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Reactions of Monosaccharide Derivatives with Diazocarbonyl Compounds. Reactivity and Synthetic Applications.

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Abstract: The reaction of monosaccharide derivatives with different stabilized diazo compounds is reported. Studies on the reactivity of the condensation products have been undertaken, finding out novel transfromations of β-oxy-α-diazo carbonyl compounds with sinthetic applications. Thus, a stereoselective Wolff rearrangement provided *syn* 2-hydroxy-1-methyl compounds, which represent macrolide type structural subunits. On the other hand, rhodium (II) mediated rearrangements of β-acetoxy-α-diazo carbonyl compounds derived from monosaccharides have led to an efficient synthesis of the natural aldonic acids KDG and DAH.
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INTRODUCTION

Diazo compounds represent an important and useful class of reagents in organic synthesis. Their ease of preparation[1] and reactivity[2] has propelled them to the forefront of the organic synthesis area.[3] The principle synthetic applications of these compounds rely on their transformation into carbene species, generated by photochemical or metal mediated methods,[4] and their subsequent intra- or inter-molecular insertions to form a new C-C bond[5] or a heteroatom-C bond.[6] In addition, the acidic character of the hydrogen alpha to the diazo carbon[7] makes it possible to use diazo compounds in aldol reactions. In these cases, stabilized diazo carbonyl compounds produce β-keto carbonyl derivatives when Lewis acids are used,[8] whereas, under basic conditions, β-hydroxy-α-diazo carbonyl compounds are formed.[9] Synthetically, the latter products are interesting, even though their chemistry is extremely limited by their tendency to give the corresponding β-keto carbonyl

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compounds by a hydrogen shift rearrangement process.[10] However, despite their chemical behaviour, a number of useful transformations has been reported so far,[11] with applications in the synthesis of natural products.[12] Our interest in the synthesis of macrolide type structures[13] led us to the development of the stereoselective synthesis of epoxy amides by reaction of monosaccharide derivatives with stabilized sulfur ylides.[14] More recently, we have begun an extensive study on the synthesis and reactivity of β-hydroxy-α-diazo compounds[15] derived from monosaccharides in order to prepare macrolide synthons in a stereoselective fashion. The results obtained from these investigations not only have found synthetic applications in the synthesis of macrolide fragments, but also in the synthesis of the natural aldonic acids such as KDG, DAH and KDO.[16] Additionally, the synthesis of C-disaccharides has also been performed using non-stabilized diazo compounds derived from carbohydrates.[17]

RESULTS AND DISCUSSION

Initially, we targeted fragments of the type **A**, **B**, **C** or **D** (see Figure 1), present in the macrolide type antibiotics and many other natural products derived from the polypropionate biosynthetic pathway.[18] The asymmetric induction of 2,3-O-isopropylidene-D-glyceraldehyde **1** in aldol reactions is well-known[19] and for this reason, we decided to use it as starting material. Initially, we focused on the photochemistry of β-oxy-α-diazo methyl ketones as a method of alkylation on the diazo carbon via a Wolff rearrangement. This transformation proved to be a difficult task due to the more favored hydrogen shift rearrangement leading to β-keto carbonyl derivatives.

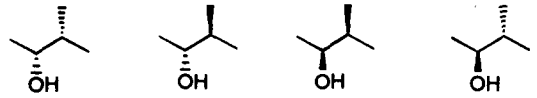
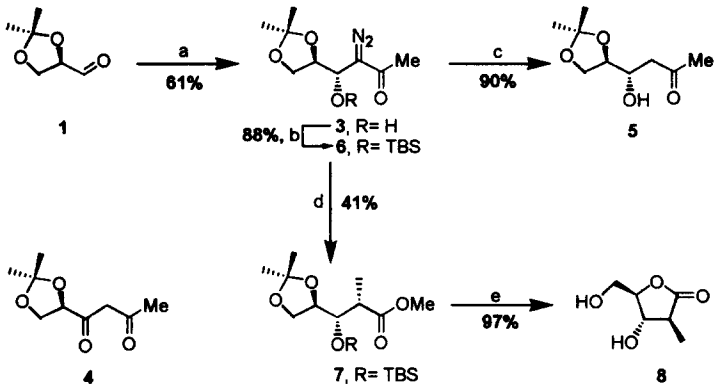


Figure 1. Fragments of Macrolide Type Antibiotics.

In fact, the hydroxy diazo compound **3**, obtained via reaction of **1** with diazoacetone **2**[20] under non-basic conditions, produced quantitatively compound **4** when it was exposed to the UV light (λ = 253.7 nm). Previuosly, we established the stereochemistry at C-4 of **3** by its transformation into the known β-hydroxy ketone **5**[21] by catalytic hydrogenation and proved it had the S configuration at C-4. We analyzed the possible influence of the hydroxyl protecting group on the migratory capacity of the α-hydrogen in order to determine the factors that favor the Wolff rearrangement over the H-rearrangement. Thus, the silyl ether **6**, prepared from **3** by conventional methods, was treated with UV light to give the Wolff rearrangement product **7** and the corresponding H-shift product in 41 and 55% yield, respectively.



Scheme 1. *Reagents and Conditions.* (a) 2.0 equiv of HCN_2COMe (**2**), neat, 0 °C, 2 days, 61%. (b) 1.5 equiv of TBSCl, 2.0 equiv of imidazole, DMF, 25 °C, 12 h, 88%. (c) H_2, Pd-C, EtOAc, 5 h, 90%. (d) hv (λ = 253.7 nm), MeOH:THF (1:1), 4 °C, 8 h, 41%. (e) F_3B-Et_2O, 0 °C, 2 h, 97%.

This result prompted us to continue this study in order to improve the yield of the Wolff rearrangement product. Interestingly, **7** was the only diastereoisomer observed by spectroscopic analysis (^{1}H-NMR and GC-MS), and its stereochemistry at C-2 was assigned as 2-(S), by the transformation of **7** into the known lactone **8**.[22] A possible explanation for the observed stereoselectivity in this reaction is based on a cyclic intermediate (Figure 2, Type A) with participation of the silicon atom in a temporary Si-O bond after the attack of methanol on the formed ketene. Related intermediates (Figure 2, Type B) have been proposed in protonation reactions of chiral nitro alcohols.[23]

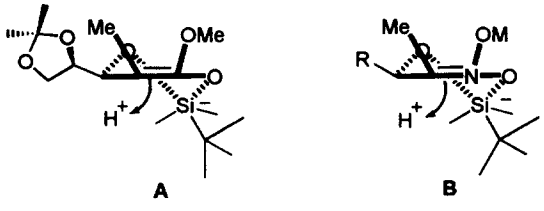
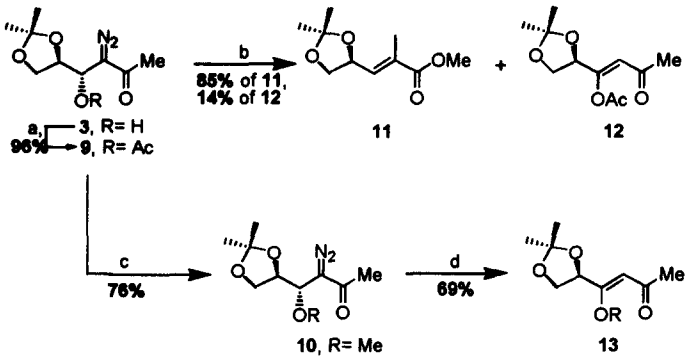


Figure 2. Intermediates Structures in the Stereoselective Protonatio

A possible inductive effect of the protecting group on the migratory capacity of the α-hydrogen was the reason for the preparation of derivatives of **3** containing electron withdrawing groups. The acetylated product **9** was prepared by standard methods and was exposed to UV-light to obtain the ester **11** (85% yield) and the olefin **12** (14% yield) as a 1:1 *Z*:*E* mixture. This result confirmed our predictions regarding the hydroxyl protecting group effect, but unfortunately elimination of the acetoxy group occurred during the photochemical reaction.[24] Contrary to compound **9**, the methyl ether **10** furnished as major product, the olefin **13** (69% yield).

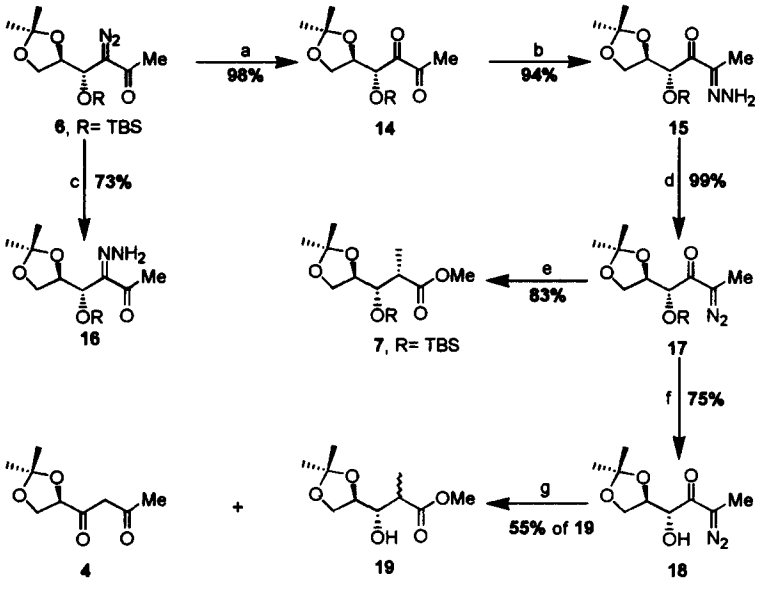


Scheme 2. *Reagents and Conditions.* (a) 2.0 equiv of Ac_2O, pyr, 25 °C, 8 h, 96%. (b) hν (λ = 253.7 nm), MeOH:THF (1:9), -30 °C, 17 h, 85% of **11**, 14% of **12**. (c) 4.0 equiv of MeI, 2.0 equiv of NaOH (powder), DMF, 25 °C, 24 h, 76%. (d) hν (λ = 253.7 nm), MeOH:THF (1:9), 4 °C, 10 h, 69%.

A second alternative towards improving the yield of the Wolff rearrangement product was based on the possibility that the hydrogen rearrangement was being caused by activation of the hydroxyl group. So, the problem was how to get the Wolff rearrangement product having in hand an intermediate with non-activated hydrogens. The solution was possible by the efficient and easy interconversion of diazo-ketone groups, performed in three quantitative steps as depicted in Scheme 3. Silyl ether **6** was treated with *meta*-chloroperbenzoic acid to give the diketone **14** in 92% yield. The reaction of **14** with hydrazine at -60 °C furnished the hydrazone **15** quantitatively. When this reaction was carried out at higher temperatures, a mixture of hydrazones **15** and **16** was obtained, reaching a 1:1 ratio at 25 °C. Structures of hydrazones **15** and **16** were confirmed by transformation of **6** into **16** by treatment with triphenylphosphine. Mild oxidation of **15** with manganese dioxide provided the diazo compound **17** (99% yield), which was treated with UV light to give **7** (83% yield). At this point, compound **17** was used to demonstrate the role of the silicon atom in the stereoselectivity of the photochemical Wolff rearrangement. Thus, TBAF deprotection of **17** and photochemistry of the resulting alcohol **18** gave a 1:1 mixture of the C-2 epimeric esters **19** (53%) together with the β-diketone **4** (40%) as a result of a ketocarbene-oxirane-ketocarbene equilibrium.[25]

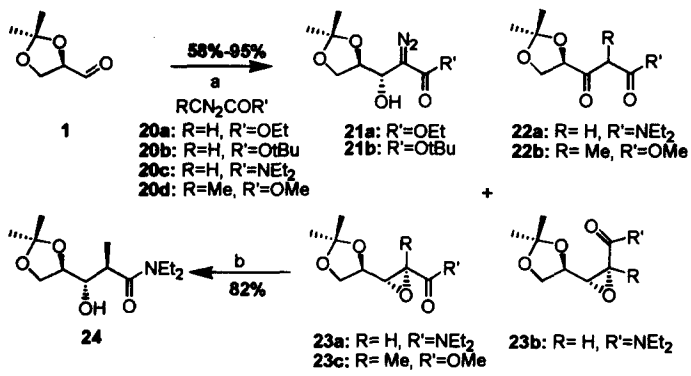
We envisioned shorter alternatives to synthesize this kind of products by direct alkylation on the diazo carbon of β-hydroxy-α-diazo esters or by introduction of the alkyl group in the condensation step. In order to investigate all these possibilities, condensations of **1** with the diazo compounds **20a**, **20b**, **20c** and **20d** were done. In the cases of diazo acetate derivatives **20a** and **20b**, the condensation products **21a** and **21b** were obtained in 68 and 70% yields, respectively. For the diazoamide **20c**,[26] the result was different than the acetate derivatives.[27] Thus, epoxiamides **23a** and **23b** and the β-keto amide **22a** were obtained in a roughly 6:3:1 proportion in the absence of solvent and catalyst at 4 °C. When this reaction was carried out in dichloromethane at 0°C, the epoxiamides **23a** and **23b**[14a] were obtained quantitatively in a 1:1 ratio. The regioselective opening of the epoxiamide **23a** by the action of lithium dimethyl cuprate[28] provided the *anti* product **24** in 82% yield. In the

last case, reaction of **1** with methyl diazopropionate[29] gave the β-keto ester **22b** as the major product (78% yield) and a mixture of diastereomeric epoxides **23c** in 20% yield which were inseparatable by column chromatography.

