Tetrahedron Letters 51 (2010) 3575–3579

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Photochromism of new diarylethenes bearing both thiazole and benzene moieties

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ARTICLE INFO

Article history:
Received 30 March 2010
Revised 4 May 2010
Accepted 5 May 2010
Available online 8 May 2010

Keywords:
Photochromism
Diarylethene
Thiazole and benzene moieties

ABSTRACT

A new class of photochromic diarylethenes bearing both thiazole and benzene moieties has been developed, and the effects of substitution on their properties, including photochromism, fatigue resistance, and fluorescence properties have been investigated. They exhibited good photochromism and functioned as a fluorescence switch upon alternating irradiation with UV and visible light both in solution and in PMMA film. The electron-donating substituents could significantly enhance the cyclization quantum yield and depress the cycloreversion quantum yield whereas the electron-withdrawing groups functionalized an inverse action for these diarylethene derivatives. Relatively big differences exist among the properties of these diarylethenes which may be attributed to the different substituent effects.

There has been considerable interest in photochromic compounds because of their potential ability for optical memories, photo switches, and display devices.[1] During the past several decades, photochromic diarylethenes have been extensively explored for optoelectric applications because of their high conversion efficiency in reversible photochromic reactions, excellent thermal stability of both isomers, and remarkable fatigue resistance.[2] Upon photoirradiation, diarylethene derivatives can undergo photochromic cyclization/cycloreversion reactions either in solution or in the solid state. The reversible photochromic cyclization/cycloreversion reactions can lead to changes in their absorption spectra and other characteristics such as fluorescence, oxidation/reduction potentials, refractive indices, etc.[3] The most important difference is that the π-systems of two aryl rings are separated in the open-ring isomer, while the π-conjugation is delocalized throughout the molecule in the closed-ring isomer.[4] Till now, most of diarylethene compounds colored in magenta or cyan have been well studied, yellow color photochromic diarylethene derivatives are more less than them.[5]

Theoretical consideration based on a molecular orbital theory revealed that the thermal stability of both isomers of the diarylethene compounds can be improved by introducing aryl groups that have low aromatic stabilization energy,[6] and it was demonstrated by the synthesis of diarylethenes with various types of aryl groups.[7] When the aryl groups are thiophene or benzothiophene rings that have low aromatic stabilization energy, the closed-ring isomers are thermally stable and do not return to the open-ring isomers in the dark.[6b] Maybe for this reason, among diarylethenes hitherto reported, most of the heteroaryl moieties have been thiophene or benzothiophene rings, with just a few reports concerning other heteroaryl moieties such as furan,[8] indene,[9] indole,[10] benzofuran,[11] pyrrole,[12] pyrazole,[13] etc. Thiazole is a heterocyclic ring which has low aromatic stabilization energy,[6b] and its structure is similar to that of thiophene and pyrrole. Therefore, introduction of a thiazole ring into the heteroaryl moieties of diarylethene derivatives can be expected to undergo excellent photochromic reactions.

Up to date, there are a few examples of photochromic diarylethene derivatives bearing thiazole rings. Irie et al. reported a series of diarylethenes bearing thiazole rings. They demonstrated that thiazole moieties could significantly shift the λ_{max} of the closed-ring isomer to shorter wavelengths.[6b,14] Hasegawa and Kawai and co-workers developed a new type of photochromic terarylene system bearing thiazole rings and elucidated some special properties of these derivatives.[15] Tanaka et al. synthesized some bis(thiazolyl)ethene derivatives and revealed their good thermal stability.[16] From these reports, it can be easily concluded that the hexatriene backbone of all photochromic systems having thiazole moieties is composed of five-membered heterocyclic rings or a combination of a five-membered aryl ring and a vinyl group. The results have contributed to a broad understanding of the effects of thiazole rings on the properties of photochromic diarylethenes, and they have also given us valuable insight to design some new photochromic diarylethene systems. To the best of our knowledge, photochromic hybrid diarylethene derivatives bearing both thiazole and six-membered moieties have not hitherto been reported.

