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Synthesis and Photochemical Properties of 3,6-Di-*tert*-butyl-9*H*-carbazole Derivatives

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Abstract—Method of synthesis has been developed for a series of 3,6-di-*tert*-butyl-9*H*-carbazole derivatives and their photochemical properties have been investigated. The dependence of the Steglich esterification reaction on the nature of the catalyst was studied. The synthesized compounds show fluorescent emission in the range 400–600 nm with a high quantum yield.

Keywords: carbazole, Steglich esterification, luminophores, fluorescent emission, Stokes shift

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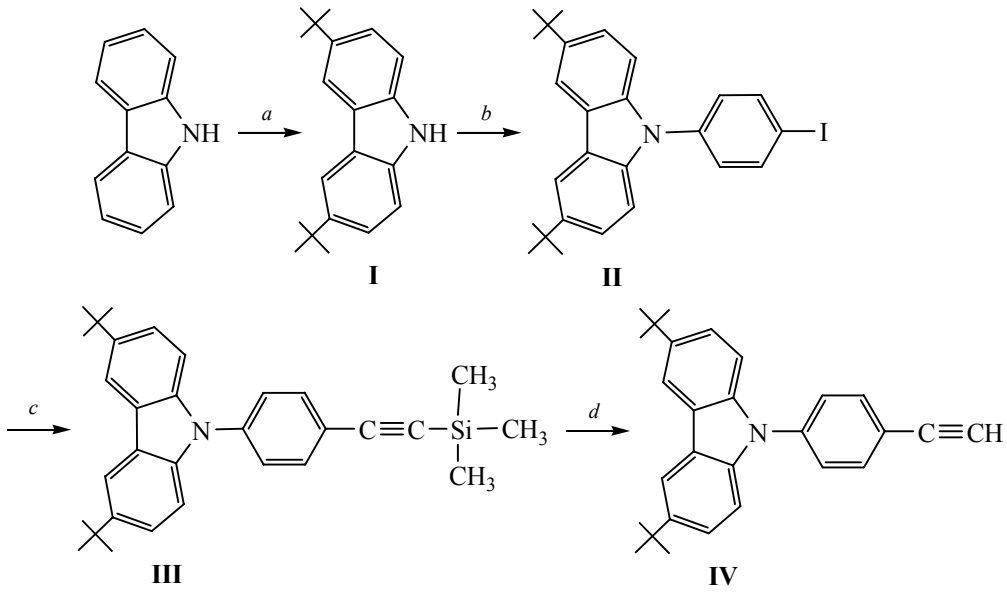
One of promising directions in modern organic chemistry and material science is the creation of organic light-emitting diods (OLEDs), including those on the basis of luminophores [1]. In this sense carbazole and its derivatives are of great interest, and they are actively studied due to their use in material science, coordination chemistry, pharmacy, etc. [2–6]. Thus, carbazole derivatives are used as synthons for preparation of luminophores [7], and branched 3,6-disubstituted derivatives of carbazole are applied as building blocks for creation of more complex organic molecules [8]. Compounds of this type are now used for the synthesis of OLEDs because of their high hole conductivity, photochemical stability, and electroconductivity [9–11]. The carbazole-based dendrites are shown to act as luminescent gelators for ordered organogels [16, 17].

The goal of the present work was the synthesis of linear esters of the carbazole series with active functional group in the focal point, which can further act as a basis for the formation of azomethine ligands in the reaction of complex formation [14, 15]. First, we intended to synthesize 4-[3,6-di-*tert*-butyl-9-(4-ethynylphenyl)-carbazol-9-yl]benzoyloxy-2-hydroxybenzaldehyde by the Sonogashira reaction of 3,6-di-*tert*-butyl-9-(4-ethynylphenyl)-carbazole with 4-(4'-bromobenzoyloxy)-2-hydroxybenzaldehyde. 3,6-Di-*tert*-butyl-9-(4-ethynylphenyl)carbazol (**IV**) was prepared by the reaction of 3,6-di-*tert*-butyl-9-(4'-iodophenyl)carbazol (**II**) with trimethylethynylsilane under the Sonogashira reaction conditions with subsequent elimination of the trimethylsilyl group by the action of tetrabutylammonium fluoride (TBAF) (Scheme 1).

It turned out that the reaction of 3,6-di-*tert*-butyl-9-(4-ethynylphenyl)carbazol (**IV**) with 4-(4'-bromobenzoyloxy)-2-hydroxybenzaldehyde (**V**) under the Sonogashira reaction conditions does not lead to the expected products of condensation irrespective of the temperature, reaction time, solvent, sequence of mixing of the reagents. Replacement of aldehyde **V** by 4-(4'-iodobenzoyloxy)-2-hydroxybenzaldehyde did not lead to the desired result, either. The only isolated product was the product of elimination of the ethynyl group from the starting carbazol **IV,** 3,6-di-*tert*-butyl-9-phenylcarbazole (**VI**) (Scheme 2).

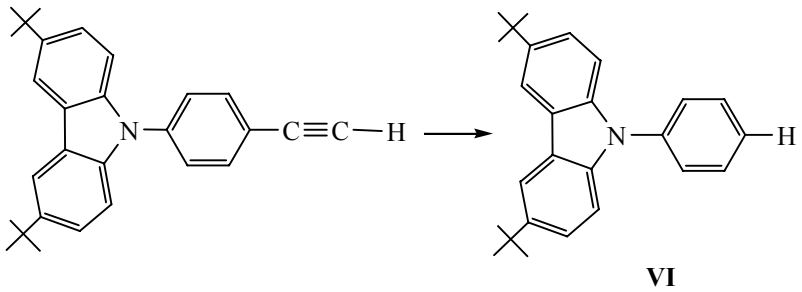
Product **VI** was isolated in 75% yield by chromatography. Its structure was proved by mass spectrometry and ^{1}H NMR spectroscopy as well as by

Scheme 1.



a, $AlCl_3$, *t*-BuCl, CH_2Cl_2; *b*, $C_6H_4I_2$, Cu_2O, dimethylacetamide; *c*, $[Pd(PPh_3)_2Cl_2]$, CuI, $(CH_3)_3SiC{\equiv}CH$, Et_3N, THF; *d*, TBAF, THF.

