Synthesis and Molecular Design of 4,8-Diaryl- and 4,8-Di(arylethynyl)pyrido[4,3-*d*]pyrimidines: Potential Applications in Nonlinear Optics. Diazines Part 49.

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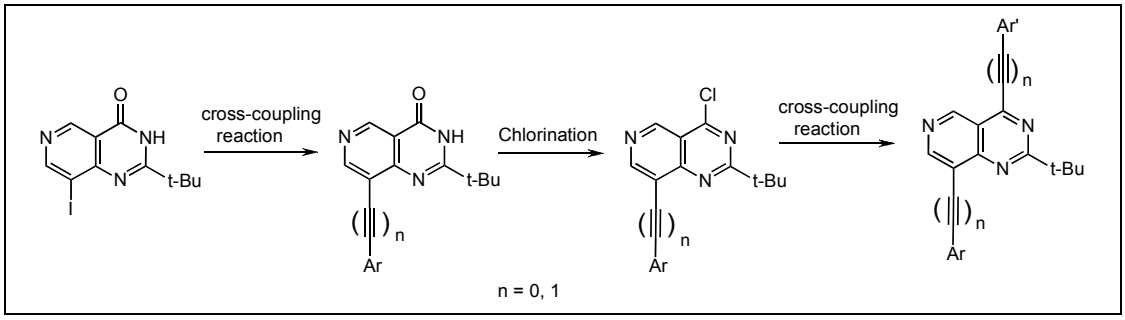

Using metallation and cross-coupling reactions, we report the synthesis of a new series of push-pull compounds with a pyrido[4,3-*d*]pyrimidine system as the central core. Two of them were tested and their NLO properties highlighted. Incorporation of triple and double bonds as spacer between the central core and the substituted aryl groups has been performed to allow an extension of conjugation.

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INTRODUCTION

Organic molecules with delocalized π-electron systems which may have applications in nonlinear optics (NLO) and electrooptics (EO) materials were extensively studied for their applications in optical data storage, telecommunications and optical signal processing.

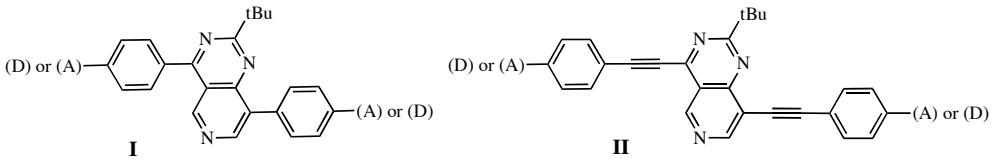
A typical NLO chromophore consists of an electron-withdrawing group (A) and an electron-donating group (D) connected by a π-conjugated system. There is widespread interest in the synthesis and study of optoelectronic properties of new conjugated oligoarenes containing electron-deficient heterocycles in the backbone or as pendant groups [1]. Azaheterocycles can be used as an electron-deficient unit in π-conjugated materials [2]. So it was established that pyridine [3], pyrimidine [4], quinoline [5] and 1,3,5-triazine [6] units improve electron characteristics compared to their phenylene analogues. Moreover, the introduction of aromatic rings improves the transparency-non linearity trade-off and the thermal stability, both factors being critical for electro-optical applications [7].

RESULTS AND DISCUSSION

In previous papers the synthesis of new materials with NLO properties comprising a cinnoline or quinazoline moiety [8] have been reported. In continuation of our work dealing with the functionalization of benzo- and pyridodiazines, we describe herein the synthesis, structure determination and potential optoelectronic properties of novel 4,8-diaryl pyrido[4,3-*d*]pyrimidines **I** and 4,8-diarylethynylpyrido[4,3-*d*]pyrimidines **II** (Scheme 1). In this last series an extension of the conjugation can be obtained *via* incorporation of ethynyl linkages between the central core and phenyl moieties substituted by electron-donor or acceptor groups.

In order to find relations between NLO properties and chemical structures, theoretical calculations have been performed to investigate the role of the different parts (A, D, π-system) in the molecule. The main goal of this work is to evaluate the quadratic NLO interest of structures **I** and **II** and not to optimize the values of the quadratic hyperpolarizability β. Standard donor (OMe, NMe_2) and acceptor groups (CN) have been used to compare properties

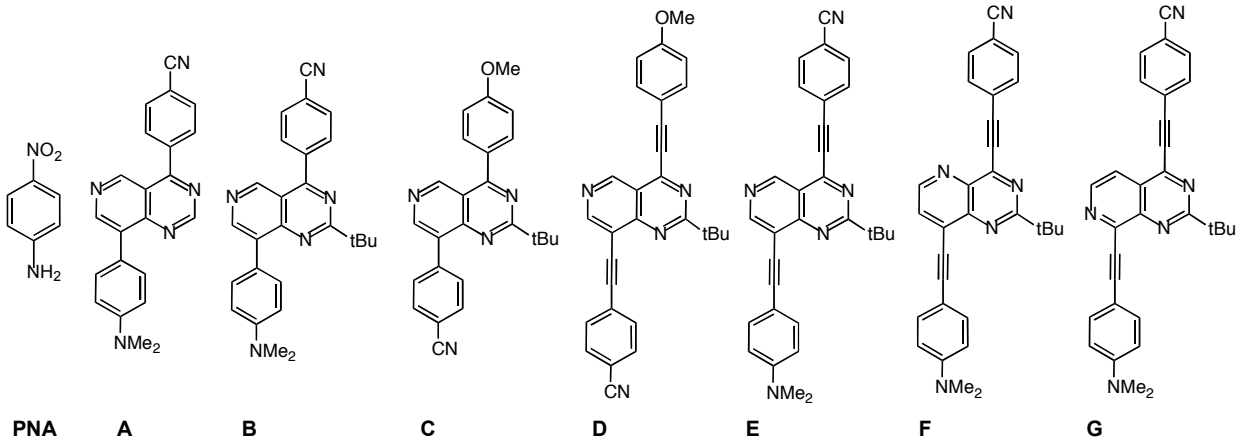
Scheme 1



of various systems. These properties have been also compared to those of *p*-nitroaniline (PNA), as a reference molecule in the field of quadratic NLO (Scheme 2).

Similar properties were observed for molecules **A** and **B**, which have the same backbone but differ only by the substituent at C_2. This result indicates that the presence of a bulky and non polar substituent such as the *tert*-butyl group at C_2 position does not modify significantly the properties of these molecules.

Scheme 2



Calculated hyperpolarizabilities values of structures **A**-**G** were established on the classical two-level model [9] and reported in Table 1.

Table 1

Theoretical NLO properties for structures **A**-**G**: maximum absorption wavelength (λ_{max}), dipole moment (μ), dipole moment difference ($\Delta\mu$) between the ground and the first excited charge transfer states and first-order hyperpolarizability (β_0).

