Samarium diiodide-induced reductive coupling of chiral nitrones with methyl acrylate

Juraj Rehák,[a] Lubor Fišera,*[a] Jozef Kožíšek,[b] Lucia Perašínová,[b] Bohumil Steiner,[c] and Miroslav Kóš[c]

[a] *Institute of Organic Chemistry, Catalysis and Petrochemistry, Slovak University of Technology, SK-812 37 Bratislava, Slovak Republic*
[b] *Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology, SK-812 37 Bratislava, Slovak Republic*
[c] *Institute of Chemistry, Slovak Academy of Sciences, 84538 Bratislava, Slovak Republic*
E-mail: lubor.fisera@stuba.sk

Dedicated to Professor Arlette Solladie-Cavallo on the occasion of her 70th birthday

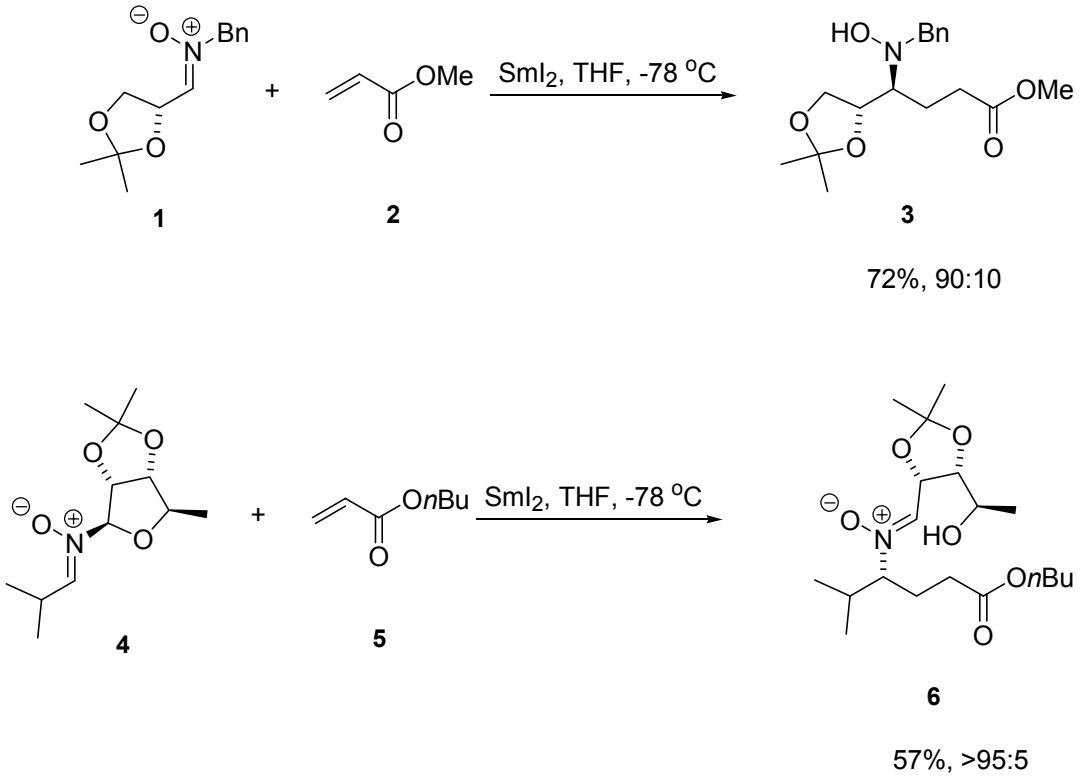
Abstract
D-Lyxose derived nitrone **7** was found to effectively undergo an SmI_2-mediated radical addition to methyl acrylate affording γ-*N*-hydroxylamino ester **8** with high diastereomeric control. The pyrrolidinone **9** was prepared in a single step from **8** involving N-O bond cleavage with Zn/AcOH and subsequent spontaneous cyclization. D-Xylose derived nitrone **10** afforded in the SmI_2-induced coupling with methyl acrylate the γ-*N*-hydroxylamino ester **11** as minor product. The major product the nitrone **12** is formed by unusual reductive deoxygenation of the starting nitrone.

