EurJOC
European Journal of Organic Chemistry

A Journal of
ChemPubSoc Europe

Accepted Article

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To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201800688

Link to VoR: http://dx.doi.org/10.1002/ejoc.201800688

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FULL PAPER

An Intramolecular C(sp^2)-H Amidation using *N*-Iodosuccinimide

Md Toufique Alam, Saikat Maiti and Prasenjit Mal*

Abstract: Herein, *N*-iodosuccinimide (NIS) mediated an intramolecular dehydrogenative C(sp^2)-H amidation is reported for an easy and convenient access to 1,2-disubstituted benzimidazoles. The non-prefunctionalized C(sp^2)-H and N(sp^3)-H bonds were directly coupled using the NIS in trifluoroethanol and proved to be mild alternative to strong oxidative iodine(III) reagents. The reaction worked at room temperature, under open atmosphere and any additive (base) free condition.

Introduction

Benzimidazoles are well known heterocyclic systems for their extensive use in pharmaceutical chemistry and material science.[1] These molecules have also shown anti-cancer,[2] anti-infective,[3] anti-inflamatory,[4] anti-hepatitis B,[5] anti-HIV,[6] anti-depressant,[7] and anti-tumor[8] activities. Interestingly, benzimidazole moiety containing drug esomeprazole (Nexium) was reported to be one of the best-selling drugs in 2009 (Figure 1a).[9] The *N*-substituted benzimidazole systems are also well known in various biologically active molecules.[4-5, 10] Therefore, synthesis of benzimidazoles gained huge attention in organic synthesis.

The development towards exploring environmentally benign methods[11] for C-N bond synthesis are of huge significance.[12] Compared to metal mediated C-N coupling reactions,[13] metal-free direct C-H amination are of importance to deliver various amines by sustainable methods.[14] The cost effective and waste free methods for construction of C-N bonds using metal free iodine based reagents are popular[15] and therefore various cross-dehydrogenative coupling (CDC) or oxidative cross C-N coupling reactions are reported.[16] However, limited examples are available for C-H amination reaction using *N*-iodosuccinimide (NIS).[17]

The small molecules system chemistry approach[18] is gaining popularity by understanding the complexity of chemical reactions and towards implementing them in a simplified manner. Cooperative multiple weak interactions[19] like hydrophobic effect,[20] halogen bonding,[21] charge-transfer,[22] cation-π, anion-π,[23] Soft-Hard Acid Base (SHAB) control,[24] etc. are significantly being explored in chemical reaction systems.[25] Therefore, in order to control a chemical reaction within a system through weak supramolecular interactions it's important to understand the reactivity of the system as a whole.[26]

Results and Discussion

In continuation of our research interests towards controlling chemical reactions using weak interactions[27] in non-prefunctionalized aromatic systems,[28] we report here an intramolecular C(sp^2)-H amidation reaction (Figure 1c) for 1,2-disubstituted benzimidazole synthesis using NIS by replacing strong oxidant like phenyliodine diacetate (PIDA).[29] Till date, numerous methods have been established for synthesis of N-H benzimidazoles,[30] but a very few reports are available for metal-free direct access to *N*-substituted benzimidazoles.[31]

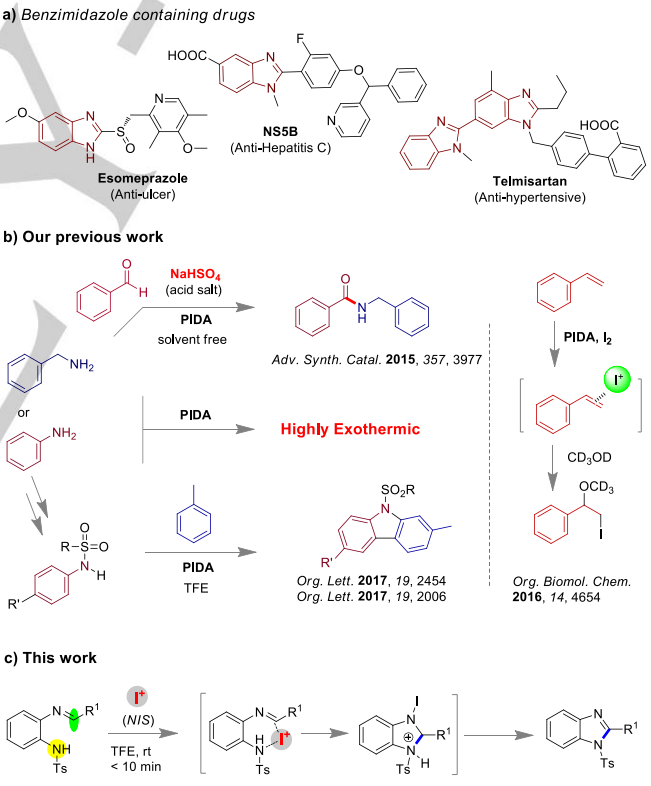

Figure 1. a) Benzimidazole containing drug molecules. b) The reactivity control of amines in presence of phenyliodine diacetate (PIDA). For example, benzyl amine-PIDA explosion was controlled by $NaHSO_4$.[22] sulphonamides in fluorinated solvents led to carbazoles,[28] styrene was difunctionalized *via* cation-π.[32] c) Understanding of the dehydrogenative C(sp^2)-H amidation by NIS (this work).

Amines are highly reactive towards hypervalent iodine reagents and therefore intra- or intermolecular control of the reactions are necessary. A successful CDC reaction was done from contact-explosives mixture primary amines and PIDA under solvent free

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ball milling condition i.e., at maximum contacts of the reactants (Figure 1b).[22] Using the acid-salt $NaHSO_4$, charge transfer basicity of the amine nitrogen was reduced towards the reaction with iodine(III). We have also recently shown that reactivity of protected aryl amines i.e., sulphonamides in 2,2,2-trifluoroethanol (TFE) can be performed towards synthesis of carbazoles,[28] At mixing certain aryl amines also led to exothermic reactions with PIDA. It was established that the I^+ generated form the PIDA-I_2 mixture promoted the olefin-difunctionalization reactions in TFE or CD_3OD *via* cation-π interaction (Figure 1b).[32] In Figure 1c, we have shown the intramolecular dehydrogenative C(sp^2)-H amination towards synthesis of 1,2-disubstituted benzimidazoles. We anticipate that I^+ helped to promote the C(sp^2)-H – NH coupling. Being highly polar and non-nucleophilic in nature, fluorinated solvents are anticipated to stabilize the cationic intermediates when the reactions are carried out using iodine reagents.[33]

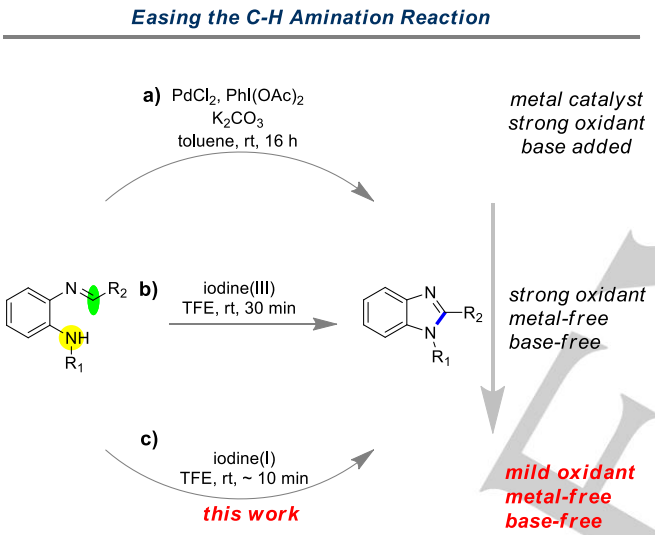
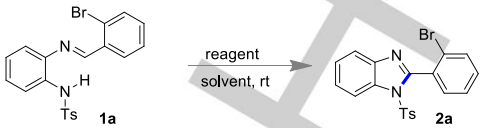


Figure 2. Easing the dehydrogenative C(sp^2)-H amidation reaction. a) Zeng's Pd-catalyzed intramolecular amidation in presence of PIDA oxidant.[34] b) The iodine(III) mediated Pd-free approach.[29] c) Work on amidation using mild oxidant NIS.

