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# Selective Synthesis of *N*-Unsubstituted and *N*-Aryl Indoles by the Reaction of Arynes with Azirines

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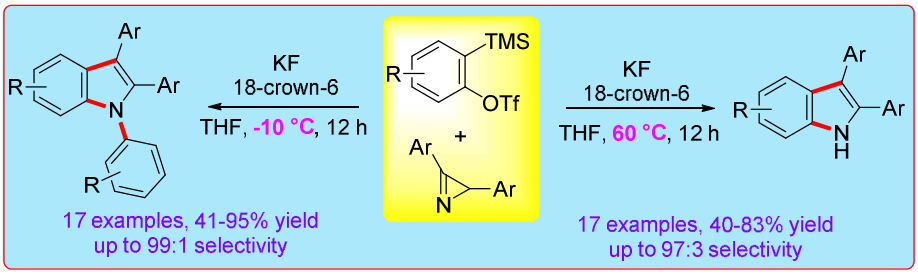


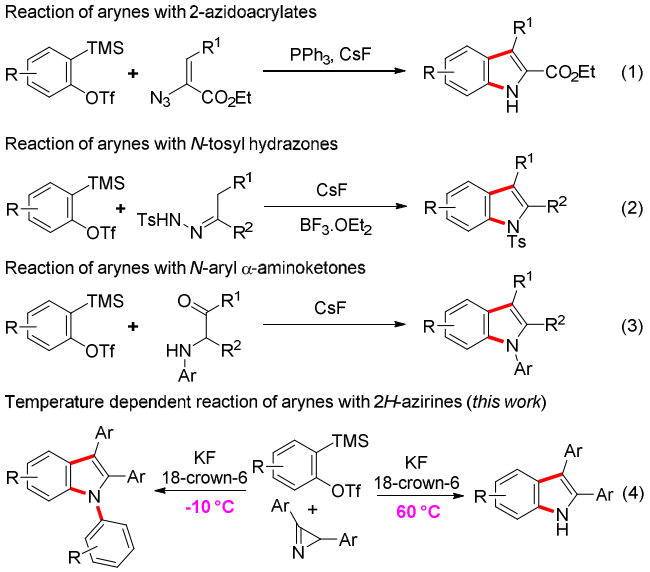

**ABSTRACT:** The transition-metal-free and temperature dependent highly selective reaction of arynes with 2*H*-azirines allowing the synthesis of either *N*-unsubstituted or *N*-aryl indoles has been developed. At 60 °C, arynes generated from 2-(trimethylsilyl)aryl triflates smoothly insert into 2*H*-azirines to form 2,3-diaryl indoles with high selectivity. Interestingly, when the reaction was performed at -10 °C, the selectivity was switched to the formation of 1,2,3-triaryl indoles in good yields.

The indole nucleus is a structural motif present in numerous biologically active natural products, pharmaceutical compounds and agrochemicals.[1] Consequently, development of straightforward and flexible synthetic routes for the construction of functionalized indoles is of great importance.[2] Among the various routes to indoles, the Fischer indole synthesis stands as one of the most widely used procedure.[3] Additionally, the annulation of 2-alkynyl anilines under metal-catalysis,[4] cyclization of 2-halogenated anilines with alkynes,[5] reductive annulation of 2-

nitro aromatics[6] etc. offers convenient route to achieve indoles. Methods employing transition-metal-catalyzed C-H bond functionalization reactions has emerged as one of the convenient and efficient protocols for the synthesis of indoles.[7] Furthermore, transition-metal-free transformations are also uncovered recently for the synthesis of indole derivatives.[8]

The transition-metal-free synthesis of indoles employing arynes[9] as the aryl source has been a convenient method, which obviates the use of hydrazines/amines as the starting materials. The use of 2-(trimethylsilyl)aryl triflate precursor in the presence of fluoride source allows the mild method for aryne generation.[10] In 2010, Wang and co-workers demonstrated the synthesis of 2,3-disubstituted indoles from arynes and 2-azidoacrylates (Scheme 1, eq 1).[11] In addition, Greaney and co-workers used *N*-tosyl hydrazones as the coupling partner for arynes resulting in the synthesis of *N*-tosyl indoles via the benzyne Fischer indole reaction (eq 2).[12] Recently, Zhu and co-workers engaged arynes in the Bischler-Möhlau synthesis of indoles, where arynes undergo an insertion-cyclization sequence with *N*-aryl α-aminoketones (eq 3).[13] Notably, a common method for the highly selective synthesis of both *N*-unsubstituted as well as *N*-aryl indoles using aryne chemistry has not been reported. Herein, we report the transition-metal-free and highly selective synthesis of both *N*-unsubstituted and *N*-aryl indoles by the reaction of arynes with 2*H*-azirines, and importantly, the product selectivity depends on the temperature used. When the reaction was carried out at -10 °C, *N*-aryl indoles are formed in high yields. Gratifyingly, when the reaction was performed at 60 °C, 2,3-diaryl *N*-unprotected indoles are formed in moderate to good yields and excellent selectivity. It may be noted in this context that the reaction of 2,3-diphenyl-1-azirine with aryne generated by the thermal decomposition of benzene diazonium 2-carboxylate leading to the mixture of 2,3-diphenyl indole and 1,2,3-triphenyl indole was reported by the Nair group as early as 1975.[14] This seminal work also

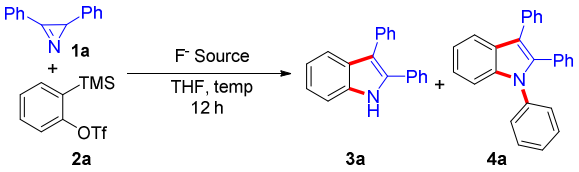
demonstrates the mechanism for the formation of *N*-unsubstituted and *N*-aryl indoles by the reaction of arynes with azirines.




**Scheme 1.** Synthesis of Indoles via Arynes

Against the literature backdrop and given the importance of functionalized indoles in organic synthesis, the present study was initiated by treating 2,3-diphenyl-1-azirine **1a** with the benzyne generated from the 2-(trimethylsilyl)aryl triflate precursor **2a** using KF in presence of 18-crown-6 as additive in THF at 30 °C. Under these conditions, the 2,3-diaryl indole **3a** was formed in 40% yield and 1,2,3-triaryl indole **4a** was formed in 21% yield in 54:46 ratio (Table 1, entry 1). Interestingly, when the reaction was performed at 60 °C, **3a** was isolated in 65% yield and 97:3 selectivity (entry 2). Under this condition, only traces of **4a** was formed. The use of other fluoride sources such as CsF and tetrabutyl ammonium fluoride (TBAF) did not improve the yield of **3a** and **4a** (entries 3,4). When the reaction was carried out at -10 °C and warmed to 30 °C, a complete switching in selectivity from **3a** to **4a** was observed (98:2) and **4a** was isolated in 76% yield. Finally, the yield of **4a** was improved to 83% when the reaction was done at -10 °C (entry 6).[15]