Scheme 2.



V, $[Pd(PPh_3)_2Cl_2]$, CuI, Et_3N, THF.

elemental analysis. The formation of **VI** can be explained by the fact that Pd(0) particles are not formed due to the presence of a polar group (HC=O, OH, COO) in one of the substrates, and, as a result, the rupture of the Ph–C bond.

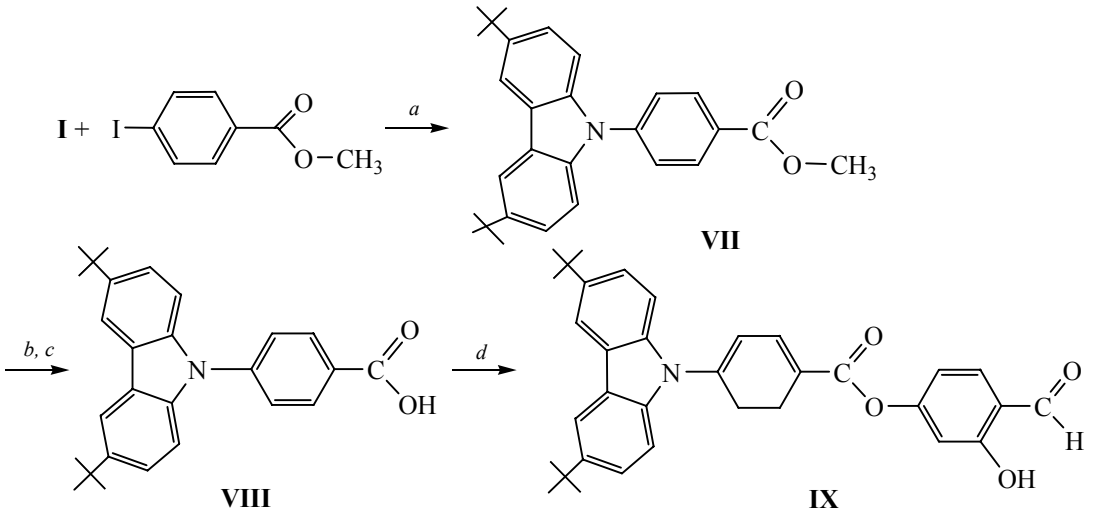
In view of this, an alternative approach was chosen for the synthesis of 3,6-disubstituted carbazoles with the aldehyde group in the focal point, by esterification of 3,6-di-*tert*-butylcarbazol-9-ylbenzoic acid (**VIII**) with 4-hydroxysalicyl aldehyde.

Acid **VIII** was prepared by the Ullmann reaction from compound **I** and methyl 4-iodobenzoate in dimethylacetamide with subsequent hydrolysis of the formed 3,6-di-*tert*-butyl-9-(4'-methoxycarbonyl)carbazole (**VII**). The yield of compound **VII** was ~80% and increased to 91% when small amount of 18-crown-6 was added.

Esterification of acid **VIII** with 4-hydroxysalicylic aldehyde by Steglich reaction [16] in the presence of dicyclohexylcarbodiimide (DCC) and catalytic amounts of dimethylaminopyridine (DMAP) or its salts leads to the formation of aldehyde **IX**. The structure and purity of the products was proved by the methods of IR and ^1H, ^{13}C NMR spectroscopy, mass spectrometry, chromatography and the data of elemental analysis (Scheme 3).

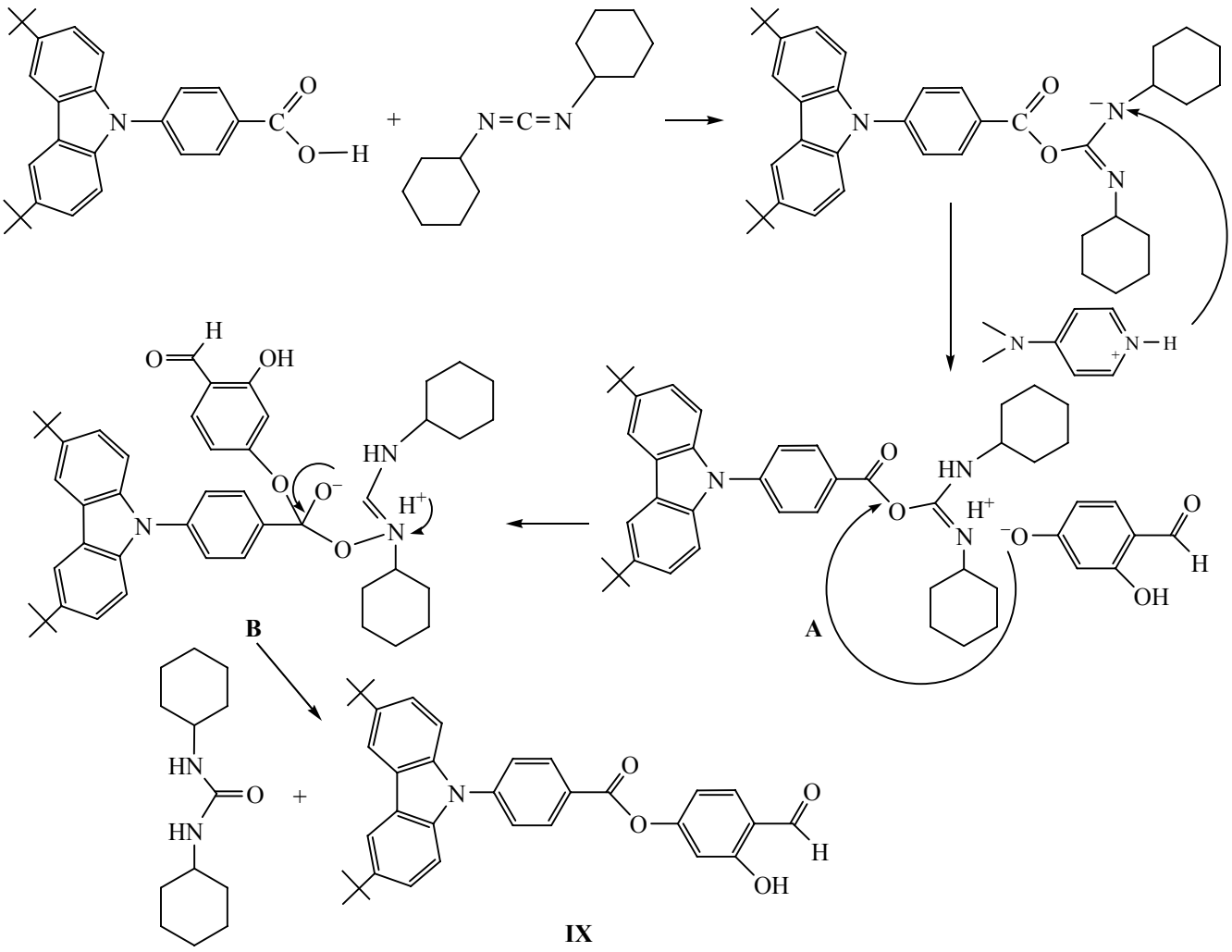
When esterification of acid **VIII** by Steglich was performed in CH_2Cl_2–DMF (99 : 1) solution, in the

