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Tetrahedron
Tetrahedron 63 (2007) 9153–9162

Base catalyzed cyclization of *N*-aryl and *N*-alkyl-*O*-propargyl carbamates to 4-alkylidene-2-oxazolidinones

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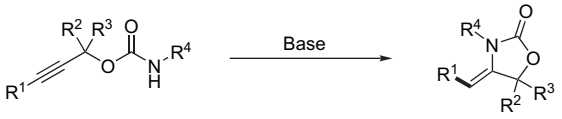
Received 4 April 2007; revised 5 June 2007; accepted 21 June 2007
Available online 27 June 2007

Abstract—The base catalyzed cyclization of *N*-aryl and *N*-alkyl-*O*-propargyl carbamates is studied in detail. The effect of various bases and solvents on the efficacy of this cyclization reaction is analyzed and a new base–solvent system (LiOH in DMF) for effective cyclization of these carbamates is reported. A number of differentially substituted *O*-propargyl carbamates were cyclized to the corresponding 2-oxazolidinones under these conditions. The reaction conditions reported here are mild and no side reactions were observed in any of the substrates studied. A propargyl carbonate group was unaffected during the course of the cyclization of the *O*-propargyl carbamate group. The propargyl carbamates were prepared from the corresponding alkyl or aryl amines and the corresponding propargyl chloroformate, resulting in oxazolidinones diversely substituted at the nitrogen atom. *N*-Aryl-*O*-propargyl carbamates cyclized readily to the corresponding oxazolidinones with LiOH in DMF, whereas *N*-alkyl-*O*-propargyl carbamates reacted slowly under the same conditions. *O*-Propargyl carbamates substituted at the 1-position tend to cyclize faster whereas those substituted at 3-position cyclize considerably slower than the unsubstituted carbamates.

1. Introduction

Oxazolidinones have been found to have a large range of applications in organic synthesis as potential intermediates, as chiral auxiliaries, and in the preparation of organometallic reagents.[1] They often show good antibacterial properties and hence these heterocyclic compounds are widely used in the pharmaceutical chemistry.[2] Among them, 4-alkylidene-2-oxazolidinones, functionalized with enamine and allylic alcohol moieties, could be of special interest as synthetic intermediates. The base promoted cyclization of *O*-propargyl carbamates to give 4-methylene-2-oxazolidinones has long been established (Scheme 1).[3] Similar cyclization reactions yielding 4-alkylidene-2-oxazolidinones starting from 2-propyn-1-ols and aryl and alkyl amines have been achieved under high pressure of carbon dioxide and at high temperatures, in the presence of tertiary phosphines[4] and more recently, in ionic liquids.[5]

Tamaru et al. have provided the most comprehensive studies on the base catalyzed cyclization of *O*-propargyl carbamates.[6] They have classified propargyl carbamates into three categories based on the ease of cyclization, which in turn is based on the nature of the substituents on the nitrogen atom. *N*-Tosyl and *N*-acyl-*O*-propargyl carbamates cyclize to the corresponding oxazolidinones only in the presence of a metal catalyst that can coordinate with the triple bond. The cyclization of *N*-aryl or *N*-alkyl propargyl carbamates is reported to be most feasible in the presence of a strong base like potassium *tert*-butoxide in THF and in the absence of metal salts. The addition of metal salts to the reaction mixture lowers the reaction rate. Although the yields are fairly high and the catalytic base is used, the reaction times were longer, ranging from 20 to 24 h for unsubstituted propargyl carbamates. Although the methodology reported was high yielding, the number of examples studied with respect to the substitutions on the nitrogen atom was limited. The propargyl carbamates were prepared from the corresponding isocyanates and propargyl alcohol. This has restricted the studies to carbamates obtained from readily available isocyanates and thus, along with the increased reaction time has limited the scope of this reaction. Hence, a detailed study of this reaction is required to standardize the conditions



Scheme 1. Base promoted cyclization of *O*-propargyl carbamates to 4-alkylidene-2-oxazolidinones.

Keywords: Carbamates; Oxazolidinones; Cyclization; Solvent effects; Chloroformates.
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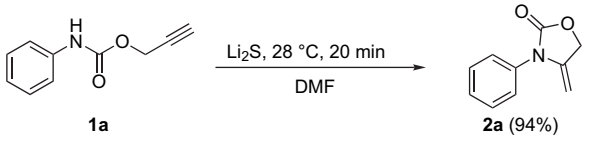
doi:10.1016/j.tet.2007.06.066

for achieving these cyclization reactions easily and efficiently.

In our laboratory, we have developed propargyl carbamates as a means of protecting amines.[7] Propargyl carbamates can easily be deblocked to the corresponding amines using benzyltriethylammonium tetrathiomolybdate.[7] As part of our efforts to understand the mechanism of this deprotection reaction, we treated propargyl carbamates with various sulfur nucleophiles. To our surprise, we observed the cyclization of *N*-phenyl-*O*-propargyl carbamate (**1a**) to 1-phenyl-4-methylene-2-oxazolidinone (**2a**) (Scheme 2) on treatment with stoichiometric lithium sulfide (94%, 20 min, 28 °C, DMF). This prompted us to study this cyclization reaction in more detail. The cyclization reactions of *N*-alkyl and *N*-aryl-*O*-propargyl carbamates in the presence of various bases and in different solvents were studied. The propargyl carbamates were easily synthesized from the corresponding amines and the propargyl chloroformates, enabling the synthesis of oxazolidinones from the corresponding amines, unlike the earlier reports[3,6] where the corresponding isocyanates were used. The results of our systematic investigation in this area are reported here.



Scheme 2. Cyclization of *N*-phenyl-*O*-propargyl carbamate in the presence of Li_2S.

2. Results and discussion

We initiated our studies by examining the effectiveness of different bases on the cyclization of *O*-propargyl carbamates. A solution of **1a** in DMF was treated with 0.1 equiv of different bases and the reaction was followed by TLC. The extent of cyclization after 24 h was measured from the NMR spectrum of the crude reaction mixture (Table 1). There was no cyclization of **1a** to **2a** in the presence of organic bases such as DMAP, pyridine, and triethylamine. KOH, LiOH, and KO^{t}Bu had the same effect on the cyclization of **1a** whereas the reaction with K_2CO_3 gave **2a**, but the rate was considerably lower. The experiments with LiOH, KOH, and KO^{t}Bu (entries 1–3) have given the best conditions (0.1 equiv, 30 min, 28 °C) available for the intramolecular cyclization of *O*-propargyl carbamates. Lithium hydroxide, which is relatively less hygroscopic and more crystalline, seemed to be a better choice for these cyclization reactions over KOH and KO^{t}Bu.

Table 1. Effect of bases on the cyclization of *N*-phenyl-*O*-propargyl carbamate (**1a**) in DMF

Entry	Base	% Conversion after 24 h[a]
1	LiOH	100 (0.5 h)[b]
2	KOH	100 (0.5 h)[b]
3	KO^{t}Bu	100 (0.5 h)[b]
4	K_2CO_3	56
5	DMAP	0
6	Pyridine	0
7	Triethylamine	0

[a] Extent of conversion is calculated based on the integration values for the starting material (**1a**) and the product (**2a**) in ^{1}H NMR spectra of the reaction mixture.
[b] Time taken for the completion of the reaction as observed from the TLC is given in the bracket.

