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Facile One-Pot Synthesis of 6-Monosubstituted and 6,12-Disubstituted 5,11-Dihydroindolo[3,2-*b*]carbazoles and Preparation of Various Functionalized Derivatives

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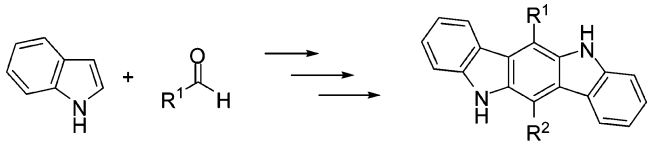

A facile three-stage, one-pot approach for the synthesis of a variety of novel 6-monosubstituted and 6,12-disubstituted 5,11-dihydroindolo[3,2-*b*]carbazoles, in moderate to good yields (20−50%), has been developed, based on the condensation of an indole and an aldehyde with a catalytic amount of iodine, followed by an acid-catalyzed intramolecular cyclization with an ortho ester. The parent indolo[3,2-*b*]-carbazoles (ICZs) could be converted to various functional derivatives. Both N-alkylation and N-arylation were successfully accomplished, and azo-coupling, formylation, as well as bromination were performed in a regioselective way leading to the formation of novel functional 6,12-disubstituted indolo[3,2-*b*]-carbazoles. Starting from a monoformylated indolocarbazole, novel benzimidazolyl-substituted derivatives were synthesized, while Suzuki cross-couplings on a monobrominated building block afforded a novel pathway toward functionally arylated ICZs.

Introduction

Over the years, interest in electro- and photoactive molecules has greatly increased because of their utilization as active components in a number of electronic devices, such as light emitting diodes (LEDs),[1] field effect transistors (FETs),[2] and photovoltaic cells.[3] Organic materials are very attractive for incorporation in such devices because of their good mechanical properties, low cost, and tunable electrical and optical properties (by structural modifications), and the main focus nowadays is on the optimization of their stability, processability, and charge transport properties. Because of their thermal stabilities, intense luminescence, and reversible oxidation processes, (oligo)-carbazole compounds are widely being used in molecular electronics.[4] Much less attention has, however, been devoted to the indolo[3,2-*b*]carbazole (ICZ) analogues, despite their promising electronic characteristics, mainly because of the lack of simple synthetic procedures toward variously functionalized derivatives. In 1999, Hu et al. reported indolo[3,2-*b*]carbazole derivative **1a**, which shows an unusual atropisomerism and excellent hole-transport properties in organic LEDs.[5] In 2004, the first organic FET (OFET) using ICZ **1b** as an active layer was successfully fabricated.[6] N,N-Disubstituted indolo[3,2-*b*]-carbazoles and polyindolo[3,2-*b*]carbazoles have also been reported recently as new classes of high-performance p-channel

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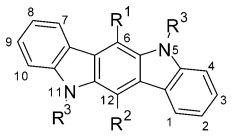
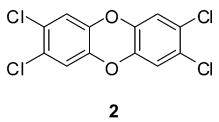
semiconductors, and they could be used to fabricate high-mobility organic thin-film transistors (OTFTs).[7]



1a R^1=R^2=H, R^3=Naphthyl
1b R^1=R^2=Methyl, R^3=Octyl
1c R^1=CHO, R^2=R^3=H
1d R^1=R^2=CHO, R^3=H



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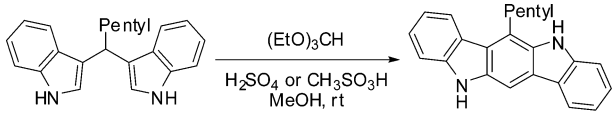
Indolo[3,2-*b*]carbazoles have also gained significant importance because of their high affinity to the receptor for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin **2** (TCDD), which is called aryl hydrocarbon or Ah receptor and involved in organogenesis, in detoxification of endo- and xenobiotics, and in mediating diverse organ-specific toxic responses of dioxins.[8] 6-Formylindolo[3,2-*b*]carbazole (**1c**) and 6,12-diformylindolo[3,2-*b*]carbazole (**1d**) have been demonstrated as extremely efficient ligands for the Ah receptor, especially ICZ **1c** which binds 5−8 times as strong to the receptor as TCDD itself.[9]

Over the decades, a number of methods for the preparation of indolo[3,2-*b*]carbazoles have been developed,[10] such as (i) Pt-mediated cyclodehydrogenation of *N*,*N*′-diphenyl-*p*-phenylenediamine,[11a] (ii) double Fischer indolization of cyclohexane-1,4-dione bis(phenylhydrazone),[11b] (iii) condensation of indole and formaldehyde in the presence of a strong acid, air, and sensitizers,[11c] (iv) Lewis acid catalyzed dimerization of 1-(1-benzotriazol-1-yl-alkyl)indoles,[11d] (v) intramolecular cyclization of 2-(1*H*-indol-3-yl-methyl)-1*H*-indole carbaldehyde,[11e] (vi) condensation of indole with aliphatic aldehydes under acidic conditions,[11f] and (vii) cyclization of 3,3′-bis(indolyl)methanes[11g] or 2,3′-bis(indolyl)methanes[11h] via an acid-catalyzed reaction in the presence of triethyl orthoformate. However, most of these methods involve multistep routines starting from indoles to afford the corresponding ICZs in low overall yields. Moreover, the poor solubility of these unsubstituted or symmetrically disubstituted ICZs in organic solvents makes further modifications very difficult.[9,12]

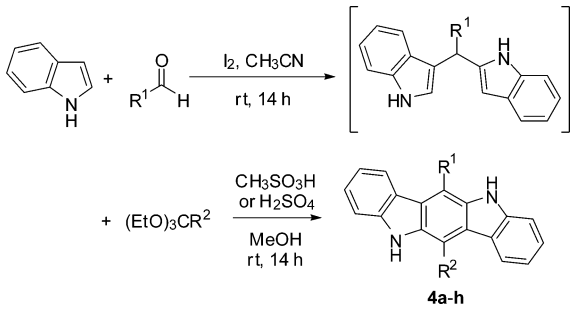
Recently, we have communicated our preliminary results on an efficient three-stage one-pot approach toward 6-monosubstituted 5,11-dihydroindolo[3,2-*b*]carbazoles.[13] The better solubility of these asymmetrical ICZs allowed easier structural modifications. Herein, we wish to report an extension of our method to the synthesis of both 6-monosubstituted and asymmetrically 6,12-disubstituted ICZs. Moreover, a variety of functionalized 6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole derivatives have been prepared via N-alkylation, N-arylation, azo-coupling, formylation, and bromination. Regioselectively monoformylated and monobrominated ICZs were proven to be useful starting materials for further modifications of the chromophore structures, through the preparation of benzimidazolyl-substituted ICZs and Suzuki cross-coupling reactions, respectively.

