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Trimethylsilyl Chloride Assisted Conjugate Addition-Elimination of Organocopper Reagents to 2-Bis(methylthio)nitroethylene: An Efficient and Highly Stereoselective Synthesis of 2-Methylthio-2-alkyl/aryl-1-nitroethylenes and their Application for Synthesis of Nitroheterocycles

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Abstract: An efficient method for the synthesis of novel 2-methylthio-2-alkyl/aryl-1-nitroethylenes **2** has been developed via conjugate addition-elimination of organocopper reagents to nitroketene dithioacetal **1** in the presence of TMSCl. The product nitroethylenes **2** have been further utilized for the synthesis of substituted 3-nitro-2-alkyl/arylpyrroles **5** by their reaction with aminoacetaldehyde dimethylacetal followed by acid catalyzed cyclization in ethereal HCl. The reaction of **2** with propargyl alcohol has also been investigated. © 1998 Elsevier Science Ltd. All rights reserved.

Introduction

Nitroalkenes are excellent Michael acceptors[1] which undergo facile addition with stabilized carbon nucleophiles such as organolithium reagents, silyl enolates, silyl keteneacetals and enamines to afford the corresponding nitroalkanes in excellent yields.[2] Additions of nonstabilized organometallics generally derived from Li, Mg, Zn, Al and Cu have also been examined although their reactions with nitroolefins are invariably accompanied with undesirable polymerization and redox processes.[2,3] The nitroolefins with leaving groups in the β–position such as dialkylamino, alkylthio or phenylsulfonyl group follow addition-elimination sequence, when reacted with amines, enolates, RMgX and RLi nucleophiles to afford the corresponding β–substituted nitroolefins in varying yields.[4] We have recently reported the conjugate addition of organocopper reagents to α-oxoketene S,S-[5] and O,S-acetals[6] and observed that the addition-elimination sequence follows highly stereoselective pathway to afford high yields of β–substituted-β-alkylthio (or alkoxy) enones with ***Z*** configuration. We further became interested in extending these additon-elimination reactions of organocopper reagents to 2-bis(methylthio)nitroethylene **1** with a view to develop a new general synthetic route for 2-alkyl/aryl-2-alkylthionitroethylenes **2**, a class of potentially versatile yet unexplored synthetic intermediates which only appeared in the literature for the first time in 1984.[7] These nitroethylenes are of further synthetic value as they would undergo another addition-elimination sequence with various O-, N- and carbon nucleophiles. The synthetic application of these compounds has not been explored although the corresponding β-phenylsulfonyl nitroalkenes are shown to be useful nitroacetylene equivalents in Diels-Alder cycloaddition reactions especially for the synthesis of nitroaromatic compounds.[8] Much of these studies are limited to only a few systems apparently due to the lack of suitable methods for their synthesis. The only method described in

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the literature[7,8] constitutes a multistep tedious process involving preparation of α-nitroketones, their conversion to diphenyl/ethylthioketals followed by Lewis acid / base [$AlCl_3$, KF, Hg(II)trifluoroacetate / Li_2CO_3] assisted or oxidative (MCPBA) elimination of one of the ethyl/phenylthio groups to afford a stereoisomeric mixture of the corresponding 2-phenyl/ethylthio-1-nitroalkenes in moderate to good yields.

It is therefore important that a more convenient general method for the synthesis of this class of nitroalkenes would catalyze further studies, particularly on the synthetic application of these intermediates. We have therefore examined the reaction of organocopper reagents with nitroketene S,S- acetal **1**[9] and observed that the reaction proved to afford hitherto unknown β-methylthio-β-alkyl/arylnitroethylenes in highly stereoselective manner involving the expected addition-elimination sequence. The intermediates thus obtained have been shown to be useful precursors for the synthesis of 3-nitro-2-alkyl/arylpyrroles and a few 3-nitrofurans in good yields. These results are described in this paper.

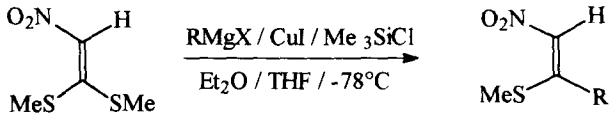
Results and Discussion

A. Synthesis of β-Methylthio-β-aryl/alkylnitroethylenes (2a-j)

Knochel and coworkers have recently reported[4] a useful preparative route for polyfunctionalized nitroolefins by addition-elimination of copper-zinc organometallic reagents to β-methylthio-β-phenylsulfonyl nitroolefins. They have also reported the reaction of 2-bis(methylthio)nitroethylene **1** with copper-zinc reagent (3 eqv.) to afford β-disubstituted nitroethylenes formed by concomitant displacement of both the methylthio groups. No attempts were made by these workers for selective displacement of one of the methylthio groups of **1** by zinc-copper reagent. This, to our knowledge is the only report of the addition of nonstabilized organometallic reagents to nitroketene dithioacetal **1**.

Our initial attempt to react Grignard reagents or butyllithium with **1** were not successful and the reaction generally resulted in intractable polymeric product mixtures. Similarly, the addition of Grignard reagents to **1** in the presence of Cu (I) halides (catalytic or stoichiometric) did not give any clear cut products and formed only the polymeric mixtures. However when **1** was reacted with ethylmagnesium iodide, cuprous iodide in the presence of trimethylsilyl chloride in tetrahydrofuran at -78°C, the reaction mixture after work up yielded the corresponding β-ethyl-β-methylthionitroethylene **2a** in 61% yield (Scheme 1).[10] Similarly, the other higher organocopper reagents were reacted with **1** in the presence of trimethylsilyl chloride to afford the corresponding β-alkyl-β-methylthionitroethylenes **2b-f** in 68-72% overall yields. The reagent apparently displaced only one methylthio group and no trace of β,β–bisalkylnitroolefins or any polymeric side product was observed. Interestingly, addition of these trimethylsilyl chloride assisted organocopper reagents to **1** was found to be highly stereoselective yielding only one stereoisomer in all the systems examined. The stereo chemistry of a few 2-methylthio-1-nitroalkenes (**2a, 2c-d**) was established by differential NOE experiment and was found to be of *Z* configuration. Thus irradiation of olefinic proton at δ 7.23 in **2a** displayed n.O.e enhancement (5.8%) of methylene proton ($\underline{CH_2}$-CH_3, δ 2.62), while no intensity enhancement was observed for olefinic proton signal when SMe proton signal (δ 2.41) was irradiated. The reaction was equally facile with benzyl organocopper reagent under similar reaction conditions to afford the corresponding β-benzylnitroethylene **2g** in 71% yield. The other aryl Grignard reagents similarly reacted with **1** under identical reaction conditions as described to afford the corresponding β-arylnitroethylenes **2h-j** in 65-70% overall

