Synthesis of novel polypyridylcarbonylpyridines from triazolopyridines. Building blocks in supramolecular chemistry

Belén Abarca,* Rafael Ballesteros, and Mimoun Chadlaoui

Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia
Avda. Vicente Andrés Estellés s/n, 46100 Burjassot (Valencia), Spain
E-mail: Belen.Abarca@uv.es

Dedicated to Professor Guy Quèguiner on the occasion of his 70th birthday

Abstract

The synthesis from triazolopyridines **1**, of novel triazolopyridylcarbonylpyridylcarbonyltriazolo-pyridines (TPyCOPyCOTPy) (tpcpctp) **7**, and polypyridylcarbonylpyridines (pPyCOPy) (ppcp) **14**, building blocks in supramolecular chemistry, is described. These compounds are interesting polynitrogenated ligands as potential molecular sensors, new magnetic materials, single molecular magnets, or in the emerging science of nanomaterials.

Keywords: Triazolopyridines, pyridylcarbonylpyridines, polynitrogenated ligands, nanomaterials supramolecular receptors, chemosensors, clusters, fluorescent compounds, magnetic materials

Introduction

We are involved in a project whose objectives spread from the preparation of new molecular receptors to the building up of hybrid nano-materials containing organic and inorganic components. Parts of the organic receptors are based on triazolopyridine and carbonylpyridine units. These molecules may have ability to complex heavy metals and other cationic, neutral or anionic species of biomedical or environmental relevance. The supramolecular compounds that could be formed may have interesting magnetic or fluorescent properties and can act as luminescent molecular chemosensors. In this context we have recently reported the synthesis of new polynitrogenated ligands **2-6** from triazolopyridines **1** (Figure 1), by Suzuki cross-coupling reactions (compounds **2** and **3**),[1] or by regioselective lithiation at -40 ºC, subsequent reaction with ethyl picolinate (compound **4**),[2] and then triazolo ring opening by SeO_2 with loss of dinitrogen (compound **5**).[3] When the co-reagent for the reaction with lithio derivative was cyanopyridine, compound **6** was formed.[4] We have study different properties of these ligands.

Compounds **2** and **3** are highly fluorescent with very high quantum yield.[1] We have synthesized, study the crystal structure, and the interesting antiferromagnetic behavior of the tetranuclear cubane compound $[Cu(\mathbf{4^*})]_4(NO_3)_4{\cdot}8H_2O$ where the ligand **4*** is the hemiacetal of **4** formed *in situ*.[5] The triazolpyridine system **6** is a molecular chemosensor for metal ions, anions and amino acids. The crystal structure of the $[Zn(\mathbf{6})(H_2O)_3](ClO_4)_2]{\cdot}H_2O$ complex shows the coordination of Zn^{2+} through the terpyridine moiety.[6] Compound **5**, a dipyridylcarbonylpyridine (dPyCOPy) (dpcp), have form the first icosanuclear Co^{II} cluster exhibiting superparamagnetic relaxation, which is also a rare example of 3d-metal clusters with O and N ligation.[7] Other reports by Mak and co-workers on a series of Cu^{II},[8] Fe^{III},[9] Cu^{I} and Ag^{I},[10] complexes emphasizes the versatility of **5** as supramolecular ligand. We therefore have supposed that bigger terms of pyridylcarbonyl-pyridines (PyCOPy) (pcp) family, with additional donor atoms, could have even more interesting behavior as receptor with different applications based on its potential rich photo-physical and photo-chemical properties,[11] as luminescent molecular sensors,[12] helicating ligands,[13] new magnetic materials,[14] single molecular magnets,[15-18] or in the emerging science of nanomaterials.[19] With this objective in mind we wish to report here the synthesis of triazolopyridylcarbonylpyridylcarbonyltriazolopyridines (TPyCOPyCOTPy) (tpcpctp) **7**, and polypyridylcarbonylpyridines (pPyCOPy) (ppcp) **14** from triazolopyridines **1**, as building blocks in supramolecular chemistry.