SCHEME 1. Synthesis of Monosubstituted ICZ 4c



3 **4c**

SCHEME 2. Synthesis of 6-Monosubstituted and 6,12-Disubstituted ICZs



4a-h

Results and Discussion

In 2003, Bandgar and Shaikh reported the reaction of indoles with various aldehydes or ketones using iodine as a catalyst to afford 3,3′-bis(indolyl)methanes in excellent yields.[14] On the basis of their method, 3,3′-bis(indolyl)hexane (**3**) could be obtained in 70% yield by condensation of indole and hexanal in acetonitrile with a catalytic amount of I_2 (0.1 equiv). When compound **3** was treated with triethyl orthoformate in methanol using either sulfuric acid or methanesulfonic acid as a catalyst (Scheme 1), 6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (**4c**) was formed only in trace amounts (as evidenced by MS analysis of the crude reaction mixture).

Interestingly, however, we discovered that, if the condensations of indole and aldehyde were carried out for a longer time (14 h), the 3,3′-bis(indolyl)methanes isomerized to 2,3′-bis(indolyl)methanes (as monitored by ^{1}H NMR spectroscopy). Such isomerizations, involving acid-induced cleavage of one of the indoles from the 3,3′-bis(indolyl)methanes and formation of an indoleinium intermediate followed by recombination, have been described previously.[15] Fourteen hours is indeed optimal reaction time, and shorter or longer reaction time gave much lower yields of **4c**.[13] Because of their instability, the 2,3′-isomers were not purified after workup, and acid-catalyzed intramolecular cyclizations were accomplished directly by treating the crude 2,3′-isomers with different ortho esters in the presence of sulfuric acid or methanesulfonic acid as a catalyst to afford the corresponding 6-monosubstituted or 6,12-disubstituted ICZs in acceptable overall yields (Scheme 2, Table 1).

When sulfuric acid was used as a catalyst, the overall yield of the reaction was much lower than when methanesulfonic acid was used (Table 1, entry 3). The optimum reaction conditions that were developed for the cyclization step involved 1 equiv

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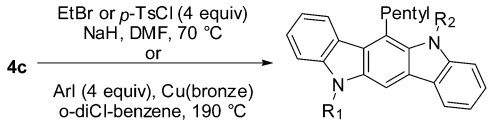
TABLE 1. Three-Stage, One-Pot Synthesis of 6-Monosubstituted and 6,12-Disubstituted 5,11-Dihydroindolo[3,2-*b*]carbazoles

entry	ICZ	R^1	R^2	yield (%)
1	**4a**	methyl	H	46[a]
2	**4b**	isobutyl	H	50[a]
3	**4c**	pentyl	H	47[a] (20)[b]
4[c]	**4d**	undecyl	H	36[a]
5[d]	**4e**	phenyl	H	20[a]
6	**4f**	pentyl	methyl	23[a] (10)[b]
7	**4g**	pentyl	ethyl	30[a] (30)[b]
8	**4h**	pentyl	phenyl	23[b] (9)[a]

[a] Using CH_3SO_3H as a catalyst. [b] Using H_2SO_4 as a catalyst. [c] Using CH_2Cl_2 as solvent. [d] 30 min reaction time for the first step.

SCHEME 3. Synthesis of N-Substituted ICZs

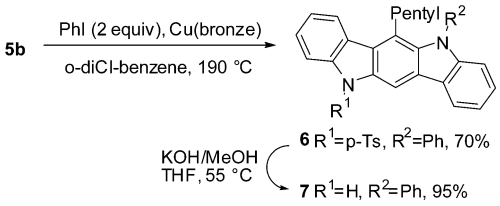


5a $R^1=R^2=$Et, 83%
5b $R^1=$*p*-Ts,$R^2=$H, 60%
5c $R^1=R^2=$Ph, 70%
5d $R^1=R^2=$2-Thienyl, 53%
5e $R^1=R^2=$4-NO_2-Ph, 65%

of 2,3′-bis(indolyl)methane, 1 equiv of the ortho ester, and 0.2 equiv of methanesulfonic acid in methanol at room temperature for 14 h. On applying these conditions, a number of 6-monosubstituted ICZs were obtained in comparable yields (36−50%), except for 6-phenyl-substituted derivative **4e** (20%, entry 5). Aromatic aldehydes are less suitable for the formation of ICZs because the corresponding 3,3′- and 2,3′-isomers are less stable, quickly forming an insoluble precipitate that is difficult to characterize. Asymmetrically 6,12-disubstituted ICZs were also successfully obtained using orthoacetate, orthopropionate, or orthobenzoate esters. Because of their lower reactivity compared to that of the orthoformate ester, the overall yields were somewhat lower than those obtained for the 6-monosubstituted ICZs. To prepare ICZ **4h** (R^2 = phenyl) in an acceptable yield (23%), sulfuric acid had to be used (entry 8). Compounds **4a**−**e** were crystallized from the reaction medium. Investigation of the mother liquor of the crystallization showed the presence of a trace amount of further **4a**−**e** together with highly colored tarry material. However, no substantial amount of the indolocarbazoles **4a**−**e** could be obtained after chromatographic purification.

