Clean chemical synthesis of 2-amino-chromenes in water catalyzed by nanostructured diphosphate $Na_2CaP_2O_7$

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Supporting Information

1) General

All commercial reagents were purchased from Aldrich Chemical Company. X-ray diffraction (XRD) patterns of the catalyst were obtained at room temperature on a Bruker AXS D-8 diffractometer using Cu-K_α radiation in Bragg-Brentano geometry (θ-2θ). Fourier transform infrared (FT-IR) spectra of samples in KBr pellets were measured on a Bruker Vector 22 spectrometer. SEM micrographs were recorded on a Hitachi S-4500 apparatus. The specific surface areas were determined from the nitrogen adsorption/desorption isotherms (at -196 C) measured with a Micromeritics ASAP 2010 automatic analyzer, using the BET equation at $p/p_0 = 0.98$. The TEM micrographs were performed on a FEI microscope at 120 kV. NMR spectra were recorded on a Bruker ARX 300 spectrometer. Mass spectra were carried out on Polaris Q apparatus (Thermo-Electron), and the fragmentations were obtained by electronic impact (EI) at 70 eV. The data are given as mass-to-charge ratio (m/z), and nominal masses were used for the calculation of molecular weights of the prepared products. Melting points were determined using a Stuart SN5228 apparatus.

2) Preparation and characterization of the catalyst

The synthesis of the $Na_2CaP_2O_7$ was carried out by the dry technique. The diphosphate $Na_2CaP_2O_7$ was prepared is a white powder obtained starting from Na_2CO_3, $CaCO_3$ and $NH_4H_2PO_4$ in high purity grade and in 1:1:2 proportions, respectively. These materials were mixed together in an agate mortar and heated in porcelain crucible progressively to 873 K. However, it is necessary to make sure of the perfect homogeneity of the finished product and the total reaction of all the components. It requires, also, of many intermediate crushings after each heat treatment. The size of the finished product does not depend only on the quality of the starting products but also of the precision of the weighings and a good crushing.

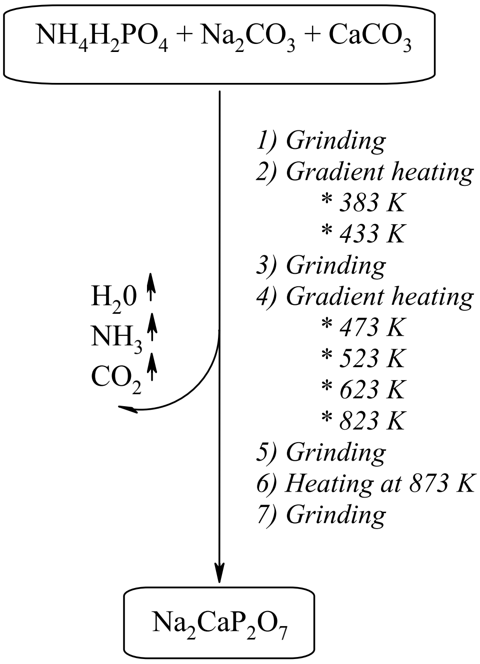


Fig. S1 Preparation of $Na_2CaP_2O_7$

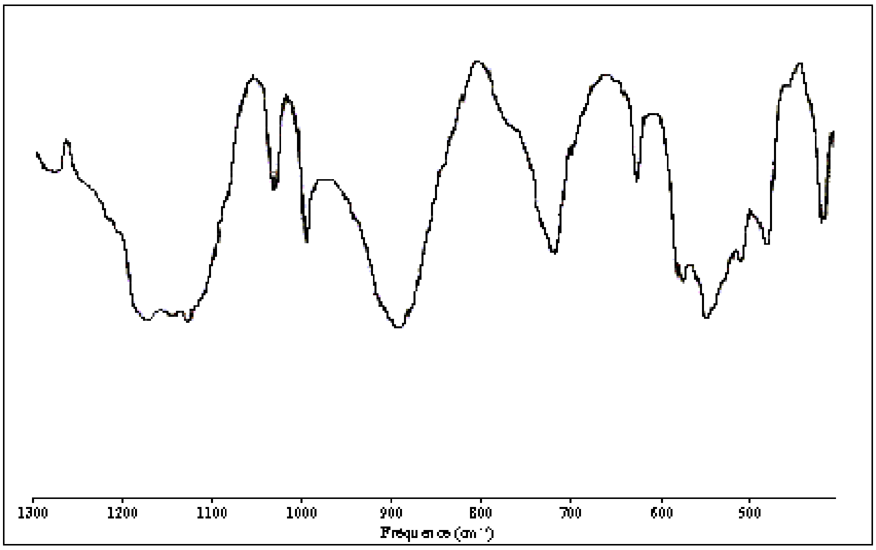


Fig. S2 FT-IR spectrum of $Na_2CaP_2O_7$

Table S1 Attribution of the observed bands of $Na_2CaP_2O_7$ analyzed by FTIR spectroscopy