Keywords: Nitrones, samarium diiodide, chiral, hydroxylamino acids

Introduction

Nitrogen-containing heterocycles and their derivatives have broad application in synthetic materials, and biological chemistry, and as a result their synthesis and reactivity is subject of considerable interest. Over the years, nitrones have become important building blocks in organic synthesis.[1] During the last years we have learned know-how about the preparation of optically active nitrone templates for the asymmetric 1,3-dipolar cycloadditions.[2,3] Py, Vallée and coworkers[4a,b] have recently described the first samarium diiodide-induced umpolung of nitrones, which were able to undergo reductive coupling with α,β-unsaturated esters. D-Glyceraldehyde derived nitrone **1** reacted with methyl acrylate in presence of 2 equivalents SmI_2 in THF at –78

°C with the formation of γ-*N*-hydroxylamino esters **3** in fairly good yields, with a 90: 10 diastereomeric ratio (Scheme 1). When chiral nitrones were used as substrates, significant diastereoselectivities were observed in this reactions.[4]



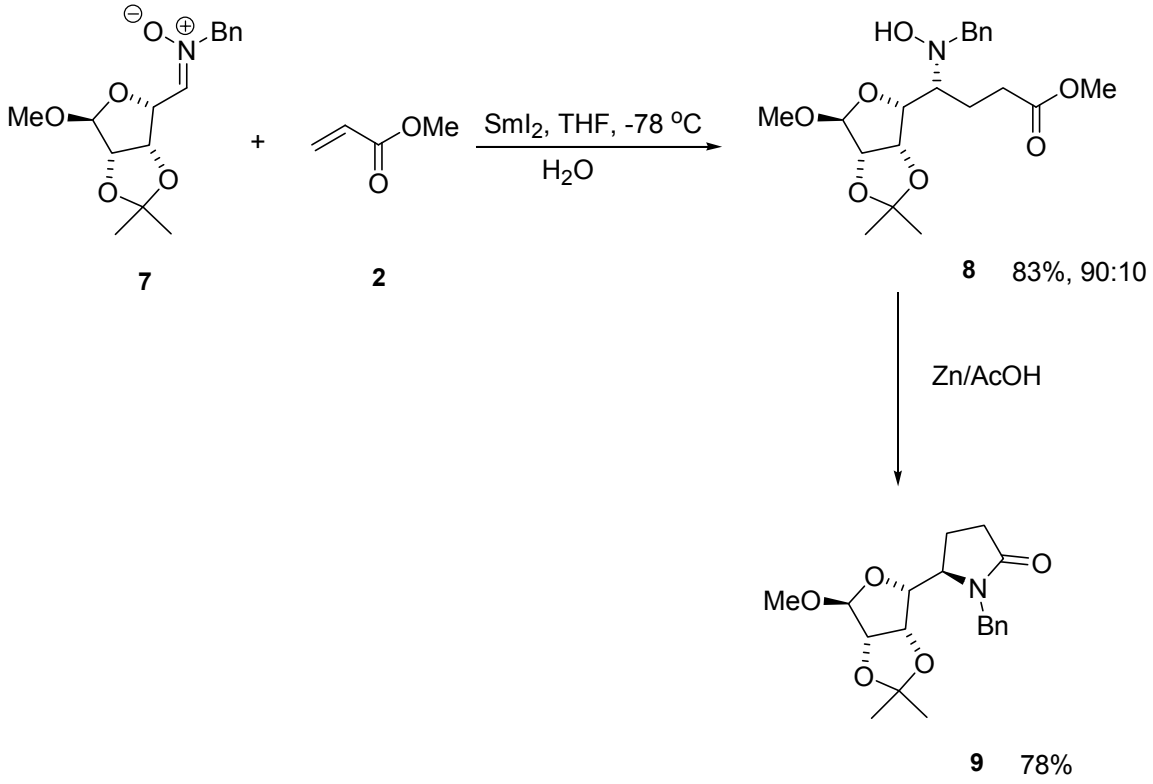
Scheme 1

Moreover, Skrydstrup et al. have found that alkyl nitrones **4** possessing *N*-substituted sugars as chiral auxiliaries effectively undergo an SmI_2-mediated radical addition to *n*-butyl acrylate affording γ-amino acid derivatives **6** with high diastereomeric control (Scheme 1).[5] This methodology opens a direct route to γ-*N*-hydroxylamino esters.[4,5] The derivatives of γ-amino buryric acid (GABA) could be potential, selective and irreversible inhibitors of GABA amino transferase, the enzyme involved in the catabolism of GABA.[6,7] As in principle γ-lactams should be easily obtained from the corresponding γ-*N*-hydroxylamino esters we have paid our attention to the synthesis of biologically important γ-amino acids from the sugar-derived nitrones previously used by us in the chiral cycloadditions.