Compared to the previously reported unsubstituted or symmetrically substituted ICZs in literature, the better solubility of these asymmetrical analogues **4a**−**h** in apolar organic solvents allows for easy further structural modifications. Since N-alkylated derivatives of ICZs have attracted considerable interest,[6,7] we first explored N,N-disubstitution reactions. 6-Monosubstituted ICZ **4c** was chosen as the substrate of preference for the investigation of ICZ derivatizations because of its high yield and good solubility. N,N-Diethylation of **4c** was performed with bromoethane (4 equiv) in DMF at 70 °C with sodium hydride as a base to afford compound **5a** in 83% yield (Scheme 3). On the other hand, tosylation of **4c** under similar reaction conditions was found to occur at only one of the two nitrogen atoms (opposite to the pentyl chain) to produce monotosylated derivative **5b** selectively in 60% yield (Scheme 3). Hence, the reaction of **4c** with *p*-toluenesulfonyl chloride is highly regioselective. This remarkable result can be employed to prepare

SCHEME 4. Synthesis of N-Monoarylated ICZ 7



both N-monosubstituted and asymmetrically N,N-disubstituted ICZ derivatives (see later paragraphs).

The Ullmann-type coupling of aryl halides with indolocarbazoles is a straightforward and inexpensive approach to obtain N-arylated ICZs. Under the Ullmann coupling conditions we have previously reported for the synthesis of oligocarbazoles,[16] the desired N,N-diarylated products **5c**−**e** (Scheme 3) were obtained in good yields (53−70%).

To synthesize an N-monoarylated derivative, ICZ **4c** was treated with only 1 equiv of iodobenzene under the same Ullmann coupling conditions as described earlier. The reaction gave in all cases only N,N-diarylated derivative **5c** (together with starting material **4c**). To solve this problem, we designed an alternative synthetic strategy. First, N-arylation of monotosyl derivative **5b** was performed to obtain the corresponding monoarylated product **6** in 70% yield. Afterward, deprotection of the *p*-tosyl group of **6** could be effected under basic conditions to afford the desired N-monoarylated ICZ **7** in 95% yield (Scheme 4).

Next, formylation of **4c** was investigated under traditional Vilsmeier conditions ($POCl_3$/DMF). With a large excess of Vilsmeier reagent, we observed both C- and N-formylated products and purification of the complex reaction mixture was not straightforward. However, on using only 1.2 equiv of Vilsmeier reagent in 1,2-dichloroethane under reflux conditions, 6-formyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (**8**) was selectively obtained and isolated in 50% yield (Scheme 5).

Benzimidazoles are very useful intermediates or subunits for the development of molecules with pharmaceutical or biological interest.[17] Moreover, polybenzimidazoles have been reported as electroactive and conducting polymers and widely studied as a fuel-cell membrane.[18] Using a known method reported by Black et al.,[19] we converted ICZ **8** to benzimidazoles **9a**−**c** in acceptable to good yields (48−70%) by reacting the aldehyde with *o*-phenylenediamines in DMF at 120−150 °C (Scheme 5).

Similar to the C-formylation, azo-coupling reactions have also been achieved regioselectively at the 12-position. On reacting ICZ **4c** with arenediazonium tetrafluoroborates in THF with pyridine as a base, diaza-indolocarbazoles **10a**−**c** were synthesized in 28−42% yield (Scheme 6).

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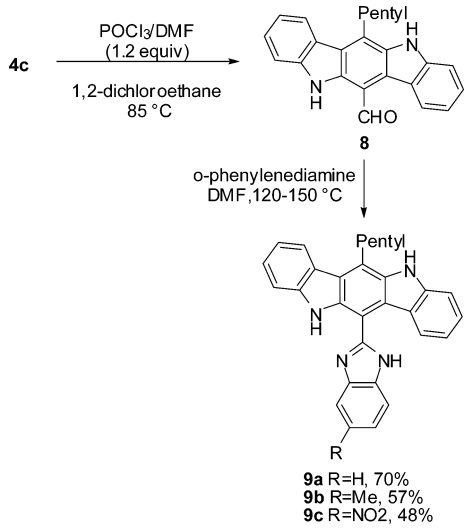
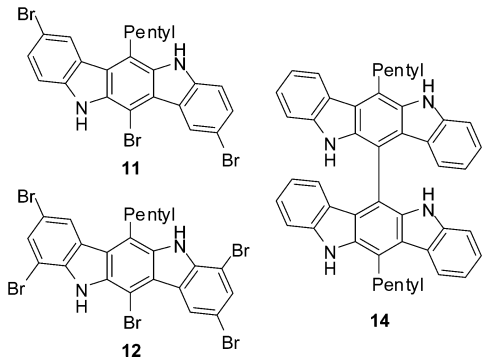
SCHEME 5. Synthesis of 6-Formyl ICZ 8 and Benzimidazolyl Derivatives 9a−c

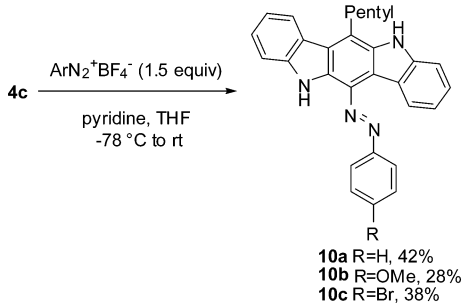


In contrast to formylation and azo-coupling, bromination of ICZ **4c** with *N*-bromosuccinimide (NBS) or bromine was not selective, and brominated products depended on the reaction conditions, such as the amount of halogenation reagent and reaction temperature. Tribrominated ICZ **11** and pentabrominated ICZ **12** were obtained on treating **4c** with 3 equiv of NBS in dichloromethane (at room temperature, rt) or 5 equiv of Br_2 in acetic acid (under reflux conditions), respectively.[13] On the other hand, the 2,8-dibrominated compound **13** was synthesized with our one-pot approach starting from 5-bromoindole. Initially, the reaction failed because of the very slow isomerization of the corresponding 3,3′-bis(indolyl)hexane to the 2,3′-isomer. However, when the more active hydroiodic acid was used as a catalyst for the condensation reaction, dibromo derivative **13** was obtained in 26% overall yield (Scheme 7).