In the Zeng's Pd-catalyzed intramolecular amidation in presence of PIDA oxidant, toluene was used as the solvent and the reaction was continued for 16 h (Figure 2a).[34] Interestingly, similar reaction could be performed in absence of any Pd-metal catalyst and using PIDA or under any base free[35] condition. The reaction time was dramatically reduced to < 30 min upon changing to the fluorinated solvent TFE at room temperature (Figure 2b).[29] We have recently reported that reactions using hypervalent iodine regents could be performed to its best in fluorinated solvents.[28] Various coupling reactions are known using I^+ as the reagent.[36] However, in this work the formation of N…I^+…π intermediate might be crucial to bring the imine double bond and nitrogen center for the oxidative coupling.[26b, 37] As a result the reaction was done at mild condition (Figure 3c). Hence, this C-N coupling reaction of non-prefunctionalized C-H and N-H bonds anticipated to be worked under metal-free, base-free and mild condition. Operational simplicity, open atmosphere reaction and excellent yield of the 1,2-disubstituted benzimidazoles at room temperature are the major advantages of this amination protocol.

Table 1 Optimization of reaction condition



Entry	Reagent (equiv)	Solvent	Time	Yield[b] (%)
1	NIS (1.1)	TFE	15 min	81
2	NIS (1.5)	TFE	15 min	91
3	NIS (1.8)	TFE	10 min	98
4	NIS (1.8)	ACN	10 min	81
5	NIS (1.8)	DCE	30 min	85
6	NIS (1.8)	DCM	20 min	86
7	NIS (1.8)	THF	30 min	40
8	NIS (1.8)	DMF	10 min	56
9	NIS (1.8)	EtOAc	25 min	61
10	NIS (1.8)	EtOH	15 min	85
11	NIS (1.8)	Acetone	20 min	61
12	NIS (1.8)	1,4-Dioxane	30 min	80
13	NIS (1.8)	$MeNO_2$	25 min	50
14	I_2 (1.8)	TFE	40 min	50
15	TBAI (1.8) [a]	TFE	1 h	--[b]
16	TEAI (1.8) [c]	TFE	1 h	--[b]

[a]Tetrabutyl ammonium iodide. [b]No Reaction. [c] Tetraethyl ammonium iodide.

During optimization of the reaction condition, *N*-(2-((2-bromobenzylidene)amino)phenyl)-4-methylbenzenesulfonamide (**1a**)[34] was used as model substrate. The product 2-(2-bromophenyl)-1-tosyl-benzo[d]imidazole (**2a**) was isolated in 98% yield when 1.8 equiv of NIS was used in solvent 2,2,2-trifluoroethanol (TFE) at room temperature (Table 1, entry 3). None of the non-fluorinated solvents such as ACN (acetonitrile), DCM (dichloromethane), DCE (1,2-dichloroethane), THF (tetrahydrofuran), DMF (*N*,*N*-dimethylformamide), ethyl acetate, EtOH (ethanol), acetone, 1,4-dioxane, nitromethane, etc. led to better result compared to TFE (Table 1, entries 5-13). Using TFE, in absence of any base and within 40 min, 50% yield of the product was obtained using molecular iodine (Table 1, entry 14). The attempts to use of (tetra)alkyl ammonium iodides as reagent were also in vain (Table 1, entries 15-16). Use of 1.8 equiv of NIS as oxidant was standardized as the optimum (Table 1, entry 3).

Using the optimized reaction condition, substrates scope for this C-H amination protocol was explored for the synthesis of 1,2-disubstituted benzimidazoles (Figure 3). *N*-Tosyl substituted benzimidazoles containing differently substituted aryl group at 2-position were isolated in excellent yield within relatively shorter reaction time (ca. 10 min). Multi-substituted benzimidazole derivatives bearing electron withdrawing halogen groups (**2a-f**), -NO_2 (**2j-k**), -CN (**2i**) groups on aryl rings were isolated in excellent yields. Likewise, electron donating alkyl (**2g-h**) or alkoxy (**2f**) groups containing benzimidazole products were also synthesized with high efficiency. Synthesis of benzimidazole derivatives with fused aromatics such as anthracenyl (**2l**), pyrenyl (**2m**) and heteroaromatic (**2n**) at 2-position were also found to be successful. Cyclohexyl substituted benzimidazole derivative (**2o**) was isolated with 96% yield. The structure of compound **2h** was confirmed by X-ray crystallographic analysis (Figure 3).

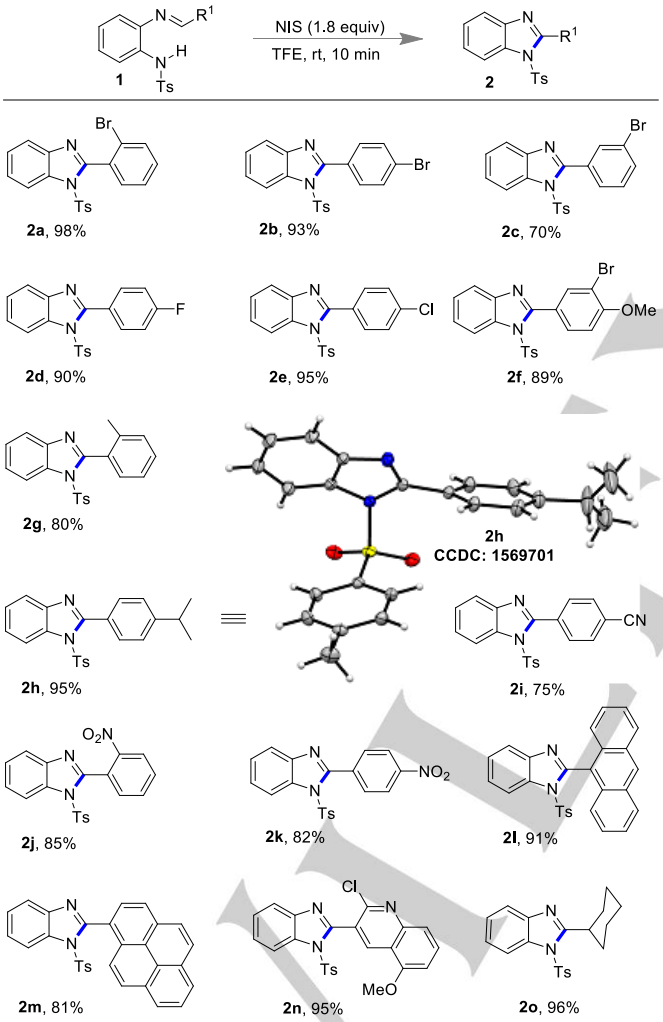


Figure 3. Scope of C-H amidation reaction.