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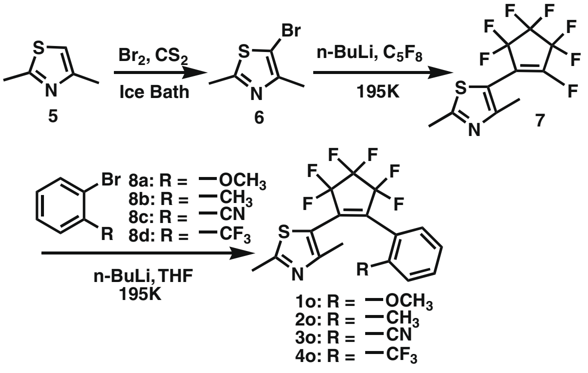
doi:10.1016/j.tetlet.2010.05.004

In this Letter, we designed a new class of diarylethenes bearing both thiazole and benzene moieties. The synthesized diarylethenes are 1-(2,4-dimethyl-5-thiazolyl)-2-(2-methoxyphenyl)perfluorocyclopentene (**1o**), 1-(2,4-dimethyl-5-thiazolyl)-2-(2-methylphenyl)perfluorocyclo-pentene (**2o**), 1-(2,4-dimethyl-5-thiazolyl)-2-(2-cyanophenyl)perfluorocyclopentene (**3o**), and 1-(2,4-dimethyl-5-thiazolyl)-2-(2-trifluoromethylphenyl)perfluorocyclopentene (**4o**). All of these diarylethene derivatives showed good photochromism both in solution and in PMMA amorphous film. The photochromic scheme of **1o**–**4o** is shown in Scheme 1.

The synthetic route for diarylethenes **1o**–**4o** is shown in Scheme 2. First, compound **6** was prepared in 80% yield by brominating compound **5** in carbon disulfide at 0 °C. Lithiation of compound **6** followed by the addition of excess octafluorocyclopentene generated compound **7** in 44% yield at −78 °C. Finally, compounds **8a**–**d** were separately lithiated and then coupled with **7** to give diarylethenes **1o**–**4o**. The structures of **1o**–**4o** were confirmed by elemental analysis, NMR, and IR.[17]

Diarylethenes **1**–**4** showed good photochromism and could be toggled between the colorless open-ring isomers (**1o**–**4o**) and the colored closed-ring isomers (**1c**–**4c**) by alternating irradiation with UV light and appropriate wavelength visible light both in hexane and in PMMA film. The absorption spectral change of diarylethene **1** and the color changes of diarylethenes **1**–**4** are shown in Figure 1. The absorption maximum of diarylethene **1o** was observed at 294 nm in hexane (ε, 1.08×10^4 L mol^{-1} cm^{-1}), which arose from $\pi \rightarrow \pi^*$ transition.[18] Upon irradiation with 297 nm light, the colorless solution of **1o** turned yellow, in which the absorption maximum was observed at 469 nm (ε, 2.51×10^3 L mol^{-1} cm^{-1}). The yellow color was due to the formation of the closed-ring isomer **1c**. Alternatively, the yellow solution turned colorless upon irradiation with visible light (λ >400 nm) because **1c** reverted to the initial state **1o**. As with diarylethene **1**, compounds **2–4** also show good photochromism in hexane. Their color changes upon photoirradiation are shown in Figure 1B. When arriving at the photostationary state, the absorption maxima of diarylethenes **2–4** appeared at 449, 441, and 444 nm, respectively. In PMMA films, diarylethenes **1**–**4** showed similar photochromism as in hexane. Compared to those in hexane, the absorption maxima of both the open-ring and the closed-ring isomers of diarylethenes **1**–**4** in PMMA films are at longer wavelengths. The red-shift phenomena may be attributed to the polar effect of the polymer matrix and the stabilization of molecular arrangement in solid medium.[19] The absorption spectral parameters of these compounds are summarized in Table 1.



