ChemPubSoc Europe

DOI: 10.1002/ejoc.201600674

EurJOC European Journal of Organic Chemistry

Full Paper

Pyrrolocarbazoles

Synthetic Approach to Dictyodendrins: A Facile Synthesis of Pyrrolo[2,3-*c*]carbazole, Pyrrolodibenzothiophene, and Benzo[*e*]indole

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Abstract: The $FeCl_3$/DDQ-PTSA/NBS-mediated cyclization (DDQ = 2,3-dichoro-5,6-dicyano-1,4-benzoquinone, PTSA = *p*-toluenesulfonic acid, NBS = *N*-bromosuccinimide) of 2-arylvinyl-3-indolylpyrrole led to the formation of the pyrrolo[2,3-*c*]carbazole core unit of dictyodendrins in yields of 75–90 %. The cyclization method was also successfully applied to the syntheses of pyrrolodibenzothiophene and benzo[*e*]indole derivatives.

Introduction

The telomerase inhibitory dictyodendrins A–E (Figure 1) were isolated by Fusetani and co-workers[1] from the South Japanese marine sponge *Dictyodendrilla verongiformis*. The structural novelty and biological importance of these marine natural products have attracted the interests of synthetic chemists.

The total syntheses of dictyodendrins B, C, and E were first reported by Fürstner and co-workers[2] who achieved their preparation by exploiting the photochemical cyclization of a suitably substituted 2-vinyl-3-(pyrrol-3-yl)indole as a key step in the assembly of the tetracyclic pyrrolo[2,3-*c*]carbazole core unit. Tokuyama and co-workers reported[3] the next total synthesis of dictyodendrins A and B, in which the tetracyclic framework was realized through an intramolecular nitrene insertion of 2-azidoarylindole. Subsequently, the total synthesis of dictyodendrins B and E was achieved by Jia and co-workers[4] who employed a Pd-catalyzed one-pot Buchwald–Hartwig amination/C–H activation reaction sequence. Very recently, Gaunt and co-workers[5] also reported the total synthesis of dictyodendrin B by involving an intramolecular nitrene insertion reaction to build the pyrrolo[2,3-*c*]carbazole core unit.

Apart from these total syntheses, several reports of the construction of the pyrrolo[2,3-*c*]carbazole framework of dictyodendrin have also appeared. Fürstner and co-workers reported the synthesis of dictyodendrin-inspired natural product-like targets.[6] Some of these synthetic dictyodendrin analogues[6] cleave double-stranded DNA under oxidative conditions. Ishibashi and co-workers[7] achieved the synthesis of the pyrrolo[2,3-*c*]carbazole core by an intramolecular condensation of a suitably substituted 3-(2-anisoylpyrrol-3-yl)-2-cyanomethylindole. The same group also reported[8] a formal total synthesis of dictyodendrin B by using a SmI_2-mediated intramolecular cyclization of 3-(2-anisoylpyrrol-3-yl)indole-2-carbaldehyde followed by subsequent dehydration using acetic anhydride. Ayats et al. outlined[9] the synthesis of the pyrrolo[2,3-*c*]carbazole core of dictyodendrin by utilizing a photochemical cyclization. The tetracyclic framework of dictyodendrin was also achieved by Viji and Nagarajan[10] by employing a $Zn(OTf)_2$-catalyzed (OTf = trifluoromethanesulfonate) annulation of 3-aminocarbazole with propargyl alcohols. Recently, Copon and co-workers

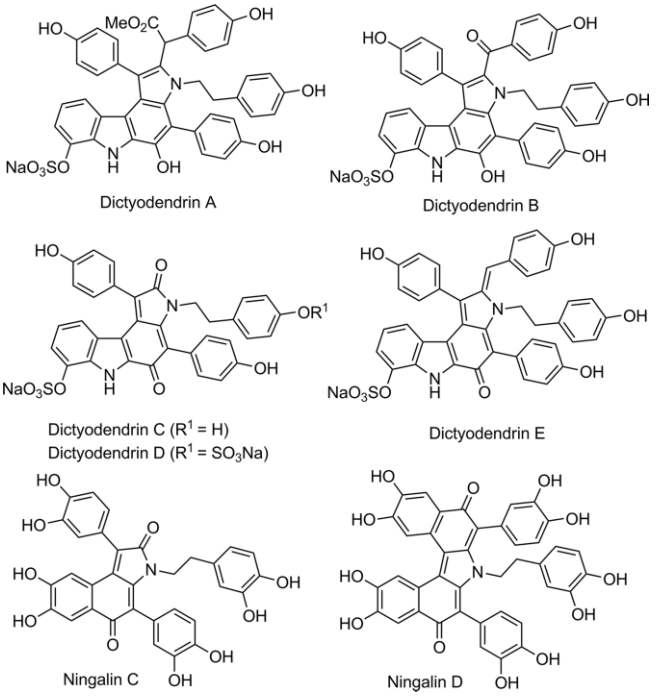

Figure 1. Examples of pyrrolo[2,3-*c*]carbazole and benzo[*e*]indole natural products.

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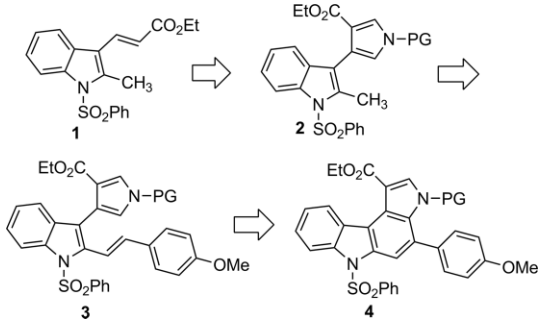
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201600674.

reported the isolation and characterization of additional natural products of the dictyodendrin family, dictyodendrins F–J, from an Australian marine sponge.[11]

Despite the above-mentioned multistep protocols, there remains a need for an efficient route to more readily access either the dictyodendrins or their core units. Very recent reports of the synthesis of benz[*e*]indoles through an iodocyclization approach by Zhang et al.[12] as well as Silveria and co-workers[13] prompted us to disclose our strategy for the construction of the core skeleton of dictyodendrin and other related compounds.

Results and Discussion

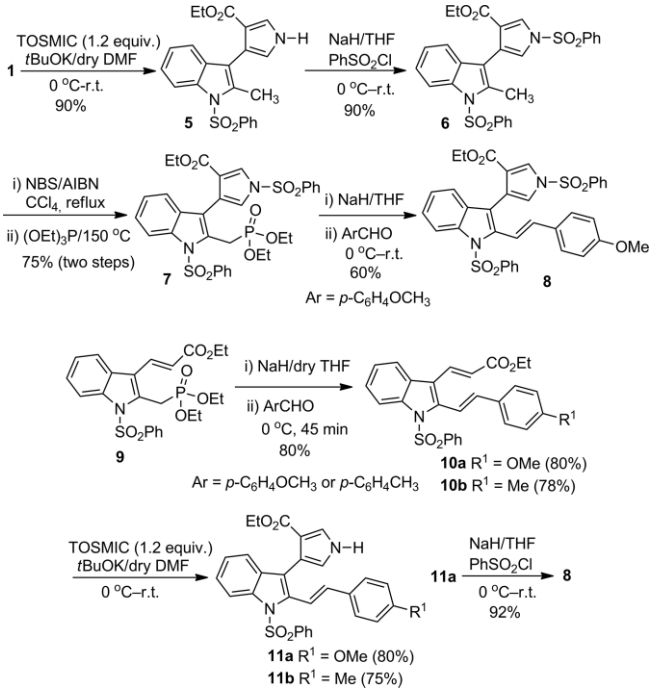
The synthesis of the tetracyclic core unit **4** of dictyodendrin started from ethyl 2-methyl-1-phenylsulfonylindol-3-ylacrylate (**1**).[14] The 1,3-dipolar cycloaddition of 3-vinylindole **1** under van Leusen reaction conditions[15] followed by protection of the pyrrole nitrogen atom leads to indolylpyrrole **2**. The allylic bromination of **2** followed by an Arbuzov and Wittig–Horner reaction with *p*-anisaldehyde affords 2-anisylvinyl-3-pyrrol-3-ylindole **3**. The subsequent oxidative cyclization of the triene system of **3** then leads to target compound **4** (Scheme 1).



Scheme 1. Schematic pathway for pyrrolo[2,3-*c*]carbazole (PG = protecting group).

We initiated our synthetic route by carrying out the cycloaddition of indole-3-vinyl ester **1** with tosylmethyl isocyanide (TOSMIC) and *t*BuOK as the base in dry *N*,*N*-dimethylformamide (DMF) to afford 3-indolylpyrrole **5** in 90 % yield.[16] The phenylsulfonylation of 3-indolylpyrrole **5** by using NaH in dry tetrahydrofuran (THF) gave *N*,*N*′-bis(phenylsulfonyl)-3-indolylpyrrole **6** (Scheme 2).

The benzylic bromination of **6** by using 1.1 equiv. of *N*-bromosuccinimide (NBS) in the presence of a catalytic amount of azobis(isobutyronitrile) (AIBN) in CCl_4 at reflux led to the isolation of a bromo compound as a thick liquid. The Michaelis–Arbuzov reaction of the crude product was carried out by treatment with triethyl phosphite at an elevated temperature to afford phosphonate ester **7** as a brown liquid in 75 % yield. Next, the Wittig–Horner reaction of **7** with *p*-anisaldehyde and NaH as the base in dry THF at 0 °C furnished 3-indolylpyrrole **8** as a yellow solid in 60 % yield. Alternatively, known phosphonate ester **9**[14] can undergo a Wittig–Horner reaction with an aryl aldehyde to lead to 2,3-divinylindole **10a** or **10b**, whereupon the aryl vinyl moiety at the 2-position can undergo a base-

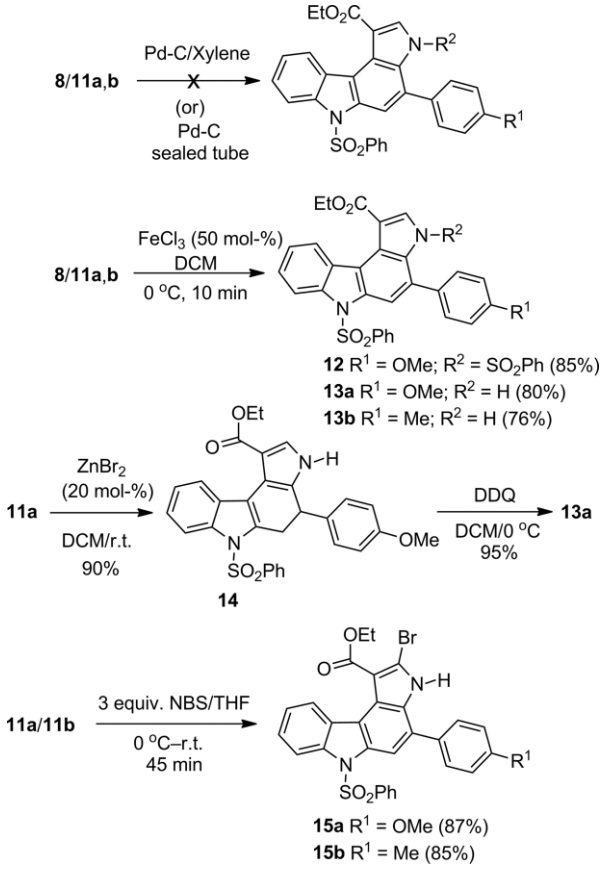


Scheme 2. Synthesis of 3-indolylpyrroles **8**, **11a**, and **11b**.

mediated cycloaddition reaction with TOSMIC to furnish 3-indolylpyrroles **11a** and **11b**, respectively, in good yields. As a representative case, the phenylsulfonylation of pyrrole **11a** led to compound **8** (Scheme 2).