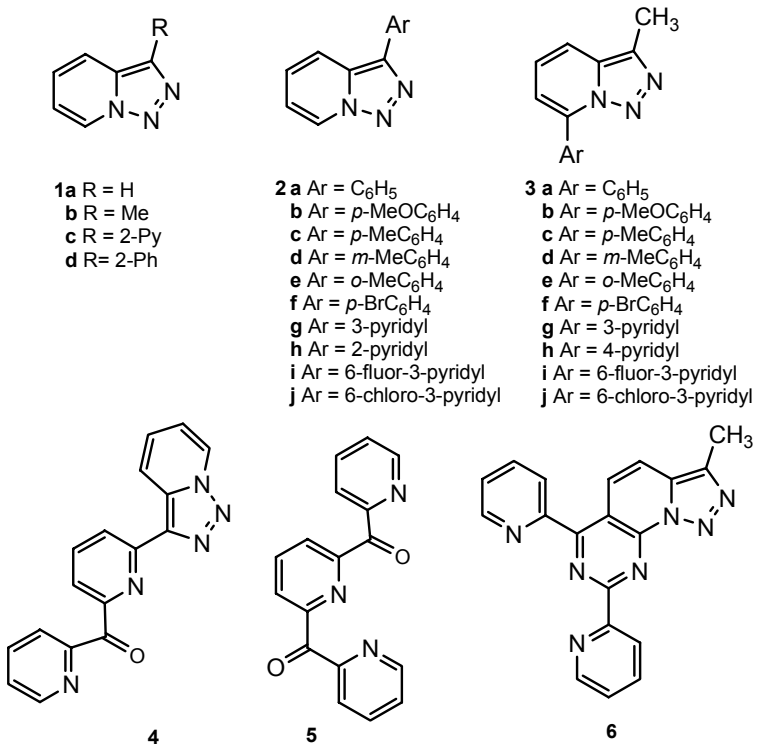
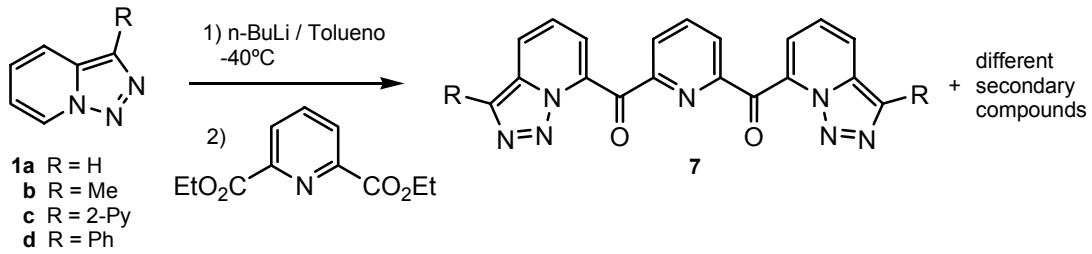


Figure 1

Results and Discussion

Lithiation of triazolopyridines **1a-d** and reaction with ethyl picolinate, followed by triazolo ring opening reaction was the methodology used by us to synthesize dpcp **5**.[3] Now we have change the co-reagent in the second step by diethyl 2,6-pyridindicarboxilate with the aim to obtain tpcpctp **7** (Scheme 1).



Scheme 1

When the reaction was done with **1a**, a unique yellow solid compound was isolated (43%) from a complex polymeric mixture, characterized as **7a** by analytical and spectral properties. The ^{1}H and ^{13}C NMR data reveal a great symmetry (C_2 axis), the ^{1}H- NMR show an AMX system corresponding to two equivalent 7-substituted triazolopyridines and an AB_2 system from one 2,6-disubstituted pyridine (see table). The reaction with **1b** was more difficult to manipulate and a complex mixture was found. The majority isolated, a fluorescent yellow compound, was identified as **7b** (47%). A minor component (14%) was also isolate and identified as **8** (Z,Z isomer) (Figure 2), similar dienes have been previously reported, as secondary compounds in triazolpyridines lithiation reactions,[3,20] and its stereochemistry discussed.[21] With **1d** as starting material the reaction give **7d** as a florescent yellow solid in 75% yield.

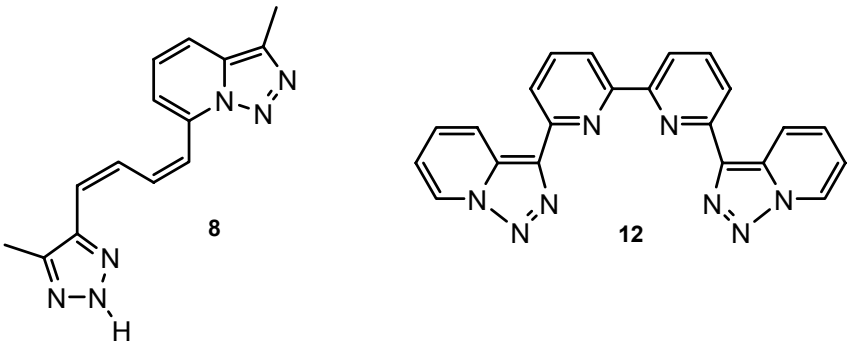
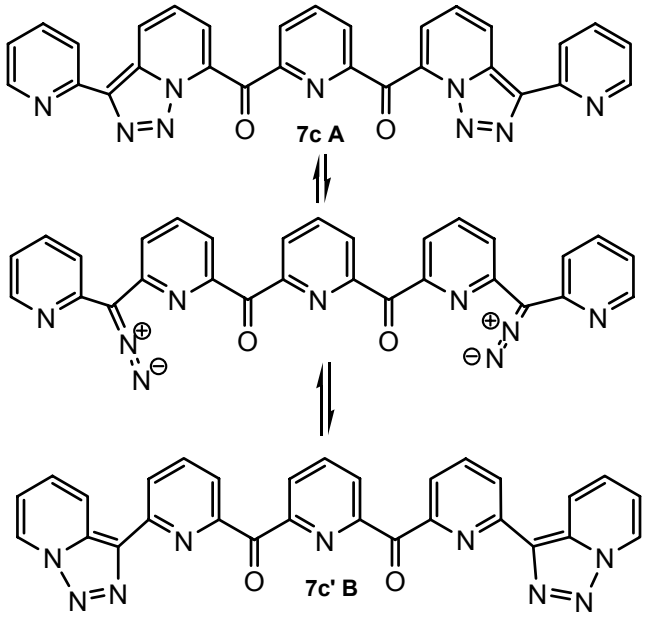


