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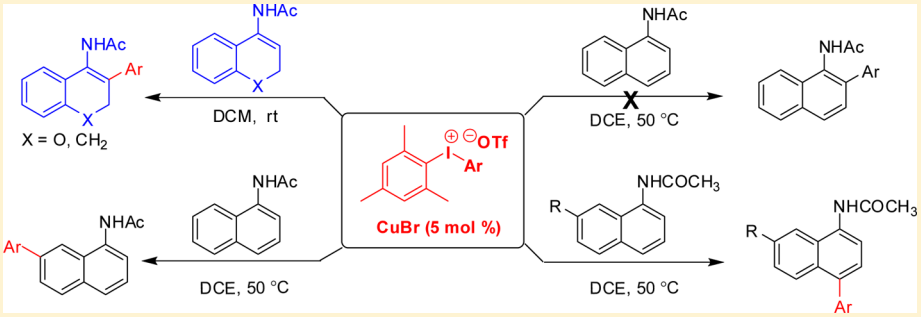
Copper(I) Bromide Catalyzed Arylation of Cyclic Enamides and Naphthyl-1-acetamides Using Diaryliodonium Salts

Muthuraj Prakash, Subramaniam Muthusamy, and Venkitasamy Kesavan*

Chemical Biology Lab, Department of Biotechnology, Bhupat and Jyothi Mehta School of Biosciences Building, Indian Institute of Technology Madras, Chennai-600036, India

Supporting Information



ABSTRACT: Copper(I) bromide catalyzed direct C−H arylation of cyclic enamides was achieved using diaryliodonium salts in the absence of base/additive at ambient temperature with high yields. A biologically active dihydro[*a*]benzocarbazole scaffold was synthesized using the established protocol. The scope of the current methodology was further extended for the synthesis of C4-, C7-aryl-substituted 1-naphthyl acetamides in good yields.

INTRODUCTION

Enamides are prevalent intermediates for synthesis of valuable chiral amines and natural products.[1,2] Although acyclic enamides are well exploited in a number of interesting synthetic transformations with electrophiles,[3−8] exploration of cyclic enamides as nucleophiles is very limited.[9−12] Synthetic utility of cyclic enamides in forming a C−C bond was demonstrated by Zhou et al.,[13,14] by synthesizing *β*-aryl cyclic enamides **4** through Suzuki−Hiyama-type coupling. These protocols rely on an expensive palladium(II) catalyst in conjunction with additives such as copper or silver salts/base at elevated temperature. Inseparable aromatized byproduct **6** also forms along with the expected *β*-aryl cyclic enamide **4** due to high temperature (Scheme 1).[13,14] Under the established catalytic conditions, only enamide **2** provided the expected product in good yields. In due course, Gigant et al., reported the first copper-catalyzed C3-arylation of cyclic enesulfonamide **I** using diaryliodonium salts in the presence of base at 80 °C.[15]

Although, *β*-aryl cyclic enamides (**4**, **5**) are important structural precursors for the synthesis of biologically important compounds, such as indole carboline ring systems (**8**, **9**, **10**), phenanthridine scaffolds (**11**), and 2-aryl-tetrahydronaphthyl-amines (**12**),[16−23] their preparation remains a challenge for the aforementioned reasons (Figure 1). The importance of *β*-aryl cyclic enamides **4** and drawbacks of existing methods stimulated us to develop an operationally simple and base/additive-free C−H arylation of cyclic enamides at ambient temperature.

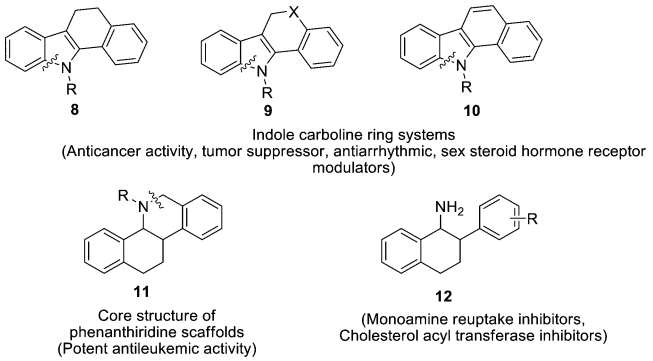


Figure 1. Biologically important scaffolds can be made from *β*-aryl cyclic enamides.

Although secondary enamides are stable under neutral conditions, the presence of triflic acid or a triflate/trifluoroborate counterion would lead to isomerization of secondary enamides **III** to imines.[24,25] Hence, we hypothesize that use of a suitably activated electrophile with a triflate/trifluoroborate counterion will facilitate the *β*-substitution of secondary cyclic enamides.

Seminal contributions from Gaunt and Macmillan groups independently showcased the ability of diaryliodonium salts in forming C−C bonds.[26−29] These reports encouraged us to use

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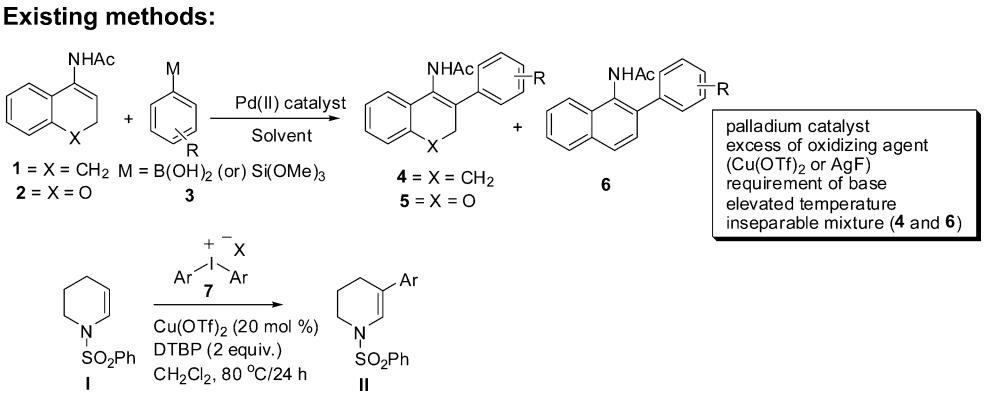
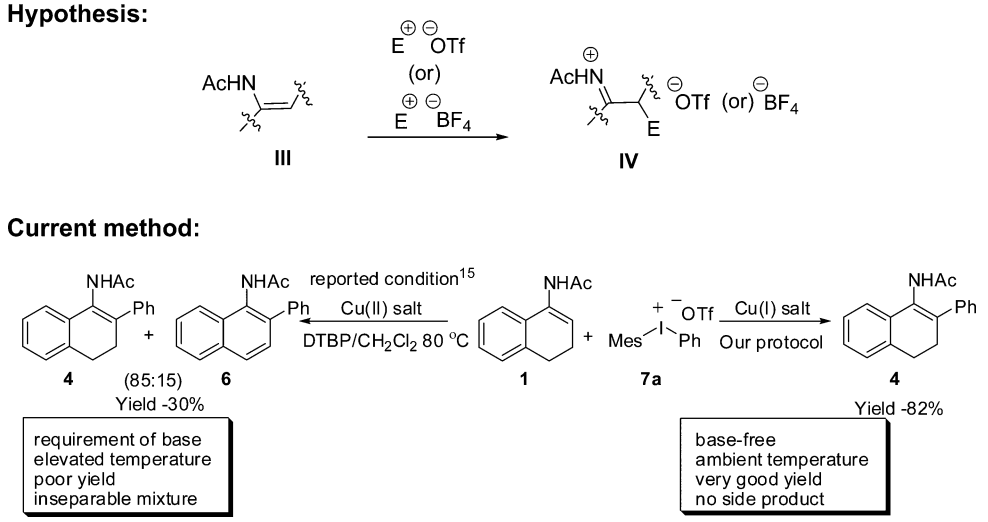
Scheme 1. Strategies for C−H Arylation of Cyclic Enamides



Scheme 2. Hypothesis and Current Protocol



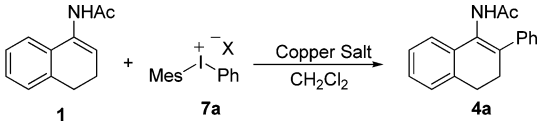
diaryliodonium salt as an electrophile for the C−H arylation of secondary enamides in the presence of a copper catalyst.[30,31] To the best of our knowledge, this is the first report to demonstrate the β-arylation of cyclic enamides at ambient conditions in the absence of additive/base using CuBr. Easy, one-pot synthesis, air- and moisture-stable diaryliodonium salts[32−34] are an added advantage.