yields. However, the reaction of methylmagnesium iodide with **1** under the described conditions failed to afford the corresponding β-methyl-β-methylthionitroethylene **2k** (R = Me) and resulted only in polymeric product mixture.



1 **2**

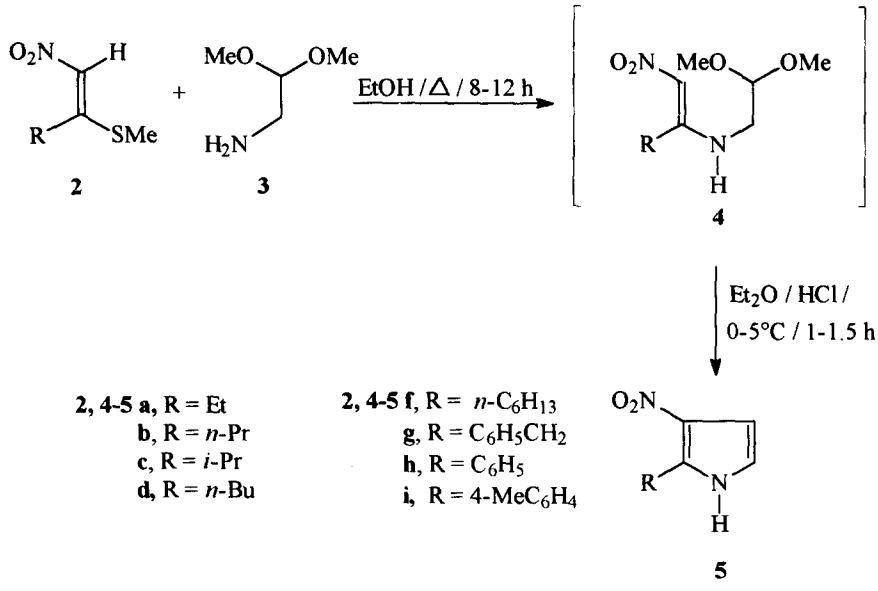
2	R	yield(%)	2	R	yield(%)
a	Et	61	**f**	n-C_6H_{13}	70
b	n-Pr	72	**g**	$C_6H_5CH_2$	71
c	i-Pr	71	**h**	C_6H_5	65
d	n-Bu	68	**i**	4-MeC_6H_4	70
e	t-Bu	68	**j**	4-$MeOC_6H_4$	69

Scheme 1

B. Cyclization of 2 with Aminoacetaldehyde dimethylacetal: A New General Method for the Synthesis of 2-Alkyl/aryl-3-nitropyrroles (5a-d, 5f-i)

Nitroketene S,S-acetal **1** was earlier reacted with aminoacetaldehyde diethylacetal **3** to yield the corresponding N,S-acetal which was shown to undergo ethereal hydrochloric acid assisted cyclization to afford the corresponding 2-methylthio-3-nitropyrrole in 70% yield.[11] Also, a number of heterocyclic N-ylides have been shown to undergo cyclization with bis(methylthio)nitroethylene and other polarized nitroolefins to afford pyrrolo fused heterocycles in good yields.[12] The β-methylthionitroethylenes **2a-j** now available from **1** are therefore an important group of functionalized nitroolefins useful for the synthesis of 2-substituted-3-nitropyrroles. The direct synthesis of 3-nitropyrroles from pyrrole itself or 2-substituted pyrroles using classical nitration involving electrophilic substitution is not possible since it affords 2 or 5-substituted pyrroles.[13] The reported method for 1,2-disubstituted-3-nitropyrroles involves the nitration of 1,2-disubstituted 5-alkoxycarbonyl pyrroles followed by hydrolysis and decarboxylation of the 5-alkoxycarbonyl group.[14] The alkoxycarbonyl group is shown to be playing both as protecting and directing group. The overall yields of the corresponding nitropyrroles were consequently low by this procedure. Similarly a series of 3-nitropyrroles have been synthesized by base induced cycloaddition of tosylmethyl isocyanides to nitroalkenes[15]. The present method which carries the nitro group from the open chain nitroethylene precursor to the product pyrrole appears to be a useful alternative for the synthesis of 3-nitropyrrole derivatives. Besides, 3-nitropyrroles are structural constituents of important pharmaceutical drugs[14b-d,15] and precursors for biologically important compounds like Distamycin and pyrrole polyamides used in sequence specific

recognition of double helical DNA.[16] We have now developed a facile synthesis of 3-nitro-2-substituted pyrroles by reacting **2** with aminoacetaldehyde dimethylacetal to yield the corresponding nitroenamines followed by their cyclization. Thus when **2a** was refluxed with aminoacetadehyde dimethylacetal **3** in ethanol, the reaction mixture after work up yielded the corresponding nitroenamine **4a** in 80% yield (Scheme 2).



