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# Novel Synthesis of 5-methyl-5,10-dihydroindolo[3,2-*b*]indoles by Pd-catalyzed C-C and two-fold C-N coupling reactions

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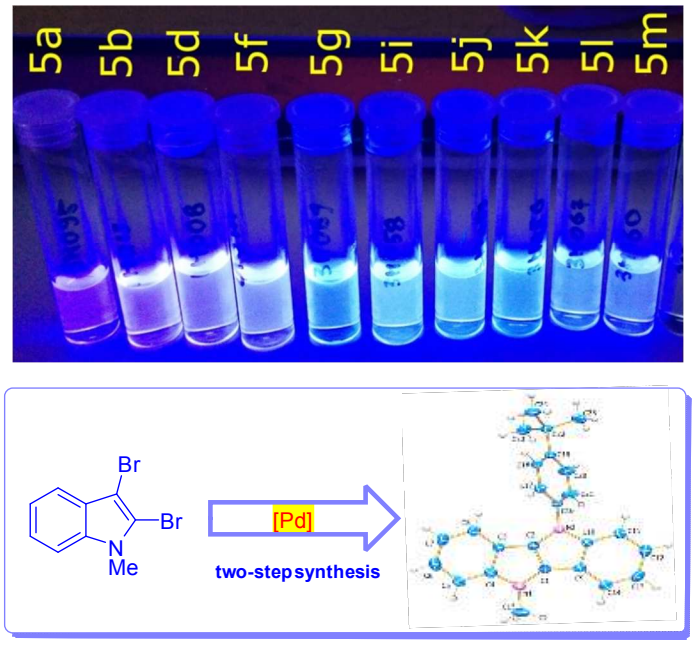
**Abstract**



**Abstract**

A series of 5,10-dihydroindolo[3,2-*b*]indoles was successfully prepared by an efficient two-step strategy based on site-selective Pd-catalyzed cross-coupling reaction with N-methyl-2,3-dibromoindole and subsequent cyclization by two-fold Pd-catalyzed C-N coupling with amines. The products show a strong fluorescence.

**Introduction**

Acenes and heteroacenes have found many applications in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaic cells.[1] Tetracene, which represents a p-type semiconductor, is one of the most studied acenes. It has been reported[2] that this molecule, in the form of single crystal devices, possesses hole mobilities as high as 1.3 $cm^2V^{-1}s^{-1}$. The introduction of heteroatoms into acenes plays an important role in tuning the electronic properties and crystal packing of the molecules as well as in improving the stability of the materials.[1b] Therefore, the preparation of new heterotetracenes has received much attention. In 2009, Liu and coworkers showed that tetrathienoacenes (TTAs) could be used in potential OFETs applications, due to their high hole mobilities and on/off current ratio.[3] Recently, Takimiya and co-workers reported the synthesis and interesting electronic properties of naphthodithiophenes (NDTs) and other chalcogenotetracenes.[4] A series of highly substituted benzothieno[3,2-*b*]benzothiophenes and benzoselenopheno[3,2-*b*]benzoselenophenes were prepared and investigated by Takimiya's group.[5] Recently, parent 5,10-dihydroindolo[3,2-*b*]indole was found to be a promising candidate for OFET applications.[6] Functionalized 5,10-dihydroindolo[3,2-*b*]indoles are known as important heterotetracenes which represent core building blocks in OLED polymers and high-spin organic polymers.[7]

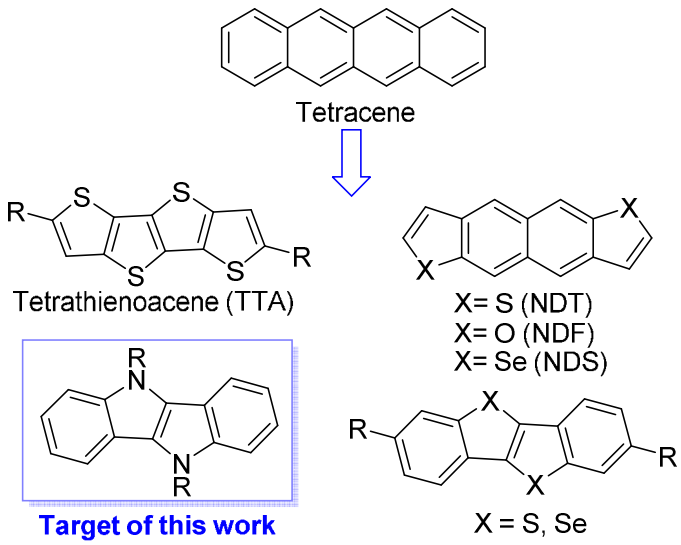


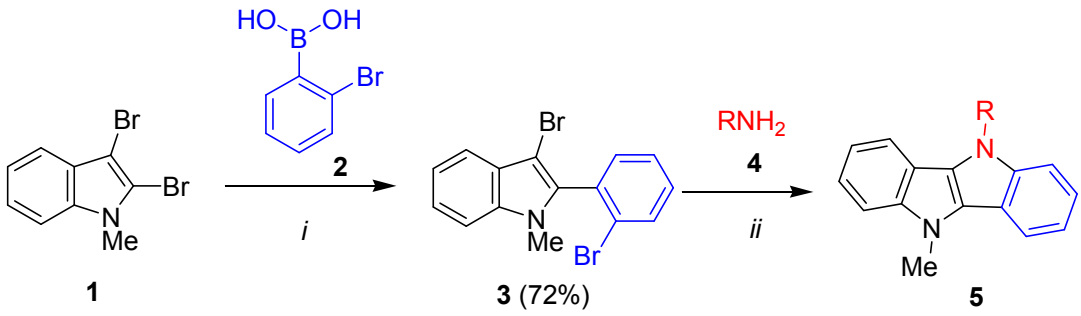

**Figure 1**: Molecular structures of tetracene and heterotetracenes for OFET applications

Several synthetic approaches to 5,10-dihydroindolo[3,2-*b*]indoles have been developed so far. Most of the conventional methods rely on a C-N bond formation as the key step.[8] Heller reported the first synthesis of 5,10-dihydroindolo[3,2-*b*]indole by reduction of *o,o'*-dinitrobenzil with zinc chloride in the presence of acetic acid.[9] Reduction of 2-(*o*-nitrophenyl)indole with $P(OEt)_3$ was reported to afford the product in moderate yields.[10] Later, Grinyov *et al.* described an interesting synthesis of 5,10-dihydroindolo[3,2-*b*]indoles by Fischer condensation of indolones with hydrazine derivatives.[11] Recently, Liu *et al.* reported a convenient method for the synthesis of 5,10-dihydroindolo[3,2-*b*]indoles by reduction of 6,12-dichlorodibenzo[*b,f*][1,5]diazocines by using an excess of zinc under acidic conditions.[6] In general, most of the known syntheses of highly functionalized 5,10-dihydroindolo[3,2-*b*]indoles are difficult to carry out, low yielding or require many synthetic steps. Because of their importance in materials science, we were interested to develop a new and efficient two-step strategy for the synthesis of highly functionalized 5,10-dihydroindolo[3,2-*b*]indoles. Our strategy relies on the site-selective Pd-catalyzed Suzuki-Miyaura reaction of *N*-methyl-2,3-dibromoindole and subsequent cyclization by Pd-catalyzed two-fold C-N coupling with amines. We have previously reported the synthesis of diindolo[3,2-*b*:4,5-b']thiophenes and indolo[2,3-*b*]quinoxalines based on the cyclization of *o*-

bromophenylboronic acid with tetrabromothiophene and 2,3-dibromoquinoxaline, respectively.[12a,b] Site-selective Suzuki-Miyaura reactions of *o*-bromophenylboronic acid with various substrates, such as 2,3-dibromopyridine, 2,3-dibromothiophene, 2,3,5-tribromothiophene, 2,3-dibromobenzothiophene, 3'-bromo-4'-iodo-2-nitro-1,1'-biphenyl, have been previously reported.[13]

## Result and discussion

2,3-Dibromo-*N*-methylindole **1** was synthesized from *N*-methylindole in 72% yield by bromination of *N*-methylindole with bromine at -78 ºC.[14] The site-selective Suzuki-Miyaura reaction of 2,3-dibromo-*N*-methylindole **1** with *o*-bromophenylboronic acid **2,** using our reported procedure,[14] afforded 2-aryl-3-bromoindole **3** in 72% yield.