**Table 1.** Optimization of the reaction conditions[a]

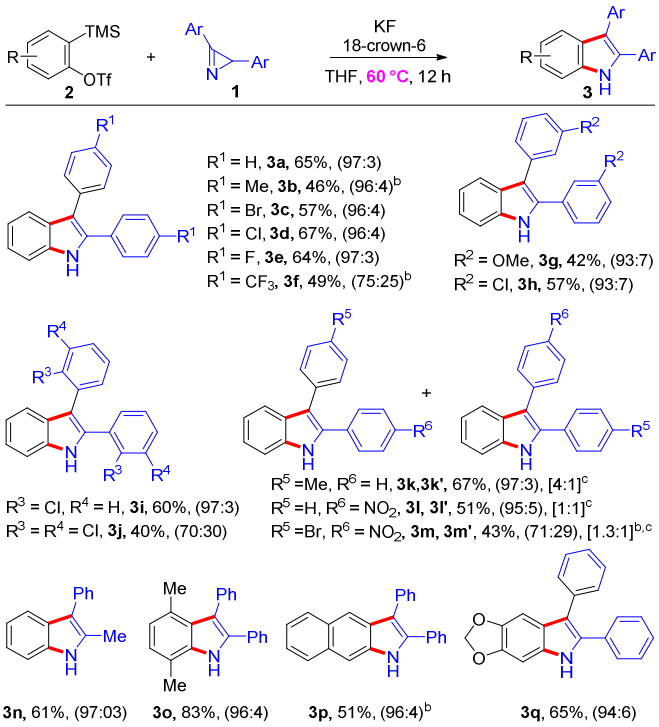



| entry | fluoride source | temp (°C) | yield of **3a** (%)[b] | yield of **4a** (%)[b] | **3a:4a**[c] |
|---|---|---|---|---|---|
| 1 | KF/18-crown-6 | 30 | 40 | 21 | 54:46 |
| *2*[d] | *KF/18-crown-6* | *60* | *65* | *<5* | *97:3* |
| 3[e] | CsF | 60 | 57 | <5 | 83:17 |
| 4 | TBAF.3H$_2$O | 60 | <5 | <5 | ND |
| 5[f] | KF/18-crown-6 | -10 to 30 | <5 | 76 | 2:98 |
| *6*[f] | *KF/18-crown-6* | *-10* | *<5* | *83* | *1:99* |

[a] General conditions: **1a** (0.25 mmol), **2a** (0.30 mmol), KF (2.4 equiv), 18- crown-6 (2.4 equiv), THF (1.0 mL), for the indicated temperature and 12 h. [b] Yield of the isolated products are given. [c] Selectivity was determined using GC analysis of the crude reaction mixture. [d] Reaction performed using 1.8 equiv of **2a** and 3.6 equiv of KF/18-crown-6 and 6.0 mL THF. [e] Reaction performed using 1.0 mL $CH_3CN$. [f] Reaction carried out using 3.0 equiv of **2a** and 6.0 equiv of KF/18-crown-6 and 1.0 mL THF.

After optimizing the reaction conditions for the selective synthesis of *N*-unsubstituted and *N*-aryl indoles, we then examined the substrate scope of both transformations. First, we evaluated the scope of the synthesis of N-H indoles (Scheme 2). A series of symmetrical 2*H*-azirines bearing electron-releasing and -withdrawing groups at the 4-position of the aryl moiety of **1** are well tolerated at 60 °C leading to the selective synthesis of 2,3-diaryl indoles in moderate to good yield and good selectivity (**3a-3f**). Notably, in the case of 4-$CF_3$ substituted 2*H*-azirine, the selectivity was moderate only. The structure of **3f** was further confirmed by single-crystal X-ray analysis.[16] Moreover, the substitution at the 2-position, 1-position as well as disubstitution on the 2,3-diaryl moiety of **1** did not affect the aryne reactivity and furnished the desired products in moderate yield and high selectivity (**3g-3j**). As expected, the unsymmetrical 2*H*-azirines afforded the inseparable mixture of regioisomers in moderate to good yield (**3k-3m**). Interestingly, unsymmetrical 2-methyl-3-phenyl-2*H*-azirine afforded the single regioisomer **3n** in 61% yield

and 97:3 selectivity. Additionally, symmetrical arynes generated from the corresponding precursors readily underwent smooth reaction with 2*H*-azirine **1a** to furnish the N-H indoles in moderate to good yields and high selectivity (**3o-3q**).

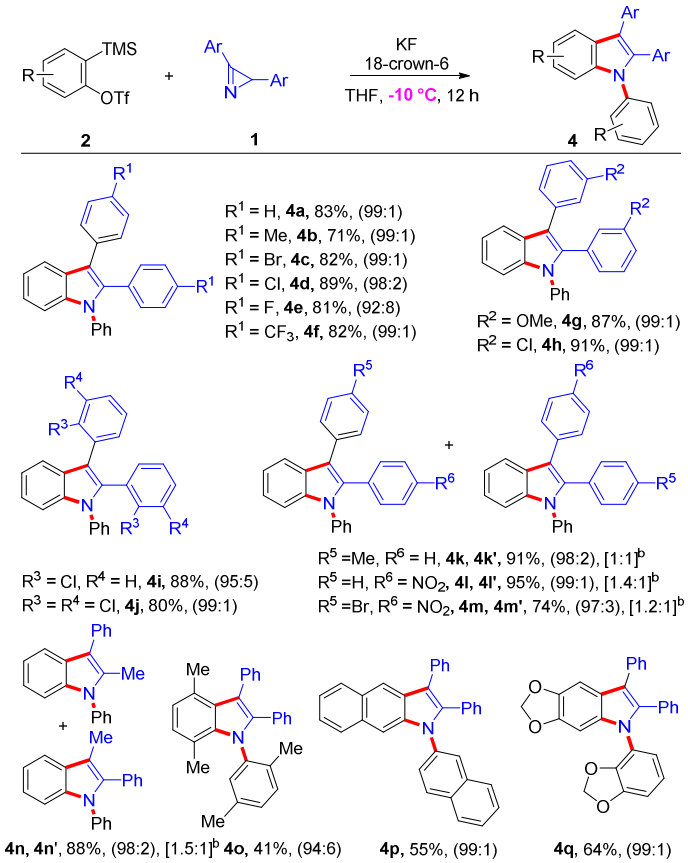



[a] General conditions: **1** (0.50 mmol), **2** (0.90 mmol), KF (1.80 mmol), 18-crown-6 (1.80 mmol), THF (12.0 mL), 60 °C, 12 h. Yields of the isolated products are given. Selectivity determined by GC analysis of crude reaction mixture is given in parentheses. [b] Reaction run on 0.25 mmol scale. [c] Regioisomer ratio determined by GC analysis.

**Scheme 2.** Substrate Scope for the Synthesis of *N*-Unsubstituted Indoles

With this result in hand, we then focused our attention on the synthesis of 1,2,3-trisubstituted indoles (Scheme 3). As in the case of reactions performed at 60 °C for the selective synthesis of N-H indoles, the experiments carried out at -10 °C also showed good functional group compatibility and high selectivity towards the synthesis of trisubstituted indoles. A wide variety of symmetrical 2*H*-azirines with different substitution pattern readily underwent efficient aryne reactions leading to the synthesis of 1,2,3-triaryl indoles in good yields (>71% in all cases)

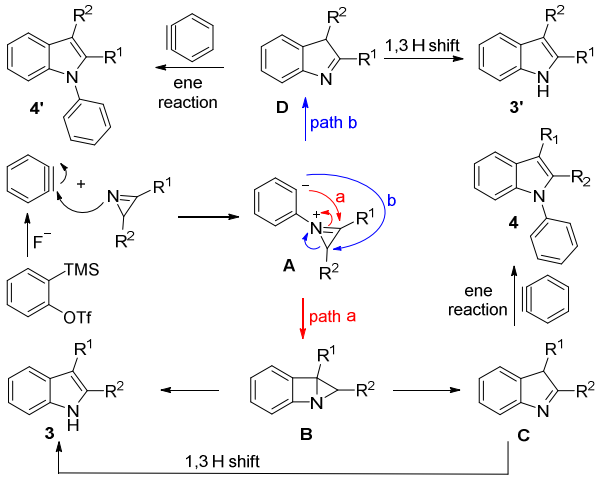
and excellent selectivity (>92:8 in all cases) (**4a-4j**). In the case of **4h**, the structure was confirmed by single-crystal X-ray analysis.[16] Moreover, the reaction of arynes with unsymmetrical 2*H*-azirines at -10 °C furnished the regioisomeric mixture of 1,2,3-triaryl indoles, where the selectivity over the N-H indoles are excellent in all cases (**4k-4m**). In contrast to the reaction of 2-methyl-3-phenyl-2*H*-azirine with aryne at 60 °C, the reaction at -10 °C afforded regioisomeric mixture of products (1.5:1) **4n** and **4n'** in 88% yield. Furthermore, the variation of aryne moiety was also feasible, leading to the formation of the corresponding trisubstituted indoles in moderate to good yield and high selectivity thus further expanding the scope of this aryne reaction (**4o-4q**).



