b	5.03 (s, 1H), 5.02 (s, 1H) ppm and 4.41 (t, 1H) ppm
2c	4.41 (t, 1H) ppm

[4.41 (t, 1H) ppm]: 2b + 2c = 0.75

[5.03 (s, 1H), 5.02 (s, 1H) ppm]: 2b = 0.97/2=0.49 => [4.41 (t, 1H) ppm]: 2c = 0.75-0.49 = 0.26

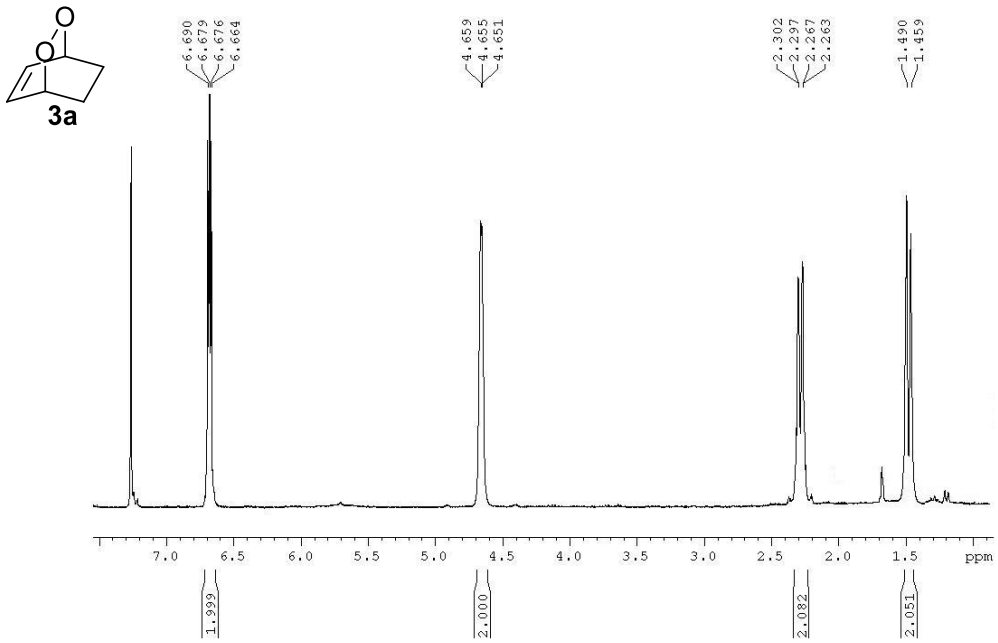
Selectivity = 2a + 2b +2c = 2.07 + 0.97 + (0.26×2) = 3.56 (100%)

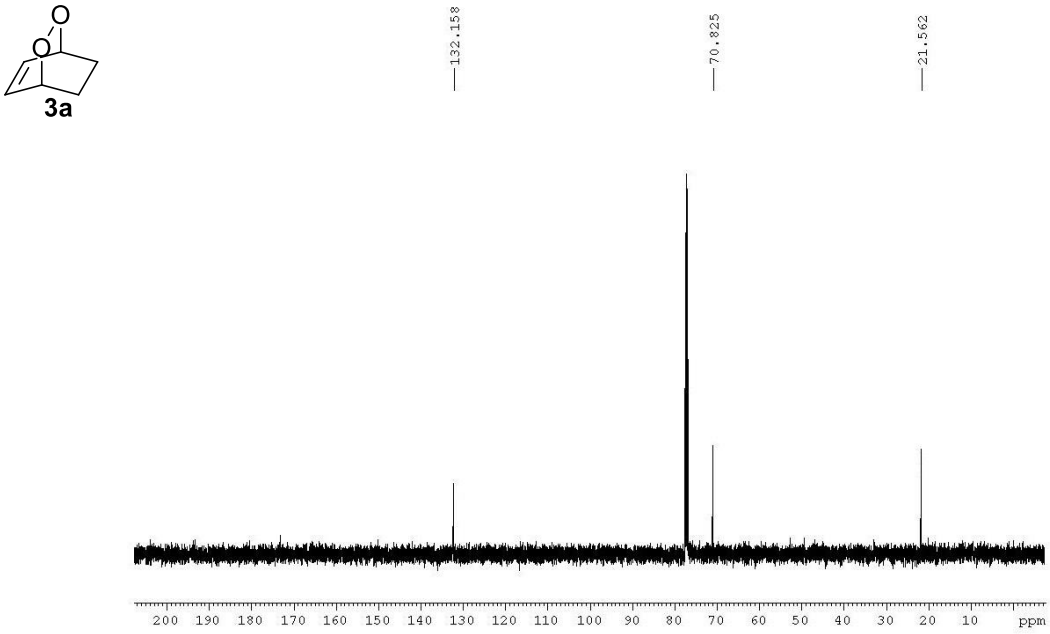
Selectivity of 2a = (2.07/3.56) ×100 = 58%