In this communication we wish to describe the SmI_2-induced coupling of *N*-benzylsubstituted D-xylose and D-lyxose derived nitrones with methyl acrylate under the formation of chiral 4-substituted γ-*N*-hydroxylamino esters.

Results and Discussion

Initial experiments were performed with the D-lyxose derived nitrone **7** that was easily prepared from the corresponding aldehyde following the described procedure.[2i,8] When treated with samarium diiodide[9] (3 equiv.) at –78 °C, nitrone **7** was reduced to an α-amino radical species, that was trapped in situ with methyl acrylate (**2**, 1.4 equiv.). In our attempt to optimize the reaction conditions, we found that the yield of product **8** could be increased to 83% when more SmI_2 (3 equiv. instead of 2 equiv., 62%) was used. The reaction was performed in the presence of water since it has been demonstrated that the addition of water to SmI_2 has a rate accelerating effect on the radical addition to α,β-unsaturated esters.[4b] A new C-C bond was thus formed to afford γ-*N*-hydroxylamino ester **8** in good yield (83%) and high diastereoselectivity (90: 10). The relative configuration at the new stereogenic center in **8** could not be assigned at this stage; however it was deduced from the structure of a cyclized derivative **9** (Scheme 2). Considering the well-known propensity of *N*-hydroxylamines to be reduced to amines, we have prepared pyrrolidinone **9** in a single step from **8** involving N-O bond cleavage with Zn/AcOH and subsequent spontaneous cyclization. The newly created stereogenic center in **8** was assigned the (*R*)-configuration on the basis of a single crystal X-ray structure of the pyrrolidinone **9** (Fig. 1). The formation of major anti isomer **8** is consistent with a β-chelated transition state suggested by previously work.[4,5]



7 **2** **8** 83%, 90:10

9 78%

Scheme 2

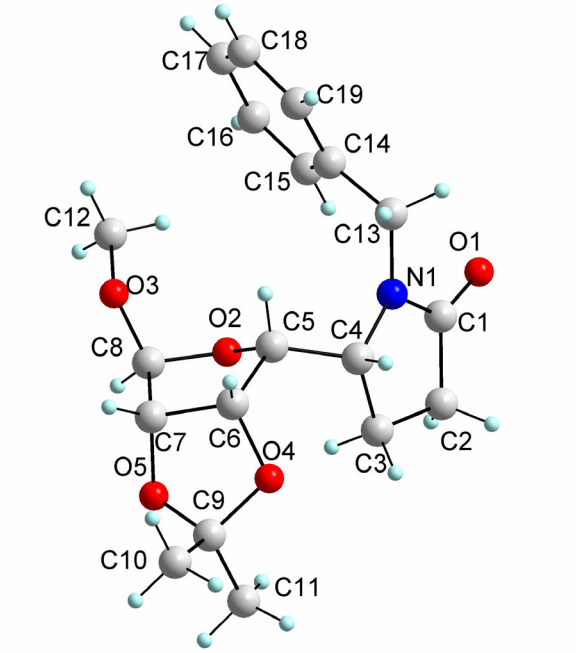
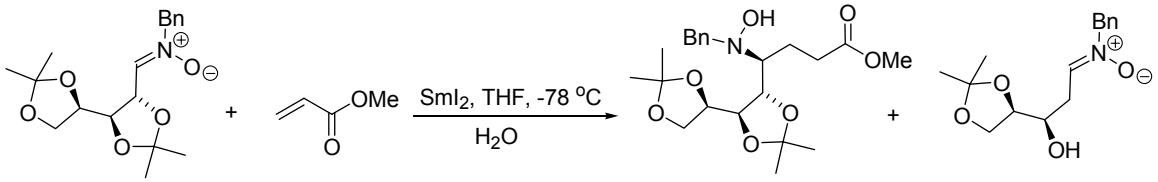


Figure 1. Structure determination of compound **9** by X-ray diffraction with crystallographic numbering and 30% ellipsoids.

