JOC The Journal of Organic Chemistry

Subscriber access provided by NATIONAL UNIV OF SINGAPORE

Article

Towards Soluble 5,10-Diheterotruxenes: Synthesis and Reactivity of 5,10-Dioxa-, 5,10-Dithia- and 5,10-Diazatruxenes

Krzysztof Górski, Justyna Mech-Piskorz, Barbara Le#niewska,
Oksana Pietraszkiewicz, and Marek Pietraszkiewicz

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b03387 • Publication Date (Web): 17 Mar 2020

Downloaded from pubs.acs.org on March 17, 2020

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W.,
Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society.
However, no copyright claim is made to original U.S. Government works, or works
produced by employees of any Commonwealth realm Crown government in the course
of their duties.

Towards Soluble 5,10-Diheterotruxenes: Synthesis and Reactivity of 5,10-Dioxa-, 5,10-Dithia- and 5,10-Diazatruxenes

Krzysztof Górski*, Justyna Mech-Piskorz*, Barbara Leśniewska, Oksana Pietraszkiewicz, Marek Pietraszkiewicz

Institute of Physical Chemistry, Polish Academy of Sciences; Kasprzaka 44/52, 01-224 Warsaw, Poland

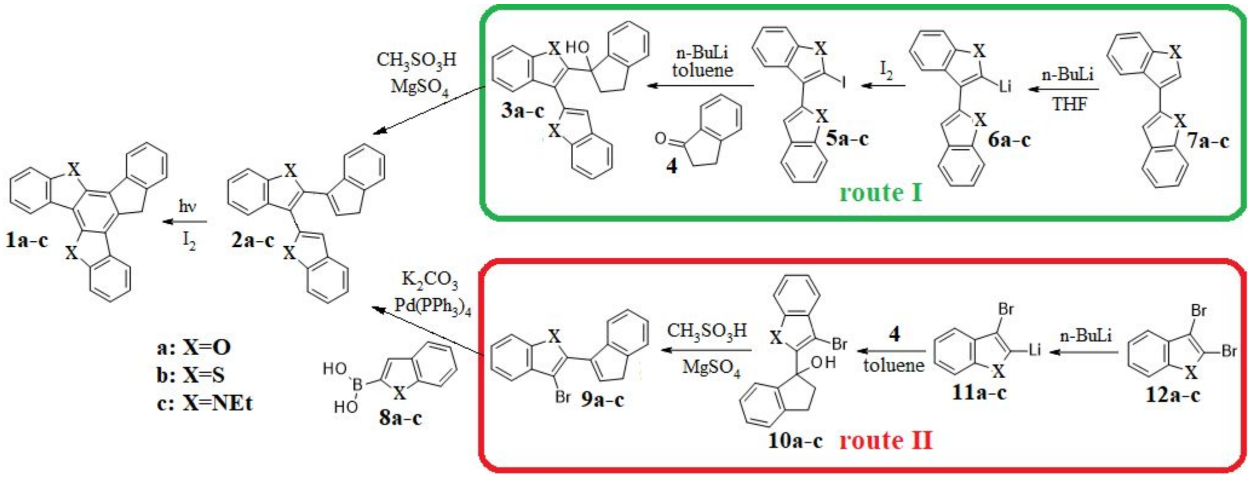
KEYWORDS: truxene, heterotruxene, thiatruxene, diheterotruxene, azatruxene, oxatruxene, synthesis, reactivity, condensation, photocyclization, alkylation, bromination, lithiation

---

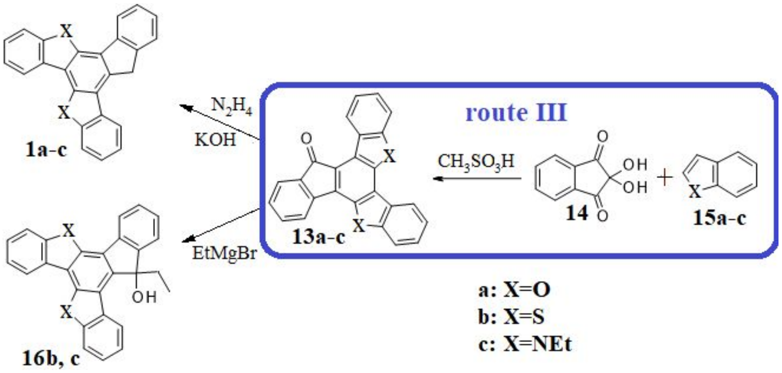
ABSTRACT: The following work presents three general approaches allowing for the first time the synthesis of 5,10-diheterotruxene derivatives containing two identical heteroatoms, namely oxygen **OOC**, nitrogen **NNC** or sulfur **SSC**. Two of described pathways involve the photocyclisation of the corresponding triene **2** as a key step leading to heptacyclic aromatic system. The third approach is based on the acidic condensation between ninhydrin **14** and benzo[*b*]heteroole **15**. Typical functionalizations of 5,10-diheterotruxene core have been also 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

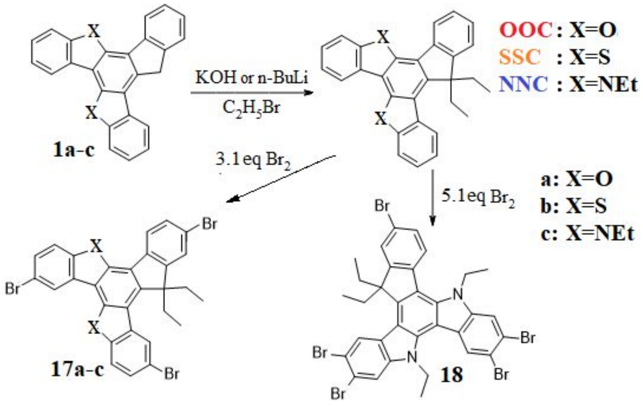
Truxenes are a family of heptacyclic carbo- and heteroaromatic systems. Currently, the synthesis of truxene[1-5] and its triheteroanalogues[6-9] as well as their reactivity[10-20] are well known. In the 80s, liquid crystal properties of some alkyl derivatives invoked an interest in this class of substances, 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], exhibit non-linear properties.[35-38] For example, the use of 5,10,15-triazatruxene as a donor subunit in the D-A_3 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 noteworthy 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-trithiatruxene[54] 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 and[56] 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-one,[59] 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.



Scheme 1. The first and the second approach to synthesis of 5,10-diheterotruxenes through photocyclization.



Scheme 2. The third approach to synthesis 5,10-diheterotruxenes through ketone intermediate and synthesis of the alcohols **16b,c**.



