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A NEW WAY FOR SYNTHETIZING (E)-METHYL METHYLSULFANYL(PHENYLAMINO)METHYLENE CARBAMATES *VIA* BECKMANN TRANSPOSITION IN TRIFLIC ACID

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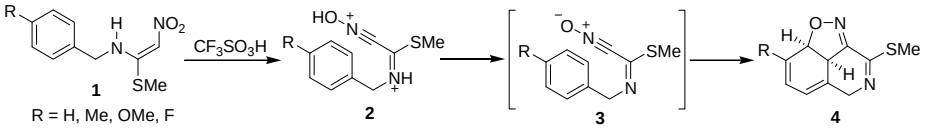
ABSTRACT. At low temperature in triflic acid, nitroketene S,N-acetals with a tethered phenyl ring react to form the corresponding hydroxynitrilium ions. Quenching with methanol leads to the formation of dications which undergo an unexpected Beckmann transposition affording new (*E*)-methyl methylsulfanyl(phenylamino) methylene carbamates.

KEY WORDS: Nitroketene S,N-acetals, Electrophilic aromatic substitution, Superacids, Triflic acid, Beckmann transposition

INTRODUCTION

Nitroethene compounds 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 reactions) [2, 3]. In superacids, non-tethered phenyl ring substrates, such as alkyl or aryl amines derivatives are polyprotonated to lead to multicharged species that can be trapped by suitable nucleophiles [4, 5].

We have previously described the behaviour and the reactivity of 1-benzylamino-1-methylsulfanyl-2-nitroethylene derivatives **1** in triflic acid. It was shown that these compounds are firstly C,O-diprotonated to give hydroxynitrilium ions **2**. By quenching with water, these ions were transformed into a reactive nitrile oxide **3**, which undergoes an intramolecular-1,3-dipolar cyclization to afford cyclic products **4** (Scheme 1) [6].



Scheme 1. Formation of isoxazolines from 1-benzylamino-1-methylsulfanyl-2-nitroethylenes.

Recently, we have shown that when 1-phenylalkylamino-1-methylthio-2-nitroethenes derivatives are dissolved with benzene in TFSA, in situ trapping occurs to afford 2-(hydroxyimino)-2-phenyl-N-(phenylalkyl) acetamides derivatives (Scheme 2) [7].

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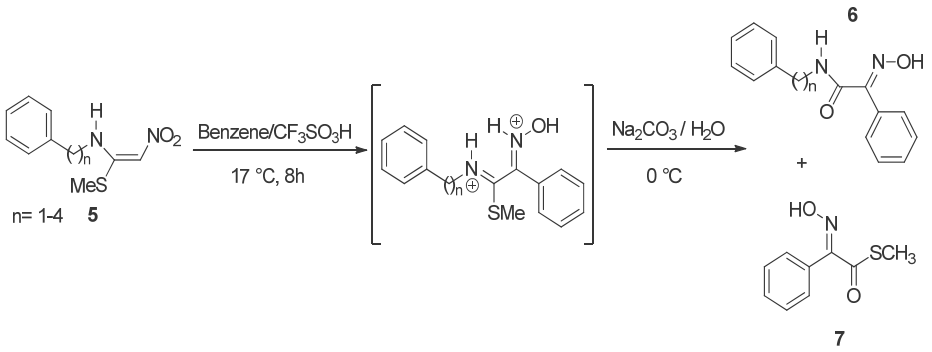


Scheme 2. Synthesis of 2-(hydroxyimino)-2-phenyl-N-(phenylalkyl)acetamides derivatives.

In the present paper, we report the synthesis of new (E)-methyl methylsulfanyl (phenylamino)methylene carbamates *via* Beckmann transposition in triflic acid from nitroketene S,N-acetals with a tethered phenyl ring.