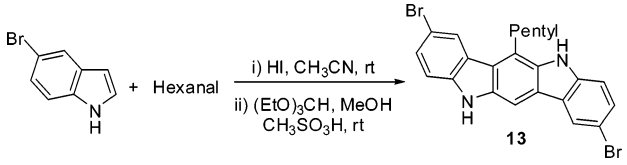


Inspired by our preceding work on the regioselective chlorination of ICZ **4c** with anhydrous ferric chloride,[20] we have examined a similar method for the bromination of **4c** with ferric bromide. Our previous study in fact showed that a chlorinated ICZ derivative was obtained with anhydrous ferric chloride, whereas the use of ferric chloride hexahydrate resulted in an oxidative dimerization. Contrary to our expectations, an opposite result was obtained with anhydrous ferric bromide. The dimerization product **14** was obtained as the main compound on using anhydrous ferric bromide in chloroform, and only a small amount of the desired brominated compound **15** was observed (as indicated by MS analysis). Because of the high hygroscopicity of anhydrous ferric bromide, we envisaged that water was the vital factor for the bromination of ICZ **4c**. Therefore, the reaction was carried out in a solvent mixture of chloroform and water. The desired ICZ derivative **15** was now formed, together with a trace amount of the dimer **14**, but starting material **4c** was only partially consumed after reaction overnight. Finally, under optimized reaction conditions (1 equiv of **4c**, 3 equiv of anhydrous $FeBr_3$, homogeneous solvent mixture THF/H_2O, 5:2), the regioselectively brominated ICZ derivative **15** was obtained in an excellent yield of 96% (Scheme 8).

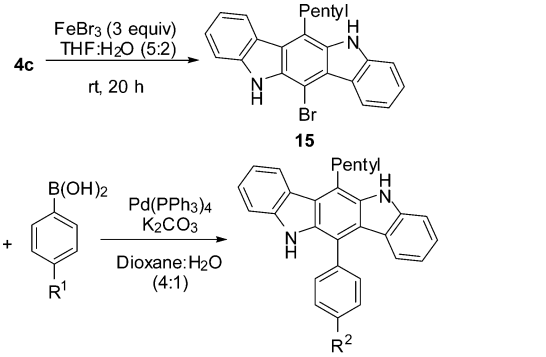
SCHEME 6. Synthesis of Arylazo Derivatives 10a−c



SCHEME 7. Synthesis of Dibromo ICZ 13



SCHEME 8. Synthesis of Monobrominated ICZ 15 and Suzuki Coupling Reactions



Finally, Suzuki coupling reactions of ICZ **15** with various phenylboronic acids were studied under standard reaction conditions (0.5 mol % $Pd(PPh_3)_4$ as a catalyst and K_2CO_3 as a base). The ideal solvent (mixture) for the reaction was explored, for example, THF, THF/H_2O (4:1), dioxane/EtOH (4:1), and dioxane/H_2O (4:1). The more polar and higher boiling point solvent mixture dioxane/H_2O (4:1) gave the best yields for the desired products **4h** and **16a**,**b** (Scheme 8). Indeed, **4h** is better prepared by this method than by the condensation of 2,3′-bis(indolyl)hexane with triethyl orthobenzoate, and the interesting

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dimer **16b** would be very difficult to prepare with any other reported methods.

Conclusions

In summary, an easy and efficient three-stage, one-pot synthetic approach toward various 6-monosubstituted and 6,-12-disubstituted 5,11-dihydroindolo[3,2-*b*]carbazoles has been developed. Iodine was found to be a highly convenient catalyst, promoting the electrophilic reaction of indoles with aliphatic aldehydes under mild conditions to afford 2,3′-bis(indolyl)-alkanes, which were converted to the corresponding 6-mono-substituted or 6,12-disubstituted ICZs with ortho esters using methanesulfonic acid as a catalyst. Enhanced solubility and stability toward oxidative degradation of the novel ICZs allowed for easy modification of the parent indolocarbazole skeleton. Thus, ICZ **4c** was substituted under different conditions, including N-alkylation, N-tosylation, copper-catalyzed Ullmann coupling, Vilsmeier reaction, azo-coupling, and bromination. More complex functional ICZs, such as benzimidazole derivatives **9a**−**c** and dimer **16b**, were obtained on the basis of regioselectively C-formylated and brominated compounds.

Experimental Section

One-Pot Approach for the Synthesis of 6-Monosubstituted and 6,12-Disubstituted ICZs (General Procedure 1). To a solution of indole (3.7 mmol) and the appropriate aldehyde (1.8 mmol) in CH_3CN (5 mL), I_2 (0.37 mmol) was added, and the reaction mixture was stirred at rt for 14 h. Na_2SO_3 (aq, saturated) was added, and the solution was extracted with EtOAc. After concentration of the organic layer, the crude product and the appropriate ortho ester (1.8 mmol) were dissolved in MeOH (2 mL). Methanesulfonic acid (0.37 mmol) was added, and the reaction mixture was stirred overnight at rt. The formed precipitate was filtered off, carefully dried in vacuum until constant weight, and, if required, purified by column chromatography.

6-Isobutyl-5,11-dihydroindolo[3,2-*b*]carbazole (4b). This compound was prepared according to General Procedure 1 using indole (0.43 g, 3.7 mmol), 3-methyl butyraldehyde (0.16 g, 1.8 mmol), and triethyl orthoformate (0.27 g, 1.8 mmol). The precipitate was filtered off and carefully dried to yield **4b** (0.29 g, 50%) as an off-white solid. Mp: 294−296 °C. IR (neat, cm^{-1}): 3447, 3401, 2950, 2863, 1612, 1583, 1526, 1459. ^1H NMR (300 MHz, DMSO-d_6): δ 1.05 (d, J = 6.3 Hz, 6H), 2.27−2.31 (m, 1H), 3.40 (br, 2H), 7.09−7.18 (m, 2H), 7.34−7.39 (m, 2H), 7.47−7.51 (m, 2H), 7.98 (s, 1H), 8.10−8.18 (m, 2H), 10.87 (s, 1H), 11.06 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 23.2 (CH_3), 29.2 (CH_3), 37.7 (CH_2), 98.9 (CH), 111.2 (CH), 111.4 (CH), 118.1, 118.3 (CH), 118.5 (CH), 121.1 (CH), 121.3, 122.9 (CH), 123.5, 123.6, 125.6 (CH), 126.2 (CH), 135.5, 136.4, 142.0, 142.1. HRMS (EI) calcd for $C_{22}H_{20}N_2$ $[M]^+$, 312.1627; found, 312.1621.