Observed band (cm^{-1})	Awarding	
407	$\delta(P_2O_7)$	Distortion vibrations
419		
483		
511		
548		
577		
626		
720	υ_{sym}(P-O-P)	Valence vibrations
893	$\upsilon_{antisym}$(P-O-P)	
996	$\upsilon_{sym}(PO_4)$	
1031		
1130	$\upsilon_{antisym}(PO_4)$	
1175		
1278		

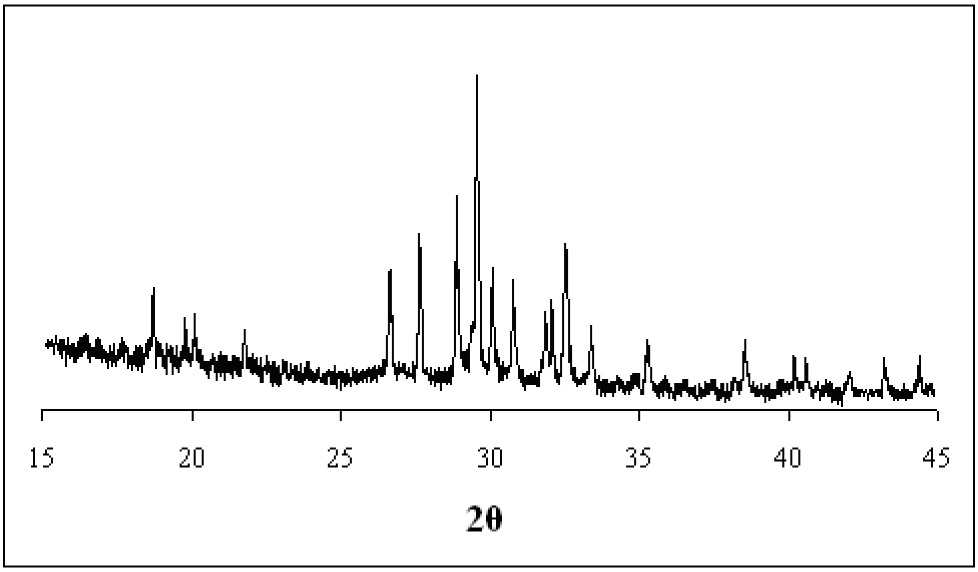
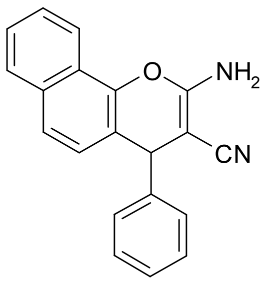


Fig. S3 XRD patterns of $Na_2CaP_2O_7$

3) Product characterizations (Note that copies of all NMR (^{1}H and ^{13}C), Mass Spectra and FTIR spectra are provided at the end of this document)

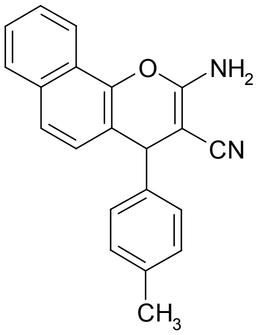
All synthesized products were characterized by spectroscopic methods including ^{1}H NMR, ^{13}C, IR and EI mass spectrometry, as well as by their melting points.

