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N^1- and N^3-Arylations of Hydantoins Employing Diaryliodonium Salts *via* Copper(I) Catalysis at Room Temperature

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Dedicated to Prof. Viktor V. Zhdankin for his outstanding contribution to Hypervalent Iodine Chemistry.

Copper(I)-catalyzed *N*-arylation (both N^1- and N^3-) of hydantoins with diaryliodonium salts as aryl partners at room temperature is reported. The transformation allows diverse scopes on both hydantoins and diaryliodonium salts delivering functionalized N^3-arylated products under mild reaction conditions. The presence of hydrogens at C^5- and N^1- position of the hydantoin does not lead to other side products. Chiral hydantoins can also be synthesized via this methodology. Sterically complicated *ortho*-substituted diaryliodonium salts are tolerated and delivered challenging *ortho*-arylated products. In addition, this strategy can also be effectively extended to N^1-arylation of hydantoins.

Introduction

Biologically active arylated hydantoin (imidazolidine-2,4-dione) derivatives[1] have marked skeletal appearances in a wide array of natural products[2] and synthetic products.[3] This motif is purposely and effectively used in medicinal chemistry,[4] coordination chemistry,[5] agrochemistry,[6] and polymer sciences.[7] Though, structurally simple and first synthesized[8] in 1861, intense research efforts have been devoted to synthetic developments and studies of this class of five-membered compound.[1a] Hydantoin based drugs such as Nilutamide (**1**) and Enzalutamide (**3**) (Figure 1) have been used as *anti*-androgen and *anti*-prostate cancer agents respectively. GLGP-0492 (**2**), BMS-587101 (**4**), and BMS-564929 (**5**) are candidates under clinical development (Figure 1).

In the traditional approach, condensation of aryl isocyanates with amino acid derivatives afforded N^3-arylated hydantoins (Scheme 1a).[9] This strategy required strong acidic or basic conditions during the cyclization of ureido derivatives. Moreover, substituted aryl isocyanates needed extra steps for their syntheses. Moreover, isocyanates are often toxic and unstable under ambient conditions.[10]

Menendez *et al.* pioneered Cu-mediated N^3-arylation of hydantoins (only one example) with *p*-tolyllead triacetate[11] as an arylating source. Thereafter, triarylbismuthane,[12] aryl boronic acid,[12] and aryl iodide[13] were also employed as aryl partners in Cu-mediated protocols (Scheme 1b). Recently, Petit's group re-established the Cu-mediated N^3-arylation and subsequently Cu-catalysed N^1-arylation of N^3-aryl hydantoins using aryl halides (Scheme 1c).[14] Although the method highlighted broad substrate scopes, *ortho*-substituted aryl groups failed to tolerate the reaction condition. Also, N^3-arylation of hydantoins containing both acidic C^5–H and N^1–H exhibited poor selectivity and hence limited hydantoins were studied.

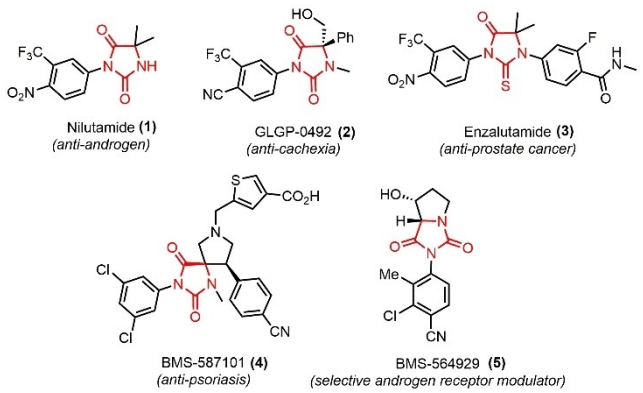

Figure 1. Important hydantoin based drugs.

Diaryliodonium salts have emerged as a versatile arylating partner over the past decades because of their ease of synthesis, less environmental impact, affordability, and reactivity within a wide range of nucleophiles.[15] Owing to the presence of an excellent leaving group (aryl iodide), diaryliodonium salts have encompassed their importance in metal-free and transition-metal catalyzed arylation chemistry.[16] Arylation of lactams and primary amides with diaryliodonium salts with the aid of Cu-catalysis has been achieved.[17] Pioneering works on metal-free arylation of a wide range of secondary amides have been reported by Olofsson's group.[18] But, hydantoins (containing imide and amide functional groups)

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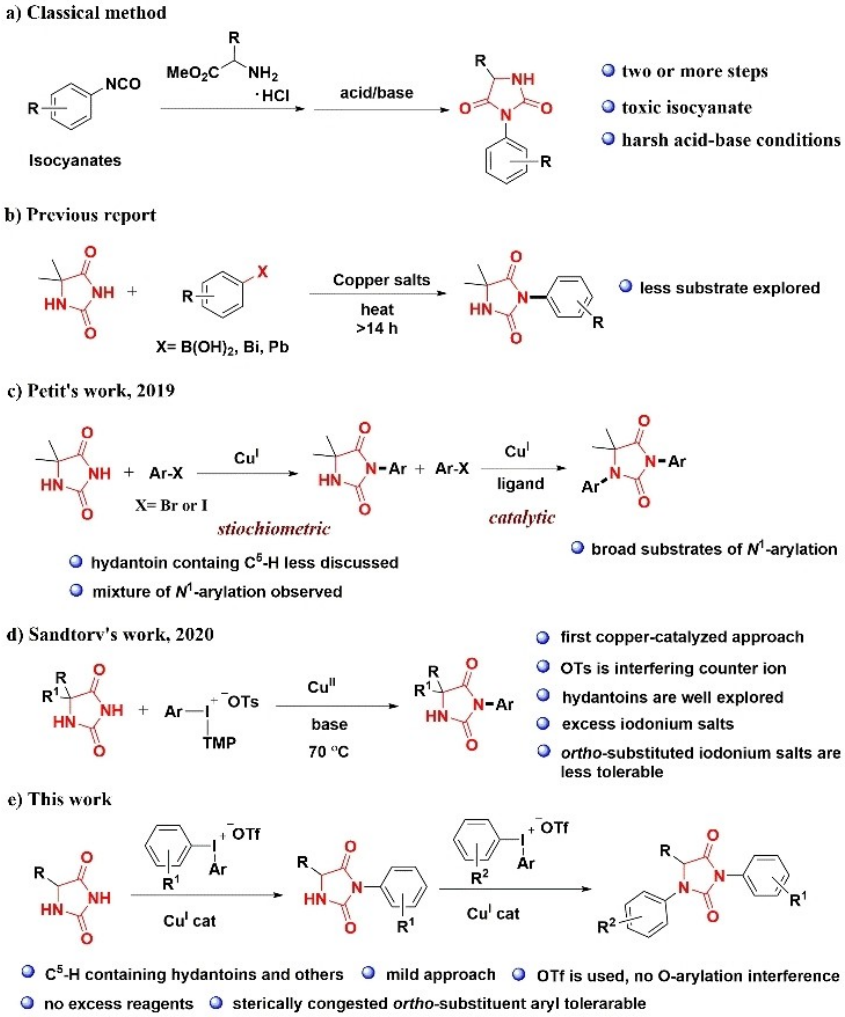


Scheme 1. Strategies for N^3-arylation of hydantoins.

have not been extensively discussed in the report.[19] Recently, Cu-catalysed N^3-arylation has been reported utilizing aryl(TMP) OTs, as the aryl source with a broad substrate scope in the aryl part (Scheme 1d).[20] In this first Cu-catalysed protocol, they highlighted the efficiency of regioselective arylation without epimerization at C^5- and N^1- position of hydantoins, even though an excess amount of iodonium salts were utilized and trace amounts of both N^1-regiomer and N^1,N^3-biarylated side products were observed. However, highly congested *ortho*-substituents were also not tolerated under this protocol.

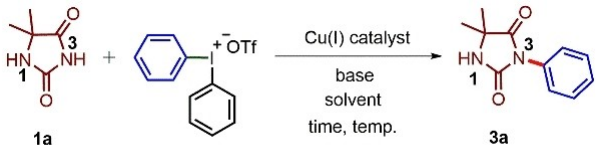
Considering the limitations of existing methodologies for the arylation of hydantoins, we have come up with a mild protocol for *N*-arylation (both N^1- and N^3-) of hydantoins with diaryliodonium salts as the arylating partner. Our protocol compatibility of congested *ortho*-substituted substrates exhibits the advantages of 1) room temperature reaction, 2)compatibility of congested *ortho*-substituted substrates (Sandtorv's observed only one example with less yield), 3) lower stoichiometry (~1 equiv.) of iodonium salt (both in symmetrical and unsymmetrical salts) and 4) non-interfering iodonium salts (triflate & tertrafluoroborate) (Scheme 1e).

