Title: One-pot chemoenzymatic synthesis of chiral disubstituted 1,2,3-triazoles in aqueous media

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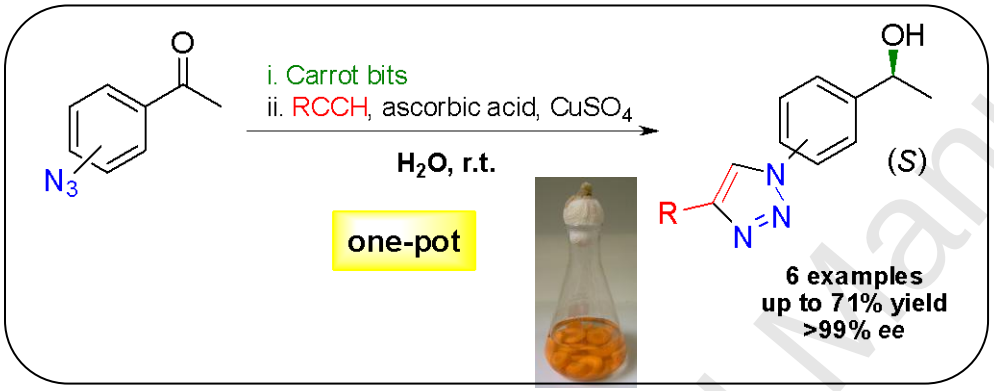

HIGHLIGHTS

- 1,3-dipolar cycloaddition reaction and bioreduction with carrot bits in one-pot.
- Excellent enantiomeric excesses were obtained for all reactions (>99%).
- Only water as solvent was needed for all reactions.
- Cheap catalysts were employed.

One-pot chemoenzymatic synthesis of chiral disubstituted 1,2,3-triazoles in aqueous media

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ABSTRACT: A one-pot, two-step procedure combining 1,3-dipolar cycloaddition and an enantioselective reduction mediated by *Daucus carota* (carrot root) is described. The synthesis was accomplished by first employing the biocatalyst followed by a "click" reaction under very mild conditions to yield the corresponding chiral disubstituted 1,2,3-triazoles.

KEYWORDS: *Daucus carota*, Biocatalysis, Click chemistry, Water chemistry.

1. Introduction

In organic chemistry, the development of one-pot multistep synthetic methods deserves attention because it minimizes the time and cost of complex molecule synthesis. This continuously challenging area can be more powerful if we consider sustainable aspects.[1] The creation of methods with all catalytic steps (Tandem Catalysis)[2] is one example. In addition to sustainability, aspects such as the simplicity and efficiency of the method and the usefulness of the product determine the potential and importance of the synthetic method and therefore must be also considered.

The "click" chemistry concept brings together a universe of reliable, quick and highly selective reactions.[3] The most recognized is the copper(I)-catalyzed 1,3-dipolar cycloaddition of azides and alkynes to form 1,4-disubstituted-1,2,3-triazoles.[4] Given the ease in achieving these products, a growing interest from many chemical fields in this type of compound has been noted.[5] As such, the range of applications of 1,2,3-triazoles involves many chemical fields, including drug discovery,[6] medicinal[7] and coordination chemistry,[8] chemosensors,[9] material and polymer chemistry[10] and many others.

Another interesting and emerging synthetic method is the enzymatic reduction of prochiral ketones using pieces of *Daucus carota* (carrot root). Although evidence for

endophytic microorganisms being the source of activity has been reported,[11] the use of the plant tissue is cheaper and easier to handle. Additionally, this biocatalyst often offers high levels of enantioselectivity and the reaction is carried out under milder conditions and has easier work-up and eco-friendly procedures in comparison with other catalytic systems.[12] Acetophenones, α-azido aryl ketones, β-ketoesters, aliphatic acyclic and cyclic ketones were converted to their corresponding optically active secondary alcohols using this method.[13] This achievement is significant because chiral alcohols are important intermediates for the synthesis of a vast range of compounds, including fragrances, flavors and chiral auxiliaries.

In this contribution, we report a tandem catalysis protocol based on the combination of chemical and enzymatic catalysis[14] for the preparation of chiral disubstituted 1,2,3-triazoles from azidoacetophenones in water.

