

3. Synthesis of Glycosylphosphine Oxides and Related Compounds

by Andrej Lopusiński, Bruno Bernet, Anthony Linden, and Andrea Vasella*

Organisch-chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

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The benzyl-protected glycosyl acetates **1**, **6**, **11**, and **15** react with MeOPPh₂ under catalysis by TMSOTf to yield diastereoselectively the glycosylphosphine oxides **2**, **3**, **8**, **12**, **13**, and **16**, with a strong preference for the 1,2-*cis*-configured anomers. Hydrogenolysis of the major products gave the crystalline, unprotected phosphine oxides **4**, **9**, **14**, and **17**, of which **4** was transformed into the acetate **5**, and **9** into the benzoate **10**. The benzylated phosphine oxides **2**, **8**, **12**, and **16** were reduced with Cl₃SiH in the presence of a tertiary amine to form the phosphines **18**, **21**, **24**, and **26**, which were transformed into the phosphine sulfides **19**, **22**, **25**, and **27**. Moreover, **18** and **21** were characterized as the borane adducts **20** and **23**. The structure of the (arabinofuranosyl)phosphine oxide **12**, the corresponding sulfide **25**, and of the borane complex **20** were established by X-ray analysis. According to NMR spectroscopy, the equatorial pyranosylphosphine oxide **8**, the sulfide **22**, and the borane complex **23** adopt a ⁴C₁ conformation. The axial phosphine oxide **2** is a flattened ⁴C₁, the sulfide **19** exists as a B_{2,5}, and the borane complex **20** is a flattened ⁴C₁ in the solid state and a B_{2,5} in solution. Thus, the conformational behavior of these α-D-glucopyranose derivatives reflects the steric requirement of the P-substituents.

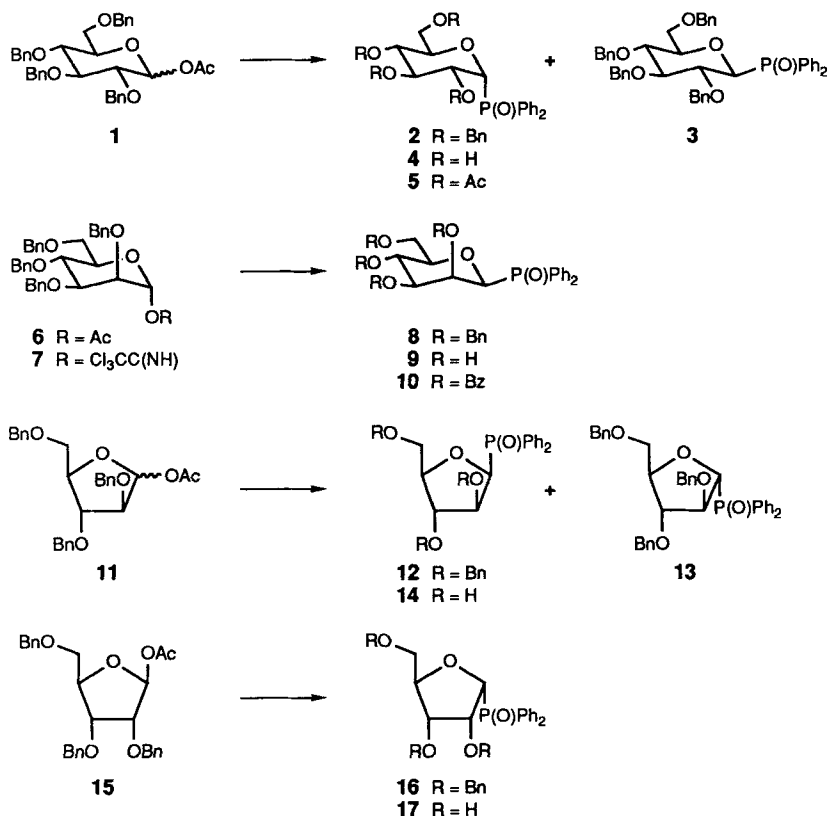
Introduction. – The synthesis of carbohydrate-derived organophosphorus compounds containing a C–P bond, especially of glycosylphosphonates, has been a subject of interest for some time [1–10]¹⁾. Until recently, there was no general and efficient route to compounds possessing a bond between the P-atom and the anomeric center. *Meuwly* and *Vasella* have shown that *O*-benzylated glycosyl acetates react under mild conditions in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) with trialkyl phosphites to form diastereoselectively 1,2-*cis*-configured glycosylphosphonates in good yield [5]. The scope of this modified *Michaelis-Arbusov* reaction appears to be broad [5–9] and includes various phosphites. Harsher reaction conditions give products resulting from dealkylation of the phosphonoyl group, apparently under thermodynamic control with regard to anomeric configuration [10].

Vasella and coworkers recently described the first syntheses of two glycosylphosphine oxides by reaction of the anomeric tetra-*O*-benzyl-D-glucopyranosyl acetates **1** with methyl diphenylphosphinite (MeOPPh₂), and by the oxidation of glucosyl phosphines, which were prepared from a 1-*azi*-glucose and diphenylphosphine [15]. We have studied the scope of the first method, applying it to derivatives of mannopyranose, arabino-, and ribofuranose, the reduction of phosphine oxides to glycosylphosphines, and the transformation of these phosphines into glycosylphosphine sulfides. In two cases, glycosylphosphines were transformed into their borane adducts.

¹⁾ For derivatives containing phosphorus as the ring heteroatom, see [11] [12] and earlier papers of *Yamamoto*. For α-heterosubstituted phosphonates and phosphine oxides, see [13] [14].

Results and Discussion. – Reaction of the glucopyranosyl acetates **1** [16] (α/β 10:1) with a slight excess of MeOPPh₂ and TMSOTf in CH₂Cl₂ at 0–25° gave 52% of an 87:13 mixture of the anomeric (glucopyranosyl)(diphenyl)phosphine oxides **2** and **3** (Scheme 1). A higher yield (74%) of **2** and **3** (85:15) was obtained from a mixture of the acetates **1** enriched in the β -anomer (α/β 1:9) [17], in agreement with earlier results [15].

Scheme 1



Under analogous conditions, the mannopyranosyl acetate **6** gave 44% of the 1,2-*cis*-configured (β -D-mannopyranosyl)(diphenyl)phosphine oxide **8**. The more reactive [8] trichloroacetimidate **7** [18] yielded 60% of **8**. Similarly, the *O*-benzylated arabinofuranosyl acetates **11** [19] (α/β 63:27) reacted with MeOPPh₂ to afford 71% of the phosphine oxides **12** and **13**, with the 1,3-*cis*-isomer dominating to an extent of 95:5. The 1,2-*cis*-configured (ribofuranosyl)phosphine oxide **16** was obtained in 76% yield as a single isomer from the ribofuranosyl acetate **15** [20]. Thus, under mild reaction conditions, the 1,2-*cis*-configured phosphine oxides are formed as the major products, similarly to what has been observed for the synthesis of glycosylphosphonates, and presumably for analogous reasons [5]. Hydrogenolysis of the glycosylphosphine oxides **2**, **8**, **12**, and **16**

(10% Pd/C, MeOH, 8 bar) yielded the corresponding, unprotected phosphine oxides **4**, **9**, **14**, and **17** as crystalline compounds which are soluble in EtOH and in DMSO, but not in H₂O. Acetylation of the crude phosphine oxide **4** ($\delta(^{31}\text{P}) = 29.39$ ppm) gave the crystalline tetraacetate **5**. Similarly, **9** was benzoylated to yield **10**. Attempts to obtain crystals of **5** suitable for X-ray crystallography were unsuccessful.

The spectroscopic data of **2** and **3** have been reported [15] (for some relevant NMR data, see *Tables 1* and *2*). These phosphine oxides follow *Hudson's* rule of isorotation [2]. In the ^1H -NMR spectrum (*Table 1*), the deprotected phosphine oxide **4** exhibits similar couplings as **3**, consistent with a flattened 4C_1 conformation. The acetate **5** shows $J(1,2) = 7.0$, $^3J(\text{P,H-C}(2)) = 21.1$, $J(2,3) = 9.7$, and $J(4,5) = 9.9$ Hz. These coupling constants and $J(3,4) = 8.9$ Hz suggest an axial orientation of H-C(2), H-C(3), and H-C(4). Thin, plate-like crystals of **5** were subjected to X-ray analysis, but proved to be of poor quality and poor diffractors. Unfortunately, larger crystals of suitable quality could not be obtained. The quality and paucity of observable reflections proved insufficient to refine the structure satisfactorily, and the structural results are not reported here. Nevertheless, the basic skeleton of the molecule was clearly defined. Approximate torsion angles are 46° for O(5)-C(1)-C(2)-C(3), -58° for O(5)-C(5)-C(4)-C(3), 53° for H-C(1)-C(2)-H, -171° for H-C(2)-C(3)-H, 169° for H-C(3)-C(4)-H, and -169° for H-C(4)-C(5)-H, where the H-atoms are in geometrically calculated positions based on the heavy atoms. A flattened 4C_1 conformation is evident, and the H-atoms at C(2), C(3) and C(4) are all axial, in agreement with the spectroscopic data.

The ^1H -NMR spectra of the (mannopyranosyl)phosphine oxides **8** and **10** show small $J(1,2)$ of 0.6–0.7 Hz (*Table 1*). H-C(2) appear as br. s. Selective irradiations reveal that the values of $J(2,3)$ and $J(\text{P,H-C}(2))$ are 2–3 Hz. The relatively small couplings of H-C(2) with both H-C(1) and H-C(3) indicate an equatorial P(O)Ph₂ group. In β -D-mannopyranoses, $J(1,2)$ should be smaller than in the corresponding α -D-anomers [21]. Analysis of a NOE experiment on **8** shows a positive effect for both H-C(3) and H-C(5) upon irradiation of the H-C(1) signal at 4.22 ppm. This confirms the axial orientation of H-C(1) and the β -D-configuration of **8**. $^3J(\text{P,C}(3))$ and $^3J(\text{P,C}(5))$ of **8** and **10** between 11.8 and 12.9 Hz (*Table 2*) suggest a nearly 180° dihedral angle between ^{31}P and both C(5) and C(3), corresponding to an equatorial orientation of the P(O)Ph₂ group. These spectroscopic data, together with large $J(3,4)$ and $J(4,5)$ (9.3–10.1 Hz) suggest a 4C_1 conformation for **8** and **10**. The ^1H -NMR spectrum ($(\text{D}_6)\text{DMSO}$) of **9** shows a d for H-C(1) with $^2J(\text{P,H}) = 8.6$ Hz. Poorly resolved peaks for H-C(2) (4.05 ppm) and one broad signal for H-C(3) and H-C(4) (3.35 ppm) do not permit conformational analysis. Nevertheless, the presence of a 4C_1 conformation of **9** is evidenced by the heteronuclear $J(\text{P,C})$ (*Table 2*), especially by $^3J(\text{P,C}(3)) = 13.1$ Hz and $^3J(\text{P,C}(5)) = 12.3$ Hz.

The structure of the (arabinofuranosyl)phosphine oxide **12** was established by X-ray analysis (*Fig. 1* and *Tables 3* and *4*). The P=O bond length is consistent with the mean P=O bond length of 1.49 (3) Å calculated from the data for 289 R₃P=O compounds stored in the *Cambridge Crystallographic Data Base* [22]. The furanosyl ring possesses a 2T_3 conformation with a pseudoequatorial Ph₂P(O), and pseudoaxial BnOCH₂ and BnO groups (*Table 5*). This is also the preferred conformation in CDCl₃ solution indicated by small values for $J(2,3)$ and $J(3,4)$ (*Table 1*). As expected, the α -D-anomer **13** possesses a 3T_2 conformation where all substituents are in pseudoequatorial positions leading to relatively large values for $J(1,2)$, $J(2,3)$, and $J(3,4)$. $^3J(\text{P,H-C}(2)) = 12.1$ Hz for **13**

Table 1. Selected ^1H -NMR (CDCl_3) Chemical Shifts [ppm] and Coupling Constants [Hz] of Glycosylphosphine Oxides, Sulfides, and Borane Adducts