Having the required 3-indolylpyrroles **8**, **11a**, and **11b** in hand, we proceeded with their intramolecular cyclization reactions to achieve the synthesis of the core unit of the dictyodendrins. Our experience with thermal electrocyclizations of *N*-protected 2,3-divinylindoles,[14,17] encouraged us to explore the same strategy with these 3-indolylpyrroles. However, the thermolysis of 3-indolylpyrroles **8**, **11a**, and **11b** in the presence of 10 % Pd-C in either xylene at reflux or in a sealed tube failed to produce the expected pyrrolocarbazoles (Scheme 3). The failure of the electrocyclization reaction prompted us to explore a Lewis acid mediated cyclization approach[18] to transform 3-indolylpyrroles **8**, **11a**, and **11b** into the respective pyrrolocarbazoles. After considerable experimentation, the reaction of 3-indolylpyrroles **8**, **11a**, and **11b** with 0.5 equiv. of $FeCl_3$ in dichloromethane (DCM) at 0 °C for 10 min led to the formation of the respective pyrrolo[2,3-*c*]carbazoles **12**, **13a**, and **13b** in excellent yields (Scheme 3). 3-Indolylpyrrole **11a** was treated with 20 mol-% $ZnBr_2$ in DCM at room temperature to furnish dihydropyrrolo[2,3-*c*]carbazole **14**, which then underwent a DDQ-mediated (DDQ = 2,3-dichoro-5,6-dicyano-1,4-benzoquinone) dehydrogenation to produce the aromatized carbazole **13a** in 95 % yield. Next, the reaction of the mono-*N*-protected 3-indolylpyrroles **11a** and **11b** with 3 equiv. of NBS in THF at room temperature led to the formation of 2-bromopyrrolo-[2,3-*c*]carbazoles **15a** and **15b** in 87 and 85 % yield, respectively.

To understand the mechanism of the pyrrolo[2,3-*c*]carbazole formation, the cyclization reactions of 3-indolylpyrroles **8**, **11a**,



Scheme 3. Synthesis of pyrrolo[2,3-*c*]carbazoles.

and **11b** were performed in the presence of different catalysts, and the results are presented in Table 1. The reaction of the 3-indolylpyrrole **11a** with 1 equiv. of DDQ/*p*-toluenesulfonic acid (PTSA) in dry benzene at room temperature gave pyrrolocarbazole **13a** in 89 % yield (Table 1, Entry 1). The transformation of **11a** into **13a** was unsuccessful by using only DDQ or PTSA, which confirmed the need for both DDQ and PTSA to be present for the cyclization to occur. Heating **11a** at reflux with 30 mol-% $Pd(OAc)_2$ in dioxane furnished pyrrolocarbazole **13a** in low yield (Table 1, Entry 2). Similar to the results obtained by using $ZnBr_2$, the reaction of **11a** with Lewis acids such as $InCl_3$, $BF_3{\cdot}OEt_2$, and $Cu(OTf)_2$ led to the isolation of dihydropyrrolocarbazole **14** in 72–83 % yield (Table 1, Entries 3–5). Under identical conditions, the reaction of *p*-tolyl-containing 3-indolylpyrrole **11b** failed to produce the respective dihydrocarbazole,

Table 1. Effect of catalysts on intramolecular cyclization of 3-indolylpyrroles **8**, **11a**, and **11b**.

Entry	Substrate	Conditions	Product [%][a]
1	**11a**	DDQ/PTSA (1 equiv.), benzene, r.t., 45 min	**13a** (89)
2	**11a**	$Pd(OAc)_2$ (30 mol-%), dioxane, reflux, 12 h	**13a** (30)
3	**11a**	$InCl_3$ (30 mol-%), DCM, r.t., 30 min	**14** (83)
4	**11a**	$BF_3{\cdot}OEt_2$ (50 mol-%), DCM, r.t., 30 min	**14** (72)
5	**11a**	$Cu(OTf)_2$ (20 mol-%), DCM, r.t. to reflux, 5 h	**14** (75)
6	**11b**	$ZnBr_2/BF_3{\cdot}OEt_2/InCl_3$ (20 mol-%), DCM, r.t., 12 h	SMR[b]
7	**11b**	DDQ/PTSA (1 equiv.), benzene, r.t., 1 h	**13b** (75)
8	**8**	DDQ/PTSA (1 equiv.), benzene, reflux, 5 h	**12** (90)
9	**8**	$ZnBr_2/BF_3{\cdot}OEt_2$ (20 %), DCM, r.t., 12 h	SMR[b]
10	**8**	NBS (1.5 equiv.), THF, reflux, 5 h	**12** (88)

[a] Isolated yields of pyrrolo[2,3-*c*]carbazoles are reported. [b] Starting material was recovered (SMR).

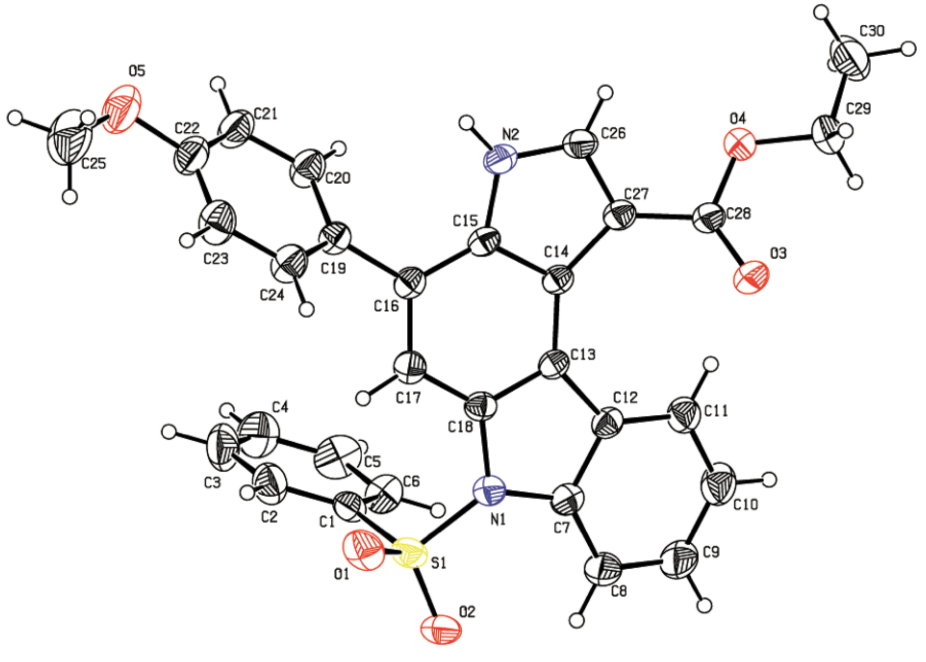
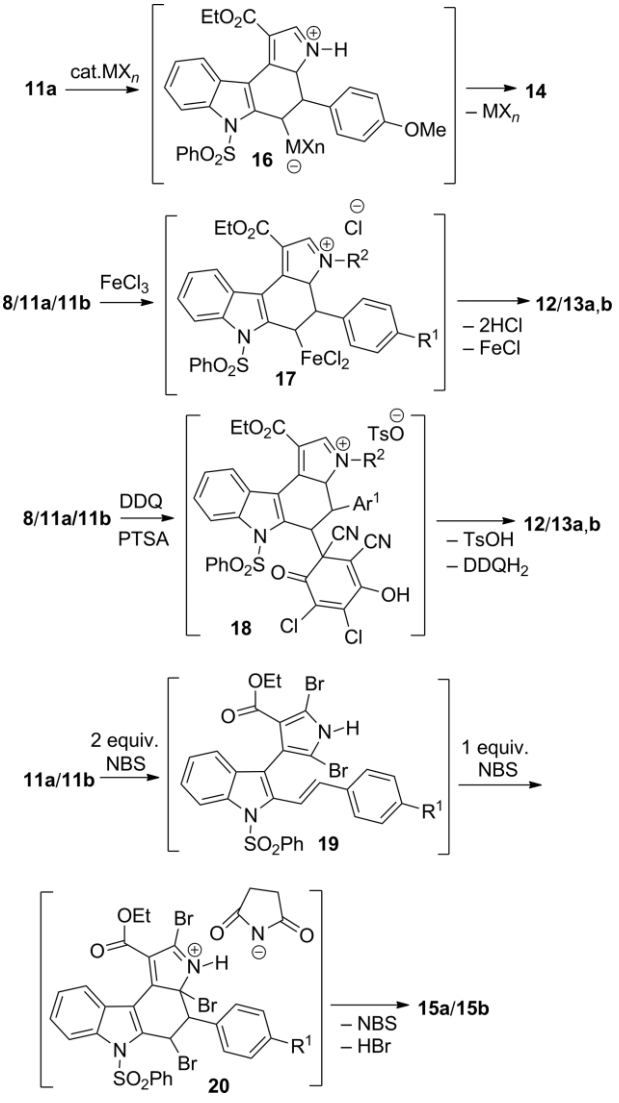


Figure 2. Single-crystal X-ray structure of pyrrolocarbazole **13a**.

