

Synthesis and fluorescent behavior of Pyran and Pyridine-3,5-dicarbonitrile derivatives

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Abstract

Novel chalcones were synthesized by Aldol condensation of aromatic aldehydes and the hitherto not described 3-(2,5-dimethoxyphenyl)-3-oxopropanenitrile in basic medium followed by cyclization with malononitrile to corresponding pyran derivatives. The well characterized pyran derivatives were further transformed into pyridine derivatives by neat heating with ammonium acetate. The fluorescence properties and quantum yield of these synthesized compounds were studied.

Keywords: Chalcones, pyrans-3,5-dicarbonitriles, ppyridine-3,5-dicarbonitriles, HOMO-LUMO, fluorescence, quantum yields.

Introduction

Derivatives of pyridine have application as light emitting diode¹ and in electroluminescence devices². Apart from this, 3-pyridinedicarbonitriles has been used as dyes for synthetic fabrics^{3,4} and in security paper^{5,6}. The heterocycles which have high extinction coefficient, large stokes shift and quantum yield near to one are fluorescent brighter and these three parameters largely determine color strength and brightness. Heterocycles which fluoresces between 400 to 700nm and have an electron hole gap between 2.7 to 7 eV are suitable for organic light emitting diodes (OLED)⁷. Suitable blue-emitting material with high brightness, low hole gap and high quantum yield still remain to be developed. As a part of our ongoing interest in this area^{8,9}, we have reported the synthesis of dipyrazolo [3,4-b:3,4-d] pyridines (DPP)¹⁰ and 3-pyridinedicarbonitriles and studied their photophysical properties. Recently, the synthesis and fluorescent behavior of pyrazolo-pyrrolo-pyrimidine (PPP) derivatives¹¹ has been reported, these literature reports encouraged us to syntheses of novel pyran and pyridine dicarbonitriles and study of their photophysical properties.

Material and Methods

Melting points were determined on a Gallenkamp melting point apparatus Mod.MFB595 in open capillary tubes and are uncorrected. ¹H and ¹³C NMR Spectra were recorded on Varian XL-300 spectrometer (300MHz). Infrared spectra were taken on Shimadzu FTIR-408, instrument in potassium bromide pellets. UV and Fluorescence spectra were recorded on a Shimadzu, UV-1601 UV-VIS RF-5301-PC-Spectrofluorophotometer respectively; UV and fluorescence scans were recorded between 200 to 600 nm. Mass spectra were recorded on a Shimadzu GC-MS QP 2010A mass spectrometer with an ionization potential of (70eV).

Solutions were concentrated in a rotary evaporator under reduced pressure. All reactions were monitored by thin layer chromatography, carried out on 0.2 mm silica gel 60 F₂₅₄ (Merck) plates using UV light (250 and 400 nm) and fluorescence light (400 and 600 nm) for detection. Common reagents grade chemicals are either commercially available and were used further purification or prepared by standard literature procedures.

The GAMESS software (MOPAC-2009, PM6) is used for HOMO-LUMO, by semi empirical methods

General Procedure for the synthesis of Chalcone 3a-g: A mixture of compound 1 (0.001 mole) and aromatic aldehydes 2(a-g) (0.001mole) in ethanol (10 ml) containing 2-3 drops of piperidine was heated for 4-5 h (TLC toluene: acetone, 9:1), then reaction mixture was cooled at room temperature. The solid obtained was isolated by filtration, dried and recrystallized from ethanol to afford as pale yellow prisms in 70-80% yields.

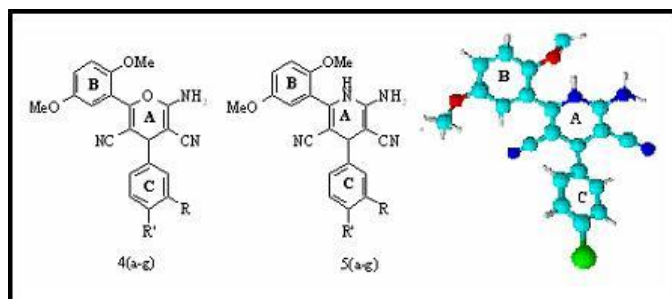


Figure - 1

Molecular modeling of pyrans 4(a-g) and pyridine-3,5-dicarbonitriles 5(a-g)

(3E) – 4 - (4- Chlorophenyl) - 3 - [(2, 5-dimethoxyphenyl) carbonyl] but-3-enenitrile (3a): Yield: 0.245g (75%), mp. 106-108 °C. ir (potassium bromide): 2940, 2210, 1676, 1610, cm^{-1} . ^1H nmr (DMSO- d_6): δ = 3.32 (s, 3H, OCH₃), 3.73 (s, 3H, OCH₃), 6.85 (s, 1H, CH) 6.95 (dd, 1H, J = 2.3 & 8.2 Hz, Ar-H), 7.12 (d, 1H, J = 8.2 Hz, Ar-H), 7.13 (d, 1H, J = 2.3 Hz, Ar-H), 7.16 (d, 2H, J = 8.5 Hz, Ar-H), 7.72 (d, 2H, J = 8.5 Hz, Ar-H) ppm; MS(70 eV): m/z 327 (M^+). Anal.Calcd for C₁₈H₁₄ClNO₃ (327.76): C, 66.05; H, 4.28; N, 4.28 Found C, 66.02; H, 4.31, N, 4.30.

