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Reaction of Sugar Thiocyanates with Grignard Reagents. New Synthesis of Thioglycosides#

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Abstract: *Glycosyl thiocyanates having hydroxyl groups protected with acetyl or benzoyl groups react readily at -40°C with Grignard reagents to afford the corresponding alkyl or aryl thioglycosides in good yields. Monosaccharide derivatives having the SCN grouping at other positions form under similar conditions thioethers. Axial thiocyanates do not react. Elevated temperatures induce side reactions leading to mercaptans.*

INTRODUCTION

Alkyl or aryl thiocyanates have found up to now rather limited application in organic synthesis.[1-4] These compounds should be, however, useful in nucleophilic ("thiophilic") substitution at the sulfur atom.[3]

$$R\text{-}SCN + Nu^- \rightarrow R\text{-}SNu + CN^-$$

Adams, Bramlet and Tendick[5] published in 1920 a study of the reaction between alkyl or aryl thiocyanates and Grignard reagents. They have found that two reactions had occurred paralelly, the one leading to dialkyl sulfides, and the other leading to mercaptans and alkyl cyanides. The conclusion of this work was that: "the use of this reaction for the preparation of either thioethers or mercaptans can hardly be recommended because mixtures are always obtained and the separation of the two products by fractionation is necessary".[5] It is probable that this statement discouraged many chemists from using this reaction.

More than fifty years later Mąkosza and Fedoryński[6] have found that aliphatic and aromatic thiocyanates are effective alkyl- and arylthiolating agents reacting easily with carbanions generated in two-phase systems.

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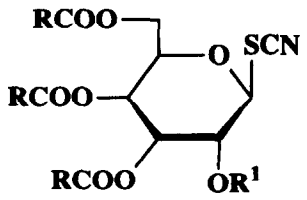
Sugar thiocyanates and, especially, glycosyl thiocyanates (**1**) are known since 1941.[7] These compounds have been employed to a limited extent in carbohydrate synthesis.[8] Recently Kochetkov and his coworkers[9-12] have proposed to use 1,2-*trans* glycosyl thiocyanates (**2**), having a non-participating group at C-2, for highly stereoselective 1,2-*cis* glycosylation.



1: R^1 = COR

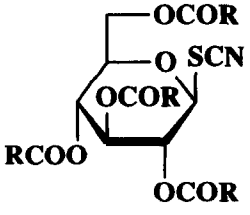
2: R^1 = Me, Bzl

In this work we would like to demonstrate that sugar thiocyanates are practical substrates for the synthesis of thioethers and, particularly, thioglycosides *via* the reaction with various Grignard reagents. Side reactions are negligible or can be largely eliminated by the proper choice of reaction conditions.

RESULTS

Monosaccharide thiocyanates can be readily obtained by a S_N2 reaction of p-toluenesulfonyl derivatives or glycosyl bromides with potassium thiocyanate.

Reaction of acetylated α-D-glucopyranosyl, α-D-galactopyranosyl, α-D-mannopyranosyl, and β-L-arabinopyranosyl bromides with KSCN in the presence of crown ether 18-c-6 yielded the corresponding 1,2-*trans* thiocyanates (**3a** - **6a**, 30 - 40%) accompanied by 8 - 18% of the isothiocyanates.[9] Thiocyanates **3a** - **6a** were purified by chromatography. The same procedure applied to benzoylated glycosyl bromides led to 1,2-*trans* thiocyanates (**3b** - **6b**) in far better yields of 70 - 88% with only a few per cent of the contaminating isothiocyanates.



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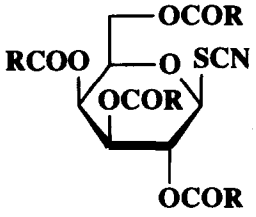

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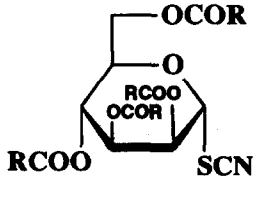

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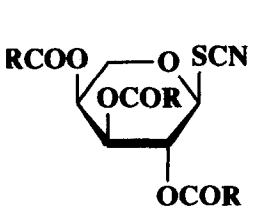

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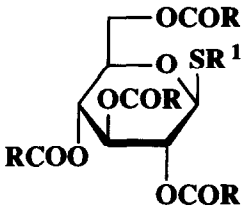
a: R = CH_3, **b**: R = C_6H_5

Acetylated glycosyl thiocyanates **3a** - **5a**, kept at low temperature, are stable during at least 1 month. Benzoylated derivatives (**3b** - **5b**) are even more stable. Thiocyanates of esterified L-arabinopyranose (**6a** and

6b) are stable during only a few days.

Tetrahydrofuran solutions of glycosyl thiocyanates (**3a,b** - **6a,b**) were next reacted at -40°C with an excess (ca. 3 mol. equiv.) of Grignard reagents in ether. The time of the reaction was short: in case of acetylated derivatives ca. 5 minutes and ca. 10 minutes in case of benzoylated derivatives. The work-up consisted in decomposition of the excessive Grignard reagent at low temperature with sat. aqueous ammonium chloride, addition of silicagel, evaporation of the suspension to dryness under diminished pressure, and isolation of the product on a silicagel column with hexane - ethyl acetate (2 : 1) as eluent.

Thiocyanates of β-D-glucopyranose, β-D-galactopyranose, and α-L-arabinopyranose gave alkyl or aryl thioglycosides (**7a,b** - **24a,b**) in good yields. Configuration of the thiocyanate was fully preserved in the thioglycosides. No side products, derived from the reaction of the ester groupings with the Grignard reagents were observed, most probably due to the low temperature and the short reaction time. Isopropylmagnesium iodide, a single secondary Grignard reagent employed, did not react with the thiocyanates. Also, peracetylated and perbenzoylated α-D-mannopyranosyl thiocyanates (**5a** and **5b**) remained unchanged on treatment with all Grignard reagents.



7: $R^1 = Me$

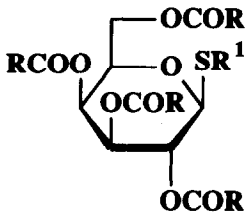
8: $R^1 = Et$

9: $R^1 = {}^nBu$

10: $R^1 = {}^iBu$

11: $R^1 = Bzl$

12: $R^1 = Ph$



13: $R^1 = Me$

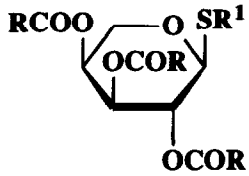
14: $R^1 = Et$

15: $R^1 = {}^nBu$

16: $R^1 = {}^iBu$

17: $R^1 = Bzl$

18: $R^1 = Ph$



19: $R^1 = Me$

20: $R^1 = Et$

21: $R^1 = {}^nBu$

22: $R^1 = {}^iBu$

23: $R^1 = Bzl$

24: $R^1 = Ph$

a: $R = CH_3$, **b**: $R = C_6H_5$

Thioglycosides obtained were readily identified on the basis of ^{1}H-NMR spectral data and, whenever possible, by comparison of the physicochemical data with the literature values. Signal of the anomeric proton in acetylated derivatives was found at δ 4.3 - 4.7 ($J_{1,2}$ 9.6 - 10.0 Hz for **7a** - **18a** and $J_{1,2}$ 7.7 - 8.7 Hz for **19a** - **24a**) and δ 4.7 - 5.0 ($J_{1,2}$ 9.8 - 10.0 Hz for **7b** - **18b** and $J_{1,2}$ 7.3 - 7.9 Hz for **19b** - **24b**) in benzoylated derivatives. The data are collected in the **Table 1**.

Failure of the α-D-mannopyranosyl thiocyanate in the substitution reaction prompted us to investigate the reactivity of sugar derivatives having the SCN grouping at other positions than at C-1. From

TABLE 1
Reaction of glycosyl thiocyanate **3**, **4**, and **6** with Grignard reagents

