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## SYNTHESIS AND OPTICAL STUDIES OF 2,4,5-TRI[2-(ARYL)-ETHENYL]-1H-IMIDAZOLES

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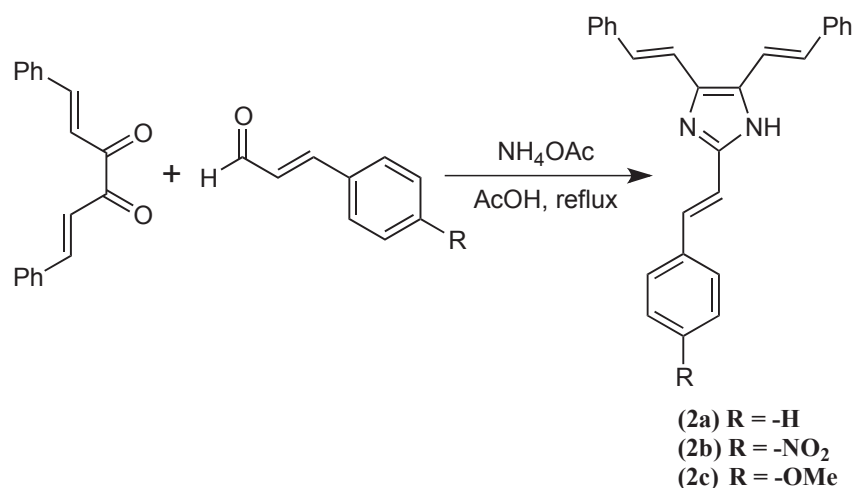
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**Abstract** – A series of Y-shaped 2,4,5-tri(arylethenyl)-1H-imidazoles (**2a-2c**) has been synthesized. The synthesized compounds have been characterized by IR, NMR, Mass and elemental analyses. The optical properties were investigated by using absorption and emission measurements. The compound **2b**, containing nitro group has been found non-fluorescent. The absorption and emission properties have helped us to find the effect of substituent on the optical properties.

Synthesis of imidazole derivatives has been a matter of great interest for chemists. Debus-Radziszewski method has been used to construct differently substituted imidazoles for decades.<sup>1</sup> Till now a variety of tri and tetra substituted imidazole derivatives have been prepared, using different catalysts and techniques.<sup>2,3</sup> There are numerous examples of naturally occurring biological compounds that possess the imidazole scaffold, such as histamine, histidine, biotin, vitamin B<sub>12</sub>, purines and haem.<sup>4</sup> Literature shows that imidazole derivatives not only have various pharmacological and medicinal applications<sup>5</sup> but they also exhibit number of uses as NLO material. Such compounds have found applications as optoelectronic compounds, chemosensors, fluorescent switches, biosensors and signaling. Imidazole derivatives exhibit variety of applications in OLEDs, PVCs, and switches. Some imidazole-based push-pull molecules have also been investigated as photoredox catalysts.<sup>6-9</sup>

Literature depicts that imidazole can successfully act as a robust  $\pi$ -conjugated backbone in organophores. Synthesis of Y-shaped imidazoles has gained great interest over few decades. In these compounds imidazole moiety can act as an electron acceptor or donor.<sup>10-12</sup> In this paper, synthesis of novel Y-shaped imidazoles has been described. Although there are numerous examples of tri-substituted imidazoles but imidazoles containing aryl groups appended at the 2, 4 and 5 positions of imidazole nucleus via vinyl group have not been reported yet. We have synthesized such imidazoles and investigated their optical properties. We are also working on the designing and synthesis of large  $\pi$ -extended imidazoles.

The compounds **2a-2c** were synthesized by three component condensation of 1,6-diphenyl-1,5-hexadiene-3,4-dione, ammonium acetate and appropriate cinnamaldehydes in glacial acetic acid (**Scheme 1**). The products were obtained in good yields (73-77%).



