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ARTICLE

Glycerol conversion to high-value chemicals: Implication of unnatural α-amino acids syntheses using natural resources

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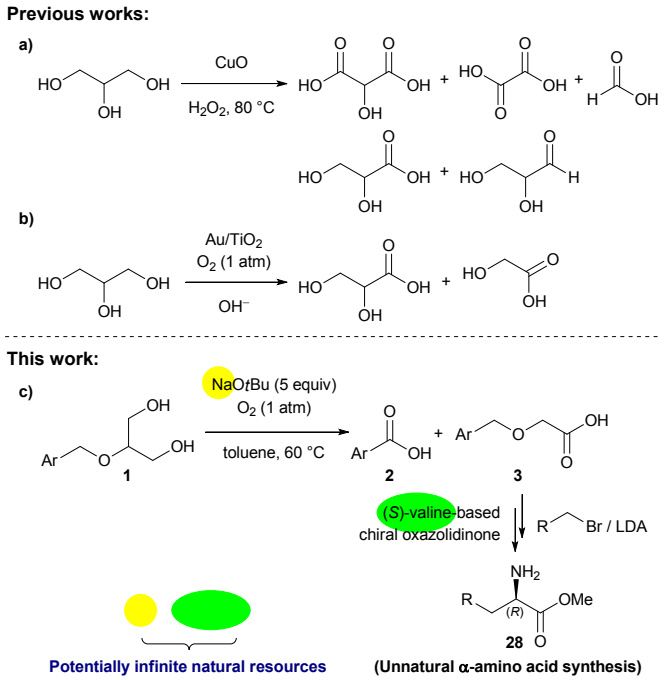
Glycerol derivatives are an important class of compounds, which have great applications as basic structural building blocks in organic synthesis. *O*-Benzylglycerol was oxidised to produce a high-value compound in high yield using a NaO*t*Bu-O_2 system. Furthermore, the synthetic utility of the resulting product was demonstrated by its transformation into unnatural α-amino acids, thus showing the valorisation of glycerol biomass.

Introduction

Glycerol, known as glycerine, is a triol that can be generated as a by-product during the synthesis of biodiesel from vegetable oils, such as soybean and sunflower oils.[1] Nowadays, there have been made efforts to synthesise renewable materials utilising biomass derivatives containing overproduced glycerol in industrial research.[2] Glycerol is no longer considered a by-product of biodiesel production and is recognised as a privileged scaffold due to its potential as a high-value carbon and oxygen source and alternative to our gradually depleting existing natural resources. Therefore, a diverse range of organic transformations are needed for glycerol conversion.[3] *O*-Benzylglycerol (**1**), as a non-viscous glycerol derivative, is one of the most valuable synthons in a variety of applications, including solvents, cosmetics, pharmaceuticals, creams, detergents, and additives for printing inks, lubricants, and fuels.[4] To date, the most common use of glycerol and its derivatives reported in the literature is in transition-metal-catalysed oxidation reactions (Scheme 1). Research on these reactions is at an early stage and is mainly focused on synthesising various chemical feedstocks rather than controlling the selectivity of the products formed using precious transition metal catalysts (e.g., Co, Au, Cu, Pt, and Ag).[5] According to the trend shown in a previous study, bimetallic systems[6] exhibit superior selectivity during the selective oxidation of glycerol when compared to monometallic systems[7] (Scheme 1a and 1b).[8,9]

Herein, we describe a transition-metal-free chemoselective oxidative dehomologation of 2-*O*-benzylglycerol (Ar = Ph, **1**) to give aromatic carboxylic acid (**2**)[10] and 2-(aryloxy)acetic acid (**3**)[11], which represents an unprecedented product pattern, under an oxygen atmosphere. Further transformation of **3** to the unnatural α-amino acid **28**[12] was investigated using potentially infinite natural resources, such as sodium and (*S*)-α-amino acids, which are derived from the electrolysis of sodium chloride in seawater and common components of chiral pool from nature, respectively (Scheme 1c). Therefore, this protocol may provide an opportunity for new categories of biomass conversions using natural resources and non-depleting molecular oxygen as a terminal oxidant.