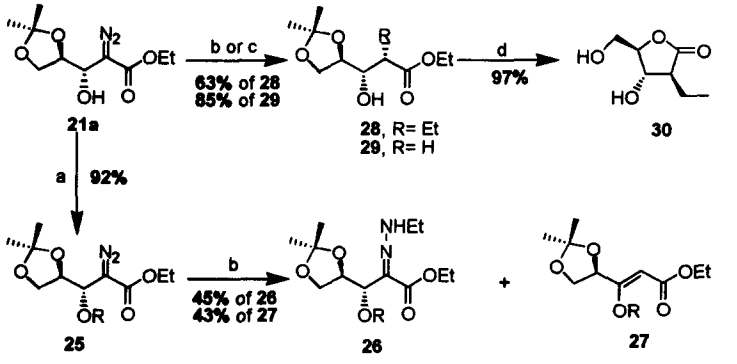


Scheme 3. *Reagents and Conditions.* (a) 1.2 equiv of *m*CPBA, CH_2Cl_2, 0 °C, 2 h, 98%. (b) 1.1 equiv of NH_2NH_2, MeOH, -60 °C, 1 h, 94%. (c) 1.5 equiv of Ph_3P, THF, 25 °C, 5 h, then H_2O, 0 °C, 2 h, 73%. (d) 1.5 equiv of MnO_2, $HCCl_3$, 25 °C, 0.5 h, 99%. (e) hν (λ = 253.7 nm), MeOH:THF (1:1), 4 °C, 5 h, 83%. (f) 1.2 equiv of TBAF, THF, 0 °C, then 25 °C, 1 h, 75%. (g) hν (λ = 253.7 nm), MeOH:THF (1:1), 4 °C, 1 h, 55% of **19**, 45% of **4**.

An alternative method for alkylation on the diazo carbon was attempted by reaction of **21a** by reaction with triethylborane.[30] In a first attempt, **21a** was silylated by treatment with TBDMSCl in DMF to obtain the silyl ether **25** in 92% yield. Treatment of **25** with triethylborane in THF at 25°C furnished as the main product, hydrazone **26**, together with a small amount of the decomposition compound **27**. Since the steric hinderance of the bulky TBS protecting group favored this result, we decided to carry out this reaction with the hydroxyl derivative **21a**, obtaining the C-alkylation product **28** as a single diastereoisomer in a 63% yield after flash cromatography. The stereochemistry of **28** on C-2 was established by the transformation of **28** into the lactone **30**.[31] We postulate that the observed stereoselectivity of this reaction is caused by the hidroxyl group which can participate in an intramolecular alkylation of the diazo carbon via a boronate intermediate. In order to explore the applicability of this C-C bond formation methodology, we reacted **21a** with 9-BBN to give **29**[32] in 85% yield. This reaction provides a new and stereoselective C-alkylation synthesis and is currently under further investigation.



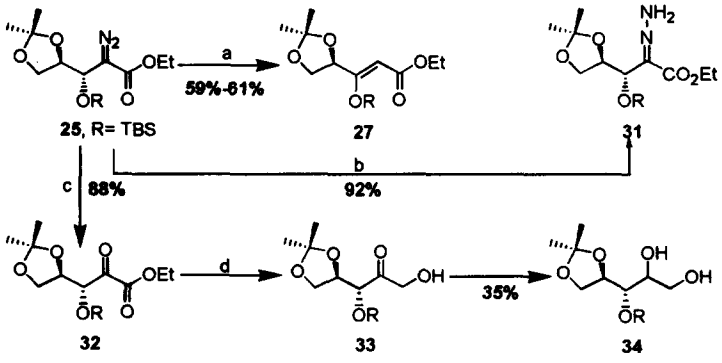
Scheme 4. *Reagents and Conditions.* (a) i. 1.5 equiv of **20a**, neat, 4 °C, 12 h, 68% of **21a**. ii. 1.5 equiv of **20b**, neat, 4 °C, 12 h, 70% of **21b**. iii. 1.5 equiv of **20c**, neat, 25 °C, 12 h, 12% of **22a**, 18% of **23a**, 28% of **23b**. iv. 1.5 equiv of **20c**, $CHCl_3$, 25 °C, 12 h, 40% of **23a**, 45% of **23b**. v. 1.5 equiv of **20d**, neat, 4 °C, 12 h, 68% of **22b**, 23% of **23c**. (b) 1.5 equiv of Me_2CuLi, diethyl ether, -10 °C, 2 h, 82%.



Scheme 5. *Reagents and Conditions.* (a) 1.5 equiv of TBSCl, 2.0 equiv of imidazole, DMF, 25 °C, 12 h, 92% (b) 1.2 equiv of Et_3B (1 M in THF), THF, 25 °C, 12 h, 45% of **26**, 43% of **27**, 63% of **28**. (c) 1.5 equiv of 9-BBN (0.5 M in THF), THF, 25 °C, 6 h, 85% (d) 20% TFA in EtOH, EtOH-H_2O, 0 °C, 5 h, 97%.

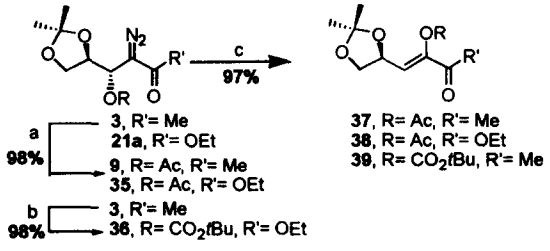
Continuing with our studies on alkylation reactions of diazo compounds, we carried out reactions of **21a** and **25** with trimethylaluminum and diethylzinc in order to prepare the 2-C-methyl and -ethyl derivatives, respectively. However, in both cases, only decomposition product **27** was obtained. On the other hand, reaction of **25** with Super-H produced the hydrazone **31** in good yield. In order to develope a new methodology for monosaccharide homologation, diazo **25** was transformed into the α-keto ester **32** in 88% yield by treatment with *meta*-chloroperbenzoic acid. Reduction of **32** with sodium borohydride gave the 1:1 epimeric mixture of

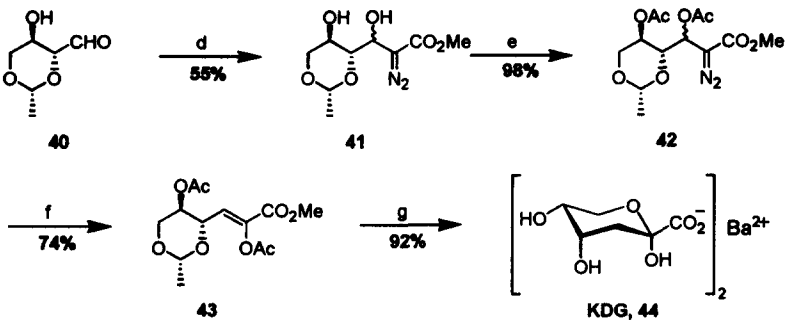
pentitols **34** via the ketone **33** in low yield (35%), and O-isopropylidene-D-glycerol as the major product, as a result of the degradation of the starting keto ester **32**.



Scheme 6. *Reagents and Conditions.* (a) 1.1 equiv of Me_3Al (2 M in toluene), toluene, -78 °C → 0 °C, 2 h, 59% or 1.1 equiv of Et_2Zn (1 M in toluene), toluene, -78 °C → 0 °C, 2 h, 61%. (b) 3.0 equiv of $LiHEt_3B$ (1 M in THF), THF, 0 °C, 1 h, 92%. (c) 1.5 equiv of *m*CPBA, CH_2Cl_2, 0 °C, 6 h, 88%. (d) 4.0 equiv of $NaBH_4$, MeOH, 0 °C, 0.5 h, 35%.

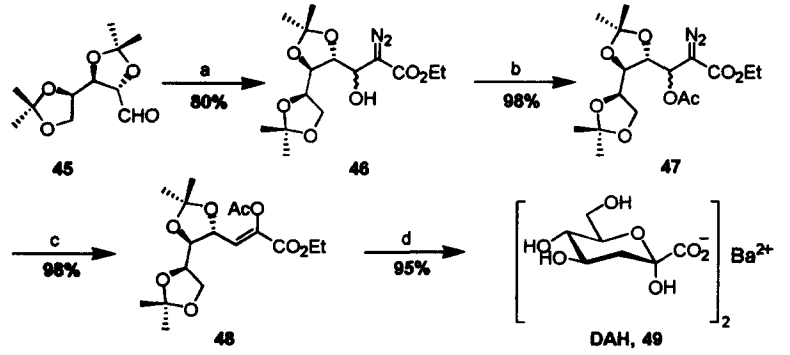
Finally, we utilized the condensations of diazo carbonyl compounds with longer monosaccharide derivatives with synthetic purposes. In particular, we used the known rearrangement of β-acetoxy-α-diazo esters mediated with rhodium(II).[33] In initial studies, the efficiency of this reaction was determined with the acetate derivatives **9**, **35** and carbonate **36** which were transformed quantitatively into the α-enol esters **37**, **38** and **39** respectively, by reaction with dirhodium tetracetate in chloroform (scheme 7). This transformation was used in the synthesis of KDO and 2-deoxy KDO[16] and has also been used successfully in the synthesis of the related natural products KDG and DAH. KDG[34] is a component of the uronic acids metabolism in bacteria and is responsible for soft-rot disease in many plant species.[35] DAH[36] is a key intermediate in the biosynthesis of aromatic aminoacids in plants, fungi and bacteria.[37] The synthesis of KDG (**44**) begins with 2,4-O-ethylidene-D-erythrose **40**.[38] Reaction of **40** with methyl diazoacetate (10% KOH in methanol), gave the condensation product **41** as diastereoisomeric mixture in 55% yield. Acetylation and rhodium decomposition furnished the enol ester **43**, which was subjected to acidic conditions followed by barium hydroxide to give KDG (**44**) as the barium salt.[34]





Scheme 7. *Reagents and Conditions.* (a) 2.0 equiv of Ac_2O, pyr, 25 °C, 5 h, 98%. (b) 2.= equiv of $O[OCO_2tBu]_2$, pyr, 25 °C, 12 h, 98%. (c) $Rh_2(OAc)_4$ (catalytic), $CHCl_3$, 25 °C, 0.5 h, 97%. (d) 2.0 equiv of HCN_2CO_2Me, 0.5 equiv of KOH (10% solution in MeOH), MeOH, 25 °C, 1 h, 55%. (e) 2.0 equiv of Ac_2O, pyr, 25 °C, 5 h, 98%. (f) $Rh_2(OAc)_4$ (catalytic), $CHCl_3$, 25 °C, 0.5 h, 74%. (g) 20 % TFA in MeOH, MeOH-H_2O, 60 °C, 8 h, then 3.0 equiv of $Ba(OH)_2$, MeOH-H_2O, 25 °C, 3 h, 92%.

In a similar synthetic sequence, DAH (**49**) was obtained in good yields from 2,3:4,5-di-O-isopropylidene-D-arabinosaldehyde **45**[39] via intermediates **46**, **47** and **48**. DAH (**49**) was identified as its barium salt and compared with the data available in the literature.[35a]



Scheme 8. *Reagents and Conditions.* (a) 2.0 equiv of HCN_2CO_2Et, neat, 25 °C, 12 h, 80%. (b) 2.0 equiv of Ac_2O, pyr, 25 °C, 5 h, 98%. (c) $Rh_2(OAc)_4$ (catalytic), $CHCl_3$, 25 °C, 0.5 h, 98%. (f) 20% TFA in EtOH, EtOH-H_2O, MeOH, 25 °C, 12 h, then 3.0 equiv of $Ba(OH)_2$, MeOH-H_2O, 25 °C, 3 h, 95%.

CONCLUSIONS

Several synthetic applications of diazo compounds derived from monosaccharides have been discovered. Among these applications, we have achieved the stereoselective synthesis of *syn* or *anti* 1-alkyl-2-hydroxy fragments by novel reactions of α-diazo-β-hydroxy carbonyl compounds via an interesting photochemical Wolff

rearrangement and by reaction with borane reagents. Finally, the use of this reaction in the carbohydrate field was demonstrated to be useful in efficient and high yielding syntheses of the natural 2-keto-3-deoxy aldonic acids KDG and DAH. The present contribution is sure to complement the many benefits of diazo chemistry in organic synthesis.

EXPERIMENTAL SECTION

General Techniques. All reactions were carried out under a dry argon atmosphere using freshly distilled solvents unless otherwise noted. Reactions were monitored by thin layer chromatography (TLC) on E. Merck silica gel plates (0.25 mm) and visualized using UV light (254 nm) and/or heating with *p*-anisaldehyde solution (340 mL ethanol, 9.2 mL *p*-anisaldehyde, 12.5 mL sulfuric acid and 3.75 mL acetic acid). Flash chromatography was performed on E. Merck silica gel (60, particle size 0.040-0.063 mm). Melting points are given uncorrected. IR spectra were recorded on a Beckman Aculab IV spectrophotometer, wavenumbers are expressed in cm^{-1}. NMR spectra were recorded at 200 MHz on a Bruker WP200SY spectrometer at ambient temperature. Chemical shifts are reported relative to the residual solvent peak. Multiplicities are designated as: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad singlet (bs). Coupling constants are expressed as *J* values in Hertz units. Mass spectra were recorded on a Hewlett-Packard 5988A instrument. Microanalyses were performed by the Servicio de Microanálisis de la Universidad de Málaga. Exact masses were recorded on a Kratos MS 80 RFA instrument of the University of Seville. Specific rotations were measured with a Perkin-Elmer 241 polarimeter. Photochemical reactions were carried out in a Rayonet device using mercury lamps of low pressure (8 w).

Diazo ketone 3. Condensation of 1 with diazoacetone 2. A mixture of aldehyde **1** (3.0 g, 23.0 mmol) and diazoacetone **2** (3.8 g, 46.0 mmol, 2.0 equiv) was kept neat at 0 °C for 2 days. After this time, the crude mixture was purified by flash column chromatography (silica gel, 40% EtOAc in hexanes) to obtain **3** as a yellow solid (3.0 g, 61%): R_f = 0.48 (silica gel, 50% EtOAc in hexanes); m. p. 47 °C; $[\alpha]^{22}_{D}$ + 16.0 (*c* 0.8, $CHCl_3$); IR (thin film) ν_{max} 3300, 2100, 1650 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.48 (t, *J* = 6.5 Hz, 1 H, C*H*(OH)), 4.23 (ddd, *J* = 6.5, 6.3, 4.8 Hz, 1 H, C*H*CH(OH)), 4.08 (dd, *J* = 8.8, 6.3 Hz, 1 H, CH_2(O)CH), 3.93 (dd, *J* = 8.8, 4.8 Hz, 1 H, CH_2(O)CH), 3.61 (d, *J* = 6.5 Hz, 1 H, CHO*H*), 2.25 (s, 3 H, CH_3), 1.38 (s, 3 H, $C(CH_3)_2$), 1.31 (s, 3 H, $C(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 192.0, 123.1, 110.5, 76.9, 68.9, 66.7, 26.8, 26.1, 25.3; MS *m/e* 171 (M^+-15-28, 16), 101 (100); Anal. Calcd. for $C_9H_{14}N_2O_4$: C 50.47%, H 6.54%, N 13.08%; found: C 50.00 %, H 7.06%, N 12.97%.

