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Synthesis and reactivity of *N*-sugar-maleimides: an access to novel highly substituted enantiopure pyrazolines

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ABSTRACT

Two diastereomeric isoxazolines were synthesized in a stereoselective manner with 6.64–20.36% *diastereoisomeric excess*. The cycloaddition of *N*-sugar-maleimide in the presence of $MgBr_2$ afforded isoxazolines with high *diasterioselectivities* (76–84% de). The 1,3-dipolar cycloaddition reaction was diastereospecific and enantiomerically pure (3*R*,4*S*,5*S*,6*S*,3a*R*,6a*S*)-pyrazolines were obtained from *N*-sugar-maleimides via 1,3-proton migration.

1. Introduction

It is known that oligosaccharides in glycoconjugates, such as glycoproteins and glycolipids, play important roles in many biological processes and consequently their biological functions have been investigated extensively by chemists, biochemists, and biologists.[1,2] Carbohydrates have been widely used as chiral templates for introducing chirality in synthetic asymmetric processes due to their rigid structure with a high degree of functionalization, and the presence of several contiguous stereogenic centers.[3,4] Due to the remarkable biological relevance of carbohydrates, the synthesis of oligosaccharides or carbohydrate derivatives has long been the goal pursued by researchers in different areas. 1,3-Dipolar cycloaddition reactions, involving heterocyclic rings, have been largely studied as a useful synthetic strategy to obtain various heterocyclic systems.[5–7]

Since Lewis acids are a powerful tool in organic synthesis, one of today's challenges in the field of 1,3-dipolar cycloadditions is Lewis acid-induced control of the regio- and stereoselectivity in these reactions.[8] The Lewis acid-catalyzed reaction of nitrile oxide cycloadditions is an important research area.[9] As part of our continuing interest in the chemistry of highly substituted heterocycles, we herein report the synthesis of optically active pyrazolines from *N*-sugar-maleimides containing five stereogenic centers.

2. Results and discussion

The synthesis of the 6-amino derivatives of galactose has been widely investigated.[10–12] Sugar **1** was converted into the corresponding azido-sugar **2** by substitution of the hydroxyl group with azide under biphasic conditions. The reduction of azide **2** was successfully accomplished in quantitative yield with Pd/C and H_2. The reaction of the resultant glycosylamine with maleic anhydride in EtOH afforded amic acid in high yields. Cyclization of amic acid **4** with 4-dimethylaminopyridine (DMAP) in the presence of *N*,*N*′-*dicyclohexylcarbodiimide* (DCC) gave the desired product **5** (Method A).

The primary alcohol **1** was converted into maleimidosugar **5** in 89% yield by a Mitsunobu reaction[13] (Method B) with maleimide in the presence of Ph_3P and diethyl azodicarboxylate (DEAD) (Scheme 1).

The reaction of maleimidosugar **5** with aromatic nitrile oxide **6** at 110 °C in toluene, without the preference of metal ions, gave a mixture of inseparable diastereomeric cycloadducts. The mixture of [(3*R*,4*S*,5*S*,6*S*,3a*S*,6a*R*)-**7**/(3*R*,4*S*,5*S*,6*S*,3a*R*,6a*S*)-**8**] was chromatographed on silica gel. The ratio of the two NMR peaks for H1 at 5.5 ppm was approximately 50:50. These results confirmed that the two diastereomers were responsible for signal doubling (Table 1).

The diastereomeric ratios for all of the results shown in Table 1 were established from the ^1H NMR integration of the crude materials of the isoxazolines as shown in Figure 1.

In general, maleimidosugar **5** (Table 1, entries 1–12) produced isoxazoline products with good yields (80–95%) but with low diastereoisomeric excess, that is, [(3*R*,4*S*,5*S*,6*S*,3a*S*,6a*R*)-**7**/(3*R*,4*S*,5*S*,6*S*,3a*R*,6a*S*)-**8**] (6.64–20.36%). From the experimental results, there was no obvious relationship between the electron density of the Ar group of the nitrile oxides and the yields of the corresponding isoxazoline products. Finally, the stereochemistry of the isoxazoline products was established and assigned by a NOESY spectrum. The *cis*-relationship between the H1 and H3a protons in the minor diastereoisomers **7** was deduced from the presence of an NOE effect as shown in Figure 2. The irradiation of H-3a in the minor diastereoisomer **7** showed a positive NOE for H-1.