**Scheme 1.** Synthesis of compounds **2a-2c**

The IR spectra of synthesized compounds *2,4,5-tristyryl-1H-imidazole* (**2a**), *2-(4-nitrostyryl)-4,5-bis[2-(phenyl)ethenyl]-1H-imidazole* (**2b**) and *2-(4-methoxystyryl)-4,5-bis[2-(phenyl)ethenyl]-1H-imidazole* (**2c**) were taken in 650-4000 cm<sup>-1</sup> region. The synthesis of imidazole nucleus is confirmed from the -N-H stretching frequency which appeared at 3192-3340 cm<sup>-1</sup> range. The mass spectra showed that *m/z* values of molecular ion peaks are in perfect agreement with the calculated mass values of the synthesized compounds. The nuclear magnetic spectroscopy is quite helpful in providing the structural diagnosis of these synthesized compounds. The chemical shift values and multiplicities of proton signals appear according to their surroundings. The characteristic proton signal that confirms the condensation has occurred and imidazole backbone has been constructed, is the signal of -N-H of imidazole nucleus. The -N-H proton singlet appeared in the 12.318-12.622 ppm range except for compounds **2a** (its signal is out of scanned range 0-12 ppm). The downfield appearance of this signal is because of the electron withdrawing inductive effect of nitrogen atom to which hydrogen is attached. The <sup>1</sup>H NMR spectral data of the compounds **2a-2c** revealed that the signals of vinyl and phenyl protons appeared in the 8.247-6.883 ppm range. The coupling constants of vinyl protons are in 15.5-16.5 Hz range and confirm the *trans* stereochemistry of vinyl protons. The chemical shift values of <sup>1</sup>H NMR spectra of these compounds **2a-2c** are in good agreement with the values reported in literature for similar compounds.<sup>13</sup> The signal of 3'-H & 5'-H for compound **2b** appeared downfield at 8.247 ppm as compared to that of **2a** and **2c**. Such downfield appearance of signal is because of the presence of electron

withdrawing  $-\text{NO}_2$  at 4'-position that draws the electron density towards itself and deshields the 3'-H & 5'-H. For compound **2b** the signal of 2'-H and 6'-H also appeared downfield as compared to that of **2a** and **2c**. For compound **2c**, there is a distinct singlet that appeared at 3.792 ppm which is due to three protons of methoxy group attached at 4' position. The signal of 3'-H and 5'-H for compound **2c** has appeared upfield as compared to that of **2a** and **2b**. This is attributed to the electron donating methoxy group at 4' position that shielded the 3'-H and 5'-H.

The  $^{13}\text{C}$  NMR spectral data revealed that the signals of carbons of phenyl, vinyl and imidazole appeared in the same range as reported in literature for similar compounds.<sup>10,13</sup> The signals of 2-C for the synthesized compounds (**2a-2c**) appeared downfield because of the presence of neighbouring nitrogen atoms. The carbon bearing nitro group for compound **2b** is also expected to appear downfield, therefore it is difficult to assign specific signal to 2-C and 4'-C. For compound **2c**, the 4'-carbon bearing the methoxy group appeared downfield at 175.329 ppm. This is attributed to the electron withdrawing inductive effect of oxygen atom. The distinct signal of methoxy carbon appeared at 55.255 ppm, also provided the evidence that desired compound has been synthesized.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data have provided the conformational analysis. The synthesized compounds have large  $\pi$ -extensions and styryl substitutions are tailored at 2, 4 and 5 positions of imidazole nucleus. These styryl groups are appended via  $\text{sp}^2\text{-sp}^2$  bonds. This provides the p-orbital overlapping and delocalization of  $\pi$ -electronic cloud.

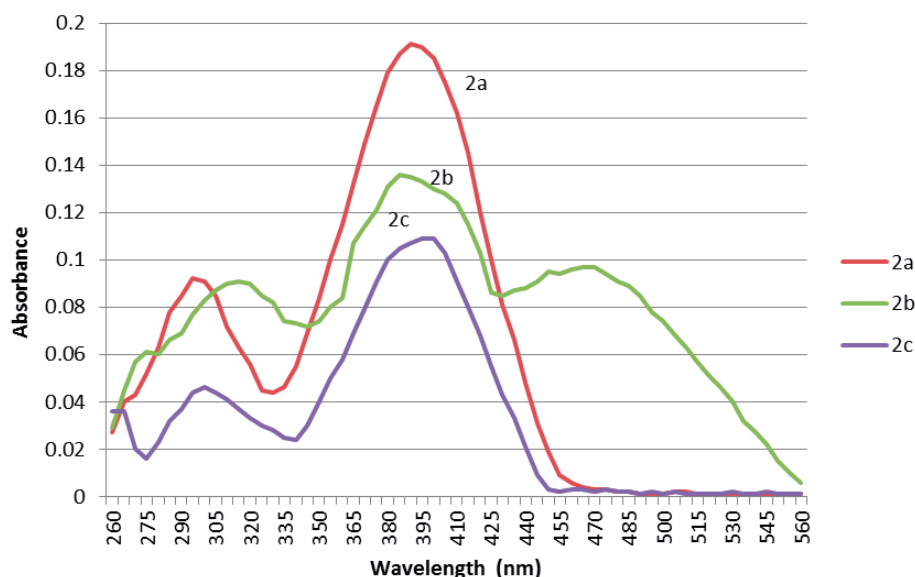
Optical studies of synthesized compounds include the maximum absorption wavelength ( $\lambda_{\text{max}}^{\text{abs}}$ , nm), maximum emission wavelength ( $\lambda_{\text{max}}^{\text{emis}}$ , nm), Stokes shift ( $\Delta\lambda$ , nm) and singlet energy ( $E_s$ , Kcal/mol). The absorption and emission spectra have been recorded in dichloromethane. The absorption and emission data have been summarized in **Table 1**.

