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Indium-mediated allylation and Reformatsky reaction on glyoxylic oximes under ultrasound irradiation

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ABSTRACT

A novel and more convenient method for the indium-promoted allylation of glyoxylic oximes based on the use of ultrasonic waves is reported. A similar procedure was used to develop the first example reported in the literature of an indium-mediated Reformatsky reaction on oxime ethers.

1. Introduction

The Mannich reaction, namely the nucleophilic addition to C=N bonds, is well recognized as a fundamental C–C bond forming reaction for the preparation of useful β-amino carbonyl compounds and β-lactams [1].

Aldimines are the most common electrophiles for the Mannich reaction, despite being unstable and very prone to hydrolysis. Oximes and oxime ethers are more attractive starting materials for the synthesis of amino compounds due to their easier preparation and inherently higher stability, especially for aliphatic aldoximes derived from enolizable aldehydes, and because the N–O bond of alkoxyamines is much easier to cleave than the amine C–N bond [2].

However, if aldimines reacting as electrophiles usually require a Lewis acid or activating agent to prevent the strongly basic nucleophiles deprotonating the α-position and forming azaenolates [3], nucleophilic additions to oximes and oxime ethers have proven even more troublesome due to the increased acidity of the α-protons, giving rise to side products such as aziridines [4]. Furthermore, the lower electrophilicity of the iminyl bond of oximes, in comparison to imines, requires more forcing conditions to allow nucleophilic addition to occur. For example allyl boronates can be added to aldimines but aldoximes require prolonged reaction times and elevated temperatures [5]. To achieve even moderate yields of *N*-alkyl *O*-alkyl hydroxylamines from oxime ethers it is demanded the use of unstabilized organometallics (typically RLi or RMgX) [6] often in the presence of a Lewis acid [7].

The harsh conditions required for the addition of classical organometallic reagents to the C–N double bond of oxime ethers, which are incompatible with many functionalities, prompted the investigation of organometallic reagents that could be added to oximes under single electron transfer (SET) conditions.

Indium is an ideal reagent for mediating C–C bond formation in SET reactions, due to its very low first ionization energy. This property, together with its stability to oxygen and water, prompted exhaustive studies focused on the chemistry of indium with organic molecules in the past several years [8].

Although indium mediated allylations of imines are known (aldimines [9], aryl/tosyl hydrazones and aldonitrones [10] all react) examples of additions to oximes, oxime esters or oxime ethers are scarcer, mainly due to their lower electrophilicity. However, glyoxylic acid oximes, which combine enhanced electrophilic character and an additional chelation site, are more reactive [11]. For example, glyoxylic acid oximes [12] were used in indium mediated allylation reactions. Compared to allylzinc reagents [13], allylindium reagents add smoothly to oxime esters in higher yields, but long reaction times and the aid of an acid are usually needed.

Indium-mediated intermolecular alkyl radical additions to glyoxylic imine derivatives were also described [14]. However, no examples of indium-mediated Reformatsky addition to glyoxylic oximes have been reported to date. In fact, to the best of our knowledge, there is only one example in the literature of a Mannich-type Reformatsky reaction between simple esters and oxime

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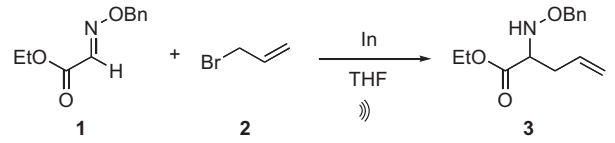
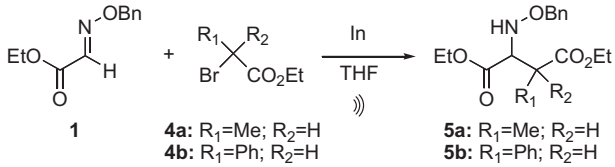
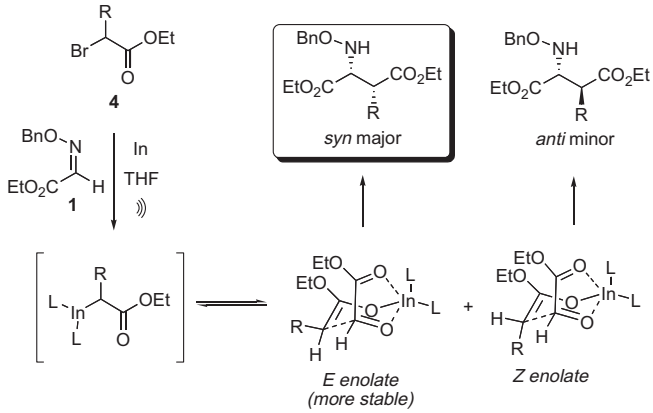


