

New NO-Donors with Antithrombotic Activities and Vasodilating Activities, III: 3,4-Disubstituted *N*-Nitroso-5-sydnone Imines

Klaus Rehse* and Klaus-Jürgen Schleifer^{†)}

Institut für Pharmazie der Freien Universität Berlin, Königin-Luise-Str. 2 + 4, D-1000 Berlin 33

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38 title compounds have been synthesized. They bear a wide variety in substituents including alkyl-, aryl-, arylalkyl-, and styryl groups. The antiplatelet activities elucidated in the *Born*-test with collagen cover more than two orders of magnitude ($IC_{50} = 0.3\text{--}45\text{ }\mu\text{mol/L}$). These effects depend on the presence of the *N*-NO-group. This is shown by comparison with the corresponding sydnone imines, sydnone cyanimines, and sydnones. The most suitable substituents were phenylethyl, styryl, and hexyl at either position of the molecule. Seven compounds, most of them styryl derivatives, have IC_{50} values below $1\text{ }\mu\text{mol/L}$. It is suggested that the differences in activity are connected with the ability of the compounds to bind to the platelet membrane.

Recently we reported on the strong platelet aggregation inhibiting activities of 3-substituted *N*-nitroso-sydnone-5 imines. The *in vitro* antiplatelet effects were accompanied by *in vivo* antithrombotic and antihypertensive properties. These results encouraged us to investigate the influence of a further substituent in position 4 of the sydnone-5 imine. The synthesis of the desired compounds was carried out in principle as described¹⁾. Briefly the amine $R^1\text{-NH}_2$ (Table 1) is reacted with an aldehyde $R^2\text{-CHO}$ and KCN. After nitrosation and acid catalyzed ring closure the type **a** sydnone-5 imines are obtained. A second nitrosation yields the wanted type **b** compounds. The amines were selected according to the results in 3-monosubstituted derivatives. In addition the aromatic amine *p*-toluidine for type **17** compounds was assayed. A wide variety of aldehydes was used including aliphatic (**1-12**, **17**), alicyclic (**13**), arylalkyl (**14-16**), olefinic (**28-38**), and aromatic (**18-27**) species. The outstanding feature of the nitrosimines is their colour. It varies from yellow, (e.g. **11b**, **12b**) via orange-yellow (**9b**), orange (**1b**, **2b**), orange-red (**5b**, **21b**), carmine (**8b**, **6b**, **22b**), and different reds to violet (**17b**, **27b**), caused by an absorption in the electronic spectra in the range between 484 nm (**0b**) and 515 nm (i.e. **30b**, **32-34b**). Its intensity is rather low but nevertheless characteristic. The log ϵ values vary from 2.06 (**1b**) to 2.55 (**38b**).

Neue NO-Pharmaka mit antithrombotischen und gefäßerweiternden Eigenschaften, 3. Mitt.: 3,4-Disubstituierte *N*-Nitroso-5-sydnon-imine

38 3,4-disubstituierte Nitrososydnonimine wurden dargestellt. Sie weisen eine große Variationsbreite von Substituenten auf. Sowohl Alkyl-, Aryl-, Arylalkyl- als auch Styrylgruppen wurden verwendet. Die im *Born*-Test mit Collagen ermittelten Hemmwirkungen auf die Thrombocytenaggregation überstreichen mehr als zwei Größenordnungen ($IC_{50} = 0.3\text{--}45\text{ }\mu\text{mol/L}$). Für diese Aktivitäten ist die *N*-Nitrosfunktion essentiell, wie der Vergleich mit den entspr. Iminen, Cyaminen oder den Sydnonen selbst zeigt. Die geeignetsten Substituenten waren 2-Phenylethyl-, Styryl- oder Hexyl-Reste sowohl in 3- wie in 4-Position. Sieben Verbindungen, vornehmlich Styrylderivate, hatten eine halbmaximale Hemmkonzentration von weniger als $1\text{ }\mu\text{mol/L}$. Die Befunde deuten daraufhin, daß die Wirkungsunterschieden mit der unterschiedlichen Fähigkeit der Substanzen, an die Thrombocytenmembran hydrophob zu binden, verknüpft sind.

The correlation between structure and light absorption is exemplified by the comparison shown in Scheme 1.

In the IR-spectra strong bands between $1350\text{--}1400\text{ cm}^{-1}$ indicate the presence of an N=O group. In FAB-mass spectra the molecular ion could be shown²⁾. The intensities varied strongly from one to one hundred % (e.g. **2b**, **8b**, **22b**). In all three cases R^1 was hexyl.

Two surprising observations were made in the $^1\text{H-NMR}$ spectra: In compound **11b** the protons of the methylene group in R^2 are diastereotopic and form the AB part of an ABX_3 spin system.

This effect is even more pronounced in the corresponding imine **11a**. This effect is connected with the presence of the hydroxy group in R^1 . As no diastereomers are seen a steric fixation of R^1 by an interaction of the hydroxy group with the electron rich N-2 of the sydnone imine might be the reason for the anisochronic behaviour of the protons in the methylene group.

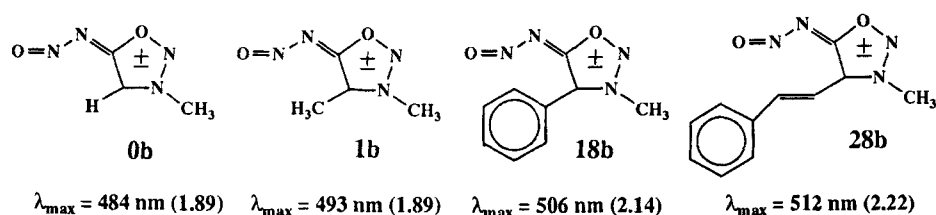
In compound **27b** (Scheme 2) a hindered rotation of the naphthalene ring was recognized by recording the $^1\text{H-NMR}$ spectra at various temp.

At the usual probe temp. of 310 K the methylene protons in R^1 -position form the non first order AB-part of an ABX_3 spin system at 4.47 ppm which is shown in the upper panel of fig. 2. When the temp. is raised the multiplett is gradually converted into a quartett ($A \rightarrow B \rightarrow C$). Simultaneously at 4.32 ppm a quartett arises. This signal corresponds to the formation of the sydnone **27c** by elimination of N_2 .

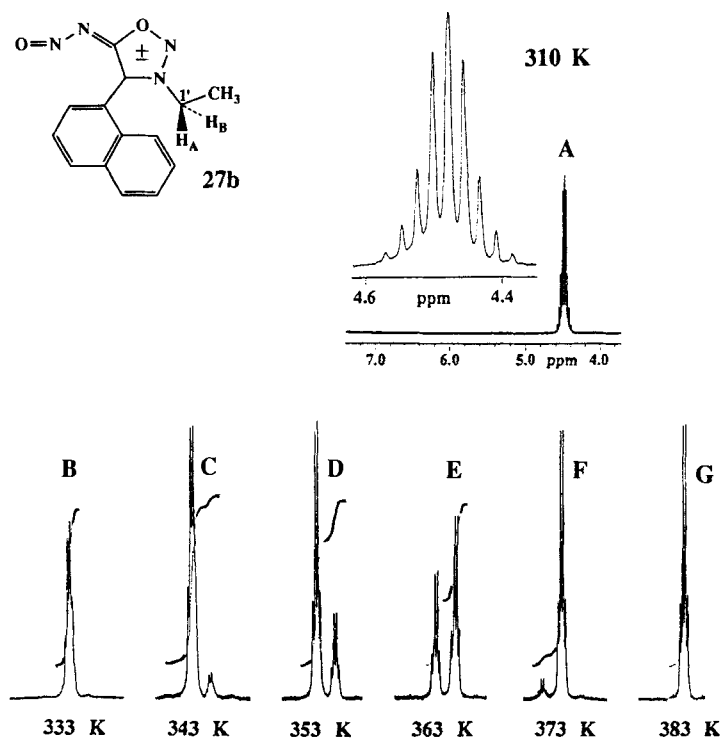
The antiplatelet effects of all compounds are summarized in Table 1. In general the type **a** imines show low or no activity (IC_{50} between 13 (**34a**) and > 500 (**18a**, **21a**, **27a**)).

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²⁾ We thank Mrs. U. Ostwald and Dr. G. Holzmann for skilful recording and discussions.



Scheme 1: Light absorption characteristics of different types of substitution in nitrososydnone imines



Scheme 2: ^1H -NMR spectra of **27b** (details)

$\mu\text{mol/L}$). Nitrosation of the imines to the type **b** nitros-imines is accompanied by a dramatic rise in the capability to inhibit collagen induced platelet aggregation. The IC_{50} drops down below $1 \mu\text{mol/L}$ (e.g. **13b**, **32b**, **34b**, **35b**, **36b**). This is most markedly expressed by the ratio of activity IC_{50a} which reaches $r \geq 250$ in **27a/b**. Nevertheless there are pronounced structure activity relationships. For instance the IC_{50} of **3b** ($86 \mu\text{mol/L}$) is highly indicating lack of activity. On the other hand especially in the series of styryl derivatives (**28b-38b**) for many compounds the IC_{50} is below $1 \mu\text{mol/L}$ so that the range of activity differences covers two orders of magnitude. The sydnone of type **c** (e.g. **27c**) or the type **d** cyanimines (e.g. **4d**) show no activity. This indicates that the NO-part of the nitrosoimino group is an essential structural feature.

In more detail the following structure activity relationships emerge. Comparison of **0b** and **1b** at first gave the - wrong - impression that a second substituent in 4-position

(R^2) is unfavourable. This effect is less obvious when optimal substituents in 3-position (R^1) are present (**2b**, **4b**, **7b**). When R^2 becomes more lipophilic (ethyl: **10b**, **11b**; isopropyl: **8b**, **9b**; isobutyl **12b**) more pronounced antiplatelet effects are observed. When suitable R^1 rests are present as well in R^2 very active compounds are obtained (**13b-16b**).

An aromatic substitution in 3-position is not easily obtained as the basicity of the starting aromatic amines is rather low. Nevertheless **17b** could be synthesized. As the activity was rather low and in the same range as in **18b** ($\text{R}^1 = \text{CH}_3$; $\text{R}^2 = \text{Ph}$) no further compounds of this series were designed. Having an aromatic substituent in 4-position (i.e. **18b**) the activity could be enhanced markedly by suitable substitution in 3-position as it is clearly shown by the rising activities in the line **18b** < **19b** < **20b** < **23b** < **22b** < **24b** < **26b**. Comparison of the pairs **20b/22b** and **23b/25b** furnishes evidence that more lipophilic substituents are more favourable. The same conclusion is suggested by compari-

son of **19b** and **27b**, where $R^2 = \text{Ph}$ is replaced by a 1-naphthyl residue. The activity thereby is raised by one order of magnitude. These results prompted us to introduce styryl rests in 4-position. This variation yielded the most active substances so far found in the sydnone nitrosimines. The IC_{50} of seven compounds was below $1 \mu\text{mol/L}$ (e.g. **28b**, **29b**, **32b-35b**). The peak activities were observed when R^1 was a 2-phenylethyl substituent (**32b**, **33b**). Interestingly the aromatic ring could be exchanged by the quasiaromatic furane without loss of activity (compare **32b** with **36b**). Polar groups (**37b**, **38b**) i.e. ether, ester or hydroxy moieties in the lipophilic R^1 decrease the antiplatelet effect.

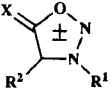
We have pointed out¹⁾ that the *in vitro* antiplatelet activities are due to photolytic cleavage of the nitrosoimino group. Therefore, the question arises why such enormous structure dependence of this effect is observed although the nitrosimino group is the same in all type **b** compounds.

Firstly it has to be discussed whether the electronic properties especially the ability for the absorption of light are

modified by the various substituents. This can be elucidated by comparison of the activities of compounds with identical electronic spectra. For instance **3b** (λ_{max} , $\log \epsilon$): 347 (4.20); 498 (2.07) and **4b** (346 (4.25); 498 (2.11)) show nearly identical light absorption but differ by more than one order of magnitude in their activities ($\text{IC}_{50} = 86$ vs. $6 \mu\text{mol/L}$). The same is true for the pairs **19b** (352 (4.14); 505 (2.15); $\text{IC}_{50} = 24 \mu\text{mol/L}$) and **22b** (352 (4.17); 507 (2.15); $\text{IC}_{50} = 2 \mu\text{mol/L}$) or **33b** (345 (4.32); 515 (2.26); $\text{IC}_{50} = 0.3 \mu\text{mol/L}$) and **37b** (344 (4.42); 514 (2.25); $\text{IC}_{50} = 3.5 \mu\text{mol/L}$). Many other examples could be added. Therefore, a different susceptibility to light cleavage can be ruled out or has a minor effect only.

