



New photochromic 1,2-diarylperfluorocyclopentenes bearing unsymmetrical six-membered aryl units

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ABSTRACT

A new class of unsymmetrical photochromic diarylethenes based on the six-membered naphthalene-benzene and naphthalene-pyridine backbones has been firstly developed and their properties have been discussed. The two different six-membered aryl moieties were connected directly to the central cyclopentene ring and available to participate in the photoinduced cyclization reaction. The three diarylethenes exhibit distinctly different photochromism by photoirradiation in solution: they turn red, yellow, and orange upon photocyclization, which may be resulted from the different substituent and six-membered aryl moiety effects. Compared with the analog bearing a benzene unit, diarylethene bearing a pyridine moiety has a shorter absorption maximum and a smaller fluorescent quantum yield, and it shows a dual-addressable photo-switch by photoirradiation and acid/base stimulation.

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Organic photochromic materials have received intense interest due to their potential promising photonic applications in optical data storage and switching devices.¹ Among the various photochromic systems, dithienyl perfluorocyclopentenes are the most representative class of photochromic compounds with thermally irreversible and high fatigue resistance, which have received most attention because they can be potentially applied in optical switches and high-density optical recording materials.^{2,3} So far, many studies concerning the photochromic properties of dithienylethene derivatives have been reported.⁴

For the application to optical recording, it is very important to develop photochromic diarylethenes with different absorption wavelengths, especially the shorter absorption wavelength because the recording capacity is proportional to the recording laser wavelength.⁵ However, among the diarylethenes hitherto reported, most of them have an absorption peak with the region between 550 and 750 nm,⁶ and just a few reports concerning photochromic diarylethenes whose absorption peaks below this wavelength range. Therefore, developing diarylethene derivatives with absorption band around 500 nm or even shorter for making use of short-wavelength optical recording materials is very necessary. One approach to achieve this expected goal is to attach the naphthalene ring to the ethene moiety, for example, the absorption maximum of the closed-ring isomer of diarylethene bearing two naphthalene rings is observed at 471 nm.⁷

Presently, the synthesis of new photochromic diarylethene with different aryl moieties has become an active area of research.

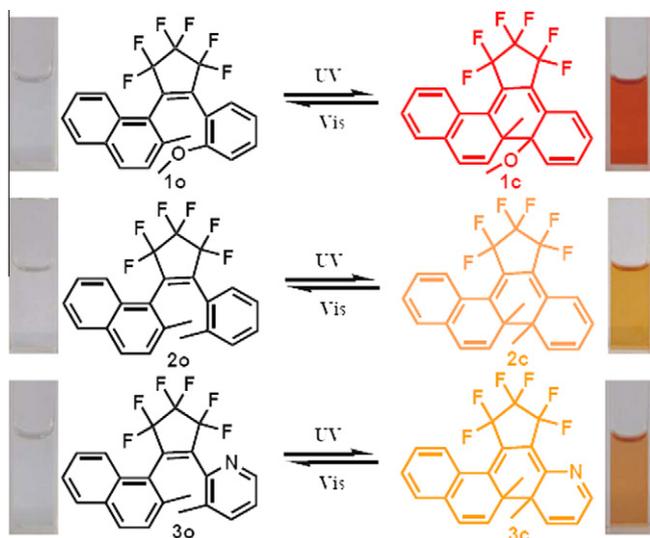
Among the reported diarylethenes, their hexatriene backbones are mainly confined to the five-membered heteroaryl moieties.^{2a,c} In the case of six-membered aryl rings, only a few symmetrical diarylethenes bearing two phenyl/naphthyl groups have been reported.^{7,8} The majority of these derivatives are thermally reversible with poor photochromism. Previously, we reported diarylethenes bearing both naphthalene and thiophene moieties, in which the absorption peak band around 510 nm.⁹ In this Letter, one of the main purposes was to develop a new class of diarylethenes bearing unsymmetrical six-membered aryl units with evident photochromism. The synthesized diarylethenes are 1-(2-methylnaphthyl)-2-(1-methoxyphenyl)perfluorocyclopentene (**1o**), 1-(2-methylnaphthyl)-2-(1-methylphenyl)perfluorocyclopentene (**2o**), and 1-(2-methylnaphthyl)-2-(3-methyl-2-pyridyl)perfluorocyclopentene (**3o**). Each of the diarylethenes exhibited notable photochromism and fluorescent photo-switch in solution; to the best of our knowledge, they are the first examples of photochromic diarylethenes bearing unsymmetrical six-membered aryl moieties. The photochromic scheme and the color changes of diarylethenes **1–3** by photoirradiation are illustrated in Scheme 1.

