Vietnam Journal of Catalysis and Adsorption
Tạp chí xúc tác và hấp phụ Việt Nam

https://jca.edu.vn

Synthesis and photophysical characterization of 4,7-bis(4-hydroxyphenyl)-5,6-BINOL-Benzo[2,1,3]thiadiazole and 4,7-bis(4-hydroxystyryl)-5,6-BINOL-Benzo[2,1,3]thiadiazole and application for luminescent hair dyes

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ARTICLE INFO

Received: 09/04/2026
Accepted: 21/05/2026
Published: 30/06/2026

Keywords:
Benzothiadiazole;
Binol; palladium; heck;
Suzuki; hair dyes

ABSTRACT

Two new chiral luminescent organic compounds were synthesized by Palladium catalyzed cross coupling reaction. While the 4,7-bis(4-hydroxyphenyl)-5,6-BINOL-benzo[2,1,3]thiadiazole was synthesized by Suzuki reaction, the 4,7-bis(4-hydroxystyryl)-5,6- BINOL-benzo[2,1,3]thiadiazole was synthesized via Heck reaction. Two compounds were highly luminescent in the solid state. All the photophysical properties have been investigated and characterized. The application for luminescent hair dyes has been executed and confirmed by our group.

Introduction

Human hair is a biologically significant structure mainly composed of keratin proteins rich in sulfur-containing cysteine residues. Structurally, hair consists of three layers: the cuticle, cortex, and medulla. The cuticle acts as a protective barrier, while the cortex contains keratin macrofibrils and melanin pigments responsible for the natural hair color [1,2]. Hair proteins are stabilized by hydrogen bonds, salt bridges, and disulfide cross-links. Under alkaline conditions, the hair fiber swells, allowing external molecules to diffuse into the cortex [2]. As melanin production decreases with aging, hair dyeing has become increasingly important in cosmetic applications [3].

Hair dyeing involves the penetration of chromophores into the hair structure to modify its optical properties. Alkalizing agents such as ammonia raise the pH and open the cuticle, while oxidizing agents like hydrogen peroxide bleach natural melanin and promote color formation [4,5]. Permanent hair dyes rely on oxidative reactions between small colorless precursors and couplers inside the hair shaft, producing large colored molecules trapped within the keratin matrix [6]. Although effective, conventional aromatic amine-based dyes may cause toxicological concerns, motivating the development of safer and more sustainable alternatives [7,8].

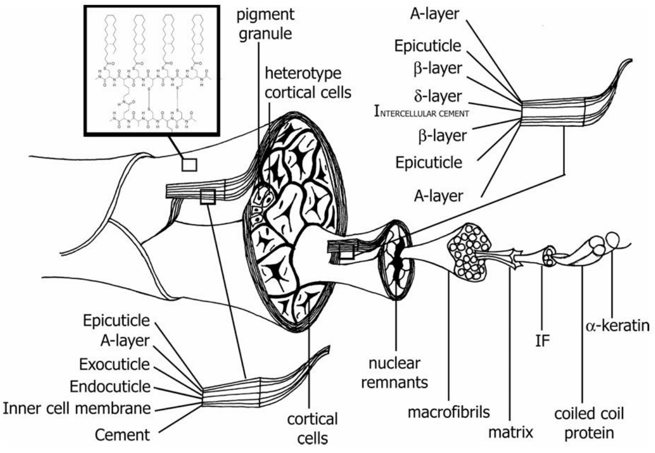


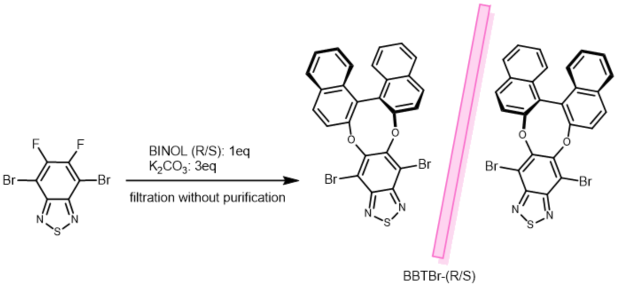
Figure 1: Structure of human hair. Adapted from [9]

https://doi.org/10.62239/jca.2026.022

Hair dyes are generally classified into temporary, semi-permanent, and permanent systems based on their durability and interaction with hair fibers [1]. Temporary dyes remain on the hair surface, semi-permanent dyes partially penetrate the cortex through weak intermolecular interactions, while permanent dyes form large insoluble pigments inside the hair through oxidative coupling reactions [5,6]. Inspired by commercial hydroxy-containing dyes, we developed two novel luminescent organic compounds and evaluated their potential for hair dye applications.