Scheme 1. Previous reports on the oxidation of glycerol using monometallic and bimetallic catalysts (**a**-**b**). Our current work on the transition-metal-free oxidative dehomologation reaction of glycerol under an O_2 atmosphere and its application to unnatural α-amino acid synthesis using a chiral auxiliary approach (**c**).

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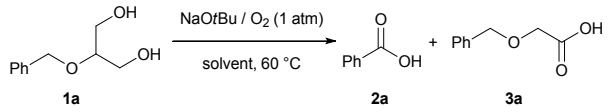
Results and discussion

We began our study by examining the transformation of two different types of *O*-benzylglycerol derivatives (**1a** and **1'a**) to high-value chemicals, such as benzoic acid **2a** and 2-(phenyloxy)acetic acid **3a** under the reaction conditions previously established for the oxidative cleavage of alcohols[13] or lignin model compounds[14] utilising a NaO*t*Bu-O_2 system (Table 1 and 2).

Table 1. Screening of the reaction parameters used for the oxidative dehomologation of 2-*O*-benzylglycerol (**1a**)[a]

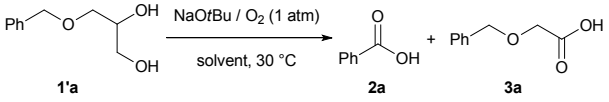


Entry	Solvent	Equiv. of NaO*t*Bu	Time (h)	Ratio of **2a**:**3a**[b]	Yield (%)[c]
1	MeOH	5	18	-	n.d
2	EtOH	5	18	-	n.d
3	*n*-BuOH	5	18	-	n.d
4	*t*-BuOH	5	18	64:36	53
5	CH_2Cl_2	5	18	>99:n.d	37
6	DMSO	5	18	86:14	28
7	THF	5	18	56:45	55
8	DMF	5	18	83:17	29
9	Toluene	3	18	55:45	29
10	Toluene	4	18	66:34	64
11	Toluene	5	18	76:24	90
12	Toluene	5	12	80:20	78
13	Toluene	5	24	78:22	86
14[d]	Toluene	5	18	72:28	69
15[e]	Toluene	5	18	75:25	80
16	-	5	18	90:10	39

[a] General conditions: **1a** (0.5 mmol), NaO*t*Bu (5 equiv), solvent (4 mL), O_2 (1 atm), 18 h, 60 °C. [b] Determined by ^{1}H NMR spectroscopy. [c] Isolated yield. [d] Reaction performed at 30 °C. [e] Reaction performed at 100 °C.

In the presence of alcoholic solvents, the target products were not detected in the reaction mixture with the exception of *t*-BuOH (Table 1, entries 1-4 and Table 2, entries 1-4). In the case of **1a**, the selectivity toward benzoic acid (**2a**) was extremely high, but the product yield was low when using CH_2Cl_2 as the reaction solvent (Table 1, entry 5). The selectivity observed between products **2a** and **3a** was low when using THF, but high in DMSO and DMF although in low yield (Table 1, entries 6-8). After screening parameters including the adjustment of NaO*t*Bu equivalents, reaction temperature, and reaction time (Table 1, entries 9-10 and 12-15), the optimal result was obtained using 5 equivalents of NaO*t*Bu in toluene at 60 °C for 18 h (Table 1, entry 11). Upon lowering the reaction temperature to 30 °C, the ratio of **2a** and **3a** was not significantly different, but the target products were obtained in low yield (Table 1, entry 14). The reaction was also investigated under solvent-free conditions, which resulted in the formation of the target products in 39% yield (Table 1, entry 16). In the case of **1'a**, the reaction was carried out in CH_2Cl_2, DMSO, THF, DMF, toluene, and THF. Among these solvents, THF gave the best results in terms of both the yield and ratio of the target products, which are the same outcomes as observed in the previous experiment using 2-*O*-benzylglycerol **1a** (Table 2, entries 5-15). After screening parameters including the adjustment of NaO*t*Bu equivalents, reaction temperature, and reaction time, the optimal conditions were found to be include **1'a** (0.5 mmol), NaO*t*Bu (5 equiv) and O_2 (1 atm) in THF at 30 °C for 18 h (Table 2, entry 11). As the reaction temperature increased, the yield of the product decreased (Table 2, entries 14 and 15). A trace amount of the target products (2% yield) was obtained when the reaction was carried out under solvent-free conditions (Table 2, entry 16).