(3E) – 4 - (4 - Bromophenyl) – 3 - [(2, 5dimethoxyphenyl) carbonyl]but-3-enenitrile(3b):Yield: 0.267g (72%), mp.130-132°C. ir (potassium bromide): 3010, 2211, 1722,1605, cm^{-1} . ^1H nmr (DMSO- d_6): δ = 3.35 (s, 3H, OCH₃), 3.76 (s, 3H, OCH₃), 6.80 (s, 1H, CH) 6.94 (dd, 1H, J = 2.5 & 8.1 Hz, Ar-H), 7.14 (d, 1H, J = 8.1 Hz, Ar-H), 7.16 (d, 1H, J = 2.5 Hz, Ar-H), 7.18 (d, 2H, J = 8.8 Hz, Ar-H), 7.78 (d, 2H, J = 8.8 Hz, Ar-H) ppm; MS(70eV): m/z 372 (M^+). Anal.Calcd for C₁₈H₁₄O₃NBr (372.21): C, 58.06; H, 3.76; N, 3.76. Found C, 58.08; H, 3.77; N, 3.77.

(3E)–3-[(2,5–Dime thoxyphenyl) carbonyl] – 4 - (4-fluoro phenyl) but-3-enenitrile(3c): Yield:0.233g(75%),m.p.124-126°C. ir (potassium bromide):3002, 2227,1715,1608 cm^{-1} . ^1H nmr (DMSO- d_6): δ = 3.36 (s, 3H, OCH₃), 3.75 (s, 3H, OCH₃), 6.75 (s,1H,CH) 6.96 (dd, 1H, J = 2.1& 8.4 Hz, Ar-H), 7.16 (d, 1H, J = 8.4 Hz, Ar-H), 7.18 (d, 1H, J = 2.1 Hz, Ar-H), 7.15 (d, 2H, J = 8.5 Hz, Ar-H) 7.79 (d, 2H, J = 8.5 Hz, Ar-H) ppm; MS(70 eV): m/z 311(M^+). Anal.Calcd for C₁₈H₁₄O₃NF (311.31): C, 69.45; H, 4.50; N, 4.50. Found C, 69.41; H, 4.52; N, 4.51.

(3E)-3-[(2,5-Dimethoxyphenyl) carbonyl]-4-(3-ethoxyphenyl)but-3-enenitrile(3d): Yield: 0.239g (74%), mp.103-105°C. ir (potassium bromide): 3040,2226,1730,1615 cm^{-1} . ^1H nmr (DMSO- d_6): δ = 3.37 (s, 3H, OCH₃), 3.78 (s, 3H, OCH₃), 3.97 (s, 3H, OCH₃), 6.82 (s, 1H, CH), 6.96 (dd, 1H, J = 2.7 & 8.1 Hz, Ar-H), 7.11 (d, 2H, J = 8.1 Hz, Ar-H), 7.16 (d, 1H, J = 2.7 Hz, Ar-H), 6.69 (d, 1H, J = 8.8 Hz, Ar-H), 6.77 (s, 1H, Ar-H), 7.21 (dd, 1H, J = 8.6 & 8.8 Hz, Ar-H), 7.28 (d, 1H, J = 8.6 Hz, Ar-H) ppm; MS(70eV): m/z 323 (M^+). Anal.Calcd for C₁₉H₁₇O₄N (323.31): C, 70.80; H, 5.27; N,4.34. Found C, 70.81; H, 5.26; N, 4.36.

(3E)-4- (3,4-Dimethoxyphenyl) -3-[(2,5 dimethoxyphenyl) carbonyl] but-3-enenitrile(3e): Yield: 0.253g (78%), mp. 99-101°C. ir (potassium bromide): 2980, 2216, 1605,1710 cm^{-1} . ^1H nmr (DMSO- d_6): δ = 3.32 (s, 3H, OCH₃), 3.73(s, 3H, OCH₃), 3.78 (s, 3H, OCH₃), 3.86 (s, 3H, OCH₃), 6.82 (s,1H, CH) 6.95 (dd, 1H, J = 2.3 & 8.1Hz, Ar-H), 7.12 (d, 1H, J = 8.1 Hz, Ar-H), 7.13 (d, 1H, J = 2.3 Hz, Ar-H), 7.16 (d, 1H, J = 8.5 Hz, Ar-H), 7.72 (d, 1H, J = 2.5 Hz, Ar-H), 7.49 (dd, 1H, J = 8.5 & 2.5 Hz, Ar-H) ppm; MS(70eV): m/z 353 (M^+). Anal.Calcd for C₂₀H₁₉O₅N

(353.37): C,67.98; H, 5.38; N,3.96. Found C,67.96; H, 5.36; N,3.95.