Benzimidazoles having different functional groups like hydroxy, carbonyl, olefin, alkyne, etc. were also efficiently synthesized (Figure 4). The yields of the reactions were also found to be good.

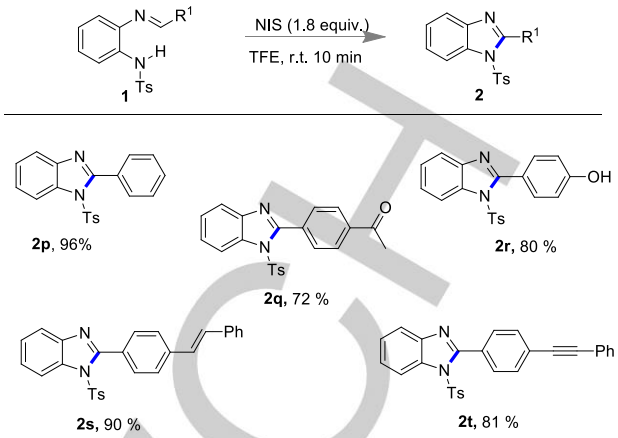


Figure 4. Functional group tolerance in the synthesis of benzimidazole.

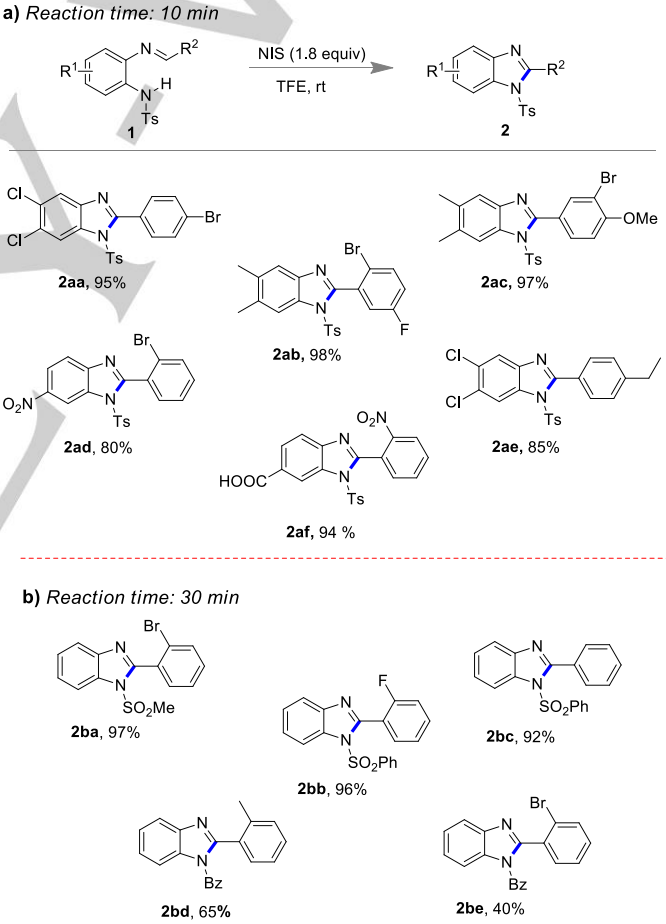


Figure 5. Scope of C-H amination reaction. The benzimidazoles a) core-modified and b) with different protecting groups.

Benzene core substituted benzimidazoles (Figure 5a) were also efficiently synthesized with substituents like -Cl, -Me, -NO_2, -COOH, etc. The products with electron donating methyl substituents (**2ab-ac**) were isolated in better yields than with electron withdrawing groups (**2aa**, **2ad-af**). Also, benzimidazoles were synthesized with different *N*-protecting groups. In addition to

tosyl (Ts) groups, other protecting groups like methane sulfonyl, benzene sulfonyl and benzoyl groups were also explored towards 1,2-disubstituted benzimidazole synthesis (Figure 5b). Notably, products with carbonyl protecting groups were isolated in relatively lower yields (**2bd-be**) than sulfonyl protecting groups (**2ba-bc**).

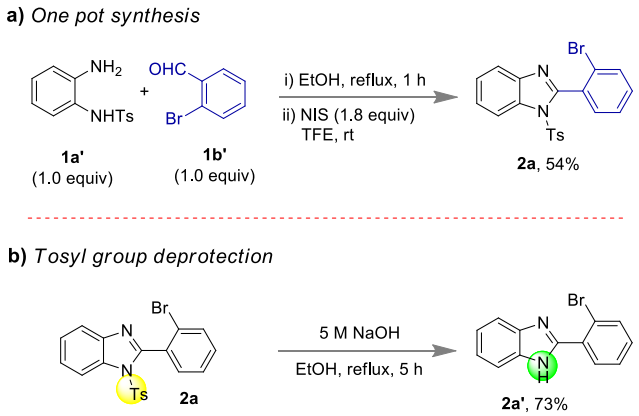


Figure 6. a) One pot synthesis approach. b) N-H Benzimidazole synthesis.

Synthesis of *N*-substituted benzimidazole could also be achieved in one-pot approach without going *via* imine substrate. Condensation of equimolecular amounts of amine and aldehyde under reflux in ethanol and followed by treatment with NIS at room temperature, the benzimidazole **2a** could be isolated in good yield (Figure 7a). For further synthetic utility, the deprotection of the tosyl (-Ts) from **2a** could successfully be done using 5 M NaOH under refluxing ethanol condition (Figure 6b)[38] and the corresponding N-H benzimidazole product 2-(2-bromophenyl)-1H-benzo[d]imidazole(**2a'**) was isolated in 73% yield.

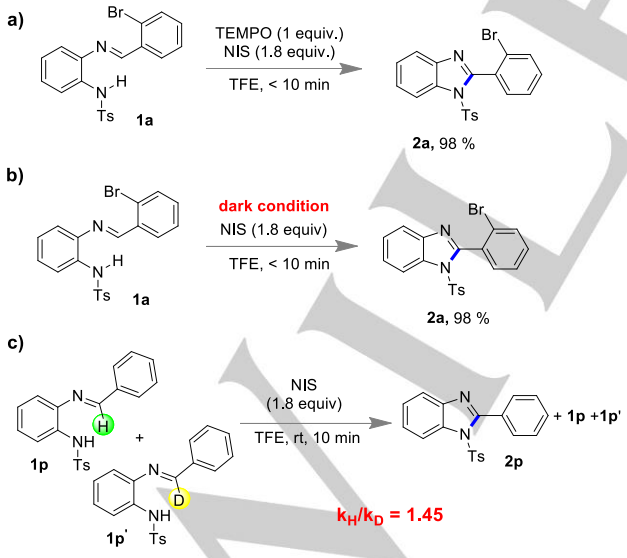


Figure 7. Control experiments. a) TEMPO radical experiment. b) Reaction under dark condition. c) Kinetic isotope effect experiment.

