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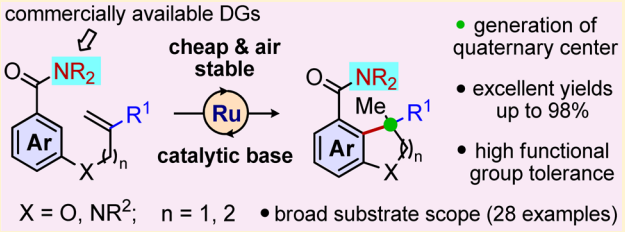
Ruthenium-Catalyzed Intramolecular Hydroarylation of Arenes and Mechanistic Study: Synthesis of Dihydrobenzofurans, Indolines, and Chromans

Raja K. Rit,* Koushik Ghosh, Rajib Mandal, and Akhila K. Sahoo*

School of Chemistry, University of Hyderabad, Hyderabad 500046, India

Supporting Information

ABSTRACT: A ruthenium-catalyzed, amide-directed intramolecular hydroarylation of alkene-tethered benzamide derivatives is discussed. This method proficiently constructs dihydrobenzofuran, indoline, and chroman skeletons of biological significance in good to excellent yields; the overall process is atom-economical and step-efficient. The reaction exhibits broad scope, tolerating common functional groups, labile protecting units, and heteroaryl motifs. The use of a catalytic amount of base suffices the need. Deuterium scrambling and kinetic studies offer valuable facts for understanding the reaction mechanism.



INTRODUCTION

Murai's discovery of directing group (DG)-aided Ru-catalyzed C−C bond formation of aromatic ketones fuelled a surge in the development of novel transition-metal-catalyzed (TMC) synthetic regimes for the direct functionalization of unactivated C−H bonds, which are ubiquitous.[1,2] These elegant manifestations surface in bringing the step- and atom-efficient construction of versatile molecular architectures from simple precursors.[3] In particular, the intramolecular functionalization of C−H bonds of the heteroatom bearing scaffolds proficiently manufactures heterocyclic motifs, adequately infusing regioselectivity in the molecule.[4] Therefore, realization of such synthetic manifolds would coherently add value to the rapidly progressing paradigm of C−H activation, which eventually would be useful for the construction of versatile heterocycle motifs.

Dihydrobenzofuran and indoline skeletons are invariably found in various biologically and pharmaceutically important molecules, such as lithospermic acid, ramelteon, etc. (Figure 1).[5] Of note, the intramolecular hydroarylation of heteroatom (O/N) bearing olefin-tethered arenes effectively delivers medium-ring-sized heterocycles. In this regard, Ellman and Bergman's group first demonstrated the Rh-catalyzed aldimine-directed C−H hydroarylation of olefin-tethered arenes to yield various carbo/heterocycles (Figure 2A).[6] The Rovis,[7] Cramer,[8] and Yoshikai[9] groups have independently developed the Rh- and Co-catalyzed hydroarylation of arenes (Figure 2A). Recently, we demonstrated an efficient Ru-catalyzed intramolecular hydroarylation of methylphenylsulfoximine (prepared from thioanisole) DG-enabled benzoic acid derivatives with olefins for the first time.[10] It therefore becomes apparent to survey the identical reaction in a readily accessible common amide derivative, employed for various intermolecular C−H functionalizations,[11] under the cost-effective and air-stable Ru catalysis,[12−14] which is so far unprecedented. To broaden the synthetic potential and the utility of the Ru-catalyzed

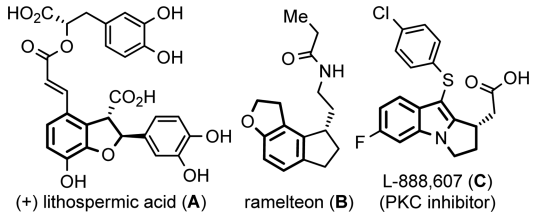


Figure 1. Biologically active and drug molecules.

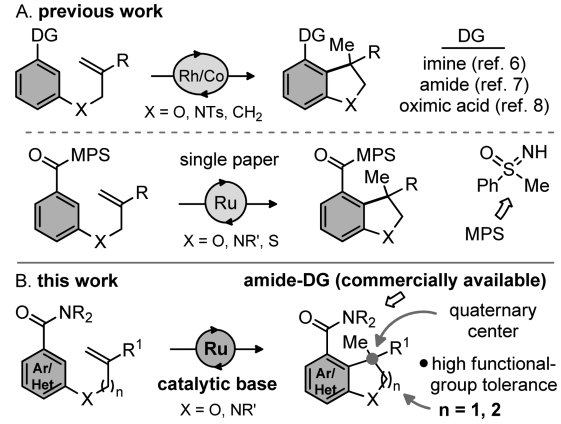


Figure 2. Intramolecular hydroarylation reactions.

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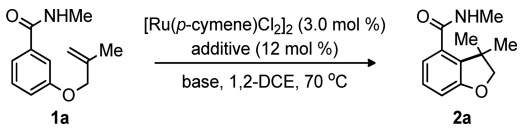
intramolecular hydroarylation of arenes, we herein report *N*-alkylamide-directed hydroarylation reaction of the O/N-tethered olefin bearing arenes for the construction of dihydrobenzofurans, indolines, and chromans. The isotopic labeling and kinetic experiments offer insightful data for deducing the reaction mechanism.

RESULTS AND DISCUSSION

The investigation of amide-directed intramolecular hydroarylation was initiated by submitting **1a** to $[Ru(p\text{-cymene})Cl_2]_2$ (3.0 mol %) and $AgSbF_6$ (12 mol %) in $ClCH_2CH_2Cl$ (1,2-DCE) (Table 1); we were pleased to notice the formation of

Table 1. Optimization of Reaction Parameters[a]



1a **2a**

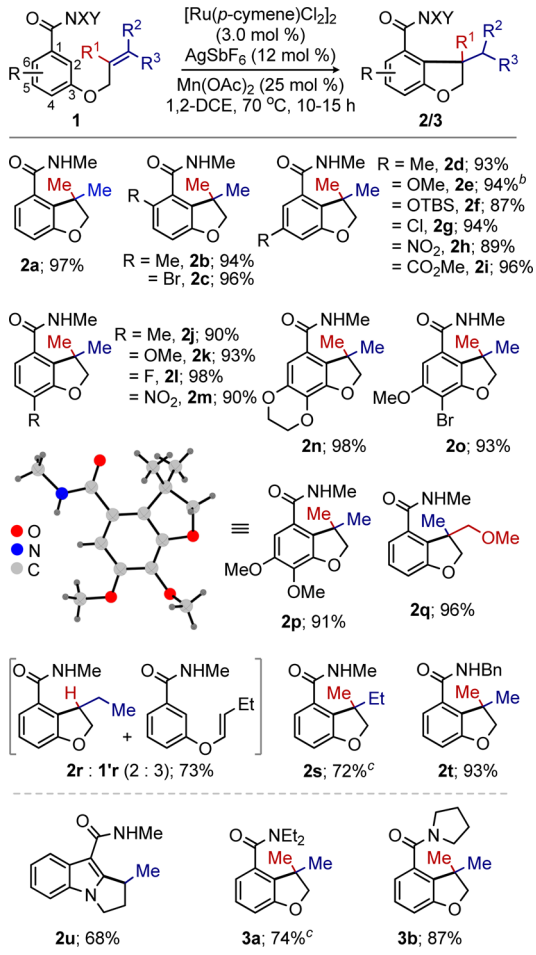
entry	additive (12 mol %)	base (1.0 equiv)	yield of **2a** (%)
1	$AgSbF_6$		<5[b]
2	$AgSbF_6$	$Cu(OAc)_2$	68
3	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	56
4	$AgSbF_6$	KOAc	36
5	$AgSbF_6$	NaOAc	21
6	$AgSbF_6$	$Zn(OAc)_2$	92
7	$AgSbF_6$	$Mn(OAc)_2$	98
8	$AgBF_4$	$Mn(OAc)_2$	<10[b]
9	KPF_6	$Mn(OAc)_2$	nr
10	$NaPF_6$	$Mn(OAc)_2$	nr
11[c]	$AgSbF_6$	$Mn(OAc)_2$	96
12[d]	**$AgSbF_6$**	**$Mn(OAc)_2$**	**96**
13[e]	$AgSbF_6$	$Mn(OAc)_2$	74
14[f]	$AgSbF_6$	$Mn(OAc)_2$	72

[a]Reactions were carried out with **1a** (50 mg, 0.24 mmol), Ru catalyst (3.0 mol %), additive (12 mol %), base (1.0 equiv) in $ClCH_2CH_2Cl$ (1,2-DCE) at 70 °C for 5 h. [b]^1H NMR yield. [c]50 mol % of $Mn(OAc)_2$, 5 h. [d]25 mol % of $Mn(OAc)_2$, 10 h. [e]10 mol % of $Mn(OAc)_2$, 20 h. [f]In the presence of AcOH (1.0 equiv); nr = no reaction.

the expected dihydrobenzofuran **2a** even in a trace amount (entry 1). Interestingly, the introduction of $Cu(OAc)_2$ (1.0 equiv) in combination with Ru catalyst enhanced the reactivity, producing 68% of **2a** in 5 h (entry 2), indicating the role of base in this transformation. Other acetate bearing bases were moderate (entries 3−5); in contrast, $Zn(OAc)_2$ and $Mn(OAc)_2$ worked remarkably well, affording 92 and 98% of **2a**, respectively (entries 6 and 7). The additives $AgBF_4$, KPF_6, and $NaPF_6$ instead of $AgSbF_6$ were found to be inferior (entries 8−10). The exceptional efficiency of $AgSbF_6$ over $AgBF_4$ is not clear to us; presumably, the SbF_6^- anion in the active catalyst $[Ru^{II}(p\text{-cymene})OAc]^+[SbF_6]^-$ plays a vital role for the better outcome. The reaction was equally efficient when a catalytic amount of $Mn(OAc)_2$ (50 and 25 mol %) was used, although the reaction took a little longer time for completion (entries 11 and 12). The role of $Mn(OAc)_2$ in this C−H hydroarylation was not known and yet to be established; we believe that $Mn(OAc)_2$ or $Zn(OAc)_2$ presumably facilitates the formation of the active catalyst $[Ru(p\text{-cymene})(OAc)]^+$ in the reaction. Use of $Mn(OAc)_2$ (10 mol %) provided 74% of **2a** in 20 h (entry 13). The reaction in the presence of AcOH (1.0 equiv), an acetate as well as proton donor, produced 72% of **2a** (entry 14). Thus, the catalytic conditions in entry 12 were considered to be optimum for the amide-directed intramolecular hydroarylation reaction.

