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$NaNO_2$–Ceric ammonium nitrate mediated conversion of acrylic esters and Baylis–Hillman derived acrylic esters into corresponding β-nitro acrylic esters☆

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Abstract—A variety of acrylic esters, including those derived from Baylis–Hillman reactions, react with $NaNO_2$–ceric ammonium nitrate to form the corresponding β-nitro alcohols **2** and **5** whose dehydration, via their mesylates, leads to β-nitro acrylic esters, in good to excellent yields. Further, β-nitro acrylic esters containing a mesylate group **6**, obtained from the Baylis–Hillman products, react with NaN_3 to form 2-cyano-3-substituted acrylic esters **10** in excellent yields.
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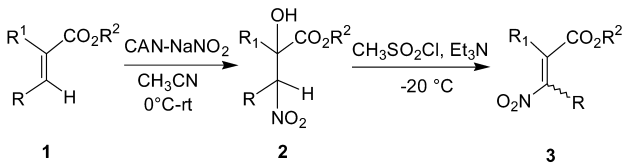
β-Nitro acrylic esters have been found to be excellent dienophiles[2] in organic synthesis. The nitro group in the β-nitro acrylic esters, owing to its more powerful electron withdrawing nature than the ester moiety, directs[2e] the regiochemical outcome in Diels–Alder reactions. This aspect has been elegantly used in the synthesis of isogabaculine,[3] gelesmine,[4] and calicheamycinone.[5] In addition, the nitro group can be eliminated[2b,h] using a base such as DBU thereby making β-nitro acrylic esters as propiolic ester equivalents. Further, the nitro group can be reduced[5] to an amino functionality with $NaBH_4$–$NiCl_2$, and to an amino[4] and amino hydroxyl[2c,d] functionalities with Al–Hg. Recently, such reductions of β-nitro acrylate derived Diels–Alder adducts have been used in the synthesis of polyhydroxylated cyclohexyl-β-amino acids[6a] and in the asymmetric synthesis of (−)-oryzoxymycin.[6b] Besides this, possibilities of employing the Nef reaction,[1] and reductive elimination[7] of the nitro group in Diels–Alder adducts also exist to obtain nitro free products. Apart from the studies in Diels–Alder reactions, β-nitro acrylic esters have also been used as Michael acceptors. Recently,[8a] nucleophiles derived from some amino acids and organo-zinc cuprates[8b–d] have been added to β-nitro acrylic esters especially in procuring optically active β-amino acids.[8c,d] Michael addition on a β-nitro acrylic ester has also been used in the synthesis of a 'template for stabilization of a peptide α-helix'.[9] Overall, these studies clearly indicate the importance of β-nitro acrylic esters in organic synthesis.

Preparation of β-nitro acrylic esters has been reported by Shechter et al.[10a] by nitrating the corresponding acrylic esters with dinitrogen tetroxide.[10b] Besides this, nitryl chloride,[11] nitrosyl chloride,[12] fuming nitric acid[12] and $NaNO_2$–aq.CH_3CO_2H[13] have also been employed to prepare β-nitro acrylic esters from the corresponding acrylic esters. Although these methods have found application, the low boiling nature of some of these reagents makes them inconvenient, especially if the reactions need to be done on small scales. Further, a general and simple approach is needed to prepare these class of compounds. Recently we have reported[14] $NaNO_2$–ceric ammonium nitrate (CAN) in CH_3CN as a novel reagent system for one pot conversion of olefins into vicinal nitro amides. In an attempt to explore the scope of this reagent system, we have now found that acrylic esters undergo smooth reaction with this reagent system forming β-nitro alcohols **2** in good yields along with a small amount (~5%) of β-nitro acrylates **3** (Scheme 1). Compounds **2** were readily converted into **3** via their mesylates by following modified McMurry's method[15] in good yields (entries 1–3, Table 1). Thus, in our initial



1 **2** **3**

Scheme 1.

☆ Part 11 in the series, 'Chemistry of Nitro Compounds'. For part 10, see Ref. 1.

Keywords: Ceric ammonium nitrate; Sodium nitrite; β-Nitro acrylic esters; Baylis–Hillman derived acrylic esters.
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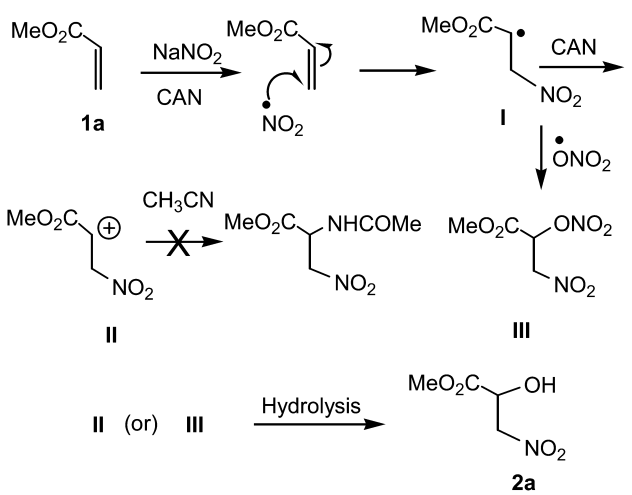
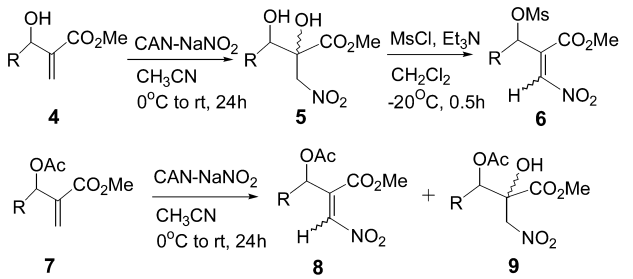
Table 1.