RESULTS AND DISCUSSION

Enamide derived from α-tetralone was selected to identify a suitable copper salt to facilitate the formation of a C−C bond. Cyclic enamide **1** was treated with various copper salts (10 mol %) and 1.2 equiv of mesitylphenyliodonium salt **7a** in dichloromethane at ambient temperature, and the results are tabulated in Table 1. Although copper(II) triflate catalyzed β-arylation of cyclic enesulfonamides,[15] it failed to catalyze β-arylation of cyclic enamide **1** efficiently (Table 1, entry 1). Copper(II) salts furnished the expected β-arylated product **4a** only in poor yields (entries 1 and 2).

Among the various Cu(I) salts screened (entries 3−6), reaction proceeded smoothly when CuBr was employed (entry 6). Further, to emphasize the importance of the present methodology, cyclic enamide **1** was treated with mesitylphenyliodonium triflate **7a** under the reported condition for enesulfonamides.[15] The obtained result indicates that the yield of the expected product **4** was not only poor, aromatized byproduct **6** also formed as an inseparable mixture (Scheme 2). In addition, to prove the requirement of copper(I) catalyst, the reaction was performed in the absence of copper(I)

Table 1. Optimization of Reaction Conditions[a]



entry	metal	X	mol (%)	time (h)	yield (%)[b]
1	$Cu(OTf)_2$	OTf	10	14	25
2	$Cu(OAc)_2$	OTf	10	9	20
3	CuOTf	OTf	10	5	70
4	$CuPF_6$	OTf	10	7	67
5	CuI	OTf	10	5	73
6	CuBr	OTf	10	3.5	81
7	CuBr	OTf	05	6	82
8	CuBr	OTf	01	36	70
9	CuBr	BF_4	05	9	77
10	CuBr	OTs	05	14	25
11	CuBr	Cl	05	36	
12	CuBr	Br	05	36	

[a]Reaction conditions: **1** (1 equiv), **7a** (1.2 equiv), and copper catalyst (X mol %) in CH_2Cl_2 at rt for the indicated time. [b]Isolated yield after column chromatography.

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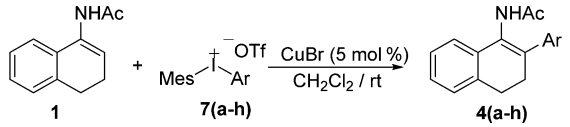
bromide. No detectable arylated product **4** was observed at room temperature; hence, the reaction was carried out in a sealed tube at 80 °C. The arylation occurred with poor conversion and inseparable mixture of expected product **4** and byproduct **6**, was obtained in 14% yield. This experiment reveals that copper(I) bromide plays a vital role and it activates the diaryliodonium salt by forming active electrophilic species. Encouraged by the performance of copper(I) bromide, we sought to identify the optimal catalytic loading without compromising the yield. The yield of the reaction was unaffected when 5 mol % of the catalyst was used (entry 7). Although 1 mol % of CuBr was sufficient enough to catalyze the arylation with 70% yield, prolonged reaction time was observed (entry 8). Hence, further optimization studies were carried out using 5 mol % of CuBr. The effect exerted by counteranions of diaryliodonium salt **7a** was studied (entries 9−12). No improvement in either yield or rate of the reaction was observed when the triflate ion was replaced by tetrafluoroborate or tosylate ions (entries 9 and 10). Arylation failed to proceed when mesitylphenyliodonium chloride or mesitylphenyliodonium bromide salts were used (entries 11 and 12). Thus, we optimized the condition for C−C bond formation of cyclic enamides through *β*-arylation using CuBr as a catalyst at 25 °C.

With these optimized reaction conditions, evaluation of the substrate scope was undertaken. The influence of methyl substitution at different positions was investigated initially. Reaction proceeded with ease when compounds **7b** and **7c** were employed as substrates. Corresponding arylated products **4b** and **4c** were isolated in good yields within 6 h (Table 2, entries 2 and 3). We also examined the steric effect of methyl substitution at *ortho*-positions by using dimesityliodonium triflate **7d** as the reagent. The corresponding arylated product **4d** was isolated in 72% yield after 36 h (entry 4). After examining the effect of alkyl substitutions, we moved on to study the tolerability of halogen-substituted iodonium salts. The examination of halogen substitutions exposed that the position and nature of the halogen present in the aryl ring did not affect the catalytic efficiency, and the reaction proceeded smoothly to afford the corresponding arylated products **7e−g** in good yields (entries 5−7).

Table 2. Synthesis of Various Substituted *β*-Aryl Cyclic Enamides[a]



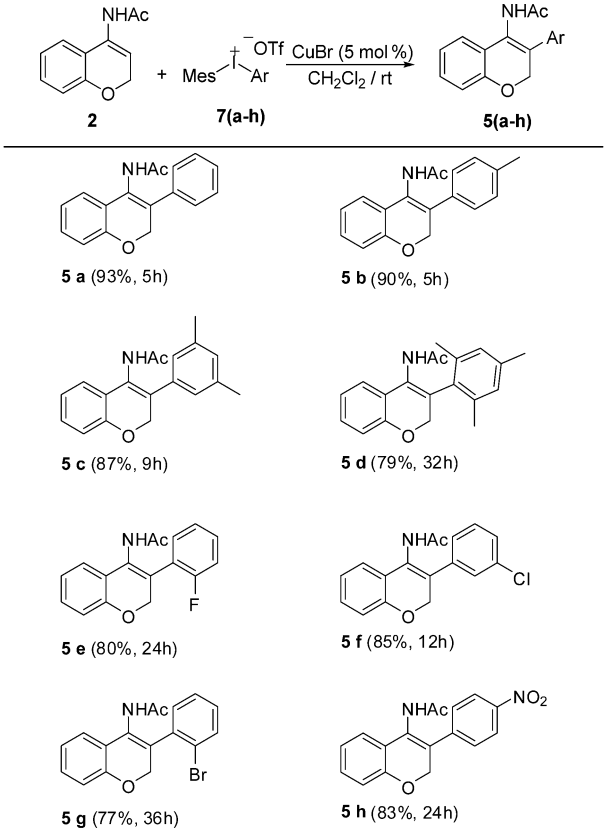
1 7(a-h) 4(a-h)

entry	(Ar =)	time (h)	yield (**4a−h**) (%)[b]
1	C_6H_5 (**7a**)	6	82
2	4-CH_3−C_6H_4 (**7b**)	6	81
3	3,5-$(CH_3)_2$-C_6H_3 (**7c**)	9	80
4	2,4,6-$(CH_3)_3$-C_6H_2 (**7d**)	36	72
5	2-F-C_6H_4 (**7e**)	24	77
6	3-Cl-C_6H_4 (**7f**)	12	83
7	2-Br-C_6H_4 (**7g**)	36	71
8	4-NO_2-C_6H_4 (**7h**)	24	80

[a]Reaction conditions: **1** (1 equiv), **7** (1.2 equiv), and Cu(I)Br (5 mol %) in CH_2Cl_2 at rt for the indicated time. [b]Isolated yield after column chromatography.

