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**Title:** Iodocarbamation of homopropargyl N-carbamates: mild and stereoselective entry to functionalized oxazinan-2-ones

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# Iodocarbamation of homopropargyl *N*-carbamates: mild and stereoselective entry to functionalized oxazinan-2-ones

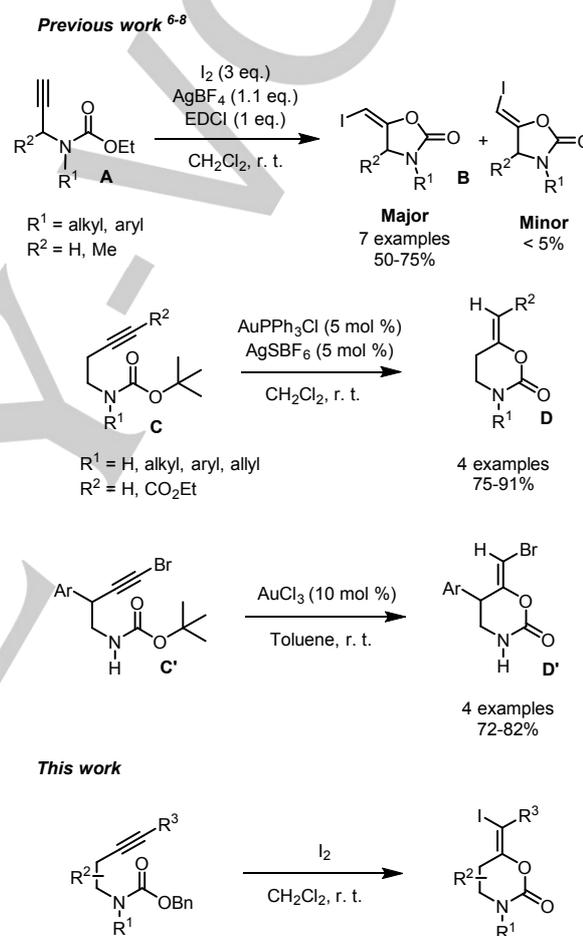
Pierre Quinodoz, Alexandre Quelhas, Karen Wright, Bruno Drouillat, Jérôme Marrot and François Couty\* <sup>[a]</sup>

**Abstract:** An efficient and general iodocarbamation of homopropargyl *N*-Cbz carbamates was developed using iodine as the electrophilic agent. This regio- and stereoselective cyclization yields (*E*)-6-iodomethylen-oxazinan-2-ones, which can be further transformed through palladium cross-coupling reactions followed by hydrogenation, to produce 1,3-oxazinan-2-ones.

## Introduction

Halocyclization of alkenes and alkynes is a very popular reaction that has a vast array of variations usually displaying high regio- and stereoselectivity. Since the seminal report of Bougault<sup>1</sup> with the first report of an iodolactonization, its long history has only recently culminated in enantioselective versions,<sup>2</sup> and has also found myriad of synthetic applications.<sup>3</sup> When *N*-carbamates are used as the nucleophilic partner, these moieties react on the activated  $\alpha$ - or  $\beta$ -alkene through their oxygen atom, followed by fragmentation, leading to oxazolidin-2-ones<sup>4</sup> or oxazinan-2-ones<sup>5</sup> with moderate to high diastereoselectivity. When the electrophilic partner is an alkyne, such halocarbamation reactions are more difficult to control, since the produced haloalkene is prone to react with the halogen source. Nevertheless, iodocarbamation of propargyl *N*-carbamates **A** promoted by iodine in the presence of EDCl and silver tetrafluoroborate as additives has been described<sup>6</sup> and gives stereoselectively (*E*)-5-iodomethylene oxazolidinones **B**. Concerning homopropargyl *N*-carbamates **C** or **C'**, Au(I)<sup>7</sup> and Au(III)<sup>8</sup>-mediated cyclocarbamations were reported recently and lead stereoselectively to oxazinan-2-ones **D** or **D'**. We report herein an in depth study of the halocarbamation of homopropargyl-*N*-Cbz carbamates and show that molecular iodine, is a suitable activating agent to promote such reactions (Scheme 1). This halogen, being cheap and non-toxic, has always played a central role in such reactions<sup>9</sup> but its use alone without other reagents has never been reported in this particular type of cyclocarbamation. We also report the reactivity of the obtained cyclized products towards cross-coupling and reduction reactions in order to demonstrate their synthetic relevance to access saturated oxazinan-2-ones, which are precursors of 1,3-

amino alcohols.<sup>10</sup>



**Scheme 1.** Cyclization of propargyl- and homopropargyl *N*-carbamates

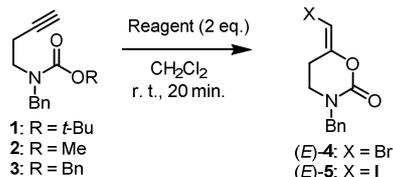
## Results and Discussion

The nature of the halogen source ( $\text{Br}_2$  or NBS, and  $\text{I}_2$  or NIS) and of the carbamate (*N*-Boc, *N*-Cbz or *N*-Carbomethoxymethyl) were first screened in the cyclocarbamation process with *N*-Bn, *N*-carbamoyl homopropargylamines **1-3** (Table 1). Within these combinations, it soon appeared that iodine (2 equiv.), combined with *N*-Cbz carbamate was the best (entry 5). Under these conditions, an excellent yield (94%) of isolated pure (*E*)-oxazinan-2-one **5** was obtained. The structure of this compound

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was determined by X-ray crystallography (Figure 1, left). It is noteworthy that crude reaction mixture showed a small amount (3%) of the (*Z*)-isomer of **5**, that was separated by flash chromatography. Furthermore, the cyclization reaction was fast and required only 20 min to reach completion. Other combinations were far less efficient: reactions with Br<sub>2</sub> or NBS (entries 1,2) were not complete after 20 min. These electrophiles also led to by-products **6-7** resulting from reaction of **4** with bromine or produced HBr (through deprotonation of the *t*-butyl cation), thus complicating purification. Structures of **6** and **7** were determined by X-Ray crystallography (Figure 1, right). Reaction with NIS was also more sluggish and required protracted reaction time (12 h) to reach completion (entry 6). With iodine as the electrophile, the nature of the carbamate proved to be a key parameter (entries 3-5). When a *N*-Boc group (entry 3) was used, cyclocarbamation was rapid but the release of HI also leads to by-products by reaction with the produced compound. Addition of a base (Et<sub>3</sub>N, 2 equiv.) as an acid scavenger did not avoid these side-reactions. Methyl carbamate reacted more sluggishly and the reaction did not reach completion after 20 min. Only *N*-Cbz carbamate, leading to the formation of benzyl iodide as a neutral by-product through nucleophilic attack of I<sup>-</sup> on the benzylic carbon in the cationic intermediate (as shown by <sup>1</sup>H NMR in the crude reaction mixture) secured stability of the produced alkenyl iodide.



