

A Simple Access to the Synthesis of 5,6-Dihydro-4H-1,3-Oxazines Under Solvent-Free Conditions and Microwave Irradiation

M.R. Taati¹, M. Mamaghani^{1,*}, N.O. Mahmoodi¹ and A. Loghmanifar¹

Abstract. 2-Arylsubstituted 5,6-dihydro-4H-1,3-oxazines were conveniently synthesized by the condensation of 3-aminopropanol and desired carboxylic acids under solvent-free and microwave conditions, in short reaction times, and moderate to good yields. Also a comparison was made between this method and the classical protocols using acid halides and nitrile substrates.

Keywords: Oxazine; *N*-acylaminoalcohol; Aminoalcohol; Solvent-free; Microwave.

INTRODUCTION

The synthetic utility of dihydro-1,3-oxazines as a useful intermediate for the synthesis of ketones [1], unusual aldehydes such as trans β -inoglidene acetaldehyde [2-5], carboxylic acids, stereoselective synthesis of trans-olefins, complex heterocyclic systems and biologically active compounds has been well documented [6-8]. Recently, a 1,3-oxazine ring system was employed in the design of a molecular switch based on the photoinduced opening and thermal closing of the oxazine ring [9].

Several synthetic approaches to 1,3-oxazine derivatives have been reported in the literature. Some highly prevailing examples of these methods are: Using azido-1-propanol [10]; Ritter reaction, consisting of reacting a diol with a nitrile under strongly acidic conditions [11]; synthesis, utilizing nitriles and aminoalcohols in the presence of a mild Lewis acid ($\text{Cu}(\text{OAc})_2$, ZnCl_2) as a catalyst [12]; the [4+2] cycloaddition of an *N*-acylimine and an alkene [13]; using *N*-acyl-4-acyloxy- β -lactams under basic conditions [14]; intramolecular hydroamination of trichloroacetimidate in the presence of Au(I) complex [15]; cycloaddition reactions, using 2-azadienes with electron-rich and electron deficient alkynes [16]; the kinetic resolution of racemic Betti base based on an enantioselective *N,O*-

deketalization [17]; and the intramolecular cyclization of *N*-thioacyl 1,3-amino alcohols with Bu_4NF and EtI [18]. Other methods such as utilizing the reaction of *o*-iodophenols or *o*-iodoanilines with heterocumulenes and carbon monoxide in the presence of palladium catalyst in classical organic solvents have also been employed for the synthesis of 1,3-oxazine derivatives [19]. However, most of these reactions require harsh reaction conditions, expensive starting materials or reagents and longer reaction times. Therefore, the objective of this study is to find a simple method for the synthesis of 1,3-oxazine derivatives.

RESULTS AND DISCUSSION

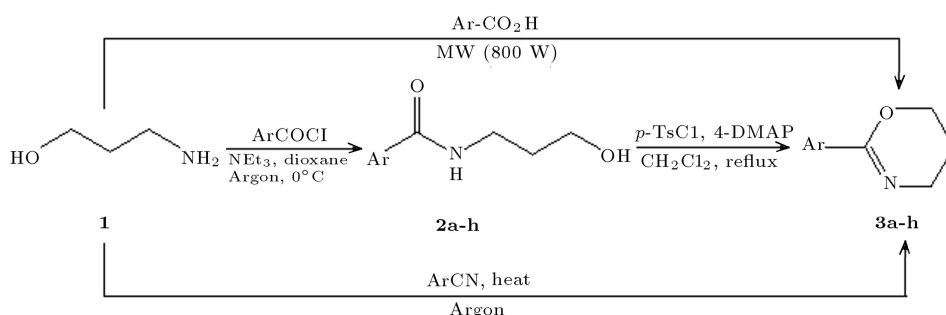
Our ongoing efforts to develop a new methodology for the synthesis of useful heterocyclic products [20] have prompted us to study the synthesis of 2-arylsubstituted 5,6-dihydro-1,3-oxazines through utilizing a new approach. Accordingly, a range of aromatic carboxylic acids was reacted with 3-aminopropanol under microwave irradiation (800 W) and solvent-free conditions (Scheme 1). This reaction proceeded elegantly to produce the desired dihydro-1,3-oxazine (**3a-h**) in a short reaction time (3-4 mins) and with moderate to good yields. The result of this study has been summarized in Table 1.