6-Phenyl-5,11-dihydroindolo[3,2-*b*]carbazole (4e). This compound was prepared according to General Procedure 1 using indole (0.46 g, 3.9 mmol), benzaldehyde (0.21 g, 1.9 mmol), and triethyl orthoformate (0.29 g, 1.9 mmol). The first step was carried out at rt for 30 min. The precipitate was filtered off and carefully dried to yield **4e** (0.13 g, 20%) as a brown solid. Mp: 278−280 °C. IR (neat, cm^{-1}): 3397, 1611, 1528, 1456. ^1H NMR (300 MHz, DMSO-d_6): δ 6.86 (t, J = 7.49 Hz, 1H), 7.12 (d, J = 7.92 Hz, 1H), 7.17 (t, J = 7.49 Hz, 1H), 7.32 (t, J = 7.32 Hz, 1H), 7.38 (t, J = 7.40 Hz, 1H), 7.48−7.51 (m, 2H), 7.64−7.77 (m, 5H), 8.20 (s, 1H), 8.26 (d, J = 7.75 Hz, 1H), 10.48 (s, 1H), 11.22 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 100.1 (CH), 110.8 (CH), 111.4 (CH), 117.6 (CH), 118.0, 118.1 (CH), 120.3, 120.6 (CH), 121.6 (CH), 122.6, 122.87, 122.93, 125.5 (CH), 125.8 (CH), 128.3 (CH), 129.6 (CH), 130.3 (CH), 133.7, 135.7, 137.5, 141.7, 141.9. HRMS (EI) calcd for $C_{24}H_{16}N_2$ $[M]^+$, 332.1314; found, 332.1313.

6-Methyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (4f). This compound was prepared according to General Procedure 1 using indole (0.50 g, 4.3 mmol), *n*-hexanal (0.21 g, 2.1 mmol), and triethyl orthoacetate (0.35 g, 2.2 mmol). The reaction mixture was purified by column chromatography on basic alumina (eluent EtOAc/heptane, 1:4) to yield **4f** (0.17 g, 23%) as an off-white solid. Mp: 260−261 °C. IR (neat, cm^{-1}): 3415, 2929, 2855, 1611, 1535, 1463, 1378. ^1H NMR (300 MHz, DMSO-d_6): δ 0.88 (t, J = 7.27 Hz, 3H), 1.32−1.44 (m, 2H), 1.50−1.60 (m, 2H), 1.76−1.86 (m, 2H), 3.01 (s, 3H), 3.44−3.49 (m, 2H), 7.11−7.17 (m, 2H), 7.38 (t, J = 7.8 Hz, 2H), 7.50−7.53 (m, 2H), 8.11 (d, J = 7.9 Hz, 1H), 8.24 (d, J = 7.81 Hz, 1H), 10.93 (s, 1H), 10.97 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.4 (CH_3), 14.8 (CH_3), 22.7 (CH_2), 28.5 (CH_2), 29.3 (CH_2), 32.0 (CH_2), 110.3, 110.7 (CH), 110.8 (CH), 115.5, 117.9 (CH), 118.1 (CH), 120.0, 120.7, 122.2 (CH), 122.5 (CH), 123.2, 123.9, 125.1 (CH), 134.4, 135.0, 141.6. HRMS (EI) calcd for $C_{24}H_{24}N_2$ $[M]^+$, 340.1940; found, 340.1944.

2,8-Dibromo-6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (13). This compound was prepared according to General Procedure 1 using 5-bromoindole (0.31 g, 1.6 mmol), *n*-hexanal (0.08 g, 0.8 mmol), four drops of HI as a catalyst, and triethyl orthoformate (0.12 g, 0.8 mmol). The reaction mixture was purified by column chromatography (silica, eluent EtOAc/heptane, 1:4) to yield **13** (0.10 g, 26%) as a slightly yellow solid. Mp: 265−267 °C. IR (neat, cm^{-1}): 3420, 3370, 1601, 1528, 1452, 1412, 1284. ^1H NMR (300 MHz, DMSO-d_6): δ 0.90 (t, J = 6.75 Hz, 3H), 1.41−1.43 (m, 2H), 1.55 (br, 2H), 1.80 (br, 2H), 3.44 (br, 3H), 7.44−7.50 (m, 4H), 8.08 (s, 1H), 8.20 (s, 1H), 8.45 (s, 1H), 11.18 (s, 1H), 11.39 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.4 (CH_3), 22.5 (CH_2), 28.5 (CH_2), 28.7 (CH_2), 31.9 (CH_2), 99.2 (CH), 109.9, 112.7 (CH), 112.8 (CH), 119.0, 120.0, 122.3, 123.4 (CH), 124.4 (CH), 124.5, 125.0, 127.7 (CH), 128.3 (CH), 134.8, 136.4, 140.29, 140.36. HRMS (EI) calcd for $C_{23}H_{20}{}^{79}Br_2N_2$ $[M]^+$, 481.9992; found, 481.9993.

N-Alkylation of 6-Pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (4c) (General Procedure 2). To a flame-dried, N_2-flushed, round-bottomed flask containing a solution of **4c** (1.5 mmol) in dry THF (10 mL), cooled to −20 °C, NaH (15 mmol) was added portionwise. After the addition of alkyl halide (6 mmol), the mixture was allowed to warm slowly to rt and was then heated at 70 °C overnight under N_2 atmosphere. The reaction mixture was cooled to rt, H_2O was added, and the solution was extracted with EtOAc. The organic extracts were combined, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude residue was purified by column chromatography.

