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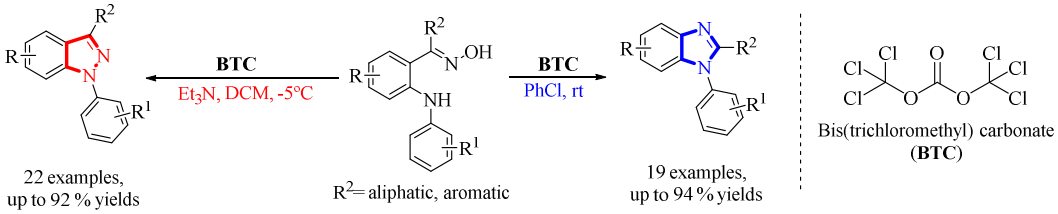
Graphic Abstract



mild conditions excellent chemoselectivity simple execution broad substrate scope

Divergent Strategy for the Chemoselective Synthesis of *N*-Arylbenzimidazoles and *N*-Arylindazoles from Arylamino Oximes

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Abstract

An efficient and divergent synthesis of *N*-arylbenzimidazoles and *N*-arylindazoles from arylamino oximes based on reaction conditions selection was developed. The synthesis was approached by treating oximes with BTC and the chemoselectivity was regulated by the amount of Et_3N. This switchable N−N and N−C bond formation process features mild reaction conditions, simple execution, high chemoselectivity and broad substrate scope.

Keywords: Divergent synthesis, Chemoselectivity, *N*-arylbenzimidazoles, *N*-arylindazoles, Bis(trichloromethyl)carbonate

1. Introduction

The isomeric *N*-arylbenzimidazoles and *N*-arylindazoles are ubiquitous in the realms of pharmacologically active agents and natural products.[1] For instance, molecules based on *N*-arylbenzimidazoles have attracted extensive attention due to their numerous pharmaceutically activities, including antifungal drugs,[2] NIMA-related kinase2 (Nek2) inhibitors, lymphocyte specific kinase (Lck) inhibitors, $GABA_A$ receptor agonists and the hepatitis C virus (HCV) NS5B polymerase inhibitors (Figure 1).[1a,3] *N*-arylbenzimidazoles have also been used as the backbone in dyes, polymers and ligands.[4] *N*-arylindazoles, the isomer of *N*-arylbenzimidazoles, also exhibited a broad spectrum of bioactivities, including heat shock protein 90 (HSP90) inhibitors, NF-κB inducing kinase (NIK) inhibitors, selective GPR120 agonists (Figure 1).[5] Given the importance of the class of heterocycles as biologically active substances has continued to inspire the pursuit of their general and efficient synthesis.

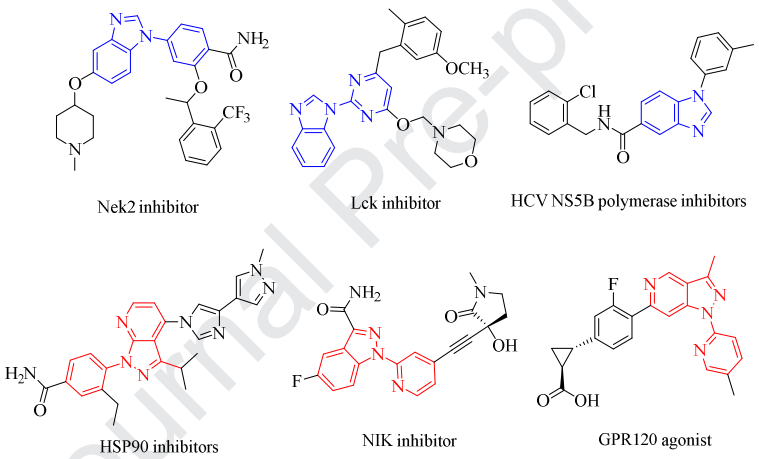
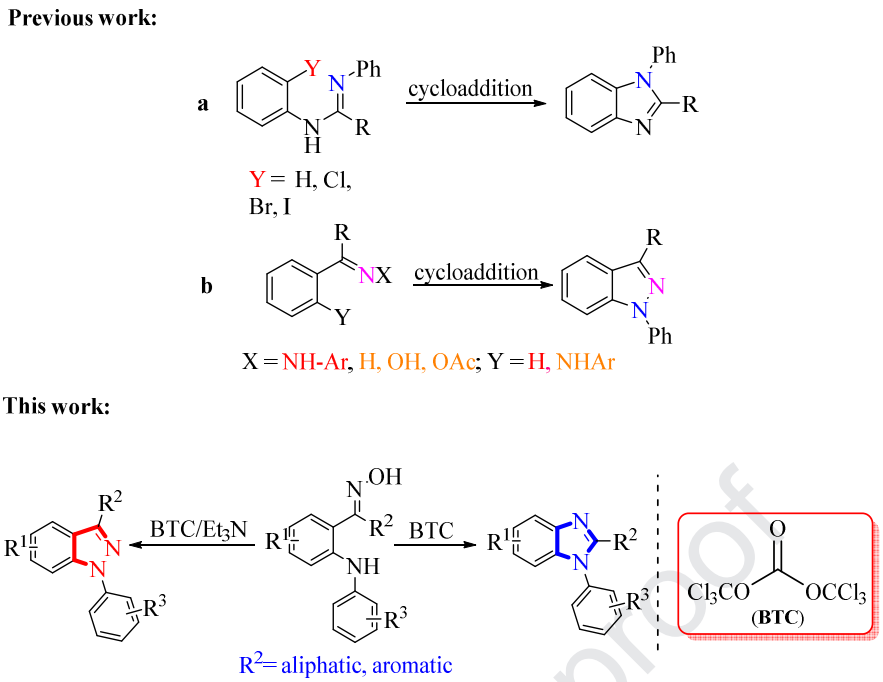