2. Experimental

2.1. General Methods

All reagents and chemicals were purchased from Sigma–Aldrich and used directly without further purification. Solvents (reagent grade) were used for extraction and flash chromatography. The solvent compositions reported for all chromatographic separations are on a volume/volume (v/v) basis. ^{1}H NMR spectra were recorded at either 300 or 500 MHz and are reported in parts per million (ppm) on the δ scale relative to tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were recorded at either 75 or 125 MHz and are reported in parts per million (ppm) on the δ scale relative to $CDCl_3$ (δ 77.00). High-resolution mass spectrometry (HRMS) data were recorded on a MicroTOF instrument (Bruker Daltonics) with ion mass/charge (m/z) ratios as values in atomic mass units. Optical rotation values were measured on a Perkin-Elmer Polarimeter. The FT-IR spectra were recorded with a Bomem MB100 instrument in the wavenumber range 4,000 cm^{-1} to 400 cm^{-1}. GC/MS was acquired on a GC-17A instrument (Shimadzu) equipped with a GCMS-QP5050A MS detector operating at 70 eV. All melting points were recorded on a Büchi Melting Point B-540 melting point apparatus. Chiral GC-FID analyses were recorded on a GC-17A instrument (Shimadzu) with a Chirasil-Dex CB-β-cyclodextrin (25 m x 0.25 mm) column using H_2 as carrier gas. The enantiomeric excess values of the samples of alcohol **5** and **6** were determined

according to the following conditions: (i) compound **5**: rate 1 ◦C/min; oven 100–180 °C (30 min); retention time [(*R*)-isomer: 12.0 min; (*S*)-isomer: 12.8 min].(ii) compound **6**: : rate 1 ◦C/min; oven 100–180 °C (30 min); retention time [(*R*)-isomer: 9.6 min; (*S*)-isomer: 10.1 min].

General procedure for the synthesis of **3**, **4**, **5** and **6** and respective analytical data are specified in Supplementary information.

2.2. General procedure for biocatalytic reduction of azidoacetophenones mediated by *Daucus carota* bits

Compounds **(*S*)-(5)** and **(*S*)-(6)** were prepared from the corresponding ketone precursors following the procedure reported previously [15].

2.2.1. (*S*)-3-azido-α-methyl-benzenemethanol (*S*)-(5): 0.494g**, y**ield 53%. : -51° (*c.* 3.1, $CHCl_3$).

2.2.2. (*S*)-4-azido-α-methyl-benzenemethanol (*S*)-(6): 0.410g, yield 44%. : -12º (*c.* 0.7, $CHCl_3$).

2.3. Cyclization of (6) with phenylacetylene

To a solution of compound (*S*)-(**6**) (0.252 g, 1.55 mmol) and phenylacetylene (0.158 g, 1.55 mmol) in *n*-butanol and water (1:1) was added 0.148 g (0.93 mmol, 0.6 equiv.) of copper sulfate ($CuSO_4$) and 0.327 g (1.86 mmol) of ascorbic acid. The mixture was stirred at room temperature until complete conversion, as indicated by TLC. After extraction with dichloromethane (3 x 50 mL), the organic phases were combined and dried over $MgSO_4$. The solvent was removed under vacuum, and a brown solid was obtained by crystallization as compound (*S*)-(**12).**

2.3.1. (*S*)-1-(4-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyl)ethanol (*S*)-(12): Yellow solid, 0.399 g, yield 97%. mp: 156 ^oC. ^1H NMR (300 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.92 (d, *J* = 6.0 Hz, 2H), 7.78 (d, *J* = 9.0 Hz, 2H), 7.56 (d, *J* = 9.0 Hz, 2H), 7.47 (t, *J* = 6.0 Hz, 2H), 7.38 (t, *J* = 6.0 Hz, 1H), 5.01 (q, *J* = 6.0 Hz, 1H), 1.55 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ 148.3, 146.8, 136.1, 130.2, 128.9, 128.4, 126.7, 125.8, 120.5, 117.6, 69.5, 25.4. IR (cm^{-1}, KBr): 3409, 2921, 1741, 1594, 1446, 1255, 1087. GCMS (70 eV,

EI): *m/z* (%) 237 (21) $[M-28]^+$, 222 (42), 194 (31), 193 (100), 165 (16), 116 (28). HRMS: m/z calcd for $C_{16}H_{16}N_3O$ $[M+H]^+$ 266.1293, found 266.1296 $[M+1]^+$. : -20° (*c*. 0.82, $CHCl_3$).