**Table 1.** Experimental conditions optimization.

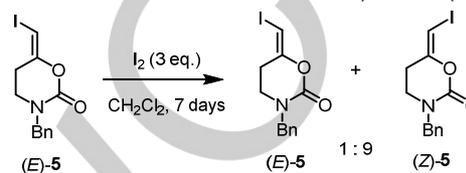
Entry	R	Reagent	Yield(%) <sup>[a]</sup>
1	<i>t</i> -Bu	Br <sub>2</sub>	52
2	<i>t</i> -Bu	NBS	53
3	<i>t</i> -Bu	I <sub>2</sub>	55
4	Me	I <sub>2</sub>	75
5	Bn	I <sub>2</sub>	94
6	Bn	NIS	18

<sup>[a]</sup> Yields refer to isolated product.

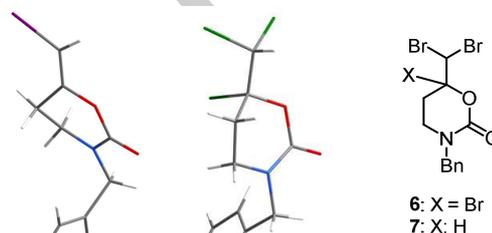
It is worthy to note that reaction time is also a key parameter, since iodine induces a slow isomerization<sup>11</sup> of the kinetically produced (*E*)-double bond, so that the (*Z*)-isomer was also often detected in the crude mixture, the two diastereoisomers being easily separated by chromatography. In order to minimize the presence of this (*Z*)-side-product, the reaction was followed by TLC until completion and was quenched immediately with an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to destroy the excess iodine. To confirm the isomerization process, we reacted isolated (*E*-

isomer **5** with 3 equivalents of iodine at room temperature. After 20 min, the (*Z*)-isomer was already detectable by <sup>1</sup>H NMR and the isomerization was almost complete after 7 days, with a 90:10 (*Z*):(*E*) ratio, from which (*Z*)-**5** was isolated pure with a 60% yield (Scheme 2).

Thermodynamic stabilities of these compounds were also evaluated by AM1 calculations (B3LYP 6.31G + level of theory), with SDD and DGDZVP basis set, and showed indeed a slight increased stability (0.24 Kcal. mol<sup>-1</sup> with the SDD basis set and 0.25 Kcal. mol<sup>-1</sup> with the DGDZVP basis set) for the (*Z*)-**5** isomer.



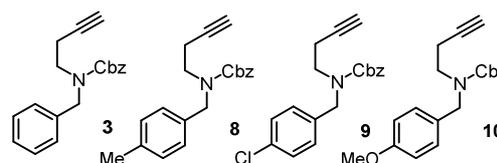
**Scheme 2.** Iodine mediated isomerization of the double bond

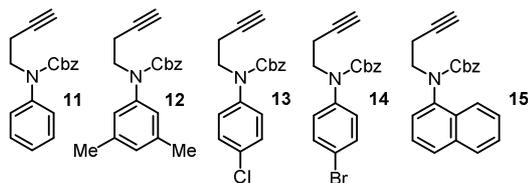
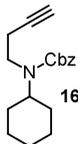


**Figure 1.** X-Ray structures of (*E*)-**5** (left) and of **6** (right). The crystalline lattice of **6/7** mixture shows a distribution of **6** (61%) and **7** (39%). Only **6** is shown.<sup>12</sup>

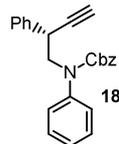
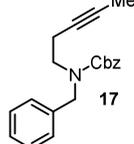
We next examined the scope of this iodocarbamation by varying the substituents on the nitrogen atom, the homopropargyl chain, and on the alkyne (Figures 2,3). We also examined the case of a propargyl *N*-carbamate **19**. Ethynyl *N*-benzylcarbamates **3** and **8-10** led to excellent yields of (*E*)-**5** and **20-22**, the (*Z*)-isomer being very minor (1-5%) in the crude reaction mixture. With the cyclohexylcarbamate **16**, the isomerization process is more rapid, and the yield of isolated (*E*)-**28** was lowered. On the contrary, electron poor *N*-Cbz anilines **11-15** reacted more slowly (90 min are required), so that isomerization occurs more significantly than with *N*-Cbz benzylamines. Substituted alkyne **17** gave a good yield of **29**, whose (*E*) stereochemistry was also confirmed by X-ray radiocrystallography,<sup>12</sup> and substituted substrate **18** gave **30** with high yield and total stereoselectivity. Finally, cyclization of propargylcarbamate **19** also gave (*E*)-oxazolidin-2-one **31** in excellent yield and total stereoselectivity.

#### *N*-benzyl substrates

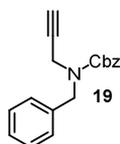


*N*-aryl substrates*N*-alkyl substrate

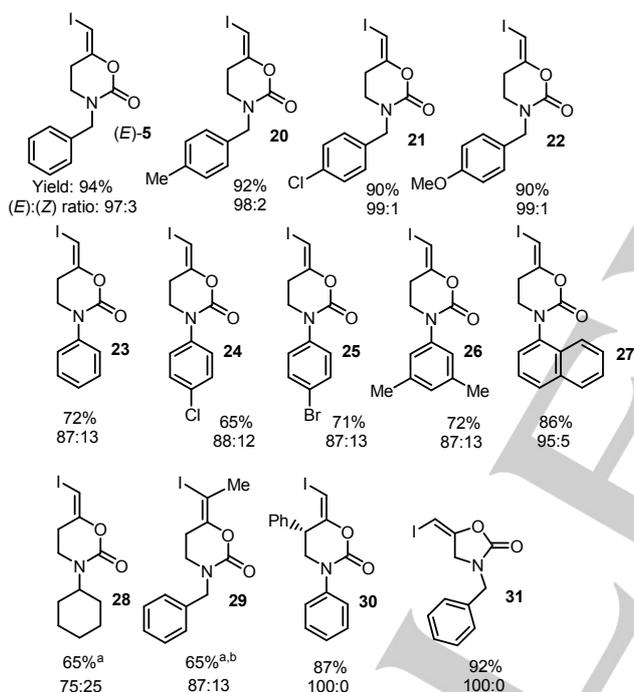
## Substituted substrates



## Propargylic substrate

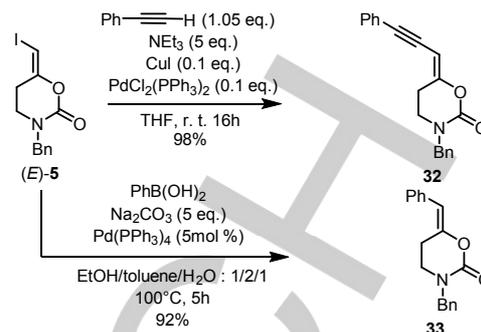


**Figure 1.** Structure of the carbamates **3** and **8-19** used to examine the scope of the iodocarbamation reaction.<sup>13</sup>



