Organotransition Metal-Modified Sugars, Part 10[+]

Chromium Iminoglycosylidenes: Synthesis and Application to Photoinduced C-Glycosidation

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Dedicated to Professor Ernst Otto Fischer on the occasion of his 80th birthday

Abstract: The iminoglycosylidene complexes **3a**,**b**, **9**, and **16a**,**b** are conveniently prepared from the sugar lactams **2a**,**b**, **8**, and **15a**,**b** by reaction with $K_2Cr(CO)_5$ and subsequent deoxygenation with trimethylsilyl chloride (TMSCl). The $Cr(CO)_5$-stabilized carbene moiety of the imino-D-*ribo*-pyranosylidene complexes **9** and **16a**,**b** has been exploited in the photoinduced generation of ketene-like species on irradiation with UV light. These intermediates were trapped with methanol to produce the methyl 2,6-imino-D-allonates **10** and **17a**,**b**. The C-glycosidation is β-selective and has been applied further to the preparation of the galactosyl 2,6-imino-D-allonate **19**. Solvent effects suggest that the diastereoselectivity originates in the chromium fragment, which shields the *re* face of the proposed ketene intermediate.

Keywords: chromium · carbene complexes · glycosides · iminosugars · photolysis

Introduction

Naturally occurring and synthetic iminosugars are the focus of much attention, as they are found to be potent glycosidase inhibitors.[1] They are therefore useful as antiviral, antidiabetic, antimetastatic, and metabolic regulation agents.[2] Several hundred of them have been synthesized to date by a broad variety of approaches based mainly on ring-closing reactions, such as intramolecular reductive amination,[3] amination of C=C bonds,[4] or intramolecular nucleophilic amination.[5] However, synthetic methods for the carbon-chain elongation/C-glycosidation of iminopyranoses are rarely found in the literature,[6] and to our knowledge, there is only one general route to the various C-glycosides of nojirimycin, reported recently by Schmidt and co-workers.[7]

The use of organometallic chemistry in stereoselective organic synthesis is well established, but its application to carbohydrate chemistry is limited to a few examples, except in the case of lithiated or stannylated compounds. However, some stable glycosyl complexes of various metals have been prepared.[8] Our aim was to transfer the synthetic potential of Fischer-type amino carbene complexes $[(CO)_5Cr{=}CR(NR'R'')]$ to iminosugar chemistry. We focused on insertion reactions with alkynes for the construction of polycyclic N-heterocycles,[9] and especially on the photolytic generation of ketene equivalents, which may be trapped by imines and oxygen or nitrogen nucleophiles to produce natural and synthetic β-lactams, α-amino acid esters, or dipeptides.[10]

We now describe the synthesis of chromium- and tungsten-stabilized imino-furanosylidene and -pyranosylidene complexes and report the photolytic conversion of pentacarbonyl-[iminopyranosylidene]chromium complexes to methyl[11] and glycosyl 2,6-imino-D-aldonates. This represents the first application of a metal-stabilized carbene moiety to the carbon-chain elongation of iminosugars.

Results and Discussion

The two available synthetic pathways to amino carbene complexes are i) the aminolysis of alkoxy carbene complexes and ii) the Hegedus route[12] (Scheme 1), which is based on the combination of amide or unsubstituted lactam electrophiles with $K_2Cr(CO)_5$ as an organometalate nucleophile. Subsequent deoxygenation with TMSCl affords the desired amino carbene complexes.

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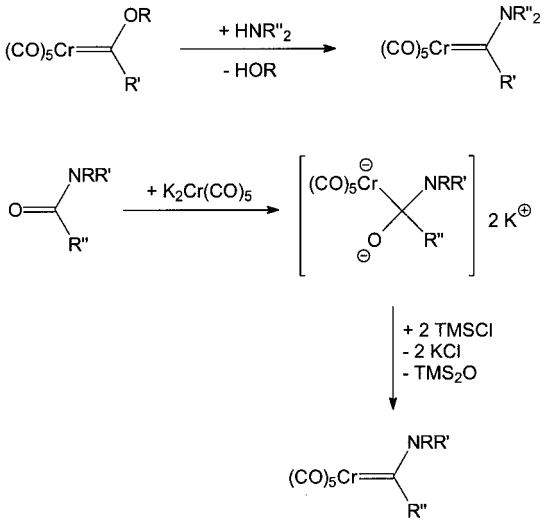
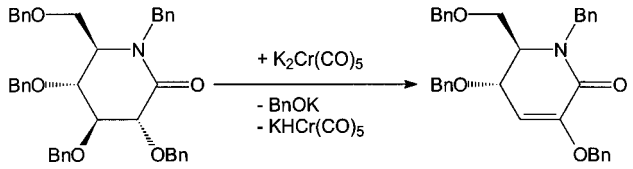


Scheme 1. Synthesis of amino carbene complexes.

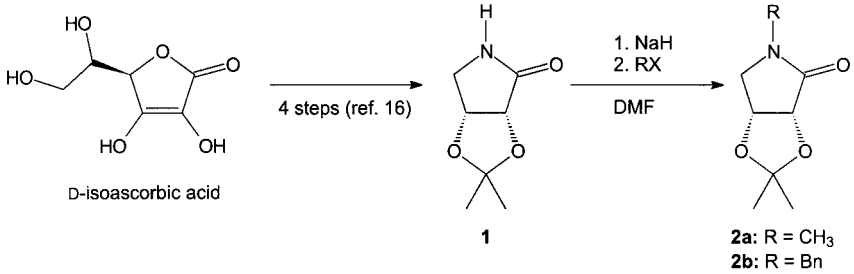
Although we have shown previously that aminolysis of furanosylidene complexes followed by intramolecular Mitsunobu reaction provides a route to both N-protected and N-unprotected iminofuranosylidene complexes,[13] the Hegedus procedure seems to be the method of choice to obtain the iminoglycosylidene complexes directly from the fully protected sugar lactams.



Scheme 2. Elimination of the C3-benzyloxy group in nojirilactam.

We started with the D-erythrono-1,4-lactam **1**, which was readily prepared from commercially available D-isoascorbic acid.[16] Subsequent N-protection with either methyl iodide or benzyl chloride resulted in the formation of the lactams **2a** and **2b**, respectively (Scheme 3).

The D-ribono-1,5-lactam **8** was synthesized in 56% yield in five steps from D-ribono-1,4-lactone, which was first protected as its 2,3-*O*-cyclohexylidene acetal **4** by acid (H_2SO_4)-catalyzed condensation in cyclohexanone. Comparable results have been reported for the reaction catalyzed by Amberlite IR 120(H^+) in benzene, but these conditions also afforded the



Scheme 3. Synthesis of the sugar lactams **2a**,**b**.

Synthesis of iminoglycosylidene complexes: The pentacarbonyl chromate dianion is not only a potent nucleophile, but is also a strong base. Consequently, earlier studies with perbenzylated nojirilactam[14] had indicated that the benzyloxy group at C-3 tends to undergo easy elimination, initiated by proton abstraction at C-2[15] (Scheme 2). To avoid this undesired reaction we turned our attention to the synthesis of sugar lactams with an acetal protecting group at positions 2 and 3.

Abstract in German: *Die Iminoglycosylidenkomplexe **3a,b**, **9** und **16a,b** können leicht aus den Zuckerlactamen **2a,b**, **8** und **15a,b** durch Reaktion mit $K_2Cr(CO)_5$ und nachfolgender Deoxygenierung durch Chlortrimethylsilan dargestellt werden. Die Pentacarbonylchrom-stabilisierte Carbenfunktionalität in den Imino-D-ribo-pyranosyliden-Komplexen **9** und **16a,b** wurde durch Bestrahlung mit UV-Licht für die photoinduzierte Generierung von ketenähnlichen Spezies ausgenutzt, welche durch Methanol unter Bildung der 2,6-Imino-D-allonsäuremethylester **10** und **17a,b** abgefangen wurden. Die C-Glycosidierung verläuft β-selektiv und wurde auf die Darstellung des Galactosyl-2,6-imino-D-allonates **19** übertragen. Lösungsmitteleffekte wiesen darauf hin, daß die Diastereoselektivitäten durch das Chromfragment gesteuert werden, welches die re-Seite des angenommenen Ketenintermediates abschirmt.*

3,4-protected isomer as a side product.[17] The acetal **4** was converted quantitatively to the tosylate **5** and then treated with sodium azide in DMF to give the azido lactone **6**. Hydrogenation in the presence of 6 mol% palladium on charcoal and subsequent protection of the resulting lactam **7** with methyl iodide produced the desired D-ribono-1,5-lactam **8** in an overall yield of 49% (Scheme 4).

A similar reaction sequence was used in the preparation of lactams **15a** and **15b**. The azido derivative **13**[19] was obtained from the tosylated ribono-1,4-lactone **12** (synthesized by a modified Mitchell reaction) in a yield of 88% after purification. (Isolation of highly pure **13** is vital to the success of the subsequent palladium-catalyzed hydrogenation.) Attempts to perform this step from the crude azide as reported[20] were unseccessful in our hands. Finally, the sugar lactam **14** was treated with either methyl iodide or benzyl chloride to afford the fully N- and O-protected D-ribono-1,5-lactams **15a** and **15b** in overall yields of 52% (**15a**) and 44% (**15b**) (Scheme 4).

The sugar lactams **2a**,**b**, **8**, and **15a**,**b** were converted to the iminoglycosylidene complexes **3a–c**, **9**, and **16a**,**b** by an efficient general procedure.[12] $Cr(CO)_6$ was allowed to react with a suspension of C_8K in THF at −78 °C to produce $K_2Cr(CO)_5$. Addition of a solution of the appropriate lactam in THF, followed by the introduction of TMSCl, formed the carbene complexes **3a**,**b** and **16a**,**b** in good yield, but the

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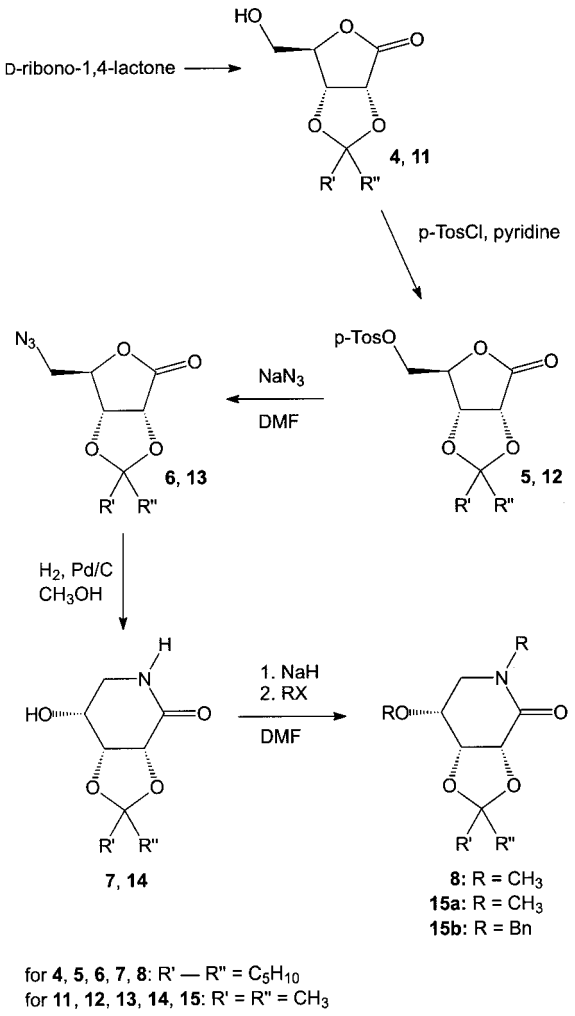
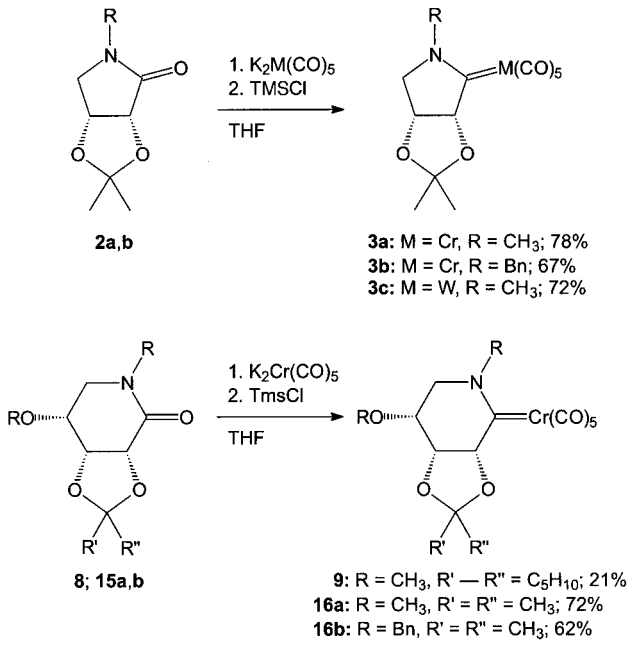


Scheme 4. Synthesis of the sugar lactams **8** and **15a**,**b**.