**Table 1.** The maximum absorption wavelength ( $\lambda_{\text{max}}^{\text{abs}}$ ), maximum emission wavelength ( $\lambda_{\text{max}}^{\text{emis}}$ ), Stokes shift ( $\Delta\lambda$ ) and singlet energy ( $E_s$ )

Compounds	$\lambda_{\text{max}}^{\text{abs}}$ (nm)	$\lambda_{\text{max}}^{\text{emis}}$ (nm)	$\Delta\lambda$ (nm)	$E_s$ (Kcal/mol)
<b>2a</b>	295 390	486.4	96.4	58.78
<b>2b</b>	315 385 470	---	---	---
<b>2c</b>	300 400	479.6	79.6	59.61

The absorption spectra of compounds **2a** and **2c** revealed that there are two absorption peaks while compound **2b** has three absorption peaks. These absorption maxima have been attributed to  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  electronic transitions. The first absorption maxima appeared at 295 nm and 300 nm, and second absorption maxima appeared at 390 nm and 400 nm for compounds **2a** and **2c**, respectively (**Table 1**). The first absorption maxima at lower wavelength is of low intensity and second absorption maxima is of higher intensity (**Figure 1**). Introduction of electron donating group *i.e.* methoxy group at the 4'-position has shifted the both absorption maxima slightly towards the longer wavelength. It is suggested that the lone pairs of oxygen atom of methoxy group are delocalized over the chromophore and thus extended the conjugation.

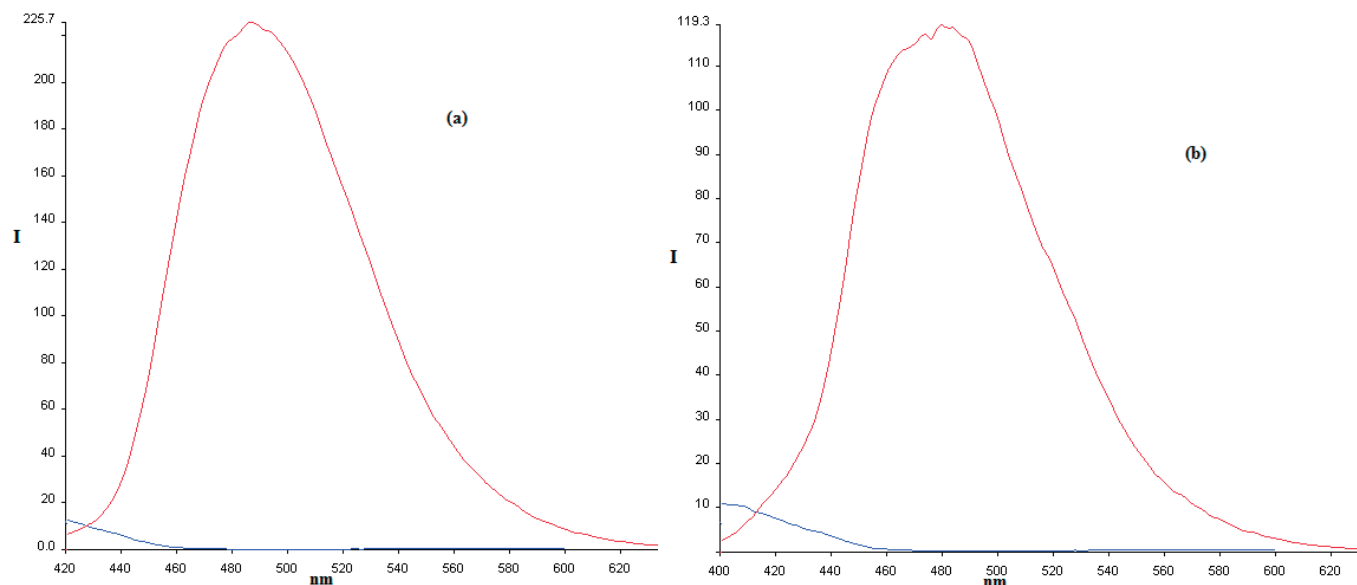
For compound **2b**, three absorption maxima have been observed (*i.e.* at 315, 385 and 470 nm) and absorption maxima have shifted towards the longer wavelength as compared to **2a** and **2c** (**Figure 1**). The order of bathochromicity of these chromophores is **2b** > **2c** > **2a**. The red shift in absorption maxima for compound **2b** is attributed to the enhancement of conjugation due to  $-\text{NO}_2$  group at 4' position that is a strong electron withdrawing group. It is postulated that appearance three peaks is attributed to distortions in the  $\pi$ -extended system of **2b** in the excited state. The multippeak profile of the chromophores has been explained in the literature as well.<sup>14,15</sup>