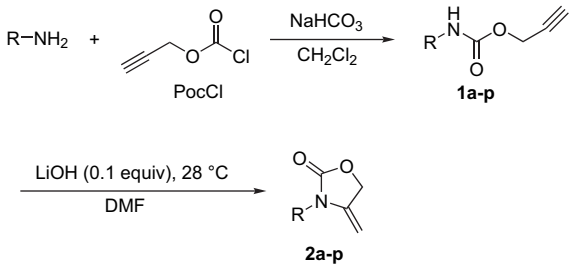
Table 2. Effect of solvents on the cyclization of *N*-phenyl-*O*-propargyl carbamate (**1a**) with LiOH

Entry	Solvent	% Conversion after 24 h[a]
1	DMF	100 (0.5 h)[b]
2	DMSO	100 (1 h)[b]
3	Acetonitrile	35
4	THF	26
5	Methanol	46
6	Acetone	22
7	Toluene	0

[a] Extent of conversion is calculated based on the integration values for the starting material (**1a**) and the product (**2a**) in ^{1}H NMR spectra of the reaction mixture.
[b] Time taken for the completion of the reaction as observed from the TLC is given in the brackets.

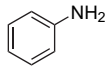
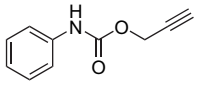
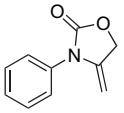
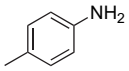
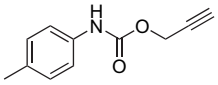
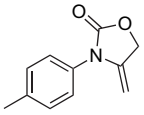
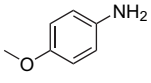
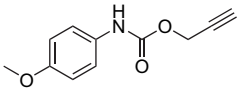
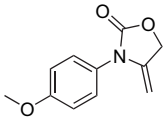
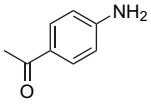
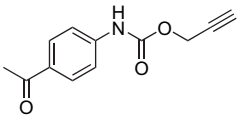
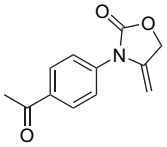
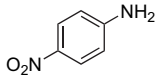
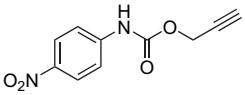
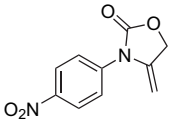
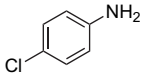
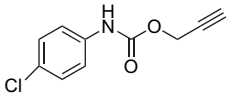
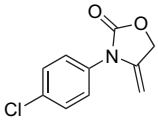
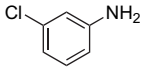
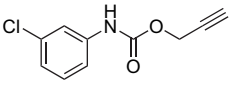
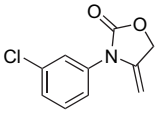
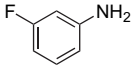
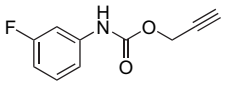
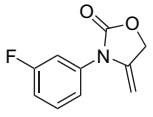
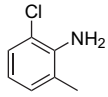
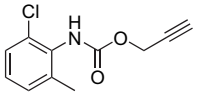
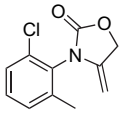
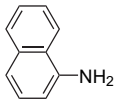
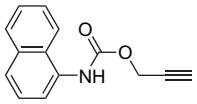
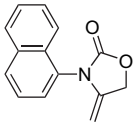
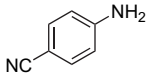
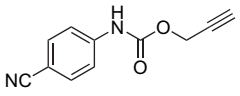
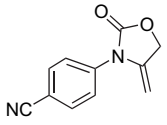
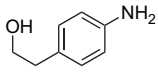
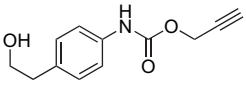
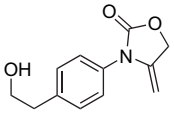
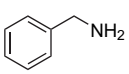
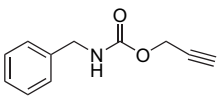
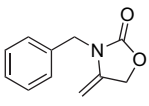
Tamaru et al. have reported KO^{t}Bu as the most suitable base for the cyclization of **1a**, and used THF as the solvent (91%, 24 h, rt).[6] Our experiments with KO^{t}Bu in DMF resulted in a much faster cyclization (entry 3, Table 1) suggesting that the role of solvents in these cyclization reactions is significant. We carried out a set of reactions to understand the role of different solvents in the cyclization reaction of **1a**, while using LiOH (0.1 equiv, 28 °C) as the base. The reactions were followed using TLC and the extent of cyclization after 24 h was measured using the NMR spectrum of the crude reaction mixture (Table 2). Polar aprotic solvents like DMF and DMSO (entries 1 and 2) were the most suitable solvents for the cyclization of **1a**. DMF was found to be a better solvent than DMSO and there was no particular order for the rate of cyclization with respect to the dielectric constant or dipole moment of the solvents. A protic solvent like methanol (entry 5) was found to be less effective in the cyclization of **1a** than DMF or DMSO. No cyclization was observed in nonpolar aprotic solvents like toluene (entry 7). The two sets of experiments listed in Tables 1 and 2 suggest that LiOH in DMF could be the best base–solvent combination for the cyclization of *O*-propargyl carbamates.

We prepared a number of *O*-propargyl carbamates from the corresponding amines and propargyloxycarbonyl chloride (PocCl) and the cyclization of these carbamates using LiOH (0.1 equiv) in DMF was studied (Scheme 3, Table 3).



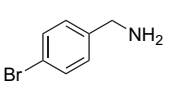
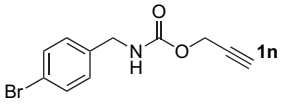
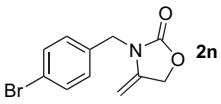
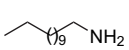
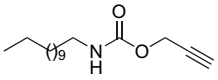
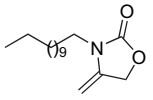
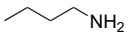
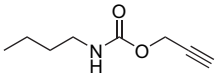
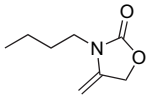
Scheme 3. Preparation of 4-methylene-2-oxazolidinones from amines.

Table 3. Preparation of 4-methylene-2-oxazolidinones from the corresponding amines

Entry	Amine	*O*-Propargyl carbamate	Time, temp	4-Methylene-2-oxazolidinone	Yield[a] (%)
1		 **1a**	0.5 h, 28 °C	 **2a**	99
2		 **1b**	1 h, 28 °C	 **2b**	99
3		 **1c**	1.5 h, 28 °C	 **2c**	98
4		 **1d**	1.5 h, 28 °C	 **2d**	93
5		 **1e**	1 h, 28 °C	 **2e**	98
6		 **1f**	1 h, 28 °C	 **2f**	98
7		 **1g**	1 h, 28 °C	 **2g**	96
8		 **1h**	1 h, 28 °C	 **2h**	97
9		 **1i**	2 h, 28 °C	 **2i**	95
10		 **1j**	1 h, 28 °C	 **2j**	96
11		 **1k**	1 h, 28 °C	 **2k**	92
12		 **1l**	1.5 h, 28 °C	 **2l**	90
13		 **1m**	5 h, 70 °C	 **2m**	96

(*continued*)

Table 3. (*continued*)

Entry	Amine	*O*-Propargyl carbamate	Time, temp	4-Methylene-2-oxazolidinone	Yield[a] (%)
14		 **1n**	5 h, 70 °C	 **2n**	96
15		 **1o**	8 h, 70 °C	 **2o**	76
16		 **1p**	8 h, 70 °C	 **2p**	68

[a] Yield of isolated compounds.

