Novel multiple acidic ionic liquids: catalysts for environmentally friendly benign synthesis of *trans*-β-nitrostyrenes under solvent-free conditions

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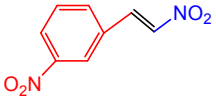
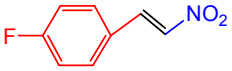
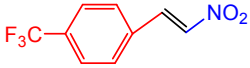
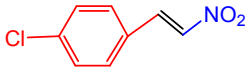
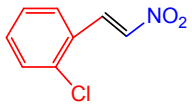
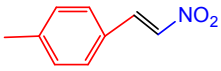
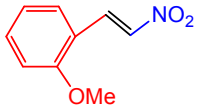
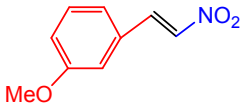
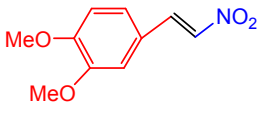
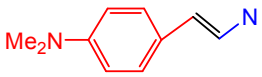
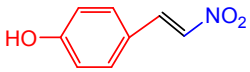
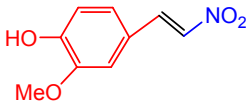
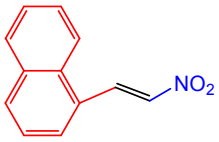
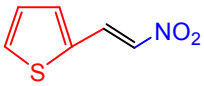
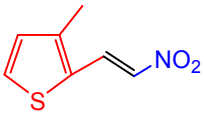
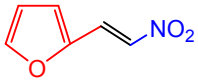
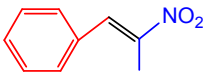
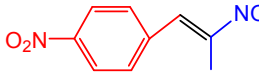
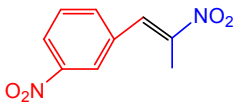
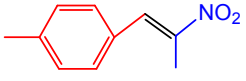
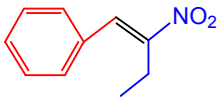
1.**Table 1** Henry reaction of various aldehydes and nitroalkanes catalyzed by [SFHEA][HSO_4][a].

Entry	Aldehyde	Nitroalkane	Time (h)	Product	Yield (%)[b]	Mp (℃)/Lit.
1	4-O_2N-C_6H_4-	CH_3NO_2	1.5		89	198-200/201[1]
2	3-O_2N-C_6H_4-	CH_3NO_2	2.0		84	124-126/122-125[2]
3	4-F-C_6H_4-	CH_3NO_2	1.5		88	99-102/101-102.5[1]
4	4-F_3C-C_6H_4-	CH_3NO_2	1.0		93	90-91/89-91[3]
5	4-Cl-C_6H_4-	CH_3NO_2	2.0		90	110-112/113-114[4]
6	2-Cl-C_6H_4-	CH_3NO_2	2.5		92	47-49/47[5]
7	4-Me-C_6H_4-	CH_3NO_2	5.0		83	103-105/103[6]
8	4-MeO-C_6H_4-	CH_3NO_2	3.0		95	85-88/84-86[6]
9	2-MeO-C_6H_4-	CH_3NO_2	3.0		88	51-53/50[7]
10	3-MeO-C_6H_4-	CH_3NO_2	3.5		90	91/91-92[8]
11	3,4-(MeO)$_2$-C_6H_4-	CH_3NO_2	4.0		86	140-142/142[9]

12	4-Me_2N-C_6H_4 -	CH_3NO_2	5.0		98	183/182-183[10]
13	4-HO-C_6H_4-	CH_3NO_2	5.0		85	168/167-168[11]
14	3-MeO,4-HO-C_6H_3-	CH_3NO_2	3.5		83	163-165/166-168[12]
15	2-Naphthyl-	CH_3NO_2	4.0		96	86/84-86[13]
16	2-Thienyl-	CH_3NO_2	2		87	78-80/79-80[14]
17	3-Methyl-2-thienyl-	CH_3NO_2	3.5		81	63-64
18	2-Furyl-	CH_3NO_2	5.0		80	74-76/72-74[15]
19	C_6H_5-	$CH_3CH_2NO_2$	3.5		86	64/64-65[15]
20	4-O_2N-C_6H_4-	$CH_3CH_2NO_2$	3.0		83	116/114-115[3]
21	3-O_2N-C_6H_4-	$CH_3CH_2NO_2$	3.0		78	55
22	4-Me-C_6H_4-	$CH_3CH_2NO_2$	6.5		83	53-55/55[7]

23	C_6H_5-	$CH_3(CH_2)_2N$ O_2		0	-

[a] Reaction conditions: the mixture of aldehydes (5 mmol) and nitroalkanes (5 mmol) was stirred in the presence of 20 mol % [SFHEA][HSO_4] at 110 ℃ under solvent-free conditions. [b] Isolated yield.

2. FT-IR, NMR spectral and elemental analysis datas of four novel ILs:

[SFHEA][HSO_4] FT-IR (NaCl) 1491, 878, 773 cm^{-1}. ^1H NMR (400 MHz, D_2O): δ=3.43 (t, 2H, *J*=4.0 Hz), 2.76 (t, 2H, *J*=4.0 Hz); ^{13}C NMR (100 MHz, D_2O): δ=57.4, 41.1. Anal. Calcd for $C_2H_9NO_{11}S_3$: C, 7.52; H, 2.84; N, 4.39; O, 55.12, S, 30.13; Found: C, 7.47; H, 2.91; N, 4.32; O, 55.27; S, 30.03.

[SFHEA][NO_3] FT-IR (NaCl) 1504, 881, 764 cm^{-1}. ^1H NMR (400 MHz, D_2O): δ=3.93 (t, 2H, *J*=3.6 Hz), 2.99 (t, 2H, *J*=3.6 Hz); ^{13}C NMR (100 MHz, D_2O): δ=64.1, 38.6. Anal. Calcd for $C_2H_8N_2O_{10}S_2$: C, 8.45; H, 2.84; N, 9.86; O, 56.29, S, 22.56; Found: C, 8.41; H, 2.89; N, 9.78; O, 56.41; S, 22.51.

[SFHEA][CF_3COO] FT-IR (NaCl) 1504, 883, 771 cm^{-1}. ^1H NMR (400 MHz, D_2O): δ=3.87 (t, 2H, *J*=4.0 Hz), 2.93 (t, 2H, *J*=4.0 Hz); ^{13}C NMR (100 MHz, D_2O): δ=164.5, 63.7, 56.8, 38.3. Anal. Calcd for $C_4H_8F_3NO_9S_2$: C, 14.33; H, 2.41; F, 17.00; N, 4.18; O, 42.95, S, 19.13; Found: C, 14.27; H, 2.47; F, 16.97; N, 4.12; O, 43.09; S, 19.08.

[SFHEA][CH_3SO_3] FT-IR (NaCl) 1504, 881, 768 cm^{-1}. ^1H NMR (400 MHz, D_2O): δ=3.91 (t, 2H, *J*=4.0 Hz), 2.98 (t, 2H, *J*=4.0 Hz), 2.43 (s, 3H); ^{13}C NMR (100 MHz, D_2O): δ=63.9, 57.1, 38.0, 37.8. Anal. Calcd for $C_3H_{11}NO_{10}S_3$: C, 11.36; H, 3.49; N, 4.41; O, 50.42, S, 30.32; Found: C, 11.31; H, 3.55; N, 4.36; O, 50.53; S, 30.25.

3. Representative ^{1}H NMR, Mass spectra and elemental analysis of products

4-Methyoxy-*trans*-β-nitrostyrene (Table 3, entry 8)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, 1H, *J*=2.8 Hz), 7.54-7.50 (m, 3H), 6.95 (d, 2H, *J*=7.2 Hz), 3.87 (s, 3H); ESI-MS: m/z= 180 [M+H]; Anal. Calc. for $C_9H_9O_3N$: C 60.28, H 5.09, O 26.80, N 7.83. Found: C 60.35, H 5.05, O 26.78, N 7.82.

3-Methyl-2-(2-nitroethenyl)-thiophene (Table 3, entry 17)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, 1H, *J*=10.8 Hz), 7.45-7.42 (m, 2H), 6.96 (d, 1H, *J*=4.0 Hz), 2.42 (s, 3H); ESI-MS: m/z= 170 [M+H]; Anal. Calc. for $C_7H_7O_2NS$: C 49.52, H 4.25, O 18.93, S 18.86, N 8.44. Found: C 49.70, H 4.17, O 18.91, S 18.95, N 8.27 .

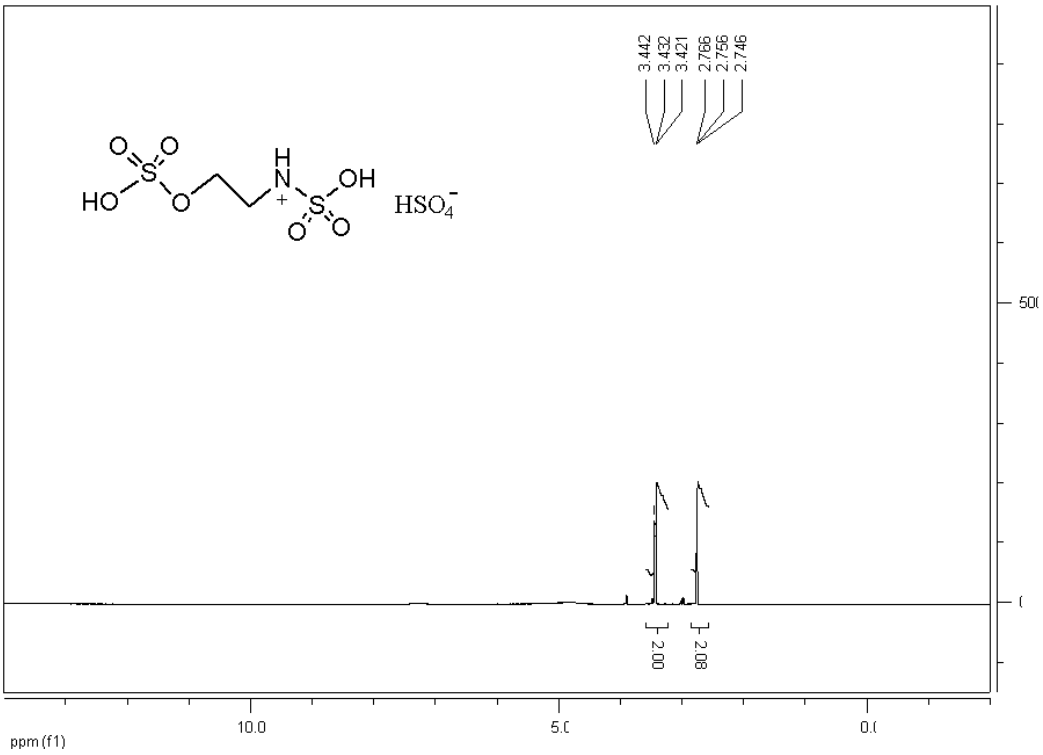
1-Nitro-4-[(1*E*)-2-nitro-1-propen-1-yl]-benzene (Table 3, entry 20)