Figure 1. *N*-arylbenzimidazoles and indazoles as medicinal agents and biologically active compounds

Generally, *N*-arylbenzimidazoles were prepared through the condensation of *ortho*-substituted aniline derivatives with carbonyls under oxidative conditions or metal catalysis,[6] benzylamines[7] and benzylalcohols[8] were also employed as the substrates instead of the carbonyls. As an alternative, intramolecular cyclization of amidines is a straightforward method for the synthesis of *N*-arylbenzimidazole moiety (Scheme 1, a).[9] On the other hand, the synthetic methods of *N*-arylindazoles included (i) condensations of aryl hydrazines with *ortho*-halobenzoyl derivatives,[10] (ii) the 1,3-dipolar cycloadditions of benzynes with diazo compounds or aryl hydrazines,[11] (iii) intramolecular cyclizations of hydrazones,[12] N−H ketimines,[13] oximes and oxime derivatives (Scheme 1, b).[14]



Scheme 1 Synthesis of *N*-arylbenzimidazole or *N*-Arylindazoles via intramolecular cyclizations

Especially, oximes were a class of essential compounds in organic synthesis,[15] due to their easy preparation, efficient reactivity and harmless byproducts. Generally, they were widely employed in the construction of nitriles and amides.[16] Besides, they provided convenient methods to prepare functionalized *N*-containing heterocycles via S_N2 reaction,[17] radical cyclization,[18] and other routes.[19] In 2010, Stambuli and co-workers reported a method for the selectively produce *N*-arylindazoles and benzimidazoles from common arylamino oximes by using methanesulfonyl chloride and different base.[14a] Despite the advance, this processes still suffered some limitations, such as corrosive reagent, tedious procedures, limited in the substrate range. Thus, development of an operationally simple, tunable synthetic method for *N*-substituted benzimidazoles and indazoles from the same substrate has remained a challenging task.

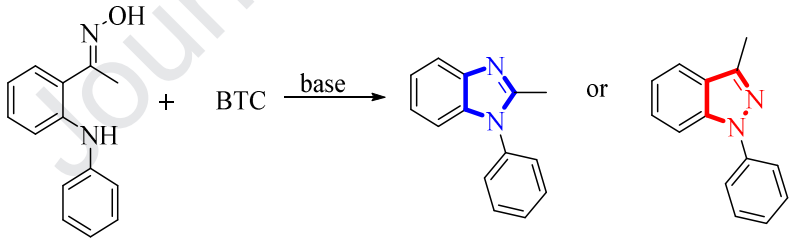
Bis(trichloromethyl)carbonate (BTC), also known as triphosgene or solid phosgene, has been considered as an easily handled alternative to highly toxic phosgene.[20] The reagent has been used in various situations, including chlorination, acylation, rearrangement and cyclization, *etc*.[21] As part of our ongoing research in developing the BTC system to synthesize biologically relevant heterocyclic compounds,[21d,22] we demonstrated herein an efficient protocol for the divergent synthesis of *N*-arylbenzimidazoles and *N*-arylindazoles from arylamino oximes mediated by BTC controlled by Et_3N with more substrate scope and providing moderate to excellent yields.