Scheme 1. Indium-mediated reaction of glyoxylic oxime **1** and allyl bromide **2** under sonication.



Scheme 2. Indium-mediated reaction of glyoxylic oxime **1** and 2-bromoesters **4** under sonication.



Scheme 3. Reaction pathway.

ethers, which is mediated by $TiCl_4$ [15]. This can be attributed to the low reactivity of oxime derivatives under Reformatsky reaction conditions.

In recent years, ultrasound has been employed in various chemical transformations with considerable enhancement in rate and yield, and in several cases facilitates organic transformations which otherwise require drastic conditions of temperature and pressure, or even unachievable reactions [16]. The SET reactions promoted by metallic reagents are specially improved by the use of sonication in terms of both reactivity and yields. Besides the activation due to cavitation, shock waves propel metals at really fast speeds, which can collide with other metals thus modifying significantly electron transfer processes. Then, the important acceleration effect of sonic waves was assigned in part to the mechanical erosion of the metal surface, resulting in its activation [17]. Accordingly, sonication has been widely used in indium mediated reactions, including both allylations [18] and Reformatsky reactions [19].

In connection with our interest in indium chemistry [20] and keeping in view the advantages of ultrasonic irradiation in SET reactions promoted by indium, we decided to investigate the effect of the ultrasonic waves in indium mediated additions to glyoxylic oximes.

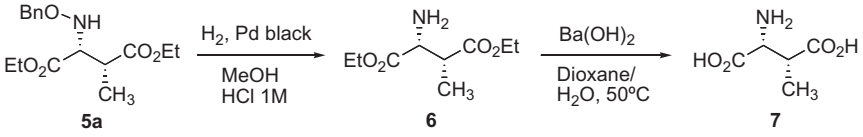
2. Results and discussion

Firstly, indium-mediated allylation of glyoxylic oxime **1** was investigated. The best results were achieved with solutions of 1 equiv. of oxime **1**, 1 equiv. of indium and 1.5 equiv. of allyl bromide in THF under sonication. After 4 h the corresponding allyl amine was obtained in 89% yield (Scheme 1).

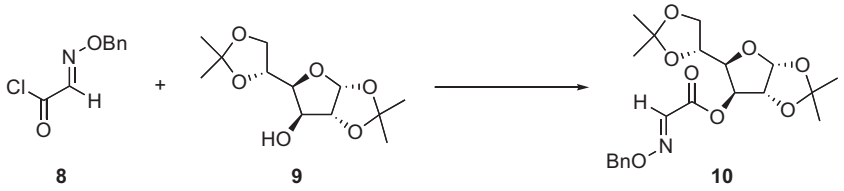
Encouraged by these excellent results, we investigated next the indium-mediated Reformatsky addition of bromoesters to glyoxylic oxime **1**. Sonication of mixtures of oxime **1**, indium powder and ethyl 2-bromopropionate **4a** in THF at room temperature for 6 h allowed to obtain compound **5a** in 81% yield as a 3:2 mixture of *syn*/*anti* isomers. Similarly, reaction of oxime **1** and ethyl 2-bromophenylacetate **4b** provided the adduct **5b** in 88% yield as a 2:1 mixture of *syn*/*anti* isomers (Scheme 2).

It is noteworthy that no reaction occurred in the absence of sonication. Thus, ultrasonic irradiation was in this case necessary to complete the reaction.

