

Microwave-Assisted Synthesis of Nitroketene *N,S*-Arylaminoacetals

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Neste trabalho nós relatamos o uso de microondas como fonte de energia para promover a síntese de uma série de nitroeteno *N,S*-acetais com bons rendimentos. Estes compostos são intermediários muito úteis para a síntese de sistemas heterocíclicos nitrogenados.

In this paper we report the use of microwaves as heat source to promote the synthesis of a series of nitroketene *N,S*-acetals with good to excellent isolated yields. These compounds are very useful intermediates for synthesizing nitrogen-containing heterocycles.

Keywords: nitroketene *N,S*-arylaminoacetals, microwaves, quinoxalines

Introduction

Nitroketene *N,S*-acetals are very useful intermediates for synthesizing nitrogen-containing heterocycles, such as 2-amino-3-nitro-4*H*-chromenes,¹ 4-imino-3,4-dihydropyrimidin-2(1*H*)-ones,² and quinoxalines.^{3,4} Substituted quinoxalines have displayed a large number of biological activities including antiviral, antibacterial and as kinase inhibitors.^{5,6} 1-Methylamino-1-methylthio-2-nitroethene is a crucial intermediate for the manufacture of ranitidine.⁷

The synthesis of nitroketene *N,S*-acetals (**3**) are usually performed by reaction of 1,1-bis(methylthio)-2-nitroethene (**1**) with one equivalent of several primary or secondary amines (Scheme 1).^{1,8,9} A second approach to the synthesis of nitroketene *N,S*-acetals is performed by adding nitromethane anion to methyl isocyanate, followed by *S*-methylation.^{8,10} In a different approach, nitromethane has been condensed with bis(methylthio)methaneimine in the presence of a rare-earth exchanged NaY zeolite.¹¹

Nowadays, it is noteworthy to connect research in chemistry and environmental protection. One of the principles of green chemistry is energy efficiency, thus the synthetic methods should be conducted whenever possible at room temperature and pressure, to reduce the energy spent during a chemical process. One option is to replace the conventional heating by alternative energy sources such as microwave.¹²

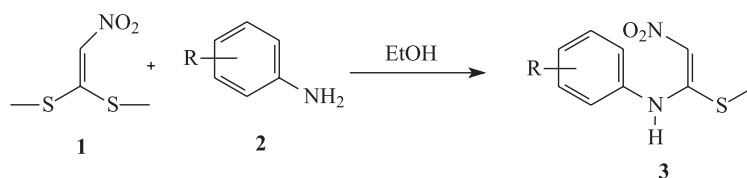
Microwave-assisted organic synthesis has had a profound impact on the way that chemists approach organic and parallel synthesis. Clearly, reductions in reaction times, improved yields and suppression of side products, relative to conventional thermal heating, are some benefits of this emerging technology.¹³⁻¹⁵

In this paper we report the use of microwaves as heat source to promote the synthesis of a series of nitroketene *N,S*-acetals with good to excellent isolated yields.

Results and Discussion

In a ongoing program towards the synthesis of quinoxalines, we investigated the reaction of nitroethene **1** with aniline using ethanol as solvent and microwave (MW) irradiation (Scheme 1). In our first trial, we obtained 43% yield of the desired product after 30 min at 110 °C and 70 W. We then performed a series of experiments in order to optimize this result, which are summarized in Table 1. We observed that the rate of conversion of reagents increased with temperature and power of microwave (entries 1 and 2); however when the temperature increased up to 140 °C and power to 150 W, by-products were formed (entry 3). Thus, we decided to investigate the time reaction by keeping temperature at 110 °C and power at 70 W (entries 4, 5 and 6). The desired product was obtained in 85% yield, gradually increasing the reaction time, without formation of by-products after 90 min. We confirmed the optimization with *p*-methoxyaniline, which furnished higher yields in the same conditions.

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Scheme 1. Synthesis of nitroketene *N,S*-arylaminoacetals (**3**).

After optimizing the reaction, we performed the coupling of different amines possessing electron donating and electron withdrawing groups to evaluate the scope of this protocol. Good to excellent isolated yields were obtained in most cases, excepting the reaction

Table 1. Microwave-assisted reaction of nitroethene **1** with aniline and *p*-methoxyaniline

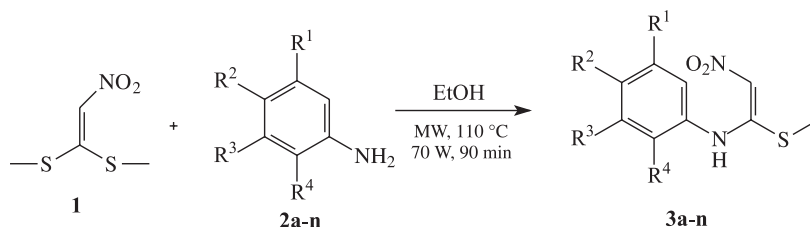
Entry	time (min)	Potency (W)	Temperature (°C)	3, yield (%) ^a	
				R=H	R=4-OMe
1	30	20	80	35	53
2	30	70	110	43	64
3	30	150	140	40	35
4	45	70	110	61	84
5	60	70	110	73	94
6	90	70	110	85	100

^aIsolated yield after purification. Purity was determined by GC-MS.

with anilines **2k** and **2n**, probably due to the presence of the strong electron withdrawing group. We have also observed that groups in the 2-position may cause steric hindrance effect, as for example for anilines **2d** and **2g** (Table 2). The reaction with cyclohexylamine (**4**) was performed (Scheme 2) and furnished the corresponding *N*-[1-(methylthio)-2-nitroethenyl]-cyclohexanamine (**5**) in 98% yield.

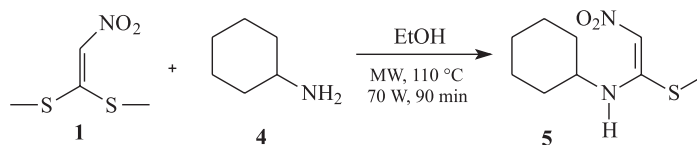
Due to the failure of the methodology as a result of the presence of strongly electron-withdrawing groups, we performed further tests with the 4-trifluoromethylaniline (Table 3). Therefore, we attempt the same procedure by using higher power and temperature (entry 2). We have also tested different solvents (entries 3 and 4). In general a reaction medium with a high loss tangent ($\tan \delta$) at the standard operating frequency of a microwave synthesis reactor (2.45 GHz) is required for good absorption and, consequently, for efficient heating.¹³ However, even in this

Table 2. Microwave-assisted reaction of nitroethene **1** with different anilines



Aniline 2	R ¹	R ²	R ³	R ⁴	3, yield (%) ^a	mp (°C)	mp (°C) literature
a	OMe	OMe	OMe	H	80	190 dec.	-
b	OMe	H	OMe	H	87	148-150	142-143 ^{3,4}
c	OMe	H	H	H	91	125-126	122-123 ^{3,4}
d	OMe	H	H	OMe	51	126-127	121-123 ^{3,4}
e	H	OMe	H	H	>99	157-158	157-158 ^{3,4}
f	H	OH	H	H	89	189 dec.	-
g	H	H	H	OH	- ^b	-	-
h	H	F	H	H	98	157-158	154-156 ²¹
i	H	H	F	H	traces	-	126-127 ^{3,4}
j	H	Br	H	H	97	174-175	173-174 ¹⁸
k	H	NO ₂	H	H	- ^b	-	177-179 ²²
l	H	-OCH ₂ O-	-OCH ₂ O-	H	93	151-152	-
m	H	H	H	H	85	152-153	152-153 ¹⁸
n	H	CF ₃	H	H	- ^b	-	-

^a Isolated yield after purification; ^b No reaction was observed.



Scheme 2. Synthesis of *N*-[1-(methylthio)-2-nitroethenyl]-cyclohexanamine (**5**).

Table 3. Microwave-assisted reaction of nitroethene **1** with *p*-trifluoromethylaniline (**2n**)

Entry	Solvent	Potency (W)	Temperature (°C)	Product 3n
1	EtOH	70	110	– ^a
2	EtOH	150	140	traces
3	DMF	70	110	– ^a
4	<i>i</i> -PrOH	70	110	– ^a

^a No reaction was observed and starting materials were recovered after 30 min of irradiation.

case we have gotten just unreacted starting materials and traces of the desired products.

All products were characterized by ¹H and ¹³C NMR, infrared, GCMS spectra and melting point. The spectroscopic data were identical with those described in the literature.^{3,4,9,16–20} The geometry of the 1-aryl-1-methylthio-nitroketenes are probably all *E* in which orientation intramolecular hydrogen bonding is possible; this was verified for **3e** by the observation of an nOe between the thiomethyl and the vinylic hydrogens.²¹

Conclusions

In summary, we have demonstrated that reactions between amines and 1,1-bis(methylthio)-2-nitroethene (**1**) employing microwave heating is an advantage method since desired products can be obtained in good yields and shorter reaction time when compared to the conventional heating. This protocol afforded a series of nitroketene *N,S*-acetals (**3**) in with good to excellent yields.

Experimental

Unless otherwise noted, all commercially available reagents were purchased from Aldrich Chemical Co. and used without purification. ¹H and ¹³C NMR spectra were recorded on a Bruker ARX-400 (400 and 100 MHz respectively). The IR spectra refer to tablets in KBr and were measured on a Bomem M102 spectrometer. Mass Spectra were recorded on a Shimadzu GCMS-QP5000. Elemental analyses were performed on a Fisons EA 1108 CHNS-O. Analytical thin-layer chromatography was performed on a 0.25 μm film of silica gel containing fluorescent indicator UV₂₅₄ supported on an aluminum sheet (Sigma-Aldrich).

Flash column chromatography was performed using silica gel (Kieselgel 60, 230–400 mesh, E. Merck). Gas chromatography was performed in a Shimadzu GC-17A with N₂ as carrier and using a DB-5 column. Melting points were performed in Microquímica MQAPF - 301.

Typical experimental procedure: nitroethene **1** (30 mg 0.182 mmol), amine **2** (0.182 mmol) and ethanol (1 mL) were placed in a glass tube, purged with oxygen-free nitrogen during 10 min sealed and irradiated in during 90 min in a CEM Discovery® focused microwave oven at 110 °C and 70 W. The nitroketene *N,S*-acetals **3** were purified by flash chromatography employing hexanes:ethyl acetate (4:1 ratio) as eluent.

3,4,5-Trimethoxy-*N*-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3a**)¹⁷

¹H NMR (400 MHz, CDCl₃): δ 2.39 (s, 3H), 3.86 (s, 6H), 3.87 (s, 3H), 6.52 (s, 2H), 6.68 (s, 1H), 11.82 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 14.77, 56.36, 60.98, 103.66, 107.82, 131.70, 153.65, 163.40, 170.87. IR (KBr) ν_{max} /cm⁻¹: 3159.67, 3066.59, 3008.73, 2947.01, 2842.87, 1595.01, 1548.73, 1415.65, 1330.79, 1234.35, 1126.35, 1004.84, 671.18. GC-MS (70 eV) *m/z* (%): 300 (M⁺, 10), 266 (80), 251 (100), 223 (33), 194 (37), 167 (20). (Found: C, 47.34; H, 5.56; N, 9.17; S, 10.18. Calc. for C₁₂H₁₆N₂O₅S: C, 47.99; H, 5.37; N, 9.33; S, 10.68%).

3,5-Dimethoxy-*N*-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3b**)^{3,4}

¹H NMR (400 MHz, CDCl₃): δ 2.39 (s, 3H), 3.80 (s, 6H), 6.45–6.42 (m, 3H), 6.68 (s, 1H), 11.80 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 14.81, 55.58, 100.11, 103.98, 108.08, 137.82, 161.32, 162.99. IR (KBr) ν_{max} /cm⁻¹: 3170.70, 3093.59, 2995.23, 2839.01, 1612.37, 1542.94, 1471.58, 1427.22, 1319.21, 1195.78, 1153.35, 1060.77, 972.05, 848.62, 690.47, 597.89. GC-MS (70 eV) *m/z* (%): 270 (M⁺, 12), 236 (52), 221 (100), 177 (66), 137 (93), 122 (70), 107 (45).

3-Methoxy-*N*-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3c**)^{3,4}

¹H NMR (400 MHz, CDCl₃): δ 2.39 (s, 3H), 3.83 (s, 3H), 6.70 (s, 1H), 6.90 (t, 1H, *J* 2.15 Hz), 6.92–6.87 (m, 2H), 7.33 (t, 1H, *J* 8.26 Hz), 11.82 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 14.71, 54.01, 111.44, 113.76, 117.89, 130.09,

137.19, 160.25, 163.28. IR (KBr) ν_{\max} /cm⁻¹: 3159.17, 3070.45, 2995.23, 1602.73, 1546.80, 1465.79, 1417.58, 1330.79, 1269.07, 1222.78, 1157.20, 958.55, 848.62, 684.68, 570.89, 532.31. GC-MS (70 eV) m/z (%): 240 (M⁺, 12), 206 (41), 159 (38), 147 (64), 107 (100), 77 (99).

