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O-Arylsulfonyl hydroxylamines via a decarboxylative rearrangement

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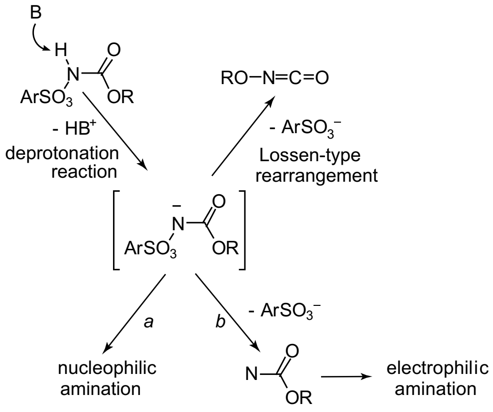
(*E*)-*O*-Arylsulfonyl-*N*-(2-nitroalk-2-enyl)hydroxylamines were easily obtained in good yields starting from (*E*)-nitro allylic alcohols, the crucial step being an inorganic base-catalyzed decarboxylative rearrangement of proposed labile unsaturated carbamates. A possible mechanism for the outcome of the reaction, characterized by the unusual retention of the sulfonyloxy group, is proposed.

1. Introduction

Hydroxylamines (RO–NR$_1$R$_2$) represent an interesting class of electrophilic aminating agents, especially those carrying a good leaving group that can be easily displaced by a nucleophile, leading to the introduction of an amino residue into carbon chains. Among these compounds, *O*-arylsulfonyl hydroxylamines (ArSO$_3$–NHR) have been considered as useful reagents for the electrophilic amination process.[1]

Similarly, arylsulfonyloxy carbamates (ArSO$_3$–NHCO$_2$R)[2] have been used in organic synthesis as aminating reagents, due to the ability of the nitrogen center to act either as an electrophile or as a nucleophile as well as being able to provide in situ a source of other chemical aminating species such as isocyanates (Scheme 1).

The reaction outcome can be controlled by the reaction conditions, namely by the organic or the inorganic base used to promote the deprotonation step, by the R group as well as by the substrate electronic features. While a highly stereoselective aza-MIRC (Michael Initiated Ring Closure) reaction (path a) on EWG substituted olefins led to the synthesis of different functionalized aziridines in very good yields,[3] the electrophilic amination (path b) most frequently led to different amination products, depending on the nature of the substrates.[4] The Lossen-type rearrangement was observed for R=*t*-Bu, leading to cyclization[5] or acylation[6] of β-dicarbonyl compounds. Anyway, the arylsulfonyloxy group is a good leaving group, according to the chemical behavior of sulfonyl-activated hydroxy carbamates.



Scheme 1.

2. Results and discussion

Continuing our studies on the synthesis and the reactivity of such carbamates, a different rearrangement characterized by the retention of the arylsulfonyloxy group coupled with a deacylation reaction giving *O*-arylsulfonyl hydroxylamines was found.

In order to obtain bicyclic aziridines by an intramolecular version of the aza-MIRC reaction, a possible synthesis of unsaturated nitro carbamates **1** (Ns=4-NO$_2$C$_6$H$_4$SO$_2$)[7] was considered, starting from suitable (*E*)-nitro allylic alcohols **2**, following standard procedures (Scheme 2).[4b,8]

2-Nitroethanol was chosen as the starting alcohol for the condensation reactions with some aliphatic or aromatic aldehydes. The synthesis of (*E*)-nitro alkenes was performed by using the

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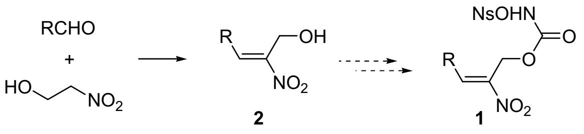


Scheme 2.

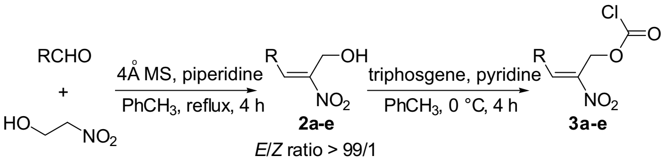
Table 1
Synthesis of (*E*)-nitro allylic alcohols **2**

Entry	2	R	Yield of **2**[a] (%)
1	**a**	*i*-Pr	91
2	**b**	*i*-Bu	89
3	**c**	Pentyl	92
4	**d**[b]	Phenyl	70
5	**e**[b]	2-Furyl	90

[a] After filtration of the crude on Celite using CH_2Cl_2 as eluent.
[b] See Ref. 10.

stereoselective one-pot method we recently reported for the unfunctionalized nitro alkenes.[9] Thus, (*E*)-**2a**–**e** were obtained in good yields (Table 1) by performing the reaction on activated 4 Å molecular sieves at toluene reflux, under an atmosphere of argon, and using piperidine as catalyst (Scheme 3).