The scope of the present Ru-catalyzed intramolecular hydroarylation was surveyed on benzamides **1** under the optimized conditions in entry 12, Table 1, and the results are displayed in Scheme 1. Compound **2a** was isolated in 97% yield

Scheme 1. Hydroarylation of Benzamides[a]



[a]Reaction conditions: **1** (0.3 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.0 mol %), $AgSbF_6$ (12 mol %), $Mn(OAc)_2$ (25 mol %), 1,2-DCE (1.0 mL) at 70 °C for 10−15 h. [b]Reaction was continued for 18 h. [c]Reaction at 100 °C.

from **1a**. The 6-Me (**1b**) and 6-Br (**1c**) bearing substrates, even though being sterically encumbered, smoothly produced **2b** and **2c** in excellent yields. Gratifyingly, the electron perturbation of arenes in terms of electron-donating (Me, OMe, OTBS; **1d−f**) as well as electron-withdrawing (halo, nitro, ester; **1g−i**) substitution did not hamper the reaction efficiency, constructing **2d−i** in lucrative yields (87−96%). Notably, the labile OTBS group in **2f** survived; the directing ability of the ester moiety (**2i**) for the respective hydroarylation was unsuccessful under the catalytic conditions.[2g] Likewise, highly peripherally decorated dihydrobenzofurans **2j−p** were fabricated from the benzamides **1j−p** having substituents at the 4- or 4,5-position on arene in excellent yield. The structure of **2p** was unambiguously characterized by X-ray crystallographic study (Scheme 1).[15] Other terminal olefins (e.g., methoxymethyl bearing compound **1q**) gave the desired **2q** (96%). An inseparable mixture of **2r** and the isomerized arylvinyl ether

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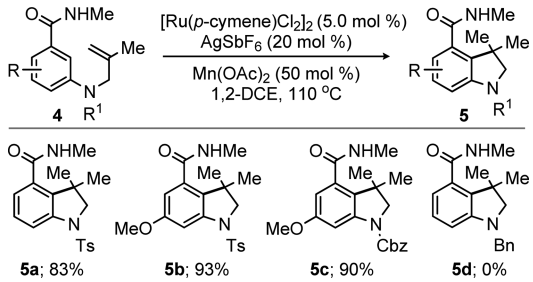
1′r was obtained from the hydroarylation of the internal alkene bearing **1r**.[15] The trisubstituted internal alkene in **1s** also participated, yielding 72% of **2s**. The *N*-benzylamide bearing dihydrobenzofuran **2t** was prepared in 93% yield. The current manifestation consequently featured accessing wide arrays of highly functionalized dihydrobenzofurans from the benzamide derivatives.

Interestingly, the indole skeleton successfully participated in the hydroarylation, producing indole-fused pyrrolidine **2u** (68%), which was otherwise difficult to access (Scheme 1). In general, the acidic N−H moiety of the amide DG is indispensable in TMC C−H activation.[11c,d] We thus turned our attention to investigate the directing ability of tertiary amides in this intramolecular hydroarylation reaction (Scheme 1). Gratifyingly, the tertiary amides (**1v,w**; Et_2N, pyrrolidinyl) effectively supported the hydroarylation reaction to yield **3a** (74%) and **3b** (87%) (Scheme 1).

The successful exhibition of hydroarylation of 3-*O*-tethered olefin bearing arene amides motivated us to probe the identical reactions with the *N*-tethered olefin substrates. Thus, subjecting the 3-N-Ts/Cbz-protected tethered olefin bearing benzamides **4a−c** to the optimized catalytic conditions in the presence of $Mn(OAc)_2$ (50 mol %) at 110 °C successfully provided the desired indolines **5a−c** in appreciable yields (83−93%; Scheme 2). Disappointingly, the N-Bn-protected benzamide **4d** did not

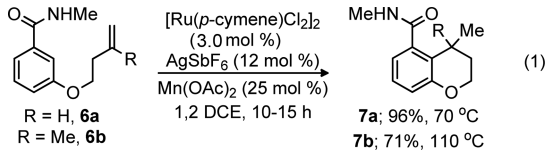
Scheme 2. Synthesis of Indolines[a]



[a]Reaction conditions: **4** (0.3 mmol), Ru catalyst (5.0 mol %), Ag salt (20 mol %), $Mn(OAc)_2$ (50 mol %) in DCE (3.0 mL) at 110 °C for 20−24 h.

deliver the product **5d**; presumably the coordination ability of the lone pair of N-Bn to Ru species hampers the C−H activation.

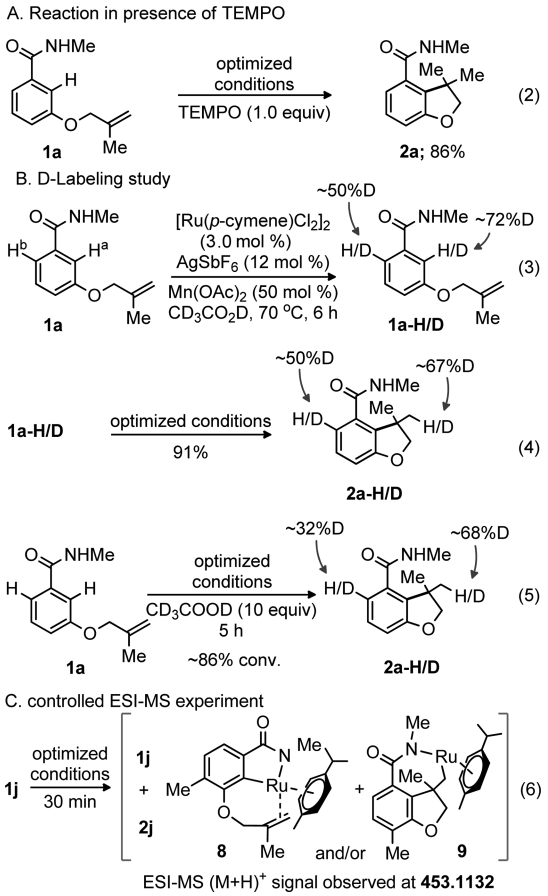
Next, we explored scrutinizing the hydroarylation of 3-*O*-homoallyl-tethered benzamides; this would ultimately lead to chromans (eq 1), an important pharmacophore present in



various biologically active molecules.[16] Pleasingly, the corresponding chroman derivatives **7a** (96%) and **7b** (71%) were reliably synthesized from **6a** and **6b**, respectively, under the optimized reaction conditions. To the best of our knowledge, Ru-catalyzed amide-group-assisted functionalization of C−H bonds for the construction of chroman derivatives is shown for the first time. This preliminary result would find broad synthetic potential for the efficient fabrication of novel chroman derivatives.

To gain insight into the probable mechanistic pathways involved in the DG-promoted Ru-catalyzed hydroarylation reaction, various control experiments, deuterium labeling, and Hammett studies were designed and performed. Interestingly, Ru-catalyzed hydroarylation of **1a** in the presence of TEMPO smoothly delivered **2a** in 86% yield, consequently refuting the possible participation of stable radical species in this reaction (eq 2; Scheme 3A).[17] To understand the preference of site-

Scheme 3. Mechanistic Studies



selective cyclometalation, compound **1a** was subjected to the hydroarylation conditions in CD_3CO_2D for 6 h. The incorporation of deuterium at both *ortho*-positions of the compound **1a** (eq 3, Scheme 3B) undoubtedly suggests the reversible cleavage of the *o*-C−H bond, which generally occurs via a base-mediated concerted metalation−deprotonation pathway under the Ru-catalyzed conditions.[11c,17] The incorporation of D into the *o*-C−H^a bond (72%) over the *o*-C−H^b bond (50%) in **1a-H/D** undoubtedly advocates the assistance of a tethered olefin moiety for the facile activation of a *o*-C−H^a bond (eq 3, Scheme 3B). Interestingly, the hydroarylation of H/D scrambled products **1a-H/D** under the hydroarylation conditions produced **2a-H/D** (eq 4, Scheme 3B). As hypothesized, a significant incorporation of 67% of D to 3-methyl (CH_2−D) in **2a-H/D** was observed, almost transposing the *o*-C−D to 3-methyl (CH_2−D) (eq 4, Scheme 3B). Moreover, 68% of D was incorporated in the newly generated 3-methyl moiety of dihydrobenzofuran **2a-H/D** upon hydroarylation of **1a** under optimized conditions in the presence of CD_3CO_2D (10.0 equiv) (eq 5, Scheme 3B). Presumably, the AcOD and AcOH generated during reversible activation of

