SYNTHESIS OF 4*H*-PYRIDO[3,2-*b*][1,4]OXAZINE AND 3-SUBSTITUTED-4*H*-PYRIDO[3,2-*b*][1,4]OXAZINES *VIA* PALLADIUM-CATALYSED REACTIONS

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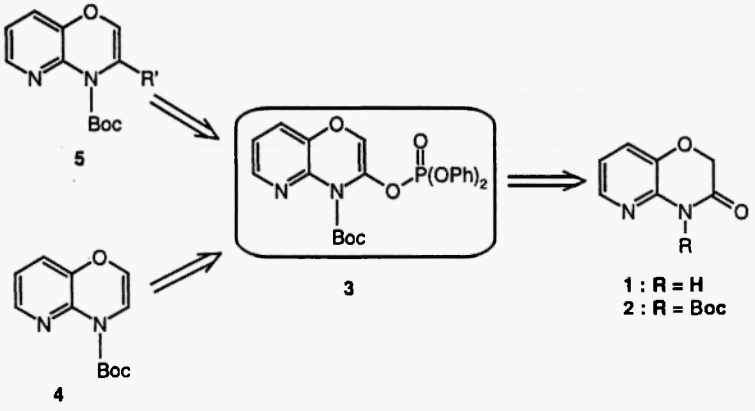
Abstract : Here is described a high yield synthesis of 4-(*tert*-butoxycarbonyl)-3-[(diphenoxyphosphoryl)oxo]-4*H*-pyrido[3,2-*b*][1,4]oxazine from a pyridoxazin-3-one derivative. The hydrogenolysis of this compound provides a convenient route to 4*H*-pyrido[3,2-*b*][1,4]oxazine and palladium-catalysed coupling reactions between this vinylphosphate and organostannanes gained access to 3-substituted-4*H*-pyrido[3,2-*b*][1,4]oxazines.

Introduction

In our continuous interest for the preparation of unusual heterocyclic systems we recently reported two complementary methods giving easy access to 3-substituted-4*H*-1,4-benzoxazines.[1] The first one involves a regioselective lithiation of position C_3 directed by the nearby N-Boc group, the second one a palladium catalysed coupling reaction between organostannanes and a vinylphosphate derivative. We wish to report herein the extension of the latter procedure to the synthesis of pyridoxazines, which constitute a very unusual heterocyclic system.[2,3] The vinylphosphate **3** constituted a key intermediate for our purpose allowing both an easy access by hydrogenolysis to unknown pyridoxazine **4** and to 3-substituted heterocycles **5** using palladium-catalysed coupling reactions (scheme 1).



Scheme 1

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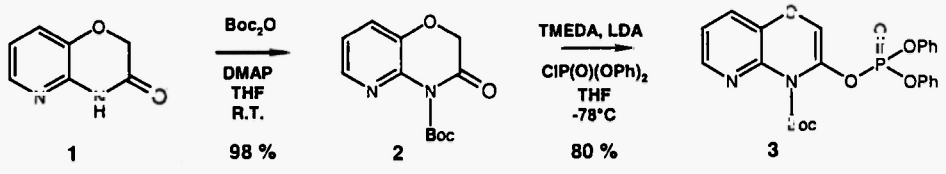
Results and Discussions

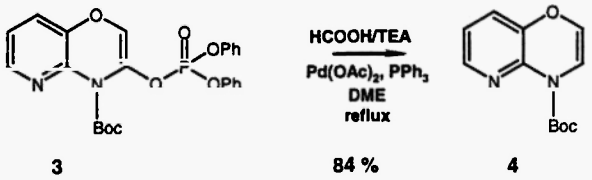
N-Boc derivative **2** was obtained in almost quantitative yield by treatment of commercially available 2*H*-pyrido[3,2-*b*]-1,4-oxazin-3(4*H*)-one **1** with di-*tert*-butyldicarbonate (1.1 eq.) in the presence of DMAP (1.1 eq.) , at room temperature, in dry tetrahydrofuran. The lithium enolate of **2** was obtained at -78°C with LDA (1.2 eq.) in the presence of TMEDA (1.2 eq.) in dry tetrahydrofuran and quenched with diphenylchlorophosphate (1.2 eq.). Vinyl phosphate **3**. the required key intermediate, was stable enough to be purified by flash chromatography on silicagel and was eventually obtained in 80 % yield (scheme 2).



