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Selective Synthesis of *N*-Unsubstituted and *N*-Arylindoles by the Reaction of Arynes with Azirines

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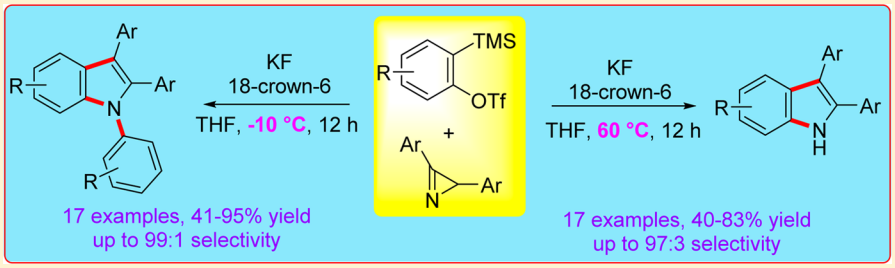
Supporting Information

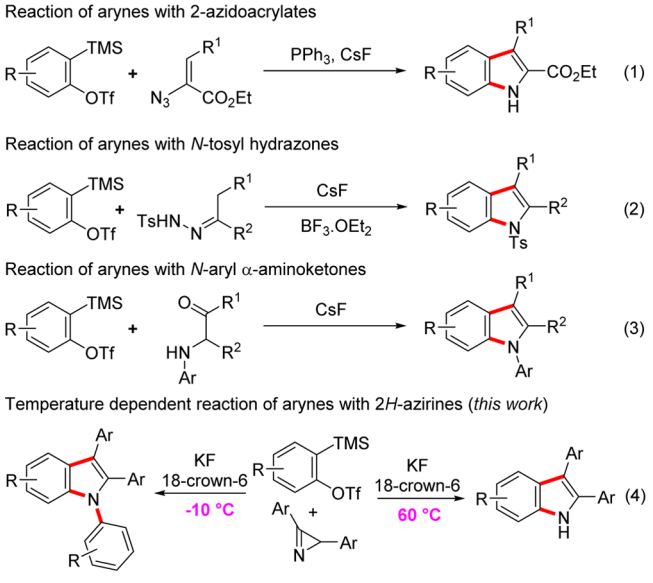


ABSTRACT: The transition-metal-free and temperature-dependent highly selective reaction of arynes with 2*H*-azirines allowing the synthesis of either *N*-unsubstituted or *N*-arylindoles has been developed. At 60 °C, arynes generated from 2-(trimethylsilyl)aryl triflates smoothly insert into 2*H*-azirines to form 2,3-diarylindoles with high selectivity. Interestingly, when the reaction was performed at −10 °C, the selectivity was switched to the formation of 1,2,3-triarylindoles 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 procedures.[3] Additionally, the annulation of 2-alkynylanilines under metal catalysis,[4] cyclization of 2-halogenated anilines with alkynes,[5] reductive annulation of 2-nitro aromatics,[6] etc. offer convenient routes to achieve indoles. Methods employing transition-metal-catalyzed C−H bond functionalization reactions have emerged as some of the most convenient and efficient protocols for the synthesis of indoles.[7] Furthermore, transition-metal-free transformations have also been developed 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 that 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 to proceed.[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*-tosylhydrazones as the coupling partner for arynes resulting in the synthesis of *N*-tosylindoles 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*-arylindoles using aryne chemistry has not been reported.

Scheme 1. Synthesis of Indoles via Arynes



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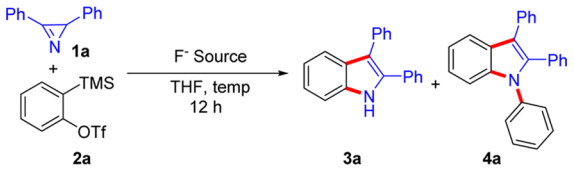
Herein, we report the transition-metal-free and highly selective synthesis of both *N*-unsubstituted and *N*-arylindoles by the reaction of arynes with 2*H*-azirines, and importantly, the product selectivity depends on the temperature used. When the reaction was carried out at −10 °C, *N*-arylindoles were formed in high yields. Gratifyingly, when the reaction was performed at 60 °C, 2,3-diaryl *N*-unprotected indoles were 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-diphenylindole and 1,2,3-triphenylindole 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*-arylindoles by the reaction of arynes with azirines.