When D-xylose derived nitrone **10**[2a] was treated with 3 equivalents of samarium diiodide in THF at low temperature with methyl acrylate was less rewarding in its coupling reaction, the expected γ-*N*-hydroxylamino ester **11** was obtained as a minor product in low yield (19%, Scheme 3). On the other hand the reaction is completely diastereoselective within the limits of ^{1}H NMR analysis of the crude product. This observation is in good agreement with the studies realized by Py and Skrydstrup.[4,5]



Scheme 3

The major product was surprisingly not the ester **11** but the nitrone **12**. The stereochemical arrangement and absolute configuration of this unexpected product was subsequently confirmed by X-ray-crystallographic analysis (Figure 2 and experimental section). Its origin can be explained by very unusual and as yet not described deoxygenation of the starting α-

alkoxysubstituted nitrone **10** by SmI_2-induced reduction. The analogous deoxygenation was described in the reduction of α-alkoxy ketones at –78 °C on addition of the substrate in THF/MeOH to a solution of SmI_2 in THF.[10] For example; benzoin methyl ether is converted to deoxybenzoin quantitatively. It was also found that small-membered ring ethers can be cleaved with SmI_2.[11] A relevant precedent exists also in the SmI_2-promoted deoxygenation of carbohydrate-derived to α,β-unsaturated esters.[12]

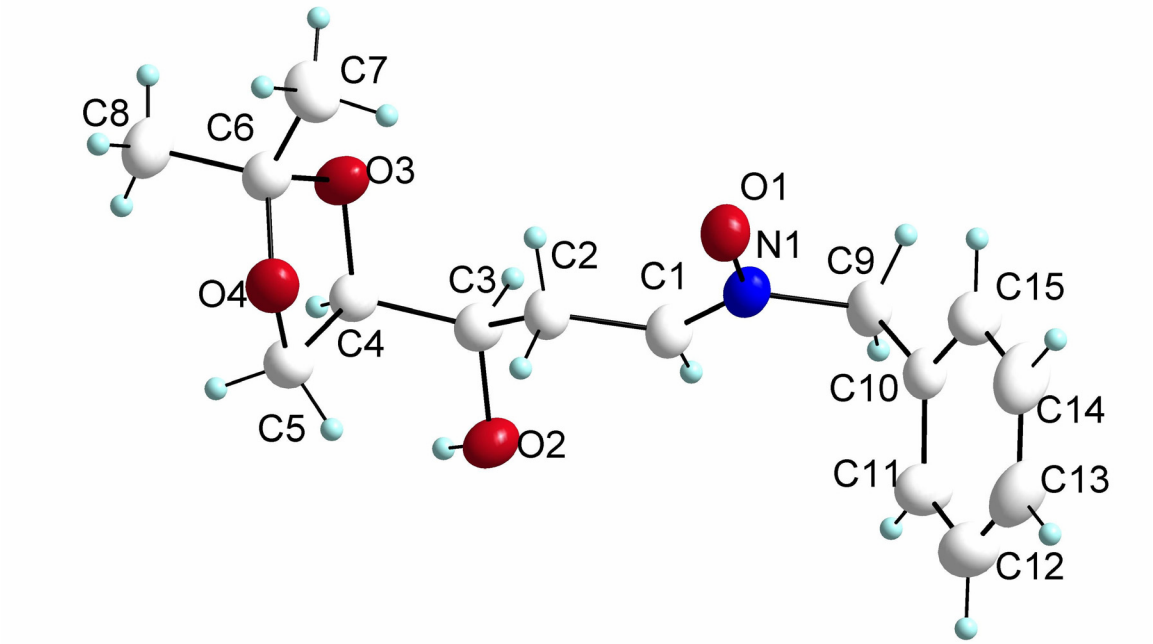


Figure 2. Structure Determination of compound **12** by X-ray diffraction with crystallographic numbering and 30% ellipsoids.