2. Results and Disscussion

Initially, we commenced our investigation by the model reaction of *N*-phenyl *o*-amino acetophenone oxime

(**2a**) with BTC/TPPO[14d,22a] which gave compounds **3a** and **4a** in 15% and 20% yields, respectively (Table 1, entry 1). Subsequently, we investigated different BTC systems in order to afford compound **3a** with a higher yield. The BTC/DMF system (Vilsmeier reagent)[21e] could not afford the desired result (Table 1, entry 2). To our delight, the *N*-Arylbenzimidazole **3a** was obtained in 73% yield with high chemoselectivity only mediated by BTC (Table 1, entry 3). Next, the yield of **3a** reached 88% when the molar ratio of **2a**: BTC was tuned to 1: 0.4 (Table 1, entries 4-6). The solvents and reaction temperature were also investigated (Table 1 entries 7-8),[23] the yield of **3a** improved to 94% with the optimal reaction conditions (Table 1, entry 8). Encouraged by the above results and with the optimal conditions of the *N*-arylbenzimidazole synthesis in hand, we turned our attention to select the appropriate reaction conditions which favor the formation of *N*-arylindazoles. Considering that Beckmann rearrangement (BR) reactions commonly catalyzed by acids, we explored whether the BR progress could be inhibited by the addition of bases.[14a] In further experimental research, we found that base and low temperature could favor the formation of *N*-arylindazoles **4a**. After investigated temperature, solvents and the molar ratio of **2a**: BTC: Et_3N, the yield of **4a** could reach 89% in DCM at -5 °C when the molar equivalent ratio of **2a**: BTC: Et_3N was 1: 0.75: 6 (Table 1, entries 9-14). Screening of other bases such as pyridine, DIPEA, DBU, DMAP, DABCO, Na_2CO_3 showed that Et_3N was the appropriate base for this reaction (Table 1, entries 15-20).

Table 1 Optimization of the reaction conditions[a,b]