The presence of sterically hindered *ortho*-bromo substitution is well tolerated under our catalytic conditions (entry 7). Moreover, halogen-substituted *β*-aryl enamides serve as valuable synthetic handles for transformation, such as cross-coupling reactions and intramolecular cyclization in the case of *ortho*-bromo-substituted products. This accomplishment clearly demonstrates the efficiency of the current methodology, because such products are difficult to obtain using a palladium-catalyzed method due to oxidative insertion. The established protocol was not only limited to electron releasing and halogen substituents; a strong electron-withdrawing group like nitro substitution at the *para*-position also furnished the expected arylated product **7h** in 80% yield (entry 8). The highlight of this methodology is that no aromatized side product **6** was observed, unlike earlier protocols.[13,14] Under the identical conditions, chromone derived cyclic enamide **2** underwent *β*-arylation with ease to afford the corresponding arylated products **5a−h** in very good yields (Table 3).

Table 3. Substrate Scope[a]



[a]Reaction conditions: **2** (1 equiv), **7** (1.2 equiv), and Cu(I)Br (5 mol %) in CH_2Cl_2 at rt for the indicated time.

When mono- and dimethyl-substituted iodonium salts **7b** and **7c** were employed as substrates, arylation occurred with excellent yields to afford **5b** and **5c**, respectively. Yield of the product was not affected in the case of sterically hindered dimesityliodonium salt **7d.** The expected arylated product **5d** was obtained in 79% yield after 32 h. The presence of halogen substituents as well as an electron-withdrawing nitro group did not exert any influence on the efficiency of the reaction. We were delighted to observe that diaryliodonium salts with aryl groups possessing electron-rich, electron-deficient and halogen

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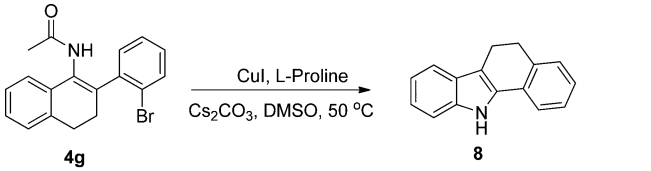
functionalities worked well under our catalytic conditions. Thus, we developed a copper(I) bromide catalyzed β-arylation of cyclic enamides with no additive/base at ambient temperature.

To demonstrate the applicability of β-aryl cyclic enamides, biologically important dihydrobenzo[*a*]carbazole was synthesized from *ortho*-bromo arylated product **4g** through intramolecular cyclization. *N*-(3-(2-Bromophenyl)-2*H*-chromen-4-yl)acetamide **4g** was treated with 5 mol % of CuI and 10 mol % of L-proline in the presence of Cs_2CO_3 in DMSO at 50 °C. Dihydro[*a*]benzocarbazole (**8**) was isolated with a moderate yield of 63% (Scheme 3). The existing protocols to synthesize

Scheme 3. Synthesis of Dihydrobenzo[*a*]carbazole via Intramolecular Cyclization



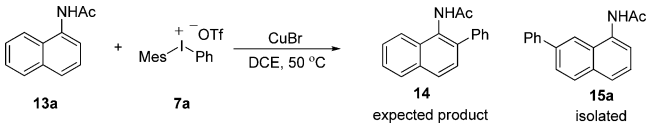
4g **8**

6,11-dihydro-5H-benzo[a]carbazole
Yield - 63%

dihydrobenzo[*a*]carbazole derivatives involve multistep reaction processes and expensive palladium catalyst.[35] This new catalytic method paves the way to synthesize diverse substituted dihydrobenzo[*a*]carbazoles effectively.

To further expand the scope of the current methodology, arylation of naphthenyl-1-acetamide was undertaken. Despite that various coupling strategies were employed to synthesize arylated anilides, arylation of naphthyl-1-acetamides is not well explored in the literature.[36−39] Naphthyl-1-acetamide **13a** was treated with 5 mol % of CuBr and 1.2 equiv of diaryliodonium salt in dichloromethane. Only a trace amount of product was observed by TLC at ambient temperature; hence, the reaction was carried out using 5 mol % of CuBr in dichloroethane at 50 °C (Scheme 4).

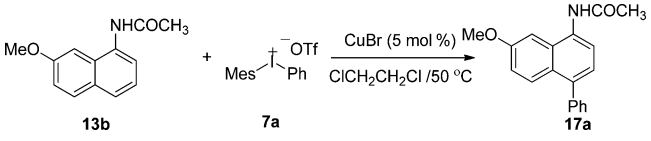
Scheme 4. Phenylation of Naphthyl-1-acetamide



13a **7a** **14** expected product **15a** isolated

2D NMR studies revealed that the isolated product was not the expected 2-phenyl-naphthyl-1-acetamide **14**, but its regioisomer 7-phenyl-naphthyl-1-acetamide **15a** (see the Supporting Information). In order to direct the phenylation at the C2-position, we chose 7-methoxy-naphthyl-1-acetamide **13b** as a substrate. Under identical reaction conditions, 4-phenyl-7-methoxy-naphthyl-1-acetamide **17a** was isolated as a major product instead of the C2-arylated product (Scheme 5).

Scheme 5. Phenylation of 7-Methoxynaphthyl-1-acetamide 13b

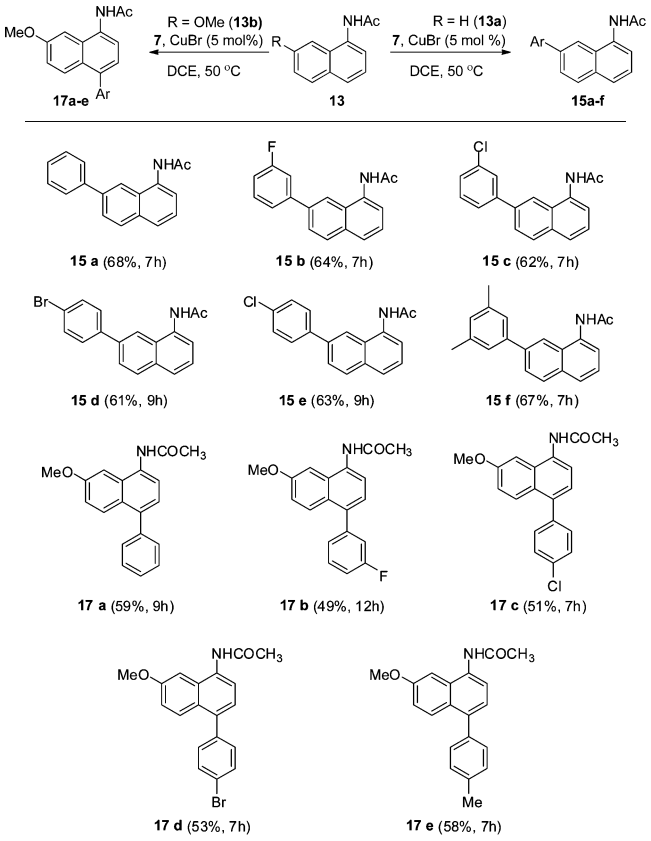


13b **7a** **17a**

It is reasonable to anticipate that steric hindrance plays a crucial role in determining the formation of regioisomers. An *ortho* effect as well as *peri*-hydrogen interaction favors the synthesis of the C7-isomer over the C2-isomer and C4-, C5-isomers. Thus, this methodology enables directed arylation of naphthyl-1-acetamides at either the C7- or the C4-position. Synthesis of C7-aryl-substituted naphthyl-1-acetamides was explored in standard reaction conditions using various diaryliodonium salts.