2-1. Characterization of 2-amino-2-chromenes 4



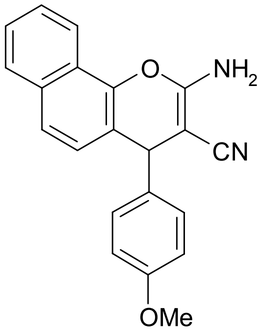
Linear formula : $C_{20}H_{14}N_2O$
Molecular weight : 298 g/mol

***2-Amino-3-cyano-4-phenyl-4H-benzo[h]chromene (4a)*:** Yellow solid, mp = 207-210°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ en ppm : 4,79 (2H, s, NH_2). 4,86 (1H, s, H-4). 7,02 (1H, d, J_{HH} = 8,4 Hz, H-5). 7,12 -7,38 (5H, m, H-2’, 3’, 4’, 5’, 6’). 7,44 -7,6 (3H, m, H-6, 8, 9). 7,8 (1H, d, J_{HH} = 7,8 Hz, H-7). 8,17 (1H, d, J_{HH} = 7,8 Hz, H-10). ^{13}C NMR ($CDCl_3$, 75 MHz) δ en ppm : 41,47 (s, C-4). 61,34 (s, C-3). 117,26 (s, CN). 119,75 (s, C-4a). 120,77 (s, C-10). 123,23 (s, C-10a). 124,62 (s, C-6), 126,22 (s, C-5). 126,66 (s, C-8). 126,74 (s, C-9). 127,36 (s, C-4’). 127,74 (s, C-7). 128,84 (s, C-3’, 5’). 129,19 (s, C-2’, 6’), 133,3 (C-6a). 142,4 (C-1’). 144,41(C-10b). 159,02 (C-2). FTIR (KBr) cm^{-1}: 3436 (CH), 3317 (NH_2), 2183 (CN), 1655 (NH_2). MS (EI) m/z (%) : 298 (M^+), 221,(100).



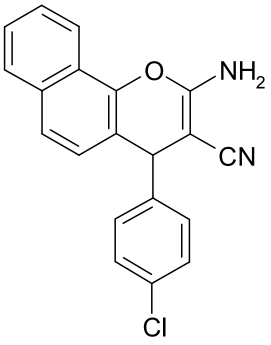
Linear formula : $C_{21}H_{16}N_2O$
Molecular weight : 312 g/mol

2-Amino-3-cyano-4-(4-methylphenyl)-4H-benzo[h]chromene (4b) : Yellow solid, mp = 206-209°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ en ppm : 2,35 (3H, s, $C_6H_4CH_3$). 4,79 (2H, s, N*H*$_2$). 4,84 (1H, s, *H*-4). 7,04 (1H, d, J_{HH} = 8,4 Hz, *H*-5). 7,11-7,37 (4H, m, *H*-2’, 3’, 5’, 6’). 7,45 -7,61 (3H, m, *H*-6, 8, 9). 7,8 (1H, d, J_{HH} = 8,4 Hz, *H*-7). 8,20 (1H, d, J_{HH} = 8,1 Hz, *H*-10). ^{13}C NMR ($CDCl_3$, 75 MHz) δ en ppm : 21,38 (s, $C_6H_4CH_3$), 41,37 (s, C-4). 61,3 (s, C-3). 117,76 (s, CN). 119,75 (s, C-4a). 120,77 (s, C-10). 123,23 (s, C-10a). 124,90 (s, C-6), 126,57 (s, C-5). 126,95 (s, C-8). 127,01 (s, C-9). 128,06 (s, C-7). 128,3 (s, C-3’, 5’). 128,92 (s, C-2’, 6’). 130,23 (s, C-6a). 133,59 (C-1’). 137,32 (C-4’). 141,86(C-10b). 159,28 (C-2). FTIR (KBr) cm^{-1}: 3435 (CH), 3320 (NH_2), 2180 (CN), 1657 (NH_2). MS (EI) m/z (%) : 312 (M^+), 221 (100).



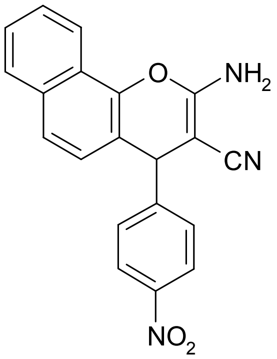
Linear formula : $C_{21}H_{16}N_2O$
Molecular weight : 328 g/mol