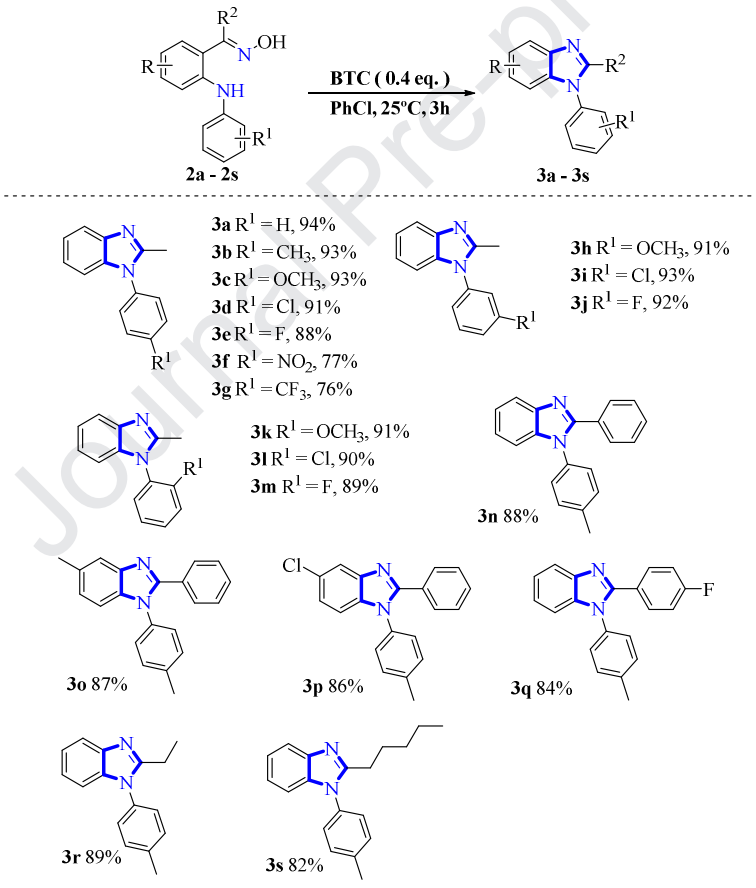
2a **3a** **4a**

entry	BTC system	BTC (eq.)[c]	Base (eq.)[c]	Solvent	T (°C)	3a Yield (%)[d]	4a Yield (%)[d]
1	BTC/TPPO[e]	0.33	/	DCE	25	15	20
2	BTC/DMF[f]	0.33	/	DCE	25	18	16
3	BTC	0.33	/	DCE	25	73	trace
4	BTC	0.35	/	DCE	25	75	trace
5	BTC	0.4	/	DCE	25	88	trace
6	BTC	0.5	/	DCE	25	88	trace
7	BTC	0.4	/	DCM	25	85	trace
8	***BTC***	***0.4***	***/***	***PhCl***	***25***	***94***	***trace***
9	BTC	0.5	Et_3N (5.5)	DCM	25	30	65
10	BTC	0.5	Et_3N	DCM	25	27	67

11	***BTC***	***0.75***	***Et_3N***	***DCM***	***-5***	***trace***	***89***
12	BTC	1	Et_3N	DCM	-10	trace	87
13	BTC	0.75	Et_3N	PhCl	-10	32	70
14	BTC	0.75	Et_3N (7)	DCM	-5	trace	84
15	BTC	0.75	Pyridine	DCM	-5	45	trace
16	BTC	0.75	DIPEA	DCM	-5	50	trace
17	BTC	0.75	DBU	DCM	-5	55	trace
18	BTC	0.75	DMAP	DCM	-5	0	0
19	BTC	0.75	DABCO	DCM	-5	46	trace
20	BTC	0.75	Na_2CO_3	DCM	-5	34	30

[a]Unless otherwise specified, the reaction conditions: **2a** (0.5 mmol, 1eq.), BTC (x mmol, x eq.), base (3 mmol, 6 eq.) and solvent (8 or 10 ml), 3h. [b] BTC is short for bis(trichloromethyl)carbonate, TPPO is short for triphenylphosphine oxide. [c]molar equivalent ratio [d]Isolated yields based on 2a. [e]the molar equivalent ratio of BTC:TPPO =1: 3. [f]the molar equivalent ratio of BTC:DMF=1: 3

Table 2 Synthesis of *N*-arylbenzimidazole 3 from oxime 2[a, b]

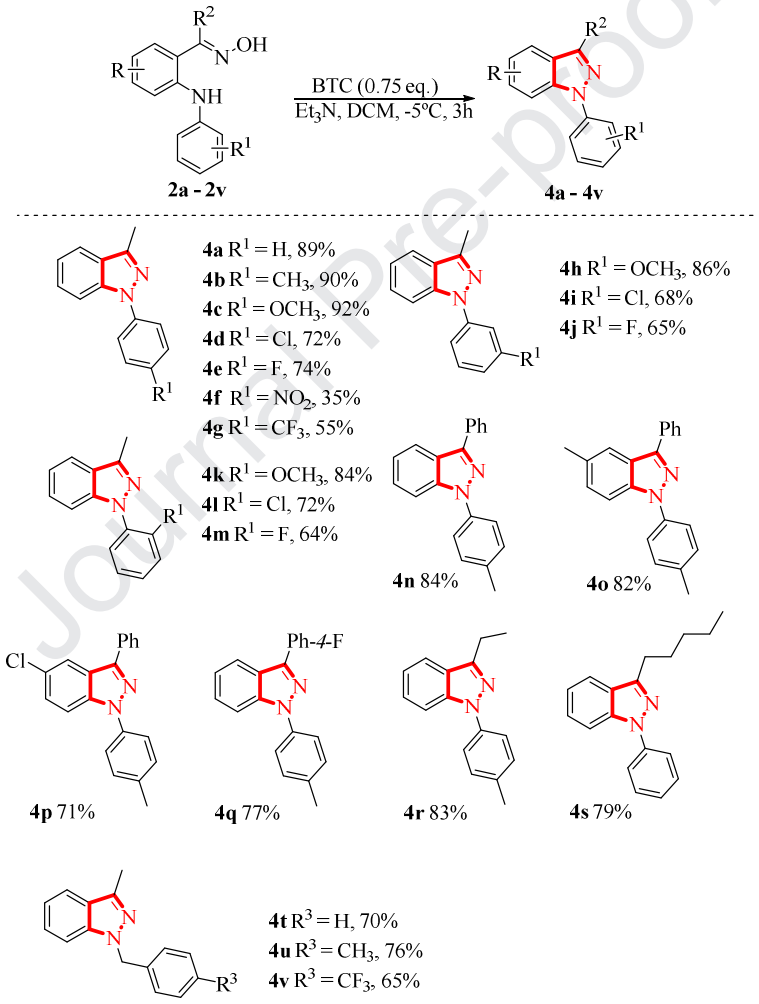


[a]Reaction conditions A: **2** (0.5 mmol, 1 eq.), BTC (0.2 mmol, 0.4 eq.), PhCl (8 ml), 25 °C for 3 h. [b]Isolated yield based on compound **2**.