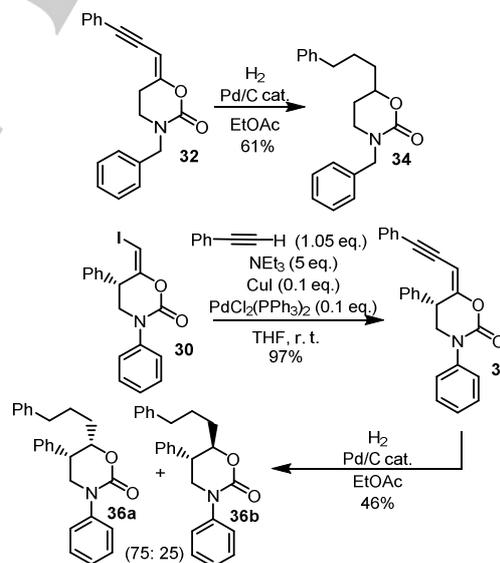
**Figure 2.** Structure and yields of the cyclized products. Yields refers to isolated pure (*E*)-isomer. <sup>a</sup>Reaction conducted at 0°C. <sup>b</sup>Structure of **29** was determined by X-ray radiocristallography.<sup>12</sup>

Carbon-carbon coupling reactions on vinylic iodide (*E*)-**5** were next investigated. Though  $\beta$ -lithio vinyl ether were reported to be stable,<sup>14</sup> lithium-iodide exchange in (*E*)-**5** promoted by *n*-Buli in THF at -78°C only led to rapid  $\beta$ -elimination and loss of CO<sub>2</sub> and gave *N*-Bn homopropargylamine as the only isolable product. On the other hand, Sonogashira and Suzuki-Miyaura cross-couplings<sup>15</sup> occurred uneventfully and gave **32** and **33** with high yields and full retention of configuration in the alkene (Scheme 3).



**Scheme 3.** C-C coupling reactions on (*E*)-**5** occur uneventfully.

Reduction of the iodomethylene moiety in **23** was next investigated. Surprisingly, this compound was found to be completely inert under classical hydrogenation conditions (H<sub>2</sub>, Pd/C cat., AcOEt, 16h). Enyne **32** could be hydrogenated to give fully saturated oxazinan-2-one **34** in fair yield. In order to evaluate the diastereoselectivity of such reaction, iodomethylene **30** was coupled with phenylacetylene to give **35**, which was hydrogenated to give in modest yield a non-separable mixture (75:25) of diastereoisomers **36a,b**. Structure of major isomer **36a** was not unambiguously ascertained but is proposed to be *cis* on the basis of AM1 calculations performed on each compound to determine its preferred conformation, combined with nOe experiments (see SI and Scheme 4).



**Scheme 4.** Hydrogenations of enynes leads to oxazinan-2-ones.

## Conclusions

In conclusion, we have developed an efficient iodine-mediated iodocarbamation of diversely substituted homopropargyl-carbamates. We have also demonstrated that both (*E*) and (*Z*)

isomers of the produced iodomethylene are accessible as respectively kinetic or thermodynamic products. Furthermore, reactivity towards reduction and functionalization of the vinylic iodide was evaluated. Thus, through a cross-coupling/hydrogenation sequence, we obtained functionalized saturated oxazinan-2-ones, synthetically relevant as 1-3-aminoalcohol precursors.

## Experimental Section

**General information:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 200 or 300 and 75 MHz, respectively; chemical shifts ( $\delta$ ) are reported in ppm and coupling constants ( $J$ ) reported in Hertz and rounded up to 0.1 Hz. Splitting patterns are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), septuplet (sep), multiplet (m), broad (br), or a combination of these. Solvents were used as internal standard when assigning NMR spectra ( $\delta$  H:  $\text{CDCl}_3$  7.26 ppm;  $\delta$  C:  $\text{CDCl}_3$  77.0 ppm). Assignments for signals from  $^1\text{H}$  and  $^{13}\text{C}$  in the NMR spectra were validated by two-dimensional correlated spectroscopy (2D COSY) and Heteronuclear Multiple Bond Correlation (HMBC). IR data were collected with an ATR-FT-IR spectrometer. All reactions were carried out under argon. Column chromatography was performed on silica gel (230–400 mesh) with use of various mixtures of  $\text{CH}_2\text{Cl}_2$ , EtOAc, petroleum ether (35–60°C fraction) (PE) and methanol. TLC was performed on Merck Kieselgel 60 F254 plates. Melting points are uncorrected. THF was distilled under argon from sodium using benzophenone as indicator. Dichloromethane was distilled from calcium hydride. Isomeric ratios were determined by NMR analysis of crude reaction mixtures before purification.

### General procedure for iodine mediated iodocarbation

Homopropargylcarbamate **3** or **8-19** (1 mmol) was dissolved in distilled dichloromethane (6 mL) and iodine (2 eq.) was then added at 0°C. The mixture was allowed to warm up to room temperature and was stirred until complete TLC conversion (from 15 min to 2 hours). It was then quenched by adding a saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  (10 mL) and stirred vigorously for 10 minutes. The phases were separated and the aqueous layer extracted with dichloromethane (3 x 15 mL). The organic layers were then washed with brine, dried on  $\text{MgSO}_4$  and the solvent was evaporated. The residue was purified by flash chromatography (eluent PE/EtOAc).

#### (E)-3-benzyl-6-(iodomethylene)-1,3-oxazinan-2-one (E)-5

Reaction time: 20 mn. White solid (309 mg, 94%); m.p. 80–82°C, Rf = 0.3 (AcOEt/EP : 20/80);  $^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) : 7.42–7.24 (m, 5H, Ph), 5.87 (s, 1H, CHI), 4.58 (s, 2H,  $\text{CH}_2\text{Ph}$ ), 3.22 (t,  $J = 6.3$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ), 2.77 (t,  $J = 6.3$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ) ppm.;  $^{13}\text{C}$  RMN (75 MHz,  $\text{CDCl}_3$ ) : 151.7 ( $\text{C}_q$ ), 150.4 ( $\text{C}_q$ ), 135.8 ( $\text{C}_q$ ), 128.9 ( $\text{C}_{Ar}$ ), 128.1 ( $\text{C}_{Ar}$ ), 128.1 ( $\text{C}_{Ar}$ ), 58.3 (CHI), 52.8 ( $\text{CH}_2\text{Ph}$ ), 42.4 ( $\text{NCH}_2\text{CH}_2$ ), 26.3 ( $\text{NCH}_2\text{CH}_2$ ) ppm.; IR (film)  $\nu_{\text{max}}$  3056, 1717, 1634, 1423, 1210, 1130, 740, 713, 693  $\text{cm}^{-1}$ ; ESIHRMS (positive mode) calcd. for  $\text{C}_{12}\text{H}_{13}\text{INO}_2$  [ $\text{M}+\text{H}$ ] $^+$ : 329.9991, found 329.9991.

