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Graphical Abstract

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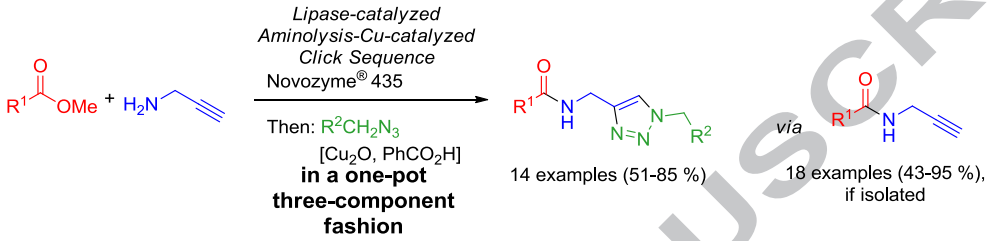

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Three-component chemoenzymatic synthesis of amide ligated 1,2,3-triazoles

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ABSTRACT

CAL-B (*Candida antarctica* lipase B) immobilized on an acrylic resin (Novozyme® 435) smoothly catalyzes the aminolysis of methyl esters with propargyl amine furnishing propargyl amides. In the same reaction vessel these propargyl derivatives are consecutively transformed into amide ligated 1,2,3-triazoles in a Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) click reaction in good to excellent yields.

1. Introduction

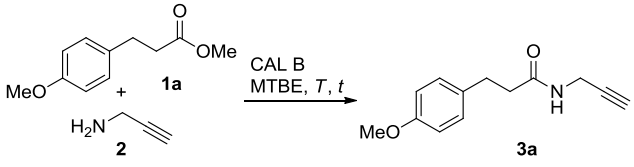
The advent of the Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) click reaction[1-3] regiospecifically furnishing 1,4-disubstitued 1,2,3-triazoles has stimulated numerous applications in many emerging fields ranging from materials to life sciences.[3,4] In particular, the synthesis of 1,2,3-triazole peptidomimetics has been considerably developed by CuAAC due to the structural and electronic similarities of 1,2,3-triazoles to the peptide linkage.[5-7] Hence, a control of the conformation in the resulting tagged peptide sequence can easily be achieved.[8]

Chemoenzymatic transformations have become increasingly important over the years and many applications have been focusing on chiral resolution of racemic or *meso* substrates as catalytic accesses to enantiomerically enriched chiral building blocks in organic syntheses.[9] With the exception of chemoenzymatic Suzuki sequences by Gröger,[10] and a very recent chemoenzymatic CuAAC by Gotor,[11] the one-pot combination of enzymes and transition metal catalysts is dominated by dynamic kinetic resolution as an important tool in asymmetric synthesis.[12] As an alternative a chemoenzymatic continuous flow process has just recently become important.[13]

Chemoenzymatic syntheses of azides and their applicability in other reactions have been reported[14] one-pot multicomponent enzyme-CuAAC sequences have remained unexplored to date. Inspired by the idea to concatenate several catalytic events in a one-pot process in the sense of sequential, consecutive, domino or tandem catalysis,[15] we set out to combine lipase-catalyzed aminolysis of methyl esters with propargyl amine to be consecutively transformed via CuAAC click reaction in a one-pot fashion. Here we report the design of a novel three-component chemoenzymatic synthesis of amide ligated 1,2,3-triazoles.

2. Results and discussion

It was already shown that lipases, which are excellent esterification and transesterification catalysts, could also catalyze amidation reactions in the sense of ammonolysis or aminolysis.[16-18] However, propargyl amine containing an alkynyl moiety for further functionalization has never been applied in lipase catalyzed aminolyses of carboxylic esters so far. As a model reaction, we chose the aminolysis of methyl *p*-methoxy dihydrocinnamate (**1a**) with propargyl amine (**2**) furnishing the propargyl amide **3a** (Scheme 1, Table 1). A quick screening for a suitable solvent system revealed that methyl *t*-butyl ether (MTBE) as a solvent with a log *P* value of 1.49[19] displayed considerable conversion within 30 min whereas other more hydrophobic or more hydrophilic solvents were less suited. A screening of six commercially available lipases revealed that only CAL-B (*Candida antarctica* lipase B) immobilized on immobead® 150 or on an acrylic resin (Novozyme® 435) was able to catalyze the model amidation of propargyl amine while the other lipases failed. However, the reaction temperature had to be set between 40 to 45 °C to observe conversion of the substrates (Table 1, entries 2 and 4). Indeed Novozyme® 435 led to full conversion within half of the reaction time (Table 1, entry 4) in comparison to CAL B immobilized immobead® 150 (Table 1, entry 2) and, therefore former was applied as a suitable CAL B source for all further methodological studies.