Scheme 2

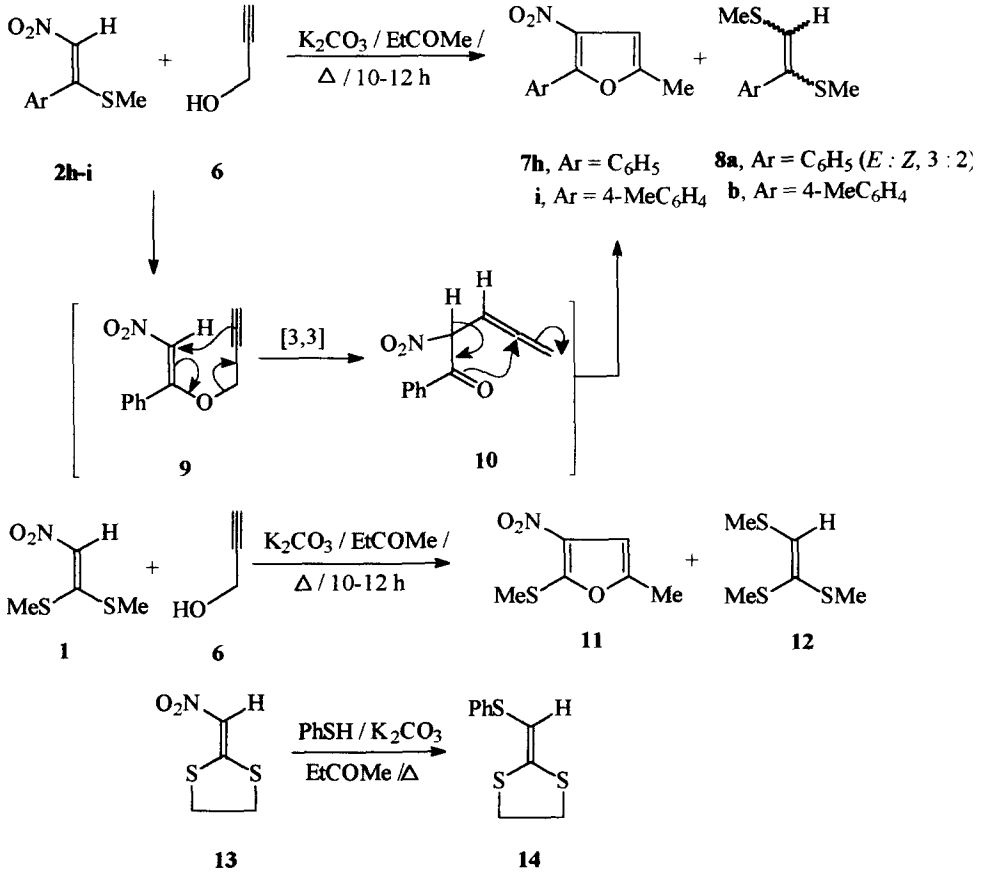
The enamine **4a** was cyclized in the presence of ethereal hydrochloric acid which after work up yielded the corresponding 2-ethyl-3-nitropyrrole **5a** in 50% yield. The other 2-alkyl (**2b-d, 2f**), 2-benzyl (**2g**), 2-aryl (**2h-i**) nitroolefins were similarly reacted with aminoacetaldehyde dimethylacetal to yield the corresponding enamines **4b-d, 4f-i** in overall high yields, which were cyclized as described to afford the corresponding 2-substituted-3-nitropyrroles **5b-d, 5f-i** in 51-69% overall yields (Scheme 2) . The structural assignments of the newly synthesized pyrroles were fully established by their analytical and spectral data.

C. Base Catalyzed Addition of Propargyl Alcohol to 2: Synthesis of 2-Aryl-3-nitro-5-methylfurans 7h-i

Logically, the preceding pyrrole approach was extended to 2-substituted-3-nitrofurans (Scheme 3). Our earlier strategy to construct furans from α-oxoketene dithioacetals using propargyl alcohol was employed.[17] Under normal base catalyzed reaction conditions, propargyl alcohol does not react with α-oxoketene dithioacetals. Therefore the corresponding dimethylsulphonium salts were reacted with propargyl alcohol in the presence of anhydrous K_2CO_3 to afford the respective O-propargyl-S-methyl acetals which underwent spontaneous Oxa-claisen rearrangement and cyclization to yield the corresponding 3-acyl-5-methylfurans in good yields.[17] Under similar reaction conditions, however, the β-methylthio-β-alkylnitroethylenes **2a-b** gave only intractable reaction mixture and our attempts to obtain 3-nitro-2-alkyl-5-methylfurans under varying conditions were unsuccessful. However when the β-phenylnitroethylene **2h** was reacted with propargyl alcohol in the presence of K_2CO_3 in refluxing ethylmethyl ketone, the reaction mixture after work up yielded a

mixture of two products, of which the expected 2-phenyl-3-nitro-5-methylfuran **7h** was obtained in 46% yield (Scheme 3) as a second product during column chromatography separation. The first product obtained in 48% yield was characterized as α,β-bis(methylthio) styrene (**8a**) as stereoisomeric *E:Z* mixture in 3:2 ratio. Similarly, **2i** reacted with propargyl alcohol to afford the corresponding 3-nitrofuran **7i** in 65% yield under the described conditions. The styrene derivative **8b** though observed on TLC (R_f = 0.6, 1% ethylacetate in hexane) as a minor spot, could not be isolated in pure form (Scheme 3).

The mechanism of the formation of furans **7h-i** evidently involves Oxa-claisen rearrangement of the intermediate vinylpropargyl ether **9** under the thermal conditions to give unstable allenic nitroketone **10** which undergoes base mediated ring closure to afford nitrofurans **7h-i** (Scheme 3). The mechanism governing the formation of **8** is an interesting example of nucleophilic displacement of NO_2 by RSH group in nitroolefins. The methylthiolate anion eliminated during the reaction of **2h-i** with propargyl alcohol adds on α-carbon of nitroethylene **2h-i** followed by elimination of nitrate anion on reversal of negative charge. It appears that these nitroethylenes do behave like push pull ethylenes[4b,18] with both the carbon atoms displaying electrophilic properties and the carbon α to the nitro group being softer than the β-carbon atom. This difference in electrophilicity is of interest and needs further investigation. In order to further ascertain the mechanism and



Scheme 3

course of this unusual formation of **8**, the nitroketene S,S acetal **1** was reacted with propargyl alcohol under similar conditions, when the reaction mixture after work up yielded the expected tris(methylthio)ethylene **12** in 46% yield along with the expected 3-nitrofuran **11** in 51% yield. Similarly, the phenylthiolate anion was added to cyclic dithioacetal **13** under similar reaction conditions to afford the cyclic tris(thio)ethylene **14** in 78% yield as the sole product.

