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# Synthesis and reactivity of 5-heterotruxenes containing sulfur or nitrogen as heteroatom

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*KEYWORDS: truxene, heterotruxene, thiatruxene, azatruxene, synthesis, reactivity, condensation, photocyclization, alkylation*

**ABSTRACT:** This paper presents an alternative path of the synthesis of 5-thiatruxene and the synthetic approach for 5-azatruxene, not known so far. New method for 5-thiatruxene improves an overall reaction yield from 17.5% to 22.6%, diminishes the synthesis time and costs by reducing synthetic steps from 5 to 2, and simplifies the isolation of intermediate and final products. The overall reaction yield for 5-azatruxene is 32.4%. The typical reactivity of both aromatic systems is also demonstrated. Recent research results suggest the use of 5-thiatruxene as the acceptor subunit of soluble blue emitters.[1]

## INTRODUCTION

Truxene is the name of an aromatic hydrocarbon consisting of seven condensed rings – three five-membered and four six-membered. Actually, this name is used to describe the entire family of aromatic compounds that are heteroanalogues of the starting hydrocarbon (Figure 1). Currently, there are many papers, which describe the synthesis and physicochemical properties of parent hydrocarbon,[2-6] and its symmetrical heteroderivatives containing nitrogen,[7-11] oxygen,[12,13] silicon,[14] phosphorus[15] or sulfur atom [16,17]

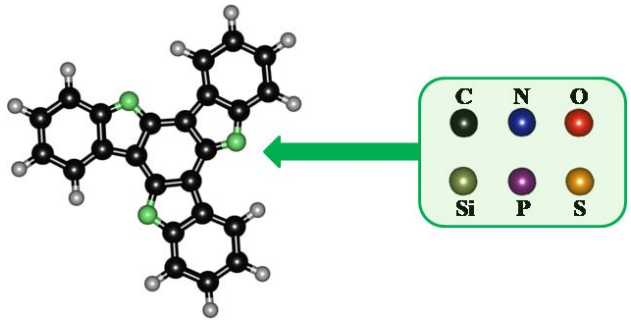



Figure 1. Structure of heterotruxenes.

Initially, an interest of this class of compounds resulted from the possibility of their use for liquid crystal displays.[12,18-20] However, the progress of optoelectronics and the demand for new stable materials significantly influenced the development of truxene chemistry. Many blue fluorescent emitters containing truxene moiety are known and have been used successfully in Organic Light Emitting Diodes or lasers. [21-24] The latest reports indicate truxene as a core in third generation OLED emitters. The presence of 5,10,15-triazatruxene in D-$A_3$ system, results in strong couplings of particular oscillation states of the singlet and triplet levels, resulting in a significant reduction of an emission time.[25] Truxenes may exhibit semiconductor properties depending on the heteroatom introduced into the π-electronic system.[26,27] 5,10,15-Triazatruxene[28-31] and 5,10,15-trithiatruxene[32] were used as a charge transporting materials in a prototype solar cells. Truxenes in general were used to develop fluorescent sensors that are able to detect of ions,[33,34] explosives[35-38] and biologically active substances.[39-41]

The nonsymmetrical truxenes containing one or two different heteroatoms are interesting and relatively little known subclass of truxenes. Currently known representatives of this class of substances are: 5,10-dithiatruxene-15-one,[42] 5,10-diazatruxene-15-one[43] and its derivatives,[44] 5-oxatruxene[45] and 5-thiatruxene.[46] 5-Thiatruxene was also used to develop stable donor-acceptor emitters,[1] which fulfill requirements for blue emitters used in HD displays. In this paper we present an alternative synthetic route leading to 5-thiatruxene derivative **SCC**, and protocol enabling the preparation of soluble derivative of 5-azatruxene, **NCC**. Possible functionalizations, for both π-electronic systems, are also presented.

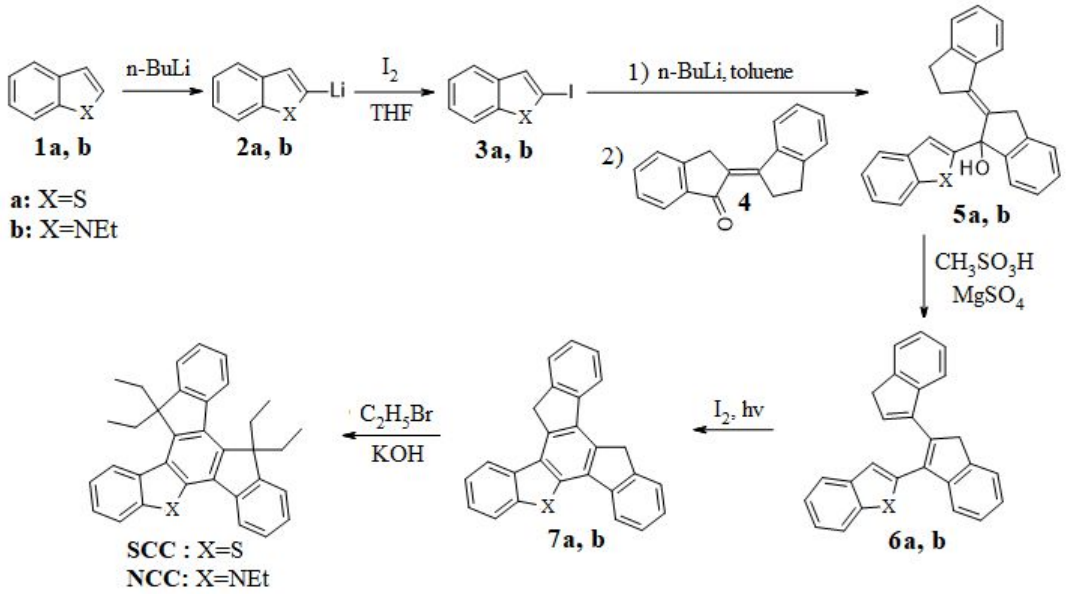
## RESULTS AND DISCUSSION

### 5–Thiatruxene

Photocyclization was successfully applied to the synthesis of 5-oxatruxene.[45] There was an idea of adopting photocyclization procedure for obtaining another 5-heterotruxenes, especially containing sulfur or nitrogen. Application of this synthetic route in 5-thiatruxene synthesis, would lead to the shortening of the preparation procedure, increase of the overall reaction yield and decrease the production costs. First step of the synthesis was direct lithiation of benzo[b]thiophene **1a** in tetrahydrofuran (Scheme 1). Afterwards, the obtained organolithium compound **2a** reacted with iodine to form 2-iodobenzo[b]thiophene **3a**. The synthesis of iododerivative **3a** is necessary to perform successful nucleophilic addition to carbonyl group of the ketone **4**. Reaction between **2a** and **4** in tetrahydrofuran did not lead to the alcohol **5a**. This is mostly caused by the fact that the ketone **4** in a polar solvents occurs in the enol form, which efficiently protonates generated organolithium compound **2a**. On the other hand, direct lithiation of benzo[b]thiophene **1a** in nonpolar solvents, such as toluene, by using n-butyllithium, is hard to carry out without other reagents. To avoid both obstacles, **3a** was synthesized in tetrahydrofuran and then reacted with n-butyllithium in toluene to form the