Results and Discussion

N^3-Arylation of hydantoins with diaryliodonium salts:

We embarked on our initial optimization of the reaction conditions using diphenyliodonium triflate (**2a**) as the aryl source and 5,5-dimethylhydantoin (**1a**) as the model substrates (Table 1). No arylation was observed under base-mediated conditions and in the absence of Cu catalyst (see ESI, Table S3). Initially, arylation at N^3-position was obtained when the reaction was conducted utilizing a stoichiometric amount of copper(I) iodide and Na_2CO_3 at room temperature (30 °C) affording the desired product (**3a**) in 74% yield (entry 1). Reducing the amount of copper to a catalytic scale (entry 2) took a longer time for completion along with decomposition of the iodonium salt and the yield came down to 45%. Different solvents and

Table 1. Optimization with diphenyliodonium salts.[a]



1a 2a 3a

Entry	Solvent	Base (equiv.)	Cu [x mol %]	T [°C]	Time [h]	Yield [%][b]
1	DCE	Na_2CO_3 (1.0)	CuI (100)	rt	5	74
2	DCE	Na_2CO_3 (1.0)	CuI (20)	rt	24	45
3	DCE	Na_2CO_3 (2.0)	CuI (20)	rt	24	54
4	DCE	Et_3N (1.0)	CuI (20)	rt	24	Trace
5	DCE	K_3PO_4 (1)	CuI (20)	rt	5	77 (52)[c]
6	DCE	K_3PO_4 (2)	CuI (20)	rt	24	Trace
7	Toluene	K_3PO_4 (1)	CuI (30)	rt	24	44
8	DMF	K_3PO_4 (1)	CuI (20)	rt	24	23
9	DCE	Cs_2CO_3 (1)	CuI (20)	rt	24	34
10	DCE	^{t}BuOK	CuI (20)	rt	24	n.r
11	DCE	K_3PO_4 (1)	$Cu(OTf)_2$ (20)	rt	24	Trace
12	DCE	K_3PO_4 (1)	CuCl (20)	rt	15	65
13	DCE	K_3PO_4 (1)	$Cu(acac)_2$ (20)	rt	24	n.r
14	DCE	K_3PO_4 (1)	CuI (20)	rt	12	67[d]
15	DCE	K_3PO_4 (1)	CuI (20)	rt	12	34[e]
16	DCE	K_3PO_4 (1)	CuI (20)	rt	12	n.r[f]
17	**DCE**	**K_3PO_4 (1)**	**CuI (20)**	**rt**	**5**	**84**[g]

[a] Reaction conditions: Diphenyliodonium salts (0.1 mmol), hydantoin **1a** (0.1 mmol), base and copper sources were added into a Schlenk tube under N_2 atmosphere. Anhydrous and degassed toluene (0.5 mL) was added to it and mixture was stirred at specified temperature. Anhydrous DCE was used (2 mL). [b] ^{1}H NMR yield. [c] CuI (10 mol%). [d] Ph_2IBF4 (1 equiv.). [e] Ph_2IBr (1 equiv.). [f] Ph_2IOTs (1 equiv.). [g] **2a** (1.2 equiv.).

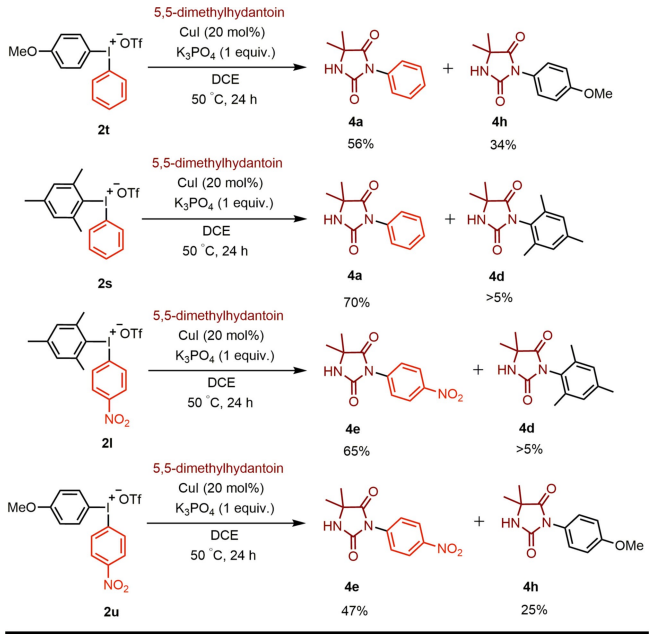
bases were screened to optimize the reaction conditions and surprisingly, in the presence of K_3PO_4, complete consumption of starting compounds was observed while maintaining the higher product yield (entry 5) in shorter reaction time. With two equivalents of base (K_3PO_4) and longer reaction time (entry 6), we observed mostly decomposition of **2a** with a trace amount of product formation. Further optimization for base and solvent was examined but, the yield of the reaction did not improve and other side products were monitored (entries 7–10). In toluene, a lower yield of the desired product was observed (entry 7). Cu^I and Cu^{II} catalysts such as $Cu(OTf)_2$, $Cu(acac)_2$, CuCl etc. were evaluated, but CuI was found to be the superior catalyst (entries 11–13). Finally, the impact of the anion in iodonium salts was optimized; where tetraflouroborate salt showed better yield in comparison to other salts (entries 14–16).

Since different synthetic routes to iodonium salts ease the incorporation of different structure and aryl groups, other anions (OTs, PF_6, TFA, Br) were also investigated but, decomposition of the iodonium salt was observed with these anions containing iodonium salts. In the case of –OTs iodonium salt, *O*-arylation at the tosyl group was primarily observed which is opposite to Sandtorv's result.[20] Nevertheless, *O*-arylation is possible with –OTs,[21] but –OTs acts as a good counter anion depending on the reaction conditions both in metal-free and metal-catalyzed reactions.[20,22] Our Cu-catalysed version of *N*-arylation of hydantoins was achieved because of the lesser nucleophilicity of the diaryliodonium triflate.

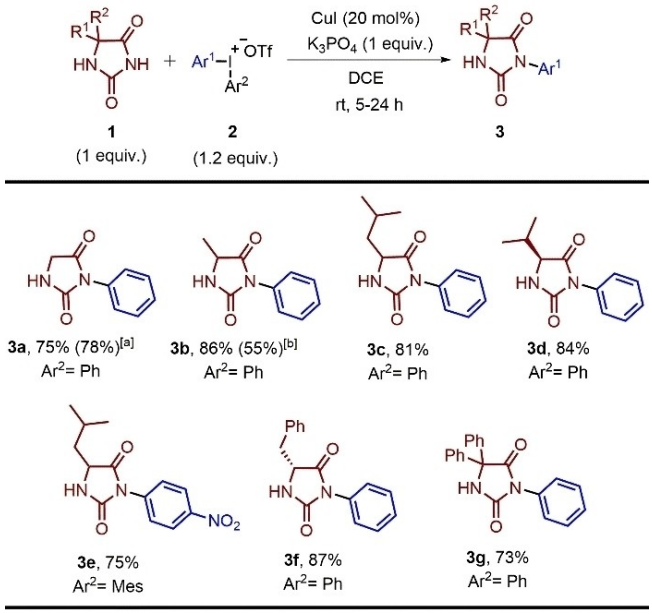
Chemoselective pattern study of the reaction is very interesting with a range of iodonium salts having both electron-donating and electron-withdrawing groups.[23] Symmetrical iodonium salts could be easily synthesized from direct arenes or aryl iodides and when approached by *O*-, *N*- and *C*-nucleophiles, one of the aryl groups got involved in the subsequent arylation. But, in most cases of unsymmetrical diaryliodonium salts, one aryl part is electron-withdrawing and the other is electron-donating and also bears *ortho*-substituted groups like mesityl or triisopropylphenyl; around the hypervalent iodine center. This brings the chemoselectivity factor between the aryl groups. Good atom economy of the reaction can be considered only when one aryl group exclusively takes part in arylation and the other aryl group leaves as "dummy" iodoarene.

The chemoselectivity study (Scheme 2) was performed under optimized reaction conditions between hydantoin (**1a**) and four selected iodonium salts (**2l**, **2s**, **2t**, and **2u**). A mixture of products was observed in the case of **2t** and the electron-deficient group was found to get transferred to furnish **4a**, as the major product. In comparison to *p*-anisyl as dummy ligand, mesityl containing iodonium salts showed higher selectivity in both the cases (**2l** and **2s**). The observed trend is matching with previous studies under metal-catalyzed conditions which implies "mesityl" as a dummy group is more reliable due to steric factor.[24]

Having the chemoselectivity study in hand, the scope of the reaction was first examined for the arylation of hydantoins with iodonium salts (**2a**) (Scheme 3). Simple hydantoin (**1b**) was arylated selectively at N^3-position without showing any traces of by-product(s). The presence of one α-hydrogen in compounds (**3a**–**3f**) did not hinder the selective arylation at N^3-position of



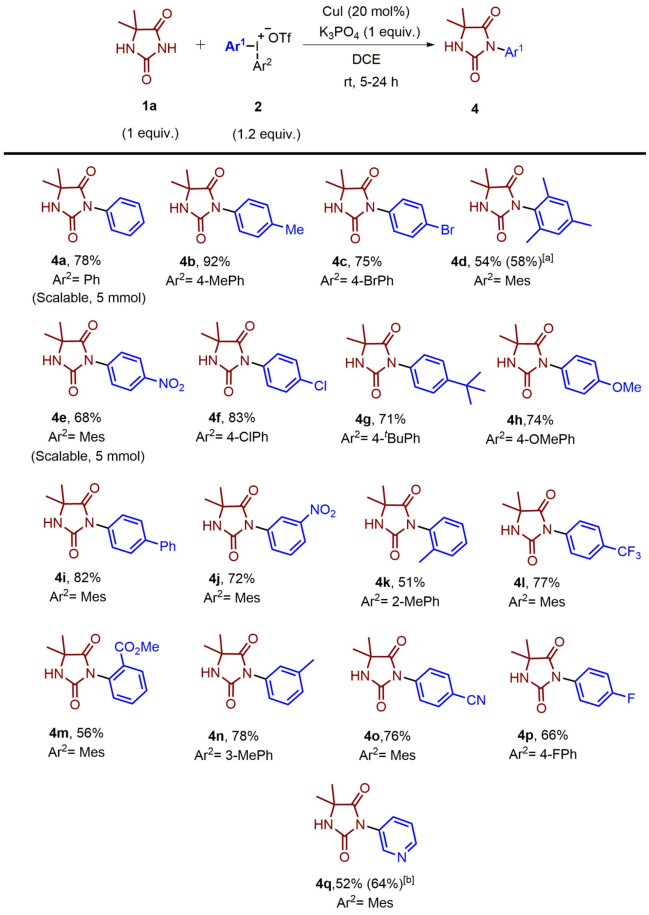
Scheme 2. Chemoselectivity trend. Yields are based on ^{1}H NMR using DMF as internal standard.



