Carbohydrate Research, 109 (1982) 143–160
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

SYNTHETIC STUDIES ON GLYCOCINNAMOYLSPERMIDINES. SYNTHESIS OF A KEY INTERMEDIATE OF THE DIAMINOHEXOSE MOIETY: ETHYL *p*-[4-AMINO-2-(*tert*-BUTOXYCARBONYL)AMINO-2,4,6-TRIDEOXY-α-D-GLUCOPYRANOSYLOXY]CINNAMATE*†

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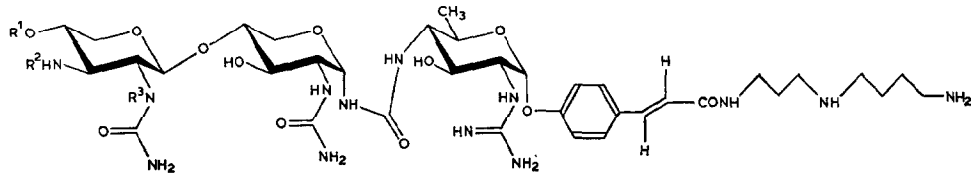
(Received March 12th, 1982; accepted for publication, June 18th, 1982)

ABSTRACT

A key synthetic intermediate for the diaminohexosyloxycinnamate moiety of glycocinnamoylspermidines was synthesized from D-galactose by two routes, via 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-D-galactopyranosyl nitrate (**20**) and via 1,6-anhydro-2-azido-2-deoxy-β-D-galactopyranose (**12**), in 16 and 22 steps, respectively.

INTRODUCTION

Glycocinnamoylspermidines, LL-BM 123β (**1**), γ_1 (**2**), and γ_2 (**3**), produced by an unidentified species of *Nocardia*, are new broad-spectrum antibiotics. The γ_1 and γ_2 components are of special interest because of their broad-spectrum activity against Gram-negative microorganisms and their protective effect against infections in mice[2]. An improvement of the activity by chemical modification has also been reported[3a]. The structures of these antibiotics were elucidated recently, mainly by X-ray analysis of degradation products, and by ^{1}H- and ^{13}C-n.m.r. spectroscopy[3b].



1 $R^1 = R^2 = R^3 = H$
2 $R^1, R^2 = CO, R^3 = H$
3 $R^1 = H, R^2, R^3 = CO$

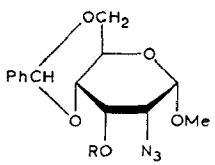
*Dedicated to Professor Sumio Umezawa on the occasion of his 73rd birthday and the 25th anniversary of the Microbial Chemistry Research Foundation.
†Amino sugars Part XXXV. For a preliminary report, see ref. 1a, for Part XXXIV, see ref. 1b.
**To whom correspondence should be addressed.

Unusual structural features of these antibiotics are summarized by the following aspects: (*a*) a new type of interglycosidic linkage, namely, α-ureido; (*b*) the *p*-hydroxycinnamoylspermidine aglycon; (*c*) diamino sugars, namely, 2,4-diamino-2,4,6-trideoxy-D-glucose (bacillosamine) and 2,3-diamino-2,3-dideoxy-D-xylose: the former is known as a component of bacterial polysaccharides[4] and the latter occurs[5] as the methyl ether in seldomycin factor 5; and (*d*) a variety of substitution modes (carbamoyl and amidino) on the amino groups. These characteristics, and interest in defining the structural unit necessary for activity, prompted us to attempt total synthesis of these antibiotics. In this paper, we report syntheses of ethyl *p*-[4-amino-2-(*tert*-butoxycarbonyl)amino-2,4,6-trideoxy-α-D-glucopyranosyl]oxycinnamate (**55**), a key intermediate for the diaminohexose moiety of glycocinnamoylspermidines.

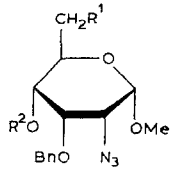
RESULTS AND DISCUSSION

In order to effect α-glycosylation with *p*-hydroxycinnamate, the use of 2-azido sugars seemed feasible. D-Glucosamine was used for the synthesis of 2,4-diacetamido-2,4,6-trideoxy-D-glucose by Liav *et al.*[6]. This route requires conversion of an amino into an azido group. Although this conversion could be effected with some model amino sugar derivatives by use of butyllithium and *p*-toluenesulfonyl azide in benzene[7], the yield was lower than required for such an early stage in the total synthesis*.

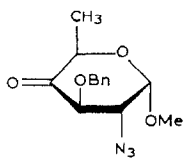
On the other hand, methyl 2-azido-4,6-*O*-benzylidene-2-deoxy-D-allopyranoside (**4**) may be obtained from D-glucose in 7 steps[8]. To explore the conversion of **4** into a 2-azido-2-deoxy-D-galactose derivative, **4** was benzylated with sodium hydride and benzyl chloride in *N*,*N*-dimethylformamide (DMF) to give its 3-benzyl ether (**5**) in 94% yield. The debenzylidenated analog (**6**) was tosylated selectively with *p*-toluenesulfonyl chloride and 4-(dimethylamino)pyridine in dichloromethane-DMF to give the 6-ester (**7**) in 67% yield, together with the 4,6-diester **8** (12%).



4 R = H
5 R = Bn



6 R^1 = OH, R^2 = H
7 R^1 = OTs, R^2 = H
8 R^1 = OTs, R^2 = Ts
9 R^1 = R^2 = H



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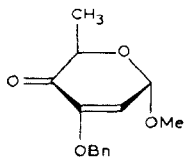

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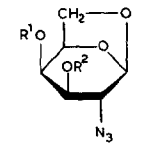
*Methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-α-D-altro- and -α-D-allopyranosides were treated with butyllithium and *p*-toluenesulfonyl azide in benzene, to give the corresponding 2-azido derivatives in 21 and 45% yield, respectively. The results will be reported elsewhere.

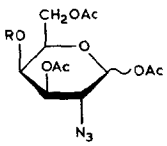
Treatment of **7** with sodium iodide and sodium cyanoborohydride in hexamethylphosphoramide[9] (HMPA) gave the 6-deoxygenated derivative (**9**) in 81% yield. An attempt to convert **9** into the corresponding D-*galacto* isomer by inversion of configuration at C-3 and C-4 failed at the next step. Very mild oxidation of **9** with dimethyl sulfoxide and trifluoroacetic anhydride in dichloromethane gave the enolone derivative (**11**), rather than the desired glycos-4-ulose (**10**).

D-Galactose was therefore selected as the starting hexose. The following sequence of operations for conversion of D-galactose into **55** was chosen: (1) introduction of the 2-amino(azido) group, (2) α-glycosylation with *p*-hydroxycinnamate, (3) 6-deoxygenation, and (4) introduction of the 4-amino(azido) group. The last two steps were initially thought to be interchangeable. We considered conducting operation (3) first, but abandoned this route because of the low yield and difficult preparation of D-fucal acetate, an intermediate for the 2-azido-2,6-dideoxy-D-galactose derivative.

The first synthetic operation may be effected by azidolysis of 1,6:2,3-dianhydro-β-D-talopyranose or by azidonitration of D-galactal triacetate. By the former method, Paulsen *et al.*[10] synthesized 1,6-anhydro-2-azido-2-deoxy-β-D-galactopyranose (**12**),



12 $R^1 = R^2 = H$
13 $R^1 = Ts, R^2 = H$
14 $R^1 = Ts, R^2 = Ac$
15 $R^1 = R^2 = Ts$



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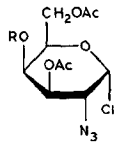
17 R = Ac



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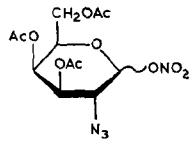
19 R = Ac



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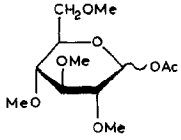

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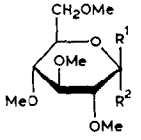
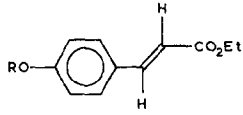
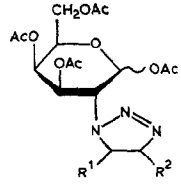


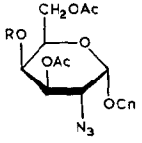
22 $R^1 = H, R^2 = Cl$
23 $R^1 = H, R^2 = OCn$
24 $R^1 = OCn, R^2 = H$



25 R = H(HOCn)
26 R = Na
27 R = Me_3Si



28 $R^1 = p\text{-}HOC_6H_4$, $R^2 = CO_2Et$
29 $R^1 = CO_2Et$, $R^2 = p\text{-}HOC_6H_4$



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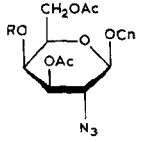
31 R = Ac



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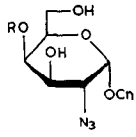
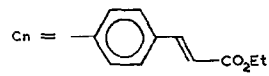
33 R = Ac



34 R = H
35 R = Ts



which has an advantage for our synthesis in that the equatorial hydroxyl group at C-4 may be expected to undergo substitution selectively. The latter method, reported recently by Lemieux and Ratcliffe[11], provides 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl nitrate (**20**) in fewer steps. Both routes were examined comparatively. The 1-acetates (**16** and **17**) and 1-chlorides (**18** and **19**) were first prepared as glycosylating agents. Selective tosylation of **12** gave, in 68% yield, the 4-ester (**13**), which was further characterized as its 3-acetate (**14**), together with the 3,4-diester (**15**) in 6% yield. Acetolysis of **13** gave the 1,3,6-triacetate (**16**) in 95% yield, which was converted into the α-glycosyl chloride (**18**) with titanium tetrachloride in dichloromethane. Similarly, the corresponding 1-acetate (**17**) and 1-chloride (**19**) could be obtained as reported from **20**. The latter was also prepared in 96% yield by treatment of **17** with titanium tetrachloride.