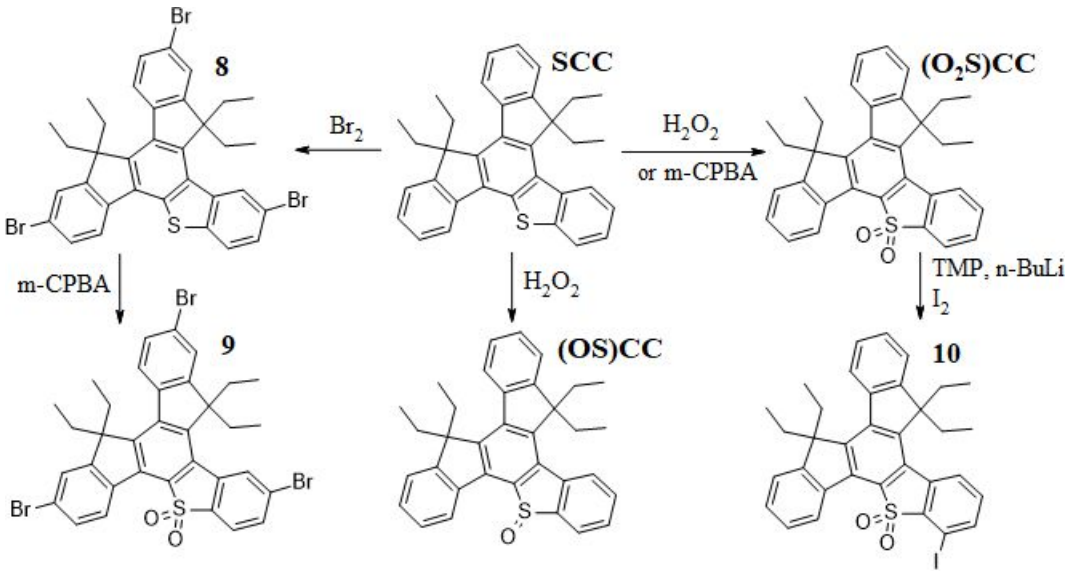
organometallic compound **2a**. The alcohol **5a**, obtained by nucleophilic addition, was very sensitive to acidic media and underwent dehydration even on the surface of the silica gel. Due to the high reactivity of **5a,** this compound was used without further purification. Reaction of **5a** in the presence of methanesulfonic acid in boiling 1,2-dichloroethane led to the formation of the trimeric compound **6a**.

**Scheme 1. Synthesis of SCC and NCC via photocyclisation approach.**




The next step in the synthesis of **SCC** was photocyclization. Irradiation of **6a** with the UV-*C* light in the presence of iodine induced conversion of **6a** into **7a**. The obtained insoluble brown solid was used to alkylation without further purification. Introduction of four ethyl groups into 5-thiatruxene core was conducted in dimethylformamide saturated with argon. The final product, **SCC,** was isolated from the reaction mixture by column chromatography. Overall yield of this synthetic route was 22.6%, which is higher of about 5% from that already known in literature.[45] **SCC** possess good solubility in most of organic solvents, which facilitate further functionalization of 5-thiatruxene core. **SCC** underwent characteristic reactions for both aromatic systems and sulfides. Treatment of **SCC** with bromine allows introduction up to three bromine atoms into the 5-thiatruxene core, **8** (Scheme 2) which can be further exchanged by using lithiation or organopalladium chemistry. **8** oxidized by m-chloroperbenzoic acid led to the formation of sulfone **9**. In a presence of oxidizers, such as hydrogen peroxide or m-chloroperbenzoic acid, **SCC** can be converted into sulfoxide **(OS)CC** as racemic mixture or sulfone **($O_2S$)CC**. Oxygenated 5-thiatruxenes, due to ambipolar character of the molecules, possess good solubility in both polar and nonpolar solvents. This property may cause some problems during purification of those substances, which results in lower reaction yield. Introduction of one sulfur atom into the truxene core breaks its symmetry, allowing monofunctionalization of 5-thiatruxene system. For example, sulfone **($O_2S$)CC** in a presence of lithium 2,2,6,6-tetramethylpiperidide underwent direct lithiation. Generated organolithium compound, after reaction with iodine, forms iododerivative **10**, which is useful reagent for further functionalization of 5-thiatruxene core.

**Scheme 2 Reactivity of SCC.**




5–Azatruxene

Another target, among the family of non-symmetrical heterotruxenes, was the synthesis of 5-azatruxene. Our experience, gained in the synthesis of previous compounds, 5-oxa- and 5-thiatruxene was utilized in the first approach. Due to the lower reactivity of **1b**, in comparison to **1a**, the direct lithiation was carried out in boiling ether in the presence of an excess of n-butyllithium. The generated organometallic derivative **2b** reacted with iodine to form **3b**. The addition of the organolithium compound **2b** to the ketone **4** was done in toluene, analogously as in the case of **SCC**. The obtained alcohol **5b** showed higher tendency to dehydration, compared to the sulfur analogue **5a**. The trimer **6b**, created after dehydration of the **5b**, appeared to be relatively unstable, which was observed as slowly darkening in contact with air. The high reactivity of **6b** can be explained by the presence of nitrogen atom, whose donating properties increase the electron density of the π-electron system, which in turn, significantly destabilizes the HOMO level, making **6b** more prone to oxidation. The photocyclisation of trimer **6b**, performed immediately after isolation, leads to a black substance. The following ethylation resulted in trace amount of **NCC**. Due to the high reactivity of trimer **6b**, an efficient synthesis of **NCC**, by using photocyclization, turned out to be impossible. The synthesis of **NCC** needed an alternative path. The introduction of a nitrogen atom into an aromatic system can be accomplished, for example, by the use of catalytic N-arylation,[47] reduction of nitro compounds[48] or decomposition of aryl azides.[49] The first step of the new synthetic pathway was the cyclotrimerization of 2'-bromoacetophenone **11,** leading to the bromoderivative **12**. Unfortunately, despite many attempts, the condensation of **11** in trifluoromethanesulfonic acid at 130°C turned out to be difficult to repeat. [50] The obtained reaction yield was 40%, which was about half as low as in the literature one. For this reason, it was necessary to optimize the cyclotrimerization of **11.**

Scheme 3 Condensation process of 11

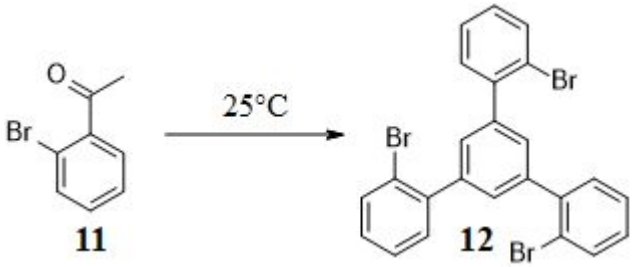



**Table 1. Optimization of condensation process of 17.**

| Conditions | Reaction yield for 12 |
|---|---|
| HCl, $HC(OEt_3)$ (1.2eq), benzene | 5% |
| $HSO_3Cl$, DCM | 0% |
| $HSO_3Cl$, $Si(OEt)_4$ (1eq), DCM | 32% |
| $HSO_3Cl$, $Si(OEt)_4$ (2eq), DCM | 75% |

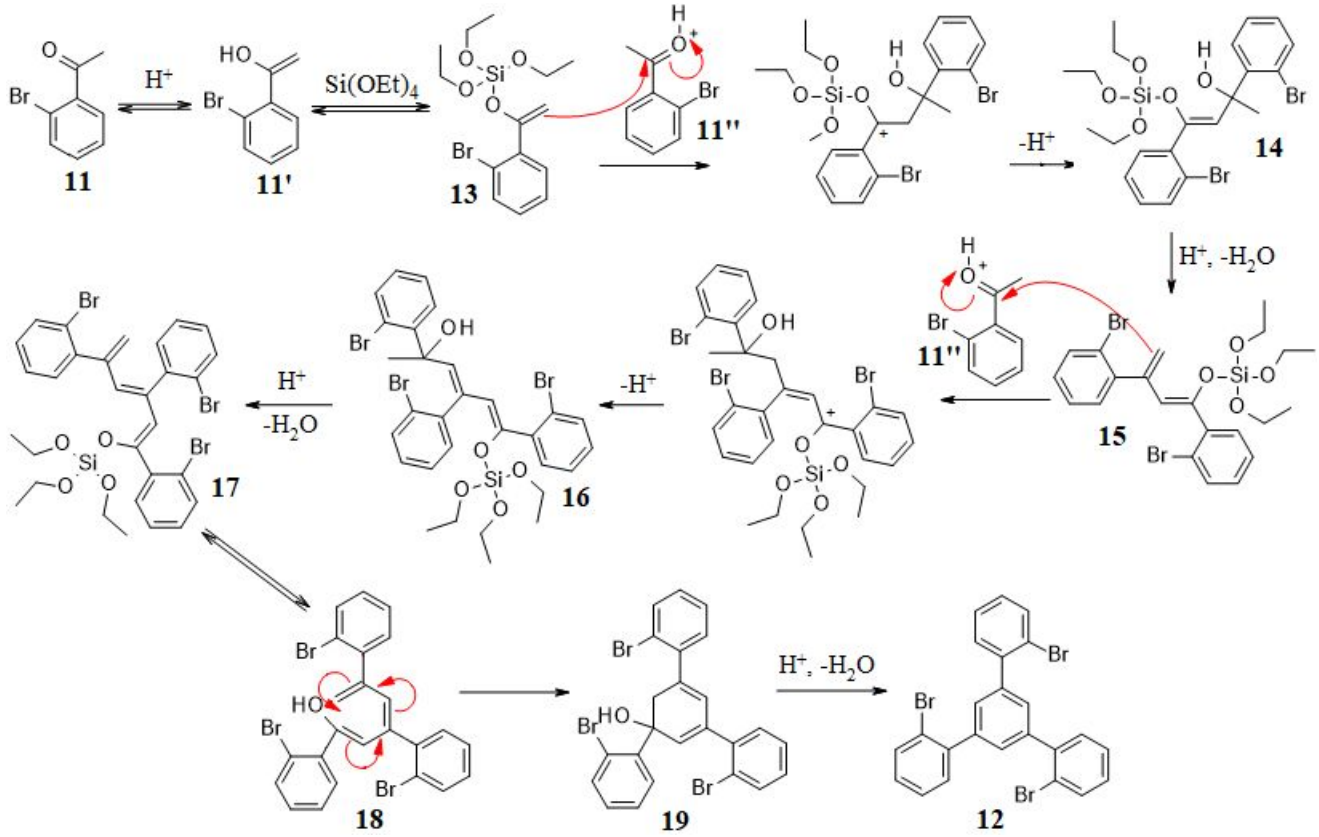
Our studies showed that the condensation of **11,** leading to **12**, can be performed without using very strong trifluoromethanesulfonic acid and high temperatures (