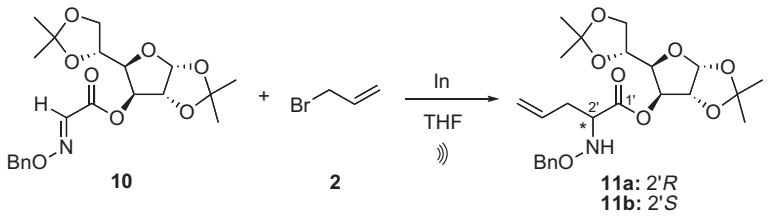
The observed diastereoselectivity of **5a** and **5b** could be explained considering a mechanism involving discrete indium species as intermediates [21] and is in accordance with a chair-like transition state in which the carbonyl of the ester moiety is chelating the indium atom (Scheme 3). The predominant formation of the *syn* isomers over the *anti* isomers, which was confirmed by the transformation of **5a** in methyl aspartic acid and comparison with the reported data for this compound (Scheme 4), suggests the participation of the stereochemically preferred transient *E* enolates [22] in the transition state.



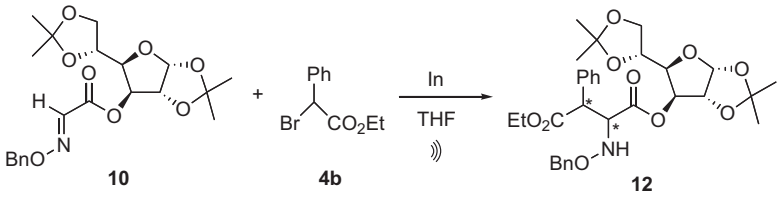
Scheme 4. Preparation of methylaspartic acid from **5a**.



Scheme 5. Preparation of chiral glucose derived glyoxylic oxime **10**.



Scheme 6. Indium-mediated reaction of chiral glyoxylic oxime **10** and allyl bromide **2** under sonication.



Scheme 7. Indium-mediated reaction of chiral glyoxylic oxime **10** and ethyl 2-bromophenylacetate **4b** under sonication.

The satisfactory results obtained in the preparation of racemic compounds **3** and **5a–b** prompted us to test the usefulness of this methodology for the synthesis of enantiopure derivatives using as starting materials chiral oxime ethers.

For this purpose, chiral glucose derived glyoxylic oxime **10** was easily prepared from commercially available diaceton-D-glucose **9** (Scheme 5).

Indium-mediated allylation of **10** in THF under sonication afforded a separable mixture of the epimeric *O*-benzyl hydroxylamines **11a** and **11b** in a ratio 4:3 in 41% and 31% yield, respectively (Scheme 6).

On other hand, indium mediated Reformatsky addition of ethyl 2-bromophenylacetate **4b–10** was carried out in THF under sonication. The elongation-chain product **12** was obtained in 34% yield as a 24:1:1 mixture of isomers. According to the proposed mechanism (Scheme 3), the formation of the *anti* isomer with configuration (2′*R*,3′*R*) would be favoured (Scheme 7).

3. Conclusions

We have developed a more efficient procedure for the indium-mediated allylation of glyoxylic oximes using ultrasonic waves. Under these conditions, the reaction is faster and more efficient than the previously reported procedure and does not need the aid of an acid.

Moreover, we have reported the first example of an indium-mediated Reformatsky reaction on glyoxylic oximes in which sonication has proven to be essential. Despite the usefulness of the obtained products as intermediates in the synthesis of peptidic isosters, to the best of our knowledge, there is only one example in the literature of a Mannich-type Reformatsky reaction between simple esters and oxime ethers [15].

The reaction was also successful with a chiral sugar-derived glyoxylic oxime, thus opening an interesting research field: the development of asymmetric versions of this Reformatsky reaction.

Work is in progress in the laboratory aimed at the preparation of chiral enantiopure peptidic isosters using this novel Reformatsky reaction on oxime ethers under sonication.