The synthetic routes for diarylethenes **1o–3o** are shown in Scheme 2. 1-Bromo-2-methoxybenzene, 1-bromo-2-methylbenzene, and 2-bromo-3-methylpyridine were separately lithiated, and then coupled with 2-methyl-1-naphthyl-perfluorocyclopentene **5^o** to give diarylethenes **1o–3o**. The synthetic details were described in Supplementary Information (SI). Their structures were confirmed by elemental analysis, NMR, and IR.¹⁰

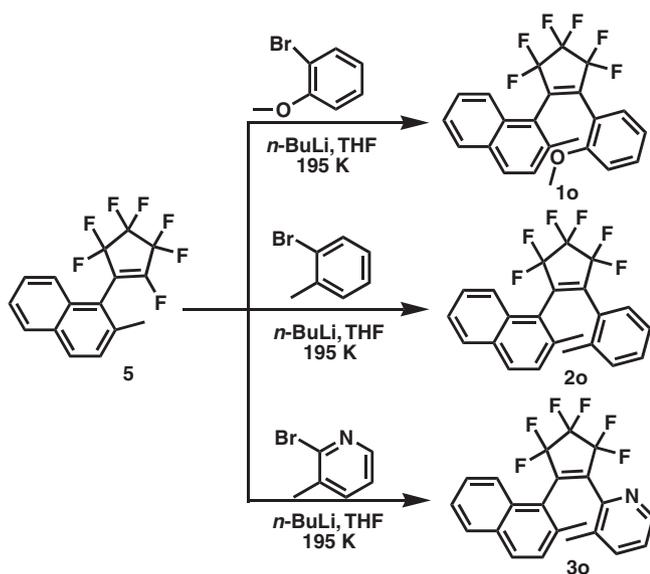
The absorption spectral changes of diarylethenes **1–3** upon alternating irradiation with UV and visible light in hexane (5.0×10^{-5} mol/L) are shown in Figure 1. In hexane, diarylethene

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Scheme 1. Photochromism and the color changes of diarylethenes **1–3** in hexane.



Scheme 2. Synthetic route for diarylethenes **1o–3o**.

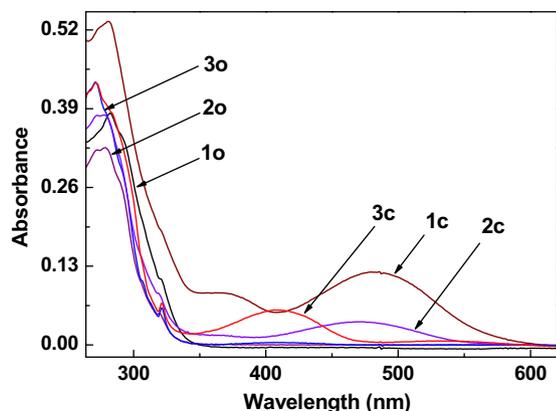


Figure 1. Absorption spectral changes of diarylethenes **1–3** by photoirradiation in hexane (5.0×10^{-5} mol/L) at room temperature.