Table 2. Screening of the reaction parameters used for the oxidative dehomologation of 1-*O*-benzylglycerol (**1'a**)[a]



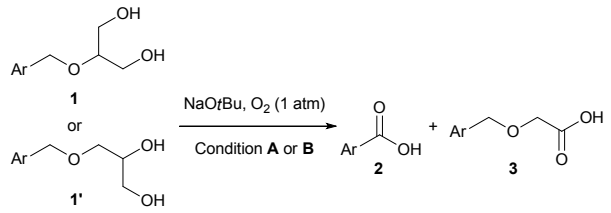
Entry	Solvent	Equiv. of NaO*t*Bu	Time (h)	Ratio of **2a**:**3a**[b]	Yield (%)[c]
1	MeOH	5	18	-	n.d
2	EtOH	5	18	-	n.d
3	*n*-BuOH	5	18	-	n.d
4	*t*-BuOH	5	18	34:66	76
5	CH_2Cl_2	5	18	61:39	75
6	DMSO	5	18	80:20	60
7	DMF	5	18	85:15	65
8	Toluene	5	18	67:33	89
9	THF	3	18	22:78	64
10	THF	4	18	71:29	85
11	THF	5	18	79:21	85
12	THF	5	12	72:28	82
13	THF	5	24	84:16	71
14[d]	THF	5	18	76:24	75
15[e]	THF	5	18	83:17	68
16	-	5	18	33:67	2

[a] General conditions: **1'a** (0.5 mmol), NaO*t*Bu (5 equiv), solvent (4 mL), O_2 (1 atm), 18 h, 30 °C. [b] Determined by ^{1}H NMR spectroscopy. [c] Isolated yield. [d] Reaction performed at 60 °C. [e] Reaction performed at 100 °C.

The substrate scope of the oxidative dehomologation of *O*-benzylglycerol (**1a** and **1'a**) was then explored under the optimal conditions and the results are summarised in Table 3. The highest yields (81-90%) were obtained with substrates **1a** and **1'a** (Table 3, entries 1 and 2). Substrates bearing electron-donating substituents on the aromatic ring gave high yields (81-83%; Table 3, entries 5 and 6). Electron-withdrawing substituents at the *para*-position (62-86%; Table 3, entries 7-12) showed better results than with substituents at the *meta*-position (20-36%; Table 3, entries 13 and 14).

Based on our previous ^{18}O-isotope labelling experiments on the oxidative cleavage reaction of alcohols[13] or direct oxidation of allylic alcohols,[15] the reaction mechanism was proposed, as shown in Scheme 2. 2-*O*-Benzylglycerol (**1a**) was oxidised to aldehyde **4** with the release of hydroperoxide anion **5** in the NaO*t*Bu-O_2 system.

Table 3. Substrate scope for the oxidation of various *O*-benzylglycerol derivatives[a]