Scheme 5. Conversion of sugar lactams to the iminoglycosylidene complexes **3a–c** and **9**, **16a**,**b**.

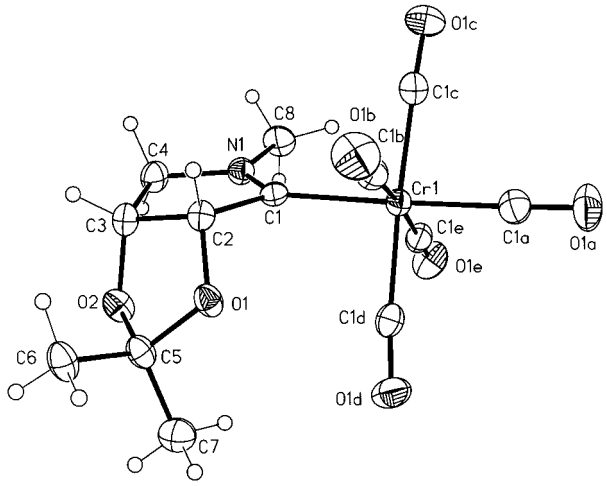


Figure 1. Molecular structure of complex **3a**. Thermal ellipsoids are drawn at the 50% probability level. Selected distances [pm] and angles [°]: Cr–C1 208.93(14), C1–N1 130.59(19), C1–C2 152.78(19), C2–C3 153.28(19), C3–C4 151.0(2), C4–N 147.89(19); Cr-C1-N1 132.20(10), Cr-C1-C2 122.14(9), N-C1-C2 105.63(11), C1-N-C5 127.70(12), C1-N-C4 117.17(12), C8-N-C4 115.12(12).

preparation of the cyclohexylidene acetal **9** was less efficient. In this case, formation of the tetrahedral intermediate (Scheme 1) may be hampered by the enhanced steric hindrance of the acetal protecting group in **8** compared with that in **15**. The complexes are easily separated from the graphite precipitate by chromatography on a short silica column. An analogous procedure can be applied to the generation of pentacarbonyl tungsten-stabilized complexes as demonstrated for **3c** in Scheme 5.

The molecular structures of complexes **3a** and **3c** exhibit similar $^4T_3$ and $^2T_3$ conformations in the solid state (Figures 1 and 2), whereas **16a** adopts a $^4S_2$ conformation (Figure 3). In these three compounds the carbene carbon atom C1 is sp^2-hybridized and therefore coplanar with its nearest neighbors. In addition, the pronounced double-bond character of the C1–N bond is indicated by the significantly short bond lengths (**3a**: 130.59, **3c**: 131.0, **16a**: 130.8 pm), combined with a planar arrangement at the nitrogen atom, which reflects the peculiar bonding of the metal-carbene fragment. In contrast bond lengths of 132.6 pm and 136.0 pm (together with a distinct pyramidalization at nitrogen) are reported for nojirilactam[21a] and for D-gluconhydroximo-1,5-lactam,[21b] respectively.

Synthesis of methyl and glycosyl 2,6-iminoaldonates: In 1982, McGuire and Hegedus discovered that irradiation of chromium carbene complexes into the metal-to-ligand charge transfer (MLCT) band (350–450 nm) resulted in the insertion of a CO ligand into the metal–carbene bond to generate short-lived alkoxy- or amino-substituted metal-bound ketenes.[10a] This process is proposed to be reversible with regeneration of the carbene complex (unless a reactive substrate is present), and has been applied to a series of acyclic and cyclic amino carbene complexes.[22] We speculated whether this methodology could be exploited in a novel route to iminosugar C-glycosides. Complexes **9** and **16a**,**b** were dissolved in

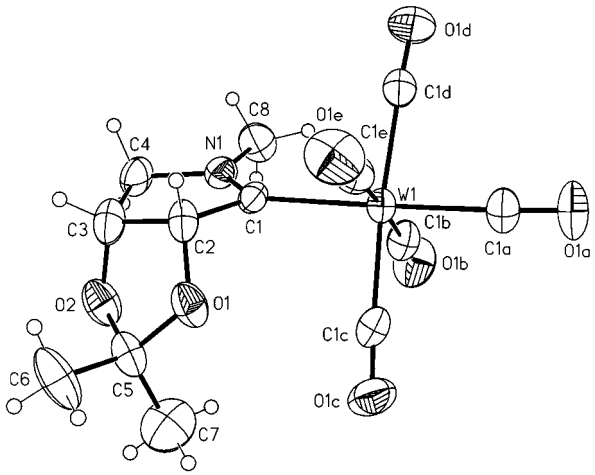


Figure 2. Molecular structure of complex **3c**. Thermal ellipsoids are drawn at the 30% probability level. Selected distances [pm] and angles [°]: W–C1 221.5(5), C1–N1 131.0(8), C1–C2 151.7(9), C2–C3 152.9(9), C3–C4 150.6(11), C4–N 148.0(8); W-C1-N1 131.9(5), W-C1-C2 121.9(4), N-C1-C2 106.1(5), C1-N-C5 127.7(5), C1-N-C4 116.6(5), C8-N-C4 115.7(6).

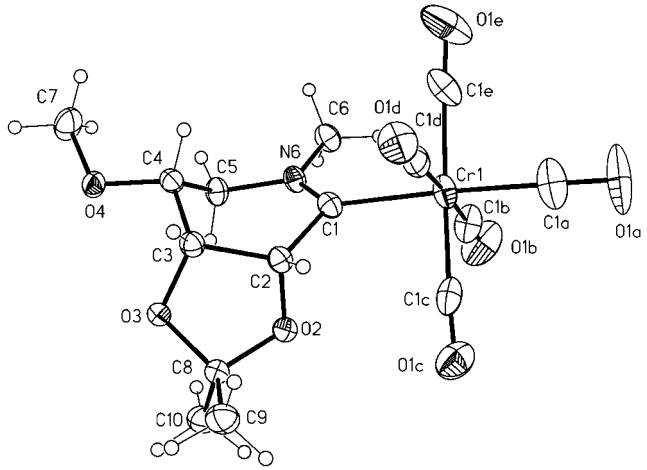
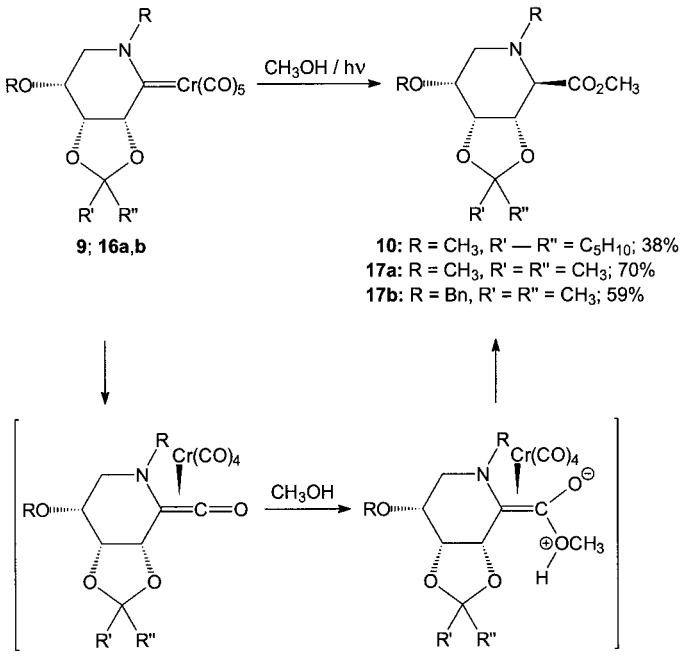


Figure 3. Molecular structure of complex **16a**. Thermal ellipsoids are drawn at the 50% probability level. Selected distances [pm] and angles [°]: Cr–C1 210.66(14), C1–N1 130.8(2), C1–C2 154.6(2), C2–C3 155.0(2), C3–C4 151.0(2), C4–C5 152.3(2), C5–N 148.86(16); Cr-C1-N1 130.57(10), Cr-C1-C2 116.67(10), N-C1-C2 112.68(12), C1-N-C6 124.37(12), C1-N-C5 123.44 (12), C6-N-C5 112.18(11).

methanol and irradiated with a 125 W mercury lamp at room temperature. The reaction afforded the methyl 2,6-iminoaldonates **10** and **17a**,**b** within five days in moderate-to-fair yields after oxidative and chromatographic workup (see Experimental Section and Scheme 6).

Despite our use of various protecting groups with different steric demands, we isolated only a single diastereomer with D-*allo* configuration, as established by NOE experiments within the accuracy of ^{1}H NMR spectroscopy in combination with GC-MS analysis or HPLC. No alternative 2,6-imino-D-altronate isomer was detected. We suppose that the stereocontrol in favor of the β-*C*-glycosidation products **10** and **17a**,**b** arises from the coordination of the chromium carbonyl fragment to the *re* face of the sugar ketene intermediate, which is generated upon photolysis of the chromium iminoglycosylidene precursor. This would explain the stereoselective protonation by the alcohol, which occurs from the generally less congested opposite face. In order to verify this hypothesis we replaced methanol by the more efficiently coordinating CH_3CN. This solvent is expected to complete successfully with the ketene for the $Cr(CO)_4$ fragment prior to the addition of the alcohol. Irradiation of a solution of **16a** and methanol (1.0 equiv) in THF led again to the formation of the single D-*allo* isomer **17a** in 65% yield. However, the diastereoselectivity decreased significantly when the reaction was run under identical conditions but with CH_3CN as the solvent. The ^{1}H NMR spectrum of the residue, obtained after oxidative workup, contained signals which could be assigned to three products: imino D-allonate **17a** and its diastereomer in an approximate ratio of 2:1 (confirmed by GC-MS analysis), and lactam **15a**, which is formed by oxidation of the unconverted starting material **16a**.



Scheme 6. Photoinduced synthesis of the methyl 2,6-imino-D-allonates **10** and **17a**,**b**.