2,5-Dimethoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (3d)^{3,4}

¹H NMR (400 MHz, CDCl₃): δ 2.40 (s, 3H), 3.78 (s, 3H), 3.84 (s, 3H), 6.82 (dd, 1H, J_1 9.27, J_2 2.98 Hz), 6.90 (d, 1H, J 9.27 Hz), 7.01 (d, 1H, J 2.98 Hz), 6.71 (s, 1H), 11.79 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 14.86, 55.91, 56.33, 108.39, 112.33, 112.41, 113.13, 125.96, 147.24, 153.18, 162.78. IR (KBr) ν_{\max} /cm⁻¹: 3161.10, 3074.31, 2995.23, 1544.87, 1508.22, 1473.51, 1411.79, 1321.14, 1226.64, 1114.77, 1045.34, 802.33, 709.75. GC-MS (70 eV) m/z (%): 270 (M⁺, 19), 236 (69), 207 (56), 189 (55), 179 (100), 107 (55).

4-Methoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (3e)^{3,4}

¹H NMR (400 MHz, CDCl₃): δ 2.36 (s, 3H), 3.84 (s, 3H), 6.68 (s, 1H), 6.93 (d, 2H, J 8.64 Hz), 6.92-6.87 (d, 2H, J 8.64 Hz), 11.64 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 14.62, 55.51, 107.43, 127.72, 128.84, 159.43, 164.41. IR (KBr) ν_{\max} /cm⁻¹: 3145.67, 3001.02, 2960.52, 2839.01, 1606.59, 1510.15, 1467.72, 1427.22, 1334.64, 1247.85, 1182.28, 1157.20, 908.41, 825.47, 765.68, 684.68, 597.89, 532.31. GC-MS (70 eV) m/z (%): 240 (M⁺, 14), 206 (42), 159 (79), 134 (100), 107 (68), 77 (99).

4-[[1-(Methylthio)-2-nitroethenyl]amino]-phenol (3f)^{16,17}

¹H NMR (400 MHz, MeOD): δ 2.42 (s, 3H), 6.79 (s, 1H), 6.83 (d, 2H, J 9.24 Hz), 7.14 (d, 2H, J 9.24 Hz). ¹³C NMR (100 MHz, MeOD): δ 14.91, 108.08, 117.04, 129.27, 129.49, 159.16, 167.98. IR (KBr) ν_{\max} /cm⁻¹: 3199.67, 3164.95, 3055.02, 2931.58, 1610.44, 1552.58, 1517.87, 1442.65, 1425.29, 1313.43, 1271.00, 1230.49, 1168.78, 906.48, 509.17. GC-MS (70 eV) m/z (%): 226 (M⁺, 9), 192 (20), 145 (55), 133 (89), 119 (47), 93 (55), 65 (100). (Found: C, 47.16; H, 4.74; N, 12.23; S, 13.45. Calc. for C₉H₁₀N₂O₃S: C, 47.78; H, 4.45; N, 12.38; S, 14.17%).

4-Fluoro-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (3h)^{9,16,17}

¹H NMR (400 MHz, CDCl₃): δ 2.40 (s, 3H), 6.70 (s, 1H), 7.16-7.12 (m, 2H), 7.33-7.29 (m, 2H), 11.67 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 14.67, 107.90, 116.35 and 116.57 (C-F), 128.30 and 128.39 (C-F), 132.14, 160.82 and 163.89 (C-F), 163.29. IR (KBr) ν_{\max} /cm⁻¹: 3161.10, 3051.16, 3016.45, 1577.66, 1512.08, 1477.36, 1415.65, 1361.64, 1274.85, 1188.06, 914.19, 837.04, 761.83, 684.68.

GC-MS (70 eV) m/z (%): 228 (M⁺, 7), 194 (11), 135 (54), 122 (45), 95 (100), 75 (47).

*4-Bromo-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (3j)*¹⁹

¹H NMR (200 MHz, CDCl₃): δ 2.39 (s, 3H), 6.69 (s, 1H), 7.19 (d, 2H, J 8.77 Hz), 7.55 (d, 2H, J 8.77 Hz), 11.70 (s, 1H). ¹³C NMR (50 MHz, CDCl₃): δ 14.74, 108.32, 127.58, 131.06, 132.62, 135.30, 159.24. IR (KBr) ν_{\max} /cm⁻¹: 3151.45, 3083.95, 3060.81, 1585.37, 1564.15, 1479.29, 1411.79, 1396.36, 1348.14, 1265.21, 1168.78, 1010.63, 910.33, 759.90, 678.89. GC-MS (70 eV) m/z (%): 290 (M+2, 5), 288 (M⁺, 6), 256 (16), 254 (16), 209 (44), 207 (44), 157 (68), 155 (69), 75 (100). (Found: C, 38.08; H, 3.49; N, 9.44; S, 10.44. Calc. for C₉H₉N₂O₂SBr: C, 37.38; H, 3.14; N, 9.69; S, 11.09%).

*N-[1-(Methylthio)-2-nitroethenyl]-1,3-benzodioxol-5-amine (3l)*¹⁶

¹H NMR (400 MHz, CDCl₃): δ 2.37 (s, 3H), 6.04 (s, 2H), 6.66 (s, 1H), 6.76-6.74 (m, 2H), 6.82 (d, 1H, J 8.08 Hz), 11.59 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 14.62, 107.82, 125.91, 128.10, 129.37, 138.18, 163.40. IR (KBr) ν_{\max} /cm⁻¹: 3139.88, 3024.16, 2908.44, 1610.44, 1566.08, 1504.37, 1473.51, 1336.57, 1174.56, 1029.91, 867.90, 761.83. GC-MS (70 eV) m/z (%): 254 (M⁺, 16), 220 (57), 207 (24), 173 (83), 121 (100), 65 (87). (Found: C, 47.04; H, 4.25; N, 10.80; S, 11.47. Calc. for C₁₀H₁₀N₂O₄S: C, 47.24; H, 3.96; N, 11.02; S, 12.61%).

N-[1-(Methylthio)-2-nitroethenyl]-benzenamine (3m)^{3,4,9,16-18}

¹H NMR (400 MHz, CDCl₃): δ 2.38 (s, 3H), 6.70 (s, 1H), 7.45-7.27 (m, 5H), 11.81 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 14.67, 101.95, 107.54, 107.69, 108.35, 120.12, 129.94, 147.66, 148.29, 164.09. IR (KBr) ν_{\max} /cm⁻¹: 3147.60, 2999.09, 1542.94, 1531.37, 1461.94, 1425.29, 1336.57, 1265.21, 1178.42, 896.83, 756.04, 690.47, 534.24. GC-MS (70 eV) m/z (%): 210 (M⁺, 10), 176 (8), 163 (16), 117 (69), 77 (100).

*N-[1-(Methylthio)-2-nitroethenyl]-cyclohexanamine (5)*²⁰

¹H NMR (400 MHz, CDCl₃): δ 1.47-1.32 (m, 5H), 1.67-1.60 (m, 1H), 1.83-1.74 (m, 2H), 2.05-1.95 (m, 2H), 2.44 (s, 3H), 3.67 (m, 1H), 6.56 (s, 1H), 10.59 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 14.34, 24.25, 25.07, 32.78, 53.79, 105.86, 163.29. IR (KBr) ν_{\max} /cm⁻¹: 3136.02, 2993.30, 2927.73, 2852.51, 1564.15, 1461.94, 1423.36, 1348.14, 1315.36, 1218.92, 1081.99, 964.34, 852.47. GC-MS (70 eV) m/z (%): 216 (M⁺, 1), 182 (1), 135 (17), 83 (79), 55 (100).

Supplementary Information

Supplementary information is available free of charge at <http://jbcs.org.br>, as PDF file.

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Experimental

¹H and ¹³C NMR spectra were recorded on a Bruker ARX-400 (400 and 100 MHz respectively). The IR spectra refer to tablets in KBr and were measured on a Bomem M102 spectrometer. Mass Spectra were recorded on a Shimadzu GCMS-QP5000.

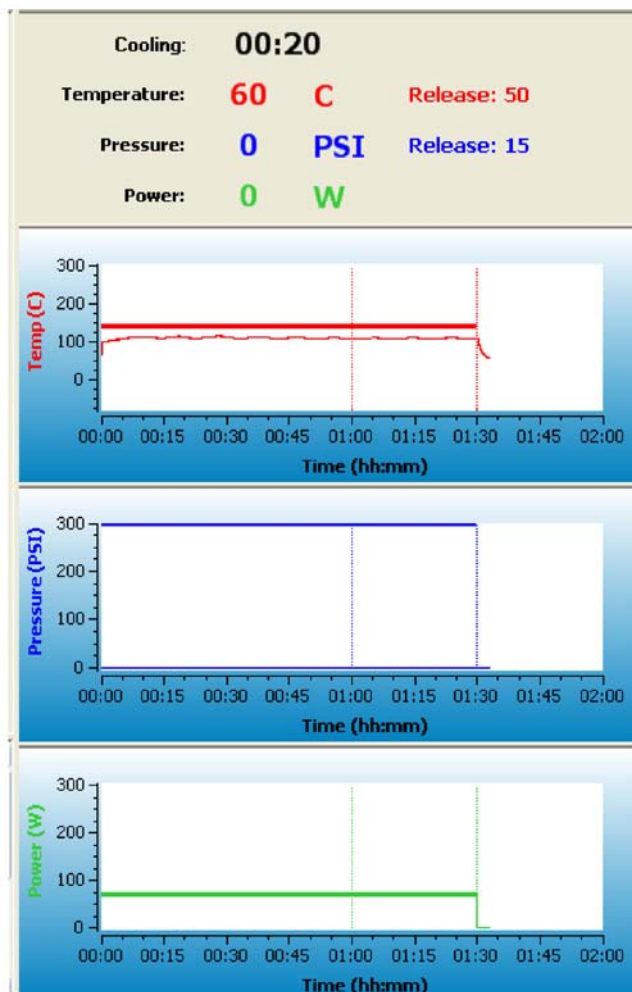
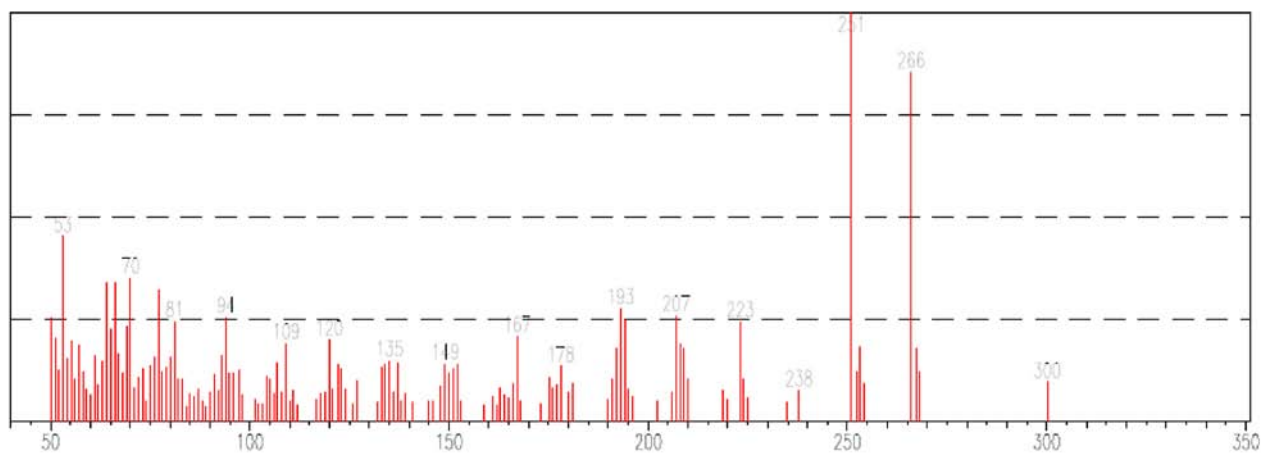
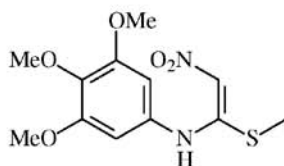
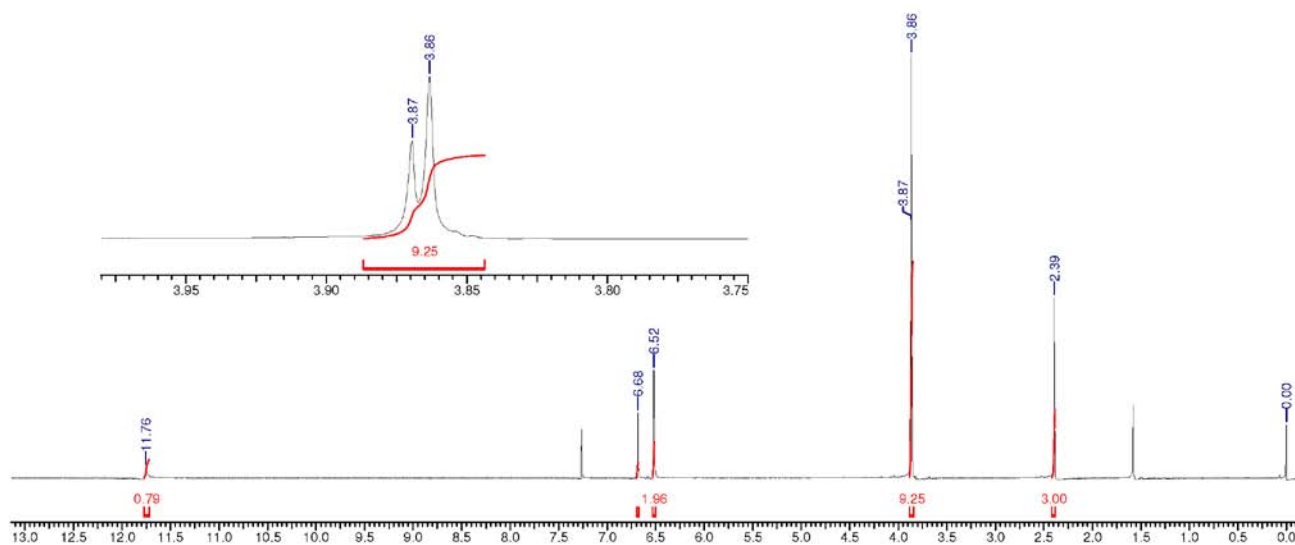


Figure S1. Representative graphic of the reaction of aniline with nitroethene **1** irradiated during 90 min in a CEM Discovery® focused microwave oven at 110 °C and 70 W.