More probably the differences in activity are connected with pharmacokinetic parameters. It is striking that the lowest IC_{50} values are obtained with substituents (phenylethyl, styryl, hexyl) which we have found to stand for high membrane affinity because of their hydrophobic binding properties²⁾. We, therefore, assume that in the test tube these com-

Tab. 1: Antiplatelet activities (*Born*-test, collagen) of 3,4-disubstituted nitrososydnone imines (**b**) compared to some corresponding sydnone imines (**a**), sydnones (**c**), and cyano sydnone imines (**d**). An asterisk means that the test has been carried out in pure Hepes buffer without addition of DMSO.

				a $\text{X} = \text{NH}_2^+\text{Cl}^-$ b $\text{X} = \text{NNO}$ c $\text{X} = \text{O}$ d $\text{X} = \text{NCN}$			
No	R^1	R^2	IC_{50} [$\mu\text{mol/L}$]	No	R^1	R^2	IC_{50} [$\mu\text{mol/L}$]
0b	CH_3	H	2.5	17a	4- CH_3 -Ph	CH_3	125*
1b	CH_3	CH_3	8.5	17b	4- CH_3 -Ph	CH_3	23
2b	C_6H_{13}	CH_3	8.5	18a	CH_3	Ph	>500*
3b	PhCH_2	CH_3	86	18b	CH_3	Ph	45
4b	$\text{Ph}(\text{CH}_2)_2$	CH_3	6	19b	C_2H_5	Ph	24
4d	$\text{Ph}(\text{CH}_2)_2$	CH_3	87	20b	C_6H_{13}	Ph	5
5b	$\text{Ph}(\text{CH}_2)_3$	CH_3	38	21a	Allyl	Ph	>500*
6a	$\text{Ph}(\text{CH}_2)_4$	CH_3	>300*	21b	Allyl	Ph	8.5
6b	$\text{Ph}(\text{CH}_2)_4$	CH_3	18	22b	C_6H_3	4-Cl-Ph	2
7b	Ph-CHOH-CH-CH_3	CH_3	6	23a	$\text{Ph}(\text{CH}_2)_2$	Ph	53
8b	C_6H_{13}	$\text{CH}(\text{CH}_3)_2$	1.5	23b	$\text{Ph}(\text{CH}_2)_2$	Ph	5
9b	$\text{Ph}(\text{CH}_2)_2$	$\text{CH}(\text{CH}_3)_2$	5	24b	Ph-CHOH-CH-CH_3	Ph	2
10b	$\text{Ph}(\text{CH}_2)_2$	C_2H_5	3	25a	$\text{Ph}(\text{CH}_2)_2$	4-Cl-Ph	53
11b	Ph-CHOH-CH-CH_3	C_2H_5	4	25b	$\text{Ph}(\text{CH}_2)_2$	4-Cl-Ph	1.5
12b	$\text{Ph}(\text{CH}_2)_2$	$\text{CH}_2\text{-CH}(\text{CH}_3)_2$	4.5	26b	$\text{Ph}(\text{CH}_2)_3$	Ph	1.5
13b	$\text{Ph}(\text{CH}_2)_2$	Cyclohexyl	0.5	27a	C_2H_5	1-naphthyl	>500*
14a	$\text{Ph}(\text{CH}_2)_2$	PhCH_2	125*	27b	C_2H_5	1-naphthyl	2
14b	$\text{Ph}(\text{CH}_2)_2$	PhCH_2	2	27c	C_2H_5	1-naphthyl	70
15b	$\text{Ph}(\text{CH}_2)_3$	PhCH_2	1	28a	CH_3	PhCH=CH	46*
16a	$\text{Ph}(\text{CH}_2)_2$	$\text{Ph}(\text{CH}_2)_2$	119*	28b	CH_3	PhCH=CH	1
16b	$\text{Ph}(\text{CH}_2)_2$	$\text{Ph}(\text{CH}_2)_2$	3	28c	CH_3	PhCH=CH	70

Tab. 1: continued

No	R ¹	R ²	IC ₅₀ [μmol/L]	No	R ¹	R ²	IC ₅₀ [μmol/L]
29b	C ₂ H ₅	PhCH=CH	0.7	34a	PhCHOHCH ₂	PhCH=CH	13
30a	Allyl	PhCH=CH	34	34b	PhCHOHCH ₂	PhCH=CH	0.6
30b	Allyl	PhCH=CH	1.5	35a	Ph(CH ₂) ₃	PhCH=CH	70
31a	Cyclohexyl	PhCH=CH	43	35b	Ph(CH ₂) ₃	PhCH=CH	0.7
31b	Cyclohexyl	PhCH=CH	2.5	36a	Ph(CH ₂) ₂	1-furanyl	70
32a	Ph(CH ₂) ₂	PhCH=CH	42*	36b	Ph(CH ₂) ₂	1-furanyl	0.4
32b	Ph(CH ₂) ₂	PhCH=CH	0.3	37b	HO-(CH ₂) ₂ -O-(CH ₂) ₂	PhCH=CH	3.5
33a	3,4-(CH ₃ O)Ph(CH ₂) ₂	PhCH=CH	75	38b	CH ₃ O-CO-(CH ₂) ₃	PhCH=CH	1.5
33b	3,4-(CH ₃ O)Ph(CH ₂) ₂	PhCH=CH	0.3				

pounds concentrate at the platelet membrane. The metabolite (presumably NO) which is now released by interaction with the aggregometer light beam has an extremely short way to diffuse into the platelet. There it activates the soluble guanylat cyclase, raises the level of c-GMP and inhibits platelet aggregation. In summary this results in a reciprocal correlation between membrane affinity and IC₅₀ values: Compounds docking best to the platelet membrane will have the highest antiplatelet activities *i.e.* the lowest IC₅₀ values.

Experimental Part

Devices, synthetic procedures and test methods correspond to the previous communications of this series^{1,3).}

3-Methyl-N-nitroso-5-sydnone imine (0b)

Ochre yellow crystals (ethanol), mp. 133°C (Lit.⁴⁾; 128°C). Yield 63%.- C₈H₄N₄O₂ (128.1) Calcd. C 28.1 H 3.14 N 43.7 Found C 27.9 H 3.11 N 43.5.- IR (KBr): 3417; 3052; 2953; 1646; 1565; 1468; 1445; 1416; 1403; 1360; 1347; 1235; 1107; 1087; 1067; 1017; 960; 878; 830; 678; 640 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 333 (4.26), 484 nm (1.89).- ¹H-NMR/250 MHz ([D₆]DMSO): δ (ppm) = 8.75 (s; 1H, syd-H), 4.39 (s; 3H, N-CH₃).- ¹³C-NMR/75.47 MHz ([D₆]DMSO): δ (ppm) = 182.6 (s; syd-C-5), 106.5 (s; syd-C-4), 40.0 (s; N-CH₃).- MS (100°C): m/z = 128 (9%, [M]⁺), 100 (33), 99 (12), 98 (15), 68 (25), 67 (47), 42 (48), 30 (100), 28 (47).- MS (+ FAB/DMSO/glycerol): m/z = 129 (21%, [M + H]⁺), 99 (4), 93 (100%, [gly + H]⁺), 55 (35).

3,4-Dimethyl-N-nitroso-5-sydnone imine (1b)

Orange powder (ethanol/ether), mp. 108°C. Yield 45%.- C₁₀H₆N₄O₂ (142.1) Calcd. C 33.8 H 4.25 N 39.4 Found C 33.9 H 4.27 N 39.1.- IR (KBr): 3429; 3044; 2956; 1618; 1583; 1559; 1473; 1433; 1401; 1383; 1371; 1353; 1341; 1173; 1150; 1115; 1075; 1008; 941; 903; 715; 662 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 268 (3.69), 342 (4.21), 493 nm (2.06).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 4.34 (s; 3H, N-CH₃), 2.40 (s; 3H, syd-CH₃).- MS (+ FAB/DMSO/glycerol): m/z = 143 (14%, [M + H]⁺), 129 (4), 114 (7), 93 (100%, [gly - H]⁺), 73 (6).

3-Hexyl-4-methyl-N-nitroso-5-sydnone imine (2b)

Orange crystals (rosettes) (isopropanol/petrolether), mp. 37°C. Yield 78%.- C₉H₁₆N₄O₂ (212.3) Calcd. C 50.9 H 7.59 N 26.4 Found C 50.8 H

7.78 N 26.6.- IR (KBr): 3432; 2950; 2924; 2858; 1609; 1577; 1463; 1401; 1365; 1345; 1160; 1111; 1071; 932; 713 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 268 (3.59), 344 (4.21), 494 nm (2.09).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 4.68 (t; J = 7.3 Hz, 2H, N-CH₂), 2.42 (s; 3H, syd-CH₃), 1.95 (tt; J = 7/7 Hz, 2H, N-CH₂-CH₂), 1.40-1.29 (m; 6H, (CH₂)₃-CH₃), 0.87 (t; J = 7 Hz, 3H, CH₃).- MS (+ FAB/DMSO/glycerol): m/z = 213 (100%, [M + H]⁺), 212 (8), 184 (35), 183 (29), 170 (22), 149 (13), 126 (15), 85 (12), 78 (18).

3-Benzyl-4-methyl-N-nitroso-5-sydnone imine (3b)

Orange crystals (methanol), mp. 103°C (Lit.⁴⁾; 105-106°C). Yield 80%.- C₁₀H₁₀N₄O₂ (218.2) Calcd. C 55.0 H 4.62 N 25.7 Found C 54.8 H 4.57 N 25.6.- IR (KBr): 2988; 2089; 1785; 1621; 1587; 1497; 1443; 1403; 1355; 1313; 1227; 1172; 1134; 1031; 1016; 961; 924; 905; 835; 715; 696; 652; 627 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 267 (3.58), 347 (4.20), 498 nm (2.07).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.53-7.46 (m; 5H arom.), 6.01 (s; 2H, N-CH₂), 2.39 (s; 3H, syd-CH₃).- MS (+ FAB/DMSO/glycerol): m/z = 219 (1%, [M + H]⁺), 149 (16), 171 (4), 93 (100), 91 (16).

4-Methyl-N-nitroso-3-(2-phenylethyl)-5-sydnone imine (4b)

Orange needles (methanol/isopropanol), mp. 101°C. Yield 78%.- C₁₁H₁₂N₄O₂ (232.2) Calcd. C 56.9 H 5.21 N 24.1 Found C 56.9 H 5.17 N 24.1.- IR (KBr): 3429; 2992; 2936; 2180; 1606; 1573; 1492; 1452; 1406; 1372; 1315; 1162; 1131; 1081; 1004; 941; 900; 847; 757; 736; 702; 676; 639 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 267 (3.72), 346 (4.25), 498 nm (2.11).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.36-7.25 (m; 5H arom.), 4.97 (t; J = 7 Hz, 2H, N-CH₂), 3.30 (t; J = 7 Hz, 2H, Ph-CH₂), 2.33 (s; 3H, syd-CH₃).- MS (+ FAB/DMSO/glycerol): m/z = 233 (49%, [M + H]⁺), 203 (14), 149 (20), 105 (98), 93 (100), 91 (12), 78 (14).

N-Cyano-4-methyl-3-(2-phenylethyl)-5-sydnone imine (4d)

Pink small crystals (methanol), mp. 117°C. Yield 35%.- C₁₂H₁₂N₄O (228.3) Calcd. C 63.1 H 5.30 N 24.5 Found C 63.0 H 5.13 N 24.4.- IR (KBr): 2994; 2960; 2167; 1633; 1496; 1466; 1454; 1385; 1367; 1336; 1253; 1186; 1155; 1126; 1081; 1052; 982; 914; 843; 763; 740; 700; 657; 627 cm⁻¹.- UV (CH₃OH): λ max (log ε) = 208 (4.30), 335 nm (4.01).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.34-7.24 (m; 5H arom.), 4.77 (t; J = 7.1 Hz, 2H, N-CH₂), 3.20 (t; J = 7.1 Hz, 2H, Ph-CH₂), 2.08 (s; 3H, syd-CH₃).- ¹³C-NMR/75.47 MHz ([D₆]DMSO): δ (ppm) = 167.9 (s; syd-C-5), 135.9 (s; Ph-C-1''), 128.8 (s; Ph-C-3' and -C-5''), 128.4 (s; Ph-C-2' and -C-6''), 127.0 (s; Ph-C-4''), 115.2 (s; -CN), 112.6 (s; syd-C-4), 52.0 (s; N-CH₂), 33.1 (s; Ph-CH₂), 6.3 (s; -CH₃).- MS (110°C): m/z = 228

(5%, [M]⁺), 105 (100), 104 (29), 103 (15), 91 (80), 81 (12), 80 (15), 79 (21), 77 (25), 65 (16), 51 (16), 41 (12), 39 (14).