β-diketone 4. Photochemistry of 3. A solution of diazo **3** (300 mg, 1.40 mmol) in MeOH (5 mL) was exposed to UV radiation (λ = 253.7 nm) at 25° C for 8 h. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (silica gel, 20% EtOAc in hexanes) to obtain **4** (240 mg, 95%) as a colorless oil: R_f = 0.75 (silica gel, 50% EtOAc in hexanes); $[\alpha]^{22}_D$ + 9.8° (*c* 1.7, $CHCl_3$); IR (thin film) ν_{max} 3300, 1620 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.85 (s, 1 H, C(OH)=C*H*COCH$_3$), 4.46 (dd, *J* = 7.4, 5.7 Hz, 1 H, C*H*C(OH)), 4.22 (dd, *J* = 8.4, 7.4 Hz, 1 H, CH_2(O)CH), 3.95 (dd, *J* = 8.4, 5.7 Hz, 1 H, CH_2(O)CH), 2.06 (s, 3 H, CH_3), 1.44 (s, 3 H, C(CH_3)$_2$), 1.36 (s, 3 H, C(CH_3)$_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 197.0, 192.7, 110.8, 96.6, 76.4, 67.7, 25.9, 25.2, 24.8; MS *m/e* 171 (M^+-15, 20), 101 (100).

Hydroxy ketone 5. Hydrogenolysis of diazo 3. To a solution of diazo ketone **3** (200 mg, 0.93 mmol) in ethyl acetate (75 mL) was added Pd/C (20 mg, 10%). The reaction was allowed to proceed under an atmosphere of H_2 at a pressure of 50 psi and at 25 °C (Parr hydrogenator apparatus). After 5 h, no starting diazo was detected by TLC and the mixture was filtered through Celite. The solution was concentrated under reduced pressure, and the resulting crude product was purified by flash column chromatography (silica gel, 20% EtOAc in hexanes) to give alcohol **5** (158 mg, 90%) as a colorless oil: R_f = 0.60 (silica gel, 50% EtOAc in hexanes); $[\alpha]^{22}_D$ – 19.6 (*c* 2.9, $CHCl_3$); IR (thin film) ν_{max} 3500-3300, 1650 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.05 (ddd, *J* = 8.2, 6.2, 1.5 Hz, 1 H, C*H*(OH)), 3.90-3.70 (m, 3 H, C*H*CH(OH), CH_2(O)CH), 3.32 (bs, 1 H, OH), 2.75 (dd, *J* = 17.5, 1.5 Hz, 1 H, CH_2COCH$_3$), 2.51 (dd, *J* = 17.5, 8.2 Hz, 1 H, CH_2COCH$_3$), 2.12 (s, 3 H, CH_3), 1.31 (s, 3 H, C(CH_3)$_2$), 1.25 (s, 3 H, C(CH_3)$_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 193.5, 110.0, 77.8, 69.0, 66.6, 46.2, 31.0, 26.7, 25.1.

Silyl ether 6. Silylation of 3. Diazo alcohol **3** (1.0 g, 4.7 mmol) was dissolved in DMF (7.0 mL), the solution was cooled to 0 °C and imidazole (0.64 g, 9.4 mmol, 2.0 equiv) and *tert*-butyldimethylsilyl chloride (1.1 g, 7.1 mmol, 1.5 equiv) were added. The reaction mixture was allowed to stir at 25 °C for 12 h. Methanol (1.0 mL) was added at 0 °C, then ether (50 mL) and saturated aqueous NH_4Cl solution (20 mL) were sequentially added and the organic layer was separated. The aqueous phase was extracted with ether (2 x 20 mL), and the combined organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, 10% EtOAc in hexanes) provided silyl ether **6** (1.4 g, 88%) as a yelow oil: R_f = 0.26 (silica gel, 20% EtOAc in hexanes); $[\alpha]^{22}_D$ + 3.8 (*c* 0.5, $CHCl_3$); IR (thin film) ν_{max} 2956, 2086, 1685 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.70 (d, *J* = 6.0 Hz, 1 H, CH(OSi)), 4.15 (ddd, *J* = 6.0, 5.8, 4.8 Hz, 1 H, C*H*CH(OSi)), 4.07 (dd, *J* = 8.8, 5.8 Hz, 1 H, CH_2(O)CH), 3.78 (dd, *J* = 8.8, 4.8 Hz, 1 H, CH_2(O)CH), 2.20 (s, 3 H, CH_3), 1.40 (s, 3 H, C(CH_3)$_2$), 1.30 (s, 3 H, C(CH_3)$_2$), 0.85 (s, 9 H, SiC(CH_3)$_3$), 0.10 (s, 3 H, Si(CH_3)$_2$), 0.00 (s, 3 H, Si(CH_3)$_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 192.0, 109.7, 77.6, 67.0, 66.4, 26.5, 25.3, 25.2, 25.1,

17.8, -0.4, -0.5; MS *m/e* 285 (M^+-15 -28, 20); Anal. Calcd. for $C_{15}H_{28}N_2O_4Si$: C 54.87%, H 8.53%, N 8.53%; found: C 54.94 %, H 9.28%, N 8.16%.

Ester 7. Photochemistry of diazo silyl ether 6. A solution of diazo **6** (1.0 g, 3.0 mmol) in MeOH/THF (20 mL, 1/1) was cooled at 0 °C, and irradiated with UV light (λ = 253.7 nm) for 8 h. After this time, the reaction was complete by TLC analysis, and the solvents were removed under *vacuo*. The crude product was purified by flash column chromatography (silica gel, 5% EtOAc in hexanes) to obtain the ester **7** (415 mg, 41%) as a colorless oil: R_f = 0.73 (silica gel, 20% EtOAc in hexanes); $[\alpha]^{22}_D$ + 14.9 (*c* 0.9, $CHCl_3$); IR (thin film) ν_{max} 2956, 1748 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.16 (dd, *J* = 5.6, 2.9 Hz, 1 H, CH(OSi)), 4.02 (dd, *J* = 7.0, 4.0 Hz, 1 H, C*H*$_2$C(O)CH), 3.94 (ddd, *J* = 5.6, 5.0, 4.0 Hz, 1 H, C*H*CH(OSi)), 3.79 (dd, *J* = 7.0, 5.0 Hz, 1 H, C*H*$_2$(O)CH), 3.65 (s, 3 H, CO_2CH_3), 2.70 (dq, *J* = 7.1, 2.9 Hz, 1 H, C*H*(CH_3)), 1.37 (s, 3 H, C(CH_3)$_2$), 1.30 (s, 3 H, C(CH_3)$_2$), 1.13 (d, *J* = 7.1 Hz, 3 H, CH(C*H*$_3$)), 0.85 (s, 9 H, SiC(CH_3)$_3$), 0.10 (s, 3 H, Si(CH_3)$_2$), -0.05 (s, 3 H, Si(CH_3)$_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 175.1, 109.0, 76.5, 73.9, 67.3, 51.6, 42.4, 26.7, 25.8, 25.3, 18.1, 9.6, -0.6; MS *m/e* 317 (M^+-15, 32); Anal. Calcd. for $C_{16}H_{32}O_5Si$: C 57.83%, H 9.60%; found: C 57.79%, H 9.53%.

Lactone 8. Hydrolysis of 7. To a solution of **7** (50 mg, 0.15 mmol) in ether (1.0 mL) was added a F_3B:Et_2O solution (100 μL) at 0 °C. After 2 h, the lactone **8** was formed quantitatively and precipitated in the ethereal solution. The suspension was filtered and the solid was washed with cold ether and chloroform, and dried to obtain **8** (21 mg, 97%) as a white solid: ^1H NMR (200 MHz, D_2O) δ 4.21 (m, 1 H, CHOCO), 3.95 (t, *J* = 7.0 Hz, 1 H, C*H*(OH)CH(CH_3)), 3.85 (dd, *J* = 7.6, 5.0 Hz, 1 H, C*H*$_2$OH), 3.62 (dd, *J* = 7.6, 5.0 Hz, 1 H, C*H*$_2$OH), 2.69 (dq, *J* = 7.1, 2.9 Hz, 1 H, C*H*(CH_3)), 1.15 (d, *J* = 7.1 Hz, 3 H, CH(C*H*$_3$)); ^{13}C NMR (50.3 MHz, D_2O) δ 178.8, 85.6, 74.1, 60.8, 44.3, 13.3.

Acetoxy diazo 9. Acetylation of 3. Diazo alcohol **3** (1.0 g, 4.7 mmol) was dissolved in pyridine (10.0 mL), and acetic anhydride (1.0 mL, 9.4 mmol, 2.0 equiv) was added at 25 °C. The reaction mixture was stirred at 25 °C for 8 h. After this time, CH_2Cl_2 (50 mL) and saturated aqueous NH_4Cl solution (50 mL) were sequentially added and the organic layer was separated. The aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL), and the combined organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, 20% EtOAc in hexanes) provided acetate **9** (1.1 g, 96%) as a yelow oil: R_f = 0.33 (silica gel, 25% EtOAc in hexanes); $[\alpha]^{22}_D$ + 4.5 (*c* 0.6, $CHCl_3$); IR (thin film) ν_{max} 2956, 2100, 1750, 1650 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.67 (m, 1 H, CH(OAc)), 4.57 (m, 1 H, C*H*CH(OAc)), 4.10 (m, 1 H, C*H*$_2$(O)CH), 3.70 (m, 1 H, C*H*$_2$(O)CH), 2.27 (s, 3 H, CH_3), 2.10 (s, 3 H, $OCOCH_3$), 1.58 (s, 3 H, C(CH_3)$_2$), 1.50 (s, 3 H, C(CH_3)$_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 192.0, 169.6,

110.3, 75.6, 68.1, 65.9, 25.8, 25.3, 24.6, 20.7; MS *m/e* 213 (M^+ -15 -28, 25); Anal. Calcd. for $C_{11}H_{16}N_2O_5$: C 51.56%, H 6.25%, N 10.93%; found: C 51.53 %, H 6.64%, N 10.10%.

Methoxy ether 10. O-methylation of diazo 3. To a solution of diazo **3** (200 mg, 0.93 mmol) in DMF (5.0 mL) was added powdered sodium hydroxide (75 mg, 1.86 mmol, 2.0 equiv) in small portions for 15 min at 0 °C. After the addition was completed, MeI (0.5 mL, 3.72 mmol, 4.0 equiv) was added dropwise for 30 min. The reaction mixture was allowed to stir at 25 °C for 24 h. Water (15.0 mL) was added at 0 °C, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure to obtain a crude product which was purified by flash column chromatography (silica gel, 20% EtOAc in hexanes) obtaining the ether **10** (160 mg, 76%) as a yelow oil: R_f = 0.45 (silica gel, 20% EtOAc in hexanes); $[\alpha]^{22}_D$ + 5.3 (*c* 0.5, $CHCl_3$); IR (thin film) ν_{max} 2956, 2100, 1650 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.35 (m, 2 H, C*H*(OCH_3), C*H*CH(OCH_3)), 4.07 (m, 1 H, CH_2(O)CH), 3.73 (m, 1 H, CH_2(O)CH), 3.30 (s, 3 H, OCH_3), 2.30 (s, 3 H, CH_3), 1.41 (s, 3 H, $C(CH_3)_2$), 1.37 (s, 3 H, $C(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 190.0, 110.2, 76.2, 74.7, 66.4, 56.9, 26.0, 25.5, 24.7; MS *m/e* 185 (M^+-15 -28, 25); FAB HRMS (NBA) *m/e* 185.0907, M - 15 - 28 calcd for $C_{10}H_{16}N_2O_4$ 185.0926.

Synthesis of the olefins 11 and 12. Photochemistry of 9. A solution of diazo **9** (212 mg, 0.83 mmol) in THF/MeOH (10 mL, 9/1) was cooled at -30 °C, and irradiated with UV light (λ = 253.7 nm) for 17 h. After this time, the reaction was complete by TLC analysis, and the solvents were removed under *vacuo*. The crude product was purified by flash column chromatography (silica gel, 20% EtOAc in hexanes) to obtain the ester **11** (132 mg, 85%) and the olefin **12** (*Z*:*E* 1:1, 27 mg, 14%) as colorless oils. **[11]**: R_f = 0.63 (silica gel, 20% EtOAc in hexanes); IR (thin film) ν_{max} 2956, 1715, 1650 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.70 (dq, *J* = 6.7, 1.5 Hz, 1 H, C*H*=C(Me)CO_2Me), 4.87 (q, *J* = 6.7 Hz, 1 H, C*H*CH=C(CH_3)), 4.17 (dd, *J* = 8.2, 6.7 Hz, 1 H, CH_2(O)CH), 3.75 (s, 3 H, CO_2CH_3), 3.67 (dd, *J* = 8.2, 6.7 Hz, 1 H, CH_2(O)CH), 1.87 (d, *J* = 1.5 Hz, 3 H, CH=C(CH_3)), 1.46 (s, 3 H, $C(CH_3)_2$), 1.42 (s, 3 H, $C(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 167.7, 138.5, 130.6, 109.7, 72.6, 68.6, 51.9, 26.5, 25.7, 12.9; Anal. Calcd. for $C_{10}H_{16}O_4$: C 59.98%, H 8.05%; found: C 60.06%, H 8.12%. **[12]**(1:1 *Z*:*E* mixture): R_f = 0.35 (silica gel, 20% EtOAc in hexanes); IR (thin film) ν_{max} 2956, 1750, 1646 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.50 (s, 0.5 H, C=C*H*COMe), 5.90 (s, 0.5 H, C=C*H*COMe), 4.50 (dd, *J* = 7.0, 5.8 Hz, 0.5 H, C*H*C(OAc)=CH), 4.45 (dd, *J* = 7.1, 5.8 Hz, 0.5 H, C*H*C(OAc)=CH), 4.22 (dd, *J* = 7.3, 7.0 Hz, 0.5 H, CH_2(O)CH), 4.19 (dd, *J* = 7.4, 7.1 Hz, 0.5 H, CH_2(O)CH), 4.06 (dd, *J* = 7.4, 5.8 Hz, 0.5 H, CH_2(O)CH), 3.98 (dd, *J* = 7.3, 5.8 Hz, 0.5 H, CH_2(O)CH), 2.35 (s, 3 H, C(OCOCH_3)=CH), 2.17 (s, 1.5 H, $COCH_3$), 2.10 (s, 1.5 H, $COCH_3$), 1.47 (s, 1.5 H, $C(CH_3)_2$), 1.45 (s, 1.5 H, $C(CH_3)_2$), 1.38 (s, 1.5 H, $C(CH_3)_2$), 1.37 (s, 1.5 H, $C(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 183.5, 169.1,

165.0, 111.1, 110.5, 81.3, 67.2, 26.1, 25.5, 21.5, 19.3; MS *m/e* 213 (M^+-15), 171, 169, 127, 101, 85 (100), 73; FAB HRMS (NBA) *m/e* 228.0975, M^+ calcd for $C_{11}H_{16}O_5$ 228.0998.