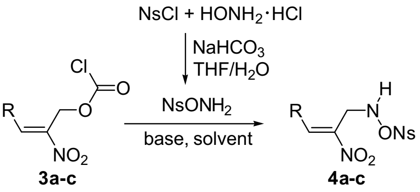
In all cases, the nitro allylic alcohols were obtained in very high purity (*E*/*Z* ratio>99:1), as confirmed by ^{1}H NMR spectra performed on the crude, and then quantitatively converted by standard procedures[4b] to the corresponding unsaturated chloroformates (*E*)-**3a**–**e** (Scheme 3).



Scheme 3.

Surprisingly these chloroformates did not react with hydroxylamine under standard conditions[8a] (Et_3N in CH_2Cl_2) giving expected unsaturated nitro carbamates **1**.

Therefore, a different procedure involving the synthesis of *O*-nosyl hydroxylamine ($NsONH_2$) followed by the reaction with **3** was attempted (Scheme 4).



Scheme 4.

While chloroformates **3d**–**e** led to complex reaction mixtures, aliphatic **3a**–**c** led to unsaturated *O*-nosyl hydroxylamines (*E*)-**4a**–**c** in all tested conditions. The results are reported in Table 2.

As shown in Table 2, nitro allylic *O*-nosyl hydroxylamines (*E*)-**4** were obtained as the only isolable products with variable yields while the desired carbamates **1** were not observed even as by-products, even under other conditions, using different inorganic bases, solvent, and/or reaction temperatures. On the other hand, while the reaction occurred even without a base albeit in a lower yield (entry 5), no product was detected using a tertiary organic base (entry 6).

Table 2
Synthesis of nitro allylic (*E*)-*O*-nosyl hydroxylamines **4a**–**c**

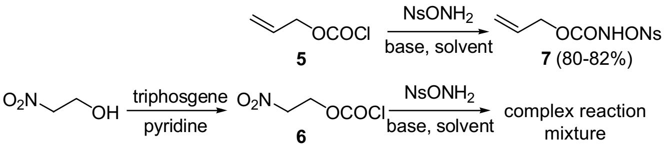
Entry	Product	R	Base	Solvent	*T* (°C)	Reaction time (h)	Yield[a] (%)
1	**4a**	*i*-Pr	CaO	Et_2O	25	24	63
2			CaO	Et_2O	−40	100	39
3			NaH	THF	25	6	61
4			K_2CO_3	Et_2O	25	6	65
5			—	Et_2O	25	100	29
6[b]			Et_3N	CH_2Cl_2	25	6	—
7	**4b**	*i*-Bu	CaO	Et_2O	25	24	65
8			NaH	THF	25	6	67
9			NaH	THF	−40	100	23
10	**4c**	Pentyl	CaO	Et_2O	25	24	63
11			NaH	THF	25	6	60

[a] After flash chromatography on silica gel.
[b] Standard reaction conditions using NH_2OH (Ref. 8a).

This last result seems to be in disagreement with that recently reported in literature for the decarboxylative [1,3]-sigmatropic rearrangement reactions found for similar carbamates. Allylic amine derivatives were in fact obtained also with high enantioselectivity starting from stable unsaturated carbamates by a domino S_N2'–S_N2' mechanism involving a tertiary organic base.[11]

With the aim of rationalizing these results, we turned our attention toward the relationship between the reagents (chloroformates and hydroxylamines) and the reaction outcome.

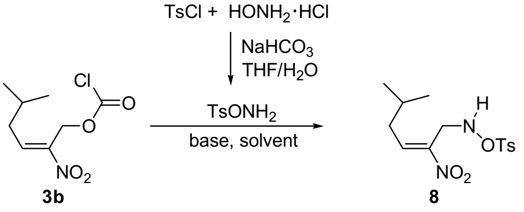
First of all, two different chloroformates, the commercially available allyl chloroformate **5** and the saturated chloroformate **6**,[12] obtained by reaction of nitroethanol with triphosgene, were considered in the reaction with $NsONH_2$ (Scheme 5).



Scheme 5.

