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Graphical abstract

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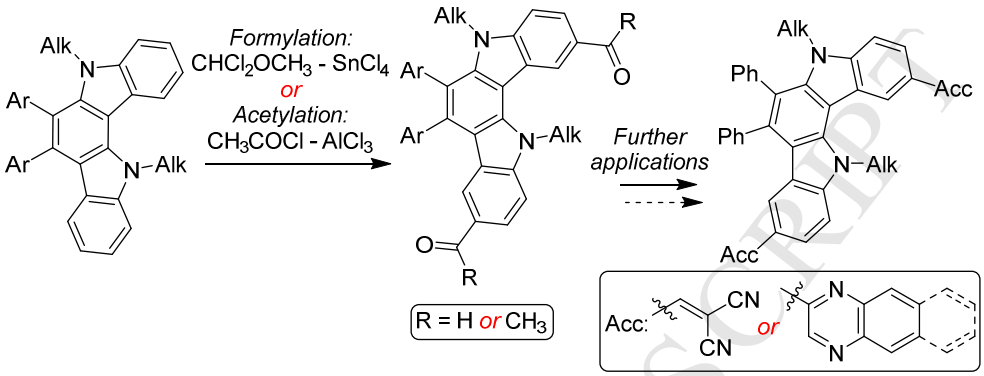

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Modifications of 5,12-dihydroindolo[3,2-*a*]carbazole scaffold *via* its regioselective C2,9-formylation and C2,9-acetylation

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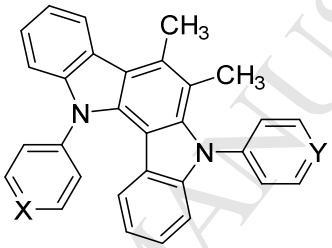
Keywords: 5,12-Dihydroindolo[3,2-*a*]carbazoles; Formylation; Acetylation; Heteroacenes

ABSTRACT

The effective approaches for regioselective double formylation and acetylation of 5,12-dialkyl-6,7-diaryl-substituted 5,12-dihydroindolo[3,2-*a*]carbazoles by their treatment with dichloromethyl methyl ether in the presence of $SnCl_4$ or with acetyl chloride in the presence of $AlCl_3$ to afford the 2,9-diformyl or 2,9-diacetyl derivatives, respectively, were developed. Furthermore, new 2,9-bis(2,2-dicyanovinyl) derivatives were synthesized by the Knoevenagel condensation of diformyl-containing substrates with malononitrile, when new 2,9-bis(quinoxaline-2-yl)- and 2,9-bis(benzo[*g*]quinoxaline-2-yl) derivatives were formed via microwave-promoted oxidation of diacetyl-containing substrates with SeO_2 to the corresponding diglyoxals, followed by the reaction of these intermediates with *o*-phenylendiamine or 2,3-diaminonaphthalene, respectively. The basic optical and electrochemical properties of some 5,12-dihydroindolo[3,2-*a*]carbazoles were investigated.

1. Introduction

Indolocarbazoles represent wide family consisting of five classes of isomeric ring-fused heterocycles, which have attracted considerable research attention during past decades thanks to a number of their valuable applications [1,2]. Indeed, derivatives of each of the five indolocarbazole systems have been found to be useful for both medicinal chemistry and materials science [1,2]. In the latter field, these π-conjugated fused systems, most often 5,11-dihydroindolo[3,2-*b*]carbazoles [3], have been utilized for designing (electro)luminescent or charge transport materials and light-harvesting dyes for organic electronics and photovoltaics [2]. In turn, some 5,12-dihydroindolo[3,2-*a*]carbazoles (indolo[3,2-*a*]carbazoles) also proved to be effective for use in organic light-emitting diodes (OLEDs) [4–6]. For instance, structures of indolo[3,2-*a*]carbazole-based host materials **ICDP**, **4ICDPy** and **4ICPPy** (see ref. [5]) for phosphorescent organic light-emitting diode (PhOLED) applications are shown in Figure 1.



ICDP (X = Y = CH)
4ICDPy (X = Y = N)
4ICPPy (X = N; Y = CH)

Figure 1. Indolo[3,2-*a*]carbazole-based host materials for PhOLEDs

A number of effective methods for the construction of indolo[3,2-*a*]carbazoles has previously been reported in the literature [7–16], while known options for further modification are very limited. Taking into account π-excessive character of indolocarbazoles, one of the most appropriate and attractive tools for framework modification is electrophilic aromatic substitution (S_EAr). In particular, we have previously described procedures for regioselective 2,8-formylation [17,18], 2,8-acetylation [19], 2,8-aroylation [17,20] and 2,8-nitration [21] of 6,12-di(hetero)aryl-5,11-dihydroindolo[3,2-*b*]carbazoles. Continuing our study, we report herein synthetic protocols for double formylation and acetylation of 6,7-diaryl-substituted 5,12-dihydroindolo[3,2-*a*]carbazoles, shown in Figure 2, and the further applications of the formyl- and acetyl-substituted substrates for the construction of more π-extended derivatives.

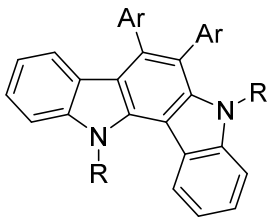
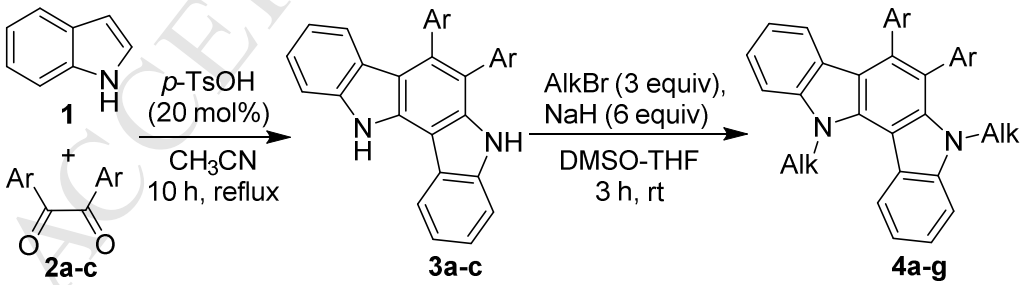


Figure 2. The structure of studied 5,12-dihydroindolo[3,2-*a*]carbazoles

2. Results and Discussion

2.1. Synthesis

There are few known ways for synthesis of indolo[3,2-*a*]carbazoles, bearing aromatic moieties at C-6 and C-7 positions, such as palladium-catalyzed cascade reaction of 2,3-unsubstituted indoles with 1,2-diarylacetylenes [22], palladium-catalyzed oxidative annulation of 2',3-unsubstituted 2,3'-biindoles with 1,2-diarylacetylenes [23] and condensation of 2,3-unsubstituted indoles with 1,2-diarylethane-1,2-dione (benzils) under catalysis of *p*-toluenesulfonic acid (*p*-TsOH) [24]. The latter protocol was chosen by us as the most attractive one for preparing multigram-scale amounts of the desired indolo[3,2-*a*]carbazoles due to the transition-metal-free process and commercially available starting materials. Unfortunately, using the originally reported procedure [24], indolo[3,2-*a*]carbazole **3a** (Ar = Ph) was obtained in 17% yield instead of stated 62%, since, as soon as the solution of indole **1** and benzil **2a** with *p*-TsOH (20 mol%) in toluene was heated to a boil, there was a fast separation of a very viscous gum from the reaction mixture, and further reaction had to proceed in the biphasic system. Nevertheless, product **3a** could be obtained in 77% yield, when this condensation was performed by refluxing the reaction mixture for 10 h in acetonitrile solution instead of toluene one. The reaction intermediates proved to be highly soluble in acetonitrile due to its greater polarity compared to toluene, in contradiction to the desired product **3a**, which precipitated from the hot solution after 3-4 h. In the same manner, indolo[3,2-*a*]carbazoles **3b,c** were prepared from indole **1** and 4,4'-disubstituted benzils **2b,c** (Scheme 1, Table 1). The treatment of compounds **3** with the appropriate alkyl halide (3 equiv) in the presence of NaH (6 equiv) in the DMSO-THF mixture (2:8, v/v) allowed us to obtain derivatives **4a-g** in 56-96% yields (Scheme 1, Table 1).



Scheme 1. Synthesis of indolo[3,2-*a*]carbazole derivatives **3** and **4**

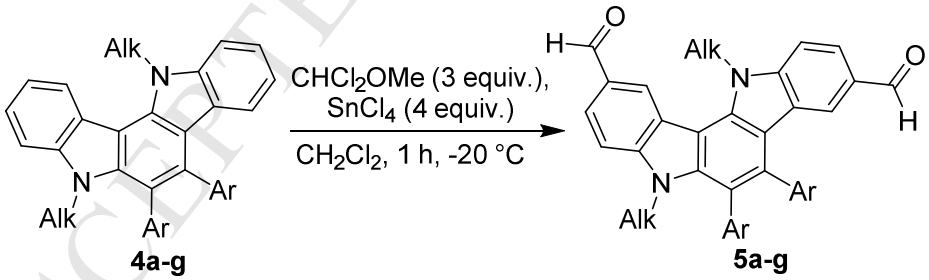
Table 1. Scope and yields of indolo[3,2-*a*]carbazoles **3** and **4**

Entry	Product **3** or **4**	Ar	Alk	Yield (%)
1	**3a**	phenyl	-	77 (17)[a]
2	**3b**	4-methoxyphenyl	-	80
3	**3c**	4-bromophenyl	-	71

4	**4a**	phenyl	*n*-C_6H_{13}	85
5	**4b**	phenyl	*n*-C_4H_9	89
6	**4c**[b]	phenyl	$C_6H_5CH_2$	81
7	**4d**	phenyl	C_2H_5	92
8	**4e**[c]	phenyl	CH_3	88
9	**4f**	4-methoxyphenyl	*n*-C_6H_{13}	96
10	**4g**	4-bromophenyl	*n*-C_6H_{13}	56

[a] Toluene was used as a solvent to perform the reaction.
[b] Benzylchloride was used to prepare compound **4c**.
[c] Iodomethane was used to prepare compound **4e**.