We observed that the efficiency of arylation on naphthyl-1-acetamide **13a** is inferior to that of cyclic enamides (**1** and **2**). TLC observation indicated the presence of starting material **13a** under standard reaction conditions. Extending the reaction time further up to 2−3 days did not improve the conversion. For example, substrate **13a** was treated with mesitylphenyliodonium salt **7a** under standard conditions to give 7-phenyl-naphthyl-1-acetamide **15a** as a major product in 68% yield along with 22% of recovered **13a** (Table4). Although only the

Table 4. Synthesis of C7-, C4-Aryl-Substituted Naphthenyl-1-acetamides[a,b]



[a]Reaction conditions: **3** (1 equiv), **7** (1.2 equiv), and Cu(I)Br (5 mol %) in $ClCH_2CH_2Cl_2$ at 50 °C for the indicated time. [b]Isolated yields.

conversion was affected, the regioselectivities of the products (**15b−e**) remain unchanged when halogen-substituted diaryliodonium salts were employed as substrates. The effect of disubstitution was also studied by employing 3,5-dimethyl phenyliodonium salt **7c** as a substrate, and the resultant arylated product **15h** was isolated in 60% yield. In all of these cases, starting material **13a** was recovered in the range of 22−36%. Based on the recovered starting material **13a**, the yields of the products are in the range of 85−93%. Thus, we achieved C7-

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arylation of naphthyl-1-acetamide under mild reaction conditions using CuBr.

Under the identical conditions, various C4-aryl-substituted 7-methoxynaphthyl-1-acetamides (**17a−e**) were successfully synthesized with moderate yields. It is noteworthy that this is the first method that discloses C4-, C7-arylation of naphthy-1-acetamides using inexpensive copper(I) salt.

In summary, we established an operationally simple, economical, and mild catalytic protocol for the direct C−H arylation of cyclic enamides derived from tetralone and chromonone for the first time using CuBr at ambient temperature in the absence of base/additives. This strategy enables the efficient synthesis of dihydrobenzo[*a*]carbazoles in good yield. The scope of this catalytic system was further extended to synthesize various C4-, C7-aryl-substituted naphthenyl-1-acetamides in moderate yields.

EXPERIMENTAL SECTION

General Remarks. Solvents used for reactions and column chromatography were commercial grade and distilled prior to use. Toluene and THF were dried over sodium/benzophenone, whereas CH_2Cl_2 and $CHCl_3$ were dried over CaH_2. Column chromatography was performed using silica gel 60−100 mesh. Melting points were determined by an open glass capillary method and uncorrected. ^{1}H NMR and ^{13}C NMR were recorded on a 500 and 125 MHz using DMSO-d_6 or $CDCl_3$ as solvents, and multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet) bs (broad singlet). Coupling constants *J* are reported in hertz (Hz). High-resolution mass spectra were obtained by ESI using Q-TOF and Orbitrap mass spectrometers. IR spectra were recorded on an FT/IR-420 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Melting points were measured in open capillaries and are uncorrected.

Typical Experimental Procedure for *β*-Arylation of Cyclic Enamides. The solution of cyclic enamide **1** or **2** (0.267 mmol), diaryliodonium salt **7** (0.32 mmol), and CuBr (1.91 mg, 5 mol %) in dry CH_2Cl_2 (1 mL) was stirred under a nitrogen atmosphere at ambient temperature for 5−36 h. The completion of the reaction was ascertained by TLC. The reaction mixture was concentrated under reduced pressure, and the residue was purified over silica gel using hexane/EtOAc as eluent (gradient mixture ratio from 90:10 to 60:40) to afford the corresponding arylated product **4** or **5**.

*N-(2-Phenyl-3,4-dihydronaphthalen-1-yl)acetamide (**4a**).* Isolated as colorless solid; 58 mg, Yield 83%; Melting Point: 167−171 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.05 (s, 1H), 7.36 (d, *J* = 4.5 Hz, 4H), 7.28−7.25 (m, 1H), 7.2−7.16 (m, 3H), 7.14−7.12 (m, 1H), 2.86 (t, *J* = 8 Hz, 2H), 2.67 (t, *J* = 8 Hz, 2H), 1.88 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.8, 141.1, 135.8, 134.9, 133.8, 133.9, 129.0, 128.6, 128.2, 127.5, 127.4, 126.7, 123.3, 29.6, 27.7, 22.8; IR (KBr): ν = 3279, 1653, 1622, 1523, 769, 702 cm^{-1}.

*N-(2-(p-Tolyl)-3,4-dihydronaphthalen-1-yl)acetamide (**4b**).* Isolated as colorless solid; 60 mg, Yield 81%; Melting Point: 181−183 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.00 (bs, 1H), 7.26 (m, 2H), 7.18−7.11 (m, 6H), 2.85 (t, *J* = 8 Hz, 2H), 2.65 (t, *J* = 8 Hz, 2H), 2.31(s, 3H) 1.89 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.7, 138.1, 136.6, 135.7, 134.7, 133.9, 129.0, 128.7, 127.5, 127.5, 127.3, 126.6, 123.3, 29.6, 27.7, 22.9, 21.2; IR (KBr): ν = 3251,1654,1627,1520,721 cm^{-1}.

*N-(2-(3,5-Dimethylphenyl)-3,4-dihydronaphthalen-1-yl)-acetamide (**4c**).* Isolated as colorless solid; 62 mg, Yield 80%; Melting Point: 185−189 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.97 (bs, 1H), 7.18−7.11 (m, 4H), 6.97 (s, 2H), 6.90 (s, 1H), 2.84 (t, *J* = 8 Hz, 2H), 2.64 (t, *J* = 8 Hz, 2H), 2.27 (s, 6H) 1.88 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.7, 141.0, 137.2, 135.7, 134.8, 133.9, 128.9, 128.8, 127.5, 127.3, 126.6, 125.3, 123.3, 29.6, 27.7, 22.8, 21.4; IR (KBr): ν = 3226, 1633, 1298, 1039, 1008, 845, 773 cm^{-1}; HRMS (ESI): *m*/*z* calculated for $C_{20}H_{21}NONa$ [M^+ + Na] 314.1521, found: 314.1516.

*N-(2-Mesityl-3,4-dihydronaphthalen-1-yl)acetamide (**4d**).* Isolated as colorless solid; 59 mg, Yield 72%; Melting Point: 175−180 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.54 (bs, 1H), 7.20−7.16 (m, 3H),7.10−7.08 (m, 1H), 6.84 (s, 2H), 2.89 (t, *J* = 8 Hz, 2H), 2.37 (t, *J* = 8 Hz, 2H), 2.28(s, 3H), 2.15(s, 6H) 1.76 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 168.8, 137.4, 135.8, 135.6, 135.0, 134.8, 133.6, 129.9, 128.2, 127.6, 127.2, 126.5, 123.1, 28.6, 28.0, 22.9, 21.0, 20.1; IR (KBr): ν = 3234, 1656, 1531, 1278, 1035, 1015, 852, 766 cm^{-1}; HRMS (ESI): *m*/*z* calculated for $C_{21}H_{23}NONa$ [M^+ + Na] 328.1677, found: 328.1684.

*N-(2-(2-Fluorophenyl)-3,4-dihydronaphthalen-1-yl)acetamide (**4e**).* Isolated as colorless solid; 58 mg, Yield 77%; Melting Point: 243−247 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.01 (bs, 1H), 7.33−7.31 (m, 2H), 7.23−7.19 (m, 6H), 2.86 (t, *J* = 8 Hz, 2H), 2.59 (t, *J* = 8 Hz, 2H), 1.82 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.2, 160.4, 158.5, 136.0, 133.2, 130.9, 130.2, 130.1, 130.0, 129.5, 129.5, 128.5, 128.4, 127.9, 127.6, 126.7, 127.4, 124.4, 123.6, 116.2, 116.0, 29.0, 27.6, 22.8; IR (KBr): ν = 3233, 1659, 1099, 1037, 1009, 805, 764 cm^{-1}; HRMS (ESI): *m*/*z* calculated for $C_{18}H_{17}NOF$ [M^+ + H] 282.1294, found: 282.1293.