In order to examine the formation of an aryl glycoside having no neighbouring participating group at C-2, 2,3,4,6-tetra-*O*-methyl-α-D-glucopyranosyl acetate (**21**) and chloride (**22**), were coupled with ethyl *p*-hydroxycinnamate (**25**) under several typical sets of conditions[12-14]. The results are summarized in Table I.

TABLE I

GLUCOSYLATION OF ETHYL *p*-HYDROXYCINNAMATE WITH 2,3,4,6-TETRA-*O*-METHYL-α-D-GLUCOPYRANOSYL ACETATE (**21**) OR CHLORIDE (**22**)

Methods	*Coupling partners*		*Reaction conditions*[a]	*Yields of products (%)*	
	Sugars	*Phenols*		*α-glucoside* (**23**)	*β-glucoside* (**24**)
A[12,13]	**21**	**25**	$ZnCl_2$, *in vacuo*, 30 min, 110–120°	53	21
B[13]	**22**	**25**	$CdCO_3$–toluene 3 h, reflux	26	23
C[12,13]	**22**	**25**	$AgClO_4$–Ag_2CO_3–CH_2Cl_2, 24 h, r.t.	27	19
D[13,14]	**22**	**26**	HMPA, 12 h, r.t.	7	68

[a]R.t. = room temperature.

TABLE II

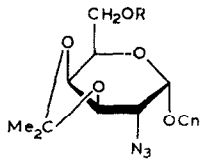
GLYCOSYLATION WITH 2-AZIDO-2-DEOXY-α-D-GALACTOPYRANOSYL CHLORIDE DERIVATIVES (**18** AND **19**) BY METHOD *C*

Runs	*Coupling partners*		*Yields and ratios of α- and β-glycosides*		
	Sugars	*Phenols*	*Yields (%)*		*α/β*
1	**18**	**25**	46	(**30**/**32**)	2.7
2	**19**	**25**	42	(**31**/**33**)	5.5
3	**18**	**27**	73	(**30**/**32**)	4.2
4	**19**	**27**	63	(**31**/**33**)	5.5

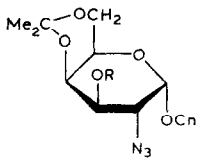
Despite promising preliminary results with **21** and **22**, Methods *A* and *B* turned out to be unsuccessful for **17** or **19**. In Method *A*, the so-called fusion methods, 1,3-dipolar cycloaddition between the 2-azido group of **17** and the alkenic double bond of **25** preceded the expected glycosylation to give two isomers (presumably **28** and **29**). In contrast, Method *B* gave no reaction between **19** and **25**. This result may be explained by the lower reactivity of **19** as compared with **22**. Successful results were obtained by Method *C*, as shown in Table II. Both **18** and **19** gave mainly the α-glycosides (**30** and **31**, respectively), in moderate yields. The yields were improved remarkably by using the *O*-trimethylsilyl phenol derivative **27** instead of **25**, presumably because of prevention of water formation. This modified method seems effective for the preparation of phenyl glycosides. Presumably, the last reaction (Method *D*) proceeds exclusively by the SN2 mechanism and the β-chloride corresponding to **19** (ref. 11) may be expected to give a better yield.

Of the remaining two synthetic operations, namely, (*3*) and (*4*), the former was examined first. Treatment of **31** with sodium ethoxide in ethanol–dichloromethane gave the *O*-deacetylated derivative **34**. For eventual 6-*O*-tosylation, initial selective 3,4-di-*O*-isopropylidenation by acetone and cupric sulfate was attempted and gave the 3,4-*O*- (**36**) and 4,6-*O*-isopropylidene (**39**) derivatives in 44 and 50% yields, respectively. Accordingly **34** was tosylated selectively with tosyl chloride in pyridine at −10° to give, in 77% yield, the 6-ester (**41**), which was also obtained from **36** via its 6-*O*-tosyl derivative (**38**). In order to avoid formation of the 3,6-anhydro derivative, **41** was converted into the 3,4-diacetate (**43**) and subjected to deoxygenation with sodium iodide and sodium cyanoborohydride in HMPA[8] to give the desired 6-deoxygenated compound (**44**) but in only 20% yield, together with the 5-enopyranoside (**46**) in 10% yield. In the absence of sodium cyanoborohydride, the 6-iodo derivative (**45**) was obtained in 70% yield. The substitution of the iodo group by hydride was presumably[15] retarded strongly by the axially oriented substituent at C-4. Therefore, 4-substitution by azide prior to 6-deoxygenation was examined. Because the two amino groups must be differentiated from each other in the total synthesis, the 2-azido group in the deacetylated compound (**35**) was hydrogenated in the presence of palladium-on-barium sulfate and quinoline to give the 2-amino derivative (**47**) in 90% yield. The 2-*N*-(*tert*-butoxycarbonyl) derivative (**48**) was obtained from **47** by treatment with 2-(*tert*-butoxycarbonyl)thio-4,6-dimethylpyrimidine and converted into its 3,6-diacetate (**49**). Compound **48** was heated with sodium azide in HMPA at 70° to give the 4-azido derivative (**50**) in 60% yield. Compound **50** was converted into the 6-*O*-tosyl derivative (**52**) in 90% yield by deacetylation and partial tosylation. Under the same reduction conditions used for **41**, the desired 6-deoxy derivative (**53**) was obtained in 74% yield. Thus, 6-substitution by hydride of the D-*gluco* compound was much easier than for the D-*galacto* isomer. Finally, compound **53** was hydrogenolyzed in the same manner as mentioned for **47**, to give the desired compound **55** in 76% yield.

The intermediate **51** could also be obtained from **34** by reduction of the 2-azido group, *N*-(*tert*-butoxycarbonylation), partial 3,6-di-*O*-benzoylation, 4-*O*-mesylation,



36 R = H
37 R = Ac
38 R = Ts



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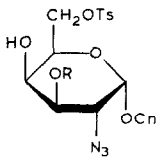

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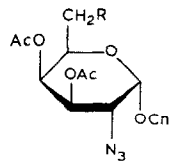
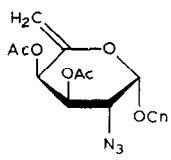
42 R = Ts



43 R = OTs
44 R = H
45 R = I



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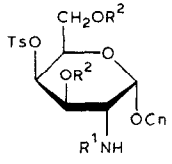
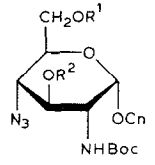
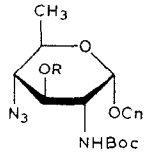


47 $R^1 = R^2 = H$
48 R^1 = Boc, R^2 = H
49 R^1 = Boc, R^2 = Ac



50 $R^1 = R^2$ = Ac
51 $R^1 = R^2 = H$
52 R^1 = Ts, R^2 = H



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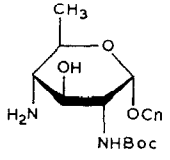
54 R = Ac



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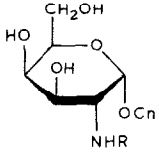

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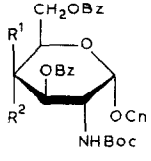
57 R = Boc



58 R^1 = OH, R^2 = H
59 R^1 = OMs, R^2 = H
60 R^1 = H, R^2 = N_3

Boc = Me_3COCO

4-azidation, and debenzoylation, via compounds **56**, **57**, **58**, **59**, and **60**. This route (via the glycal : D-galactose→4 steps→**20**→**19**→**31**→**34**→**56**→**57**→**58**→**59**→**60**→**51**→**52**→**53**→**55**) is more favorable for total synthesis of **55** than the former (via the 1,6 : 2,3-dianhydro sugar: D-galactose→9 steps→**12**→**13**→**16**→**18**→**30**→**35**→**47**→**48**→**49**→**50**→**51**→**52**→**53**→**55**) because of the fewer steps from D-galactose (16 steps versus 22 steps, giving 3.8 and 2.7% overall yields, respectively).

EXPERIMENTAL

General methods. — Melting points were determined with a Mel-Temp apparatus and are not corrected. Optical rotations were measured in chloroform at $c = 1.0$, unless stated otherwise, using a 0.5-dm tube and a Carl Zeiss LEP-Al or JASCO DIP-4 polarimeter. I.r. spectra were recorded with a Hitachi EPI-G2 grating spectrometer. N.m.r. spectra were recorded at 100 MHz with a JEOL JNM PS-100 spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard, unless stated otherwise. Column chromatography and preparative t.l.c. were performed on Wakogel C-200

(Wako Pure Chemical Industries, Ltd.) and Kieselgel 60 HF_{254} (Merck), respectively. Evaporations were conducted under diminished pressure at $\leqslant 50°$.

*Methyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-*D*-allopyranoside* (**5**).— To a chilled solution of compound[3] **4** (5.0 g, 16.3 mmol) in DMF (30 mL) were added sodium hydride (1.6 g, 50% in oil) and then benzyl chloride (2.8 mL, 24.8 mmol). After 16 h at room temperature, the solution was poured into ice–water and the crystals that precipitated were recrystallized from ethanol to give **5** in 94% yield; m.p. 93–95°, $[\alpha]_D$ +126.0°; n.m.r.: δ 4.80 (d, $J_{1,2}$ 3.8 Hz, H-1), 2.97 (dd, $J_{2,3}$ 4.2 Hz, H-2), 3.50 (s, OMe), 5.48 (s, CH in benzylidene), 4.98 and 4.76 (ABq, J_{AB} 12.0 Hz, CH_2 in Bn), and 7.1–7.6 (m, 10 H, aromatic).

Anal. Calc. for $C_{21}H_{23}N_3O_5$: C, 63.46; H, 5.83; N, 10.58. Found: C, 63.71; H, 5.93; N, 10.16.

*Methyl 2-azido-3-*O*-benzyl-2-deoxy-α-*D*-allopyranoside* (**6**). — A suspension of **5** (603 mg, 1.5 mmol) in 70% aqueous acetic acid was heated for 2 h at 100°. The resulting, clear solution was evaporated to give syrupy **6** in quantitative yield; $[\alpha]_D$ +131.9°; n.m.r.: δ 3.82 (d, $J_{1,2}$ 3.9 Hz, H-1), 3.12 (dd, $J_{2,3}$ 3.8 Hz, H-2), 4.04 (t, $J_{3,4}$ 3.8 Hz, H-3), 3.47 (s, OMe), 5.03 and 4.64 (ABq, J_{AB} 11.9 Hz, CH_2 in Bn), and 7.38 (s, 5 H, aromatic).

Anal. Calc. for $C_{14}H_{19}N_3O_5$: C, 54.39; H, 6.19; N, 13.59. Found: C, 54.50; H, 6.39; N, 13.15.

*Methyl 2-azido-3-*O*-benzyl-2-deoxy-6-*O*-(p-tolylsulfonyl)-α-*D*-allopyranoside* (**7**) and *methyl 2-azido-3-*O*-benzyl-2-deoxy-4,6-di-*O*-(p-tolylsulfonyl)-α-*D*-allopyranoside* (**8**). — To a solution of **6** (488 g, 15.8 mmol) in dry dichloromethane (80 mL) and DMF (8 mL) were added triethylamine (4 mL, 28.7 mmol), 4-(dimethylamino)pyridine (90 mg, 0.74 mmol), and *p*-toluenesulfonyl chloride (3.4 g, 21.0 mmol), and the solution kept at room temperature for 16 h. Dichloromethane was added and the mixture was washed with water, dried with anhydrous magnesium sulfate, and then evaporated to give a crude mixture of **7** and **8**, which was separated on a column of silica gel with 9:1 benzene–acetone to afford **7** in 67% and **8** in 12% yield.

Compound **7** was a syrup, $[\alpha]_D$ +101.1°; n.m.r.: δ 4.78 (d, $J_{1,2}$ 3.9 Hz, H-1), 3.12 (t, $J_{2,3}$ 3.9 Hz, H-2), 4.06 (t, $J_{3,4}$ 3.9 Hz, H-3), 3.50 (dd, $J_{4,5}$ 10.2 Hz, H-4), 4.00 (dt, $J_{5,6}$ 3.6 Hz, H-5), 4.26 (d, 2 H, H-6 and H-6′), 3.44 (s, OMe), 2.44 (s, Me in Ts), 4.63 and 5.02 (ABq, J_{AB} 12.0 Hz), and 7.24–7.88 (m, 9 H, aromatic).

Anal. Calc. for $C_{21}H_{25}N_3O_7S$: C, 55.42; H, 5.44; N, 9.07. Found: C, 55.84; H, 5.69; N, 8.74.

Compound **8** was a syrup, $[\alpha]_D$ +136.7°; n.m.r.: δ 4.67 (d, $J_{1,2}$ 4.2 Hz, H-1), 2.90 (dd, $J_{2,3}$ 3.0 Hz, H-2), 3.33 (s, OMe), 2.44 and 2.47 (each s, Me in Ts), 4.76 (s, CH_2 in Bn), and 7.20–7.88 (m, 13 H, aromatic).

Anal. Calc. for $C_{28}H_{31}N_3O_9S_2$: C, 54.45; H, 5.06; N, 6.80. Found: C, 54.25; H, 5.22; N, 6.44.

*Methyl 2-azido-3-*O*-benzyl-2,6-dideoxy-α-*D*-allopyranoside* (**9**). — To a solution of **7** (980 mg, 2.12 mmol) in HMPA (20 mL) was added sodium iodide (640 mg,

4.27 mmol) and sodium cyanoborohydride (955 mg, 15.4 mmol). The mixture was stirred for 20 h at 70–80°, mixed with ethyl acetate (40 mL), washed with water, dried, and evaporated. The syrupy residue was purified on silica gel with 4 : 1 hexane–ethyl acetate to give **9** in 81% yield; syrup, $[\alpha]_D$ +166.4°; n.m.r.: δ 4.75 (d, $J_{1,2}$ 4.2 Hz, H-1), 3.13 (t, $J_{2,3}$ 4.2 Hz, H-2), 3.96 (t, $J_{3,4}$ 4.2 Hz, H-3), 3.12 (dd, $J_{4,5}$ 9.8 Hz, H-4), 3.90 (dq, $J_{5,6}$ 6.6 Hz, H-5), 1.21 (d, 3 H, H-6), 3.47 (s, OMe), 4.59 and 5.01 (ABq, J_{AB} 11.7 Hz), and 7.35 (s, 5 H, phenyl).

Anal. Calc. for $C_{14}H_{19}N_3O_4$: C, 57.32; H, 6.53; N, 14.33. Found: C, 57.80; H, 6.56; N, 13.89.

*Methyl 3-*O*-benzyl-2,6-dideoxy-*α*-*D*-*glycero*-hex-2-enopyranosid-4-ulose* (**11**). — To a solution of **9** (121 mg, 0.41 mmol) and dimethyl sulfoxide (161 mg, 2.06 mmol) in dry dichloromethane (7 mL) was added with stirring at −78° a solution of trifluoroacetic anhydride (260 mg, 1.24 mmol) in dichloromethane (7 mL), and the temperature was maintained for 30 min. Triethylamine (0.5 mL, 3.59 mmol) was added, the mixture was kept at room temperature and then diluted with dichloromethane, and the solution was washed with water, dried, and evaporated to give **11**. n.m.r.: δ 5.19 (d, $J_{1,2}$ 4.2 Hz, H-1), 5.80 (d, H-2), 4.61 (q, $J_{5,6}$ 6.8 Hz, H-5), 1.34 (d, 3 H, H-6), 4.83 (s, CH_2 in Bn), 3.49 (s, OMe), and 7.34 (s, 5 H, aromatic).

*1,6-Anhydro-2-azido-2-deoxy-4-*O*-(p-tolylsulfonyl)-β-D-galactopyranose* (**13**). — To a solution of **12** (1.12 g, 5.66 mmol) in pyridine (15 mL) was added *p*-toluenesulfonyl chloride (1.4 g, 7.35 mmol) with stirring. The mixture was kept for 48 h at room temperature and then poured into ice–water. The product was extracted with chloroform and the dried extract was evaporated. The resulting residue was fractionated on a column of silica gel with 9 : 1 benzene–acetone to afford **13** in 68% yield. The 4,6-disulfonate (**15**) was also obtained as a faster-moving component in 6% yield.

Compound **13** had m.p. 92–93°, $[\alpha]_D$ −0.73°; n.m.r.: 5.42 (m, $J_{1,2}$ 1.0, $J_{1,3}$ 1.5 Hz, H-1), 3.67 (m, $J_{2,3}$ 1.5 Hz, H-2), 4.07 (m, $J_{3,4}$ 4.2 Hz, H-3), 4.52 (t, $J_{4,5}$ 4.2 Hz, H-4), 2.49 (s, Me in Ts), and 7.37 and 7.82 (each d, each 2 H, aromatic).

Anal. Calc. for $C_{13}H_{15}N_3O_6S$: C, 45.74; H, 4.43; N, 12.31; S, 9.39. Found: C, 45.76; H, 4.42; N, 11.90; S, 9.64.

Compound **15** had m.p. 128–129°, $[\alpha]_D$ −26.1°.

Anal. Calc. for $C_{20}H_{21}N_3O_8S_2$: C, 48.48; H, 4.27; N, 8.48; S, 12.94. Found: C, 48.29; H, 4.11; N, 8.39; S, 13.02.

*3-*O*-Acetyl-1,6-anhydro-2-azido-2-deoxy-4-*O*-(p-tolylsulfonyl)-β-D-galactopyranose* (**14**). — Compound **13** was acetylated conventionally with acetic anhydride in pyridine to give **14** in quantitative yield; syrup, $[\alpha]_D$ +59.0°; n.m.r.: δ 5.36 (m, $J_{1,2} = J_{1,3} = 1.5$ Hz, H-1), 3.52 (m, $J_{2,3}$ 1.5 Hz, H-2), 4.56 (dt, $J_{3,4}$ 5.4 Hz, H-3), 4.70 (dd, $J_{4,5}$ 4.2 Hz, H-4), 4.54 (dd, $J_{5,6}$ 5.4, $J_{5,6'}$ ~0 Hz, H-5), 3.72 (dd, $J_{6,6'}$ 8.0 Hz, H-6), 4.39 (d, H-6'), 2.47 (s, Me in Ts), 2.06 (s, Ac), and 7.37 and 7.77 (each d, each 2 H, aromatic).