Further in this study, we focused our effort on finding suitable reaction conditions for the regioselective formylation of substrates **4**, that to obtain indolo[3,2-*a*]carbazole compounds with aldehyde groups at the both terminal benzene rings of the fused frameworks. First, we tried to perform formylation of indolo[3,2-*a*]carbazole **4a** by the Vilsmeier–Haack protocol [25], that is often used to prepare formyl derivatives of electron-rich (hetero)aromatic compounds. However, the treatment of compound **4a** with the Vilsmeier reagent ($POCl_3$-DMF complex) gave a mixture of several formyl-substituted products, which we failed to separate by crystallization or column chromatography due to the close nature. At the same time, we succeeded to achieve regioselective formylation of substrate **4a** using the Rieche method [26,27], consisting in the treatment of the starting compound with dichloromethyl methyl ether in the presence of $SnCl_4$ in dry CH_2Cl_2 solution at -20 °C for 1 h to form dialdehyde **5a** as the single reaction product in 71% yield. Other 2,9-dialdehydes **5** were also prepared in the same manner in 55-86% yields (Scheme 2, Table 2).

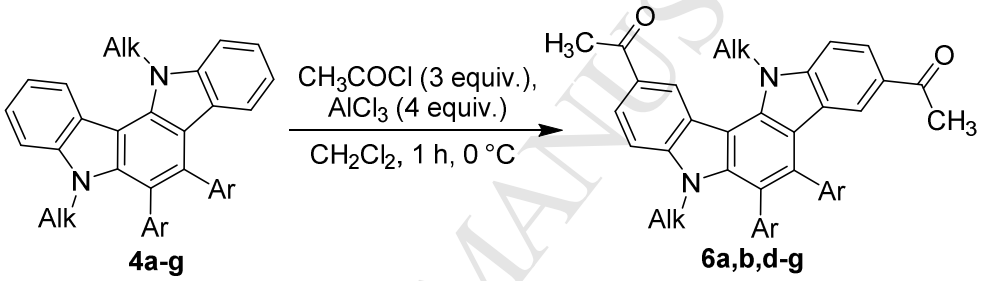


Scheme 2. Formylation of indolo[3,2-*a*]carbazoles **4** at C-2 and C-9 positions

Table 2. Scope and yields of 2,9-diformyl-substituted derivatives **5**

Entry	Substrate **4**	Ar	Alk	Product **5**	Yield (%)
1	**4a**	phenyl	*n*-C_6H_{13}	**5a**	71
2	**4b**	phenyl	*n*-C_4H_9	**5b**	68
3	**4c**	phenyl	$C_6H_5CH_2$	**5c**	55
4	**4d**	phenyl	C_2H_5	**5d**	59
5	**4e**	phenyl	CH_3	**5e**	61
6	**4f**	4-methoxyphenyl	*n*-C_6H_{13}	**5f**	78
7	**4g**	4-bromophenyl	*n*-C_6H_{13}	**5g**	86

In turn, the regioselective double acetylation of indolo[3,2-*a*]carbazoles **4** proceeded smoothly by treatment with acetyl chloride in the presence of anhydrous $AlCl_3$ in dry CH_2Cl_2 solution at 0 °C for 1 h, thus afforded 2,9-diacetyl-substiuted derivatives **6** in 71-88% yields (Scheme 3, Table 3). The only exception was the *N*,*N'*-dibenzyl-substituted substrate **4c** (Table 3, entry 3), which undergone rapid decomposition under these reaction conditions and formed a complex mixture of compounds. This fact can be explained by unwanted acetylation of the benzyl groups of compound **4c** as well as its debenzylation with $AlCl_3$, similar to a previously described reaction for *N*-benzylcarbazoles [28]. However, we also failed to perform acetylation of **4c** using acetyl chloride with milder Lewis acids, such as $SnCl_4$ and $TiCl_4$, as well as acetic anhydride with BF_3 etherate. The latter reaction conditions were previously used by us for acetylation of 5,11-dihydroindolo[3,2-*b*]carbazole derivatives [19].



Scheme 3. Acetylation of indolo[3,2-*a*]carbazoles **4** at C-2 and C-9

Table 3. Scope and yields of 2,9-diacetyl-substituted derivatives **6**

Entry	Substrate **4**	Ar	Alk	Product **6**	Yield (%)
1	**4a**	phenyl	*n*-C_6H_{13}	**6a**	76
2	**4b**	phenyl	*n*-C_4H_9	**6b**	72
3	**4c**	phenyl	$C_6H_5CH_2$	**6c**	-
4	**4d**	phenyl	C_2H_5	**6d**	78
5	**4e**	phenyl	CH_3	**6e**	71
6	**4f**	4-methoxyphenyl	*n*-C_6H_{13}	**6f**	88
7	**4g**	4-bromophenyl	*n*-C_6H_{13}	**6g**	73

Notably, the structures of the diformyl- and diacetyl-substituted derivatives **5a-g** and **6a**,**b**,**d-g** is fully consistent with NMR data and elemental analysis. For instance, ^{1}H NMR spectra of products **5** and **6** contained characteristic signals of two non-equivalent formyl groups at 9.5-9.6 ppm and 9.6-10.2 ppm or two non-equivalent acetyl group at 2.1-2.2 ppm and 2.7-2.8 ppm, respectively. However, to confirm unequivocally disposition of formyl and acetyl functions in these molecules, we performed X-ray diffraction analysis for the single crystals of derivatives **5d** and **6e**; the results are shown in Figures 3 and 4.

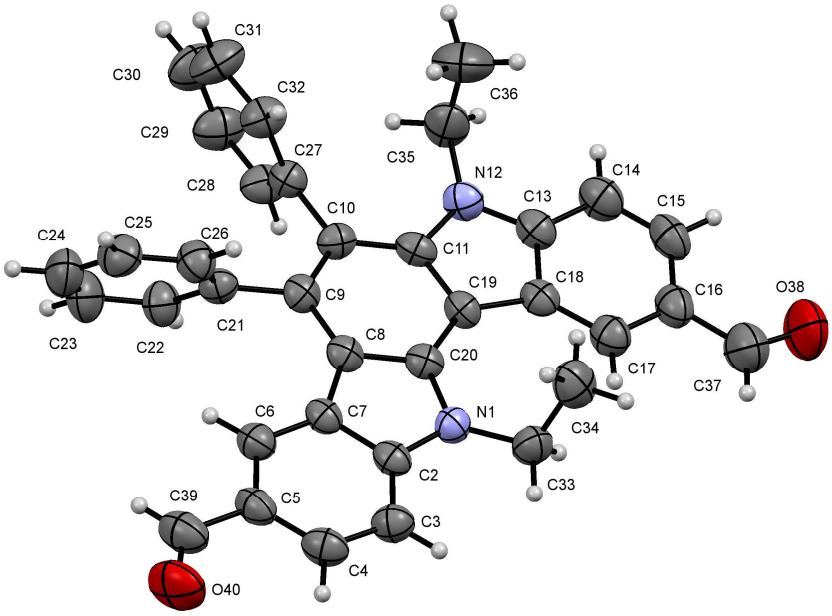


Figure 3. ORTEP diagram for the X-ray structure of **5d**. Thermal ellipsoids of 50% probability are shown

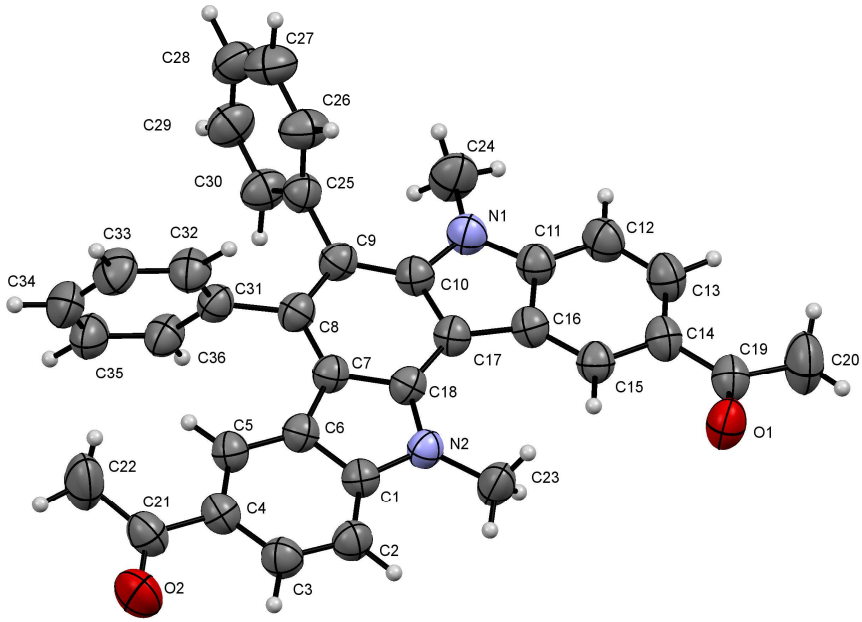
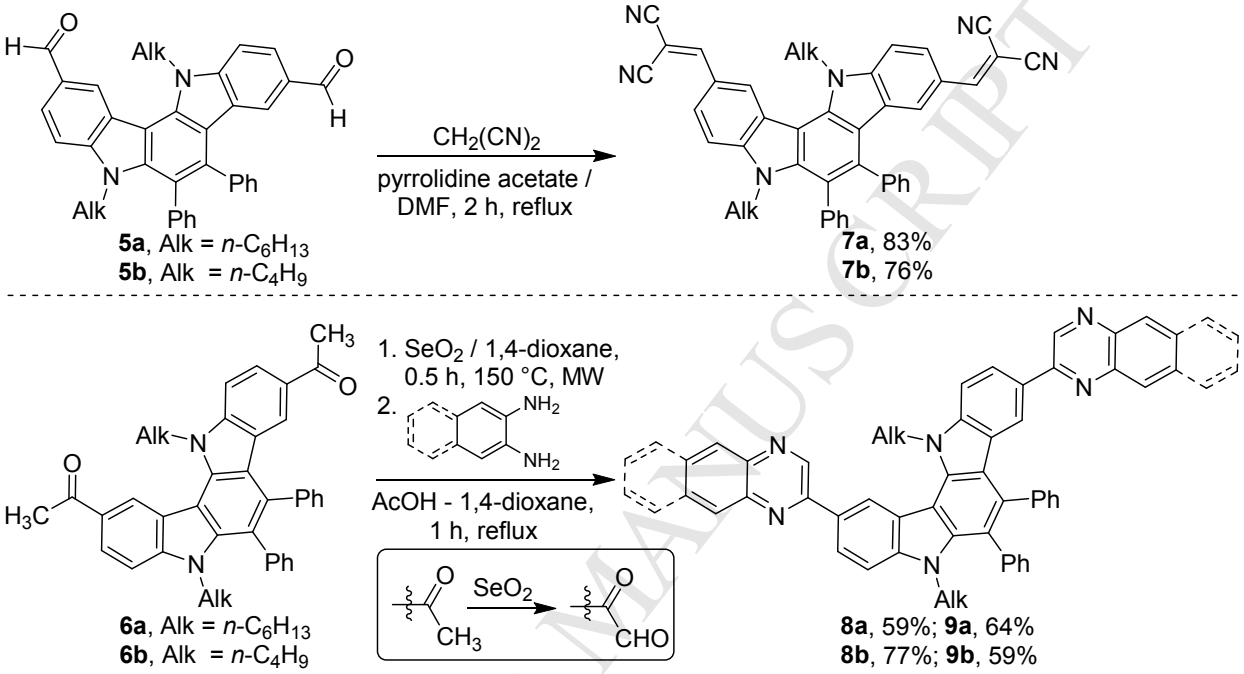