Synthesis of the olefin 13. Photochemistry of 10. Diazo **10** (100 mg, 0.45 mmol) was exposed to UV light according to the procedure described above for **9** at 4 °C and for 10 h. to afford olefin **13** (61 mg, 69%) as a colorless oil: R_f = 0.26 (silica gel, 20% EtOAc in hexanes); IR (thin film) ν_{max} 2930, 1648 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.64 (dd, *J* = 7.0, 5.5 Hz, 1 H, C*H*C(OMe)=CH), 5.48 (s, 1 H, CHC(OMe)=C*H*), 4.37 (dd, *J* = 8.5, 7.0 Hz, 1 H, CH_2(O)CH), 3.77 (dd, *J* = 8.5, 5.5 Hz, 1 H, CH_2(O)CH), 3.69 (s, 3 H, C(OCH_3)=CH), 2.17 (s, 3 H, $COCH_3$), 1.46 (s, 3 H, $C(CH_3)_2$), 1.38 (s, 3 H, $C(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 196.6, 172.2, 110.6, 99.9, 73.4, 69.1, 56.3, 31.7, 25.8, 25.5; MS *m/e* 200 (M^+), 185, 142, 127, 125 (100); FAB HRMS (NBA) *m/e* 185.0917, M^+ - 15 calcd for $C_{10}H_{16}O_4$ 185.0926.

Diketone 14. Oxidation of diazo 6. To a solution of diazo **6** (1.34 g, 4.10 mmol) in CH_2Cl_2 (20.0 mL) at 0 °C was added *m*-chloroperbenzoic acid (1.50 g, 57% purity, 4.92 mmol, 1.2 equiv), and the reaction mixture was stirred at that temperature for 2 h, at which time TLC indicated completion of the reaction. The reaction mixture was diluted with hexanes (50 mL), precipitating the benzoic acid derivative. The suspension was filtered and the filtrate was washed with hexanes (3 x 20 mL). The combined organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, 5% EtOAc in hexanes) provided diketone **14** (1.26 g, 98%) as a pale yelow oil: R_f = 0.75 (silica gel, 10% EtOAc in hexanes); $[\alpha]^{22}_D$ + 35.8 (*c* 0.7, $CHCl_3$); IR (thin film) ν_{max} 2975, 1725, 1718 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.89 (d, *J* = 7.5 Hz, 1 H, CH(OSi)), 4.05 (m, 2 H), 3.95 (m, 1 H), 2.30 (s, 3 H, CH_3), 1.33 (s, 3 H, $C(CH_3)_2$), 1.25 (s, 3 H, $C(CH_3)_2$), 0.85 (s, 9 H, $SiC(CH_3)_3$), 0.00 (s, 3 H, $Si(CH_3)_2$), -0.10 (s, 3 H, $Si(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 200.7, 199.2, 110.5, 77.6, 73.1, 67.4, 26.0, 25.6, 25.0, 24.2, 18.1, -4.7, -5.2; MS *m/e* 301 (M^+-15), 241, 201, 155 (100), 101; Anal. Calcd. for $C_{15}H_{28}O_5Si$: C 56.93%, H 8.92%; found: C 56.97%, H 8.81%.

Hydrazone 15. Treatment of diketone 14 with hydrazine. Diketone **14** (1.03 g, 3.3 mmol) was dissolved in MeOH (5 mL) and the solution was cooled to -60 °C. A solution of NH_2NH_2 (116 mg, 3.6 mmol, 1.1 equiv) in MeOH (5 mL) was slowly added, and the resulting mixture was stirred for 1 h. After this time, CH_2Cl_2 (20 mL) and saturated aqueous NH_4Cl solution (20 mL) were sequentially added at -60 °C, and the mixture was allowed to warm to 25 °C. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, 20% EtOAc in hexanes) furnished hydrazone **15** (1.01 g, 94%) as a pale yellow solid: R_f = 0.53 (silica gel, 20% EtOAc in hexanes); m p 96 °C; $[\alpha]^{22}_D$ + 15.8 (*c* 0.7, $CHCl_3$); IR (thin film) ν_{max} 3500, 3450, 3400, 2960, 1715 cm^{-1}; ^1H NMR (200 MHz,

$CDCl_3$) δ 6.11 (bs, 2 H, NNH_2), 5.42 (d, J = 5.6 Hz, 1 H, CHOSi), 4.26 (ddd, J = 6.2, 5.7, 5.6 Hz, 1 H, C*H*CHOSi), 4.01 (dd, J = 8.4, 5.7 Hz, 1 H, CH_2(O)CH), 3.87 (dd, J = 8.4, 6.2 Hz, 1 H, CH_2(O)CH), 1.83 (s, 3 H, CH_3), 1.36 (s, 3 H, $C(CH_3)_2$), 1.28 (s, 3 H, $C(CH_3)_2$), 0.84 (s, 9 H, $SiC(CH_3)_3$), 0.02 (s, 3 H, $Si(CH_3)_2$), -0.05 (s, 3 H, $Si(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 196.9, 143.3, 109.1, 77.1, 70.1, 65.3, 26.4, 25.7, 25.4, 18.1, 6.9, -4.7, -4.9; MS *m/e* 315 (M^+-15), 173 (100), 101; Anal. Calcd. for $C_{15}H_{30}O_4N_2Si$: C 54.51%, H 9.15%, N 8.48%; found: C 54.54%, H 9.06%, N 8.22%.

Hydrazone 16. Treatment of diazo 6 with triphenylphosphine. To a solution of diazo **6** (600 mg, 1.83 mmol) in THF (5 mL) was added Ph_3P (720 mg, 2.75 mmol, 1.5 equiv) at room temperature. After being stirred for 5 h, the solution was cooled to 0 °C and water (10 mL) was added. The reaction mixture was stirred at this temperature for 2 h, and then was allowed to warm to 25 °C. The organic layer was separated and the aqueous phase was extracted with ether (2 x 10 mL). The combined organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Flash column chromatography (silica gel, 20% EtOAc in hexanes) provided hydrazone **16** (440 mg, 73%) as a colorless oil: R_f = 0.49 (silica gel, 20% EtOAc in hexanes); m p 4 °C; $[\alpha]^{22}_D$ - 116.9 (*c* 0.3, $CHCl_3$); IR (thin film) ν_{max} 3440, 3323, 3237, 2960, 1664, 1560 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.30 (bs, 2 H, NNH_2), 5.14 (d, J = 6.5 Hz, 1 H, CH(OSi)), 4.41 (ddd, J = 6.5, 6.2, 5.3 Hz, 1 H, C*H*CH(OSi)), 3.98 (dd, J = 8.7, 6.2 Hz, 1 H, CH_2(O)CH), 3.82 (dd, J = 8.7, 5.3 Hz, 1 H, CH_2(O)CH), 2.27 (s, 3 H, CH_3), 1.34 (s, 3 H, $C(CH_3)_2$), 1.27 (s, 3 H, $C(CH_3)_2$), 0.85 (s, 9 H, $SiC(CH_3)_3$), 0.08 (s, 3 H, $Si(CH_3)_2$), -0.01 (s, 3 H, $Si(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 196.9, 142.5, 109.1, 75.5, 68.9, 66.3, 26.4, 25.7, 25.4, 24.1, 18.1, -4.7, -4.9; MS *m/e* 315 (M^+-15), 230 (100), 101; Anal. Calcd. for $C_{15}H_{30}O_4N_2Si$: C 54.51%, H 9.15%, N 8.48%; found: C 55.04%, H 9.26%, N 8.39%.

Diazo 17. Oxidation of hydrazone 15. To a solution of hydrazone **15** (500 mg, 1.51 mmol) in $CHCl_3$ (10 mL) was added activated manganese dioxide (175 mg, 2.0 mmol, 1.5 equiv) at 25 °C. After stirring for 30 min, no starting hydrazone was detected by TLC and the mixture was filtered through Celite. The clear yellow solution was concentrated under reduced pressure, and the resulting crude product was purified by flash column chromatography (silica gel, 10% EtOAc in hexanes) to give diazo **17** (490 mg, 99%) as a yellow oil: R_f = 0.72 (silica gel, 20% EtOAc in hexanes); $[\alpha]^{22}_D$ + 28.0 (*c* 0.9, $CHCl_3$); IR (thin film) ν_{max} 2958, 2086, 1685 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.21 (s, 1 H, CHOSi), 4.18 (dd, J = 6.0, 5.4 Hz, 1 H, C*H*CHOSi), 4.02 (dd, J = 8.8, 6.0 Hz, 1 H, CH_2(O)CH), 3.86 (dd, J = 8.8, 5.4 Hz, 1 H, CH_2(O)CH), 1.96 (s, 3 H, CH_3), 1.38 (s, 3 H, $C(CH_3)_2$), 1.30 (s, 3 H, $C(CH_3)_2$), 0.87 (s, 9 H, $SiC(CH_3)_3$), 0.06 (s, 3 H, $Si(CH_3)_2$), 0.05 (s, 3 H, $Si(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 193.4, 109.9, 78.9, 77.5, 66.2, 26.3, 25.7, 25.2, 18.2, 9.4, -4.9, -5.2; MS *m/e* 285 (M^+ -15 -28); Anal. Calcd. for $C_{15}H_{28}O_4N_2Si$: C 54.85%, H 8.59%, N 8.53%; found: C 55.16%, H 8.72%, N 8.17%.

Synthesis of the ester 7. Photochemistry of diazo 17. Diazo **17** (100 mg, 0.31 mmol) was exposed to UV light according to the procedure described above for **6** to afford ester **7** (84 mg, 83%) with identical spectroscopic and physical properties than that obtained from **6**.

Hydroxy diazo 18. Desilylation of diazo 17. A solution of diazo **17** (125 mg, 0.38 mmol) in THF (2.0 mL) at 0 °C was treated with TBAF (0.46 mL, 1 M solution in THF, 0.46 mmol, 1.2 equiv). After being stirring for 1 h, the reaction mixture was diluted with EtOAc (5.0 mL) and washed with saturated aqueous NH_4Cl solution (10.0 mL). The aqueous phase was extracted with EtOAc (2 x 10 mL), and the combined organic layer was washed with brine (10.0 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, 40% EtOAc in hexanes) to provide hydroxy diazo **18** (61 mg, 75%) as a yellow oil: R_f = 0.30 (silica gel, 20% EtOAc in hexanes); $[\alpha]^{22}_D$ - 5.0 (*c* 0.6, $CHCl_3$); IR (thin film) ν_{max} 3500, 2958, 2090, 1617 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.21 (d, *J* = 7.4 Hz, 1 H, CHOH), 4.11 (m, 1 H, C*H*CHOH), 3.97 (dd, *J* = 14.1, 5.8 Hz, 1 H, CH_2(O)CH), 3.86 (dd, *J* = 14.1, 5.8 Hz, 1 H, CH_2(O)CH), 2.00 (s, 3 H, CH_3), 1.40 (s, 3 H, C$(CH_3)_2$), 1.29 (s, 3 H, C$(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 192.9, 110.2, 77.6, 73.6, 67.5, 25.9, 24.9, 24.8; MS *m/e* 171 (M^+-15 -28), 101 (100); Anal. Calcd. for $C_9H_{14}N_2O_4$: C 50.47%, H 6.54%, N 13.08%; found: C 50.32 %, H 7.02%, N 12.97%.

Synthesis of ester 19. Photochemistry of diazo 18. Diazo **18** (60 mg, 0.28 mmol) was exposed to UV light according to the procedure described above for **6** to afford ester **19** (34 mg, 55%), as a 1:1 C-2 epimeric mixture, and β-diketone **4** (24 mg, 45%). **[19]**: R_f = 0.35 (silica gel, 50% EtOAc in hexanes); IR (thin film) ν_{max} 3480, 2975, 1725 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.20-3.90 (m, 4 H), 3.80 (s, 3 H, OCH_3), 2.80 (m, 1 H), 1.45 (s, 3 H, C$(CH_3)_2$), 1.30 (s, 3 H, C$(CH_3)_2$), 1.25 (d, *J* = 7.1 Hz, 3 H, CH(CH_3)); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 176.6, 109.3, 75.2, 74.6, 72.2, 67.1, 66.7, 51.9, 51.8, 40.9, 40.6, 26.8, 26.7, 25.2, 14.7, 10.4; MS *m/e* 203 (M^+-15), 175, 161, 129, 117, 101 (100).

