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An efficient asymmetric synthesis of nitroolefinic lactones with chiral nitroenamines possessing bulky chiral leaving groups

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Abstract: An efficient asymmetric nitroolefination of enolates **4a–c**, **5** afforded multifunctional group nitroolefinic lactones **7a–e** and **8a,b** containing stereogenic quaternary carbon centers using bulky chiral nitroenamines **1a,b–3a,b** as chiral auxiliaries. Studies on the effect of the bulkiness of leaving group showed that bulky nitroenamines **1a,b** gave higher ees and yields than those of the less bulky **2a,b–3a,b**. A possible cyclic transition model is proposed to elucidate the *S* selectivity. © 1997 Elsevier Science Ltd

Introduction

The efficient synthesis of enantiomerically pure multifunctional molecules containing stereogenic quaternary carbon centers has long fascinated organic chemists due to their considerable utilities as chiral blocks for many biologically active natural products such as terpenes, steroids, and alkaloids.[1] A number of reactions,[2] for example, asymmetric Heck reactions, asymmetric Michael reactions, asymmetric alkylations, and Diels–Alder cyclozations, have been employed for the asymmetric synthesis of quaternary carbon centers since the pioneering work of Yamada and his coworkers.[3] Among the methods reported so far,[4] the synthesis of nitroolefinic lactones containing stereogenic quaternary carbon centers in enantiomerically pure form through an asymmetric nitroolefination reaction was attractive because these compounds are multifunctional molecules, readily transformed into other functional groups, and versatile intermediates as chiral building blocks for the synthesis of natural products.[5] Using them as chiral starting materials, the asymmetric synthesis of 5-methyl-8-hydroxybicyclo[3,3,0]-2-octanone, a key intermediate of marine sesquiterpene-(−)-$\Delta^{9(12)}$-capnellene, *Aspidosperma* and *Hunteria* types indole alkaloids, (−)-physostigmine, and diterpenoids have been accomplished.[6] In this asymmetric nitroolefination reaction, (*S*)-2-methoxymethyl- pyrrolidine (SMP) was used as the chiral auxiliary and leaving group. However, a drawback of this asymmetric reaction was that enantioselectivities as well as the yields with some substrates such as α-substituted ketones and γ-lactones were low.[5a,b] Recently, the Node group improved the asymmetric nitroolefination with modified nitroenamines.[7] Here, we wish to report some new progress for this reaction. On the basis of the strategy that increasing the bulkiness of the auxiliary can increase enantioselectivities,[8] and in order to study the effects of the R_1 group in the chiral auxiliary on the reaction, we synthesized bulky chiral nitroenamines **1a**,[9] **1b–3a,b**. Under their induction, the asymmetric nitroolefination of zinc enolates **4a–c**, **5** of α-substituted-γ-lactones, α-methyl-δ-lactone gave a series of multifunctional nitroolefinic lactones **7a–e**, **8a,b** possessing a stereogenic quaternary carbon in high enantioselectivity as well as the yield through an addition–elimination process (Scheme 1).[10] The effects of the bulkiness of the R_1 group, α-substituent on the enolates, the equivalent number of enolates, and the solvent on the asymmetric nitroolefination reactions were studied.

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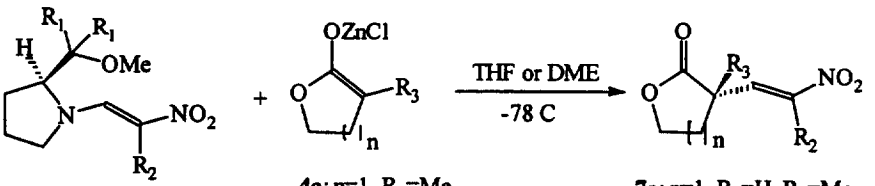


1a: R_1=Ph, R_2=H
1b: R_1=Ph, R_2=Me
2a: R_1=Et, R_2=H
2b: R_1=Et, R_2=Me
3a: R_1=Me, R_2=H
3b: R_1=R_2=Me

