ACTION OF PRIMARY AMINES AND HYDROXYLAMINE ON ETHOXYMETHYLENEAMINONAPHTOPYRANES: SYNTHESIS OF NEW NAPHTOPYRANO [2, 3-d] PYRIMIDINES DERIVATIVES

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Abstract: A variety of naphtopyrans 1 has been prepared by reaction of 2-naphtol with aryl (or alkyl) idenemalononitriles. The reaction of the naphtopyrans with triethylorthoformiate and then with primary amines and hydroxylamine, leads to new naphtopyrano [2, 3-d] pyrimidines 3 and 4, whose structures were confirmed by IR and NMR spectroscopy.

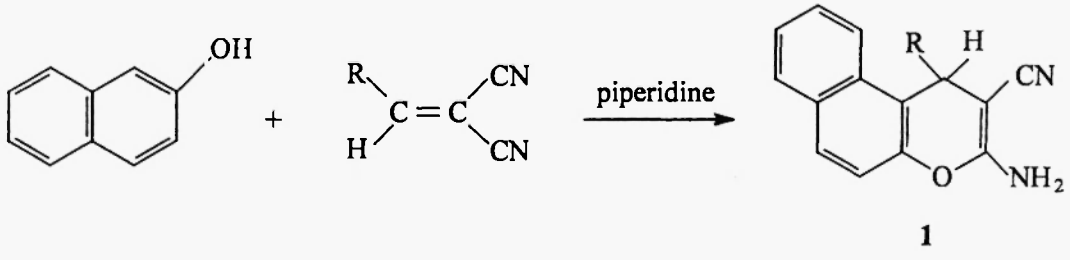
Introduction

The analysis of the bibliographical data shows that pyrans are biologically interesting compounds (1-4). Infact, some pyran derivatives present antibacterial activities (5-6); antifungal activities (7); antitumor activity (8) and they can have a hypotensive effect (9). We report here the synthesis of a variety of new 2-amino-3-cyano-4H-naphto [2,1-b] pyrans 1, and we show their usefulness as building blocks for the preparation of new pyranopyrimidine 3 and 4 .

Results and discussion

Synthesis of 2-amino-3-cyano-4H-naphto [2, 1-b] pyrans 1

Several recent work mentioned the synthesis of the 2-amino-3-cyano-4H-naphto [2,1-b] pyrans (10-14). These products were prepared via a standard addition of Michael of naphtol on arylidenemalononitriles with piperidine as a base.
To generalize the synthesis of compounds **1**, we have prepared a new serie of 2-amino-4-aryl-3-cyano-4H-naphto[2,1-b] pyrans and for the first time a new variety of 2-amino-4-alkyl-3-cyano-4H-naphto[2,1-b]pyrans by condensation of 2-naphtol and alkylidenemalononitriles .(Scheme 1)



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SCHEME 1

Table-I: Synthesis of naphto[2,1-b]pyrans **1a-h**

compound	1a	1b	1c	1d	1e	1f	1g	1h
R	**Ph**	**o-ClC_6H_4**	**p-ClC_6H_4**	**p-$CH_3C_6H_4$**	**(3,4)$Cl_2C_6H_3$**	**Furyle**	**Ipr**	**pentyle**
Yields	**82%**	**83%**	**84%**	**77%**	**79%**	**72%**	**74%**	**78%**

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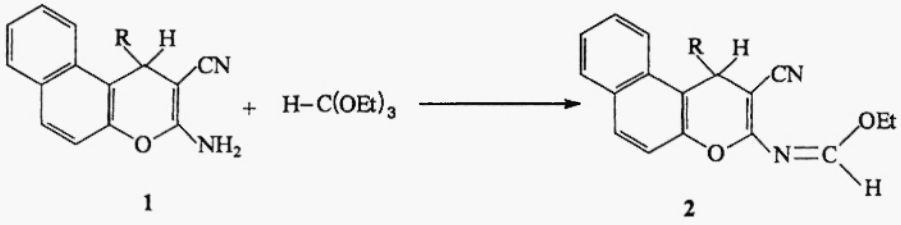
The structure of compounds 1 was deduced from their IR, ^1H and ^{13}C NMR spectra. Indeed, IR spectra of these compounds showed two bands towards 3330 and 3420 cm^{-1} due to the vibration of the amino group. Another intense peak at 2180 cm^{-1} is revealed and which can be ascribed to the nitrile group.
^1H NMR spectrum clearly showed the presence of a singlet characteristic of the 4-H pyran towards 4.0-5.0 ppm for the compounds 1g et 1h (R=alkyl) and towards 5.0-5.5 ppm for the compounds 1a-1f (R=aryl). ^{13}C NMR of these compounds confirms without ambiguity the structure of the obtained product by comparison with the known chemical shifts of similar compounds (11).