Structure	λ_{max} (nm)	μ (D)	$\Delta\mu$ (D)	β_0 (10^{-30} esu)
PNA	310	8.2	6.8	8
A	361	9.1	11.6	15
B	357	9.2	10.4	15
C	343	8.2	1.6	8
D	385	9.6	1.8	23
E	430	5.6	19.4	43
F	426	9.0	13.7	53
G	420	4.1	11.2	36

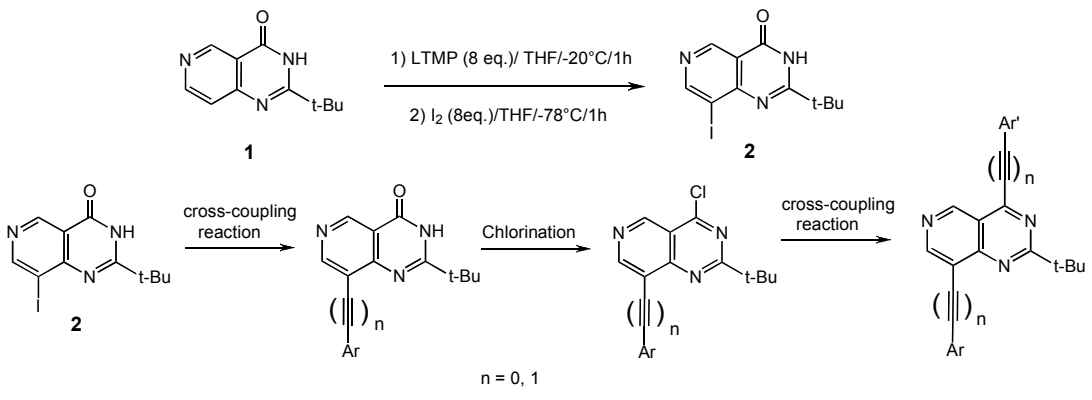
Molecule **C** presents the weakest static β_0 value of 8.10^{-30} esu, identical to the PNA molecule.

Introduction of alkynyl linkages at C_4 and C_8 positions **D**-**G** increases by two to three times the values of quadratic hyperpolarizability β_0.

We can note that for molecules **A**-**D** the quadratic hyperpolarizability β_0 and the linear absorption are influenced by the position of the electron-donor group. When this one is at C_8 on the pyridine moiety, the values of β_0 and λ_{max} are higher than when it is at C_4, fixed to the more π-deficient pyrimidine moiety. Moreover, the red-shift absorption becomes more important between **B** and **E** ($\Delta\lambda$= 73 nm) than between **C** and **D** ($\Delta\lambda$=42 nm).

Comparison between structures **E**, **F** and **G** shows the influence of the position of the nitrogen atom on the pyridine moiety. For these molecules similar maximum absorption wavelengths were calculated whereas the best

Scheme 3



value of β_0 was predicted for **F** when the nitrogen atom was at C_5.

We report here the synthesis of several molecules with a pyrido[4,3-*d*]pyrimidine as central core comprising one electron-rich aryl substituted by an electron-donor (D) while the other aryl group has a reduced electronic density resulting of substitution with an electron-withdrawing group (A) or is a π-deficient heteroarene. These aryl substituents are directly attached or connected by a triple bond to the core of the molecule.

According to the general synthetic route, the target compounds **I** and **II** were obtained using cross-coupling reactions from 2-*tert*-butyl-8-iodopyrido[4,3-*d*]pyrimidin-4(3*H*)-one **2** as starting material (Scheme 2). The key intermediate **2** was synthesized *via* metallation reaction of 2-*tert*-butyl-pyrido[4,3-*d*]pyrimidin-4(3*H*)-one **1** with lithium tetramethylpiperidide (LTMP) at low temperature (-20°C), followed by reaction with iodine as the electrophile (Scheme 3) [10]

Synthesis of the 4,8-diaryl pyrido[4,3-*d*]pyrimidines **I** involves formation of the first aryl-aryl bond at the C_8 position obtained by a Suzuki cross-coupling reaction of **2** leading to compounds **3**-**5**. The 4-oxo derivatives were converted with phosphorus oxychloride to their 4-chloro analogues **6**-**8**. In a last step these compounds reacted with arylboronic acid to give the expected compounds **9**-**12** (Scheme 4).

Experimental results for β showed values approximately twice as high as the theoretical data. As was predicted by calculation, we observed a higher value for β when the electron-donor group was at C_8 on the pyridine moiety.

Table 2

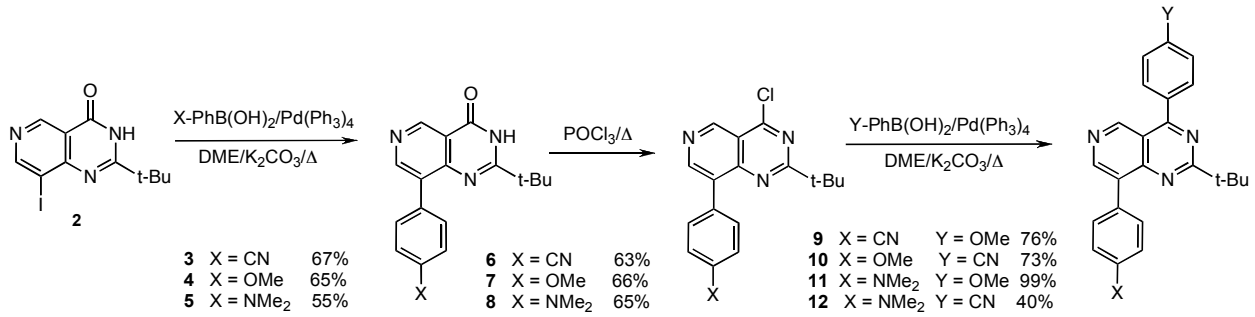
Theoretical and experimental data **PNA**, **9** and **12**: maximum absorption wavelength (λ_{max}) and first-order hyperpolarizability (β_0).

Compound	λ^{th}_{max} (nm)	λ^{exp}_{max} (nm)	ε^{exp}	β_0^{th} (10^{-30} esu)	β_0^{exp} (10^{-30} esu)
PNA	312	310	-	8	7
9	343	333	14418	8	13
12	357	397	6394	15	33

A new series of pyrido[4,3-*d*]pyrimidines bearing one or two arylethynyl groups at C_8 or at C_4 and C_8 positions were also synthesized by Pd-catalyzed Sonogashira coupling reaction. Starting from compound **2** a first coupling reaction was performed at C_8 position leading to compounds **13**-**16**. As previously, reaction with phosphorus oxychloride gave the C_4 chlorinated compounds **17-19** which underwent a further coupling reaction to give the diarylethynyl compounds **20** and **21** (Scheme 5).

When the second Sonogashira coupling was performed with the difluoro derivative **19** and 2-

Scheme 4



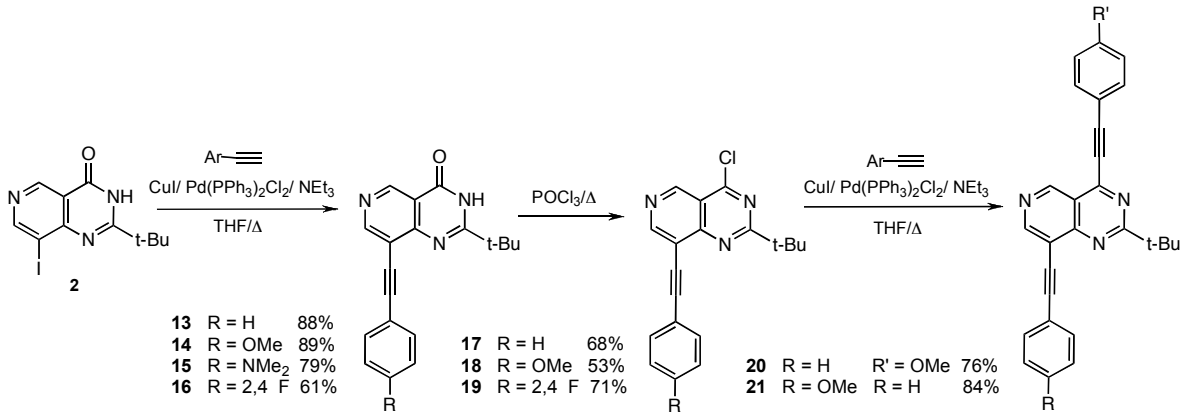
Starting from 2-*tert*-butylpyrido[4,3-*d*]pyrimidin-4(3*H*)-one **1**, four new push-pull compounds **9**-**12** were obtained in four steps with an overall yield varying from 14 to 33%. These compounds present a high thermal stability with melting points between 171°C and 232°C.

