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Note

Synthesis of *S*-glycosyl thiophosphates, thiophosphonates and thiophosphinates by the Michaelis–Arbuzov rearrangement of anomeric thiocyanates

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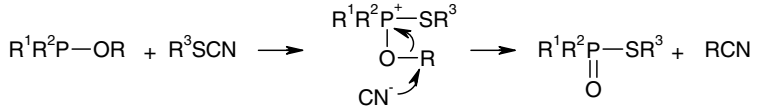
Abstract—Reaction of anomeric thiocyanates with a series of *O*-alkyl or *O*-trimethylsilyl phosphite, phenylphosphonite and diphenylphosphinite derivatives afforded the corresponding *S*-glycosyl thiophosphates, thiophosphonates and thiophosphinates in good yields. These derivatives had been previously applied as glycosyl donors in the synthesis of benzyl glycosides and disaccharides with excellent stereoselectivity.

Keywords: Thiocyanates; Thiophosphates; Thiophosphonates; Thiophosphinates; Glycosyl donors

The effectiveness of glycosylation is a key problem in oligosaccharide synthesis and strongly depends upon the nature of the leaving group at the anomeric centre and its method of activation. Numerous versatile leaving groups are known;[1] however, a universally applicable method for glycoside bond formation is not available. Therefore, the need for new, readily accessible, stable and reactive glycosyl donors still persists. During our studies directed towards the synthesis of oligosaccharides[2] we focused our attention on the leaving groups containing a phosphorus–sulfur bond. Recently, we reported that *S*-glycosyl thiophosphates, thiophosphonates and thiophosphinates are very promising glycosyl donors and give glycosides and disaccharides with excellent stereoselectivity.[3] Numerous synthetic methods for the introduction of a phosphorothioate moiety into a saccharide structure have been reported[4] but they often lead to a mixture of anomers or O,S-isomerisation. *S*-Glycosyl thiophosphates have also been used in the synthesis of glycosyl cyanides and glycosyl 1-*O*-acyl esters,[5] *S*-glycosyl thiophosphonates for studies of phosphorus stereochemistry,[6] whereas *S*-glycosyl thiophosphinates have not been described yet.

The Michaelis–Arbuzov reaction (also known as the Arbuzov reaction or Arbuzov rearrangement) is well known and widely used in general organic chemistry for the creation of carbon–phosphorus bonds.[7] It has also been demonstrated that alkyl and aryl thiocyanates are highly reactive reagents in this reaction.[8] The reaction involves S–CN bond fission and gives alkyl cyanates and *O*,*O*,*S*-trialkyl thiophosphates (Scheme 1).



Scheme 1.

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Therefore, organic thiocyanates are potentially very promising substrates for the highly regioselective preparation of unsymmetrical *O*,*O*,*S*-trialkyl thiophosphates.[9] In this regard, anomeric thiocyanates[10,11] are particularly interesting starting materials for the preparation of anomeric thiophosphorus derivatives.

In this paper, we report a highly efficient method for the preparation of *S*-glycosyl thiophosphates, thiophosphonates and thiophosphinates via Michaelis–Arbuzov reaction of glycosyl thiocyanates with simple phosphorus reagents.

As we described earlier,[3] peracetylated glycosyl thiocyanates are thermally unstable and at high temperature (usually required for the Arbuzov reaction) easily isomerise to the corresponding glycosyl isothiocyanates. We decided, therefore, to use the much more thermally stable perbenzoylated glycosyl thiocyanates **1**–**4** (Fig. 1) as the starting materials. These compounds are readily available by the treatment of the corresponding glycosyl bromides with potassium thiocyanate in the presence of 18-crown-6,[10] or by a slightly modified method in which the relatively expensive crown ether is replaced by 1-butyl-3-methylimidazolium chloride ([bmim]Cl) without decreasing the yields.

Reaction of 2,3,4,6-tetra-*O*-benzoyl-D-mannopyranosyl bromide with potassium thiocyanate afforded the known α-D-mannopyranosyl thiocyanate **4**, and small amount of its β-epimer **3** which was not characterised before. The $^{1}J_{1H-13C}$ coupling constants of 179.5 Hz observed at the anomeric carbon atom of **4**, and 160.8 Hz of **3** clearly characterise the α- and β-epimers, respectively.[12]

Initially, the Michaelis–Arbuzov reaction with the tetra-*O*-benzoyl-D-glucose-derived thiocyanate **1** was carried out in neat triethylphosphite [$P(OEt)_3$] at various temperatures and afforded the expected thiophosphate **5** (Fig. 1). The highest yield of thiophosphate **5** (51%) was obtained at 120 °C. Similar reaction with tributylphosphite afforded thiophosphate **8**. The same reactions performed on galactopyranosyl thiocyanate **2** and β-mannopyranosyl thiocyanate **3** afforded the expected glycosyl thiosphosphates **6**, **7** and **9**, **10** in moderate yields; the results are summarised in Table 1.

Based on the ^{31}P NMR data, the purity of thiophosphates **5**–**7** obtained by the treatment of thiocyanates **1**–**3** with triethylphosphite fluctuated between 77% and 99% and the products were contaminated with $H_2P(O)(OEt)$, $HP(O)(OEt)_2$ and $HOP(O)(OEt)_2$. The purities of compounds **8**–**10** obtained by the treatment of thiocyanates **1**–**3** with tributylphosphite were only 30–46%; byproducts including $HP(O)(OBu)_2$ and $HOP(O)(OBu)_2$ were formed.[3]

Unsatisfying reaction yields and contamination of the desired products with inseparable compounds prompted us to search for more efficient organophosphorus reagents. A known method of activation of the phosphorus(III) acids is their conversion into the trimethylsilyloxy derivatives.[13] This approach was successful; we have found that the reaction of thiocyanates **1**–**3** with diethyltrimethylsilylphosphite [$(EtO)_2$P–OTMS] proceeded smoothly at slightly elevated temperature (even room temperature) and afforded (after simple chromatographic separation) pure *S*-glycosyl thiophosphates **5**–**7** in very good yields (Table 1).

