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# Palladium on carbon catalyzed cross-coupling between alk-1-ynes and 2-chloro-4,6-dialkoxy-1,3,5-triazines

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Dedicated to Professor Luciano Lardicci on the occasion of his 75th birthday, with sincere gratefulness for introducing us to heterocycle and organometallic chemistry

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**Abstract**—2-(Alk-1′-ynyl)-4,6-dialkoxy-1,3,5-triazines have been synthesized in satisfactory yields by (Pd/C)/$PPh_3$/CuI catalyzed cross-coupling between alk-1-ynes and 2-chloro-4,6-dialkoxy-1,3,5-triazines carried out in the presence of diisopropylethylamine or $K_2CO_3$/18-crown-6. 

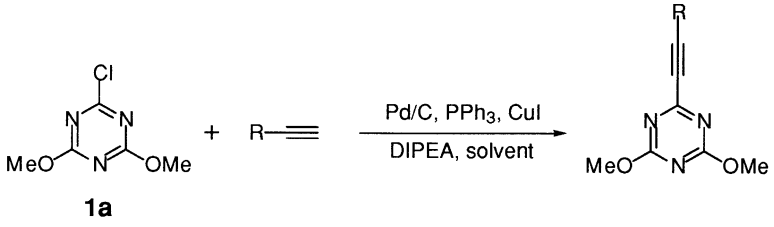
Our studies concerning the chemistry[1–5] and the biological properties[6–11] of 1,3,5-triazine derivatives recently prompted us to prepare 1,3,5-triazines bearing a C–C bonded residue functionalized in the α and/or β positions. In this context, a suitably functionalized nucleophile able to convert cyanuric chloride and/or its mono- or disubstituted derivatives into the desired heterocyclic compounds should be the best strategy.

Acetylenic Grignard reagents are simple and efficient carbon nucleophiles allowing the introduction of a versatile triple bond, but our findings[5] showed that, while the synthesis of 2-(alk-1′-ynyl)-4,6-dialkylamino-1,3,5-triazines can be conveniently carried out by alkynylation of cyanuric chloride followed by amination of the intermediate, the same approach, at least under the experimental conditions we used, fails for the preparation of 2-(alk-1′-ynyl)-4,6-dialkoxy-1,3,5-triazines. On the contrary, preliminary results[3] showed that these compounds can be successfully prepared by $Pd(PPh_3)_4$ mediated cross-coupling of alk-1-ynes and 2-chloro-4,6-dimethoxy-1,3,5-triazine (**1a**).

Although experiments in which the easier to handle Pd/C was used instead of $Pd(PPh_3)_4$ did not suggest this catalytic system for a general approach to 2-(alk-1′-ynyl)-4,6-dialkoxy-1,3,5-triazines,[3] further studies on Pd/C mediated alkynylation of **1a** were carried out and the results obtained are hereby described.

In our former investigation we evaluated the possibility of replacing $Pd(PPh_3)_4$ with the system (Pd/C)/$PPh_3$, in the presence of CuI and diisopropylethylamine (DIPEA) (Scheme 1) for the cross-coupling between 2-chloro-4,6-dimethoxy-1,3,5-triazine (**1a**) and alk-1-ynes.[3]

The results obtained (Table 1, entries 1–5) showed that, while the reaction between **1a** and phenylethyne (Table 1, entry 1) as well as cyclohexylethyne (Table 1, entry 2) afforded **2a** and **3a**, respectively, in yields comparable to those obtained in the presence of $Pd(PPh_3)_4$,[3] some problems arose in further cases; in particular: (i) when hex-1-yne was used (Table 1, entry 3) the yield in **4a** was significantly lowered owing to the formation (42%) of isomeric 2-(hexa-1′,3′-dienyl)-4,6-dimethoxy-1,3,5-triazine;[3] (ii)




**Scheme 1.**

*Keywords*: coupling reactions; triazines; alk-1-ynes; Pd/C; 18-crown-6.