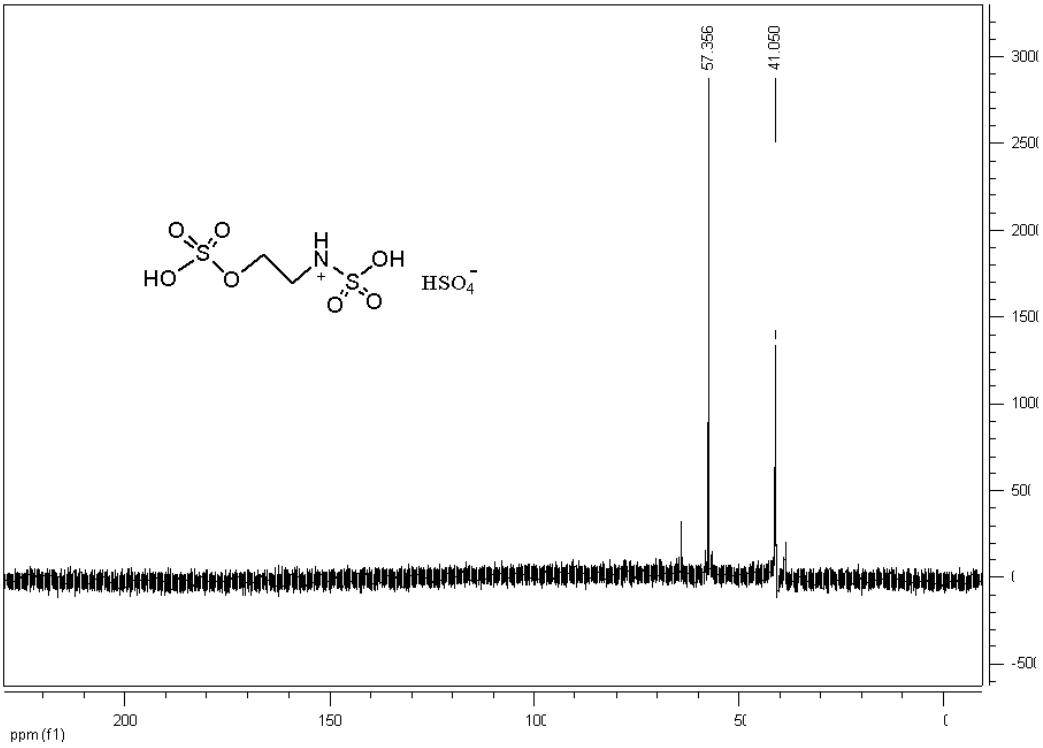
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, 2H, *J*=6.0 Hz), 8.10 (s, 1H), 7.60 (d, 2H, *J*=6.0 Hz), 2.47 (s, 3H); ESI-MS: m/z= 209 [M+H]; Anal. Calc. for $C_9H_8O_4N_2$: C 51.86, H 3.91, O 30.76, N 13.47. Found: C 51.94, H 3.87, O 30.74, N 13.45.

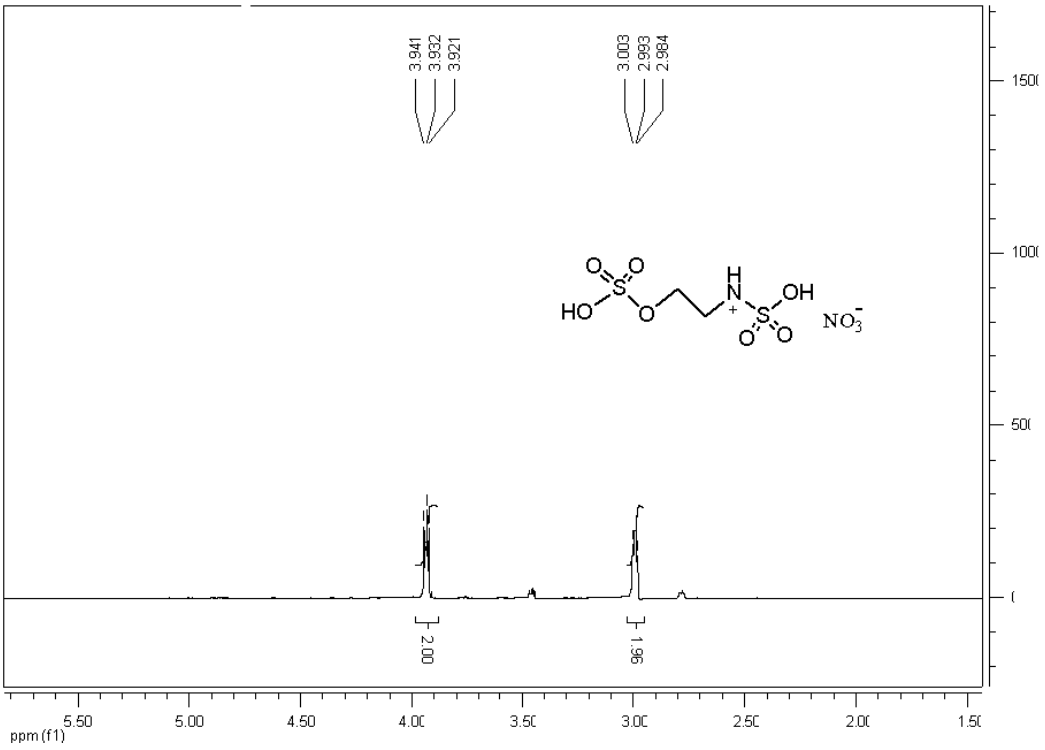
1-Nitro-3-[(1*E*)-2-nitro-1-propen-1-yl]-benzene (Table 3, entry 21)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.45 (s, 1H), 8.34-8.33 (m, 1H), 8.13 (d, 1H, *J*=6.4 Hz), 7.65 (t, 1H, *J*=6.4 Hz), 2.27 (s, 3H); ESI-MS: m/z= 209 [M+H]; Anal. Calc. for $C_9H_8O_4N_2$: C 51.83, H 3.98, O 30.81, N 13.38. Found: C 51.94, H 3.87, O 30.74, N 13.45.