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3,4,5-Trimethoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (3a)**Figure S2.** GC-MS of *3,4,5-Trimethoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (3a)*.**Figure S3.** ^1H NMR of *3,4,5-Trimethoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (3a)*.

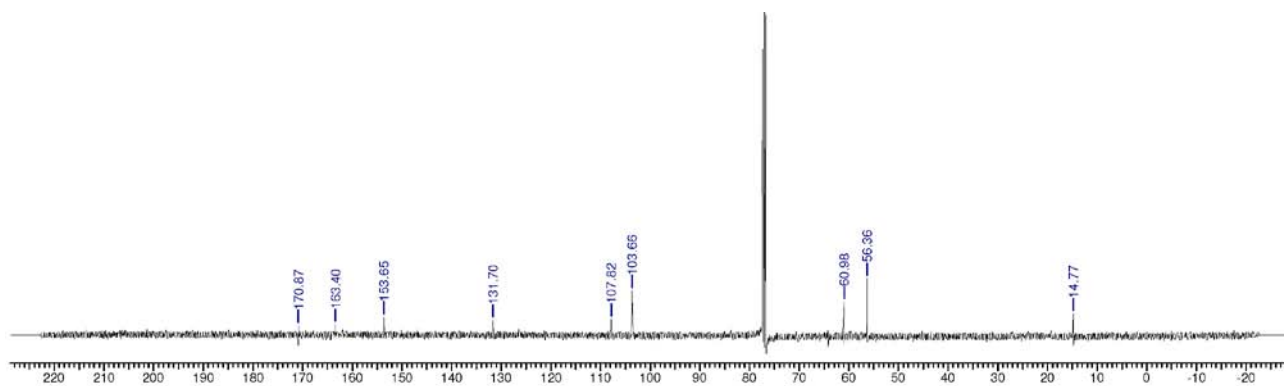


Figure S4. ¹³C NMR of 3,4,5-Trimethoxy-N-[1-(methylthio)-2-nitroethyl]-benzenamine (3a).

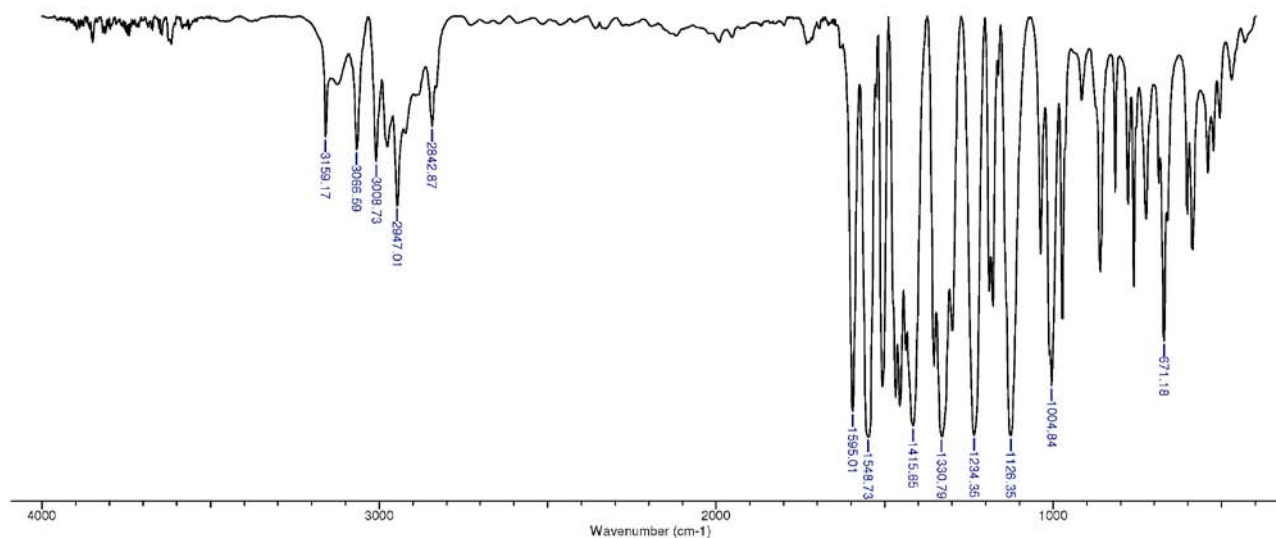
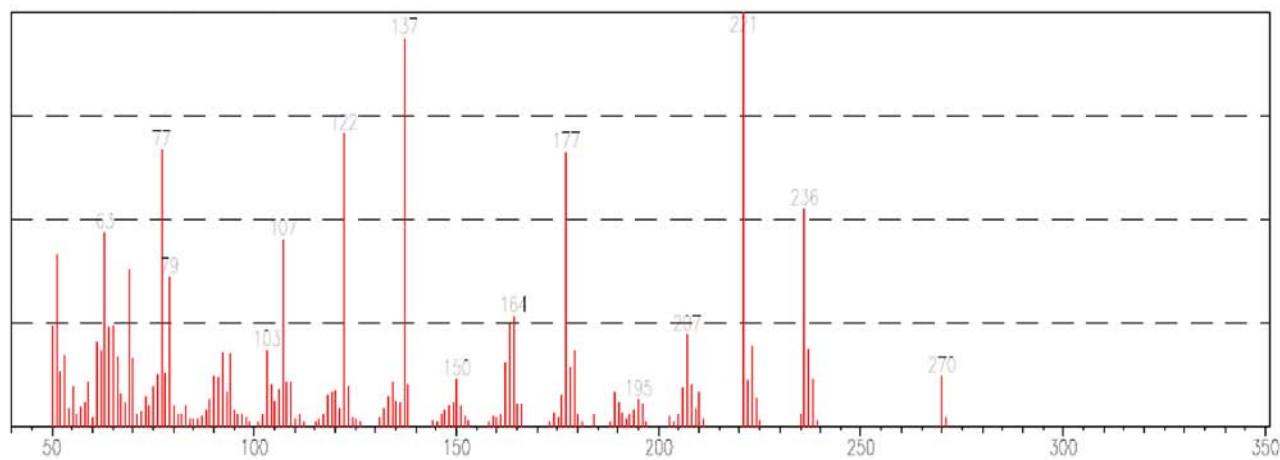
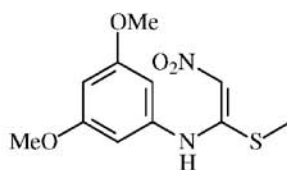
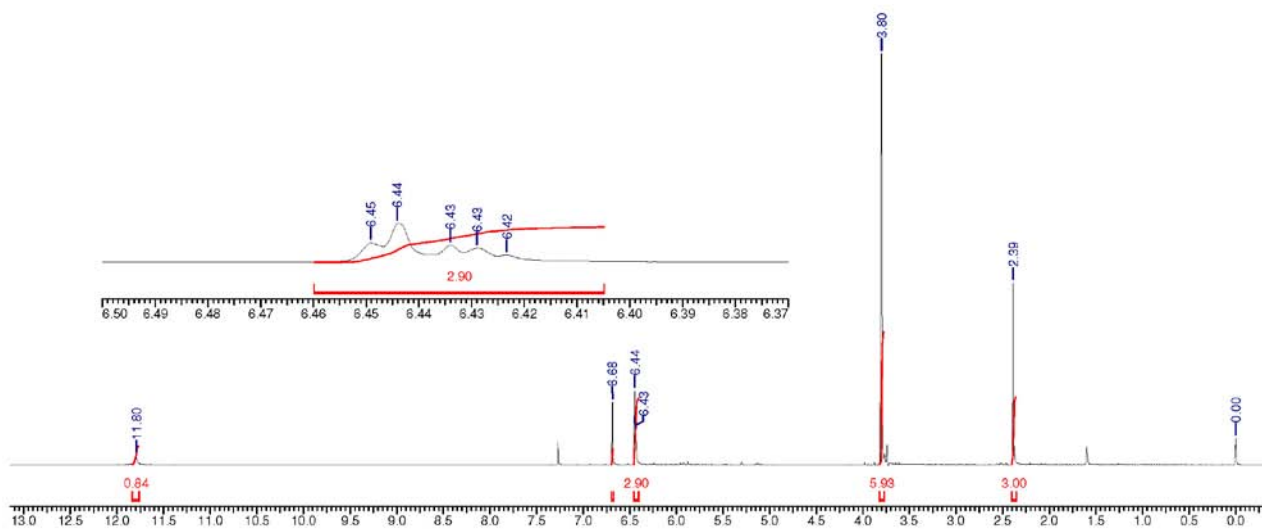


Figure S5. IR of 3,4,5-Trimethoxy-N-[1-(methylthio)-2-nitroethyl]-benzenamine (3a)

3,5-Dimethoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (3b)**Figure S6.** GC-MS of 3,5-Dimethoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3b**).**Figure S7.** ¹H NMR of 3,5-Dimethoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3b**)

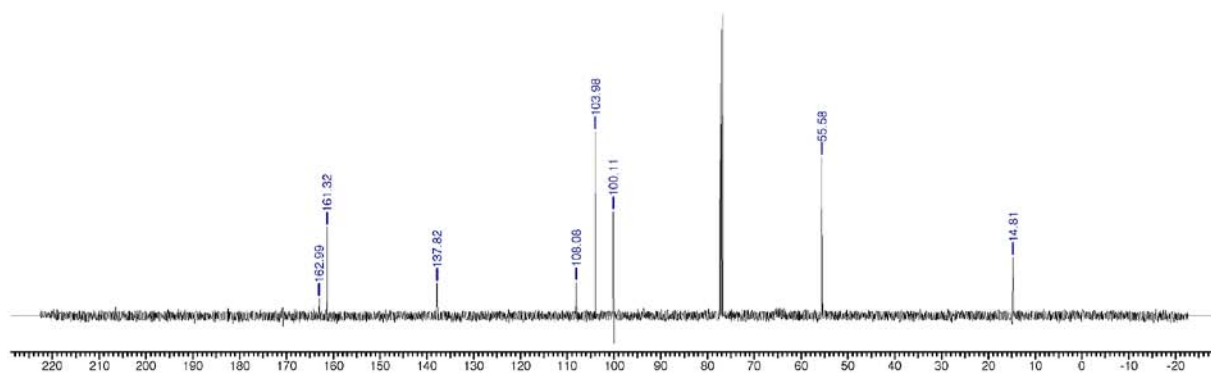


Figure S8. ¹³C NMR of 3,5-Dimethoxy-N-[1-(methylthio)-2-nitroethyl]-benzenamine (3b).