Scheme 3.

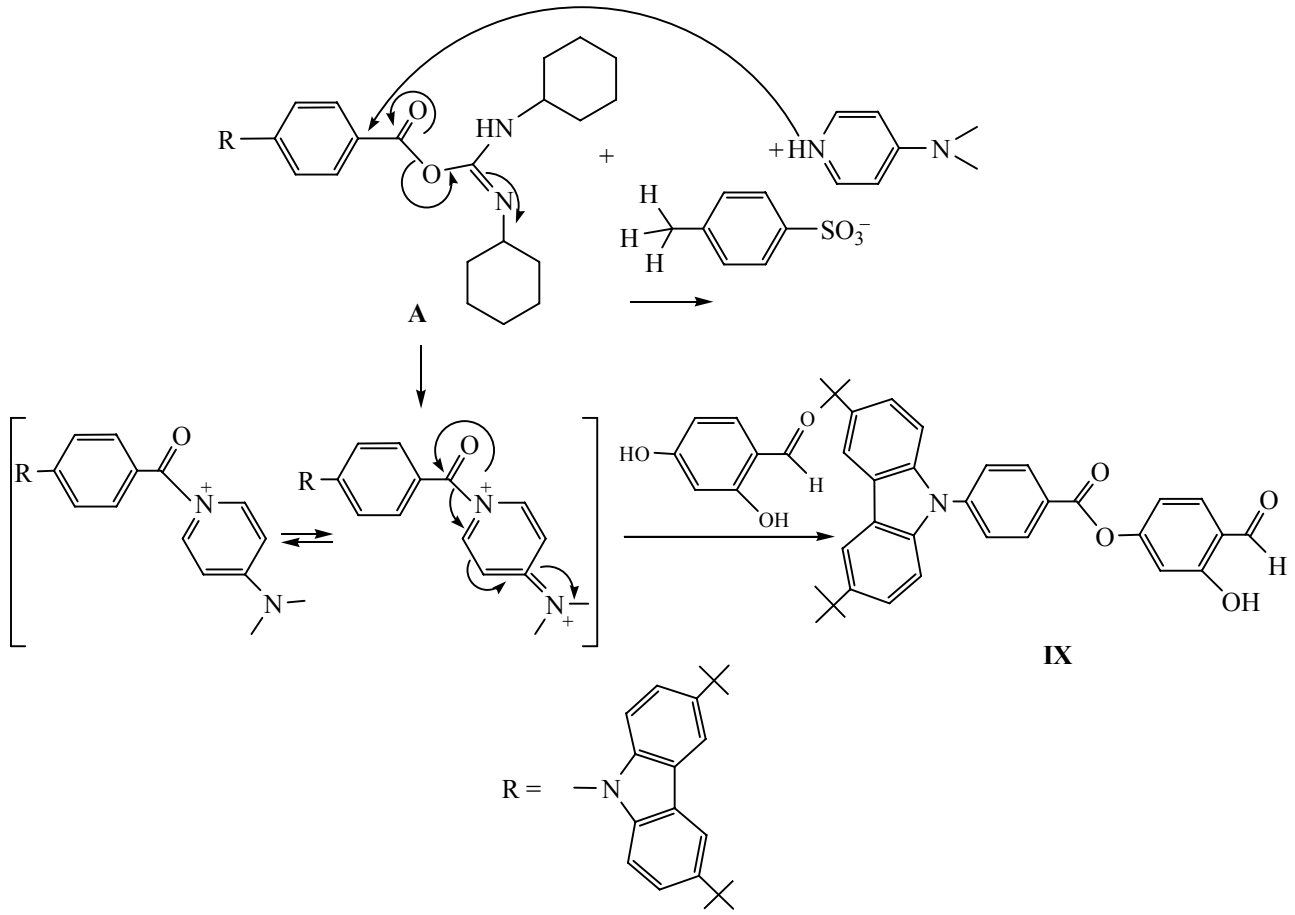


a, Cu_2O, dimethylacetamide; *b*, NaOH, EtOH; *c*, HCl, H_2O; *d*, 4-hydroxysalicyl aldehyde , DCC, DMAP, CH_2Cl_2.

Scheme 4.



Scheme 5.



first step a stable *O*-acylisourea intermediate is formed [17], which only partly enters further reaction with the phenol group of the aldehyde in the presence of dimethylaminopyridine catalyst, giving rise to aldehyde **IX** in as low as 10–15% yield. To optimize this stage, we have performed step-by-step analysis of the intermediates of the reaction and isolated the most stable of them (Scheme 4).

Thus, by the method of column chromatography the *O*-acylisourea intermediate (**A**) was separated and characterized by the data of NMR spectroscopy and mass spectrometry (Fig. 1). Besides, intermediate **B** was chromatographically isolated and characterized by the method of ^{1}H NMR spectroscopy (Fig. 2).

The formation of intermediate **A** and its partial involvement in further reaction governs the yield of the target product. As a rule, 4-dimethylaminopyridine is a stronger nucleophile as compared with hydroxyl-containing compounds, and reacts with the *O*-acylisourea intermediate to form the so-called "active ester" [18]. Under the conditions of the studied reaction this does not occur due to insufficient nucleophilic ability of the reaction catalyst (the organic base) to accept and to donate the proton of the carboxy group [19, 20]. In order to increase the yield of the reaction product **IX** we have performed the esterification of acid **VIII** by Steglich reaction in the presence of various catalysts (Table 1).

The highest yield of the reaction product was achieved using 4-dimethylaminopyridinium *p*-tosylate. Apparently, this can be attributed to a higher catalytic activity due to the protonation of the pyridine nitrogen and the ability to participate in the attack of the *O*-acylisourea adduct (**A**) acting as the acyl group carrier (Scheme 5).

In the second stage of our work we have studied the photochemical properties of the synthesized derivatives of 3,6-di-*tert*-butyl-9*H*-carbazol (**III, IV, VII–IX**).

The data on electron absorption spectra of compounds **III, IV, VII–IX** are presented in Table 2.

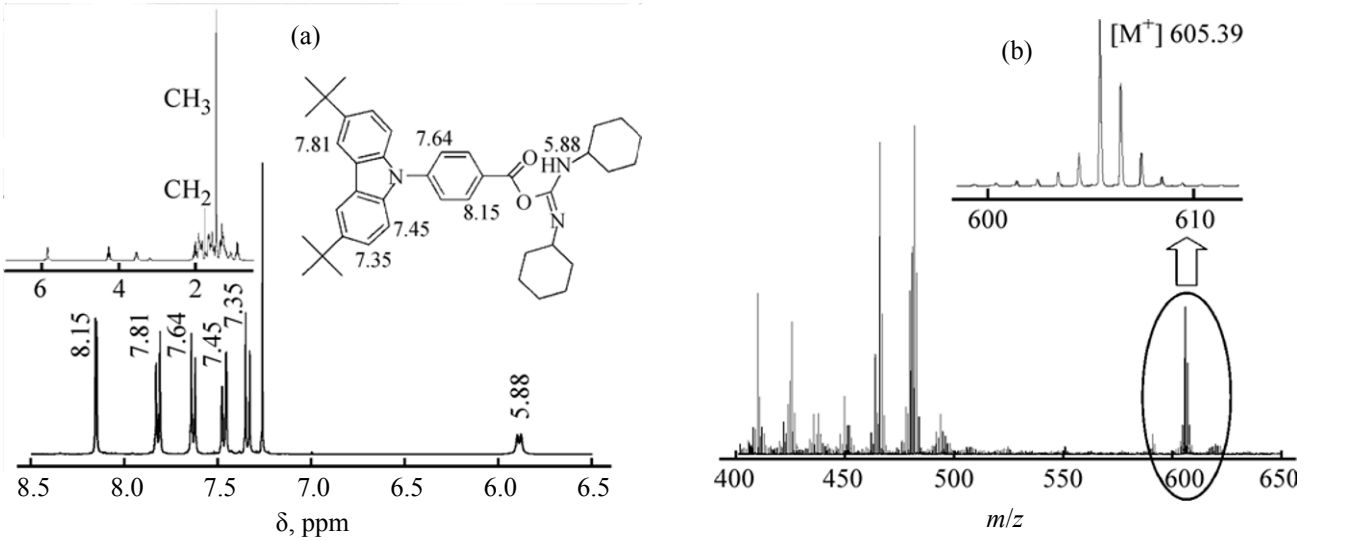


Fig. 1. (a) ^{1}H NMR spectrum and (b) fragment of mass-spectrum of *O*-acylisourea adduct (**A**).

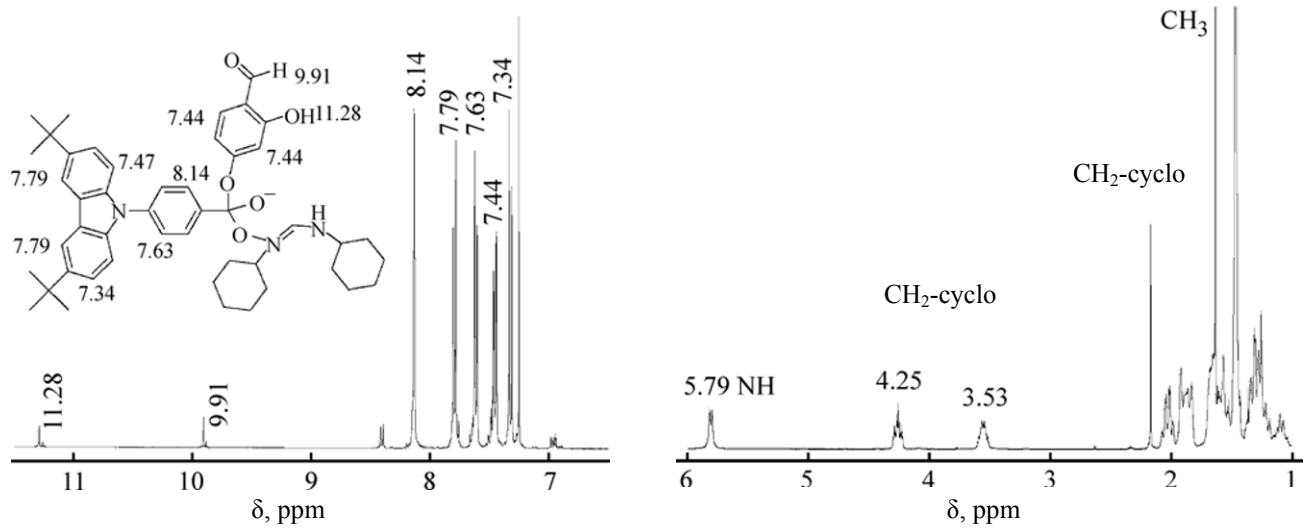


Fig. 2. ^{1}H NMR spectrum of intermediate **B**.

The investigated compounds show bright fluorescence. For example, in Fig. 3 the electronic spectrum of fluorescence and excitation/fluorescence of compound **VII** is shown. As can be seen, the spectrum of fluorescence does not depend on the wavelength of the exciting light. This is indicative of the fact that the observed fluorescence is connected with the nature of the studied object. A similar result was obtained for other compounds.

Table 1. Conditions of the Steglich esterification and the yield of product **VIII** (10 mol% of catalyst, 14 h)

Catalyst	Solvent	Yield of aldehyde **IX**, %
4-Dimethylaminopyridine	CH_2Cl_2–DMF, 99 : 1	13
4-Dimethylaminopyridine 4-tosylate	CH_2Cl_2	87
p-Aminopyridine	CH_2Cl_2–DMF, 99 : 1	5
4-Pyrrolidinopyridine	CH_2Cl_2	27
4-Pyrrolidinopyridine 4-tosylate	CH_2Cl_2–DMF, 99 : 1	20

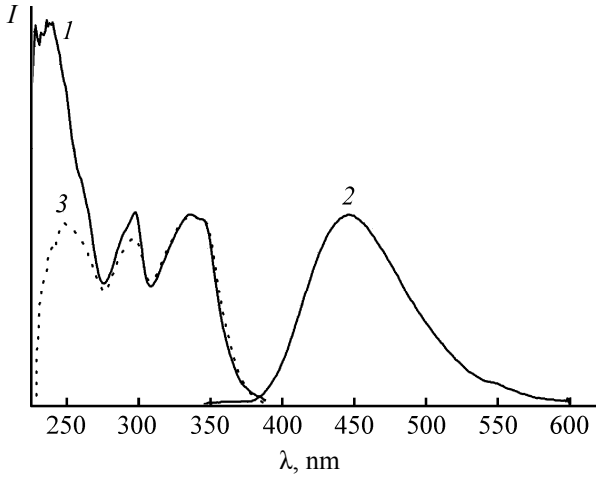


Fig. 3. Normalized absorption spectra of (*1*) electron absorption, (*2*) fluorescence, and (*3*) fluorescence excitation of compound **VI** in CH_2Cl_2.

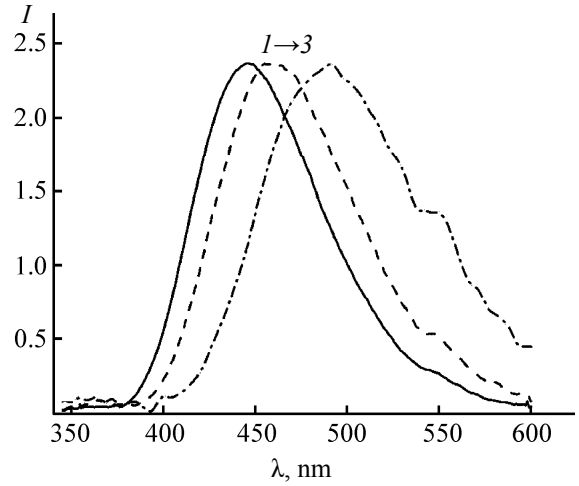


Fig. 4. Normalized fluorescence spectra of compounds **VI–VIII** (*1*→*3*) in CH_2Cl_2.

The band in the fluorescence spectra of compounds **III, VII–IX** suffers a red shift, and its value is increased in the order **III** < **VII** < **VIII** < **IX**. The same is true for the Stokes shift (Fig. 4).

This may be due to the increase in the dipole moment of the studied molecules in the excited singlet state [21]. As follows from the data of Table 2, the functionalization of the carbazole leads to a decrease in the quantum yield of fluorescence and its lifetime. These data point to a high probability of nonadiative quenching of the excited singlet states of the studied molecules.

Taking into account the nature of the functional groups, the decrease in the luminescent activity of the studied compounds may be connected with the decrease in the π-electron density on the carbazole moiety and the participation in nonradiative decay processes of the excited singlet molecules with intramolecular charge transfer.

Table 2. Spectral luminescent parameters of compounds **III, IV, VII–IX**[a]

Comp. no.	λ_{abs}^{max}, nm	λ_{fl}^{0-0}, nm	τ_{fl}, ns	φ_{fl}
III	~250 sh, ~287 sh, 298, ~316 sh, 325, ~332 sh, ~343 sh	398	7.1	0.71
IV[b]	320.5, 295, 259	379	6.3	0.09
VII	237, 258 sh, 287, 296, ~320 sh, 335, 345	446	9.3	0.49
VIII	238, ~260 sh, ~288 sh, 296, 336 sh, 345	459	9.4	0.39
IX	240, ~259 sh, 288, 295, ~336 sh, 347	491	6.3	0.11

[a] Solvent is CH_2Cl_2. [b] Data of [8].

EXPERIMENTAL

IR spectra were taken on a Bruker Vertex 80 instrument in the range 7500–350 cm^{-1} in KBr. ^1H and ^{13}C NMR spectra were taken on a Bruker 500 (500.13 MHz) spectrometer in $CDCl_3$ with TMS as an internal reference. Thin layer chromatography was carried out on RoTH UV 254 plates, development under UV lamp with λ = 254–310 nm. Elemental analysis was performed on a FlashEA 1112 analyzer. Mass spectra were registered on instruments JMS-700 JEOL (FAB) and JMS-100GCV JEOL (EI). The spectra of absorption, fluorescence and excitation/ fluorescence were recorded on a SOLAR CM2203 spectrofluorimeter.

The quantum yield of fluorescence (φ_{fl}) was determined by the relative method using quinine bisulfate in 0.1N H_2SO_4 as a standard [22], according to formula (1).

$$\varphi_{fl} = \varphi_{st}(A_{st}Sn^2)/(AS_{st}n_{st}^2). \quad (1)$$

where φ_{st} = 0.55 [23]; S and S_{st} denote areas under the fluorescence curves of the sample and the standard; A and A_{st} denote the absorption of the sample and the standard at the length of the exciting light (0.13 at λ_{exc} = 326 nm); n and n_{st} denote the refraction indices of the used solvents equal to 1.42 (CH_2Cl_2) and 1.33 (H_2O). The kinetics of quenching of fluorescence was measured on a laser pulse fluorimeter LIF-200. As the source of the laser exciting light ILGI-503 (λ_{exc} = 337.1 nm) was used. The lifetime of the fluorescence (τ_{fl}) was calculated by formula (2).

$$\tau_{fl}^2 = \tau^2 - \tau_p^2, \quad (2)$$

where τ denotes the observed lifetime of fluorescence, τ_p is the lifetime of the laser pulse [23]. All measurements were performed in square quartz cells 1 cm thick at room temperature (22ºC) in the presence of air oxygen.

4-Dimethylaminopyridinium *p*-tosylate [24, 25] was prepared by stirring equimolar amounts of dimethylaminopyridine and toluenesulfonic acid monohydrate in dry tetrahydrofurane in the course of 1 h. The formed precipitate was filtered off and dried in a vacuum.

Similarly, 4-pyrrolidinopyridinium *p*-tosylate was obtained.

3,6-Di-*tert*-butyl-9*H*-carbazole (I). Carbazole (5.0 g, 0.03 mol) was dissolved in 100 mL of CH_2Cl_2, cooled to 0°C, and slowly added the solution of 2-chloro-2-methylpropane (6.6 mL, 0.06 mol) in 20 mL of CH_2Cl_2. $AlCl_3$ (4.0 g, 0.03 mol) was introduced in small portions in the course of 1 h with constant stirring, and the reaction mixture was stirred for 8 h at room temperature. Then the flask was cooled with ice, 300 mL of water was added in small portions at stirring, the mixture was poured in 500 mL of water, extracted with CH_2Cl_2 (7 × 100 mL). The organic layer was washed with water, dried over Na_2SO_4, the solvent was removed on a rotary evaporator. The residue was thrice crystallized from hexane to give white crystalline powder. Yield 4.5 g (54 %), mp 229–231ºC. IR spectrum, ν, cm^{-1}: 3414 (NH), 3064 (Ph–H), 2960–2862 (CH_3). ^{1}H NMR spectrum, δ, ppm: 8.07 s (2H, Ar–H), 7.84 s (1H, NH), 7.46 d (2H, Ar–H), 7.32 d (2H, Ar–H), 1.45 s (18H, –CH_3). ^{13}C NMR spectrum, δ, ppm: 143.2, 138.0, 123.5, 123.3, 116.1, 110.0, 34.7, 32.1. Mass spectrum, *m/z*: 279.19 $[M]^+$. Found, %: C 85.25; H 9.89; N 6.16. $C_{20}H_{25}N$. Calculated, %: C 85.97; H 9.02; N 5.01.

3,6-Di-*tert*-butyl-9-(4'-iodophenyl)carbazole (II). The mixture of 3,6-di-*tert*-butyl-9*H*-carbazole (1 g, 3.58 mmol), *p*-diiodobenzene (3.54 g, 10.8 mmol), potassium carbonate (1 g, 7.2 mmol) and Cu_2O (0.25 g) was heated for 12 h in dimethylacetamide (60 mL) at 165°C. Then the reaction mixture was cooled, 100 mL of CH_2Cl_2 was added, filtered, washed thrice with water, the solvent was removed, the residue was chromatographed on silica gel, eluent hexane–dichloromethane (99 : 1). The product was crystallized from the mixture toluene/ethanol to obtain white crystalline powder. Yield 1.37 (80 %), mp 174ºC. IR spectrum, ν, cm^{-1}: 3064 (Ph–H), 2962–2866 (CH_3), 595, 500 (PhC–I). ^{1}H NMR spectrum, δ, ppm: 8.05 d (2H, Ar-H); 7.81 d (2H, Ar-H); 7.38 d (2H, Ar-H); 7.24 d (4H, Ph-H); 1.38 s (18H, CH_3). ^{13}C NMR spectrum, δ, ppm: 143.2, 138.9, 138.8, 138.0, 128.5, 123.7, 123.5, 116.3, 109.0, 34.7, 91.3, 32.0. Mass spectrum, *m/z*: 482 $[M - H]^+$, 426 $[M$ – *tert*-butyl$]^+$, 354 $[M - I]^+$. Found, %: C 64.80; H 5.94; N 2.86. $C_{26}H_{28}NI$. Calculated, %: C 64.87; H 5.86; N 2.91.

3,6-Di-*tert*-butyl-9-[(4-trimethylsilyl)ethynyl]-phenylcarbazole (III). To the mixture of 3,6-di-*tert*-butyl-9-(4'-iodophenyl)carbazole (2.02 g, 9.22 mmol), bis(triphenylphosphine)palladium(II) chloride (129 mg, 0.184 mmol), CuI (9 mg, 0.047 mmol), and 20 mL of dry triethylamine trimethylsilylacetylene (1.6 mL, 11.3 mmol) was added, the reaction mixture was stirred for 8 h at 60°C, cooled, CH_2Cl_2 was added, and the solvents were removed in a vacuum, the residue was chromatographed on silica gel, eluent hexane–CH_2Cl_2 (9 : 1), to obtain light-yellow solid. Yield 1.07 g (85 %), mp 208ºC. IR spectrum, ν, cm^{-1}: 3050 (Ph-H), 2962–2862 (CH_3), 2156 (C≡C), 866-841 ($SiMe_3$). ^{1}H NMR spectrum, δ, ppm: 8.04 d (2H, Ar-H), 7.57 d (2H, Ph-H), 7.40 d (2H, Ar-H), 7.35 d (2H, Ph-H), 7.25 d (2H, Ar-H), 1.36 s (18H, CH_3), 0.20 s (9H, $SiMe_3$). ^{13}C NMR spectrum, δ, ppm: 143.2, 138.8, 138.3, 133.4, 126.2, 123.7, 123.6, 121.5, 116.3, 109.2, 104.4, 95.1, 34.7, 32.0, 1.1. Mass spectrum, *m/z*: 251.1 $[M]^+$, 436.4 $[M - CH_3]^+$. Found, %: C 82.25; H 7.95; N 3.23. $C_{31}H_{37}NSi$. Calculated, %: C 82.42; H 8.19; N 3.10.

3,6-Di-*tert*-butyl-9-(4-ethynylphenyl)carbazole (IV). To the solution of 3,6-di-*tert*-butyl-9-[(4-trimethylsilyl)ethynyl]phenylcarbazole (1.00 g, 2.2 mmol) in THF (10 mL) tetrabutylammonium fluoride (2.88 g, 11 mmol) was added. The reaction mixture was stirred in the dark for 5 min at room temperature in an argon atmosphere, the solution was passed through the

column packed with silica gel, the filtrate evaporated in a vacuum to obtain light-yellow solid. Yield 0.60 g (98 %), mp 135ºC. IR spectrum, ν, cm^{-1}: 3255 (RC≡CH), 3045 (Ph-H), 2964–2862 (CH_3). ^1H NMR spectrum, δ, ppm: 8.14 d (2H, Ar-H), 7.7 m (2H, Ar-H), 7.54 m (2H, Ar-H), 7.47 d (2H, Ph-H), 7.37 d (2H, Ph-H), 3.17 m (1H, C≡CH), 1.47 s (18H, –CH_3). ^{13}C NMR spectrum, δ, ppm: 143.2, 138.8, 138.6, 133.6, 126.3, 123.7, 123.6, 120.4, 116.3, 109.1, 83.0, 77.9, 34.7, 32.0. Mass spectrum, *m/z*: 379.1 $[M]^+$, 364 $[M - CH_3]^+$. Found, %: C 88.47; H 7.99; N 3.67. $C_{28}H_{29}N$. Calculated, %: C 88.61; H 7.7; N 3.69.

4-(4'-Bromobenzoyloxy)-2-hydroxybenzaldehyde (V). 4-Bromobenzoic acid (5 g, 25 mmol) was dissolved in the mixture of CH_2Cl_2 and DMF, 2,4-dihydroxybenzaldehyde (3.45 g, 25 mmol) was added and after 10 min dicyclohexylcarbodiimide (5.78 g, 28 mmol) and catalytic amount of dimethylaminopyridine, the reaction mixture was stirred for 12 h at room temperature. The formed precipitate was filtered off, the filtrate was successively washed with 5% acetic acid (2 × 25 mL), 5% cold solution of NaOH (2 × 25 mL) and water (3 × 25 mL), dried over anhydrous Na_2SO_4. The solvent was distilled off on a rotary evaporator, yellowish solid residue was chromatographed on silica gel, eluent $CHCl_3$. Yield 2.57 g (53.4 %), mp 187ºC. IR spectrum, ν, cm^{-1}: 3215 (OH), 3067 (Ph-H), 2926 (CHO), 1735 (–COO–), 1673 (CHO), 1268 (C–O), 678. 625 (C–Br). ^1H NMR spectrum, δ, ppm: 11.19 s (1H, OH), 9.82 s (1H, CHO), 7.97 d (2H, Ph-H), 7.61 d (2H, Ph-H), 7.57 d (1H, Ph-H), 6.83 m (2H, Ph-H). ^{13}C NMR spectrum, δ, ppm: 195.5, 163.2, 157.4, 152.2, 135.0, 132.2, 131.8, 129.4, 127.8, 118.9, 113.9, 110.8. Mass spectrum, *m/z*: 321 $[M]^+$; calculated 321.1. Found, %: C 52.69; H 2.92; O 19.00; Br 25.38. $C_{14}H_9BrO_4$. Calculated, %: C 52.36; H 2.82; O 19.93; Br 24.9.

3,6-Di-*tert*-butyl-9-phenylcarbazole (VI) was prepared similarly to compound **II** from 4-(4'-bromobenzoyloxy)-2-hydroxybenzaldehyde (0.42 g, 1.32 mmol), bis(triphenylphosphine)palladium (**II**) chloride (129 mg, 0.184 mmol), CuI (9 mg, 0.047 mmol), 20 mL of trimethylamine, and 3,6-di-*tert*-butyl-9-(4-ethynylphenyl)carbazole (0.5 g, 1.32 mmol). Yield 0.6 g (75%), mp 186ºC. IR spectrum, ν, cm^{-1}: 3050 (Ph-H), 2962–2862 (CH_3). ^1H NMR spectrum, δ, ppm: 8.35 d (2H, Ar-H), 8.15 s (2H, Ph-H), 7.75 d (2H, Ar-H), 7.49 d (2H, Ph-H), 7.28 s (1H, Ar-H), 1.36 s (18H, CH_3). ^{13}C NMR spectrum, δ, ppm: 151.2, 138.6, 128.2, 127.1, 123.5, 121.5, 117.4, 36.4, 31.4. Mass spectrum, *m/z*: 355.2 $[M]^+$. Found, %: C 88.15; H 7.98; N 3.87. $C_{31}H_{37}N$. Calculated, %: C 87.84; H 8.22; N 3.94.

3,6-Di-*tert*-butyl-9-(4-methoxycarbonyl)carbazole (VII) was prepared similarly to compound **II** from 3,6-di-*tert*-butyl-9*H*-carbazole (3.5 g, 13.0 mmol), 1-iodo-4-methylbenzoate (3.73 g, 14.23 mmol), Cu_2O (3.73 g, 26.0 mmol), reaction time 24 h. The product was isolated by column chromatography, eluent hexane–ethyl acetate (10 : 1). Yield 4.3 g (80 %), mp 156ºC. IR spectrum, ν, cm^{-1}: 3059 (Ph-H), 2957–2862 (CH_3), 1749 (–COO–). ^1H NMR spectrum, δ, ppm: 8.14 s (2H, Ar-H), 7.43 m (4H, Ph-H), 7.25 d (2H, Ar-H), 7.09 d (2H, Ar-H), 3.89 s (3H, –$COOCH_3$), 1.46 s (18H, CH_3). ^{13}C NMR spectrum, δ, ppm: 158.6, 142.5, 139.8, 130.8, 128.3, 123.5, 123.1, 116.2, 115.0, 109.1, 55.6, 34.8, 32.1. Mass spectrum, *m/z*: 414.3 $[M - H]^+$; calculated 413.5. Found, %: C 80.79; H 7.03; N 3.60; O 8.58. $C_{28}H_{31}NO_2$. Calculated, %: C 81.32; H 7.56; N 3.39; O 7.74.

4-(3,6-Di-*tert*-butylcarbazol-9-yl)benzoic acid (VIII). The mixture of 3,6-di-*tert*-butyl-9-(4-methoxycarbonyl)carbazole (2.5 g, 6.0 mmol), 50 mL of ethanol, and 20 mL of 1 M solution of NaOH was stirred under reflux for 10 h, cooled to room temperature, poured into 100 mL of distilled water and acidified by adding 40 mL of 1 M HCl. The crude product was separated by filtration, chromatographed on silica gel, eluent hexane–ethyl acetate (1 : 1), to obtain the product as fine white powder. Yield 2.2 g (92 %), mp 287ºC. IR spectrum, ν, cm^{-1}: 3414 (OH), 3000 (Ph-H), 2959–2866 (CH_3), 1688 (C=O), 1604 (Ph-H), 1471 (CH_3), 1289 (C–N). ^1H NMR spectrum, δ, ppm: 8.52 s (1H, OH), 8.36 d (2H, Ar-H), 8.15 s (2H, Ar-H), 7.73 d (2H, Ar-H), 7.47 m (4H, Ph-H), 1.47 s (18H, CH_3). ^{13}C NMR spectrum, δ, ppm: 171.2, 143.7, 143.4, 138.4, 132.0, 127.0, 125.8, 123.9, 116.4, 110.0, 109.3, 34.8, 31.9. Mass spectrum, *m/z*: 399.4 $[M]^+$; calculated 399.2. Found, %: C 81.27; H 7.15; N 3.24; O 8.34. $C_{27}H_{29}NO_2$. Calculated, %: C 81.17; H 7.32; N 3.51; O 8.01.

4-(3,6-Di-*tert*-butylcarbazol-9-yl)benzoyloxy-2-hydroxybenzaldehyde (IX). 4-(3,6-Di-*tert*-butyl-9*H*-carbazol-9-yl)benzoic acid (1.5 g, 3.8 mmol) was dissolved in CH_2Cl_2, 2,4-dihydroxybenzaldehyde (0.53 g, 3.8 mmol), the calculated amount of dicyclohexylcarbodiimide (0.78 g, 3.8 mmol), and a catalytic amount of dimethylaminopyridine tosylate was added, and the mixture was stirred at room temperature for 14 h. The formed precipitate was filtered off, the

filtrate was successively washed with 5% acetic acid (2 × 25 mL), 5% solution of cold NaOH (2 × 25 mL) and water (3 × 25 mL), dried over anhydrous Na_2SO_4. The solvent was removed, the solid residue was chromatographed on silica gel, eluent hexane–$CHCl_3$ (1 : 1), to obtain the product as fine powder of light-yellow color. Yield 1.48 g (87 %), mp 246ºC. IR spectrum, ν, cm^{-1}: 3062 (Ph-H), 29566–2863 (CH_3), 1742 (–COO–), 1658 (CHO), 1253 (C–N). ^{1}H NMR spectrum, δ, ppm: 11.29 s (1H, OH), 9.88 s (1H, COH), 8.39 d (2H, Ar-H), 8.15 s (2H, Ar-H), 7.77 d (2H, Ar-H), 7.63 d (1H, Ar-H), 7.47 m (4H, Ar-H), 6.97 s (1H, Ar-H), 6.94 m (1H, Ar-H), 1.47 t (18H, $-CH_3$). ^{13}C NMR spectrum, δ, ppm: 195.5, 163.5, 163.2, 157.5, 143.8, 143.6, 138.3, 135.0, 132.0, 126.3, 125.9, 123.9, 118.7, 116.4, 114.0, 110.8, 109.2, 34.7, 31.9. Mass spectrum, *m/z*: 520.6 $[M - H]^+$; calculated 519.6. Found, %: C 77.85; H 6.59; N 2.13; O 13.4. $C_{34}H_{33}NO_4$. Calculated, %: C 78.59; H 6.40; N 2.70; O 12.32.

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