(3E) – 3 - [(2,5-Dimethoxyphenyl) carbonyl] -4- (4-nitro phenyl) but-3-enenitrile(3f): Yield:0.260g(77%),mp.107-109°C.ir(potassiumbromide):2990,2250,1730,1612,1535,1360 cm^{-1} . ^1H nmr (DMSO- d_6): δ = 3.39 (s, 3H, OCH₃), 3.69 (s, 3H, OCH₃), 6.76 (s, 1H, CH), 6.98 (dd, 1H, J = 2.3 & 8.5 Hz, Ar-H), 7.22 (d, 1H, J = 8.5 Hz, Ar-H), 7.53 (d, 1 H, J = 2.3 Hz, Ar-H), 7.76 (d, 2H, J = 8.8 Hz, Ar-H), 7.82 (d, 2H, J = 8.8 Hz, Ar-H) ppm; MS (70eV): m/z 338 (M^+). Anal.Calcd for C₁₈H₁₄O₅N₂ (338.31): C, 63.90; H, 4.14; N, 8.28. Found C, 63.87; H, 4.16; N, 8.30.

(3E)-3-[(2,5-Dimethoxyphenyl)carbonyl]-4-phenylbut-3-enenitrile(3g) : Yield: 0.233g (80%), mp.102-105°C. ir (potassium bromide): 2996,2250,1730,1614 cm^{-1} . ^1H nmr (DMSO- d_6): δ = 3.75 (s, 3H, OCH₃), 3.74 (s, 3H, OCH₃), 6.78 (s, 1H, CH), 6.85 (d, 1H, J = 2.1 Hz, Ar-H), 7.05 (dd, 1H, J = 2.1 & 8.4 Hz, Ar-H), 7.34 (m, 3H, Ar-H), 7.36 (d, 1H, J = 8.4 Hz, Ar-H), 7.51 (m, 2H, Ar-H) ppm; MS (70eV): m/z 292 (M^+). Anal. Calcd for C₁₈H₁₄O₃N (292.31): C, 73.72; H, 4.77; N, 4.77. Found C, 73.71; H, 4.75; N, 4.76.

General Procedure for the synthesis of Pyran 4a-g: A mixture of chalcone **3** (0.001 mole) and malononitrile (0.001mole) in ethanol (10 mL) containing catalytic amount of ethanolic potassium hydroxide (50mg of KOH was dissolved in 2 mL ethanol) was stirred at room temperature for 5-6 h (TLC, toluene:acetone, 9:1). The solid obtained was collected by filtration, dried and recrystallized from ethanol to furnish **4** as a colorless solid in 80 -85%.

2,2'-[2-Amino-4-(4-chlorophenyl)-6-(2,5 dimethoxyphenyl)-4H- pyran – 3 ,5 diyl] diacetoneitrile (4a): Yield: 0.314g (80%), mp. 93-95 °C. ir (potassium bromide): 3312, 3280, 2240, 1640, 1560 cm^{-1} . ^1H nmr (DMSO- d_6): δ = 3.70 (s, 3H, OCH₃), 3.75 (s, 3H, OCH₃), 4.75 (s, 1H, CH), 7.13 (d, 1H, J = 2.5 Hz, Ar-H), 7.21 (dd, 1H, J = 2.5 & 8.5 Hz, Ar-H), 7.29 (bs, 2H, NH₂), 7.36 (d, 1H, J = 8.5 Hz, Ar-H), 7.51 (d, 2H, J = 8.2 Hz, Ar-H), 7.65 (d, 2H, J = 8.2 Hz, Ar-H) ppm; MS (70 eV): m/z 393 (M^+). Anal.Calcd for C₂₁H₁₆ClN₃O₃ (393.82): C, 64.12; H, 4.07; N, 10.68. Found C, 64.10; H, 4.06; N, 10.66.

2,2'-[2-Amino-4-(4-bromophenyl)-6-(2,5 dimethoxyphenyl)-4H-pyran-3,5diyl]- diacetoneitrile (4b): Yield: 0.359g (82%), mp.115-117 °C. ir (potassium bromide): 3302, 3285, 2240, 1630, 1590 cm^{-1} . ^1H nmr (DMSO- d_6): δ = 3.75 (s, 3H, OCH₃), 3.81 (s, 3H, OCH₃), 4.75 (s, 1H, CH), 7.33(d, 1H, J = 2.7 Hz, Ar-H), 7.22 (dd, 1H, J = 2.7 & 8.4 Hz, Ar-H), 7.27(bs, 2H, NH₂), 7.35 (d, 1H, J = 8.4 Hz, Ar-H), 7.55(d, 2H, J = 8.3 Hz, Ar-H), 7.75(d, 2H, J = 8.3 Hz, Ar-H) ppm; MS (70eV): m/z 438 (M^+). Anal.Calcd for C₂₁H₁₆BrN₃O₃ (438.27): C, 57.53; H, 3.65; N, 9.58. Found C, 57.54; H, 3.67; N, 9.57.