**Scheme 1.** Synthesis of 5,10-dihydroindolo[3,2-*b*]indoles **5a-o**. Conditions: (i) 1.2 equiv. of **2**, 5 mol% of $Pd(PPh_3)_4$ catalyst, 3 equiv. of NaOH, THF, $H_2O$, 70 ºC, 4h. (ii) 3 equiv. of **4**, 3 equiv. of NaO*t*Bu, 5% mol of $Pd_2(dba)_3$, 10 mol% of XantPhos, toluene, 90 ºC, 6-10h.

The cyclization of **3** with *p*-toluidine (**4b**) was chosen for the optimization of conditions (Table 1). Some important parameters that can influence the reaction, including ligand, palladium source, solvent and temperature, were examined. Interestingly, up to 89% yield of **5b** was achieved by employment of XantPhos as ligand in combination with $Pd_2(dba)_3$. The yields decreased when $Pd(OAc)_2$ was used as the palladium source and when other solvents were

employed. When the temperature was reduced to 90 °C, the yield increased to 91% and the reaction mixture contained a smaller amount of side products.

**Table 1:** Optimizations for the synthesis of **5b**

| Entry | Catalyst | Ligand | Solvent | Temperature (ºC) | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 | $Pd_2(dba)_3$ | BINAP | Tol | 100 | 11 |
| 2 | $Pd_2(dba)_3$ | XantPhos | Tol | 100 | 89 |
| 3 | $Pd_2(dba)_3$ | DPEPhos | Tol | 100 | - |
| 4 | $Pd_2(dba)_3$ | Dppe | Tol | 100 | 7 |
| 5 | $Pd_2(dba)_3$ | Dppf | Tol | 100 | - |
| 6 | $Pd_2(dba)_3$ | $PCy_3 \cdot HBF_4$ | Tol | 100 | - |
| 7 | $Pd_2(dba)_3$ | $PBu_3 \cdot HBF_4$ | Tol | 100 | 4 |
| 8 | $Pd_2(dba)_3$ | XPhos | Tol | 100 | 79 |
| 9 | $Pd_2(dba)_3$ | XPhos·*t*$Bu_2$ | Tol | 100 | - |
| 10 | $Pd_2(dba)_3$ | SPhos | Tol | 100 | 72 |
| 11 | $Pd_2(dba)_3$ | DavePhos | Tol | 100 | 4 |
| 12 | $Pd_2(dba)_3$ | RuPhos | Tol | 100 | 11 |
| 13 | $Pd(OAc)_2$ | XantPhos | Dioxane | 100 | 57 |
| 14 | $Pd_2(dba)_3$ | XantPhos | DMF | 100 | 20 |
| **15** | **$Pd_2(dba)_3$** | **XantPhos** | **Tol** | **90** | **91** |
| 16 | $Pd_2(dba)_3$ | XantPhos | Tol | 80 | 82 |

[a]Yield was calculated by $^1$H-NMR of the crude product using 4-nitroacetophenone as an internal standard

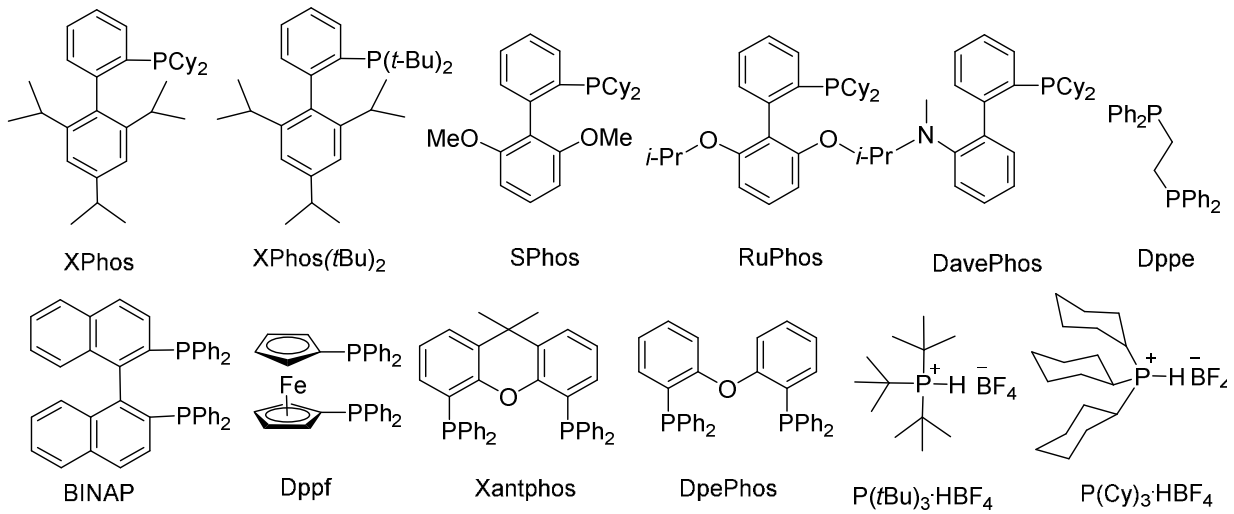



**Figure 2.** Monodentate and bidentate ligands

With the optimized condition in hand, we explored the scope of the two-fold C-N coupling reaction of **3** with different aniline derivatives. The employment of various anilines afforded the corresponding products **5a-o** in good to excellent yields (Table 2). Very good yields were obtained for both aniline derivatives bearing electron donating and withdrawing substituents. On the other hand, the cyclization of **3** with aliphatic amines gave lower yields (products **5j-o**, Table 2).

**Table 2:** Synthesis of **5a-t**

| 5 | R | Time (h) | Temperature (°C) | Yield (%)[a] |
|---|---|---|---|---|
| **a** | Ph | 6 | 90 | 80 |
| **b** | 4-(*t*Bu)$C_6H_4$ | 6 | 90 | 84 |
| **c** | 4-Me$C_6H_4$ | 6 | 90 | 81 |
| **d** | 4-F$C_6H_4$ | 6 | 90 | 82 |
| **e** | 3-($CF_3$)$C_6H_4$ | 6 | 90 | 84 |

| 5 | R | Time (h) | Temperature (°C) | Yield (%)[a] |
|---|---|---|---|---|
| **f** | 4-(MeO)$C_6H_4$ | 6 | 90 | 76 |
| **g** | 4-(MeS)$C_6H_4$ | 6 | 90 | 83 |
| **h** | (4-CN)$C_6H_4$ | 6 | 90 | 82 |
| **i** | *n*-$C_3H_7$ | 10 | 90 | 86 |
| **j** | Allyl | 10 | 90 | 84 |
| **k** | Bn | 10 | 90 | 72 |
| **l** | 4-(MeO)$C_6H_4CH_2$ | 10 | 90 | 79 |
| **m** | (4-$FC_6H_4$)$CH_2$ | 10 | 80 | 64 |
| **n** | 3-($CF_3$)$C_6H_4CH_2$ | 10 | 80 | 60 |
| **o** | $PhCH_2CH_2$ | 10 | 90 | 83 |

[a]Yield of isolated products

The structures of products **5a-o** were established by spectroscopic methods. The structure of **5b** was independently confirmed by X-ray crystal structure analysis (Figure 3). As expected, the heterocyclic core structure is planar. The aryl group is twisted out of plane.

