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Multifold C–C Coupling and Unorthodox Cyclization Catalysis for Selective Synthesis of Indolotriarylmethanes, Indolocarbazoles, and Their Analogues: A Control Experiment Study

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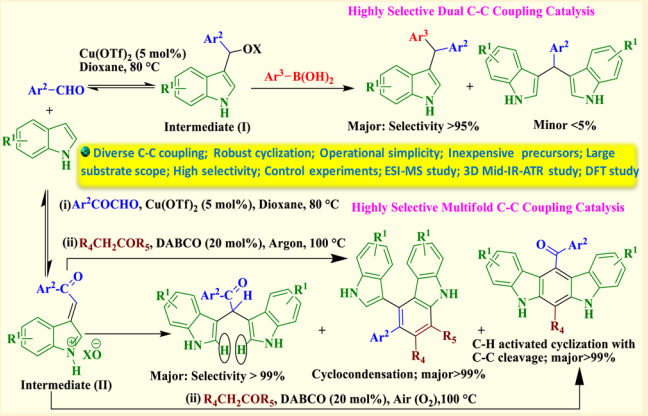
Supporting Information

ABSTRACT: The selective construction of medicinally and synthetically important indole-based unsymmetrical triarylmethanes using indoles and aldehydes is challenging because the significant nucleophilicity of indole leads to C–C coupling with an azafulvene intermediate to build up the alternative bis(indolyl)methane products, which may be useful synthons. A new, straightforward, ligand-free Cu^{II} catalytic strategy for easy syntheses of unsymmetrical indolotriarylmethanes and new bisindolylbenzoyl analogues is established through the dual C–C coupling of an assembly of three reaction partners comprising aldehydes, indoles, and arylboronic acids. More importantly, this approach is exploited for multifold C–C coupling cyclization reactions with C–C cleavage using symmetrical bisindolylbenzoylmethanes in the presence of an organic base and aerial molecular oxygen as a stoichiometric oxidant. In contrast to the formation of a simple cyclocondensation product indolocarbazole, it undergoes unprecedented selective pseudo-four-component tandem oxidative cyclization with fragmentation from a 1,3-dicarbonyl compound to produce valuable fused 5,7-dihydroindolo[2,3-*b*]carbazoles through the functionalization of two indole $C(sp^2)$–H and one $C(sp^3)$–H bond of the active methylene residue. For a better understanding of the new reactions, we have studied various competition experiments and ESI-MS and 3D Mid-IR-ATR spectral analyses of the ongoing reactions. The predicted DFT transition state model is also in agreement with the experimental results.



INTRODUCTION

C–C bond formation is a fundamental reaction, and multifold C–C coupling catalysis[1] has recently attracted considerable attention as a convenient way to frame desirable molecular complexity for the design of an appropriate assembly of simple precursors.[2] The selective construction of valuable unsymmetrical indole-based triarylmethanes[3] (**4**, path a, Scheme 1) using indoles (**1**) and aldehydes (**2**) is challenging because the significant nucleophilicity of indole leads to the formation of the alternative product bis(indolyl)methane (**5**, path b) through C–C coupling with an azafulvene intermediate (**II**). In most reports, two of the three aryl groups are the same, imposing an obstacle to the fine tuning of the chemical, medicinal, and material properties of the resulting triarylmethanes. On the other hand, arylboronic acids[4] are used extensively in organic chemistry as chemical building blocks because of their commercial availability, low toxicity, and wide tolerance. One of the important chemical reactivities of boronic acids is the transmetalation of its organic residue with an appropriate transition metal.[5] Thus, it would be beneficial if we could use arylboronic acid (**3**) as the third reaction partner during indole (**1**)–aldehyde (**2**) coupling through the development of an efficient catalyst for the selective dual C–C coupling process (path a) to achieve unsymmetrical triarylmethanes (**4**). Another properly designed and synthesized possible product, bisindolylmethane (path b, **5**) analogues, would be useful synthons if the two $C(sp^2)$–H groups undergo cyclization with release of the $C(sp^3)$–H, leading to the highly selective construction of ubiquitous carbazole[6] and indolocarbazole[7] core structures. Thus, the transformation of two competing pathways (**4** and **5**; path a/path b) for the selective building up of complex frameworks through a suitable catalysis strategy should be useful in modern organic synthesis.

Indole is a key building block in a wide range of valuable natural products, pharmaceuticals, agrochemicals, and materials,[8−10] which prompted us to develop a mild catalysis approach to achieve simple and complex indole architectures. Indole-based triarylmethanes constitute an important class of compounds because of their omnipresence in reductase inhibitors, antiviral agents, anticancer drugs, dye materials, bioactive alkaloids, and other natural products.[9] Indole-based compounds were developed as an anti breast cancer active nonsteroidal aromatase inhibitor (**A**, Figure 1),[10a] antibiotic and

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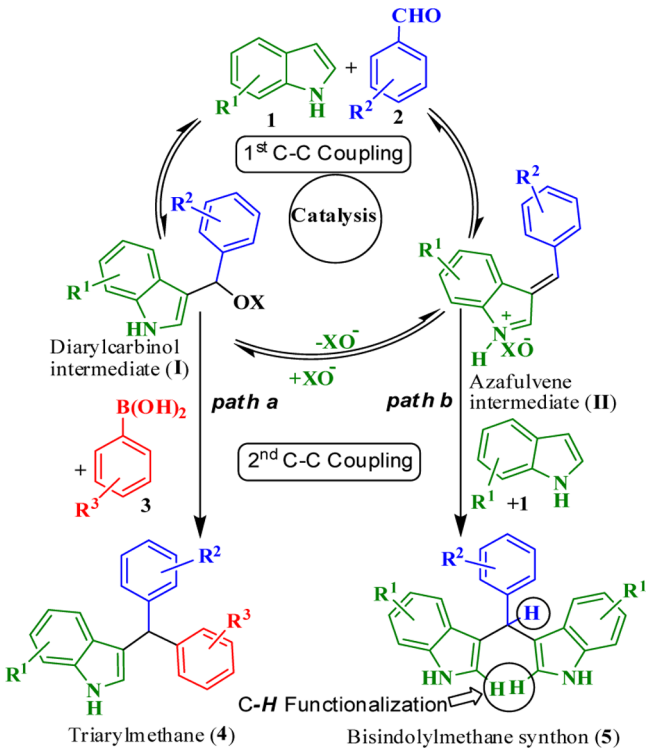
Scheme 1. Two Possible Catalytic Pathways to Triarylmethanes



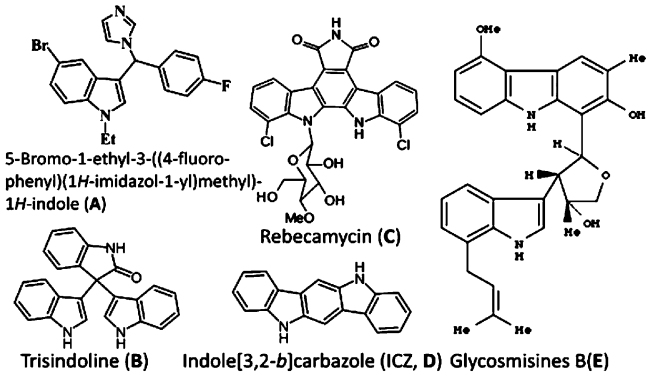


Figure 1. Valuable indole-based natural and synthetic compounds.

anticancer trisindoline alkaloid (**B**),[10b] the antitumor drug rebecamycin (**C**),[10c] the high-performance OFET material indolo[3,2-*b*]carbazole (ICZ, **D**),[10d] and multiple cancer cell line active natural product glycosmisine B (**E**).[10e] The syntheses of symmetrical bisindolotriarylmethanes were investigated via the Friedel–Crafts addition of electron-rich arenes to aldehydes and imines.[11] However, the direct synthesis of unsymmetrical indole-based triarylmethanes has been less explored, and recent reports have involved $InCl_3$-, $FeCl_3$-, $(EtCp)_2ZrCl_2$-$C_8F_{17}SO_3Ag$-, $ZnCl_2$-, and $PdCl_2$-catalyzed reactions.[12] The syntheses of common unsymmetrical triarylmethanes have been studied thoroughly.[13] However, the methods have limitations in terms of utilizing expensive metallic compounds, two catalysts, stoichiometric oxidants, ligands, hazardous and specially designed substrates, stringent reaction conditions, and multistep reactions, as well as the formation of symmetrical analogues. Moreover, mechanistic pathway for the synthesis of unsymmetrical indole-based triarylmethanes is not studied thoroughly.

Indolocarbazole was first isolated in 1977 and showed important biological activities and pharmaceutical applications (Figure 1).[14] Rigid coplanar structural features with the strong π-electron density of 5,11-dihydroindolo[3,2-*b*]carbazole have led to electron-rich π-conjugated backbones for innovative materials displaying properties useful for photophysical, electronic, optoelectronic, OFET, and other organic electronic applications of extreme sensitivity.[10b−d,15] In contrast to the diverse applications of indolo[2,3-*b*]carbazole and isomeric indole-bearing carbazoles, their general synthesis remains unexplored due to the construction restraints. The typical indole−aldehyde condensation widely used for the synthesis of indolo[3,2-*b*]carbazoles failed to provide the isomeric indolo-[2,3-*b*]carbazoles; however, a few methods have been reported, such as oxidative indole−arylaldehyde condensation with $POCl_3$ and acids, the intramolecular cyclization of specially designed iron carbonyl activated aromatic diamine precursors, the double-intramolecular Buchwald−Hartwig reaction, and Pd(II)−Cu(II) catalyzed carbazole−indole cyclization.[16] Interestingly, the carbazole-bearing indole moiety also displayed important medicinal[10e] and solar cell applications.[17] Thus, it will be beneficial to develop an efficient general strategy for the diverse syntheses of valuable indole-based functionalized unsymmetrical triarylmethanes, diindolylbenzoyl analogues, indole-substituted carbazoles, and indolo[3,2-*b*]carbazoles, which possess innovative medicinal and organic electronic properties.

RESULTS AND DISCUSSION

At the outset, we studied the dual C−C coupling process using indole (**1a**), 4-methylbenzaldehyde (**2a**), and phenylboronic acid (**3a**) as three reacting partners to survey the reaction parameters, and the results are summarized in Table 1. The reaction was first performed at ambient temperature (not shown), and subsequently the temperature was raised to 100 °C for 12−18 h with potential catalysts such as rare-earth-metal (entries 1−3) and transition-metal compounds (entries 4−7). The desired product **4a** or byproduct **5a** was not detected in the postreaction mixtures. To our delight, with the use of $Cu(OTf)_2$ as a catalyst (entry 8), **4a** was obtained in 65% yield. Both the yield (79%) and catalyst loading (5 mol %) were greatly improved on performing the reaction at 80 °C (entry 9). The reaction did not occur at room temperature (entry 10), and the yield was reduced if the reaction temperature was reduced even slightly to 70 °C (entry 11). Similar observations were made upon conducting the reaction under an argon atmosphere (entry 12). The results of changing the aprotic polar to nonpolar solvents (entries 13−17) or using various Cu^{II} and Cu^{I} compounds (entries 18−22), different ligands (entries 23 and 24), bases (entries 25 and 26), and combination catalysts (entry 27) were not encouraging.

