Aryl *C*-Glycosides from *O*-Glycosyltrichloroacetimidates and Phenol Derivatives with Trimethylsilyl Trifluoromethanesulfonate (TMSOTf) as the Catalyst[1]

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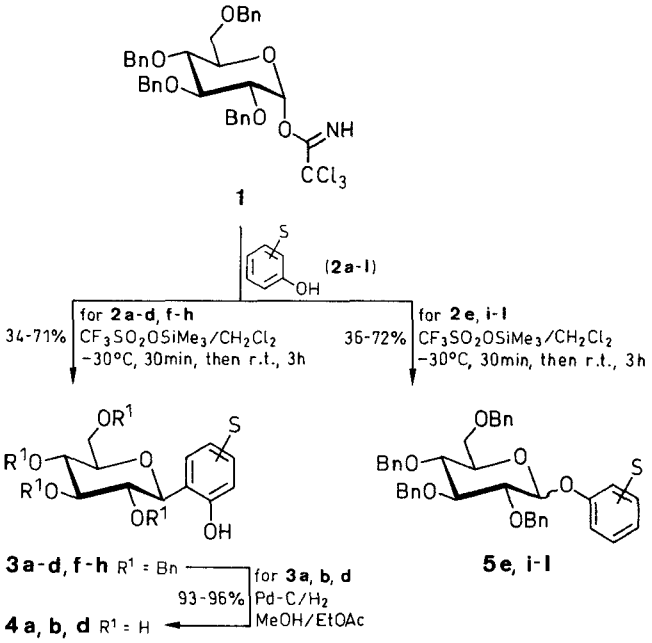
The reaction of *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)trichloracetimidate (**1**), as glycosyl donor with phenol and naphthol derivatives **2a–d** and **2f–h**, as glycosyl acceptors, furnished in the presence of catalytic amounts of TMSOTf the corresponding *o*-hydroxyaryl *C*-β-D-glucopyranosides **3a–d, f–h** regio- and stereoselectively. The less reactive 4-methoxyphenol (**2e**), α-naphthol (**2i**), the hydroxy substituted coumarines **2j, k** and the flavone **2l** afforded under these conditions *O*-glycosides **5e, i–l**. Hydrogenolytic *O*-debenzylation of **3a,b,d** afforded compounds **4a,b,d**.

Aryl *C*-glycosides found in nature are generally derived from phenols and their derivatives.[2] They have recently attracted considerable attention because various representatives possess interesting physiological properties.[3,4] The most straightforward approach to their synthesis is the Friedel-Crafts type reaction between glycosyl donors and electronrich aromatic compounds (for instance, phenol derivatives) as glycosyl acceptors,[4,5] a process accordingly employed by nature.[6] In the chemical synthesis, matching of the reactivities of the donor/acceptor pair seems to be an important prerequisite for successful results; otherwise competing side reactions of one or either one of the two components are observed. Additionally, often regio- and stereoselectivity problems are encountered.[4,5]

Recently Fries-type rearrangement of *O*-aryl glycosides to α-hydroxyaryl *C*-glycosides has been detected furnishing generally only one regioisomer.[7,8] Thus, *O*-unprotected phenols can be transformed either via their *O*-glycosides or directly (with *O*-glycosides as possible intermediates) into α-hydroxyaryl *C*-glycosides. Later reports refer generally to relatively reactive glycosyl fluorides and/or phenol derivatives as glycosyl donors and acceptors, respectively, and employ preferably $Cp_2ZrCl_2/AgClO_4$ or $Cp_2HfCl_2/AgClO_4$ as promoters which are used in up to a fivefold molar excess.[9] We would like to report on earlier results with *O*-glucosyltrichloroacetimidate **1** as donor which requires only catalytic amounts of TMSOTf as promoter for reaction with phenol derivatives **2a–l**.[10] Because the reactive glycopyranosyl species (generated from **1** or any other structurally related glucopyranosyl donor) possesses typical reactivity amongst the various glycosylating species, these investigations exhibit the scope and limitations of this process; in our hands the results obtained with the convenient catalytic procedure described in this paper were not surpassed by the fluoride zirconium or hafneium promoter system.[11]

The reaction of glycosyl donor **1** with phenol derivatives **2a–l** was initiated with catalytic amounts of TMSOTf at − 30 °C resulting in rapid *O*-glycoside formation, and for phenol derivatives **2a–d, f–h**, by warming up to room temperature, to ensure rearrangement to *C*-glucosides. As products, only *o*-hydroxyaryl *C*-β-D-glucopyranosides **3a–d, f–h** were obtained; yields and physical data are summarized in Table 1.