Scheme 2

We prepared unsubstituted derivative **4** by hydrogenolysis of **3** with the view of using ulteriorly, the N-*tert*-butoxycarbonyl moiety as directing group for the regioselective metallation then fonctionalisation on the position 3 of the heterocyclic system.

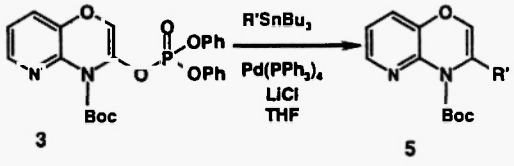
The hydrogenolysis of vinyl phosphate **3** was performed in 84 % yield by adapting a procedure previously described by Ortar and al[4] for the conversion of enol triflates into the corresponding alkenes (Scheme 3). The reaction was carried out by refluxing DME in the presence of formic acid (2 eq.), triethylamine (3 eq.), palladium acetate (0.04 eq.) and triphenylphosphine (0.08 eq.).



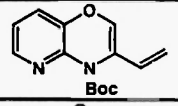
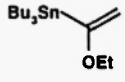
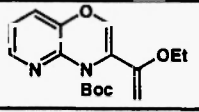
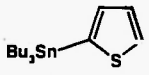
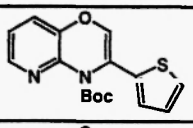
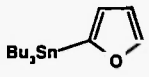
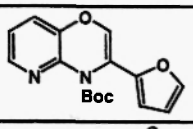
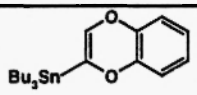
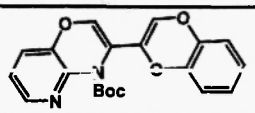
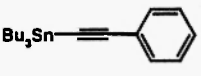
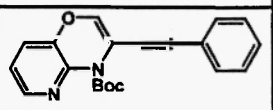
Scheme 3

On the other hand, the vinylphosphate **3** was also engaged in coupling reactions involving vinyl, alkynyl and heteroaryl organostannanes[5] with the view of obtaining 3-substituted derivatives **5** (Table 1).

Table 1. Palladium-Catalysed Coupling of vinyl phosphate **3** with organostannanes $R'SnBu_3$



3 5

5	R'SnBu$_3$	Products	Yield
5a			78 %
5b			65 %
5c			70 %
5d			96 %
5e			94 %
5f			72 %

A typical procedure is as follows : a mixture of $Pd(PPh_3)_4$ (0.05 eq.), LiCl (3 eq.), vinylphosphate **3** (1 eq.) and organostannane (2 eq.) was stirred in dry THF at reflux. Stirring was continued until the vinylphosphate had disappeared (indicated by TLC).

The reaction proved to be quite efficient for the synthesis of pyridoxazines bearing vinyl, alkynyl, or heteroaryl substituents on C_3.

Conclusion

We have developed a new and versatile method allowing an easy access to the little known 4*H*-pyrido[3,2-*b*][1,4]oxazine. The coupling reaction involving a vinyl phosphate allows the introduction of various vinyl or heteroaryl groups.

Further work is going on to prepare other 3-substituted derivatives from 4 *via* the regioselective formation of a 3-lithioderivative and its condensation on various electrophilic reagents.

Experimental

General. Melting points were determined with a Büchi SMP-20 melting point apparatus and were uncorrected. IR spectra were recorded on a Perkin-Elmer FT PARAGON 1000 PC. ^1H and ^{13}C NMR were recorded on a Bruker Avance DPX250 spectrometer (250.19 MHz ^1H, 62.89 MHz ^{13}C), multiplicities were determined by the DEPT 135 sequence. MS were recorded on a Perkin-Elmer

SCIEX API 3000 spectrometer. All reactions were carried out in a flame-dried glassware under an argon atmosphere. Thin-layer chromatography (TLC) was carried out on Merck silica gel $60F_{254}$ precoated plates. "Usual workup" means extraction with EtOAc, drying with $MgSO_4$, filtration and evaporation.