Scheme 2. Synthesis of diarylethenes **1o**–**4o**.

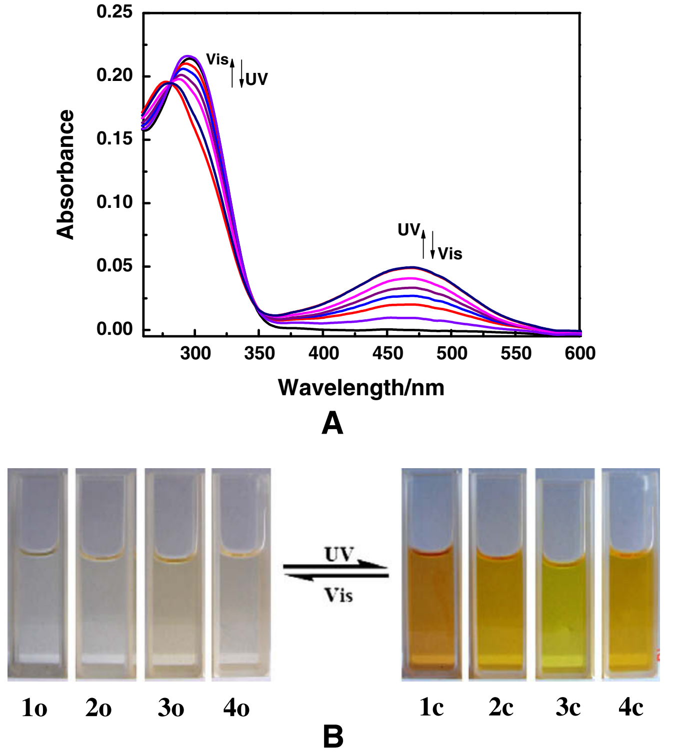
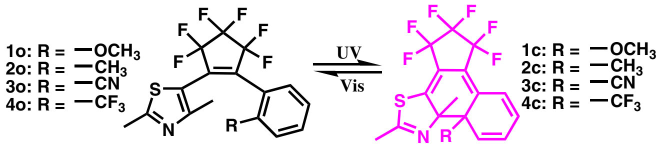


Figure 1. Absorption spectral changes of diarylethene **1** (A) and the color changes of diarylethenes **1**–**4** (B) by photoirradiation in hexane (2.0×10^{-5} mol L^{-1}) at room temperature.



Scheme 1. Photochromism of diarylethenes **1o**–**4o**.

The cyclization and cycloreversion quantum yields of diarylethenes **1–4** were measured in hexane at room temperature, and the results are also summarized in Table 1. The results indicated that different substituents at 2-position of the benzene ring had a significant effect on the photochromic features of diarylethenes **1–4**, including the absorption maxima, molar absorption coefficients, and quantum yields. The absorption maxima of **1c**–**4c** showed a notable red-shift with the increase in electron-donating ability both in hexane and in PMMA film. On the one hand, the absorption maximum of **1c** was much longer than that of **2c**, as a result of the electron-donating ability of methoxy group which was larger than that of the methyl group.[4a,20] The molar absorption coefficients of diarylethenes bearing an electron-donating substituent (methoxy or methyl group such as in compound **1c** or **2c**) were much larger than those of compounds bearing an electron-withdrawing group (cyano or trifluoromethyl group such as in compound **3c** or **4c**). The cyclization quantum yields enhanced significantly when the electron-donating groups were substituted at the 2-position of the benzene ring of these diarylethenes, while the cycloreversion quantum yields were improved when the electron-withdrawing groups were substituted at the same position. Therefore, the cyclization quantum yields of diarylethenes **1** and **2** bearing electron-donating groups were higher than those of diarylethenes **3** and **4** bearing electron-withdrawing groups, but a reverse case for the cycloreversion quantum yields. This indicated that the electron-donating substituents could significantly enhance the cyclization quantum yield and depress the cycloreversion quantum yield, while the electron-withdrawing groups functionalized an inverse