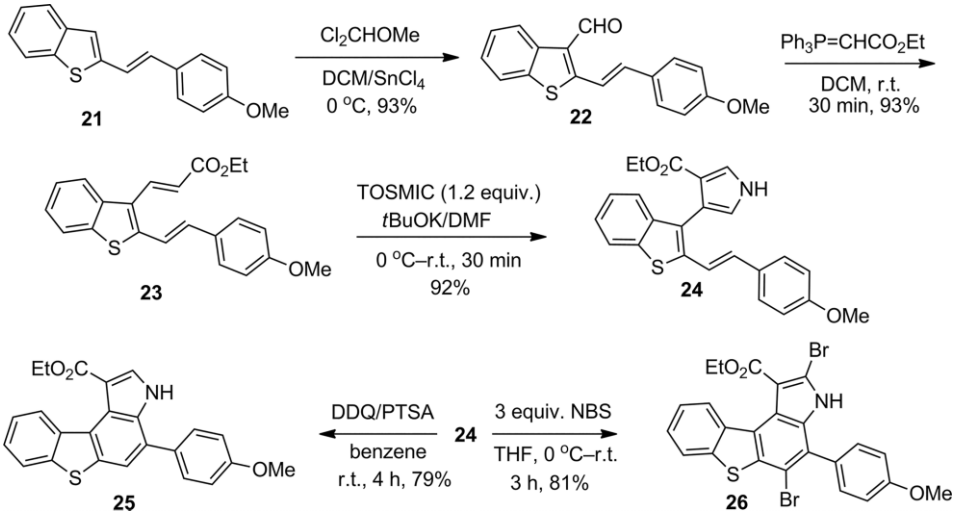
even after extending the reaction time, and the starting material was recovered instead (Table 1, Entry 6). This clearly confirms the comparatively lower coordination ability of the *p*-methylstyryl moiety relative to that of the *p*-methoxystyryl unit. However, 3-indolylpyrrole **11b** underwent a smooth cyclization process upon treatment with 1 equiv. of DDQ/PTSA in dry benzene at room temperature to give the corresponding pyrrolocarbazole **13b** in 75 % yield (Table 1, Entry 7). The DDQ-PTSA-mediated cyclization 3-indolyl-*N*,*N*′-di(phenylsulfonyl)pyrrole **8** in benzene at room temperature was unsuccessful, but under refluxing conditions, 2-*p*-anisylvinylindole **8** underwent a smooth cyclization to yield pyrrolo[2,3-*c*]carbazole **12** in 90 % yield (Table 1, Entry 8).

Lewis acids such as $ZnBr_2$ and $BF_3{\cdot}OEt_2$ failed to induce any cyclization reaction of 3-indolyl-*N*,*N*′-di(phenylsulfonyl)pyrrole **8** (Table 1, Entry 9). Finally, heating **8** at reflux with 1.5 equiv. of NBS in THF afforded pyrrolo[2,3-*c*]carbazole **12** in 88 % yield (Table 1, Entry 10). As a representative case, the structure of pyrrolo[2,3-*c*]carbazole **13a** was confirmed by single-crystal X-ray structure analysis (Figure 2).[19]

Mechanistically, the formation of dihydro compound **14** from 3-indolylpyrrole **11a** can occur through the formation of intermediate **16** (Scheme 4). However, the similar reaction of indolyl pyrroles **8**, **11a**, and **11b** with $FeCl_3$ may generate tetracyclic intermediate **17**, which upon elimination of HCl and FeCl leads to pyrrolocarbazoles **12**, **13a**, and **13b**, respectively. On the other hand, the DDQ/PTSA-mediated transformation of divinylindoles **8**, **11a**, and **11b** into pyrrolocarbazoles **12**, **13a**, and **13b**, respectively, can proceed through the formation of intermediate **18**. In the NBS-mediated cyclization of indolyl pyrroles **11a** and **11b**, the first two equivalents of NBS led to the formation of the intermediate dibromopyrrole **19**. The third equivalent of NBS triggered a vinylic bromination followed by a cyclization and aromatization reaction sequence to afford target compounds **15a** and **15b** (Scheme 4). In the case of 3-indolyl-*N*,*N*′-di(phenylsulfonyl)pyrrole **8**, however, using 1.5 equiv. of NBS leads to a straightforward bromination at the vinylic unit



Scheme 4. Proposed mechanistic details for pyrrolo[2,3-*c*]carbazoles (Ts = *p*-tolylsulfonyl).

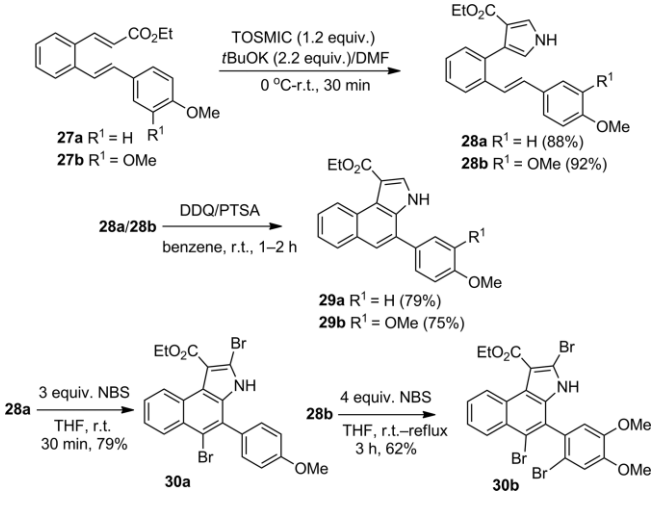


Scheme 5. Synthesis of pyrrolodibenzothiophenes **25** and **26**.

followed by aromatization to form pyrrolo[2,3-*c*]carbazole **12** (Table 1, Entry 10).

In an effort to expand the synthetic utility of this protocol, the cyclization method was applied to the synthesis of pyrrolodibenzothiophenes **25** and **26** (Scheme 5). A Rieche formylation (*E*)-2-(4-methoxystyryl)benzo[*b*]thiophene (**21**) by using dichloromethyl methyl ether and $SnCl_4$ in DCM at 0 °C gave (*E*)-2-(4-methoxystyryl)benzo[*b*]thiophene-3-carbaldehyde (**22**). A Wittig reaction by treating aldehyde **22** with (carbethoxymethylene)triphenylphosphorane in DCM at room temperature furnished benzo[*b*]thiophenyl-3-vinyl ester **23**. As expected, under van Leusen reaction conditions, **23** led to 3-benzo[*b*]thienylpyrrole **24** in 92 % yield, whereupon a facile DDQ/PTSA-mediated cyclization and subsequent aromatization furnished pyrrolo[2,3-*c*]dibenzothiophene **25**. However, the reaction of benzo[*b*]thienylpyrrole **24** with 3 equiv. of NBS in THF led to the isolation of dibromo pyrrolodibenzothiophene **26** in 81 % yield.

The electrophile-induced cyclization/aromatization strategy was then extended to access benzo[*e*]indole frameworks (Scheme 6). The reaction of vinyl esters **27a** and **27b** with TOSMIC and *t*BuOK as the base in DMF gave pyrroles **28a** and **28b**, which underwent a DDQ/PTSA-mediated intramolecular cyclization to furnish benzo[*e*]indoles **29a** and **29b** in 79 and 75 % yield, respectively. Similarly, the NBS-mediated cyclization of divinyl compounds **28a** and **28b** also led to the isolation of corresponding monobrominated benzo[*e*]indole **30a** and tribrominated benzo[*e*]indole **30b**, respectively.



Scheme 6. Synthesis of benzo[*e*]indoles **29a**, **29b**, **30a**, and **30b**.

Conclusions

In summary, we have reported a simple and easily accessible approach for the preparation of the core skeletal framework of dictyodendrins by employing Lewis acid, NBS-, and DDQ-PTSA-mediated intramolecular cyclization reactions of 3-(2-styrylaryl/heteroaryl)pyrroles. The present protocol of a vinylic precursor as a two-carbon synthon was highly useful to construct the core units of biologically important heterocycles. We anticipate our method to be applicable towards the total syntheses of pyrrolocarbazole natural products, dictyodendrins,[1,11] ningalins,[20] and other related natural products.[21]

Experimental Section

General Methods: Solvents were dried by standard procedures. All experiments were carried out under nitrogen unless otherwise stated. The progress of all of the reactions was monitored by TLC analysis using mixtures of hexanes and ethyl acetate. Column chromatography was carried out on silica gel (230–400 mesh, Merck) by increasing the polarity of the eluent. The ^1H and ^{13}C NMR spectroscopic data and DEPT spectra were recorded with a Bruker 300 MHz spectrometer at room temperature. $CDCl_3$ was used as the NMR solvent with TMS as the internal standard. Chemical shift values are reported in parts per million, and coupling constants are reported in hertz. Elemental analysis data was recorded on an Elementar Vario Series Analyzer [Indian Institute of Science Education and Research (IISER), Pune]. HRMS data were recorded with a JEOL GC Mate II (EI).

Preparation of Starting Materials: The required starting materials ethyl 4-(2-methyl-1-phenylsulfonyl-indol-3-yl)pyrrole-3-carboxylate (**5**),[16] (*E*)-ethyl 3-{2-[(diethoxyphosphoryl)methyl]-1-(phenylsulfonyl)-1*H*-indol-3-yl}acrylate (**9**),[14] diethyl benzo[*b*]thiophen-2-ylmethylphosphonate,[22] (*E*)-2-(4-methoxystyryl)benzaldehyde,[23] and (*E*)-2-(3,4-dimethoxystyryl)benzaldehyde[23] were prepared according to procedures reported in the literature.

Ethyl 4-(2-Methyl-1-phenylsulfonyl-indol-3-yl)-1-phenylsulfonyl-pyrrole-3-carboxylate (6): To a suspension of hexane washed sodium hydride (0.94 g, 19.58 mmol) in dry THF (70 mL) at 0 °C under N_2 was slowly added ethyl 4-(2-methyl-1-phenylsulfonyl-indol-3-yl)pyrrole-3-carboxylate (**5**,[16] 4 g, 9.79 mmol) in dry THF (30 mL), and the resulting mixture was stirred for 1 h. To the reaction mixture was added a solution of benzenesulfonyl chloride (2 g, 11.75 mmol) in dry THF (5 mL), and the stirring was continued for an additional 2 h. Then, the reaction mixture was poured over crushed ice (100 g) and then acidified with concentrated HCl (5 mL). The resulting solid was removed by filtration and dried. The crude product was crystallized (methanol) to afford *N*-sulfonated pyrrole **6** (4.85 g, 90 %) as a colorless solid; m.p. 138–140 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.19 (d, J = 8.1 Hz, 1 H), 7.99–7.94 (m, 3 H), 7.83 (d, J = 8.1 Hz, 2 H), 7.74–7.69 (m, 1 H), 7.63–7.53 (m, 3 H), 7.47–7.42 (m, 2 H), 7.28–7.08 (m, 4 H), 3.99–3.94 (m, 2 H), 2.47 (s, 3 H), 0.84 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.9, 139.3, 138.0, 136.0, 134.8, 134.7, 133.6, 130.6, 129.8, 129.3, 127.3, 126.6, 126.4, 124.2, 123.5, 121.1, 120.6, 119.5, 119.3, 114.4, 114.2, 60.3, 13.9, 13.7 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 134.7, 133.6, 129.8, 129.3, 127.2, 126.5, 126.4, 124.1, 123.4, 121.0, 119.2, 114.3, 60.2, 13.9, 13.6 ppm. $C_{28}H_{24}N_2O_6S_2$ (548.63): calcd. C 61.30, H 4.41, N 5.11; found C 61.51, H 4.71, N 5.19.

