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Synthesis and Properties of 2,7-Phenylethenyl- and Benzoxazol-2-ylethenyl *N*-Ethylcarbazole Derivatives

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Abstract—A number of new symmetrically and unsymmetrically substituted 2,7-phenylethenyl and benzoxazol-2-ylethenyl *N*-ethylcarbazole derivatives were synthesized by successive Wittig and Knoevenagel olefinations of 9-ethylcarbazole-2,7-dicarbaldehyde. The resulting compounds showed strong photoluminescence in the blue region. The spectral parameters of unsymmetrically substituted 9-ethylcarbazoles with a donor–donor–acceptor conjugation type are determined by intramolecular interaction in the donor–acceptor fragment.

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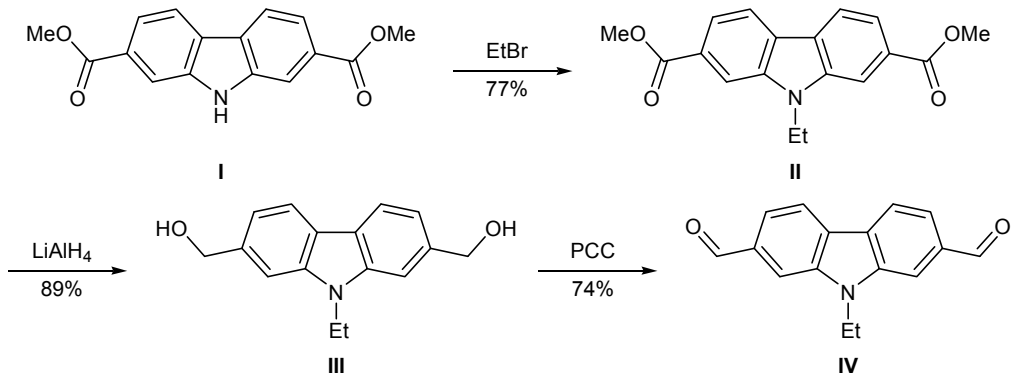
In the past decades much attention has been given to possible applications of organic molecules as molecular conductors, switchers, field-effect transistors, organic light-emitting diodes, etc. [1–3]. An advantage of organic electroactive and photoactive materials over inorganic is the possibility for directed tuning of molecular properties via relatively simple chemical modifications. Poly-π-conjugated carbazole derivatives constitute an extensively studied group of organic compounds which possess a good (predominantly hole) conductivity and high stability and display strong photo- and electroluminescence [4]. Therefore, they attract interest as promising materials for the design of organic light-emitting devices [5–7]. Most publications in this field are concerned with the synthesis and properties of symmetrical 3,6- or 2,7-disubstituted polyconjugated oligomeric and polymeric carbazole derivatives.

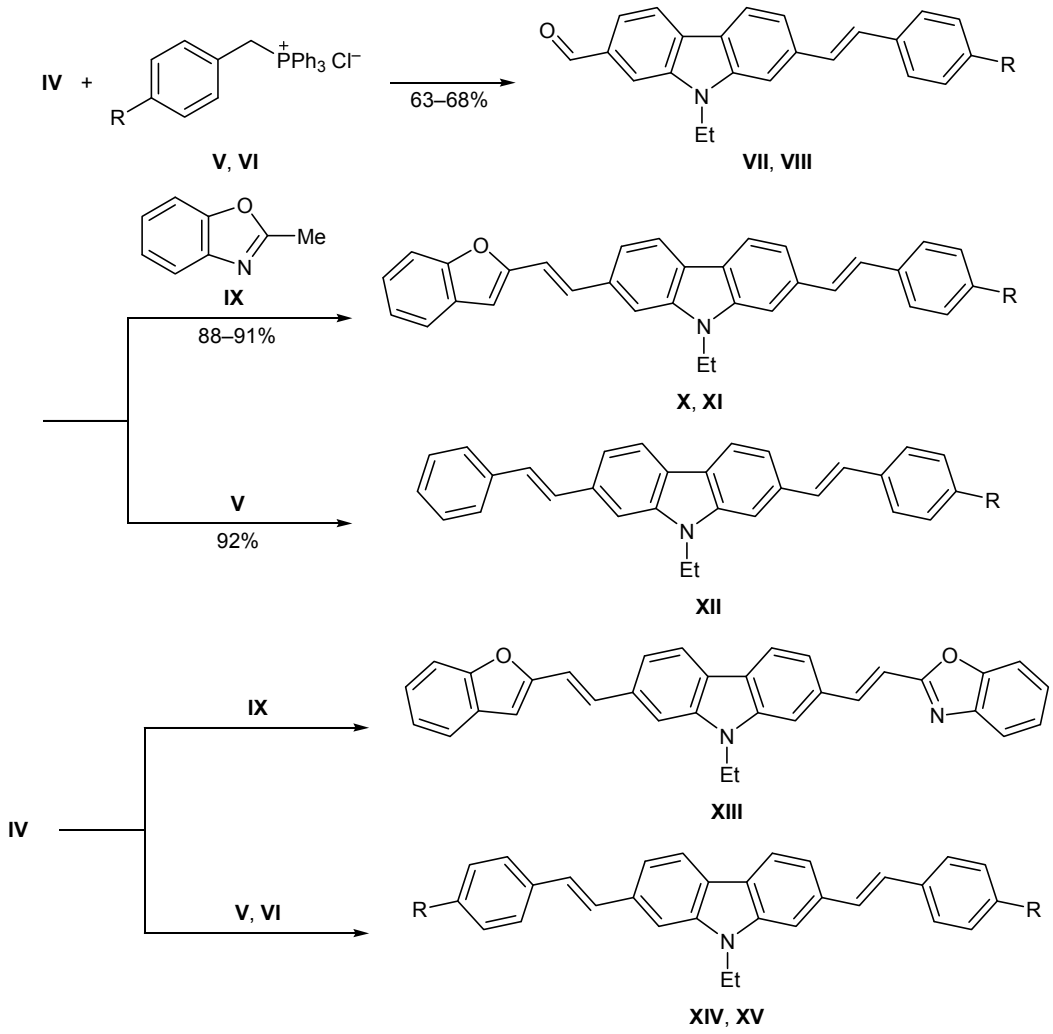
In the present article we report on the synthesis and spectral parameters of new unsymmetrically substituted poly-π-conjugated carbazole derivatives having electron-donating and electron-withdrawing groups in positions *2* and *7*. Such compounds may be regarded as donor–donor–acceptor (D–D–A), donor–donor–donor (D–D–D), or acceptor–donor–acceptor (A–D–A) polyconjugated systems. As electron-acceptor fragment we introduced benzoxazole ring which was conjugated with the carbazole core via ethylene bridge. The other side chain was phenylethenyl or 4-fluorophenylethenyl substituent.