In conclusion, the reductive cross-coupling of chiral sugar derived nitrones with alkyl acrylates allows the stereoselective synthesis of 4-substituted γ-*N*-hydroxylamino esters and their reduction provides entry to the optically active pyrrolidinones possessing structural similarities to the HIV inhibitors. This method opens a novel, short, and general route for the synthesis of biologically important trihydroxy- and tetrahydroxysubstituted γ-amino acids and pyrrolidinones. We are currently extending the scope of this synthetically useful reaction to various chiral sugar derived nitrones.

Experimental Section

General Procedures. Melting points were determined using a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VRX-300 in $CDCl_3$ solution using TMS as internal standard. Chemical shifts are reported in ppm. IR spectra were

recorded on FTIR NICOLET MAGNA 750 instrument. Specific rotations [α] were measured on an IBZ Messtechnik Polar-LμP polarimeter at the sodium D line (589 nm) using a 1 dm cell. Elemental analyses were conducted using the Fisons EA 1108 Analysator. Nitrones **7**[2i] and **10**[2a] were prepared from the corresponding aldehyde by the reaction with *N*-benzylhydroxylamine according to the procedure already described.[8] TLC analysis was carried out using Merck TLC silica gel 60 F254 aluminium sheets and visualized by UV light or oxidized in KMnO4 solution ($NaOH/KMnO_4/K_2CO_3/H_2O$ 1:8:80:1200).

General procedure for preparation of 8, 11 and 12

A stirred and carefully deoxygenated solution of the corresponding nitrone (0.5 mmol) in dry THF (5 mL) was cooled to –78 °C under argon. Methyl acrylic ester (**2**) and water were degassed by boiling under a stream of argon for 20 min. Methyl acrylic ester (0.7 mmol), water (4 mmol) and solution of SmI_2 (15 mL of 0.1 M in THF, 1.5 mmol) were then added. The temperature was kept at –78 °C until the reaction was judged to be complete by TLC (1.5 h for **7** and 2 h for **10**), whereupon a saturated aqueous solution of $Na_2S_2O_3$ (40 mL) was added. The mixture was extracted with EtOAc (4 x 30 mL) and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in rotatory evaporator. The residue was purified by silica gel column chromatography using AcOEt/hexanes (1:2).

Methyl 4-(*R*)-(*N*-benzyl-*N*-hydroxylamino)-4-(2,3-*O*-isopropylidene-1-*O*-methyl-α-D-lyxo-tetrafuranosyl) butanoate (8). Colorless oil (82%); R_f: 0.67 (hexanes/EtOAc 50:50, $KMnO_4$, yellow spot); ^{1}H NMR (300 MHz) δ: 7.32-7.20 (m, 5H), 5.30-5.20 (bs, 1H), 4.85 (s, 1H), 4.84-4.80 (dd, 1H, *J* = 6.0, 4.0 Hz), 4.56-4.54 (d, 1H, *J* = 6.0 Hz), 4.31-4.28 (dd, 1H, *J* = 8.0 Hz, *J* = 4.0 Hz), 3.95-3.85 (2 x d, 2H, *J* = 14 Hz), 3.55 (s, 3H), 3.21 (s, 3H), 3.25-3.15 (m, 1H), 2.55-2.45 (m, 2H), 2.20-2.03 (m, 2H), 1.42 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (75 MHz) δ: 175.7, 138.8, 129.0, 128.0, 126.9, 112.1, 105.9, 85.1, 80.1, 77.1, 63.7, 61.2, 54.3, 51.5, 32.1, 26.1, 24.9, 23.6; IR (KBr, cm^{-1}), ν: 3449, 3030, 2989, 2949, 2835, 1736; Anal. Calcd for $C_{20}H_{29}NO_7$: C, 60.74; H, 7.39; N, 3.54. Found: C, 60.63; H, 7.54; N, 3.17.