We have shown the control experiments in Figure 7. TEMPO radical experiment (Figure 7a) and the reactions under dark condition (Figure 7b) did not affect the yield of the reaction. The kinetic isotopic effect[39] was found to be as k_H/k_D = 1.45. This indicate that the C(sp^2)-H is actively participating during the reaction.

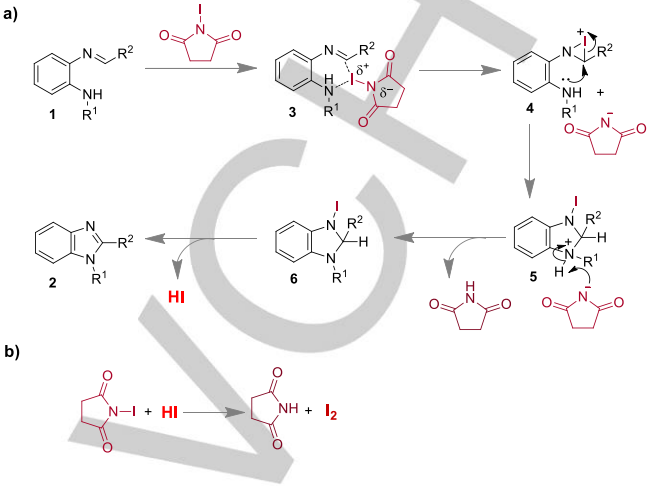


Figure 8. a) Plausible mechanism and b) Neutralization of by-product HI.

Based on the control experiments and our previous work,[32] a plausible mechanistic pathway for the transformation is shown in Figure 8a. Iodide center of NIS being electrophilic in nature, is expected to interact with the electron rich imine bond and *N*-center of –NH simultaneously to create an intermediate **3** and lead to subsequent formation of bridged iodonium intermediate **4**. Following, the C–N bond formation with the generation of another intermediate **5** was expected. Anion generated from succinimide would help the abstraction of proton to form **6** and followed by HI elimination to drive the aromatization of product **2**.

One of the by-product of the reaction is hydroiodic acid (HI), which bear capacity to protonate the *N*-center of amide group and the nucleophilicity of *N*-center would be diminished. Requirement of excess amount of NIS for the transformation might be justified by the need of neutralization of by-product HI with the help of succinimide. Isolation of succinimide was possible using 3:2 (hexane: ethyl acetate) mixture as eluent by column chromatography during detection of polar compound 2-(2-nitrophenyl)-1-tosyl-1H-benzo[d]imidazole-6-carboxylic acid (**2af**, Figure 5a). Iodine was liberated during the evaporation to dryness of reaction mixture which proves HI may react with excess NIS (Figure 8b). Also from ^{1}H NMR spectra of separate reaction mixtures of deuterated aldimine (**1p'**) and aldimine (**1p**), it has been confirmed that the proton of succinimide comes from NH proton but not from C (sp^2)-H proton of aldimine (see supporting information).

The role of the use of fluorinated solvent[33, 40] TFE can be rationalized as follows. Kita and co-workers have successfully shown that hypervalent iodine reagents when mixed with fluorinated solvent like hexafluoroisopropanol (HFIP), the radical cationic intermediate get stabilized due to the high polarity and low-nucleophilic nature of the solvent.[40d] Recently, Donohoe and Compton with co-workers have also demonstrated the role of HFIP towards activation of the hypervalent iodine reagents.[41] Similarly trifluoroethanol is also established as one of the potential fluorinated solvents to stabilize cationic or cation-radical species

generated using iodine regents.[40b, 40c, 40e] Therefore we anticipated that TFE promoted the reaction by stabilizing intermediate **4** and **5** (Figure 8a).

Conclusions

In conclusion, the above demonstrated chemical reaction system and the proposed mechanism may suggest an efficient pathway towards developing designed functional molecules using multiple weak interactions. Therefore, by choosing appropriate reaction conditions many difficult reactions can be performed easily. During the C(sp^2)-H amination reaction using *N*-iodosuccinimide 1,2-disubstituted benzimidazole were synthesized easily. Thus we could develop a reaction by an operationally simple, metal, additive and base free methodology. Overall, a library of 1,2-disubstituted benzimidazoles were accessed from easily affordable starting materials. We anticipate that this method will be highly desirable in pharmaceutical chemistry and drug discovery efforts.

Experimental Section

Instrumentation and Chemicals. All the reactions were performed under open atmosphere and isolated yields after column chromatography are presented. For NMR spectra the chemical shift values are given in parts per million (ppm) with respect to residual chloroform (7.26 ppm for ^{1}H and 77.16 for ^{13}C) (in case of DMSO-d_6: 2.5 ppm for ^{1}H and 39.5 for ^{13}C). The peak patterns are indicated as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet). The coupling constants (*J*) are reported in hertz (Hz). High-resolution mass spectra (HRMS) were obtained on an ESI-TOF (time of flight) mass spectrometer. FT-IR spectra were recorded in wave number (cm^{-1}) after making thin layer of the compounds on the surface of NaCl crystal using dichloromethane. Melting points of the compounds were measured using a digital melting point apparatus and are uncorrected. Thin-layer chromatography (TLC) was done on Merck Silica Gel F254 plates (0.25 mm).

All starting materials (*N*-substituted imine **1**) were prepared by following literature report.[34]

General Procedure for Preparation of *N*-Substituted Benzimidazoles. NIS (0.251 mmol, 1.8 equiv) was added to a stirred solution of *N*-substituted imine **1** (0.139 mmol, 1 equiv) in TFE (2,2,2-trifluoroethanol) at room temperature. The progress of the reaction was monitored by thin layer chromatography (TLC) using appropriate mixture of ethyl acetate and hexane as eluent. Upon completion of the reaction, solvent was completely evaporated to dryness. Then the crude reaction mixture was purified by silica gel column chromatography using n-hexane and ethyl acetate as eluent.

Procedure for Preparation of 2-(2-Bromophenyl)-1-tosyl-benzo[d]imidazole (2a). NIS (57 mg, 0.251 mmol) was added to a stirred solution of *N*-(2-((2-bromobenzylidene)amino)phenyl)-4-methylbenzenesulfonamide **1a** (60 mg, 0.139 mmol) in TFE (0.5 mL) at room temperature. Upon completion (ca. 10 min) of the reaction, TFE was completely evaporated to dryness. The crude mixture was purified by silica gel column chromatography using n-hexane and ethyl acetate (92:8) as eluent to 2-(2-bromophenyl)-1-tosyl-benzo[d]imidazole **2a** (58.5 mg, 0.137 mmol, yield: 98%).

Kinetic Isotopic Effect (KIE) Experiment.[39] The kinetic isotopic study shown in Figure 7c, were performed by following the general procedure of the preparation of *N*-substituted benzimidazoles. The reaction was done using equimolar amount of aldimine (**1p**) and deuterated aldimine (**1p'**) in presence of 1.8 equiv NIS in TFE. After that, the reaction mixture was evaporated to dryness and crude mixture was passed through a short-pad silica gel column using 9:1 hexane: ethyl acetate mixture as eluent. The ^{1}H NMR spectra of the mixture was recorded for whole sample in CD_3Cl for the determination of k_H/k_D (Fig. S71, supporting information)

2-(2-Bromophenyl)-1-tosyl-benzo[d]imidazole (2a)[29]**:** 58.5 mg; Yield: 98%; R_f = 0.5 (hexane:ethyl acetate 4:1); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8 Hz, 1H), 7.8 (d, *J* = 8 Hz, 1H), 7.66 (d, *J* = 8 Hz, 1H), 7.54 (d, *J* = 8 Hz, 2H), 7.48–7.39 (m, 5H), 7.19 (d, *J* = 8 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 146.1, 142.2, 135.1, 132.8, 132.6, 132.4, 132.0, 131.7, 129.9, 127.5, 126.5, 125.8, 125.1, 124.7, 120.8, 114.2, 21.7.