In the second approach, 3-aminopropanol was converted to its corresponding amides (**2**) by reacting with acid halides in dry dioxane in the presence of NEt_3 under an argon atmosphere at 0°C (Scheme 1). This reaction furnished the desired amides in 85-95% yields.

1. Department of Chemistry, Faculty of Sciences, University of Guilan, Rasht, P.O. Box 41335-1914, Iran.

*. Corresponding author. E-mail: m-chem41@guilan.ac.ir

Received 21 August 2007; received in revised form 22 February 2008; accepted 15 November 2008



Scheme 1. Synthetic routes to 2-aryl-5,6-dihydro-4H-1,3-oxazines.

Table 1. The reaction of carboxylic acids with 3-amino-1-propanol under solvent free condition and MW irradiation.

Entry	Ar	Time (min)	Yield (%) ^{a,b}
a		4	71
b		3	74
c		3	74
d	C ₆ H ₅ -	4	72 [10]
e	4-NO ₂ C ₆ H ₄ -	3	68 [10]
f	3-NO ₂ C ₆ H ₄ -	3	70
g	3,5-(NO ₂) ₂ C ₆ H ₃ -	3	65
h	4-MeOC ₆ H ₄ -	4	69 ^c [10]

a: All compounds have been fully characterized by ¹H NMR and IR; b: Isolated yields; c: By comparison with authentic sample.

Cyclization of *N*-acylaminoalcohol (**2a-h**) in dry CH₂Cl₂ with *p*-TSCl and 4-DMAP under a reflux condition gave 5,6-dihydro-1,3-oxazine (**3a-h**) in 67-77% yields (Table 2).

For further comparison of the first procedure (MW condition) with the literature method [12], dihydro-1,3-oxazine **3a** was prepared by the reaction of thieophene-2-carbonitrile and 3-amino-1-propanol in the presence of ZnCl₂ (Scheme 1). This reaction afforded the desired product in lower yield (65%) with much longer reaction time (48 h).

In conclusion an efficient one-pot protocol for the preparation of 2-arylsubstituted 5,6-dihydro-1,3-oxazines was developed under solvent-free condition and microwave irradiation, producing 5,6-dihydro-1,3-oxazines from 3-amino-1-propanol and readily available carboxylic acids, in short reaction times (3-4 min) and with moderate to good yields (65-74%) (Table 1).

Table 2. Cyclization of *N*-acylaminoalcohols (**2a-h**) to 5,6-dihydro-1,3-oxazines (**3a-h**).

Entry	Ar	Time (h)	Yield (%) ^{a,b}
a		22	75
b		24	77
c		22	77
d	C ₆ H ₅ -	30	75 [10]
e	4-NO ₂ C ₆ H ₄ -	24	72 [10]
f	3-NO ₂ C ₆ H ₄ -	24	75
g	3,5-(NO ₂) ₂ C ₆ H ₃ -	24	67
h	4-MeOC ₆ H ₄ -	24	74 [10]

a: All compounds have been fully characterized by ¹H NMR and IR; b: Isolated yields.

EXPERIMENTAL

General

¹H NMR spectra were obtained on a Bruker DRX-500. FTIR spectra were recorded on a Shimadzu FTIR-8400S spectrometer. Chemical shifts of ¹H spectra were expressed in ppm, downfield from tetramethylsilane. Microwave experiments were carried out in a DeLonghi 5510. Melting points were measured on a Buchi melting point B-540 instrument and are uncorrected. All the chemicals were purchased from Merck and used without further purification.

General Procedure for the Preparation of 2-Substituted 5,6-Dihydro-4H-1,3-Oxazine (**3a-h**) Under Solvent-Free Conditions and Microwave Irradiation

A mixture of aromatic carboxylic acids (5 mmol) and 3-amino-1-propanol (5 mmol) was irradiated (800 W)

in a microwave oven and the progress of the reaction was monitored by TLC (petroleum ether/ethyl acetate: 3:1). After completion of the reaction (3-4 min) (Table 1), the reaction mixture was purified by a preparative thin layer chromatography (petroleum ether/ethyl acetate 3:1) to afford **3a-h** in 65-74% yields (Table 1).