Lewis acids were successfully employed as catalysts for the 1,3-dipolar cycloaddition reactions between aromatic nitrile oxides and maleimidosugar **5**. While the reactions proceeded in the pres-

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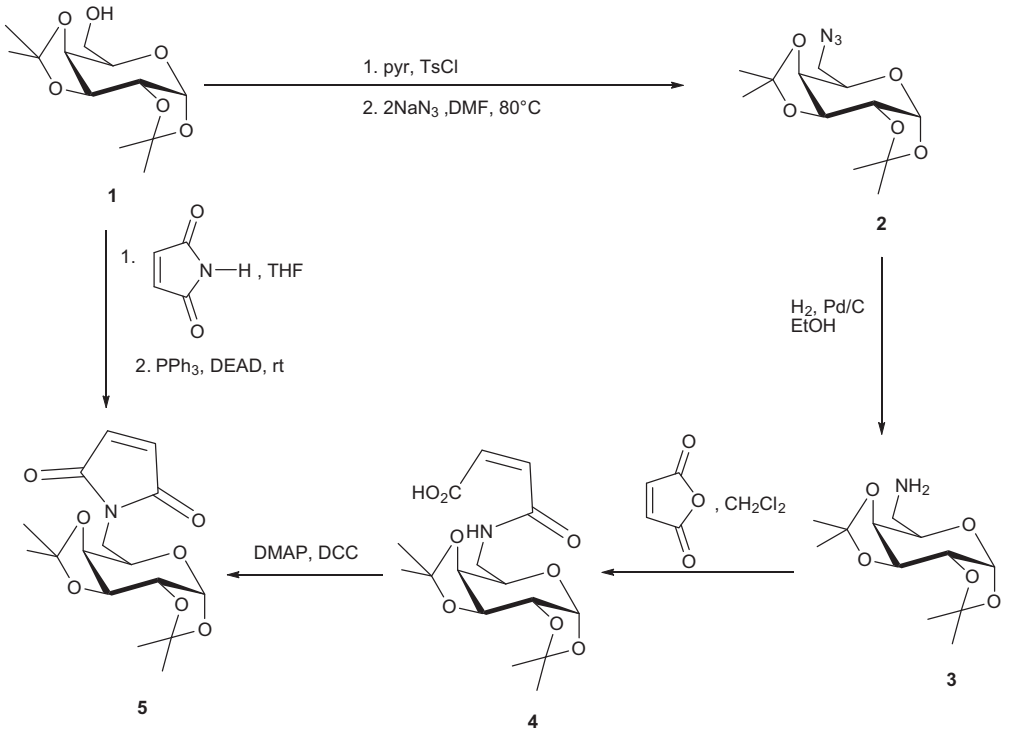
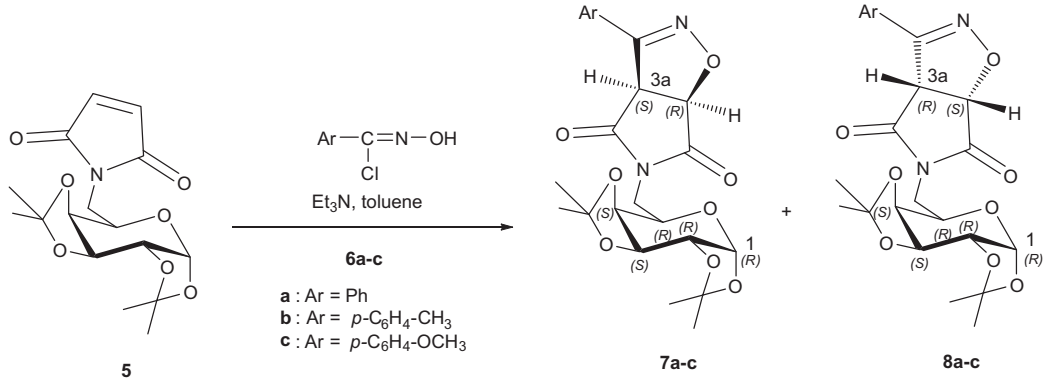


Scheme 1.