Figure 2

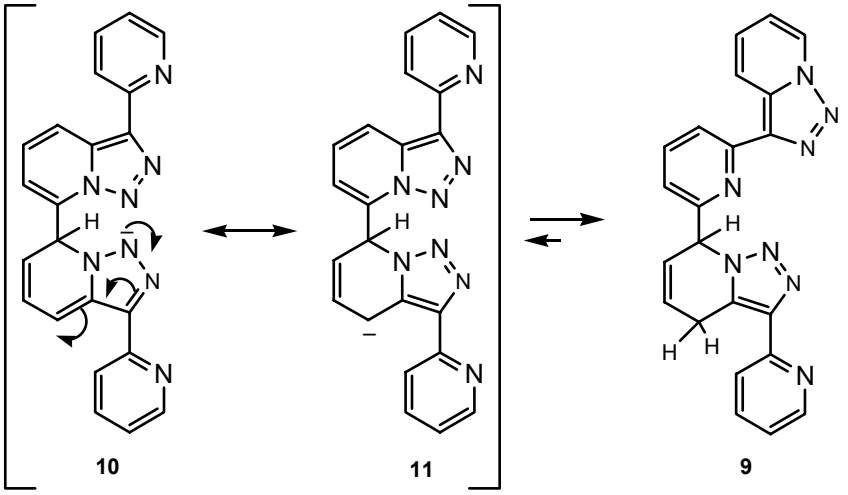
Table 1. ^{1}H NMR data from compounds **7**

	2H4	2H5	2H6	2H7	1H3'	1H4'	1H5'	Others
7a	7.62, dd, J_1=8.8 J_2=1.1	6.98, dd, J_1=8.8 J_2=6.8	6.89, dd, J_1=6.8 J_2=1.1	-	8.39, d, J=7.9	8.19, t, J=7.9	8.39, d, J=7.9	7.95, s, 2H3
7b	7.52, dd, J_1=8.6 J2=1.3	6.88, dd, J_1=8.6 J_2=6.8	6.81, dd, J_1=6.8 J_2=1.3	-	8.39, d, J=7.7	8.16, d, J=7.7	8.39, d, J=7.7	2.54, s, 6H, CH_3
7c ⇅ **7c'**	8.10, d, J=8.8	7.15, ddd, J_1=8.8 J_2=6.8 J_3=0.7	6.89, ddd, J_1=7.0 J_2=6.8 J_3=1.3	8.63, d, J=7.0	8.22, dd, J_1=8.3 J_2=1.3	8.12, t, J=8.3	8.22, dd, J_1=8.3 J_2=1.3	8.37, dd, J_1=7,9, J_2=1.1, 2H3'' 7.97, dd, J_1=7.7, J_2=1.1, 2H5'' 7.97, dd, J_1=7.9, J_2=7.7, 2H4''
7d	7.71-7.67, m	6.79-6.77, m	6.79-6.77, m	-	8.40, d, J=7,8	8.18, d, J=7,8	8.40, d, J=7,8	7.83-7.80, m, 4H*o* 7.51-7.45, m, 4H*m* 7.40-7.36, m, 2H*p*

More complicated was the reaction with **1c**; three compounds were isolated from a complex mixture. In the ^{1}H- NMR spectrum of the major compound (50%), the δ and J values prove that it has a pyridyltriazolopyridine (PyTPy) structure with great symmetry (C_2 axis). The signal at δ=8.63, d, J=7.0Hz, 2H characteristic of H7 triazolopyridine protons show that there are two equivalent 3-substituted triazolopyridines. Two different AB_2 systems indicate the presence of two types of 2,6-disubstituted pyridines. All these data are in agree with the structure **7c'** (Scheme 2). We know that 7-substituted 3-(2-pyridyl)-triazolopyridines are in equilibrium between a type **A** isomer, 3-(2-pyridyl)-[1,2,3]triazolo[1,5-*a*]pyrid-7-yl derivative, and a type **B** isomer, 6-{[1,2,3]triazolo[1,5-*a*]pyrid-3-yl}-2-pyridyl derivative, through a diazo intermediate.[22] To account for structure **7c'** we assume that this equilibrium is shifted to the **B** isomer, as we have described when the substituent is electron-withdrawing as pyridylcarbonyl.[22] The second compound isolated, **9** (10%) (Scheme 3), is a surprising new compound, that could be formed if in the lithiation reaction the intermediate **10**↔**11** had been formed, in a similar manner as we described for triazolopyridine **1b**,[20] then treatment with water give **9**. The last compound isolated was **12** (Figure 2), a dimer isolated also as secondary compound in lithiation reactions of triazolopyridines.[2]