Diethyl {3-[4-(Ethoxycarbonyl)-1-phenylsulfonyl-pyrrol-3-yl]-1-phenylsulfonyl-indol-2-yl}methylphosphonate (7): A mixture of 2-methylindole **6** (3 g, 5.46 mmol) and NBS (1.16 g, 6.56 mmol) in dry CCl_4 (80 mL) that contained a catalytic amount of AIBN (71 mg, 0.43 mmol) was heated at reflux for 2 h. The reaction mixture was then cooled to room temperature. The suspended succinimide was removed by filtration, and the filtrate was concentrated in vacuo to afford the crude bromo compound (2.83 g, 82 %) as a thick brown liquid. A solution of the crude bromo compound (2 g, 3.18 mmol) and triethyl phosphite (1.58 g, 9.56 mmol) was heated at reflux under N_2 for 2 h. Upon consumption of the bromo compound (monitored by TLC), the reaction mass was poured over crushed ice

(100 g) that was combined with concentrated HCl (5 mL). The resulting mixture was extracted with $CHCl_3$ (2 × 25 mL). The combined organic layers were then washed with brine and dried with Na_2SO_4. The solvent was removed in vacuo to give the crude phosphonate ester **7** (2.00 g, 91 %) as a thick brown liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.95–7.92 (m, 3 H), 7.86 (d, *J* = 2.4 Hz, 1 H), 7.66–7.59 (m, 4 H), 7.53–7.48 (m, 2 H), 7.40–7.35 (m, 1 H), 7.30–7.25 (m, 2 H), 7.20–7.11 (m, 1 H), 7.06–6.96 (m, 2 H), 4.11–3.33 (m, 8 H), 1.29–1.14 (m, 6 H), 0.53 (m, 3 H) ppm.

Ethyl 4-[2-(4-Methoxystyryl)-1-phenylsulfonyl-indol-3-yl]-1-phenylsulfonyl-pyrrole-3-carboxylate (8): To a suspension of hexane washed sodium hydride (175 mg, 3.65 mmol) in dry THF (10 mL) at –10 °C under N_2 was slowly added phosphonate ester **7** (1 g, 1.46 mmol) in dry THF (25 mL), and the resulting mixture was stirred for 1 h. Then, a solution of *p*-anisaldehyde (0.22 g, 1.60 mmol) in dry THF (5 mL) was added, and the stirring was continued for an additional 2 h. The yellow solution was then poured over crushed ice (50 g), and the mixture was then acidified with concentrated HCl (3 mL). The solid was removed by filtration and dried to give the crude product, which was crystallized (MeOH) to give 2-*p*-anisylvinylindole **8** (0.59 g, 60 %) as a colorless solid; m.p. 170–172 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.4 Hz, 1 H), 7.89 (d, *J* = 2.1 Hz, 1 H), 7.84 (d, *J* = 7.8 Hz, 2 H), 7.73 (d, *J* = 7.8 Hz, 2 H), 7.57 (t, *J* = 7.2 Hz, 1 H), 7.49–7.26 (m, 7 H), 7.20–7.06 (m, 5 H), 6.83 (d, *J* = 8.4 Hz, 2 H), 6.23 (d, *J* = 16.2 Hz, 1 H), 3.92–3.80 (m, 5 H), 0.67 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.8, 159.8, 138.5, 138.0, 136.3, 136.1, 134.8, 134.4, 133.6, 131.6, 129.7, 129.5, 128.9, 127.9, 126.9, 126.8, 126.6, 125.0, 124.0, 121.0, 120.7, 120.2, 119.8, 115.9, 115.1, 114.6, 114.1, 60.2, 55.4, 13.5 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 134.8, 134.4, 133.6, 129.6, 128.9, 127.9, 126.9, 126.8, 126.6, 125.0, 124.0, 121.0, 119.8, 115.9, 115.1, 114.1, 60.2, 55.4, 13.5 ppm. $C_{36}H_{30}N_2O_7S_2$ (666.76): calcd. C 64.85, H 4.54, N 4.20; found C 65.05, H 4.68, N 4.32.

Ethyl (*E*)-3-[2(*E*)-(4-Methoxystyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl]acrylate (10a): To a suspension of hexane washed sodium hydride (710 mg, 14.83 mmol) in dry THF (20 mL) at –10 °C under N_2, was slowly added (*E*)-ethyl 3-{2-[(diethoxyphosphoryl)methyl]-1-(phenylsulfonyl)1*H*-indol-3-yl}acrylate (**9**,[14] 3 g, 5.93 mmol) in dry THF (40 mL), and the resulting mixture was stirred for 1 h. Then, a solution of *p*-anisaldehyde (0.89 g, 6.52 mmol) in dry THF (8 mL) was added, and the stirring was continued for an additional 2 h. The yellow solution was then poured over crushed ice (100 g), and the mixture was acidified with concentrated HCl (5 mL). The solid was removed by filtration and dried to give the crude product, which was crystallized (MeOH) to give divinyl indole **10a** (2.35 g, 80 %) as a yellow solid; m.p. 140–142 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.33 (d, *J* = 7.8 Hz, 1 H), 7.86–7.68 (m, 4 H), 7.57–7.29 (m, 8 H), 6.96 (d, *J* = 8.4 Hz, 2 H), 6.62–6.51 (m, 2 H), 4.17 (q, *J* = 7.2 Hz, 2 H), 3.80 (s, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.3, 160.5, 141.3, 139.2, 138.1, 136.9, 136.8, 134.0, 129.2, 129.1, 128.6, 128.1, 126.9, 125.6, 124.7, 120.5, 119.1, 117.2, 115.3, 115.2, 114.4, 60.4, 55.4, 14.4 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 139.2, 136.8, 134.0, 129.1, 128.7, 126.9, 125.6, 124.7, 120.5, 119.1, 115.3, 114.3, 60.4, 55.4, 14.4 ppm.

Ethyl (*E*)-3-[2(*E*)-(4-Methylstyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl]acrylate (10b): To a suspension of hexane washed sodium hydride (470 mg, 9.89 mmol) in dry THF (10 mL) at –10 °C under N_2 was slowly added (*E*)-ethyl 3-{2-[(diethoxyphosphoryl)methyl]-1-(phenylsulfonyl)-1*H*-indol-3-yl}acrylate (**9**,[14] 2.5 g, 4.94 mmol) in dry THF (30 mL), and the resulting mixture was stirred for 1 h. Then, a solution of *p*-anisaldehyde (0.65 g, 5.43 mmol) in dry THF (5 mL) was added, and the stirring was continued for an additional 2 h. The yellow solution was then poured over crushed ice (100 g), and the mixture was acidified with concentrated HCl (5 mL). The solid was removed by filtration and dried to give the crude product, which was crystallized (MeOH) to afford divinyl indole **10b** (1.81 g, 78 %) as a yellow solid; m.p. 136–138 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 8.1 Hz, 1 H), 7.78–7.76 (m, 4 H), 7.56 (d, *J* = 16.2 Hz, 1 H), 7.43–7.15 (m, 9 H), 6.53 (d, *J* = 16.2 Hz, 1 H), 6.46 (d, *J* = 16.2 Hz, 1 H), 4.16 (q, *J* = 7.05 Hz, 2 H), 2.33 (s, 3 H), 1.22 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.2, 141.0, 139.5, 139.2, 138.0, 136.9, 136.7, 134.0, 133.6, 129.6, 129.0, 128.0, 127.1, 126.8, 125.7, 124.7, 120.5, 119.3, 117.4, 116.5, 115.3, 60.4, 21.4, 14.3 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 139.5, 136.7, 134.0, 129.6, 129.0, 127.1, 126.8, 125.7, 124.7, 120.5, 119.3, 116.5, 115.3, 60.4, 21.4, 14.3 ppm.

Ethyl 4-[2(*E*)-(4-Methoxystyryl)-1-phenylsulfonyl-1*H*-indol-3-yl]-1*H*-pyrrole-3-carboxylate (11a): To a suspension of *t*BuOK (350 mg, 3.07 mmol) in dry DMF (8 mL) at 0 °C under N_2 was added TOSMIC (0.44 g, 2.25 mmol) in dry DMF (5 mL). The reaction mixture was stirred for 15 min at the same temperature and then treated dropwise with a solution of divinyl compound **10a** (1 g, 2.05 mmol) in dry DMF (10 mL). After the starting material was consumed (monitored by TLC), the reaction mixture was quenched with crushed ice (50 g), and the resulting mixture was extracted with $CHCl_3$ (2 × 20 mL). The combine organic layers were dried with Na_2SO_4, and the solvent was removed. The crude residue was purified by column chromatography [hexane/ethyl acetate (EA), 9:1] to afford pyrrole compound **11a** (0.87 g, 80 %) as a yellow solid; m.p. 220–223 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.64 (s, 1 H), 8.17 (d, *J* = 8.1 Hz, 1 H), 7.69 (d, *J* = 7.5 Hz, 2 H), 7.45 (d, *J* = 16.2 Hz, 1 H), 7.40–7.35 (m, 2 H), 7.27–7.19 (m, 5 H), 7.10–7.08 (m, 2 H), 6.77 (d, *J* = 8.4 Hz, 2 H), 6.56 (s, 1 H), 6.39 (d, *J* = 16.2 Hz, 1 H), 3.81–3.70 (m, 5 H), 0.51 (t, *J* = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.6, 159.6, 138.6, 136.2, 135.7, 134.2, 133.4, 132.8, 130.1, 128.8, 127.9, 126.9, 125.0, 124.6, 123.8, 120.3, 119.1, 117.4, 116.3, 116.2, 116.0, 115.1, 114.1, 59.4, 55.4, 13.5 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 138.6, 138.5, 133.8, 132.5, 131.4, 130.0, 129.3, 128.6, 125.2, 124.4, 121.0, 119.6, 118.9, 63.6, 60.1, 18.6 ppm. $C_{30}H_{26}N_2O_5S$ (526.61): calcd. C 68.42, H 4.98, N 5.32; found C 68.63, H 4.71, N 5.41.

