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Ionic liquid-promoted three-component domino reaction of propargyl alcohols, carbon dioxide and 2-aminoethanols: A thermodynamically favourable synthesis of 2-oxazolidinones

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Abstract: To circumvent the thermodynamic limitation of the synthesis of oxazolidinones starting from 2-aminoethanols and CO_2 and realize incorporation CO_2 under atmospheric pressure, a protic ionic liquid-facilitated three-component reaction of propargyl alcohols, CO_2 and 2-aminoethanols was developed to produce 2-oxazolidinones along with equal amount of α-hydroxyl ketones. The ionic liquid structure, reaction temperature and reaction time were in detail investigated. And 15 mol% [TBDH][TFE] (1,5,7-triazabicylo[4.4.0]dec-5-ene trifluoroethanol) was found to be able to synergistically activate the substrate and CO_2, thus catalyzing this cascade reaction under atmospheric CO_2 pressure. By employing this task-specific ionic liquid as sustainable catalyst, 2-aminoethanols with different substituents were successfully transformed to 2-oxazolidinones with moderate to excellent yield after 12 h at 80 °C. This three-component reaction running under atmospheric pressure proves to be a clever detour to avoid the thermodynamic issue in the synthesis of 2-oxazolidinones starting from 2-aminoethanols and CO_2.

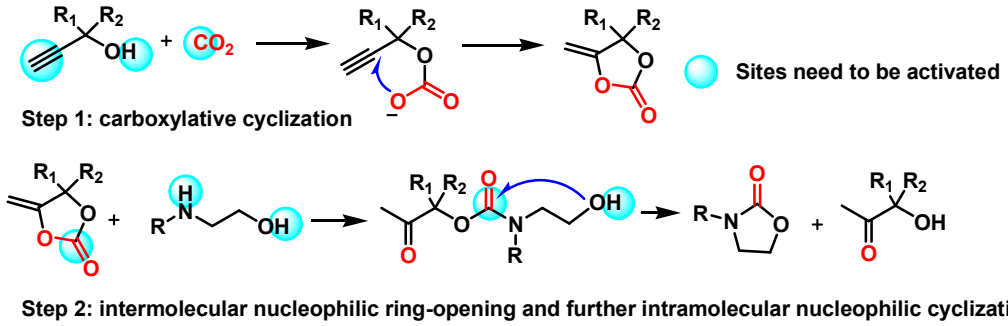
Keywords: Ionic liquid; synergistic activation; aminoethanol; 2-oxazolidinone; atmospheric CO_2; sustainable catalysis

1. Introduction

The accumulation of CO_2 in atmosphere has aroused considerable concern due to its link to the climate change; hence effective strategies are urgently needed to mitigate the increasing CO_2 buildup [1-3]. Among the various strategies, transforming CO_2 to valuable chemicals has received much attention by utilizing CO_2 as economic and nontoxic C_1 source [4, 5]. Nowadays, CO_2 has been employed in the synthesis of carboxylic acids [6-8], carbonates [9-12], carbamates [13-18], formate [19-21], methanol [21-24], ureas [25-27] and polymers [28-30] as well.

Oxazolidinones, which are in the family of carbamates, are important chiral auxiliaries in organic synthesis [31, 32] and are also common structural units in drugs [33, 34] and agrochemicals [35]. However, the conventional synthetic methods of 2-oxazolidinones rely on hazardous or expensive reagents such as isocyanides [36] and phosgene [37]. Recently, synthesis of 2-oxazolidinones using CO_2 and appropriate substrates has attracted much attention [14, 38, 39], among which the direct synthesis of oxazolidinones starting from 2-aminoethanols and CO_2 is considered as an ideal route because the aqueous amino alcohols have been widely utilized to capture CO_2 in industry [40, 41]. Unfortunately, the direct reaction between amino alcohols and CO_2 occurs difficultly due to the thermodynamic limitation [42]. To shift the equilibrium to 2-oxazolidinones, harsh reaction conditions [43-47], dehydrating agents or auxiliaries are often needed [13, 48-51]; thus the generation of wasteful by-products is unavoidable. As an alternative strategy, our group introduced propargyl alcohols into the reaction system of amino alcohols and CO_2 to circumvent this thermodynamic limitation [52-54]. As descripted in Scheme 1, this

three-component cascade reaction is composed of carboxylative cyclization and the following intermolecular nucleophilic ring-opening and further intramolecular nucleophilic cyclization. Although Ag- and Cu-based catalysts have been developed for this three-component reaction to coproduce 2-oxazolidinones and α-hydroxyl ketones, high CO_2 pressure is still needed. In this context, efficient catalyst is still highly desirable to run this reaction at atmospheric pressure.



Scheme 1 Stepwise reaction in the three-component domino reaction and sites need to be activated

It is speculated the synergistic activation of the substrate and CO_2 may facilitate this tandem reaction running at atmospheric pressure. Promisingly, the ionic liquids (ILs) show the potential of multi-site activation in many organic syntheses by choice or functionalization of cations or anion [55-58]. Especially, the ILs-promoted carboxylative cyclization of propargyl alcohols and CO_2 has been reported [59]. Considering this carboxylative cyclization reaction is the crucial step in this three-component cascade reaction of propargyl alcohols, amino alcohols and CO_2, we envisioned that the ILs-catalyzed three-component reaction is feasible.

Herein, a task-specific ILs-catalyzed three-component reaction of propargyl alcohols, CO_2 and 2-aminoethanols was reported. By subtly selecting the cations and anions of the ionic liquid, [TBDH][TFE] was found to be the most suitable catalyst and excellent yield of 2-oxazolidinones and α-hydroxyl ketones could be obtained at atmospheric CO_2 pressure.

