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Glycosidation

Cooperative Catalysis in Glycosidation Reactions with *O*-Glycosyl Trichloroacetimidates as Glycosyl Donors**

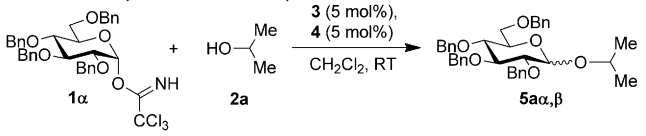
*Yiqun Geng, Amit Kumar, Hassan M. Faidallah, Hassan A. Albar, Ibrahim A. Mhkalid, and Richard R. Schmidt**

Thioureas form strong hydrogen bonds with such anions as chloride, cyanide, and carboxylates and also with neutral compounds containing groups properly aligned to accept two hydrogen bonds, thus leading to coordination complexes.[1,2] This observation was very successfully employed in organocatalysis and, with chiral thiourea derivatives, in asymmetric synthesis.[3,4] It was found that thioureas are able to catalyze acetal formation from aldehydes and alcohols in the presence of orthoesters as condensing agent[5] and also from highly reactive α-halogen ethers and alcohols.[6] Recently, this approach to the synthesis of acetals was extended by Galan and co-workers[7] to the addition of alcohols to glycals, providing a specific class of glycosides, namely 2-deoxyglycosides. However, not even the quite acidic *N*,*N*′-bis[3,5-bis-(trifluoromethyl)phenyl]thiourea (Table 1, **4**) with a pK_a of 8.5[8] is expected to activate such highly reactive glycosyl donors as the *O*-glycosyl trichloroacetimidates under standard conditions. Generally, acids with a lower pK_a value (≤ 5) are required; commonly, catalytic amounts of TMSOTf or $BF_3{\cdot}OEt_2$ are used.[9]

In work by the Schreiner group,[10] the Jacobsen group,[11] and others,[12] cooperativity between Brønsted acids and hydrogen-bonding cocatalysts, as for instance thiourea derivatives, was observed in organocatalysis that was also successfully applied to asymmetric synthesis.[10a] Therefore, the study of cooperative phenomena with thiourea cocatalysts in glycoside bond formation with *O*-glycosyl trichloroacetimidates as efficient glycosyl donors[9] is of great promise. As these donors, which are different from most other commonly used glycosyl donors,[9] are accessible to activation with catalytic amounts of an acid, they are ideally suited for such studies. Obviously, it is hoped that not only the reaction rate and the product yield but also the anomeric selectivity will be governed by the interaction of a thiourea cocatalyst with the substrates (glycosyl donor and acceptor) and the catalyst. As compound **4** has proven to be very successful in previous thiourea-based studies,[2,5b,8,13–15] this achiral compound was selected for our work. Thus in these first studies, the anomeric selectivity will be determined essentially by the chirality of the glycosyl donor and, in the absence of directing groups, essentially by the configuration of the anomeric center.

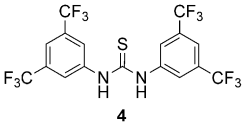
For the basic studies, α-D-glucopyranosyl trichloroacetimidate **1α**[9,16] was selected as donor, isopropanol (**2a**) as acceptor, and benzoic acid (**3a**, p$K_a = 4.2$)[10b] as catalyst. As previously observed,[9,16] **3a** led with **1α** to slow formation of β-D-glucopyranosyl benzoate **6aβ** until **3a** was consumed;

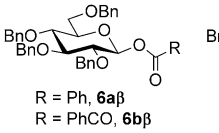
Table 1: Reactions of donor **1α** and acceptor **2a** in the presence of different catalysts **3** and cocatalyst **4**.[a]

