

Bis-DCM Type Dyes: Convenient Method for Synthesis of 2-(2, 6-bis(4-(dialkylamino)styryl)-4H -pyran-4-ylidene) Malononitrile Derivatives

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ABSTRACT: An efficient and convenient method for synthesis of 2,6-bis (4-(dialkylamino) styryl)-4H-pyran-4-one starting from 4- (dialkylamino) benzaldehyde with 2,6-dimethyl-4H-pyran-4-one in the presence of MeONa as the base was described. Additionally, preparation of novel compounds with bis-DCM-type skeleton for application in organic light-emitting diodes was developed via reaction of malononitrile as active methylene group with 2,6-bis (4-(dialkylamino) styryl) -4H-pyran-4-one derivatives. ¹H and ¹³C NMR, FT-IR spectroscopy supported the predicted structure of the products. The UV-Vis absorption spectra of synthesis compound were measured in diluted dichloromethane solution. Maximum absorption (λ_{max}) values differ from 460 to 496 nm, this absorption is due to π - π^* transition.

KEYWORDS: Knoevenagel condensation; Bis-DCM; Malononitrile; 2,6-bis(4-(dialkylamino) styryl)-4H-pyran-4-one.

INTRODUCTION

Organic compounds with low molecular mass properties of internal load transfer are widely photonics adopted for organic materials such as the creation of molecular electronics elements, solar cells, and magnets (organic light emitting diodes OLEDs) for full display panels [1-4]. A considerable and large amount of attention research efforts have been devoted over the four decades to the preparation of polarized olefinic systems [5-8]. These materials contain push-pull chromophores, characterized by electron-donating and electron-accepting moieties linked through a conjugated π -system [9-11].

Among the primary color emitters of Red, Green, and Blue (RGB) required for full-color displays, red fluorescent emitters are necessary to improve their electroluminescent properties [12,13]. One of the light-emitting materials most widely used red contains pyranilydene (4H-pyran-4-ylidene) or isophorene (5, 5-dimethylcyclohex-2-enylidene) backbone fragments of the molecule, which is conjugated in a system with electron acceptor and electron donor fragments [14-31]. Among the luminescent materials applied in red emitters, bis-DCM type dyes are the most efficient materials.

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4-(Dicyanomethylene)-2-methyl-6-[*p*-(dialkylamino)styryl]-4*H*-pyran (bis-DCM) derivatives have attracted considerable interest due to their excellent electronic and optical properties, can be used to improve the luminance efficiency, and color purity [32-35]. Bis -DCM also has more red-shifted emission than the mono-substituted DCM derivatives [36].

Herein, we describe the design and synthesis of 2,6-bis(4-(dialkylamino)styryl)-4*H*-pyran-4-one **3** via an efficient and convenient new method from 4-(dialkylamino)benzaldehyde with 2,6-dimethyl-4*H*-pyran-4-one in the presence of MeONa. In continuous 2-(2, 6-bis(4-(dialkylamino) styryl)-4*H*-pyran-4-ylidene) malononitrile **6** was synthesized by Knoevenagel condensation.

EXPERIMENTAL SECTION

Material

Chemicals were either prepared in our laboratory or purchased from Merck, Fluka, Sigma, Aldrich and Yantai Suny Chem. International Co., Ltd. Commercial solid reagents were used without further purification. Liquid reactants were distilled prior to use. Solvents were dried and distilled prior to use according to standard laboratory practices; Column chromatography was performed on silicagel 60 (Merck, grain size 0.063-0.2 mm). All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring.

Instrumentation

The ¹H NMR and ¹³C NMR spectra were recorded using a Bruker FT-400 MHz spectrometer at room temperature. The FT-IR spectra were recorded on a Bruker-Tensor 270 spectrophotometer as KBr disks or smears between salt plates. Operating at 70 eV. Elemental analyses were carried out with an Elementor Vario EL. III instrument. The electronic absorption spectra were obtained using SPECORD 250 analytik jena UV/Vis spectrophotometer.