2. Results and Discussion

2.1. Optimization of the reaction conditions

The initial attempt to perform the three-component domino reaction of 2-(benzylamino)ethanol (**1a**), 2-methylbut-3-yn-2-ol (**2a**) and CO_2 using ILs as catalyst was carried out under 1 atm CO_2 at 80 ^oC for 12 h, as summarized in Table 1. Considering the anion may play an important role in activation of substrate **2a**, **1a** and CO_2, the anions of ILs were firstly screened. Thus five DBU-based ILs with different anions were investigated for this purpose (entries 1-5). As a result, the IL with anion $[TFE]^-$ presented the highest activity with 23% yield of the target product **3a** (3-benzyl oxazoline-2-ketone) and 27% yield of **4a** (3-hydroxyl-3-methyl butanone) (entry 3,), which is attributed to the activation capacity of $[TFE]^-$ to CO_2 [65] and to **1a** as well, being consistent with the reaction mechanism as depicted in Scheme 1. On the other hand, the cation of IL is supposed to activate the triple bond of **2a** and also carbonyl group of the intermediate i.e. α-alkylidene cyclic carbonate, thus facilitate the carboxylative cyclization of **2a** and the following intermolecular nucleophilic ring-opening and further intramolecular nucleophilic cyclization. Therefore, a variety of cations, including $[DBUH]^+$, $[TBDH]^+$, $[TMGH]^+$ and $[P_{4444}]^+$, were further evaluated with $[Im]^-$ as the anion (entries 1, 6-8), and $[TBDH]^+$ was found to be the most effective cation, which may be related with its stronger interaction with the substrate **1a** and the intermediate. The above findings showed that both the anions and cations can affect the the catalytic ability of the ILs in this reaction. With this in mind, we speculated that the IL with the combination of $[TBDH]^+$ and $[TFE]^-$ would be

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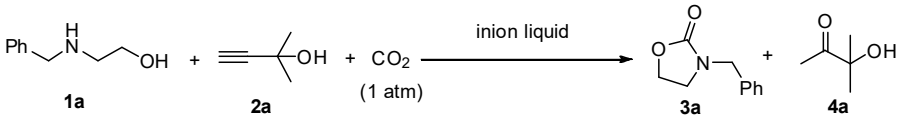
an efficient catalyst for this domino reaction. As expected, the yield of the products were improved, and 33% yield of **3a** and 39% of **4a** were obtained when [TBDH][TFE] was used as catalyst (entry 9).

Table 1. Screening ILs for the three-component domino reaction [a]



Entry	IL (mol%)	Yield/% [b]	
		3a	4a
1	[DBUH][Im]	14	13
2	[DBUH][OAc]	19	21
3	[DBUH][TFE]	23	27
4	[DBUH][TFA]	21	21
5	[DBUH]Cl	13	9
6	[TBDH][Im]	27	30
7	[TMGH][Im]	22	21
8	[P_{4444}][Im]	trace	trace
9	[TBDH][TFE]	33	39

[a] Unless otherwise specified, the reaction conditions were: **1a** (302.4 mg, 2.0 mmol), **2a** (168.2 mg, 2.0 mmol), IL (5 mol%), CO_2 (1 atm), 80 °C, 12 h. [b] Determined by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as the internal standard. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, [DBUH][Im]= DBU imidazolide, [DBUH][OAc]= DBU acetate, [DBUH][TFE] = DBU trifluoroethanol, [DBUH][TFA] = DBU trifluoracetic acid, [DBUH]Cl = DBU chloride, [TBDH][Im] = 1,5,7-Triazabicylo[4.4.0]dec-5-ene imidazolide, [TMGH][Im] = 1,1,3,3-tetramethylguanidinium imidazolide, [P_{4444}][Im]= hexyltributylphosphonium imidazolide, [TBDH][TFE] = 1,5,7-Triazabicylo[4.4.0]dec-5-ene trifluoroethanol.

Considering the IL amount may also affect the catalytic capability, the amount of the IL was increased to further improve the reaction (Table 2). Surprisingly, the reduction of yields was observed for most of the ionic liquids when the amount of the tested IL was increased from 5 mol% to 10 mol% (entries 1-6). It is inferred that the interaction between the cations of ILs and the nucleophilic sites of the substrate became dominant with the increase of the amount of the IL, which can deactivate these nucleophilic sites and thus impede the domino reaction. Conversely, increasing the amount of [TMGH][Im], [P_{4444}][Im] and [TBDH][TFE] would promote the reaction (entries 7-9), wherein [TBDH][TFE] showed higher activity than other ionic liquids used in this study. With [TBDH][TFE] as catalyst, the reaction time and reaction temperature were further studied. The

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results showed that extending the reaction time (entry 10) or raising the reaction temperature (entries 11, 12) had no obvious impact on the reaction results. But if the loading of [TBDH][TFE] was increased to 15 mol%, the **3a** yield of up to 94% was obtained (entry 13). Further improving the loading of [TBDH][TFE] to 20 mol% reduced the yield greatly (entry 14), which may be attributed to the solvent effect of the IL and also the deactivation of the nucleophilic sites by $[TBDH]^+$. No target product was obtained with only TBD or TFE as catalyst (entries 15, 16), which indicates the importance of free anion and cation in activating substrate and CO_2. Therefore, 15 mol% [TBDH][TFE] was used as catalyst and the reactions were performed at 80 °C for 12 h in subsequent studies.

Table 2. Optimization of the reaction conditions.[a]

Entry	IL (mol%)	Yield/% [b]	
		3a	**4a**
1	[DBUH][Im] (10)	13	11
2	[DBUH][OAc] (10)	7	6
3	[DBUH][TFE] (10)	3	5
4	[DBUH][TFA] (10)	9	9
5	[DBUH]Cl (10)	13	16
6	[TBDH][Im] (10)	5	9
7	[TMGH][Im] (10)	33	37
8	$[P_{4444}]$[Im] (10)	25	26
9	[TBDH][TFE] (10)	59	55
10[c]	[TBDH][TFE] (10)	57	58
11[d]	[TBDH][TFE] (10)	47	47
12[e]	[TBDH][TFE] (10)	56	53
13	[TBDH][TFE] (15)	94	97
14	[TBDH][TFE] (20)	44	46
15	TBD (15)	trace	trace