4-Methyl-N-nitroso-3-(3-phenylpropyl)-5-sydnone imine (5b)

Orange-red needles (ethanol), mp. 87°C. Yield 80%. C₁₂H₁₄N₄O₂ (246.3) Calcd. C 58.5 H 5.73 N 22.7 Found C 58.2 H 5.66 N 22.5. IR (KBr): 3437; 2995; 2958; 1578; 1479; 1452; 1407; 1348; 1329; 1221; 1177; 1132; 1107; 1011; 975; 944; 902; 779; 746; 701 cm⁻¹. UV (CH₃CN): λ max (log ε) = 210 (3.67), 267 (3.57), 345 (4.25), 496 (2.10). ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.33-7.08 (m; 5H arom.), 4.70 (t; J = 7 Hz, 2H, N-CH₂), 2.76 (t; J = 7 Hz, 2H, Ph-CH₂), 2.40 (s; 3H, syd-CH₃), 2.28 (tt; J = 7/7 Hz, 2H, N-CH₂-CH₂). MS (+ FAB/DMSO/glycerol): m/z = 247 (15%, [M + H]⁺), 246 (6), 218 (5), 217 (9), 186 (12), 119 (9), 92 (10), 91 (100), 81 (16). MS (130°C): m/z = 218 (8%, [M - N₂]⁺), 119 (15), 92 (8), 91 (100).

4-Methyl-3-(4-phenylbutyl)-5-sydnone imine hydrochloride (6a)

Powder (ethanol/ether), mp. 146°C. Yield 72%. C₁₃H₁₈ClN₃O (267.8) Calcd. C 58.3 H 6.78 N 15.7 Found C 58.0 H 6.77 N 15.7. IR (KBr): 3006; 2624; 2087; 1669; 1598; 1501; 1469; 1450; 1399; 1345; 1257; 1218; 1153; 1092; 939; 904; 803; 757; 729; 704 cm⁻¹. UV (CH₃OH): λ max (log ε) = 206 (4.11), 300 nm (3.93). ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 9.70 (s; 2H, =NH₂⁺, D₂O exchange), 7.31-7.16 (m; 5H arom.), 4.59 (t; J = 7.1 Hz, 2H, N-CH₂), 2.63 (t; J = 7.6 Hz, 2H, Ph-CH₂), 2.35 (s; 3H, syd-CH₃), 1.89 (m; 2H, N-CH₂-CH₂), 1.66 (m; 2H, Ph-CH₂-CH₂). MS (50°C): m/z = 231 (6%, [M]⁺), 133 (13), 91 (100), 36 (12).

4-Methyl-N-nitroso-3-(4-phenylbutyl)-5-sydnone imine (6b)

Carmine platelets (methanol/isopropanol), mp. 58°C. Yield 82%. C₁₃H₁₆N₄O₂ (260.3) Calcd. C 59.9 H 6.19 N 21.5 Found C 59.5 H 6.17 N 21.5. IR (KBr): 3439; 3019; 2927; 1671; 1610; 1577; 1493; 1465; 1451; 1382; 1346; 1163; 1134; 1087; 939; 903; 795; 750; 700 cm⁻¹. UV (CH₃CN): λ max (log ε) = 209 (3.53), 267 (3.38), 344 (4.17), 495 nm (2.09). ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.31-7.16 (m; 5H arom.), 4.71 (t; J = 7.2 Hz, 2H, N-CH₂), 2.65 (t; J = 7.4 Hz, 2H, Ph-CH₂), 2.40 (s; 3H, syd-CH₃), 1.97 (tt; J = 7.5/7.5 Hz, 2H, N-CH₂-CH₂), 1.71 (tt; J = 7.5/7.5 Hz, 2H, Ph-CH₂-CH₂). MS (+ FAB/DMSO/glycerol): m/z = 261 (2%, [M + H]⁺), 241 (6), 149 (25), 117 (7), 93 (100), 91 (7), 78 (5).

DL-erythro-[2-[4-Methyl-5-nitrosoimino-sydnone-3-yl]-phenyl]-propanol (7b)

Citrous platelets (methanol), mp. 155°C. Yield 48%. C₁₂H₁₄N₄O₃ (262.3) Calcd. C 54.9 H 5.38 N 21.4 Found C 54.8 H 5.42 N 21.4. IR (KBr): 3267; 3021; 2972; 2941; 2872; 1699; 1675; 1587; 1486; 1449; 1405; 1391; 1376; 1363; 1327; 1314; 1250; 1231; 1170; 1140; 1067; 1046; 1014; 998; 946; 903; 850; 761; 725; 702; 682; 673; 652; 622 cm⁻¹. UV (CH₃CN): λ max (log ε) = 266 (3.67), 348 (4.22), 498 nm (2.12). ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.36 (m; 5H arom.), 6.23 (d; J = 4.8 Hz, 1H, OH, D₂O exchange), 5.34 (m; 1H, N-CH(CH₃)), 5.12 (dd; after D₂O exchange d; J = 4.5 Hz, 1H, Ph-CH(OH)), 2.40 (s; 3H, syd-CH₃), 1.54 (d; J = 6.8 Hz, 3H, N-CH(CH₃)). MS (+ FAB/DMSO/glycerol): m/z = 263 (63%, [M + H]⁺), 262 (41), 234 (12), 233 (43), 201 (14), 135 (100), 129 (40), 128 (37), 118 (12), 117 (46), 107 (27), 105 (30), 96 (29), 91 (32), 83 (65), 79 (38), 77 (34).

3-Hexyl-4-isopropyl-N-nitroso-5-sydnone imine (8b)

The intermediate sydnone imine cannot be isolated (very hygroscopic) and is nitrosated in the two phase system water/ether: Carmine needles (isopropanol/ether), mp. 80°C. Yield ~ 45%. C₁₁H₂₀N₄O₂ (240.3) Calcd.

C 55.0 H 8.38 N 23.3 Found C 54.7 H 8.47 N 23.4. IR (KBr): 3433; 3009; 2959; 2944; 2926; 2855; 1592; 1480; 1456; 1410; 1401; 1366; 1345; 1250; 1212; 1171; 1159; 1132; 1110; 1081; 1054; 1021; 1006; 963; 941; 893; 874; 767; 743; 729; 659; 626 cm⁻¹. UV (CH₃CN): λ max (log ε) = 266 (3.78), 354 (4.24), 504 nm (2.22). ¹H-NMR/300 MHz (CDCl₃): δ (ppm) = 4.53 (t; J = 7.4 Hz, 2H, N-CH₂), 3.19 (sept; J = 7 Hz, 1H, syd-CH(CH₃)₂), 2.06 (tt; J = 7.5/7.5 Hz, 2H, N-CH₂-CH₂), 1.43-1.35 (m; 12 H, syd-CH(CH₃)₂ and (CH₂)₃-CH₃), 0.92 (t; J = 7.0 Hz, 3H, CH₃). MS (+ FAB/DMSO/m-NO₂-benzyl alcohol): m/z = 241 (100%, [M + H]⁺), 240 (40), 212 (15), 211 (28), 210 (29), 179 (21), 154 (32), 137 (22), 85 (12), 83 (22), 77 (10).

4-Isopropyl-N-nitroso-3-(2-phenylethyl)-5-sydnone imine (9b)

Orange-yellow crystals (chloroform/ether), mp. 117°C. Yield 56%. C₁₃H₁₆N₄O₂ (260.3) Calcd. C 60.0 H 6.20 N 21.5 Found C 60.0 H 6.26 N 21.7. IR (KBr): 3414; 2968; 2934; 1592; 1551; 1490; 1476; 1456; 1444; 1401; 1354; 1334; 1289; 1214; 1175; 1161; 1140; 1110; 1088; 1017; 979; 957; 947; 757; 705; 659 cm⁻¹. UV (CH₃CN): λ max (log ε) = 266 (3.80), 356 (4.24), 508 nm (2.24). ¹H-NMR/300 MHz (CDCl₃): δ (ppm) = 7.34 (m; 3H arom., H-3'', H-4'', H-5''), 7.18 (dd; J = 8/1.5 Hz, 2H arom., H-2'', H-6''), 4.79 (t; J = 7.1 Hz, 2H, N-CH₂), 3.39 (t; J = 7.1 Hz, 2H, Ph-CH₂), 2.98 (sept; J = 7 Hz, 1H, CH(CH₃)₂), 1.22 (d; J = 7 Hz, 6H, J = 7 Hz, (CH₃)₂). MS (+ FAB/DMSO/glycerol): m/z = 261 (11%, [M + H]⁺), 260 (10), 231 (5), 105 (100), 91 (11), 77 (6).

4-Ethyl-N-nitroso-3-(2-phenylethyl)-5-sydnone imine (10b)

Orange crystals (ethanol/ether), mp. 92°C. Yield 78%. C₁₂H₁₄N₄O₂ (246.3) Calcd. C 58.5 H 5.73 N 22.7 Found C 58.4 H 5.77 N 22.7. IR (KBr): 3428; 2996; 2971; 2937; 1603; 1565; 1495; 1456; 1406; 1372; 1346; 1296; 1158; 1127; 1098; 1057; 964; 893; 840; 782; 756; 726; 700; 659; 635 cm⁻¹. UV (CH₃CN): λ max (log ε) = 267 (3.69), 347 (4.23), 499 nm (2.10). ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.36-7.25 (m; 5H arom.), 4.99 (t; J = 7.1 Hz, 2H, N-CH₂), 3.32 (t; J = 7.2 Hz, 2H, Ph-CH₂), 2.77 (q; J = 7.5 Hz, 2H, syd-CH₂), 1.05 (t; J = 7.3 Hz, 3H, CH₃). MS (+ FAB/DMSO/glycerol): m/z = 247 (14%, [M + H]⁺), 246 (12), 217 (7), 106 (9), 105 (100), 91 (15), 78 (6).

DL-erythro-[2-[4-Ethyl-5-nitrosoimino-sydnone-3-yl]-phenyl]-propanol (11b)

Yellow needles (methanol/isopropanol), mp. 126°C. Yield 37%. C₁₃H₁₆N₄O₃ (276.3) Calcd. C 56.5 H 5.83 N 20.3 Found C 56.2 H 5.77 N 20.2. IR (KBr): 3404; 3239; 2974; 2920; 1605; 1568; 1494; 1452; 1428; 1380; 1371; 1329; 1295; 1236; 1192; 1175; 1118; 1104; 1053; 1031; 1000; 970; 898; 874; 846; 827; 757; 701; 678; 635 cm⁻¹. UV (CH₃CN): λ max (log ε) = 209 (3.57), 267 (3.55), 349 (4.20), 499 nm (2.10). ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.37-7.34 (m; 5H arom.), 6.29 (d; J = 4.7 Hz, 1H, -OH, D₂O exchange), 5.35 (m; 1H, N-CH(CH₃)), 5.07 (dd; J = 5/5 Hz, 1H, Ph-CH(OH)), 2.81 (q; J = 7.4 Hz, 2H, syd-CH₂), 1.59 (d; J = 6.8 Hz, 3H, N-CH(CH₃)), 1.05 (t; J = 7.4 Hz, 3H, CH₂-CH₃). MS (+ FAB/DMSO/glycerol): m/z = 277 (46%, [M + H]⁺), 276 (31), 248 (12), 247 (32), 190 (31), 135 (100), 117 (57), 105 (42), 97 (44), 91 (45), 79 (47), 77 (42).

4-Isobutyl-N-nitroso-3-(2-phenylethyl)-5-sydnone imine (12b)

Yellow crystals (chloroform/ether), mp. 87°C. Yield 62%. C₁₄H₁₈N₄O₂ (274.3) Calcd. C 61.3 H 6.61 N 20.4 Found C 61.2 H 6.67 N 20.3. IR (KBr): 3430; 3057; 3016; 2955; 2921; 2867; 1596; 1561; 1493; 1454; 1430; 1400; 1352; 1337; 1293; 1245; 1231; 1204; 1153; 1139; 1119; 1098; 1035; 1021; 960; 950; 923; 897; 879; 860; 758; 746; 699; 666; 639 cm⁻¹. UV (CH₃CN): λ max (log ε) = 206 (3.87), 268 (3.67), 352 (4.21), 504 nm

(2.16).- $^1\text{H-NMR}$ /300 MHz (CDCl_3): δ (ppm) = 7.34 (m; 3H arom., H-3'', H-4'', H-5''), 7.18 (d; 2H arom., H-2'', H-6''), 4.74 (t; J = 7 Hz, 2H, N-CH₂), 3.42 (t; J = 7 Hz, 2H, Ph-CH₂), 2.48 (d; J = 7.3 Hz, 2H, syd-CH₂), 1.95 (m; 1H, CH-(CH₃)₂), 0.87 (d; J = 6.6 Hz, 6H, (CH₃)₂)-MS (+ FAB/DMSO/glycerol): m/z = 275 (11%, [M + H]⁺), 274 (10), 123 (15), 106 (9), 105 (100), 91 (9), 78 (6).