General procedure for the synthesis of 2, 6-Bis-[2-(4-dialkylaminophenyl) vinyl]-4*H*-Pyran-4-one (**3**)

To a magnetically stirred solution of 4-(dialkylamino)benzaldehyde **1** (6.7 mmol) and 2, 6-dimethyl-4*H*-pyran-4-one **2** (3.35 mmol) in 8 mL of dry MeOH, NaOMe (6.7 mmol) was added under gentle stirring and allowed to react for 24 h at room temperature. The obtained

precipitate, was collected by filtration and washed with cold MeOH, then recrystallized MeOH to give **3**.

2, 6-bis(4-(dimethylamino) styryl)-4*H*-pyran-4-one (**3a**)

Pale brown powder. Yield: 1.81 g (70%); mp 385-390 °C; IR: ν 1643(C=O), 1639, 1602 (C=C), 1157 (C=O) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 3.04 (s, 12H, Me₂N); 6.16 (s, 2H, pyran); 6.52 (d, 2H, =CH, *J* = 15.9); 6.71 (d, 4H, =CH Aromatic, *J* = 8.7); 7.41 (d, 2H, =CH, *J* = 15.9); 7.47 (d, 4H, =CH Aromatic, *J* = 8.7); ¹³C-NMR (100 MHz, CDCl₃): δ 39.2 (CH₃), 111.1 (=CH, pyran), 111.3 (HC=CH), 113.6 (HC=CH), 121.9 (=CH, Aromatic), 128.0 (=CH, Aromatic), 129.5 (=CH, Aromatic), 135.0 (=CH, Aromatic), 150.2(=C, pyran), 161.1 (=C, pyran), 179.0 (C=O); Anal. calc. for C₂₅H₂₆N₂O₂ (386.20): C 77.69; H 6.78; N 7.25; found: C 77.54, H 6.68, N 7.14%.

2,6-bis(4-(pyrrolidin-1-yl)styryl)-4*H*-pyran-4-one (**3b**)

Brown powder. Yield: 2.34 g (80%); mp 265-270 °C; IR: ν 1639 (C=O), 1585, 1519 (C=C), 1169 (C-O) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 2.03 (m, 8H, CH₂); 3.33-3.36 (m, 8H, CH₂N); 6.18 (s, 2H, pyran); 6.55 (d, 4H, =CH Aromatic, *J* = 8.3); 6.87 (d, 2H, =CH, *J* = 15.6); 7.50 (d, 4H, =CH Aromatic, *J* = 8.3); 7.68 (d, 2H, =CH, *J* = 8.4); ¹³C-NMR (100 MHz, CDCl₃): δ 28.6 (CH₂), 46.5 (CH₂N), 110.6 (=CH, pyran), 119.7 (HC=CH), 121.2 (HC=CH), 123.48 (=CH, Aromatic), 126.44 (=CH, Aromatic), 129.2 (=CH, Aromatic), 142.1 (=C, pyran), 148.2 (C-N), 187.8 (C=O). Anal. calc. for C₂₉H₃₀N₂O₂ (438.23): C 79.42, H 6.89, N 6.39; found: C 79.12, H 6.82, N 6.23%.

2,6-bis(4-(piperidin-1-yl)styryl)-4*H*-pyran-4-one (**3c**)

Brown powder. Yield: 2.34 g (75%); mp 276-280 °C; IR:ν 1639 (C=O), 1598, 1558 (C=C), 1178 (C-O) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 1.69-1.70 (m, 12H, CH₂); 3.29 (t, 8H, CH₂); 6.18 (s, 2H, pyran); 6.54 (d, 2H, =CH, *J* = 15.9); 6.91 (d, 4H, =CH Aromatic, *J* = 8.7); 7.39 (d, 2H, =CH, *J* = 15.9); 7.46 (d, 4H, =CH Aromatic, *J* = 8.7); ¹³C-NMR (100 MHz, CDCl₃): δ 24.6 (CH₂), 28.6 (CH₂), 48.3 (CH₂N), 111.5 (=CH, pyran), 114.1 (HC=CH), 114.8 (HC=CH), 127.9 (=CH, Aromatic), 128.9 (=CH, Aromatic), 129.4 (=CH, Aromatic), 134.7 (=C, pyran), 161.0 (C-N), 179.5 (C=O). Anal. calc. for C₃₁H₃₄N₂O₂ (466.26): C 79.79, H 7.34, N 6.00; found: C 79.5, H 7.24, N 5.96%.