II-2: Action of ethyl orthoformiate on compounds 2

Compounds such as 2-amino-8-bromo-2-cyano-1-(p-methoxyphenyl)-1H-naphto[2,1-b] pyrans and 3-amino-2-cyano-9-chloro-1-(4-halophenyl)-1H-benzo[h]chromene have an important synthetic use in the field of condensed heterocyclic compounds incorporating the pyrimidinic nucleus (5,14) . The chemical behaviour of compounds 1 towards ethyl orthoformiate was investigated. Thus treating compounds 1 with ethyl orthoformiate under reflux of acetic anhydride was carried out at the purpose of production of the corresponding ethoxymethyleneamino derivatives 2. (Scheme 2)



1 2

Scheme-2

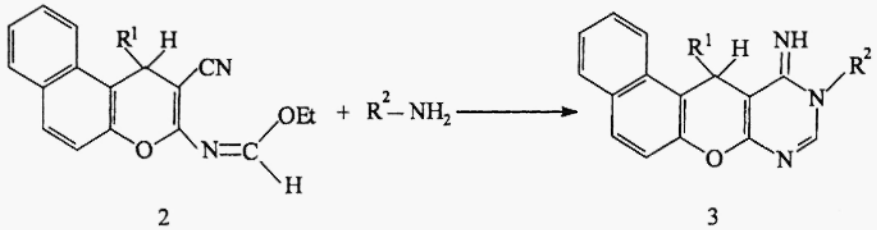
Table-II: **Synthesis of iminoethers 2a-g**

compound	2a	2b	2c	2d	2e	2f	2g
R	**Ph**	**o-ClC_6H_4**	**p-ClC_6H_4**	**p-$CH_3C_6H_4$**	**(3,4)$Cl_2C_6H_3$**	**Furyle**	**Ipr**
Yields	**83%**	**81%**	**84%**	**80%**	**78%**	**79%**	**75%**

The structure of compounds 2 was determined by IR, ^1H and ^{13}C NMR spectra. I.R. spectra revealed in particular the absence of the absorption bands corresponding to the amino group (3330 -3420 cm^{-1}) while exhibiting a band corresponding to C=N group at 1610 cm^{-1}. ^1H NMR of compounds 2 gave us useful information about the nature of protons in this molecule, thus we observe the appearence of a triplet towards 1.4 ppm and a quadruplet towards 4.5 ppm corresponding to the protons of ethoxy group. We can also observe a singlet towards 8.4 ppm corresponding to the proton of the N=C(OEt)H group.

II-3: Action of primary amines on compounds 2

During the course of cyclization reaction between primary amins and iminoethers 2, the latter react with their two electrophilic sites 1, 5 to yielding the corresponding pyrimidinic derivatives 3. This condensation was carried out in boiling toluene with the presence of some drops of acetic acid for 24 hours. (Scheme 3)



2 3

Scheme-3

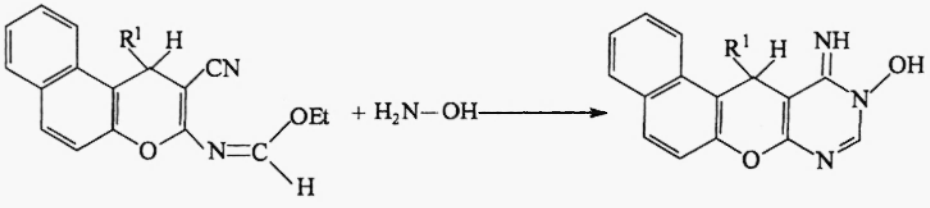
Table-II: **Synthesis of naphtopyrano [2, 3-d] pyrimidine** 3a-e

compound	R^1	R^2	Yields
3a	**o-ClC_6H_4**	**CH_2Ph**	**62%**
3b	**p-ClC_6H_4**	**CH_2Ph**	**54%**
3c	**3,4-$Cl_2C_6H_3$**	**p-$CH_3C_6H_4$**	**82%**
3d	**Ipr**	**Ph**	**78%**
3e	**Ipr**	**CH_2Ph**	**56%**