Figure 4. ORTEP diagram for the X-ray structure of **6e**. Thermal ellipsoids of 50% probability are shown.

We also showed usefulness of the formyl- and acetyl-functionalized substrates **5** and **6** as the building blocks for the synthesis of π-extended indolo[3,2-*a*]carbazole compounds. To this end, 2,9-dialdehydes **5a**,**b** were treated with malononitrile in the presence of pyrrolidine acetate (20 mol%) to obtain 2,9-bis(2,2-dicyanovinyl)-substituted indolo[3,2-*a*]carbazoles **7a** and **7b** in 83% and 76% yields (Scheme 4). At the same time, two 2,9-diacetyl derivatives **6** were utilized by as us for the construction of 2,6,7,9-tetra(hetero)aryl-substituted indolo[3,2-*a*]carbazoles **8**

and **9**, bearing quinoxaline-2-yl or benzo[*g*]quinoxaline-2-yl units at C-2 and C-9 positions, respectively. Thus, the oxidation of substrates **6a,b** with SeO_2 in 1,4-dioxane solution at 150 °C under microwave irradiation conditions for 30 min transformed both acetyl groups of **6** into glyoxyloyl (COCHO) functions. The formed crude bis-glyoxal intermediates were further treated with *o*-phenylendiamine or 2,3-diaminonaphthalene to afford desired products **8a,b** and **9a,b** in 59-77% yields, respectively (Scheme 4).



Scheme 4. Synthesis of π-extended indolo[3,2-*a*]carbazole derivatives **7a,b**, **8a,b** and **9a,b**

2.2. Optical and electrochemical study

Cyclic voltammetry (CV) measurements of compounds **4a,f-g**, **7a, 8a** and **9a** were performed to study their electrochemical properties. The HOMO (E_{HOMO}) and LUMO (E_{LUMO}) (of compounds **8a** and **9a**) energy values were estimated from the onset potentials of the first oxidation or reduction event according to the following equations:

$$E_{HOMO} = -[E_{[onset,\ ox\ vs.\ Fc/Fc+]} + 5.1]$$

$$E_{LUMO} = -[E_{[onset,\ red\ vs.\ Fc/Fc+]} + 5.1]$$

All the LUMO energy levels were also calculated from HOMO energy levels and the optical band gaps (E_g^{opt}) using equation:

$$E_{LUMO} = E_{HOMO} + E_g^{opt}.$$

The obtained data are listed in Table 4.

Table 4. The electrochemical and optical characteristics of indolo[3,2-*a*]carbazoles derivatives **4a**,**f-g**, **7a**, **8a** and **9a**. All experiments were carried out in CH_2Cl_2 solution

Compound	E_g^{opt}, eV,[a]	$E_{[onset, ox vs. Fc/Fc+]}$, V	E_{HOMO}, eV	$E_{[onset, red vs. Fc/Fc+]}$, V	E_{LUMO}, eV
4a	3.24	0.28	-5.38	-	-2.14
4f	3.24	0.25	-5.35	-	-2.11
4g	3.23	0.34	-5.44		-2.21
7a	2.54	0.65	-5.75		-3.21
8a	2.79 (2.63)[b]	0.39	-5.49	-2.24	-2.70 (-2.86)[c]
9a	2.53 (2.33)[b]	0.39	-5.49	-1.94	-2.96 (-3.16)[c]

[a] Estimated from the absorption spectra ($E_g^{opt} = 1240/\lambda_{edge}$) [29].

[b] Electrochemical E_g was calculated from the equation $E_g = E_{LUMO} - E_{HOMO}$

[c] Determined from the onset potential in cyclic voltammogram

The results of voltammetry shows that the oxidation potentials of the studied indolo[3,2-*a*]carbazoles derivatives are quite sensitive to changes in the electron-donor properties of the substituents. Thus, the introduction of an electron-withdrawing 2,2-dicyanovinyl fragment (compound **7a**) into indolo[3,2-*a*]carbazole core leads to a significant increase in $E_{onset, ox}$ (~ 370 mV). The comparison of $E_{onset, ox}$ of compound **4a** with ones of **4f-g** shows, that the introduction of an electron-withdrawing *p*-bromo substituents increases the oxidation potential by 60 mV, at the same time the introduction of an electron-donating methoxy groups gives a slight decrease. For compounds **8a** and **9a** the reduction processes are observed, apparently related to the heterocyclic moieties in the molecules.

The UV/visible absorption and photoluminescence spectra of compounds **4a**, **4f**, **4g**, **7a**, **8a** and **9a** were recorded in CH_2Cl_2 solution ($5 \cdot 10^{-5}$M) at ambient temperature, and the results are summarized in Tables 4 and 5.

All selected compounds are wide-bandgap semiconductors with E_g^{opt} of ~3.24 eV for **4a, 4f-g** and 2.50-2.80 eV for **7a**, **8a** and **9a**. Thus, an increase in π-conjunction in indolo[3,2-*a*]carbazole derivatives **7a**, **8a**, **9a** leads to a significant decrease in the bandgap value.

Table 5. UV/Vis and photoluminescence data for **4a, 4f, 4g, 7a, 8a** and **9a**

Compound	Absorption	Photoluminescence		
	λmax, nm (ε, 10^3 $M^{-1}\cdot cm^{-1}$)	Excitation λmax, nm	Emission λmax, nm	Φ_F, (±10) %
4a	370 (28.6), 354 (17.2), 296 (89.9), 252 (74.3)	370, 354, 296, 252	388	52[a]
4f	370 (15.8), 354 (9.7), 295 (50.2), 280 (44.5), 254 (39.1)	370, 354, 295, 280, 254	387	24[a]
4g	371 (17.3), 355 (10.6), 296 (54.9), 250 (48.6)	371, 355, 296, 250	396	55[a]
7a	429 (63.9), 345 (34.9), 294 (49.3)	429, 345, 294	555	3[b]
8a	397 (49.3),	397,	528	33[b]

9a	300 (81.4), 238 (60.4) 423 (38.3), 309 (101.1), 267 (77.6), 232 (57.9)	300, 238 423, 309, 267, 232	588	11[b]

[a] Solution of quinine bisulfate in 0.1 N H_2SO_4 was used as a relative standard (Φ_F = 52%, $^{ex}\lambda$ = 300 nm) [30]
[b] Solution of 3-aminophthalimide in ethanol was used as a relative standard (Φ_F = 60%, $^{ex}\lambda$ = 400 nm) [31]

The various aryl substituents at C-6 ad C-7 positions of the indolo[3,2-*a*]carbazole core have no effect on the absorption spectrum maxima in a series of compounds **4a**, **4f**, **4g** (Figure 5). It can be caused by non-planar disposition of aryls due to steric factors. On the other hand, there is a bathochromic shift of absorption bands in the spectra of indolo[3,2-*a*]carbazole derivatives **7a**, **8a**, **9a** due to the π-extended system compared with **4a** one (Figure 6, also see Supplementary Information).