2,6-bis(4-morpholinostyryl)-4H-pyran-4-one (3d)

Pale brown powder. Yield: 2.45 g (78%); mp 290-292 °C; IR:v 1656 (C=O), 1593 (C=C), 1154 (C-O) cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 3.24 (t, 8H, CH_2); 3.86 (t, 8H, CH_2); 6.16 (s, 2H, pyran); 6.51 (d, 2H, =CH, $J = 16.0$); 6.89 (d, 4H, =CH Aromatic, $J = 8.2$); 7.30 (d, 2H, =CH, $J = 16.0$); 7.45 (d, 4H, =CH Aromatic, $J = 8.2$); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 47.1 (CH_2N), 65.6 (CH_2O), 113.1 (=CH, pyran), 115.2 (HC=CH), 116.4 (HC=CH), 125.0 (=CH, Aromatic), 127.8 (=CH, Aromatic), 134.3 (=CH, Aromatic), 150.9 (=C, pyran), 163.7 (C-N), 179.3 (C=O). Anal. calc. for $\text{C}_{29}\text{H}_{30}\text{N}_2\text{O}_4$ (470.22): C 74.02, H 6.43, N 5.95; found: C 73.83, H 6.12, N 5.86%.

General procedure for synthesis of 2-(2,6-bis(4-dialkylamino)styryl)-4H-pyran-4-ylidene)malononitrile (5)

A mixture of compound 3 (2.59 mmol) and malononitrile (2.64 mmol) in 6 ml acetic anhydride was stirred for 1 h at 150 °C. The reaction was controlled with TLC by the quantity of compound 3 in solution of reaction, after completion of the reaction, saturated NaHCO_3 was added, and the mixture was extracted with CH_2Cl_2 (3 \times 5 mL). The organic phase was concentrated under vacuum and the residue was purified by column chromatography over silica gel and hexane: EtOAc (3:2) as eluent to afford corresponding products.

2-(2,6-bis(4-dimethylamino)styryl)-4H-pyran-4-ylidene)malononitrile (5a)

Green powder. Yield: 0.67 g (60%); mp 295-300 °C; IR:v 2192 ($\text{C}\equiv\text{N}$), 1639, 1591 (C=C) cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 3.05 (s, 12H, Me_2N); 6.47 (d, 2H, =CH, $J = 15.7$); 6.49 (s, 2H, pyran); 6.69 (d, 4H, =CH Aromatic, $J = 8.6$); 7.41 (d, 2H, =CH, $J = 15.7$); 7.44 (d, 4H, =CH Aromatic, $J = 8.6$); $^{13}\text{C-NMR}$: δ 39.1 (CH_3), 70.1 (C-CN), 110.9 (=CH, pyran), 112.0 (HC=CH), 115.3 ($\text{C}\equiv\text{N}$), 121.3 (HC=CH), 128.5 (=CH, Aromatic), 137.1 (=CH, Aromatic), 150.6 (=CH, Aromatic), 155.1 (=CH-N, Aromatic), 158.2 (=C, pyran), 178.9 (C=C-CN, pyran). Anal. Calc. for $\text{C}_{28}\text{H}_{26}\text{N}_4\text{O}$ (434.21): C 77.39, H 6.03, N 12.89; found: C 77.1, H 5.95, N 12.63.

2-(2,6-bis(4-pyrrolidin-1-yl)styryl)-4H-pyran-4-ylidene)malononitrile (5b)

Green powder. Yield: 0.63 g (50%); mp 303-306 °C; IR:v 2195 ($\text{C}\equiv\text{N}$), 1638, 1592 (C=C) cm^{-1} ; $^1\text{H-NMR}$ (400