	H-C(1)	H-C(2)	H-C(3)	H-C(4)	H-C(5)	$J(1,2)$	$J(2,3)$	$J(3,4)$	$J(4,5)$	$^2J(\text{P,H-C}(1))$	$^3J(\text{P,H-C}(2))$	$^4J(\text{P,H-C}(3))$
2	4.91	4.17	4.61	3.68	4.06	5.9	7.4	7.2	9.7	0	17.8	0
4 ^{a)}	4.98	3.83–3.70	4.15	3.23	3.78–3.70	4.7	7.5	8.1	9.0	0	b)	0
5	5.12	5.31	6.27	5.03	4.60	7.0	9.7	8.9	9.9	3.2	21.1	0
19	5.14	4.68–4.63	4.12–3.97	3.70	4.12–3.97	3.4	b)	3.4	9.7	1.9	b)	b)
19 ^{c)}	5.30	4.94	4.11	3.78	4.44	3.2	3.5	3.7	9.4	2.7	4.7	3.7
20	5.13	4.29	4.09	3.73	3.97	3.7	4.2	4.4	9.4	2.8	6.2	ca. 3.5
3	4.24	3.97	3.78	3.62–3.54	3.47	10.1	8.9	8.9	9.8	2.5	9.6	0
8	4.22	4.72	3.68	4.02	3.53	0.7	2.8	9.3	9.5	10.4	ca. 3	0
9 ^{a)}	4.33	4.05	3.37–3.32	3.37–3.32	3.32–3.18	0	< 3	b)	b)	8.6	< 2	b)
10 ^{c)}	4.77	6.53	5.70	5.97	4.20	0.6	3.3	10.1	9.9	11.7	ca. 3	0
22	4.25	5.06	3.71	4.03	3.54	0.6	2.7	9.2	9.0	7.8	3.5	0
23	4.21	4.67	3.71	4.03	3.50	0.6	2.6	9.4	9.6	4.1	3.2	0
13	4.82	4.55	4.10	3.90	3.57, 3.53	5.6	3.9	5.8	4.4, 5.4	2.7	12.1	0
12	4.93	4.53	3.89	4.32	3.48, 3.32	3.9	< 0.5	ca. 1	6.3, 6.9	2.2	< 0.5	ca. 2
14 ^{a)}	4.47	4.19	3.89	3.84	3.44	3.9	1.7	2.0	5.4	2.9	ca. 2	ca. 2
25	5.14	4.62	3.83	4.46–4.42	3.46, 3.27	3.7	0.5	1.2	6.5, 7.1	0.5	0	2.3
16	4.88	4.62	4.06	4.18	3.75, 3.56	3.4	4.0	9.2	2.1, 3.8	3.6	0	0
17 ^{a)}	5.09	4.44	3.87	3.80	3.50, 3.39	5.6	5.1	6.2	3.6, 5.0	6.1	9.6	0
27	5.01	4.75	4.13	4.28	3.74, 3.56	3.2	3.7	9.3	3.6, 2.2	0	0	0

^{a)} In $(\text{D}_6)\text{DMSO}$. ^{b)} Not determined. ^{c)} In C_6D_6 .

Table 2. Selected ^{13}C - and ^{31}P -NMR (CDCl_3) Chemical Shifts [ppm] and P , C Coupling Constants [Hz] of Glycosylphosphine Oxides, Sulfides, and Borane Adducts

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	^{31}P	$^1J(\text{P}, \text{C}(1))$	$^2J(\text{P}, \text{C}(2))$	$^3J(\text{P}, \text{C}(3))$	$^3J(\text{P}, \text{C}(5))$
2 ^{a)}	74.14	78.70	80.76	77.55	74.95	68.66	23.27	79.5	0	2.5	0
5	71.26	70.46	70.46	68.51	73.11	61.98	27.61	74.6	0	0	ca. 3
19	77.27	77.21	75.34	77.29	73.18	69.47	39.20	69.8	0	1.7	2.3
20 ^{b)}	73.87	77.05	77.67	77.14	74.00	69.28	19.44 ^{b)}	39.4	0	6.0	ca. 1.5
3 ^{a)}	76.84	78.26	87.43	77.68	81.06	68.93	21.96	89.7	0	12.9	13.1
8 ^{a)}	79.86	73.01	84.28	74.76	81.77	69.68	24.84	93.7	2.4	12.0	12.9
9 ^{c)}	77.79	68.20	74.41	67.19	83.78	61.45	24.64	93.8	< 2	13.1	12.3
10	77.74	67.47	72.71	66.60	78.80	62.30	21.33	90.4	< 2	11.8	12.0
22	83.15	72.82	84.81	74.64	81.78	69.56	39.62	74.0	2.6	13.6	11.8
23 ^{a)}	79.47	74.27	85.11	74.56	81.96	69.56	18.62	43.9	0	12.8	8.0
13 ^{a)}	81.38	83.99	84.27	82.21	68.91	–	27.42	78.0	3.9	4.8	5.4 ^{d)}
12 ^{a)}	81.23	83.29	83.09	85.50	70.07	–	26.15	92.6	4.5	5.3	8.4 ^{d)}
14 ^{c)}	79.75	77.81	78.22	88.69	61.72	–	25.06	92.5	5.0	5.0	7.1 ^{d)}
25	84.77	83.66	82.19	86.67	70.01	–	37.47	73.8	3.3	5.6	7.4 ^{d)}
16 ^{a)}	81.15	77.52	79.18	79.96	69.05	–	24.46	94.5	4.4	6.1	3.5 ^{d)}
17 ^{c)}	79.17	71.81	72.31	85.15	61.38	–	26.35	88.0	4.1	4.0	1.5 ^{d)}
27	85.15	77.78	78.97	81.27	69.00	–	36.49	75.0	3.7	7.1	3.2 ^{d)}

^{a)} Assignment based upon a ^1H , ^{13}C inverse correlation spectrum. ^{b)} In C_6D_6 . ^{c)} In $(\text{D}_2)\text{DMSO}$. ^{d)} $J(\text{P}, \text{C}(4))$.

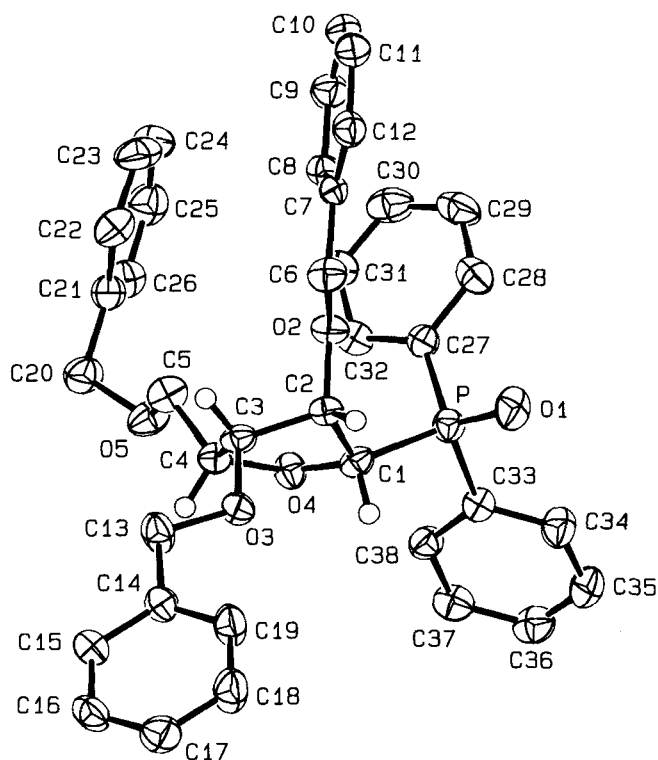
Fig. 1. X-Ray structure of **12**

Table 3. Data Collection and Structure Refinement Parameters

	12	25	20
Molecular formula	$C_{38}H_{37}O_5P$	$C_{38}H_{37}O_4PS$	$C_{46}H_{48}BO_5P$
Formula weight	604.68	620.74	722.67
Crystal color, habit	colorless, prism	colorless, needle	colorless, prism
Crystal dimensions [mm]	$0.19 \times 0.32 \times 0.40$	$0.10 \times 0.20 \times 0.40$	$0.15 \times 0.20 \times 0.50$
Crystallized from	ethyl acetate/hexane	ethyl acetate/hexane	hexane
Data-collection temp.	213 ± 1 K	173 ± 1 K	173 ± 1 K
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Cell determination reflections; 2θ range [°]	25; 23–30	25; 21–36	21; 22–30
Unit cell parameters: a [Å]	9.490(1)	9.647(1)	12.836(2)
b [Å]	9.650(1)	35.239(5)	24.669(2)
c [Å]	34.078(4)	9.375(1)	12.679(2)
V [Å ³]	3120.9(7)	3187.2(7)	4014.8(9)
Z	4	4	4
D_x [g·cm ⁻³]	1.287	1.294	1.195
Linear absorption coefficient [cm ⁻¹]	1.263	1.842	1.080
Diffractometer	Nicolet R3	Rigaku AFC5R	Rigaku AFC5R
Reflection scan mode	Wyckoff ω -scans	ω - 2θ	ω - 2θ
$2\theta_{\text{max}}$ [°]	55	55	60

Table 3 (cont.)

	12	25	20
Total reflections measured	4706	4820	7221
Unique reflections	4567	4688	7137
R_{int}	0.017	0.015	0.016
Reflections used in refinement	3096 [$I > 2\sigma(I)$]	3421 [$I > 3\sigma(I)$]	4998 [$I > 3\sigma(I)$]
Parameters refined	435	435	545
R	0.0473	0.0391	0.0446
wR	0.0476	0.0351	0.0393
Goodness of fit s	1.312	1.396	1.680
Weighting factor g	0.0004	0.000025	0.000025
Data/parameter ratio	7.12	7.86	9.17
Final $\Delta_{\text{max}}/\sigma$	0.0002	0.001	0.001
$\Delta\rho$ (max; min) [$\text{e } \text{\AA}^{-3}$]	0.25; -0.26	0.30; -0.24	0.29; -0.29

Table 4. Selected Bond Lengths [$\text{\AA}$] with E.s.d.'s in Parentheses^{a)}

	12	25	20
P–C(1)	1.833(4)	1.848(3)	1.889(3)
P–X	1.482(3)	1.954(1)	1.936(3)
O(2)–C(2)	1.415(5)	1.414(4)	1.432(3)
O(3)–C(3)	1.426(5)	1.417(4)	1.432(3)
O(4)–C(1)	1.438(4)	1.432(4)	–
O(4)–C(4)	1.461(5)	1.456(4)	1.430(3)
O(5)–C(1)	–	–	1.431(3)
O(5)–C(5)	–	–	1.435(3)
C(1)–C(2)	1.519(5)	1.522(4)	1.537(4)
C(2)–C(3)	1.525(6)	1.532(5)	1.527(4)
C(3)–C(4)	1.531(5)	1.534(4)	1.522(4)
C(4)–C(5)	1.494(6)	1.505(5)	1.523(4)
C(5)–C(6)	–	–	1.511(4)

^{a)} Atom X is O(1), S, and B for **12**, **25**, and **20**, respectively.

reflects a dihedral angle of nearly 0° and agrees with the value expected from the *Karplus* relation [23]. The ^{31}P -NMR chemical shifts of 26.15 ppm for **12** and of 27.42 ppm for **13**, as well as $^2J(\text{P}, \text{C}(1)) = 92.6$ Hz for **12** and 78.0 Hz for **13** agree well with the assigned orientation of the $\text{Ph}_2\text{P}(\text{O})$ group at C(1). The minor anomer **13** is strongly dextrarotatory, while **12** is levorotatory, in keeping with the chiroptical properties of anomeric glycosylphosphonates [2]. A 3T_3 conformation of the (β -D-arabinofuranosyl)phosphine oxide **14** is suggested by the similarity of the signal patterns in the ^1H - and ^{13}C -NMR spectra of **12** and **14** (Tables 1 and 2).

The ^1H -NMR spectrum of the (ribofuranosyl)phosphine oxide **16** (Table 1) suggests an α -D-configuration. Irradiation of H–C(1) at 4.88 ppm shows NOE's for the signals of H–C(2) ($\delta = 4.62$ ppm) and H–C(3) ($\delta = 4.06$ ppm). Similar NOE's were observed for H–C(1) and H–C(3) upon irradiation of H–C(2), confirming the *cis*-dipseudoaxial orientation of H–C(1) and H–C(3) and the α -D-configuration. The data are consistent with a northern conformation [24]. The large value for $J(3,4) = 9.2$ Hz agrees well with a distinct 3T_2 conformation where H–C(3) and H–C(4) are pseudodiaxial. The relatively