RESULTS AND DISCUSSION

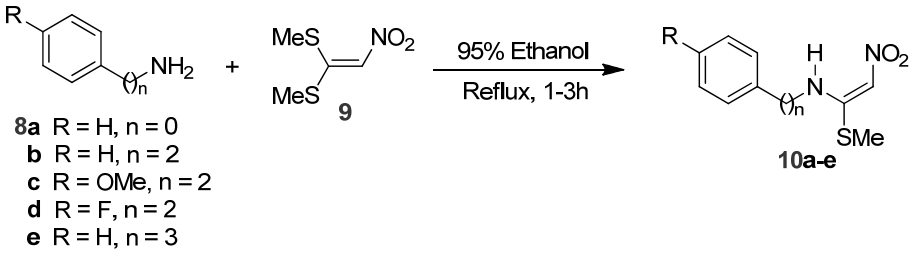
Starting compounds

The starting compounds **10a-e** were prepared by nucleophilic substitution between aniline **8a** or the corresponding ω-phenylalkylamines **8b-e** and 1,1-bis(methylthio)-2-nitroethylene **9** (1.1 molar equivalent) in refluxing 95% ethanol [8] (Scheme 3) in yields varying from 64 to 82% (Table 1). In all cases, the di-substituted products were formed in a small range.

Table 1. Yields of compounds **10b-e**.

Starting compounds	**8b**	**8c**	**8d**	**8e**
Products	**10b**	**10c**	**10d**	**10e**
Yield (%)	82	74	64	76

Starting materials have not been described before, except for (E)-N-(1-(methylthio)-2-nitrovinyl)aniline **10a** [8] and 1-methylsulfanyl-2-nitro-N-phenethylethenamine **10b** [9].



Scheme 3. Synthesis of starting products **10a-e**.

Compounds **10a-e** were characterized from their ^{1}H and ^{13}C NMR spectra, with vinylic and amino protons respectively in the range of δ_H 6.47-6.58 ppm and 10.32-10.52 ppm. The C-1 and C-2 carbons resonate at δ_C 165.0-165.5 ppm and 106.5-106.7 ppm, respectively.

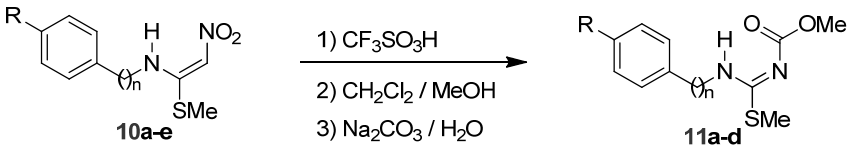
In organic solvent, compounds **10a-e** exist as a sole isomer as shown by a single set of signals in the ^{13}C NMR spectra. They are probably all (*E*)-isomers because this conformation allows formation of an intramolecular hydrogen bond between the N-H and one of the oxygen atoms of $–NO_2$ group, as previously reported for the 1-arylamino-1-methylthio-2-nitroethenes **10a** [8].

Reactions in triflic acid

In the present study, the reactions were carried out in triflic acid at low temperature between -5 to 0 °C and under nitrogen atmosphere. The molar ratio of triflic acid/starting compounds **10a-e** was 50:1. The starting materials were fully transformed within 1 to 5 h of reaction time, depending on the substituent. The observed reaction, reported in Scheme 4, was generally clean with yields varying from 18 to 50% (Table 2) except for **10e**, because of degradation reactions leading to the formation of dark polar products which has not been identified by NMR study.

Table 2. Yields of products **11a-d** and **16**.

Starting compounds	**10a**		**10b**	**10c**	**10d**
Products	**11a**	**16**	**11b**	**11c**	**11d**
Yield (%)	50	14	30	18	42



Scheme 4. Reaction of compounds **10a-e** in triflic acid.