Table 1
Absorption spectral properties of diarylethenes **1–4** in hexane (2.0×10^{-5} mol L^{-1}) and in PMMA film (10% w/w) at room temperature

Compound	$\lambda_{o,max}$/nm[a] (ε/L mol^{-1} cm^{-1})		$\lambda_{c,max}$/nm[b] (ε/L mol^{-1} cm^{-1})		Φ[c]	
	Hexane	PMMA	Hexane	PMMA	Φ_{o-c}	Φ_{c-o}
1	294(1.08×10^4)	304	469(2.51×10^3)	472	0.46	0.095
2	293(9.28×10^3)	303	449(2.72×10^3)	462	0.42	0.052
3	307(8.72×10^3)	308	441(2.27×10^3)	446	0.37	0.19
4	296(1.09×10^4)	301	444(2.11×10^3)	445	0.35	0.16

[a] The maximum absorption peak of the open-ring isomers.
[b] The maximum absorption peak of the closed-ring isomers.
[c] Quantum yields of cyclization (Φ_{o-c}) and cycloreversion (Φ_{c-o}), respectively.

action for these diarylethene derivatives. The result is contrary to that of diarylethenes bearing both thiophene and benzene moieties.[21] When replacing the thiazole moiety with the thiophene unit, the molar absorption coefficients and the absorption maxima increased significantly, but the changing trends of the cyclization and cycloreversion quantum yields are reversed compared with thiazole moiety.[21] On the side, the photochromic features of diarylethenes **1**–**4** were also remarkably different from those of other diarylethenes bearing a thiazole unit when replacing the benzene ring with other groups.[14,22] Compared to the symmetrical/unsymmetrical analogs bearing thiazole ring(s),[6b] the cyclization/cycloreversion quantum yields of **1**–**4** are greater, but the molar absorption coefficients of their closed-ring isomers are much lower. Compared to those bearing two six-membered rings,[23] the photochromic features of **1**–**4** are much more excellent.

Fatigue-resistant property, that is, how many times photocyclization and cycloreversion reaction cycles can be repeated without loss of performance,[2a,12b] is a very important factor for practical applications in optical devices.[2a,c] The fatigue resistances of diarylethenes **1**–**4** were tested both in hexane and in PMMA films by alternatively irradiating with UV and visible light in air at room temperature. The fatigue resistance of diarylethene **1** is shown in Figure 2. In hexane, 88% of **1c** was destroyed after 10 repeat cycles, which may be attributed to degradation resulting from the formation of an epoxide.[24] However, its fatigue resistance in PMMA film is much stronger than that in hexane. After 10 repeat cycles, diarylethene **1** still showed good photochromism with only ca. 28% degradation of **1c** in PMMA film. Similarly, the fatigue resistances of diarylethenes **2–4** in PMMA films are also much stronger than those in solution. After 10 repeat cycles, they showed good photochromism with only ca. 17% degradation of **2c**, 6% of **3c**, and 5% of **4c**, respectively. But, the degradation percents of diarylethenes **2–4** in hexane are 71% of **2c**, 53% of **3c**, and 39% of **4c**, respectively. This remarkable improvement may result from effectively suppressing the oxygen diffusion in the solid medium.[2a] In addition, the fatigue resistances of diarylethenes with an electron-withdrawing group (such as in diarylethenes **3** and **4**) are much better than those of diarylethenes with an electron-donating group (such as in diarylethenes **1** and **2**) both in hexane and in PMMA films. The result is well in agreement with that reported for analogs bearing both thiophene and benzene moieties, where fatigue resistance markedly increased with the increase of electron-withdrawing ability.[21]