Next, we studied the general applicability of the developed reaction conditions (entry 9, Table 1) using various substituted aldehydes (**1**), indoles (**2**), and arylboronic acids (**3**) to obtain functionalized indole-based unsymmetrical triarylmethanes (**4**, Scheme 2), though we were not totally successful in eliminating the bisindolyl byproduct **5** (<5%). Both aliphatic and aromatic aldehydes were tried and were transformed into the corresponding desired products (**4a−r**) under the reaction conditions. Aldehydes substituted with both electron-withdrawing (**4c,e−j,l**) and electron-donating groups (**4a,b,d,o,r**)

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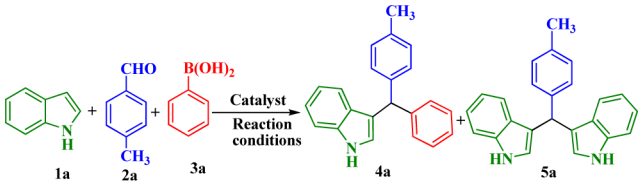
Table 1. Survey of Dual C−C Coupling Reaction To Give Triarylmethane (4a)[a]



entry	catalyst[b]	reaction conditions[c]	yield (%):[d] 4a, 5a
1	$Sc(OTf)_3$	dioxane, 100 °C, air, 15 h	15, 20
2	$Ce(OTf)_3$	dioxane, 100 °C, air, 12 h	15, 8
3	$Tb(OTf)_3$	dioxane, 100 °C, air, 12 h	25, 30
4	$In(OTf)_3$	dioxane, 100 °C, air, 18 h	5, 10
5	$Sn(OTf)_3$	dioxane, 100 °C, air, 14 h	10, 8
6	AgOTf	dioxane, 100 °C, air, 15 h	0, 0
7	$Pd(OAc)_2$	dioxane, 100 °C, air, 12 h	0, 0
8	$Cu(OTf)_2$	dioxane, 100 °C, air, 3 h	65, 10
9	**$Cu(OTf)_2$**[e]	**dioxane, 80 °C, air, 4 h**	**79, 4**
10	$Cu(OTf)_2$[e]	dioxane, room temp, air, 24 h	0, 65
11	$Cu(OTf)_2$[e]	dioxane, 70 °C, air, 5 h	52, 22
12	$Cu(OTf)_2$[e]	dioxane, 80 °C, Ar, 4 h	79, 5
13	$Cu(OTf)_2$[e]	THF, reflux, air, 4 h	15, 12
14	$Cu(OTf)_2$[e]	DME, 80 °C, air, 4 h	5, 8
15	$Cu(OTf)_2$[e]	CH_3NO_2, 80 °C, air	20, 25
16	$Cu(OTf)_2$[e]	DMF, 80 °C, air	0, 0
17	$Cu(OTf)_2$[e]	toluene, 80 °C, air	25, 35
18	$Cu(OTf).PhCH_3$	dioxane, 80 °C, air, 4 h	70, 11
19	$CuBr_2$	dioxane, 80 °C, air, 4 h	5, 45
20	$CuCl_2$	dioxane, 80 °C, air, 4 h	10, 50
21	$CuSO_4{\cdot}5H_2O$	dioxane, 80 °C, air, 4 h	8, 55
22	$Cu(OAc)_2$	dioxane, 80 °C, air, 4 h	15, 52
23	PPh_3,[f] $Cu(OTf)_2$[e]	dioxane, 80 °C, air, 4 h	0, 0
24	BINAP,[f] $Cu(OTf)_2$[e]	dioxane, 80 °C, air, 4 h	0, 0
25	K_3PO_4,[g] $Cu(OTf)_2$[e]	dioxane, 80 °C, air, 4 h	0, 0
26	Cs_2CO_3,[g] $Cu(OTf)_2$[e]	dioxane, 80 °C, air, 4 h	0, 0
27	Ag_2O,[e] $Cu(OTf)_2$[e]	dioxane, 80 °C, air, 4 h	0, 0

[a]Reaction conditions: **1a** (1.2 mmol), **2a** (1 mmol), and **3a** (1.2 mmol). [b]Catalyst loading: 10 mol %. [c]Volume of solvent: 3 mL. [d]Yield of pure **4a** and **5a** after silica gel column chromatography. [e]5 mol %. [f]10 mol %. [g]1 mmol.

were able to respond to the reaction. Among the synthesized indole derivatives, the reaction went very well when sterically hindered aldehydes (**4b,e,g,h,k,n−p**) were used. Even 5-methoxy-, 5-bromo-, 5-nitro-, and 2-methylindole and *N*-methylindole derivatives (**4f,h−j,r**) yielded the corresponding triarylmethanes. In the case of arylboronic acids, other than phenylboronic acid, a 2-methyl analogue is also capable of yielding the desired product (**4g**), allowing the installation of a great diversity of substituents on the triarylmethane template.

To obtain a close look into the probable reaction pathway of the three-component reaction, we have performed some control experiments (Scheme 3). We started the reaction using the possible intermediate phenyl(*p*-tolyl)methanol (**6a**) and reactant indole (**1a**, eq i, Scheme 3) as well as the alternative intermediate (1*H*-indol-3-yl)(*p*-tolyl)methanol (**6b**) and substrate phenylboronic acid (**3a**, eq ii) in a 1:1 ratio under similar reaction conditions (entry 9, Table 1). Both reactions were quenched in 1 h, and the desired product **4a** was obtained for both reactions, though the yields were distinctly different. A much better yield (88%) was found for the first reaction between indole (**1a**) and phenyl(*p*-tolyl)methanol (**6a**). A relatively low yield (**4a**, 67%) was afforded (eq ii) from coupling between (1*H*-indol-3-yl)(*p*-tolyl)methanol (**6b**) and phenylboronic acid (**3a**). Interestingly, if we added *p*-tolylbenzaldehyde (**2a**) and phenylboronic acid (**3a**) under similar reaction conditions, phenyl(*p*-tolyl)methanol (**6a**) was not generated even after 12 h (eq iii). From these control experiments, it is concluded that the reaction passes through the formation of the intermediate (1*H*-indol-3-yl)(*p*-tolyl)-methanol (**I**), which was also detected in the mass spectra of the reaction mixture (vide infra, intermediate **I-1** in Scheme 4).

A reasonable mechanism for the formation of the indolotriarylmethane product is proposed in Scheme 4 and was corroborated by the mass study data on the reaction mixture containing the reaction partner 4-nitrobenzaldehyde, phenylboronic acid, and indole. The two proposed intermediates **I-1** and **I-2** were detected by ESI-MS analyses (Supporting Information). We also attempted a theoretical DFT study for the $Cu(OTf)_2$-catalyzed synthesis of triarylmethane. All calculations were performed using the Gaussian 09 package of programs. The structures were optimized using the DFT method B3LYP with basis set SDD. Vibration analyses were performed to check stable geometries with no imaginary frequencies. The transition state was determined using the QST3 approach. For the located transition structure, only one imaginary frequency was found. Intrinsic reaction coordinate (IRC) calculations were performed to connect the transition structure unambiguously with the reactants. The energy profile diagram of the final step (Scheme 4) of the reaction is displayed in Figure 2 along with the DFT-optimized structures of the intermediate (**I-2**), transition state (TS), and final product. The transition state energy barrier is 0.0015 kcal/mol. Thus, the prediction is in agreement with the experimental data on the rapid dual C−C coupling reaction.

We have also monitored the progress of the catalytic process using 3D Mid-IR-ATR spectral analyses of the ongoing reaction among 4-nitrobenzaldehyde, phenylboronic acid, and indole. As a reference compound, we found two symbolic peaks for 4-nitrobenzaldehyde (1712 and 1536 cm^{-1}; red line, Figure 3) and one distinct peak at 1604 $cm^{-1}$for phenylboronic acid (deep green, Figure 3). As expected, the peaks at 1712 and 1536 cm^{-1} for aldehyde vanished entirely within 30 min after the commencement of the reaction (Figure 4). However, there was no prominent change in the characteristic peaks for indole in the 3D surface, since the product itself bears the indole residue. After 30 min, the peak attributable to phenylboronic acid at 1604 cm^{-1} started decreasing (marked portion in the 3D surface diagram), and a new peak at 1600 cm^{-1} appeared at 55 min, corresponding to the desired product (pink line, Figure 3), and its peak intensity increased significantly with time. Although the decreasing portion and the increasing portion were found to be merged, the distinct nature of these two peaks was understood to a considerable extent (Supporting Information).

The formation of symmetrical bisindolyltriarylmethane (**5** in Table 1) as a side product encouraged us to examine it in the formation of a new series of synthons, 2,2-bis(1*H*-indol-3-yl)-1-phenylethanone derivatives (**5a−c**, Scheme 5) starting from phenyl glyoxal and indole (excess) using $Cu(OTf)_2$ catalyst (5 mol %) in dioxane, utilized in situ for the construction of complex indolocarbazole analogues. To our delight, under similar reaction conditions, a new class of 2,2-bis(1*H*-indol-3-

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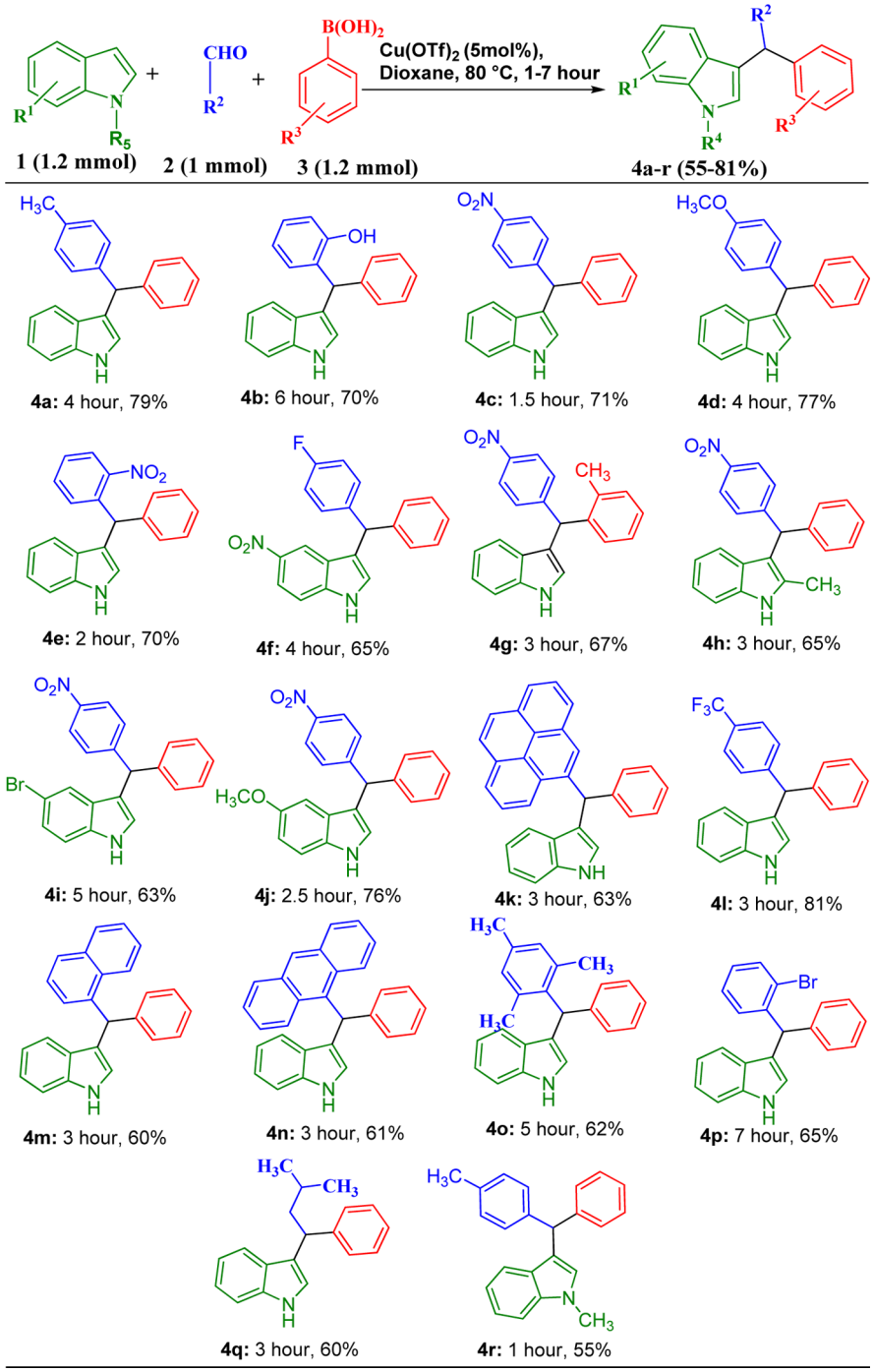
Scheme 2. Selective Synthesis of Indolotriarylmethanes (4)



yl)-1-phenylethanone and its bromo and methoxy derivatives (**5b–d**) were rapidly (15 min to 2 h) synthesized in excellent yield (82–91%).