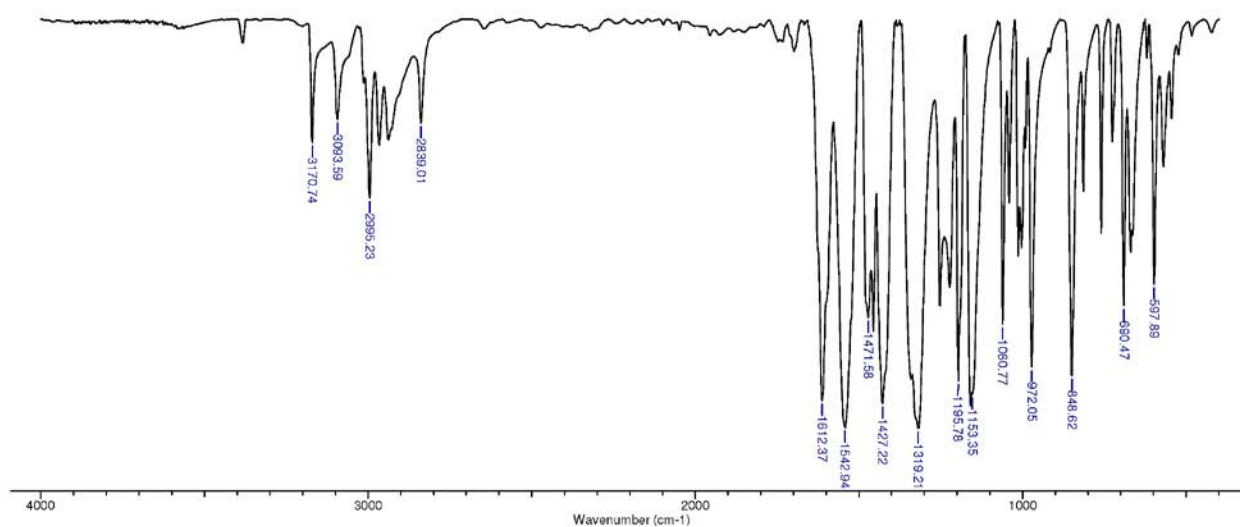
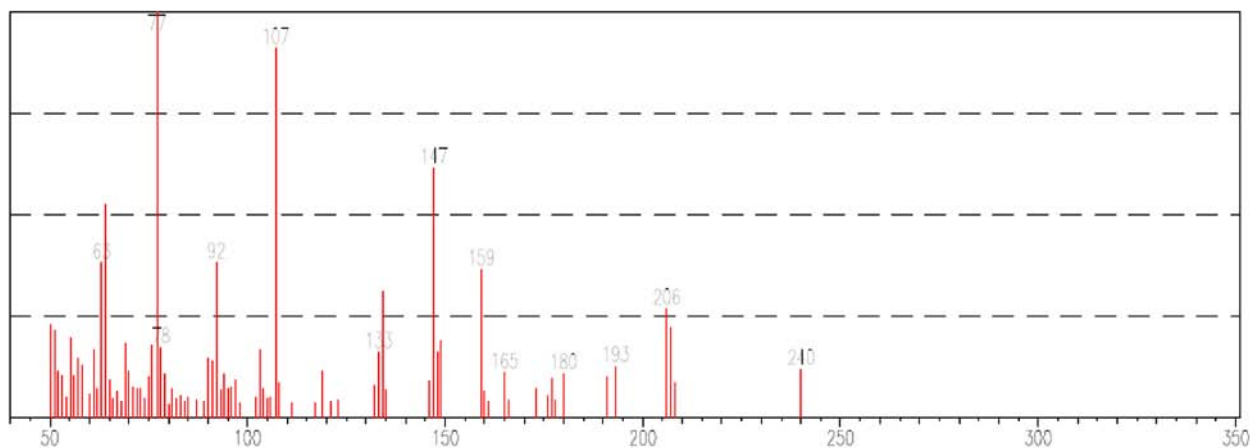
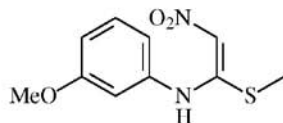
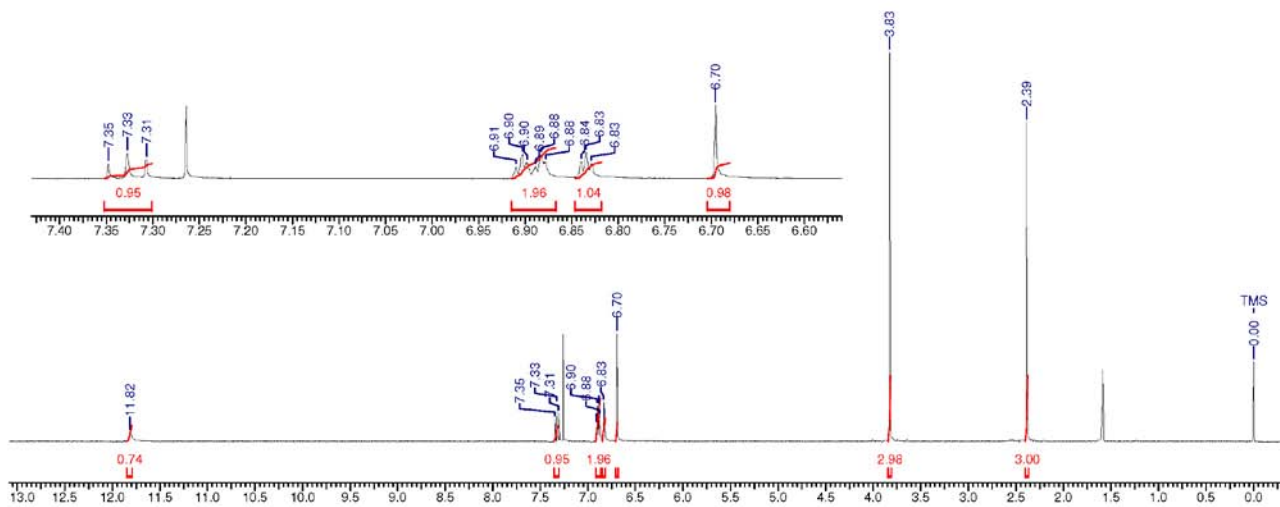


Figure S9. IR of 3,5-Dimethoxy-N-[1-(methylthio)-2-nitroethyl]-benzenamine (3b)

3-Methoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (3c)**Figure S10.** GC-MS of *3-Methoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (3c)*.**Figure S11.** ^1H NMR of *3-Methoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (3c)*.

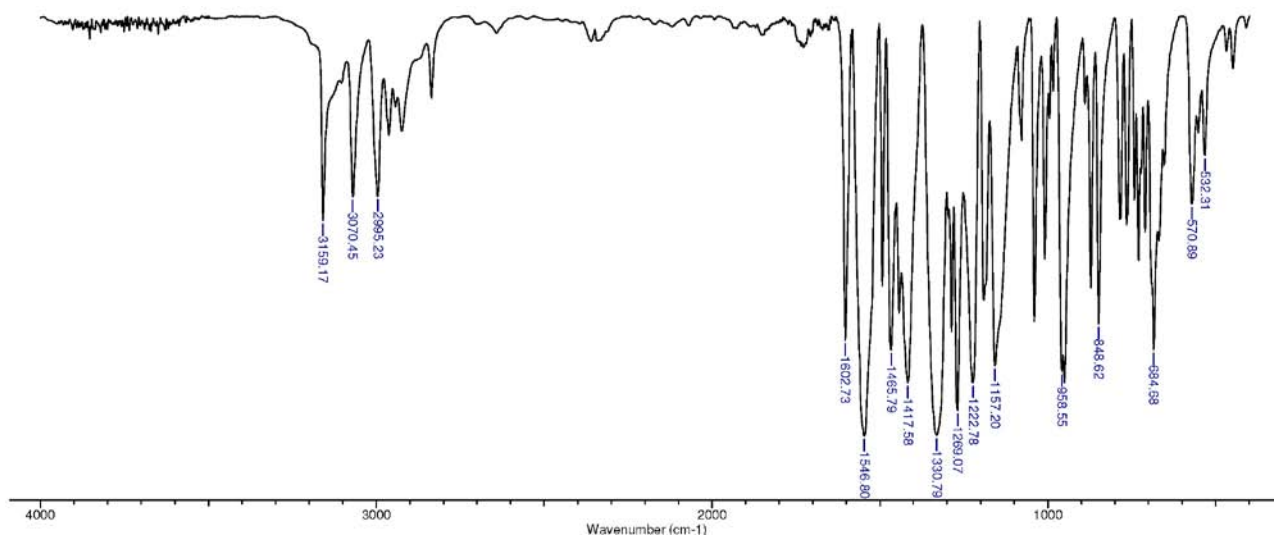


Figure S12. IR of 3-Methoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3c**).

2,5-Dimethoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (3d)

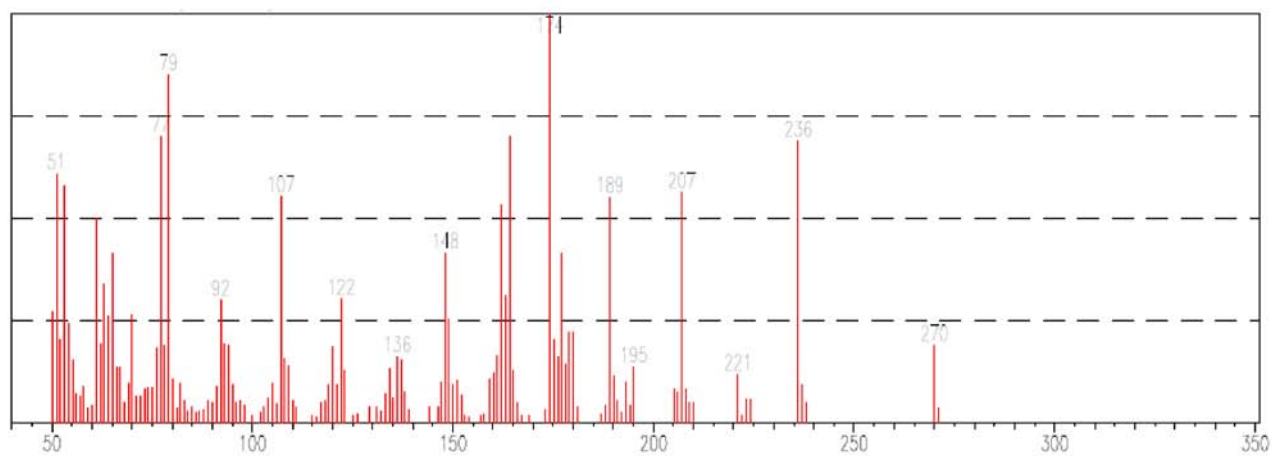
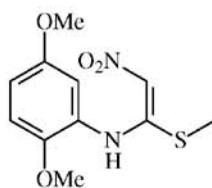


Figure S13. GC-MS of 2,5-Dimethoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3d**).

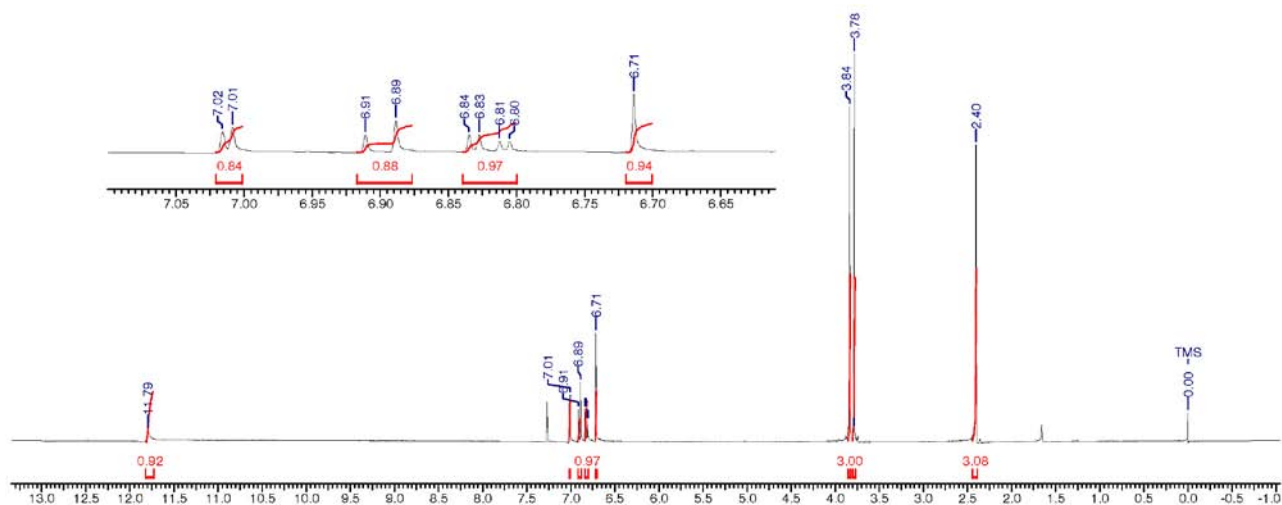


Figure S14. ¹H NMR of 2,5-Dimethoxy-*N*-[1-(methylthio)-2-nitroethenyl]-benzenamine (3d).

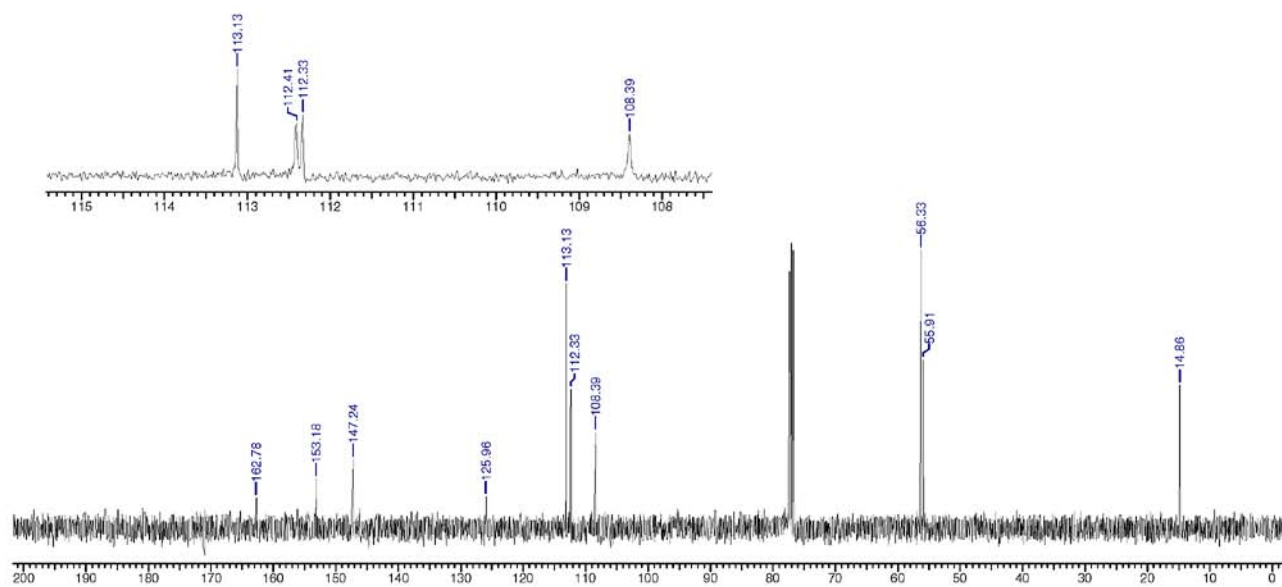


Figure S15. ¹³C NMR of 2,5-Dimethoxy-*N*-[1-(methylthio)-2-nitroethenyl]-benzenamine (3d).