Hydrogenolytic *O*-debenzylation of **3a,b,d** in the presence of palladium on carbon as catalyst furnished compounds **4a,b,d** (Table 2). The less electron rich phenol derivatives **2e** and **2i–l** afforded under the above described glycosylation conditions only *O*-glycosides **5e, i–l** with the α-anomer generally predominating (Table 3). Investigations towards their rearrangement to *C*-glycosides resulted under more forcing conditions in product decomposition. The structures of compounds **3a–d, f–k, 4a,b,d** and **5e, i–l** were assigned with the help of their ^{1}H NMR data which exhibited typical shifts and coupling constants for H-1 for the α- and β-anomers; The regioselectivity of the attack could be derived from the ^{1}H NMR data of the aromatic moiety.



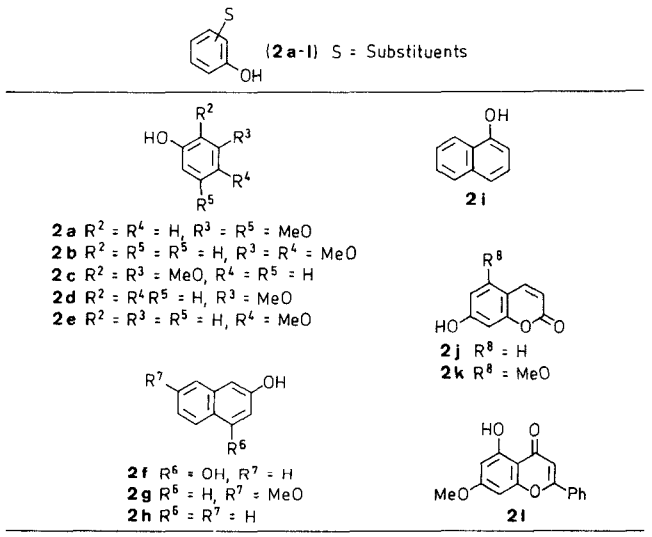
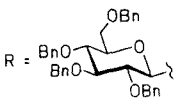
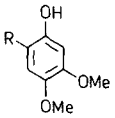
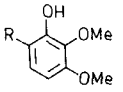
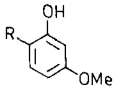
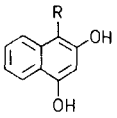
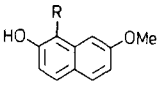
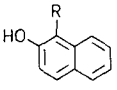


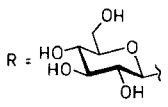
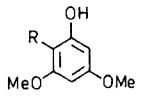
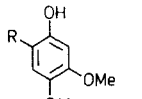
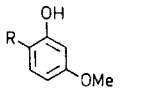
Table 1. *C*-Glycosylated Products **3a–d, f–h** Prepared