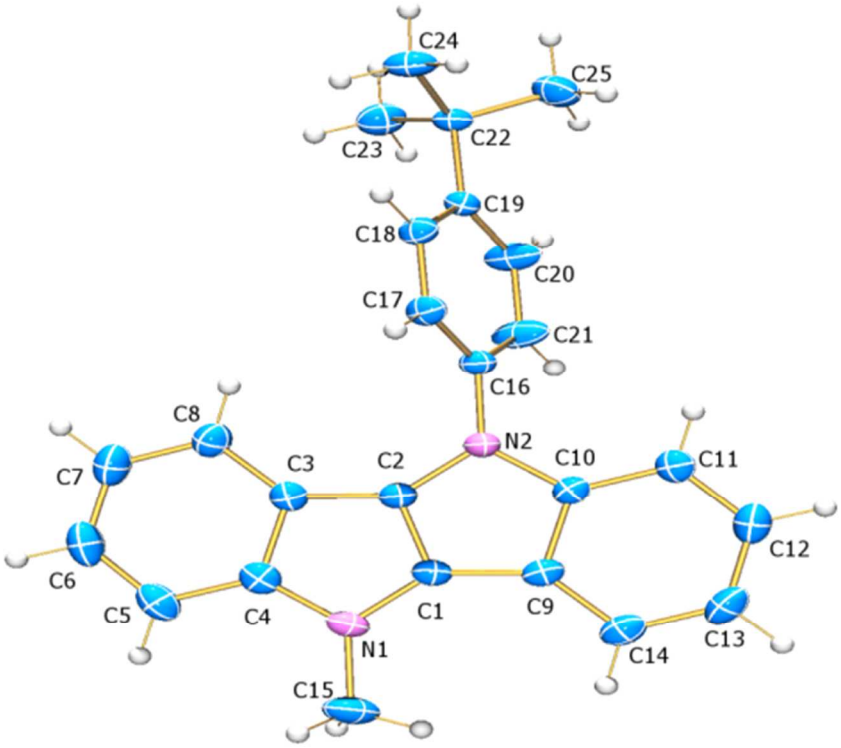



**Figure 3.** Ortep plot of **5b**

## Absorption and Fluorescence Properties

We studied UV-VIS and fluorescence properties of some selected 5,10-dihydroindolo[3,2-*b*]indoles **5** which contain different types of substituents located at the nitrogen atom N2 (see Figure 3). The measurements were carried out in acetonitrile and the spectra are shown in Figure 4. The corresponding spectral data are summarized in Table 3. The UV-VIS absorption spectra of the compounds exhibit three absorption bands around 361, 351, 324 and 261 nm with increasing absorption strength. The spectra of all derivatives **5** are quite similar suggesting that the substituent located at the nitrogen atom has only a weak influence. The bands of derivative **5i** are slightly red-shifted while derivative **5a**, bearing a phenyl group at N-position, exhibits a very slight shift to shorter wavelenghs. No clear correlation between structure and absoption spectrum

can be established since the observed shifts are extremely small and close or below the experimental accuracy. The prime influence is probably induced by the lone pair of the nitrogen atom conjugated to the heteroaromatic chromophore.

**Table 3.** Spectroscopic data characterizing the absorption properties of selected example **5**

| Comp. | $\lambda_{1abs}^{max}$ [nm] | Log$\varepsilon$ $\lambda_{1abs}^{max}$ (L·mol$^{-1}$·cm$^{-1}$) | $\lambda_{2abs}^{max}$ [nm] | Log$\varepsilon$ $\lambda_{2abs}^{max}$ (L·mol$^{-1}$·cm$^{-1}$) | $\lambda_{3abs}^{max}$ [nm] | Log$\varepsilon$ $\lambda_{3abs}^{max}$ (L·mol$^{-1}$·cm$^{-1}$) | $\lambda_{4abs}^{max}$ [nm] | Log$\varepsilon$ $\lambda_{4abs}^{max}$ (L.mol$^{-1}$·cm$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| **5a** | 361 | 4.49 | 349 | 4.51 | 324 | 4.86 | 260 | 5.23 |
| **5b** | 363 | 3.56 | 351 | 3.57 | 324 | 3.93 | 260 | 4.33 |
| **5d** | 362 | 3.34 | 351 | 3.35 | 324 | 3.73 | 261 | 4.15 |
| **5f** | 363 | 3.65 | 352 | 3.64 | 324 | 4.02 | 261 | 4.47 |
| **5g** | 363 | 3.43 | 351 | 4.05 | 323 | 4.08 | 259 | 3.62 |
| **5i** | 365 | 3.34 | 354 | 3.35 | 325 | 3.83 | 263 | 3.28 |
| **5j** | 363 | 3.41 | 351 | 3.42 | 325 | 3.89 | 262 | 4.33 |
| **5k** | 363 | 3.24 | 351 | 4.10 | 323 | 4.10 | 259 | 4.02 |
| **5l** | 362 | 4.29 | 351 | 4.28 | 325 | 4.75 | 262 | 5.18 |
| **5m** | 363 | 3.49 | 351 | 3.53 | 325 | 4.02 | 262 | 3.57 |

The fluorescence spectra were again measured in actonitrile with excitation at 340 nm (see Figure 4). The fluorescence quantum yields were determined by comparison to the standard quinine hemisulfate salt monohydrate (in 0.05M $H_2SO_4$), which exhibits a fluorescence yield of 52%.[15] The corresponding spectroscopic data are summarized in table 4. All emission spectra have their maximum around 400 nm and exhibit a shoulder at around 363 nm. Derivatives **5a** and **5b**, containing an aromatic substituent located at the nitrogen atom, exhibit the most blue-shifted emission with a maximum at a wavelength of 398 nm, while **5l**, containing a 4-methoxybenzyl group, shows a slight red-shift (404 nm). The Stokes shift is similar for all compounds and varies only in the range of 19 nm and 25 nm. It is important to note that the quantum yields of 5,10-dihydroindolo[3,2-*b*]indoles **5** are quite high. This is also illustrated by the abstract image which shows the strongly fluorescing samples irradiated by an UV-lamp. The highest quantum yield (47%) was observed for **5m**. The band gaps, determined from the crossing

of the absorption and fluorescence spectra, vary again only slightly among the compounds studied. Derivative **5a**, bearing a phenyl group, has the largest band gap of 3.344 eV, while the smallest band gap of 3.313 eV is observed for **5l** which bears a 4-methoxybenzyl group as the substituent.