General Procedure for the Preparation of *N*-Acylaminoalcohol (**2a-h**)

A solution of 3-amino-1-propanol (20 mmol) and triethylamine (39 mmol) in dioxane (30 mL) was cooled to 0°C under an atmosphere of dry Argon. A solution of acid halide (19 mmol) in dioxane (25 mL) was added and the reaction mixture was stirred at this temperature for 1.45 h. The reaction mixture was filtered and the filtrate was evaporated in a vacuum to afford the desired amides (**2a-h**).

General Procedure for the Preparation of 2-Substituted 5,6-Dihydro-4H-1,3-Oxazines (**3a-h**) Under Classical Conditions

To a magnetically stirred solution of *N*-acylaminoalcohol (**2**) (10 mmol), triethylamine (50 mmol) and 4-dimethylaminopyridine (0.5 mmol) in CH₂Cl₂ (30 mL), *p*-TSCl (14 mmol) was added, at room temperature. The reaction mixture was heated under reflux for the specified reaction time (Table 2). Water was added and the organic layer was separated and dried under magnesium sulfate (MgSO₄). Concentration of the organic phase under vacuum and the subsequent purification of the crude product by preparative TLC (petroleum ether/ethyl acetate 3:1) afforded the desired dihydro-1,3-oxazine **3a-h** (Table 2).