[a] General conditions: **1** (0.25 mmol), **2** (0.75 mmol), KF (1.5 mmol), 18-crown-6 (1.5 mmol), THF (1.0 mL), -10 °C, 12 h. Yields of the isolated products are given. Selectivity was determined by GC analysis of crude reaction mixture is given in parentheses. [b] Regioisomer ratio determined by GC analysis.

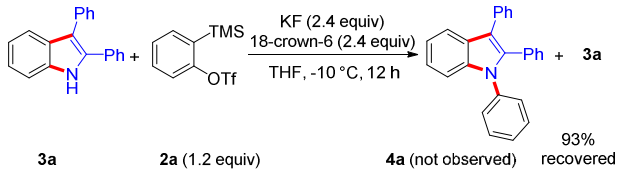
**Scheme 3.** Substrate Scope for Synthesis of *N*-aryl Indoles[a]

Considering the mixture of regioisomers obtained in the reaction of arynes with unsymmetrical 2*H*-azirines, a tentative mechanism of this reaction is showed in Scheme 4. The nucleophilic addition of 2*H*-azirines onto arynes generate the 1,4 zwitterionic intermediate **A**.[17,18] The zwitterion **A** could cyclize in two pathways. In path a, the aryl anion adds to the C=N bond (1,2-addition) to generate the intermediate **B**. A 1,2-hydrogen shift to nitrogen can result in the formation of **3**. Alternatively, a 1,2-hydrogen shift to carbon can generate the intermediate **C**, which can undergo another 1,3 hydrogen shift to afford **3**.[19] An ene reaction of **C** with another molecule of aryne can furnish **4**. In path b, the aryl anion adds to carbon attached to $R^2$ (breaking of C-N bond) to generate the intermediate **D**. A 1,3-hydrogen shift on **D** can afford the regioisomer **3'**. Moreover, the ene reaction of **D** with another molecule of aryne can result in the formation of *N*-aryl indole **4'**.



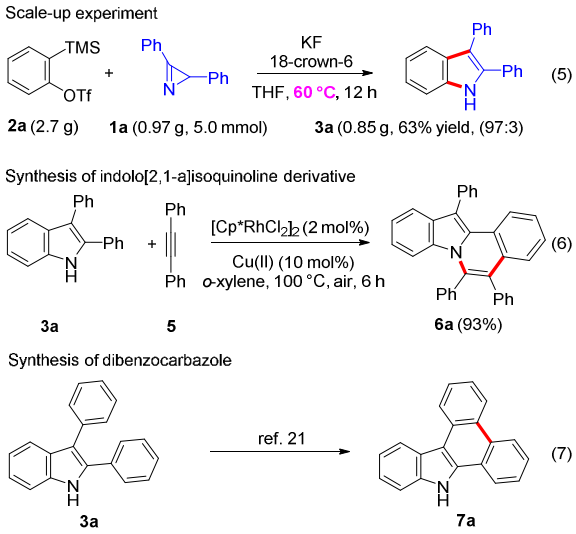

**Scheme 4.** Proposed Mechanism of the Reaction

Treatment of the N-H indole **3a** with excess aryne at -10 °C did not afford the *N*-aryl indole **4a** (Scheme 5). This experiment rules out the possibility of initial formation of **3a** in the reaction of **1a** and **2a** for the synthesis of **4a**. This also sheds light on the mechanism proposed in Scheme 4.




**Scheme 5.** Attempted Reaction of **3a** with Arynes

To demonstrate the synthetic utility of the reaction, a scale-up experiment was performed. Carrying out the reaction in a 5.0 mmol scale of **1a** afforded **3a** in 63% yield and 97:3 selectivity indicating the practical nature of the reaction (Scheme 6, eq 5). Reaction of **3a** with alkyne **5** under Rh(III)-catalysis following the procedure of Miura, Satoh and co-workers[20] with a minor modification afforded the indolo[2,1-a]isoquinoline derivative **6a** in 93% yield (eq 6). Moreover, **3a** could easily be transformed to the dibenzocarbazole derivative **7a** via dehydrogenative coupling reaction (eq 7).[21] Compounds **6a** and **7a** are nitrogen-doped conjugated systems (π-expanded) having potential organic semiconductor applications.




**Scheme 6.** Synthetic Utility of the Method

In conclusion, we have demonstrated the highly selective and transition-metal-free reaction of arynes with 2*H*-azirines leading to the synthesis of either *N*-unsubstituted or *N*-aryl indoles. The reaction of arynes with 2*H*-azirines at 60 °C afforded 2,3-diaryl indoles. Interestingly, the selectivity was switched to the formation of 1,2,3-triaryl indoles when the reaction was performed at -10 °C. Both reactions took place with high selectivity and broad substrate scope.

## Experimental Section

**General Information:** Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. Reaction temperatures are reported as the temperature of the bath surrounding the reaction vessel. 30 °C corresponds to the room temperature of the lab, when the experiments were carried out. THF was freshly purified by distillation over Na-benzophenone and was transferred under argon. 18-Crown-6 was recrystallized from dry $CH_3CN$ and KF was dried by heating at 110 °C for 12 h and left to cool under argon and stored in glove box. The 2(trimethylsilyl)phenyl trifluoromethane sulfonate **2a** and the other symmetric and unsymmetric aryne precursors were synthesized following literature procedure.[22] The azirines used in this work were prepared from the corresponding diaryl 1,2-diones following the literature procedure.[23] Melting points were determined with a melting apparatus. $^{1}H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ as solvent. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). HRMS measurements were carried out using ESI method and ion-trap mass analyzer. Infrared (IR) spectra were recorded on a FT-IR spectrometer as thin films using NaCl plates.

**General Procedure for the synthesis of *N*-Unsubstituted indoles**

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added 18-crown-6 (0.475 g, 1.8 mmol), KF (0.105 g, 1.8 mmol) inside the glove box. Then the corresponding 2*H*-azirine **1** (0.5 mmol) was added outside the glovebox. Then the mixture was dissolved in 12.0 mL of THF and the resultant reaction mixture was kept stirring at 30 °C for 5 min. To the stirring solution was added aryne precursor **2** (0.90 mmol). Then the reaction mixture was immediately placed in a preheated oil bath at 60 °C. When TLC control showed the completion of the reaction (typically after 12 h), the solvent was evaporated and subsequently the crude residue was purified by flash column chromatography on silica gel (using Pet. ether-EtOAc) to afford the corresponding *N*-unsubstituted indoles **3** in moderate to good yields. Selectivity ratio was determined by GC analysis of crude reaction mixture.