The reaction worked very well for carbamates derived from aromatic amines (entries 1–12). The electronic nature of the substituents on the aromatic ring seemed to have no effect on the cyclization reaction. The propargyl carbamate derived from aniline (**1a**) cyclized faster than all the other propargyl carbamates studied (entry 1). The carbamates derived from both 4-anisidine and 4-nitroaniline (**1c** and **1e**, respectively) reacted slower than **1a**. The cyclization reaction is tolerant of all types of substitutions on the aromatic ring. The propargyl carbamate **1d** derived from 4-aminoacetophenone underwent the expected cyclization without any other base catalyzed side reactions (entry 4). The cyclization reactions were independent on the position of the substituents and the nature of the aromatic ring. *N*-Aryl propargyl carbamates with substitutions on the *meta* position (entries 7 and 8) reacted as well as those with substitutions on the *para* position. The sterically demanding carbamate **1i**, with substitutions on the 2- and 6-position reacted to give the oxazolidinone **2i** in 2 h (entry 9). The carbamate **1j** derived from 1-naphthylamine cyclized to give **2j** in excellent yield (entry 10) as effectively as **1a**. A free hydroxyl group in **1l** has no effect on its cyclization to **2l** (entry 12). However, the cyclization of propargyl carbamates derived from alkyl amines is not so facile. The propargyl carbamate **1m**, derived from benzylamine did not undergo complete cyclization even after 24 h under the conditions used for **1a** (0.1 equiv LiOH, DMF, 28 °C). Nevertheless, when the reaction mixture was heated (70 °C, 5 h), **1m** cyclized to **2m** in excellent yield. The carbamate **1n**, which is similar to **1m** also yielded the corresponding oxazolidinone **2n** in 96% yield under the same reaction conditions. The reaction of carbamates **1o** and **1p** was much slower and the corresponding oxazolidinones **2o** and **2p** could be obtained in 76 and 68%, respectively, after 8 h at 70 °C. Heating the reaction mixture for longer time or at higher temperatures did not seem to have increased effects on these reactions. Propargyl carbamates in which the nitrogen is attached to an aliphatic secondary carbon atom did not cyclize under these conditions. The carbamates **1q–1s** (Fig. 1) did not yield any cyclized product even after 24 h at 70 °C.

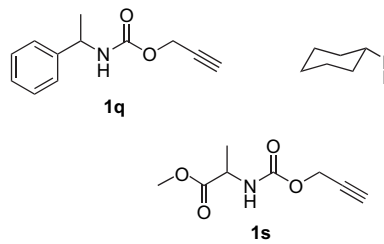
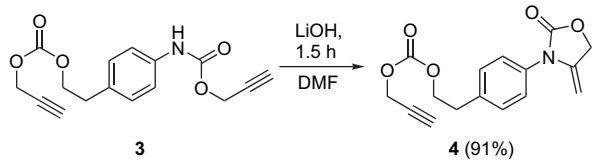


Figure 1. Propargyl carbamates that did not cyclize to the corresponding oxazolidinones with LiOH.

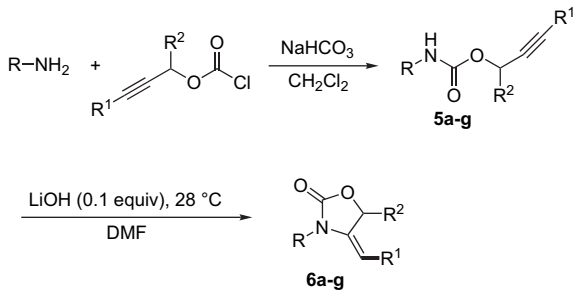
The use of LiOH in DMF for the cyclization of propargyl carbamates works extremely well for the carbamates derived from aromatic amines, and also for those derived from simple aliphatic amines. The reaction conditions are mild and did not bring about any side reactions in the examples studied. Compound **3**, which bears a propargyl carbonate and a propargyl carbamate group, when treated with LiOH gave **4** in excellent yield resulting from the cyclization of the carbamate group and the carbonate group in **4** was left unaffected (Scheme 4).



Scheme 4. Cyclization of propargyl carbamate, keeping the propargyl carbonate intact.

Having found that LiOH in DMF could be an efficient reaction medium for the cyclization of simple *O*-propargyl carbamates, we explored the possibility of using the same reaction conditions for the preparation of 2-oxazolidinones from substituted *O*-propargyl carbamates. Substituted propargyl carbamates **5a–g** were prepared in good yields from the corresponding amines and prop-2-ynyl chloroformates. These carbamates were then treated with 0.1 equiv of LiOH in DMF and their cyclization reactions were followed (Scheme 5, Table 4).

As observed by Tamaru et al. the cyclization of propargyl carbamates, which are substituted at the 1-position (when R^2 is not H in Scheme 5) was faster than the corresponding unsubstituted compounds. The phenyl derivative **5a** reacted as fast as the carbamate **1a** (in 30 min at 28 °C) to give **6a** (Table 4, entry 1), while the 1-naphthyl derivative **5b** (Table

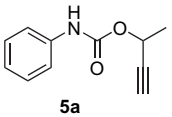
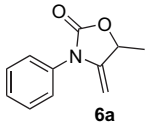
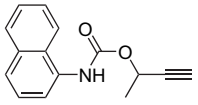
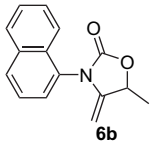
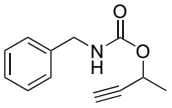
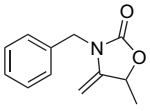
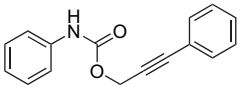
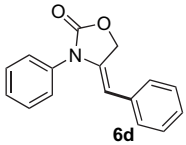
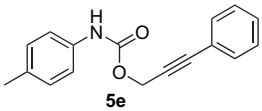
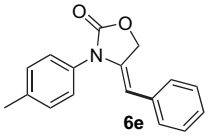
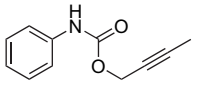
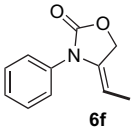
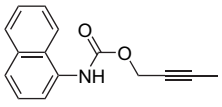
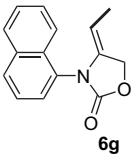


Scheme 5. Synthesis of 4-alkylidene-2-oxazolidinones from substituted propargyl carbamates.