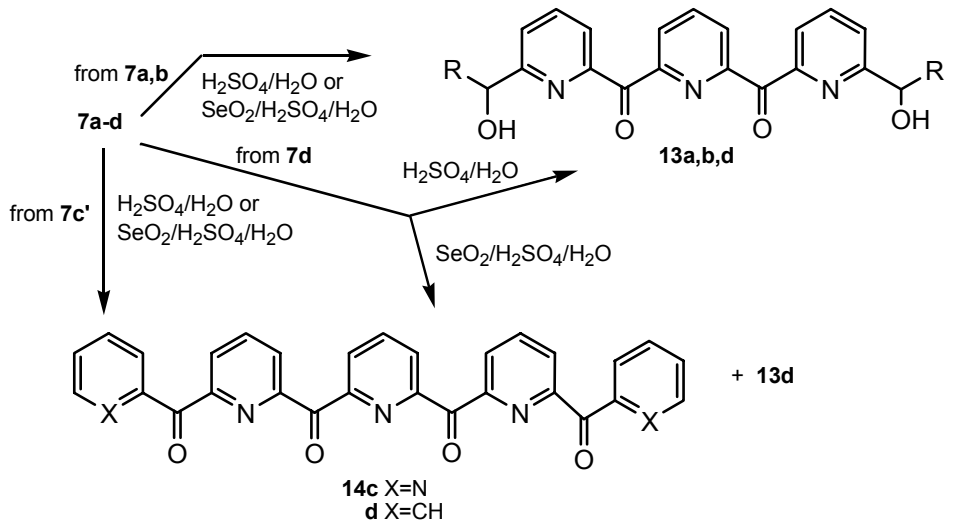


Scheme 2



Scheme 3

Triazolo ring opening reactions[23] of compounds **7** have been studied. Compounds **7a,b,d** reacted with aqueous sulfuric acid to give in quantitative yields the keto alcohols **13a,b,d**. Nevertheless, in the same conditions, compound **7c'** gave tetra-2-pyridylcarbonylpyridine **14c**. With selenium dioxide as co-reagent in sulfuric acid medium, compound **7c'** gave again compound **14c** in 100% yield as expected. However, with this reagent and compounds **7a,b** unexpected results were found, and again compounds **13a,b** were obtained. In similar conditions, compound **7d** gave a mixture of **13d** and **14d** (Scheme 4).



Scheme 4

Polynitrogenated ligands are very interesting structures. Carbonyl fragments give additional possibilities for creating different coordination compounds. All new synthesized compounds should be able to form polynuclear complexes with different metal ions. As we have mentioned in the Introduction, the supramolecular compounds that could be formed may have interesting magnetic or fluorescent properties, and act as luminescent molecular chemosensors. We are at present investigating these possibilities.

Experimental Section

General Procedures. Melting points were determined on a Kofler heated stage and are uncorrected. NMR spectra were recorded on a Bruker AC300MHz in $CDCl_3$ as solvent. COSY experiments were done for all compounds. HRMS (EI) determinations were made using a VG Autospec Trio 1000 (Fisons). Infrared spectra were recorded in KBr discs on a Bio-Rad FTS-7. Ultraviolet spectra were recorded on a Shimazu UV-2101 instrument. Chromatography was performed on a Chromatotron, using 2 cm plates of Merck Pf254 silica.

[1,2,3]Triazolo[1,5-*a*]pyridine (1a), 3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (1b), 3-(2-pyridyl)-[1,2,3]triazolo[1,5-*a*]pyridine (1c), and **3-phenyl-[1,2,3]triazolo[1,5-*a*]pyridine (1d)** were prepared as described elsewhere.[23-26]

General procedure for lithiation of [1,2,3]triazolo[1,5-*a*]pyridines 1a-d and reaction with diethyl 2,6-pyridinedicarboxylate. To a solution of the corresponding [1,2,3]triazolo[1,5-*a*]pyridine **1** in anhydrous toluene at –40ºC, a solution of *n*-butyllithium in hexane (2.5*M*) was added with stirring. A deep red color developed. The mixture was kept at –40ºC (4 h). Treatment

with a dry toluene solution (10 mL) of diethyl 2,6-pyridinedicarboxylate produced a color change to yellow. The mixture was left at –40ºC (2 h) and allowed at room temperature overnight, then was treated with a saturated solution of ammonium chloride. The organic layer was separated and the aqueous layer extracted with dichloromethane. After drying over anhydrous Na_2SO_4 and evaporation of the organic solvents, a residue was obtained. Precipitation with ethyl acetate gave compounds **7a–d** as brown or yellow solids. In some cases the filtrate was evaporated to dryness and the residue obtained was purified. The yield and conditions of purification are given for each compound.