2,2'-[2-Amino-6-(2,5-dimethoxyphenyl)-4-(4 fluorophenyl)-4H-pyran-3,5-diyl]-diacetonitrile(4c): Yield: 0.316g (84%), mp.125-127 °C. ir (potassium bromide): 3286, 3240, 2235, 1605, 1560 cm⁻¹. ¹H nmr (DMSO-*d*₆): δ = 3.72 (s, 3H, OCH₃), 3.80 (s, 3H, OCH₃), 4.88 (s, 1H, CH), 7.10 (d, 1H, *J* = 2.5 Hz, Ar-H), 7.12 (dd, 1H, *J* = 2.5 & 8.5 Hz, Ar-H), 7.29 (bs, 2H, NH₂), 7.36 (d, 1H, *J* = 8.5 Hz, Ar-H), 7.54 (d, 2H, *J* = 8.2 Hz, Ar-H), 7.65 (d, 2H, *J* = 8.2 Hz, Ar-H) ppm; MS (70eV): *m/z* 377 (M⁺). Anal.Calcd for C₂₁H₁₆FN₃O₃ (377.37): C, 67.02; H, 4.25; N, 11.17. Found C, 67.01; H, 4.24; N, 11.18.

2,2'-[2-Amino-6-(2,5-dimethoxyphenyl)-4-(3-methoxyphenyl)-4H-pyran-3,5-diyl]-diacetonitrile(4d) : Yield: 0.315g (81%), m.p. 111-114 °C. ir (potassium bromide): 3286, 3190, 2245, 1620 cm⁻¹. ¹H nmr (DMSO-*d*₆): δ = 3.70 (s, 3H, OCH₃), 3.79 (s, 3H, OCH₃), 3.94 (s, 3H, OCH₃), 5.02 (s, 1H, CH), 6.82 (s, 1H, Ar-H), 6.94 (d, 1H, *J* = 8.2 Hz, Ar-H), 7.05 (dd, 1H, *J* = 8.2 & 8.4 Hz, Ar-H), 7.09 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.12 (d, 1H, *J* = 2.5 Hz, Ar-H), 7.19 (dd, 1H, *J* = 2.5 & 8.8 Hz, Ar-H), 7.25 (bs, 2H, NH₂), 7.36 (d, 1H, *J* = 8.8 Hz, Ar-H) ppm; MS (70eV):*m/z* 389 (M⁺). Anal.Calcd for C₂₂H₁₉N₃O₄ (389.40): C, 67.86; H, 4.88; N, 10.79. Found C, 67.85; H, 4.87; N, 10.76.

2,2'-[2-Amino-6-(2,5-dimethoxyphenyl)-4-(3,4dimethoxyphenyl)-4H-pyran-3,5-diyl]-diacetonitrile (4e): Yield: 0.343g (82%), m.p. 103-105 °C. ir (potassium bromide): 3260, 3180, 2245, 1600 cm⁻¹. ¹H nmr (DMSO-*d*₆): δ = 3.41 (s, 3H, OCH₃), 3.52 (s, 3H, OCH₃), 3.58 (s, 3H, OCH₃), 3.82 (s, 3H, OCH₃), 4.68 (s, 1H, CH), 6.84 (dd, 1H, *J* = 2.3 & 8.4 Hz, Ar-H), 7.12 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.13 (d, 1H, *J* = 2.3 Hz, Ar-H), 7.20 (d, 1H, *J* = 2.5 Hz, Ar-H), 7.21 (bs, 2H, NH₂), 7.27 (dd, 1H, *J* = 2.5 & 8.7 Hz, Ar-H), 7.32 (d, 1H, *J* = 8.7 Hz, Ar-H) ppm; ¹³C nmr (75MHz, CDCl₃) δ: 55.45, 55.67, 56.06, 56.30, 93.87, 111.15, 111.92, 113.14, 115.16, 116.15, 117.23, 119.43, 119.21, 120.11, 129.12, 134.32, 136.78, 148.39, 148.84, 150.25, 152.21, 155.09, 158.56. ppm; MS (70 eV): *m/z* 419 (M⁺). Anal.Calcd for C₂₃H₂₁N₃O₅ (419.43): C, 65.87; H, 5.01; N, 10.02. Found C, 65.86; H, 5.03; N, 10.01.

2,2'-[2-Amino-6-(2,5-dimethoxyphenyl)-4-(4-nitrophenyl)-4H-pyran-3,5-diyl]-diacetonitrile(4f): Yield: 0.342g (85%), mp. 130-132°C. ir (potassium bromide): 3255, 3150, 2240, 1605, 1540, 1315 cm⁻¹. ¹H nmr (DMSO-*d*₆) δ =: 3.75 (s, 3H, OCH₃), 3.81 (s, 3H, OCH₃), 4.75 (s, 1H, CH), 7.13 (d, 1H, *J* = 2.7 Hz, Ar-H), 7.12 (dd, 1H, *J* = 2.7 & 8.7 Hz, Ar-H), 7.27 (bs, 2H, NH₂), 7.36 (d, 1H, *J* = 8.7 Hz, Ar-H), 7.51 (d, 2H, *J* = 8.2 Hz, Ar-H), 7.68 (d, 2H, *J* = 8.2 Hz, Ar-H) ppm; MS (70eV): *m/z* 404 (M⁺). Anal.Calcd for C₂₁H₁₆N₄O₅ (404.38): C, 62.53 H, 3.97; N, 13.89. Found C, 62.52 H, 3.95; N, 13.85.