2-(4-Bromophenyl)-1-tosyl-benzo[d]imidazole (2b): 55 mg; Yield: 93%; R_f = 0.5 (hexane: ethyl acetate 4:1); white solid; mp 135-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8 Hz, 1H), 7.10 (d, *J* = 8 Hz, 1H), 7.61 (d, *J* = 8, 2H), 7.50 (d, *J* = 8, 2H), 7.41 (m, 2H), 7.33 (d, *J* = 8, 2H), 7.11 (d, 2H), 2.32 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 153.1, 146.0, 142.7, 134.9, 133.9, 132.5, 131.4, 129.9, 129.1, 127.0, 125.8, 125.6, 125.5, 120.5, 115.3, 121.7; IR (KBr): ν = 2921, 1562, 1480, 1450, 1377, 12 50, 1189, 1177, 1072, 1057 cm^{-1}; HR-MS (ESI-TOF): m/z = 427.0114, calculated for $C_{20}H_{15}BrN_2O_2S$ ($M+H^+$): 427.0110.

2-(3-Bromophenyl)-1-tosyl-benzo[d]imidazole (2c): 62 mg; Yield: 70%; R_f = 0.5 (hexane :ethyl acetate 4:1); white semi-solid; ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.60 (s, 2H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 3H), 7.13 (d, *J* = 8.4 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 152.2, 146.1, 142.5, 135.0, 133.9, 133.5, 133.4, 132.0, 130.0, 129.7, 129.3, 127.1, 125.8, 125.5, 121.7, 120.3, 115.2, 21.8; IR (KBr): ν = 2924, 2108, 1640, 1536, 1448, 1381, 1253, 1177, 1084, 1012 cm^{-1}; HR-MS (ESI-TOF): m/z = 427.0106, calculated for $C_{20}H_{15}BrN_2O_2S$ ($M+H^+$): 427.0110.

2-(4-Fluorophenyl)-1-tosyl-benzo[d]imidazole (2d)[29]**:** 32 mg; Yield: 90%; R_f = 0.5 (hexane :ethyl acetate 4:1); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8 Hz, 1H), 7.71 (d, *J* = 8 Hz, 1H), 7.62 (dd, J_1 = 8 Hz, J_2 = 4 Hz, 2H), 7.46–7.37 (m, 2H), 7.31 (d, *J* = 8 Hz, 2H), 7.18–7.10 (m, 4H), 2.33 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 164.3 (d, $^1J_{C,F}$ = 249.9 Hz), 153.2, 146.0, 142.6, 135.0, 134.0, 131.7 (d,$^3J_{C,F}$ = 8. Hz), 129.9, 127.0, 126.1 (d, $^4J_{C,F}$ = 3.5 Hz), 125.7, 125.6, 120.5, 115.3, 115.1 (d, $^2J_{C,F}$ =21.7 Hz), 21.7.

2-(4-Chlorophenyl)-1-tosyl-benzo[d]imidazole (2e)[35]**:** 76 mg; Yield: 95%; R_f = 0.5 (hexane:ethyl acetate 4:1); white solid; ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.42 (m, 3H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 153.1, 146.1, 142.7, 137.1, 135.0, 134.0, 132.3, 130.0, 128.6, 128.2, 127.0, 125.8, 125.6 120.6, 115.3, 21.8.

2-(3-Bromo-4-methoxyphenyl)-1-tosyl-benzo[d]imidazole (2f)[29]**:** 53 mg; Yield: 89%; R_f = 0.4 (hexane:ethyl acetate 4:1); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8 Hz, 1H), 7.70 (d, *J* = 8 Hz, 1H), 7.66–7.64 (m, 2H), 7.44–7.37 (m, 2H), 7.34 (d, *J* = 8 Hz, 2H), 7.12 (d, *J* = 8 Hz, 2H), 6.99 (d, *J* = 8 Hz, 1H), 4.00 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 157.8, 152.6, 146.0, 142.6, 135.4, 135.0, 134.0, 131.9, 129.9, 127.0, 125.6, 125.5, 123.5, 120.4, 115.3, 110.9, 110.8, 56.5, 21.8.

2-(Ortho-Tolyl)-1-tosyl-benzo[d]imidazole (2g)[29]**:** 25 mg; Yield: 80%; R_f = 0.5 (hexane:ethyl acetate 4:1); white solid; ^{1}H NMR (400 MHz, $CDCl_3$):

δ 8.27 (d, J = 8 Hz, 1H), 7.79 (d, J= 8 Hz, 1H), 7.50–7.44 (m, 5H), 7.31–7.28 (m, 2H), 7.22–7.18 (m, 3H), 2.40 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 152.5, 146.0, 142.3, 139.1, 135.4, 133.3, 130.8, 130.5, 130.3, 129.9, 129.8, 127.5, 125.5, 125.0, 124.9, 120.5, 114.5, 21.8, 20.0.

2-(4-Isopropylphenyl)-1-tosyl-benzo[d]imidazole (2h)[29]**:** (CCDC: 1569701); 48 mg; Yield: 95%; R_f = 0.5 (hexane:ethyl acetate 4:1); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8 Hz, 1H), 7.71 (d, *J* = 8 Hz, 1H), 7.53 (d, *J* = 8 Hz, 2H), 7.42–7.29 (m, 6H), 7.07 (d, *J* = 8 Hz, 2H), 3.01 (sept, *J* = 8 Hz, 1H), 2.32(s, 3H), 1.32 (d, *J* = 8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 151.8, 145.7, 142.8, 135.1, 134.1, 131.0, 129.8, 127.5,127.2, 125.9, 125.4, 125.3, 120.4, 115.3, 34.3, 24.0, 21.7.

4-(1-Tosyl-benzo[d]imidazol-2-yl)benzonitrile (2i)[29]**:** 45 mg**;** Yield: 75%; R_f = 0.4 (hexane:ethyl acetate 4:1); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8 Hz, 1H), 7.77–7.73 (m, 5H), 7.50–7.44 (m, 2H), 7.34 (d, *J* = 8 Hz, 2H), 7.13 (d, *J* = 8 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 152.0, 146.4, 142.7, 134.8, 134.7,133.9, 131.7, 131.5, 130.1, 126.9, 126.3, 125.9, 120.8, 118.3, 115.2, 114.3, 21.8.

2-(2-Nitrophenyl)-1-tosyl-benzo[d]imidazole (2j): 68 mg; Yield: 85%, R_f = 0.3 (hexane:ethyl acetate 4:1); Yellow solid, mp 80-81 ^{o}C ; ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 3H), 7.54 – 7.45 (m, 4H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 148.9, 148.5, 146.4, 142.4, 134.9, 133.2, 133.1, 132.9, 131.6, 130.1, 127.4, 126.3, 126.0, 125.2, 124.8, 120.8, 114.0, 21.8; IR (KBr): ν = 2924, 1638, 1531, 1448, 1347, 1253, 1176, 1087, 1013 cm^{-1}; HR-MS (ESI-TOF): m/z = 394.0855, calculated for $C_{20}H_{15}N_3O_4S$ ($M+H^+$): 394.0856.