Scheme 3. Scope of Hydantoins. Reaction conditions: 3-aryl-5,5-dimethylhydantoin (0.25 mmol), iodonium salt (0.3 mmol), CuI (20 mol%) and K_3PO_4 (0.25 mmol) in DCE (0.1 M). [a] 2 equiv. of **2a**. [b] 2 equiv. of **1b**. Isolated yields.

these hydantoins without showing any mixture of C^5- and N^1-arylation. Alanine-derived hydantoin, **3b** was less reactive than other bulky amino acid-derived hydantoins (**3c** and **3d**). Nitrophenylation of leucine-derived hydantoin **3e** also showed good conversion (75% isolated yield) and we successfully observed regioselective arylation. D-valine (**3d**) and L-phenylalanine-derived hydantoin (**3f**) reacted without affecting the chirality with the yield of 84% and 87% respectively. Bulky hydantoins (**3g**) also tolerated the reaction condition and showed arylation in a similar pattern.

Next, the scope of the Cu-catalysed N^3-arylation of hydantoins was studied (Scheme 4). Various symmetrical and unsymmetrical iodonium salts were employed as a coupling partner. The use of 5,5-dimethylhydantoin (**1a**) and diaryliodonium salts containing electron-donating, electron-withdrawing, and electron-neutral groups afforded the desired products (**4a**–**4q**) in moderate to good yields. Halide substituents such as –F, –Cl, and –Br were easily transferred from its corresponding symmetrical iodonium salts and products **4c**, **4f**, and **4p** were obtained in good yields in less than 10 hrs, which is a rather difficult to accomplish in metal-catalyzed reactions with other aryl sources.[25] *Ortho*-substituted groups such as mesityl, –Me and –CO_2Me were found to be well tolerated under this protocol and furnished the products **4d**, **4k**, and **4m**. As found in the chemoselectivity study, electron-withdrawing groups such as –NO_2, –CF_3, –CO_2Me, and -CN were selectively transferred to the hydantoin core affording **4e**, **4l**, **4m**, and **4o** respectively with moderate yields. Similarly, *tert*-butyl salt, **4g** underwent arylation at room temperature, though it took a

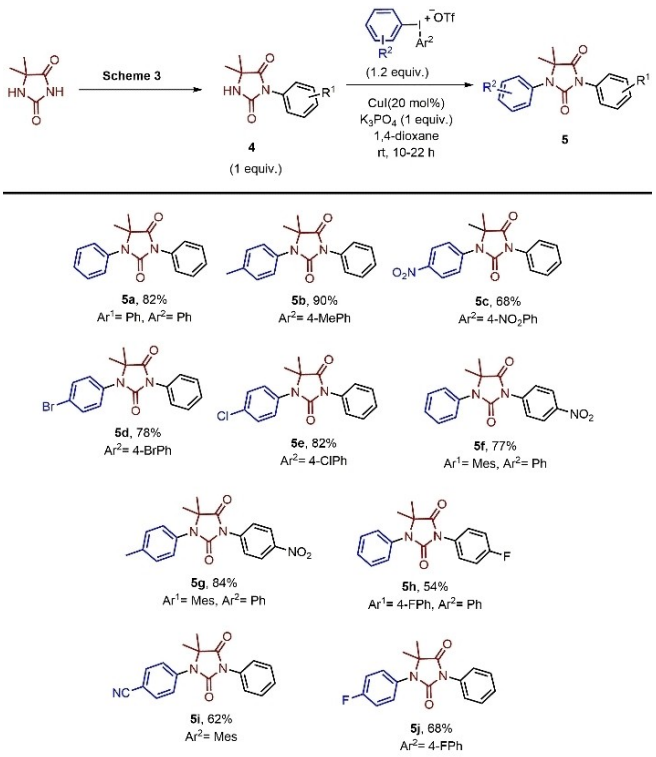


Scheme 4. Scope of diaryliodonium salts. Reaction conditions: 5,5-dimethylhydantoin (0.25 mmol), iodonium salt (0.3 mmol), CuI (20 mol%), K_3PO_4 (0.25 mmol), DCE (0.1 M). [a] 2 equiv. of iodonium salt. [b] 80 °C. Isolated yields.

longer time for the completion of the reaction. Very few reports are found on the transfer of electron-donating groups to hydantoins in metal-catalyzed reaction with aryl halides; but, in our protocol a *p*-methoxyphenyl group, **4h** is easily used as the arylating partner from bis-(4-methoxyphenyl)iodonium salt, in 74% yield. Biphenyl group from (biphenyl)mesityl iodonium salt was also selectively induced in the hydantoin core, **4i** with excellent yields. **4n** and **4j** are the examples for *meta*-substituted hydantoins from bis-(3-methylphentyl)iodonium tertrafluoroborate (**2k**) and mesityl-(3-nitrolphenyl)iodonium triflate (**2o**) respectively. Heterocyclic moiety containing iodonium salts were also employed in this protocol and pyridine ring containing **4q** was isolated despite the formation of **4d** as the side product.

N^1-Arylation of hydantoins with diaryliodonium salts

After the comprehensive study on N^3-arylation of hydantoins, we next focused on a more challenging aspect, i.e. arylation of the remaining nitrogen, i.e. N^1.[26] We initially attempted one-pot double arylations from the single iodonium salt by utilizing the eliminated aryl iodide. Temperature and base for the reaction were screened in order to achieve N^1-arylation, but the reaction didn't proceed beyond N^3-arylation (ESI, Table S9). The same reaction conditions were imposed in a step-wise manner using the N^3-arylated product for the N^1-arylation (Scheme 5)

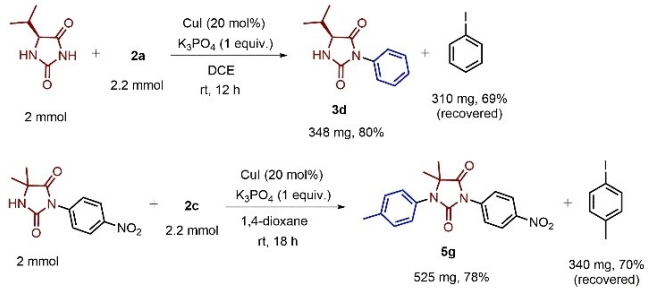


Scheme 5. Synthesis of N^1,N^3-diaryl-hydantoin. Reaction conditions: 3-aryl-5,5-dimethylhydantoin (0.25 mmol), iodonium salt (0.3 mmol), CuI (20 mol%) and K_3PO_4 (0.25 mmol) in DCE (0.1 M). Isolated yields.

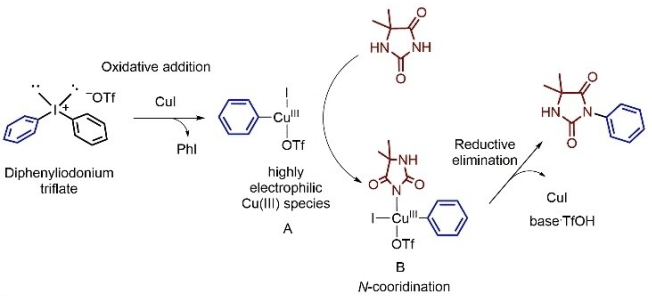
(ESI, Table S10), but the yield of the reaction was low with DCE as the solvent. Temperature and solvents were screened again for the reaction between N^3-phenyl-5,5-dimethylhydantoin and diphenyliodonium triflate, while maintaining the other parameters. It was observed that 1,4-dioxane was the solvent of choice at room temperature, and gratifyingly, the yield of **5a** increased to 82%. Other Cu^I and Cu^{II} sources and different bases were tested, but the yield did not improve. The synthesis of all the N^1,N^3-arylated compounds (**5a**–**5j**) proceeded smoothly under the optimized condition in moderate to good yields. Symmetrical iodonium salts containing electron-neutral and electron-donating and unsymmetrical iodonium salts containing electron-deficient groups were easily tolerated under the reaction conditions. Hereby, we have demonstrated substrate scopes on both the nitrogen atoms of the hydantoin motif.

The protocol was extended successfully to a larger scale (Scheme 6) for **4a** and **4e** showcasing the gram-scale applicability of this method.

Aiming the mechanistic study (Scheme 7), the reaction was performed in the presence of 2 equiv. of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) as a radical scavenger. But, the N^3-arylated product was obtained in 65% yield which indicates that radicals are not involved.[27] The plausible mechanism of this simple and robust *N*-arylation starts with the reaction between the copper(I) catalyst and the diaryliodonium salt. Ph – Cu(III) species **A**, a highly electrophilic copper centre is generated after the oxidative addition of iodonium salts to CuI. The N^3 atom of the hydantoin undergoes coordination with species **A** and forms species **B**, from which reductive elimination delivers the arylated product while making the copper source



Scheme 6. Larger-scale synthesis.