Scheme 3). The direct application of the methods used during the cyclotrimerization of acetophenone, for example, condensation in the presence of ethyl orthoformate and hydrogen chloride did not lead to satisfactory yields (Table 1).[51] One of the factors affecting the result of the reaction is the lower reactivity of the ketone **11,** compared to acetophenone, therefore the use of a stronger acid should generate enol form **11'** in a higher concentration, increasing the condensation yield. Chlorosulfonic acid plays a double role in the cyclotrimerization reaction. Firstly, chlorosulfonic acid, as a strong acid, is responsible for the shift of the keto-enol equilibrium and condensation of **11**. Secondly, the presence of the reactive Cl–S bond is responsible for binding water, produced during the

cyclotrimerization. Unfortunately, the chlorosulfonic acid alone does not induce condensation at room temperature, however, the introduction of tetraethoxysilane to the reaction mixture allows to obtain **12** with a yield reaching 75%. It turns out that tetraethoxysilane present in the reaction mixture, acts not only as a scavenger of produced water. Lowering the condensation temperature from 130°C to 25°C suggests a significant reduction of activation energy. Thus the conclusion is that, the tetraethoxysilane increases the reactivity of **11** in the condensation reaction. Interaction between **11** and tetraethoxysilane results in silyl ether of the enol form (Scheme 4).

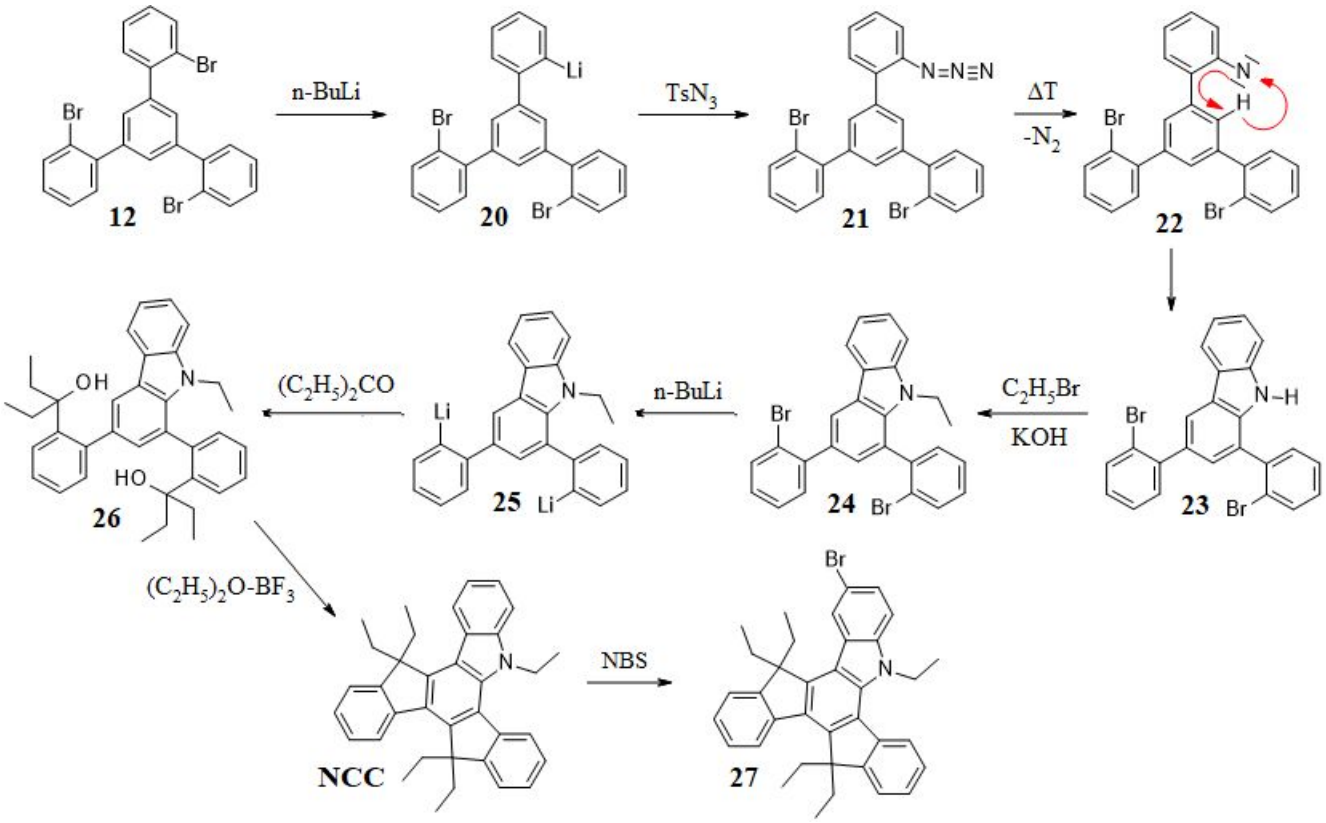
These types of systems are very susceptible to electrophilic attack, because of the stabilizing properties of the silicon atom towards the cation in the $\beta$ position.[52] The reaction between ether **13** and protonated ketone **11"** resulted in dimer formation **15**, which in turn reacted with **11"** giving the trimer **17.** As a result of following electrocyclization and elimination, **12** was obtained as a final product. Strong acid and tetraethoxysilane can be also generated In situ by performing condensation in ethanol in presence of silicon tetrachloride.[53]

**Scheme 4. Condensation mechanism in a presence of tetraethoxysilane.**




The next step of the synthetic route was a single lithiation of **12,** leading to an organometallic compound **20,** which afterwards reacted with tosyl azide, to form monoaziderivative **21 (**Scheme 5**)**. The isolation of the product by column chromatography turned out to be problematic, because both substrates and byproducts possessed similar polarity to **21**. The solution of this obstacle was thermal decomposition of reaction mixture in boiling 1,2-dichlorobenzene.

**Scheme 5. Synthesis of NCC and its bromoderivative 27.**




Nitrene **22,** created during thermolysis, underwent insertion into the C–H bond of the central benzene ring to form the carbazole derivative **23**. At this step, the product of thermal decomposition **23**, was separated from the substrates of the previous reaction. The final step was alkylation of **23** to give the N-ethylderivative **24**.The bromoderivative **24** was double lithiated and generated organometallic compound **25** was used in the reaction with pentan-3-one to form alcohol **26**. Diol **26** in the presence of a boron trifluoride underwent cyclization leading to **NCC**. In order to obtain higher reaction yield, the temperature during cyclization had to be controlled. Every drop of borontrifluorideetherate added to the reaction mixture, significantly increased the temperature. The uncontrolled reaction resulted in the creation of elimination byproducts, which reduced the yield and made the isolation of **NCC** difficult. In this case separation of the reaction mixture using liquid chromatography with reversed-phase polarity was necessary. The presence of one nitrogen atom allowed selective and efficient functionalization of the 5-azatruxene core, e.g. the reaction with N-bromosuccinimide resulted in monobromoderivative **27** formation**. 27** can be used to the further functionalization of 5-azatruxene core.

