Tetrahedron 69 (2013) 7492–7504

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

One-pot synthesis of arylated 1-methyl-1*H*-indoles by Suzuki–Miyaura cross-coupling reactions of 2,3-dibromo-1-methyl-1*H*-indole and 2,3,6-tribromo-1-methyl-1*H*-indole

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ARTICLE INFO

Article history:
Received 18 March 2013
Received in revised form 15 May 2013
Accepted 21 May 2013
Available online 18 June 2013

Keywords:
Catalysis
Cross-coupling
Suzuki–Miyaura reaction
Palladium
N-Heterocycles

ABSTRACT

Arylated 1-methyl-1*H*-indoles were prepared by Suzuki–Miyaura cross-coupling reactions of 2,3-dibromo-1-methyl-1*H*-indole and 2,3,6-tribromo-1-methyl-1*H*-indole. The reactions proceed with very good regioselectivity in favour of position 2.

1. Introduction

The substituted indole core is a structural component of agrochemicals, functional materials, of a broad number of biologically active compounds, and especially of many pharmaceutical agents.[1] Due to its capability of binding with many receptors with excellent affinity, indole is referred to as a so-called privileged structure.[2] They are structural motifs of a variety of biologically active compounds, such as novel COX-2 inhibitors for the treatment of arthritic pain.[3] For example, 2,3-bis(4-methoxyphenyl)indole ('indoxole') represents a potent anti-inflammatory agent.[4] The chemistry and biology of indoles have been reviewed several times.[5] Various well-established classical methods have been applied for the synthesis and functionalization of indoles for more than 100 years. A great deal of recent work has been focused on the development of transition metal-catalysed reactions for the direct arylation of indoles.[6] In this context, impressive strategies have been developed to synthesize C2- and C3-functionalized indoles.[7] Traditional methods of their synthesis mostly involve multistep syntheses.[7,8] Gribble and Liu reported the synthesis of *N*-phenylsulfonyl-2,3-diarylindoles by twofold Suzuki–Miyaura reactions of 2,3-dihalo-*N*-(phenylsulfonyl)indoles.[9] However, all attempts to develop a site-selective reaction failed, because of a similar reactivity of positions 2 and 3 and formation of diarylated products. Recently, we developed the first site-selective Suzuki–Miyaura cross-coupling reactions of 2,3-dibromoindoles.[10] The success of these reactions, which provide a convenient one-pot synthesis of various 2,3-diarylindoles, relies on the use of *N*-methyl-2,3-dibromoindole as the starting material and on a proper optimization. Herein, we report full details of this work. In addition, we report what are, to the best of our knowledge, the first Suzuki–Miyaura of 2,3,6-tribromoindole.

2. Results and discussion

The Suzuki–Miyaura reaction of 2,3-dibromo-*N*-methylindole[11] (**1**) with arylboronic acids **2a**–**e** (2.3 equiv) afforded 2,3-diarylindoles **3a**–**e** (Scheme 1, Table 1). It was found that the reaction is sensitive to the presence of water. The use of tetrahydrofuran in combination with an aqueous solution of K_2CO_3 resulted in the formation of a mixture containing products in which the loss of

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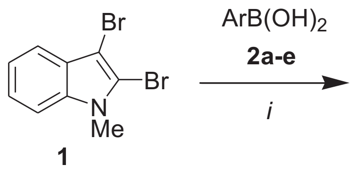
http://dx.doi.org/10.1016/j.tet.2013.05.100



Scheme 1. Synthesis of **3a**–**e**. Conditions: (i) **1** (1.0 equiv), Ar^1–$B(OH)_2$ (2.3 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 110 °C, 6 h.

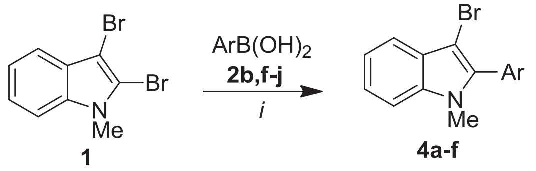
Table 1
Synthesis of **3a**–**e**

2,3	Ar	3[a] (%)
a	4-MeC_6H_4	90
b	4-EtC_6H_4	86
c	3,5-$Me_2C_6H_3$	90
d	4-ClC_6H_4	83
e	4-$^tBuC_6H_4$	79

[a] Yields of isolated products.

bromine from C3 was accompanied with the formation of monoarylated and diarylated indoles. The best yields were obtained when 1,4-dioxane was used as the solvent. However, the use of dry tetrahydrofuran resulted in low yields. The employment of DMF and toluene as solvents required high reaction times and gave relatively low yields. Finally, K_3PO_4 was found to be the best base, followed by K_2CO_3, while organic bases such as triethylamine or hydroxylamine resulted in low yields. The reaction was also optimized with regard to the catalyst. It was found that $Pd(PPh_3)_4$ (3 mol %) resulted in good yields, while S-Phos and X-Phos also gave satisfactory results. Good yields were obtained for both electron-rich and electron-poor arylboronic acids.

The regioselective Suzuki–Miyaura reaction of **1** with arylboronic acids **2f**–**k** (1.0 equiv) afforded the 2-aryl-3-bromo-1-methyl-1*H*-indoles **4a**–**f** in good yields (Scheme 2, Table 2). The reaction was optimized in case of product **4e** (Table 3). The use of wet solvents resulted in replacement of the bromine by a hydrogen atom at carbon 3 (vide infra). Thus, solvents had to be thoroughly dried. It was found that dioxane and the base K_3PO_4 gave excellent yields of mono-coupling products and no formation of other products was observed. While in case of other solvents, such as dichloromethane, mixtures of products were observed. In case of THF and acetone, the other isomers were also observed by TLC. The use of $Pd(OAc)_2$ in the presence of X-Phos or S-Phos gave similar yield as compared to the use of $Pd(PPh_3)_4$ (3–4 mol %). $Pd(PPh_3)_4$ was used as the catalyst in all reactions because of its relatively low price. The structure of **4e** was independently confirmed by X-ray crystal structure analysis (Fig. 1).[12]



Scheme 2. Synthesis of **4a**–**f**. Conditions: (i) **1** (1.0 equiv), $ArB(OH)_2$ (1.1 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane, 70 °C, 6 h.

Table 2
Synthesis of **4a**–**f**

4	2	Ar	4[a] (%)
a	**b**	2-EtC_6H_4	73
b	**f**	C_6H_5	84
c	**g**	3-$(C_6H_5)C_6H_4$	77
d	**h**	3-$(CF_3)C_6H_4$	81
e	**i**	3,4-$(MeO)_2C_6H_3$	79
f	**j**	2-$(MeO)C_6H_4$	71

[a] Yields of isolated products.

Table 3
Optimization of the synthesis of **4e**

Entry	Solvent	Base	**4e**[a] (%)
1	CH_2Cl_2	Et_3N	Mixture
2	CH_2Cl_2	K_3PO_4	41
3	CH_2Cl_2	K_2CO_3	33
4	THF	K_3PO_4	59
5	THF	K_2CO_3	53
6	Dioxane	K_3PO_4	79
7	Acetone	K_3PO_4	52
8	THF/dioxane (1:1)	K_3PO_4	53

[a] Yields of isolated products.

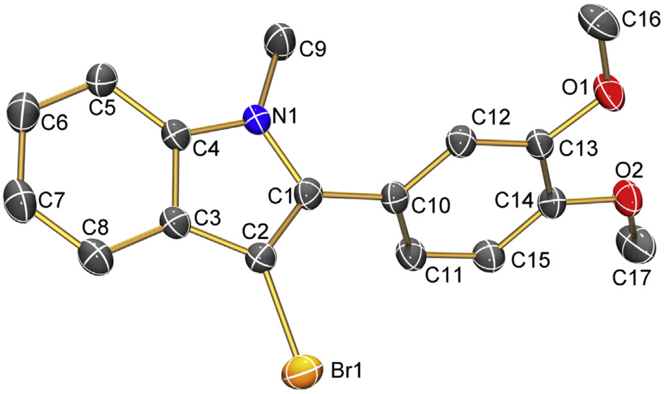
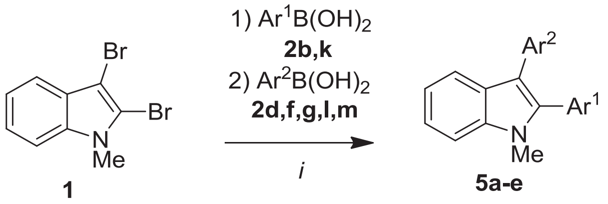


Fig. 1. ORTEP drawing of the molecular structure of **4e** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms are omitted for clarity.

Our next goal was to develop a regioselective synthesis of diarylated indoles **5a**–**e** by application of a one-pot double Suzuki–Miyaura reaction. This reaction was successfully realized when **1** was reacted with arylboronic acid (1.0 equiv) in the presence of catalyst and base at 70 °C for 6 h and, subsequently, the next boronic acid (1.3 equiv) was added and stirring was continued at 110 °C for 8 h (Scheme 3, Table 4). Good yields were obtained for both electron-rich and electron-deficient arylboronic acids.



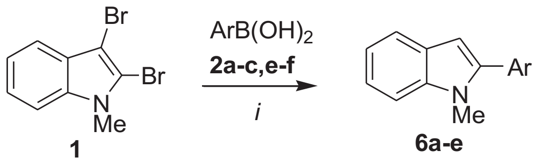
Scheme 3. Synthesis of **5a**–**e**. Conditions: (i) (1) **1** (1.0 equiv), **2b**,**k** (1.1 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (4 mol %), 1,4-dioxane, 70 °C, 6 h; (2) **2d**,**f**,**g**,**l**,**m** (1.3 equiv), K_3PO_4 (1.5 equiv), 110 °C, 8 h.

Table 4
Synthesis of **5a**–**e**

5	2	Ar^1	Ar^2	5[a] (%)
a	**b g**	4-EtC_6H_4	3-PhC_6H_4	71
b	**k**,**d**	2,5-$(MeO)_2C_6H_3$	Ph	69
c	**k**,**f**	2,5-$(MeO)_2C_6H_3$	4-ClC_6H_4	59
d	**k**,**l**	2,5-$(MeO)_2C_6H_3$	4-FC_6H_4	71
e	**k**,**m**	2,5-$(MeO)_2C_6H_3$	4-$(F_3C)C_6H_4$	63

[a] Yields of isolated products.

We have mentioned above that the use of wet solvents resulted in the formation of mixtures including products derived from loss of the bromine atom from position 3 of the indole. We tried to use this observation with the goal to develop conditions for the selective synthesis of these products. The reaction of **1** with arylboronic acids, carried out in a 1:1 mixture of dioxane and water, allowed for the synthesis of products **6a**–**e** in good yields (Scheme 4, Table 5). The employment of pure water as the solvent resulted in a decrease of the yield. The structure of **6a** was independently confirmed by X-ray crystal structure analysis (Fig. 2).[12]



Scheme 4. Synthesis of **6a**–**e**. Conditions: (1) **2** (1.0 equiv), **2a**–**c**,**e**–**f** (1.1 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane/water=1:1, 90 °C, 6 h.

Table 5
Synthesis of **6a**–**e**

6	2	Ar	6^a (%)
a	**a**	$4\text{-}MeC_6H_4$	92
b	**b**	$4\text{-}EtC_6H_4$	95
c	**c**	$3,5\text{-}Me_2C_6H_3$	83
d	**e**	$4\text{-}(^tBu)C_6H_4$	81
e	**f**	C_6H_5	97

[a] Yields of isolated products.

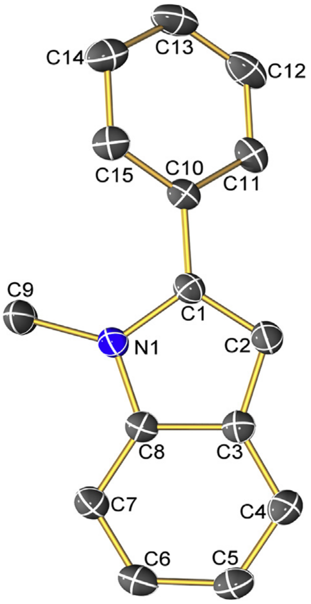
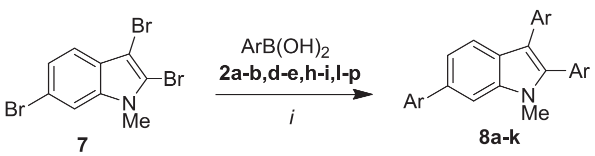


Fig. 2. ORTEP drawing of the molecular structure of **6a** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms are omitted for clarity.

2,3,6-Tribromo-1-methyl-1*H*-indole (**7**) was prepared as reported[10] and was further used in the following reactions as starting material. 2,3,6-Triaryl-1-methyl-1*H*-indoles **8a**–**k** were prepared in good yields (78–94%) by Suzuki–Miyaura cross-coupling reactions of **7** with 3.4 equiv of arylboronic acids **2a**,**b**,**d**,**e**,**h**,**i**,**l**–**p** (Scheme 5, Table 6). Products **8b** and **8g** were selected for optimization studies. Compound **8b** is derived from an electron-rich arylboronic acid, while **8g** is derived from an electron-poor arylboronic acid. The best yields were obtained when the reactions were carried out at 110 °C for 8 h. The use of 1,4-dioxane as solvent gave the best results. In contrast to the synthesis of products **3**, the employment of an aqueous solution of potassium carbonate gave better yields than the use of potassium phosphate. The use of $Pd(PPh_3)_4$ (4 mol %) gave higher yields than $Pd(PPh_3)_2Cl_2$ or $Pd(OAc)_2$ (3 mol %), with X-Phos or S-Phos (6 mol %) as a catalyst. Good yields were obtained for both electron-rich and electron-poor arylboronic acids. The structures of **8b** and **8k** were independently confirmed by X-ray crystallography (Figs. 3 and 4) . The crystal structures were found to show monoclinic *P*21/*n* symmetry. The asymmetric unit contains single molecule.



Scheme 5. Synthesis of **8**. Conditions: (1) **7** (1.0 equiv), **2a**–**b**,**d**,**e**,**h**–**j**,**l**–**p** (3.3 equiv), K_2CO_3 (4 equiv), $Pd(PPh_3)_4$ (4 mol %), 1,4-dioxane, 2 mL H_2O, 110 °C, 8 h.

Table 6
Synthesis of **8a**–**k**

8	2	Ar	8^a (%)
a	**a**	$4\text{-}MeC_6H_4$	87
b	**b**	$4\text{-}EtC_6H_4$	94
c	**d**	$4\text{-}ClC_6H_4$	91
d	**e**	$4\text{-}^tBuC_6H_4$	85
e	**h**	$3\text{-}(CF_3)C_6H_4$	78
f	**i**	$3,4\text{-}(MeO)_2C_6H_3$	82
g	**l**	$4\text{-}FC_6H_4$	84
h	**m**	$4\text{-}(CF_3)C_6H_4$	82
i	**n**	$4\text{-}(MeO)C_6H_4$	87
j	**o**	$3\text{-}ClC_6H_4$	80
k	**p**	$2\text{-}(EtO)C_6H_4$	85

[a] Yields of isolated products.

2,6-Diaryl-3-bromo-1-methyl-1*H*-indoles **9a**–**e** were prepared by reaction of **7** with arylboronic acids **2a**,**b**,**d**,**l**,**n** (2.1 equiv). The reaction proceeded in good yields (73–83%) and with excellent site-selectivity (Scheme 6, Table 7). The first attack occurred at carbon atom C-2 and C-6, while position 3 remained unattacked. The reactions were best carried out at 90 °C using exactly 2.1 equiv of the arylboronic acid and 5 mol % of $Pd(PPh_3)_4$ as the catalyst. Both electron-donating and withdrawing groups were examined in this reaction. K_3PO_4 (3.0 equiv) gave better yields than K_2CO_3. The structure of **9b** (Fig. 5) was independently confirmed by X-ray crystal structure analysis . Both aryl groups and the indole moiety are twisted out of plane.

The Suzuki–Miyaura cross-coupling reaction of **7** with arylboronic acids **2c**,**b**,**e**,**f** (1.1 equiv) afforded the 2-aryl-3,6-dibromo-1-methyl-1*H*-indoles **10a**–**d** in 77–84% yields and with very good site-selectivity (Scheme 7, Table 8). A solvent mixture of toluene/1,4-dioxane (4:1), K_3PO_4 (1.5 equiv) as base and $Pd(PPh_3)_4$ (3 mol %) as a catalyst were used. Compounds **10a** and **10d** were selected for optimization studies (Table 9). Compound **10a** is derived from an electron-rich arylboronic acid, while **10d** is derived from an electron-poor arylboronic acid. During the optimization, we have found that the best yields were obtained when the reactions were carried out at 65 °C. Significant amounts of side-products, derived from multi-fold coupling, were formed when the temperature was higher than 65 °C. A solvent mixture of toluene/1,4-dioxane (4:1), K_3PO_4 (1.5 equiv) as base and $Pd(PPh_3)_4$ (3 mol %) as a catalyst were used. The structures of all products were confirmed by spectroscopic methods.

The structure of **10b** was independently confirmed by 2D-NMR experiments. In the NOESY spectrum, an interaction was observed between the aromatic proton attached to carbon atom (C-6′) to the *N*-methyl group (Fig. 6). In addition, a strong correlation was observed between the aromatic proton of C-7 to the *N*-methyl group. In the HMBC spectrum, the aromatic proton of C-2 showed a strong coupling with carbon C-3 of ring A.