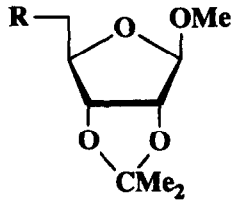
Entry	RMgX	Prod.[a] No	Yield (%)[b]	^{1}H-NMR: δ[c]		$[\alpha]_D$ (c)[d]	m.p.[e] (°C)	literature data		
				H-1	$J_{1,2}$ (Hz)			$[\alpha]_D$ (c)	m.p. (°C)	lit.
1	MeMgI	**7a**	63	4.40	9.7	-11.9 (0.7)	90 - 91	-12.0 (1.0)	96	14
2	EtMgBr	**8a**	91	4.50	10.0	-24.4 (1.1)	80 - 81	-24.4 (1.16)	81 - 82	15
3	EtMgBr	**8b**	79	4.82	10.0	+27.3 (1.1)		+27 (1.8)		18
4	^{n}BuMgBr	**9a**	65	4.48	9.9	-27.2 (0.8)	68 - 69	-25 (1.11)	67 - 68	15
5	^{n}BuMgBr	**9b**	67	4.82	9.9	+47.2 (1.6)				
6	^{i}BuMgBr	**10a**	31	4.46	9.8	-22.0 (0.6)	90 - 91	-2.03 (0.98)	93 - 94	16
7	^{i}BuMgBr	**10b**	30	4.82	9.9	+15.9 (2.7)				
8	BzlMgCl	**11a**	81	4.28	9.6	-84.4 (1.1)	103 - 104	-90.8 (1.01)	100 - 101	15
9	BzlMgCl	**11b**	76			+23.2 (1.6)				
10	PhMgBr	**12a**	66	4.70	10.0	-15.1 (1.5)	115 - 116	-16.5 (0.61)	113 - 114	16
11	PhMgBr	**12b**	74	4.85	9.9	+5.4 (1.3)		+34		22
12	MeMgI	**13a**	21	4.39	9.8	+4.9 (1.1)	85 - 86	+4.3 (1)	110 - 111	14
13	MeMgI	**13b**	31	4.69	9.9	+97.2 (0.6)				
14	EtMgBr	**14a**	61	4.50	9.8	-10.5 (0.9)		-8.0 (1.0)		14
15	EtMgBr	**14b**	78	4.80	9.8	+145.3 (2.1)				
16	^{n}BuMgBr	**15a**	48	4.48	9.8	-8.3 (0.7)		-11.6 (0.86)		16
17	^{n}BuMgBr	**15b**	50	4.84	10.0	+25.7 (0.2)				
18	^{i}BuMgBr	**16a**	34	4.46	9.8	-4.8 (0.5)		-10.6 (0.94)		16
19	^{i}BuMgBr	**16b**	29	4.82	9.9	+32.8 (0.5)				

TABLE 1
continued

20	BzlMgCl	**17a**	72	4.29	10.0	-66.5 (0.9)	95 - 96	-67.5 (0.75)	95 - 96	16
21	BzlMgCl	**17b**	71	4.83	9.8	+4.4 (0.5)				
22	PhMgBr	**18a**	71	4.72	9.8	+4.9 (0.8)		+3.0 (0.5)		17
23	PhMgBr	**18b**	85	5.02	9.8	+151.4 (4.1)				
24	MeMgI	**19a**	49	4.39	8.7	+8.2 (0.7)	74 - 75			
25	MeMgI	**19b**	32	4.79	7.9	+116.3 (1.0)				
26	EtMgBr	**20a**	50	4.52	8.3	-4.8 (0.8)	70 - 71			
27	EtMgBr	**20b**	74	4.97	7.5	+213.6 (1.8)				
28	^{n}BuMgBr	**21b**	57	4.88	7.5	+94.1 (0.7)				
29	^{i}BuMgBr	**22b**	59	4.89	7.5	+58.3 (0.4)				
30	BzlMgCl	**23a**	59	4.36	8.4	-57.2 (0.8)				
31	BzlMgCl	**23b**	87	4.92	7.3	+132.6 (0.5)				
32	PhMgBr	**24a**	62	4.82	7.7	+6.4 (0.8)				
33	PhMgBr	**24b**	72			+306.9 (2.3)				

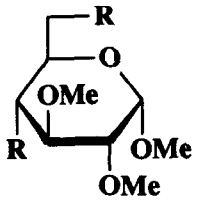
[a] All products gave correct m/z values for LSIMS $(M+H)^+$ ions.
[b] Isolated yields after chromatography
[c] All spectra were recorded in $CDCl_3$ solution.
[d] In chloroform at 22 ± 2°C.
[e] Crystallized from ethanol.

p-toluenesulfonyl esters **25** - **27** the corresponding thiocyanates **28** - **30** have been prepared in very good yields.



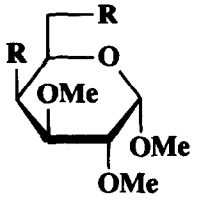
25: R = OTs

28: R = SCN



27: R = OTs

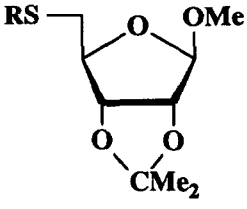
29: R = SCN



26: R = OTs

30: R = SCN

Methyl 5-deoxy-2,3-O-isopropylidene-5-thiocyanato-β-D-ribofuranoside (**28**) reacted readily at low temperature (-40°C), within 20 min, with ethyl, n-butyl, and phenylmagnesium bromides to give the corresponding 5-alkylthioethers in good yields (**Table 2**, Entries 7, 11, and 15) . At room temperature methylmagnesium iodide furnished the 5-methylthio derivative in only 28% yield (entry 5). When the reactions mixtures with methylmagnesium iodide, ethyl and phenylmagnesium bromides, and benzylmagnesium chloride were refluxed, besides the corresponding 5-alkyl(aryl)thio derivatives some formation of 5-mercapto derivative **39**, and, in a single case, of disulfide **40**, was also observed (entries 4, 6, 14, and 16); under these conditions isopropylmagnesium iodide, n-butyl, and isobutylmagnesium bromides yielded cleanly 5-alkylthioethers (entries 8, 10, and 12). For comparison purposes compounds **39** and **40** have been synthesized independently from **28** (see Experimental).



31: R = Me

32: R = Et

33: R = ^{i}Pr

34: R = ^{n}Bu

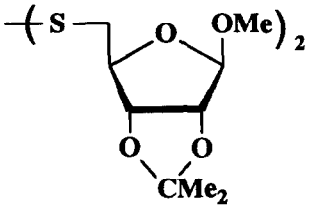
35: R = ^{i}Bu

36: R = Bzl

37: R = Ph

38: R = ^{t}Bu

39: R = H



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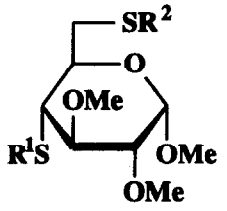
In contrast, the reaction of **28** with alkyllithium reagents required only 5 min at -78°C and led to the corresponding alkylthioethers in good yields (entries 1-3).

TABLE 2
Reactions of methyl 5-deoxy-2,3-O-isopropylidene-5-thiocyanato-β-D-ribofuranoside (**28**) with organolithium and organomagnesium compounds

Entry	Organometallic reagent	Reaction conditions	Product	Yield [%][a]
1	^{n}BuLi	-78°C, 5 min, THF	**34**	74
2	CH_3Li	-78°C, 5 min, THF	**31**	90
3	^{t}BuLi	-78°C, 5 min, THF	**38**	40
4	MeMgI	reflux, 10 min, Et_2O	mixture of **31** and **39**	
5	MeMgI	r.t., 20 min, Et_2O	**31**	28
6	EtMgBr	reflux, 10 min, Et_2O	mixture of **32** and **39**	
7	EtMgBr	-40°C, 20 min, Et_2O/THF	**32**	57
8	^{i}PrMgI	reflux, 10 min, Et_2O	**33**	97
9	^{i}PrMgI	-40°C, 1 h, Et_2O/THF	no reaction	
10	^{n}BuMgBr	reflux, 10 min, Et_2O	**34**	65
11	^{n}BuMgBr	-40°C, 20 min, Et_2O/THF	**34**	97
12	^{i}BuMgBr	reflux, 10 min, Et_2O	**35**	70
13	^{i}BuMgBr	-40°C, 20 min, Et_2O/THF	**32** **28**	38 54
14	PhMgBr	reflux, 10 min, Et_2O	mixture of **37** and **39**	
15	PhMgBr	-40°C, 20 min, Et_2O/THF	**37**	68
16	$PhCH_2MgCl$	reflux, 10 min, Et_2O	mixture of **36**, **39** and **40**	
17	$PhCH_2MgCl$	-40°C, 20 min, Et_2O/THF	**36** and unknown products	7

[a] Isolated yields after chromatography.

Reactions of methyl 4,6-dideoxy-2,3-di-O-methyl-4,6-di(thiocyanato)-α-D-glucopyranoside (**29**) with ethyl, n-butyl, and phenylmagnesium bromides at -40°C during 20 min led to 4,6-di-alkyl(aryl)thioethers in good yields (**Table 3**, entries 1, 4, and 7). Secondary Grignard reagent, isopropylmagnesium iodide, gave at low temperature as well as at 0°C mixtures of 4,6-di(isopropylthio)- and 6-isopropylthio-ethers; a few per cent of the substrate remained unchanged (entries 2 and 3). The result of the reaction of **29** with isobutylmagnesium bromide was similar (entries 5 and 6).



41: $R^1 = R^2 = Et$

42: $R^1 = R^2 = {}^iPr$

43: $R^1 = SCN$, $R^2 = {}^iPr$

44: $R^1 = R^2 = {}^nBu$

45: $R^1 = R^2 = {}^iBu$

46: $R^1 = SCN$, $R^2 = {}^iBu$

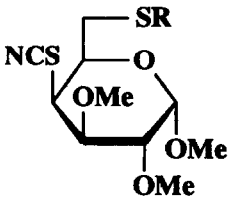
47: $R^1 = R^2 = Ph$

TABLE 3
Reactions of methyl 4,6-dideoxy-2,3-di-O-methyl-4,6-di(thiocyanato)-α-D-glucopyranoside (**29**) with organomagnesium compounds

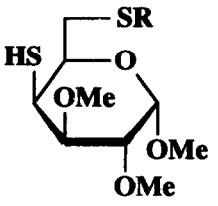
Entry	Grignard reagent	Reaction conditions	Product	Yield [%][a]
1	EtMgBr	-40°C, 20 min, Et_2O/THF	**41**	86
2	^iPrMgI	-40°C, 20 min, Et_2O/THF	**42** **43** **29**	23 31 29
3	^iPrMgI	0°C, 20 min, Et_2O/THF	**42** **43** **29**	35 25 9
4	^nBuMgBr	-40°C, 20 min, Et_2O/THF	**44**	83
5	^iBuMgBr	-40°C, 20 min, Et_2O/THF	**45** **46**	31 57
6	^iBuMgBr	0°C, 20 min, Et_2O/THF	**45** **46**	63 19
7	PhMgBr	-40°C, 20 min, Et_2O/THF	**47**	86

[a] Isolated yields after chromatography.