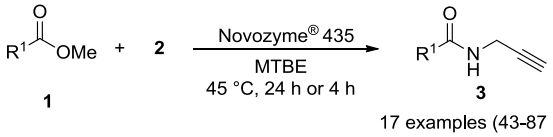
Scheme 1. CAL-B catalyzed aminolysis of methyl p-methoxy dihydrocinnamate (**1a**) with propargyl amine (**2**).

Table 1. Screening of conditions for the CAL-B catalyzed aminolysis of *p*-methoxy dihydro cinnamate (**1a**) with propargyl amine (**2**).[a]

Entry	CAL-B	*T* [°C]	*t* [h]	Yield of amide **3a** [%]
1	CAL-B immobilized on immobead® 150	21	48	n. i.[b]
2	CAL-B immobilized on immobead® 150	45	48	68
3	Novozyme® 435[c]	21	24	n. i.[b]
4	**Novozyme® 435[c]**	**45**	**24**	**67**

[a]A molar ratio of 1.2 for **1a**/**2** was chosen to achieve full conversion. [b]Not isolated. [c]CAL B immobilized on an acrylic resin.

With these optimized conditions in hand, the scope of suitable methyl carboxylates **1** furnishing the corresponding propargyl amides **3** was tested on a preparative scale (Scheme 2, Table 2).



Scheme 2. CAL-B catalyzed aminolysis of methyl carboxylates **1** with propargyl amine (**2**) (Reaction Conditions: c_0(**1**) = 0.6 mmol/mL, c_0(**2**) = 0.5 mmol/mL, Novozyme® 450 (50 % w/w with respect to **1**), 2.0 mL of MTBE, 45 °C, shaker @ 290 rpm).

Table 2. Propargyl amides **3** synthesized by CAL-B catalysis.[a]

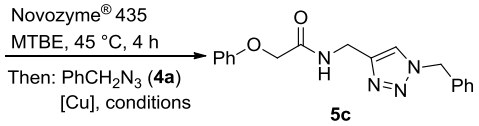
Entry	Methyl ester **1**	Propargyl amide **3** (yield after isolation)
1	R^1 = *p*-$MeOC_6H_4CH_2CH_2$ (**1a**)	**3a** (68%)[a]
2	R^1 = $PhCH_2CH_2$ (**1b**)	**3b** (62%)[a]
3	R^1 = $PhOCH_2$ (**1c**)	**3c** (87%)[b]
4	R^1 = $PhCH_2OCH_2$ (**1d**)	**3d** (86%)[b]
5	R^1 = $PhSCH_2$ (**1e**)	**3e** (77%)[b]
6	R^1 = $PhCH_2SCH_2$ (**1f**)	**3f** (82%)[b]
7	R^1 = $PhNHCH_2$ (**1g**)	**3g** (81%)[b]
8	R^1 = 2-thienyl (**1h**)	**3h** (77%)[a]
9	R^1 = 2-furyl (**1i**)	**3i** (71%)[a]
10	R^1 = PhC≡C (**1j**)	**3j** (80%)[a]
11	R^1 = *p*-$(MeO_2CCH_2CH_2)C_6H_4OCH_2$ (**1k**)	**3k** (80%)[b]
12	R^1 = (*R*)-$H_3CCH(NHCOCF_3)$ (**1l**)	**3l** (80%)[a]
13	R^1 = (*R*)-$H_3CCH(NHCbz)$ (**1m**)	**3m** (82%)[b]
14	R^1 = (*S*)-$H_3CCH(NHCbz)$ (**1n**)	**3n** (87%)[b]
15	R^1 = (*S*)-$HOCH_2CCH(NHCbz)$ (**1o**)	**3o** (43%)[b]
16	R^1 = (*S*)-*N*-Cbz-pyrrolidin-2-yl (**1p**)	**3p** (68%)[a]
17	R^1 = $(CH_2)_5NCH_2$ (**1q**)	**3q** (70%)[b]

[a]Reaction time of 24 h to complete conversion. [b]Reaction time of 4 h to complete conversion. Cbz: carboxybenzyl

While methyl esters **1** lacking an α-heteroatom substituent (Table 2, entries 1, 2, and 8-10) have to be reacted for 24 h at 45 °C, methyl esters containing oxygen atoms in the α-position, as already previously observed for CAL-B catalyzed amidations,[3] displayed complete conversion already after 4 h. In addition, other heteroatoms in α-position such as sulfur (Table 2, entries 5 and 6) and nitrogen (Table 2, entries 7, and 13-17) are transformed with comparable rates.