Entry	Acrylic esters (**1**)			Yield (%)	
	R	R^1	R^2	**2**	**3** (*E*:*Z*)
a	H	H	C_2H_5	62	75 (1:0)
b	CH_3	H	CH_3	62	90 (1:0)
c	H	CH_3	CH_3	78	73 (1:0)
d	Ph	H	C_2H_5	—	64[12] (1:1.7)
e	*p*-Tolyl	H	CH_3	—	81 (1:2)
f	*p*-Anisyl	H	CH_3	—	57 (1:1)

experiments, the reaction of ethyl acrylate with $NaNO_2$–CAN in acetonitrile resulted in the formation of ethyl 2-hydroxy-3-nitro propionate **2a**[10a] in 62% yield. Conversion of this alcohol to *trans*-ethyl 3-nitro acrylate **3a** (entry 1, Table 1) was performed via its mesylate in 75% yield. Likewise, methyl methacrylate **1c** and methyl crotonate **1b** also gave 2-hydroxy-3-nitro propionates **2b** and **2c** in 62 and 78% yields (entries b and c, Table 1) which were converted to the corresponding β-nitro acrylates in 90 and 73% yields, respectively. Interestingly, these β-nitro acrylates were found to be exclusively *E*-isomers, possibly because of the ensuing E_1cB reaction on the corresponding mesylates. On the other hand, cinnamic esters directly gave the corresponding β-nitro acrylates, (entries d–f, Table 1) without forming the intermediate hydroxy compounds, possibly because of the extended conjugation in these molecules. However, each of these compounds (**3d**–**f**) was obtained as a mixture of the corresponding *E* and *Z* isomers as revealed by their ^1H NMR spectra (Section 1). Although the mechanism of this reaction has not been investigated by us, we presume that nitrite radicals formed upon oxidation[16] of nitrite ions by CAN, add on to an acrylic ester as shown in Scheme 2 forming an intermediate **I**. This intermediate radical **I** can either be further oxidised to a carbocation **II** or react with a nitrate radical to form **III**. Hydrolysis of **III**, during work up, will lead to the observed product **2a**. Alternatively, the carbocation **II** will react with water to form **2a**. It is also likely that the intermediate **III** is derived from carbocation **II** upon reaction with nitrate ions from CAN.[17] However, hydration of the carbocation **II** is unlikely since the reaction conditions are anhydrous. Further, had the



Scheme 2.



Scheme 3.

Table 2.

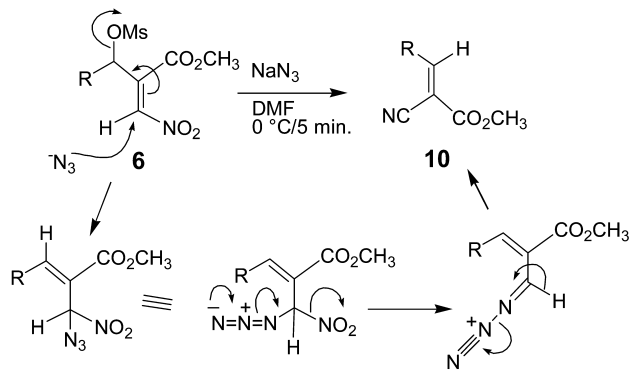
Entry		Yield (%)	
	4 *R*	**5**	**6** (*E*:*Z*)
a	Ph	62	37 (0:1)
b	*m*-Cl-Ph	56	70 (0:1)
c	*p*-Cl-Ph	63	79 (0:1)
d	C_2H_5	47	51 (1:13)
e	C_3H_7	45	51 (0:1)

carbocation formed it would have also reacted with acetonitrile to form the corresponding amide via a typical Ritter reaction[18] which we have not observed. We, therefore, feel that the pathway via the radical formation is most likely in the present case. This is also because the carbocation **II** is of high energy and thus less likely to form.

To further extend the scope of this reaction we considered using acrylic esters **4** (Scheme 3) derived from the Baylis–Hillman reaction.[19] Thus, a series of such esters were reacted with the present reagent system to form the corresponding diols **5** which could be readily dehydrated via their mesylates into the corresponding β-nitro acrylates **6** in fair to good yields (Table 2). β-Nitro acrylates **6** were found be exclusively the *Z*-isomers (entries 6a–c and e) or with the *Z*-isomer as the major product (entry 6d). The geometry of the olefinic bond was established on the basis of nOe experiments in which irradiation of either of the allylic proton or the olefinic proton led to the enhancement of the other peak. The corresponding acetates **7** were also reacted with $NaNO_2$–CAN, however, they gave almost 1:1 mixture of nitro olefin **8** and nitro alcohol **9** in modest yields (Table 3). Compound **8** was obtained as a mixture of *E*- and *Z*-isomers in which either the *Z*-isomer was the major product (entries a, c, f and g, Table 3) or the only product (entries b, d and e, Table 3). Once again the geometry of the

Table 3.