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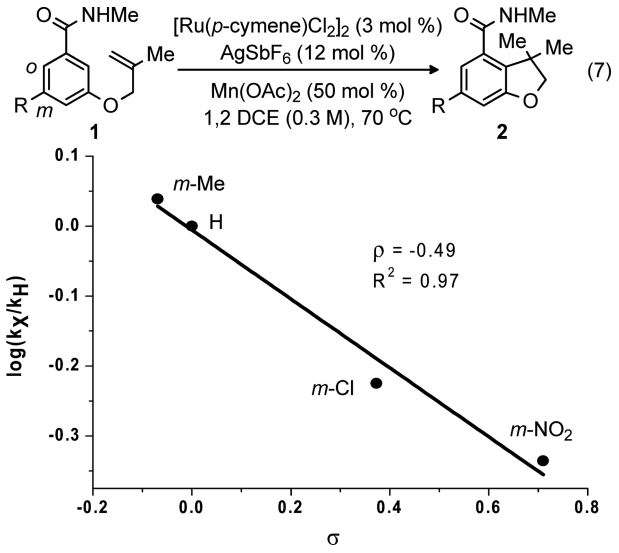
both *o*-C−H[a] and *o*-C−H[b] bond is accountable for the incorporation of both D and H in the newly generated 3-methyl group in the 2,3-dihydrobenzofuran product in the proto-demetalation process. These results explicitly support the involvement of a proto-demetalation.[18] The ESI-MS studies were exhibited in **1j** under the optimized conditions within 30 min; the appearance of a signal at 453.1132 clearly indicated the presence of ruthenium complex **8** and/or **9** (eq 6, Scheme 3C).[15] We thus surmise that the species **8** and/or **9** is liable for the delivery of the desired hydroarylation product.

The Hammett study was next executed in various benzamides having *meta*-substitution in arenes to understand and generalize the electronic substituent effect on this hydroarylation (eq 7, Scheme 4).[19] The negative reaction

Scheme 4. Hammett Analysis



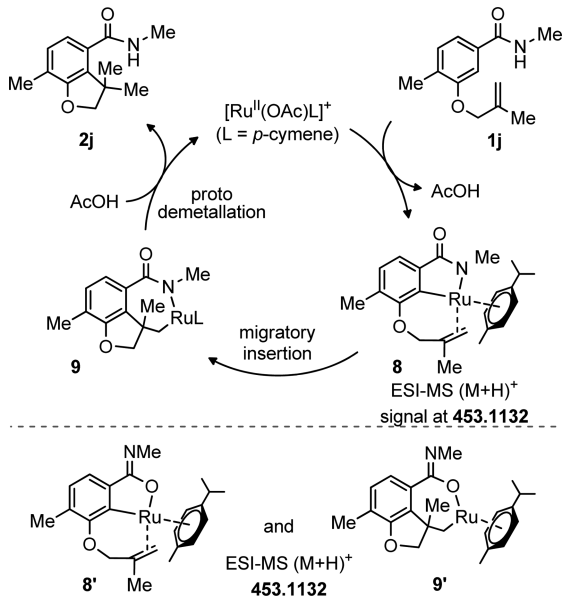
constant value (ρ = −0.49) clearly reflects the occurrence of electron dispersion away from the ring in the rate-limiting step. However, the lower amplitude of ρ value and appropriate fitting of σ_m values with respect to the amide DG in the Hammett plot suggest a probable non-rate-determining C−H activation. Consequently, we speculate the electron-donating group on arene in benzamide derivatives would facilitate the hydroarylation process; the result in Scheme 4 agrees consistently with the fact.

On the basis of the above mechanistic investigations and literature support, a probable reaction pathway for this amide-directed intramolecular hydroarylation is outlined in Scheme 5.[20] The active catalyst, generated from $[RuCl_2(p\text{-cymene})]_2$, $AgSbF_6$, and $Mn(OAc)_2$, coordinates to the amide DG and activates the *o*-C−H bonds to produce cyclometalated complex **8** (eq 6; detected by ESI-MS).[15] However, we cannot rule out the participation of amide oxygen as the DG, as shown in **8′** and **9′** (Scheme 5), in this reaction. The additional interaction of oxygen-tethered olefin to the metal probably facilitates the activation of the sterically hindered C−H bond. Finally, the migratory insertion and proto-demetalation produce the desired product **2**.

CONCLUSION

In conclusion, a novel and efficient Ru-catalyzed hydroarylation of arenes is demonstrated with the aid of a commercially

Scheme 5. Probable Mechanism



available amide DG for the first time. The reaction exhibits broad scope, manufacturing dihydrobenzofurans and indolines. Deuterium scrambling experiments and Hammett studies offer insightful information about the reaction mechanism. The hydroarylation of the *O*-homoallyl-tethered compound for the synthesis of chromans is revealed. Effort to achieve the stereoselective hydroarylation of unactivated C−H bonds is currently underway.

EXPERIMENTAL SECTION

General Information. All the reactions were performed in an oven-dried Schlenk flask. Commercial grade solvents were distilled prior to use. Column chromatography was performed using 100−200 mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel GF254 plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over an I_2 chamber. Proton, carbon, and fluorine nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR, and ^{19}F NMR) were recorded based on the resonating frequencies as follows: ^{1}H NMR, 400 MHz; ^{13}C NMR, 101 MHz; ^{19}F NMR, 376 MHz and ^{1}H NMR, 500 MHz; ^{13}C NMR, 126 MHz; ^{19}F NMR, 470 MHz having the solvent resonance as internal standard (^{1}H NMR, $CDCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; bs = broad singlet; d = doublet; bd = broad doublet, t = triplet; bt = broad triplet; q = quartet; m = multiplet), coupling constants, *J*, in hertz, and integration. Data for ^{13}C NMR and ^{19}F NMR were reported in terms of chemical shift (ppm). IR spectra were reported in cm^{-1}. High-resolution mass spectra were obtained in ESI mode. Melting points were determined by electrothermal heating and are uncorrected. X-ray data were collected at 298 K using graphite monochromated Mo Kα radiation (0.71073 Å).

Preparation of *N*-Alkylbenzamide Derivatives (1,4, and 6): General Procedure (GP-1). Following the known procedure, the desired *N*-alkylbenzamide derivatives were prepared from the corresponding benzoic acids in excellent yield (80−95%) and subsequently used for the hydroarylation reaction.[7a,10]

*N-2-Dimethyl-5-((2-methylallyl)oxy)benzamide (**1b**):* Colorless solid; mp = 115−116 °C; R_f = 0.39 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 2.8 Hz, 1H), 6.84 (dd, *J* = 8.4, 2.8 Hz, 1H), 5.88 (bs, 1H), 5.05 (s, 1H), 4.96 (s, 1H), 4.38 (s, 2H), 3.04 (dd, *J* = 1.6, 4.8 Hz, 3H), 2.32 (s, 3H), 1.80 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.5, 156.4, 140.6,

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137.1, 131.7, 127.6, 116.0, 113.2, 112.5, 71.7, 26.4, 19.2, 18.6; IR (neat) ν_{max} 3282, 1632, 1539, 1320, 1243, 1167, 1068, 805 cm^{-1}; HRMS (ESI) for $C_{13}H_{18}NO_2$ $(M + H)^+$ calcd 220.1332, found 220.1334.

*2-Bromo-N-methyl-5-((2-methylallyl)oxy)benzamide (**1c**):* Colorless solid; mp = 145−146 °C; R_f = 0.19 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.8 Hz, 1H), 7.08 (d, J = 2.8 Hz, 1H), 6.82 (dd, J = 8.8, 3.2 Hz, 1H), 6.12 (bs, 1H), 5.05 (s, 1H), 4.98 (s, 1H), 4.40 (s, 2H), 2.99 (d, J = 4.8 Hz, 3H), 1.79 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.9, 158.0, 140.1, 138.3, 134.1, 118.3, 115.7, 113.1, 109.4, 72.0, 26.7, 19.2; IR (neat) ν_{max} 3320, 1638, 1600, 1545, 1397, 1156, 904, 821 cm^{-1}; HRMS (ESI) for $C_{12}H_{14}BrNNaO_2$ $(M + Na)^+$ calcd 306.0100, found 306.0114.

*N-3-Dimethyl-5-((2-methylallyl)oxy)benzamide (**1d**):* Colorless viscous liquid; R_f = 0.32 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 1H), 7.11 (s, 1H), 6.82 (s, 1H), 6.60 (bs, 1H), 5.04 (s, 1H), 4.94 (s, 1H), 4.38 (s, 2H), 2.94 (d, J = 4.8 Hz, 3H), 2.28 (s, 3H), 1.78 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.3, 158.8, 140.5, 139.5, 135.7, 119.8, 118.7, 112.6, 110.1, 71.6, 26.7, 21.3, 19.3; IR (neat) ν_{max} 3315, 3079, 2915, 1643, 1594, 1320, 1063 cm^{-1}; HRMS (ESI) for $C_{13}H_{18}NO_2$ $(M + H)^+$ calcd 220.1332, found 220.1343.