4. Experimental

Reactions under sonication were carried out on a Selecta cleaning bath (320 W) at 20 °C. Nuclear magnetic resonance spectra were recorded on a Varian Mercury plus 200 spectrometer. Mass spectra were obtained on a Hewlett Packard 5988A mass spectrometer. Thin layer chromatography (TLC) was performed using Merck GF-254 type 60 silica gel and ethyl acetate/hexane mixtures as eluants; the TLC spots were visualized with Hanessian mixture. Column chromatography was carried out using Merck type 9385 silica gel.

4.1. Ethyl 2-(benzyloxyamino)-pent-4-enoate (3)

cTo a suspension of indium powder (57.4 mg, 0.5 mmol) in THF (1 mL) was added allyl bromide **2** (0.07 mL, 0.75 mmol) and the mixture was sonicated for 10 min. The glyoxylic oxime **1** (103.6 mg, 0.5 mmol) was added and sonication was continued for a further 4 h. The reaction mixture was neutralized with saturated aqueous sodium hydrogen carbonate, diluted with water (10 mL) and extracted with ether (3 × 25 mL). The combined organic layers were dried over magnesium sulfate, filtered and the solvent was evaporated *in vacuo*. The residue was purified by flash column chromatography (ethyl acetate/hexane 1:8) to afford ethyl 2-(benzyloxyamino)-pent-4-enoate (0.11 g, 89%). R_f = 0.29 (ethyl acetate/hexane 1:8). ν_{max} (neat)/cm^{-1} 3350 (NH), 3032 (CH), 2982 (CH), 1734 (CO). ^{1}HNMR (300 MHz, $CDCl_3$): 1.28 (m, 3H, $-CH_3$), 2.34 (m, 2H), 7.33 (5H, s, 5× ArH), 3.68 (t, 1H, *J* 6.7 Hz), 4.09–4.12 (h, 2H), 4.71 (ABq, 2H, $-OCH_2Ph$), 5.12 (m, 2H), 5.69 (m, 1H), 5.91 (1H, bs, 1H, NH). ^{13}CNMR (75 MHz, $CDCl_3$): 14.1 ($-CH_3$), 33.8 (–CH–), 60.9 ($-CH_2-$), 63.1 (–CH–), 76.1 ($-CH_2-$), 118.0 ($-CH_2-$), 127.7, 128.3, 128.5 (5× –CHAr–), 133.0 (–CH–), 137.6 (–CAr–), 173.0 (C=O). *m/z* (CI) 250 [$(MH)^+$, (61%)]; HRMS calculated for $C_{14}H_{20}NO_3$: 250.1443. Found: 250.1449.

4.2. General procedure for the reaction of ethyl 2-bromoalkanoates 4 and glyoxylic oxime 1

To a suspension of indium powder (0.5 mmol) in THF (1 mL) was added the corresponding ethyl 2-bromoalkanoate (0.75 mmol) and the mixture was sonicated for 10 min. The oxime **1** (0.5 mmol) was added and sonication was continued for a further 6 h. The reaction mixture was neutralized with saturated aqueous sodium hydrogen carbonate, diluted with water (10 mL) and extracted with ether (3 × 25 mL). The combined organic layers were dried over magnesium sulfate, filtered and the solvent was evaporated *in vacuo*. The residue was purified by flash column chromatography

with mixtures of ethyl acetate/hexane as eluents to give the pure compounds **5**.