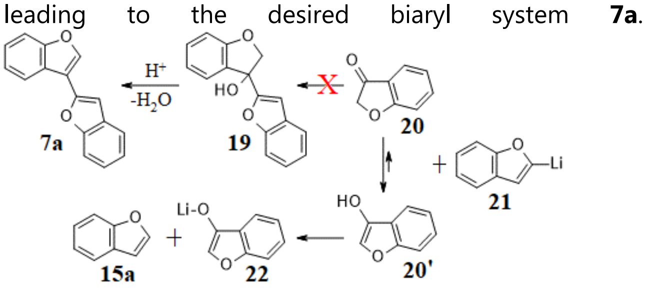
Scheme 3. Synthesis of the soluble 5,10-dihetrotruxenes: **OOC**, **SSC** and **NNC** and their reactivity.

RESULTS AND DISCUSSION

Scheme 1 and Scheme 2 present three general procedures, **route 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 slightly different approach.

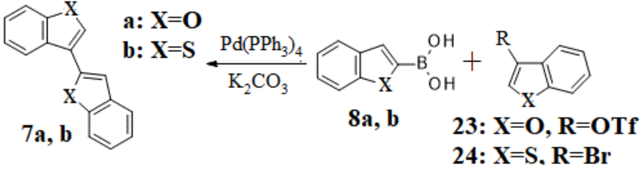
5,10–Dioxatruxene, **OOC**

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 the 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. 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 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 dehydratation 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 synthesis of **OOC**. 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 dehydratation can be converted into 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** and the deprotonation product **22**. Therefore, it was necessary to develop an alternative synthesis path leading to the desired biaryl system **7a**.



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

To perform successful synthesis of **7a,** well known arene transformation, called Suzuki reaction, was applied, Scheme 5. As a result of reaction between ketone **20** and trifluoromethanesulfonic anhydride in the presence of triethylamine, triflate **23** was obtained. 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.

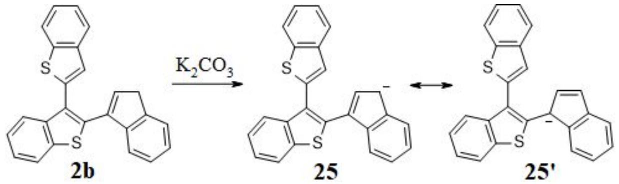


Scheme 5. Synthesis of biaryls **7a** and **7b**.

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. Generated organolithium derivative **6a** after reaction with iodine, led to a iododerivative **5a**. As a result of lithiation of **5a** in toluene, an organometallic compound is obtained, which afterwards reacted with ketone **4**, leads 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 catalytic amount of iodine which leads to the photocyclization product **1a.** As obtained, nearly insoluble, orange solid containing **1a** was used in the next step, Scheme 3. Alkylation of 5,10-dioxatruxene **1a** under argon atmosphere, in the basic environment results in the formation of 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 tetraethylated derivative of 5-oxatruxene. The described effect is a consequence of increased intermolecular interactions occurring between benzo[*b*]furan subunits (Figure S1).

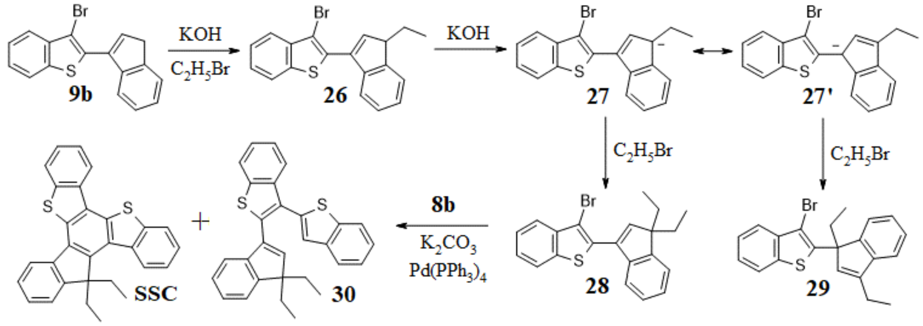
5,10–Dithiatruxene

Route III, Scheme 2 was successfully applied in the synthesis of ketone **13b**.[59] The use of methanesulfonic acid in 1,2-dichloroethane allows 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 in order to obtain an organometallic compound **6b** which, after reacting with iodine, leads to monoiododerivative **5b**. However, very low solubility of **5b** in toluene caused iodine to lithium exchange insufficient. 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**, bromoderivative **9b** was formed. Reaction between boronic acid **8b** and 9**b** 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 1*H*-indene subunit of trimer **2b**, which may undergo ionization under Suzuki reaction conditions (Scheme 6). Formed reactive anion **25**, could undergo further transformations leading to colored byproducts present in the reaction mixture.



Scheme 6. Ionization of trimer **2b**

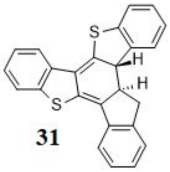
To confirm or disprove proposed explanation of the reaction course, the trimer **30** with protected by ethyl groups indene subunit, was synthesized (Scheme 7). The first step was the alkylation of **9b** which led to a mixture of two isomeric ethylated products **28** : **29** in a ratio of ~ 1:5.



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 were 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 with the flat structure of the benzo[b]thiophene subunit. In order 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. Bromoderivative **28** underwent palladium catalysed 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 by-products. 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 a cyclic product **31** (Scheme 8)**.** Low solubility of **31** in hexane prevents subsequent reaction with iodine leading to 5,10-dithiatruxsene **1b**. For this reason, it was necessary to use 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 diethylderivative of 5,10-dithiatruxene, **SSC**.



Scheme 8. Probable structure of **31**.

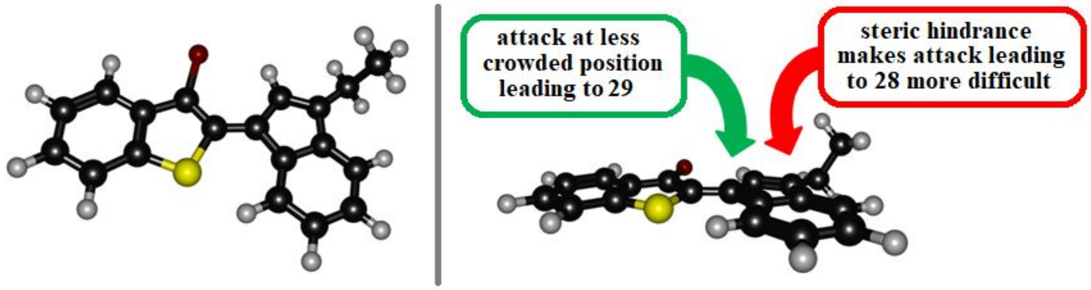


Figure 1. Structure of anion **27** and possible attacks of alkylating agent

5,10–Diazatruxene

The known in the literature 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] Photocyclisation approach, successful in 5-azatruxene synthesis, was not suitable due to the high reactivity of the trimer **2c**. What is more, the nitrene insertion, successfully used in the synthesis of 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 previously discussed carbonyl compound **13b**, ketone **13c** has two ethyl groups, as solubilizing agent, allowing Wolff–Kizhner 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 °C in dimethylformamide, saturated with argon. Despite lower temperature, than in the case of **OOC** and **SSC**, amount of bromoethane during ethylation increased from 4.4 eq to 20.8 eq. 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 the 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 experiments enabled a distinct increase in the alkylation yield up to 45.1%. To achieve such a result, n-butyllithium at -78 °C was added as the ionizing agent. All soluble 5,10-diheterotruxene 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 eq. of bromine in dichloromethane, while using the excess of bromine results in up to five bromine atoms in 5,10-diazatruxene core, **18**. Bromoderivatives, **17** and **18**, can be used for further functionalization in order to tune the physicochemical properties for optoelectronic application. Another possible way to modify the 5,10-diheterotruxene core is to use the reactivity of the carbonyl group present in compounds **13a-c**. Despite poor solubility of ketones **13b**,**c**, their reactions with organometallic compounds such as ethylmagnesium bromide at elevated temperature resulted in efficient conversion to **16b**,**c**.

