Synthesis of Six- to Nine-Membered Ring Oximinoorthodithiolactones by Cyclization of Nitroketene *S,S*-Acetals in Trifluoromethanesulfonic Acid

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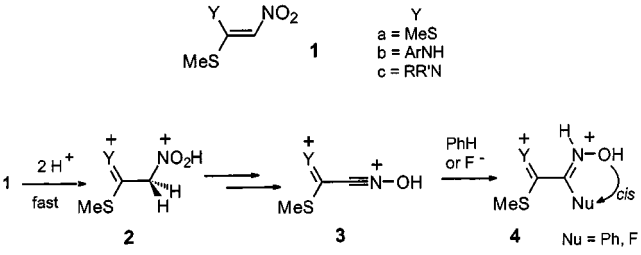
2-Nitro-1,1-bis(phenylalkylthio)ethene or 1-(methylthio)-2-nitro-1-(phenylalkylthio)ethene derivatives tethered to an aromatic ring undergo a fast intramolecular cyclization in trifluoromethanesulfonic acid, with the intermediate formation of dications, which can be detected by NMR spectroscopy. Quenching with methanol at low temperature affords cyclic orthothioesters of isothiochromanones, 4,5-dihydrobenzo[*d*]-thiepin-1-one, 5,6-dihydro-4*H*-benzo[*d*]thiocin-1-one and 8,9,10,11-tetrahydro-7-thiabenzocyclononen-5-one oximes. The yields are usually fair to good, except for the nine-membered ring derivatives.

Introduction

Nitroethene derivatives are well-known synthons in organic chemistry. For instance, they are used in the field of drug synthesis[1,2] and for intramolecular cyclizations involving nitrile oxides (INOC reaction).[2,3] Generally, thio derivatives also tend to be useful synthetic substrates, for example, in heterocyclic synthesis using tandem reactions. This good reactivity is due to the formation of transient thiocarbenium cations that react with nitrogen or in an ene-type reaction.[4] Thiocarbenium cations are formed either from a sulfoxide in a Pummerer-type reaction,[5,6] from dithioacetals treated with dimethyl(methylthio)sulfonium tetrafluoroborate,[4−7] or by α-halogenation of sulfides.[8] α-Halosulfites are useful reagents as aldehyde or ketone equivalents that can react either as nucleophiles by halogen substitution or as electrophiles in the presence of Lewis acids. Superelectrophilic methylthiomethylation of aromatic rings with a thio-substituted carbenium ion generated under superacidic conditions are also reported.[9]

1,1-Bis(methylthio)-2-nitroethene (**1a**) is also a good starting substrate for various syntheses because of the easy nucleophilic substitution of both MeS groups.[10−12] Reactions with aromatic[13] or nonaromatic amines[14] afford nitroketene S,N-acetals. An intermediate in the manufacture of the anti-ulcer drug ranitidine can be prepared in this way.[15] Nitroketeneaminals are obtained by nucleophilic substitution of both MeS groups with an amine group.[16] Similar reactions with Grignard reagents are also reported.[18]

Cyclic tetrathioorthocarbonates and cyclic trithioorthoesters are also potential reagents to afford alkenes by Ni-catalyzed cross-coupling reactions with Grignard reagents.[19] Cyclic orthotrithioesters are also used in the field of sugar synthesis.[20] In the superacids HF/SbF_5 or trifluoromethanesulfonic acid (TFSA or trific acid), 1-heterosubstituted-2-nitroethene derivatives **1**, with either nitrogen or sulfur as heteroatoms, are kinetically diprotonated to form cations **2**. They are then transformed into conjugated dications **3** with a heterosubstituted carbocationic center and a hydroxynitrilium site − or *O*-protonated nitrile oxide − as shown in Scheme 1.



Scheme 1. Reactivity of heterosubstituted nitroethylene derivatives **1** in triflic acid

These cations were observed by ^1H and ^{13}C NMR spectroscopy.[21−23] They are fair electrophiles that react with various nucleophiles to afford, in agreement with theoretical considerations,[24,25] the kinetic product **4** in which the attacking group and the OH oxime group are in *cis* configuration.[26,27]

In the present paper, the reactivity of conjugated hydroxynitrilium ions is applied to new syntheses in the field of sulfur heterocyclic compounds. New derivatives such as orthodithioesters of thiochromanone, 4,5-dihydrobenzo[*d*]-thiepin-1-one, 5,6-dihydro-4*H*-benzo[*d*]thiocin-1-one and 8,9,10,11-tetrahydro-7-thiabenzocyclononen-5-one oximes were easily prepared.

Results and Discussion

Starting Material

Starting compounds **6a−d** were obtained from 2 mol-equiv. of the corresponding phenylalkyl bromide with dipotassium salt **7** in DMSO, and starting compound **5a−d**

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were obtained from 1 mol-equiv. of the corresponding phenylalkyl bromide followed by the addition of 1 mol-equiv. of iodomethane (Figure 1).

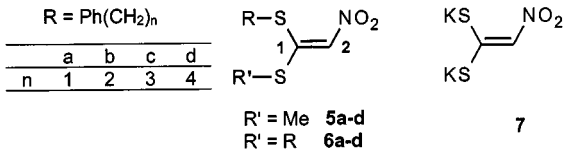


Figure 1. Starting products **5a**–**d** and **6a**–**d** and dipotassium salt **7** used for their synthesis

Starting materials have not been described before, except for 1,1-bis(benzylthio)-2-nitroethene (**6a**).[28] The products were purified by flash chromatography, followed by crystallization from various solvents to eliminate a small amount of co-eluted yellow compounds.

Compounds **5a**–**d** exist as mixtures of (*Z*) and (*E*) isomers in organic solvent solutions. The NMR spectra of **5a**–**d** are characterized by: (i) the presence of signals assigned to two vinylic protons at $\delta_H \approx 7.0$ ($\Delta\delta_H$ for the two isomers in the range 0.02–0.20 ppm), (ii) by two sets of signals for C-1 at $\delta_C \approx 163.5$ ($\Delta\delta_C = 0.12$–0.36 ppm) and for the C-2 at $\delta_C = 124.5$ ($\Delta\delta_C = 0.3$–0.95 ppm). Such a rotation about a C–C double bond in solution was previously reported for the thio derivative **1a**, with both methyl protons giving rise to one signal at room temperature, and a coalescence temperature of approximately 0 °C (60 MHz).[29] In the present study, this equilibrium was also observed by HPLC for compounds **5a**–**d**, as indicated by their plateau-like elution profiles. Such an elution behavior is typical for quickly equilibrating isomers during analysis, as reported for other products either on analytical or on theoretical grounds.[30–32]

Reactions in Trifluoromethanesulfonic Acid

In the present study, the reactions were carried out in trifluoromethanesulfonic acid at 0 °C or at lower temperature under nitrogen. The thio derivatives were added to cold, stirred trifluoromethanesulfonic acid. The trifluoromethanesulfonic acid/thio derivative molar ratio was > 50:1. At the end of the reaction, the acidic solution was poured into a mixture of methanol/CH_2Cl_2 (about 15:85 v/v) at −60 to −80 °C. The extraction was carried out at approximately 0 °C, as described in the Exp. Sect. The reactions were usually clean, except with **5d** and **6d** for which polar by-products were formed, probably because of extensive intermolecular reactions.[33] By-products were also observed in the reactions with **6b**,**c** with longer reaction times, or at higher temperatures, probably because of the reactivity of the second tethered phenyl ring.