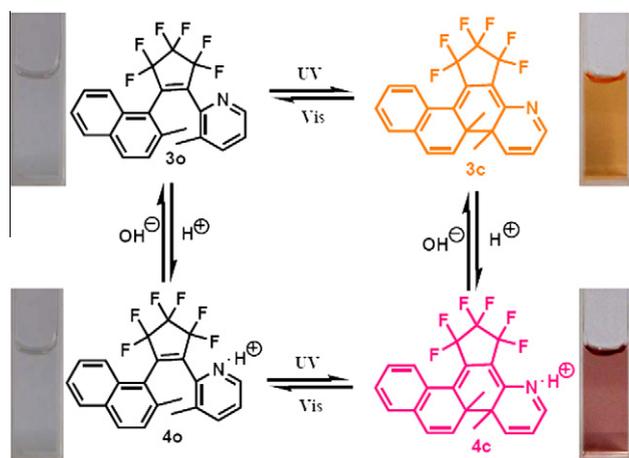
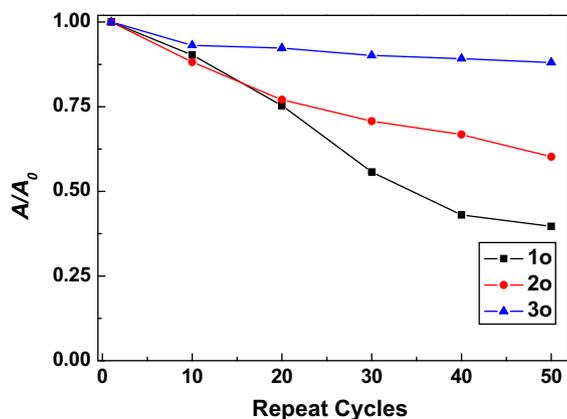
1o exhibited a sharp absorption peak at 280 nm in hexane due to a $\pi \rightarrow \pi^*$ transition.^{4j,11} Upon irradiation with UV light, a new visible absorption band centered at 480 nm, corresponding to the color change of the solution from colorless to red, as a result of the formation of the closed-ring isomer **1c**. The red-colored solution of **1c** can be decolorized completely upon irradiation with visible light ($\lambda > 400$ nm) again, due to the conversion of the compound back to the open-ring isomer **1o**. As with diarylethene **1**, diarylethenes **2**, and **3** also showed photochromism in hexane. Upon irradiation with UV light, the colorless solution of **2o** and **3o** turned to yellow and orange, and their absorption maxima centered at 469 for **2c** and 406 nm for **3c**. The photochromic features of diarylethenes **1–3** in hexane are summarized in Table 1. The absorption maxima of both open- and closed-ring isomers of diarylethene **1** are much longer than those of diarylethene **2**, which may be attributed to the stronger electron-donating ability of methoxy group as compared to a methyl group. Compared with the analogous diarylethene bearing a benzene unit (such as in **1** or **2**), the introduction of pyridine unit (such as in **3**) can be effective to shift the absorption maximum to a shorter wavelength. The cyclization and cycloreversion quantum yields of diarylethenes **1–3** were measured by the reported method.¹² The cyclization quantum yields of diarylethenes **1–3** were determined to be 0.16 for **1**, 0.06 for **2**, and 0.11 for **3**, and the cycloreversion quantum yields were 0.05 for **1**, 0.03 for **2**, and 0.13 for **3**. The result suggests that the photochromic reaction of diarylethene can be effectively modulated by the introduction of the different substituent or six-membered aryl unit. For diarylethenes bearing a benzene unit (**1** and **2**), the cyclization quantum yields are greater than their respective cycloreversion quantum yields. However, the cyclization quantum yield of diarylethene **3** is lower than its cycloreversion quantum yield. Among these derivatives, the cyclization quantum yield of diarylethene **1** is the biggest, and the cycloreversion quantum yield of **3** is the biggest. In addition, the photoconversion ratios of the three diarylethenes were analyzed by HPLC in the photostationary state, with the value of 33% for **1**, 22% for **2**, and 17% for **3**, respectively (Table 1). Compared to the reported analogs,⁹ the photoconversion ratios of the three diarylethenes were significantly decreased in hexane, which may be attributed to the higher aromatic stabilization energy of the six-membered aromatic ring.^{2a}

Furthermore, the switching properties between **3** and **4** bearing a pyridine moiety were also investigated by protonation of **3o** and **3c** with trifluoroacetic acid in acetonitrile (1.3×10^{-3} mol/L) and neutralization of **4o** and **4c** with triethylamine base (7.2×10^{-3} mol/L), respectively. The molecular structural and color changes between **3** and **4** are illustrated in Scheme 3. Addition of trifluoroacetic acid (20 μ L) to the solution of **3o** in acetonitrile produces a protonated diarylethene **4o**, and **4o** can return to **3o** by neutralization with triethylamine base. Similarly, addition of trifluoroacetic acid to the solution of **3c** produced a protonated diarylethene **4c** in photostationary state. As has been observed for the reported diarylethenes,¹³ the yellow solution (**3c**) changed to a reddish one (**4c**) by protonation, and the absorption maximum bathochromic shifted from 444 to 479 nm. The reddish solution of **4c** either returns completely back to orange (**3c**) after neutralization with the amine or gets bleached to colorless (**4o**) upon irradiation with visible light.