[1,2,3]Triazolo[1,5-*a*]pyridin-7-yl-6-{[1,2,3]triazolo[1,5-*a*]pyridin-7-ylcarbonyl}-2-pyridyl-methanone (7a). 1a (1.50 g, 12.6 mmol), toluene (50 mL), *n*-BuLi (6 mL), diethyl 2,6-pyridindicarboxylate (1.65 g, 7.4 mmol). The precipitate was purified by recrystallization from ethyl acetate giving **7a** (0.70 g), additional amount of **7a** (0.30 g) was isolate by purification on chromatotron from the filtrate (total yield 43 %). Mp > 300ºC. HRMS found for M^+-N_2 341.0847; $C_{19}H_{11}N_5O_2$ requires 341.0786. $\nu_{max.}$ (KBr) (cm^{-1}) 1694 (CO), 1328, 1058, 843, 808, 748. λ_{max} (nm) (log ε) (EtOH) 290.5 (3.87), 358 (3.61). ^{13}C NMR δ 186.90 (CO), 151.22 (C), 140.35 (CH), 133.17 (C), 132.57 (C), 125.79 (CH), 124.71 (CH), 123.69 (CH), 120.61 (CH), 117.72 (CH). MS *m/z* (%) 341(94), 313(46), 285(51), 257(99.7), 256(100), 231(21), 230(27), 179(25), 140(24), 63(32).

3-Methyl-[1,2,3]triazolo[1,5-*a*]pyridin-7-yl-6-(3-methyl-[1,2,3]triazolo[1,5-*a*]pyridin-7-yl-carbonyl)-2-pyridylmethanone (7b). 1b (1.50 g, 11.3 mmol), toluene (50 mL), *n*-BuLi (5.5 mL), diethyl 2,6-pyridinedicarboxylate (1.26 g, 5.65 mmol). The precipitate was purified by recrystallization from ethyl acetate giving **7b** (0.65 g), additional amount of **7b** (0.15 g) was isolate by purification on chromatotron from the filtrate (47 %). Mp > 300ºC. HRMS found for M^++1 398.1367; $C_{21}H_{16}N_7O_2$ requires 398.11365. ν_{max} (KBr) (cm^{-1}) 1691 (CO), 1320, 745. λ_{max} (nm) (log ε) (EtOH) 290(3.95), 377.5(3.74). ^{13}C NMR δ 187.01 (CO), 152.31 (C), 139.37 (CH), 134.72 (C), 134.01 (C), 131.94 (C), 127.82 (CH), 123.06 (CH), 120.05 (CH), 119.11 (CH), 10.80 (CH_3). MS *m/z* (%) 398(0.1), 370(11), 369(42), 341(67), 340(100), 301(30), 104(41), 77(22). A secondary compound was also obtained, identified as **(1Z, 3Z)-1-(3-methyl-[1,2,3]-triazolo[1,5-*a*]pyridine-7-yl)-4-(5-methyl-2*H*-[1,2,3]triazol-4-yl)-1,3-butadiene** (**8)** (14%). Mp 190-192ºC (ethyl acetate/hexane). HRMS found for M^++1 266.1272; $C_{14}H_{15}N_6$ requires 266.1279. ν_{max} (KBr) (cm^{-1}) 3478 (broad, NH), 3150, 3042, 2965, 2901, 1623, 1540, 1437, 1145, 962, 796, 769. λ_{max} (nm) (log ε) (EtOH) 317(4.14), 360.5(4.22). ^{1}H NMR δ 7.84 (dd, J_1=11.8, J_2=11.7Hz, Hb), 7.52 (d, J=8.7Hz, H4), 7.28 (d, J=11.9Hz, Ha), 7.17 (dd, J_1=8.7, J_2=6.8Hz, H5), 7.0 (d, J=6.8Hz, H6), 6.75 (ddd, J_1=11.5, J_2=11.5, J_3=1.1Hz, Hc), 6.37 (ddd, J_1=11.5, J_2=1.3, J_3=1.1Hz, Hd), 2.6 (s, CH_3(1)), 2.3 (s, CH_3(2)). ^{13}C NMR δ 135.03 (C), 134.08 (C), 132.88 (CH), 132.13 (C), 129.10 (C), 126.17 (CH), 123.65 (CH), 121.38 (CH), 120.17 (CH), 116.41 (CH), 116.13 (CH), 10.48 (CH_3 (1)), 9.62(CH_3 (2)). MS *m/z* (%) 266 (100), 238 (42), 237 (52), 209 (57), 195 (35), 168 (52), 154 (58), 142 (44), 77 (23).