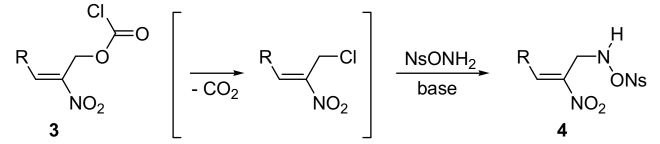
While the reaction between allyl chloroformate and *O*-nosyl hydroxylamine in the presence of CaO or K_2CO_3 gave the allyl nosyloxycarbamate **7** in good yield, a complex reaction mixture was once again obtained starting from **6**. The last result is consistent with the observed reactivity of the chloroformates **3d**–**e**, where the aromatic ring influences the reactivity. On the other hand, the data reported in literature[7] and the formation of **7** suggest that the reaction outcome might be sensitive to the presence of the nitro group.

Then, to test the possible influence of the nosyl group, we decided to replace it with the tosyl group. Again, the reaction of *O*-tosyl hydroxylamine[13] with (*E*)-**3b** performed in the presence of CaO or K_2CO_3 gave (*E*)-**8** as the only characterizable product in 65% and 71% yields, respectively (Scheme 6).



Scheme 6.

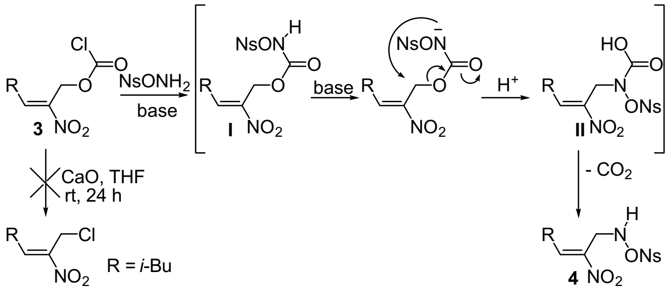
Finally, since some chloroformates were reported to undergo a decarboxylation reaction leading to the corresponding halides,[14] it might be possible that decarboxylation of **3** would lead to the corresponding allylic halides (Scheme 7).



Scheme 7.

However, **4a** was obtained also in the reaction performed without base, although in lower yields and longer times (Table 2, entry 5). Nevertheless, a solution of **3b** and CaO was stirred at room temperature for 24 h but the chloroformate was quantitatively recovered.

As shown in Scheme 8 for reactions with $NsONH_2$, a catalyzed rearrangement reaction of labile allylic arylsulfonyloxy carbamate **I** accompanied by decarboxylation of **II** and characterized by the retention of the nosyloxy group is proposed to explain the formation of **4**. Decarboxylation of stable allylic carbamates were reported on heating to 200–240 °C in the presence of NaH[15] or in different catalyzed conditions.[16]



Scheme 8.

The obtained *O*-nosyl hydroxylamines **4** can be regarded as useful precursors of functionalized allylic primary and secondary amines. The former would be obtained by a selective cleavage of the weak N–O bond[17] while the secondary amines can be synthesized using **4** as electrophilic nitrogen sources in the copper-catalyzed reaction with aryl or alkyl nucleophiles.[18] Finally, it is well known that *O*-nosyl hydroxylamines are considered as effective electrophiles involved in different amination reactions.[19]

3. Conclusions

In conclusion we report a decarboxylative rearrangement in which the arylsulfonyloxy group is surprisingly retained, in spite of its well-known character of leaving group. In fact, in the presence of a base $ArSO_3NHCO_2R$ are reported to undergo either an α-elimination reaction or a Lossen-type rearrangement, the $ArSO_3^-$ acting as a good leaving group in both cases.

4. Experimental

4.1. General methods

IR spectra were recorded on a Perkin Elmer 1600 FT/IR spectrophotometer in $CHCl_3$ as the solvent, and reported in cm^{-1}. ^1H NMR and ^{13}C NMR spectra were recorded at 300 and 75 MHz or at 200 and 50 MHz with a Varian XL-300 or Gemini 200 NMR spectrometer, respectively, and reported in δ units. $CDCl_3$ was used as the solvent and $CHCl_3$ as the internal standard. HRMS analyses were performed using a Micromass Q-TOF Micro quadrupole-time of flight (TOF) mass spectrometer equipped with an ESI source and a syringe pump. The experiments were conducted in the positive ion mode. Anhydrous toluene and CH_2Cl_2 were used as such. Molecular sieves (4 Å) (*Fluka*, beads, diameter 1.7–2.4 mm) were activated by heating at 280 °C for 2 h under vacuum. Compounds **2d**,**e**[10] and $TsONH_2$[13] were reported in the literature. *Caution! Nitro alkenes are lachrymatory and allergenic. All the procedures should be carried out in a fume hood by a gloved operator.* $TsONH_2$ *in one case was found to decompose spontaneously and vigorously.*[13a]