In summary, we have demonstrated selective and efficient displacement of one of the methylthio groups of nitroketene dithioacetal **1** by organocopper reagents under mild conditions to afford hitherto unreported β-alkyl/aryl-β-methylthionitroethylenes in synthetically useful yields. The successes of the reaction is based on the use of trimethylsilyl chloride as activating reagent. The utility of these newly synthesized β-methylthionitroethylenes as "C=C-NO_2" synthon is demonstrated in facile synthesis of 2-substituted-3-nitropyrrole derivatives which are not easily available by other synthetic methods. Besides, the base catalyzed addition rearrangement of propargyl alcohol on β-arylnitroethylenes **2h-i** further demonstrates potential utility of these intermediates for the synthesis of 3-nitro-2-arylfuran derivatives. The formation of bis(methylthio)styrene **8** in reasonable yield in this reaction suggests alternative reactivity pattern of these β-methylthionitroalkenes which demands further probe to utilize it for the synthesis of poly alkyl/arylthioethylenes, a class of important donor organic molecules. The work in this direction is under progress and will be published later.

Experimental Section

Melting points were obtained on a Thomas Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 297 and 983 spectrometer. ^{1}H NMR (90MHz and 300 MHz), ^{13}C NMR (75.43 MHz) spectra were recorded on either EM-390 or Brucker ACF-300 spectrometer. Chemical shifts are reported in δ (ppm) relative to Me_4Si and coupling constants (*J*) are given in Hertz. Mass spectra are obtained on a Jeol-D-300 mass spectrometer. Elemental analyses were carried out on a Heraeus CHN-O-Rapid analyser.

All reactions were conducted in oven dried (120°C) glassware. The reactions were monitored by TLC on glass plates coated with silica gel (ACME'S) containing 13% calcium sulfate as binder and visualization of compounds was accomplished by exposure to iodine vapour or by spraying potassium permangnate (acidic) solution. Column chromatography was carried out using ACME'S silica gel (60-120 mesh).

General Procedure for Reaction of Organocopper Reagents with Bis(methylthio)nitroethylene 1: Synthesis of 1-Alkyl/aryl-1-methylthio-2-nitroethylenes (2a-j)

To a stirred suspension of anhydrous CuI (1.9gm, 10 mmol) in dry THF (25 ml) under a nitrogen atmosphere at –78°C, alkyl/aryl Grignard reagent [10 mmol, prepared from magnesium (0.96 gm, 40 mmol) and alkyl/aryl halide (10 mmol) in 60 ml of Et_2O:THF (1:3)] was added dropwise followed by further stirring for 20 min. A solution of nitroketene dithioacetal **1** (0.8 gm, 5 mmol) and trimethylsilyl chloride (0.6 ml, 50 mmol) in dry THF (15 ml) was added dropwise at –78°C and the reaction mixture was further stirred for 1hr (monitored by TLC) at the same temperature. It was then poured into satd. NH_4Cl solution (100 ml), extracted

with $CHCl_3$ (3 x 50 ml), dried (Na_2SO_4) and evaporated to give viscous residues, which were purified by column chromatography over silica gel using hexane as eluent to afford pure **2a-j**.

2-Methylthio-1-nitrobut-1-ene (2a). Viscous liquid; yield 61%; IR (CCl_4): 1276, 1464, 1556 cm^{-1}; ^1H NMR (300 MHz, CCl_4): δ 1.40 (t, J = 7.5 Hz, 3H), 2.41 (s, 3H), 2.62 (q, J = 7.5 Hz, 2H), 7.23 (s, 1H); MS (m/z, %): 147 (M^+, 11.6), 101 (M^+, -NO_2, 11.2); Anal. Calcd for $C_5H_9NO_2S$ (147.20): C, 40.80; H, 6.16; N, 9.52%. Found: C, 40.52; H, 6.24; N, 9.48%.

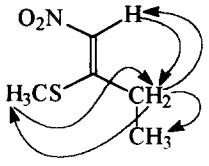


Fig. Important n .O.e. correlations

2-Methylthio-1-nitropent-1-ene (2b). Viscous liquid; yield 72%; IR (CCl_4): 1259, 1477, 1557, 1634 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3/CCl_4$): δ 0.95 (t, J = 7.5 Hz, 3H), 1.56 (sext, J = 7.5 Hz, 2H), 2.31 (s, 3H), 2.39 (t, J = 7.5 Hz, 2H), 7.10 (s, 1H); MS (m/z, %): 161 (M^+, 23.4); Anal. Calcd for $C_6H_{11}NO_2S$ (161.22): C, 44.70; H, 6.88; N, 8.69%. Found: C, 44.84; H, 6.77; N, 8.73%.

3-Methyl-2-methylthio-1-nitrobut-1-ene (2c). Yellow viscous liquid; yield 71%; IR (CCl_4): 1268, 1476, 1498, 1566 cm^{-1}; ^1H NMR (300 MHz, CCl_4): δ 1.25 (d, J = 7.5 Hz, 6H), 2.47 (s, 3H), 2.90 (sept, J = 7.5 Hz, 1H), 7.23 (s, 1H); MS (m/z, %): 161 (M^+, 18.7), 99 (15.1); Anal. Calcd for $C_6H_{11}NO_2S$ (161.22): C, 44.70; H, 6.88; N, 8.69%. Found: C, 44.88; H, 6.91; N, 8.74%.