2,3,6-Triaryl-1-methyl-1*H*-indoles **11a**–**d** were prepared by site-selective Suzuki cross-coupling reactions. A one-pot synthesis was carried out for product **11a**. The first cross-coupling reaction proceeded by reaction of **7** with 1.1 equiv of **2l** at 65 °C for 8 h. Subsequently, **2e** was added (2.1 equiv) to give product **11a** in good

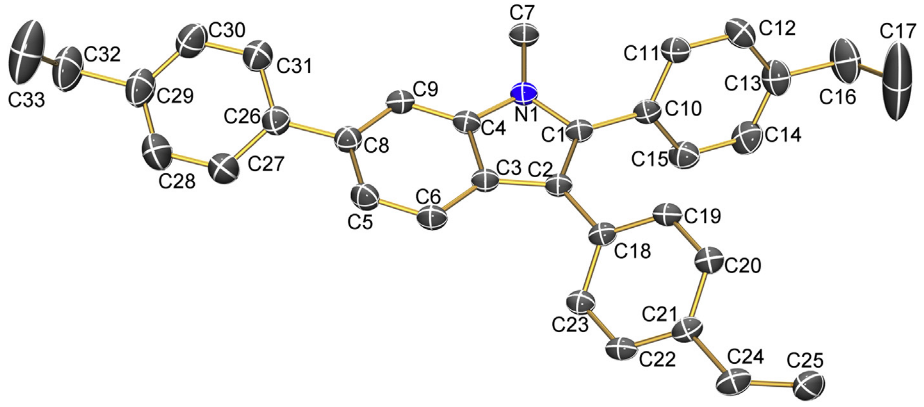


Fig. 3. ORTEP drawing of the molecular structure of **8b** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms are omitted for clarity.

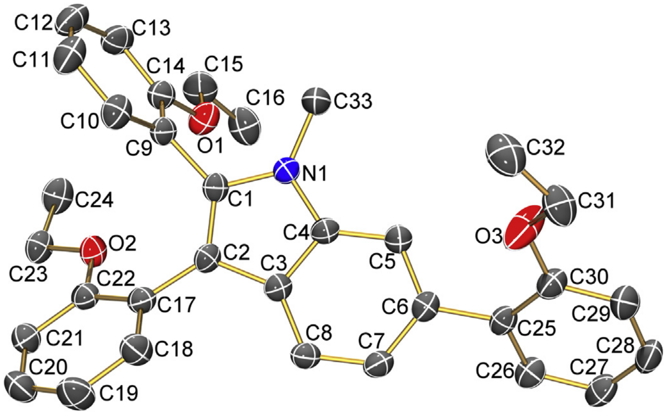
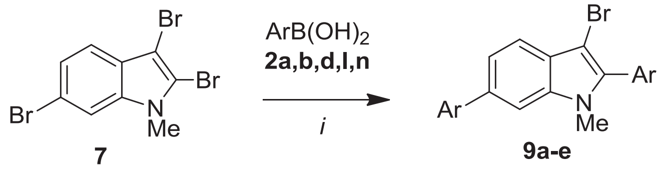


Fig. 4. ORTEP drawing of the molecular structure of **8k** in the crystal. Thermal ellipsoids with 50% probability at 173 K. Hydrogen atoms are omitted for clarity.



Scheme 6. Synthesis of **9a**–**e**. Reagents and conditions: (i) **7** (1.0 equiv), **2a**,**b**,**d**,**l**,**n** (2.1 equiv), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (3.0 equiv), 1,4-dioxane, 90 °C, 8 h.

Table 7
Synthesis of **9a**–**e**

9	2	Ar	9[a] (%)
a	**a**	$4\text{-}MeC_6H_4$	73
b	**b**	$4\text{-}EtC_6H_4$	79
c	**d**	$4\text{-}ClC_6H_4$	80
d	**l**	$4\text{-}FC_6H_4$	83
e	**n**	$4\text{-}(MeO)C_6H_4$	83

[a] Yields of isolated products.

yield (74%). A mixture of the solvents toluene and 1,4-dioxane (4:1), K_3PO_4 (1.5 equiv) and $Pd(PPh_3)_4$ (5 mol %) were used. Derivatives **11b**–**d** were synthesized in two steps via products **10**, which were isolated. Products **11a**–**d** were isolated in good yields (72–82%) (Scheme 8, Table 10). To achieve a good site-selectivity in favour of position 2 of the substrate, it is important that the first step is carried out at 65 °C to avoid double coupling and the second step at 90 °C. Both electron-donating and withdrawing groups were examined for the synthesis of compounds **11a**–**d**.

Unfortunately, the stepwise or one-pot synthesis of indoles containing three different aryl groups proved to be unsuccessful. A number of side-products were formed and not clean products could be isolated.

3. Conclusions

The order of reactivity of the three different positions of 2,3,6-tribromo-1-methyl-1*H*-indole is C-2>C-6>C3 (Scheme 9). The first attack occurred at carbon atom C-2. The site-selectivity can be explained by the fact that carbon atom C-2 is considerable more electron-deficient than positions 3 and 6. The second attack occurred at position 6, which is electronically less deficient than position 2. Carbon atom C-3 is less electron-deficient than C-6 because of the electron-donating effect of the nitrogen atom.

In conclusion, a variety of arylated indoles were synthesized with excellent site-selectivity by Suzuki–Miyaura reactions of 2,3-dibromo-1-methyl-1*H*-indole and 2,3,6-tribromo-1-methyl-1*H*-indole. The site-selectivity can be explained by electronic reasons. In several cases, monoarylated bromoindoles were found to be very sensitive to moisture and decompose rapidly with loss of bromine. In contrast, 2,3-diarylindoles proved to be stable for several days even at the air. Likewise, the triarylated indoles are highly stable and can be stored for months.

4. Experimental section

4.1. General procedure for the synthesis of 3a–e, 4a–f and 6a–e

The reaction was carried out in a pressure tube. A 1,4-dioxane (for compounds **3** and **4**) or 1:1 dioxane/water (for compounds **6**) solution (4 mL) of **1**, K_3PO_4, $Pd(PPh_3)_4$ and arylboronic acid **2** was stirred at 110 °C (for compounds **3**), 70 °C (for compounds **4**) or 90 °C (for compounds **6**) for 6 h (for compounds **3**, **4** and **6**). After cooling to 20 °C, a saturated aqueous solution of NH_4Cl was added. The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (silica gel, heptanes).

4.1.1. 1-Methyl-2,3-di-p-tolyl-1H-indole (***3a***). Starting with **1** (289 mg, 1.0 mmol), **2a** (313 mg, 2.3 mmol), K_3PO_4 (636 mg, 3.0 mmol), $Pd(PPh_3)_4$ (3 mol %) and 1,4-dioxane (4 mL), **3a** was isolated as a colourless oil (280 mg, 90%). ^1H NMR (250.13 MHz, $CDCl_3$): δ=3.28 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.63 (s, 3H, NCH_3), 7.05–7.27 (m, 10H, ArH), 7.45 (dt, J=8.0, 0.9 Hz, 1H, ArH), 7.67 (dt, J=8.0, 0.9 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ=21.2, 21.3 (CH_3), 31.1 (NCH_3), 110.7 (CH), 115.3 (C), 119.9, 120.7, 122.7 (CH), 128.1 (C), 129.7 (2CH), 129.9 (2CH), 130.1 (C), 130.5, 131.9 (2CH),

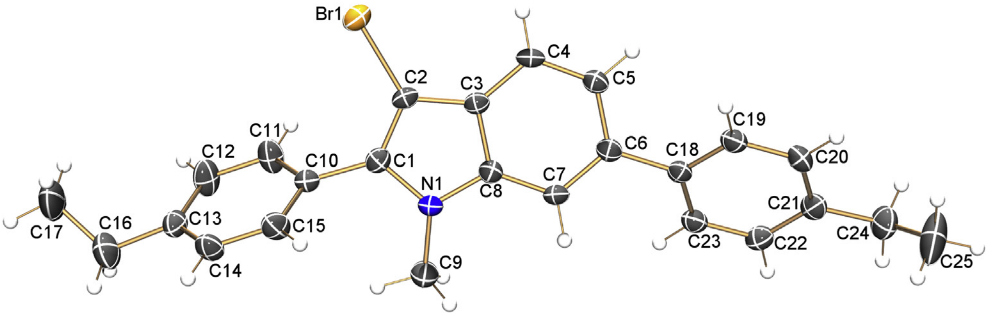
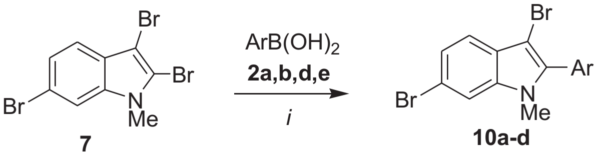


Fig. 5. Molecular structure of compound **9b**.



Scheme 7. Synthesis of **10a**–**d**. Reagents and conditions: (i) **7** (1.0 equiv), **2a**,**b**,**d**,**e** (1.1 equiv), Pd(PPh$_3$)$_4$ (3 mol %), K$_3$PO$_4$ (1.5 equiv), toluene/1,4-dioxane (4:1), 65 °C, 8 h.

Table 8
Synthesis of **10a**–**d**

10	2	Ar	10[a] (%)
a	**a**	4-MeC$_6$H$_4$	**77**
b	**b**	4-EtC$_6$H$_4$	**83**
c	**d**	4-ClC$_6$H$_4$	**79**
d	**e**	4-^{t}BuC$_6$H$_4$	**84**

[a] Yields of isolated products.

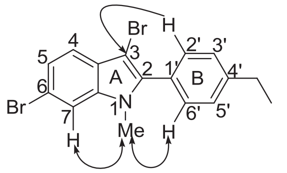
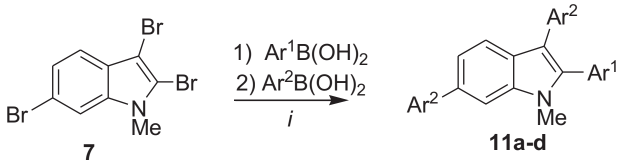


Fig. 6. 2D-NMR correlations of compound **10b**.



Scheme 8. Synthesis of **25a**–**d**. Reagents and conditions: (i) 1) Ar^{1}B(OH)$_2$ **2d**,**e**,**l** (1.1 equiv), Pd(PPh$_3$)$_4$ (5 mol %), K$_3$PO$_4$ (1.5 equiv), toluene/1,4-dioxane (4:1), 65 °C, 8 h, (2) Ar^{2}B(OH)$_2$ **2d**,**e**,**k**,**m**,**o** (2.1 equiv), K$_2$CO$_3$ (aq) (2 M, 1 mL), 1,4-dioxane, 90 °C, 8 h.

Table 10
Synthesis of **11a**–**d**

11	2	Ar^1	Ar^2	11[a] (%)
a	**l**,**e**	4-FC$_6$H$_4$	4-^{t}BuC$_6$H$_4$	74[c]
b	**e**,**n**	4-^{t}BuC$_6$H$_4$	4-(MeO)C$_6$H$_4$	81[b]
c	**d**,**n**	4-ClC$_6$H$_4$	4-(MeO)C$_6$H$_4$	82[d]
d	**e**,**j**	4-^{t}BuC$_6$H$_4$	2-(MeO)C$_6$H$_4$	72[b]

[a] Yields of isolated products.
[b] Yield based on **11c** (stepwise synthesis).
[c] Yield based on **7** (one-pot synthesis).
[d] Yield based on **11d** (stepwise synthesis).

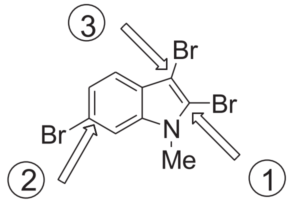
133.4, 135.6, 138.3, 138.4, 138.7 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3044 (w), 3015 (m), 2942 (m), 2914 (m), 2860 (w), 1904 (w), 1613 (w), 1564 (w), 1553 (m), 1519 (m), 1494 (w), 1480 (m), 1464 (m), 1446 (m), 1428 (m), 1414 (w), 1366 (m), 1326 (m), 1258 (m), 1232 (m), 1182 (m), 1150 (m), 1089 (m), 1018 (m), 940 (m), 858 (m), 825 (s), 816 (s), 802 (s), 773 (m), 747 (s), 738 (s), 719 (s), 694 (m), 652 (m), 627 (s), 561 (m), 540 (m). GC–MS (EI, 70 eV): *m*/*z* (%)=312 ([M+1]$^+$, 26), 311 ([M]$^+$, 100), 295 (8), 281 (8), 140 (8), 139 (6). HRMS (EI) calcd for C$_{23}$H$_{21}$N [M]$^+$ is 311.16685, found 311.166454.

*4.1.2. 2,3-Bis(4-ethylphenyl)-1-methyl-1H-indole (**3b**).* Starting with **1** (289 mg, 1.0 mmol), **2b** (262 mg, 2.3 mmol), K$_3$PO$_4$ (636 mg, 3.0 mmol), Pd(PPh$_3$)$_4$ (3 mol %) and 1,4-dioxane (4 mL), **3b** was isolated as a yellowish oil (291 mg, 86%). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ=1.01 (t, *J*=7.5 Hz, 3H, CH$_3$), 1.05 (t, *J*=7.5 Hz, 3H, CH$_3$), 2.40 (q, *J*=7.5 Hz, 2H, CH$_2$), 2.48 (q, *J*=7.5 Hz, 2H, CH$_2$), 3.42 (s, 3H, NCH$_3$), 6.90–6.96 (m, 3H, ArH), 7.02–7.10 (m, 7H, ArH), 7.25 (d, *J*=8.2 Hz, 1H, ArH), 7.51 (d, *J*=7.8 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, CDCl$_3$): δ=15.8, 16.0 (CH$_3$), 29.1, 29.2 (CH$_2$), 31.2 (NCH$_3$), 110.7 (CH), 115.4 (C), 120.0, 121.0, 123.0 (CH), 128.1 (C), 128.5, 128.7 (2CH), 130.3 (C), 130.6, 132.0 (2CH), 133.7, 138.3, 138.4, 142.0, 144.9 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3047 (w), 3022 (w), 2961 (s), 2928 (w), 1797 (w), 1765 (w), 1726 (w), 1519 (m), 1463 (s), 1362 (m), 1325 (m), 1257 (m), 1131 (w), 1115 (w), 1089 (m), 1060 (w), 1017 (m), 967 (w), 923 (w), 869 (m), 836 (s), 801 (w), 740 (s), 652 (w), 629 (m), 545 (m). MS (EI, 70 eV): *m*/*z* (%)=340 ([M+1]$^+$, 28), 339 ([M]$^+$, 100), 324 (34), 309

Table 9
Optimization of the synthesis of **10a** and **10d**

Entry	Solvent	Base	Ligand	*T* (°C)	% (**10a**)[a]	% (**10d**)[a]
1	Dioxane	2 M K$_2$CO$_3$	(PPh$_3$)$_4$Pd	70	Mixture	Mixture
2	Dioxane	2 M K$_2$CO$_3$	Cy$_3$P, Pd(OAc)$_2$	70	Mixture	Mixture
3	Dioxane	2 M K$_2$CO$_3$	S-Phos, Pd(OAc)$_2$	70	Mixture	Mixture
4	Dioxane	2 M K$_2$CO$_3$	(PPh$_3$)$_2$PdCl$_2$	70	Mixture	Mixture
5	Dioxane	1.5 equiv K$_3$PO$_4$	(PPh$_3$)$_4$Pd	65	Mixture	Mixture
6	Dioxane	1.5 equiv K$_3$PO$_4$	Cy$_3$P, Pd(OAc)$_2$	65	Mixture	Mixture
7	Toluene	2 M K$_2$CO$_3$	(PPh$_3$)$_4$Pd	65	No reaction	No reaction
8	Toluene	2 M K$_2$CO$_3$	(PPh$_3$)$_4$Pd	70	No reaction	No reaction
9	Dioxane/toluene (1:1)	2 M K$_2$CO$_3$	(PPh$_3$)$_4$Pd	65	Mixture	Mixture
10	Dioxane/toluene (4:1)	1.5 equiv K$_3$PO$_4$	(PPh$_3$)$_4$Pd	65	30	25
11	*Dioxane/toluene (1:4)*	*1.5 equiv K$_3$PO$_4$*	*(PPh$_3$)$_4$Pd*	*65*	*84*	*79*

[a] Yields of isolated products.



Scheme 9. Order of reactivity.

(5), 294 (5), 281 (5), 278 (4), 146 (5). HRMS (EI) calcd for $C_{25}H_{25}N$ $[M]^+$ is 339.19815, found 339.197901.

*4.1.3. 2,3-Bis(3,5-dimethylphenyl)-1-methyl-1H-indole (**3c**).* Starting with **1** (289 mg, 1.0 mmol), **2c** (345 mg, 2.3 mmol), K_3PO_4 (636 mg, 3.0 mmol), $Pd(PPh_3)_4$ (3 mol %) and 1,4-dioxane (4 mL), **3c** was isolated as colourless crystals (305 mg, 90%), mp 108–109 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ=2.22 (s, 6H, $2CH_3$), 2.30 (s, 6H, $2CH_3$), 3.64 (s, 3H, NCH_3), 6.82 (d, *J*=0.8 Hz, 1H, ArH), 6.97 (s, 2H, ArH), 7.03 (s, 2H, ArH), 7.06 (s, 1H, ArH), 7.11–7.16 (m, 1H, ArH), 7.25 (ddd, *J*=8.2, 7.0, 1.2 Hz, 1H, ArH), 7.46 (dt, *J*=8.3, 0.9 Hz, 1H, ArH), 7.73 (dt, *J*=7.8, 0.9 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ=21.3, 21.4 ($2ArCH_3$), 31.1 (NCH_3), 110.6 (CH), 115.5 (C), 120.1, 120.7, 122.6, 127.9 (CH), 128.1 (C), 128.4, 129.7 (2CH), 130.4 (CH), 132.9, 136.2 (C), 137.9 (2C), 138.3 (C), 138.5 (2C), 138.7 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3026 (w), 2912 (m), 2857 (m), 2728 (w), 2687 (w), 1783 (m), 1598 (m), 1573 (m), 1549 (m), 1538 (m), 1519 (w), 1480 (m), 1467 (m), 1435 (m), 1392 (m), 1379 (m), 1366 (m), 1323 (m), 1288 (m), 1237 (m), 1196 (m), 1153 (m), 1132 (m), 1101 (m), 1036 (m), 1015 (m), 997 (m), 966 (m), 948 (m), 914 (m), 903 (m), 889 (m), 862 (m), 845 (m), 836 (m), 781 (m), 738 (s), 702 (s), 693 (s), 666 (m), 648 (m), 603 (m), 588 (m), 567 (m), 541 (m). MS (EI, 70 eV): *m*/*z* (%)=340 ($[M+1]^+$, 30), 339 ($[M]^+$, 100), 308 (5). HRMS (EI) calcd for $C_{25}H_{25}N$ $[M]^+$ is 339.19815, found 339.198033.