The fluorescence spectra of diarylethenes **1o**–**4o** both in solution (2.0×10^{-5} mol/L) and in PMMA amorphous films (10% w/w) were measured at room temperature. In hexane, the emission peaks of **1o**–**4o** were observed at 463, 452, 476, and 457 nm when excited at 397 nm (Fig. 3). In PMMA films, the emission peaks of diarylethenes **1o**–**4o** were observed at 465, 465, 487, and 465 nm when excited at 395 nm. Compared to those in hexane, the emission peaks of diarylethenes **1o**–**4o** showed a bathochromic shift in PMMA film consistently across their maxima absorption wavelengths with values of 2 nm for **1**, 13 nm for **2**, 11 nm for **3**, and 8 nm for **4**. Among compounds **1o**–**4o**, the emission intensity of **2o** is the strongest and that of **4o** is the smallest in hexane, however, the emission peak of **3o** is at the lowest energy both in hexane and in PMMA film. The result suggested that different substituents attached at the 2-position of the benzene ring had a significant effect not only on the emission peak but also on the emission intensity.

As has been observed for most of the reported diarylethenes,[25] diarylethenes **1**–**4** exhibited a very good fluorescent switch on changing from the open-ring isomers to the closed-ring isomers by photoirradiation both in hexane and in PMMA. During the process of photoisomerization, diarylethene **1** exhibited changes in its fluorescence in hexane as shown in Figure 4. Upon irradiation with 313 nm UV light, the photocyclization reaction was carried out and the non-fluorescent closed-ring isomer **1c** was produced. Back irradiation of the appropriate wavelength of visible light regenerated the open-ring isomer **1o** and duplicated the original emission spectra. When arriving at the photostationary state, the emission inten-

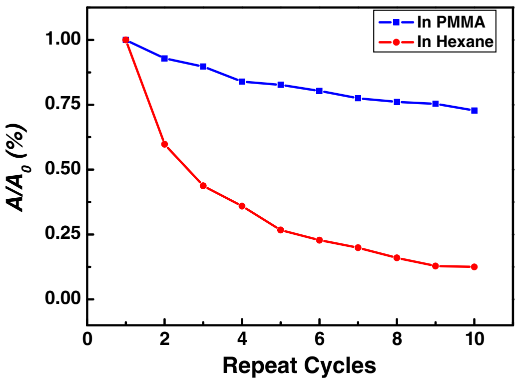


Figure 2. Fatigue resistance of diarylethene **1** in hexane and in PMMA film in air atmosphere at room temperature. Initial absorptance of the sample was fixed to 1.0.

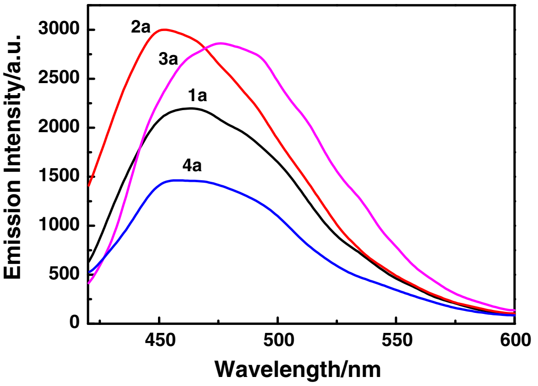


Figure 3. Fluorescence emission spectra of diarylethenes **1–4** in hexane (2.0×10^{-5} mol L^{-1}) at room temperature when excited at 397 nm.