NMR Spectroscopic Analysis of Cations

The nitro derivatives **5a**–**c** and **6a**–**c** were dissolved in trifluoromethanesulfonic acid and the resulting solutions were observed by NMR spectroscopy either at room temperature or at 255 K. The starting material quickly disappeared to afford the only observable cations **8a**–**c** and **9a**–**c**, respectively, which are characterized by a dithiocarbenium center and a hydroxyiminium group. The dithiocarbenium carbon atoms resonate in the range $\delta_C = 209.1$–220.9 and the hydroxyiminium carbon atoms between $\delta_C = 148.2$ and 159.0. Figure 2 shows the observed NMR spectra for cation **8a**.

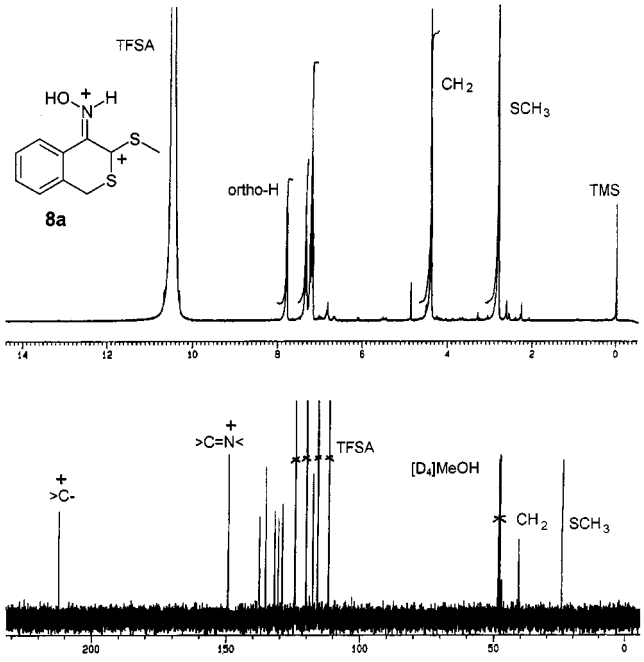


Figure 2. NMR spectra of cyclic cation **8a** in trifluoromethanesulfonic acid at room temp. (reference TMS in [D_4]methanol)

In both cases, the more shielded carbon atoms are observed in the six-membered series, probably because of the conformation of the nonaromatic ring, which allows for some kind of conjugation with the aromatic ring,[34] as observed with cation **10** in the acyclic series (Figure 3).[21] The increase in the ring size may also account for the increase in the chemical shift, as observed with cyclic ketones.[35]

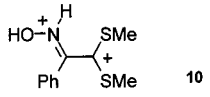
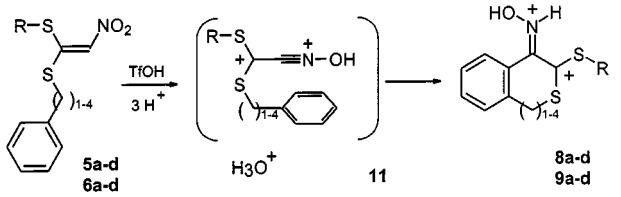


Figure 3. Acyclic cation **10** previously observed

The formation of cations **8a**–**c** and **9a**–**c** may be explained in the light of previously observed reactions in the acyclic series: Starting products undergo multiple protonation, leading quickly to the formation of conjugated hydroxynitrilium cation **11**, which were not observed. As soon as it is formed, the cation **11** reacts with the tethered phenyl ring by means of an electrophilic aromatic substitution mechanism, to afford the observed cations **8** and **9** (Scheme 2).

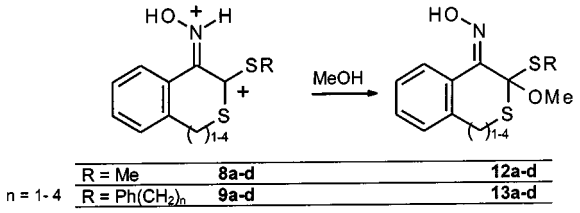


Scheme 2. Formation of cations **8a**–**d** and **9a**–**d** from nitroethylene derivatives **5a**–**d** and **6a**–**d**

The addition mechanism at the C−N triple bond of the hydroxynitrilium ions implies that the phenyl group of the attacking species and the OH of the formed hydroxyiminium groups must adopt a *cis* configuration, as previously observed[21−23] and also predicted on theoretical grounds.[24,25] This mechanism explains why single isomers of cations **8a−d** and **9a−d** are obtained, and why they must have an (*E*) configuration.

Quenching with Methanol

The cations **8** and **9** can be trapped by methanol at low temperature (Scheme 3) to afford, in fair to good yields, six- to nine-membered ring cyclic orthodithioesters with an oxime group in the benzylic position. These are derivatives of isothiochromanones (**12a**, **13a**), 4,5-dihydrobenzo[*d*]thiepin-1-one (**12b**, **13b**), 5,6-dihydro-4*H*-benzo[*d*]thiocin-1-one (**12c**, **13c**) and 8,9,10,11-tetrahydro-7-thiabenzocyclononen-5-one oximes (**12d** and **13d**).



Scheme 3. Trapping of cations **8a−d** and **9a−d** by methanol

The yields are reported in Table 1. Some difficulties were experienced in reproducing the yields of the nine-membered ring system where the yields are low, probably because intermolecular reactions are favored over cyclization, as is generally observed in such large ring systems.[33]

Table 1. Yields of cyclic dithioorthoesters **12a−d** and **13a−d**

Starting product	**5a**	**6a**	**5b**	**6b**	**5c**	**6c**	**5d**	**6d**
Product	**12a**	**13a**	**12b**	**13b**	**12c**	**13c**	**12d**	**13d**
Yield (%)	70	83	74	73	82	71	28	12