We designed and synthesized bisindolylbenzoylmethanes for the construction of two new series of complex carbazole compounds (Scheme 6) possessing both electron-rich (e.g., indole) and electron-deficient (e.g., benzoyl) moieties, which are innovative organic materials for the fabrication of a new generation of organic electronic devices of ultimate sensitivity. The formation of these bisindolyltriarylmethanes (**5a**, Scheme 3) prompted us to construct 2,2-bis(1*H*-indol-3-yl)-1-phenylethanone (**III**, Scheme 6) utilizing α-ketoaldehyde **2n**. We envisioned that the condensation of **5** with substrate **7** (**III**, path a) bearing an active ketomethylene group would provide the complex carbazole **8** possessing an indole substituent. The mechanism for construction of compound **9** is unknown to us. However, it is expected that in the presence of the Cu^{II} catalyst under oxidative conditions, robust cyclization catalysis is carried out through the tandem functionalization of two $C(sp^2)$–H groups with the oxidative coupling of an active CH_2 (**7**, **IV**),[1a] the release of $C(sp^3)$–H and selective C–C cleavage leading to the construction of the valuable complex indolocarbazoles (**9**, path b). Both indole-based carbazole compounds (**8** and **9**) are useful nanobuilding blocks possessing a wide range of gluing weak interactions such as H-bonding donors and acceptors, π–π stacking, and van der Waals and dipole–dipole attractive

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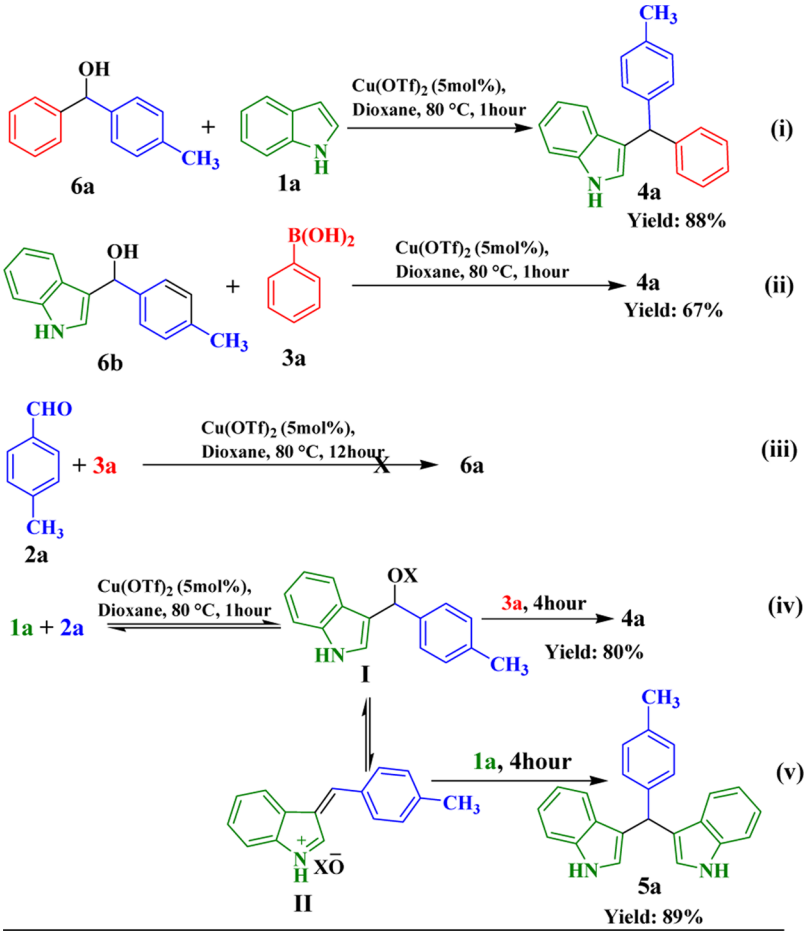
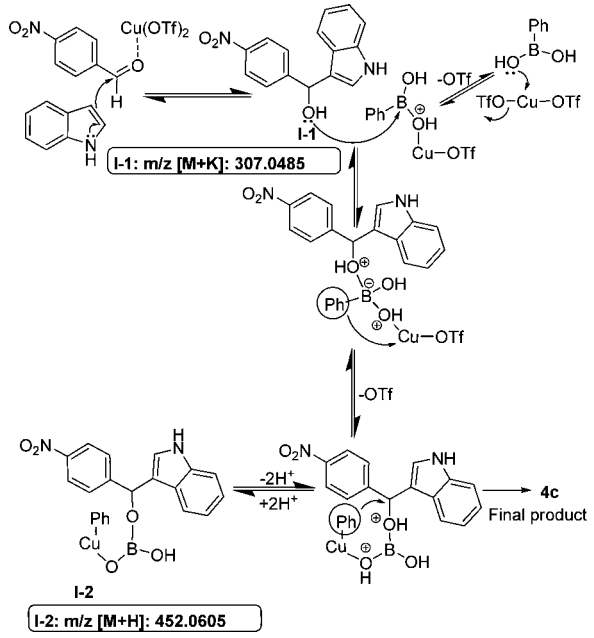
Scheme 3. Control Experiment Study



Scheme 4. Plausible Mechanistic Pathway to Indolotriarylmethane



interactions operating between nanobuilding blocks to offer self-aggregated organic nanomaterials.

Gratifyingly, the treatment of an assembly of precursors including indole (**1a**, 2.1 mmol) and phenyl glyoxal (**2n**, 1 mmol) using $Cu(OTf)_2$ catalyst (5 mol %) in dioxane at 80 °C (1 h) for the in situ generation of 2,2-bis(1*H*-indol-3-yl)-1-phenylethanone (**5b**) and subsequent addition of 4,4,4-trifluoro-1-phenylbutane-1,3-dione (**7a**, 1 mmol) and DMAP (1 mmol) under oxygen-free (argon atmosphere) reflux conditions (10 h) produced the desired multifold C−C coupled product, indole-bearing carbazoles **8a**, with 76% yield (Scheme 7). This multifold C−C coupling catalysis is also selective because formation of the unsymmetrical keto-methylene compound **7a** did not occur to construct the other possible regioisomer **8b**. Herein, the strong carbonyl characteristic of the $-COCF_3$ moiety led to selective condensation with the indole C_2 of **5b**, and thus **8b** was not detected in the postreaction mixture.

Next, we turn our attention to the more challenging synthesis of valuable symmetrical indolo[2,3-*b*]carbazoles (**9**, Scheme 8) through an oxidative multifold C−C coupling cyclization reaction. The selective synthesis of compound **9** over the more thermodynamically stable unsymmetrical isomer indolo-[3,2-*b*]carbazoles (**10**) is a challenging goal, and we focused on testing various oxidants (I_2, DDQ, O_2, air, and $Cu(OAc)_2{\cdot}H_2O$) and bases (K_2CO_3, piperidine, DMAP, and DABCO) with changes in temperature (Supporting Information). Among the different bases, DABCO (20 mol %) was found to be efficient in combination with aerial oxygen as a stoichiometric oxidant for the C−H functionalized cyclization process. Another

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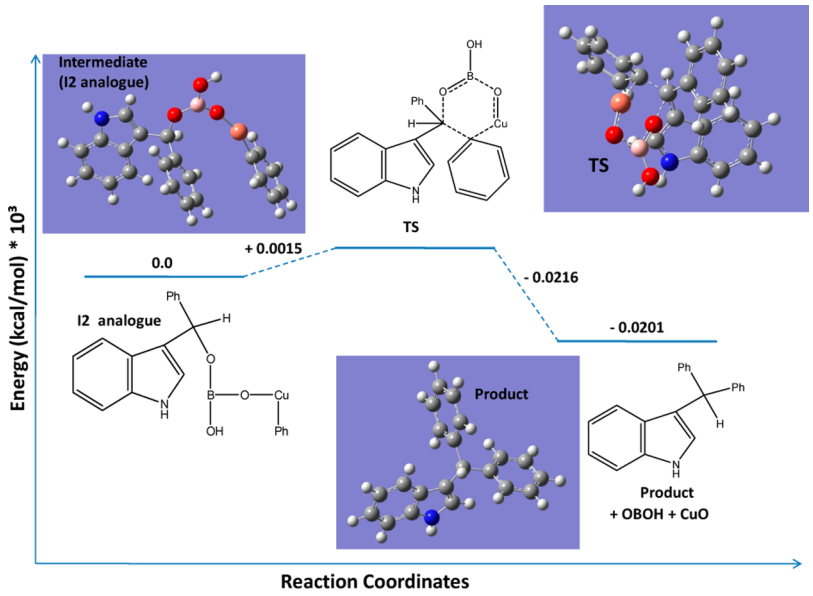


Figure 2. Important transition state and expected intermediate as predicted by DFT calculations (Gaussian 09). DFT-optimized structures are given in violet boxes.