In contrast, the increasing steric demand of the alcohol substrate has no influence on the stereocontrol of the C-glycosidation. The reaction of **16a** with galactose derivative **18** (1.1 equiv)[23] in THF is highly diastereoselective, even though it was considerably slower and gave only a 25% yield of the galactosyl 2,6-imino-D-allonate **19** after five days of irradiation (Scheme 7).

Conclusion

We have shown that iminoglycosylidene complexes of chromium are readily synthesized from sugar lactams in good yields. The metal-stabilized carbene moiety in iminopyranosylidene complexes can be exploited in a photoinduced carbon-chain elongation. We propose that the chromium carbonyl fragment in the iminopyranosylidene complexes not only mediates the generation of ketene equivalents, but also

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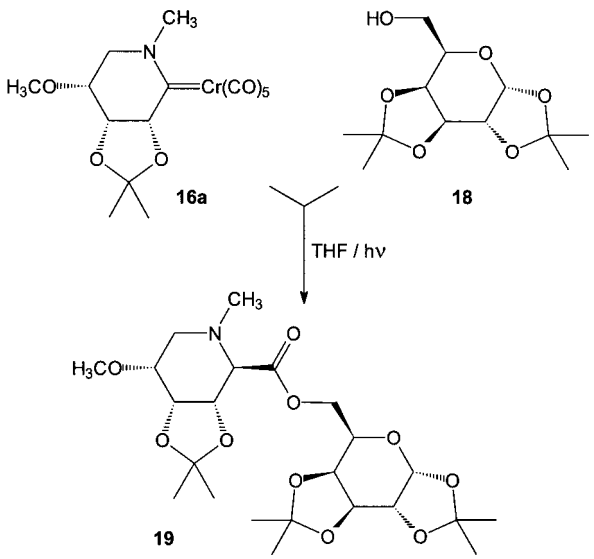

Scheme 7. Photoinduced synthesis of the galactosyl 2,6-imino-D-allonate **19**.

controls the stereochemical course of the reaction with alcohols. This may be the result of the coordination of the metal fragment to the zwitterion opposite the acetal protection group. The importance of metal coordination to the ketene intermediate is demonstrated by the fact that the diastereoselectivity of C-glycosidation decreases significantly if methanol is replaced by the better coordinating CH_3CN.

This reaction provides a novel, complementary, and highly diastereoselective pathway to 2,6-iminoaldonic acid derivatives[3–5] and a straightforward, yet unconventional, approach to *allo*-configured iminosugars.[19, 24]

Experimental Section

All solvents were dried by standard procedures and then saturated with argon. Organic products were purified by chromatography carried out at room temperature on silica gel (Merck 60, 0.062–0.200 nm). Chromatographic workup of organometallic products was carried out between −5 and −12 °C with dry solvents on degassed silica gel (Merck 60, 0.062–0.200 nm). TLC: Merck plates, silica gel 60F254. HPLC: Chiracel OD (4.6 × 250 mm), Eurospher (16 × 250 mm). UV irradiation was performed with a high-pressure mercury lamp, Philips TPK125, combined with a transformer DEMA HPK125. ^{1}H and ^{13}C NMR (298 K): Bruker DRX 500, AM 400. Chemical shifts refer to those of residual solvent signals based on δ(TMS) = 0.00 ppm, coupling constants J are given in Hz. FTIR: Nicolet 550. MS-EI: Kratos Analytical MS50. GC-MS: Hewlett–Packard 5890 Series-II-Gas-Chromatograph, column HP-5 MS (30m × 0.2 cm), 5972 Series-Mass Selective Detector. Elemental analysis: Heraeus CHN-Rapid and Elementar Analysensysteme GmbH Vario EL. Optical rotations: Perkin–Elmer Polarimeter 341, 1 mL cell, 20 °C, 589 nm. Melting points: Büchi SMP 20, uncorrected. X-ray crystal structure analysis: Nonius Kappa CCD.

X-ray structural analysis of 3a, 3c, and 16a: The structures were solved by direct methods (SHELXS-97).[25] The non-hydrogen atoms were refined anisotropically on F^2 (SHELXL-97).[26] Hydrogen atoms were refined isotropically with a riding model. An extinction correction (**3a**, **3c**, and **16a**) and an empirical absorption correction were applied (**3c**: $T_{max/min}$ = 0.47906/0.35685). The absolute configuration is determined by refining Flack's x parameter.[27] Further details are given in Table 1.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102572 (**3a**), CCDC-102573 (**3c**), CCDC-102574 (**16a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic data and summary of data collection and refinement of **3a**, **3c** and **16a**.

	3a	**3c**	**16a**
formula	$C_{13}H_{13}NO_7Cr$	$C_{13}H_{13}NO_7W$	$C_{15}H_{17}NO_8Cr$
M_r	347.24	479.09	391.30
crystal system	orthorhombic	orthorhombic	orthorhombic
space group	$P2_12_12_1$ (no.19)	$P2_12_12_1$ (no.19)	$P2_12_12_1$ (no.19)
a [Å]	7.7241(2)	7.7210(1)	8.9292(3)
b [Å]	12.6238(4)	13.1660(3)	10.0482(3)
c [Å]	16.1620(5)	16.3970(3)	20.2145(4)
V [Å^3]	1575.92(8)	1666.83(5)	1813.69(4)
Z	4	4	4
crystal size [mm^3]	0.10 × 0.20 × 0.50	0.20 × 0.40 × 0.50	0.10 × 0.15 × 0.25
ρ_{calcd} [g cm^{-3}]	1.46	1.91	1.43
μ [mm^{-1}]	0.76	6.96	0.67
F(000)	712	912	808
diffractometer	Nonius Kappa-CCD		
radiation	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$
λ [Å]	0.71073	0.71073	0.71073
T [K]	123(2)	293(2)	123(2)
max 2θ [°]	56.6	56.4	56.6
index range	$-9 \le h \le 9$	$-7 \le h \le 7$	$-10 \le h \le 10$
	$-16 \le k \le 16$	$-15 \le k \le 15$	$-12 \le k \le 12$
	$-19 \le hl \le 19$	$-19 \le l \le 19$	$-22 \le l \le 22$
no. of data	72437	22653	27662
no. of unique data	3607	3185	3890
R_{int}	0.029	0.058	0.033
no. of data with $I > 2\sigma(I)$	3343	3533	3491
parameters	201	201	231
absolute structure parameter x	−0.01(1)	0.02(2)	−0.01(1)
$R(F)$ for $I > 2\sigma(I)$	0.023	0.027	0.025
w$R2(F^2)$ for all data	0.059	0.068	0.065
goodn. of fit on F^2	1.04	1.11	1.06
largest diff. peak and hole e Å^{-3}	0.26/−0.26	1.20/−0.81	0.22/−0.26

***N*-Methyl-4-amino-4-deoxy-2,3-*O*-isopropylidene-D-erythronolactam (2a)**: A solution of lactam **1**[16] (3.97 g, 25.3 mmol) in DMF (25 mL) was cooled to 0 °C. NaH (0.85 g, 35.4 mmol) was added and the mixture was stirred at 25 °C for 1.5 h. After addition of CH_3I (12.6 mL, 202.4 mmol), the solution was stirred for a further 8 h. The solvent was then evaporated and the residue was purified by chromatography (eluent CH_2Cl_2/CH_3OH, 5:1). Colorless crystals of **2a** (2.89 g, 66%) were obtained after distillation at 100 °C (5×10^{-2} mbar). M.p. 86–87 °C; R_f = 0.80 (CH_2Cl_2/CH_3OH, 5:1); MS (70 eV, EI): m/z (%): 171 ([M]$^+$, 6.4), 156 ([$M - CH_3$]$^+$, 100), 128 ([$M - CH_3 - CO$]$^+$, 7.8), 114 (6.4), 96 (60); HR-MS: $C_8H_{13}NO_3$: calcd 171.0895; found 171.0905; IR (KBr): $\tilde{\nu}$ = 1693 cm^{-1}; $C_8H_{13}NO_3$ (171.19): calcd C 56.13, H 7.65, N 8.18; found C 55.76, H 7.57, N 8.10; ^{1}H NMR (500 MHz, CD_3OD): δ = 1.27 (s, 3H; CH_3), 1.28 (s, 3H; CH_3), 2.76 (s, 3H; NCH_3), 3.34 (dd, $^2J_{4/4'}$ = 11.72, $^3J_{4/3}$ = 0.39, 1H; H-4), 3.58 (dd, $^2J_{4'/4}$ = 11.72, $^3J_{4'/3}$ = 4.87, 1H; H-4′), 4.56 (d, $^3J_{2/3}$ = 5.96, 1H; H-2), 4.67 (pt, 1H; H-3); ^{13}C NMR (125 MHz, CD_3OD): δ = 26.1, 27.6 (2C, CH_3), 30.3 (1C, NCH_3), 54.4 (1C, C-4), 74.1, 79.5 (2C, C-2, C-3), 113.5 (1C, Me_2C), 173.8 (1C, C-1).

***N*-Benzyl-4-amino-4-deoxy-2,3-*O*-isopropylidene-D-erythronolactam (2b)**: As described in the previous procedure, treatment of **1** (0.91 g, 5.8 mmol) with NaH (0.19 g, 8.1 mmol) and benzyl chloride (2.7 mL, 23.2 mmol) in DMF (10 mL) yielded **2b** as colorless needles (1.02 g, 71%) after chromatographic workup (eluent CH_2Cl_2/CH_3OH, 20:1) and distillation at 100 °C (5×10^{-2} mbar). M.p. 89–90 °C; R_f = 0.54 (CH_2Cl_2/CH_3OH, 20:1); MS (70 eV, EI): m/z (%): 247 ([M]$^+$, 17.8), 232 ([$M - CH_3$]$^+$, 6.4), 189 ([$M - Me_2CO$]$^+$, 4.2), 172 (68.5), 132 (5.7), 91 (100), 65 (12.1); HR-MS: $C_{14}H_{17}NO_3$ calcd 247.1028; found 247.1202; IR (KBr): $\tilde{\nu}$ = 1685 cm^{-1}; [α]$_D$ =

+7.3 ($c = 0.994$, CH_3OH). $C_{14}H_{17}NO_3$ (247.29): calcd C 68.00, H 6.93, N 5.66; found C 67.98, H 6.86, N 5.37; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 1.23$ (s, 3H; CH_3), 1.42 (s, 3H; CH_3), 2.69 (dd, $^2J_{4'/4} = 11.22$, $^3J_{4'/3} = 4.96$, 1H; H-4′), 2.96 (d, $^2J_{4/4'} = 11.22$, 1H; H-4), 4.00 (pt, 1H; H-3), 4.20 (d, $^2J = 14.60$, 1H; PhCH_2), 4.25 (d, $^2J = 14.60$, 1H; PhCH_2), 4.31 (d, $^3J_{2/3} = 6.06$, 1H; H-2), 7.05 – 7.14 (m, 5H; H-aryl); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 25.8$, 27.3 (2C, CH_3), 46.4 (1C, CH_2Ph), 49.6 (1C, C-4), 72.3, 77.9 (2C, C-3, C-2), 111.9 (1C, Me_2C), 127.7, 128.4, 128.8 (5C, aryl-C), 136.5 (1C, C_{ipso}), 170.0 (1C, C-1).