All these cyclic orthodithioesters are characterized by the quaternary orthodithiolactone carbon atoms whose chemical shifts increase steadily from δ_C = 93.5 for the six-membered ring, to δ_C = 101.3 for the nine-membered ring system. The lactone methoxy group resonates at δ_C = 50.5−52.0 and the oxime carbon atoms in the range δ_C = 148.9−159.6, with more shielded values being observed for the six-membered ring derivatives. The downfield shift of the signal for the oxime carbon atom may be related to the ring size, as was also observed in the cyclic ketone series.[35] Only the (*E*)-configured oxime was observed, except in the case of the seven-membered ring system. The (*E*) configuration was confirmed by X-ray crystallographic analysis.[36] These results are in full agreement with the expected mechanism of the reaction concerning the addition to a C−N triple bond of nitrile oxide in which the attacking group and the O atom are in the *cis* configuration in the final product.[24,25]

Conclusion

The present study is an application of the usefulness of arylalkyl-substituted nitroethylenedithiocetals in the field of heterocyclic synthesis. Cyclic orthodithioester derivatives such as isothiochromanones, 4,5-dihydrobenzo[*d*]thiepin-1-one, 5,6-dihydro-4*H*-benzo[*d*]thiocin-1-one, and 8,9,10,11-tetrahydro-7-thiabenzocyclononen-5-one oximes can be prepared in good to fair yields in trifluoromethanesulfonic acid, with the transient formation of conjugated hydroxynitrilium ions. Work is in progress in the field of heterocyclic synthesis with other heteroatoms, and results will be published in due course

Experimental Section

General Remarks: Melting points were determined with a Büchi Melting Point B545 apparatus using capillary tubes (temperature rate 2 °C/min) and were not corrected. − A Bruker DPX 300 spectrometer, equipped with a low-temperature probe, was used for ^{1}H and ^{13}C NMR spectra recorded at 300.13 MHz and 75.47 MHz, respectively. NMR spectra of cations were recorded in TFSA at low temperature or at room temperature. Chemical shifts are reported relative to Me_4Si in [D_4]methanol, contained in a sealed capillary tube placed inside the NMR cell. The reproducibility of ^{13}C NMR shifts was about ± 0.05 ppm, but from experiment to experiment small-scale shifts were also observed depending on concentration, temperature and on the NMR cell used. Chemical shift assignments were made using DEPT 135 techniques and usual chemical shift assignment rules. − Electron-impact ionization (70 eV) mass spectra were obtained with a Finnigan Incos 500 instrument. − Microanalyses were performed with an N.A. 2000 Analyzer. − Flash chromatography was achieved on silica gel (20 to 45 μm particle size). − HPLC was used to check the purity or to identify the various compounds described below. A Waters 600 pump equipped with a Rheodyne 7125 injector valve (20 μL loop) and an Applied Biosystem 785 A programmable or a Waters 486 UV detector, column 250 × 4 mm I.D., 5 μm Spherisorb silica, were used. Triflic acid came from Acros and was used without further purification. No attempt was made to optimize the yields.

Starting Material

1-(Benzylthio)-1-(methylthio)-2-nitroethene (5a). − Typical Procedure: $PhCH_2Br$ (1.46 mL, 12.3 mmol) was added over 5 min to a stirred suspension of dipotassium salt **7** (2.62 g, 12.3 mmol) in DMSO (50 mL) at room temp. The reaction was carried out under N_2 at room temp. for 17 h and then for 3 h at 50 °C. Iodomethane (0.766 mL, 12.3 mmol) was then added all at once at room temp. After 2 h at 40 °C, the reaction mixture was left for 14 h at room temp. The reaction was monitored by TLC. At the end of the reaction, CH_2Cl_2 (220 mL) was added to the DMSO solution. The organic phase was washed with slightly acidified water (40 mL), then with water (2 × 20 mL) and finally with brine (30 mL). The organic phase was dried with $MgSO_4$, and the solvent was eliminated under vacuum. The resulting caramel-like oil was purified by chromatography on silica gel to afford the nitro derivative **5a** (eluent CH_2Cl_2/AcOEt/hexanes,10:30:460), which was further crystallized from MTBE/hexanes as pale yellow crystals (910 mg; 30.7% yield). − M.p. 104−105 °C (MTBE). − IR ($CHCl_3$): $\tilde{\nu}$ = 1271 (m), 1313 and 1317 (strong, NO_2), 1525 (strong, NO_2) 3025 and 3067

(CH), 3142 (CH). − ^{1}H NMR ($CDCl_3$); solution of both (*Z*)/(*E*) isomers in a 1:1 ratio at room temp.: δ = 2.50 and 2.52 (s, 3 H, SCH_3), 4.16 and 4.27 (s, 2 H, $PhCH_2S$), 7.03 and 7.20 (s, 1 H, vinylic H), 7.3−7.4 (m, 5 H, aromatic H). − ^{13}C NMR ($CDCl_3$); both (*Z*) and (*E*) isomers: δ = 15.2 and 17.8 (S−CH_3) 36.5 and 39.5 (Ph−CH_2−S), 124.8 and 125.7 (=CH−NO_2), 128.1, 128.6, 128.9, 129.1, 129.2 and 129.4 (aromatic CH), 132.6 and 134.2 (*ipso*-C), 163.2 and 163.4 [$(RS)_2C$=]. − MS (70 eV); *m*/*z* (%): 194 (7) [$M^+ - CH_3S$], 91 (100) [$PhCH_2^+$]. − $C_{10}H_{11}NO_2S_2$ (241.32): calcd. C 49.77, H 4.59, N 5.80, S 26.57; found C 49.78, H 4.58, N 5.80, S 26.55.

1-(Methylthio)-2-nitro-1-(2-phenylethylthio)ethene (5b): Yield 35%. − M.p. 87−8 °C (acetonitrile/*tert*-butyl methyl ether). − IR ($CHCl_3$): $\tilde{\nu}$ = 1267, 1314 (strong, NO_2), 1454, 1497, 1525 (strong, NO_2), 2856 (CH_2), 2927 (CH_2), 3015 and 3026 (CH). − ^{1}H NMR ($CDCl_3$); solution of both (*Z*)/(*E*) isomers in an approximate 1:1 ratio at room temp. δ = 2.43 and 2.45 (s, 2 × 3 H, 2 × SCH_3), 2.96 (m, 2 H, CH_2), 3.14 (t, *J* = 7.2 Hz, 2 H, CH_2 for one isomer) and 3.22 (t, *J* = 7.2 Hz, 2 H, CH_2 for the other isomer), 7.00 (s, 1 H, vinylic H of the first isomer) and 7.10 (s, 1 H, vinylic H of the second isomer), 7.21 (br. t, *J* = 7 Hz, 6 H, aromatic H), 7.29 (br. t, *J* = 7 Hz, 4 H, aromatic-H). − ^{13}C NMR [(*Z*) and (*E*) isomers in $CDCl_3$]: δ = 15.3 and 17.6 (SCH_3), 32.8 and 33.2 (CH_2), 34.7 and 35.8 (CH_2), 125.0 and 125.3 (=CH−NO_2), 126.8 and 127.1 (aromatic CH), 128.4 (aromatic CH), 128.6 and 128.7 (aromatic CH), 138.2 and 139.0 (*ipso*-C), 163.6 and 163.9 [$(RS)_2$>C=)]. − MS (70 eV); *m*/*z* (%): 206 (15) [$M^+ - NO_2$], 104 (100). − $C_{11}H_{13}NO_2S_2$ (255.34): calcd. C 51.74, H 5.13, N 5.49, S 25.11; found C 51.55, H 5.11, N 5.44, S 24.99.