Diazo ester 21a. Condensation of 1 with ethyl diazoacetate 20a. A mixture of aldehyde **1** (3.6 g, 27.6 mmol) and ethyl diazoacetate **20a** (4.7 g, 41.4 mmol, 1.5 equiv) was kept neat at 4 °C for 12 h. After this time, the crude mixture was purified by flash column chromatography (silica gel, 20% EtOAc in hexanes) to obtain diazo ester **21a** (4.6 g, 68%) as a yellow oil: R_f = 0.61 (silica gel, 50% EtOAc in hexanes); IR (thin film) ν_{max} 3400, 2980, 2080, 1670 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.49 (t, *J* = 5.9 Hz, 1 H, C*H*OH), 4.25 (q, *J* = 7.0 Hz, 2 H, OC$H_2$$CH_3$), 4.15 (ddd, *J* = 6.3, 5.9, 5.0 Hz, 1 H, C*H*CHOH), 4.05 (dd, *J* = 8.7, 6.3 Hz, 1 H, CH_2(O)CH), 3.93 (dd, *J* = 8.7, 5.0 Hz, 1 H, CH_2(O)CH), 1.39 (s, 3 H, C$(CH_3)_2$), 1.35 (s, 3 H, C$(CH_3)_2$), 1.25

(t, J = 7.0 Hz, 3 H, OCH_2CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 167.2, 110.5, 76.7, 68.1, 67.0, 61.5, 27.0, 24.9, 14.1; MS *m/e* 201 (M^+-15-28), 101 (100).

Diazo ester 21b. Condensation of 1 with *tert*-butyl diazoacetate 20b. Aldehyde **1** (3.0 g, 23.0 mmol) and *tert*-butyl diazoacetate **20b** (9.4 g, 34.5 mmol, 1.5 equiv) were condensed according to the same procedure described above for **20a** to obtain diazo ester **21b** (4.4 g, 70%) as a yellow solid: R_f = 0.65 (silica gel, 50% EtOAc in hexanes); IR (thin film) ν_{max} 3420, 2980, 2080, 1670 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.41 (dd, J = 6.7, 5.6 Hz, 1 H, C*H*OH), 4.18 (ddd, J = 6.7, 6.3, 5.1 Hz, 1 H, C*H*CHOH), 4.04 (dd, J = 8.5, 6.3 Hz, 1 H, CH_2(O)CH), 3.87 (dd, J = 8.5, 5.1 Hz, 1 H, CH_2(O)CH), 1.42 (s, 9 H, $C(CH_3)_3$), 1.36 (s, 3 H, $C(CH_3)_2$), 1.29 (s, 3 H, $C(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 166.4, 110.1, 82.3, 76.8, 68.1, 66.8, 28.5, 26.7, 25.2; MS *m/e* 229 (M^+-15 -28), 101 (100); Anal. Calcd. for $C_{12}H_{20}O_5N_2$: C 52.93%, H 7.40%, N 10.29%; found: C 52.79%, H 7.45%, N 10.12%.

β-keto amide 22a and epoxy amides 23a and 23b. Condensation of 1 with *N,N*-diethyl diazoacetamide 20c. Procedure A: Aldehyde **1** (0.9 g, 7.1 mmol) and *N,N*-diethyl diazoacetamide **20c** (1.5 g, 10.6 mmol, 1.5 equiv) were condensed according to the same procedure described above for **20a** to obtain β-keto amide **22a** (0.21 g, 12%) and epoxy amides **23a** (0.30 g, 18%) and **23b** (0.48 g, 28%). **Procedure B:** To a solution of aldehyde **1** (2.2 g, 16.9 mmol) in $CHCl_3$ (10 mL) was added *N,N*-diethyl diazoacetamide **20c** (3.6 g, 25.3 mmol, 1.5 equiv) dropwise and at 25 °C. After being stirred at room temperature for 12 h, the solution was concentrated under reduced pressure and the crude mixture purified by flash column chromatography (silica gel, 40% EtOAc in hexanes) to obtain pure epoxy amides **23a** (1.6 g, 40%) and **23b** (1.8 g, 45%). **[22a]**: R_f = 0.51 (silica gel, 40% EtOAc in hexanes); IR (thin film) ν_{max} 2980, 2870, 1730, 1650 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.40 (d, J = 0.7 Hz, 1 H, C(OH)=C*H*), 4.49 (dd, J = 7.1, 5.9 Hz, 1 H, C*H*C(OH)=CH), 4.17 (dd, J = 8.4, 7.1 Hz, 1 H, CH_2(O)CH), 3.94 (dd, J = 8.4, 5.9 Hz, 1 H, CH_2(O)CH), 3.68 (d, J = 15.7, 2 H, $COCH_2CONEt_2$), 3.38-3.13 (m, 4 H, $N(CH_2CH_3)_2$), 1.41 (s, 3 H, $C(CH_3)_2$), 1.35 (s, 3 H, $C(CH_3)_2$), 1.18-1.06 (m, 6 H, $N(CH_2CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 174.9, 170.9, 110.2, 110.7, 84.9, 79.9, 74.8, 68.0, 66.2, 44.7, 42.6, 42.1, 40.1, 40.0, 25.9, 25.3, 24.8, 14.0, 13.1, 12.8; MS *m/e* 170 (M^+-15 -2 x 29), 140, 127, 112, 101, 83 (100); Anal. Calcd. for $C_{12}H_{21}O_4N$: C 59.24%, H 8.70%, N 5.76%; found: C 58.63%, H 8.63%, N 5.93%. **[23a]**: R_f = 0.35 (silica gel, 40% EtOAc in hexanes); $[\alpha]^{22}_D$ - 1.4 (*c* 1.2, $CHCl_3$); IR (thin film) ν_{max} 2980, 2870, 1662, 1395, 1375 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.12 (dd, J = 10.4, 8.4 Hz, 1 H, CH_2(O)CH), 3.95 (ddd, J = 8.4, 5.4, 5.1 Hz, 1 H, CH_2(O)C*H*), 3.92 (dd, J = 10.4, 5.1 Hz, 1 H, CH_2(O)CH), 3.55 (d, J = 2.0 Hz, 1 H, C*H*$CONEt_2$), 3.49-3.27 (m, 4 H, $N(CH_2CH_3)_2$), 3.19 (dd, J = 5.4, 2.0 Hz, 1 H, C*H*(O)CHCONEt_2), 1.41 (s, 3 H, $C(CH_3)_2$), 1.32 (s, 3 H, $C(CH_3)_2$), 1.21 (t, J = 7.2 Hz, 3 H, NCH_2CH_3), 1.10 (t, J = 7.2 Hz, 3 H, NCH_2CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 165.6, 109.9, 74.9, 66.9, 57.6, 51.7, 41.4,

40.7, 26.4, 25.0, 14.6, 12.8; MS *m/e* 228 (M^+-15), 200, 180, 142 (100), 130, 100, 72. **[23b]**: R_f = 0.31 (silica gel, 40% EtOAc in hexanes); $[\alpha]^{22}_D$ + 12.3 (*c* 0.6, $CHCl_3$); IR (thin film) ν_{max} 2980, 2870, 1662, 1395, 1375 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.12 (dd, *J* = 8.7, 6.4 Hz, 1 H, C*H*$_2$(O)CH), 4.02 (dd, *J* = 8.7, 4.6 Hz, 1 H, C*H*$_2$(O)CH), 3.85 (ddd, *J* = 7.9, 6.4, 4.6 Hz, 1 H, CH$_2$(O)C*H*), 3.64 (d, *J* = 4.3 Hz, 1 H, C*H*CONEt$_2$), 3.55-3.30 (m, 4 H, N(C*H*$_2$CH$_3$)$_2$), 3.22 (dd, *J* = 7.9, 4.3 Hz, 1 H, C*H*(O)CHCONEt$_2$), 1.45 (s, 3 H, C(CH$_3$)$_2$), 1.30 (s, 3 H, C(CH$_3$)$_2$), 1.20 (t, *J* = 7.1 Hz, 3 H, NCH$_2$C*H*$_3$), 1.11 (t, *J* = 7.1 Hz, 3 H, NCH$_2$C*H*$_3$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 164.8, 109.7, 72.9, 67.7, 56.8, 53.4, 41.1, 40.0, 26.8, 25.1, 14.1, 12.7; MS *m/e* 228 (M^+-15), 184, 172, 143 (100), 130, 100; Anal. Calcd. for $C_{12}H_{21}NO_4$: C 59.24%, H 8.70%, N 5.76%; found: C 59.34%, H 9.06%, N 5.97%.

β-keto ester 22b and epoxy ester 23c. Condensation of 1 with methyl diazopropionate 20d. Aldehyde **1** (300 mg, 2.31 mmol) and methyl diazopropionate **20d** (395 mg, 3.46 mmol, 1.5 equiv) were condensed according to the same procedure described above for **20a** to obtain β-keto ester **22b** (338 mg, 68%) as a 1:1 mixture of C-2 epimers and epoxy ester **23c** (113 mg, 23%) as a 2:1 mixture of C-2 epimers. **[22b]**: R_f = 0.46 (silica gel, 20% EtOAc in hexanes); IR (thin film) ν_{max} 2980, 2880, 1740, 1715 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.54 (dd, *J* = 7.8, 5.2 Hz, 1 H, C*H*COCH$_2$), 4.47 (dd, *J* = 7.9, 5.9 Hz, 1 H, C*H*COCH$_2$), 4.16 (dd, *J* = 8.5, 5.9 Hz, I H, C*H*$_2$(O)CH), 4.12 (dd, *J* = 8.6, 5.2 Hz, 1 H, C*H*$_2$(O)CH), 4.02 (dd, *J* = 8.5, 7.9 Hz, 1 H, C*H*$_2$(O)CH), 3.98 (dd, *J* = 8.6, 7.8 Hz, 1 H, C*H*$_2$(O)CH), 3.87 (q, *J* = 7.1, 1 H, COC*H*(CH$_3$)), 3.80 (q, *J* = 7.0, 1 H, COC*H*(CH$_3$)), 3.65 (s, 3 H, OCH$_3$), 3.64 (s, 3 H, OCH$_3$), 1.39 (s, 3 H, C(CH$_3$)$_2$), 1.27 (s, 3 H, C(CH$_3$)$_2$), 1.23 (d, *J* = 7.0, 3 H, COCH(C*H*$_3$)); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 196.5, 196.2, 170.6, 170.5, 110.9, 110.8, 79.5, 79.4, 66.6, 52.1, 52.0, 48.3, 48.2, 25.6, 25.5, 24.6, 24.5, 12.5, 12.1; MS *m/e* 201 (M^+-15), 171, 101 (100); Anal. Calcd. for $C_{10}H_{16}O_5$: C 55.55%, H 7.46%; found: C 55.86%, H 7.48%. **[23c]**(2:1 C-2 epimeric mixture): R_f = 0.39 (silica gel, 20% EtOAc in hexanes); IR (thin film) ν_{max} 2980, 2880, 1740 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.14 (dd, *J* = 8.6, 6.3 Hz, 1 H, C*H*$_2$(O)CH), 4.05 (dd, *J* = 8.6, 4.8 Hz, 1 H, C*H*$_2$(O)CH), 4.02 (ddd, *J* = 8.2, 6.3, 4.8 Hz, 1 H, CH$_2$(O)C*H*), 4.00-3.85 (m, 3 H, minor isomer), 3.78 (s, 3 H, OCH$_3$, minor isomer), 3.74 (s, 3 H, OCH$_3$), 3.22 (d, *J* = 8.2 Hz, 1 H, C*H*(O)C(CH$_3$)), 2.96 (d, *J* = 7.5 Hz, 1 H, C*H*(O)C(CH$_3$), minor isomer), 1.45 (s, 3 H, CH(O)C(C*H*$_3$)), 1.37 (s, 3 H, C(CH$_3$)$_2$, minor isomer), 1.35 (s, 3 H, C(CH$_3$)$_2$), 1.31 (s, 3 H, C(CH$_3$)$_2$, minor isomer), 1.30 (s, 3 H, C(CH$_3$)$_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 171.5, 171.0 (minor isomer), 110.9, 110.2 (minor isomer), 73.1, 72.9 (minor isomer), 68.5, 68.1 (minor isomer), 66.1, 64.1 (minor isomer), 62.2, 53.0, 52.9 (minor isomer), 26.7, 25.7 (minor isomer), 25.1, 24.9 (minor isomer), 19.5, 14.5 (minor isomer); MS *m/e* 201 (M^+-15, 100), 183, 145, 127, 115, 99, 71; MS *m/e* (minor isomer) 201 (M^+-15), 185, 171, 159, 141, 101 (100), 73.

Hydroxy amide 24. Treatment of epoxy amide 23a with lithium dimethyl cuprate. To a cold suspension (-10 °C) of copper (I) iodide (4.8 g, 25.2 mmol, 1.5 equiv) in ether (250 mL) was slowly added MeLi (1.0 M in THF, 50.4 mL, 50.4 mmol, 3.0 equiv). The reaction mixture was stirred for 20 min at -10 °C and was added dropwise to a cold solution (-10 °C) of epoxy amide **23a** (4.1 g, 16.8 mmol) in ether. After addition, the reaction mixture was stirred for 2 h at -10 °C, and then, it was diluted with EtOAc (200 mL) and quenched by carefull addition of saturated aqueous NH_4Cl solution (100 mL). The aqueous phase was extracted with EtOAc (2 x 100 mL), and the combined organic layer was washed with brine (100 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude product so obtained was purified by flash column chromatography (silica gel, 50% EtOAc in hexanes) to give hydroxy amide **24** (3.5 g, 82%) as a colorless oil: R_f = 0.36 (silica gel, 40% EtOAc in hexanes); $[\alpha]^{22}_D$ - 29.5 (*c* 0.8, $CHCl_3$); IR (thin film) ν_{max} 3470, 2980, 2870, 1650 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.24 (d, *J* = 9.7 Hz, 1 H, CHO*H*), 4.07 (dd, *J* = 8.4, 6.1 Hz, 1 H, C*H*$_2$(O)CH), 3.86 (dd, *J* = 8.4, 5.9 Hz, 1 H, C*H*$_2$(O)CH), 3.72 (ddd, *J* = 9.3, 6.1, 5.9 Hz, 1 H, CH$_2$(O)C*H*), 3.42-3.17 (m, 5 H, N(C*H*$_2$CH$_3$)$_2$, C*H*OH), 2.99 (dq, *J* = 7.2, 2.5 Hz, 1 H, C*H*(CH$_3$)), 1.31 (s, 3 H, C(CH$_3$)$_2$), 1.26 (d, *J* = 7.2 Hz, 1 H, CH(C*H*$_3$)), 1.23 (s, 3 H, C(CH$_3$)$_2$), 1.18 (t, *J* = 7.2 Hz, 3 H, NCH$_2$C*H*$_3$), 1.06 (t, *J* = 7.0 Hz, 3 H, NCH$_2$C*H*$_3$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 176.3, 109.1, 77.2, 76.6, 68.4, 42.3, 40.3, 34.7, 26.8, 25.2, 15.5, 14.3, 12.9; MS *m/e* 244 (M^+-15), 158, 141, 129, 100 (100), 72; Anal. Calcd. for $C_{13}H_{25}O_4N$: C 60.21%, H 9.72%, N 5.40%; found: C 59.98%, H 9.63%, N 5.70%.