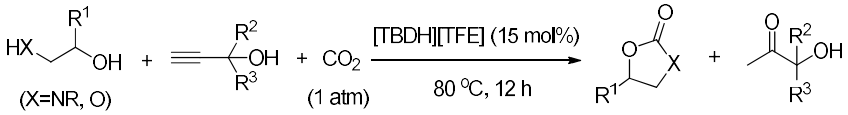
16	TFE (15)	trace	trace

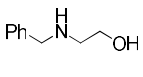
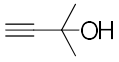
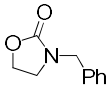
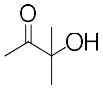
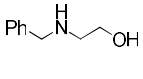
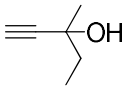
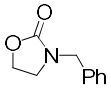
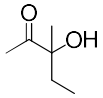
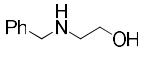
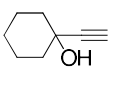
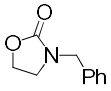
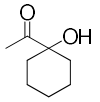
[a] Reactions were carried out at 80 °C for 12 h with **1a** (302.4 mg, 2.0 mmol), **2a** (168.2 mg, 2.0 mmol) and CO_2 (1 atm). [b] Determined by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as the internal standard. [c] 18 h. [d] 60 °C. [e] 100 °C.

2.2. Investigation of substrate applicability

Having selected suitable IL as catalyst, we proceeded to investigate the substrate applicability as listed in Table 3. The propargyl alcohols, 2-aminoalcohols and even glycols with different substituents were employed in this cascade reaction. A wide range of propargyl alcohols with methyl, ethyl, cyclohexyl, aryl and even other complicated substitute at the propargylic position (**2a**-**2e**), could be transformed effectively to afford the corresponding 2-oxazolidinone and *α*-hydroxyl ketones in moderate to high yields (entries 1-5). Notably, this protocol showed its potential application in pharmaceutical industry by realizing the transformation of ethisterone (**2e**) to *α*-hydroxyprogesterone (**4e**) with 63% of yield and the chiral structure retained (entry 5). Subsequently, the suitability of 2-aminoalcohols with different substitutes was further examined (entries 6-11). Both aryl-substituted and alkyl-substituted 2-aminoalcohols proceeded smoothly and generated the corresponding products in excellent yields with the exception of aromatic 2-aminoalcohols bearing nitro group at *para*-position (entry 10). The results may be interpreted by the weakened nucleophilicity of amino caused by the strong electron-withdrawing nitro group at benzene ring [60, 61]. Besides 2-aminoalcohols, glycols (**1h**-**1j**) were also converted to the corresponding cyclic carbonates in moderate to good yields (entries 12-14).

Table 3. Substrate scope.[a]



Entry	Substrate		Yiled/% [b]	
	1	2	3	4
1	 **1a**	 **2a**	 **3a** (94, 90[c])	 **4a** (97, 93[c])
2	 **1a**	 **2b**	 **3a** (80)	 **4b** (79)
3	 **1a**	 **2c**	 **3a** (73)	 **4c** (76)

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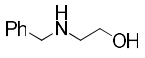
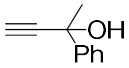
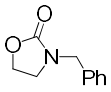
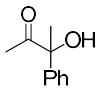
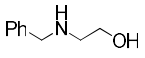
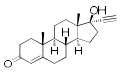
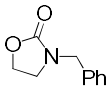
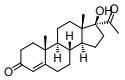
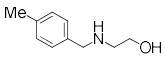
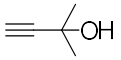
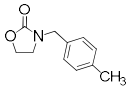
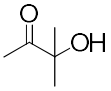
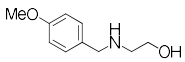
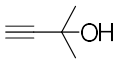
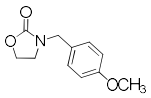
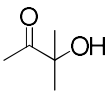
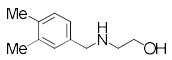
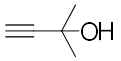
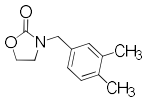
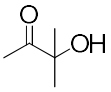
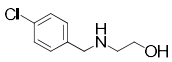
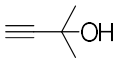
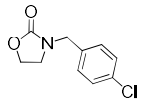
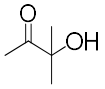
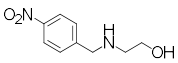
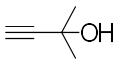
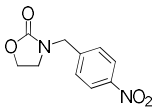
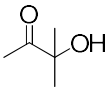
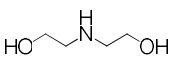
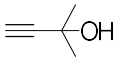
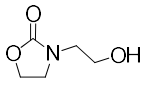
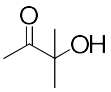
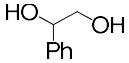
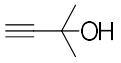
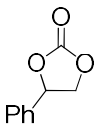
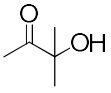
4		**1a**		**2d**	 **3a** (99)	 **4d** (99)
5		**1a**		**2e**	 **3a** (61)	 **4e** (63)
6		**1b**		**2a**	 **3b** (89)	 **4a** (89)
7		**1c**		**2a**	 **3c** (85)	 **4a** (82)
8		**1d**		**2a**	 **3d** (99)	 **4a** (99)
9		**1e**		**2a**	 **3e** (82)	 **4a** (80)
10		**1f**		**2a**	 **3f** (24)	 **4a** (23)
11		**1g**		**2a**	 **3g** (93)	 **4a** (92)
12		**1h**		**2a**	 **3h** (95)	 **4a** (97)

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13	**1i**	**2a**	**3i** (58)	**4a** (57)
14	**1j**	**2a**	**3j** (94)	**4a** (98)

[a] Reactions were performed using **1** (2.0 mmol), **2** (, 2.0 mmol), [TBDH][TFE] (71.8 mg, 15 mol%) with CO_2 pressure of 1 atm at 80 °C for 12 h. [b] Determined by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as the internal standard. [c] Isolated yield.