2,3-*O*-Cyclohexylidene-D-ribono-1,4-lactone (**4**): D-Ribono-1,4-lactone was protected by treatment with cyclohexanone (50 mL) and concentrated H_2SO_4 (5 drops) over 20 h at 25 °C. The solvent was then evaporated in vacuo at 45 – 60 °C in the presence of solid $NaHCO_3$ (0.5 g). Chromatography of the residue (eluent EtOAc/PE, 2:1) gave **4** as a white solid (6.48 g, 56 %). M.p. 120 – 121 °C; $R_f = 0.42$ (EtOAc/PE, 2:1); MS (70 eV, EI): *m*/*z* (%): 228 ([*M*]$^+$, 96.0), 199 ([*M* – H – CO]$^+$, 21.4), 185 ([*M* + H – CO_2]$^+$, 100), 169 (3.2), 99 (4.2), 85 (10), 55 (53.5); HR-MS: $C_{11}H_{16}O_5$: calcd 228.0997; found 228.0993; IR (KBr): $\tilde{\nu} =$ 3465, 1780 cm^{-1}; $[\alpha]_D = -53.1°$ ($c = 1.440$, $CHCl_3$). $C_{11}H_{16}O_5$ (228.24): calcd C 57.89, H 7.07; found C 57.63, H 6.96; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.33 – 1.40$ (m, 2H; C_6H_{10}), 1.50 – 1.67 (m, 8H; C_6H_{10}), 2.61 (b, 1H; OH), 3.77 (dd, $^2J_{5/5'} = 12.32$, $^3J_{5/4} = 1.69$, 1H; H-5), 3.96 (dd, $^2J_{5'/5} = 12.32$, $^3J_{5'/4} = 2.28$, 1H; H-5′), 4.61 (pt, $^3J_{4/5} \approx {}^3J_{4/5'} \approx 1.98$, 1H; H-4), 4.74 (d, $^3J_{3/2} = 5.67$, 1H; H-3), 4.81 (d, $^3J_{2/3} = 5.67$, 1H; H-2); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 23.6$, 23.7, 24.7, 34.8, 36.2 (5C, C_6H_{10}), 61.8 (1C, C-5), 75.2, 77.7, 82.9 (3C, C-2, C-3, C-4), 113.8 (1C, C_{spiro}), 175.3 (1C, C-1).

2,3-*O*-Cyclohexylidene-5-*O*-*p*-toluenesulfonyl-D-ribono-1,4-lactone (**5**): *p*-Toluenesulfonyl chloride (8.0 g, 42.0 mmol) was added to a solution of the acetal **4** (3.5 g, 21.0 mmol) in cold pyridine (20 mL, – 20 °C) in one portion. After the mixture had been kept for 20 h at – 28 °C, water (2.0 mL) was added, and the solution was then poured slowly into ice water (500 mL) with vigorous stirring. The crystals formed were collected, dried, and purified chromatographically (eluent EtOAc/PE, 2:1) to furnish the tosylate **5** as a colorless liquid (8.0 g, 100 %). $R_f = 0.87$ (EtOAc/PE, 2:1); MS (70 eV, EI): *m*/*z* (%): 382 ([*M*$^+$], 35.6), 353 ([*M* – HCO]$^+$, 23.7), 339 ([*M* + H – CO_2]$^+$, 100), 155 ([$C_7H_7O_2S$]$^+$, 23.7), 139 ([C_7H_7OS]$^+$, 8.4), 91 ([C_7H_7]$^+$, 25.4), 55 (35.3); HR-MS: $C_{18}H_{22}O_7S$: calcd 382.1086; found 382.1091; IR (film): $\tilde{\nu} =$ 1795, 1733 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6): $\delta =$ 1.08 – 1.17 (m, 2H; C_6H_{10}), 1.27 – 1.63 (m, 8H; C_6H_{10}), 1.81 (s, 3H; PhCH_3), 3.53 (dd, $^2J_{5/5'} = 11.22$, $^2J_{5/4} = 2.08$, 1H; H-5), 3.58 (dd, $^2J_{5'/5} = 11.22$, $^3J_{5'/4} =$ 2.58, 1H; H-5′), 4.00 (pt, $^3J_{4/5} \approx {}^3J_{4/5'} \approx 2.28$, 1H; H-4), 4.16 (d, $^3J_{3/2} = 5.66$, 1H; H-3), 4.60 (d, $^3J_{2/3} = 5.66$, 1H; H-2), 6.70 (d, $^3J = 8.54$, 2H; H-aryl), 7.61 (d, $^3J = 8.54$, 2H; H-aryl); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 21.1$ (1C, PhCH_3), 23.9, 24.0, 24.9, 35.0, 36.5 (5C, C_6H_{10}), 68.2 (1C, C-5), 74.9, 77.1, 78.7 (3C, C-2, C-3, C-4), 114.1 (1C, C_{spiro}), 128.0, 130.1, 132.4 (5C, aryl-C), 145.2 (1C, C_{ipso}), 172.7 (1C, C-1).

5-Azido-2,3-*O*-cyclohexylidene-5-deoxy-D-ribono-1,4-lactone (**6**): Sodium azide (1.07 g, 16.5 mmol) was added to a solution of **5** (1.96 g, 5.0 mmol) in DMF (50 mL) and the suspension was warmed to 100 °C for 6 h. After evaporation of the solvent in vacuo at 40 °C, the residue was taken up in water (40 mL) and extracted with Et_2O (6 × 50 mL). The combined extracts were dried over $MgSO_4$ and then concentrated to give white needles of the azido lactone **6** (1.26 g, 100 %). M.p. 80 – 81 °C; MS (70 eV, EI): *m*/*z* (%): 253 ([*M*]$^+$, 20), 224 ([*M* – H – CO]$^+$, 19.2), 210 ([*M* – HN_3]$^+$, 38.5), 196 ([224 – N_2], 2.1), 182 ([210 – CO], 7.8), 55 (100); HR-MS: $C_{11}H_{15}N_3O_4$: calcd 253.1062; found 253.1067; IR (KBr): $\tilde{\nu} =$ 2112, 1784 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.33 – 1.39$ (m, 2H; C_6H_{10}), 1.48 – 1.67 (m, 8H; C_6H_{10}), 3.63 (dd, $^2J_{5/5'} = 13.21$, $^3J_{5/4} = 2.28$, 1H; H-5), 3.75 (dd, $^2J_{5'/5} = 13.21$, $^3J_{5'/4} = 3.17$, 1H; H-5′), 4.59 (d, $^3J_{3/2} = 5.77$, 1H; H-3), 4.64 (pt, $^3J_{4/5} \approx {}^3J_{4/5'} \approx$ 2.73, 1H; H-4), 4.81 (d, $^3J_{2/3} = 5.77$, 1H; H-2); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 23.6$, 23.7, 24.6, 34.8, 36.2 (5C, C_6H_{10}), 52.4 (1C, C-5), 74.7, 77.5, 80.1 (3C, C-2, C-3, C-4), 114.3 (1C, C_{spiro}), 173.5 (1C, C-1).

5-Amino-2,3-*O*-cyclohexylidene-5-deoxy-D-ribono-1,5-lactam (**7**): Azido lactone **6** (1.26 g, 5.0 mmol) was dissolved in methanol (100 mL) and hydrogenated in the presence of palladium on charcoal (6 mol %) at 1.5 bar H_2 and 25 °C. After 2 h, the catalyst was filtered through a short column filled with silica gel. Evaporation of the solvent yielded the lactam **7** as a white solid (1.07 g, 94 %). M.p. 202 °C; MS (70 eV, EI): *m*/*z* (%): 227 ([*M*]$^+$, 31.4), 198 ([*M* – H – CO]$^+$, 22.8), 184 ([*M* – HNCO]$^+$, 100), 171 (2.1), 130 (3.5), 112 (10.0), 84 (6.4), 55 (57.1); HR-MS: $C_{11}H_{17}NO_4$: calcd 227.1157; found 227.1158; IR (KBr): $\tilde{\nu} =$ 3412, 3257, 1656 cm^{-1}; $[\alpha]_D = +14.9$ ($c =$ 0.705, CH_3OH); $C_{11}H_{17}NO_4$ (227.26): calcd C 58.14, H 7.54, N 6.16; found C 57.96, H 7.58, N 6.02; ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 1.28 – 1.38$ (m, 2H; C_6H_{10}), 1.45 – 1.58 (m, 8H; C_6H_{10}), 2.91 (m, 1H; H-5′), 3.17 (t, $^2J_{5/5'} = {}^3J_{5/4} = 10.43$, 1H; H-5), 3.86 (m, 1H; H-4), 4.26 (d, $^3J_{2/3} = 6.36$, 1H; H-2), 4.35 (m, 1H; H-3), 5.19 (d, $^2J_{OH/4} = 5.06$, 1H; OH), 7.61 (d, $^2J = 3.97$, 1H; NH); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 23.5$, 23.7, 24.7, 34.7, 36.2 (5C, C_6H_{10}), 41.5 (1C, C-5), 64.8, 73.5, 75.6 (3C, C-2, C-3, C-4), 109.8 (1C, C_{spiro}), 168.3 (1C, C-1).

***N*-Methyl-5-amino-2,3-*O*-cyclohexylidene-5-deoxy-4-*O*-methyl-D-ribono-1,5-lactam** (**8**): Lactam **7** (909 mg, 4.0 mmol) was dissolved in DMF (50 mL) and cooled to 0 °C. NaH (249 mg, 10.4 mmol) was added, and the mixture was stirred at 25 °C for 1.5 h. After addition of CH_3I (4.0 mL, 64.0 mmol), the solution was stirred for a further 8 h. The solvent was then evaporated and the residue was purified by chromatography (eluent CH_2Cl_2/CH_3OH, 10:1). Further purification was achieved by distillation at 120 °C (5×10^{-2} mbar) to give **8** as a colorless syrup (950 mg, 93 %). $R_f = 0.60$ (CH_2Cl_2/CH_3OH, 10:1); MS (70 eV, EI): *m*/*z* (%): 255 ([*M*]$^+$, 43.5), 226 ([*M* – H – CO]$^+$, 27.8), 212 ([*M* – H_2CNCH_3]$^+$, 100), 140 (58.3), 98 (17.1), 71 (17.8), 55 (31.4); HR-MS: $C_{13}H_{21}NO_4$: calcd 255.1470; found 255.1468; IR (film): $\tilde{\nu} =$ 1662 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 1.12 – 1.24$ (m, 2H; C_6H_{10}), 1.49 – 1.71 (m, 8H; C_6H_{10}), 2.53 (dddd, $^2J_{5/5'} = 11.33$, $^3J_{5/4} = 4.67$, $^3J_{5/3} = 1.39$, $^5J_{5/2} = 0.50$, 1H; H-5), 2.57 (s, 3H; NCH_3), 2.75 (dddd, $^3J_{4/5'} =$ 10.13, $^3J_{4/5} = 4.67$, $^3J_{4/3} = 2.69$, $^4J_{4/2} = 0.55$, 1H; H-4), 2.98 (s, 3H; OCH_3), 3.43 (dd, $^2J_{5'/5} = 11.33$, $^3J_{5'/4} = 10.13$, 1H; H-5′), 4.15 (m, 1H; H-3), 4.28 (d, $^3J_{2/3} =$ 6.16, 1H; H-2); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 24.0$, 24.1, 25.2 (3C, C_6H_{10}), 34.3 (1C, NCH_3), 35.2, 36.8 (2C, C_6H_{10}), 46.9 (1C, C-5), 56.2 (1C, OCH_3), 72.8 (1C, C-3), 73.9 (1C, C-4), 74.6 (1C, C-2), 111.1 (1C, C_{spiro}), 166.5 (1C, C-1).