- 2a:** Brown oil, IR (CHCl₃): ($\nu_{\max}/\text{cm}^{-1}$); 3450 (OH), 1640 (C=O), 1590 (N-H), ¹H NMR (500 MHz, CDCl₃): δ : 7.87; (dd, J=1.1, 3.75 Hz, 1H, ArH), 7.62 (dd, J= 1.1, 4.9 Hz, 1H, ArH), 7.15 (dd, J= 3.75, 4.9 Hz, 1H, ArH), 6.56 (s, 1H, NH), 4.50 (t, J= 5.95 Hz, 2H, CH₂O), 3.60 (q, J= 6.55 Hz, 2H, CH₂N), 2.1 (quint., J= 6.1 Hz, 2H, CH₂-CH₂-CH₂), 1.6 (s, 1H, OH) ppm.
- 2b:** Violet oil, IR (CH₂Cl₂): ($\nu_{\max}/\text{cm}^{-1}$); 3347 (OH), 1650 (C=O), 1590 (N-H), ¹H NMR (500 MHz, CDCl₃): δ : 7.49 (dd, J= 0.64, 1.75 Hz, 1H), 7.16 (dd, J= 0.64, 3.5 Hz, 1H), 6.75 (s, 1H, NH), 6.55 (dd, J= 1.75, 3.5 Hz, 1H), 3.74 (t, J= 5.7 Hz, 2H, CH₂O), 3.64 (q, J= 6.35 Hz, 2H, CH₂N), 1.83 (quint., J= 6.1 Hz, 2H, CH₂-CH₂-CH₂), 1.69 (s, 1H, OH) ppm.
- 2c:** Brown oil, IR (CH₂Cl₂): ($\nu_{\max}/\text{cm}^{-1}$); 3400 (OH), 1640 (C=O), 1550 (N-H), ¹H NMR (500 MHz, CDCl₃): δ : 8.5 (s, 1H, NH), 7.75 (d, J= 3.3 Hz, 1H, ArH), 7.70 (d, J= 4.70 Hz, 1H, ArH), 7.1 (dd, J= 3.3, 4.70 Hz, 1H, ArH), 4.52 (s, 1H, OH), 3.45 (t, J= 6.1 Hz, 2H, CH₂O), 3.35 (s, 2H), 3.27 (q, J= 6.2 Hz, 2H, CH₂N), 1.66 (quint, J= 6.5 Hz, 2H, CH₂-CH₂-CH₂) ppm.
- 2d:** Colorless oil, IR (CH₂Cl₂): ($\nu_{\max}/\text{cm}^{-1}$); 3400 (OH), 1640 (C=O, N-H), ¹H NMR (500 MHz, CDCl₃): 8.09 (dt, J= 1.3, 8.4 Hz, 2H, ArH), 7.61 (t, J= 7.4, 1H, ArH), 7.52 (t, J= 7.5 Hz, 2H, ArH), 6.75 (s, 1H, NH), 4.53 (t, J= 6.0 Hz, 2H, CH₂O), 3.63 (q, J= 6.3 Hz, 2H, CH₂N), 2.14 (quint., J= 6.3 Hz, 2H, CH₂-CH₂-CH₂), 1.75 (s, 2H, OH) ppm.
- 2e:** Yellow solid, mp 118-119°C, IR (KBr): ($\nu_{\max}/\text{cm}^{-1}$); 3450 (OH), 1640 (C=O, N-H), 1530, 1350 (NO₂), ¹H NMR (500 MHz, CDCl₃): δ : 8.28 (d, J = 8.70 Hz, 2H, ArH), 8.02 (d, J = 8.70 Hz, 2H, ArH), 6.80 (s, 1H, NH), 4.59 (t, J = 6.0 Hz, 2H, CH₂O), 3.67 (q, J = 6.30, 2H, CH₂N), 2.19 (quint., J = 6.35 Hz, 2H, CH₂-CH₂-CH₂), 1.75 (s, 1H, OH) ppm.
- 2f:** Yellow solid, mp 114.5-116°C, IR (KBr): ($\nu_{\max}/\text{cm}^{-1}$); 3300 (OH), 1640 (C=O), 1600 (N-H), 1520, 1340 (NO₂), ¹H NMR (500 MHz, CDCl₃): δ : 8.65 (s, 1H, ArH), 8.22 (dd, J = 1.0, 7.95 Hz, 1H, ArH), 8.16 (d, J = 7.75 Hz, 1H, ArH), 7.53 (t, J = 7.95 Hz, 1H, ArH), 6.80 (s, 1H, NH), 3.98 (t, J = 5.7 Hz, 2H, CH₂O), 3.48 (q, J = 6.25, 2H, CH₂N), 1.71 (quint., J = 5.85 Hz, 2H, CH₂-CH₂-CH₂), 1.14 (s, 1H, OH) ppm.
- 2g:** Yellow solid, mp 139-141°C, IR (KBr): ($\nu_{\max}/\text{cm}^{-1}$); 3400 (OH), 1640 (C=O, N-H), 1540, 1340 (NO₂), ¹H NMR (500 MHz, CDCl₃): δ : 9.46 (s, 1H, ArH), 9.25 (d, J = 1.55 Hz, 2H, ArH), 6.9 (s, 1H, NH), 4.61 (t, J = 6.0 Hz, 2H, CH₂O), 3.69 (q, J = 6.30 Hz, 2H, CH₂N), 2.20 (quint., J = 6.35 Hz, 2H, CH₂-CH₂-CH₂), 1.76 (s, 1H, OH) ppm.
- 2h:** Colorless oil, IR (CDCl₃): ($\nu_{\max}/\text{cm}^{-1}$); 3400 (OH), 1640 (C=O, N-H), 1250 (-OMe), ¹H NMR (500 MHz, CDCl₃): δ : 7.73 (d, J= 8.80 Hz, 2H, ArH), 6.91 (d, J= 8.80 Hz, 2H, ArH), 6.45 (s, 1H, NH), 3.85 (s, 3H, OCH₃), 3.70 (t, J= 5.25 Hz, 2H, CH₂O), 3.62 (q, J= 6.0, 2H, CH₂N), 3.10 (s, 1H, OH), 1.79 (quint, J= 6.0 Hz, 2H, CH₂-CH₂-CH₂) ppm.
- 3a:** Brown oil, IR (CHCl₃): ($\nu_{\max}/\text{cm}^{-1}$); 1600 (C=N), 1520, 1460 (C=C), 1075 (C-O), ¹H NMR (500 MHz, CDCl₃): δ : 7.5 (dd, J= 1.1, 3.70 Hz, 1H, ArH), 7.36 (dd, J= 1.1, 5.0 Hz, 1H, ArH), 7.0 (dd, J= 3.70, 5.0 Hz, 1H, ArH), 4.38 (t, J= 5.5, 2H, CH₂O), 3.61 (t, J= 5.85 Hz, 2H, CH₂N), 2.0 (quint., J= 5.77 Hz, 2H, CH₂-CH₂-CH₂) ppm.