#### (E)-6-(iodomethylene)-3-(4-methylbenzyl)-1,3-oxazinan-2-one 20

Reaction time: 20 mn. White solid (316 mg, 92%); m.p. 93–95°C, Rf = 0.45 (AcOEt/EP : 20/80);  $^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) :  $\delta = 7.19$  (d part of AB syst.,  $J = 8.7$  Hz, 2H, Ar), 7.16 (d part of AB syst.,  $J = 8.7$  Hz, 2H, Ar), 5.87 (s, 1H, CHI), 4.55 (s, 2H,  $\text{CH}_2\text{Ar}$ ), 3.21 (t,  $J = 6.3$  Hz, 2H,

$\text{NCH}_2\text{CH}_2$ ), 2.76 (t,  $J = 6.3$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ), 2.35 (s, 3H, Me) ppm.;  $^{13}\text{C}$  RMN (75 MHz,  $\text{CDCl}_3$ ) : 151.7 ( $\text{C}_q$ ), 150.4 ( $\text{C}_q$ ), 137.9 ( $\text{C}_q$ ), 132.7 ( $\text{C}_q$ ), 129.5 ( $\text{C}_{Ar}$ ), 128.2 ( $\text{C}_{Ar}$ ), 58.0 (CHI), 52.5 ( $\text{CH}_2\text{Ar}$ ), 42.2 ( $\text{NCH}_2\text{CH}_2$ ), 26.3 ( $\text{NCH}_2\text{CH}_2$ ), 21.1 (Me) ppm.; IR (film)  $\nu_{\text{max}}$  3069, 2910, 2850, 1709, 1697, 1638, 1425, 1133, 754  $\text{cm}^{-1}$ ; ESIHRMS (positive mode) calcd. for  $\text{C}_{13}\text{H}_{15}\text{INO}_2$  [ $\text{M}+\text{H}$ ] $^+$ : 344.0148, found 344.0149.

#### (E)-3-(4-chlorobenzyl)-6-(iodomethylene)-1,3-oxazinan-2-one 21

Reaction time: 20 mn. White solid (326 mg, 90%); m.p. 100–102°C, Rf = 0.40 (AcOEt/EP : 20/80);  $^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) :  $\delta = 7.35$  (d,  $J = 8.4$  Hz, 2H, Ar), 7.25 (d,  $J = 8.4$  Hz, 2H, Ar), 5.90 (s, 1H, CHI), 4.55 (s, 2H,  $\text{CH}_2\text{Ar}$ ), 3.23 (t,  $J = 6.3$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ), 2.79 (t,  $J = 6.2$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ) ppm.;  $^{13}\text{C}$  RMN (75 MHz,  $\text{CDCl}_3$ ) : 151.5 ( $\text{C}_q$ ), 150.4 ( $\text{C}_q$ ), 134.4 ( $\text{C}_q$ ), 134.0 ( $\text{C}_q$ ), 129.5 ( $\text{C}_{Ar}$ ), 129.1 ( $\text{C}_{Ar}$ ), 58.4 (CHI), 52.2 ( $\text{CH}_2\text{Ar}$ ), 42.5 ( $\text{NCH}_2\text{CH}_2$ ), 26.3 ( $\text{NCH}_2\text{CH}_2$ ) ppm.; IR (film)  $\nu_{\text{max}}$  3069, 2920, 1696, 1638, 1477, 1426, 1133, 1081, 1011, 755  $\text{cm}^{-1}$ ; ESIHRMS (positive mode) calcd. for  $\text{C}_{12}\text{H}_{12}\text{ClIO}_2$  [ $\text{M}+\text{H}$ ] $^+$ : 363.9609, found 363.9601

#### (E)-6-(iodomethylene)-3-(4-methoxybenzyl)-1,3-oxazinan-2-one 22

Reaction time: 20 mn. White solid (323 mg, 90%); m.p. 105–107°C, Rf = 0.60 (AcOEt/EP : 30/70);  $^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) :  $\delta = 7.15$  (d,  $J = 8.7$  Hz, 2H, Ar), 6.80 (d,  $J = 8.7$  Hz, 2H, Ar), 5.78 (s, 1H, CHI), 4.44 (s, 2H,  $\text{CH}_2\text{Ar}$ ), 3.73 (s, 3H, OMe), 3.13 (t,  $J = 6.4$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ), 2.68 (t,  $J = 6.3$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ) ppm.;  $^{13}\text{C}$  RMN (75 MHz,  $\text{CDCl}_3$ ) : 159.5 ( $\text{C}_q$ ), 151.7 ( $\text{C}_q$ ), 150.3 ( $\text{C}_q$ ), 129.6 ( $\text{C}_q$ ), 127.8 ( $\text{C}_{Ar}$ ), 114.2 ( $\text{C}_{Ar}$ ), 58.0 (CHI), 55.3 (OMe), 52.2 ( $\text{CH}_2\text{Ar}$ ), 42.1 ( $\text{NCH}_2\text{CH}_2$ ), 26.3 ( $\text{NCH}_2\text{CH}_2$ ) ppm.; IR (film)  $\nu_{\text{max}}$  3065, 2970, 2917, 1696, 1638, 1513, 1416, 1127, 830  $\text{cm}^{-1}$ ; ESIHRMS (positive mode) calcd. for  $\text{C}_{13}\text{H}_{15}\text{INO}_3$  [ $\text{M}+\text{H}$ ] $^+$ : 360.0097, found 360.0096.

#### (E)-6-(iodomethylene)-3-phenyl-1,3-oxazinan-2-one 23

Reaction time: 90 mn. White solid (226 mg, 72%); m.p. 138–140°C, Rf = 0.30 (AcOEt/EP : 15/85);  $^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) : 7.46–7.28 (m, 5H, Ph), 5.99 (t,  $J = 1.0$  Hz, 1H, CHI), 3.77 (t,  $J = 6.3$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ), 3.01 (td,  $J = 6.3$ , 1.0 Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ) ppm.;  $^{13}\text{C}$  RMN (75 MHz,  $\text{CDCl}_3$ ) : 151.6 ( $\text{C}_q$ ), 149.2 ( $\text{C}_q$ ), 141.9 ( $\text{C}_q$ ), 129.3 ( $\text{C}_{Ar}$ ), 127.2 ( $\text{C}_{Ar}$ ), 125.1 ( $\text{C}_{Ar}$ ), 58.4 (CHI), 46.5 ( $\text{NCH}_2\text{CH}_2$ ), 26.9 ( $\text{NCH}_2\text{CH}_2$ ) ppm.; IR (film)  $\nu_{\text{max}}$  3065, 1711, 1643, 1496, 1479, 1398, 1139, 760  $\text{cm}^{-1}$ ; ESIHRMS (positive mode) calcd. for  $\text{C}_{11}\text{H}_{11}\text{INO}_2$  [ $\text{M}+\text{H}$ ] $^+$ : 315.9835, found 315.9842.