2,3-*O*-Isopropylidene-5-*O*-*p*-toluenesulfonyl-D-ribono-1,4-lactone (**12**): 2,3-*O*-Isopropylidene-D-ribono-1,4-lactone **11**[18] (6.03 g, 32.0 mmol) was dissolved in cold pyridine (30 mL, – 20 °C) and *p*-toluenesulfonyl chloride (12.22 g, 64.0 mmol) was introduced to the solution in one portion. The solution was left at – 28 °C for 20 h. Water (2 mL) was then added (2 mL), and the solution was poured into ice water (2400 mL). The crystals formed were filtered and dried in vacuo to give the tosylate **12** as a slightly yellow solid (9.24 g, 84 %). M.p. 110 – 114 °C; MS (70 eV, EI): *m*/*z* (%): 327 ([*M* – CH_3]$^+$, 100), 172 ([p-TosOH]$^+$, 2.5), 155 ([*M* – H – p-TosOMe]$^+$, 64.4), 127 (45.7), 85 (59.3), 68 (45.7), 59 (9.3); HR-MS: $C_{14}H_{15}O_7S$ (M – CH_3): calcd 327.0538; found 327.0541; IR (KBr): $\tilde{\nu} =$ 1786 cm^{-1}; $[\alpha]_D = -16.8$ ($c = 2.51$, acetone); $C_{15}H_{18}O_7S$ (342.36): calcd C 52.62, H 5.30, S 9.36; found C 52.60, H 5.33, S 9.18; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.35$ (s, 3H; CH_3), 1.43 (s, 3H; CH_3), 2.44 (s, 3H; PhCH_3), 4.15 (dd, $^2J_{5/5'} = 11.13$, $^3J_{5/4} = 2.43$, 1H; H-5), 4.31 (dd, $^2J_{5'/5} = 11.13$, $^3J_{5'/4} = 1.89$, 1H; H-5′), 4.65 (pt, $^3J_{4/5} \approx {}^3J_{4/5'} \approx$ 2.14, 1H; H-4), 4.72 (d, $^3J_{3/2} = 5.56$, 1H; H-3), 4.75 (d, $^3J_{2/3} = 5.56$, 1H; H-2), 7.35 (d, ^{3}J = 8.44, 2H; H-aryl), 7.72 (d, ^{3}J = 8.44, 2H; H-aryl); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 21.6$ (1C, PhCH_3), 25.4 (1C, CH_3), 26.6 (1C, CH_3), 68.2 (1C, C-5), 74.9, 77.3, 78.9 (3C, C-4, C-3, C-2), 113.8 (1C, Me_2C), 127.9, 130.2, 131.4 (5C, aryl-C), 145.8 (1C, C_{ipso}), 173.0 (1C, C-1).

5-Azido-5-deoxy-2,3-*O*-isopropylidene-D-ribono-1,4-lactone (**13**): A suspension of tosylate **12** (9.00 g, 26.2 mmol) and sodium azide (5.12 g, 78.8 mmol) in DMF (150 mL) was heated for 6 h at 100 °C. After evaporation of the solvent, the residue was taken up in water (200 mL) and extracted with Et_2O (7 × 200 mL). The combined extracts were dried over $MgSO_4$ and evaporated. The residue was then purified by column chromatography (eluent Et_2O/PE/CH_3OH, 15:5:1). The azido lactone **13** was obtained as yellowish needles (4.95 g, 88 %). M.p. 39 °C; $R_f = 0.58$ (Et_2O/PE/CH_3OH, 15:5:1); MS (70 eV, EI): *m*/*z* (%): 214 ([*M* + H]$^+$, 0.7), 198 ([*M* – CH_3]$^+$, 100), 170 ([*M* – HN_3]$^+$, 12.1), 129 (12.8), 112 (2.8), 100 (10.0), 85 (25.7), 59 (52.1), 55 (26.4); HR-MS: $C_8H_{11}N_3O_4$ (*M* – CH_3): calcd 198.0514; found 198.0513; IR (KBr): $\tilde{\nu} =$ 2115, 1787 cm^{-1}; $[\alpha]_D = +15.0$ ($c = 1.001$, $CHCl_3$); $C_8H_{11}N_3O_4$ (213.19): calcd C 45.07, H 5.20, N 19.71; found C 45.13, H 5.19, N 19.26; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.35$ (s, 3H; CH_3), 1.44 (s, 3H; CH_3), 3.64 (dd, $^2J_{5/5'} = 13.21$, $^3J_{5/4} = 1.89$, 1H; H-5), 3.76 (dd, $^2J_{5'/5} = 13.21$, $^3J_{5'/4} = 2.89$, 1H; H-5′), 4.60 (d, $^3J_{3/2} = 5.66$, 1H; H-3), 4.63 (m, 1H; H-4), 4.82 (d, $^3J_{2/3} = 5.66$; H-2); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 25.3$ (1C, CH_3), 26.5 (1C, CH_3), 52.3 (1C, C-5), 75.0, 77.9, 79.9 (3C, C-4, C-3, C-2), 113.5 (1C, Me_2C), 173.3 (1C, C-1).

5-Amino-5-deoxy-2,3-*O*-isopropylidene-D-ribono-1,5-lactam (**14**): Azido lactone **13** (4.95 g, 23.0 mmol) was hydrogenated in methanol (250 mL) in the presence of palladium on charcoal (6 mol %) at 1.0 bar H_2 and 25 °C. After 2.5 h, the catalyst was filtered through a short column filled with silica gel. The filtrate was concentrated to a sticky foam, which was triturated

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with a mixture of acetone/Et_2O (1:1, 100 mL) with vigorous stirring to induce precipitation of the product. After filtration, the residue obtained was concentrated again and the procedure was repeated (acetone/Et_2O, 1:1, 30 mL) to give the lactam **14** as a white solid (2.93 g, 67%). M.p. 139–140 °C. MS (70 eV, EI): *m/z* (%): 188 ($[M+H]^+$, 0.6), 172 ($[M-CH_3]^+$, 100), 144 ($[M-HNCO]^+$, 6.4), 130 ($[M+H-Me_2CO]^+$, 32.8), 112 (9.6), 101 (10.7), 84 (23.9), 73 (19.6), 59 ($[Me_2COH]^+$, 46.7); HR-MS: $C_7H_{10}NO_4$ ($M-CH_3$): calcd 172.0609; found 172.0610; IR (KBr): $\tilde{\nu}$ = 3529, 3427, 3290, 1664, 1633 cm^{-1}; $[\alpha]_D = +22.6$ ($c = 1.030$, $CHCl_3$); $C_8H_{13}NO_4$ (187.19): calcd C 51.33, H 7.00, N 7.48; found C 51.08, H 6.86, N 7.28; ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 1.28$ (s, 3H; CH_3), 1.32 (s, 3H; CH_3), 2.92 (dpt, $^2J_{5'/5} = 11.42$, $^3J_{5'/4} \approx {}^3J_{5'/NH} \approx 4.6$, 1H; H-5′), 3.17 (dd, $^2J_{5/5'} = 11.42$, $^3J_{5/4} = 11.13$, 1H; H-5), 3.87 (dddd, $^3J_{4/5} = 11.13$, $^3J_{4/OH} = 5.15$, $^3J_{4/5'} = 4.77$, $^3J_{4/3} = 2.59$, 1H; H-4), 4.25 (d, $^3J_{2/3} = 6.35$, 1H; H-2), 4.35 (dd, $^3J_{3/2} = 6.35$, $^3J_{3/4} = 2.59$, 1H; H-3), 5.20 (d, $^3J_{OH/4} = 5.15$, 1H; OH), 7.63 (d, $^3J_{NH/5'} \approx 4.6$, 1H; NH); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 25.4$ (1C, CH_3), 26.8 (1C, CH_3), 41.5 (1C, C-5), 64.7, 73.8, 75.9 (3C, C-4, C-3, C-2), 109.3 (1C, Me_2C), 168.1 (1C, C-1).

***N*-Methyl-5-amino-5-deoxy-2,3-*O*-isopropylidene-4-*O*-methyl-D-ribono-1,5-lactam (15a)**: As in the procedure reported for **8**, reaction of **14** (1.49 g, 8.0 mmol) with NaH (0.50 g, 20.8 mmol) and CH_3I (8.0 mL, 128.0 mmol) in DMF (100 mL) yielded the lactam **15a** as a colorless solid (1.53 g, 88%) after chromatographic workup (eluent CH_2Cl_2/CH_3OH, 10:1) and distillation at 120 °C (5×10^{-2} mbar). M.p. 65 °C; $R_f = 0.56$ (CH_2Cl_2/CH_3OH, 10:1); MS (70 eV, EI): *m/z* (%): 215 ($[M]^+$, 7.1), 200 ($[M-CH_3]^+$, 100), 182 ($[M-CH_3OH]^+$, 14.2), 172 ([200 – CO], 5.7), 158 ($[M-CH_3NCO]^+$, 31.4), 140([172 – CH_3OH], 23.5), 71 ($[H_2CNCH_3CO]^+$, 34.2), 58 ($[Me_2CO]^+$, 27.1); HR-MS: $C_9H_{14}NO_4$ ($M-CH_3$): calcd 200.0922; found 200.0922; IR (KBr): $\tilde{\nu}$ = 1660 cm^{-1}. $[\alpha]_D = -3.6$ ($c = 1.006$, CH_3OH); $C_{10}H_{17}NO_4$ (215.24): calcd C 55.80, H 7.96, N 6.51; found C 55.81, H 7.97, N 6.33; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 1.27$ (s, 3H; CH_3), 1.41 (s, 3H; CH_3), 2.59 (dd, $^2J_{5'/5} = 11.63$, $^3J_{5'/4} = 4.67$, 1H; H-5′), 2.61 (s, 3H; NCH_3), 2.82 (ddd, $^3J_{4/5} = 10.00$, $^3J_{4/5'} = 4.67$, $^3J_{4/3} = 2.69$, 1H; H-4), 3.03 (s, 3H; OCH_3), 3.44 (dd, $^2J_{5/5'} = 11.63$, $^3J_{5/4} = 10.00$, 1H; H-5), 4.15 (dd, $^3J_{3/2} = 6.16$, $^3J_{3/4} = 2.69$, 1H; H-3), 4.31 (d, $^3J_{2/3} = 6.16$, 1H; H-2); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 25.3$ (1C, CH_3), 26.8 (1C, CH_3), 34.6 (1C, NCH_3), 46.9 (1C, C-5), 56.2 (1C, OCH_3), 73.0 (1C, C-3), 73.8 (1C, C-4), 74.9 (1C, C-2), 110.3 (1C, Me_2C), 166.3 (1C, C-1).