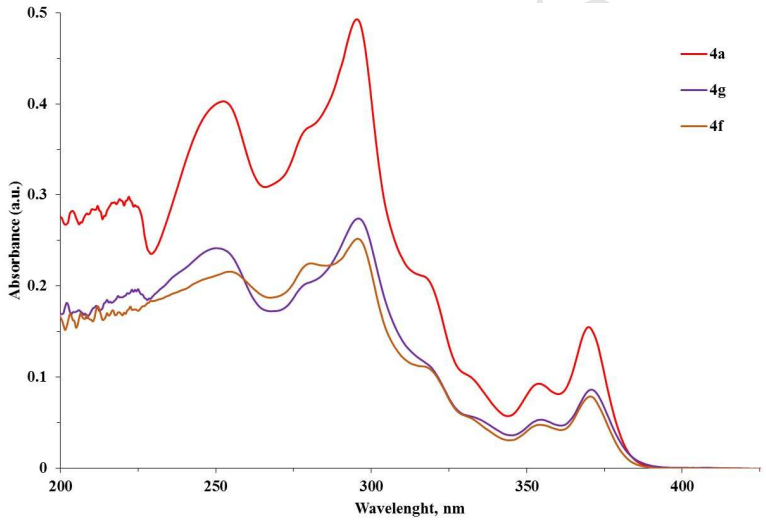


Figure 5. UV/Vis spectra of compounds **4a**, **4f**, **4g**

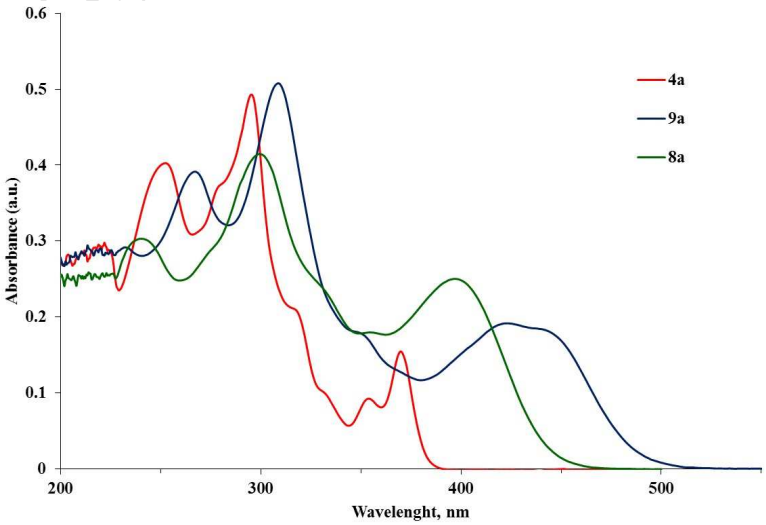


Figure 6. UV/Vis spectra of compounds **4a**, **8a**, **9a**

It was found that all selected compounds exhibit photoluminescent properties (Table 5). The excitation spectra coincide with the absorption ones. The influence of the structure of compounds **4a, 4f, 4g, 7a, 8a, 9a** on the fluorescence spectra seems to be similar to that observed for the absorption spectra. Thus, the fluorescence maxima of indolo[3,2-*a*]carbazoles (**4a, 4f, 4g**) are in narrow range of values (380-400 nm). At the same time, the fluorescence spectrum maxima of π-extended indolo[3,2-*a*]carbazole derivatives **7a, 8a, 9a** (λ_{max} = 520 – 590 nm) have a significant bathochromic shift in respect to compound **4a** (λ_{max} = 388 nm).

3. Conclusion

In summary, we demonstrated that electrophilic aromatic substitution reactions are effective synthetic tools for the primary functionalization of 5,12-dihydroindolo[3,2-*a*]carbazoles framework on examples of its formylation and acetylation. Thus, the convenient procedures for the synthesis of new 2,9-diformyl- and 2,9-diacetyl-substituted indolo[3,2-*a*]carbazoles with aromatic fragments at C-6,7 positions were elaborated during this study. In addition, a few π-extended derivatives of indolo[3,2-*a*]carbazole ring system, bearing 2,2-dicyanovinyl groups as well as quinoxaline-2-yl or benzo[*g*]quinoxaline-2-yl parts at C-2 and C-9 positions, were prepared starting from the above mentioned diformyl and diacetyl substrates to show synthetic usefulness.

4. Experimental part

All reagents were purchased from commercial sources and used without further purification.

Analytical studies were carried out using equipment of the Center for Joint Use "Spectroscopy and Analysis of Organic Compounds" at the Postovsky Institute of Organic Synthesis of the Russian Academy of Sciences (Ural Division). Melting points were determined on combined heating stages and are uncorrected. Elemental analysis was carried on an automated CHN analyzer. Mass spectrometry was performed using a high resolution Q-TOF LC-MS/MS spectrometer. NMR measurements were performed on NMR spectrometers at 400 MHz and 500 MHz for ^{1}H, 101 MHz, 126 MHz and 151 MHz for 13C spectra in DMSO-d_6 or $CDCl_3$ with tetramethylsilane as an internal standard. The ^{13}C NMR spectra of indolo[3,2-*a*]carbazoles **3b** and **3c** could not be determined due to a poor solubility of these compounds in a majority of deuterated solvents.

Cyclic voltammetry was carried out on a Metrohm Autolab PGSTAT**128N** potentiostat with a standard three-electrode configuration. Typically, a three electrodes cell equipped with a glass carbon working electrode, a $Ag/AgNO_3$ (0.01M) reference electrode, and a glass carbon

rod counter electrode was employed. The measurements were done in dichloromethane with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte under an argon atmosphere at a scan rate of 100 mV/s. The potential of $Ag/AgNO_3$ reference electrode was calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc^+), which has a known oxidation potential of +5.1 eV.

Optical spectra were obtained in CH_2Cl_2 solution ($5 \cdot 10^{-5}$ M) at ambient temperature using a Shimadzu UV-2600 double-beam UV/Vis spectrophotometer, a Varian Cary Eclipse fluorescence spectrophotometer and a Hellma QS-101 high precision quartz cell.

5. General procedure for the synthesis of 6,7-bisaryl-5,12-dihydroindolo[3,2-*a*]carbazoles (3)

p-Toluenesulfonic acid monohydrate (0.38 g; 20.00 mol%) was added to a solution of indole **1** (2.92 g, 25.00 mmol) and the corresponding benzil **2a-c** (10.00 mmol) in acetonitrile (25 ml), and the resulting mixture was refluxed for 10 hours. The solution turned red, and the formed precipitate of desired product **3** was filtered off, washed with 3 × 5 ml of EtOH, and dried at 120 °C.

5.1 6,7-Diphenyl-5,12-dihydroindolo[3,2-a]carbazole (3a)

White powder (3.14 g, 77%), m.p. (321–322 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.86 (s, 1H), 10.75 (s, 1H), 8.71 (d, *J* = 7.8 Hz, 1H), 7.61 (dd, *J* = 13.1, 8.0 Hz, 2H), 7.43 – 7.19 (m, 13H), 6.81 (td, *J* = 7.6, 7.1, 1.0 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 1H).

Compound **3a** was previously described in the literature and its analytical data are identical to the reported data [24].

5.2 6,7-Bis(4-methoxyphenyl)-5,12-dihydroindolo[3,2-a]carbazole (3b)

White powder (3.75 g, 80%), m.p. (> 360 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.80 (s, 1H), 10.66 (s, 1H), 8.68 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.26 – 7.17 (m, 5H), 6.97 – 6.88 (m, 4H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 3.79 (d, *J* = 15.3 Hz, 6H). Anal. Calcd for $C_{32}H_{24}N_2O_2$: C, 82.0; H, 5.2; N, 6.0; Found: C, 81.9; H, 5.3; N, 6.1.

5.3 6,7-Bis(4-bromophenyl)-5,12-dihydroindolo[3,2-a]carbazole (3c)

White powder (4.02 g, 71%), m.p. (> 360 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.93 (s, 1H), 10.87 (s, 1H), 8.71 (d, *J* = 7.8 Hz, 1H), 7.92 – 7.82 (m, 4H), 7.67 – 7.57 (m, 2H), 7.57 – 7.51 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.36 – 7.22 (m, 4H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* =

7.9 Hz, 1H). Anal. Calcd for $C_{30}H_{18}Br_2N_2$: C, 63.6; H, 3.2; N, 4.95; Found: C, 63.9; H, 3.1; N, 4.9.

6. General procedure for the synthesis of 5,12-alkyl-6,7-diaryl-5,12-dihydroindolo[3,2-*a*]carbazoles (4)

The corresponding alkyl halide (3.00 mmol) was added to the ice-cooled suspension of **3** (1.00 mmol) in a mixture of THF (8 ml) and DMSO (2 ml), and then sodium hydride (0.14 g, 6.00 mmol) was added in small portions. The resulting mixture was stirred for 3 hours at room temperature. Then unreacted sodium hydride was decomposed with 2 ml of methanol, the reaction mixture was diluted with water (20 ml), and the formed precipitate was filtered off and recrystallized from DMF (8 ml), washed with 2 × 5 ml of EtOH and dried.

6.1 5,12-Dihexyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole (4a)

White powder (0.49 g, 85%), m.p. (119-120 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.43 (t, *J* = 8.1 Hz, 1H), 7.52 – 7.40 (m, 3H), 7.35 – 7.23 (m, 7H), 7.20 (dt, *J* = 6.9, 2.1 Hz, 5H), 6.86 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.43 (dd, *J* = 8.0, 1.1 Hz, 1H), 4.94 – 4.88 (m, 2H), 3.74 – 3.67 (m, 2H), 2.28 – 2.18 (m, 2H), 1.62 – 1.56 (m, 2H), 1.52 – 1.31 (m, 7H), 1.23 – 1.12 (m, 2H), 1.12 – 1.02 (m, 2H), 0.95 – 0.88 (m, 3H), 0.84 – 0.75 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.1, 140.9, 140.3, 138.8, 138.2, 136.2, 135.9, 131.9, 130.3, 127.8, 127.3, 126.6, 126.5, 124.5, 124.1, 123.5, 122.4, 121.18, 121.16, 119.11, 119.07, 118.1, 115.0, 109.5, 109.0, 107.3, 46.5, 44.6, 31.6, 31.4, 30.9, 28.7, 26.5, 26.2, 22.6, 22.5, 14.01, 13.97. Anal. Calcd for $C_{42}H_{44}N_2$: C, 87.45; H, 7.7; N, 4.9; Found: C, 87.6; H, 7.8; N, 4.9.

6.2 5,12-Dibutyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole (4b)

White powder (0.46 g, 89%), m.p. (182-183 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.38 (m, 3H), 7.36 – 7.23 (m, 6H), 7.17 (dt, *J* = 12.1, 6.9 Hz, 6H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 4.90 (t, *J* = 8.0 Hz, 2H), 3.70 (t, *J* = 8.2 Hz, 2H), 2.19 (p, *J* = 7.8 Hz, 2H), 1.58 (h, *J* = 7.4 Hz, 2H), 1.42 (p, *J* = 7.8 Hz, 2H), 1.03 (t, *J* = 7.4 Hz, 3H), 0.82 (h, *J* = 7.5 Hz, 2H), 0.70 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.1, 140.9, 140.3, 138.8, 138.3, 136.2, 135.9, 131.9, 130.3, 127.8, 127.3, 126.6, 126.5, 124.5, 124.1, 123.5, 122.4, 121.2, 121.1, 119.12, 119.08, 118.1, 115.2, 109.5, 109.0, 107.4, 46.2, 44.4, 33.0, 30.8, 20.2, 19.8, 14.0, 13.6. Anal. Calcd for $C_{38}H_{36}N_2$: C, 87.65; H, 7.0; N, 5.4; Found: C, 87.6; H, 7.0; N, 5.3.