Silyl ether 25. Silylation of 21a. Silyl ether **25** was prepared from hydroxy diazo **21a** (132 mg, 0.54 mmol) by treatment with *tert*-butyldimethylsilyl chloride according to the procedure described above for the preparation of **6**, to obtain pure silyl ether **25** (178 mg, 92%) as a yellow oil: R_f = 0.70 (silica gel, 20% EtOAc in hexanes); $[\alpha]^{22}_D$ + 7.5 (*c* 0.5, $CHCl_3$); IR (thin film) ν_{max} 2956, 2100, 1750 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.51 (d, *J* = 6.1 Hz, 1 H, CHOSi), 4.28-4.09 (m, 3 H, OC*H*$_2$CH$_3$, C*H*CH(OSi)), 3.99 (dd, *J* = 12.1, 6.7 Hz, 1 H, C*H*$_2$(O)CH), 3.82 (dd, *J* = 12.1, 4.8 Hz, 1 H, C*H*$_2$(O)CH), 1.39 (s, 3 H, C(CH$_3$)$_2$), 1.31 (s, 3 H, C(CH$_3$)$_2$), 1.25 (t, *J* = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 0.85 (s, 9 H, SiC(CH$_3$)$_3$), 0.09 (s, 3 H, Si(CH$_3$)$_2$), 0.05 (s, 3 H, Si(CH$_3$)$_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 167.5, 109.9, 77.5, 68.1, 66.5, 60.8, 26.4, 26.1, 25.4, 17.9, 14.5, -5.0, -5.4; Anal. Calcd. for $C_{16}H_{30}N_2O_5Si$: C 53.60%, H 8.43%, N 7.81%; found: C 53.60 %, H 8.66%, N 8.12%.

Hydrazone 26 and olefin 27. Treatment of 25 with triethylborane. Compound **25** (300 mg, 0.84 mmol) was dissolved in THF (5 mL). Triethylborane (1.0 mL, 1 M solution in THF, 1.00 mmol, 1.2 equiv) was added, and the reaction mixture was stirred for 12 h at 25 °C. Water (10 mL) was added with stirring, and after 1 h at 25 °C, the reaction mixture was diluted with ether (10 mL). The organic solution was separated, and the aqueous phase was extracted with ether (2 x 10 mL). The combined organic layer was washed with brine (10 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Flash column chromatography (silica gel, 20% EtOAc

in hexanes) furnished the hydrazone **26** (147 mg, 45%) and the olefin **27** (119 mg, 40%) as colorless oils. **[26]**: R_f = 0.30 (silica gel, 10% EtOAc in hexanes); $[\alpha]^{22}_D$ + 40.8 (*c* 0.5, $CHCl_3$); IR (thin film) ν_{max} 3440, 2956, 1750, 1560 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.37 (bs, 1 H, NNHEt), 5.18 (d, *J* = 6.5 Hz, 1 H, CHOSi), 4.33 (ddd, *J* = 6.5 Hz, 1 H, C*H*CH(OSi)), 4.25 (q, *J* = 7.0 Hz, 2 H, OCH_2CH_3), 3.96 (dd, *J* = 8.2, 6.5 Hz, 1 H, CH_2(O)CH), 3.75 (dd, *J* = 8.2, 6.5 Hz, 1 H, CH_2(O)CH), 3.38 (m, 2 H, $NNH(CH_2CH_3)$), 1.33 (s, 3 H, $C(CH_3)_2$), 1.27 (s, 3 H, $C(CH_3)_2$), 1.25 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 1.21 (t, *J* = 7.0 Hz, 3 H, $NNH(CH_2CH_3)$), 0.85 (s, 9 H, $SiC(CH_3)_3$), 0.10 (s, 3 H, $Si(CH_3)_2$), -0.01 (s, 3 H, $Si(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 167.5, 137.1, 109.4, 77.2, 68.6, 66.0, 61.5, 45.9, 26.2, 25.7, 25.6, 18.7, 15.5, 14.2, -0.2, -0.4; MS *m/e* 388 (M^+); FAB HRMS (NBA) *m/e* 388.2407, M calcd for $C_{18}H_{36}N_2O_5Si$ 388.2393. **[27]**: R_f = 0.70 (silica gel, 10% EtOAc in hexanes); $[\alpha]^{22}_D$ + 20.8 (*c* 0.5, $CHCl_3$); IR (thin film) ν_{max} 2970, 1740 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.99 (s, 1 H, C(OSi)=CH), 4.36 (dd, *J* = 7.5, 5.9 Hz, 1 H, C*H*C(OSi)=CH), 4.25 (q, *J* = 7.0 Hz, 2 H, OCH_2CH_3), 4.18 (dd, *J* = 8.3, 7.5 Hz, 1 H, CH_2(O)CH), 3.94 (dd, *J* = 8.3, 5.9 Hz, 1 H, CH_2(O)CH), 1.33 (s, 3 H, $C(CH_3)_2$), 1.27 (s, 3 H, $C(CH_3)_2$), 1.25 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 0.85 (s, 9 H, $SiC(CH_3)_3$), 0.10 (s, 3 H, $Si(CH_3)_2$), -0.01 (s, 3 H, $Si(CH_3)_2$); FAB HRMS (NBA) *m/e* 330.1884, M calcd for $C_{16}H_{30}O_5Si$ 330.1862.

Ester 28. Treatment of 21a with triethylborane. Ester **28** was prepared from hydroxy diazo **21a** (350 mg, 1.43 mmol) by treatment with triethylborane (1 M solution in THF) according to the procedure described above for the preparation of **26**, to obtain ester **28** (221 mg, 63%) as a colorless oil: R_f = 0.35 (silica gel, 10% EtOAc in hexanes); $[\alpha]^{22}_D$ + 13.0 (*c* 1.1, $CHCl_3$); IR (thin film) ν_{max} 3440, 2956, 1750 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.16 (q, *J* = 7.3 Hz, 2 H, OCH_2CH_3), 4.11-4.00 (m, 2 H), 3.94 (dd, *J* = 8.7, 3.5 Hz, 1 H, CH_2(O)CH), 3.85 (ddd, *J* = 5.0, 3.5 Hz, 1 H, C*H*CH(OSi)), 2.46 (q, *J* = 5.0 Hz, 1 H, $CH(CH_2CH_3)$), 1.84-1.56 (m, 2 H, $CH(CH_2CH_3)$), 1.38 (s, 3 H, $C(CH_3)_2$), 1.32 (s, 3 H, $C(CH_3)_2$), 1.26 (t, *J* = 7.3 Hz, 3 H, OCH_2CH_3), 0.92 (t, *J* = 7.5 Hz, 3 H, $CH(CH_2CH_3)$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 175.0, 109.1, 75.9, 71.9, 66.1, 60.6, 48.9, 26.6, 25.2, 20.1, 14.2, 11.8; MS *m/e* 231 (M^+-15), 201, 171, 145, 125, 101 (100), 73; Anal. Calcd. for $C_{12}H_{22}O_5$: C 58.52%, H 9.00%; found: C 58.98 %, H 8.73%.

Ester 29. Treatment of 21a with 9-BBN. To a solution of compound **21a** (150 mg, 0.61 mmol) in THF (3 mL) was added 9-BBN (1.8 mL, 0.5 M solution in THF, 0.92 mmol, 1.5 equiv) at 25 °C. The reaction mixture was allowed to stirr at room temperature for 6 h, and after that time, water (5 mL) was added. The crude mixture was diluted with ether (10 mL), the organic solution was separated, and the aqueous phase was extracted with ether (2 x 10 mL). The combined organic layer was washed with brine (10 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Flash column chromatography (silica gel, 20% EtOAc in hexanes) furnished the ester **29** (113 mg, 85%) as a colorless oil: R_f = 0.47 (silica gel, 20% EtOAc in hexanes); $[\alpha]^{22}_D$ - 11.8 (*c* 0.6,

$CHCl_3$); IR (thin film) ν_{max} 3450, 2970, 1750 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.15 (q, J = 7.3 Hz, 2 H, OCH_2CH_3), 4.14-3.95 (m, 4 H), 2.70 (dd, J = 16.7, 2.8 Hz, 1 H, CH_2CO_2Et), 2.46 (dd, J = 16.7, 8.4 Hz, 1 H, CH_2CO_2Et), 1.38 (s, 3 H, $C(CH_3)_2$), 1.32 (s, 3 H, $C(CH_3)_2$), 1.25 (t, J = 7.3 Hz, 3 H, OCH_2CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 172.1, 109.7, 77.6, 68.3, 65.6, 60.1, 38.1, 26.3, 25.1, 14.2.

Lactone 30. Hydrolysis of 28. To a solution of **28** (50 mg, 0.20 mmol) in ethanol/water (1.0 mL, 5:1), cooled to 0 °C, was added a freshly prepared 20% (v/v) TFA solution in EtOH (200 μL). The reaction mixture was allowed to stirr for 5 h at that temperature, and then, the solvents were evaporated under reduced pressure. The lactone **30** was formed quantitatively and precipitated after addition of ether, obtaining **30** (26 mg, 97%) as a white solid: ^1H NMR (200 MHz, D_2O) δ 4.11 (dd, J = 5.9, 1.4 Hz, 1 H, $CHOH$), 4.10 (ddd, J = 4.0, 2.2, 1.4 Hz, 1 H, $CH(OCO)$), 3.86 (dd, J = 12.7, 2.2 Hz, 1 H, CH_2OH), 3.65 (dd, J = 12.7, 4.0 Hz, 1 H, CH_2OH), 2.52 (dt, J = 7.2, 5.9 Hz, 1 H, $CH(CH_2CH_3)$), 1.82-1.66 (m, 1 H, $CH(CH_2CH_3)$), 1.05 (t, J = 7.4 Hz, 3 H, $CH(CH_2CH_3)$); ^{13}C NMR (50.3 MHz, D_2O) δ 178.1, 85.1, 71.2, 60.3, 49.5, 20.7, 10.4.

Olefin 27. Treatment of 25 with trimethylaluminum and diethylzinc. Compound **25** (150 mg, 0.42 mmol) in toluene (2 mL) was treated with trimethylaluminum (0.23 mL, 2 M in toluene, 0.46 mmol, 1.1 equiv) and diethylzinc (0.46 mL, 1 M in toluene, 0.46 mmol, 1.1 equiv) respectively at -78 °C. Both reaction mixtures were warmed to 0 °C, and after stirring for 2 h at this temperature were quenched with MeOH (1 mL). Water (5 mL) was added with stirring, and after 30 min at 25 °C, the reaction mixture was diluted with ether (5 mL). The organic solution was separated, and the aqueous phase was extracted with ether (2 x 5 mL). The combined organic layer was washed with brine (5 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Flash column chromatography (silica gel, 20% EtOAc in hexanes) furnished olefin **27** (54 mg, 59% for Me_3Al reaction and 56 mg, 61% for Et_2Zn reaction) whose spectroscopic and physical properties were identical than **27** obtained above.

Hydrazone 31. Treatment of 25 with lithium triethylborohydride. Compound **25** (24 mg, 0.07 mmol) was dissolved in THF (1 mL) and cooled to 0 °C. Lithium triethylborohydride (210 μL, *Super*-hydride, 1 M solution in THF, 0.21 mmol, 3.0 equiv) was added, and the reaction mixture was stirred for 1 h at 0 °C. Water (5 mL) was added with stirring, and the reaction mixture was diluted with EtOAc (5 mL). The organic solution was separated, and the aqueous phase was extracted with EtOAc (2 x 5 mL). The combined organic layer was washed with brine (10 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash column chromatography (silica gel, 50% EtOAc in hexanes) provided pure hydrazone **31** (22 mg, 92%) as a colorless oil: R_f = 0.33 (silica gel, 50% EtOAc in hexanes); $[\alpha]^{22}_D$ + 25.8 (*c* 0.7, $CHCl_3$); IR (thin film) ν_{max} 2956, 1715, 1576 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.20 (bs, 2 H, NNH_2), 4.99 (d, J = 7.1 Hz, 1 H, CHOSi), 4.49 (ddd, J = 7.1, 6.1, 5.2 Hz, 1 H, $CHCH(OSi)$), 4.32 (q, J = 7.1 Hz, 2 H, OCH_2CH_3), 4.02 (dd, J = 8.6, 6.1 Hz, 1 H,

CH_2(O)CH), 3.87 (dd, J = 8.6, 5.2 Hz, 1 H, CH_2(O)CH), 1.37 (s, 3 H, $C(CH_3)_2$), 1.34 (t, J = 7.1 Hz, 3 H, OCH_2CH_3), 1.31 (s, 3 H, $C(CH_3)_2$), 0.86 (s, 9 H, $SiC(CH_3)_3$), 0.12 (s, 3 H, $Si(CH_3)_2$), 0.05 (s, 3 H, $Si(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 134.4, 109.7, 74.9, 70.8, 66.4, 61.1, 26.3, 25.7, 25.3, 18.1, -0.2, -0.4; FAB HRMS (NBA) *m/e* 360.2105, M calcd for $C_{16}H_{32}N_2O_5Si$ 360.2080.