Anal. Calc. for $C_{15}H_{17}N_3O_7S$: C, 46.99; H, 4.47; N, 10.96; S, 8.36. Found: C, 47.19; H, 4.46; N, 11.14; S, 8.49.

*1,3,6-Tri-*O*-acetyl-2-azido-2-deoxy-4-*O*-p-tolylsulfonyl-D-galactopyranose* (**16**).

— To a solution of **13** (280 mg, 0.80 mmol) in acetic anhydride (6 mL) was added with stirring one drop of concentrated sulfuric acid, and stirring was continued for 90 min. The solution was poured into ice-cold, saturated sodium hydrogencarbonate and the product extracted with chloroform. The chloroform layer was washed with water, dried, and evaporated to give **16** in 95% yield as a 1.8:1 α,β-anomeric mixture. A portion of the mixture was separated on a column of silica gel with 7:3 hexane–ethyl acetate to give each anomer. These were characterized only by n.m.r. spectra. N.m.r.: α anomer, δ 6.22 (d, $J_{1,2}$ 3.5 Hz, H-1), 3.99 (dd, $J_{2,3}$ 10.7 Hz, H-2), 5.22 (dd, $J_{3,4}$ 3.5 Hz, H-3), 5.17 (d, $J_{4,5}$ ~0 Hz, H-4), 4.20 (dd, $J_{5,6}$ 7.5, $J_{5,6'}$ 6.0 Hz, H-5), 3.61 (dd, $J_{6,6'}$ 11.3 Hz, H-6), 3.92 (dd, H-6'), 2.00, 2.15 and 2.19 (each s, Ac), 2.46 (s, Me in Ts), and 7.33 and 7.77 (each d, each 2 H, aromatic); β anomer, δ 5.47 (d, $J_{1,2}$ 8.6 Hz, H-1), 4.82 (dd, $J_{2,3}$ 10.5, $J_{3,4}$ 3.0 Hz, H-3), 5.06 (d, $J_{4,5}$ ~0 Hz, H-4), 1.99, 2.15 and 2.17 (each s, Ac), 2.45 (s, Me in Ts), and 7.30 and 7.76 (each d, each 2 H, aromatic).

Anal. Calc. for $C_{18}H_{23}N_3O_{10}S$: C, 47.01; H, 4.78; N, 8.66; S, 6.60. Found: C, 47.03; H, 4.80; N, 8.46; S, 6.94.

*3,6-Di-*O*-acetyl-2-azido-2-deoxy-4-*O*-*p*-tolylsulfonyl-*α*-*D*-galactopyranosyl chloride* (**18**). — To a solution of **16** (385 mg, 0.78 mmol) in dichloromethane (7 mL) was added titanium tetrachloride (400 mg, 2.11 mmol), and the mixture was boiled for 16 h under reflux. The mixture was diluted with chloroform and successively washed with water, saturated aqueous sodium hydrogencarbonate, and water, dried, and evaporated. The syrup obtained was purified on a column of silica gel with 4:1 hexane–ethyl acetate to give **18** in 85% yield; m.p. 138–139°, $[\alpha]_D$ +149.4°; ν_{max}^{KBr} 2130 (N_3), 1755 and 1750 (ester) cm^{-1}; n.m.r.: δ 6.15 (d, $J_{1,2}$ 3.9 Hz, H-1), 4.19 (dd, $J_{2,3}$ 10.8 Hz, H-2), 5.17–5.42 (m, H-3 and H-4), 4.47 (t, $J_{4,5}$ ~0, $J_{5,6}$ = $J_{5,6'}$ 6.8 Hz, H-5), 3.96 (dd, $J_{6,6'}$ 11.7 Hz, H-6), 3.70 (dd, H-6'), 2.45 (s, Me), 2.00 and 2.18 (each s, Ac), and 7.43 and 7.88 (each d, each 2 H, aromatic).

Anal. Calc. for $C_{17}H_{20}ClN_3O_8S$: C, 44.40; H, 4.38; N, 9.14. Found: C, 44.47; H, 4.28; N, 8.76.

*3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl chloride* (**19**). — Compound **19** was prepared from **17** as described for **18**. The n.m.r. data were in accord with those reported[11].

Ethyl p-(*2,3,4,6-tetra-*O*-methyl-α-D-glucopyranosyloxy)cinnamate* (**23**) *and its β anomer* (**24**). — *Method* A. A mixture of **21** (112 mg, 0.40 mmol), **25** (240 mg, 1.26 mmol), and zinc chloride (20 mg) was heated for 30 min at 110–120° with shaking under diminished pressure (7 mmHg). The resulting melt was dissolved in chloroform, and the solution was washed with water, dried, and evaporated to give a mixture of **23** and **24**, which was separated on a column of silica gel with 7:3 hexane–ethyl acetate.

Method B. A mixture of **25** (378 mg, 1.97 mmol), cadmium carbonate (397 mg, 2.30 mmol), and 4A molecular sieves (1.0 g) in dry toluene (25 mL) was boiled for 1 h under reflux in a flask equipped with a Dean–Stark trap. A solution of **22** in dry toluene (15 mL) was then added and heating was continued for 3 h. Undissolved

materials were filtered off and the filtrate was evaporated to give a syrupy residue from which **23** and **24** were separated as already described.

Method C. To a solution of **22** (240 mg, 0.94 mmol) and **25** (362 mg, 1.89 mmol) in dry dichloromethane (10 mL) were added 4A molecular sieves, silver carbonate (460 mg, 1.67 mmol), and silver perchlorate (205 mg, 0.99 mmol). The mixture was stirred for 24 h at room temperature with shielding from light. Chloroform was added, undissolved materials were filtered off, and the filtrate was washed with water, dried and evaporated to give a crude mixture of **23** and **24**. They were fractionated as in Method *A*.

Method D. To a solution of sodium (79 mg, 3.43 mmol) in abs. ethanol (10 mL) was added **25** (700 mg, 3.65 mmol), and after 10 min the solution was evaporated to give **26** as a yellow solid, which was washed twice with dry ether and dried in a desiccator. Next, compound **26** was added to a solution of **22** (455 mg, 1.79 mmol) in HMPA (10 mg), and the solution was stirred for 24 h at room temperature. The solution was shaked with ethyl acetate and water. The organic layer was washed with water, dried, and evaporated to give a syrupy mixture of **23** and **24**, which was resolved as described in Method *A*.

Yields of **23** and **24** for Methods A–D are summarized in Table I.

Compound **23** was a syrup $[\alpha]_D$ +183.1°; ν_{max}^{NaCl} 1708 (ester), 1630 (alkene), 1603 and 1508 cm^{-1} (phenyl); n.m.r.: δ 5.66 (d, $J_{1,2}$ 3.3 Hz, H-1), 7.12, 7.47 (*J* 9.3 Hz), 7.62, 6.32 (*J* 15.9 Hz), and 4.26 and 1.34 (*J* 7.2 Hz) (Cn*).

Anal. Calc. for $C_{21}H_{30}O_8$: C, 61.45; H, 7.37. Found: C, 61.68; H, 7.35.

Compound **24** had m.p. 187°, $[\alpha]_D$ −46.0°; ν_{max}^{KBr} 1718 (ester), 1638 (alkene), 1605 and 1508 cm^{-1} (phenyl); n.m.r.: δ 4.85 (d, $J_{1,2}$ 7.2 Hz, H-1), 6.95, 7.42 (*J* 9.0 Hz), 7.60, 6.28 (*J* 15.9 Hz), and 4.23 and 1.33 (*J* 7.5 Hz) (Cn*).

Anal. Calc. for $C_{21}H_{30}O_8$: C, 61.45; H, 7.37. Found: C, 61.63; H, 7.30.

Fusion reaction of **17** *with* **25** *in the presence of zinc chloride* (*formation of* **28** *and* **29**). — The fusion reaction of **17** (125 mg, 0.41 mmol) with **25** (230 mg, 1.20 mmol) was performed in the presence of zinc chloride (7 mg, 0.05 mmol) for 30 min at 130°. The same isolation as described for **23** and **24** gave, in low yield, two 1,3-dipolar cycloaddition products (A and B), whose structures were tentatively assigned as **28** and **29**.

Compound A was a syrup; ν_{max}^{NaCl} 1745 cm^{-1} (ester); n.m.r.: δ 6.45 (d, $J_{1,2}$ 3.9 Hz, H-1), 5.20 (dd, $J_{2,3}$ 11.0, $J_{3,4}$ 3.3 Hz, H-3), 5.45 (d, $J_{4,5}$ ~0 Hz, H-4), 1.22 (t, Me in Et), 2.02, 2.05, 2.17, and 2.22 (each s, Ac), and 6.60–7.26 (m, 4 H, aromatic).