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 the presence of 18-crown-6 as additive in THF at 30 °C. Under these conditions, the 2,3-diarylindole **3a** was formed in 40% yield, and 1,2,3-triaryl indole **4a** was formed in 21% yield in a 54:46 ratio (Table 1, entry 1). Interestingly,

Table 1. Optimization of the Reaction Conditions[a]



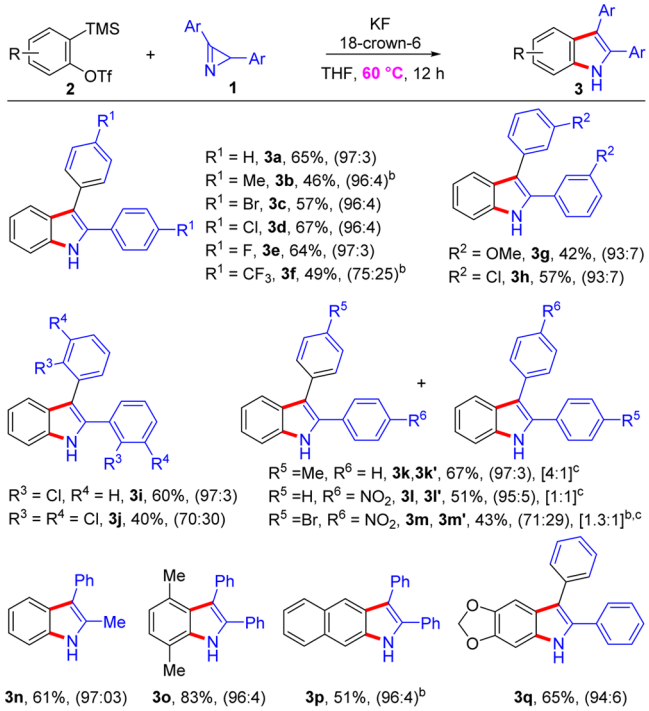
entry	fluoride source	temp (°C)	yield of **3a**[b] (%)	yield of **4a**[b] (%)	**3a**:**4a**[c]
1	KF/18-crown-6	30	40	21	54:46
2[d]	*KF/18-crown-6*	60	65	<5	97:3
3[e]	CsF	60	57	<5	83:17
4	TBAF.3H$_2$O	60	<5	<5	ND
5[f]	KF/18-crown-6	−10 to +30	<5	76	2:98
6[f]	*KF/18-crown-6*	*−10*	<5	83	*1:99*

[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]Yields 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**, 3.6 equiv of KF/18-crown-6, and 6.0 mL of THF. [e]Reaction performed using 1.0 mL of CH_3CN. [f]Reaction carried out using 3.0 equiv of **2a**, 6.0 equiv of KF/18-crown-6, and 1.0 mL of THF.

when the reaction was performed at 60 °C, **3a** was isolated in 65% yield and 97:3 selectivity (entry 2). Under these conditions, only traces of **4a** were formed. The use of other fluoride sources such as CsF and tetrabutylammonium fluoride (TBAF) did not improve the yield of **3a** and **4a** (entries 3 and 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 performed at −10 °C (entry 6).[15]

After optimizing the reaction conditions for the selective synthesis of *N*-unsubstituted and *N*-arylindoles, we examined the substrate scope of both transformations. First, we evaluated the scope of the synthesis of N−H indoles (Scheme 2). A series

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



[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.

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-diarylindoles in moderate to good yield and good selectivity (**3a**−**f**). Notably, in the case of 4-CF_3-substituted 2*H*-azirine, the selectivity was only moderate. The structure of **3f** was further confirmed by single-crystal X-ray analysis.[16] Moreover, the substitution at the 2-position and 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**−**j**). As expected, the unsymmetrical 2*H*-azirines afforded the inseparable mixture of regioisomers in moderate to good yield (**3k**−**m**). 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**−**q**).