4.3. Diethyl 2-(benzyloxyamino)-3-methylsuccinate (5a)

Purification by flash column chromatography (EtOAc/Hex 1:9 1:8) to yield **5a** (125.3 mg, 81%). Data for the *syn* isomer: R_f = 0.28 (ethyl acetate/hexane 1:9). ν_{max} (neat)/cm^{-1} 3251 (NH), 1742 (CO), 1739 (CO). ^{1}HNMR (300 MHz, $CDCl_3$): 1.20–1.29 (m, 9H, 3× –CH_3), 3.34–3.36 (m, 1H, H-3), 4.07–4.28 (m, 5H), 4.59 (ABq, 2H, –OCH_2Ph), 5.72 (bs, 1H, –NH–), 7.19–7.32 (m, 5H, Ar–H). ^{13}CNMR (75 MHz, $CDCl_3$): 11.5 (–CH_3), 14.1 (–CH_3), 34.2 (–CH–), 61.5 (–CH_2–), 61.7 (–CH_2–), 65.7 (–CH–), 76.7 (–CH_2–), 128.1, 128.5, 129.1 (5× –CH–), 135.5 (–C–), 171.1, 172.5 (2× C=O). Data for the *anti* isomer: R_f = 0.29 (ethyl acetate/hexane 1:8). ν_{max} (neat)/cm^{-1} 3248 (NH), 1740 (CO), 1738 (CO). ^{1}HNMR (300 MHz, $CDCl_3$): 1.22–1.29 (m, 9H, 3× –CH_3), 3.34–3.38 (m, 1H, H-3), 4.06–4.29 (m, 5H), 4.57 (ABq, 2H, –OCH_2Ph), 5.72 (bs, 1H, –NH–), 7.17–7.32 (m, 5H, Ar–H). ^{13}CNMR (75 MHz, $CDCl_3$): 11.2 (–CH_3), 14.1 (–CH_3), 34.3 (–CH–), 61.3 (–CH_2–), 61.6 (–CH_2–), 65.8 (–CH–), 77.0 (–CH_2–), 127.8, 128.5, 129.0 (5× –CH–), 135.7 (–C–), 171.5, 173.0 (2× C=O). *m/z* (CI) 310 [(MH)$^+$, (66%)]; HRMS calculated for $C_{16}H_{24}NO_5$: 310,1654. Found 310.1660.

4.4. Diethyl 2-(benzyloxyamino)-3-phenylsuccinate (5b)

Purification by flash column chromatography (EtOAc/Hex 1:9 1:8) to yield the *syn* isomer (59%) and the *anti* isomer (29%). Data for the *syn* isomer: R_f = 0.30 (ethyl acetate/hexane 1:9). ν_{max} (neat)/cm^{-1} 3220 (NH), 1739 (CO), 1688 (CO). ^{1}HNMR (300 MHz, $CDCl_3$): 1.25–1.30 (m, 6H, 2× –OCH_2CH_3), 4.05–4.29 (m, 6H), 4.53 (ABq, 2H, –OCH_2Ph), 5.81 (bs, 1H, –NH–), 7.17–7.42 (m, 10H, Ar–H). ^{13}CNMR (75 MHz, $CDCl_3$): 13.5, 13.8 (2× –CH_3), 43.8 (–CH–), 60.8, 61.0 (2× –CH_2–), 66.2 (–CH–), 75.8 (–CH_2–), 127.2, 128.1, 128.2, 128.4, 128.5, 128.8, 129.0, 129.1 (10× –CH–), 133.6, 137.4 (2× –C–), 171.9, 174.0 (2× C=O). Data for the *anti* isomer: R_f = 0.29 (ethyl acetate/hexane 1:8). ν_{max} (neat)/cm^{-1} 3225 (NH), 1740 (CO), 1687 (CO). ^{1}HNMR (300 MHz, $CDCl_3$): 1.21 (t, 3H, –OCH_2CH_3), 1.28 (t, 3H, –OCH_2CH_3), 4.02–4.29 (m, 6H), 4.51 (ABq, 2H, –OCH_2Ph), 5.76 (bs, 1H, –NH–), 7.18–7.42 (m, 10H, Ar–H). ^{13}CNMR (75 MHz, $CDCl_3$): 13.8, 14.0 (2× –CH_3), 41.9 (–CH–), 61.3 (–CH_2–), 65.6 (–CH–), 77.1 (–CH_2–), 127.5, 128.1, 128.3, 128.4, 128.5, 128.8, 129.1, 129.5 (10× –CH–), 134.8, 136.7 (2× –C–), 171.3, 173.7 (2× C=O). *m/z* (CI) 372 [(MH)$^+$, (47%)]; HRMS calculated for $C_{21}H_{26}NO_5$: 372.1811. Found: 372.1815.