Table 1
Effect of metal ion, molar concentration of nitrile oxides with **5**



Entries 7:8[a]	Ar	Additive (equiv)	Yield[b] (%)	Diastereomeric ratio
1	Ph	None	80	44:56
3	*p*-C_6H_4-CH_3	None	85	46:54
5	*p*-C_6H_4-OCH_3	None	85	40:60
7	Ph	$MgBr_2$ (0.5 equiv)	80	40:60
8	Ph	$MgBr_2$ (1 equiv)	90	35:65
9	Ph	$ZnCl_2$ (1 equiv)	85	10:90
10	*p*-C_6H_4-CH_3	$MgBr_2$ (1 equiv)	85	12:88
12	*p*-C_6H_4-OCH_3	$MgBr_2$ (1 equiv)	95	8:92

[a] Determined by integrations of H1 signal in the ^1H proton NMR spectra as discussed in the text.
[b] Combined yield.

ence of a Lewis acid (0.5 equiv), the diastereoselectivities of the reactions did not improve. Increase of the amount of $MgBr_2$ from 0.5 equiv to 1 equiv augmented diastereoselectivity (80–95% yields with [(3*R*,4*S*,5*S*,6*S*,3a*S*,6a*R*)-**7**/(3*R*,4*S*,5*S*,6*S*,3a*R*,6a*S*)-**8**] 40:60 to 8:92; Table 1, entry 12). We also examined the effect of the electronic nature of the benzonitrile oxides. As can be seen in Table 1 (entry 3), the nitrile oxides with a methoxy electron-donating substituent showed higher diastereoselectivities (see Table 2).

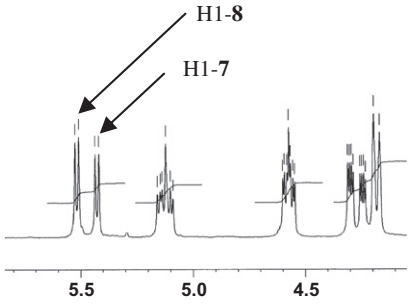


Figure 1. 4–6 ppm enlargement of the ^{1}H NMR spectrum of isoxazolines **7a** and **8a** in $CDCl_3$.

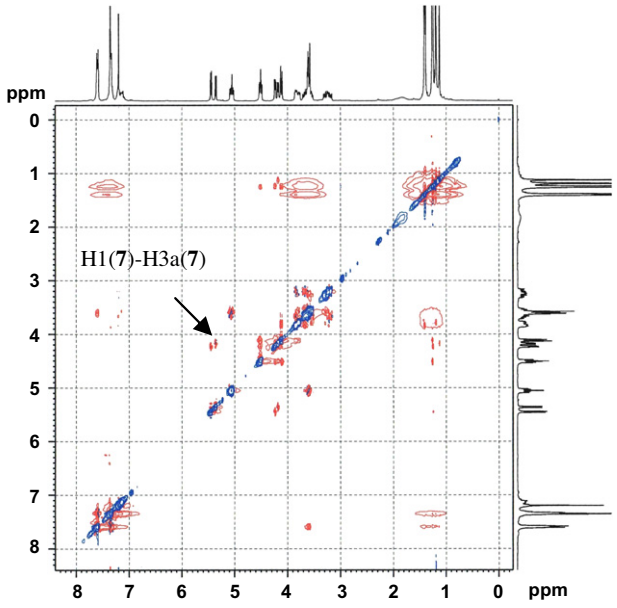


Figure 2. NOESY spectrum of isoxazolines **7a** and **8a** in $CDCl_3$.

The 1,3-dipolar cycloaddition reaction of excess diazoalkanes **9** with sugar **4** at 0 °C led first to the unstable pyrazoline intermediate **10** which then underwent a prototropic shift to yield pyrazolines **11**. Microanalysis and FAB mass spectrometry indicated that **11** was the result of the addition of two diazoalkane equivalents. In this case, alkylation of the carboxylic acids was carried out using diazoalkanes (Scheme 2).[14]

The structure elucidation for stereoisomers **11a** and **11b** was achieved in part with the aid of 1D NOE and 2D NMR techniques (NOESY). In 1D NOE experiments with a $CDCl_3$ solution of **11a**, the selective irradiation of 4′-H showed a positive NOE for 4-H and 5-H. For instance, adduct **11a** displayed cross-peaks between signal at 3.83 (4′-H) and 3.15 ppm (5-H) in the two-dimensional NOESY ^{1}H NMR spectrum. This observation clearly indicated that the 4′-H and 3-H protons attached to the pyrazoline ring pointed in opposite directions. From the data collected, we were able to establish the configuration at C-4′ as (*S*) for the cycloadducts considered.