Entry		Yield (%)	
	7 *R*	**8** (*E*:*Z*)	**9**
a	Ph	49 (1:6)	31
b	*o*-Cl	45 (0:1)	53
c	*m*-Cl	46 (1:4)	51
d	*p*-Cl	50 (0:1)	47
e	*o*-NO_2	43 (0:1)	50
f	C_2H_5	48 (1:6)	50
g	C_3H_7	40 (1:6)	58



Scheme 4.

Table 4.

Entry	**6** *R*	**10** Yield (%)
a	Ph	90
b	*m*-Cl–Ph	81
c	*p*-Cl–Ph	76

double bond in **8** was established using nOe experiments (vide supra) after chromatographically separating the mixture of **8** and **9**.

Compounds **6a–e** appear to be very interesting since they possess a good leaving group as a mesylate along with the β-nitro acrylate system. In our preliminary experiments, we have reacted some of these compounds **6a–c** (with R=aryl) with NaN_3, and it was interesting to find that these compounds led to the formation of the corresponding cyano derivatives **10a–c**[20] (Scheme 4, Table 4) in a highly stereoselective manner. The geometry of the double bond was established by comparison with the reported ^{1}H NMR spectral data[20] for these compounds and also by the X-ray analysis of **10a** (R=Ph). A tentative mechanism for the formation of **10** could be written as shown in Scheme 4. When *R* is an aliphatic moiety, the reaction was found to be unclean and hence was not further pursued. Although, these compounds **10a–c** can be readily obtained by the classical Knovenagel type condensation of cyanoacetic esters with aldehydes, the mechanism through which these are obtained in the present cases is interesting.

In summary, we have demonstrated that $NaNO_2$–CAN is an excellent reagent to obtain β-nitro acrylic esters from a variety of acrylic esters in good to excellent yields. We have performed this preparation on scales ranging from 1 to 50 mmol without any change in the yields. In view of the fact that such nitro acrylates have already found use in organic synthesis[2–6] and since our method of preparation is very simple and high yielding, this methodology should find widespread application in organic synthesis. Some of these products, derived from the Baylis–Hillman based acrylic esters **6**, which contain a mesylate group also, lead to 2-cyano-3-substituted acrylic esters in excellent yields. Further work to explore the potential of compounds **6** and **8** and also to explore the potential of $NaNO_2$–CAN reagent system with other α,β-unsaturated compounds is in progress.

1. Experimental

1.1. General

Infrared spectra were recorded on Bruker FT/IR Vector 22 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on JEOL LA-400 (400 and 100 MHz, respectively) spectrometer in solutions of $CDCl_3$ using tetramethylsilane as the internal standard. The mass spectra were recorded on a Micromass Quattro II Triple Quadrupole Mass Spectrometer. Elemental analyses were carried out on a Thermoquest CE-instruments EA-1110 C, H, N, S analyser. Column chromatography was performed on silicagel (100–200 mesh) and thin layer chromatography (TLC) was performed on Silica gel plates made by using grade G silica gel obtained from s.d.fine-chem Ltd, Mumbai. Melting points were determined using a Fischer–John melting point apparatus. All solvents and common reagents were purified by established procedures.[21] Ceric ammonium nitrate and sodium nitrite were dried at 80 °C/0.2 mm for 3 h.

1.2. General procedure for the nitration of acrylic esters

To a stirred solution of an acrylic ester (1 mmol) in anhydrous CH_3CN (5 mL) were added CAN (1.64 g, 3 mmol) and $NaNO_2$ (207 mg, 3 mmol) at 0 °C under nitrogen. The reaction mixture was vigorously stirred for 24 h at rt, diluted with water and extracted with ethyl acetate. The organic layer was washed sequentially with saturated solution of $NaHCO_3$, brine and dried over anhydrous Na_2SO_4. The residue obtained after evaporation of the solvent was purified by column chromatography to get the nitro alcohols.

1.3. General procedure for the dehydration of nitro alcohols

To a stirred solution of a nitro alcohol (1 mmol) in dry CH_2Cl_2 (mL) were added $MeSO_2Cl$ (0.2 mL, 3 mmol), Et_3N (0.4 mL, 3 mmol) at −20 °C in succession. After the reaction was over (TLC monitoring), it was poured into ice-cold water and extracted with CH_2Cl_2, washed with water, brine and then dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a crude product, which was purified by column chromatography.

1.4. General procedure for the conversion of mesylates into cyano derivatives

To a stirred solution of a mesylate (0.15 mmol) in dry DMF (1 mL) at 0 °C was added NaN_3 (12 mg, 0.17 mmol) under nitrogen. After disappearance of the mesylate (TLC monitoring after 5 min), the reaction mixture was poured into ice water, extracted with diethyl ether followed by washing with brine, drying over anhydrous Na_2SO_4, and then concentrated in vacuum. The crude solid residue was purified by column chromatography.

1.4.1. Methyl 2-hydroxy-3-nitro-butyrate (2b). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47–5.16 (m, 2H), 3.85 (br s, 3H), 3.84 (br s, 1H), 1.21 and 1.20 (2d, J=6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 163.1, 87.8, 87.7, 87.1, 87.0, 53.9, 53.8, 11.9, 11.8; ν_{max}

(neat film) 3487 (br), 1736, 1555, 1367 cm^{-1}. ESMS: *m/z* 186 $[M+Na]^+$. Anal. calcd for $C_5H_9NO_5$: C, 36.81; H, 5.56; N, 8.59%. Found: C, 36.77; H, 5.58; N, 8.57%.