All of the newly obtained compounds were charaterized using I.R. ^1H and ^{13}C NMR spectroscopy. I.R. spectra of compounds 3 showed the absence of the absorption band corresponding to C≡N group (2180 cm^{-1}) and the appearance of another band at 1645 cm^{-1} corresponding to C=NH group. ^1H NMR spectrum clearly showed that the ethoxy group disappeared and aromatic and aliphatic protons were integrated in the spectrum chart.

II-3: Action of hydroxylamine on compounds 2

Reaction of hydroxylamine with iminoethers 2 gave a new variety of hydroxypyranopyrimidine 4. (Scheme 4).
The structure of compounds 4 was confirmed on the basis of their spectral analyses. It's clear that –like for the previous condensation- the reaction pathway proceed via a double nucleophilic attack of the amino group on nitrile group and on imidic carbon.



2 4

Scheme -4

Table-III: **Synthesis of hydroxypyranopyrimidine** 4a-e

compound	4a	4b	4c	4d	4e
R^1	Ph	o-$CH_3OC_6H_4$	p-$CH_3C_6H_4$	(3,4)$Cl_2C_6H_3$	Ipr
Yields	63%	71%	54%	53%	58%

The I.R spectra of these compounds showed the absence of the absorption band corresponding to CN group and the appearance of new bands corresponding to –OH and –NH groups (3460-3370 cm^{-1}).
The ^1H NMR spectra of compounds 4 are in agreement with the proposed structure. Infact, we note the same observations that we have mentioned for compounds 3, like the disappearance of the signals of the ethoxy group.
In the ^{13}C NMR spectra we could unequivocally assign the signals on the basis of the observed chemical shifts. In particular we observe the disappearance of the signal of nitril's carbon.

III- EXPERIMENTAL SECTION

III-1-General information

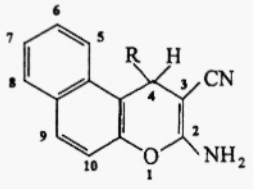
- NMR: NMR spectra were recorded on a Bruker A C 200 (^1H: 300 MHz, ^{13}C: 75 MHz) in $CDCl_3$ solution or in DMSO-d_6 solution. All chemical shifts are recorded in parts per million (ppm) downfield from tetramethylsilane. Coupling constants (^3J) are given in hertz (Hz).

- IR: IR spectra were determined for KBr discs on a JASCO FT-IR-420 spectrometer with the incertitude as ± 2 cm^{-1} in the field of 4000-400 cm^{-1}.
- Melting point: the melting points were determined in Electrothermal 9100 apparatus and are uncorrected.

The reactions were monitored by thin layer chromatography using aluminium sheets with silica gel 60 F_{254} (Merck).

III-2- Synthesis of naphto [2, 1-b] pyrans 1

A mixture of 2-naphtol (0,01mmol) and enaminonitrile (0,01mmol) in ethanol (30 ml) was refluxed for 10 h, with the presence of 0,2 equivalent of piperidine. The solvent was evaporated to dryness under reduced pressure. The solid was collected by filtration. The crude product was purified by recrystallization from toluene to give compounds **1a-h** .



Compound 1a:
Yield:82%; Mp: 277°C; IR: νCN :2178 cm^{-1}; νNH_2:3337-3428 cm^{-}; RMN ^1H (DMSO d_6):5.29(s,1H);7.11-7.91(m,13H) RMN ^{13}C (DMSO d_6): 38.39(C-4); 58.18(C-3); 116.01(CN); 120.89-146.06(C arom); 147.15(C ipso); 159.99(C-2).

Compound 1b:
Yield: 83%; Mp: 265 °C; IR: νCN :2176 cm^{-1} ; νNH_2:3335-3431 cm^{-1}, RMN ^1H ($CDCl_3$): 4.75(s, 2H), 5.43(s, 1H); 7.14-7.86(m, 10H); RMN ^{13}C ($CDCl_3$): 38.13(C-4); 60.43(C-3); 115.22(CN); 120.65-142.33(C arom); 147.08(C ipso) ; 159.26(C-2).