Reactions of methyl 4,6-dideoxy-2,3-di-O-methyl-4,6-di(thiocyanato)-α-D-galactopyranoside (**30**) with the Grignard reagents were essentially uniform: at -40°C during 20 min reacted only the 6-thiocyanate giving the 6-alkyl(aryl)thioethers in good yields and leaving the 4-SCN grouping intact (**Table 4**). When the reaction of **30** with n-butylmagnesium bromide was performed at 0°C, 4-mercapto derivative **52** was obtained as the single product in a good yield (entry 4).



48: R = Et
49: R = ^{i}Pr
50: R = ^{n}Bu
51: R = Ph



52: R = ^{n}Bu

TABLE 4
Reactions of methyl 4,6-dideoxy-2,3-di-O-methyl-4,6-di(thiocyanato)-α-D-galactopyranoside (**30**) with organomagnesium compounds

Entry	Grignard reagent	Reaction conditions	Product	Yield [%][a]
1	EtMgBr	-40°C, 20 min, Et_2O/THF	**48**	61
2	^{i}PrMgI	-40°C, 20 min, Et_2O/THF	**49** **30**	26 46
3	^{n}BuMgBr	-40°C, 20 min, Et_2O/THF	**50**	38
4	^{n}BuMgBr	0°C, 20 min, Et_2O/THF	**52**	73
5	PhMgBr	-40°C, 20 min, Et_2O/THF	**51**	72

[a] Isolated yields after chromatography.

The conclusions of this study can be summarized as follows:

1. Thiocyanate grouping is very reactive against simple, primary Grignard reagents. Substitution at the sulfur atom occurs readily at low temperature and in a short time leading cleanly to thioethers. In case of glycosyl thiocyanates this route leads efficiently to thioglycosides, a valuable class of sugar derivatives. From a single thiocyanate a variety of thioglycosides or thioethers can be obtained. It is important to note that alkyl and aryl thioglycosides are gaining interest as glycosylating agents in the synthesis of oligosaccharides[13].
2. Higher temperatures (0°C or reflux temperatures) can lead - in accord with Adams[5] observations - to side products (mercaptans).
3. The reaction is susceptible to conformational factors: whereas equatorial thiocyanate reacts readily, the axial thiocyanate grouping does not undergo nucleophilic substitution, at least, under the mild reaction conditions employed.
4. Isopropylmagnesium iodide and isobutylmagnesium bromide are less reactive than Grignard reagents obtained from simple primary alkyl bromides.
5. ***From the preparative point of view it is important to note that all operations in this method leading to thioglycosides are completely odorless!***

EXPERIMENTAL

General methods. All manipulations on organometallic reagents were performed under argon. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from $LiAlH_4$ prior to use. Butyllithium was used as a 1.6M solution in hexane, tert-butyllithium as 1.4M solution in pentane, and methyllithium as 1.6M solution in ethyl ether. Grignard reagents were used as a 1M solution in ether. Optical rotations were measured with a JASCO DIP-360 automatic polarimeter. TLC was performed on Silica Gel HF-254 and column chromatography on Silica Gel 230 - 400 mesh (Merck). NMR spectra were recorded with a Bruker AM-500 (500 MHz) and Varian AC-200 (200 MHz) spectrometers in $CDCl_3$ with Me_4Si as internal standard. High resolution mass spectra (HR-MS) were measured with AMD-604 mass spectrometer. IR spectra were recorded on a Perkin - Elmer 1640 FT - IR spectrophotometer. Compound **3a** was prepared according to literature.[9]

Preparation of glycosyl thiocyanates (3 - 6). General procedure.

A mixture of glycosyl bromide (10.0 mM), potassium thiocyanate (30.0 mM) and crown ether (18-c-6, 300 mg) in acetone (25 mL) was stirred for 7 h. The mixture was filtered through Celite and concentrated to dryness. Column chromatography (hexane - ethyl acetate, 2 : 1) of the residue gave pure glycosyl thiocyanates.

2,3,4,6-Tetra-O-benzoyl-β-D-glucopyranosyl thiocyanate (**3b**), yield 5.48 g (83%); m.p. 146 - 147°C; $[\alpha]_D^{20}$ +46° (*c* 0.8, chloroform); ν_{max} (KBr): 2164 cm^{-1}. ^1H NMR: δ 5.81 (t, 1H, $J_{4,3}$ 9.5, $J_{4,5}$ 10.5 Hz, H-4), 5.42 - 5.67 (m, 2H, H-2,3), 4.93 (d, 1H, $J_{1,2}$ 9.7 Hz, H-1), 4.44 - 4.82 (m, 3H, H-5,6,6'). ^{13}C NMR: δ 108.04 (SCN), 83.89 (C-1), 73.26, 71.17, 68.60, 62.59 and 60.34. HR-MS/LSIMS $C_{35}H_{28}NNaO_9S$ $(M+Na)^+$. Calc.: 660.1304. Found: 660.1309.

2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl thiocyanate (**4a**), yield 1.44 g (37%); m.p. 108 - 110°C; $[\alpha]_D^{20}$ +3° (*c* 1.2, chloroform); ν_{max} (KBr): 2160 cm^{-1}. ^1H NMR: δ 5.46 (dd, 1H, $J_{4,3}$ 3.3, $J_{4,5}$ 0.9 Hz, H-4), 5.35 (t, 1H, H-2), 5.10 (dd, 1H, $J_{3,2}$ 10.0 Hz, H-3), 4.90 (d, 1H, $J_{1,2}$ 9.7 Hz, H-1), 4.04 - 4.24 (m, 3H, H-5,6,6'), 2.19, 2.17, 2.07 and 2.01 (4s, 12H, 4 × OAc). ^{13}C NMR: δ 108.14 (SCN), 84.11 (C-1), 75.78, 71.21, 67.95, 66.73, 61.15, 20.66, 20.59, 20.51. HR-MS/LSIMS $C_{15}H_{19}NNaO_9S$ $(M+Na)^+$. Calc.: 412.0682. Found: 412.0678.

2,3,4,6-Tetra-O-benzoyl-β-D-galactopyranosyl thiocyanate (**4b**), yield 5.81 g (88%); $[\alpha]_D^{20}$ +10° (*c* 0.1, chloroform); ν_{max} (KBr): 2164 cm^{-1}. ^1H NMR: δ 6.21 (dd, 1H, $J_{4,3}$ 3.8, $J_{4,5}$ 1.2 Hz, H-4), 5.84 (t, 1H, $J_{1,2}$ = $J_{2,3}$ = 9.9 Hz, H-2), 5.68 (dd, 1H, $J_{3,2}$ 10.0 Hz, H-3), 4.82 (d, 1H, H-1), 4.67 (m, 1H, H-5), 4.43 (m, 1H, H-6), 4.32 (m, 1H, H-6'). ^{13}C NMR: δ 108.21 (SCN), 83.78 (C-1), 71.98, 68.82, 67.71, 61.87 and 60.34. HR-MS/LSIMS $C_{35}H_{28}NNaO_9S$ $(M+Na)^+$. Calc.: 660.1304. Found: 660.1296.

2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyl thiocyanate (**5a**), yield 1.17 g (30%); $[\alpha]_D^{20}$ +152° (*c* 0.8, chloroform); ν_{max} (KBr): 2162 cm^{-1}. ^1H NMR: δ 5.91 (dd, 1H, $J_{1,2}$ 1.8, $J_{1,5}$ 0.7 Hz, H-1), 5.32 - 5.36 (m, 2H, H-2,4), 5.18 (dd, 1H, $J_{3,2}$ 3.5, $J_{3,4}$ 9.6 Hz, H-3), 4.39 (dd, 1H, $J_{6,5}$ 6.0, $J_{6,6'}$ 12.4 Hz, H-6), 4.26 (m, 1H, $J_{5,6'}$ 2.3, $J_{5,4}$ 9.8 Hz, H-5), 4.18 (dd, 1H, H-6'), 2.19, 2.12, 2.09 and 2.02 (4s, 12H, 4 × OAc). ^{13}C NMR: δ 107.50 (SCN), 84.57 (C-1), 72.11, 68.76, 68.22, 65.31, 61.43, 20.60, 20.57, 20.54, 20.42. HR-MS/LSIMS $C_{15}H_{19}NNaO_9S$ $(M+Na)^+$. Calc.: 412.0682. Found: 412.0688.