Scheme 7. Plausible Mechanism.

available for the next cycle. The mechanism for the arylation of the N^1-position can also be proposed in the same line. This similar pattern of mechanism has also been proposed in the literature.[28]

Conclusion

In conclusion, we have developed a mild and robust Cu-catalyzed *N*-arylation of hydantoins at room temperature with diaryliodonium salts. Broad substrate scopes of hydantoins were discussed for N^3-arylation including chiral hydantoins. Our protocol showed moderate to good yields for the formation of simple to congested hydantoins. Electron-neutral, electron-donating and electron-withdrawing groups from both symmetrical and unsymmetrical iodonium salts were well tolerated. *Ortho*-substituted arylating partners were also employed and successful transformation with moderate yields was achieved. Our methodology was also extended to N^1-arylation and substantial scopes of diaryliodonium salts were discussed. We believe this methodology could be of interest to organic chemists and affords many medicinally active scaffolds.

Experimental Section

All reactions were performed in oven-dried Schlenk-tubes or round bottom flasks under nitrogen condition unless otherwise stated. Dichloromethane (DCM), dichloroethane (DCE), and acetonitrile (ACN) were dried by refluxing over CaH_2 under nitrogen condition and stored over 4 Å molecular sieves. Toluene and 1,4-dioxane were dried utilizing conventional drying procedures using sodium/benzophenone as an indicator and stored over 4 Å molecular sieves. All chemicals were purchased from commercial suppliers and used as received unless otherwise stated. NaOH, Cs_2CO_3, K_3PO_4, and *t*BuOK were stored in a desiccator. For experimental details, see the reference for each method used. *m*-CPBA (Aldrich, 77% active oxidant) was dried at room temperature over high vacuum for 1 hour and titrated by iodometric titration[29] prior to use in the synthesis of diaryliodonium salts. Thin Layer Chromatography (TLC) analysis was performed on pre-coated Merck silica gel 60 F_{254} plates using UV (254 nm) light and/or with $KMnO_4$-stain. Column chromatography was performed on 100–200 mesh silica gel using the gradient system, freshly distilled ethyl acetate-hexane mixture. All NMR data were recorded at 400 MHz at 298 K using $CDCl_3$ and DMSO-d_6 as solvents. Chemical shifts are given in ppm relative to the residual solvent peak (^{1}H NMR: $CDCl_3$ δ 7.26 and sometimes δ 1.56 ($CDCl_3$-water) and in DMSO-d_6 δ 2.50 and δ 3.3 (DMSO-water); ^{13}C NMR: $CDCl_3$ δ 77.16, DMSO-d_6 δ 39.52) with multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, sep = septet, m = multiplet, app = apparent), coupling constants (in Hz) and integration. Chemical shifts for ^{19}F-NMR are given in ppm relative to monofluorobenzene (−113.15 ppm) used as internal standard. The raw data of NMR were processed by MestReNova software.

5,5′-dimethylhydantoin (**1 a)** is commercially available and others (**1 b**–**1 g)** are known compounds and were prepared by literature procedures.[30] The diaryliodonium salts **(2 a–2 u)** were synthesized according to literature procedures (see ESI).[31]

General procedure A: N^3-arylation of hydantoins

To an oven-dried Schlenck-tube, hydantoin **1** (0.25 mmol), diaryliodonium salt **2** (0.3 mmol), CuI (50 μmol, 0.2 equiv.) and K_3PO_4 (0.25 mmol) was added under N_2 atmosphere. The tube was sealed and DCE (3 mL) was added under N_2 atmosphere. The reaction mixture was stirred at room temperature for the indicated time. The reaction was filtered through celite and concentrated *in vacuo.* The crude product was purified as described.

3-phenylimidazolidine-2,4-dione (3 a)[32] Synthesized following **general procedure A** starting from imidazolidine-2,4-dione (**1 b**) (25 mg, 0.25 mmol, 1 equiv.), diphenyliodonium triflate (**2 a)** (129 mg, 0.3 mmol, 1.2 equiv.), CuI (9.5 mg, 0.05 mmol, 0.2 equiv.) and K_3PO_4 (53 mg, 0.25 mmol). The reaction mixture was stirred at room temperature for 10 h. The mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 40/60) to afford **3 a** (33 mg, 0.187 mmol, 75%) as white solid. R_f 0.45 (AcOEt /Hexane: 40/60). M.p. 191–192 °C (lit. 194 °C); ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.51–7.49 (m, 2H, ArH), 7.41–7.38 (m, 3H, ArH), 4.07 (s, 2H, methylene); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 170.3, 157.8, 131.3, 129.0, 128.4, 126.0, 46.2; IR (ν_{max}, cm^{-1}): 3173 (b), 3056 (m), 2932 (s), 1835 (s), 1744 (s), 1595 (s), 1503 (s), 1449 (s), 1405 (s). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_9H_8N_2O_2$ 177.0659; found 177.0688.

5-methyl-3-phenylimidazolidine-2,4-dione (3 b)[33] Synthesized following **general procedure A** starting from 5-methylimidazolidine-2,4-dione (**1 c**) (29 mg, 0.25 mmol) and diphenyliodonium triflate (**2 a)** (129 mg, 0.3 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 20/80) to afford **3 b** (41 mg, 0.215 mmol, 86%) as a off-white solid. R_f 0.35 (AcOEt /Hexane: 40/60). M.p. 146–148 °C (lit. 151 °C); ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.50–7.47 (m, 2H, ArH), 7.41–7.37 (m, 3H, ArH), 6.58 (br s, 1H, amide), 4.22 (qd, J = 6.9, 1.3 Hz, 1H, methine), 1.52 (d, J = 8 Hz, 3H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 173.1, 156.2, 131.5, 129.1, 128.3, 126.1, 52.3, 17.4; IR (ν_{max}, cm^{-1}): 3216 (b), 3080 (b), 3311 (m), 1780 (s), 1720 (s), 1404 (s), 1377 (s), 1240 (s), 1041 (s), 916 (s) 818 (s), 639 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{10}H_{10}N_2O_2$ 191.0815; found 191.0866.

5-isobutyl-3-phenylimidazolidine-2,4-dione (3 c) Synthesized following **general procedure A** starting from 5-isobutylimidazolidine-2,4-dione (**1 d**) (39 mg, 0.25 mmol) and diphenyliodonium triflate (**2 a)** (129 mg, 0.3 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 40/60) to afford **3 c** (47 mg, 0.202 mmol, 81%) as a white solid. R_f 0.42 (AcOEt /Hexane: 40/60). M.p. 174–176 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.49–7.45 (m, 2H, ArH), 7.41–7.36 (m, 3H, ArH), 6.49 (br s, 1H, amide NH), 4.20–4.17 (m, 1H, methine), 1.92–1.82 (m, 2H, methylene), 1.69–1.64 (m, 1H, methine), 1.01–0.98 (m, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 173.1, 156.2, 131.5, 129.1, 128.3, 126.1, 52.3, 17.4; IR (ν_{max}, cm^{-1}): 3255 (b), 3112 (m), 3311 (m), 1776 (s), 1726 (s), 1430 (s), 1402 (s), 1160 (s), 860 (s), 712 (s), 648 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{16}N_2O_2$ 233.1285; found 233.1294.

(S)-5-isopropyl-3-phenylimidazolidine-2,4-dione (3 d) Synthesized following **general procedure A** starting from 5-isopropylimidazolidine-2,4-dione (**1 e**) (36 mg, 0.25 mmol) and diphenyliodonium triflate (**2 a)** (129 mg, 0.3 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 40/60) to afford **3 d** (47 mg, 0.202 mmol, 81%) as an off-white solid. R_f 0.4 (AcOEt /Hexane: 40/60). M.p. 136–138 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.50–7.46 (m, 2H, ArH), 7.40–7.37 (m, 3H, ArH), 6.69 (br s, 1H, amide NH) 4.06–4.07 (m, 1H, methine), 2.37–2.29 (m, 1H, methine), 1.09 (d, J = 7 Hz, 3H, methyl), 1.01 (d, J = 7 Hz, 3H, methyl); ^{13}C NMR (100 MHz,

Chloroform-*d*): δ 172.6, 157.4, 131.1, 129.3, 127.9, 126.1, 62.1, 30.4, 18.2, 15.6; IR (ν_{max}, cm^{-1}): 3273 (b), 3116 (m), 3311 (m), 2966 (s), 1720 (s), 1429 (s), 1171 (s), 762 (s), 633 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{13}N_3O_4$ 219.1128; found 219.1181.

5-isobutyl-3-(4-nitrophenyl)imidazolidine-2,4-dione (3e) Synthesized following **general procedure A** starting from 5-isobutylimidazolidine-2,4-dione (**1d**) (39 mg, 0.25 mmol) and (4-nitrophenyl)(2,4,6-trimethylphenyl)iodonium triflate (**2l**) (155 mg, 0.30 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 40/60) to afford **3e** (51 mg, 0.187 mmol, 75%) as a white solid. R_f 0.35 (AcOEt /Hexane: 40/60). M.p. 155–157 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.81 (br s, 1H, amide), 8.34 (d, J = 8 Hz, 2H, ArH), 7.73 (d, J = 8 Hz, 2 h, ArH), 4.27 (t, J = 4 Hz, 1H, methine), 1.90–1.82 (m, 1H, methine), 1.64–1.58 (m, 2H, methylene), 0.93 (d, J = 7 Hz, 6H, methyl); ^{13}C NMR (100 MHz, DMSO-d_6): δ 173.6, 155.3, 146.2, 138.1, 127.2, 124.5, 55.1, 24.6, 23.2, 21.3; IR (ν_{max}, cm^{-1}): 3258 (b), 2955 (s), 2840 (s), 1756 (s), 1540 (s), 1310 (s), 1135 (s), 848 (s), 768 (s), 667 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{16}N_2O_2$ 278.1135; found 279.1141.

(R)-5-benzyl-3-phenylimidazolidine-2,4-dione (3f) Synthesized following **general procedure A** starting from *(R)*-5-benzylimidazolidine-2,4-dione (**1e**) (47 mg, 0.25 mmol) and diphenyliodonium triflate (**2a)** (129 mg, 0.3 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 40/60) to afford **3f** (57 mg, 0.214 mmol, 87%) as a white solid. R_f 0.35 (AcOEt /Hexane: 40/60). M.p. 126 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.46–7.42 (m, 2H, ArH), 7.38–7.31 (m, 2H, ArH), 7.26–7.22 (m, 2H, ArH), 5.81 (br s, 1H, amide), 4.22 (app. qd, J = 7 and 1.3 Hz, 1H, methine), 3.33 (dd, J = 7 and 1.3 Hz, 1H, methylene), 3.03 (dd, J = 7 and 1.3 Hz, 1H, methylene); ^{13}C NMR (100 MHz, Chloroform-d_6): δ 171.7, 155.8, 134.7, 131, 129.4, 129.0, 128.8, 128.3, 127.5, 126.2, 57.7, 37.7; IR (ν_{max}, cm^{-1}): 3205 (b), 3110 (m), 2944 (m), 1743 (s), 1402 (s), 1317 (s), 1139 (s), 746 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{16}H_{14}N_2O_2$ 267.1128; found 267.1134.

3,5,5-triphenylimidazolidine-2,4-dione (3g) [CAS: 52461–02-6]*[33] Synthesized following **general procedure A** starting from 5,5-diphenylimidazolidine-2,4-dione (**1f**) (63 mg, 0.25 mmol) and diphenyliodonium triflate (**2a)** (129 mg, 0.3 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 30/70) to afford **3g** (59 mg, 0.182 mmol, 73%) as a white solid. R_f 0.48 (AcOEt /Hexane: 40/60). M.p. 208–210 °C (lit. 206–207 °C); ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.50–7.42 (m, 15H, ArH), 6.83 (br s, 1H, amide); ^{13}C NMR (100 MHz, Chloroform-d_6): δ 172.2, 155.8, 139.1, 131.4, 129.1, 127.1, 126.3, 70.07; IR (ν_{max}, cm^{-1}): 3237 (b), 3105 (m), 3311 (m), 2931 (m), 1715 (s), 1431 (s), 1350 (s), 1169 (s), 689 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{21}H_{16}N_2O_2$ 329.1285; found 329.1295.

***5,5-Dimethyl-3-phenylhydantoin (4a)*[34]** Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol, 1 equiv.), diphenyliodonium triflate (**2a)** (129 mg, 0.3 mmol, 1.2 equiv.), CuI (9.5 mg, 0.05 mmol, 0.2 equiv.) and K_3PO_4 (53 mg, 0.25 mmol). The reaction mixture was stirred at room temperature for 5 h. The crude was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 30/70) to afford **4a** (42 mg, 0.205 mmol, 81%) as white solid. R_f 0.4 (AcOEt /Hexane: 40/60). M.p. 162–165 °C (lit. 164–167 °C); ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.42–7.38 (m, 2H, ArH), 7.34–7.28 (m, 3H, ArH), 1.43 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 176.4, 155.7, 131.5, 128.6, 127.9, 126.1, 58.3, 25.12; IR (ν_{max}, cm^{-1}): 3217 (b), 3101 (s), 1728 (s), 1427 (s), 1295 (s), 1148 (s), 861 (s), 765 (m), 708 (s), 604 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{11}H_{12}N_2O_2$ 205.0972; found 209.0998.

5,5-dimethyl-3-(p–tolyl)imidazolidine-2,4-dione (4b) Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and bis(4-methylphenyl)iodonium triflate (**2c**) (138 mg, 0.30 mmol). The reaction was stirred for 7 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 20/80) to afford **4b** (49 mg, 0.225 mmol, 92%) as a light yellow solid. R_f 0.4 (AcOEt /Hexane: 40/60). M.p. 168–170 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.19 (s, 4H, ArH), 2.30 (s, 3H, methyl), 1.42 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 176.7, 156.4, 138.5, 129.9, 129.1, 126.1, 58.9, 25,1, 21.3; IR (ν_{max}, cm^{-1}): 3217 (b), 2911 (m), 1720 (s), 1421 (s), 1387 (s), 1260 (s), 818 (s), 792 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{14}N_2O_2$ 219.1128; found 219.1159.

3-(4-bromophenyl)-5,5-dimethylimidazolidine-2,4-dione (4c) Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and bis(4-bromophenyl) iodonium triflate (**2c**) (176 mg, 0.30 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 20/80) to afford **4c** (53 mg, 0.187 mmol, 75%) as a brown solid. R_f 0.45 (AcOEt /Hexane: 40/60). M.p. 158–161 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.52 (d, J = 8 Hz, 2H, ArH), 7.26 (d, J = 8 Hz, 2H, ArH), 6.82 (s, 1H, amide NH), 1.44 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 176.1, 155.6, 132.5, 130.8, 128.1, 122.3, 58.6, 25.1; IR (ν_{max}, cm^{-1}): 3241 (b), 3110 (m), 2089 (m), 2929 (s), 1706 (m), 1492 (s), 1427 (s), 821 (m), 732 (m), 604 (m); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{11}H_{11}N_2O_2Br$ 283.0077; found 283.0091.

3-mesityl-5,5-dimethylimidazolidine-2,4-dione (4d) Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and bis(2,4,6-trimethylphenyl))iodonium triflate (**2h**) (154 mg, 0.30 mmol). The reaction was stirred for 16 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 20/80) to afford **4d** (33.21 mg, 0.135 mmol, 54%) as a white solid. R_f 0.56 (AcOEt /Hexane: 40/60). M.p. 147–150 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.97 (s, 2H, ArH), 6.80 (s, 1H, amide NH), 2.30 (s, 3H, methyl), 2.14 (s, 6H, methyl) 1.44 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 176.2, 155.5, 139.2, 136.5, 129.1, 126.4, 59.4, 25.5, 21.1, 17.4; IR (ν_{max}, cm^{-1}): 3227 (b), 3106 (m), 2918 (s), 2860 (s), 1746 (s), 1724 (s), 1603 (s), 1468 (m), 1283 (s), 1253 (s), 835 (m), 674 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{18}N_2O_2$ 247.1441; found 247.1475.

***5,5-dimethyl-3-(4-nitrophenyl)imidazolidine-2,4-dione (4e)*[14]** Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and (4-nitrophenyl)(2,4,6-trimethylphenyl)iodonium triflate (**2l**) (155 mg, 0.30 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90 followed by 30/70) to afford **4e** (43 mg, 0.172 mmol, 68%) as a white solid. R_f 0.3 (AcOEt /Hexane: 40/60). M.p. 162–164 °C (lit. 168 °C); ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.33 (d, J = 8 Hz 2H, ArH), 7.77 (d, J = 8 Hz, 2H, ArH), 6.00 (s, 1H, amide NH), 1.58 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 175.3, 154.2, 146.4, 137.6, 125.6, 124.2, 58.6, 25.0; IR (ν_{max}, cm^{-1}): 3261 (b), 2920 (s), 2852 (s), 1731 (s), 1521 (s), 1337 (s), 1135 (s), 831 (s), 725 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{11}H_{11}N_3O_4$ 250.0822; found 250.0847.

3-(4-chlorophenyl)-5,5-dimethylimidazolidine-2,4-dione (4f) Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and bis(4-chlorophenyl)iodonium triflate (**2e**) (149.7 mg, 0.30 mmol). The reaction was stirred for 6 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 20/80) to afford **4f** (49 mg, 0.205 mmol, 83%) as a brownish solid. R_f 0.45 (AcOEt /Hexane: 40/60). M.p. 152–154 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.45–7.38 (m, 4H, ArH), 6.19 (s, 1H, amide NH), 1.54 (s, 6H, methyl); ^{13}C

NMR (100 MHz, Chloroform-*d*): δ 176.5, 155.7, 139.2, 134.7, 130.4, 129.6, 127.7, 58.8, 25.4; IR (ν_{max}, cm^{-1}): 3298 (s), 2915 (s), 2849 (s), 1715 (s), 1497 (s), 1426 (s), 1309 (s), 1148 (s), 1089 (s), 819 (s), 740 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{11}H_{11}N_2O_2Cl$ 239.0589; found 239.0591.

3-(4-(tert-butyl)phenyl)-5,5-dimethylimidazolidine-2,4-dione (4g)[14] Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and bis(4-*tert*-butylphenyl)iodonium triflate (**2g**) (162.72 mg, 0.30 mmol). The reaction was stirred for 24 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 20/70) to afford **4g** (46 mg, 0.177 mmol, 71%) as a brownish solid. R_f 0.43 (AcOEt /Hexane: 40/60). M.p. 173–175 °C (lit. 177 °C); ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.48 (d, *J* = 8 Hz, 2H, ArH), 7.32 (d, *J* = 8 Hz, 2H, ArH), 6.71 (s, 1H, amide NH), 1.51 (s, 6H, methyl), 1.33 (s, 9H, *tert*-butyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 176.1, 156.1, 151.2, 128.5, 126.0, 58.3, 34.7, 30.9, 25.1; IR (ν_{max}, cm^{-1}): 3277 (s), 2972 (s), 1717 (s), 1528 (s), 1420 (s), 1141 (s), 846 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{20}N_2O_2$ 261.1598; found 261.1635.

3-(4-methoxyphenyl)-5,5-dimethylimidazolidine-2,4-dione (4h) Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and bis(4-methoxyphenyl) iodonium triflate (**2i**) (147.06 mg, 0.30 mmol). The reaction was stirred for 8 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 20/80) to afford **4h** (44 mg, 0.185 mmol, 74%) as a white solid. R_f 0.35 (AcOEt /Hexane: 40/60). M.p. 134–136 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.32 (d, *J* = 8 Hz, 2H, ArH), 6.97 (d, *J* = 8 Hz, 2H, ArH), 6.28 (s, 1H, amide NH), 3.28 (s, 3H, methyl), 1.55 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 176.5, 159.1, 155.7, 127.4, 124.0, 114.2, 58.2, 55.5, 24.8; IR (ν_{max}, cm^{-1}): 3268 (s), 2942 (s), 1731 (s), 1707 (s) 1460 (m), 1283 (s), 1228 (s), 1086 (s), 867 (m), 741 (s), 674 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{14}N_2O_3$ 235.1077; found 235.1109.

3-([1,1′-biphenyl]-4-yl)-5,5-dimethylimidazolidine-2,4-dione (4i)[14] Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and (biphenyl)(2,4,6-trimethylphenyl)iodonium triflate (**2h**) (164 mg, 0.30 mmol). The reaction was stirred for 16 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90 followed by 30/70) to afford **4i** (58 mg, 0.205 mmol, 82%) as a white solid. R_f 0.4 (AcOEt /Hexane: 40/60). M.p. 188–190 °C (lit. 185 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8 Hz, 2H, ArH), 7.60 (d, *J* = 8 Hz, 2H, ArH), 7.52–7.44 (m, 4H, ArH), 7.38 (t, *J* = 8 Hz, 1H, ArH), 6.75 (s, 1H, amide NH), 1.55 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 175.8, 155.1, 141, 139.3, 130.1, 128.4, 127.4, 126.7, 126, 58.4, 24.8; IR (ν_{max}, cm^{-1}): 3221 (b), 2908 (s), 1755 (s), 1489 (s), 1318 (s), 1156 (s), 810 (s), 743 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{16}N_2O_2$ 281.1285; found 281.1308.

5,5-dimethyl-3-(3-nitrophenyl)imidazolidine-2,4-dione (4j) Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and (3-nitrophenyl)(2,4,6-trimethylphenyl)iodonium triflate (**2h**) (155 mg, 0.30 mmol). The reaction was stirred for 18 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90 followed by 40/60) to afford **4j** (44 mg, 0.176 mmol, 72%) as a white solid. R_f 0.35 (AcOEt /Hexane: 40/60). M.p. 143–146 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.72 (s, 1H, amide NH), 8.37 (s, 1H, ArH), 8.25 (d, *J* = 8 Hz, 1H, ArH), 7.87 (d, *J* = 8 Hz, 1H, ArH), 7.75 (d, *J* = 8 Hz, 1H, ArH), 1.43 (s, 6H, methyl); ^{13}C NMR (100 MHz, DMSO-d_6): δ 176.3, 154, 148.1, 133.8, 133.4, 130.5, 122.8, 121.7, 58.1, 24.6; IR (ν_{max}, cm^{-1}): 3223 (b), 2933 (s), 1732 (s), 1509 (s), 1321 (s), 1176 (s), 866 (s), 790 (s); HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{11}H_{11}N_3O_4$ 250.0822; found 250.9121.

5,5-dimethyl-3-(o–tolyl)imidazolidine-2,4-dione (4k) Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and bis(2-methylphenyl)iodonium tetrafluoroborate (**2j**) (118 mg, 0.30 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 30/70) to afford **4k** (28 mg, 0.128 mmol, 51%) as a pink solid. R_f 0.46 (AcOEt /Hexane: 40/60). M.p. 166–168 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.37–7.26 (m, 4H, ArH), 7.17 (d, *J* = 8 Hz, 1H, ArH), 6.57 (s, 1H, amide NH), 2.21 (s, 3H, methyl), 1.53 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 176.3, 154, 148.1, 133.8, 133.4, 130.5, 122.8, 121.7, 58.1, 24.6; IR (ν_{max}, cm^{-1}): 3205 (b), 2943 (m), 1744 (s), 1440 (s), 1345 (s), 1225 (s), 867 (s), 765 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{14}N_2O_2$ 219.1128; found 219.1154.

5,5-dimethyl-3-(4-(trifluoromethyl)phenyl)imidazolidine-2,4-dione (4l)[14] Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and mesityl(4-trifluoromethylphenyl)iodonium triflate (**2n**) (162 mg, 0.30 mmol). The reaction was stirred for 16 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90 followed by 30/80) to afford **4k** (54 mg, 0.212 mmol, 77%) as a white solid. R_f 0.35 (AcOEt /Hexane: 40/60). M.p. 174–176 °C (lit. 179 °C); ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.49 (d, *J* = 8 Hz, 2H, ArH), 7.30 (d, *J* = 8 Hz 2H, ArH), 6.57 (s, 1H, amide NH), 1.53 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 176, 154.8, 148.8, 130.1, 127.5, 121.7, 121.6, 58.7, 25.3; ^{19}F (376 MHz, Chloroform-*d*): δ −57.4; IR (ν_{max}, cm^{-1}): 3217 (b), 2949 (m), 2377 (m), 1743 (s), 1739 (s), 1408 (s), 1332 (s), 1164 (s), 1121 (s), 1038 (s), 843 (s), 713 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{14}N_2O_2$ 273.0845; found 273.1756.

Methyl 2-(4,4-dimethyl-2,5-dioxoimidazolidin-1-yl)benzoate (4m) Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and mesityl(2-(methoxycarbonyl)phenyl)iodonium triflate (**2p**) (159 mg, 0.30 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 20/80) to afford **4m** (36 mg, 0.140 mmol, 56%) as a brown-coloured liquid. R_f 0.42 (AcOEt /Hexane: 40/60). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.12 (d, *J* = 8 Hz, 1H, ArH), 7.68 (dt, *J* = 8 Hz & 1.6 Hz, 1H, ArH), 7.53 (dt, *J* = 8 Hz & 1.3 Hz, 1H, ArH), 7.37 (d, *J* = 8 Hz, 1H, ArH), 6.36 (s, 1H, amide NH), 3.85 (s, 3H, methyl), 1.53 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 176.3, 165.1, 155.6, 133.3, 131.6, 131.5, 130.0, 129.2, 128.0, 58.7, 52.07, 25.3; IR (ν_{max}, cm^{-1}): 3215 (b), 2918 (m), 1777 (s), 1729 (s), 1715 (s), 1434 (s), 1263 (s), 1107 (s), 710 (s), 678 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{14}N_2O_4$ 263.1026; found 263.1031.

5,5-dimethyl-3-(m–tolyl)imidazolidine-2,4-dione (4n) Synthesized following **general procedure A** starting from 5,5-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and bis(m-tolyl)iodonium tetrafluoroborate (**2k**) (119 mg, 0.30 mmol). The reaction was stirred for 10 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 20/80) to afford **4n** (42 mg, 0.195 mmol, 78%) as a white solid. R_f 0.48 (AcOEt /Hexane: 40/60). M.p. 145–147 °C; ^{1}H NMR (400 MHz, Chloroform-d): δ 7.38 (t, J = 8 Hz, 1H, ArH), 7.22–7.20 (m, 3H, ArH), 6.33 (s, 1H, amide NH), 2.42 (s, 3H, methyl), 1.55 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-d): δ 176.7, 156.0, 139.4, 131.4, 129.4, 129.1, 127.2, 123.4, 58.8, 25.3, 21.4; IR (ν_{max}, cm^{-1}): 3212 (b), 2955 (m), 1734 (s), 1438 (s), 1342 (s), 1228 (s), 865 (s), 769 (s); HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{14}N_2O_2$ 219.1128; found 219.1159.

4-(4,4-dimethyl-2,5-dioxoimidazolidin-1-yl)benzonitrile (4o) Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and (4-cyanophenyl)(mesityl) iodonium triflate (**2m**) (149 mg, 0.30 mmol). The reaction was stirred for 15 h. The reaction mixture was purified by column

chromatography (AcOEt/Hexane: 10/90 followed by 20/80) to afford **4q** (43 mg, 0.1 mmol, 52%) as a white solid. R_f 0.38 (AcOEt /Hexane: 40/60). M.p. 182 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.76 (d, *J* = 8 Hz, 1H, ArH), 7.69 (d, *J* = 8 Hz, 1H, ArH), 6.47 (s, 1H, amide NH), 1.56 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 175.5, 154.4, 135.4, 132.4, 125.6, 118.2, 111.1, 58.3, 24.8; IR (ν_{max}, cm^{-1}): 3214 (b), 2948 (s), 2270 (s), 1766 (s), 1643 (s), 1532 (s), 1406 (s), 1141 (s), 894 (s), 776 (s), 684 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{11}N_3O_2$ 230.0924; found 230.0934.

3-(4-fluorophenyl)-5,5-dimethylimidazolidine-2,4-dione (4p) Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and bis(4-fluorophenyl)iodonium triflate (**2f**) (139 mg, 0.30 mmol). The reaction was stirred for 9 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 30/80) to afford **4p** (36 mg, 0.165 mmol, 66%) as a white solid. R_f 0.38 (AcOEt /Hexane: 40/60). M.p. 176–178 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.42–7.39 (app. dd, *J* = 8 and 4 Hz, 2H, ArH), 7.16 (app. t, *J* = 8 Hz, 2H, ArH), 6.36 (s, 1H, amide NH), 1.54 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 175.7, 162.4, 161.56 (d, $J_{C\text{-}F}$ = 247 Hz), 155.2, 127.69 (d, $J_{C\text{-}F}$ = 9 Hz), 127.15 (d, $J_{C\text{-}F}$ = 3 Hz), 115.69 (d, $J_{C\text{-}F}$ = 15 Hz), 58.3, 24.5; ^{19}F (376 MHz, Chloroform-*d*): δ −112.9; IR (ν_{max}, cm^{-1}): 3218 (b), 2908 (s), 1765 (s), 1711 (s), 1530 (s), 1258 (s), 1130 (s), 884 (s), 712 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{11}H_{11}N_2O_2F$ 223.0877; found 223.0891.

5,5-dimethyl-3-(pyridin-3-yl)imidazolidine-2,4-dione (4q) Synthesized following **general procedure A** starting from *5,5*-dimethylhydantoin (**1a**) (32 mg, 0.25 mmol) and mesityl(pyridin-3-yl) iodonium triflate (**2r**) (141 mg, 0.30 mmol). The reaction was stirred for 18 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 10/90 followed by 30/80) to afford **4p** (29 mg, 0.165 mmol, 56%) as a white solid. R_f 0.32 (AcOEt /Hexane: 40/60). M.p. 154–157 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.79 (s, 1H, ArH), 8.62 (d, *J* = 8 Hz, 1H, ArH), 7.84 (d, *J* = 9.5 Hz, 1H, ArH), 7.45–7.42 (m, 1H, ArH), 6.69 (s, 1H, amide NH), 1.57 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 175.9, 154.6, 148.9, 146.8, 133.4, 129.3, 123.5, 59.1, 25.3; IR (ν_{max}, cm^{-1}): 3209 (b), 2920 (s), 1762 (s), 1712 (s), 1534 (s), 1354 (s), 1347 (s), 1076 (s), 862 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{10}H_{11}N_3O_2$ 206.0924; found 206.0949.

General procedure B: for N^1-Arylation

To an oven-dried Schlenck-tube, 3-arylated-hydantoin **4** (0.25 mmol), diaryliodonium salt **2** (0.3 mmol), CuI (50 μmol, 0.2 equiv.) and K_3PO_4 (0.25 mmol) was added under N_2 atmosphere. The tube was sealed and DCE (3 mL) was added under N_2 atmosphere. The reaction mixture was stirred at room temperature for indicated time period. The reaction was filtered through celite and concentrated *in vacuo*. The crude product was purified as described.

5,5-dimethyl-1,3-diphenylhydantoin (5a)[35] To an oven-dried Schlenck-tube, 3-phenyl-5,5-dimethylhydantoin (**4a**) (51 mg, 0.25 mmol, 1 equiv.), diphenyliodonium triflate (**2a**) (129 mg, 0.3 mmol, 1.2 equiv.), CuI (9.5 mg, 0.05 mmol, 0.2 equiv.) and K_3PO_4 (53 mg, 0.25 mmol) were added under N_2 atmosphere. The tube was sealed and 1,4-dioxane (3 mL) was added under N_2 atmosphere. The reaction mixture was stirred at room temperature for 10 h. The reaction mixture was filtered through celite and concentrated *in vacuo*. The crude was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 20/80) to afford **5a** (57 mg, 0.205 mmol, 82%) as white solid. R_f 0.5 (AcOEt /Hexane: 30/70). M.p. 124–126 °C (lit. 130 °C); ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.52–7.32 (m, 10H, ArH), 1.43 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 174.9, 153.8, 134.1, 131.9, 129.6, 129.0, 128.7, 128.1, 126.1, 63.2, 23.6; IR (ν_{max}, cm^{-1}): 2976 (s), 2929 (s), 1780 (s), 1714 (s), 1496 (s), 1412 (s), 1366 (s), 1200 (s) 878 (m), 755 (s), 692 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{16}N_2O_2$ 281.1285; found 281.1352.

5,5-dimethyl-3-phenyl-1-(p–tolyl)hydantoin (5b) Synthesized following **general procedure B** starting from 3-phenyl-5,5-dimethylhydantoin (**4a**) (51 mg, 0.25 mmol) and bis(4-methylphenyl) iodonium triflate (**2c**) (138 mg, 0.30 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 20/80) to afford **5b** (66 mg, 0.225 mmol, 90%) as a white solid. R_f 0.52 (AcOEt /Hexane: 30/70). M.p. 143–145 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.50–7.44 (m, 4H, ArH), 7.35–7.33 (m, 1H, ArH), 7.26 (d, *J* = 8 Hz, 2H, ArH), 7.19 (d, *J* = 8 Hz, 2H, ArH), 2.39 (s, 3H, methyl), 1.52 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 175.2, 154.0, 138.5, 131.8, 130.0, 128.8, 127.9, 126.4, 63.3, 23.7, 21.1; IR (ν_{max}, cm^{-1}): 2975 (s), 2930 (s), 1779 (s), 1713 (s), 1493 (s), 1406 (s), 1198 (s), 1143, 767 (s), 687 (s), 517 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{18}N_2O_2$ 295.1441; found 295.1468.

5,5-dimethyl-1-(4-nitrophenyl)-3-phenylhydantoin (5c)[14] Synthesized following **general procedure B** starting from 3-phenyl-5,5-dimethylhydantoin (**4a**) (51 mg, 0.25 mmol) and (4-nitrophenyl) (2,4,6-trimethylphenyl)iodonium triflate (**2l**) (155 mg, 0.30 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 20/80) to afford **5c** (55 mg, 0.170 mmol, 68%) as a pale yellow solid. R_f 0.45 (AcOEt /Hexane: 30/70). M.p. 133–135 °C (lit. 131 °C); ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.32 (d, *J* = 8 Hz, 2H, ArH), 7.62 (d, *J* = 8 Hz, 2H, ArH), 7.52–7.41 (m, 5H, ArH), 1.66 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 174.3, 153.5, 146.2, 141.0, 131.3, 129.0, 127.4, 126.4, 124.7, 64.0, 24.5; IR (ν_{max}, cm^{-1}): 2923 (m), 1776 (s), 1724 (s), 1522 (s), 1497 (s), 1403 (s), 1333 (s), 1194, 854 (s), 751 (s), 619 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}N_3O_4$ 326.1135; found 326.1175.

1-(4-bromophenyl)-5,5-dimethyl-3-phenylhydantoin (5d) Synthesized following **general procedure B** starting from 3-phenyl-5,5-dimethylhydantoin (**4a**) (51 mg, 0.25 mmol) and bis(4-bromophenyl)iodonium triflate (**2c**) (176 mg, 0.30 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 20/80) to afford **5e** (69 mg, 0.170 mmol, 78%) as a beige solid. R_f 0.56 (AcOEt /Hexane: 30/70). M.p. 122–124 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.51 (d, *J* = 8 Hz, 2H, ArH), 7.40–7.39 (app. d, *J* = 4 Hz, 4H, ArH), 7.32–7.28 (m, 1H, ArH), 7.13 (d, *J* = 8 Hz, 2H, ArH), 1.46 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 173.7, 152.5, 132.1, 131.8, 130.5, 129.4, 128.1, 127.2, 125.1, 121.5, 62.5, 23.0; IR (ν_{max}, cm^{-1}): 2927 (s), 2856 (s), 1772 (s), 1715 (s), 1494 (s), 1416 (s), 1203 (s), 1154 (s), 1069 (s), 879 (s), 804 (s), 767 (s), 687 (s), 518 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}N_2O_2Br$ 359.0390; found 359.0434.

1-(4-chlorophenyl)-5,5-dimethyl-3-phenylhydantoin (5e) Synthesized following **general procedure B** starting from 3-phenyl-5,5-dimethylhydantoin (**4a**) (51 mg, 0.25 mmol) and bis(4-chlorophenyl)iodonium triflate (**2e**) (149.7 mg, 0.30 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 20/80) to afford **5d** (63 mg, 0.2 mmol, 82%) as a white solid. R_f 0.5 (AcOEt /Hexane: 30/70). Mp: 118–120 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.57 (d, *J* = 8 Hz, 2H, ArH), 7.46–7.45 (app. d, *J* = 4 Hz, 4H, ArH), 7.34–7.33 (m, 1H, ArH), 7.19 (d, *J* = 8 Hz, 2H, ArH), 1.52 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 174.6, 153.6, 133, 132.7 131.4, 130.3, 130.2, 128.9, 128.1, 125.9, 122.3, 63.5, 23.7; IR (ν_{max}, cm^{-1}): 2981 (s), 2917 (s), 1768 (s), 1707 (s), 1491 (s), 1416 (s), 1206 (s), 1150 (s), 1088 (s), 878 (s), 697 (s), 519 (s); HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $C_{17}H_{15}N_2O_2Cl$ 359.0471; found 359.0433.