We believed that the most practical synthetic approach to such system should be based on successive Wittig and Knoevenagel olefinations of appropriate dialdehyde. As starting compound we used *N*-ethylcarbazole-2,7-dicarbaldehyde (**IV**) which was synthesized

Scheme 1.



Scheme 2.



V, **VII**, **X**, **XIV**, R = H; **VI**, **VIII**, **XI**, **XV**, R = F.

in three steps from dimethyl 9*H*-carbazole-2,7-dicarboxylic acid (**I**) as shown in Scheme 1. Alkylation of the carbazole nitrogen atom was performed with a view to enhance electron-donor power of the carbazole core and improve the solubility of the resulting polyconjugated systems. Consistent effects of two electron-withdrawing ester groups in positions *2* and *7* of the carbazole ring considerably reduced the basicity of the carbazole nitrogen atom, and *N*-ethyl derivative **II** was obtained in acceptable yields only by prolonged heating of 9*H*-carbazole **I** in xylene in the presence of a large excess of ethyl bromide and potassium carbonate. The alkylation of **I** with the use of strong bases, e.g., potassium *tert*-butoxide, in aprotic polar solvents was accompanied by side transesterification.

Dialdehyde **IV** was synthesized in two steps. The ester groups in **II** were reduced to hydroxymethyl with lithium tetrahydridoaluminate in tetrahydrofuran. The subsequent oxidation of diol **III** to the corresponding dialdehyde **IV** was performed using pyridinium chlorochromate (PCC). This reaction can be carried out in methylene chloride, chloroform, 1,2-dichloroethane, or dioxane with equal success. With a view to obtain unsymmetrically substituted carbazoles **X**–**XII**, phenylethenyl and benzoxazolylethenyl groups were introduced into the carbazole core in two steps with necessary isolation of intermediate monoaldehydes **VII** and **VIII** (Scheme 2). An attempt to synthesize compound **XII** by reaction of dialdehyde **IV** with an equimolar mixture of phosphonium salts **V** and **VI** according to Wittig gave a mixture of symmetrically and unsymmetrically substituted carbazole derivatives **XII**, **XIV**, and **XV**. Monosubstituted carbazoles **VII** and **VIII** were obtained by reaction of dialdehyde **IV**

with the corresponding phosphonium salts. Coupling of **IV** with ylide generated from phosphonium salt **V** or **VI** by the action of potassium *tert*-butoxide in tetrahydrofuran was characterized by high stereoselectivity, and compounds **VII** and **VIII** were formed exclusively as *trans* isomers. Electron-acceptor benzoxazole group was introduced by condensation of monoaldehydes **VII** and **VIII** with 2-methylbenzoxazole (**IX**) in DMSO in the presence of potassium *tert*-butoxide. The yields of unsymmetrically substituted carbazoles **X** and **XI** isolated by column chromatography were 55–62% calculated on the initial dialdehyde **IV**. By two consecutive Wittig reactions we synthesized unsymmetrically substituted 9-ethyl-2-[(*E*)-2-(4-fluorophenyl)-ethenyl]-7-[(*E*)-2-phenylethenyl]-9*H*-carbazole (**XII**) in an overall yield of 63%. The condensation of aldehyde **VIII** with phosphonium salt **V** was also highly stereoselective, and the major product was *trans*,*trans* isomer **XII**.