2.3 Recycle tests

As ILs are non-volatile and thermal stable, they can be easily recovered by evaporating the low boiling point components. So we subsequently explored the recycle performance of [TBDH][TFE] for this tandem reaction using **1a** and **2a** as model substrates under the optimum conditions. After reaction, the gas was released and vacuum-rotary evaporation was conducted at 180 °C. After removing the reactants and products, the catalyst was directly used in the next round of catalytic reaction. As depicted in Fig. 1, the IL can be reused without considerable activity loss for at least four times. The target product could still be obtained at a 75% yield after the catalyst was reused for 5 times, suggesting that the system has a good recyclability (as shown in Fig. 1).

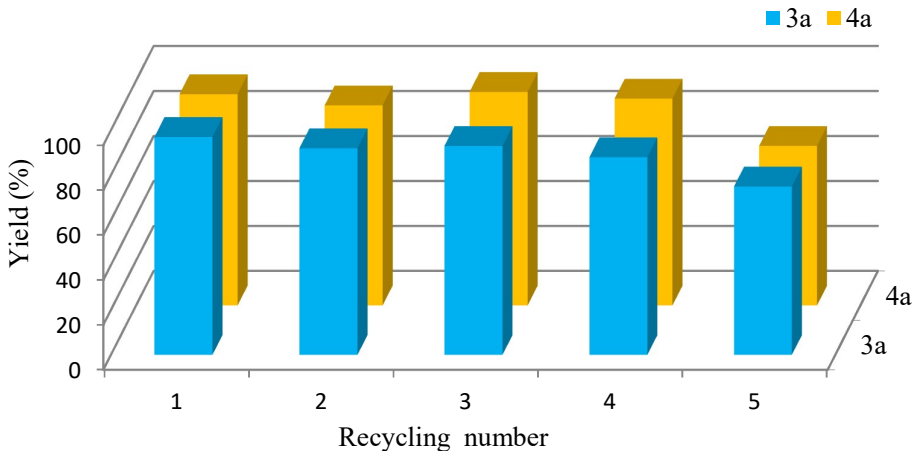

Fig. 1 Reusability of the [TBDH][TFE] system. Reaction conditions: **1a** (302.4 mg, 2.0 mmol), **2a** (168.2 mg, 2.0 mmol), [TBDH][TFE] (71.8 mg, 15 mol%), CO_2 (1 atm), 80 °C, 12 h.

2.4 Mechanism study

According to our early reports [53, 54], this cascade reaction is composed of carboxylative cyclization and the following intermolecular nucleophilic ring-opening and further intramolecular nucleophilic cyclization. To gain deeper insight on the role of [TBDH][TFE] in the catalysis, the stepwise reactions were conducted (Table 4). To begin with, we performed the

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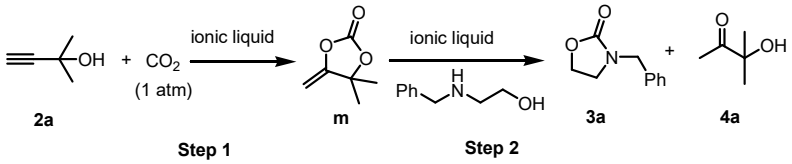
carboxylative cyclization of 2-methylbut-3-yn-2-ol (**2a**) with CO_2 using 10 mol% of IL as catalyst. A variety of DBU-based ILs such as [DBUH][Im]), [DBUH][OAc], [DBUH][Cl], and Im-based ILs including [TBDH][Im], [TMGH][Im] showed high efficiency to produce 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (**m**) with excellent yield under mild conditions (entries 1-2, 5-7). Unexpectedly, [TBDH][TFE] and [DBUH][TFE], which showed higher activity in the cascade reaction, but showed lower activity in the carboxylative cyclization reaction, probably due to the weaker hydrogen bond receptors of anions (entries 3, 4, 9, vs. 1-2, 5-7) [62-64]. The same reason may be used to explain the low activity of [DBUH][TFA]. For [P_{4444}][Im](tetra butylphosphonium imidazolide), the large steric hindrance may impedes the interaction of cation and carbon-carbon triple bond and thus the substrate can't be activated efficiently (entry 8).

Table 4. Stepwise reaction results of the domino reaction.[a]



Entry	IL	Yield/% [b]		
		m	**3a**	**4a**
1	[DBUH][Im]	87	97	99
2	[DBUH][OAc]	88	90	93
3	[DBUH][TFE]	46	63	62
4	[DBUH][TFA]	54	55	54
5	[DBUH]Cl	75	50	50
6	[TBDH][Im]	75	57	54
7	[TMGH][Im]	76	49	46
8	[P_{4444}][Im]	34	44	43
9	[TBDH][TFE]	43	99	99

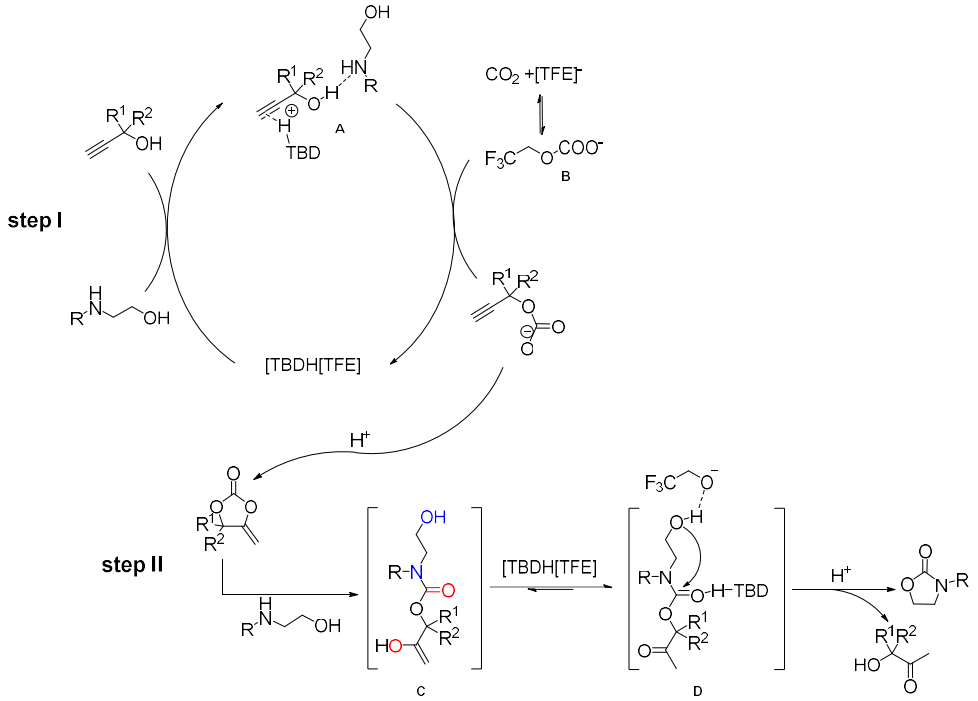
[a] Reaction conditions: 1a (302.4 mg, 2.0 mmol), 2a (168.2 mg, 2.0 mmol), IL (47.8 mg, 10%), CO_2 (1 atm), 80 °C, 12 h. [b] Determined by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as the internal standard.

