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SYNTHESIS AND TWO-PHOTON ABSORPTION PROPERTIES OF TWO LONG π CONJUGATED ASYMMETRIC CARBAZOLE DERIVATIVES

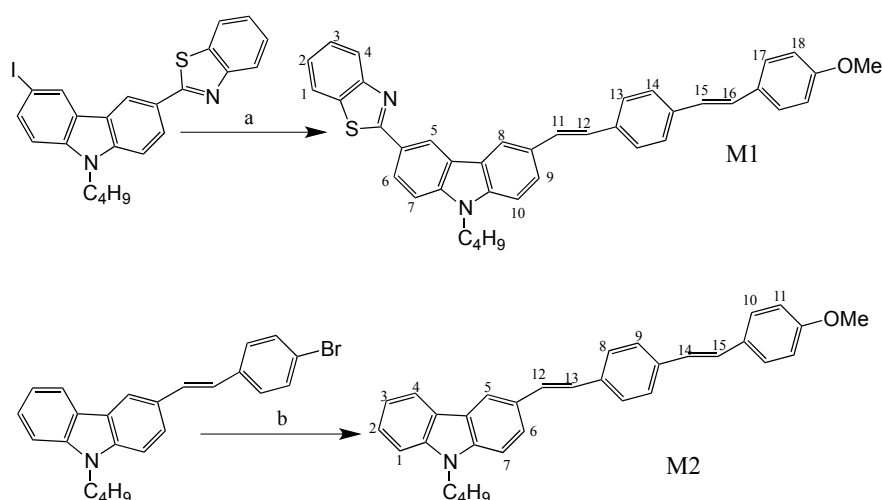
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Abstract – Two long π conjugated asymmetric carbazole derivatives, 3-benzothiazolyl-6-(4-(4-methoxystyryl)-styryl)-9-butylcarbazole (**M1**) and 3-(4-(4-methoxystyryl)styryl)-9-butylcarbazole (**M2**), were synthesized and characterized by FT-IR, ^1H NMR and elemental analyses. Their linear photophysical and two-photon absorption (TPA) properties were investigated by UV-vis absorption, fluorescence emission spectra and the two-photon excited fluorescence (TPEF) measurements in DMF, respectively. The results show that both compounds have strong fluorescence emission and the fluorescence quantum yield (Φ) of **M2** (0.36) is higher than **M1** (0.25), **M1** exhibits larger TPA cross-section (1538 GM) than **M2** (564 GM) in the femtosecond regime, indicating their potential applications as excellent optoelectronic material in optical field.

Fluorescent compounds with large two-photon absorption (TPA) crosssections have attracted much attention because of their potential applications in the areas of optical power limiting, two-photon microscopy, two-photon up-conversion laser, data storage, photodynamic therapy.¹ Various design ideas had been put forward to enhancing TPA cross section (δ_{TPA}) of the molecular by changing donor (D) and acceptor (A) symmetrically or asymmetrically with the π -conjugated group to form D- π -D, D- π -A, D- π -A- π -D and A- π -D- π -A structures. Furthermore, research on structure-property relationship indicates that the D or A strength, chain length, and planarity of the π -center have a great influence on the δ_{TPA} .² Carbazole group with heterocyclic structure containing a nitrogen atom and a condensed ring with a special rigid structure is a good fluorescence group. In recent years, carbazole derivatives have been widely investigated in nonlinear optical (NLO) materials for their good coplanarity of the conjugated system, strong intramolecular charge-transfer (ICT), excellent solubility, stability and the excellent

hole-transporting capability.³ These research results encourage us to develop new carbazole derivatives for optical application. At present, mostly of the structural modification of the carbazole derivatives is based on the 3, 6-position of the symmetric modification of small organic molecules, however, there are few reported on the 3, 6-position asymmetric structural modification of the carbazole derivatives.⁴ Benzimidazole compounds are a particular class of heterocyclic compounds, which have great significance in pharmaceutical chemistry. At the same time, benzothiazole moiety is an excellent acceptor, by fixing the benzothiazole unit as an optimized acceptor, the change by a series of different donors or π -bridges of the molecular structures may further optimize the NLO property of the compounds.⁵ Based on these above ideas, in this paper, we have synthesized two long π conjugated asymmetric carbazole derivatives by Heck coupling reactions (**Scheme 1**). The only difference between the structure of **M1** and **M2** is if the conjugated connection of benzothiazole group at 6-position of carbazole. Their linear absorption, fluorescence and two-photon absorption properties were investigated. The results demonstrated that the TPA cross sections of **M1** increase with introduction of benzothiazole ring.