Theoretical and experimental NLO properties of PNA and compounds **9** and **12** could be compared (Table 2).

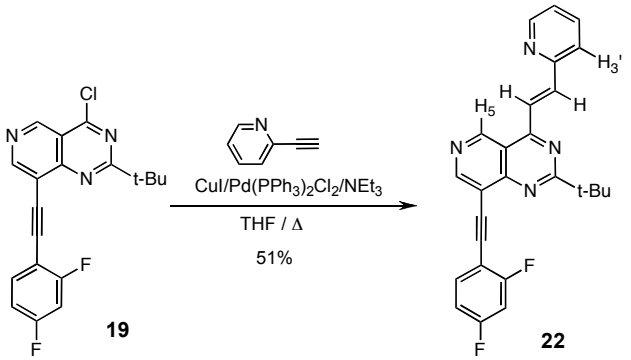
The hyperpolarizability value β_0 was calculated and measured using the EFISH method for compounds **9** and **12** which present a higher quadratic hyperpolarizability than *p*-nitroaniline.

pyridylethyne, the compound **22** bearing an arylethynyl group and an arylvinyl group was obtained in 51% yield. The ^{1}H NMR spectrum presents two signals at 8.54 and 8.35 ppm which were assigned to the vinylic protons. The coupling constant of 14.7 Hz was attributed to an *E* configuration for the double bond. To determine which triple bond had been reduced, a NOESY NMR experiment was performed, the correlations between H_5 (9.72 ppm) the pyridyl $H_{3'}$ (7.60 ppm) with the two vinylic protons respectively at 8.54 and 8.35 ppm indicated that the double bond was located between the pyridine ring and the pyridopyrimidine moiety (Scheme 6).

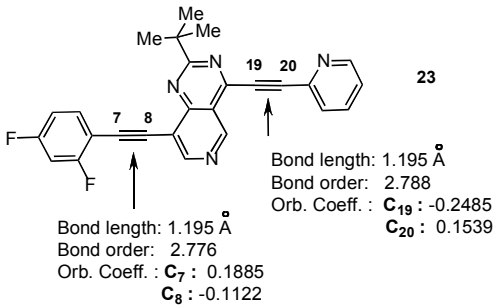
Scheme 5



Scheme 6



Scheme 7



To explain the regioselective reduction of the triple bond fixed at the C_4 position a semi-empirical calculation using PM3 method has been performed with the hypothetical compound **23** bearing two triple bonds. Geometry optimization obtained with PM3 method reveals a planar structure for molecule **23** without sterical hindrance (Figure 1).

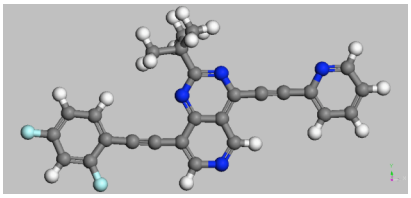


Figure 1

Bond length, bond order and orbital coefficients in the LUMO have been calculated for each triple bond and reported (Scheme 7).

The bond lengths of the two triple bonds are identical, a slightly higher value of bond order is observed for the triple bond between the central core and the pyridine moiety. Comparison of the orbital coefficients in the LUMO for the carbon atoms of the triple bonds reveals higher values for the triple bond fixed on the pyridine ring and could explain the better reactivity of this bond towards the reduction reaction.

CONCLUSION

Using metallation and cross-coupling reactions, we have synthesized a new series of push-pull compounds with a pyrido[4,3-*d*]pyrimidine system as central core. Two of these compounds were tested and have highlighted NLO properties. In addition, incorporation of triple and double bonds as spacer between the central core and the substituted aryl groups allowed an extension of conjugation which could improve NLO properties. Synthesis of similar compounds with various central cores and substituted aryl groups are in progress and their NLO properties will be studied in the future.

EXPERIMENTAL

The geometry of the molecules was optimized by using Sybyl, *i.e*. Tripos force field and PM3 from MOPAC package [11]. The experimental quadratic hyperpolarizability was determinated by using the well-known EFISH (Electric Field Induced Second Harmonic) method [12] at the wavelength of 1.907 μm.

Melting points were determined on a Kofler hot-stage. The ir spectra were obtained as potassium bromide pellets with a Perkin-Elmer Paragon 500 spectrophotometer. The ^{1}H, ^{13}C and

^{19}F nmr spectra were recorded on a Bruker AC 300 (300 MHz ^{1}H, 75 MHz ^{13}C, 282 MHz ^{19}F) instrument. Mass spectra were recorded on a JEOL JMS AX500. Microanalyses were performed on a Carlo Erba CHNOS 1160 apparatus.

All reagents were of commercial quality and were purchased from Acros, Aldrich Chemical Co. or Avocado. The Pd(0)-catalyst $Pd(PPh_3)_4$ was prepared according to the literature. 4-Methoxyphenyl-, 4-*N*,*N*-dimethylaminophenyl- and 4-cyanophenylboronic acids were synthesized by halogen-metal exchange followed by reaction with trimethylborate or triisopropylborate from the commercially available 4-bromoanisole, 4-bromo-*N*,*N*-dimethylaniline or 4-bromobenzonitrile.

General cross-coupling procedure A of arylboronic acid with heteroaryl halide. A mixture of the heteroaryl halide (2 mmol), the arylboronic acid (1.3 equiv.), $Pd(PPh_3)_4$ (0.05 equiv.), aqueous 2M sodium carbonate (2 equiv.) and water (2 mL) in degassed dimethoxyethane (15 mL) was heated under reflux and under nitrogen for 40-60 hours. After cooling to room temperature, the organic solvent was evaporated under reduced pressure, the residue was diluted with water and extracted with dichloromethane (3x15 mL), the combined organic extracts were dried over magnesium sulfate and evaporated. The crude product was purified by column chromatography on silica gel.

General cross-coupling procedure B of alkynes with heteroaryl halide. To a mixture of the heteroaryl halide, copper(I) iodide (0.03 equiv.), bis(triphenylphosphine)palladium(II) chloride (0.03 equiv.), in degassed tetrahydrofuran, triethylamine (2.5 equiv.) and alkyne (1.2 equiv) were added under nitrogen. The mixture was heated under reflux for 24-60 hours. After cooling to room temperature, the organic solvent was evaporated under reduced pressure, the residue was diluted with water and extracted with dichloromethane (3x15 mL), the combined organic extracts were dried over magnesium sulfate and evaporated. The crude product was purified by column chromatography on silica gel.

2-*tert*-Butylpyrido[4,3-*d*]pyrimidin-4(3*H*)-one **(1)** [10] mp 248-249°C, mp(litt) 248-249°C .

2-*tert*-Butyl-8-iodopyrido[4,3-*d*]pyrimidin-4(3*H*)-one **(2)** [10] mp > 250°C, mp(litt) > 250°C.