4, entry 2) reacted faster than **1j**. *N*-Benzyl-*O*-propargyl carbamate (**1m**) required heating up to 70 °C for 5 h to achieve complete cyclization (Table 3,entry 13), whereas the corresponding substituted *N*-benzyl carbamate **5c** cyclized in 4 h at room temperature (Table 4, entry 3). Substitutions on the 3-position (when R_1 is not H in Scheme 4) tend to make the cyclization reaction slower. The carbamates **5d** and **5e** reacted much slower than **1a** and the cyclization reaction proceeded at a reasonable rate only when the reaction mixture was heated to 70 °C for 5 h. However, the carbamates **5f** and **5g**, where R^1 is a methyl group, did not cyclize to any noticeable extent (entries 6 and 7, Table 4) and resulted in the hydrolysis of the carbamates to the corresponding amines when heated for longer time with excess LiOH. The chloroformate used for the synthesis of the carbamates **5a**–**5c** was racemic and hence racemic mixtures of the oxazolidinones **6a**–**6c** were formed. Compounds **6d** and **6e** were isolated as mixtures of *E*- and *Z*-isomer and were crystalline solids. The structure of the *E*-isomer of **6d** was confirmed by X-ray crystallography (Fig. 2).[8]

Although the cyclization of *O*-propargyl carbamates worked well with LiOH as the catalyst in DMF, our efforts to cyclize *O*-but-3-ynyl carbamates to get the corresponding 4-methylenetetrahydro-1,3-oxazin-2-one derivatives under the same reaction conditions were unsuccessful (Scheme 6). The carbamate **7** did not yield any cyclized product on treatment with LiOH (0.1 equiv, 70 °C, 24 h, DMF). Reaction of **7**

Table 4. Synthesis of 4-alkylidene-2-oxazolidinones from substituted *O*-propargyl carbamates

Entry	Carbamates	Time, temp	2-Oxazolidinones	Yield[a] (%)
1	 **5a**	0.5 h, 28 °C	 **6a**	98
2	 **5b**	0.5 h, 28 °C	 **6b**	96
3	 **5c**	4 h, 28 °C	 **6c**	97
4	 **5d**	36 h, 28 °C or 5 h, 70 °C	 **6d**	85 [50 (*E*):50 (*Z*)]
5	 **5e**	5 h, 70 °C	 **6e**	90 [50 (*E*):50 (*Z*)]
6	 **5f**	24 h, 28 °C or 5 h, 70 °C	 **6f**	0
7	 **5g**	5 h, 70 °C	 **6g**	0

[a] Yield of isolated compounds.

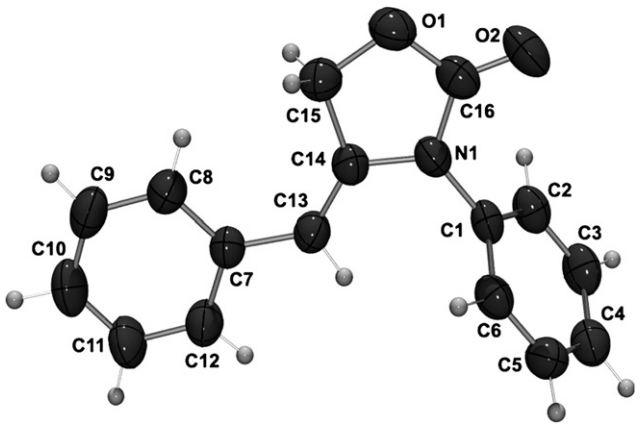
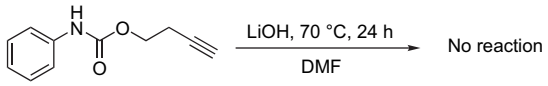


Figure 2. X-ray crystallographic structure of the *E*-isomer of compound **6d**.

with stoichiometric amounts of LiOH resulted in gradual hydrolysis of the carbamate to aniline.



7

Scheme 6. Reaction of *O*-but-3-ynyl carbamates with LiOH.

3. Conclusion

We have studied the effect of various bases and solvents on the well-known cyclization reaction of *O*-propargyl carbamates to 2-oxazolidinones and have developed a new catalyst–solvent system, LiOH in DMF, for easy and efficient cyclization of *N*-alkyl and *N*-aryl-*O*-propargyl carbamates. Cyclization reactions of various *O*-propargyl carbamates have been analyzed to understand the scope and limitations of this methodology. The carbamates were prepared from the corresponding amines using chloroformates allowing the inspection of carbamates diversely substituted on nitrogen. The method developed is the most efficient for the cyclization of *N*-aryl and *N*-alkyl propargyl carbamates. The conditions used are mild, which tolerate a number of other functionalities and even a propargyl carbonate group is unaffected. Substitutions at 3-position of the propargyl group tend to reduce the rate of the cyclization reaction whereas substitutions at 1-position of the propargyl group increases the cyclization rate. *O*-But-3-ynyl carbamates cannot be cyclized to the corresponding 4-methylene-1,3-oxazin-2-ones derivatives under the same reaction conditions. The present study extends the scope of a well-known reaction to practical levels.

4. Experimental section

4.1. General

All reactions were performed in oven dry apparatus and were stirred magnetically. Melting points reported are uncorrected. Infrared spectra were recorded using an FTIR instrument and the frequencies are reported in wave number (cm^{-1}) and intensities of the peaks are denoted as s (strong), w (weak), and m (medium). ^1H and ^{13}C NMR spectra were recorded on a 300 and 75 MHz spectrometer, respectively. Chemical shifts are reported in parts per million downfield from the internal reference, tetramethylsilane. Multiplicity is indicated using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), qu (quintet), m (multiplet), and br s (broad singlet). Coupling constants are reported wherever it is necessary in hertz (Hz). Mass spectra were recorded on a Q-TOF electrospray instrument.

4.2. General procedure for the preparation of propargyl chloroformates

To a stirred solution of triphosgene (2.23 g, 7.5 mmol) in dry ether (30 mL), activated charcoal (0.05 g) was added and stirred for 1 h at room temperature (28 °C). The solution was cooled to 0 °C and the propargyl alcohol (15 mmol) in dry ether (10 mL) was added dropwise. The resultant solution was stirred for 12 h and filtered. The ether layer was concentrated under reduced pressure and the remaining liquid was used for the reactions without further purification.

4.2.1. Propargyloxycarbonyl chloride. Greenish yellow liquid; ^1H NMR (300 MHz, $CDCl_3$): δ 2.6 (t, J=2.4, 1H), 4.7 (d, J=2.4, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.2, 77.6, 74.9, 58.3.

4.2.2. But-3-ynyl-2-oxycarbonyl chloride. Yellow liquid; ^1H NMR (300 MHz, $CDCl_3$): δ 5.40–5.45 (m, 1H), 2.64 (d, J=1.8, 1H), 1.63 (d, J=6.6, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.8, 79.4, 77.0, 68.0, 20.9.

4.2.3. But-2-ynyl-1-oxycarbonyl chloride. Greenish yellow liquid; ^1H NMR (300 MHz, $CDCl_3$): δ 4.83 (q, J=2.4, 2H), 1.89 (t, J=2.4, 3H); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 150.2, 86.2, 70.8, 59.5, 3.5.

4.2.4. 3-Phenylpropargyloxycarbonyl chloride. Yellowish brown oil; ^1H NMR (300 MHz, $CDCl_3$): δ 7.43–7.46 (m, 2H), 7.28–7.35 (m, 3H), 5.05 (s, 2H); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 150.2, 131.8, 129.2, 128.3, 121.2, 88.9, 80.9, 59.4.

4.2.5. But-3-ynyl-1-oxycarbonyl chloride. Pale yellow liquid; ^1H NMR (300 MHz, $CDCl_3$): δ 4.41 (t, J=6.9, 2H), 2.62–2.67 (m, 2H), 2.08 (t, J=2.4, 1H); ^{13}C NMR (75.45 MHz, $CDCl_3$): δ 150.5, 78.2, 70.8, 68.8, 18.6.