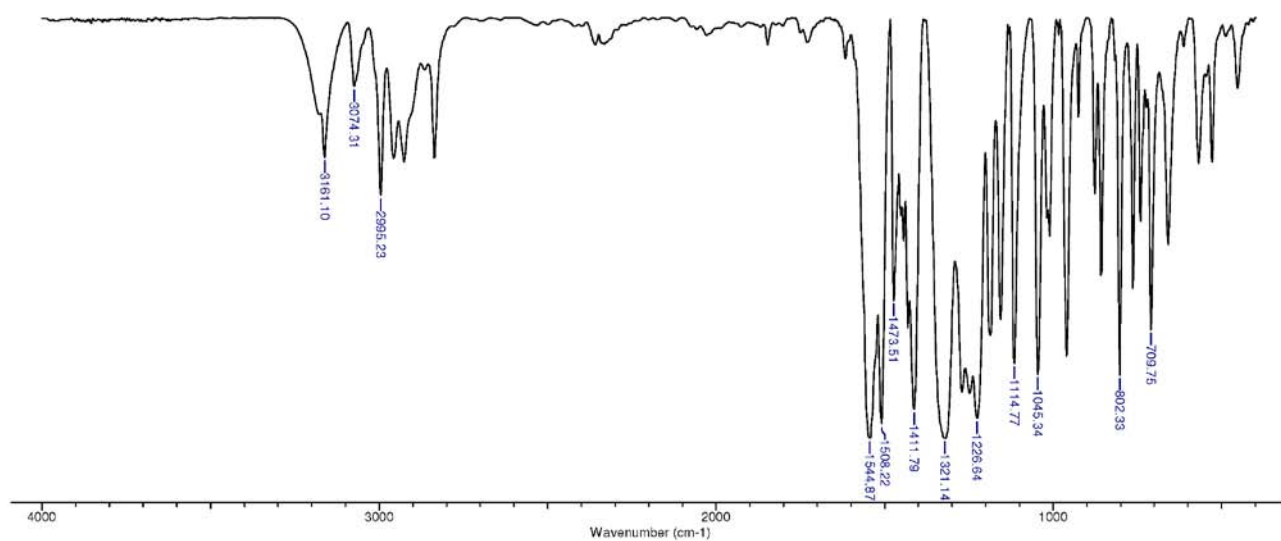


Figure S16. IR of 2,5-Dimethoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3d**).

*4-Methoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3e**)*

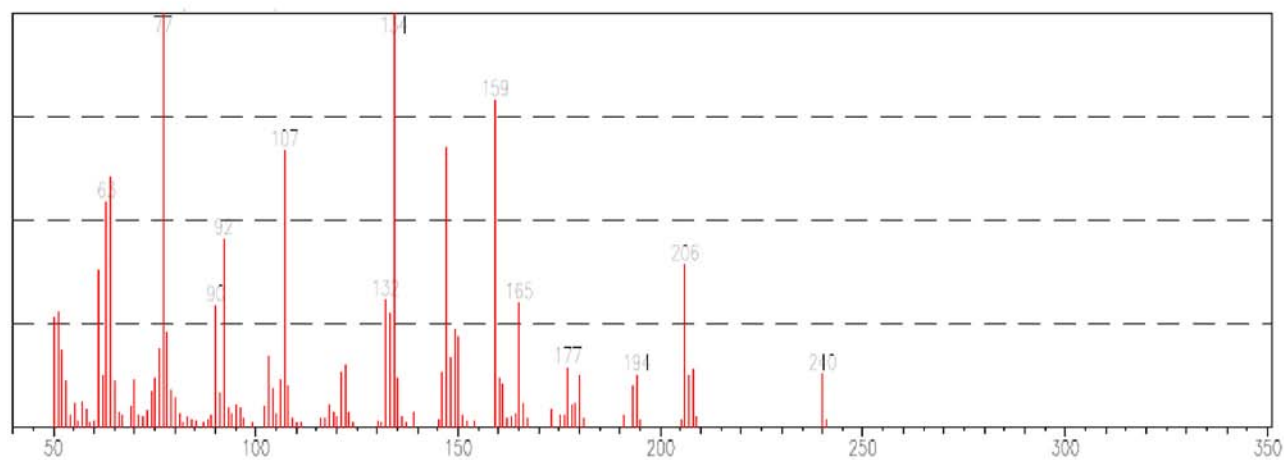
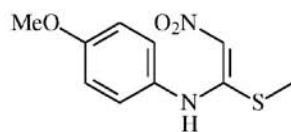


Figure S17. GC-MS of 4-Methoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3e**).

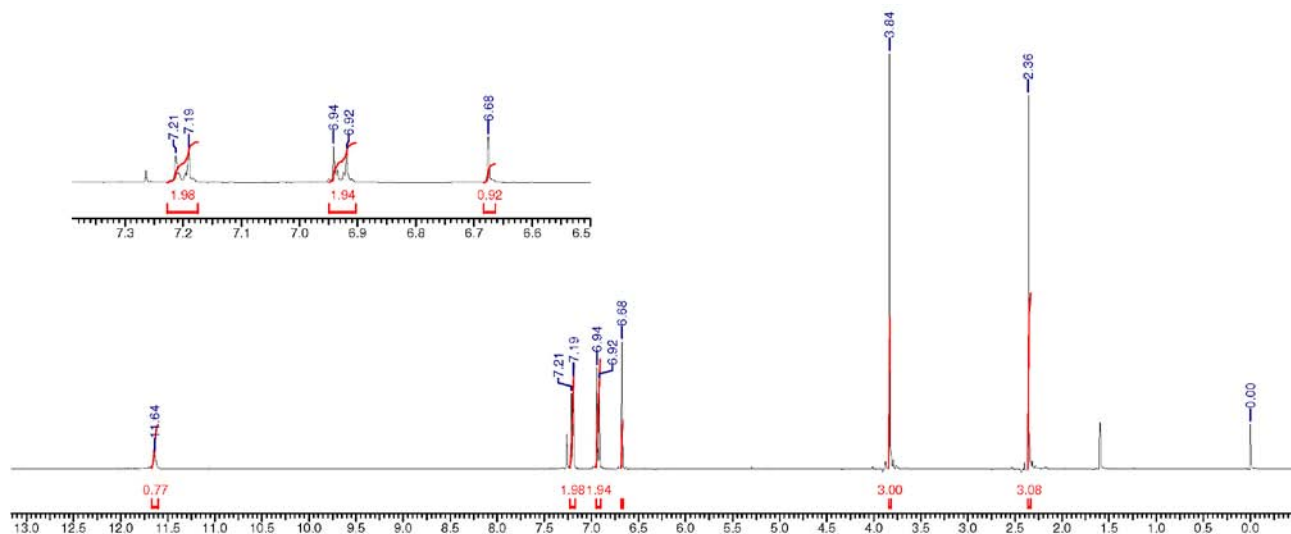


Figure S18. ¹H NMR of 4-Methoxy-N-[1-(methylthio)-2-nitroethyl]-benzenamine (3e).

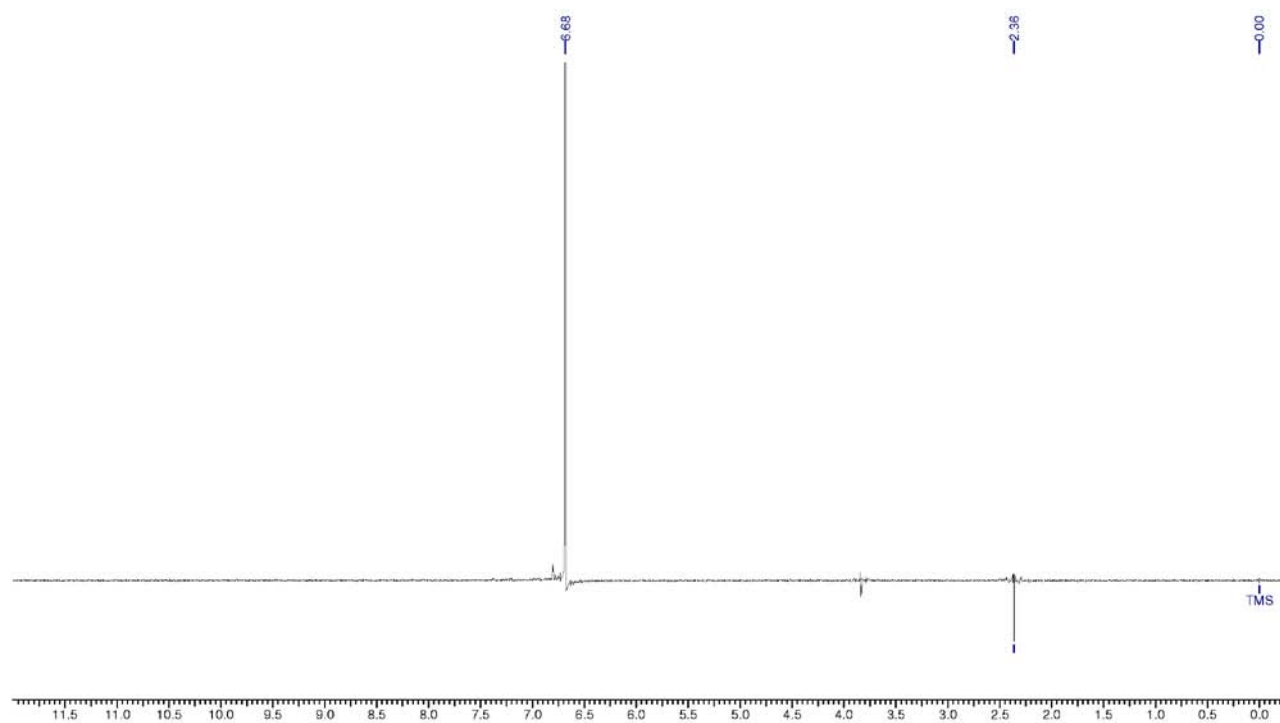


Figure S19. ¹H NMR-NOE of 4-Methoxy-N-[1-(methylthio)-2-nitroethyl]-benzenamine (3e).

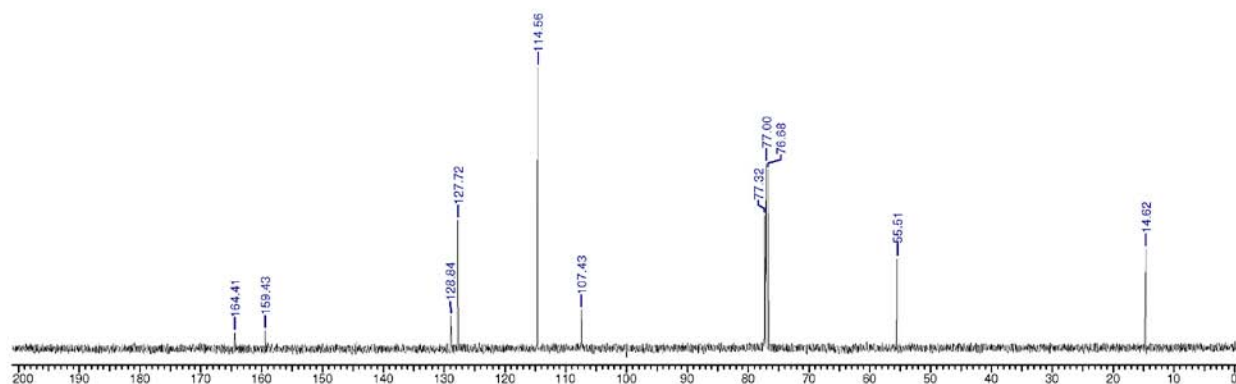


Figure S20. ¹³C NMR of 4-Methoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (3e).