*3-Methoxy-N-methyl-5-((2-methylallyl)oxy)benzamide (**1e**):* Colorless viscous liquid; R_f = 0.26 (1:1 hexane/EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 6.89 (t, J = 1.7 Hz, 1H), 6.88 (t, J = 1.7 Hz, 1H), 6.58−6.53 (m, 1H), 6.49 (bs, 1H), 5.05 (s, 1H), 4.96 (s, 1H), 4.39 (s, 2H), 3.76 (d, J = 1.5 Hz, 3H), 2.94 (dd, J = 4.7, 1.2 Hz, 3H), 1.78 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 168.1, 160.7, 159.8, 140.4, 136.7, 112.8, 105.6, 104.8, 104.1, 71.8, 55.4, 26.8, 19.3; IR (KBr) ν_{max} 3320, 3079, 2942, 1588, 1352, 1160, 1062 cm^{-1}; HRMS (ESI) for $C_{13}H_{18}NO_3$ $(M + H)^+$ calcd236.1281, found 236.1290.

*3-((tert-Butyldimethylsilyl)oxy)-N-methyl-5-((2-methylallyl)oxy)-benzamide (**1f**):* Colorless viscous liquid; R_f = 0.45 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 6.93 (t, J = 1.8 Hz, 1H), 6.78 (t, J = 1.6 Hz, 1H), 6.52 (t, J = 2.2 Hz, 1H), 6.11 (bs, 1H), 5.08 (s, 1H), 4.98 (s, 1H), 4.42 (s, 2H), 2.98 (d, J = 5.2 Hz, 3H), 1.81 (s, 3H), 0.97 (s, 9H), 0.20 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.0, 159.9, 156.8, 140.5, 136.7, 112.9, 111.2, 109.9, 106.4, 71.9, 26.8, 25.6 (3C), 19.3, 18.1, −4.4 (2C); IR (KBr) ν_{max} 3331, 2958, 2849, 1589, 1435, 1156, 832 cm^{-1}; HRMS (ESI) for $C_{18}H_{30}NO_3Si$ $(M + H)^+$ calcd 336.1989, found 336.1996.

*3-Chloro-N-methyl-5-((2-methylallyl)oxy)benzamide (**1g**):* Colorless solid; mp = 90−91 °C; R_f = 0.39 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.30−7.25 (m, 1H), 7.24 (dd, J = 2.4, 1.6 Hz, 1H), 7.01 (t, J = 2.2 Hz, 1H), 6.49 (bs, 1H), 5.07 (s, 1H), 5.00 (s, 1H), 4.43 (s, 2H), 2.98 (d, J = 4.8 Hz, 3H), 1.81 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.9, 159.5, 139.9, 137.1, 135.0, 119.1, 118.0, 113.2, 111.9, 72.0, 26.9, 19.3; IR (KBr) ν_{max} 3369, 3315, 3084, 2931, 1654, 1578, 1545, 1243, 1008, 673 cm^{-1}; HRMS (ESI) for $C_{12}H_{15}ClNO_2$ $(M + H)^+$ calcd 240.0785, found 240.0791.

*N-Methyl-3-((2-methylallyl)oxy)-5-nitrobenzamide (**1h**):* Pale yellow solid; mp = 158−159 °C; R_f = 0.19 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 1.6 Hz, 1H), 7.81 (t, J = 2.2 Hz, 1H), 7.74−7.69 (m, 1H), 6.81 (bs, 1H), 5.09 (s, 1H), 5.02 (s, 1H), 4.51 (s, 2H), 3.02 (d, J = 4.8 Hz, 3H), 1.81 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.8, 159.4, 148.9, 139.3, 136.9, 120.2, 113.8, 113.5, 112.1, 72.5, 27.0, 19.2; IR (KBr) ν_{max} 3282, 3101, 2926, 1632, 1528, 1336, 1073, 887 cm^{-1}; HRMS (ESI) for $C_{12}H_{15}N_2O_4$ $(M + H)^+$ calcd 251.1026, found 251.1037.

*Methyl-3-((2-methylallyl)oxy)-5-(methylcarbamoyl)benzoate (**1i**):* Colorless solid; mp = 113−115 °C; R_f = 0.29 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (t, J = 1.4 Hz, 1H), 7.68 (dd, J = 2.4, 1.2 Hz, 1H), 7.61 (dd, J = 2.4, 1.6 Hz, 1H), 6.36 (bs, 1H), 5.09 (s, 1H), 5.00 (s, 1H), 4.49 (s, 2H), 3.91 (s, 3H), 3.01 (d, J = 4.8 Hz, 3H), 1.82 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.0, 166.2, 158.9, 140.0, 136.1, 131.4, 119.5, 118.4, 118.3, 113.1, 71.9, 52.3, 26.8, 19.3; IR (KBr) ν_{max} 3336, 2953, 2350, 1720, 1643, 1589, 1435, 904 cm^{-1}; HRMS (ESI) for $C_{14}H_{18}NO_4$ $(M + H)^+$ calcd 264.1230, found 264.1233.

*N-4-Dimethyl-3-((2-methylallyl)oxy)benzamide (**1j**):* Colorless solid; mp = 139−141 °C; R_f = 0.28 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.73 (bs, 1H), 5.07 (s, 1H), 4.95 (s, 1H), 4.39 (s, 2H), 2.94 (d, J = 4.8 Hz, 3H), 2.24 (s, 3H), 1.79 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.2, 156.8, 140.6, 133.2, 130.6, 130.2, 118.2, 112.1, 110.0, 71.3, 26.7, 19.3, 16.2; IR (KBr) ν_{max} 3364, 3095, 2915, 1638, 1556, 1506, 1243, 1057, 893 cm^{-1}; HRMS (ESI) for $C_{13}H_{18}NO_2$ $(M + H)^+$ calcd 220.1332, found 220.1338.

*4-Methoxy-N-methyl-3-((2-methylallyl)oxy)benzamide (**1k**):* Colorless solid; mp = 114−116 °C; R_f = 0.17 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 2.0 Hz, 1H), 7.26 (dd, J = 8.4, 2.0 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.12 (bs, 1H), 5.10 (s, 1H), 4.99 (s, 1H), 4.54 (s, 2H), 3.90 (s, 3H), 2.98 (d, J = 4.8 Hz, 3H), 1.82 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.8, 151.9, 147.8, 140.2, 126.9, 119.7, 112.8, 112.4, 110.6, 72.4, 55.8, 26.7, 19.2; IR (KBr) ν_{max} 3331, 3090, 2931, 2356, 1841, 1726, 1506, 1216, 1139, 904 cm^{-1}; HRMS (ESI) for $C_{13}H_{18}NO_3$ $(M + H)^+$ calcd 236.1281, found 236.1291.

*4-Fluoro-N-methyl-3-((2-methylallyl)oxy)benzamide (**1l**):* Colorless solid; mp = 121−122 °C; R_f = 0.28 (1:1 hexane/EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, J = 8.0, 2.0 Hz, 1H), 7.24−7.17 (m, 1H), 7.08 (dd, J = 10.5, 8.5 Hz, 1H), 6.15 (bs, 1H), 5.12 (s, 1H), 5.01 (s, 1H), 4.54 (s, 2H), 2.99 (d, J = 5.0 Hz, 3H), 1.83 (s, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 167.3, 154.5 (d, J = 252.0 Hz), 146.7 (d, J = 10.1 Hz), 139.9, 130.9 (d, J = 2.5 Hz), 119.4, 115.8 (d, J = 20.2 Hz), 114.6, 113.3, 72.8, 26.8, 19.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −129.3; IR (KBr) ν_{max} 3369, 1873, 1638, 1600, 1501, 1052 cm^{-1}; HRMS (ESI) for $C_{12}H_{15}FNO_2$ $(M + H)^+$ calcd 224.1081, found 224.1088.

*N-Methyl-3-((2-methylallyl)oxy)-4-nitrobenzamide (**1m**):* Pale yellow solid; mp = 133−134 °C; R_f = 0.18 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.4 Hz, 1H), 7.58 (s, 1H), 7.32−7.26 (m, 1H), 6.49 (bs, 1H), 5.16 (s, 1H), 5.04 (s, 1H), 4.61 (s, 2H), 3.02 (d, J = 4.8 Hz, 3H), 1.84 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.1, 152.0, 141.2, 139.6, 139.0, 125.6, 117.7, 114.2, 113.8, 73.0, 27.0, 19.2; IR (KBr) ν_{max} 3370, 1875, 1678, 1660, 1561, 1161, 865 cm^{-1}; HRMS (ESI) for $C_{12}H_{15}N_2O_4$ $(M + H)^+$ calcd 251.1026, found 251.1026.

*N-Methyl-8-((2-methylallyl)oxy)-2,3-dihydrobenzo[b][1,4]-dioxine-6-carboxamide (**1n**):* Colorless solid; mp = 151−153 °C; R_f = 0.20 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, J = 2.0 Hz, 1H), 6.85 (d, J = 2.0 Hz, 1H), 6.05 (bs, 1H), 5.11 (s, 1H), 4.99 (s, 1H), 4.53 (s, 2H), 4.37−4.31 (m, 2H), 4.29−4.23 (m, 2H), 2.97 (d, J = 4.8 Hz, 3H), 1.83 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.6, 147.9, 143.5, 140.2, 136.2, 126.4, 113.0, 108.6, 105.2, 72.6, 64.4, 64.0, 26.7, 19.3; IR (KBr) ν_{max} 3287, 3052, 2926, 1758, 1632, 1353, 1134, 882 cm^{-1}; HRMS (ESI) for $C_{14}H_{18}NO_4$ $(M + H)^+$ calcd 264.1230, found 264.1232.