The structure of compounds **X** and **XI** was determined on the basis of their ^{1}H NMR, IR, and mass spectra. Signals from protons in the two (*E*)-ethenyl groups appear in the ^{1}H NMR spectra as four doublets at δ 7.42, 7.51, 8.02, and 8.18 ppm with coupling constants ^3J of 16.0–16.5 Hz. The chemical shifts of protons in the benzoxazole fragment are as follows, δ, ppm: 7.40 t and 7.42 t (1H each, 5-H or 6-H), 7.74 d and 7.76 d (1H each, 4-H or 7-H). Signals from protons in the benzene ring of compound **X** were observed at δ 7.25, (t or d.d, 2H, *m*-H)), 7.71 (d.d, 2H, *o*-H), and 7.29 ppm (t, 1H, *p*-H). In the ^{1}H NMR spectrum of *para*-fluorophenylethenyl-substituted compound **XI**, additional couplings between the *ortho*- and *meta*-protons, on the one hand, and fluorine nucleus, on the other, were observed with constants J_{HF} of 9.0 and 5.5 Hz, respectively. Analogous couplings were found in the ^{19}F NMR spectrum. The unsymmetrically substituted carbazole fragment gave rise to six proton signals at δ, ppm: 7.43 d (1H, 6-H), 7.51 d and 7.65 d (1H each, 4-H, 5-H), 7.85 s (1H, 8-H), 8.16 d (1H, 3-H), 8.18 s (1H, 1-H). In the IR spectra of **X** and **XI** absorption bands corresponding to stretching vibrations of the exocyclic double C=C bonds were observed at 1640–1647 cm^{-1}.

The ^{1}H NMR spectral pattern of compound **XII** also demonstrated unsymmetrical substitution in the carbazole core (four groups of signals were present). However, taking into account similar electronic effects of (*E*)-2-phenylethenyl and (*E*)-2-(4-fluorophenyl)-ethenyl substituents, different chemical shifts were found only for the 1-H and 8-H protons in the carbazole core. δ, ppm: 7.44 d (2H, 3-H, 6-H), 7.82 s and 7.84 s (1H each, 1-H, 8-H), 8.12 d (2H, 4-H, 5-H). Protons at the exocyclic double bonds gave rise to a multiplet at δ 7.38–7.43 ppm (4H); taking into account the above stated, the most probable configuration of the vinylic fragments in **XII** is *trans* (*E*). The chemical shifts of protons in the unsubstituted phenyl ring are 7.28 (t, 1H, *p*-H), 7.49 (t, 2H, *m*-H), and 7.66 ppm (d, 2H, *o*-H). Protons in the *p*-fluorophenyl ring displayed coupling not only with each other but also with the fluorine nucleus, δ, ppm: 7.25 d.d (2H, *m*-H), 7.70 d.d (2H, *o*-H). In the IR spectrum of **XII**, stretching vibrations of the exocyclic double C=C bonds gave rise to absorption at 1600 cm^{-1}.

In order to estimate the effect of unsymmetrical structure of compounds **X**–**XII** on their spectral properties we also synthesized the corresponding symmetrically substituted derivatives, namely 2,7-bis[(*E*)-2-(benzoxazol-2-yl)ethenyl]-9-ethyl-9*H*-carbazole (**XIII**), 2,7-bis[(*E*)-2-phenylethenyl]-9-ethyl-9*H*-carbazole (**XIV**), and 2,7-bis[(*E*)-2-(4-fluorophenyl)ethenyl]-9-ethyl-9*H*-carbazole (**XV**). Compounds **XIII**–**XV** were synthesized in one step from aldehyde **IV** as shown in Scheme 2 (by Knoevenagel or Wittig reaction). Compounds **XIII** was obtained in 76% yield by condensation of aldehyde **IV** with 2.5 equiv of 2-methylbenzoxazole in the presence of potassium *tert*-butoxide in DMSO. Symmetrically substituted 2,7-bis[(*E*)-2-phenylethenyl]carbazoles **XIV** and **XV** were prepared by reaction of dialdehyde **IV** with 2.5 equiv of the corresponding phosphonium ylide in THF; the yields were 64–68%.

The results showed insignificant effect of electronegative fluorine atom on the spectral parameters of unsymmetrically substituted carbazole derivatives. Compounds like D–D–A (**X**, **XI**) displayed photoluminescence in the blue region with its maximum at λ 471–472 nm. Likewise, the emission maximum of compound **XII** weakly depended on the substituent in the benzene ring of the phenylethenyl fragment (λ_{max} 434 nm). No appreciable differences in the position of absorption and emission maxima were also observed between compound **XII** and symmetrically substituted derivatives **XIV** and **XV**. The blue shift (Δλ = 35–38 nm) in the luminescence spectra of D–D–D (**XII**, **XIV**, **XV**) and D–D–A type compounds (**X**, **XI**) is likely to result from replacement of the electron-deficient benzoxazole fragment by phenyl group, while the size of the π-conjugation chain in these compounds remained almost unchanged.