6-[1,2,3]Triazolo[1,5-*a*]pyridin-3-yl-2-pyridyl-6-(6-[1,2,3]triazolo[1,5-*a*]pyridin-3-yl-2-pyridylcarbonyl)-2-pyridylmethanone (7c'). 1c (1.0 g, 5.1 mmol), toluene (40 mL), *n*-BuLi

(2.7 mL), diethyl 2,6-pyridincarboxylate (0.65 g, 2.5 mmol). The precipitate was purified by recrystallization from ethyl acetate, giving **7c'** (0.60 g). The filtrate was purified by chromatotron, elution with ethyl acetate/hexane with increasing amount of ethyl acetate gave first starting material **1c** (0.100 g, 10 %), then a white solid identified as **3-(2-pyridyl-7-(6-[1,2,3]triazolo[1,5-*a*]pyridine-3-yl-2-pyridyl)-4,7-dihydro[1,2,3]triazolo[1,5-*a*]pyridine (9)** (10 % yield). Mp 252-254ºC (AcOEt). HRMS found for M^+ 392.1526; $C_{22}H_{16}N_8$ requires 392.1497. ν_{max} (KBr) (cm^{-1}) 1624, 1599, 1569, 1533, 1493, 799, 738. λ_{max} (nm) (log ε) (EtOH) 298.5(4.35), 329(4.10). ^{1}H NMR δ 8.63 (ddd, J_1=7.0, J_2=J_3=0.9Hz, 1H, H7), 8.57 (ddd, J_1=4.9, J_2=J_3=1.0Hz, 1H, H6'''), 8.31 (ddd, J_1=8.8, J_2=J_3=0.9Hz, 1H, H4), 8.21 (m, 2H, H3''', H3'), 7.73 (dd, J_1=7.7, J_2=7.7Hz, 1H, H4'''), 7.65 (dd, J_1=J_2=7.9Hz, 1H, H4'), 7.43 (m, 1H, H6''), 7.17 (ddd, J_1=7.5, J_2=4.9, J_3=1.1Hz, 1H, H5'''), 7.03 (ddd, J_1=8.8, J_2=6.6, J_3=0.9, 1H, H5), 6.89 (ddd, J_1=7.0, J_2=6.8, J_3=1.3Hz, 1H, H6), 6.68 (d, J=7.7Hz, 1H, H5'), 6.07 (m, 2H, H5'', H7''), 3.24 (m, 2H, H4''). ^{13}C NMR δ 157.12 (C), 151.69 (C), 149.44 (CH), 141.60 (C), 137.64 (CH), 136.90 (C), 136.68 (CH), 131.99 (C), 131.04 (C), 126.43 (2CH), 125.15 (CH), 122.39 (CH), 121.13 (CH), 120.85 (CH), 119.58 (CH), 118.62 (CH), 118.03 (CH), 115.86 (CH), 59.01 (CH), 30.79 (CH_2). MS *m/z* (%) 392(96), 364(30), 336(43), 335(100), 308(23), 258(42), 231(50), 229(12), 197(59), 168(25), 142(16), 78(13). Further elution gave **12** (8 % yield). Mp > 350ºC, lit.[2] > 350ºC. The last compound eluted was an additional amount of **7c'** (0.1 g) as a yellow solid (50% total yield). Mp > 300ºC (AcOEt). HRMS found for M^+ 523.1489; $C_{29}H_{17}N_9O_2$ requires 523.1505. ν_{max} (KBr) (cm^{-1}) 3125, 1684(CO), 1594, 1528, 1323, 1238, 1158, 1043, 993, 748. λ_{max} (nm) (log ε) (EtOH) 297.5(4.90), 326(4.87). ^{13}C NMR δ 192.36 (CO), 154.69 (C), 152.65 (C), 151.43 (C), 137.71 (CH), 137.29 (CH), 132.21 (C), 126.88 (CH), 126.53 (CH), 125.18 (CH), 123.53 (CH), 123.42 (CH), 120.42 (CH), 116.03 (CH). MS m/z (%) 523(10), 495 (26), 467 (50), 566 (100), 438 (8), 389 (17), 333 (8), 243 (6), 167 (15), 78 (3).

3-Phenyl-[1,2,3]triazolo[1,5-*a*]pyridin-7-yl-6-(3-phenyl-[1,2,3]triazolo[1,5-*a*]pyridin-7-yl-carbonyl)-2-pyridylmetanone (7d). 1d (0.5 g, 2.56 mmol), toluene (30 mL), n-BuLi (1.4 mL), diethyl 2,6-pyridinedicarboxylate (0.28 g, 1.28 mmol). The precipitate was purified by recrystallization from ethyl acetate giving **7d** (0.50 g), (75 %). Mp 235-237ºC. HRMS found for M^+-N_2 493.1542; $C_{31}H_{19}N_5O_2$ requires 493.1539. ν_{max} (KBr) (cm^{-1}) 3065, 1694(CO), 1313, 1058, 698. λ_{max} (nm) (log ε) (EtOH) 294(4.91), 391(3.74). ^{13}C NMR δ 186.77 (CO), 151.71 (CH), 138.99(C), 137.54 (C), 134.43 (C), 131.03 (C), 129.94 (C), 129.22 (CH), 128.27 (CH), 127.32 (CH), 126.56 (CH), 124.87 (CH), 120.09 (CH), 117.66 (CH). MS m/z (%) 493 (100), 465 (40), 464 (42), 437 (12), 271 (8), 243 (6), 166 (8).