2,2'-[2-Amino-6-(2,5-dimethoxyphenyl)-4-phenyl-4H-pyran-3,5-diyl]diacetonitrile (4g): Yield: 0.290g (81%), mp. 112-115°C. ir (potassium bromide): 3285, 3180, 2235, 1615 cm⁻¹. ¹H nmr (DMSO-*d*₆): δ = 3.70 (s, 3H, OCH₃), 3.74 (s, 3H, OCH₃), 4.64 (s, 1H, CH), 6.85 (d, 1H, *J* = 2.3 Hz, Ar-H), 7.05 (dd, 1H, *J* = 2.3 & 8.3 Hz, Ar-H), 7.24 (bs, 2H, NH₂), 7.38-7.52 (m, 5H, Ar-H), 7.36 (d, 2H, *J* = 8.3 Hz, Ar-H) ppm; ¹³CNMR (DMSO-*d*₆) δ: 55.79, 56.31, 93.24, 113.44, 115.54, 116.52, 117.82, 118.98, 120.17, 127.68, 127.78, 128.86, 142.25, 150.98, 152.77, 156.08, 158.53. ppm; MS (70 eV): *m/z* 359 (M⁺). Anal.Calcd for C₂₁H₁₇N₃O₃ (359.38): C,70.19; H, 4.73; N, 11.69. Found C, 70.17; H, 4.71; N, 11.68.

General Procedure for synthesis of pyridine 3, 5-dicarbonitrile 5a-g: A mixture of pyran 4 (0.001 mole) and ammonium acetate (0.01 mole) was heated at 110-120°C for 5-6 h. After completion of reaction (TLC) cold water (30 mL) was added to the viscous reaction mixture and stirred for further 30-min to remove excess of ammonium acetate. Then it was extracted with ethyl acetate, organic layer was dried over anhyd. Sodium sulphate and evaporated to furnish yellow solid. It was recrystallized from ethanol to furnish compound 5 in 80-85% yields.

2-Amino-4-(4-chlorophenyl)-1,4-dihydro-6-(2,5-dimethoxyphenyl)pyridine-3,5-dicarbonitrile(5a): Yield: 0.313g (80%), m.p. 117-116°C. ir (potassium bromide): 3440, 3312, 3275, 2245, 1640,1570 cm⁻¹. ¹H nmr (DMSO-*d*₆): δ = 3.71 (s, 3H, OCH₃), 3.73 (s, 3H, OCH₃), 4.66 (s, 1H, CH), 6.88 (d, 1H, *J* = 2.3 Hz, Ar-H), 7.10 (dd, 1H, *J* = 2.3 & 8.5 Hz, Ar-H), 7.29 (bs, 2H, NH₂), 7.36 (d, 1H, *J* = 8.5 Hz, Ar-H), 7.49 (d, 2H, *J* = 8.9 Hz, Ar-H), 7.64 (d, 2H, *J* = 8.9 Hz, Ar-H), 9.86 (bs, 1H, NH) ppm; MS(70eV): *m/z* 392 (M⁺). Anal.Calcd. for C₂₁H₁₇ClN₄O₂ (392.84): C, 64.28; H, 4.33; N, 14.28. Found C, 64.27; H,4.32; N, 14.26.

2-Amino-4-(4-bromophenyl)-1,4-dihydro-6-(2,5-dimethoxyphenyl)pyridine-3,5-dicarbonitrile (5b): Yield: 0.358g (82%), m.p. 154-155°C. ir (potassium bromide): 3392, 3304, 3225, 2235, 1640, 1575 cm⁻¹. ¹H nmr (DMSO-*d*₆): δ = 3.72 (s, 3H, OCH₃), 3.74 (s, 3H, OCH₃), 4.64 (s, 1H, CH), 6.85 (d, 1H, *J* = 2.2 Hz, Ar-H), 7.05 (dd, 1H, *J* = 2.2 & 8.4 Hz, Ar-H), 7.27 (bs, 2H, NH₂), 7.36 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.44 (d, 2H, *J* = 8.7 Hz, Ar-H), 7.59 (d, 2H, *J* = 8.7 Hz, Ar-H), 9.88 (s, 1H, NH) ppm; MS(70eV): *m/z* 437 (M⁺). Anal.Calcd for C₂₁H₁₇BrN₄O₂ (437.29): C, 57.66; H, 3.89; N, 12.81. Found C, 57.65; H, 3.87; N, 12.80.