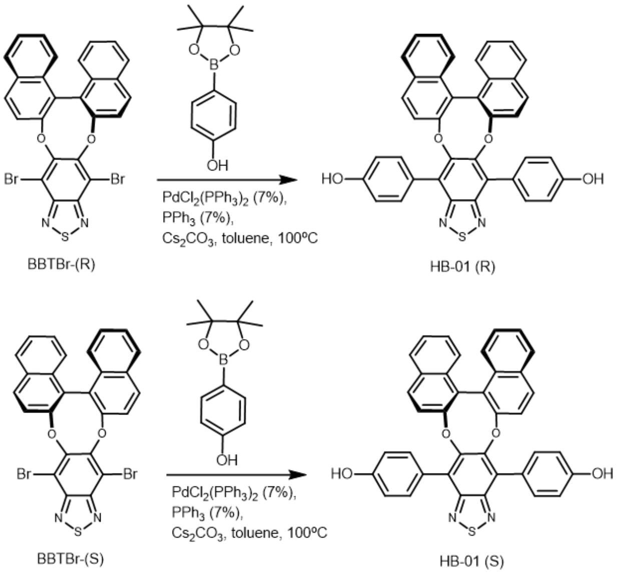
Experimental

Starting reagents were purchased commercially and used without further purification, except for 4,7-dibromo-5,6-BINOL-Benzo[2,1,3]thiadiazole, which was synthesized and modified according to the literature methods reported by Nguyen *et al.* [10].

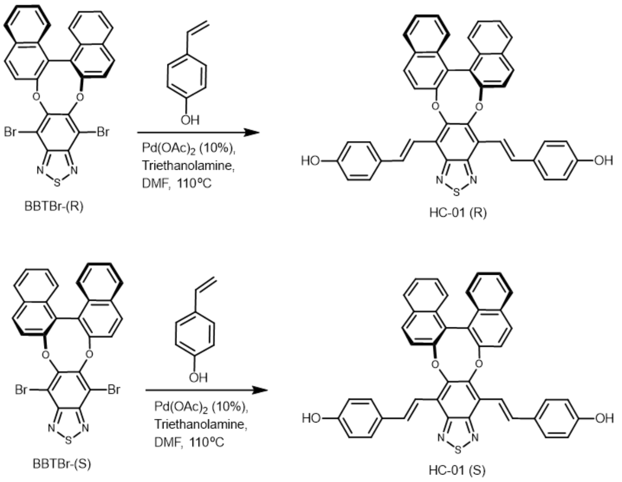


Scheme 1: Synthesis of 4,7-dibromo-5,6-(R/S)-BINOL-O-2,1,3-benzothiadiazole

The Suzuki-Miyaura reaction is a key method for forming C-C bonds via palladium-catalyzed coupling of aryl halides and organoboron compounds, widely used due to its mild conditions and high selectivity [11]. Benzothiadiazole (BTD), a strong electron acceptor, is often functionalized through this reaction to extend π-conjugation. Unsymmetrical BTD derivatives can be efficiently synthesized from dibromo-BTD and boronic esters, enabling precise tuning of optoelectronic properties [12]. Accordingly, HB-01 (R/S) was prepared via Suzuki coupling to yield an extended conjugated system with potential applications in luminescent and organic electronic materials. The palladium-catalyzed Heck reaction is a key method for forming C–C bonds between aryl halides and olefins, valued for its high regioselectivity and functional group tolerance [13]. However, challenges remain in controlling stereochemistry and maintaining efficiency for sterically hindered internal alkenes. To address this, an optimized ligand-controlled Heck protocol was developed, enabling moderate-yield and regioselective synthesis of the congested disubstituted compounds HC-01 (R/S).