Compound 1c:
Yield: 84% ; Mp: 218 °C; IR: νCN :2189 cm^{-1} ; νNH_2:3319-3405 cm^{-1}; RMN ^1H ($CDCl_3$): 4.66(s, 2H); 5.23(s, 1H); 7.11-7.83(m, 10H); RMN ^{13}C ($CDCl_3$): 38.26(C-4); 61.80(C-3); 114.36(CN); 119.65-142.81(C arom); 147.07(C ipso) ; 158.63(C-2).

Compound 1d:
Yield: 77% ; Mp: 270°C; IR: νCN :2178 cm^{-1} ; νNH_2:3331-3423 cm^{-1}; RMN ^1H (DMSO d_6):2.17(s,3H); 5.23(s, 1H); 6.94-7.87(m, 12H); RMN ^{13}C (DMSO d_6): 20.52(CH_3); 37.74(C-4) ; 58.04(C-3); 115.77(CN); 120.53-142.79(C arom); 146.75(C ipso) ; 159.60(C-2).

Compound 1e:
Yield: 79% ; Mp: 230 °C; IR: νCN : 2175cm^{-1} ; νNH_2:3331-3421cm^{-1}; RMN ^1H (DMSO d_6): 5.43(s, 1H); 7.08-8.30(m,11H); RMN ^{13}C (DMSO d_6):37.35(C-4); 57.28(C-3); 114.85(CN); 120.51-147.05(Carom);147.22(C ipso) ; 160.21(C-2).

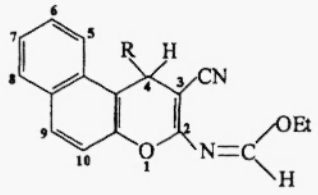
Compound 1f :
Yield: 72%; Mp: 268 °C; IR: νCN :2178cm^{-1} ; νNH_2:3332-3415cm^{-1}; RMN ^1H (DMSO d_6):5.28(s, 1H); 6.20-7.92(m, 11H); RMN ^{13}C (DMSO d_6):32.41(C-4); 67.46(C-3); 115.78(CN); 119.26-144.29(Carom);151.32(C ipso); 159.63(C-2).

Compound 1g :
Yield: 74%; Mp: 196°C; IR: νCN :2178cm^{-1} ; νNH_2:3331-3434cm^{-1}; RMN ^1H ($CDCl_3$):0.68(d,^3J=7;3H); 1.24(d,^3J=7.2;3H); 2.20(m,1H); 4.16(d,^3J=7.2 ;1H); 4.70(s,2H); 7.13-7.89(m, 6H); RMN ^{13}C ($CDCl_3$): 16.17((CH_3)$_2$CH); 21.31((CH_3)$_2$CH); 35.43((CH_3)$_2$CH); 38.89(C-4) ; 55.45(C-3); 116.81(CN); 118.05-131.83(C arom); 148.02(C ipso) ; 162.42(C-2).

Compound 1h:
Yield: 78%; Mp: 192°C; IR: νCN : 2187cm^{-1} ; νNH_2: 3329-3401cm^{-1}; RMN ^1H ($CDCl_3$): 0.87(t, ^3J=7.2 , 3H); 1.2-1.5(m, 6H); 2.31(td, 2H); 4.42(t, ^3J=7.4 , 1H); 4.70(s,2H); 7.20-7.71(m, 6H); RMN ^{13}C ($CDCl_3$): 14.04($CH_3CH_2CH_2CH_2CH_2$); 14.19($CH_3CH_2CH_2CH_2CH_2$); 24.46($CH_3CH_2CH_2CH_2CH_2$); 31.71($CH_3CH_2CH_2CH_2CH_2$); 32.41($CH_3CH_2CH_2CH_2CH_2$); 36.29(C-4);59.98(C-3); 117.75(CN);121.05-131.83(C arom);149.31(C ipso); (C-2)159.26

III-3-Synthesis of iminoethers 2

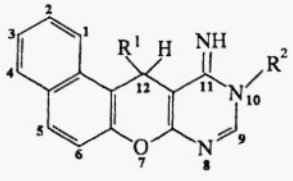
A mixture of ethyl orthoformiate (0.01mmol) and naphto[2,1-b] pyran (0.01mmol) in acetic anhydride (30 ml) was refluxed for 6 h. On cooling, the solid that separated out was collected by filtration. The crude product was purified by recrystallization from ethanol to give iminoethers **2**.