CONCLUSIONS

The presented three general methods for creating the 5,10-diheterotruxene skeleton, presented in this paper, allow the introduction of two heteroatoms of the same type. During the synthesis of diheterotruxenes the particular attention should be paid to the photocyclization approach, presented at Scheme 1 (route I and II). Due to the availability of reagents, benzo[b]heterools, further exploration of the diheterotruxene family is possible. What's more, it can be used in the synthesis of novel diheterotruxenes 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-diheterotruxenes. Hence the special attention has been paid to the matter of solubility. Good solubility connected with increased aggregation of 5,10-diheterotruxenes in the solid state, comparing 5-heterotruxenes, 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-diheterotruxenes, 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 electronic supporting info, will be discussed in detail in a separate paper.

EXPERIMENTAL

General Information. All solvents used were of analytical grade. Toluene and tetrahydrofuran used in lithiation reaction were freshly distilled from $LiAlH_4$ under argon atmosphere. Benzo[*b*]thiophene, benzo[*b*]furan, indole, indan-1-one, were delivered from ABCR. All reaction requiring heating were carried out using a heating mantle. 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. Emission spectrum of the UV-C lamp can be found in SI. Mass spectra were collected at Applied Biosystems 4000Q TRAP with electron impact as ionization method. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured at Bruker DRX 500MHz in CD_2Cl_2 or $CDCl_3$. Shift of the residual peak of solvents was taken as an internal chemical shift. 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 recorder using spectrophotometer UV 2401, Shimazu, Japan. Emission spectra were collected using 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 b3lyp/6-31g(d,p) set for molecules in a vacuum.

Benzofuran-3(2H)-one – ***20.*** 7.61 g (50 mmol) of phenoxyacetic acid was dissolved in 50 mL of thionyl chloride and was refluxed. After 4 hours, 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 to 0 °C. After 15 min from the 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 stationary phase and 10% ethyl acetate in hexane solution as eluent, to give 2.41 g of a yellow solid, with the reaction yield of 36%. The mp. 97 °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 Hz, 2H).

Benzo[b]furan-3-yl trifluoromethanesulfonate – ***23***. To 5 mL of dichloromethane distilled from H_2SO_4, 670 mg (5 mmol) of benzo[*b*]furan-3(2H)-one **20** and 1.05 mL (7.5 mmol, d = 0.735 g/mL) of triethylamine distilled from CaH_2 was added. The solution, kept under argon, turned red and then was cooled to -40 °C. Next, 1.26 mL (7.5 mmol, d = 1.667 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 stationary phase and 10% dichloromethane in hexane solution as 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 Hz, 1H), 7.44 (td, *J* = 7.2, 1.3 Hz, 1H), 7.54 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.65 (dd, *J* = 7.2. 1.3 Hz, 1H), 7.84 (s, 1H); $^{13}C\{^1H\}$ 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, 4.4 mL (40 mmol, d = 1.072 g/mL) of benzo[*b*]furan **15a** was added and the mixture was cooled 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 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. 4.41 g of white solid 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, d_6-DMSO: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, d_6-DMSO: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 argon atmosphere, 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 was added and then solution was refluxed. The mixture turned muddy light brown. After 21 hours, reaction was cooled and evaporated to dryness. The crude product was purified via column chromatography using silica gel as stationary phase and hexane as 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-ylo)benzo[b]furan – ***5a***. To 6 mL of tetrahydrofuran, 702 mg (3 mmol) of 3-(benzo[*b*]furan-2-yl)benzo[*b*]furan **7a** was added and then cooled 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; fund, 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-dioxatruxene – ***OOC***. Step I (synthesis of trimer **2a**): To 12 mL of toluene, 720 mg (2 mmol) of 2-iodo-3-(benzo[*b*]furan-2-yl)benzo[*b*]furan **5a** was added and the mixture was cooled 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 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, the organic layer was separated, dried over $MgSO_4$ and evaporated. The crude product was purified via column chromatography using silica gel as stationary phase and hexane → 10% solution of dichloromethane in hexane → 15% solution of ethyl acetate in hexane as eluent to obtain 370 mg of **2a** as white solid, with the reaction yield of 53%. Step II (photocyclisation and alkylation): To 1.06 l of hexane, 370 mg (1.06 mmol) of **2a** and 26.71 mg (0.106 mmol) of iodine were added. Than 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 was dried over $MgSO_4$ and evaporated. The crude product was purified via column chromatography using silica gel as stationary phase and 10% solution of dichloromethane in hexane as 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 = 7.25Hz, 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***. 45.7 g (341 mmol) of benzo[*b*]thiophene **15b** 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. 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 re-cooled, and the formed solid was filtered. (The process was repeated several times, because there was still a lot of product in the post-crystallization 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, 16.06 g (55 mmol) of 2,3-dibromobenzo[*b*]thiophene **12b** was added and cooled to -40 °C, followed by slowly 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 stirring, at constant temperature, 22 mL of water was added to the solution, 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, 5.36 g (40 mmol) of benzo[*b*]thiophene **15b** was added and then the mixture was cooled 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 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 to 0 °C and filtered. 5.49g of a white solid, 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); $^{13}C\{^1H\}$ 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 argon atmosphere, 123 mg (1 mmol) of 3-bromobenzo[*b*]thiophene **24**, 178 mg (1 mmol) of benzo[*b*]thien-2-ylboronic acid **8b**, 7mg (0.04 mmol) of palladium(II) chloride, 42 mg (0.16 mmol) of triphenylphosphine and 1.5 mL (3 mmol, 2 M) of K_2CO_3 aqueous solution was added, then obtained solution was kept under reflux. The mixture turned muddy light brown that changed into red-brown as the reaction proceeded. After 3h, the solution was cooled and evaporated to dryness. The crude product was purified via column chromatography using silica gel as stationary phase and hexane as eluent. 126.5 mg of a white solid, with the reaction yield of 48%, was obtained. The analysis is consistent with the literature data.[68] ^1H NMR (400 MHz, $CDCl_3$) 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); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 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, 399 mg (1.5 mmol) of 3-(benzo[*b*]thien-2-yl)benzo[*b*]thiophene **7b** was added. Then solution was cooled 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 solution was brought to room temperature. After warming, 1.5 mL of a saturated aqueous Na_2SO_3 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 $MgSO_4$ 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, CD_2Cl_2) 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); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) 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 $C_{16}H_9IS_2$, 391.9190; found, 391.9193; elemental analysis (%): calcd for $C_{16}H_9IS_2$: C, 48.99; H, 2.31. Found: C, 48.45; H, 2.41.