4.5. (2S,3R)/(2R,3S)-3-Methylaspartic acid 7

To a degassed solution of diester **5a** (50 mg, 0.16 mmol) in methanol and two drops of 1 M aqueous solution of hydrochloric acid, palladium black was added and the mixture was stirred at r.t. under hydrogen atmosphere for 14 h. After filtering over a celite pad, the filtrate was evaporated *in vacuo* to give the crude amine **6**, which was used in the next step without any further purification. To a solution of the amine in dioxane/water 1:1 (mL), barium hydroxide was added (83.34 mg, 0.48 mmol) and the mixture was heated at 50 °C for 12 h. After cooling to r.t., a DOWEX 50 W resin was added to pH 4 and the mixture was stirred for 1 h. Then, the resin was filtered, washed with water until no reaction with silver nitrate was observed and stirred with 1 M aqueous solution of ammonium hydroxide. After 2 h., the resin was filtered off and the filtrate evaporated under reduced pressure to give **7** (30.69 mg, 62%). ^{1}HNMR (300 MHz, D_2O): 1.01 (d, 3H, J = 7.6 Hz), 2.90–2.99 (m, 1H), 3.88 (d, 1H, J = 3.3 Hz); ^{13}C NMR (75 MHz, D_2O): 11.2 (–CH_3), 51.7 (–CH–), 61.0 (–CH–), 172.9 (–C=O).

4.6. 3-O-[2-(Benzyloxyamino)pent-4-enoyl]-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (11)

To a suspension of indium powder (40.3 mg, 0.35 mmol) in THF (1 mL) was added allyl bromide (0.05 mL, 0.52 mmol) and the mixture was sonicated for 10 min. The oxime **10** (0.15 g, 0.35 mmol) was added and sonication was continued for a further 4 h. The reaction mixture was neutralized with saturated aqueous sodium hydrogen carbonate, diluted with water (10 mL) and extracted with ether (3 × 25 mL). The combined organic layers were dried over magnesium sulfate, filtered and the solvent was evaporated *in vacuo*. The residue was purified by flash column chromatography (ethyl acetate/hexane 2:9) to give 3-*O*-[2(*R*)-(benzyloxyamino)pent-4-enoyl]-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **11a** (65 mg, 41%) and 3-*O*-[2(*S*)-(benzyloxyamino)pent-4-enoyl]-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **11b** (50 mg, 31%). Data for **11a**: R_f = 0.29 (ethyl acetate/hexane 2:9). ν_{max} (neat)/cm^{-1} 3230 (NH), 3030 (CH), 2950 (CH), 1740 (CO). ^{1}HNMR (300 MHz, $CDCl_3$): 1.25 (s, 3H, –CH_3), 1.26 (s, 3H, –CH_3), 1.41 (s, 3H, –CH_3), 1.51 (s, 3H, –CH_3), 2.25–2.49 (m, 2H), 3.65–3.73 (m, 1H), 3.98–4.02 (m, 1H), 4.12–4.21 (m, 3H), 4.44 (d, 1H, J = 6.4 Hz), 4.71 (s, 2H, –OCH_2Ph), 5.02–5.18 (m, 2H), 5.27 (d, 1H, J = 2.2 Hz), 5.69–5.78 (m, 2H), 5.89 (bs, 1H), 7.29–7.41 (m, 5H, Ar–H). ^{13}CNMR (75 MHz, $CDCl_3$): 25.4, 26.4, 26.6, 27.1 (4× –CH_3), 33.0 (–CH_2–), 51.1 (–CH–), 61.5 (–CH_2–), 65.7 (–CH–), 73.3 (–CH–), 76.8 (–CH_2–), 77.5 (–CH–), 79.4 (–CH–), 82.7 (–CH–), 105.8 (–CH–), 108.9, 112.8 (2× –C–), 116.5 (–CH_2), 125.2, 128.2, 128.5, 129.0 (5× –CH–), 134.4 (–CH–), 135.7 (–C–), 171.6 (C=O). Data for **11b**: R_f = 0.25 (ethyl acetate/hexane 2:9). ^{1}HNMR (300 MHz, $CDCl_3$): 1.24 (s, 3H, –CH_3), 1.26 (s, 3H, –CH_3), 1.43 (s, 3H, –CH_3), 1.50 (s, 3H, –CH_3), 2.27–2.48 (m, 2H), 3.65–3.74 (m, 1H), 3.89–4.24 (m, 4H), 4.32 (d, 1H, J = 6.4 Hz), 4.72 (s, 2H, –OCH_2Ph), 5.04–5.12 (m, 2H), 5.28 (s, 1H), 5.69–5.79 (m, 2H), 5.85 (bs, 1H), 7.31–7.42 (m, 5H, Ar–H). ^{13}CNMR (75 MHz, $CDCl_3$): 25.5, 26.4, 26.8, 27.3 (4× –CH_3), 33.0 (–CH_2–), 53.0 (–CH–), 61.5 (–CH_2–), 65.6 (–CH–), 73.5 (–CH–), 76.2 (–CH–), 77.0 (–CH_2–), 78.5 (–CH–), 81.5 (–CH–), 105.3 (–CH–), 109.3, 112.8 (2× –C–), 117.0 (–CH_2), 127.2, 128.0, 128.4, 129.0 (5× –CH–), 134.4 (–CH–), 135.2 (–C–), 172.1 (C=O). *m/z* (CI) 464 [(MH)$^+$, (58%)]; HRMS calculated for $C_{24}H_{33}NO_8$: 464.2284. Found: 464.2288.