Ethyl 4-[2(*E*)-(4-Methylstyryl)-1-(phenylsulfonyl)-1*H*-indol-3-yl]-1*H*-pyrrole-3-carboxylate (11b): To a suspension of *t*BuOK (360 mg, 3.18 mmol) in dry DMF (8 mL) at 0 °C under N_2 was added TOSMIC (0.45 g, 2.33 mmol) in dry DMF (5 mL). The reaction mixture was stirred for 15 min at the same temperature and then treated dropwise with a solution of divinyl indole **10b** (1 g, 2.12 mmol) in dry DMF (8 mL). After the starting material was consumed (monitored by TLC), a similar workup procedure as that of 2-*p*-anisylvinylindole **11a** was followed to afford 2-*p*-tolylvinylindole **11b** (0.81 g, 75 %) as a yellow solid; m.p. 230–232 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 11.61 (s, 1 H), 8.54 (d, *J* = 6.9 Hz, 1 H), 8.12 (d, *J* = 7.8 Hz, 2 H), 7.89–7.74 (m, 5 H), 7.65–7.49 (m, 7 H), 7.06 (s, 1 H), 6.90 (d, *J* = 16.2 Hz, 1 H), 4.21 (q, *J* = 7.8 Hz, 2 H), 2.71 (s, 3 H), 1.10 (t, *J* = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.1, 143.0, 142.5, 140.8, 139.9, 139.2, 138.8, 138.5, 137.5, 134.1, 133.8, 131.4, 131.2, 130.1, 129.4, 128.6, 125.2, 124.4, 123.1, 122.1, 119.6, 119.5, 63.6, 26.0, 18.5 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 138.8, 138.5, 134.1, 133.8, 131.4, 131.1, 130.1, 129.4, 128.6, 125.2, 124.4, 122.1, 119.5, 63.6, 26.0, 18.5 ppm. $C_{30}H_{26}N_2O_4S$ (510.61): calcd. C 70.57, H 5.13, N 5.49; found C 70.71, H 5.22, N 5.28.

Ethyl 4-(4-Methoxyphenyl)-3,6-bis(phenylsulfonyl)-3,6-dihydropyrrolo[2,3-*c*]carbazole-1-carboxylate (12)

Method 1: To a solution of 2-*p*-anisylvinylindole **8** (0.20 g, 0.30 mmol) in dry DCM (10 mL) at 0 °C was added anhydrous $FeCl_3$

(24 mg, 0.15 mmol), and the resulting mixture was stirred at reflux for 3 h. Upon completion of the reaction (monitored by TLC), the mixture was poured into ice water (20 mL) and then acidified with concentrated HCl (2 mL). The resulting mixture was extracted with DCM (2 × 10 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 8:2) to afford pyrrolo[2,3-*c*]carbazole **12** (0.17 g, 85 %) as a colorless solid; m.p. 193–195 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50 (s, 1 H), 8.40 (d, J = 8.4 Hz, 1 H), 8.18 (s, 1 H), 7.97 (d, J = 7.8 Hz, 1 H), 7.71 (d, J = 7.8 Hz, 2 H), 7.51–7.25 (m, 10 H), 7.03 (d, J = 8.4 Hz, 2 H), 6.70 (d, J = 8.4 Hz, 2 H), 4.50 (q, J = 7.2 Hz, 2 H), 3.86 (s, 3 H), 1.41 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.7, 159.1, 138.8, 138.1, 137.7, 136.6, 136.1, 133.9, 133.6, 132.2, 132.1, 131.1, 129.5, 129.0, 126.9, 126.4, 126.1, 125.7, 124.7, 123.6, 122.5, 118.3, 116.9, 115.7, 114.8, 112.9, 61.5, 55.3, 14.3 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 136.7, 133.9, 133.6, 131.1, 129.0, 127.0, 126.5, 126.1, 124.7, 123.6, 116.8, 114.8, 112.9, 61.5, 55.3, 14.3 ppm. HRMS (EI): calcd. for $C_{36}H_{28}N_2O_7S_2$ $[M]^+$ 664.1338; found 664.1328.

Method 2: (Table 1, Entry 8). To a solution of 2-*p*-anisylvinylindole **8** (0.1 g, 0.15 mmol) in dry benzene (10 mL) at room temperature were added DDQ (34 mg, 0.15 mmol) and PTSA (26 mg, 0.15 mmol), and the resulting mixture was stirred at reflux for 5 h. Upon completion of the reaction (monitored by TLC), the mixture was poured into water (20 mL) and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford pyrrolo[2,3-*c*]carbazole **12** (90 mg, 90 %) as a colorless solid.

Method 3: (Table 1, Entry 10). To a solution of 2-*p*-anisylvinylindole **8** (0.1 g, 0.15 mmol) in dry THF (10 mL) at room temperature was added NBS (0.40 g, 0.22 mmol), and the resulting mixture was stirred at reflux for 5 h. Upon completion of the reaction (monitored by TLC), the mixture was poured into ice water (10 mL) and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford pyrrolo[2,3-*c*]carbazole **12** (88 mg, 88 %) as a colorless solid.

Ethyl 4-(4-Methoxyphenyl)-6-(phenylsulfonyl)-3,6-dihydropyrrolo[2,3-*c*]carbazole-1-carboxylate (13a)

Method 1: To a solution of 2-*p*-anisylvinylindole **11a** (0.1 g, 0.19 mmol) in dry DCM (10 mL) at −10 °C was added anhydrous $FeCl_3$ (15 mg, 0.09 mmol), and the resulting mixture was stirred at the same temperature for 10 min. Upon completion of the reaction (monitored by TLC), the mixture was poured into ice water (20 mL) and then was acidified with concentrated HCl (2 mL). The mixture was extracted with DCM (2 × 10 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 8:2) to afford pyrrolo[2,3-*c*]carbazole **13a** (80 mg, 80 %) as a colorless solid; m.p. 225–227 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.98 (s, 1 H), 8.45–8.41 (m, 3 H), 7.94 (d, J = 3.0 Hz, 1 H), 7.76 (d, J = 7.5 Hz, 2 H), 7.55 (d, J = 8.7 Hz, 2 H), 7.53–7.36 (m, 3 H), 7.27–7.22 (m, 2 H), 7.07 (d, J = 8.7 Hz, 2 H), 4.43 (q, J = 7.2 Hz, 2 H), 3.88 (s, 3 H), 1.38 (t, J = 7.05 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.4, 159.6, 138.5, 137.9, 135.5, 133.6, 132.6, 131.7, 130.4, 129.8, 128.9, 126.9, 126.4, 126.1, 125.7, 125.3, 123.6, 118.2, 118.0, 114.9, 114.7, 111.4, 111.1, 60.5, 55.4, 14.5 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 133.6, 131.8, 129.8, 128.9, 126.4, 126.1, 125.3, 123.6, 114.9, 114.7, 111.4, 60.5, 55.4, 14.5 ppm. HRMS (EI): calcd. for $C_{30}H_{24}N_2O_5S$ $[M]^+$ 524.1406; found 524.1421. For the single-crystal X-ray analysis of **13a**, all calculations were performed with the SHELXL-97 program.[24] Crystal data of **13a**: $C_{30}H_{24}N_2O_5S$, MW = 524.58 g mol^{-1}, triclinic crystal system, space group $P\bar{1}$, Z = 4, a = 8.8507(4) Å, b = 11.3879(5) Å, c = 25.6008(12) Å, α = 90°, β = 90°, γ = 90°, V = 2580.3(2) Å^3, and $D_{calcd.}$ = 1.350 Mg m^{-3}. In total, 5653 independent reflections were collected, of which 4655 were considered as observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least-squares procedures to a final R-value of 3.30 %.

Method 2: To a solution of tetrahydropyrrolo[2,3-*c*]carbazole **14** (0.1 g, 0.19 mmol) in dry DCM (10 mL) at room temperature was added DDQ (43 mg, 0.19 mmol), and the resulting mixture was stirred at room temperature for 45 min. Upon completion of the reaction (monitored by TLC), the mixture was poured into water (20 mL) and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford pyrrolo[2,3-*c*]carbazole **13a** (95 mg, 95 %) as a colorless solid.

Method 3: (Table 1, Entry 1). To a solution of 2-*p*-anisylvinylindole **11a** (0.1 g, 0.19 mmol) in dry benzene (10 mL) at 0 °C were added DDQ (43 mg, 0.19 mmol) and PTSA (32 mg, 0.19 mmol), and the resulting mixture was stirred at room temperature for 45 min. Upon completion of the reaction (monitored by TLC), the mixture was poured into water (20 mL) and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford pyrrolo[2,3-*c*]carbazole **13a** (89 mg, 89 %) as a colorless solid.

Method 4: (Table 1, Entry 2). To a solution of 2-*p*-anisylvinylindole **11a** (0.1 g, 0.19 mmol) in dry dioxane (10 mL) was added $Pd(OAc)_2$ (13 mg, 0.06 mmol), and the resulting mixture was stirred at reflux for 12 h. Upon completion of the reaction (monitored by TLC), the mixture was poured into water (20 mL) and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford pyrrolo[2,3-*c*]-carbazole **13a** (30 mg, 30 %) as a colorless solid.

Ethyl 6-(Phenylsulfonyl)-4-*p*-tolyl-3,6-dihydropyrrolo[2,3-*c*]-carbazole-1-carboxylate (13b)

Method 1: To a solution of 2-*p*-tolylvinylindole **11b** (0.12 g, 0.23 mmol) in dry DCM (10 mL) at 0 °C was added anhydrous $FeCl_3$ (20 mg, 0.11 mmol), and the resulting mixture was stirred at the same temperature for 30 min. Upon completion of the reaction (monitored by TLC), the mixture was poured into ice water (20 mL) and then acidified with concentrated HCl (2 mL). The mixture was extracted with DCM (2 × 10 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 8:2) to afford pyrrolo[2,3-*c*]carbazole **13b** (91 mg, 76 %) as a colorless solid; m.p. 265–267 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.90 (s, 1 H), 8.39 (s, 1 H), 8.37 (d, J = 8.1 Hz, 2 H), 7.89 (d, J = 3.0 Hz, 1 H), 7.70 (d, J = 7.5 Hz, 2 H), 7.47 (d, J = 7.8 Hz, 2 H), 7.43–7.29 (m, 5 H), 7.22–7.17 (m, 2 H), 4.37 (q, J = 7.05 Hz, 2 H), 2.40 (s, 3 H), 1.32 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.4, 138.6, 138.1, 137.9, 135.5, 135.1, 133.6, 132.5, 131.7, 130.1, 128.9, 128.5, 128.3, 126.9, 126.4, 126.1, 125.3, 123.6, 118.4, 118.0, 114.7, 111.4, 111.1, 60.5, 21.2, 14.5 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 133.6, 131.7, 130.1, 128.9, 128.5, 126.4, 126.1, 125.3, 123.6, 114.7, 111.4, 60.5, 21.3, 14.5 ppm. HRMS (EI): calcd, for $C_{30}H_{24}N_2O_4S$ $[M]^+$ 508.1457; found 508.1437.