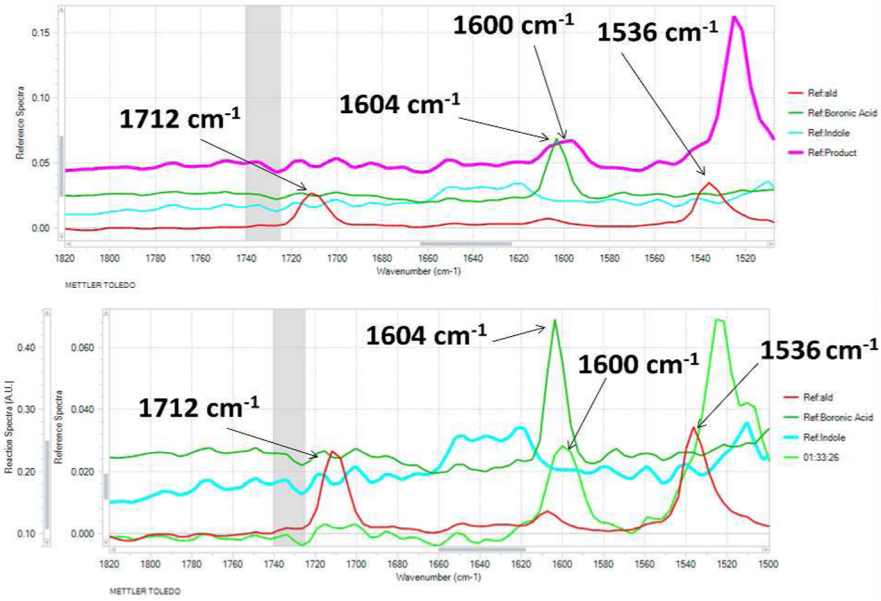


Figure 3. FTIR spectra of individual reaction partners.

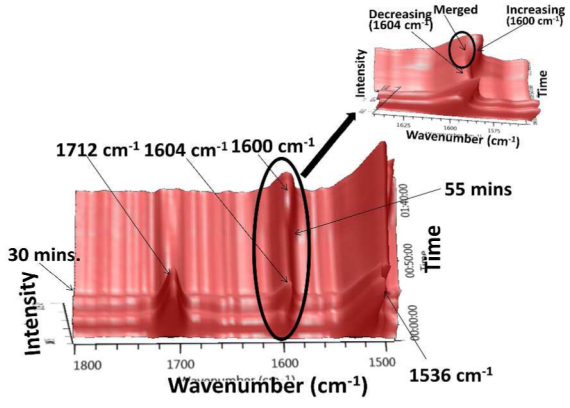
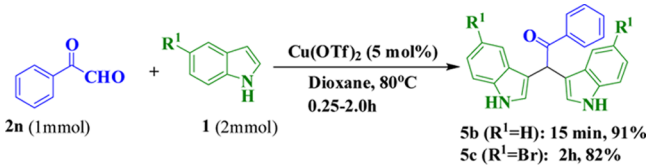


Figure 4. Mid-IR-ATR 3D surface of the ongoing reaction.

Scheme 5. Synthesis of Bisindolylbenzoylmethanes (5)



2n (1mmol) 1 (2mmol)

5b (R^1=H): 15 min, 91%
5c (R^1=Br): 2h, 82%
5d (R^1=OMe): 1h, 85%

noteworthy observation is that in no case was the corresponding nonoxidative multifold C−C coupling condensation product (**8**, Scheme 7) or isomeric byproduct **10** detected. With the optimized conditions in hand, we explored the synthesis of various 5,7-dihydroindolo[2,3-*b*]carbazole structures using indole, indole bearing electron-donating (5-OMe) and electron-withdrawing (5-Br) substituents (**1**),

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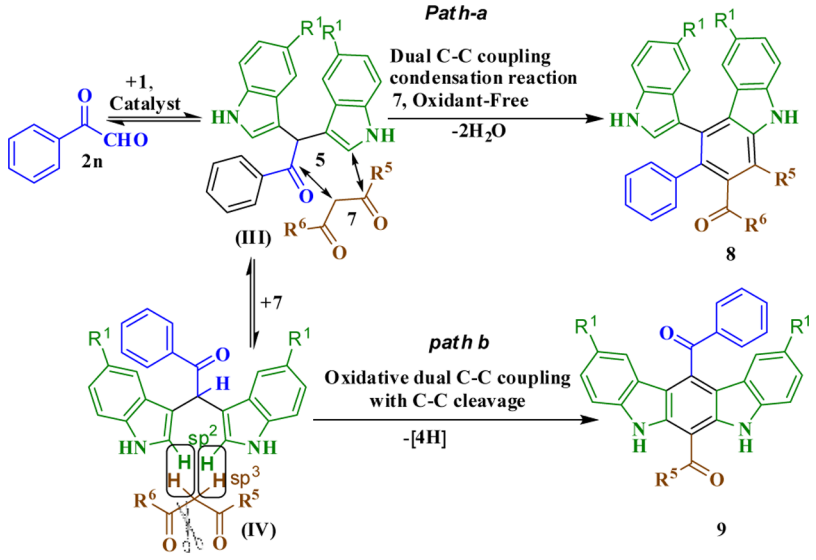
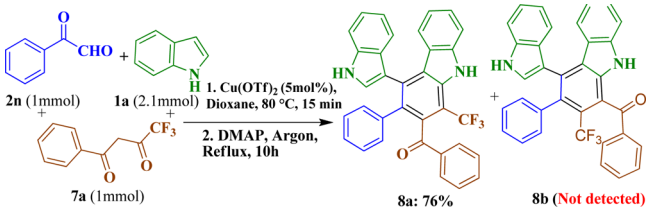
Scheme 6. Multifold C−C Coupled Selective Cyclization Reactions



Scheme 7. Selective Pseudo-Four-Component Coupling Catalysis To Give Indole-Substituted Carbazole



phenylglyoxal (**2n**), and symmetrical active methylene compounds (**7**) such as acetylacetone (**7b**, entry 1), benzoylacetophenone (**7c**, entries 2, 3, and 5), diethyl malonate (**7d**, entry 4), dimethyl malonate (**7e**, entry 6), 3,5-dioxoheptane (**7f**, entry 7), malononitrile (**7g**, entry 8), and *N*,*N*-diphenylmalonoamide (**7h**, entry 9). Herein, the pseudo-four-component assembly rapidly passed through a domino oxidative cyclization catalysis through the formation of multiple C−C bonds to obtain valuable symmetrical functionalized indolo[2,3-*b*]carbazoles (**9a−i**) with outstanding selectivity and good yield. These heterocycles possess both electron-donating and electron-withdrawing chromophores along with several weak attractive forces, making them potential nanobuilding blocks with gluing interactions to construct organic nanomaterials for innovative organic electronic applications. The structure of compound **9h** was confirmed through analyses of single-crystal X-ray diffraction data (CCDC no. 1508780; Supporting Information).

To shed light on the possible reaction pathways, we have performed control experiments for the two-step reaction (Scheme 9). In the first control experiment, phenylglyoxal (1 mmol), indole (2.1 mmol) and unsymmetrical 1,3-diketone $PhCOCH_2COCF_3$ were reacted under aerobic conditions. Surprisingly, a mixture of carbazoles was obtained (eq vi, Scheme 9) with 48% of the condensation product (**8a**) along with 25% oxidative cyclization product (**9b**). This result clearly indicates that the strong carbonyl characteristics of $COCF_3$ (**7a**) led to the construction of the condensation product (**8a**) at a faster reaction rate even under oxidative reaction conditions (path a, Scheme 6). However, 1,3-dicarbonyl compounds (**7b−h**, Scheme 8) bearing relatively less electrophilic carbonyl centers preferred to undergo an oxidative cyclization pathway even through C−C bond cleavage (path b, Scheme 6). We also investigated oxidative cyclization reactions using unsymmetrical 1,3-dicarbonyl compounds (**7i−l**, eqs vii−x, Scheme 9), which produced a mixture of products in each case. The major products contained relatively less electrophilic carbonyl moieties such as −CONHPh (**9i**, 51%, eq vii), −CONHPh (**9i**, 54%, eq viii), −COPh (**9b**, 45%, eq ix), and −CN (**9h**, 70%, eq x), in comparison to −COPh (**9b**, 23%), COMe (**9a**, 15%), COMe (**9a**, 23%), and CO_2Et (**9d**, 1%), respectively. From these results, it can be concluded that the selective nucleophilic attack of the DABCO on the more electrophilic carbon of the active methylene compound is crucial to achieve the major product. Thus, cleavage of the C−C bond for removal of the second carbonyl moiety may be considered as the rate-determining transition state. However, this reaction was completely arrested in the absence of molecular oxygen or air, which verifies the necessity of oxidant for the three C−H bond-activated cyclizations. To understand the influence of activated and deactivated indole in the reaction, we conducted a reaction (eq xi) using phenyl glyoxal (**2n**, 1 mmol), 5-methoxyindole (**1i**, 2 mmol), 5-bromoindole (**1j**, 2 mmol), and 1,3-diphenylpropane-1,3-dione (**7c**, 1 mmol) under the developed reaction conditions. Surprisingly, the product incorporating two 5-methoxyindole groups, **9c**, was found as the exclusive product (65%) alongside a negligible amount of the **1i** and **1j** insertion product **9j**. We were unable to detect the third possible product **9k** with both 5-bromoindoles relatively deactivated (**1j**). Thus, the reaction is more favorable for activated indoles.

On the basis of ESI-MS analysis data of the ongoing multifold C−C coupling cyclization reaction, the possible mechanism is depicted in Scheme 10. Formation of the bisindolylbenzoylmethane (**I-3**) intermediate was confirmed by the *m*/*z* [M + Na] symbolic peak in the ESI-MS spectra (Supporting Information). It is expected that the cyclization reaction should pass through the first C−C coupling between the activated C(sp^3)−H of **7c** and one of the two C(sp^2)−H groups[1a] of the two indole residues with a powerful Cu^{II} catalyst under oxidative conditions, followed by coupling with the other C(sp^2)−H. Intermediates **I-4** and **I-5** were both

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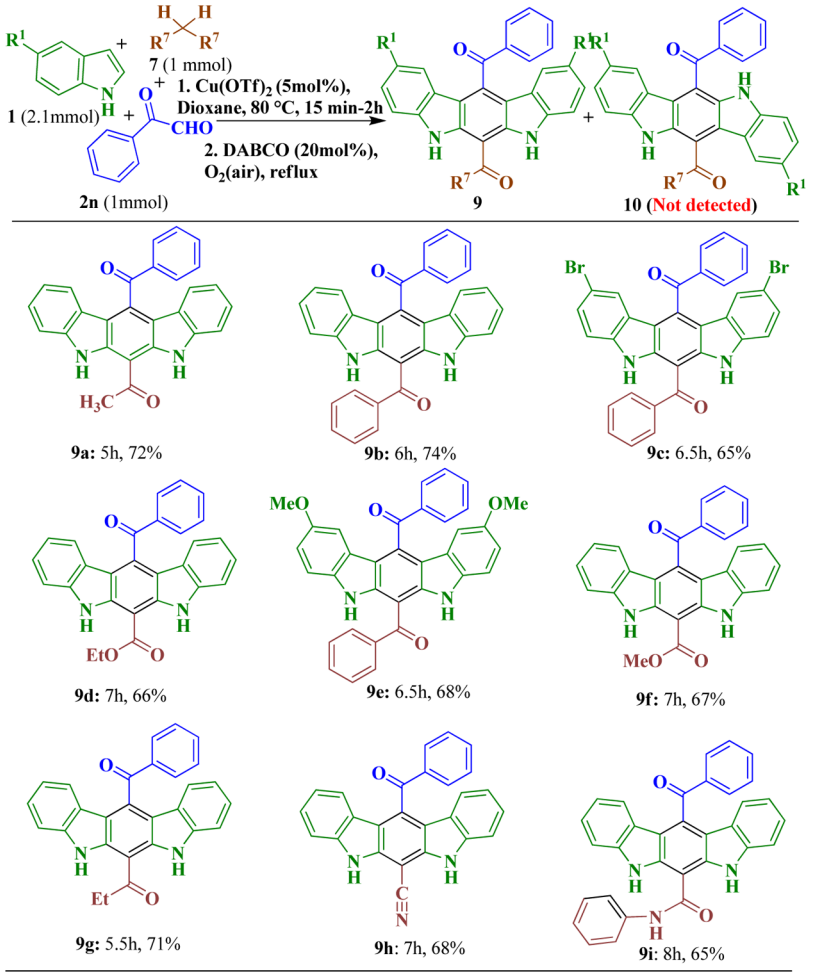
Scheme 8. Selective Synthesis of Indolo[2,3-*b*]carbazoles



detected in the ESI-MS experiment (Supporting Information). In the final step, DABCO mediated C−C cleavage of **I-5** with oxidation to afford the desired product **9b**.