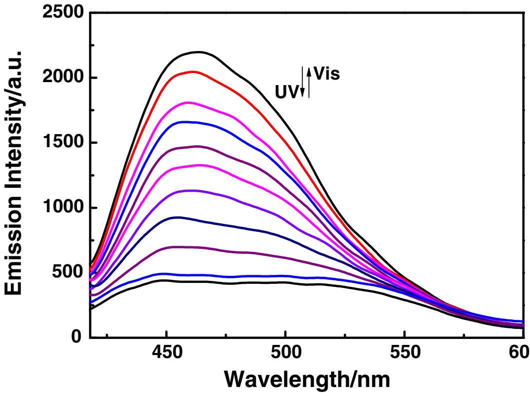


Figure 4. Change in the intensity of the fluorescence spectra of diarylethene **1** in hexane (2.0×10^{-5} mol L^{-1}) upon photoirradiation.

sity of diarylethene **1** was quenched to ca. 20% in hexane and ca. 27% in PMMA film. Similarly, diarylethenes **2**–**4** also functioned as a good fluorescent switch upon photoirradiation both in hexane and in PMMA films. In the photostationary state, their emission intensities were quenched to ca. 36% for **2**, 37% for **3**, and 39% for **4** in hexane and ca. 51% for **2**, 47% for **3**, and 58% for **4** in PMMA films. The result showed that the fluorescent modulation efficiencies of diarylethenes **1**–**4** in hexane were much higher than those in PMMA film. The result is also contrary to that reported for diarylethenes bearing both thiophene and benzene moieties, where the fluorescent modulation efficiencies in hexane were much lower than those in PMMA film.[21] The incomplete cyclization reaction and the existence of parallel conformations with relatively strong fluorescence may be the main cause for the lower fluorescent conversion.[26] Among diarylethenes **1**–**4**, diarylethene **1** showed the highest fluorescent modulation efficiency both in solution and in PMMA film, suggesting that it is the most promising candidate for application on photoswitchable devices such as optical memory and fluorescent modulation switches.[27]

In conclusion, four new unsymmetrical photochromic diarylethenes with both thiazole and benzene moieties have been synthesized and their properties have been investigated. This new photochromic system showed good photochromism and acted as a remarkable fluorescent switch both in solution and in PMMA film. The results indicated that the substituents at 2-position of the benzene ring had a significant effect on the properties of these diarylethene derivatives. Diarylethenes based on thiazole and benzene moieties induced some new characteristics differing from other reported diarylethenes. The results will be helpful for the synthesis of efficient photoactive diarylethene derivatives with new molecular skeletons and to design new photochromic systems for further potential applications.

Acknowledgments

This work was supported by Program for the NSFC of China (20962008), New Century Excellent Talents in University (NCET-08-0702), Project of Jiangxi Youth Scientist, the Key Scientific Project from Education Ministry of China (208069), National Natural Science Foundation of Jiangxi Province (2008GZH0020), and Graduated Research and Innovation Fund of Jiangxi Province.