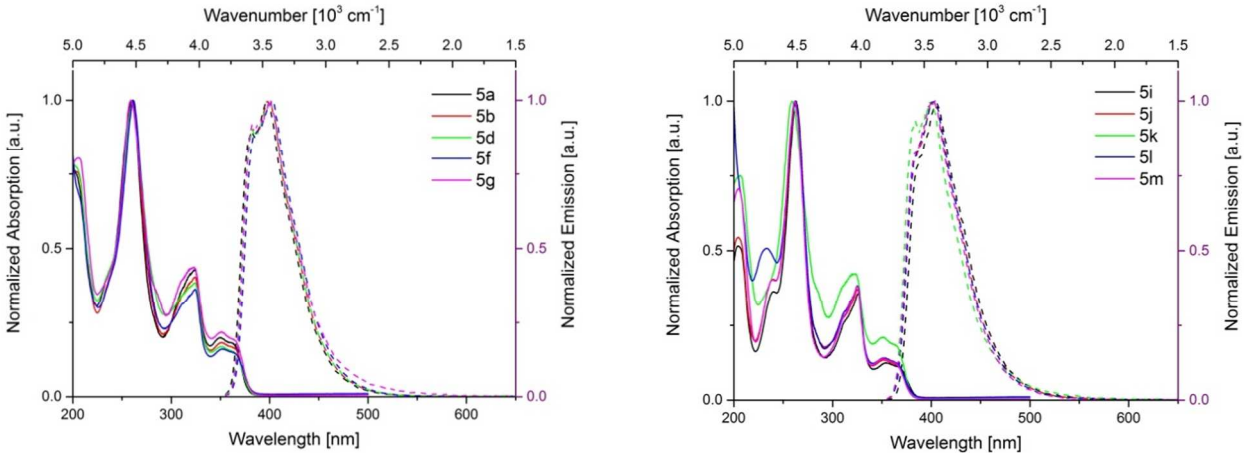



**Figure 4**. Normalized absorption and emission spectra of selected compounds **5** measured in acetonitrile. Emission spectra were recorded with excitation at 340 nm.

**Table 4.** Spectroscopic data characterizing the absorption and emission properties of **5**

| Comp. | $\lambda_{1abs}^{max}$ [nm] | $\lambda_{1em}^{max}$ [nm] | $\lambda_{2em}^{max}$ [nm] | Stokes shift [nm] | $\lambda_{00}$ [a] [nm] | Band gaps [b] (eV) | $\Phi_{fluo}$ Quantum yield |
|---|---|---|---|---|---|---|---|
| **5a** | 361 | 382 | 398 | 21 | 370.8 | 3.344 | 46% |
| **5b** | 363 | 383 | 398 | 20 | 372.6 | 3.328 | 46% |
| **5d** | 362 | 382 | 400 | 20 | 372.6 | 3.328 | 44% |
| **5f** | 363 | 387 | 403 | 24 | 374.0 | 3.315 | 43% |
| **5g** | 363 | 382 | 399 | 19 | 372.8 | 3.326 | 30% |
| **5i** | 365 | 388 | 403 | 23 | 377.0 | 3.289 | 41% |
| **5j** | 363 | 385 | 400 | 22 | 374.0 | 3.315 | 42% |
| **5k** | 363 | 383 | 399 | 20 | 372.6 | 3.328 | 31% |
| **5l** | 362 | 387 | 404 | 25 | 374.2 | 3.313 | 43% |
| **5m** | 363 | 386 | 403 | 23 | 373.4 | 3.320 | 47% |

[a] $\lambda_{00}$ is determined from the crossing point of the normalized absorption and emission spectra.[16]

[b] optical band gaps were calculated from $\lambda_{00}$. [16]

## Conclusions

In conclusion, we reported a short, practical and efficient strategy to prepare highly functionalized 5,10-dihydroindolo[3,2-*b*]indoles in very good yields. The reactions proceeded with very good site-selectivity in favour of positions 2 and 6. The site-selectivity of the reaction of the 2-bromophenylboronic acid with *N*-methyl-2,3-dibromoindole can be explained by the fact that position 2 is less electron rich than position 3. It has been previously reported that the oxidative addition of Pd(0) catalysed cross-coupling reactions of polyhalogenated substrates proceed by predominant attack at the more electron poor position.[17] Absorption and fluorescence properties of the 5,10-dihydroindolo[3,2-*b*]indoles were studied. Although the substituents have only a small influence on the absorption and fluorescence, very good quantum yields were generally observed.

## Experimental Section

**General.** Chemicals were purchased from alfa aesar, sigma Aldrich and were used without further purification. NMR spectra were recorded on Brucker AV 300 and 250 MHz instruments. IR spectra were recorded on a Perkin Elmer FT IR 1600 spectrometer (ATR). Mass spectra were obtained on a Hewlett-Packard HPGC/MS 5890/5972 instrument (EI, 70 eV) by GC inlet or on an MX-1321 instrument (EI, 70 eV) by direct inlet. Column chromatography was performed on silica gel (63e200 mesh, Merck) and silica gel Merck 60F254 plates were used for TLC. Commercially available solvents were distilled for column chromatography. All other solvents

were purified and dried by standard methods. Starting material **1** contains a small amount of impurity which could not be completely separated, due to the formation of tribrominated product. However, the material could be successfully used as the products in the following steps could be isolated in pure form.

**Procedure for the preparation of *2,3-dibromo-1-methyl-1H-indole*.** To solution of 1-methyl-1*H*-indole (1 mL, 8 mmol) in 20 mL THF was added wisely NBS (3.14 g, 17.6 mmol) at -78 ºC. Then the mixture was stirred for 5h at this temperature. The reaction mixture was treated with water (20 mL). The solvent THF was partial removed by evaporator *in vacuo* and then extracted with dihloromethane (3 x 20 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$ and then evaporated *in vacuo* affording yellow syrup. The mixture was separated over column chromatography (silica gel, heptanes) to yield 2,3-dibromo-1-methyl-1*H*-indole **1** (2 g, 86%) as white solid; m.p. 38-40 ºC; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.41 (dt, *J* = 7.6, 1.1 Hz, 1H), 7.15 (dd, *J* = 4.9, 1.2 Hz, 2H), 7.13 – 7.02 (m, 1H), 3.66 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 136.3, 126.9, 122.9, 120.8, 118.8, 114.9, 109.6, 92.6, 32.3; GC/MS (EI, 70eV): m/z (%) = 289 (100), 291 (50), 288 (20), 274 (18), 129 (15), 114 (23), 88 (12); HRMS (EI): calculated for $C_9H_7Br_2N_1$ ([$M^+$]): 286.89398; found: 286.89391, calculated for $C_9H_7Br_1{}^{81}Br_1N_1$ ([$M^+$]): 288.8919; found: 288.8918, calculated for $C_9H_7{}^{81}Br_2N_1$ ([$M^+$]): 290.88988; found: 290.88980.

**Procedure for the preparation of *3-bromo-2-(2-bromophenyl)-1-methyl-1H-indole* 3.** 2,3-dibromoindole **1** (1 g, 3.46 mmol), 2-bromophenyl boronic acid **2** (0.83 g, 4.15 mmol), $Pd(PPh_3)_4$ (200 mg, 173 µmol) and sodium hydroxide (415 mg, 10.38 mmol) were added to 500 mL Schlenk flask. The mixture was back-filled several times with Argon. To the mixture 70 mL THF and 10 mL distilled water were added, then, back-filled several times. The reaction was heated at 70 ºC for 4h. The solvent was evaporated *in vacuo*. The residue was extracted with dichloromethane and water. The organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated *in vacuo*. The yellow residue was purified by column chromatography (silica gel, Heptane/ethylacetate/dichloromethane 3:1:1) to yield *3-bromo-2-(2-bromophenyl)-1-methyl-1H-*

*indole* **3** (0.91 g, 72 %) as white solid; m.p. 83-85 °C; $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 1H), 7.59 – 7.52 (m, 1H), 7.44 – 7.12 (m, 6H), 3.50 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 137.1, 136.3, 133.3, 132.9, 132.2, 130.9, 127.4, 126.8, 125.5, 122.9, 120.4, 119.4, 109.7, 90.7, 31.2; IR (ATR, $cm^{-1}$): ν = 3053 (m), 3018 (w), 2939 (w), 2875 (w), 2833 (w), 1498 (m), 1473 (m), 1460 (s), 1427 (m), 1412 (m), 1356 (m), 1325 (s), 1319 (s), 1230 (s), 1201 (m), 1173 (w), 1153 (s), 1126 (m), 1105 (m), 1084 (m), 1009 (m), 947 (m), 922 (m), 808 (w), 729 (vs), 606 (m), 546 (m); GC-MS (EI, 70 eV): m/z (%) = 365 (100), 204 (82), 176 (22), 102 (26), 88 (13); HRMS (EI): calcd. for $C_{15}H_{11}Br_2N_1$ ($[M^+]$): 362.9253; found: 362.9248, calculated for $C_{15}H_{11}Br_1{}^{81}Br_1N_1$ ($[M^+]$): 364.92323; found: 364.92292, calculated for $C_{15}H_{11}{}^{81}Br_2N_1$ ($[M^+]$): 366.92118; found: 366.92109.