2-*tert*-Butyl-8-(4'-cyanophenyl)pyrido[4,3-*d*]pyrimidin-4(3*H*)-one (3). Coupling of 4-cyanophenylboronic acid (1.3 equiv.) with **2** (747 mg, 2 mmol) according to the general procedure A (*t* = 40 hours) gave after purification by column chromatography (silica gel, eluent:petroleum ether:ethyl acetate (6:4)) 408 mg (67%) of **3** as a slight yellow solid, mp >250°C; ir : 3191, 3106, 2970, 2905, 2226, 1711, 1698, 1586, 1489, 1465, 1388, 835, 811 cm^{-1}; ^{1}H nmr (deuteriochloroform) : δ 11.41 (s, 1H, NH); 9.53 (s, 1H, H_5); 8.91 (s, 1H, H_7); 7.86 (d, J = 8.3 Hz, 2H, $H_{2'/6'}$); 7.78 (d, J = 8.3 Hz, 2H, $H_{3'/5'}$); 1.45 (s, 9H, 3 $CH_{3\ tert\text{-}butyl}$); ^{13}C nmr (deuteriochloroform) : δ 167.2 (C_2), 163.4 (C_4), 153.8 (C_7), 151.5 (C_{8a}), 150.9 (C_5), 140.0 ($C_{1'}$), 132.1 ($C_{3'}$,$C_{5'}$), 131.6 ($C_{2'}$,$C_{6'}$), 131.4 (C_8), 119.2 (CN), 116.7 (C_{4a}), 112.1 ($C_{4'}$), 38.9 ($C_{tert\text{-}butyl}$), 28.5 (3 $CH_{3\ tert\text{-}butyl}$); ms (IC) : 305 ($MH^+$). *Anal.* Calcd for $C_{18}H_{16}N_4O$ (304.35) : C, 71.04; N, 18.41; H, 5.30. Found: C, 70.91; N, 18.74; H, 5.39.

2-*tert*-Butyl-8-(4'-methoxyphenyl)pyrido[4,3-*d*]pyrimidin-4(3*H*)-one (4). Coupling of 4-methoxyphenylboronic acid (1.3 equiv.) with **2** (747 mg, 2 mmol) according to the general procedure A (*t* = 40 hours) gave after purification by crystallization in dichloromethane, 359 mg (58%) of **4** as a beige solid, mp >250°C; ir : 3189, 1693, 1593, 1514, 1463, 1390, 1293, 1247, 1178, 833, 812 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6) : δ 12.36 (s, 1H, NH); 9.22 (s, 1H, H_5); 8.88 (s, 1H, H_7); 7.78 (d, J = 8.3 Hz, 2H, $H_{2'/6'}$); 7.06 (d, J = 8.7 Hz, 2H, $H_{3'/5'}$); 3.84 (s, 3H, OCH_3); 1.34 (s, 9H, 3 $CH_{3\ tert\text{-}butyl}$); ^{13}C nmr (dimethyl sulfoxide-d_6) : δ 166.9 (C_2), 162.0 (C_4), 159.1, 152.4 (C_7), 150.1, 147.8 (C_5), 131.7 ($C_{2'}$,$C_{6'}$), 131.4, 126.8, 116.5 (C_{4a}), 113.4 ($C_{3'}$,$C_{5'}$), 55.2 (OCH_3), 38.1 ($C_{tert\text{-}butyl}$), 27.6 (3 $CH_{3\ tert\text{-}butyl}$). *Anal.* Calcd for $C_{18}H_{19}N_3O_2$ (309.37) : C, 69.88; N, 13.58; H, 6.19. Found: C, 69.49; N, 13.29; H, 6.23.

2-*tert*-Butyl-8-(4'-*N*,*N*-dimethylaminophenyl)pyrid-[4,3-*d*]-pyrimidin-4(3*H*)-one (5). Coupling of 4-*N*,*N*-Dimethylaminophenylboronic acid (1.3 equiv.) with **2** (747 mg, 2 mmol) according to the general procedure A (*t* = 40 hours) gave after purification by column chromatography (silica gel, eluent : ethyl acetate) 355 mg (55%) of **5** as a yellow solid, mp >250°C; ir : 3175, 3040, 2965, 2908, 1683, 1609, 1522, 1460, 1390, 1156, 818 cm^{-1};^{1}H nmr (deuteriochloroform) : δ 11.14 (s, 1H, NH); 9.39 (s, 1H, H_5); 8.92 (s, 1H, H_7); 7.73 (d, J = 8.7 Hz, 2H, $H_{2'/6'}$); 6.83 (d, J = 8.7 Hz, 2H, $H_{3'/5'}$); 3.04 (s, 6H, $N(CH_3)_2$); 1.47 (s, 9H, 3 $CH_{3\ tert\text{-}butyl}$); ^{13}C nmr (deuteriochloroform) : δ 166.0 (C_2), 164.1 (C_4), 153.1 (C_7), 151.0 (C_{8a} or $C_{4'}$), 150.3 (C_{8a} or $C_{4'}$), 148.0 (C_5), 132.9 (C_8), 131.6 ($C_{2'}$,$C_{6'}$), 122.5 ($C_{1'}$), 116.4 (C_{4a}), 112.0 ($C_{3'}$,$C_{5'}$), 40.5 (2 CH_3), 38.6 ($C_{tert\text{-}butyl}$), 28.3 (3 $CH_{3\ tert\text{-}butyl}$); ms (IC) : 323 ($MH^+$). *Anal.* Calcd for $C_{19}H_{22}N_4O$ (322.41) : C, 70.78; N, 17.28; H, 6.88. Found: C, 70.58; N, 16.87; H, 6.82.

2-*tert*-Butyl-4-chloro-8-(4'-cyanophenyl)pyrido[4,3-*d*]pyrimidine (6). Reaction of **3** (400 mg, 1.3 mmol) in $POCl_3$ (20 mL) under reflux for 5 hours, followed by removal of excess of $POCl_3$ under reduced pressure and partitionning of the residue between CH_2Cl_2 and cold aqueous Na_2CO_3 solution, gave after purification by column chromatography (silica gel, eluent : petroleum ether:ethyl acetate (4:6)) 264 mg (63%) of **6** as a yellow solid, mp >250°C; ir : 3042, 2965, 2854, 2230, 1593, 1558, 1460, 1341, 1143, 838 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 9.63 (s, 1H, H_5); 8.99 (s, 1H, H_7); 7.91 (d, J = 8.3 Hz, 2H, $H_{2'/6'}$); 7.79 (d, J = 8.3 Hz, 2H, $H_{3'/5'}$); 1.40 (s, 9H, 3 $CH_{3\ tert\text{-}butyl}$); ^{13}C nmr (deuteriochloroform) : δ 177.6 (C_2), 163.2 (C_4), 151.8 (C_{8a}), 151.3 (C_5), 151.1 (C_7), 139.1 ($C_{1'}$), 132.1 ($C_{3'}$,$C_{5'}$), 131.5 ($C_{2'}$,$C_{6'}$), 131.1 (C_8), 118.9 (CN), 117.6 (C_{4a}), 112.4 ($C_{4'}$), 40.9 ($C_{tert\text{-}butyl}$), 29.3 (3 $CH_{3\ tert\text{-}butyl}$). *Anal.* Calcd for $C_{18}H_{15}ClN_4$ (322.80) : C, 66.98; N, 17.36; H, 4.68. Found: C, 67.34; N, 17.97; H, 5.18.

2-*tert*-Butyl-4-chloro-8-(4'-methoxyphenyl)pyrido[4,3-*d*]-pyrimidine (7). Reaction of **4** (350 mg, 1.1 mmol) in $POCl_3$ (20 mL) under reflux for 6 hours, followed by removal of excess of $POCl_3$ under reduced pressure and partitionning of the residue between CH_2Cl_2 and cold aqueous Na_2CO_3 solution, gave after purification by column chromatography (silica gel, eluent: petroleum ether:ethyl acetate (8:2)) 238 mg (66%) of **7** as a yellow oil; ir : 1502, 1574, 1556, 1461, 1341, 1250, 1180, 1143, 1035, 830, 808 cm^{-1};^{1}H nmr (deuteriochloroform) : δ 9.53 (s, 1H, H_5); 8.98 (s, 1H, H_7); 7.78 (d, J = 8.3 Hz, 2H, $H_{2'/6'}$); 7.04 (d, J = 8.7 Hz, 2H, $H_{3'/5'}$); 3.88 (s, 3H, OCH_3); 1.44 (s, 9H, 3 $CH_{3\ tert\text{-}butyl}$); ^{13}C nmr (deuteriochloroform) : δ 176.8 (C_2), 163.1 (C_4), 160.0 (2 C_q), 151.9, 150.3 (C_5 or C_7), 149.1 (C_5 or C_7), 132.1 ($C_{2'}$,$C_{6'}$), 126.4 (2 C_q), 113.8 ($C_{3'}$,$C_{5'}$), 55.4 (OCH_3), 40.7 ($C_{tert\text{-}butyl}$), 29.2 (3 $CH_{3\ tert\text{-}butyl}$). *Anal.* Calcd for $C_{18}H_{18}ClN_30$ (327.82) : C, 65.95; N, 12.82; H, 5.53. Found: C, 65.55; N, 12.92; H, 5.96.