2,3,4,6-Tetra-O-benzoyl-α-D-mannopyranosyl thiocyanate (**5b**), yield 4.69 g (71%); $[\alpha]_D^{20}$ +29° (*c* 0.5, chloroform); ν_{max} (KBr): 2164 cm^{-1}. ^1H NMR: δ 5.93 (dd, 1H, H-1), 5.28 - 5.36 (m, 2H, H-2,4), 5.24 (dd, 1H, $J_{3,2}$ 3.5, $J_{3,4}$ 9.7 Hz, H-3), 4.39 (dd, 1H, $J_{6,5}$ 6.0, $J_{6,6'}$ 12.4 Hz, H-6), 4.25 (m, 1H, $J_{5,6'}$ 2.3, $J_{5,4}$ 9.8 Hz, H-5), 4.18 (dd, 1H, H-6'). ^{13}C NMR: δ 108.17 (SCN), 83.52 (C-1), 74.01, 71.25, 68.25, 62.94 and 61.27. HR-MS/LSIMS $C_{35}H_{28}NNaO_9S$ $(M+Na)^+$. Calc.: 660.1304. Found: 660.1307.

2,3,4-Tri-O-acetyl-α-L-arabinopyranosyl thiocyanate (**6a**), yield 1.05 g (33%); $[\alpha]_D^{20}$ -70° (*c* 1.5, chloroform); ν_{max} (KBr): 2164 cm^{-1}. ^1H NMR: δ 5.19 - 5.38 (m, 4H, H-1,2,3,4), 4.16 (dd, 1H, $J_{5,4}$ 6.4, $J_{5,5'}$ 12.4 Hz, H-5), 3.85 (dd, 1H, $J_{5',4}$ 3.2 Hz, H-5'), 2.15, 2.12 and 2.11 (3s, 9H, 3 × OAc). ^{13}C NMR: δ 109.50 (SCN), 85.08 (C-1), 69.04, 68.55, 65.86, 63.82, 20.75, 20.62. HR-MS/LSIMS $C_{12}H_{15}NNaO_7S$ $(M+Na)^+$. Calc.: 340.0467. Found: 340.0466.

2,3,4-Tri-O-benzoyl-α-L-arabinopyranosyl thiocyanate (**6b**), yield 3.89 g (74%); $[\alpha]_D^{20}$ +6° (*c* 0.6, chloroform); ν_{max} (KBr): 2162 cm^{-1}. ^1H NMR: δ 5.83 (d, 1H, H-2), 5.71 (m, 1H, H-4), 5.63 (dd, 1H, H-3), 4.92 (d, 1H, H-1), 4.42 (dd, 1H, $J_{5,4}$ 3.8, $J_{5,5'}$ 12.8 Hz, H-5), 3.98 (dd, 1H, $J_{5',4}$ 2.0 Hz, H-5'). ^{13}C NMR: δ 108.11 (SCN), 82.57 (C-1), 69.33, 66.81, 64.09 and 60.38. HR-MS/LSIMS $C_{27}H_{21}NNaO_7S$ $(M+Na)^+$. Calc.: 504.1117. Found: 504.1121.

Methyl 5-deoxy-2,3-O-isopropylidene-5-thiocyanato-β-D-ribofuranoside (**28**)

To a solution of methyl 2,3-O-isopropylidene-5-O-(p-toluenosulfonyl)-β-D-ribofuranoside[19] (**25**, 10.7 g, 30 mM) in DMF (150 mL) was added potassium thiocyanate (15.5 g, 160 mM), and the mixture was heated at 120 - 130°C for 6 h. The mixture was cooled to r.t., water (100 mL) was added, and product was extracted with dichloromethane (4 × 100 mL). Combined organic extracts were washed with water (100 mL) and dried over $MgSO_4$. The solvents were evaporated. Column chromatography (hexane - acetone, 6 : 1) of the residue gave **28** (6.7 g, 91%), m.p. 48 - 49°C; $[\alpha]_D^{20}$ -42° (*c* 1.7, chloroform); ν_{max} (KBr): 2151 cm^{-1}. ^1H NMR: δ 5.01 (s, 1H, H-1), 4.71 (dd, 1H, $J_{3,2}$ 5.9, $J_{3,4}$ 0.6 Hz, H-3), 4.64 (d, 1H, H-2), 4.42 (m, 1H, H-4), 3.38 (s, 3H, OCH_3), 3.19 (dd, 1H, $J_{5,4}$ 7.9, $J_{5,5'}$ 13.1 Hz, H-5), 3.08 (dd, 1H, $J_{5',4}$ 7.3 Hz, H-5'), 1.49 and 1.33 (2s, 6H, CMe_2). ^{13}C NMR: δ 113.01 (CMe_2), 111.41 (SCN), 109.94 (C-1), 85.11 (C-2), 85.01 (C-4), 82.79 (C-3), 55.51 (OCH_3), 37.20 (C-5), 26.34 and 24.92 (CMe_2). HR-MS/EI $C_9H_{12}NO_4S$ $(M-CH_3)^+$. Calc.: 230.0487. Found: 230.0486.

Methyl 2,3-di-O-methyl-4,6-di-O-(p-toluenesulfonyl)-α-D-galactopyranoside (**26**)

To a solution of methyl 2,3-di-O-methyl-α-D-galactopyranoside[20] (930 mg, 4.2 mM) in pyridine (10 mL), p-toluenesulfonyl chloride (3.8 g, 20.0 mM) was added and the mixture was stirred for 5 days at room temperature. Solvents were evaporated. Column chromatography (hexane - ethyl acetate, 1 : 1) of the residue gave **26** (1.93 g, 87%), syrup, $[\alpha]_D^{20}$ +156° (*c* 1.1, chloroform). ^1H NMR: δ 5.04 (d, 1H, $J_{1,2}$ 2.9 Hz, H-1), 4.81 (d, 1H, $J_{4,3}$ 3.5 Hz, H-4), 4.11 (m, 3H, H-5,6,6'), 3.52 (dd, 1H, $J_{2,3}$ 10.1 Hz, H-2), 3.40 and 3.23 (2s, 6H, 2 × OCH_3), 3.39 (m, 4H, H-3, OCH_3), 2.46 and 2.44 (2s, 6H, 2 × $CH_3C_6H_4$). HR-MS/LSIMS $C_{23}H_{30}NaO_{10}S_2$ $(M+Na)^+$. Calc.: 553.1178. Found: 553.1177.

Methyl 4,6-dideoxy-2,3-di-O-methyl-4,6-di(thiocyanato)-α-D-glucopyranoside (**29**)

To a solution of **26** (1.90g, 3.6 mM) in DMF (20 mL) potassium thiocyanate (4.0 g, 41 mM) was

added, and the mixture was heated at 120 - 130°C for 8 h. The mixture was cooled to r.t., water (100 mL) was added, and the product was extracted with dichloromethane (3 x 50 mL). Combined organic extracts were washed with water (100 mL) and dried over $MgSO_4$. The solvents were evaporated. Column chromatography (hexane - ethyl acetate, 2 : 1) of the residue gave **29** (807 mg, 74%), $[\alpha]_D^{20}$ +43° (*c* 0.6, chloroform); ν_{max} (film): 2155 cm^{-1}. ^1H NMR: δ 4.93 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.17 (m, 1H, H-5), 3.70, 3.56 and 3.51 (3s, 9H, 3 x OCH_3), 3.66 (dd, 1H, $J_{3,2}$ 9.2, $J_{3,4}$ 10.4 Hz, H-3), 3.57 (dd, 1H, $J_{6,5}$ 2.7, $J_{6,6'}$ 13.9 Hz, H-6), 3.30 (m, 2H, $J_{6',5}$ 7.0 Hz, H-2,6'), 2.83 (t, 1H, $J_{4,5}$ 10.4 Hz, H-4). ^{13}C NMR: δ 111.56 and 108.38 (SCN), 97.76 (C-1), 82.93 (C-2), 78.83 (C-3), 68.90 (C-5), 62.01, 59.19 and 56.07 (OCH_3), 51.25 (C-4), 36.39 (C-6). HR-MS/EI: $C_{10}H_{13}N_2O_3S_2$ $(M\text{-}OCH_3)^+$. Calc.: 273.0368. Found: 273.0368.

Methyl 4,6-dideoxy-2,3-di-O-methyl-4,6-di(thiocyanato)-α-D-galactopyranoside (**30**)[21]

Compound **30** was obtained from methyl 2,3-di-O-methyl-4,6-di-O-(p-toluenesulfonyl)-α-D-glucopyranoside[21] (**27**, 2.65 g, 5.0 mM) according to the previous method. Yield 1.20 g (79%) of **30**, m.p. 90 - 92°C; $[\alpha]_D^{20}$ +200° (*c* 0.6, chloroform); [lit.[21]: m.p. 91 - 92°C; $[\alpha]_D^{20}$ +182° (*c* 0.4, chloroform)]; ν_{max} (film) 2152 cm^{-1}. ^1H NMR: δ 4.88 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.39 (ddd, 1H, $J_{5,4}$ 1.6, $J_{5,6}$ 9.3, $J_{5,6'}$ 3.8 Hz, H-5), 4.10 (dd, 1H, $J_{4,3}$ 4.1 Hz, H-4), 3.90 (dd, 1H, $J_{3,2}$ 9.8 Hz, H-3), 3.55, 3.54 and 3.53 (3s, 9H, 3 x OCH_3), 3.37 (dd, 1H, H-2), 3.36 (dd, 1H, $J_{6,6'}$ 13.9 Hz, H-6), 3.25 (dd, 1H, H-6'). ^{13}C NMR: δ 111.51 and 111.19 (SCN), 98.15 (C-1), 77.72 (C-3), 77.19 (C-2), 67.49 (C-5), 59.55, 57.91 and 56.03 (OCH_3), 55.18 (C-4), 35.94 (C-6). HR-MS/EI: $C_{11}H_{17}N_2O_4S_2$ $(M+H)^+$. Calc.: 305.0630. Found: 305.0626.