**General procedure for double C-N coupling with aniline derivatives, exemplified by *5-methyl-10-phenyl-5,10-dihydroindolo[3,2-b]indole* 5a.** Aniline (75 µL, 0.82 mmol) was added to pressure tube charged with **3** (100 mg, 0.27 mmol), $Pd_2(dba)_3$ (12.5 mg, 14 µmol), ligand Xanthphhos (15.9 mg, 28 µmol) and sodium *tert*-butoxide (79 mg, 0.82 mmol) under Argon. The mixture was back-filled with Argon several times. The mixture was dissolved in anhydrous toluene (10 mL) and heated to 90 ºC for 6 h. After cooling, the reaction mixture was diluted with dichloromethane (20 mL) and filtered through a celite pad, washing with dichloromethane (40 mL). The filtrate was evaporated *in vacuo*. The product was separated via flash chromatography (silica gel, heptanes/dichloromethane 5:1) to yield **5a** (65 mg, 80 %) as a white solid; m.p. 130-131 ºC; $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 1H), 7.66 – 7.41 (m, 6H), 7.37 – 7.26 (m, 2H), 7.24 – 7.08 (m, 3H), 6.97 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 4.03 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 141.3, 140.7, 139.1, 129.6, 127.8, 126.4, 125.5, 125.2, 122.5, 121.9, 119.6, 118.4, 118.2, 117.6, 116.0, 114.6, 110.9, 109.5, 31.6; IR (ATR, $cm^{-1}$): ν = 3047 (w), 2928 (w), 1593 (m), 1576 (m), 1500 (s), 1471 (s), 1460 (s), 1435 (m), 1423 (m), 1398 (s), 1365 (m), 1340 (m), 1323 (m), 1309 (m), 1282 (m), 1267 (w), 1232 (s), 1174 (m), 1151 (m), 1126 (m), 1103 (m), 1076 (m), 1061 (m), 1028 (m), 1014 (m), 987 (w), 966 (w), 949 (m), 918 (w), 910 (m), 883 (w), 831 (w), 823 (m), 779 (w), 729 (vs), 700 (vs), 677 (s), 650 (s), 617 (m),

596 (m), 588 (s), 565 (m), 542 (m); GC-MS (EI, 70 eV): m/z (%) = 296 (100), 281 (45); HRMS (EI): calculated for $C_{21}H_{16}N_2$ ([$M^+$]): 296.1308; found: 296.1304.

***5-(4-(tert-Butyl)phenyl)-10-methyl-5,10-dihydroindolo[3,2-b]indole*** **5b** was prepared following general procedure A using compound **3** (100 mg, 0.27 mmol) and 4-(tert-butyl)aniline (131 µL, 0.82 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane 5:1) to yield **5b** (81 mg, 84%) as a white solid; m.p. 210-213 ºC; $^1$H NMR (250 MHz, $C_6D_6$) δ 7.99 – 7.89 (m, 2H), 7.84 – 7.75 (m, 1H), 7.73 – 7.65 (m, 2H), 7.48 – 7.33 (m, 5H), 7.33 – 7.18 (m, 2H), 3.56 (s, 3H), 1.36 (s, 9H); $^{13}$C NMR (63 MHz, $C_6D_6$) δ 149.2, 141.8, 141.4, 137.0, 127.8, 126.6, 125.4, 122.8, 122.2, 119.8, 118.9, 118.6, 117.9, 116.6, 115.3, 111.4, 109.8, 34.5, 31.4, 30.9; IR (ATR, cm$^{-1}$): ν = 3057 (w), 2960 (m), 2929 (w), 2901 (w), 2864 (w), 1516 (s), 1495 (m), 1471 (s), 1441 (m), 1423 (m), 1402 (s), 1365 (m), 1329 (m), 1309 (w), 1265 (w), 1234 (s), 1200 (m), 1184 (m), 1161 (w), 1151 (w), 1136 (m), 1111 (m), 1030 (w), 1022 (w), 1012 (m), 955 (w), 922 (w), 833 (m), 823 (m), 775 (w), 729 (vs), 712 (m), 685 (m), 665 (w), 607 (w), 590 (m), 571 (w), 561 (w), 550 (m); GC/MS (EI, 70eV): m/z (%) = 352 (100), 337 (22), 322 (19),155 (20); HRMS (EI): calculated for $C_{25}H_{24}N_2$ ([$M^+$]): 352.1934; found: 352.1929.

***5-Methyl-10-(p-tolyl)-5,10-dihydroindolo[3,2-b]indole*** **5c** was prepared following general procedure A using compound **3** (100 mg, 0.27 mmol) and *p*-toluidine (88 mg, 0.82 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane 5:1) to yield **5c** (69 mg, 81 %) as a white solid; m.p. 140-141 ºC; $^1$H NMR (300 MHz, Acetone) δ 7.92 – 7.85 (m, 1H), 7.48 – 7.29 (m, 7H), 7.14 – 7.00 (m, 3H), 6.87 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 4.02 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (63 MHz, Acetone) δ 142.2, 141.6, 137.3, 137.2, 131.1, 128.4, 126.0, 125.8, 123.3, 122.7, 120.4, 118.9, 118.7, 118.7, 116.8, 115.3, 111.5, 110.6, 31.8, 21.1; IR (ATR, cm$^{-1}$): ν = 3057 (w), 3036 (w), 2918 (w), 1514 (s), 1487 (m), 1473 (m), 1454 (m), 1441 (m), 1421 (m), 1402 (m), 1365 (m), 1325 (m), 1304 (w), 1232 (m), 1174 (w), 1153 (m), 1126 (m), 1109 (m), 1063 (w), 1032 (m), 1012 (m), 968 (w), 951 (m), 918 (m), 822 (m), 796 (w), 760 (w), 748 (m), 727 (vs), 683 (m), 665 (w), 640 (w), 615 (w), 590 (m), 563

(m), 542 (w); GC/MS (EI, 70eV): m/z (%) = 310 (100), 295 (40); HRMS (EI): calculated for $C_{22}H_{18}N_2$ ([$M^+$]): 310.1465; found: 310.1470.