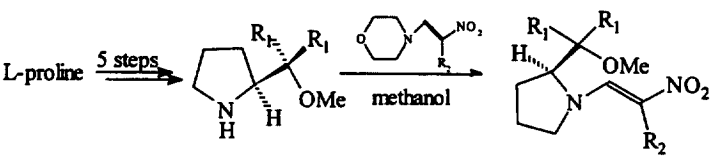
4a: n=1, R_3=Me
4b: n=1, R_3=Et
4c: n=1, R_3=allyl
5: n=2, R_3=Me
6: n=3, R_3=Me

7a: n=1, R_2=H, R_3=Me
7b: n=1, R_2=R_3=Me
7c: n=1, R_2=H, R_3=Et
7d: n=1, R_2=Me, R_3=Et
7e: n=1, R_2=H, R_3=allyl
8a: n=2, R_2=H, R_3=Me
8b: n=2, R_2=R_3=Me

Scheme 1.

Results and discussion

2-(Methoxydisubstituted)methylpyrrolidines **9a–c** were prepared in a five-step sequence, esterification of carbonyl group, *N*-protection, Grignard reaction, methylation of hydroxy group, and deprotection, starting from L-proline.[11] Amine exchange reaction of **9a–c** with morpholino enamines **10a,b**[6a] in an anhydrous methanol solution afforded the desired chiral nitroenamines **1a,b–3a,b** (Scheme 2). All the new nitroenamines were crystalline, therefore, they were obtained in enantiomerically pure form by recrystallization. The *E* configuration of the double bond was determined mainly by NMR data including the chemical shift and the coupling constant.[12]



9a: R_1=Ph
9b: R_1=Et
9c: R_1=Me

10a: R_2=H
10b: R_2=Me

1a,b–3a,b

Scheme 2.

At first DL-morpholino enamines **10a,b** were used to explore the reaction conditions. The reaction of **10a,b** with zinc enolates **4a–c**, **5** gave racemic nitroolefinic lactones **7a–e** and **8a,b**. On the basis of the conditions, chiral nitroenamines **1a,b–3a,b** reacted quickly with 4 equivalents of zinc enolates in tetrahydrofuran (THF) or dimethoxyethane (DME) at −78°C to give chiral **7a–e** and **8a,b** in high enantioselectivity and yield.

The results of the asymmetric nitroolefination are compiled in Table 1. Enantisoelectivities with nitroenamines **1a,b–3a,b** having bulky group (R_1=Ph, Et, Me) were remarkably improved, compared with the previous results using SMP (R_1=H) as a chiral auxiliary.[5a] Both the ees and the yields increased when the bulkiness of the R_1 group was increased (run 1–8–10; 3–9–11; 13–16–18; 15–17–19). The enantioselectivity depended on the bulkiness of R_1 in the chiral nitroenamines, namely, the order was Ph>Et>Me>H, which indicated that increase in the bulkiness of the chiral auxiliary increased the enantioselectivity of the reaction. The bulkiness of α-substituent (R_3) in the enolate too had a little effect on the reaction (run 1–5–7; 3–6): the ee value decreased 20% and the yields decreased ~12% when the bulkiness of R_3 was increased. After many experiments, we found that three equivalents

Table 1. Asymmetric nitroolefination of α-substituted lactone enolates[a]

run	enolate		nitroenamine		solv.	time	prod.	yield[b]	ee[c]	$[\alpha]_D^{18}$
	n	R_3	R_1	R_2		(min)		(%)	(%)	$(CHCl_3)$[d]
1	1	Me	Ph	H	THF	10	7a	98	95	- 35.6
2[e]	1	Me	Ph	H	THF	20	7a	89	86	- 34.3
3	1	Me	Ph	Me	THF	10	7b	96	>99	- 55.6
4[e]	1	Me	Ph	Me	THF	30	7b	89	88	- 54.7
5	1	Et	Ph	H	THF	10	7c	93	78	- 31.8
6	1	Et	Ph	Me	THF	10	7d	88	86	- 29.9
7	1	allyl	Ph	H	THF	10	7e	86	75	- 34.8
8	1	Me	Et	H	THF	5	7a	94	92	- 35.0
9	1	Me	Et	Me	THF	5	7b	94	97	- 56.1
10	1	Me	Me	H	THF	5	7a	90	89	- 35.2
11	1	Me	Me	Me	THF	5	7b	87	94	- 55.5
12	2	Me	Ph	H	DME	15	8a	86	96	- 11.6
13	2	Me	Ph	H	THF	30	8a	95	93	- 10.9
14	2	Me	Ph	Me	DME	15	8b	82	94	- 49.0
15	2	Me	Ph	Me	THF	15	8b	93	>99	- 47.4
16	2	Me	Et	H	THF	10	8a	89	87	- 9.7
17	2	Me	Et	Me	THF	10	8b	91	92	- 48.8
18	2	Me	Me	H	THF	5	8a	84	81	- 8.3
19	2	Me	Me	Me	THF	5	8b	86	87	- 48.2
20	3	Me	no reaction under the above conditions							