1-(Methylthio)-2-nitro-1-(3-phenylpropylthio)ethene (5c): A brown oil that slowly crystallized (1.705 g, 53% yield). Further crystallization afforded light yellow crystals. M.p. 78 °C (CH_2Cl_2/ether/pentane). − IR ($CHCl_3$) $\tilde{\nu}$ = 1268, 1307 and 1320 (strong, NO_2), 1429, 1434, 1497, 1523 and 1525 (strong, NO_2), 2859 and 2927 (CH_2), 3014 and 3026 (aromatic CH), 3065 and 3087 (CH). − ^{1}H NMR [$CDCl_3$ solution of both (*Z*)/(*E*) isomers in an approximate 1:1 ratio]: δ = 2.01 (m, 4 H, $CH_2CH_2CH_2$), 2.40 (s, 3 H, SCH_3), 2.46 (s, 3 H, SCH_3), 2.73 (m, 4 H, CH_2S), 2.83 (t, *J* = 7 Hz, 2 H, Ph−CH_2) and 2.98 (t, *J* = 7 Hz, 2 H, Ph−CH_2), 7.00 (s, 1 H, =C−H) and 7.02 (s, 1 H, =C−H), 7.21 (m, 6 H, aromatic H) and 7.28 (m, 4 H, aromatic H). − ^{13}C NMR [$CDCl_3$ solution of both (*Z*)/(*E*) isomers in a roughly 1:1 ratio]: δ = 15.0 and 17.3 (SCH_3), 28.3, 29.7, 30.4, 33.3, 34.2 and 34.3 (CH_2), 124.6 and 124.84 (=CH−NO_2), 125.89 and 124.84 (aromatic CH), 128.1 and 128.2 (aromatic CH), 128.1 and 128.3 (aromatic CH), 139.7 and 140.2 (*ipso*-C), 163.9 and164.0 [$(RS)_2C$=]. − MS (70 eV); *m*/*z* (%): 223 (35) [$M^+ - NO_2$], 175 (50) [$M^+ - NO_2 - CH_3SH$], 117 (65) [$C_9H_9^+$], 91 (100). − $C_{12}H_{15}NO_2S_2$ (269.27): calcd. C 53.50, H 5.61, N 5.20, S 23.81; found C 53.43, H 5.57, N 5.29, S 23.02.

1-Methylthio-2-nitro-1-(4-phenylbutylthio)ethene (5d): Flash chromatography of the crude product (petroleum ether/ethyl acetate, 85:15) afforded **5d** (2.22 g, 65%) as an oil that slowly crystallized. − M.p. 46−49 °C (petroleum ether/ethyl acetate). − IR ($CHCl_3$) $\tilde{\nu}$ =1268, 1307 and 1320 (strong, NO_2), 1430, 1453, 1497, 1525 (NO_2), 2859 and 2929 (CH_2), 3014 (aromatic CH), 3134 (CH). − ^{1}H NMR ($CDCl_3$) mixture of isomers: δ = 1.71 (br. m, 4 H, CH_2), 2.47 and 2.49 (s, 2.2:3 ratio, 3 H, SCH_3), 2.64 (br. q, *J* ≈ 5 Hz, 2 H, benzylic CH_2), 2.92 and 3.03 (t, *J* = 7 Hz, 2 H, S−CH_2), 7.02 and 7.08 (s, in a 2.2:3 ratio, 1 H, vinylic H), 7.14 (m, 3 H, aromatic H), 7.25 (m, 2 H, aromatic H). − ^{13}C NMR ($CDCl_3$); mixture of isomers: δ = 15.3 and 17.6 (SCH_3), 26.6, 27.9, 30.4, 30.5, 31.3, 34.4, 35.1 and 35.2 (CH_2), 124.9 and 125.2 (=CH−NO_2), 125.9 and 126.1, 128.32, 128.36 and 128.4 (aromatic CH), 141.3 and 141.5 (*ipso*-C), 164.0 and 164.2 [$(RS)_2C$=]. − MS (70 eV); *m*/*z* (%): 237 (52) [$M^+ - NO_2$], 189 (11) [$M^+ - NO_2 - CH_3SH$], 165 (25) [$Ph(CH_2)_4S^+$], 131 (53), 104 (51) [$C_8H_8^+$], 91 (100) [$C_7H_7^+$]. − $C_{13}H_{17}NO_2S_2$ (283.40): calcd. C 55.09, H 6.05, N 4.94, S 22.63; found C 55.06, H 6.01, N 4.85, S.22.33

2-Nitro-1,1-bis(2-phenylethylthio)ethene (6b). − Typical Procedure: Dipotassium salt **7** (2.63 g, 12.3 mmol) was dissolved in DMSO (35 mL) and a solution of $Ph(CH_2)_2Br$ (4.46 g, 26.2 mmol) in DMSO (10 mL) was added. Then the reaction medium was heated at 40 °C for 20 h under nitrogen. After cooling, CH_2Cl_2 was added (200 mL). The organic phase was washed with diluted HCl (2 × 40 mL), then with brine (2 × 40 mL), and dried with $MgSO_4$. A brown oil was recovered after distillation of the solvent. Flash chromatography (AcOEt/Et_2O/hexane, 5:3:42), followed by crystallization from MTBE afforded **6b** (2.75 g, 65%). − M.p. 95−96 °C. − IR ($CHCl_3$) $\tilde{\nu}$ = 1263, 1311 and 1314 (strong, NO_2), 1454, 1497, 1525 (strong, NO_2), 2856 and 2933 (CH_2), 2927 (CH_2), 3014 and 3029 (CH), 3066 and 3089 (CH). − ^{1}H NMR ($CDCl_3$): δ = 2.93 (m, 4 H, 2 CH_2), 3.20 (m, 4 H, 2 CH_2), 7.08 (s, 1 H, vinylic H), 7.15−7.35 (m, 10 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 33.0, 33.3, 34.9 and 35.9 (CH_2), 126.7 (=CH−NO_2), 126.8, 127.1, 128.4, 128.6 and 128.8 (aromatic CH), 138.1 and 139.0 (*ipso*-C), 162.0 [$(RS)_2C$=]. − MS (70 eV); *m*/*z* (%): 299 (18) [$M^+ - NO_2$], 194 (15) [$M^+ - NO_2 - PhCH_2CH_2$], 105 (100) [$PhCH_2CH_2^+$]. − $C_{18}H_{19}NO_2S_2$ (345.47): calcd. C 62.58, H 5.54, N 4.05, S 18.56; found C 62.53, H 5.58, N 4.16, S 18.55.