4.3. General procedure for the preparation of different propargyl carbamates

To a solution of the amine (2 mmol) in anhydrous dichloromethane (5 mL), $NaHCO_3$ (0.5 g) was added. The suspension was cooled to 0 °C and then propargyl chloroformate (2.1 mmol) was added dropwise over a period of 15 min. The reaction was followed by TLC till the disappearance of the starting material and was then filtered. The carbamate was then purified using column chromatography on a silica gel (100–200 mesh) column eluting with a solution of ethyl acetate in hexane.

4.3.1. Compound 1a. Colorless solid; yield: 95%; melting point: 62 °C; FTIR (Neat): 3297 (s), 2128 (w), 1716 (s);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36–7.39 (m, 2H), 7.24–7.31 (m, 2H), 7.04–7.09 (m, 1H), 6.91 (br s, 1H), 4.77 (d, J=2.4, 2H), 2.51 (t, J=2.4, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.5, 137.3, 128.9, 123.7, 118.8, 77.7, 74.9, 52.6; high resolution ESMS (*m/z*) calculated for $C_{10}H_9NO_2$+Na: 198.0531, observed: 198.0533.

4.3.2. Compound 1b. Data available in the literature.[9]

4.3.3. Compound 1c. Pale yellow solid; yield: 98%; melting point: 115 °C; FTIR (Neat): 3304 (s), 2129 (w), 1694 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29 (d, J=8.4, 2H), 6.85 (d, J=8.4, 2H), 6.70 (br s, 1H), 4.77 (d, J=2.4, 2H), 3.78 (s, 3H), 2.51 (t, J=2.4, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.1, 152.7, 130.3, 120.7, 114.2, 77.9, 74.9, 55.4, 52.6; high resolution ESMS (*m/z*) calculated for $C_{11}H_{11}NO_3$+Na: 228.0637, observed: 228.0636.

4.3.4. Compound 1d. Pale yellow solid; yield: 73%; melting point: 158 °C; FTIR (Neat): 3297 (s), 2130 (w), 1711 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.60 (br s, 1H), 7.88 (d, J=8.7, 2H), 7.62 (d, J=8.7, 2H), 4.79 (d, J=2.7, 2H), 2.63 (t, J=2.7, 1H), 2.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.5, 152.2, 142.8, 131.1, 129.0, 117.3, 77.4, 74.9, 51.9, 25.8; high resolution ESMS (*m/z*) calculated for $C_{12}H_{11}NO_3$+Na: 240.0637, observed: 240.0630.

4.3.5. Compound 1e. Yellow crystalline solid; yield: 58%; melting point: 178 °C; FTIR (Neat): 3301 (s), 2128 (w), 1718 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.91 (br s, 1H), 8.15 (d, J=9.3, 2H), 7.70 (d, J=9.3, 2H), 4.81 (d, J=2.7, 2H), 2.59 (t, J=2.7, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.3, 144.7, 142.1, 124.5, 117.7, 77.4, 75.1, 52.4; high resolution ESMS (*m/z*) calculated for $C_{10}H_8N_2O_4$+Na: 243.0382, observed: 243.0387.

4.3.6. Compound 1f. Pale yellow solid; yield: 90%; melting point: 126 °C; FTIR (Neat): 3297 (s), 2130 (w), 1698 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (d, J=9.0, 2H), 7.27 (d, J=9.0, 2H), 6.79 (br s, 1H), 4.78 (d, J=2.4, 2H), 2.52 (t, J=2.4, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.3, 135.9, 129.0, 128.8, 119.9, 77.6, 75.1, 52.8; high resolution ESMS (*m/z*) calculated for $C_{10}H_8{}^{35}ClNO_2$+Na: 232.0141; observed: 232.0144.

4.3.7. Compound 1g. Pale yellow solid; yield: 83%; melting point: 45 °C; FTIR (Neat): 3300 (s), 2131 (w), 1702 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (br s, 1H), 7.21–7.23 (m, 2H), 7.03–7.07 (m, 1H), 6.94 (br s, 1H), 4.78 (d, J=2.4, 2H), 2.53 (t, J=2.4, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.2, 138.5, 134.7, 130.0, 123.8, 118.7, 116.6, 77.5, 75.2, 52.9; high resolution ESMS (*m/z*) calculated for $C_{10}H_8{}^{35}ClNO_2$+Na: 232.0141, observed: 232.0145.

4.3.8. Compound 1h. White crystalline solid; yield: 82%; melting point: 59 °C; FTIR (Neat): 3302 (s), 2129 (w), 1709 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49–7.51 (m, 1H), 7.26–7.37 (m, 1H), 6.80–7.06 (m, 1H), 6.74–7.81 (m, 1H), 4.78 (d, J=2.4, 2H), 2.53 (t, J=2.4, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.0 (d, J_{C-F}=243), 152.3, 138.9 (d, J_{C-F}=11), 130.1 (d, J_{C-F}=10), 114.0, 110.4 (d, J_{C-F}=21), 106.2 (d, J_{C-F}=27), 77.5, 75.2, 52.8; high resolution ESMS (*m/z*) calculated for $C_{10}H_8FNO_2$+Na: 216.0437, observed: 216.0435.

4.3.9. Compound 1i. Pale yellow solid; yield: 76%; melting point: 102 °C; FTIR (Neat): 3304 (s), 2128 (w), 1699 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25–7.28 (m, 1H), 7.09–7.16 (m, 2H), 6.41 (br s, 1H), 4.77 (br s, 2H), 2.51 (br s, 1H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.9, 155.2, 138.1, 132.0, 129.3, 127.9, 127.0, 77.7, 75.0, 53.1, 18.7; high resolution ESMS (*m/z*) calculated for $C_{11}H_{10}{}^{35}ClNO_2$+Na: 246.0298, observed: 246.0297.

4.3.10. Compound 1j. Yellow solid; yield: 74%; melting point: 143 °C; FTIR (Neat): 3302 (s), 2130 (w), 1696 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84–7.87 (m, 3H), 7.66–7.69 (m, 1H), 7.43–7.54 (m, 3H), 7.08 (br s, 1H), 4.83 (d, J=2.4, 2H), 2.54 (t, J=2.4, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.8, 133.9, 131.9, 128.5, 126.8, 126.2, 125.7, 125.4, 125.3, 120.3, 77.8, 75.1, 52.9; high resolution ESMS (*m/z*) calculated for $C_{14}H_{11}NO_2$+Na: 248.0687, observed: 248.0691.

4.3.11. Compound 1k. Yellow solid; yield: 74%; melting point: 162 °C; FTIR (Neat): 3299 (s), 2135 (w), 1718 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.70 (br s, 1H), 7.66 (d, J=8.7, 2H), 7.55 (d, J=8.7, 2H), 4.80 (d, J=2.7, 2H), 2.59 (t, J=2.7, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.2, 142.7, 132.6, 118.9, 118.2, 105.1, 77.0, 75.0, 52.3; high resolution ESMS (*m/z*) calculated for $C_{11}H_8N_2O_2$+Na: 223.0483, observed: 223.0489.