2-Amino-3-cyano-4-(4-methoxylphenyl)-4H-benzo[h]chromene (4c) : Yellow solid, mp = 182-184°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ en ppm : 3,5 (3H, s, $C_6H_4OCH_3$). 4,81 (2H, s, N*H*$_2$). 4,88 (1H, s, *H*-4). 7,03 (1H, d, J_{HH} = 8,4 Hz, *H*-5). 7,23 -7,35 (4H, m, *H*-2’, 3’, 5’, 6’). 7,5 -7,59 (3H, m, *H*-6, 8, 9). 7,8 (1H, d, J_{HH} = 8,1 Hz, *H*-7). 8,19 (1H, d, J_{HH} = 7,8 Hz, *H*-10). ^{13}C NMR ($CDCl_3$, 75 MHz) δ en ppm : 41,79 (s, C-4). 55,3 (s, $C_6H_4OCH_3$). 61,65 (s, C-3). 117,58 (s, CN). 120 (s, C-4a). 121,1 (s, C-10). 123,55 (s, C-10a). 124,95 (s, C-6), 126,55 (s, C-5). 126,99 (s, C-8). 127,07 (s, C-9). 127,69 (s, C-7). 128,43 (s, C-3’, 5’). 128,17 (s, C-2’, 6’). 129,52 (s, C-1’). 133,62 (C-6a). 144,74 (C-10b). 154 (s, C-4’). 159,35 (C-2). FTIR (KBr) cm^{-1}: 3416 (CH), 3316 (NH_2), 2183 (CN), 1633 (NH_2). MS (EI) m/z (%) : 328 (M^+); 221 (100).



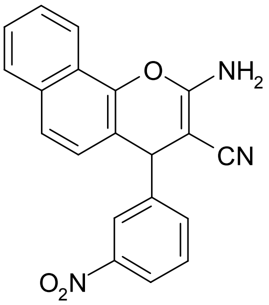
Linear formula : $C_{20}H_{13}ClN_2O$
Molecular weight : 332 g/mol

2-Amino-3-cyano-4-(4-chlorphenyl)-4H-benzo[h]chromene (4d) : Yellow solid, mp = 232-234°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ en ppm : 4,81 (2H, s, N*H*$_2$). 4,87 (1H, s, *H*-4). 6,99 (1H, d, J_{HH} = 8,52 Hz, *H*-5).7,18 (2H, d, J_{HH} = 8,4 Hz, *H*-2’, 6’). 7,31 (2H, d, J_{HH} = 8,4 Hz, 3’, 5’). 7,52-7,62 (3H, m, *H*-6, 8, 9). 7,81 (1H, d, J_{HH} = 7,35 Hz, *H*-7). 8,19 (1H, d, J_{HH} = 7,92 Hz, *H*-10). ^{13}C NMR ($CDCl_3$, 75 MHz) δ en ppm : 40,93 (s, C-4). 60,96 (s, C-3). 116,66 (s, CN). 119,52 (s, C-4a). 120,78 (s, C-10). 123,21 (s, C-10a). 124,82 (s, C-6). 125,97 (s, C-5). 126,82 (s, C-8). 126,94 (s, C-9). 127,80 (C-7). 129,05 (s, C-3’,5’). 129,48 (s, C-2’, 6’). 133,27 (s, C-4’), 133,38 (s, C-6a). 142,93 (s, C-1’). 143,30 (s, C-10b). 159 (s, C-2). FTIR (KBr) cm^{-1}: 3433 (CH), 3316 (NH_2), 2183 (CN), 1650 (NH_2). MS (EI) m/z (%): 332 (M^+), 221 (100).



Linear formula : $C_{20}H_{13}N_3O_3$
Molecular weight : 343 g/mol

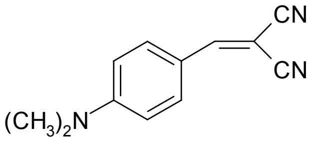
2-Amino-3-cyano-4-(4-nitrophenyl)-4H-benzo[h]chromene (4e) : Yellow solid, mp = 239-241°C. ^1H NMR ($CDCl_3$, 300 MHz) δ en ppm : 4,96 (2H, s, N*H*$_2$). 5 (1H, s, *H*-4). 6,95 (1H, d, J_{HH} = 8,4 Hz, *H*-5). 7,4 (2H, d, J_{HH} = 8,4 Hz, *H*-2’, 6’). 7,52 -7,62 (3H, m, *H*-6, 8, 9). 7,81 (1H, d, J_{HH} = 7,2 Hz, *H*-7). 8,17 (2H, d, J_{HH} = 8,7 Hz, *H*-3’, 5’). 8,28 (1H, d, J_{HH} = 8,7 Hz, *H*-10). ^{13}C NMR ($CDCl_3$, 75 MHz) δ en ppm : 41,70 (s, C-4). 61,30 (s, C-3). 117,00 (s, CN). 119,2 (s, C-4a). 121,14 (s, C-10). 123,5 (s, C-10a). 124,59 (s, C-3’, 5’). 125,50 (s, C-6). 125,89 (s, C-5). 127,39 (s, C-8). 127,75 (s, C-9).128,20 (s, C-7). 129,35 (s, C-2’, 6’). 130,74 (s, C-6a). 133,89 (s, C-4’). 148 (s, C-1’). 151,73 (C-10b). 159,72 (C-2). FTIR (KBr) cm^{-1}: 3454 (CH), 3330 (NH_2), 2182 (CN), 1614 (NH_2). MS (EI) m/z (%): 343 (M^+), 221 (100).