**Figure 1.** The absorption spectra of compounds (**2a-2c**)

The compounds **2a** and **2c** have exhibited emission maxima at 486.4 nm and 479.6 nm, respectively. It is observed from the emission analysis that the compound **2b** containing nitro group is non-fluorescent. The methoxy group in the compound **2c** has found to show no good effect on emission, and intensity of emission has decreased (**Figure 2**).<sup>16</sup> The red shift of absorption maxima showed that compound **2c** have

poor transparency. It is suggested that the increased intermolecular electrostatic interactions among the chromophores due to the presence of certain groups and poor transparency are responsible for the enhancement of scattering-induced optical loss.<sup>17</sup>



**Figure 2.** (a) Emission spectrum of compound **2a** (b) Emission spectrum of compound **2c**

Excited Singlet Energy  $E_s$  was calculated using the following equation (1).<sup>18</sup>

$$E_s = h.c/(\lambda_{max}^{emis}) \quad (1)$$

Where,  $h$  is the Planck constant,  $c$  is the speed of light, and  $\lambda_{max}^{emis}$  is the maximum emission wavelength. The compounds **2a** and **2c** have exhibited the moderate values of Stokes shift. These values exhibit geometrical differences between the excited state and the ground state.<sup>19</sup>

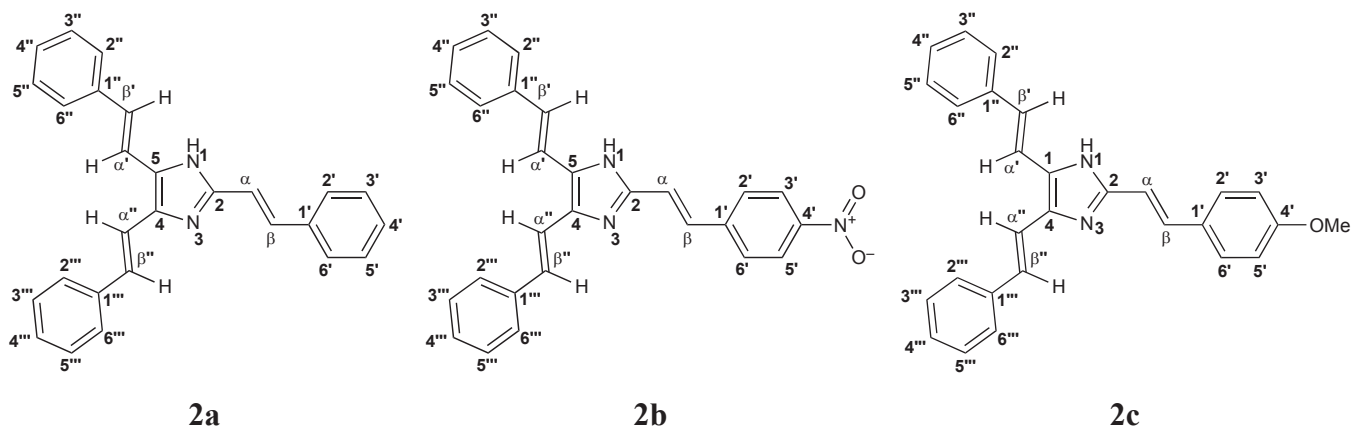
In conclusion, a novel series of 2,4,5-tri(arylethenyl)-1*H*-imidazoles has been designed and synthesized via three component condensation reaction. The absorption measurement showed that compounds have large  $\pi$ -extended framework. The chromophores **2a** and **2c** have exhibited two absorption maxima while chromophore **2b** has shown three absorption maxima. The emission analysis revealed that the compounds **2a** and **2c** have maximum emission wavelength in the blue region. The compound **2b** did not show the fluorescence. The fluorophore **2a** and **2c** have moderate values of Stokes shift which reveals the benefits of better spectral resolution in emission based studies. This study gives a comprehensive glance of the effect of substituents and structural modification on the optical properties of chromophores. This study has prompted us to synthesize more  $\pi$ -extended Y-shaped imidazoles. We wish to present the more promising fluorophores in near future.