4-(*tert*-Butoxycarbonyl)-3,4-dihydro-2*H*-pyrido[3,2-*b*][1,4]oxazin-3-one (2)
To a solution of 3,4-dihydro-2*H*-pyrido[3,2-*b*][1,4]oxazin-3-one **1** (3.49 g, 23.2 mmol) in THF (60 mL) was added 4-dimethylaminopyridine (3.12 g, 25.6 mmol) and di-*tert*-butyldicarbonate (5.58 g, 25.6 mmol). The resulting mixture was stirred at room temperature 3 hours. After concentration and hydrolysis, the reaction mixture was extracted with EtOAc. The combined organic phases were washed with hydrochloric acid solution (5 %), brine, dried over $MgSO_4$ and concentrated to give **2** as a white solid (5.82 g, 98 %). m.p. : 70°C. IR (KBr) : ν cm^{-1} 1778 and 1722 (C=O), 1599 and 1463 (C=C, C=N). ^1H NMR ($CDCl_3$) : δ ppm 1.63 (s, 9H, $(CH_3)_3C$) ; 4.64 (s, 2H, H_2) ; 6.99 (dd, 1H, H_7, $J_{6,7}$ = 5 Hz, $J_{7,8}$ = 8 Hz) ; 7.27 (dd, 1H, H_8, $J_{6,8}$ = 1.5 Hz, $J_{7,8}$ = 8 Hz) ; 8.00 (dd, 1H, H_6, $J_{6,7}$ = 5 Hz, $J_{6,8}$ = 1.5 Hz). ^{13}C NMR ($CDCl_3$) : δ ppm 27.85 ($3CH_3$, $(CH_3)_3C$) ; 67.55 (CH_2, C_2) ; 86.45 (C, $(CH_3)_3C$) ; 120.55 (CH, C_7) ; 124.35 (CH, C_8) ; 139.65 and 140.40 (2C, C_9 and C_{10}) ; 141.95 (CH, C_6) ; 148.65 (C, C=O) ; 162.85 (C, C_3). MS : *m/z* 251 (M+1).

4-(*tert*-Butoxycarbonyl)-3-[(diphenoxyphosphoryl)oxo]-4*H*-pyrido[3,2-*b*][1,4]oxazine (3)
To a cold (-78°C) solution of **2** (4 g, 16 mmol) in dry THF (60 mL) and N,N,N',N'-tetramethylenediamine (2.9 mL, 19.2 mmol) was added a solution of LDA (2M) in heptane / THF (9.6 mL, 19.2 mmol). The reaction mixture was stirred at -78°C for 2 hours and diphenyl chlorophosphate freshly distilled (4 mL, 19.2 mmol) was added , then the mixture was stirred for 3 hours at -78°C, allowed to warm to room temperature and treated with 5 % ammonium hydroxide solution (30 mL). After the usual workup and flash chromatography on silica gel with petroleum ether/EtOAc/triethylamine (75/15/10), **3** was obtained as white crystals (6.2 g, 80 %). m.p. : 94°C. IR (KBr) : ν cm^{-1} 1713 (C=O), 1590, 1487 and 1439 (C=C, C=N), 1313 (P=O). ^1H NMR ($CDCl_3$) : δ ppm 1.46 (s, 9H, $(CH_3)_3C$) ; 6.75 (d, 1H, H_2, $J_{H,P}$ = 3.5 Hz) ; 7.12 (dd, 1H, H_7, $J_{6,7}$ = 5 Hz, $J_{7,8}$ = 8 Hz) ; 7.19 - 7.37 (m, 11H, $10H_{arom}$ and H_8) ; 8.29 (dd, 1H, H_6, $J_{6,7}$ = 5 Hz, $J_{6,8}$ = 1.5 Hz). ^{13}C NMR ($CDCl_3$) : δ ppm 28.20 ($3CH_3$, $(CH_3)_3C$) ; 84.10 (C, $(CH_3)_3C$) ; 120.30 (4CH) ; 122.70 (CH, C_7) ; 124.45 (CH) ; 126.05 (CH) ; 128.10 (CH) ; 128.20 (CH, C_2) ; 130.20 (4CH) ; 133.00 (C) ; 141.75 (C) ; 144.10 (CH, C_6) ; 147.00 (C) ; 150.50 (2C) ; 151.50 (C). MS : *m/z* 483 (M+1).