4. Copies of ^{1}H and ^{13}C NMR of the novel ionic liquids



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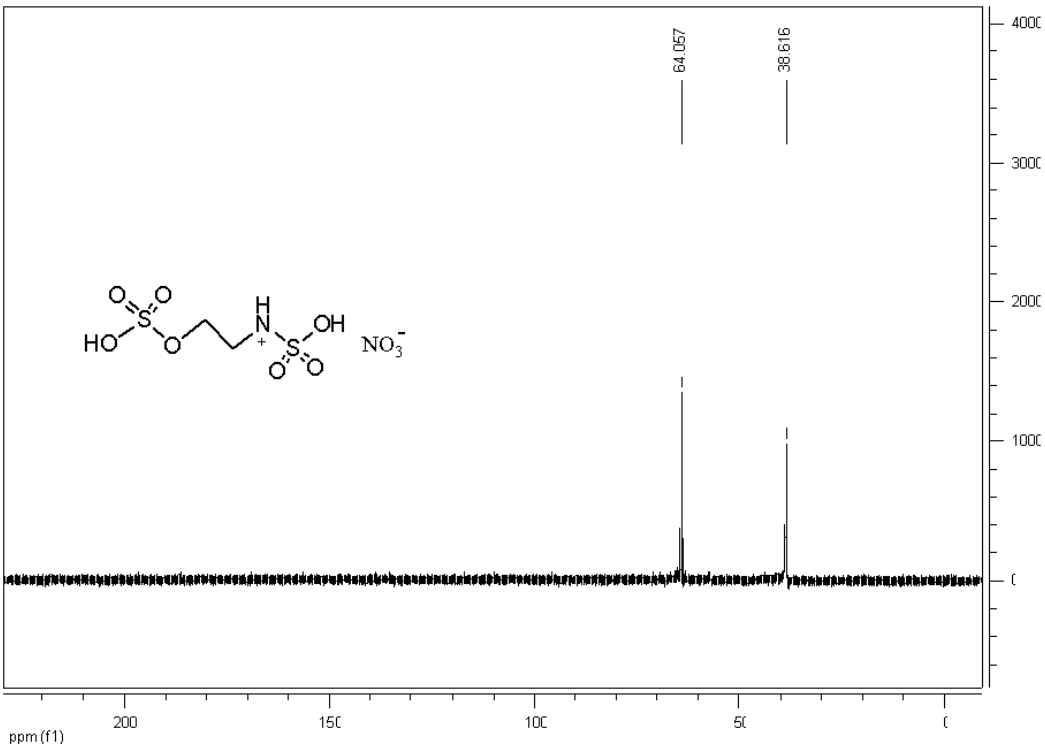
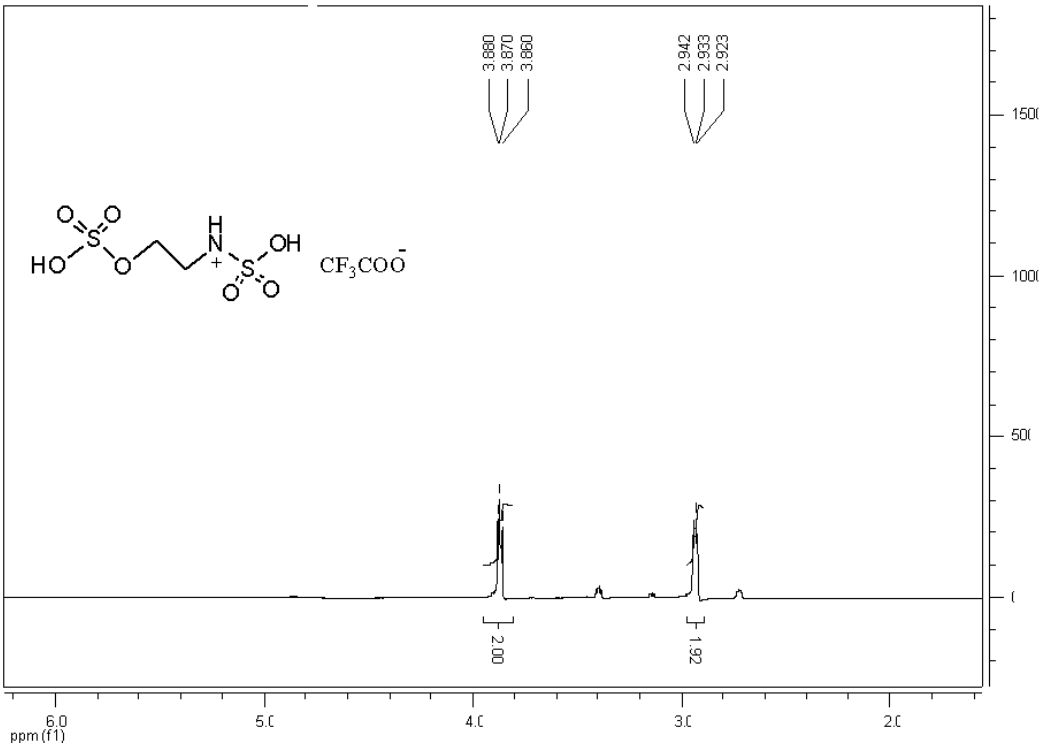
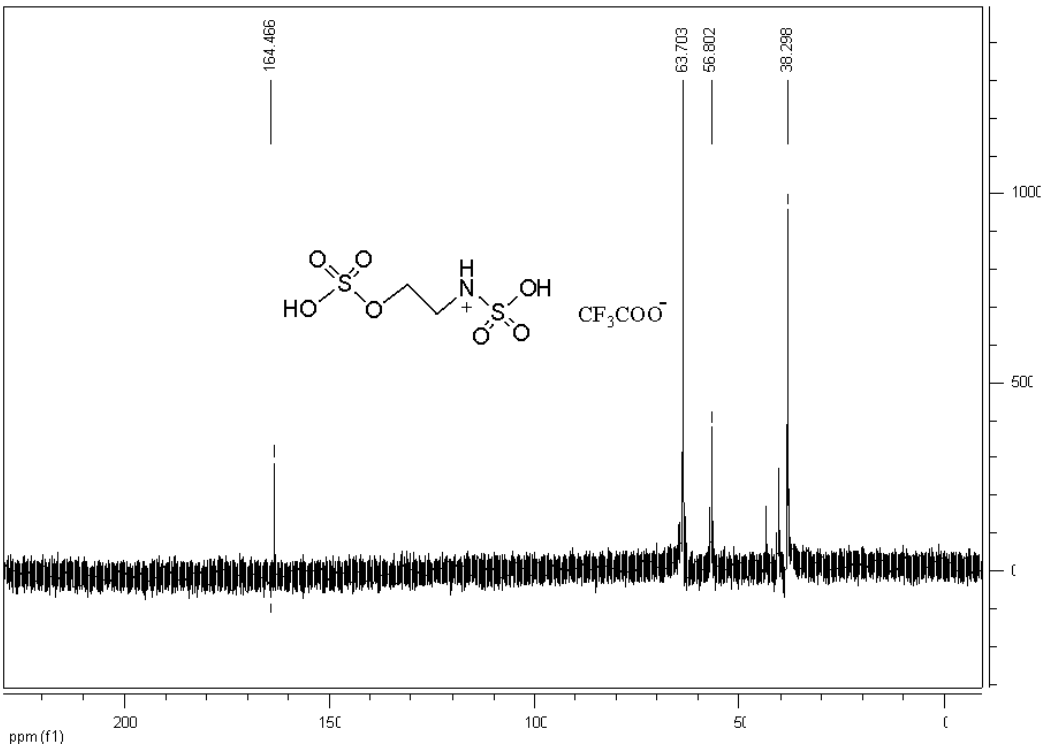
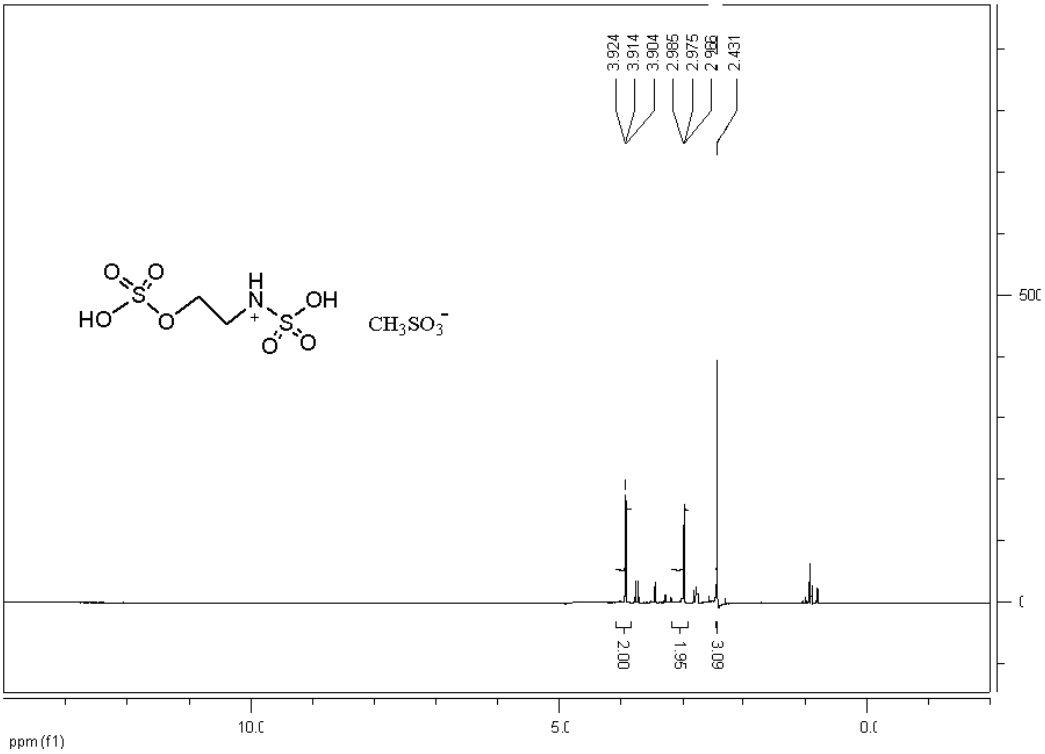
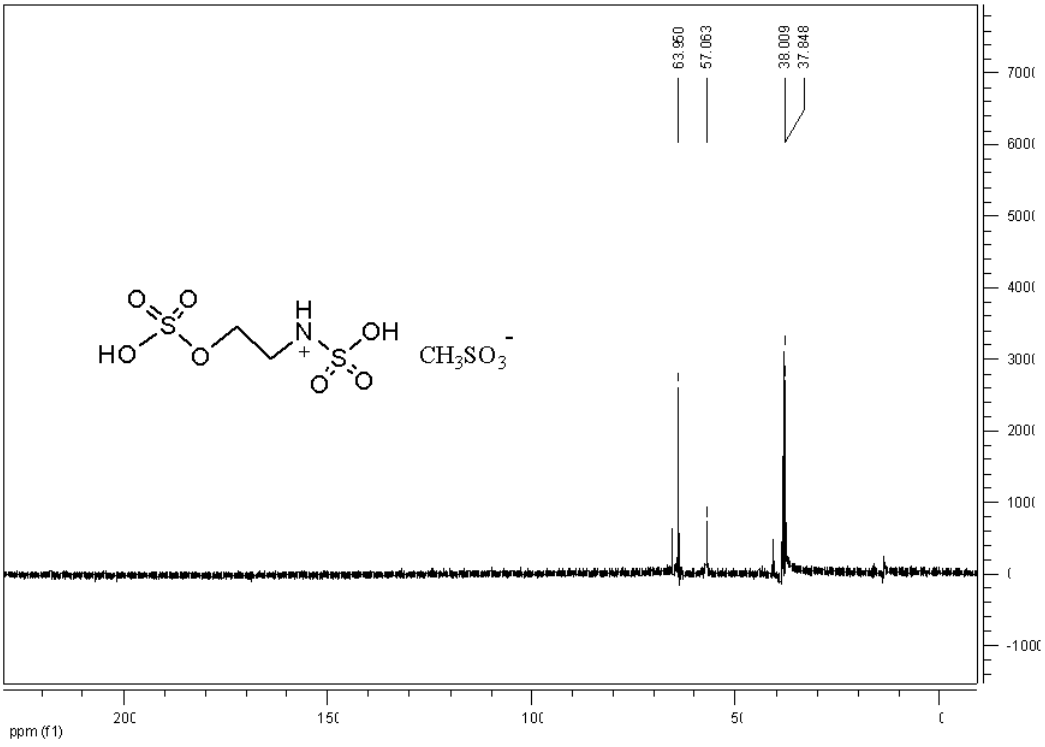
3.932
3.921
3.003
2.993
2.984
2.00
1.96
ppm (f1)


64.057
38.616
ppm (f1)

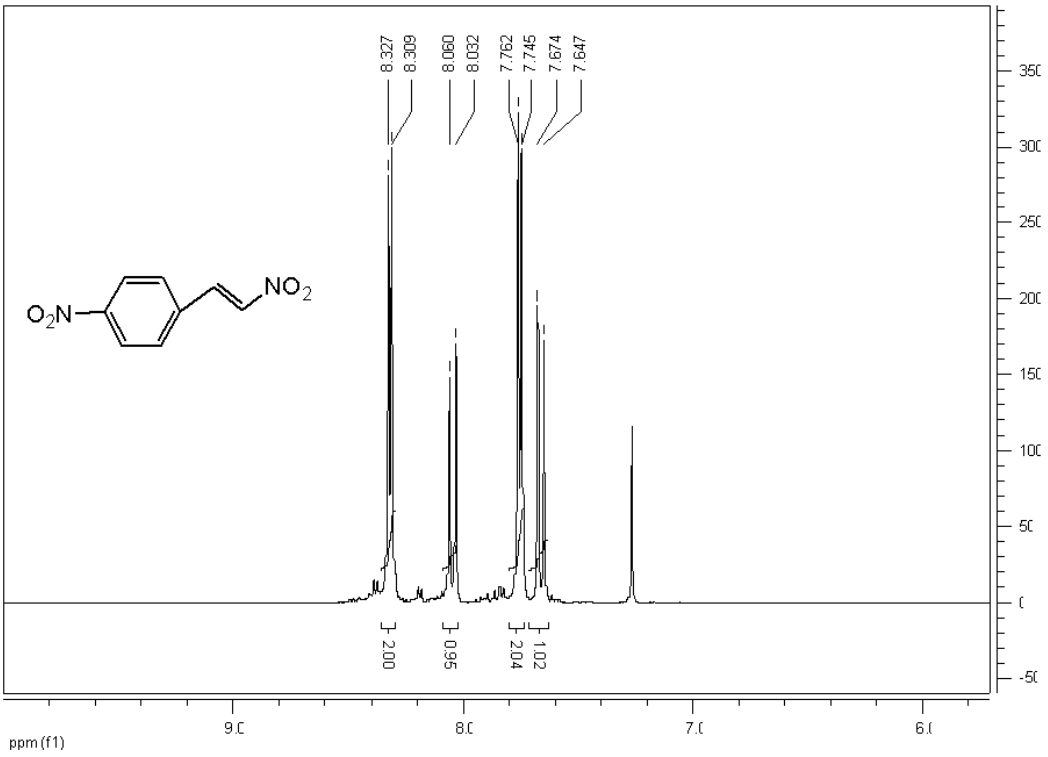

3.880
3.870
3.860
2.942
2.933
2.923
CF3COO-
2.00
1.92
ppm (f1)