Application of dimethylphenylphosphonite [PhP-$(OMe)_2$] (instead of triethylphosphite) in the reaction with glycosyl thiocyanates **1**–**3** under similar conditions afforded the expected *S*-glycosyl thiophosphonates **11**–**13** (Fig. 1) as an inseparable mixture of diastereoisomers and in acceptable yields. The purity of thiophosphonates **11**–**13** varied between 70% and 99%; HP(O)(Ph)(OMe) and HP(O)(Ph)(OH) were detected as contaminants by ^{31}P NMR.[3]

Again, the use of silylated phenylphosphonite—ethyltrimethylsilylphenylphosphonite[14] [PhP(OEt)(OTMS)]—instead of dimethylphenylphosphonite in the reaction with glycosyl thiocyanates **1**–**3** gave *S*-glycosyl thiophosphonates **14**–**16** in much higher yield, and the products were completely free from any undesirable byproducts (Table 1).

Extension of these reaction conditions to methyl diphenylphosphinite [$Ph_2P(OMe)$] as a starting material

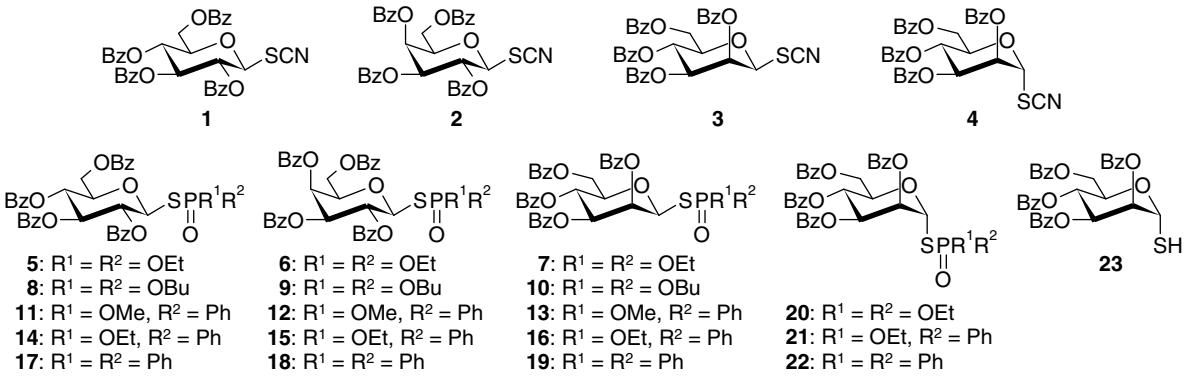
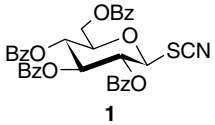
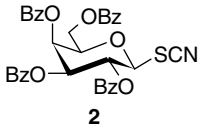
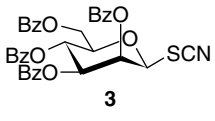
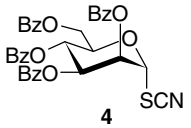


Figure 1.

Table 1. The Michaelis–Arbuzov rearrangement of glycosyl thiocyanates **1**–**4**

RSCN	$R_2P(OR')$	Product	Temp[a] (°C)	Time	Isolated yield (%)
 **1**	$P(OEt)_3$	**5**	120	30 min	51[b]
	$(EtO)_2P$–OTMS	**5**	rt	24 h	70
	$(EtO)_2P$–OTMS	**5**	50	1 h	82
	$P(OBu)_3$	**8**	120	30 min	33[b]
	$PhP(OMe)_2$	**11**	40	30 min	51[b]
	PhP(OEt)(OTMS)	**14**	rt	18 h	90
	PhP(OEt)(OTMS)	**14**	40	1 h	94
	$Ph_2P(OMe)$	**17**	40	30 min	20[b]
	$Ph_2P(OMe)$	**17**	80	10 min	25[b]
	Ph_2P(OTMS)	**17**	rt	18 h	80
	Ph_2P(OTMS)	**17**	40	1 h	71
 **2**	$P(OEt)_3$	**6**	80	2 h	30[b]
	$(EtO)_2P$–OTMS	**6**	rt	24 h	68
	$(EtO)_2P$–OTMS	**6**	60	2 h	77
	$P(OBu)_3$	**9**	80	8 h	30[b]
	$PhP(OMe)_2$	**12**	40	30 min	53[b]
	PhP(OEt)(OTMS)	**15**	rt	18 h	85
	PhP(OEt)(OTMS)	**15**	40	1 h	83
	$Ph_2P(OMe)$	**18**	rt	24 h	20[b]
	$Ph_2P(OMe)$	**18**	40	30 min	25[b]
	Ph_2P(OTMS)	**18**	rt	18 h	74
	Ph_2P(OTMS)	**18**	40	1 h	71
 **3**	$P(OEt)_3$	**7**	80	3.5 h	24[b]
	$(EtO)_2P$–OTMS	**7**	rt	24 h	68
	$(EtO)_2P$–OTMS	**7**	40	3 h	68
	$P(OBu)_3$	**10**	120	30 min	40[b]
	$PhP(OMe)_2$	**13**	50	1 h	41[b]
	PhP(OEt)(OTMS)	**16**	rt	24 h	85
	PhP(OEt)(OTMS)	**16**	40	90 min	89
	Ph_2P(OTMS)	**19**	rt	24 h	82
	Ph_2P(OTMS)	**19**	40	90 min	66
 **4**	$(EtO)_2P$–OTMS	**20**	rt	24 h	35
	$(EtO)_2P$–OTMS	**20**	60	24 h	62
	$(EtO)_2P$–OTMS	**20**	100	4 h	53
	PhP(OEt)(OTMS)	**21**	rt	24 h	42
	PhP(OEt)(OTMS)	**21**	60	24 h	51
	PhP(OEt)(OTMS)	**21**	100	4 h	33
	Ph_2P(OTMS)	**22**	60	24 h	20[c]

[a] Bath temperature.
[b] Purity determined by ^{31}P NMR spectroscopy and the yield was calculated for pure product.
[c] Product decomposed during chromatographic purification; contains significant amount of thiol **23**. Pure thiol **23** (50%) was also isolated.

led to *S*-glycosyl thiophosphinates **17** and **18** (Fig. 1), but in very low yields. Thiocyanate **3** was unreactive under these reaction conditions. In this case, due to the instability of the final products at higher temperatures, the reactions were conducted below 80 °C. Because of their high polarity, chromatographic separation of *S*-glycosyl thiophosphinates **17** and **18** was relatively simple and purities of the products usually exceeded 95%; $Ph_2P(O)(OMe)$, $Ph_2P(OH)$ and $H_2P(O)(OMe)$ were detected as side products by ^{31}P NMR.[3] In contrast to the above reaction, the use of trimethylsilyldiphenylphosphinite[15] [Ph_2P(OTMS)] afforded *S*-glycosyl thiophosphinates **17**–**19** in excellent yield. All products were pure and free from any contaminants (Table 1).