Table 5. *Selected Torsion Angles [°] with E.s.d.'s in Parentheses^{a)}*

	12	25	20		12	25	20
P–C(1)–O(4)–C(4)	–150.8(3)	–149.0(2)	–	C(1)–O(5)–C(5)–C(4)	–	–	62.6(3)
P–C(1)–O(5)–C(5)	–	–	70.0(3)	C(1)–O(4)–C(4)–C(5)	124.5(3)	125.3(3)	–
P–C(1)–C(2)–O(2)	43.6(4)	44.1(3)	43.3(3)	C(1)–O(5)–C(5)–C(6)	–	–	–173.6(2)
P–C(1)–C(2)–C(3)	160.5(3)	160.5(2)	–77.1(2)	C(1)–C(2)–C(3)–C(4)	–33.6(4)	–33.6(4)	–50.2(3)
X–P–C(1)–O(4)	173.5(2)	172.1(2)	–	C(2)–C(1)–O(4)–C(4)	–23.4(4)	–23.1(4)	–
X–P–C(1)–O(5)	–	–	–85.6(2)	C(2)–C(1)–O(5)–C(5)	–	–	–59.7(3)
X–P–C(1)–C(2)	51.5(3)	50.5(3)	42.4(3)	C(2)–C(3)–C(4)–C(5)	–99.2(4)	–99.9(3)	53.5(3)
O(2)–C(2)–C(1)–O(4)	–81.7(4)	–81.0(3)	–	C(3)–C(4)–C(5)–C(6)	–	–	179.9(2)
O(2)–C(2)–C(1)–O(5)	–	–	172.8(2)	P–C(1)–C(2)–H(2)	–80.2(4)	–80.1(4)	162
O(2)–C(2)–C(3)–O(3)	–159.8(3)	–159.1(2)	67.3(3)	O(2)–C(2)–C(1)–H(1)	164	164	–71
O(2)–C(2)–C(3)–C(4)	81.1(4)	81.5(3)	–172.7(2)	O(2)–C(2)–C(3)–H(3)	–38	–38	–54
O(3)–C(3)–C(2)–C(1)	85.4(3)	85.8(3)	–170.2(2)	O(3)–C(3)–C(2)–H(2)	–34	–34	–53
O(3)–C(3)–C(4)–O(4)	–95.4(4)	–94.3(3)	–67.7(3)	O(3)–C(3)–C(4)–H(4)	22	23	56
O(3)–C(3)–C(4)–C(5)	144.5(3)	144.6(3)	174.0(2)	C(5)–C(4)–C(3)–H(3)	20	19	–
O(4)–C(1)–C(2)–C(3)	35.3(4)	35.4(3)	–	O(4)–C(4)–C(3)–H(3)	–	–	55
O(5)–C(1)–C(2)–C(3)	–	–	52.4(3)	O(4)–C(4)–C(5)–H(5)	–	–	–60
O(4)–C(4)–C(3)–C(2)	20.8(4)	21.2(4)	171.8(2)	C(6)–C(5)–C(4)–H(4)	–	–	–61
O(5)–C(5)–C(4)–C(3)	–	–	–58.5(3)	H(1)–C(1)–C(2)–H(2)	40	40	48
O(4)–C(4)–C(5)–O(5)	–	–	–178.3(2)	H(2)–C(2)–C(3)–H(3)	88	88	–174
O(4)–C(4)–C(5)–C(6)	–	–	60.1(3)	H(3)–C(3)–C(4)–H(4)	–103	–103	178
C(1)–O(4)–C(4)–C(3)	1.4(4)	0.9(4)	–	H(4)–C(4)–C(5)–H(5)	–	–	179

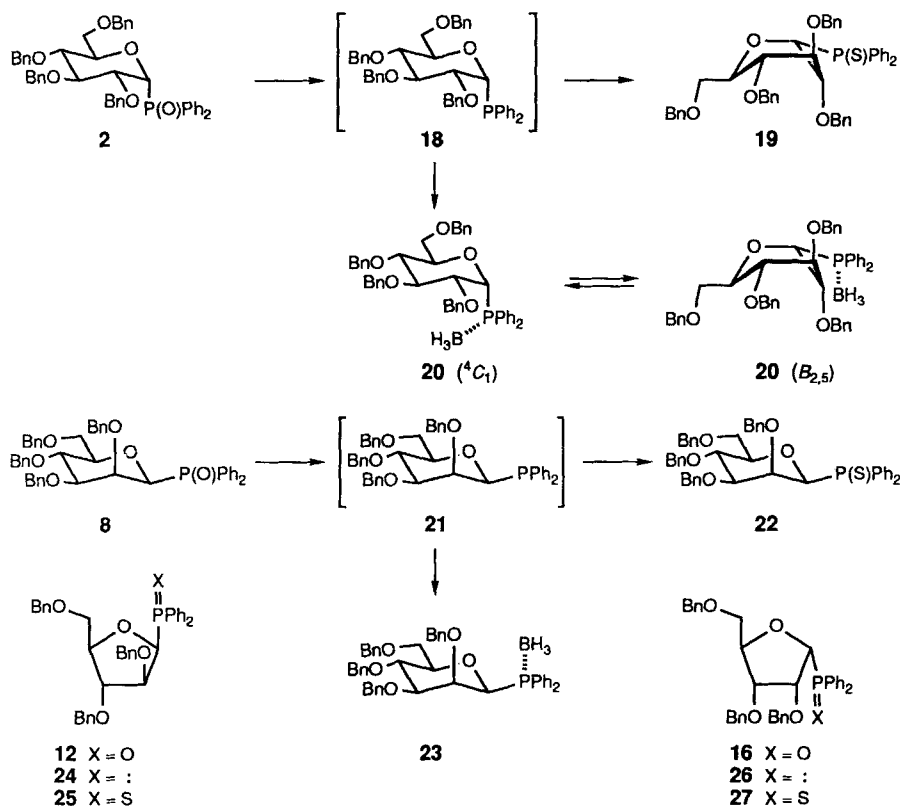
^{a)} Atom X is O(1), S and B for **12**, **25**, and **20**, respectively.

small $^3J(\text{C,P}) = 6.1$ Hz for **16** (Table 2) is well accommodated by the pseudoequatorial orientation of the $\text{Ph}_2\text{P}(\text{O})$ group [25] [26]. Similar coupling constants corresponding to a dihedral angle of *ca.* 150° were reported for acyclic phosphonates [27] [28] and dialkylphosphine sulfides and oxides [29]. *Dreiding* models suggest a $\text{C}(3)\text{--C}(2)\text{--C}(1)\text{--P}$ angle of $150\text{--}155^\circ$ for the 3T_2 conformation of **16**. The deprotected (ribofuranosyl)-phosphine oxide **17** adopts also a 3T_2 conformation. A larger $J(1,2)$ and a smaller $J(3,4)$ than observed for **16** indicate some flattening. $^2J(\text{P,H--C}(1))$ (**16**: 3.6, **17**: 6.1 Hz) and $^3J(\text{P,H--C}(2))$ (**16**: 0, **17**: 9.6 Hz) differ, whereas the corresponding $J(\text{P,C})$ are similar. These coupling constants were unambiguously assigned by a ^{31}P -decoupled spectrum of **17** and by selective ^1H -decoupling experiments (see *Exper. Part*). They may be a hint for the presence of different rotamers around the $\text{C}(1)\text{--P}$ bond in the protected and deprotected phosphine oxide.

The simple access to (glycosyl)(diphenyl)phosphine oxides suggests the use of these compounds as starting materials for the synthesis of glycosylphosphines, which are of interest as ligands in low-valent transition-metal catalysts for enantioselective organic transformations [30] [31].

The glycosylphosphine oxides **2**, **8**, **12**, and **16** were reduced (Scheme 2) with an excess of Cl_3SiH and Et_3N or *N,N*-dimethyl-*p*-toluidine (molar ratio of silane to amine 1:1) at 80° in benzene [32–36]. As the resulting phosphines **18**, **21**, **24**, and **26** are readily oxidized to the starting phosphine oxides, the crude products were immediately transformed to phosphine sulfides by the addition of elemental sulfur. The (glucopyranosyl)-, (mannopyranosyl)-, (arabinofuranosyl)-, and (ribofuranosyl)phosphine sulfides **19**, **22**, **25**, and **27** were thus isolated in 57 to 85%. As the reaction of phosphines with sulfur is a

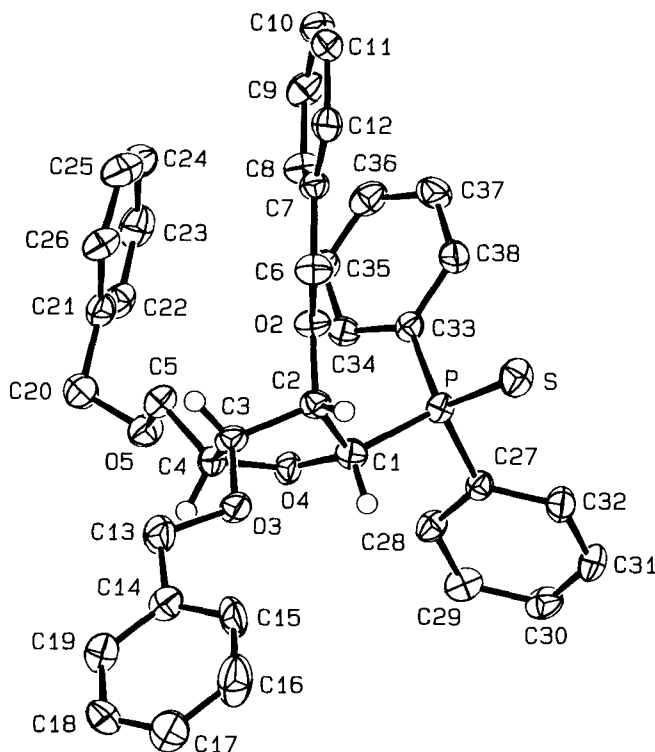
Scheme 2



quantitative process [37], these yields reflect the reduction of glycosylphosphine oxides by Cl_3SiH .

The resonances of ${}^{31}\text{P}$ [38] and C(1) the glycosylphosphine sulfides are shifted to lower field by 11–16 and 3–4 ppm, respectively, as compared to those of their phosphine-oxide analogs (Table 2). Their IR spectra show medium (KBr) or strong (CHCl_3) bands at 610–615 and 645–672 cm^{-1} , respectively, characteristic for the $\text{P}=\text{S}$ group, and corresponding to the absorptions observed for (alkyl)(diaryl)phosphine sulfides [39]. The ${}^1\text{H}$ -NMR spectrum (C_6D_6 or CDCl_3) of the phosphine sulfide 19 (Table 1) suggests a $B_{2,5}$ conformation, which is different from the one of the corresponding phosphine oxide (flattened 4C_1), presumably reflecting the larger *van der Waals* radius of sulfur. The effect of the transition from the $\text{Ph}_2\text{P}(\text{O})$ to the $\text{Ph}_2\text{P}(\text{S})$ group on the conformation of these anomeric glycosylphosphine derivatives is, thus, similar to that which has been observed for the transition from a Ph_2P to a $\text{Ph}_2\text{P}(\text{O})$ group attached to C(2) and C(4) of 1,6-anhydro- β -D-glucopyranose [31]. The NMR spectra of the mannopyranosyl sulfide 22, which suggest an equatorial $\text{Ph}_2\text{P}(\text{S})$ group, evidence the β -D-configuration of the strongly levorotatory 22 and a 4C_1 conformation.

X-Ray analysis of the (arabinofuranosyl)phosphine sulfide 25 establishes its β -D-configuration (Fig. 2 and Tables 3 and 4). The crystal data and atomic coordinates show that

Fig. 2. X-Ray structure of **25**

12 and **25** are isostructural. The P=S bond length is consistent with the mean P=S bond length of 1.95 (3) Å calculated from the data for 106 $R_3P=S$ compounds stored in the *Cambridge Crystallographic Data Base* [22]. The high, negative value for the specific rotation of **25** is in keeping with Hudson's rule. The NMR spectra (*Tables 1* and *2*) are consistent with a 2T_3 conformation, similar to what is found for the solid state (*Table 4*). The 1H -NMR spectrum of the sulfide **27** is similar to the one of the phosphine oxide **16** and confirms the expectation that both compounds possess the same conformation. No coupling between P and H—C(1) was observed, but the P signal is broadened, even when the *ortho*-H—Ph are decoupled, suggesting a small coupling between P and H—C(1) and probably also H—C(2).

The synthesis of (glycopyranosyl)phosphine sulfides by reduction of phosphine oxides, followed by addition of elemental sulfur to the intermediate phosphines takes place with retention of the configuration at the anomeric center, showing that the phosphines **21** and **24** are stable to the reduction conditions.

Boron compounds form stable adducts with electron-donating tri-coordinated phosphorus compounds [40] [41]. Some of them [42] catalyze the enantioselective reduction of ketones [43]. Others show potent hypolipidemic, antineoplastic, and antiinflammatory activities in rodents [44]. A cytotoxic activity of some borane complexes against murine and human tissue culture cell lines has been demonstrated [45] [46].

The crude phosphine **18**, obtained from **2**, was treated at 80° with 10 equiv. of $\text{Me}_3\text{N} \cdot \text{BH}_3$ in benzene [47] [48]. The crystalline product (m.p. 89–94°) was isolated in 55% yield by column chromatography and identified as the borane adduct **20**. In an analogous way, the crude phosphine **21**, obtained from **8**, gave 55% of the (mannopyranosyl)phosphine borane complex **23**. Similarly to what has been reported for phenyloxazaphospholidine borane complexes [42], **20** ($\delta(^{31}\text{P})$ 19.4 ppm) reacted readily with a small excess of Et_3NH . The reaction is conveniently monitored by ^{31}P -NMR spectroscopy. Immediately after addition of the amine, only one resonance line was detected (–22.4 ppm), corresponding to the phosphine **18**. Addition of elemental sulfur caused a shift of this resonance to 39.1 ppm, corresponding to the phosphine sulfide **19**. Reduction of acetophenone in toluene at 110°, with 1 equiv. of $\text{Me}_2\text{S} \cdot \text{BH}_3$ in the presence of 2 mol % of **20**, gave (–)-(S)-1-phenylethanol (**28**, $[\alpha]_{\text{D}}^{25} = -10.7$ ($c = 4.12$, MeOH)) with 24% e.e.²⁾.