Interestingly, the α-heteroatom substitution can nicely be exploited in the regioselective transformation of the diester **1k** to the exclusive formation of product **3k** (Table 2, entry 11) in very good yield. Amino acid methyl esters with Cbz (carboxylbenzyl) as *N*-protection group can be efficiently employed (Table 2, entries 14-17). Lipases, unlike proteases, do not possess amidase activity and, therefore, lipases can occasionally act as catalysts for peptide syntheses.[20] Although, the synthesis of a β-dipeptide has been reported using CAL-A as an acylation catalyst for β-amino esters,[21] CAL-B has not previously been employed as an enzyme of choice for acylating amino acids to the best of our knowledge.

As model reaction for the catenation of the Cu(I) catalyzed click reaction in a one-pot fashion, the CAL-B catalyzed aminolysis of methyl ester **1c** with propargyl amine (**2**) furnishing the corresponding propargyl amide **3c** and its subsequent Cu-catalyzed alkyne-azide cycloaddition with benzyl azide (**4a**) as a substrate to give the triazole **5c** was chosen (Scheme 3, Table 3).



Scheme 3. Model reaction for the optimization of the Cu-AAC step in the chemoenzymatic one-pot sequence furnishing propargyl amide **5a**.

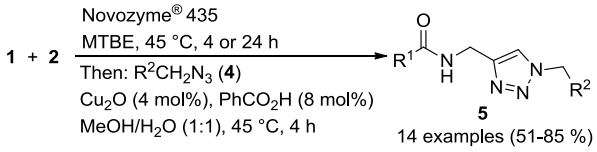
Whereas the classical Medal-Sharpless system, i.e. $CuSO_4 \cdot 5\ H_2O$ and sodium ascorbate, in various added solvent systems gave only moderate yields (Table 3, entries 1-6), even in added dichloromethane,[22] the addition of *L*-proline as a ligand[23] proofed to accelerate the reaction and led to higher isolated yields (Table 3, entries 9-11). However, even simpler than cupric sulfate, cupric acetate (Table 3, entry 7),[24] and cuprous iodide (Table 3, entry 8), and yet comparably efficient turned out to be Cu_2O as direct Cu(I) source in the presence of benzoic acid as a bidentate Cu(I) stabilizing ligand (Table 3, entries 12 and 13).[25]

Table 3. Screening of conditions for the Cu-catalyzed click step in the chemoenzymatic aminolysis-azide addition sequence of methyl α-phenoxy acetate (**1c**) with propargyl amine (**2**) and benzyl azide (**4a**).[a]

Entry	Cu catalyst	Na ascorbate [mol%]	Ligand	Base	Solvent	*T* [°C]	*t* [h]	Yield of triazole **5c** [%]
1	$CuSO_4 \cdot 5\ H_2O$[b]	20	-	-	THF/H_2O (2:1)	21	48	35
2	$CuSO_4 \cdot 5\ H_2O$[b]	20	-	-	$EtOH/H_2O$ (1:1)	21	24	52
3	$CuSO_4 \cdot 5\ H_2O$[c]	20	-	Na_2CO_3[d]	$EtOH/H_2O$ (1:1)	21	24	42
4	$CuSO_4 \cdot 5\ H_2O$[c]	20	-	Na_2CO_3[d]	$EtOH/H_2O$ (2:1)	21	24	38
5	$CuSO_4 \cdot 5\ H_2O$[b]	15	-	-	CH_2Cl_2/H_2O (1:1)	21	48	60
6	$CuSO_4 \cdot 5\ H_2O$[b]	15	-	-	CH_2Cl_2/H_2O (1:1)	45	24	63
7	$Cu(OAc)_2 \cdot H_2O$[e]	6	-	-	$MeCN/H_2O$ (1:1)	21	42	72
8	CuI[f]	-	ethylenediamine[g]	$EtNiPr_2$[h]	THF	21	24	61
9	$CuSO_4 \cdot 5\ H_2O$[b]	20	*L*-proline[i]	Na_2CO_3[d]	$MeOH/H_2O$ (1:1)	21	24	61
10	$CuSO_4 \cdot 5\ H_2O$[b]	20	*L*-proline[i]	Na_2CO_3[d]	$MeOH/H_2O$ (1:1)	45	19	85
11	$CuSO_4 \cdot 5\ H_2O$[b]	20	*L*-proline[i]	Na_2CO_3[d]	CH_2Cl_2/H_2O (1:1)	45	19	82
12	Cu_2O[c]	-	benzoic acid[j]	-	H_2O	21	8	61
13	**Cu_2O[c]**	-	**benzoic acid[j]**	-	**H_2O**	**45**	**4**	83