CONCLUSION

We have demonstrated a three-component coupling method for selective synthesis of unsymmetrical indolotriarylmethanes using readily available aldehydes, indoles, and arylboronic acids as well as bisindolylarylmethanes through Cu^{II}-catalyzed dual C−C coupling. This novel strategy is advantageous in terms of easily available inexpensive precursors, simplicity of execution, large substrate scope, excellent functional group tolerance, a wide range of indole-based new compounds, chemo- and regioselectivity, product selectivity, and high yields. We have also found useful reaction insights through several control experiments and 3D mid-IR-ATR and mass spectral analysis of the ongoing reaction as well as DFT studies for the crucial transition state. The development of a robust catalysis approach to diverse C−C coupling reactions and the synthesis of indole-based functionalized molecules is expected to find considerable application in organic synthesis, medicinal chemistry, and materials science.

EXPERIMENTAL SECTION

General Methods. All reagents were purchased from commercial suppliers and used without further purification. Petroleum ether used in our experiments was in the boiling range of 60−80 °C. Column chromatography was performed on silica gel (100−200 and 230−400 mesh). Reported melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature in $CDCl_3$/DMSO-d_6 solution. Chemical shifts are reported in ppm (δ) relative to the internal reference tetramethylsilane. Coupling constants are quoted in Hz (J). Proton multiplicities are represented as s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), and m (multiplet). Splitting patterns that could not be interpreted were designated as multiplets (m). Infrared spectra were recorded ona FT-IR spectrometer as thin films. HR-MS data were acquired by the electron spray ionization technique on a Q-tof-micro quadruple mass spectrophotometer. X-ray crystallographic data were obtained using an X-ray diffractometer.

General Procedure for Synthesis of Indolyltriarylmethanes (GP-I) 4a−r. To a mixture of arylboronic acid (1.2 mmol), indole (1.2 mmol), aldehyde (1 mmol), and $Cu(OTf)_2$ (5 mol %) was added dioxane (3 mL), and this mixture was stirred at 80 °C in air to complete the reaction, which was monitored by TLC. Dioxane was removed from the reaction mixture and extracted with ethyl acetate. The combined organic phase was washed with brine, dried on activated Na_2SO_4, and concentrated in a rotary evaporator under reduced pressure at ambient temperature. The residue was purified by silica gel column chromatography using a suitable eluent to afford the desired product.

*3-(Phenyl(p-tolyl)methyl)-1H-indole (**4a**).* The compound was prepared following GP-I employing 4-methylbenzaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and indole (1.2 mmol). Purification by column chromatography (3% petroleum ether−acetone) afforded the title compound as a reddish brown solid (234 mg, 0.79 mmol, 79% yield): mp 78−80 °C; ^{1}H NMR (300 MHz,

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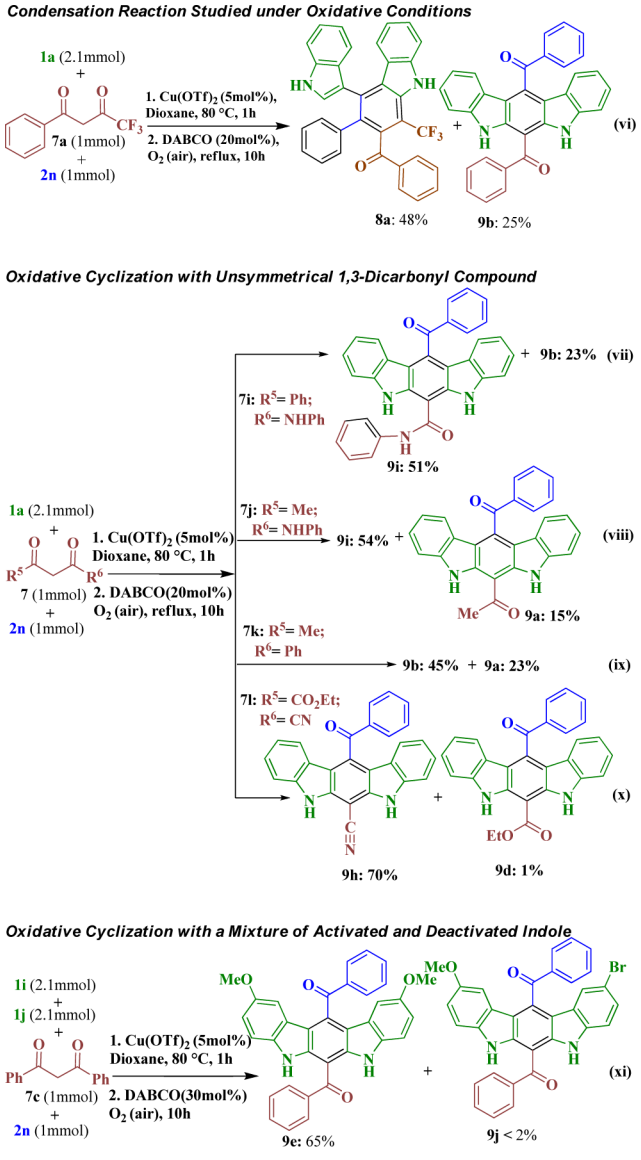
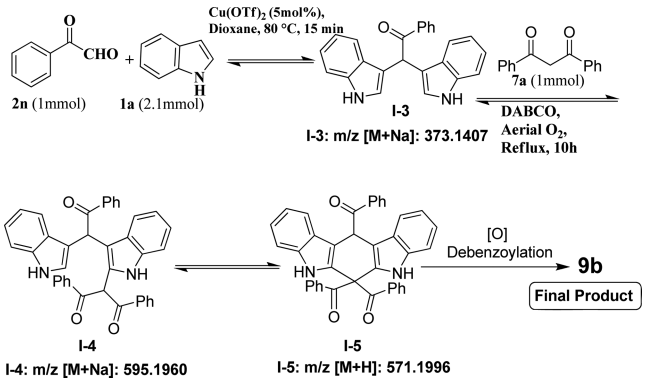
Scheme 9. Control Experiments under Oxidative Conditions



Scheme 10. Plausible Reaction Pathway for Oxidative Multifold C−C Coupling



CDCl$_3$) δ 2.30 (s, 3H), 5.61 (s, 1H), 6.51 (d, J = 1.2 Hz, 1H), 6.93−7.30 (m, 13H), 7.84 (br s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 21.2, 48.6, 111.2, 119.5, 120.1, 120.2, 122.2, 124.1, 126.3, 127.2, 128.4, 129.0, 129.1, 135.8, 136.8, 141.1, 144.3; FT-IR (KBr, cm^{-1}) 1094.8, 1415.3, 1456.1, 1492.7, 1511.0, 1642.6, 3418.5; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{18}N$ [M − H] 296.1439, found 296.1468.

*2-((1H-Indol-3-yl)(phenyl)methyl)phenol (**4b**).*[18] The compound was prepared following GP-I employing 2-hydroxylbenzaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and indole (1.2 mmol). Purification by column chromatography (15% petroleum ether−acetone) afforded the title compound as a brown solid (209.3 mg, 0.70 mmol, 70% yield): mp 76−78 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.09 (br s, 1H), 5.82 (s, 1H), 6.64 (d, J = 2.1 Hz, 1H), 6.81−6.85 (m, 2H), 6.92−7.02 (m, 2H), 7.11−7.35 (m, 9H), 8.02 (br s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 43.3, 111.2, 116.3, 117.7, 119.7, 119.8, 120.8, 122.5, 124.0, 126.7, 126.9, 128.0, 128.6, 1129.0, 129.7, 130.1, 136.9, 142.3, 153.9; FT-IR (KBr, cm^{-1}) 699.0, 742.3, 1090.9, 1454.0, 1591.9, 2922.5, 3413.1.

*3-((4-Nitrophenyl)(phenyl)methyl)-1H-indole (**4c**).* The compound was prepared following GP-I employing 4-nitrobenzaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and indole (1.2 mmol). Purification by column chromatography (15% petroleum ether−acetone) afforded the title compound as a deep yellow solid (233 mg, 0.71 mmol, 71% yield): mp 89−91 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.79 (s, 1H), 6.59 (s, 1H), 7.05 (t, J = 7.5 Hz, 1H), 7.20−7.29 (m, 4H), 7.32−7.35 (m, 3H), 7.38−7.43 (m, 2H), 8.15 (d, J = 8.7 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 48.6, 111.3, 118.2, 119.4, 119.6, 122.4, 123.5, 124.1, 126.4, 126.8, 128.6, 128.8, 129.8, 136.6, 142.3, 146.4, 151.6; FT-IR (KBr, cm^{-1}) 701.6, 473.0, 1097.1, 1343.8, 1516.3, 1593.9, 3414.3; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{15}N_2O_2$ [M − H] 327.1134, found 327.1128.

*3-((4-Methoxyphenyl)(phenyl)methyl)-1H-indole (**4d**).*[19] The compound was prepared following GP-I employing 4-methoxybenzaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and indole (1.2 mmol). Purification by column chromatography (20% petroleum ether−DCM) afforded the title compound as a sticky liquid (241 mg, 0.77 mmol, 77% yield): ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.73 (s, 3H), 5.57 (s, 1H), 6.49 (s, 1H), 6.77 (d, J = 8.7 Hz, 2H), 6.94 (t, J = 7.5 Hz, 1H), 7.08−7.30 (m, 9H), 7.88 (br s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 48.0, 55.2, 111.0, 113.6, 119.4, 120.0, 122.1, 124.0, 126.1, 127.0, 128.3, 128.9, 129.9, 136.2, 136.7, 144.3, 158.0; FT-IR (neat, cm^{-1}) 1031.8, 1246.7, 1456.0, 1509.3, 1599.9, 3420.1.

*3-((2-Nitrophenyl)(phenyl)methyl)-1H-indole (**4e**).* The compound was prepared following GP-I employing 2-nitrobenzaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and indole (1.2 mmol). Purification by column chromatography (15% petroleum ether−acetone) afforded the title compound as a deep yellow solid (230 mg, 0.70 mmol, 70% yield): mp 153−155 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.40 (s, 1H), 6.51 (s, 1H), 6.96−7.01 (m, 1H), 7.14−7.41 (m, 11H), 7.85 (dd, J = 7.8 Hz, 1.2 Hz, 1H), 8.01 (br s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 43.3, 111.2, 118.3, 119.5, 119.7, 122.4, 124.4, 124.5, 126.6, 126.7, 127.4, 128.4, 129.0, 131.5, 132.4, 136.8, 137.9, 141.8, 149.8; FT-IR (KBr, cm^{-1}) 747.1, 1357.6, 1456.7, 1514.9, 1521.8, 2853.4, 2924.2, 3420.0; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{15}N_2O_2$ [M − H] 327.1133, found 327.1112.