The unique chemical properties of α-D-mannopyranosyl thiocyanate **4** should be mentioned here. As we had observed previously, α-D-mannopyranosyl thiocyanate **4** was completely unreactive towards Grignard reagents.[10] This compound also remained unchanged during the Michaelis–Arbuzov rearrangement, and we did not observe any reaction with triethylphosphite, dimethylphenylphosphonite or methyldiphenylphosphinite. The reason for the lack of reactivity of α-D-mannopyranosyl thiocyanate **4** remains unknown. However, when the more active silylated phosphorus(III) acid derivatives were used, the Michaelis–Arbuzov reaction took place. Although the required reaction temperature was higher and the yields were usually lower than for the corresponding β-D-*manno* isomer, *S*-glycosyl thiophosphate **20** and *S*-glycosyl thiophosphonate **21** were isolated in good yield (Fig. 1, Table 1). Reaction of thiocyanate **4** with trimethylsilyldiphenylphosphinite afforded *S*-glycosyl

thiophosphinate **22**, which was confirmed by ^{31}P NMR spectra of the crude reaction mixture (in which a suitable signal at 40.6 ppm was observed). This compound was, however, unstable and almost complete decomposition of **22** occurred during flash chromatography and yielded several decomposition products from which only thiol **23**[16] (obtained in 50% yield) could be identified. A small amount (20%) of the desired product **22** was also isolated but contaminated with a significant amount of **23**. We suppose that thiol **23** was obtained by the hydrolysis of *S*-glycosyl thiophosphinate **22** in the presence of residual water on silica. This process may be considered as similar to the known transesterification reaction of simple alkyl and aryl thiophosphorus esters leading to the corresponding thiols.[17] It should be noted that traces of **23** were also detected during chromatographic purification of *S*-glycosyl thiophosphonate **21**.

In conclusion, we have developed an efficient synthesis of *S*-glycosyl thiophosphates, thiophosphonates and thiophosphinates from anomeric thiocyanates by treatment with diethyltrimethylsilylphosphite, ethyltrimethylsilylphenylphosphonite or trimethylsilyldiphenylphosphinite, respectively. It should be emphasised that in all the cases studied, the configuration at the stereogenic centre connected to the sulfur atom (anomeric position) was fully preserved. Reactions were also regioselective affording *S*-glycosyl derivatives as the only products.

1. Experimental

1.1. General methods

TLC was performed on silica gel HF-254 and column chromatography on silica gel 230–400 mesh (Merck). The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 303 K with a Varian Mercury 400BB spectrometer (400 MHz, 100 MHz and 161.9 MHz, respectively). TMS was used as the internal standard for ^{1}H and ^{13}C NMR spectra, and H_3PO_4 as the external standard for ^{31}P NMR spectra. Signals of the aromatic groups observed for typical values were omitted for simplicity. High-resolution mass spectra (HR-MS) were measured with a MARINER mass spectrometer. Optical rotations were measured with a JASCO P-1020 automatic polarimeter. IR spectra were recorded on Perkin–Elmer 1640 FT-IR spectrophotometer. Unless otherwise stated, all products were isolated as a foam. Structural assignments of the *S*-glycosyl derivatives prepared above were based on NMR measurements including DEPT. All isolated compounds gave ^{1}H and ^{13}C NMR spectra fully consistent with the indicated structures. Positions of the ^{31}P NMR signals were in good conformity with the literature data for the corresponding compounds and were consistent with the expected structures.[18]

1.2. Typical procedure for the preparation of glycosyl thiocyanate[10]

A mixture of glycosyl bromide (10.0 mM), potassium thiocyanate (30.0 mM) and crown ether (18-crown-6, 300 mg) or [bmim]Cl (350 mg) in acetone (50 mL) was stirred at room temperature for 7 h, and then filtered through Celite and concentrated. Column chromatography (hexane–EtOAc 20:1→7:3) of the residue gave pure glycosyl thiocyanates **1**–**4**.

1.2.1. 2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl thiocyanate (4) and 2,3,4,6-tetra-*O*-benzoyl-β-D-mannopyranosyl thiocyanate (3). As the first product, 2,3,4,6-tetra-*O*-benzoyl-D-mannopyranosyl isothiocyanate (29%) was eluted, the second fraction comprised 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl thiocyanate (**4**, 47%) and the third fraction contained 2,3,4,6-tetra-*O*-benzoyl-β-D-mannopyranosyl thiocyanate (**3**, 16%).

Data for thiocyanate **3**: ν_{max} (film): 2164 cm^{-1}; $[\alpha]_D^{20}$ −89.2 (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 6.06 (m, 2H, H-2, H-4), 5.66 (m, 2H, H-1, H-3), 4.77 (dd, 1H, $J_{6,5} = 2.6$, $J_{6,6'} = 12.3$ Hz, H-6), 4.55 (dd, 1H, $J_{6',5} = 4.8$ Hz, H-6′), 4.30 (m, 1H, H-5); ^{13}C NMR ($CDCl_3$) δ: 166.0 (C═O), 165.4 (C═O), 165.1 (C═O), 165.0 (C═O), 108.8 (SCN), 83.1 (C-1), 77.5, 72.0, 70.3, 65.5, 62.4 (C-6); HRMS-ESI calcd for $C_{35}H_{27}NNaO_9S$ $[M+Na]^+$: 660.1299. Found: 660.1274. Anal. Calcd for $C_{35}H_{27}NO_9S$: C, 65.92; H, 4.27; N, 2.20; S, 5.03. Found: C, 65.90; H, 4.37; N, 2.05; S, 5.14.

1.3. Typical procedure for the Michaelis–Arbuzov rearrangement

A mixture of $(EtO)_2P$–OTMS (3 equiv) and thiocyanate **1** (1 equiv) was heated under an argon atmosphere in a screw cap tube (for reaction details see Table 1). Column chromatography of the residue (hexane–EtOAc, 9:1→1:1) afforded *S*-glycosyl phosphate **5**.