Selectivity of 2b = (1.03/3.56) ×100 = 29%

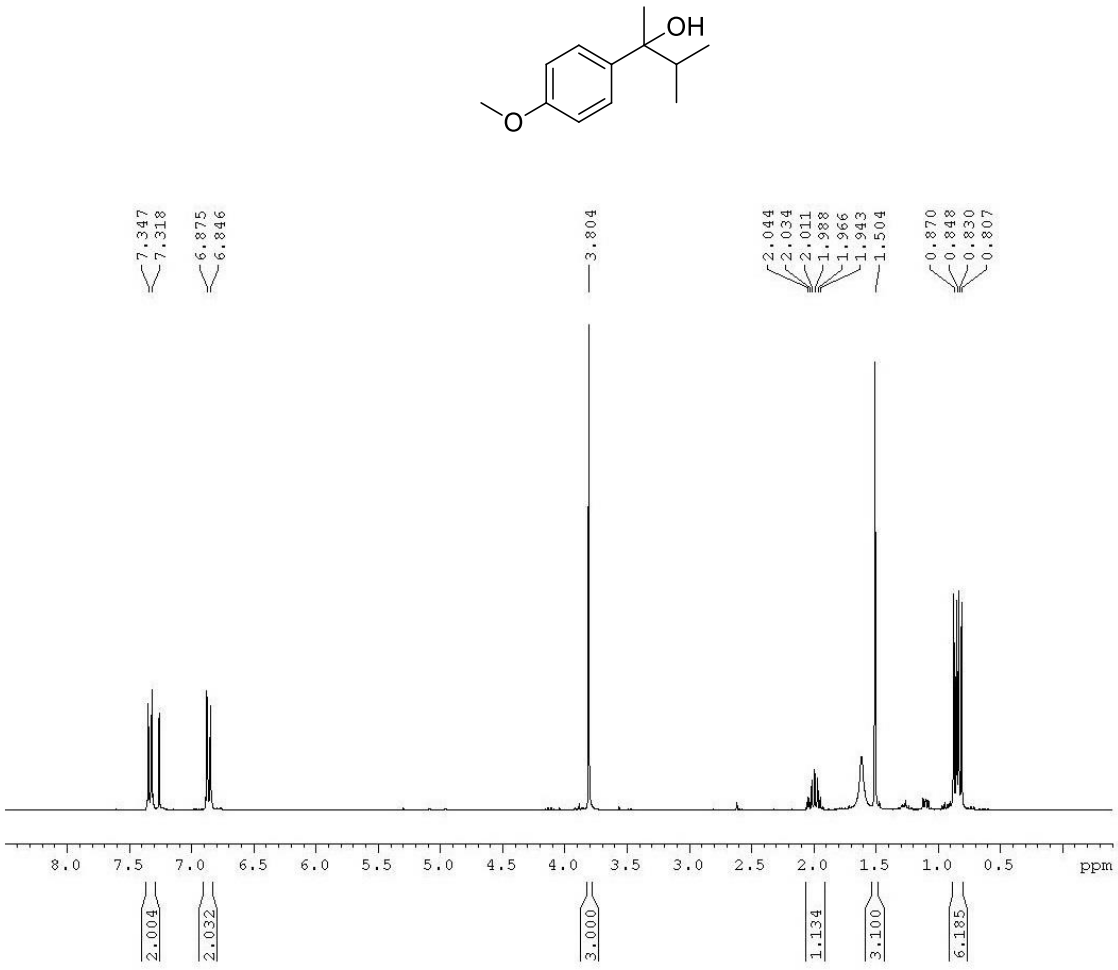
Selectivity of 4c = (0.26×2/3.56) ×100 = 13%

1.8 ^{1}H and ^{13}C NMR spectra of **3a** product of photooxidation of 1,3-cyclohexadiene **3**.