4-(*tert*-Butoxycarbonyl)-4*H*-pyrido[3,2-*b*][1,4]oxazine (4)
To a solution of phosphate **3** (2 g, 4.14 mmol), triphenylphosphine (90 mg, 0.34 mmol) and palladium acetate (40 mg, 0.16 mmol) in 1,2-dimethoxyethane (6 mL) was added a solution of triethylamine (1.75 mL, 12.44 mmol) and formic acid (0.32 mL, 8.28 mmol) in 1,2-dimethoxyethane (6 mL). The reaction mixture was refluxed for 40 minutes, allowed to cool to room temperature and hydrolyzed with distilled water (20 mL). After usual workup and flash chromatography on silica gel with petroleum ether/EtOAc (60/40), **4** was obtained as a white solid (815 mg, 84 %). m.p. : 83°C. IR (KBr) : ν cm^{-1} 1720 (C=O), 1577 and 1451 (C=C, C=N). ^1H NMR ($CDCl_3$) : δ ppm 1.52 (s, 9H, $(CH_3)_3C$) ; 5.91 and 6.22 (2d, 2H, H_2 and H_3, $J_{2,3}$ = 4.5 Hz) ; 6.88 (dd, 1H, H_7, $J_{6,7}$ = 4.5 Hz, $J_{7,8}$ = 8 Hz) ; 6.97 (dd, 1H, H_8, $J_{6,8}$ = 2 Hz, $J_{7,8}$ = 8 Hz) ; 8.04 (dd, 1H, H_6, $J_{6,7}$ = 4.5 Hz, $J_{6,8}$ = 2 Hz). ^{13}C NMR ($CDCl_3$) : δ ppm 28.45 ($3CH_3$, $(CH_3)_3C$) ; 82.75 (C, $(CH_3)_3C$) ; 111.70 and 130.55 (2CH, C_2 and C_3) ; 121.65 (CH, C_7) ; 123.70 (CH, C_8) ; 142.00 (C) ; 142.95 (CH, C_6) ; 144.10 (C) ; 149.20 (C, C=O). MS : *m/z* 235 (M+1). Anal. calc. for $C_{12}H_{14}N_2O_3$: C 57.6; H 6.0; N 12.0; Found: C 57.7; H 6.0; N 11.8.

4-(*tert*-Butoxycarbonyl)-3-vinyl-*4H*-pyrido[3,2-*b*][1,4]oxazine (5a)

Phosphate **3** (482 mg, 1 mmol) and tributyl(vinyl)tin (634 mg, 2 mmol) were dissolved in dry THF (3 mL). Tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.05 mmol) and lithium chloride (127 mg, 3 mmol) were added and the reaction was refluxed for 24 hours. After usual workup, extraction with acetonitrile/pentane and flash chromatography on silica gel with petroleum ether/EtOAc (80/20), **5a** was obtained as a brown solid (203 mg, 78 %). m.p. : 71°C. IR (KBr) : ν cm^{-1} 1710 (C=O), 1658 ($C=CH_2$), 1591 and 1443 (C=C, C=N). ^1H NMR ($CDCl_3$) : δ ppm 1.48 (s, 9H, $(CH_3)_3C$) ; 5.13 (d, 1H, vinyl-H_{2trans}, J_{cis} = 11 Hz) ; 5.44 (d, 1H, vinyl-H_{2cis} J_{trans} = 17.5 Hz) ; 6.20 (dd, 1H, vinyl-H_1, J_{trans} = 17.5 Hz, J_{cis} = 11 Hz) ; 6.66 (s, 1H, H_2) ; 7.10 (dd, 1H, H_7, $J_{6,7}$ = 5 Hz, $J_{7,8}$ = 8 Hz) ; 7.27 (dd, 1H, H_8, $J_{6,8}$ = 2 Hz, $J_{7,8}$ = 8 Hz) ; 8.27 (dd, 1H, H_6, $J_{6,7}$ = 5 Hz, $J_{6,8}$ = 2 Hz). ^{13}C NMR ($CDCl_3$) : δ ppm 28.25 ($3CH_3$, $(CH_3)_3C$) ; 82.95 (C, $(CH_3)_3C$) ; 113.65 (CH_2, vinyl-C_2) ; 122.20 (CH, C_7) ; 124.10 (CH, C_8) ; 126.50 (C) ; 128.10 (CH, vinyl-C_1) ; 138.10 (CH, C_2) ; 142.35 (C) ; 143.80 (CH, C_6) ; 146.85 (C) ; 152.20 (C, C=O). MS : *m/z* 261 (M+1). Anal. calc. for $C_{14}H_{16}N_2O_3$: C 64.6; H 6.2; N 10.8; Found: C 64.4; H 6.1; N 11.0.