1.3.1. *O,O′*-Diethyl-*S*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl) thiophosphate (5). $[\alpha]_D^{20}$ +50.3 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 5.94 (t, 1H, $J_{3,2} = J_{3,4} = 9.5$ Hz, H-3), 5.71 (t, 1H, $J_{4,5} = 9.9$ Hz, H-4), 5.65 (t, 1H, $J_{2,1} = 10.1$ Hz, H-2), 5.42 (dd, 1H, $J_{P,H} = 12.5$ Hz, H-1), 4.63 (dd, 1H, $J_{6,5} = 2.6$; $J_{6,6'} = 12.4$ Hz, H-6), 4.47 (dd, 1H, $J_{6'5} = 5.4$ Hz, H-6′), 4.28 (m, 1H, H-5), 3.89–4.14 (m, 4H, 2 × CH_2), 1.21 (dt, $J = 7.1$, $J_{H,P} = 0.9$ Hz, 3H, CH_3), 1.11 (dt, $J = 7.1$, $J_{H,P} = 0.8$ Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ: 166.0 (C═O), 165.6 (C═O), 165.1 (C═O), 165.0 (C═O), 83.9 (d, $J_{C,P} = 3.4$ Hz, C-1), 76.6 (C-5), 73.8 (C-3), 71.2 (d, $J_{P,C} = 9.5$ Hz, C-2), 69.0 (C-4), 64.0 (d, $J_{C,P} = 5.2$ Hz, CH_2), 63.9 (d, $J_{C,P} = 5.2$ Hz, CH_2), 62.9 (C-6), 15.8 (d, $J_{C,P} = 2.6$ Hz, CH_3), 15.7 (d, $J_{C,P} = 2.6$ Hz, CH_3); ^{31}P NMR ($CDCl_3$) δ: 22.6; HRMS-ESI calcd for

$C_{38}H_{37}NaO_{12}PS$ $[M+Na]^+$: 771.1636. Found: 771.1640. Anal. Calcd for $C_{38}H_{37}O_{12}PS$: C, 60.96; H, 4.98; S, 4.28. Found: C, 60.97; H, 4.77; S, 4.35.

1.3.2. *O,O′*-Diethyl-*S*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl) thiophosphate (6). $[\alpha]_D^{20}$ +108.6 (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ: 6.05 (dd, 1H, $J_{4,3}=3.4$, $J_{4,5}$ <1.0 Hz, H-4), 5.90 (t, 1H, $J_{2,1}=J_{2,3}=10.0$ Hz, H-2), 5.68 (dd, 1H, H-3), 5.44 (dd, 1H, $J_{P,H}=13.1$ Hz, H-1), 4.64 (dd, 1H, $J_{6,5}=6.7$, $J_{6,6'}=11.2$ Hz, H-6), 4.48 (m, 1H, H-5), 4.40 (dd, 1H, $J_{6',5}=5.6$ Hz, H-6′), 3.89–4.15 (m, 4H, 2 × CH_2), 1.22 (dt, $J=7.1$, $J_{H,P}=0.9$ Hz, 3H, CH_3), 1.11 (dt, $J=7.1$, $J_{H,P}=0.8$ Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ: 165.9 (C═O), 165.5 (C═O), 165.3 (C═O), 165.2 (C═O), 84.4 (d, $J_{C,P}=4.3$ Hz, C-1), 75.7, 72.4, 68.8 (d, $J_{C,P}=9.5$ Hz), 68.3, 63.9 (2d, $J_{C,P}=5$ Hz, 2 × CH_2), 62.4 (C-6), 15.8 (2d, 2 × CH_3); ^{31}P NMR ($CDCl_3$) δ: 22.9; HRMS-ESI calcd for $C_{38}H_{37}NaO_{12}PS$ $[M+Na]^+$: 771.1636. Found: 771.1644. Anal. Calcd for $C_{38}H_{37}O_{12}PS$: C, 60.96; H, 4.98; S, 4.28. Found: C, 60.75; H, 4.83; S, 4.51.

1.3.3. *O,O′*-Diethyl-*S*-(2,3,4,6-tetra-*O*-benzoyl-β-D-mannopyranosyl) thiophosphate (7). $[\alpha]_D^{20}$ −80.3 (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ: 6.01 (m, 2H, $J_{4,3}=J_{4,5}=10.1$ Hz, H-2, H-4), 5.66 (m, 2H, $J_{1,2}=1.1$, $J_{H,P}=12.5$, $J_{3,2}=3.3$ Hz, H-1, H-3), 4.73 (dd, 1H, $J_{6,5}=2.5$, $J_{6,5}=12.3$ Hz, H-6), 4.48 (dd, 1H, $J_{6',5}=4.7$ Hz, H-6′), 4.29 (m, 1H, H-5), 4.10–4.25 (m, 4H, 2 × CH_2), 1.33 (dt, 3H, $J=7.1$, $J_{H,P}=0.8$ Hz, CH_3), 1.28 (dt, 3H, $J=7.1$, $J_{H,P}=0.9$ Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ: 166.0 (C═O), 165.5 (C═O), 165.3 (C═O), 165.2 (C═O), 82.4 (d, $J_{C,P}=2.6$ Hz, C-1), 76.8, 72.6, 71.8 (d, $J_{C,P}=8.5$ Hz), 66.0, 64.3 (d, $J_{C,P}=5.2$ Hz, CH_2), 64.1 (d, $J_{C,P}=5.6$ Hz, CH_2), 62.9 (C-6); ^{31}P NMR ($CDCl_3$) δ: 23.2. HRMS-ESI calcd for $C_{38}H_{37}NaO_{12}PS$ $[M+Na]^+$: 771.1636. Found: 771.1614. Anal. Calcd for $C_{38}H_{37}O_{12}PS$: C, 60.96; H, 4.98; S, 4.28. Found: C, 60.04; H, 4.93; S, 4.20.