***5-(4-Fluorophenyl)-10-methyl-5,10-dihydroindolo[3,2-b]indole*** **5d** was prepared following general procedure A using compound **3** (100 mg, 0.27 mmol) and 4-fluoroaniline (78 µL, 0.82 mmol). The product was purified by flash chromatography (silica gel, heptanes/ dichloromethane 4:1) to yield **5d** (71 mg, 82 %) as a white solid; m.p. 106-108 ºC; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.48 – 7.28 (m, 3H), 7.23 – 7.08 (m, 5H), 6.96 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 4.01 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 161.1 (d, *J* = 246.0 Hz), 141.2, 140.9, 135.1 (d, *J* = 3.0 Hz), 127.7, 127.2 (d, *J* = 8.4 Hz), 125.3, 122.6, 122.0, 119.7, 118.3, 118.1, 117.6, 116.5 (d, *J* = 22.8 Hz), 116.0, 114.4, 110.6, 109.6, 31.6; IR (ATR, $cm^{-1}$): ν = 3055 (w), 2922 (w), 1504 (s), 1471 (s), 1439 (m), 1423 (m), 1398 (s), 1367 (m), 1323 (m), 1281 (w), 1230 (s), 1217 (s), 1153 (m), 1134 (m), 1124 (m), 1095 (m), 1061 (m), 1032 (m), 1016 (m), 949 (m), 918 (m), 872 (m), 841 (m), 827 (s), 808 (s), 785 (m), 760 (m), 725 (vs), 710 (s), 679 (m), 636 (m), 611 (m), 588 (s), 565 (s), 542 (m); GC/MS (EI, 70eV): m/z (%) = 314 (100), 299 (48), 157 (10); HRMS (EI): calculated for $C_{21}H_{15}F_1N_2$ ([$M^+$]): 314.1214; found: 314.1214.

***5-Methyl-10-(3-(trifluoromethyl)phenyl)-5,10-dihydroindolo[3,2-b]indole*** **5e** was prepared following general procedure A using compound **3** (100 mg, 0.27 mmol) and 3-(trifluoromethyl)aniline (103 µL, 0.82 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane 4:1) to yield **5e** (84 mg, 84 %) as a white solid; m.p. 86-87 ºC; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.88 – 7.74 (m, 2H), 7.64 – 7.46 (m, 3H), 7.35 (dd, *J* = 15.7, 8.2 Hz, 2H), 7.22 – 7.12 (m, 3H), 6.99 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 4.00 (s, 3H); $^{19}$F NMR (282 MHz, $CDCl_3$) δ = -62.54 (s); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 141.2, 140.5, 139.8, 132.2 (q, *J* = 32.7 Hz), 130.2, 128.4 (d, *J* = 0.9 Hz), 128.3, 124.6, 123.0, 122.7 (q, *J* = 3.8 Hz), 122.5 (q, *J* = 272.7 Hz ), 122.5 (d, *J* = 272.7 Hz), 122.1, 122.0 (q, *J* = 7.8, 4.1 Hz), 120.3, 118.5, 117.8, 116.5, 114.4, 110.6, 109.7, 31.6; IR (ATR, $cm^{-1}$): ν = 3061 (w), 2931 (w), 1612 (w), 1595 (m), 1574 (w), 1514 (w), 1495 (s), 1471 (s), 1441 (s), 1421 (m),

1396 (m), 1373 (m), 1335 (s), 1321 (s), 1308 (s), 1286 (s), 1263 (m), 1232 (s), 1176 (s), 1163 (s), 1113 (vs), 1095 (s), 1066 (s), 1034 (m), 1020 (m), 1001 (m), 968 (m), 957 (m), 924 (m), 916 (m), 899 (m), 872 (w), 839 (s), 802 (s), 729 (vs), 706 (vs), 696 (s), 679 (m), 665 (s), 650 (m), 638 (m), 596 (m), 588 (m), 569 (m), 542 (m); GC/MS (EI, 70eV): m/z (%) = 364 (100), 349 (39); HRMS (EI): calculated for $C_{22}H_{15}F_3N_2$ ([$M^+$]): 364.1182; found: 364.1179.

***5-(4-Methoxyphenyl)-10-methyl-5,10-dihydroindolo[3,2-b]indole*** **5f** was prepared following general procedure A using compound **3** (100 mg, 0.27 mmol) and *p*-anisidine (101 mg, 0.82 mmol). The product was purified by flash chromatography (silica gel, heptanes/ethylacetate 5:1) to yield **5f** (68 mg, 76 %) as a white solid; m.p. 114-116 ºC; $^1$H NMR (300 MHz, Acetone) δ 7.91 – 7.81 (m, 1H), 7.49 – 7.41 (m, 2H), 7.40 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 7.14 – 7.00 (m, 5H), 6.86 (m, 1H), 4.01 (s, 3H), 3.75 (s, 3H); $^{13}$C NMR (75 MHz, Acetone) δ 159.4, 142.2, 141.9, 132.6, 128.1, 127.7, 126.2, 123.2, 122.7, 120.2, 118.9, 118.6, 116.6, 115.7, 115.3, 111.4, 110.6, 55.9, 31.8; IR (ATR, $cm^{-1}$): ν = 3057 (m), 2955 (m), 2926 (m), 2912 (m), 2835 (m), 1510 (s), 1473 (s), 1464 (s), 1441 (s), 1421 (m), 1400 (s), 1367 (m), 1331 (m), 1296 (m), 1284 (m), 1234 (s), 1182 (m), 1169 (m), 1161 (m), 1151 (m), 1132 (m), 1124 (m), 1107 (s), 1065 (m), 1030 (s), 1018 (m), 968 (m), 953 (m), 947 (m), 931 (m), 914 (m), 870 (m), 827 (s), 806 (m), 795 (m), 756 (m), 742 (m), 723 (vs), 685 (m), 675 (m), 665 (m), 640 (m), 613 (m), 590 (s), 573 (s), 542 (m); GC/MS (EI, 70eV): m/z (%) = 326 (100), 311 (25), 268 (12); HRMS (EI): calculated for $C_{21}H_{15}N_2O_1$ ([$M^+$]): 326.1414; found: 326.1412.

***5-Methyl-10-(4-(methylthio)phenyl)-5,10-dihydroindolo[3,2-b]indole*** **5g** was prepared following general procedure A using compound **3** (100 mg, 0.27 mmol) and 4-(methylthio)aniline (102 µL, 0.82 mmol). The product was purified by flash chromatography (silica gel, heptanes/ethylacetate 5:1) to yield **5f** (78 mg, 83 %) as a white solid; m.p. 107-108 ºC; $^1$H NMR (250 MHz, $CDCl_3$) δ 8.04 – 7.95 (m, 1H), 7.75 – 7.58 (m, 4H), 7.58 – 7.46 (m, 3H), 7.43 – 7.24 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 4.17 (s, 3H), 2.64 (s, 3H); $^{13}$C NMR (63 MHz, $CDCl_3$) δ 141.2, 140.7, 136.4, 136.3, 127.7, 125.9, 125.1, 122.5, 121.9, 119.6, 118.3, 118.2,

117.6, 116.0, 114.5, 110.9, 109.5, 31.6, 16.2; IR (ATR, $cm^{-1}$): ν = 3057 (w), 2916 (m), 1495 (s), 1468 (s), 1439 (s), 1419 (m), 1396 (s), 1365 (m), 1323 (s), 1302 (m), 1284 (m), 1265 (m), 1228 (s), 1180 (m), 1161 (m), 1153 (m), 1132 (m), 1090 (s), 1065 (m), 1030 (m), 1011 (m), 962 (m), 957 (m), 949 (m), 924 (m), 916 (m), 870 (w), 835 (w), 822 (s), 773 (m), 735 (vs), 727 (vs), 700 (s), 687 (s), 679 (s), 634 (m), 602 (m), 588 (s), 569 (m), 544 (m); GC/MS (EI, 70eV): m/z (%) = 342 (100), 327 (35), 171 (8); HRMS (EI): calculated for $C_{22}H_{18}N_2S_1$ ([$M^+$]): 342.1185; found: 342.1185.