Product	Yield (%)[a] (solvent for Chromatography)	$[\alpha]_D^{20}$ ($c = 1$, solvent)	mp (°C) (solvent)	Molecular Formula[b]	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)
 **3a**	65–71 (PE/Et_2O)	+31 ($CHCl_3$)	105–107 (PE/EtOAc)	$C_{42}H_{44}O_8$ (676.9)	3.67 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.55–3.89 (m, 6H, H-2' to H-7'), 3.85 (d, 1H, H-1', $J_{H\text{-}1',H\text{-}2'}$ = 10.2), 4.42–4.46 (m, 4H, 2 × CH_2), 4.83–5.03 (m, 4H, 2 × CH_2), 6.05 (d, 1H, H-6, $J_{H\text{-}6,H\text{-}4}$ = 2.3), 6.15 (d, 1H, H-4, $J_{H\text{-}4,H\text{-}6}$ = 2.3), 6.99–7.34 (m, 20H, 4 × C_6H_5), 8.04 (s, 1H, OH)
 **3b**	59–63 (PE/EtOAc)	+12° ($CHCl_3$)	155–156 (PE/EtOAc)	$C_{42}H_{44}O_8$ (676.9)	3.68 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.55–3.94 (m, 6H, H-2' to H-7'), 4.45–4.49 (d, 1H, H-1', $J_{H\text{-}1',H\text{-}2'}$ = 9.9), 4.50–5.02 (m, 8H, 4 × CH_2), 6.55 (s, 1H, H-6), 6.62 (s, 1H, H-3), 6.99–7.36 (m, 20H, 4 × C_6H_5), 7.51 (s, 1H, OH)
 **3c**	53–55 (Toluene/ EtOAc)	+5° ($CHCl_3$)	colourless oil	$C_{42}H_{44}O_8$ (676.9)	3.87 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.60–3.96 (m, 6H, H-2' to H-7'), 3.92–3.96 (d, 1H, CH_2), 4.49–4.53 (d, 1H, H-1', $J_{H\text{-}1',H\text{-}2'}$ = 9.1), 4.41–4.97 (m, 7H, CH_2), 6.46–6.49 (d, 1H, H-4, $J_{H\text{-}4,H\text{-}3}$ = 8.7), 6.96 (s, 1H, OH), 6.95–6.98 (d, 1H, H-3, $J_{H\text{-}3,H\text{-}4}$ = 8.7), 6.95–7.00 (m, 2H, C_6H_5), 7.15–7.34 (m, 18H, C_6H_5)
 **3d**	69 (PE/EtOAc)	−2° ($CHCl_3$)	104–106 (PE/EtOAc)	$C_{41}H_{42}O_7$ (646.8)	3.54–3.58 (d, 1H, H-5'), 3.77 (s, 3H, OCH_3), 3.67–3.89 (m, 5H, H-2' to H-4', H-6', H-7'), 3.84–3.88 (d, 1H, CH_2), 4.35–4.43 (dd, 2H, H-1', $J_{H\text{-}1',H\text{-}2'}$ = 8.1, CH_2), 4.42–4.98 (m, 6H, CH_2), 6.43–6.48 (dd, 1H, H-4, $J_{H\text{-}4,H\text{-}6}$ = 2.5), $J_{H\text{-}4,H\text{-}3}$ = 8.3), 6.51–6.52 (d, 1H, H-6, $J_{H\text{-}6,H\text{-}4}$ = 2.5), 7.04–7.07 (d, 1H, H-3, $J_{H\text{-}3,H\text{-}4}$ = 8.3), 7.01–7.34 (m, 20H, 4 × C_6H_5), 7.84 (s, 1H, OH)
 **3f**	59 (PE/EtOAc)	−2°[c] (MeOH)	colourless oil[c]	