2-*tert*-Butyl-4-chloro-8-(4'-*N*,*N*-dimethylaminophenyl)pyrido[4,3-*d*]pyrimidine (8). Reaction of **5** (355 mg, 1.1 mmol) in $POCl_3$ (20 mL) under reflux for 4 hours, followed by removal of excess of $POCl_3$ under reduced pressure and partitionning of the residue between CH_2Cl_2 and cold aqueous Na_2CO_3 solution, gave 377 mg (65%) of **8** as an orange solid; ^{1}H nmr (deuteriochloro-

form): δ 9.49 (s, 1H, H_5); 9.00 (s, 1H, H_7); 7.82 (d, J = 8.7 Hz, 2H, $H_{2'/6'}$); 6.85 (d, J = 8.7 Hz, 2H, $H_{3'/5'}$); 3.06 (s, 3H, $N(CH_3)_2$); 1.47 (s, 9H, 3 CH_3 *tert*-butyl); ^{13}C nmr (deuteriochloroform): δ 175.2, 162.0, 150.8 (C_{8a} or $C_{4'}$), 149.6 (C_{8a} or $C_{4'}$), 149.3 (C_5 or C_7), 147.3 (C_5 or C_7), 131.8 (C_8), 130.8 ($C_{2'}$,$C_{6'}$), 120.7 ($C_{1'}$), 116.7 (C_{4a}), 111.0 ($C_{3'}$,$C_{5'}$), 39.7 (C *tert*-butyl), 39.5 (2x CH_3), 28.4 (3xCH_3 *tert*-butyl). *Anal.* Calcd for $C_{19}H_{21}ClN_4$ (340.86) : C, 66.95; N, 16.44; H, 6.21. Found: C, 66.65; N, 15.92; H, 6.06.

2-*tert*-Butyl-8-(4''-cyanophenyl)-4-(4'-methoxyphenyl)pyrido[4,3-*d*]pyrimidine (9). Coupling of 4-methoxyphenylboronic acid (1.3 equiv.) with **6** (646 mg, 2 mmol) according to the general procedure A (*t* = 48 hours) gave after purification by column chromatography (silica gel, eluent:petroleum ether:ethyl acetate (6:4)) 600 mg (76%) of **9** as a yellow solid, mp 171°C; ir : 2223, 1605, 1544, 1470, 1380, 1254, 1175, 843, 830 cm^{-1}; ^1H nmr (deuteriochloroform) : δ 9.55 (s, 1H, H_5); 8.92 (s, 1H, H_7); 8.00 (d, J = 8.3 Hz, 2H, $H_{2''/6''}$); 7.91 (d, J = 8.7 Hz, 2H, $H_{2'/6'}$); 7.82 (d, J = 8.3 Hz, 2H, $H_{3''/5''}$); 7.14 (d, J = 8.7 Hz, 2H, $H_{3'/5'}$); 1.47 (s, 9H, 3 CH_3 *tert*-butyl); ^{13}C nmr (deuteriochloroform): δ 177.3 (C_2), 168.7 (C_4), 162.3 ($C_{4'}$), 152.9 (C_5), 152.1 (C_{8a}), 149.5 (C_7), 140.2 ($C_{1''}$), 132.7 , 132.1 , 131.8 , 131.4 (C_8), 129.1 ($C_{1'}$), 119.3 (CN), 116.7 (C_{4a}), 114.7 , 112.0 ($C_{4''}$), 55.9 (OCH_3), 40.9 (C *tert*-butyl), 29.7 (3xCH_3 *tert*-butyl). *Anal.* Calcd for $C_{25}H_{22}N_4O$ (394.48): C, 76.12; N, 14.20; H, 5.62. Found: C, 76.37; N, 13.88; H, 5.35.

2-*tert*-Butyl-4-(4'-cyanophenyl)-8-(4''-methoxyphenyl)pyrido[4,3-*d*]pyrimidine (10). Coupling of 4-cyanophenylboronic acid (1.3 equiv.) with **7** (655 mg, 2 mmol) according to the general procedure A (*t* = 60 hours) gave after purification by column chromatography (silica gel, eluent:petroleum ether:ethyl acetate (8:2)) 576 mg (73%) of **10** as a yellow solid, mp 232°C; ir : 2228, 1590, 1570, 1547, 1468, 1381, 1252, 1178, 831, 812 cm^{-1}; ^1H nmr (deuteriochloroform) : δ 9.31 (s, 1H, H_5); 8.95 (s, 1H, H_7); 7.99 (d, J = 8.3 Hz, 2H, $H_{2'/6'}$); 7.91 (d, J = 8.7 Hz, 2H, $H_{3'/5'}$); 7.85 (d, J = 8.7 Hz, 2H, $H_{2''/6''}$); 7.07 (d, J = 8.7 Hz, 2H, $H_{3''/5''}$); 3.90 (s, 3H, OCH_3); 1.49 (s, 9H, 3 CH_3 *tert*-butyl); ^{13}C nmr (deuteriochloroform) : δ 176.6 (C_2), 171.3 (C_4), 167.1, 160.0, 151.8, 149.7 (C_5), 149.4 (C_7), 141.0, 132.9, 132.6 ($C_{2''/6''}$), 132.2 ($C_{3'}$,$C_{5'}$), 131.2 ($C_{2'/6'}$), 126.9, 118.3, 116.3, 114.4, 113.8 ($C_{3''}$,$C_{5''}$), 55.4 (OCH_3), 40.8 (C *tert*-butyl), 29.5 (3 CH_3 *tert*-butyl). *Anal.* Calcd for $C_{25}H_{22}N_4O$ (394.48): C, 76.12; N, 14.20; H, 5.62. Found: C,75.91; N, 13.99; H, 5.82.

2-*tert*-Butyl-8-(4''-*N*,*N*-dimethylaminophenyl)-4-(4'-methoxyphenyl)pyrido[4,3-*d*]pyrimidine (11). Coupling of 4-methoxyphenylboronic acid (1.3 equiv.) with **8** (681 mg, 2 mmol) according to the general procedure A (*t* = 48 hours) gave after purification by column chromatography (silica gel, eluent: petroleum ether:ethyl acetate (6:4)) 800 mg (97%) of **11** as a yellow solid, mp 203°C; ir : 1613, 1586, 1544, 1526, 1484, 1466, 1380, 1253, 1174, 1159, 1030, 827, 812 cm^{-1}; ^1H nmr (deuteriochloroform) : δ 9.39 (s, 1H, H_5); 8.92 (s, 1H, H_7); 7.90 (m, 4H, $H_{2'/6'/2''/6''}$); 7.12 (d, J = 8.7 Hz, 2H, $H_{3'/5'}$); 6.89 (d, J = 8.7 Hz, 2H, $H_{3'/5'}$); 6.89 (d, J = 8.7 Hz, 2H, $H_{3''/5''}$); 3.93 (s, 3H, OCH_3), 1.52 (s, 9H, 3 CH_3 *tert*-butyl); ^{13}C nmr (deuteriochloroform): δ 176.2 (C_2), 168.4 (C_4), 162.0 ($C_{4'}$), 152.2 (C_{8a}), 150.6 ($C_{4''}$), 150.1 (C_5 or C_7), 148.7 (C_5 or C_7), 133.1 (C_8), 132.6 (2xCH_{Ar}), 132.0 (2xCH_{Ar}), 129.7 ($C_{1'}$), 123.0 ($C_{1''}$), 116.9 (C_{4a}), 114.5 ($C_{3'}$,$C_{5'}$), 112.2 ($C_{3''}$,$C_{5''}$), 55.9 (OCH_3), 40.8 (C *tert*-butyl), 40.7 2x CH_3), 29.9 (3xCH_3 *tert*-butyl). *Anal.* Calcd for $C_{26}H_{28}N_4O$ (412.54) : C, 75.70; N, 13.58; H, 6.84. Found: C, 75.77; N, 13.25; H, 6.91.