*N-(2-(2-Chlorophenyl)-3,4-dihydronaphthalen-1-yl)acetamide (**4f**).* Isolated as colorless solid; 66 mg, Yield 83%; Melting Point: 238−242 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.10 (bs, 1H), 7.41−7.38 (m, 2H), 7.34−7.30 (m, 2H), 7.21−7.16 (m, 4H), 2.87 (t, *J* = 8 Hz, 2H), 2.67 (t, *J* = 8 Hz, 2H), 1.89 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.6, 143.3, 135.9, 133.4, 133.4, 133.1, 130.3, 129.8, 127.9, 127.6, 127.3, 127.2, 126.7, 126.2, 123.5, 29.2, 27.6, 22.8; IR (KBr): ν = 3280, 1654, 1620, 1519, 769 cm^{-1}; HRMS (ESI): *m*/*z* calculated for $C_{18}H_{17}NOCl$ [M^+ + H] 298.0999, found: 298.1005.

*N-(2-(2-Bromophenyl)-3,4-dihydronaphthalen-1-yl)acetamide (**4g**).* Isolated as colorless solid; 65 mg, Yield 71%; Melting Point: 203−207 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.87 (bs, 1H), 7.67−7.65 (dd, *J* = 8 Hz, 1H), 7.36−7.34 (m, 1H), 7.27−7.24(m, 2H), 7.22−7.19 (m, 3H), 7.16−7.12 (m, 1H), 2.99−2.94 (m, 1H), 2.90−2.85 (m, 1H), 2.71−2.66 (m, 1H), 2.49−2.47 (m, 1H), 1.77 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.3, 141.7, 136.0, 135.4, 133.2, 132.9, 130.4, 130.3, 129.4, 127.8, 127.7, 127.6, 126.7, 123.6, 122.2, 29.1, 27.8, 22.7; IR (KBr): ν = 3268, 1665, 1498, 1024, 1009, 956, 762 cm^{-1}; HRMS (ESI): *m*/*z* calculated for $C_{18}H_{17}NOBr$ [M^+ + H] 342.0494, found: 342.0494.

*N-(2-(4-Nitrophenyl)-3,4-dihydronaphthalen-1-yl)acetamide (**4h**).* Isolated as yellow solid; 66 mg, Yield 80%; Melting Point: > 250 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.20 (bs, 1H), 8.24−8.22 (dd, *J* = 7 Hz, *J* = 2 Hz, 2H), 7.62−7.61 (dd, *J* = 7 Hz, *J* = 2 Hz, 2H), 7.24−7.22 (m, 4H), 2.89 (t, *J* = 8 Hz, 2H), 2.72 (t, *J* = 8 Hz, 2H), 1.91 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.5, 148.6, 146.3, 136.2, 133.1, 132.5, 131.1, 128.7, 128.3, 127.7, 126.8, 123.8, 123.7, 29.1, 27.5, 22.9; IR (KBr): ν = 3260, 1661, 1593, 1509, 1341, 1287, 1108, 857, 774 cm^{-1}; HRMS (ESI): *m*/*z* calculated for $C_{18}H_{17}N_2O_3$ [M^+ + H] 309.1239, found: 309.1248.

*N-(3-Phenyl-2H-chromen-4-yl)acetamide (**5a**).* Isolated as colorless solid; 65 mg, Yield 93%; Melting Point: 160−163 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.22 (bs, 1H), 7.41−7.38 (m, 4H), 7.33 (m, 1H), 7.20−7.17 (td, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.11 (dd, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 6.96−6.93 (td, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 6.87(dd, *J* = 8 Hz, 1H), 5.08 (d, *J* = 1.5 Hz, 2H), 1.93 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.9, 154.2, 136.4, 129.7, 128.8, 128.2, 128.2, 127.6, 126.6, 124.2, 122.7, 121.7, 115.9, 69.0, 22.9; IR (KBr): ν = 3235, 1665, 1600, 1537, 1208, 1037, 1005, 723 cm^{-1}.

*N-(3-(p-Tolyl)-2H-chromen-4-yl)acetamide (**5b**).* Isolated as colorless solid; 66 mg, Yield 90%; Melting Point: 174−177 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.17 (bs, 1H), 7.29 (d, *J* = 8 Hz, 2H), 7.21 (d, *J* = 8 Hz, 2H), 7.19−7.15 (td, *J* = 8 Hz, *J* = 1.5 Hz, 1H), 7.10 (dd, *J* = 8 Hz, *J* = 1.5 Hz, 1H), 6.95−6.92 (td, *J* = 7.5 Hz, *J* = 1 Hz, 1H), 6.86 (dd, *J* = 8 Hz, *J* = 1 Hz, 1H), 5.05 (d, *J* = 1.5 Hz, 2H), 2.32(s, 3H) 1.93 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.8, 154.2, 137.6, 133.4, 129.5, 129.3, 128.1, 127.5, 126.2, 124.1, 122.8, 121.7, 115.8,

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69.0, 22.9, 21.3; IR (KBr): ν = 3240, 1653, 1641, 1514, 1040, 1009, 814, 765 cm^{-1}.

*N-(3-(3,5-Dimethylphenyl)-2H-chromen-4-yl)acetamide (**5c**).* Isolated as colorless solid; 67 mg, Yield 87%; Melting Point: 179−183 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.16 (bs, 1H), 7.17 (td, J = 8 Hz, J = 1.5 Hz, 1H), 7.09 (dd, J = 7.5 Hz, J = 1.5 Hz, 1H), 6.99 (s, 2H), 6.96 (s, 1H), 6.95−6.91 (td, J = 7.5 Hz, J = 1 Hz, 1H), 6.86 (dd, J = 8 Hz, J = 1 Hz, 1H), 5.03 (d, J = 1 Hz, 2H), 2.27(s, 6H) 1.92 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.9, 154.2, 137.7, 136.2, 129.7, 129.5, 128.3, 126.4, 125.3, 124.2, 122.8, 121.7, 115.8, 69.0, 22.8, 21.4; IR (KBr): ν = 3238, 1652, 1646, 1598, 1038, 1015, 848, 753 cm^{-1}; HRMS (ESI): m/z calculated for $C_{19}H_{20}NO_2$ [M^+ + H] 294.1494, found: 294.1507.

*N-(3-Mesityl-2H-chromen-4-yl)acetamide (**5d**).* Isolated as colorless solid; 66 mg, Yield 79%; Melting Point: 170−175 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.76 (bs, 1H), 7.16 (td, J = 7.5 Hz, J = 1.5 Hz, 1H), 7.07 (dd, J = 7.5 Hz, J = 1.5 Hz, 1H), 6.92 (m, 1H), 6.86 (s, 3H), 4.76 (s, 2H), 2.23(s, 3H), 2.19(s, 6H), 1.79 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.0, 154.3, 136.7, 136.2, 132.5, 129.3, 129.0, 128.4, 127.5, 124.0, 122.3, 121.5, 115.9, 68.3, 22.9, 21.0, 19.9; IR (KBr): ν = 3235, 1663, 1651, 1511, 1036, 1005, 803, 756 cm^{-1}; HRMS (ESI): m/z calculated for $C_{20}H_{22}NO_2$ [M^+ + H] 308.1651, found: 308.1644.

*N-(3-(2-Fluorophenyl)-2H-chromen-4-yl)acetamide (**5e**).* Isolated as colorless solid; 60 mg, Yield 80%; Melting Point: 200−204 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.21 (bs, 1H), 7.41−7.34 (m, 1H), 7.27−7.21 (m, 3H), 7.17 (dd, J = 7.5 Hz, J = 1.5 Hz, 1H), 6.97 (td, J = 7.5 Hz, J = 1 Hz, 1H), 6.90 (dd, J = 8 Hz, J = 1 Hz, 1H), 4.94 (s, 2H), 1.87 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.3, 160.9, 158.9, 154.6, 130.4, 130.3, 130.2, 130.2, 130.1, 128.8, 124.8, 124.7, 124.4, 124.3, 124.1, 122.8, 122.3, 121.8, 116.3, 116.1, 68.3, 68.3, 22.9; IR (KBr): ν = 3234, 1664, 1575, 1272, 1039, 1005, 790, 759 cm^{-1}; HRMS (ESI): m/z calculated for $C_{17}H_{14}NO_2FNa$ [M^+ + Na] 306.0902, found: 306.0906.