*4.1.4. 2,3-Bis(4-chlorophenyl)-1-methyl-1H-indole (**3d**).* Starting with **1** (289 mg, 1.0 mmol), **2d** (360 mg, 2.3 mmol), K_3PO_4 (636 mg, 3.0 mmol), $Pd(PPh_3)_4$ (3 mol %) and 1,4-dioxane (4 mL), **3d** was isolated as a yellowish oil (292 mg, 83%). ^1H NMR (300.13 MHz, $CDCl_3$): δ=3.68 (s, 3H, NCH_3), 7.12–7.18 (m, 1H, ArH), 7.23–7.32 (m, 5H, ArH), 7.35–7.40 (m, 2H, ArH), 7.44–7.51 (m, 2H, ArH), 7.51 (d, *J*=8.0 Hz, 1H, ArH), 7.67 (d, *J*=7.8 Hz, 1H, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ=31.2 (CH_3), 110.9 (CH), 114.7 (C), 119.8, 121.3, 123.3 (CH), 127.5 (C), 129.3, 129.6 (2CH), 131.3, 131.8 (C), 132.1, 133.7 (2CH), 134.8, 134.9, 137.4, 138.5 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3078 (w), 3051 (w), 2919 (m), 2850 (m), 1916 (w), 1894 (w), 1567 (w), 1538 (m), 1496 (m), 1478 (m), 1464 (m), 1456 (m), 1430 (m), 1410 (m), 1389 (m), 1364 (m), 1326 (m), 12 97 (w), 1257 (m), 1233 (m), 1177 (w), 1152 (m), 1135 (w), 1121 (w), 1106 (w), 1088 (s), 1044 (m), 1011 (s), 967 (m), 938 (m), 930 (m), 856 (m), 846 (m), 836 (m), 830 (m), 820 (s), 794 (m), 761 (w), 743 (s), 727 (s), 719 (s), 705 (m), 688 (m), 666 (m), 644 (m), 622 (m), 607 (m), 578 (m), 557 (m), 540 (m). MS (EI, 70 eV): *m*/*z* (%)=354 ($[M+1]^+$, ^{37}Cl, 15), 353 ($[M]^+$, ^{37}Cl, 67), 352 ($[M+1]^+$, ^{35}Cl, 24), 351 ($[M]^+$, ^{35}Cl, 100), 315 (9), 314 (5), 301 (6), 266 (7), 265 (6), 140 (17), 139 (13). HRMS (EI): calcd for $C_{21}H_{15}Cl_2N$ $[M]^+$ is 351.05761, found 351.057126.

*4.1.5. 2,3-Bis(4-tert-butylphenyl)-1-methyl-1H-indole (**3e**).* Starting with **1** (289 mg, 1.0 mmol), **2e** (409 mg, 2.3 mmol), K_3PO_4 (636 mg, 3.0 mmol), $Pd(PPh_3)_4$ (3 mol %) and 1,4-dioxane (4 mL), **3e** was isolated as a greenish oil (313 mg, 79%). ^1H NMR (250.13 MHz, $CDCl_3$): δ=1.18 (s, 9H, $[C(CH_3)_3]$), 1.23 (s, 9H, $[C(CH_3)_3]$), 3.52 (s, 3H, NCH_3), 6.39–7.54 (m, 12H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ=31.1 (NCH_3), 31.6 (s, 3C, $C(CH_3)_3$), 31.7 (s, 3C, $C(CH_3)_3$), 34.9, 35.2 ($C(CH_3)_3$), 110.6 (CH), 116.9 (C), 120.0, 120.7, 122.7 (CH), 125.8, 126.1 (2CH), 126.8, 128.1 (C), 130.2, 131.7 (2CH), 133.9 (C), 138.3 (2C), 149.9, 150.8 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3052 (w), 2954 (m), 2928 (m), 2903 (m), 2865 (m), 1716 (m), 1661 (m), 1651 (m), 1606 (m), 1520 (m), 1464 (s), 1392 (m), 1362 (s), 1326 (m), 1266 (m), 1233 (s), 1201 (m), 1150 (m), 1109 (m), 1086 (m), 1016 (m), 941 (m), 932 (m), 880 (w), 861 (m), 838 (m), 823 (m), 795 (w), 763 (w), 737 (s), 711 (m), 699 (m), 651 (m), 633 (m), 619 (m), 601 (m), 552 (m). MS (EI, 70 eV): *m*/*z* (%)=396 ($[M+1]^+$, 32), 395 ($[M]^+$, 100), 380 (59), 350 (6), 183 (9), 154 (15). HRMS (EI) calcd for $C_{29}H_{33}N$ $[M]^+$ is 395.26075, found 395.260299.

*4.1.6. 3-Bromo-1-methyl-2-phenyl-1H-indole (**4a**).* Starting with **1** (289 mg, 1.0 mmol), **2f** (134 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %) and 1,4-dioxane (4 mL), **4a** was isolated as a brownish oil (240 mg, 84%). ^1H NMR (300.13 MHz, $CDCl_3$): δ=3.68 (s, 3H, NCH_3), 7.18–7.23 (m, 1H, ArH), 7.26–7.32 (m, 1H, ArH), 7.48 (dt, *J*=8.1, 0.8 Hz, 1H, ArH), 7.48–7.57 (m, 6H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ=32.0 (NCH_3), 90.0 (C), 111.2, 119.6, 121.4, 123.7 (CH), 128.0 (C), 129.4 (2CH), 129.7 (CH), 131.3 (C), 131.6 (2CH), 137.9, 139.0 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3055 (m), 3028 (m), 2937 (m), 2880 (w), 2836 (m), 1887 (w), 1714 (w), 1651 (w), 1604 (m), 1574 (m), 1479 (m), 1462 (s), 1441 (m), 1428 (m), 1380 (m), 1356 (m), 1339 (m), 1320 (m), 1234 (m), 1214 (m), 1176 (m), 1154 (m), 1127 (m), 1103 (m), 1074 (m), 1022 (m), 1010 (m), 968 (w), 944 (m), 921 (m), 828 (m), 792 (m), 735 (s), 697 (s), 677 (m), 614 (m), 583 (m), 547 (m). MS (EI, 70 eV): *m*/*z* (%)=288 ($[M+1]^+$, ^{81}Br, 18), 287 ($[M]^+$, ^{81}Br, 100), 286 ($[M+1]^+$, ^{79}Br, 20), 285 ($[M]^+$, ^{79}Br, 98), 206 (7), 205 (21), 204 (35), 191 (13), 190 (12), 178 (8), 176 (7), 164 (6), 163 (6), 102 (14). HRMS (EI) calcd for $C_{15}H_{12}BrN$ $[M]^+$ is 285.01476, found 285.014285.

*4.1.7. 2-(Biphenyl-3-yl)-3-bromo-1-methyl-1H-indole (**4b**).* Starting with **1** (289 mg, 1.0 mmol), **2g** (218 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %) and 1,4-dioxane (4 mL), **4b** was isolated as a yellowish oil (279 mg, 77%). ^1H NMR (250.13 MHz, $CDCl_3$): δ=3.70 (s, 3H, NCH_3), 7.24 (td, *J*=6.9, 1.1 Hz, 1H, ArH), 7.32 (td, *J*=6.9, 1.1 Hz, 1H, ArH) 7.38–7.42 (m, 1H, ArH), 7.46–7.67 (m, 6H, ArH), 7.72–7.80 (m, 3H, ArH), 7.87 (t, *J*=1.5 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ=32.1 (NCH_3), 90.3 (C), 111.2, 119.7, 121.4, 123.8 (CH), 127.9 (2CH), 128.0 (C), 128.1, 128.6 (CH), 129.9 (2CH), 130.0, 130.1, 130.4 (CH), 131.9, 137.9, 138.8, 141.2, 142.1 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3055 (m), 3028 (m), 2922 (m), 2851 (m), 1949 (w), 1884 (w), 1712 (w), 1599 (m), 1574 (m), 1537 (m), 1500 (w), 1462 (s), 1450 (m), 1430 (m), 1412 (m), 1355 (m), 1338 (m), 1321 (m), 1234 (m), 1204 (m), 1154 (m), 1103 (m), 1019 (w), 1011 (m), 945 (m), 899 (m), 854 (m), 806 (m), 737 (s), 699 (s), 671 (m), 638 (m), 613 (m), 586 (m), 548 (m). MS (EI, 70 eV): *m*/*z* (%)=364 ($[M+1]^+$, ^{81}Br, 22), 363 ($[M]^+$, ^{81}Br, 100), 362 ($[M+1]^+$, ^{79}Br, 24), 361 ($[M]^+$, ^{79}Br, 100), 281 (10), 280 (20), 267 (7), 266 (6), 204 (8), 181 (5), 180 (5), 133 (7), 120 (5). HRMS (EI) calcd for $C_{16}H_{14}BrNO$ $[M]^+$ is 361.04606, found 361.045430.

*4.1.8. 3-Bromo-2-(3-(trifluoromethyl)phenyl)-1-methyl-1H-indole (**4c**).* Starting with **1** (289 mg, 1.0 mmol), **2h** (209 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %) and 1,4-dioxane (4 mL), **4c** was isolated as a yellowish oil (287 mg, 81%). ^1H NMR (300 MHz, $(CD_3)_2CO$): δ=3.73 (s, 3H, NCH_3), 7.21–7.26 (m, 1H, ArH), 7.30–7.36 (m, 1H, ArH), 7.51 (dt, *J*=8.3, 0.8 Hz, 1H, ArH), 7.56 (dq, *J*=7.9, 0.6 Hz, 1H, ArH), 7.79–7.89 (m, 3H, ArH), 7.94–7.95 (m, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ=32.1 (NCH_3), 111.3, 119.8, 121.6 (CH), 123.4 (C), 124.2 (CH), 125.2 (q, $J_{F,C}$=271 Hz, $ArCF_3$), 126.3 (q, $J_{F,C}$=3.9 Hz, CH, ArH), 127.8 (C), 128.2 (q, $J_{F,C}$=3.9 Hz, CH, ArCH), 130.5 (CH), 131.2 (q, $J_{F,C}$=32 Hz, ArC), 132.4 (C), 135.4 (d, *J*=1.1 Hz, CH, ArH), 137.2, 138.0 (C). ^{19}F NMR (282.40 MHz, $(CD_3)_2CO$): δ=−114.49 (3F, CF_3). IR (ATR, cm^{-1}): $\tilde{\nu}$=3056 (m), 2940 (m), 1613 (m), 1592 (m), 1574 (m), 1462 (m), 1423 (m), 1380 (m), 1356 (m), 1340 (m), 1321 (s), 1310 (s), 1278 (m), 1235 (m), 1211 (m), 1165 (s), 1120 (s), 1105 (s), 1095 (s), 1073 (s), 1052 (m), 1010 (m), 946 (m), 926 (w), 907 (m), 858 (m), 808 (m), 781 (w), 770 (w), 737 (s), 701 (s), 694 (s), 651 (m), 643 (m), 608 (w), 586 (m), 547 (m). MS (EI, 70 eV): *m/z* (%)=356 ([M+1]$^+$, ^{81}Br, 18), 355 ([M]$^+$, ^{81}Br, 98), 354 ([M+1]$^+$, ^{79}Br, 20), 353 ([M]$^+$, ^{79}Br, 100), 274 (6), 273 (14), 272 (15), 205 (10), 204 (23), 190 (5). HRMS (EI) calcd for $C_{16}H_{11}BrF_3N$ [M]$^+$ is 353.00215, found 353.001842.

*4.1.9. 3-Bromo-2-(2-ethylphenyl)-1-methyl-1H-indole (**4d**).* Starting with **1** (289 mg, 1.0 mmol), **2b** (165 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %) and 1,4-dioxane (4 mL), **4d** was isolated as a brownish oil (229 mg, 73%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ=1.21 (t, *J*=7.7 Hz, 3H, CH_3), 2.63 (q, *J*=7.6 Hz, 2H, OCH_2), 3.64 (s, 3H, NCH_3), 7.02–7.07 (m, 1H, ArH), 7.12–7.18 (m, 1H, ArH), 7.19–7.28 (m, 3H, ArH), 7.32–7.36 (m, 2H, ArH), 7.54 (dt, *J*=7.9, 0.9 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ=15.5 (CH_3), 28.7 (CH_2), 31.1 (NCH_3), 101.2 (C), 109.6, 119.8, 120.4, 121.5 (CH), 128.0 (2CH), 128.0 (C), 129.4 (2CH), 130.2, 138.3, 141.7, 144.0 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3049 (m), 3023 (m), 2963 (m), 2929 (m), 2873 (m), 1916 (w), 1609 (m), 1543 (m), 1495 (m), 1462 (s), 1429 (s), 1412 (m), 1374 (m), 1357 (s), 1337 (s), 1313 (s), 1238 (m), 1213 (m), 1163 (m), 1129 (m), 1116 (m), 1099 (m), 1063 (w), 1050 (w), 1004 (m), 966 (w), 945 (w), 924 (w), 895 (w), 837 (s), 792 (s), 783 (s), 749 (s), 733 (s), 700 (m), 666 (m), 623 (w), 586 (m), 568 (m), 546 (m). MS (EI, 70 eV): *m/z* (%)=315 (95), 313 (100), 300 (40), 299 (42), 235 (5), 204 (10).

*4.1.10. 3-Bromo-2-(3,4-dimethoxyphenyl)-1-methyl-1H-indole (**4e**).* Starting with **1** (289 mg, 1.0 mmol), **2i** (200 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %) and 1,4-dioxane (4 mL), **4e** was isolated as a yellowish solid (272 mg, 79%), mp 146–148 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ=3.59 (s, 3H, NCH_3), 3.84 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 6.93–6.95 (m, 2H, ArH), 7.11–7.27 (m, 4H, ArH), 7.50–7.53 (m, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ=30.6 (CH_3), 54.9, 55.0 (OCH_3), 88.9 (C), 108.6, 109.9, 112.8, 118.2, 119.5, 121.7 (CH), 121.8 (C), 122.4 (CH), 126.1, 135.7, 137.0, 147.8, 148.4 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3052 (w), 2960 (w), 2924 (W), 1607 (w), 1584 (w), 1502 (m), 1462 (m), 1445 (m), 1404 (w), 1379 (w), 1339 (w), 1317 (w), 1257 (s), 1239 (s), 1168 (m), 1136 (s), 1022 (s), 945 (m), 911 (w), 858 (m), 812 (m), 777 (w), 750 (s), 654 (m), 575 (w), 547 (w). MS (EI, 70 eV): *m/z* (%)=348 ([M+1]$^+$, ^{81}Br, 18), 347 ([M]$^+$, ^{81}Br, 100), 346 ([M+1]$^+$, ^{79}Br, 19), 345 ([M]$^+$, ^{79}Br, 98), 302 (5), 302 (5), 300 (4), 251 (5), 223 (24), 180 (10), 152 (7), 102 (5). HRMS (EI) calcd for $C_{17}H_{16}Br^{79}NO_2$ [M]$^+$ is 345.03589, found 345.035679.

*4.1.11. 3-Bromo-2-(2-methoxyphenyl)-1-methyl-1H-indole (**4f**).* Starting with **1** (289 mg, 1.0 mmol), **2j** (167 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %) and 1,4-dioxane (4 mL), **4f** was isolated as a yellowish oil (224 mg, 71%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ=3.39 (s, 3H, CH_3), 3.62 (s, 3H, NCH_3), 6.95 (td, *J*=7.5, 0.9 Hz, 1H, ArH), 6.98–7.04 (m, 2H, ArH), 7.07–7.12 (m, 1H, ArH), 7.21 (dd, *J*=7.6, 1.7 Hz, 1H, ArH), 7.27 (dt, *J*=8.1, 0.8 Hz, 1H, ArH), 7.31–7.37 (m, 2H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ=31.6 (NCH_3), 55.9 (OCH_3), 90.3 (C), 110.8, 112.3, 119.4 (CH), 120.1 (C), 120.9, 121.4, 123.3 (CH), 127.9 (C), 132.0, 133.8 (CH), 136.7, 137.5, 158.9 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3052 (w), 3002 (w), 2929 (m), 2835 (m), 2716 (w), 2555 (w), 1604 (m), 1579 (m), 1545 (m), 1461 (s), 1434 (s), 1379 (m), 1362 (m), 1338 (m), 1321 (m), 1294 (m), 1278 (m), 1246 (s), 1232 (s), 1209 (m), 1179 (m), 1154 (m), 1118 (m), 1103 (m), 1054 (m), 1021 (m), 1011 (m), 945 (m), 837 (w), 779 (w), 734 (s), 668 (m), 618 (m), 592 (m), 565 (m). MS (EI, 70 eV): *m/z* (%)=318 ([M+1]$^+$, ^{81}Br, 18), 317 ([M]$^+$, ^{81}Br, 98), 316 ([M+1]$^+$, ^{79}Br, 20), 315 ([M]$^+$, ^{79}Br, 98), 237 (11), 236 (56), 235 (9), 234 (15), 222 (12), 221 (47), 220 (58), 219 (12), 218 (11), 208 (12), 206 (12), 205 (15), 204 (22), 193 (16), 192 (14), 191 (12), 178 (9), 177 (9), 165 (22), 118 (13), 102 (13). HRMS (EI) calcd for $C_{16}H_{14}BrNO$ [M]$^+$ is 315.02533, found 315.024969.

4.2. General procedure for the synthesis of 5a–e

The reaction was carried out in pressure tube. To a dioxane suspension (4 mL) of **1** (215 mg, 0.75 mmol), $Pd(PPh_3)_4$ (4 mol %) and $Ar^1B(OH)_2$ (0.82 mmol) was added K_3PO_4 (234 mg, 1.1 mmol) and the solution was degassed by bubbling argon through the solution for 10 min. The mixture was heated at 70 °C under argon atmosphere for 6 h. The mixture was cooled to 20 °C. To the solution was added $Ar^2B(OH)_2$ (0.90 mmol) and K_3PO_4 (254 mg, 1.2 mmol) and the solution was degassed again. The reaction mixture was heated under argon atmosphere for 8 h at 110 °C. After cooling to 20 °C, the solution was diluted with water and extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (silica gel, heptanes).