*3-((4-Fluorophenyl)(phenyl)methyl)-5-nitro-1H-indole (**4f**).* The compound was prepared following GP-I employing 4-fluorobenzaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and 5-nitroindole (1.2 mmol). Purification by column chromatography (10% petroleum ether−EtOAc) afforded the title compound as a yellow solid (225 mg, 0.65 mmol, 65% yield): mp 246−248 °C; ^{1}H NMR (300 MHz, CDCl$_3$ + DMSO-d_6) δ 5.68 (s, 1H), 6.73 (s, 1H), 6.97 (t, J = 8.4 Hz, 2H), 7.15−7.31 (m, 7H), 7.41 (d, J = 9.0 Hz, 1H), 7.99 (d, J = 9.0 Hz, 1H), 8.10 (s, 1H), 11.04 (br s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$+DMSO-d_6) δ 47.0, 111.0, 114.4, 114.7, 116.2 (d, ^2J = 40.6 Hz, C-CF), 120.5, 125.4, 126.0, 127.2, 127.9, 128.1, 129.6, 129.7, 139.7, 140.3, 140.6 (d, ^1J = 294.8 Hz, CF), 162.4; FT-IR (KBr, cm^{-1}) 700.4, 740.5, 1089.0, 1232.7, 1321.5, 1506.0, 2356.3, 2923.7, 3291.9; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{16}FN_2O_2$ [M + H] 347.1196, found 347.1192.

*3-((4-Nitrophenyl)(o-tolyl)methyl)-1H-indole (**4g**).* The compound was prepared following GP-I employing 4-nitrobenzaldehyde (1 mmol), 2-methylphenylboronic acid (1.2 mmol), and 5-nitroindole (1.2 mmol). Purification by column chromatography (10% petroleum ether−EtOAc) afforded the title compound as a sticky liquid (229 mg,

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0.67 mmol, 67% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 5.93 (s, 1H), 6.48 (d, J = 1.5 Hz, 1H), 6.91 (d, J = 7.5 Hz, 1H), 7.01−7.14 (m, 2H), 718−7.29 (m, 4H), 7.35−7.42 (m, 3H), 8.07−8.16 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.7,45.0, 111.3, 117.9, 119.4, 119.7, 122.5, 124.0, 124.3, 126.2, 126.7, 126.9, 128.8, 130.0, 130.7, 136.3, 136.8, 140.6, 146.6, 151.4; FT-IR (neat, cm^{-1}) 1345.4, 1596.4, 1604.6, 1655.0, 3418.5; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{19}N_2O_2$ [M + H] 343.1447, found: 343.1472.

2-Methyl-3-((4-nitrophenyl)(phenyl)methyl)-1H-indole (**4h**). The compound was prepared following GP-I employing 4-nitrobenzaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and 2-methylindole (1.2 mmol). Purification by column chromatography (10% petroleum ether−EtOAc) afforded the title compound as a thick liquid (222 mg, 0.65 mmol, 65% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.11 (s, 3H), 5.73 (s, 1H), 6.83−6.89 (m, 2H), 6.98−7.04 (m, 1H), 7.11−7.13 (m, 2H), 7.17−7.30 (m, 6H), 7.91 (br s, 1H), 8.04 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4, 47.8,110.5, 112.6, 119.1, 119.5, 121.2, 123.5, 126.7, 127.9, 128.6, 129.0, 130.0, 132.4, 135.3, 142.2, 146.4, 151.9; FT-IR (neat, cm^{-1}) 746.7, 1344.9, 1459.7, 1517.1, 1594.4, 1705.8, 3403.6; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{19}N_2O_2$ [M + H] 343.1447, found: 343.1470.

5-Bromo-3-((4-nitrophenyl)(phenyl)methyl)-1H-indole (**4i**). The compound was prepared following GP-I employing 4-nitrobenzaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and 5-bromoindole (1.2 mmol). Purification by column chromatography (5% petroleum ether−EtOAc) afforded the title compound a as thick liquid (256 mg, 0.63 mmol, 63% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (s, 1H), 6.59 (s, 1H), 7.16−7.22 (m, 2H), 7.27−7.38 (m, 7H), 8.13−8.16 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 48.4, 112.8, 113.0, 118.1, 121.9, 123.7, 125.3, 125.4, 127.0, 128.3, 128.7, 128.8, 129.6, 129.7, 135.3, 141.9, 146.7, 151.1; FT-IR (neat, cm^{-1}) 1345.0, 1451.9, 1518.1, 1587.4, 3412.2; HRMS (ESI-TOF) m/z calcd for due $C_{21}H_{16}BrN_2O_2$ [M + H] 407.0395, found 405.0368, 407.0373.

5-Methoxy-3-((4-nitrophenyl)(phenyl)methyl)-1H-indole (**4j**). The compound was prepared following GP-I employing 4-nitrobenzaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and 5-methoxylindole (1.2 mmol). Purification by column chromatography (8% petroleum ether−EtOAc) afforded the title compound as a thick liquid (272 mg, 0.76 mmol, 76% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 3H), 5.72 (s, 1H), 6.57 (dd, J = 2.4 Hz, 9.9 Hz, 2H), 8.86 (dd, J = 2.4 Hz, 8.7 Hz, 1H), 7.20−7.33 (m, 6 H), 7.40 (d, J = 8.7 Hz, 2H), 8.03 (br s, 1H), 8.14 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 48.7, 55.8, 101.6, 112.0, 112.3, 118.0, 123.6, 124.8, 126.9, 127.0, 128.6, 128.9, 129.8, 131.9, 142.3, 146.5, 151.6, 154.0; FT-IR (neat, cm^{-1}) 1208.4, 1345.2, 1519.5, 1627.2, 3434.2; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{19}N_2O_3$ [M + H] 359.1396, found 397.1428.

3-(Phenyl(pyren-4-yl)methyl)-1H-indole (**4k**). The compound was prepared following GP-I employing pyrene-4-carbaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and indole (1.2 mmol). Purification by column chromatography (5% petroleum ether−EtOAc) afforded the title compound as a deep yellow solid (256 mg, 0.63 mmol, 63% yield): mp 77−79 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.43 (s, 1H), 6.76 (s, 1H), 6.96−7.01 (m, 1H), 7.17−7.38 (m, 8H), 7.69−7.71 (m, 1H), 7.93−8.05 (m, 6H), 8.13−8.18 (m, 2H), 8.39 (d, J = 9.3, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.0, 111.1, 115.2, 119.4, 119.8, 120.1, 120.6, 122.2, 123.6, 124.7, 124.9, 125.0, 125.1, 125.8, 126.3, 126.9, 127.0, 127.1, 127.5, 128.4, 128.8, 129.3, 129.6, 130.0, 130.2, 130.7, 131.3, 136.7, 137.6, 143.9; FT-IR (KBr, cm^{-1}) 713.5, 841.1, 1417.0, 1455.0, 2852.3, 2922.9, 3458.5; HRMS (ESI-TOF) m/z calcd for $C_{31}H_{21}NNa$ [M + Na] 430.1572, found 430.1605.

3-(Phenyl(4-(trifluoromethyl)phenyl)methyl)-1H-indole (**4l**). The compound was prepared following GP-I employing 4-(trifluoromethyl)benzaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and indole (1.2 mmol). Purification by column chromatography (8% petroleum ether−EtOAc) afforded the title compound as a light brown solid (284 mg, 0.81 mmol, 81% yield): mp 112−114 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69 (s, 1H), 6.49 (d, J = 1.2 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 7.13−7.32 (m, 10H), 7.50 (d, J = 8.1 Hz, 2H), 7.94 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 48.7, 111.3, 115.3, 119.0, 119.6, 119.7, 122.4, 125.27, 125.30 (q, ^1J = 225.0 Hz, CF_3), 125.32, 126.8, 128.5, 128.8, 129.0, 129.4, 136.7, 143.0, 148.1; FT-IR (KBr, cm^{-1}) 743.8, 805.8, 1067.2, 1108.2, 1165.1, 1323.9, 3424.0; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{15}F_3N$ [M − H] 350.1157, found 350.1167.

3-(Naphthalen-1-yl(phenyl)methyl)-1H-indole (**4m**). The compound was prepared following GP-I employing 1-naphthaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and indole (1.2 mmol). Purification by column chromatography (2% petroleum ether−EtOAc) afforded the title compound as a brown solid (200 mg, 0.60 mmol, 60% yield): mp 68−70 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.45 (d, J = 4.5 Hz, 2H),7.00−7.05 (m, 1H), 7.13−7.50 (m, 12H), 7.78 (d, J = 8.1 Hz, 1H), 7.90 (d, J = 7.8 Hz, 2H), 8.14 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.7, 111.1, 115.3, 119.5, 119.8, 122.2, 124.3, 124.8, 125.4, 126.0, 126.3, 126.9, 127.0, 127.2, 128.4, 128.7, 129.3, 131.9, 134.0, 136.7, 139.6, 143.7; FT-IR (KBr, cm^{-1}) 1093.1, 1415.6, 1455.7, 1492.4, 1596.0, 3056.1, 3418.5; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{18}N$ [M − H] 332.1439, found 332.1416.

3-(Anthracen-9-yl(phenyl)methyl)-1H-indole (**4n**). The compound was prepared following GP-I employing anthracene-9-carbaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and indole (1.2 mmol). Purification by column chromatography (3% petroleum ether−EtOAc) afforded the title compound as a brown solid (234 mg, 0.61 mmol, 61% yield): mp 84−86 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.65 (s, 1H), 7.08−7.29 (m, 9H), 7.36−7.43 (m 3H), 7.48 (d, J = 7.8 Hz, 1H), 7.92 (br s, 1H), 8.03 (d, J = 8.4 Hz, 2H), 8.34 (d, J = 9.0 Hz, 2H), 8.47 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.7, 111.2, 119.6, 119.8, 122.2, 124.7, 125.3, 125.7, 125.9, 127.4, 127.9, 128.2, 128.5, 129.2, 130.5, 132.1, 136.4, 144.5; FT-IR (KBr, cm^{-1}) 704.6, 730.3, 1096.0, 1338.5, 1446.0, 1455.9, 1491.2, 2923.4, 3050.1, 3414.6; HRMS (ESI-TOF) m/z calcd for $C_{29}H_{20}N$ [M − H] 382.1596, found 382.1622.

3-(Mesityl(phenyl)methyl)-1H-indole (**4o**).[20] The compound was prepared following GP-I employing 2,4,6-trimethylbenzaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and indole (1.2 mmol). Purification by column chromatography (5% petroleum ether−EtOAc) afforded the title compound as a brown solid (202 mg, 0.62 mmol, 62% yield): mp 45−47 °C;^{1}H NMR (300 MHz, $CDCl_3$) δ 2.09 (s, 6H), 2.31 (s, 3H), 6.13 (s, 1H), 6.63 (s, 1H), 6.87 (2H), 7.03−7.08 (m, 1H), 7.16−7.33 (m, 5H), 7.39 (d, J = 8.1 Hz, 1H), 7.96 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9, 21.7, 42.9, 111.1, 116.8, 119.4, 119.9, 122.0, 123.9, 125.6, 127.8, 128.0, 128.9, 130.1, 135.7, 136.6, 137.3, 137.8, 143.4; FT-IR (KBr, cm^{-1}) 741.1, 1093.2, 1149.3, 1337.1, 1455.8, 1491.9, 2916.9, 3413.4.