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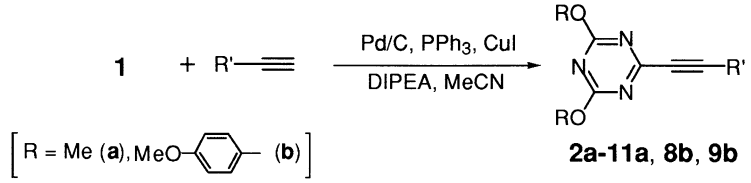
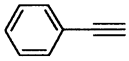
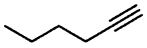
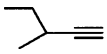
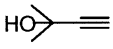
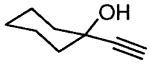
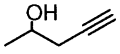
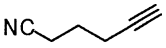
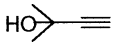
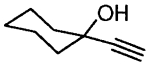
**Table 1.** Reaction of 2-chloro-4,6-dialkoxy-1,3,5-triazines (**1a**,**b**) with alk-1-ynes in the presence of (Pd/C)/$PPh_3$/CuI catalytic system and DIPEA




| Entry | 1 | R' | *T* (°C), *t* (h) | Product (% yield)[a] |
|---|---|---|---|---|
| 1[b] | **a** |  | 65, 70 | **2a**(65) |
| 2[b] | |  | 65, 86 | **3a**(75) |
| 3[b] | |  | 65, 70 | **4a**(40)[c] |
| 4[b] | |  | 36, 70 | **5a**(0) |
| 5[b] | |  | 65, 144 | **6a**(25) |
| 6 | |  | 110, 90[d] | **7a**(20)[e] |
| 7 | |  | 82, 40 | **8a**(66) |
| 8 | |  | 82, 26 | **9a**(92) |
| 9 | |  | 82, 26 | **10a**(50) |
| 10 | |  | 82, 48 | **11a**(0) |
| 11 | **b** |  | 82, 48 | **8b**(62) |
| 12 | |  | 82, 48 | **9b**(90) |

**1**/(Pd/C)/$PPh_3$/CuI/DIPEA=1/0.04/0.16/0.04/2.5 molar ratio, solvent MeCN.
[a] Isolated yield on chemically pure compound.
[b] See Ref. 3.
[c] An appreciable amount (42%) of 2-(hexa-1′,3′-dienyl)-4,6-dimethoxy-1,3,5-triazine was isolated along with **4a**.
[d] Reaction carried out in a Carius tube.
[e] The main (60%) component of the reaction mixture was 2-(*N*-ethyl, *N*-isopropyl)amino-4,6-dimethoxy-1,3,5-triazine.

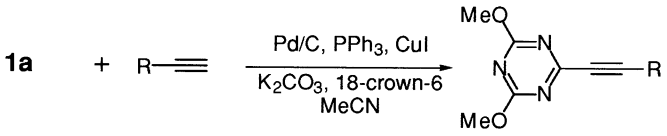
when 3,3-dimethylbut-1-yne was used (Table 1, entry 4), only unreacted **1a** was recovered, and (iii) the cross-coupling with 3-methylpent-1-yn-3-ol (Table 1, entry 5) led to the formation (25%) of **6a** along with appreciable amounts of unidentified by-products.

In order to establish if the isomerization process observed in the preparation of **4a** but not in the preparation of **3a** depended on the structure of the acetylenic reagent (Table 1, entry 2 vs entry 3), in a further reaction **1a** was reacted with acyclic, α-branched 3-methylpent-1-yne under the usual reaction conditions in a Carius tube (see Section 1) at 110°C (Table 1, entry 6): as a matter of fact in our opinion the failure in the preparation of **5a** (Table 1, entry 4) could be reasonably ascribed to the low boiling point (36°C) of 3,3-dimethylbut-1-yne which did not allow the reaction to be carried out at the usual (65°C) temperature.[3] As expected, the conversion of **1a** was complete after 90 h, but, along with a minor amount (20%) of **7a**, the main product (60%) was 2-(*N*-ethyl,*N*-isopropyl)amino-4,6-dimethoxy-1,3,5-triazine arising from the amination of **1a** by DIPEA followed by the elimination of an *iso*propyl residue; anyway, no traces of isomerization by-products were observed.

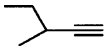
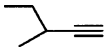
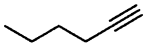
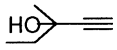
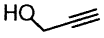
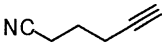
On the contrary, the cross-coupling between **1a** and some functionalized alk-1-ynes (Table 1, entries 7–10) generally allowed the preparation of the corresponding products in moderate (**10a**, 50%) to very good (**9a**, 92%) yields, with the exception of **11a**: in this last case no traces of unreacted **1a** were detected and a complex mixture of by-products was obtained.