Scheme 1. The synthetic route of **M1** and **M2**: (a) 4-Methoxy-4'-vinyl-1,2-stilbene, Pd(OAc)₂, triethylamine, DMF; (b) 4-Methoxystyrene, Pd(OAc)₂, triethylamine, DMF

The linear absorption and fluorescence spectral studies

The linear absorption and one-photon excited fluorescence (OPEF) of **M1** and **M2** are studied by UV-vis absorption and photoluminescence emission spectra in DMF solutions. The absorption and emission spectra for two compounds are shown in **Figure 1** and the data are listed in **Table 1**. It can be seen from **Figure 1** that **M1** exhibits one major absorption peak at about 388 nm, which is attributed to the extended π -delocalization and the charge transfer type π - π^* transition from the electron-donating methoxy to the electron-accepting benzothiazole group. **M2** has a shorter conjugation length (compared to **M1**) exhibits an 8 nm blue shift absorption. The charge transfer absorption band of **M1** and **M2** strongly depends on the

conjugation length.

As listed in **Figure 1** and **Table 1**, **M1** and **M2** both exhibit strong photoluminescent band at 460 and 483 nm, respectively. The blue-shift of emission spectra of **M1** is due to introduce the electron-accepting benzothiazole moieties, which make **M1** own D- π -A structures and has a high photoluminescence (PL) emission ability. The single peak in the PL emission spectra manifests that the state responsible for the PL emission is not the localized excited state but the ICT state. The different dipole moments of the ICT state and the ground state lead to the shift in PL spectra. Similar phenomenon is also reported, respectively.^{5,6} The fluorescence quantum yields (Φ) are measured in DMF using quinine sulfate ($\Phi = 0.55$) as standard.⁷ The photophysical data are summarised in **Table 1**. From **Table 1**, we can be seen that the fluorescence quantum yield of **M2** ($\Phi = 0.36$) is higher than that of **M1** ($\Phi = 0.25$). This difference of Φ might be happened during the process of exciton migration or might be due to the change of the molecular size.⁵ This result clearly indicates that the interaction between donor and acceptor plays a significant role in modulating planarity and photophysical properties.

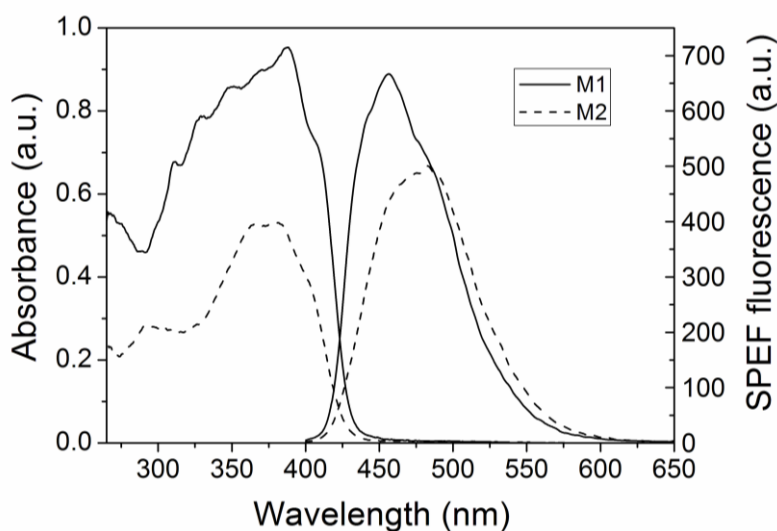


Figure 1. UV-vis spectra and fluorescence emission spectra of compound **M1** (solid line) and compound **M2** (dash line) in DMF solution (concentration: 1.0×10^{-5} mol L⁻¹)

Two-photon absorption cross-sections (δ_{TPA}) of the samples were obtained by two-photon excited fluorescence (TPEF) method at femtosecond laser pulse and Ti: sapphire system (680-1080 nm, 80 MHz, 140 fs) as the light source.⁸ The δ_{ref} value of reference was taken from the literature.⁹ Two-photon fluorescence spectra (TPEF) of **M1** and **M2** in DMF pumped by femtosecond laser pulses under different pumped powers at their maximum excitation wavelengths were presented in **Figure 2**. The insets show logarithmic plots of the fluorescence integral versus pumped powers with a slope of 2.02/2.03, with the increase of the input laser power. Because no linear absorption was observed in the range from 475 nm to

1000 nm, the emission excited by 680-780 nm laser wavelengths can be attributed to the TPEF mechanism. As shown in **Figure 3**, **M1** and **M2** display TPA activity in the range of 680-780 nm in DMF, and the optimal excitation wavelengths for the TPA cross-sections are 700 nm.