4.2. Synthesis of (*E*)-nitro allylic alcohols 2. General procedure

An equimolar solution (10 mmol) of 2-nitroethanol and aldehyde in anhydrous toluene (25 mL) was added under Ar into a round-bottom flask containing previously activated 4 Å molecular sieves (10 g). A catalytic amount of piperidine was added (0.6 mmol). The reactions were kept at reflux and followed by ^1H NMR analysis until disappearance of the aldehyde proton signal (4 h). The crude mixtures were filtered under Ar through plugs of Celite using CH_2Cl_2 as eluent. After solvent removal, the *E* isomers were obtained in the yields reported in Table 1.

*4.2.1. (2E)-4-Methyl-2-nitropent-2-en-1-ol (**2a**)*

Pale yellow oil, 91%. IR: 3594, 1671 cm^{-1}. ^1H NMR: 1.10 (d, J=6.6 Hz, 6H), 2.64–2.78 (m, 1H), 2.97 (br, 1H), 4.50 (s, 2H), 7.01 (d, J=10.7 Hz, 1H). ^{13}C NMR: 22.0 (two C), 27.7, 55.4, 146.1, 148.3. HRMS (ES Q-TOF) calcd for $C_6H_{12}NO_3$ $(M+H)^+$: 146.0817; found: 146.0820.

*4.2.2. (2E)-5-Methyl-2-nitrohex-2-en-1-ol (**2b**)*

Pale yellow oil, 89%. IR: 3596, 1670 cm^{-1}. ^1H NMR: 0.97 (d, J=6.5 Hz, 6H), 1.77–1.91 (m, 1H), 2.20–2.26 (m, 2H), 2.80 (br, 1H), 4.53 (s, 2H), 7.27 (t, J=8.2 Hz, 1H). ^{13}C NMR: 22.1, 22.2, 28.2, 36.4, 55.2, 139.3, 150.3. HRMS (ES Q-TOF) calcd for $C_7H_{14}NO_3$ $(M+H)^+$: 160.0974; found: 160.0981.

*4.2.3. (2E)-2-Nitrooct-2-en-1-ol (**2c**)*

Pale yellow oil, 92%. IR: 3589, 1672 cm^{-1}. ^1H NMR: 0.89 (t, J=7.3 Hz, 3H), 1.20–1.40 (m, 6H), 2.20–2.45 (m, 2H), 2.86 (br, 1H), 4.53 (s, 2H), 7.37 (t, J=7.1 Hz, 1H). ^{13}C NMR: 13.7, 22.2, 27.7, 28.0, 31.2, 55.4, 140.4, 149.9. HRMS (ES Q-TOF) calcd for $C_8H_{16}NO_3$ $(M+H)^+$: 174.1130; found: 174.1122.

4.3. Synthesis of (*E*)-nitro allylic chloridates 3. General procedure

(*E*)-Nitro allylic alcohol (10 mmol) and pyridine (15 mmol) were added at 0 °C to a solution of triphosgene (15 mmol) in anhydrous toluene (50 mL). After stirring (4 h), the mixture was filtered and the solvent removed in vacuo to obtain (*E*)-nitro allylic chloridates **3** in quantitative yields.

*4.3.1. (2E)-4-Methyl-2-nitropent-2-en-1-yl carbonochloridate (**3a**)*

Pale yellow oil, 96%. IR: 1776, 1664 cm^{-1}. ^1H NMR: 1.11 (d, J=6.6 Hz, 6 H), 2.71–2.80 (m, 1 H), 4.61 (s, 2 H), 7.02 (d, J=10.6 Hz, 1 H). ^{13}C NMR: 22.1 (two C), 27.5, 63.4, 145.3, 147.9, 149.4. HRMS (ES Q-TOF) calcd for $C_7H_{11}ClNO_4$ $(M+H)^+$: 208.0377; found: 208.0388.

*4.3.2. (2E)-5-Methyl-2-nitrohex-2-en-1-yl carbonochloridate (**3b**)*

Yellow oil, 94%. IR: 1774, 1665 cm^{-1}. ^1H NMR: 0.99 (d, J=6.6 Hz, 6H), 1.83–1.97 (m, 1H), 2.25 (dd, J_1=6.8 Hz, J_2=1.2 Hz, 2H), 4.54 (s, 2H), 7.37 (t, J=8.1 Hz, 1H). ^{13}C NMR: 22.4 (two C), 28.1, 37.1, 65.4, 141.1, 148.0, 149.4. HRMS (ES Q-TOF) calcd for $C_8H_{13}ClNO_4$ $(M+H)^+$: 222.0533; found: 222.0527.