The activity of different ILs on the subsequent reaction of vinyl cyclic carbonate (**m**) and aminoethanol (**1a**) was further examined under the otherwise identical conditions (Table 3). Noticeably, [DBUH][Im], [DBUH][OAc] and [TBDH][TFE] exhibited similar catalytic behavior to afford quantitative yield of **3a** and **4a** (entries 1, 2 and 9, Table 3), while other ILs showed moderate activities (entries 3-8, Table 3).

The interesting results can be obtained by comparing the results of stepwise reaction with three-component cascade reaction. Most ionic liquids, which can promote the stepwise reaction, display reduced performance in the three-component reaction (Table 2 and Table 4).

Depressingly, the reason for the decreased catalytic activity of ILs in the three-component reaction is not clear at this stage. Fortunately, the catalytic activity of [TBDH][TFE] is retained in the three-component reaction and its catalytic performance can be improved by increasing the loading amount from 10 mol% to 15 mol% (Table 2). It is inferred that α-alkylidene cyclic carbonate is the key intermediate in this multistep cascade reaction [52-54]. Although [TBDH][TFE] was not so efficient in the carboxylative cyclization, we speculated that the added ethanolamine can act as a base to facilitate the activation of hydroxyl in propargyl alcohol, thus efficiently promoting carboxylative cyclization of 2-methylbut-3-yn-2-ol (**2a**) with CO_2.

On the basis of the experimental studies and previous reports [53], the possible mechanism for the [TBDH][TFE]-catalyzed three-component reaction was proposed as depicted in Scheme 2. This cascade reaction includes the initial carboxylative cyclization of 2-methylbut-3-yn-2-ol (**2a**) with CO_2 and the subsequent nucleophilic addition of α-alkylidene cyclic carbonate with 2-aminoalcohol. In step **I**, propargyl alcohol is simultaneously activated by the coordination of the C≡C bond with cation $[TBDH]^+$ and hydrogen bonding with 2-aminoethanol to form the intermediate **A**, while CO_2 is activated through the formation of the anion $[TFECOO]^-$. Then the α-alkylidene cyclic carbonate intermediate is generated by the nucleophilic attack of O atom in the intermediate **A** to CO_2 and subsequent intramolecular cyclization. In step **II**, the nucleophilic N atom of 2-aminoethanol attacks α-alkylidene cyclic carbonate to form the corresponding β-oxopropylcarbamate species C [53]. Finally, 2-oxazolidinones and equal amount of α-hydroxyl ketones are formed through the intramolecular cyclization of intermediate C facilitated by $[TBDH]^+$.



Scheme 2. Plausible mechanism.

3. Conclusion

In summary, We have developed a new strategy to promote three-component cascade reaction of propargyl alcohols, atmospheric CO_2 and 2-aminoethanols efficiently under mild conditions by utilizing ILs as both catalyst and solvent, which sucessfully avoids the thermodynamic issue in the synthesis of 2-oxazolidinones starting from 2-aminoethanols with CO_2 and the generation of wasteful by-products. [TBDH][TFE] showed the best performance by subtly choosing ILs. The protic IL is found to synergistically activate the substrate by its cation and anion and can be easily

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recovered and reused at least for 5 times without obvious loss of its activity. A wide range of propargyl alcohols and 2-aminoethanols, were successfully transformed to 2-oxazolidinones and α-hydroxyl ketones with moderate to excellent yield after 12 h at 80 °C. We believe that this high-efficient and greener IL catalytic system exhibits great potential in conversion of CO_2 to valuable chemicals.

4. Materials and Methods

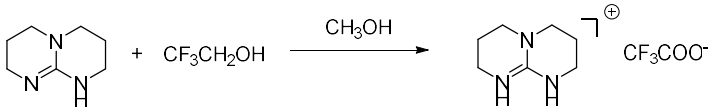
4.1. Materials and general analytic methods

Unless otherwise noted, carbon dioxide (99.999%), commercially available DBU, TBD, TMG, Imidazole, TFE and TFA were obtained from Aladdin, TCI. All starting materials including propargyl alcohols, monoethanolamine and aromatic aldehydes, were obtained from Aladdin, Alfa Aesar and Heowns and used as received. All operations were carried out by using standard high vacuum and Schlenk technique unless otherwise noted. ^{1}H NMR spectra were recorded on 400 MHz spectrometer using $CDCl_3$ or DMSO-*d6* as solvent referenced to $CDCl_3$ (7.26 ppm) or DMSO-*d6* (2.50 ppm). ^{13}C NMR was recorded at 100.6 MHz in $CDCl_3$ (77.00 ppm). Multiplets were assigned as singlet, doublet, triplet, doublet of doublet, multiplet and broad singlet. Mass spectra were recorded on a Shimadzu GCMS-QP2010 equipped with a RTX-5MS capillary column at an ionization voltage of 70 eV. The data are given as mass units per charge (m/z).