[a]The reaction conditions for the CAL-B catalyzed aminolysis was chosen as in Scheme 2. [b]5 mol% of the catalyst. [c]4 mol% of the catalyst. [d]20 mol% of the base. [e]6 mol% of the catalyst. [f]10 mol% of the catalyst. [g]100 mol% of the ligand. [h]100 mol% of the base. [i]20 mol% of the ligand. [j]8 mol% of the ligand.

Therefore, this straightforward copper catalyst system was employed to scout the scope of the consecutive three-component chemoenzymatic synthesis of the amido methylsubstituted 1,2,3-triazoles **5** on a preparative scale (Scheme 4, Table 4).



Scheme 4. Consecutive three-component chemoenzymatic synthesis of the amido methylsubstituted 1,2,3-triazoles **5**.

Table 4. Amido methylsubstituted 1,2,3-triazoles **5** synthesized by CAL B catalysis.

Entry	Methyl ester **1**	Azide **3**	1,2,3-Triazoles **5** (yield after isolation)
1	R^1 = *p*-$MeOC_6H_4CH_2CH_2$ (**1a**)	R^2 = Ph (**3a**)	**5a** (71%)[a]
2	R^1 = $PhCH_2CH_2$ (**1b**)	**3a**	**5b** (61%)[a]
3	R^1 = $PhOCH_2$ (**1c**)	**3a**	**5c** (83%)[b]
4	R^1 = $PhCH_2OCH_2$ (**1d**)	**3a**	**5d** (70%)[b]
5	R^1 = $PhSCH_2$ (**1e**)	**3a**	**5e** (74%)[b]
6	R^1 = $PhNHCH_2$ (**1g**)	**3a**	**5f** (85%)[b]
7	R^1 = 2-furyl (**1i**)	**3a**	**5g** (68%)[a]
8	R^1 = PhC≡C (**1j**)	**3a**	**5h** (71%)[a]
9	R^1 = *p*-$(MeO_2CCH_2CH_2)C_6H_4OCH_2$ (**1k**)	**3a**	**5i** (51%)[b]
10	R^1 = (*R*)-$H_3CCH(NHCbz)$ (**1m**)	**3a**	**5j** (73%)[b]
11	R^1 = (*S*)-$H_3CCH(NHCbz)$ (**1n**)	**3a**	**5k** (70%)[b]
12	R^1 = $PhSCH_2$ (**1e**)	R^2 = PhS (**3b**)	**5l** (59%)[b]
13	R^1 = $PhNHCH_2$ (**1g**)	**3b**	**5m** (78%)[b]
14	R^1 = 2-furyl (**1i**)	**3b**	**5n** (85%)[a]

[a]Reaction time of 24 h of the aminolysis. [b]Reaction time of 4 h of the aminolysis. Cbz: carboxybenzyl

This novel chemoenzymatic multicomponent synthesis of especially decorated 1,2,3-triazoles combines the mild reaction conditions of the CAL-B catalyzed propargyl aminolysis of methyl esters and the efficient Medal-Sharpless Cu-AAC triazole synthesis with a high level of functional group tolerance.

The regio- and chemoselective click reaction easily allows distinguishing between terminal and internal triple bonds as demonstrated by the synthesis of compound **5h**, and although the alkynoate is even activated towards the thermal [3+2] cycloaddition, the click reaction proceeds faster. Other interesting showcases are the efficient formation of the compounds **5j** and **5k** derived from Cbz-protected *D*- and *L*-alanine, respectively.

3. Conclusion

All this accounts for a suitable application of this enzyme-metal catalyzed methodology for the application to more sophisticated peptides and azides as substrates for the efficient generation of peptidomimetics in a one-pot fashion. Additional studies directed to expand and to develop further chemoenzymatic sequences with this reactivity principle, are currently underway.

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Supplementary Material

Electronic Supplementary Information (ESI) available.