*4.3.3. (2E)-2-Nitrooct-2-en-1-yl carbonochloridate (**3c**)*

Yellow oil, 97%. IR: 1774, 1659 cm^{-1}. ^1H NMR: 0.90 (t, J=7.3 Hz, 3H), 1.10–1.65 (m, 6H), 2.27–2.41 (m, 2H), 4.54 (s, 2H), 7.36 (t,

J=8.1 Hz, 1H). ^{13}C NMR: 13.7, 22.2, 27.7, 28.2, 31.3, 61.8, 142.2, 147.6, 150.1. HRMS (ES Q-TOF) calcd for $C_9H_{15}ClNO_4$ $(M+H)^+$: 236.0690; found: 236.0688.

4.3.4. *(2E)-2-Nitro-3-phenylprop-2-en-1-yl carbonochloridate (**3d**)*

Orange oil, 91%. IR: 1770, 1655 cm^{-1}. ^{1}H NMR: 4.73 (s, 2H), 7.45–7.62 (m, 5H), 8.27 (s, 1H). ^{13}C NMR: 64.5, 129.3 (two C), 130.1, 130.9 (two C), 131.3, 138.2, 146.5, 150.1. HRMS (ES Q-TOF) calcd for $C_{10}H_9ClNO_4$ $(M+H)^+$: 242.0220; found: 242.0212.

4.3.5. *(2E)-3-(Furan-2-yl)-2-nitroprop-2-en-1-yl carbonochloridate (**3e**)*

Bright-yellow oil, 94%. IR: 1770, 1657 cm^{-1}. ^{1}H NMR: 5.05 (s, 2H), 6.64–6.71 (m, 1H), 7.02–7.10 (m, 1H), 7.75–7.81 (m, 1H), 7.98 (s, 1H). ^{13}C NMR: 63.4, 111.9, 113.6, 122.9, 123.5, 146.6, 148.3, 158.2. HRMS (ES Q-TOF) calcd for $C_8H_7ClNO_5$ $(M+H)^+$: 232.0013; found: 232.0021.

4.4. Synthesis of 1-[(aminooxy)sulfonyl]-4-nitrobenzene ($NsONH_2$)

To a solution of 4-nitrophenylsulfonyl chloride (50 mmol) in 200 mL of THF a solution of hydroxylamine hydrochloride (20 mmol) in 30 mL of H_2O was added at −10 °C. Then, 160 mL of a solution of 10 M $NaHCO_3$ was added dropwise during 45 min. After stirring at −10 °C for additional 2 h, the aqueous phase was extracted with CH_2Cl_2, dried with Na_2SO_4, and the solvents evaporated to give a stable colorless solid that was crystallized from hexane (needles). Mp 142–143 °C (hexane). ^{1}H NMR (DMSO): 8.03–8.06 (m, 2H), 8.36–8.39 (m, 2H), 9.95 (br, 2H). ^{13}C NMR (DMSO): 124.8 (two C), 130.3 (two C), 143.1, 150.7. HRMS (ES Q-TOF) $C_6H_6N_2NaO_5S$ $(M+Na)^+$: 240.9895; found: 240.9897.

4.5. Synthesis of (*E*)-nitro allylic *O*-nosyl hydroxylamines 4. General procedure

To a solution of **3** (20 mmol) in 40 mL of Et_2O, 20 mmol of $NsONH_2$ and 20 mmol of base were added in quick succession. After stirring at rt (see Table 2), the crude mixture was filtered, the solvent evaporated, and the crude product was directly purified by flash chromatography (hexane/ethyl acetate=75:25).

4.5.1. *(2E)-4-Methyl-2-nitro-N-{[(4-nitrophenyl)sulfonyl]oxy}pent-2-en-1-amine (**4a**)*

Colorless oil, 65%. IR: 3438, 1651 cm^{-1}. ^{1}H NMR: 1.20 (d, J=6.5 Hz, 6H), 2.75–2.87 (m, 1H), 4.61 (s, 2H), 4.71 (br, 1H), 7.41 (d, J=11.4 Hz, 1H), 8.10–8.11 (m, 2H), 8.39–8.42 (m, 2H). ^{13}C NMR: 22.1 (two C), 31.1, 54.5, 124.6 (two C), 131.0 (two C), 131.4, 144.0, 146.2, 151.0. HRMS (ES Q-TOF) calcd for $C_{12}H_{16}N_3O_7S$ $(M+H)^+$: 346.0709; found: 346.0712.