Compound 2a:
Yield: 83% ; Mp: 215 °C; IR: νC=N :1614cm^{-1} ; νCN:2203cm^{-1}; RMN ^{1}H (DMSO d_6): 1.17(t,^{3}J=7; 3H); 4.20(q,^{3}J=7; 2H); 5.42(s, 1H); 7.03-8.15(m, 11H); 8.57(s, 1H); RMN ^{13}C (DMSO d_6): 14.22($OCH_2\underline{C}H_3$) ; 38.46(C-4) ; 64.30($O\underline{C}H_2CH_3$) ;79.51(C-3); 114.38(CN); 118.31-144.13(C arom);157.19(N=CH-OEt) ;162.28(C-2).
Compound 2b:
Yield: 81% ; Mp: 228 °C; IR: νC=N :1615 cm^{-1} ; νCN:2207 cm^{-1}; RMN ^{1}H (DMSO d_6): 1.30(t,^{3}J=7; 3H); 4.32(q,^{3}J=7; 2H); 5.93(s, 1H); 7.20-8.29(m, 10H); 8.72(s, 1H); RMN ^{13}C ($DMSOd_6$):14.36(OCH_2CH_3) ; 39.15(C-4); 63.40($O\underline{C}H_2CH_3$) ; 79.66(C-3); 114.85(CN); 120.51-147.05(Carom); 156.19(N=CH-OEt); 160.21(C-2).
Compound 2c:
Yield: 84% ; Mp: 191 °C; IR: νC=N :1610 cm^{-1} ; νCN:2201 cm^{-1}; RMN ^{1}H ($CDCl_3$): 1.39(t,^{3}J=7; 3H); 4.43(q,^{3}J=7; 2H); 5.34(s, 1H); 7.16-7.86(m, 10H); 8.45(s, 1H); RMN ^{13}C ($CDCl_3$): 13.86($OCH_2\underline{C}H_3$) ; 40.24(C-4) ; 64.22($O\underline{C}H_2CH_3$) ;81.60(C-3); 113.29(CN); 118.07-147.56(Carom); 156.78(N=CH-OEt) ; 159.58(C-2).
Compound 2d:
Yield: 80% ; Mp: 186 °C; IR: νC=N :1610 cm^{-1} ; νCN:2207 cm^{-1}; RMN ^{1}H (DMSO d_6): 1.23(t,^{3}J=7; 3H); 2.01(s, 3H) ; 4.31(q,^{3}J=7; 2H); 5.54(s, 1H);6.96-8.11(m, 10H); 8.39(s, 1H); RMN ^{13}C (DMSO d_6): 14.03($OCH_2\underline{C}H_3$) ;20.32($\underline{C}H_3$); 39.76(C-4) ; 64.13($O\underline{C}H_2CH_3$) ;66.52(C-3); 114.62(CN); 119.83-147.71(C arom);157.19(N=CH-OEt) ; 160.17(C-2).
Compound 2e:
Yield: 78% ; Mp: 168 °C; IR: νC=N :1611cm^{-1} ; νCN:2204 cm^{-1}; RMN ^{1}H (DMSO d_6): 1.29(t,^{3}J=7; 3H); 4.32(q,^{3}J=7; 2H); 5.70(s,1H);7.19-8.29(m,9H);8.71(s,1H);RMN ^{13}C(DMSO d_6): 14.35(OCH_2CH_3) ; 38.74(C-4) ; 64.56($O\underline{C}H_2CH_3$) ;80.48(C-3); 113.38(CN); 118.20-145.21(C arom);157.84(N=CH-OEt) ; 162.81(C-2).
Compound 2f:
Yield: 79% ; Mp: 179 °C; IR: νC=N : 1610cm^{-1} ; νCN:2201 cm^{-1}; RMN ^{1}H ($CDCl_3$): 1.37(t,^{3}J=7; 3H); 4.45(q,^{3}J=7; 2H); 5.52(s, 1H); 6.13-7.88(m, 9H); 8.44(s, 1H); RMN ^{13}C ($CDCl_3$): 13.97(OCH_2CH_3) ; 34.43(C-4) ; 64.33($O\underline{C}H_2CH_3$) ;107.06(C-3); 111.05(CN); 118.22-142.46(Carom);154.34(N=CH-OEt) ; 159.75(C-2).
Compound 2g:
Yield: 75% ; Mp: 137 °C; IR: νC=N :1612 cm^{-1} ; νCN:2205 cm^{-1}; RMN ^{1}H ($CDCl_3$):0.73(d,^{3}J=7 ;3H) ; 1.29(d,^{3}J=7 ;3H) ; 1.41(t,^{3}J=7; 3H);2.26(m, 1H);4.29(d,^{3}J=7 ;1H) ;4.47(q,^{3}J=7; 2H);7.17-7.89(m, 6H); 8.41(s, 1H); RMN ^{13}C ($CDCl_3$): 14.01(OCH_2CH_3) ; 16.71($(CH_3)_2CH$); 21.25($(CH_3)_2CH$); 35.18($(CH_3)_2CH$); 40.48(C-4) ; 64.20 (OCH_2CH_3) ;116.40(CN); 119.88-148.30(C arom);159.12(N=CH-OEt) ; 160.35(C-2).