α-keto ester 32. Oxidation of diazo 25. To a solution of diazo **25** (1.30 g, 3.63 mmol) in CH_2Cl_2 (35.0 mL) at 0 °C was added *m*-chloroperbenzoic acid (1.57 g, 57% purity, 5.44 mmol, 1.5 equiv), and the reaction mixture was stirred at that temperature for 6 h. Then, saturated aqueous $NaHCO_3$ solution (20 mL) was added and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL), and the combined organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, 10% EtOAc in hexanes) provided keto ester **32** (1.10 g, 88%) as a pale yellow oil: R_f = 0.80 (silica gel, 10% EtOAc in hexanes); $[\alpha]^{22}_D$ - 11.9 (*c* 0.3, $CHCl_3$); IR (thin film) ν_{max} 2965, 2942, 1771, 1747 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.10 (d, J = 6.1 Hz, 1 H, CHOSi), 4.31 (q, J = 7.0 Hz, 2 H, OCH_2CH_3), 4.17 (ddd, J = 6.4, 6.1, 4.7 Hz, 1 H, CHCH(OSi)), 4.09 (dd, J = 8.5, 6.4 Hz, 1 H, CH_2(O)CH), 3.92 (dd, J = 8.5, 4.7 Hz, 1 H, CH_2(O)CH), 1.39 (s, 3 H, $C(CH_3)_2$), 1.35 (t, J = 7.0 Hz, 2 H, OCH_2CH_3), 1.26 (s, 3 H, $C(CH_3)_2$), 0.88 (s, 9 H, $SiC(CH_3)_3$), 0.15 (s, 3 H, $Si(CH_3)_2$), 0.08 (s, 3 H, $Si(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 157.4, 156.7, 110.2, 94.4, 76.7, 65.2, 63.1, 26.3, 25.5, 25.1, 17.7, 13.8, -4.7, -5.3; MS *m/e* 347 (M^+ + 1), 287, 245, 175, 147 (100), 101, 73; Anal. Calcd. for $C_{16}H_{30}O_6Si$: C 55.46%, H 8.73%; found: C 55.89%, H 8.58%.

Pentitol 34. Treatment of 32 with sodium borohydride. A solution of α-keto ester **32** (107 mg, 0.31 mmol) in MeOH (5 mL) was treated with $NaBH_4$ (47 mg, 1.23 mmol) at 0 °C for 30 min. The solution was diluted with EtOAc (10 mL), and then saturated aqueous NH_4Cl solution (5 mL) was carefully added. The organic phase was separated and the aqueous phase was extracted with EtOAc (2 x 10 mL). The combined organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Flash column chromatography (silica gel, 50% EtOAc in hexanes) gave pentitol **34** (1:1 C-2 epimeric mixture, 33 mg, 35%) as a colorless oil: R_f = 0.27 (silica gel, 50% EtOAc in hexanes); IR (thin film) ν_{max} 3500, 2956, 1495 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.52-4.10 (m, 2 H), 4.09-3.98 (m, 2 H), 3.83-3.65 (m, 2 H), 3.55 (dd, J = 8.5, 4.7 Hz, 1 H, CH_2(O)CH), 1.41 (s, 3 H, $C(CH_3)_2$), 1.32 (s, 3 H, $C(CH_3)_2$), 0.87 (s, 9 H, $SiC(CH_3)_3$), 0.12 (s, 3 H, $Si(CH_3)_2$), 0.07 (s, 3 H, $Si(CH_3)_2$); MS *m/e* 307 (M^+ + 1), 245, 205, 187, 161, 145, 133, 131, 129 (100), 101, 75; FAB HRMS (NBA) *m/e* 291.1809, M - 15 calcd for $C_{14}H_{30}O_5Si$ 291.1862.

Acetoxy diazo 35. Acetylation of 21a. Diazo alcohol **21a** (310 mg, 1.27 mmol) was acetylated with Ac_2O in pyridine according to the procedure described above for the preparation of **9** to obtain **35** (356 mg, 98%) as a yellow liquid: R_f = 0.45 (silica gel, 20% EtOAc in hexanes); $[\alpha]^{22}_D$ + 10.5 (*c* 0.8, $CHCl_3$); IR (thin film) ν_{max} 2956, 2060, 1720, 1700, 1675 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.53 (d, *J* = 4.8 Hz, 1 H, CHOAc), 4.52 (ddd, *J* = 6.7, 5.7, 4.8 Hz, 1 H, C*H*CH(OAc)), 4.25 (q, *J* = 7.0 Hz, 2 H, OCH_2CH_3), 4.09 (dd, *J* = 8.8, 6.7 Hz, 1 H, CH_2(O)CH), 3.74 (dd, *J* = 8.8, 5.7 Hz, 1 H, CH_2(O)CH), 2.07 (s, 3 H, $CH(OCH_3)$), 1.44 (s, 3 H, $C(CH_3)_2$), 1.35 (t, *J* = 7.0 Hz, 2 H, OCH_2CH_3), 1.33 (s, 3 H, $C(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 169.6, 165.4, 110.3, 75.4, 69.6, 66.2, 60.4, 25.9, 24.7, 20.6; FAB HRMS (NBA) *m/e* 243.0687, M -N_2 -Me calcd for $C_{12}H_{18}N_2O_6$ 243.0708.

Diazo carbonate 36. Treatment of 3 with di-*tert*-butyl dicarbonate. Diazo **3** (500 mg, 2.34 mmol) in pyridine (5 mL) was treated with $O[OC(OtBu)]_2$ (1.1 mL, 4.68 mmol) at 0 °C, and the reaction mixture was allowed to warm at 25 °C. After being stirred for 5 h at this temperature, ether (20 mL) was added and the resulting mixture was washed with saturated aqueous NH_4Cl solution (20 mL). The organic solution was separated, and the aqueous phase was extracted with ether (2 x 20 mL). The combined organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a crude product which was purified by flash column chromatography (silica gel, 20% EtOAc in hexanes). Diazo carbonate **36** (720 mg, 96%) was obtained as a yellow oil: R_f = 0.70 (silica gel, 40% EtOAc in hexanes); $[\alpha]^{22}_D$ + 35.5 (*c* 0.7, $CHCl_3$); IR (thin film) ν_{max} 2956, 2080, 1715, 1700, 1675 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.50 (d, *J* = 5.0 Hz, 1 H, $CH(OCO_2tBu)$), 4.47 (m, 1 H, C*H*CH(OCO_2tBu)), 4.17 (m, 1 H, CH_2(O)CH), 3.84 (dd, *J* = 8.8, 5.7 Hz, 1 H, CH_2(O)CH), 2.25 (s, 3 H, $COCH_3$), 1.48 (s, 9 H, $OCO_2C(CH_3)_3$), 1.40 (s, 3 H, $C(CH_3)_2$), 1.30 (s, 3 H, $C(CH_3)_2$).

α-Enol ester 37. Treatment of diazo 9 with dirhodium tetracetate. To a solution of diazo **9** (100 mg, 0.39 mmol) in $CHCl_3$ (2 mL) was added $Rh_2(OAc)_4$ (10 mg, catalytic amount) at 25 °C. After stirring for 30 min, with intense nitrogen release, no starting diazo was detected by TLC and the mixture was filtered through Celite. The clear colorless solution was concentrated under reduced pressure, and the resulting crude product was purified by flash column chromatography (silica gel, 20% EtOAc in hexanes) to give α-enol ester **37** (87 mg, 98%) as a colorless oil: R_f = 0.58 (silica gel, 20% EtOAc in hexanes); IR (thin film) ν_{max} 2958, 1774, 1685 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.87 (d, *J* = 6.5 Hz, 1 H, CH=C(OAc)), 5.15 (q, *J* = 6.5 Hz, 1 H, C*H*CH=C(OAc)), 4.41 (dd, *J* = 8.3, 6.5 Hz, 1 H, CH_2(O)CH), 3.68 (dd, *J* = 8.3, 6.5 Hz, 1 H, CH_2(O)CH), 2.25 (s, 3 H, $COCH_3$), 2.17 (s, 3 H, $CH=C(OCOCH_3)$), 1.41 (s, 3 H, $C(CH_3)_2$), 1.37 (s, 3 H, $C(CH_3)_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 195.6, 169.7, 144.6, 133.2, 109.9, 72.3, 69.5, 26.6, 25.8, 25.4, 21.3.

α-Enol ester 38. Compound **38** was prepared from diazo **35** (100 mg, 0.35 mmol) by treatment with $Rh_2(OAc)_4$ according to the procedure described above for the preparation of **37**, obtaining pure **38** (89 mg, 98%) as a colorless oil: R_f = 0.65 (silica gel, 20% EtOAc in hexanes); IR (thin film) ν_{max} 2958, 1774, 1740, 1375 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.94 (d, *J* = 7.3 Hz, 1 H, CH=C(OAc)), 5.28 (q, *J* = 6.9 Hz, 1 H, C*H*CH=C(OAc)), 4.24 (dd, *J* = 8.3, 6.8 Hz, 1 H, CH_2(O)CH), 4.14 (q, *J* = 7.1 Hz, 2 H, OCH_2CH$_3$), 3.61 (dd, *J* = 8.3, 6.5 Hz, 1 H, CH_2(O)CH), 2.09 (s, 3 H, CH=C(OCOCH_3)), 1.34 (s, 3 H, C(CH_3)$_2$), 1.29 (s, 3 H, C(CH_3)$_2$), 1.19 (t, *J* = 7.1 Hz, 3 H, OCH$_2$CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 169.0, 161.1, 138.2, 133.0, 109.7, 71.5, 69.4, 61.5, 26.3, 25.2, 20.0, 13.7; MS *m/e* 243 (M^+ - 15), 201, 186, 158, 141 (100), 113, 85; Anal. Calcd. for $C_{12}H_{18}O_6$: C 55.81%, H 6.97%; found: C 55.50%, H 6.53%.

α-Enol ester 39. Compound **39** was prepared from diazo **36** (30 mg, 0.09 mmol) by treatment with $Rh_2(OAc)_4$ according to the procedure described above for the preparation of **37**, obtaining pure **38** (26 mg, 96%) as a colorless oil: R_f = 0.71 (silica gel, 20% EtOAc in hexanes); IR (thin film) ν_{max} 2958, 1774, 1680, 1375 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.93 (d, *J* = 6.9 Hz, 1 H, CH=C(OCO*t*Bu)), 5.17 (q, *J* = 6.8 Hz, 1 H, C*H*CH=C(OCO*t*Bu)), 4.36 (dd, *J* = 8.4, 6.9 Hz, 1 H, CH_2(O)CH), 3.63 (dd, *J* = 8.4, 6.9 Hz, 1 H, CH_2(O)CH), 2.17 (s, 3 H, CH_3), 1.49 (s, 9 H, OCOC(CH_3)$_3$), 1.39 (s, 3 H, C(CH_3)$_2$), 1.33 (s, 3 H, C(CH_3)$_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 194.8, 151.6, 144.4, 131.8, 109.9, 84.5, 71.9, 69.6, 27.5, 26.6, 26.5, 25.3.

Diazo ester 41. Condensation of 40 with methyl diazoacetate. A mixture of aldehyde **40** (500 mg, 4.16 mmol) and methyl diazoacetate (832 mg, 8.32 mmol, 2.0 equiv) in MeOH (5 mL) was treated with a KOH solution in MeOH (0.723 mL, 10% KOH in MeOH, 0.5 equiv) at 25 °C. After being stirred for 1 h, the reaction mixture was diluted with EtOAc (20 mL) and water (20 mL) was added. The organic layer was separated and the aqueous phase was extracted with EtOAc (2 x 10 mL). The combined organic layer was dried ($MgSO_4$), filtered and concentrated under *vacuo*. The crude product was purified by flash column chromatography (silica gel, 50% EtOAc in hexanes), obtaining diazo ester **41** (595 mg, 55%) as a yellow oil: R_f = 0.33 (silica gel, 50% EtOAc in hexanes); IR (thin film) ν_{max} 3460, 2995, 2946, 2100, 1710, 1475, 1375 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.92-4.85 (m, 1 H, C*H*(OH)C(N_2)), 4.66 (q, *J* = 5.2 Hz, 1 H, C*H*CH$_3$), 4.16-4.03 (m, 1 H), 3.96-3.83 (m, 1 H), 3.74 (s, 3 H, CO_2CH_3), 3.56 (dd, *J* = 8.9, 1.6 Hz, 1 H, CH_2(O)CH), 3.38 (dd, *J* = 8.9, 7.0 Hz, 1 H, CH_2(O)CH), 1.27 (d, *J* = 5.2 Hz, 3 H, CHCH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 169.5, 99.7, 98.9, 77.6, 73.5, 71.5, 67.4, 66.9, 63.9, 63.5, 62.2, 52.2, 20.6; Anal. Calcd. for $C_9H_{14}N_2O_6$: C 43.30%, H 5.73%, N 11.38%; found: C 43.22%, H 5.77%, N 11.55%.

***Di*-acetoxy diazo 42. Acetylation of 41.** Dihydroxy diazo **41** (361 mg, 1.38 mmol) was acetylated with Ac_2O in pyridine according to the procedure described above for the preparation of **9** to obtain **42** (450 mg,

98%) as a yellow liquid: R_f = 0.65 (silica gel, 20% EtOAc in hexanes); IR (thin film) ν_{max} 3000, 2877, 2128, 1750, 1700, 1436, 1370 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.88 (d, J = 1.9 Hz, 1 H, CHOAc), 5.75 (d, J = 1.9 Hz, 1 H, CHOAc), 4.68-4.60 (m, 2 H), 4.23-4.00 (m, 2 H), 3.72 (s, 3 H, CO_2CH_3), 3.69 (s, 3 H, CO_2CH_3, other isomer), 3.34 (dd, J = 10.3, 9.7 Hz, 1 H, CH_2(O)CH), 2.03 (s, 3 H, CH(OCOCH_3)), 1.99 (s, 3 H, CH(OCOCH_3)), 1.28 (d, J = 5.3 Hz, 3 H, CHCH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 169.6, 169.5, 99.7, 98.9, 80.1, 79.3, 67.4, 66.9, 63.9, 63.5, 61.1, 52.2, 20.8, 20.6, 19.9; Anal. Calcd. for $C_{13}H_{18}N_2O_8$: C 47.27%, H 5.49%, N 8.48%; found: C 47.65%, H 5.67%, N 8.82%.