General procedures for triazolo ring opening reactions of triazolopyridines (7).

Procedure A:

A suspension of the corresponding triazolopyridine **7a–d** and selenium dioxide (3 equivalents) in aqueous sulfuric acid was heated at reflux for 24 h. Then was cooled, neutralized with aqueous saturated solution of sodium bicarbonate, and extracted with dichloromethane. The organic layers were dried, and the solvent evaporated. The yield and conditions of purification are given for each compound.

Procedure B:

A suspension of the corresponding triazolopyridine **7a–d** in aqueous sulfuric acid (10 mL, 1 *M*) was heated to reflux for 24 h. The solution was neutralized with a saturated aqueous solution of sodium bicarbonate and extracted with dichloromethane. The organic solvent was dried, and evaporated. The residue was almost pure compounds in quantitative yield.

6-Hydroxymethyl-2-pyridyl-6-(6-hydroxymethyl-2-pyridylcarbonyl)-2-pyridylmethanone (13a). The title compound was obtained by procedure A from **7a** (50 mg, 0.13 mmol), SeO_2 (45 mg, 0.4 mmol), H_2SO_4 (10 mL, 2.5 M) almost pure. (100 %). Recrystallization from dichloromethane/hexane. Mp 92-94ºC. HRMS found for M^+ 349.1096; $C_{19}H_{15}N_3O_4$ requires 349.1062. ν_{max} (KBr) (cm^{-1}) 3426(OH), 1681(CO), 1587, 1450, 1331, 1070, 992, 754. ^{1}H NMR δ 8.14(d, J=8.4Hz, 2H, H3', H5'), 8.00(dd, J_1=J_2=8.4Hz, 1H, H4'), 7.89(d, J=7.5Hz, 2H, H3), 7.69(dd, J_1=7.8, J_2=7.5Hz, 2H, H4), 7.36(d, J=7.8Hz, 2H, H5), 4.66(s, 4H, CH_2), 3.89(brs, 2H, OH). ^{13}C NMR δ 191.73 (CO), 159.18 (C), 153.47 (C), 152.37 (C), 137.62 (CH), 137.16 (CH), 127.09 (CH), 124.21 (CH), 123.50 (CH), 64.21 (CH_2). *m/z* (%) 349 (3), 289 (51), 271 (27), 243 (18), 211 (10), 182 (100), 167 (63), 128 (11), 105 (78), 77 (91).

6-Hydroxyethyl-2-pyridyl-6-[6-(1-hydroxyethyl)-2-pyridylcarbonyl]-2-pyridylmethanone (13b). The title compound was obtained by procedure A from **7b** (50 mg, 0.12 mmol), SeO_2 (42 mg, 0.37 mmol), H_2SO_4 (10 mL, 2.5 *M*) almost pure in quantitative yield as a yellow oil. HRMS found for M^+ 377.1323; $C_{21}H_{19}N_3O_4$ requires 377.1375. ν_{max} (KBr) (cm^{-1}) 3387(OH), 2974, 1681(CO), 1586, 1448, 1393, 1118, 992, 753. ^{1}H NMR δ 8.14(d, J=8.4Hz, 2H, H3', H5'), 8.01(dd, J_1=J_2=8.4Hz, 1H, H4'), 7.92(d, J=7.5Hz, 2H, H3), 7.74(dd, J_1=7.8, J_2=7.5Hz, 2H, H4), 7.39 (d, J=7.8Hz, 2H, H5), 4.81 (q, J=6.6Hz, 1H, CH), 4.80 (q, J=6.6Hz, 1H, CH), 4.14 (brs, 2H, OH), 1.37 (d, J=6.6Hz, 3H, CH_3), 1.35 (d, J=6.6Hz, 3H, CH_3). ^{13}C NMR δ 191.76(CO), 162.91(C), 153.68(C), 152.02(C), 137.40(CH), 137.37(CH), 126.99(CH), 123.85(CH), 122.84(CH), 68.97(CH-OH), 23.92(CH_3). *m/z* (%) 377 (100), 362 (43), 344 (31), 316 (27), 288 (7), 227 (68), 122 (13), 104 (38), 78 (30).