The thermal stabilities of the open- and closed-ring isomers of diarylethenes **1–3** were tested in ethanol at room temperature and 371 K, respectively. Storing these solutions in ethanol at room temperature in the dark and then exposing them to air for more than 10 days, no changes in their colors and spectra were observed and, indeed, no decomposition was detected when these derivatives were exposed to air for more than three months. Compared with the reported diarylethenes bearing two benzene ring whose closed-ring isomers gradually return to the open-ring isomers at

Table 1Photochromic parameters of diarylethenes **1–3** in hexane (5.0×10^{-5} mol/L) at room temperature

Compound	$\lambda_{o,max}$ /nm ^a	$\lambda_{c,max}$ /nm ^b	Φ^c		PR/% ^d
	($\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1}$)	($\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1}$)	Φ_{o-c}	Φ_{c-o}	
	Hexane				
1	282 (7.65×10^3)	480 (7.82×10^3)	0.16	0.05	33
2	278 (6.51×10^3)	469 (3.46×10^3)	0.06	0.03	22
3	271 (8.48×10^3)	406 (6.79×10^3)	0.11	0.13	17

^a Absorption maxima of open-ring isomers.^b Absorption maxima of closed-ring isomers.^c Quantum yields of cyclization (Φ_{o-c}) and cycloreversion (Φ_{c-o}), respectively.^d Photoconversion ratios of diarylethenes **1–3** (PR%) in the photostationary state.**Scheme 3.** Structural and color changes between **3o**, **3c**, **4o**, and **4c** in acetonitrile (1.3×10^{-3} mol/L).**Figure 2.** Fatigue resistant characteristics of diarylethenes **1–3** in hexane in air atmosphere at rt. Initial absorbance of the sample was fixed to 1.0.

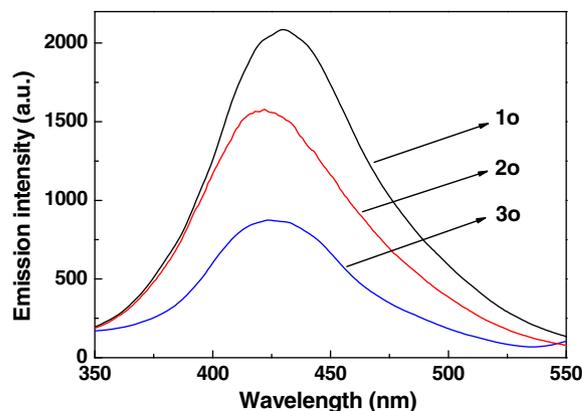
ambient temperature,⁸ the thermal stabilities of diarylethenes **1–3** are very good at room temperature. However, storing these solutions in ethanol at 371 K, the colored solutions of **1c–3c** gradually disappeared after 5 min. Hence the thermal stabilities of diarylethenes **1–3** are relatively weak at high temperature, compared with the reported diarylethenes bearing five-membered aryl moieties,^{2a,14}

Fatigue resistance of photochromic diarylethene is a critical factor for practical applications in optical devices.^{2a,15} As with the reported method,^{2a,16} the fatigue resistant characteristics of diarylethenes **1–3** were measured in hexane by alternating irradiating with UV and visible light in air at room temperature, as

shown in Figure 2. In hexane, the coloration and decoloration cycles of diarylethenes **1–3** were irradiated alternatively with 297 nm and visible light, and the irradiation time was long enough for coloration to reach the photostationary state. The fatigue resistant characteristics of diarylethenes **1–3** in solution indicated that 10% of **1c**, 12% of **2c**, and 8% of **3c** were destroyed after 10 repeat cycles, respectively. After 50 repeat cycles, diarylethene **3** still exhibited good photochromism with only 12% degradation of **3c**. However, 61% of **1c** and 40% of **2c** were destroyed after 50 repeat cycles at the same experimental condition. Therefore, the fatigue resistance of diarylethene **3** bearing a pyridine moiety is much better than that of diarylethene **1** or **2** bearing a benzene moiety, which may be attributed to the lower aromatic stabilization energy of pyridine ring. The result is well in agreement with that of the reported analogs bearing both six-membered and five-membered aryl moieties, where the fatigue resistances of diarylethenes bearing a pyridine moiety are much better than those of diarylethenes bearing a benzene moiety.^{12,14}