4.5.2. *(2E)-5-Methyl-2-nitro-N-{[(4-nitrophenyl)sulfonyl]oxy}hex-2-en-1-amine (**4b**)*

Pale yellow oil, 67%. IR: 3436, 1649 cm^{-1}. ^{1}H NMR: 1.02 (d, J=6.6 Hz, 6H), 1.85–2.02 (m, 1H), 2.37 (t, J=7.3 Hz, 2H), 4.61 (s, 2H), 4.97 (br, 1H), 7.67 (t, J=7.9 Hz, 1H), 8.06–8.11 (m, 2H), 8.38–8.42 (m, 2H). ^{13}C NMR: 22.4 (two C), 28.3, 37.8, 53.7, 124.5 (two C), 130.5 (two C), 131.0, 144.1, 145.9, 151.3. HRMS (ES Q-TOF) calcd for $C_{13}H_{18}N_3O_7S$ $(M+H)^+$: 360.0865; found: 360.0856.

4.5.3. *(2E)-2-Nitro-N-{[(4-nitrophenyl)sulfonyl]oxy}oct-2-en-1-amine (**4c**)*

Colorless solid, 60%. Mp 81–83 °C. IR: 3435, 1650 cm^{-1}. ^{1}H NMR: 0.80 (t, J=7.3 Hz, 3H), 1.09–1.36 (m, 6H), 2.07–2.28 (m, 2H), 4.45 (br, 1H), 4.78 (s, 2H), 7.60 (t, J=8.0 Hz, 1H), 8.02–8.09 (m, 2H), 8.30–8.43 (m, 2H). ^{13}C NMR: 14.4, 23.4 (two C), 29.2, 35.3, 62.9, 124.9 (two C), 129.8 (two C), 130.9, 131.1, 144.5, 151.3. HRMS (ES Q-TOF) calcd for $C_{14}H_{20}N_3O_7S$ $(M+H)^+$: 374.1022; found: 374.1031.

4.6. Synthesis of prop-2-en-1-yl {[(4-nitrophenyl)-sulfonyl]oxy}carbamate (7)

The general procedure for the synthesis of (*E*)-nitro allylic *O*-nosyl hydroxylamines **4** was followed. White solid, 82%. Mp 73–75 °C. IR: 1751 cm^{-1}. ^{1}H NMR: 4.74 (dd, J_1=5.9 Hz, J_2=27.1 Hz, 2H), 5.25–5.40 (m, 2H), 5.70–6.06 (m, 1H), 8.01 (br, 1H), 8.23–8–27 (m, 2H), 8.37–8.41 (m, 2H). ^{13}C NMR: 69.0, 124.1 (two C), 129.8 (two C), 130.6, 142.0, 149.4, 151.1, 152.9. HRMS (ES Q-TOF) calcd for $C_{10}H_{11}N_2O_7S$ $(M+H)^+$: 303.0287; found: 303.0278.

4.7. Synthesis of (2*E*)-5-methyl-*N*-{[(4-methylphenyl)-sulfonyl]oxy}-2-nitrohex-2-en-1-amine (8)

Starting from **3b**, the general procedure for the synthesis of **4** was followed but using 1-[(aminooxy)sulfonyl]-4-methylbenzene ($TsONH_2$) as reagent. Pale yellow oil, 82%. IR: 3436, 1651 cm^{-1}. ^{1}H NMR: 0.97 (d, J=6.7 Hz, 6H), 2.14–2.33 (m, 1H), 2.40–2.48 (m, 2H), 2.45 (s, 3H), 4.54 (s, 2H), 4.98 (br, 1H), 7.33–7.37 (m, 2H), 7.56 (t, J=7.8 Hz, 1H), 7.79–7.85 (m, 2H). ^{13}C NMR: 21.6, 22.2 (two C), 29.2, 38.1, 54.2, 129.6 (two C), 129.8 (two C), 131.7, 140.0, 146.0, 152.0. HRMS (ES Q-TOF) calcd for $C_{14}H_{21}N_2O_5S$ $(M+H)^+$: 329.1171; found: 329.1177.

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Supplementary data

^{1}H NMR spectra of all new compounds synthesized are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.05.016.

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