2.4. General Procedure for one-pot synthesis of chiral 1,2,3-Triazoles

To a 125 mL Erlenmeyer flask was added 40 mL of distilled water, 10 g of fresh carrot (cut into small, thin slices, 5 mm) and 50 mg (0.72 mmol) of azidoacetophenone. The mixture was incubated in an orbital shaker (200 rpm) at room temperature for 48 h. Alkyne (0.72 mmol, 1 equiv.), $CuSO_4$ (0.064 g, 0.4 mmol) and ascorbic acid (0.176 g, 0.9 mmol) were then added to the Erlenmeyer Flask, and the reaction was stirred in an orbital shaker and monitored by TLC. After completion, the suspension was filtered off, and the carrot root was washed three times with water (3 x 15 mL) and dichloromethane (3 x 20 mL). Filtrates were then extracted with more dichloromethane (3 x 125 mL). The organic phases were combined, dried (Na_2SO_4) and then evaporated under vacuum. The final products were purified by flash chromatography when necessary.

2.4.1. (*S*)-1-(3-(4-pentyl-1H-1,2,3-triazol-1-yl)phenyl)ethanol (7): Eluent: EtOAc/hexane (2:3), pale yellow oil, 0.106 g, yield 57%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (t, *J* = 1.8 Hz, 1H), 7.73 (s, 1H), 7.63 (dt, *J* = 2.1, 2.1 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 5.01 (q, *J* = 6.3 Hz, 1H), 2.80 (t, *J* = 7.5 Hz, 2H), 1.74 (qn, *J* = 7.5 Hz, 2H), 1.56~1.31 (m, 7H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ 148.0, 130.2, 129.7, 125.4, 119.3, 118.9, 117.4, 69.8, 31.4, 29.1, 27.2, 26.6, 25.4, 22.4, 14.0. HRMS: m/z calcd for $C_{15}H_{22}N_3O$ $[M+H]^+$ 260.1763, found 260.1750. -5° (*c* 1.4, $CHCl_3$). IR (cm^{-1}, KBr): 3363, 2919, 1741,1612, 1454, 1226, 1047.

2.4.2. (*S*)-1-(4-(4-pentyl-1H-1,2,3-triazol-1-yl)phenyl)ethanol (8): Eluent: EtOAc/hexane (2:3), orange oil, 0.127 g, yield 68%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.5 Hz, 3H), 7.45 (d, *J* = 5.5 Hz, 2H), 4.92 (m, 1H), 2.72 (t, *J* = 8 Hz, 2H), 1.66 (qn, J = 1.0 Hz, 2H), 1.46 (d, *J* = 6.5 Hz, 3H), 1.30 (qn, *J* = 8.5 Hz, 4H), 0.84 (t, *J* = 1.5 Hz, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ 146.3, 126.7, 120.5, 31.5, 25.6, 22.4, 14.0.

HRMS: m/z calcd for $C_{15}H_{22}N_3O$ $[M+H]^+$ 260.1763, found 260.1750. : -13° (*c* 0.63, $CHCl_3$). IR (cm^{-1}, KBr): 3367, 2929, 1743, 1592, 1452, 1230, 1049.

2.4.3. (*S*)-1-(3-(4-(hydroxymethyl)-1H-1,2,3-triazol-1-yl)phenyl)ethanol (9): Eluent: EtOAc/hexane (4:1), orange oil, 0.039 g, yield 25%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.78 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.45 (d, 7.0 Hz, 1H), 5.01 (q, *J* = 6.5 Hz, 1H), 4.89 (s, 2H), 1.55 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ 175.5, 148.1, 136.9, 129.6, 127.5, 125.9,119.2, 117.5, 69.5, 55.9, 22.6. HRMS: m/z calcd for $C_{11}H_{14}N_3O_2$ $[M+H]^+$ 220.1086, found 220.1072. -11° (*c* 0.4, $CHCl_3$). IR (cm^{-1}, KBr): 3370, 2921, 2107, 1614, 1452, 1220, 1058.