2-Nitro-1,1-bis(3-phenylpropylthio)ethene (6c): Yield 69%. − M.p. 47−48 °C (MTBE). − IR ($CHCl_3$) $\tilde{\nu}$ = 1270, 1311 and 1313 (both strong, NO_2), 1454, 1497, 1524 (strong, NO_2), 2860 and 2941 (CH_2), 3014 and 3027 (aromatic CH), 3066 and 3087 (CH). − ^{1}H NMR ($CDCl_3$): δ = 2.03 (complex sext, *J* ≈ 7 Hz, 4 H, 2 $CH_2CH_2CH_2$), 2.73 (t, *J* = 7 Hz, 2 H, CH_2S), 2.75 (t, *J* = 7 Hz, 2 H, CH_2S), 2.85 (t, *J* = 7.3 Hz, 2 H, benzylic H), 3.00 (t, *J* = 7 Hz, 2 H, benzylic H), 7.00 (s, 1 H, vinylic H), 7.10−7.45 (m, 10 H, aromatic H). − ^{13}C NMR ($CDCl_3$): δ = 28.6, 30.1, 30.9, 33.6, 34.5 and 34.6 (CH_2), 125.4 (=CH−NO_2), 126.2, 126.4, 128.3, 128.4, 128.5 and 128.6 (aromatic CH), 139.9 and 140.4 (*ipso*-C), 162.8 [$(RS)_2C$=]. − MS (70 eV): *m*/*z* (%) = 327 (25) [$M^+ - NO_2$], 265 (17) [$M^+ - PhC_3H_5$], 222 (40) [$M^+ - PhCH_2CH_2CH_2S$], 175 (50), 151 (40) [$PhC_3H_6^+$],117 (60), 91 (100) [$C_7H_7^+$]. − $C_{20}H_{23}NO_2S_2$ (373.52): calcd. C 64.31, H 6.21, N 3.75, S 17.17; found C 64.24, H 6.16, N 3.87, S 16.79.

2-Nitro1,1-bis(4-phenylbutylthio)ethene (6d): Viscous oil that crystallized on standing. Yield 85%. − M.p. 45−7 °C. − IR ($CHCl_3$) $\tilde{\nu}$ = 1273, 1309 and 1317 (strong, NO_2), 1454, 1496, 1523 (strong, NO_2), 2860 and 2939 (CH_2), 3013 and 3027 (CH), 3064 and 3086 (CH). − ^{1}H NMR ($CDCl_3$): δ = 1.76 (br. signal, 8 H, 2 × $CH_2CH_2CH_2CH_2$), 2.62 (t, *J* = 6.9 Hz, 2 H, CH_2−S) and 2.64 (t, *J* = 6.9 Hz, 2 H, CH_2−S), 2.87 (t, *J* = 6.75 Hz, 2 H, benzylic H), 2.99 (t, *J* = 6.75 Hz, 2 H, benzylic H), 7.02 (s, 1 H, vinylic H), 7.18 (m, 6 H), 7.25 (m, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 26.7, 27.9, 30.4, 30.4, 31.5, 34.4, 35.1 and 35.2 (all CH_2), 125.3 (=CH−NO_2), 125.9, 126.1, 128.3, 128.3, 128.3 and 128.4 (aromatic CH), 141.3 and 141.5 (*ipso*-C), 163.2 [$(RS)_2C$=]. − MS (70 eV); *m*/*z* (%): 402 (0.001) [$M^+ + 1$], 384 (0.14), 371 (0.15), 355 (10) [$M^+ - NO_2$], 191 (3) [$M^+ - NO_2 - Ph(CH_2)_3CH{=}S$], 165 (5) [$Ph(CH_2)_4S^+$], 131 (20), 104 (15) [$C_8H_8^+$], 91 (100) [$C_7H_7^+$]. − $C_{22}H_{27}NO_2S_2$ (401.58): calcd. C 65.80, H 6.78, N 3.49, S 15.97; found C 65.38, H 6.70, N 3.38, S 15.94.

Dications

Cation 8a: ^{1}H NMR (room temp./TMS, [D$_4$]MeOH): δ = 2.83 (s, 3 H, S−C*H*$_3$), 4.52 (s, 2 H, Ph−C*H*$_2$−S), 7.19 (d, *J* = 6.4 Hz, 1 *o*-H), 7.26 (dd, *J* = 7.8, 7.8 Hz, 1 H), 7.35 (dd, *J* = 7.8, 7.8 Hz, 1 H), 7.79 (d, *J* = 8 Hz, 1 *o*-H). − ^{13}C NMR: δ = 24.2 (S*C*H$_3$), 40.7 (benzylic *C*H$_2$), 117.7 (*ipso*-C), 129.1, 130.7 and 132.1 (aromatic *C*H), 135.4 (*ipso*-C), 137.7 (aromatic *C*H), 149.2 (>C=N$^+$<), 212.3 (>C$^+$).

Cation 8b: ^{1}H NMR (room temp.): δ = 1.89 (br. s, 2 H, CH$_2$<), 2.50 (br. s, 2 H, benzylic H), 2.89 (br. s, 3 H, SCH$_3$), 3.54 (br. s, 2 H, SCH$_2$), 6.91 (d, *J* = 7.7 Hz, 1 H), 6.97 (t, *J* = 7.7 Hz, 1 H), 7.16 (t, *J* = 7.7 Hz, 1 H), 7.21 (d, *J* = 8.5 Hz, 1 H). − ^{13}C NMR: δ = 23.7 (SCH$_3$), 31.5 (CH$_2$), 36.5 (CH$_2$), 118.1 (*ipso*-C), 128.3, 129.1 and 132.5 (aromatic CH), 136.9 (*ipso*-C), 138.2 (aromatic CH), 158.3 (>C=N$^+$<), 220.1 (C$^+$<).

Cation 8c: ^{1}H NMR (255 K): δ = 1.85 (br. s, 2 H, CH$_2$), 2.47 (br. s, 2 H, CH$_2$), 2.86 (s, 3 H, S−CH$_3$), 3.51 (br. s, 2 H, CH$_2$), 7.01 (m, 1 H), 7.20 (br. s, 1 H), 7.56 (br. s, 1 H), 6.92 (m, 1 H). − ^{13}C NMR: δ = 26.2 (S−CH$_3$), 29.6, 33.4 and 44.6 (CH$_2$), 122.5, 129.5 (=C−H), 134.5, 140.0, 158.5 (>C=N$^+$<), 220.1 (C$^+$<).