Method 2: (Table 1, Entry 7). To a solution of 2-*p*-tolylvinylindole **11b** (0.1 g, 0.19 mmol) in dry benzene (10 mL) at room temperature were added DDQ (44 mg, 0.19 mmol) and PTSA (34 mg, 0.19 mmol),

and the resulting mixure was stirred at room temperature for 1 h. Upon completion of the reaction (monitored by TLC), the mixture was poured into water (20 mL) and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford pyrrolo[2,3-*c*]carbazole **13b** (75 mg, 75 %) as a colorless solid.

Ethyl 4-(4-Methoxyphenyl)-6-(phenylsulfonyl)-3,4,5,6-tetrahydropyrrolo[2,3-*c*]carbazole-1-carboxylate (14)

Method 1: To a solution of 2-*p*-anisylvinylindole **11a** (0.1 g, 0.19 mmol) in dry DCM (10 mL) was added $ZnBr_2$ (10 mg, 0.04 mmol) at 0 °C, and the resulting mixture was stirred at room temperature for 1 h. Upon completion of the reaction (monitored by TLC), the mixture was poured into ice water (20 mL) and then acidified with concentrated HCl (2 mL). The mixture was extracted with DCM (2 × 10 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 8:2) to afford dihydropyrrolocarbazole **14** (90 mg, 90 %) as a green solid; m.p. 130–132 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25 (s, 1 H), 8.17–8.14 (m, 1 H), 7.75–7.72 (m, 1 H), 7.57 (d, *J* = 7.5 Hz, 2 H), 7.44–7.39 (m, 1 H), 7.28–7.23 (m, 5 H), 7.06 (d, *J* = 8.4 Hz, 2 H), 6.79 (d, *J* = 8.1 Hz, 2 H), 4.29 (q, *J* = 7.2 Hz, 2 H), 4.10–4.06 (m, 1 H), 3.81–3.73 (m, 4 H), 3.72–3.48 (m, 1 H), 1.24 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.4, 158.9, 138.5, 136.9, 133.5, 132.3, 131.9, 131.7, 129.1, 129.0, 127.4, 126.3, 123.8, 123.2, 123.1, 122.1, 117.3, 114.4, 114.3, 113.9, 113.3, 60.1, 55.3, 39.6, 32.2, 14.3 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 133.5, 129.1, 129.0, 126.3, 123.8, 123.2, 123.1, 122.1, 114.4, 114.3, 60.1, 55.3, 39.6, 32.2, 14.3 ppm.

Method 2: (Table 1, Entry 3). To a solution of 2-*p*-anisylvinylindole **11a** (0.1 g, 0.19 mmol) in dry DCM (10 mL) was added $InCl_3$ (13 mg, 0.06 mmol) at 0 °C, and the resulting mixture was stirred at room temperature for 30 min. Upon completion of the reaction (monitored by TLC), the mixture was poured into ice water (20 mL) and then acidified with concentrated HCl (2 mL). The mixture was extracted with DCM (2 × 10 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 8:2) to afford dihydropyrrolocarbazole **14** (83 mg, 83 %) as a green solid.

Method 3: (Table 1, Entry 4). To a solution of 2-*p*-anisylvinylindole **11a** (0.1 g, 0.19 mmol) in dry DCM (10 mL) was added BF_3•OEt_2 (14 mg, 0.09 mmol) at 0 °C, and the resulting mixture was stirred at room temperature for 30 min. Upon completion of the reaction (monitored by TLC), the mixture was poured into ice water (20 mL) and then acidified with concentrated HCl (2 mL). The mixture was extracted with DCM (2 × 10 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 8:2) to afford dihydropyrrolocarbazole **14** (72 mg, 72 %) as a green solid.

Method 4: (Table 1, Entry 5). To a solution of 2-*p*-anisylvinylindole **11a** (0.1 g, 0.19 mmol) in dry DCM (10 mL) was added $Cu(OTf)_2$ (14 mg, 0.04 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 2 h and then heated at reflux for 3 h. Upon completion of the reaction (monitored by TLC), the mixture was poured into ice water (20 mL) and then acidified with concentrated HCl (2 mL). The mixture was extracted with DCM (2 × 10 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 8:2) to afford dihydropyrrolocarbazole **14** (75 mg, 75 %) as a green solid.

Ethyl 2-Bromo-4-(4-methoxyphenyl)-6-(phenylsulfonyl)-3,6-dihydropyrrolo[2,3-*c*]carbazole-1-carboxylate (15a): To a solution of 2-*p*-anisylvinylindole **11a** (0.20 g, 0.38 mmol) in dry THF (10 mL) at 0 °C was added NBS (0.20 g, 1.14 mmol), and the resulting mixture was stirred at room temperature for 30 min. Upon completion of the reaction (monitored by TLC), the mixture was poured into ice water (10 mL) and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford bromopyrrolo[2,3-*c*]carbazole **15a** (0.20 g, 87 %) as a colorless solid; m.p. 190–193 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.90 (s, 1 H), 8.43 (d, *J* = 8.4 Hz, 1 H), 8.36 (s, 1 H), 7.83 (d, *J* = 7.8 Hz, 1 H), 7.76 (d, *J* = 7.5 Hz, 2 H), 7.55 (d, *J* = 8.7 Hz, 2 H), 7.50–7.34 (m, 3 H), 7.27 (t, *J* = 7.05 Hz, 2 H), 7.09 (d, *J* = 8.7 Hz, 2 H), 4.51 (q, *J* = 7.2 Hz, 2 H), 3.87 (s, 3 H), 1.35 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.3, 159.8, 138.5, 137.8, 135.3, 133.7, 131.9, 129.9, 129.7, 129.0, 126.4, 126.3, 124.9, 123.9, 123.5, 119.0, 116.9, 115.0, 113.9, 111.3, 61.3, 55.4, 14.2 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 133.7, 129.7, 129.0, 126.4, 126.3, 123.9, 123.6, 115.0, 111.3, 61.3, 55.4, 14.2 ppm. HRMS (EI): calcd. for $C_{30}H_{23}BrN_2O_5S$ $[M]^+$ 602.0511; found 602.0500.

Ethyl 2-Bromo-6-(phenylsulfonyl)-4-*p*-tolyl-3,6-dihydropyrrolo-[2,3-*c*]carbazole-1-carboxylate (15b): To a solution of 2-*p*-tolylvinylindole **11b** (0.12 g, 0.23 mmol) in dry THF (10 mL) at 0 °C was added NBS (0.12 g, 0.70 mmol), and the resulting mixture was stirred at room temperature for 30 min. Upon completion of the reaction (monitored by TLC), the mixture was poured into ice water (20 mL) and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford bromopyrrolo[2,3-*c*]carbazole **15b** (120 mg, 85 %) as a yellow solid; m.p. 255–257 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.77 (s, 1 H), 8.37 (d, *J* = 8.4 Hz, 1 H), 8.33 (s, 1 H), 7.77 (d, *J* = 7.8 Hz, 1 H), 7.70 (d, *J* = 7.5 Hz, 2 H), 7.48–7.19 (m, 9 H), 4.45 (q, *J* = 7.05 Hz, 2 H), 2.41 (s, 3 H), 1.28 (t, *J* = 7.05 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 138.5, 138.3, 137.8, 135.3, 134.7, 133.7, 131.8, 130.2, 128.9, 128.4, 126.4, 126.3, 126.2, 125.1, 123.9, 123.5, 119.0, 117.1, 114.9, 113.8, 111.4, 111.2, 61.3, 21.2, 14.2 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 132.7, 129.2, 127.9, 127.4, 125.4, 125.3, 122.9, 122.5, 113.9, 110.3, 60.3, 20.2, 13.2 ppm. HRMS (EI): calcd. for $C_{30}H_{23}BrN_2O_4S$ $[M]^+$ 586.0562; found 586.0542.

(*E*)-2-(4-Methoxystyryl)benzo[*b*]thiophene (21): To a suspension of hexane washed sodium hydride (1.69 g, 35.17 mmol) in dry THF (30 mL) at −10 °C under N_2 was slowly added the diethyl benzo[*b*]thiophen-2-ylmethylphosphonate[22] (5 g, 17.58 mmol) in dry THF (50 mL), and the resulting mixture was stirred for 1 h. Then, a solution of *p*-anisaldehyde (2.63 g, 19.34 mmol) in dry THF (10 mL) was added, and the stirring was continued for an additional 2 h. The reaction mixture was poured onto crushed ice (150 g) and then acidified with concentrated HCl (5 mL). The solid was removed by filtration and washed with methanol. The crude product was crystallized (MeOH) to afford (*E*)-2-(4-methoxystyryl)benzo[*b*]thiophene (**21**, 4.50 g, 96 %) as a colorless solid; m.p. 210–212 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 6.6 Hz, 1 H), 7.61 (d, *J* = 7.5 Hz, 1 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 7.24–7.09 (m, 4 H), 6.90–6.82 (m, 3 H), 3.76 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.6, 143.3, 140.3, 138.7, 130.5, 129.4, 127.8, 124.5, 124.4, 123.2, 122.4, 122.1, 120.2, 114.2, 55.3 ppm; DEPT-135 (75 MHz, $CDCl_3$): δ = 130.5, 127.8, 124.5, 123.2, 122.4, 122.1, 120.2, 114.2, 55.3 ppm.

(*E*)-2-(4-Methoxystyryl)benzo[*b*]thiophene-3-carbaldehyde (22): To a solution of (*E*)-2-(4-methoxystyryl)benzo[*b*]thiophene (**21**, 3 g, 11.26 mmol) in dry DCM (30 mL) at 0 °C were added dichloromethyl methyl ether (1.55 g, 13.51 mmol) and $SnCl_4$ (3.52 g, 13.51 mmol), and the resulting mixture was stirred at the same temperature for

30 min. Upon completion of the reaction (monitored by TLC), the mixture was poured into ice water (100 mL) and then acidified with concentrated HCl (5 mL). The mixture was extracted with DCM (2 × 10 mL), and the combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford (*E*)-2-(4-methoxystyryl)benzo[*b*]thiophene-3-carbaldehyde (**22**, 3.10 g, 93 %) as a yellow solid; m.p. 116–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.50 (s, 1 H), 8.47 (d, *J* = 7.8 Hz, 1 H), 7.81 (d, *J* = 15.9 Hz, 1 H), 7.69 (d, *J* = 7.8 Hz, 1 H), 7.46 (d, *J* = 8.7 Hz, 2 H), 7.40–7.29 (m, 2 H), 7.19 (d, *J* = 6.3 Hz, 1 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 3.78 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 184.2, 160.8, 156.9, 137.9, 136.7, 136.6, 128.9, 128.6, 128.4, 126.0, 125.9, 124.0, 121.6, 116.1, 114.5, 55.4 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 184.2, 136.6, 128.9, 126.0, 125.9, 124.0, 121.6, 116.0, 114.4, 55.4 ppm.

