

Toward Soluble 5,10-Diheterotruxenes: Synthesis and Reactivity of 5,10-Dioxatruxenes, 5,10-Dithiatruxenes, and 5,10-Diazatruxenes

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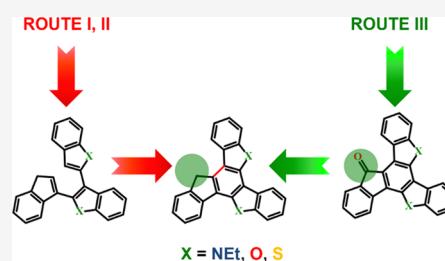


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ABSTRACT: The following work presents three general approaches allowing, for the first time, the synthesis of 5,10-diheterotruxene derivatives containing two identical heteroatoms, namely, oxygen OOC, nitrogen NNC, or sulfur SSC. Two of described pathways involve the photocyclization of the corresponding triene **2** as a key step leading to a heptacyclic aromatic system. The third approach is based on the acidic condensation between ninhydrin **14** and benzo[*b*]heteroole **15**. Typical functionalizations of the 5,10-diheterotruxene core have also been presented. In addition, the article discusses the advantages and limitations of the three suggested paths for receiving specific 5,10-diheterotruxene derivatives because the universal method suitable for obtaining molecules with any type of heteroatoms is not known so far.



INTRODUCTION

Truxenes are a family of heptacyclic carbo- and heteroaromatic systems. Currently, the synthesis of truxene^{1–5} and its triheteroanalogues^{6–9} as well as their reactivity^{10–20} are well known. In the 80s, the liquid crystal properties of some alkyl derivatives invoked an interest in this class of substances, in particular, of truxene,^{21,22} 5,10,15-trioxatruxene,²³ and 5,10,15-trithiatruxene.^{24,25} Currently, truxenes are used in optoelectronics as blue emitters,^{26–30} or in lasing media^{31–34} and exhibit nonlinear properties.^{35–38} For example, the use of 5,10,15-triazatruxene as a donor subunit in the D-A₃ system significantly reduced the time of thermally activated delayed fluorescence (TADF).³⁹ Nevertheless, not only the emissive properties of truxenes have been practically used. It is worth noting that the presence of heteroatoms in the truxene π -electron system allows the modulation of physicochemical properties, including electric conductivity, so that 5,10,15-triazatruxene^{40–53} and 5,10,15-trithiatruxene⁵⁴ derivatives have been used as hole transporting materials in prototype photovoltaic devices. A relatively new class of aromatic systems based on the truxene core are 5-hetero- and 5,10-diheterotruxenes. The synthesis and reactivity of 5-heterotruxenes has been described for compounds containing nitrogen,⁵⁵ oxygen,⁵⁶ and sulfur.⁵⁷ 5-Thiatruxene derivatives were also used to develop deep blue emitters used in the prototype OLED device characterized by high stability.⁵⁸ In the case of 5,10-dihetero compounds, only the carbonyl derivatives are known, namely, 5,10-dithiatruxen-15-one⁵⁹ and 5,10-diazatruxen-15-one,⁶⁰ which can be applied as ambipolar semiconductors.⁶¹ Due to the fact that the synthesis, reactivity, and physicochemical properties of nonsymmetric heterotruxenes are barely known, there is still a lot to explore.

RESULTS AND DISCUSSION

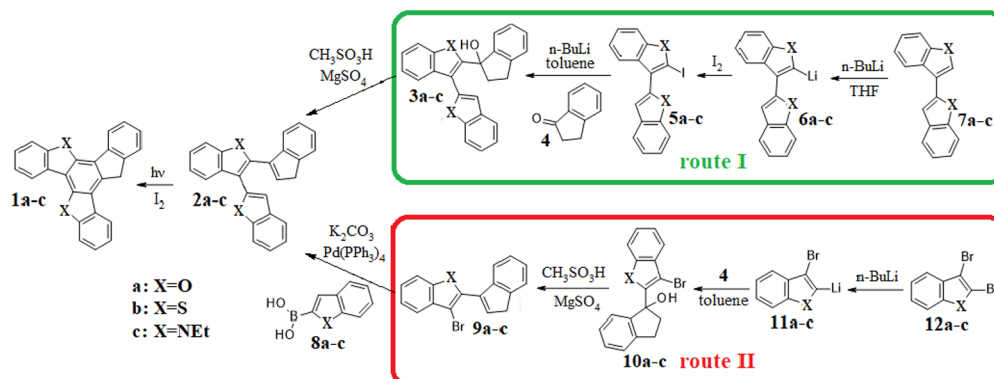
Schemes 1 and 2 present three general procedures, routes I, II, and III, leading to the formation of 5,10-diheterotruxene core. Despite the very useful knowledge gained during the synthesis of 5-heterotruxenes,^{56,55} the obtaining of 5,10-diheterotruxenes demands a slightly different approach.

5,10-Dioxatruxene OOC. The work on the soluble derivatives of 5,10-diheterotruxenes began with the synthesis of ethylated 5,10-dioxatruxene OOC. The first and the most promising attempt to obtain OOC was a synthesis according to route III (Scheme 2). During acidic condensation between **14** and **15a**, the ketone **13a** was formed but in a trace amount; therefore, alternative synthetic routes had to be developed. An alternative synthetic strategy of OOC is based on photocyclization of **2a**, which enables the formation of 5,10-dioxatruxene **1a** (Scheme 1). As a result of alkylation, **1a** is converted to the diethylated derivative OOC. The trimer **2a** can be synthesized in two different ways. Route I is based on addition of organolithium compound **6a** to indan-1-one **4**. The resulting alcohol **3a** undergoes dehydration in the presence of strong acidic media, for example, methanesulfonic acid. Another approach, route II, uses a palladium-catalyzed cross-coupling reaction between **8a** and **9a**. Due to the availability of reagents and the ease of synthesis of the corresponding precursors, route I seems to be the most appropriate for the synthesis of OOC.

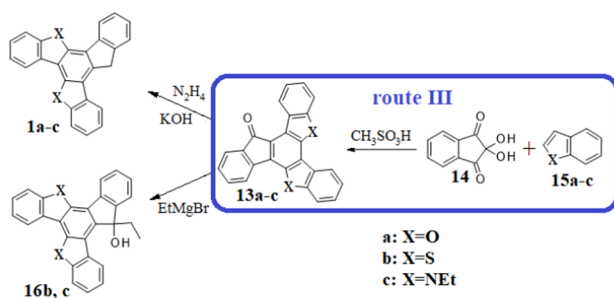
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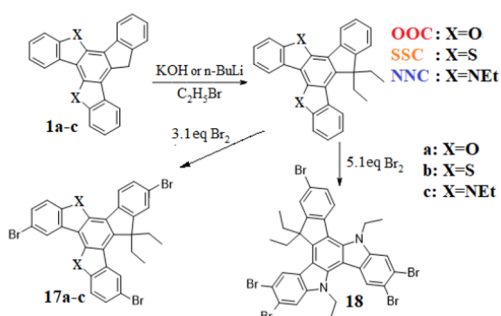
Scheme 1. First and Second Approach to Synthesis of 5,10-Diheterotruxenes through Photocyclization



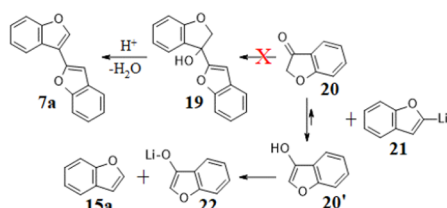
Scheme 2. Third approach to Synthesis of 5,10-Diheterotruxenes through Ketone Intermediate and Synthesis of the Alcohols 16b and 16c



Scheme 3. Synthesis of the Soluble 5,10-Diheterotruxenes OOC, SSC, and NNC and Their Reactivity



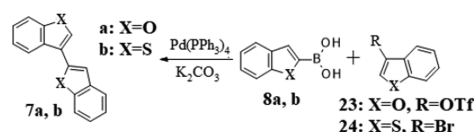
Research leading to OOC began with the synthesis of dimer 7a (route I). The first approach that could enable the formation of 7a was the addition of an organolithium compound 21 to benzo[*b*]furan-3-one 20, leading to alcohol 19, which, after dehydration, can be converted into the final compound 7a (Scheme 4). However, due to the significant shift of equilibrium into the enol form 20', the nucleophilic addition carried out in toluene was unsuccessful, leading mainly to benzo[*b*]furan 15a

Scheme 4. Reaction of 18 with Benzo[*b*]furan-3-one 20

and the deprotonation product 22. Therefore, it was necessary to develop an alternative synthesis path leading to the desired biaryl system 7a.