2-Amino-4-(4-fluorophenyl)-1,4-dihydro-6-(2,5-dimethoxyphenyl)pyridine-3,5-dicarbonitrile (5c): Yield: 0.319g (85%),m.p.142-143°C. ir (potassium bromide): 3384, 3325, 3265, 2250, 1610, 1550, 1325 cm⁻¹. ¹H nmr (DMSO-*d*₆): δ = 3.77 (s, 3H, OCH₃), 3.71 (s, 3H, OCH₃), 4.62 (s, 1H, CH), 6.82 (d, 1H, *J* = 2.3 Hz, Ar-H), 7.15 (dd, 1H, *J* = 2.3 & 8.2 Hz, Ar-H), 7.30 (bs, 2H, NH₂), 7.32 (d, 1H, *J* = 8.2 Hz, Ar-

H), 7.39 (d, 2H, $J = 8.8$ Hz, Ar-H), 7.72 (d, 2H, $J = 8.8$ Hz, Ar-H), 9.85 (s, 1H, NH) ppm; MS (70eV): m/z 376 (M^+). Anal. Calcd. for $C_{21}H_{17}FN_4O_2$ (376.38): C, 67.02; H, 4.52; N, 14.89. Found C, 67.01; H, 4.53; N, 14.86.

2-Amino-1,4-dihydro-6-(2,5-dimethoxyphenyl)-4(3methoxyphenyl)pyridine-3,5-dicarbonitrile(5d): Yield: 0.322g (83%). m.p.123-124°C. ir (potassium bromide): 3410, 3310, 3265, 2242, 1635, 1560 cm^{-1} . 1H nmr (DMSO- d_6): $\delta = 3.77$ (s, 3H, OCH₃), 3.81 (s, 3H, OCH₃), 3.91 (s, 3H, OCH₃), 4.75 (s, 1H, CH), 6.82 (d, 1H, $J = 8.2$ Hz, Ar-H), 6.90 (s, 1H, Ar-H), 6.94 (dd, 1H, $J = 8.2$ & 8.4 Hz, Ar-H), 7.12 (d, 1H, $J = 8.4$ Hz, Ar-H), 7.13 (d, 1H, $J = 2.5$ Hz, Ar-H), 7.12 (dd, 1H, $J = 2.5$ & 8.5 Hz, Ar-H), 7.25 (bs, 2H, NH₂), 7.36 (d, 1H, $J = 8.5$ Hz, Ar-H), 9.92 (s, 1H, NH) ppm; MS(70eV): m/z 388 (M^+). Anal.Calcd for $C_{22}H_{20}N_4O_3$ (388.42): C, 68.04; H, 5.15; N, 14.43. Found C, 68.03; H, 5.12; N, 14.42.

2-Amino-1,4-dihydro-6-(2,5-dimethoxyphenyl)-4-(3,4-dimethoxyphenyl)-pyridine-3,5-dicarbonitrile(5e): Yield: 0.334g (80%), m.p.128-129 °C. ir (potassium bromide): 3408, 3322, 3255, 2245, 1635,1595 cm^{-1} . 1H nmr (DMSO- d_6): $\delta = 3.41$ (s, 3H, OCH₃), 3.52 (s, 3H, OCH₃), 3.58 (s, 3H, OCH₃), 3.82 (s, 3H, OCH₃), 4.68 (s, 1H, CH), 6.84 (dd, 1H, $J = 2.5$ & 8.4 Hz, Ar-H), 7.12 (d, 1H, $J = 8.4$ Hz, Ar-H), 7.13 (dd, 1H, $J = 2.4$ & 8.2 Hz, Ar-H), 7.20 (d, 1H, $J = 2.5$ Hz, Ar-H), 7.27 (d, 1H, $J = 8.2$ Hz, Ar-H), 7.29 (bs, 2H, NH₂), 7.32 (d, 1H, $J = 2.4$ Hz, Ar-H), 9.90 (s, 1H, NH) ppm; ^{13}C nmr (DMSO- d_6) δ : 55.01, 45.05, 55.08, 67.14, 56.06, 56.30, 93.09, 111.15, 111.92, 113.01, 115.08, 116.05, 117.12, 119.09, 119.22, 120.23, 134.31, 148.39, 148.84, 150.06, 152.08, 155.33, 158.21 ppm; MS(70eV): m/z 418 (M^+). Anal.Calcd for $C_{23}H_{22}N_4O_4$ (418.45): C, 66.02; H,5.26; N, 13.39. Found C, 66.01; H,5.24; N, 13.34.

2-Amino-1,4-dihydro-6-(2,5-dimethoxyphenyl)-4-(4-nitrophenyl)pyridine-3,5-dicarbonitrile (5f): Yield: 0.338g (84%). m.p158-159°C. ir (potassium bromide): 3398, 3305, 3275, 2250, 1640, 1520, 1350 cm^{-1} . 1H nmr (DMSO- d_6): $\delta = 3.69$ (s, 3H, OCH₃), 3.74 (s, 3H, OCH₃), 4.61 (s, 1H, CH), 6.85 (d, 1H, $J = 2.5$ Hz, Ar-H), 7.15 (dd, 1H, $J = 2.5$ & 8.6 Hz, Ar-H), 7.27 (bs, 2H, NH₂), 7.38 (d, 1H, $J = 8.6$ Hz, Ar-H), 7.47 (d, 2H, $J = 8.9$ Hz, Ar-H), 7.89(d, 2H, $J = 8.9$ Hz, Ar-H), 9.86 (s, 1H, NH) ppm; MS(70eV): m/z 403 (M^+). Anal.Calcd for $C_{21}H_{17}N_5O_4$ (403.39): C, 62.37; H,4.49; N,17.32. Found C, 62.61; H,4.52; N,17.21.