Methyl 4-(*R*)-(*N*-benzyl-*N*-hydroxylamino)-4-(1,2:3,4-di-*O*-isopropylidene-D-xylo) butanoate (11). Yellow crystals (19%); mp 83-86 °C; R_f: 0.81 (hexanes/EtOAc 1:1, $KMnO_4$, yellow spot); $[\alpha]_D^{25}$ = –25.2 (c= 0.5 mol.dm^{-3}, $CHCl_3$); ^{1}H NMR (300 MHz) δ: 7.36-7.25 (m, 5H), 5.37-5.28 (bs, 1H), 4.46-4.40 (dd, 1H, *J* = 5.0, 7.8 Hz), 4.28-4.21 (m, 1H), 4.12-3.84 (m, 5H), 3.65 (s, 3H), 2.85-2.78 (m, 1H), 2.69-2.42 (m, 2H), 2.31-1.82 (m, 2H), 1.43 (s, 6H), 1.39 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (75 MHz) δ: 174.5, 137.8, 129.6, 128.3, 127.3, 109.6, 109.5, 78.9, 76.1, 75.3, 65.8, 65.3, 59.9, 51.5, 31.4, 27.2, 27.0, 26.1, 25.7, 21.0; IR (KBr, cm^{-1}), ν: 3432, 2986, 2948, 2902, 2889, 2834, 1737, 1708; Anal. Caldc for $C_{22}H_{33}NO_7$: C, 62.39; H, 7.85; N, 3.31. Found: C, 62.68; H, 7.88; N, 3.09.

(*Z*)-*N*-(1,2-Dideoxy-4,5-*O*-isopropylidene-3-hydroxy-D-xylo-1-ylidene)-benzylamine-*N*-oxide (12). Yellow crystals (39%); mp 110-112 °C; R_f: 0.02 (hexanes/ AcOEt 1:1, $KMnO_4$, yellow spot); $[\alpha]_D^{25}$ = 12.6 (c= 0.45 mol.dm^{-3}, $CHCl_3$); ^{1}H NMR (300 MHz) δ: 7.48-7.30 (m, 5H), 7.01-6.94 (t, 1H, *J* = 5.9 Hz), 4.9 (s, 2H), 4.06-3.97 (m, 2H), 3.89-3.79 (m, 2H), 2.68-2.63

(t, 2H, *J* = 5.9 Hz), 1.41 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (75 MHz) δ: 137.4, 132.4, 129.3, 129.1, 128.9, 109.5, 78.4, 70.2, 69.0, 65.6, 30.9, 29.5, 25.1; IR (KBr, cm^{-1}), ν: 3416, 3141, 3030, 2980, 2936, 2911, 2841, 1610; Anal. Calcd for $C_{15}H_{21}NO_4$: C, 64.50; H, 7.58; N, 5.01. Found: C, 64.82; H, 7.53; N, 4.68.

Preparation of 1-benzyl-5-(*R*)-(2,3-*O*-isopropylidene-1-*O*-methyl-α-D-lyxo-tetrafuranosyl)-pyrrolidin-2-one (9). Hydroxylamino ester **8** (0.313 g, 0.791 mmol) was dissolved in mixture AcOH/THF/H_2O (50 mL, 2:1:1). Zinc dust (0.308 g, 4.74 mmol) was added and reaction mixture was stirred at 75 °C for 2.5h. Reaction was controlled with TLC. Saturated solution $NaHCO_3$ was added after reaction and mixture was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in rotatory evaporator. The resulting mixture was separated by chromatography on a silica gel using EtOAc/toluene (1:1). Product was obtained as colorless crystals in 78% yield. mp 156-158 °C; R_f: 0.45 (hexanes/EtOAc 1:4, $KMnO_4$, yellow spot); $[\alpha]_D^{25}$ = 31.4 (c = 0.5 mol.dm^{-3}, $CHCl_3$); ^{1}H NMR (300 MHz) δ: 7.33-7.21 (m, 5H), 4.95-4.19 (2 x d, 2H, *J* = 15.1 Hz), 4.85 (s, 1H), 4.53-4.48 (m, 2H), 3.95-3.92 (dd, 1H, *J* = 5.2, 2.8 Hz), 3.89-3.84 (m, 1H), 3.26 (s, 3H), 2.64-2.33 (m, 2H), 2.32-2.02 (m, 2H), 1.42 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (75 MHz) δ: 176.0, 137.1, 128.4, 127.7, 127.2, 112.5, 106.5, 85.1, 79.5, 78.5, 56.3, 54.6, 44.8, 29.9, 25.6, 24.3, 21.5; IR (KBr, cm^{-1}), ν: 3011, 2986, 2962, 2938, 2904, 2893, 1668; Anal. Calcd for $C_{19}H_{25}NO_5$: C, 65.69; H, 7.25; N, 4.03. Found: C, 65.56; H, 7.39; N, 3.68.