4.3.12. Compound 1l. Data available in the literature.[9]

4.3.13. Compound 1m. Data available in the literature.[9]

4.3.14. Compound 1n. Colorless crystalline solid; yield: 95%; melting point: 71 °C; FTIR (Neat): 3297 (s), 2128 (w), 1716 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, J=8.4, 2H), 7.15 (d, J=8.4, 2H), 5.34 (br s, 1H), 4.69 (d, J=2.4, 2H), 4.31 (d, J=6.0, 2H), 2.48 (t, J=2.4, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.4, 137.1, 131.6, 129.1, 121.3, 78.0, 74.7, 52.6, 44.4; high resolution ESMS (*m/z*) calculated for $C_{11}H_{10}{}^{79}BrNO_2$+Na: 289.9793, observed: 289.9797.

4.3.15. Compound 1o. Data available in the literature.[9]

4.3.16. Compound 1p. Pale yellow oil; yield: 97%; FTIR (Neat): 3297 (s), 2129 (w), 1716 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.93 (br s, 1H), 4.68 (d, J=2.4, 2H), 3.19 (q, J=6.3, 2H), 2.48 (t, J=2.4, 1H), 1.44–1.54 (m, 2H), 1.28–1.40 (m, 2H), 0.92 (t, J=7.2, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.3, 78.3, 74.4, 52.2, 40.7, 31.8, 19.7, 13.6; high resolution ESMS (*m/z*) calculated for $C_8H_{13}NO_2$+Na: 178.0844, observed: 178.0846.

4.3.17. Compound 3. Data available in the literature.[9]

4.3.18. Compound 5a. Dark yellow oil; yield: 82%; FTIR (Neat): 3302 (s), 2127 (w), 1700 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27–7.40 (m, 4H), 7.07 (t, J=7.2, 1H), 6.77 (br s, 1H), 5.46–5.53 (m, 1H), 2.49 (d, J=1.8, 1H), 1.56 (d, J=6.6, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.1, 137.4, 129.0, 123.6, 118.7, 82.1, 73.1, 61.0, 21.4; high resolution

ESMS (*m*/*z*) calculated for $C_{11}H_{11}NO_2$+Na: 212.0687, observed: 212.0692.

4.3.19. Compound 5b. Yellow solid; yield: 85%; melting point: 119 °C; FTIR (Neat): 3299 (s), 2130 (w), 1710 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85–7.88 (m, 3H), 7.65–7.68 (m, 1H), 7.44–7.55 (m, 3H), 7.03 (br s, 1H), 5.52–5.60 (m, 1H), 2.52 (d, J=2.1, 1H), 1.60 (d, J=6.6, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.0, 134.0, 132.1, 128.7, 126.2, 126.0, 125.7, 125.1, 120.3, 119.1, 82.2, 73.2, 61.3, 21.5; high resolution ESMS (*m*/*z*) calculated for $C_{15}H_{13}NO_2$+Na: 262.0844, observed: 262.0849.

4.3.20. Compound 5c. Pale yellow solid; yield: 90%; melting point: 58 °C; FTIR (Neat): 3300 (s), 2131 (w), 1718 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26–7.35 (m, 5H), 5.39–5.46 (m, 1H), 5.13 (br s, 1H), 4.37 (d, J=6.0, 2H), 2.46 (d, J=2.1, 1H), 1.50 (d, J=6.6, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 138.1, 128.6, 127.4, 82.5, 72.7, 60.7, 45.0, 21.5; high resolution ESMS (*m*/*z*) calculated for $C_{12}H_{13}NO_2$+Na: 226.0844, observed: 226.0841.

4.3.21. Compound 5d. Yellow solid; yield: 82%; melting point: 81 °C; FTIR (Neat): 2139 (w), 1710 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39–7.47 (m, 4H), 7.27–7.32 (m, 5H), 7.04–7.09 (m, 1H), 6.88 (br s, 1H), 5.01 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.6, 137.4, 131.8, 129.0, 128.7, 128.2, 123.6, 122.0, 118.7, 86.6, 83.0, 53.5; high resolution ESMS (*m*/*z*) calculated for $C_{16}H_{13}NO_2$+Na: 274.0844, observed: 274.0848.

4.3.22. Compound 5e. Yellow solid; yield: 84%; melting point: 99 °C; FTIR (Neat): 2135 (w), 1712 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44–7.47 (m, 2H), 7.26–7.33 (m, 5H), 7.11 (d, J=8.4, 2H), 6.71 (br s, 1H), 5.01 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.7, 134.8, 133.3, 131.8, 129.5, 128.7, 128.2, 122.1, 118.9, 86.5, 83.1, 53.5, 20.7; high resolution ESMS (*m*/*z*) calculated for $C_{17}H_{15}NO_2$+Na: 288.1000, observed: 288.1003.

4.3.23. Compound 5f. White solid; yield: 85%; melting point: 66 °C; FTIR (Neat): 2131 (w), 1699 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37–7.40 (m, 2H), 7.26–7.32 (m, 2H), 7.02–7.08 (m, 1H), 6.87 (br s, 1H), 4.74 (q, J=2.4, 1H), 1.85 (t, J=2.4, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.7, 137.5, 128.9, 123.5, 118.7, 83.3, 73.2, 53.4, 3.5; high resolution ESMS (*m*/*z*) calculated for $C_{11}H_{11}NO_2$+Na: 212.0687, observed: 212.0694.

4.3.24. Compound 5g. Pale yellow solid; yield: 80%; melting point: 126 °C; FTIR (Neat): 2132 (w), 1704 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84–7.87 (m, 3H), 7.65–7.68 (m, 1H), 7.43–7.52 (m, 3H), 7.06 (br s, 1H), 4.81 (q, J=2.4, 2H), 1.88 (t, J=2.4, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.3, 134.0, 132.1, 128.7, 126.2, 125.9, 125.7, 125.1, 120.3, 119.0, 83.4, 73.3, 53.8, 3.6; high resolution ESMS (*m*/*z*) calculated for $C_{15}H_{13}NO_2$+Na: 262.0844, observed: 262.0847.

4.3.25. Compound 7. Pale yellow solid; yield: 93%; melting point: 54 °C; FTIR (Neat): 3297 (s), 2127 (w), 1698 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37–7.40 (m, 2H), 7.25–7.32 (m, 2H), 7.03–7.09 (m, 1H), 6.84 (br s, 1H), 4.27 (t, J=6.9, 2H), 2.55–2.60 (m, 2H), 2.04 (t, J=2.7, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.1, 137.6, 129.0, 123.5, 118.6, 80.2, 69.9, 62.8, 19.2; high resolution ESMS (*m*/*z*) calculated for $C_{11}H_{11}NO_2$+Na: 212.0688, observed: 212.0691.

4.4. General procedure for the cyclization of different *O*-propargyl carbamates

To a stirred solution of the *O*-propargyl carbamate (1 mmol) in DMF (2 mL), lithium hydroxide (2.4 mg, 0.1 mmol) was added. The reaction was followed by TLC until the complete disappearance of the starting material. DMF was then removed under vacuum and the residue was extracted with dichloromethane and filtered through a silica gel (60–120 mesh) column to get the corresponding 4-alkylidene-2-oxazolidinone.