Subsequent work was to investigate the substrate scopes of this method to synthesize *N*-arylbenzimidazoles **3** under the optimized conditions (Table 2). Satisfactorily, the substituents on the *N*-substituted arenes had no significant effect on the reaction and afforded the products in good to excellent yields of 74% to 94% including

electron-withdrawing or electron-donating groups (Table 2, **3a**-**3m**). Among them, the yields of **3f** and **3g** decreased slightly. The lower yields might be caused by electron-withdrawing groups reduced the nucleophilic ability of the amino group. The R^2 groups including aryl or aliphatic groups on oximes **2** also worked well resulting in a slight decrease in yields due to steric hindrance but still affording the products in good yields of 82% to 89% (Table 2, **3n**-**3s**). Unfortunately, the reaction results of *N*-benzyl-*o*-aminoacetophenone oxime and *N*-methyl-*o*-aminoacetophenone oxime were complicated and did not afford the products, which indicated that the alkyl group and benzyl group might not be suitable for this position in this method.

Table 3 Synthesis of N-Arylindazoles 4 from oxime 2[a, b]

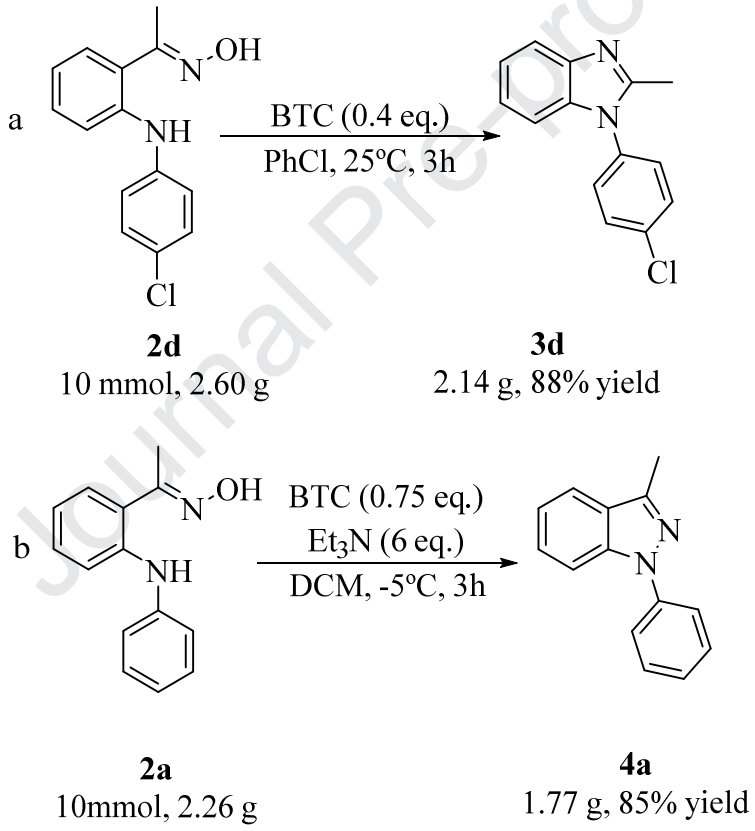


[a]Reaction conditions B: **2** (0.5 mmol, 1 eq.), BTC (0.375 mmol, 0.75 eq.), Et_3N (3 mmol, 6 eq.), DCM (10 ml) at -5 °C for 3 h. [b]Isolated yield based on **2**.

Next, we investigated the selective formation of *N*-arylindazoles **4** using the optimized condition (Table 3). Medium yields were obtained for the substrates that contained arenes with electron-donating groups at the *para*, *meta* or *ortho* positions (Table 3, **4a**-**4c**, **4h**, **4k**). However, lower yields of indazoles were obtained with the

N-substituted arenes including electron-withdrawing substituents (Table 3, **4d**-**4g**, **4i**-**4j**, **4l**-**4m**), this might be caused by the electronics of the group attached to the arene. When the R^2 groups were aryl or aliphatic groups on oximes **2**, the yields decreased slightly due to steric hindrance (Table 3, **4n**-**4s**). Interestingly, *N*-benzyl-*o*-aminoacetophenone oxime (Table 3, **2t**-**2v**) afforded the corresponding products with moderate yields of 70%, 76% and 65%, respectively. However, *N*-methyl-*o*-aminoacetophenone oxime still failed in the tests.