III-4- Synthesis of naphtopyrano [2, 3-d] pyrimidine 3

A mixture of iminoethers **2** (0.01mmol), primary amine (0.01mmol), toluene (30 ml) and few drops of acetic acid was refluxed for 24 h. On cooling, the separated solid was collected by filtration and dried. The crude product was purified by recrystallization from dioxan to give the pyrimidine derivative **3**.

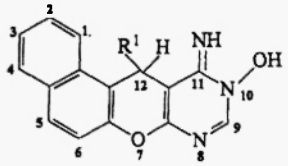


Compound 3a:
Yield: 62% ; Mp: 200 °C; IR: νC=N :1648 cm^{-1} ; νNH:3434 cm^{-1}; RMN ^{1}H ($CDCl_3$): 4.89(d,^{2}J=15; 1H); 5.27(d,^{2}J=15; 1H); 5.53(s, 1H); 7.19-7.48(m, 16H); 7.98(s, 1H); RMN ^{13}C ($CDCl_3$): 37.31(C-12) ; 51.12($\underline{C}H_2Ph$); 99.94(C-11a) ; 115.47-156.22 (C arom) ;156.97(C=NH).
Compound 3b:
Yield: 54% ; Mp: 217 °C; IR: νC=N :1647 cm^{-1} ; νNH:3348 cm^{-1}; RMN ^{1}H ($CDCl_3$): 4.87(d,^{2}J=15; 1H); 5.30(s, 1H); 5.49(d,^{2}J=15; 1H); 7.06-7.87(m, 16H); 8.25(s, 1H); RMN ^{13}C ($CDCl_3$): 34.45(C-12) ; 51.31($\underline{C}H_2Ph$) ; 101.03(C-11a) ;116.88 -157.02(C arom) ; 157.55(C=NH).

Compound 3c:
Yield: 82%; Mp: 250°C; IR: νC=N :1643 cm^{-1} ; νNH:3411cm^{-1}; RMN ^{1}H (DMSO d_6): 2.34(s, 3H); 5.80(s, 1H); 6.58-7.88(m, 14H); 8.05(s, 1H); RMN ^{13}C (DMSO d_6): 21.62($C_6H_4\underline{C}H_3$) ; 33.42(C-12) ; 98.69(C-11a); 116.53-159.08(C arom); 162.48(C=NH).