Linear formula : $C_{20}H_{13}N_3O_3$
Molecular weight : 343 g/mol

2-Amino-3-cyano-4-(3-nitrophenyl)-4H-benzo[h]chromene (4f): Yellow solid, mp = 213-215°C. ^1H NMR ($CDCl_3$, 300 MHz) δ en ppm : 4,97 (2H, s, N*H*$_2$). 5,03 (1H, s, *H*-4). 6,96 (1H, d, J_{HH} = 8,4 Hz, *H*-5).7,49-7,66 (5H, m, *H*-6, 8, 9, 4’, 5’). 7,82 (1H, d, J_{HH} = 7,5 Hz, *H*-7). 8,11 (2H, m, *H*-2’, 6’). 8,21 (1H, d, J_{HH} = 7,8 Hz, *H*-10). ^{13}C NMR ($CDCl_3$, 75 MHz) δ en ppm : 41,67 (s, C-4). 61,2 (s, C-3). 116,00 (s, CN). 119,63 (s, C-4a). 121,19 (s, C-10). 122,94 (s, C-9). 123,36 (s, C-6). 123,74 (s, C-10a). 125,47 (s, C-2’). 125,86 (s, C-4’). 127,36 (s, C-7). 127,54 (s, C-5).128,15 (s, C-8). 130,21 (s, C-6’). 133,85 (C-6a). 134,61 (s, C-5’). 144 (C-1’). 146,88 (s, C-3’). 149,05 (s, C-10b). 159,73 (C-2). FTIR (KBr) cm^{-1}: 3457 (CH), 3350 (NH_2), 2180 (CN), 1614 (NH_2). MS (EI) m/z (%) : 343 (M^+), 221 (100).

Characterisation of the Knœvenagel condensation product 4’g

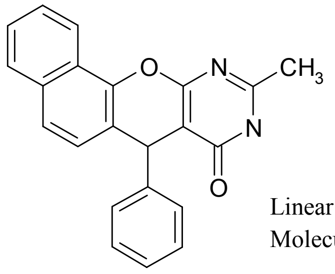


Linear formula : $C_{12}H_{11}N_3$
Molecular weight : 197 g/mol

2-(4-Dimethylamino-benzylidene)-malononitrile (4’g): Orange solid, mp = 180-182°C. ^1H NMR ($CDCl_3$, 300 MHz) δ en ppm: 2,89 (6H, s, $C_6H_4N(CH_3)_2$). 7,50-7,69 (4H, m, Ph). 7,76 (1H, s, PhC*H*=C). ^{13}C NMR ($CDCl_3$, 75 MHz) δ en ppm : 41,6 (6H, s, $C_6H_4N(CH_3)_2$). 83,7 (s, =*C*(CN)$_2$). 112,5 (s, CN). 113,75 (s, CN). 129,62 (s, *C*H=C(CN)$_2$). 129,94 (2C, s, Ph). 130,5 (2C, s, Ph). 132,5 (s, Ph). 150,1 (s, Ph). FTIR (KBr) cm^{-1}: 2231 (CN), 1587 (C=C). MS (EI) m/z (%): 197 $[M]^+$ (100).