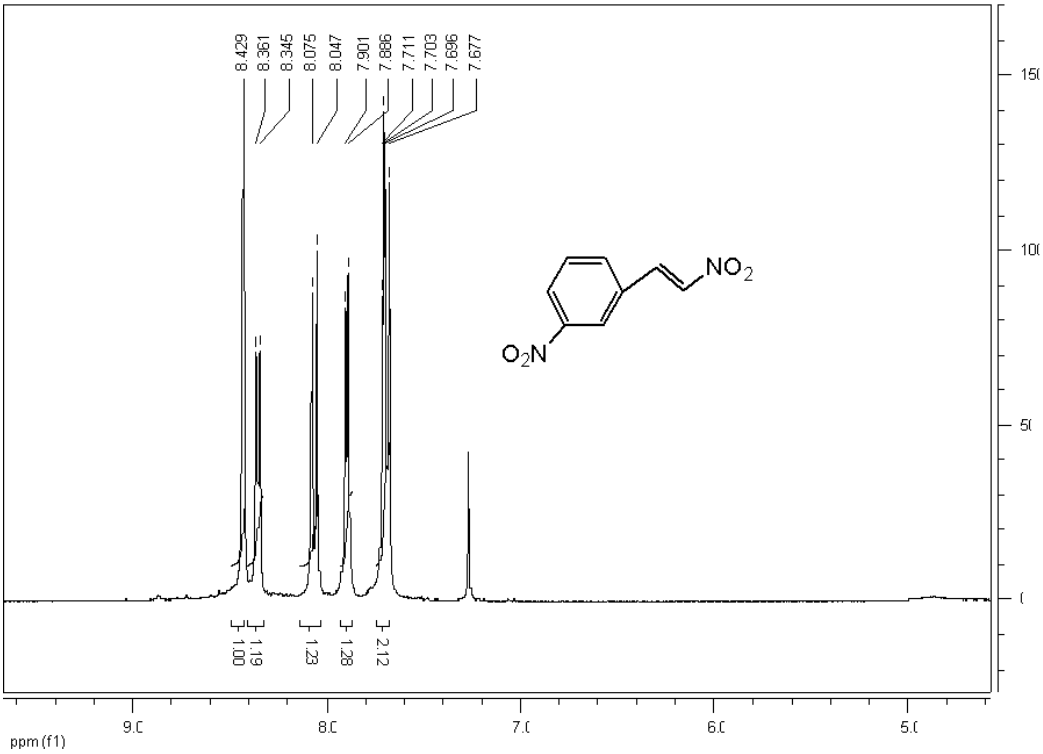

164.466
63.703
56.802
38.298
CF3COO-
ppm (f1)

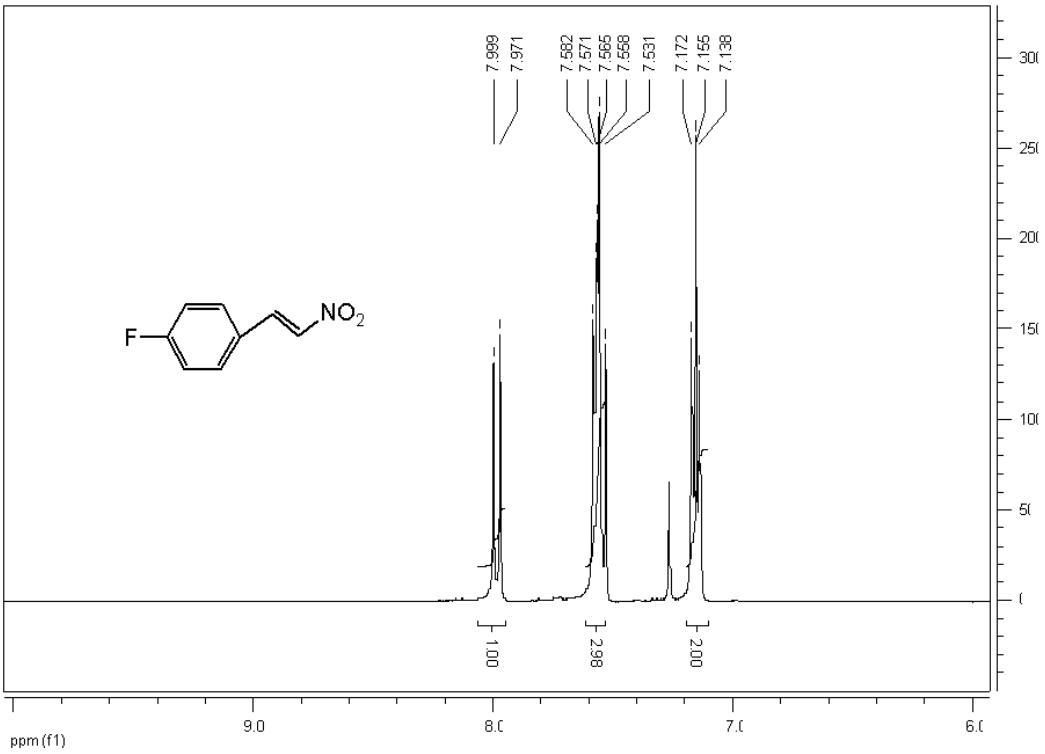

3.924
3.914
3.904
2.985
2.975
2.966
2.431
2.00
1.95
3.09
ppm (f1)

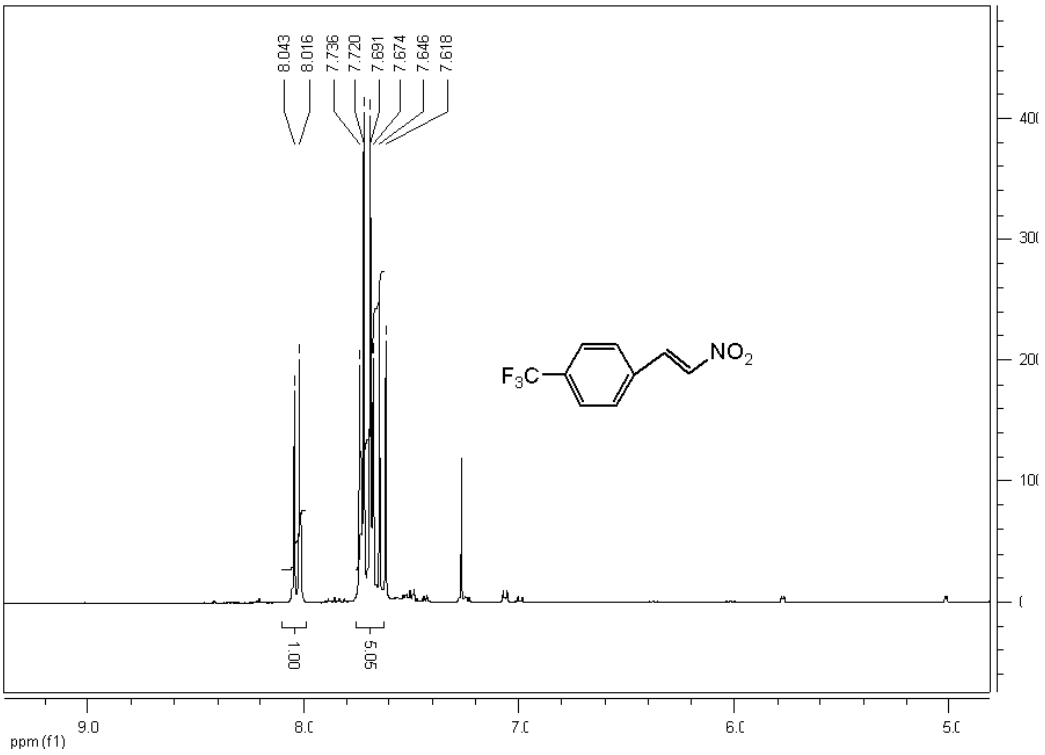

63.960
57.063
38.009
37.848
ppm (f1)

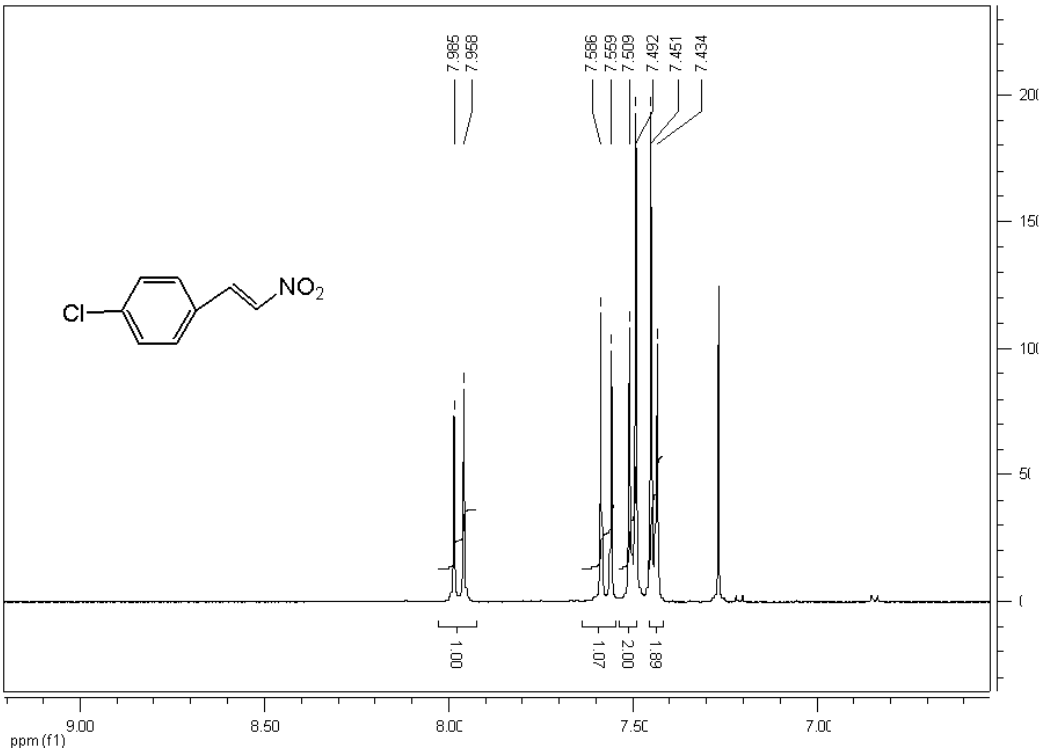
5. Copies of ^{1}H NMR of the nitrostyrenes in Table 1