Scheme 2: Synthesis of 4,7-bis(4-hydroxyphenyl)-5,6 BINOL-Benzo[2,1,3]thiadiazole



Scheme 3: synthesis of 4,7-bis(4-hydroxystyryl)-5,6-BINOL-Benzo[2,1,3]thiadiazole

Measurement. 1H NMR spectra were recorded on a BRUKER 500 MHz Ascend spectrometer with tetramethylsilane (TMS) as the internal standard. UV-visible absorption spectra were obtained using Aligent Cary 5000. Steady-state fluorescence spectra and excitation spectra were measured using NanoLog Horiba.

Synthesis of 4,7-dibromo-5,6-(R/S)-BINOL-O-2,1,3-benzothiadiazole (BBTBr-(R/S)): An 48 mL heavy-walled pressure vessel equipped with a Teflon-coated magnetic stir bar is charged with 4,7-dibromo-5,6-difluorobenzo[2,1,3]thiadiazole (5.0 g, 15.15 mmol, 1 equiv.), potassium carbonate (5.23 g, 37.88 mmol, 2.5

equiv.), and enantiopure BINOL (4.34 g, 15.15 mmol, 1 equiv.). DMF (50 mL) were then added to the vessel, and the mixture was stirred at 80ºC overnight. After the reaction completion, the mixture was cooled to room temperature and filtered with silica gel to obtain BBTBr as brown solid in 97% yield.

Synthesis of 4,7-bis(4-hydroxyphenyl)-5,6 BINOL-Benzo[2,1,3]thiadiazole (HB-01 (R/S)): A reaction tube equipped with a magnetic stirrer was charged under an argon atmosphere with 4,7-dibromo-5,6-(R/S)-BINOL-O-2,1,3-benzothiadiazole (BBTBr) (50 mg, 0.087 mmol), 4-hydroxyphenylboronic acid pinacol ester (0.42 mmol), bis(triphenylphosphine)palladium(II) dichloride (4.2 mg), triphenylphosphine (1.6 mg), and cesium carbonate (50 mg), followed by the addition of 3 mL of toluene at room temperature. The mixture was heated to 100ºC and stirred for 48 hours. Upon completion, the reaction mixture was cooled to room temperature. The desired product was purified by column chromatography using a hexane/ethyl acetate (EtOAc) solvent system to afford the product in 90% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.93–7.90 (m, 1H), 7.87–7.85 (m, 1H), 7.65–7.60 (m, 3H), 7.50–7.47 (m, 1H), 7.41–7.38 (m, 1H), 7.11–7.10 (d, J ≈ 8.5 Hz, 1H), 6.98–6.97 (d, J ≈ 8.5 Hz, 2H).

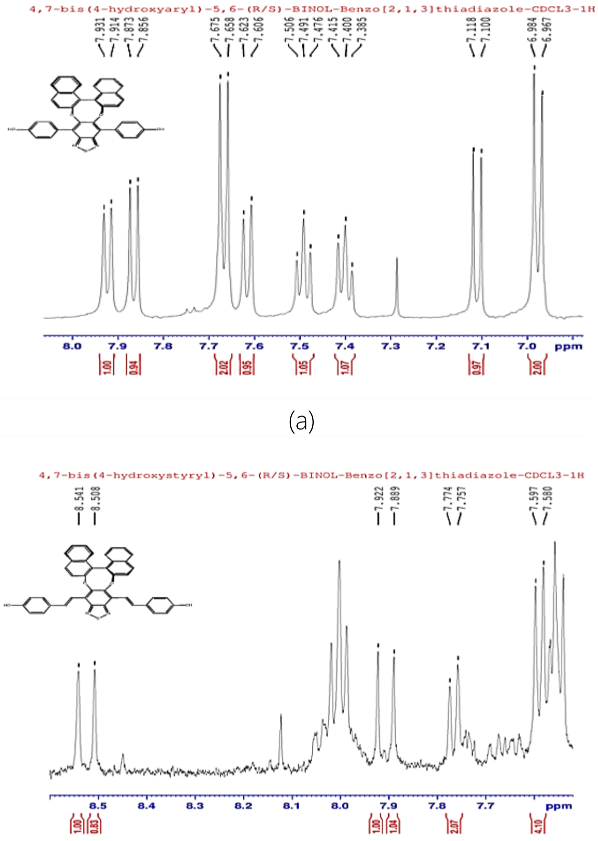
Synthesis of 4,7-bis(4-hydroxystyryl)-5,6-BINOL-Benzo[2,1,3]thiadiazole (HC-01 (R/S)): A reaction tube equipped with a magnetic stirrer was charged under an argon atmosphere with 4,7-dibromo-5,6-(R/S)-BINOL-O-2,1,3-benzothiadiazole (50 mg, 0.087 mmol), 4-vinylphenol (0.32 mmol), palladium(II) acetate (2.4 mg), and triethanolamine (56 µL), followed by the addition of 3 mL of dimethylformamide at room temperature. The mixture was heated to 110ºC and stirred for 48 hours. Upon completion, the reaction mixture was cooled to room temperature and extracted with ethyl acetate (three times). The combined organic layers were dried over anhydrous $CaCl_2$ and concentrated under reduced pressure. The crude product was purified by column chromatography using a hexane/ethyl acetate (EtOAc) solvent system to afford the desired product in 40% yield. The moderate yield of the Heck coupling reaction may be attributed to incomplete double coupling, likely due to steric hindrance and reduced reactivity of the second bromide site after the first coupling step. In addition, the highly conjugated and bulky structure of the product may decrease its solubility in the reaction medium, further limiting the overall conversion and complicating purification.