*N-(3-(3-Chlorophenyl)-2H-chromen-4-yl)acetamide (**5f**).* Isolated as colorless solid; 67 mg, Yield 85%; Melting Point: 186−192 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.26 (bs, 1H), 7.44−7.42 (m, 2H), 7.40−7.38 (dt, J = 7.5 Hz, J = 1.5 Hz, 1H), 7.35−7.33 (dt, J = 7.5 Hz, J = 1.5 Hz, 1H), 7.22−7.19 (td, J = 7.5 Hz, J = 1.5 Hz, 1H), 7.14 (dd, J = 7.5 Hz, J = 1.5 Hz, 1H), 6.97−6.94 (td, J = 7.5 Hz, J = 1 Hz, 1H), 6.87 (dd, J = 8 Hz, J = 1 Hz, 1H), 5.07 (d, J = 1 Hz, 2H), 1.93 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.8, 154.4, 138.6, 133.5, 130.6, 130.1, 128.0, 127.5, 127.4, 126.7, 126.3, 124.3, 122.4, 121.8, 116.0, 68.6, 22.9; IR (KBr): ν = 3238, 1651, 1633, 1523, 1278, 1038, 1009, 877, 750 cm^{-1}; HRMS (ESI): m/z calculated for $C_{17}H_{15}NO_2Cl$ [M^+ + H] 300.0791, found: 300.0792.

*N-(3-(2-Bromophenyl)-2H-chromen-4-yl)acetamide (**5g**).* Isolated as colorless solid; 70 mg, Yield 77%; Melting Point: 176−181 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.09 (bs, 1H), 7.68 (dd, J = 8 Hz, J = 1.5 Hz, 1H), 7.39 (td, J = 7.5 Hz, J = 1.5 Hz, 1H), 7.30−7.28 (m, 2H), 7.23 (td, J = 7.5 Hz, J = 1.5 Hz, 1H), 7.14 (dd, J = 7.5 Hz, J = 1.5 Hz, 1H), 6.97 (td, J = 7.5 Hz, J = 1 Hz, 1H), 6.89 (dd, J = 5 Hz, J = 0.5 Hz, 1H), 5.01 (d, J = 15 Hz, 1H), 4.84 (d, J = 13.5 Hz, 1H), 1.82 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.4, 154.6, 137.5, 133.1, 131.2, 130.2, 130.1, 128.4, 128.1, 128.0, 124.5, 122.5, 122.2, 121.8, 116.1, 68.3, 22.8; IR (KBr): ν = 3268, 1670, 1604, 1485, 1366, 1036, 1002, 856, 756 cm^{-1}; HRMS (ESI): m/z calculated for $C_{17}H_{15}NO_2Br$ [M^+ + H] 344.0286, found: 344.0293.

*N-(3-(4-Nitrophenyl)-2H-chromen-4-yl)acetamide (**5h**).* Isolated as yellow solid; 68 mg, Yield 83%; Melting Point: 229−235 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.39 (bs, 1H), 8.25 (d, J = 7 Hz, 2H), 7.64 (d, J = 7 Hz, 2H), 7.25−7.20 (m, 2H), 6.99 (td, J = 7.5 Hz, J = 1 Hz, 1H), 6.90 (dd, J = 7.5 Hz, J = 1 Hz, 1H), 5.11 (d, J = 1 Hz, 2H), 1.95 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.6, 154.7, 146.7, 143.7, 130.6, 128.9, 128.8, 125.3, 124.7, 124.0, 122.2, 121.9, 116.1, 68.4, 23.0; IR (KBr): v = 3260, 1666, 1594, 1278, 1039, 1008, 757 cm^{-1}; HRMS (ESI): m/z calculated for $C_{17}H_{14}N_2O_4Na$ [M^+ + Na] 333.0851, found: 333.0868.

Synthesis of Dihydrobenzo[*a*]carbazole (8). The mixture of 0.2 mmol of enamide **4g** (35 mg, 0.2 mmol), proline (2.35 mg, 10 mol %), Cs_2CO_3 (97 mg, 0.3 mmol), and CuI (1.94 mg, 5 mol %) in DMSO (3 mL) was heated at 50 °C for 12 h under an inert atmosphere. The reaction mixture was cooled to room temperature, and 5 mL of water was added. The aqueous layer was extracted with AcOEt (10 mL × 2). The combined organic layer was washed with brine (10 mL × 2) and dried over $MgSO_4$. The organic layer was concentrated in vacuo. The obtained crude product was purified with column chromatography on silica gel (elution with hexane/AcOEt = 70:30) to give **8** (20 mg, 63% yield) as a colorless solid. Melting Point: 162−165 °C; ^{1}H NMR (500 MHz, DMSO- d_6): δ 11.41 (br s, 1H), 7.63−7.64 (m, 1H), 7.63−7.64 (m, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8 Hz, 1H), 7.27−7.29 (m, 2H), 7.14−7.17 (m, 1H), 7.08−7.11 (m, 1H), 6.98−7.01 (m, 1H), 2.98−3.01 (m, 2H), 2.88−2.91 (m, 2H); ^{13}C NMR (125 MHz, DMSO- d_6): δ 137.5, 136.3, 133.5, 129.5, 128.7, 127.1, 127.1, 126.9, 122.0, 121.3, 119.3, 118.8, 111.8, 111.2, 29.4, 19.7; IR (KBr): ν = 3410, 3048, 1451, 1319, 743 cm^{-1}.

Typical Experimental Procedure for Synthesis of Various Substituted 7-Aryl-1-naphthenyl Acetamides 15a−f. To the stirred solution of 1-naphthenyl acetamide **13a** (50 mg, 0.27 mmol) and diaryliodonium salt **7** (0.32 mmol) in dry dichloroethane (1 mL) was added CuBr (1.93 mg, 5 mol %) under a nitrogen atmosphere, and the mixture was heated at 50 °C for 7−9 h. The reaction progress was monitored by TLC. After 7−9 h, the crude mixture was concentrated under reduced pressure, and the residue was purified to afford the corresponding 7-aryl-1-naphthenyl acetamides **15a−f** and unreacted substrate **13a**.

*N-(7-Phenylnaphthalen-1-yl)acetamide (**15a**).* The crude product was purified by flash chromatography using hexane/AcOEt as eluent (gradient mixture ratio from 95:05 to 80:20) to provide the compounds in order of elution, arylated product **15a** as a colorless solid (48 mg, 68%) and the recovered starting material **13a** (11 mg, 22%). Melting Point: 161−165 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 10.01 (bs, 1H), 8.35 (s, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.86 (dt, J = 7.5, 1 Hz, 3H), 7.79 (d, J = 7.5, 1H), 7.77 (d, J = 8.5, 1H), 7.55 (t, J = 8 HZ, 2H), 7.50 (t, J = 8 HZ, 1H), 7.42 (t, J = 7.5 HZ, 1H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.4, 140.7, 137.9, 134.4, 133.3, 129.5, 129.4, 128.1, 127.9, 127.6, 126.2, 125.6, 125.0, 121.9, 120.7, 24.1; IR (KBr): ν = 3266, 3052, 2926, 1672, 1606, 1547, 1517, 1467, 1388, 1291, 1188, 1131, 1099, 1042, 889, 798, 772 cm^{-1}. HRMS (ESI): m/z calculated $C_{18}H_{16}ON$ [M^+ + H] 262.1226, found: 262.1221.