Compound B was a syrup; ν_{max}^{NaCl} 1740 cm^{-1} (ester); n.m.r.: δ 6.17 (d, $J_{1,2}$ 3.8 Hz, H-1), 5.06 (dd, $J_{2,3}$ 14.3, $J_{3,4}$ 3.0 Hz, H-3), 5.39 (d, $J_{4,5}$ ~0 Hz, H-4), 1.24 (t, Me in Et), 2.01, 2.06, and 2.20 (each s, Ac), and 6.64–7.51 (m, 4 H, aromatic).

Ethyl p-(*3,6-di*-O-*acetyl-2-azido-2-deoxy-4*-O-p-*tolylsulfonyl*-α-D-*galactopyra*-

*The last six signals listed arise from the cinnamoyl (Cn) group, namely, the first two of these (each d) for aromatic protons, the second two (each d) for alkenic, and the last two (q and t, respectively) for those of the ethyl group.

nosyloxy)cinnamate (**30**) *and its β anomer* (**32**). — *Method* A. Compound **18** was coupled with **25** as described for **23** and **24** (method *C*) to give a mixture of **30** and **32**, which were separated on a column of silica gel with 3:1 hexane–ethyl acetate.

Method B. The same reaction as just described was repeated with **27** instead of **25**. The yields and the ratio of **30** and **32** are summarized in Table II.

Compound **30** had m.p. 123–125°, $[\alpha]_D$ +146.9°; ν_{max}^{KBr} 2105 (N_3), 1750 and 1700 (ester), 1630 (alkene), 1600 and 1505 cm^{-1} (phenyl); n.m.r.: δ 5.59 (d, $J_{1,2}$ 3.0 Hz, H-1), 3.90 (dd, $J_{2,3}$ 10.8 Hz, H-2), 5.48 (dd, $J_{3,4}$ 3.0 Hz, H-3), 5.21 (d, $J_{4,5}$ ~0 Hz, H-4), 3.70 (dd, $J_{5,6}$ 6.5, $J_{6,6'}$ 11.0 Hz, H-6), 3.90 (dd, $J_{5,6'}$ 6.8 Hz, H-6'), 2.47 (s, Me in Ts), 1.89 and 2.18 (each s, Ac), 7.35 and 7.80 (each d, each 2 H, aromatic in Ts), 7.05, 7.45, 7.60, 6.30 (*J* 16.0 Hz), 4.24 and 1.32 (Cn*).

Anal. Calc. for $C_{28}H_{31}N_3O_{11}S$: C, 54.45; H, 5.06; N, 6.80; S, 5.19. Found: C, 54.42; H, 5.11; N, 6.78; S, 5.43.

Compound **32** was a syrup, $[\alpha]_D$ +21.5°; ν_{max}^{NaCl} 2110 (N_3), 1742 and 1705 (ester), 1635 (alkene), and 1605 and 1510 cm^{-1} (phenyl); n.m.r.: δ 4.81 (d, $J_{1,2}$ 7.7 Hz, H-1), 4.84 (dd, $J_{,23}$ 12.8, $J_{3,4}$ 3.0 Hz, H-3), 5.10 (d, $J_{4,5}$ ~0 Hz, H-4), 2.46 (s, Me in Ts), 2.03 and 2.18 (each s, Ac), 7.34 and 7.80 (each d, each 2 H, aromatic in Ts), 7.00, 7.44, 7.60, 6.30 (*J* 16.1 Hz), 4.24 and 1.31 (Cn*).

*Anal.*Calc. for $C_{28}H_{31}N_3O_{11}S$: C, 54.45; H, 5.06; N, 6.80; S, 5.19. Found: C, 54.49; H, 5.14; N, 6.62; S, 5.01.

Ethyl p-(*3,4,6-tri*-O-*acetyl-2-azido-2-deoxy-α*-D-*galactopyranosyloxy)cinnamate* (**31**) *and its β anomer* (**33**). — *Method* A. Compound **19** was coupled with **25** as described for **23** (Method *C*) to give a mixture of **31** and **33**, which was separated on a column of silica gel with 7:3 hexane–ether.

Method B. The same reaction as just described was conducted with **27** instead of **25**. The yields and the ratios of **31** and **33** are summarized in Table II.

Compound **31** had m.p. 95–97°, $[\alpha]_D$ +164.9°; ν_{max}^{KBr} 2125 (N_3), 1755, 1740 and 1715 (ester), 1630 (alkene), and 1605 and 1510 cm^{-1} (phenyl); n.m.r.: δ 5.65 (d, $J_{1,2}$ 3.8 Hz, H-1), 3.82 (dd, $J_{2,3}$ 10.5 Hz, H-2), 5.55 (dd, $J_{3,4}$ 3.2 Hz, H-3), 5.50 (m, H-4), 1.94, 2.10 and 2.17 (each s, Ac), 7.07, 7.45 (*J* 9.0 Hz), 7.61, 6.30 (*J* 16.2 Hz), 4.24 and 1.34 (*J* 7.2 Hz) (Cn*).

Compound **33** was a syrup, $[\alpha]_D$ +11.3°; ν_{max}^{NaCl} 2110 (N_3), 1745 and 1705 (ester), 1638 (alkene), and 1605 and 1510 cm^{-1} (phenyl); n.m.r.: δ 5.00 (d, $J_{1,2}$ 7.8 Hz, H-1), 3.99 (dd, $J_{2,3}$ 10.7 Hz, H-2), 4.92 (dd, $J_{3,4}$ 3.2 Hz, H-3), 5.41 (d, $J_{4,5}$ ~0 Hz, H-4), 2.08, 2.10 and 2.20 (each s, Ac), 7.08, 7.49 (*J* 9.0 Hz), 7.63, 6.35 (*J* 16.2 Hz), 4.26, and 1.35 (*J* 7.4 Hz) (Cn*).

Anal. Calc. for $C_{23}H_{27}N_3O_{10}$: C, 54.65; H, 5.38; N, 8.31. Found: C, 54.69; H, 5.45; N, 8.16.

Ethyl p-(*2-azido-2-deoxy-α*-D-*galactopyranosyloxy)cinnamate* (**34**). — To a solution of **31** (1.08 g, 2.14 mmol) in abs. ethanol (7 mL) and dichloromethane (7 mL) was added with stirring abs. ethanol (7 mL) in which had been dissolved a catalytic amount of sodium. The solution was kept for 30 min at room temperature, made neutral with acetic acid, and evaporated. The resulting syrup was purified on a

column of silica gel with 6:1:1 benzene–ethyl acetate–ethanol to give pure **34** in 92% yield, $[\alpha]_D$ +146.9°; ν_{max}^{NaCl} 3400–3500 (OH), 2120 (N_3), and 1710 cm^{-1} (ester); n.m.r.: δ 5.52 (d, $J_{1,2}$ 3.0 Hz, H-1), 7.02, 7.39, 7.54, 6.25 (J 16.0 Hz), 4.25, and 1.33 (Cn*).

Anal. Calc. for $C_{17}H_{21}N_3O_7$: C, 53.82; H, 5.58; N, 11.08. Found: C, 53.84; H, 5.65; N, 10.92.

Ethyl p-(*2-azido-2-deoxy-4-*O-p-*tolylsulfonyl-*α-D-*galactopyranosyloxy)cinnamate* (**35**). — Compound **30** was deacetylated as described for **34**. The solution was made neutral with acetic acid, diluted with chloroform, washed with saturated sodium hydrogencarbonate and water, dried, and evaporated to give **35** as a sysup in quantitative yield; $[\alpha]_D$ +127.4°; ν_{max}^{NaCl} 3450 (OH), 2125 (N_3), 1710 (ester), and 1640 cm^{-1} (alkene); n.m.r.: δ 5.51 (d, $J_{1,2}$ 3.8 Hz, H-1), 3.53 (dd, $J_{2,3}$ 11.0 Hz, H-2), 4.42 (dd, $J_{3,4}$ 3.0 Hz, H-3), 5.22 (d, $J_{4,5}$ ~0 Hz, H-4), 5.12 (t, $J_{5,6} = J_{5,6'}$ 7.2 Hz, H-5), 3.62 (d, H-6), 2.46 (s, Me in Ts), 7.33 and 7.86 (each d, each 2 H, aromatic in Ts), 7.03, 7.42, 7.54, 6.28 (J 16.2 Hz), 4.23, and 1.33 (Cn*).

Anal. Calc. for $C_{24}H_{27}N_3O_9S$: C, 54.03; H, 4.92; N, 7.88. Found: C, 53.80; H, 5.16; N, 7.53.

Ethyl p-(*2-azido-2-deoxy-3,4-*O-*isopropylidene-*α-D-*galactopyranosyloxy)cinnamate* (**36**) *and its 4,6-*O-*isopropylidene isomer* (**39**). — To a solution of **34** (768 mg, 2.07 mmol) in dry acetone (25 mL) were added anhydrous cupric sulfate (4.0 g, 25 mmol) and one drop of concentrated sulfuric acid, and the mixture was stirred for 16 h at room temperature. Undissolved materials were filtered off. The filtrate was mixed with chloroform (40 mL), washed with saturated sodium hydrogencarbonate and water, dried, and evaporated to give a mixture of two isomers, which were separated on a column of silica gel with 3:2 hexane–ethyl acetate to afford **36** and **39** in 44 and 50% yield, respectively. Structures of each isomer were ascertained by n.m.r. spectra of the respective 6-acetate (**37**) and 3-acetate (**40**).