*4.2.1. 3-(Biphenyl-3-yl)-2-(4-ethylphenyl)-1-methyl-1H-indole (**5a**).* Starting with **1** (215 mg, 0.75 mmol), **2b** (123 mg, 0.82 mmol), **2g** (178 mg, 0.9 mmol), K_3PO_4 (488 mg, 2.3 mmol), $Pd(PPh_3)_4$ (4 mol %) and 1,4-dioxane (4 mL), **5a** was isolated as a brownish oil (206 mg, 71%). ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ=1.29 (t, *J*=7.6 Hz, 3H, CH_3), 2.73 (q, *J*=7.6 Hz, 2H, CH_2), 3.70 (s, 3H, NCH_3), 7.14–7.20 (m, 1H, ArH), 7.24–7.43 (m, 14H, ArH), 7.51 (dt, *J*=8.1, 1 Hz, 1H, ArH), 7.81 (dt, *J*=7.9, 0.9 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ=16.1 (CH_3), 29.3 (CH_2), 31.1 (NCH_3), 110.8 (CH), 115.2 (C), 119.9, 121.0, 122.8, 124.8 (CH), 127.7 (2CH), 127.7 (C), 128.0 (CH), 128.9 (2CH), 129.2, 129.3 (CH), 129.6 (2CH), 129.7 (CH), 130.4 (C), 132.1 (2CH), 136.9, 138.4, 139.0, 141.6, 142.1, 145.4 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3400 (br), 3051 (m), 3025 (m), 2962 (m), 2928 (m), 2871 (m), 1710 (m), 1650 (w), 1643 (w), 1609 (m), 1599 (m), 1582 (m), 1518 (w), 1493 (m), 1463 (s), 1428 (m), 1410 (m), 1363 (s), 1325 (m), 1261 (m), 1247 (m), 1218 (m), 1182 (m), 1152 (w), 1131 (m), 1115 (m), 1088 (m), 1049 (w), 1016 (m), 974 (w), 918 (w), 897 (m), 879 (m), 856 (m), 834 (s), 812 (s), 799 (m), 784 (m), 742 (s), 699 (s), 648 (m), 630 (m), 615 (m), 578 (m), 567 (m), 548 (m). MS (EI, 70 eV): *m/z* (%)=388 ([M+1]$^+$, 32), 387 ([M]$^+$, 100), 372 (5), 357 (5), 343 (6). HRMS (EI) calcd for $C_{29}H_{25}N$ [M]$^+$ is 387.19815, found 387.198028.

*4.2.2. 2-(2,5-Dimethoxyphenyl)-1-methyl-3-phenyl-1H-indole (**5b**).* Starting with **1** (215 mg, 0.75 mmol), **2k** (150 mg, 0.82 mmol), **2d** (110 mg, 0.9 mmol), K_3PO_4 (488 mg, 2.3 mmol), $Pd(PPh_3)_4$ (4 mol %) and 1,4-dioxane (4 mL), **5b** was isolated as a colourless oil (177 mg, 69%). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ=3.40 (s, 3H, NCH_3), 3.44 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3), 6.54 (d, *J*=3.1 Hz, 1H, ArH), 6.77–6.82 (m, 1H, ArH), 6.87–6.98 (m, 3H, ArH), 7.04–7.18 (m, 5H, ArH), 7.28 (d, *J*=8.3 Hz, 1H, ArH), 7.56 (d, *J*=7.8 Hz, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=30.7 (NCH_3), 55.9, 56.3 (OCH_3), 110.5, 113.3 (CH), 115.7 (C), 115.8, 119.5, 119.8, 120.6 (CH), 122.5 (C), 122.6, 126.2 (CH), 127.7 (C), 129.0, 130.1 (2CH), 135.7, 136.7, 138.1, 153.7, 154.4 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3051 (w), 2936 (w), 2832 (w), 1736 (w), 1712 (w), 1602 (w), 1549 (w), 1502 (m), 1485 (m), 1463 (m), 1366 (m), 1273 (m), 1225 (m), 1210 (m), 1039 (m), 1020 (m), 941 (w), 918 (w), 876 (w), 805 (w), 772 (m), 735 (s), 700 (s), 616 (w), 570 (w), 531 (w). MS (EI, 70 eV): *m/z* (%)=345 ([M+2]$^+$, 3), 344 ([M+1]$^+$, 24), 343 ([M]$^+$, 100), 342 (15), 297 (6), 230 (5), 220 (5), 156 (7). HRMS (EI) calcd for $C_{23}H_{21}NO_2$ [M]$^+$ is 343.15668, found 343.156270.

*4.2.3. 3-(4-Chlorophenyl)-2-(2,5-dimethoxyphenyl)-1-methyl-1H-indole (**5c**).* Starting with **1** (215 mg, 0.75 mmol), **2k** (150 mg, 0.82 mmol), **2f** (141 mg, 0.9 mmol), K_3PO_4 (488 mg, 2.3 mmol), $Pd(PPh_3)_4$ (4 mol %) and 1,4-dioxane (4 mL), **5c** was isolated as a colourless oil (167 mg, 59%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ=3.58 (s, 3H, OCH_3), 3.65 (s, 3H, NCH_3), 3.71 (s, 3H, OCH_3), 6.71 (d, *J*=3 Hz, 1H, ArH), 7.01 (dd, J=9.0, 3.0 Hz, 1H, ArH), 7.08–7.16 (m, 2H, ArH), 7.22–7.26 (m, 1H, ArH), 7.28–7.32 (m, 4H, ArH), 7.47 (dt, J=8.0, 1.0 Hz, 1H, ArH), 7.70 (dt, J=8.0, 1.0 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ=30.1 (NCH_3), 55.9, 56.3 (OCH_3), 110.6, 113.3 (CH), 114.3 (C), 116.0, 119.4, 119.6, 120.8 (CH), 122.2 (C), 122.7 (CH), 127.5 (C), 129.1 (2CH), 131.4 (C), 131.5 (2CH), 135.6, 136.0, 138.1, 153.6, 154.4, (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3047 (w), 2921 (m), 2851 (m), 1732 (w), 1667 (w), 1609 (w), 1544 (w), 1499 (m), 1483 (m), 1463 (m), 1431 (m), 1417 (m), 1366 (m), 1326 (m), 1302 (m), 1274 (m), 1263 (m), 1225 (s), 1209 (s), 1178 (m), 1150 (m), 1133 (m), 1091 (s), 1038 (s), 1013 (s), 934 (m), 912 (m), 879 (m), 866 (m), 835 (m), 810 (s), 761 (m), 732 (s), 719 (m), 712 (m), 699 (m), 675 (m), 649 (m), 630 (m), 603 (m), 585 (m), 571 (m), 551 (m). MS (EI, 70 eV): m/z (%)=380 ($[M+1]^+$, ^{37}Cl, 8), 379 ($[M]^+$, ^{37}Cl, 35), 378 ($[M+1]^+$, ^{35}Cl, 30), 377 ($[M]^+$, ^{35}Cl, 100), 376 (14), 327 (6), 241 (6), 133 (9), 127 (6). HRMS (EI) calcd for $C_{23}H_{20}ClNO_2$ $[M]^+$ is 377.11771, found 377.117256.

*4.2.4. 3-(4-Fluorophenyl)-2-(2,5-dimethoxyphenyl)-1-methyl-1H-indole (**5d**).* Starting with **1** (215 mg, 0.75 mmol), **2k** (150 mg, 0.82 mmol), **2l** (126 mg, 0.9 mmol), K_3PO_4 (488 mg, 2.3 mmol), $Pd(PPh_3)_4$ (4 mol %) and 1,4-dioxane (4 mL), **5d** was isolated as a yellowish oil (192 mg, 71%). ^1H NMR (300 MHz, $(CD_3)_2CO$): δ=3.58 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 3.69 (s, 3H, NCH_3), 6.73 (d, J=3.0 Hz, 1H, ArH), 6.97–7.08 (m, 4H, ArH), 7.12–7.17 (m, 1H, ArH), 7.26 (td, J=7.6, 1.0 Hz, 1H, ArH), 7.30–7.38 (m, 2H, ArH), 7.47 (d, J=8.3 Hz, 1H, ArH), 7.72 (d, J=7.7 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ=30.8 (NCH_3), 55.9, 56.3 (OCH_3), 110.6, 113.3 (CH), 114.7 (C), 115.7 (d, $J_{F,C}$=21.4 Hz, 2CH), 116.0, 119.5, 119.7, 120.7 (CH), 122.3 (C), 122.7 (CH), 127.7 (C), 131.7 (d, $J_{F,C}$=7.8 Hz, 2CH), 132.9 (d, $J_{F,C}$=3.0 Hz, C), 135.7, 138.1, 153.7, 154.4 (C), 161.9 (d, $J_{F,C}$=242 Hz, C). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ=−112.53 (ArF). IR (ATR, cm^{-1}): $\tilde{\nu}$=3046 (w), 2997 (w), 2934 (m), 2832 (m), 1712 (w), 1608 (w), 1589 (w), 1549 (m), 1508 (s), 1487 (s), 1463 (s), 1431 (s), 1417 (m), 1366 (m), 1326 (m), 1301 (m), 1273 (m), 1212 (s), 1179 (m), 1155 (m), 1133 (m), 1089 (m), 1038 (s), 1019 (m), 941 (m), 911 (m), 877 (m), 839 (m), 821 (m), 785 (m), 762 (w), 734 (s), 719 (m), 693 (m), 678 (m), 673 (m), 651 (m), 633 (m), 609 (m), 589 (m), 574 (m), 559 (s). MS (EI, 70 eV): m/z (%)=362 ($[M+1]^+$, 26), 361 ($[M]^+$, 100), 360 (16), 347 (8), 329 (5), 315 (7), 272 (5), 259 (5), 248 (9), 238 (6). HRMS (EI) calcd for $C_{29}H_{25}N$ $[M]^+$ is 361.14726, found 361.147102.

*4.2.5. 3-[4-(Trifluoromethyl)phenyl]-2-(2,5-dimethoxyphenyl)-1-methyl-1H-indole (**5e**).* Starting with **1** (215 mg, 0.75 mmol), **2k** (150 mg, 0.82 mmol), **2m** (171 mg, 0.9 mmol), K_3PO_4 (488 mg, 2.3 mmol), $Pd(PPh_3)_4$ (4 mol %) and 1,4-dioxane (4 mL), **5e** was isolated as a yellowish oil (194 mg, 63%). ^1H NMR (300.13 MHz, $CDCl_3$): δ=3.61 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.71 (s, 3H, NCH_3), 6.74 (d, J=3.2 Hz, 1H, ArH), 7.05 (d, J=3.2 Hz, 1H, ArH), 7.10–7.21 (m, 2H, ArH), 7.29 (ddd, J=8.1, 7.0, 1.1 Hz, 1H, ArH), 7.50–7.62 (m, 5H, ArH), 7.79 (d, J=7.7 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ=30.8 (NCH_3), 55.9, 56.3 (OCH_3), 110.8, 113.4 (CH), 114.2 (C), 116.2, 119.3, 119.5, 121.1 (CH), 122.0 (C), 122.9 (CH), 123.5 (C), 125.6 (q, $J_{F,C}$=271 Hz, $ArCF_3$), 125.9 (q, $J_{F,C}$=3.8 Hz, 2CH, C), 127.4 (q, $J_{F,C}$=32 Hz, C), 130.2 (2CH), 136.6, 138.2 (C), 141.1 (d, J=1.4 Hz, C), 153.6, 154.5 (C). ^{19}F NMR (282.40 MHz, acetone): δ=−114.49 ($ArCF_3$). IR (ATR, cm^{-1}): $\tilde{\nu}$=3057 (w), 2953 (m), 2921 (m), 2852 (m), 1732 (w), 1613 (m), 1574 (w), 1566 (w), 1549 (m), 1494 (w), 1465 (m), 1435 (w), 1415 (w), 1394 (w), 1367 (w), 1320 (s), 1260 (m), 1190 (w), 1166 (m), 1106 (s), 1090 (s), 1064 (s), 1014 (m), 961 (m), 941 (m), 930 (m), 863 (m), 851 (m), 833 (m), 802 (m), 768 (m), 748 (m), 734 (s), 695 (m), 674 (m), 650 (m), 631 (m), 597 (m), 574 (m), 557 (m).

*4.2.6. 1-Methyl-2-phenyl-1H-indole (**6a**).* Starting with **1** (289 mg, 1.0 mmol), **2a** (134 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane (2 mL) and H_2O (2 mL) **6a** was isolated as colourless crystals (201 mg, 97%), mp 93–95 °C. ^1H NMR (300 MHz, $(CD_3)_2CO$): δ=3.77 (s, 3H, NCH_3), 6.55 (d, J=0.8 Hz, 1H, ArH), 7.05–7.11 (m, 1H, ArH), 7.17–7.23 (m, 1H, ArH), 7.37–7.61 (m, 7H, ArH). ^{13}C NMR ($(CD_3)_2CO$, 62.89 MHz): δ=31.5 (NCH_3), 102.2, 110.7, 120.5, 121.1, 122.3 (CH), 129.0 (C), 129.5, 130.1 (2CH), 133.8, 139.5, 142.3 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3053 (m), 3026 (m), 2919 (m), 2850 (m), 1601 (m), 1539 (w), 1464 (s), 1433 (m), 1382 (m), 1366 (m), 1340 (m), 1319 (m), 1307 (m), 1241 (m), 1233 (m), 1207 (m), 1178 (m), 1168 (m), 1147 (m), 1129 (m), 1119 (m), 1100 (m), 1074 (m), 1035 (w), 1007 (m), 996 (w), 988 (w), 975 (w), 924 (m), 893 (w), 842 (m), 796 (m), 765 (s), 747 (s), 731 (s), 700 (s), 672 (m), 659 (m), 616 (m), 582 (m), 576 (m), 532 (s). MS (EI, 70 eV): m/z (%)=208 ($[M+1]^+$, 16), 207 ($[M]^+$, 100), 206 (44), 204 (10), 165 (10). HRMS (EI) calcd for $C_{15}H_{13}N$ $[M]^+$ is 207.10425, found 207.103624.

*4.2.7. 1-Methyl-2-p-tolyl-1H-indole (**6b**).* Starting with **1** (289 mg, 1.0 mmol), **2b** (149 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane (2 mL) and H_2O (2 mL) **6b** was isolated as colourless crystals (203 mg, 92%), mp 88–89 °C. ^1H NMR (250.13 MHz, $(CD_3)_2CO$): δ=2.39 (s, 3H, $ArCH_3$), 3.74 (s, 3H, NCH_3), 6.50 (d, J=0.8 Hz, 1H, ArH), 7.06 (td, J=6.9, 1.1 Hz, 1H, ArH), 7.18 (td, J=6.9, 1.1 Hz, 1H, ArH), 7.29–7.39 (m, 2H, ArH), 7.42–7.48 (m, 2H, ArH), 7.72–7.80 (m, 3H, ArH), 7.56 (dt, J=8.0, 0.9 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ=21.2 (CH_3), 31.4 (NCH_3), 101.9, 110.6, 120.4, 121.0, 122.2 (CH), 129.1 (C), 130.0, 130.1 (2CH), 130.9, 138.5, 139.4, 142.4 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3051 (m), 3018 (m), 2920 (m), 2853 (m), 2726 (w), 1925 (w), 1907 (w), 1755 (w), 1607 (w), 1495 (w), 1477 (w), 1462 (m), 1432 (w), 1409 (w), 1382 (m), 1366 (m), 1337 (m), 1317 (m), 1305 (m), 1239 (m), 1219 (m), 1189 (w), 1026 (w), 1006 (m), 955 (m), 918 (m), 895 (w), 826 (m), 773 (s), 749 (s), 734 (s), 716 (m), 666 (m), 636 (m), 623 (w), 581 (m), 556 (s), 526 (m). MS (EI, 70 eV): m/z (%)=222 ($[M+1]^+$, 18), 221 ($[M]^+$, 100), 220 (38), 205 (10), 204 (14), 178 (6), 110 (8). HRMS (EI) calcd for $C_{16}H_{15}N$ $[M]^+$ is 221.11990, found 221.119448.

*4.2.8. 2-(4-Ethylphenyl)-1-methyl-1H-indole (**6c**).* Starting with **1** (289 mg, 1.0 mmol), **2c** (165 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane (2 mL) and H_2O (2 mL) **6c** was isolated as a colourless solid (223 mg, 95%), mp 133–135 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ=1.19 (t, J=7.6 Hz, 3H, CH_3), 2.61 (q, J=7.6 Hz, 2H, CH_2), 3.60 (s, 3H, NCH_3), 7.00–7.05 (m, 1H, ArH), 7.10–7.24 (m, 4H, ArH), 7.29–7.34 (m, 2H, ArH), 7.31 (dt, J=8.1, 1.7 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ=15.6 (CH_3), 28.8 (CH_2), 31.2 (NCH_3), 109.7, 119.9, 120.5, 121.6 (CH), 128.1 (2CH), 128.2 (C), 129.5 (2CH), 130.7, 138.1, 138.4, 141.9, 144.2 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3045 (w), 3024 (w), 2960 (m), 2922 (m), 2852 (m), 1682 (w), 1598 (m), 1567 (w), 1504 (w), 1495 (w), 1463 (m), 1455 (m), 1432 (m), 1409 (m), 1385 (m), 1362 (m), 1325 (m), 1310 (m), 1250.13 (m), 1228 (m), 1183 (m), 1149 (m), 1132 (m), 1115 (m), 1093 (m), 1085 (m), 1053 (m), 1018 (m), 1001 (m), 970 (m), 955 (m), 922 (m), 901 (m), 856 (m), 834 (m), 801 (m), 763 (s), 755 (s), 738 (s), 707 (s), 701 (s), 670 (m), 646 (m), 614 (m), 598 (m), 575 (m), 567 (m), 547 (m). MS (EI, 70 eV): m/z (%)=236 ($[M+1]^+$, 19), 235 ($[M]^+$, 100), 234 (9), 221 (11), 220 (62), 218 (6), 205 (10), 204 (21), 178 (5), 110 (6), 102 (5). HRMS (EI) calcd for $C_{17}H_{17}N$ $[M]^+$ is 235.13555, found 235.135424.