Cation 9a: ^{1}H NMR (254 K): δ = 4.31 (s, 2 H, CH$_2$), 4.37 (s, 2 H, CH$_2$), 6.6 to 6.9 (br. m, 5 H, Ph), 7.17 (d, *J* = 7.6 Hz, 1 H, *ortho*-H), 7.21 (dd, *J* = 7.6 and 8 Hz, 1 H), 7.34 (dd, *J* = 7.7 and 7.7 Hz, 1 H), 7.77 (d, *J* = 8 Hz, 1 H, *ortho*-H). − ^{13}C NMR (room temp.): δ = 41.0 (benzylic C), 48.4, 117.7 (*ipso*-C), 125.6, 129.0 (br. s, aromatic CH), 129.4 (aromatic CH), 129.6, 130.4, 135.3 (*ipso*-C), 148.2 (>C=N$^+$<), 209.0 (>C$^+$).

Cation 9b: ^{1}H NMR (255 K): δ = 2.62 (m, 2 H, CH$_2$CH$_2$CH$_2$), 2.82 (m, 2 H, CH$_2$CH$_2$CH$_2$), 3.19 (br. d, 1 H), 3.40 (m, 2 H), 3.65 (t, *J* = 14 Hz, 1 H, CH$_2$S), 6.56 (m, 5 H), 6.92 (d, *J* = 7.8 Hz, 1 H), 6.98 (t, *J* = 7.7 Hz, 1 H), 7.16 (d, *J* = 7.6 Hz, 1 H) 7.19 (t, *J* = 7.8 Hz, 2 H), 12.70 (v br. s, =NH$^+$−O*H*). − ^{13}C NMR: δ = 32.3, 32.5, 37.2, 46.8 (br. s), 119.1, 128.8, 129.2, 129.4, 129.9, 130.0, 133.5, 136.2, 137.8, 139.3, 159.0 (>C=N$^+$<), 216.6 (>C$^+$).

Cation 9c: ^{1}H NMR (255 K): δ = 1.80 (br. s, 4 H, 2 CH$_2$−CH$_2$−CH$_2$), 2.22 (br. s, 2 H, benzylic H), 2.30 (br. s, 2 H benzylic H), 3.21 (br. s, 2 H, CH$_2$S), 3.33 (br. s, 2 H, CH$_2$S), 6.12 (br. s, 1 H, aromatic H), 6.33 (br. s, 2 H, aromatic H), 6.50 (br. s, 2 H, aromatic H), 6.96 (br. s, 2 H, aromatic H), 7.23 (br. s, 1 H, aromatic H), 7.60 (br. s, 1 H, aromatic H). − ^{13}C NMR: δ = 27.3, 29.2, 33.0, 34.4, 43.1 and 45.0 (CH$_2$−S), 122.8, 128.0, 128.7, 129.7, 130.0, 133.5, 134.8, 139.5, 143.9, 155.7 (>C=N$^+$<), 214.3 (C$^+$<). Mostly broadened signals and slow decomposition at 255 K.

Cyclic Compounds. − 3-Methoxy-3-(methylsulfanyl)isothiochroman-4-one Oxime (12a). − Typical Procedure: Nitroethylene derivative **5a** (322 mg, 1.33 mmol) was dissolved in TFSA (5.0 mL, 56 mmol) at a temperature between −10 and +2 °C, and left for 40 min. The solution was quenched with MeOH/CH$_2$Cl$_2$ (18:52, 70 mL) at a temperature between −60 and −80 °C, and then CH$_2$Cl$_2$ (100 mL) was added. At a temperature between −10 and 0 °C, the resulting organic phase was washed with water (30 mL), then brine (20 mL), and finally with brine containing NaHCO$_3$. The organic phase was dried with MgSO$_4$ and the solvent was evaporated under vacuum to afford a crystallized product. Flash chromatography led to the recovery of some starting material (petroleum ether/AcOEt, 9:1, 9 mg, 2.7%). Further elution (petroleum ether/AcOEt/CH$_2$Cl$_2$, 40:7:3) afforded the cyclic derivative **12a** (236 mg; 70%), which was further crystallized from AcOEt as white crystals. − M.p. 134−136 °C (dec.). − IR (CHCl$_3$) ν̃ = 940, 1059, 2860 1454, 1495, 1602 (weak, C=N−OH), 1827, 2935, 3007, 3276 (br. band, OH), 3564 (oxime, OH). − ^{1}H NMR ([D$_6$]DMSO/CDCl$_3$): δ = 2.07 (s, 3 H, SCH$_3$), 3.20 (s, 3 H, OCH$_3$), 3.65 (d, *J* = 15.9 Hz, 1 H, axial benzylic H), 4.20 (d, *J* = 15.9 Hz, 1 H, equatorial benzylic H), 7.15−7.35 (m, 3 H, aromatic H), 8.12 (dd, *J* = 7.5 and 1.7 Hz, 1 H, *o*-H), 11.37 (s, 1 H, =N−OH). − ^{13}C NMR ([D$_6$]DMSO/CDCl$_3$): δ = 11.9 (SCH$_3$), 30.2 (CH$_2$), 51.5 (OCH$_3$), 93.5 (orthodithioester C), 125.9 and 127.1 (aromatic CH), 127.1 (*ipso*-C), 128.9 and 131.0 (aromatic CH), 135.6 (*ipso*-C), 148.9 (>C=N−OH). − MS (70 eV); *m*/*z* (%): 224 (1) [M$^+$ − CH$_3$O], 208 (70) [M$^+$ − CH$_3$S], 176 (5) [M$^+$ − CH$_3$S − CH$_3$OH], 148 (20), 134 (32), 116 (70) [C$_4$H$_6$ONS$^+$], 89 (65) [C$_3$H$_5$OS$^+$], 75 (100) [C$_2$H$_3$OS$^+$]. − C$_{11}$H$_{13}$NO$_2$S$_2$ (255.34): calcd. C 51.74, H 5.13, N 5.49, S 25.11; found C 51.64, H 5.16, N 5.35, S 24.36.