As shown in **Figure 4** and **Table 1**, these two compounds display TPA activity in the range of 680-780 nm in DMF and the fluorescence peak of wavelengths were obviously red-shifted by 21-46 nm compared to those of OPEF in DMF due to the reabsorption effect. For one-photon induced emission measurements, we used dilute solutions (1×10^{-5} mol L⁻¹), thus the reabsorption of the fluorescence within the samples can be negligible. However, the reabsorption of the shorter wavelength fluorescence by the concentrated

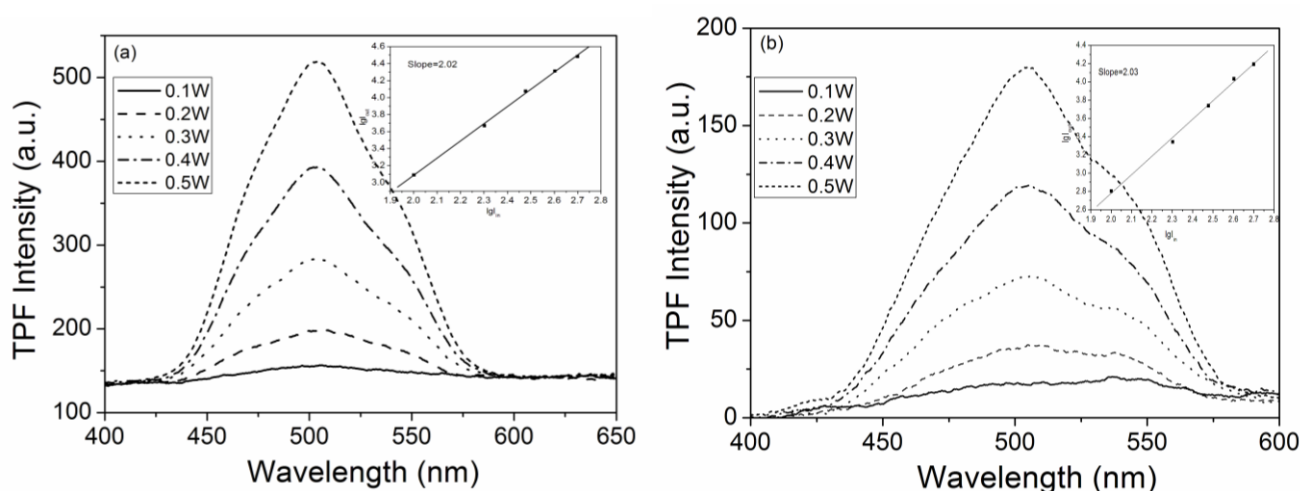


Figure 2. TPF spectra of compound **M1** (a) and **M2** (b) in DMF pumped by femtosecond laser pulses under different pumped powers at their maximum excitation wavelength (inset: the logarithmic plots of the fluorescence integral of chromophores versus different excitation intensities)

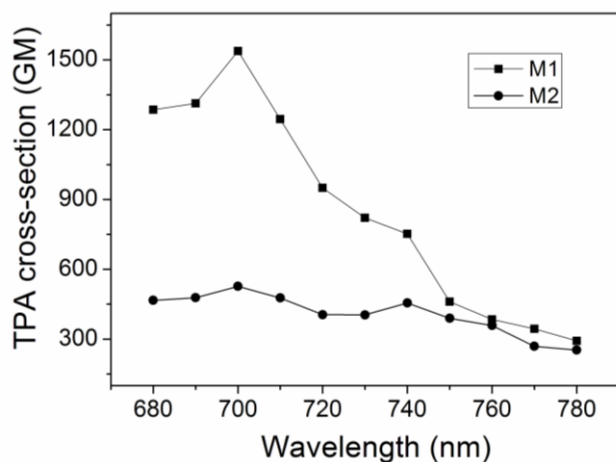


Figure 3. TPA cross sections of **M1** and **M2** in DMF versus excitation wavelengths of identical energy of 0.5 w (experimental uncertainties: 10%)