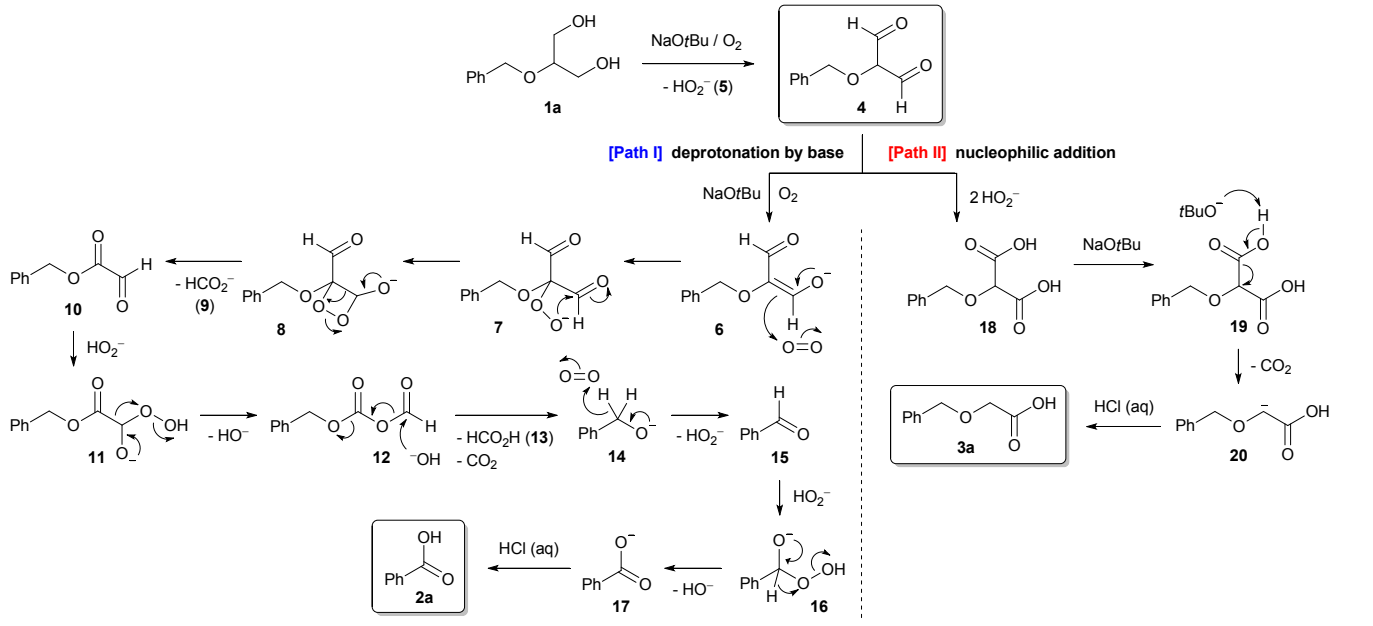
Entry	Substrate	Ar	Condition	Products (**2** and **3**)	Yields of **2**:**3** (%) [b]
1	**1a**	Ph	A	**2a** + **3a**	76:24
2	**1'a**		B		63:18
3	**1b**	β-Naphthyl	A	**2b**+ **3b**	59:8
4	**1'b**		B		57:15
5	**1c**	3-OMe-C_6H_4	A	**2c** + **3c**	70:13
6	**1'c**		B		65:16
7	**1d**	4-Cl-C_6H_4	A	**2d** + **3d**	74:12
8	**1'd**		B		64:11
9	**1e**	4-Br-C_6H_4	A	**2e** + **3e**	57:6
10	**1'e**		B		50:12
11	**1f**	4-CF_3-C_6H_4	A	**2f** + **3f**	62:17
12	**1'f**		B		63:12
13	**1g**	3-NO_2-C_6H_4	A	**2g** + **3g**	19:17
14	**1'g**		B		16:5

[a] Condition A: **1** (0.5 mmol), NaO*t*Bu (5 equiv), toluene (4 mL), O_2 (1 atm), 18 h, 60 °C; Condition B: **1'** (0.5 mmol), NaO*t*Bu (5 equiv), THF (4 mL), O_2 (1 atm), 18 h, 30 °C. [b] Isolated yield.

The next step was determined to follow either Path I or Path II. In Path I, treating aldehyde **4** with NaO*t*Bu forms nucleophilic enolate **6**, which attacks molecular oxygen to afford 1,2-dioxetan-3-olate **8** via the intramolecular nucleophilic addition of the hydroperoxyl anion to the carbonyl group.