3. Conclusion

Our studies have shown that $MgBr_2$ catalysts are extremely effective in affording high levels of asymmetric induction (up to 84% de) for 1,3-dipolar cycloaddition reactions between nitrile oxides and *N*-sugar-maleimides. This synthesis allows us to obtain one diastereoisomer of enantiomerically pure pyrazolines with six stereogenic centers.

4. Experimental section

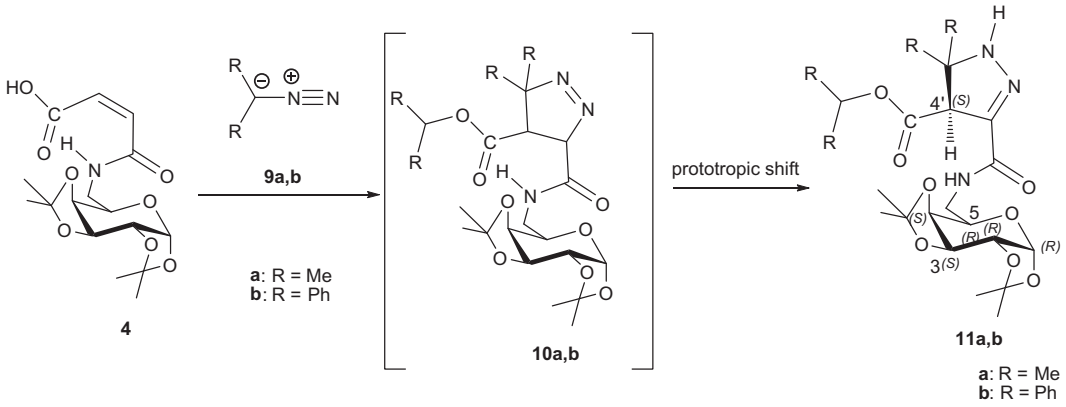
Caution: Diazoalkanes are toxic and should be used in an efficient fume hood.

4.1. General

Chemicals were of reagent-grade, purchased from commercial suppliers, and used without further purification. CH_2Cl_2 and toluene used in reactions were prepared by distillation over a drying

Table 2
The characteristic peaks in the 300 MHz ^{1}H NMR spectra ($CDCl_3$) of **7** and **8**

	Ar	^{1}H NMR ($CDCl_3$) δ
7a	Ph	1.15(CH_3); 1.19(CH_3); 1.45(CH_3); 1.47(CH_3); 5.42 (H1)
7b	*p*-CH_3-C_6H_4	1.17(CH_3); 1.22(CH_3); 1.31(CH_3); 1.46(CH_3); 2.38(CH_3); 5.33 (H1)
7c	*p*-CH_3O-C_6H_4	1.29(CH_3); 1.30(CH_3); 1.43(CH_3); 1.46(CH_3); 3.89(OCH_3); 5.35 (H1)
8a	Ph	1.31(CH_3); 1.32(CH_3); 1.33(CH_3); 1.46(CH_3); 5.51(H1)
8b	*p*-CH_3-C_6H_4	1.30(CH_3); 1.33(CH_3); 1.48(CH_3); 1.51(CH_3); 2.39(CH_3); 5.35 (H1)
8c	*p*-CH_3O-C_6H_4	1.23(CH_3); 1.37(CH_3); 1.47(CH_3); 1.48(CH_3); 3.88(OCH_3); 5.34 (H1)



Scheme 2.

agent (CH_2Cl_2:CaH_2; toluene:Na). TLC analysis was performed on Merck Kieselgel 60 F254 plates. Flash chromatography was performed using silica gel Merck 60 (particle size 0.040–0.063 mm). All anhydrous reactions were performed under nitrogen using anhydrous solvents. NMR spectra were obtained on a Bruker AC 300 spectrometer operating at 300 MHz for ^1H and at 75.64 MHz for ^{13}C. Melting points were determined on a Buchi-510 capillary melting point apparatus. Chemical shifts are given in parts per million relative to tetramethylsilane (TMS) and the coupling constants *J* are given in Hertz. The spectra were recorded in $CDCl_3$ as solvent at room temperature. Elemental analysis was recorded on a PERKIN–ELMER 240B microanalyzer. Mass spectra were recorded on a Finnigan LCQ DECA XP plus.