sample can no longer be neglected because in this case the concentration of solutions is high (1×10^{-3} mol L⁻¹). The results show that **M2** without substitution at 6-position of carbazole with a δ_{TPA} of 564 GM, while the substitution of benzothiazole group makes **M1** possess larger δ_{TPA} (1538 GM). As shown in **Figure 4**, the intensities of TPEF of **M1** and **M2** exhibit the sequence of **M2** < **M1**. These similarities between TPEF and OPEF indicate that both the emissions for a given compound are from the same excited state. It can be seen from **Table 1**, the δ_{TPA} increases obviously, it indicates that the increased conjugated length led to enlarged δ_{TPA} and red shift in the UV absorption, which is consistent with the experiment results. Therefore, the structure of substitution on carbazole molecules has an important effect on their optical properties and this will provide some foundation for the structure design of emitting molecules in future.

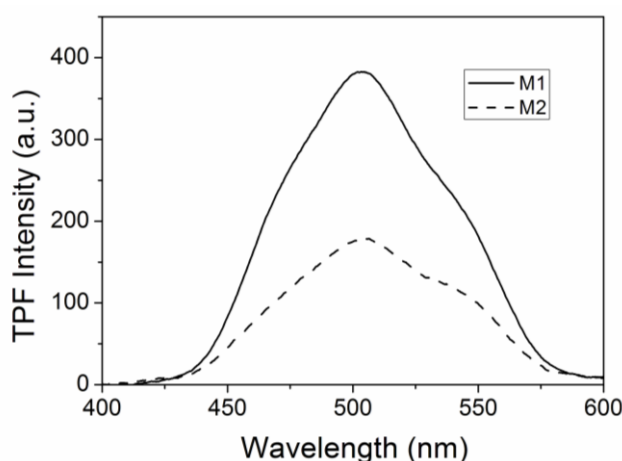


Figure 4. The two-photon fluorescence spectra of **M1** and **M2** in DMF ($c = 1 \times 10^{-3}$ mol L⁻¹) pumped by femtosecond laser pulses at 500 mw at their maximum excitation wavelength

Table 1. The linear and two-photon absorption properties of compounds **M1** and **M2**

Compound	$\lambda_{\text{max}}^{\text{a}}$	$\epsilon_{\text{max}}^{\text{b}}$	$\lambda_{\text{max}}^{\text{c}}$	Φ^{d}	$\lambda_{\text{max}}^{\text{e}}$	δ^{f}
M1	388	9.53	460	0.25	506	1538
M2	380	5.31	483	0.36	504	564

^a Absorption peak position in nm (1.0×10^{-5} mol L⁻¹).

^b Maximum molar absorbance in 10^4 mol⁻¹ L cm⁻¹.

^c Peak position of OPEF in nm (1.0×10^{-5} mol L⁻¹), excited at the absorption maximum.

^d Quantum yields determined by using quinine sulfate (1.0×10^{-5} mol L⁻¹) as the standard.

^e TPEF peak position in nm pumped by femtosecond laser pulses at 500 mw at their maximum excitation wavelength.

^f TPA cross section in GM.

In conclusion, two π long conjugated asymmetric compounds **M1** and **M2**, which were based on carbazole moiety with and without the attachment of benzothiazole group, have been synthesized and

their optical properties were investigated. The results show that two compounds exhibited excellent strong fluorescence emission and larger TPA cross-section, indicating their potential application excellent optoelectronic material in optical field.

EXPERIMENTAL

Materials

Palladium (II) acetate, 4-methoxystyrene and triphenylphosphine were purchased from Aldrich. Triethylamine and *N,N*-dimethylformamide were purified before use. 4-Methoxy-4'-vinyl-1,2-stilbene, 3-benzothiazolyl-6-iodo-9-butylcarbazole and 3-[(4-bromophenyl)-*N*-butyl]carbazole were synthesized according to references.^{5,10}

Characterization

The FT-IR spectrum was recorded with KBr pellets on a Nicolet 170 sx spectrometer. ¹H NMR spectrum was obtained on a Bruker AV-400 spectrometer at room temperature. Elemental analysis was determined on an Elementar Vario EL III spectrometer. All spectral characterizations were carried out in HPLC-grade solvents at 20 °C within a 10 mm quartz cell. UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Corrected steady-state excitation and emission spectra were recorded on a Perkin Elmer LS-55 FL spectrophotometer. The excitation source for the TPEF experiments was a mode-locked femtosecond Ti: Sapphire laser (Spectra-physics, 100 fs, 82 MHz) tuned to 720 nm. The maximum average laser power available for these experiments was about 100 mW.