3-(3-Bromobenzo[b]thien-2-yl)-1H-indene – ***9b***. To 60 mL of toluene, 2.92 g (10 mmol) of 2,3-dibromobenzo[*b*]thiophene **12b** was added and then the obtained solution was cooled 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 NH_4Cl was added. The aqueous layer was extracted with 60 mL of dichloromethane and then the combined extracts were evaporated. Obtained residue was dissolved in 10 mL of 1,2-dichloroethane and 0.973 mL (15 mmol, d = 1.48 g/mL) of CH_3SO_3H and 1.2 g of $MgSO_4$ were added. The solution was refluxed 30 min and then cooled. 5 mL (10 mmol, 2 M) of a K_2CO_3 aqueous solution and 5 mL of dichloromethane were added. The organic layer was separated, dried over $MgSO_4$ 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, CD_2Cl_2) 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); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) 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 $C_{17}H_9SBr$, 325.9725; found, 325.9760; elemental analysis (%): calcd for $C_{17}H_9SBr$: C, 62.40; H, 3.39. Found: C, 62.74; H, 3.83.

3-(3-Bromobenzo[b]thien-2-yl)-1,1-diethyl-1H-indene – **28**, *3-(3-Bromobenzo[b]thien-2-yl)-1,3-diethyl-1H-indene* – **29**. To 50 mL of dimethylformamide (saturated with argon at 0 °C for 1h), 3.27 g (10 mmol) of 3-(3-bromobenzo[*b*]thien-2-yl)-*1H*-indene **9b** was added followed by the 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 $MgSO_4$ and evaporated The crude product was purified via column chromatography using silica gel as stationary phase and petroleum ether as 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 (SiO_2 / hexane) compared to **29** and changed color to orange after irradiation with UV-C light. For **28**: ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 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 $C_{21}H_{19}SBr$, 382.0391; found, 382,0392; elemental analysis (%): calcd for $C_{21}H_{19}SBr$: C, 65.80; H, 5.00. Found: C, 65.91; H, 5.11. For **29**: ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) 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 $C_{21}H_{19}SBr$, 382.0391; found, 382,0390; elemental analysis (%): calcd for $C_{21}H_{19}SBr$ 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)-1H-indene – ***2b***. To 120 mL of tetrahydrofuran, 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**, 924.45 mg (0.8 mmol) of $Pd(PPh_3)_4$, were added and after the dissolution of the substrates, 15 mL (30 mmol, 2 M) of K_2CO_3 aqueous solution was introduced. The solution was refluxed under argon atmosphere. The mixture turned muddy dark brown. After 24 h, it was cooled, the organic layer was separated and evaporated. The crude product was purified via column chromatography using silica gel as stationary phase and hexane → 4% solution of dichloromethane in hexane (after collecting the substrate) as 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. ^{1}H NMR (500 MHz, CD_2Cl_2) 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); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) 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 $C_{25}H_{16}S_2$, 380.0693; found, 380.0698; elemental analysis (%): calcd for $C_{25}H_{16}S_2$: C, 78.91; H, 4.24. Found: C, 78.57; H, 4.49.

15,15-Diethyl-5,10-dithiatruxene – **SSC**. 95 mg (0.25 mmol) of trimer **2b** and 9.53 mg (0.0375 mmol) of iodine were dissolved in 250 mL of toluene, and irradiated with UV-C light. After 3 h the reaction mixture was evaporated, the resulting orange solid was suspended in 5 mL of methanol and filtered. 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 stationary phase and 1 → 10% solution of dichloromethane in hexane as eluent to obtain 51 mg of a white solid, with the reaction yield of 47%. The mp. was 255 °C. ^{1}H 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}C{^{1}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 $C_{29}H_{22}S_2$, 434.1163; found, 434.1160; elemental analysis (%): calcd for $C_{29}H_{22}S_2$: C, 80.14; H, 5.10. Found: C, 80.04; H, 5.32.

5,10–Dithiatruxene–15–one – ***13b***. 1.34 g (10 mmol) of benzo[*b*]thiophene **15b** was dissolved in 20 mL of 1,2-dichloroethane, followed by the 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. Formed participate was filtrated, 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 $C_{25}H_{12}OS_2$: C, 76.50; H, 3.08. Found: C, 76.74; H, 3.11.

N-ethylindole – ***15c***. To 50 mL of dimethylformamide, 11.7 g (100 mmol) of indole and 8.4 g (150 mmol) of potassium hydroxide were added, and the mixture was cooled 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 x 50 mL of hexane. The combined extracts were washed with 50 mL of brine, dried over $MgSO_4$, and evaporated. 14.35 g of a colorless liquid, 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); $^{13}C\{^1H\}$ 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***. 10.74 g (74 mmol) of N-ethylindole **15c** was dissolved in 74 mL of 1,2-dichloroethane, followed by the 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 were 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 stationary phase and 20% → 40% dichloromethane solution in hexane as 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); $^{13}C\{^1H\}$ 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 $C_{29}H_{22}N_2O$, 414.1732; found, 414.1721; elemental analysis (%): calcd for $C_{29}H_{22}N_2O$: 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***. 207 mg (0.5 mmol) of 5.10-diethyl-5.10-diazatruxene-15-one **13c** was dissolved in 4 mL of ethylene glycol, then 0.121 mL (2.5 mmol, d = 1.032 g/mL) of hydrazine monohydrate was added. Obtained mixture was refluxed under 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 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 stationary phase and 20% dichloromethane in hexane as 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); $^{13}C\{^1H\}$ 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 $C_{29}H_{24}N_2$, 400.1939; found, 400.1931; elemental analysis (%): calcd for $C_{29}H_{24}N_2$: 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***. 1.6 g (4 mmol) of 5,10–diethyl–5,10–diazatruxene **1c** was suspended in 40 mL of tetrahydrofuran and cooled to -78 °C. Then 2 mL (5 mmol, 2.5 M) of n-butyllithium solution in hexane was added – 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 stationary phase and 5% dichloromethane in hexane as eluent to obtain 822.8

mg of a white solid, with the reaction yield of 45%. The mp. was 170 °C. ^{1}H 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}C{^{1}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 $C_{33}H_{32}N_2$, 456.2565; found, 456.2560; elemental analysis (%): calcd for $C_{33}H_{32}N_2$: 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**: 0.25 mmol of **13** was suspended in 1 mL of anhydrous toluene followed by addition of 0.1 mL (0.3 mmol, 1.2 eq) of a solution of ethylmagnesium bromide in diethyl ether (3 M). After 0.5 h in reflux mixture was cooled to room temperature and 5 mL of water and 5 mL of dichloromethane were added. Collected organic phase was dried over $MgSO_4$ and then evaporated to obtain alcohols **16**.