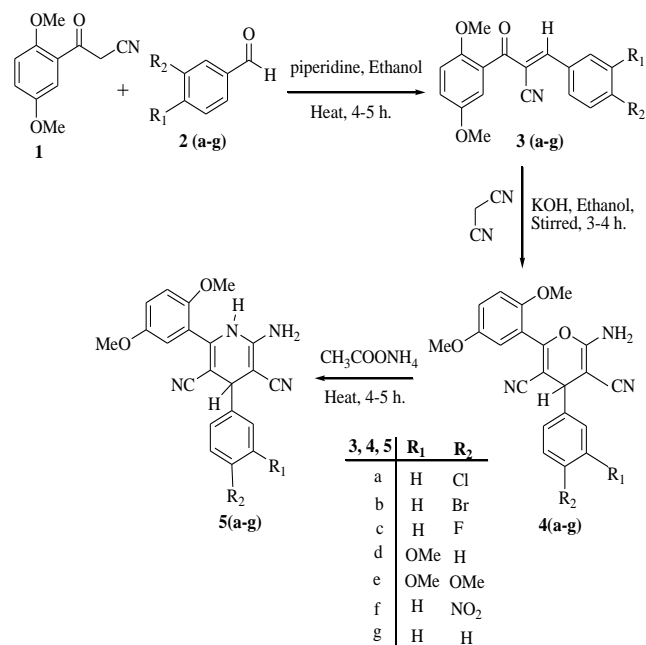
2-Amino-1,4-dihydro-6-(2,5-dimethoxyphenyl)-4-phenylpyridine-3,5-dicarbonitrile(5g): Yield: 0.289g (81%), mp. 138-139°C. ir (potassium bromide): 3398, 3310, 3250, 2245, 1635 cm^{-1} . 1H nmr (DMSO- d_6): $\delta = 3.71$ (s, 3H, OCH₃), 3.73 (s, 3H, O CH₃), 4.60 (s, 1H, CH), 6.81 (d, 1H, $J = 2.4$ Hz, Ar-H), 7.15 (dd, 1H, $J = 2.4$ & 8.7 Hz, Ar-H), 7.24 (m, 3H, Ar-H), 7.29 (bs, 2H, NH₂), 7.36 (d, 1H, $J = 8.7$ Hz, Ar-H), 7.51 (m, 2H, Ar-H), 9.84 (s, 1H, NH) ppm; MS (70eV): m/z 358 (M^+). Anal.Calcd for $C_{21}H_{18}N_4O_2$ (358.39):

C, 70.39;H, 5.02; N, 15.64. Found C, 70.37; H, 5.03; N, 15.62.

Results and Discussion

The required chalcones for the synthesis of title compounds were prepared by aldol condensation of 3-(2,5-dimethoxyphenyl)-3-oxopropanenitrile and aromatic aldehydes. Thus, equimolar solution of 3-(2,5-dimethoxyphenyl)-3-oxopropanenitrile **1** and aromatic aldehydes **2** in ethanol, heating in basic medium furnished chalcones **3** in 70-80 % yield (scheme 1). Compounds **3** were characterized by spectral and analytical methods. The chalcones **3**, were further utilized for Michael addition with malononitrile in presence of catalytic amount of KOH in ethanol to yield pyran derivatives **4** in 80-85 % yield. Previously we have noted the formation of pyridine derivative by condensation of chalcone, different than reported here, with malononitrile under similar reaction condition, Compounds **4** were transformed in to pyridine derivative **5** by heating with ammonium acetate at 110-120 °C (scheme 1).

This reaction did not require any solvent and aqueous work up of the reaction allowed for the isolation of 100 % of the product **5**.and were characterized by IR, mass, 1H and ^{13}C NMR data. Further semiempirical study and photophysical properties of compounds **4** and **5** were under taken.



Scheme- 1
Scheme-1

Table-1
The molecular electronic properties (HOMO-LUMO energy and GAP value) of pyrans 4(a-g) and pyridine-3,5-dicarbonitriles 5(a-g)

Comp.	R ¹	R ²	HOMO eV	LUMO eV	GAP eV
4a	H	Cl	-8.898	-1.086	7.812
4b	H	Br	-8.894	-1.088	7.806
4c	H	F	-8.887	-1.071	7.816
4d	OMe	H	-8.775	-0.951	7.824
4e	OMe	OMe	-8.257	-0.932	7.325
4f	H	NO ₂	-9.224	-1.319	7.905
4g	H	H	-8.819	-0.979	7.840
5a	H	Cl	-8.910	-1.042	7.868
5b	H	Br	-8.920	-1.054	7.866
5c	H	F	-8.890	-1.024	7.866
5d	OMe	H	-8.660	-0.914	7.746
5e	OMe	OMe	-8.150	-0.897	7.253
5f	H	NO ₂	-9.170	-1.288	7.882
5g	H	H	-8.805	-0.938	7.867

Table-2
The photophysical data for electronic absorption (UV λMax), fluorescence (Em λMax) and quantum yield (φ_F) of pyran 4(a-g) and pyridine-3,5-dicarbonitrile 5(a-g) for 0.1M Conc. in CHCl₃ at 25°C.