4.2. General procedure for the synthesis of 2-aminoethanol derivatives [33]

A mixture of an aromatic aldehyde (10 mmol), 2-aminoethanol (0.61 g, 10 mmol) and Na_2SO_4 (1.42 g, 10 mmol) in CH_3OH (20.0 mL) was added into a 100 mL round bottom flask and stirred for 2 h at room temperature. Then, the solution was obtained after removing the drying agent. The solution was treated with the addition of $NaBH_4$ (0.19 g, 5 mmol) in ice water and stirred for 1 h. The mixture was concentrated under vacuum, and the residue was extracted with CH_2Cl_2 (3 × 20 mL), washed with water (20.0 mL), and dried with Na_2SO_4. The CH_2Cl_2 solution was concentrated under vacuum and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v, 10:1-1:2) as eluent to give the desired products.

4.3. General procedure for the synthesis of ILs [68].

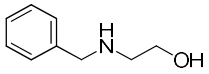


All ionic liquids (ILs) were synthesized based on the procedures reported [59]. Typically, for the synthesis of [TBDH][TFE], TBD was added to the methanol solution of CF_3CH_2OH by using the anion-exchange resin method. Then the mixture was stirred at room temperature for 24 h. Subsequently, methanol was distilled off at 70 °C under vacuum for 24 h. The as-synthesized ILs were characterized by NMR spectroscopy. ^{1}H and ^{13}C NMR analyses were performed on a Bruker Avance NMR spectrometer (400 MHz), and the NMR data are listed as follows.

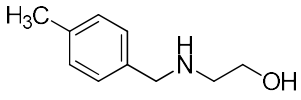
4.4. General procedure for the synthesis of 2-oxazolidinones and α-hydroxyl ketones.

[TBDH][TFE] (69.9 mg, 15 mol%), propargylic alcohol 1a (2.0 mmol) and 2-aminoethanol (2.0 mmol) were added successively to a 10 mL Schlenk tube equipped with a magnetic stir bar. Then the flask was capped and attached to a CO_2 balloon with purity of 99.95%. Subsequently, the reaction mixture was stirred at 80 °C for 12 h. When the reaction completed, the vessel was cooled with an ice-bath, and remove the balloon. The residue was flushed with 2 × 3 mL CH_2Cl_2 and purified by column chromatography on silica gel (*n*-butylamine saturation) using petroleum ether/ethyl acetate (v/v, 50:1-1:1) as eluent to give the desired products.

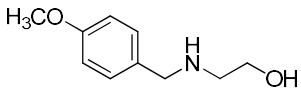
4.5. Characterization Data for Substrates and Products

 **1a**

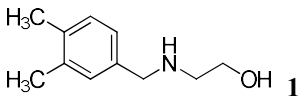
2-(Benzylamino)ethanol[53]. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5H), 3.80 (s, 2H), 3.66 (t, J= 6.0 Hz, 2H), 2.79 (t, J= 6.0 Hz, 2H), 2.71 (-OH, -NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 139.6, 128.4, 128.1, 127.1, 60.7, 53.4, 50.5 ppm. GC-MS (EI, 70 eV) m/z (%) 120.15 (48.51), 91.15 (100).

 **1b**

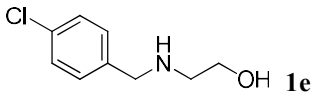
2-(4-Methylbenzylamino)ethanol[53]. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.12 (m, 4H), 3.74 (s, 2H), 3.63 (t, J= 6.0 Hz, 2H), 2.75 (t, J= 6.0 Hz, 2H), 2.67 (-OH, -NH), 2.33 (s, 3H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 136.7, 136.6, 129.1, 128.1, 60.7, 53.2, 50.5, 21.0 ppm. GC-MS (EI, 70 eV) m/z (%) 134.15 (35.23), 105.10 (100), 77.05 (8.65).

 **1c**

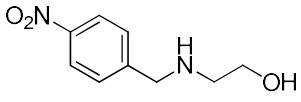
2-(4-Methoxybenzylamino)ethanol[53]. Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.20 (m, 2H), 6.86-6.84 (m, 2H), 3.78 (s, 3H), 3.70 (t, J= 6.0 Hz, 2H), 3.62 (t, J= 6.0 Hz, 2H), 2.73 (4H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 158.6, 131.9, 129.3, 113.7, 60.7, 55.2, 52.9, 50.5 ppm. GC-MS (EI, 70 eV) m/z (%) 150.20 (17.75), 122.10 (9.08), 121.15 (100), 91.10 (5.24), 78.10 (6.03), 77.05 (7.48).

 **1d**

2-(3,4-Dimethylbenzylbenzylamino)ethanol[53]. Colorless solid. M.P. 43 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10-7.03 (m, 3H), 3.73 (s, J= 6.0 Hz, 2H), 3.65 (t, J= 6.0 Hz, 2H), 2.78 (t, 2H), 2.72 (-OH, -NH), 2.26-2.25 (m, 6H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 137.1, 136.7, 135.4, 129.7, 129.6, 125.7, 60.8, 53.2, 50.5, 19.7, 19.4 ppm. GC-MS (EI, 70 eV) m/z (%) 148.20 (26.96), 120.15 (10.86), 119.15 (100), 91.10 (11.06), 77.10 (5.90).

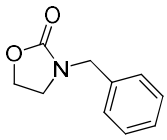
 **1e**

2-(4-Chlorobenzylbenzylamino)ethanol[53]. Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 4H), 3.77 (s, 2H), 3.66 (t, J= 6.0 Hz, 2H), 2.78 (t, J= 6.0 Hz, 2H), 2.40 (-OH, -NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 138.2, 132.9, 129.5, 128.6, 60.8, 52.7, 50.4 ppm. GC-MS (EI, 70 eV) m/z (%) 156.10 (9.60), 154.10 (30.14), 127.10 (32.04), 126.10 (7.91), 125.10 (100), 89.05 (14.34).