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17. Data for **1o**: Mp 55–56 °C; Calcd for $C_{17}H_{13}F_6NOS$ (%): Calcd C, 51.91; H, 3.33; N, 3.56. Found C, 51.89; H, 3.37; N, 3.51; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.90 (s, 3H, $-CH_3$), 2.67 (s, 3H, $-CH_3$), 3.60 (s, 3H, $-OCH_3$), 6.88(d, 1H, $J = 8.0$ Hz, benzene-H), 7.03 (t, 1H, $J = 6.0$ Hz, benzene-H), 7.34 (d, 1H, $J = 8.0$ Hz, benzene-H), 87.40(t, 1H, $J = 8.0$ Hz, benzene-H); ^{13}C NMR(100 MHz, $CDCl_3$, ppm): δ 16.12, 19.04, 55.24, 111.48, 116.88, 117.16, 120.96, 129.90, 132.07, 153.36, 157.02, 167.63; IR(KBr, v, cm^{-1}): 707, 760, 790, 831, 864, 985, 1023, 1047, 1073, 1126, 1190, 1271, 1338, 1400, 1438, 1463, 1532, 1630. Data for **2o**: Calcd for $C_{17}H_{13}F_6NS$ (%): Calcd C, 54.11; H, 3.47; N, 3.71. Found C, 54.17; H, 3.50; N, 3.68; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.96 (s, 3H, $-CH_3$), 1.99 (s, 3H, $-CH_3$), 2.53 (s, 3H, $-CH_3$), 7.13 (d, 1H, $J = 8.0$ Hz benzene-H), 7.20 (t, 2H, $J = 6.0$ Hz, benzene-H), 7.25–7.29 (m, 1H, benzene-H); ^{13}C NMR(100 MHz, $CDCl_3$, ppm): δ 16.85, 19.03, 19.55, 116.40, 126.31, 127.02, 129.17, 130.16, 130.95, 136.92, 154.44, 168.42; IR (KBr, v, cm^{-1}): 586, 744, 833, 866, 989, 1072, 1132, 1193, 1276, 1342, 1400, 1456, 1627. Data for **3o**: 77–78 °C; Calcd for $C_{17}H_{10}F_6N_2S$ (%): Calcd C, 52.58; H, 2.60; N, 7.21. Found: C, 52.63; H, 2.57; N, 7.19; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.97 (s, 3H, $-CH_3$), 2.67 (s, 3H, $-CH_3$), 7.62–7.66 (m, 2H, benzene-H), 7.73 (d, 1H, $J = 8.0$ Hz, benzene-H), 7.77 (t, 1H, $J = 8.0$ Hz, benzene-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 16.75, 19.17, 113.23, 115.64, 116.08, 129.93, 130.75, 131.28, 133.30, 134.01, 154.85, 169.74; IR (KBr, v, cm^{-1}): 767, 834, 867, 949, 990, 1036, 1073, 1137, 1199, 1282, 1341, 1399, 1445, 1524, 1624, 1628, 1986, 2232, 2931, 2968, 3197. Data for **4o**: Calcd for $C_{17}H_{10}F_9NS$ (%): Calcd C, 47.34; H, 2.34; N, 3.25. Found: C, 47.39; H, 2.38; N, 3.60; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.23 (s, 3H, $-CH_3$), 2.60 (s, 3H, $-CH_3$), 7.42 (d, 1H, $J = 8.0$ Hz, benzene-H), 7.64–7.70 (m, 2H, benzene-H), 7.76 (d, 1H, $J = 8.0$ Hz, benzene-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.90, 19.21, 115.64, 121.77, 125.20, 127.59, 127.63, 130.63, 131.25, 131.98; IR (KBr, v, cm^{-1}): 727, 771, 800, 834, 865, 950, 991, 1036, 1076, 1139, 1398, 1276, 1315, 1342, 1398, 1446, 1529, 1627, 1629, 2932. Data for **1c**: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.66 (s, 3H, $-CH_3$), 2.35 (s, 3H, $-CH_3$), 3.35 (s, 3H, $-OCH_3$), 5.92 (d, 1H, $J = 8.0$ Hz, benzene-H), 6.09 (t, 1H, $J = 8.0$ Hz, benzene-H), 6.41 (t, 1H, benzene-H), 6.52 (d, 1H, $J = 8.0$ Hz, benzene-H). Data for **2c**: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.25 (s, 3H, $-CH_3$), 1.57 (s, 3H, $-CH_3$), 2.34 (s, 3H, $-CH_3$), 6.15 (d, 1H, $J = 8.0$ Hz, benzene-H), 6.28 (t, 2H, $J = 8.0$ Hz, benzene-H), 6.32 (t, 1H, $J = 8.0$ Hz, benzene-H). Data for **3c**: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.50 (s, 3H, $-CH_3$), 2.45 (s, 3H, $-CH_3$), 6.20–6.28 (m, 2H, benzene-H), 6.54 (d, 1H, benzene-H), 6.58 (t, 1H, $J = 8.0$ Hz, benzene-H). Data for **4c**: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.69 (s, 3H, $-CH_3$), 1.92 (s, 3H, $-CH_3$), 6.07 (d, 1H, $J = 8.0$ Hz, benzene-H), 6.20–6.24 (m, 2H, benzene-H), 6.51 (d, 1H, benzene-H).
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