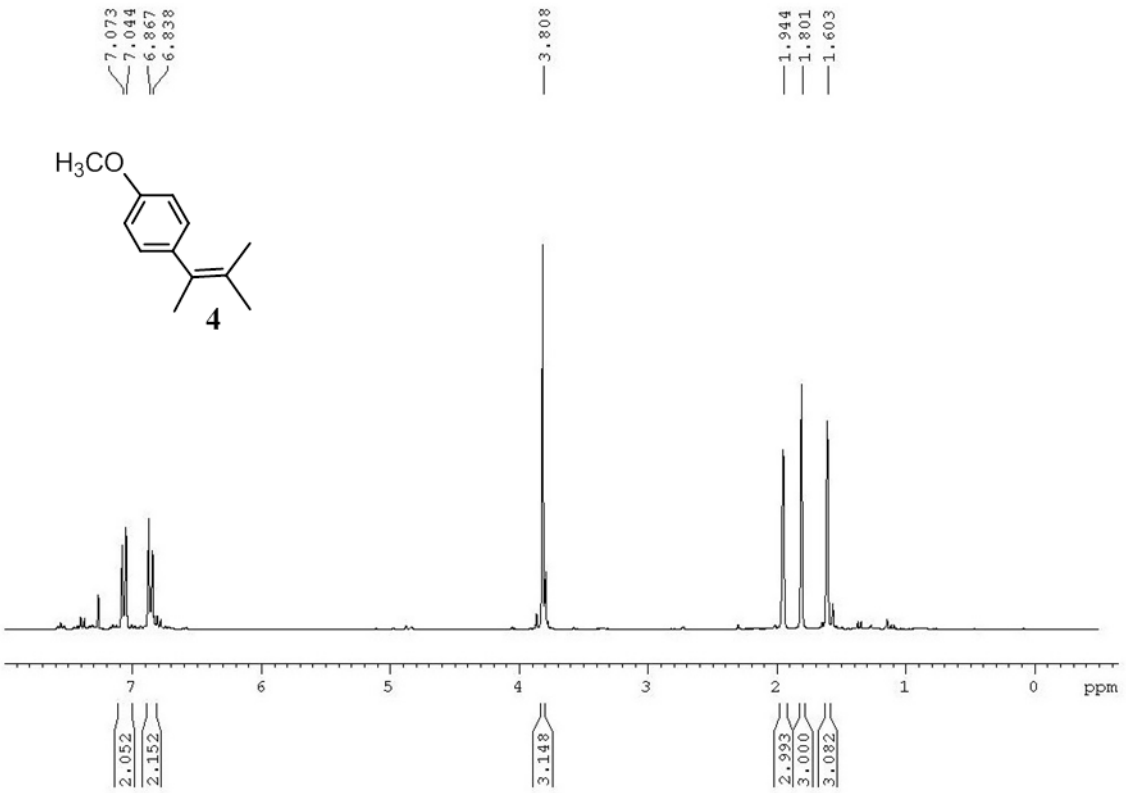


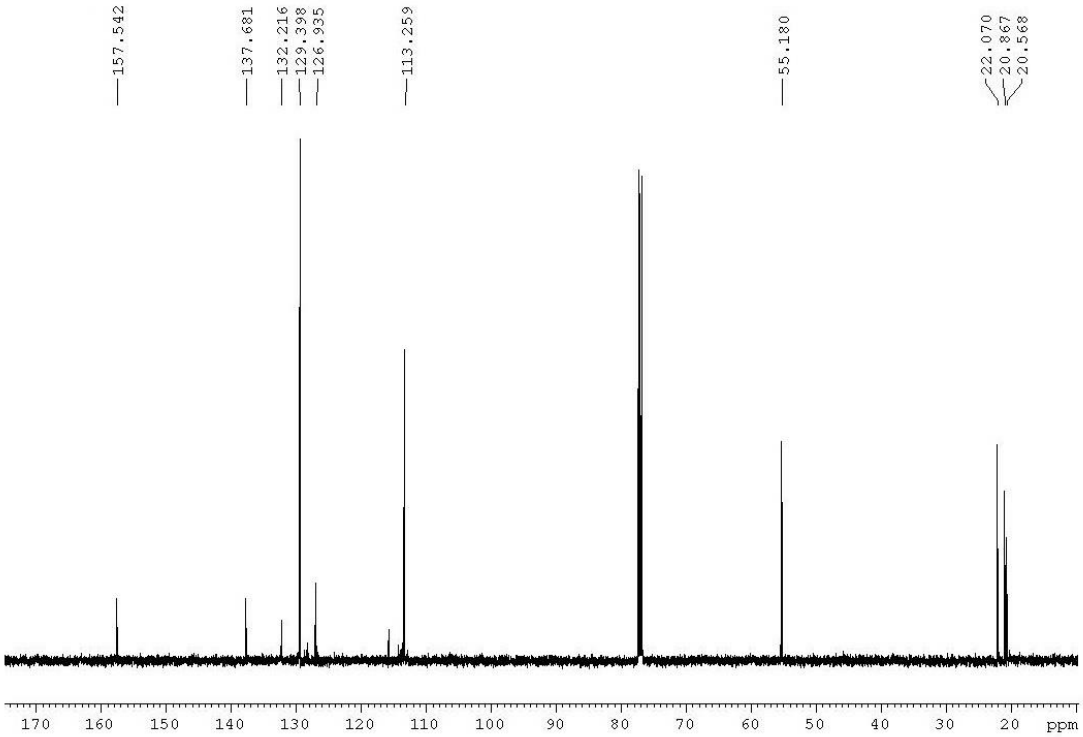


1.9 ^{1}H NMR spectrum of 2-(4-methoxyphenyl)-3-methylbutan-2-ol, precursor of **4**