#### (E)-3-(4-chlorophenyl)-6-(iodomethylene)-1,3-oxazinan-2-one 24

Reaction time: 90 mn. White solid (227 mg, 65%); m.p. 122–124°C, Rf = 0.60 (AcOEt/EP : 20/80);  $^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) : 7.36 (d,  $J = 8.7$  Hz, 2H, Ar), 7.25 (d,  $J = 8.6$  Hz, 2H, Ar), 5.97 (s, 1H, CHI), 3.71 (t,  $J = 6.2$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ), 2.98 (t,  $J = 6.2$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ) ppm.;  $^{13}\text{C}$  RMN (75 MHz,  $\text{CDCl}_3$ ) : 151.3 ( $\text{C}_q$ ), 149.0 ( $\text{C}_q$ ), 140.3 ( $\text{C}_q$ ), 132.7 ( $\text{C}_q$ ), 129.4 ( $\text{C}_{Ar}$ ), 126.4 ( $\text{C}_{Ar}$ ), 58.8 (CHI), 46.4 ( $\text{NCH}_2\text{CH}_2$ ), 26.8 ( $\text{NCH}_2\text{CH}_2$ ) ppm.; IR (film)  $\nu_{\text{max}}$  3061, 1708, 1697, 1641, 1421, 1321, 1149, 822  $\text{cm}^{-1}$ ; ESIHRMS (positive mode) calcd. for  $\text{C}_{11}\text{H}_{10}\text{ClINO}_2$  [ $\text{M}+\text{H}$ ] $^+$ : 349.9452, found 349.9448.

#### (E)-3-(4-bromophenyl)-6-(iodomethylene)-1,3-oxazinan-2-one 25

Reaction time: 90 mn. White solid (279 mg, 71%); m.p. 135–138°C, Rf = 0.70 (AcOEt/EP : 15/85);  $^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) : 7.54 (d,  $J = 8.7$  Hz, 2H, Ar), 7.22 (d,  $J = 8.7$  Hz, 2H, Ar), 5.99 (s, 1H, CHI), 3.74 (t,  $J = 6.2$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ), 3.01 (t,  $J = 6.2$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ) ppm.;  $^{13}\text{C}$  RMN (75 MHz,  $\text{CDCl}_3$ ) : 151.3 ( $\text{C}_q$ ), 148.9 ( $\text{C}_q$ ), 140.8 ( $\text{C}_q$ ), 132.4 ( $\text{C}_q$ ), 126.7 ( $\text{C}_{Ar}$ ), 120.6 ( $\text{C}_{Ar}$ ), 58.8 (CHI), 46.3 ( $\text{NCH}_2\text{CH}_2$ ), 26.8 ( $\text{NCH}_2\text{CH}_2$ )

ppm.; IR (film)  $\nu_{\max}$  3059, 1708, 1697, 1641, 1490, 1467, 1422, 1322, 1150, 822, 721  $\text{cm}^{-1}$ ; ESIHRMS (positive mode) calcd. for  $\text{C}_{11}\text{H}_{10}\text{BrINO}_2$   $[\text{M}+\text{H}]^+$ : 393.8940, found 393.8949.

#### (E)-3-(3,5-dimethylphenyl)-6-(iodomethylene)-1,3-oxazinan-2-one 26

Reaction time: 90 mn. White solid (247 mg, 72%); m.p. 138-140°C, Rf = 0.60 (AcOEt/EP : 20/80);  $^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) : 6.93 (s, 3H, Ar), 5.96 (s, 1H, CHI), 3.70 (t,  $J = 6.3$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ), 2.98 (t,  $J = 6.3$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ), 2.33 (s, 6H, Me) ppm.;  $^{13}\text{C}$  RMN (75 MHz,  $\text{CDCl}_3$ ) : 151.7 ( $\text{C}_q$ ), 149.2 ( $\text{C}_q$ ), 141.7 ( $\text{C}_q$ ), 139.2 ( $\text{C}_q$ ), 129.1 ( $\text{C}_{Ar}$ ), 123.0 ( $\text{C}_{Ar}$ ), 58.2 (CHI), 46.7 ( $\text{NCH}_2\text{CH}_2$ ), 26.9 ( $\text{NCH}_2\text{CH}_2$ ), 21.2 (Me) ppm.; IR (film)  $\nu_{\max}$  3065, 2913, 1716, 1637, 1481, 1409, 1154, 1113  $\text{cm}^{-1}$ ; ESIHRMS (positive mode) calcd. for  $\text{C}_{13}\text{H}_{15}\text{INO}_2$   $[\text{M}+\text{H}]^+$ : 344.0147, found 344.0148.

#### (E)-6-(iodomethylene)-3-(naphthalen-1-yl)-1,3-oxazinan-2-one 27

Reaction time: 90 mn. White solid (314 mg, 86%); m.p. 183-185°C, Rf = 0.40 (AcOEt/EP : 20/80);  $^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) : 7.97-7.85 (m, 2H, Ar), 7.85-7.76 (m, 1H, Ar), 7.65-7.42 (m, 4H, Ar), 6.08 (s, 1H, CHI), 3.86-3.67 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ), 3.25-3.01 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ) ppm.;  $^{13}\text{C}$  RMN (75 MHz,  $\text{CDCl}_3$ ) : 151.8 ( $\text{C}_q$ ), 149.4 ( $\text{C}_q$ ), 138.1 ( $\text{C}_q$ ), 134.8 ( $\text{C}_q$ ), 129.2 ( $\text{C}_q$ ), 129.0 ( $\text{C}_{Ar}$ ), 128.8 ( $\text{C}_{Ar}$ ), 127.3 ( $\text{C}_{Ar}$ ), 126.6 ( $\text{C}_{Ar}$ ), 125.8 ( $\text{C}_{Ar}$ ), 124.9 ( $\text{C}_{Ar}$ ), 121.8 ( $\text{C}_{Ar}$ ), 58.8 (CHI), 47.3 ( $\text{NCH}_2\text{CH}_2$ ), 26.9 ( $\text{NCH}_2\text{CH}_2$ ) ppm.; IR (film)  $\nu_{\max}$  3059, 1708, 1641, 1412, 1320, 1152, 1109, 805, 778, 746  $\text{cm}^{-1}$ ; ESIHRMS (positive mode) calcd. for  $\text{C}_{15}\text{H}_{13}\text{INO}_2$   $[\text{M}+\text{H}]^+$ : 365.9991, found 365.9990.

#### (E)-3-cyclohexyl-6-(iodomethylene)-1,3-oxazinan-2-one 28

Reaction time: 20 mn at 0°C. White solid (209 mg, 65%); m.p. 126-128°C, Rf = 0.60 (AcOEt/EP : 30/70);  $^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) : 5.82 (s, 1H, CHI), 4.20-4.05 (m, 1H, NCH), 3.24 (t,  $J = 6.3$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ), 2.78 (t,  $J = 6.2$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ), 1.90-1.52 (m, 6H, Cy), 1.44-1.34 (m, 3H, Cy), 1.08 (m, 1H, Cy) ppm.;  $^{13}\text{C}$  RMN (75 MHz,  $\text{CDCl}_3$ ) : 151.6 ( $\text{C}_q$ ), 149.8 ( $\text{C}_q$ ), 57.1 (CHI), 56.0 (NCH), 37.5 ( $\text{NCH}_2\text{CH}_2$ ), 29.7 (Cy), 26.8 ( $\text{NCH}_2\text{CH}_2$ ), 25.5 (Cy), 25.3 (Cy) ppm.; IR (film)  $\nu_{\max}$  3062, 2914, 2849, 1705, 1638, 1420, 1305, 1175, 1112, 819, 739  $\text{cm}^{-1}$ ; ESIHRMS (positive mode) calcd. for  $\text{C}_{11}\text{H}_{17}\text{INO}_2$   $[\text{M}+\text{H}]^+$ : 322.0304, found 322.0304.