1.3.4. *O,O′*-Diethyl-*S*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl) thiophosphate (20). $[\alpha]_D^{20}$ −3.1 (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ: 6.18 (t, 1H, $J_{4,3}=J_{4,5}=10.0$ Hz, H-4), 6.03 (dd, 1H, $J_{1,2}=1.7$, $J_{H,P}=12.5$ Hz, H-1), 5.87 (dd, 1H, $J_{2,3}=3.2$ Hz, H-2), 5.82 (ddd, 1H, $J_{H,P}=1.4$ Hz, H-3), 4.67 (m, 2H), 4.53 (m, 1H), 4.25 (m, 4H, 2 × CH_2), 1.38 (m, 6H, 2 × CH_3); ^{13}C NMR ($CDCl_3$) δ: 166.0 (C═O), 165.5 (C═O), 165.3 (C═O), 165.1 (C═O), 83.1 (d, $J_{C,P}=2.5$ Hz, H-1), 72.4 (d, $J_{C,P}=9.4$ Hz), 71.4, 69.9, 66.4, 64.3 (2 × d, 2 × CH_2), 62.5 (C-6), 16.0 (2 × d, 2 × CH_3); ^{31}P NMR ($CDCl_3$) δ: 22.1; HRMS-ESI calcd for $C_{38}H_{37}NaO_{12}PS$ $[M+Na]^+$: 771.1636. Found: 771.1621. Anal. Calcd for $C_{38}H_{37}O_{12}PS$: C, 60.96; H, 4.98; S, 4.28. Found: C, 60.94; H, 4.82; S, 4.32.

1.3.5. *O,O′*-Dibutyl-*S*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl) thiophosphate (8). ^1H NMR ($CDCl_3$) δ: 5.93 (t, 1H, $J_{3,2}$ 9.5 $=J_{3,4}=9.5$ Hz, H-3), 5.72 (t, 1H, $J_{4,5}=9{,}8$ Hz, H-4), 5.65 (t, 1H, $J_{2,1}=10.1$, H-2), 5.43 (dd, 1H, $J_{H,P}=12.5$ Hz, H-1), 4.62 (dd, 1H, $J_{6,5}=2.8$, $J_{6,6'}=12.3$ Hz, H-6), 4.47 (dd, 1H, $J_{6',5}=5.1$ Hz, H-6′), 4.27 (m, 1H, H-5); ^{13}C NMR ($CDCl_3$) δ: 166.0 (C═O), 165.6 (C═O), 165.1 (C═O), 84.0 (d, $J_{C,P}=3.4$ Hz, C-1), 76.6, 73.8, 71.2 (d, $J_{C,P}=10.0$ Hz), 62.9 (C-6); ^{31}P NMR ($CDCl_3$) δ: 22.8. HRMS-ESI calcd for $C_{42}H_{45}NaO_{12}PS$ $[M+Na]^+$: 827.2262. Found: 827.2242.

1.3.6. *O,O′*-Dibutyl-*S*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl) thiophosphate (9). ^{31}P NMR ($CDCl_3$) δ: 23.1; HRMS-ESI calcd for $C_{42}H_{45}NaO_{12}PS$ $[M+Na]^+$: 827.2262. Found: 827.2269.

1.3.7. *O,O′*-Dibutyl-*S*-(2,3,4,6-tetra-*O*-benzoyl-β-D-mannopyranosyl) thiophosphate (10). ^{31}P NMR ($CDCl_3$) δ: 23.4. HRMS-ESI calcd for $C_{42}H_{45}NaO_{12}PS$ $[M+Na]^+$: 827.2262. Found: 827.2301.

1.3.8. *O*-Methyl-*S*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl) phenylthiophosphonate (11). Obtained as a mixture of diastereoisomers **11a** and **11b** in a ratio of 1.2:1.0. ^1H NMR ($CDCl_3$) δ: 5.95 (t, 1H, $J_{3,2}=J_{3,4}=9.5$ Hz, H-3, **11b**), 5.88 (t, 1H, $J_{3,2}=J_{3,4}=9.4$ Hz, H-3, **11b**), 5.62–5.75 (m, 4H, H-2, H-4, both isomers), 5.51 (dd, 1H, $J_{1,2}=10.2$, $J_{H,P}=11.8$ Hz, H-1, **11b**), 5.32 (t, 1H, $J_{1,2}=J_{P,H}=10.3$ Hz, H-1, **11a**), 4.55 (dd, 1H, $J_{6,5}=2.8$, $J_{6,6'}=12.4$ Hz, H-6, **11b**), 4.45 (m, 2H, H-6, H-6, both isomers), 4.36 (dd, 1H, $J_{6'5}=5.2$, $J_{6,6'}=12.4$ Hz, H-6, **11a**), 4.25 (m, 1H, H-5, **11b**), 4.17 (m, 1H, H-5, **11a**), 3.82 (d, 3H, $J_{H,P}=12.9$ Hz, OCH_3, **11b**), 3.73 (d, 3H, $J_{H,P}=12.8$ Hz, OCH_3, **11a**); ^{13}C NMR ($CDCl_3$) δ: 83.3 (d, $J_{C,P}=2.2$ Hz, C-1, **11a**), 82.9 (d, $J_{C,P}=2.6$ Hz, C-1, **11b**), 76.6 (**11b**), 76.5 (**11a**), 74.0 (**11b**), 73.8 (**11a**), 71.2 (d, $J_{C,P}=7.3$ Hz, **11b**), 71.1 (d, $J_{C,P}=8.2$ Hz, **11a**), 69.1, 63.0 (C-6, **11a**), 62.9 (C-6, **11b**), 52.5 (d, $J_{C,P}=6.9$ Hz, OCH_3, **11b**), 52.4 (d, $J_{C,P}=7.3$ Hz, OCH_3, **11a**); ^{31}P NMR ($CDCl_3$) δ: 42.9 (**11a**), 41.1 (**11b**); HRMS-ESI calcd for $C_{41}H_{35}NaO_{11}PS$ $[M+Na]^+$: 789.1530. Found: 789.1551.