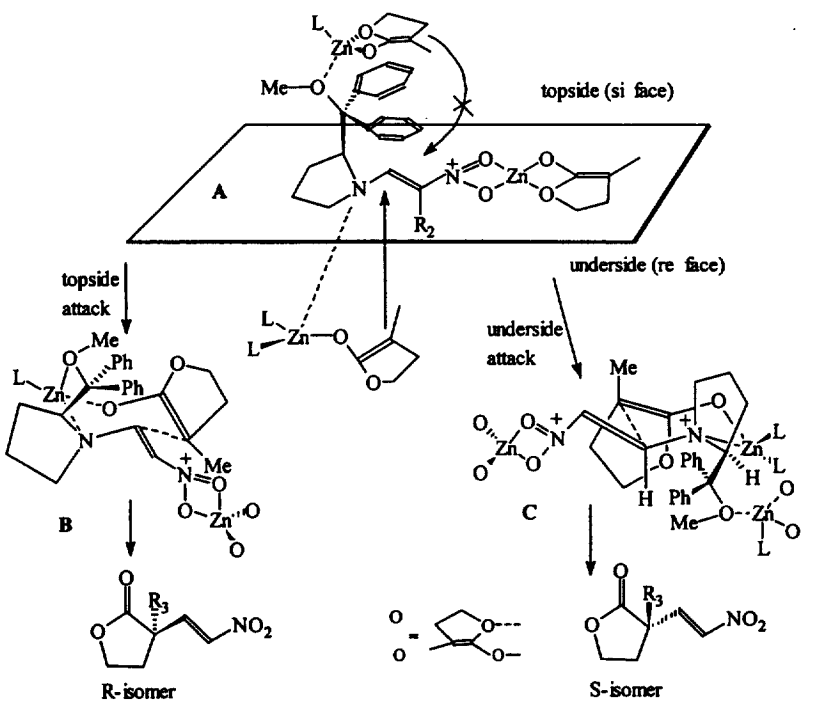
a) 4 equivalents of zinc enolate were used; b) isolated yield; c) determined by 400M Hz ^{1}HNMR with $Eu(hfc)_3$ as chiral shift reagent; d) absolute configuration was S; e) 3 equivalents of zinc enolate were used.

of zinc enolate were essential for completing the reaction and four equivalents of zinc enolate were necessary to obtain high enantioselectivity as well as high yield. Both the ee and the yield rose and the reaction time shortened when the equivalent number of zinc enolates was increased (run 1–4). Studies on the effect of solvent on the reaction showed that the reaction yields using THF as a solvent were higher than those using DME as a solvent (run 12–15). The reaction of α-methyl-ε-lactone enolate **6** with **1a,b**–**3a,b** didn't give the desired products under different conditions (run 20). It was presumed that the zinc enolate **6** was unstable at −78°C.

The *S* configuration of stereogenic quaternary carbon of **7a–e**, **8a,b** was determined by circular dichroism (CD) spectra.[7] The stereochemistry of the double bond was determined by chemical shift and the coupling constant: the chemical shift of olefinic hydrogen in the nitroolefinic lactones was deshielded 1.67 ppm when the double bond was the *E* configuration, and deshielded 0.46 ppm when the double bond was the *Z* configuration, compared with those of the normal olefinic hydrogen. On the basis of the value (δ5.25 ppm) of the normal olefinic hydrogen, the chemical shift of the *E* double bond of nitroolefinic lactones should be 6.92 ppm and that of the *Z* double bond should be 5.71 ppm.[13] The chemical shift of the above products **7b**, **7d**, and **8b** (R_2=Me) was $\delta_{7.0\ ppm}$, proving the *E*

configuration of the double bond. The coupling constant of **7a**, **7c**, **7e**, and **8a** (R_2=H) was 13.5–13.8 Hz, which proved that the stereochemistry of the double bond was the *E* type also.