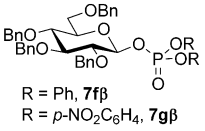


Entry	Catalyst (**3a–g**)	Cocatalyst **4**	Reaction time	β/α ratio[b] (yield[c])
1[d]	$PhCO_2H$ (**3a**)	–	24 h	1:1 (<5%)[e]
2[d]	**3a**	+	4 h	8:1
3	–	+	48 h	No reaction[f]
4	$PhCOCO_2H$ (**3b**)	–	18 h	**6bβ** (5%)
5	**3b**	+	5 h	>20:1[g]
6	CH_3COCO_2H (**3c**)	+	48 h	5:1
7	*p*-$MeOC_6H_4COCO_2H$ (**3d**)	+	10 h	>20:1[g]
8	*p*-$NO_2C_6H_4COCO_2H$ (**3e**)	+	50 min	>20:1[g]
9	$(PhO)_2PO_2H$ (**3f**)	–	48 h	1:1 (30%)
10	**3f**	+	3 h	>20:1[g]
11	(*p*-$NO_2C_6H_4O)_2PO_2H$ (**3g**)	–	48 h	3:2 (80%)
12	**3g**	+	**40 min**	**>20:1[g] (90%)**

[a] General procedure: **1α** (1.0 equiv), **2a** (1.2 equiv), and **4** (5 mol%) were dissolved in CH_2Cl_2 and then the catalyst **3a–g** (5 mol%) was added at room temperature. After completion of the reaction (if not otherwise indicated, ≥90% formation of **5a**), the reaction mixture was worked up. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined after purification by flash silica gel chromatography. [d] 15 mol% of catalyst **3a** and **4** were employed to increase the reaction rate. [e] About 5% of β-D-glucopyranosyl benzoate **6aβ** was formed. [f] Under reflux after 48 h, about 40% **5aα,β** was obtained; β/α ratio = 4:1. [g] Detection limit of the minor isomer.







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only a minor amount of a 1:1 anomeric ratio of glycosides **5aα,β** was obtained (Table 1, entry 1). However, when cocatalyst **4** was added (entry 2), the result was totally different: in much shorter reaction time, exclusive formation of glycoside **5a** in an 8:1 β/α ratio was observed; thus, a strong influence of thiourea **4** on reaction rate, yield, and stereoselectivity became evident. As expected, the cocatalyst **4** alone did not catalyze the glycosidation at room temperature (entry 3). To attain faster reaction rates, the more acidic phenylglyoxylic acid (**3b**, $pK_a = 2.1$)[10b] was investigated (entries 4, 5). In the absence of **4**, the catalyst **3b** was consumed, leading to glycosyl carboxylate **6bβ**; however, in the presence of cocatalyst **4**, fast and practically exclusive formation of **5aβ** was observed. Also the studies with pyruvic acid (**3c**) and aryl glyoxylic acids **3d** and **3e** (entries 6–8) showed that with increasing acidity of the Brønsted acid catalyst, the reaction rate increases without losing the high β-selectivity. Therefore, we turned our attention to phosphorous acids as catalysts (entries 9–12), which are also known to react with **1α** directly to β-D-glucopyranosyl phosphates **7β**.[17] In the presence of **2a** as acceptor and with **3f** and **3g** as catalyst, essentially α,β-mixtures of **5aα,β** were formed in slow reactions (entries 9, 11). However, when cocatalyst **4** was added, the β-anomeric glucoside **5aβ** was obtained practically exclusively in fast reactions (entries 10, 12). This result is independent of the addition procedure of the reagents: that is, addition of catalyst **3g** to a mixture of **1α**, **2a**, and **4** (normal procedure; see Table 1) or addition of donor **1α** to a mixture of **2a**, **3g**, and **4** (inverse procedure)[9b,c,18] led to the same result.