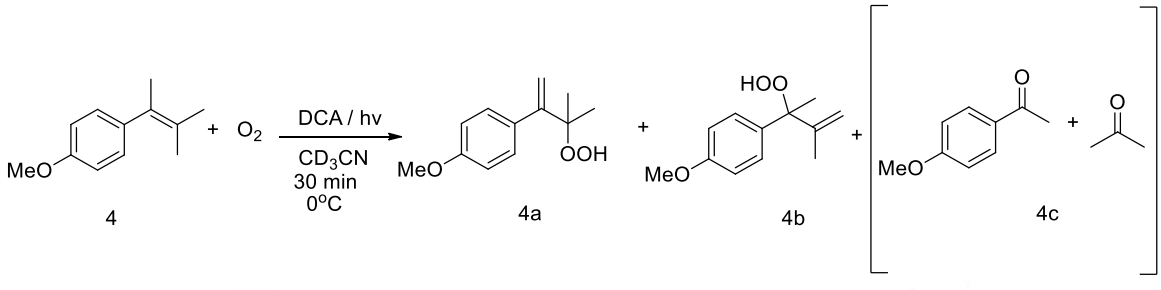


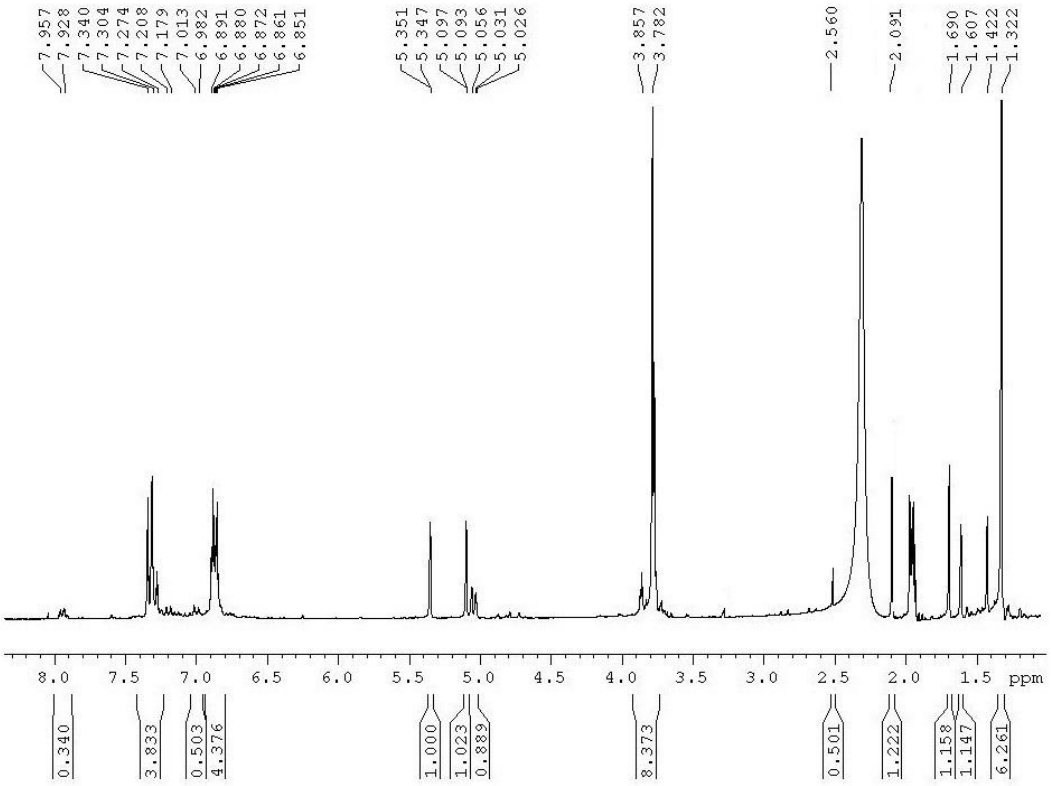
1.10 ^{1}H and ^{13}C NMR spectra of aryl alkene **4**





1.11 ^{1}H NMR (CD_3CN) spectrum of **4a, 4b, 4c**, products from the photooxidation of alkene **4**





Calculation of the conversion and selectivity (Table 2, Entry 4)

	δ (CD_3CN)
4a	5.35 (d, 1H, J=1.1Hz), 5.10 (d, 1H, J=1.1Hz) ppm
4b	5.06 (d, 1H, J=1.1Hz), 5.03 (d, 1H, J=1.1Hz) ppm
4c	2.51 (s, 3H) ppm and 2.09 (s, 6H) ppm
4	7.00 (d, 2H, J=8.7Hz) ppm

Calculation of the conversion and selectivity

Total amount of compounds 4 + 4a + 4b +4c = 0.50 + 2.02 + 0.90 + (1.22/3) = 3.83 (100%)