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 toward the synthesis of trisubstituted indoles. A wide variety of symmetrical 2*H*-azirines with different substitution patterns readily underwent efficient aryne reactions leading to the synthesis of 1,2,3-triarylindoles in good yields (>71% in all cases) and excellent selectivity (>92:8 in all cases) (**4a**−**j**). In the case of **4h**, the structure was confirmed

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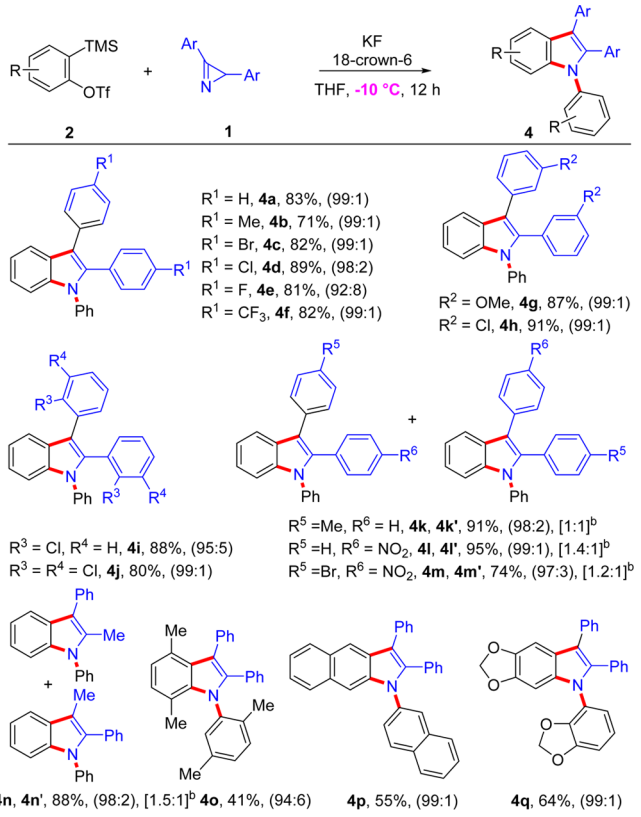
Scheme 3. Substrate Scope for Synthesis of *N*-Arylindoles[a]

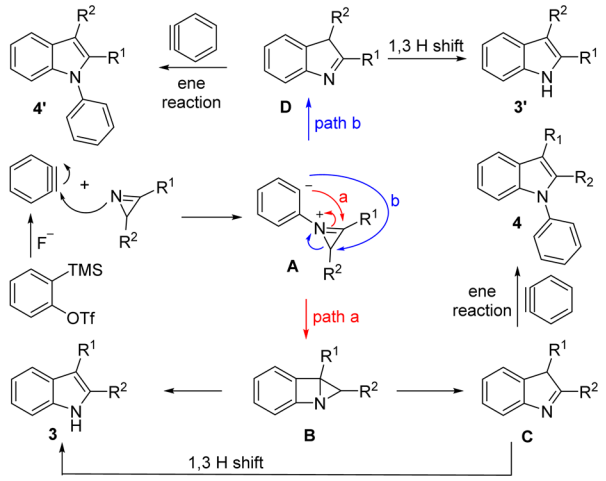


[a]General conditions: **1** (0.25 mmol), **2** (0.75 mmol), KF (1.5 mmol), 18-crown-6 (1.5 mmol), THF (1.0 mL), −10 °C, 12 h. Yields of the isolated products are given. Selectivity as determined by GC analysis of crude reaction mixture is given in parentheses. [b]Regioisomer ratio determined by GC analysis.

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**−**m**). In contrast to the reaction of 2-methyl-3-phenyl-2*H*-azirine with aryne at 60 °C, the reaction at −10 °C afforded a regioisomeric mixture of products (1.5:1) **4n** and **4n′** in 88% yield. Furthermore, variation of the 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**−**q**).

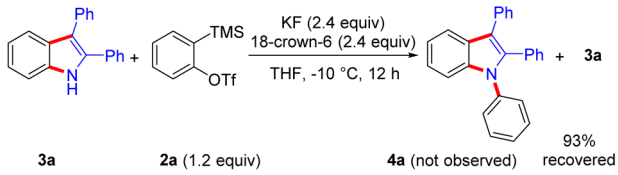
Considering the mixture of regioisomers obtained in the reaction of arynes with unsymmetrical 2*H*-azirines, a tentative mechanism of this reaction is shown in Scheme 4. The nucleophilic addition of 2*H*-azirines onto arynes generates the 1,4 zwitterionic intermediate **A**.[17,18] The zwitterion **A** 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*-arylindole **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*-arylindole **4a** (Scheme 5).