**2,3-Diphenyl-1*H*-indole (3a)**[24]**:** (yellow solid, 0.087 g, 65%, 97:3). $R_f$ (Pet. ether /EtOAc = 95/05): 0.35; Melting point: 109-111 °C; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.22 (bs, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.48 -7.39 (m, 6H), 7.35 -7.26 (m, 5H), 7.23-7.13 (m, 2H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 136.0, 135.2, 134.2, 132.8, 130.3, 128.9, 128.8, 128.6, 128.3, 127.8, 126.3, 122.8, 120.5, 119.8, 115.1, 111.1. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{20}H_{16}N$: 270.1277, found: 270.1278. **FTIR (cm$^{-1}$)**: 3679, 3458, 3415, 3060, 3018, 1722, 1670, 1598, 1496, 1449, 1319, 1217, 1031, 764, 702.

**2,3-Di-*p*-tolyl-1*H*-indole (3b)**[25]**:** (pale sticky yellow liquid, 0.034 g, 46%, 96:4, reaction performed on a 0.25 mmol scale of **1b**). $R_f$ (Pet. ether /EtOAc = 95/05): 0.35; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.19 (bs, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.45-7.37 (m, 5H), 7.30 -7.17 (m, 6H), 2.46 (s, 3H), 2.41 (s, 3H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 137.6, 135.9, 135.8, 134.2, 132.3, 130.1, 130.0, 129.5, 129.4, 129.1, 128.1, 122.6, 120.4, 119.8, 114.7, 110.9, 21.4. **HRMS (ESI)**

calculated $[M+H]^+$ for $C_{22}H_{20}N$: 298.1590, found: 298.1585. **FTIR ($cm^{-1}$)**: 3463, 3018, 1605, 1582, 1453, 1326, 1248, 1115, 1043, 930, 821, 772.

**2,3-Bis(4-bromophenyl)-1*H*-indole (3c)[24]:** (yellow solid, 0.122 g, 57%, 96:4). $R_f$ (Pet. ether /EtOAc = 95/05): 0.24; Melting point: 151-153 °C; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.23 (bs, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.55-7.44 (m, 5H), 7.32-7.28 (m, 5H), 7.20 (t, *J* = 7.4 Hz, 1H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 136.1, 133.8, 133.2, 132.2, 132.0, 131.8, 131.4, 129.8, 128.5, 123.4, 122.2, 121.0, 120.6, 119.6, 114.4, 111.2. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{20}H_{14}NBr_2$: 425.9488, found: 425.9484. **FTIR ($cm^{-1}$)**: 3458, 3018, 1587, 1544, 1499, 1453, 1392, 1312, 1215, 1070, 996, 772.

**2,3-Bis(4-chlorophenyl)-1*H*-indole (3d)[25]:** (pale yellow solid, 0.114 g, 67%, 96:4). $R_f$ (Pet. ether /EtOAc = 95/05): 0.25; Melting point: 129-131 °C; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.24 (bs, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.41 -7.29 (m, 9H), 7.23 -7.20 (m, 1H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 136.1, 134.0, 133.4, 133.2, 132.4, 131.4, 131.0, 129.5, 129.2, 129.0, 128.5, 123.3, 120.9, 119.6, 114.3, 111.2. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{20}H_{14}NCl_2$: 338.0498, found: 338.0500. **FTIR ($cm^{-1}$)**: 3450, 3058, 1546, 1482, 1432, 1328, 1296, 1215, 1014, 966, 831, 769.

**2,3-Bis(4-fluorophenyl)-1*H*-indole (3e)[24]:** (pale yellow solid, 0.098 g, 64%, 97:3). $R_f$ (Pet. ether /EtOAc = 95/05): 0.28; Melting point: 130-132 °C; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.21 (bs, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.47-7.38 (m, 5H), 7.31 -7.27 (m, 1H), 7.21 -7.18 (m, 1H), 7.13-7.04 (m, 4H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 162.5 (d, *J* = 248.2 Hz), 161.8 (d, *J* = 246.0 Hz), 135.9, 133.4, 131.7 (d, *J* = 7.8 Hz), 130.9 (d, *J* = 3.4 Hz), 130.1 (d, *J* = 8.5 Hz), 128.8, 123.1, 120.8, 119.6, 116.0 (d, *J* = 21.9 Hz), 115.7 (d, *J* = 21.5 Hz), 114.2, 111.1. **HRMS (ESI)**

calculated $[M+H]^+$ for $C_{20}H_{14}NF_2$: 306.1089, found: 306.1083. **FTIR (cm$^{-1}$)**: 3460, 3018, 1651, 1560, 1494, 1436, 1328, 1218, 1096, 838, 772.

**2,3-Bis(4-(trifluoromethyl)phenyl)-1*H*-indole (3f):** (yellow solid, 0.099 g, 49%, 75:25, reaction performed on a 0.25 mmol scale of **1f**). $R_f$ (Pet. ether /EtOAc = 95/05): 0.27; Melting point: 130-132 °C; **$^1$H NMR (400 MHz, CDCl$_3$)** δ 8.38 (s, 1H), 7.68-7.66 (m, 3H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.55-7.49 (m, 5H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H). **$^{13}$C NMR (100 MHz, CDCl$_3$)** δ 138.6, 136.3, 135.9, 133.2, 130.4, 128.5, 128.4, 126.1 (q, *J* = 3.7 Hz), 125.9 (q, *J* = 3.5 Hz), 123.9, 121.3, 121.1, 119.8, 118.7, 115.2, 111.4. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{22}H_{14}NF_6$: 406.1025, found: 406.1024. **FTIR (cm$^{-1}$)**: 3457, 1674, 1494, 1323, 1216, 1125, 1066, 966, 845, 768.

**2,3-Bis(3-methoxyphenyl)-1*H*-indole (3g)[26]:** (yellow viscous liquid, 0.069 g, 42%, 97:3). $R_f$ (Pet. ether /EtOAc = 95/05): 0.14; **$^1$H NMR (400 MHz, CDCl$_3$)** δ 8.32 (bs, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.29-7.24 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.08-7.05 (m, 3H), 7.00 (s, 1H), 6.90-6.85 (m, 2H), 3.78 (s, 3H), 3.69 (s, 3H). **$^{13}$C NMR (100 MHz, CDCl$_3$)** δ 159.8, 159.7, 136.6, 135.9, 134.1, 134.0, 129.8, 129.6, 128.8, 122.9, 122.9, 120.6, 120.5, 119.8, 115.6, 115.2, 113.8, 113.6, 112.3, 111.1, 55.3, 55.2. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{22}H_{20}O_2N$: 330.1489, found: 330.1486. **FTIR (cm$^{-1}$)**: 3459, 3017, 1603, 1583, 1482, 1430, 1284, 1216, 1046, 771, 668.

**2,3-Bis(3-chlorophenyl)-1*H*-indole (3h)[26]:** (pale sticky yellow liquid, 0.097 g, 57%, 93:7). $R_f$ (Pet. ether /EtOAc = 95/05): 0.28; **$^1$H NMR (400 MHz, CDCl$_3$)** δ 8.27 (bs, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.49-7.44 (m, 3H), 7.33 -7.21 (m, 8H). **$^{13}$C NMR (100 MHz, CDCl$_3$)** δ 136.7, 136.1, 134.8, 134.5, 134.2, 133.0, 130.2, 130.1, 130.0, 128.5, 128.4, 128.1, 127.9, 126.8, 126.7, 123.5,

121.0, 119.7, 114.6, 111.2. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{20}H_{14}NCl_2$: 338.0498, found: 338.0503. **FTIR ($cm^{-1}$)**: 3457, 3019, 1597, 1487, 1328, 1217, 1077, 928, 771, 699.