Unreacted material = (0.50/3.83)×100 = 13%, Conversion = 100%–13% = 87%

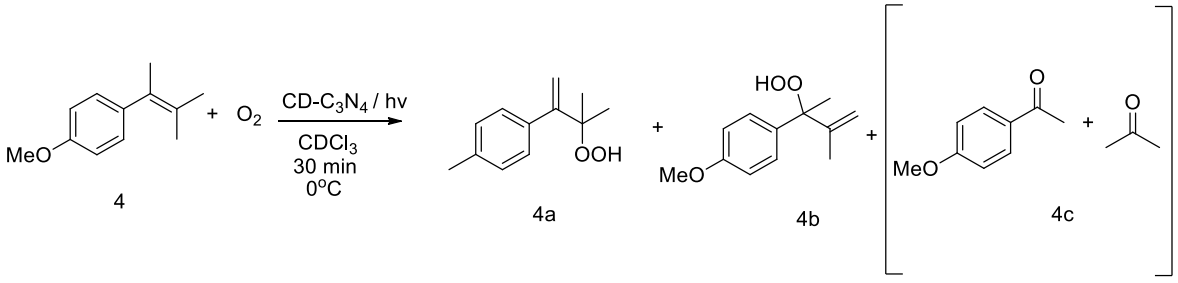
Selectivity: 4a+4b+4c= 2.02 + 0.90 + (1.22/3) = 3.33(100%).

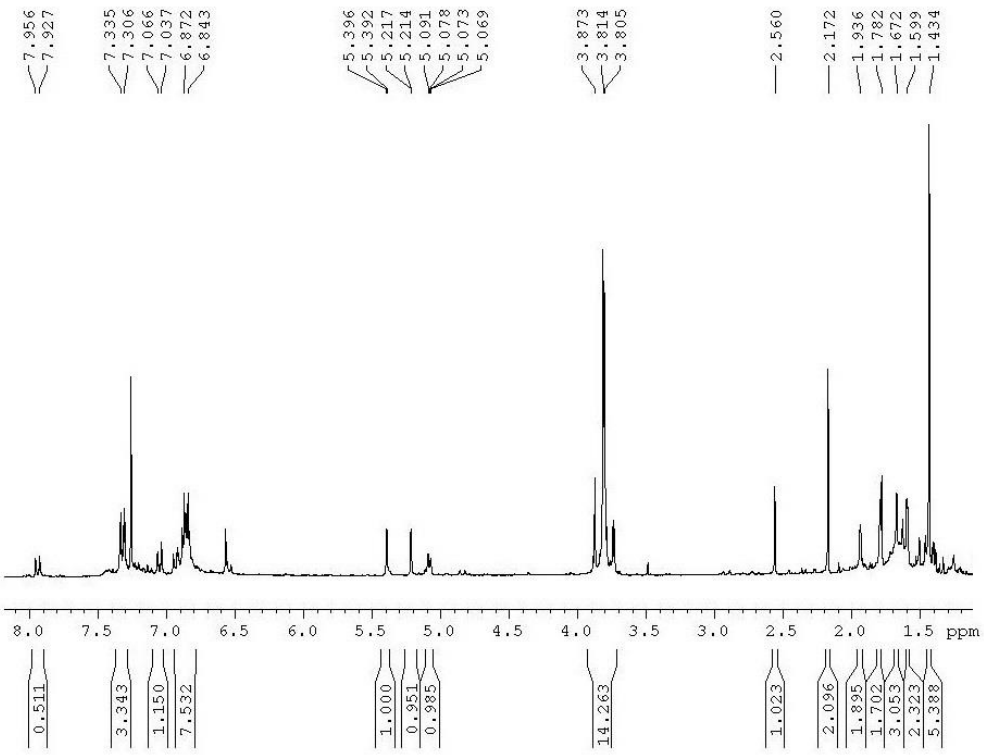
Selectivity of 4a = (2.02/3.33) ×100 = 61%