$C_{44}H_{42}O_7$[c] (682.9)	3.45–3.49 (d, 1H, CH_2, J = 9.7), 3.66–4.14 (m, 6H-2' to H-7'), 4.16–4.20 (d, 1H, CH_2, J = 9.7), 4.44–5.00 (m, 6H, 3 × CH_2), 5.28–5.32 (d, 1H, H-1', $J_{H\text{-}1',H\text{-}2}$ = 9.0), 5.83 (s, 1H, OH), 6.30–6.32 (d, 2H, H_{ortho} of one phenyl), 6.52 (s, 1H, H-2), 6.92–6.98 (dt, 2H, H_{meta} of one phenyl), 7.04–7.09 (tt, 1H, H_{para} of one phenyl), 7.14–7.42 (m, 17H, H-6, H-7, 3 × C_6H_5, 7.89–7.93 (dd, 1H, H-8, $J_{H\text{-}8,H\text{-}7}$ = 8.7), 8.11–8.14 (dd, 1H, H-5, $J_{H\text{-}5,H\text{-}6}$ = 8.8, $J_{H\text{-}5,H\text{-}7}$ = 1.4), 8.63 (s, 1H, OH)
 **3g**	34 (PE/Et_2O)	−6°[d] ($CHCl_3$)	colourless oil[d]	$C_{45}H_{44}O_7$[d] (696.9)	3.47–3.51 (d, 1H, CH_2, J = 9.9), 3.72 (s, 3H, OCH_3), 3.61–4.04 (m, 6H, H-2' to H-7'), 4.21–4.25 (d, 1H, CH_2, J = 9.9), 4.44–5.01 (m, 6H, 3 × CH_2), 5.26–5.30 (d, 1H, H-1', $J_{H\text{-}1',H\text{-}2'}$ = 9.4), 6.40–6.43 (2 × d, 2H, H_{ortho} of one phenyl), 6.96–7.01 (dt, 2H, H_{meta} of one phenyl), 7.02–7.06 (d, 1H, H-3, $J_{H\text{-}3,H\text{-}4}$ = 8.9), 7.08–7.11 (tt, 1H, H_{para} of one phenyl), 7.16 (d, 1H, H-8, $J_{H\text{-}8,H\text{-}6}$ = 2.1), 7.18–7.35 (m, 16H, H-6, 3 × phenyl), 7.64–7.67 (d, 1H, H-5, $J_{H\text{-}5,H\text{-}6}$ = 8.9), 7.65–7.69 (d, 1H, H-4, $J_{H\text{-}4,H\text{-}3}$ = 8.8), 8.66 (s, 1H, OH)
 **3h**	65 (PE/EtOAc)	+76° ($CHCl_3$)	colourless oil	$C_{44}H_{42}O_6$ (666.9)	3.39–3.41 (d, 1H, CH_2, J = 9.5), 3.65–3.70 (dd, 2H, J = 10, H-6', H-7'), 3.77–3.80 (q, 1H, J = 8.5, H-5'), 3.84–3.89 (t, 1H, J = 9, H-3'), 3.95–3.99 (t, 1H, J = 9.3, H-2'), 4.00–4.04 (t, 1H, J = 9.5, H-4'), 4.16–4.18 (d, 1H, CH_2, J = 9.8), 4.42–5.00 (m, 6H, 3 × CH_2), 5.39–5.41 (d, 1H, H-1', $J_{H\text{-}1',H\text{-}2'}$ = 9.8), 6.29–6.27 (dd, 2H, H_{ortho} of one phenyl), 6.92–6.96 (t, 2H$_{meta}$ of one phenyl), 7.03–7.06 (t, 1H, H_{para} of one phenyl), 7.16–7.18 (d, 1H, J = 8.9, H-3), 7.24–7.28 (t, 1H, J = 10, H-6), 7.28–7.34 (m, 15H, 3 × C_6H_5), 7.35–7.41 (t, 1H, J = 7.5, H-7), 7.73–7.77 (dd, 2H, J = 9, H-4, H-5), 7.99–8.01 (d, 1H, J = 8.5, H-8), 8.68 (s, 1H, OH)