Compound **36** had $[\alpha]_D$ +193.4°; n.m.r.: δ 5.58 (d, $J_{1,2}$ 2.9 Hz, H-1), 3.54 (dd, $J_{2,3}$ 8.7 Hz, H-2), 4.62 (dd, $J_{3,4}$ 5.4 Hz, H-3), 4.35 (t, $J_{4,5}$ 5.4 Hz, H-4), 1.59 and 1.63 (each s, Me_2C), 7.09, 7.48, 7.63, 6.32 (J 16.0 Hz), 4.19, and 1.35 (Cn*).

Anal. Calc. for $C_{20}H_{25}O_7N_3$: C, 57.27; H, 6.01; N, 10.02. Found: C, 57.67; H, 6.24; N, 9.65.

Compound **37** had $[\alpha]_D$ +205.1°; n.m.r.: δ 5.53 (d, $J_{1,2}$ 3.2 Hz, H-1), 3.54 (dd, $J_{2,3}$ 7.8 Hz, H-2), 4.58 (dd, $J_{3,4}$ 5.1 Hz, H-3), 1.97 (s, Ac), 1.35 and 1.55 (each s, Me_2C), 7.09, 7.46, 7.62, 6.32 (J 16.0 Hz), 4.25, and 1.33 (Cn*).

Anal. Calc. for $C_{22}H_{27}N_3O_8$: C, 57.26; H, 5.90; N, 9.11. Found: C, 57.68; H, 6.09; N, 9.20.

Compound **39** had $[\alpha]_D$ +126.1°; n.m.r.: δ 5.67 (d, $J_{1,2}$ 3.2 Hz, H-1).

Anal. Calc. for $C_{20}H_{25}O_7N_3$: C, 57.27; H, 6.01; N, 10.02. Found: C, 57.58; H, 6.07; N, 10.05.

Compound **40** had $[\alpha]_D$ +183.7°; n.m.r.: δ 5.73 (d, $J_{1,2}$ 3.8 Hz, H-1), 4.06 (dd, $J_{2,3}$ 10.8 Hz, H-2), 5.44 (dd, $J_{3,4}$ 3.3 Hz, H-3), 4.49 (d, $J_{4,5}$ ~0 Hz, H-4), 3.70 (m, H-5), 3.83 (dd, $J_{5,6}$ 1.5, $J_{6,6'}$ 13.2 Hz, H-6), 4.04 (dd, $J_{5,6'}$ 2.2 Hz, H-6'), 2.19

(s, Ac), 1.43 and 1.49 (each s, Me_2C), 7.09, 7.45, 7.61, 6.30 (J 16.0 Hz), 4.24, and 1.31 (Cn*).

Anal. Calc. for $C_{22}H_{27}N_3O_8$: C, 57.26; H, 5.90; N, 9.11. Found: C, 57.68; H, 6.12; N, 8.88.

Ethyl p-(*2-azido-2-deoxy-3,4-*O*-isopropylidene-6-*O*-*p*-tolylsulfonyl-α-*D*-galacto-pyranosyloxy)cinnamate* (**38**). — Compound **36** was *p*-toluenesulfonylated conventionally to give **38** in 92% yield, syrup, $[\alpha]_D$ +110.9°; n.m.r.: δ 5.44 (d, $J_{1,2}$ 3.3 Hz, H-1), 3.48 (dd, $J_{2,3}$ 8.1 Hz, H-2), 4.54 (dd, $J_{3,4}$ 5.3 Hz, H-3), 2.43 (s, Me in Ts), 1.35 and 1.50 (each s, Me_2C), 7.25 and 7.70 (each d, each 2 H, aromatic in Ts), 7.02, 7.43, 7.62, 6.32 (J 16.0 Hz), 4.22, and 1.35 (Cn*).

Anal. Calc. for $C_{26}H_{33}N_3O_9S$: C, 56.54; H, 5.45; N, 7.33; S, 5.59. Found: C, 56.59; H, 5.48; N, 7.01; S, 5.91.

Ethyl p-(*2-azido-2-deoxy-6-*O*-p-tolylsulfonyl-α-*D*-galactopyranosyloxy)cinnamate* (**41**). — To a solution of **34** (197 mg, 0.63 mmol) in pyridine (5 mL) was added *p*-toluenesulfonyl chloride (134 mg, 0.70 mmol) at − 10° with stirring, and stirring was continued for 16 h. The mixture was diluted with chloroform (20 mL), washed with water, dried, and evaporated to give a syrupy mixture of **41** and its 3,6-di-*p*-toluenesulfonate (**42**), which were separated by preparative t.l.c. to afford **41** and **42** in 77 and 20% yields, respectively.

Compound **41** had m.p. 120–123°, $[\alpha]_D$ +101.9°; ν_{max}^{KBr} 3420 (OH), 2125 (N_3), 1710 (ester), 1638 (alkene), 1610, 1515, and 760 cm^{-1} (phenyl); n.m.r.: δ 5.53 (d, $J_{1,2}$ 3.3 Hz, H-1), 2.43 (s, Me in Ts), 7.35 and 7.70 (each d, each 2 H, aromatic in Ts), 7.03, 7.43, 7.62, 6.32 (J 15.8 Hz), 4.27, and 1.35 (Cn*).

Anal. Calc. for $C_{24}H_{27}N_3O_9S$: C, 54.03; H, 5.10; N, 7.88; S, 6.01. Found: C, 53.90; H, 4.99; N, 7.63; S, 6.31.

Compound **42** was a syrup, $[\alpha]_D$ +175.7°; ν_{max}^{NaCl} 3475 (OH), 2110 (N_3), 1700 (ester), 1633 (alkene), 1600 and 1510 (phenyl), and 1363 cm^{-1} (SO_2); n.m.r.: δ 5.50 (d, $J_{1,2}$ 3.0 Hz, H-1), 3.78 (dd, $J_{2,3}$ 10.7 Hz, H-2), 5.00 (dd, $J_{3,4}$ 3.0 Hz, H-3), ~4.2 (H-4), 2.43 and 2.47 (each s, Me in Ts), 1.31 and 4.24 (t and q, respectively, Et), 6.30 and 7.61 (each d, alkene, J 16.0 Hz), and 6.9–8.0 (m, 12 H, aromatic).

Anal. Calc. for $C_{31}H_{33}N_3O_{11}S_2$: C, 54.14; H, 4.84; N, 6.11; S, 9.32. Found: C, 54.35; H, 5.07; N, 5.85; S, 9.30.

Ethyl p-(*3,4-di-*O*-acetyl-2-azido-2-deoxy-6-*O*-p-tolylsulfonyl-α-*D*-galactopyra-nosyloxy)cinnamate* (**43**). — Compound **41** was acetylated with acetic anhydride and pyridine to give **43** quantitatively; syrup, $[\alpha]_D$ +158.4°; ν_{max}^{NaCl} 2090 (N_3), 1740 and 1698 (ester), 1625 (alkene), 1596 and 1500 (phenyl), and 1358 cm^{-1} (SO_2); n.m.r.: δ 5.62 (d, $J_{1,2}$ 3.5 Hz, H-1), 3.80 (dd, $J_{2,3}$ 10.8 Hz, H-2), 5.46–5.60 (m, $J_{3,4}$ 10.8 Hz, H-3 and H-4), 5.45 (s, Me in Ts), 2.09 and 2.12 (each s, Ac), 1.34 and 4.27 (t and q, respectively, Et), 6.31 (d, alkenic, J 16.0 Hz), and 7.00–7.76 (m, 8 H, aromatic).

Anal. Calc. for $C_{28}H_{31}N_3O_{11}S$: C, 54.45; H, 5.06; N, 6.80; S, 5.19. Found: C, 54.41; H, 5.11; N, 6.45; S, 5.90.

Ethyl p-(*3,4-di-*O*-acetyl-2-azido-2,6-dideoxy-α-*D*-galactopyranosyloxy)cinna-mate* (**44**) *and* p-(*3,4-di-*O*-acetyl-2-azido-2,6-dideoxy-β-*L*-arabino-hex-5-enopyrano-*

syloxy)cinnamate (**46**). — Compound **43** (762 mg, 1.39 mmol) was reduced with sodium iodide (1.1 g, 7.3 mmol) and sodium cyanoborohydride (0.75 g, 11.9 mmol) in HMPA (7 mL) for 60 h at 70°. As the two products obtained in admixture as described for **9** could not be separated, the mixture was deacetylated with sodium ethoxide in ethanol, fractionated by preparative t.l.c. with 3:2 hexane–ethyl acetate, and reacetylated to give **44** and **46** in 20 and 10% yield, respectively.

Compound **44** was a syrup, $[\alpha]_D$ +184.9°; n.m.r.: δ 5.66 (d, $J_{1,2}$ 3.2 Hz, H-1), 3.82 (dd, $J_{2,3}$ 11.0 Hz, H-2), 5.61 (dd, $J_{3,4}$ 3.2 Hz, H-3), 5.38 (dd, $J_{4,5}$ 1.5 Hz, H-4), 1.14 (d, 3 H, $J_{5,6}$ 6.6 Hz, H-6), 2.11 and 2.21 (s, Ac), and 7.12, 7.52, 7.67, 6.35 (J 16.2 Hz), 4.27, and 1.37 (Cn*).

Anal. Calc. for $C_{21}H_{25}N_3O_8$: C, 56.37; H, 5.63; N, 9.39. Found: C, 56.13; H, 5.67; N, 9.11.