*4-Bromo-3-methoxy-N-methyl-5-((2-methylallyl)oxy)benzamide (**1o**):* Colorless solid; mp = 124−126 °C; R_f = 0.40 (1:1 hexane/EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 6.93 (s, 1H), 6.91 (s, 1H), 6.26 (bs, 1H), 5.17 (s, 1H), 5.01 (s, 1H), 4.51 (s, 2H), 3.92 (s, 3H), 2.99 (d, J = 4.5 Hz, 3H), 1.84 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.7, 157.2, 156.2, 139.9, 134.9, 113.0, 105.1, 104.4, 103.2, 72.8, 56.6, 26.9, 19.3; IR (neat) ν_{max} 3276, 3090, 2942, 1632, 1561, 1419, 1336, 1243, 1123, 1035, 860, 767 cm^{-1}; HRMS (ESI) for $C_{13}H_{17}BrNO_3$ $(M + H)^+$ calcd 314.0386, found 314.0395.

*3,4-Dimethoxy-N-methyl-5-((2-methylallyl)oxy)benzamide (**1p**):* Colorless solid; mp = 146−148 °C; R_f = 0.14 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, J = 2.0 Hz, 1H), 6.96 (d, J = 2.0 Hz, 1H), 6.12 (bs, 1H), 5.10 (s, 1H), 4.99 (s, 1H), 4.50 (s, 2H), 3.89 (s, 3H), 3.88 (s, 3H), 2.99 (d, J = 4.8 Hz, 3H) 1.83 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.9, 153.1, 152.1, 141.0, 140.3, 129.8, 112.7, 105.9, 104.3, 72.6, 60.7, 56.1, 26.8, 19.3; IR (neat) ν_{max} 3276, 3084, 2936, 1638, 1495, 1342, 1243, 1134, 849 cm^{-1}; HRMS (ESI) for $C_{14}H_{20}NO_4$ $(M + H)^+$ calcd 266.1386, found 266.1392.

*3-((2-(Methoxymethyl)allyl)oxy)-N-methylbenzamide (**1q**):* Colorless solid; mp = 89−90 °C; R_f = 0.22 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.36−7.27 (m, 2H), 7.09−7.02 (m, 1H), 6.15 (bs, 1H), 5.34 (s, 1H), 5.28 (s, 1H), 4.59 (s, 2H), 4.02 (s, 2H), 3.36 (s, 3H), 3.01 (d, J = 4.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz,

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$CDCl_3$) δ 168.0, 158.8, 141.0, 136.0, 129.5, 118.9, 118.1, 115.1, 113.2, 73.3, 68.5, 58.1, 26.8; IR (KBr) ν_{max} 3326, 3079, 2816, 1643, 1578, 1545, 1304, 920, 756 cm^{-1}; HRMS (ESI) for $C_{13}H_{17}NNaO_3$ $(M + Na)^+$ calcd 258.1100, found 258.1109.

*(E)-3-(But-2-en-1-yloxy)-N-methylbenzamide (**1r**):* Colorless solid; mp = 97−98 °C; R_f = 0.30 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40−7.33 (m, 1H), 7.33−7.23 (m, 2H), 7.06−6.99 (m, 1H), 6.23 (bs, 1H), [5.93−5.81 (m, 0.8H), 5.78−5.66 (m, 1.2H)], [4.63 (d, J = 6.0 Hz, 0.4H), 4.49 (d, J = 6.0 Hz, 1.6H)], 3.00 (d, J = 4.8 Hz, 3H), 1.79−1.72 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.1, 158.8, 135.9, 130.7, [129.4 and 128.9], [125.6 and 125.1], 118.7, 118.2, 112.9, [68.7 and 63.8], 26.7, [17.7 and 13.3]; IR (neat) ν_{max} 3298, 2915, 1643, 1545, 1479, 1309, 1238, 1013, 805 cm^{-1}; HRMS (ESI) for $C_{12}H_{16}NO_2$ $(M + H)^+$ calcd 206.1175, found 206.1182.

*1-(But-3-en-1-yl)-N-methyl-1H-indole-3-carboxamide (**1u**):* Colorless solid; mp = 143−144 °C; R_f = 0.13 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.96−7.90 (m, 1H), 7.69 (s, 1H), 7.42−7.36 (m, 1H), 7.32−7.21 (m, 2H), 5.94 (bs, 1H), 5.83−5.68 (m, 1H), 5.10−5.06 (m, 1H), 5.07−5.02 (m, 1H), 4.19 (t, J = 7.0 Hz, 2H), 3.05 (d, J = 4.8 Hz, 3H), 2.64−2.55 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 165.9, 136.4, 133.9, 131.3, 125.3, 122.4, 121.3, 120.1, 118.0, 111.0, 110.2, 46.3, 34.1, 26.3; IR (KBr) ν_{max} 3331, 3101, 2920, 2361, 1627, 1550, 1282, 750 cm^{-1}; HRMS (ESI) for $C_{14}H_{16}N_2NaO$ $(M + Na)^+$ calcd 251.1154, found 251.1159.

*N-Methyl-3-(4-methyl-N-(2-methylallyl)phenylsulfonamido)-benzamide (**4a**):* Colorless solid; mp = 162−164 °C; R_f = 0.22 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.6 Hz, 1H), 7.50−7.41 (m, 3H), 7.33 (t, J = 8.0 Hz, 1H), 7.29−7.22 (m, 2H), 7.19−7.11 (m, 1H), 6.24 (bs, 1H), 4.74 (s, 1H), 4.71 (s, 1H), 4.10 (s, 2H), 2.98 (d, J = 4.8 Hz, 3H), 2.42 (s, 3H), 1.72 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.1, 143.8, 139.2, 139.1, 135.3, 134.7, 131.0, 129.5 (2C), 128.8, 127.5 (2C), 126.9, 126.1, 115.5, 56.4, 26.8, 21.5, 19.8; IR (KBr) ν_{max} 3282, 3090, 3057, 2937, 2865, 1632, 1556, 1342, 701 cm^{-1}; HRMS (ESI) for $C_{19}H_{22}N_2NaO_3S$ $(M + Na)^+$ calcd 381.1243, found 381.1249.

*3-Methoxy-N-methyl-5-(4-methyl-N-(2-methylallyl)-phenylsulfonamido)benzamide (**4b**):* Colorless solid; mp = 172−173 °C; R_f = 0.19 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.0 Hz, 2H), 7.29−7.23 (m, 3H), 7.03 (t, J = 1.4 Hz, 1H), 6.65 (t, J = 2.2 Hz, 1H), 6.19 (bs, 1H), 4.76 (s, 1H), 4.72 (s, 1H), 4.07 (s, 2H), 3.77 (s, 3H), 2.97 (d, J = 4.8 Hz, 3H), 2.43 (s, 3H), 1.73 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.0, 159.7, 143.8, 140.1, 139.2, 136.1, 134.7, 129.5 (2C), 127.6 (2C), 118.9, 117.3, 115.4, 111.4, 56.4, 55.5, 26.7, 21.5, 19.8; IR (KBr) ν_{max} 3353, 3101, 2915, 2854, 1632, 1589, 1550, 1342, 1167, 810 cm^{-1}; HRMS (ESI) for $C_{20}H_{25}N_2O_4S$ $(M + H)^+$ calcd 389.1529, found 389.1535.

*Benzyl-(3-methoxy-5-(methylcarbamoyl)phenyl)(2-methylallyl)-carbamate (**4c**):* Colorless viscous liquid; R_f = 0.22 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38−7.29 (m, 5H), 7.20−7.13 (m, 2H), 6.91 (bs, 1H), 6.08 (bs, 1H), 5.18 (s, 2H), 4.86 (s, 1H), 4.80 (s, 1H), 4.23 (s, 2H), 3.79 (s, 3H), 2.94 (d, J = 4.8 Hz, 3H), 1.73 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.6, 159.9, 155.2, 143.2, 140.7, 136.23, 136.18, 128.4 (2C), 128.1, 127.9 (2C), 116.7, 115.2, 112.2, 109.8, 67.5, 55.9, 55.5, 26.8, 20.1; IR (KBr) ν_{max} 3358, 3084, 2936, 1709, 1643, 1326, 1232, 1145 cm^{-1}; HRMS (ESI) for $C_{21}H_{25}N_2O_4$ $(M + H)^+$ calcd 369.1808, found 369.1812.

*3-(But-3-en-1-yloxy)-N-methylbenzamide (**6a**):* Colorless solid; mp = 74−75 °C; R_f = 0.28 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.32 (m, 1H), 7.33−7.24 (m, 2H), 7.04−6.97 (m, 1H), 6.42 (bs, 1H), 5.96−5.81 (m, 1H), 5.16 (dd, J = 17.2, 1.2 Hz, 1H), 5.11 (d, J = 10 Hz, 1H), 4.03 (t, J = 6.6 Hz, 2H), 2.98 (d, J = 4.8 Hz, 3H), 2.53 (q, J = 6.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$)δ 168.1, 159.0, 136.0, 134.2, 129.4, 118.6, 118.0, 117.1, 112.9, 67.3, 33.5, 26.8; IR (KBr) ν_{max} 3358, 1632, 1578, 1534, 1304, 1243, 1030 cm^{-1}; HRMS (ESI) for $C_{12}H_{16}NO_2$ $(M + H)^+$ calcd 206.1175, found 206.1183.