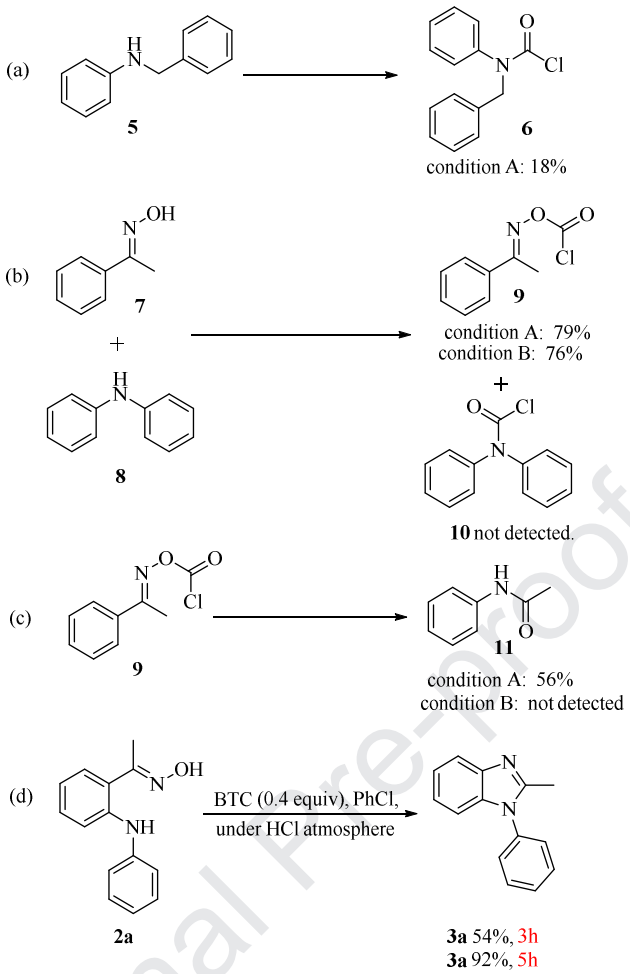
In order to demonstrate the utility of this method, several larger scale reactions were conducted, as shown in scheme 2. To our delight, the method exhibited good stability. When the oxime **2d** was magnified to 10 mmol (2.60 g), the product **3d** still afforded in 2.14 g, 88% isolated yield (Scheme 2a). And the oxime **2a** was magnified to 10 mmol (2.26 g), the product **4a** afforded in 1.77 g, 85% isolated yield (Scheme 2b).