## EXPERIMENTAL

The compound 1,6-diphenyl-1,5-hexadiene-3,4-dione (**1**) was prepared according to method available in literature.<sup>20</sup> All the solvents used are of analytical grade and used as such. However, they were distilled under vacuum when required. Cinnamaldehyde was obtained from Fluka (Steinheim, Germany). *Trans*-4-methoxycinnamaldehyde was purchased from Acros Organics (New Jersey, USA). 4-Nitrocinnamaldehyde was purchased from Alfa Aesar (Karlsruhe, Germany). Thin layer chromatography was carried with silica gel 60F<sub>254</sub> (Merck, Darmstadt, Germany). Melting points were taken on Gallenkamp melting point apparatus and are uncorrected.

Fourier transform infrared spectra were taken on Agilent Technologies Carry 630 FTIR. Mass spectra were obtained from JOEL JMS 600H, EI-positive mode. UV-vis spectral data was collected from PerkinElmer T90-UV/VIS Spectrometer. Emission maxima were obtained from PerkinElmer LS 45 Fluorescence Spectrometer. <sup>1</sup>H NMR spectra were recorded on Avance AV-500 spectrometer. <sup>13</sup>C NMR spectrum of **2a** was taken on 75 MHz, Avance AV-300 spectrometer and <sup>13</sup>C NMR spectra of **2b** and **2c** were recorded on 100 MHz, Avance 400 spectrometer, using TMS as internal standard. Elemental analysis was done by LECO CHN 628.

**General Procedure for the Synthesis of 2,4,5-Tri(arylethenyl)-1H-imidazoles (2a-2c).** A mixture of 1,6-diphenyl-1,5-hexadiene-3,4-dione (524 mg, 2 mmol), appropriate cinnamaldehyde (2 mmol) and ammonium acetate (308 mg, 4 mmol) was added in glacial acetic acid (50 mL). The reaction mixture was heated at reflux. The completion of reaction was monitored through TLC. The reaction mixture was stayed overnight and precipitates appeared. The crude product was filtered and dried. Recrystallization was carried in mixture of MeOH and DMF.



**Figure 3.** Newly-synthesized Y-shaped imidazoles

**2,4,5-Tristyryl-1H-imidazole (2a):** The compound **2a** (**Figure 3**) was synthesized by heating a mixture of 1,6-diphenyl-1,5-hexadiene-3,4-dione (524 mg, 2 mmol), cinnamaldehyde (264 mg, 2 mmol),