- 3b:** Red oil, IR (CHCl₃): ($\nu_{\max}/\text{cm}^{-1}$); 1600 (C=N), 1520, 1470 (C=C), 1200 (C-O), ¹H NMR (500 MHz, CDCl₃): δ ; 7.40 (dd, J = 0.60, 1.80 Hz, 1H), 7.10 (dd, J = 0.60, 3.50 Hz, 1H), 6.52 (dd, J = 1.8, 3.50 Hz, 1H), 4.30 (t, J = 5.5 Hz, 2H, CH₂O), 3.74 (t, J = 5.53 Hz, 2H, CH₂N), 1.80 (quint., J = 5.7 Hz, 2H, CH₂-CH₂-CH₂) ppm.
- 3c:** Dark brown oil, IR (CHCl₃): ($\nu_{\max}/\text{cm}^{-1}$); 1650 (C=N), 1573, 1473 (C=C), 1218 (C-O), ¹H NMR (500 MHz, CDCl₃): δ ; 7.49 (dd, J = 1.0, 3.70 Hz, 1H, ArH), 7.36 (dd, J = 1.0, 5.0 Hz, 1H, ArH), 7.04 (dd, J = 3.70, 5.0 Hz, 1H, ArH), 4.37 (t, J = 5.4 Hz, 2H, CH₂O), 3.67 (s, 2H), 3.6 (t, J = 5.8 Hz, 2H, CH₂N), 2.01 (quint., J = 5.7 Hz, 2H, CH₂-CH₂-CH₂) ppm.
- 3d:** Colorless oil, IR (neat): ($\nu_{\max}/\text{cm}^{-1}$); 1645 (C=N), 1580, 1475 (C=C), 1020 (C-O), ¹H NMR (500 MHz, CDCl₃): 7.84 (dd, J = 1.1, 8.1 Hz, 2H, ArH), 7.54 (t, J = 7.50 Hz, 1H, ArH), 7.45 (t, J = 7.5, 2H, ArH), 3.85 (t, J = 5.6, 2H, CH₂O), 3.25 (t, J = 6.13, 2H, CH₂N), 1.82 (quint., J = 5.7 Hz, 2H, CH₂-CH₂-CH₂) ppm.
- 3e:** Yellow oil, IR (neat): ($\nu_{\max}/\text{cm}^{-1}$); 1604 (C=N), 1519, 1350 (NO₂), 1118 (C-O), ¹H NMR (500 MHz, CDCl₃): δ ; 7.79 (d, J = 8.10 Hz, 2H, ArH), 7.36 (d, J = 8.10 Hz, 2H, ArH), 3.79 (t, J = 5.60 Hz, 2H, CH₂O), 3.15 (t, J = 6.20 Hz, 2H, CH₂N), 1.75 (quint., J = 5.90 Hz, 2H, CH₂-CH₂-CH₂) ppm.
- 3f:** Yellow oil, IR (neat): ($\nu_{\max}/\text{cm}^{-1}$); 1650 (C=N), 1520, 1350 (NO₂), 1060 (C-O), ¹H NMR (500 MHz, CDCl₃): δ ; 8.97 (s, 1H, ArH), 8.5 (d, J = 8.15 Hz, 1H, ArH), 8.45 (d, J = 7.8 Hz, 1H, ArH), 7.74 (t, J = 8.0 Hz, 1H, ArH), 3.83 (t, J = 5.65 Hz, 2H, CH₂O), 3.43 (t, J = 6.65 Hz, 2H, CH₂N), 1.89 (quint., J = 5.7 Hz, 2H, CH₂-CH₂-CH₂) ppm.
- 3g:** Yellow oil, IR (CH₂Cl₂): ($\nu_{\max}/\text{cm}^{-1}$); 1640 (C=N), 1530, 1350 (NO₂), 1085 (C-O), ¹H NMR (500 MHz, CDCl₃): 9.2 (s, 1H, ArH), 9.01 (d, J = 1.6 Hz, 2H, ArH), 3.94 (t, J = 5.2 Hz, 2H, CH₂O), 3.15 (t, J = 6.0 Hz, 2H, CH₂N), 1.96 (quint., J = 5.5 Hz, 2H, CH₂-CH₂-CH₂) ppm.