MHz, CDCl_3): δ 2.03 (m, 8H, CH_2); 3.37 (m, 8H, CH_2N); 6.47 (d, 2H, =CH, $J = 15.8$); 6.51 (s, 2H, pyran); 6.56 (d, 4H, =CH Aromatic, $J = 8.4$); 7.44 (d, 2H, =CH, $J = 15.7$); 7.45 (d, 4H, =CH Aromatic, $J = 8.4$); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 24.4 (CH_2), 46.5 (CH_2N), 70.4 (C-CN), 110.6 (=CH, pyran), 115.4 ($\text{C}\equiv\text{N}$), 120.8 (HC=CH), 121.4 (HC=CH), 128.7 (=CH, Aromatic), 137.4 (=CH, Aromatic), 148.2 (=CH, Aromatic), 155.1 (=CH-N, Aromatic), 158.4 (=C, pyran), 178.5 (C=C-CN, pyran). Anal. calc. for $\text{C}_{32}\text{H}_{30}\text{N}_4\text{O}$ (486.24): C 78.98, H 6.21, N 11.51; found: C 78.7, H 6.15, N 10.89.

2-(2,6-bis(4(piperidin-1-yl)styryl)-4H-pyran-4-ylidene)malononitrile (5c)

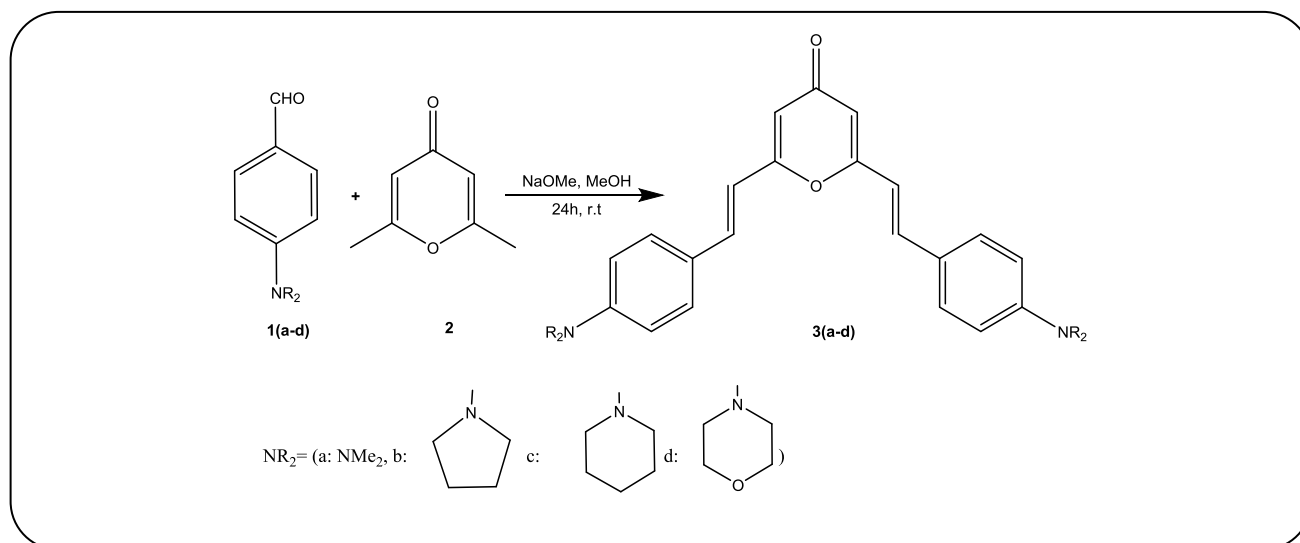
Red powder. Yield: 0.73 g (55%); mp 347-350 °C; IR:v 2201 ($\text{C}\equiv\text{N}$), 1636, 1597 (C=C) cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 1.68-1.70 (m, 12H, CH_2); 3.33 (t, 8H, CH_2N); 6.55 (d, 2H, =CH, $J = 15.8$); 6.58 (s, 2H, pyran); 6.91 (d, 4H, =CH Aromatic, $J = 8.6$); 7.44 (d, 2H, =CH, $J = 15.6$); 7.46 (d, 4H, =CH Aromatic, $J = 8.6$); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 29.1 (CH_2), 30.4 (CH_2), 47.9 (CH_2N), 70.3 (C-CN), 104.7 (=CH, pyran), 113.0 ($\text{C}\equiv\text{N}$), 123.0 (HC=CH), 128.4 (HC=CH), 136.9 (=CH, Aromatic), 150.2 (=CH, Aromatic), 158.4 (=CH-N, Aromatic), 158.8 (=C, pyran), 178.8 (C=C-CN, pyran). Anal. calc. for $\text{C}_{34}\text{H}_{34}\text{N}_4\text{O}$ (514.27): C 79.35, H 6.66, N 10.89; found: C 79.72, H 6.50, N 10.86.