2-(4-Nitrophenyl)-1-tosyl-benzo[d]imidazole (2k)[35]**:** 65 mg; Yield: 82%; R_f = 0.4 (hexane:ethyl acetate 4:1): Yellow solid, ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.7 Hz, 2H), 8.20 (d, *J* = 7.7 Hz, 1H), 7.85 (d, *J* = 7.7 Hz, 2H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.50−7.43 (m, 2H), 7.35 (d, *J* = 6.3 Hz, 2H), 7.15 (d, *J* = 6.3 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 151.7, 149.0, 146.4, 142.7, 136.5, 134.8, 133.9, 132.1, 130.1, 126.9, 126.4, 125.9, 122.9, 120.9, 115.3, 21.8.

2-(Anthracen-9-yl)-1-tosyl-benzo[d]imidazole (2l)[29]**:** 54 mg; Yield: 91%; R_f = 0.45 (hexane:ethyl acetate 4:1); yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 1H), 8.36 (d, *J* = 8 Hz, 1H), 8.05 (d, *J* = 8 Hz, 2H), 7.89 (d, *J* = 8 Hz, 1H), 7.56–7.50 (m, 2H), 7.44-7.40 (m, 2H), 7.23–7.17 (m, 4H), 6.97 (d, *J* = 8 Hz, 2H), 6.77 (d, *J* = 8 Hz, 2H), 2.22 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 150.3, 145.6, 142.6, 134.4, 133.6, 131.9, 130.9, 130.4, 130.1, 129.5, 128.5, 127.5, 127.2, 126.6, 125.8, 125.7, 125.3, 125.0, 123.6, 120.8, 114.5, 21.7.

2-(Pyren-1-yl)-1-tosyl-benzo[d]imidazole (2m)[29]**:** 42 mg; Yield: 81%; R_f = 0.45 (hexane:ethyl acetate 4:1); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8 Hz, 1H), 8.26 (d, *J* = 8 Hz, 2H), 8.20–8.13 (m, 4H), 8.04 (t, *J* = 8 Hz, 1H), 7.90 (d, *J* = 8 Hz, 1H), 7.82 (d, *J* = 9.2 Hz, 1H), 7.57–7.49 (m, 3H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 145.7, 142.6, 134.8, 133.8, 132.8, 131.2, 131.0, 130.6, 129.4, 129.3, 129.0, 128.4, 127.4, 127.2, 126.4, 126.0, 125.8, 125.7, 125.2, 124.4, 124.29, 124.26, 124.1, 123.6, 120.7, 114.9, 21.3.

2-Chloro-6-methoxy-3-(1-tosyl-benzo[d]imidazol-2-yl)-quinolone (2n)[29]**:** 57 mg; Yield: 95%; R_f = 0.4 (hexane:ethyl acetate 3:1); white solid; ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.17 (s, 2H), 8.02 (d, *J* = 9.1 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.51-7.45 (m, 5H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.12 (s, 1H), 3.96 (s, 3H), 2.37 (s, 3H) ; ^{13}C NMR (175 MHz, $CDCl_3$): δ 158.8, 148.2, 146.7, 146.4, 144.2, 142.3, 140.5, 134.9, 133.0, 130.2, 130.1 127.4, 126.9, 126.2, 125.3, 124.8, 124.3, 121.0, 114.3, 105.6, 55.9, 21.8.

2-Cyclohexyl-1-tosyl-benzo[d]imidazole (2o)[29]**:** 65 mg; Yield: 96%; R_f = 0.5 (hexane: ethyl acetate 4:1); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–8.03 (m, 1H), 7.75 (d, *J* = 8 Hz, 2H), 7.68–7.66 (m, 1H), 7.35–7.30 (m, 2H), 7.27 (d, *J* = 8 Hz, 2H), 3.52–3.45 (m, 1H), 2.38 (s, 3H), 1.93–1.84 (m, 4H), 1.75–1.66 (m, 3H), 1.43–1.30 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 159.8, 145.9, 142.1, 136.1, 133.0, 130.3, 126.7, 124.8, 124.7, 119.9, 114.1, 38.3, 32.7, 26.4, 25.9, 21.8.

2-Phenyl-1-tosyl-1H-benzo[d]imidazole (2p)[35]: 57 mg; Yield: 96 %; R_f = 0.4 (hexane:ethyl acetate 4:1): white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8 Hz, 1H), 7.73 (d, *J* = 8 Hz, 1H), 7.62 (d, *J* = 8 Hz, 2H), 7.55 (t, *J* = 8 Hz, 1H), 7.50 – 7.36 (m, 4H), 7.33 (d, J = 8.0 Hz, 2H), 7.08 (d, *J* = 8 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 145.8, 142.7, 135.0, 133.9, 130.9, 130.6, 130.1, 129.8, 127.7, 127.0, 125.5, 125.4, 120.5, 115.2, 21.7.

1-(4-(1-Tosyl-1H-benzo[d]imidazol-2-yl)phenyl)ethanone (2q) : 40 mg; Yield: 72 %; R_f = 4.5 (hexane:ethyl acetate 4:1); white solid; mp 164-165 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.81 – 7.68 (m, 3H), 7.48-7.39 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.69 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 153.0, 146.1, 142.8, 138.4, 134.9, 134.7, 133.9, 131.3, 130.0, 127.7, 127.0, 126.0, 125.7, 120.8, 115.3, 26.9, 21.8. ; IR (KBr): ν = 2063, 1645, 1380, 1256, 1174, 1080 cm^{-1}; HR-MS (ESI-TOF): m/z = 391.1112, calculated for $C_{22}H_{18}N_2O_3S$ ($M+H^+$): 391.1111.

4-(1-Tosyl-1H-benzo[d]imidazol-2-yl)phenol (2r)[35]: 48 mg; Yield: 80 %; R_f = 0.4 (hexane:ethyl acetate 7:3); light brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.22 (d, *J* = 8 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8 Hz, 2H), 7.08 (d, *J* = 8 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 154.9, 145.9, 145.8, 141.8, 134.9, 133.8, 132.7, 129.8, 127.2, 125.6, 120.5, 119.8, 115.5, 115.2, 21.7. HR-MS (ESI-TOF): m/z = 365.0984, calculated for $C_{20}H_{16}N_2O_3S$ ($M+H^+$): 365.0954.

(E)-2-(4-styrylphenyl)-1-tosyl-1H-benzo[d]imidazole (2s): 54 mg; Yield: 90%; R_f = 0.5 (hexane:ethyl acetate 9:1); white solid; mp 170 – 172 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.47 – 7.41 (m, 2H), 7.41 – 7.27 (m, 5H), 7.26 (d, *J* = 8 Hz, 1H), 7.19 (d, *J* = 16.4 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 145.8, 142.9, 139.7, 137.1, 135.1, 134.1, 131.4, 130.6, 129.83, 129.0, 128.9, 128.2, 127.9, 127.1, 126.9, 125.8, 125.6, 125.5, 120.5, 115.4, 21.7. IR (KBr): ν = 2081, 1629, 1378, 1187, 1172, 1117 1072 cm^{-1}; HR-MS (ESI-TOF): m/z = 451.1471, calculated for $C_{28}H_{22}N_2O_2S$ ($M+H^+$): 451.1475.