The subsequent ring-opening reaction of **8** takes place due to ring strain to give formyl ester **10** and formate **9**. Formyl carbonate **12** may be formed as a transient intermediate by nucleophilic addition of hydroperoxide anion to aldehyde **10** followed by Baeyer-Villiger rearrangement[16] with acyl group migration. Formyl carbonate **12** may decompose to benzyl alkoxide **14** with the loss of formic acid **13** and carbon dioxide in the presence of hydroxide ion. Benzoic acid **2a** was then obtained via α-hydride transfer from **14** to molecular oxygen and Dakin-type oxidation reaction[17] of **16** followed by an acidic work-up procedure. In Path II, 2-(benzyloxy)malonic acid **18** was serendipitously isolated and confirmed using ^{1}H and ^{13}C NMR spectroscopy, which allowed a better understanding of the following reaction mechanism. Di-aldehyde **4** was oxidised to the di-carboxylic acid using 2 equivalents of hydroperoxide anion, which then formed the final target compound **3a** via the mono-decarboxylation of **19** followed by an acidic work-up procedure.

The mechanism for oxidative dehomologation of 1-*O*-benzylglycerol **1'a** was also determined using a competing reaction between the deprotonation of **4'** by NaO*t*Bu and the nucleophilic addition of **4'** with hydroperoxide anion, as shown in Scheme 2. As a result, benzoic acid **2a** and 2-(benzyloxy) acetic acid **3a**, which are the same products formed in the previous experiments using 2-*O*-benzylglycerol (**1a**), were produced (Scheme 3). Similar to Path I in Scheme 2, enolate **6'** was formed by the abstraction of the α-acidic proton in the ketone by *tert*-butoxide base. Benzyl formate **10'**, as a transient intermediate, can be generated via consecutive transformations including the nucleophilic addition of hydroperoxyl anion to the carbonyl group **7'** and ring-opening of 1,2-dioxetan-3-olate (**8'**) with the release of glyoxylate **9'**.



Scheme 2. Proposed mechanism for the oxidative dehomologation of 2-*O*-benzylglycerol **1a**.