2-(2,6-bis(4-morpholinostyryl)-4H-pyran-4-ylidene)malononitrile (5d)

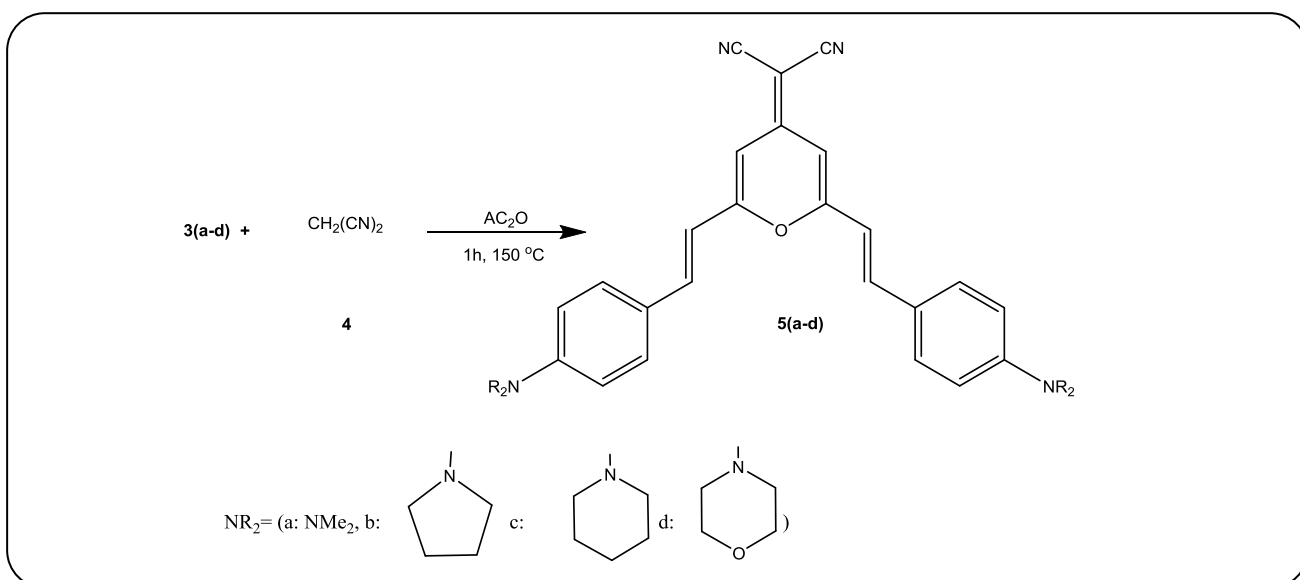
Red powder. Yield: 0.87 g (65%); mp 363-367 °C; IR:v 2197 ($\text{C}\equiv\text{N}$), 1639, 1597 (C=C) cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 3.28 (t, 8H, CH_2); 3.87 (t, 8H, CH_2); 6.59 (d, 2H, =CH, $J = 15.9$); 6.6 (s, 2H, pyran); 6.92 (d, 4H, =CH Aromatic, $J = 8.7$); 7.45 (d, 2H, =CH, $J = 15.9$); 7.50 (d, 4H, =CH Aromatic, $J = 8.7$); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 46.9 (CH_2N), 59.3 (CH_2O), 69.6 (C-CN), 105.1 (=CH, pyran), 113.7 ($\text{C}\equiv\text{N}$), 119.0 (HC=CH), 124.5 (HC=CH), 128.3 (=CH, Aromatic), 136.6 (=CH, Aromatic), 151.4 (=CH, Aromatic), 157.8 (=CH-N, Aromatic), 158.2 (=C, pyran), 179.2 (C=C-CN, pyran). Anal. calc. for $\text{C}_{32}\text{H}_{30}\text{N}_4\text{O}_3$ (518.23): C 74.11, H 5.83, N 10.80; found: C 73.75, H 5.75, N 10.66.