2-(4-(Phenylethynyl)phenyl)-1-tosyl-1H-benzo[d]imidazole (2t)[42]**:** 48 mg; Yield: 81 %; R_f = 0.5 (hexane:ethyl acetate 9:1); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.64 (m, 4H), 7.59 (dd, J_1 = 7.6, J_2 = 4 Hz, 2H), 7.51 – 7.41 (m, 2H), 7.41 – 7.32 (m, 5H), 7.11 (d, *J* = 8.4 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6 145.9, 142.8, 135.0, 134.1, 131.8, 131.0, 130.9, 129.9, 129.7, 128.8, 128.6, 127.0, 125.7, 125.5, 123.0, 120.5, 115.4, 91.7, 88.9, 21.7. HR-MS (ESI-TOF): m/z = 449.1333, calculated for $C_{28}H_{20}N_2O_2S$ ($M+H^+$): 449.1318

2-(4-Bromophenyl)-5,6-dichloro-1-tosyl-benzo[d]imidazole (2aa)[29]**:** 57 mg; Yield: 95%; R_f = 0.7 (hexane:ethyl acetate 4:1); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.79 (s, 1H), 7.62 (d, *J* = 8 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8 Hz, 2H), 2.20 (s, 3H); ^{13}C NMR (175, MHz, $CDCl_3$): δ 154.8, 146.7, 142.0, 134.5, 133.1, 132.5, 131.3, 130.2, 130.00, 129.9, 128.2, 127.1, 126.1, 121.7, 116.8, 21.6.

2-(2-Bromo-5-fluorophenyl)-5,6-dimethyl-1-tosyl-benzo[d]imidazole (2ab)[29]**:** 59 mg; Yield: 98%; R_f = 0.5 (hexane:ethyl acetate 4:1); white

solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.63 – 7.58 (m, 1H), 7.56 (s, 1H), 7.54 (d, *J* = 4.0 Hz, 2H), 7.22 (d, *J* = 8 Hz, 2H), 7.16 – 7.10 (m, 1H), 7.07 (dd, J_1 = 8.4, J_2 = 3.2 Hz, 1H), 2.46 (s, 3H), 2.38 (s, 6H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 160.5 (d, $^1J_{C,F}$ = 247.1 Hz), 148.6, 146.3, 140.4, 135.7, 135.2, 134.6, 134.0 (d, $^3J_{C,F}$ = 8.0 Hz), 133.6 (d, $^3J_{C,F}$ = 8.4 Hz), 131.2, 130.1, 127.5, 120.9, 119.9 (d, $^2J_{C,F}$ = 23.6 Hz), 119.5 (d, $^4J_{C,F}$ = 3.0 Hz), 119.1 (d, $^2J_{C,F}$ =21.7 Hz), 114.4, 21.9, 21.0, 20.3.

2-(3-Bromo-4-methoxyphenyl)-5,6-dimethyl-1-tosyl-benzo[d]imidazole (2ac): 59 mg; Yield: 97 %; R_f = 0.4 (hexane: ethyl acetate 4:1), white solid; mp 140-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.68 – 7.56 (m, 2H), 7.46 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8 Hz, 2H), 6.98 (d, *J* = 9.2 Hz, 1H), 4.00 (s, 3H), 2.45 (s, 3H), 2.36 (s, 3H), 2.34 (s, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 157.6, 151.8, 145.8, 135.4, 135.2, 135.1, 134.7, 132.4, 131.9, 130.4, 129.8, 127.0, 123.6, 120.4, 115.5, 110.9, 110.8, 56.5, 21.8, 20.9, 20.3; IR (KBr): $\tilde{\nu}$ = 2920, 1847, 1629, 1487, 1377, 1269, 1175, 1081, 1019 cm^{-1}; HR-MS (ESI-TOF): m/z = 485.0534, calculated for $C_{23}H_{21}BrN_2O_3S$ (M+H$^+$): 485.0529.

2-(2-Bromophenyl)-6-nitro-1-tosyl-benzo[d]imidazole (2ad): 42 mg; Yield: 90%; R_f = 0.4 (hexane:ethyl acetate 4:1); white solid; mp 150-152 °C; ^{1}H NMR (700 MHz, $CDCl_3$): δ 9.10 (s, 1H), 8.36 (dd, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 9.1 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.42 (m, 3H), 7.30 – 7.19 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 155.1, 147.1, 146.2, 145.7, 134.3, 132.8, 132.5, 132.4, 132.3, 131.0, 130.4, 128.0, 126.8, 124.5, 121.2, 120.7, 111.2, 22.0; IR (KBr): $\tilde{\nu}$ = 2097, 1641, 1595, 1523, 1461, 1385, 1271, 1176, 1086, 1012; HR-MS (ESI-TOF): m/z = 471.9937, calculated for $C_{20}H_{14}BrN_3O_4S$ (M+H$^+$): 471.9961.

2-(4-Ethylphenyl)-5, 6-dichloro-1-tosyl-benzo[d]imidazole (2ae): 51 mg; Yield: 85%; R_f = 0.6 (hexane:ethyl acetate 4:1) white solid; mp 170-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.78 (s, 1H), 7.49 (d, *J* = 8 Hz, 2H), 7.37 – 7.21 (m, 4H), 7.11 (d, *J* = 8 Hz, 2H), 2.76 (q, *J* = 8 Hz, 2H), 2.34 (s, 3H), 1.31 (t, *J* = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 147.8, 146.3, 142.1, 134.6, 133.2, 131.0, 130.0, 129.6, 129.5, 127.5, 127.2, 126.6, 121.5, 116.8, 29.0, 21.8, 15.5; IR (KBr): $\tilde{\nu}$ = 2965, 2362, 1624, 1595, 1433, 1383, 1281, 1190, 1177, 1075, 1018 cm^{-1}; HR-MS (ESI-TOF): m/z = 445.0539, calculated for $C_{22}H_{18}Cl_2N_2O_2S$ (M+H$^+$): 445.0539.

2-(2-nitrophenyl)-1-tosyl-1H-benzo[d]imidazole-6-carboxylic acid (2af)[29]**:** 56 mg; Yield: 94%; R_f = 0.3 (hexane:ethyl acetate 1:1); white solid; ^{1}H NMR (400 MHz, DMSO-D_6) δ 8.58 (s, 1H), 8.41 (m, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.96 (m, 2H), 7.89 (d, *J* = 8.0, 1H), 7.71 (m, 1H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, DMSO-D_6) δ 166.9, 151.2, 147.7, 147.0, 145.0, 134.3, 133.3, 132.9, 132.6, 131.9, 130.6, 128.3, 126.9, 126.3, 124.8, 124.8, 120.5, 114.8, 21.2.