**2,3-Bis(2-chlorophenyl)-1*H*-indole (3i):** (yellow solid, 0.101 g, 60%, 97:3). $R_f$ (Pet. ether /EtOAc = 95/05): 0.34; Melting point: 129-131 °C; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.55 (bs, 1H), 7.52-7.45 (m, 4H), 7.34-7.11 (m, 8H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 135.5, 134.8, 133.9, 133.3, 133.1, 132.8, 132.7, 131.5, 130.3, 129.9, 129.6, 128.4, 127.8, 126.9, 126.7, 123.0, 120.4, 120.3, 114.7, 111.2. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{20}H_{14}NCl_2$: 338.0498, found: 338.0496. **FTIR ($cm^{-1}$)**: 3457, 3060, 3010, 1596, 1489, 1330, 1244, 1122, 1063, 1033, 969, 754.

**2,3-Bis(3,4-dichlorophenyl)-1*H*-indole (3j)[27]:** (sticky yellow liquid, 0.081 g, 40%, 70:30). $R_f$ (Pet. ether /EtOAc = 95/05): 0.28; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.33 (bs, 1H), 7.66 (d, $J$ = 8.0 Hz, 1H), 7.59 (s, 2H), 7.50-7.43 (m, 3H), 7.36 -7.30 (m, 2H), 7.23-7.21 (m, 2H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 136.1, 134.7, 133.3, 132.9, 132.4, 132.2, 131.7, 131.0, 130.9, 130.8, 129.5, 128.2, 127.8, 123.9, 121.4, 119.5, 114.6, 113.9, 111.4. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{20}H_{12}NCl_4$: 405.9718, found: 405.9723. **FTIR ($cm^{-1}$)**: 3453, 3019, 1648, 1595, 1469, 1377, 1215, 1134, 1030, 928, 883, 757.

**3-Phenyl-2-(*p*-tolyl)-1*H*-indole (3k) and 2-Phenyl-3-(*p*-tolyl)-1*H*-indole (3k')[28]:** (yellow viscous oil, 0.095 g, 67%, regioisomer ratio: 4:1, selectivity: 97:3). $R_f$ (Pet. ether /EtOAc = 95/05): 0.29; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.20 (bs, 1H), 7.71 (d, $J$ = 8.0 Hz, 1H), 7.47-7.14 (m, 12H), 2.43 (s, 3H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 136.0, 135.9, 134.0, 133.0, 132.1, 130.1, 129.4, 128.8, 128.3, 127.7, 126.3, 122.8, 120.5, 119.9, 111.0, 21.4. ***Representative peaks of Minor Isomer*: $^1$H NMR (400 MHz, $CDCl_3$)** δ 2.38 (s). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 130.3, 129.5, 129.0, 128.6, 128.2, 122.7, 119.7, 115.1. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{21}H_{18}N$:

284.1434, found: 284.1436. **FTIR (cm$^{-1}$)**: 3460, 3018, 1602, 1514, 1452, 1327, 1043, 929, 771, 697.

**2-(4-Nitrophenyl)-3-phenyl-1*H*-indole (3l) and 3-(4-Nitrophenyl)-2-phenyl-1*H*-indole (3l')[25]:** (orange solid, 0.080 g, 51%, regioisomer ratio: 1:1, selectivity: 95:5). ***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.14; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.42-8.38 (m, 1H), 8.22 (d, *J* = 8.6 Hz, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 7.73-7.65 (m, 1H), 7.60-7.55 (m, 2H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.43-7.29 (m, 6H), 7.25-7.17 (m, 1H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 146.7, 146.0, 142.9, 139.3, 136.7, 136.1, 134.3, 132.0, 131.4, 130.4, 130.3, 129.2, 129.1, 128.9, 128.7, 128.6, 128.4, 127.9, 127.2, 124.2, 124.1, 123.4, 121.4, 121.2, 120.4, 119.2, 118.4, 113.0, 111.5, 111.4. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{20}H_{14}O_2N_2Na$: 337.0974, found: 337.0945. **FTIR (cm$^{-1}$)**: 3455, 3020, 1596, 1552, 1451, 1343, 1250, 1150, 1072, 855, 756.

**3-(4-Bromophenyl)-2-(4-nitrophenyl)-1*H*-indole (3m) and 2-(4-Bromophenyl)-3-(4-nitrophenyl)-1*H*-indole (3m'):** (red solid, 0.042 g, 43%, regioisomer ratio: 1.3:1, selectivity: 71:29, reaction performed on a 0.25 mmol scale of **1m**). ***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.14; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.53-8.51 (m, 1H), 8.26-8.18 (m, 2H), 7.64-7.48 (m, 6H), 7.39-7.24 (m, 4H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 146.8, 146.1, 138.9, 136.7, 134.7, 133.3, 132.4, 132.3, 130.5, 130.1, 128.5, 124.4, 124.3, 123.7, 122.9, 121.4, 120.0, 119.3, 116.9, 111.5. ***Representative peaks of Minor Isomer*: $^1$H NMR (400 MHz, $CDCl_3$)** δ 8.51 (bs). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 142.5, 136.2, 131.8, 121.5, 111.5. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{20}H_{14}O_2N_2Br$: 393.02332, found: 393.02335. **FTIR (cm$^{-1}$)**: 3393, 3061, 1658, 1513, 1451, 1343, 1247, 1109, 855, 754.

**2-Methyl-3-phenyl-1*H*-indole (3n)[24]:** (pale sticky yellow liquid, 0.104 g, 61%, 97:3). ***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.25; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.86 (bs, 1H), 7.79 (d, *J* = 7.3 Hz,

1H), 7.62-7.54 (m, 4H), 7.42 -7.34 (m, 2H), 7.27-7.20 (m, 2H), 2.52 (s, 3H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 135.5, 135.3, 131.6, 129.5, 128.6, 127.9, 125.9, 121.6, 120.1, 118.9, 114.5, 110.5, 12.6. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{15}H_{14}N$: 208.1121, found: 208.1118. **FTIR ($cm^{-1}$)**: 3464, 3058, 1618, 1562, 1495, 1330, 1255, 1188, 1019, 771.

**4,7-Dimethyl-2,3-diphenyl-1*H*-indole (3o):** (pale sticky yellow liquid, 0.124 g, 83%, 96:4). ***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.38; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.23 (bs, 1H), 7.50-7.41 (m, 7H), 7.36-7.27 (m, 3H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 7.1 Hz, 1H), 2.62 (s, 3H), 2.19 (s, 3H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 137.2, 135.2, 133.9, 133.0, 131.9, 129.6, 129.3, 128.8, 128.6, 127.9, 127.8, 127.3, 127.1, 126.8, 123.1, 122.1, 117.8, 117.1, 20.2, 16.5. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{22}H_{20}N$: 298.1590, found: 298.1587. **FTIR ($cm^{-1}$)**: 3316, 3058, 1659, 1599, 1477, 1317, 1217, 1072, 801, 766.

**2,3-Diphenyl-1*H*-benzo[*f*]indole (3p):** (pale yellow viscous liquid, 0.041 g, 51%, 96:4, reaction performed on a 0.25 mmol scale of **1p**). ***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.23; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.55 (bs, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.67-7.59 (m, 2H), 7.55-7.47 (m, 5H), 7.38-7.21 (m, 7H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 137.3, 132.9, 132.8, 132.4, 131.6, 130.2, 128.9, 128.7, 127.6, 127.3, 127.2, 125.6, 124.2, 123.4, 122.1, 118.1, 112.6. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{18}N$: 320.1434, found: 320.1432. **FTIR ($cm^{-1}$)**: 3459, 3018, 1602, 1494, 1370, 1320, 1216, 1067, 926, 765, 669.