^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 8.54 (d, J ≈ 8.5 Hz, 1H), 8.50 (d, J ≈ 8.5 Hz, 1H), 7.92 (d, J ≈ 16.0 Hz, 1H), 7.89 (d, J ≈ 16.0 Hz, 1H), 7.77 (d, J ≈ 8.0 Hz, 2H), 7.60–7.58 (m, 4H).

Hair dyeing process: A reaction tube (Tube 1) was charged under ambient air with a hair tress (approximately 15 cm in length, consisting of about 20 strands), 1 mL of deionized water, H_2O_2 3% (10mL), and triethylamine (0.3mL) at room temperature. The mixture was allowed to stand for 1 hour while being heated at 50 ºC. Separately, a second reaction tube (Tube 2) was charged under ambient air with compound HB-01 (R/S), followed by the addition of 2mL of ethanol. After 1 hour, the contents of Tube 2 were poured into Tube 1, and the resulting mixture was left undisturbed for 4 hours at 50 ºC.

Results and Discussion

Synthesis and Structural Characterization



(a)

(b)

Figure 2: ^{1}H NMR of (a) HC-01 (R/S) and (b) HB-01 (R/S) in aromatic field

The target compounds HB-01 (R/S) and HC-01 (R/S) were successfully synthesized from the dibromo precursor BBTBr through palladium-catalyzed cross-coupling reactions. HB-01 (R/S) was obtained via Suzuki–Miyaura coupling with 4-hydroxyphenylboronic acid pinacol ester in 90% yield, whereas HC-01 (R/S) was synthesized through Heck coupling with 4-vinylphenol in 40% yield. The lower yield observed for HC-01 (R/S) is likely associated with the steric hindrance generated after the first coupling step and the reduced reactivity of the remaining bromide position. Furthermore, the highly conjugated structure of HC-01 (R/S) may decrease its solubility during the reaction and purification processes.

The structures of both compounds were confirmed by ^{1}H NMR spectroscopy in Figure 2. For HC-01 (R/S), the appearance of characteristic vinyl proton doublets at δ=7.92 and 7.89 ppm with a coupling constant of approximately 16 Hz confirmed the formation of the trans-styryl moiety. The aromatic resonances observed for both compounds were fully consistent with the proposed molecular structures.