As about 1 mol% of TMSOTf is generally used as catalyst for the activation of *O*-glycosyl trichloroacetimidate donors,[9] corresponding comparison studies were also performed with this catalyst (Table 2). Reaction of donor **1α** and acceptor **2a** with TMSOTf as catalyst showed the known strong dependence of the α,β-selectivity on the reaction temperature (entries 1–3).[9] This result is explained by acid-catalyzed activation of the donor leading to temperature-dependent ion-pair formation, thus favoring an S_N2-type reaction at low temperature and S_N1-type at high temperature.[9] Addition of cocatalyst **4** to these reactions obviously leads to a competing reaction course that further increases the β-selectivity (entries 4–6). However, owing to a very fast reaction at temperatures as low as −78°C, no major reaction rate difference was observed for complete formation of product **5a**. Overall, in the presence of the strong catalyst TMSOTf, the cooperativity effect is less dramatic than found for the Brønsted acids in Table 1.

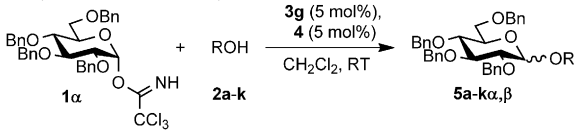
Studies with other acceptors were based on the highly promising results with **3g** as catalyst and **4** as cocatalyst (Table 1, entry 12). Thus, reaction of **1α** with allyl alcohol (**2b**) led practically exclusively to allyl β-D-glucopyranoside **5bβ** (Table 3,[19] entry 1). Other primary alcohols, such as 4-pentenol (**2c**) and propargyl alcohol (**2d**), also gave glucosides **5cβ** and **5dβ**, respectively, preferentially or exclusively (entries 2, 3). With decreasing nucleophilicity of the acceptor hydroxy group (through steric and/or inductive effects), as in acceptors **2e–g** and **2h**, the reaction rate and the high preference for β-product formation decreased and different from isopropanol **2a** as acceptor (entry 7), the α-anomer could also be detected (entries 4–6 and 8; formation of **5e–gα,β** and **5hα,β**). A particularly interesting case is sterically

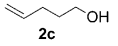
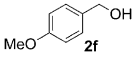
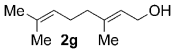
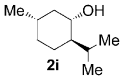
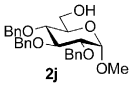
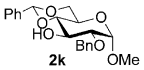
Table 2: Reaction of donor **1α** with isopropanol (**2a**) as acceptor in the presence of TMSOTf as catalyst and **4** as cocatalyst at different temperatures.[a]

Entry	Addition of **4**	Reaction temperature [°C]	Reaction time [min]	**5aα,β** β/α ratio
1	−	0	5	1:1
2	−	−40	10	5:1
3	−	−78	30	12:1
4	+	0	5	1.3:1
5	+	−40	10	11:1
6	+	−78	30	> 20:1[b]

[a] General procedure: **1α** (1.0 equiv), **2a** (1.2 equiv), and **4** (5 mol%) were dissolved in CH_2Cl_2 and then TMSOTf (1 mol%) was added. After completion of the reaction, yielding ≥90% of **5aα,β**, the reaction mixture was worked up and the product ratio determined by ^1H NMR spectroscopy. [b] Detection limit of the minor isomer.

Table 3: Reaction of donor **1α** with acceptors **2a–k** in the presence of **3g** as catalyst and **4** as cocatalyst.[a]



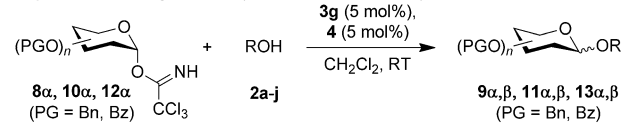
Entry	ROH	Reaction time	Product	Yield [%][b]	β/α ratio[c]
1	 **2b**	15 min	**5bβ**	93	> 20:1[d]
2	 **2c**	30 min	**5cα,β**	91	10:1
3	 **2d**	10 min	**5dβ**	95	> 20:1[d]
4	 **2e**	1.5 h	**5eα,β**	85	5:1
5	 **2f**	30 min	**5fα,β**	87	7:1
6	 **2g**	10 min	**5gα,β**	83	4:1
7	 **2a**	40 min	**5aβ**	90	> 20:1[d]
8	 **2h**	4 h	**5hα,β**	88	6:1
9[e]	 **2i**	1 h	**5iα,β**	87	4:1
10[e]	 **2j**	2 h	**5jα,β**	82	5:1
11[e]	 **2k**	3.5 h	**5kα,β**	78	6:1