4.2. Synthesis of sugar 4 and maleimidosugar 5

Method A: To a solution of sugar **1** (177 mg, 0.68 mmol) in dry pyridine (2 mL) was added *p*-toluenesulfonyl chloride (142 mg, 0.75 mmol) and the reaction mixture was stirred at room temperature for 10 h. The solvent was then removed in vacuo, after which EtOAc was added and washed successively with 1 M HCl and satd aq $NaHCO_3$. The organic phase was dried (Na_2SO_4) and concentrated in vacuo. The crude product was dissolved in DMF (2 mL) and sodium azide (110 mg, 1.7 mmol) was added. The reaction mixture was stirred at 50 °C for 10 h after which H_2O was added and the aqueous phase was extracted with EtOAc. The organic phase was dried over $MgSO_4$, concentrated in vacuo, and purified by column chromatography over silica gel using petroleum ether–EtOAc (v/v = 7/3) as the eluent. A mixture of azido-sugar **2** (200 mg, 0.7 mmol) and 5% palladium–carbon (82 mg) in EtOH (10 mL) was hydrogenated under an atmospheric pressure of hydrogen using a balloon with vigorous stirring for 6 h. The mixture was filtered through Celite, and the solvent removed in vacuo to give the title compound in quantitative yield as a colorless solid.

Amino-sugar **3** (300 mg, 1.16 mmol) was dissolved in CH_2Cl_2 (25 mL) to which maleic anhydride (114 mg, 1 mmol) was added. TLC control showed a quantitative reaction after which the product was not purified further. Compound **4** (350 mg, 98%) was obtained as a white solid. A solution of compound **4** (392 mg, 1.1 mmol), DCC (223.4 mg, 1.1 mmol), and DMAP (11.1 mg, 91 μmol) in dichloromethane was stirred at room temperature for 2 h and then heated at 40 °C for a further 1 h. The crude reaction mixture was filtered and the solvent removed in vacuo. The crude material was purified by flash column chromatography using ethyl acetate/hexanes as eluant to afford maleimidosugar **5** as a white solid (228 mg, 70%).

Method B: Maleimide (1.0 mmol, 97 mg) was added to a solution of alcohol **1** (1.1 mmol, 260 mg) and phosphine reagent (1.1 mmol, 262 mg) in anhydrous CH_2Cl_2 under an N_2 atmosphere at 0 °C. The resulting suspension/solution was treated with diethyl azodicarboxylate (1.1 mmol, 174 mg) and the reaction mixture was then continued to stir at room temperature up until completion of the reaction, as indicated by TLC monitoring (the reaction mixture was filtered to recover the reduced diethyl azodicarboxylate). The solvent was then evaporated and the residue dissolved in cyclohexane. The triphenylphosphane oxide precipitated and then filtered off after which the filtrate was evaporated under reduced pressure. The product was purified by column chromatography on silica gel to afford the pure products (302 mg, 89%).

4.2.1. (*Z*)-4-Oxo-4-(((3*R*,4*S*,5*S*,6*S*)-1,2;3,4-di-*O*-isopropylidene-tetrahydro-2*H*-pyran-2-yl)methylamino)but-2-enoic acid 4