To perform successful synthesis of 7a, well-known arene transformation, called the Suzuki reaction, was applied (Scheme 5). As a result of the reaction between ketone 20 and

Scheme 5. Synthesis of Biaryls 7a and 7b

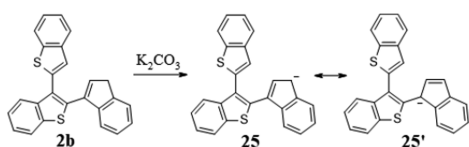


trifluoromethanesulfonic anhydride in the presence of triethylamine, triflate 23 was obtained. The cross-coupling reaction of 23 with 8a led to biaryl 7a. It should be mentioned that the esterification ought to be carried out in solvents such as chlorinated hydrocarbons, which do not react with trifluoromethanesulfonic acid, present in triflic anhydride as impurity.

The biaryl 7a underwent direct lithiation in the presence of *n*-butyllithium in tetrahydrofuran (route I, Scheme 1). Lithiation of derivative 7a is easier than lithiation of benzo[*b*]furan 15a, which results from coordination of the lithium atom with the external oxygen atom of the neighboring benzo[*b*]furan subunit. The generated organolithium derivative 6a after the reaction with iodine led to the iododerivative 5a. As a result of lithiation of 5a in toluene, an organometallic compound is obtained, which afterward reacted with ketone 4, leading to the alcohol 3a. The nucleophilic addition turns out to be very sensitive to temperature; therefore, the indan-1-one-4 solution should be added very slowly to increase the efficiency of the addition to the carbonyl group. The resulting hydroxyl derivative 3a was then treated with methanesulfonic acid, which initiated dehydration, finally leading to the formation of trimer 2a. Directly after the isolation, trimer 2a was irradiated with UV-C light in the presence of a catalytic amount of iodine, which leads to the photocyclization product 1a. As obtained, a nearly insoluble, orange solid containing 1a was used in the next step (Scheme 3). Alkylation of 5,10-dioxatruxene 1a under an argon atmosphere in the basic environment results in the formation of a soluble derivative, OOC. The introduction of two ethyl groups to the aromatic system of 1a significantly increased its solubility. However, solubility of 1a is much lower corresponding to the tetraethylated derivative of 5-oxatruxene. The described effect is a consequence of increased intermolecular interactions occurring between benzo[*b*]furan subunits (Figure S1).

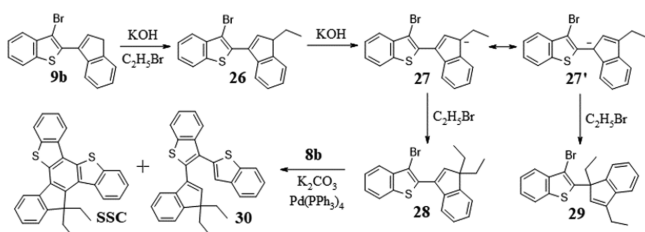
5,10-Dithiatruxene. Route III (Scheme 2) was successfully applied in the synthesis of ketone **13b**.⁵⁹ The use of methanesulfonic acid in 1,2-dichloroethane allows us to increase the reaction yield from 68 to 74%. Due to very low solubility of **13b**, the carbonyl group does not undergo reduction, preventing quick conversion of **13b** to **1b** and then to SSC. The first synthetic approach, leading to a soluble derivative of 5,10-dithiatruxene SSC, was analogous to OOC synthesis (route I, Scheme 1). Biaryl **7b**, obtained from the Suzuki reaction between **8b** and **24** (Scheme 5), was subjected to direct lithiation to obtain an organometallic compound **6b**, which, after reacting with iodine, leads to the monoiododerivative **5b**. However, very low solubility of **5b** in toluene caused insufficient iodine to lithium exchange. Generation of the organolithium compound **6b** in toluene became complicated and its addition to the ketone **4** was impossible to achieve. Replacement of an iodine atom with a bromine one did not significantly change the solubility of the compound. On the other hand, the addition to the carbonyl group in tetrahydrofuran leads only to the protonation of the organolithium compound **5b**. For this reason, it was necessary to use an alternative synthetic path, enabling the preparation of trimer **2b**. The trimer **2b** can also be obtained by palladium-catalyzed cross-coupling route II (Scheme 1). For this purpose, the generated organolithium compound **11b** was reacted with indan-1-one **4**. After the subsequent dehydration of alcohol **10b**, the bromoderivative **9b** was formed. The reaction between boronic acid **8b** and **9b** in the presence of the base and the palladium catalyst led to both trimer **2b** and traces of 5,10-dithiatruxene **1b**. In addition to the expected products, a large amount of colored byproducts was also created. The unexpected course of the described transformation could be a consequence of the acidic nature of the hydrogen atoms in the 1*H*-indene subunit of trimer **2b**, which may undergo ionization under Suzuki reaction conditions (Scheme 6). The formed reactive anion **25** could undergo further transformations, leading to colored byproducts present in the reaction mixture.

Scheme 6. Ionization of Trimer 2b



To confirm or disprove the proposed explanation of the reaction course, the trimer **30** protected by an ethyl group indene subunit was synthesized (Scheme 7). The first step was the alkylation of **9b**, which led to a mixture of two isomeric ethylated products **28/29** in a ratio of ~1:5.

Scheme 7. Synthesis of Trimer 30



The composition of the reaction mixture after alkylation can be estimated by analysis of the spatial structure of the intermediate anion **27**. Possible structures differ in the places where the bromoethane attack occurs, leading to the generation of the expected product **28** and the side product **29**. A seemingly more crowded position, located closer to the benzo[*b*]thiophene subunit, turns out to be much more susceptible to the attack of the alkylating agent (Figure 1). This is directly related to the flat structure of the benzo[*b*]thiophene subunit. To obtain the lowest possible molecular energy, which is equivalent to achieving the most effective electron coupling between π -electron systems, the whole molecule is flattened as much as possible. Such orientation of aromatic subunits leads to the more stable carbanion **27'**, resulting in a smooth approach of the alkylating agent. Attack on an adjacent position to the ethyl group is more difficult due to the steric hindrance. The bromoderivative **28** underwent palladium-catalyzed cross-coupling with boronic acid **8b** despite the presence of the ethyl moieties. This process leads to the trimer **30**, traces of SSC, and a large number of colored byproducts. A similar reaction result in the case of **2b** or **30** indicated its instability in Suzuki coupling conditions associated with the electronic structure rather than their ionization capability. Photocyclization of trimer **2b** in the presence of iodine in hexane, under UV-C light (Scheme 1), led to an insoluble substance, which did not undergo alkylation. Mass spectrometry analysis suggests that the obtained compound is the cyclic product **31** (Scheme 8). Low solubility of **31** in hexane prevents the subsequent reaction with iodine, leading to 5,10-dithiatruxene **1b**. For this reason, it was necessary to use the toluene solvent as the proper environment for photocyclization of **2b**. **2b** was irradiated with UV-C light and the obtained orange solid was subjected to alkylation reaction, leading to diethyl derivative of 5,10-dithiatruxene SSC.

5,10-Diazatruxene. The literature-known acidic condensation of ninhydrin with indoles seems to be the only way leading to the 5,10-diazatruxene core (route I, Scheme 1).^{60,61} The photocyclization approach, successful in 5-azatruxene synthesis, was not suitable due to the high reactivity of the trimer **2c**. In addition, the nitrene insertion, successfully used in the synthesis of the 5-azatruxene core, in this case, leads to a complicated mixture of products.⁵⁵ In the presence of strong protic acid, ninhydrin **14** undergoes condensation with indole derivative **15c**, leading to ketone **13c**. In contrast to the previously discussed carbonyl compound **13b**, ketone **13c** has two ethyl groups as a solubilizing agent, allowing Wolff–Kishner reduction. Surprisingly, the most problematic step in the synthesis of soluble derivative NNC turns out to be the double ethylation of the methylene group. Ethylation of 5,10-diethyl-5,10-diazatruxene **1c**, carried out in the same conditions as previously used in the synthesis of OOC and SSC, leads to multiple colored products. This rather unusual behavior of **1c** in alkaline conditions suggests decomposition of anions formed in the reaction environment. Numerous experiments have made it possible to obtain the desired structure of NNC. **1c** was alkylated at $-40\text{ }^{\circ}\text{C}$ in dimethylformamide, saturated with argon. Despite lower temperature than in the case of OOC and SSC, the amount of bromoethane during ethylation increased from 4.4 to 20.8 equiv. Such conditions were dictated by the faster conversion of unstable anions. Also, the order of adding reagents has changed. The alkylating agent was added first into the reaction mixture, followed by addition of the base. The described procedure finally allows for the synthesis of NNC but still with a relatively low reaction yield, i.e., 14%. Further

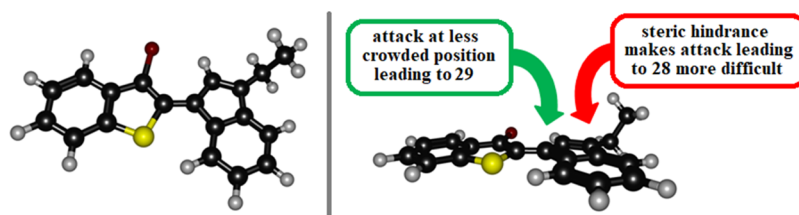
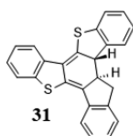


Figure 1. Structure of anion 27 and possible attacks of the alkylating agent.