2-(2-Bromophenyl)-1-methylsulfonyl-benzo[d]imidazole (2ba): 78 mg; Yield: 97%; R_f = 0.3 (hexane:ethyl acetate 4:1); yellow solid; mp 155-156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, J_1 = 6.8, J_2 = 2 Hz, 1H), 7.89 – 7.84 (m, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.53 – 7.46 (m, 3H), 7.45 – 7.37 (m, 2H), 3.28 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 150.7, 132.5, 132.4, 132.3, 132.3, 131.8, 127.1, 126.1, 125.4, 123.5, 121.2, 113.5, 42.27; IR (KBr): $\tilde{\nu}$ = 1604, 1641, 1462, 1450, 1185, 1049 cm^{-1}; HR-MS (ESI-TOF): m/z = 350.9791, calculated for $C_{14}H_{11}BrN_2O_2S$ (M+H$^+$): 350.9797.

2-(2-Fluorophenyl)-1-(phenylsulfonyl)-benzo[d]imidazole (2bb): 76 mg; Yield: 96%; R_f = 0.5 (hexane:ethyl acetate 4:1); white semi-solid, ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.51 (m, 2H), 7.47 – 7.42 (m, 2H), 7.38 (dt, J_1= 21.0, J_2 = 7.7 Hz, 3H), 7.30 – 7.24 (m, 1H), 7.18 - 7.16 (m, 1H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 161.1 (d, $^1J_{C,F}$ = 250.25 Hz), 147.9, 143.0, 137.9, 134.6, 133.3, 132.8 (d, $^3J_{C,F}$ = 8.75 Hz), 132.2, 129.4, 127.1, 125.9, 125.3, 123.7 (d, $^4J_{C,F}$ = 3.5 Hz), 120.8, 118.8 (d, $^3J_{C,F}$ = 14 Hz), 115.7 (d, $^2J_{C,F}$ = 21 Hz), 114.4; IR (KBr): $\tilde{\nu}$ = 2096, 1624, 1583, 1482, 1448, 1382, 1311, 1253, 1187, 1125, 1187, 1079, 1018 cm^{-1}; HR-MS (ESI-TOF): m/z = 353.0767, calculated for $C_{19}H_{13}FN_2O_2S$ (M+H$^+$): 353.0755.

2-Phenyl-1-(phenylsulfonyl)-benzo[d]imidazole (2bc)[35]**:** 72 mg; Yield: 92%; R_f = 0.5 (hexane:ethyl acetate 4:1); white solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8 Hz, 1H), 7.73 (d, *J* = 8 Hz, 1H), 7.59 (d, *J* = 8 Hz, 2H), 7.53 (m , 1H), 7.50 – 7.45 (m, 2H), 7.50 – 7.39 (m, 5H), 7.28 (t, *J* = 8 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 154.0, 142.6, 137.9, 134.5, 133.9, 130.9, 130.6, 129.9, 129.2, 127.7, 126.9, 125.6, 125.4, 120.5, 115.2.

2-(Ortho-Tolyl)-1-benzoyl-benzo[d]imidazole (2bd): 25 mg; Yield: 65%; R_f = 0.5 (hexane:ethyl acetate 4:1); yellow semi-solid; ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.31 (dt, J_1 = 21.0, J_2 = 7.7 Hz, 4H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.07-7.10 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 168.8, 153.6, 142.9, 137.1, 134.1, 133.6, 133.3, 130.8, 130.5, 130.5, 130.1, 129.8, 128.5, 125.6, 124.8, 124.6, 120.3, 113.7, 20.2; IR (KBr): $\tilde{\nu}$ = 2107, 1641, 1311, 1259, 1223, 1146, 1101, 1073 cm^{-1}; HR-MS (ESI-TOF): m/z = 313.1308, calculated for $C_{21}H_{16}BrN_2O$ (M+H$^+$): 313.1335.

2-(2-Bromophenyl)-1-benzoyl-benzo[d]imidazole (2be): 16 mg; Yield: 40%; Rf = 0.6 (hexane:ethyl acetate 4:1); semi-solid; ^{1}H NMR (700 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.45 – 7.38 (m, 3H), 7.35 (d, *J* = 8.4 Hz, 4H), 7.19 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$): δ 168.2, 152.2, 142.3, 133.9, 133.8, 132.9, 132.8, 132.6, 131.4, 130.7, 128.5, 127.5, 125.4, 124.9, 123.0, 120.6, 114.1; IR (KBr): $\tilde{\nu}$ = 2093.07, 1642, 1448, 1310, 1225, 1147 cm^{-1}; HR-MS (ESI-TOF): m/z = 377.0271, calculated for $C_{20}H_{13}BrN_2O$ (M+H$^+$): 377.0284.

2-(2-Bromophenyl)-1H-benzo[d]imidazole (2a')[43]**:** 37 mg; Yield: 73%; R_f = 0.4 (hexane:ethyl acetate 4:1); white solid; ^{1}H NMR (700 MHz, DMSO-D_6): δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.29 – 7.23 (m, 2H); ^{13}C NMR (175 MHz, DMSO-D_6): δ 150.3, 133.4, 132.3, 132.1, 131.5, 127.8, 122.4, 121.6.

1p': Mp 102-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8 Hz, 2H), 7.72 (s, 1H), 7.63 (d, *J* = 8 Hz, 1H), 7.58 (d, *J* = 8 Hz, 2H), 7.53-7.48 (m, 3H), 7.22 (dd, J_1 = 16, J_2 = 8 Hz, 1H), 7.12-7.08 (m,1H), 7.03 (d, *J* = 8. Hz, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (t, *J* = 25.0 Hz), 143.7, 140.9, 136.1, 135.5, 132.3, 132.2, 129.5, 129.1, 128.9, 127.8, 127.2, 125.5, 121.3, 117.0, 21.6; IR (KBr): $\tilde{\nu}$ =3285, 2165, 1916, 1613, 1485, 1337, 1165, 1215 cm^{-1}; HR-MS (ESI-TOF): m/z = 352.1215, calculated for $C_{20}H_{17}DN_2O_2S$ (M+H$^+$): 352.1225.

Acknowledgements

We thank DST (New Delhi, India) for support and Dr. Milan Kr. Barman (NISER) for crystallography. M.T.A. and S.M. thank UGC (India) and CSIR (India), respectively, for fellowships.

Keywords: C(sp2)-H Amidation• C-N coupling• 1,2-Disubstituted Benzimidazole • *N*-Iodosuccinimide • Weak Interactions

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10.1002/ejoc.201800688

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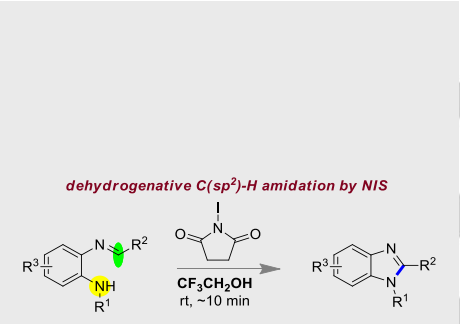
FULL PAPER

An intramolecular dehydrogenative C(sp2)H-NH coupling reaction is being reported by using *N*-iodosuccinimide as the metal-free and sole reagent. The reactions were carried out in trifluoroethanol as solvent to access several *N*-substituted benzimidazoles with very high yields and in short reaction times.



Synthetic Methods

*Md Toufique Alam, Saikat Maiti and Prasenjit Mal**

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An Intramolecular C(sp²)-H Amidation by *N*-Iodosuccinimide