4-Cyclohexyl-N-nitroso-3-(2-phenylethyl)-5-sydnone imine (**13b**)

Carmine crystals (methanol), mp. 117°C. Yield 53%. - $\text{C}_{16}\text{H}_{20}\text{N}_4\text{O}_2$ (300.4) Calcd. C 64.0 H 6.71 N 18.7 Found C 63.7 H 6.76 N 18.6.- IR (KBr): 3428; 3051; 3019; 2980; 2926; 2851; 1587; 1494; 1467; 1447; 1401; 1365; 1355; 1340; 1268; 1233; 1153; 1105; 1051; 994; 967; 946; 890; 880; 813; 763; 740; 700; 669; 644 cm^{-1} .- UV (CH_3CN): λ max (log ϵ) = 268 (3.83), 358 (4.22), 509 nm (2.23).- $^1\text{H-NMR}$ /300 MHz ($[\text{D}_6]\text{DMSO}$): δ (ppm) = 7.30 (m; 5H arom.), 5.05 (t; J = 6.8 Hz, 2H, N-CH₂), 3.29 (t; J = 6.8 Hz, 2H, Ph-CH₂), 2.83 (m; 1H, cyclohexyl-H-1'' ax), 1.70-1.03 (m; 10 H, cyclohexyl-H).- MS (+ FAB/DMSO/glycerol): m/z = 301 (13%, [M + H]⁺), 300 (8), 149 (12), 106 (9), 105 (100), 91 (7), 76 (8).

4-Benzyl-3-(2-phenylethyl)-5-sydnone imine hydrochloride (**14a**)

Crystals (ethanol/acetone), mp. 161°C (decompn.). Yield 43%. - $\text{C}_{17}\text{H}_{18}\text{ClN}_3\text{O} \cdot 1/4 \text{H}_2\text{O}$ (320.3) Calcd. C 63.8 H 5.82 N 13.1 Found C 64.1 H 5.74 N 13.2.- IR (KBr): 3421; 3274; 3230; 3108; 2963; 1590; 1560; 1490; 1430; 1388; 1362; 1229; 1211; 1189; 1062; 1027; 1005; 930; 912; 895; 845; 770; 716; 690 cm^{-1} .- UV (CH_3OH): λ max (log ϵ) = 206 (4.33), 303 nm (3.92).- $^1\text{H-NMR}$ /300 MHz ($[\text{D}_6]\text{DMSO}$): δ (ppm) = 10.07 (s; 2H, =NH₂⁺, D₂O exchange), 7.41-7.07 (m; 10 H arom.), 4.79 (t; J = 7.1 Hz, 2H, N-CH₂), 4.39 (s; 2H, syd-CH₂), 2.96 (t; J = 7.1 Hz, 2H, N-CH₂-CH₂).- MS (110°C): m/z = 279 (3%, [M]⁺), 105 (93), 104 (32), 103 (14), 91 (100), 79 (13), 77 (17), 65 (16), 36 (16).

4-Benzyl-N-nitroso-3-(2-phenylethyl)-5-sydnone imine (**14b**)

Orange powder (methanol), mp. 116°C. Yield 47%. - $\text{C}_{17}\text{H}_{16}\text{N}_4\text{O}_2$ (308.3) Calcd. C 66.2 H 5.23 N 18.2 Found C 66.1 H 5.18 N 18.2.- IR (KBr): 3418; 3057; 3022; 2998; 2952; 2934; 1954; 1885; 1603; 1582; 1570; 1493; 1462; 1452; 1429; 1403; 1375; 1349; 1342; 1334; 1314; 1287; 1276; 1190; 1157; 1149; 1107; 1080; 1028; 1002; 985; 953; 922; 901; 886; 844; 805; 779; 757; 737; 727; 698; 686; 649; 617 cm^{-1} .- UV (CH_3CN): λ max (log ϵ) = 268 (3.85), 348 (4.22), 503 nm (2.12).- $^1\text{H-NMR}$ /300 MHz ($[\text{D}_6]\text{DMSO}$): δ (ppm) = 7.36-7.27 (m; 8H arom.), 7.13 (d; J = 6.2 Hz, 2H, syd-CH₂-Ph-H-2'' and -H-6''), 4.97 (t; J = 7.3 Hz, 2H, N-CH₂), 4.28 (s; 2H, syd-CH₂), 3.10 (t; J = 7.3 Hz, 2H, Ph-CH₂-CH₂).- MS (+ FAB/DMSO/glycerol): m/z = 309 (3%, [M + H]⁺), 157 (8), 105 (100), 103 (11), 91 (27), 79 (19), 77 (16).

4-Benzyl-N-nitroso-3-(3-phenylpropyl)-5-sydnone imine (**15b**)

Orange needles (methanol/ether), mp. 78°C. Yield 41%. - $\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_2$ (322.4) Calcd. C 67.1 H 5.63 N 17.4 Found C 67.1 H 5.52 N 17.5.- IR (KBr): 3436; 3020; 2992; 2953; 1571; 1492; 1476; 1450; 1399; 1377; 1354; 1323; 1277; 1222; 1162; 1102; 1080; 1041; 998; 923; 906; 775; 726; 695 cm^{-1} .- UV (CH_3CN): λ max (log ϵ) = 269 (3.74), 346 (4.21), 500 nm (2.10).- $^1\text{H-NMR}$ /300 MHz (CDCl_3): δ (ppm) = 7.36-7.04 (m; 10 H arom.), 4.30 (t; J = 7.6 Hz, 2H, N-CH₂), 4.17 (s; 2H, syd-CH₂), 2.71 (t; J = 7.1 Hz, 2H, Ph-CH₂-CH₂), 2.22 (tt; J = 7.4/7.1 Hz, 2H, N-CH₂-CH₂).- MS (+ FAB/DMSO/*m*-NO₂-benzyl alcohol): m/z = 323 (17%, [M + H]⁺), 322 (9), 294 (6), 293 (7), 171 (33), 119 (11), 103 (8), 91 (100), 76 (6).

3,4-Bis-(2-phenylethyl)-5-sydnone imine hydrochloride (**16a**)

Crystals (ethanol), mp. 155°C. Yield 32%. - $\text{C}_{18}\text{H}_{20}\text{ClN}_3\text{O}$ (329.8) Calcd. C 65.5 H 6.11 N 12.7 Found C 65.5 H 6.18 N 12.6.- IR (KBr): 2964; 2702; 2612; 1673; 1598; 1495; 1450; 1420; 1403; 1361; 1307; 1280; 1189; 1162; 1084; 1062; 1029; 982; 958; 949; 920; 889; 841; 769; 760; 749; 730; 706 cm^{-1} .- UV (CH_3OH): λ max (log ϵ) = 207 (4.28), 304 nm (3.92).- $^1\text{H-NMR}$ /300 MHz ($[\text{D}_6]\text{DMSO}$): δ (ppm) = 9.94 (s; 2H, =NH₂⁺, D₂O exchange), 7.35-7.20 (m; 10 H arom.), 4.77 (t; J = 7 Hz, 2H, N-CH₂), 3.16 (t; J = 7 Hz, 2H, N-CH₂-CH₂), 3.06 (t; J = 7 Hz, 2H, syd-CH₂), 2.77 (t; J = 7 Hz, 2H, syd-CH₂-CH₂).- MS (60°C): m/z = 293 (2%, [M]⁺), 181 (18), 105 (52), 104 (50), 91 (100), 77 (10), 68 (12), 65 (11), 44 (10), 42 (10).

N-Nitroso-3,4-bis-(2-phenylethyl)-5-sydnone imine (**16b**)

Bright red, hygroscopic crystals (ethanol), mp. 95°C. Yield 45%. - $\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_2$ (322.4) Calcd. C 67.1 H 5.63 N 17.4 Found C 67.0 H 5.57 N 17.4.- IR (KBr): 3421; 3020; 2927; 1596; 1567; 1494; 1452; 1404; 1365; 1339; 1222; 1166; 1116; 1076; 1055; 968; 943; 924; 753; 702; 645 cm^{-1} .- UV (CH_3CN): λ max (log ϵ) = 268 (3.78), 346 (4.22), 500 nm (2.07).- $^1\text{H-NMR}$ /300 MHz (CDCl_3): δ (ppm) = 7.33-7.01 (m; 10 H arom.), 3.98 (t; J = 7.4 Hz, 2H, N-CH₂), 3.06 (t; J = 7.4 Hz, 2H, N-CH₂-CH₂), 2.89 (m; 4H, syd-(CH₂)₂).- MS (+ FAB/DMSO/*m*-NO₂-benzyl alcohol): m/z = 323 (11%, [M + H]⁺), 322 (8), 293 (5), 171 (13), 106 (9), 105 (100), 91 (23), 79 (7), 77 (6).

4-Methyl-3-(*p*-tolyl)-5-sydnone imine hydrochloride (**17a**)

Needles (ethanol), mp. 191°C (decompn.). Yield 31%. - $\text{C}_{10}\text{H}_{12}\text{ClN}_3\text{O}$ (225.7) Calcd. C 53.2 H 5.36 N 18.6 Found C 53.5 H 5.37 N 18.8.- IR (KBr): 3124; 3029; 2954; 1954; 1671; 1594; 1488; 1450; 1411; 1399; 1317; 1295; 1238; 1213; 1191; 1130; 1043; 1011; 994; 918; 831; 802; 779; 711; 648 cm^{-1} .- UV (CH_3OH): λ max (log ϵ) = 206 (4.04), 312 nm (3.97).- $^1\text{H-NMR}$ /300 MHz ($[\text{D}_6]\text{DMSO}$): δ (ppm) = 10.06 (s; 2H, =NH₂⁺, D₂O exchange), 7.72 (d; J = 8.4 Hz, 2H arom., Ph-H-2', Ph-H-6'), 7.57 (d; J = 8.4 Hz, 2H arom., Ph-H-3', Ph-H-6'), 2.46 (s; 3H, syd-CH₃), 2.29 (s; 3H, Ph-CH₃).- MS (140°C): m/z = 189 (16%, [M]⁺), 133 (12), 132 (100), 91 (83), 65 (31), 38 (10), 36 (32).

4-Methyl-N-nitroso-3-(*p*-tolyl)-5-sydnone imine (**17b**)

Purple powder (methanol), mp. 131°C. Yield 43%. - $\text{C}_{10}\text{H}_{10}\text{N}_4\text{O}_2$ (218.2) Calcd. C 55.0 H 4.62 N 25.7 Found C 55.0 H 4.56 N 25.9.- IR (KBr): 3033; 2920; 1673; 1606; 1584; 1505; 1456; 1378; 1359; 1312; 1296; 1240; 1208; 1156; 1114; 1069; 1040; 1014; 955; 934; 843; 830; 800; 715; 682; 662 cm^{-1} .- UV (CH_3CN): λ max (log ϵ) = 272 (3.90), 354 (4.25), 507 nm (2.15).- $^1\text{H-NMR}$ /300 MHz ($[\text{D}_6]\text{DMSO}$): δ (ppm) = 7.81 (d; J = 8.3 Hz, 2H arom., H-2', H-6'), 7.60 (d; J = 8.3 Hz, 2H arom., H-3', H-5'), 2.47 (s; 3H, syd-CH₃), 2.32 (s; 3H, Ph-CH₃).- MS (+ FAB/DMSO/glycerol): m/z = 219 (66%, [M + H]⁺), 218 (12), 190 (64), 189 (28), 158 (24), 132 (100), 107 (26), 91 (71), 78 (27), 74 (25), 64 (20).- MS (100°C): m/z = 190 (9%, [M - N₂]⁺), 158 (10), 132 (88), 91 (100), 89 (10), 65 (36), 63 (12), 51 (10), 39 (21).