Scheme 8. Probable Structure of 31



experiments enabled a distinct increase in the alkylation yield up to 45.1%. To achieve such a result, *n*-butyllithium at $-78\text{ }^{\circ}\text{C}$ was added as the ionizing agent. All soluble 5,10-diheterotruexene derivatives (OOC, SSC, and NNC) underwent a characteristic reaction for aromatic systems, namely, electrophilic substitution. Triple bromination, leading to 17 (Scheme 3), can be easily carried out in the presence of 3 equiv of bromine in dichloromethane, while using the excess of bromine results in up to five bromine atoms in the 5,10-diazatruexene core, 18. Bromoderivatives 17 and 18 can be used for further functionalization to tune the physicochemical properties for optoelectronic application. Another possible way to modify the 5,10-diheterotruexene core is to use the reactivity of the carbonyl group present in compounds 13a–13c. Despite poor solubility of ketones 13b and 13c, their reactions with organometallic compounds such as ethylmagnesium bromide at elevated temperature resulted in efficient conversion to 16b and 16c.

CONCLUSIONS

The presented three general methods for creating the 5,10-diheterotruexene skeleton, presented in this paper, allow the introduction of two heteroatoms of the same type. During the synthesis of diheterotruexenes, particular attention should be paid to the photocyclization approach presented in Scheme 1 (routes I and II). Due to the availability of reagents, benzo[*b*]heteroatoms, further exploration of the diheterotruexene family is possible. In addition, it can be used in the synthesis of novel diheterotruexenes having two different heteroatoms. The dramatically low solubility of the appropriate reagents in the most common solvents was the most serious obstacle to obtain unsubstituted 5,10-diheterotruexenes. Hence, special attention has been paid to the matter of solubility. Good solubility connected with increased aggregation of 5,10-diheterotruexenes in the solid state, comparing 5-heterotruexenes, suggests the use of OOC, SSC, and NNC derivatives as a solution-processible organic semiconductors. In turn, the functionalization of positions 2, 8, 13, and 15 allows the synthesis of new fluorophores for optoelectronics industry or for detection of volatile substances. The presented synthetic approach, leading to unsymmetrical 5,10-diheterotruexenes, also opens the possibility of synthesis of other hard-to-reach soluble condensed aromatic and heteroaromatic systems. The crystallographic and spectroscopic experimental data, placed in the Supporting Information, will be discussed in detail in a separate paper.

EXPERIMENTAL SECTION

General Information. All solvents used were of analytical grade. Toluene and tetrahydrofuran used in the lithiation reaction were freshly distilled from LiAlH_4 under an argon atmosphere. Benzo[*b*]thiophene, benzo[*b*]furan, indole, and indan-1-one were delivered from ABCR. All reactions requiring heating were carried out using a heating mantle. An OSRAM UV-C Puritec HNS L 2G11, 55 W, lamp was the source of UV-C radiation during the photocyclization. The photocyclization was carried out directly in the reaction vessel. The emission spectrum of the UV-C lamp can be found in the Supporting Information. The mass spectra were collected at an Applied Biosystems 4000Q TRAP with electron impact as the ionization method. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were measured at a Bruker DRX 500 MHz in CD_2Cl_2 or CDCl_3 . The shift of the residual peak of solvents was taken as an internal chemical shift. The absorption and emission spectra were measured for diluted samples (absorbance below 0.1). Dichloromethane used as a solvent was distilled prior to the experiment. Absorption was recorded using a UV 2401 spectrophotometer (Shimadzu, Japan). The emission spectra were collected using a Fluorolog FL3-22 (Horiba Jobin Yvon, France). Quantum yield values were obtained by the absolute method using an integrating sphere. Calculations were performed using DFT theory with the b3lyp/6-31g(d,p) set for molecules in vacuum.

Benzofuran-3(2*H*)-one (20). Phenoxyacetic acid (7.61 g, 50 mmol) was dissolved in 50 mL of thionyl chloride and refluxed. After 4 h, the mixture was cooled and excess of thionyl chloride was evaporated under reduced pressure. The liquid residue was dissolved in 50 mL of dichloromethane. The obtained solution was added to a suspension of 13 g (98 mmol) of anhydrous aluminum chloride in 50 mL of dichloromethane cooled down to $0\text{ }^{\circ}\text{C}$. After 15 min from addition of the acid chloride, the mixture was brought to room temperature, and after a further 30 min, the solution was poured onto ice. The organic layer was separated, while aqueous layer was extracted three times with 50 mL of dichloromethane. Next, combined extracts were dried over MgSO_4 and evaporated. The crude product was purified via column chromatography using silica gel as the stationary phase and 10% ethyl acetate in hexane solution as the eluent to give 2.41 g of a yellow solid, with the reaction yield of 36%. The mp $97\text{ }^{\circ}\text{C}$ is consistent with literature data.⁶² ^1H NMR (400 MHz, CDCl_3) δ : 7.80–7.51 (m, 2H), 7.23–6.99 (m, 2H), 4.65 (d, $J = 15.6\text{ Hz}$, 2H).

Benzo[*b*]furan-3-yl Trifluoromethanesulfonate (23). To 5 mL of dichloromethane distilled from H_2SO_4 were added 670 mg (5 mmol) of benzo[*b*]furan-3(2*H*)-one 20 and 1.05 mL (7.5 mmol, $d = 0.735\text{ g/mL}$) of triethylamine distilled from CaH_2 . The solution, kept under argon, turned red and then was cooled down to $-40\text{ }^{\circ}\text{C}$. Next, 1.26 mL (7.5 mmol, $d = 1.667\text{ g/mL}$) of trifluoromethanesulfonic anhydride was added slowly and the mixture was brought to room temperature. After about 0.5 h, 5 mL of water was added, the organic layer was separated, and the aqueous phase was extracted with 5 mL of dichloromethane. The combined extracts were dried over MgSO_4 and evaporated. The crude product was purified via column chromatography using silica gel as the stationary phase and 10% dichloromethane in hexane solution as the eluent to give 1.05 g of a light yellow liquid, with the reaction yield of 80%. The analysis is consistent with the literature data.⁶³ ^1H NMR (300 MHz, CDCl_3) δ : 7.38 (td, $J = 7.2, 1.3\text{ Hz}$, 1H), 7.44 (td, $J = 7.2, 1.3\text{ Hz}$, 1H), 7.54 (dd, $J = 7.2, 1.3\text{ Hz}$, 1H), 7.65 (dd, $J = 7.2, 1.3\text{ Hz}$, 1H), 7.84 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, CDCl_3) δ : 111.2, 118.1, 118.8, 120.2, 124.1, 126.2, 134.1, 135.3, 153.2.

Benzo[b]furan-2-ylboronic Acid (8a). To 40 mL of tetrahydrofuran was added 4.4 mL (40 mmol, $d = 1.072$ g/mL) of benzo[b]furan **15a**, the mixture was cooled down to -78 °C, and 16 mL (40 mmol, 2.5 M) of a solution of *n*-butyllithium in hexane was added; a white precipitate appeared. After 1 h, the mixture was brought to room temperature and cooled down again to -78 °C. Then, 5 mL (45 mmol, $d = 0.932$ g/mL) of trimethylborate was added and the obtained solution was slowly elevated to room temperature. After that, 10 mL of aqueous HCl (1:9, HCl/water) was added to the mixture and extracted three times with 40 mL of dichloromethane. The combined extracts were dried over $MgSO_4$ and evaporated. The obtained solid residue was treated with 40 mL of hexane, cooled to 0 °C, and filtered. A white solid (4.41 g) as a final product was obtained, with the reaction yield of 68%. The analysis is consistent with the literature data.⁶⁴ 1H NMR (500 MHz, $DMSO-d_6/D_2O$, 95:5) δ : 7.71 (d, $J = 8.0$ Hz, 1H), 7.60 (d, $J = 8.5$ Hz, 1H), 7.50 (s, 1H), 7.37 (t, $J = 8.0$ Hz, 1H), 7.26 (t, $J = 7.5$ Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $DMSO-d_6/D_2O$, 95:5) δ : 156.4, 127.6, 125.3, 122.5, 121.8, 117.5, 111.4.