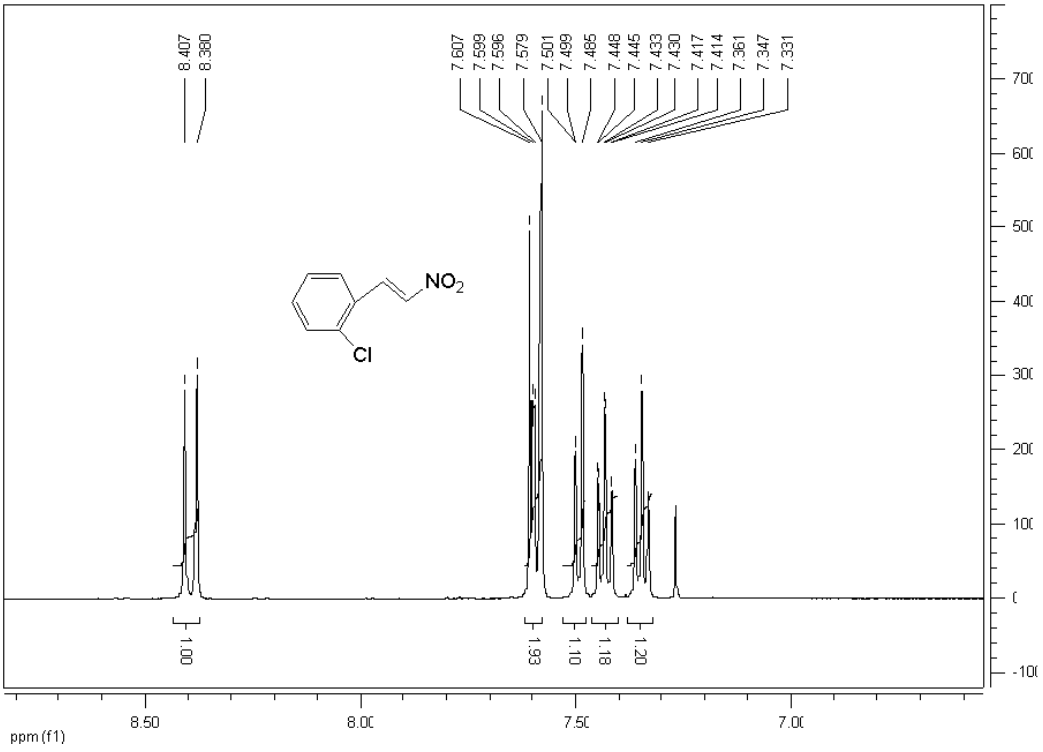


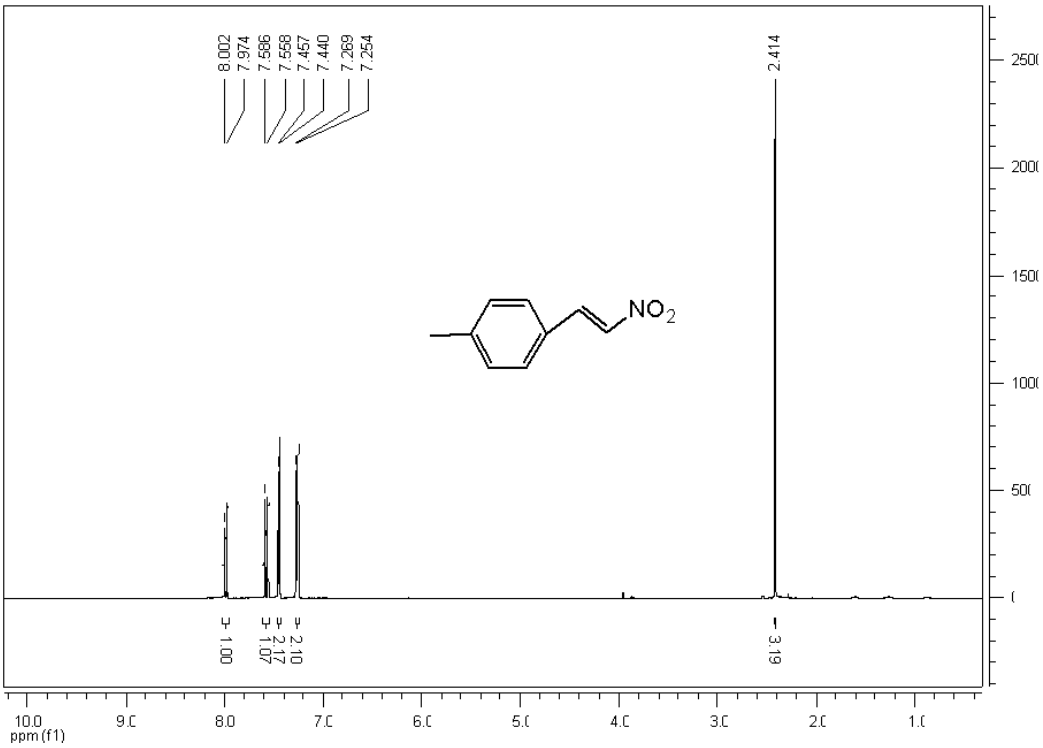



7.999
7.971
7.582
7.571
7.565
7.558
7.531
7.172
7.155
7.138
F
NO2
1.00
2.98
2.00
ppm (f1)


8.043
8.016
7.736
7.720
7.691
7.674
7.646
7.618
F3C
NO2
1.00
5.05
ppm (f1)


7.985
7.958
7.586
7.559
7.509
7.492
7.451
7.434
Cl
NO2
1.00
1.07
2.00
1.89
9.00
8.50
8.00
7.50
7.00
ppm (f1)


8.407
8.380
7.607
7.599
7.596
7.579
7.501
7.499
7.485
7.448
7.445
7.433
7.430
7.417
7.414
7.361
7.347
7.331
NO2
Cl
1.00
1.93
1.10
1.18
1.20
8.50
8.00
7.50
7.00
ppm (f1)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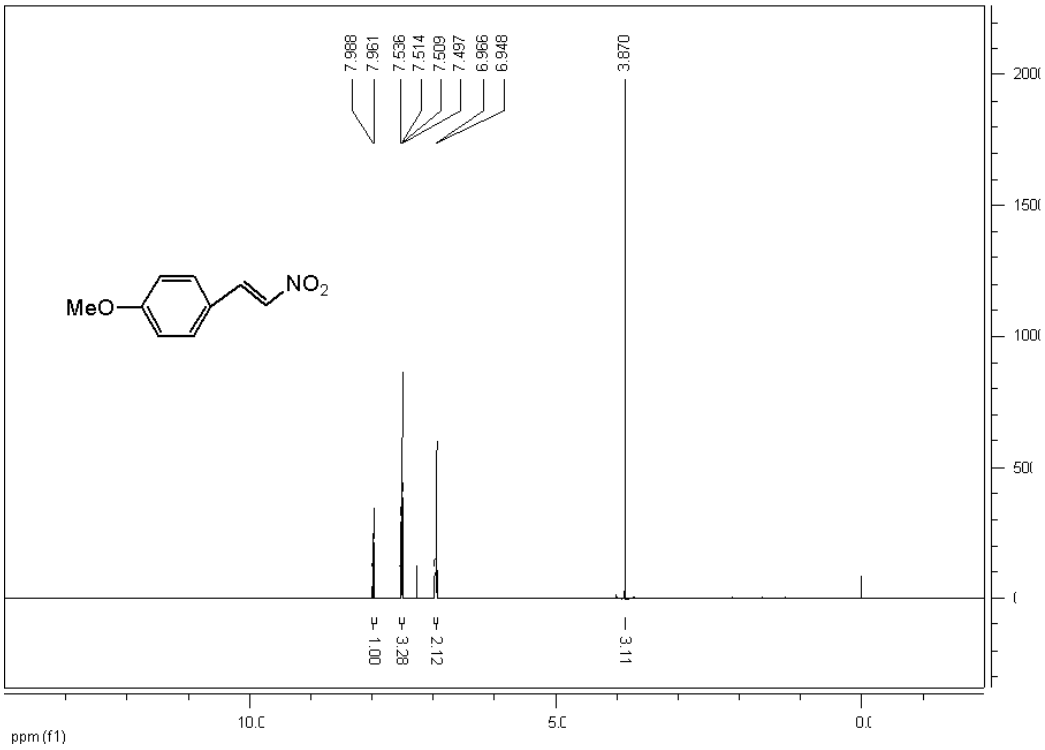
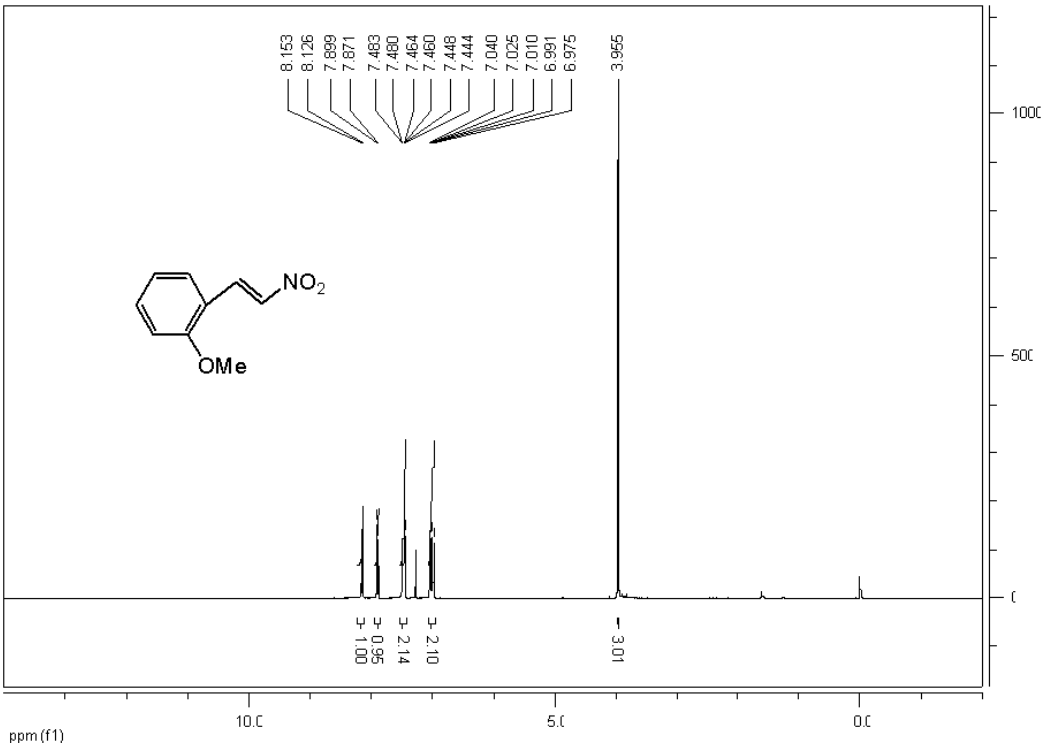
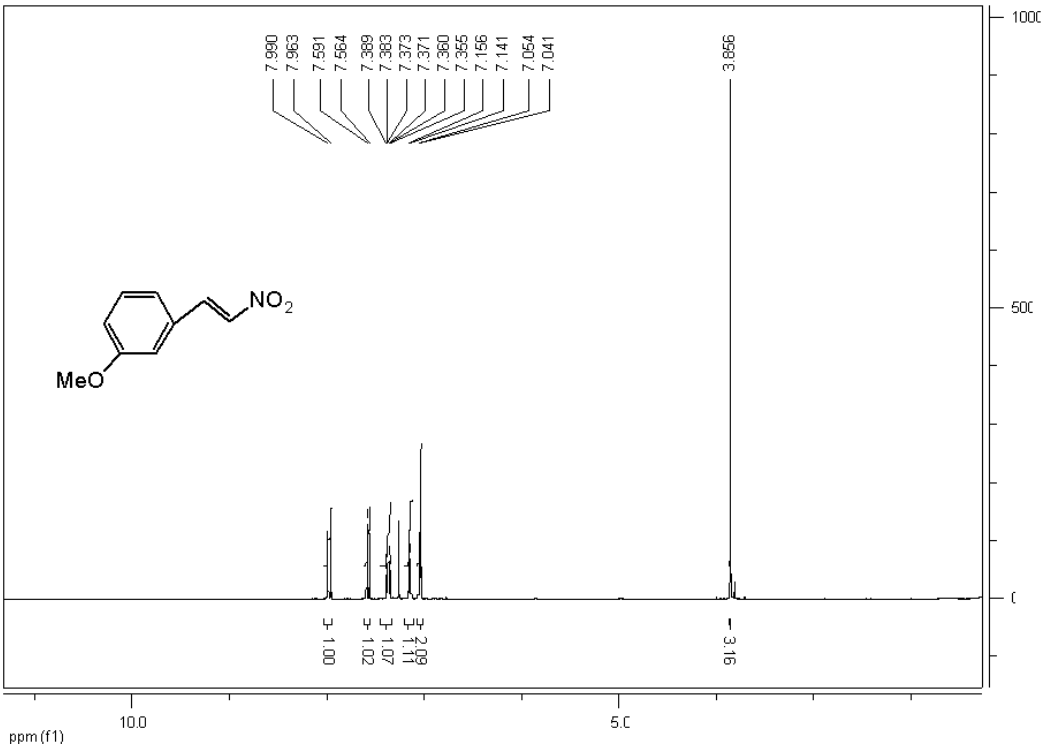
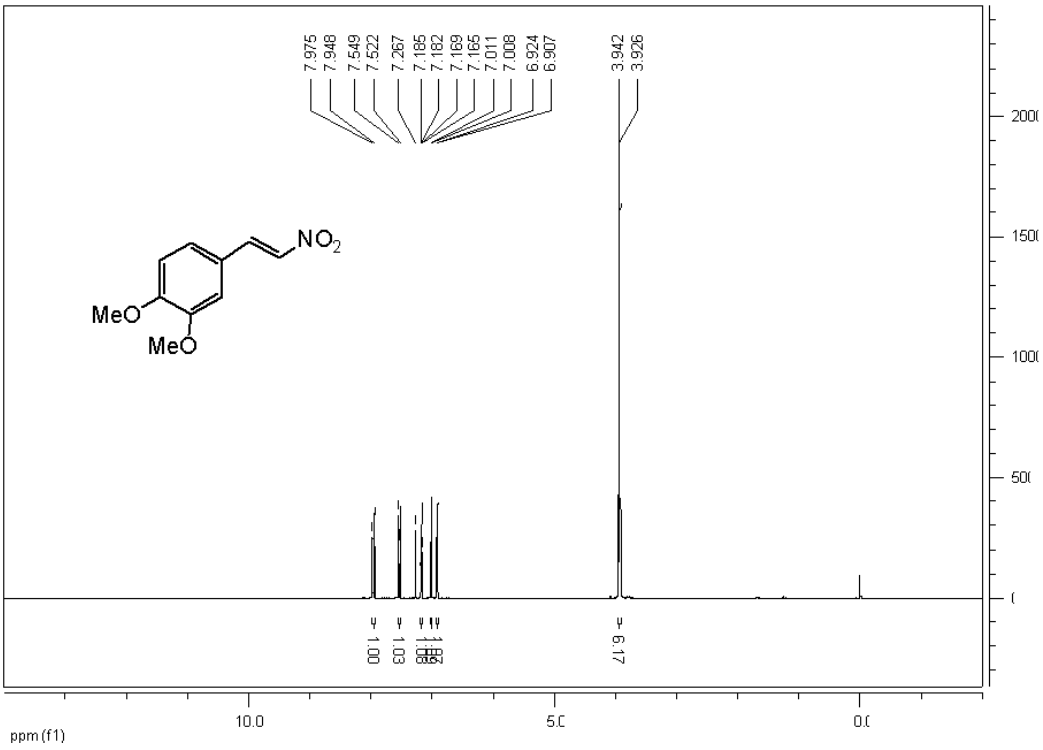
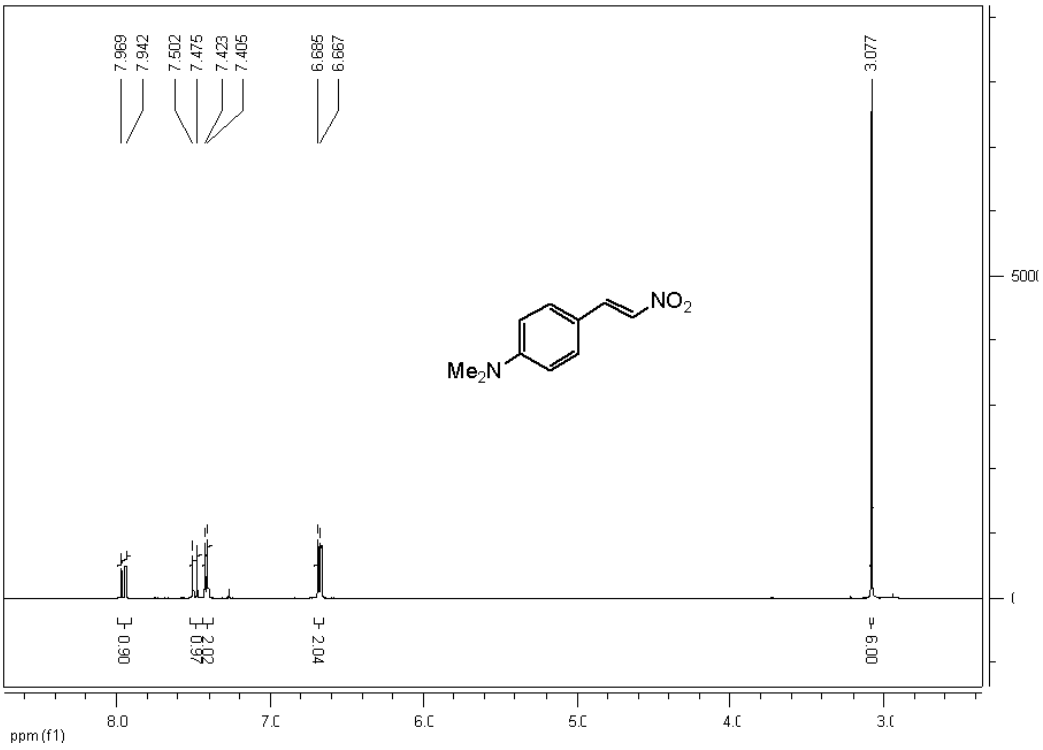
7.974
7.586
7.568
7.457
7.440
7.269
7.254
2.414
NO2
1.00
1.07
2.17
2.10
3.19
ppm (f1)