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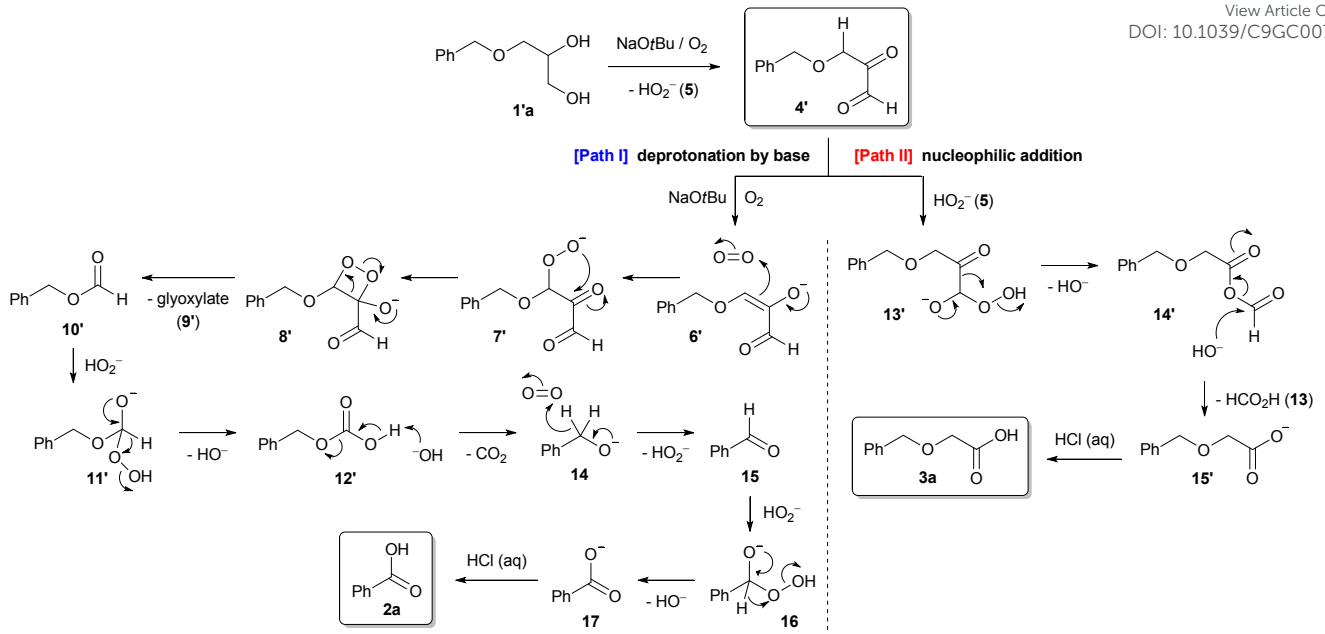
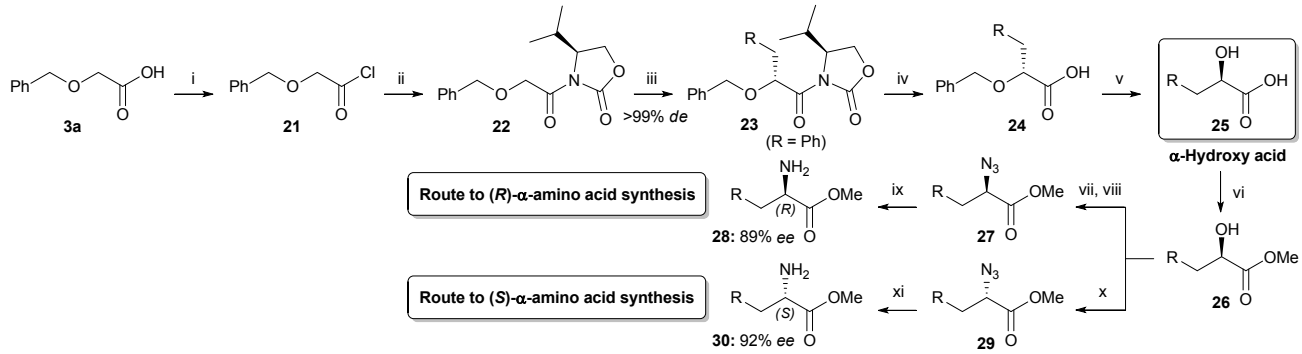


Scheme 3. Plausible mechanism for the oxidative dehomologation of 1-*O*-benzylglycerol **1'a**.

Benzyl oxide **14** can be produced after the 1,2-hydride shift of **11'** and decarboxylation of **12'**. Subsequently, the target product (**2a**) was formed via the iterative routes from **14** to **17** as described in Scheme 2. In Path II, the nucleophilic addition reaction takes place by the hydroperoxide anion **5** with more electrophilic aldehyde **4'** to give tetrahedral intermediate **13'**. *O*-Formyl ester **14'** and hydroxide ion are formed via Baeyer-Villiger rearrangement[16] with acyl group migration. Deformylation can be promoted by hydroxide ion and thus, release carboxylate **15'** and formic acid **13**. After an acidic work-up procedure, carboxylate **15'** was converted into 2-(phenyloxy)acetic acid **3a**.