It is also noteworthy that the replacement of **1a** with 2-chloro-4,6-di(4′-methoxyphenoxy)-1,3,5-triazine (**1b**, Table 1, entries 11 and 12) did not affect the good results

**Table 2.** Reaction of 2-chloro-4,6-dimethoxy-1,3,5-triazine (**1a**) with alk-1-ynes in the presence of catalytic systems (Pd/C)/$PPh_3$/CuI and $K_2CO_3$/18-crown-6




**4a, 5a, 7a, 11a**

| Entry | R | *T* (°C), *t* (h) | Product (% yield)[a] |
|---|---|---|---|
| 1 |  | 100, 24[b,c,d] | **7a**(40)[e] |
| 2 |  | 100, 17[b,c] | **7a**(58) |
| 3 |  | 90, 8[c] | **5a**(60) |
| 4 |  | 82, 8 | **4a**(63) |
| 5 |  | 82, 24 | **6a**(0)[f] |
| 6 |  | 82, 24 | (0)[f] |
| 7 |  | 82, 8 | **11a**(65) |

**1a**/(Pd/C)/$PPh_3$/CuI=1/0.04/0.16/0.04 and **1a**/$K_2CO_3$/18-crown-6=1/2.5/0.05 molar ratio, solvent MeCN.
[a] Isolated yield on chemically pure compounds.
[b] Solvent dimethoxyethane.
[c] Reaction carried out in a Carius tube.
[d] Reaction carried out according to Ref. 12 (**1a**/$K_2CO_3$/$H_2O$=1/2.5/5 molar ratio).
[e] Unidentified by-products were also present.
[f] No traces of unreacted **1a** were detected and a complex mixture of untreatable by-products was obtained.

previously obtained using **1a** and the same acetylenic substrates (Table 1, entry 11 vs entry 7 and entry 12 vs entry 8).

Since we had found[3] that the isomerization degree observed in the preparation of **4a** could depend, among other factors, on the concentration of DIPEA used in the cross-coupling and taking into account that the competitive amination of **1a** by DIPEA occurred in the preparation of **7a**, the replacement of the amine with an inorganic base seemed very attractive. Thus, according to an experimental procedure[12] described for the synthesis of aryl- and heteroarylalkynes, cross-coupling between **1a** and 3-methylpent-1-yne was attempted in the presence of the system $K_2CO_3$/$H_2O$ (**1a**/[$K_2CO_3$]/[$H_2O$]=1/2.5/5 molar ratio,Table 2, entry 1) in a Carius tube. Under these experimental conditions, complete conversion of **1a** was detected after a shorter reaction time and a better yield of **7a** was obtained (Table 2, entry 1 vs Table 1, entry 6), but appreciable amounts of unidentified by-products were formed probably due to both base catalyzed solvolysis of **1a** and nucleophilic addition of water to the triple bond.[13] In order to minimize this problem, in a further experiment (Table 2, entry 2) the cross-coupling was attempted under anhydrous conditions, in the presence of $K_2CO_3$ and a catalytic amount of 18-crown-6;[†] after a significantly shorter reaction time, **1a** afforded **7a** in satisfactory yield (Table 2, entry 2 vs entry 1).

This encouraging result prompted us to take up these last reaction conditions (Table 2, entries 3–7) for the preparation of 1,3,5-triazine derivatives which could not have been synthesized in the presence of DIPEA.

While repeated efforts to carry out the cross-coupling between **1a** and alk-1-ynes bearing hydroxy substituents always failed (Table 2, entries 5 and 6), the system $K_2CO_3$/18-crown-6 proved very useful for the preparation of derivatives **5a**, **4a** and **11a** (Table 2, entries 3, 4 and 7, respectively): when 3,3-dimethylbut-1-yne was used the conversion was complete after only 8 h and the yield in **5a** was satisfactory (60%, Table 2, entry 3); moreover, it has to be underlined that, when hex-1-yne was used (Table 2, entry 4), no traces of isomerized by-products were observed, so that the yield of **4a** could be appreciably improved (Table 2, entry 4 vs Table 1, entry 1); eventually, the cross-coupling between **1a** and 5-hexynenitrile (Table 2, entry 7) led to the desired **11a** without the formation of the untreatable by-products previously obtained (Table 1, entry 10) in the presence of DIPEA.

To conclude, the cross-coupling between 2-chloro-4,6-dialkoxy-1,3,5-triazines and alk-1-ynes can be conveniently carried out in the presence of the catalytic system (Pd/C)/$PPh_3$/CuI under suitable basic conditions.