[a] Purification was carried out by flash chromatography.
[b] Satisfactory microanalyses obtained: C ± 0.47, H ± 0.29. Exceptions: **3f**, C − 0.54; **3h**, C − 0.49.
[c] Data for di-*O*-acetylated product.
[d] Data for mono-*O*-acetylated product.

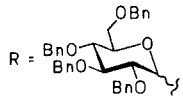
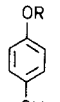
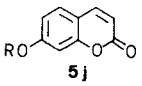
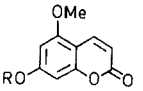
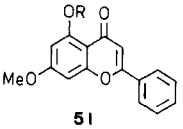
^{1}H NMR spectra were recorded at 250 MHz (Bruker, AC 250) and 400 MHz (Jeol, JNM-GX 400) with TMS as internal standard. – Optical rotations: Perkin-Elmer 241 MC polarimeter. Melting points are uncorrected. All solvents were distilled before use, petroleum ether (PE) (bp 35–60 °C). TLC: DC-Plastikfolien, silica gel 60 F_{254} (Merck, layer thickness 0.2 mm), detection by UV light (254 mm) or 10% H_2SO_4 and heating to 110 °C. Flash chromatography: silica gel 60 (J.T. Baker, 230–400 mesh ASTM).

Table 2. Debenzylated *C*-Glycosides **4a, b, d** Prepared

Product	Yield (%)[a] (solvent for Chromatography)	$[\alpha]_D^{20}$ ($c = 1$, solvent)	mp (°C) (solvent)	Molecular Formula[b]	^{1}H NMR (MeOH-d_4) δ, J (Hz)
 R =					
 **4a**	96 (Toluene/MeOH)	+21° (MeOH)	84–86 (Toluene/MeOH)	$C_{14}H_{20}O_8 \cdot \frac{3}{4}H_2O$ (329.8)	3.34–3.95 (m, 6H, H-2′ to H-7′), 3.68 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 4.77 (d, 1H, H-1′, $J_{H\text{-}1',H\text{-}2'} = 9.9$), 6.00 (d, 1H, H-6, $J_{H\text{-}6,H\text{-}4} = 2.3$), 6.04 (d, 1H, H-4, $J_{H\text{-}4,H\text{-}6} = 2.3$)
 **4b**[c]	94 (Toluene/MeOH)	+31° (Acetone)	118–120 (Toluene/MeOH)	$C_{14}H_{20}O_8 \cdot \frac{3}{4}H_2O$ (329.8)	3.34–3.85 (m, 6H, H-2′ to H-7′), 3.72 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 4.47 (d, 1H, H-1′, $J_{H\text{-}1',H\text{-}2'} = 9.2$), 6.43 (s, 1H, H-6), 6.89 (s, 1H, H-3)
 **4d**	93 (Toluene/MeOH)	+20° (MeOH)	70–73 (Toluene/MeOH)	$C_{13}H_{18}O_7 \cdot \frac{1}{2}H_2O$ (295.3)	3.38–3.87 (m, 6H, H-2′ to H-7′), 3.72 (s, 3H, OHC_3), 4.48–4.51 (d, 1H, H-1′, $J_{H\text{-}1',H\text{-}2'} = 9.2$), 6.38 (d, 1H, H-3, $J_{H\text{-}3,H\text{-}5} = 2.4$), 6.41–6.45 (dd, 1H, H-5, $J_{H\text{-}5,H\text{-}6} = 8.5$, $J_{H\text{-}5,H\text{-}3} = 2.5$), 7.19–7.23 (d, 1H, H-6, $J_{H\text{-}6,H\text{-}5} = 8.5$)

[a] Purified by flash chromatography.
[b] Satisfactory microanalyses obtained: C ± 0.22, H ± 0.16.
[c] Product was tested as inhibitor for β-glucosides from sweet almonds,[13] but inhibition was not detected.