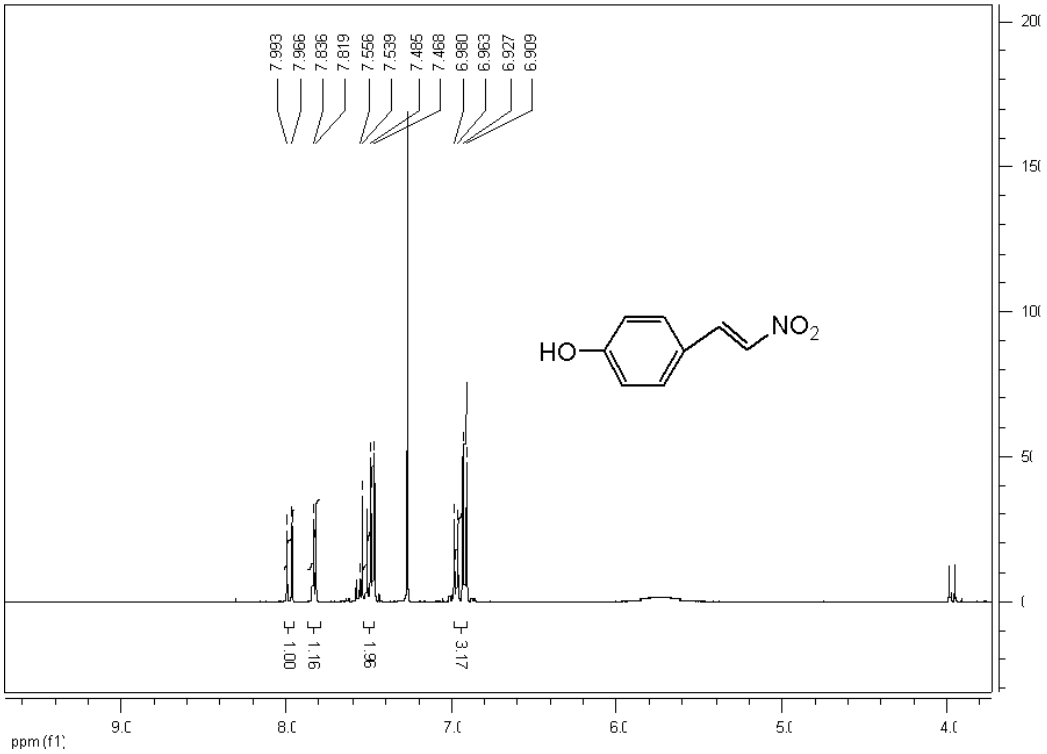

7.988
7.961
7.536
7.514
7.509
7.497
6.966
6.948
3.870
MeO
NO2
1.00
3.28
2.12
3.11
ppm (f1)

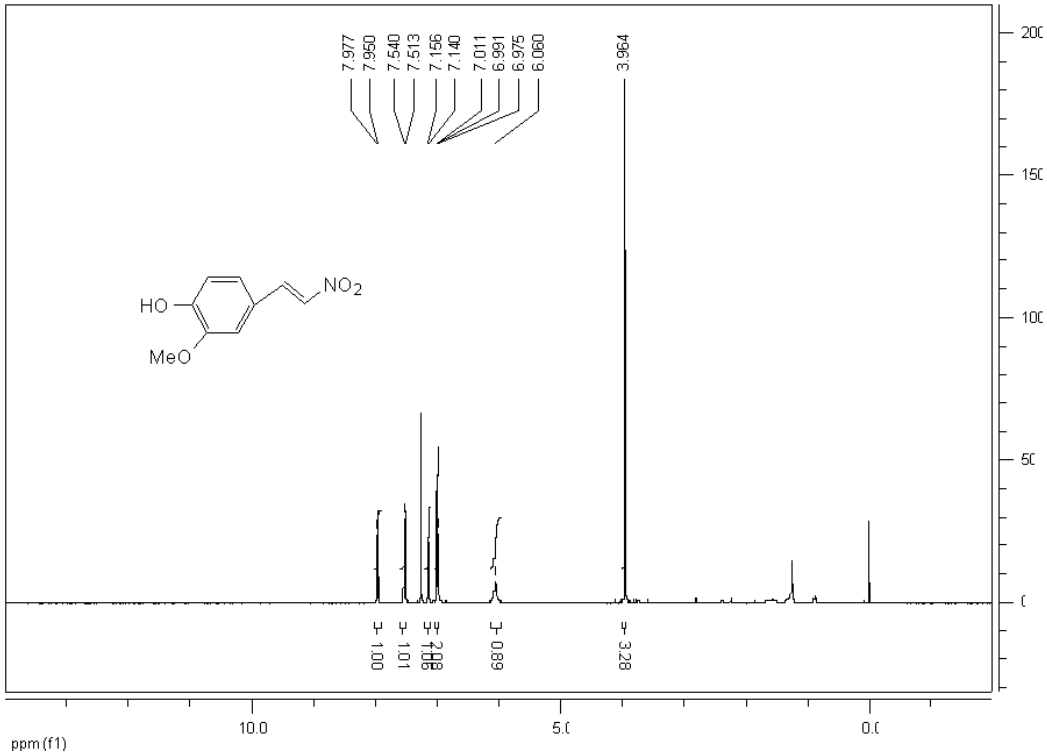

8.153
8.126
7.899
7.871
7.483
7.480
7.464
7.460
7.448
7.444
7.040
7.025
7.010
6.991
6.975
3.955
NO2
OMe
1.00
0.95
2.14
2.10
3.01
ppm (f1)