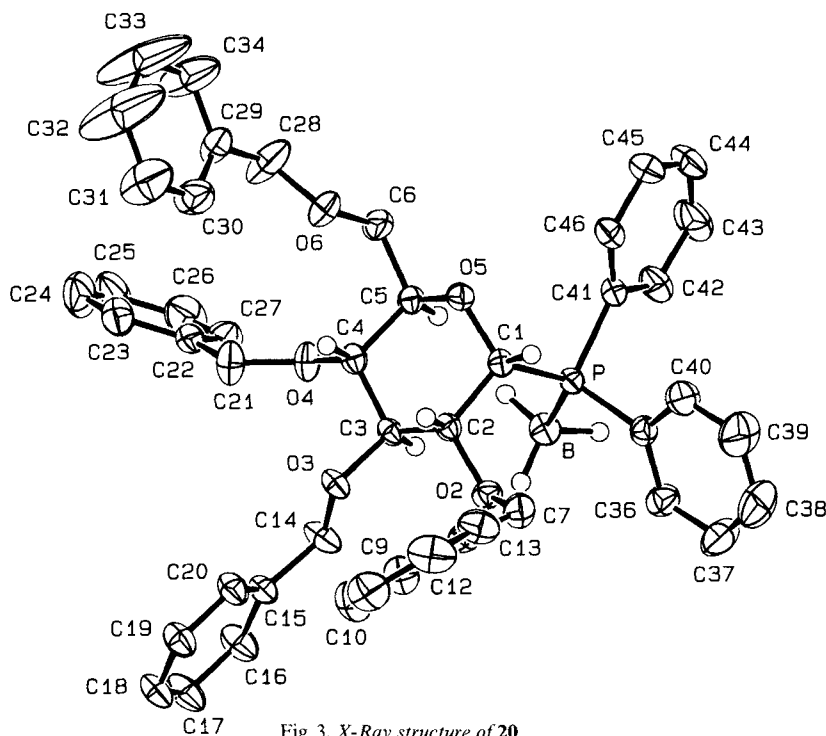


Fig. 3. X-Ray structure of **20**

The structure of the borane adduct **20** was established by X-ray analysis (Fig. 3 and Tables 3 and 4). The P–B bond length is not significantly different to that observed in triphenylphosphine borane (1.93(1) and 1.90(2) Å) [50a] and trimethylphosphine borane (1.901(7) Å) [50b]. The pyranose ring adopts a slightly flattened 4C_1 conformation (Table 5), which differs from the solution conformation, for which NMR spectra suggest a $B_{2,5}$,

²⁾ The maximum value of $[\alpha]_{\text{D}}^{25}$ for (–)-(S)-**28** is –45 ($c = 5.0$, MeOH) [49].

quite similar to the conformation of the corresponding phosphine sulfide **19**. The A value of the diphenylphosphine-borane group (3.3 kcal/mol [51a]) is indeed intermediary between the one of the $\text{Ph}_2\text{P}(\text{O})$ (2.74 kcal/mol [51b]) and $\text{Ph}_2\text{P}(\text{S})$ groups (3.61 kcal/mol [51c]), as it is suggested by their *van der Waals* radii. The lengths of the C(1)–P and the C(1)–O bonds of the phosphine oxide **12**, sulfide **25**, and borane adduct **20** do not reflect an anomeric effect³⁾. The ^1H - and ^{13}C -NMR spectra of the adduct **23** are similar to the ones of the corresponding phosphine oxide **8** (Tables 1 and 2). In all other aspects, the ^1H -, ^{13}C -, ^{31}P -, and ^{11}B -NMR spectra are similar to those reported for analogous complexes [42] [53–57].

We thank the *Anna Feddersen-Wagner Foundation* and the *Swiss National Science Foundation* for generous support.

Experimental Part

General. MeOPPh_2 was synthesized according to [58]. Cl_3SiH was distilled from quinoline immediately before use. Flash chromatography (FC): silica gel *Merck* (0.040–0.063 mm). ^1H -, ^{13}C -, ^{31}P -, and ^{11}B -NMR spectra were recorded on a *Varian XL-200* or *Bruker AM-400* spectrometer of CDCl_3 soln., unless specified otherwise. Chemical shifts in ppm relative to TMS as internal standard for ^1H - and ^{13}C -, relative to H_3PO_4 (external reference) for ^{31}P - and relative to $\text{Et}_2\text{O} \cdot \text{BF}_3$ (external reference) for ^{11}B -NMR spectra. CI-MS: *Varian-112S* spectrometer (NH_3 or isobutane). FAB-MS: *Varian-711* spectrometer (8-keV Xe-atoms, glycerol matrix).

General Procedure for the Preparation of Protected (Glycosyl)(diphenyl)phosphine Oxides. Under Ar, trimethylsilyl trifluoromethanesulfonate (TMSOTf, 0.8–1.1 mmol) was added dropwise during 5–10 min to a cooled (0°) mixture of the glycosyl acetate (1 mmol), MeOPPh_2 (1.0–1.3 mmol), and 4-Å molecular sieves (300–350 mg) in CH_2Cl_2 (2–5 ml). The mixture was stirred for 10–15 min at 0 – 5° , allowed to warm up to r.t., and stirred for 6–8 h at 20 – 25° . After the addition of a second portion of MeOPPh_2 (0.5–0.8 mmol) and TMSOTf (0.4–0.5 mmol), the mixture was stirred for 48–85 h at r.t., diluted with CH_2Cl_2 (10–15 ml), filtered, cooled to 0° , and treated with sat. aq. NaHCO_3 soln. (3–5 ml). The org. layer was washed with H_2O , dried (MgSO_4), and evaporated. The residue was purified by FC.

Diphenyl(2,3,4,6-tetra-O-benzyl- α -D- and - β -D-glucopyranosyl)phosphine Oxide (2 and 3). a) The reaction of **1** [16] (α/β 10:1, 0.86 g, 1.63 mmol) with MeOPPh_2 (685 μl , 3.03 mmol) and TMSOTf (547 μl , 2.71 mmol) in CH_2Cl_2 (5 ml), and FC (toluene/AcOEt 10:1) gave **2** (530 mg, 45%) and **3** (76 mg, 7%).

b) The reaction of **1** [17] (α/β 1:9, 530 mg, 0.909 mmol) with MeOPPh_2 (390 μl , 1.83 mmol) and TMSOTf (300 μl , 1.45 mmol) in CH_2Cl_2 (5 ml), and FC (toluene/AcOEt 10:1) gave **2** (415 mg, 63%) and **3** (73 mg, 11%).

Diphenyl(2,3,4,6-tetra-O-benzyl- β -D-mannopyranosyl)phosphine Oxide (8). a) The reaction of **6** (1.68 g, 2.88 mmol) with MeOPPh_2 (975 μl , 4.33 mmol) and TMSOTf (901 μl , 4.45 mmol) in CH_2Cl_2 (2.5 ml), and FC (hexane/AcOEt 7:3 $\rightarrow$ 1:1) gave **8** (915 mg, 44%).

b) The reaction of **7** [18] (1.7 g, 2.48 mmol) with MeOPPh_2 (2.55 ml, 11.32 mmol), TMSOTf (810 μl , 3.93 mmol), and 4-Å molecular sieves (350 mg) in CH_2Cl_2 (3 ml), and FC (toluene/AcOEt 7:2) gave **8** (1.094 g, 60%).

Data of 8: R_f (hexane/ CH_2Cl_2 /AcOEt 1:1:1) 0.22. $[\alpha]_{\text{D}}^{25} = -51.3$ ($c = 0.55$, CHCl_3). IR (CHCl_3): 3060m, 2995m, 2930m, 2910m, 2870m, 1955w, 1810w, 1725w, 1595w, 1495m, 1485w, 1455m, 1440m, 1395w, 1360m, 1310w, 1275w, 1240w, 1170s, 1130s, 1120s, 1095s, 1040s, 1030w, 1000m, 910w, 840w, 700s, 660w. ^1H -NMR (400 MHz, CDCl_3): 7.97–7.88 (m, 4 arom. H); 7.50–7.20 (m, 18 arom. H); 7.20–7.08 (m, 6 arom. H); 6.95 (br. d, $J = 6.8$, 2 arom. H); 4.905 (d, $J = 10.6$, PhCH); 4.90 (d, $J = 11.0$, PhCH); 4.78 (d, $J = 11.8$, PhCH); 4.72 (br. s, $\text{HW}_{50} = 7.0$; irradi. at 3.68: br. s, $\text{HW}_{50} = 5.0$; irradi. at 4.22: strong NOE; irradi. at 3.68: strong NOE, H–C(2)); 4.65 (d, $J = 11.8$, PhCH); 4.63 (d, $J \approx 11.0$, PhCH); 4.60 (d, $J \approx 12.0$, PhCH); 4.57 (d, $J \approx 12.0$, PhCH); 4.45 (d, $J = 11.9$, PhCH); 4.22 (dd, $J = 10.4$, 0.7; irradi. at 4.72: d, $J = 10.4$; irradi. at 3.68: strong NOE; irradi. at 3.53: strong NOE, H–C(1)); 4.02 (t, $J = 9.4$; irradi. at 3.68: d, $J = 9.3$; irradi. at 3.53: d, $J = 9.3$, H–C(4)); 3.84–3.76 (ABX; irradi. at

³⁾ For the anomeric effect in 2-(diphenylphosphinyl)-1,3-dithianes and -1,3-dioxanes, compare [13] [51d] [52] and references quoted there. Other compounds are known, where a strong anomeric effect is not reflected in significant changes in bond length [51e].

3.53: *AB*; irradi. at 3.53: medium NOE, 2 H–C(6)); 3.68 (*dd*, $J = 9.3, 2.8$; irradi. at 4.72: $d, J = 9.3$; irradi. at 4.22: strong NOE; irradi. at 3.53: strong NOE, H–C(3)); 3.53 (*ddd*, $J = 9.5, 4.7, 2.3$; irradi. at 4.22: strong NOE; irradi. at 3.68: strong NOE, H–C(5)). ^{13}C -NMR (50 MHz, CDCl_3): 138.45 (*s*); 138.29 (*s*, 2 C); 137.91 (*s*); 134.65–130.06 (*m*); 128.83–126.70 (*m*); 84.28 (*dd*, $J(\text{C},\text{P}) = 12.0, \text{C}(3)$); 81.77 (*dd*, $J(\text{C},\text{P}) = 12.9, \text{C}(5)$); 79.86 (*dd*, $J(\text{C},\text{P}) = 93.7, \text{C}(1)$); 75.21 (*t*, PhCH_2); 74.76 (*d*, $\text{C}(4)$); 74.24 (*t*, PhCH_2); 73.19 (*t*, PhCH_2); 73.01 (*dd*, $J(\text{C},\text{P}) = 2.4, \text{C}(2)$); 71.94 (*t*, PhCH_2); 69.68 (*t*, $\text{C}(6)$). ^{31}P -NMR (80 MHz, CDCl_3): +24.84. CI-MS: 726 (50), 725 (100, $[M + 1]^+$). Anal. calc. for $\text{C}_{46}\text{H}_{45}\text{O}_6\text{P}$ (724.83): C 76.23, H 6.26, P 4.27; found: C 76.29, H 6.40, P 4.50.

Diphenyl(2,3,5-tri-O-benzyl- α -D- and β -D-arabinofuranosyl)phosphine Oxide (13 and 12). The reaction of **11** [19] (α/β 63:27, 1.45 g, 3.13 mmol) with MeOPPh_2 (1.37 ml, 6.14 mmol) and TMSOTf (885 μl , 4.29 mmol) in CH_2Cl_2 (2 ml), and FC (toluene/ AcOEt 20:3) gave **13** (67 mg, 4%) and **12** (1.268 g, 67%).