1.3.9. *O*-Methyl-*S*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl) phenylthiophosphonate (12). Obtained as a mixture of diastereoisomers **12a** and **12b** in a ratio of 1.1:1.0. ^1H NMR ($CDCl_3$) δ: 6.04 (dd, 1H, $J_{4,3}=3.4$, $J_{4,5}=1.1$ Hz, H-4, **12b**), 6.01 (dd, 1H, $J_{4,3}=3.4$, $J_{4,5}=1.0$ Hz, H-4, **12a**), 5.95 (t, 1H, $J_{2,1}=J_{2,3}$ 10.0 Hz, H-2, **12b**), 5.89 (t, 1H, $J_{2,1}=J_{2,3}$ 10.0 Hz, H-2, **12a**), 5.67 (dd, 1H, H-3, **12b**), 5.60 (dd, 1H, H-3, **12a**), 5.51 (dd, 1H, $J_{P,H}=12.1$ Hz, H-1, **12b**), 5.33 (dd, 1H, $J_{H,P}=11.1$ Hz, H-1, **12a**), 4.57 (dd, 1H, $J_{6,5}=6.7$, $J_{6,6'}=11.1$ Hz, H-6, **12b**), 4.48 (dd, 1H, $J_{6,5}=6.6$,

$J_{6,6'} = 11.1$ Hz, H-6, **12a**); 4.43 (m, 1H, H-5, **12b**); 4.33–4.39 (m, 2H, $J_{6,5} = 6.1$ Hz, H-5, H-6), 4.29 (dd, 1H, $J_{6,5} = 5.6$ Hz, H-6, **12a**), 3.80 (d, 3H, $J_{P,H} = 12.0$ Hz, OCH_3, **12a**), 3.77 (d, 3H, $J_{P,H} = 11.3$ Hz, OCH_3, **12b**); ^{13}C NMR ($CDCl_3$) δ: 83.9 (d, $J_{C,P} = 2.6$ Hz, C-1, **12a**), 83.2 (d, $J_{C,P} = 3.0$ Hz, C-1, **12b**), 75.6, 72.5 (**12b**), 72.4 (**12a**), 68.7 (2 × d), 68.2, 62.3 (C-6, **12a**), 62.1 (C-6, **12b**), 52.7 (d, $J_{C,P} = 5.6$ Hz, OCH_3), 52.1 (d, $J_{C,P} = 6.4$ Hz, OCH_3); ^{31}P NMR ($CDCl_3$) δ: 42.7 (**12a**), 41.3 (**12b**); HRMS-ESI calcd for $C_{41}H_{35}NaO_{11}PS$ $[M+Na]^+$: 789.1530. Found: 789.1555.

1.3.10. *O*-Methyl-*S*-(2,3,4,6-tetra-*O*-benzoyl-β-D-manno-pyranosyl) phenylthiophosphonate (13). Obtained as a mixture of diastereoisomers **13a** and **13b** in a ratio of 1.2:1.0. ^1H NMR ($CDCl_3$) δ: 6.02 (m, 3H, H-2, H-2, H-4), 5.97 (t, 1H, $J_{4,3} = J_{4,5} = 10.0$ Hz, H-4), 5.77 (dd, 1H, $J_{1,2} = 1.1$, $J_{H,P} = 11.2$ Hz, H-1, **13b**), 5.69 (dd, 1H, $J_{3,2} = 3.3$, $J_{3,4} = 10.3$ Hz, H-3, **13b**), 5.62 (m, 2H, $J_{1,2} = 1.1$, $J_{3,2} = 3.3$, $J_{H,P} = 11.2$ Hz, H-1, H-3, **13a**), 4.70 (dd, 1H, $J_{6,5} = 2.4$, $J_{6,6'} = 12.3$ Hz, H-6, **13b**), 4.54 (dd, 1H, $J_{6,5} = 2.6$, $J_{6,6'} = 12.3$ Hz, H-6, **13a**), 4.47 (dd, 1H, $J_{6',5} = 4.8$ Hz, H-6, **13b**), 4.40 (dd, 1H, $J_{6',5} = 4.8$ Hz, H-6, **13a**), 4.29 (m, 1H, H-5, **13b**), 4.19 (m, 1H, H-5, **13a**), 3.91 (d, 3H, $J_{H,P} = 12.6$ Hz, OCH_3, **13a**), 3.90 (d, 3H $J_{H,P} = 12.8$ Hz, OCH_3, **13b**); ^{13}C NMR ($CDCl_3$) δ: 82.1 (bs, $J_{C,P}$ <1 Hz, C-1, **13a**), 81.2 (d, $J_{C,P} = 2.1$ Hz, C-1, **13b**), 76.8 (**13a**), 76.7 (**13b**), 72.7 (**13b**), 72.6 (**13a**), 72.0 (d, $J_{C,P} = 6.8$ Hz, **13b**), 71.8 (d, $J_{C,P} = 6.8$ Hz, **13a**), 66.1, 62.9 (C-6, **13a**), 62.8 (C-6, **13b**), 52.8 (d, $J_{C,P} = 2.6$ Hz, OCH_3), 52.7 (d, $J_{C,P} = 2.6$ Hz, OCH_3); ^{31}P NMR ($CDCl_3$) δ: 43.1 (**13a**), 41.1 (**13b**); HRMS-ESI calcd for $C_{41}H_{35}NaO_{11}PS$ $[M+Na]^+$: 789.1530. Found: 789.1559. Anal. Calcd for $C_{41}H_{35}O_{11}PS$: C, 64.22; H, 4.60; S, 4.18. Found: C, 64.51; H, 4.83; S, 3.79.

1.3.11. *O*-Ethyl-*S*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyr-anosyl) phenylthiophosphonate (14). Obtained as a mixture of diastereoisomers **14a** and **14b** in a ratio of 1.3:1.0. ^1H NMR ($CDCl_3$) δ: 5.93 (t, 1H, $J_{3,2} = J_{3,4} = 9.4$ Hz, H-3, **14a**), 5.89 (t, 1H, $J_{3,2} = J_{3,4} = 9.4$ Hz, H-3, **14b**), 5.62–5.74 (m, 4H, H-2, H-4), 5.49 (dd, 1H, $J_{1,2} = 10.1$, $J_{H,P} = 11.9$ Hz, H-1, **14a**), 5.40 (t, 1H, $J_{1,2} = J_{P,H} = 10.4$ Hz, H-1, **14b**), 4.53 (dd, 1H, $J_{6,5} = 2.8$, $J_{6,6'} = 12.3$ Hz, H-6, **14a**), 4.42 (m, 2H, H-6, H-6, **14ab**), 4.34 (dd, 1H, $J_{6'5} = 5.0$, $J_{6,6'} = 12.3$ Hz, H-6, **14b**), 4.00–4.30 (m, other protons), 1.28 (t, 3H, $J = 7.1$ Hz, CH_3, **14a**), 1.18 (t, 3H, $J = 7.1$ Hz, CH_3, **14b**); ^{13}C NMR ($CDCl_3$) δ: 83.5 (d, $J_{C,P}$ <1 Hz, C-1, **14b**), 83.0 (d, $J_{C,P} = 2.6$ Hz, C-1, **14a**), 76.6 (**14b**), 76.5 (**14a**), 74.0 (**14a**), 73.8 (**14b**), 71.2 (2d), 69.1, 63.0 (C-6, **14b**), 62.9 (C-6, **14a**), 62.6 (2d, 2 × CH_2), 16.1 (CH_3, **14b**), 16.0 (CH_3, **14a**); ^{31}P NMR ($CDCl_3$) δ: 40.6 (**14b**), 38.9 (**14a**); HRMS-ESI calcd for $C_{42}H_{37}O_{11}NaPS$ $[M+Na]^+$: 803.1686. Found: 803.1725. Anal. Calcd for $C_{42}H_{37}O_{11}PS$: C, 64.61; H, 4.78; S, 4.11. Found: C, 64.68; H, 4.52; S, 4.07.