White solid. Mp = 141–143 °C. $[\alpha]_D^{22} = +86$ (*c* 1, CH_2Cl_2), R_f = 0.35 (hexane/AcOEt 3:1). ^1H NMR (300 MHz, $CDCl_3$) δ 15.66 (br s, 1H, CO_2H), 6.87 (br s, 1H, NH), 6.42 (d, J_{Heth} = 13.1, 1H, Heth), 6.26 (d, J_{Heth} = 13.1, 1H, Heth), 5.51 (d, $J_{H1\text{-}2}$ = 4.9, 1H, H1), 4.63 (dd, $J_{H3\text{-}4}$ = 3.9, $J_{H3\text{-}2}$ = 2.0, 1H, H3), 4.46 (dd, $J_{H2\text{-}3}$ = 2.0, $J_{H2\text{-}1}$ = 3.9, 1H, H2), 4.26 (d, $J_{H6\text{-}5}$ = 8.3, 1H, H6), 3.97 (d, $J_{H6'\text{-}5}$ = 8.3, 1H, H6′), 3.88–3.79 (m, 1H, H4), 3.34–3.22 (m, 1H, H5), 1.50, 1.47, 1.36, 1.34 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.20, 164.57, 137.07, 130.38, 109.79, 109.09, 96.31, 71.81, 70.83, 70.49, 65.42, 41.15, 26.06, 25.98, 24.92, 24.28, HRMS Calcd for $C_{16}H_{23}NO_8$ 357.1424. Found: 357.1421; IR (KBr) ν_{max}/cm^{-1} 3350, 2956, 1720, 1725 cm^{-1}; Anal. Calcd for $C_{16}H_{23}NO_8$: C, 53.78, H, 6.49, N, 3.92. Found: C, 53.75, H, 6.41, N, 3.89.

4.2.2. 1-(6′-Deoxy-1′,2′:3′,4′-di-*O*-isopropylidene-α-D-glucopyranos-6′-yl)-1*H*-pyrrole-2,5-dione 5

Yield (228 mg, 70%), white solid. Mp = 132–134 °C. $[\alpha]_D^{22} = +24$ (*c* 1, CH_2Cl_2), R_f = 0.4 (hexane/AcOEt 3:1). ^1H NMR (300 MHz, $CDCl_3$) δ 6.42 (s, 2H, H2,4), 6.11 (d, $J_{H1'\text{-}2'}$ = 3.6, 1H, H1′), 5.62 (dd, $J_{H3'\text{-}4'}$ = 3.7, $J_{H3'\text{-}2'}$ = 2.3, 1H, H3′), 5.21–5.10 (m, 2H, H2′,4′), 4.45–4.38 (m, 1H, H5′), 4.20–4.15 (m, 1H, H6′), 4.02–3.90 (m, 1H, H6′), 2.02, 1.98, 1.97, 1.87 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.69, 132.67, 109.52, 108.89, 96.08, 70.45, 70.36, 70.28, 68.22, 65.83, 25.95, 25.79, 24.89, 24.31, HRMS Calcd for $C_{16}H_{21}NO_7$ 339.1318. Found: 339.1323; IR (KBr) ν_{max}/cm^{-1} 2954, 1710, 1715 cm^{-1}; Anal. Calcd for $C_{16}H_{21}NO_7$: C, 56.63, H, 6.24, N, 4.13. Found: C, 56.60, H, 6.27, N, 4.11.

4.2.3. 1,3-Dipolar cycloaddition of nitrile oxides with maleimidosugar 5

A solution of maleimidosugar **5** (1 mmol, 326 mg) and chloroximes **6** (1.2 mmol) in toluene (10 mL) was stirred at 110 °C. To this solution trimethylamine (0.2 mL), dissolved in toluene (10 mL), was added dropwise. The precipitated triethylammonium chloride was removed by filtration and the filtrate was concentrated in vacuo, which was then submitted to chromatography (SiO_2; ethyl acetate/petroleum ether, 2:1) to afford compounds **7** and **8**.

4.3. Procedure for trapping 2-diazopropane 9a with sugar 4

To a solution of sugar **4** (1.0 mmol, 357 mg) in CH_2Cl_2, cooled at 20 °C was added portionwise a 2.6 M ether solution of diazopropane. The reaction was kept at the same temperature for 2 h after which the solvent was removed in vacuo without heating to give a brown oil, which was subjected to flash column chromatography (SiO_2; ethyl acetate/petroleum ether, 3:1) to afford compounds **11**.