4.4.1. Compound 2a. Colorless crystalline solid; yield: 99%; melting point: 93 °C; FTIR (Neat): 1760 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46–7.51 (m, 2H), 7.33–7.41 (m, 3H), 5.039 (t, J=2.4, 2H), 4.22–4.24 (m, 1H), 4.13–4.15 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.9, 141.7, 133.5, 129.5, 128.3, 126.8, 81.9, 67.0; high resolution ESMS (*m*/*z*) calculated for $C_{10}H_9NO_2$+Na: 198.0531, observed: 198.0533.

4.4.2. Compound 2b. Colorless crystalline solid; yield: 99%; melting point: 102 °C; FTIR (Neat): 1765 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (d, J=8.1, 2H), 7.21 (d, J=8.1, 2H), 5.03 (t, J=2.4, 2H), 4.18–4.21 (m, 1H), 4.11–4.13 (m, 1H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.1, 141.9, 138.4, 130.8, 130.2, 126.7, 81.8, 67.0, 21.1; high resolution ESMS (*m*/*z*) calculated for $C_{11}H_{11}NO_2$+Na: 212.0688, observed: 212.0694.

4.4.3. Compound 2c. Pale yellow crystalline solid; yield: 98%; melting point: 120 °C; FTIR (Neat): 1756 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24 (d, J=9, 2H), 6.99 (d, J=9, 2H), 5.03 (t, J=2.4, 2H), 4.14–4.17 (m, 1H), 4.10–4.13 (m, 1H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.3, 156.2, 142.2, 128.2, 126.0, 114.8, 81.7, 67.0, 55.4; high resolution ESMS (*m*/*z*) calculated for $C_{11}H_{11}NO_3$+Na: 228.0637, observed: 228.0636.

4.4.4. Compound 2d. Pale yellow solid; yield: 93%; melting point: 92 °C; FTIR (Neat): 1769 (s), 1704(s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (d, J=8.7, 2H), 7.49 (d, J=8.7, 2H), 5.07 (t, J=2.4, 2H), 4.35–4.38 (m, 1H), 4.23–4.26 (m, 1H), 2.63 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.8, 155.3, 140.6, 137.7, 136.3, 129.5, 126.5, 82.7, 67.1, 26.5; high resolution ESMS (*m*/*z*) calculated for $C_{12}H_{11}NO_3$+Na: 240.0637, observed: 228.0636.

4.4.5. Compound 2e. Yellow solid; yield: 98%; melting point: 172 °C; FTIR (Neat): 1774 (s); ^{1}H NMR (300 MHz, CD_3SOCD_3): δ 8.37 (d, J=9.3, 2H), 7.69 (d, J=9.3, 2H), 5.13 (t, J=2.4, 2H), 4.29–4.32 (m, 1H), 4.24–4.27 (m, 1H); ^{13}C NMR (75 MHz, CD_3SOCD_3): δ 154.8, 146.2, 141.0, 139.6, 127.8, 124.8, 82.2, 67.4; high resolution ESMS (*m*/*z*) calculated for $C_{10}H_8N_2O_4$+Na: 243.0382, observed: 243.0390.

4.4.6. Compound 2f. Pale yellow solid; yield: 98%; melting point: 119 °C; FTIR (Neat): 1768 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (d, J=8.7, 2H), 7.30 (d, J=8.7, 2H), 5.05

(t, J=2.4, 2H), 4.23–4.26 (m, 1H), 4.16–4.19 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.7, 141.3, 134.1, 132.0, 129.8, 128.2, 82.3, 67.1; high resolution ESMS (m/z) calculated for $C_{10}H_8{}^{35}ClNO_2$+Na: 232.0141, observed: 232.0140.

4.4.7. Compound 2g. Pale yellow solid; yield: 96%; melting point: 117 °C; FTIR (Neat): 1768 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33–7.47 (m, 3H), 7.25–7.31 (m, 1H), 5.05 (t, J=2.4, 2H), 4.27–4.30 (m, 1H), 4.19–4.22 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.6, 141.0, 134.9, 134.6, 130.5, 128.5, 127.1, 125.0, 82.5, 67.1; high resolution ESMS (m/z) calculated for $C_{10}H_8{}^{35}ClNO_2$+Na: 232.0141, observed: 232.0137.

4.4.8. Compound 2h. White solid; yield: 97%; melting point: 70 °C; FTIR (Neat): 1769 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43–7.50 (m, 1H), 7.08–7.19 (m, 3H), 5.05 (t, J=2.4, 2H), 4.311–4.33 (m, 1H), 4.19–4.22 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.8 (d, J_{C-F}=247), 155.5, 141.0, 134.8 (d, J_{C-F}=10), 130.7 (d, J_{C-F}=9), 122.5 (d, J_{C-F}=4), 115.3 (d, J_{C-F}=20), 114.3 (d, J_{C-F}=23), 82.5, 67.1; high resolution ESMS (m/z) calculated for $C_{10}H_8FNO_2$+Na: 216.0437, observed: 216.0441.

4.4.9. Compound 2i. Pale yellow solid; yield: 95%; melting point: 85 °C; FTIR (Neat): 1770 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36–7.39 (m, 1H), 7.23–7.31 (m, 2H), 5.124 (q, J=2.7, 2H), 4.12–4.15 (m, 1H), 3.81–3.84 (m, 1H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.0, 139.7, 139.5, 133.6, 130.3, 129.5, 129.3, 128.0, 81.9, 67.5, 17.7; high resolution ESMS (m/z) calculated for $C_{11}H_{10}{}^{35}ClNO_2$+Na: 246.0298, observed: 246.0300.

4.4.10. Compound 2j. Pale yellow solid; yield: 96%; melting point: 116 °C; FTIR (Neat): 1765 (s); ^{1}H NMR (300 Hz, $CDCl_3$): δ 7.91–7.99 (m, 2H), 7.71–7.74 (m, 1H), 7.46–7.59 (m, 4H), 5.12–5.26 (m, 2H), 4.10–4.12 (m, 1H), 3.81–3.84 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3, 142.3, 134.6, 129.8, 129.6, 129.5, 128.5, 127.1, 126.8, 126.6, 125.7, 122.2, 82.8, 67.4; high resolution ESMS (m/z) calculated for $C_{14}H_{11}NO_2$+Na: 248.0688, observed: 248.0691.

4.4.11. Compound 2k. Yellow solid; yield: 92%; melting point: 47 °C; FTIR (Neat): 1769 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, J=8.1, 2H), 7.55 (d, J=8.1, 2H), 5.08 (br s, 2H), 4.38–4.42 (m, 1H), 4.27–4.30 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.1, 140.2, 137.8, 133.4, 127.1, 117.9, 111.7, 83.1, 67.2; high resolution ESMS (m/z) calculated for $C_{11}H_8N_2O_2$+Na: 223.0484, observed: 223.0480.

4.4.12. Compound 2l. Colorless gummy solid; yield: 90%; FTIR (Neat): 3400 (br), 1763 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (d, J=8.4, 2H), 7.27 (d, J=8.4, 2H), 5.04 (t, J=2.4, 2H), 4.21–4.24 (m, 1H), 4.13–4.16 (m, 1H), 3.84 (t, J=6.6, 2H), 2.88 (t, J=6.6, 2H), 1.97 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.1, 141.7, 139.2, 131.7, 130.2, 126.9, 82.0, 67.1, 63.2, 38.6; high resolution ESMS (m/z) calculated for $C_{12}H_{13}NO_3$+Na: 242.0793, observed: 242.0795.