1.4.2. Methyl 2-hydroxy-2-methyl-3-nitro-propionate (2c). Pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 4.80 (d, J=13.7 Hz, 1H), 4.52 (d, J=13.7 Hz, 1H), 3.81 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 80.9, 72.5, 53.5, 23.6; ν_{max} (neat film) 3550 (br), 1759, 1565, 1384 cm^{-1}. ESMS: *m/z* 186 $[M+Na]^+$. Anal. calcd for $C_5H_9NO_5$: C, 36.81; H, 5.56; N, 8.59%. Found: C, 36.83; H, 5.61; N, 8.56%.

1.4.3. (*E*)-Ethyl 3-nitro-acrylate (3a). Yellow solid, mp 39–40 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J=13.6 Hz, 1H), 7.09 (d, J=13.6 Hz, 1H), 4.33 (q, J=7.1 Hz, 2H), 1.35 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 148.8, 127.6, 62.3, 13.9; ν_{max} (neat film) 1730, 1541, 1356 cm^{-1}. ESMS: *m/z*: 145 $[M^+]$, 116 $[M^+-29]$. Anal. calcd for $C_5H_7NO_4$: C, 41.38; H, 4.86; N, 9.65%. Found: C, 41.44; H, 4.79; N, 9.54%.

1.4.4. (*E*)-Methyl 3-nitro-but-2-enoate (3b). Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 6.90 (q, J=1.7 Hz, 1H), 3.89 (s, 3H), 2.11 (d, J=1.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 140.6, 135.9, 53.1, 17.5; ν_{max} (neat film) 1734, 1526, 1349 cm^{-1}. ESMS: *m/z* 145 $[M^+]$. Anal. calcd for $C_5H_7NO_4$: C, 41.38; H, 4.86; N, 9.65%. Found: C, 41.53; H, 4.85; N, 9.63%.

1.4.5. (*E*)-Methyl 2-methyl-3-nitro-acrylate (3c). Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (q, J=1.2 Hz, 1H), 3.84 (s, 3H), 2.60 (d, J=1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 160.1, 120.9, 52.6, 14.0; ν_{max} (neat film) 1731, 1540, 1368 cm^{-1}. ESMS: *m/z* 168 $[M+Na]^+$. Anal. calcd for $C_5H_7NO_4$: C, 41.38; H, 4.86; N, 9.65%. Found: C, 41.36; H, 4.90; N, 9.54%.

1.4.6. (*E*)-Ethyl 3-nitro-3-phenyl-acrylate (3d). Mixture with (*Z*)-**3d**. Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53–7.42 (m, 6H), 4.38 (q, J=7.1 Hz, 2H), 1.35 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 136.5, 132.1, 130.4, 129.7, 129.3, 63.0, 14.0.

1.4.7. (*Z*)-3d. ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.53–7.42 (m, 5H), 4.44 (q, J=7.1 Hz, 2H), 1.37 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 140.1, 132.9, 132.3, 129.3, 128.2, 63.1, 13.7; ν_{max} (neat film) 1732, 1644, 1535, 1321 cm^{-1}. ESMS: *m/z* 244 $[M+Na]^+$. Anal. calcd for $C_{11}H_{11}NO_4$: C, 59.73; H, 5.01; N, 6.33%. Found: C, 59.71; H, 5.04; N, 6.24%.

1.4.8. (*E*)-Methyl 3-nitro-3-*p*-tolyl-acrylate (3e). Mixture with (*Z*)-**3e**. Yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.36–7.22 (m, 4H), 3.94 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 143.6, 140.5, 136.9, 130.4, 129.9, 125.8, 53.4, 21.4.

1.4.9. (*Z*)-3e. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.29–7.17 (m, 4H), 3.87 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 143.2, 138.7, 132.9, 129.9, 129.7, 125.7, 53.2, 21.3; ν_{max} (neat film) 1740, 1546, 1362 cm^{-1}. ESMS: *m/z* 244 $[M+Na]^+$. Anal. calcd for $C_{11}H_{11}NO_4$: C, 59.73; H, 5.01; N, 6.33%. Found: C, 59.81; H, 5.03; N, 6.24%.

1.4.10. Methyl 3-anisyl-3-nitro-acrylate (3f). (1:1, *E:Z* isomers). Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49–6.90 (m, 5H), 3.89 (2s, 3H), 3.84 (2s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 160.0, 137.6, 136.9, 132.9, 132.1, 121.1 (m), 114.9, 114.8, 114.2, 114.1, 55.5, 55.4, 53.5, 53.3; ν_{max} (neat film) 1732, 1602, 1528 cm^{-1}. ESMS: *m/z* 260 $[M+Na]^+$, 238 $[M+1]^+$. Anal. calcd for $C_{11}H_{11}NO_5$: C, 55.70; H, 4.67; N, 5.90%. Found: C, 55.62; H, 4.70; N, 5.98%.

1.4.11. Methyl 2,3-dihydroxy-2-nitromethyl-3-phenyl-propionate (5a). Viscous oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.24 (m, 5H), 5.46 (s, 1H), 5.33–4.77 (m, 2H), 3.87 (s, 3H), 3.70 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 141.3, 136.7, 128.3, 126.7, 78.8, 75.4, 71.1, 53.2; ν_{max} (neat film) 3493 (br), 1743, 1561, 1379 cm^{-1}. ESMS: *m/z* 278 $[M+Na]^+$. Anal. calcd for $C_{11}H_{13}NO_6$: C, 51.77; H, 5.13; N, 5.49%. Found: C, 51.69; H, 5.09; N, 5.47%.