#### (E)-3-benzyl-6-(1-iodoethylidene)-1,3-oxazinan-2-one 29

Reaction time: 20 mn at 0°C. White solid (223 mg, 65%); m.p. 110-112°C, Rf = 0.30 (AcOEt/EP : 15/85);  $^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) : 7.41-7.24 (m, 5H, Ph), 4.59 (s, 2H,  $\text{CH}_2\text{Ph}$ ), 3.19 (t,  $J = 6.3$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ), 2.84 (td,  $J = 6.3$ , 1.3 Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ), 2.51 (t,  $J = 1.3$  Hz, 3H, Me) ppm.;  $^{13}\text{C}$  RMN (75 MHz,  $\text{CDCl}_3$ ) : 150.8 ( $\text{C}_q$ ), 145.4 ( $\text{C}_q$ ), 136.0 ( $\text{C}_q$ ), 128.8 ( $\text{C}_{Ar}$ ), 128.2 ( $\text{C}_{Ar}$ ), 128.0 ( $\text{C}_{Ar}$ ), 78.0 ( $\text{C}_q$ ), 52.8 ( $\text{NCH}_2\text{Ph}$ ), 42.8 ( $\text{NCH}_2\text{CH}_2$ ), 29.0 ( $\text{NCH}_2\text{CH}_2$ ), 24.9 (Me) ppm.; IR (film)  $\nu_{\max}$  2942, 2907, 1711, 1660, 1444, 1204, 1168, 1104, 1076, 697, 604  $\text{cm}^{-1}$ ; ESIHRMS (positive mode) calcd. for  $\text{C}_{13}\text{H}_{15}\text{INO}_2$   $[\text{M}+\text{H}]^+$ : 344.0148, found 344.0153.

#### (R,E)-6-(iodomethylene)-3,5-diphenyl-1,3-oxazinan-2-one 30

Reaction time: 90mn. White solid (340 mg, 87%); m.p. 162-164°C, Rf = 0.30 (AcOEt/EP : 5/95);  $[\alpha]_D^{20} = -61$  (c.1.4,  $\text{CHCl}_3$ );  $^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) : 7.54-7.13 (m, 9H, Ph), 6.99 (d,  $J = 5.6$  Hz, 2H, Ph), 6.20 (s, 1H, CHI), 4.61-4.53 (m, 1H, CHPh), 4.29 (dd,  $J = 12.4$ , 3.8 Hz, 1H, NCHH), 3.79 (dd,  $J = 12.4$ , 2.0 Hz, 1H, NCHH) ppm.;  $^{13}\text{C}$  RMN (75 MHz,  $\text{CDCl}_3$ ) : 153.3 ( $\text{C}_q$ ), 149.0 ( $\text{C}_q$ ), 141.7 ( $\text{C}_q$ ), 136.5 ( $\text{C}_q$ ), 129.3 ( $\text{C}_{Ar}$ ), 129.2 ( $\text{C}_{Ar}$ ), 128.0 ( $\text{C}_{Ar}$ ), 127.3 ( $\text{C}_{Ar}$ ), 127.1 ( $\text{C}_{Ar}$ ), 125.4 ( $\text{C}_{Ar}$ ), 60.3 (CHI), 53.1 ( $\text{NCH}_2$ ), 41.7 (CHPh) ppm.; IR (film)  $\nu_{\max}$  3065, 3021, 1707, 1631,

1492, 1408, 1137, 1116, 694  $\text{cm}^{-1}$ ; ESIHRMS (positive mode) calcd. for  $\text{C}_{17}\text{H}_{15}\text{INO}_2$   $[\text{M}+\text{H}]^+$ : 392.0148, found 392.0143.

#### (E)-3-benzyl-5-(iodomethylene)-1,3-oxazolidin-2-one 31

Reaction time: 20 mn. White solid (290 mg, 92%); m.p. 104-106°C, Rf = 0.4 (AcOEt/EP : 10/90);  $^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) : 7.47-7.25 (m, 5H, Ph), 5.75 (t,  $J = 2.7$  Hz, 1H, CHI), 4.51 (s, 2H,  $\text{CH}_2\text{Ph}$ ), 3.97 (d,  $J = 2.7$  Hz, 2H,  $\text{CH}_2\text{CHI}$ ) ppm.;  $^{13}\text{C}$  RMN (75 MHz,  $\text{CDCl}_3$ ) : 155.40 ( $\text{C}_q$ ), 148.31 ( $\text{C}_q$ ), 134.61 ( $\text{C}_q$ ), 129.13 ( $\text{C}_{Ar}$ ), 128.48 ( $\text{C}_{Ar}$ ), 128.2 ( $\text{C}_{Ar}$ ), 50.91 (CHI), 50.29 ( $\text{CH}_2\text{CHI}$ ), 48.05 ( $\text{CH}_2\text{Ph}$ ) ppm.; IR (film)  $\nu_{\max}$  3069, 2948, 1769, 1664, 1422, 1226, 1051, 741, 692  $\text{cm}^{-1}$ ; ESIHRMS (positive mode) calcd. for  $\text{C}_{13}\text{H}_{15}\text{INO}_2$   $[\text{M}+\text{H}]^+$ : 315.9829, found 315.9824.

#### Pd-catalyzed coupling reactions

*Sonogashira cross-coupling.* In a flame dried roundbottom, the oxazinanone (1 mmol) was dissolved in dry THF (15 mL). Copper iodide (0.1 mmol, 19 mg), triethylamine (5 mmol, 0.7 mL) and phenylacetylene (1.05 mmol, 115  $\mu\text{L}$ ) were added. The reaction mixture was degassed by argon bubbling for 15 min and palladium catalyst  $\text{PdCl}_2(\text{PPh}_3)_2$  was added afterwards. After stirring 12h at room temperature, THF was removed, the crude product dissolved in EtOAc and water, then extracted with EtOAc (3x 20 mL). The organic layers were washed with brine, dried on  $\text{MgSO}_4$  and the solvent was evaporated. The residue was purified by flash chromatography (eluent PE/EtOAc).

*Suzuki-Miyaura cross-coupling.* In a sealed tube, a solution of oxazinanone (1 mmol.) in toluene (5 mL), a solution of phenylboronic acid (244 mg, 2 mmol.) in absolute EtOH (3 mL) and a 2M aqueous solution of  $\text{Na}_2\text{CO}_3$  (3 mL) were stirred together while argon was bubbled through the mixture for 15 min.  $\text{Pd}(\text{PPh}_3)_4$  (57 mg, 5 mol%) was then added and the mixture was stirred at 100°C under argon for 5h, then cooled to room temperature and poured into EtOAc and water. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, then dried over  $\text{MgSO}_4$ . The residue was then purified by flash chromatography.