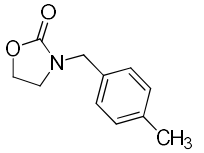
1f

2-(4-Nitrobenzylbenzylamino)ethanol[53]. Brown solid. M.P. 82-83.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.15 (m, 2H), 7.50-7.48 (m, 2H), 3.91 (s, 2H), 3.68 (t, *J*= 6.0 Hz, 2H), 2.79 (t, *J*= 6.0 Hz, 2H), 2.16 (-OH, -NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 147.7, 147.0, 128.6, 123.6, 61.0, 52.7, 50.6 ppm. GC-MS (EI, 70 eV) m/z (%) 166.10 (10.39), 165.10 (100), 137.10 (5.32), 136.10 (62.21), 120.10 (8.87), 119.10 (7.69), 106.10 (31.23), 105.05 (5.28), 91.10 (10.32), 90.10 (24.52), 89.05 (24.99), 78.05 (33.75), 77.05 (7.24).



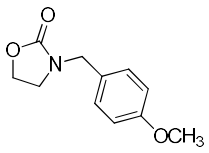
3a

3-Benzyloxazolidin-2-one[36]. Light yellow solid. M.P. 77-78.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5H), 4.43 (s, 2H), 4.30 (t, *J* = 8.0 Hz, 2H), 3.42 (t, *J* = 8.0 Hz, 2H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 158.5 (C=O), 135.7, 128.7, 128.0, 127.9, 61.7, 48.3, 43.9 ppm. GC-MS (EI, 70 eV) m/z (%) 178.10 (7.73), 177.10 (62.67), 176.10 (61.59), 132.15 (19.98), 105.10 (27.09), 104.10 (100), 92.10 (14.18), 91.10 (86.07), 78.10 (18.29), 77.10 (11.92), 65.10 (27.49).



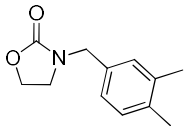
3b

3-(4-Methylbenzyl)oxazolidin-2-one[66]. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.14 (m, 4H), 4.39 (s, 2H), 4.28 (t, *J* = 8.0 Hz, 2H), 3.42 (t, *J* = 8.8 Hz 2H), 2.34 (s, 3H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 158.5 (C=O), 137.7, 132.7, 129.5, 128.2, 61.7, 48.1, 43.8, 21.1 ppm. GC-MS (EI, 70 eV) m/z (%) 191.20 (48.54), 176.20 (58.84), 146.25 (7.91), 132.20 (15.10), 119.15 (24.23), 118.15 (100), 105.15 (60.83), 91.10 (23.07), 77.10 (25.82).



3c

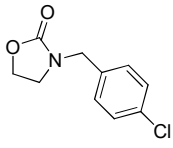
3-(4-Methoxybenzyl)oxazolidin-2-one[36]. Colorless solid. M.P. 72-73.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.20 (m, 2H), 6.88-6.86 (2H), 4.36 (s, 2H), 4.28 (t, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 3.39 (t, *J* = 7.6 Hz, 2H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 159.3, 158.4, 129.5, 127.8, 114.1, 61.7, 55.3, 47.8, 43.8 ppm. GC-MS (EI, 70 eV) m/z (%) 208.20 (6.69), 207.20 (48.54), 206.20 (26.48), 179.15 (20.05), 176.20 (29.66), 162.20 (9.17), 135.15 (23.28), 134.20 (100), 121.15 (68.48), 91.10 (12.46), 78.10 (20.27), 77.10 (20.87), 65.10 (8.26), 63.05 (5.09).



3d

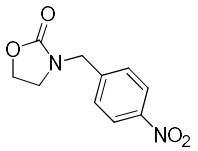
Peer-reviewed version available at Molecules 2018, 23, 3033; doi:10.3390/molecules23113033

3-(3,4-Dimethylbenzyl)oxazolidin-2-one[53]. Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-6.99 (m, 3H), 4.35 (s, 2H), 4.27 (t, J = 8.0 Hz, 2H), 3.40 (t, J = 8.0 Hz, 2H), 2.25 (s, 6H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 158.4 (C=O), 136.9, 136.1, 132.9, 129.8, 129.3, 125.5, 61.6, 47.9, 43.7, 19.5, 19.2 ppm. GC-MS (EI, 70 eV) m/z (%) 146.20 (24.14), 133.20 (25.43), 132.20 (100), 119.20 (72.16), 106.15 (12.16), 105.15 (18.44), 104.15 (8.77), 91.10 (42.09), 77.10 (24.38), 65.10 (10.50). HRMS (ESI): $C_{12}H_{16}NO_2$ for $[M+H]^+$ calculated 206.1176, found 206.1181.



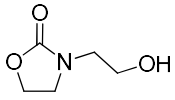
3e

3-(4-Chlorobenzyl)oxazolidin-2-one[53]. M.P. 72-73 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.30 (m, 2H), 7.22-7.20 (m, 2H), 4.38 (s, 2H), 4.29 (t, J = 8.0 Hz, 2H), 3.40 (t, J = 8.0 Hz, 2H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 158.4 (C=O), 134.2, 133.8, 129.4, 128.9, 61.7, 47.7, 43.9 ppm. GC-MS (EI, 70 eV) m/z (%) 213.15 (14.97), 211.15 (47.48), 210.15 (14.92), 176.15 (52.54), 166.15 (9.45), 138.15 (100), 132.20 (25.87), 125.10 (72.60), 112.10 (12.73), 89.10 (37.59), 77.10 (12.46), 63.00 (15.51).



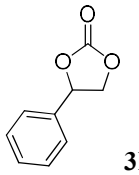
3f

3-(4-Nitrobenzyl)oxazolidin-2-one[36]. Light yellow solid. M.P. 148-150 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.22 (4H), 4.40 (s, 2H), 4.32 (t, J = 8.0 Hz, 2H), 3.43 (t, J = 8.0 Hz, 2H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 158.4 (C=O), 134.2, 133.8, 129.4, 128.9, 61.7, 47.6, 43.8 ppm. GC-MS (EI, 70 eV) m/z (%) 213.15 (16.79), 212.10 (10.73), 211.10 (49.09), 210.10 (15.33), 177.25 (6.14), 176.15 (51.73), 166.15 (9.83), 140.10 (35.32), 139.10 (25.34), 138.10 (100), 132.20 (26.26), 127.10 (22.41), 126.10 (7.12), 125.10 (73.59), 112.10 (12.93), 89.10 (35.12), 77.10 (12.20), 76.10 (8.47), 63.05 (14.85).