4.3.1. 5,5-Dimethyl-3-[(2,2,7,7-tetramethyl-tetrahydro-bis[1,3]-dioxolo[4,5-*b*;4′,5′-*d*]pyran-5-ylmethyl)-carbamoyl]-4,5-dihydro-1*H*-pyrazole-4-carboxylic acid isopropyl ester 11a

Yield (375.4 mg, 83%), white solid. Mp = 189–191 °C. $[\alpha]_D^{22} = +45$ (*c* 1, CH_2Cl_2), R_f = 0.5 (hexane/AcOEt 3:1). ^1H NMR (300 MHz, $CDCl_3$) δ 5.99 (br s, 1H, NH), 5.39 (d, $J_{H1\text{-}2}$ = 5.1, 1H, H1), 4.99–5.07 (h, $J_{HCH3\text{-}Hiso}$ = 6.0, 1H, H_{iso}), 4.02 (d, $J_{H3\text{-}2}$ = 6.9, 1H, H3), 4.18–4.20 (dd, $J_{H3\text{-}2}$ = 1.2, 3.9, 1H, H2), 4.10–4.06 (t, $J_{H3\text{-}2}$ = 6.3, 1H, H4), 3.83–3.60 (m, 2H, H6′,H4′), 3.37 (d, *J* = 13.2, 1H, H6), 3.15–3.05 (m, 1H, H5), 1.58 1.46 1.44 1.41 1.37 1.29 1.22 1.19 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.99, 167.80, 162.19, 109.77, 109.11, 109.04, 72.00, 71.97, 71.13, 70.74, 69.25, 68.33, 61.18, 40.46, 26.33, 25.29, 24.66, 23.16, 23.01, 22.73, 22.29, 22.18, HRMS Calcd for $C_{22}H_{35}N_3O_8$ 469.2424. Found: 469.2412; IR (KBr) ν_{max}/cm^{-1} 3315, 2927, 1733, 1728, 1640 cm^{-1}; Anal. Calcd for $C_{22}H_{35}N_3O_8$: C, 56.28, H, 7.51, N, 8.95. Found: C, 56.21, H, 7.54, N, 8.92.

4.4. Procedure for trapping diphenyldiazomethane 9b with sugar 4

To a solution of **4** (1 mmol, 357) in ethyl acetate (20 mL), diphenyldiazomethane (6 mmol, 1.17 g) was added and the resulting

solution was heated under an argon atmosphere at 40 °C for 2 h, after which time the mixture was cooled to ambient temperature and concentrated under reduced pressure. Pyrazoline **11b** was crystallized from ethanol.

4.4.1. 5,5-Diphenyl-3-[(2,2,7,7-tetramethyl-tetrahydro-bis[1,3]-dioxolo[4,5-*b*;4′,5′-*d*]pyran-5-ylmethyl)-carbamoyl]-4,5-dihydro-1*H*-pyrazole-4-carboxylic acid benzhydryl ester 11b

Yield (516.5 mg, 72%), white solid. Mp = 165–167 °C. $[\alpha]_D^{22} = +34$ (*c* 1, CH_2Cl_2), $R_f = 0.45$ (hexane/AcOEt 3:1). ^1H NMR (300 MHz, $CDCl_3$) δ 6.72–7.74 (m, 10H, H arom), 6.01 (br s, 1H, NH), 5.41 (d, $J_{H1\text{-}2} = 5.2$, 1H, H1), 4.95–5.02 (h, $J_{HCH3\text{-}Hiso} = 6.0$, 1H, H_{iso}), 4.06 (d, $J_{H3\text{-}2} = 6.7$, 1H, H3), 4.15–4.22 (dd, $J_{H3\text{-}2} = 1.3$, 3.7, 1H, H2), 4.11–4.09 (t, $J_{H3\text{-}2} = 6.3$, 1H, H4), 3.84–3.61 (m, 2H, H6′,H4′), 3.39 (d, $J = 13.1$, 1H, H6), 3.14–3.05 (m, 1H, H5), 1.40, 1.37, 1.28, 1.23 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.76, 166.97, 162.20, 140.10, 139.5, 139.4, 138.97, 129.2, 128.94, 128.87, 128.21, 127.43, 127.22, 126.94, 126.91, 126.21, 125.67, 125.23, 109.76, 109.14, 109.09, 72.01, 71.94, 71.16, 70.70, 69.22, 62.31, 56.19, 44.41, 25.28, 24.65, 23.00, 21.93, HRMS Calcd for $C_{42}H_{43}N_3O_8$ 717.3050. Found: 717.3053; IR (KBr) ν_{max}/cm^{-1} 3310, 2929, 1730, 1725, 1638 cm^{-1}; Anal. Calcd for $C_{42}H_{43}N_3O_8$: C, 70.28, H, 6.04, N, 5.85. Found: C, 70.26, H, 6.07, N, 5.79.

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