1.3.12. *O*-Ethyl-*S*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galacto-pyranosyl) phenylthiophosphonate (15). Obtained as a mixture of diastereoisomers **15a** and **15b** in a ratio of 1.5:1.0. ^1H NMR ($CDCl_3$) δ: 6.04 (dd, 1H, $J_{4,3} = 3.4$, $J_{4,5} = 1.0$ Hz, H-4, **15b**), 6.01 (dd, 1H, $J_{4,3} = 3.4$, $J_{4,5} = 1.0$ Hz, H-4, **15a**), 5.94 (t, 1H, $J_{2,1} = J_{2,3}$ 10.1 Hz, H-2, **15b**), 5.89 (t, 1H, $J_{2,1} = J_{2,3}$ 10.0 Hz, H-2, **15a**), 5.67 (dd, 1H, H-3, **15b**), 5.63 (dd, 1H, H-3, **15a**), 5.51 (dd, 1H, $J_{P,H} = 12.1$ Hz, H-1, **15b**), 5.42 (dd, 1H, $J_{H,P} = 11.3$ Hz, H-1, **15a**), 4.56 (dd, 1H, $J_{6,5} = 6.6$, $J_{6,6'} = 11.1$ Hz, H-6, **15b**), 4.47 (dd, 1H, $J_{6,5} = 6.5$, $J_{6,6'} = 11.1$ Hz, H-6, **15a**), 4.43 (m, 1H, H-5, **15b**), 4.38 (m, 1H, H-5, **15a**), 4.00–4.30 (m, other protons), 1.28 (t, 3H, $J = 7.0$ Hz, CH_3, **15b**), 1.19 (t, 3H, $J = 7.0$ Hz, CH_3, **15a**); ^{13}C NMR ($CDCl_3$) δ: 84.0 (d, $J_{C,P}$ <1 Hz, C-1, **15a**), 83.4 (d, $J_{C,P}$ <1 Hz, C-1, **15b**), 75.6 (**15b**), 75.5 (**15a**), 72.5 (**15b**), 72.4 (**15a**), 68.8 (2 × d), 68.2, 62.6 (2 × d, 2 × CH_2), 62.2 (C-6, **15a**), 62.1 (C-6, **15b**), 16.1 (CH_3, **15b**), 16.0 (CH_3, **15a**); ^{31}P NMR ($CDCl_3$) δ: 40.4 (**15a**), 39.0 (**15b**); HRMS-ESI calcd for $C_{42}H_{37}O_{11}NaPS$ $[M+Na]^+$: 803.1686. Found: 803.1691. Anal. Calcd for $C_{42}H_{37}O_{11}PS$: C, 64.61; H, 4.78; S, 4.11. Found: C, 64.52; H, 4.69; S, 4.10.

1.3.13. *O*-Ethyl-*S*-(2,3,4,6-tetra-*O*-benzoyl-β-D-manno-pyranosyl) phenylthiophosphonate (16). Obtained as a mixture of diastereoisomers **16a** and **16b** in a ratio of 1.3:1.0. ^1H NMR ($CDCl_3$) δ: 5.94–6.05 (m), 5.76 (dd, $J = 1.0$ and 11.1 Hz), 5.62–5.70 (m), 4.69 (dd, $J = 2.5$ and 12.4 Hz), 4.15–4.53 (m), 1.39 (t, $J = 7.0$ Hz, CH_3, **16a**), 1.32 (t, $J = 7.0$ Hz, CH_3, **16b**); ^{13}C NMR ($CDCl_3$) δ: 82.1 (C-1, **16a**), 81.3 (C-1, **16b**), 76.7, 72.7, 72.6, 71.9, 71.8, 66.1, 62.9 (CH_2), 16.3; ^{31}P NMR ($CDCl_3$) δ: 41.1 (**16a**), 38.8 (**16b**); HRMS-ESI calcd for $C_{42}H_{37}O_{11}NaPS$ $[M+Na]^+$: 803.1686. Found: 803.1725. Anal. Calcd for $C_{42}H_{37}O_{11}PS$: C, 64.61; H, 4.78; S, 4.11. Found: C, 64.55; H, 4.69; S, 4.19.

1.3.14. *O*-Ethyl-*S*-(2,3,4,6-tetra-*O*-benzoyl-α-D-manno-pyranosyl) phenylthiophosphonate (21). Obtained as a mixture of diastereoisomers **21a** and **21b** in a ratio of 1.3:1.0. ^1H NMR ($CDCl_3$) δ: 6.18 (m, 3H, H-1, H-4), 6.00 (dd, 1H, $J_{1,2} = 0.8$, $J_{H1,P} = 10.4$ Hz, H-1, **21b**), 5.90 (dd, 1H, $J_{2,3} = 3.1$ Hz, H-2, **21a**), 5.76–5.84 (m, 3H), 4.59 (m, 1H, H-5, **21b**), 4.32–4.46 (m, 6H), 4.28 (m, 1H, H-5, **21a**), 4.11 (dd, 1H, $J_{6,5} = 1.8$, $J_{6,6'} = 12.5$ Hz, H-6, **21a**), 3.95 (dd, 1H, $J_{6',5} = 2.6$ Hz, H-6, **21a**), 1.45 (2t, 6H, 2 × CH_3); ^{13}C NMR ($CDCl_3$) δ: 83.2 (C-1, **21a**), 82.2 (C-1, **21b**), 72.5 (d, $J_{C,P} = 7.7$ Hz, **21b**), 71.9 (d, $J_{C,P} = 7.7$ Hz, **21a**), 71.0 (**21a**), 70.6 (**21b**), 70.2 (**21a**), 70.1 (**21b**), 66.3 (**21b**), 66.2 (**21a**), 63.3 (d, $J_{C,P} = 6.8$, CH_2, **21a**), 62.8 (d, $J_{C,P} = 6.9$ Hz, CH_2, **21a**), 62.2 (C-6, **21b**), 61.6 (C-6, **21b**), 16.3 (**21a**),