6.3 5,12-Dibenzyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole (4c)

Beige powder (0.46 g, 81%), m.p. (283-284 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.43 – 7.35 (m, 1H), 7.33 – 7.15 (m, 9H), 7.15 – 6.97 (m, 7H), 6.97 – 6.84 (m, 3H), 6.55 (dd, *J* = 7.4, 2.1 Hz, 2H), 6.49 (d, *J* = 8.0 Hz, 1H), 6.12 (s, 2H), 5.07 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.3, 141.3, 140.0, 138.7, 138.4, 137.84, 137.80, 137.4, 136.1, 131.8, 130.3, 129.2, 128.1, 127.8, 127.5, 127.1, 126.6, 126.5, 125.5, 124.9, 124.5, 124.1, 122.6, 121.2, 120.9, 119.8, 119.7, 118.8, 115.6, 109.9, 109.8, 107.5, 50.9, 47.9. (2 signal ($2C_{Ar}$) was not found due to overlapping peaks). Anal. Calcd for $C_{44}H_{32}N_2$: C, 89.8; H, 5.5; N, 4.8; Found: C, 89.7; H, 5.5; N, 4.6.

6.4 5,12-Diethyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole (4d)

White powder (4.27 g, 92%), m.p. (269–270 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.50 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.52 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.36 – 7.31 (m, 2H), 7.31 – 7.15 (m, 11H), 6.88 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.45 (dt, *J* = 7.9, 0.9 Hz, 1H), 5.04 (q, *J* = 7.2 Hz, 2H), 3.82 (q, *J* = 7.1 Hz, 2H), 1.85 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.1 Hz, 3H).

Compound **4d** was previously described in the literature and its analytical data are identical to the reported data [24].

6.5 5,12-Dimethyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole (4e)

White powder (3.84 g, 88%), m.p. (314–315 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 8.1 Hz, 1H), 7.48 (ddd, *J* = 7.0, 5.3, 2.7 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.33 (dtd, *J* = 8.2, 7.0, 1.2 Hz, 2H), 7.32 – 7.14 (m, 4H), 6.90 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.55 – 6.48 (m, 1H), 4.52 (s, 3H), 3.28 (s, 3H).

Compound **4e** was previously described in the literature and its analytical data are identical to the reported data [24].

6.6 5,12-Dihexyl-6,7-bis(4-methoxyphenyl)-5,12-dihydroindolo[3,2-a]carbazole (4f)

White powder (0.61 g, 96%), m.p. (178-179 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.34 (d, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.36 (m, 2H), 7.29 – 7.18 (m, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.82 – 6.74 (m, 1H), 6.74 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 6.30 (d, *J* = 7.9 Hz, 1H), 4.90 (t, *J* = 7.9 Hz, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 3.66 (q, *J* = 8.1, 7.5 Hz, 2H), 2.02 (p, *J* = 7.5 Hz, 2H), 1.51 – 1.39 (m, 2H), 1.38 – 1.22 (m, 6H), 1.16 (p, *J* = 7.0 Hz, 2H), 1.05 (p, *J* = 7.0 Hz, 2H), 0.89 – 0.73 (m, 8H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.2, 158.0, 141.1, 140.9, 138.6, 136.1, 136.0, 132.74, 132.66, 131.2, 131.0, 124.6, 124.0, 123.4, 122.3, 121.3, 121.2, 119.1, 119.0, 118.2, 115.5, 113.2, 112.7, 109.5, 108.9, 107.2, 55.1, 55.0, 46.5, 44.6, 31.6, 31.4, 30.9, 28.7, 26.5, 26.4, 22.6, 22.5, 13.99, 13.95. Anal. Calcd for $C_{44}H_{48}N_2O_2$: C, 83.0; H, 7.6; N, 4.4; Found: C, 82.8; H, 7.8; N, 4.5.

6.*7 6,7-Bis(4-bromophenyl)-5,12-dihexyl-5,12-dihydroindolo[3,2-a]carbazole* (4g)

Beige powder (0.41 g, 56%), m.p. (184-185 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.46 – 7.39 (m, 3H), 7.39 – 7.30 (m, 4H), 7.16 – 7.08 (m, 2H), 7.12 – 7.00 (m, 2H), 6.97 – 6.89 (m, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 4.95 – 4.86 (m, 2H), 3.74 – 3.66 (m, 2H), 2.27 – 2.14 (m, 2H), 1.62 – 1.52 (m, 3H), 1.49 – 1.29 (m, 6H), 1.27 – 1.13 (m, 2H), 1.13 – 1.02 (m, 2H), 0.91 (t, *J* = 7.1 Hz, 3H), 0.88 – 0.78 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.1, 140.9, 139.0, 138.0, 137.6, 136.4, 134.2, 133.4, 132.0, 131.3, 130.6, 124.4, 124.1, 123.9, 122.4, 121.1, 120.97, 120.95, 119.38, 119.37, 119.36, 116.5, 114.8, 109.6, 109.2, 107.7, 46.5, 44.7, 31.6, 31.2, 30.8, 28.7, 26.5, 26.3, 22.6, 22.5, 13.98, 13.99. Anal. Calcd for $C_{42}H_{42}Br_2N_2$: C, 68.7; H, 5.8; N, 3.8; Found: C, 68.7; H, 5.8; N, 4.1.

7. General procedure for the synthesis of 5,12-dialkyl-6,7-diaryl-5,12-dihydroindolo[3,2-*a*]carbazole-2,9-dicarbaldehydes (5)

1,1-Dichloromethyl methyl ether (0.28 ml, 3.00 mmol) was added dropwise to the cooled to -20 °C solution of **4** (1.00 mmol) and $SnCl_4$ (0.47 ml, 4.00 mmol) in dichloromethane (20 ml), and the resulting solution was incubated for 1 hour. The reaction mixture turned red. Then water (50 ml) was added, and the mixture was stirred for 0.5 hours until discoloration. The organic phase was separated, the solvent was distilled off, and the resulting residue of product **5** was recrystallized from DMF (8-10 ml), washed with 2 × 5 ml of EtOH and dried at 120 °C.

***7.1 5,12-Dihexyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole-2,9-dicarbaldehyde* (5a)**

White powder (0.45 g, 71%), m.p. (213-214 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.17 (s, 1H), 9.59 (s, 1H), 8.97 (d, *J* = 1.4 Hz, 1H), 8.03 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.94 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.32 (ddd, *J* = 18.5, 4.2, 2.0 Hz, 5H), 7.26 – 7.15 (m, 5H), 6.80 (d, *J* = 1.5 Hz, 1H), 5.09 – 4.94 (m, 2H), 3.87 – 3.62 (m, 2H), 2.41 – 2.22 (m, 2H), 1.73 (p, *J* = 7.4 Hz, 2H), 1.53 – 1.30 (m, 6H), 1.26 – 1.12 (m, 2H), 1.14 – 1.01 (m, 2H), 0.91 (t, *J* = 7.1 Hz, 3H), 0.87 – 0.76 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.8, 191.3, 144.5, 144.3, 139.24, 139.19, 137.7, 137.2, 136.4, 131.6, 129.9, 129.0, 128.9, 128.3, 127.6, 127.21, 127.17, 126.9, 126.5, 125.4, 123.94, 123.89, 120.9, 119.6, 116.2, 109.8, 109.4, 107.8, 46.7, 45.0, 31.7, 31.30, 31.27 , 28.7, 26.3, 26.1, 22.5, 22.4, 14.0, 13.9. Anal. Calcd for $C_{44}H_{44}N_2O_2$: C, 83.5; H, 7.0; N, 4.4; Found: C, 83.7; H, 7.1; N, 4.6.

***7.2 5,12-Dibutyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole-2,9-dicarbaldehyde* (5b)**

White powder (0.39 g, 68%), m.p. (206-207 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.16 (s, 1H), 9.58 (s, 1H), 8.97 (d, *J* = 1.5 Hz, 1H), 8.06 – 7.98 (m, 1H), 7.94 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.42 – 7.13 (m, 10H), 6.80 (d, *J* = 1.6 Hz, 1H), 5.06 – 4.97 (m, 2H), 3.84 – 3.75 (m, 2H), 2.34 – 2.21 (m, 2H), 1.82 – 1.67 (m, 2H), 1.47 (p, *J* = 8.1 Hz, 2H), 1.10 (t, *J* = 7.3 Hz, 3H), 0.87 (h, *J* = 7.1, 6.6 Hz, 2H), 0.74 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.8, 191.4, 144.6, 144.4, 139.3, 139.2, 137.6, 137.2, 136.4, 131.6, 129.9, 129.0, 128.9, 128.3, 127.6, 127.24, 127.18, 127.0, 126.6, 125.4, 124.0, 123.9, 121.0, 119.6, 116.2, 109.8, 109.5, 107.9, 46.6, 44.8, 33.4, 30.8, 20.0, 19.8, 14.0, 13.6. Anal. Calcd for $C_{40}H_{36}N_2O_2$: C, 83.3; H, 6.3; N, 4.9; Found: , 83.3; H, 6.25; N, 4.8.