Data of 12: R_f (hexane/ CH_2Cl_2 / AcOEt 1:1:1) 0.26. M.p. 94–95° (hexane/ AcOEt). $[\alpha]_D^{25} = -51.1$ ($c = 0.135$, CHCl_3). IR (KBr): 3055w, 3035w, 2920m, 2895m, 2860m, 1495w, 1480w, 1455m, 1435m, 1395w, 1370w, 1355w, 1335w, 1310w, 1285w, 1265w, 1245w, 1210m, 1190s, 1125s, 1110s, 1090s, 1075s, 1040m, 1025m, 1000m, 985w, 950w, 915w, 865m, 850w, 760m, 745s, 700s. ^1H -NMR (400 MHz, CDCl_3): 7.95–7.82 (*m*, 4 arom. H); 7.50–7.20 (*m*, 19 arom. H); 6.98 (*dd*, $J = 7.4, 1.9, 2$ arom. H); 4.93 (*dd*, $J = 3.9, 2.2$, H–C(1)); 4.53 (*d*, $J = 3.9$; irradi. at 4.93; *s*, H–C(2)); 4.51 (*d*, $J = 11.8$, PhCH); 4.44 (*d*, $J \approx 12.0$, PhCH); 4.415 (*d*, $J \approx 11.5$, PhCH); 4.41 (*d*, $J \approx 12.5$, PhCH); 4.37 (*d*, $J = 11.9$, PhCH); 4.35 (*d*, $J = 12.1$, PhCH); 4.32 (*br. td*, $J \approx 6.7, 1.1$; irradi. at 3.89: *t*, $J = 6.7$; irradi. at 3.48: *br. d*, $J \approx 6.3$; irradi. at 3.32: *br. d*, $J \approx 5.9$, H–C(4)); 3.89 (*br. d*, $J \approx 0.6$, $\text{HW}_{50} = 4.5$, H–C(3)); 3.48 (*dd*, $J = 9.9, 6.3$, H–C(5)); 3.32 (*dd*, $J = 9.9, 6.9$, H–C(5)). ^{13}C -NMR (50 MHz, CDCl_3): 138.05 (*s*); 137.30 (*s*); 137.27 (*s*); 132.25–130.59 (*m*); 128.52–127.28 (*m*); 85.50 (*dd*, $J(\text{C},\text{P}) = 8.4, \text{C}(4)$); 83.29 (*dd*, $J(\text{C},\text{P}) = 4.5, \text{C}(2)$); 83.09 (*dd*, $J(\text{C},\text{P}) = 5.3, \text{C}(3)$); 81.23 (*dd*, $J(\text{C},\text{P}) = 92.6, \text{C}(1)$); 73.20 (*t*, PhCH_2); 72.29 (*t*, PhCH_2); 71.46 (*t*, PhCH_2); 70.07 (*t*, $\text{C}(5)$). ^{31}P -NMR (80 MHz, CDCl_3): +26.15. CI-MS: 607 (9), 606 (41), 605 (100, $[M + 1]^+$). Anal. calc. for $\text{C}_{38}\text{H}_{37}\text{O}_5\text{P}$ (604.68): C 75.48, H 6.17, P 5.12; found: C 75.10, H 6.51, P 5.22.

Data of 13: R_f (hexane/ CH_2Cl_2 / AcOEt 1:1:1) 0.39. M.p. 90–91° (hexane/ AcOEt). $[\alpha]_D^{25} = +45.5$ ($c = 0.25$, CHCl_3). IR (KBr): 3050w, 3020w, 2925w, 2880w, 2860w, 1495w, 1450m, 1440m, 1365m, 1180s, 1135s, 1125s, 1105s, 1085w, 1070s, 1050m, 1030m, 1000w, 975m, 745s, 735s, 695s. ^1H -NMR (400 MHz, CDCl_3): 7.98–7.83 (*m*, 4 arom. H); 7.58–7.23 (*m*, 19 arom. H); 7.10 (*dd*, $J = 7.1, 2.8, 2$ arom. H); 4.82 (*dd*, $J = 5.6, 2.7$; irradi. at ^{31}P : $d, J = 5.6$, H–C(1)); 4.57 (*d*, $J = 11.6$, PhCH); 4.55 (*ddd*, $J = 12.1, 5.6, 3.9$; irradi. at ^{31}P : *dd*, $J = 5.6, 3.9$; irradi. at 4.82: *dd*, $J = 12.1, 3.9$; irradi. at 4.10: *dd*, $J = 12.1, 5.6$, H–C(2)); 4.545 (*d*, $J = 12.1$, PhCH); 4.51 (*d*, $J = 11.6$, PhCH); 4.49 (*d*, $J = 12.2$, PhCH); 4.36 (*d*, $J = 11.9$, PhCH); 4.32 (*d*, $J = 11.9$, PhCH); 4.10 (*dd*, $J = 5.8, 3.9$; irradi. at 3.90: $d, J = 3.9$, H–C(3)); 3.90 (*q*, $J \approx 5.1$; irradi. at 4.10: *t*, $J \approx 4.9$, H–C(4)); 3.57 (*dd*, $J = 10.8, 4.4$; irradi. at 3.90: $d, J = 10.4$, H–C(5)); 3.53 (*dd*, $J = 10.8, 5.4$; irradi. at 4.10: $d, J = 10.6$, H–C(5)). ^{13}C -NMR (50 MHz, CDCl_3): 138.07 (*s*); 137.73 (*s*); 137.69 (*s*); 132.44–131.08 (*m*); 128.68–127.60 (*m*); 84.23 (*dd*, $J(\text{C},\text{P}) = 4.8, \text{C}(3)$); 83.99 (*dd*, $J(\text{C},\text{P}) = 3.9, \text{C}(2)$); 82.27 (*dd*, $J(\text{C},\text{P}) = 5.4, \text{C}(4)$); 81.38 (*dd*, $J(\text{C},\text{P}) = 78.0, \text{C}(1)$); 73.19 (*t*, PhCH_2); 72.25 (*t*, PhCH_2); 71.69 (*t*, PhCH_2); 68.91 (*t*, $\text{C}(5)$). ^{31}P -NMR (80 MHz, CDCl_3): +27.42. CI-MS: 607 (7), 606 (35), 605 (100, $[M + 1]^+$). Anal. calc. for $\text{C}_{38}\text{H}_{37}\text{O}_5\text{P}$ (604.68): C 75.48, H 6.17, P 5.12; found: C 75.19, H 6.26, P 5.26.

Diphenyl(2,3,5-tri-O-benzyl- α -D-ribofuranosyl)phosphine Oxide (16). The reaction of **15** [20] (1.56 g, 3.38 mmol) with MeOPPh_2 (1.449 ml, 6.43 mmol), TMSOTf (1.114 ml, 5.38 mmol), and 4-Å molecular sieves (300 mg) in CH_2Cl_2 (2 ml), and FC (hexane/ AcOEt 3:1→3:2) gave **16** (1.551 g, 76%).

Data of 16: R_f (hexane/ CH_2Cl_2 / AcOEt 1:1:1) 0.18. $[\alpha]_D^{25} = +27.3$ ($c = 0.11$, CHCl_3). IR (CHCl_3): 3060w, 3000m, 2980m, 2935m, 2860m, 1495w, 1455m, 1440m, 1360w (*br.*), 1310w, 1255m (*br.*), 1170s, 1120s, 1085s, 1070s, 1040m, 1030s, 1000m, 910w, 880w, 700s. ^1H -NMR (400 MHz, CDCl_3): 7.94–7.86 (*m*, 4 arom. H); 7.50–7.12 (*m*, 21 arom. H); 4.88 (*t*, $J \approx 3.5$; irradi. at 4.62: $d, J = 3.6$; irradi. at 4.62: medium NOE, H–C(1)); 4.71 (*s*; irradi. at 4.62: medium NOE, PhCH_2); 4.62 (*t*, $J \approx 3.7$; irradi. at 4.88: medium NOE, H–C(2)); 4.54 (*d*, $J = 12.3$, PhCH); 4.50 (*d*, $J = 12.3$, PhCH); 4.46 (*d*, $J = 11.8$, PhCH); 4.30 (*d*, $J = 11.8$, PhCH); 4.18 (*ddd*, $J = 9.2, 3.6, 2.2$, H–C(4)); 4.06 (*dd*, $J = 9.2, 4.0$; irradi. at 4.62: $d, J = 9.2$; irradi. at 4.88: medium NOE; irradi. at 4.62: medium NOE, H–C(3)); 3.75 (*dd*, $J = 11.2, 2.1$, H–C(5)); 3.56 (*dd*, $J = 11.2, 3.8$, H–C(5)). ^{13}C -NMR (50 MHz, CDCl_3): 138.18 (*s*); 137.82 (*s*); 137.39 (*s*); 132.55–130.78 (*m*); 128.66–127.15 (*m*); 81.15 (*dd*, $J(\text{C},\text{P}) = 94.5, \text{C}(1)$); 79.96 (*dd*, $J(\text{C},\text{P}) = 3.5, \text{C}(4)$); 79.18 (*dd*, $J(\text{C},\text{P}) = 6.1, \text{C}(3)$); 77.52 (*dd*, $J(\text{C},\text{P}) = 4.4, \text{C}(2)$); 73.97 (*t*, PhCH_2); 73.16 (*t*, PhCH_2); 72.66 (*t*, PhCH_2); 69.06 (*t*, $\text{C}(5)$). ^{31}P -NMR (80 MHz, CDCl_3): +24.46. CI-MS: 607 (6), 606 (33), 605 (100, $[M + 1]^+$). Anal. calc. for $\text{C}_{38}\text{H}_{37}\text{O}_5\text{P}$ (604.68): C 75.48, H 6.17, P 5.12; found: C 75.23, H 6.51, P 5.24.

General Procedure for the Hydrogenolysis of Benzylated Glycosylphosphine Oxides. A stirred soln. of phosphine oxide (0.1–0.2 mmol) in MeOH (10 ml) was hydrogenated in the presence of 10% Pd/C (40–50 mg) for 40–80 h at 8 bar and at r.t. After filtration (*Celite*) and evaporation of the filtrate, the product was purified by FC or by crystallization.

(α -D-Glucopyranosyl) (diphenyl)phosphine Oxide (**4**). The hydrogenolysis of **2** (110 mg, 0.15 mmol) with 10% Pd/C (40 mg) and FC (hexane/AcOEt/MeOH 10:2:1) gave slightly soiled **4** (38 mg, 70%). M.p. 90–96°. ¹H-NMR (400 MHz, (D₆)DMSO): 7.88–7.80 (*m*, 4 arom. H); 7.47–7.40 (*m*, 6 arom. H); 4.98 (*d*, *J* = 4.8, 1 H exchanged with D₂O; after the addn. of D₂O: *d*, *J* = 4.7, OH, H–C(1)); 4.94 (*d*, *J* = 4.6, exchanged with D₂O, OH); 4.85 (*d*, *J* = 5.1, exchanged with D₂O, OH–C(4)); 4.15 (*td*, *J* = 7.8, 4.3; after the addn. of D₂O: *t*, *J* = 7.8, H–C(3)); 3.99 (*t*, *J* ≈ 5.6, exchanged with D₂O, OH–C(6)); 3.83–3.70 (*m*, H–C(2), H–C(5)); 3.36 (*dt*, *J* ≈ 11.5, 5.6; after the addn. of D₂O: *dd*, *J* = 11.5, 5.5, H–C(6)); 3.23 (*dt*, *J* = 8.6, 5.1; after the addn. of D₂O: *t*, *J* = 8.6, H–C(4)); 3.08 (*ddd*, *J* = 11.5, 5.3, 3.0; after the addn. of D₂O: *dd*, *J* = 11.5, 3.0, H–C(6)). ³¹P-NMR (80 MHz, (D₆)DMSO): +29.39. CI-MS: 366 (20), 365 (100, [*M* + 1]⁺).

(Diphenyl) (2,3,4,6-tetra-O-acetyl- α -D-glucopyranosyl)phosphine Oxide (**5**). A mixture of **4** (40 mg, 0.1 mmol) and Ac₂O (1 ml) in pyridine (5 ml) was stirred for 1 h at 0° and 36 h at r.t. Evaporation of the solvent and FC (toluene/AcOEt 7:3) of the residue gave crystalline **5** (47 mg, 88%). *R*_f (AcOEt/MeOH 5:1) 0.73. M.p. 150–151° (hexane/AcOEt). [α]_D²⁵ = +57.7 (*c* = 0.13, CHCl₃). IR (KBr): 3060w, 2940w (br.), 1750s, 1485w, 1440m, 1370s, 1235s, 1190s, 1115m, 1095m, 1045s, 1000w, 980w, 915w, 755w, 725m, 705m. ¹H-NMR (400 MHz, CDCl₃): 7.93–7.79 (*m*, 4 arom. H); 7.53–7.43 (*m*, 6 arom. H); 6.27 (*dd*, *J* = 9.7, 8.9, H–C(3)); 5.31 (*ddd*, *J* = 21.1, 9.7, 7.0; irradi. at ³¹P: *dd*, *J* = 9.8, 7.0, H–C(2)); 5.12 (*dd*, *J* = 7.0, 3.2; irradi. at ³¹P: *d*, *J* = 7.0, H–C(1)); 5.03 (*dd*, *J* = 9.9, 8.9, H–C(4)); 4.60 (*ddd*, *J* = 9.9, 5.2, 2.1, H–C(5)); 4.03 (*dd*, *J* = 12.4, 5.2, H–C(6)); 3.68 (*dd*, *J* = 12.4, 2.1, H–C(6)); 2.03 (*s*, Ac); 2.01 (*s*, Ac); 1.97 (*s*, Ac); 1.83 (*s*, Ac). ¹³C-NMR (50 MHz, CDCl₃): 170.38 (*s*, C=O); 170.22 (*s*, C=O); 169.82 (*s*, C=O); 169.55 (*s*, C=O); 133.51–128.51 (*m*); 73.11 (*dd*, *J*(C,P) = 2.3); 71.26 (*dd*, *J*(C,P) = 74.6, C(1)); 70.46 (*d*, 2 C); 68.51 (*d*, C(6)); 61.98 (*t*, C(6)); 20.65 (*q*, Me); 20.62 (*q*, Me); 20.51 (*q*, Me); 19.36 (*dq*, *J*(C,P) = 1.7, Me). ³¹P-NMR (80 MHz, CDCl₃): +27.61. CI-MS: 534 (28), 533 (100, [*M* + 1]⁺). Anal. calc. for C₂₆H₂₉O₁₀P (532.48): C 58.65, H 5.49, P 5.82; found: C 58.46, H 5.58, P 5.65.