1.4.12. Methyl 3-(3-chloro-phenyl)-2,3-dihydroxy-2-nitromethyl-propionate (5b). Colourless solid, mp 122–123 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.13 (m, 4H), 5.47 and 5.31 (2s, 1H), 5.08–4.37 (m, 2H), 3.87 and 3.75 (2s, 3H), 3.14 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 170.9, 139.20, 139.1, 134.5, 134.3, 129.7, 129.6, 129.2, 129.0, 127.4, 127.1, 125.4, 125.0, 78.7, 78.6, 78.3, 78.1, 75.8, 74.9, 53.8, 53.2; ν_{max} (neat film) 3503 (br), 1750, 1566, 1382 cm^{-1}. ESMS: *m/z* 312 $[M+Na]^+$. Anal. calcd for $C_{11}H_{12}ClNO_6$: C, 45.61; H, 4.18; N, 4.84%. Found: C, 45.57; H, 4.19; N, 4.81%.

1.4.13. Methyl 3-(4-chloro-phenyl)-2,3-dihydroxy-2-nitromethyl-propionate (5c). Colourless solid, mp 132–133 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.29 (m, 4H), 5.50 and 5.29 (2s, 1H), 4.99–4.30 (m, 2H), 3.88 and 3.86 (2s, 3H), 3.73 (br s, 1H), 3.57 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 171.0, 136.7, 136.4, 134.1, 134.0, 128.7, 128.5, 128.1, 128.0, 79.1, 78.9, 76.6, 75.5, 74.6, 72.8, 53.1, 52.7; ν_{max} (neat film) 3522 (br), 1753, 1566, 1388 cm^{-1}. ESMS: *m/z* 312 $[M+Na]^+$. Anal. calcd for $C_{11}H_{12}ClNO_6$: C, 45.61; H, 4.18; N, 4.84%. Found: C, 45.59; H, 4.17; N, 4.81%.

1.4.14. Methyl 2,3-dihydroxy-2-nitromethyl-pentanoate (5d). Colourless solid, mp 96–97 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 4.95–4.59 (2dd, J=13.9 Hz, 2H), 4.11 (br d, J=13.1 Hz, 1H), 3.81 and 3.80 (2s, 3H), 3.50 (m, 1H), 2.70 (br s, 1H), 1.59–1.36 (m, 1H), 1.22 (m,1H), 0.95–0.90 (2t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 172.0, 79.2, 78.6, 78.3, 78.2, 75.8, 74.7, 53.6, 53.5, 24.0, 23.6, 10.1, 9.9; ν_{max} (neat film) 3498 (br), 1743, 1561, 1381 cm^{-1}. ESMS: *m/z* 230 $[M+Na]^+$. Anal. calcd for $C_7H_{13}NO_6$: C, 40.58; H, 6.32; N, 6.76%. Found: C, 40.56; H, 6.28; N, 6.72%.

1.4.15. Methyl 2,3-dihydroxy-2-nitromethyl-hexanoate (5e). Colourless solid, mp 84–86 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 5.02–4.66 (2d, J=13.9 Hz, 2H), 3.94 (br s, 1H), 3.92 (s, 3H), 3.68 (t, J=8.4 Hz, 1H), 2.24 (br d, J=8.5 Hz,

1H), 1.63–1.51 (m, 2H), 1.39–1.26 (m, 2H), 0.94 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 78.7, 78.1, 74.3, 53.8, 33.2, 18.9, 13.6; ν_{max} (neat film) 3484 (br), 1740, 1559, 1372 cm^{-1}. ESMS: m/z 244 $[M+Na]^+$. Anal. calcd for $C_8H_{15}NO_6$: C, 43.44; H, 6.83; N, 6.33%. Found: C, 43.42; H, 6.79; N, 6.32%.

1.4.16. (*Z*)-Methyl 2-(methanesulfonyloxy-phenyl-methyl)-3-nitro-acrylate (6a). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.34 (m, 5H), 7.16 (d, J=1.7 Hz, 1H), 6.40 (d, J=1.7 Hz, 1H), 3.70 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 139.2, 138.1, 132.3, 130.5, 129.2, 127.6, 78.6, 53.2, 39.0; ν_{max} (neat film) 1743, 1543, 1363 cm^{-1}. ESMS: m/z 338 $[M+Na]^+$. Anal. calcd for $C_{12}H_{13}NO_7S$: C, 45.71; H, 4.16; N, 4.44; S, 10.17%. Found: C, 45.85; H, 4.02; N, 4.32; S, 10.12%.

1.4.17. (*Z*)-Methyl 2-[(3-chloro-phenyl)-methanesulfonyloxy-methyl]-3-nitro-acrylate (6b). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.31 (m, 4H), 7.15 (d, J=1.7 Hz, 1H), 6.37 (d, J=1.7 Hz, 1H), 3.75 (s, 3H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 138.6, 138.5, 135.3, 134.5, 130.8, 130.7, 127.7, 125.8, 77.5, 53.6, 39.4; ν_{max} (neat film) 1743, 1545, 1363 cm^{-1}. ESMS: m/z 372 $[M+Na]^+$. Anal. calcd for $C_{12}H_{12}ClNO_7S$: C, 41.21; H, 3.46; N, 4.00; S, 9.17%. Found: C, 41.10; H, 3.41; N, 4.07; S, 9.19%.