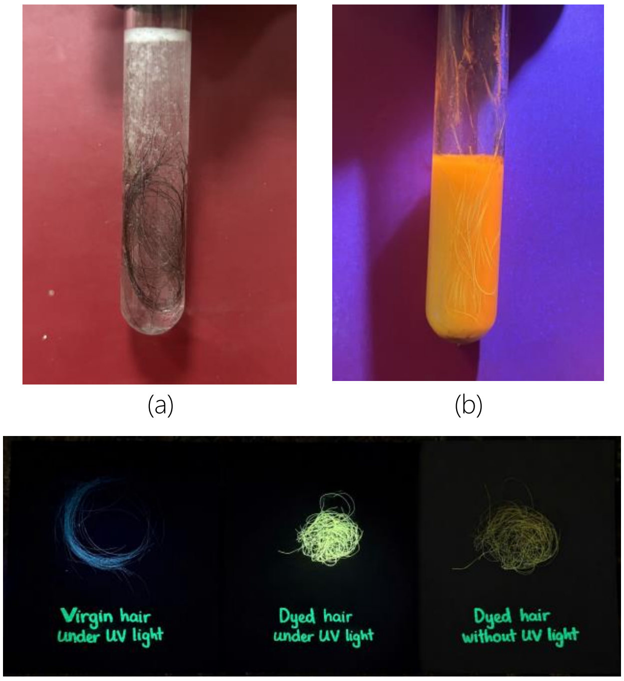
Hair dyeing performance

The luminescent hair-dyeing performance of HB-01 was evaluated under oxidative conditions using hydrogen peroxide and triethylamine. As shown in Figure 3, untreated hair exhibited negligible fluorescence under UV irradiation, whereas hair treated with HB-01 (R/S) displayed intense green luminescence. The retention of fluorescence after the dyeing process indicates successful incorporation of the dye into the hair matrix. The presence of hydroxy groups may facilitate hydrogen-bonding interactions between the dye molecules and keratin proteins, thereby enhancing dye retention on hair fibers. In addition, the bulky BINOL-containing structure may reduce dye diffusion out of the hair shaft, contributing to improved durability.

Although the current results clearly demonstrate visible fluorescence on dyed hair, the evaluation remains primarily qualitative. Further investigations involving wash-fastness testing, fluorescence retention measurements, colorimetric analysis, and long-term stability studies are required to fully assess the practical performance of these materials as commercial luminescent hair dyes.

Photophysical Properties

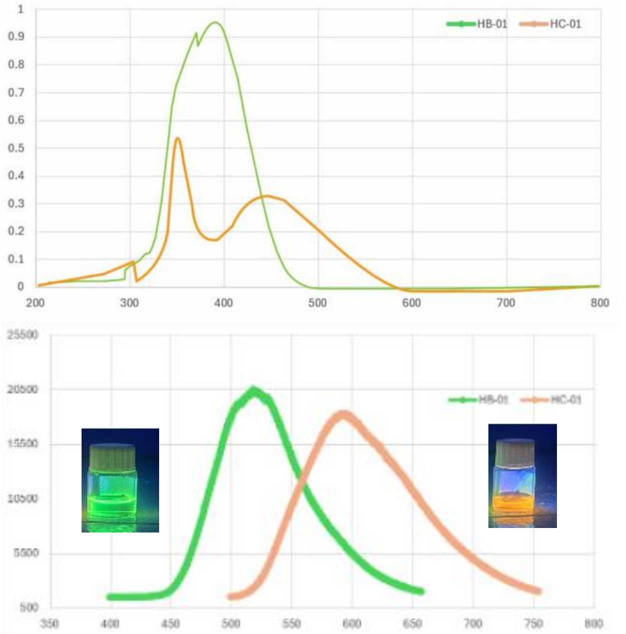
The UV-Vis absorption and fluorescence spectra of HB-01 (R/S) and HC-01 (R/S) are shown in Figure 4. HB-01 (R/S) exhibited a maximum absorption wavelength at 380 nm and an emission maximum at 525 nm, corresponding to green fluorescence. In contrast, HC-01 (R/S) displayed a significantly red-shifted absorption band at 450 nm and an emission maximum at 590 nm, resulting in orange fluorescence.



(a) (b)

(c)

Figure 3: (a) Hair treated with the oxidizing solution in the absence of HB-01 (R/S) under UV light. (b) The oxidizing solution after the addition of HB-01 (R/S) under UV light. (c) Virgin hair and dyed hair under UV light vs dyed hair without UV light



Compound	λ_{abs} (nm)	λ_{em} (nm)	Emission color
HB-01	380	525	green
HC-01	450	590	orange

Figure 4: (a) UV-vis and (b) FL spectra of HB-01 (R/S) (green) and HC-01 (R/S) (orange)

The pronounced bathochromic shift observed for HC-01 (R/S) can be attributed to the incorporation of styryl bridges, which extend the π-conjugation pathway and strengthen intramolecular charge transfer (ICT) between the hydroxy donor groups and the electron-deficient benzothiadiazole acceptor core. Consequently, the HOMO-LUMO energy gap is reduced, leading to longer-wavelength absorption and emission.