5,11-Diethyl-6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (5a). This compound was prepared according to General Procedure 2 using **4c** (2.0 g, 6.1 mmol), NaH (60% in mineral oil, 2.4 g, 61 mmol), and bromoethane (2.7 g, 24.8 mmol). The crude residue was dispersed in *n*-pentane (40 mL), and the resulting precipitate was filtered off and carefully dried to give **5a** (1.94 g, 83%) as a yellow solid. Mp: 144−145 °C. IR (neat, cm^{-1}): 2963, 2929, 1608, 1506, 1451, 1417. ^1H NMR (300 MHz, DMSO-d_6): δ 0.94 (t, J = 7.25 Hz, 3H), 1.33−1.51 (m, 8H), 1.62−1.68 (m, 2H), 1.88 (br, 2H), 3.61 (br, 2H), 4.49−4.59 (m, 4H), 7.16−7.24 (m, 2H), 7.43−7.48 (m, 2H), 7.54−7.61 (m, 2H), 8.17 (d, J = 7.93 Hz, 1H), 8.24 (s, 1H), 8.27 (d, J = 7.69 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 13.7 (CH_3), 14.4 (CH_3), 15.3 (CH_3), 22.4 (CH_2), 28.8 (CH_2), 30.2 (CH_2), 31.9 (CH_2), 37.2 (CH_2), 39.9 (CH_2), 97.3 (CH), 108.9 (CH), 109.3 (CH), 118.5 (CH), 118.6 (CH), 120.0, 120.5 (CH), 121.1, 122.5 (CH), 122.6, 123.0, 124.2, 125.4 (CH), 126.3 (CH), 133.1, 135.7, 141.1, 142.5. HRMS (EI) calcd for $C_{27}H_{30}N_2$ $[M]^+$, 382.2409; found, 382.2406.

N-Arylation of 6-Pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (4c) via Ullmann Coupling (General Procedure 3). A solution of **4c** (1 mmol), K_2CO_3 (2 mmol), iodoarene (4 mmol), and copper bronze (2.4 mmol) in *o*-dichlorobenzene (7 mL) was heated

overnight at 190 °C. The reaction mixture was allowed to cool to rt, and $CHCl_3$ (20 mL) was added. The mixture was filtered, and the filtrate was concentrated. To the residue, MeOH (20 mL) was added, and the formed precipitate was filtered off and purified by column chromatography.

6-Pentyl-5,11-diphenyl-5,11-dihydroindolo[3,2-*b*]carbazole (5c). This compound was prepared according to General Procedure 3 using **4c** (0.33 g, 1 mmol), K_2CO_3 (0.28 g, 2 mmol), iodobenzene (0.82 g, 4 mmol), and copper bronze (1.5 g, 2.4 mmol). Column chromatographic purification (silica, eluent EtOAc/heptane, 3:7) yielded **5c** (0.34 g, 70%) as a slightly yellow solid. Mp: 183−185 °C. IR (neat, cm^{-1}): 2922, 2854, 1592, 1496, 1448, 1415. ^1H NMR (300 MHz, $CDCl_3$): δ 0.84 (t, 3H), 1.07−1.26 (m, 4H), 1.63 (br, 2H), 3.03 (br, 2H), 6.93 (d, J = 8.10 Hz, 1H), 7.15−7.20 (m, 1H), 7.27−7.34 (m, 1H), 7.38−7.40 (m, 2H), 7.52−7.59 (m, 6H), 7.66−7.68 (m, 4H), 7.91 (s, 1H), 8.06 (d, J = 7.51 Hz, 1H), 8.13 (d, J = 8.01 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.6 (CH_3), 22.9 (CH_2), 28.8 (CH_2), 29.4 (CH_2), 32.6 (CH_2), 97.8 (CH), 109.7 (CH), 110.4 (CH), 119.5 (CH), 119.7 (CH), 120.3 (CH), 121.8, 122.2, 123.1 (CH), 123.6, 124.0, 124.9, 125.6 (CH), 126.4 (CH), 127.9 (CH), 128.3 (CH), 128.8 (CH), 130.0 (CH), 130.4 (CH), 136.0, 137.9, 138.6, 141.6, 142.7, 145.3. HRMS (EI) calcd for $C_{35}H_{30}N_2$ $[M]^+$, 478.2409; found, 478.2413.

6-Pentyl-5-phenyl-5,11-dihydroindolo[3,2-*b*]carbazole (7). The first step was performed according to General Procedure 3 using **5b** (0.40 g, 0.83 mmol), K_2CO_3 (0.23 g, 1.6 mmol), iodobenzene (0.34 g, 1.7 mmol), and copper bronze (0.127 g, 2 mmol). Column chromatographic purification (silica, eluent EtOAc/heptane, 3:7) yielded **6** (0.32 g, 70%). A solution of **6** (0.32 g, 0.6 mmol) and 2 M KOH (in MeOH, 3 mL) in THF (25 mL) was heated at 55 °C for 3 h. When the reaction mixture was cooled to rt, H_2O was added, and the solution was extracted with EtOAc. The organic extracts were combined, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude residue was purified by column chromatography (silica, eluent EtOAc/heptane, 3:7) to afford **7** (0.22 g, 95%) as a slightly yellow solid. Mp: 229−231 °C. IR (neat, cm^{-1}): 3406, 2921, 2861, 1611, 1591, 1515, 1495, 1453, 1414. ^1H NMR (300 MHz, DMSO-d_6): δ 0.78 (t, 3H), 1.00 (br, 2H), 1.06−1.16 (m, 2H), 1.49 (br, 2H), 2.91 (br, 2H), 6.84 (d, J = 8.01 Hz, 1H), 7.12 (d, J = 7.45 Hz, 1H), 7.21 (d, J = 7.38 Hz, 1H), 7.30−7.40 (m, 2H), 7.50−7.68 (m, 6H), 7.99 (d, J = 7.99 Hz, 1H), 8.12 (s, 1H), 8.28 (d, J = 7.59 Hz, 1H), 11.24 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.3, 22.2, 28.2, 28.8, 31.9, 98.9, 109.9, 110.9, 118.4, 119.4, 120.4, 120.5, 121.6, 122.3, 122.8, 123.1, 124.1, 125.3, 126.4, 128.8, 129.6, 130.1, 134.7, 136.3, 141.0, 141.6, 144.6. HRMS (EI) calcd for $C_{29}H_{26}N_2$ $[M]^+$, 402.2096; found, 402.2092.