(*E*)-Ethyl 3-[2-(4-Methoxystyryl)benzo[*b*]thiophen-3-yl]acrylate (23): To a solution of (*E*)-2-(4-methoxystyryl)benzo[*b*]thiophene-3-carbaldehyde (**22**, 1 g, 3.40 mmol) in dry DCM (20 mL) was added (carbethoxymethylene)triphenylphosphorane (1.53 g, 4.41 mmol), and the resulting mixture was stirred for 30 min. Upon completion of the reaction (monitored by TLC), the solvent was removed in vacuo followed by column chromatographic purification (hexane/EA, 9:1) to afford divinylbenzo[*b*]thiophene **23** (1.15 g, 93 %) as a yellow solid; m.p. 123–125 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 15.9 Hz, 1 H), 7.86 (d, *J* = 7.2 Hz, 1 H), 7.69 (d, *J* = 6.9 Hz, 1 H), 7.44–7.27 (m, 5 H), 7.00 (d, *J* = 15.6 Hz, 1 H), 6.85 (d, *J* = 7.8 Hz, 2 H), 6.42 (d, *J* = 16.2 Hz, 1 H), 4.25 (q, *J* = 7.2 Hz, 2 H), 3.77 (s, 3 H), 1.31 (t, *J* = 7.05 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.4, 160.1, 145.1, 138.6, 137.7, 136.1, 133.2, 129.0, 128.4, 127.6, 125.3, 125.0, 122.5, 122.3, 120.6, 117.7, 114.3, 60.7, 55.3, 14.4 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 136.1, 133.2, 128.4, 125.3, 125.0, 122.5, 122.3, 120.6, 117.7, 114.3, 60.7, 55.3, 14.4 ppm. $C_{22}H_{20}O_3S$ (364.46): calcd. C 72.50, H 5.53; found C 72.68, H 5.72.

(*E*)-Ethyl 4-[2-(4-Methoxystyryl)benzo[*b*]thiophen-3-yl]-1*H*-pyrrole-3-carboxylate (24): To a suspension of *t*BuOK (461 mg, 4.11 mmol) in dry DMF (8 mL) at 0 °C under N_2 was added TOSMIC (0.59 g, 3.02 mmol) in dry DMF (5 mL). The resulting mixture was stirred for 15 min at the same temperature and then treated dropwise with a solution of divinyl compound **23** (1 g, 2.74 mmol) in dry DMF (8 mL). After the starting material was consumed (monitored by TLC), the reaction was quenched with ice water (50 mL), and the resulting mixture was extracted with $CHCl_3$ (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford 2-*p*-anisylvinylbenzo[*b*]thiophene **24** (1.02 g, 92 %) as a yellow solid; m.p. 180–182 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.80 (s, 1 H), 7.66 (d, *J* = 7.2 Hz, 1 H), 7.55 (s, 1 H), 7.33–7.14 (m, 5 H), 7.05–6.83 (m, 2 H), 6.76 (d, *J* = 8.1 Hz, 2 H), 6.70 (s, 1 H), 3.89 (q, *J* = 6.6 Hz, 2 H), 3.72 (s, 3 H), 0.75 (t, *J* = 7.05 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.8, 159.3, 141.8, 139.1, 137.2, 129.9, 129.6, 128.9, 127.8, 125.0, 124.5, 124.0, 123.2, 121.8, 120.1, 120.0, 117.4, 116.4, 114.1, 59.6, 55.3, 13.6 ppm; DEPT-135 (75 MHz, $CDCl_3$): δ = 129.6, 127.8, 125.0, 124.5, 124.0, 1123.2, 121.8, 120.1, 120.0, 114.1, 59.6, 55.3, 13.6 ppm. $C_{24}H_{21}NO_3S$ (403.49): calcd. C 71.44, H 5.25, N 3.47; found C 71.61, H 5.32, N 3.12.

Pyrrolodibenzothiophene 25: To a solution of 2-*p*-anisylvinylbenzo[*b*]thiophene **24** (0.1 g, 0.25 mmol) in dry benzene (10 mL) at 0 °C were added DDQ (56 mg, 0.25 mmol) and PTSA (42 mg, 0.25 mmol), and the resulting mixture was stirred at room temperature for 4 h. Upon completion of the reaction (monitored by TLC), the mixture was poured into water (20 mL) and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford pyrrolodibenzothiophene **25** (79 mg, 79 %) as a yellow solid; m.p. 150–152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.00 (s, 1 H), 8.22–8.19 (m, 1 H), 7.91–7.88 (m, 2 H), 7.68 (s, 1 H), 7.54–7.42 (m, 4 H), 7.05 (d, *J* = 8.7 Hz, 2 H), 4.45 (q, *J* = 7.0 Hz, 2 H), 3.87 (s, 3 H), 1.33 (t, *J* = 7.05 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.1, 159.6, 139.6, 135.8, 135.2, 133.3, 130.5, 130.0, 129.6, 126.9, 126.7, 125.7, 125.2, 123.2, 122.1, 119.5, 117.7, 114.8, 111.4, 60.6, 55.4, 14.4 ppm; DEPT-135 (75 MHz, $CDCl_3$): δ = 130.5, 129.6, 126.7, 125.2, 123.2, 122.1, 117.7, 114.8, 60.6, 55.4, 14.4 ppm. HRMS (EI): calcd. for $C_{24}H_{19}NO_3S$ $[M]^+$ 401.1086; found 401.1086.

Dibromopyrrolodibenzothiophene 26: To a solution of 2-*p*-anisylvinylbenzo[*b*]thiophene **24** (0.1 g, 0.25 mmol) in dry THF (10 mL) at 0 °C was added NBS (0.14 g, 0.75 mmol), and the resulting mixture was stirred at room temperature for 30 min. Upon completion of the reaction (monitored by TLC), the mixture was poured into cold water (20 mL) and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford dibromopyrrolodibenzothiophene **26** (112 mg, 81 %) as a yellow solid; m.p. 205–207 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.68 (s, 1 H), 7.83–7.77 (m, 2 H), 7.37–7.34 (m, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 6.94 (d, *J* = 8.4 Hz, 2 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 3.74 (s, 3 H), 1.14 (t, *J* = 7.05 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.5, 159.9, 139.4, 137.5, 136.0, 134.2, 131.1, 127.8, 126.3, 125.9, 125.8, 124.8, 123.7, 122.4, 119.3, 114.5, 113.9, 112.5, 111.2, 61.4, 55.3, 14.1 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 131.2, 125.9, 125.8, 123.7, 122.4, 114.5, 61.4, 55.3, 14.1 ppm. HRMS (EI): calcd. for $C_{24}H_{17}Br_2NO_3S$ $[M]^+$ 556.9296; found 556.9296.

(*E*)-Ethyl 3-[2-(4-Methoxystyryl)phenyl]acrylate (27a): To a solution of (*E*)-2-(4-methoxystyryl)benzaldehyde[23] (1.2 g, 5.04 mmol) in dry DCM (20 mL) was added (carbethoxymethylene)triphenylphosphorane (2.28 g, 6.54 mmol), and the reaction mixture was stirred for 30 min. Upon completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure followed by column chromatographic purification (hexane/EA, 9:1) to afford divinylbenzene **27a** (1.45 g, 93 %) as a colorless solid; m.p. 78–80 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 15.6 Hz, 1 H), 7.52–7.18 (m, 7 H), 6.88–6.82 (m, 3 H), 6.29 (d, *J* = 15.9 Hz, 1 H), 4.20 (q, *J* = 7.2 Hz, 2 H), 3.76 (s, 3 H), 1.26 (t, *J* = 7.05 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.9, 159.6, 142.4, 137.8, 132.5, 132.0, 129.9, 129.8, 128.0, 127.3, 127.2, 126.6, 123.2, 120.1, 114.1, 60.5, 55.3, 14.3 ppm; DEPT-135 (75 MHz, $CDCl_3$): δ = 142.5, 132.1, 130.0, 128.1, 127.4, 127.2, 126.7, 123.3, 120.2, 114.1, 60.5, 55.3, 14.3 ppm. $C_{20}H_{20}O_3$ (308.38): calcd. C 77.90, H 6.54; found C 77.98, H 6.69.

(*E*)-Ethyl 3-[2-(3,4-Dimethoxystyryl)phenyl]acrylate (27b): To a solution of (*E*)-2-(3,4-dimethoxystyryl)benzaldehyde[23] (1 g, 3.72 mmol) in dry DCM (30 mL) was added (carbethoxymethylene)triphenylphosphorane (1.68 g, 4.48 mmol), and the resulting mixture was stirred for 30 min. Upon completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure followed by column chromatographic purification (hexane/EA, 9:1) to afford divinylbenzene **27b** (1.20 g, 95 %) as a colorless solid; m.p. 81–83 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 15.9 Hz, 1 H), 7.58 (t, *J* = 8.4 Hz, 2 H), 7.40–7.25 (m, 3 H), 7.10–7.08 (m, 2 H), 6.90–6.86 (m, 2 H), 6.39 (d, *J* = 15.9 Hz, 1 H), 4.28 (q, *J* = 7.05 Hz, 2 H), 3.96 (s, 3 H), 3.91 (s, 3 H), 1.35 (t, *J* = 7.05 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.8, 149.2, 149.0, 142.3, 137.6, 132.5, 132.3, 130.1, 129.9, 127.3, 127.1, 126.7, 123.4, 120.1, 111.1, 109.0, 60.4, 55.9, 55.8, 14.2 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 142.4, 132.5, 130.0, 127.4, 127.2, 126.8, 123.6, 120.2, 111.2, 109.1, 60.5, 55.9, 55.8,

14.3 ppm. $C_{21}H_{22}O_4$ (338.40): calcd. C 74.54, H 6.55; found C 74.33, H 6.73.