#### (E)-3-benzyl-6-(3-phenylprop-2-yn-1-ylidene)-1,3-oxazinan-2-one 32

Yellow solid (297 mg, 98%); m.p. 117-119°C, Rf = 0.30 (AcOEt/EP : 20/80);  $^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) : 7.50-7.19 (m, 10H, Ph), 5.54 (s, 1H,  $\text{PhCCCH}$ ), 4.63 (s, 2H,  $\text{CH}_2\text{Ph}$ ), 3.30 (t,  $J = 6.3$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ), 2.91 (t,  $J = 6.2$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ) ppm.;  $^{13}\text{C}$  RMN (75 MHz,  $\text{CDCl}_3$ ) : 157.7 ( $\text{C}_q$ ), 150.4 ( $\text{C}_q$ ), 135.8 ( $\text{C}_q$ ), 131.2 ( $\text{C}_{Ar}$ ), 128.9 ( $\text{C}_{Ar}$ ), 128.4 ( $\text{C}_{Ar}$ ), 128.2 ( $\text{C}_{Ar}$ ), 128.1 ( $\text{C}_{Ar}$ ), 128.1 ( $\text{C}_{Ar}$ ), 123.2 ( $\text{C}_q$ ), 94.1 ( $\text{C}_q$ ), 90.6 ( $\text{PhCCCH}$ ), 83.5 ( $\text{PhCCCH}$ ), 52.9 ( $\text{CH}_2\text{Ph}$ ), 42.3 ( $\text{NCH}_2\text{CH}_2$ ), 23.9 ( $\text{NCH}_2\text{CH}_2$ ) ppm.; IR (film)  $\nu_{\max}$  3053, 2910, 2847, 1720, 1632, 1485, 1429, 1139, 753  $\text{cm}^{-1}$ ; ESIHRMS (positive mode) calcd. for  $\text{C}_{20}\text{H}_{17}\text{NO}_2$   $[\text{M}+\text{H}]^+$ : 304.1338, found 304.1343.

#### (E)-3-benzyl-6-benzylidene-1,3-oxazinan-2-one 33

Yellow solid (257 mg, 92%); m.p. 86-88°C, Rf = 0.75 (AcOEt/EP : 20/80);  $[\alpha]_D^{20} = -297$  (c.1.55,  $\text{CHCl}_3$ );  $^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ) :  $\delta$  (ppm) : 7.39-6.95 (m, 10H, Ph), 6.28 (s, 1H, CHPh), 4.54 (s, 2H,  $\text{CH}_2\text{Ph}$ ), 3.12 (t,  $J = 6.1$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ), 2.75 (t,  $J = 6.1$  Hz, 2H,  $\text{NCH}_2\text{CH}_2$ ) ppm.;  $^{13}\text{C}$  RMN (75 MHz,  $\text{CDCl}_3$ ) : 151.4 ( $\text{C}_q$ ), 148.3 ( $\text{C}_q$ ), 136.1 ( $\text{C}_q$ ), 134.3 ( $\text{C}_q$ ), 128.9 ( $\text{C}_{Ar}$ ), 128.7 ( $\text{C}_{Ar}$ ), 128.5 ( $\text{C}_{Ar}$ ), 128.2 ( $\text{C}_{Ar}$ ), 128.0 ( $\text{C}_{Ar}$ ), 126.9 ( $\text{C}_{Ar}$ ), 110.2 (CHPh), 52.7 ( $\text{CH}_2\text{Ph}$ ), 42.7 ( $\text{NCH}_2\text{CH}_2$ ), 23.1 ( $\text{NCH}_2\text{CH}_2$ ) ppm.; IR (film)  $\nu_{\max}$  3050, 2894, 1701, 1656, 1492, 1445, 1419, 1219, 1133, 694  $\text{cm}^{-1}$ ; ESIHRMS (positive mode) calcd. for  $\text{C}_{18}\text{H}_{18}\text{NO}_2$   $[\text{M}+\text{H}]^+$ : 280.1338, found 280.1342.

**(R,E)-3,5-diphenyl-6-(3-phenylprop-2-yn-1-ylidene)-1,3-oxazinan-2-one 35**

Brown oil (354 mg, 97%); Rf = 0.30 (AcOEt/EP : 5/95);  $[\alpha]_D^{20} = -297$  (c.1.55, CHCl<sub>3</sub>); <sup>1</sup>H RMN (300 MHz, CDCl<sub>3</sub>) :  $\delta$  (ppm) : 7.37-7.12 (m, 13H, Ph), 6.98 (d,  $J = 8.3$  Hz, 2H, Ph), 5.69 (s, 1H, PhCCH), 4.63 (dd,  $J = 3.8, 2.1$  Hz, 1H, NCH<sub>2</sub>C<sup>H</sup>Ph), 4.24 (dd,  $J = 12.3, 3.9$  Hz, 1H, NCH<sub>2</sub>C<sup>H</sup>Ph), 3.78 (dd,  $J = 12.3, 2.2$  Hz, 1H, NCH<sub>2</sub>C<sup>H</sup>Ph) ppm.; <sup>13</sup>C RMN (75 MHz, CDCl<sub>3</sub>) : 159.4 (C<sub>q</sub>), 149.0 (C<sub>q</sub>), 141.9 (C<sub>q</sub>), 137.4 (C<sub>q</sub>), 131.3 (C<sub>Ar</sub>), 129.4 (C<sub>Ar</sub>), 129.2 (C<sub>Ar</sub>), 128.3 (C<sub>Ar</sub>), 128.3 (C<sub>Ar</sub>), 127.9 (C<sub>Ar</sub>), 127.3 (C<sub>Ar</sub>), 127.1 (C<sub>Ar</sub>), 125.4 (C<sub>Ar</sub>), 123.1 (C<sub>q</sub>), 94.9 (C<sub>q</sub>), 92.2 (PhCCH), 83.3 (C<sub>q</sub>), 52.7 (NCH<sub>2</sub>C<sup>H</sup>Ph), 39.3 (NCH<sub>2</sub>C<sup>H</sup>Ph) ppm.; IR (film)  $\nu_{\max}$  3062, 3034, 1724, 1634, 1490, 1401, 1162, 1130, 753, 689 cm<sup>-1</sup>; ESIHRMS (positive mode) calcd. for C<sub>25</sub>H<sub>20</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 366.1494, found 366.1491.

**General procedure for hydrogenations**

The oxazinanone (1 mmol) was dissolved in EtOAc (4 mL) and 10% Pd on charcoal (1 wt eq.) was added. The mixture was stirred under a H<sub>2</sub> atmosphere (1 bar) for 12 hours, it was then filtered on Celite®. The solvent was evaporated and residue purified by flash chromatography (eluent PE/EtOAc).