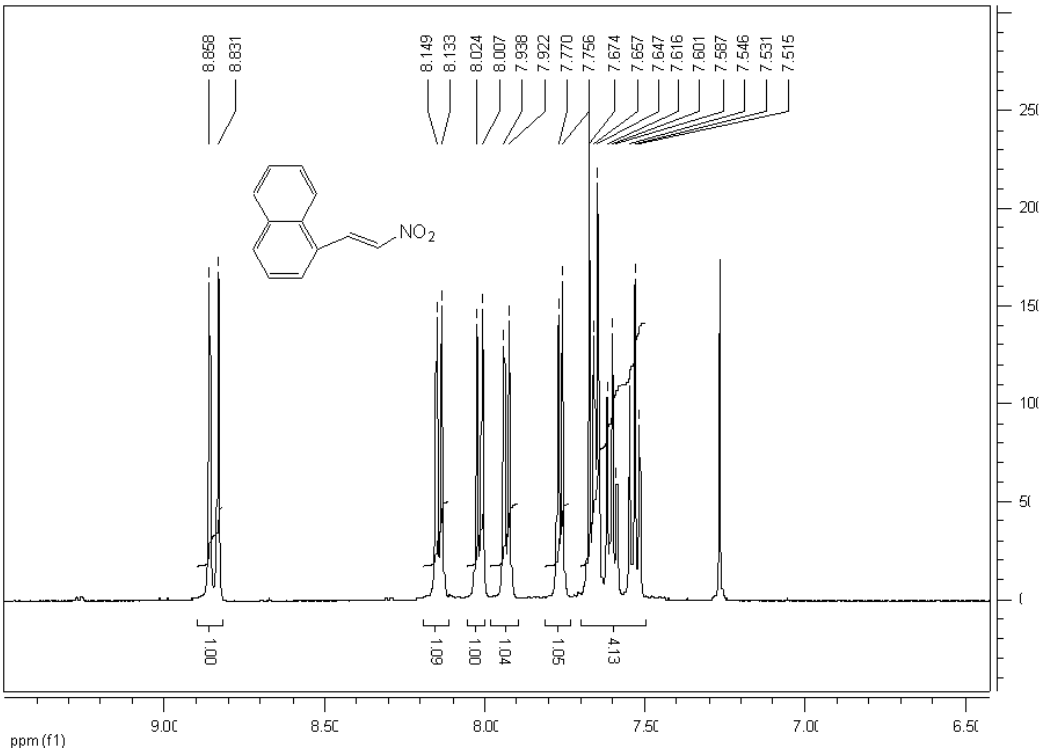

7.990
7.963
7.591
7.564
7.389
7.383
7.373
7.371
7.360
7.355
7.156
7.141
7.054
7.041
3.856
NO2
MeO
1.00
1.02
1.07
2.09
1.11
3.16
ppm (f1)

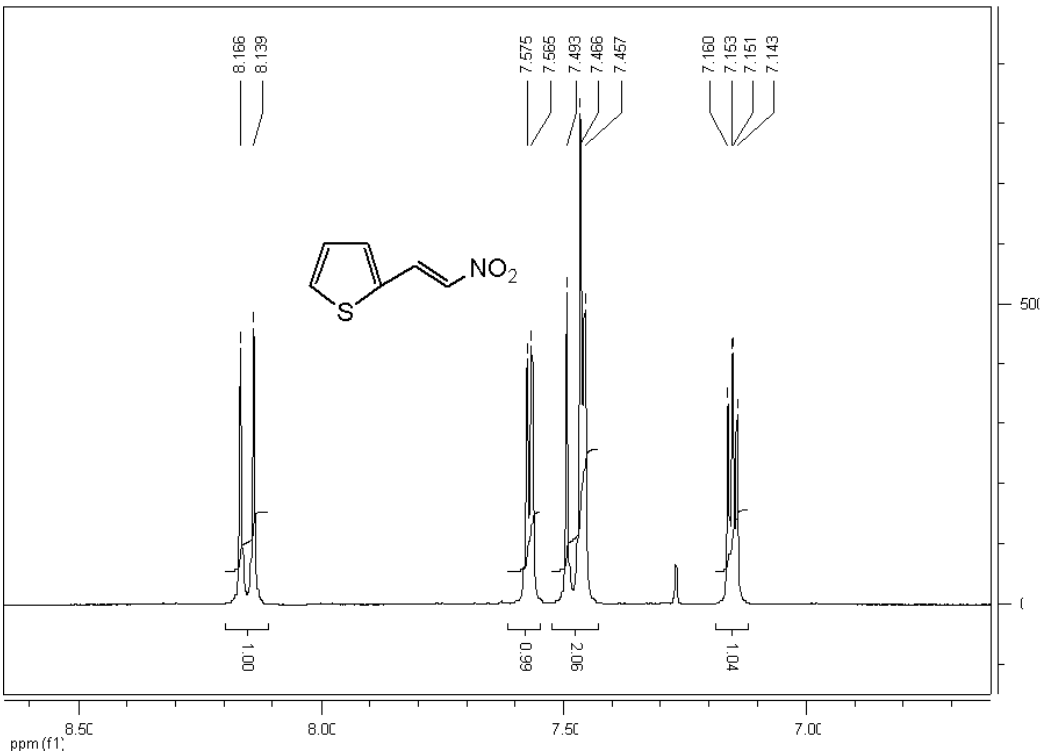

7.975
7.948
7.549
7.522
7.267
7.185
7.182
7.169
7.165
7.011
7.008
6.924
6.907
3.942
3.926
NO2
MeO
MeO
1.00
1.03
6.17
10.0
5.0
0.0
ppm (f1)

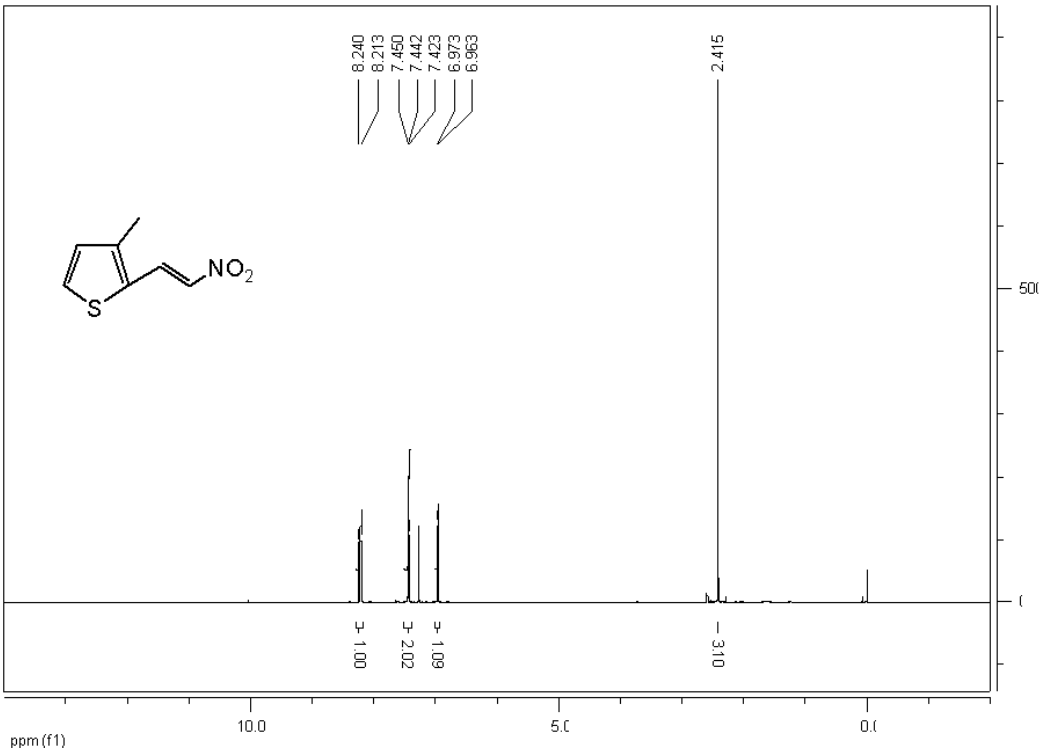

7.969
7.942
7.502
7.475
7.423
7.405
6.685
6.667
3.077
NO2
Me2N
0.90
2.04
9.00
8.0
7.0
6.0
5.0
4.0
3.0
ppm (f1)

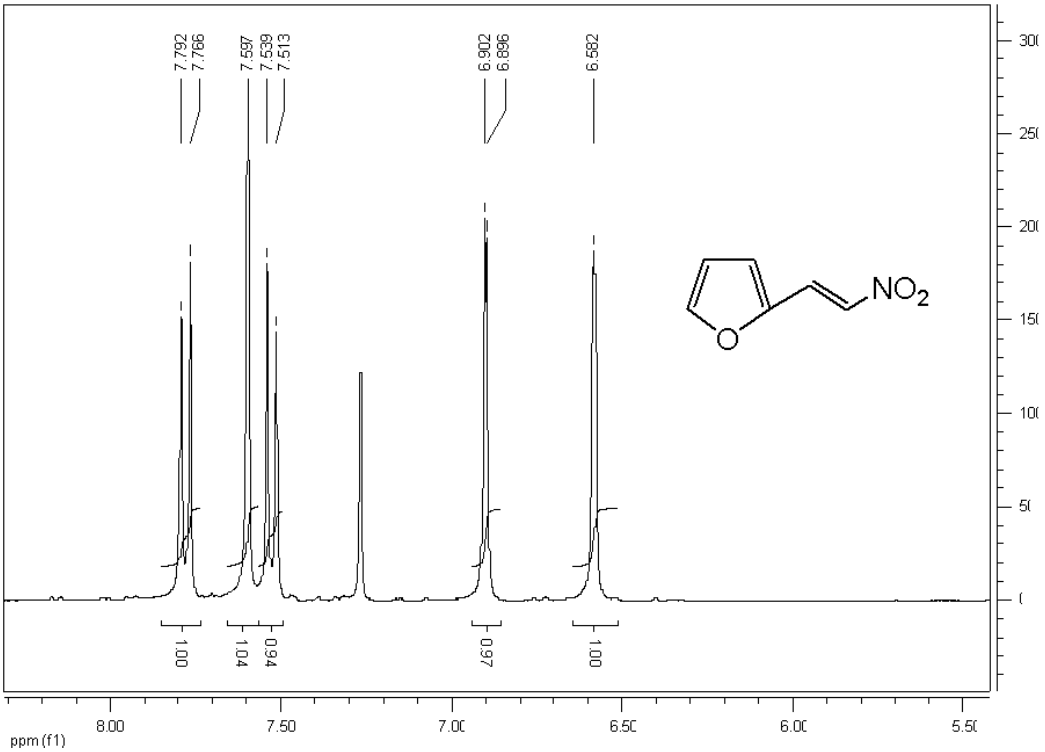

7.993
7.966
7.836
7.819
7.556
7.539
7.485
7.468
6.980
6.963
6.927
6.909
HO
NO2
1.00
1.16
1.96
3.17
ppm (f1)