2-Methylthio-1-nitrohex-1-ene (2d). Viscous liquid; yield 68%; IR (CCl_4): 1325, 1429, 1557, 2959 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.97 (t, J = 7.2 Hz, 3H), 1.45 (sext, J = 6.30, 2H), 1.57 (quint, J = 6.9 Hz, 2H), 2.41 (s, 3H), 2.49 (t, J = 6 Hz, 2H), 7.21 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.69, 14.16, 22.15, 31.50, 33.23, 96.07, 130.87, 161.42; MS (m/z, %): 175 (M^+, 34.7), 81 (100); Anal. Calcd for $C_7H_{13}NO_2S$ (175.25): C, 47.97; H, 7.48; N, 7.99%. Found: C, 48.13; H, 7.56; N, 7.89%.

3,3-Dimethyl-2-methylthio-1-nitrobut-1-ene (2e). Viscous liquid; yield 68%; IR (CCl_4): 1199, 1308, 1392, 1449 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 0.85 (s, 9H), 2.21 (s, 3H), 6.69 (s, 1H); Anal. Calcd for $C_7H_{13}NO_2S$ (175.25): C, 47.97; H, 7.48; N, 7.99%. Found: C, 47.89; H, 7.61; N, 7.91%.

2-Methylthio-1-nitrooct-1-ene (2f). Viscous liquid; yield 70%; IR (CCl_4): 1328, 1496, 1579, 2926 cm^{-1}; ^1H NMR (300 MHz, CCl_4): δ 0.90 (t, J = 7.5 Hz, 3H), 1.29-1.40 (m, 6H), 1.56-1.63 (m, 2H), 2.49 (s, 3H), 2.52 (t, J = 7.5 Hz, 2H), 7.24 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.00, 14.34, 22.49, 28.75, 29.61, 31.70, 33.69, 130.98, 162.06; MS (m/z, %): 203 (M^+, 28.2) , 102 (27.2); Anal. Calcd for $C_9H_{17}O_2NS$ (203.31): C, 53.17; H, 8.43; N, 6.89%. Found: C, 53.28; H, 8.48; N, 6.79%.

2-Methylthio-3-phenyl-1-nitroprop-1-ene (2g). Viscous liquid; yield 71%; IR (CCl_4): 1016, 1252, 1374, 1593, 2922 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.34 (s, 3H), 4.24 (s, 2H), 6.72 (s, 1H), 7.24-7.27 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.29, 38.37, 95.95, 126.98, 127.76, 127.91, 127.99, 128.30, 128.64, 128.77, 129.43, 135.76; MS (m/z, %): 209 (M^+, 8.8), 161 (82.9), 114 (100); Anal. Calcd for $C_{10}H_{11}O_2SN$ (209.27): C, 57.40; H, 5.30; N, 6.69%. Found: C, 57.51; H, 5.37; N, 6.73%.

1-Phenyl-1-methylthio-2-nitroethylene (2h). Yellow viscous liquid; yield 65%; IR (CCl_4): 1073, 1176, 1268, 1329, 1474 cm^{-1}; ^1H NMR (90 MHz, CCl_4): δ 1.98 (s, 3H), 7.20 (s, 1H), 7.33-7.67 (m, 5H); MS (m/z, %): 195 (M^+, 7.2), 134 (100); Anal. Calcd for $C_9H_9NO_2S$ (195.24): C, 55.37; H, 4.65; N, 7.17%. Found: C, 55.28; H, 4.71; N, 7.24%.

1-(4'-Methylphenyl)-1-methylthio-2-nitroethylene (2i). Viscous liquid; yield 70%; IR (CCl_4): 1267, 1380, 1404, 1505 cm^{-1}; ^1H NMR (90 MHz, CCl_4): δ 1.85 (s, 3H), 2.35 (s, 3H), 7.18 (s, 1H), 7.22-7.43 (m,

4H); MS (m/z, %): 209 (M^+, 6.2), 182 (9.3), 192 (14.1), 130 (88.4); Anal. Calcd for $C_{10}H_{11}NO_2S$ (209.27): C, 57.40; H, 5.30; N, 6.69%. Found: C, 57.53; H, 5.42; N, 6.61%.

1-(4'-Methoxyphenyl)-1-methylthio-2-nitroethylene (2j). Viscous liquid; yield 69%; IR (CCl_4): 1175, 1253, 1603, 2925 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 2.00 (s, 3H), 3.89 (s, 3H), 7.01 (d, J = 9 Hz, 2H), 7.25 (d, J = 9 Hz, 2H), 7.31 (s, 1H); MS (m/z, %): 226 (M^+, 28.8), 135 (100); Anal. Calcd for $C_{10}H_{11}NO_3S$ (225.27): C, 53.32; H, 4.92; N, 6.22%. Found: C, 53.27; H, 5.06; N, 6.28%.

General Procedure for the Reaction of 1-Alkyl/aryl-1-methylthio-2-nitroethylene 2a-d, 2f-i with Aminoacetaldehyde dimethylacetal 3: Synthesis of Nitroenamines (4a-d, 4f-i)

A solution of aminoacetaldehyde dimethylacetal **3** (1.4 ml, 10 mmol) and 1-alkyl/aryl-1-methylthio-2-nitroethylene **2a-d, 2f-i** (10 mmol) in ethanol (50 ml) was refluxed for 8-12 hr (monitored by TLC). The solvent was removed under vaccum to give viscous residues, which were dissolved in chloroform (50 ml), washed thoroughly with water (3 x 50 ml), the combined organic layer was dried (Na_2SO_4) and evaporated to give crude products, which on column chromatography over silica gel using hexane-ethyl acetate (94:6) as eluent gave pure **4a-d, 4f-i**.

2-(2',2'-Dimethoxyethyl)amino-1-nitrobut-1-ene (4a). Thick viscous liquid; yield 80%; IR (CCl_4): 1013, 1167, 1299, 2922, 3105 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$): δ 1.20 (t, J = 7.5 Hz, 3H), 2.30 (q, J = 7.5 Hz, 2H), 3.41 (s, 6H), 3.50 (dd, J = 7 Hz, 2H), 4.50 (t, J = 7 Hz, 1H), 6.50 (s,1H), 10.10 (brs, 1H); MS (m/z, %): 204 (M^+, 22.7); Anal.Calcd for $C_8H_{16}N_2O_4$ (204.23): C, 47.05; H, 7.90; N, 13.72%. Found: C, 46.93; H, 7.83; N, 13.82%.