General Procedure for Hydroarylation of *O*-Tethered Compounds (1) (GP-2). The hydroarylation reactions were conducted in a 20 mL Schlenk tube having a high-pressure valve and side arm. The tube was charged with **1** (0.3 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5.5 mg, 3.0 mol %), and $Mn(OAc)_2$ (13 mg, 0.075 mmol). Subsequently, the additive $AgSbF_6$ (12 mg, 0.036 mmol) was introduced to the flask in a glovebox. 1,2-Dichloroethene (DCE) (1.0 mL) was added to the mixture, and the resulting mixture was stirred at 70 °C for 10−15 h. The reaction mixture was filtered through a small plug of Celite and washed with dichloromethane (3 × 5.0 mL). The solvents were evaporated under the reduced pressure, and the crude material was purified through column chromatography on silica gel using hexane/ethyl acetate (9:1 to 7:3) as eluent.

*N-3,3-Trimethyl-2,3-dihydrobenzofuran-4-carboxamide (**2a**):* 60 mg, 97%; as colorless solid; mp = 116−117 °C; R_f = 0.37 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (t, J = 7.6 Hz, 1H), 6.85−6.79 (m, 2H), 5.98 (bs, 1H), 4.15 (s, 2H), 2.94 (d, J = 4.8 Hz, 3H), 1.42 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.6, 160.2, 133.8, 133.6, 128.2, 118.9, 111.7, 85.2, 42.9, 26.6, 25.9 (2C); IR (neat) ν_{max} 3287, 2926, 2876, 1643, 1545, 1435, 1260, 1057 cm^{-1}; HRMS (ESI) for $C_{12}H_{16}NO_2$ $(M + H)^+$ calcd 206.1175, found 206.1190.

*N-3,3,5-Tetramethyl-2,3-dihydrobenzofuran-4-carboxamide (**2b**):* 62 mg, 94%; as colorless solid; mp = 176−178 °C; R_f = 0.40 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, J = 8.0 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 5.81 (bs, 1H), 4.12 (s, 2H), 2.97 (d, J = 4.8 Hz, 3H), 2.20 (s, 3H), 1.34 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.5, 157.6, 133.6, 131.9, 129.8, 126.0, 110.3, 84.8, 42.8, 26.22, 26.17 (2C), 18.0; IR (neat) ν_{max} 3282, 2964, 2926, 1632, 1457, 1298 cm^{-1}; HRMS (ESI) for $C_{13}H_{18}NO_2$ $(M + H)^+$ calcd 220.1332, found 220.1328.

*5-Bromo-N-3,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (**2c**):* 84 mg, 96%; as colorless solid; mp = 170−171 °C; R_f = 0.44 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8.4 Hz, 1H), 6.66 (d, J = 8.4 Hz, 1H), 5.83 (bs, 1H), 4.17 (s, 2H), 2.99 (d, J = 4.8 Hz, 3H), 1.35 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.3, 159.0, 134.84, 134.77, 132.2, 112.2, 109.5, 85.1, 43.2, 26.4, 26.0 (2C); IR (neat) ν_{max} 3304, 2958, 2882, 1638, 1545, 1287 cm^{-1}; HRMS (ESI) for $C_{12}H_{15}BrNO_2$ $(M + H)^+$ calcd 284.0280, found 284.0284.

*N-3,3,6-Tetramethyl-2,3-dihydrobenzofuran-4-carboxamide (**2d**):* 61 mg, 93%; as colorless viscous liquid; R_f = 0.39 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 6.65 (s, 2H), 5.97 (bs, 1H), 4.14 (s, 2H), 2.93 (d, J = 4.8 Hz, 3H), 2.26 (s, 3H), 1.40 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.7, 160.4, 138.4, 133.1, 130.9, 119.6, 112.3, 85.4, 42.6, 26.5, 25.9 (2C), 21.2; IR (neat) ν_{max} 3229, 2952, 1643, 1534, 1435, 1200 cm^{-1}; HRMS (ESI) for $C_{13}H_{18}NO_2$ $(M + H)^+$ calcd 220.1332, found 220.1342.

*6-Methoxy-N-3,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (**2e**):* 66 mg, 94%; as colorless solid; mp = 135−136 °C; R_f = 0.33 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 6.42 (d, J = 2.4 Hz, 1H), 6.39 (d, J = 2.4 Hz, 1H), 5.86 (bs, 1H), 4.18 (s, 2H), 3.75 (s, 3H), 2.96 (d, J = 4.8 Hz, 3H), 1.41 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.4, 161.6, 160.0, 133.6, 125.9, 104.9, 97.9, 86.0, 55.6, 42.4, 26.6, 26.1 (2C); IR (neat) ν_{max} 3304, 2986, 2947, 2865, 2361, 1649, 1550, 1326 cm^{-1}; HRMS (ESI) for $C_{13}H_{18}NO_3$ $(M + H)^+$ calcd 236.1281, found 236.1284.

*6-((tert-Butyldimethylsilyl)oxy)-N-3,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (**2f**):* 88 mg, 87%; as colorless solid; mp = 150−153 °C; R_f = 0.60 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 6.35 (d, J = 2.4 Hz, 1H), 6.33 (d, J = 2.0 Hz, 1H), 5.77 (bs, 1H), 4.18 (s, 2H), 2.97 (d, J = 4.8 Hz, 3H), 1.42 (s, 6H), 0.97 (s, 9H), 0.19 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.4, 161.4, 155.8, 133.5, 126.7, 110.7, 103.9, 85.9, 42.4, 26.6, 26.2 (2C), 25.6 (3C), 18.1, −4.4 (2C); IR (KBr) ν_{max} 3238, 2958, 2854, 1638, 1473, 1139 cm^{-1}; HRMS (ESI) for $C_{18}H_{30}NO_3Si$ $(M + H)^+$ calcd 336.1989, found 336.1992.

*6-Chloro-N-3,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (**2g**):* 68 mg, 94%; as colorless solid; mp = 158−160 °C; R_f = 0.50 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 2H), 5.98 (bs, 1H), 4.19 (s, 2H), 2.95 (d, J = 4.8 Hz, 3H), 1.40 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.2, 161.2, 134.1, 133.3, 132.7, 118.9, 112.2, 85.9, 42.6, 26.6, 25.8 (2C); IR (KBr) ν_{max} 3243, 3079, 2942, 1638, 1408, 1320, 1243 cm^{-1}; HRMS (ESI) for $C_{12}H_{15}ClNO_2$ $(M + H)^+$ calcd 240.0785, found 240.0781.

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*N-3,3-Trimethyl-6-nitro-2,3-dihydrobenzofuran-4-carboxamide (**2h**):* 67 mg, 89%; as pale yellow solid; mp = 236−238 °C; R_f = 0.38 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.61 (s, 1H), 6.04 (bs, 1H), 4.30 (s, 2H), 3.01 (d, J = 5.2 Hz, 3H), 1.47 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.2, 161.2, 148.0, 141.7, 133.6, 114.7, 106.7, 86.2, 43.2, 26.8, 25.5 (2C); IR (KBr) ν_{max} 3232, 3101, 2953, 1638, 1528, 1342 cm^{-1}; HRMS (ESI) for $C_{12}H_{15}N_2O_4(M + H)^+$ calcd 251.1026, found 251.1035.

*Methyl-3,3-dimethyl-4-(methylcarbamoyl)-2,3-dihydrobenzofuran-6-carboxylate (**2i**):* 76 mg, 96%; as colorless viscous liquid; R_f = 0.37 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 1.2 Hz, 1H), 7.43 (d, J = 1.6 Hz, 1H), 6.01 (bs, 1H), 4.22 (s, 2H), 3.89 (s, 3H), 2.99 (d, J = 5.2 Hz, 3H), 1.45 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.5, 166.2, 160.6, 139.4, 133.3, 130.4, 120.8, 112.4, 85.6, 52.3, 43.1, 26.7, 25.6 (2C); IR (KBr) ν_{max} 3293, 2958, 1715, 1638, 1413, 1276, 1238, 1013 cm^{-1}; HRMS (ESI) for $C_{14}H_{18}NO_4$ (M + H)$^+$ calcd 264.1230, found 264.1230.

*N-3,3,7-Tetramethyl-2,3-dihydrobenzofuran-4-carboxamide (**2j**):* 59 mg, 90%; as colorless viscous liquid; R_f = 0.37 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, J = 7.6 Hz, 1H), 6.78 (d, J = 7.6 Hz, 1H), 5.81 (bs, 1H), 4.18 (s, 2H), 2.98 (d, J = 4.8 Hz, 3H), 2.22 (s, 3H), 1.45 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.7, 158.5, 133.2, 131.1, 129.2, 122.4, 118.8, 85.1, 43.2, 26.6, 25.9 (2C), 15.2; IR (neat) ν_{max} 3298, 2947, 2865, 1643, 1539, 1408, 1320, 1265 cm^{-1}; HRMS (ESI) for $C_{13}H_{18}NO_2$ (M + H)$^+$ calcd 220.1332, found 220.1338.