***N*-Benzyl-5-amino-4-*O*-benzyl-5-deoxy-2,3-*O*-isopropylidene-D-ribono-1,5-lactam (15b)**: As in the procedure reported for **8**, reaction of **14** (1.49 g, 8.0 mmol) with NaH (0.50 g, 20.8 mmol) and benzyl chloride (7.4 mL, 64.0 mmol) in DMF (100 mL) yielded the lactam **15b** as a colorless solid (2.23 g, 75%) after chromatographic workup (eluent CH_2Cl_2/CH_3OH, 20:1). M.p. 99–100 °C; $R_f = 0.50$ (CH_2Cl_2/CH_3OH, 20:1); MS (70 eV, EI): *m/z* (%): 367 ($[M]^+$, 16.9), 309 ($[M-Me_2CO]^+$, 3.3), 280 ([309 – H – CO], 6.7), 261 ($[M-PhCHO]^+$, 8.4), 218 ([309 – C_7H_7], 11.8), 203 ([309 – PhCHO], 11.8), 174 ([280 – PhCHO], 11.0), 91 ($[C_7H_7]^+$, 100); HR-MS: $C_{22}H_{25}NO_4$: calcd 367.1783; found 367.1783; IR (KBr): $\tilde{\nu}$ = 1660 cm^{-1}; $[\alpha]_D = +34.6$ ($c = 1.006$, CH_3OH). $C_{22}H_{25}NO_4$ (367.44): calcd C 71.91, H 6.86, N 3.81; found C 71.83, H 6.76, N 3.58; ^{1}H NMR (500 MHz, C_6D_6/TMS): $\delta = 1.31$ (s, 3H; CH_3), 1.46 (s, 3H; CH_3), 2.87 (ddd, $^2J_{5'/5} = 11.63$, $^3J_{5'/4} = 4.27$, $^4J_{5'/3} = 1.29$, 1H; H-5′), 3.28 (ddd, $^3J_{4/5} = 9.63$, $^3J_{4/5'} = 4.27$, $^3J_{4/3} = 2.68$, 1H; H-4), 3.55 (dd, $^2J_{5/5'} = 11.63$, $^3J_{5/4} = 9.63$, 1H; H-5), 4.23 (d, $^2J = 11.82$, 1H; PhCH_2), 4.25 (ddd, $^3J_{3/2} = 6.56$, $^3J_{3/4} = 2.68$, $^4J_{3/5'} = 1.29$, 1H; H-3), 4.34 (d, $^2J = 14.61$, 1H; PhCH_2), 4.35 (d, $^2J = 11.82$, 1H; PhCH_2), 4.45 (d, $^3J_{2/3} = 6.56$, 1H; H-2), 4.55 (d, $^2J = 14.61$, 1H; PhCH_2), 7.11–7.29 (m, 10H; H-aryl); ^{13}C NMR (125 MHz, C_6D_6/TMS): $\delta = 25.2$, 26.7 (2C, CH_3), 44.6 (1C, PhCH_2N), 50.4 (1C, C-5), 70.9 (1C, PhCH_2O), 72.4 (1C, C-3), 73.8 (1C, C-4), 75.2 (1C, C-2), 110.5 (1C, Me_2C), 127.6, 127.7, 127.8, 128.5, 128.6, 128.7 (10C, aryl-C), 137.3, 138.4 (2C, C_{ipso}), 166.3 (1C, C-1).

General procedure for preparation of the iminoglycosylidene complexes 3a–c, 9, and 16a,b: In order to prepare C_8K, graphite (17.6 equiv) was stirred in vacuo for 20 min at 165 °C. Potassium (2.2 equiv) was then added under a flow of argon, and the mixture was kept at 165 °C for 1.5 h to complete the formation of C_8K. The laminate was cooled to 25 °C and then suspended in freshly distilled THF (the volume used was that required for a 0.15–0.3 M solution of the pentacarbonyl metalate). The suspension was cooled to −78 °C, and either $Cr(CO)_6$ or $W(CO)_6$ (1.1 equiv) was added. The reaction mixture was stirred for 0.5 h at −78 °C and then kept between −10 and −5 °C until no more carbon monoxide was evolved (approximately 1.5–2 h). The solution was cooled again to −78 °C, and the appropriate lactam (**2a**,**b**, **8**, or **15a**,**b**; 1.0 equiv in THF) was added by syringe. The mixture was kept for 0.5 h at −78 °C, 1.5 h at −5 °C, and then cooled again to −78 °C. TMSCl (3.1 equiv) was added in one portion and the reaction mixture was stirred for 0.5 h. Neutral Al_2O_3 was used to adsorb the product, and the solvent was then removed under reduced pressure. The resulting dry powder was eluted on a silica gel column (eluent Et_2O/PE/CH_3OH, 15:5:1 for **3a–c**, **9**, **16a**; Et_2O/PE/CH_3OH, 15:10:1 for **16b**).

Pentacarbonyl[1,4-dideoxy-2,3-*O*-isopropylidene-1,4-(methylimino)-D-*erythro*-furanosylidene]chromium (3a): Compound **3a** (2.36 mmol, 820 mg, 78%) was isolated as an orange solid by reaction of graphite (634 mg, 52.8 mmol), potassium (258 mg, 6.6 mmol), and $Cr(CO)_6$ (726 mg, 3.3 mmol) with **2a** (513 mg, 3.0 mmol) and TMSCl (1.17 mL, 9.3 mmol) in THF (15 mL) (see general procedure above). M.p. 87 °C (decomp); R_f = 0.58 (Et_2O/PE/CH_3OH, 15:5:1); MS (70 eV, EI): *m/z* (%): 347 ($[M]^+$, 10.0), 332 ($[M-CH_3]^+$, 5.0), 319 ($[M-CO]^+$, 5.0), 291 ($[M-2CO]^+$, 2.1), 263 ($[M-3CO]^+$, 3.2), 235 ($[M-4CO]^+$, 21.6), 207 ($[M-5CO]^+$, 100), 192 ([207 – CH_3], 15.3), 149 ([207 – Me_2CO], 20.2), 93 ($[H_3CN{=}C{=}Cr]^+$, 20.7); HR-MS: $C_{13}H_{13}{}^{52}CrNO_7$: calcd 347.0097; found 347.0098; IR (PE): $\tilde{\nu}$ = 2058, 1978, 1940, 1930 cm^{-1}; $[\alpha]_D = -61$ ($c = 0.278$, Et_2O); $C_{13}H_{13}CrNO_7$ (347.24): calcd C 44.97, H 3.77, N 4.03; found C 44.98, H 3.79, N 3.90; ^{1}H NMR (500 MHz, CD_3OD): $\delta = 1.23$ (s, 3H; CH_3), 1.28 (s, 3H; CH_3), 3.60 (s, 3H; NCH_3), 3.88 (d, $^2J_{4/4'} = 13.91$, 1H; H-4), 4.02 (ddd, $^2J_{4'/4} = 13.91$, $^3J_{4'/3} = 4.96$, $^4J_{4'/2} = 0.70$, 1H; H-4′), 4.60 (pt, $J \approx 5.2$, 1H; H-3), 5.13 (dd, $^3J_{2/3} = 5.57$, $^4J_{2/4'} = 0.70$, 1H; H-2); ^{13}C NMR (100 MHz, CD_3OD): $\delta = 26.2$, 27.7 (2C, CH_3), 43.3 (1C, NCH_3), 69.5 (1C, C-4), 75.9 (1C, C-3), 100.2 (1C, C-2), 112.8 (1C, Me_2C), 219.5 (4C, CO_{cis}), 224.7 (1C, CO_{trans}), 265.1 (1C, C-1).

Pentacarbonyl[1,4-(benzylimino)-1,4-dideoxy-2,3-*O*-isopropylidene-D-*erythro*-furanosylidene]chromium (3b): Compound **3b** (1.00 mmol, 424 mg, 67%) was obtained as a red-orange solid by reaction of graphite (317 mg, 26.4 mmol), potassium (129 mg, 3.3 mmol), and $Cr(CO)_6$ (363 mg, 1.6 mmol) with **2b** (371 mg, 1.5 mmol) and TMSCl (0.59 mL, 4.6 mmol) in THF (8 mL), as described for compound **3a**. M.p. 145–146 °C; R_f = 0.40 (Et_2O/PE/CH_3OH, 15:5:1); MS (70 eV, EI): *m/z* (%): 423 ($[M]^+$, 4.1), 408 ($[M-CH_3]^+$, 0.9), 395 ($[M-CO]^+$, 2.0), 339 ($[M-3CO]^+$, 21.6), 311 ($[M-4CO]^+$, 7.5), 283 ($[M-5CO]^+$, 40.0), 268 ([283 – CH_3], 7.5), 225 ([283 – Me_2CO], 11.7), 172 (27.5), 157 (20.0), 133 ([283 – C_7H_8], 28.3), 91 ($[C_7H_7]^+$, 100); HR-MS: $C_{19}H_{17}{}^{52}CrNO_7$: calcd 423.0410; found 423.0407; IR (PE): $\tilde{\nu}$ = 2058, 1977, 1940, 1931 cm^{-1}; $[\alpha]_D = -91$ ($c = 0.29$, Et_2O); $C_{19}H_{17}CrNO_7$ (423.34): calcd C 53.91, H 4.05, N 3.31; found C 53.58, H 4.21, N 3.03; ^{1}H NMR (500 MHz, CD_3COCD_3): $\delta = 1.36$ (s, 3H; CH_3), 1.41 (s, 3H; CH_3), 3.82 (d, $^2J_{4/4'} = 13.81$, 1H; H-4), 4.06 (dd, $^2J_{4'/4} = 13.81$, $^3J_{4'/3} = 4.76$, 1H; H-4′), 4.79 (pt, $J \approx 5.1$, 1H; H-3), 5.26 (d, $^2J = 14.90$, 1H; PhCH_2), 5.43 (d, $^3J_{2/3} = 5.47$, 1H; H-2), 5.55 (d, $^2J = 14.90$, 1H; PhCH_2), 7.36–7.45 (m, 5H; H-aryl); ^{13}C NMR (125 MHz, CD_3COCD_3): $\delta = 25.9$, 27.4 (2C, CH_3), 59.5 (1C, PhCH_2), 65.8 (1C, C-4), 75.0 (1C, C-3), 99.3 (1C, C-2), 112.0 (1C, Me_2C), 218.7 (4C, CO_{cis}), 224.2 (1C, CO_{trans}), 266.0 (1C, C-1).

Pentacarbonyl[1,4-dideoxy-2,3-*O*-isopropylidene-1,4-(methylimino)-D-*erythro*-furanosylidene]tungsten (3c): Compound **3c** (1.82 mmol, 872 mg, 72%) was obtained as an orange solid by reaction of graphite (538 mg, 44.8 mmol), potassium (219 mg, 5.6 mmol), and $W(CO)_6$ (985 mg, 2.8 mmol) with **2a** (436 mg, 2.5 mmol) and TMSCl (0.99 mL, 7.9 mmol) in THF (15 mL), as described for compound **3a**. M.p. 104 °C; R_f = 0.41 (Et_2O/PE/CH_3OH, 15:5:1); MS (70 eV, EI): *m/z* (%): 479 ($[M]^+$, 2.1), 464 ($[M-CH_3]^+$, 2.5), 451 ($[M-CO]^+$, 8.4), 423 ($[M-2CO]^+$, 20.1), 408 ([464 – 2CO], 5.0), 395 ($[M-3CO]^+$, 2.5), 380 ([464 – 3CO], 8.4), 367 ($[M-4CO]^+$, 3.3), 352 ([464 – 4CO], 3.3), 339 ($[M-5CO]^+$, 3.3), 324 ([464 – 5CO], 6.7), 309 ([367 – Me_2CO], 39.4), 281 ([339 – Me_2CO], 53.7), 253 (12.6), 82 (100); HR-MS: $C_{13}H_{13}NO_7{}^{182}W$: calcd 477.0174; found 477.0166; IR (PE): $\tilde{\nu}$ = 2065, 1975, 1940, 1928 cm^{-1}; $[\alpha]_D = -51$ ($c = 0.250$, Et_2O); $C_{13}H_{13}NO_7W$ (479.09): calcd C 32.59, H 2.73, N 2.92; found C 32.64, H 2.78, N 2.80; ^{1}H NMR (500 MHz, CD_3OD): $\delta = 1.24$ (s, 3H; CH_3), 1.28 (s, 3H; CH_3), 3.53 (s, 3H; NCH_3), 3.88 (d, $^2J_{4/4'} = 14.01$, 1H; H-4′), 4.01 (dd, $^2J_{4/4'} = 14.01$, $^3J_{4/3} = 4.77$, 1H; H-4), 4.62 (pt, $J \approx 5.2$, 1H; H-3), 5.12 (d, $^3J_{2/3} = 5.46$, 1H; H-2); ^{13}C NMR (125 MHz, CD_3OD): $\delta = 26.0$, 27.5 (2C, CH_3), 44.8 (1C, NCH_3), 68.3 (1C, C-4), 76.1 (1C, C-3), 100.9 (1C, C-2), 112.5 (1C, Me_2C), 199.3 (4C, CO_{cis}), 204.0 (1C, CO_{trans}), 247.0 (1C, C-1).