α-Enol ester 43. Compound **43** was prepared from diazo **42** (60 mg, 0.16 mmol) by treatment with $Rh_2(OAc)_4$ according to the procedure described above for the preparation of **37**, obtaining pure **43** (45 mg, 74%) as a colorless oil: R_f = 0.70 (silica gel, 20% EtOAc in hexanes); IR (thin film) ν_{max} 2965, 2875, 1763, 1676, 1437, 1374 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.34 (d, J = 8.6 Hz, 1 H, CHCH=C(OAc)), 5.76 (d, J = 9.3 Hz, 1 H, CHOAc), 5.20-5.09 (m, 1 H), 4.78-4.65 (m, 1 H), 4.24-4.10 (m, 1 H), 3.76 (s, 3 H, CO_2CH_3), 3.48 (dd, J = 10.5, 9.0 Hz, 1 H, CH_2(O)CH), 2.15 (s, 3 H, CH(OCOCH_3)), 1.96 (s, 3 H, CH=C(OCOCH_3)), 1.31 (d, J = 5.1 Hz, 3 H, CHCH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 169.8, 169.1, 127.1, 126.7, 125.3, 98.9, 73.9, 73.8, 73.4, 67.6, 67.5, 67.4, 65.3, 52.7, 52.3, 20.5, 20.3, 13.9; Anal. Calcd. for $C_{13}H_{18}O_8$: C 51.66%, H 6.00%; found: C 51.73%, H 6.27%.

KDG 44. Hydrolysis of α-enol ester 43. A solution containing compound **43** (100 mg, 0.33 mmol) in ethanol-water (3 mL, 2:1) was treated with TFA (1 mL, 20% solution in EtOH) at 60 °C for 8 h. Then, the solution was concentrated under reduced pressure and the resulting crude was dissolved in MeOH-H_2O (5 mL, 1:1) and $Ba(OH)_2$ (25 mg, 3.0 equiv) was added in one portion at 25 °C. The resulting mixture was allowed to stand at 25 °C for 3 h. Then, the solvent was removed under high vacuum and the crude was redissolved in water (2 mL) and liophilized. The resulting solid (95 mg, 92%) exhibited identical NMR spectra and analytical features as reported in the literature:[34a] ^1H NMR (200 MHz, D_2O) δ 4.30-3.45 (m, 4 H), 2.65-2.10 (m, 1 H), 1.90-1.85 (m, 1 H); ^{13}C NMR (50.3 MHz, D_2O) δ 176.4, 99.3, 67.3, 65.1, 64.3, 39.5.

Diazo ester 46. Condensation of 45 with ethyl diazoacetate 20a. The preparation of **46** was accomplished from **45** (1.3 g, 5.65 mmol) by reaction with ethyl diazoacetate **20a** (1.2 g, 11.30 mmol, 2.0 equiv) by the same procedure described above for **21a** to obtain **46** (1.43 g, 80%) as a 3:2 C-3 epimeric mixture, which were separated by flash column chromatography (silica gel, 20% EtOAc in hexanes): R_f = 0.45 (silica gel, 50% EtOAc in hexanes); IR (thin film) ν_{max} 3462, 2996, 2946, 2110, 1706, 1475, 1375 cm^{-1}; **[46] (major isomer)**: $[\alpha]^{22}_D$ + 3.6 (*c* 1.1, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 4.72 (dd, J = 6.1, 4.5 Hz, 1 H, CHOH), 4.20 (q, J = 7.0 Hz, 2 H, OCH_2CH$_3$), 4.13-4.02 (m, 2 H), 4.00 (dd, J = 8.5, 5.4 Hz, 1 H, CH_2(O)CH), 3.90 (dd, J = 8.1,

4.2 Hz, 1 H, C*H*$_2$(O)CH), 3.88 (dd, *J* = 8.1, 6.5 Hz, 1 H, C*H*$_2$(O)CH), 2.80 (d, *J* = 6.1 Hz, 1 H, CHO*H*), 1.41 (s, 3 H, C(CH$_3$)$_2$), 1.36 (s, 6 H, C(CH$_3$)$_2$), 1.31 (s, 3 H, C(CH$_3$)$_2$), 1.24 (t, *J* = 7.0 Hz, 3 H, OCH$_2$C*H*$_3$); ^{13}C NMR (50.3 MHz, CDCl$_3$) δ 167.1, 110.4, 109.8, 82.0, 77.9, 77.0, 67.8, 66.2, 60.9, 27.3, 26.9, 26.4, 25.1, 14.4; MS *m/e* 301 (M$^+$-15 -28), 229 (100), 201, 143, 85. **[46] (minor isomer)**: $[\alpha]^{22}_D$ + 6.6 (*c* 1.0, CHCl$_3$); ^{1}H NMR (200 MHz, CDCl$_3$) δ 4.67 (dd, *J* = 6.3, 2.5 Hz, 1 H, C*H*OH), 4.20 (q, *J* = 7.2 Hz, 2 H, OC*H*$_2$CH$_3$), 4.19-4.03 (m, 3 H), 3.96 (dd, *J* = 7.5, 4.2 Hz, 1 H, C*H*$_2$(O)CH), 3.74 (dd, *J* = 7.5 Hz, 1 H, C*H*$_2$(O)CH), 3.45 (d, *J* = 2.5 Hz, 1 H, CHO*H*), 1.42 (s, 3 H, C(CH$_3$)$_2$), 1.37 (s, 3 H, C(CH$_3$)$_2$), 1.35 (s, 3 H, C(CH$_3$)$_2$), 1.33 (s, 3 H, C(CH$_3$)$_2$), 1.25 (t, *J* = 7.2 Hz, 3 H, OCH$_2$C*H*$_3$); ^{13}C NMR (50.3 MHz, CDCl$_3$) δ 167.4, 110.2, 109.8, 81.4, 80.1, 76.6, 67.8, 67.6, 60.9, 26.8, 26.6, 26.3, 25.0, 14.4; MS *m/e* 301 (M$^+$-15 -28), 255 (100), 213, 153, 101, 83; Anal. Calcd. of the mixture for $C_{15}H_{24}N_2O_7$: C 52.94%, H 7.05%, N 8.23%; found: C 52.64%, H 7.25%, N 7.63.

Diazo ester 47. Acetylation of 46. Acetylation of **46** (1.0 g, 2.9 mmol) was accomplished with Ac_2O in pyridine by the same procedure described above for **3** to obtain **47** (1.1 g, 98%) as a yellow oil: R_f = 0.67 (silica gel, 50% EtOAc in hexanes); IR (thin film) ν_{max} 2997, 2945, 2112, 1753, 1735, 1480 cm^{-1}; **[47] (major isomer)**: $[\alpha]^{22}_D$ + 27.2 (*c* 2.2, CHCl$_3$); ^{1}H NMR (200 MHz, CDCl$_3$) δ 5.72 (d, *J* = 5.5 Hz, 1 H, C*H*OAc), 4.30 (dd, *J* = 5.8, 5.5 Hz, 1 H, C*H*CHOAc), 4.18 (q, *J* = 7.1 Hz, 2 H, OC*H*$_2$CH$_3$), 4.07 (dd, *J* = 7.8, 5.8 Hz, 1 H, C*H*CHCHOAc), 3.98 (ddd, *J* = 7.8, 6.0, 4.4 Hz, 1 H, CH$_2$(O)C*H*), 3.86 (dd, *J* = 8.0, 4.4 Hz, 1 H, C*H*$_2$(O)CH), 3.73 (dd, *J* = 8.0, 6.0 Hz, 1 H, C*H*$_2$(O)CH), 2.07 (s, 3 H, CHOCOC*H*$_3$), 1.36 (s, 3 H, C(CH$_3$)$_2$), 1.34 (s, 3 H, C(CH$_3$)$_2$), 1.32 (s, 3 H, C(CH$_3$)$_2$), 1.28 (s, 3 H, C(CH$_3$)$_2$), 1.22 (t, *J* = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$); ^{13}C NMR (50.3 MHz, CDCl$_3$) δ 169.4, 164.9, 110.7, 109.8, 80.8, 78.3, 76.9, 68.1, 67.5, 61.1, 27.6, 26.7, 26.3, 25.0, 20.7, 14.3; MS *m/z* 343 (M$^+$-15-28), 301, 243, 215, 157, 128, 101, 43 (100). **[47] (minor isomer)**: $[\alpha]^{22}_D$ - 14.2 (*c* 0.5, CHCl$_3$); ^{1}H NMR (200 MHz, CDCl$_3$) δ 5.84 (d, *J* = 3.1 Hz, 1 H, C*H*OAc), 4.35 (dd, *J* = 7.3, 3.1 Hz, 1 H, C*H*CHOAc), 4.21 (q, *J* = 7.1 Hz, 2 H, OC*H*$_2$CH$_3$), 4.08 (dd, *J* = 9.0, 6.3 Hz, 1 H, C*H*$_2$(O)CH), 4.05 (dd, *J* = 9.0, 6.0 Hz, 1 H, C*H*$_2$(O)CH), 3.93 (ddd, *J* = 7.7, 6.3, 6.0 Hz, 1 H, CH$_2$(O)C*H*), 3.68 (dd, *J* = 7.7, 7.3 Hz, 1 H, C*H*CHCHOAc), 2.09 (s, 3 H, CHOCOC*H*$_3$), 1.44 (s, 3 H, C(CH$_3$)$_2$), 1.42 (s, 3 H, C(CH$_3$)$_2$), 1.36 (s, 3 H, C(CH$_3$)$_2$), 1.25 (s, 3 H, C(CH$_3$)$_2$), 1.24 (t, *J* = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$); ^{13}C NMR (50.3 MHz, CDCl$_3$) δ 169.4, 164.9, 111.0, 110.0, 81.1, 78.8, 76.9, 68.8, 67.5, 61.2, 27.0, 26.7, 26.4, 25.1, 20.9, 14.4; MS *m/z* 343 (M$^+$-15-28), 300, 255, 215, 183, 128, 115, 101, 43 (100); Anal. Calcd. of the mixture for $C_{17}H_{26}N_2O_8$: C 52.84%, H 6.78%, N 7.25%; found: C 52.88%, H 6.95%, N 6.91.

α-Enol ester 48. Compound **48** was prepared from diazo **47** (1.0 g, 2.59 mmol) by treatment with $Rh_2(OAc)_4$ according to the procedure described above for the preparation of **37**, obtaining pure **48** (0.91 g, 98%) as a colorless oil: R_f = 0.76 (silica gel, 50% EtOAc in hexanes); IR (thin film) ν_{max} 2995, 2891, 1773,

1735, 1370 cm^{-1}; **[48] (major isomer)**: $[\alpha]^{22}_D$ - 23.0 (*c* 0.5, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 5.80 (d, *J* = 9.2 Hz, 1 H, C*H*=C(OAc)), 5.27 (dd, *J* = 9.2, 7.9 Hz, 1 H, C*H*CH=C(OAc)), 4.20 (q, *J* = 7.2 Hz, 2 H, OC$H_2$$CH_3$), 4.12-4.05 (m, 2 H), 3.94 (ddd, *J* = 6.1, 6.0, 4.7 Hz, 1 H, CH_2(O)C*H*), 3.74 (dd, *J* = 7.9, 6.1 Hz, 1 H, C*H*CHCH=C(OAc)), 2.14 (s, 3 H, CH=C(OCOCH_3)), 1.37 (s, 3 H, C(CH_3)$_2$), 1.33 (s, 3 H, C(CH_3)$_2$), 1.27 (s, 6 H, C(CH_3)$_2$), 1.26 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 168.9, 161.2, 140.4, 128.6, 110.1, 109.5, 80.8, 75.9, 73.8, 66.3, 61.5, 27.0, 26.8, 26.4, 25.3, 20.2, 13.9; MS *m/e* 343 (M^+-15). **[48] (minor isomer)**: $[\alpha]^{22}_D$ - 17.4 (*c* 1.4, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 6.41 (d, *J* = 8.3 Hz, 1 H, C*H*=C(OAc)), 4.71 (dd, *J* = 8.3, 7.3 Hz, 1 H, C*H*CH=C(OAc)), 4.22 (q, *J* = 7.1 Hz, 2 H, OC$H_2$$CH_3$), 4.13-3.77 (m, 4 H), 2.20 (s, 3 H, CH=C(OCOCH_3)), 1.40 (s, 3 H, C(CH_3)$_2$), 1.39 (s, 3 H, C(CH_3)$_2$), 1.35 (s, 3 H, C(CH_3)$_2$), 1.29 (s, 3 H, C(CH_3)$_2$), 1.27 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 168.0, 161.5, 140.5, 126.7, 110.5, 109.8, 80.9, 76.2, 73.8, 66.8, 61.7, 26.9, 26.4, 25.1, 20.3, 14.0; MS *m/e* 343 (M^+-15); Anal. Calcd. for $C_{17}H_{26}O_8$: C 56.98%, H 7.26%; found: C 56.45%, H 7.30%.

DAH 49. Hydrolysis of α-enol ester 48. A solution containing compound **48** (1.0 g, 2.79 mmol) in ethanol-water (7 mL, 5:2) was treated with TFA (5 mL, 20% solution in EtOH) at 25 °C for 12 h. Then, the solution was concentrated under reduced pressure and the resulting crude was dissolved in MeOH-H_2O (20 mL, 1:1) and $Ba(OH)_2$ (0.43 g, 3.0 equiv) was added in one portion at 25 °C. The resulting mixture was allowed to stand at 25 °C for 3 h. Then, the solvent was removed under high vacuum and the crude was redissolved in water (5 mL) and liophilized. The resulting solid (1.46 g, 95%) exhibited identical NMR spectra and analytical features as reported in the literature. Further purification was carried out by recrystallization in acetone/water (85/15): $[\alpha]^{22}_D$ + 33.3 (*c* 0.6, H_2O); ^1H NMR (200 MHz, D_2O) δ 3.90-3.57 (m, 4 H), 3.30 (t, 1 H), 2.23 (dd, *J* = 13.1, 5.0 Hz, 1 H, CHCH_2C(CO_2)), 1.82 (dd, *J* = 13.1, 12.2 Hz, 1 H, CHCH_2C(CO_2)); ^{13}C NMR (50.3 MHz, D_2O) δ 177.4, 97.3, 74.5, 71.4, 69.7, 61.2, 40.0; Anal. Calcd. for $C_{14}H_{22}O_{14}Ba$ x $2H_2O$: C 28.61%, H 4.46%; found: C 28.69%, H 4.22%.

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