*7-Methoxy-N-3,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (**2k**):* 66 mg, 93%; as colorless solid; mp = 137−139 °C; R_f = 0.27 (1:1 hexane/EtOAc); 1H NMR (400 MHz, $CDCl_3$) δ 6.85 (d, J = 8.4 Hz, 1H), 6.68 (d, J = 8.4 Hz, 1H), 5.92 (bs, 1H), 4.23 (s, 2H), 3.86 (s, 3H), 2.94 (d, J = 4.8 Hz, 3H), 1.44 (s, 6H); 13C{1H} NMR (101 MHz, $CDCl_3$) δ169.4, 148.3, 146.1, 135.3, 125.9, 120.1, 110.2, 85.9, 55.9, 43.7, 26.6, 25.7 (2C); IR (neat) ν_{max} 3282, 3101, 2953, 1643, 1506, 1287, 1057 cm^{-1}; HRMS (ESI) for $C_{13}H_{18}NO_3$ (M + H)$^+$ calcd 236.1281, found 236.1283.

*7-Fluoro-N-3,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (**2l**):* 66 mg, 98%; as colorless solid; mp = 112−113 °C; R_f = 0.36 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92−6.84 (m, 1H), 6.83−6.76 (m, 1H), 5.95 (bs, 1H), 4.26 (s, 2H), 2.94 (d, J = 4.8 Hz, 3H), 1.44 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.8, 148.6 (d, J = 251 Hz), 146.9 (d, J = 10 Hz), 137.9 (d, J = 2.0 Hz), 129.2 (d, J = 3.0 Hz), 119.7 (d, J = 6.1 Hz), 115.1 (d, J = 17 Hz), 86.5, 43.8, 26.6, 25.6 (2C); ^{19}F NMR (376 MHz, $CDCl_3$) δ −135.8; IR (neat) ν_{max} 3282, 2958, 1638, 1495, 1265, 997, 953, 821 cm^{-1}; HRMS (ESI) for $C_{12}H_{15}FNO_2$ (M + H)$^+$ calcd 224.1081, found 224.1090.

*N-3,3-Trimethyl-7-nitro-2,3-dihydrobenzofuran-4-carboxamide (**2m**):* 68 mg, 90%; as pale yellow solid; mp = 130−132 °C; R_f = 0.23 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.4 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 6.01 (bs, 1H), 4.44 (s, 2H), 3.00 (d, J = 4.8 Hz, 3H), 1.47 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.6, 155.3, 138.82, 138.80, 133.5, 124.3, 119.0, 87.2, 42.7, 26.7, 25.7 (2C); IR (neat) ν_{max} 3216, 3079, 2964, 1643, 1600, 1523, 1200 cm^{-1}; HRMS (ESI) for $C_{12}H_{15}N_2O_4$ (M + H)$^+$ calcd 251.1026, found 251.1029.

*N-7,7-Trimethyl-2,3,7,8-tetrahydro-[1,4]dioxino[2,3-g]-benzofuran-6-carboxamide (**2n**):* 78 mg, 98%; as colorless solid; mp = 189−190 °C; R_f = 0.30 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (s, 1H), 5.83 (bs, 1H), 4.33−4.26 (m, 2H), 4.27−4.21 (m, 4H), 2.94 (d, J = 4.8 Hz, 3H) 1.43 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.9, 148.3, 143.2, 130.8, 127.9, 124.9, 108.1, 86.9, 64.6, 64.4, 43.3, 26.6, 25.9 (2C); IR (KBr) ν_{max} 3325, 2920, 2312, 1654, 1621, 1501, 1304 cm^{-1}; HRMS (ESI) for $C_{14}H_{18}NO_4$ (M + H)$^+$ calcd 264.1230, found 264.1232.

*7-Bromo-6-methoxy-N-3,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (**2o**):* 88 mg, 93%; as colorless solid; mp = 202−204 °C; R_f = 0.27 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (s, 1H), 5.94 (bs, 1H), 4.27 (s, 2H), 3.83 (s, 3H), 2.96 (d, J = 4.8 Hz, 3H), 1.41 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.8, 158.8, 156.0, 132.0, 127.2, 102.4, 94.9, 86.1, 56.7, 43.6, 26.6, 26.1 (2C); IR (KBr) ν_{max} 3293, 2964, 1634, 1463, 1260, 1106 cm^{-1}; HRMS (ESI) for $C_{13}H_{17}BrNO_3$ (M + H)$^+$ calcd 314.0386, found 314.0388.

*6,7-Dimethoxy-N-3,3-trimethyl-2,3-dihydrobenzofuran-4-carboxamide (**2p**):* 73 mg, 91%; as colorless solid; mp = 171−173 °C; R_f = 0.22 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.40 (s, 1H), 5.87 (bs, 1H), 4.21 (s, 2H), 3.92 (s, 3H), 3.81 (s, 3H), 2.96 (d, J = 4.8 Hz, 3H), 1.41 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.3, 152.2, 151.7, 135.0, 128.8, 127.0, 103.5, 86.3, 60.6, 56.5, 42.9, 26.6, 25.9 (2C); IR (KBr) ν_{max} 3408, 2936, 1665, 1605, 1238, 1106 cm^{-1}; HRMS (ESI) for $C_{14}H_{20}NO_4$ (M + H)$^+$ calcd 266.1386, found 266.1391.

*3-(Methoxymethyl)-N-3-dimethyl-2,3-dihydrobenzofuran-4-carboxamide (**2q**):* 68 mg, 96%; as colorless solid; mp = 150−152 °C; R_f = 0.28 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.60 (bs, 1H), 4.48 (d, J = 8.8 Hz, 1H), 4.06 (d, J = 8.8 Hz, 1H), 3.66 (d, J = 8.8 Hz, 1H), 3.60 (d, J = 8.8 Hz, 1H), 3.33 (s, 3H), 2.96 (d, J = 4.8 Hz, 3H), 1.40 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.3, 160.9, 134.5, 129.6, 128.7, 119.7, 111.9, 81.1, 77.5, 59.2, 47.6, 26.5, 20.7; IR (neat) ν_{max} 3304, 2931, 1649, 1539, 1441, 1101 cm^{-1}; HRMS (ESI) for $C_{13}H_{18}NO_3$ (M + H)$^+$ calcd 236.1281, found 236.1291.

*3-Ethyl-N-methyl-2,3-dihydrobenzofuran-4-carboxamide (**2r**) and (E)-3-(But-1-en-1-yloxy)-N-methylbenzamide (**1′r**):* 45 mg, 73%; as colorless solid; R_f = 0.30 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 7.6, 1.6 Hz, 1H), 7.46 (s, 1H), 7.31−7.23 (m, 3H), 7.14 (t, J = 7.8 Hz, 1.5H), 6.96 (d, J = 7.6 Hz, 1.5H), 6.87 (d, J = 8.0 Hz, 1.5H), 6.03 (bs, 1.5H), 5.94 (bs, 1H), 4.55 (t, J = 8.2 Hz, 1.5H), 4.40 (dd, J = 8.8, 3.6 Hz, 1.5H), 3.88−3.79 (m, 1.5H), 3.05 (d, J = 4.8 Hz, 3H), 2.99 (d, J = 5.2 Hz, 4.5H), 2.80−2.71 (m, 1.5H), 1.80−1.68 (m, 2H), 1.58−1.46 (m, 1.5H), 1.24 (t, J = 7.4 Hz, 3H), 0.88 (t, J = 7.4 Hz, 4.5H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.6, 168.6, 160.7, 156.1, 142.2, 132.4, 130.8, 130.6, 128.3, 125.0, 123.6, 122.6, 120.9, 118.2, 113.4, 111.8, 76.2, 42.8, 27.1, 26.8, 26.6, 18.1, 13.5, 11.0; IR (neat) ν_{max} 3282, 2969, 1632, 1545, 1238, 1095, 1057, 810 cm^{-1}; HRMS (ESI) for $C_{12}H_{16}NO_2$ (M + H)$^+$ calcd 206.1175, found 206.1184.

*3-Ethyl-N-3-dimethyl-2,3-dihydrobenzofuran-4-carboxamide (**2s**):* 48 mg, 72%; as colorless viscous liquid; R_f = 0.48 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, J = 7.8 Hz, 1H), 6.88−6.81 (m, 2H), 5.81 (bs, 1H), 4.36 (d, J = 8.4 Hz, 1H), 4.11 (d, J = 8.8 Hz, 1H), 2.98 (d, J = 4.8 Hz, 3H), 2.03−1.90 (m, 1H), 1.82−1.69 (m, 1H), 1.42 (s, 3H), 0.80 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.7, 160.8, 133.9, 132.5, 128.3, 118.9, 111.6, 82.3, 46.9, 31.5, 26.6, 24.6, 9.2; IR (neat) ν_{max} 3304, 2926, 1643, 1539, 1441, 1254 cm^{-1}; HRMS (ESI) for $C_{13}H_{18}NO_2$ (M + H)$^+$ calcd 220.1332, found 220.1332.

*N-Benzyl-3,3-dimethyl-2,3-dihydrobenzofuran-4-carboxamide (**2t**):* 79 mg, 93%; as colorless solid; mp = 119−120 °C; R_f = 0.42 (7:3) hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.33 (m, 4H), 7.33−7.25 (m, 1H), 7.11 (t, J = 7.8 Hz, 1H), 6.89 (d, J = 6.8 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.20 (bs, 1H), 4.61 (d, J = 5.6 Hz, 2H), 4.18 (s, 2H), 1.46 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.6, 160.3, 138.0, 134.1, 133.3, 128.7 (2C), 128.2, 127.8 (2C), 127.6, 118.9, 111.9, 85.2, 43.9, 43.0, 25.9 (2C); IR (neat) ν_{max} 3276, 2980, 2953, 1649,1627, 1523, 1194 cm^{-1}; HRMS (ESI) for $C_{18}H_{20}NO_2$ (M + H)$^+$ calcd 282.1488, found 282.1490.