Table 3. *O*-Glycosylated Products **5e, i–l** Prepared

Product	Yield (%)[a] (solvent for Chromatography)	$[\alpha]_D^{20}$ ($c = 1$, solvent)	Ratio of $\alpha:\beta$[b]	Molecular Formula[c]	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)
 R =					
 **5e**	72 (PE/EtOAc)	–	1:1.1	$C_{41}H_{42}O_7$ (646.8)	3.74 (2 × s, 3H, OCH_3), 3.57–4.23 (m, 6H, H-2′ to H-7′, α/β-product), 4.37–4.93 (m, 8H, 4 × CH_2), 5.05 (d, 0.5H, H-1′, $J_{H\text{-}1',H\text{-}2'} = 10.9$, β-product), 5.36 (d, 0.5H, H-1′, $J_{H\text{-}1',H\text{-}2'} = 3.6$, α-product), 6.77–6.81 (m, $2H_{arom}$), 7.00–7.06 (m, $2H_{arom}$), 7.12–7.39 (m, 20H, 4 × C_6H_5)
 **5i**	56 (Toluene/EtOAc)	–	3:1	$C_{44}H_{42}O_6$ (666.9)	3.59–4.00 (m, 6H, H-2′ to H-7′), 4.32–5.42 (m, 8H, 4 × CH_2), 5.64 (d, 1H, H-1′, $J_{H\text{-}1',H\text{-}2'} = 3.45$, α-product), 7.12–7.55 (m, 25H, 4 × C_6H_5, $5H_{naphthyl}$, 7.78–7.81 (m, $1H_{naphthyl}$), 8.38–8.42 (m, $1H_{naphthyl}$)
 **5j**	45–48[d] (Toluene/EtOAc)	+145° ($CHCl_3$)	1:0	$C_{43}H_{40}O_8$ (684.8)	3.52–3.56 (d, 1H, H-5′), 3.66–3.80 (m, 4H, H-3′, H-4′, H-6′, H-7′), 4.16–4.21 (m, 1H, H-2′), 4.40–5.04 (m, 8H, 4 × CH_2), 5.48 (d, 1H, H-1′, $J_{H\text{-}1',H\text{-}2'} = 3.5$), 6.27–6.31 (d, 1H, H-4, $J_{H\text{-}4,H\text{-}3} = 9.5$), 6.97–7.02 (dd, 1H, H-6, $J_{H\text{-}6,H\text{-}8} = 2.4$, $J_{H\text{-}6,H\text{-}5} = 8.5$), 7.05 (d, 1H, H-8, $J_{H\text{-}8,H\text{-}6} = 2.3$), 7.11–7.39 (m, 21H, 4 × C_6H_5, H-5), 7.62–7.65 (d, 1H, H-3, $J_{H\text{-}3,H\text{-}4} = 9.5$)
 **5k**	36[e,f] (Toluene/EtOAc)	+116° ($CHCl_3$)	1:0	$C_{44}H_{42}O_9$ (714.9)	3.52–4.16 (m, 6H, H-2′ to H-7′), 3.85 (s, 3H, OCH_3), 4.41–5.05 (m, 8H, 4 × CH_2), 5.44 (d, 1H, H-1′, $J_{H\text{-}1',H\text{-}2'} = 3.5$), 6.19 (d, 1H, H-4, $J_{H\text{-}4,H\text{-}3} = 9.7$), 6.44 (d, 1H, H-8, $J_{H\text{-}8,H\text{-}6} = 2.1$), 6.64 (d, 1H, H-6, $J_{H\text{-}6,H\text{-}8} = 2.0$), 7.10–7.41 (m, 20H, 4 × C_6H_5), 7.97 (d, 1H, H-3, $J_{H\text{-}3,H\text{-}4} = 9.6$)
 **5l**	44 (Toluene/EtOAc)	not determined	1:0	$C_{50}H_{46}O_9$ (790.9)	3.46–4.00 (m, 6H, H-2′ to H-7′), 3.84 (s, 3H, OCH_3), 4.30–5.16 (m, 8H, 4 × CH_2), 5.61 (d, 1H, H-1′, $J_{H\text{-}1',H\text{-}2'} = 3.2$), 6.49 (d, 1H, H-8, $J_{H\text{-}8,H\text{-}6} = 2.3$), 6.62 (d, 1H, H-6, $J_{H\text{-}6,H\text{-}8} = 2.3$), 6.66 (s, 1H, H-3), 7.12–7.42 (m, 20H, 4 × C_6H_5), 7.49–7.53 (m, 3H, H-3″), 7.84–7.88 (m, 2H, H-2″, H-6″)

[a] Purification by flash chromatography.
[b] α/β-ratio from NMR data.
[c] Satisfactory microanalyses obtained: C ± 0.41, H ± 0.38. Exception **5i**, C – 0.69.
[d] Reaction was carried out in dry acetonitrile.
[e] Reaction was carried out in dry 1,2-dimethoxyethane.
[f] Reaction was also carried out as described by Suzuki, K. et al. (see ref. 8).

The following starting materials are commercially available: **2a,g**: Fluka; **2b–e, h–j**: Aldrich; **2f**: Janssen. Compound **2k** was prepared as described in Ref. 12; **2l** was obtained by methylation of 5,7-dihydroxyflavone (Aldrich) with NaH/MeI in DMF.

o-Hydroxyaryl C-β-D-Glucopyranosides 3a–d, f,h and O-Glycosides 5e, i–l; General Procedure:
A mixture of **2** (1.1 mmol) and **1** (1.0 mmol) in anhydrous CH_2Cl_2 (5 mL) was treated under N_2 at −30 °C with TMSOTf (0.05–0.1 mmol) for 30 min. The temperature was gradually raised to r.t. within 3 h (TLC monitoring). The reaction was quenched by addition of sat. $NaHCO_3$ solution (2 mL); stirring was continued for 15 min and then water (5 mL) added. Extraction with CH_2Cl_2 (4 × 5 mL), drying of the organic extracts ($MgSO_4$), and evaporation of the solvent in vacuo provided the crude product which was purified by flash chromatography (Tables 1, 3).

O-Debenzylation of 3a,b,d; General Procedure:
Compounds **3a,b,d** (0.5 mmol) were hydrogenated in MeOH/EtOAc (4 mL, 1:1) with Pd/C (20 mg) at r.t. The catalyst was filtered, the filtrate evaporated and the residue purified by flash chromatography (Table 2).

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