Compound **46** showed n.m.r.: δ 5.67 (d, $J_{1,2}$ 3.2 Hz, H-1), 3.99 (dd, $J_{2,3}$ 11.1 Hz, H-2), 5.58 (dd, $J_{3,4}$ 3.8 Hz, H-3), 5.77 (d, $J_{4,5}$ ~0 Hz, H-4), 4.68 (d, $J_{6,6'}$ 1.5 Hz, H-6), 4.76 (d, H-6'), 2.10 and 2.16 (each s, Ac), 7.16, 7.44, 7.58, 6.29 (J 16.1 Hz), 4.22, and 1.32 (Cn*).

Ethyl p-(*3,4-di*-O-*acetyl-2-azido-2,6-dideoxy-6-iodo*-α-D-*galactopyranosyloxy*)-*cinnamate* (**45**). — A suspension of **43** (187 mg, 0.34 mmol) and sodium iodide (277 mg, 1.85 mmol) in HMPA (5 mL) was heated with stirring for 12 h at 100°. The same processing as just described, followed by preparative t.l.c., gave **45** in 70% yield: n.m.r.: δ 3.80 (dd, $J_{1,2}$ 3.2, $J_{2,3}$ 11.0 Hz, H-2), 5.46–5.64 ($J_{3,4}$ 3.0 Hz, H-1, H-3, and H-4), 3.11 (d, 2 H, $J_{5,6}$ 7.2 Hz, H-6), 2.10 and 2.16 (each s, Ac), 7.12, 7.46, 7.60, 6.30 (J 16.0 Hz), 4.23, and 1.33 (Cn*). Further characterisation was not performed.

Ethyl p-(*2-amino-2-deoxy-4*-O-p-*tolylsulfonyl*-α-D-*galactopyranosyloxy*)*cinnamate* (**47**). — A solution of **35** (3.96 g, 7.43 mmol) in methanol (65 mL) was shaken for 20 h under hydrogen (1 atm) at room temperature in the presence of 5% palladium-on-barium sulfate (1.0 g) and quinoline (0.3 mL). The catalyst was filtered off and the syrupy residue obtained by evaporation of the filtrate was purified on a column of silica gel with 15:1:1 benzene–ethyl acetate–ethanol to give **47** in 90% yield; $[\alpha]_D$ +124.7°: ν_{max}^{NaCl} 3400 (OH, NH_2), 1705 (ester), and 1630 cm^{-1} (alkene); n.m.r.: δ 5.41 (d, $J_{3,4}$ 3.6 Hz, H-1), 3.02 (dd, $J_{2,3}$ 10.5 Hz, H-2), 3.80 (dd, $J_{3,4}$ 2.7 Hz, H-3), 5.10 (d, $J_{4,5}$ ~0 Hz, H-4), 4.01 (t, $J_{5,6}$ 6.6 Hz, H-5), 3.60 (d, 2 H, H-6), 2.43 (s, Me in Ts), 2.23 (broad s, 3 H, OH and NH_2), 7.23 and 7.76 (each d, each 2 H, aromatic in Ts), 6.94, 7.35, 7.52, 6.23 (J 15.8 Hz), 4.20, and 1.32 (Cn*).

Anal. Calc. for $C_{24}H_{29}NO_9S$: C, 56.79; H, 5.76; N, 2.76; S, 6.32. Found: C, 56.62; H, 5.77; N, 2.90; S, 6.53.

Ethyl p-[*2*-(tert-*butoxycarbonyl*)*amino-2-deoxy-4*-O-p-*tolylsulfonyl*-α-D-*galactopyranosyloxy*]*cinnamate* (**48**). — To a solution of **47** (157 mg, 0.31 mmol) in 1:1 1,4-dioxane–water (10 mg) were added with stirring 2-(*tert*-butoxycarbonylthio)-4,6-dimethylpyrimidine (97 mg, 0.43 mmol) and triethylamine (50 mg, 0.50 mmol), and stirring was continued for 16 h. The residue obtained by direct evaporation of the solution was purified by preparative t.l.c. with 7:1:1 benzene–ethyl acetate–ethanol

to give **48** in 87% yield; syrup, $[\alpha]_D$ +110.3°; n.m.r.: δ 5.44 (d, $J_{1,2}$ 2.0 Hz, H-1), 5.08 (d, $J_{3,4}$ 1.0, $J_{4,5}$ ~0 Hz, H-4), 2.43 (s, Me in Ts), 1.42 (s, 9 H, Me_3C), 7.26 and 7.77 (each d, each 2 H, aromatic in Ts), 6.92, 7.34, 7.50, 6.20 (J 16.2 Hz), 4.18, and 1.30 (Cn*).

Anal. Calc. for $C_{29}H_{37}NO_{11}S$: C, 57.32; H, 6.14; N, 2.31; S, 5.28. Found: C, 57.49; H, 6.32; N, 2.37; S, 5.39.

Ethyl p-[*3,6-di*-O-*acetyl-2*-(tert-*butoxycarbonyl*)*amino-2-deoxy-4*-O-p-*tolylsulfonyl*-α-D-*galactopyranosyloxy*]*cinnamate* (**49**). — Compound **48** was acetylated with acetic anhydride and pyridine to give **49** quantitatively; syrup, $[\alpha]_D$ +123.9°; ν_{max}^{NaCl} 3350 (NH), 1700–1740 (ester and urethan) and 1635 cm^{-1} (alkene); n.m.r.: δ 5.54 (d, $J_{1,2}$ 3.3 Hz, H-1), 4.36 (dt, $J_{2,3} = J_{2,NH}$ = 10.5 Hz, H-2), 5.08–5.28 (m, H-3 and H-4), 4.70 (d, NH), 2.44 (s, Me in Ts), 1.85 and 2.01 (each s, Ac), 1.43 (s, 9 H, Me_3C), 7.29 and 7.78 (each d, each 2 H, aromatic in Ts), 6.98, 7.40, 7.50, 6.25 (J 16.2 Hz), 4.20, and 1.30 (Cn*).

Anal. Calc. for $C_{33}H_{41}NO_{13}S$: C, 57.30; H, 5.97; N, 2.02; S, 4.64. Found: C, 57.22; H, 6.02; N, 1.96; S, 4.74.

Ethyl p-[*3,6-di*-O-*acetyl-4-azido-2*-(tert-*butoxycarbonyl*)*amino-2,4-dideoxy*-α-D-*glucopyranosyloxy*]*cinnamate* (**50**). — A mixture of **49** (250 mg, 0.41 mmol) and sodium azide (50 mg, 0.77 mmol) in HMPA (5 mL) was heated for 15 h at 80° with stirring. The cooled mixture was diluted with aqueous sodium chloride and extracted with ethyl acetate. The extract was washed with water, dried, and evaporated to give crude **50**, which was purified by preparative t.l.c. with 4:1 hexane–ethyl acetate; yield, 60%, syrup, $[\alpha]_D$ +184.9°; ν_{max}^{NaCl} 3350 (NH), 2110 (N_3), 1745 and 1710 (ester and urethan), and 1635 cm^{-1} (alkene); n.m.r. (C_6D_6): δ 5.20 (d, $J_{1,2}$ 3.3 Hz, H-1), 4.24 (m, H-2), 5.52 (dd, $J_{2,3}$ 10.5, $J_{3,4}$ 9.6 Hz, H-3), 3.33 (t, $J_{4,5}$ 9.9 Hz, H-4), 5.06 (d, $J_{2,NH}$ 9.6 Hz, NH), 1.58 and 1.88 (each s, Ac), 1.40 (s, 9 H, Me_3C), and 6.50, 6.98, 7.78, 6.38 (J 16.4 Hz), 4.13 and 1.08 (Cn*).

Anal. Calc. for $C_{26}H_{34}N_4O_{10}$: C, 55.51; H, 6.09; N, 9.96. Found: C, 55.58; H, 6.21; N, 9.48.

Ethyl p-[*4-azido-2*-(tert-*butoxycarbonyl*)*amino-2,4-dideoxy*-α-D-*glucopyranosyloxy*]*cinnamate* (**51**). — Compounds **50** or **60** were deacylated as described for **34** to give **51** in 95% yield in both instances, syrup, $[\alpha]_D$ +186.0°; ν_{max}^{NaCl} 3340 (OH and NH), 2110 (N_3), 1700 (ester), 1690 and 1530 (urethan), and 1630 cm^{-1} (alkene); n.m.r.: δ 5.62 (d, $J_{1,2}$ 0.5 Hz, H-1), 1.20 (s, 9 H, Me_3C), 7.05, 7.46, 7.62, 6.32 (J 15.9 Hz), 4.26, and 1.38 (Cn*).

Anal. Calc. for $C_{22}H_{30}N_4O_8$: C, 55.22; H, 6.32; N, 11.70. Found: C, 55.04; H, 6.32; N, 11.60.

Although **51** was also obtained by the same substitution of **48** as described for **50**, the yield was lower and the processing was more tedious because of formation of an unidentified by-product.