2-(2',2'-Dimethoxyethyl)amino-1-nitropent-1-ene (4b). Thick viscous liquid; yield 78%; IR (CCl_4): 1095, 1259, 1557, 2854, 2923 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$): δ 1.08 (t, J = 7.5 Hz, 3H), 1.62 (sext, J = 7.5 Hz, 2H), 2.30 (t, J = 7.5 Hz, 2H), 3.42 (s, 6H), 3.55 (dd, J = 6Hz, 2H), 4.50 (t, J = 6 Hz, 1H), 6.55 (s, 1H), 10.20 (brs, 1H); MS (m/z, %): 218 (M^+, 7.1), 187 (7.5), 126 (30.3); Anal. Calcd for $C_9H_{18}N_2O_4$ (218.25): C, 49.53; H, 8.31; N, 12.84%. Found: C, 49.66; H, 8.38; N, 12.89%.

2-(2',2'-Dimethoxyethyl)amino-3-methyl-1-nitrobut-1-ene (4c): The crude product **4c** was used as such for cyclization without further purification to give pyrrole **5c**.

2-(2',2'-Dimethoxyethyl)amino-1-nitrohex-1-ene (4d). Viscous liquid; yield 80%; IR (CCl_4): 1193, 1243, 1603, 2960 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.95 (t, J = 7.5 Hz, 3H), 1.42 (sext, J = 6 Hz, 2H), 1.51 (quint, J = 6 Hz, 2H), 2.23 (t, J = 7.2 Hz, 2H), 3.46 (s, 6H), 3.47 (dd, J = 5.4 Hz, 2H), 4.49 (t, J = 6 Hz, 1H), 6.56 (s, 1H), 10.35 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.68, 22.40, 29.68, 30.42, 45.29, 55.03, 102.64, 110.65, 161.95; MS (m/z, %): 202 (M^+ OMe, 3.9); Anal. Calcd for $C_{10}H_{20}N_2O_4$ (232.28): C, 51.71; H, 8.68; N, 12.06%. Found: C, 51.84; H, 8.73; N, 12.17%.

2-(2',2'-Dimethoxyethyl)amino-1-nitrooct-1-ene (4f). Viscous liquid; yield 79%; IR (CCl_4): 1162, 1192, 1492, 2910 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.90 (t, J = 6 Hz, 3H), 1.31-1.37 (m, 6H), 1.52-1.56 (m, 2H), 2.26 (t, J = 6 Hz, 2H), 3.45 (s, 6H), 3.46 (dd, J = 6 Hz, 2H), 4.48 (dd, J = 6 Hz, 1H), 6.43 (s, 1H), 10.10 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.91, 22.33, 27.50, 28.86, 30.46, 31.26, 44.96, 54.52, 96.00, 102.43, 110.20, 161.04; Anal. Calcd for $C_{12}H_{24}N_2O_4$ (260.33): C, 55.36; H, 9.29; N, 10.76%. Found: C, 55.27; H, 9.33; N, 10.81%.

2-(2',2'-Dimethoxyethyl)amino-3-phenyl-1-nitroprop-1-ene (4g). Viscous liquid; yield 79%; IR (CCl_4): 1030, 1128, 1215, 1358, 1605, 2937, 3017 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 3.30 (s, 6H), 3.35 (dd,

J = 6 Hz, 2H), 3.65 (s, 2H), 4.33 (t, J = 6 Hz, 1H), 6.66 (s, 1H), 7.25-7.55 (m, 5H), 9.68 (brs, 1H); Anal. Calcd for $C_{13}H_{18}N_2O_4$ (266.30): C, 58.63; H, 6.81; N, 10.52%. Found: C, 58.72; H, 6.87; N, 10.61%.

2-(2',2'-Dimethoxyethyl)amino-2-phenyl-1-nitroethene (4h). Viscous liquid; yield 82%; IR (CCl_4): 1107, 1276, 1651, 2919 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.31 (dd, J = 4.2 Hz, 2H), 3.36 (s, 6H), 4.37 (t, J = 6 Hz, 1H), 6.49 (s, 1H), 7.27-7.52 (m, 5H), 10.00 (brs. 1H); Anal. Calcd for $C_{12}H_{16}N_2O_4$ (252.27): C, 57.13; H, 6.39; N, 11.10%. Found: C, 57.21; H, 6.44; N, 11.19%.

2-(2',2'-Dimethoxyethyl)amino-1-(4'-methylphenyl)-1-nitroethene (4i). Light yellow viscous liquid; yield 90%; IR (CCl_4): 1130, 1359, 1457, 1595, 2935 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.41 (s, 3H), 3.37 (dd, J = 5 Hz, 2H), 3.80 (s, 6H), 4.39 (t, J = 5 Hz, 1H), 6.57 (s, 1H), 7.23-7.30 (m, 4H), 10.16 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.41, 46.69, 54.83, 96.08, 102.63, 111.81, 127.85, 128.39, 129.69, 141.22, 160.33; MS (m/z, %): 226 (M^+, 9.1); Anal.Calcd for $C_{13}H_{18}N_2O_4$ (266.30): C, 58.63; H, 6.81; N, 10.52%. Found: C, 58.71; H, 6.73; N, 10.58%.

General Procedure for the Cyclization of Nitroenamines 4a-d, 4f-i: Synthesis of 2-Alkyl/aryl-3-nitropyrroles (5a-d, 5f-i)

A solution of enamines **4a-d**, **4f-i** (3 mmol) in ethereal hydrochloric acid (15 ml) was stirred at 0-5°C for 1.5-2 hr (monitored by TLC). The reaction mixture was then poured into crushed ice, the ether layer was separated and the water layer extracted with $CHCl_3$ (3 x 50 ml). The combined organic extracts were dried (Na_2SO_4) and evaporated to give crude pyrroles which were purified by column chromatography over silica gel using hexane-ethylacetate (98:2) as eluent.