Compounds **X** and **XI** having one electron-withdrawing side-chain group absorb at longer wavelengths as compared to symmetrically substituted 2,7-bis[(*E*)-2-(benzoxazol-2-yl)ethenyl]-9-ethyl-9*H*-carbazole (**XIII**, A–D–A), and the red shift reached 20.5 nm. However, the difference in the photoluminescence maxima of benzoxazole-containing compounds **X**, **XI** and **XIII** was not large, $\Delta\lambda$ = 4–6 nm. Presumably, the reason is that the effect of the donor–acceptor fragment, i.e., (*E*)-2-(benzoxazol-2-yl)ethenylcarbazole chromophore, in compounds **X** and **XI** on the position of the emission maximum is much stronger than the effect of the (*E*)-2-phenylethenyl group.

EXPERIMENTAL

The melting points were measured on a Kofler hot stage equipped with a Hanna HI 93530 electronic thermometer. The ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker Biospin Avance 500 spectrometer at 500, 125, and 470 MHz, respectively, using DMSO-d_6 as solvent. The IR spectra (400–4000 cm^{-1}) were obtained in KBr on a Specord M-80 instrument. The UV and fluorescence spectra were measured from solutions in DMF or microcrystalline samples using a Solar CM2203 spectrofluorimeter (excitation at λ 365.0 nm). The mass spectra (atmospheric pressure chemical ionization) were recorded on an Accela-LCQ Fleet instrument. The solvents and reagents were purified (pure or analytical grade) and dehydrated according to standard procedures. The progress of reactions was monitored by TLC on silica gel 60 F_{254} (Merck) applied to aluminum plates.

Dimethyl 9*H*-carbazole-2,7-dicarboxylate (**I**) was synthesized as described in [8].

Dimethyl 9-ethyl-9*H*-carbazole-2,7-dicarboxylate (II). Powdered potassium carbonate, 1382 mg (10.0 mmol), and ethyl bromide, 0.3 ml (~4.0 mmol), were added to a solution of 285 mg (1.0 mmol) of dimethyl 9*H*-carbazole-2,7-dicarboxylate (**I**) in *o*-xylene, and the mixture was heated for 50 h under reflux, 0.7 ml (~10.0 mmol) of ethyl bromide being added in small portions. When the reaction was complete, the solvent was removed on a rotary evaporator, and the residue was recrystallized from benzene and dried under reduced pressure. Yield 240 mg (0.8 mmol, 77%), mp 145.0–145.5°C. UV spectrum, λ_{max}, nm: 256.0, 278.5, 307.5, 320.5. IR spectrum, ν, cm^{-1}: 3107, 3093, 3043, 3027, 2997, 2977, 2910, 2897, 2867, 1723, 1707, 1637, 1610, 1577, 1503, 1487, 1477, 1457, 1443, 1433, 1383, 1373, 1347, 1333, 1290, 1250, 1237, 1220, 1210, 1150, 1143, 1103, 1067, 1000, 957, 943, 880, 837, 830, 793, 767. ^{1}H NMR spectrum, δ, ppm: 1.44 t (3H, $CH_2C\mathbf{H}_3$, J = 7.0 Hz), 3.94 s (6H, CH_3), 4.55 q (2H, NCH_2, J = 7.2 Hz), 7.84 d (2H, 3-H, 6-H, J = 8.0 Hz), 8.14 s (2H, 1-H, 8-H), 8.22 d (2H, 4-H, 5-H, J = 8.0 Hz).

(9-Ethyl-9*H*-carbazole-2,7-diyl)dimethanol (III). Dimethyl 9-ethyl-9*H*-carbazole-2,7-dicarboxylate (**II**), 311 mg (1.0 mmol), was dissolved in anhydrous THF, 350 mg (~9.0 mmol) of lithium tetrahydridoaluminate was added, and the mixture was stirred for 1 h at room temperature and then heated for 2 h under reflux, the progress of the reaction being monitored by TLC. When the reaction was complete, ethyl acetate and 50% aqueous potassium hydroxide were added until aluminum hydroxide separated. The precipitate was filtered off and washed with several portions of hot THF. The solvent was removed on a rotary evaporator, and the residue was recrystallized from aqueous ethanol and dried in air. Yield 217 mg (0.9 mmol, 89%), white powder, mp 133.5–134.0°C. IR spectrum, ν, cm^{-1}: 3650–3100 sh, 3083, 3067, 3030, 2983, 2953, 2940, 2910, 2873, 2863, 1630, 1610, 1570, 1503, 1480, 1463, 1460, 1447, 1437, 1377, 1353, 1323, 1267, 1240, 1173, 1140, 1133, 1120, 1090, 1060, 1047, 1027, 1003, 997, 970, 943, 937, 860, 847, 813, 790, 763, 747, 733. ^{1}H NMR spectrum, δ, ppm: 1.41 t (3H, CH_3, J = 7.3 Hz), 4.42 q (2H, NCH_2, J = 7.2 Hz), 4.67 d (4H, $C\mathbf{H}_2OH$, J = 5.5 Hz), 5.05 t (2H, OH, J = 5.8 Hz), 7.09 d.d (2H, 3-H, 6-H, J = 7.8, 1.3 Hz), 7.45 s (2H, 1-H, 8-H), 7.95 d (2H, 4-H, 5-H, J = 8.0 Hz).