7.3 5,12-Dibenzyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole-2,9-dicarbaldehyde **(5c)**

White powder (0.37 g, 55%), m.p. (304-305 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.62 (s, 1H), 9.48 (s, 1H), 8.50 (d, *J* = 1.4 Hz, 1H), 7.87 (ddd, *J* = 8.5, 5.1, 1.5 Hz, 2H), 7.59 – 7.48 (m, 4H), 7.42 (dd, *J* = 22.2, 7.9 Hz, 2H), 7.36 – 7.28 (m, 4H), 7.23 – 7.08 (m, 6H), 7.02 – 6.93 (m, 4H), 6.90 (d, *J* = 1.5 Hz, 1H), 6.55 – 6.47 (m, 2H), 6.23 (s, 2H), 5.14 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.9, 191.5, 145.7, 144.8, 139.6, 138.9, 137.4, 137.2, 137.0, 136.69, 136.66, 131.5, 129.9, 129.63, 129.58, 128.4, 128.3, 128.2, 127.35, 127.27, 127.1, 127.0, 126.6, 126.1, 125.2, 124.7, 124.6, 124.5, 120.4, 120.3, 116.7, 110.5, 110.2, 107.9, 50.8, 48.3. Anal. Calcd for $C_{46}H_{32}N_2O_2$: C, 85.7; H, 5.0; N, 4.3; Found: C, 85.5; H, 5.1; N, 4.6.

7.4 5,12-Diethyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole-2,9-dicarbaldehyde **(5d)**

White powder (0.32 g, 59%), m.p. (315-316 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.18 (s, 1H), 9.60 (s, 1H), 9.06 (d, *J* = 1.4 Hz, 1H), 8.03 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.96 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.38 – 7.31 (m, 5H), 7.30 – 7.18 (m, 5H), 6.82 (d, *J* = 1.6 Hz, 1H), 5.14 (q, *J* = 7.2 Hz, 2H), 3.90 (q, *J* = 7.1 Hz, 2H), 1.96 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.9, 191.6, 144.4, 144.1, 139.24, 139.18, 137.7, 137.2, 136.4, 131.5, 129.9, 129.2, 129.0, 128.3, 127.6, 127.3, 127.2, 127.0, 126.8, 125.4, 124.15, 124.09, 121.2, 119.6, 116.3, 109.8, 109.3, 107.9, 41.6, 39.5, 16.6, 14.1. Anal. Calcd for $C_{36}H_{28}N_2O_2$: C, 83.05; H, 5.4; N, 5.4; Found: C, 83.1; H, 5.5; N, 5.35.

7.5 5,12-Dimethyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole-2,9-dicarbaldehyde **(5e)**

White powder (0.30 g, 61%), m.p. (284-285 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.16 (s, 1H), 9.62 (s, 1H), 9.16 (d, *J* = 1.5 Hz, 1H), 7.99 (ddd, *J* = 23.7, 8.6, 1.5 Hz, 2H), 7.55 (dd, *J* =

27.7, 8.6 Hz, 2H), 7.36 (ddt, *J* = 5.6, 3.9, 2.2 Hz, 3H), 7.35 – 7.17 (m, 7H), 6.89 (d, *J* = 1.6 Hz, 1H), 4.65 (s, 3H), 3.35 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.9, 191.7, 145.40, 145.36, 140.3, 139.0, 137.6, 137.1, 137.0, 132.0, 129.9, 129.0, 128.9, 128.3, 127.5, 127.3, 127.2, 126.8, 126.6, 125.4, 124.3, 124.0, 120.7, 119.8, 116.1, 109.5, 109.4, 107.7, 35.7, 33.5. Anal. Calcd for $C_{34}H_{24}N_2O_2$: C, 82.9; H, 4.9; N, 5.7; Found: C, 82.8; H, 4.9; N, 5.6.

7.6 5,12-Dihexyl-6,7-bis(4-methoxyphenyl)-5,12-dihydroindolo[3,2-a]carbazole-2,9-dicarbaldehyde (5f)

Cream powder (0.54 g, 78%), m.p. (225-226 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.10 (s, 1H), 9.56 (s, 1H), 8.88 (d, *J* = 1.3 Hz, 1H), 7.97 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.81 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.18 – 7.12 (m, 2H), 7.08 – 7.01 (m, 2H), 6.90 – 6.84 (m, 2H), 6.81 – 6.77 (m, 2H), 6.76 (d, *J* = 1.5 Hz, 1H), 5.02 (t, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 3.81 – 3.74 (m, 5H), 2.10 (p, *J* = 8.0 Hz, 2H), 1.62 (p, *J* = 7.4 Hz, 2H), 1.44 – 1.26 (m, 6H), 1.21 – 1.14 (m, 2H), 1.12 – 1.04 (m, 1H), 0.84 (dt, *J* = 18.1, 7.2 Hz, 8H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.9, 191.3, 158.7, 158.6, 144.6, 144.3, 139.7, 137.4, 136.3, 132.4, 131.6, 130.9, 129.8, 129.0, 128.8, 127.2, 126.4, 125.4, 124.0, 123.7, 121.0, 119.7, 116.7, 113.8, 113.1, 109.8, 109.4, 107.8, 55.3, 55.2, 46.7, 45.0, 31.7 , 31.31, 31.32, 28.8, 26.28, 26.35, 22.6, 22.5, 14.0, 13.9. Anal. Calcd for $C_{46}H_{48}N_2O_4$: C, 79.7; H, 7.0; N, 4.0; Found: C, 79.8; H, 6.9; N, 4.1.

7.7 6,7-Bis(4-bromophenyl)-5,12-dihexyl-5,12-dihydroindolo[3,2-a]carbazole-2,9-dicarbaldehyde (5g)

Cream powder (0.68g, 86%), m.p. (253-254 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.12 (s, 1H), 9.60 (s, 1H), 8.92 (d, *J* = 1.4 Hz, 1H), 8.01 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.85 – 7.82 (m, 2H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.49 – 7.42 (m, 2H), 7.31 – 7.23 (m, 2H), 7.19 – 7.10 (m, 2H), 6.76 (d, *J* = 1.4 Hz, 1H), 5.06 (t, *J* = 7.9 Hz, 2H), 3.89 – 3.73 (m, 2H), 2.23 – 1.99 (m, 2H), 1.64 – 1.56 (m, 2H), 1.45 – 1.27 (m, 6H), 1.26 – 1.14 (m, 2H), 1.13 – 1.03 (m, 2H), 0.88 – 0.82 (m, 8H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.6, 191.3, 144.6, 144.4, 139.1, 137.9, 136.6, 136.5, 135.6, 133.1, 131.7, 131.6, 131.0, 129.2, 129.1, 126.9, 126.6, 125.4, 124.1, 123.5, 121.7, 121.6, 120.8, 118.1, 116.0, 109.9, 109.7, 108.2, 46.8, 45.2, 31.7, 31.30, 31.26, 28.8, 26.3, 26.2, 22.55, 22.49, 13.98, 13.94. Anal. Calcd for $C_{44}H_{42}Br_2N_2O_2$: C, 66.8; H, 5.35; N, 3.5; Found: C, 66.8; H, 5.4; N, 3.55.

8. General procedure for the synthesis of 1,1'-(5,12-dialkyl-6,7-diaryl-5,12-dihydroindolo[3,2-*a*]carbazole-2,9-diyl)bis(ethan-1-one)s (6)

Acetyl chloride (0.21 ml, 3.00 mmol) was added dropwise to the ice-cooled solution of **4** (1 mmol) and $AlCl_3$ (0.53 g, 4.00 mmol) in dichloromethane (20 ml), and the resulting solution was incubated for 1 hour. The reaction mixture turned red. Then 50 ml of water was added, and the mixture was stirred for 0.5 hours until discoloration. The organic phase was separated, the solvent was distilled off, and the resulting residue of product **6** was recrystallized from DMF (8-10 ml), washed with 2 × 5 ml of EtOH and dried at 120 °C.

8.1 1,1'-(5,12-Dihexyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole-2,9-diyl)bis(ethan-1-one) **(6a)**

White powder (0.50 g, 76%), m.p. (208-209 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.18 (d, *J* = 1.6 Hz, 1H), 8.11 (dd, *J* = 8.7, 1.4 Hz, 1H), 8.05 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.39 – 7.28 (m, 6H), 7.24 (dd, *J* = 4.5, 2.1 Hz, 4H), 6.96 (d, *J* = 1.7 Hz, 1H), 5.02 (t, *J* = 7.9 Hz, 2H), 3.92 – 3.60 (m, 2H), 2.77 (s, 3H), 2.27 – 2.15 (m, 2H), 2.19 (s, 3H), 1.65 (q, *J* = 7.7 Hz, 2H), 1.47 (p, *J* = 8.5 Hz, 2H), 1.42 – 1.28 (m, 4H), 1.27 – 1.14 (m, 2H), 1.09 (p, *J* = 6.9 Hz, 2H), 0.92 – 0.72 (m, 10H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.8, 197.2, 143.69, 143.66, 139.7, 139.1, 137.9, 136.7, 136.4, 131.6, 130.1, 129.2, 129.0, 128.1, 127.5, 127.1, 127.0, 125.5, 123.92, 123.87, 123.8, 123.3, 120.8, 119.1, 116.2, 109.0, 108.8, 108.1, 46.7, 44.9, 31.7, 31.3, 31.2, 28.7, 26.7, 26.2, 26.1, 26.0, 22.5, 22.4, 13.99, 13.92. Anal. Calcd for $C_{46}H_{48}N_2O_2$: C, 83.6; H, 7.3; N, 4.2; Found: C, 83.5; H, 7.4; N, 4.5.

8.2 1,1'-(5,12-Dibutyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole-2,9-diyl)bis(ethan-1-one) **(6b)**

White powder (0.44g, 72%), m.p. (257-258 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.20 (d, *J* = 1.6 Hz, 1H), 8.11 (dd, *J* = 8.8, 1.5 Hz, 2H), 8.05 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.40 – 7.29 (m, 5H), 7.25 (s, 3H), 7.30 – 7.22 (m, 2H), 6.97 (d, *J* = 1.7 Hz, 1H), 5.03 (t, *J* = 7.9 Hz, 2H), 3.82 – 3.75 (m, 2H), 2.77 (s, 3H), 2.29 – 2.21 (m, 5H), 2.19 (s, 3H), 1.77 – 1.61 (m, 2H), 1.46 (p, *J* = 7.7 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H), 0.87 (q, *J* = 7.5 Hz, 2H), 0.74 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.8, 197.3, 143.7, 139.7, 139.1, 137.88, 137.86, 136.7, 136.4, 131.6, 130.1, 129.1, 129.0, 128.1, 127.5, 127.1, 127.0, 125.6, 123.91, 123.86, 123.7, 123.3, 120.8, 119.1, 116.2, 109.0, 108.8, 108.1, 46.5, 44.7, 33.4, 30.8, 26.7, 26.0, 20.0, 19.8, 14.0, 13.6. Anal. Calcd for $C_{42}H_{40}N_2O_2$: C, 83.4; H, 6.7; N, 4.6; Found: C, 83.3; H, 6.7; N, 4.8.