[†] The crown ether was added in order to guarantee a certain extent of solubilization of the base in the organic solvent.

With the exception of 3-methylpent-1-yn-3-ol, DIPEA can be used with 2- as well as 3-hydroxyalk-1-ynes and with high boiling, not isomerizable alk-1-ynes; low boiling alk-1-ynes can be reacted with 2-chloro-4,6-dialkoxy-1,3,5-triazines in a Carius tube but DIPEA must be replaced with the system $K_2CO_3$/18-crown-6: it is noteworthy that the yield in biologically active **5a**[11] (60%) obtained under these conditions is better than that (46%) previously obtained by using $Pd(PPh_3)_4$.[3]

Finally, the replacement of DIPEA with $K_2CO_3$/18-crown-6 solved the problem of isomerization observed in the preparation of biostatic **4a**,[11] the yield of which is now at least comparable to that obtained in the presence of $Pd(PPh_3)_4$.[3]

In summary, the use of the $K_2CO_3$/18-crown-6 system, that allowed us to prepare in satisfactory yields **4a**, **5a**, **7a** and **11a**, could be suggested whenever the cross-coupling process is affected by side reactions caused by organic bases.

## 1. Experimental

### 1.1. General procedures and materials

GLC analyses were performed on a Perkin–Elmer 8500 instrument (a DB1, 12 m×0.22 mm capillary column was used) equipped with a flame ionization detector and a split-splitless injector, with He as carrier gas. Analytical HPLC were performed on a Perkin–Elmer series 410 HPLC (a Supelcosil 5 mm LC-18-DB 25 cm×46 mm column was used) equipped with a Perkin–Elmer 785 programmable absorbance detector. TLC analyses were performed on silica gel 60 plates (Fluka) and flash chromatography purifications were carried out on silica gel 60 (Fluka, 230–400 mesh) using the solvent eluting mixtures (v/v) reported for each case. Melting points were determined using a Kofler hot-stage apparatus and are not corrected. $^1$H and $^{13}$C NMR (200 and 50 MHz, respectively) spectra were recorded on a Varian Gemini 200 spectrometer; all NMR data were obtained using $CDCl_3$ solutions. Chemical shifts ($\delta$ ppm) are referred to tetramethylsilane (TMS) ($^1$H NMR) or $CDCl_3$ ($^{13}$C NMR) as internal standard. Mass spectra (*m/z*, *I*%) were taken on a Perkin–Elmer Q-Mass 910 instrument; IS mass spectra ($[M+1]^+$) were acquired on a Perkin–Elmer–Sciex API III mass spectrometer (Sciex Thornhill, Ontario, Canada). Infrared spectra were recorded on a Perkin–Elmer Spectrum GX FT-IR spectrophotometer.

**1.1.1. Preparation of 2-(alk-1′-ynyl)-4,6-dialkoxy-1,3,5-triazines.** In a round bottomed, two necked flask[‡] equipped with a reflux condenser and a magnetic stirrer, Pd/C (10%, Fluka), $PPh_3$, CuI, **1a**[14] or **1b**[1] were placed under nitrogen along with the suitable base (DIPEA for compounds **2**–**3a**, **6a**, **8**–**10a** and **8**–**9b**, or $K_2CO_3$/18-crown-6 for compounds **4**–**5a**, **7a** and **11a**, see Tables 1 and 2, respectively). After accurately purging with nitrogen, a solution of 1.5 mol equiv. of the suitable alk-1-yne in 10 mL of MeCN[§] was added, the temperature was raised and the mixture kept under vigorous stirring until the complete conversion of **1** was achieved (TLC and/or GLC). After cooling and filtering the reaction mixture on a short package of celite, solvents were removed at reduced pressure and the crude products were purified by flash chromatography. The isolated, chemically pure (GLC and/or HPLC) compounds (substrate, alk-1-yne, time (h), temperature (°C), flash chromatography conditions, yield) showed:

**1.1.2. 2-Phenylethynyl-4,6-dimethoxy-1,3,5-triazine (2a).** (**1a**, phenylethyne, 70, 65, hexane/ethyl acetate 55/45, 65%, brown oil): *m/z* (*I*%): 241 (38), 211 (14), 196 (17), 128 (100), 100 (30), 69 (93); $^1$H NMR: 7.69–7.64 (m, 2H, $H_o$), 7.46–7.34 (m, 3H, $H_m$+$H_p$), 4.08 (s, 6H, OC$H_3$); $^{13}$C NMR: 172.3, 162.8, 132.9, 130.3, 128.4, 120.4, 90.9, 86.6, 55.4; IR ($\nu$ cm$^{-1}$): 3070, 3002, 2949, 2225, 1532, 1345, 1108, 817; Anal. calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42%. Found: C, 64.75; H, 4.55; N, 17.48%.