1.4.18. (*Z*)-Methyl 2-[(4-chloro-phenyl)-methanesulfonyloxy-methyl]-3-nitro-acrylate (6c). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.23 (m, 4H), 7.15 (d, J=1.5 Hz, 1H), 6.39 (br s, 1H), 3.74 (s, 3H), 2.89 (s, 3H); ^{13}C NMRδ 162.4, 138.8, 138.3, 136.8, 131.0, 129.7, 129.2, 77.7, 53.6, 39.4; ν_{max} (neat film) 1750, 1551, 1373 cm^{-1}. ESMS: m/z 372 $[M+Na]^+$. Anal. calcd for $C_{12}H_{12}ClNO_7S$: C, 41.21; H, 3.46; N, 4.00; S, 9.17%. Found: C, 41.29; H, 3.42; N, 3.97; S, 9.12%.

1.4.19. (*E*)-Methyl 3-methanesulfonyloxy-2-nitromethylene-pentanoate (6d). Mixture with (*Z*)-**6d**. Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 5.82 (m, 1H), 3.87 (s, 3H), 3.02 (s, 3H), 1.99–1.88 (m, 2H), 1.06 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 143.2, 136.4, 71.4, 53.2, 37.9, 28.1, 10.1.

1.4.20. (*Z*)-6d. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 1H), 5.26 (t, J=6.2 Hz, 1H), 3.92 (s, 3H), 3.10 (s, 3H), 1.99–1.88 (m, 2H), 1.04 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 139.9, 137.9, 78.4, 53.6, 38.9, 27.1, 8.9; ν_{max} (neat film) 1742, 1541, 1357 cm^{-1}. ESMS: m/z 290 $[M+Na]^+$. Anal. calcd for $C_8H_{13}NO_7S$: C; 35.95; H, 4.90; N, 5.24; S, 12.00%. Found: C, 36.04; H, 4.94; N, 5.19; S, 12.17%.

1.4.21. (*Z*)-Methyl 3-methanesulfonyloxy-2-nitromethylene-hexanoate (6e). Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J=1.0 Hz, 1H), 5.31 (br t, J=6.5 Hz, 1H), 3.92 (s, 3H), 3.10 (s, 3H), 1.86 (m, 2H), 1.48 (m, 2H), 0.98 (t, J=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 140.2, 137.9, 77.1, 53.6, 38.9, 35.8, 18.0, 13.2; ν_{max} (neat film) 1744, 1543, 1359 cm^{-1}. ESMS: m/z 304 $[M+Na]^+$. Anal. calcd for $C_9H_{15}NO_7S$: C, 38.43; H, 5.38; N, 4.98; S, 11.40%. Found: C, 38.37; H, 5.32; N, 5.01; S, 11.38%.

1.4.22. (*E*)-Methyl 2-(acetoxy-phenyl-methyl)-3-nitro-acrylate (8a). Mixture with (*Z*)-**8a**. Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.02 (s, 1H), 7.42–7.34 (m, 5H), 3.76 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 163.2, 142.8, 135.1, 132.8, 128.8, 128.5, 127.3, 70.5, 53.1, 20.4.

1.4.23. (*Z*)-8a. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.34 (m, 5H), 7.05 (d, J=1.7 Hz, 1H), 6.62 (d, J=1.7 Hz, 1H), 3.72 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 163.3, 141.5, 137.2, 134.0, 129.6, 128.9, 127.5, 72.3, 53.1, 20.6; ν_{max} (neat film) 1747, 1359, 1359 cm^{-1}. ESMS: m/z 302 $[M+Na]^+$. Anal. calcd for $C_{13}H_{13}NO_6$: C, 55.92; H, 4.69; N, 5.02%. Found: C, 55.86; H, 4.70; N, 5.06%.

1.4.24. (*Z*)-Methyl-2-[acetoxy-(2-chloro-phenyl)-methyl]-3-nitro-acrylate (8b). Yellow solid, mp 96–97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.21 (m, 4H), 6.98 (d, J=1.4 Hz, 1H), 6.96 (d, J=1.4 Hz, 1H), 3.74 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 162.9, 140.1, 137.9, 133.0, 132.0, 130.7, 129.9, 128.6, 127.4, 69.0, 53.3, 20.4; ν_{max} (neat film) 1750, 1538, 1355 cm^{-1}. ESMS: m/z 336 $[M+Na]^+$. Anal. calcd for $C_{13}H_{12}NO_6Cl$: C, 49.78; H, 3.86; N, 4.47%. Found: C, 49.81; H, 3.88; N, 4.43%.

1.4.25. (*E*)-Methyl-2-[acetoxy-(3-chloro-phenyl)-methyl]-3-nitro-acrylate (8c). Mixture with (*Z*)-**8c**. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.53–7.26 (m, 4H), 7.00 (s, 1H), 3.79 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 163.0, 143.7, 137.2, 134.4, 132.4, 129.8, 128.9, 127.3, 125.4, 69.4, 53.2, 20.3.

1.4.26. (*Z*)-8c. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.26 (m, 4H), 7.09 (s, 1H), 6.58 (s, 1H), 3.74 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 162.9, 143.4, 140.5, 137.5, 136.0, 134.8, 130.2, 127.5, 125.7, 71.6, 53.2, 20.6; ν_{max} (neat film) 1748, 1540, 1360 cm^{-1}. ESMS: m/z 336 $[M+Na]^+$. Anal. calcd for $C_{13}H_{12}NO_6Cl$: C, 49.78; H, 3.86; N, 4.47%. Found: C, 49.74; H, 3.82; N, 4.49%.