## CONCLUSIONS

Numerous synthetic steps and low reaction yield are the obvious obstacles to get new heterotruxene compounds. Application of completely new synthetic approach, or optimization of the synthesis of already known heterotruxenes is one of the goals of this research considering benefits from this class of compounds. The star-shaped structure is chemically and physically stable which is crucial in construction of new materials for optoelectronic application. This was confirmed by recent studies involving **(SO2)CC**, where the obtained emissive materials reveal high external quantum efficiencies at brightness up to 10 000 cd/m$^2$ and good thermal stability.[1] The synthetic route for unknown so far compound, **NCC**, opens a new research field in truxene-based donor-acceptor systems. In D-A molecules, heterotruxenes can act both as a donor (**NCC**) or acceptor (**(SO2)CC**). In this case, essential is the adjustment of energy levels of individual heterotruxene subunits, which is possible by introduction of particular heteroatom, or changing its oxidation state, as in the case of sulfur. Fast, effective and remarkable yield performance was developed, as described in this paper, giving rise to better accessibility of new truxene compounds which will have a great impact on the advanced organic electronics. The crystallographic and other experimental data placed in the electronic supporting info will be discussed in detail in a separate paper.

## EXPERIMENTAL

**General Information.** All solvents used were analytical grade. Toluene and tetrahydrofuran used in lithiation reaction were freshly distilled from $LiAlH_4$ under argon atmosphere. Benzo[b]thiophene, indan-1-one, 2'-bromoacetophenone and tetraethoxysilane were delivered with ABCR. Mass spectra was collected at Applied Biosystems 4000Q TRAP with electron impact as ionization method. $^1$H and $^{13}$C NMR spectra were measured at Bruker

DRX 500MHz in $CD_2Cl_2$ or $C_6D_6$. Shift of the residual peak of solvents was taken as an internal chemical shift.

*2-(indan-2-ylideno)-indan-1-one* – ***4.***[45] To 100 mL of methanol 26.4 g (0.2 mol) of indan-1-one, 89.2 mL (d = 0.964 g/mL, 0.4 mmol) of tetraethoxysilane and 10.68 mL (d = 1.836 g/mL, 0.2 mol) of $H_2SO_4$ was added. Mixture turns to yellow. After 5 days of stirring at room temperature the mixture was filtrated. The solid was washed with methanol until colorless filtrate was obtained. Crude product was purified by Soxhlet extraction with toluene and filtrated. 12.44 g of **4** as a pale yellow solid state was obtained with a yield 50.57 %. $^1$H NMR analysis confirms the structure of the compound.

*2-iodobenzo[b]thiophene* – ***3a.*** To 20 mL of tetrahydrofuran, 2.68 g (20 mmol) of benzo[b]thiophene **1** was added. The obtained mixture was cooled to -40ºC and 12 mL (2.5 M, 30 mmol) of n-butyllithium solution in hexane was added, then white participate was formed. After 1 h of stirring in constant temperature the solution of 7.62 g (30 mmol) of iodine in 20 mL of THF was added, then the solution was elevated to room temperature. After extraction with 50 mL of saturated aq solution of $Na_2S_2O_3$ and 20 mL of ethyl acetate, organic layer was separated, dried over $MgSO_4$ and evaporated. Crude 2-iodobenzo[b]thiophene **3** (5.2 g ~100%) as a white solid was taken to the next step without further purification. NMR analysis is in accordance with literature data.[54] $^1$H NMR (500 MHz, $CDCl_3$) δ: 7.41-7.45 (m, 2H), 7.64 (s, 1H), 7.81- 7.92 (m, 2H)$^{13}$C NMR (126 MHz, $CDCl_3$) δ: 79.3, 121.3, 122.4, 124.5, 124.6, 133.9, 140.9, 144.5

*3-(3-(benzo[b]thiophene-2-yl)-1H-inden-2-yl)-1H-indene* – ***6a***. To 60 mL of toluene, freshly distillated from $LiAlH_4$ under argon atmosphere, 5.2 g (20 mmol) 2-iodobenzo[b]thiophene **3a** was added. Obtained mixture was cooled to -78ºC and 8 mL (2.5 M, 20 mmol) of n-butyllithium solution in hexane was added, then white participate was formed. After 10 min the solution of 4.92 g (20 mmol) 2-(indan-2-ylideno)-indan-1-one **4** in 100 mL of toluene was added dropwise within 1 h. After that the solution was slowly elevated to room temperature (~1 h). There was a change of the color to dark red. After 3 h $NH_4Cl$ solution (1.07 g, 20 mmol, in 20 mL of water) and 100 mL of dichloromethane was added. Organic phase was separated and evaporated. Obtained dark oil residue was dissolved in 20 mL of 1,2-dichloroethane followed by the addition of 2.4 g (20 mmol) of $MgSO_4$ and 1.3 mL (d = 1.48 g/mL, 20 mmol) methanesulphonic acid. After 30 min of stirring in reflux, to cool down, the mixture, 40 mL of water and 60 mL of dichloromethane, was added. Organic phase was separated and water phase was extracted 3 times with 30 mL of dichloromethane. Combined organic phases were dried over $MgSO_4$ and evaporated. Crude product was purified via column chromatography using silica gel as the stationary phase and 10% dichloromethane in hexane to obtain 3.20 g (44.1%) of a final product **6a** as a white solid, m.p. 194°C. $^1$H NMR (500 MHz, $CD_2Cl_2$) δ: 7.78 – 7.72 (m, 3H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.43 (s, 1H), 7.39 (td, *J* = 7.5, 0.5 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.13 (td, *J* = 7.4, 1 Hz, 1H), 7.05 (td, *J* = 7.5, 0.5 Hz, 1H), 6.64 (t, *J* = 2.2 Hz, 1H), 3.95 (s, 2H), 3.53 (d, *J* = 2.1 Hz, 2H); $^{13}$C NMR (126 MHz, $CD_2Cl_2$) δ: 144.5, 143.7, 143.5, 142.3, 140.3, 140.2, 139.5, 139.4, 136.7, 133.9, 133.1, 126.2, 125.4, 124.9, 124.2, 123.7, 123.3, 123.3, 123.2, 123.0, 121.5, 120.2, 120.0, 42.7, 38.3; HRMS (EI – TOF) m/z (M+): Calcd for $C_{26}H_{18}S$ 362.1129; Found 362.1117; Elemental analysis (%). Calcd for $C_{26}H_{18}S$: C 86.15, H 5.01; Found: C 86.21, H 4.98

*10,10,15,15-tetraethyl-5-thiatruxene* – ***SCC.*** To 3.65 mL of hexane 1.32 g (3.65 mmol) of 3-(3-(benzo[b]thiophene-2-yl)-1H-inden-2-yl)-1H-indene **6a** and 92.7 mg (0.365 mmol) of iodine was added, then the irradiation of mixture with UV-C lamp (55 W) was started. After 3 h solvent was evaporated and brown solid was collected. Next it was suspended in 18.25 mL of dimethylformamide (saturated with argon in 0°C for 1 h). Afterwards 1.8 g (32.16 mmol) of shredded KOH and 2.4 mL (32.16 mmol, d = 1.46 g/mL) of ethyl bromide was added. After 24 h of stirring 20 mL of water was added to the brown solution. The mixture was extracted three times with 10 mL of dichloromethane, combined organic phases were dried over $MgSO_4$ and evaporated. Crude product was purified via column chromatography using silica gel as the stationary phase and 10% dichloromethane in hexane as eluent to obtain 880.42 mg (51.2%) of **SCC** as a white solid, mp 207-209°C. $^1$H NMR (500 MHz, $CD_2Cl_2$) δ: 8.95 (d, *J* = 8.1 Hz, 1H), 8.37 (d, *J* = 7.1 Hz, 1H), 8.20 – 8.16 (m, 1H), 8.06 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.60-7.51 (m, 5H), 7.48-7.40 (m, 3H), 3.13 (dq, *J* = 14.4, 7.2 Hz, 2H), 3.00 (dq, *J* = 14.6, 7.3 Hz, 2H), 2.34-2.26 (m, 4H), 0.24 (t, *J* = 7.3 Hz, 6H), 0.22 (t, *J* = 7.3 Hz, 6H); $^{13}$C NMR (126 MHz, $CD_2Cl_2$) δ: 152.0, 151.9, 145.9, 142.5, 140.7, 140.4, 140.1, 137.7, 135.7, 134.3, 132.70, 132.68, 127.08, 127.05, 126.9, 126.6, 126.4, 125.9, 124.1, 123.9, 123.1, 122.3, 122.1, 121.5, 58.8, 57.8, 29.7, 29.4, 8.5, 8.4; HRMS (EI – TOF) m/z (M+): Calcd for $C_{34}H_{32}S$ 472.2225, Found 472.2215; Elemental analysis (%). Calcd for $C_{34}H_{32}S$: C 86.39, H 6.82; Found: C 86.44, H 6.88.