**1.1.3. 2-Cyclohexylethynyl-4,6-dimethoxy-1,3,5-triazine (3a).** (**1a**, cyclohexylethyne, 86, 65, petroleum ether/ethyl acetate 80/20, 75%, pale yellow solid): mp 75–78°C; *m/z* (*I*%): 247 (25), 232 (27), 218 (48), 179 (100), 134 (12), 69 (15); $^1$H NMR: 4.04 (s, 6H, OC$H_3$), 2.64 (tt, 1H, $J$=9.1 Hz, $J'$=3.7 Hz, $CH_2CHCH_2$), 1.98–1.35 (m, 10H, c.hexyl); $^{13}$C NMR: 172.3, 162.9, 97.9, 78.9, 55.2, 31.6, 29.5, 25.6, 24.7; IR ($\nu$ cm$^{-1}$): 2937, 2858, 2234, 1542, 1329, 1125, 820; Anal. calcd for $C_{13}H_{17}N_3O_2$: C, 63.14; H, 6.93; N, 16.99%. Found: C, 63.20; H, 6.91; N, 16.91%.

**1.1.4. 2-(Hex-1′-ynyl)-4,6-dimethoxy-1,3,5-triazine (4a).** (**1a**, hex-1-yne, 8, 82, hexane/ethyl acetate 55/45, 63%, brown oil): *m/z* (*I*%): 221 (9), 206 (56), 192 (60), 179 (80), 149 (20), 108 (51), 79 (47), 69 (100); $^1$H NMR: 4.05 (s, 6H, OC$H_3$), 2.47 (t, 2H, $J$=7.0 Hz, C+CC$H_2$), 1.68–1.45 (m, 4H, C$H_2$C$H_2$CH$_3$), 0.94 (t, 3H, $J$=7.2 Hz, CH$_2$C$H_3$); $^{13}$C NMR: 172.2, 162.7, 94.5, 78.7, 56.3, 29.7, 21.9, 19.0, 13.4; IR ($\nu$ cm$^{-1}$): 2937, 2873, 2238, 1537, 1346, 1103, 821; Anal. calcd for $C_{11}H_{15}N_3O_2$: C, 59.71; H, 6.83; N, 18.99%. Found: C, 59.76; H, 6.80; N, 18.89%.

**1.1.5. 2-(3′,3′-Dimethylbut-1′-ynyl)-4,6-dimethoxy-1,3,5-triazine (5a).** (**1a**, 3,3-dimethylbut-1-yne, 8, 90, hexane/ethyl acetate 75/25, 60%, white glassy solid): *m/z* (*I*%): 221 (33), 206 (31), 191 (8), 176 (4), 106 (45), 58 (100); $^1$H NMR: 4.05 (s, 6H, OC$H_3$), 1.36 (s, 9H, *t-Bu*); $^{13}$C NMR: 172.2, 162.8, 101.3, 77.5, 55.1, 30.0, 27.8; IR ($\nu$ cm$^{-1}$): 2978, 2938, 2230, 1541, 1380, 1348, 1127, 821; Anal. calcd for $C_{11}H_{15}N_3O_2$: C, 59.71; H, 6.83; N, 18.99%. Found: C, 59.74; H, 6.85; N, 19.01%.

**1.1.6. 2-(3′-Hydroxy-3′-methylpent-1′-ynyl)-4,6-dimethoxy-1,3,5-triazine (6a).** (**1a**, 3-methylpent-1-yn-3-ol, 144, 65, petroleum ether/ethyl acetate 50/50, 25%, brown oil): $[M+1]^+$=238; $^1$H NMR: 4.04 (s, 6H, OC$H_3$), 2.38 (bs, 1H, O*H*), 1.82 (q, 2H, $J$=7.3 Hz, C$H_2$CH$_3$), 1.58 (s, 3H, COHC$H_3$), 1.10 (t, 3H, $J$=7.3 Hz, CH$_2$C$H_3$); $^{13}$C NMR: 172.3, 162.4, 95.3, 80.8, 68.8, 55.4, 36.0, 28.5, 8.8; IR ($\nu$ cm$^{-1}$) 3384, 2975, 2941, 2236, 1548, 1377, 1352,

[‡] The preparation of **5a** and **7a** was carried out in a Carius tube fitted with a Rotaflo stopcock.