From the above results, we concluded: (1) the enantioselectivities of the asymmetric nitroolefination reaction with nitroenamines **1a,b–3a,b** were much higher than those with the previous nitroenamines,[5a] and increased when the bulkiness of the chiral auxiliary was increased. The best results were obtained using chiral nitroenamines **1a,b** having a bulkier Ph group, and the steric effect of chiral induced reagents was very important; (2) three equivalents of zinc enolate were essential for completing the asymmetric nitroolefination reaction. A possible cyclic transition model is shown in Scheme 3. Two equivalents of zinc enolate were consumed to form complex **A** by the coordination with nitroenamine. Zinc enolate can attack **A** from the topside or the underside. When it attacks **A** from the topside, two equivalents of zinc enolate seem to be enough to complete the reaction. However, the steric effect of the R_1 group inhibits the approach from the topside.[14] When it attacks **A** from the underside, another zinc enolate has to be consumed. Although it is necessary to consume three equivalents of enolate, the approach of the enolate to **A** was easy.[15] In addition, it is clear that transition state **C** was more stable than transition state **B**, because the zinc chelation involving 5,6-ring system is too strained to form a new carbon–carbon bond.[7] So, zinc enolate attacked mainly from the underside, leading to the *S* isomer, which explains the very high enantio-selectivities of the reaction and why it is necessary to consume three equivalents of zinc enolate.



Scheme 3.

Experimental

All reactions were carried out under an argon atmosphere with dry, freshly distilled solvent under anhydrous condition unless otherwise stated. THF, DME, and ether were distilled from sodium-benzophenone and diisopropylamine was distilled from calcium hydride under argon atmosphere before use. n-Butyllithium (1.55 M in n-hexane) and $ZnCl_2$ solution (0.85 M in Et_2O) were prepared in the normal way.[6a]

Melting points were uncorrected, and recorded on X-4 melting point apparatus; ^{1}H NMR spectra were recorded on Bruker AM80, AM400 MHz instruments in $CDCl_3$ with TMS as an internal standard; IR spectra were recorded on a Nicolet 170SX spectrometer; mass spectra were recorded on VG-ZAB mass spectrometer; optical rotations were taken on a WZZ automatic polarimeter.

General procedure for nitroenamines ***1a,b–3a,b***

To a solution of morpholino nitroenamine **10** (14 mmol) in 40 ml methanol was added dropwise a 7 ml methanol solution of pyrrolidine **9** (7 mmol). The mixture was stirred at room temperature for 5 h. After filtration the residue was washed with methanol (10 ml×5). The filtrate was combined and evaporated to give a red solid, which was purified by flash column chromatography (ethyl acetate:petroleum ether) to give a yellow solid. The resulting solid was recrystallized to give the optically pure nitroenamines.

(E)-1-[(S)-2-(Methoxydiphenyl)methylpyrrolidino]-2-nitroethene ***1a***

Pale yellow crystals, yield 71.3%; m.p. 185°C (EtOH); $[\alpha]_D^{25}$ −473 (c 0.19, $CHCl_3$): ^{1}H NMR ($CDCl_3$) δ: 1.41–1.72 (m, 2H, CH_2), 1.81–2.50 (m, 3H, CH_2, CHN), 2.82 (m, 1H, CHN), 2.97 (s, 3H, CH_3), 4.86 (m, 1H, CHN), 6.59, 8.67 (ABq, 2H, J=10.8 Hz), 7.36–7.42 (m, 10H, Ar); IR (KBr) γ: 1610 (C=N$^+$), 1470, 1312, 1255, 766, 703 cm^{-1}; MS m/z: 338 (M$^+$).

(E)-1-[(S)-2-(Methoxydiphenyl)methylpyrrolidino]-2-nitropropene ***1b***

Pale yellow crystals, yield 80.2%; m.p. 181°C (EtOH); $[\alpha]_D^{25}$ −75 (c 0.18, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 1.41–2.10 (m, 4H, CH_2CH_2), 2.81 (s, 3H, CH_3), 2.40 (m, 1H, CH_2N), 2.92 (s, 3H, CH_3), 3.21 (m, 1H, CH_2N), 4.76 (m, 1H, CHN), 7.38–7.42 (m, 10H, Ar), 8.63 (s, 1H); IR (KBr) γ: 1620 (C=N$^+$), 1440, 1261, 768, 703 cm^{-1}; MS m/z: 352 (M$^+$).

(E)-1-[(S)-2-(Methoxydiethyl)methylpyrrolidino]-2-nitroethene ***2a***

Colourless crystals, yield 78%; m.p. 73°C (Et_2O); $[\alpha]_D^{25}$ −68.7 (c 0.36, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 0.7–1.1 (m, 6H, CH_3×2), 1.2–2.1 (m, 8H, CH_2×2, CH_2CH_2), 3.0–3.2 (m, 5H, CH_3O, CH_2N), 3.86 (m, 1H, CHN), 6.61, 8.71 (ABq, 2H, J=10.8 Hz); IR (KBr) γ: 2999, 1608 (C=N$^+$), 1305, 1240 cm^{-1}; MS m/z: 242 (M$^+$).

(E)-1-[(S)-2-(Methoxydiethyl)methylpyrrolidino]-2-nitropropene ***2b***

Pale yellow crystals, yield 81%; m.p. 118°C (n-hexane); $[\alpha]_D^{18}$ +354 (c 0.34, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 0.78–0.97 (m, 6H, CH_3×2), 1.41–2.01 (m, 8H, CH_2×2, CH_2CH_2), 2.27 (s, 3H, CH_3), 3.21 (s, 3H, CH_3O), 3.47–3.80 (m, 3H, CH_2N, CHN), 8.58 (s, 1H); IR (KBr) γ: 2949, 1618 (C=N$^+$), 1388, 1234 cm^{-1}; MS m/z 256 (M$^+$).

(E)-1-[(S)-2-(Methoxydimethyl)methylpyrrolidino]-2-nitroethene ***3a***

Pale yellow crystals, yield 83.2%; m.p. 81°C (n-hexane); $[\alpha]_D^{17}$ −47.6 (c 0.56, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 1.06, 1.16 (ds, 6H, CH_3×2), 1.76–2.2 (m, 4H, CH_2CH_2), 3.14–3.3 (m, 5H, CH_3O, CH_2N), 3.5–3.7 (m, 1H, CHN), 6.68, 8.66 (ABq, 2H, J=10.8 Hz); IR (KBr) γ: 2929, 1607 (C=N$^+$), 1468, 1304, 1236 cm^{-1}; MS m/z 214 (M$^+$).

(E)-1-[(S)-2-(Methoxydimethyl)methylpyrrolidino]-2-nitropropene ***3b***

Yellow crystals, yield 87.1%; m.p. 86–87°C (n-hexane); $[\alpha]_D^{17}$ +539.8 (c 0.25, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 1.04, 1.11 (ds, 6H, CH_3×2), 1.6–2.1 (m, 4H, CH_2CH_2), 2.26 (s, 3H, CH_3), 3.19 (m, 3H, CH_3O), 3.48–3.7 (m, 3H, CHN, CH_2N), 8.5 (s, 1H); IR (KBr) γ: 2947, 1614 (C=N$^+$), 1385, 1246 cm^{-1}; MS m/z: 228 (M$^+$).

General procedure for asymmetric nitroolefination

Lithium diisopropylamine (LDA) was prepared by adding 1.3 ml n-BuLi in hexane (1.55 M, 2 mmol) to a solution of diisopropylamine (0.29 ml, 2.1 mmol) in dry THF or DME (2.5 ml) at −78°C followed by stirring for 10 min at 0°C. A solution of α-substituted lactone (2 mmol) in THF or DME (4 ml) was added dropwise to the resulting LDA solution at −78°C by syringe. After being stirred for 1 h at −78°C, an equimolar amount of $ZnCl_2$ (0.85 M in Et_2O) was added to the above lithium enolate. To the resulting zinc enolate was added a solution of chiral nitroenamine (0.5 mmol) in 0.4 ml THF (DME) at −78°C. The reaction mixture was performed under the conditions shown in Table 1. After no change was detected by TLC, the reaction mixture was transferred into a solution of 0.5 N HCl–ice by a tube, extracted with Et_2O (15 ml×4), washed with saturated brine, and dried over $MgSO_4$. The resulting residue was purified by column chromatography (silica gel, AcOEt–petroleum ether) to give the desired nitroolefins, which were identified by ^1H NMR, MS, and IR.

2-Methyl-2-[(E)-2-nitroethenyl]-4-butanolide ***7a***

Pale yellow oil, ^1H NMR ($CDCl_3$) δ: 1.52 (s, 3H, CH_3), 2.35 (m, 1H, CH_2), 2.52 (m, 1H, CH_2), 4.45 (m, 2H, CH_2O), 7.16, 7.32 (ABq, 2H, J=13.9 Hz); IR ($CHCl_3$) γ: 771, 531, 352, 1177 cm^{-1}; MS m/z: 172 (M^++1).

2-Methyl-2-[(E)-2-nitroprop-1-enyl]-4-butanolide ***7b***

Pale yellow crystals, m.p. 41°C (n-hexane); ^1H NMR ($CDCl_3$) δ: 1.53 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.47 (m, 2H, CH_2), 4.40 (m, 2H, CH_2O), 7.36 (s, 1H); IR ($CHCl_3$) γ: 1769, 1521, 1331, 1191 cm^{-1}; MS m/z: 186 (M^++1).

2-Ethyl-2-[(E)-2-nitroethenyl]-4-butanolide ***7c***

Pale yellow oil, ^1H NMR ($CDCl_3$) δ: 1.0 (t, 3H, CH_3, J=7.6 Hz), 1.70–1.84 (m, 2H, CH_2), 2.3–2.4 (m, 2H, CH_2), 4.26 (dd, 2H, CH_2O, J=7.6 Hz), 7.15, 7.32 (ABq, 2H, J=13.8 Hz); IR ($CHCl_3$) γ: 1770, 1529, 1352, 1181 cm^{-1}; MS m/z: 186 (M^++1).

2-Ethyl-2-[(E)-2-nitroprop-1-enyl]-4-butanolide ***7d***

Pale yellow oil, ^1H NMR ($CDCl_3$) δ: 1.04 (t, 3H, CH_3, J=7.6 Hz), 1.70–1.84 (m, 2H, CH_2), 2.26 (s, 3H, CH_3), 2.33–2.51 (m, 2H, CH_2), 4.26 (dd, 2H, CH_2O, J=7.6 Hz), 7.33 (s, 1H); IR ($CHCl_3$) γ: 1771, 1528, 1333, 1192 cm^{-1}; MS m/z: 200 (M^++1).

2-Allyl-2-[(E)-2-nitroethenyl]-4-butanolide ***7e***

Pale yellow oil, ^1H NMR ($CDCl_3$) δ: 2.37 (m, 1H, CH_2), 2.51 (m, 1H, CH_2), 2.56 (d, 2H, CH_2, J=7.4 Hz), 4.40 (m, 2H, CH_2O), 5.30 (dd, 2H, $CH{=}CH_2$, J=10.3, 10.9 Hz), 5.76 (m, 1H, $CH{=}CH_2$), 7.12, 7.27 (ABq, 2H, J=13.5 Hz); IR ($CHCl_3$) γ: 1771, 1532, 1352, 1177 cm^{-1}; MS m/z: 198 (M^++1).

2-Methyl-2-[(E)-2-nitroethenyl]-5-pentanolide ***8a***

Pale yellow oil; ^1H NMR ($CDCl_3$) δ: 1.54 (s, 3H, CH_3), 1.92–2.12 (m, 4H, CH_2CH_2), 4.39–4.45 (m, 2H, CH_2O), 7.08, 7.34 (ABq, 2H, J=13.5 Hz); IR ($CHCl_3$) γ: 1723, 1525, 1346, 1265 cm^{-1}; MS m/z: 186=(M^++1).

2-Methyl-2-[(E)-2-nitroprop-1-enyl]-5-pentanolide ***8b***

Colorless needles, m.p. 60°C (n-hexane); ^1H NMR ($CDCl_3$) δ: 1.56 (s, 3H, CH_3), 1.9–2.15 (m, 4H, CH_2CH_2), 2.24 (s, 3H, CH_3), 4.42 (m, 2H, CH_2O), 7.19 (s, 1H); IR ($CHCl_3$) γ: 1730, 1524, 1330, 1153 cm^{-1}; MS m/z: 200 (M^++1).

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