Preparation of thioglycosides. General procedure.

To a solution of a glycosyl thiocyanate (0.25 mM) in THF (2 mL) cooled to -40°C an excess of a Grignard reagent (0.75 mM) was added. After 5 min. (in case of acetylated derivatives) or 10 min. (in case of benzoylated derivatives) the reaction was quenched by adding saturated ammonium chloride (0.2 mL), whereupon silica gel (3 g) was added, and the suspension was concentrated under diminished pressure. Column chromatography (hexane - ethyl acetate, 2 : 1) of the residue gave pure thioglycoside. Physical properties and yields of the thioglycosides are given in **Table 1**. The ^1H NMR signals of the sugar part in alkyl(aryl)thioglucopyranosides were similar. For illustration full data for **8a**, **8b**, **14a**, **14b**, **20a** and **20b** are given below:

Ethyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranoside (**8a**), $[\alpha]_D^{20}$ -24° (*c* 1.1, chloroform). ^1H NMR: δ 4.99 - 5.28 (m, 3H, H-2,3,4), 4.50 (d, 1H, $J_{1,2}$ 10.0 Hz, H-1), 4.25 (dd, 1H, $J_{6,5}$ 4.8, $J_{6,6'}$ 12.4 Hz, H-6), 4.14 (dd, 1H, $J_{6',5}$ 2.4 Hz, H-6'), 3.72 (m, 1H, $J_{5,4}$ 9.9 Hz, H-5), 2.71 (m, 2H, CH_2), 2.08, 2.06, 2.03, 2.01 (4s, 12H, 4 x OAc), 1.28 (t, 3H, *J* 7.5 Hz, CH_3). MS/LSIMS: 807 $(2M+Na)^+$, 785 $(2M+H)^+$, 723 $(2M+H\text{-}SEt)^+$, 415 $(M+Na)^+$, 393 $(M+H)^+$.

Ethyl 2,3,4,6-tetra-O-benzoyl-1-thio-β-D-glucopyranoside (**8b**), $[\alpha]_D^{20}$ +27° (*c* 1.1, chloroform). ^1H NMR: δ 5.93 (t, 1H, H-4), 5.64 (dd, 1H, $J_{3,2}$ 9.9, $J_{3,4}$ 9.5 Hz, H-3), 5.40 (t, 1H, H-2), 4.82 (d, 1H, $J_{1,2}$ 10.0 Hz, H-1), 4.40 - 4.64 (m, 3H, H-5,6,6'), 2.73 (q, 2H, CH_2), 1.21 (t, 3H, CH_3). MS/LSIMS: 663 $(M+Na)^+$, 641 $(M+H)^+$.

Ethyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside (**14a**), $[\alpha]_D^{22}$ -11° (*c* 0.9, chloroform). ^{1}H NMR: δ 5.43 (dd, 1H, $J_{4,3}$ 3.3, $J_{4,5}$ 1.1 Hz, H-4), 5.24 (t, 1H, H-2), 5.05 (dd, 1H, $J_{3,2}$ 10.0 Hz, H-3), 4.50 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1), 4.14 (m, 2H, H-6,6'), 3.93 (m, 1H, H-5), 2.73 (m, 2H, CH_2), 2.16, 2.07, 2.05, 1.99 (4s, 12H, 4 × OAc), 1.29 (t, 3H, *J* 7.5 Hz, CH_3). MS/LSIMS: 415 $(M+Na)^+$, 391 $(M-H)^+$.

Ethyl 2,3,4,6-tetra-O-benzoyl-1-thio-β-D-galactopyranoside (**14b**), $[\alpha]_D^{22}$ +145° (*c* 2.1, chloroform). ^{1}H NMR: δ 6.04 (d, 1H, $J_{4,3}$ 3.3, H-4), 5.85 (t, 1H, H-2), 5.66 (dd, 1H, $J_{3,2}$ 9.9 Hz, H-3), 4.80 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1), 4.65 (m, 1H, H-5), 4.38 (m, 2H, H-6,6'), 2.84 (q, 2H, *J* 7.5 Hz, CH_2), 1.32 (t, 3H, CH_3). MS/LSIMS: 663 $(M+Na)^+$, 641 $(M+H)^+$.

Ethyl 2,3,4-tri-O-acetyl-1-thio-α-L-arabinopyranoside (**20a**), $[\alpha]_D^{22}$ -5° (*c* 0.8, chloroform). ^{1}H NMR: δ 5.29 (m, 1H, H-4), 5.24 (t, 1H, H-2), 5.07 (dd, 1H, $J_{3,2}$ 8.9, $J_{3,4}$ 3.6 Hz, H-3), 4.52 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.10 (dd, 1H, $J_{5,4}$ 3.5, $J_{5,5'}$ 12.9 Hz, H-5), 3.68 (dd, 1H, $J_{5',4}$ 1.9 Hz, H-5'), 2.72 (m, 2H, CH_2), 2.14, 2.09, 2.04 (3s, 9H, 3 × OAc), 1.28 (t, 3H, *J* 7.4 Hz, CH_3). MS/LSIMS: 663 $(2M+Na)^+$, 641 $(2M+H)^+$, 343 $(M+Na)^+$, 321 $(M+H)^+$.

Ethyl 2,3,4-tri-O-benzoyl-1-thio-α-L-arabinopyranoside (**20b**), $[\alpha]_D^{22}$ +214° (*c* 1.8, chloroform). ^{1}H NMR: δ 5.62 - 5.85 (m, 3H, H-2,3,4), 4.97 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.42 (dd, 1H, $J_{5,4}$ 4.4, $J_{5,5'}$ 12.8 Hz, H-5), 3.95 (dd, 1H, $J_{5',4}$ 1.2 Hz, H-5'), 2.80 (q, 2H, *J* 7.1 Hz, CH_2), 1.26 (t, 3H, CH_3). MS/LSIMS: 529 $(M+Na)^+$, 507 $(M+H)^+$.

*Reaction of **28** with organolithium derivatives. General procedure.*

To a solution of **28** (245 mg, 1.0 mM) in THF (5 mL), cooled to -78°C, organolithium reagent (3.0 mM) was added. The mixture was stirred for 5 min. Methanol (1 mL) was added and the mixture was allowed to attain room temp. The solution was concentrated to dryness. Column chromatography (hexane - ethyl acetate, 10 : 1) of the residue gave products, yields of which are given in **Table 2.**

*Reaction of **28** with organomagnesium derivatives. General procedure.*

To a solution of **28** (123 mg, 0.5 mM) in THF (4 mL) Grignard reagent (1.5 mM) was added and the mixture was stirred whereupon the saturated ammonium chloride solution (0.2 mL) was added. The mixture was concentrated to dryness. Column chromatography (hexane - ethyl acetate, 10 : 1) of the residue afforded pure products. Reactions conditions and yields are given in **Table 2.**

Methyl 2,3-O-isopropylidene-5-S-methyl-5-thio-β-D-ribofuranoside (**31**), $[\alpha]_D^{20}$ -102° (*c* 1.6, chloroform). ^{1}H NMR: δ 4.98 (s, 1H, H-1), 4.72 (bd, 1H, H-3), 4.61 (d, 1H, $J_{2,3}$ 6.0 Hz, H-2), 4.28 (m, 1H, $J_{4,3}$ 0.9 Hz, H-4), 3.35 (s, 3H, OCH_3), 2.72 (dd, 1H, $J_{5,4}$ 6.1, $J_{5,5'}$ 13.6 Hz, H-5), 2.58 (dd, 1H, $J_{5',4}$ 9.6 Hz, H-5'), 2.16 (s, 3H, SCH_3), 1.49 and 1.33 (2s, 6H, CMe_2). HR-MS/EI: $C_{10}H_{18}O_4S$ $(M)^+$. Calc.: 234.0926. Found.: 234.0924.

Methyl 5-S-ethyl-2,3-O-isopropylidene-5-thio-β-D-ribofuranoside (**32**), $[\alpha]_D^{22}$ -104°(*c* 0.7, chloroform). ^{1}H NMR: δ 4.97 (s, 1H, H-1), 4.72 (dd, 1H, $J_{3,2}$ 6.0, $J_{3,4}$ 0.6 Hz, H-3), 4.61 (d, 1H, H-2), 4.25 (m, 1H, $J_{4,5}$ 6.1, $J_{4,5'}$ 9.8 Hz, H-4), 3.35 (s, 3H, OCH_3), 2.78 (dd, 1H, $J_{5,5'}$ 13.5 Hz, H-5), 2.53 - 2.64 (m, 3H, H-5', SCH_2),

1.49 and 1.33 (2s, 6H, CMe_2), 1.27 (t, 3H, *J* 7.4 Hz, CH_3). HR-MS/EI: $C_{12}H_{20}O_4S$ $(M)^+$. Calc.: 248.1082. Found: 248.1090.