9-Ethyl-9*H*-carbazole-2,7-dicarbaldehyde (IV). A solution of 500 mg (2.3 mmol) of pyridinium chlorochromate in a minimal amount of 1,4-dioxane was added dropwise under vigorous stirring to a suspension of 200 mg (0.8 mmol) of diol **III** in anhydrous methylene chloride, and the mixture was stirred for 8 h at room temperature. When the initial compound disappeared (TLC), excess isopropyl alcohol was added, and the mixture was filtered through a layer of silica gel. The solvent was removed on a rotary evaporator, and the residue was subjected to column chromatography on silica gel using chloroform as eluent. The eluate was evaporated, and the product was dried under reduced pressure. Yield 148 mg (0.6 mmol, 74%). Yellow–green crystals, mp 201.0–201.5°C. IR spectrum, ν, cm^{-1}: 2993, 2944, 2925, 2885, 2869, 2833, 2787, 2734, 1700, 1636, 1603, 1570, 1505, 1489, 1459, 1403, 1387, 1367, 1338, 1302, 1292, 1250, 1203, 1193, 1154, 1138, 1100, 1085, 1069, 1016, 984, 967, 882, 869, 830, 790, 764, 757. ^{1}H NMR spectrum, δ,

ppm: 1.47 t (3H, CH_3, J = 6.5 Hz), 4.65 q (2H, NCH_2, J = 6.5 Hz), 7.77 d (2H, 3-H, 6-H, J = 8.0 Hz), 8.21 s (2H, 1-H, 8-H), 8.37 d (2H, 4-H, 5-H, J = 8.0 Hz), 10.16 s (2H, CHO).

9-Ethyl-7-[(*E*)-2-phenylethenyl]-9*H*-carbazole-2-carbaldehydes VII and VIII (*general procedure*). Potassium *tert*-butoxide, 244 mg (2.0 mmol), was added under vigorous stirring at room temperature to a suspension of 466–488 mg (1.2 mmol) of benzyl(triphenyl)phosphonium chloride **V** or **VI** in anhydrous tetrahydrofuran. The mixture was stirred for 15–20 min, and the resulting solution was added dropwise to a solution of 251 mg (1.0 mmol) of dialdehyde **IV** in THF. The mixture was stirred for 1 h at room temperature, the progress of the reaction being monitored by TLC. When the initial compound disappeared, the solvent was removed on a rotary evaporator, and the residue was purified by column chromatography on silica gel using CH_2Cl_2 as eluent. The products were isolated as yellow crystalline substances.

9-Ethyl-7-[(*E*)-2-phenylethenyl]-9*H*-carbazole-2-carbaldehyde (VII). Yield 205 mg (0.6 mmol, 63%), mp 185.0–186.0°C. IR spectrum, ν, cm^{-1}: 3067, 3037, 2990, 2943, 2890, 2870, 2840, 2783, 2740, 1700, 1637, 1623, 1607, 1570, 1517, 1500, 1483, 1460, 1450, 1363, 1350, 1343, 1303, 1293, 1250, 1190, 1177, 1110, 1100, 1077, 1023, 1013, 980, 950, 917, 907, 880, 857, 830, 803, 787, 773, 737, 723. ^{1}H NMR spectrum, δ, ppm: 1.39 t (3H, CH_3, J = 7.0 Hz), 4.58 q (2H, NCH_2, J = 7.0 Hz), 7.26 t (2H, *m*-H, J = 8.8 Hz), 7.30 t (1H, *p*-H, J = 8.3 Hz), 7.43 d (1H, =CH, J = 14.5 Hz), 7.49 d (1H, =CH, J = 16.5 Hz), 7.56 d.d (1H, 6-H, J = 8.5, 0.5 Hz), 7.72 d.d (2H, *o*-H, J = 8.8, 3.0 Hz), 7.75 d (1H, 3-H, J = 8.0 Hz), 7.92 s (1H, 8-H), 8.21 s (1H, 1-H), 8.26 d (1H, 5-H, J = 8.0 Hz), 8.34 d (1H, 4-H, J = 8.0 Hz), 10.14 s (1H, CHO).

9-Ethyl-7-[(*E*)-2-(4-fluorophenyl)ethenyl]-9*H*-carbazole-2-carbaldehyde (VIII). Yield 234 mg (0.7 mmol, 68%), mp 175.0–175.5°C. IR spectrum, ν, cm^{-1}: 3077, 3037, 2993, 2947, 2890, 2863, 2840, 2790, 2747, 1700, 1640, 1630, 1607, 1570, 1517, 1500, 1483, 1460, 1447, 1367, 1350, 1343, 1307, 1293, 1250, 1193, 1177, 1110, 1100, 1070, 1027, 1013, 980, 950, 920, 880, 857, 830, 817, 807, 787, 777, 740, 727. ^{1}H NMR spectrum, δ, ppm: 1.39 t (3H, CH_3, J = 7.0 Hz), 4.58 q (2H, NCH_2, J = 7.0 Hz), 7.25 d.d (2H, *m*-H, J_{HH} = J_{HF} = 8.8 Hz), 7.42 d (1H, =CH, J = 16.5 Hz), 7.49 d (1H, =CH, J = 16.5 Hz), 7.56 d.d (1H, 6-H, J = 8.0, 0.5 Hz), 7.71 d.d (2H, *o*-H, J_{HH} = 8.5, J_{HF} = 5.5 Hz), 7.75 d.d (1H, 3-H, J = 8.0, 0.5 Hz), 7.91 s (1H, 8-H), 8.20 s (1H, 1-H), 8.25 d (1H, 5-H, J = 8.0 Hz), 8.33 d (1H, 4-H, J = 8.0 Hz), 10.14 s (1H, CHO).