4-(*tert*-Butoxycarbonyl)-3-(1-ethoxyvinyl)-*4H*-pyrido[3,2-*b*][1,4]oxazine (5b)

The reaction was carried out as described above for the synthesis of the compound **5a** with tributyl(1-ethoxyvinyl)tin (722 mg, 2 mmol) and 2.5 hours at reflux. After flash chromatography with petroleum ether/EtOAc (80/20), **5b** was obtained as a yellow oil (198 mg, 65 %). ^1H NMR ($CDCl_3$) : δ ppm 1.34 (t, 3H, CH_3CH_2O, J = 7 Hz) ; 1.47 (s, 9H, $(CH_3)_3C$) ; 3.85 (q, 2H, CH_3CH_2O, J = 7 Hz) ; 4.13 and 4.47 (2d, 2H, ethoxyvinyl-H_2, J_{gem} = 2.5 Hz) ; 6.90 (s, 1H, H_2) ; 7.09 (dd, 1H, H_7, $J_{6,7}$ = 5 Hz, $J_{7,8}$ = 8 Hz) ; 7.26 (dd, 1H, H_8, $J_{6,8}$ = 1.5 Hz, $J_{7,8}$ = 8 Hz) ; 8.26 (dd, 1H, H_6, $J_{6,7}$ = 5 Hz, $J_{6,8}$ = 1.5 Hz). ^{13}C NMR ($CDCl_3$) : δ ppm 13.85 (CH_3, CH_3CH_2O) ; 28.25 ($3CH_3$, $(CH_3)_3C$) ; 63.60 (CH_2, CH_3CH_2O) ; 82.75 (C, $(CH_3)_3C$) ; 82.95 (CH_2, ethoxyvinyl-C_2) ; 122.20 (CH, C_7) ; 124.10 (CH, C_8) ; 126.15 (C) ; 137.55 (CH, C_2) ; 142.55 (C) ; 143.75 (CH, C_6) ; 147.00 (C) ; 152.10 (C) ; 154.50 (C). MS : *m/z* 305 (M+1). Anal. calc. for $C_{16}H_{20}N_2O_4$: C 63.1; H 6.6; N 9.2; Found: C 63.1; H 6.5; N 9.3.

4-(*tert*-Butoxycarbonyl)-3-(2-thienyl)-*4H*-pyrido[3,2-*b*][1,4]oxazine (5c)