Further transformation of 2-(benzyloxy) acetic acid **3a** to an unnatural α-amino acid utilising a diastereoselective alkylation reaction of a chiral metal enolate was carried out using Evans' chiral auxiliary[18], as shown in Scheme 4. Acid chloride **21** was coupled with the chiral auxiliary [(*S*)-4-isopropyloxazolidin-2-one] to give acylated derivative **22**. Reaction of the corresponding lithium enolate, which was generated from **22** using LDA at -78 °C, with benzyl bromide gave the corresponding α-alkylated adduct **23** as a single diastereomer (>99% *de*). The pure diastereomer **23** was cleaved from the chiral auxiliary upon treatment with $LiOH/H_2O_2$ (*aq*) to give the (*R*)-configured carboxylic acid **24**. The chiral oxazolidinone was recovered almost quantitatively and can be recycled (see ESI).[19] α-Hydroxy acid **25**,[20] as a versatile chiral building block and intermediate, was obtained via debenzylation of **24** using 10% Pd/C with H_2 gas. The absolute configuration of product **25** was determined by comparison of optical rotation with the literature and assigned to be (*R*)-configuration.[21] Methyl ester **26** was synthesized using a conventional Fischer esterification reaction of compound **25**. A series of stepwise transformations starting from **26** enable its elaboration into unnatural α-amino acid **28** and potential unnatural α-amino acid **30**, depending on



Scheme 4. *Reagents and conditions*: i) $SOCl_2$, CH_2Cl_2, reflux, 4 h, 99%; ii) (*S*)-4-isopropyloxazolidin-2-one, *n*-BuLi, THF, -78 °C to 0 °C, 4.5 h, 70%; iii) BnBr, LDA, THF, -78 °C to -45 °C, 3.5 h, 74%; iv) 28% H_2O_2 (*aq*), LiOH, THF, 0 °C, 1 h, 84%; v) 10% Pd/C, H_2, EtOH, rt, 12 h, 84%; vi) H_2SO_4 (*cat.*), MeOH, reflux, 3.5 h, 87%; vii) Tf_2O, pyridine, LiBr, CH_2Cl_2, $(CH_3)_2CO$, -45 °C to 0 °C, 1 h, 90%; viii) NaN_3, DMF, 40 °C, 1 h, 92%; ix) 10% Pd/C, H_2, EtOH, rt, 12 h, 78%; x) DBU, DPPA, THF, 0 °C to 40 °C , 1d, 89%; xi) 10% Pd/C, H_2, EtOH, rt, 12 h, 85%.

the R group used and the stereochemistry of the chiral secondary alcohol **26** formed via an inversion or retention step. The (*R*)-configured hydroxy group in **26** was readily converted into (*R*)-configured azido group in **27** via a double inversion of stereochemistry involving bromination [reaction conditions: Tf_2O, pyridine, LiBr, CH_2Cl_2, $(CH_3)_2CO$, -45 °C to 0 °C, 1 h][22] and azidonation [reaction conditions: NaN_3, DMF, 40 °C, 1 h][23]. Catalytic hydrogenation of **27** gave (*R*)-phenylalanine methyl ester **28** in 89% ee. The absolute configuration of (*R*)-α-amino acid **28** was established based on a comparison of its specific optical rotation {$[\alpha]_D^{20}$ -26.2° (*c* 4.0, EtOH)} with reported in the literature {$[\alpha]_D^{23}$ -25.0° (*c* 4.04, EtOH)}[24].

(*R*)-configured hydroxy group in **26** was readily converted into an (*S*)-configured azido group in **29** via a Mitsunobu inversion reaction using diphenylphosphoryl azide (DPPA) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[25] Catalytic hydrogenation of **29** using 10% Pd/C and H_2 gas, gave the potential unnatural α-amino acid **30** in 92% ee. The absolute stereochemistry of (*S*)-**30** was determined by comparison of its specific optical rotation {$[\alpha]_D^{20}$ +26.5° (*c* 4.0, EtOH)} with that previously reported {$[\alpha]_D^{23}$ +25.0° (*c* 4.04, EtOH)}[24].

Conclusions

In summary, *O*-benzylglycerol derivatives have been synthesised from glycerol, which can act as a promising carbon source from a myriad of biomass obtained from nature. These derivatives were subjected to a transition-metal-free oxidative dehomologation reaction using a NaO*t*Bu-O_2 system, leading to the two different carboxylic acid products. The use of 1-*O*-benzylglycerol enables the construction of unnatural α-amino acids utilising potentially infinite natural resources, such as sodium and (*S*)-α-amino acid, thereby contributing to a new type of glycerol valorisation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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