*4.2.9. 2-(3,5-Dimethylphenyl)-1-methyl-1H-indole (**6d**).* Starting with **1** (289 mg, 1.0 mmol), **2e** (165 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane (2 mL) and H_2O (2 mL) **6d** was isolated as a yellowish gel (195 mg, 83%). ^1H NMR (300.13 MHz, $CDCl_3$): δ=2.22 (s, 6H, $2CH_3$), 3.60 (s, 3H, NCH_3), 6.35 (d, J=0.8 Hz, 1H, ArH), 6.89–6.94 (m, 2H, ArH), 7.00–7.06 (m, 3H, ArH), 7.25 (dd, J=8.1, 0.8 Hz, 1H, ArH), 7.41 (dt, J=7.7, 1 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ=21.4 ($2ArCH_3$), 31.5 (NCH_3), 102.0, 110.6, 120.4, 121.0, 122.2 (CH), 127.9 (2CH), 129.1 (C), 130.3

(CH), 133.6 (C), 138.8 (2C), 139.5, 142.6 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3052 (w), 2919 (m), 2853 (m), 2725 (w), 1599 (m), 1537 (m), 1465 (s), 1432 (m), 1376 (m), 1362 (m), 1338 (m), 1312 (s), 1281 (w), 1262 (w), 1230 (m), 1162 (m), 1146 (m), 1129 (m), 1099 (m), 1074 (m), 1036 (m), 1009 (m), 960 (w), 946 (w), 922 (w), 903 (m), 857 (m), 772 (s), 748 (s), 731 (s), 700 (s), 666 (s), 608 (w), 584 (m), 576 (m), 548 (m), 536 (m). MS (EI, 70 eV): *m/z* (%)=236 ($[M+1]^+$, 19), 235 ($[M]^+$, 100), 234 (30), 220 (8), 219 (8), 218 (11), 217 (5), 205 (6), 204 (14). HRMS (EI) calcd mass for $C_{17}H_{17}N$ $[M]^+$ is 235.13555, found 235.135292.

*4.2.10. 2-(4-tert-Butylphenyl)-1-methyl-1H-indole (**6e**).* Starting with **1** (289 mg, 1.0 mmol), **2f** (196 mg, 1.1 mmol), K_3PO_4 (318 mg, 1.5 mmol), $Pd(PPh_3)_4$ (3 mol %), 1,4-dioxane (2 mL) and H_2O (2 mL) **6e** was isolated as a yellowish solid (213 mg, 81%), mp 108–110 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ=1.37 (s, 3H, CH_3), 3.76 (s, 3H, NCH_3), 6.51 (s, 1H, ArH), 7.03–7.09 (m, 1H, ArH), 7.14–7.21 (m, 1H, ArH), 7.48 (dt, *J*=8.2, 0.8 Hz, 1H, ArH), 7.49–7.57 (m, 5H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ=31.5 (NCH_3), 31.6 (CH_3), 35.2 (C), 101.9, 110.6, 120.4, 121.0, 122.2 (CH), 126.3 (2CH), 129.1 (C), 129.8 (2CH), 130.9, 139.5, 142.3, 151.6 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3049 (w), 2954 (w), 2901 (w), 2860 (w), 1613 (w), 1494 (w), 1463 (m), 1454 (m), 1430 (w), 1406 (w), 1358 (m), 1336 (m), 1317 (w), 1266 (w), 1242 (w), 1216 (w), 1196 (w), 1165 (w), 1120 (m), 1098 (m), 1023 (w), 1004 (m), 922 (w), 846 (m), 840 (m), 794 (m), 782 (m), 747 (s), 736 (s), 671 (w), 589 (m), 559 (m), 542 (m). MS (EI, 70 eV): *m/z* (%)=264 ($[M+1]^+$, 20), 263 ($[M]^+$, 100), 249 (19), 248 (85), 233 (18), 232 (7), 220 (8), 218 (6), 217 (5), 204 (9), 110 (19), 109 (7), 102 (6). HRMS (EI): calcd for $C_{19}H_{21}N$ $[M]^+$ is 263.16685, found 263.166607.

4.3. General procedure for the synthesis of 8a–k

The reaction was carried out in a pressure tube. The mixture of **7**, 1,4-dioxane (2 mL), H_2O (2 mL), K_2CO_3, $Pd(PPh_3)_4$ and arylboronic acid **2** was stirred at 110 °C for 8 h. After cooling to 20 °C, a saturated aqueous solution of NH_4Cl was added. The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (silica gel, heptanes).

*4.3.1. 1-Methyl-2,3,6-tri-p-tolyl-1H-indole (**8a**).* Starting with **7** (100 mg, 0.27 mmol), **2a** (126 mg, 0.93 mmol), $Pd(PPh_3)_4$ (4 mol %), K_2CO_3 (152 mg, 1.1 mmol), 1,4-dioxane (2 mL) and H_2O (2 mL), **8a** was isolated as a white solid (96 mg, 87%), mp 174–177 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=2.23 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 3.58 (s, 3H, NCH_3), 6.99 (d, 2H, *J*=7.86 Hz, ArH), 7.07–7.18 (m, 8H, ArH), 7.32 (dd, 1H, *J*=1.53, 8.28 Hz, ArH), 7.46 (d, 1H, *J*=1.02 Hz, ArH), 7.51 (d, 2H, *J*=8.10 Hz, ArH), 7.71 (d, 1H, *J*=8.31 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=21.1, 21.2, 21.4 (CH_3), 31.0 (NCH_3), 107.9 (CH), 114.8 (C), 119.8, 119.9 (CH), 126.4 (C), 127.3, 129.0, 129.2 (CH), 129.3 (C), 129.5, 129.7, 131.0 (CH), 132.4, 135.0, 135.6, 136.3, 137.8, 137.9, 138.3, 139.8 (C). IR (KBr): ν=3018, 2917, 2860, 2733, 1610, 1567, 1548 (w), 1518, 1468 (m), 1449, 1428, 1403, 1391 (w), 1373 (m), 1337, 1319, 1304, 1256, 1229, 1212, 1185, 1147, 1112 (w), 1087 (m), 1039, 1015, 971, 962 (w), 944, 852 (m), 840, 820, 810, 801 (s), 777, 755, 726 (m), 698, 689, 642, 633 (w), 612 (m), 577, 567, 539 (w) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=402 ($[M+H]^+$, 33), 401 ($[M]^+$, 100), 371 (6). HRMS (ESI, 70 eV): calcd for $C_{30}H_{28}N$ $[M+H]^+$: 402.22163, found: 402.22112.

*4.3.2. 2,3,6-Tris(4-ethylphenyl)-1-methyl-1H-indole (**8b**).* Starting with **7** (100 mg, 0.27 mmol), **2b** (139.5 mg, 0.93 mmol), $Pd(PPh_3)_4$ (4 mol %), K_2CO_3 (152 mg, 1.1 mmol), 1,4-dioxane (2 mL) and H_2O (2 mL), **8b** was isolated as colourless crystals (113 mg, 94%), mp 154–156 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ=1.29 (t, *J*=7.5 Hz, 3H, CH_3), 1.32 (t, *J*=7.5 Hz, 3H, CH_3), 1.34 (t, *J*=7.5 Hz, 3H, CH_3), 2.69 (q, *J*=7.5 Hz, 2H, CH_2), 2.74 (q, *J*=7.5 Hz, 2H, CH_2), 2.76 (q, *J*=7.6 Hz, 2H, CH_2), 3.74 (s, 3H, NCH_3), 7.02–7.05 (m, 2H, ArH), 7.12–7.19 (m, 6H, ArH), 7.21–7.23 (m, 2H, ArH), 7.34 (dd, *J*=8.3, 1.5 Hz, 1H, ArH), 7.49 (d, *J*=0.9 Hz, 1H, ArH), 7.56 (m, 2H, ArH), 7.74 (d, *J*=8.3 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ=15.3, 15.3, 15.7 (CH_3), 28.5, 28.5, 28.7 (CH_2), 31.0 (NCH_3), 107.9 (CH), 114.8 (C), 119.8 (2CH), 126.3 (C), 127.4, 127.7, 127.9, 128.2 (2CH), 129.2 (C), 129.7, 131.0 (2CH), 132.5, 135.6, 137.8, 138.2, 140.0, 141.2, 142.7, 144.0 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3020 (w), 2962 (m), 2922 (m), 2871 (m), 2852 (m), 1915 (w), 1886 (w), 1800 (w), 1651 (w), 1609 (m), 1566 (w), 1545 (m), 1517 (m), 1464 (m), 1429 (m), 1410 (m), 1393 (m), 1374 (m), 1318 (m), 1278 (m), 1257 (m), 1228 (m), 1206 (w), 1119 (m), 1088 (m), 1060 (m), 1047 (m), 944 (m), 856 (m), 822 (s), 806 (s), 783 (m), 754 (m), 730 (m), 700 (w), 688 (w), 641 (w), 629 (m), 611 (m), 584 (m), 536 (m). MS (EI, 70 eV): *m/z* (%)=445 ($[M+2]^+$, 12), 444 ($[M+1]^+$, 43), 443 ($[M]^+$, 100), 429 (9), 428 (12), 200 (11), 192 (37), 191 (23), 184 (37), 178 (13), 171 (10). HRMS (EI) calcd for $C_{33}H_{33}N$ $[M]^+$ is 443.26075, found 443.260766.

*4.3.3. 2,3,6-Tris(4-chlorophenyl)-1-methyl-1H-indole (**8c**).* Starting with **7** (100 mg, 0.27 mmol), **2d** (145 mg, 0.93 mmol), $Pd(PPh_3)_4$ (4 mol %), K_2CO_3 (152 mg, 1.1 mmol), 1,4-dioxane (2 mL) and H_2O (2 mL), **8c** was isolated as white powder (113 mg, 91%), mp 198–200 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ=3.74 (s, 3H, NCH_3), 7.22–7.32 (m, 6H, ArH), 7.35–7.48 (m, 5H, ArH), 7.58 (d, *J*=1.1 Hz, 1H, ArH), 7.63–7.67 (m, 2H, ArH), 7.49 (dd, *J*=8.3, 0.6 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ=31.1 (NCH_3), 108.9 (CH), 114.4 (C), 119.8, 120.2, 126.3 (C), 128.6 (4CH), 128.9, 129.0 (2CH), 129.8 (C), 130.9 (2CH), 131.7 (C), 132.3 (2CH), 132.9, 133.2, 134.6, 134.9, 137.4, 137.9, 140.6 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3078 (w), 3030 (w), 2930 (w), 1538 (w), 1496 (m), 1463 (m), 1427 (m), 1396 (m), 1370 (m), 1334 (m), 1315 (m), 1299 (w), 1254 (m), 1234 (m), 1177 (w), 1163 (w), 1089 (s), 1013 (m), 958 (w), 946 (m), 854 (m), 831 (m), 812 (s), 760 (m), 747 (m), 733 (m), 721 (m), 706 (m), 662 (m), 644 (m), 626 (w), 615 (m), 584 (m). MS (EI, 70 eV): *m/z* (%)=465 (30), 464 (25), 463 (100), 465 (30), 461 (99), 376 (5), 178 (12), 177 (6), 170 (6), 69 (5), 44 (6), 43 (5). HRMS (EI) calcd for $C_{27}H_{18}ClN$ $[M]^+$ is 461.04993, found, 461.049515.

*4.3.4. 2,3,6-Tris(4-(tert-butyl)phenyl)-1-methyl-1H-indole (**8d**).* Starting with **7** (100 mg, 0.27 mmol), **2e** (166 mg, 0.93 mmol), $Pd(PPh_3)_4$ (4 mol %), K_2CO_3 (152 mg, 1.1 mmol), 1,4-dioxane (2 mL) and H_2O (2 mL), **8d** was isolated as a white solid (123 mg, 85%), mp 116–117 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.24 (s, 9H, $3CH_3$), 1.28 (s, 9H, $3CH_3$), 1.30 (s, 9H, $3CH_3$), 3.60 (s, 3H, NCH_3), 6.16–7.21 (m, 5H, ArH), 7.30–7.37 (m, 3H, ArH), 7.39 (d, 3H, *J*=3.54 Hz, ArH), 7.49 (d, 1H, *J*=1.05 Hz, ArH), 7.57 (d, 2H, *J*=8.49 Hz, ArH), 7.76 (d, 1H, *J*=8.04 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=31.0 (NCH_3), 31.3, 31.4, 31.5 (CH_3), 34.4, 34.5, 34.7 (C), 107.9 (CH), 114.7 (C), 119.8, 119.9, 125.4, 125.5, 125.7 (CH), 126.4 (C), 127.1 (CH), 128.9 (C), 129.3, 130.8 (CH), 132.2, 135.4, 137.8, 138.2, 139.7, 148.0, 149.5, 150.9 (C). IR (KBr): ν=3029 (w), 2956 (s), 2902, 2865 (m), 1911, 1673, 1604, 1548, 1519 (w), 1461 (s), 1426, 1392 (w), 1361 (s), 1335, 1318, 1307 (w), 1267 (m), 1201, 1181, 1166 (w), 1108 (m), 1086, 1047 (w), 1014, 947 (m), 921, 907 (w), 860 (m), 835, 809 (s), 769, 756 (w), 732 (m), 711, 699, 672, 651 (w), 623, 599 (m), 554 (s) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%)=528 ($[M+H]^+$, 38), 527 ($[M]^+$, 100), 513 (11), 512 (26), 471 (12), 249 (9). HRMS (EI, 70 eV): calcd for $C_{39}H_{45}N$ $[M]^+$: 527.35465, found: 527.35464.

*4.3.5. 1-Methyl-2,3,6-tris(3-(trifluoromethyl)phenyl)-1H-indole (**8e**).* Starting with **7** (100 mg, 0.27 mmol), **2h** (177 mg, 0.93 mmol), $Pd(PPh_3)_4$ (4 mol %), K_2CO_3 (152 mg, 1.1 mmol), 1,4-dioxane (2 mL) and H_2O (2 mL), **8e** was isolated as a white solid (120 mg, 78%), mp 158–160 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.66 (s, 3H, NCH_3), 7.28–7.46 (m, 8H, ArH), 7.48–7.58 (m, 4H, ArH), 7.71 (d, 1H, *J*=8.34 Hz, ArH), 7.76–7.78 (m, 1H, ArH), 7.85 (br s, 1H, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−62.9, −62.8, −62.5. ^{13}C NMR

(75.5 MHz, $CDCl_3$): δ=30.1 (NCH_3), 107.5 (CH), 113.7 (C), 118.9, 119.5 (CH), 121.6 (q, $J_{F,C}$=3.74 Hz, CH), 122.5 (q, $J_{F,C}$=3.75 Hz, CH), 122.7 (q, $J_{F,C}$=272.5 Hz, CF_3), 123.0 (q, $J_{F,C}$=272.5 Hz, CF_3), 123.1 (q, $J_{F,C}$=3.79 Hz, CH), 123.3 (q, $J_{F,C}$=272.5 Hz, CF_3), 124.2 (q, $J_{F,C}$=3.67 Hz, CH), 125.4 (q, $J_{F,C}$=3.76 Hz, CH), 126.7 (q, $J_{F,C}$=3.72 Hz, CH), 127.9, 128.2, 128.3, 129.7 (CH), 129.8 (q, $J_{F,C}$=25.3 Hz, C–CF_3), 130.1 (q, $J_{F,C}$=27.4 Hz, C–CF_3), 130.2 (q, $J_{F,C}$=30.7 Hz, C–CF_3), 130.9 (C), 131.8, 133.3 (CH), 134.0, 134.2, 136.4, 137.1, 141.8 (C). IR (KBr): ν=3073, 3046, 2960, 2924, 2853, 1610, 1590, 1551, 1494, 1465, 1439, 1424, 1411, 1375 (w), 1334, 1326, 1308 (s), 1270 (w), 1251, 1159, 1112, 1094, 1071 (s), 1049, 1034 (m), 1000, 986, 964 (w), 912 (s), 879, 862, 829, 809 (m), 795 (s), 783 (m), 764 (w), 724 (m), 698 (s), 677 (w), 670 (s), 644, 622, 612, 595, 571, 528 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)= 564 ($[M+H]^+$, 27), 563 ($[M]^+$, 100), 547 (15), 69 (19). HRMS (ESI, 70 eV): calcd for $C_{30}H_{19}F_9N$ $[M+H]^+$: 564.13683, found: 564.13740.

*4.3.6. 2,3,6-Tris(3,4-dimethoxyphenyl)-1-methyl-1H-indole (**8f**).* Starting with **7** (100 mg, 0.27 mmol), **2i** (154.4 mg, 0.93 mmol), $Pd(PPh_3)_4$ (4 mol %), K_2CO_3 (152 mg, 1.1 mmol), 1,4-dioxane (2 mL) and H_2O (2 mL), **8f** was isolated as a white powder (120.1 mg, 85%), mp 176 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ=3.72 (s, 3H, NCH_3), 3.78 (s, 6H, $2ArOCH_3$), 3.91 (s, 3H, $ArOCH_3$), 3.96 (s, 3H, $ArOCH_3$), 3.98 (s, 3H, $ArOCH_3$), 4.03 (s, 3H, $ArOCH_3$), 6.86–6.89 (m, 3H, ArH), 6.95–6.98 (m, 3H, ArH), 7.02 (d, J=8.3 Hz, 1H, ArH), 7.27–7.31 (m, 2H, ArH), 7.44 (dd, J=8.3, 1.5 Hz, 1H, ArH), 7.18 (d, J=0.9 Hz, 1H, ArH), 7.85 (d, J=8.3 Hz, 1H, ArH). ^{13}C NMR (62.89 MHz, $(CD_3)_2CO$): δ=30.9 (NCH_3), 55.6, 55.8 ($ArOCH_3$), 55.9, 56.0 ($2ArOCH_3$), 107.7, 110.9, 111.0, 111.1, 111.6, 113.1, 114.2 (CH), 114.5 (C), 119.58, 119.6, 119.9, 121.8, 123.6 (CH), 124.4, 126.0, 127.9, 135.5, 135.6, 137.7, 137.9, 147.0, 148.2, 148.5, 148.7, 148.9, 149.1 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3644 (br), 3068 (w), 2999 (m), 2923 (m), 2839 (m), 1731 (w), 1605 (w), 1585 (m), 1552 (m), 1607 (w), 1517 (m), 1501 (m), 1486 (m), 1462 (m), 1444 (m), 1421 (m), 1403 (m), 1387 (m), 1369 (m), 1333 (m), 1315 (m), 1301 (m), 1274 (s), 1227 (s), 1169 (m), 1132 (s), 1094 (m), 1064 (m), 1021 (s), 982 (m), 933 (m), 910 (m), 867 (m), 842 (m), 815 (s), 806 (m), 790 (s), 761 (s), 751 (s), 697 (m), 655 (m), 642 (m), 622 (m), 612 (m), 591 (m), 580 (m), 570 (m). MS (EI, 70 eV): m/z (%)=541 ($[M+2]^+$, 7), 540 ($[M+1]^+$, 34), 539 (M^+, 100), 270 (3). HRMS (EI) calcd mass for $C_{33}H_{33}NO_6$ $[M^+]$ is 539.23024, found 539.231334.