The yields of isolated products **11a-d** were low, probably because the formed hydroxynitrilium ions can either react (i) to afford degradation products or (ii) with triflate anion to form the nucleophilic addition, that easily decomposed during the hydrolysis step of the reaction medium, as previously observed in situ with 1-amino-2-nitroethylene derivatives [4]. The structure of compounds **11a-d** was determined by NMR and HRMS spectroscopy. The CH_3O protons appear in the range of δ_H 3.64-3.71 ppm and the NH proton as a broad singlet in the range of δ_H 9.80-10.07 ppm. Methoxy, imine and carbamate carbons resonate respectively at δ_C 52.95-53.00 ppm, δ_C163.12-163.14 ppm and 174.43-174.50 ppm. The structure of compounds **11** was corroborated by X-ray crystallographic analysis of **11a** [10-12] (Figure 1). The X-ray analysis indicated the trapping of a methoxy group, the loss of oxime group and the formation of carbamate derivatives.

Compounds **11a-d** are presumably (*E*)-isomers because this conformation allows formation of intramolecular hydrogen bond between the N-H and O=C-OMe groups. The formation of compounds **11** may be explained by the mechanism described in Scheme 5. In this mechanism, starting materials **10a-e** undergo a protonation on the carbon bearing the nitro group and an O-protonation of the nitro group. This last O-protonation occurred through a fast proton exchange process with the acidic medium, as demonstrated in fluorosulfonic acid at -80 °C [13, 14]. Prototropic exchanges and the formal loss of a molecule of water lead to the formation of the reacting conjugated hydroxynitrilium ion **12**. Such hydroxynitrilium cations were previously observed with 1,1-heterodisubstitud-2-nitroethylene derivatives by NMR experiments [4-6, 15-17]. They are electrophilic species which can react in situ with aromatic ring [7, 15-20]. In the

present case, starting compounds **10a-e** lead to hydroxynitrilium ions **12** which do not react through an intramolecular process, probably because of the excessively high activation energy of the reaction at this low temperature or the length of alkyl chain between the aryl and the NH.

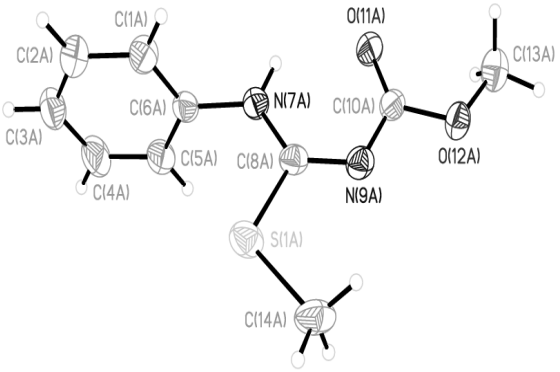
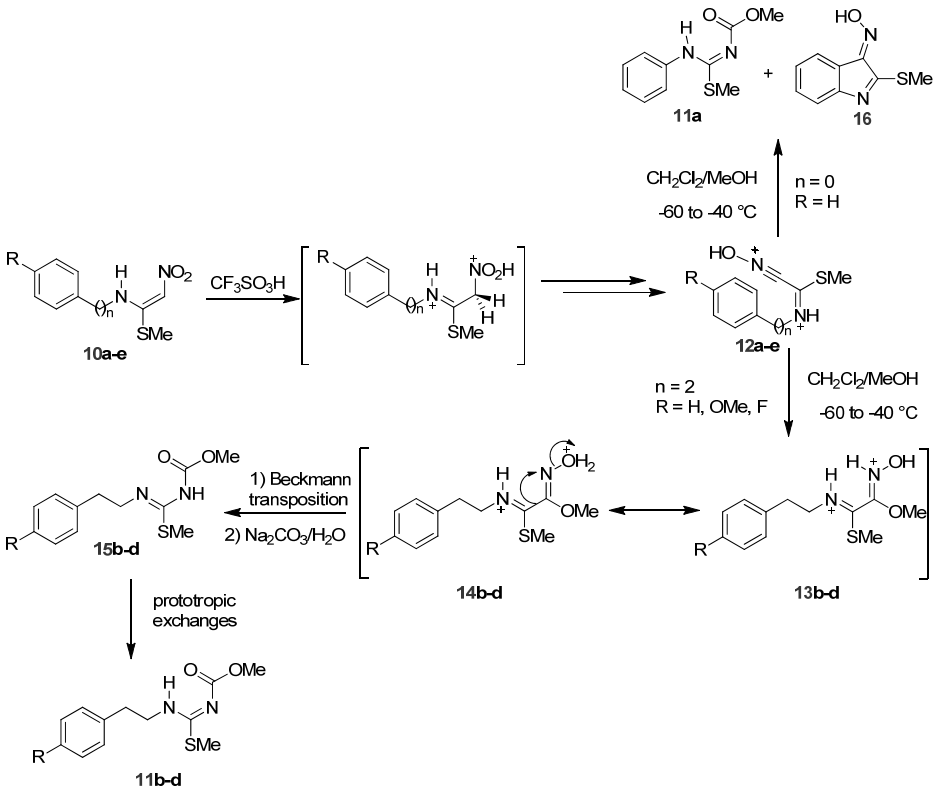