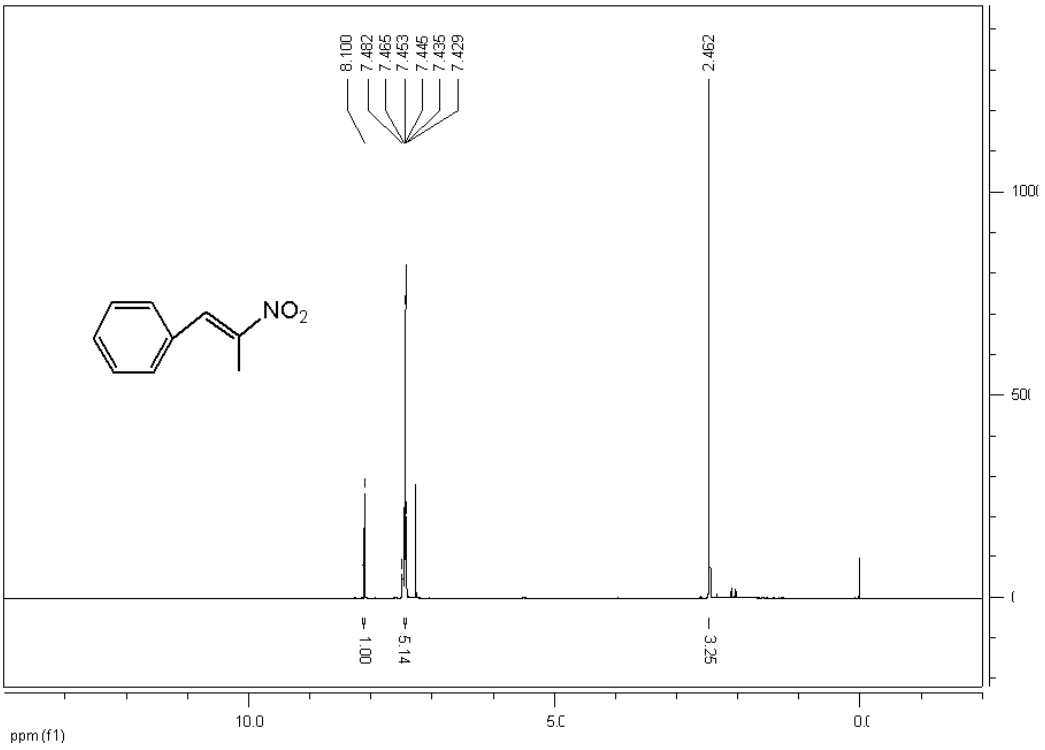

7.977
7.950
7.540
7.513
7.156
7.140
7.011
6.991
6.975
6.060
3.964
HO
MeO
NO2
1.00
1.01
2.08
0.89
3.28
ppm (f1)

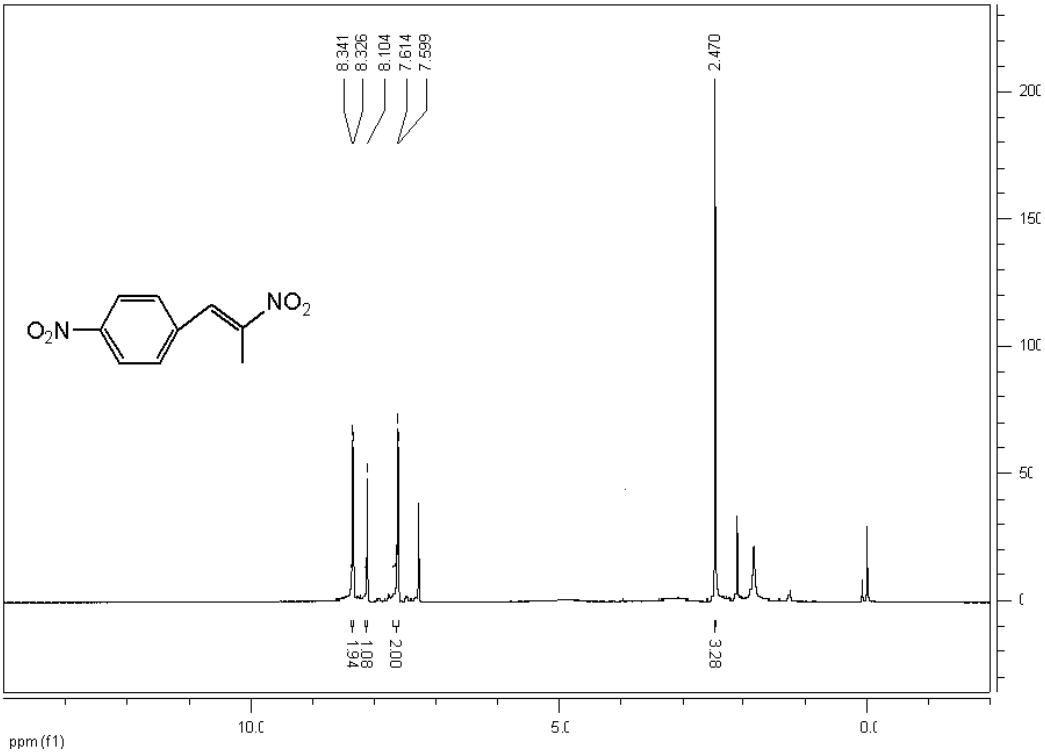

8.858
8.831
8.149
8.133
8.024
8.007
7.938
7.922
7.770
7.756
7.674
7.657
7.647
7.616
7.601
7.587
7.546
7.531
7.515
NO2
1.00
1.09
1.00
1.04
1.05
4.13
9.00
8.50
8.00
7.50
7.00
6.50
ppm (f1)

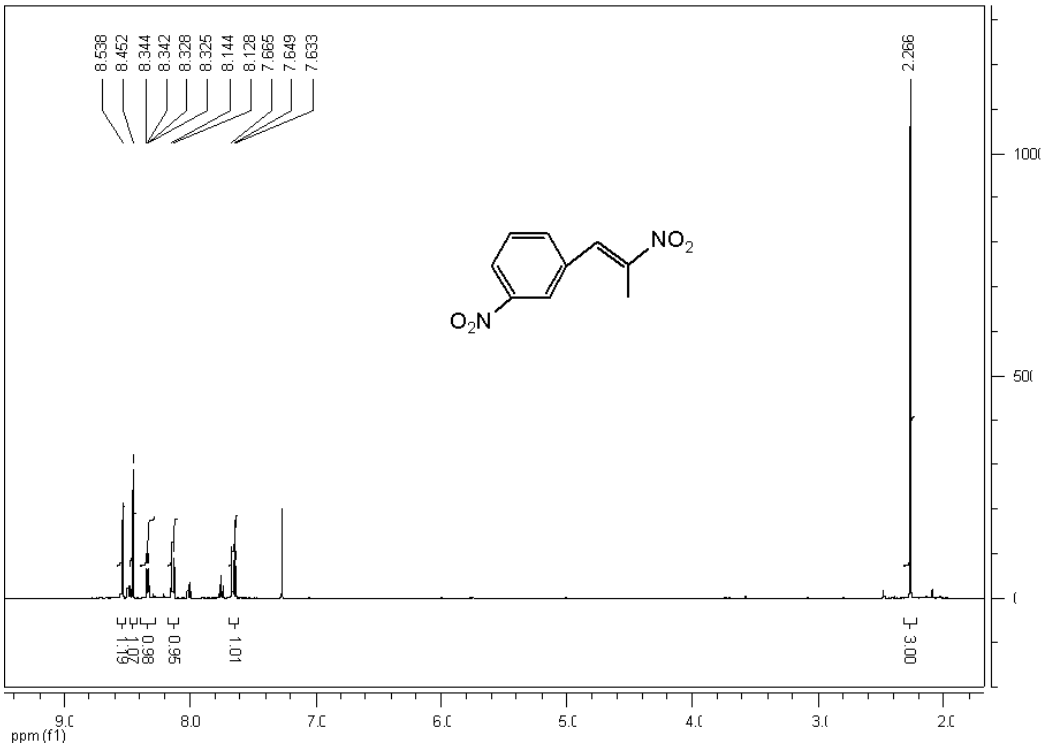

8.166
8.139
7.575
7.565
7.493
7.466
7.457
7.160
7.153
7.151
7.143
NO2
S
1.00
0.99
2.06
1.04
8.50
8.00
7.50
7.00
ppm (f1)

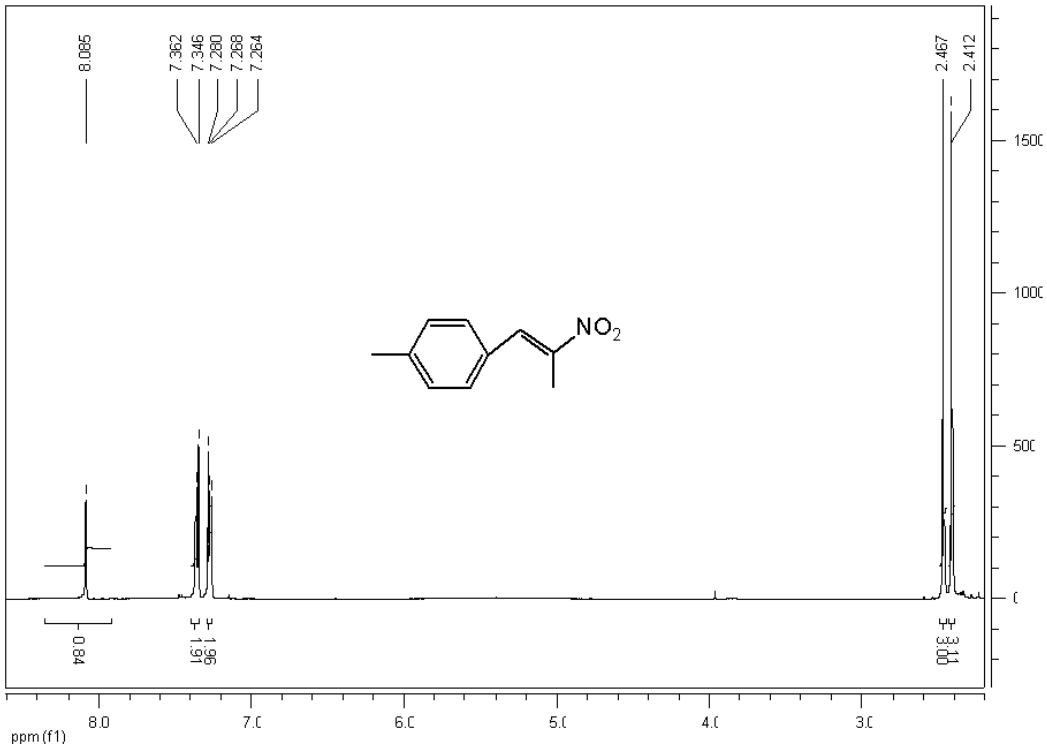

8.240
8.213
7.450
7.442
7.423
6.973
6.963
2.415
NO2
S
1.00
2.02
1.09
3.10
ppm (f1)
10.0
5.0
0.0


7.792
7.766
7.597
7.539
7.513
6.902
6.896
6.582
NO2
O
1.00
1.04
0.94
0.97
1.00
ppm (f1)
8.00
7.50
7.00
6.50
6.00
5.50


8.100
7.482
7.465
7.453
7.445
7.435
7.429
2.462
NO2
1.00
5.14
3.25
ppm (f1)


8.341
8.326
8.104
7.614
7.599
2.470
O2N
NO2
1.94
1.08
2.00
3.28
ppm (f1)


8.538
8.452
8.344
8.342
8.328
8.325
8.144
8.128
7.665
7.649
7.633
2.266
NO2
O2N
1.19
1.07
0.98
0.95
1.01
3.00
ppm (f1)


8.085
7.362
7.346
7.280
7.268
7.264
2.467
2.412
NO2
0.84
1.91
1.96
3.00
3.11
ppm (f1)

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