(β -D-Mannopyranosyl) (diphenyl)phosphine Oxide (**9**). The hydrogenolysis of **8** (135 mg, 0.19 mmol) with 10% Pd/C (45 mg) for 68 h and FC (AcOEt/MeOH 5:1) gave **9** (48 mg, 73%). *R*_f (AcOEt/MeOH 5:1) 0.18. [α]_D²⁵ = –14.5 (*c* = 0.2, MeOH). IR (KBr): 3400s (br.), 2920w, 1590w, 1560w, 1540w, 1485w, 1440s, 1245m, 1180s, 1120s, 1080s 1050s (sh), 1000w, 965w, 915w, 860w, 825w, 755m, 725s, 695s. ¹H-NMR (600 MHz, (D₆)DMSO): 7.90–7.84 (*m*, 4 arom. H); 7.55–7.38 (*m*, 6 arom. H); 4.82 (*d*, *J* = 4.4, exchanged with D₂O (*ca.* 5 equiv.), OH–C(4)); 4.71 (*d*, *J* = 2.7, exchanged with D₂O, OH–C(3)); 4.54 (*t*, *J* ≈ 5.6, exchanged with D₂O, OH–C(6)); 4.49 (*d*, *J* = 4.0; irradi. at 4.05: *s*; exchanged with D₂O, OH–C(2)); 4.33 (*d*, *J* = 8.6, H–C(1)); 4.05 (br. *s*, HW₅₀ = 8.5; after the addn. of D₂O: br. *s*, HW₅₀ = 4, H–C(2)); 3.73 (*ddd*, *J* = 11.3, 4.4, 1.6; irradi. at 3.20: *dd*, *J* = 11.6, 4.5; after the addn. of D₂O: *dd*, *J* = 11.3, 1.6, H–C(6)); 3.43 (*dt*, *J* ≈ 11.5, 6.3; irradi. at 3.20: *dd*, *J* = 11.6, 6.3; after the addn. of D₂O: *dd*, *J* = 11.5, 6.7, H–C(6)); 3.37–3.32 (*m*; irradi. at 4.05: smaller *m*; irradi. at 3.20: *AB*; after the addn. of D₂O: *ABM*, H–C(3), H–C(4)); 3.23–3.18 (*m*, H–C(5)). ¹³C-NMR (50 MHz, (D₆)DMSO): 134.00 (*d*, *J*(C,P) = 96.6); 132.88 (*d*, *J*(C,P) ≈ 97.5); 131.91–130.60 (*m*); 128.55–127.50 (*m*); 83.78 (*dd*, *J*(C,P) = 12.3, C(5)); 77.79 (*dd*, *J*(C,P) = 93.8, C(1)); 74.41 (*dd*, *J*(C,P) = 13.1, C(3)); 68.20 (*d*, C(2)); 67.19 (*d*, C(4)); 61.45 (*t*, C(6)). ³¹P-NMR (80 MHz, (D₆)DMSO): +24.64. CI-MS: 366 (18), 365 (100, [*M* + 1]⁺). Anal. calc. for C₁₈H₂₁O₆P (364.32): C 59.34, H 5.80, P 8.50; found: C 57.87, H 6.35, P 8.10.

Diphenyl (2,3,4,6-tetra-O-benzoyl- β -D-mannopyranosyl)phosphine Oxide (**10**). A cooled (0°) soln. of **9** (204 mg, 0.56 mmol) in dry pyridine (9 ml) was treated with freshly distilled benzoyl chloride (647 μ l, 5.6 mmol) and stirred for 30 h at 0° and 30 h at r.t. The soln. was evaporated at 0.5 Torr. FC (toluene/AcOEt 7:3) of the residue gave **10** (370 mg, 85%). *R*_f (toluene/AcOEt 7:3) 0.23. M.p. 110–111° (cyclohexane). [α]_D²⁵ = –297.8 (*c* = 0.5, CHCl₃). IR (KBr): 3060w, 2930w, 2850w, 1730s, 1600m, 1585w, 1490w, 1450s, 1440m, 1335w, 1315m, 1285s, 1265s, 1180m, 1160m, 1130s, 1095s, 1070s, 1025s, 1000w, 935w, 875w, 820w, 800w, 750w, 710s, 695s, 650w. ¹H-NMR (400 MHz, C₆D₆): 8.20–6.92 (*m*, 30 arom. H); 6.53 (br. *s*, HW₅₀ = 7.5; irradi. at ³¹P: br. *d*, *J* = 3.2; irradi. at 5.70: br. *s*, HW₅₀ = 4.5, H–C(2)); 5.97 (*t*, *J* = 10.0; irradi. at 5.70: *d*, *J* = 9.9, H–C(4)); 5.70 (*dd*, *J* = 10.1, 3.3; irradi. at 6.53; *d*, *J* = 10.1, H–C(3)); 4.91 (*dd*, *J* = 12.3, 2.1, H–C(6)); 4.77 (*dd*, *J* = 11.7, 0.6; irradi. at ³¹P: br. *s*; irradi. at 6.53: *d*, *J* = 11.7, H–C(1)); 4.52 (*dd*, *J* = 12.3, 4.8, H–C(6)); 4.20 (*ddd*, *J* = 9.8, 4.8, 2.1, H–C(5)). ¹³C-NMR (50 MHz, CDCl₃): 165.98 (*s*); 165.25 (*s*); 165.22 (*s*); 164.20 (*s*); 133.54–127.84 (*m*); 78.80 (*dd*, *J*(C,P) = 12.0, C(5)); 77.74 (*dd*, *J*(C,P) = 90.4, C(1)); 72.71 (*dd*, *J*(C,P) = 11.8, C(3)); 67.48 (*d*); 66.60 (*d*); 62.30 (*t*, C(6)). ³¹P-NMR (80 MHz, CDCl₃): +21.33. CI-MS: 782 (22), 781 (45, [*M* + 1]⁺), 659 (100, [*M* – PhCO₂]⁺). Anal. calc. for C₄₆H₃₇O₁₀P (780.77): C 70.76, H 4.77, P 3.96; found: C 70.73, H 4.92, P 4.19.

(β -D-Arabinofuranosyl) (diphenyl)phosphine Oxide (**14**). The hydrogenolysis of **12** (100 mg, 0.165 mmol) with 10% Pd/C (45 mg) for 48 h and FC (AcOEt/MeOH 10:1) gave **14** (37 mg, 67%). *R*_f (AcOEt/MeOH 5:1) 0.36. M.p. 185–187°. [α]_D²⁵ = +10.0 (*c* = 0.1, MeOH). IR (KBr): 3600–2000s, 2935s, 2920s, 2860s, 1590w, 1560w, 1540w, 1485w, 1455w, 1440s, 1395m, 1385m, 1340m, 1310m, 1270m, 1250m, 1235w, 1210m, 1165s, 1125s, 1085s, 1060s, 1040m, 1015s, 970w, 920w, 840s, 810w, 750m, 735m, 710m, 695s. ¹H-NMR (400 MHz, (D₆)DMSO): 7.86–7.76 (*m*,

4 arom. H); 7.55–7.44 (*m*, 6 arom. H); 5.27 (*d*, *J* = 4.0, exchanged with D₂O, OH–C(3)); 5.24 (*d*, *J* = 5.5; irradi. at 4.19: *s*, exchanged with D₂O, HO–C(2)); 4.84 (*t*, *J* = 5.2, exchanged with D₂O, HO–C(5)); 4.77 (*dd*, *J* = 4.0, 2.9; irradi. at ³¹P: *d*, *J* = 4.0; irradi. at 4.19: *d*, *J* = 2.0, H–C(1)); 4.19 (*m*, HW₃₀ = 14; irradi. at ³¹P: *ddd*, *J* = 5.5, 3.8, 1.7; irradi. at 4.77: *m*, HW₃₀ = 10.5, H–C(2)); 3.89 (*br. dq*, *J* ≈ 4.0, 2.0; irradi. at ³¹P: *br. dt*, *J* ≈ 4.0, 2.0; irradi. at 4.19: *br. dt*, *J* ≈ 4.0, 2.0, H–C(3)); 3.84 (*td*, *J* = 5.5, 2.0, H–C(4)); 3.44 (*t*, *J* = 5.4, 2 H–C(5)). ¹³C-NMR (50 MHz, (D₆)DMSO): 133.86 (*d*, *J*(C,P) = 96.4); 132.65 (*d*, *J*(C,P) ≈ 99); 131.66–127.84 (*m*); 88.69 (*dd*, *J*(C,P) = 7.1, C(4)); 79.75 (*dd*, *J*(C,P) = 92.5, C(1)); 78.22 (*dd*, *J*(C,P) = 5.0, C(2)); 77.81 (*dd*, *J*(C,P) = 5.0, C(3)); 61.72 (*t*, C(5)). ³¹P-NMR (80 MHz, (D₆)DMSO): +25.06. CI-MS: 336 (17), 335 (100, [*M* + 1]⁺). Anal. calc. for C₁₇H₁₉O₃P (334.66): C 61.01, H 5.82, P 9.25; found: C 61.20, H 5.77, P 9.16.

(Diphenyl)(α-D-ribofuranosyl)phosphine Oxide (17). The hydrogenolysis of **16** (1.06 g, 1.75 mmol) with 10% Pd/C (180 mg) in MeOH (20 ml) for 68 h, filtration through Celite, evaporation of the filtrate, and washing of the crystalline residue with hot AcOEt (3 × 15 ml) gave pure **17** (456 mg, 78%). *R*_f (AcOEt/MeOH 5:1) 0.25. M.p. 193–195°. [α]_D²⁵ = +54.2 (*c* = 0.19, MeOH). IR (KBr): 3430s (*br.*), 2920m, 2860w, 1610w, 1580w, 1485m, 1440s, 1390w, 1335w, 1250w, 1155s, 1130s, 1120s, 1090m, 1070s, 1040m, 1020m, 1000m, 925w, 875w, 855w, 830w, 755m, 725m, 705s, 690s, 650w. ¹H-NMR (400 MHz, (D₆)DMSO): 7.84–7.77 (*m*, arom. H); 7.52–7.43 (*m*, 6 arom. H); 5.24 (*d*, *J* = 9.4, exchanged with D₂O, OH–C(3)); 5.09 (*t*, *J* = 6.0; irradi. at ³¹P: *d*, *J* = 5.6; irradi. at 4.44: *d*, *J* = 6.1 H–C(1)); 5.00 (*d*, *J* = 3.9; irradi. at 4.44: *s*, exchanged with D₂O, OH–C(2)); 4.69 (*br. t*, *J* ≈ 4.8, exchanged with D₂O, OH–C(5)); 4.44 (*dq*, *J* = 9.6, 4.8; irradi. at ³¹P: *q*, *J* = 5.0; irradi. at 5.09: *dt*, *J* = 9.2, 4.5; after the addn. of D₂O: *dt*, *J* = 9.6, 5.5, H–C(2)); 3.87 (*dt*, *J* ≈ 9.3, 5.5; irradi. at 4.44: *dd*, *J* = 9.2, 6.2; after the addn. of D₂O: *t*, *J* = 5.5, H–C(3)); 3.80 (*br. q*, *J* ≈ 4.8, H–C(4)); 3.50 (*dt*, *J* = 11.9, 3.9; after the addn. of D₂O: *dd*, *J* = 11.9, 3.6, H–C(5)); 3.39 (*dt*, *J* = 11.9, 5.0; after the addn. of D₂O: *dd*, *J* = 11.9, 5.0, H–C(5)). ¹³C-NMR (50 MHz, (D₆)DMSO): 133.80 (*d*, *J*(C,P) = 100.8); 133.05 (*d*, *J*(C,P) = 99.7); 131.27–127.93 (*m*); 85.15 (*dd*, *J*(C,P) = 1.5, C(4)); 79.19 (*dd*, *J*(C,P) = 88.0, C(1)); 72.31 (*dd*, *J*(C,P) = 4.0, C(3)); 71.81 (*dd*, *J*(C,P) = 4.1, C(2)); 61.38 (*t*, C(5)). ³¹P-NMR (80 MHz, (D₆)DMSO): +26.35. CI-MS: 336 (19), 335 (100, [*M* + 1]⁺). Anal. calc. for C₁₇H₁₉O₃P (334.66): C 61.01, H 5.82, P 9.25; found: C 60.82, H 5.78, P 9.40.

General Procedure for the Preparation of Glycosylphosphine Sulfides. Under Ar, a soln. of (glycosyl)(diphenyl)-phosphine oxide (1 mmol) and Et₃N (or *N,N*-dimethyl-*p*-toluidine, 5–10 mmol) in benzene (10 ml) was treated with freshly distilled Cl₃SiH (5–10 mmol) and heated to reflux for 3.5–5.0 h. The mixture was cooled to 0°, diluted with benzene (10 ml), and treated with 30% aq. NaOH soln. (5–8 ml). The org. layer was separated, dried under Ar (MgSO₄), and filtered. The filtrate was treated with elemental sulfur (2.5 mmol) and stirred for 24–35 h at r.t. Evaporation and FC gave the pure sulfide.