The reaction was carried out as described above for the synthesis of the compound **5a** with tributyl(2-thienyl)tin (746 mg, 2 mmol) and 8.5 hours at reflux. After flash chromatography with petroleum ether/EtOAc (80/20), **5c** was obtained as a brown solid (221 mg, 70 %). m.p. : 163°C. IR (KBr) : ν cm^{-1} 1719 (C=O), 1654, 1589 and 1443 (C=C, C=N). ^1H NMR ($CDCl_3$) : δ ppm 1.28 (s, 9H, $(CH_3)_3C$) ; 6.74 (s, 1H, H_2) ; 6.98 (dd, 1H, thienyl-H_4, $J_{3,4}$ = 3.5 Hz, $J_{4,5}$ = 5 Hz) ; 7.10 - 7.18 (m, 2H, H_7 and thienyl-H_3) ; 7.20 (dd, 1H, thienyl-H_5, $J_{3,5}$ = 1 Hz, $J_{4,5}$ = 5 Hz) ; 7.27 (dd, 1H, H_8, $J_{6,8}$ = 1.5 Hz, $J_{7,8}$ = 8 Hz) ; 8.31 (dd, 1H, H_6, $J_{6,7}$ = 5 Hz, $J_{6,8}$ = 1.5 Hz). ^{13}C NMR ($CDCl_3$) : δ ppm 27.90 ($3CH_3$, $(CH_3)_3C$) ; 82.85 (C, $(CH_3)_3C$) ; 122.25 (CH, C_7) ; 122.85 (C) ; 123.95 and 124.00 (3CH, C_8, thienyl-C_3 and -C_5) ; 126.95 (CH, thienyl-C_4) ; 134.75 (CH, C_2) ; 137.15 (C) ; 142.30 (C) ; 143.70 (CH, C_6) ; 146.95 (C) ; 151.60 (C, C=O). MS : *m/z* 317 (M+1). Anal. calc. for $C_{12}H_{14}N_2O_3$: C 60.7; H 5.1; N 8.8; Found: C 60.8; H 5.2; N 8.7.

4-(*tert*-Butoxycarbonyl)-3-(2-furyl)-*4H*-pyrido[3,2-*b*][1,4]oxazine (5d)

The reaction was carried out as described above for the synthesis of the compound **5a** with tributyl(2-furyl)tin (714 mg, 2 mmol) and 3 hours at reflux. After flash chromatography with petroleum ether/EtOAc (80/20), **5d** was obtained as a white solid (288 mg, 96 %). m.p. : 144°C. IR (KBr) : ν cm^{-1} 1722 (C=O), 1590 and 1444 (C=C, C=N). ^1H NMR ($CDCl_3$) : δ ppm 1.36 (s, 9H, $(CH_3)_3C$) ; 6.38 - 6.42 (m, 2H, furyl-H_3 and -H_4) ; 6.93 (s, 1H, H_2) ; 7.12 (dd, 1H, H_7, $J_{6,7}$ = 4.5 Hz,

$J_{7,8}$ = 8 Hz) ; 7.27 - 7.34 (m, 2H, $\mathbf{H_8}$ and furyl-$\mathbf{H_5}$) ; 8.29 (dd, 1H, $\mathbf{H_6}$, $J_{6,7}$ = 4.5 Hz, $J_{6,8}$ = 1.5 Hz). ^{13}C NMR ($CDCl_3$) : δ ppm 27.90 ($3CH_3$, $(CH_3)_3C$) ; 82.75 (C, $(CH_3)_3\mathbf{C}$) ; 106.80 and 111.15 (2CH, furyl-$\mathbf{C_3}$ and -$\mathbf{C_4}$) ; 119.65 (C) ; 122.20 (CH, $\mathbf{C_7}$) ; 124.05 (CH, $\mathbf{C_8}$) ; 135.60 (CH, $\mathbf{C_2}$) ; 141.25 (CH, furyl-$\mathbf{C_5}$) ; 142.10 (C) ; 143.70 (CH, $\mathbf{C_6}$) ; 146.85 (C) ; 147.50 (C) ; 151.70 (C, **C=O**). MS : *m/z* 301 (M+1).

3-(2-benzo[1,4]dioxino)-4-(*tert*-Butoxycarbonyl)-*4H*-pyrido[3,2-*b*][1,4]oxazine (5e)