*4.3.7. 2,3,6-Tris(4-fluorophenyl)-1-methyl-1H-indole (**8g**).* Starting with **7** (100 mg, 0.27 mmol), **2l** (130 mg, 0.93 mmol), $Pd(PPh_3)_4$ (4 mol %), K_2CO_3 (152 mg, 1.1 mmol), 1,4-dioxane (2 mL) and H_2O (2 mL), **8g** was isolated as a white solid (95 mg, 84%), mp 178–180 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.62 (s, 3H, NCH_3), 6.87–6.93 (m, 2H, ArH), 6.98–7.10 (m, 4H, ArH), 7.12–7.24 (m, 4H, ArH), 7.30 (dd, 1H, J=1.56, 8.28 Hz, ArH), 7.45 (d, 1H, J=1.02 Hz, ArH), 7.53–7.59 (m, 2H, ArH), 7.67 (d, 1H, J=8.28 Hz, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−116.8, −116.6, −112.7. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=29.9 (NCH_3), 107.0 (CH), 113.3 (C), 114.2 (d, $J_{F,C}$=21.2 Hz, CH), 114.6 (d, $J_{F,C}$=21.4 Hz, CH), 114.7 (d, $J_{F,C}$=21.6 Hz, CH), 118.6, 119.1 (CH), 125.2 (C), 126.5 (d, $J_{F,C}$=3.54 Hz, C), 127.9 (d, $J_{F,C}$=8.00 Hz, CH), 129.7 (d, $J_{F,C}$=3.28 Hz, C), 130.2 (d, $J_{F,C}$=7.76 Hz, CH), 131.8 (d, $J_{F,C}$=8.20 Hz, CH), 134.1, 136.3, 136.7 (C), 137.4 (d, $J_{F,C}$=3.19 Hz, C), 160.2 (d, $J_{F,C}$=245.1 Hz, C–F), 160.7 (d, $J_{F,C}$=246.1 Hz, C–F), 161.6 (d, $J_{F,C}$=248.1 Hz, C–F). IR (KBr): ν=3068, 3043, 2961, 2853, 1907, 1891 (w), 1601, 1593, 1556 (m), 1513 (s), 1493 (m), 1463 (s), 1425, 1403 (w), 1367, 1335 (m), 1315, 1299 (w), 1258 (m), 1219, 1156, 1087, 1014 (s), 946 (m), 907 (w), 860, 837 (m), 819, 811, 800, 794 (s), 762 (w), 730 (m), 724, 686, 643, 628 (w), 608 (s), 576 (w), 566 (m), 538 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=414 ($[M+H]^+$, 30), 413 ($[M]^+$, 100), 397 (9). HRMS (EI, 70 eV): calcd for $C_{27}H_{18}F_3N$ $[M]^+$: 413.13859, found: 413.13909.

*4.3.8. 1-Methyl-2,3,6-tris(4-(trifluoromethyl)phenyl)-1H-indole (**8h**).* Starting with **7** (100 mg, 0.27 mmol), **2m** (177 mg, 0.93 mmol), $Pd(PPh_3)_4$ (4 mol %), K_2CO_3 (152 mg, 1.1 mmol), 1,4-dioxane (2 mL) and H_2O (2 mL), **8h** was isolated as a white solid (127 mg, 82%), mp 200–202 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.67 (s, 3H, NCH_3), 7.30 (d, 2H, J=1.56 Hz, ArH), 7.36–7.42 (m, 3H, ArH), 7.47 (d, 2H, J=8.13 Hz, ArH), 7.56 (d, 1H, J=0.84 Hz, ArH), 7.59–7.65 (m, 4H, ArH), 7.71–7.76 (m, 3H, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−62.7, −62.3, −62.3. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=30.2 (NCH_3), 107.7 (CH), 113.8 (C), 119.0, 119.7 (CH), 122.9 (q, $J_{F,C}$=273.3 Hz, CF_3), 123.5 (q, $J_{F,C}$=272.7 Hz, CF_3), 123.7 (q, $J_{F,C}$=272.0 Hz, CF_3), 124.4 (q, $J_{F,C}$=3.74 Hz, CH), 124.6 (q, $J_{F,C}$=3.79 Hz, CH), 124.9 (q, $J_{F,C}$=3.56 Hz, CH), 125.5 (C), 126.6 (CH), 127.0 (q, $J_{F,C}$=32.4 Hz, C–CF_3), 127.9 (q, $J_{F,C}$=32.4 Hz, C–CF_3), 128.8 (CH), 129.6 (q, $J_{F,C}$=32.6 Hz, C–CF_3), 130.3 (CH), 133.9, 134.0, 136.6, 137.1, 137.3, 144.5 (C). IR (KBr): ν=3051, 2957, 2923, 2852, 2640 (w), 1613 (m), 1574, 1553, 1520, 1494 (w), 1465 (m), 1431, 1416, 1407, 1397, 1369 (w), 1321 (s), 1257 (m), 1187 (w), 1160 (m), 1105, 1089, 1163, 1012 (s), 960, 946 (w), 858, 841 (m), 828, 807 (s), 779, 771, 761, 742, 712 (w), 696 (m), 675, 654, 650 (w), 634, 614, 599 (m), 576 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%)=564 ($[M+H]^+$, 39), 563 ($[M]^+$, 100), 97 (10), 84 (13), 71 (18), 69 (27), 57 (28). HRMS (EI, 70 eV): calcd for $C_{30}H_{18}F_9N$ $[M]^+$: 563.12900, found: 563.12941.

*4.3.9. 2,3,6-Tris(4-methoxyphenyl)-1-methyl-1H-indole (**8i**).* Starting with **7** (100 mg, 0.27 mmol), **2n** (142 mg, 0.93 mmol), $Pd(PPh_3)_4$ (4 mol %), K_2CO_3 (152 mg, 1.1 mmol), 1,4-dioxane (2 mL) and H_2O (2 mL), **8i** was isolated as a white solid (107 mg, 87%), mp 124–126 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.67 (s, 3H, NCH_3), 3.72 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 6.68 (d, 1H, J=2.94 Hz, ArH), 6.75–6.94 (m, 6H, ArH), 7.14–7.16 (m, 3H, ArH), 7.30 (dd, 1H, J=1.50, 8.28 Hz, ArH), 7.44 (d, 1H, J=0.99 Hz, ArH), 7.55 (d, 2H, J=8.76 Hz, ArH), 7.68 (d, 1H, J=8.25 Hz, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=30.9 (NCH_3), 55.2, 55.3, 55.4 (OCH_3), 107.6, 113.8, 114.2 (CH), 114.3 (C), 114.8, 116.0, 119.6 (CH), 124.2, 126.1, 127.8 (C), 128.4, 130.8, 132.3 (CH), 135.2, 137.6, 137.7, 149.5, 157.5, 158.7, 159.3 (C). IR (KBr): ν=3053, 3037, 2994, 2961, 2928, 2838, 1607, 1573, 1551 (w), 1515 (m), 1478 (w), 1466, 1455, 1440 (m), 1426, 1392, 1370, 1338, 1303 (w), 1286 (m), 1239, 1173 (s), 1148, 1107, 1089 (m), 1036, 1026 (s), 961, 944, 932, 856 (w), 838 (m), 820, 809, 795 (s), 755 (m), 729, 721 (w), 688 (m), 646, 640, 628, 625 (w), 611 (s), 586, 576 (m), 556 (w), 537 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 449 ($[M]^+$, 100), 435 (11), 434 (36). HRMS (EI, 70 eV): calcd for $C_{30}H_{27}O_3N$ $[M]^+$: 449.19855, found: 449.19913.

*4.3.10. 2,3,6-Tris(3-chlorophenyl)-1-methyl-1H-indole (**8j**).* Starting with **7** (100 mg, 0.27 mmol), **2o** (145 mg, 0.93 mmol), $Pd(PPh_3)_4$ (4 mol %), K_2CO_3 (152 mg, 1.1 mmol), 1,4-dioxane (2 mL) and H_2O (2 mL), **8j** was isolated as a white solid (101 mg, 80%), mp 120–123 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=3.63 (s, 3H, NCH_3), 6.99–7.02 (m, 1H, ArH), 7.09–7.11 (m, 3H, ArH), 7.21–7.35 (m, 7H, ArH), 7.46–7.49 (m, 2H, ArH), 7.59–7.60 (m, 1H, ArH), 7.70 (d, 1H, J=8.13 Hz, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=30.1 (NCH_3), 107.3 (CH), 113.4 (C), 118.9, 119.3, 124.5, 125.0 (CH), 125.3 (C), 125.8, 126.4, 126.9, 127.7, 128.3, 128.5, 128.6, 128.9, 129.0, 129.7 (CH), 132.1, 133.1, 133.4, 133.6, 133.8, 135.4, 136.3, 136.8, 143.0 (C). IR (KBr): ν=3066, 2917, 2849 (w), 1592 (s), 1564 (w), 1550 (m), 1485 (w), 1467 (s), 1455 (m), 1427, 1410, 1397 (w), 1373 (s), 1334 (m), 1308, 1296 (w), 1256 (m), 1165, 1140 (w), 1099, 1088, 1077 (m), 1050, 1034, 995 (w), 963 (m), 910 (w), 894, 866, 856 (m), 825, 787, 781, 771, 758, 717, 700, 688, 676 (s), 661 (w), 646 (s), 603, 583, 557, 551, 541 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 464 ($[(M+H), {}^{35}Cl, {}^{35}Cl, {}^{37}Cl]^+$, 29), 463 ($[M, {}^{35}Cl, {}^{35}Cl, {}^{37}Cl]^+$, 98), 462 ($[(M+H), {}^{35}Cl, {}^{35}Cl, {}^{35}Cl]^+$, 29), 461 ($[M, {}^{35}Cl, {}^{35}Cl, {}^{35}Cl]^+$, 100). HRMS (EI, 70 eV): calcd for $C_{27}H_{18}Cl_3N$ $[M, {}^{35}Cl, {}^{35}Cl, {}^{37}Cl]^+$: 463.04698, found: 463.04738, calcd for $C_{27}H_{18}Cl_3N$ $[M, {}^{35}Cl, {}^{35}Cl, {}^{35}Cl]^+$: 461.04993, found: 461.05006.

*4.3.11. 2,3,6-Tris(2-ethoxyphenyl)-1-methyl-1H-indole (**8k**).* Starting with **7** (100 mg, 0.27 mmol), **2p** (154.4 mg, 0.93 mmol), $Pd(PPh_3)_4$

(4 mol %), K_2CO_3 (152 mg, 1.1 mmol) and 1,4-dioxane (2 mL) and H_2O (2 mL), **8k** was isolated as white powder (114 mg, 85%), mp 166 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ=1.19 (br s, 3H, CH_3), 1.32 (t, J=7.0 Hz, 3H, CH_3), 1.40 (t, J=7.0 Hz, 3H, CH_3), 3.68 (s, 3H, NCH_3), 3.97–4.04 (m, 2H, $ArOCH_2$), 4.10 (q, J=7.0 Hz, 4H, $2ArOCH_2$), 6.83–6.91 (m, 3H, ArH), 6.97 (d, J=7.9 Hz, 1H, ArH), 7.02–7.22 (m, 4H, ArH), 7.28–7.34 (m, 3H, ArH), 7.38 (dd, J=8.2, 1.4 Hz, 1H, ArH), 7.52 (dd, J=7.6, 1.7 Hz, 1H, ArH), 7.60 (d, J=8.3 Hz, 1H, ArH), 7.63 (d, J=0.8 Hz, 1H, ArH). ^{13}C NMR (262.89 MHz, $CDCl_3$): δ=14.5, 14.7, 14.9 (CH_3), 30.9 (NCH_3), 63.4 ($2CH_2$), 64.1 (CH_2), 110.2, 111.5 (2CH), 112.0 (C), 112.9 (2CH), 120.0, 120.2, 120.8, 121.3 (CH), 121.9, 125.0, 126.6 (C), 127.0, 127.7, 129.4 (CH), 131.3 (2CH), 131.8, 132.5, 132.6, 133.2, 136.3, 137.1, 156.1 (C). IR (ATR, cm^{-1}): $\tilde{\nu}$=3045 (w), 2978 (m), 2922 (m), 2874 (m), 1595 (w), 1577 (m), 1554 (m), 1499 (m), 1467 (m), 1451 (m), 1439 (m), 1387 (m), 1371 (m), 1333 (m), 1312 (m), 1281 (s), 1239 (s), 1158 (m), 1117 (s), 1084 (m), 1040 (s), 950 (m), 921 (m), 850 (m), 814 (m), 794 (m), 748 (s), 721 (s), 698 (m), 681 (m), 642 (m), 633 (m), 601 (m), 545 (m). MS (EI, 70 eV): m/z (%)=493 ($[M+2]^+$, 7), 492 ($[M+1]^+$, 37), 491 ($[M]^+$, 100), 433 (9), 29 (5). HRMS (EI) calcd for $C_{33}H_{33}NO_3$ $[M]^+$ is 491.24550, found 491.245592.

*4.3.12. 3-Bromo-1-methyl-2,6-di-p-tolyl-1H-indole (**9a**).* Starting with **7** (100 mg, 0.27 mmol), **2a** (77 mg, 0.57 mmol), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (172 mg, 0.82 mmol) and 1,4-dioxane (5 mL), **9a** was isolated as a white solid (78 mg, 73%), mp 135–137 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.30 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.62 (s, 3H, NCH_3), 7.06–7.11 (m, 1H, ArH), 7.21–7.27 (m, 3H, ArH), 7.33 (d, 2H, J=8.24 Hz, ArH), 7.39 (dd, 1H, J=1.45, 8.24 Hz, ArH), 7.43 (br s, 1H, ArH), 7.49–7.57 (m, 3H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.1, 21.4 (CH_3), 31.7 (NCH_3), 89.9 (C), 107.9, 119.4, 120.8 (CH), 120.8, 123.1, 126.4 (C), 127.3, 129.2, 129.5, 130.5 (CH), 136.3, 136.6, 137.3, 138.7, 139.3 (C). IR (KBr): ν=3022, 2916, 2852, 2729, 1908, 1613, 1556 (w), 1518, 1492 (m), 1455 (s), 1423 (w), 1368, 1341 (m), 1312, 1299, 1253, 1231 (w), 1218 (m), 1183, 1139 (w), 1105 (m), 1059, 1039, 1018, 965 (w), 950 (s), 939 (m), 907, 854 (w), 840, 821 (m), 806 (s), 779 (m), 748 (w), 721 (m), 687, 672, 649, 631 (w), 622, 598 (m), 570, 537 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 392 ($[(M+H), ^{81}Br]^+$, 24), 391 ($[M, ^{81}Br]^+$, 100), 390 ($[(M+H), ^{79}Br]^+$, 31), 389 ($[M, ^{79}Br]^+$, 100), 295 (11), 294 (14). HRMS (EI, 70 eV): calcd for $C_{23}H_{20}BrN$ $[M, ^{81}Br]^+$: 391.07532, found: 391.07571, calcd for $C_{23}H_{20}BrN$ $[M, ^{79}Br]^+$: 389.07736, found: 389.07745.

*4.3.13. 3-Bromo-2,6-bis(4-ethylphenyl)-1-methyl-1H-indole (**9b**).* Starting with **7** (100 mg, 0.27 mmol), **2b** (85 mg, 0.57 mmol), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (172 mg, 0.81 mmol) and 1,4-dioxane (5 mL), **9b** was isolated as a white solid (90 mg, 79%), mp 119–121 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.19–1.26 (m, 6H, $2CH_3$), 2.59–2.70 (m, 4H, $2CH_2$), 3.61 (s, 3H, NCH_3), 7.24 (q, 4H, J=8.31 Hz, ArH), 7.35 (d, 2H, J=8.25 Hz, ArH), 7.39 (dd, 1H, J=1.47, 8.19 Hz, ArH), 7.43 (d, 1H, J=0.75 Hz, ArH), 7.50–7.57 (m, 3H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=15.3, 15.7 (CH_3), 28.6, 28.8 (CH_2), 31.7 (NCH_3), 89.9 (C), 108.1, 119.5, 120.4 (CH), 126.5 (C), 127.4 (CH), 127.6 (C), 127.8, 127.9, 130.6 (CH), 136.4, 137.4, 138.7, 139.6, 143.0, 144.9 (C). IR (KBr): ν=3050, 3019, 2966, 2930, 2872, 2853, 1517, 1492 (w), 1456 (s), 1423, 1410 (w), 1370, 1342 (m), 1309, 1272, 1231 (w), 1216 (m), 1182, 1139, 1115 (w), 1101 (m), 1051, 1017, 964 (w), 949 (s), 908, 858 (w), 844, 835 (m), 812 (s), 771, 763 (m), 750, 732, 685, 676, 647, 631 (w), 619, 603 (m), 562 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 419 ($[M, ^{81}Br]^+$, 99), 418 ($[(M+H), ^{79}Br]^+$, 28), 417 ($[M, ^{79}Br]^+$, 100), 404 (27), 402 (26). HRMS (EI, 70 eV): calcd for $C_{25}H_{24}BrN$ $[M, ^{81}Br]^+$: 419.10662, found: 419.10785, calcd for $C_{25}H_{24}BrN$ $[M, ^{79}Br]^+$: 417.10866, found: 417.10911.