3-Methyl-4-phenyl-6-sydnone imine monohydrochloride (**18a**)

Crystals (isopropanol/ether), mp. 153°C. Yield 70%. - $\text{C}_9\text{H}_9\text{ClN}_3\text{O}$ (211.7) Calcd. C 51.1 H 4.76 N 19.8 Found C 51.1 H 4.80 N 19.7.- IR (KBr): 3327; 3182; 3115; 2994; 1903; 1660; 1612; 1575; 1519; 1482; 1450; 1424; 1374; 1327; 1273; 1164; 1128; 1103; 1083; 1009; 977; 948; 798; 757; 722; 696; 645; 617 cm^{-1} .- UV (CH_3OH): λ max (log ϵ) = 205 (3.98), 242 (3.69), 307 nm (3.73).- $^1\text{H-NMR}$ /300 MHz ($[\text{D}_6]\text{DMSO}$): δ

(ppm) = 9.78 (s; 2H, =NH₂⁺, D₂O exchange), 7.65 (bs; 5H arom.), 4.19 (s; 3H, N-CH₃).- MS (140°C): m/z = 175 (14%, [M]⁺), 144 (13), 143 (22), 129 (22), 120 (25), 118 (54), 116 (100), 91 (12), 89 (20), 77 (41), 69 (19), 51 (28), 43 (24), 42 (28), 30 (16).

3-Methyl-N-nitroso-4-phenyl-5-sydnone imine (**18b**)

Red crystals (ethanol/ether), mp. 106°C. Yield 58%.- C₉H₈N₄O₂ (204.2) Calcd. C 52.9 H 3.95 N 27.4 Found C 53.2 H 3.80 N 27.3.- IR (KBr): 3435; 3047; 3018; 2950; 1680; 1618; 1594; 1499; 1470; 1443; 1422; 1379; 1358; 1317; 1189; 1145; 1084; 1066; 1030; 1007; 953; 869; 853; 775; 733; 696; 631 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 291 (3.96), 354 (4.12), 506 nm (2.14).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.69-7.55 (m; 5H arom.), 4.33 (s; 3H, CH₃).- MS (+ FAB/DMSO/glycerol): m/z = 205 (20%, [M + H]⁺), 204 (10), 176 (13), 175 (14), 174 (17), 144 (9), 118 (100), 105 (13), 91 (10), 77 (27).- MS (80°C): m/z = 176 (40%, [M - N₂]⁺), 118 (100), 103 (20), 77 (51), 76 (11), 69 (10), 55 (19), 51 (18), 50 (10), 44 (14), 39 (11).

3-Ethyl-N-nitroso-4-phenyl-5-sydnone imine (**19b**)

Orange crystals (ethanol/ether), mp. 114°C. Yield 63%.- C₁₀H₁₀N₄O₂ (218.2) Calcd. C 55.0 H 4.62 N 25.7 Found C 55.0 H 4.50 N 25.7.- IR (KBr): 3417; 3045; 2982; 1607; 1579; 1570; 1495; 1457; 1381; 1339; 1240; 1173; 1126; 1109; 1093; 1082; 1021; 997; 992; 938; 893; 770; 739; 707; 696; 674; 655; 618 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 289 (3.88), 352 (4.14), 505 nm (2.15).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.67-7.57 (m; 5H arom.), 4.69 (q; J = 7.2 Hz, 2H, CH₂), 1.48 (t; J = 7.2 Hz, 3H, CH₃).- MS (70°C): 190 (47%, [M - N₂]⁺), 132 (84), 104 (100), 91 (10), 77 (69), 63 (27), 51 (46), 36 (61).- MS (+ FAB/DMSO/glycerol): m/z = 219 (15%, [M + H]⁺), 190 (9), 149 (32), 117 (9), 104 (8), 93 (100).

3-Hexyl-N-nitroso-4-phenyl-5-sydnone imine (**20b**)

Dark-red crystals (methanol/ether), mp. 76.5°C. Yield 51%.- C₁₄H₁₈N₄O₂ (274.3) Calcd. C 61.3 H 6.61 N 20.4 Found C 61.3 H 6.61 N 20.6.- IR (KBr): 2952; 2925; 2858; 1609; 1591; 1501; 1449; 1395; 1348; 1215; 1186; 1106; 1074; 1056; 1026; 989; 944; 754; 696; 664 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 285 (3.94), 352 (4.16), 506 nm (2.15).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.65-7.57 (m; 5H arom.), 4.65 (t; J = 7.2 Hz, 2H, N-CH₂), 1.81 (tt; J = 7.2/7.2 Hz, 2H, N-CH₂-CH₂), 1.30-1.17 (m; 6H, (CH₂)₃-CH₃), 0.80 (t; J = 6.6 Hz, 3H, CH₃).- MS (+ FAB/DMSO/glycerol): m/z = 275 (39%, [M + H]⁺), 274 (33), 246 (19), 245 (29), 244 (17), 213 (34), 188 (29), 185 (12), 131 (11), 118 (11), 117 (12), 105 (36), 104 (100), 103 (10), 91 (13), 89 (15), 85 (13), 78 (22), 77 (24).

3-Allyl-4-phenyl-5-sydnone imine hydrochloride (**21a**)

Crystals (ethanol/ether), mp. 110.5°C. Yield 80%.- C₁₁H₁₂ClN₃O (237.7) Calcd. C 55.6 H 5.09 N 17.7 Found C 55.7 H 5.08 N 17.7.- IR (KBr): 3180; 2934; 2860; 1666; 1636; 1595; 1575; 1503; 1492; 1448; 1387; 1340; 1305; 1278; 1256; 1232; 1190; 1156; 1089; 1077; 1004; 951; 901; 848; 817; 797; 768; 747; 710; 687; 628 cm⁻¹.- UV (CH₃OH): λ max (log ε) = 205 (4.02), 243 (3.79), 309 nm (3.90).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 9.82 (s; 2H, =NH₂⁺, D₂O exchange), 7.64 (m; 5H arom.), 5.90 (m; 1H, CH=), 5.36 (d; J = 17.1 Hz, 1H, *cis*=CH₂), 5.33 (d; J = 10.3 Hz, 1H, *trans*=CH₂), 5.24 (d; J = 5.8 Hz, 2H, N-CH₂).- MS (100°C): m/z = 201 (38%, [M]⁺), 145 (11), 144 (100), 116 (35), 104 (30), 89 (15), 77 (36), 76 (15), 63 (20), 51 (24), 50 (10).

3-Allyl-N-nitroso-4-phenyl-5-sydnone imine (**21b**)

Orange-red needles (ethanol), mp. 104°C. Yield 71%.- C₁₁H₁₀N₄O₂ (230.2) Calcd. C 57.4 H 4.37 N 24.3 Found C 57.4 H 4.24 N 24.3.- IR

(KBr): 3039; 1719; 1605; 1578; 1566; 1495; 1448; 1433; 1421; 1384; 1366; 1342; 1194; 1173; 1117; 1096; 1071; 1019; 990; 982; 932; 920; 887; 775; 757; 732; 706; 686; 652; 607 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 289 (3.92), 355 (4.15), 509 nm (2.16).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.66-7.55 (m; 5H arom.), 6.01 (m; 1H, CH=), 5.40 (m; 4H, CH₂-CH=CH₂).- MS (+ FAB/DMSO/glycerol): m/z = 231 (79%, [M + H]⁺), 230 (14), 202 (59), 201 (45), 200 (9), 169 (26), 157 (12), 144 (54), 130 (16), 129 (22), 117 (14), 115 (17), 105 (78), 104 (41), 93 (100%, [gly + H]⁺), 91 (28), 78 (45), 76 (31).

4-(4-Chlorophenyl)-3-hexyl-N-nitroso-5-sydnone imine (**22b**)

Carmine needles (ethanol), mp. 87°C. Yield 54%.- C₁₄H₁₇ClN₃O₂ (308.8) Calcd. C 54.5 H 5.55 N 18.2 Found C 54.3 H 5.54 N 18.3.- IR (KBr): 3437; 3042; 2954; 2924; 2856; 1619; 1608; 1588; 1577; 1562; 1497; 1463; 1386; 1342; 1242; 1188; 1105; 1088; 1057; 1018; 999; 966; 954; 943; 892; 834; 739; 731; 711; 653 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 220 (4.08), 295 (3.99), 352 (4.17), 507 nm (2.15).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.68 (s; 4H arom.), 4.64 (t; J = 7.2 Hz, 2H, N-CH₂), 1.81 (tt; J = 7.2/7.2 Hz, 2H, N-CH₂-CH₂), 1.33-1.17 (m; 6H, (CH₂)₃-CH₃), 0.81 (t; J = 6.8 Hz, 3H, CH₃).- MS (+ FAB/DMSO/glycerol): m/z = 311 (28%, [M + H]⁺[³⁷Cl]), 310 (28%, [M]⁺[³⁷Cl]), 309 (100%, [M + H]⁺[³⁵Cl]), 308 (100%, [M]⁺[³⁵Cl]), 280 (34), 279 (41), 278 (17), 222 (30), 154 (91), 138 (71), 136 (59), 91 (12), 89 (47), 77 (44).

4-Phenyl-3-(2-phenylethyl)-5-sydnone imine hydrochloride (**23a**)

Crystals (ethanol/ether), mp. 142°C. Yield 55%.- C₁₆H₁₆ClN₃O (301.8) Calcd. C 63.7 H 5.34 N 13.9 Found C 63.8 H 5.25 N 13.9.- IR (KBr): 3043; 3020; 2943; 1665; 1600; 1515; 1494; 1476; 1462; 1450; 1386; 1355; 1330; 1257; 1172; 1153; 1091; 1081; 1040; 1026; 1004; 947; 861; 840; 798; 769; 748; 701; 659; 620 cm⁻¹.- UV (CH₃OH): λ max (log ε) = 208 (4.17), 240 (3.83), 310 nm (3.93).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 9.81 (s; 2H, =NH₂⁺, D₂O exchange), 7.65-7.59 (m; 5H arom., syd-Ph), 7.27 (m; 3H arom., CH₂-Ph-H-3'', H-4'', H-5''), 7.10 (''d''); 2H arom., CH₂-Ph-H-2'' and H-6''), 4.80 (t; J = 7 Hz, 2H, N-CH₂), 3.05 (t; J = 7 Hz, 2H, Ph-CH₂).- MS (+ FAB/DMSO/glycerol): m/z = 266 (29%, [M + H]⁺), 117 (6), 106 (12), 105 (100), 91 (18), 78 (12), 76 (10).

N-Nitroso-4-phenyl-3-(2-phenylethyl)-5-sydnone imine (**23b**)

Red platelets (methanol), mp. 110°C (decompn.). Yield 83%.- C₁₆H₁₄N₄O₂ (294.3) Calcd. C 65.3 H 4.79 N 19.0 Found C 65.4 H 4.53 N 19.0.- IR (KBr): 3411; 3053; 3017; 2966; 1612; 1594; 1496; 1454; 1448; 1434; 1371; 1348; 1235; 1189; 1147; 1105; 1077; 1068; 1031; 1004; 966; 874; 857; 773; 756; 732; 696; 630 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 289 (3.83), 355 (4.12), 509 (2.16).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.57 (bs; 5H arom., syd-Ph), 7.26 (m; 3H arom., CH₂-Ph-H-3'', H-4'', H-5''), 7.13 (''d''), J = 6.1 Hz, 2H arom., CH₂-Ph-H-2'' and H-6''), 4.94 (t; J = 7.1 Hz, 2H, N-CH₂), 3.15 (t; J = 7.1 Hz, 2H, Ph-CH₂).- MS (+ FAB/DMSO/glycerol): m/z = 295 (8%, [M + H]⁺), 266 (10), 105 (100), 91 (18), 76 (11).

DL-erythro-[2-[5-Nitrosoimino-4-phenyl-sydnone-3-yl]-phenyl]-propanol (**24b**)

Orange powder (methanol), mp. 131°C. Yield 64%.- C₁₇H₁₆N₄O₃ (324.3) Calcd. C 63.0 H 4.97 N 17.3 Found C 63.0 H 4.95 N 17.3.- IR (KBr): 3407; 3052; 1614; 1592; 1495; 1447; 1398; 1375; 1335; 1256; 1206; 1179; 1104; 1084; 1036; 1009; 991; 954; 877; 760; 701 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 285 (3.86), 354 (4.16), 507 nm (2.19).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.64-7.52 (m; 5H arom., syd-Ph), 7.27 (m; 3H arom., CH(OH)-Ph-H-3', H-4', H-5'), 6.90 (m, 2H arom., CH(OH)-Ph-H-2' and H-6'), 6.15 (d; J = 5.3 Hz, 1H, OH, D₂O

exchange), 5.09 (m; 1H, CH(CH₃)), 4.84 (dd; J = 4.7/4.7 Hz, 1H, CH(OH)), 1.59 (d; J = 6.8 Hz, 3H, CH(CH₃)).- MS (+ FAB/DMSO/glycerol): m/z = 325 (21%, [M + H]⁺), 324 (17), 295 (17), 158 (16), 135 (56), 132 (35), 120 (42), 118 (49), 117 (59), 105 (100), 91 (47), 77 (79).

4-(4-Chlorophenyl)-3-(2-phenylethyl)-5-sydnone imine hydrochloride (25a)

Crystals (ethanol/ether), mp. 152°C. Yield 31%.- C₁₆H₁₅Cl₂N₃O (336.2) Calcd. C 57.1 H 4.49 N 12.5 Found C 56.9 H 4.44 N 12.5.- IR (KBr): 3417; 3018; 2992; 2922; 1666; 1589; 1509; 1473; 1454; 1438; 1426; 1405; 1364; 1329; 1263; 1221; 1165; 1090; 1029; 1005; 966; 945; 843; 790; 770; 754; 707; 651 cm⁻¹.- UV (CH₃OH): λ max (log ε) = 206 (4.20), 248 (3.87), 310 nm (3.88).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 9.77 (s; 2H, =NH₂⁺, D₂O exchange), 7.71 (d; J = 8.4 Hz, 2H arom., syd-Ph-H-2', H-6'), 7.59 (d; J = 8.4 Hz, 2H arom., syd-Ph-H-3', H-5'), 7.29-7.23 (m; 3H arom., CH₂-Ph-H-3'', -H-4'', -H-5''), 7.14 (d; 2H arom., CH₂-Ph-H-2'', H-6''), 4.79 (t; 2H, N-CH₂), 3.07 (t; 2H, Ph-CH₂).- MS (+ FAB/DMSO/*m*-NO₂-benzyl alcohol): m/z = 302 (12%, [M + H]⁺[³⁷Cl]), 300 (34%, [M + H]⁺[³⁵Cl]), 154 (5), 136 (4), 106 (9), 105 (100), 91 (9), 79 (6), 77 (11).

4-(4-Chlorophenyl)-3-(2-phenylethyl)-N-nitroso-5-sydnone imine (25b)

Orange crystals (methanol), mp. 104°C. Yield 62%.- C₁₆H₁₃ClN₄O₂ (328.8) Calcd. C 58.4 H 3.99 N 17.0 Found C 58.1 H 3.94 N 17.0.- IR (KBr): 3420; 3052; 3015; 1601; 1587; 1572; 1494; 1453; 1390; 1352; 1343; 1226; 1181; 1165; 1098; 1092; 1077; 1013; 991; 963; 890; 829; 764; 751; 720; 699; 653; 631 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 295 (3.92), 355 (4.12), 511 (2.14).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.66 (d; J = 8.5 Hz, 2H arom., syd-Ph-H-2', H-6'), 7.58 (d; J = 8.5 Hz, 2H arom., syd-Ph-H-3', H-5'), 7.26 (m; 3H arom., CH₂-Ph-H-3'', H-4'', H-5''), 7.17 (d; J = 7.5 Hz, 2H arom., CH₂-Ph-H-2'', H-6''), 4.94 (t; J = 7.1 Hz, 2H, N-CH₂), 3.17 (t; J = 7.1 Hz, 2H, Ph-CH₂).- MS (+ FAB/DMSO/*m*-NO₂-benzyl alcohol): m/z = 331 (2%, [M + H]⁺[³⁷Cl]), 329 (8%, [M + H]⁺[³⁵Cl]), 299 (3), 154 (11), 136 (9), 106 (10), 105 (100), 91 (25), 77 (16).

N-Nitroso-4-phenyl-3-(3-phenylpropyl)-sydnone imine (26b)

Red crystals, mp. 104°C. Yield 50%.- C₁₇H₁₆N₄O₂ (308.3) Calcd. C 66.2 H 5.23 N 18.2 Found C 66.1 H 5.08 N 18.2.- IR (KBr): 3052; 2911; 1614; 1597; 1499; 1469; 1446; 1385; 1366; 1355; 1194; 1148; 1078; 1066; 1032; 1007; 982; 962; 912; 857; 772; 750; 726; 698; 655; 605 cm⁻¹.- UV (CH₃OH): λ max (log ε) = 204 (4.29), 275 (3.91), 346 (4.03).- ¹H-NMR/250 MHz ([D₆]DMSO): δ (ppm) = 7.7-7.5 (m; 5H, arom.), 7.3-7.1 (m; 5H, arom.), 4.66 (t; J = 7 Hz, 2H, syd-CH₂), 2.67 (t; J = 7 Hz, CH₂-Ph), 2.14 (tt; J = 7/7 Hz, 2H, CH₂-CH₂-CH₂).- MS (+ FAB/DMSO/glycerol): 309 (18%, [M + H]⁺), 280 (16), 279 (11), 144 (13), 133 (31), 117 (11), 105 (26), 91 (100).- MS (100°C): m/z = 280 (15%, [M - N₂]⁺), 235 (6), 222 (17), 119 (17), 104 (28), 91 (100).

3-Ethyl-4-naphthyl-5-sydnone imine hydrochloride (27a)

Powder (isopropanol/ether), mp. 151°C (decompn.). Yield 74%.- C₁₄H₁₄ClN₃O (275.7) Calcd. C 61.0 H 5.11 N 15.2 Found C 60.7 H 5.10 N 15.2.- IR (KBr): 3402; 3040; 3008; 2995; 2936; 2867; 2838; 2822; 1667; 1591; 1512; 1496; 1459; 1397; 1355; 1236; 1191; 1161; 1143; 1119; 1089; 1018; 980; 958; 934; 921; 868; 808; 778; 769; 726; 665; 646 cm⁻¹.- UV (CH₃OH): λ max (log ε) = 222 (4.78), 292 nm (4.07).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 9.58 (bs; 2H, =NH₂⁺, D₂O exchange), 8.29-7.63 (m; 7H, arom.), 4.39 (q; J = 7.2 Hz, 2H, N-CH₂), 1.28 (t; J = 7 Hz, 3H, CH₃).- MS (+ FAB/DMSO/glycerol): m/z = 240 (100%, [M + H]⁺), 182 (8), 167 (7), 155 (11), 154 (28), 141 (6), 127 (12), 115 (6).

3-Ethyl-4-naphthyl-N-nitroso-5-sydnone imine (27b)

Violet crystals (ethanol), mp. 104°C. Yield 82%.- C₁₄H₁₂N₄O₂ (268.3) Calcd. C 62.6 H 4.50 N 20.9 Found C 62.4 H 4.45 N 20.8.- IR (KBr): 3418; 3044; 2986; 2939; 1966; 1733; 1605; 1584; 1573; 1508; 1474; 1461; 1443; 1386; 1365; 1344; 1256; 1239; 1209; 1170; 1160; 1112; 1080; 1058; 1028; 1016; 976; 956; 918; 868; 808; 792; 777; 740; 706; 661; 631 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 220 (4.69), 343 (4.16), 501 nm (2.07).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 8.21-7.53 (m; 7H, arom.), 4.47 (m; 2H, N-CH₂), 1.34 (t; J = 7.3 Hz, 3H, CH₃).- MS (+ FAB/DMSO/glycerol): m/z = 269 (16%, [M + H]⁺), 241 (6), 215 (11), 182 (12), 155 (14), 154 (11), 149 (21), 93 (100%, [gly + H]⁺), 78 (6), 72 (6).

3-Ethyl-4-naphthyl-sydnone (27c)

Light yellow crystals (isopropanol), mp. 90°C. Yield 57%.- C₁₄H₁₂N₂O₂ (240.3) Calcd. C 70.0 H 5.03 N 11.7 Found C 70.1 H 5.03 N 11.7.- IR (KBr): 3437; 3050; 2974; 1722; 1590; 1514; 1499; 1456; 1443; 1371; 1334; 1240; 1142; 1119; 1103; 1073; 1030; 1014; 974; 954; 887; 800; 776; 745; 666; 608 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 216 (4.62), 309 nm (4.01).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 8.15-7.56 (m; 7H, arom.), 4.32 (m; 2H, N-CH₂, AB-spin system), 1.23 (t; J = 7.3 Hz, 3H, CH₃).- MS (120°C): m/z = 240 (38%, [M]⁺), 182 (43), 155 (11), 154 (100), 153 (19), 127 (27), 126 (10), 77 (4), 29 (16).

E-3-Methyl-4-styryl-5-sydnone imine hydrochloride (28a)

Yellow crystals (methanol/isopropanol), mp. 192°C. Yield 57%.- C₁₁H₁₂ClN₃O (237.7) Calcd. C 55.6 H 5.09 N 17.7 Found C 55.5 H 5.06 N 17.7.- IR (KBr): 3422; 3178; 2969; 1660; 1631; 1591; 1508; 1486; 1442; 1348; 1317; 1269; 1201; 1103; 1079; 957; 851; 805; 748; 690; 669; 607 cm⁻¹.- UV (CH₃OH): λ max (log ε) = 204 (4.34), 294 (4.15), 342 nm (4.18).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 10.18 (bs; 2H, =NH₂⁺, D₂O exchange), 7.79 (d; J = 7.6 Hz, 2H arom., Ph-H-2'', Ph-H-6''), 7.52 (d; J = 17 Hz, 1H, Ph-CH=), 7.45-7.37 (m; 3H, arom.), 7.26 (d; J = 17 Hz, 1H, syd-CH=), 4.40 (s; 3H, -CH₃).- MS (+ FAB/DMSO/glycerol): m/z = 202 (100%, [M + H]⁺), 185 (13), 144 (8), 115 (12), 91 (6), 77 (6).

E-3-Methyl-N-nitroso-4-styryl-5-sydnone imine (28b)

Bright red crystals (methanol), mp. 162°C (decompn.). Yield 38%.- C₁₁H₁₀N₄O₂ (230.2) Calcd. C 57.4 H 4.37 N 24.3 Found C 57.1 H 4.38 N 24.1.- IR (KBr): 3411; 3050; 3022; 2996; 2941; 1724; 1598; 1583; 1492; 1481; 1440; 1406; 1364; 1338; 1325; 1313; 1295; 1275; 1208; 1156; 1109; 1082; 1024; 995; 965; 941; 918; 846; 778; 761; 720; 691; 612 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 230 (3.95), 259 (4.03), 343 (4.43), 512 nm (2.22).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.69 (d; J = 7.6 Hz, 2H arom., H-2'', H-6''), 7.46-7.30 (m; 5H, Ph-H-3'', H-4'', H-5'', CH=CH), 4.48 (s; 3H, CH₃).- MS (+ FAB/DMSO/glycerol): m/z = 231 (25%, [M + H]⁺), 202 (16), 201 (16), 185 (10), 171 (11), 170 (15), 169 (17), 157 (52), 145 (11), 144 (87), 116 (11), 115 (33), 103 (16), 91 (19), 78 (100), 77 (18), 76 (16).- MS (90°C): m/z = 202 (45%, [M - N₂]⁺), 169 (18), 145 (11), 144 (100), 129 (13), 115 (29), 103 (25), 102 (15), 77 (27), 51 (12), 28 (13).

E-3-Methyl-4-styryl-sydnone (28c)

Light yellow crystals (isopropanol/acetone), mp. 163°C. Yield 58%.- C₁₁H₁₀N₂O₂ (202.2) Calcd. C 65.3 H 4.98 N 13.8 Found C 65.4 H 4.97 N 13.8.- IR (KBr): 3418; 3019; 1793; 1726; 1621; 1515; 1483; 1441; 1327; 1292; 1269; 1202; 1115; 1065; 1047; 967; 921; 750; 728; 690; 619 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 270 (3.95), 346 nm (4.46).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.62 (d; J = 7.6 Hz, 2H arom., Ph-H-2'', H-6''), 7.44-7.29 (m; 4H, 3H arom., Ph-CH=), 7.18 (d; J = 16.1 Hz, 1H,

syd-CH=), 4.20 (s; 3H, N-CH₃).- MS (200°C): m/z = 202 (55%, [M]⁺), 145 (11), 144 (100), 129 (11), 115 (30), 103 (25), 102 (14), 77 (25), 63 (8), 51 (11), 39 (7).

E-3-Ethyl-N-nitroso-4-styryl-5-sydnone imine (29b)

Bright red crystals (methanol), mp. 109°C. Yield 43%.- C₁₂H₁₂N₄O₂ (244.3) Calcd. C 59.0 H 4.95 N 22.9 Found C 59.2 H 4.83 N 22.8.- IR (KBr): 2984; 1625; 1597; 1581; 1469; 1444; 1415; 1382; 1376; 1364; 1349; 1234; 1207; 1161; 1119; 1110; 1080; 1039; 1008; 980; 960; 922; 813; 771; 750; 723; 690 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 259 (3.88), 344 (4.33), 512 nm (2.24).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.70 (d; J = 7.2 Hz, 2H arom., Ph-H-2'', H-6''), 7.48-7.34 (m; 5H, CH=CH, Ph-H-3'', H-4'', H-5''), 4.93 (q; J = 7.2 Hz, 2H, CH₂), 1.61 (t; J = 7.2 Hz, 3H, CH₃).- MS (+ FAB/DMSO/glycerol): m/z = 245 (54%, [M + H]⁺), 217 (11), 216 (28), 215 (14), 199 (19), 158 (32), 149 (100), 131 (59), 130 (42), 117 (46), 103 (29), 91 (29), 78 (88), 77 (16), 73 (37), 60 (54).- MS (110°C): m/z = 216 (58%, [M - N₂]⁺), 183 (11), 158 (41), 131 (11), 130 (100), 115 (12), 105 (21), 103 (29), 91 (10), 77 (23), 29 (18), 28 (51).

E-3-Allyl-4-styryl-5-sydnone imine hydrochloride (30a)

Yellow needles (isopropanol), mp. 156°C. Yield 48%.- C₁₃H₁₄ClN₃O (263.7) Calcd. C 59.2 H 5.35 N 15.9 Found C 59.2 H 5.33 N 15.9.- IR (KBr): 3185; 2993; 1660; 1636; 1590; 1504; 1492; 1445; 1428; 1389; 1359; 1330; 1241; 1212; 1153; 1077; 995; 982; 952; 941; 853; 811; 780; 747; 688; 613 cm⁻¹.- UV (CH₃OH): λ max (log ε) = 204 (4.24), 295 (4.11), 345 nm (4.14).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 10.38 (bs; 2H, =NH₂⁺, D₂O exchange), 7.81 (d; J = 7 Hz, 2H arom., Ph-H-2'', H-6''), 7.61 (d; J = 17 Hz, 1H, Ph-CH=), 7.43 (dd; J = 7/7 Hz, 2H arom., Ph-H-3'', H-5''), 7.36 (dd; J = 7/7 Hz, 1H arom., Ph-H-4''), 7.29 (d; J = 17 Hz, 1H, syd-CH=), 6.06 (m; 1H, CH=), 5.61 (d; J = 18.6 Hz, 1H, =CH₂), 5.57 (d; J = 6 Hz, 2H, N-CH₂), 5.49 (d; J = 10.4 Hz, 1H, =CH₂).- MS (60°C): m/z = 227 (100%, [M]⁺), 195 (40), 170 (74), 155 (48), 142 (80), 115 (91), 91 (29), 77 (45), 63 (23), 51 (30).

E-3-Allyl-N-nitroso-4-styryl-5-sydnone imine (30b)

Bright red crystals (ethanol), mp. 100°C. Yield 67%.- C₁₃H₁₂N₄O₂ (256.3) Calcd. C 60.9 H 4.72 N 21.8 Found C 60.8 H 4.57 N 21.5.- IR (KBr): 3425; 2995; 1717; 1625; 1599; 1578; 1489; 1468; 1445; 1393; 1358; 1327; 1203; 1167; 1113; 1074; 1048; 998; 964; 938; 917; 847; 791; 759; 718; 694 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 259 (4.05), 345 (4.40), 515 nm (2.23).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.68 (d; J = 7 Hz, 2H arom., H-2'', H-6''), 7.58-7.37 (m; 4H, Ph-H-3'', H-4'', H-5'', Ph-CH=), 7.33 (d; J = 16.3 Hz, 1H, syd-CH=), 6.16 (m; 1H, Ph-CH=), 5.65 (m; 3H, CH₂, =CH₂), 5.52 (d; J = 11 Hz, 1H, =CH₂).- MS (+ FAB/DMSO/glycerol): m/z = 257 (58%, [M + H]⁺), 229 (27), 228 (70), 227 (30), 170 (42), 131 (39), 116 (33), 115 (100), 103 (25), 91 (48), 78 (94), 77 (24).

E-3-Cyclohexyl-4-styryl-5-sydnone imine hydrochloride (31a)

Small yellow crystals (ethanol), mp. 183°C. Yield 66%.- C₁₆H₂₀ClN₃O (305.8) Calcd. C 62.8 H 6.59 N 13.7 Found C 62.8 H 6.75 N 13.7.- IR (KBr): 3414; 2933; 2860; 1664; 1593; 1486; 1448; 1341; 1277; 1257; 1232; 1189; 1144; 1077; 1006; 955; 900; 817; 798; 750; 689; 630 cm⁻¹.- UV (CH₃OH): λ max/nm (log ε) = 204 (4.34), 295 (4.11), 340 (4.15).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 10.20 (bs; 2H, =NH₂⁺, D₂O exchange), 7.86 (d; J = 7.4 Hz, 2H arom., Ph-H-2'', H-6''), 7.56 (d; J = 16.8 Hz, 1H, Ph-CH=), 7.44 (m; 2H arom., Ph-H-3'', H-5''), 7.39-7.31 (m; 2H, Ph-H-4'', syd-CH=), 5.30 (m; 1H, N-CH(R₁)ax), 2.25-1.25 (m; 10

H, cyclohexyl-H).- MS (220°C): m/z = 269 (18%, [M]⁺), 159 (13), 143 (13), 142 (22), 130 (59), 116 (33), 115 (34), 91 (6), 83 (37), 77 (10), 55 (100).

E-3-Cyclohexyl-N-nitroso-4-styryl-5-sydnone imine (31b)

Cobalt red crystals (methanol), mp. 101°C. Yield 67%.- C₁₆H₁₈N₄O₂ (298.3) Calcd. C 64.4 H 6.08 N 18.8 Found C 64.4 H 6.14 N 19.0.- IR (KBr): 3431; 3019; 2940; 2859; 1621; 1598; 1580; 1490; 1448; 1401; 1383; 1359; 1348; 1343; 1301; 1276; 1265; 1225; 1209; 1189; 1157; 1098; 1074; 1024; 1003; 971; 952; 891; 842; 773; 757; 734; 718; 691; 639; 629 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 259 (4.12), 344 (4.42), 511 nm (2.29).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.71 (d; J = 7.3 Hz, 2H arom., Ph-H-2'', H-6''), 7.51-7.35 (m; 5H, CH=CH, Ph-H-3'', H-4'', H-5''), 5.32 (m; 1H, N-CH(R₁)ax), 2.33-1.28 (m; 10 H, cyclohexyl-H).- MS (+ FAB/DMSO/glycerol): m/z = 299 (6%, [M + H]⁺), 270 (7), 269 (6), 239 (16), 238 (14), 157 (19), 140 (12), 131 (18), 130 (83), 128 (10), 117 (11), 116 (13), 115 (45), 103 (11), 100 (10), 91 (24), 82 (42), 80 (33), 78 (87), 77 (100).

E-3-(2-Phenylethyl)-4-styryl-5-sydnone imine hydrochloride (32a)

Yellow crystals (ethanol), mp. 173°C. Yield 39%.- C₁₈H₁₈ClN₃O (327.8) Calcd. C 65.9 H 5.53 N 12.8 Found C 65.8 H 5.55 N 12.8.- IR (KBr): 3394; 2935; 1659; 1631; 1493; 1451; 1320; 1233; 1169; 1079; 1028; 952; 837; 803; 748; 698 cm⁻¹.- UV (CH₃OH): λ max (log ε) = 205 (4.55), 295 (4.10), 348 (4.11).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 10.11 (bs; 2H, =NH₂⁺, D₂O exchange), 7.76 (d; J = 7 Hz, 2H, arom., =CH-Ph-H-2'', H-6''), 7.47-7.17 (m; 10 H, 8H arom., 2H olef.), 5.12 (t; J = 7 Hz, 2H, N-CH₂), 3.27 (t; J = 7 Hz, 2H, Ph-CH₂).- MS (+ FAB/DMSO/*m*-NO₂-benzyl alcohol): m/z = 292 (33%, [M + H]⁺), 115 (8), 106 (9), 105 (100), 91 (10), 78 (10), 76 (10).

E-N-Nitroso-3-(2-phenylethyl)-4-styryl-5-sydnone imine (32b)

Bright carmine crystals (methanol/ethanol), mp. 107°C. Yield 52%.- C₁₈H₁₆N₄O₂ (320.4) Calcd. C 67.5 H 5.03 N 17.5 Found C 67.5 H 4.88 N 17.3.- IR (KBr): 3429; 3020; 2220; 1659; 1623; 1577; 1493; 1469; 1449; 1399; 1381; 1353; 1333; 1219; 1198; 1153; 1098; 1077; 1023; 971; 935; 895; 852; 747; 721; 699; 633 cm⁻¹.- UV (CH₃CN): λ max (log ε) = 206 (4.05), 259 (4.06), 345 (4.40), 515 nm (2.24).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.66 (d; J = 7.2 Hz, 2H arom., =CH-Ph-H-2'', H-6''), 7.45-7.23 (m; 10 H, 8H arom., CH=CH), 5.20 (t; J = 7.1 Hz, 2H, N-CH₂), 3.36 (t; J = 7 Hz, 2H, Ph-CH₂).- MS (+ FAB/DMSO/*m*-NO₂-benzyl alcohol): m/z = 321 (12%, [M + H]⁺), 291 (7), 260 (10), 115 (10), 105 (100), 91 (18), 76 (14).

E-3-[2-(3,4-Dimethoxyphenyl)-ethyl]-4-styryl-5-sydnone imine hydrochloride (33a)

Light yellow crystals (methanol/ether), mp. 183°C (decompn.). Yield 43%.- C₂₀H₂₂ClN₃O₃ (387.9) Calcd. C 61.9 H 5.72 N 10.8 Found C 61.5 H 5.72 N 10.9.- IR (KBr): 2940; 1659; 1630; 1591; 1513; 1462; 1440; 1422; 1357; 1336; 1263; 1253; 1228; 1188; 1169; 1151; 1139; 1078; 1038; 1023; 957; 846; 823; 809; 752; 712; 690; 629 cm⁻¹.- UV (CH₃OH): λ max (log ε) = 204 (4.61), 283 (4.15), 349 nm (4.11).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 10.27 (s; 2H, =NH₂⁺, D₂O exchange), 7.76 (d; J = 7.1 Hz, 2H arom., =CH-Ph-H-2'', H-6''), 7.49 (d; J = 17 Hz, 1H, Ph-CH=), 7.43-7.34 (m; 3H arom., =CH-Ph-H-3'', H-4'', H-5''), 7.15 (d; J = 17 Hz, 1H, syd-CH=), 6.93 (s; 1H arom., CH₂-Ph-H-2''), 6.83 (d; J = 8.2 Hz, 1H arom., CH₂-Ph-H-5''), 6.75 (dd; J = 8/2 Hz, 1H arom., CH₂-Ph-H-6''), 5.12 (t; 2H, N-CH₂), 3.71 (s; 3H, 4''-OCH₃), 3.63 (s; 3H, 3'''-OCH₃), 3.18 (t; 2H, Ph-CH₂).- MS (+ FAB/DMSO/glycerol): m/z =

352 (50%, [M + H]⁺), 166 (20), 165 (100), 164 (17), 151 (22), 150 (14), 115 (11), 91 (14), 76 (10).

E-3-[2-(3,4-Dimethoxyphenyl)-ethyl]-N-nitroso-4-styryl-5-syndnone imine (33b)

Small orange crystals (methanol), mp. 105°C. Yield 30%. C₂₀H₂₀N₄O₄ · 1/4 H₂O (384.9) Calcd. C 62.4 H 5.42 N 14.5 Found C 62.5 H 5.29 N 14.1. IR (KBr): 3490; 2996; 2932; 2831; 1626; 1578; 1514; 1464; 1446; 1383; 1347; 1253; 1235; 1148; 1096; 1075; 1028; 960; 842; 811; 760; 719; 694 cm⁻¹. UV (CH₃CN): λ max (log ε) = 201 (4.53), 232 (4.08), 261 (3.96), 345 (4.32), 515 nm (2.26). ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.62 (d; J = 7.1 Hz, 2H arom., =CH-Ph-H-2''', H-6'''), 7.42-7.33 (m; 4H, 3H arom., =CH-Ph-H-3''', H-4''', H-5''', Ph-CH=), 7.20 (d; J = 16.2 Hz, 1H, syd-CH=), 6.93 (s; 1H arom., CH₂-Ph-H-2''), 6.84-6.76 (m; 2H arom., CH₂-Ph-H-5'', H-6''), 5.18 (t; 2H, N-CH₂), 3.69 (s; 3H, OCH₃), 3.61 (s; 3H, OCH₃), 3.26 (t; 2H, Ph-CH₂). MS (+ FAB/DMSO/glycerol): m/z = 381 (4%, [M + H]⁺), 352 (6), 165 (100), 151 (30), 149 (23), 131 (14), 103 (9), 91 (11), 78 (16).