3-((2-Bromophenyl)(phenyl)methyl)-1H-indole (**4p**). The compound was prepared following GP-I employing 2-bromobenzaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and indole (1.2 mmol). Purification by column chromatography (8% petroleum ether−EtOAc) afforded the title compound as a brown solid (235 mg, 0.65 mmol, 65% yield): mp 86−88 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 (s, 1H), 6.45 (s, 1H), 6.45−7. 31 (m, 12H), 7.55 (d, J = 8.1 Hz, 1H), 7.92 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 47.9, 111.1, 115.3, 119.0, 119.5, 119.8, 122.2, 124.3, 125.1, 126.4, 127.3, 128.0, 128.3, 129.2, 129.6, 130.9, 133.0, 136.7, 142.4, 142.8; FT-IR (KBr, cm^{-1}) 700.2, 718.3, 741.3, 751.2, 1020.4, 1091.9, 1415.0, 1454.7, 3387.2, 3437.8; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{17}BrN$ [M + H] 362.0544, found 360.0502, 362.0515.

3-(4-Methyl-1-phenylpentyl)-1H-indole (**4q**). The compound was prepared following GP-I employing 3-methylbutanal (1 mmol), phenylboronic acid (1.2 mmol), and indole (1.2 mmol). Purification by column chromatography (5% petroleum ether−EtOAc) afforded the title compound as a brown solid (158 mg, 0.60 mmol, 60% yield): mp 80−82 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88−0.91 (m, 3H), 0.95−0.98 (m, 3H), 1.47−1.56 (m, 1H), 1.88−2.06 (m, 2H), 4.25−4.30 (m, 1H), 6.95−7.03 (m, 2H), 7.09−7.15 (m, 2H), 7.20−7.31 (m, 5H), 7.47 (d, J = 7.8 Hz, 1H), 7.86 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.4, 23.2, 25.6, 40.4, 45.6, 111.0, 119.2, 119.4, 120.6, 121.0, 121.9, 125.9, 127.1, 127.9, 128.3, 136.5, 145.6; FT-IR (KBr, cm^{-1}) 701.0, 740.9, 1456.9, 2951.2, 3411.5; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{22}N$ [M + H] 264.1752, found 264.1780.

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*1-Methyl-3-(phenyl(p-tolyl)methyl)-1H-indole (**4r**).* The compound was prepared following GP-I employing 4-methylbenzaldehyde (1 mmol), phenylboronic acid (1.2 mmol), and 1-methylindole (1.2 mmol). Purification by column chromatography (0.5% petroleum ether−EtOAc) afforded the title compound as a brown solid (171 mg, 0.55 mmol, 55% yield): mp 78−80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 3H), 3.68 (s, 3H), 5.62 (s, 1H), 6.40 (s, 1H), 6.94−6.99 (m, 1H), 7.06−7.16 (m, 4H), 7.19−7.29 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2, 31.8, 47.5, 108.2, 117.6, 117.9, 119.1, 120.7, 125.2, 126.5, 127.4, 127.8, 128.0, 128.1, 134.7, 136.6, 140.3, 143.5; FT-IR (KBr, cm^{-1}) 1116.0, 1228.2, 1329.0, 1370.2, 1469.4, 1510.2, 2853.4, 2923.8; HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{20}N$ [M − H] 310.1596, found 310.1623.

General Procedure for Synthesis of 5a−d (GP-II). To a mixture of indole/substituted indole (2.0 mmol), 4-methylbenzaldehyde/phenyl glyoxal (1.0 mmol), and $Cu(OTf)_2$ (5 mol %) was added dioxane (4 mL), and this mixture was stirred at 80 °C in air to complete the reaction, which was monitored by TLC. Dioxane was removed from the reaction mixture and extracted with ethyl acetate. The combined organic phase was washed with brine, dried on activated Na_2SO_4, and concentrated in a rotary evaporator under reduced pressure at ambient temperature. The residue was purified by silica gel column chromatography using a suitable eluent to afford the desired product **5**.

*3,3′-(p-Tolylmethylene)bis(1H-indole) (**5a**):*[21] ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.22 (s, 3H), 5.74 (s, 1H), 6.47 (d, 2H, *J* = 1.5 Hz), 6.87−6.93 (m, 2H), 6.98 (d, *J* = 7.1 Hz, 2H), 7.03−7.14 (m, 4H), 7.20 (d, *J* = 7.1 Hz, 2H), 7.29 (d, *J* = 7.1 Hz, 2H), 7.65 (br s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 39.7, 111.0, 119.1, 119.8, 119.9, 121.8, 123.5, 127.0, 128.5, 128.9, 135.5, 136.6, 141.0.

*2,2-Bis(1H-indol-3-yl)-1-phenylethanone (**5b**).*[16g] The compound was prepared following GP-II employing indole (2.0 mmol), phenyl glyoxal (1.0 mmol), and $Cu(OTf)_2$ (5 mol %). Purification by column chromatography (DCM) afforded the title compound as a red solid (319 mg, 0.91 mmol, 91% yield): mp 200−202 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.51 (s, 1H), 6.88 (s, 2H), 7.09 (d, *J* = 7.2 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.38−7.43 (m, 2H), 7.50−7.57 (m, 3H), 8.07−8.12 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.1, 111.3, 114.2, 118.9, 119.7, 122.2, 124.0, 126.6, 128.6, 128.7, 128.8, 132.9, 136.5, 136.9, 198.6.

*2,2-Bis(5-bromo-1H-indol-3-yl)-1-phenylethanone (**5c**).* The compound was prepared following GP-II employing 5-bromoindole (2.0 mmol), phenyl glyoxal (1.0 mmol), and $Cu(OTf)_2$ (5 mol %). Purification by column chromatography (20% petroleum ether−EtOAc) afforded the title compound as a red solid (417 mg, 0.82 mmol, 82% yield): mp 98−100 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.28 (s, 1H), 6.52 (s, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 7.30−7.35 (m, 2H), 7.43−7.47 (m, 1H), 7.57 (s, 2H), 8.01 (d, *J* = 8.1 Hz, 2H), 8.30 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.2, 112.8, 112.9, 113.2, 121.2, 125.0, 125.4, 127.9, 128.8, 128.9, 133.5, 135.2, 136.1, 199.1; FT-IR (KBr, cm^{-1}) 794.0, 884.8, 1098.0, 1213.3, 1447.2, 1458.3, 1674.0, 2923.0, 3341.2, 3419.5; HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{17}Br_2N_2O$ [M + H] 506.9708, found 506.9734, 508.9737, 510.9964.

*2,2-Bis(5-methoxy-1H-indol-3-yl)-1-phenylethanone (**5d**).* The compound was prepared following GP-II employing 5-methoxyindole (2.0 mmol), phenyl glyoxal (1.0 mmol), and $Cu(OTf)_2$ (5 mol %). Purification by column chromatography (20% petroleum ether−EtOAc) afforded the title compound as a red solid (349 mg, 0.85 mmol, 85% yield): mp 172−174 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.72 (s, 6H), 6.37 (s, 1H), 6.67 (s, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.98 (s, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.49 (d, *J* = 6.9 Hz, 1H), 8.11 (d, *J* = 7.5 Hz, 2H), 8.23 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 42.4, 55.8, 101.0, 111.9, 112.2, 113.2, 125.1, 126.8, 128.6, 128.7, 121.8, 132.9, 136.9, 153.9, 199.2; FT-IR (KBr, cm^{-1}) 685.8, 787.6, 1024.4, 1076.1, 1169.2, 1175.3, 1210.4, 1246.7, 1290.1, 1450.3, 1486.5, 1668.4, 2930.4, 3334.1, 3419.0; HRMS (ESI-TOF) *m*/*z* calcd for $C_{26}H_{22}NaN_2O_3$ [M + Na] 433.1528, found 433.1529.

Procedure for the Synthesis of 4-(1*H*-Indol-3-yl)-3-phenyl-1-(trifluoromethyl)-9*H*-carbazol-2-yl)(phenyl)methanone (8a). To a mixture of indole (2.1 mmol), phenyl glyoxal (1 mmol), and $Cu(OTf)_2$ (5 mol %) was added dioxane (4 mL), and this mixture was heated at 80 °C for 15 min for in situ generation of 2,2-bis(1*H*-indol-3-yl)-1-phenylethanone (**5b**). 4,4,4-Trifluoro-1-phenylbutane-1,3-dione (1 mmol) and DMAP (1 mmol) were added and refluxed under an argon atmosphere for 10 h (Scheme 7).The reaction mixture was extracted with ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using 5% petroleum ether−EtOAc as an eluent to afford **8a** (403 mg, 0.76 mmol, 76% yield): deep yellow solid, mp 250−205 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.45 (d, *J* = 8.1 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 7.26−7.33 (m, 1H), 7.45−7.53 (m, 4H), 7.61−7.82 (m, 7H), 7.97−8.01 (m, 3H), 8.30 (q, *J* = 8.4 Hz, *J* = 12.0 Hz, 2H), 9.07 (s, 1H), 10.88 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 111.0, 119.6, 119.8, 121.5, 121.6, 122.2, 122.3, 125.67, 125.72, 125.9, 127.3, 127.9, 128.4, 128.7, 128.8 (q, ^1J = 240.5 Hz, CF_3), 129.1, 129.7, 130.0, 132.6, 138.4, 138.9, 139.6, 142.8, 142.9, 158.2, 198.0; FT-IR (KBr, cm^{-1}) 1225.4, 1101.9, 1610.8, 1634.6, 2852.8, 2924.4, 3402.9; HRMS (ESI-TOF) *m*/*z* calcd for due $C_{34}H_{22}F_3N_2O$ [M + H] 531.1684, found 531.1680.

General Procedure for Synthesis of 9a−i (GP-III). To a mixture of indole derivative (2.0 mmol), phenyl glyoxal (1.0 mmol) and $Cu(OTf)_2$ (5 mol %) was added dioxane (4 mL), and this mixture was stirred at 80 °C for 15 min to 2 h depending on the substrate. Next, active methylene compound (1.0 mmol) and DABCO (20 mol %) were added to the reaction mixture and refluxed for the specified time in air. The reaction mixture was extracted with ethyl acetate. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using the appropriate eluent to give the desired product.

*1-(12-Benzoyl-5,7-dihydroindolo[2,3-b]carbazol-6-yl)ethanone (**9a**).* The compound was prepared following GP-III employing phenyl glyoxal (1 mmol), indole (2.1 mmol) and acetylacetone (1 mmol). Purification by column chromatography (10% petroleum ether−EtOAc) afforded the title compound as a deep yellow solid (289 mg, 0.72 mmol, 72% yield): mp 210−212 °C dec; ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.11 (s, 3H), 6.98−7.03 (m, 2H), 7.30−7.38 (m, 4H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.66−7.79 (m, 3H), 7.96 (d, *J* = 7.2 Hz 2H), 11.64 (br s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 31.8, 103.9, 111.8, 113.7, 119.4, 120.0, 124.7, 128.9, 129.1, 132.0, 134.5, 135.0, 138.5, 140.3, 196.3, 197.3; FT-IR (KBr, cm^{-1}) 723.9, 1202.5, 1233.5, 1321.5, 1463.9, 1577.9, 1593.2, 1642.5, 2853.4, 2924.3, 3342.3, 3390.3; HRMS (ESI-TOF) *m*/*z* calcd for $C_{27}H_{18}N_2NaO_2$ [M + Na] 425.1266, found 425.1264.