3-(Benzo[b]furan-2-yl)benzo[b]furan (7a). To 60 mL of a mixture of xylene/ethanol (2:1) under an argon atmosphere were added 810 mg (5 mmol) of benzo[b]furan-2-ylboronic acid **8a**, 1.33 g (5 mmol) of benzo[b]furan-3-yl trifluoromethanesulfonate **23**, 231.12 mg (0.2 mmol) of $Pd(PPh_3)_4$, and 7.5 mL (15 mmol, 2 M) of an aqueous solution of K_2CO_3 , and then the solution was refluxed. The mixture turned muddy light brown. After 21 h, the reaction was cooled and evaporated to dryness. The crude product was purified via column chromatography using silica gel as the stationary phase and hexane as the eluent to give 625 mg of a white solid, with the reaction yield of 53%. The mp was 85 °C. 1H NMR (500 MHz, CD_2Cl_2) δ : 8.18 (s, 1H), 8.03–7.99 (m, 1H), 7.64 (broad d, $J = 7.52$ Hz, 1H), 7.60 (m, 1H), 7.55 (dd, $J = 8.0, 0.7$ Hz, 1H), 7.44–7.40 (m, 2H), 7.32 (dt, $J = 7.81, 1.35$, 1H), 7.27 (dt, $J = 7.85, 1.02$, 1H), 7.10 (s, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ : 155.5, 148.1, 143.2, 129.3, 128.9, 125.6, 124.8, 123.9, 123.4, 121.1, 112.2, 111.6, 111.2, 102.9; HRMS (EI–TOF) m/z (M^+): calcd for $C_{16}H_{10}O_2$, 234.0681; found, 234.0684; elemental analysis (%): calcd for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30. Found: C, 82.91; H, 4.88.

2-Jodo-3-(benzo[b]furan-2-yl)benzo[b]furan (5a). To 6 mL of tetrahydrofuran was added 702 mg (3 mmol) of 3-(benzo[b]furan-2-yl)benzo[b]furan **7a**, then the mixture was cooled down to -40 °C, and 1.8 mL (4.5 mmol, 2.5 M) solution of *n*-butyllithium in hexane was added; the mixture grew muddy and turned green. After 1 h, 1.14 g (4.5 mmol) of iodine was added and the mixture was brought to room temperature. Then, 3 mL of a saturated Na_2SO_3 aqueous solution and 6 mL of dichloromethane were added. After discoloration of the mixture, the phases were separated, the aqueous layer was extracted with 6 mL of dichloromethane, and the combined extracts were dried over $MgSO_4$ and evaporated. The solid residue was suspended in 6 mL of methanol and filtrated to give 1.02 g of a light yellow solid, with the reaction yield of 94%. 1H NMR (500 MHz, CD_2Cl_2) δ : 8.18–8.13 (m, 1H), 7.71–7.68 (m, 1H), 7.63 (dd, $J = 8.1, 0.7$ Hz, 1H), 7.57–7.55 (m, 1H), 7.43 (d, $J = 0.9$ Hz, 1H), 7.39–7.34 (m, 3H), 7.32–7.28 (dt, $J = 7.2, 1.1$, 1H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ : 158.6, 154.9, 149.3, 128.7, 126.6, 125.6, 125.0, 124.1, 123.6, 121.4, 121.2, 120.0, 111.5, 111.3, 104.6, 97.5; HRMS (EI–TOF) m/z (M^+): calcd for $C_{16}H_9IO_2$, 359.9647; found, 359.9639; elemental analysis (%): calcd for $C_{16}H_9IO_2$: C, 53.36; H, 2.52. Found: C, 54.04; H, 2.74.

15,15-Diethyl-5,10-dioxatruene (OOC). For step I (synthesis of trimer **2a**), to 12 mL of toluene was added 720 mg (2 mmol) of 2-iodo-3-(benzo[b]furan-2-yl)benzo[b]furan **5a**, and the mixture was cooled down to -78 °C. Next, 0.8 mL (2 mmol, 2.5 M) of *n*-butyllithium in hexane was added; the solution turned yellow. After 10 min, 264 mg (2 mmol) of indan-1-one **4** dissolved in 10 mL of anhydrous toluene was slowly added and then brought to room temperature. After 1.5 h, an NH_4Cl aqueous solution (107 mg in 2 mL of water) was added, the phases were separated and the organic layer was evaporated. The mixture was then dissolved in 2 mL of 1,2-dichloroethane and 0.13 mL (2 mmol, $d = 1.48$ g/mL) of CH_3SO_3H , and 240 mg of $MgSO_4$ was added followed by boiling. After 0.5 h, the mixture was cooled, 4 mL of water and 6 mL of dichloromethane were added, and the organic layer was separated, dried over $MgSO_4$, and

evaporated. The crude product was purified via column chromatography using silica gel as the stationary phase and hexane \rightarrow 10% solution of dichloromethane in hexane \rightarrow 15% solution of ethyl acetate in hexane as the eluent to obtain 370 mg of **2a** as a white solid, with the reaction yield of 53%. For step II (photocyclization and alkylation), to 1.06 L of hexane were added 370 mg (1.06 mmol) of **2a** and 26.71 mg (0.106 mmol) of iodine. Then, the solution was irradiated with UV-C light. After 1 h, the reaction mixture was concentrated, and the resulting orange precipitate was filtered. The obtained material was then suspended in 5.3 mL of dimethylformamide (saturated with argon at 0 °C for 1 h) and 0.35 mL (4.66 mmol, $d = 1.46$ g/mL) of ethyl bromide, and 0.26 g (4.66 mmol) of ground KOH was added with stirring. After 24 h, 5.8 mL of water was added and the mixture was extracted three times with 2.9 mL of dichloromethane. Combined organic layers were dried over $MgSO_4$ and evaporated. The crude product was purified via column chromatography using silica gel as the stationary phase and 10% solution of dichloromethane in hexane as the eluent to obtain 183 mg of a white solid, with the reaction yield of 43%. The mp was 230 °C. 1H NMR (500 MHz, $CDCl_3$) δ : 8.41 (d, $J = 7.53$ Hz, 1H), 8.34 (d, $J = 7.16$ Hz, 1H), 8.33 (d, $J = 7.18$ Hz, 1H), 7.78 (d, $J = 7.78$ Hz, 1H), 7.76 (d, $J = 7.55$ Hz, 1H), 7.57–7.44 (m, 6H), 7.39 (td, $J = 7.4, 1.0$ Hz, 1H), 2.84–2.77 (m, 2H), 2.42–2.28 (m, 2H), 0.27 (t, $J = 7.25$ Hz, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ : 157.0, 156.3, 151.2, 150.4, 149.4, 144.1, 139.7, 127.3, 126.8, 126.4, 125.9, 123.7, 123.6, 123.4, 123.0, 122.4, 122.3, 122.2, 122.1, 121.9, 115.8, 112.1, 111.8, 109.1, 59.1, 30.6, 8.7; HRMS (EI–TOF) m/z (M^+): calcd for $C_{29}H_{22}O_2$, 402.1620; found, 402.1636 (M^+); elemental analysis (%): calcd for $C_{29}H_{22}O_2$: C, 86.54; H, 5.51. Found: C, 86.44; H, 6.01.

2,3-Dibromobenzo[b]thiophene (12b). Benzo[b]thiophene **15b** (45.7 g, 341 mmol) was dissolved in 480 mL of chloroform and then 39 mL (755 mmol, $d = 3.1028$ g/mL) of bromine was slowly added. After 20 h, 60.9 mL of dichloromethane and 60.9 mL of saturated aqueous solution of $Na_2S_2O_3$ were added. The organic layer was separated, dried over $MgSO_4$, and evaporated. The obtained oil was treated with 250 mL of hexane and cooled in the freezer. After solidifying, the mixture was brought to room temperature and the resulting precipitate was filtered off. The filtrate was concentrated and recooled and the formed solid was filtered. (The process was repeated several times because there was still a lot of product in the postcrystallization liquor.) Finally, 83.58 g of a white solid, with the reaction yield of 84%, was obtained. The mp was 54 °C. The analysis is consistent with the literature data.⁶⁵ 1H NMR (400 MHz, $CDCl_3$) δ : 7.72 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 8.0$ Hz, 2H), 7.41–7.36 (m, 2H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ : 139.1, 137.7, 125.9, 125.7, 123.5, 122.1, 114.4, 111.9.

3-Bromobenzo[b]thiophene (24). To 55 mL of tetrahydrofuran was added 16.06 g (55 mmol) of 2,3-dibromobenzo[b]thiophene **12b**, and the mixture was cooled down to -40 °C, followed by slow addition of 22 mL (55 mmol, 2.5 M) of a solution of *n*-butyllithium in hexane. After addition, the mixture turned yellow and the precipitate appeared. After 1 h of stirring, at a constant temperature, 22 mL of water was added to the solution and the organic layer was separated, whereas the aqueous layer was extracted two times with 55 mL of dichloromethane. Then, combined extracts were dried over $MgSO_4$ and evaporated. The crude product was distilled under reduced pressure to give 10.43 g of a colorless liquid, with the reaction yield of 89%. The analysis is consistent with the literature data.⁶⁶ 1H NMR (300 MHz, $CDCl_3$) δ : 7.88–7.86 (m, 2H), 7.52–7.41 (m, 3H).