E-[2-[5-Imino-4-styryl-syndnone-3-yl]-phenyl]-ethanol hydrochloride (34a)

Yellow green small crystals (ethanol), mp. 191°C (decompn.). Yield 35%. C₁₈H₁₈ClN₃O (343.8) Calcd. C 62.8 H 5.28 N 12.2 Found C 62.5 H 5.28 N 12.1. IR (KBr): 3254; 3042; 1659; 1636; 1505; 1492; 1448; 1396; 1359; 1267; 1201; 1103; 1067; 1027; 950; 891; 847; 805; 752; 714; 699; 604 cm⁻¹. UV (CH₃OH): λ max (log ε) = 205 (4.30), 296 (4.08), 350 nm (4.11). ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 10.15 (s; 2H, =NH₂⁺, D₂O exchange), 7.78 (d; J = 7.4 Hz, 2H arom., =CH-Ph-H-2'', H-6''), 7.52-7.30 (m; 10H, 8 arom., CH=CH), 6.31 (d; J = 4.1 Hz, 1H, OH, D₂O exchange), 5.15 (m; 2H, CH(OH)-CH₂ [X- and A-part]), 4.99 (dd; J = 13.9/9 Hz, 1H, CH(OH)-CH₂ [B-part]). MS (200°C): m/z = 307 (8%, [M]⁺), 171 (68), 143 (52), 142 (97), 115 (77), 107 (100), 91 (70), 79 (82), 77 (84), 51 (35).

E-[2-[5-Nitrosoimino-4-styryl-syndnone-3-yl]-phenyl]-ethanol (34b)

Small orange crystals (washed with methanol and water), mp. 97°C. Yield 41%. C₁₈H₁₆N₄O₃ · 1/2 H₂O (345.4) Calcd. C 62.6 H 4.93 N 16.2 Found C 62.9 H 4.70 N 16.2. IR (KBr): 3418; 3050; 1625; 1582; 1491; 1448; 1363; 1171; 1110; 1059; 964; 846; 754; 696 cm⁻¹. UV (CH₃CN): λ max (log ε) = 230 (4.04), 259 (4.13), 345 (4.41), 515 nm (2.29). ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.67 (d; J = 7.2 Hz, 2H arom., Ph-H-2''', H-6'''), 7.55 (d; J = 7.2 Hz, 2H arom., Ph-H-2''', H-6'''), 7.47-7.33 (m; 8H, 6H arom., CH=CH), 6.23 (d; J = 4.6 Hz, 1H, OH, D₂O exchange), 5.22-5.07 (m; 3H, CH₂-CH(OH)). MS (+ FAB/DMSO/glycerol): m/z = 337 (28%, [M + H]⁺), 308 (15), 307 (13), 171 (11), 170 (11), 149 (16), 131 (34), 130 (39), 121 (18), 117 (18), 115 (45), 103 (41), 93 (100), 91 (39), 78 (24), 76 (25).

E-3-(3-Phenylpropyl)-4-styryl-5-syndnone imine hydrochloride (35a)

Yellow crystals (ethanol), mp. 164°C (decompn.). Yield 31%. C₁₉H₂₀ClN₃O (341.8) Calcd. C 66.8 H 5.89 N 12.3 Found C 66.8 H 5.91 N 12.5. IR (KBr): 2952; 1655; 1632; 1592; 1494; 1452; 1403; 1341; 1304; 1273; 1253; 1219; 1181; 1089; 1028; 951; 921; 851; 802; 776; 747; 702; 690 cm⁻¹. UV (CH₃OH): λ max/nm (log ε) = 205 (4.29), 296 (4.09), 344 (4.14). ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 10.28 (bs; 2H, =NH₂⁺, D₂O exchange), 7.82 (d; J = 7.5 Hz, 2H arom., =CH-Ph-H-2'', =CH-Ph-H-6''), 7.58 (d; J = 17 Hz, 1H, Ph-CH=), 7.44 (m; 2H arom., =CH-Ph-H-3'', =CH-Ph-H-5''), 7.38 (m; 1H arom., =CH-Ph-H-4''), 7.32-7.18 (m; 6H, 5 Phenyl-H, syd-CH=), 4.86 (t; J = 6.9 Hz, 2H, N-CH₂), 2.76 (t; J = 7.6 Hz, 2H, Ph-CH₂), 2.23 (m; 2H, Ph-CH₂-CH₂). MS

(120°C): m/z = 305 (8%, [M]⁺), 261 (20), 201 (12), 200 (26), 171 (13), 170 (17), 169 (11), 143 (12), 142 (55), 130 (12), 117 (18), 115 (31), 91 (100), 77 (10), 41 (15).

E-N-Nitroso-3-(3-phenylpropyl)-4-styryl-5-syndnone imine (35b)

Cherry red crystals (methanol), mp. 97°C. Yield 49%. C₁₉H₁₈N₄O₂ (334.4) Calcd. C 68.2 H 5.42 N 16.8 Found C 68.0 H 5.38 N 16.8. IR (KBr): 2996; 2942; 2872; 1724; 1666; 1584; 1494; 1474; 1464; 1453; 1444; 1406; 1381; 1358; 1271; 1257; 1208; 1157; 1107; 1082; 1070; 1056; 1027; 999; 979; 964; 942; 885; 866; 849; 806; 784; 752; 733; 714; 701; 686; 628 cm⁻¹. UV CH₃CN): λ max (log ε) = 207 (4.05), 259 (4.04), 345 (4.40), 513 nm (2.24). ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.67 (d; J = 7 Hz, 2H arom., =CH-Ph-H-2'', H-6''), 7.48-7.18 (m; 10H, 8H arom., CH=CH), 4.92 (t; J = 7 Hz, 2H, N-CH₂), 2.80 (t; 2H, Ph-CH₂), 2.31 (t; J = 7/7 Hz, 2H, Ph-CH₂-CH₂). MS (+ FAB/DMSO/glycerol): m/z = 335 (2%, [M + H]⁺), 170 (6), 131 (7), 117 (11), 115 (15), 103 (8), 91 (100), 78 (22), 76 (13). MS (120°C): m/z = 306 (53%, [M - N₂]⁺), 276 (3), 170 (6), 130 (17), 119 (18), 91 (100), 77 (6), 41 (10).

E-4-[2-(2-Furanylenyl)-3-(2-phenylethyl)-5-syndnone imine hydrochloride (36a)]

Yellow green small crystals (ethanol/chloroform), mp. 175°C. Yield 34%. C₁₆H₁₆ClN₃O₂ (317.8) Calcd. C 60.5 H 5.07 N 13.2 Found C 60.4 H 5.04 N 13.2. IR (KBr): 3185; 2982; 1665; 1637; 1598; 1504; 1495; 1471; 1453; 1389; 1323; 1290; 1229; 1199; 1176; 1076; 1041; 1010; 961; 938; 883; 807; 736; 695; 651 cm⁻¹. UV (CH₃OH): λ max (log ε) = 205 (4.14), 307 (4.16), 368 nm (4.15). ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 10.15 (bs; 2H, =NH₂⁺, D₂O exchange), 7.85 (s; 1H arom., Fu-H-5''), 7.39 (d; J = 16.6 Hz, 1H, syd-CH=), 7.33-7.23 (m; 5H arom., Phenyl-H), 6.86 (d; J = 16.6 Hz, 1H, Fu-CH=), 6.80 (d; J = 3.5 Hz, 1H arom., Fu-H-3''), 6.65 (dd; J = 3/1 Hz, 1H arom., Fu-H-4''), 5.06 (t; J = 7 Hz, 2H, N-CH₂), 3.24 (t; J = 7 Hz, 2H, Ph-CH₂). MS (120°C): m/z = 281 (23%, [M]⁺), 177 (12), 159 (23), 132 (22), 105 (100), 91 (21), 79 (12), 77 (14).

E-4-[2-(2-Furanylenyl)-N-nitroso-3-(2-phenylethyl)-5-syndnone imine (36b)]

Blood red needles (methanol), mp. 112°C. Yield 48%. C₁₆H₁₄N₄O₃ (310.3) Calcd. C 61.9 H 4.54 N 18.0 Found C 61.5 H 4.52 N 17.9. IR (KBr): 3430; 3106; 3049; 3023; 1720; 1629; 1585; 1484; 1451; 1405; 1387; 1364; 1354; 1336; 1219; 1160; 1141; 1098; 1077; 1021; 958; 936; 892; 807; 744; 707; 676; 633 cm⁻¹. UV (CH₃CN): λ max (log ε) = 272 (4.00), 357 (4.43), 508 nm (2.32). ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.83 (d; J = 1.5 Hz, 1H arom., Fu-H-5''), 7.32-7.22 (m; 6H, 5 Ph-H, syd-CH=), 6.98 (d; J = 16 Hz, 1H, Fu-CH=), 6.85 (d; J = 3.4 Hz, 1H, Fu-H-3''), 6.63 (dd; J = 3.4/1.5 Hz, 1H, Fu-H-4''), 5.15 (t; J = 6.5 Hz, 2H, N-CH₂), 3.33 (t; J = 6.5 Hz, 2H, Ph-CH₂). MS (+ FAB/DMSO/glycerol): m/z = 311 (2%, [M + H]⁺), 159 (7), 106 (9), 105 (100), 91 (18), 78 (28), 77 (9), 76 (12).

E-2-[2-[5-Nitrosoimino-4-styryl-syndnone-3-yl]-ethoxy]-ethanol (37b)

Red crystals (methanol/ethanol), mp. 107°C (decompn.). Yield 42%. C₁₄H₁₆N₄O₄ (304.3) Calcd. C 55.3 H 5.30 N 18.4 Found C 55.3 H 5.37 N 17.8. IR (KBr): 3415; 3047; 3009; 2893; 1626; 1571; 1496; 1474; 1447; 1409; 1395; 1372; 1343; 1282; 1261; 1196; 1165; 1158; 1119; 1098; 1081; 1055; 1028; 983; 968; 952; 920; 849; 821; 752; 721; 688; 679; 640 cm⁻¹. UV (CH₃CN): λ max (log ε) = 259 (4.18), 344 (4.42), 514 nm (2.25). ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.68 (d; J = 7 Hz, 2H arom., Ph-H-2''', H-6'''), 7.44-7.36 (m; 5H, Ph-H-3''', H-4''', H-5''', CH=CH), 5.14 (t; J = 4.8 Hz, 2H, N-CH₂), 4.63 (t; J = 5 Hz, 1H, D₂O

exchange, OH), 4.02 (t; $J = 4.8$ Hz, 2H, N-CH₂-CH₂), 3.53-3.44 (m; 4H, O-(CH₂)₂-OH).- MS (+ FAB/DMSO/glycerol): $m/z = 305$ (9%, [M + H]⁺), 276 (3), 245 (8), 218 (3), 149 (14), 131 (14), 115 (10), 75 (64).

Methyl E-4-[5-Nitrosoimino-4-styryl-sydnone-3-yl]-butanoate (38b)

Blood red needles (methanol), mp. 102°C. Yield 33%.- C₁₅H₁₆N₄O₄ (316.3) Calcd. C 57.0 H 5.09 N 17.7 Found C 57.1 H 5.09 N 17.5.- IR (KBr): 2944; 1718; 1576; 1473; 1413; 1383; 1361; 1257; 1207; 1152; 1100; 1071; 1009; 964; 935; 876; 843; 757; 731; 711; 691; 639 cm⁻¹.- UV (CH₃CN): λ max (log ϵ) = 230 (4.27), 259 (4.36), 345 (4.72), 514 nm (2.55).- ¹H-NMR/300 MHz ([D₆]DMSO): δ (ppm) = 7.70 (d; $J = 7.1$ Hz, 2H arom., Ph-H-2'', H-6''), 7.50-7.35 (m; 5H, 3H arom., CH=CH), 4.93 (t; $J = 7$ Hz, 2H, N-CH₂), 3.60 (s; 3H, OCH₃), 2.61 (t; $J = 7$ Hz, 2H,

CH₂-CO), 2.24 (tt; $J = 7/7$ Hz, 2H, CH₂-CH₂).- MS (+ FAB/DMSO/glycerol): $m/z = 317$ (1%, [M + H]⁺), 140 (5), 130 (6), 115 (19), 101 (100), 91 (8), 78 (8), 77 (6).

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