*4.3.14. 3-Bromo-2,6-bis(4-chlorophenyl)-1-methyl-1H-indole (**9c**).* Starting with **7** (100 mg, 0.27 mmol), **2d** (89 mg, 0.57 mmol), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (172 mg, 0.81 mmol) and 1,4-dioxane (5 mL), **9c** was isolated as a white solid (94 mg, 80%), mp 173–175 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.61 (s, 3H, NCH_3), 7.31–7.44 (m, 8H, ArH), 7.49–7.58 (m, 3H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=30.7 (NCH_3), 88.5 (C), 107.1, 118.8, 119.4 (CH), 125.8 (C), 127.6, 127.8, 127.9, 130.9 (CH), 131.2, 132.0, 134.0, 134.4, 136.4, 136.5, 139.4 (C). IR (KBr): ν=3069, 3054, 3013, 2961, 2924, 2872, 2851, 1598, 1557, 1542, 1498 (w), 1478, 1463 (m), 1426, 1399, 1367, 1340, 1306, 1296 (w), 1258 (m), 1236, 1213, 1180, 1124 (w), 1104 (m), 1089 (s), 1056 (m), 1009 (s), 950, 939 (m), 907, 861 (w), 838 (s), 823, 813 (m), 797 (s), 742, 733 (w), 725 (m), 715, 698, 673, 666, 648, 639, 626 (w), 609 (m), 592, 582, 538 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 431 ($[(M+H), ^{81}Br, ^{35}Cl]^+$, 100), 430 ($[M, ^{81}Br, ^{35}Cl]^+$, 15), 429 ($[(M+H), ^{79}Br, ^{35}Cl]^+$, 63), 393 (8), 314 (10), 139 (16). HRMS (EI, 70 eV): calcd for $C_{21}H_{14}BrCl_2N$ $[M, ^{81}Br, ^{35}Cl]^+$: 430.96607, found: 430.96755, calcd for $C_{21}H_{14}BrCl_2N$ $[M, ^{79}Br, ^{35}Cl]^+$: 428.96812, found: 428.96935.

*4.3.15. 3-Bromo-2,6-bis(4-fluorophenyl)-1-methyl-1H-indole (**9d**).* Starting with **7** (100 mg, 0.27 mmol), **2l** (79 mg, 0.57 mmol), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (172 mg, 0.81 mmol) and 1,4-dioxane (5 mL), **9d** was isolated as a white solid (90 mg, 83%), mp 115–117 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.60 (s, 3H, NCH_3), 7.06 (t, 2H, J=5.22 Hz, ArH), 7.14 (t, 2H, J=5.22 Hz, ArH), 7.35 (dd, 1H, J=0.87, 4.92 Hz, ArH), 7.39–7.42 (m, 3H, ArH), 7.53–7.57 (m, 3H, ArH). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ=−116.3, −111.9. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=31.7 (NCH_3), 90.3 (C), 108.2 (CH), 115.5 (d, $J_{F,C}$=6.51 Hz, CH), 117.3 (d, $J_{F,C}$=6.83 Hz, CH), 119.7, 120.5 (CH), 126.2, 126.3 (C), 128.9 (d, $J_{F,C}$=7.92 Hz, CH), 132.5 (d, $J_{F,C}$=8.32 Hz, CH), 135.7, 137.3, 137.7, 138.1 (C), 162.3 (d, $J_{F,C}$=245.9 Hz, C–F), 162.9 (d, $J_{F,C}$=249.2 Hz, C–F). IR (KBr): ν=2925, 2852 (w), 1603, 1591 (m), 1574, 1557 (w), 1539 (m), 1515, 1488 (s), 1456 (m), 1424, 1405, 1371, 1339, 1308, 1298 (w), 1229, 1158, 1100 (s), 1022 (w), 1010, 951 (m), 860 (w), 846, 834, 824 (w), 794 (s), 726, 718, 686, 667, 644, 629 (w), 619 (m), 599 (s), 566 (m), 536 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 399 ($[M, ^{81}Br]^+$, 100), 398 ($[(M+H), ^{79}Br]^+$, 25), 397 ($[M, ^{79}Br]^+$, 99), 317 (11), 316 (15), 303 (14). HRMS (EI, 70 eV): calcd for $C_{21}H_{14}F_2BrN$ $[M, ^{81}Br]^+$: 399.02517, found: 399.02549, calcd for $C_{21}H_{14}F_2BrN$ $[M, ^{79}Br]^+$: 397.02722, found: 397.02732.

*4.3.16. 3-Bromo-2,6-bis(4-methoxyphenyl)-1-methyl-1H-indole (**9e**).* Starting with **7** (100 mg, 0.27 mmol), **2n** (86 mg, 0.57 mmol), $Pd(PPh_3)_4$ (5 mol %), K_3PO_4 (172 mg, 0.81 mmol) and 1,4-dioxane (5 mL), **9e** was isolated as a white solid (96 mg, 83%), mp 163–165 °C (CH_2Cl_2/EtOH 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.58 (s, 3H, NCH_3), 3.77 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 6.87–6.98 (m, 4H, ArH), 7.31–7.37 (m, 4H, ArH), 7.49–7.54 (m, 3H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=30.6 (NCH_3), 54.3, 54.4 (OCH_3), 88.8 (C), 106.7, 112.9, 113.2, 118.3, 119.1 (CH), 121.5, 125.2 (C), 127.4, 130.9 (CH), 133.7, 134.9, 136.2, 137.3, 157.8, 158.8 (C). IR (KBr): ν=3033, 2998, 2961, 2932, 2833 (w), 1606 (m), 1573, 1562, 1542 (w), 1518, 1489, 1461, 1443, 1424 (m), 1372 (w), 1345, 1305, 1288, 1274 (m), 1246, 1175 (s), 1105, 1035 (m), 1019 (s), 950 (m), 864 (w), 845, 832 (m), 815, 804, 781 (s), 747, 732, 704, 687, 668, 643, 629 (w), 621, 600, 576 (m), 556 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 424 ($[(M+H), ^{81}Br]^+$, 25), 423 ($[M, ^{81}Br]^+$, 99), 422 ($[(M+H), ^{79}Br]^+$, 28), 421 ($[M, ^{79}Br]^+$, 100), 408 (34), 406 (33), 212 (13). HRMS (EI, 70 eV): calcd for $C_{23}H_{20}BrNO_2$ $[M, ^{79}Br]^+$: 421.06719, found: 421.06734, calcd for $C_{23}H_{20}BrNO_2$ $[M, ^{81}Br]^+$: 421.06515, found: 421.06567.

*4.3.17. 3,6-Dibromo-1-methyl-2-(p-tolyl)-1H-indole (**10a**).* Starting with **7** (100 mg, 0.27 mmol), **2a** (40 mg, 0.29 mmol), $Pd(PPh_3)_4$ (3 mol %), K_3PO_4 (86 mg, 0.40 mmol) and toluene/1,4-dioxane (4:1) (5 mL), **10a** was isolated as a white solid (79 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.37 (s, 3H, CH_3), 3.54 (s, 3H, NCH_3), 7.21–7.32 (m, 5H, ArH), 7.35–7.39 (m, 1H, ArH), 7.42 (d, 1H, J=1.77 Hz, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ=21.4 (CH_3), 31.7 (NCH_3), 90.1 (C), 112.7 (CH), 116.2 (C), 120.5, 123.7 (CH), 126.2, 126.9 (C), 129.3, 130.4 (CH), 137.5, 138.8, 139.0 (C). IR (KBr): ν=3206, 3070, 3021 (w), 2918 (m), 2866, 2584, 2550, 2417, 2357, 2326, 2142, 1965, 1910, 1869, 1801, 1732, 1673, 1604, 1562 (w), 1492 (m), 1462, 1450 (s), 1419, 1370 (m), 1336 (s), 1289, 1217, 1182 (m), 1131 (w), 1110, 1054 (m), 1040 (w), 1018 (m), 964 (w), 943 (s), 830, 797 (s), 781 (m), 759, 736 (w), 720 (m), 677, 658, 633 (w), 620, 586 (s), 549 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 381 ([(M+H), ^{81}Br]$^{+}$, 49), 380 ([M, ^{81}Br]$^{+}$, 19), 379 ([(M+H), ^{79}Br, ^{81}Br]$^{+}$, 100), 377 ([(M+H), ^{79}Br]$^{+}$, 50), 218 (11), 204 (13). HRMS (EI, 70 eV): calcd for C$_{16}$H$_{13}$Br$_2$N [M, ^{81}Br]$^{+}$: 380.93683, found: 380.93821, calcd for C$_{16}$H$_{13}$Br$_2$N [M, ^{79}Br, ^{81}Br]$^{+}$: 378.93888, found: 378.93905, calcd for C$_{16}$H$_{13}$Br$_2$N [M, ^{79}Br]$^{+}$: 376.94093, found: 376.94069.

*4.3.18. 3,6-Dibromo-2-(4-ethylphenyl)-1-methyl-1H-indole (**10b**).* Starting with **7** (100 mg, 0.27 mmol), **2b** (44 mg, 0.29 mmol), Pd(PPh$_3$)$_4$ (3 mol %), K$_3$PO$_4$ (86 mg, 0.40 mmol) and toluene/1,4-dioxane (4:1) (5 mL), **10b** was isolated as a white solid (88 mg, 83%), mp 94–96 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ=1.24 (t, 3H, CH$_3$), 2.67 (q, 2H, J=7.59, CH$_2$), 3.56 (s, 3H, NCH$_3$), 7.20–7.26 (m, 2H, ArH), 7.29 (d, 3H, J=8.40 Hz, ArH), 7.33–7.39 (m, 1H, ArH), 7.42 (d, 1H, J=1.41 Hz, ArH). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ=15.3 (CH$_3$), 28.7 (CH$_2$), 31.7 (NCH$_3$), 90.1 (C), 112.7 (CH), 116.2 (C), 120.5, 123.7 (CH), 126.2, 127.1 (C), 128.0, 130.5 (CH), 137.5, 138.8, 145.1 (C). IR (KBr): ν=3070, 3022, 2960, 2868 (w), 1492, 1463, 1448 (m), 1414, 1371 (w), 1338 (m), 1305, 1289, 1231 (w), 1214 (m), 1183, 1130, 1117 (w), 1109, 1054 (m), 1040, 1015, 966 (w), 943, 934, 843, 837, 829 (s), 811 (w), 800 (s), 765, 734, 677 (w), 659 (m), 632 (w), 617 (m), 587 (s), 560 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 395 ([(M+H), ^{81}Br]$^{+}$, 49), 394 ([M, ^{81}Br]$^{+}$, 19), 393 ([(M−H), ^{81}Br]$^{+}$, 100), 392 ([M, ^{81}Br]$^{+}$, 11), 391 ([(M+H), ^{79}Br]$^{+}$, 51), 378 (32), 376 (16). HRMS (EI, 70 eV): calcd for C$_{17}$H$_{15}$Br$_2$N [M, ^{81}Br]$^{+}$: 394.95248, found: 394.95330, calcd for C$_{17}$H$_{15}$Br$_2$N [M, ^{79}Br]$^{+}$: 390.95658, found: 390.95765.

*4.3.19. 3,6-Dibromo-2-(4-chlorophenyl)-1-methyl-1H-indole (**10c**).* Starting with **7** (100 mg, 0.27 mmol), **2d** (46 mg, 0.29 mmol), Pd(PPh$_3$)$_4$ (3 mol %), K$_3$PO$_4$ (86 mg, 0.40 mmol) and toluene/1,4-dioxane (4:1) (5 mL), **10c** was isolated as a white solid (86 mg, 79%), reaction temperature: 65 °C for 8 h. ^{1}H NMR (300 MHz, CDCl$_3$): δ=3.54 (s, 3H, NCH$_3$), 7.23–7.26 (m, 1H, ArH), 7.32–7.36 (m, 3H, ArH), 7.39–7.44 (m, 3H, ArH). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ=31.8 (NCH$_3$), 90.7 (C), 112.8 (CH), 116.7 (C), 120.8, 124.0 (CH), 126.1, 128.4 (C), 128.9, 131.9 (CH), 135.2, 137.4, 137.6 (C). IR (KBr): ν=3079, 3064, 2925, 2854, 1915, 1872, 1728, 1692, 1599, 1562, 1536, 1503, 1478 (w), 1461, 1454 (m), 1418, 1400, 1361 (w), 1336 (m), 1288, 1268, 1232, 1212, 1179, 1129, 1104 (w), 1088 (m), 1051, 1036 (w), 1011 (m), 966 (w), 944, 939 (m), 835 (s), 803 (m), 795 (s), 737 (w), 724 (m), 674, 648, 625 (w), 607 (m), 589 (s), 570 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 399 ([(M+H), ^{79}Br, ^{81}Br, ^{35}Cl]$^{+}$, 100), 398 ([M, ^{79}Br, ^{81}Br, ^{35}Cl]$^{+}$, 8), 397 ([(M+H), ^{79}Br, ^{79}Br, ^{35}Cl]$^{+}$, 45), 204 (11). HRMS (EI, 70 eV): calcd for C$_{15}$H$_{10}$Br$_2$ClN [M, ^{79}Br, ^{81}Br, ^{35}Cl]$^{+}$: 398.88426, found: 398.88410, calcd for C$_{15}$H$_{10}$Br$_2$ClN [M, ^{79}Br, ^{79}Br, ^{35}Cl]$^{+}$: 396.88630, found: 396.88615.

*4.3.20. 3,6-Dibromo-2-(4-(tert-butyl)phenyl)-1-methyl-1H-indole (**10d**).* Starting with **7** (100 mg, 0.27 mmol), **2e** (52 mg, 0.29 mmol), Pd(PPh$_3$)$_4$ (3 mol %), K$_3$PO$_4$ (86 mg, 0.40 mmol) and toluene/1,4-dioxane (4:1) (5 mL), **10d** was isolated as a white solid (97 mg, 84%), mp 156–158 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ=1.31 (s, 9H, 3CH$_3$), 3.55 (s, 3H, NCH$_3$), 7.23 (dd, 1H, J=1.92, 10.11 Hz, ArH), 7.31–7.46 (m, 6H, ArH). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ=31.3 (CH$_3$), 31.8 (NCH$_3$), 33.2, 90.0 (C), 112.7 (CH), 116.2 (C), 120.5, 123.7, 125.5 (CH), 126.2, 126.8 (C), 130.2 (CH), 137.5, 138.8, 151.9 (C). IR (KBr): ν=3026 (w), 2959 (m), 2901, 2865, 2707, 1920, 1868, 1731, 1681, 1599, 1563, 1556 (w), 1491, 1461, 1451, 1416 (m), 1405, 1390 (w), 1360 (m), 1336 (s), 1289, 1267 (w), 1217 (m), 1199, 1131 (w), 1109, 1053, 1014 (m), 968 (w), 945, 842, 800 (s), 738, 723, 689 (w), 654 (m), 628 (w), 615 (s), 589 (m), 576, 553, 543 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 421 ([(M+H), ^{79}Br, ^{81}Br]$^{+}$, 100), 420 ([M, ^{79}Br, ^{81}Br]$^{+}$, 11), 419 (52), 408 (23), 406 (45), 404 (23), 378 (8). HRMS (EI, 70 eV): calcd for C$_{19}$H$_{19}$Br$_2$N [M, ^{79}Br, ^{81}Br]$^{+}$: 420.98583, found: 420.98605.

*4.3.21. 3,6-Bis(4-(tert-butyl)phenyl)-2-(4-fluorophenyl)-1-methyl-1H-indole (**11a**).* The reaction was carried out in a pressure tube. To a mixture solvent of toluene/dioxane (4:1) (5 mL) suspension of the brominated-*N*-methylindole, Pd(PPh$_3$)$_4$ (5 mol %) and of the Ar^{1}B(OH)$_2$ (1.1 equiv), K$_3$PO$_4$ (1.5 equiv) was added also. The mixture was heated at the indicated temperature (65 °C) under argon atmosphere for the indicated period of time (8 h) and cooled to room temperature. Then Ar^{2}B(OH)$_2$ (2.1 equiv), K$_2$CO$_{3(aq)}$ (2 M, 1 mL) and 1,4-dioxane (3 mL) were added. The reaction mixture was further heated for 8 h at 110 °C. The reaction mixture was again cooled to room temperature and diluted with water and extracted with CH$_2$Cl$_2$ (3×25 mL). The combined organic layers were dried (Na$_2$SO$_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (silica gel, EtOAc/heptanes). Starting with **7** (100 mg, 0.27 mmol), **2l** (41 mg, 0.29 mmol), Pd(PPh$_3$)$_4$ (5 mol %), K$_3$PO$_4$ (86 mg, 0.40 mmol) and toluene/1,4-dioxane (4:1) (5 mL), **2e** (99 mg, 0.57 mmol), K$_2$CO$_3$ (2 M, 1 mL) and 1,4-dioxane (3 mL), **11a** was isolated as a yellowish solid (99 mg, 74%), mp 148–150 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ=1.22 (s, 9H, 3CH$_3$), 1.29 (s, 9H, 3CH$_3$), 3.56 (s, 3H, NCH$_3$), 6.97 (t, 2H, J=8.64 Hz, ArH), 7.10–7.25 (m, 6H, ArH), 7.34 (dd, 1H, J=1.35, 8.31 Hz, ArH), 7.40 (d, 2H, J=8.34 Hz, ArH), 7.47 (d, 1H, J=0.90 Hz, ArH), 7.56 (d, 2H, J=8.31 Hz, ArH), 7.75 (d, 1H, J=8.31 Hz, ArH). ^{19}F NMR (282.4 MHz, CDCl$_3$): δ=−113.2. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ=30.9 (NCH$_3$), 31.4, 31.5 (CH$_3$), 34.4, 34.5 (C), 107.9 (CH), 115.2 (C), 115.6 (d, $J_{F,C}$=21.5 Hz, CH), 120.1, 125.2, 125.7 (CH), 126.3 (C), 127.1 (CH), 128.1 (d, $J_{F,C}$=3.49 Hz, CH), 129.3 (CH), 131.9 (C), 132.4 (d, $J_{F,C}$=8.15 Hz, CH), 135.8, 136.9, 137.9, 139.6, 148.4, 149.7 (C), 162.6 (d, $J_{F,C}$=247.9 Hz, C–F). IR (KBr): ν=3030 (w), 2957 (m), 2902, 2865, 2244, 1900, 1605, 1593, 1563, 1549 (w), 1516 (m), 1491 (w), 1462 (s), 1426, 1404, 1392 (w), 1363 (m), 1334, 1319, 1307, 1296 (w), 1267 (m), 1221 (s), 1202 (w), 1156 (m), 1108, 1093, 1086, 1045, 1014 (w), 947 (m), 906 (s), 860 (m), 836, 823, 810, 802 (s), 761, 750 (w), 729 (s), 694, 672, 649 (w), 624, 604 (m), 561 (s), 538 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 490 ([M+H]$^{+}$, 61), 489 ([M]$^{+}$, 100), 474 (38), 444 (8), 229 (23), 215 (36), 201 (96), 189 (16), 183 (15), 134 (14). HRMS (EI, 70 eV): calcd for C$_{35}$H$_{36}$FN [M]$^{+}$: 489.28263, found: 489.28253.