*N-(7-(3-Fluorophenyl)naphthalen-1-yl)acetamide (**15b**).* The crude product was purified by flash chromatography using hexane/AcOEt as eluent (gradient mixture ratio from 95:05 to 80:20) to provide the compounds in order of elution, arylated product **15b** as a colorless solid (51 mg, 67%) and the recovered starting material **13a** (10 mg, 20%). Melting Point: 182−187 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 10.01 (bs, 1H), 9.71 (s, 1H), 8.01−7.94 (m, 3H), 7.59−7.58 (m, 2H), 7.56−7.49 (m, 2H), 7.30−7.26 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 170.0, 162.4 (d, J = 241 Hz), 142.6 (d, J = 8.75 Hz), 135.9, 133.7, 131.4, 131.3, 130.6 (d, J = 8.75 Hz), 128.4, 128.1, 127.9, 127.3, 126.9, 125.5 (d, J = 3.75 Hz), 124.4, 116.0 (d, J = 22.5 Hz), 114.4 (d, J = 21.25 Hz), 23.0; IR (KBr): ν = 3253, 3046, 2327, 1667, 1607, 1590, 1537, 1501, 1456, 1433, 1271, 1185, 1161, 1131, 1185, 1131, 869, 832, 753, 699 cm^{-1}. HRMS (ESI): m/z calculated $C_{18}H_{15}ONF$ [M^+ + H] 280.1132, found: 280.1130.

*N-(7-(3-Chlorophenyl)naphthalen-1-yl)acetamide (**15c**).* The crude product was purified by flash chromatography using hexane/AcOEt as eluent (gradient mixture ratio from 95:05 to 80:20) to provide the compounds in order of elution, arylated product **15c** as a colorless solid (49 mg, 61%) and the recovered starting material **13a** (14 mg, 28%). Melting Point: 187−192 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 10.03 (bs, 1H), 8.39 (s, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.94 (t, J = 2 Hz, 1H), 7.88 (dd, J = 8.5, 2 Hz, 1H), 7.85−7.82 (m, 2H), 7.77 (d, J = 8 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.54−7.49 (m, 2H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.4, 142.9, 136.3, 134.5, 134.3, 133.6, 131.3, 130.5, 129.6, 127.9, 127.3, 126.5, 126.4, 125.4, 124.9, 121.9, 121.0, 24.2; IR (KBr): ν 3293, 3066, 2961, 2934, 2868, 1739, 1676, 1621, 1548, 1476, 1391, 1278, 1133, 1103,

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1083, 1057, 1021, 978, 898, 834, 743 cm^{-1}. HRMS (ESI): m/z calculated $C_{18}H_{15}ONCl$ $[M^+ + H]$ 296.0837, found: 296.0832.

*N-(7-(4-Bromophenyl)naphthalen-1-yl)acetamide (**15d**).* The crude product was purified by flash chromatography using hexane/AcOEt as eluent (gradient mixture ratio from 95:05 to 80:20) to provide the compounds in order of elution, arylated product **15d** as a colorless solid (53 mg, 58%) and the recovered starting material **13a** (18 mg, 36%). Melting Point: 194−197 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 10.02 (bs, 1H), 8.36 (s, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.87−7.82 (m, 3H), 7.76−7.73 (m, 3H), 7.54−7.49 (m, 2H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.4, 139.9, 137.4, 133.5, 132.4, 129.7, 129.5, 128.6, 126.4, 125.3, 125.0, 123.2, 122.0, 121.6, 120.7, 24.2; IR (KBr): ν = 3274, 3041, 2944, 2917, 2847, 1719, 1651, 1598, 1527, 1439, 1363, 1259, 1112, 1081, 1059, 1028, 1001, 947, 875, 807, 738 cm^{-1}. HRMS (ESI): m/z calculated $C_{18}H_{15}ONBr$ $[M^+ + H]$ 340.0332, found: 340.0327.

*N-(7-(4-Chlorophenyl)naphthalen-1-yl)acetamide (**15e**).* The crude product was purified by flash chromatography using hexane/AcOEt as eluent (gradient mixture ratio from 95:05 to 80:20) to provide the compounds in order of elution, arylated product **15e** as a colorless solid (52 mg, 65%) and the recovered starting material **13a** (15 mg, 30%). Melting Point: 220−225 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 10.04 (bs, 1H), 8.33 (s, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.89−7.84 (m, 3H), 7.77 (d, J = 8.0 Hz, 2H), 7.61−7.59 (m, 2H), 7.51 (dd, J = 7.5, 8.0 Hz, 1H), 3.10 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.4, 139.5, 136.5, 134.5, 133.5, 133.0, 129.5, 129.5, 129.4, 127.8, 126.4, 125.3, 125.0, 122.0, 120.7, 24.2; IR (KBr): ν = 3280, 3056, 2957, 2926, 2856, 1728, 1664, 1608, 1537, 1461, 1377, 1272, 1125, 1094, 1070, 1041, 1009, 962, 881, 821, 751 cm^{-1}. HRMS (ESI): m/z calculated $C_{18}H_{15}ONCl$ $[M^+ + H]$ 296.0837, found: 296.0827

*N-(7-(3,5-Dimethylphenyl)naphthalen-1-yl)acetamide (**15f**).* The crude product was purified by flash chromatography using hexane/AcOEt as eluent (gradient mixture ratio from 95:05 to 80:20) to provide the compounds in order of elution, arylated product **15f** as a colorless solid (52 mg, 66%) and the recovered starting material **13a** (13 mg, 26%). Melting Point: 179−182 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 10.01 (bs, 1H), 8.30 (s, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.82 (dd, J = 8.5, 1.5 Hz, 1H), 7.78 (d, J = 7.5 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.49 (dd, J = 8,8 Hz 1H), 7.44 (s, 2H), 7.06 (s, 1H), 2.39 (s, 6H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.4, 140.7, 138.4, 138.2, 137.5, 134.4, 133.3, 129.5, 129.2, 127.1, 126.0, 125.8, 125.0, 122.0, 120.4, 24.2, 21.6; IR (KBr): v =3254, 3073, 3030, 3012, 2972, 2927, 2809, 2302, 1603, 1587, 1521, 1485, 1442, 1417, 1364, 1350, 1319, 1223, 1225, 1200, 1133, 1107, 1011, 942, 958, 801, 733, 721, 676 cm-1. HRMS (ESI): m/z calculated $C_{20}H_{20}ON$ $[M^+ + H]$ 290.1539, found: 290.1534.

Typical Experimental Procedure for Synthesis of Various Substituted 7-Methoxy-4-aryl-1-naphthenyl Acetamides 17a−e. To the stirred solution of 7-methoxy-1-naphthenyl acetamide **13b** (50 mg, 0.23 mmol) and diaryliodonium salt 7 (0.28 mmol) in dry dichloroethane (1 mL) was added CuBr (1.66 mg, 5 mol %) under a nitrogen atmosphere, and the mixture was heated at 50 °C for 7−12 h. The reaction completion was monitored by TLC. After completion, the crude mixture was concentrated and purified to the corresponding 7-methoxy-4-aryl-1-naphthenyl acetamides **17a−e**.

*N-(7-Methoxy-4-phenylnaphthalen-1-yl)acetamide (**17a**).* The crude product was purified by flash chromatography using hexane/AcOEt as eluent (gradient mixture ratio from 95:05 to 80:20) to provide the compounds in order of elution, arylated product **17a** as a colorless solid (38 mg, 56%) and the recovered starting material **13b** (16 mg, 32%). Melting Point: 223−226 °C; Isolated as a colorless solid; 60 mg, Yield 81%; Melting Point: 181−183 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.59 (bs, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.46−7.45 (m, 4H), 7.35 (d, J = 8.5 Hz, 2H), 7.25−7.23 (dd, J = 8 Hz, J = 2.5 Hz, 1H), 7.20 (d, J = 4 Hz, 1H), 3.87 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.8, 158.4, 140.5, 137.8, 132.8, 130.2, 130.1, 129.2, 129.0, 128.6, 127.5, 127.5, 126.0, 118.7, 103.1, 55.6, 23.0. IR (KBr): v = 3266, 3085, 3050, 3026, 2999, 2938, 2829, 2330, 1633, 1602, 1534, 1501, 1468, 1434, 1390, 1370, 1330, 1273, 1250, 1218, 1162, 1134, 1034, 1010, 961, 914, 824, 764, 742, 698 cm^{-1}. HRMS (ESI): m/z calculated C19 H18 O2 N $[M^+ + H]$ 292.1332, found: 292.1330.

*N-(4-(3-Fluorophenyl)-7-methoxynaphthalen-1-yl)acetamide-(**17b**).* The crude product was purified by flash chromatography using hexane/AcOEt as eluent (gradient mixture ratio from 95:05 to 80:20) to provide the compounds in order of elution, arylated product **17b** as a colorless solid (37 mg, 52%) and the recovered starting material **13b** (15 mg, 30%). Melting Point: 214−219 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.66 (bs, 1H), 7.93 (d, J = 9.0 Hz, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.52−7.48 (m, 1H), 7.36 (d, J = 8.5 Hz, 1H), 7.29−7.22 (m, 5H), 3.88 (s, 3H); 1.99 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.9, 162.4 (d, J = 241 Hz), 158.5, 142.7 (d, J = 7.5 Hz), 136.5, 132.7, 130.5 (d, J = 8.75 Hz), 130.3, 130.2, 129.2, 127.6, 125.6, 125.4 (d, J = 2.5 Hz), 119.0, 115.9 (d, J = 22.5 Hz), 114.3 (d, J = 21.25 Hz), 103.0, 55.6, 23.0; IR (KBr): v = 3293, 3085, 3030, 3005, 2983, 2928, 1643, 1616, 1538, 1509, 1472, 1390, 1280, 1256, 1226, 1190, 1056, 1027, 752, 737 cm-1. HRMS (ESI): m/z calculated $C_{19}H_{17}O_2NF$ $[M^+ + H]$ 310.1238, found: 310.1237.

*N-(4-(4-Chlorophenyl)-7-methoxynaphthalen-1-yl)acetamide (**17c**).* The crude product was purified by flash chromatography using hexane/AcOEt as eluent (gradient mixture ratio from 95:05 to 80:20) to provide the compounds in order of elution, arylated product **17c** as a colorless solid (42 mg, 55%) and the recovered starting material **13b** (16 mg, 32%). Melting Point: 205−212 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.63 (bs, 1H), 7.92 (d, J = 9 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.52 (d, J = 9 Hz, 2H), 7.46 (d, J = 8 Hz, 2H), 7.34 (d, J = 8.5 Hz, 1H), 7.26−7.24 (dd, J = 8.5 Hz, J = 2.5 Hz, 1H), 7.22 (d, J = 1.5 Hz, 1H), 3.88 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.8, 158.5, 139.4, 136.5, 132.7, 132.4, 131.0, 130.2, 130.1, 129.1, 128.6,127.6,125.6, 118.9, 103.0, 55.6, 23.0. IR (KBr): v = 3240, 3010, 2961, 2832, 1657, 1627, 1513, 1492, 1460, 1424, 1390, 1334, 1275, 1225, 1180, 1141, 1095, 1032, 1015, 831, 760 cm^{-1}. HRMS (ESI): m/z calculated $C_{19}H_{17}O_2NCl$ $[M^+ + H]$ 326.0942, found: 326.0944.

*N-(4-(4-Bromophenyl)-7-methoxynaphthalen-1-yl)acetamide (**17d**).* The crude product was purified by flash chromatography using hexane/AcOEt as eluent (gradient mixture ratio from 95:05 to 80:20) to provide the compounds in order of elution, arylated product **17d** as a colorless solid (49 mg, 57%) and the recovered starting material **13b** (14 mg, 28%). Melting Point: 211−216 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.63 (bs, 1H), 7.92 (d, J = 9 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.65 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8 Hz, 1H), 7.26−7.24 (dd, J = 8.5 Hz, J = 2.5 Hz, 1H), 7.22 (d, J = 2.5 Hz, 1H), 3.88 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.9,158.5, 139.7, 136.52, 132.7, 131.5, 131.3, 130.2, 130.2, 129.1, 127.6, 125.6, 121.1, 118.9, 103.0, 55.6, 23.0. IR (KBr): v = 3262, 2958, 2927, 2855, 1723, 1658, 1605, 1511, 1490, 1373, 1275, 1226, 1180, 829, 752 cm^{-1}. HRMS (ESI): m/z calculated $C_{19}H_{17}O_2NBr$ $[M^+ + H]$ 370.0437, found: 370.0439.

*N-(7-Methoxy-4-p-tolylnaphthalen-1-yl)acetamide (**17e**).* The crude product was purified by flash chromatography using hexane/AcOEt as eluent (gradient mixture ratio from 95:05 to 80:20) to provide the compounds in order of elution, arylated product **17e** as a colorless solid (45 mg, 59%) and the recovered starting material **13b** (10 mg, 20%). Melting Point: 224−227 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.55 (bs, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.35−7.32 (m, 3H), 7.26 (d, J = 8 Hz, 2H), 7.23−7.21 (dd, J = 8.5 Hz, J = 2.5 Hz, 1H), 7.18 (d, J = 2.5 Hz, 1H), 3.86 (s, 3H), 2.36 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 169.9, 158.4, 137.7, 137.5, 136.7, 132.9, 130.1, 130.1, 129.2, 129.1, 128.9, 127.4, 126.0, 118.6, 103.1, 55.6, 23.0, 21.2. (KBr): v = 3260, 2957, 2924, 2856, 1725, 1659, 1626, 1576, 1505, 1459, 1423, 1373, 1334, 1273, 1225, 1182, 1137, 1121, 1073, 1033, 968, 892, 841, 823 cm^{-1}. HRMS (ESI): m/z calculated $C_{20}H_{20}O_2N$ $[M^+ + H]$ 306.1489, found: 306.1488

Typical Procedure for (2-Bromophenyl)(mesityl)iodonium Trifluoromethanesulfonate (7g). To the stirred solution of *m*-CPBA (~55% assay, dried under high vacuum for 2−3 h prior to use) (2.4 g, 7.77 mmol) in dry CH_2Cl_2 (70 mL) were added 2-bromo iodobenzene (2.0 g, 7.07 mmol) and mesitylene (0.935 g, 7.77 mmol)

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under an argon atmosphere. The resulting solution was cooled to 0 °C, and trifluoromethanesulfonic acid (1.9 mL, 22 mmol) was added dropwise over a period of 10−15 min. The reaction mixture was stirred at room temperature for 8 h. Volatiles are removed under vacuum and titurated with Et_2O. This process was repeated 3−4 times until detectable formation of precipitate was observed. Once precipitation initiated, the solution was cooled to −20 °C for 30 min to obtain (2-bromophenyl)(mesityl)iodonium trifluoromethanesulfonate **7g** (3.4 g, 87%). Melting Point: 155−157 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.77 (dd, J = 8 Hz, J = 1.5 Hz, 1H), 7.47 (td, J = 8 Hz, J = 1.5 Hz, 1H), 7.35 (td, J = 8 Hz, J = 1.5 Hz, 1H), 7.23 (s, 2H), 6.88 (dd, J = 8 Hz, J = 1.5 Hz, 1H), 2.64 (s, 6H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, CDCl3) δ: 145.4, 142.8, 134.5, 133.2, 131.4, 131.0, 130.9, 124.6, 121.6, 120.2 (q, J = 318 Hz), 115.4, 27.1, 21.0; IR (KBr): ν = 2919, 1619, 1443, 1251, 1159, 1026 cm^{-1}; HRMS (ESI): m/z calculated for $C_{15}H_{15}BrI$ [M^+] 400.9402, found: 400.9402. All other aryliodonium salts were prepared according to the literature procedure.[32−34,40−44]

■ ASSOCIATED CONTENT

Supporting Information

General information and NMR spectra are given for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vkesavan@iitm.ac.in.

Notes

The authors declare no competing financial interest.

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