Comp.	R ¹	R ²	λ _{Abs.} (CHCl ₃) Nm	λ _{Emi.} (CHCl ₃) nm	φ _F
4a	H	Cl	358 nm	445	0.171
4b	H	Br	359 nm	448	0.173
4c	H	F	353 nm	451	0.174
4d	OMe	H	357 nm	464	0.186
4e	OMe	OMe	367 nm	475	0.197
4f	H	NO ₂	344 nm	423	0.151
4g	H	H	358 nm	456	0.181
5a	H	Cl	406 nm	455	0.177
5b	H	Br	376 nm	453	0.175
5c	H	F	358 nm	457	0.178
5d	OMe	H	381 nm	469	0.189
5e	OMe	OMe	413 nm	479	0.208
5f	H	NO ₂	347 nm	430	0.156
5g	H	H	355 nm	461	0.184

Semi-empirical study: The gain interest into the atomic contribution on the frontier orbital, we analyzed the three-dimensional HOMO and LUMO coefficient contribution by software MOPAC-2009 (Version 8.331) and are given in table 1. From this table we observed that pyran derivative **4e** and pyridine-3, 5-dicarbonitriles **5e** showed low gap values (eV= 7.325 and 7.253), while compounds **4f** and **5f** showed high gap values (eV= 7.905 and 7.882). The observed low gap value for **4e** and **5e** may be due to strong electron donating group such as -OCH₃ and high gap value for **4f** and

5f due to -NO₂ group which is electron acceptor present on ring C (figure-1) The 3D picture (molecular modeling)of representative pyran and pyridine dicarbonitriles .

Photophysical properties: Fluorescence quantum yields of compound **4** and **5** were determined by standard literature procedure using quinine sulphate as reference standard and are listed in table 2. From this table we observed that compound **4e** and **5e** showed maximum absorption, emission and high quantum yields (φ_F = 0.197 & 0.208 respectively). This may be due to electron donating group (-OCH₃) present on benzene ring at C₄-position in ring C of pyran **4e** and pyridine **5e** (figure-1). The electron accepting group such as -NO₂ on benzene ring at C₄-position in **4f** and **5f** showed absorption, emission to shorter wavelength also low quantum yields (φ_F = 0.151 and 0.156 respectively). The graphical representation of absorption and emission spectra of compound **4e** and **5e** are shown in figure 2.

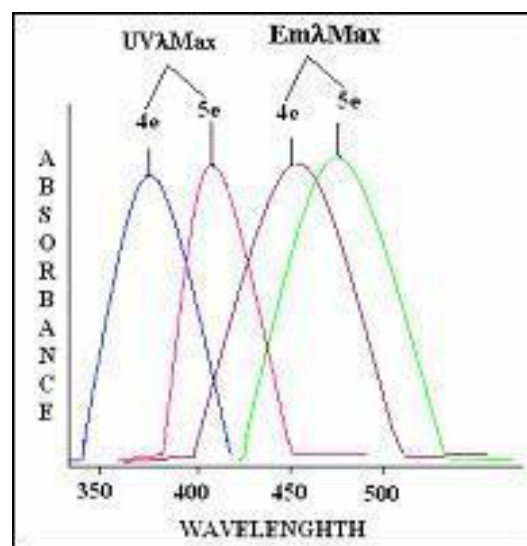


figure-2.
Comparative absorption (UV λ Max) and emission (Em λ Max) spectra of compounds (4e) and (5e) respectively.

Conclusion

In summary we have developed an efficient and simple method for synthesis of pyran derivatives **4** in excellent yields, the transformation of **4** into pyridine derivative **5** was achieved using ammonium acetate as ecofriendly reagent. This method has several advantages in terms of yields, mild reaction condition and lack of side product. The photophysical studies of compound **4** and **5** revealed that the donor substituents -OCH₃ on benzene ring at C₄-position (C-ring, figure-1) of **4e** and **5e** showed red shift (Bathochromic shift), while acceptor group -NO₂ leads to absorption and emission to shorter wavelength i.e. blue shift (hypsochromic shift). From these studies we can conclude that the

fluorescent properties of compounds **4** and **5** depend upon the nature of substituents present on benzene ring at (C-ring, figure-1) C₄-position of pyran and pyridine nucleus. These compounds may be useful as organic light emitting diodes (OLED) and are addition in the library of new heterocyclic compounds.

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