2-Ethyl-3-nitropyrrole (5a). Viscous semisolid; yield 50%; IR (CCl_4): 1170, 1330, 1573, 2899, 2971 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.30 (t, J = 7.5 Hz, 3H), 3.08 (q, J = 7.5 Hz, 2H), 6.57 (t, J = 3 Hz, 1H), 6.76 (t, J = 3 Hz, 1H), 8.60 (brs, 1H); MS (m/z, %): 140 (M^+, 68.5), 123 (100); Anal. Calcd for $C_6H_8N_2O_2$ (140.14): C, 51.42; H, 5.75; N, 19.99%. Found: C, 51.53; H, 5.83; N, 19.87%.

2-Propyl-3-nitropyrrole (5b). White crystals (ether); mp 54-55°C; yield 59%; IR (KBr): 1169, 1308, 1573, 2871, 2972 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$): δ 1.10 (t, J = 7.5 Hz, 3H), 1.75 (sext, J = 7 Hz, 2H), 3.05 (t, J = 7 Hz, 2H), 6.55 (t, J = 3Hz, 1H), 6.75 (t, J = 3Hz, 1H), 8.55 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.80, 21.46, 29.35, 106.57, 115.62; MS (m/z, %): 154 (M+, 73.1), 137 (100); Anal. Calcd for $C_7H_{10}N_2O_2$ (154.17): C, 54.53; H, 6.54; N, 18.17%. Found: C, 54.67; H, 6.49; N, 18.21%.

2-(*i*-Propyl)-3-nitropyrrole (5c). White crystals (hexane-ether); mp 122-123°C; yield 52%; IR (KBr): 1169, 1331, 1573, 2871, 2972 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$): δ 1.30 (d, J = 6 Hz, 6H), 3.80 (sept, J = 6 Hz, 1H), 6.50 (t, J = 3 Hz, 1H), 6.68 (t, J = 3Hz, 1H), 8.80 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.95, 26.29, 106.57, 115.87, 132.38, 141.83; MS (m/z, %): 154 (M^+, 52.9), 137 (100); Anal. Calcd for $C_7H_{10}N_2O_2$ (154.17): C, 54.53; H, 6.54; N, 18.17%. Found: C, 54.65; H, 6.63; N, 18.21%.

2-(*n*-Butyl)-3-nitropyrrole (5d). White crystals (hexane-ether); mp 98-99°C; yield 69%; IR (KBr): 1128, 1332, 1414, 1574, 2929 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.95 (t, J = 7 Hz, 3H), 1.40 (sext, J = 5Hz, 2H), 1.66 (m, 2H), 3.04 (t, J = 7 Hz, 2H), 6.56 (brs, 1H), 6.75 (brs, 1H), 8.60 (brs, 1H); MS (m/z, %): 168 (M^+, 100), 151 (93.1); Anal. Calcd for $C_8H_{12}N_2O_2$ (168.19): C, 57.13; H, 7.19; N, 16.65%. Found: C, 57.21; H, 7.21; N, 16.68%.

2-(*n*-Hexyl)-3-nitropyrrole (5f). White crystals (ether); mp 101-102°C; yield 66%; IR (KBr): 1312, 1465, 1574, 2916 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, J = 7 Hz, 3H), 1.33-1.40 (m, 6H), 1.71 (quint,

J = 7 Hz, 2H), 3.04 (t, J = 7.5 Hz, 2H), 6.58 (brs, 1H), 6.72 (brs, 1H), 9.36 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.93, 22.39, 27.33, 28.03, 28.89, 31.35, 106.22, 115.77, 132.90, 136.89; MS (m/z, %): 196 (M^+, 36.0), 119 (68.6); Anal. Calcd for $C_{10}H_{16}N_2O_2$ (196.25): C, 61.20; H, 8.22; N, 14.27%. Found: C, 61.31; H, 8.16; N, 14.31%. .

2-Benzyl-3-nitropyrrole (5g). Viscous semisolid; yield 57%; IR (CCl_4): 1106, 1302, 1321, 2839 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$): δ 4.50 (s, 2H), 6.65 (brs, 1H), 6.85 (brs, 1H), 7.35-7.60 (brs, 5H); Anal. Calcd for $C_{11}H_{10}N_2O_2$ (202.21): C, 65.34; H, 4.98; N, 13.85%. Found: C, 65.41; H, 4.88; N, 13.91%.

2-Phenyl-3-nitropyrrole (5h). Pale yellow crystals (hexane-ether); mp 153-154°C; yield 64%; IR (KBr): 1307, 1423, 1455, 1573, 2972 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$/DMSO-d_6): δ 6.74 (brs, 1H), 6.91 (brs, 1H), 7.45-7.47 (m, 3H), 7.56-7.60 (m, 2H), 11.8 (brs, 1H); MS m/z, %): 188 (M^+, 100), 115 (50); Anal. Calcd for $C_{10}H_8N_2O_2$ (188.19): C, 63.82; H, 4.28; N, 14.88%. Found: C, 63.91; H, 4.31; N, 14.91%.

2-(4'-Methylphenyl)-3-nitropyrrole (5i). Pale yellow crystals (hexane-ethylacetate); mp 159-160°C; yield 80%; IR (KBr): 1106, 1302, 1321, 2839 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.40 (s, 3H), 6.70 (t, J = 3 Hz, 1H), 6.87 (t, J = 3 Hz, 1H), 7.24-7.26 (m, 2H), 7.44-7.48 (m, 2H), 8.64 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.42, 107.71, 117.12, 126.84, 127.82, 128.96, 129.23, 129.75, 133.09, 139.62; Anal. Calcd for $C_{11}H_{10}N_2O_2$ (202.21): C, 65.34; H, 4.98; N, 13.85%. Found: C, 65.42; H, 4.88; N, 13.91%.