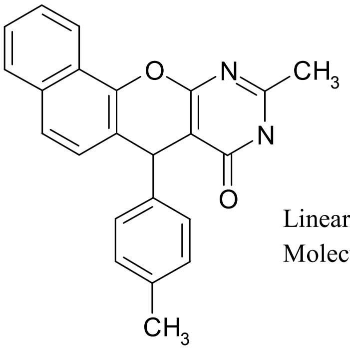
Characterisation of benzo[*a*]anthracenes:

Purification of these products as follows: after 6 hrs reaction, the obtained residue was purified by silica gel flash chromatography (n-hexane/AcOEt: 80/20).



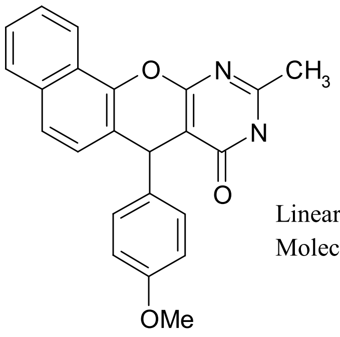
Linear formula : $C_{22}H_{16}N_2O_2$
Molecular weight : 340 g/mol

10-methyl-7-phenyl-8,9-dihydro-7H-12-oxa-9,11-diaza-benzo[a]anthracene-8-one(5a): Yellow solid, mp = 110-112°C. ^1H NMR ($CDCl_3$, 300 MHz) δ en ppm : 2,51 (3H, s, C*H*$_3$). 5,09 (1H, s, *H*-7). 7,25 (1H, d, J_{HH} = 10,17 Hz, *H*-6). 7,24 - 7,37 (6H, m, *H*-2', 3', 4', 5', 6', N*H*). 7,52 -7,61 (3H, m, *H*-2, 3, 5). 7,79 (1H, d, J_{HH} = 9 Hz, *H*-4). 8,12 (1H, d, J_{HH} = 9 Hz, *H*-1). ^{13}C NMR ($CDCl_3$, 75 MHz) δ en ppm : 25,56 (s, *C*H$_3$). 43,89 (s, C-7). 93,43 (s, C_q). 115,59 (s, C_q). 115,6 (s, C_q). 120,98 (s, C-1). 123,36 (s, C-12b). 125,7 (s, C-5). 126,22 (s, C-6). 127,38 (s, C-2 ou C-3). 127,44 (s, C-2 ou C-3). 127,91 (s, C-4). 128,39 (s, C-4'). 128,56 (s, C-3', 5'). 129,38 (s, C-2', 6'). 133,64 (s, C_q). 141,98 (s, C_q). 143,95 (s, C-12a). 152,42 (C-11a). 170,63 (s, C-8). FTIR (KBr) cm^{-1}: 3265 (NH), 1720 (CO lactone). MS (EI) m/z : 340 (M^+).



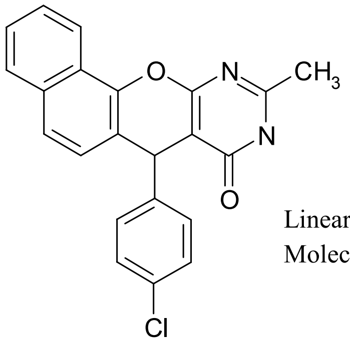
Linear formula : $C_{23}H_{18}N_2O_2$
Molecular weight : 354 g/mol

10-methyl-7-(4-methylphenyl)-8,9-dihydro-7H-12-oxa-9,11-diaza-benzo[a]anthracene-8-one (5b) : Yellow solid, mp = 148-149°C. ^1H NMR ($CDCl_3$, 300 MHz) δ en ppm : 2,31 (3H, s, C_6H_4C*H*$_3$). 2,51 (3H, s, C*H*$_3$). 5,05 (1H, s, *H*-7). 7,02 (1H, d, J_{HH} = 9,81 Hz, *H*-6). 7,2 -7,4 (5H, m, *H*-2', 3', 5', 6', N*H*). 7,5 -7,65 (3H, m, *H*-2, 3, 5). 7,78 (1H, d, J_{HH} = 9 Hz, *H*-4). 8,11 (1H, d, J_{HH} = 9 Hz, *H*-1). ^{13}C NMR ($CDCl_3$, 75 MHz) δ en ppm : 21,23 (s, C_6H_4*C*H$_3$). 25,55 (s, *C*H$_3$). 43,49 (s, C-7). 93,91 (s, C_q). 115,22 (s, C_q). 115,77 (s, C_q). 120,96 (s, C-1). 123,36 (s, C-12b). 125,74 (s, C-5). 126,15 (s, C-6). 127,32 (s, C-2 ou C-3). 127,46 (s, C-2 ou C-3). 127,89 (s, C-4). 128,44 (s, C-3', 5'). 130,06 (s, C-2', 6'). 133,60 (s, C_q). 138,17 (s, C_q). 139,15 (s, C_q). 143,9 (s, C-12a). 152,21 (C-11a). 170,63 (s, C-8). FTIR (KBr) cm^{-1}: 3270 (NH), 1719 (CO lactone). MS (EI) m/z : 354 (M^+).