In both compounds, the BINOL framework contributes additional rigidity and steric hindrance, which restrict intramolecular rotation and suppress non-radiative decay pathways. This structural feature is expected to enhance fluorescence efficiency and improve the solid-state emissive properties of the molecules.

Conclusion

In conclusion, a series of hydroxyl-functionalized compounds were successfully synthesized via Heck and Suzuki cross-coupling reactions. The structures and photophysical properties were confirmed by ^{1}H NMR, UV-Vis, and fluorescence spectroscopy. The compounds were successfully incorporated into hair fibers and exhibited strong fluorescence under UV irradiation. These results suggest their potential as promising candidates for the first generation of luminescent hair dyes. Further studies on scalp biocompatibility and safety are still required.

Acknowledgement

This research is funded by Ministry of Education and Training, Vietnam under grant number BK2024.BKA.03.

References

1. O.J.X. Morel, R.M. Christie, Chem. Rev., 111(4) (2011) 2537–2561. https://doi.org/10.1021/cr1000145
2. D. Lewis, J. Mama, J. Hawkes, Materials, 6(2) (2013) 517–534. https://doi.org/10.3390/ma6020517
3. Z.F. Gao, X.Y. Wang, J.B. Gao, F. Xia, RSC Adv., 9(35) (2019) 20492–20496. https://doi.org/10.1039/C9RA03177D
4. S.A. da França, M.F. Dario, V.O. Consiglieri, T.M. Kaneko, A.R. Baby, M.V.R. Velasco, Cosmetics, 2(2) (2015) 110–126. https://doi.org/10.3390/cosmetics2020110
5. A. Meyer, K. Fischer, Environ. Sci. Eur., 27(1) (2015) 11. https://doi.org/10.1186/s12302-015-0044-7
6. G. Venkatesan, Y. Dancik, A. Sinha, S. Valiyaveettil, P. Bigliardi, G. Pastorin, New J. Chem., 43(11) (2019) 4109–4117. https://doi.org/10.1039/C9NJ03362A
7. G. Venkatesan, Y. Dancik, A. Sinha, H.M. Kyaw, R. Srinivas, T.L. Dawson Jr, M. Bigliardi, P. Bigliardi, G. Pastorin, J. Hazard. Mater., 402 (2021) 123712. https://doi.org/10.1016/j.jhazmat.2020.123712
8. R.A.G. de Oliveira, T.B. Zanoni, G.G. Bessegato, D.P. Oliveira, G.A. Umbuzeiro, M.V.B. Zanoni, Quim. Nova, 37(6) (2014) 1037–1046. https://doi.org/10.5935/0100-4042.20140143
9. M. Feughelman, Mechanical Properties and Structure of Alpha-Keratin Fibres: Wool, Human Hair and Related Fibres, UNSW Press, Sydney (1997).
10. N.V. Gioi, M.T. Phung, P.T.M. Ngo, T.T.T. Pham, D.H. Ta, Q.T. Tran, L.P. Giang, T.T. Dang, Vietnam J. Catal. Adsorpt., 14(4) (2025) 37–41. https://doi.org/10.62239/jca.2025.060
11. L. Caliò, B.R. Patil, J. Benduhn, K. Vandewal, H.-G. Rubahn, M. Madsen, Sustain. Energy Fuels, 2(9) (2018) 2296–2302. https://doi.org/10.1039/C8SE00251G
12. J.P. Heiskanen, P. Vivo, N.M. Saari, T.I. Hukka, T. Kastinen, K. Kaunisto, H.J. Lemmetyinen, O.E.O. Hormi, J. Org. Chem., 81(4) (2016) 1535–1546. https://doi.org/10.1021/acs.joc.5b02689
13. J. Zhang, A. Konsmo, A. Sandberg, X. Wu, S. Nyström, U. Obermüller, B.M. Wegenast-Braun, P. Konradsson, M. Lindgren, P. Hammarström, J. Med. Chem., 62(4) (2019) 2038–2048. https://doi.org/10.1021/acs.jmedchem.8b01681