Typical Procedure for Base Catalyzed Addition of Propargyl Alcohol to β-Methylthio-β-arylnitroethylenes 2h-i:

To a refluxing suspension of anhydrous K_2CO_3 (0.83g, 6 mmol) in ethylmethyl ketone (30 ml), a mixture of ß-phenylnitroethylene **2h** (0.58g, 3 mmol) and propargyl alcohol (0.30 ml, 5 mmol) were added and the reaction mixture was refluxed for 10-12 hr (monitored by TLC). It was then cooled and filtred to remove K_2CO_3, the filtrate was evaporated to give a viscous residue which was diluted with chloroform (40 ml). The chloroform layer was washed with water (2 x 25 ml), dried (Na_2SO_4), evaporated and the residue was column chromatographed on silica gel using hexane:ethylacetate (99:1) as eluent to give products **7h** and **8a**.

5-Methyl-3-nitro-2-phenylfuran (7h). (EtOAc/hexane, 1:99, R_f = 0.3); light yellow liquid; yield 46%; IR (CCl_4): 1136, 1343, 1376, 1500 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4): δ 2.30 (s, 3H), 7.30 (s, 1H), 7.45-7.65 (m, 3H), 7.80-8.10 (m, 2H); Anal. Calcd for $C_{11}H_9NO_3$ (203.20): C, 65.02; H, 4.46; N, 6.89%. Found: C, 65.09; H, 4.55; N, 6.94%.

1,2-Bis(methylthio)-1-phenylethylene (8a). (EtOAc/hexane, 1:99, R_f = 0.7); viscous liquid; yield 48%; IR (CCl_4): 1499, 1437, 1375, 1342 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$, *E*:*Z*, 3:2): δ 2.05 (s, 3H, SMe for *E*), 2.26 (s, 3H, SMe for *Z*), 2.30 (s, 3H, SMe for *Z*), 3.35 (s, 3H, SMe for *E*), 6.30 (s, 1H, olefinic for *Z*), 6.41 (s, 1H, olefinic for *E*), 7.20-8.05 (m, 10H, ArH for *E* and *Z*); Anal Calcd for $C_{10}H_{12}S_2$ (196.33): C, 61.17; H, 6.16%. Found: C, 61.44; H, 6.03%.

2-(4'-Methylphenyl)-5-methyl-3-nitrofuran (7i). **7i** was similarly obtained from β-phenylnitroethylene **2i** and propargyl alcohol under identical reaction conditions (EtOAc/hexane, 1:99, R_f = 0.6). viscous liquid; yield 65%; IR (CCl_4): 1140, 1346, 1377, 1504, 2922 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.26 (s, 3H), 2.39 (s, 3H), 7.19 (s, 1H), 7.25 (d, J = 9 Hz, 2H), 7.66 (d, J = 9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.57, 21.51, 118.59, 125.19, 127.15, 128.53, 128.86, 138.68, 140.83, 153.96; Anal. Calcd for $C_{12}H_{11}NO_3$ (217.22): C, 66.35; H, 5.10; N, 6.45%. Found: C, 66.42; H, 5.19; N, 6.59%.

Reaction of 2-Bis(methylthio)nitroethylene with Propargyl Alcohol: The nitroketene dithioacetal **1** (4.95g, 30 mmol) and propargyl alcohol (2.65 ml, 45 mmol) were reacted with anhydrous K_2CO_3 (6.20g, 45 mmol) under identical conditions as described for **2h** and propargyl alcohol. Work up of the reaction mixture as described, afforded 2-methylthio-5-methyl-3-nitrofuran **11** and 2,2,2-tris(methylthio)ethylene **12.**

2-Methylthio-5-methyl-3-nitrofuran (11). (EtOAc/hexane, 1:99, R_f = 0.4); pale yellow crystals (ether); mp 83-84°C; yield 51%; IR (KBr): 1127, 1330, 1398, 1490, 1546, 1932, 2927 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$): δ 2.30 (brs, 3H), 2.65 (s, 3H), 7.32 (brs,1H); MS (m/z, %): 173 (M^+, 62.5), 149 (100); Anal. Calcd for $C_6H_7NO_3S$ (173.19): C, 41.61; H, 4.07; N, 8.09%. Found: C, 41.76; H, 4.18; N, 8.17%.

2,2,1-Tris(methylthio)ethylene (12). (EtOAc/hexane, 1:99, R_f = 0.8); viscous liquid; yield 46%; IR (neat): 796, 1421, 2907 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.26 (s, 3H), 2.32 (s, 3H), 2.34 (s, 3H), 6.47 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.13, 17.20, 17.64, 96.02, 126.55, 133.94; MS (m/z, %): 166 (M^+, 100); Anal. Calcd for $C_5H_{10}S_3$ (166.33): C, 36.10; H, 6.06%. Found: C, 36.24; H, 6.11%.

Base Catalyzed Addition of Phenylthiol to 2-(Nitro)methylene-1,3-dithiolane 13: Cyclic nitroketene dithioacetal **13** (3.26g, 20 mmol) was reacted with phenylthiol (1.02 ml, 10 mmol) in the presence of K_2CO_3 (2.07g, 15 mmol) in refluxing ethylmethyl ketone (30 ml) following similar procedure as described for reaction of **2h** and propargyl alcohol. After work up of the reaction mixture as described yielded 2-(phenylthio)methylene-1,3-dithiolane **14**.

2-(Phenylthio)methylene-1,3-dithiolane (14). (EtOAc/hexane, 1:99, R_f = 0.8); viscous liquid; yield 78%; IR (CCl_4): 1237, 1398, 1470 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.86 (t, J = 6 Hz, 2H), 3.16 (t, J = 6 Hz, 2H), 7.14-7.31 (m, 4H), 7.47 (d, J = 6 Hz, 2H); ^{13}C NMR (75 MHz, CDCl3): δ 32.72, 37.42, 126.37, 126.44, 127.02, 127.29, 127.78, 128.88, 137.85; Anal. Calcd for $C_{10}H_{10}S_3$ (226.39): C, 53.05; H, 4.45%. Found: C, 53.24; H, 4.55%.

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