Pentacarbonyl[2,3-*O*-cyclohexylidene-1,5-dideoxy-4-*O*-methyl-1,5-(methylimino)-D-*ribo*-pyranosylidene]chromium (9): Compound **9** (0.78 mmol, 336 mg, 21%) was obtained as an orange solid by reaction of graphite (773 mg, 64.4 mmol), potassium (315 mg, 8.0 mmol), and $Cr(CO)_6$ (886 mg, 4.0 mmol) with **8** (934 mg, 3.6 mmol) and TMSCl (1.43 mL, 11.3 mmol) in

THF (16 mL), as described for compound **3a**. M.p. 95 °C (decomp); R_f = 0.42 (Et_2O/PE/CH_3OH, 15:5:1); MS (70 eV, EI): *m*/*z* (%): 431 ($[M]^+$, 0.6), 403 ($[M-CO]^+$, 8.2), 375 ($[M-2CO]^+$, 2.4), 319 ($[M-4CO]^+$, 16.8), 291 ($[M-5CO]^+$, 100), 110 (94.1), 94 ($[MeNH{=}C{=}Cr]^+$, 81.5), 69 (24.3), 55 (77.3); HR-MS: $C_{17}H_{21}{}^{52}CrNO_7$ (*M* − CO): calcd 403.0723; found 403.0725; IR (PE): $\tilde{\nu}$ = 2056, 1976, 1938, 1922 cm^{-1}; $[\alpha]_D$ = +81.8 (*c* = 0.592, Et_2O); $C_{18}H_{21}CrNO_8$ (431.36): calcd C 50.12, H 4.91, N 3.25; found C 50.22, H 4.87, N 3.07; ^{1}H NMR (500 MHz, CD_3COCD_3): δ = 1.30 – 1.37 (m, 1H; C_6H_{10}), 1.49 – 1.72 (m, 8H; C_6H_{10}), 1.79 – 1.82 (m, 1H; C_6H_{10}), 3.40 (s, 3H; OCH_3), 3.65 (dd, $^2J_{5/5'}$ = 13.61, $^3J_{5'/4}$ = 2.19, 1H; H-5′), 3.74 (m, 1H; H-4), 3.80 (dd, $^2J_{5/5'}$ = 13.61, $^3J_{5/4}$ = 6.46, 1H; H-5), 3.90 (s, 3H; NCH_3), 4.43 (dd, $^3J_{3/2}$ = 7.35, $^3J_{3/4}$ = 3.08, 1H; H-3), 4.88 (d, $^3J_{2/3}$ = 7.35, 1H; H-2); ^{13}C NMR (125 MHz, CD_3COCD_3): δ = 24.3, 24.7, 26.0, 34.5, 36.4 (5C, C_6H_{10}), 53.6 (1C, NCH_3), 55.9 (1C, C-5), 58.2 (1C, OCH_3), 72.2 (2C, C-3, C-4), 86.2 (1C, C-2), 110.3 (1C, C_{spiro}), 219.1 (4C, CO_{cis}), 225.0 (1C, CO_{trans}), 264.7 (1C, C-1).

Pentacarbonyl[1,5-dideoxy-2,3-*O*-isopropylidene-4-*O*-methyl-1,5-(methylimino)-D-*ribo*-pyranosylidene]chromium (**16a**): Compound **16a** (4.32 mmol, 1.69 g, 72%) was isolated as a yellow solid by reaction of graphite (1.26 g, 105.6 mmol), potassium (516 mg, 13.2 mmol), and $Cr(CO)_6$ (1.45 g, 6.6 mmol) with **15a** (1.29 g, 6.0 mmol) and TMSCl (2.35 mL, 18.6 mmol) in THF (44 mL). M.p. 110 °C (decomp); R_f = 0.38 (Et_2O/PE/CH_3OH, 15:5:1); MS (70 eV, EI): *m*/*z* (%): 391 ($[M]^+$, 1.7), 376 ($[M-CH_3]^+$, 0.3), 363 ($[M-CO]^+$, 13.7), 335 ($[M-2CO]^+$, 2.7), 307 ($[M-3CO]^+$, 1.0), 279 ($[M-4CO]^+$, 24.1), 251 ($[M-5CO]^+$, 100), 94 ($[H_3CNH{=}C{=}Cr]^+$, 51.6); HR-MS: $C_{15}H_{17}{}^{52}CrNO_8$: calcd 391.0359; found 391.0365; IR (PE): $\tilde{\nu}$ = 2056, 1976, 1930 cm^{-1}; $[\alpha]_D$ = +81.5 (*c* = 0.404, Et_2O); $C_{15}H_{17}CrNO_8$ (391.29): calcd C 46.04, H 4.38, N 3.58; found C 46.03, H 4.39, N 3.40; ^{1}H NMR (500 MHz, CD_3OD): δ = 1.47 (s, 3H; CH_3), 1.48 (s, 3H; CH_3), 3.47 (s, 3H; OCH_3), 3.58 (dd, $^2J_{5/5'}$ = 13.71, $^3J_{5/4}$ = 2.48, 1H; H-5), 3.69 (pquin, 1H; H-4), 3.76 (dd, $^2J_{5/5}$ = 13.71, $^3J_{5'/4}$ = 6.65, 1H; H-5′), 3.93 (s, 3H; NCH_3), 4.39 (dd, $^3J_{3/2}$ = 7.55, $^3J_{3/4}$ = 3.27, 1H; H-3), 4.94 (d, $^3J_{2/3}$ = 7.55, 1H; H-2); ^{13}C NMR (125 MHz, CD_3OD): δ = 24.4, 26.1 (2C, CH_3), 53.5 (1C, NCH_3), 55.6 (1C, C-5), 58.2 (1C, OCH_3), 72.7 (1C, C-3), 72.9 (1C, C-4), 86.9 (1C, C-2), 110.1 (1C, Me_2C), 219.6 (4C, CO_{cis}), 225.4 (1C, CO_{trans}), 266.9 (1C, C-1).

Pentacarbonyl[4-*O*-benzyl-1,5-(benzylimino)-1,5-dideoxy-2,3-*O*-isopropylidene-D-*ribo*-pyranosylidene]chromium (**16b**): Compound **16b** (3.09 mmol, 1.68 g, 62%) was obtained as a sticky orange foam by reaction of graphite (1.05 g, 88.0 mmol), potassium (430 mg, 11.0 mmol), and $Cr(CO)_6$ (1.21 g, 5.5 mmol) with **15b** (1.83 g, 5.0 mmol) and TMSCl (1.95 mL, 15.5 mmol) in THF (35 mL), as described above for compound **3a**. R_f = 0.36 (Et_2O/PE/CH_3OH, 15:10:1); MS (70 eV, EI): *m*/*z* (%): 459 ($[M-3CO]^+$, 3.3), 431 ($[M-4CO]^+$, 0.8), 403 ($[M-5CO]^+$, 1.2), 388 (0.7), 345 ($[403-Me_2CO]$, 1.8), 312 ($[403-C_7H_7]$, 1.8), 293 ($[345-Me_2CO]$, 2.0), 276 (3.0), 170 ($[BnNH{=}C{=}Cr]^+$, 11.6), 91 ($[C_7H_7]^+$, 100); HR-MS: $C_{24}H_{25}{}^{52}CrNO_5$ (*M* − 3CO): calcd 459.1137; found 459.1136; IR (PE): 2056, 1977, 1934 cm^{-1}; ^{1}H NMR (500 MHz, CD_3COCD_3): δ = 1.46 (s, 3H; CH_3), 1.51 (s, 3H; CH_3), 3.40 (dd, $^2J_{5/5}$ = 14.27, $^3J_{5'/4}$ = 1.94, 1H; H-5′), 3.68 (dd, $^2J_{5/5'}$ = 14.27, $^3J_{5/4}$ = 5.31, 1H; H-5), 3.95 (m, 1H; H-4), 4.45 (dd, $^3J_{3/2}$ = 8.09, $^3J_{3/4}$ = 4.57, 1H; H-3), 4.46 (d, ^2J = 12.16, 1H; PhCH_2), 4.71 (d, ^2J = 12.16, 1H; PhCH_2), 5.07 (d, $^3J_{2/3}$ = 8.09, 1H; H-2), 5.53 (d, ^2J = 14.70, 1H; PhCH_2), 5.58 (d, ^2J = 14.70, 1H; PhCH_2), 7.23 – 7.33 (m, 8H; H-aryl), 7.39 – 7.42 (m, 2H; H-aryl); ^{13}C NMR (125 MHz, CD_3COCD_3): δ = 24.2, 26.0 (2C, CH_3), 54.2 (1C, C-5), 68.8 (1C, PhCH_2), 70.1 (1C, C-4), 72.4 (1C, PhCH_2), 72.9 (1C, C-3), 86.5 (1C, C-2), 109.5 (1C, Me_2C), 127.8, 128.1, 128.9, 129.0, 129.1, 129.5 (10C, aryl-C), 134.9, 139.5 (2C, C_{ipso}), 218.7 (4C, CO_{cis}), 224.9 (1C, CO_{trans}), 267.5 (1C, C-1).

General procedure for the photoinduced generation of the methyl 2,6-imino-D-allonates 10 and 17a,b: Carbene complex **9** or **16a**,**b** and methanol were loaded into a flame-dried Schlenk tube. The resulting solution (under argon) was irradiated with a 125 W high-pressure mercury lamp at 25 °C for five days. The solvent was evaporated and the residue was taken up in Et_2O/PE (1:1, 40 mL). Unconverted carbene complex and chromium precipitates were oxidized by vigorous stirring in air. After filtration of the solids and evaporation of the solvent, the crude product was purified by column chromatography.

Methyl 3,4-*O*-cyclohexylidene-2,6-dideoxy-5-*O*-methyl-2,6-(methylimino)-D-allonate (**10**): As in the general procedure above, compound **9** (164 mg, 0.38 mmol) was irradiated in solution in methanol (9 mL). After oxidation and chromatographic purification (eluent Et_2O/PE/CH_3OH, 15:5:1), **10** was obtained as a colorless syrup (0.14 mmol, 43 mg, 38%). R_f = 0.32 (Et_2O/PE/CH_3OH, 15:5:1); MS (70 eV, EI): *m*/*z* (%): 299 ($[M]^+$, 1.4), 240 ($[M-CO_2CH_3]^+$, 100), 208 ($[240-CH_3OH]$, 1.0), 184 (10.0), 152 (2.8), 142 (35.0), 126 (2.8), 114 (8.2), 82 (5.7), 71 (14.2); HR-MS: $C_{15}H_{25}NO_5$: calcd 299.1732; found 299.1741; IR (film): $\tilde{\nu}$ = 1743 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6): δ = 1.20 – 1.27 (m, 2H; C_6H_{10}), 1.54 – 1.59 (m, 4H; C_6H_{10}), 1.63 – 1.72 (m, 2H; C_6H_{10}), 1.83 – 1.93 (m, 2H; C_6H_{10}), 2.11 (s, 3H; NCH_3), 2.47 (pt, $^2J_{6/6'}$ = 10.83, $^3J_{6/5}$ = 10.83, 1H; H-6), 2.76 (dd, $^2J_{6'/6}$ = 10.83, $^3J_{6'/5}$ = 5.30, 1H; H-6′), 3.04 (d, $^3J_{2/3}$ = 8.54, 1H; H-2), 3.17 (s, 3H; OCH_3), 3.39 (s, 3H; CO_2CH_3), 3.58 (m, 1H; H-5), 4.27 (dd, $^3J_{4/3}$ = 4.57, $^3J_{4/5}$ = 3.87, 1H; H-4), 4.55 (dd, $^3J_{3/2}$ = 8.54, $^3J_{3/4}$ = 4.57, 1H; H-3); ^{13}C NMR (125 MHz, C_6D_6): δ = 23.9, 24.2, 25.2, 35.7, 38.3 (5C, C_6H_{10}), 43.2 (1C, NCH_3), 51.6 (1C, CO_2CH_3), 54.1 (1C, C-6), 55.9 (1C, OCH_3), 70.9 (1C, C-2), 71.9 (1C, C-4), 74.4 (1C, C-5), 76.2 (1C, C-3), 110.7 (1C, C_{spiro}), 172.0 (1C, C-1).