12-Pentyl-5,11-dihydroindolo[3,2-*b*]carbazole-6-carbaldehyde (8). To a solution of **4c** (2.5 g, 7.7 mmol) in 1,2-dichloroethane (25 mL), DMF (0.71 mL, 9.2 mmol) was added, and subsequently $POCl_3$ (0.84 mL, 9.2 mmol) was added dropwise at rt under N_2 atmosphere. The mixture was heated at reflux overnight under N_2 atmosphere. The mixture was cooled to rt, poured into ice water, and extracted with EtOAc. The organic extracts were combined, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude residue was purified by column chromatography (silica, eluent Et_2O/heptane, 5:6) to give **8** (1.36 g, 50%) as a yellow solid. Mp: 266−268 °C. IR (neat, cm^{-1}): 3420, 3354, 2922, 2862, 1688, 1653, 1596, 1524, 1463. UV−vis (CH_2Cl_2) λ_{max} (log ϵ): 253 (4.5), 315 (4.3), 382 (4.3), 451 (4.0). ^1H NMR (300 MHz, DMSO-d_6): δ 0.88 (t, 3H), 1.34−1.42 (m, 2H), 1.58 (br, 2H), 1.84 (br, 2H), 3.56−3.62 (m, 2H), 7.19 (t, J = 7.48 Hz, 1H), 7.27 (t, J = 7.47 Hz, 1H), 7.42−7.51 (m, 2H), 7.64 (d, J = 8.08 Hz, 1H), 7.82 (d, J = 8.08 Hz, 1H), 8.16 (d, J = 7.80 Hz, 1H), 8.54 (d, J = 8.11 Hz, 1H), 11.32 (s, 1H), 11.53 (s, 1H), 11.82 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.4 (CH_3), 22.6 (CH_2), 28.9 (CH_2), 29.2 (CH_2), 31.9 (CH_2), 110.8, 111.9 (CH), 112.5 (CH), 119.2 (CH), 119.9 (CH), 120.9, 121.5, 121.6, 121.7, 122.1 (CH), 125.0 (CH), 125.9 (CH), 126.8 (CH), 129.4, 134.2, 136.3, 141.9, 189.8. HRMS (EI) calcd for $C_{24}H_{22}N_2O[M]^+$, 354.1732; found, 354.1742.

Synthesis of Benzimidazole Derivatives of 6-Pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (4c) (General Procedure 4). A solution of **8** (0.42 mmol) and the appropriate *o*-phenylenediamine (0.64 mmol) in DMF (5 mL) was heated at 120 °C for 14 h under a N_2 atmosphere. After removal of the solvent, the crude residue was purified by column chromatography.

6-(1*H*-Benzimidazol-2-yl)-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (9a). This compound was prepared according to General Procedure 4 using **8** (0.15 g, 0.42 mmol) and 1,2-phenylenediamine (0.07 g, 0.65 mmol). Column chromatographic purification (silica, eluent EtOAc/heptane, 3:7) yielded **9a** (0.13 g, 70%) as a brown solid. Mp: 248−250 °C. IR (neat, cm^{-1}): 3438, 3386, 2924, 2856, 1611, 1583, 1547, 1450, 1413. UV−vis (CH_2Cl_2) λ_{max} (log ϵ): 257 (4.5), 314 (4.5), 355 (4.3), 434 (4.1). ^1H NMR (300 MHz, DMSO-d_6): δ 0.92 (t, 3H), 1.39−1.46 (m, 2H), 1.62 (br, 2H), 1.90 (br, 2H), 3.61 (br, 2H), 6.94 (t, J = 7.44 Hz, 1H), 7.21 (t, J = 7.38 Hz, 1H), 7.35−7.42 (m, 4H), 7.51−7.59 (m, 3H), 7.77 (br, 2H), 8.20 (d, J = 7.8 Hz, 1H), 10.86 (s, 1H), 11.25 (s, 1H), 13.01 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.4 (CH_3), 22.7 (CH_2), 28.8 (CH_2), 29.1 (CH_2), 32.0 (CH_2), 103.9, 111.2 (CH), 111.5 (CH), 118.0 (CH), 118.7 (CH), 120.3, 120.5, 120.9, 122.1 (CH), 122.2 (CH), 122.3, 122.5, 125.6 (CH), 126.0 (CH), 134.4, 135.2, 141.8, 149.6. HRMS (EI) calcd for $C_{30}H_{26}N_4$ $[M]^+$, 442.2158; found, 442.2154.

Azo-Coupling Reactions of 6-Pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (4c) (General Procedure 5). A solution of **4c** (0.31 mmol) and pyridine (1.53 mmol) in THF (4 mL) was cooled to −78 °C, and the appropriate arenediazonium tetrafluoroborate salt (0.46 mmol) was added. The mixture was allowed to warm to rt and stirred overnight. EtOAc was added, and the organic solution was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude residue was purified by column chromatography.