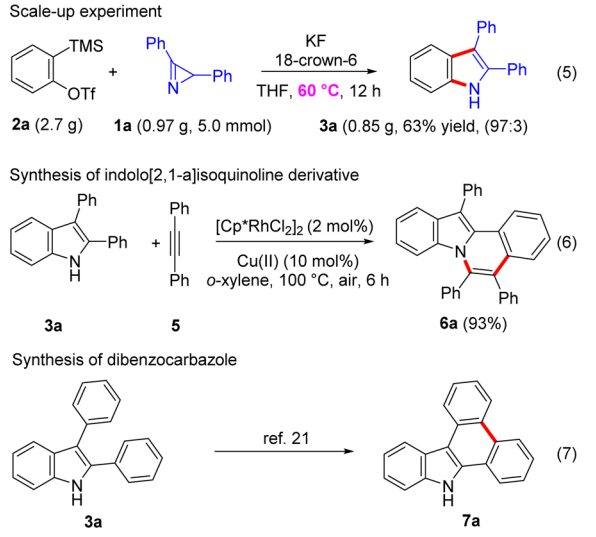
Scheme 5. Attempted Reaction of 3a with Arynes



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.

To demonstrate the synthetic utility of the reaction, a scale-up experiment was performed. Carrying out the reaction on 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).

Scheme 6. Synthetic Utility of the Method



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

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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.

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*-arylindoles. The reaction of arynes with 2*H*-azirines at 60 °C afforded 2,3-diarylindoles. Interestingly, the selectivity was switched to the formation of 1,2,3-triarylindoles 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. The room temperature of the laboratory was 30 °C 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, left to cool under argon, and stored in a glovebox. The 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** and the other symmetric and unsymmetric aryne precursors were synthesized following the 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 were converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). HRMS measurements were carried out using the ESI method and an ion-trap mass analyzer. Infrared (IR) spectra were recorded on an 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 were added 18-crown-6 (0.475 g, 1.8 mmol) and KF (0.105 g, 1.8 mmol) inside the glovebox. Then the corresponding 2*H*-azirine **1** (0.5 mmol) was added outside the glovebox. The mixture was dissolved in 12.0 mL of THF, and the resultant reaction mixture was allowed to stir 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 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 petroleum ether−EtOAc) to afford the corresponding *N*-unsubstituted indoles **3** in moderate to good yields. Selectivity ratio was determined by GC analysis of the crude reaction mixture.

*2,3-Diphenyl-1H-indole (**3a**):*[24] yellow solid, 0.087 g, 65%, 97:3; R_f (pet ether/EtOAc = 95/05) 0.35; mp 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) calcd $[M + H]^+$ 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-1H-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) calcd $[M + H]^+$ 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)-1H-indole (**3c**):*[24] yellow solid, 0.122 g, 57%, 96:4; R_f (pet ether/EtOAc = 95/05) 0.24; mp 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) calcd $[M + H]^+$ 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)-1H-indole (**3d**):*[25] pale yellow solid, 0.114 g, 67%, 96:4; R_f (pet ether/EtOAc = 95/05) 0.25; mp 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) calcd $[M + H]^+$ 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)-1H-indole (**3e**):*[24] pale yellow solid, 0.098 g, 64%, 97:3; R_f (pet ether/EtOAc = 95/05) 0.28; mp 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) calcd $[M + H]^+$ 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)-1H-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; mp 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) calcd $[M + H]^+$ 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)-1H-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) calcd $[M + H]^+$ 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)-1H-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) calcd $[M + H]^+$ 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)-1H-indole (**3i**):* yellow solid, 0.101 g, 60%, 97:3; R_f (pet ether/EtOAc = 95/05) 0.34; mp 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) calcd $[M + H]^+$ 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)-1H-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),