*5-oxo-10,10,15,15-tetraethyl-5-thiatruxene* – ***(SO)CC.*** To the mixture of acetic acid and dichloromethane (11 mL and 4 mL respectively), 130 mg (0.275 mmol) of **SCC** and 0.102 mL (0.825 mmol) of a 30% aqueous solution of hydrogen peroxide was added. After 24 h, 10 mL of water and 10 mL of dichloromethane were added. The organic layer was washed with an aqueous $NaHCO_3$ solution, dried over $MgSO_4$, filtrated and evaporated. The crude product was adsorbed at $SiO_2$ and purified via column chromatography using silica gel as a stationary phase and 5% → 20% ethyl acetate in hexane as an eluent. After evaporation of the fractions, the product was dissolved in methanol and aqueous NaCl was added. The obtained white solid (mp. 194-196°C) was collected by filtration to give 79 mg (58.8%) of the product **(SO)CC**. $^1$H NMR (500 MHz, $CD_2Cl_2$) δ: 8.59 – 8.52 (m, 2H), 8.38 (dd, *J* = 6.0, 2.4 Hz, 1H), 8.12 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.73 (t, *J* = 7.4Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.56 – 7.44 (m, 6H), 3.04 – 2.87 (m, 4H), 2.32 – 2.14 (m, 4H), 0.33 (t, *J* = 7.4 Hz, 3H), 0.28 (t, *J* = 7.3 Hz, 3H), 0.19 (t, *J* = 7.3 Hz, 3H), 0.16 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (126 MHz, $CD_2Cl_2$) δ: 153.3, 152.7, 146.0, 145.3, 145.2, 145.0, 143.3, 139.1, 138.5, 137.00, 136.98, 133.9, 132.3, 129.1, 129.0, 128.6, 128.2, 127.9, 127.8, 127.1, 125.4, 124.5, 122.9, 122.6, 58.8, 57.8, 30.4, 30.0, 29.5, 29.5, 8.9, 8.8, 8.71, 8.68; HRMS

(EI – TOF) m/z (M+):Calcd for $C_{34}H_{32}SO$ 488.2174, Found 488.2172; Elemental analysis (%). Calcd for $C_{34}H_{32}OS$: C 83.56, H 6.60; Found: C 83.71, H 6.68.

*5,5-dioxo-10,10,15,15-tetraethyl-5-thiatruxene* – ***(SO$_2$)CC.*** 283.6 mg (0.6 mmol) of **SCC** and 443.75 mg (1.8 mmol, 70%) of m-chloroperbenzoic acid were introduced into 5 mL of dichloromethane. After 1 h, 5 mL (3 M) of aqueous NaOH solution was added. The organic layer was separated, the aqueous layer was washed with 5 mL dichloromethane and the combined extracts were dried over $MgSO_4$, filtrated, evaporated and dried in vacuo to give 283.2 mg (93.61%) of white solid, mp 221-223°C. NMR analyzes are in accordance with literature data.[46] $^1$H NMR (500 MHz, $CDCl_3$) δ: 8.68 – 8.77 (m, 1H). 8.45 (d, *J* = 8.1 Hz, 1H), 8.37 (d, *J* = 7.3 Hz, 1H),8.00 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.72 (ddd, *J* = 8.3, 7.4, 1.4 Hz, 1H), 7.59 (td, *J* = 7.5, 0.7 Hz, 1H), 7.43 – 7.52 (m, 6H), 2.89 (m, *J* = 14.0, 7.2 Hz, 4H), 2.21 (m, *J* = 14.1, 7.4 Hz, 4H), 0.27 (t, *J* = 7.3, 12H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ:153.2, 152.3, 146.3, 145.5, 145.2, 139.9, 138.4, 138.1, 136.6, 133.2, 131.9, 129.6, 129.4, 129.3, 128.6, 127.8, 127.6, 127.4, 126.9, 125.3, 125.0, 122.6, 122.5, 122.0, 58.3, 57.3, 29.7, 29.6, 8.8, 8.7; HRMS (EI – TOF) m/z (M+):Calcd for $C_{34}H_{32}SO_2$ 504.2123, Found 504.2128; Elemental analysis (%). Calcd for $C_{34}H_{32}O_2S$: C 80.92, H 6.39; Found: C 81.06, H 6.47.

*6-iodo-5,5-dioxo-10,10,15,15-tetraethyl-5-thiatruxene* – ***10.*** To 1 mL of tetrahydrofuran 0.204 mL (1.2 mmol, d = 0.83 g/mL) 2,2,6,6-tetramethylpiperidine was added and cooled to -78°C. After that 0.48 mL (1.2 mmol, 2.5 M) of a solution of n-butyllithium in hexane was added and the mixture was elevated to room temperature. White solid precipitation was obtained in one minute. The mixture was kept at constant temperature 10 min and then cooled down and the solution of 302.5 mg (0.6 mmol) of **(SO$_2$)CC** in 6 mL of tetrahydrofuran was added. The mixture was dark green at this step. After 0.5 h, 304.8 mg (1.2 mmol) of iodine was added and the mixture was elevated to room temperature, followed by the addition of 600 mg of $Na_2S_2O_3$ and 5 mL of water. The organic phase was separated, whereas the aqueous layer was extracted with 6 mL of ethyl acetate. The combined extracts were dried over $MgSO_4$ and evaporated to give 373.2 mg (98.7%) of a gray-brown solid. In order to obtain a pure analytical sample, the product **10** was purified via column chromatography using silica gel as a stationary phase and 20% ethyl acetate in hexane solution as an eluent. In this way, iododerivative **10** was obtained in the form of a pale yellow solid, m.p. 231°C.$^1$H NMR (500 MHz, $CD_2Cl_2$) δ: 8.69 (d, *J* = 7.8 Hz, 1H), 8.51 (d, *J* = 8.1 Hz, 1H), 8.39 (d, *J* = 7.1 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.56 – 7.46 (m, 6H), 7.41 (t, *J* = 7.9 Hz, 1H), 2.95 – 2.89 (m, 2H), 2.88 – 2.76 (m, 2H), 2.30 – 2.16 (m, 4H), 0.29 – 0.26 (m, 6H), 0.26 – 0.23 (m, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ: 153.0, 152.4, 148.2, 147.3, 146.5, 144.4, 143.2, 140.6, 137.8, 134.2, 131.4, 131.1, 129.94, 129.85, 129.6, 129.2, 127.8, 127.6, 127.3, 125.8, 125.2, 123.0, 122.7, 100.4, 58.8, 57.8, 30.00, 29.9, 8.9, 8.8; HRMS (EI – TOF) m/z (M+): Calcd for $C_{34}H_{31}SO_2I$ 630.1090, Found 630.1104 . Elemental analysis (%). Calcd for $C_{34}H_{31}O_2SI$: C 64.76, H 4.96; Found: C 64.69, H 4.97.

*2,8,12-tribromo-5,5-dioxo-10,10,15,15-tetraethyl-5-thiatruxene* – ***9.*** Step I (bromination): 472 mg (1 mmol) of **SCC** was dissolved in 10 mL of dichloromethane and 0.207 mL (4 mmol d = 3.119 g/mL) of bromine was added. The mixture was heated to the boiling temperature- the solution became muddy. After 1 h it was cooled down, to add 20 mL of hexane and then continuously cooled down to reach 0°C. The mixture was filtered to get **8** as a white solid. Step II (oxidation): The obtained bromination product **8** was dissolved in 10 mL of dichloromethane and 737 mg (3 mmol, C = 70%) of water-stabilized m-chloroperbenzoic acid were added. After 1 h the whole mixture was evaporated and the solid residue obtained was washed with aqueous NaOH solution, 280 mg (6 mmol) in 10 mL of water, and mixture of 10 mL of water and 20 mL of methanol. After drying, 904 mg (91%) of **9** in a form of white solid were obtained. NMR analyzes are in accordance with literature data.[46] $^1$H NMR (500 MHz, $CDCl_3$) δ: 8.56 (d, *J* = 1.1 Hz 1H), 8.55 (d, *J*=8.5 Hz,1H), 8.18 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.75 (dd, *J* = 8.1 Hz, 1.3 Hz, 1H), 7.58–7.64 (m, 4H), 2.70–2.86 (m, 4H), 2.12–2.25 (m, 4H), 0.31 (t, *J* = 7.2 Hz, 6H), 0.27 (t, J=7.2 Hz, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ:155.5, 154.5, 146.7, 144.7, 145.6, 139.3, 137.0, 136.8, 135.3, 133.6, 132.7, 131.2, 130.7, 130.6, 130.3, 128.3, 127.0, 126.7, 126.6, 126.1, 125.6, 124.3, 123.9, 123.8, 58.9, 57.8, 29.8, 29.7, 8.9, 8.8; HRMS (EI – TOF) m/z (M+): Calcd for $C_{34}H_{29}SO_2Br_3$ 737.9438, Found 737.9405; Elemental analysis (%). Calcd for $C_{34}H_{29}O_2SBr_3$: C 55.08, H 3.94; Found C 55.16, H 3.98.

*1,3,5-tri(2-bromophenyl)benzene* – ***12***. To 15 mL of dichloromethane 1.35 mL (10 mmol, d = 1.476 g/mL) of 2'-bromoacetophenone, 666 µL (10 mmol, d = 1.753 g/mL) of chlorosulfonic acid and 2.94 mL (20 mmol, d = 1.032 g/mL) of tetraethoxysilane was added. There was a change in the color of the solution to red, which was darkening with time. After 48 h, 10 mL (1 M) aqueous $Na_2CO_3$ solution was added. The produced silica was filtered on Celite and washed 3 times with 10 mL of dichloromethane. The organic phase was separated, dried over $MgSO_4$, filtrated and evaporated. The crude product was suspended in 5 mL of a 20 % solution of acetone in hexane and filtered to give 1.36 g (75%) of **12** as a pale yellow solid, mp 158-160°C.[55] NMR analysis is in accordance with literature data.[56] $^1$H NMR (400MHz, $CDCl_3$) δ: 7.69 (d, *J* = 7.8 Hz, 3H), 7.51-7.26 (m, 9H), 7.22 (m, 3H); $^{13}$C NMR (99MHz, $CDCl_3$) δ: 142.3, 140.9, 133.6, 131.9, 130.1, 129.4, 128.0, 122.9; LR MS FD: 543.80 (M+).

*Tosyl azide.* To the solution of water and acetone (300 mL and 500 mL respectively) 71.5 g (1.1 mol) of $NaN_3$ was added. Than the solution of 190.7 g (1 mol) of p-toluenesulfonyl chloride in 500 mL of acetone was added quickly during intense stirring. The mixture was heated up, what results in the formation of a two-phase system. After 2 h, the acetone was evaporated under reduced pressure, in temperature not exceeding 35°C. The aqueous layer was extracted with 200 mL of dichloromethane and the separated organic layer was washed with 2×200 mL of water and dried over $Na_2SO_4$, then was filtrated and evaporated not exceeding 35°C. 195.24 g (99%) of a colorless liquid was obtained.[57] NMR analysis is in accordance with literature data.[58] $^1$H NMR (300 MHz, $CDCl_3$) δ: 7.80 (d, *J*=8.4 Hz, 2H), 7.38 (d, *J*=8.7 Hz, 2H), 2.45 (s, 3H); $^{13}$C NMR (75 MHz. $CDCl_3$) δ: 146.0, 135.1, 130.0, 127.2, 21.6.

*1,3-(2-bromophenyl)-9-ethylcarbazole* – ***24.*** Step I (bromine to azide exchange): To 20 mL of tetrahydrofuran, 2.715 g (5 mmol) of 1,3,5-tri(2-bromophenyl)benzene **12** was added. Obtained mixture was cooled down to -78°C and 2.1 mL (2.5 M, 5.25 mmol) of n-butyllithium solution in hexane was added - mixture turns brown. After 1 h of stirring in constant temperature 1 g (5.5 mmol) tosyl azide was added. Color of the solution becomes dark brown. Then the mixture was slowly elevated to room temperature. After 12 h the 5.25 mL (1 M) of aq solution of $NH_4Cl$ and 10 mL of dichloromethane was added. Organic phase was separated whereas water phase was extracted with 10 mL of dichloromethane. Mixed organic phases were dried over $MgSO_4$ and evaporated. Crude product was purified via column chromatography using silica gel as the stationary phase and 10% dichloromethane in hexane as eluent to obtain 2.39 g of monoazide derivative **21** in the form of pale yellow oil. The product was contaminated with substrates. Step II (nitrene insertion): **21** was dissolved in 4.74 mL of o-dichlorobenzene and the mixture was heated to temperature 180°C. The mixture turns dark brown. After 1 h the reaction was cooled to room temperature and crude product was purified via column chromatography using silica gel as a stationary phase and hexane→10% dichloromethane in hexane→5% ethyl acetate in hexane as an eluent. Obtained 1.48 g of carbazole derivative **23** as a pale orange solid was used in the next step. Step III (carbazole alkylation): To 6.2 mL of dimethylsulphoxide, 1.48 g (3.1 mmol) of **23** and 347.22 mg (6.2 mmol) of shredded KOH was added. After that 0.465 mL (6.2 mmol, d = 1.46 g/mL) of ethyl bromide was added dropwise. After 24 h 6.2 mL of water and 6.2 mL of dichloromethane was added. Organic phase was separated, whereas water phase was extracted with 6.2 mL of dichloromethane. Mixed organic phases were dried over $MgSO_4$ and evaporated. Crude product was purified via column chromatography using silica gel as a stationary phase and 5→10% dichloromethane in hexane as an eluent. 1.46 g (58% after 3 steps) of **24** as a white solid was obtained, m.p. 175°C. $^1$H NMR (500 MHz, $CD_2Cl_2$) δ: 8.20 (d, *J* = 1.8 Hz, 1H), 8.14 (d, *J* = 7.73 Hz, 1H), 7.76 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.72 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.59 (dd, *J* = 8.1, 2.5 Hz, 1H), 7.53 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.48 (m, 2H), 7.42 (m, 2H), 7.36 (ddd, *J* = 10.0, 6.1, 2.1 Hz, 1H), 7.29 (d, *J* = 1.8 Hz, 1H), 7.26 (ddd, *J*= 1H), 7.23 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 3.99 (dq, *J* = 14.3, 7.1 Hz, 1H), 3.84 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.03 (t, *J* =7.2Hz, 3H); $^{13}$C NMR (126 MHz, $CD_2Cl_2$) δ: 143.1, 141.5, 141.2, 136.6, 133.5, 132.7, 132.3, 132.2, 131.8, 130.2, 130.0, 128.8, 127.8, 127.6, 126.4, 125.4, 124.3, 124.2, 123.4, 123.4, 121.0, 120.5, 119.7, 109.5, 39.1, 14.3; HRMS (EI – TOF) m/z (M+): Calcd for $C_{26}H_{19}NBr_2$ 502.9884, Found 502.9870; Elemental analysis (%). Calcd for $C_{26}H_{19}Br_2N$: C 61.81, H 3.79, N 2.77; Found: C 61.87, H 3.81, N 2.71.

*5,10,10,15,15-pentaethyl-5-azatruxene* – ***NCC.*** Step I (diol synthesis): To 10 mL of tetrahydrofuran, 757 mg (1.5 mmol) of 1,3-(2-bromophenyl)-9-ethylcarbazole **24** was added. Obtained mixture was cooled down to -78°C. Than 1.2 mL (2.5 M, 3 mmol) of n-butyllithium solution in hexane was added. The mixture turns to yellow. After 20 min of stirring at constant temperature 0.32 mL (d = 0.815 g/mL, 3 mmol) of pentan-3-one was added. The solution turns to dark brown. Next the solution was slowly elevated to room temperature. After 12 h the 3 mL (1 M) of aq solution of $NH_4Cl$ and 10 mL dichloromethane was added. Organic phase was separated and water phase was extracted with 10 mL of dichloromethane. Mixed organic phases were dried over $MgSO_4$ and evaporated. Crude product was dissolved in toluene and adsorbed with 4 g of silica gel. Product was purified via column chromatography using silica gel (40 g) as a stationary phase and 3→10% ethyl acetate in hexane as an eluent to obtain 503 mg (64.6%)of **26** as a colorless oil. Step II (rings formation): To 10 mL of dichloromethane, freshly distilled from $H_2SO_4$, 518.6 mg (1 mmol) of **26** was added. Obtained mixture was cooled to 0°C and 0.278 mL of $Et_2O$-$BF_3$, freshly distilled under argon atmosphere, was slowly added. Mixture turns yellow, and started darkening during the reaction. After 30 min 1 mL of methanol was added and solution was evaporated. Crude product was purified via column chromatography using aluminum oxide as stationary phase and hexane as an eluent to obtain 404.7 mg (86.5%) of **NCC** as a white solid, mp 181-182 °C. (In the case of many byproducts, presented in the reaction mixture after step II, purification with RP18 as stationary phase and acetonitrile as eluent is necessary). $^1$H NMR (500 MHz, $C_6D_6$) δ: 8.67 (d, *J* = 7.9 Hz, 1H), 8.43 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.44 – 7.20 (m, 9H), 4.33 (q, *J* = 7.0 Hz, 2H), 3.11 (m, 4H), 2.17 (m, 4H), 0.67 (t, *J* = 7.0 Hz, 3H), 0.42 (t, *J* = 7.3 Hz, 6H), 0.32 (t, *J* = 7.3 Hz, 6H); $^{13}$C NMR (126 MHz, $C_6D_6$) δ: 151.5, 151.2, 145.3, 145.0, 143.3, 142.0, 140.6, 139.0, 132.8, 127.9, 126.6, 126.4, 126.2, 126.0, 125.6, 125.3, 124.9, 123.6, 122.8, 122.5, 122.3, 122.2, 120.2, 112.2, 58.2, 56.9, 42.1, 30.0, 29.8, 12.5, 8.6, 8.4; HRMS (EI – TOF) m/z (M+): Calcd for $C_{36}H_{37}N$ 483.2926, Found 483.2916; : Elemental analysis (%). Calcd for $C_{36}H_{37}N$: C 89.39, H 7.71, N 2.90; Found: C 89.45, H 7.73. N 2.87.

*8-bromo-5,10,10,15,15-pentaethyl-5-azatruxene* – ***27.*** 43.5 mg (0.09 mmol) of **NCC** and 24 mg (0.135 mmol) of N-bromosuccinimide was added to 4.5 mL dichloromethane. The progress of the reaction was monitored on TLC. After 4 h 10 mL of dichloromethane and 10 mL of saturated aqueous $NaHCO_3$ solution were added. The phases were separated and the organic phase was dried over $MgSO_4$ and evaporated. The solid residue was suspended in methanol and filtered to give 50.46 mg (~100%) of **27** as a white solid. $^1$H NMR (500 MHz, $CD_2Cl_2$) δ: 8.65 (s, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.62 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.57 – 7.34 (m, 7H), 4.72 (q, *J* = 7.0 Hz, 2H), 3.02 (dq, *J* = 14.4, 7.2 Hz, 2H), 2.91 (dq, *J* = 14.3, 7.2 Hz, 2H), 2.27 (dq, *J* = 14.4, 7.2 Hz, 4H), 0.97 (t, *J* = 7.0 Hz, 3H), 0.25 (t, *J* = 7.3 Hz, 6H), 0.18 (t, *J* = 7.3 Hz, 6H); $^{13}$C NMR (126 MHz, $CD_2Cl_2$) δ: 152.0, 151.5, 145.4, 144.7, 144.3, 142.0, 140.5, 139.6, 133.5, 128.3, 127.7, 127.4, 127.0, 126.7, 126.5, 126.1, 124.1, 122.8, 122.7, 122.6, 121.8, 114.0, 113.2, 58.7, 57.4, 43.1, 30.4, 30.0, 13.1, 8.8, 8.7; HRMS (EI – TOF) m/z (M+): Calcd for $C_{36}H_{36}NBr$ 561.2031, Found 561.2038; Elemental analysis (%). Calculated for $C_{36}H_{36}$ BrN: C 76.86, H 6.45, N 2.49; Found: C 76.95, H 6.51, N 2.43.

## ASSOCIATED CONTENT

**Supporting Information.**

Crystal structures and NMR are available free of charge via the Internet at http://pubs.acs.org.

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## REFERENCES

(1) 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.* **2018**, *1807572*, 1–13.

(2) Tisch, T. L.; Lynch, T. J.; Dominguez, R. Polymetallic Compounds of Extended Polyaromatic Ligands. Rhenium and Manganese Carbonyl Derivatives of Truxene. *J. Organomet. Chem.* **1989**, *377*, 265–273.

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

(4) Li, L.-L.; Hu, P.; Wang, B.-Q.; Yu, W.-H.; Shimizu, Y.; Zhao, K.-Q. Synthesis and Mesomorphism of Ether-Ester Mixed Tail C3-Symmetrical Truxene Discotic Liquid Crystals. *Liq. Cryst.* **2010**, *37* (5), 499–506.

(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) 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.

(7) Manini, P.; d'Ischia, M.; Milosa, M.; Prota, G. Acid-Promoted Competing Pathways in the Oxidative Polymerization of 5,6-Dihydroxyindoles and Related Compounds: Straightforward Cyclotrimerization Routes to Diindolocarbazole Derivatives. *J. Org. Chem.* **1998**, *63* (20), 7002–7008.

(8) Wang, F.; Li, X.-C.; Lai, W.-Y.; Chen, Y.; Huang, W.; Wudl, F. Synthesis and Characterization of Symmetric Cyclooctatetraindoles: Exploring the Potential as Electron-Rich Skeletons with Extended π-Systems. *Org. Lett.* **2014**, *16* (11), 2942–2945.

(9) Sanguinet, L.; Williams, J. C.; Yang, Z.; Twieg, R. J.; Mao, G.; Singer, K. D.; Wiggers, G.; Petschek, R. G. Synthesis and Characterization of New Truxenones for Nonlinear Optical Applications. *Chem. Mater.* **2006**, *18*, 4259–4269.

(10) Bura, T.; Leclerc, N.; Bechara, R.; Lévêque, P.; Heiser, T.; Ziessel, R. Triazatruxene-Diketopyrrolopyrrole Dumbbell-Shaped Molecules as Photoactive Electron Donor for High-Efficiency Solution Processed Organic Solar Cells. *Adv. Energy Mater.* **2013**, *3* (9), 1118–1124.

(11) Robertson, N.; Parsons, S.; MacLean, E. J.; Coxall, R. A.; Mount, A. R. Preparation, X-Ray Structure and Properties of a Hexabrominated, Symmetric Indole Trimer and Its TCNQ Adduct: A New Route to Functional Molecular Systems. *J. Mater. Chem.* **2000**, *10* (9), 2043–2047.

(12) 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.

(13) 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.

(14) 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.

(15) Kojima, T.; Furukawa, S.; Tsuji, H.; Nakamura, E. Synthesis of Triphosphatruxene via Sextuple Aromatic Nucleophilic Substitution and Simple Isolation of Stereoisomers. *Chem. Lett.* **2014**, *43* (5), 676–677.

(16) Bergman, J.; Egestad, B. Cyclotrimerization of 3(2H)-Benzo[b]Furanone, 3-Acetoxybenzo[b]Thiophene and 3(2H)-Benzo[b]Selenophenone in Trifluoroacetic Acid. *Chem. Scr.* **1986**, *26* (2), 287–292.

(17) Bergman, J.; Egestad, B. Cyclocondensation of 3(2H)-Benzo[b]Thiophenone and Oxidation Products Obtained During These Reaction. *Tetrahedron* **1986**, *42* (2), 763–773.

(18) 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.

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

(20) Tinh, N. H.; Malthete, J.; Destrade, C. Reentrant Phenomenon in Disc-Like Liquid Crystal. *Mol. Cryst. Liq. Cryst.* **1981**, *64*, 291–298.

(21) 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.

(22) Lai, W.-Y.; Xia, R.; He, Q.-Y.; Levermore, P. A.; Huang, W.; Bradley, D. D. C. Enhanced Solid-State Luminescence and Low-Threshold Lasing from Starburst Macromolecular Materials. *Adv. Mater.* **2009**, *21* (3), 355–360.

(23) 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).

(24) 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.

(25) 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–A3 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).

(26) Grisorio, R.; Iacobellis, R.; Listorti, A.; De Marco, L.; Cipolla, M. P.; Manca, M.; Rizzo, A.; Abate, A.; Gigli, G.; Suranna, G. P. Rational Design of Molecular Hole-Transporting Materials for Perovskite Solar Cells: Direct versus Inverted Device Configurations. *ACS Appl. Mater. Interfaces* **2017**, *9* (29), 24778–24787.

(27) Rakstys, K.; Paek, S.; Gao, P.; Gratia, P.; Marszalek, T.; Grancini, G.; Cho, K. T.; Genevicius, K.; Jankauskas, V.; Pisula, W.; et al. Molecular Engineering of Face-on Oriented Dopant-Free Hole Transporting Material for Perovskite Solar Cells with 19% PCE. *J. Mater. Chem. A* **2017**, *5* (17), 7811–7815.

(28) Andrikaityte, E.; Simokaitiene, J.; Tomkeviciene, A.; Grazulevicius, J. V.; Jankauskas, V. Synthesis and Properties of Triindole-Based Monomers and Polymers. *Mol. Cryst. Liq. Cryst.* **2014**, *590*, 121–129.

(29) Qian, X.; Lu, L.; Zhu, Y.-Z.; Gao, H.-H.; Zheng, J.-Y. Triazatruxene-Based Organic Dyes Containing a Rhodanine-3-Acetic Acid Acceptor for Dye-Sensitized Solar Cells. *Dye. Pigment.* **2015**, *113*, 737–742.

(30) 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.

(31) 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.

(32) 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.

(33) Yang, P.-C.; Wen, H.-W.; Huang, C.-W.; Zhu, Y.-N. Synthesis and Chemosensory Properties of Two-Arm Truxene-Functionalized Conjugated Polyfluorene Containing Terpyridine Moiety. *RSC Adv.* **2016**, *6* (90), 87680–87689.

(34) 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.

(35) Xu, Y.; Wu, X.; Chen, Y.; Hang, H.; Tong, H.; Wang, L. Star-Shaped Triazatruxene Derivatives for Rapid Fluorescence Fiber-Optic Detection of Nitroaromatic Explosive Vapors. *RSC Adv.* **2016**, *6* (38), 31915–31918.

(36) Earmrattana, N.; Sukwattanasinitt, M.; Rashatasakhon, P. Water-Soluble Anionic Fluorophores from Truxene. *Dye. Pigment.* **2012**, *93* (1), 1428–1433.

(37) Sam-ang, P.; Raksasorn, D.; Sukwattanasinitt, M.; Rashatasakhon, P. A Nitroaromatic Fluorescence Sensor from a Novel Tripyrenyl Truxene. *RSC Adv.* **2014**, *4* (101), 58077–58082.

(38) Xu, Y.; Wu, X.; Chen, Y.; Hang, H.; Tong, H.; Wang, L. Fiber-Optic Detection of Nitroaromatic Explosives with Solution-Processable Triazatruxene-Based Hyperbranched Conjugated Polymer Nanoparticles. *Polym. Chem.* **2016**, *7* (27), 4542–4548.

(39) Wang, K.-R.; An, H.-W.; Han, D.; Qian, F.; Li, X.-L. Fluorescence Quenching of Triazatruxene-Based Glycocluster Induced by Peanut Agglutinin Lectin. *Chinese Chem. Lett.* **2013**, *24* (6), 467–470.

(40) Wang, K.-R.; Wang, Y.-Q.; An, H.-W.; Zhang, J.-C.; Li, X.-L. A Triazatruxene-Based Glycocluster as a

Fluorescent Sensor for Concanavalin A. *Chem. - A Eur. J.* **2013**, *19* (8), 2903–2909.

(41) Huang, W.; Smarsly, E.; Han, J.; Bender, M.; Seehafer, K.; Wacker, I.; Schröder, R. R.; Bunz, U. H. F. Truxene-Based Hyperbranched Conjugated Polymers: Fluorescent Micelles Detect Explosives in Water. *ACS Appl. Mater. Interfaces* **2017**, *9* (3), 3068–3074.

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

(43) 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.

(44) 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.

(45) 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.

(46) 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.

(47) Jiang, Q.; Duan-Mu, D.; Zhong, W.; Chen, H.; Yan, H. Amino-Directed RhIII-Catalyzed C–H Activation Leading to One-Pot Synthesis of N–H Carbazoles. *Chem. - A Eur. J.* **2013**, *19* (6), 1903–1907.

(48) Kim, M.; Lee, J. Y. Synthesis of 2- and 4-Substituted Carbazole Derivatives and Correlation of Substitution Position with Photophysical Properties and Device Performances of Host Materials. *Org. Electron.* **2013**, *14* (1), 67–73.

(49) Ullah, E.; Mcnulty, J.; Robertson, A. Highly Chemoselective Mono-Suzuki Arylation Reactions on All Three Dichlorobenzene Isomers and Applications Development. *European J. Org. Chem.* **2012**, *2012* (11), 2127–2131.

(50) Feng, X.; Wu, J.; Enkelmann, V.; Müllen, K. Hexa-Peri-Hexabenzocoronenes by Efficient Oxidative Cyclodehydrogenation: The Role of the Oligophenylene Precursors. *Org. Lett.* **2006**, *8* (6), 1145–1148.

(51) Khotina, I. A.; Consonni, R.; Kushakova, N. S.; Porzio, W.; Giovanella, U.; Kovalev, A. I.; Babushkina, M. A.; Peregudov, A. S.; Destri, S. Branched Polyphenylenes and Phenylene Dendrimers : NMR and Optical Studies. *Eur. Polym. J.* **2013**, *49* (12), 4224–4237.

(52) Lambert, J. B.; Zhao, Y.; Emblidge, R. W.; Salvador, L. A.; Liu, X.; So, J.-H.; Chelius, E. C. The β Effect of Silicon and Related Manifestations of σ Conjugation. *Acc. Chem. Res.* **1999**, *32* (2), 183–190.

(53) Trawny, D.; Quennet, M.; Rades, N.; Lentz, D.; Paulus, B.; Reissig, H.-U. Syntheses, Structures and Conformational Dynamics of 1,3,5-Tris(3′′-Ethynylbiphenyl-2′-Yl)Benzene Derivatives. *European J. Org. Chem.* **2015**, *2015* (21), 4667–4674.

(54) L'Helgoual'ch, J. M.; Seggio, A.; Chevallier, F.; Yonehara, M.; Jeanneau, E.; Uchiyama, M.; Mongin, F. Deprotonative Metalation of Five-Membered Aromatic Heterocycles Using Mixed Lithium-Zinc Species. *J. Org. Chem.* **2008**, *73* (1), 177–183.

(55) Pietraszkiewicz, M.; Maciejczyk, M. R.; Górski, K. P. Sposób Wytwarzania Pochodnych 1,3,5-Triarylobenzenu i Truksenu. 404606, 2013.

(56) Maciejczyk, M.; Pietraszkiewicz, M.; Górski, K. Process for Preparing Derivatives of 1,3,5-Triarylbenzene and Truxene, 2015.

(57) Curphey, T. J. Preparation of P-Toluenesulfonylazide. A Cautionary Note. *Org. Prep. Proced. Int.* **1981**, *13* (2), 112–115.

(58) Waser, J.; Gaspar, B.; Nambu, H.; Carreira, E. M. Hydrazines and Azides via the Metal-Catalyzed Hydrohydrazination and Hydroazidation of Olefins. *J. Am. Chem. Soc.* **2006**, *128* (35), 11693–11712.

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