*N-1-Dimethyl-2,3-dihydro-1H-pyrrolo[1,2-a]indole-9-carboxamide (**2u**):* 47 mg, 68%; as colorless solid; mp = 218−220 °C; R_f = 0.19 (1:1 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79−7.73 (m, 1H), 7.31−7.24 (m, 1H), 7.23−7.17 (m, 2H), 5.87 (bs, 1H), 4.18−4.04 (m, 2H), 3.81−3.71 (m, 1H), 3.05 (d, J = 4.8 Hz, 3H), 2.91−2.78 (m, 1H), 2.32−2.21 (m, 1H), 1.45 (d, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.2, 154.4, 132.2, 129.2, 121.3, 121.0, 119.3, 110.3, 102.4, 42.9, 35.6, 33.3, 26.2, 19.2; IR (KBr) ν_{max} 3287, 2926, 2849, 1742, 1621, 1463 cm^{-1}; HRMS (ESI) for $C_{14}H_{17}N_2O$ (M + H)$^+$ calcd 229.1335, found 229.1348.

*N,N-Diethyl-3,3-dimethyl-2,3-dihydrobenzofuran-4-carboxamide (**3a**):* 55 mg, 74%; as colorless viscous liquid; R_f = 0.29 (7:3 hexane/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (bt, J = 7.6 Hz, 1H), 6.77 (bd, J = 8.0 Hz, 1H), 6.66 (bd, J = 7.2 Hz, 1H), 4.17 (bs, 2H),

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3.79 (bs, 1H), 3.34 (bs, 1H), 3.16 (bs, 2H), 1.50−1.20 (m, 9H), 1.09 (t, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.4, 160.0, 133.4, 131.7, 128.2, 117.9, 110.2, 84.7, 43.0, 42.8, 38.4, 13.8, 12.5; IR (neat) ν_{max} 2964, 2865, 1632, 1430, 1282, 1117 cm^{-1}; HRMS (ESI) for $C_{15}H_{22}NO_2$ $(M + H)^+$ calcd 248.1645, found 248.1643.

*(3,3-Dimethyl-2,3-dihydrobenzofuran-4-yl) (pyrrolidin-1-yl)-methanone (**3b**):* 64 mg, 87%; as colorless viscous liquid; R_f = 0.33 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, J = 7.8 Hz, 1H), 6.79 (dd, J = 8.4, 0.8 Hz, 1H), 6.71 (dd, J = 7.6, 0.8 Hz, 1H), 4.17 (s, 2H), 3.64 (t, J = 7.0 Hz, 2H), 3.21 (t, J = 6.8 Hz, 2H), 2.01−1.91 (m, 2H), 1.90−1.79 (m, 2H), 1.36 (s, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 168.4, 160.1, 134.1, 131.7, 128.4, 118.2, 110.4, 84.9, 49.0, 45.3, 42.7, 26.0, 25.9 (2C), 24.6; IR (neat) ν_{max} 2969, 2865, 2350, 1627, 1430, 1249, 1189 cm^{-1}; HRMS (ESI) for $C_{15}H_{20}NO_2$ $(M + H)^+$ calcd 246.1488, found 246.1495.

General Procedure for Hydroarylation of N-Tethered Compounds (4) (GP-3). The hydroarylation reaction was conducted in a 20 mL Schlenk tube having high-pressure valve and side arm. The tube was charged with **4** (0.3 mmol), $[RuCl_2(p\text{-cymene})]_2$ (9.2 mg, 5.0 mol %), and $Mn(OAc)_2$ (27 mg, 0.15 mmol). Subsequently, the additive $AgSbF_6$ (21 mg, 0.06 mmol) was introduced to the flask in a glovebox. 1,2-DCE (1.0 mL) was added to the mixture, and the resulting mixture was stirred at 110 °C for 24 h. The reaction mixture was filtered through a small plug of Celite and washed with dichloromethane (3 × 5.0 mL). The solvents were evaporated under the reduced pressure, and the crude material was purified through column chromatography on silica gel using hexane/ethyl acetate (5:1 to 3:2) as eluent.

*N-3,3-Trimethyl-1-tosylindoline-4-carboxamide (**5a**):* 89 mg, 83%; as colorless solid; mp = 242−243 °C; R_f = 0.25 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73−7.66 (m, 3H), 7.28−7.21 (m, 2H), 7.18 (t, J = 8.0, 1H), 6.91 (dd, J = 7.6, 0.8 Hz, 1H), 5.80 (s, 1H), 3.58 (s, 2H), 2.92 (d, J = 4.8 Hz, 3H), 2.37 (s, 3H), 1.22 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.7, 144.3, 141.9, 137.1, 134.0, 133.9, 129.7 (2C), 128.1, 127.2 (2C), 122.0, 115.8, 64.5, 41.3, 26.6, 26.5 (2C), 21.5; IR (neat) ν_{max} 3287, 2920, 2860, 1638, 1353, 1260 1161 cm^{-1}; HRMS (ESI) for $C_{19}H_{23}N_2O_3S$ $(M + H)^+$ calcd 359.1423, found 359.1430.

*6-Methoxy-N-3,3-trimethyl-1-tosylindoline-4-carboxamide (**5b**):* 108 mg, 93%; as colorless solid; mp = 230−232 °C; R_f = 0.20 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 2.4 Hz, 1H), 7.26 (d, J = 7.6 Hz, 2H), 6.46 (d, J = 2.4 Hz, 1H), 5.74 (bs, 1H), 3.81 (s, 3H), 3.60 (s, 2H), 2.93 (d, J = 4.8 Hz, 3H), 2.39 (s, 3H), 1.20 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.4, 159.5, 144.3, 143.0, 134.2, 134.0, 129.7 (2C), 129.0, 127.2 (2C), 107.6, 102.0, 65.0, 55.6, 40.5, 26.6 (2C), 26.5, 21.5; IR (neat) ν_{max} 3315, 2931, 1649, 1556, 1347, 1320, 1167 cm^{-1}; HRMS (ESI) for $C_{20}H_{25}N_2O_4S$ $(M + H)^+$ calcd 389.1529, found 389.1535.

*6-Methoxy-N,3,3-trimethyl-1-tosylindoline-4-carboxamide (**5c**):* 99 mg, 90%; as colorless solid; mp = 160−161 °C; R_f = 0.24 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (bs, 1H), 7.41−7.30 (m, 5H), 6.44 (s, 1H), 6.02 (bs, 1H), 5.23 (s, 2H), 3.77−3.70 (m, 5H), 2.93 (d, J = 4.8 Hz, 3H), 1.38 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.8, 159.4, 153.0, 136.0, 133.8, 128.6 (3C), 128.2 (2C), 128.0 (2C), 107.6, 102.0, 63.7, 55.5, 40.1, 29.6, 27.1, 26.6 (2C); IR (neat) ν_{max} 3320, 2964, 1665, 1600, 1539, 1391, 1221 cm^{-1}; HRMS (ESI) for $C_{21}H_{25}N_2O_4$ $(M + H)^+$ calcd 369.1808, found 369.1813.

*N-4-Dimethylchroman-5-carboxamide (**7a**):* 59 mg, 96%; as colorless solid; mp = 152−154 °C; R_f = 0.30 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (t, J = 7.8 Hz, 1H), 6.88−6.82 (m, 2H), 5.83 (bs, 1H), 4.26−4.13 (m, 2H), 3.61−3.54 (m, 1H), 2.98 (d, J = 4.8 Hz, 3H), 2.19−2.06 (m, 1H), 1.73−1.64 (m, 1H), 1.26 (d, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.7, 154.5, 137.0, 126.9, 125.9, 118.9, 118.8, 62.0, 28.8, 26.6, 24.8, 22.6; IR (neat) ν_{max} 3326, 2953, 2915, 1627, 1523, 1287, 1216 cm^{-1}; HRMS (ESI) for $C_{12}H_{16}NO_2$ $(M + H)^+$ calcd 206.1175, found 206.1184.

*N-4,4-Trimethylchroman-5-carboxamide (**7b**):* 47 mg, 71%; as colorless solid; mp = 175−177 °C; R_f = 0.35 (1:1 hexane/EtOAc); ^1H NMR (400 MHz, $CDCl_3$) δ 7.03 (t, J = 7.8 Hz, 1H), 6.80 (dd, J = 8.2, 1.4 Hz, 1H), 6.73 (dd, J = 7.4, 1.4 Hz, 1H), 5.85 (bs, 1H), 4.25−4.19 (m, 2H), 2.94 (d, J = 4.8 Hz, 3H), 1.80−1.73 (m, 2H), 1.44 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 172.8, 154.1, 138.0, 128.2, 127.0, 120.1, 118.9, 62.4, 39.4, 31.5, 29.2 (2C), 26.7; IR (neat) ν_{max} 3271, 3002, 2931, 1627, 1446, 1243, 1167, 1002 cm^{-1}; HRMS (ESI) for $C_{13}H_{18}NO_2$ $(M + H)^+$ calcd 220.1332, found 220.1340.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01734.

NMR spectra for all compounds, Hammett analysis, deuterium studies (PDF)

X-ray crystallographic data of **2p** (CCDC 1488804) (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: ritchem2009@gmail.com.

*E-mail: akhilchemistry12@gmail.com.

Notes

The authors declare no competing financial interest.

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