The reaction was carried out as described above for the synthesis of the compound **5a** with 2-tributyltin-1,4-benzodioxine (828 mg, 2 mmol) and 4 hours at reflux. After flash chromatography with petroleum ether/EtOAc (80/20), **5e** was obtained as a light brown solid (344 mg, 94 %). m.p. : 170°C (d). IR (KBr) : ν cm^{-1} 1732 (C=O), 1600, 1494 and 1443 (C=C, C=N). ^{1}H NMR ($CDCl_3$) : δ ppm 1.49 (s, 9H, $(\mathbf{CH_3})_3C$) ; 6.25 (s, 1H, benzodioxino-$\mathbf{H_3}$) ; 6.25 - 6.34 (m, 2H, $\mathbf{H_{arom}}$) ; 6.83 (s, 1H, $\mathbf{H_2}$) ; 6.84 - 6.88 (m, 2H, $\mathbf{H_{arom}}$) ; 7.13 (dd, 1H, $\mathbf{H_7}$, $J_{6,7}$ = 5 Hz, $J_{7,8}$ = 8 Hz) ; 7.29 (dd, 1H, $\mathbf{H_8}$, $J_{6,8}$ = 1.5 Hz, $J_{7,8}$ = 8 Hz) ; 8.28 (dd, 1H, $\mathbf{H_6}$, $J_{6,7}$ = 5 Hz, $J_{6,8}$ = 1.5 Hz). ^{13}C NMR ($CDCl_3$) : δ ppm 28.30 ($3\mathbf{CH_3}$, $(\mathbf{CH_3})_3C$) ; 83.60 (C, $(CH_3)_3\mathbf{C}$) ; 116.50 and 116.55 (2CH) ; 119.75 (C) ; 122.60 (CH, $\mathbf{C_7}$) ; 124.40 ; 124.45 and 124.50 (4CH, $\mathbf{C_8}$ and benzodioxino-$\mathbf{C_3}$) ; 131.85 (C) ; 136.10 (CH, $\mathbf{C_2}$) ; 142.05 ; 142.30 and 142.50 (3C) ; 144.00 (CH, $\mathbf{C_6}$) ; 147.10 (C) ; 152.00 (C, **C=O**). MS : *m/z* 367 (M+1). Anal. calc. for $C_{12}H_{14}N_2O_3$: C 65.6; H 5.0; N 7.7; Found: C 65.5; H 4.9; N 7.9.

4-(*tert*-Butoxycarbonyl)-3-(phenylethynyl)-*4H*-pyrido[3,2-*b*][1,4]oxazine (5f)

The reaction was carried out as described above for the synthesis of the compound **5a** with tributyl(phenylethynyl)tin (824 mg, 2 mmol) and 1.5 hour at reflux. After flash chromatography with petroleum ether/EtOAc (80/20), **5f** was obtained as a colorless oil (241 mg, 72 %). IR (NaCl) : ν cm^{-1} 2233 (C≡C), 1730 (C=O), 1573 and 1444 (C=C, C=N). ^{1}H NMR ($CDCl_3$) : δ ppm 1.55 (s, 9H, $(\mathbf{CH_3})_3C$) ; 6.75 (s, 1H, $\mathbf{H_2}$) ; 7.07 (dd, 1H, $\mathbf{H_7}$, $J_{6,7}$ = 5 Hz, $J_{7,8}$ = 8 Hz) ; 7.23 (dd, 1H, $\mathbf{H_8}$, $J_{6,8}$ = 1.5 Hz, $J_{7,8}$ = 8 Hz) ; 7.27 - 7.33 (m, 3H, $\mathbf{H_{arom}}$) ; 7.41 - 7.45 (m, 2H, $\mathbf{H_{arom}}$) ; 8.27 (dd, 1H, $\mathbf{H_6}$, $J_{6,7}$ = 5 Hz, $J_{6,8}$ = 1.5 Hz). ^{13}C NMR ($CDCl_3$) : δ ppm 28.50 ($3CH_3$, $(CH_3)_3C$) ; 82.00 and 90.05 (2C, C≡C) ; 83.40 (C, $(CH_3)_3\mathbf{C}$) ; 110.85 (C) ; 122.20 (CH, $\mathbf{C_7}$) ; 122.90 (C) ; 124.30 (CH, $\mathbf{C_8}$) ; 128.75 and 128.80 (3CH) ; 131.55 (2CH) ; 141.95 (C) ; 142.20 (CH, $\mathbf{C_2}$) ; 144.30 (CH, $\mathbf{C_6}$) ; 145.90 (C) ; 151.15 (C, **C=O**). MS : *m/z* 335 (M+1). Anal. calc. for $C_{12}H_{14}N_2O_3$: C 71.8; H 5.4; N 8.4; Found: C 71.7; H 5.4; N 8.3.

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