Figure 1. The X-ray analysis of compound **11a**.



Scheme 5. Suggested mechanism for the formation of compounds **11a-d** and **16**.

In agreement with this hypothesis is the fact that with the **10a**, hydroxynitrilium ion formed reacts with the tethered phenyl ring by way of an electrophilic aromatic substitution mechanism to give a cyclic subproduct **16** [5]. By quenching with a cold mixture of CH_2Cl_2/MeOH, hydroxynitrilium ions **12a-d** are trapped with MeOH to give dications**13**, which undergo an Beckmann transposition *via* dications **14**, followed by prototropic exchanges [13-20] to afford carbamic esters compounds **11**.

CONCLUSION

New (*E*)-methyl methylsulfanyl(phenylamino)methylene carbamates have been easily prepared *via* Beckmann transposition in triflic acid. The mechanism of the reaction implies the formation of a stable hydroxynitrilium ion which was trapped by methanol leading to a reactive dication. A Beckmann transposition of this dication leads to the methyl carbamate derivatives. The present study constitutes an extension of the transformation of nitroketene S,N-acetals with a tethered phenyl ring in triflic acid.

EXPERIMENTAL

General remarks

Melting points were determined with a Büchi Melting point B545 apparatus using capillary tubes (temperature rate 2 ^{o}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 and 75 MHz, respectively. NMR spectra were recorded at room temperature and chemical shifts reported relative to Me_4Si. The reproducibility of ^{13}C NMR shift was about ±0.05 ppm, depending on cell and concentration. Chemical assignments were made using DEPT-135 techniques and usual chemical shift assignments rules. Electron-impact ionization (70 eV) mass spectra were obtained with a FinniganIncos 500 Instrument. High resolution mass spectrometry was performed by the "Centre Régional de Mesures Physiques de l'Ouest - Université de Rennes, France". Flash chromatography was achieved on silica gel (20 to 45 μm particle size). Triflic acid was purchased from Acros and 1,1-bis(methylthio)-2-nitroethene from Lancaster and were used without further purification. No attempt was made to optimize the yields.

*(E)-1-Methylthio-2-nitro-N-phenethylethenamine (**10b**)*

1,1-Bis(methylthio)-2-nitroethene (2.2 g, 13.32 mmol) and phenethylamine **8b** (1.5 mL, 12.00 mmol) were heated together in refluxing 95% ethanol (75 mL) under nitrogen atmosphere. The reaction was followed by thin-layer chromatography (CH_2Cl_2). After disappearance of the phenethylamine (3 h) and cooling, the mixture was concentrated under reduced pressure and the resulting oily product was purified by flash chromatography with AcOEt/EP (30/70) and then crystallized from CH_2Cl_2/petroleum ether to afford **10b** (2.34 g, 82%) as white crystals, m.p. 95.4 ^{o}C (CH_2Cl_2/petroleum ether). ^{1}H NMR ($CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 2.90 (t, *J* = 7.23 Hz, 2H, C*H*$_2$-Ph), 3.59 (dd, *J* = 6.99 and 13.00 Hz, 2H, CH_2-N<), 6.47 (s, 1H, H-vinylic), 7.14-7.23 (m, 3H, *o*-H and *p*-H, Ar), 7.23-7.28 (m, 2H, *m*-H, Ar), 10,32 (broad s, NH). ^{13}C NMR ($CDCl_3$): δ = 14.7 (SCH_3), 42.6 (*C*H_2-Ph), 46.4 (CH_2-N<), 106.6 (=CH-NO_2), 127.4 (CH-Ar), 127.7 (2 CH-Ar), 129.2 (2 CH-Ar), 137.8 (*ipso*-C), 165.3 (-NH-C=). HRMS for $C_{11}H_{14}N_2O_2S$ $[M]^+$: calcd. 238.0776, found 238.0788.