*5-Hydroxy-15-ethyl-5,10-dithiatruxene – **16b***. 99 mg as a pale yellow solid, with the reaction yield of 94%, was obtained. ^{1}H NMR (500 MHz, CD2Cl2) 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}C{^{1}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 $C_{27}H_{18}OS_2$, 422.0799; found, 422.0791; elemental analysis (%): calcd for $C_{27}H_{18}OS_2$: C, 76.74; H, 4.29. Found: C, 76.81; H, 4.38. 1H NMR signal from OH group proton was not visible.

*15-Hydroxy-5,10,15-triethyl-5,10-diazatruxene – **16c***. 106.7 mg as a pale yellow solid, with the reaction yield of 96%, was obtained. ^{1}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}C{^{1}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 $C_{31}H_{28}N_2O$, 444.2202; found, 444.2206; elemental analysis (%): calcd for $C_{31}H_{28}N_2O$: 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**: 1 mmol of soluble 5,10-diheterotruxene (**OOC**, **SSC** or **NNC**) was dissolved in 1 mL of dichloromethane at 0 °C and 0.16 mL (3.1 mmol, 3.1 eq) 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***. 641 mg, as white solid was obtained, with the reaction yield of 96%. The mp. was >300 °C. ^{1}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 $C_{29}H_{19}Br_3S_2$, 667.8478; found, 667.8476; elemental analysis (%): calcd for $C_{29}H_{19}Br_3S_2$: C, 51.89; H, 2.85. Found: C, 52.01; H, 2.99. Due to low solubility ^{13}C{^{1}H} NMR cannot be measured.

*2,8,13-Tribromo-5,10,15,15-tetraethyl-5,10-diazatruxene – **17c***. 635 mg as a white solid, with the reaction yield of 92%, was obtained. The mp. was 145°C. ^{1}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}C{^{1}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 $C_{33}H_{29}Br_3N_2$, 689.9881; found, 689.9875; elemental analysis (%): calcd for $C_{33}H_{29}Br_3N_2$: 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***. 456.6 mg (1 mmol) of **NNC** was dissolved in 1 mL of dichloromethane and 0.26 mL (5.1 mmol, 5.1 eq)of bromine was slowly added. After 0.5 h 10 mL of methanol was added dropwise and formed participate was filtrated to obtain 808.5 mg of white solid, with the reaction yield of 95%. The mp. was 195 °C. ^{1}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); $^{13}C\{^1H\}$ 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, 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 $C_{33}H_{27}Br_5N_2$, 845.8091; found, 845.8082; elemental analysis (%): calcd for $C_{33}H_{27}Br_5N_2$: 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 on the ACS publication website.

Crystallographic information on **OOC** in dichloromethane (CIF)

Crystallographic information on **SSC** in dichloromethane (CIF)

Crystallographic information on **NNC** in methanol (CIF)

Crystallographic information on **13b** in chlorobenzene (CIF)

Crystallographic information on **13c** in dichloromethane (CIF)

Crystallographic information on **1c** in methanol (CIF)

Crystallographic information on **1c** in acetonitrile (CIF)

Crystallographic information on **1c** in acetone (CIF)

Crystal structures and NMR (PDF)

Emission spectrum of the UV-C lamp (PDF)

Absorption vs emission spectrum and quantum yield of 5,10-diheterotruxenes in CH2Cl2

Calculated energy diagram

AUTHOR INFORMATION

Corresponding Authors

*kgorski@ichf.edu.pl ORCID ID 0000-0002-6439-2651

*jmech@ichf.edu.pl ORCID ID 0000-0002-4778-7918

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

ACKNOWLEDGMENTS

This work was supported by National Science Centre (FUGA 4, grant no. 2015/16/S/ST4/00427), and in part by the Institute of Physical Chemistry, Polish Academy of Sciences. The Authors cordially thank MSc Eng. Agnieszka Wiśniewska, of the Institute of Physical Chemistry of the Polish Academy of Sciences, for measurements of thermal properties.

REFERENCES

(1) Dehmlow, E. V.; Kelle, T. Synthesis of New Truxene Derivatives: Possible Precursors of Fullerene Partial Structures? *Synth. Commun.* **1997**, *27* (11), 2021–2031.

(2) Gómez-Lor, B.; de Frutos, Ó.; Ceballos, P. A.; Thierry, G.; Echavarren, A. M. Synthesis of New C_{3h} and C_{3v} Truxene Derivatives. *European J. Org. Chem.* **2001**, *2001* (11), 2107–2114.

(3) Kimura, M.; Kuwano, S.; Sawaki, Y.; Fujikawa, H.; Noda, K.; Taga, Y.; Takagi, K. New 9-Fluorene-Type Trispirocyclic Compounds for Thermally Stable Hole Transport Materials in OLEDs. *J. Mater. Chem.* **2005**, *15*, 2393–2398.

(4) Kao, M.-T.; Chen, J.-H.; Chu, Y.-Y.; Tseng, K.-P.; Hsu, C.-H.; Wong, K.-T.; Chang, C.-W.; Hsu, C.-P.; Liu, Y.-H. Facile Synthesis of 5,10,15-Hexaaryl Truxenes: Structure and Properties. *Org. Lett.* **2011**, *13* (7), 1714–1717.

(5) Amick, A. W.; Scott, L. T. Trisannulated Benzene Derivatives by Acid Catalyzed Aldol Cyclotrimerizations of Cyclic Ketones. Methodology Development and Mechanistic Insight. *J. Org. Chem.* **2007**, *72* (9), 3412–3418.

(6) Ogaki, T.; Ohta, E.; Oda, Y.; Sato, H.; Matsui, Y.; Kumeda, M.; Ikeda, H. Intramolecular Triple Cyclization Strategy for Sila- and Oxa-Analogues of Truxene with Long-Lived Phosphorescence. *Asian J. Org. Chem.* **2017**, *6* (3), 290–296.

(7) Ginnari-Satriani, L.; Casagrande, V.; Bianco, A.; Ortaggi, G.; Franceschin, M. A Hydrophilic Three Side-Chained Triazatruxene as a New Strong and Selective G-Quadruplex Ligand. *Org. Biomol. Chem.* **2009**, *7* (12), 2513–2516.

(8) Gómez-Lor, B.; Echavarren, A. M. Synthesis of a Triaza Analogue of Crushed-Fullerene by Intramolecular Palladium-Catalyzed Arylation. *Org. Lett.* **2004**, *6* (17), 2993–2996.

(9) Kaida, H.; Satoh, T.; Nishii, Y.; Hirano, K.; Miura, M. Synthesis of Benzobis- and Benzotrisbenzofurans by Palladium-Catalyzed Multiple Intramolecular C–H/C–H Coupling. *Chem. Lett.* **2016**, *45* (9), 1069–1071.