Ethyl p-[*4-azido-2*-(tert-*butoxycarbonyl*)*amino-2,4-dideoxy-6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyloxy*]*cinnamate* (**52**). — Compound **51** (997 mg, 2.62 mmol) was treated conventionally with *p*-toluenesulfonyl chloride (805 mg, 4.23 mmol) in

pyridine (25 mL) to give **52** as crystals, which were recrystallized from ethanol; yield 96%, m.p. 133–136°, $[\alpha]_D$ +145.6°; ν_{max}^{KBr} 3350 (NH and OH), 2120 (N_3), 1710 (ester), 1665 and 1510 (urethan), and 1640 cm^{-1} (alkene); n.m.r.: δ 5.46 (d, $J_{1,2}$ 2.7 Hz, H-1), 4.96 (d, $J_{2,NH}$ 8.2 Hz, NH), 2.45 (s, Me in Ts), 1.46 (s, 9 H, Me_3C), 7.32 and 7.76 (each d, each 2 H, aromatic in Ts), 7.61, 6.32 (J 16.1 Hz), 4.25 and 1.33 (Cn*).

Anal. Calc. for $C_{29}H_{36}N_4O_{10}S$: C, 55.05; H, 5.74; N, 8.86; S, 5.07. Found: C, 54.96; H, 5.84; N, 8.64; S, 5.15.

Ethyl p-[*4-azido-2-*(tert-*butoxycarbonyl)amino-2,4,6-trideoxy-*α-D-*glucopyranosyloxy*]*cinnamate* (**53**). — Compound **52** (206 mg, 0.39 mmol) was reduced with sodium iodide (322 mg, 2.15 mmol) and sodium cyanoborohydride (180 mg, 2.90 mmol) in HMPA (5 mL) for 16 h at 70–75°. Processing as for **9** gave **53** in 74% yield; m.p. 110–112°, $[\alpha]_D$ +192.2°; ν_{max}^{KBr} 3400 and 3280 (NH and OH), 2095 (N_3), 1700–1630 cm^{-1} (broad: ester, urethan and alkene); n.m.r.: δ 5.53 (d, $J_{1,2}$ 1.5 Hz, H-1), 3.22 (t, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3), 3.64 (dq, $J_{4,5}$ 9.9 Hz, H-5), 1.28 (d, 3 H, $J_{5,6}$ 6.0 Hz, H-6), 5.04 (d, NH), 1.47 (s, 9 H, Me_3C), 7.05, 7.42, 7.64, 6.33 (J 16.0 Hz), 4.26, and 1.33 (Cn*).

Anal. Calc. for $C_{22}H_{30}N_4O_7$: C, 57.13; H, 6.54; N, 12.12. Found: C, 56.90; H, 6.65; N, 11.84.

Acetylation of **53** gave the corresponding 3-acetate (**54**) in quantitative yield as a syrup, $[\alpha]_D$ +220.4°; n.m.r.: δ 5.49 (d, $J_{1,2}$ 3.6 Hz, H-1), ~4.1 (m, H-2), 5.34 (t, $J_{2,3} = J_{3,4}$ 10.2 Hz, H-3), 3.31 (t, $J_{4,5}$ 10.2 Hz, H-4), 3.68 (dq, $J_{5,6}$ 7.1 Hz, H-5), 1.26 (d, 3 H, H-6), 4.96 (d, $J_{2,NH}$ 9.8 Hz, NH), 1.41 (s, 9 H, Me_3C), 7.04, 7.42, 7.63, 6.31 (J 16.0 Hz), 4.24, and 1.37 (Cn*).

Anal. Calc. for $C_{24}H_{32}N_4O_8$: C, 57.13; H, 6.39; N, 11.11. Found: C, 56.92; H, 6.36; N, 11.21.

Ethyl p-[*4-amino-2-*(tert-*butoxycarbonyl)amino-2,4,6-trideoxy-*α-D-*glucopyranosyloxy*]*cinnamate* (**55**). — Compound **53** was hydrogenolyzed as described for **47** to give **55** in 76% yield; m.p. 167–170°, $[\alpha]_D$ +151.0°; ν_{max}^{KBr} 3450 (NH and OH), 1710 (ester), 1680 and 1520 (urethan), and 1630; n.m.r.: 5.56 (d, $J_{1,2}$ 3.0 Hz, H-1), 2.63 (t, $J_{3,4} = J_{4,5}$ 9.3 Hz, H-4), 1.23 (d, 3 H, $J_{5,6}$ 8.0 Hz, H-6), 5.20 (d, $J_{2,NH}$ 8.3 Hz, NH), 1.44 (s, 9 H, Me_3C), 7.06, 7.46, 7.64, 6.32 (J 16.0 Hz), 4.26, and 1.28 (Cn*).

Anal. Calc. for $C_{22}H_{32}N_2O_7$: C, 60.53; H, 7.39; N, 6.42. Found: C, 60.24; H, 7.39; N, 6.29.

Ethyl p-[*3,6-di-*O-*benzoyl-2-*(tert-*butoxycarbonyl)amino-2-deoxy-*α-D-*galactopyranosyloxy*]*cinnamate* (**58**). — Compound **34** (8.6 g, 27.7 mmol) was hydrogenolyzed in methanol (100 mL) in the presence of 5% palladium-on-barium sulfate (2.0 g) and quinoline (0.8 mL) for 24 h as described for **47** to give the 2-amino derivative (**56**). Compound **56** was treated with 2-(*tert*-butoxycarbonylthio)-4,6-dimethylpyrimidine (8.2 g, 36.0 mmol) and triethylamine (7 mL, 50.3 mmol) in 1:1 1,4-dioxane–water (80 mL) for 16 h. Evaporation of the mixture gave a syrup containing **57** as the major component. The completely dry syrup was dissolved in dry acetone (100 mL). To the solution was added benzoyl chloride (13 mL, 112

mmol) and triethylamine (15.4 mL, 111 mmol) with stirring at −10°, and the temperature was maintained for 16 h. Water was added and the solution was extracted with chloroform. The extract was washed with water, dried, and evaporated to give a syrup that was purified on a column of silica gel with 9:1 benzene–acetone; yield of **58** from **34**, 75%, syrup, $[\alpha]_D$ +161.5°; ν_{max}^{NaCl} 3500 (OH), 3340 (NH), 1710 (ester and urethane), and 1630 cm^{-1} (alkene); n.m.r.: δ 5.70 (d, $J_{1,2}$ 3.3 Hz, H-1), 5.48 (dd, $J_{2,3}$ 10.5, $J_{3,4}$ 2.9 Hz, H-3), 1.29 (s, 9 H, Me_3C), 1.34 and 4.26 (t and q, respectively, Et), 6.23 (d, J 15.9 Hz, alkenic), and 7.0–8.2 (m, 15 H, aromatic).

Anal. Calc. for $C_{36}H_{39}NO_{11}$: C, 65.35; H, 5.94; N, 2.12. Found: C, 65.21; H, 6.08; N, 2.32.

Ethyl p-(*3,6-di-*O*-benzoyl-2-*(tert-*butoxycarbonyl*)*amino-2-deoxy-4-*O*-(methylsulfonyl)-α-*D*-galactopyranosyloxy*]*cinnamate* (**59**). — Compound **58** was mesylated conventionally to give **59** in 82% yield; m.p. 69–71°, $[\alpha]_D$ +159.6°; ν_{max}^{KBr} 3340 (NH), 1705 and 1680 (ester and urethane), and 1625 cm^{-1} (alkene); n.m.r.: δ 5.73 (d, $J_{1,2}$ 3.0 Hz, H-1), ~2.8 (m, H-2), 5.56 (dd, $J_{2,3}$ 9.8, $J_{3,4}$ 2.7 Hz, H-3), 5.43 (d, $J_{4,5}$ ~0 Hz, H-4), 3.11 (s, Ms), 1.31 (s, 9 H, Me_3C), 1.34 and 4.28 (t and q, respectively, Et), 6.24 (d, J 15.9 Hz, alkenic), and 7.0–8.2 (m, 15 H, aromatic).

Anal. Calc. for $C_{37}H_{41}NO_{13}S$: C, 60.07; H, 5.59; N, 1.89; S, 4.33. Found: C, 60.26; H, 5.62; N, 2.18; S, 4.59.

Ethyl p-[*4-azido-3,6-di-*O*-benzoyl-2-*(tert-*butoxycarbonyl*)*amino-2,4-dideoxy-α-*D*-glucopyranosyloxy*]*cinnamate* (**60**). — Compound **59** (2.87 g, 4.35 mmol) was treated with sodium azide (0.57 g, 8.77 mmol) in HMPA (40 mL) for 10 h at 80°. Isolation as described for **50** gave **60** in 77% yield; syrup, $[\alpha]_D$ +160.9°; ν_{max}^{NaCl} 3350 (NH), 2120 (N_3), 1720 (ester and urethan), and 1640 cm^{-1} (alkene); n.m.r.: δ 5.66 (d, $J_{1,2}$ 3.2 Hz, H-1), 4.48 (m, H-2), 5.84 (dd, $J_{2,3}$ 9.0, $J_{3,4}$ 10.5 Hz, H-3), 3.92 (t, $J_{4,5}$ 10.5 Hz, H-4), 4.58 (m, 2 H, H-6), 5.08 (d, $J_{2,NH}$ 10.2 Hz, NH), 1.20 (s, 9 H, Me_3C), 1.34 and 4.27 (t and q, respectively, Et), 6.30 (d, $_B$ 15.9 Hz, alkenic), and 7.0–8.2 (m, 15 H, aromatic).

Anal. Calc. for $C_{36}H_{38}N_4O_{10}$: C, 62.96; H, 5.58; N, 8.16. Found: C, 62.94; H, 5.49; N, 7.74.

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