Benzo[b]thien-2-ylboronic Acid (8b). To 40 mL of tetrahydrofuran was added 5.36 g (40 mmol) of benzo[b]thiophene **15b**, and then the mixture was cooled down to -78 °C. Next, 16 mL (40 mmol, 2.5 M) of a solution of *n*-butyllithium in hexane was added; a white precipitate appeared. After 1 h, the mixture was brought to room temperature and cooled down again to -78 °C. Then, 5 mL (45 mmol, $d = 0.932$ g/mL) of trimethylborate was added and obtained solution was slowly elevated to room temperature. After that, 10 mL of aqueous HCl (1:9, HCl/water) was added to the mixture and extracted three times with 40 mL of dichloromethane. Combined extracts were dried over $MgSO_4$ and evaporated. The solid residue was treated with 40 mL of hexane, cooled down to 0 °C, and filtered. A white solid (5.49 g), with

the reaction yield of 77%, was obtained. The analysis is consistent with the literature data.⁶⁷ ¹H NMR (500 MHz, acetone-*d*₆) δ : 7.99–7.93 (m, 2H), 7.91 (m, 1H), 7.59 (s, 2H), 7.41–7.33 (m, 2H); ¹³C{¹H} NMR (126 MHz, acetone-*d*₆) δ : 143.4, 140.8, 132.6, 124.8, 124.0, 123.8, 122.2.

3-(Benzo[*b*]thien-2-yl)benzo[*b*]thiophene (7b). To 12 mL of tetrahydrofuran under an argon atmosphere were added 123 mg (1 mmol) of 3-bromobenzo[*b*]thiophene **24**, 178 mg (1 mmol) of benzo[*b*]thien-2-ylboronic acid **8b**, 7 mg (0.04 mmol) of palladium(II) chloride, 42 mg (0.16 mmol) of triphenylphosphine, and 1.5 mL (3 mmol, 2 M) of K₂CO₃ aqueous solution, and then the obtained solution was kept under reflux. The mixture turned muddy light brown that changed into red-brown as the reaction proceeded. After 3 h, the solution was cooled and evaporated to dryness. The crude product was purified via column chromatography using silica gel as the stationary phase and hexane as the eluent. A white solid (126.5 mg), with the reaction yield of 48%, was obtained. The analysis is consistent with the literature data.⁶⁸ ¹H NMR (400 MHz, CDCl₃) δ : 8.31 (d, *J* = 8.00 Hz, 1H), 7.98 (d, *J* = 7.60 Hz, 1H), 7.93 (d, *J* = 7.60 Hz, 1H), 7.89 (d, *J* = 7.60 Hz, 1H), 7.66 (s, 1H), 7.62 (s, 1H), 7.56–7.41 (m, 4H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ : 140.8, 140.4, 139.4, 137.7, 137.3, 130.8, 125.5, 125.0, 124.9, 124.7, 124.5, 123.7, 123.2, 123.1, 122.3, 121.6.

2-Jodo-3-(benzo[*b*]thien-2-yl)benzo[*b*]thiophene (5b). To 3 mL of tetrahydrofuran was added 399 mg (1.5 mmol) of 3-(benzo[*b*]thien-2-yl)benzo[*b*]thiophene **7b**. Then, the solution was cooled down to –40 °C and 0.9 mL (2.25 mmol, 2.5 M) of a solution of *n*-butyllithium in hexane was added; the mixture turned purple, and after a while, a pink precipitate was formed. After 1 h, 571.3 mg (2.25 mmol) of iodine was added and the solution was brought to room temperature. After warming, 1.5 mL of a saturated aqueous Na₂SO₃ solution and 3 mL of dichloromethane were added. After discoloration of the mixture, the phases were separated, the aqueous layer was extracted with 3 mL of dichloromethane, and the combined extracts were dried over MgSO₄ and evaporated. The solid residue was suspended in 3 mL of methanol and filtered to give 547.4 mg of a light yellow solid, with the reaction yield of 93%. The mp was 165 °C. ¹H NMR (500 MHz, CD₂Cl₂) δ : 7.93 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.82 (t, *J* = 8.4 Hz, 2H), 7.47 (s, 1H), 7.46–7.40 (m, 2H), 7.39–7.32 (m, 2H); ¹³C{¹H} NMR (126 MHz, CD₂Cl₂) δ : 144.0, 141.0, 140.1, 139.0, 136.9, 136.5, 126.0, 125.4, 125.3, 125.1, 124.9, 124.3, 123.1, 122.6, 121.9, 84.3; HRMS (EI–TOF) *m/z* (*M*⁺): calcd for C₁₆H₉IS₂, 391.9190; found, 391.9193; elemental analysis (%): calcd for C₁₆H₉IS₂: C, 48.99; H, 2.31. Found: C, 48.45; H, 2.41.

3-(3-Bromobenzo[*b*]thien-2-yl)-1*H*-indene (9b). To 60 mL of toluene was added 2.92 g (10 mmol) of 2,3-dibromobenzo[*b*]thiophene **12b**, and then the obtained solution was cooled down to –78 °C. After that, 4 mL (10 mmol, 2.5 M) of a solution of *n*-butyllithium in hexane was added; a white precipitate appeared. After 30 min, a solution of 1.32 g (10 mmol) of indan-1-one **4** in 20 mL of toluene was slowly added; after a while, the precipitate dissolves. The solution transferred to room temperature turned yellow. After 1 h, 10 mL (10 mmol, 1 M) of an aqueous NH₄Cl was added. The aqueous layer was extracted with 60 mL of dichloromethane and then the combined extracts were evaporated. The obtained residue was dissolved in 10 mL of 1,2-dichloroethane, and 0.973 mL (15 mmol, *d* = 1.48 g/mL) of CH₃SO₃H and 1.2 g of MgSO₄ were added. The solution was refluxed 30 min and then cooled. A K₂CO₃ aqueous solution (5 mL, 10 mmol, 2 M) and dichloromethane (5 mL) were added. The organic layer was separated, dried over MgSO₄, and evaporated. The solid residue was dissolved in 10 mL of dichloromethane, and 20 mL of methanol was added. Then, dichloromethane was slowly evaporated. The resulting white solid was collected by filtration to give 2.4 g, with the reaction yield of 73%. The mp was 109 °C. ¹H NMR (500 MHz, CD₂Cl₂) δ : 7.91 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.55–7.50 (m, 1H), 7.48–7.43 (m, 1H), 7.34 (dd, *J* = 7.4, 6.9 Hz, 1H), 7.30 (td, *J* = 7.4, 0.9 Hz, 1H), 7.00 (t, *J* = 2.1 Hz, 1H), 3.64 (d, *J* = 2.0 Hz, 2H); ¹³C{¹H} NMR (126 MHz, CD₂Cl₂) δ : 144.2, 143.6, 139.0, 138.3, 137.7, 136.8, 133.2, 126.6, 125.9, 125.8, 125.6, 124.4, 123.7, 122.7, 121.4, 106.9, 39.3; HRMS (EI–TOF) *m/z* (*M*⁺): calcd

for C₁₇H₉SBr, 325.9725; found, 325.9760; elemental analysis (%): calcd for C₁₇H₉SBr: C, 62.40; H, 3.39. Found: C, 62.74; H, 3.83.