Fluorescence is widely applicable to molecular-scale optoelectronics, ion-sensors, and digital fluorescent photoswitches.¹⁷ So far, the fluorescent properties of many diarylethene derivatives have been extensively studied.¹⁸ In this work, the fluorescent features of diarylethenes **1–3** in hexane (5.0×10^{-5} mol/L) were measured using a Hitachi F-4500 fluorimeter at room temperature. As shown in Figure 3, the emission peaks of **1o–3o** were observed at 430, 422 and 424 nm when excited at 290 nm. Although there is not remarkable difference among the emission peaks of diarylethenes **1o–3o**, the emission intensities of them exist significant difference. The emission intensity of diarylethene **1o** or **2o** is notably stronger than that of **3o**. Using anthracene as a reference, the fluorescence quantum yields of diarylethenes **1o**, **2o**, and **3o** were determined as 0.057, 0.048, and 0.033, respectively. The result indicates that the six-membered aryl ring attached at ethene moiety has a significant effect on the emission intensity and fluorescence quantum yield of diarylethene. Compared to the reported analogs,⁹ the six-membered aryl ring could notably increase the fluorescence quantum yield.

As has been observed for most of the reported diarylethenes,¹⁹ diarylethenes **1–3** exhibited changes in the fluorescence between the open-ring isomers and the closed-ring isomers during the process of photoisomerization by photoirradiation in hexane. The fluorescent changes of diarylethene **1** during the process of photoisomerization are shown in Figure 4. Upon irradiation with 297 nm UV light, the photocyclization reaction was occurred and the emission intensity of diarylethene decreased significantly when excited at 290 nm. When the samples arrived at the photostationary state by irradiation with UV light, the emission intensity of diarylethene

**Figure 3.** Emission spectra of diarylethenes **1–3** in hexane (5.0×10^{-5} mol/L) at rt when excited at 290 nm.

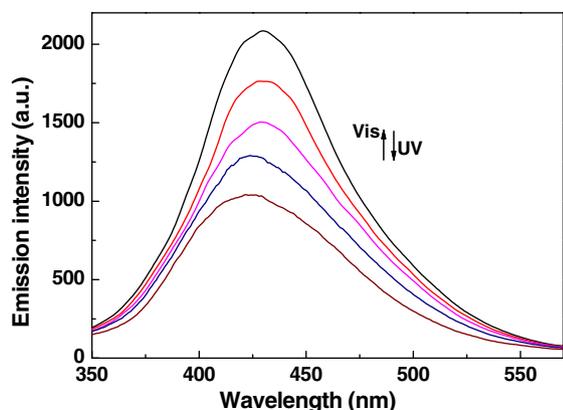


Figure 4. Emission intensity changes of diarylethene **1** in hexane (5.0×10^{-5} mol/L) by photoirradiation at rt when excited at 290 nm.

1 was quenched to ca. 49%. Back irradiation of the appropriate wavelength of visible light regenerated the open-ring isomer **1o** and duplicated the original emission spectra. As with diarylethene **1**, diarylethenes **2** and **3** also exhibited the similar fluorescent switching properties upon photoirradiation. In the photostationary state, their emission intensities were quenched to ca. 67% for **2** and 64% for **3**. The result shows that diarylethene **1** exhibits a more marked change in fluorescence upon photocyclization than **2** and **3** because of its higher photoconversion efficiency. Upon irradiation with appropriate wavelength visible light, their open-ring isomers were regenerated and the original emission intensities were recovered. Compared with diarylethenes bearing two thiophene moieties,^{4g,20} the fluorescent modulation efficiencies of diarylethenes **1–3** were significantly decreased in solution. One reason is the lower photoconversion efficiency resulted from the relatively high aromatic stabilization energy of the six-membered aryl backbone.^{2a,7} The other reason for the lower fluorescent change induced by photoirradiation may be attributed to the existence of parallel conformations of **1o**, **2o**, and **3o** in the photostationary state.^{20,21}

In conclusion, three new photochromic diarylethenes based on the unsymmetrical six-membered aryl backbone have been developed and their properties have been investigated. The new photochromic system showed evident photochromism and acted as a remarkable fluorescent switch in solution at room temperature. It has been demonstrated that the categories of six-membered aryl units and substituents have a significant effect on the properties of these diarylethene derivatives. The results of this work may be useful for new strategy in exploring photochromic diarylethenes based on different six-membered aryl units.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.11.035.