2-*tert*-Butyl-4-(4'-cyanophenyl)-8-(4''-*N*,*N*-dimethylaminophenyl)pyrido[4,3-*d*]pyrimidine (12). Coupling of 4-cyanophenylboronic acid (1.3 equiv.) with **8** (681 mg, 2 mmol) according to the general procedure A (*t* = 48 hours) gave after purification by column chromatography (silica gel, eluent: petroleum ether:ethyl acetate (6:4)) 326 mg (40%) of **12** as a yellow solid, mp 228°C; ir : 2226, 1610, 1584, 1542, 1525, 1466, 1379, 1359, 1202, 1160, 851, 826, 811 cm^{-1}; ^1H nmr (deuteriochloroform) : δ 9.23 (s, 1H, H_5); 8.94 (s, 1H, H_7); 7.97 (d, J = 8.3 Hz, 2H, $H_{2'/6'}$); 7.86 (m, 4H, $H_{2''/6''/3'/5'}$); 6.86 (d, J = 8.7 Hz, 2H, $H_{3''/5''}$); 3.05 (s, 6H, $N(CH_3)_2$, 1.49 (s, 9H, 3 CH_3 *tert*-butyl); ^{13}C nmr (deuteriochloroform): δ 176.4 (C_2), 167.1 (C_4), 152.0 (C_{8a}), 150.7 ($C_{4''}$), 149.0 (C_7), 148.8 (C_5), 141.3 ($C_{1'}$), 133.4 (C_8), 132.7 (2xCH_{Ar}), 132.0 (2xCH_{Ar}), 131.3 ($C_{2'/6'}$), 122.2 ($C_{1''}$), 118.5 (CN), 116.5 (C_{4a}), 114.4 ($C_{4'}$), 112.1 ($C_{3''}$,$C_{5''}$), 40.9 (C *tert*-butyl), 40.6 (2 CH_3), 29.7 (3 CH_3 *tert*-butyl); *Anal.* Calcd for $C_{26}H_{25}N_5$ (407.21) : C, 76.63; N, 17.19; H, 6.18. Found: C, 76.59; N, 16.92; H, 6.65.

2-*tert*-Butyl-8-(phenylethynyl)pyrido[4,3-*d*]pyrimidin-4(3*H*)-one (13). Coupling of phenylacetylene (1.2 equiv.) with **2** (373 mg, 1 mmol) according to the general procedure B (*t* = 24 hours) gave after purification by column chromatography (silica gel, eluent:petroleum ether:ethyl acetate (6:4)) 267 mg (88%) of **13** as a yellow solid, mp >250°C; ir : 2210, 1707, 1585, 1493, 1395, 1160, 813, 760, 690 cm^{-1}; ^1H nmr (deuteriochloroform): δ 10.15 (s, 1H, NH); 9.38 (s, 1H, H_5); 9.01 (s, 1H, H_7); 7.62 (m, 2H, $H_{2'/6'}$); 7.39 (m, 3H, $H_{3'/4'/5'}$); 1.52 (s, 9H, 3 CH_3 *tert*-butyl); ^{13}C nmr (deuteriochloroform): δ 167.8 (C_2), 163.4 (C_4), 156.3 (C_7), 154.4 (C_{8a}), 149.1 (C_5), 132.0 ($C_{2'}$,$C_{6'}$), 129.0 ($C_{4'}$), 128.6 ($C_{3'}$,$C_{5'}$), 123.0 ($C_{4'}$), 117.9, 116.1, 98.4, 83.4, 38.6 (C *tert*-butyl), 28.3 (3 CH_3 *tert*-butyl). *Anal.* Calcd for $C_{19}H_{17}N_3O$ (303.37) : C, 75.23; N, 13.85; H, 5.65. Found: C, 75.12; N, 13.68; H, 5.92.

2-*tert*-Butyl-8-(4'-methoxyphenylethynyl)pyrido[4,3-*d*]pyrimidin-4(3*H*)-one (14). Coupling of 4-methoxyphenylethyne [13] (1.2 equiv.) with **2** (373 mg, 1 mmol) according to the general procedure B (*t* = 24 hours) gave after purification by column chromatography (silica gel, eluent:petroleum ether:ethyl acetate (6:4)) 297 mg (89%) of **14** as a yellow solid, mp >250°C; ir : 3178, 2209, 1677, 1563, 1510, 1465, 1253, 1164 1029, 825, 808 cm^{-1}; ^1H nmr (deuteriochloroform): δ 11.13 (s, 1H, NH); 9.37 (s, 1H, H_5); 8.99 (s, 1H, H_7); 7.56 (d, J = 8.7 Hz, 2H, $H_{2'/6'}$); 6.92 (d, J = 8.7 Hz, 2H, $H_{3'/5'}$); 3.85 (s, 3H, OCH_3); 1.55 (s, 9H, 3 CH_3 *tert*-butyl); ^{13}C nmr (deuteriochloroform): δ 167.4 (C_2), 163.0 (C_4), 160.3 ($C_{4'}$),156.1 (C_7), 154.2 (C_{8a}), 148.7 (C_5), 133.6 ($C_{2'}$,$C_{6'}$), 118.2 (C_8), 116.1 (C_{4a}), 115.1 ($C_{1'}$), 114.3 ($C_{3'}$,$C_{5'}$), 98.7, 82.2, 55.5 (OCH_3), 38.5 (C *tert*-butyl), 28.3 (3 CH_3 *tert*-butyl). *Anal.* Calcd for $C_{20}H_{19}N_3O_2$ (333.39) : C, 72.05; N, 12.60; H, 5.74. Found: C, 71.66; N, 12.45; H, 5.89.

2-*tert*-Butyl-8-(4'-*N*,*N*-dimethylphenylethynyl)pyrido[4,3-*d*]-pyrimidin-4(3*H*)-one (15). Coupling of 4-*N*,*N*-dimethyl-aminophenylethyne [13, 14] (1.2 equiv.) with **2** (373 mg, 1 mmol) according to the general procedure B (*t* = 24 hours) gave after purification by column chromatography (silica gel, eluent: petroleum ether:ethyl acetate (7:3)) 274 mg (79%) of **15** as a yellow solid, mp >250°C; ir : 3177, 2201, 1673, 1607, 1586, 1558, 1520, 1462, 1391, 1359, 1222, 1151, 1115, 810 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 12.41 (s, 1H, NH); 9.12 (s, 1H, H_5); 8.89 (s, 1H, H_7); 7.40 (d, J = 8.7 Hz, 2H, $H_{2'/6'}$); 6.77 (d, J = 8.7 Hz, 2H, $H_{3'/5'}$); 3.98 (s, 6H, $N(CH_3)_2$); 1.42 (s, 9H, 3 CH_3 *tert*-butyl); ^{13}C nmr (deuteriochloroform): δ 168.0 (C_2), 161.9 (C_4), 154.4 (C_7), 153.1 (C_{8a}), 150.4 ($C_{4'}$), 147.4 (C_5), 132.5 ($C_{2'}$,$C_{6'}$), 117.4, 116.3, 112.0 ($C_{3'}$,$C_{5'}$), 108.2 ($C_{1'}$), 99.4, 82.1, 38.0 (C *tert*-butyl), 30.7 ($N(CH_3)_2$), 28.3 (3 CH_3 *tert*-butyl). *Anal.* Calcd for $C_{21}H_{22}N_4O$ (346.44) : C, 72.81; N, 16.17; H, 6.40. Found: C, 72.47; N, 15.89; H, 6.03.