3-(3-Bromobenzo[*b*]thien-2-yl)-1,1-diethyl-1*H*-indene (28) and 3-(3-Bromobenzo[*b*]thien-2-yl)-1,3-diethyl-1*H*-indene (29). To 50 mL of dimethylformamide (saturated with argon at 0 °C for 1 h) was added 3.27 g (10 mmol) of 3-(3-bromobenzo[*b*]thien-2-yl)-1*H*-indene **9b**, followed by addition of 2.46 g (44 mmol) of shredded potassium hydroxide and 3.28 mL (44 mmol, *d* = 1.46 g/mL) of bromoethane; the mixture turned dark yellow. After stirring for 24 h, 50 mL of water was added and the mixture was extracted three times with 50 mL of hexane. The organic layer was dried over MgSO₄ and evaporated. The crude product was purified via column chromatography using silica gel as the stationary phase and petroleum ether as the eluent to obtain 351 mg of **28** as a white solid, with the reaction yield of 92%. The mp was 91 °C. Without changing the eluent (petroleum ether), 1.89 g of **29**, with the reaction yield of 49%, as a white solid was obtained. The mp was 59 °C. **28** has slightly larger *R*_f (SiO₂/hexane) compared to **29** and changed color to orange after irradiation with UV-C light. For **28**: ¹H NMR (400 MHz, CDCl₃) δ : 7.89 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.50 (dd, *J* = 9.5, 5.5 Hz, 2H), 7.46–7.39 (m, 1H), 7.32–7.26 (m, 3H), 6.71 (s, 1H), 2.05–1.84 (m, 4H), 0.70 (t, *J* = 7.4 Hz, 6H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ : 150.8, 147.0, 143.6, 139.0, 138.2, 135.1, 133.1, 126.7, 126.0, 125.7, 125.5, 123.9, 122.6, 122.2, 121.4, 107.1, 58.7, 30.5, 9.4; HRMS (EI–TOF) *m/z* (*M*⁺): calcd for C₂₁H₁₉SBr, 382.0391; found, 382.0392; elemental analysis (%): calcd for C₂₁H₁₉SBr: C, 65.80; H, 5.00. Found: C, 65.91; H, 5.11. For **29**: ¹H NMR (400 MHz, CDCl₃) δ : 7.78 (ddd, *J* = 8.1, 1.1, 0.7 Hz, 1H), 7.66–7.63 (m, 1H), 7.63–7.59 (m, 1H), 7.41–7.37 (m, 1H), 7.34 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.33–7.28 (m, 2H), 7.25 (td, *J* = 7.2, 1.8 Hz, 1H), 6.56 (t, *J* = 1.6 Hz, 1H), 2.77 (dq, *J* = 14.6, 7.3 Hz, 1H), 2.63–2.53 (m, 2H), 2.43–2.30 (m, 1H), 1.32 (t, *J* = 7.4 Hz, 3H), 0.74 (t, *J* = 7.3 Hz, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ : 150.1, 146.0, 145.1, 141.5, 140.1, 136.1, 133.4, 127.9, 125.6, 125.2, 125.1, 124.0, 122.8, 122.1, 119.8, 105.1, 58.7, 29.7, 20.9, 12.5, 9.4; HRMS (EI–TOF) *m/z* (*M*⁺): calcd for C₂₁H₁₉SBr, 382.0391; found, 382.0390; elemental analysis (%): calcd for C₂₁H₁₉SBr: C, 65.80; H, 5.00. Found: C, 65.74; H, 5.08.

3-(3-(Benzo[*b*]thien-2-yl)benzo[*b*]thien-2-yl)-1*H*-indene (2b). To 120 mL of tetrahydrofuran were added 1.78 g (10 mmol) of benzo[*b*]thien-2-ylboronic acid **8b**, 3.27 g (10 mmol) of 3-(3-bromobenzo[*b*]thien-2-yl)-1*H*-indene **9b**, and 924.45 mg (0.8 mmol) of Pd(PPh₃)₄, and after the dissolution of the substrates, 15 mL (30 mmol, 2 M) of K₂CO₃ aqueous solution was introduced. The solution was refluxed under an argon atmosphere. The mixture turned muddy dark brown. After 24 h, it was cooled and the organic layer was separated and evaporated. The crude product was purified via column chromatography using silica gel as the stationary phase and hexane → 4% solution of dichloromethane in hexane (after collecting the substrate) as the eluent. The obtained product was dissolved in 15 mL of dichloromethane and very slowly evaporated. Then, 30 mL of methanol was added. The precipitate was collected by filtration to give 1.91 g of a white solid, with the reaction yield of 50%. The mp was 180 °C. ¹H NMR (500 MHz, CD₂Cl₂) δ : 8.04–8.01 (m, 1H), 7.96–7.93 (m, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.78–7.75 (m, 1H), 7.51–7.48 (m, 1H), 7.48–7.44 (m, 2H), 7.40 (s, 1H), 7.38–7.37 (m, 1H), 7.35 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.33–7.29 (m, 1H), 7.21–7.14 (m, 2H), 6.75 (t, *J* = 2.1 Hz, 1H), 3.54 (d, *J* = 2.0 Hz, 2H); ¹³C{¹H} NMR (126 MHz, CD₂Cl₂) δ : 144.7, 144.6, 141.2, 140.7, 140.6, 139.7, 138.2, 137.8, 137.4, 137.0, 129.0, 126.9, 125.9, 125.8, 125.7, 125.3, 125.1, 125.1, 124.7, 124.4, 124.0, 123.0, 122.8, 121.3, 39.7. HRMS (EI–TOF) *m/z* (*M*⁺): calcd for C₂₅H₁₆S₂, 380.0693; found, 380.0698; elemental analysis (%): calcd for C₂₅H₁₆S₂: C, 78.91; H, 4.24. Found: C, 78.57; H, 4.49.

15,15-Diethyl-5,10-dithiatruxene (SSC). Trimer **2b** (95 mg, 0.25 mmol) and iodine (9.53 mg, 0.0375 mmol) were dissolved in 250 mL of toluene and irradiated with UV-C light. After 3 h, the reaction mixture was evaporated and the resulting orange solid was suspended in 5 mL of methanol and filtered. The obtained material was then suspended in 1.25 mL of dimethylformamide (saturated with argon at 0 °C for 1 h), and 0.082 mL (1.1 mmol, *d* = 1.46 g/mL) of bromoethane and 61 mg (1.1 mmol) of shredded potassium hydroxide were added.

After stirring for 24 h, 5 mL of water was added and obtained solution was extracted three times with 2.5 mL of dichloromethane. The organic layer was dried over MgSO_4 and evaporated. The crude product was purified via column chromatography using silica gel as the stationary phase and 1 \rightarrow 10% solution of dichloromethane in hexane as the eluent to obtain 51 mg of a white solid, with the reaction yield of 47%. The mp was 255 °C. ^1H NMR (400 MHz, CDCl_3) δ : 8.97 (d, J = 8.0 Hz, 1H), 8.75 (d, J = 8.0 Hz, 1H), 8.19–8.16 (m, 1H), 8.13–8.09 (m, 2H), 7.76–7.70 (m, 1H), 7.65–7.61 (m, 2H), 7.60–7.53 (m, 3H), 7.50–7.45 (m, 1H), 3.12 (dq, J = 14.5, 7.3 Hz, 2H), 2.41 (dq, J = 14.8, 7.4 Hz, 2H), 0.29 (t, J = 7.3 Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ : 151.7, 144.6, 141.0, 140.2, 139.6, 135.0, 134.9, 134.5, 134.3, 132.3, 131.4, 129.8, 127.5, 127.4, 126.6, 126.6, 126.1, 125.4, 124.8, 124.5, 123.5, 123.3, 122.4, 121.7, 60.1, 30.3, 9.3; HRMS (EI–TOF) m/z (M^+): calcd for $\text{C}_{29}\text{H}_{22}\text{S}_2$, 434.1163; found, 434.1160; elemental analysis (%): calcd for $\text{C}_{29}\text{H}_{22}\text{S}_2$: C, 80.14; H, 5.10. Found: C, 80.04; H, 5.32.

5,10-Dithiatruxene-15-one (13b). Benzo[*b*]thiophene 15b (1.34 g, 10 mmol) was dissolved in 20 mL of 1,2-dichloroethane, followed by addition of 890 mg (5 mmol) of ninhydrin 14 and 1.29 mL (20 mmol) of methanesulfonic acid. The solution was stirred for 0.5 h at room temperature and refluxed. After 3 h, it was cooled and left overnight. The formed participate was filtrated and washed with 20 mL of dichloromethane and 20 mL of methanol to obtain 1.45 g of an orange solid, with the reaction yield of 74%. The NMR analysis is in accordance with the literature data.⁵⁹ ^1H NMR (500 MHz, CDCl_3) δ : 9.95 (d, J = 8.6 Hz, 1H), 8.60 (d, J = 7.9 Hz, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H), 7.80 (d, J = 7.3 Hz, 1H), 7.75 (d, J = 7.3 Hz, 1H), 7.69 (t, J = 7.3 Hz, 1H), 7.63–7.57 (m, 4H), 7.37 (t, J = 6.7 Hz, 1H); elemental analysis (%): calcd for $\text{C}_{25}\text{H}_{12}\text{OS}_2$: C, 76.50; H, 3.08. Found: C, 76.74; H, 3.11.

N-Ethylindole (15c). To 50 mL of dimethylformamide were added 11.7 g (100 mmol) of indole and 8.4 g (150 mmol) of potassium hydroxide, and the mixture was cooled down to 0 °C. After 20 min, 22.8 mL (150 mmol, d = 1.46 g/mL) of bromoethane was added. After stirring for 24 h, 100 mL of water was added and the solution was extracted with 6 \times 50 mL of hexane. The combined extracts were washed with 50 mL of brine, dried over MgSO_4 , and evaporated. A colorless liquid (14.35 g), with the reaction yield of c.a. 100%, was obtained. The analysis is in accordance with the literature data.⁶⁹ ^1H NMR (300 MHz, CDCl_3) δ : 7.72 (d, J = 7.8 Hz, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.30 (t, J = 8.1 Hz, 1H), 7.22–7.17 (m, 2H), 6.59 (d, J = 3.9 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 1.58 (t, J = 7.2 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 16.0, 41.4, 101.5, 109.7, 119.7, 121.5, 121.8, 127.5, 129.2, 136.2.