[a] General procedure: **1α** (1.0 equiv), **2** (1.2 equiv), and **4** (5 mol%) were dissolved in CH_2Cl_2 and then **3g** (5 mol%) was added. After completion of the reaction by TLC detection, the reaction mixture was worked up. [b] Determined after purification by flash silica gel chromatography. [c] Determined by ^1H NMR spectroscopy. [d] Detection limit of the minor isomer. [e] CH_3CN was used as the solvent.

demanding (+)-menthol (**2i**). With **3g** as catalyst and **4** as cocatalyst, a 4:1 ratio in favor of the β-isomer **5iβ** was obtained (entry 9) when the reaction was carried out in acetonitrile as solvent, which allowed a rate increase. Studies with two additional carbohydrate acceptors (**2j** and **2k**, entries 10 and 11), again using acetonitrile as solvent, showed that also the β-(1-6)- and β-(1-3)-connected disaccharides (**5jβ** and **5k,β** respectively) can be successfully obtained as major products with this method.

Other glycosyl donors were also investigated (Table 4).[19] Studies with α-D-galactosyl trichloroacetimidate **8α**[9b] were of particular interest, as this glycosyl donor generally provides

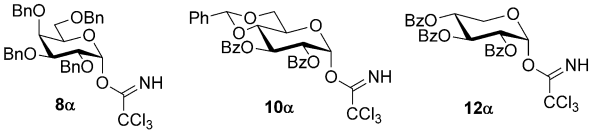
Table 4: Reactions of donor **8α**, **10α** and **12α** with different acceptors in the presence of **3g** as catalyst and **4** as cocatalyst.[a]



8α, 10α, 12α (PG = Bn, Bz) — **2a-j** — **9α,β, 11α,β, 13α,β** (PG = Bn, Bz)

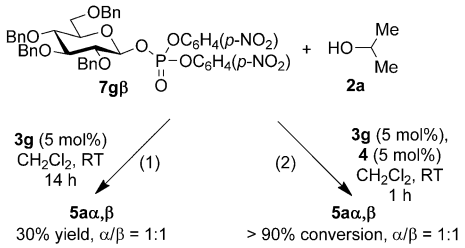
Entry	Donor	ROH	Reaction time	Product	Yield [%][b]	β/α ratio[c]
1	**8α**	**2b**	30 min	**9bα,β**	91	12:1
2	**8α**	**2d**	20 min	**9dβ**	93	>20:1[d]
3	**8α**	**2f**	1.5 h	**9fα,β**	87	9:1
4	**8α**	**2a**	3 h	**9aα,β**	89	7:1
5[e]	**8α**	**2i**	2 h	**9iα,β**	86	4:1
6[e]	**8α**	**2j**	3.5 h	**9jα,β**	81	5:1
7	**10α**	**2a**	5 h	**11aβ**	95	>20:1[d]
8	**12α**	**2a**	22 h	**13aβ**	88	>20:1[d]

[a] General procedure: **8α** or **10α** or **12α** (1.0 equiv), **2** (1.2 equiv), and **4** (5 mol%) were dissolved in CH_2Cl_2 and was then added at room temperature **3g** (5 mol%). After completion of the reaction by TLC detection, the reaction mixture was worked up. [b] Determined after purification by flash silica gel chromatography. [c] Determined by ^{1}H NMR spectroscopy. [d] Detection limit of the minor isomer. [e] CH_3CN was used as the solvent.