Synthesis of M1 and M2

The synthetic route of **M1** and **M2** is described in **Scheme 1**. To obtain target product **M1**, 0.50 g (1 mmol) 3-benzothiazolyl-6-iodo-9-butylcarbazole, 0.24 g (1 mmol) 4-methoxy-4'-vinyl-1,2-stilbene, 22.4 mg Pd(OAc)₂ (0.1 mmol), 26.2 mg (0.10 mmol) PPh₃ were dissolved in 30 mL DMF. The mixture was refluxed for 48 h under nitrogen. After cooling down to room temperature, the reaction solution was dumped to water to precipitate the product. The crude product of **M1** was purified by column chromatography (Al₂O₃, EtOAc: petroleum ether = 1 : 2 as eluent) and dark yellowish green resultant product was obtained in 57.6% yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.88 (s, 1H, H⁴), 8.35 (s, 1H, H¹), 8.22 (d, *J* = 7.53 Hz, 1H, H¹⁰), 8.08 (d, *J* = 8.70, 1H, H⁸), 7.93-7.83 (m, 2H, H¹⁷), 7.70 (d, *J* = 8.28 Hz, 1H, H³), 7.59-7.35 (m, 9H, H^{2,5-7,9,13,14}), 7.31 (s, 1H, H¹¹), 7.20 (s, 1H, H¹²), 7.08 (s, 1H, H¹⁵), 7.02 (s, 1H, H¹⁶), 6.91 (d, 2H, *J* = 7.78 Hz, H¹⁸), 4.34 (t, 2H, -N-CH₂-), 3.86 (s, 3H, Ar-OCH₃), 1.91-1.87 (m, 2H, -CH₂-), 1.55-1.42 (m, 2H, -CH₂-), 0.96 (t, 3H, CH₃-). Anal. Calcd for C₄₀H₃₄N₂OS: C 81.32; H 5.80; N 4.74; S, 5.43. Found C 81.25; H 5.84; N 4.68; S 5.41.

M2 was prepared as above from 3-[(4-bromophenyl)-*N*-butyl]carbazole and 4-methoxystyrene. The precipitate was washed three times using EtOH to give yellow green powder in 75.4% yield. ¹H NMR

(400 MHz, CDCl₃) δ (ppm): 8.26 (s, 1H, H⁴), 8.15 (s, $J = 7.6$ Hz, 1H, H⁵), 7.70 (d, $J = 8.4$ Hz, 1H, H⁷), 7.55 (m, 4H, H^{1-3,6}), 7.44 (m, 6H, H^{8,9,11}), 7.36 (d, 1H, $J = 16.4$ Hz, H¹²), 7.20 (d, $J = 7.8$ Hz, 3H, H¹³⁻¹⁵), 7.12 (d, $J = 7.2$ Hz, 2H, H¹⁰), 4.34 (t, $J = 7.2$ Hz, 2H, -N-CH₂-), 3.86 (s, 3H, Ar-OCH₃), 1.92~1.86 (m, 2H, -CH₂-), 1.47~1.41 (m, 2H, -CH₂-), 0.98 (t, 3H, CH₃-). Anal. Calcd for C₃₃H₃₁NO: C, 86.61; H 6.83; N 3.06. Found C 86.57; H 6.86; N 3.01.