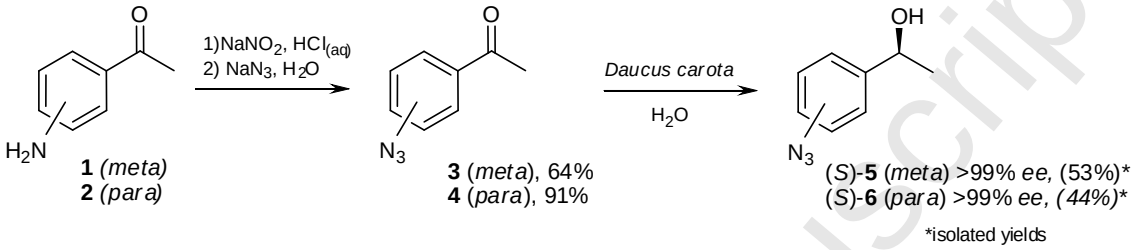
2.4.4. (*S*)-1-(4-(4-(hydroxymethyl)-1H-1,2,3-triazol-1-yl)phenyl)ethanol (10): Eluent: EtOAc/hexane (2:3), orange oil, 0.111 g, yield 71%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.63 (d, *J* = 9.0 Hz, 2H), 7.47 (d, *J* = 9.5 Hz, 2H), 4.92 (q, *J* = 6.5 Hz, 1H), 4.81 (s, 2H), 1.47 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ 148.2, 146.8, 136.1, 126.9, 120.7, 129.9, 69.7, 56.6, 25.4. HRMS: m/z calcd for $C_{11}H_{14}N_3O_2$ $[M+H]^+$ 220.1086, found 220.1071. -8º (c 0.8, $CHCl_3$). IR (cm^{-1}, KBr): 3409, 2921, 1741, 1594, 1446, 1255, 1087.

2.4.5. (*S*)-1-(3-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyl)ethanol (11): Eluent: EtOAc/hexane (1:4), orange oil, 0.097 g, yield 51%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.77 (s, 1H), 7.64 (d, *J* = 6.5 Hz, 1H), 7.45 (t, *J* = 10.0 Hz, 1H), 7.41 (m, 3H), 7.31 (t, *J* = 6.0 Hz, 1H), 4.97 (d, *J* = 6.0 Hz, 1H), 1.5 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ 148.1, 137.2, 130.2, 129.9, 128.9, 128.4, 125.9, 125.7, 119.4, 117.6, 117.5, 69.8, 25.58. HRMS: m/z calcd for $C_{16}H_{16}N_3O$ $[M+H]^+$ 266.1293, found 266.1295. : -15° (*c* 0.67, $CDCl_3$). IR (cm^{-1}, KBr): 3407, 2924, 2102, 1587, 1449, 1260, 1070.

2.4.6. (*S*)-1-(4-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyl)ethanol (*S*)-(12): Yellow solid, 0.094 g, yield 51%. The analytical data of compound (**12**) was consistent with those obtained for the compound isolated from the step-wise synthesis.

3. Results and Discussion

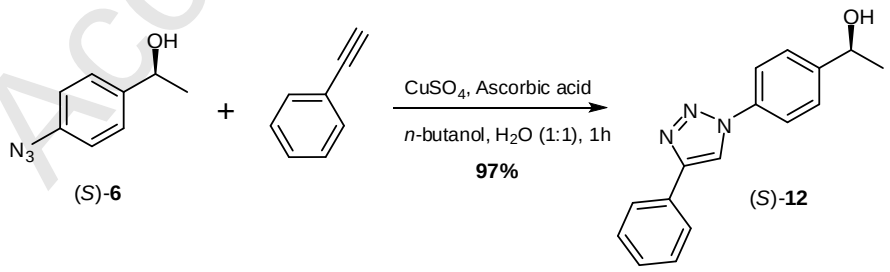
The preparation of azidoacetophenones is straightforward and can be achieved simply by diazotation of the amino group followed by substitution with sodium azide.[16] Thus, starting from commercially available *meta*- and *para*-substituted aminoacetophenones, azides **3** and **4** were obtained (Scheme 1).



Scheme 1. Synthesis and bioreduction of azidoacetophenones **3** and **4**.

To verify the influence of the azido group, the prepared azidoacetophenones **3** and **4** were first reacted with carrot bits in water (Scheme 1). The progress of the reaction was followed by TLC analysis, and the corresponding secondary alcohols **5** and **6** were obtained in the *S* configuration[17],[18] with high enantioselectivity (>99% ee) and moderate isolated yield. As expected, the enantioselectivity agreed with Prelog´s rule.[19]

To ensure the success and the regioselectivity of the cycloaddition reaction, compound **6** was reacted following the cyclization protocol with phenylacetylene. In this control experiment, the chiral disubstituted 1,2,3-triazole **12** was isolated as a single product (Scheme 2).



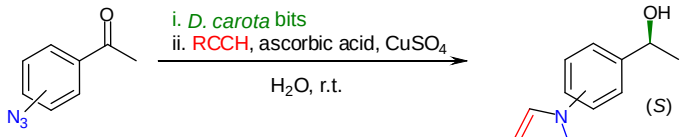
Scheme 2. Cycloaddition of phenylacetylene with compound **6**.