**6,7-Diphenyl-5*H*-[1,3]dioxolo[4,5-*f*]indole (3q):** (brown solid, 0.102 g, 65%, 94:6). ***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.1; Melting point: 135-137 °C; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.13 (bs, 1H), 7.50-7.39 (m, 5H), 7.37 -7.28 (m, 5H), 7.08 (s, 1H), 6.91 (s, 1H), 5.97 (s, 2H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 145.5, 143.7, 135.3, 132.9, 131.0, 130.7, 130.2, 128.8, 128.7, 128.1, 127.8, 127.3, 126.4, 123.1, 115.5, 105.2, 102.8, 100.8, 98.4, 91.9. **HRMS (ESI)** calculated

[M+H] $^{+}$ for $C_{21}H_{16}O_2N$: 314.1176, found: 314.1170. **FTIR (cm$^{-1}$)**: 3460, 3018, 1602, 1502, 1485, 1437, 1284, 1216, 1064, 949, 770.

**General Procedure for the synthesis of *N*-Aryl Indoles**

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added 18-crown-6 (0.396 g, 1.5 mmol), KF (0.087 g, 1.5 mmol) inside the glove box. Then the corresponding 2*H*-azirine **1** (0.25 mmol) was added outside the glovebox. Then the mixture was dissolved in 1.0 mL of solvent. The resultant reaction mixture was cooled to -10 °C and kept stirring for 5 min. To the stirring solution was added aryne precursor **2** (0.75 mmol) and kept stirring at -10 °C for 12h. When TLC control showed the completion of the reaction (typically after 12 h), the reaction was quenched and the solvent was evaporated and subsequently the crude residue was purified by flash column chromatography on silica gel (using Pet. ether-EtOAc) to afford the corresponding *N*-aryl indole derivatives **4** in moderate to good yields. Selectivity ratio was determined by GC analysis of crude reaction mixture.

**1,2,3-Triphenyl-1*H*-indole (4a)[29]:** (white solid, 0.072 g, 83%, 99:1). $R_f$ (Pet. ether /EtOAc = 95/05): 0.75; Melting point: 184-186 °C; **$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.89 -7.87 (m, 1H), 7.46 -7.35 (m, 8H), 7.33 -7.26 (m, 5H), 7.22 -7.16 (m, 5H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 138.3, 138.1, 137.2, 135.1, 131.7, 131.3, 130.4, 129.2, 128.4, 128.0, 127.7, 127.5, 127.3, 126.1, 122.9, 121.0, 119.7, 116.9, 110.8. **HRMS (ESI)** calculated [M+H] $^{+}$ for $C_{26}H_{20}N$: 346.1590, found: 346.1589. **FTIR (cm$^{-1}$)**: 3018, 2925, 1598, 1547, 1495, 1450, 1371, 1219, 1073, 1025, 763.

**1-Phenyl-2,3-di-*p*-tolyl-1*H*-indole (4b)[29]:** (yellow solid, 0.066 g, 71%, 99:1). $R_f$ (Pet. ether /EtOAc = 95/05): 0.58; Melting point: 175-177 °C; **$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.88-7.85 (m, 1H), 7.45 -7.35 (m, 6H), 7.31-7.25 (m, 4H), 7.23 (d, $J$ = 7.8 Hz, 2H), 7.07-6.96 (m, 4H), 2.44

(s, 3H), 2.33(s, 3H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 138.5, 138.0, 137.1, 135.5, 132.2, 131.1, 130.2, 129.6, 129.2, 128.9, 128.8, 128.5, 127.9, 127.1, 122.6, 120.9, 119.7, 116.5, 114.6, 110.7, 21.4. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{28}H_{24}N$: 374.1903, found: 374.1901. **FTIR ($cm^{-1}$)**: 3017, 1596, 1499, 1369, 1217, 1103, 832, 771, 668.

**2,3-Bis(4-bromophenyl)-1-phenyl-1*H*-indole (4c)[29]:** (yellow solid, 0.103 g, 82%, 99:1). ***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.69; Melting point: 223-225 °C; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.44-7.40 (m, 2H), 7.38-7.29 (m, 4H), 7.27-7.22 (m, 6H), 6.95 (d, *J* = 8.3 Hz, 2H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 138.2, 137.8, 135.9, 133.8, 132.7, 131.9, 131.8, 131.5, 130.4, 129.5, 128.4, 127.7, 127.3, 123.4, 122.1, 121.4, 120.3, 119.5, 116.0, 111.0. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{26}H_{18}NBr_2$: 501.9801, found: 501.9791. **FTIR ($cm^{-1}$)**: 3045, 1592, 1545, 1452, 1370, 1243, 1167, 1068, 822, 771, 746.

**2,3-Bis(4-chlorophenyl)-1-phenyl-1*H*-indole (4d)[29]:** (white solid, 0.092 g, 89%, 98:2). ***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.73; Melting point: 200-202 °C; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.79 - 7.77 (m, 1H), 7.46 -7.24 (m, 12H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 138.2, 137.9, 135.9, 133.8, 133.4, 132.4, 132.1, 131.5, 129.9, 129.4, 128.8, 128.6, 128.4, 127.7, 127.4, 123.33, 121.4, 119.5, 116.0, 110.9. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{26}H_{18}NCl_2$: 414.0811, found: 414.0810. **FTIR ($cm^{-1}$)**: 3019, 1650, 1571, 1498, 1406, 1369, 1216, 1106, 1016, 837, 772.

**2,3-Bis(4-fluorophenyl)-1-phenyl-1*H*-indole (4e):** (yellow solid, 0.077 g, 81%, 92:8). ***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.55; Melting point: 148-150 °C; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.81 - 7.79 (m, 1H), 7.46 -7.36 (m, 6H), 7.32-7.26 (m, 4H), 7.12-7.07 (m, 4H), 6.93-6.88 (m, 2H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 162.2, (d, *J* = 248.3 Hz), 161.6 (d, *J* = 245.5 Hz), 138.0 (d, *J* = 5.4 Hz), 136.2, 132.9 (d, *J* = 8.9 Hz), 131.8 (d, *J* = 7.7 Hz), 130.8 (d, *J* = 3.2 Hz), 129.4, 128.4,

127.5, 123.1, 121.2, 119.5, 116.0, 115.5 (d, $J$ = 21.3 Hz), 115.3 (d, $J$ = 21.53 Hz), 110.9. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{26}H_{18}NF_2$: 382.1402, found: 382.1400. **FTIR (cm$^{-1}$)**: 3048, 1597, 1497, 1369, 1216, 1157, 1093, 841, 801, 772.

**1-Phenyl-2,3-bis(4-(trifluoromethyl)phenyl)-1*H*-indole (4f)[30]:** (pale yellow solid, 0.098 g, 82%, 99:1). $R_f$ (Pet. ether /EtOAc = 95/05): 0.69; Melting point: 168-170 °C; **$^1$H NMR (400 MHz, CDCl$_3$)** δ 7.82 (d, $J$ = 6.8 Hz, 1H), 7.65 (d, $J$ = 7.4 Hz, 2H), 7.50-7.37 (m, 8H), 7.34-7.29 (m, 2H), 7.26-7.22 (m, 4H). **$^{13}$C NMR (100 MHz, CDCl$_3$)** 138.5, 138.4, 137.6, 136.0, 135.0, 131.4, 130.5, 129.9, 129.6, 128.6, 128.4, 128.0, 127.2, 125.6 (q, $J$ = 3.6 Hz), 125.3 (q, $J$ = 3.4 Hz), 123.8, 123.2, 122.8, 121.7, 119.6, 116.6, 111.2. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{28}H_{18}NF_6$: 482.1338, found: 482.1337. **FTIR (cm$^{-1}$)**: 3020, 1610, 1495, 1365, 1219, 1119, 1019, 929, 850, 745, 668.