ACKNOWLEDGEMENTS

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REFERENCES

1. W. R. Dichtel, J. M. Serin, C. Edder, J. M. J. Fréchet, M. Matuszewski, L. S. Tan, T. Y. Ohulchansky, and P. N. Prasad, *J. Am. Chem. Soc.*, 2004, **126**, 5380; Y. Qian, K. Meng, C. G. Lu, B. P. Lin, W. Huang, and Y. P. Cui, *Dyes Pigm.*, 2009, **80**, 174; B. Sadowski, H. Kita, M. Grzybowski, K. Kamada, and D. T. Gryko, *J. Org. Chem.*, 2017, **82**, 7254; J. W. Choi, S. T. Hong, D. E. Kang, K. C. Paik, M. S. Han, C. S. Lim, and B. R. Cho, *Anal. Chem.*, 2016, **88**, 9412.
2. W. Jiang, J. N. Tang, Q. Qi, W. B. Wu, Y. M. Sun, and D. W. Fu, *Dyes Pigm.*, 2009, **80**, 11; H. P. Shia, L. Xu, Y. Cheng, J. Y. He, J. X. Dai, L. W. Xing, B. Q. Chen, and L. Fang, *Spectrochim. Acta, Part A*, 2011, **81**, 730; X. P. Ge, X. P. Gan, S. Yao, K. Wang, W. J. Zhu, J. H. Yu, J. Y. Wu, Y. P. Tian, and H. P. Zhou, *J. Mater. Chem. B*, 2016, **4**, 2785; C. Brieke, F. Rohrbach, A. Gottschalk, G. Mayer, and A. Heckel, *Angew. Chem. Int. Ed.*, 2012, **51**, 8446; G. Bort, T. Gallavardin, D. Ogden, and P. I. Dalko, *Angew. Chem. Int. Ed.*, 2013, **52**, 4526; S. Piant, F. Bolze, and A. Specht, *Opt. Mat. Exp.*, 2016, 1679; M. Abe, Y. Chitose, S. Jakkampudi, P. T. T. Thuy, Q. Lin, B. T. Van, A. Yamada, R. Oyama, M. Sasaki, and C. Katan, *Synthesis*, 2017, **49**, 3337.
3. T. Fulghum, S. M. Abdual Karim, A. Baba, P. Taranekar, T. Nakai, T. Masuda, and R. C. Advincula, *Macromolecules*, 2006, **39**, 1467; W. J. Zhu, L. L. Yang, M. Fang, Z. Y. Wu, Q. Zhang, F. F. Yin, Q. Huang, and C. Li, *J. Lumin.*, 2015, **158**, 38; L. L. Yang, W. J. Zhu, M. Fang, Q. Zhang, and C. Li, *Spectrochim. Acta, Part A*, 2013, **109**, 186; Q. Peng, J. Xu, M. J. Li, and W. X. Zheng, *Macromolecules*, 2009, **42**, 5478.
4. C. N. Chuang, H. J. Chuang, Y. X. Wang, S. H. Chen, J. J. Huang, M. K. Leung, and K. H. Hsieh, *Polymer*, 2012, **53**, 4983.
5. H. Y. Wang, G. Chen, X. P. Xu, H. Chen, and S. J. Ji, *Dyes Pigm.*, 2010, **86**, 238.

6. D. X. Cao, Q. Fang, D. Wang, Z. Q. Liu, G. Xue, G. B. Xu, and W. T. Yu, [*Eur. J. Org. Chem.*, 2003, 3628](#); V. D. Gupta, V. S. Padalkar, K. R. Phatangare, V. S. Patil, P. G. Umape, and N. Sekar, [*Dyes Pigm.*, 2011, 88, 378](#).
7. Z. J. Zhao, X. J. Xu, Z. T. Jiang, P. Lu, G. Yu, and Y. Q. Liu, [*J. Org. Chem.*, 2007, 72, 8345](#).
8. H. P. Zhou, F. X. Zhou, S. Y. Tang, P. Wu, Y. X. Chen, Y. L. Tu, J. Y. Wu, and Y. P. Tian, [*Dyes Pigm.*, 2011, 92, 633](#).
9. S. K. Lee, W. J. Yang, J. J. Choi, C. H. Kim, S. J. Jeon, and B. R. Cho, [*Org. Lett.*, 2005, 7, 323](#); Z. Zheng, H. P. Zhou, F. X. Zhou, Z. P. Yu, X. F. Yang, L. H. Cheng, L. Kong, Y. Feng, J. Y. Wu, and Y. P. Tian, [*Tetrahedron*, 2012, 68, 6569](#).
10. W. J. Zhu, Z. Y. Wu, J. M. Song, and C. Li, [*Chin. Chem. Lett.*, 2011, 22, 1017](#); S. Y. Guang, S. C. Yin, H. Y. Xu, W. J. Zhu, Y. C. Gao, and Y. L. Song, [*Dyes Pigm.*, 2007, 73, 285](#).