Methyl 2,3-O-isopropylidene-5-S-isopropyl-5-thio-β-D-ribofuranoside (**33**), $[\alpha]_D^{20}$ -93° (*c* 3.2, chloroform). ^1H NMR: δ 4.98 (s, 1H, H-1), 4.73 (dd, 1H, $J_{3,2}$ 6.0, $J_{3,4}$ 0.6 Hz, H-3), 4.61 (d, 1H, H-2), 4.25 (m, 1H, H-4), 3.36 (s, 3H, OCH_3), 2.98 (m, 1H, SCH), 2.80 (dd, 1H, $J_{5,4}$ 6.1, $J_{5,5'}$ 13.4 Hz, H-5), 2.59 (dd, 1H, $J_{5',4}$ 9.9 Hz, H-5'), 1.49 and 1.33 (2s, 6H, CMe_2), 1.29 and 1.27 (2d, 6H, *J* 6.7 Hz, 2 × CH_3). HR-MS/EI: $C_{12}H_{22}O_4S$ $(M)^+$. Calc.: 262.1239. Found: 262.1239.

Methyl 5-S-n-butyl-2,3-O-isopropylidene-5-thio-β-D-ribofuranoside (**34**), $[\alpha]_D^{20}$ -95° (*c* 2.6, chloroform). ^1H NMR: δ 4.97 (s, 1H, H-1), 4.72 (dd, 1H, $J_{3,2}$ 5.9, $J_{3,4}$ 0.6 Hz, H-3), 4.61 (d, 1H, H-2), 4.25 (m, 1H, $J_{4,5}$ 6.1, $J_{4,5'}$ 9.8 Hz, H-4), 3.35 (s, 3H, OCH_3), 2.75 (dd, 1H, $J_{5,5'}$ 13.5 Hz, H-5), 2.51 - 2.64 (m, 3H, H-5', SCH_2), 1.49 and 1.33 (2s, 6H, CMe_2), 1.35 - 1.66 (m, 4H, 2 × CH_2), 0.92 (t, 3H, *J* 7.2 Hz, CH_3). HR-MS/EI: $C_{13}H_{24}O_4S$ $(M)^+$. Calc.: 276.1395. Found: 276.1392.

Methyl 5-S-isobutyl-2,3-O-isopropylidene-5-thio-β-D-ribofuranoside (**35**), $[\alpha]_D^{20}$ -95° (*c* 3.3, chloroform). ^1H NMR: δ 4.97 (s, 1H, H-1), 4.72 (bd, 1H, H-3), 4.61 (d, 1H, $J_{2,3}$ 6.0 Hz, H-2), 4.25 (m, 1H, $J_{4,3}$ 0.6 Hz, H-4), 3.35 (s, 3H, OCH_3), 2.74 (dd, 1H, $J_{5,4}$ 6.1, $J_{5,5'}$ 13.4 Hz, H-5), 2.56 (dd, 1H, $J_{5',4}$ 9.7 Hz, H-5'), 2.44 (d, 2H, *J* 6.9 Hz, SCH_2), 1.81 (m, 1H, CH), 1.49 and 1.33 (2s, 6H, CMe_2), 1.00 (d, 6H, *J* 6.6 Hz, 2 × CH_3). HR-MS/EI: $C_{13}H_{24}O_4S$ $(M)^+$. Calc.: 276.1395. Found: 276.1394.

Methyl 5-S-benzyl-2,3-O-isopropylidene-5-thio-β-D-ribofuranoside (**36**), $[\alpha]_D^{20}$ -96° (*c* 0.6, chloroform). ^1H NMR: δ 4.94 (s, 1H, H-1), 4.63 (dd, 1H, $J_{3,2}$ 5.9, $J_{3,4}$ 0.8 Hz, H-3), 4.55 (d, 1H, H-2), 4.21 (m, 1H, $J_{4,5}$ 6.4, $J_{4,5'}$ 9.4 Hz, H-4), 3.74 (s, 2H, CH_2Ph), 3.29 (s, 3H, OCH_3), 2.65 (dd, 1H, $J_{5,5'}$ 13.4 Hz, H-5), 2.49 (dd, 1H, H-5'), 1.48 and 1.31 (2s, 6H, CMe_2). HR-MS/EI: $C_{16}H_{22}O_4S$ $(M)^+$. Calc.: 310.1239. Found: 310.1235.

Methyl 2,3-O-isopropylidene-5-S-phenyl-5-thio-β-D-ribofuranoside (**37**), m.p. 31 - 32°C; $[\alpha]_D^{22}$ -67° (*c* 0.8, chloroform). ^1H NMR: δ 4.98 (s, 1H, H-1), 4.73 (d, 1H, $J_{3,2}$ 5.9 Hz, H-3), 4.61 (d, 1H, H-2), 4.25 (dd, 1H, $J_{4,5}$ 6.0, $J_{4,5'}$ 9.6 Hz, H-4), 3.36 (s, 3H, OCH_3), 3.18 (dd, 1H, $J_{5,5'}$ 13.6 Hz, H-5), 2.95 (dd, 1H, H-5'), 1.45 and 1.31 (2s, 6H, CMe_2). HR-MS/EI: $C_{15}H_{20}O_4S$ $(M)^+$. Calc.: 296.1082. Found: 296.1079.

Methyl 5-S-tert-butyl-2,3-O-isopropylidene-5-thio-β-D-ribofuranoside (**38**), $[\alpha]_D^{25}$ -69° (*c* 0.4, chloroform). ^1H NMR: δ 4.97 (s, 1H, H-1), 4.68 (dd, 1H, $J_{3,2}$ 6.0, $J_{3,4}$ 0.7 Hz, H-3), 4.60 (d, 1H, H-2), 4.25 (m, 1H, $J_{4,5}$ 6.5, $J_{4,5'}$ 9.6 Hz, H-4), 3.37 (s, 3H, OCH_3), 2.77 (dd, 1H, $J_{5,5'}$ 12.6 Hz, H-5), 2.61 (dd, 1H, H-5'), 1.48 and 1.32 (2s, 6H, CMe_2), 1.33 (s, 9H, tert-Bu). HR-MS/EI: $C_{13}H_{24}O_4S$ $(M)^+$. Calc.: 276.1395. Found: 276.1392.

Methyl 2,3-O-isopropylidene-5-thio-β-D-ribofuranoside (**39**)

To a solution of **28** (1.46 g, 5.95 mM) in ethyl ether (50 mL) lithium aluminium hydride (490 mg, 12.9 mM) was added at -20°C, and the mixture was stirred at r.t. for 1 h. Water (0.5 mL) was slowly added, and the suspension was stirred for 30 min, filtered through silica gel, and concentrated to dryness. Pure **39** (1.24 g, 95%) was obtained, $[\alpha]_D^{20}$ -86° (*c* 0.6, chloroform); ν_{max} (film): 2580 cm^{-1}. ^1H NMR: δ 4.98 (s, 1H, H-1),

4.70 (dd, 1H, $J_{3,2}$ 6.0, $J_{3,4}$ 0.8 Hz, H-3), 4.61 (d, 1H, H-2), 4.18 (m, 1H, $J_{4,5}$ 6.7, $J_{4,5'}$ 8.5 Hz, H-4), 3.36 (s, 3H, OCH_3), 2.79 (m, 1H, $J_{5,5'}$ 13.4 Hz, H-5), 2.55 (m, 1H, H-5'), 1.50 (dd, 1H, $J_{SH,5}$ 6.9, $J_{SH,5'}$ 9.9 Hz, SH), 1.49 and 1.33 (2s, 6H, CMe_2). *Anal.*: $C_9H_{16}O_4S$ (220.29). Calc.: C 49.07; H 7.32; S 14.56. Found: C 49.14; H 7.31; S 14.63.

Bis(methyl 5-deoxy-2,3-O-isopropylidene-β-D-ribofuranos-5-yl) disulfide (**40**).

To a solution of **39** (1.23 g, 5.58 mM) in benzene (20 mL), 20% aqueous sodium hydroxide (1.8 mL, 11 mM) and iodine (1.8 g) were added. The mixture was stirred for 24 h and 20% sodium hydroxide was added for decolouring. Then water (10 mL) was added, and the mixture was extracted with chloroform (3 × 20 mL). The combined organic layer was washed with water (2 × 20 mL), dried over $MgSO_4$, and concentrated to dryness. Column chromatography (hexane - acetone, 2 : 1) of the residue gave **40** (1.13g, 92%), m.p. 77 - 78°C; $[\alpha]_D^{22}$ -116° (*c* 2.3, chloroform). ^1H NMR: δ 4.98 (s, 1H, H-1), 4.74 (dd, 1H, $J_{3,2}$ 6.0 Hz, H-3), 4.62 (d, 1H, H-2), 4.46 (m, 1H, $J_{4,3}$ 0.5 Hz, H-4), 3.35 (s, 3H, OCH_3), 2.96 (dd, 1H, $J_{5,4}$ 6.6, $J_{5,5'}$ 13.6 Hz, H-5), 2.77 (dd, 1H, $J_{5',4}$ 8.8 Hz, H-5'), 1.49 and 1.33 (2s, 6H, CMe_2). HR-MS/EI: $C_{18}H_{30}O_8S_2$ $(M)^+$. Calc.: 438.1382. Found: 438.1382.