Selectivity of 4b = (0.90 /3.33) ×100 = 27%

Selectivity of 4c = ([1.22/3]/3.33) ×100 = 12%

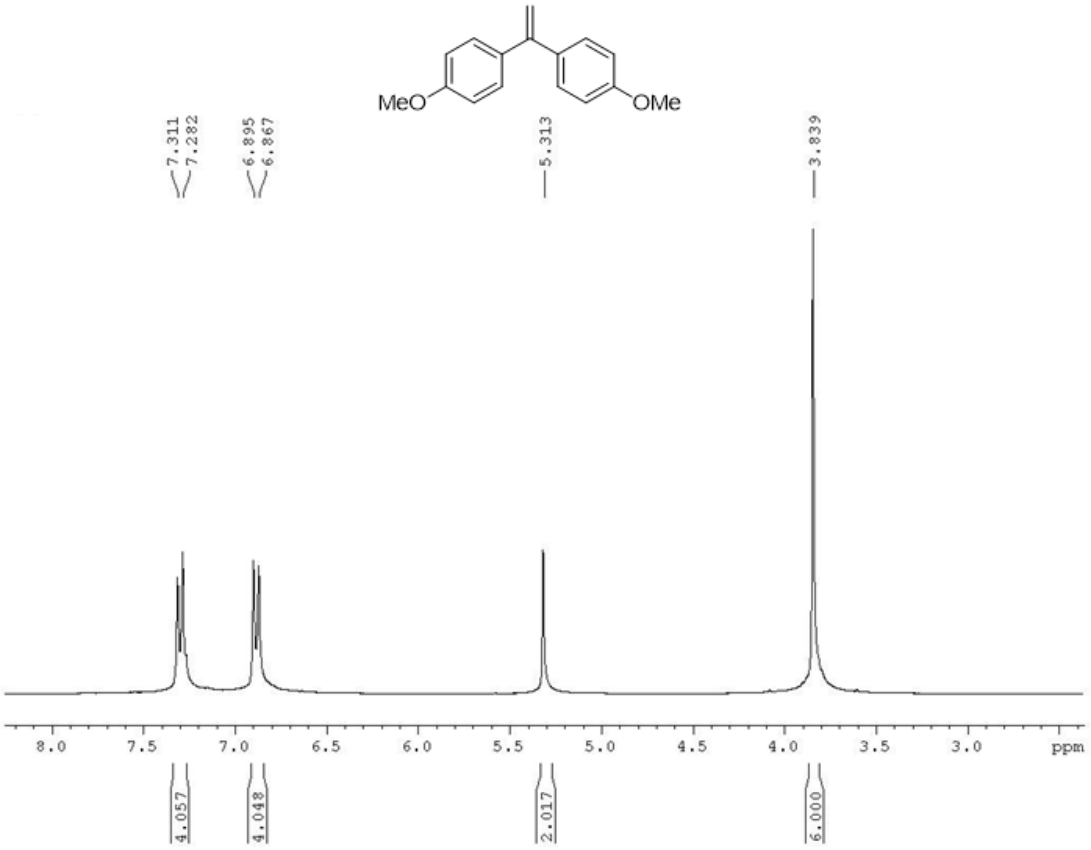
1.12 ^{1}H NMR ($CDCl_3$) spectrum of **4a, 4b, 4c**, products from the photooxidation of alkene **4**



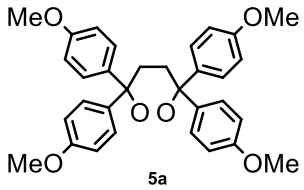


The percentage of each product was calculated from the integration of the appropriate protons using the same method as above.

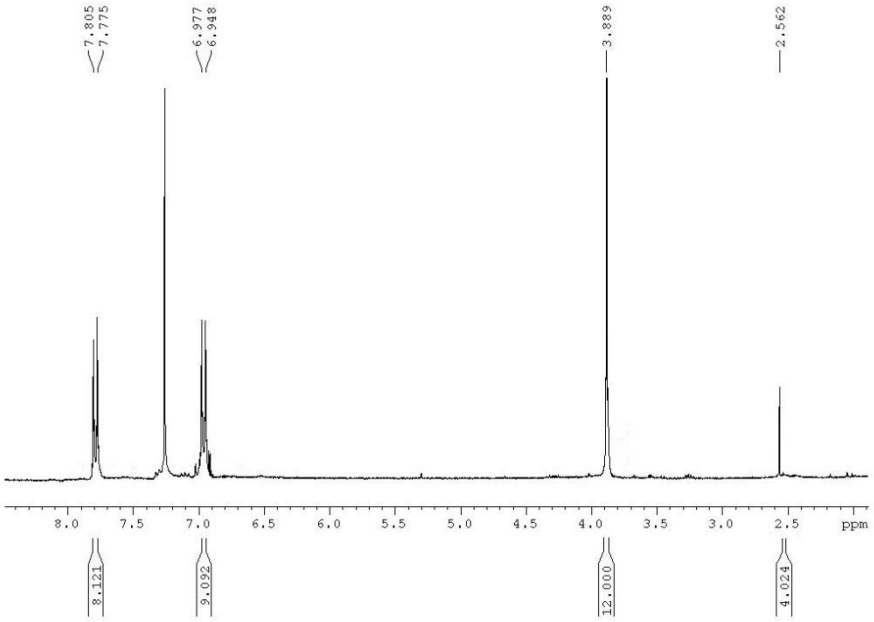
1.13 ^{1}H NMR ($CDCl_3$) spectrum of alkene **5**