(10) Pei, J.; Wang, J.-L.; Cao, X.-Y.; Zhou, X.-H.; Zhang, W.-B. Star-Shaped Polycyclic Aromatics

Based on Oligothiophene-Functionalized Truxene: Synthesis, Properties, and Facile Emissive Wavelength Tuning. *J. Am. Chem. Soc.* **2003**, *125* (33), 9944–9945.

(11) Yuan, M.-S.; Liu, Z.-Q.; Fang, Q. Donor-and-Acceptor Substituted Truxenes as Multifunctional Fluorescent Probes. *J. Org. Chem.* **2007**, *72* (21), 7915–7922.

(12) Cao, X.-Y.; Liu, X.-H.; Zhou, X.-H.; Zhang, Y.; Jiang, Y.; Cao, Y.; Cui, Y.-X.; Pei, J. Giant Extended π-Conjugated Dendrimers Containing the 10,15-Dihydro-5H-Diindeno[1,2-a;1′,2′-c]Fluorene Chromophore: Synthesis, NMR Behaviors, Optical Properties, and Electroluminescence. *J. Org. Chem.* **2004**, *69* (18), 6050–6058.

(13) Cao, X.-Y.; Zi, H.; Zhang, W.; Lu, H.; Pei, J. Star-Shaped and Linear Nanosised Molecules Functionalized with Hexa-Peri-Hexabenzocoronene: Synthesis and Optical Properties. *J. Org. Chem.* **2005**, *70* (9), 3645–3653.

(14) de Frutos, Ó.; Gómez-Lor, B.; Granier, T.; Monge, M. Á.; Gutiérrez-Puebla, E.; Echavarren, A. M. Syn-Trialkylated Truxenes: Building Blocks That Self-Associate by Arene Stacking. *Angew. Chemie - Int. Ed.* **1999**, *38* (1–2), 204–207.

(15) Liu, L.; Telfer, S. G. Systematic Ligand Modulation Enhances the Moisture Stability and Gas Sorption Characteristics of Quaternary Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2015**, *137* (11), 3901–3909.

(16) Lin, T.-C.; Tsai, B.-K.; Huang, T.-Y.; Chien, W.; Liu, Y.-Y.; Li, M.-H.; Tsai, M.-Y. Synthesis and Two-Photon Absorption Properties of Ladder-Type Chromophores with Functionalized Pyrazine Units Fused as the End-Groups. *Dye. Pigment.* **2015**, *120* (28), 99–111.

(17) Cao, X.-Y.; Zhou, X.-H.; Zi, H.; Pei, J. Novel Blue-Light-Emitting Truxene-Containing Hyperbranched and Zigzag Type Copolymers: Synthesis, Optical Properties, and Investigation of Thermal Spectral Stability. *Macromolecules* **2004**, *37* (24), 8874–8882.

(18) Shao, J.; Guan, Z.; Yan, Y.; Jiao, C.; Xu, Q.-H.; Chi, C. Synthesis and Characterizations of Star-Shaped Octupolar Triazatruxenes-Based Two-Photon Absorption Chromophores. *J. Org. Chem.* **2011**, *76* (3), 780–790.

(19) Lai, W.-Y.; He, Q.-Y.; Zhu, R.; Chen, Q.-Q.; Huang, W. Kinked Star-Shaped Fluorene/Triazatruxene Co-Oligomer Hybrids with Enhanced Functional Properties for High-Performance, Solution-Processed, Blue Organic Light-Emitting Diodes. *Adv. Funct. Mater.* **2008**, *18* (2), 265–276.

(20) Gómez-Lor, B.; Hennrich, G.; Alonso, B.; Monge, A.; Gutiérrez-Puebla, E.; Echavarren, A. M. A Redox-Active C_3-Symmetric Triindole-Based Triazacyclophane. *Angew. Chemie - Int. Ed.* **2006**, *45* (27), 4491–4494.

(21) Destrade, C.; Malthete, J.; Tinh, N. H.; Gasparoux, H. Truxene Derivatives: Temperature Inverted Nematic-Columnar Sequence in Disc-Like Mesogens. *Phys. Lett. A* **1980**, *78* (1), 82–84.

(22) Warmerdam, T. W.; Nolte, R. J. M.; Drenth, W.; Van Miltenburg, J. C.; Frenkel, D.; Zijlstra, R. J. J. Discotic Liquid Crystals: Physical Parameters of Some 2,3,7,8,12,13-Hexa(Alkanoyloxy)Truxenes. Observation of a Re-Entrant Isotropic Phase in a Pure Disc-like Mesogen. *Liq. Cryst.* **1988**, *3* (8), 1087–1104.

(23) Destrade, C.; Tinh, N. H.; Mamlok, L.; Malthete, J. Trioxatruxenes : A New Family of Disc-Like Mesogens with a Complex Polymorphism. *Mol. Cryst. Liq. Cryst.* **1984**, *114*, 139–150.

(24) Tinh, N. H.; Cayuela, R.; Destrade, C.; Malthete, J. Trithiatruxenes: A Family of Disc-like Mesogens with a New Polymorphism. *Mol. Cryst. Liq. Cryst.* **1985**, *122*, 141–149.

(25) Cayuela, R.; Nguyen, H. T.; Destrade, C.; Levelut, A. M. Two Families of Trithiatruxene Derivatives. *Mol. Cryst. Liq. Cryst.* **1989**, *177*, 81–91.

(26) Yao, C.; Yu, Y.; Yang, X.; Zhang, H.; Huang, Z.; Xu, X.; Zhou, G.; Yue, L.; Wu, Z. Effective Blocking of the Molecular Aggregation of Novel Truxene-Based Emitters with Spirobifluorene and Electron-Donating Moieties for Furnishing Highly Efficient Non-Doped Blue-Emitting OLEDs. *J. Mater. Chem. C* **2015**, *3* (22), 5783–5794.

(27) Zhao, B.; Liu, B.; Png, R. Q.; Zhang, K.; Lim, K. A.; Luo, J.; Shao, J.; Ho, P. K. H.; Chi, C.; Wu, J. New Discotic Mesogens Based on Triphenylene-Fused Triazatruxenes: Synthesis, Physical Properties, and Self-Assembly. *Chem. Mater.* **2010**, *22* (2), 435–449.

(28) Feng, G.-L.; Lai, W.-Y.; Ji, S.-J.; Huang, W. Synthesis of Novel Star-Shaped Carbazole-Functionalized Triazatruxenes. *Tetrahedron Lett.* **2006**, *47* (39), 7089–7092.

(29) Lai, W.-Y.; He, Q.-Y.; Chen, D.-Y.; Huang, W. Synthesis and Characterization of Starburst 9-Phenylcarbazole/Triazatruxene Hybrids. *Chem. Lett.* **2008**, *37* (9), 986–987.

(30) Lai, W.-Y.; Zhu, R.; Fan, Q.-L.; Hou, L.-T.; Cao, Y.; Huang, W. Monodisperse Six-Armed Triazatruxenes: Microwave-Enhanced Synthesis and Highly Efficient Pure Deep-Blue Electroluminescence. *Macromolecules* **2006**, *39* (11), 3707–3709.