***5-Methyl-10-(4-cyanophenyl)-5,10-dihydroindolo[3,2-b]indole*** **5h** was prepared following general procedure A using compound **3** (100 mg, 0.27 mmol) and 4-aminobenzonitrile (97 mg, 0.82 mmol). The product was purified by flash chromatography (silica gel, Heptane/ethylacetate 4:1) to yield **5h** (72 mg, 82 %) as a white solid; m.p. 158-160 ºC; $^1$H NMR (250 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 1H), 7.76 – 7.59 (m, 4H), 7.58 – 7.48 (m, 1H), 7.39 – 7.31 (m, 2H), 7.26 – 7.13 (m, 3H), 7.00 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 3.98 (s, 3H); $^{13}$C NMR (63 MHz, $CDCl_3$) δ 143.0, 141.2, 140.1, 133.6, 128.8, 124.9, 123.8, 123.2, 122.2, 120.8, 118.7, 118.6, 118.2, 117.9, 117.0, 114.3, 110.7, 109.8, 108.8, 31.5; IR (ATR, $cm^{-1}$): ν = 3055 (w), 2929 (w), 2218 (m), 1601 (m), 1508 (s), 1470 (s), 1441 (s), 1423 (m), 1396 (s), 1373 (m), 1346 (m), 1325 (s), 1308 (m), 1279 (w), 1230 (m), 1200 (w), 1174 (m), 1163 (m), 1155 (m), 1134 (m), 1059 (w), 1034 (m), 1024 (m), 949 (w), 872 (w), 843 (m), 831 (m), 741 (s), 729 (vs), 687 (w), 681 (w), 673 (w), 646 (w), 607 (w), 590 (m), 567 (w), 548 (m); GC/MS (EI, 70eV): m/z (%) = 321 (100), 306 (36), 219 (12), 161 (10); HRMS (EI): calculated for $C_{22}H_{15}N_3$ ([$M^+$]): 321.1261; found: 321.1260.

***5-Methyl-10-propyl-5,10-dihydroindolo[3,2-b]indole*** **5i** was prepared following general procedure A using compound **3** (100 mg, 0.27 mmol) and n-propylamine (68 µL, 0.82 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane 5:1) to yield **5i** (54 mg, 86 %) as a white solid; m.p. 121-122 ºC; $^1$H NMR (250 MHz, $CDCl_3$) δ 7.81 – 7.71 (m, 2H), 7.36 – 7.02 (m, 6H), 4.33 (s, 2H), 3.98 (s, 3H), 1.89 (sex, *J* = 7.3 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (63 MHz, $CDCl_3$) δ 141.2, 140.6, 126.5, 125.8, 121.6, 118.1, 117.9,

117.6, 117.5, 114.7, 109.7, 109.5, 46.8, 31.5, 23.6, 11.6; IR (ATR, $cm^{-1}$): ν = 3053 (w), 2960 (w), 2931 (m), 2874 (w), 1497 (m), 1475 (s), 1466 (m), 1439 (m), 1423 (m), 1406 (m), 1381 (m), 1363 (s), 1298 (m), 1267 (m), 1246 (w), 1225 (s), 1188 (m), 1151 (m), 1132 (m), 1119 (m), 1014 (m), 951 (w), 920 (m), 899 (m), 841 (m), 729 (vs), 675 (m), 660 (m), 644 (m), 590 (m), 575 (m), 567 (m), 544 (m); GC/MS (EI, 70eV): m/z (%) = 262 (100), 233 (89), 219 (48); HRMS (EI): calculated for $C_{18}H_{18}N_2$ ([$M^+$]): 262.1465; found: 262.1459.

***5-Methyl-10-allyl-5,10-dihydroindolo[3,2-b]indole*** **5j** was prepared following general procedure A using compound **3** (100 mg, 0.27 mmol) and allylamine (62 µL, 0.82 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane 5:1) to yield **5j** (60 mg, 84 %) as a white solid; m.p. 125-126 ºC; $^1$H NMR (250 MHz, $CDCl_3$) δ 8.08 – 7.65 (m, 2H), 7.62 – 6.95 (m, 6H), 6.17 – 5.90 (m, 1H), 5.20 – 4.95 (m, 4H), 4.03 (s, 3H); $^{13}$C NMR (63 MHz, $CDCl_3$) δ 141.1, 140.6, 133.4, 126.6, 125.7, 121.7, 121.6, 118.3, 118.1, 117.7, 117.4, 116.6, 115.0, 114.6, 109.8, 109.4, 47.4, 31.6; IR (ATR, $cm^{-1}$): ν = 3063 (w), 2920 (m), 2852 (w), 1643 (w), 1497 (m), 1475 (s), 1448 (m), 1433 (m), 1406 (s), 1367 (m), 1352 (m), 1294 (w), 1273 (m), 1246 (m), 1221 (s), 1174 (m), 1149 (m), 1132 (m), 1119 (m), 1061 (w), 1041 (w), 1016 (m), 993 (m), 976 (m), 953 (w), 943 (w), 924 (m), 914 (m), 904 (m), 841 (m), 831 (m), 771 (w), 741 (m), 721 (vs), 663 (m), 598 (m), 584 (s), 565 (m), 544 (m); GC/MS (EI, 70eV): m/z (%) = 260 (47), 219 (100); HRMS (EI): calculated for $C_{18}H_{16}N_2$ ([$M^+$]): 260.1308; found: 260.1308.

***5-Methyl-10-benzyl-5,10-dihydroindolo[3,2-b]indole*** **5k** was prepared following general procedure A using compound **3** (100 mg, 0.27 mmol) and benzylamine (90 µL, 0.82 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane 3:1) to yield **5k** (61 mg, 72 %) as a white solid; m.p. 151-152 ºC; $^1$H NMR (250 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 1H), 7.55 – 7.52 (m, 1H), 7.39 – 7.29 (m, 2H), 7.26 – 7.06 (m, 8H), 7.05 – 6.94 (m, 1H), 5.61 (s, 2H), 4.05 (s, 3H); $^{13}$C NMR (63 MHz, $CDCl_3$) δ 141.1, 140.8, 137.9, 128.7 (x 2C), 127.4, 126.5 (x 2C), 121.9, 121.6, 118.4, 118.2, 115.1, 114.6, 109.9, 109.4, 48.8, 31.6; IR (ATR, $cm^{-1}$): ν = 3055 (w), 3030 (w), 2935 (w), 1603 (w), 1579 (w), 1495 (m), 1475 (s), 1448 (m),

1431 (m), 1406 (m), 1387 (m), 1360 (m), 1346 (m), 1340 (m), 1317 (m), 1300 (m), 1288 (m), 1273 (m), 1246 (m), 1223 (m), 1171 (m), 1149 (w), 1132 (m), 1122 (m), 1099 (w), 1074 (w), 1028 (w), 1014 (m), 978 (m), 849 (w), 766 (w), 731 (vs), 694 (s), 658 (m), 594 (w), 584 (m), 569 (w), 536 (w); GC/MS (EI, 70eV): m/z (%) = 310 (49), 219 (100); HRMS (EI): calculated for $C_{22}H_{18}N_2$ ([$M^+$]): 310.1465; found: 310.1472.