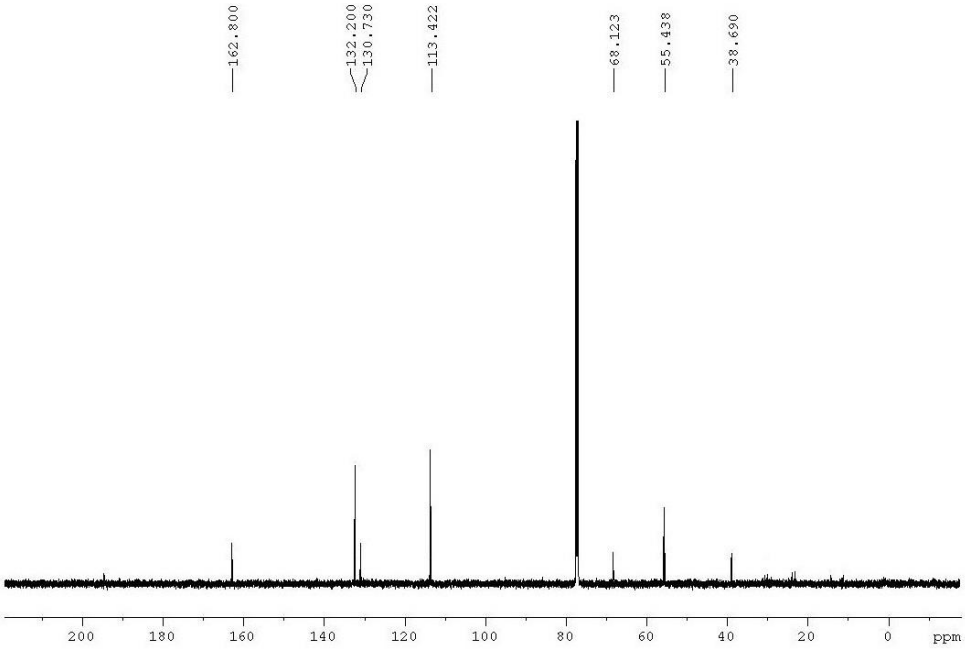


1.14 ^{1}H and ^{13}C NMR spectra of **5a** product from photooxidation of alkene **5**



5a





2. GC Chromatograms (HP-5 capillary column 30m×0.32mm×0.25µm, 5% diphenyl and 95% dimethylpolysiloxane):

The production of 3-hydroperoxy-2,3-dimethylbut-1-ene (**1a**) in solvents MeCN, $CDCl_3$, EtOAc, Hexane and CCl_4 was monitored using the following program. In case where DMSO was used, 2,3-dimethylbut-3-en-2-ol (**1b**) was monitored due to the retention time of DMSO, with the same program.

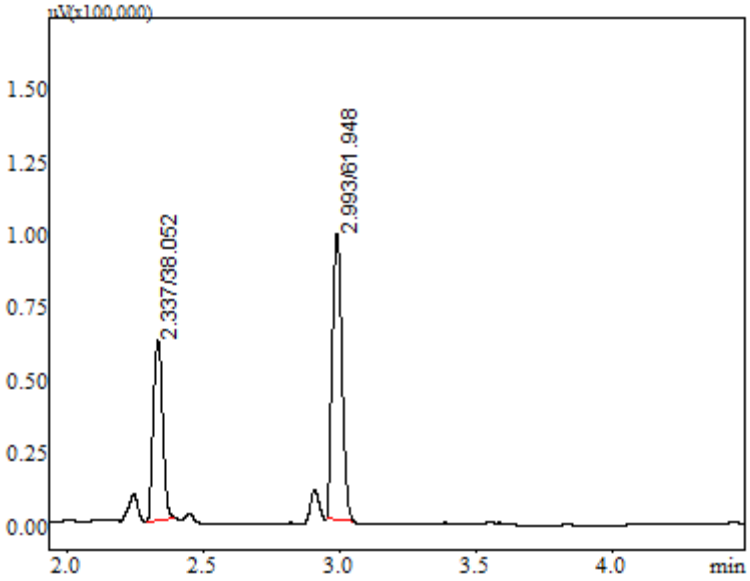
Rate (◦C/min)	Temperature (◦C)	Hold Time (min)	Column Flow
-	80.0	5.00	0.88 mL/min
5.00	100.0	5.00	
50.00	220.0	2.00	

3-hydroperoxy-2,3-dimethylbut-1-ene (**1a**): $\mathbf{t_r}$ = 2.34 min

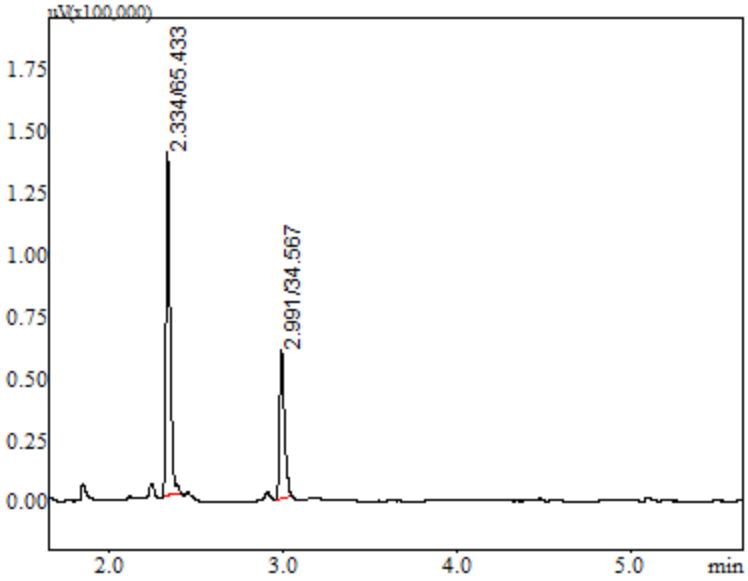
2,3-dimethylbut-3-en-2-ol (**1b**) : $\mathbf{t_r}$ = 1.50 min