8.3 1,1'-(5,12-Diethyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole-2,9-diyl)bis(ethan-1-one) **(6d)**

White powder (0.37 g, 78%), m.p. (264-265 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.26 (d, *J* = 1.6 Hz, 1H), 8.14 (dd, *J* = 8.7, 1.5 Hz, 1H), 8.07 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.57 (dd, *J* = 8.7, 4.4 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.42 – 7.26 (m, 5H), 7.30 – 7.17 (m, 5H), 6.98 (d, *J* = 1.7 Hz, 1H), 5.12 (q, *J* = 7.2 Hz, 2H), 3.88 (q, *J* = 7.1 Hz, 2H), 2.79 (s, 3H), 2.20 (s, 3H), 2.02 – 1.90 (m, 3H), 1.04 (q, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 197.9, 197.5, 143.5, 143.4, 139.7, 139.0, 138.0, 136.8, 136.5, 131.6, 130.1, 129.3, 129.2, 128.3, 127.6, 127.3, 127.1, 125.5, 124.2, 124.0, 123.9, 123.5, 120.9, 119.2, 116.2, 109.0, 108.8, 108.1, 41.6, 39.4, 26.8, 26.1, 16.6, 14.1. Anal. Calcd for $C_{38}H_{32}N_2O_2$: C, 83.2; H, 5.9; N, 5.1; Found: C, 83.3; H, 5.75; N, 5.15.

8.4 1,1'-(5,12-Dimethyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole-2,9-diyl)bis(ethan-1-one) (6e)

White powder (0.37 g, 71%), m.p. (323-324 °C). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.37 (d, *J* = 1.6 Hz, 1H), 8.12 (dd, *J* = 8.7, 1.6 Hz, 1H), 8.08 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.32 – 7.24 (m, 8H), 7.04 (d, *J* = 1.7 Hz, 1H), 4.63 (s, 3H), 3.34 (s, 3H), 2.78 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.9, 197.5, 144.7, 144.5, 140.1, 139.5, 137.9, 137.2, 136.5, 132.0, 130.1, 129.3, 129.1, 128.2, 127.5, 127.14, 127.11, 125.5, 124.3, 123.9, 123.7, 123.5, 120.5, 119.3, 116.2, 108.9, 108.7, 107.9, 35.6, 33.3, 26.7, 26.0. Anal. Calcd for $C_{36}H_{28}N_2O_2$: C, 83.05; H, 5.4; N, 5.4; Found: C, 83.1; H, 5.4; N, 5.2.

8.5 1,1'-(6,7-Bis(4-bromophenyl)-5,12-dihexyl-5,12-dihydroindolo[3,2-a]carbazole-2,9-diyl)bis(ethan-1-one) (6f)

White powder (0.72 g, 88%), m.p. (266-267 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.05 (d, *J* = 1.6 Hz, 1H), 8.10 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.89 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.50 – 7.39 (m, 2H), 7.33 – 7.26 (m, 2H), 7.21 – 7.12 (m, 2H), 6.78 (d, *J* = 1.7 Hz, 1H), 5.02 (t, *J* = 7.7 Hz, 2H), 3.87 – 3.70 (m, 2H), 2.71 (s, 3H), 2.19 (s, 3H), 2.07 (d, *J* = 8.5 Hz, 2H), 1.57 (t, *J* = 7.8 Hz, 2H), 1.39 (d, *J* = 16.0 Hz, 2H), 1.32 – 1.16 (m, 6H), 1.14 – 1.02 (m, 2H), 0.84 (td, *J* = 7.0, 3.7 Hz, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.5, 197.1, 143.67, 143.66, 138.9, 138.4, 136.7, 136.6, 135.1, 133.1, 131.8, 131.6, 131.0, 129.4, 129.2, 125.8, 124.2, 123.8, 123.4, 122.9, 121.6, 121.5, 120.7, 117.5, 116.1, 109.2, 109.0, 108.5, 46.7, 45.1, 31.6, 31.3, 31.2, 28.8, 26.7, 26.25, 26.18, 25.8, 22.50, 22.45, 13.96, 13.94. Anal. Calcd for $C_{46}H_{46}Br_2N_2O_2$: C, 67.5; H, 5.7; N, 3.4; Found: C, 67.5; H, 5.7; N, 3.6.

***8.6 1,1'-(6,7-Bis(4-methoxyphenyl)-5,12-dihexyl-5,12-dihydroindolo[3,2-a]carbazole-2,9-diyl)bis(ethan-1-one)* (6g)**

White powder (0.53 g, 73%), m.p. (208-209 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.05 (d, *J* = 1.6 Hz, 1H), 8.08 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.87 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.12 – 7.06 (m, 2H), 6.96 – 6.89 (m, 2H), 6.84 – 6.77 (m, 3H), 5.02 (t, *J* = 7.8 Hz, 2H), 3.81 (s, 3H), 3.80 – 3.68 (m, 5H), 2.71 (s, 3H), 2.15 (s, 3H), 2.06 (q, *J* = 7.8 Hz, 2H), 1.56 (q, *J* = 7.7 Hz, 2H), 1.39 (d, *J* = 6.6 Hz, 2H), 1.35 – 1.13 (m, 6H), 1.13 – 1.03 (m, 2H), 0.93 – 0.75 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.7, 197.2, 158.56, 158.52, 143.7, 139.5, 136.98, 136.92, 136.3, 132.5, 132.1, 131.1, 130.1, 129.1, 128.9, 125.5, 124.0, 123.8, 123.7, 123.4, 120.8, 119.2, 116.8, 113.7, 113.0, 109.0, 108.8, 108.1, 55.3, 55.1, 46.7, 44.9, 31.7, 31.3, 31.2, 28.7, 26.7, 26.3, 26.2, 25.9, 22.48, 22.47, 13.98, 13.91. Anal. Calcd for $C_{48}H_{52}N_2O_4$: C, 80.0; H, 7.3; N, 3.9; Found: C, 79.9; H, 7.25; N, 3.9.

9. General procedure for the synthesis of 2,2'-((5,12-dialkyl-6,7-diaryl-5,12-dihydroindolo[3,2-*a*]carbazole-2,9-diyl)bis(methaneylylidene))dimalononitriles (7)

Dicarbaldehyde **5** (0.50 mmol) and malononitrile (0.13 g, 2.00 mmol) were added in a mixture of DMF (3 ml), AcOH (2 ml) and pyrrolidine (0.17 ml, 2.00 mmol), the resulting solution was refluxed for 2 hours. Then the reaction mixture was cooled, and the formed precipitate was filtered off and crystallized from DMF (3 ml), washed with 2 × 2 ml EtOH and dried at 120 °C to give the desired product **7**.

9.1 2,2'-((5,12-Dihexyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole-2,9-diyl)bis(methaneylylidene))dimalononitrile (7a)

Orange powder (0.30 g, 83%), m.p. (253-254 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.90 (d, *J* = 1.7 Hz, 1H), 8.38 (dd, *J* = 8.9, 1.9 Hz, 1H), 8.14 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.91 (s, 1H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.30 – 7.26 (m, 6H), 7.20 – 7.12 (m, 2H), 6.44 (d, *J* = 1.9 Hz, 1H), 5.05 (t, *J* = 7.4 Hz, 2H), 3.83 – 3.70 (m, 2H), 2.16 – 2.01 (m, 2H), 1.53 – 1.44 (m, 2H), 1.44 – 1.36 (m, 2H), 1.33 – 1.16 (m, 6H), 1.15 – 1.04 (m, 2H), 0.90 – 0.77 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.5, 160.1, 144.5, 144.4, 139.5, 138.7, 137.8, 137.0, 136.3, 131.4, 129.7, 129.4, 128.4, 127.74 , 127.66, 127.56, 127.51, 127.1, 124.3, 124.0, 123.01, 122.96, 121.5, 120.5, 116.7, 115.0, 114.9, 114.1, 113.7, 110.73, 110.72, 107.8, 46.6, 45.2, 31.4, 31.2, 30.6, 28.9, 26.4, 26.0, 22.45, 22.38, 13.87, 13.86. Anal. Calcd for $C_{50}H_{44}N_6$: C, 82.4; H, 6.1; N, 11.5; Found: C, 82.3; H, 5.9; N, 11.7.

***9.2 2,2'-((5,12-Dibutyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole-2,9-diyl)bis(methaneylylidene))dimalononitrile* (7b)**

Orange powder (0.51 g, 76%), m.p. (281-282 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.95 (d, *J* = 1.7 Hz, 1H), 8.39 (dd, *J* = 9.0, 1.9 Hz, 1H), 8.13 – 8.07 (m, 1H), 7.91 (s, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.41 – 7.27 (m, 3H), 7.30 – 7.25 (m, 6H), 7.20 – 7.14 (m, 2H), 6.44 (d, *J* = 1.9 Hz, 1H), 5.08 (t, *J* = 7.2 Hz, 2H), 3.83 – 3.76 (m, 1H), 2.10 – 2.03 (m, 2H), 1.51 – 1.43 (m, 2H), 1.39 (p, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.86 (q, *J* = 7.5 Hz, 2H), 0.75 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.6, 160.2, 144.59, 144.56, 139.7, 138.7, 137.9, 137.1, 136.4, 131.5, 129.7, 129.4, 128.5, 127.9, 127.7, 127.60, 127.57, 126.9, 124.4, 124.1, 123.07, 123.05, 121.7, 120.6, 116.8, 115.1, 114.9 , 114.2, 113.8, 110.8, 110.7, 107.9, 46.5, 45.1, 32.8, 31.0, 20.2, 19.8, 13.9, 13.5. Anal. Calcd for $C_{46}H_{36}N_6$: C, 82.1; H, 5.4; N, 12.5; Found: C, 82.1; H, 5.4; N, 12.4.