***5-Methyl-10-(4-methoxybenzyl)-5,10-dihydroindolo[3,2-b]indole*** **5l** was prepared following general procedure A using compound **3** (100 mg, 0.27 mmol) and 4-methoxybenzylamine (107 µL, 0.82 mmol). The product was purified by flash chromatography (silica gel, heptanes/ethylacetate 5:1) to yield **5l** (74 mg, 79 %) as a white solid; m.p. 161-162 ºC; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.32 (dd, *J* = 8.3, 4.0 Hz, 2H), 7.25 – 6.95 (m, 6H), 6.74 – 6.62 (m, 2H), 5.49 (s, 2H), 4.00 (s, 3H), 3.60 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 158.9, 141.2, 140.8, 130.1, 128.4, 127.8, 121.9, 121.7, 118.4, 118.2, 117.7, 117.5, 115.1, 114.7, 114.2, 114.0, 110.0, 109.5, 55.2, 48.3, 31.6; IR (ATR, $cm^{-1}$): ν = 3047 (w), 2928 (w), 1610 (w), 1512 (m), 1497 (m), 1475 (m), 1450 (m), 1437 (m), 1421 (w), 1404 (m), 1363 (m), 1342 (m), 1311 (w), 1300 (w), 1294 (w), 1271 (m), 1252 (m), 1221 (m), 1171 (m), 1149 (m), 1132 (m), 1120 (m), 1109 (m), 1030 (m), 1014 (m), 984 (w), 957 (w), 926 (w), 843 (m), 831 (w), 823 (w), 810 (m), 768 (w), 752 (m), 742 (s), 727 (vs), 665 (w), 656 (w), 642 (m), 629 (w), 592 (m), 577 (w), 565 (w), 534 (m); GC/MS (EI, 70eV): m/z (%) = 340 (53), 219 (100), 121 (32); HRMS (EI): calculated for $C_{23}H_{20}N_2O_1$ ([$M^+$]): 340.1570; found: 340.1576.

***5-Methyl-10-(4-fluorobenzyl)-5,10-dihydroindolo[3,2-b]indole*** **5m** was prepared following general procedure A using compound **3** (100 mg, 0.27 mmol) and 4-fluorobenzylamine (94 µL, 0.82 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane 3:1) to yield **5m** (58 mg, 64 %) as a white solid; m.p. 153-154 ºC; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.28 (t, *J* = 8.5 Hz, 2H), 7.22 – 6.92 (m, 6H), 6.80 (dd, *J* = 12.0, 5.3 Hz, 2H), 5.44 (s, 2H), 3.95 (s, *J* = 6.4 Hz, 3H); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -115.08 (s); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.5

Hz), 141.2, 140.8, 133.8 (d, $J$ = 3.1 Hz), 128.2 (d, $J$ = 8.1 Hz), 126.8, 125.7, 122.0, 121.8, 118.7, 118.3, 117.6, 117.5, 115.7 (d, $J$ = 21.6 Hz), 115.2, 114.6, 109.9, 109.6, 48.1, 31.6; IR (ATR, $cm^{-1}$): ν = 3055 (w), 2926 (w), 1606 (m), 1508 (s), 1497 (m), 1473 (s), 1448 (m), 1433 (m), 1423 (m), 1406 (s), 1360 (m), 1340 (m), 1296 (w), 1288 (m), 1271 (m), 1244 (m), 1221 (s), 1171 (m), 1157 (s), 1132 (m), 1122 (m), 1092 (m), 1049 (w), 1014 (m), 978 (m), 957 (w), 930 (w), 920 (w), 843 (m), 814 (s), 779 (w), 729 (vs), 681 (m), 650 (m), 623 (m), 592 (m), 580 (m), 567 (m), 542 (w); GC/MS (EI, 70eV): m/z (%) = 328 (44), 219 (100), 109 (9); HRMS (EI): calculated for $C_{22}H_{17}N_2F_1$ ([$M^+$]): 328.1370; found: 328.1374.

***5-Methyl-10-(3-(trifluoromethyl)benzyl)-5,10-dihydroindolo[3,2-b]indole*** **5n** was prepared following general procedure A using compound **3** (100 mg, 0.27 mmol) and 3-(trifluoromethyl)benzylamine (118 µL, 0.82 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane 3:1) to yield **5n** (62 mg, 60 %) as a white solid; m.p. 153-154 ºC; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 1H), 7.56 – 7.45 (m, 2H), 7.45 – 7.09 (m, 8H), 7.01 (ddd, $J$ = 8.0, 7.1, 1.0 Hz, 1H), 5.63 (s, 2H), 4.05 (s, 3H); $^{19}$F NMR (282 MHz, $CDCl_3$) δ -62.55 (s); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 141.1, 140.8, 139.1, 131.1 (d, $J$ = 32.3 Hz), 129.8, 129.4, 126.9, 125.6, 124.4 (q, $J$ = 3.8 Hz), 123.9 (q, $J$ = 274.3 Hz), 123.2 (q, $J$ = 3.8 Hz), 122.1, 121.8, 118.8, 118.3, 117.6, 117.3, 115.3, 114.5, 109.8, 109.6, 48.4, 31.6; IR (ATR, $cm^{-1}$): ν = 3055 (w), 2926 (w), 1579 (w), 1497 (m), 1473 (m), 1446 (m), 1433 (m), 1406 (m), 1363 (w), 1346 (w), 1327 (s), 1288 (m), 1271 (m), 1246 (m), 1221 (m), 1186 (m), 1161 (s), 1153 (s), 1117 (vs), 1092 (s), 1072 (s), 1049 (m), 1014 (m), 1003 (m), 989 (m), 980 (m), 957 (w), 947 (w), 920 (m), 893 (m), 872 (w), 841 (m), 827 (m), 793 (s), 737 (s), 727 (vs), 700 (s), 677 (m), 665 (m), 648 (m), 613 (m), 602 (m), 586 (m), 567 (m), 552 (m), 540 (m); GC/MS (EI, 70eV): m/z (%) = 378 (52), 219 (100), 159 (8); HRMS (EI): calculated for $C_{23}H_{17}N_2F_3$ ([$M^+$]): 378.1338; found: 378.1338.

***5-Methyl-10-phenethyl-5,10-dihydroindolo[3,2-b]indole*** **5o** was prepared following general procedure A using compound **3** (100 mg, 0.27 mmol) and phenethylamine (104 µL, 0.82 mmol). The product was purified by flash chromatography (silica gel, heptanes/dichloromethane 4:1) to

yield **5o** (74 mg, 83 %) as a white solid; m.p. 138-139 ºC; $^{1}$H NMR (250 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H), 7.62 – 6.96 (m, 11H), 4.83 – 4.59 (m, 2H), 4.15 (s, 3H), 3.34 – 3.15 (m, 2H); $^{13}$C NMR (63 MHz, $CDCl_3$) δ 141.2, 140.4, 138.7, 128.8, 128.7, 126.7, 126.6, 125.3, 121.7, 121.6, 118.3, 118.2, 117.5, 117.4, 114.9, 114.7, 109.6, 109.5, 47.1, 36.7, 31.6; IR (ATR, $cm^{-1}$): ν = 3026 (w), 2929 (m), 1495 (m), 1477 (s), 1450 (m), 1439 (m), 1423 (m), 1406 (s), 1362 (m), 1348 (s), 1281 (m), 1228 (s), 1203 (m), 1167 (m), 1155 (m), 1132 (m), 1122 (m), 1082 (w), 1016 (m), 999 (m), 850 (w), 829 (w), 742 (s), 727 (vs), 694 (vs), 646 (m), 596 (m), 580 (m), 569 (w), 532 (m); GC-MS (EI, 70 eV): m/z (%) = 324 (54), 233 (100), 218 (42); HRMS (ESI): calcd. for $C_{23}H_{20}N_2$ ($[M]^+$): 324.1627; found: 324.1624.

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