diglyme: $\mathbf{t_r}$ = 3.00 min

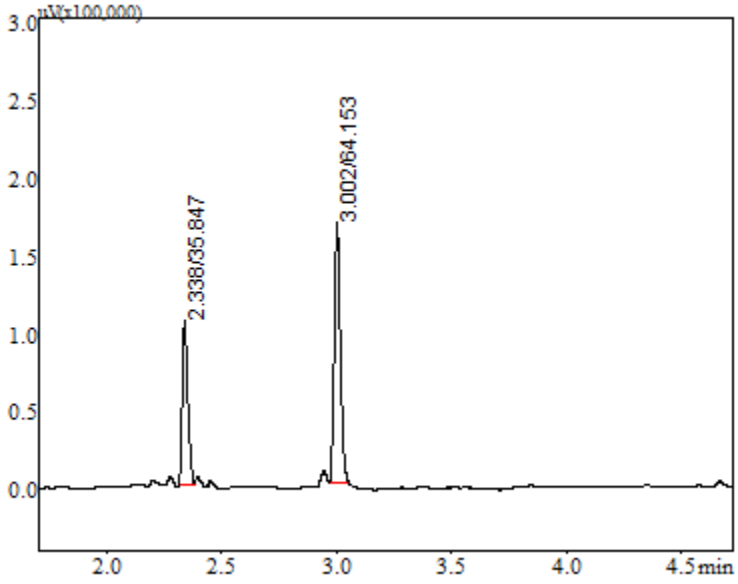
2.1. GC chromatogram of compound **1a** in Acetonitrile



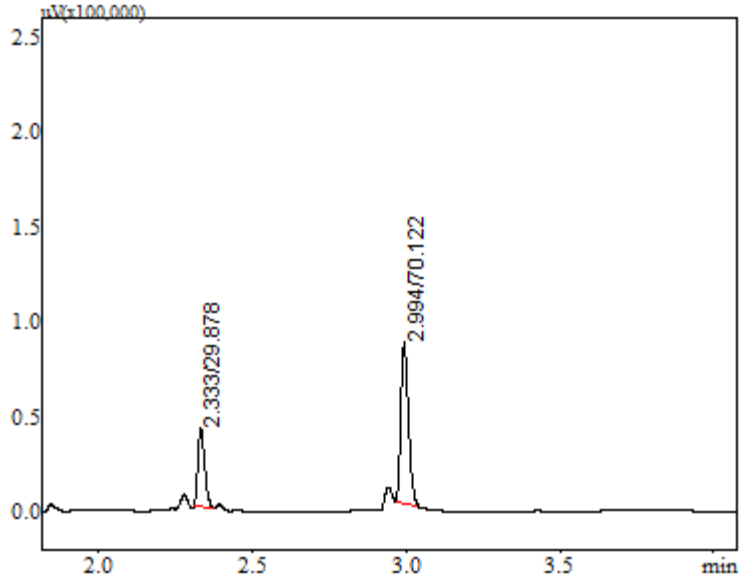
2.2. GC chromatogram of compound **1a** in Ethyl acetate



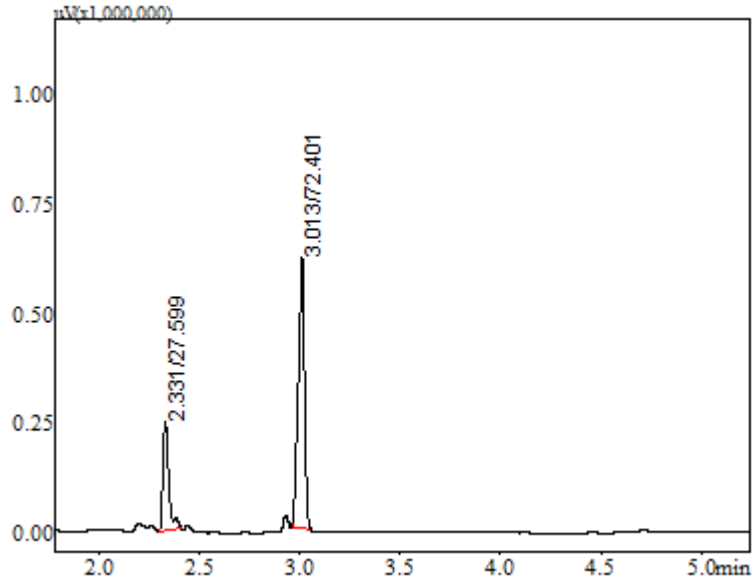
2.3 GC chromatogram of compound **1a** in Chloroform-d



2.4. GC chromatogram i of compound **1a** n Hexane



2.5. GC chromatogram of compound **1a** in Carbon tetrachloride



2.6 GC chromatogram of compound **1b** in Dimethyl sulfoxide