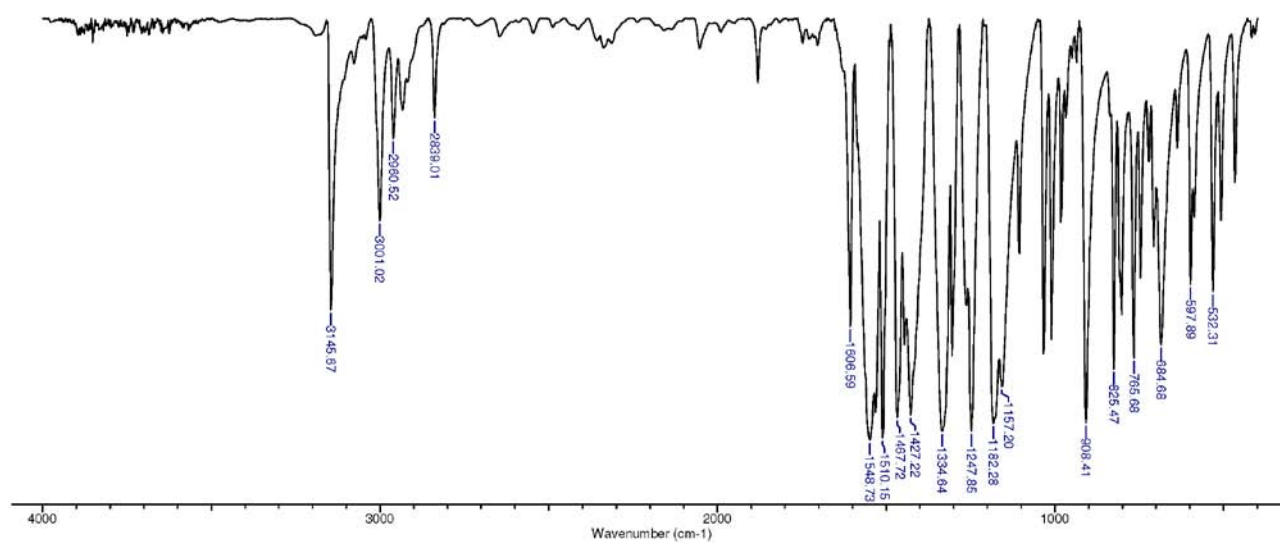
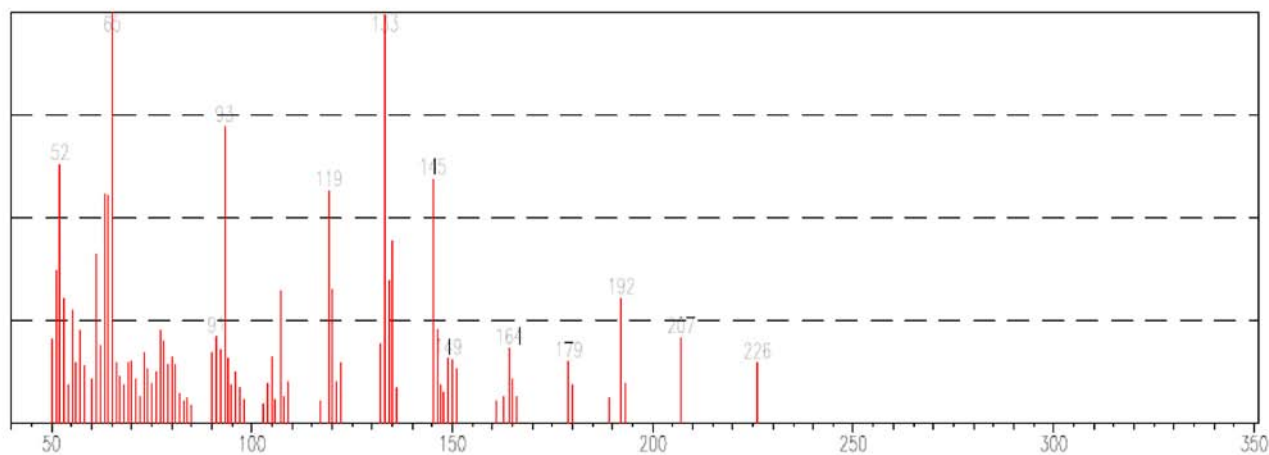
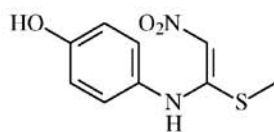
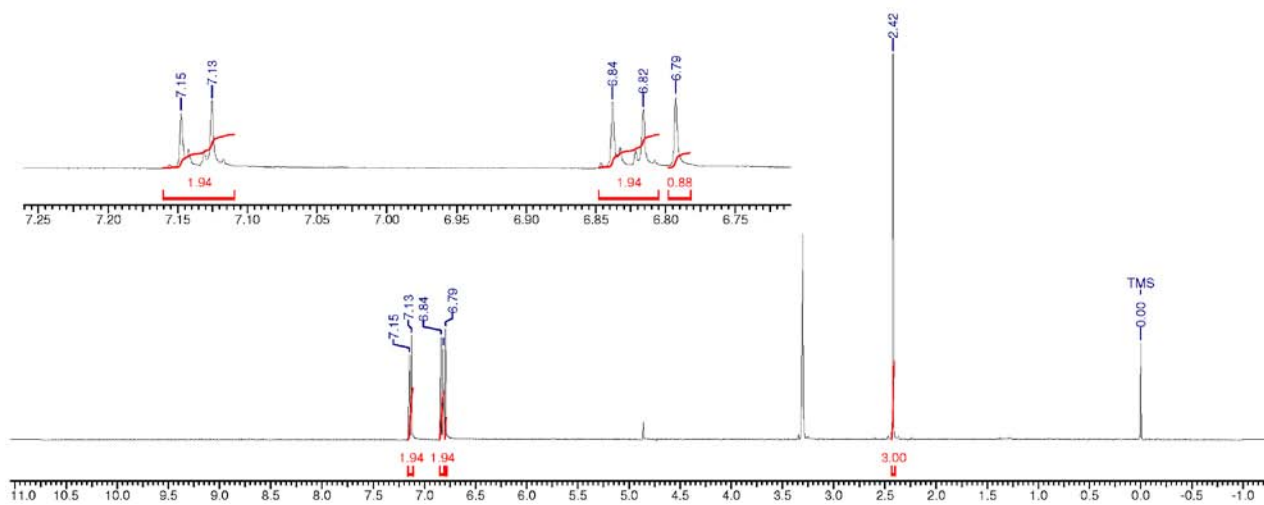


Figure S21. IR of 4-Methoxy-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (3e).

4-[[1-(methylthio)-2-nitroethenyl]amino]-phenol (**3f**)**Figure S22.** GC-MS of 4-[[1-(methylthio)-2-nitroethenyl]amino]-phenol (**3f**).**Figure S23.** ¹H NMR of 4-[[1-(methylthio)-2-nitroethenyl]amino]-phenol (**3f**).

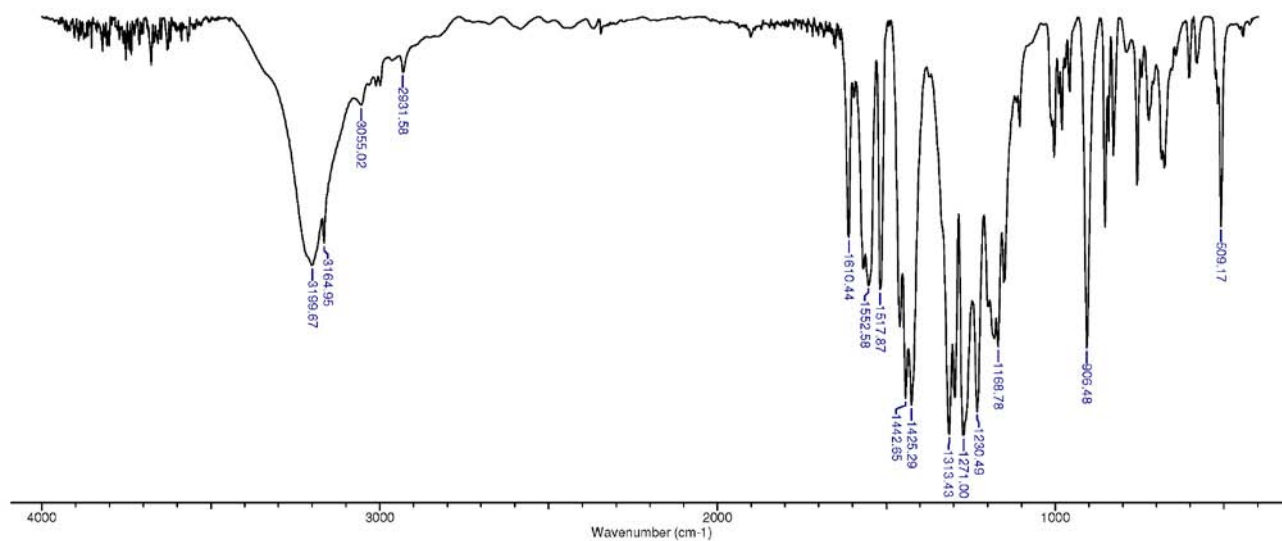


Figure S24. IR of 4-[[1-(methylthio)-2-nitroethyl]amino]-phenol (**3f**).

4-Fluoro-N-[1-(methylthio)-2-nitroethyl]-benzenamine (**3h**)

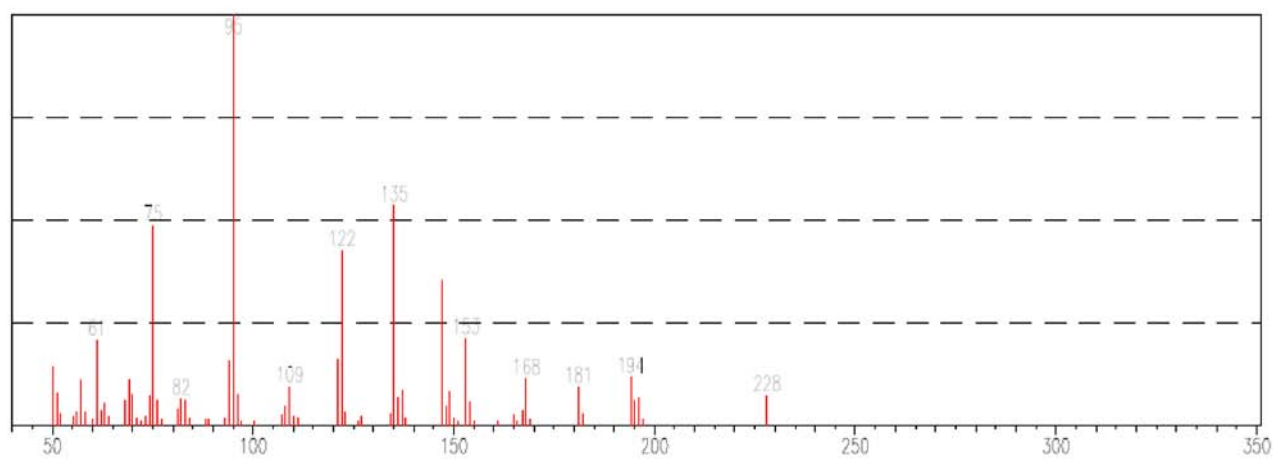
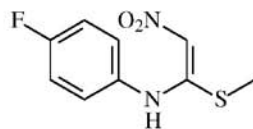


Figure S25. GC-MS of 4-Fluoro-N-[1-(methylthio)-2-nitroethyl]-benzenamine (**3h**).

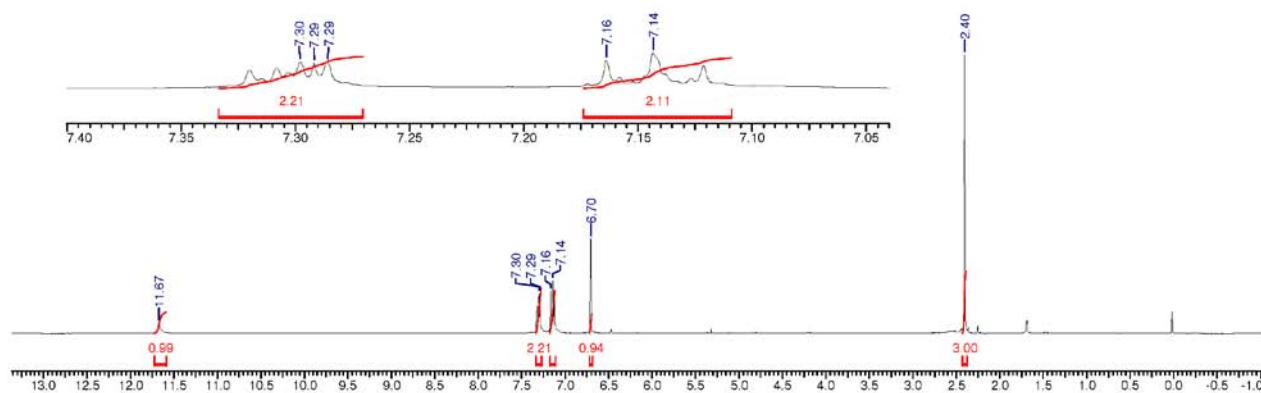


Figure S26. ¹H NMR of 4-Fluoro-N-[1-(methylthio)-2-nitroethyl]-benzenamine (3h).

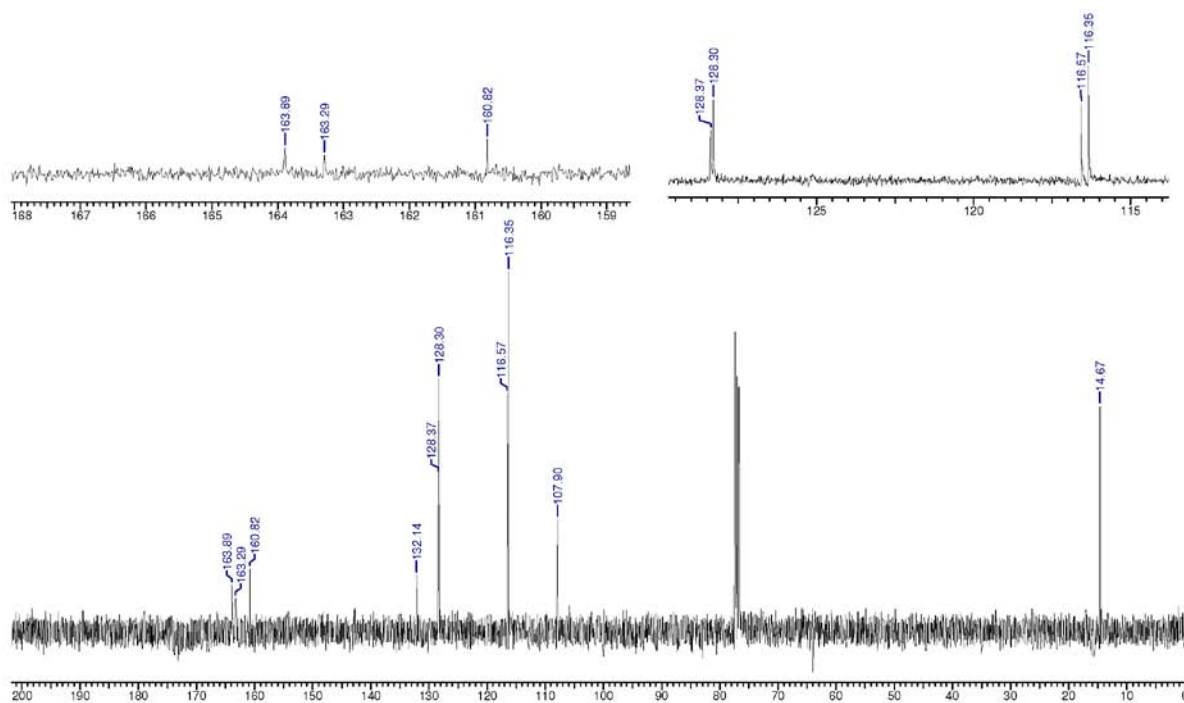


Figure S27. ¹³C NMR of 4-Fluoro-N-[1-(methylthio)-2-nitroethyl]-benzenamine (3h).