*(E)-N-(4-Methoxyphenethyl)-1-methylthio-2-nitroethenamine (**10c**)*

From 4-methoxyphenethylamine (1.8 mL, 12.30 mmol) and 1,1-bis(methylthio)-2-nitroethene (2.23 g, 13.52 mmol) was obtained **10c** (2.23 g, 74%) as yellow crystals, m.p. 112.4 ^{o}C

(CH_2Cl_2/petroleum ether). ^{1}H NMR ($CDCl_3$): δ = 2.42 (s, 3H, SCH_3), 2.92 (t, *J* = 7.0 Hz, 2H, C*H*$_2$-Ph), 3.62 (dd, *J* = 7.0 Hz and 14.2 Hz, 2H, CH_2-N<), 3.80 (s, 3H, OCH_3), 6.55 (s, 1H, H-vinylic), 6.85-6.89 (m, 2H, H-Ar), 7.13-7.16 (m, 2H, H-Ar), 10.52 (broad s, NH). ^{13}C NMR ($CDCl_3$): δ = 14.73 (SCH_3), 34.96 (*C*H_2-Ph), 46.59 (CH_2-N<), 55.66 (OCH_3), 106.67 (=CH-NO_2), 114.70 (2 CH-Ar), 129.56 (C-Ar), 130.14 (2 CH-Ar), 159.07 (C-OMe), 165.00 (-NH-C=). HRMS for $C_{12}H_{16}N_2O_3SNa$ $[M+Na]^+$: calcd. 291.0779, found 291.0779.

*(E)-N-(4-Fluorophenethyl)-1-methylthio-2-nitroethenamine (**10d**)*

From 4-fluorophenethylamine (1.5 mL, 11.43 mmol) and 1,1-bis(methylthio)-2-nitroethene (2.07 g, 12.58 mmol) was obtained **10d** (1.88 g, 64%) as white crystals, m.p. 115.4 °C (CH_2Cl_2/petroleum ether). ^{1}H NMR ($CDCl_3$): δ = 2.42 (s, 3 H, SCH_3), 2.96 (t, *J* = 7.0 Hz, 2H, C*H*$_2$-Ph), 3.65 (dd, *J* = 7.0 Hz and 13.6 Hz, 2H, CH_2-N<), 6.55 (s, 1H, H-vinylic), 6.99-7.05 (m, 2H, H-Ar), 7.16-7.21 (m, 2H, H-Ar), 10.52 (broad s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ = 14.72 (SCH_3), 35.05 (*C*H_2-Ph), 46.31 (CH_2-N<), 106.76 (=CH-NO_2), 115.95 (d, $^2J_{CF}$ = 21.4 Hz, *m*-CH-Ar), 130.62 (d, $^3J_{CF}$ = 8.2 Hz, *o*-CH-Ar), 133.41 (d, $^4J_{CF}$ = 3.3 Hz, C-Ar), 162.30 (d, $^1J_{CF}$ = 244.8 Hz, C-F), 165.05 (-NH-C=). HRMS for $C_{11}H_{13}FN_2O_2SNa$ $[M+Na]^+$: calcd. 279.0579, found 279.0580.