2-[(*E*)-2-(Benzoxazol-2-yl)ethenyl]-9-ethyl-7-[(*E*)-2-phenylethenyl]-9*H*-carbazoles X and XI (*general procedure*). Aldehyde **VII** or **VIII**, 325–343 mg (1.0 mmol), was dissolved in DMSO, 200 mg (1.5 mmol) of 2-methylbenzoxazole (**IX**) and 224 mg (2.0 mmol) of potassium *tert*-butoxide were added, and the mixture was stirred for 8 h at 40°C. When the initial compound disappeared (TLC), the mixture was poured into water and extracted with methylene chloride, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using chloroform as eluent. The product was additionally purified by recrystallization from hexane and dried. Compounds **X** and **XI** were isolated as bright yellow crystalline substances.

2-[(*E*)-2-(Benzoxazol-2-yl)ethenyl]-9-ethyl-7-[(*E*)-2-phenylethenyl]-9*H*-carbazole (X). Yield 388 mg (0.9 mmol, 88%), sublimes at ~225°C. UV spectrum, λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 410.0 (68000), 429.0 (59700). Fluorescence spectrum, λ_{max}, nm: in solution: 472.0; in the solid state: 496.0, 544.5, 606.5. IR spectrum, ν, cm^{-1}: 3073, 3043, 2973, 2940, 2887, 2870, 1643, 1623, 1603, 1570, 1540, 1517, 1500, 1473, 1457, 1447, 1353, 1343, 1243, 1193, 1173, 1013, 977, 940, 853, 827, 810, 790, 773, 750, 736. ^{1}H NMR spectrum, δ, ppm: 1.40 t (3H, CH_3, J = 7.0 Hz), 4.55 q (2H, NCH_2, J = 6.8 Hz), 7.25 t (2H, *m*-H, J = 8.8 Hz), 7.29 t (1H, *p*-H, J = 7.8 Hz), 7.40 t (1H, 5′-H or 6′-H, J = 7.3, 1.5 Hz), 7.42 d (1H, =CH, J = 17.0 Hz), 7.42 t (1H, 6′-H or 5′-H, J = 7.5, 2.0 Hz), 7.43 d (1H, 6-H, J = 5.0 Hz), 7.51 d (1H, =CH, J = 16.5 Hz), 7.51 d (1H, 4-H or 5-H, J = 9.0 Hz), 7.65 d (1H, 5-H or 4-H, J = 8.0 Hz), 7.71 d.d (2H, *o*-H, J = 8.8, 3.0 Hz), 7.74 d (1H, 4′-H or 7′-H, J = 9.0 Hz), 7.76 d (1H, 7′-H or 4′-H, J = 8.5 Hz), 7.85 s (1H, 8-H), 8.02 d (1H, =CH, J = 16.5 Hz), 8.16 d (1H, 3-H, J = 5.5 Hz), 8.18 d (1H, =CH, J = 16.0 Hz), 8.18 s (1H, 1-H). Mass spectrum: m/z 441 $[M + 1]^+$.

2-[(*E*)-2-(Benzoxazol-2-yl)ethenyl]-9-ethyl-7-[(*E*)-2-(4-fluorophenyl)ethenyl]-9*H*-carbazole (XI). Yield 417 mg (0.9 mmol, 91%), sublimes at ~230°C. UV spectrum, λ_{max}, nm (ε, lmol^{-1} cm^{-1}): 410.0 (62700), 429.0 (55400). Fluorescence spectrum, λ_{max}, nm: in solution: 471.0; in the solid state: 510.0, 547.0, 607.5. IR spectrum, ν, cm^{-1}: 3080, 3047, 2990, 2947, 2870, 1647, 1640, 1627, 1607, 1570, 1550, 1543, 1517, 1500, 1477, 1457, 1447, 1357, 1343, 1243,