*Reaction of **29** and **30** with Grignard reagents. General procedure.*

To a solution of dithiocyanate (**29** or **30**, 152 mg, 0.50 mM) in THF (4 mL), Grignard reagent (2 mM) was added. Then, the solvents were evaporated. Column chromatography (hexane - ethyl acetate, 4 : 1) of the residue gave the products. Reactions conditions and yields are given in **Tables 3** and **4**.

Methyl 4,6-di-S-ethyl-2,3-di-O-methyl-4,6-dithio-α-D-glucopyranoside (**41**), $[\alpha]_D^{20}$ +172° (*c* 1.4, chloroform). ^1H NMR: δ 4.80 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 3.69 (m, 1H, H-5), 3.63, 3.50 and 3.41 (3s, 9H, 3 × OCH_3), 3.40 (m, 1H, H-3), 3.18 (dd, 1H, $J_{6,5}$ 2.6, $J_{6,6'}$ 13.5 Hz, H-6), 3.16 (dd, 1H, $J_{2,3}$ 9.3 Hz, H-2), 2.81 (dd, 1H, $J_{6',5}$ 7.4 Hz, H-6'), 2.63 (m, 4H, 2 × CH_2), 2.47 (t, 1H, $J_{4,5}$ 7.4, $J_{4,3}$ 10.7 Hz, H-4), 1.25 (t, 6H, *J* 7.5 Hz, 2 × CH_3). ^{13}C NMR: δ 98.00 (C-1), 83.56 and 82.58 (C-2,3), 71.69 (C-5), 61.98, 59.42 and 55.68 (OCH_3), 51.55 (C-4), 35.08 (C-6), 27.57 and 27.05 (CH_2), 15.68 and 15.37 (CH_3). HR-MS/EI: $C_{13}H_{26}O_4S_2$ $(M)^+$. Calc.: 310.1272. Found: 310.1269.

Methyl 4,6-di-S-isopropyl-2,3-di-O-methyl-4,6-dithio-α-D-glucopyranoside (**42**), $[\alpha]_D^{20}$ +169° (*c* 1.3, chloroform). ^1H NMR: δ 4.84 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 3.70 (m, 1H, H-5), 3.66, 3.52 and 3.44 (3s, 9H, 3 × OCH_3), 3.41 (m, 1H, H-3), 3.24 (dd, 1H, $J_{6,5}$ 2.5, $J_{6,6'}$ 13.2 Hz, H-6), 3.18 (dd, 1H, $J_{2,3}$ 9.4 Hz, H-2), 3.01 (m, 2H, 2 × CH), 2.83 (dd, 1H, $J_{6',5}$ 7.6 Hz, H-6'), 2.52 (t, 1H, $J_{4,5} = J_{4,3}$ = 10.6 Hz, H-4), 1.30 (m, 12H, 4 × CH_3). ^{13}C NMR: δ 98.00 (C-1), 83.61 and 83.52 (C-2,3), 71.91 (C-5), 62.18, 59.46 and 55.68 (OCH_3), 51.16 (C-4), 37.66 and 36.18 (CH), 33.88 (C-6), 24.73, 24.63, 24.02 and 23.96 (CH_3). HR-MS/EI: $C_{15}H_{30}O_4S_2$ $(M)^+$. Calc.: 338.1585. Found: 338.1582.

Methyl 4-deoxy-6-S-isopropyl-2,3-di-O-methyl-6-thio-4-thiocyanato-α-D-glucopyranoside (**43**), $[\alpha]_D^{20}$ +100° (*c* 1.2, chloroform); ν_{max} (film): 2154 cm^{-1}. ^1H NMR: δ 4.87 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.07 (m, 1H, H-5), 3.70, 3.55 and 3.47 (3s, 9H, 3 × OCH_3), 3.66 (t, 1H, H-3), 3.27 (dd, 1H, $J_{2,3}$ 9.2 Hz, H-2), 3.11 (dd, 1H, $J_{6,5}$ 2.7, $J_{6,6'}$ 13.8 Hz, H-6), 2.80 - 3.05 (m, 3H, $J_{4,3} = J_{4,5}$ = 10.4 Hz; $J_{6',5}$ 6.3 Hz, H-4,6', CH), 1.28 (m, 6H, 2 × CH_3). ^{13}C NMR: δ 109.68 (SCN), 98.00 (C-1), 83.74 (C-2), 79.81 (C-3), 70.35 (C-5), 62.38, 59.61

and 56.13 (OCH_3), 52.06 (C-4), 36.42 and 33.26 (C-6, CH), 23.95 and 23.87 (CH_3). HR-MS/EI: $C_{13}H_{23}NO_4S_2$ $(M)^+$. Calc.: 321.1068. Found: 321.1067.

Methyl 4,6-di-S-n-butyl-2,3-di-O-methyl-4,6-dithio-α-D-glucopyranoside (**44**), $[\alpha]_D^{20}$ +142° (*c* 1.2, chloroform). ^1H NMR: δ 4.80 (d, 1H, $J_{1,2}$ 3.3 Hz, H-1), 3.68 (m, 1H, H-5), 3.63, 3.49 and 3.41 (3s, 9H, 3 × OCH_3), 3.39 (m, 1H, H-3), 3.11 - 3.21 (m, 2H, H-2,6), 2.80 (dd, 1H, $J_{6',5}$ 7.4, $J_{6,6'}$ 13.5 Hz, H-6'), 2.60 (m, 4H, CH_2), 2.45 (t, 1H, $J_{4,5} = J_{4,3}$ = 10.7 Hz, H-4), 1.55 and 1.40 (2m, 8H, 4 × CH_2), 0.88 (t, 6H, *J* 7.1 Hz, 2 × CH_3). ^{13}C NMR: δ 97.97 (C-1), 83.57 and 82.54 (C-2,3), 71.76 (C-5), 61.98, 59.41 and 55.67 (OCH_3), 51.78 (C-4), 35.57 (C-6), 33.44, 32.73, 32.51, 32.33 and 22.38 (CH_2), 14.15 and 14.11 (CH_3). HR-MS/EI: $C_{17}H_{34}O_4S_2$ $(M)^+$. Calc.: 366.1899. Found: 366.1902.

Methyl 4,6-di-S-isobutyl-2,3-di-O-methyl-4,6-dithio-α-D-glucopyranoside (**45**), $[\alpha]_D^{20}$ +136° (*c* 1.2, chloroform). ^1H NMR: δ 4.84 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 3.71 (m, 1H, H-5), 3.67, 3.53 and 3.44 (3s, 9H, 3 × OCH_3), 3.43 (m, 1H, H-3), 3.15 - 3.23 (m, 2H, H-2,6), 2.83 (dd, 1H, $J_{6',5}$ 7.3, $J_{6',6}$ 13.4 Hz, H-6'), 2.41 - 2.57 (m, 5H, H-4, 2 × CH_2), 1.82 (m, 2H, 2 × CH), 1.00 (d, 12H, 4 × CH_3). ^{13}C NMR: δ 98.00 (C-1), 83.61 and 82.58 (C-2,3), 71.86 (C-5), 62.03, 59.45 and 55.70 (OCH_3), 52.12 (C-4), 43.09 and 42.17 (CH_2), 36.21 (C-6), 29.38 and 29.22 (CH), 22.54 and 22.46 (CH_3). HR-MS/EI: $C_{17}H_{34}O_4S_2$ $(M)^+$. Calc.: 366.1899. Found: 366.1898.

Methyl 4-deoxy-6-S-isobutyl-2,3-di-O-methyl-6-thio-4-thiocyanato-α-D-glucopyranoside (**46**), $[\alpha]_D^{20}$ +94° (*c* 1.3, chloroform); ν_{max} (film): 2153 cm^{-1}. ^1H NMR: δ 4.88 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.05 (m, 1H, H-5), 3.70, 3.55 and 3.47 (3s, 9H, 3 × OCH_3), 3.66 (m, 1H, H-3), 3.27 (dd, 1H, $J_{2,3}$ 9.1 Hz, H-2), 3.07 (dd, 1H, $J_{6,5}$ 2.6, $J_{6,6'}$ 14.0 Hz, H-6), 2.96 (t, 1H, $J_{4,3} = J_{4,5}$ = 10 Hz, H-4), 2.86 (dd, 1H, $J_{6',5}$ 6.2 Hz, H-6'), 2.50 (2d, 4H, *J* 6.6 Hz, 2 × CH_2), 1.82 (m, 2H, 2 × CH), 1.00 (d, 12H, *J* 6.6 Hz, 4 × CH_3). ^{13}C NMR: δ 109.66 (SCN), 98.00 (C-1), 83.76 (C-2), 79.83 (C-3), 70.46 (C-5), 62.37, 59.61 and 56.12 (OCH_3), 51.97 (C-4), 43.20 (CH_2), 35.57 (C-6), 29.20 (CH), 22.49 and 22.39 (CH_3). HR-MS/EI: $C_{14}H_{25}NO_4S_2$ $(M)^+$. Calc.: 335.1225. Found: 335.1224.