5,5-dimethyl-3-(4-nitrophenyl)-1-phenylhydantoin (5f)[14] Synthesized following **general procedure B** starting from 5,5-dimethyl-3-(4-nitrophenyl)hydantoin (**4e**) (62 mg, 0.25 mmol) and diphenyliodonium triflate (**2a**) (129 mg, 0.3 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 30/70) to afford **5f** (62 mg, 0.192 mmol, 77%) as a white solid. R_f 0.45 (AcOEt /Hexane: 30/70). M.p. 206–208 °C (lit. 213 °C); ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.35 (d, *J* = 8 Hz, 2H, ArH), 7.86 (d, *J* = 8 Hz, 2H, ArH), 7.51–7.47 (m, 3H, ArH), 7.33 (m, 2H, ArH), 1.58 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 173.9, 153, 146.1, 137.7, 133.1, 129.8, 128.9, 125.8, 124.5, 63.4, 23.8; IR (ν_{max}, cm^{-1}): 2973 (b), 2923 (m), 1780 (s), 1722 (s), 1515 (s), 1416 (s), 1343 (s), 1200 (s), 847 (s), 764 (s), 695 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}N_3O_4$ 326.1136; found 326.1172.

5,5-dimethyl-3-(4-nitrophenyl)-1-(p–tolyl)hydantoin (5g) Synthesized following **general procedure B** starting from 5,5-dimethyl-3-(4-nitrophenyl)hydantoin (**4e**) (62 mg, 0.25 mmol) and bis(4-methylphenyl)iodonium triflate (**2c**) (138 mg, 0.30 mmol). The reaction was stirred for 10 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 30/70) to afford **5g** (71 mg, 0.21 mmol, 84%) as a white solid. R_f 0.5 (AcOEt /Hexane: 30/70). M.p. 186–188 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.32 (d, *J* = 8 Hz, 2H, ArH), 7.28 (d, *J* = 8 Hz, 2H, ArH), 7.84 (d, *J* = 8 Hz, 2H, ArH), 7.17 (d, *J* = 8 Hz, 2H, ArH), 2.42 (s, 3H, methyl), 1.58 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 174.6, 152.6, 145.8, 139.1, 137.7, 130.2, 128.9, 126.2, 124.1, 63.3, 23.6, 21.3; IR (ν_{max}, cm^{-1}): 31125 (m), 2920 (b), 2923 (m), 1768 (s), 1723 (s), 1524 (s), 1411 (s), 1340 (s), 1203 (s), 849 (s), 762 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{17}N_3O_4$ 340.1293; found 340.1306.

3-(4-fluorophenyl)-5,5-dimethyl-1-phenylhydantoin (5h) Synthesized following **general procedure B** starting from 3-(4-fluorophenyl)-5,5-dimethylhydantoin (**4p**) (51 mg, 0.25 mmol) and diphenyliodonium triflate (**2a**) (129 mg, 0.3 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 30/70) to afford **5h** (40 mg, 0.135 mmol, 54%) as a white solid. R_f 0.52 (AcOEt /Hexane: 30/70). M.p. 158–160 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.51–7.43 (m, 5H, ArH), 7.33–7.31 (m, 2H, ArH), 7.19–7.14 (m, 2H, ArH), 1.55 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 175.3, 161.8 (d, $J_{C\text{-}F}$ = 271 Hz), 153.6, 133.7, 129.6, 129.0, 128.8, 128.0, 127.7, 116.0 (d, $J_{C\text{-}F}$ = 7 Hz), 63.5, 24.0; ^{19}F (376 MHz, Chloroform-*d*): δ −112.16; IR (ν_{max}, cm^{-1}): 3076 (m), 2987 (b), 1760 (s), 1710 (s), 1516 (s), 1417 (s), 1366 (s), 1204 (s), 1147 (s), 830 (s), 757 (s), 701 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}N_2O_2F$ 299.1191; found 299.1234.

4-(5,5-dimethyl-2,4-dioxo-3-phenylimidazolidin-1-yl)benzonitrile (5i)[14] Synthesized following **general procedure B** starting from 3-phenyl-5,5-dimethylhydantoin (**4a**) (51 mg, 0.25 mmol) and (4-cyanophenyl)(mesityl)iodonium triflate (**2m**) (149 mg, 0.30 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 30/70) to afford **5i** (47 mg, 0.153 mmol, 62%) as a white solid. R_f 0.48 (AcOEt /Hexane: 30/70). M.p. 163–165 °C (lit. 169 °C); ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.77 (d, *J* = 8 Hz, 2H, ArH), 7.55 (d, *J* = 8 Hz, 2H, ArH), 7.50–7.46 (m, 4H, ArH), 7.43–7.39 (m, 1H, ArH), 1.63 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 174.4, 153.6, 138.9, 133.3, 131.2, 129.0, 127.8, 126.1, 118.0, 111.5, 63.8, 24.4; IR (ν_{max}, cm^{-1}): 2220 (s) 1777 (s), 1727 (s), 1497 (s), 1415 (s), 1345 (s), 1202 (s), 833 (s), 749 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{18}H_{15}N_3O_2$ 306.1237; found 306.1276.

1-(4-fluorophenyl)-5,5-dimethyl-3-phenylhydantoin (5j) Synthesized following **general procedure B** starting from 3-phenyl-5,5-dimethylhydantoin (**4a**) (51 mg, 0.25 mmol) and bis(4-fluorophenyl)iodonium triflate (**2f**) (139 mg, 0.30 mmol). The reaction was stirred for 12 h. The reaction mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 30/70) to afford **5j** (55 mg, 0.140 mmol, 56%) as a white solid. R_f 0.56 (AcOEt /Hexane: 30/70). M.p. 125–127 °C; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.50–7.47 (m, 4H, ArH), 7.40–7.35 (m, 1H, ArH), 7.32–7.28 (m, 2H, ArH), 7.19–7.14 (m, 2H, ArH), 1.54 (s, 6H, methyl); ^{13}C NMR (100 MHz, Chloroform-*d*): δ 174.8, 162.4 (d, $J_{C\text{-}F}$ = 273 Hz), 154.0, 131.7, 131.0, 129.8, 129.0, 128.1, 126.1, 116.5 (d, $J_{C\text{-}F}$ = 3 Hz), 63.5, 23.8; ^{19}F (376 MHz, Chloroform-*d*): δ −112.5; IR (ν_{max}, cm^{-1}): 2994 (m) 1788 (s), 1729 (s), 1510 (s), 1417 (s), 1214 (s), 1202 (s), 1147 (s) 691 (s); HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{17}H_{15}N_2O_2F$ 299.1190; found 299.1210.

Larger Scale Synthesis Procedure

i) (S)-5-isopropyl-3-phenylimidazolidine-2,4-dione (3d)

(*S*)-5-isopropylimidazolidine-2,4-dione (**1e**) (284 mg, 2 mmol) and diphenyliodonium triflate (**2a**) (1.032 g, 2.4 mmol), CuI (38 mg, 0.2 mmol) and K_3PO_4 (424 mg, 2 mmol) were added under N_2 atmosphere to a dried 50 mL round-flask. The flask was equipped with a rubber septa, evacuated and backfilled with nitrogen three times. The stirring was started and dry DCE (20 mL) was added. The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was filtered through celite and concentrated *in vacuo*. The mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 40/60) to afford **3d** (348 mg, 1.6 mmol, 80%) as white solid.

ii) 5,5-dimethyl-3-(4-nitrophenyl)-1-(p–tolyl)hydantoin (5g)

5,5-dimethyl-3-(4-nitrophenyl)hydantoin (**4e**) (498 mg, 2 mmol) and bis(4-methylphenyl)iodonium triflate (**2c**) (1.099 g, 2.4 mmol), CuI (38 mg, 0.2 mmol) and K_3PO_4 (424 mg, 2 mmol) were a"dded under N_2 atmosphere to a dried 50 mL round-flask. The flask was equipped with a rubber septa, evacuated and backfilled with nitrogen three times. The stirring was started and dry DCE (20 mL) was added. The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was filtered through celite and concentrated *in vacuo*. The mixture was purified by column chromatography (AcOEt/Hexane: 5/95 followed by 20/80) to afford **5g** (525 mg, 1.56 mmol, 78%) as white solid.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Copper · Hypervalent iodine · Homogeneous catalysis · N-arylation · Synthetic methods

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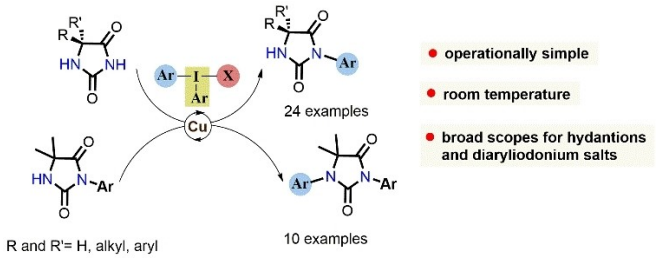

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The N^1- and N^3-arylation of hydantoins is reported employing diaryliodonium triflates as aryl source using a copper (I) catalyst. The developed protocol is performable at room temperature and easily scalable. The robustness is confirmed with a wide range of substrate studies of both hydantoins and diaryliodonium salts. Sterically complicated *ortho*-substituted diaryliodonium salts are also compatible with the reaction protocol.