1193, 1173, 1110, 1100, 1070, 1017, 980, 947, 857, 827, 810, 803, 787, 773, 757. ^{1}H NMR spectrum, δ, ppm: 1.40 t (3H, CH_3, J = 7.0 Hz), 4.55 q (2H, NCH_2, J = 7.0 Hz), 7.25 d.d (2H, *m*-H, $J_{HH} = J_{HF}$ = 9.0 Hz), 7.40 t (1H, 5′-H or 6′-H, J = 7.5, 1.5 Hz), 7.42 d (1H, =CH, J = 17.0 Hz), 7.42 t (1H, 6′-H or 5′-H, J = 7.5, 1.8 Hz), 7.43 d (1H, 6-H, J = 5.0 Hz), 7.51 d (1H, =CH, J = 16.5 Hz), 7.51 d (1H, 4-H or 5-H, J = 8.5 Hz), 7.65 d (1H, 5-H or 4-H, J = 8.0 Hz), 7.71 d.d (2H, *o*-H, J_{HH} = 8.5, J_{HF} = 5.5 Hz), 7.74 d (1H, 4′-H or 7′-H, J = 9.0 Hz), 7.76 d (1H, 7′-H or 4′-H, J = 8.5 Hz), 7.85 s (1H, 8-H), 8.02 d (1H, =CH, J = 16.0 Hz), 8.16 d (1H, 3-H, J = 5.0 Hz), 8.18 d (1H, =CH, J = 16.5 Hz), 8.18 s (1H, 1-H). ^{19}F NMR spectrum: δ_F –114.65 ppm, d.t (J = 9.4, 4.9 Hz). Mass spectrum: m/z 459 $[M + 1]^+$.

9-Ethyl-2-[(*E*)-2-(*p*-fluorophenyl)ethenyl]-7-[(*E*)-2-phenylethenyl]-9*H*-carbazole (XII). Benzyl(triphenyl)phosphonium chloride (**V**), 466 mg (1.2 mmol), was dispersed in anhydrous tetrahydrofuran, 244 mg (2.0 mmol) of potassium *tert*-butoxide was added under vigorous stirring at room temperature, and the mixture was stirred for 15–20 min. The resulting ylide solution was added dropwise to a solution of 325 mg (1.0 mmol) of carbazole-2-carbaldehyde **VIII** in THF, and the mixture was stirred for 1 h at room temperature, the progress of the reaction being monitored by TLC. When the initial compound disappeared, the mixture was filtered through a layer of silica gel, and the product was purified by column chromatography on silica gel using toluene as eluent, followed by recrystallization from toluene. Yield 384 mg (0.9 mmol, 92%), light yellow crystals, mp 256.0–257.5°C. UV spectrum, λ_{max}, nm (ε, l× mol^{-1} cm^{-1}): 384.0 (23500), 401.5 (20700). Fluorescence spectrum, λ_{max}, nm: in solution: 434.0; in the solid state: 456.0, 489.5. IR spectrum, ν, cm^{-1}: 3067, 3037, 2987, 2977, 2937, 1630, 1600, 1567, 1560, 1507, 1493, 1470, 1450, 1440, 1350, 1333, 1323, 1237, 1190, 1170, 1133, 1107, 1093, 1063, 1040, 1010, 973, 880, 853, 830, 823, 810, 800, 777, 770, 757, 737, 730, 700. ^{1}H NMR spectrum, δ, ppm: 1.39 t (3H, CH_3, J = 7.3 Hz), 4.55 q (2H, NCH_2, J = 6.8 Hz), 7.25 d.d (2H, *m*-H, $J_{HH} = J_{HF}$ = 9.0 Hz), 7.28 t (1H, *p*′-H, J = 8.0 Hz), 7.38–7.43 m (4H, =CH), 7.44 d (2H, 3-H, 6-H, J = 6.5 Hz), 7.49 t (2H, *m*′-H, J = 8.0 Hz), 7.66 d (2H, *o*′-H, J = 7.5 Hz), 7.70 d.d (2H, *o*-H, J_{HH} = 8.3, J_{HF} = 5.8 Hz), 7.82 s (1H, 1-H or 8-H), 7.84 s (1H, 9-H or 1-H), 8.12 d (2H, 4-H, 5-H, J = 8.0 Hz). ^{19}F NMR spectrum: δ_F –114.80 ppm, d.t (J = 9.3, 5.2 Hz). Mass spectrum: m/z 418 $[M + 1]^+$.

2,7-Bis[(*E*)-2-(benzoxazol-2-yl)ethenyl]-9-ethyl-9*H*-carbazole (XIII). Potassium *tert*-butoxide, 338 mg (3.0 mmol), was added under stirring to a solution of 251 mg (1.0 mmol) of dialdehyde **IV** and 320 mg (2.5 mmol) of 2-methylbenzoxazole (**IX**) in DMSO, and the mixture was stirred for 16 h on heating at 40–50°C. When the initial compound disappeared (TLC), the mixture was poured into water and extracted with chloroform. The solvent was removed from the extract under reduced pressure, and the product was purified by column chromatography on silica gel using chloroform as eluent, followed by recrystallization from toluene. Yield 144 mg (0.3 mmol, 76%), bright yellow crystals, mp 309.5–312.0°C. UV spectrum, λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 389.5 (129200), 414.0 (108800). Fluorescence spectrum, λ_{max}, nm: in solution: 466.5; in the solid state: 515.5, 548.0, 612.5. IR spectrum, ν, cm^{-1}: 3070, 3063, 3030, 2963, 1640, 1567, 1560, 1533, 1493, 1467, 1450, 1440, 1367, 1347, 1333, 1300, 1283, 1240, 1230, 1190, 1180, 1160, 1147, 1107, 1087, 1060, 1003, 970, 930, 883, 853, 833, 823, 817, 797, 783, 757, 737, 723, 703. ^{1}H NMR spectrum, δ, ppm: 1.41 t (3H, CH_3, J = 7.0 Hz), 4.60 t (2H, NCH_2, J = 7.5 Hz), 7.40 d.t (2H, 5′-H or 6′-H, J = 7.3, 1.3 Hz), 7.43 d.t (2H, 6′-H or 5′-H, J = 7.5, 1.5 Hz), 7.54 d (2H, =CH, J = 16.5 Hz), 7.67 d.d (2H, 3-H, 6-H, J = 8.5, 1.0 Hz), 7.75 d.d (2H, 4′-H or 7′-H, J = 8.5, 0.5 Hz), 7.76 d.d (2H, 7′-H or 4′-H, J = 8.5, 0.5 Hz), 8.03 d (2H, =CH, J = 16.0 Hz), 8.19 s (2H, 1-H, 8-H), 8.25 d (2H, 4-H, 5-H, J = 8.0 Hz). Mass spectrum: m/z 482 $[M + 1]^+$.