1.4.27. (*Z*)-Methyl-2-[acetoxy-(4-chloro-phenyl)-methyl]-3-nitro-acrylate (8d). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.27 (m, 4H), 7.08 (d, J=1.4 Hz, 1H), 6.58 (d, J=1.5 Hz, 1H), 3.74 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 163.0, 140.8, 137.3, 135.7, 132.6, 129.2, 129.0, 71.7, 53.3, 20.6; ν_{max} (neat film) 1747, 1539, 1360 cm^{-1}. ESMS: m/z 336 $[M+Na]^+$. Anal. calcd for $C_{13}H_{12}NO_6Cl$: C, 49.78; H, 3.86; N, 4.47%. Found: C, 49.82; H, 3.85; N, 4.46%.

1.4.28. (*Z*)-Methyl-2-[acetoxy-(2-nitro-phenyl)-methyl]-3-nitro-acrylate (8e). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–7.58 (m, 4H), 7.25 (d, J=1.4 Hz, 1H), 7.12 (d, J=1.4 Hz, 1H), 3.81 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 162.8, 147.8, 139.9, 138.3, 134.1, 130.4, 130.2, 128.9, 125.1, 67.6, 53.4, 20.5; ν_{max} (neat film) 1745, 1533, 1353 cm^{-1}. ESMS: m/z 347 $[M+Na]^+$. Anal. calcd for $C_{13}H_{12}N_2O_8$: C, 48.16; H, 3.73; N, 8.64%. Found: C, 48.12; H, 3.76; N, 8.63%.

1.4.29. (*E*)-Methyl-3-acetoxy-2-nitromethylene-pentanoate (8f). Mixture with (*Z*)-**8f**. Yellow oil; ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 5.81 (dd, J=9.1, 4.8 Hz, 1H), 3.86, (s, 3H), 2.03 (s, 3H), 1.92–1.77 (m, 2H), 1.00 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 163.6, 142.7, 135.9, 70.9, 53.3, 26.5, 20.5, 10.3.

1.4.30. (*Z*)-8f. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (d, J=1.2 Hz, 1H), 5.47 (td, J=6.3, 1.0 Hz, 1H), 3.90 (s, 3H), 2.13 (s, 3H), 1.92–1.77 (m, 2H), 0.97 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 163.7, 142.0, 137.0, 71.9, 53.4, 26.0, 20.7, 9.1; ν_{max} (neat film) 1743, 1535, 1358 cm^{-1}. ESMS: m/z 254 $[M+Na]^+$. Anal. calcd for $C_9H_{13}NO_6$: C, 46.76; H, 5.67; N, 6.06%. Found: C, 46.82; H, 5.71; N, 5.98%.

1.4.31. (*E*)-Methyl-3-acetoxy-2-nitromethylene-hexanoate (8g). Mixture with (*Z*)-**8g**. Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 5.90–5.87 (dd, J=9.5, 3.9 Hz,1H), 3.86 (s, 3H), 2.02 (s, 3H), 1.79 (q, J=6.6 Hz, 2H), 1.48–1.34 (m, 2H), 0.97 (t, J=6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 163.5, 142.4, 136.2, 69.3, 53.1, 34.9, 20.3, 18.9, 13.3.

1.4.32. (*Z*)-8g. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (s, 1H), 5.51 (t, J=6.3 Hz, 1H), 3.90 (s, 3H), 2.12 (s, 3H), 1.77 (q, J=6.6 Hz, 2H), 1.48–1.34 (m, 2H), 0.95 (t, J=6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 163.6, 142.2, 136.7, 70.6, 53.2, 34.7, 20.5, 18.0, 13.4; ν_{max} (neat film) 1744, 1538, 1363 cm^{-1}. ESMS: m/z 268 $[M+Na]^+$. Anal. calcd for $C_{10}H_{15}NO_6$: C, 48.98; H, 6.17; N, 5.71%. Found: C, 48.92; H, 6.21; N, 5.68%.

1.4.33. Methyl 3-acetoxyl-2-hydroxy-2-nitromethyl-3-phenyl-propionate (9a). Yellow solid, mp 98–99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.20 (m, 5H), 5.85 and 5.81 (2s, 1H), 4.91–4.15 (2dd, J=13.9 Hz, 2H), 3.77 and 3.71 (2s, 3H), 2.05 and 1.98 (2s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 170.5, 169.5, 168.9, 133.6, 133.5, 129.3, 129.2, 128.5, 128.3, 128.0, 127.5, 78.2, 77.9, 77.3, 77.0, 75.8, 75.6, 53.8, 53.7, 20.7, 20.5; ν_{max} (neat film) 3493 (br), 1755, 1563, 1377 cm^{-1}. ESMS: m/z 320 $[M+Na]^+$. Anal. calcd for $C_{13}H_{15}NO_7$: C, 52.53; H, 5.09; N, 4.71%. Found: C, 52.35; H, 5.13; N, 4.68%.