5,10-Diethyl-5,10-diazatruxene-15-one (13c). N-Ethylindole 15c (10.74 g, 74 mmol) was dissolved in 74 mL of 1,2-dichloroethane, followed by addition of 6.59 g (37 mmol) of ninhydrin 14 and 4.79 mL (74 mmol) of methanesulfonic acid. The solution was stirred for 0.5 h at room temperature and refluxed. After 2.5 h, it was cooled and left overnight. Then, 74 mL of water was added, the organic layer was separated, and the aqueous layer was extracted two times with 37 mL of dichloromethane. The combined extracts were dried over MgSO_4 and evaporated. The crude product was purified via column chromatography using silica gel as the stationary phase and 20% \rightarrow 40% dichloromethane solution in hexane as the eluent to obtain 4.75 g of a dark brown solid, with the reaction yield of 31%. The mp was 188 °C. ^1H NMR (500 MHz, CD_2Cl_2) δ : 9.37 (d, J = 7.9 Hz, 1H), 8.30 (d, J = 8.2 Hz, 1H), 7.60 (dd, J = 7.1, 0.6 Hz, 1H), 7.58–7.49 (m, 5H), 7.42 (dt, J = 7.5, 1.2 Hz, 1H), 7.35–7.31 (m, 2H), 7.16 (t, J = 7.3 Hz, 1H), 4.79 (q, J = 7.2 Hz, 2H), 4.63 (q, J = 7.1 Hz, 2H), 1.62 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) δ : 194.9, 145.2, 144.6, 142.7, 139.1, 137.9, 135.2, 134.3, 128.6, 127.1, 126.6, 126.6, 125.7, 124.1, 123.9, 123.6, 123.1, 123.1, 123.0, 121.0, 120.6, 116.8, 115.4, 111.9, 109.9, 42.3, 41.8, 16.0, 14.4; HRMS (EI–TOF) m/z (M^+): calcd for $\text{C}_{29}\text{H}_{22}\text{N}_2\text{O}$, 414.1732; found, 414.1721; elemental analysis (%): calcd for $\text{C}_{29}\text{H}_{22}\text{N}_2\text{O}$: C, 84.03; H, 5.35; N, 6.76. Found: C, 84.44; H, 5.88; N, 6.51.

5,10-Diethyl-5,10-diazatruxene (1c). 5,10-Diethyl-5,10-diazatruxene-15-one 13c (207 mg, 0.5 mmol) was dissolved in 4 mL of

ethylene glycol, and then 0.121 mL (2.5 mmol, d = 1.032 g/mL) of hydrazine monohydrate was added. The obtained mixture was refluxed under an argon atmosphere and left overnight. Then, the solution was cooled and 112 mg (2 mmol) of potassium hydroxide was added. After 0.5 h of refluxing under an argon atmosphere, the mixture was cooled and 4 mL of aqueous ammonium chloride solution (0.5 M) was added. The light yellow participate was filtered off. The crude product was purified via column chromatography using silica gel as the stationary phase and 20% dichloromethane in hexane as the eluent to obtain 192.2 mg of a white solid, with the reaction yield of 96%. The mp was 169 °C. ^1H NMR (500 MHz, CD_2Cl_2) δ : 8.43 (d, J = 8.1 Hz, 1H), 8.19 (d, J = 7.6 Hz, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 7.3 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.55–7.46 (m, 3H), 7.40–7.36 (m, 2H), 7.31 (t, J = 7.3 Hz, 1H), 4.97 (q, J = 7.2 Hz, 2H), 4.89 (q, J = 7.1 Hz, 2H), 4.47 (s, 2H), 1.73 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) δ : 143.8, 142.5, 141.9, 141.4, 139.0, 139.0, 137.1, 126.9, 125.3, 124.7, 124.6, 124.6, 124.4, 124.0, 122.7, 122.5, 121.0, 120.5, 120.2, 119.4, 114.4, 111.8, 109.8, 109.4, 42.5, 41.8, 38.0, 16.3, 14.6; HRMS (EI–TOF) m/z (M^+): calcd for $\text{C}_{29}\text{H}_{24}\text{N}_2$, 400.1939; found, 400.1931; elemental analysis (%): calcd for $\text{C}_{29}\text{H}_{24}\text{N}_2$: C, 86.97; H, 6.04; N, 6.99. Found: C, 87.06; H, 6.18; N, 6.76.

5,10,15,15-Tetraethyl-5,10-diazatruxene (NNC). 5,10-Diethyl-5,10-diazatruxene 1c (1.6 g, 4 mmol) was suspended in 40 mL of tetrahydrofuran and cooled down to -78 °C. Then, 2 mL (5 mmol, 2.5 M) of *n*-butyllithium solution in hexane was added; the mixture turned orange. After 0.5 h in constant temperature, 0.375 mL (5 mmol, d = 1.46 g/mL) of bromoethane was added and the temperature was slowly raised to room temperature and then lowered again to -78 °C. The whole procedure of *n*-butyllithium addition followed by addition of bromoethane was repeated two times. After warming the mixture to room temperature, the solvent was evaporated. The crude product was purified via column chromatography using silica gel as the stationary phase and 5% dichloromethane in hexane as the eluent to obtain 822.8 mg of a white solid, with the reaction yield of 45%. The mp was 170 °C. ^1H NMR (500 MHz, CD_2Cl_2) δ : 8.56 (d, J = 8.0 Hz, 1H), 8.42 (d, J = 8.1 Hz, 1H), 7.91 (d, J = 7.7 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.55–7.46 (m, 3H), 7.43 (dt, J = 7.6, 1.1 Hz, 1H), 7.40–7.36 (m, 1H), 7.33 (t, J = 7.5 Hz, 2H), 5.02 (q, J = 7.2 Hz, 2H), 4.83 (q, J = 7.0 Hz, 2H), 3.11–3.01 (m, 2H), 2.33 (dq, J = 14.6, 7.4 Hz, 2H), 1.72 (t, J = 7.2 Hz, 3H), 1.00 (t, J = 7.0 Hz, 3H), 0.23 (t, J = 7.3 Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) δ : 150.9, 145.3, 144.0, 141.9, 141.8, 139.2, 138.3, 126.7, 125.2, 124.9, 124.7, 124.2, 124.2, 123.8, 122.9, 122.6, 122.0, 120.8, 120.6, 119.8, 114.9, 112.6, 110.3, 110.2, 58.7, 42.9, 41.9, 29.8, 16.1, 13.4, 8.9; HRMS (EI–TOF) m/z (M^+): calcd for $\text{C}_{33}\text{H}_{32}\text{N}_2$, 456.2565; found, 456.2560; elemental analysis (%): calcd for $\text{C}_{33}\text{H}_{32}\text{N}_2$: C, 86.80; H, 7.06; N, 6.13. Found: C, 86.92; H, 7.15; N, 5.93.

General Procedure for Synthesis of Alcohols 16. 13 (0.25 mmol) was suspended in 1 mL of anhydrous toluene followed by addition of 0.1 mL (0.3 mmol, 1.2 equiv) of a solution of ethylmagnesium bromide in diethyl ether (3 M). After 0.5 h in reflux, the mixture was cooled down to room temperature and 5 mL of water and 5 mL of dichloromethane were added. The collected organic phase was dried over MgSO_4 and then evaporated to obtain alcohols 16.

5-Hydroxy-15-ethyl-5,10-dithiatruxene (16b). A pale yellow solid (99 mg), with the reaction yield of 94%, was obtained. ^1H NMR (500 MHz, CD_2Cl_2) δ : 9.36 (d, J = 8.0 Hz, 1H), 8.47 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.82 (d, J = 7.4 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.58 (d, J = 7.3 Hz, 1H), 7.55–7.51 (m, 1H), 7.50 (d, J = 7.4 Hz, 1H), 7.46 (t, J = 7.2 Hz, 2H), 7.38 (t, J = 7.3 Hz, 1H), 2.65 (dq, J = 14.6, 7.3 Hz, 1H), 2.40 (dq, J = 14.9, 7.6 Hz, 1H), 0.24 (t, J = 7.4 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) δ : 149.0, 142.7, 140.2, 139.3, 139.0, 134.6, 134.6, 134.3, 131.5, 131.5, 131.1, 130.6, 129.3, 128.1, 127.9, 126.8, 126.6, 125.5, 125.0, 124.4, 123.2, 123.1, 122.7, 121.8, 86.1, 30.4, 8.6; HRMS (EI–TOF) m/z (M^+): calcd for $\text{C}_{27}\text{H}_{18}\text{OS}_2$, 422.0799; found, 422.0791; elemental analysis (%): calcd for $\text{C}_{27}\text{H}_{18}\text{OS}_2$: C, 76.74; H, 4.29. Found: C, 76.81; H, 4.38. The ^1H NMR signal from the OH group proton was not visible.