Compound 3d:
Yield: 78%; Mp: 225°C; IR:νC=N :1631cm^{-1} ; νNH:3407cm^{-1};RMN ^{1}H (DMSO d_6):0.64(d,^{3}J=7; 3H); 0.90(d,^{3}J=7; 3H); 2.06(m, 1H) ; 5.37(d,^{3}J=7; 1H); 7.06-8.31(m, 12H); 9.06(s, 1H); RMN ^{13}C (DMSO d_6):18.38($(CH_3)_2CH$); 20.20($(CH_3)_2CH$); 33.69($(CH_3)_2CH$); 36.12(C-12) ; 96.95(C-11a) ; 117.58-160,35(C arom) ; 165.33(C=NH).
Compound 3e:
Yield: 56%; Mp: 153 °C;IR:νC=N :1643 cm^{-1}; νNH:3362cm^{-1};RMN^{1}H($CDCl_3$):0,80(d,^{3}J=7; 3H); 0.98(d,^{3}J=7; 3H); 2.20(m, 1H) ; 4.59(d,^{3}J=7; 1H); 5.13(d,^{2}J=15; 1H); 5.37(d,^{2}J=15; 1H); 7.16-8.06(m, 12H); 8.41(s, 1H); RMN ^{13}C ($CDCl_3$):18.84($(CH_3)_2CH$); 21.21($(CH_3)_2CH$); 35.89($(CH_3)_2CH$); 36.05(C-12) ; 51.27(CH_2Ph) ; 98.05(C-11a) ; 116.86-156.05(C arom) ; 158.81(C=NH) .

III-4- Synthesis of hydroxypyranopyrimidine 4
To a solution of hydroxylamine (0.01mmol) in toluene (20ml) containing triethylamine (0.2 ml), the iminoethers **2** (0.01mmol) was added and the mixture was heated under reflux for 2 h. the reaction mixture was left to cool and poured onto crushed ice-cold water (20 ml). The precipitate so obtained was filtered off and crystallized from DMF to give the pyrimidine derivative **4**.



Compound 4a:
Yield: 63%; Mp: 292 °C; IR: νC=N: 1644 cm^{-1}; νNH: 3372cm^{-1}; νOH: 3453 cm^{-1}; RMN^{1}H(DMSO): 6.01(s,1H); 6.83-8.07(m, 13H), 8.35(s, 1H); RMN ^{13}C (DMSO): 31.70(C-12) ; 98.28(C-11a) ; 116.72-153.38 (C arom) ; 153.44 (C=NH)
Compound 4b:
Yield: 71%; Mp: 290 °C; IR: νC=N: 1648 cm^{-1}; νNH: 3386cm^{-1}; νOH: 3460 cm^{-1}; RMN^{1}H(DMSO): 3.80(s, 3H); 6.13(s, 1H); 6.83-8.15(m, 12H); 8.57(s, 1H); RMN ^{13}C (DMSO): 35.28(C-12); 56.21(OCH_3); 96.97(C-11a) ; 112.37-153.51 (C arom) ; 156.21(C=NH) .
Compound 4c:
Yield: 54%; Mp: 290 °C; IR:νC=N: 1644 cm^{-1}; νNH: 3386cm^{-1}; νOH: 3409 cm^{-1}; RMN^{1}H(DMSO): 2.25(s, 3H); 6.12(s,1H); 7.00-8.14(m, 12H), 8.57(s, 1H); RMN ^{13}C (DMSO): 20.98(CH_3); 35.07(C-12); 98.54(C-11a) ; 116.96-148.11 (C arom) ; 153.38(C=NH) .
Compound 4d:
Yield: 53%; Mp: 285 °C; IR: νC=N: 1644 cm^{-1}; νNH: 3381cm^{-1}; νOH: 3470cm^{-1}; RMN^{1}H(DMSO): 6.27(s,1H); 7.33-8.31(m, 11H), 8.60(s, 1H); RMN ^{13}C (DMSO): 34.56(C-12); 98.63(C-11a) ; 117.96-118.15 (C arom) ; 152.11(C=NH) .
Compound 4e:
Yield: 58%; Mp: 289°C; IR: νC=N: 1644cm^{-1}; νNH: 3362cm^{-1} ; νOH: 3409cm^{-1}; RMN^{1}H(DMSO): 0.48(d,^{3}J=7; 3H); 0.50(d,^{3}J=7; 3H); 1.85(m, 1H) ; 5.00(d,^{3}J=7; 1H); 7.23-8.12(m, 8H); 8.39(s, 1H); RMN ^{13}C (DMSO):18.68($(CH_3)_2CH$); 19.81($(CH_3)_2CH$); 34.83($(CH_3)_2CH$); 36.15(C-12) ; 95.94(C-11a) ; 116.96-154.45(C arom) ; 155.84(C=NH) .

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