more α-product than glycosyl donor **1α** under the same reaction conditions. However, allyl alcohol (**2b**) and 4-methoxybenzyl alcohol (**2f**) as acceptors preferentially led to the β-anomers **9bβ** and **9fβ**, respectively, in the presence of **3g** as catalyst and **4** as cocatalyst (entries 1, 3); with propargyl alcohol (**2d**), the β-anomer **9dβ** was formed practically exclusively (entry 2). Isopropanol (**2a**), as a very reactive secondary alcohol, showed still a strong preference for the β-anomer **9aβ** (entry 4) and even sterically demanding (+)-menthol (**2i**) furnished a 4:1 mixture of **9iα,β** (entry 5). With 6-*O*-unprotected glycosyl acceptor, the β-disaccharide **9jβ** was obtained preferentially (entry 6). Therefore, there is also a strong effect of cocatalyst **4** on the glycosidation rate, yield, and α/β selectivity with galactosyl donor **8α**. Studies with glycosyl donors having anchimerically assisting groups in 2-positions, such as 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene protected glucosyl donor **10α**[19] and 2,3,4-tri-*O*-benzoyl protected xylosyl donor **12α**,[19] showed that addition of thiourea **4** to the reaction mixture containing **2a** and **3g** leads to an increase in reaction rate under formation of β-products **11aβ** and **13aβ**, respectively (entries 7 and 8). Thus, the cooperative effect of **4** in these glycosidations is also supported.

As a universal cooperative catalysis phenomenon had been observed in the catalytic glycosidations with different *O*-glycosyl trichloroacetimidates while using **3g** as catalyst and **4** as cocatalyst, further efforts were focused on the reaction mechanism. As previous observations do not rule out that glycosyl carboxylates **6** or glycosyl phosphates **7**, respectively, could be the decisive intermediates in these glycosidations (results in Table 1), **1α** was transformed with **3g** into glycosyl phosphate **7gβ** (Scheme 1). However, attempted reaction of



Scheme 1. Control experiments using **7gβ** in the glycosydations with **2a**.

7gβ with acceptor **2a** did not lead to glycoside **5a**; when **3g** (5 mol%) was added to this reaction mixture, only 30% of a 1:1-mixture of **5aα,β** was obtained after 14 h (Scheme 1, (1)). Addition of cocatalyst **4** (5 mol%) to this reaction mixture of **7gβ**, **2a**, and **3g** increased the reaction rate, and practically complete transformation to **5aα,β** was observed after 1 h; however, the anomeric ratio was still 1:1 (Scheme 1, (2)). Therefore, glycosyl phosphate **7gβ** is not the decisive intermediate in these glycosidations.

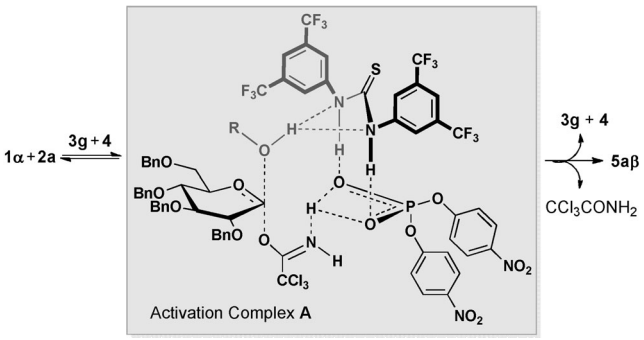
^{1}H NMR spectroscopy studies with mixtures of the cocatalyst **4** and donor **1α** or acceptor **2a**,[20] respectively, showed, in addition to the expected shifts of the -NH and -OH signals, shifts of the proton signals, for instance, of the bis(trifluoromethyl)phenyl residues. These shifts are also visible for mixtures of **1α** + **2a** + **4**. However, owing to low solubility, almost no effect was observed for 1:1 mixtures of **3g** + **4** and also for **3g** + **2a**. However, addition of **2a** to a mixture of **3g** (10 mol%) + **4** (10 mol%) led to immediate dissolution and to increased shifts of the aryl protons of **4**.

From these results, the following conclusions can be drawn:

- The thiourea **4** is decisive for the reaction rate increase and the β-selectivity.
- Glycosyl carboxylates or phosphates, respectively, are not decisive intermediates.
- Glycosyl cations, as generally discussed in the TMSOTf catalyzed activation of *O*-glycosyl trichloroacetimidates, are not the decisive intermediates in the reaction course mediated by thiourea **4**.
- Fast complex formation between acceptor **2a**, catalyst **3g**, and cocatalyst **4** seems to precede interaction with donor **1α** and the following product formation.

- This complex has steric constraints, and thus the thiourea **4** cocatalyst effect decreases with increasing steric bulk of the acceptor.

These conclusions support a reaction course as proposed in Scheme 2. The thiourea **4** effects, together with catalyst **3g** and acceptor **2a**, the hydrogen-bond-mediated formation of a complex.[21] Upon interaction with donor **1α**, this complex



Scheme 2. Proposed reaction course.

generates activation complex **A**, leading to proton transfer to the leaving group in an intramolecular reaction and concomitant proton release from the acceptor, thus facilitating an acid-base catalyzed S_N2-type glycoside bond formation.[22] Thus, thiourea **4** functions as a relay for proton transfer as, for instance, often found for the imidazole residue in the active site of hydrolases. Competing reaction courses, leading for example to α-product formation via directed attack at the trichloroacetimidate favoring an S_N1-type reaction course (or reaction between donor and catalyst), are only effective in the presence of less reactive acceptors.

In summary, thiourea **4** as cocatalyst exhibits a cooperative behavior that has a strong effect on the reaction rate, yield, and the selectivity of glycosidations. This compound enables hydrogen-bond-mediated complex formation between *O*-glycosyl trichloroacetimidate donors, acceptors, and acid catalysts; acid–base-catalyzed S_N2-type glycoside bond formation is facilitated even at room temperature and in the absence of anchimeric assistance. This finding is of great practical usefulness and of great promise for further studies to finally completely control anomeric selectivity even at ambient temperature.

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Keywords: acid–base catalysis · cooperativity · glycosylation · organocatalysis · thiourea