ammonium acetate (308 mg, 4 mmol) at reflux in AcOH for 6 h. Yield: 0.622 g, 74%. mp 220 °C. IR $\text{cm}^{-1}$ : 3340 [-N-H *str*], 3019, 2920 [=C-H *str* of phenyl and vinyl group], 1586 [-C=N *str*], 1534, 1490 [-C=C *str*], 1284 [-C-N *str*]. EI-MS *m/z*: 374.3 M<sup>+</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/TMS)  $\delta$ : 7.515 (d, 2'-H, 6''-H, 2'''-H, 6'''-H, *J* = 7.5 Hz), 7.462-7.491 (m, 4'-H, 2'-H, 6'-H), Two merged doublets appearing as a triplet [7.356 (d, 3''-H, 5''-H or 3'''-H, 5'''-H, *J* = 7.5 Hz), 7.341 (d, 3''-H, 5''-H or 3'''-H, 5'''-H, *J* = 7.5 Hz)], 7.252-7.300 (m, 3'-H, 5'-H, vinyl 1H, 4''-H, 4'''-H), 7.185 (d, two vinyl protons, *J* = 15.5 Hz), 7.069 (d, two vinyl protons, *J* = 16 Hz), 6.996 (d, vinyl 1H, *J* = 16.5 Hz). <sup>13</sup>C NMR [75 MHz, CDCl<sub>3</sub>/TMS]  $\delta$ : 137.195 [2-C], 134.686, 134.569, 133.999, 133.736, 133.079, 128.692, 128.692, 127.716, 126.488, 114.320 [carbons of phenyl, vinyl & imidazole]. Anal. Calcd for C<sub>27</sub>H<sub>22</sub>N<sub>2</sub>: C, 86.63; H, 5.88; N, 7.49. Found: C, 86.61; H, 5.92; N, 7.48.

**2-(4-Nitrostyryl)-4,5-bis[2-(phenyl)ethenyl]-1H-imidazole (2b):** The compound **2b** (Figure 3) was obtained by heating following: 1,6-diphenyl-1,5-hexadiene-3,4-dione (524 mg, 2 mmol), *p*-nitrocinnamaldehyde (354 mg, 2 mmol), ammonium acetate (308 mg, 4 mmol) at reflux in AcOH for 5 h. Yield: 0.65 g, 77%. mp 258-260 °C. IR $\text{cm}^{-1}$ : 3300 [-N-H *str*], 3029, 2924 [=C-H *str* of aryl & vinyl], 1626, 1498 [-C=N *str*], 1584, 1498 [-C=C *str*], 1321 [-NO<sub>2</sub> *str*]. EI-MS *m/z*: 419.1 M<sup>+</sup>. <sup>1</sup>H NMR (500 MHz, *d*<sub>6</sub>-DMSO/TMS)  $\delta$ : 12.622 [s, N-H], 8.247 [d, 3'-H, 5'-H, *J* = 9 Hz], 7.888 [d, 2'-H, 6'-H, *J* = 9 Hz], 7.684 [d, 2''-H, 6''-H, 2'''-H, 6'''-H, *J* = 7.5 Hz], 7.622-7.558 [m, three vinyl protons], 7.401-7.374 [m, 3''-H, 5''-H, 3'''-H, 5'''-H], 7.305-7.119 [m, three vinyl protons 4''-H, 4'''-H]. <sup>13</sup>C NMR [100 MHz, CDCl<sub>3</sub>/TMS]  $\delta$ : 136.863 [4'-NO<sub>2</sub> or 2-C], 135.603, 135.353, 132.774, 128.999, 128.886, 128.768, 128.173, 127.964, 126.834, 126.706, 124.244, 118.37, 117.445, 115.393 [carbons of phenyl, vinyl & imidazole nucleus]. Anal. Calcd for C<sub>27</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>: C, 77.33; H, 5.01; N, 10.02; O, 7.64. Found: C, 77.30; H, 5.05; N, 10.0; O, 7.65.