Based on the success of the two reactions and considering the use of aqueous media as solvent in both cases, we investigated the possibility of performing these reactions in a one-pot protocol. Initial attempts involving the addition of all reagents

(compound **6** and phenylacetylene) in a single step showed that the cyclization reaction proceeded faster than the bioreduction reaction. Because of the low solubility of the acetophenones containing the 1,2,3-triazole core in water, the desired chiral alcohol **12** was not obtained. This result indicated the synthesis should be performed in a stepwise procedure.

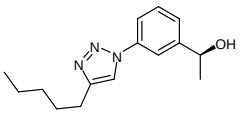
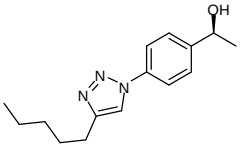
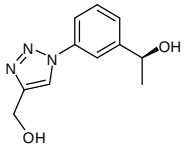
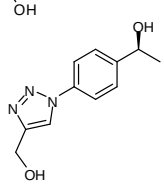
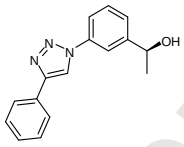
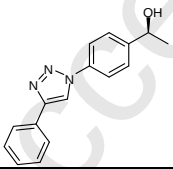
As expected, when the enzymatic reduction of azidoacetophenone **6** was performed prior to the copper-catalyzed reaction, we obtained the corresponding chiral disubstituted 1,2,3-triazole **12** as a single product. This strategy was successfully applied to three different alkynes, 1-heptyne, phenylacetylene and propargyl alcohol, reacting with *para*- and *meta*-azidoacetophenones (Scheme 3, Table 1).

Table 1. One-pot synthesis of chiral 1,2,3-triazoles from azidoacetophenones **3** and **4a**.



3 (*meta*)
4 (*para*)

7 (*meta*, R= C_5H_{11})
8 (*para*, R= C_5H_{11})
9 (*meta*, R= CH_2OH)
10 (*para*, R= CH_2OH)
11 (*meta*, R= Ph)
12 (*para*, R= Ph)

Compound	Product	Time (days)	% yield[b]	$[\alpha]_D^{20}$	% ee[c]	Config.[d]
7		6	57	-5 (c 1.4, $CDCl_3$)	>99%	*S*
8		6	68	-13 (c 0.63, $CDCl_3$)	>99%	*S*
9		4	25	-11 (c 0.4, $CDCl_3$)	>99%	*S*
10		5	71	-8 (c 0.8, $CDCl_3$)	>99%	*S*
11		6	51	-15 (c 0.67, $CDCl_3$)	>99%	*S*
12		7	51	-20 (c 0.82, $CDCl_3$)	>99%	*S*

a. Reaction conditions: azidoacetophenone (0.7 mmol), carrot (10g), water (40 ml) at room temperature for 48 h, followed by alkyne (0.7 mmol), $CuSO_4$ (0.42 mmol), and ascorbic acid (1 mmol) until completion (analyzed by TLC). **b.** Isolated Yield. **c.** The enantiomeric excess was inferred from the chiral GC analysis of (S)-1-(3-azidophenyl)ethanol and (S)-1-(4-azidophenyl)ethanol obtained from the bioreduction step. **d**. The absolute configurations were inferred from (S)-1-(3-azidophenyl)ethanol and (S)-1-(4-azidophenyl)ethanol obtained from the bioreduction step (see refs. 15 and 16).

An examination of the results in Table 1 revealed that there was no influence of the position of the azide group or the R group of the alkyne on the reaction. The only drawback was observed with the purification of compound **9**, which resulted in a low yield. Interestingly, when the azidoacetophenone was fully converted to the alcohol and

submitted to cyclization, in most cases the final product precipitated as a single compound. However, recrystallization attempts were not successful.

4. Conclusions

In summary, a useful method for the chemoenzymatic synthesis of chiral disubstituted 1,2,3-triazoles is presented. This procedure consists of the use of cheap, versatile and readily available reagents (water as solvent and carrot bits as biocatalysts). Moreover, the bioreduction and Cu-catalyzed Hüisgen 1,3-dipolar cycloaddition can be achieved in a one-pot sequence to afford the title compounds in moderate yields. Investigations into improving the yields, the use of more sophisticated terminal alkynes and biological activities of the products are ongoing.

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