(*E*)-Ethyl 4-[2-(4-Methoxystyryl)phenyl]-1*H*-pyrrole-3-carboxylate (28a): To a suspension of *t*BuOK (540 mg, 4.86 mmol) in dry DMF (8 mL) at 0 °C under N_2 was added TOSMIC (0.70 g, 3.56 mmol) in dry DMF (5 mL). The resulting mixture was stirred for 15 min at the same temperature and then treated dropwise with a solution of divinylbenzene **27a** (1 g, 2.05 mmol) in dry DMF (8 mL). When the starting material was consumed (monitored by TLC), the reaction was quenched with ice water (10 mL), and the mixture was extracted with $CHCl_3$ (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford 2-*p*-anisylvinylpyrrole **28a** (0.99 g, 88 %) as a colorless solid; m.p. 172–174 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.58 (s, 1 H), 7.63 (d, *J* = 7.8 Hz, 1 H), 7.45 (s, 1 H), 7.26–7.15 (m, 5 H), 6.91–6.89 (m, 2 H), 6.76–6.74 (m, 2 H), 6.60 (s, 1 H), 3.39 (q, *J* = 7.2 Hz, 2 H), 3.72 (s, 3 H), 0.98 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.8, 159.0, 136.9, 134.2, 131.2, 130.8, 127.9, 127.6, 127.1, 126.4, 126.1, 124.5, 124.3, 119.2, 115.8, 114.0, 59.5, 55.3, 14.0 ppm; DEPT-135 (75 MHz, $CDCl_3$): δ = 131.2, 127.9, 127.6, 127.1, 126.4, 126.1, 124.3, 119.2, 114.0, 59.6, 55.3, 14.0 ppm. $C_{22}H_{21}NO_3$ (347.41): calcd. C 76.06, H 6.09, N 4.03; found C 76.21, H 5.89, N 4.13.

(*E*)-Ethyl 4-[2-(3,4-Dimethoxystyryl)phenyl]-1*H*-pyrrole-3-carboxylate (28b): To a suspension of *t*BuOK (490 mg, 4.43 mmol) in dry DMF (8 mL) at 0 °C under N_2 was added TOSMIC (0.63 g, 3.25 mmol) in dry DMF (5 mL). The mixture was stirred for 15 min at the same temperature and then treated dropwise with a solution of divinyl compound **27b** (1 g, 2.95 mmol) in dry DMF (8 mL). When the starting material was consumed (monitored by TLC), the reaction was quenched with ice water (10 mL), and the mixture was extracted with $CHCl_3$ (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford 2-(3,4-dimethoxyphenyl)pyrrolobenzene **28b** (1.02 g, 92 %) as a colorless solid; m.p. 120–122 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.20 (s, 1 H), 7.71 (d, *J* = 7.5 Hz, 1 H), 7.48 (s, 1 H), 7.33–7.24 (m, 3 H), 7.08–6.91 (m, 4 H), 6.80 (d, *J* = 8.1 Hz, 1 H), 6.64 (s, 1 H), 4.08 (q, *J* = 7.2 Hz, 2 H), 3.86 (s, 6 H), 1.09 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.1, 148.9, 148.5, 136.7, 134.4, 131.3, 131.2, 128.1, 127.1, 126.6, 126.5, 124.5, 124.4, 124.2, 119.5, 119.4, 115.3, 111.3, 109.4, 59.6, 55.9, 55.8, 14.0 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 131.2, 128.1, 127.1, 126.6, 126.5, 124.5, 124.4, 119.5, 119.4, 111.2, 109.3, 59.6, 55.9, 55.8, 14.0 ppm. $C_{23}H_{23}NO_4$ (377.44): calcd. C 73.19, H 6.14, N 3.71; found C 73.32, H 6.02, N 3.52.

Ethyl 4-(4-Methoxyphenyl)-3*H*-benzo[*e*]indole-1-carboxylate (29a): To a solution of 2-*p*-anisylvinylpyrrole **28a** (0.1 g, 0.29 mmol) in dry benzene (10 mL) at room temperature were added DDQ (66 mg, 0.29 mmol) and PTSA (50 mg, 0.29 mmol), and the reaction mixture was stirred at room temperature for 1 h. Upon completion of the reaction (monitored by TLC), the mixture was poured into water (20 mL) and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford benzoindole **29a** (79 mg, 79 %) as a brown solid; m.p. 140–142 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.64 (d, *J* = 8.4 Hz, 1 H), 8.88 (s, 1 H), 7.91 (d, *J* = 3.0 Hz, 1 H), 7.83 (d, *J* = 7.8 Hz, 1 H), 7.55–7.38 (m, 5 H), 6.99 (d, *J* = 8.7 Hz, 2 H), 4.35 (q, *J* = 7.2 Hz, 2 H), 3.80 (s, 3 H), 1.36 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.3, 159.5, 132.5, 130.9, 130.3, 130.2, 129.6, 128.4, 127.8, 126.8, 126.5, 125.9, 124.5, 124.3, 120.8, 114.8, 112.2, 60.1, 55.4, 14.5 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 130.2, 129.6, 128.4, 126.8, 125.9, 124.5, 124.3, 114.8, 60.1, 55.4, 14.5 ppm. HRMS (EI): calcd. for $C_{22}H_{19}NO_3$ $[M]^+$ 345.1365; found 345.1335.

Ethyl 4-(3,4-Dimethoxyphenyl)-3*H*-benzo[*e*]indole-1-carboxylate (29b): To a solution of 2-(3,4-dimethoxyphenyl)pyrrolobenzene **28b** (0.1 g, 0.26 mmol) in dry benzene (10 mL) at 0 °C were added DDQ (60 mg, 0.26 mmol) and PTSA (45 mg, 0.26 mmol), and the resulting mixture was stirred at room temperature for 2 h. Upon completion of the reaction (monitored by TLC), the mixture was poured into water (20 mL) and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was remove followed by column chromatographic purification (hexane/EA, 9:1) to afford benzoindole **29b** (75 mg, 75 %) as a brown solid; m.p. 228–230 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.75 (d, *J* = 8.1 Hz, 1 H), 9.09 (s, 1 H), 8.04 (d, *J* = 2.1 Hz, 1 H), 7.94 (d, *J* = 7.8 Hz, 1 H), 7.65–7.49 (m, 3 H), 7.19–7.03 (m, 3 H), 4.45 (q, *J* = 7.05 Hz, 2 H), 3.97 (s, 3 H), 3.95 (s, 3 H), 1.46 (t, *J* = 7.05 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 149.7, 149.0, 132.4, 130.8, 130.7, 130.3, 128.4, 127.8, 126.8, 126.7, 125.9, 124.5, 124.2, 120.8, 120.6, 112.2, 111.9, 111.8, 60.1, 56.1, 56.0, 14.5 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 130.3, 128.4, 126.8, 125.9, 124.6, 124.2, 120.6, 111.8, 111.7, 60.1, 56.1, 56.0, 14.5 ppm. HRMS (EI): calcd. for $C_{23}H_{21}NO_4$ $[M]^+$ 375.1471; found 375.1445.

Ethyl 2,5-Dibromo-4-(4-methoxyphenyl)-3*H*-benzo[*e*]indole-1-carboxylate (30a): To a solution of 2-*p*-anisylvinylpyrrole **28a** (0.1 g, 0.29 mmol) in dry THF (10 mL) at 0 °C was added NBS (0.15 g, 0.87 mmol), and the resulting mixture was stirred at room temperature for 30 min. Upon completion of the reaction (monitored by TLC), the mixture was poured into cold water (20 mL) and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford dibromobenzoindole **30a** (115 mg, 79 %) as a colorless solid; m.p. 185–187 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.95 (d, *J* = 7.8 Hz, 1 H), 8.42–8.39 (m, 2 H), 7.55–7.48 (m, 2 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.03 (d, *J* = 8.1 Hz, 2 H), 4.45 (q, *J* = 7.05 Hz, 2 H), 3.84 (s, 3 H), 1.41 (t, *J* = 7.05 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.9, 159.8, 132.9, 131.0, 129.0, 128.9, 128.7, 127.4, 127.0, 126.8, 125.7, 125.5, 120.3, 120.0, 114.6, 112.2, 112.0, 61.1, 55.4, 14.3 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 131.0, 128.7, 126.8, 125.8, 125.5, 114.6, 61.1, 55.4, 14.3 ppm. HRMS (EI): calcd. for $C_{22}H_{17}Br_2NO_3$ $[M]^+$ 500.9575; found 500.9550.

Ethyl 2,5-Dibromo-4-(2-bromo-4,5-dimethoxyphenyl)-3*H*-benzo[*e*]indole-1-carboxylate (30b): To a solution of 2-(3,4-dimethoxyphenyl)pyrrolobenzene **28b** (0.1 g, 0.26 mmol) in dry THF (10 mL) at room temperature was added NBS (0.19 g, 1.05 mmol). The resulting mixture was stirred at room temperature for 1 h and then heated at reflux for 2 h. Upon completion of the reaction (monitored by TLC), the mixture was poured into ice water (20 mL) and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried with Na_2SO_4. The solvent was removed followed by column chromatographic purification (hexane/EA, 9:1) to afford dibromobenzoindole **30b** (99 mg, 62 %) as a brown solid; m.p. 130–132 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.34 (s, 1 H), 7.72 (d, *J* = 8.4 Hz, 1 H), 7.23–7.19 (m, 1 H), 7.03–6.87 (m, 3 H), 6.64 (d, *J* = 0.9 Hz, 1 H), 4.45 (q, *J* = 7.2 Hz, 2 H), 3.90 (s, 3 H), 3.83 (s, 3 H), 1.39 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.2, 150.7, 149.2, 138.8, 135.0, 134.7, 131.1, 131.0 130.3, 127.9, 127.0, 123.5, 122.8, 122.7, 118.1, 112.2, 111.1, 110.2, 109.2, 60.6, 56.2, 56.1, 14.5 ppm. DEPT-135 (75 MHz, $CDCl_3$): δ = 131.0, 127.0, 122.8, 122.7, 112.2, 111.1, 60.6, 56.2, 56.1, 14.5 ppm. HRMS (EI): calcd. for $C_{23}H_{18}Br_3NO_4$ $[M]^+$ 608.8786; found 608.8786.

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H and ^{13}C NMR spectra as well as DEPT 135 spectra of the prepared compounds.

Acknowledgments

Financial assistance from the Council of Scientific and Industrial Research (CSIR), New Delhi [02(0214)/14-EMR-II] is acknowledged. P. R. thanks the University Grants Commission (UGC), New Delhi for the fellowship. The authors thank the Department of Science and Technology – Fund for Improvement of Science and Technology (DST-FIST) for the high resolution NMR facility.

Keywords: Synthetic methods · Cyclization · Nitrogen heterocycles · Fused-ring systems · Natural products

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Received: June 2, 2016
Published Online: August 5, 2016