2,7-Bis[(*E*)-2-phenylethenyl]-9-ethyl-9*H*-carbazoles XIV and XV (*general procedure*). Potassium *tert*-butoxide, 366 mg (3.0 mmol), was added to a suspension of 972–1017 mg (2.5 mmol) of benzyl(triphenyl)phosphonium chloride **V** or **VI** in anhydrous tetrahydrofuran under vigorous stirring at room temperature. The mixture was stirred for 15–20 min, a solution of 251 mg (1.0 mmol) of 9-ethyl-9*H*-carbazole-2,7-dicarbaldehyde (**IV**) in THF was added dropwise at room temperature to the resulting phosphonium ylide solution, and the mixture was stirred for 1 h at room temperature, the progress of the reaction being monitored by TLC. When the initial compound disappeared, the mixture was filtered through a layer of silica gel, and the product was purified by column chromatography on silica gel using toluene as eluent, followed by recrystallization from toluene. Compounds **XIV** and **XV** were isolated as light yellow crystalline substances.

9-Ethyl-2,7-bis[(*E*)-2-phenylethenyl]-9*H*-carbazole (XIV). Yield 272 mg (0.7 mmol, 68%), mp 241.0–242.5°C. UV spectrum, λ_{max}, nm (ε, l× mol^{-1} cm^{-1}): 369.0 (59500), 387.0 (54500). Fluorescence spectrum, (in solution): λ_{max} 435.5 nm. IR spectrum, ν, cm^{-1}: 3090, 3067, 3043, 2977, 2943, 2870, 1607, 1516, 1463, 1423, 1307, 1267, 1240, 1210, 1170, 1140, 1110, 1090, 1027, 980, 970, 950, 856, 773. ^{1}H NMR spectrum, δ, ppm: 1.39 t (3H, CH_3, J = 7.5 Hz), 4.55 q (2H, NCH_2, J = 7.0 Hz), 7.26 t (2H, *p*-H, J = 8.5 Hz), 7.34 d (2H, =CH–, J = 16.5 Hz), 7.37 t (4H, *m*-H, J = 7.5 Hz), 7.42 d (2H, 3-H, 6-H, J = 8.0 Hz), 7.45 d (2H, =CH, J = 16.5 Hz), 7.65 d.d (2H, *o*-H, J = 8.3, 2.0 Hz), 7.84 s (2H, 1-H, 8-H), 8.10 d (2H, 4-H, 5-H, J = 8.0 Hz). Mass spectrum: *m*/*z* 400 $[M + 1]^+$.

9-Ethyl-2,7-bis[(*E*)-2-(4-fluorophenyl)ethenyl]-9*H*-carbazole (XV). Yield 276 mg (0.6 mmol, 64%), mp 235.5–236.0°C. UV spectrum, λ_{max}, nm (ε, l× mol^{-1} cm^{-1}): 365.0 (44200), 382.0 (39800). Fluorescence spectrum, λ_{max}, nm: in solution: 424.5; in the solid state: 437.0, 449.0. IR spectrum, ν, cm^{-1}: 3073, 3040, 2943, 2873, 1600, 1573, 1510, 1470, 1453, 1433, 1377, 1360, 1340, 1323, 1307, 1237, 1207, 1170, 1160, 1120, 1087, 1040, 997, 977, 923, 893, 883, 853, 820, 763, 737, 703. ^{1}H NMR spectrum, δ, ppm: 1.39 t (3H, CH_3, J = 7.5 Hz), 4.55 q (2H, NCH_2, J = 7.0 Hz), 7.25 d.d (4H, *m*-H, $J_{HH} = J_{HF}$ = 8.8 Hz), 7.33 d (2H, =CH–, J = 16.5 Hz), 7.43 d (2H, 3-H, 6-H, J = 8.0 Hz), 7.45 d (2H, =CH–, J = 16.5 Hz), 7.70 d.d (2H, *o*-H, J_{HH} = 8.5, J_{HF} = 5.5 Hz), 7.82 s (2H, 1-H, 8-H), 8.11 d (2H, 4-H, 5-H, J = 8.0 Hz). Mass spectrum: *m*/*z* 436 $[M + 1]^+$.

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