15-Hydroxy-5,10,15-triethyl-5,10-diazatruxene (16c). A pale yellow solid (106.7 mg), with the reaction yield of 96%, was obtained. $^1\text{H NMR}$ (500 MHz, CD_2Cl_2) δ : 8.92 (d, $J = 7.9$ Hz, 1H), 8.38 (d, $J = 8.1$ Hz, 1H), 7.78 (d, $J = 7.6$ Hz, 1H), 7.67 (d, $J = 8.1$ Hz, 1H), 7.62 (dd, $J = 7.3, 0.6$ Hz, 1H), 7.56 (d, $J = 8.1$ Hz, 1H), 7.54–7.50 (m, 1H), 7.48–7.44 (m, 1H), 7.44–7.40 (m, 1H), 7.39–7.34 (m, 1H), 7.32–7.29 (m, 1H), 7.29–7.26 (m, 1H), 4.96–4.87 (m, 2H), 4.84–4.75 (m, 2H), 2.74 (dq, $J = 14.7, 7.4$ Hz, 1H), 2.51 (dq, $J = 14.7, 7.4$ Hz, 1H), 2.41 (s, 1H), 1.70 (t, $J = 7.2$ Hz, 3H), 1.13 (t, $J = 7.1$ Hz, 3H), 0.51 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) δ : 149.6, 145.0, 143.5, 1141.8, 140.6, 138.7, 138.2, 128.6, 125.7, 125.4, 124.9, 124.7, 124.2, 123.4, 123.3, 123.0, 122.4, 120.7, 120.0, 117.1, 114.6, 112.1, 110.8, 109.6, 85.7, 42.5, 41.8, 31.1, 16.2, 13.8, 8.9; HRMS (EI–TOF) m/z (M^+): calcd for $\text{C}_{31}\text{H}_{28}\text{N}_2\text{O}$, 444.2202; found, 444.2206; elemental analysis (%): calcd for $\text{C}_{31}\text{H}_{28}\text{N}_2\text{O}$: C, 83.75; H, 6.35; N, 6.30. Found: C, 83.68; H, 6.24; N, 6.25.

General Procedure for Synthesis of Bromoderivatives 17. Soluble 5,10-diheterotruxene (OOC, SSC, or NNC; 1 mmol) was dissolved in 1 mL of dichloromethane at 0 °C and 0.16 mL (3.1 mmol, 3.1 equiv) of bromine was slowly added. After 1 h, 10 mL of methanol was added dropwise and the formed participate was filtrated to get bromoderivatives 17.

2,8,13-Tribromo-15,15-diethyl-5,10-dithiatruxene (17b). A white solid (641 mg) was obtained, with the reaction yield of 96%. The mp was >300 °C. $^1\text{H NMR}$ (500 MHz, CD_2Cl_2) δ : 9.15 (s, 1H), 8.85 (d, $J = 5.0$ Hz, 1H), 8.44 (d, $J = 8.6$ Hz, 1H), 8.38 (d, $J = 1.4$ Hz, 1H), 8.34 (s, 1H), 8.03 (d, $J = 8.2$ Hz, 1H), 7.96 (d, $J = 8.5$ Hz, 1H), 7.74–7.68 (m, 2H), 2.94 (dq, $J = 14.7, 7.5$ Hz, 2H), 2.40 (dq, $J = 14.6, 7.4$ Hz, 2H), 0.27 (t, $J = 7.3$ Hz, 6H); HRMS (EI–TOF) m/z (M^+): calcd for $\text{C}_{29}\text{H}_{19}\text{Br}_3\text{S}_2$, 667.8478; found, 667.8476; elemental analysis (%): calcd for $\text{C}_{29}\text{H}_{19}\text{Br}_3\text{S}_2$: C, 51.89; H, 2.85. Found: C, 52.01; H, 2.99. Due to low solubility, $^{13}\text{C}\{^1\text{H}\}$ NMR cannot be measured.

2,8,13-Tribromo-5,10,15,15-tetraethyl-5,10-diazatruxene (17c). A white solid (635 mg), with the reaction yield of 92%, was obtained. The mp was 145 °C. $^1\text{H NMR}$ (500 MHz, CD_2Cl_2) δ : 8.61 (d, $J = 1.2$ Hz, 1H), 8.50 (d, $J = 1.4$ Hz, 1H), 7.73 (d, $J = 8.2$ Hz, 1H), 7.62 (dd, $J = 8.7, 1.6$ Hz, 2H), 7.60–7.56 (m, 2H), 7.55 (dd, $J = 8.3, 1.8$ Hz, 1H), 7.53 (d, $J = 8.6$ Hz, 1H), 4.91 (q, $J = 7.1$ Hz, 2H), 4.74 (q, $J = 7.0$ Hz, 2H), 2.95 (dq, $J = 14.5, 7.3$ Hz, 2H), 2.29 (dq, $J = 14.6, 7.3$ Hz, 2H), 1.71 (t, $J = 7.2$ Hz, 3H), 0.99 (t, $J = 7.0$ Hz, 3H), 0.22 (t, $J = 7.3$ Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) δ : 153.2, 145.8, 142.4, 140.5, 140.5, 138.8, 129.8, 127.6, 127.1, 126.5, 126.3, 125.9, 125.5, 125.3, 123.3, 119.4, 113.9, 113.9, 113.0, 111.8, 109.8, 59.1, 43.0, 42.2, 30.3, 16.0, 13.5, 8.8; HRMS (EI–TOF) m/z (M^+): calcd for $\text{C}_{33}\text{H}_{29}\text{Br}_3\text{N}_2$, 689.9881; found, 689.9875; elemental analysis (%): calcd for $\text{C}_{33}\text{H}_{29}\text{Br}_3\text{N}_2$: C, 57.17; H, 4.22; N, 4.04. Found: C, 57.06; H, 4.18; N, 4.11.

2,7,8,12,13-Pentabromo-5,10,15,15-tetraethyl-5,10-diazatruxene (18). NNC (456.6 mg, 1 mmol) was dissolved in 1 mL of dichloromethane and 0.26 mL (5.1 mmol, 5.1 equiv) of bromine was slowly added. After 0.5 h, 10 mL of methanol was added dropwise and the formed participate was filtrated to obtain 808.5 mg of a white solid, with the reaction yield of 95%. The mp was 195 °C. $^1\text{H NMR}$ (500 MHz, CD_2Cl_2) δ : 8.73 (s, 1H), 8.58 (s, 1H), 7.96 (s, 1H), 7.90 (s, 1H), 7.70 (d, $J = 7.4$ Hz, 1H), 7.64 (s, 1H), 7.55 (dd, $J = 8.2, 1.7$ Hz, 1H), 4.82 (m, 2H), 4.71 (m, 2H), 2.89 (dq, $J = 14.6, 7.3$ Hz, 2H), 2.29 (dq, $J = 14.3, 7.2$ Hz, 2H), 1.71 (t, $J = 7.2$ Hz, 3H), 1.00 (t, $J = 7.0$ Hz, 3H), 0.21 (t, $J = 7.3$ Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2) δ : 143.5, 143.5, 141.5, 138.8, 129.9, 129.9, 128.1, 127.0, 126.0, 125.3, 124.3, 123.6, 123.4, 123.4, 120.3, 119.8, 117.1, 116.0, 114.9, 114.9, 109.0, 59.2, 43.2, 42.2, 30.3, 16.0, 13.5, 8.8; HRMS (EI–TOF) m/z (M^+): calcd for $\text{C}_{33}\text{H}_{27}\text{Br}_5\text{N}_2$, 845.8091; found, 845.8082; elemental analysis (%): calcd for $\text{C}_{33}\text{H}_{27}\text{Br}_5\text{N}_2$: C, 46.57; H, 3.20; N, 3.29. Found: C, 46.96; H, 3.34; N, 3.18.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.9b03387>.

Crystallographic information on OOC in dichloromethane, SSC in dichloromethane, NNC in methanol, 13b in chlorobenzene, 13c in dichloromethane, 1c in methanol, 1c in acetonitrile, and 1c in acetone (CIF)

Crystal structures and NMR, emission spectrum of the UV-C lamp, absorption vs emission spectrum and quantum yield of 5,10-diheterotruxenes in CH_2Cl_2 , and calculated energy diagram (PDF)

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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