*(5,7-Dihydroindolo[2,3-b]carbazole-6,12-diyl)bis-(phenylmethanone) (**9b**).* The compound was prepared following GP-III employing phenyl glyoxal (1 mmol), indole (2.1 mmol), and 1,3-diphenylpropane-1,3-dione (1 mmol). Purification by column chromatography (10% petroleum ether−EtOAc) afforded the title compound as a deep yellow solid (334 mg, 0.74 mmol, 74% yield): mp 178−180 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.01−7.07 (m, 2H), 7.26−7.31 (m, 4H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.53−7.56 (m, 2H), 7.59−7.66 (m, 3H), 7.71−7.74 (m, 1H), 7.82−7.86 (m, 2H), 8.12 (d, *J* = 7.5 Hz, 2H), 9.31 (br s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 102.3, 110.8, 115.3, 120.6, 121.3, 121.4, 125.5, 128.0, 129.3, 129.5, 130.1, 132.3, 134.3, 134.6, 136.0, 139.6, 140.1, 140.9, 195.3, 197.6; FT-IR (KBr, cm^{-1}) 687.3, 707.0, 968.6, 727.5, 746.9, 1214.1, 1235.9, 1321.1, 1449.1, 1460.2, 1595.4, 1630.4, 1668.1, 2852.2, 2922.8, 3362.3, 3445.7; HRMS (ESI-TOF) *m*/*z* calcd for $C_{32}H_{21}N_2O_2$ [M + H] 465.1603, found 465.1596.

*(2,10-Dibromo-5,7-dihydroindolo[2,3-b]carbazole-6,12-diyl)bis-(phenylmethanone) (**9c**).* The compound was prepared following GP-III employing phenyl glyoxal (1 mmol), 5-bromoindole (2.1 mmol), and 1,3-diphenylpropane-1,3-dione (1 mmol). Purification by column chromatography (20% petroleum ether−EtOAc) afforded the title compound as a deep yellow solid (404 mg, 0.65 mmol, 65% yield): mp 300−303 °C dec; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.49−7.55 (m, 5H), 7.64 (t, *J* = 7.5 Hz, 5H), 7.78−7.81 (m, 2H), 7.99−8.05 (d, *J* =

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7.5 Hz, 2H), 8.11 (d, J = 7.2 Hz, 2H), 11.53 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 103.6, 110.7, 112.9, 113.2, 121.8, 122.0, 127.4, 128.0, 128.5, 128.7, 129.1, 129.3, 129.5, 133.3, 134.85, 134.94, 136.8, 138.4, 139.3, 193.0, 196.8; FT-IR (KBr, cm^{-1}) 974.9, 1232.8, 1284.1, 1459.1, 1595.9, 1627.6, 1666.2, 2852.3, 2923.2, 3417.5; HRMS (ESI-TOF) m/z calcd for $C_{32}H_{19}Br_2N_2O_2$ [M + H] 620.9813, found 620.9805, 622.9797, 624.9771.

*Ethyl 12-Benzoyl-5,7-dihydroindolo[2,3-b]carbazole-6-carboxylate (**9d**).*[16g] The compound was prepared following GP-III employing phenyl glyoxal (1 mmol), indole (2.1 mmol), and diethyl malonate (1 mmol). Purification by column chromatography (8% petroleum ether−EtOAc) afforded the title compound as a deep yellow solid (285 mg, 0.66 mmol, 66% yield): ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.57 (t, J = 7.2 Hz, 3H), 4.75 (q, J = 6.9 Hz, 14.1 Hz, 2H), 7.00−7.05 (m, 2H), 7.33−7.39 (m, 4H), 7.54 (t, J = 7.5 Hz, 2H), 7.69−7.81 (m, 3H), 7.98 (d, J = 7.2 Hz, 2H), 11.57 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 14.3, 60.3, 93.6, 111.7, 113.1, 119.1, 119.3, 120.1, 124.7, 128.9, 129.1, 131.6, 134.5, 135.0, 138.9, 140.0, 165.6, 197.2; FT-IR (KBr, cm^{-1}) 695.4, 729.2, 1176.5, 1193.0, 1245.1, 1325.0, 1460.8, 1602.4, 1661.6, 1685.9, 2852.9, 2923.9, 3416.7.

*(2,10-Dimethoxy-5,7-dihydroindolo[2,3-b]carbazole-6,12-diyl)-bis(phenylmethanone) (**9e**).* The compound was prepared following GP-III employing phenyl glyoxal (1 mmol), 5-methoxyindole (2.1 mmol), and 1,3-diphenylpropane-1,3-dione (1 mmol). Purification by column chromatography (10% petroleum ether−EtOAc) afforded the title compound as a deep yellow solid (356 mg, 0.68 mmol, 68% yield): mp 246−248 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.63 (s, 6H), 6.92 (dd, J = 2.1 Hz, 9.0 Hz, 2H), 7.02 (s, 2H), 7.20 (d, J = 8.7 Hz, 1H), 7.47 (t, J = 7.5 Hz, 3H), 7.63 (t, J = 7.2 Hz, 4H), 7.82 (d, J = 6.9 Hz, 2H), 8.12 (d, J = 7.8 Hz, 2H), 9.18 (br s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.7, 102.1, 104.7, 111.3, 114.0, 115.1, 121.8, 127.8, 129.3, 129.4, 129.9, 132.1, 134.3, 134.6, 136.1, 140.8, 154.2, 195.1, 197.8; FT-IR (KBr, cm^{-1}) 687.7, 1039.6, 1204.7, 1482.6, 1588.2, 2853.2, 2924.3, 3334.2, 3434.3; HRMS (ESI-TOF) m/z calcd for $C_{34}H_{25}N_2O_4$ [M + H] 525.1814, found 525.1852.

*Methyl 12-Benzoyl-5,7-dihydroindolo[2,3-b]carbazole-6-carboxylate (**9f**).* The compound was prepared following GP-III employing phenyl glyoxal (1 mmol), indole (2.1 mmol), and dimethyl malonate (1 mmol). Purification by column chromatography (10% petroleum ether−EtOAc) afforded the title compound as a deep yellow solid (280 mg, 0.67 mmol, 67% yield): mp 200−202 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 4.23 (s, 3H), 7.04 (t, J = 7.5 Hz, 2H), 7.35−7.41 (m, 4H), 7.56 (t, J = 7.7 Hz, 2H), 7.74−7.82 (m, 3H), 8.0 (d, J = 3.6 Hz, 2H), 11.67 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 51.6, 93.4, 111.7, 113.2, 119.2, 119.4, 120.1, 124.8, 128.1, 128.8, 129.0, 129.1, 132.4, 134.5, 135.0, 138.9, 140.1, 166.1, 197.3; FT-IR (KBr, cm^{-1}) 685.3, 729.0, 1082.8, 1173.9, 1206.1, 1245.1, 1324.5, 1601.5, 1659.6, 1687.7, 2852.8, 2923.7, 3416.3, 3433.2; HRMS (ESI-TOF) m/z calcd for $C_{27}H_{18}N_2NaO_3$ [M + Na] 441.1215, found 441.1213.

*1-(12-Benzoyl-5,7-dihydroindolo[2,3-b]carbazol-6-yl)propan-1-one (**9g**).* The compound was prepared following GP-III employing phenyl glyoxal (1 mmol), indole (2.1 mmol), and heptane-3,5-dione (1 mmol). Purification by column chromatography (10% petroleum ether−EtOAc) afforded the title compound as a deep yellow solid (295 mg, 0.71 mmol, 71% yield): mp 280−282 °C dec; ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.09−1.14 (m, 3H), 3.01−3.05 (m, 2H), 6.88−6.93 (m, 2H), 7.16−7.21 (m, 2H), 7.31−7.41 (m, 6H), 7.56 (t, J = 7.5 Hz, 1H), 7.99 (d, J = 7.5 Hz, 2H), 10.09 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 7.5, 36.9, 103.3, 111.0, 114.9, 120.4, 120.7, 120.9, 125.2, 129.2, 130.0, 132.6, 134.7, 135.8, 139.3, 139.8, 198.93, 198.99; FT-IR (KBr, cm^{-1}) 733.8, 1152.3, 1239.9, 1320.5, 1464.4, 1593.9, 1644.7, 2923.9, 3335.4, 3389.4; HRMS (ESI-TOF) m/z calcd for $C_{28}H_{21}N_2O_2$ [M + H] 417.1603, found 417.1576.

*12-Benzoyl-5,7-dihydroindolo[2,3-b]carbazole-6-carbonitrile (**9h**).* The compound was prepared following GP-III employing phenyl glyoxal (1 mmol), indole (2.1 mmol), and malononitrile (1 mmol). Purification by column chromatography (15% petroleum ether−EtOAc) afforded the title compound as a deep yellow solid (262 mg, 0.68 mmol, 68% yield): mp 290−296 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.76−5.81 (m, 2H), 6.09−6.14 (m, 4H), 6.26−6.35 (m, 4H), 6.47 (t, J = 7.5 Hz, 2H), 6.72 (d, J = 7.5 Hz, 1H), 11.14 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 74.2, 111.2, 112.9, 115.2, 119.5, 119.6, 120.4, 125.2, 129.0, 129.1, 131.3, 134.6, 134.8, 140.1, 140.4, 196.7; FT-IR (KBr, cm^{-1}) 731.3, 1248.0, 1327.7, 1462.3, 1608.6, 1644.5, 2221.5, 2923.5, 3287.3, 3435.7; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{16}N_3O$ [M + H] 386.1293, found 386.1322.

*12-Benzoyl-N-phenyl-5,7-dihydroindolo[2,3-b]carbazole-6-carboxamide (**9i**).* The compound was prepared following GP-III employing phenyl glyoxal (1 mmol), indole (2.1 mmol), and *N*,*N*-diphenylmalonamide (1 mmol). Purification by column chromatography (8% petroleum ether−EtOAc) afforded the title compound as a deep yellow solid (311 mg, 0.65 mmol, 65% yield): mp 80−82 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.01 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 7.33−7.52 (m, 6H), 7.58 (t, J = 7.5 Hz, 2H), 7.66 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 7.2 Hz, 1H), 8.01 (d, J = 4.5 Hz, 4H), 10.79 (s, 1H), 11.58 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 101.2, 111.1, 113.4, 118.5, 119.5, 120.1, 120.3, 123.1, 124.6, 127.8, 128.0, 128.3, 128.9, 129.0, 134.2, 135.4, 136.8, 139.1, 140.4, 164.1, 197.6; FT-IR (KBr, cm^{-1}) 689.9, 739.1, 1245.2, 1322.3, 1439.4, 1462.3, 1501.1, 1596.0, 1644.0, 2851.6, 2922.0, 3361.8; HRMS (ESI-TOF) m/z calcd for $C_{32}H_{22}N_3O_2$ [M + H] 480.1712, found 480.1715.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02689.

Materials and methods, optimization table, general procedures, characterization data for all compounds, ^{1}H and ^{13}C spectra of the new compounds, single-crystal XRD data, and mid-IR-ATR data and spectra (PDF)

Single-crystal XRD data (CIF)

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Notes

The authors declare no competing financial interest.

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