X-Ray structure determination of 9 and 12.[13-15] The suitable crystals were obtained by slow crystallization from a mixture of ethyl acetate and hexane at room temperature. The crystallographic data were obtained by GEMINY R diffractometer. The relevant crystallographic data and structure refinement are given in Table 1 and Table 2. The structure was solved by direct methods and refined by anisotropic full-matrix least-squares technique. Perspective view and the numbering of the atoms are depicted in Figure 1 and Figure 2. The hydrogen atoms were refined isotropically in idealized positions riding on the atom to which they are attached. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The corresponding deposition numbers are CCDC 663043 and CCDC 663044. Copies of the data can be obtained free of charge on request to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Tel.: +44-1223-336408, Fax: +44-1223 336-033).

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Table 1. Crystal and experimental data for compound **9**

Empirical formula	C_{19} H_{25} N_1O_5
Formula weight	347.406
Temperature, *T* (K)	295 K
Wavelength, λ (Å)	0.71093
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions(Å)	a = 5.913(1) α = β = γ = 90°
	b = 15.861(3)
	c = 18.991(4)
Unit-cell volume, V (Å^3)	1781(1)
Formula units per unit cell, Z	4
Calculated density, D_x (g cm^{-3})	1.3
Absorption coefficient, μ (mm^{-1})	0.093
F(000)	744
Crystal size (mm)	0.630 x 0.085 x 0.050
Diffractometer	Oxford Diffraction Gemini R CCD diffractometer
Theta range for data collection, (°)	3.21 - 28.73
Index ranges	$-7 \le h \le 7$, $-19 \le k \le 19$, $-23 \le l \le 23$
Reflections collected	3764
Independent reflections [I>2σ(I)]	1635 (Rint = 0.0323)
Absorption correction	Empiric Psi-scan
Max. and min. transmission	0.8982 and 1.0668
Refinement method	Full-matrix least-squares on F^2
Data / parameters	3625 / 227
Goodness-of-fit (all)	0.698
Final R indices [I>2σ(I)]	$R1$ = 0.0329, w$R2$ = 0.0490
R indices (all data)	$R1$ = 0.1199, w$R2$ = 0.0550
Largest diff. peak and hole	0.104 and -0.101 (e Å^{-3})

Table 2. Crystal and experimental data for compound **12**

Empirical formula	C_{15} H_{22} N_1O_4
Formula weight	280.34
Temperature, *T* (K)	295 K
Wavelength, λ (Å)	0.71093
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions(Å)	a = 5.742(1) α = β = γ = 90°
	b = 9.989(3)

	c = 26.312(6)
Unit-cell volume, V (Å^3)	1509.25(6)
Formula units per unit cell, Z	4
Calculated density, D_x (g cm^{-3})	1.23
Absorption coefficient, μ (mm^{-1})	0.089
F(000)	604
Crystal size (mm)	0.37 x 0.13 x 0.05
Diffractometer	Oxford Diffraction Gemini R CCD diffractometer
Theta range for data collection, (^{o})	4.1 - 26.4
Index ranges	-7 ≤ h ≤ 7, -12 ≤ k ≤ 12, -32 ≤ l ≤ 32
Reflections collected	9915
Independent reflections [I>2σ(I)]	1344 (Rint = 0.045)
Absorption correction	Empiric Psi-scan
Max. and min. transmission	1.0000 and 0.9665
Refinement method	Full-matrix least-squares on F^2
Data / parameters	3073 / 186
Goodness-of-fit (all)	1.038
Final R indices [I>2σ(I)]	R1 = 0.0473, wR2 = 0.1315
R indices (all data)	R1 = 0.0730, wR2 = 0.1601
Extinction coefficient	0.0082(8)
Largest diff. peak and hole	0.230 and -0.151 (e Å^{-3})

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