**2-(4-Methoxystyryl)-4,5-bis[2-(phenyl)ethenyl]-1H-imidazole (2c):** The compound **2c** (Figure 3) was synthesized by heating a mixture of 1,6-diphenyl-1,5-hexadiene-3,4-dione (0.524 g, 2 mmol), *p*-methoxycinnamaldehyde (0.264 g, 2 mmol) and ammonium acetate (0.308 g, 4 mmol) at reflux in AcOH for 6 h. Yield: 0.59 g, 73%. mp 164 °C. IR $\text{cm}^{-1}$ : 3192 [-N-H *str*], 3030, 2920, 2831 [C-H *str*], 1649 [-C=N *str*], 1595, 1505 [-C=C *str*], 1240 [-C-N *str*]. EI-MS *m/z*: 404.1 M<sup>+</sup>. <sup>1</sup>H NMR (500 MHz, *d*<sub>6</sub>-DMSO/TMS)  $\delta$ : 12.318 [s, N-H], 7.672-7.661 [m, 2''-H, 6''-H, 2'''-H, 6'''-H], 7.577-7.526 [m, merged doublets 7.568 (d, 2'-H, 6'-H, *J* = 9 Hz) & 7.542 (d, vinyl 2H, *J* = 16.5 Hz)], 7.461 [d, vinyl 1H, *J* = 16.5 Hz], 7.37 [m, 3''-H, 5''-H, 3'''-H, 5'''-H], 7.247 [m, 4''-H, 4'''-H, vinyl 1H], 7.053 [d, vinyl 1H, *J* = 16 Hz], 6.986 [d, 3'-H, 5'-H, *J* = 8.5 Hz], 6.883 [d, vinyl 1H, *J* = 16.5 Hz], 3.792 [s, 3H of -OCH<sub>3</sub>]. <sup>13</sup>C NMR [100 MHz, CDCl<sub>3</sub>/TMS]  $\delta$ : 175.32 [4'-OCH<sub>3</sub>], 136.799 [2-C], 129.042, 128.743, 127.983, 126.588, 114.083 [carbons of phenyl, vinyl & imidazole nucleus], 55.255 [carbon of -OCH<sub>3</sub>]. Anal. Calcd for C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>O: C, 83.17; H, 5.94; N, 6.93; O, 3.96. Found: C, 83.15; H, 5.93; N, 6.94; O, 3.98.

## REFERENCES

1. J. A. H. Munoz, J. J. Junior, and F. M. da Silva, *Curr. Org. Synth.*, 2014, **11**, 824.
2. R. Bansal, P. K. Soni, M. K. Ahirwar, and A. K. Halve, *Int. Res. J. Pure Appl. Chem.*, 2016, **11**, 1.
3. D. H. Romero, V. E. T. Heredia, O. García-Barradas, M. Márquez López, and E. S. Pavón, *J. Chem. Biochem.*, 2014, **2**, 45.
4. L. D. Luca, *Curr. Med. Chem.*, 2006, **13**, 1.
5. K. Shalini, P. K. Sharma, and N. Kumar, *Der Chemica Sinica*, 2010, **1**, 36.
6. S. Basu, *Ind. Eng. Chem. Prod. Res. Dev.*, 1984, **23**, 183.
7. S. R. Marder, *Chem. Commun.*, 2006, 131.
8. Y.-W. Han, H. Sugiyama, and Y. Harada, *Biomater. Sci.*, 2016, **4**, 391.
9. Y. Zhu, L. Xiao, M. Zhao, J. Zhou, Q. Zhang, H. Wang, S. Li, H. Zhou, J. Wu, and Y. Tian, *BioMed Res. Int.*, 2015, **2015**, 1.
10. A. O. Eseola, W. Li, W.-H. Sun, M. Zhang, L. Xiao, and J. A. O. Woods, *Dyes Pigm.*, 2011, **88**, 262.
11. L. Zhao, S. B. Li, G. A. Wen, B. Peng, and W. Huang, *Mater. Chem. Phys.*, 2006, **100**, 460.
12. J. Ren, S.-M. Wang, L.-F. Wu, Z.-X. Xu, and B.-H. Dong, *Dyes Pigm.*, 2008, **76**, 310.
13. P. Navamani, P. Loganayaki, K. Jayamoorthy, and N. Sirinivasan, *Silicon.*, 2018, **10**, 1045.
14. Y.-F. Sun, Z.-Y. Chen, L. Zhu, S.-H. Xu, R.-T. Wu, and Y.-P. Cui, *Color. Technol.*, 2013, **129**, 165.
15. G. Ozturk, D. Karakas, F. Karadag, G. Ozturk, and C. Yorgun, *J. Fluoresc.*, 2012, **22**, 1159.
16. Z. Ghasemi and Z. Fathi, *Res. Chem. Intermed.*, 2017, **43**, 3131.
17. Z. Lei, W. Shi-min, X. Zu-xun, Z. Sheng-li, W. Chong-hao, and C. Shi-yuan, *Chem. Res. Chinese U.*, 2003, **19**, 28.
18. U. Doğru, G. Ö. Ürüt, and D. Bayramin, *J. Lumin.*, 2015, **163**, 32.
19. J. Jayabharathi, V. Thanikachalam, K. B. Devi, and N. Srinivasan, *Spectrochim. Acta, A. Mol. Biomol. Spectrosc.*, 2011, **82**, 513.
20. E. C. Constable, M. J. Hannon, and D. R. Smitha, *Tetrahedron Lett.*, 1994, **35**, 6657.