4.7. 3-O-[3-(Ethoxycarbonyl)-2-(benzyloxyamino)-3-phenylpropanoyl]-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (12)

To a suspension of indium powder (46.0 mg, 0.39 mmol) in THF (1 mL) was added ethyl 2-phenylacetate (0.1 mL, 0.59 mmol) and the mixture was sonicated for 10 min. The oxime **10** (0.16 g, 0.39 mmol) was added and sonication was continued for a further 7 h. The reaction mixture was neutralized with saturated aqueous sodium hydrogen carbonate, diluted with water (10 mL) and extracted with ether (3 × 25 mL). The combined organic layers were dried over magnesium sulfate, filtered and the solvent was evaporated *in vacuo*. The residue was purified by flash column chromatography (ethyl acetate/hexane 1:5) to give 3-*O*-[3-(ethoxycarbonyl)-2-(benzyloxyamino)-3-phenylpropanoyl]-1,2:5,6-di-*O*-isopropylid ene-α-D-glucofuranose **12** (78 mg, 34%). R_f = 0.30 (ethyl acetate/hexane 1:5). ν_{max} (neat)/cm^{-1} 3345 (NH), 1728 (CO), 1739 (CO); ^{1}HNMR (300 MHz, $CDCl_3$): 1.22–1.51 (m, 15H, 5× –CH_3), 3.82–4.75 (m, 9H), 4.49–4.52 (m, 3H) 5.78 (d, 1H, J = 3.7 Hz), 7.15–7.48 (m, 10H, Ar–H). ^{13}CNMR (75 MHz, $CDCl_3$) (major isomer): 14.1 (–CH_3), 25.4, 26.4, 26.6, 27.1 (4× –CH_3), 50.8 (–CH–), 61.5 (–CH_2–), 65.7 (–CH–), 67.7 (–CH_2–), 72.3 (–CH–), 76.8 (–CH_2–), 77.0 (–CH–), 79.9 (–CH–), 83.2 (–CH–), 105.3 (–CH–), 109.5, 112.5 (2× –C–), 125.2, 128.1, 128.2, 128.4, 128.5, 128.8, 129.0, 129.1 (10× –CH–), 135.4, 137.3 (2× –C–), 170.7,

172.2 (2× C=O). *m/z* (CI) 464 [$(MH)^+$, (58%)]; HRMS calculated for $C_{31}H_{40}NO_{10}$: 586.2652. Found: 586.2648.

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