Linear formula : $C_{23}H_{18}N_2O_3$
Molecular weight : 370 g/mol

10-methyl-7-(4-methoxylphenyl)-8,9-dihydro-7H-12-oxa-9,11-diaza-benzo[a]anthracene-8-one (5c) : Yellow solid, mp = 135-137°C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ en ppm : 2,51 (3H, s, C*H*$_3$). 3,77 (3H, s, C$_6$H$_4$OC*H*$_3$). 5,04 (1H, s, *H*-7). 6,88 (2H, d, *J*$_{HH}$ = 9 Hz, *H*-3', 5'). 7,02 (1H, d, *J*$_{HH}$ = 10,5 Hz, *H*-6). 7,24 (2H, d, *J*$_{HH}$ = 9 Hz, *H*-2', 6'). 7,55 -7,6 (4H, m, *H*-2, 3, 5, N*H*). 7,78 (1H, d, *J*$_{HH}$ = 6 Hz, *H*-4). 8,11 (1H, d, *J*$_{HH}$ = 9 Hz, *H*-1). ^{13}C NMR (CDCl$_3$, 75 MHz) δ en ppm : 25,55 (s, *C*H$_3$). 43,06 (s, C-7). 55,37 (s, C$_6$H$_4$O*C*H$_3$). 93,65 (s, C$_q$). 114,71 (s, C-3', 5'), 115,26 (s, C$_q$). 115,86 (s, C$_q$). 120,94 (s, C-1). 123,35 (s, C-12b). 125,72 (s, C-5). 126,12 (s, C-6). 127,32 (s, C-2 ou C-3). 127,35 (s, C-2 ou C-3). 127,88 (s, C-4). 129,66 (s, C-2', 6'). 133,56 (s, C$_q$). 134,37 (s, C$_q$). 143,37 (s, C-12a). 152,1 (C-11a). 159,54 (s, C-4'). 170,63 (s, C-8). FTIR (KBr) cm^{-1}: 3280 (NH), 1725 (CO lactone). MS (EI) m/z : 370 (M$^+$).



Linear formula : $C_{22}H_{15}ClN_2O_3$
Molecular weight : 374 g/mol

10-methyl-7-(4-chlorophenyl)-8,9-dihydro-7H-12-oxa-9,11-diaza-benzo[a]anthracene-8-one (5d) : Yellow solid, mp = 136-138°C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ en ppm : 2,51 (3H, s, C*H*$_3$). 5,09 (1H, s, *H*-7). 7,01 (1H, d, *J*$_{HH}$ = 9 Hz, *H*-6). 7,23 -7,37 (5H, m, *H*-2', 3', 5', 6', N*H*). 7,56 -7,79 (3H, m, *H*-2, 3, 5). 7,87 (1H, d, *J*$_{HH}$ = 9 Hz, *H*-4). 8,12 (1H, d, *J*$_{HH}$ = 9 Hz, *H*-1). ^{13}C NMR (CDCl$_3$, 75 MHz) δ en ppm : 25,5 (s, *C*H$_3$). 43,35 (s, C-7). 92,97 (s, C$_q$). 115,02 (s, C$_q$). 115,09 (s, C$_q$). 120,99 (s, C-1). 123,37 (s, C-12b). 125,44 (s, C-5). 126,44 (s, C-6). 127,55 (s, C-2 ou C-3). 127,63 (s, C-2 ou C-3). 127,98 (s, C-4). 129,65 (s, C-3', 5'). 129,89 (s, C-2', 6'). 133,72 (s, C$_q$). 134,49 (s, C$_q$). 140,49 (s, C$_q$). 143,94 (s, C-12a). 152,67 (C-11a). 170,2 (s, C-8). FTIR (KBr) cm^{-1}: 3282 (NH), 1712 (CO lactone). MS (EI) m/z : 374 (M$^+$).