Methyl 2,3-di-O-methyl-4,6-di-S-phenyl-4,6-dithio-α-D-glucopyranoside (**47**), $[\alpha]_D^{20}$ +86° (*c* 1.5, chloroform). ^1H NMR: δ 4.77 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 3.81 (m, 1H, H-5), 3.64 (dd, 1H, $J_{6,5}$ 2.3, $J_{6,6'}$ 13.3 Hz, H-6), 3.59, 3.46 and 3.31 (3s, 9H, 3 × OCH_3), 3.35 (m, 1H, H-3), 3.19 (dd, 1H, $J_{2,3}$ 9.3 Hz, H-2), 2.93 (dd, 1H, $J_{6',5}$ 8.2, H-6'), 2.87 (t, 1H, $J_{4,3} = J_{4,5}$ = 10.6 Hz, H-4). ^{13}C NMR: δ 97.91 (C-1), 83.71 and 81.37 (C-2,3), 71.24 (C-5), 62.09, 59.50, 56.23 and 55.75 (C-4,OCH_3), 37.53 (C-6). HR-MS/EI: $C_{21}H_{26}O_4S_2$ $(M)^+$. Calc.: 406.1273. Found: 406.1274.

Methyl 4-deoxy-6-S-ethyl-2,3-di-O-methyl-6-thio-4-thiocyanato-α-D-galactopyranoside (**48**), $[\alpha]_D^{20}$ +137° (*c* 5.1, chloroform); ν_{max} (film): 2155 cm^{-1}. ^1H NMR: δ 4.81 (d, 1H, $J_{1,2}$ 3.9 Hz, H-1), 4.18 (dd, 1H, $J_{4,3}$ 4.0, $J_{4,5}$ 1.7 Hz, H-4), 4.15 (m, 1H, H-5), 3.82 (dd, 1H, $J_{3,2}$ 9.8 Hz, H-3), 3.54, 3.53 and 3.45 (3s, 9H, 3 × OCH_3), 3.43 (dd, 1H, H-2), 2.92 (dd, 1H, $J_{6,5}$ 7.3 Hz, $J_{6,6'}$ 13.6 Hz, H-6), 2.80 (dd, 1H, $J_{6',5}$ 6.6 Hz, H-6'), 2.65 (q, 2H, *J* 7.4 Hz, CH_2), 1.30 (t, 3H, CH_3). ^{13}C NMR: δ 112.17 (SCN), 98.00 (C-1), 78.47 and 77.49 (C-2,3), 68.30 (C-5), 59.50, 57.75, 55.62 and 55.40 (C-4, OCH_3), 33.74 (C-6), 27.04 (CH_2), 14.71 (CH_3). HR-MS/EI: $C_{12}H_{21}NO_4S_2$ $(M)^+$. Calc.: 307.0912. Found: 307.0911.

Methyl 4-deoxy-6-S-isopropyl-2,3-di-O-methyl-6-thio-4-thiocyanato-α-D-galactopyranoside (**49**), $[\alpha]_D^{20}$ +135° (*c* 4.4, chloroform); ν_{max} (film): 2155 cm^{-1}. ^1H NMR: δ 4.81 (d, 1H, $J_{1,2}$ 3.9 Hz, H-1), 4.18 (dd, 1H, $J_{4,3}$ 4.0, $J_{4,5}$ 1.7 Hz, H-4), 4.14 (m, 1H, H-5), 3.82 (dd, 1H, $J_{3,2}$ 9.8 Hz, H-3), 3.54, 3.53 and 3.45 (3s, 9H, 3 × OCH_3), 3.43 (dd, 1H, H-2), 3.02 (m, 1H, CH), 2.94 (dd, 1H, $J_{6,5}$ 7.3 Hz, $J_{6,6'}$ 13.4 Hz, H-6), 2.80 (dd, 1H, $J_{6',5}$ 6.7 Hz, H-6'), 1.31 and 1.30 (2d, 6H, *J* 6.7 Hz, 2 × CH_3). ^{13}C NMR: δ 112.21 (SCN), 98.00 (C-1), 78.48 and 77.50 (C-2,3), 68.34 (C-5), 59.51, 57.77, 55.65 and 55.45 (C-4, OCH_3), 36.01 (C-6), 32.56 (CH), 23.40 and 23.28 (CH_3). HR-MS/EI: $C_{13}H_{23}NO_4S_2$ $(M)^+$. Calc.: 321.1068. Found: 321.1065.

Methyl 4-deoxy-6-S-n-butyl-2,3-di-O-methyl-6-thio-4-thiocyanato-α-D-galactopyranoside (**50**), $[\alpha]_D^{20}$ +117° (*c* 6.5, chloroform); ν_{max} (film): 2155 cm^{-1}. ^1H NMR: δ 4.82 (d, 1H, $J_{1,2}$ 3.9 Hz, H-1), 4.18 (dd, 1H, $J_{4,3}$ 4.0, $J_{4,5}$ 1.6 Hz, H-4), 4.14 (m, 1H, H-5), 3.82 (dd, 1H, $J_{3,2}$ 9.8 Hz, H-3), 3.54, 3.53 and 3.45 (3s, 9H, 3 × OCH_3), 3.43 (dd, 1H, H-2), 2.90 (dd, 1H, $J_{6,5}$ 7.3, $J_{6,6'}$ 13.6 Hz, H-6), 2.79 (dd, 1H, $J_{6',5}$ 6.6 Hz, H-6'), 2.62 (t, 2H, *J* 7.4 Hz, CH_2), 1.60 (m, 2H, CH_2), 1.44 (m, 2H, CH_2), 0.93 (t, 3H, *J* 7.3 Hz, CH_3). ^{13}C NMR: δ 112.12 (SCN), 97.94 (C-1), 78.43 and 77.44 (C-2,3), 68.27 (C-5), 59.43, 57.69, 55.56 and 55.34 (C-4, OCH_3), 34.15, 32.84 and 31.58 (C-6, CH_2), 21.74 (CH_2), 13.51 (CH_3). HR-MS/EI: $C_{14}H_{25}NO_4S_2$ $(M)^+$. Calc.: 335.1225. Found: 335.1221.

Methyl 4-deoxy-2,3-di-O-methyl-6-S-phenyl-6-thio-4-thiocyanato-α-D-galactopyranoside (**51**), $[\alpha]_D^{20}$ +83° (*c* 6.7, chloroform); ν_{max} (film): 2155 cm^{-1}. ^1H NMR: δ 4.80 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.16 (m, 2H, H-4,5), 3.77 (dd, 1H, $J_{3,2}$ 9.7, $J_{3,4}$ 4.0 Hz, H-3), 3.52, 3.51 and 3.39 (3s, 9H, 3 × OCH_3), 3.42 (dd, 1H, H-2), 3.32 (dd, 1H, $J_{6,5}$ 7.0, $J_{6,6'}$ 13.9 Hz, H-6), 3.21 (dd, 1H, $J_{6',5}$ 6.4 Hz, H-6'). ^{13}C NMR: δ 112.03 (SCN), 98.02 (C-1), 78.40 and 77.44 (C-2,3), 67.50 (C-5), 59.48, 57.76, 55.58 and 55.27 (C-4, OCH_3), 36.32 (C-6). HR-MS/EI: $C_{16}H_{21}NO_4S_2$ $(M)^+$. Calc.: 355.0912. Found: 355.0907.

Methyl 6-S-n-butyl-2,3-di-O-methyl-4,6-dithio-α-D-galactopyranoside (**52**), $[\alpha]_D^{20}$ +114° (*c* 3.4, chloroform); ν_{max} (film): 2570 cm^{-1}. ^1H NMR: δ 4.85 (d, 1H, $J_{1,2}$ 3.1 Hz, H-1), 4.07 (m, 1H, H-5), 3.68 (m, 3H, H-2,3,4), 3.52, 3.46 and 3.45 (3s, 9H, 3 × OCH_3), 2.84 (dd, 1H, $J_{6,5}$ 7.3, $J_{6,6'}$ 13.4 Hz, H-6), 2.73 (dd, 1H, $J_{6',5}$ 6.6 Hz, H-6'), 2.61 (t, 2H, CH_2), 1.33 - 1.68 (m, 5H, SH, 2 × CH_2), 0.92 (t, 3H, *J* 7.3 Hz, CH_3). ^{13}C NMR: δ 98.54 (C-1), 79.04 and 77.64 (C-2,3), 69.32 (C-5), 59.57, 56.61, 55.79 and 43.95 (C-4, OCH_3), 34.91, 33.28 and 32.26 (CH_2), 22.38 (CH_2), 14.14 (CH_3). HR-MS/EI: $C_{13}H_{26}O_4S_2$ $(M)^+$. Calc.: 310.1272. Found: 310.1269.

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