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- Data for **1o**: mp 79–80 °C; Calcd for C₂₃H₁₆F₆O (%): Calcd C, 65.41; H, 3.82. Found C, 65.46; H, 3.79; ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.31 (s, 3H, –CH₃), 3.36 (s, 3H, –CH₃), 6.66 (d, 1H, benzene–H), 6.80 (t, 1H, benzene–H, J = 8.0 Hz), 7.18 (s, 1H, benzene–H, J = 8.0 Hz), 7.24 (t, 2H, naphthalene–H, J = 8.0 Hz), 7.36 (t, 1H, benzene–H, J = 8.0 Hz), 7.43 (t, 1H, naphthalene–H, J = 8.0 Hz), 7.76 (m, 3H, naphthalene–H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 20.16, 54.70, 110.92, 116.85, 120.24, 123.71, 125.26, 125.87, 126.24, 127.39, 128.33, 129.47, 129.93, 131.66, 131.97, 135.25, 142.68, 157.28; IR (KBr, ν, cm⁻¹): 517, 588, 750, 771, 817, 848, 863, 875, 981, 1021, 1090, 1128, 1193, 1265, 1337, 1461, 1498, 1602. Data for **2o**: mp 86–87 °C; C₂₃H₁₆F₆O (%): Calcd C, 67.98; H, 3.97. Found C, 67.92; H, 3.94; ¹H NMR (400 MHz, CDCl₃, TMS): δ 2.22 (s, 3H, –CH₃), 2.44 (s, 3H, –CH₃), 7.02 (m, 2H, benzene–H, J = 8.0 Hz), 7.11 (m, 1H, benzene–H, J = 8.0 Hz), 7.14 (m, 1H, naphthalene–H, J = 8.0 Hz), 7.25 (t, 1H, benzene–H, J = 8.0 Hz), 7.44 (t, 1H, naphthalene–H, J = 8.0 Hz), 7.52 (t, 1H, naphthalene–H, J = 8.0 Hz), 7.75 (t, 3H, naphthalene–H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 20.35, 20.86, 122.61, 125.28, 125.44, 125.52, 126.64, 126.84, 128.21, 128.35, 129.62, 129.84, 130.56, 131.71, 131.78, 135.47, 136.91; IR (KBr, ν, cm⁻¹): 462, 495, 535, 572, 744, 783, 813, 838, 857, 986, 1056, 1095, 1110, 1132, 1192, 1274, 1344, 1400, 1453, 1511, 1637. Data for **3o**: mp 93–94 °C; Calcd for C₂₂H₁₅F₆N (%): Calcd C, 64.87; H, 3.71. Found C, 64.93; H, 3.95; ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.13 (s, 3H, –CH₃), 2.50 (s, 3H, –CH₃), 7.06 (m, 1H, naphthalene–H), 7.29 (t, 2H, naphthalene–H, J = 8.0 Hz), 7.42 (t, 1H, pyridine–H, J = 8.0 Hz), 7.50 (t, 1H, pyridine–H, J = 8.0 Hz), 7.77 (d, 3H, naphthalene–H, J = 8.0 Hz), 8.40 (s, 1H, pyridine–H, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, TMS): δ = 18.71, 20.98, 122.26, 124.01, 125.40, 125.47, 126.58, 128.07, 128.55, 129.91, 131.35, 131.57, 133.25, 136.50, 138.15, 146.48, 147.05; IR (KBr, ν, cm⁻¹): 509, 536, 571, 586, 732, 753, 788, 816, 850, 865, 880, 984, 1054, 1136, 1191, 1271, 1338, 1450, 1573.
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