(Diphenyl)(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)phosphine Sulfide (19). The reaction of **2** (181 mg, 0.25 mmol) with *N,N*-dimethyl-*p*-toluidine (361 μl, 2.5 mmol) and Cl₃SiH (250 μl, 2.5 mmol) and sulfur (80 mg, 2.5 mmol) and FC (hexane/AcOEt 5:1) gave **19** (104 mg, 56%). *R*_f (hexane/AcOEt 5:1) 0.15. M.p. 92–93° (MeOH). [α]_D²⁵ = +54.9 (*c* = 0.175, CHCl₃). IR (KBr): 3050w, 3030w, 2860w, 1500m, 1455m, 1440m, 1400w, 1365m, 1330m, 1310w, 1265w, 1210w, 1155m, 1085s (*br.*), 1030m, 1000m, 765m, 735s, 725m, 695s, 670m. ¹H-NMR (400 MHz, C₆D₆): 8.40–8.24 (*m*, 4 arom. H); 7.24–6.93 (*m*, 26 arom. H); 5.30 (*dd*, *J* = 3.2, 2.7; irradi. at 4.94: *d*, *J* = 2.5, H–C(1)); 4.94 (*br. dt*, *J* ≈ 4.7, 3.5; irradi. at 5.30: *br. dd*, *J* ≈ 4.7, 3.7; irradi. at 3.78: *dt*, *J* = 4.9, 3.5, H–C(2)); 4.62 (*d*, *J* = 11.3, PhCH); 4.54 (*d*, *J* = 11.3, PhCH); 4.48 (*d*, *J* = 11.7, PhCH); 4.46 (*d*, *J* = 11.5, PhCH); 4.44 (*br. dt*, *J* ≈ 9.5, 3.7; irradi. at 3.78: *br. t*, *J* ≈ 3.7; irradi. at 3.54: *d*, *J* ≈ 9.5, H–C(5)); 4.31 (*d*, *J* = 11.6, PhCH); 4.28 (*br. dt*, *J* ≈ 12.0, 2 PhCH); 4.23 (*d*, *J* = 12.2, PhCH); 4.11 (*br. q*, *J* ≈ 3.7; irradi. at 4.94: *br. t*, *J* = 3.7; irradi. at 3.78: *br. t*, *J* ≈ 3.5, H–C(3)); 3.78 (*br. dd*, *J* = 9.4, 3.7; irradi. at 4.94: *dd*, *J* = 9.4, 3.7, H–C(4)); 3.54 (*d*, *J* = 3.8, 2 H–C(6)). ¹H-NMR (300 MHz, CDCl₃): 8.10–7.94 (*m*, 4 arom. H); 7.47–6.85 (*m*, 26 arom. H); 5.14 (*dd*, *J* = 3.4, 1.9, H–C(1)); 4.68–4.63 (*m*, H–C(2)); 4.64 (*d*, *J* = 11.7, PhCH); 4.56 (*d*, *J* = 11.9, PhCH); 4.52 (*d*, *J* ≈ 12.0, 2 PhCH); 4.48 (*d*, *J* = 11.8, PhCH); 4.45 (*d*, *J* = 11.3, PhCH); 4.42 (*d*, *J* = 12.1, PhCH); 4.32 (*d*, *J* = 11.4, PhCH); 4.12–3.97 (*m*, H–C(3), H–C(5)); 3.70 (*dd*, *J* = 9.7, 3.4, H–C(4)); 3.55 (*dd*, *J* = 10.8, 4.5, H–C(6)); 3.50 (*dd*, *J* = 10.8, 2.4, H–C(6)). ¹³C-NMR (50 MHz, CDCl₃): 138.31 (*s*); 138.02 (*s*); 137.67 (*s*); 137.56 (*s*); 133.29–130.88 (*m*); 128.45–127.34 (*m*); 77.29 (*d*, C(4)); 77.27 (*dd*, *J*(C,P) = 69.8, C(1)); 77.21 (*d*); 75.34 (*dd*, *J*(C,P) = 1.7, C(2), C(3)); 73.18 (*dd*, *J*(C,P) = 2.3, C(5)); 73.2 (*t*, PhCH₂); 73.02 (*t*, PhCH₂); 72.15 (*t*, 2 PhCH₂); 69.47 (*t*, C(6)). ³¹P-NMR (80 MHz, CDCl₃): +39.20. CI-MS: 743 (17), 742 (51), 741 (100, [*M* + 1]⁺). Anal. calc. for C₄₆H₄₅O₃P (740.80): C 74.58, H 6.12, P 4.18; found: C 74.61, H 6.12, P 3.99.

(Diphenyl)(2,3,4,6-tetra-O-benzyl-β-D-mannopyranosyl)phosphine Sulfide (22). The reaction of **8** (166 mg, 0.23 mmol) with *N,N*-dimethyl-*p*-toluidine (331 μl, 2.3 mmol), Cl₃SiH (230 μl, 2.3 mmol), and sulfur (80 mg, 2.5 mmol) and FC (hexane/AcOEt 20:1) gave **22** (122 mg, 72%). Oil. *R*_f (hexane/AcOEt 5:1) 0.26. [α]_D²⁵ = –52.8 (*c* = 0.25, CHCl₃). IR (CHCl₃): 3060m, 3000m, 2920m, 2870m, 1950w, 1810w, 1610w, 1585w, 1495m, 1480m, 1455s, 1435s, 1395w, 1360s, 1325w, 1310m, 1275m, 1235m, 1185w, 1140s, 1000s (*br.*), 1030s, 1000m, 910w, 870w, 840w,

695s, 650s, 615m. ¹H-NMR (400 MHz, CDCl₃): 8.05–7.95 (m, 4 arom. H); 7.45–7.08 (m, 24 arom. H); 6.93 (d, *J* = 7.0, 2 arom. H); 5.06 br. t, *J* ≈ 3.0; irradi. at 3.71: br. d, *J* = 3.5, H–C(2)); 4.93 (d, *J* = 10.6, PhCH); 4.89 (d, *J* = 11.0, PhCH); 4.84 (d, *J* = 11.6, PhCH); 4.70 (d, *J* = 11.3, PhCH); 4.67 (d, *J* = 10.4, PhCH); 4.61 (d, *J* = 11.0, PhCH); 4.55 (d, *J* = 11.9, PhCH); 4.43 (d, *J* = 11.9, PhCH); 4.25 (dd, *J* = 7.8, 0.6; irradi. at 5.06: d, *J* = 7.9, H–C(1)); 4.03 (t, *J* = 9.5; irradi. at 3.71: d, *J* = 9.5, H–C(4)); 3.80 (dd, *J* = 11.3, 4.7, H–C(6)); 3.77 (dd, *J* = 11.3, 2.2, H–C(6)); 3.71 (dd, *J* = 9.4, 2.7; irradi. at 5.06: d, *J* = 9.4, H–C(3)); 3.54 (ddd, *J* = 9.6, 4.7, 2.2, H–C(5)). ¹³C-NMR (50 MHz, CDCl₃): 138.39 (s, 2 C); 138.22 (s); 137.95 (s); 134.02–130.94 (m); 129.31–126.73 (m); 84.81 (dd, *J*(C,P) = 13.6, C(3)); 83.15 (dd, *J*(C,P) = 74.0, C(1)); 81.78 (dd, *J*(C,P) = 11.8, C(5)); 75.24 (t, PhCH₂); 74.64 (d, C(4)); 74.52 (t, PhCH₂); 73.20 (t, PhCH₂); 72.82 (dd, *J*(C,P) = 2.6, C(2)); 72.10 (t, PhCH₂); 69.56 (t, C(6)). ³¹P-NMR (80 MHz, CDCl₃): +39.62. CI-MS: 759 (34), 758 (67, [M + NH₄]⁺), 743 (18), 742 (50), 741 (100, [M + 1]⁺). Anal. calc. for C₄₆H₄₅O₅PS (740.80): C 74.58, H 6.12, P 4.18; found: C 74.32, H 6.32, P 4.01.

(Diphenyl)(2,3,5-tri-O-benzyl-β-D-arabinofuranosyl)phosphine Sulfide (**25**). The reaction of **12** (733 mg, 1.2 mmol) with Et₃N (850 μl, 6.3 mmol), Cl₃SiH (620 μl, 6.2 mmol), and sulfur (70 mg, 2.2 mmol), and FC (hexane/AcOEt 8:1) gave crystalline **25** (635 mg, 85%). *R*_f (hexane/AcOEt 7:1) 0.24. M.p. 123–124° (hexane/AcOEt). [α]_D²⁵ = –43.2 (*c* = 0.22, CHCl₃). IR (KBr): 3050w, 3020w, 2920m, 2895m, 2860m, 1495m, 1475w, 1455s, 1435s, 1395m, 1365m, 1350m, 1340w, 1330w, 1310w, 1285w, 1245w, 1210m, 1180w, 1155w, 1130s, 1110s, 1100s, 1090s, 1070s, 1040s, 1030s, 1000m, 980w, 960w, 945w, 915w, 860m, 820w, 755s, 735s, 720s, 700s, 650s, 615m, 610m. ¹H-NMR (400 MHz, CDCl₃): 8.05–7.93 (m, 4 arom. H); 7.50–7.16 (m, 19 arom. H); 6.95 (br. d, *J* = 7.3, 2 arom. H); 5.14 (dd, *J* = 3.7, 0.5; irradi. at 4.62: br. s, H–C(1)); 4.62 (br. d, *J* = 3.6; irradi. at 5.14: br. s; irradi. at 3.83: d, *J* = 3.7, H–C(2)); 4.56 (d, *J* = 11.3, PhCH); 4.48 (d, *J* = 11.9, PhCH); 4.46–4.42 (m, H–C(4)); 4.44 (d, *J* = 11.4, PhCH); 4.42 (d, *J* ≈ 11.0, PhCH); 4.41 (d, *J* = 12.0, PhCH); 4.34 (d, *J* = 11.9, PhCH); 3.83 (br. dd, *J* ≈ 1.8, 0.9; irradi. at 4.62: dd, *J* = 2.3, 1.2, H–C(3)); 3.46 (dd, *J* = 9.8, 6.5, H–C(5)); 3.27 (dd, *J* = 9.8, 7.1, H–C(5)). ¹³C-NMR (50 MHz, CDCl₃): 137.89 (s); 137.13 (s, 2 C); 133.28–130.67 (m); 128.46–125.93 (m); 86.67 (dd, *J*(C,P) = 7.4, C(4)); 84.77 (dd, *J*(C,P) = 73.8, C(1)); 83.66 (dd, *J*(C,P) = 3.3, C(2)); 82.19 (dd, *J*(C,P) = 5.6, C(3)); 73.08 (t, PhCH₂); 72.77 (t, PhCH₂); 71.28 (t, PhCH₂); 70.01 (t, C(5)). ³¹P-NMR (80 MHz, CDCl₃): +37.47. CI-MS: 623 (13), 622 (42), 621 (100, [M + 1]⁺). Anal. calc. for C₃₈H₃₇O₄PS (620.75): C 73.52, H 6.00, P 4.98; found: C 73.30, H 6.18, P 4.81.

(Diphenyl)(2,3,5-tri-O-benzyl-α-D-ribofuranosyl)phosphine Sulfide (**27**). The reaction of **16** (782 mg, 1.29 mmol) with Et₃N (913 μl, 6.76 mmol), Cl₃SiH (660 μl, 6.6 mmol), and sulfur (60 mg, 1.8 mmol), and FC (hexane/AcOEt 20:1) gave **27** (333 mg, 41%). Syrup. *R*_f (hexane/AcOEt 5:1) 0.2. [α]_D²⁵ = +92.8 (*c* = 0.39, CHCl₃). IR (CHCl₃): 3060w, 3000w, 2930w, 2860m, 1900w, 1820w, 1495m, 1480w, 1455m, 1440m, 1360m (br.), 1310w, 1255m (br.), 1135s (br.), 1100s, 1070s, 1040m, 1025s, 1000m, 910w, 715m, 695s, 645s, 615m. ¹H-NMR (400 MHz, CDCl₃): 8.00–7.91 (m, 4 arom. H); 7.47–7.14 (m, 19 arom. H); 7.04 (dd, *J* = 7.8, 1.6, 2 arom. H); 5.01 (d, *J* = 3.2; irradi. at 4.75: s, H–C(1)); 4.75 (t, *J* ≈ 3.4, H–C(2)); 4.72 (d, *J* = 10.7, PhCH); 4.68 (d, *J* = 10.7, PhCH); 4.54 (d, *J* = 12.1, PhCH); 4.53 (d, *J* = 11.7, PhCH); 4.50 (d, *J* = 12.3, PhCH); 4.37 (d, *J* = 11.9, PhCH); 4.28 (ddd, *J* = 9.2, 3.5, 2.3, H–C(4)); 4.13 (dd, *J* = 9.3, 3.7; irradi. at 4.75: d, *J* = 9.3, H–C(3)); 3.74 (dd, *J* = 11.2, 2.2, H–C(5)); 3.56 (dd, *J* = 11.2, 3.7, H–C(5)). ¹³C-NMR (50 MHz, CDCl₃): 138.21 (s); 137.83 (s); 137.41 (s); 133.5–130.0 (m); 128.45–127.07 (m); 85.15 (dd, *J*(C,P) = 75.0, C(1)); 81.27 (dd, *J*(C,P) = 3.2, C(4)); 78.97 (dd, *J*(C,P) = 7.1, C(3)); 77.78 (dd, *J*(C,P) = 3.7, C(2)); 74.45 (t, PhCH₂); 73.19 (t, PhCH₂); 72.77 (t, PhCH₂); 69.01 (t, C(5)). ³¹P-NMR (80 MHz, CDCl₃): +36.49. CI-MS: 623 (12), 622 (43), 621 (100, [M + 1]⁺). Anal. calc. for C₃₈H₃₇O₄PS (620.75): C 73.52, H 6.00, P 4.98; found: C 73.39, H 5.92, P 4.75.