*4.3.22. 2-(4-(tert-Butyl)phenyl)-3,6-bis(4-methoxyphenyl)-1-methyl-1H-indole (**11b**).* The synthesis was carried out following the procedure given for the synthesis of products **8**. Starting with **10d** (71 mg, 0.17 mmol), **2n** (53 mg, 0.35 mmol), Pd(PPh$_3$)$_4$ (5 mol %), K$_2$CO$_3$ (2 M, 1 mL) and 1,4-dioxane (3 mL), **11b** was isolated as a yellowish solid (65 mg, 81%), mp 184–186 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ=1.27 (s, 9H, 3CH$_3$), 3.62 (s, 3H, NCH$_3$), 3.72 (s, 3H, OCH$_3$), 3.78 (s, 3H, OCH$_3$), 6.76 (d, 2H, J=8.76 Hz, ArH), 6.92 (d, 2H, J=8.73 Hz, ArH), 7.16–7.18 (m, 4H, ArH), 7.31 (d, 3H, J=8.28 Hz, ArH), 7.44 (d, 1H, J=0.84 Hz, ArH), 7.56 (d, 2H, J=8.70 Hz, ArH), 7.68 (d, 1H, J=8.22 Hz, ArH). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ=31.0 (NCH$_3$), 31.3 (CH$_3$), 34.7 (C), 55.2, 55.4 (OCH$_3$), 107.6, 113.7, 114.2 (CH), 114.5 (C), 119.7, 125.3 (CH), 122.1, 127.8 (C), 127.4, 128.7 (CH), 128.9 (C), 130.7, 130.9 (CH), 135.3, 137.8, 138.0, 150.9, 157.6, 158.7 (C). IR (KBr): ν=3033, 2996, 2953, 2902, 2866, 2832, 2248, 2059, 1886, 1714, 1650 (w), 1607 (m), 1573, 1548 (w), 1514 (s), 1492 (w), 1461 (s), 1440 (m), 1426, 1407, 1393 (w), 1363 (m), 1334, 1316, 1302 (w), 1278 (m), 1240, 1174 (s), 1108, 1089 (w), 1035 (s), 946, 906, 858 (m), 832, 807, 794 (s), 783, 760 (w), 727 (s), 688 (m), 648, 624 (w), 607 (s), 582, 558 (w), 531 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 476 ([M+H]$^{+}$, 36), 475 ([M]$^{+}$, 100), 460 (12). HRMS (ESI, 70 eV): calcd for C$_{33}$H$_{33}$NO$_2$ [M+H]$^{+}$: 476.25841, found: 476.25779.

*4.3.23. 2-(4-Chlorophenyl)-3,6-bis(4-methoxyphenyl)-1-methyl-1H-indole (**11c**).* The synthesis was carried out following the procedure given for the synthesis of products **8**. Starting with **10c** (67 mg, 0.17 mmol), **2n** (54 mg, 0.35 mmol), $Pd(PPh_3)_4$ (5 mol %), K_2CO_3 (2 M, 1 mL) and 1,4-dioxane (3 mL), **11c** was isolated as a yellowish solid (62 mg, 82%), mp 105–107 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.60 (s, 3H, NCH_3), 3.72 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 6.77 (d, 2H, J=8.79 Hz, ArH), 6.92 (d, 2H, J=8.79 Hz, ArH), 7.12–7.19 (m, 4H, ArH), 7.26–7.35 (m, 3H, ArH), 7.44 (br s, 1H, ArH), 7.55 (d, 2H, J=8.67 Hz, ArH), 7.67 (d, 1H, J=8.36 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=30.0 (NCH_3), 54.2, 54.4 (OCH_3), 106.6, 112.8, 113.2, 118.8 (CH), 125.1, 126.1 (C), 127.4, 127.7 (CH), 127.8, 129.4 (C), 129.8, 131.3 (CH), 133.0, 134.0, 134.7, 135.3, 137.0, 156.8, 157.8 (C). IR (KBr): ν=3033, 2999, 2958, 2920, 2836 (w), 1606 (m), 1572, 1546 (w), 1510, 1462 (s), 1441 (m), 1426, 1395 (w), 1368 (m), 1333, 1316, 1302 (w), 1279 (m), 1242, 1174, 1087, 1033, 1013 (s), 945 (m), 907, 887, 873 (w), 856, 826 (m), 815, 804, 794 (s), 760 (w), 725 (m), 698, 684, 649, 637, 618 (w), 603 (s), 578, 568 (w), 534 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 454 ($[M+H]^+$, 27), 453 ($[M]^+$, 100), 438 (25). HRMS (EI, 70 eV): calcd for $C_{29}H_{24}ClO_2N$ $[M]^+$: 453.14901, found: 453.14838.

*4.3.24. 2-(4-(tert-Butyl)phenyl)-3,6-bis(2-methoxyphenyl)-1-methyl-1H-indole (**11d**).* The synthesis was carried out following the procedure given for the synthesis of products **8**. Starting with **10d** (71 mg, 0.17 mmol), **2j** (54 mg, 0.36 mmol), $Pd(PPh_3)_4$ (5 mol %), K_2CO_3 (2 M, 1 mL) and 1,4-dioxane (3 mL), **11d** was isolated as a yellowish solid (58 mg, 72%), mp 175–177 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.24 (s, 9H, $3CH_3$), 3.38 (s, 3H, NCH_3), 3.67 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 6.77–6.86 (m, 2H, ArH), 6.92–7.00 (m, 2H, ArH), 7.12–7.17 (m, 3H, ArH), 7.19–7.28 (m, 5H, ArH), 7.33–7.36 (m, 1H, ArH), 7.43–7.46 (m, 2H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=30.2 (NCH_3), 30.3 (CH_3), 33.6 (C), 53.8, 54.7 (OCH_3), 109.5, 109.9 (CH), 110.1 (C), 110.4 (CH), 118.3, 119.3, 119.8, 120.9 (CH), 123.4 (C), 123.9 (CH), 125.8 (C), 126.4, 126.9 (CH), 128.7 (C), 129.0, 130.0 (CH), 131.2, 131.4 (C), 131.7 (CH), 136.3, 138.0, 149.3, 155.7, 156.2 (C). IR (KBr): ν=3050 (w), 2954, 2924 (m), 2854, 1716, 1699, 1683, 1669, 1652, 1635, 1615, 1597, 1578, 1558, 1501 (w), 1457 (s), 1432 (m), 1406, 1394 (w), 1363 (m), 1333, 1313, 1289 (w), 1252, 1239 (s), 1178, 1160 (w), 1117, 1083, 1050 (m), 1025 (s), 947 (m), 932, 856, 838 (w), 825, 813, 792 (m), 749 (s), 699, 654 (m), 638 (w), 628 (m), 611, 592, 560, 544 (w) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 476 ($[M+H]^+$, 36), 475 ($[M]^+$, 100). HRMS (EI, 70 eV): calcd for $C_{33}H_{33}NO_2$ $[M]^+$: 475.25058, found: 475.25047.

References and notes

1. (a) Sundberg, R. J. *The Chemistry of Indoles*; Academic: New York, NY, 1970; (b) Sundberg, R. J. Pyrroles and their benzoderivatives: synthesis and applications. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, UK, 1984; vol. 4, p 313; (c) Sundberg, R. J. *Indoles: Best Synthetic Methods*; Academic: New York, NY, 19967; (d) Joule, J. A. Indole and its derivatives Category 2. In *Science of Synthesis: Houben–Weyl Methods of Molecular Transformations*; Thomas, E. J., Ed.; George Thieme: Stuttgart, Germany, 2000; vol. 10; (Chapter 10.13); (e) Brown, R. K. In *Indoles*; Houlihan, W. J., Ed.; Wiley-Interscience: New York, NY, 1972; (f) Sundberg, R. J. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Ress, C. W., Scriven, E. F. V., Bird, C. W., Eds.; Pergamon: Oxford, UK, 1996; vol. 2, p 119; (g) Gribble, G. W. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Ress, C. W., Scriven, E. F. V., Bird, C. W., Eds.; Pergamon: Oxford, UK, 1996; vol. 2, p 207; (h) *Indoles*; Sundberg, R. J., Ed.; Academic: London, UK, 1996; (i) Barden, T. C. *Top. Heterocycl. Chem.* **2010**, *26*, 31; (j) Vicente, R. *Org. Biomol. Chem.* **2011**, *9*, 6469; (k) Lindel, T.; Marsch, N.; Adla, S. K. *Top. Curr. Chem.* **2012**, *309*, 67; (l) Bronner, S. M.; Im, G.-Y. J.; Neil, K. *Heterocycles in Natural Product Synthesis*; Wiley-VCH: Weinheim, Germany, 2011; p 221.
2. (a) Evans, B. E.; Rittle, K. E.; Bock, M. G.; DiPardo, R. M.; Freidinger, R. M.; Whitter, W. L.; Lundell, G. F.; Verber, D. F.; Anderson, P. S.; Chang, R. S. L.; Lotti, V. J.; Cerino, D. H.; Chen, T. B.; Kling, P. J.; Kunkel, K. A.; Springer, J. P.; Hirshfield, J. *J. Med. Chem.* **1988**, *31*, 2235; (b) Horton, D. A.; Bourne, G. T.; Smythe, M. L. *Chem. Rev.* **2003**, *103*, 893 and references therein.
3. McAdam, B. F.; Catella-Lawson, F.; Mardini, I. A.; Kapoor, S.; Lawson, J. A.; FitzGerald, G. A. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 272.
4. (a) Glenn, E. M.; Bowman, B. J.; Kooyers, W.; Koslowske, T.; Myers, M. L. *J. Pharmacol. Exp. Ther.* **1967**, *155*, 157; (b) Kaiser, D. G.; Glenn, E. M.; Johnson, R. H.; Johnston, R. L. *J. Pharmacol. Exp. Ther.* **1967**, *155*, 174; (c) Whitehouse, M. W. *J. Pharm. Pharmacol.* **1967**, *19*, 590; (d) Collier, H. O. J.; James, G. W. L.; Piper, P. J. *Br. J. Pharmacol.* **1968**, *34*, 76; (e) Brune, K.; Graf, P.; Glatt, M. *Agents Actions* **1976**, *6*, 159; (f) Podos, S. M.; Becker, B. *Invest. Ophthalmol.* **1976**, *15*, 841; (g) Spinelli, H. M.; Krohn, D. L. *Arch. Ophthalmol.* **1980**, *98*, 1106; (h) Klug, R. D.; Krohn, D. L.; Breitfeller, J. M.; Dieterich, D. *Ophthalmic Res.* **1981**, *13*, 122.
5. (a) Humphrey, G. R.; Kuethe, J. T. *Chem. Rev.* **2006**, *106*, 2875; (b) Cacchi, S.; Fabrizi, G. *Chem. Rev.* **2005**, *105*, 2873.
6. For direct C-arylations of indoles with (hetero)aryl halides or pseudohalides, see: (a) Lane, B. S.; Brown, M. A.; Sames, D. *J. Am. Chem. Soc.* **2005**, *127*, 8050; (b) Lane, B. S.; Sames, D. *Org. Lett.* **2004**, *6*, 2897; (c) Sezen, B.; Sames, D. *J. Am. Chem. Soc.* **2003**, *125*, 5274; (d) Bressy, C.; Alberico, D.; Lautens, M. *J. Am. Chem. Soc.* **2005**, *127*, 13148; (e) Wang, X.; Gribkov, D. V.; Sames, D. *J. Org. Chem.* **2007**, *72*, 1476; (f) Bellina, F.; Calandri, C.; Cauteruccio, S.; Rossi, R. *Tetrahedron* **2007**, *63*, 1970; (g) Zhang, Z.; Hu, Z.; Yu, Z.; Lei, P.; Chi, H.; Wang, Y.; Hen, R. *Tetrahedron Lett.* **2007**, *48*, 2415; (h) Lebrasseur, N.; Larrosa, I. *J. Am. Chem. Soc.* **2008**, *130*, 2926; (i) Bellina, F.; Benelli, F.; Rossi, R. *J. Org. Chem.* **2008**, *73*, 5529; (j) Joucla, L.; Djakovitch, L. *Adv. Synth. Catal.* **2009**, *351*, 673; (k) Ackermann, L.; Barfuesser, S. *Synlett* **2009**, 808; (l) Boorman, T. C.; Larrosa, I. *Prog. Heterocycl. Chem.* **2011**, *22*, 1; (m) Lebrasseur, N.; Larrosa, I. *Adv. Heterocycl. Chem.* **2012**, *105*, 309; (n) Roy, D.; Mom, S.; Royer, S.; Lucas, D.; Hierso, J.-C.; Doucet, H. *ACS Catal.* **2012**, *2*, 1033; (o) Dong, H.; Limberakis, C.; Liras, S.; Price, D.; James, K. *Chem. Commun.* **2012**, 11644 Review: S. Cacchi, G. Fabrizi, Chem. Rev. 111 (2011) 215.
7. Bandini, M.; Eichholzer, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 9608 and references cited therein.
8. For Rh-catalyzed arylation of NH indoles, see: (a) Wang, X.; Lane, B. S.; Sames, D. *J. Am. Chem. Soc.* **2005**, *127*, 4996 For PdII-catalyzed indole alkenylation/alkylation, see: (b) Jia, C.; Lu, W.; Kitamura, T. *Org. Lett.* **1999**, *1*, 2097; (c) Lu, W.; Jia, C.; Kitamura, T.; Fujiwara, Y. *Org. Lett.* **2000**, *2*, 2927; (d) Ferreira, E. M.; Stoltz, B. M. *J. Am. Chem. Soc.* **2003**, *125*, 9578; (e) Liu, C.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 10250; (f) Grimster, N. P.; Gauntlett, C.; Godfrey, C. R. A.; Gaunt, M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 3125; (g) Capito, E.; Brown, J. M.; Ricci, A. *Chem. Commun.* **2005**, 1854 For recent examples of Pd-catalyzed intermolecular arylations of nitrogen heterocycles, see: (h) Review: Miura, M.; Nomura, M. *Top. Curr. Chem.* **2002**, *219*, 211; (i) Park, C.-H.; Ryabova, V.; Seregin, I. V.; Sromek, A. W.; Gevorgyan, V. *Org. Lett.* **2004**, *6*, 1159; (j) Rieth, R. D.; Mankad, N. P.; Calimano, E.; Sadighi, J. P. *Org. Lett.* **2004**, *6*, 3981; (k) Gauthier, D. R.; Limanto, J.; Devine, P. N.; Desmond, R. A.; Szumigala, R. H.; Foster, B. S.; Volante, R. P. *J. Org. Chem.* **2005**, *70*, 5938; (l) Campeau, L.-C.; Rousseaux, S.; Fagnou, K. *J. Am. Chem. Soc.* **2005**, *127*, 18020; (m) Parisien, M.; Valette, D.; Fagnou, K. *J. Org. Chem.* **2005**, *70*, 7578; (n) Stuart, D. R.; Alsabeh, P.; Kuhn, M.; Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 18326; (o) Deprez, N. R.; Kalyani, D.; Krause, A.; Sanford, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 4972; (p) See Ref. 6e. (q) Phipps, R. J.; Grimster, N. P.; Gaunt, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 8172.
9. (a) Liu, Y.; Gribble, G. W. *Tetrahedron Lett.* **2000**, *41*, 8717; (b) Liu, Y.; Gribble, G. W. *Tetrahedron Lett.* **2002**, *43*, 7135 For $Pd(OAc)_2$-catalyzed regioselective arylation of indoles with arylsiloxane: (c) Liang, Z.; Yao, B.; Zhang, Y. *Org. Lett.* **2010**, *12*, 3185; (d) Regioselective oxidative arylation of indoles: Potqvathri, S.; Pereira, K. C.; Gorelsky, S. I.; Pike, A.; LeBris, A. P.; DeBoef, B. *J. Am. Chem. Soc.* **2010**, *132*, 14676; (e) Palladium-catalyzed cross-coupling of 2-indolylsilanolates: Denmark, S.; Baird, J. D.; Regens, C. S. *J. Org. Chem.* **2008**, *73*, 1440 For other syntheses of 2,3-diarylindoles, see: (f) Joucla, L.; Batail, N.; Djakovitch, L. *Adv. Synth. Catal.* **2010**, *352*, 2929; (g) Scribner, A.; Moore, J. A., III; Ouvry, G.; Fisher, M.; Wyvratt, M.; Leavitt, P.; Liberator, P.; Gurnett, A.; Brown, C.; Mathew, J.; Thompson, D.; Schmatz, D.; Biftu, T. *Bioorg. Med. Chem.* **2009**, *19*, 1517; (h) Zhang, H.-C.; Ye, H.; White, K. B.; Maryanoff, B. E. *Tetrahedron Lett.* **2001**, *42*, 4751.
10. Ibad, M. F.; Hussain, M.; Abid, O.-U.-R.; Ali, A.; Ullah, I.; Zinad, D. S.; Langer, P. *Synlett* **2010**, 411.
11. Hussain, M.; Dang, T. T.; Langer, P. *Synlett* **2009**, 1822.
12. CCDC 941362–941366 contains all crystallographic details of this publication and is available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or can be ordered from the following address: Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ; Fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk