centers in the indolizidinones by means of the ring contraction. Further investigations into the scope and limitations of the diastereoselective transannular reaction are in progress.

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An Enzyme-Labile Linker Group for Organic Syntheses on Solid Supports**

Bernd Sauerbrei, Volker Jungmann, and Herbert Waldmann*

Combinatorial chemistry has proven to be a new and valuable method for the rapid identification and further development of compounds with a predetermined profile of properties, not only for drug discovery but also for asymmetric catalysis.[1] In the majority of the cases combinatorial syntheses are carried out on solid supports. Once the desired compounds are constructed they have to be released from the supports selectively and without attack on the synthesized structures through cleavage of a suitable anchor group (linker). Combinatorial synthesis gives access to a multitude of different classes of compounds with a wide range of stability under the conditions of the releasing reactions. Therefore the development of broadly applicable linkers

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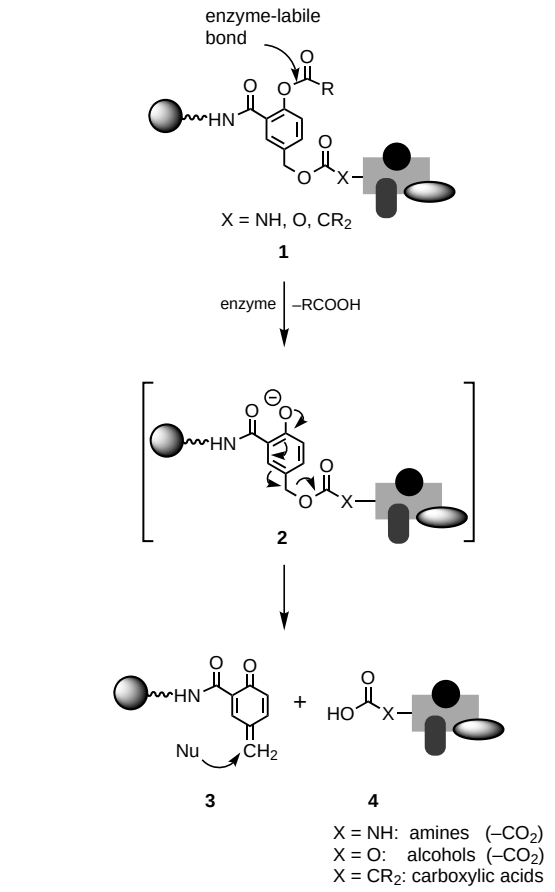
allowing for selective cleavage of the synthesized products from the polymeric support under mild conditions (preferably at pH 7 and room temperature) is of particular importance. In many cases biocatalyzed transformations have opened up advantageous alternatives to classical chemical approaches, since enzymatic reactions often proceed under very mild conditions and with pronounced chemo-, regio-, and stereoselectivity.[2] The use of enzyme-labile anchor groups could also provide new opportunities for combinatorial chemistry and solid-phase synthesis. However, a broadly applicable enzyme-labile linker has not yet been developed.[3] We now report that the 4-acyloxy-3-carboxybenzyloxy group can be employed advantageously as an enzyme-labile linker for solid-phase syntheses. The compounds built up at this anchor group can be released by means of an enzyme-initiated fragmentation.

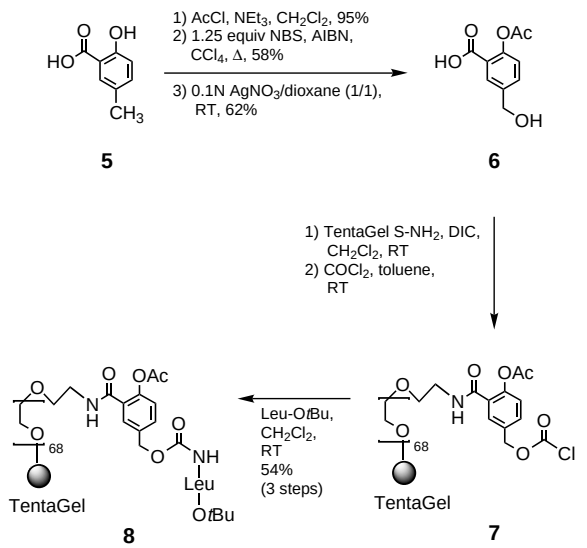
For the design of an enzyme-labile linker we have drawn from our experience in the development of enzymatically removable protecting groups.[4] The anchor group was constructed in such a way that a) it contains a functional group that is recognized and attacked by the biocatalyst, that b) cleavage of the enzyme-labile bond yields an intermediate that undergoes a spontaneous fragmentation, thereby releasing the desired compound,[5] and that c) a further functional group for attaching the linker to the solid support is present. The realization of this principle is shown in Scheme 1. The linker is attached through a carboxyl group as an amide to the solid phase (→**1**). It contains an acyl group, for example an acetate, which can be cleaved by lipases or esterases. A phenolate is thus generated (→**2**), which fragments to give a quinone methide **3** and releases the desired compound **4**, a product of, for example, combinatorial synthesis. The quinone methide remains bound to the solid phase and is trapped there by water or an additional nucleophile. In this way amines (bound as urethanes), alcohols (bound as carbonates), and carboxylic acids (bound as esters) can be detached from the polymeric carrier. The substrate specificity of the enzyme guarantees that only the intended ester is cleaved, and the mild conditions of the biocatalyzed transformations ensure that the compounds built up on the solid phase remain intact during the cleavage. Furthermore the linker is constructed in such a way that the variable part of the substrates is remote from the site of the biocatalyst's attack. This guarantees that the substrate tolerance of the enzyme in the cleaving reaction is not restricted by interfering electronic or steric interactions of the protein with the different substrates generated by combinatorial synthesis.

For the synthesis of the linker, building block 5-methylsalicylic acid (**5**) was first O-acetylated, then the methyl group was converted into a benzyl bromide with *N*-bromosuccinimide (NBS), and the bromide was finally hydrolyzed to the benzyl alcohol by treatment with $AgNO_3$ solution (Scheme 2).

The polymeric support selected for the subsequent transformations on the solid phase was TentaGel S-NH_2, a polystyrene resin onto which terminally NH_2-functionalized oligoethyleneglycol units had been grafted.[6] Its polar surface and the fact that it is well solvated in aqueous solution are particularly advantageous properties that should facilitate the enzymatic cleavage of the linker. After activation with



Scheme 1. Principle for the development of the enzyme-labile 4-acyloxybenzyloxy linker groups. The solid support is represented by a shaded sphere; the target compounds constructed by combinatorial synthesis are shown schematically (rectangles, circles, oblongs, ellipses).



Scheme 2. Synthesis of linker **6** and its attachment to TentaGel S-NH_2. AIBN = 2,2′-azobisisobutyronitrile, DIC = diisopropylcarbodiimide, Leu = leucine, RT = room temperature.

diisopropyl carbodiimide (DIC) the carboxylic acid **6** was coupled to the polymer, and the benzylic alcohol was then converted into the chloroformic acid ester **7** by treatment with phosgene. Thus, an activated intermediate is generated to

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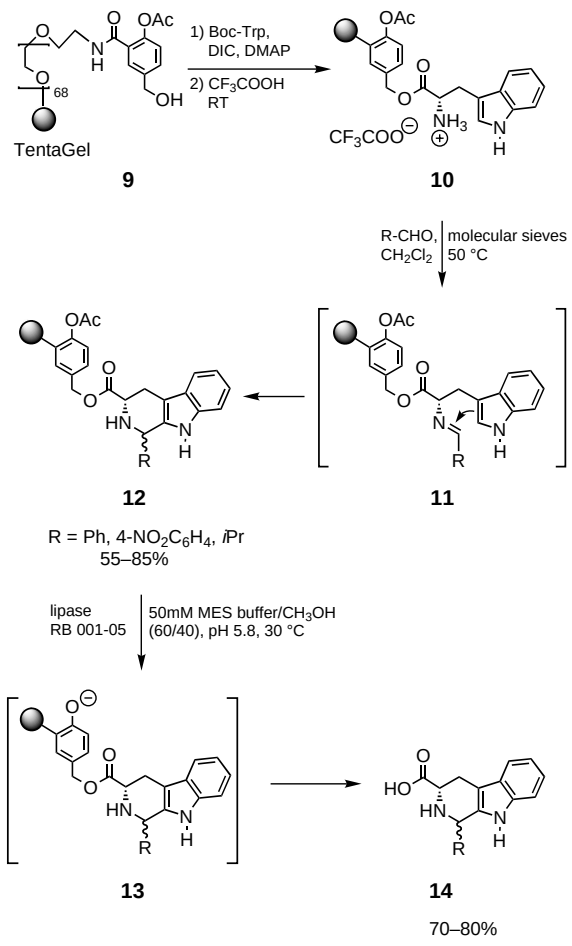
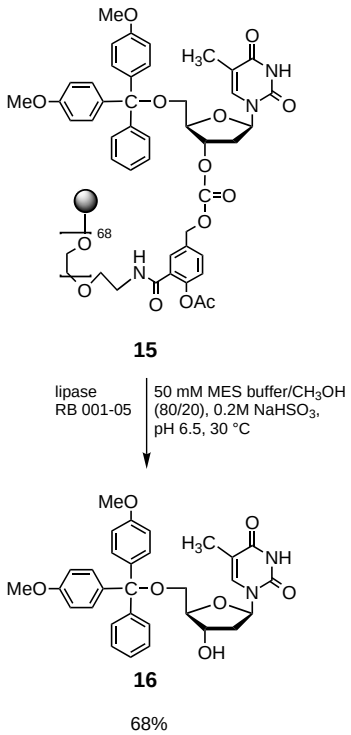
which a broad variety of amines and alcohols can be attached. Carboxylic acids can already be coupled to the polymer-bound benzyl alcohol **9** (see Scheme 3). In order to determine the best conditions for the enzyme-initiated fragmentation of the anchoring group, leucine *tert*-butyl ester was linked to **7** to give the urethane **8**.[7] Several commercially available lipases and esterases were investigated for the enzyme-initiated fragmentation of the linker. By far the best results were achieved with lipase RB 001-05 (Recombinant Biocatalysis, Diversa, San Diego, USA). This biocatalyst detaches leucine *tert*-butyl ester at pH 5.8 und 40 °C in 0.05 M morpholinoethane sulfonic acid (MES) buffer/methanol (60/40), in other words, under very gentle conditions. The amino acid ester was isolated in 73 % yield. Lipase from *Mucor miehei* also catalyzes this reaction under similarly mild conditions (0.1 M NaH_2PO_4 buffer, pH 6, 37 °C); however, the product was obtained in lower yield (50 %).

The applicability of the enzyme-labile anchor group to multistep transformations on the solid phase, which are for instance relevant to the generation of libraries in pharmaceutical research, was proven by the synthesis of tetrahydro-β-carbolines by means of the Pictet–Spengler reaction[8] and their subsequent enzyme-mediated release (Scheme 3). To this end, the benzylic OH group of the TentaGel S-NH_2 bound linker **9** was first esterified with Boc-L-tryptophan, and the Boc group was then removed by treatment with trifluoroacetic acid. The support-bound tryptophan **10** was then condensed with aliphatic and aromatic aldehydes at 50 °C in the presence of molecular sieves to give imines **11**, which under these reaction conditions cyclized immediately to the tetrahydro-β-carbolines. Starting from **9** the heterocyclic amines **12** were thus formed in 55–85 % yield.[7] The Pictet–Spengler adducts could also be released from the polymeric support under very mild conditions by lipase-initiated fragmentation of the anchor group. Upon treatment of **12** with lipase RB 001-05 at pH 5.8 in an MES buffer/methanol mixture (60/40) the enzyme selectively attacked the acetate incorporated into the linker and converted it into the corresponding phenolate (→**13**), which then fragmented spontaneously. By means of this enzyme-mediated dissection of the anchor group the desired tetrahydro-β-carbolines **14** were released in 70–80 % yield.[9] The result that the enzymatic fragmentation of the linker occurs already at pH 5.8 is not a foregone one. In the nonenzymatic cleavage of 4-acyloxybenzyloxy groups the pH has to be raised to at least 10–11 to deprotonate the corresponding phenol and thereby induce its conversion into the quinone methide.[10, 11] Active participation of the enzyme in the fragmentation, for example by means of basic amino acid side chains in or close to the active site, is therefore very probable.

To further prove the broad applicability of the enzyme-labile anchor group the polymer-bound chloroformic acid ester **7** was coupled with the very acid-labile 5′-*O*-dimethoxytrityl(DMTr)-protected thymidine (NaH, THF). Treatment of the resulting immobilized nucleoside **15** with lipase RB 001-05



Scheme 3. Solid-phase synthesis of tetrahydro-β-carbolines and subsequent detachment (→**14**) by enzyme-initiated fragmentation of the anchor group. Boc = *tert*-butyloxycarbonyl, Trp = tryptophan, DMAP = 4-dimethylaminopyridine.



Scheme 4. Detachment of DMTr-protected thymidine from the polymeric support by enzyme-initiated fragmentation of the anchor group.

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at pH 6.5 initiated the fragmentation of the linker and released the DMTr-protected thymidine **16** from the solid support under gentle conditions (Scheme 4).

The results demonstrate that the 4-acetyloxybenzyloxy linker allows for the detachment of amines (like leucine *tert*-butyl ester), carboxylic acids (like the tetrahydro-β-carbolines **14**), and alcohols (like the protected nucleoside **16**) from the polymeric support under very mild conditions (pH 5–7, room temperature) and with complete selectivity. The results are not only relevant to combinatorial chemistry, they also indicate that enzymes in general may be valuable reagents for transformations on solid supports.[12]

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[9] **14a** (R = Ph): 75% yield; ^{1}H NMR (200 MHz, CD_3OD, 25 °C, TMS): $\delta = 7.28–7.49$ (m, 6H, H-7, H-14–18), 7.12 (dd, 1H, H-10, $J = 6.8$, $J' = 1.4$ Hz), 6.96 (td, 1H, H-9, $J = 6.9$, $J' = 1.3$ Hz), 6.90 (td, 1H, H-8, $J = 6.9$, $J' = 1.4$ Hz), 5.99 (br. s, 1H, H-1 (*trans*)), 5.84 (br. s, 1H, H-1 (*cis*)), 4.12–4.26 (m, 1H, H-3), 3.35–3.51 (br. m, 2H, H-4).

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[11] If an amino group can function intramolecularly as nucleophile, the fragmentation (in these cases with cyclization) can occur even at pH 8. This principle can also be employed for the development of an anchor group that can be cleaved by classical chemical methods: B. Atrash, M. Bradley, *J. Chem. Soc. Chem. Commun.* **1997**, 1397.

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Novel Distorted Pentagonal-Pyramidal Coordination of Anionic Oxodiperoxo Molybdenum and Tungsten Complexes**

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There is currently much interest in the preparation of new polyoxo(peroxo)metalates for homogeneous catalysis[1] and heterogeneous systems[2] in order to understand the chemistry of surface species and the nature of the catalytically active sites of transition metal containing molecular sieves or other materials. While studying oxidation reactions with mesoporous materials,[1m] which are potentially interesting catalysts and/or catalyst supports,[3] we became interested in comparing anionic or neutral oxoperoxo complexes with those that can be formed on silica and/or alumina. From studies on systems of aqueous $[MoO_4]^{2-}$ and $[Mo_7O_{24}]^{6-}$ solutions and silica, it is known that Mo^{VI} uptake by SiO_2 is relatively low over the entire pH range, except for a small increase at pH 2 or lower owing to the formation of $[SiMo_{12}O_{40}]^{4-}$ ions, which can partially desorb into solution.[4] Furthermore, silica (BET specific surface area 263 $m^2 g^{-1}$) and molybdenum– (or tungsten–) oxoperoxo species interact in aqueous acidic medium to form surface peroxo species with characteristic IR bands $\tilde{\nu}_{O-O}$ near 870 cm^{-1} ($\tilde{\nu}_{O-O}$ is expected to be in the range of 845–885 cm^{-1}).[1] These observations suggest that it might be possible to synthesize oxoperoxoheterosiloxanes involving the various functionalities on the silica surface (i.e., lone

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