General Procedure for the Preparation of Glycosylphosphine Borane Adducts. Under Ar, freshly prepared glycosylphosphine (1 mmol) was treated with a soln. of Me₃N · BH₃ (10 mmol) in benzene (20–30 ml). The soln. was heated to 85–90° for 5–8 h with continuous removal of Me₃N. Evaporation and FC of the residue gave the pure adduct.

(Diphenyl)(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)phosphine Borane Adduct (**20**). The reaction of crude **18** (obtained from the reduction of **2** (506 mg, 0.68 mmol) with Cl₃SiH (690 μl, 6.9 mmol) and *N,N*-dimethyl-*p*-toluidine (999 μl, 6.8 mmol)) with Me₃N · BH₃ (510 mg, 7.0 mmol) and FC (toluene) gave crystalline **20** (270 mg, 55%). *R*_f (toluene/AcOEt 7:3) 0.7. M.p. 93–94° (hexane). [α]_D²⁵ = +75.0 (*c* = 0.62, CHCl₃). IR (KBr): 3050m, 3020m, 2930m, 2890m, 2860m, 2390s, 2350s, 2300w, 2270w, 1605w, 1590w, 1560w, 1540w, 1495m, 1455s, 1440s, 1410w, 1380w, 1370m, 1360s, 1330s, 1310m, 1270w, 1250w, 1210m, 1190m, 1160s, 1140s, 1090s (br.), 1065s, 1030s, 1000m, 985m, 950w, 900w, 875w, 845w, 780w, 730s, 690s, 650m, 620w, 605w. ¹H-NMR (400 MHz, CDCl₃): 7.92–7.81 (m, 4 arom. H); 7.42–7.09 (m, 24 arom. H); 6.92 (br. d, *J* = 7.4, 2 arom. H); 5.13 (dd, *J* = 3.7, 2.8; irradi. at 4.29: d, *J* = 2.7, H–C(1)); 4.69 (d, *J* = 11.6, PhCH); 4.60 (d, *J* = 11.6, PhCH); 4.54 (d, *J* = 11.5, PhCH); 4.49 (d, *J* = 12.1, PhCH); 4.46 (d, *J* = 10.8, PhCH); 4.395 (d, *J* = 11.3, PhCH); 4.39 (d, *J* = 12.2, PhCH); 4.36 (d, *J* = 11.0, PhCH); 4.29 (dt, *J* = 6.2, 3.9; irradi. at 5.13: dd, *J* = 6.2, 4.2, H–C(2)); 4.09 (q, *J* ≈ 4.0; irradi. at 4.29: br.

t , $J \approx 4.2$, H–C(3)); 3.97 (*ddd*, $J = 9.4$, 4.3, 2.4, H–C(5)); 3.73 (*dd*, $J = 9.4$, 4.4, H–C(4)); 3.56 (*dd*, $J = 10.8$, 4.4, H–C(6)); 3.46 (*dd*, $J = 10.8$, 2.4, H–C(6)); 2.0–0.5 (br. s ; irradi. at ^{11}B : 1.13, d , $^2J(\text{P},\text{H}) = 15.3$, H_3B). ^{13}C -NMR (50 MHz, CDCl_3): 138.25 (s); 138.09 (s); 137.73 (s); 137.31 (s); 134.41–126.70 (m); 77.59 (*dd*, $J(\text{C},\text{P}) \approx 4.2$, C(3)); 77.08 (d , C(4)); 77.00 (d , C(2)); 73.96 (d , $J(\text{C},\text{P}) = 1.5$, C(5)); 73.86 (*dd*, $J(\text{C},\text{P}) = 39.2$, C(1)); 73.21 (t , PhCH_2); 72.59 (t , 2 PhCH_2); 72.22 (t , PhCH_2); 69.21 (t , C(6)). ^{13}C -NMR (100 MHz, CDCl_3): 77.67 (*dd*, $J(\text{C},\text{P}) \approx 6.0$, C(3)); 77.14 (d , C(4)); 77.05 (d , C(2)); 74.00 (br. d , C(5)); 73.87 (*dd*, $J(\text{C},\text{P}) = 39.4$, C(1)); 73.26 (t , PhCH_2); 72.62 (t , PhCH_2); 72.60 (t , PhCH_2); 72.25 (t , PhCH_2); 69.28 (t , C(6)). ^{31}P -NMR (80 MHz, C_6D_6): +19.44 (br. s). ^{11}B -NMR (128.4 MHz, C_6D_6): –38.1 (br. s , $J(\text{B},\text{P}) \approx 16$). CI-MS: 711 (18), 710 (48), 709 (100, $[\text{M} - \text{BH}_3 + 1]^+$). Anal. calc. for $\text{C}_{46}\text{H}_{48}\text{BO}_5\text{P}$ (722.66): C 76.45, H 6.69, P 4.28; found: C 76.61, H 6.54, P 4.45.

Reaction of 20 with Et_2NH and Sulfur. Under Ar in a NMR tube, a soln. of **20** (20 mg, 0.03 mmol; ^{31}P -NMR: +19.44 ppm) in C_6D_6 (0.5 ml) was treated with dry Et_2NH (40 μl , 0.04 mmol). The ^{31}P -NMR spectrum (recorded after 5 min) showed only one signal at –22.43 ppm (**18**). After the addition of sulfur (5 mg, 0.15 mmol), the signal at –22.43 ppm had disappeared in favor of a signal at +39.10 ppm (**19**).

(Diphenyl)(2,3,4,6-tetra-O-benzyl- β -D-mannopyranosyl)phosphine Borane Adduct (23). The reaction of crude **21** (obtained from the reduction of **8** (344 mg, 0.47 mmol)) with $\text{Me}_3\text{N} \cdot \text{BH}_3$ (136 mg, 1.88 mmol) and FC (toluene) gave **23** (203 mg, 60%). Oil. R_f (toluene/AcOEt 7:3) 0.79. $[\alpha]_D^{25} = -59.7$ ($c = 0.31$, CHCl_3). IR (CHCl_3): 3060w, 3000w, 2930s, 2850m, 2390m, 2350w, 1495w, 1485w, 1455m, 1440m, 1360m, 1285w, 1205w, 1130s, 1105s, 1070s, 1030m, 1000w, 905w, 715m, 700s, 675w, 630w, 610w. ^1H -NMR (400 MHz, CDCl_3): 7.94–7.81 (m , 4 arom. H); 7.43–7.04 (m , 24 arom. H); 6.87 (br. d , $J = 7.5$, 2 arom. H); 4.99 (d , $J = 10.4$, PhCH); 4.88 (d , $J = 10.8$, PhCH); 4.85 (d , $J = 11.5$, PhCH); 4.73 (d , $J = 11.6$, PhCH); 4.67 (br. t , $J \approx 2.5$; irradi. at 4.21: t , $J \approx 2.9$; irradi. at 3.71: br. d , $J = 3.2$, H–C(2)); 4.60 (d , $J = 11.0$, PhCH); 4.595 (d , $J = 10.4$, PhCH); 4.55 (d , $J = 11.9$, PhCH); 4.43 (d , $J = 11.9$, PhCH); 4.21 (*dd*, $J = 4.1$, 0.6; irradi. at 4.67: d , $J = 4.2$, H–C(1)); 4.03 (t , $J = 9.6$; irradi. at 3.71: d , $J = 9.3$, H–C(4)); 3.81 (*dd*, $J = 11.2$, 5.0, H–C(6)); 3.76 (*dd*, $J = 11.2$, 2.0, H–C(6)); 3.71 (*dd*, $J = 9.4$, 2.6; irradi. at 4.67: d , $J = 9.4$, H–C(3)); 3.50 (*ddd*, $J = 9.6$, 4.9, 2.0, H–C(5)); 2.2–0.8 (br. s ; irradi. at ^{11}B : 1.05, d , $^2J(\text{P},\text{H}) = 15.7$, H_3B). ^{13}C -NMR (50 MHz, CDCl_3): 138.50 (s); 138.35 (s); 138.28 (s); 137.92 (s); 134.54–126.14 (m); 85.11 (*dd*, $J(\text{C},\text{P}) = 12.8$, C(3)); 81.96 (*dd*, $J(\text{C},\text{P}) = 8.0$, C(5)); 79.47 (*dd*, $J(\text{C},\text{P}) = 43.9$, C(1)); 75.24 (t , PhCH_2); 74.56 (d , C(4)); 74.27 (d , C(2)); 74.04 (t , PhCH_2); 73.22 (t , PhCH_2); 72.36 (t , PhCH_2); 69.56 (t , C(6)). ^{31}P -NMR (80 MHz, CDCl_3): +18.62 (br. s). ^{11}B -NMR (128.4 MHz, CDCl_3): –39.9 (br. s). CI-MS: 741 (7), 740 (16, $[\text{M} + \text{NH}_4]^+$), 711 (13), 710 (50), 709 (100, $[\text{M} - \text{BH}_3 + 1]^+$). Anal. calc. for $\text{C}_{46}\text{H}_{48}\text{BO}_5\text{P}$ (722.66): C 76.45, H 6.69, P 4.28; found: C 76.67, H 6.95, P 4.11.

Reduction of Acetophenone with $\text{Me}_2\text{S} \cdot \text{BH}_3$ in the Presence of 20. A soln. of $\text{Me}_2\text{S} \cdot \text{BH}_3$ (632 mg, 8.32 mmol) and **20** (120 mg, 0.166 mmol, 2 mol%) in dry toluene (20 ml) was stirred for 10 min under Ar. After the addition of freshly distilled acetophenone (1.000 g, 8.3 mmol), the soln. was heated to 120° (bath temp.) for 5 min. Evaporation *in vacuo* and FC (hexane/AcOEt 14:3) of the residue gave (–)-(S)-1-phenylethanol (**28**, 935 mg, 92%) and **20** (110 mg). Two distillations (93–94°, 15 mm Hg) gave pure **28** (71%). R_f (hexane/AcOEt 7:2) 0.33. $[\alpha]_D^{25} = -10.7$ ($c = 4.12$, MeOH) which corresponds to 23.8% e.e. ([49]: $[\alpha]_D^{25} = -45$ ($c = 5.0$, MeOH)). ^1H -NMR (300 MHz, CDCl_3): 7.37–7.26 (m , 5 arom. H); 4.87 (q , $J = 6.4$, H–C(1)); 2.24 (s , OH–C(1)); 1.49 (d , $J = 6.5$, 3 H–C(2)).

Crystal Structure Determination of 12, 25, and 20. All measurements were made with graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å). Data collection and refinement parameters are given in Table 3⁴). The intensities of three representative reflections, which were measured after every 150 reflections, remained stable throughout each data collection. Lorentz polarization, and, for **12** and **25** only, absorption corrections (DIFABS [59]), were applied to the intensities. Neutral atom scattering factors for non-H-atoms were taken from Cromer and Waber [60a], and the scattering factors for H-atoms were taken from Stewart *et al.* [61]. The scattering factors were corrected for the real and imaginary parts of the anomalous dispersion [60b] [62]. The structures were solved by direct methods [63] which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. For **20**, some of the atoms in one of the Ph rings show severely elongated thermal ellipsoids, which is probably an indication of thermal motion within this ring. No attempt was made to refine disordered positions for these atoms. Most of the H-atoms could be located in difference Fourier maps. For **12** and **25**, because of the small ratio of observed reflections to refined parameters, the H-atoms were placed in geometrically calculated positions with a C–H distance of 0.95 Å, and only individual isotropic temperature factors were refined for these atoms. For **20**, the H-atoms of the sugar ring and the BH_3 group were placed in the positions indicated by a difference Fourier map, and their positions were allowed to refine. All of the remaining H-atoms (CH_2 and Ph) were placed in geometrically

⁴) Atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, England.

calculated positions with a C–H distance of 0.95 Å, and their positions were not refined. Individual isotropic temp. factors were refined for each of the H-atoms, except where the refined temp. factor became very large, in which case the appropriate H-atom was assigned a fixed isotropic temp. factor with a value of $1.2 \times B_{eq}$ of the C-atom to which it was bonded. The structures were refined on F by full-matrix least-squares procedures using the TEXSAN [64] program system. Refinements minimized the function $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. Corrections were applied for secondary extinction. There were no significant features in any of the final difference maps. No attempt was made to determine the absolute configuration; in each case, the enantiomorph was chosen based on the known configuration of the reaction starting materials.

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