2-*tert*-Butyl-8-(2',4'-difluorophenylethynyl)pyrido[4,3-*d*]-pyrimidin-4(3*H*)-one (16). Coupling of 2,4-difluorophenylethyne (1.2 equiv.) with **2** (373 mg, 1 mmol) according to the general procedure B (*t* = 48 hours) gave after purification by column chromatography (silica gel, eluent:petroleum ether:ethyl acetate (6:4)) 207 mg (61%) of **16** as a brown solid, mp >250°C; ir : 2318, 1722, 1704, 1587, 1509, 1397, 1267, 1093, 966, 849, 810 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 12.46 (s, 1H, NH); 9.21 (s, 1H, H_5); 8.99 (s, 1H, H_7); 7.71 (m, 1H, $H_{6'}$); 7.49 (m, 1H, $H_{Ph\text{-}F2}$); 7.23 (m, 1H, $H_{Ph\text{-}F2}$); 1.39 (s, 9H, 3 CH_3 *tert*-butyl); ^{19}F nmr (dimethyl sulfoxide-d_6) : δ -105.0 (d, J = 9.7 Hz, 1F), -106.3 (d, J = 9.7 Hz, 1F); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 168.7 (C_2), 164.2 (m, C_F), 161.6, 155.4 (C_7), 154.6 (C_{8a}), 148.9 (C_5), 144.1, 134.8 (d, J = 37.6 Hz, $C_{6'}$), 116.5, 115.9, 112.8 (dd, J = 80.9 and 14.5 Hz, $C_{5'}$), 107.3, 105.0 (t, J = 98.2 Hz, $C_{3'}$), 89.0, 82.5, 38.1 ($C_{tert\text{-}butyl}$), 27.6 (3 CH_3 *tert*-butyl). *Anal.* Calcd for $C_{19}H_{15}F_2N_3O$ (339.35) : C, 67.25; N, 12.38; H, 4.46. Found: C, 67.03; N, 11.85; H, 4.21.

2-*tert*-Butyl-4-chloro-8-(phenylethynyl)pyrido[4,3-*d*]pyrimidine (17). Reaction of **13** (303 mg, 1 mmol) in $POCl_3$ (20 mL) under reflux for 6 hours, followed by removal of excess of $POCl_3$ under reduced pressure and partitioning of the residue between CH_2Cl_2 and cold aqueous Na_2CO_3 solution, gave after purification by column chromatography (silica gel, eluent: petroleum ether:ethyl acetate (6:4)) 219 mg (68%) of **17** as a yellow solid, mp 133°C; ir : 2218, 1592, 1554, 1492, 1460, 1347, 1147, 850, 759, 690 cm^{-1}; ^1H nmr (deuteriochloroform): δ 9.39 (s, 1H, H_5); 9.01 (s, 1H, H_7); 7.54 (m, 2H, $H_{2'/6'}$); 7.30 (m, 3H, $H_{3'/4'/5'}$); 1.49 (s, 9H, 3 CH_3 *tert*-butyl); ^{13}C nmr (deuteriochloroform): δ 177.4 (C_2), 162.7 (C_4), 156.3 (C_7), 154.1 (C_{8a}), 149.1 (C_5), 131.8 ($C_{2'}$,$C_{6'}$), 129.0 ($C_{4''}$), 128.3 ($C_{3'}$,$C_{5'}$), 123.0 ($C_{4'}$), 118.0, 117.1, 99.2, 82.8, 40.6 ($C_{tert\text{-}butyl}$), 29.1 (3 CH_3 *tert*-butyl). *Anal.* Calcd for $C_{19}H_{16}ClN_3$ (321.81) : C, 70.91; N, 13.06; H, 5.01. Found: C, 71.00; N, 12.58; H, 5.39.

2-*tert*-Butyl-4-chloro-8-(4'-methoxyphenylethynyl)pyrido-[4,3-*d*]pyrimidine (18). Reaction of **14** (333 mg, 1 mmol) in $POCl_3$ (20 mL) under reflux for 7 hours, followed by removal of excess of $POCl_3$ under reduced pressure and partitionning of the residue between CH_2Cl_2 and cold aqueous Na_2CO_3 solution, gave after purification by column chromatography (silica gel, eluent:petroleum ether:ethyl acetate (6:4)) 186 mg (53%) of **18** as a yellow solid, mp 163°C; ir : 2213, 1605, 1588, 1555, 1501, 1252, 1168, 1038, 837, 812, 798 cm^{-1}; ^1H nmr (deuteriochloroform): δ 9.45 (s, 1H, H_5); 9.05 (s, 1H, H_7); 7.54 (d, J = 8.7 Hz, 2H, $H_{2'/6'}$); 6.88 (d, J = 8.7 Hz, 2H, $H_{3'/5'}$); 3.82 (s, 3H, OCH_3); 1.53 (s, 9H, 3 CH_3 *tert*-butyl); ^{13}C nmr (deuteriochloroform): δ 177.4 (C_2), 162.8 (C_4), 160.4 ($C_{4'}$),154.1 (C_{8a}), 153.5 (C_7), 148.9 (C_5), 133.6 ($C_{2'}$,$C_{6'}$), 114.8 (C_8, C_{4a}, $C_{1'}$), 114.2 ($C_{3'}$,$C_{5'}$), 99.7, 81.9, 55.4 (OCH_3), 40.7 ($C_{tert\text{-}butyl}$), 29.2 (3 CH_3 *tert*-butyl). *Anal.* Calcd for $C_{20}H_{18}ClN_3O$ (351.11) : C, 68.28; N, 11.94; H, 5.16. Found: C, 68.56; N, 12.22; H, 5.48.

2-*tert*-Butyl-4-chloro-8-(2',4'-difluorophenylethynyl)pyrido[4,3-*d*]pyrimidine (19). Reaction of **16** (339 mg, 1 mmol) in $POCl_3$ (20 mL) under reflux for 6 hours, followed by removal of excess of $POCl_3$ under reduced pressure and partitioning of the residue between CH_2Cl_2 and cold aqueous Na_2CO_3 solution, gave after purification by column chromatography (silica gel, eluent: petroleum ether:ethyl acetate (6:4)) 254 mg (71%) of **19** as an orange solid, mp 153°C; ir : 2225, 1591, 1556, 1506, 1269, 1150, 1106, 967, 888, 849, 815 cm^{-1}; ^1H nmr (deuteriochloroform) : δ 9.47 (s, 1H, H_5); 9.06 (s, 1H, H_7); 7.60-7.53 (m, 1H, $H_{6'}$); 6.94-6.85 (m, 2H, $H_{2'/5'}$); 1.50 (s, 9H, 3 CH_3 *tert*-butyl); ^{19}F nmr (deuteriochloroform): δ -105.0 (d, J = 9.7 Hz, 1F), -106.3 (d, J = 9.7 Hz, 1F); ^{13}C nmr (deuteriochloroform) : δ 177.9 (C_2), 164.2 (d, J = 46.2 Hz, C_F), 154.2 (C_{8a}), 154.0 (C_7),149.8 (C_5), 134.6 (dd, J = 40.4 and 11.5 Hz, $C_{6'}$), 117.7, 117.3, 112.0 (dd, J = 89.5 and 17.3 Hz, $C_{5'}$), 107.3 (dd, J = 60.7 and 14.4 Hz, $C_{1'}$), 104.6 (t, J = 98.2 Hz, $C_{3'}$), 91.4, 82.5, 40.7 ($C_{tert\text{-}butyl}$), 29.1 (3 CH_3 *tert*-butyl). *Anal.* Calcd for $C_{19}H_{14}ClF_2N_3$ (357.79) : C, 63.78; N, 11.74; H, 3.94. Found: C, 64.15; N, 11.38; H, 4.11.

2-*tert*-Butyl-4-(4'-methoxyphenyl)-8-(phenylethynyl)pyrido[4,3-*d*]pyrimidine (20). Coupling of 4-methoxyphenylethyne (1.2 equiv.) with **17** (322 mg, 1 mmol) according to the general procedure B (*t* = 40 hours) gave after purification by column chromatography (silica gel, eluent: petroleum ether:ethyl acetate (8:2)) 351 mg (84%) of **20** as a yellow green solid, mp 180°C; ir : 2198, 1602, 1511, 1462, 1252, 1170, 1030, 820, 806, 754, 690 cm^{-1}; ^1H nmr (deuteriochloroform) : δ 9.64 (s, 1H, H_5); 9.06 (s, 1H, H_7); 7.71 (d, J = 8.7 Hz, 2H, $H_{2'/6'}$); 7.66 (m, 2H, $H_{2''/6''}$); 7.41 (m, 3H, $H_{3''/4''/5''}$); 6.96 (d, J = 8.7 Hz, 2H, $H_{3'/5'}$); 3.87 (s, 3H, OCH_3); 1.58 (s, 9H, 3 CH_3 *tert*-butyl); ^{13}C nmr (deuteriochloroform): δ 178.2 (C_2), 161.7 ($C_{4'}$), 153.9 (C_4), 153.3 (C_7), 153.1 (C_{8a}), 150.7 (C_5), 134.8 ($C_{2''}$,$C_{6'}$), 132.1 ($C_{2''}$,$C_{6''}$), 129.1 ($C_{4''}$), 128.7 ($C_{3''}$,$C_{5''}$), 123.1 ($C_{1''}$), 118.3 (C_8 or C_{4a}), 115.6 ($C_{1'}$), 114.6 ($C_{3'}$,$C_{5'}$), 112.8 (C_8 or C_{4a}), 100.8 , 99.1, 84.3, 83.3, 55.6 (OCH_3), 40.8 ($C_{tert\text{-}butyl}$), 29.6 (3 CH_3 *tert*-butyl). *Anal.* Calcd for $C_{28}H_{23}N_3O$ (417.52) : C, 80.55; N, 10.06; H, 5.55. Found: C, 80.68; N, 9.88; H, 5.82.

2-*tert*-Butyl-8-(4'-methoxyphenylethynyl)-4-phenylethynyl-pyrido[4,3-*d*]pyrimidine (21). Coupling of phenylacetylene (1.2 equiv.) with **18** (351 mg, 1 mmol) according to the general procedure B (*t* = 60 hours) gave after purification by column chromatography (silica gel, eluent:petroleum ether:ethyl acetate (8:2)) 317 mg (76%) of **21** as a yellow solid, mp 191°C; ir : 2208, 1605, 1579, 1538, 1509, 1464, 1247, 1170, 1153, 1030, 836, 821, 804, 762, 690 cm^{-1}; ^1H nmr (deuteriochloroform): δ 9.62 (s, 1H, H_5); 9.03 (s, 1H, H_7); 7.76 (dd, J = 7.9 et 1.5 Hz, 2H, $H_{2'/6'}$); 7.61 (d, J = 8.7 Hz, 2H, $H_{2''/6''}$); 7.50-7.43 (m, 3H, $H_{3'/4'/5'}$); 6.92 (d, J = 8.7 Hz, 2H, $H_{3''/5''}$); 3.85 (s, 3H, OCH_3); 1.58 (s, 9H, 3 CH_3 *tert*-butyl); ^{13}C nmr (deuteriochloroform): δ 178.0 (C_2), 160.3 ($C_{4''}$), 153.6 (C_{ar}), 153.0 (C_7 et C_{ar}), 150.1 (C_5), 133.7 ($C_{2''}$,$C_{6''}$), 132.9 ($C_{2'}$,C_6), 129.1 ($C_{4''}$), 128.9 ($C_{3'}$,$C_{5'}$), 120.9 ($C_{1'}$), 118.6 (C_{ar}), 118.4 (C_{ar}), 115.1 ($C_{1''}$), 114.3 ($C_{3''}$,$C_{5''}$), 99.6, 99.5, 84.7, 82.2, 55.5 (OCH_3), 40,8 ($C_{tert\text{-}butyl}$), 29,6 (3 $CH_{3tert\text{-}butyl}$). *Anal.* Calcd for $C_{28}H_{23}N_3O$ (417.52) : C, 80.55; N, 10.06; H, 5.55. Found: C, 80.38; N, 9.92; H, 5.74.

2-*tert*-Butyl-8-(2',4'-difluorophenylethynyl)-4-(2'-pyridyl)-pyrido[4,3-*d*]pyrimidine (22). Coupling of 2-pyridylethyne (1.2 equiv.) with **19** (351 mg, 1 mmol) according to the general procedure B (*t* = 48 hours) gave after purification by column chromatography (silica gel, eluent:petroleum ether:ethyl acetate (8:2)) 217 mg (51%) of **22** as a brown solid, mp 188°C; ir: 2219, 1584, 1539, 1506 1465, 1266, 1142, 1103, 967, 850, 812 cm^{-1}; ^1H nmr (deuteriochloroform): δ 9.72 (s, 1H, H_5); 9.04 (s, 1H, H_7); 8.73 (d, J = 3.8 Hz, 1H, $H_{6'}$); 8.54 (d, J = 14.7 Hz, 1H, CH=CH); 8.35 (d, J = 14.7 Hz, 1H, CH=CH); 7.78 (dt, J = 7.5 and 1.9 Hz, 1H, $H_{4'}$); 7.60 (m, 2H, $H_{3'}$ and H_{PhF2}); 7.31 (m, 1H, $H_{5'}$); 6.96-6.89 (m, 2H, $2H_{PhF2}$); 1.59 (s, 9H, 3 CH_3 *tert*-butyl); ^{19}F nmr (deuteriochloroform): δ -104.8 (d, J = 8.5 Hz, 1F), -106.4 (d, J = 8.5 Hz, 1F); ^{13}C nmr (deuteriochloroform) : δ 177.7 (C_2), 165.0 (m, $C_{2''}$), 162.4 (C_4), 161.6 (m, $C_{4''}$), 154.3 (C_{ar}), 153.8 (C_{ar}), 152.9 (C_7), 150.4 ($C_{6''}$), 149.0 (C_5), 139.6 ($CH_{CH=CH}$), 137.1 ($C_{4'}$), 134.8 ($C_{6''}$), 125.2 (CH), 124.3 (CH), 123.7 (CH), 117.9 (C_8), 116.4 (C_{4a}), 112.0 (m, CH_{PhF2}), 108.3 (m, C_{PhF2}), 104.6 (t, J

= 98.2 Hz, CH_{PhF2}), 90.7, 88,5, 40,8 ($C_{tert\text{-}butyl}$), 29,6 (3 $CH_{3\ tert\text{-}butyl}$). *Anal*. Calcd for $C_{26}H_{20}F_2N_4$ (426.47): C, 73.27; N, 13.14; H, 4.73. Found: C, 73.52; N, 12.96; H, 4.82.

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