6-Pentyl-12-(phenyldiazenyl)-5,11-dihydroindolo[3,2-*b*]carbazole (10a). This compound was prepared according to General Procedure 5 using **4c** (0.10 g, 0.31 mmol), pyridine (0.12 mL, 1.53 mmol), and benzenediazonium tetrafluoroborate (0.09 g, 0.46 mmol). Purification by column chromatography (silica, eluent EtOAc/heptane, 1:4) yielded **10a** (0.055 g, 42%) as a red solid. Mp: 264−266 °C. IR (neat, cm^{-1}): 3431, 3381, 2916, 2862, 1602, 1564, 1517, 1453, 1323, 1295, 1210. UV−vis (CH_2Cl_2) λ_{max} (log ϵ): 271 (4.5), 307 (4.4), 509 (4.2). ^1H NMR (300 MHz, DMSO-d_6): δ 0.90 (t, 3H), 1.37−1.45 (m, 2H), 1.57−1.67 (m, 2H), 1.89 (br, 2H), 3.61 (m, 2H), 7.24−7.34 (m, 2H), 7.49 (t, J = 7.59 Hz, 2H), 7.56 (t, J = 7.21 Hz, 1H), 7.62 (d, J = 8.12 Hz, 1H), 7.71 (t, J = 7.67 Hz, 2H), 7.90 (d, J = 8.08 Hz, 1H), 8.21 (d, J = 7.87 Hz, 1H), 8.33 (d, J = 7.83 Hz, 2H), 8.71 (d, J = 7.93 Hz, 1H), 11.45 (s, 1H), 11.79 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.4 (CH_3), 22.7 (CH_2), 29.1 (CH_2), 32.0 (CH_2), 111.6 (CH), 113.0 (CH), 119.5 (CH), 120.4 (CH), 121.4, 121.7, 121.9, 122.2 (CH), 122.7 (CH), 125.4, 125.6 (CH), 125.8 (CH), 126.7 (CH), 129.0, 129.8 (CH), 130.3 (CH), 134.8, 141.6, 142.0, 153.9. HRMS (EI) calcd for $C_{29}H_{26}N_4$ $[M]^+$, 430.2158; found, 430.2160.

6-Bromo-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (15). To a solution of **4c** (0.5 g, 1.5 mmol) in a solvent mixture of THF and H_2O (5:2, 28 mL), anhydrous $FeBr_3$ (1.36 g, 4.5 mmol) was added portionwise under N_2 atmosphere at rt. The mixture was stirred for 20 h at rt. H_2O (10 mL) was added, and the mixture was extracted with EtOAc. The organic extracts were combined, washed with brine (25 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude residue was purified by column chromatography (silica, eluent EtOAc/heptane, 1:4) to give **15** as a white solid. Mp: 185−187 °C. IR (neat, cm^{-1}): 3419, 2929, 2867, 1611, 1585, 1525, 1464, 1404, 1323, 743. UV−vis (CH_2Cl_2) λ_{max} (log ϵ): 276 (4.7), 331 (4.9), 398 (4.9). ^1H NMR (300 MHz, DMSO-d_6): δ 0.88 (t, 3H), 1.31−1.41 (m, 2H), 1.55−1.58 (m, 2H), 1.82 (br, 2H), 3.47−3.52 (m, 2H), 7.18−7.24 (m, 2H), 7.41−7.49 (m, 2H), 7.58 (d, J = 8.15 Hz, 1H), 7.62 (d, J = 8.09 Hz, 1H), 8.14 (d, J = 7.88 Hz,

1H), 8.69 (d, $J = 7.97$ Hz, 1H), 11.16 (s, 1H), 11.28 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.4 (CH_3), 22.7 (CH_2), 28.4 (CH_2), 29.1 (CH_2), 31.9 (CH_2), 93.3, 111.2 (CH), 111.6 (CH), 118.1 (CH), 118.3, 119.0 (CH), 119.8, 121.1, 121.9 (CH), 122.5 (CH), 123.1, 125.8 (CH), 126.3 (CH), 134.4, 135.0, 141.6. HRMS (EI) calcd for $C_{23}H_{21}BrN_2$ $[M]^+$, 404.0888; found, 404.0910.

Suzuki Coupling of Arylboronic Acids with 6-Bromo-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (15) (General Procedure 6). A solution of **15** (0.49 mmol), arylboronic acid (1 mmol), K_2CO_3 (1.2 mmol), and $Pd(PPh_3)_4$ (2.5 μmol) in a mixture of dioxane and H_2O (4:1, 10 mL) was degassed and flushed with N_2 and then heated at reflux overnight. After removal of the solvents, the reaction mixture was dissolved in EtOAc and washed with brine. The organic fraction was dried over Na_2SO_4 and concentrated in vacuo. The crude residue was purified by column chromatography.

6-Pentyl-12-phenyl-5,11-dihydroindolo[3,2-*b*]carbazole (4h). This compound was prepared according to General Procedure 6 using **15** (0.10 g, 0.25 mmol), phenylboronic acid (0.06 g, 0.5 mmol), K_2CO_3 (0.085 g, 0.6 mmol), and $Pd(PPh_3)_4$ (1.4 mg, 1.25 μmol). Purification by column chromatography (silica, eluent EtOAc/heptane, 1:9) yielded **4h** (0.072 g, 72%) as a slightly yellow solid. Mp: 214−215 °C. IR (neat, cm^{-1}): 3407, 2926, 2865, 1612, 1536, 1460, 1378, 1307. UV−vis (CH_2Cl_2) λ_{max} (log ϵ): 276 (4.6), 333 (4.7), 401 (3.9). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.92 (t, 3H), 1.39−1.46 (m, 2H), 1.58−1.65 (m, 2H), 1.86 (br, 2H), 3.52−3.57 (m, 2H), 6.81 (t, $J = 7.58$ Hz, 1H), 7.05 (d, $J = 7.85$ Hz, 1H), 7.16 (t, $J = 7.34$ Hz, 1H), 7.26−7.37 (m, 2H), 7.48−7.50 (m, 2H), 7.59−7.72 (m, 5H), 8.15 (d, $J = 7.92$ Hz, 1H), 10.43 (s, 1H), 11.06 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.5 (CH_3), 22.7 (CH_2), 28.7 (CH_2), 29.2 (CH_2), 32.1 (CH_2), 110.9 (CH), 111.4 (CH), 115.4, 117.5 (CH), 117.7, 118.3 (CH), 120.0, 120.3, 121.6 (CH), 122.1 (CH), 122.78, 122.84, 125.1 (CH), 125.4 (CH), 128.1 (CH), 129.5 (CH), 130.5 (CH), 134.0, 134.4, 137.6, 141.7, 141.9. HRMS (EI) calcd for $C_{29}H_{26}N_2$ $[M]^+$, 402.2096; found, 402.2096.

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Supporting Information Available: Additional experimental data and ^{1}H NMR and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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