Methyl 2,6-dideoxy-3,4-*O*-isopropylidene-5-*O*-methyl-2,6-(methylimino)-D-allonate (**17a**): As in the general procedure above, compound **16a** (274 mg, 0.70 mmol) was irradiated in solution in methanol (12 mL). After oxidation and chromatographic purification (eluent Et_2O/PE/CH_3OH, 15:5:3), **17a** was obtained as a colorless syrup (0.49 mmol, 127 mg, 70%). R_f = 0.60 (Et_2O/PE/CH_3OH, 15:5:3); MS (70 eV, EI): *m*/*z* (%): 259 ($[M]^+$, 2.4), 244 ($[M-CH_3]^+$, 4.7), 200 ($[M-CO_2CH_3]^+$, 100), 184 ($[244-HCO_2CH_3]$, 6.4), 142 ($[200-Me_2CO]$, 37.8), 114 (10.0), 100 (10.0), 82 (7.1), 71 (21.4); HR-MS: $C_{12}H_{21}NO_5$: calcd 259.1419; found 259.1430; IR (film): $\tilde{\nu}$ = 1745 cm^{-1}; $[\alpha]_D$ = −7 (*c* = 0.064, Et_2O); $C_{12}H_{21}NO_5$ (259.30): calcd C 55.58, H 8.16, N 5.40; found C 55.59, H 8.14, N 5.40; ^{1}H NMR (500 MHz, C_6D_6): δ = 1.26 (s, 3H; CH_3), 1.56 (s, 3H; CH_3), 2.11 (s, 3H; NCH_3), 2.46 (pt, $^2J_{6/6'}$ = 10.72, $^3J_{6/5}$ = 10.72, 1H; H-6), 2.72 (dd, $^2J_{6'/6}$ = 10.72, $^3J_{6'/5}$ = 5.26, 1H; H-6′), 3.03 (d, $^3J_{2/3}$ = 8.44, 1H; H-2), 3.15 (s, 3H; OCH_3), 3.38 (s, 3H; CO_2CH_3), 3.49 (ddd, $^3J_{5/6}$ = 10.72, $^3J_{5/6'}$ = 5.26, $^3J_{5/4}$ = 3.87, 1H; H-5), 4.23 (dd, $^3J_{4/3}$ = 4.67, $^3J_{4/5}$ = 3.87, 1H; H-4), 4.51 (dd, $^3J_{3/2}$ = 8.44, $^3J_{3/4}$ = 4.67, 1H; H-3); ^{13}C NMR (125 MHz, C_6D_6): δ = 26.3, 28.3 (2C, CH_3), 43.3 (1C, NCH_3), 51.6 (1C, CO_2CH_3), 54.2 (1C, C-6), 55.9 (1C, OCH_3), 70.9 (1C, C-2), 72.2 (1C, C-4), 74.5 (1C, C-5), 76.8 (1C, C-3), 109.9 (1C, Me_2C), 172.5 (1C, C-1).

Methyl 5-*O*-benzyl-2,6-(benzylimino)-2,6-dideoxy-3,4-*O*-isopropylidene-D-allonate (**17b**): As in the general procedure above, compound **16b** (380 mg, 0.70 mmol) was irradiated in solution in methanol (12 mL). After oxidation and chromatographic purification (eluent Et_2O/PE/CH_3OH, 15:5:1) **17b** was first obtained as a colorless syrup (0.42 mmol, 170 mg, 59%). Then compound **15b** (56 mg) eluted as the product of oxidative degradation. R_f = 0.49 (Et_2O/PE/CH_3OH, 15:5:1); MS (70 eV, EI): *m*/*z* (%): 411 ($[M]^+$, 4.1), 396 ($[M-CH_3]^+$, 20.8), 352 ($[M-CO_2CH_3]^+$, 85.0), 305 ($[396-C_7H_7]$, 6.6), 294 ($[352-Me_2CO]$, 13.3), 91 ($[C_7H_7]^+$, 100); HR-MS: $C_{24}H_{29}NO_5$: calcd 411.2045; found 411.2048; IR (film): $\tilde{\nu}$ = 1742 cm^{-1}; $[\alpha]_D$ = +25.8 (*c* = 0.062, Et_2O); $C_{24}H_{29}NO_5$ (411.49): calcd C 70.05, H 7.10, N 3.40; found C 69.69, H 7.19, N 3.17; ^{1}H NMR (500 MHz, C_6D_6/TMS): δ = 1.22 (s, 3H; CH_3), 1.59 (s, 3H; CH_3), 2.51 (dd, $^2J_{6/6'}$ = 10.83, $^3J_{6/5}$ = 10.53, 1H; H-6), 2.95 (dd, $^2J_{6'/6}$ = 10.83, $^3J_{6'/5}$ = 5.26, 1H; H-6′), 3.14 (d, ^2J = 13.11, 1H; PhCH_2), 3.31 (s, 3H; OCH_3), 3.38 (d, $^3J_{2/3}$ = 7.85, 1H; H-2), 3.63 (ddd, $^3J_{5/6}$ = 10.53, $^3J_{5/6'}$ = 5.26, $^3J_{5/4}$ = 3.87, 1H; H-5), 3.76 (d, ^2J = 13.11, 1H; PhCH_2), 4.19 (d, ^2J = 11.82, 1H; PhCH_2), 4.25 (dd, $^3J_{4/3}$ = 4.87, $^3J_{4/5}$ = 3.87, 1H; H-4), 4.32 (d, ^2J = 11.82, 1H; PhCH_2), 4.53 (dd, $^3J_{3/2}$ = 7.85, $^3J_{3/4}$ = 4.87, 1H; H-3), 7.03 – 7.33 (m, 10H; H-aryl); ^{13}C NMR (125 MHz, C_6D_6/TMS): δ = 26.2, 28.3 (2C, CH_3), 50.1 (1C, C-6), 51.6 (1C, CO_2CH_3), 59.7 (1C, PhCH_2), 69.5 (1C, C-2), 70.7 (1C, PhCH_2), 73.0 (1C, C-5), 73.2 (1C, C-4), 77.0 (1C, C-3), 110.1 (1C, Me_2C), 127.5, 127.6, 128.3, 128.4, 128.5, 129.3 (10C, aryl-C), 138.4, 138.8 (2C, C_{ipso}), 172.7 (1C, C-1).

(6′-Deoxy-1′,2′:3′,4′-di-*O*-isopropylidene-α-D-galactopyranos-6′-yl)-2,6-dideoxy-3,4-*O*-isopropylidene-5-*O*-methyl-2,6-(methylimino)-D-allonate (**19**): A solution of **16a** (274 mg, 0.70 mmol) and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **18**[23] (200 mg, 0.77 mmol) in THF (6 mL) was irradiated for five days. Oxidative workup of the reaction residue in Et_2O/PE (1:1, 40 mL) in air and subsequent chromatographic purification (eluent Et_2O/PE/CH_3OH, 15:5:1) give first unconverted starting material **18** (127 mg), followed by the disaccharide **19** as a colorless syrup (0.18 mmol, 88 mg, 25%), and then the lactam **15a** (83 mg). R_f = 0.30 (Et_2O/PE/CH_3OH, 15:5:1); MS (70 eV, EI): *m*/*z* (%): 487 ($[M]^+$, 0.8), 472 ($[M-CH_3]^+$, 7.8), 414 ($[472-Me_2CO]$, 1.5), 245 (2.0), 200 (100), 142 ($[200-Me_2CO]$, 16.1); HR-MS: $C_{23}H_{37}NO_{10}$: calcd 487.2417; found 487.2414; $[\alpha]_D$ = −21.3 (*c* = 0.052, Et_2O); $C_{23}H_{37}NO_{10}$ (487.54): calcd C 56.66, H 7.65, N 2.87; found C 56.37, H 7.56, N 2.68; ^{1}H NMR (500 MHz, C_6D_6): δ = 1.02 (s, 3H; CH_{3gal}), 1.10 (s, 3H; CH_{3gal}), 1.24 (s, 3H; CH_{3all}), 1.39 (s, 3H; CH_{3gal}),

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1.45 (s, 3H; CH_{3gal}), 1.58 (s, 3H; CH_{3all}), 2.22 (s, 3H; NCH_3), 2.45 (pt, $^2J_{6/6a}=10.76$, $^3J_{6/5}=10.76$, 1H; H-6), 2.70 (dd, $^2J_{6a/6}=10.76$, $^3J_{6a/5}=5.28$, 1H; H-6a), 3.09 (d, $^3J_{2/3}=8.42$, 1H; H-2), 3.12 (s, 3H; OCH_3), 3.46 (ddd, $^3J_{5/6}=10.76$, $^3J_{5/6a}=5.28$, $^3J_{5/4}=3.92$, 1H; H-5), 3.84 (dd, $^3J_{4'/3'}=7.92$, $^3J_{4'/5'}=1.85$, 1H; H-4′), 4.11 (dd, $^3J_{2'/1'}=5.09$, $^3J_{2'/3'}=2.44$, 1H; H-2′), 4.19–4.22 (m, 2H; H-4, H-5′), 4.42 (dd, $^3J_{3'/4'}=7.92$, $^3J_{3'/2'}=2.44$, 1H; H-3′), 4.51 (dd, $^3J_{3/2}=8.42$, $^3J_{3/4}=4.70$, 1H; H-3), 4.53–4.56 (m, 2H; H-6′, H-6a′), 5.44 (d, $^3J_{1'/2'}=5.09$, 1H; H-1′); ^{13}C NMR (125 MHz, C_6D_6): $\delta=24.2$ (1C, CH_{3gal}), 24.8 (1C, CH_{3gal}), 26.0 (1C, CH_{3all}), 26.1 (1C, CH_{3gal}), 26.3 (1C, CH_{3gal}), 28.3 (1C, CH_{3all}), 43.4 (1C, NCH_3), 54.2 (1C, C-6), 55.9 (1C, OCH_3), 64.4 (1C, C-6′), 66.6 (1C, C-4/5′), 70.7 (1C, C-2′), 70.9 (1C, C-2), 71.1 (1C, C-3′), 71.3 (1C, C-4′), 72.4 (1C, C-4/5′), 74.6 (1C, C-5), 76.8 (1C, C-3), 96.6 (1C, C-1′), 108.4 (1C, Me_2C_{gal}), 109.4 (1C, Me_2C_{gal}), 109.9 (1C, Me_2C_{all}), 172.0 (1C, C-1).

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