**2,3-Bis(3-methoxyphenyl)-1-phenyl-1*H*-indole (4g):** (yellow solid, 0.088 g, 87%, 99:1). $R_f$ (Pet. ether /EtOAc = 95/05): 0.37; Melting point: 123-125 °C; **$^1$H NMR (400 MHz, CDCl$_3$)** δ 7.86-7.83 (m, 1H), 7.42-7.39 (m, 2H), 7.35-7.32 (m, 2H), 7.28-7.22 (m, 5H), 7.07 (t, $J$ = 7.9 Hz, 1H), 7.01 (d, $J$ = 7.6 Hz, 1H), 6.97 (s, 1H), 6.82 (dd, $J_1$ = 8.2 Hz, $J_2$ = 1.9 Hz, 1H), 6.75-6.71 (m, 2H), 6.64 (s, 1H), 3.71 (s, 3H), 3.53 (s, 3H). **$^{13}$C NMR (100 MHz, CDCl$_3$)** δ 159.6, 159.1, 138.3, 138.0, 137.0, 136.4, 132.9, 129.4, 129.3, 129.0, 128.4, 127.6, 127.3, 123.9, 122.9, 122.8, 121.1, 119.8, 116.8, 116.2, 115.5, 113.9, 112.2, 110.8, 55.2, 55.1. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{28}H_{24}O_2N$: 406.1802, found: 406.1800. **FTIR (cm$^{-1}$)**: 3011, 2835, 1598, 1498, 1429, 1368, 1284, 1217, 1154, 1046, 756, 667.

**2,3-Bis(3-chlorophenyl)-1-phenyl-1*H*-indole (4h):** (white solid, 0.094 g, 91%, 99:1). $R_f$ (Pet. ether /EtOAc = 95/05): 0.63; Melting point: 159-161 °C; **$^1$H NMR (400 MHz, CDCl$_3$)** δ 7.83-7.81 (m, 1H), 7.48 -7.36 (m, 5H), 7.33-7.26 (m, 6H), 7.22-7.20 (m, 2H), 7.15-7.11 (m, 2H), 7.03

(d, *J* = 7.8 Hz, 1H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 138.1, 137.7, 136.6, 135.8, 134.3, 134.0, 133.2, 131.0, 130.1, 129.8, 129.4, 128.5, 128.3, 128.0, 127.8, 127.3, 126.5, 123.5, 121.5, 119.6, 116.1, 111.0. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{26}H_{18}NCl_2$: 414.0811, found: 414.0812. **FTIR ($cm^{-1}$)**: 3064, 1596, 1487, 1425, 1319, 1239, 1078, 997, 888, 758.

**2,3-Bis(2-chlorophenyl)-1-phenyl-1*H*-indole (4i):** (yellow solid, 0.091 g, 88%, 95:5). ***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.57; Melting point: 147-149 °C; **$^1$H NMR (400 MHz, $CDCl_3$)** 7.61-7.53 (m, 1H), 7.48-7.43 (m, 2H), 7.40-7.28 (m, 7H), 7.27-7.22 (m, 4H), 7.20-7.14 (m, 2H), 7.13-7.09 (m, 1H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 137.8, 137.3, 135.6, 135.4, 134.9, 133.7, 133.3, 131.4, 131.1, 129.9, 129.8, 129.4, 129.0, 128.5, 127.8, 127.3, 126.6, 126.1, 122.9, 120.8, 120.5, 116.1, 114.6, 110.8. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{26}H_{18}NCl_2$: 414.0811, found: 414.0809. **FTIR ($cm^{-1}$)**: 3059, 1596, 1499, 1435, 1320, 1216, 1121, 1062, 1032, 749.

**2,3-Bis(3,4-dichlorophenyl)-1-phenyl-1*H*-indole (4j):** (yellow solid, 0.097 g, 80%, 99:1). ***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.65; Melting point: 164-166 °C; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 7.4 Hz, 1H), 7.59 (s, 1H), 7.49-7.42 (m, 4H), 7.35-7.24 (m, 6H), 7.18 (s, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 138.2, 137.4, 134.9, 134.7, 132.7, 132.6, 132.5, 132.3, 131.7, 131.2, 130.7, 130.5, 130.4, 130.3, 129.7, 129.6, 128.3, 128.1, 126.9, 123.8, 121.7, 119.4, 117.5, 115.4, 111.1. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{26}H_{16}NCl_4$: 482.0031, found: 482.0035. **FTIR ($cm^{-1}$)**: 3061, 1594, 1498, 1451, 1375, 1258, 1215, 1110, 888, 757.

**1,2-Diphenyl-3-(*p*-tolyl)-1*H*-indole (4k) and 1,3-Diphenyl-2-(*p*-tolyl)-1*H*-indole (4k'):** (white solid, 0.082 g, 91%, regioisomer ratio: 1:1, selectivity: 98:2). ***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.64; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.83-7.81 (m, 2H), 7.41-7.11 (m, 30H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.28 (s, 3H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 138.4,

138.3, 138.0, 137.3, 137.2, 137.0, 135.6, 135.2, 132.0, 131.9, 131.3, 131.1, 130.4, 130.2, 129.2, 128.8, 128.7, 128.5, 128.4, 128.0, 127.8, 127.4, 127.2, 126.0, 122.8, 122.7, 120.9, 119.8, 119.6, 110.7, 21.4, 21.3. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{27}H_{22}N$: 360.17468, found: 360.17465. **FTIR ($cm^{-1}$)**: 3011, 1597, 1500, 1454, 1369, 1320, 1216, 1168, 1074, 1025, 827, 766, 699.

**2-(4-Nitrophenyl)-1,3-diphenyl-1*H*-indole (4l) and 3-(4-Nitrophenyl)-1,2-diphenyl-1*H*-indole (4l'):** (yellow viscous liquid, 0.093 g, 95%, regioisomer ratio: 1.4:1, selectivity: 99:1). $R_f$ (Pet. ether /EtOAc = 95/05): 0.46; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.20 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.7 Hz, 1H), 7.86-7.80 (m, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.47-7.20 (m, 13H), 7.12-7.10 (m, 1H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 146.6, 142.8, 138.8, 137.8, 137.6, 134.3, 134.1, 131.7, 130.9, 130.4, 129.7, 128.8, 128.4, 128.3, 127.8, 127.6, 126.9, 124.0, 123.3, 121.8, 120.6, 119.3, 114.6, 111.3, 111.0. ***Representative peaks of Minor Isomer*: $^{13}$C NMR (100 MHz, $CDCl_3$)** δ 145.8, 138.2, 131.2, 138.6, 129.4, 128.5, 127.9, 126.9, 123.8, 123.5, 121.6, 120.2, 119.1. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{26}H_{19}O_2N_2$: 391.1441, found: 391.1438. **FTIR ($cm^{-1}$)**: 3064, 1596, 1548, 1454, 1369, 1288, 1215, 1105, 910, 859, 777.

**3-(4-Bromophenyl)-2-(4-nitrophenyl)-1-phenyl-1*H*-indole (4m) and 2-(4-Bromophenyl)-3-(4-nitrophenyl)-1-phenyl-1*H*-indole (4m'):** (yellow solid, 0.087 g, 74%, regioisomer ratio: 1.2:1, selectivity: 97:3). $R_f$ (Pet. ether /EtOAc = 95/05): 0.46; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.24 (d, *J* = 8.7 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.84-7.76 (m, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.48-7.39 (m, 3H), 7.37-7.31 (m, 4H), 7.28-7.25 (m, 4H), 7.0 (d, *J* = 7.1 Hz, 1H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 146.7, 145.9, 138.3, 138.2, 137.5, 134.4, 133.1, 132.7, 131.8, 131.7, 130.5, 130.4, 129.9, 129.7, 127.2, 124.0, 123.7, 123.4, 122.7, 121.9, 121.7, 120.9, 119.2, 117.8, 111.3, 111.1. ***Representative peaks of Minor Isomer*: $^{13}$C NMR (100 MHz, $CDCl_3$)** δ 142.3, 138.6, 137.3, 137.2, 132.0, 131.9, 129.6, 128.3, 128.2, 128.0, 126.7, 124.2, 120.6, 119.8, 115.0, 114.6.