*1-(Methylthio)-2-nitro-1-(3-phenylpropylamino)ethene (**10e**)*

From 3-phenylpropylamine (1.4 mL, 9.85 mmol) and 1,1-bis(methylthio)-2-nitroethene (1.79 g, 10.83 mmol) was obtained **10e** (1.89 g, 76%) as yellow crystals, m.p. 84 °C (CH_2Cl_2/petroleum ether). ^{1}H NMR ($CDCl_3$): δ = 2.02 (dd, *J* = 7.49 and 14.66 Hz, 2H, CH_2), 2.40 (s, 3H, CH_3), 2.71 (t, *J* = 7.49 Hz, , 2H, C*H*$_2$-Ph), 3.40 (dd, *J* = 7.49 and 13.11 Hz, 2H, CH_2-N<), 6.58 (s, 1H, vinylic H), 7.15-7.23 (m, 3H, aromatic *o*-H and *p*-H), 7.26-7.33 (m, 2H, aromatic *m*-H), 10.32 (broad s, NH). ^{13}C NMR ($CDCl_3$): δ = 14.6 (SCH_3), 30.9 (CH_2), 33.1 (*C*H_2-Ph), 44.2 (CH_2-N<), 106.5 (=CH-NO_2), 126.7 (aromatic CH), 128.8 (2 aromatics CH), 129.0 (2 aromatics CH), 140.7 (*ipso*-C), 165.5 (-NH-C=). HRMS for $C_{12}H_{16}N_2O_2S$ $[M]^+$: calcd. 252.0932, found 252.0916.

*Methylmethylsulfanylphenethylaminomethylenecarbamate (**11b**)*

1-Methylsulfanyl-2-nitro-1-(2-phenethylamino)ethylene **10b** (238 mg, 1 mmol) was dissolved with stirring in triflic acid (4.4 mL, 50 mmol) at -5 to 0 °C for 1 h under nitrogen atmosphere. After the disappearance of the starting compound, the acidic solution was poured into a mixture 80 mL of CH_2Cl_2/MeOH (87:13) at -60 to -40 °C and let to warm at room temperature. When temperature reached about -15 °C, brine (10 mL) and anhydrous Na_2CO_3 (6 g) were added. The extraction was carried out promptly with dichloromethane (4 x 20 mL). The organic phase was dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The resulting oil was purified by flash chromatography (eluent petroleum ether/ethylacetate: 90/10) to yield **11b** (75 mg, 30%) as viscous oil. ^{1}H NMR ($CDCl_3$): δ = 2.45 (s, 3H, SCH_3), 2.93 (t, *J* = 7.6 Hz, 2H, Ph-*CH*$_2$), 3.57 (dd, *J* = 7.6 Hz and 13.7 Hz, 2H, CH_2), 3.71 (s, 3H, OMe), 7.20–7.28 (m, 3H, *p*- and *o*-H-Ar), 7.30-7.36 (m, 2H, *m*-H-Ar), 9.80 (broad s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ = 14.07 (SCH_3), 36.01 (Ph-*CH*$_2$), 45.68 (CH_2), 52.97 (OCH_3), 127.28 (CH-Ar), 129.09 (2 CH-Ar), 129.17 (2 CH-Ar), 138.08 (C-Ar), 163.12 (>C=N), 174.50 (>C=O).HRMS for $C_{12}H_{16}N_2O_2S$ $[M]^+$: calcd. 252.0932, found 252.0919.

*(E)-methyl ((methylthio)(phenylamino)methylene)carbamate (**11a**)[21]*

From (E)-N-(1-(methylthio)-2-nitrovinyl)aniline (1 mmol) was obtained **11a** (0.5 mmol, 50%), m.p. 66 °C. ^{1}H NMR ($CDCl_3$): δ = 2.40 (s, 3H, SCH_3), 3.77 (s, 3H, OCH_3), 7.20- 7.50 (m, 5H, H-Ar), 11.33 (broad s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ = 13.87 (SCH_3), 52.55 (OCH_3, 126.29,

127.60, 129.14, 136.56, 162.84 (>C=N), 173.95 (>C=O). HRMS for $C_{10}H_{12}N_2O_2S$ $[M]^+$: calcd. 224.0619, found 224.0619.

*Methyl-(4-methoxyphenethylamino)methylsulfanylmethylenecarbamate (**11c**)*

From *(E)-N*-(4-methoxyphenethyl)-1-methylthio-2-nitroethenamine (1 mmol) was obtained **11c** (0.18 mmol, 18%) as viscous oil. ^{1}H NMR ($CDCl_3$): δ = 2.45 (s, 3H, SCH_3), 2.86 (t, *J* = 7.1 Hz, 2H, Ph-*CH_2*), 3.52 (dd, *J* = 7.1 Hz and 13.3 Hz, 2H, CH_2), 3.71 (s, 3H, OMe), 3.80 (s, 3H, Ph-O*CH_3*), 6.85–6.88 (m, 2H, H-Ar), 7.12-7.15 (m, 2H, H-Ar), 10.07 (broad s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ = 14.07 (SCH_3), 35.11 (Ph-*CH_2*), 45.90 (CH_2), 52.95 (OCH_3), 55.65 (Ph-O*CH_3*), 114.56 (2 CH-Ar), 130.07 (2 CH-Ar), 152.77 (C-Ar), 158.90 (>*C*-OMe), 163.12 (>C=N), 174.44 (>C=O). HRMS for $C_{13}H_{18}N_2O_3SNa$ $[M+Na]^+$: calcd. 305.0936, found 305.0936.

*Methyl-(4-fluorophenethylamino)methylsulfanylmethylenecarbamate (**11d**)*

From *(E)-N*-(4-fluorophenethyl)-1-methylthio-2-nitroethenamine (1 mmol) was obtained **11d** (42.20 mmol, 42%) as viscous oil. ^{1}H NMR ($CDCl_3$): δ = 2.38 (s, 3H, SCH_3), 2.82 (t, *J* = 7.0 Hz, 2H, Ph-*CH_2*), 3.47 (m, 2H, CH_2), 3.64 (s, 3H, OCH_3), 6.91-6.97 (m, 2H, H-Ar); 7.08-7.12 (m, 2H, H-Ar), 9.80 (broad s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ = 14.06 (SCH_3), 35.21 (Ph-*CH_2*), 45.66 (CH_2), 53.00 (OCH_3), 115.87 (d, $^2J_{CF}$ = 21.4 Hz, *m*-CH- Ar), 130.51 (d, $^3J_{CF}$ = 7.7 Hz, *o*-CH-Ar), 133.72 (d, $^4J_{CF}$ = 3.3 Hz, C-Ar), 162.22 (d, $^1J_{CF}$ = 244.8 Hz, C-F), 163.14 (>C=N), 174.43 (>C=O). HRMS for $C_{12}H_{15}FN_2O_2SNa$ $[M+Na]^+$: calcd. 293.0736, found 293.0736.

*(E)-2-(methylthio)-3H-indol-3-one oxime (**16**)*

From (*E*)-N-(1-(methylthio)-2-nitrovinyl)aniline was obtained sub product **16** (0.14 mmol, 14%). m.p. 198 °C. ^{1}H NMR ($CDCl_3$/DMSO-d_6): δ = 2.60 (s, 3H, SCH_3), 7.11-7.18 (m, 1H, H-Ar), 7.29-7.41 (m, 2H, H-Ar), 7.93 (d, *J* = 7.0 Hz, 1H, H-Ar), 13.00 (broad s, 1H, OH). ^{13}C NMR ($CDCl_3$/DMSO-d_6): δ = 12.05 (SCH_3), 118.29, 121.89, 125.01, 126.12, 131.53, 152.72, 155.47 (>C-N=OH), 170.57 (>C=N). HRMS for $C_9H_8N_2OS$ $[M]^+$: calcd. 192.0357, found 193.0357.

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DEDICATION

This publication is dedicated in memory of Professor Jean-Marie Coustard who supervised this work but passed away at the end of August 2013. Rest in peace dear Professor.

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