3g

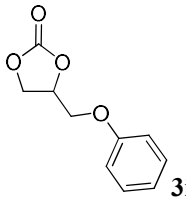
3-(2-Hydroxyethyl)oxazolidin-2-one. Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.32 (t, J = 8.0 Hz, 2H), 3.73-3.62 (m, 5H), 3.31 (t, J = 5.0 Hz, 2H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 159.2 (C=O), 62.1, 59.8, 46.5, 45.3 ppm. GC-MS (EI, 70 eV) m/z (%) 113.10 (7.88), 101.10 (66.73), 100.10 (100), 88.10 (12.34).



3h

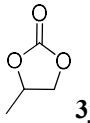
4-Phenyl-1,3-dioxolan-2-one[67]. White solid. M.P. 53 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (t, J = 8.4Hz, 1H), 4.78 (t, J = 8.4 Hz, 1H), 5.70 (t, J = 8.0 Hz, 1H), 7.35 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 6.4 Hz,

3H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 71.29, 78.11, 125.99, 129.34, 129.84, 135.86, 154.97. GC-MS (EI, 70 eV) m/z (%) 164.10 (69), 120.10 (13), 119.10 (12), 105.10 (31), 92.10 (20), 91.10 (96), 90.05 (100), 89.05 (36), 78.10 (78), 77.05 (28), 65.05 (27), 63.05 (14).



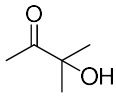
3i

4-(Phenoxymethyl)-1,3-dioxolan-2-one[67]. Yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (dd, ^3J= 4.4 Hz, ^2J = 10.8 Hz, 1H), 4.23 (dd, ^3J = 3.6 Hz, ^2J = 10.8 Hz, 1H) 4.54 (dd, ^3J = 8.4 Hz, ^2J= 6.0 Hz, 1H), 4.60 (t, J = 8.4 Hz, 1H), 5.02 (m, 1H), 6.90 (d, J = 8.0 Hz, 2H), 7.00 (t, J = 7.4 Hz, 2H), 7.31 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 44.92, 67.02, 74.43, 114.8, 122.2, 129.1, 154.39. GC-MS (EI, 70 eV) m/z (%) 194.05 (66), 107.10 (100), 94.05 (73), 77.10 (87), 65.05 (18), 51.05 (23), 43.05 (12).



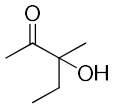
3j

4-Methyl-1,3-dioxolan-2-one. Colorless liquid[67]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (d, J = 6.0 Hz, 1H), 3.96 (t, 1H), 4.49 (t, J = 8.4 Hz, 1H), 4.79 (m, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.28, 70.72, 73.71, 155.16. GC-MS (EI, 70 eV) m/z (%) 102.05 (19), 87.05 (100).



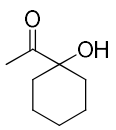
4a

3-Hydroxy-3-methylbutan-2-one[67]. Colorless oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.24 (s, 1H), 2.15 (s, 3H), 1.17 (s, 6H) ppm. ^{13}C NMR (100.6 MHz, DMSO-d_6) δ 213.6, 75.5, 25.9, 24.0 ppm. GC-MS (EI, 70 eV) m/z (%) 102.10 (8.57), 87.10 (100), 69.05 (61.60), 60.05 (92.12).



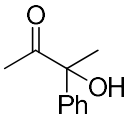
4b

3-Hydroxy-3-methylpentan-2-one[67]. Colorless oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.04 (OH, 1H), 2.13 (s, 3H), 1.64-1.42 (m, 2H), 1.12 (s, 3H), 0.74 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (100.6 MHz, DMSO-d_6) δ 214.2, 78.6, 31.8, 25.1, 24.1, 7.9 ppm. GC-MS (EI, 70 eV) m/z (%) 67.10 (100), 85.05 (66.74), 71.10 (15.76), 69.10 (12.80), 84.10 (12.44), 86.10 (12.00), 110.10 (10.92), 95.10 (10.56).



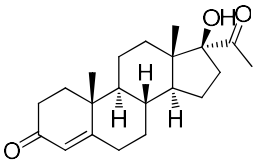
4c

1-(1-Hydroxycyclohexyl)ethanone[67]. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 3H), 1.75-1.64 (m, 6H), 1.49 (d, J = 6.5 Hz, 2H), 1.28 (dd, J_1 = 15.1 Hz, J_2 = 10.3 Hz, 2H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 212.7, 78.0, 33.8, 25.3, 23.7, 21.1 ppm. GC-MS (EI, 70 eV) *m/z* (%) 99.10 (70.66), 81.10 (100), 79.10 (20.54).



4d

3-Hydroxy-3-phenylbutan-2-one[67]. Brown oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 (d, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.26 (t, J = 7.1 Hz, 1H), 6.06 (s, 1H), 2.02 (s, 3H), 1.52 (s, 3H) ppm. ^{13}C NMR (100.6 MHz, DMSO-d_6) δ 210.0, 143.0, 127.9, 126.9, 124.7, 79.4, 25.8, 24.0 ppm. GC-MS (EI, 70 eV) *m/z* (%) 121.10 (100), 105.10 (18.88), 77.05 (30.87).



4e

White solid[53], M. p. 192−193 ºC.^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 (s, 1H), 2.96 (s, 1H), 2.38-2.27 (m, 5H), 2.23 (s, 3H), 1.98-1.95 (m, 1H), 1.86-1.83 (m, 1H), 1.74-1.36 (m, 10H), 1.16 (s, 3H), 1.06-1.02 (m, 1H), 0.95 (s, 3H), 0.90-0.82 (m, 1H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 214.2, 199.4, 171.0, 123.8, 90.7, 53.2, 49.1, 47.5, 38.5, 36.1, 35.6, 35.0, 33.8, 33.0, 32.7, 31.5, 28.2, 24.2, 20.7, 17.3, 14.1 ppm. HRMS (ESI): $C_{21}H_{31}O_3$ for $[M+H]^+$ calculated 331.2268, found 331.2274

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