ACKNOWLEDGMENT

We would like to express our gratefulness to the Research Council of the University of Guilan for partial support of this work.

REFERENCES

- Meyers, A.I. and Smith, E.M. "Synthesis of ketones from dihydro-1,3-oxazines via stepwise alkyl or aryl introduction", *J. Org. Chem.*, **37**(26), pp. 4289-4293 (1972).
- Schimdt, R.R. "1,3-oxazines and 1,3-thiazines. Intermediates of interest in organic synthesis", *Synthesis*, pp. 329-333 (1972).
- Meyers, A.I., Nabeya, A., Adickes, H.W., Politzer, I.R., Kovelesky, A.C., Malone, G.R. and Portnoy, R.C. "Synthesis of aldehydes from dihydro-1,3-oxazines", *J. Org. Chem.*, **38**, pp. 36-56 (1973).
- Meyers, A.I., Nabeya, A., Adicks, H.W., Fitzpatrick, J.M., Malone, G.R. and Politzer, I.R. "Aldehydes from dihydro-1,3-oxazines. I. Synthesis of aliphatic aldehydes and their C-1 deuterated derivatives", *J. Am. Chem. Soc.*, **91**, pp. 763-764 (1969).
- Meyers, A.I. and Malone, G.R. "Chemistry of 1,6-dihydro-1,3-oxazines. XXII. Chemistry of 2-chloromethyl-5,6-dihydro-1,3-oxazines. Grignard coupling and metalation studies. Synthesis of alpha-chloroaldehydes and arylacetic acids", *J. Org. Chem.*, **39**, pp. 618-623 (1974).
- Eckstein, Z. and Urbanski, T. "1,3-oxazine derivatives", *Adv. Heterocycl. Chem.*, **2**, pp. 311-342 (1963).
- Michelin, R.A., Belluco, U., Mozzon, M. and Berin, P. "Synthesis of 5,6-dihydro-4H-1,3-oxazines from neutral and cationic platinum(II) nitrile complexes. X-ray structure of trans-[Pt(CF₃){N=C(PH)OCH₂CH₂CH₂}(PPH₃)₂]BF₄", *Inorganica Chimica Acta*, **220**, pp. 21-33 (1994).
- Singh, O.V. and Han, H. "Stereoselective synthesis of *trans*-olefins by the copper-mediated S_N2' reaction of vinyl oxazines with Grignard reagents. Asymmetric synthesis of *D-threo*-sphingosines", *Tetrahedron Lett.*, **48**, pp. 2345-2348 (2007).
- Tomasulo, M., Sortino, S. and Raymo, F.M. "A fast and stable photochromic switch based on the opening and closing of an oxazine ring", *Org. Lett.*, **7**(6), pp. 1109-1112 (2005).
- Badiang, J.G. and Aube, J. "One-step conversion of aldehydes to oxazolines and 5,6-dihydro-4H-1,3-oxazines using 1,2- and 1,3-azido alcohols", *J. Org. Chem.*, **61**, pp. 2484-2487 (1996).
- Tillmanns, E.J. and Ritter, J.J. "Nitriles in nuclear heterocyclic syntheses I. Dihydro-1,3 oxazines", *J. Org. Chem.*, **22**, pp. 839-840 (1957).
- Lee, J., Lee, K. and Kim, H. "A facile synthesis of 5,6-dihydro-4H-1,3-oxazine derivatives", *Bull. Korean Chem. Soc.*, **17**(2), pp. 115-116 (1996).
- Toujas, J.L., Jost, E. and Vaultier, M. "Synthesis of homochiral *N*-Boc-beta-aminoaldehydes from *N*-Boc-beta-aminonitriles", *Bull. Soc. Chim. Fr.*, pp. 713-715 (1997).
- Tovar, F. and Ochoa, G. "Conversion of *N*-Acyl-4-acyloxy- β -lactams into 1,3-oxazin-6-ones: two consecutive pseudopericyclic processes", *Org. Lett.*, **2**(7), pp. 965-968 (2000).
- Kang, J.E., Kim, H.B., Lee, J.W. and Shin, S. "Gold(I)-catalyzed intramolecular hydroamination of alkyne with trichloroacetimidates", *Org. Lett.*, **8**(16), pp. 3537-3540 (2006).