2-Methoxy-2-(methylsulfanyl)-4,5-dihydrobenzo[*d*]thiepin-1-one Oxime (12b): From nitroethylene derivative **5b** (312 mg, 1.22 mmol) in TFSA (4.0 mL, 45 mmol) at room temp. for 1 h. Flash chromatography (CH$_2$Cl$_2$/AcOEt/*i*PrOH, 95:5:0.5) afforded compound **12b** (244 mg, 74%). − M.p. 181−3 °C (dec.). − ^{1}H NMR ([D$_6$]DMSO/CDCl$_3$): δ = 2.04 (s, SMe), 2.70 (m, 1 H), 3.05 (m, 3 H), 3.35 (s, 3 H, OMe), 7.14 (m, 2 H), 7.24 (m, 2 H), 11.08 (s, 1 H, =N−OH). − ^{13}C NMR ([D$_6$]DMSO/CDCl$_3$): δ = 12.1 (SCH$_3$), 27.4 (br. and weak signal for both CH$_2$ groups), 50.8 (OCH$_3$), 96.6 (orthodithioester C), 125.3, 128.3, 129.2 and 129.8 (aromatic CH), 132.9 (*ipso*-C), 136.5 (*ipso*-C), 156.6 (>*C*=N). − MS (70 eV); *m*/*z* (%): 269 (< 1) [M$^+$], 252 (5) [M$^+$ − OH], 238 (2) [M$^+$ − OCH$_3$], 222 (100) [M$^+$ − SCH$_3$], 130 (20), 116 (20) [C$_4$H$_6$ONS$^+$], 89 (17) [C$_3$H$_5$OS$^+$], 75 (58) [C$_2$H$_5$OS$^+$]. − C$_{12}$H$_{15}$NO$_2$S$_2$ (269.38): calcd. C 53.51, H 5.61, N 5.20, S 23.81; found C 53.44, H 5.44, N 5.39, S 22.92.

2-Methoxy-2-(methylsulfanyl)-5,6-dihydro-4*H*-benzo[*d*]thiocin-1-one Oxime (12c): From nitroethylene derivative **5c** (241 mg, 0.896 mmol) in TFSA (4.9 mL, 55 mmol) for 2 h at 0−5 °C. Flash chromatography (CH$_2$Cl$_2$/EtOH, 99:1) afforded compound **12c** (184 mg, 82%) as white crystals. − M.p. 191−193 °C (dec.). − ^{1}H NMR ([D$_6$]DMSO/CDCl$_3$, 4:1) mixture of isomers in 3:2 ratio (main signal with *): δ = 1.5−1.9 (m, 1.7 H), 1.9−2.1 (m, 0.3 H), 2.03 and 2.05* (s, 3 H, SCH$_3$), 2.15−2.3 (m, 0.7 H), 2.4−2.8 (m, 3.4 H), 3.38* and 3.40 (s, OCH$_3$), 6.88* and 7.03 (d, *J* = 7.2 Hz and *J* = 7.0 Hz, 1 H, *ortho*-H), 7.1−7.3 (m, 3 H, aromatic H), 11.13 and 11.17* (s, 1 H, N−OH). − ^{13}C NMR ([D$_6$]DMSO/CDCl$_3$) (two isomers, main signal with *): δ = 11.4 and 12.4* (SCH$_3$), 26.5 and 29.5* (CH$_2$S), 30.5 and 31.1* (benzylic CH$_2$), 32.2* and 34.1 (CH$_2$−CH$_2$−CH$_2$), 50.6 and 50.4* (OCH$_3$), 99.2 and 99.9* (dithioorthoester C), 124.8 and 125.3* (aromatic CH), 127.5* and 127.7 (aromatic CH), 128.3* and 128.4 (aromatic CH), 128.6 (aromatic CH), 134.1 and 134.3* (*ipso*-C), 137.9 and 140.6* (*ipso*-C), 156.1 and 157.3* (>C=N−OH). − MS (70 eV); *m*/*z* (%): 283 (2) [M$^+$], 266 (9) [M$^+$ − OH], 252 (55) [M$^+$ − OCH$_3$], 236 (100) [M$^+$ − SCH$_3$], 204 (20) [M$^+$ − SCH$_3$ − CH$_3$OH], 116 (50) [C$_8$H$_6$N]. − C$_{13}$H$_{17}$NO$_2$S$_2$ (283.40): calcd. C 55.10, H 6.05, N 4.94, S 22.63; found C 55.57, H 6.20, N 5.31, S 22.43.

6-Methoxy-6-(methylsulfanyl)-8,9,10,11-tetrahydro-7-thiabenzocyclononen-5-one Oxime (12d): From nitroethylene derivative **5d** (517 mg, 1.83 mmol) in TFSA (9 mL, 101 mmol) for 30 min at 0−5 °C. Flash chromatography (CH$_2$Cl$_2$/EtOH, 98:2) afforded compound **12d** (152 mg, 28%) as light yellow crystals after crystallization from AcOEt/hexane. − M.p. 173−174 °C (dec.). − ^{1}H NMR (CDCl$_3$), mixture of two isomers (1:7 ratio): δ = 1.28 (m, 2 H) and 1.86 (m, 4 H), 2.10 (CH$_3$S) and 2.69 (m, 4 H), 3.48 (CH$_3$O), 7.26 (d, *J* = 7.4 Hz, 2 H), 7.35 (d, *J* = 7.4 Hz, 1 H), 7.47 (d, *J* = 7.4 Hz, 1 H), 9.02, (s, =N−O*H*). − ^{13}C NMR (CDCl$_3$): δ = 12.2 (SCH$_3$),

25.1, 27.6, 27.8 and 28.6 (CH_2), 50.7 (CH_3O), 98.7 (orthodithioester C), 125.3, 127.6, 128.7 and 129.1 (aromatic CH), 131.8 and 141.3 (*ipso*-C), 156.5 (>C=N−OH). − MS (70 eV); *m/z* (%): 280 (2.8) [M^+ − OH], 250 (28) [M^+ − SCH_3], 218 (30) [M^+ − CH_3S − CH_3OH], 201 (7) [M^+ − CH_3S − CH_3OH − OH], 186 (14), 116 (45) [$C_4H_6ONS^+$], 75 (100) [$C_2H_3OS^+$]. − $C_{14}H_{19}NO_2S_2$ (297.43): calcd. C 56.53, H 6.44, N 4.71, S 21.56; found C 56.68, H 6.59, N 4.97, S 20.98.

3-(Benzylsulfanyl)-3-methoxyisothiochroman-4-one Oxime (13a): From nitroethylene derivative **6a** (343 mg, 1.08 mmol) in TFSA (5.0 mL, 56 mmol) at a temperature between −9 and −2 °C for 30 min. Flash chromatography (petroleum ether/AcOEt, 9:1) afforded starting material **6a** (11.4 mg, 11.4%), and then compound **13a** (298 mg, 83.3%) as white crystals. − M.p. 136−8 °C (dec.) from pentane/MTBE. − ^{1}H NMR ([D$_6$]DMSO/$CDCl_3$): δ = 3.34 (s, 3 H, OMe), 3.67 (d, *J* = 16 Hz, 1 H, axial benzylic H), 3.83 (d, *J* = 12.6 Hz, 1 H, Ph−CH*H*), 3.86 (d, *J* = 12.6 Hz, 1 H, Ph−CH*H*), 4.21 (d, *J* = 16 Hz, 1 H, equatorial benzylic H), 7.20−7.30 (m, 8 H, aromatic H), 8.05 (dd, *J* = 9 Hz, *J* = 1.4 Hz, 1 H, *o*-H), 11.44 (s, 1 H, =N−OH). − ^{13}C NMR ([D$_6$]DMSO/$CDCl_3$): δ = 30.2 and 33.9 (CH_2), 51.8 (OCH_3), 94.4 (orthodithioester C), 125.9, 126.7 and 127.0 (aromatic CH), 127.2 (*ipso*-C), 128.3, 128.9, 129.0 and 131.0 (aromatic CH), 135.7 (*ipso*-C), 137.6 (*ipso*-C), 148.9 (>C=N−OH). − MS (70 eV); *m/z* (%): 208 (38) [M^+ − $PhCH_2S$], 176 (3) [M^+ − $PhCH_2S$ − CH_3OH], 148 (10), 134 (24), 116 (25), 91 (100) ($C_7H_7^+$). − $C_{17}H_{17}NO_2S_2$ (331.44): calcd. C 61.60, H 5.17, N 4.23, S 19.35; found C 61.56, H 5.19, N 4.20, S 19.23.