RESULTS AND DISCUSSION

Synthetic routes employed for the preparation of pyron derivatives are shown in Scheme 1, the reaction of



Scheme 1: Synthesis of 2,6-bis-[2-(4-dialkylaminophenyl) vinyl]-4H-pyran-4-one 3.



Scheme 2: Synthesis of 2-(2,6-bis(4-(dialkylamino)styryl)-4H-pyran-4-ylidene)malononitrile 5.

two equivalent of compound **1** with **2** afforded mainly bis substituted derivative (**3**), in 52-65 % yields, without the presence of mono condensate compounds as a byproduct. The reaction was conducted under room temperature with the MeONa in dry methanol. Full characterization involving IR, ^1H NMR and ^{13}C NMR proved the identity of **3**.

The dicyanomethylenepyran derivatives (DCM analogues) have the typical donor- π -acceptor (D- π -A) structure that has attracted considerable attention because of their potential applications in Organic light-emitting devices (OLEDs). Therefore we decided to the synthesis

of 2-(2, 6-bis(4-(dialkylamino)styryl)-4H-pyran-4-ylidene) malononitrile (**5**) derivatives (Scheme 2). These Compounds were prepared from the reaction of **3** and malononitrile in AC_2O at reflux temperature for 1 h. In FT-IR spectra the appearance stretching vibration band at 2192 cm^{-1} corresponding to $\text{C}\equiv\text{N}$ and the complete disappearance of $\text{C}=\text{O}$ peaks in 1656 cm^{-1} were confirmed the preparation of respective compounds.

The structure of compounds **5a-d** was deduced from their IR, ^1H NMR and ^{13}C NMR spectra. For example the the ^1H NMR spectrum of **5a** exhibited singlet signal

Table 1: Absorption spectral data of 5(a-d) compounds in dichloromethane solution.

Compound	λ_{\max}
5a	490
5b	496
5c	471
5d	460

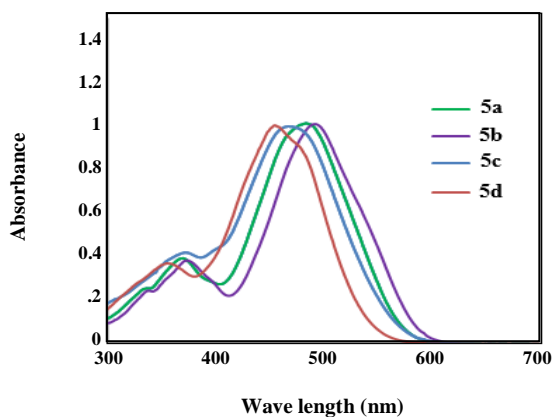


Fig. 1: Normalized UV-Vis absorption of 5(a-d) compounds in dichloromethane solution.

at ($\delta = 3.05$), ($\delta = 6.49$) due to the methyl group of NMe_3 , and pyran protons, respectively, the phenyl groups showed characteristic doublet in the appropriate region of the spectrum. Its ^{13}C NMR spectrum exhibited 11 signals which in agreement with the proposed structure.

The UV-Vis absorption spectra of synthesis compound (5a-d) were measured in the diluted dichloromethane solution (Fig 1). Maximum absorption (λ_{\max}) values differ from 460 to 496 nm, this absorption is due to π - π^* transition. This data are summarized in Table 1.

In summary, we described a convenient route to synthesis of 2-(2, 6-bis (4-(dialkylamino)styryl)-4H-pyran-4-ylidene) malononitrile (bis-DCM) that can use in organic light-emitting devices (OLEDs). The advantage of this method was the formation of bis compounds without the presence of mono condensate compounds as a byproduct.

CONCLUSIONS

In this study, we report the efficient and convenient method for synthesis of 2,6-bis (4-(dialkylamino) styryl)-4H-pyran-4-one starting through the reaction of 4- (dialkylamino) benzaldehyde with 2,6-dimethyl-4H-

pyran-4-one in the presence of NaOMe is described. Additionally, preparation of new types of bis condensed DCM derivatives for application in organic light-emitting diodes is therewith via reaction of malononitrile with 2,6-bis (4-(dialkylamino) styryl)-4H-pyran-4-one.

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