(31) Tsiminis, G.; Wang, Y.; Shaw, P. E.; Kanibolotsky, A. L.; Perepichka, I. F.; Dawson, M. D.; Skabara, P. J.; Turnbull, G. A.; Samuel, I. D. W. Low-Threshold Organic Laser Based on an Oligofluorene Truxene with Low Optical Losses. *Appl. Phys. Lett.* **2009**, *94* (24), 243304-(1-3).

(32) Wang, Y.; Tsiminis, G.; Yang, Y.; Ruseckas, A.; Kanibolotsky, A. L.; Perepichka, I. F.; Skabara, P. J.; Turnbull, G. A.; Samuel, I. D. W. Broadly Tunable Deep Blue Laser Based on a Star-Shaped Oligofluorene Truxene. *Synth. Met.* **2010**, *160* (13–14), 1397–1400.

(33) Sang, M.; Cao, S.; Yi, J.; Huang, J.; Lai, W.-Y.; Huang, W. Multi-Substituted Triazatruxene-Functionalized Pyrene Derivatives as Efficient Organic Laser Gain Media. *RSC Adv.* **2016**, *6* (8), 6266–6275.

(34) Ma, L.; Wu, Z.; Zhou, G.; Yuan, F.; Yu, Y.; Yao, C.; Ning, S.; Hou, X.; Li, Y.; Wang, S.; et al. The Molecular Picture of Amplified Spontaneous Emission of Star-Shaped Functionalized-Truxene Derivatives. *J. Mater. Chem. C* **2015**, *3* (27), 7004–7013.

(35) Ji, L.; Fang, Q.; Yuan, M.-S.; Liu, Z.-Q.; Shen, Y.-X.; Chen, H.-F. Switching High Two-Photon Efficiency: From 3,8,13-Substituted Triindole Derivatives to Their 2,7,12-Isomers. *Org. Lett.* **2010**, *12* (22), 5192–5195.

(36) Wang, L.; Fang, Q.; Lu, Q.; Zhang, S.-J.; Jin, Y.-Y.; Liu, Z.-Q. Octupolar (C_3 and S_4) Symmetric Cyclized Indole Derivatives: Syntheses, Structures, and NLO Properties. *Org. Lett.* **2015**, *17* (17), 4164–4167.

(37) Guzelturk, B.; Kanibolotsky, A. L.; Orofino-Pena, C.; Laurand, N.; Dawson, M. D.; Skabara, P. J.; Demir, H. V. Ultralow-Threshold up-Converted Lasing in Oligofluorenes with Tailored Strong Nonlinear Absorption. *J. Mater. Chem. C* **2015**, *3* (46), 12018–12025.

(38) Li, F.; Zhao, B.; Chen, Y.; Zhang, Y.; Wang, T.; Xue, S. Synthesis, Characterization, and Nonlinear Optical (NLO) Properties of Truxene-Cored Diphenylamine Derivatives. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2017**, *185*, 20–26.

(39) dos Santos, P. L.; Ward, J. S.; Congrave, D. G.; Batsanov, A. S.; Eng, J.; Stacey, J. E.; Penfold, T. J.; Monkman, A. P.; Bryce, M. R. Triazatruxene: A Rigid Central Donor Unit for a D–A_3 Thermally Activated Delayed Fluorescence Material Exhibiting Sub-Microsecond Reverse Intersystem Crossing and Unity Quantum Yield via Multiple Singlet–Triplet State Pairs. *Adv. Sci.* **2018**, *5* (6), 1700989 (1-9).

(40) García-Frutos, E. M.; Gutierrez-Puebla, E.; Monge, M. A.; Ramírez, R.; de Andrés, P.; de Andrés, A.; Ramírez, R.; Gómez-Lor, B. Crystal Structure and Charge-Transport Properties of N-Trimethyltriindole: Novel p-Type Organic Semiconductor Single Crystals. *Org. Electron. physics, Mater. Appl.* **2009**, *10* (4), 643–652.

(41) Ruiz, C.; Arrechea-Marcos, I.; Benito-Hernández, A.; Gutiérrez-Puebla, E.; Monge, M. A.; López Navarrete, J. T.; Ruiz Delgado, M. C.; Ortiz, R. P.; Gómez-Lor, B. Solution-Processed N-Trialkylated Triindoles for Organic Field Effect Transistors. *J. Mater. Chem. C* **2018**, *6* (1), 50–56.

(42) Gallego-Gõmez, F.; García-Frutos, E. M.; Villalvilla, J. M.; Quintana, J. A.; Gutiérrez-Puebla, E.; Monge, A.; Díaz-García, M. A.; Gomez-Lor, B. Very Large Photoconduction Enhancement upon Self-Assembly of a New Triindole Derivative in Solution-Processed Films. *Adv. Funct. Mater.* **2011**, *21* (4), 738–745.

(43) Han, T.; Bulut, I.; Méry, S.; Heinrich, B.; Lévêque, P.; Leclerc, N.; Heiser, T. Improved Structural Order by Side-Chain Engineering of Organic Small Molecules for Photovoltaic Applications. *J. Mater. Chem. C* **2017**, *5*, 10794–10800.

(44) Benito-Hernández, A.; Pandey, U. K.; Cavero, E.; Termine, R.; García-Frutos, E. M.; Serrano, J. L.; Golemme, A.; Gómez-Lor, B. High Hole Mobility in Triindole-Based Columnar Phases: Removing the Bottleneck of Homogeneous

Macroscopic Orientation. *Chem. Mater.* **2013**, *25* (2), 117–121.

(45) Reig, M.; Puigdollers, J.; Velasco, D. Molecular Order of Air-Stable p-Type Organic Thin-Film Transistors by Tuning the Extension of the π-Conjugated Core: The Cases of Indolo[3,2-b]Carbazole and Triindole Semiconductors. *J. Mater. Chem. C* **2015**, *3* (3), 506–513.

(46) Shelton, S. W.; Chen, T. L.; Barclay, D. E.; Ma, B. Solution-Processable Triindoles as Hole Selective Materials in Organic Solar Cells. *ACS Appl. Mater. Interfaces* **2012**, *4* (5), 2534–2540.

(47) Kim, G. W.; Lampande, R.; Choe, D. C.; Bae, H. W.; Kwon, J. H. Efficient Hole Injection Material for Low Operating Voltage Blue Fluorescent Organic Light Emitting Diodes. *Thin Solid Films* **2015**, *589*, 105–110.

(48) Zhang, F.; Yang, X.; Cheng, M.; Li, J.; Wang, W.; Wang, H.; Sun, L. Engineering of Hole-Selective Contact for Low Temperature-Processed Carbon Counter Electrode-Based Perovskite Solar Cells. *J. Mater. Chem. A* **2015**, *3* (48), 24272–24280.