2-Methoxy-2-(phenethylsulfanyl)-4,5-dihydrobenzo[*d*]thiepin-1-one Oxime (13b): From nitroethylene derivative **6b** (297 mg, 0.861 mmol) in TFSA (5.0 mL, 56 mmol) at 0−5 °C for 6 min. Flash chromatography (CH_2Cl_2/AcOEt, 9:1) afforded compound **13b** (222 mg, 72%). − M.p. 119−120 °C (white prisms from ether/pentane). − ^{1}H NMR ($CDCl_3$): δ = 2.3−3.4 (complex m, 8 H, 4 CH_2), 3.46 (br. s, 3 H, OCH_3), 7.0−7.5 (m, 9 H, aromatic H), 9.44 (br. s, 1 H, =N−OH). − ^{13}C NMR ($CDCl_3$): δ = 26.9 (CH_2), 31.4 (CH_2), 33.1 (CH_2), 35.1 (CH_2), 51.4 (OCH_3), 97.7 (orthodithioester C), 125.7 (aromatic CH) 126.4, 128.46 and 128.52 (aromatic CH), 129.2 (aromatic CH), 129.6 and 129.8 (aromatic CH), 131.8 and 136.2 (*ipso*-C), 140.3 (*ipso*-C), 157.2 (oxime C). − MS (70 eV); *m/z* (%): 359 (< 1) [M^+], 342 (5) [M^+ − OH], 328 (2) [M^+ − OCH_3], 222 (100) [M^+ − $PhCH_2CH_2S$], 130 (42), 105 (65) [$C_8H_9^+$], 91 (82) [$C_7H_7^+$]. − $C_{19}H_{21}NO_2S_2$ (359.50): calcd. C 63.48, H 5.89, N 3.90, S 17.84; found C 63.58, H 5.98, N 4.07, S 17.58.

2-Methoxy-2-(3-phenylpropylsulfanyl)-5,6-dihydro-4*H*-benzo[*d*]thiocin-1-one Oxime (13c): From nitroethylene derivative **6c** (239 mg, 0.641 mmol) in TFSA (5 mL, 56 mmol) at 0−5 °C for 20 min. Flash chromatography (CH_2Cl_2/EtOH, 99:1) afforded **13c** (163 mg, 71%) as white crystals. − M.p. 147−148 °C. − ^{1}H NMR ([D$_6$]DMSO/$CDCl_3$, 4:1, mixture of two isomers in a 45:55 ratio, major isomer *): δ = 1.8−2.3 (m, 5 H, CH_2), 2.5−2.8 (m, 7 H, CH_2), 3.28* and 3.40 (s, 3 H, OCH_3), 6.80 and 7.03* (d, *J* = 7.2 Hz and d, *J* = 7.2 Hz, 1 H, *ortho*-H), 7.1 to 7.3 (m, 9 H, aromatic H), 11.120* and 11.125 (s, 1 H, =N−OH). − ^{13}C NMR ($CDCl_3$, mixture of two isomers): δ = 26.0, 29.1, 29.6, 30.1, 30.2, 30.7, 31.1, 32.7, 34.4, 35.3, 35.33, 50.5 and 51.2* (OCH_3), 98.4 and 98.8* (orthodithioester C), 125.3, 125.6, 125.9, 126.0, 127.5, 128.0, 128.4, 128.4, 128.5, 128.8, 129.0, 129.3, 132.8, 133.5, 137.6, 140.7, 141.1, 141.4, 158.0* and 159.6 (>C=N−OH). − MS (70 eV); *m/z* (%): 370 (3) [M^+ − OH], 236 (95) [M^+ − $Ph(CH_2)_3S$], 204 (18) [M^+ − $Ph(CH_2)_3S$ − CH_3OH], 187 (15) [M^+ − $Ph(CH_2)_3S$ − CH_3OH − OH], 143 (25), 117 (55), 91 (100) [$C_7H_7^+$], 75 (72) [$C_2H_3OS^+$]. − $C_{21}H_{25}NO_2S_2$ (387.55): calcd. C 65.08, H 6.50, N 3.61, S 16.54; found C 64.92, H 6.42, N 3.69, S 16.46.

6-Methoxy-6-(4-phenylpropylsulfanyl)-8,9,10,11-tetrahydro-7-thiabenzocyclononen-1-one Oxime (13d): From nitroethylene derivative **6d** (366 mg, 0.913 mmol) in triflic acid (4.6 mL, 51.5 mmol) for 10 min at 0−5 °C. Flash chromatography (hexane/ethyl acetate, 15:85) afforded compound **13d** (54 mg, 12%). − M.p. 144 °C (pentane/CH_2Cl_2/MTBE). − ^{1}H NMR ($CDCl_3$): δ = 1.5−2.0 (m, 8 H), 2.5−2.9 (m, 6 H), 3.49 (s, 3 H, OCH_3), 7.0−7.5 (m, 9 H), 9.74 (s, =N−OH). − ^{13}C NMR ($CDCl_3$): δ = 28.1, 29.4, 30.0, 30.4, 30.9, 32.6, 35.3, 35.4 (all *C*H_2), 52.0 (O*C*H_3), 101.3 (orthodithioester C), 125.7, 125.8, 128.3, 128.3, 128.4, 141.95 and 141.97 (aromatic *C*), 152.6 (>*C*=N−OH). A slight isomerization occurred during ^{13}C NMR analysis [examples of new signals: δ = 50.8 (O*C*H_3), 141.1 (aromatic *C*), 156.9 (>*C*=N−OH)]. No reaction at −10 °C even after 30 min. − MS (70 eV); *m/z* (%): 250 (98) [M^+ − $Ph(CH_2)_4S$], 190 (35), 132 (75), 156 (40), 116 (100) [$C_4H_6ONS^+$]. − $C_{23}H_{29}NO_2S_2$ (415.60) calcd. C 66.47, H 7.03, N 3.37, S 15.43; found C 66.41, H 7.03, N 3.31, S 14.71.

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