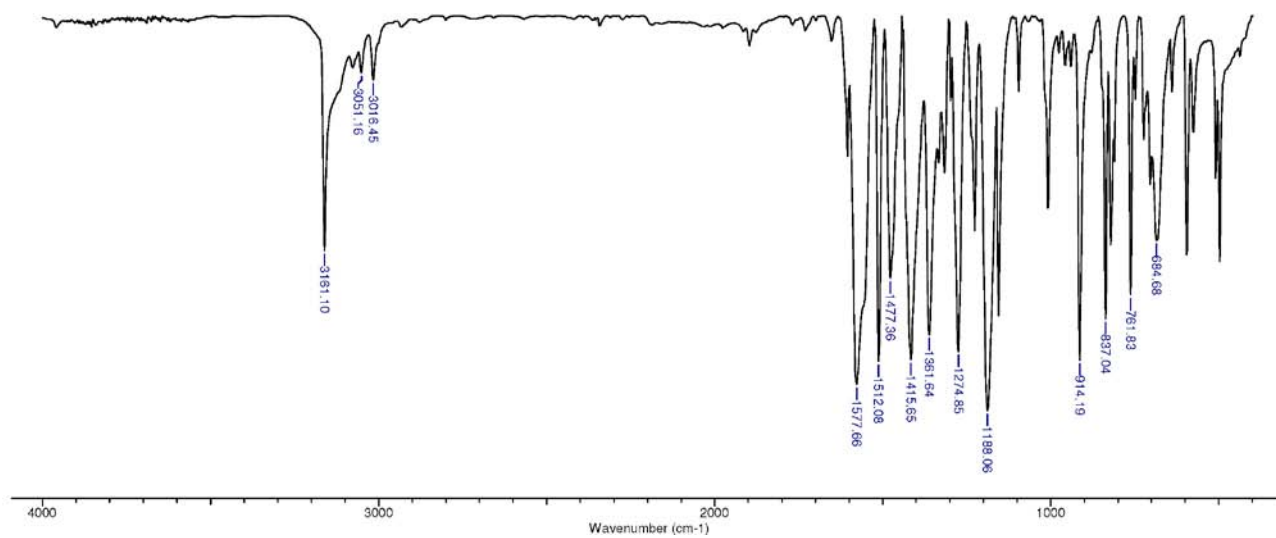


Figure S28. IR of 4-Fluoro-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3h**).

4-Bromo-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3j**)

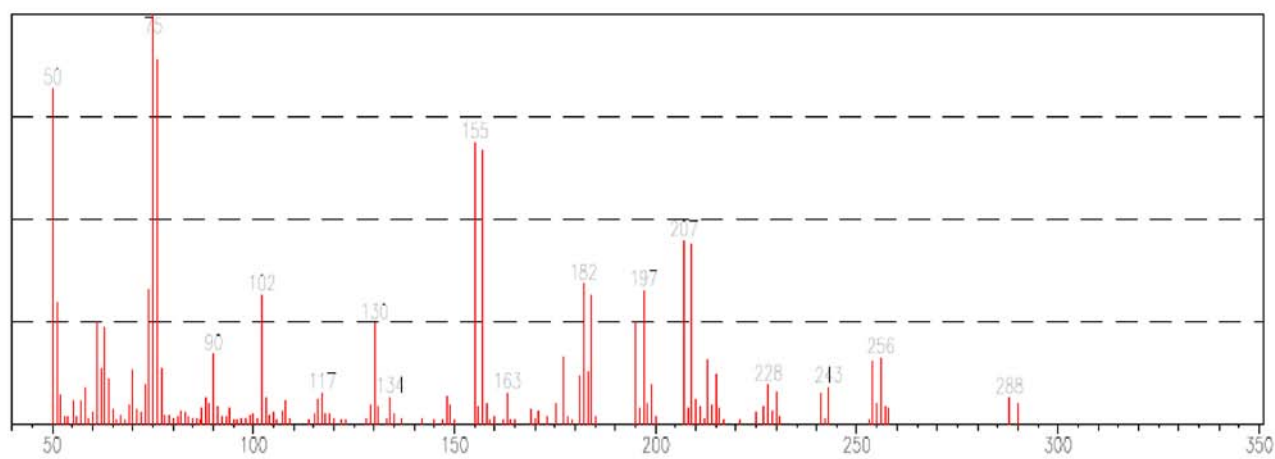
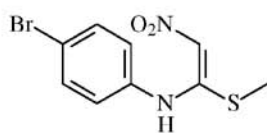


Figure S29. GC-MS of 4-Bromo-N-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3j**).

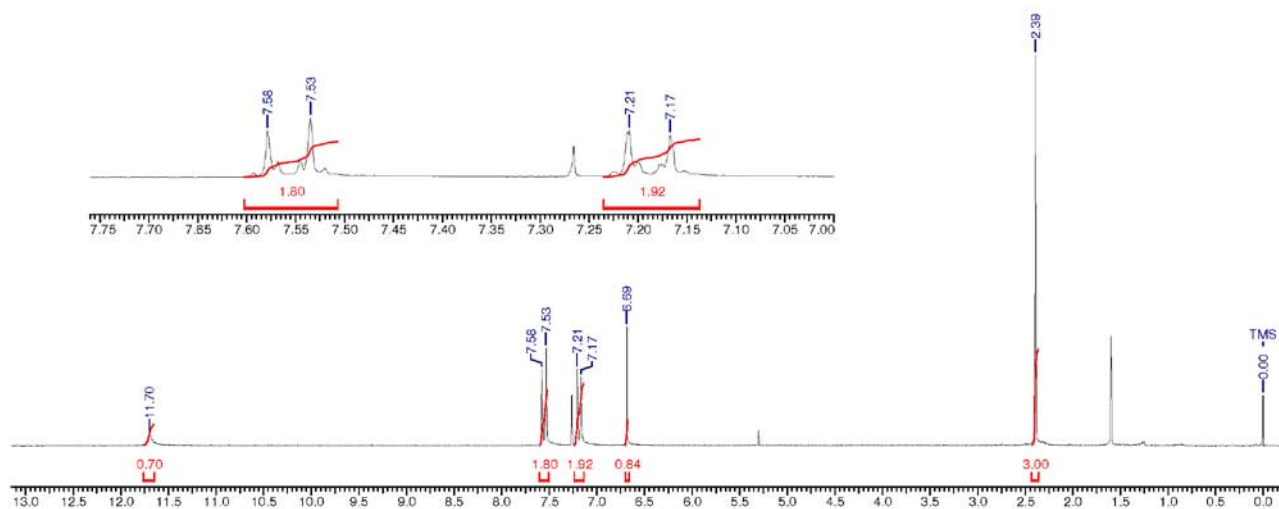


Figure S30. ¹H NMR of 4-Bromo-N-[1-(methylthio)-2-nitroethyl]-benzenamine (**3j**).

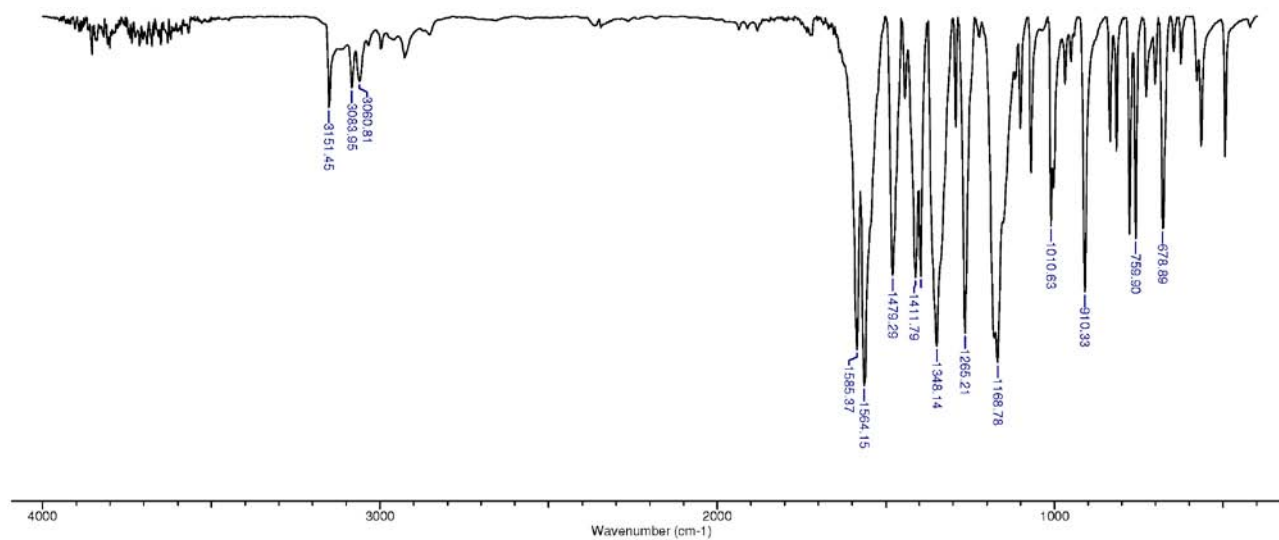


Figure S31. IR of 4-Bromo-N-[1-(methylthio)-2-nitroethyl]-benzenamine (**3j**).

N-[1-(methylthio)-2-nitroethenyl]-1,3-benzodioxol-5-amine (**31**)

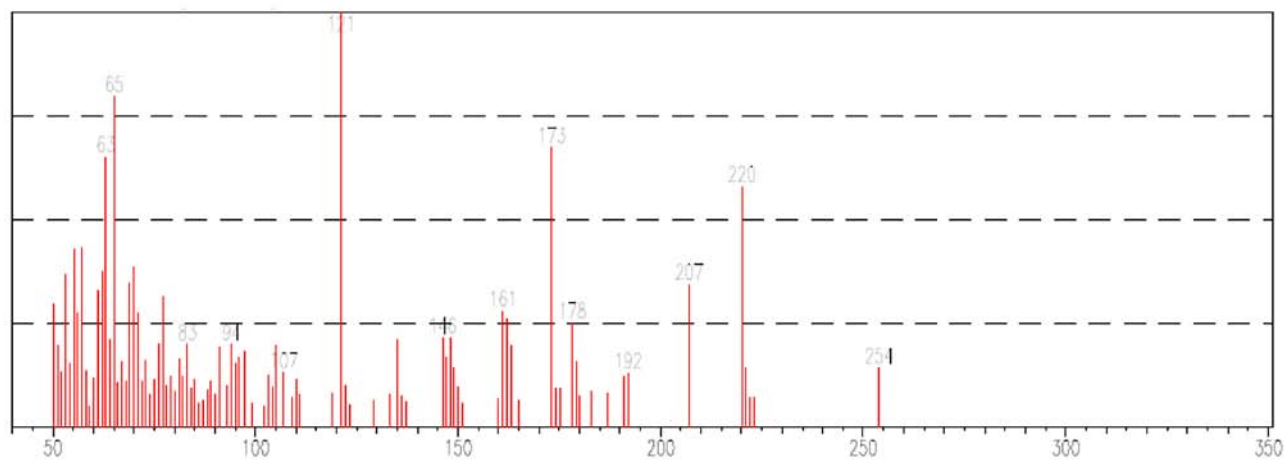
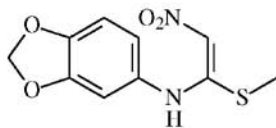


Figure S32. GC-MS of *N*-[1-(methylthio)-2-nitroethenyl]-1,3-benzodioxol-5-amine (**31**).