[§] The preparation of **7a** was carried out in dimethoxyethane (DME).

1109, 822; Anal. calcd for $C_{11}H_{15}N_3O_3$: C, 55.69; H, 6.37; N, 17.71%. Found: C, 55.72; H, 6.38; N, 17.70%.

**1.1.7. 2-(3′-Methylpent-1′-ynyl)-4,6-dimethoxy-1,3,5-triazine (7a).** (**1a**, 3-methylpent-1-yne, 17, 100, hexane/ethyl acetate 85/15, 58%, yellow oil): *m/z* (*I*%): 221 (71), 206 (34), 191 (68), 193 (60), 179 (100); $^1$H NMR: 4.05 (s, 6H, OC*H*$_3$), 2.65 (tq, 1H, *J*=6.75 Hz, CH$_3$C*H*CH$_2$), 1.61 (dq, 2H, *J*=6.75 Hz, CHC*H*$_2$CH$_3$), 1.29 (d, 3H, *J*=6.80 Hz, CHC*H*$_3$), 1.06 (t, 3H, *J*=7.40 Hz, CH$_2$C*H*$_3$); $^{13}$C NMR: 172.3, 162.8, 98.2, 79.1, 55.2, 29.1, 28.0, 19.5, 11.6; IR ($\nu$ cm$^{-1}$): 2968, 2935, 2237, 1538, 1378, 1348, 1108, 823; Anal. calcd for $C_{11}H_{15}N_3O_2$: C, 59.71; H, 6.83; N, 18.99%. Found: C, 59.75; H, 6.81; N, 18.97%.

**1.1.8. 2-(3′-Hydroxy-3′-methylbut-1′-ynyl)-4,6-dimethoxy-1,3,5-triazine (8a).** (**1a**, 2-methylbut-3-yn-2-ol, 40, 82, diethyl ether/petroleum ether 80/20, 66%, pale yellow solid): mp 63–66°C; $[M+1]^+$=224; $^1$H NMR: 4.05 (s, 6H, OC*H*$_3$), 3.22 (bs, 1H, O*H*), 1.64 (s, 6H, C*H*$_3$CC*H*$_3$); $^{13}$C NMR: 172.2, 162.4, 96.2, 79.5, 65.0, 55.4, 30.6; IR ($\nu$ cm$^{-1}$): 3451, 2984, 2940, 2243, 1547, 1393, 1346, 1128, 816; Anal. calcd for $C_{10}H_{13}N_3O_3$: C, 53.81; H, 5.87; N, 18.82%. Found: C, 53.84; H, 5.89; N, 18.78%.

**1.1.9. 2-[2′-(1″-Hydroxycyclohex-1″-yl)-ethynyl)-4,6-dimethoxy-1,3,5-triazine (9a).** (**1a**, 1-ethynylcyclohexanol, 26, 82, petroleum ether/ethyl acetate 50/50, 92%, pale yellow solid): mp 77–80°C; *m/z* (*I*%): 263 (6), 262 (33), 183 (35), 152 (5), 108 (10), 77 (9), 51 (100); $^1$H NMR: 4.05 (s, 6H, OC*H*$_3$), 2.77 (bs, 1H, O*H*), 2.15–1.15 (m, 10H, c.hexyl); $^{13}$C NMR: 172.3, 162.5, 95.4, 81.6, 68.6, 55.4, 39.2, 25.0, 22.9; IR ($\nu$ cm$^{-1}$): 3327, 2938, 2863, 2233, 1543, 1379, 1349, 1108, 817; Anal. calcd for $C_{13}H_{17}N_3O_3$: C, 59.30; H, 6.51; N, 15.96%. Found: C, 59.34; H, 6.50; N, 15.92%.