(49) Calió, L.; Momblona, C.; Gil-Escrig, L.; Kazim, S.; Sessolo, M.; Sastre-Santos, Á.; Bolink, H. J.; Ahmad, S. Vacuum Deposited Perovskite Solar Cells Employing Dopant-Free Triazatruxene as the Hole Transport Material. *Sol. Energy Mater. Sol. Cells* **2017**, *163*, 237–241.

(50) Ramos, F. J.; Rakstys, K.; Kazim, S.; Grätzel, M.; Nazeeruddin, M. K.; Ahmad, S. Rational Design of Triazatruxene-Based Hole Conductors for Perovskite Solar Cells. *RSC Adv.* **2015**, *5* (66), 53426–53432.

(51) Rakstys, K.; Abate, A.; Dar, M. I.; Gao, P.; Jankauskas, V.; Jacopin, G.; Kamarauskas, E.; Kazim, S.; Ahmad, S.; Grätzel, M.; et al. Triazatruxene-Based Hole Transporting Materials for Highly Efficient Perovskite Solar Cells. *J. Am. Chem. Soc.* **2015**, *137* (51), 16172–16178.

(52) Petrikyte, I.; Zimmermann, I.; Rakstys, K.; Daskeviciene, M.; Malinauskas, T.; Jankauskas, V.; Getautis, V.; Nazeeruddin, M. K. Efficiency Enhancement of Perovskite Solar Cells via Incorporation of Phenylethenyl Side Arms into Indolocarbazole-Based Hole Transporting Materials. *Nanoscale* **2016**, *8* (16), 8530–8535.

(53) Su, P.-Y.; Huang, L.-B.; Liu, J.-M.; Chen, Y.-F.; Xiao, L.-M.; Kuang, D.-B.; Mayor, M.; Su, C.-Y. A Multifunctional Poly-N-Vinylcarbazole Interlayer in Perovskite Solar Cells for High Stability and Efficiency: A Test with New Triazatruxene-Based Hole Transporting Materials. *J. Mater. Chem. A* **2017**, *5* (5), 1913–1918.

(54) Xiao, Q.; Sakurai, T.; Fukino, T.; Akaike, K.; Honsho, Y.; Saeki, A.; Seki, S.; Kato, K.; Takata, M.; Aida, T. Propeller-Shaped Fused Oligothiophenes: A Remarkable Effect of the Topology of Sulfur Atoms on Columnar Stacking. *J. Am. Chem. Soc.* **2013**, *135* (49), 18268–18271.

(55) Górski, K.; Mech-Piskorz, J.; Leśniewska, B.; Pietraszkiewicz, O.; Pietraszkiewicz, M. Synthesis and Reactivity of 5-Heterotruxenes Containing Sulfur or Nitrogen as the Heteroatom. *J. Org. Chem.* **2019**, *84*, 11553–11561.

(56) Górski, K.; Mech-Piskorz, J.; Noworyta, K.; Leśniewska, B.; Pietraszkiewicz, M. Efficient Synthesis of 5-Oxatruxene and the Unusual Influence of Oxygen Heteroatom on Its Physico-Chemical Properties. *New J. Chem.* **2018**, *42*, 5844–5852.

(57) Maciejczyk, M. R.; Williams, J. A. G.; Robertson, N.; Pietraszkiewicz, M. Monothiatruxene: A New Versatile Core for Functional Materials. *RSC Adv.* **2017**, *7* (78), 49532–49535.

(58) Maciejczyk, M. R.; Zhang, S.; Hedley, G. J.; Robertson, N.; Samuel, I. D. W.; Pietraszkiewicz, M. Monothiatruxene-Based, Solution-Processed Green, Sky-Blue, and Deep-Blue Organic Light-Emitting Diodes with Efficiencies Beyond 5% Limit. *Adv. Funct. Mater.* **2019**, *29* (6), 1807572.

(59) Kobayashi, K.; Suzue, N.; Ishii, R.; Kamiya, R.; Wakabayashi, H. Reactions of Ninhydrin with Benzo[b]Thiophenes. *Heterocycles* **2009**, *78* (10), 2467–2475.

(60) El-Sayed, M. T.; Wessjohann, L.; Porzel, A.; Hilgeroth, A. Diazatruxenes from the Condensation Reaction of Indoles with Ninhydrin. *J. Heterocycl. Chem.* **2016**, *54* (2), 1077–1083.

(61) Benito-Hernández, A.; El-Sayed, M. T.; López Navarrete, J. T.; Ruiz Delgado, M. C.; Gómez-Lor, B. Fused Donor-Acceptor π-Conjugated Diazatruxenones: Synthesis and Electronic Properties. *Org. Chem. Front.* **2018**, *5* (11),

1748–1755.

(62) Wu, D.; Mei, H.; Tan, P.; Lu, W.; Zhu, J.; Wang, W.; Huang, J.; Li, J. Total Synthesis of the 2-Arylbenzo[b]Furan-Containing Natural Products from Artocarpus. *Tetrahedron Lett.* **2015**, *56* (29), 4383–4387.

(63) Morice, C.; Garrido, F.; Mann, A.; Suffert, J. Palladium Assisted Substitution of 3-Benzo[b]Furan Triflates. *Synlett* **2002**, *2* (3), 501–503.

(64) Knapp, D. M.; Gillis, E. P.; Burke, M. D. A General Solution for Unstable Boronic Acids: Slow-Release Cross-Coupling from Air-Stable MIDA Boronates. *J. Am. Chem. Soc.* **2009**, *131* (20), 6961–6963.

(65) Yue, D.; Larock, R. C. Synthesis of 2,3-Disubstituted Benzo[b]Thiophenes via Palladium-Catalyzed Coupling Anphilic Cyclization of Terminal Acetylenes. *J. Org. Chem.* **2002**, *67* (6), 1905–1909.

(66) Xiong, Y.; Qiao, X.; Wu, H.; Huang, Q.; Wu, Q.; Li, J.; Gao, X.; Li, H. Syntheses and Properties of Nine-Ring-Fused Linear Thienoacenes. *J. Org. Chem.* **2014**, *79* (3), 1138–1144.

(67) Molander, G. A.; Cavalcanti, L. N.; Canturk, B.; Pan, P. S.; Kennedy, L. E. Efficient Hydrolysis of Organotrifluoroborates via Silica Gel and Water. *J. Org. Chem.* **2009**, *74* (19), 7364–7369.

(68) Yang, Y.; Oldenhuis, N. J.; Buchwald, S. L. Mild and General Conditions for Negishi Cross-Coupling Enabled by the Use of Palladacycle Precatalysts. *Angew. Chemie - Int. Ed.* **2013**, *52* (2), 615–619.

(69) Lane, B. S.; Brown, M. A.; Sames, D. Direct Palladium-Catalyzed C-2 and C-3 Arylation of Indoles: A Mechanistic Rationale for Regioselectivity. *J. Am. Chem. Soc.* **2005**, *127* (5), 8050–8057.

For Table of Contents Only