**HRMS (ESI)** calculated $[M+H]^+$ for $C_{26}H_{18}O_2N_2Br$: 469.0546, found: 469.0544. **FTIR ($cm^{-1}$)**: 1595, 1514, 1497, 1411, 1395, 1344, 1289, 1174, 1071, 860, 753.

**2-Methyl-1,3-diphenyl-1*H*-indole (4n)**[31] **and 3-Methyl-1,2-diphenyl-1*H*-indole (4n')**[32] (yellow solid, 0.062 g, 88%, regioisomer ratio: 1.5:1, selectivity: 98:2). $R_f$ (Pet. ether /EtOAc = 95/05): 0.50; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.70 -7.68 (m, 1H), 7.53 -7.49 (m, 2H), 7.37-7.33 (m, 4H), 7.24-7.20 (m, 6H), 7.18 (m, 1H), 2.44 (s, 3H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 138.8, 137.7, 135.6, 132.2, 129.8, 129.1, 128.3, 128.0, 127.4, 126.7, 122.6, 120.5, 119.0, 110.8, 110.2, 12.2. **$^1$H NMR (400 MHz, $CDCl_3$)** ***for minor isomer*** **δ:** 7.75-7.73 (m), 7.61-7.56 (m), 7.47-7.43 (m), 7.32-7.27 (m), 7.18-7.16 (m), 2.37 (s). **$^{13}$C NMR (100 MHz, $CDCl_3$)** ***for minor isomer*** δ 138.0, 137.0, 133.7, 130.7, 129.7, 128.7, 128.1, 127.2, 126.1, 120.8, 120.2, 118.8, 110.5, 9.7. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{21}H_{18}N$: 284.1434, found: 284.1433. **FTIR ($cm^{-1}$)**: 3057, 1597, 1499, 1397, 1247, 1177, 1074, 915, 794, 700.

**1-(2,5-Dimethylphenyl)-4,7-dimethyl-2,3-diphenyl-1*H*-indole (4o):** (yellow viscous liquid, 0.041 g, 41%, selectivity: 94:6). $R_f$ (Pet. ether /EtOAc = 95/05): 0.38; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.53-7.43 (m, 1H), 7.33-7.24 (m, 5H), 7.08-7.0 (m, 7H), 6.90-6.84 (m, 2H), 2.34 (s, 3H), 2.20 (s, 3H), 1.90 (s, 3H), 1.89 (s, 3H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 139.1, 138.7, 137.3, 135.3, 135.0, 132.5, 132.0, 131.8, 131.2, 129.7, 129.3, 129.0, 127.3, 127.1, 126.6, 126.3, 125.0, 122.0, 119.6, 117.8, 20.9, 20.8, 18.8, 17.3. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{30}H_{28}N$: 402.2216, found: 402.2213. **FTIR ($cm^{-1}$)**: 3006, 1647, 1507, 1414, 1352, 1285, 1113, 1033, 989, 842, 753.

**1,2,3-Triphenyl-1*H*-benzo[*f*]indole (4p)**[29]**:** (yellow viscous liquid, 0.054 g, 55%, selectivity: 99:1). $R_f$ (Pet. ether /EtOAc = 95/05): 0.49; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.33 (s, 1H), 8.0-7.83 (m, 7H), 7.59 -7.52 (m, 4H), 7.44 (t, $J$ = 7.6 Hz, 2H), 7.39 -7.33 (m, 3H), 7.25-7.16 (m,

4H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 147.1, 140.7, 139.0, 136.2, 134.9, 133.7, 132.2, 131.5, 131.2, 131.0, 130.5, 129.7, 129.6, 129.2, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.6, 126.8, 126.7, 126.5, 126.3, 124.2, 123.1, 117.3, 116.3, 106.1. **FTIR ($cm^{-1}$)**: 3020, 1660, 1596, 1502, 1443, 1383, 1216, 1110, 1061, 925, 862, 763.

**5-(Benzo[*d*][1,3]dioxol-4-yl)-6,7-diphenyl-5*H*-[1,3]dioxolo[4,5-*f*]indole (4q)[29]:** (brown solid, 0.069 g, 64%, selectivity: 99:1). ***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.27; Melting point: 184-186 °C; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.32-7.28 (m, 4H), 7.25-7.21 (m, 1H), 7.16-7.13 (m, 4H), 7.09-7.06 (m, 2H), 6.78-6.67 (m, 4H), 5.99 (s, 2H), 5.93 (s, 2H). **$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 148.1, 146.9, 145.5, 143.9, 136.1, 135.2, 133.7, 132.2, 131.8, 131.1, 130.2, 128.4, 128.0, 127.2, 126.0, 122.0, 121.4, 116.8, 109.4, 108.3, 101.8, 100.9, 98.2, 91.8. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{28}H_{20}O_4N$: 434.1387, found: 434.1380. **FTIR ($cm^{-1}$)**: 3019, 1602, 1489, 1464, 1334, 1291, 1180, 946, 879, 770, 700.

**5,6,12-Triphenylindolo[2,1-*a*]isoquinoline (6a)[33]:** To a 5 mL screw-capped test tube equipped with a magnetic stir bar, 2,3-diphenyl-1*H*-indole (3a, 30 mg, 0.1 mmol), 1,2-diphenylacetylene (5, 24 mg, 0.13 mmol, 1.2 equiv), $[(Cp^*RhCl_2)_2]$ (1.0 mg, 0.02 mmol, 2 mol%), $Cu(OAc)_2 \cdot H_2O$ (1.0 mg, 0.1 mmol, 10 mol%), and 1 mL *o*-xylene were added sequentially. The tube (not sealed) was immersed in an oil bath (100 °C) and stirred vigorously under air. When TLC control showed the completion of the reaction (after 6 h), the solvent was evaporated and subsequently the crude residue was purified by flash column chromatography on silica gel (using Pet. ether-EtOAc) to afford the corresponding indolo[2,1-a]isoquinoline derivative **6a** as a yellow solid (0.046 g, 93% yield). ***R*$_f$** (Pet. ether /EtOAc = 95/05): 0.54; Melting point: 193-195 °C; **$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.71 -7.63 (m, 4H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.41 (s, 5H), 7.31-7.17 (m, 9H), 6.90 (t, *J* = 7.8 Hz, 1H), 6.08 (d, *J* = 8.9 Hz, 1H). **$^{13}$C NMR (100**

**MHz, $CDCl_3$)** δ 137.0, 136.6, 136.1, 135.7, 132.0, 131.7, 131.3, 131.2, 131.0, 130.8, 130.7, 129.2, 128.8, 128.0, 127.4, 127.1, 126.9, 126.6, 126.2, 126.0, 124.6, 121.8, 120.9, 119.1, 114.6, 112.2. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{34}H_{24}N$: 446.1903, found: 446.1900. **FTIR ($cm^{-1}$)**: 3063, 1603, 1549, 1483, 1379, 1332, 1216, 1109, 1030, 924, 766, 670.

## Supporting Information

Crystallographic data of compounds **3f** and **4j**, Details on computational studies, and copies of $^1H$ and $^{13}C$ NMR spectra of all products, This material is available free of charge via the Internet at http://pubs.acs.org.

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