**1.1.10. 2-(4′-Hydroxypent-1′-ynyl)-4,6-dimethoxy-1,3,5-triazine (10a).** (**1a**, pent-4-yn-2-ol, 26, 82, ethyl acetate/methanol 98/2, 50%, pale yellow solid): mp 119–122°C; *m/z* (*I*%): 205 ($M^+-18$, 4), 179 (98), 79 (100), 72 (78), 69 (86), 65 (51), 58 (85); $^1$H NMR: 4.14 (tq, 1H, *J*=*J*′=6.1 Hz, CH$_2$C*H*CH$_3$), 4.05 (s, 6H, OC*H*$_3$), 3.46 (bs, 1H, O*H*), 2.66 (d, 2H, *J*=5.9 Hz, C*H*$_2$CH), 1.35 (d, 3H, *J*=6.2 Hz, CHC*H*$_3$); $^{13}$C NMR: 172.1, 162.3, 91.2, 80.2, 65.8, 55.4, 29.8, 22.5; IR ($\nu$ cm$^{-1}$): 3390, 2968, 2920, 2246, 1551, 1388, 1130, 814; Anal. calcd for $C_{10}H_{13}N_3O_3$: C, 53.81; H, 5.87; N, 18.82%. Found: C, 53.85; H, 5.86; N, 18.84%.

**1.1.11. 2-(5′-Cyanopent-1′-ynyl)-4,6-dimethoxy-1,3,5-triazine (11a).** (**1a**, 5-hexynenitrile, 8, 82, ethyl acetate/hexane 70/30, 65%, brownish oil): *m/z* (*I*%): 232 (116), 202 (12), 119 (8), 92 (14), 84 (27), 69 (100); $^1$H NMR: 4.15 (s, 6H, OC*H*$_3$), 2.69 (t, 2H, *J*=7.0 Hz, CH$_2$C*H*$_2$CN), 2.61 (t, 2H, *J*=7.0 Hz, C+CC*H*$_2$CH$_2$), 2.04 (tt, 2H, *J*=*J*′=7.0 Hz, CH$_2$C*H*$_2$CH$_2$); $^{13}$C NMR: 172.0, 161.9, 118.5, 90.1, 79.8, 55.2, 23.5, 18.0, 15.6; IR ($\nu$ cm$^{-1}$): 2944, 2887, 2243, 2197, 1548, 1343, 1127, 814; Anal. calcd for $C_{11}H_{12}N_4O_2$: C, 56.89; H, 5.21; N, 24.12%. Found: C, 56.91; H, 5.19; N, 24.11%.

**1.1.12. 2-(3′-Hydroxy-3′-methylbut-1′-ynyl)-4,6-di-(4″-methoxyphenoxy)-1,3,5-triazine (8b).** (**1b**, 2-methylbut-3-yn-2-ol, 48, 82, petroleum ether/ethyl acetate 50/50, 62%, pale yellow glass): $[M+1]^+$=408; $^1$H NMR: 7.10–6.75 (m, 8H, H$_{arom}$), 3.78 (s, 6H, OC*H*$_3$), 2.90 (bs, 1H, O*H*), 1.55 (s, 6H, C*H*$_3$CC*H*$_3$); $^{13}$C NMR: 172.4, 163.2, 157.3, 144.9, 122.1, 114.5, 97.2, 79.6, 65.1, 55.5, 30.5; IR ($\nu$ cm$^{-1}$): 3418, 2982, 2984, 2236, 1554, 1499, 1353, 1199, 827, 817; Anal. calcd for $C_{22}H_{21}N_3O_5$: C, 64.86; H, 5.20; N, 10.31%. Found: C, 64.84; H, 5.24; N, 10.32%.

**1.1.13. 2-[2′-(1″-Hydroxycyclohex-1″-yl)-ethynyl)-4,6-di-(4‴-methoxyphenoxy)-1,3,5-triazine (9b).** (**1b**, 1-ethynylcyclohexanol, 48, 82, petroleum ether/ethyl acetate 60/40, 90%, pale yellow glass): $[M+1]^+$=448; $^1$H NMR: 7.15–6.75 (m, 8H, H$_{arom}$), 3.77 (s, 6H, OC*H*$_3$), 2.45–1.16 (4m, 11H, c.hex+O*H*); $^{13}$C NMR: 172.4, 163.3, 157.4, 145.0, 122.1, 114.5, 96.6, 81.5, 68.6, 55.6, 39.0, 24.9, 22.8; IR ($\nu$ cm$^{-1}$): 3501, 3074, 2936, 2246, 1533, 1501, 1355, 1200, 1028, 835, 824, 810; Anal. calcd for $C_{25}H_{25}N_3O_5$: C, 67.10; H, 5.63; N, 9.39%. Found: C, 67.13; H, 5.65; N, 9.35%.

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