1.4.34. Methyl-3-acetoxy-3-(2-chlorophenyl)-2-hydroxy-2-nitromethyl-propionate (9b). Colourless solid, mp 70–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17–7.25 (m, 4H), 6.48 and 6.46 (2s, 1H), 5.28–4.12 (m, 2H), 3.93 and 3.83 (2s, 3H), 2.12 and 2.05 (2s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 170.5, 169.2, 168.7, 143.1, 139.1, 133.1, 133.0, 131.7, 131.5, 130.6, 130.4, 129.9, 129.3, 127.3, 126.9, 77.9, 77.4, 71.6, 71.4, 53.9, 52.2, 38.2, 31.5, 20.7, 20.5; ν_{max} (neat film) 3496, 1748, 1563, 1375 cm^{-1}. ESMS: m/z 354 $[M+Na]^+$. Anal. calcd for $C_{13}H_{14}ClNO_7$: C, 47.07; H, 4.25; N, 4.22%. Found: C, 47.13; H, 4.14; N, 4.17%.

1.4.35. Methyl-3-acetoxy-3-(3-chlorophenyl)-2-hydroxy-2-nitromethyl-propionate (9c). Colourless solid, mp 78–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.18 (m, 4H), 5.88 and 5.84 (2s, 1H), 4.98–4.25 (2dd, J=13.7, 13.8 Hz, 2H), 3.87 and 3.82 (2s, 3H), 2.16 and 2.08 (2s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.3, 169.4, 168.9, 135.6, 135.5, 134.4, 134.2, 129.7, 129.6 (2s), 129.4, 128.1, 127.7, 126.2, 125.7, 78.1, 77.8, 76.9, 77.4, 75.1, 74.9, 53.9, 53.8, 20.7, 20.5; ν_{max} (neat film) 3498 (br), 1760, 1568, 1378 cm^{-1}. ESMS: m/z 354 $[M+Na]^+$. Anal. calcd for $C_{13}H_{14}ClNO_7$: C, 47.07; H, 4.25; N, 4.22%. Found: C, 47.13; H, 4.30; N, 4.27%.

1.4.36. Methyl-3-acetoxy-3-(4-chlorophenyl)-2-hydroxy-2-nitromethyl-propionate (9d). Colourless solid, mp 82–84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.26 (m, 4H), 5.89 and 5.84 (2s, 1H), 4.98–4.22 (2dd, J=13.9, 13.7 Hz, 2H), 3.87 and 3.81 (2s, 3H), 2.14 and 2.07 (2s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.4, 169.4, 168.9, 135.4, 135.2, 132.2, 132.1, 129.5, 129.0, 128.7, 128.6, 78.2, 77.8, 77.4, 76.9, 75.1, 75.0, 53.9 (2s), 20.7, 20.5; ν_{max} (neat film) 3506, 1761, 1566, 1378 cm^{-1}. ESMS: m/z 354 $[M+Na]^+$. Anal. calcd for $C_{13}H_{14}ClNO_7$: C, 47.07; H, 4.25; N, 4.22%. Found: C, 47.13; H, 4.17; N, 4.18%.

1.4.37. Methyl-3-acetoxy-2-hydroxy-2-nitromethyl-3-(2-nitrophenyl)-propionate (9e). Yellow solid, mp 102–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.51 (m, 4H), 6.88 and 6.57 (2s, 1H), 5.32–4.19 (2dd, J=13.9, 13.8 Hz, 2H), 3.96 and 3.85 (2s, 3H), 2.16 and 2.02 (2s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 170.6, 168.8 (2s), 149.3, 148.7, 133.5, 132.9, 131.3, 130.2, 130.1, 130.0, 129.1, 128.5, 124.7, 124.3, 78.2, 77.3, 77.2, 76.3, 69.5, 69.4, 54.4, 54.3, 20.7, 20.4; ν_{max} (neat film) 3500, 1760, 1566, 1535 cm^{-1}. ESMS: m/z 365 $[M+Na]^+$. Anal. calcd for $C_{13}H_{14}N_2O_9$: C, 45.62; H, 4.12; N, 8.18%. Found: C, 45.94; H, 4.08; N, 8.13%.

1.4.38. Methyl-3-acetoxy-2-hydroxy-2-nitromethyl-pentanoate (9f). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05 (m, 1H), 4.67 (m, 2H), 3.90 and 3.86 (2s, 3H), 2.15 and 2.10 (2s, 3H), 1.65 (m, 2H), 1.17 and 1.53 (2t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 171.4, 170.5, 170.0, 78.1, 77.6, 76.8, 76.7, 75.2, 75.1, 54.0, 53.6, 21.9, 21.8, 20.5, 20.4, 9.7 (2s); ν_{max} (neat film) 3490, 1746, 1562, 1376 cm^{-1}. ESMS: m/z 272 $[M+Na]^+$. Anal. calcd for $C_9H_{15}NO_7$: C, 43.38; H, 6.07; N, 5.62%. Found: C, 43.16; H, 6.13; N, 5.58%.

1.4.39. Methyl-3-acetoxy-2-hydroxy-2-nitromethyl-hexanoate (9g). Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (m, 1H), 4.90–4.62 (2dd, J=13.9 Hz, 2H), 3.89 and 3.86 (2s, 3H), 2.13 and 2.08 (2s, 3H), 1.71–1.21 (m, 4H), 0.93 and 0.88 (2t, J=13.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 171.4, 170.4, 169.9, 78.0, 77.7, 76.8, 76.7, 73.6, 73.5, 53.9, 53.5, 30.7, 30.5, 20.5, 20.4, 18.5, 18.4, 13.5, 13.4; ν_{max} (neat film) 3502, 1747, 1563, 1377 cm^{-1}. ESMS: m/z 286 $[M+Na]^+$. Anal. calcd for $C_{10}H_{17}NO_7$: C, 45.63; H, 6.51; N, 5.32%. Found: C, 45.53; H, 6.49; N, 5.28%.

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