**(R,S)-3-benzyl-6-(3-phenylpropyl)-1,3-oxazinan-2-one 34**

Oil (188 mg, quant.); Rf = 0.30 (AcOEt/EP : 25/75); <sup>1</sup>H RMN (300 MHz, CDCl<sub>3</sub>) :  $\delta$  (ppm) : 7.40-7.13 (m, 10H, Ph), 4.63 and 4.51 (two d,  $J = 14.9$  Hz, 2H, NCH<sub>2</sub>Ph), 4.28-4.17 (m, 1H, OCH), 3.29-3.08 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 2.66 (t,  $J = 7.1$  Hz, 2H, PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.18 (s, 1H), 1.98-1.54 (m, 6H, PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> and NCH<sub>2</sub>CH<sub>2</sub>) ppm.; <sup>13</sup>C RMN (75 MHz, CDCl<sub>3</sub>) : 154.2 (C<sub>q</sub>), 141.8 (C<sub>q</sub>), 136.8 (C<sub>q</sub>), 128.7 (C<sub>Ar</sub>), 128.4 (C<sub>Ar</sub>), 128.4 (C<sub>Ar</sub>), 128.1 (C<sub>Ar</sub>), 127.6 (C<sub>Ar</sub>), 125.9 (C<sub>Ar</sub>), 77.0 (OCH) 52.5 (NCH<sub>2</sub>Ph), 43.7 (NCH<sub>2</sub>CH<sub>2</sub>), 35.6 (PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 34.5, 27.2 and 26.5 (NCH<sub>2</sub>CH<sub>2</sub> and PhCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) ppm.; IR (film)  $\nu_{\max}$  2926, 2869, 1681, 1449, 1260, 1131, 729, 698 cm<sup>-1</sup>; ESIHRMS (positive mode) calcd. for C<sub>20</sub>H<sub>24</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 310.1807, found 310.1811.

**(5R,6S)-3,5-diphenyl-6-(3-phenylpropyl)-1,3-oxazinan-2-one 36a and (5R,6R)-3,5-diphenyl-6-(3-phenylpropyl)-1,3-oxazinan-2-one 36b**

Oil (171 mg, 46%); Rf = 0.40 (Major) and 0.25 (minor) (AcOEt/EP : 25/75); <sup>1</sup>H RMN (300 MHz, CDCl<sub>3</sub>) :  $\delta$  (ppm) : 7.35-6.95 (m, 15H<sup>M</sup> and 15H<sup>m</sup>, Ph), 4.65-4.48 (m, 1H<sup>M</sup> and 1H<sup>m</sup>, OCH), 4.00 (dd,  $J = 11.8, 5.7$  Hz, 1H<sup>M</sup>, NCH<sub>2</sub>), 3.85-3.68 (m, 1H<sup>M</sup> and 1H<sup>m</sup>, NCH<sub>2</sub>), 3.64 (dd,  $J = 11.8, 5.4$  Hz, 1H<sup>m</sup>, NCH<sub>2</sub>), 3.34-3.24 (m, 1H<sup>M</sup>, C<sup>H</sup>Ph), 3.12 (td,  $J = 10.8, 5.4$  Hz, 1H<sup>m</sup>, C<sup>H</sup>Ph), 2.50 (t,  $J = 7.3$  Hz, 2H<sup>M</sup> and 2H<sup>m</sup>, CH<sub>2</sub>Ph), 1.95-1.33 (m, 4H<sup>M</sup> and 4H<sup>m</sup>, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph) ppm.; <sup>13</sup>C RMN (75 MHz, CDCl<sub>3</sub>) : 152.8 (C<sub>q</sub><sup>M</sup>), 151.9 (C<sub>q</sub><sup>m</sup>), 142.7 (C<sub>q</sub><sup>M</sup>), 142.5 (C<sub>q</sub><sup>m</sup>), 141.7 (C<sub>q</sub><sup>M</sup> and <sup>m</sup>), 137.4 (C<sub>q</sub><sup>M</sup>), 137.0 (C<sub>q</sub><sup>m</sup>), 129.8 (C<sub>Ar</sub>), 129.4 (C<sub>Ar</sub>), 129.2 (C<sub>Ar</sub>), 129.0 (C<sub>Ar</sub>), 128.4 (C<sub>Ar</sub>), 128.4 (C<sub>Ar</sub>), 128.3 (C<sub>Ar</sub>), 128.0 (C<sub>Ar</sub>), 127.9 (C<sub>Ar</sub>), 127.7 (C<sub>Ar</sub>), 127.1 (C<sub>Ar</sub>), 126.8 (C<sub>Ar</sub>), 126.1 (C<sub>Ar</sub>), 125.9 (C<sub>Ar</sub>), 125.8 (C<sub>Ar</sub>), 125.6 (C<sub>Ar</sub>), 81.3 (OC<sup>M</sup>H), 80.0 (OC<sup>m</sup>H), 54.9 (NC<sup>M</sup>H<sub>2</sub>), 53.7 (NC<sup>m</sup>H<sub>2</sub>), 44.1 (C<sup>M</sup>HPh), 41.0 (C<sup>m</sup>HPh), 35.42 (C<sup>M</sup>H<sub>2</sub>Ph), 35.37 (C<sup>m</sup>H<sub>2</sub>Ph), 32.4 (C<sup>M</sup>H<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 31.1 (C<sup>m</sup>H<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Ph), 27.1 (CH<sub>2</sub>C<sup>M</sup>H<sub>2</sub>CH<sub>2</sub>Ph), 26.0 (CH<sub>2</sub>C<sup>m</sup>H<sub>2</sub>CH<sub>2</sub>Ph) ppm.; IR (film)  $\nu_{\max}$  3059, 3024, 2929, 1692, 1494, 1420, 1152, 752, 695 cm<sup>-1</sup>; ESIHRMS (positive mode) calcd. for C<sub>25</sub>H<sub>26</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 372.1964, found 372.1957.

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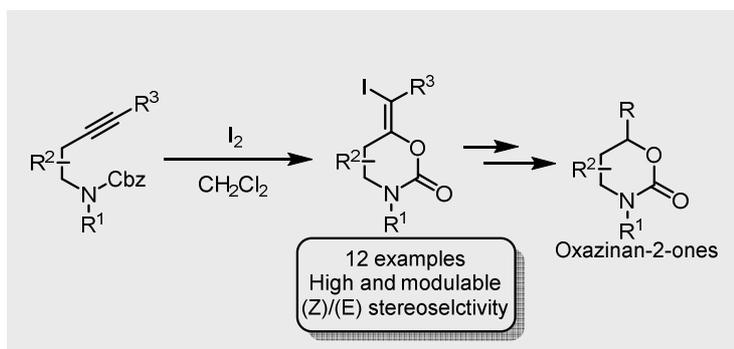
**Keywords:** halocarbamation • iodine • oxazinan-2-one

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**Halocarbamation reaction\***

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Marrot and François Couty\*

Page No. – Page No.

**Iodocarbamation of homopropargyl  
N-carbamates: mild and  
stereoselective entry to  
functionalized oxazinan-2-ones**

Iodocarbamation of *N*-Cbz homopropargylamines gives high yields of stereodefined 6-iodomethylene oxazin-2-ones, that can further be transformed into oxazinan-2-ones.