16.2 (**21b**); ^{31}P NMR ($CDCl_3$) δ: 39.2 (**21a**), 39.1 (**21b**); HR-MS (ESI) calcd for $C_{42}H_{37}O_{11}NaPS$ $[M+Na]^+$: 803.1686. Found: 803.1724. Anal. Calcd for $C_{42}H_{37}O_{11}PS$: C, 64.61; H, 4.78; S, 4.11. Found: C, 64.65; H, 4.60; S, 4.24.

1.3.15. *S*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl) diphenylthiophosphinate (17). $[\alpha]_D^{20}$ +43.0 (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 5.88 (t, 1H, $J_{3,2} = 9.5$, $J_{3,4} = 9.5$ Hz, H-3), 5.70 (m, 2H, $J_{2,1} = 9.7$ Hz, $J_{4,5} = 9.8$ Hz, H-2, H-4), 5.53 (t, 1H, $J_{PH} = 9.5$ Hz, H-1), 4.16 (m, 2H, H-6, H-6′), 4.01 (m, 1H, H-5); ^{13}C NMR ($CDCl_3$) δ: 165.9 (C=O), 165.5 (C=O), 165.3 (C=O), 165.0 (C=O), 81.2 (C-1), 76.3, 74.1, 71.4 (d, $J_{C,P} = 6.1$ Hz), 68.9, 62.6 (C-6); ^{31}P NMR ($CDCl_3$) δ: 42.4. HRMS-ESI calcd for $C_{46}H_{37}NaO_{10}PS$ $[M+Na]^+$: 835.1737. Found: 835.1704. Anal. Calcd for $C_{46}H_{37}O_{10}PS$: C, 67.97; H, 4.59; S, 3.94. Found: C, 67.68; H, 4.41; S, 4.07.

1.3.16. *S*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl) diphenylthiophosphinate (18). $[\alpha]_D^{20}$ +65.5 (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ: 5.97 (m, 2H, $J_{4,3} = 3.3$, $J_{4,5}$ <1 Hz, H-2, H-4), 5.63 (dd, 1H, $J_{3,2} = 9.9$ Hz, H-3), 5.52 (t, 1H, $J_{1,2} = J_{H,P} = 10.3$ Hz, H-1), 4.22 (m, 2H, H-5,6), 4.12 (dd, 1H, $J_{6,5} = 8.7$, $J_{6'6} = 13.1$ Hz, H-6′); ^{13}C NMR ($CDCl_3$) δ: 165.8 (C=O), 165.5 (C=O), 165.4 (C=O), 165.3 (C=O), 81.6 (C-1), 75.2, 72.5, 68.9 (d, $J_{C,P} = 6.8$ Hz), 68.2, 61.6 (C-6); ^{31}P NMR ($CDCl_3$) δ: 42.4; HRMS-ESI calcd for $C_{46}H_{37}NaO_{10}PS$ $[M+Na]^+$: 835.1737. Found: 835.1728. Anal. Calcd for $C_{46}H_{37}O_{10}PS$: C, 67.97; H, 4.59; S, 3.94. Found: C, 67.88; H, 4.63; S, 3.77.

1.3.17. *S*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-mannopyranosyl) diphenylthiophosphinate (19). $[\alpha]_D^{20}$ −74.3 (*c* 0.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 6.02 (m, 2H, $J_{4,3} = J_{4,5} = 10.1$ Hz, H-2, H-4), 5.73 (dd, 1H, $J_{1,2} = 1.1$, $J_{H,P} = 10.5$ Hz, H-1), 5.64 (dd, 1H, $J_{3,2} = 3.3$ Hz, H-3), 4.29 (dd, 1H, $J_{6,5} = 2.7$, $J_{6,6'} = 12.2$ Hz, H-6), 4.22 (dd, 1H, $J_{6',5} = 3.7$ Hz, H-6′), 3.99 (m, 1H, H-5); ^{13}C NMR ($CDCl_3$) δ: 165.9 (C=O), 165.3 (C=O), 165.2 (C=O), 165.1 (C=O), 79.6 (d, $J_{C,P} = 1.7$ Hz, H-1), 76.5, 72.6, 72.2 (d, $J_{C,P}$ 6.0 Hz), 65.9, 62.5 (C-6); ^{31}P NMR ($CDCl_3$) δ: 43.1; HRMS-ESI calcd for $C_{46}H_{37}NaO_{10}PS$ $[M+Na]^+$: 835.1737. Found: 835.1726. Anal. Calcd for $C_{46}H_{37}O_{10}PS$: C, 67.97; H, 4.59; S, 3.94. Found: C, 67.71; H, 4.62; S, 4.20.

1.3.18. *S*-(2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl) diphenylthiophosphinate (22). ^{13}C NMR ($CDCl_3$) δ: 165.9 (C=O), 165.5 (C=O), 165.1 (C=O), 164.8 (C=O), 81.4 (C-1), 72.0 (d, $J = 6.8$ Hz), 70.8, 70.4, 66.3, 61.8 (C-6); ^{31}P NMR ($CDCl_3$) δ: 40.6; HRMS-ESI calcd for $C_{46}H_{37}NaO_{10}PS$ $[M+Na]^+$: 835.1737. Found: 835.1721.

1.3.19. 2,3,4,6-Tetra-*O*-benzoyl-1-thio-α-D-mannopyranose (23). $[\alpha]_D^{20}$ −30.5 (*c* 0.5, $CHCl_3$); Lit:[16] $[\alpha]_D^{20}$ −30.5 (*c* 1.0, $CHCl_3$); ^{1}H and ^{13}C NMR spectral data matched that reported.[16]

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