16. (a) Palacios, F., Herran, E., Rubiales, G. and Ezpeleta, M.J. "Cycloaddition reaction of 2-azadienes derived from β -amino acids with electron-rich and electron-deficient alkenes and carbonyl compounds. Synthesis of pyridine and 1,3-oxazine derivatives", *J. Org. Chem.*, **67**, pp. 2131-2135 (2002); (b) Palacios, F., Alonso, C. and Rubiales, G. "Aza-Wittig reaction of *N*-vinylic phosphazenes with carbonyl compounds. Azadiene-mediated synthesis of isoquinolines and 5,6-dihydro-2*H*-1,3-oxazines", *J. Org. Chem.*, **62**, pp. 1146-1154 (1997).
17. Dong, Y., Li, R., Lu, J., Xu, X., Wang, X. and Hu, Y. "An efficient kinetic resolution of racemic Betti base based on an enantioselective *N,O*-deketalization", *J. Org. Chem.*, **70**, pp. 8617-8620 (2005).
18. Murai, T., Sano, H., Kawai, H., Aso, H. and Shibahara, F. "*N*-Thioacyl 1,3-amino alcohols: Synthesis via ring-opening of oxiranes with thioamide dianions and applications as key intermediates leading to stereochemically defined 5,6-dihydro-4*H*-1,3-oxazines and 1,3-amino alcohols", *J. Org. Chem.*, **70**, pp. 8148-8153 (2005).
19. (a) Ye, F. and Alper, H. "Ionic-liquid-promoted palladium-catalyzed multicomponent cyclocarbonylation of *o*-iodoanilines and allenes to form methylene-2,3-dihydro-1 *H*-quinolin-4-ones", *J. Org. Chem.*, **72**, pp. 3218-3222 (2007); (b) Larksarp, C. and Alper, H. "Palladium-catalyzed cyclocarbonylation of *o*-iodophenols and 2-hydroxy-3-iodopyridine with heterocumulenes: regioselective synthesis of benzo[*e*]-1,3-oxazin-4-one and pyrido[3,2-*e*]-1,3-oxazin-4-one derivatives", *J. Org. Chem.*, **64**, pp. 9194-9200 (1999).
20. (a) Badrian, A., Mamaghani, M., Tabatabaeian, K. and Valizadeh, H. "Asymmetric induction in darzens condensation by means of (R)-5,5-dimethyl-4-phenyloxazolidin-2-one as an effective chiral auxiliary", *Lett. Org. Chem.*, **4**(4), pp. 228-231 (2007); (b) Tabatabaeian, K., Mamaghani, M., Mahmoodi, N. and Khorshidi, A. "A Ru^{III} catalyzed double-conjugate 1,4-addition of indoles to symmetric enones", *J. Mol. Catal. A*, **270**, pp. 112-116 (2007); (c) Tabatabaeian, K., Mamaghani, M., Mahmoodi, N.O. and Khorshidi, A. "Efficient Ru^{III}-catalyzed condensation of indoles and aldehydes or ketones", *Canadian. J. Chem.*, **84**(11), pp. 1541-1545 (2006); (d) Mamaghani, M., Yazdanbakhsh, M.R., Badrian, A., Valizadeh, H. and Samimi, H.A. "The use of enantiomerically pure α, β -unsaturated *N*-acyloxazolidin-2-one in diastereoselective Baylis-Hillman type reaction mediated by SmI₂", *Lett. Org. Chem.*, **2**(8), pp. 721-724 (2005).