[1] a) P. J. Smith, M. V. Reddington, C. S. Wilcox, *Tetrahedron Lett.* **1992**, *33*, 6085–6088; b) E. Fan, S. A. Vanarman, S. Kincaid, A. D. Hamilton, *J. Am. Chem. Soc.* **1993**, *115*, 369–370; c) J. S. Albert, A. D. Hamilton, *Tetrahedron Lett.* **1993**, *34*, 7363–7366.
[2] For a recent review see: Z. Zhang, P. R. Schreiner, *Chem. Soc. Rev.* **2009**, *38*, 1187–1198.
[3] For reviews see: a) P. R. Schreiner, *Chem. Soc. Rev.* **2003**, *32*, 289–296; b) Y. Takemoto, *Org. Biomol. Chem.* **2005**, *3*, 4299–4306; c) S. J. Connon, *Chem. Eur. J.* **2006**, *12*, 5418–5427; d) M. S. Taylor, E. N. Jacobsen, *Angew. Chem.* **2006**, *118*, 1550–1573; *Angew. Chem. Int. Ed.* **2006**, *45*, 1520–1543; e) A. G. Doyle, E. N. Jacobsen, *Chem. Rev.* **2007**, *107*, 5713–5743.
[4] For recent reviews on asymmetric synthesis employing chiral thioureas as organocatalysts, see: a) M. Mahlau, B. List, *Angew. Chem.* **2013**, *125*, 540–556; *Angew. Chem. Int. Ed.* **2013**, *52*, 518–533; b) K. Brak, E. N. Jacobsen, *Angew. Chem.* **2013**, *125*, 558–588; *Angew. Chem. Int. Ed.* **2013**, *52*, 534–561.
[5] a) M. Kotke, P. R. Schreiner, *Tetrahedron* **2006**, *62*, 434–439; b) M. Kotke, P. R. Schreiner, *Synthesis* **2007**, 779–790.
[6] S. E. Reisman, A. G. Doyle, E. N. Jacobsen, *J. Am. Chem. Soc.* **2008**, *130*, 7198–7199.
[7] E. I. Balmond, D. M. Coe, M. C. Galan, E. M. McGarrigle, *Angew. Chem.* **2012**, *124*, 9286–9289; *Angew. Chem. Int. Ed.* **2012**, *51*, 9152–9155.
[8] G. Jakab, C. Tancon, Z. Zhang, K. M. Lippert, P. R. Schreiner, *Org. Lett.* **2012**, *14*, 1724–1727.
[9] For reviews, see: a) R. R. Schmidt, *Angew. Chem.* **1986**, *98*, 213–236; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 212–235; b) R. R. Schmidt, W. Kinzy, *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21–123; c) X. Zhu, R. R. Schmidt, *Angew. Chem.* **2009**, *121*, 1932–1967; *Angew. Chem. Int. Ed.* **2009**, *48*, 1900–1934.
[10] a) T. Weil, M. Kotke, C. M. Kleiner, P. R. Schreiner, *Org. Lett.* **2008**, *10*, 1513–1516; b) Z. Zhang, K. M. Lippert, H. Hausmann, M. Kotke, P. R. Schreiner, *J. Org. Chem.* **2011**, *76*, 9764–9776.
[11] R. S. Klausen, E. N. Jacobsen, *Org. Lett.* **2009**, *11*, 887–890.
[12] D. Uraguchi, Y. Ueki, T. Ooi, *Science* **2009**, *326*, 120–123.
[13] P. R. Schreiner, A. Wittkopp, *Org. Lett.* **2002**, *4*, 217–220.
[14] X.-S. Wang, C.-W. Zheng, S. L. Zhao, Z. Chai, G. Zhao, G.-S. Yang, *Tetrahedron: Asymmetry* **2008**, *19*, 2699–2704.
[15] X. Li, H. Deng, S. Luo, J.-P. Cheng, *Eur. J. Org. Chem.* **2008**, 4350–4356.
[16] R. R. Schmidt, J. Michel, *Angew. Chem.* **1980**, *92*, 763–764; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 731–732.
[17] a) R. R. Schmidt, M. Stumpp, J. Michel, *Tetrahedron Lett.* **1982**, *23*, 405–408; b) R. R. Schmidt, M. Stumpp, *Liebigs Ann. Chem.* **1984**, 680–691.
[18] R. R. Schmidt, A. Toepfer, *Tetrahedron Lett.* **1991**, *32*, 3353–3356.
[19] Compounds **5a**–**5e**, **5g**–**5k**, **9a**, **9b**, **9d**, **9i**, **9j**, **10α**, and **12α** have been previously prepared. For references and physical data, also of **5f**, **9f**, **11aβ**, and **13aβ**, see the Supporting Information.
[20] For the ^{1}H NMR studies of the interaction of cocatalyst **4** with donor **1α**, acceptor **2a**, or catalyst **3g**, see the Supporting Information.
[21] The authors are grateful to one of the reviewers, who drew our attention to the importance of the hydrogen-bond-mediated interaction between the catalyst (**3g**) and cocatalyst (**4**).
[22] For cases of acid–base catalysis in glycosidations, see: a) A. Kumar, V. Kumar, R. T. Dere, R. R. Schmidt, *Org. Lett.* **2011**, *13*, 3612–3615; b) A. Kumar, Y. Geng, R. R. Schmidt, *Adv. Synth. Catal.* **2012**, *354*, 1489–1499; c) A. Kumar, R. R. Schmidt, *Eur. J. Org. Chem.* **2012**, 2715–2719.