4.4.13. Compound 2m. Pale yellow solid; yield: 96%; melting point: 50 °C; FTIR (Neat): 1765 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26–7.34 (m, 5H), 4.88 (t, J=2.4, 2H), 4.65 (s, 2H), 4.13–4.16 (m, 1H), 4.06–4.08 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.4, 140.3, 134.9, 128.6, 127.7, 127.2, 81.5, 66.7, 45.1; high resolution ESMS (m/z) calculated for $C_{11}H_{11}NO_2$+Na: 212.0688, observed: 212.0685.

4.4.14. Compound 2n. Pale yellow solid; yield: 96%; melting point: 66 °C; FTIR (Neat): 1767 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (d, J=8.4, 2H), 7.18 (d, J=8.4, 2H), 4.90 (t, J=2.4, 2H), 4.60 (s, 2H), 4.09–4.13 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.5, 140.0, 133.9, 131.6, 128.9, 121.5, 81.5, 66.7, 44.4; high resolution ESMS (m/z) calculated for $C_{11}H_{10}{}^{79}BrNO_2$+Na: 289.9793, observed: 289.9801.

4.4.15. Compound 2o. White gummy solid; yield: 76%; FTIR (Neat): 1765 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.85 (t, J=2.4, 2H), 4.17–4.19 (m, 1H), 4.08–4.11 (m, 1H), 3.45 (t, J=7.2, 2H), 1.61 (q, J=7.2, 2H), 1.26 (br s, 18H), 0.88 (t, J=6.6, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.1, 140.9, 79.8, 66.6, 52.1, 41.3, 36.3, 31.7, 29.5, 29.4, 29.2, 29.1, 26.6, 26.2, 22.5, 13.9; high resolution ESMS (m/z) calculated for $C_{16}H2_9NO_2$+Na: 290.2096, observed: 290.2103.

4.4.16. Compound 2p. Colorless oil; yield: 68%; FTIR (Neat): 1765 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.86 (t, J=2.4, 2H), 4.13–4.15 (m, 1H), 4.05–4.07 (m, 1H), 3.53 (t, J=7.2, 2H), 1.56–1.68 (m, 2H), 1.30–1.43 (m, 2H), 0.95 (t, J=7.2, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.1, 140.3, 81.5, 66.7, 41.4, 31.1, 19.8, 13.6; high resolution ESMS (m/z) calculated for $C_8H_{13}NO_2$+Na: 178.0844, observed: 178.0851.

4.4.17. Compound 4. White solid; yield: 91%; melting point: 71 °C; FTIR (Neat): 3302 (s), 2129 (w), 1763 (s), 1750 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 (d, J=8.4, 2H), 7.29 (d, J=8.4, 2H), 5.05 (t, J=2.4, 2H), 4.72 (d, J=2.4, 2H), 4.39 (t, J=7.2, 2H), 4.22–4.25 (m, 1H), 4.14–4.16 (m, 1H), 3.04 (t, J=7.2, 2H), 2.55 (t, J=2.4, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.0, 154.3, 141.6, 137.5, 132.1, 130.1, 127.0, 82.0, 76.8, 75.7, 68.3, 67.1, 55.1, 34.5; high resolution ESMS (m/z) calculated for $C_{16}H_{15}NO_5$+Na: 324.0848, observed: 324.0852.

4.4.18. Compound 6a. Colorless crystalline solid; yield: 98%; melting point: 88 °C; FTIR (Neat): 1764 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26–7.50 (m, 5H), 5.22–5.29 (m, 1H), 4.19 (t, J=2.7, 1H), 4.08 (t, J=2.7, 1H), 1.61 (d, J=6, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 147.5, 133.8, 129.5, 128.2, 126.9, 81.8, 74.9, 21.1; high resolution ESMS (m/z) calculated for $C_{11}H_{11}NO_2$+Na: 212.0688, observed: 212.0688.

4.4.19. Compound 6b. Colorless crystalline solid; yield: 96% (mixture of two rotamers); melting point: 106 °C; FTIR (Neat): 1769 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90–7.98 (m, 2H), 7.44–7.75 (m, 5H), 5.33–5.47 (m, 1H), 4.03–4.06 (m, 1H), 3.76–3.79 (m, 1H), 1.74 and 1.68 (2d, J=6.6, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.4, 148.1, 148.0, 134.5, 129.8, 129.7, 129.6, 129.4, 128.55, 128.50, 127.1, 127.0, 126.8, 126.5, 125.6, 125.5, 122.2, 121.9, 82.6, 82.5, 75.4, 75.2, 21.7, 20.9; high resolution

ESMS (*m*/*z*) calculated for $C_{15}H_{13}NO_2$+Na: 262.0844, observed: 262.0839.

4.4.20. Compound 6c. Pale yellow gum; yield: 97%; FTIR (Neat): 1772 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26–7.38 (m, 5H), 5.05–5.12 (m, 1H), 4.67 (d, J=15.9, 1H), 4.60 (d, J=15.9, 1H), 4.09 (t, J=2.4, 1H), 3.99 (t, J=2.4, 1H), 1.49 (d, J=6.6, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.6, 146.0, 135.1, 128.6, 127.6, 127.1, 81.3, 74.7, 45.1, 21.0; high resolution ESMS (*m*/*z*) calculated for $C_{12}H_{13}NO_2$+Na: 226.0844, observed: 226.0846.

4.4.21. Compound 6d. Pale yellow crystalline solid; yield: 85% (mixture of *E*- and *Z*-isomer); melting point: 114 °C; FTIR (Neat): 1775 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.14–7.56 (m, 4H), 6.82–7.06 (m, 5H), 6.62–6.64 (m, 1H), 5.64 and 5.69 (2t, J=2.4, 1H), 5.37 and 5.13 (2d, J=2.4, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.0, 155.5, 136.9, 134.9, 134.6, 133.5, 132.8, 132.3, 129.8, 129.3, 128.7, 128.2, 128.1, 127.5, 127.1, 127.0, 126.9, 126.0, 125.9, 125.7, 101.5, 100.0, 68.1, 67.4; high resolution ESMS (*m*/*z*) calculated for $C_{16}H_{13}NO_2$+Na: 274.0844, observed: 274.0841.

4.4.22. Compound 6e. Pale yellow crystalline solid; yield: 90% (mixture of *E*- and *Z*-isomer); melting point: 95 °C; FTIR (Neat): 1773 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ set of multiplets from 6.63 to 7.35 (9H), 5.67 and 5.62 (2t, J=2.4, 1H), 5.37 and 5.13 (2d, J=2.4, 2H), 2.43 and 2.21 (2s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.2, 155.7, 141.1, 138.9, 137.1, 135.1, 132.9, 132.6, 132.0, 130.8, 130.4, 128.8, 128.7, 128.3, 127.4, 126.9, 126.0, 125.8, 125.6, 101.4, 99.6, 68.0, 67.4, 21.2, 20.9; high resolution ESMS (*m*/*z*) calculated for $C_{17}H_{15}NO_2$+Na: 288.1001, observed: 288.1000.

Acknowledgements

R.R. thanks CSIR, New Delhi for a Senior Research Fellowship and IISc for financial assistance.

Supplementary data

Copies of ^{1}H and ^{13}C NMR spectra of all new compounds. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.06.066.

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8. CCDC-638075 (**6d**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: 44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
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