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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) calcd $[M + H]^+$ 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)-1H-indole (**3k**) and 2-phenyl-3-(p-tolyl)-1H-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) calcd $[M + H]^+$ 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-1H-indole (**3l**) and 3-(4-Nitrophenyl)-2-phenyl-1H-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) calcd $[M + Na]^+$ 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)-1H-indole (**3m**) and 2-(4-Bromophenyl)-3-(4-nitrophenyl)-1H-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) calcd $[M + H]^+$ 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-1H-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) calcd $[M + H]^+$ 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-1H-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) calcd $[M + H]^+$ 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-1H-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) calcd $[M + H]^+$ 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-5H-[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; mp 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) calcd $[M + H]^+$ 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*-Arylindoles. To a flame-dried screw-capped test tube equipped with a magnetic stir bar were added 18-crown-6 (0.396 g, 1.5 mmol) and KF (0.087 g, 1.5 mmol) inside the glovebox. Then the corresponding 2*H*-azirine **1** (0.25 mmol) was added outside the glovebox. The mixture was dissolved in 1.0 mL of solvent. The resultant reaction mixture was cooled to −10 °C and allowed to stir for 5 min. To the stirring solution was added aryne precursor **2** (0.75 mmol), and stirring was maintained at −10 °C for 12 h. 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*-arylindole derivatives **4** in moderate to good yields. Selectivity ratio was determined by GC analysis of crude reaction mixture.

*1,2,3-Triphenyl-1H-indole (**4a**):*[29] white solid, 0.072 g, 83%, 99:1; R_f (pet ether/EtOAc = 95/05) 0.75; mp 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) calcd $[M + H]^+$ 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-1H-indole (**4b**):*[29] yellow solid, 0.066 g, 71%, 99:1; R_f (pet ether/EtOAc = 95/05) 0.58; mp 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) calcd $[M + H]^+$ 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-1H-indole (**4c**):*[29] yellow solid, 0.103 g, 82%, 99:1; R_f (pet ether/EtOAc = 95/05) 0.69; mp 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) calcd $[M + H]^+$ 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-1H-indole (**4d**):*[29] white solid, 0.092 g, 89%, 98:2; R_f (pet ether/EtOAc = 95/05) 0.73; mp 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) calcd $[M + H]^+$ 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-1H-indole (**4e**):* yellow solid, 0.077 g, 81%, 92:8; R_f (pet ether/EtOAc = 95/05) 0.55; mp 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),

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110.9; HRMS (ESI) calcd $[M + H]^+$ 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)-1H-indole (**4f**):*[30] pale yellow solid, 0.098 g, 82%, 99:1; R_f (pet ether/EtOAc = 95/05) 0.69; mp 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) calcd $[M + H]^+$ 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-1H-indole (**4g**):* yellow solid, 0.088 g, 87%, 99:1; R_f (pet ether/EtOAc = 95/05) 0.37; mp 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) calcd $[M + H]^+$ 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-1H-indole (**4h**):* white solid, 0.094 g, 91%, 99:1; R_f (pet ether/EtOAc = 95/05) 0.63; mp 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) calcd $[M + H]^+$ 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-1H-indole (**4i**):* yellow solid, 0.091 g, 88%, 95:5; R_f (pet ether/EtOAc = 95/05) 0.57; mp 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) calcd $[M + H]^+$ 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-1H-indole (**4j**):* yellow solid, 0.097 g, 80%, 99:1; R_f (pet ether/EtOAc = 95/05) 0.65; mp 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) calcd $[M + H]^+$ 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)-1H-indole (**4k**) and 1,3-Diphenyl-2-(p-tolyl)-1H-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) calcd $[M + H]^+$ 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-1H-indole (**4l**) and 3-(4-Nitrophenyl)-1,2-diphenyl-1H-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) calcd $[M + H]^+$ 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-1H-indole (**4m**) and 2-(4-Bromophenyl)-3-(4-nitrophenyl)-1-phenyl-1H-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) calcd $[M + H]^+$ 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-1H-indole (**4n**)*[31] *and 3-Methyl-1,2-diphenyl-1H-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) calcd $[M + H]^+$ 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-1H-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) calcd $[M + H]^+$ 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-1H-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-5H-[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; mp 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) calcd $[M + H]^+$ 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.

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*5,6,12-Triphenylindolo[2,1-a]isoquinoline (**6a**).*[33] To a 5 mL screw-capped test tube equipped with a magnetic stir bar were sequentially added 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. 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; mp 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) calcd $[M + H]^+$ 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.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01472.

X-ray data, details on computational studies, and ^{1}H and ^{13}C NMR spectra of all products (PDF)
X-ray crystallographic data for **3f** (CIF)
X-ray crystallographic data for **4j** (CIF)

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Notes

The authors declare no competing financial interest.

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