10. General procedure for the synthesis of 5,12-dialkyl-6,7-diphenyl-2,9-di(quinoxalin-2-yl)-5,12-dihydroindolo[3,2-*a*]carbazoles (8) and 2,9-bis(benzo[*g*]quinoxalin-2-yl)-5,12-dialkyl-6,7-diphenyl-5,12-dihydroindolo[3,2-*a*]carbazoles (9)

Diacetyl derivative **6** (0.25 mmol), SeO_2 (0.06 g, 0.50 mmol), 1,4-dioxane (5 ml), and H_2O (50 μl) were placed in a 10 ml microwave reaction vial. The resulting mixture was irradiated for 0.5 h (200 W) at 150 °C. Then the black precipitate of elemental Se was filtered off, and the bright yellow filtrate was used in the next stage. *o*-Phenylenediamine (0.08 g, 0.7 mmol) or 2,3-diaminonaphthalene (0.12 g, 0.75 mmol) and glacial AcOH (0.75 ml) were added to the previously obtained filtrate, and the resulting solution was refluxed for an hour. After cooling the reaction mixture, the precipitate of product **8** or **9** was separated by filtration and recrystallized from DMF (10 ml), washed with 2 × 2 ml EtOH and dried at 120 ° C.

***10.1 5,12-Dihexyl-6,7-diphenyl-2,9-di(quinoxalin-2-yl)-5,12-dihydroindolo[3,2-a]carbazole* (8a)**

Yellow powder (0.49 g, 59%), m.p. (220-221 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.49 (s, 1H), 9.43 (d, *J* = 1.6 Hz, 1H), 8.80 (s, 1H), 8.38 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.27 (dd, *J* = 8.6, 1.5 Hz, 1H), 8.21 (dd, *J* = 8.2, 1.4 Hz, 2H), 8.15 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.04 (td, *J* = 8.8, 1.4 Hz, 2H), 7.85 – 7.56 (m, 6H), 7.50 – 7.19 (m, 10H), 7.13 (d, *J* = 1.8 Hz, 1H), 5.14 (t, *J* = 7.9 Hz, 2H), 3.84 – 3.77 (m, 2H), 2.32 (t, *J* = 7.8 Hz, 2H), 1.68 (dt, *J* = 15.3, 7.7 Hz, 2H), 1.54 – 1.48 (m, 2H), 1.31 (q, *J* = 7.8 Hz, 2H), 1.27 – 1.06 (m, 6H), 0.90 – 0.79 (m, 5H), 0.71 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.8, 152.3, 143.6, 143.2, 142.5, 142.3, 142.24,

142.16, 141.1, 140.8, 140.0, 139.0, 138.2, 136.7, 136.5, 131.7, 130.2, 130.0, 129.7, 129.3, 129.2, 129.1, 128.8, 128.5, 128.3, 128.1, 127.50, 127.48, 127.10, 127.07, 124.5, 123.8, 123.4 122.6, 121.9, 120.6, 118.8, 115.9, 109.9, 107.9, 46.7, 44.9, 31.6, 31.33, 31.29, 28.7, 26.5, 26.2, 22.44, 22.38, 13.9, 13.8. (2 signal ($2C_{Ar}$) was not found due to overlapping peaks). Anal. Calcd for $C_{58}H_{52}N_6$: C, 83.6; H, 6.3; N, 10.1; Found: C, 83.75; H, 6.3; N, 10.1.

***10.2 5,12-Dibutyl-6,7-diphenyl-2,9-di(quinoxalin-2-yl)-5,12-dihydroindolo[3,2-a]carbazole* (8b)**

Yellow powder (0.60 g, 77%), m.p. (175-176 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.50 (s, 1H), 9.44 (d, *J* = 1.6 Hz, 1H), 8.81 (s, 1H), 8.39 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.29 (dd, *J* = 8.6, 1.5 Hz, 1H), 8.21 (dd, *J* = 8.3, 1.4 Hz, 2H), 8.16 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.09 – 7.98 (m, 2H), 7.86 – 7.58 (m, 6H), 7.50 – 7.21 (m, 10H), 7.14 (d, *J* = 1.8 Hz, 1H), 5.17 (t, *J* = 7.9 Hz, 2H), 3.95 – 3.68 (m, 2H), 2.35 (p, *J* = 7.9 Hz, 2H), 1.77 (q, *J* = 7.6 Hz, 2H), 1.51 (p, *J* = 8.0 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.90 (h, *J* = 7.3 Hz, 2H), 0.76 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.7, 152.0, 143.4, 143.0, 142.9, 142.4, 142.2, 141.0, 139.9, 139.1, 138.2, 136.7, 136.5, 131.7, 130.24, 130.18, 130.0, 129.1, 129.0, 128.9, 128.71, 128.68, 128.5, 128.3, 128.0, 127.9, 127.5, 127.1, 127.0, 124.5, 123.9, 123.64, 123.57, 122.5, 121.9, 120.8, 118.9, 115.9, 110.0, 108.0, 46.4, 44.7, 33.5, 30.9, 20.1, 19.8, 14.1, 13.6. (2 signal ($2C_{Ar}$) was not found due to overlapping peaks). Anal. Calcd for $C_{54}H_{44}N_6$: C, 83.5; H, 5.7; N, 10.8; Found: C, 83.4; H, 5.7; N, 11.0.

***10.3 2,9-Bis(benzo[g]quinoxalin-2-yl)-5,12-dihexyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole* (9a)**

Dark orange powder (0.60 g, 64%), m.p. (282-283 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.57 (s, 1H), 9.51 (d, *J* = 1.6 Hz, 1H), 8.83 (s, 1H), 8.76 (s, 1H), 8.71 (s, 1H), 8.58 (d, *J* = 5.3 Hz, 2H), 8.49 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.35 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 2H), 8.07 (t, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.65 – 7.42 (m, 8H), 7.41 – 7.32 (m, 4H), 7.33 – 7.25 (m, 3H), 7.17 (d, *J* = 1.8 Hz, 1H), 5.20 (t, *J* = 7.9 Hz, 2H), 3.82 (t, *J* = 8.2 Hz, 2H), 2.41 – 2.34 (m, 2H), 1.76 (t, *J* = 7.8 Hz, 2H), 1.57 – 1.47 (m, 2H), 1.37 (q, *J* = 7.8 Hz, 2H), 1.27 – 1.07 (m, 6H), 0.91 – 0.81 (m, 5H), 0.71 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.3, 151.2, 144.7, 144.1, 142.5, 142.3, 139.9, 139.0 , 138.8, 138.1, 137.8, 137.1, 136.6, 136.4, 134.2, 134.0, 133.2, 133.0, 131.7, 130.3, 128.5, 128.34, 128.26, 128.2, 127.9, 127.5, 127.4, 127.2, 127.1, 127.0, 126.8, 126.7, 126.4, 126.2, 124.3, 124.0, 122.7, 121.8, 121.0, 118.9, 115.8, 110.1, 109.9, 107.9, 46.6, 45.0, 31.7, 31.38, 31.35, 28.8, 26.5, 26.2, 22.50, 22.47, 14.0, 13.9. (4

signal ($4C_{Ar}$) was not found due to overlapping peaks). Anal. Calcd for $C_{66}H_{56}N_6$: C, 84.95; H, 6.05; N, 9.0; Found: C, 84.8; H, 6.2; N, 8.9.

***10.4 2,9-Bis(benzo[g]quinoxalin-2-yl)-5,12-dibutyl-6,7-diphenyl-5,12-dihydroindolo[3,2-a]carbazole* (9b)**

Orange powder (0.52 g, 59%), m.p. (319-320 °C). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.58 (s, 1H), 9.53 (d, *J* = 1.5 Hz, 1H), 8.84 (s, 1H), 8.76 (s, 1H), 8.72 (s, 1H), 8.59 (d, *J* = 6.2 Hz, 2H), 8.50 (dd, *J* = 8.5, 1.8 Hz, 1H), 8.36 (dd, *J* = 8.7, 1.5 Hz, 1H), 8.16 (dd, *J* = 7.7, 5.6 Hz, 2H), 8.08 (t, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.66 – 7.42 (m, 8H), 7.42 – 7.26 (m, 7H), 7.19 (d, *J* = 1.7 Hz, 1H), 5.22 (t, *J* = 7.9 Hz, 2H), 3.88 – 3.80 (m, 2H), 2.40 (t, *J* = 7.7 Hz, 2H), 1.83 (q, *J* = 7.6 Hz, 2H), 1.57 – 1.45 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.91 (m, 2H), 0.77 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.1, 151.0, 144.6, 143.9, 142.6, 139.8, 139.7, 139.2, 138.1, 138.0, 137.9, 136.80, 136.78, 136.51, 136.48, 134.6, 134.43, 134.38, 131.8, 131.7, 130.3, 128.9, 128.62, 128.57, 128.43, 128.39, 127.6, 127.4, 127.2, 127.0, 126.7, 124.47, 124.45, 124.3, 122.9, 121.8, 119.2, 115.9, 115.8, 110.6, 110.5, 110.3, 110.1, 108.0, 46.6, 44.8, 33.5, 30.9, 20.2, 19.9, 14.2, 13.6. (6 signal ($6C_{Ar}$) was not found due to overlapping peaks). Anal. Calcd for $C_{66}H_{56}N_6$: $C_{62}H_{48}N_6$: C, 84.9; H, 5.5; N, 9.6; Found: C, 84.9; H, 5.5; N, 9.5.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at

X-ray crystallographic data

Deposition numbers CCDC 1917414 (for compound **5d**) and CCDC 1917416 (for compound **6e**) contain the crystallographic data for these structures. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Highlights

- Modifications of 5,12-dihydroindolo[3,2-*a*]carbazole compounds were investigated
- Methods for double formylation and acetylation of these heteroacenes were elaborated
- Prepared diformyl and diacetyl derivatives were used to construct π-extended molecules