6-(2-Pyridylcarbonyl)-2-pyridyl-6-[6-(2-pyridylcarbonyl)-2-pyridylcarbonyl]-2-pyridyl-methanone (14c). The title compound was obtained by procedures A and B from **7c'** (50 mg, 0.095 mmol), SeO_2 (32 mg, 0.29 mmol), H_2SO_4 (10 mL, 2.5 *M*) almost pure in quantitative yield. Recrystallization from dichloromethane/cyclohexane. Mp 112-114ºC. HRMS found for M^+ 499.1359; $C_{29}H_{17}N_5O_4$ requires 499.1280. ν_{max} (KBr) (cm^{-1}) 1687(CO), 988, 738. ^{1}H NMR δ 8.61 (ddd, J_1=4.7, J_2=1.7, J_3=0.7Hz, 2H, H6), 8.20 (d, J=7.9Hz, 4H, H3', H3'', H5''), 8.2 (dd, J_1=7.9, J_2=1.1Hz, 2H, H5'), 8.03 (ddd, J_1=7.7, J_2=1.9, J_3=0.7Hz, 2H, H3), 7.95 (dd, J_1=J_2=7.9Hz, 2H, H4'), 7.86 (dd, J_1=J_2=7.9Hz, 1H, H4''), 7.68 (ddd, J_1=J_2=7.7, J_3=1.7Hz, 2H, H4), 7.33 (ddd, J_1=7.7, J_2=4.7, J_3=1.1Hz, 2H, H5). ^{13}C NMR δ 191.72 (CO), 191.22 (CO), 153.47 (C), 153.26 (C), 153.07 (C), 152.83 (C), 149.17 (CH), 137.61 (CH), 137.25 (CH), 136.59 (CH), 127.74 (CH), 127.71 (CH), 127.56 (CH), 126.52 (CH), 125.96 (CH). *m/z* (%) 499 (27), 366 (26), 365 (30), 337 (9), 288 (16), 231 (8), 155 (17), 78 (100).

6-Hydroxyphenylmethyl-2-pyridyl-6-[6-(hydroxyphenyl)-2-pyridylcarbonyl]-2-pyridyl-methanone (13d). The title compound was obtained by procedure A from **7d** (50 mg, 0.096

mmol), SeO_2 (33 mg, 0.29 mmol), H_2SO_4 (10 mL, 3 *M*). A residue was obtained which was purified by chromatotron using hexane/ethyl acetate as eluent. The first isolated compound was a yellow oil identified as **14d** (17 % yield). Recrystallization from ether/hexane. Mp 42-44ºC. HRMS found for M^+ 497.1302; $C_{31}H_{19}N_3O_4$ requires 497.1375. ν_{max} (KBr) (cm^{-1}) 2924, 1666(CO), 1325, 1261, 1020, 738, 692, 633. ^{1}H NMR δ 8.17 (d, J=7.9Hz, 2H, H3', H5'), 8.15-8.10 (m, 4H, H3, H5), 7.97-7.89 (m, 7H, Ho, H4, H4'), 7.42-7.36 (m, 2H, Hp), 7.24-7.19 (m, 4H, Hm). ^{13}C NMR δ 192.13 (CO), 191.87 (CO), 153.99 (C), 153.42 (C), 152.56 (C), 137.95 (CH), 137.58 (CH), 135.45 (C), 133.11 (CH), 131.25 (CH), 127.94 (CH), 127.28 (CH), 127.22 (CH), 127.14 (CH). *m/z* (%) 497 (57), 469 (3), 364 (3), 287 (10), 231 (3), 182 (100), 154 (6), 77 (49). Then a yellow oil was eluted and identified as **13d** (14 % yield). HRMS found for M^+ 501.1670; $C_{31}H_{23}N_3O_4$ requires 501.1688. ν_{max} (KBr) (cm^{-1}) 3426 (OH), 2923, 1681 (CO), 1584, 1450, 1310, 1056, 992, 753, 700. ^{1}H NMR δ 8.12 (dd, J_1=7.8, J_2=3.6Hz, 2H, H3', H5'), 8.01 (dd, J_1=J_2=7.8Hz, 1H, H4'), 7.93 (dd, J_1=7.8, J_2=3.6Hz, 2H, H5), 7.64 (dd, J_1=J_2=7.8Hz, 2H, H4), 7.23-7.16 (m, 12H, H3, Ho, Hm, Hp), 5.65 (d, J=4.2Hz, 2H, CH-OH), 4.93 (brs, 2H, OH). ^{13}C NMR δ 191.54 (CO), 191.50 (CO), 160.80 (C), 160.75 (C), 153.79 (C), 153.73(C), 151.66(C), 142.49(C), 137.57 (CH), 137,55(CH), 137.40 (CH), 137.38 (CH), 128.55 (CH), 127.91 (CH), 127,11 (CH), 127.07 (CH), 127,02 (CH), 126.99 (CH), 124,40 (CH), 124.36 (CH), 123,99 (CH), 75,06 (CH), 75.02 (CH-OH). *m/z* (%) 501(4), 497(54), 422(5), 316(6), 271(16), 231(4), 182(100), 154(8), 77(46).

Compound **13d** was obtained by procedure B from **7d** (40 mg, 0.076 mmol) and H_2SO_4 (10 mL, 4 *M*), almost pure, in quantitative yield.

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