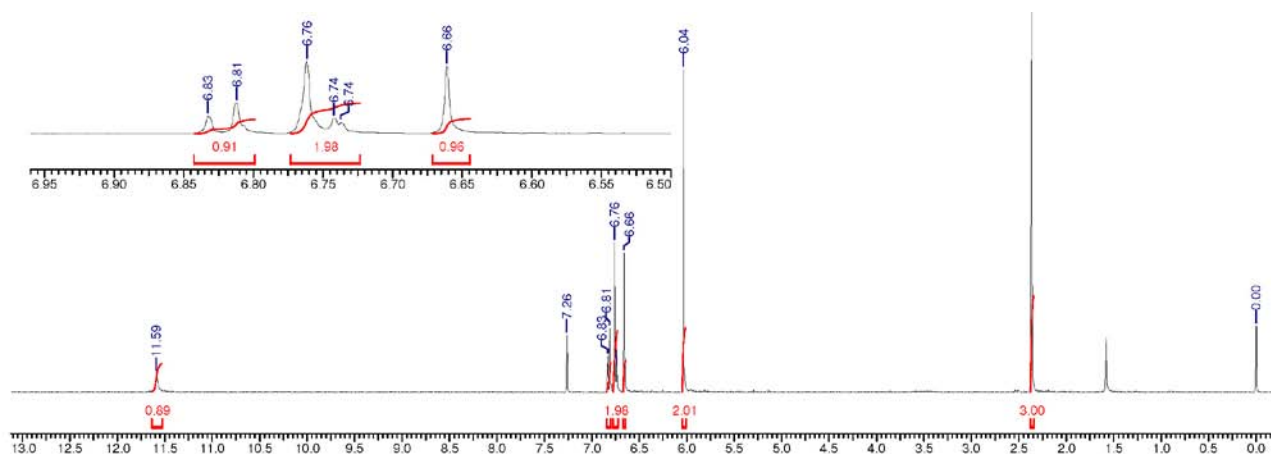


Figure S33. ^1H NMR of *N*-[1-(methylthio)-2-nitroethenyl]-1,3-benzodioxol-5-amine (**31**).

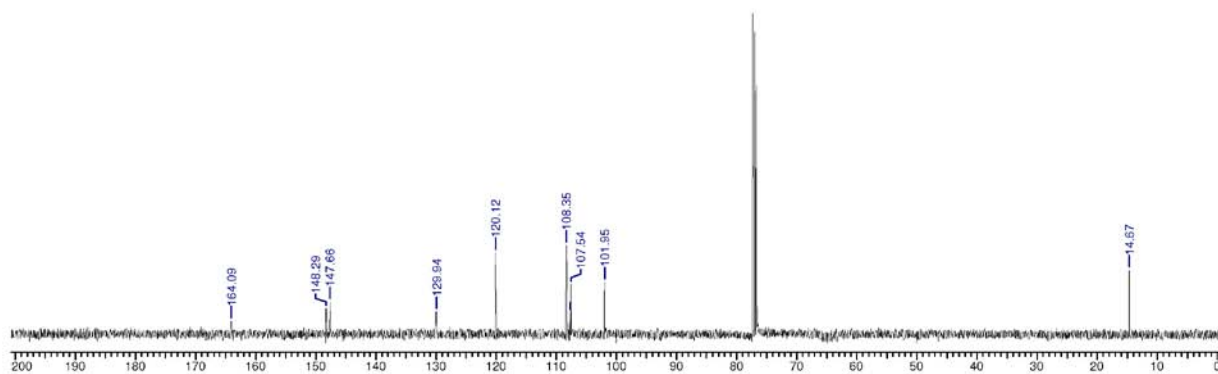


Figure S34. ¹³C NMR of *N*-[1-(methylthio)-2-nitroethyl]-1,3-benzodioxol-5-amine (31).

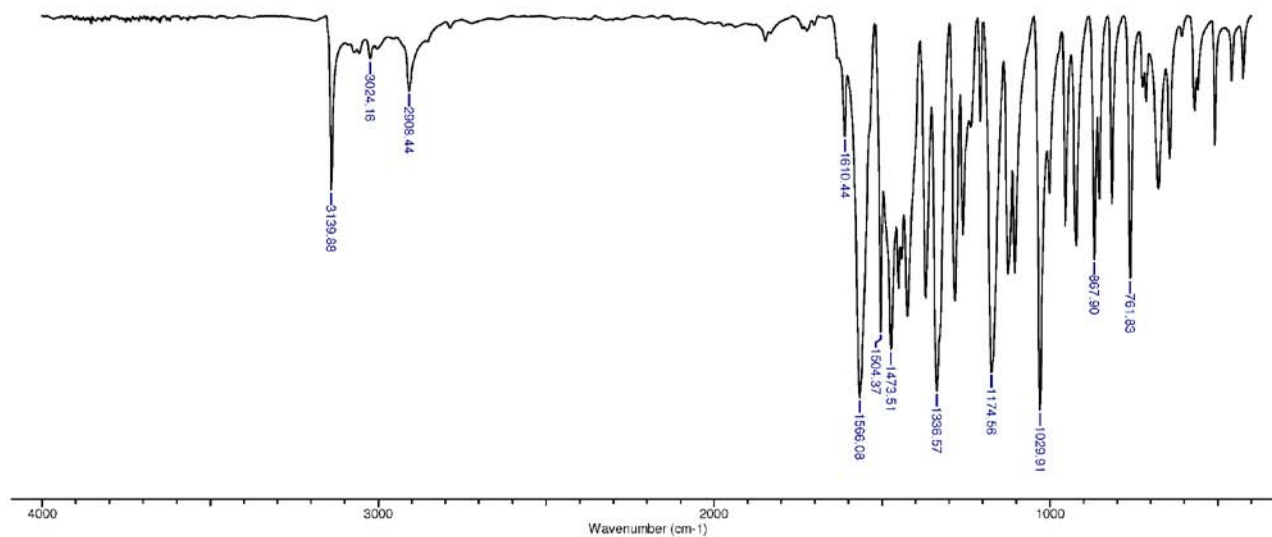
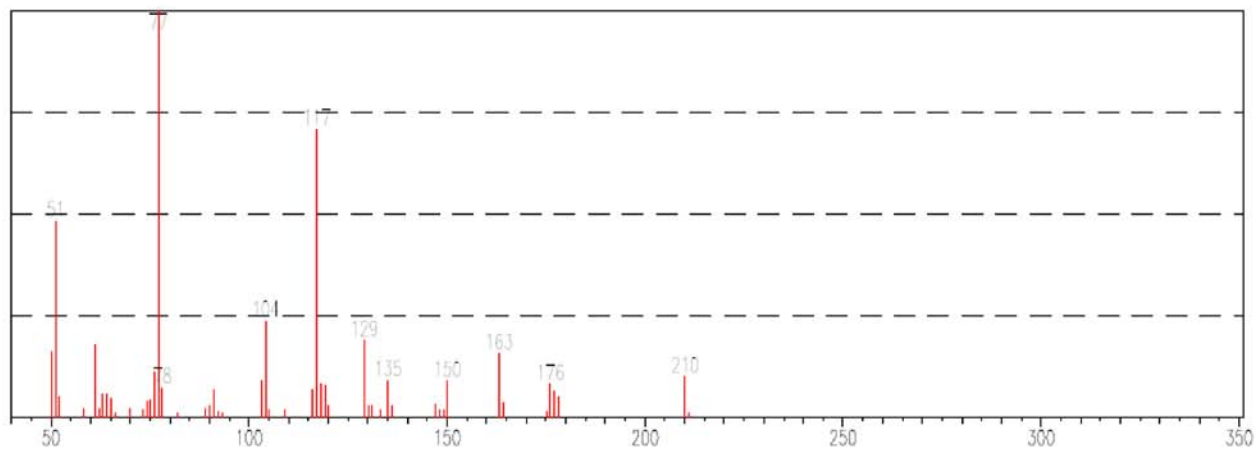
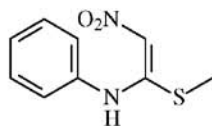
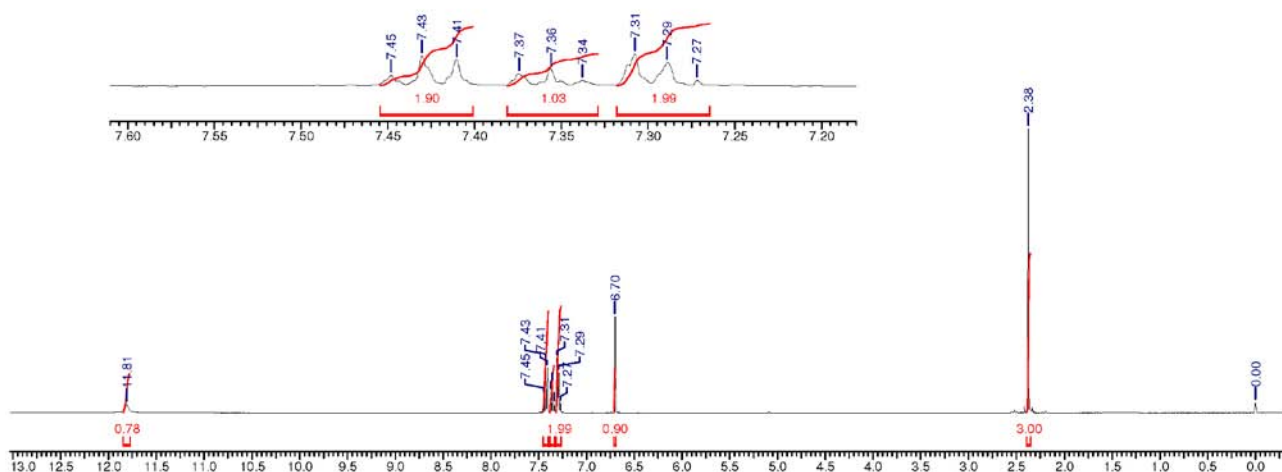


Figure S35. IR of *N*-[1-(methylthio)-2-nitroethyl]-1,3-benzodioxol-5-amine (31).

N-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3m**)**Figure S36.** GC-MS of *N*-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3m**).**Figure S37.** ^1H NMR of *N*-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3m**).

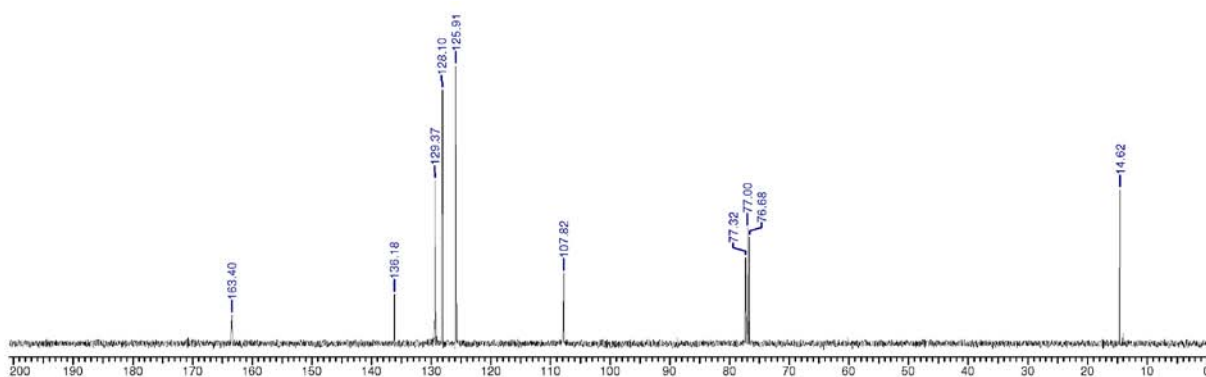


Figure S38. ¹³C NMR of *N*-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3m**).

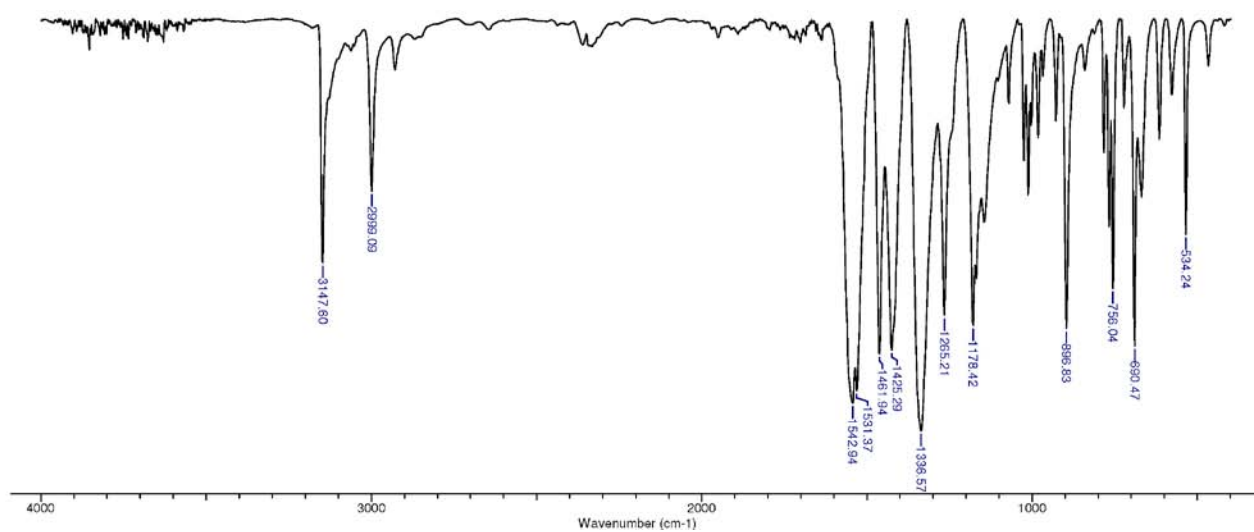


Figure S39. IR of *N*-[1-(methylthio)-2-nitroethenyl]-benzenamine (**3m**).