Scheme 2 Larger Scale Reaction

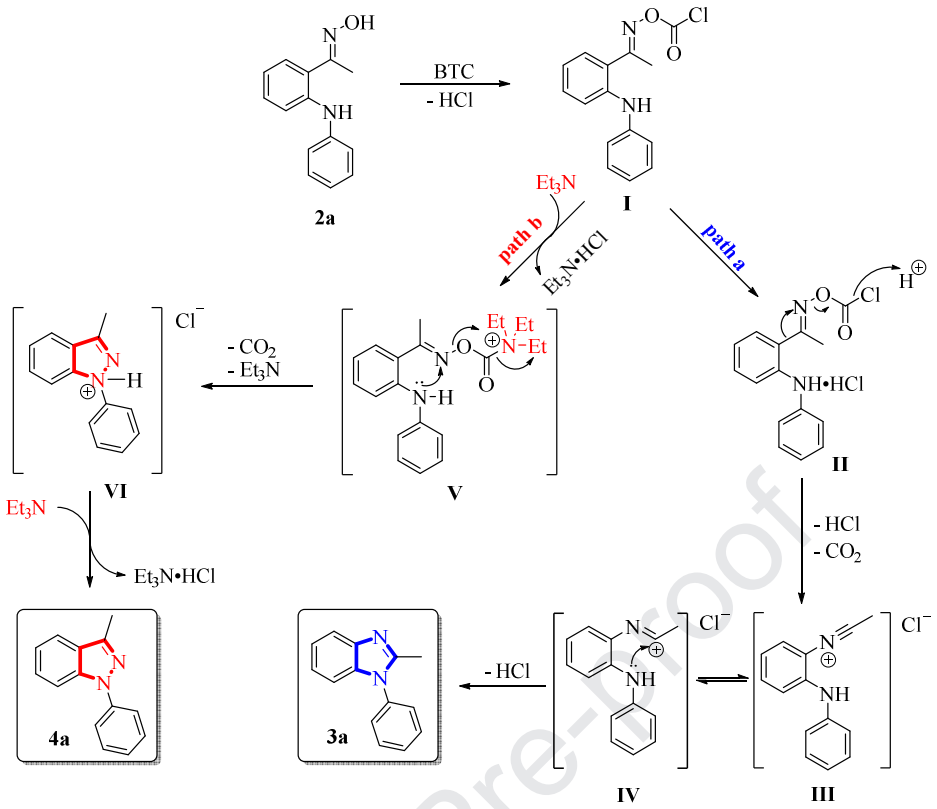
The inconsonant experimental results of *N*-alkyl-*o*-aminoacetophenone oxime (**2t**-**2v**) and *N*-aryls-*o*-aminoacetophenone oxime (**2a**-**2s**) have attracted our attention. Generally, the nucleophilicity of *N*-alkyl motifs is stronger than *N*-aryls according to the delocalization of electrons in the *N*-aryls structure. We speculate that the difference nucleophilicity of amino between *N*-alkyl-*o*-aminoacetophenone oxime (**2t**-**2v**) and *N*-aryls-*o*-aminoacetophenone oxime (**2a**-**2s**) led to different experimental results. The experiments (a) was

performed under condition A, the results were complicated and compound **6** was detected. These results indicated that due to the stronger nucleophilicity of *N*-alkyl motifs, the *N*-alkyl-*o*-aminoacetophenone oxime may reacted with BTC, which resulted in no target product generation in standard condition A (Scheme 3, a). In order to get an insight view into the reaction mechanism, several control experiments were conducted (Scheme 3). First, a competitive experiment (b) was carried out under both reaction conditions A and B. Oxime **7** could be converted into product **9** in 79% and 76% yields, respectively, while the compound **8** wa**s** not reacted with BTC and compound **10** was not detected. This result indicated that the reactivity of *N*-OH was higher than the secondary amine group. Next, the experiments (c) were performed under reaction conditions A and B. The acetanilide **11** was isolated in 56% via Beckmann rearrangement under the condition A, however **11** was not produced under condition B (Scheme 3, c). These results indicated that the compound **9** derivatives might be an important intermediate for the reaction and the Beckmann rearrangement could be inhibited with the presence of Et_3N. Finally, we carried out the template reaction under HCl atmosphere for 3h and 5h, the desired product **3a** was isolated in 54% and 92%, respectively. These results revealed that HCl partial inhibited the nucleophilicity of the amino group in the reaction (Scheme 3, d).



Scheme 3 Control experiments

Based on the above results and the literature reports,[14a,21d,24] a plausible reaction mechanism was proposed, which was elucidated in Scheme 4 using **2a** as a typical example. Initially, the oxime **2a** reacted with BTC led to intermediate **I**. Then, two pathways are possible for the following steps. In one case (path a), intermediate **I** reacted with a small amount of HCl in the reaction system to form intermediate **II**. The hydrochloride decreased the nucleophilicity of the secondary amino group and simultaneously promoted Beckmann rearrangement to form intermediate **IV**. Finally, *N*-arylbenzimidazole **3a** was obtained by an intramolecular aza-cyclization of intermediate **IV**. On the other case (Path b), the addition of Et_3N neutralized the HCl and inhibiting the Beckmann rearrangement. In addition, the Et_3N served as a nucleophilic promoter to the intermediate **I**,[21b,21f] thereby enabling a dominant intramolecular nucleophilic substitution reaction under Et_3N condition afforded *N*-arylindazoles **4a**.



Scheme 4 Proposed mechanism

3. Conclusion

In summary, an efficient and divergent synthesis of *N*-arylbenzimidazoles and *N*-arylindazoles has been developed from arylamino oximes based on reaction conditions selection. Thus, a series of *N*-arylbenzimidazoles were synthesized via sequential Beckmann rearrangement and intramolecular aza-cyclization under BTC conditions. *N*-arylindazoles were obtained via intramolecular nucleophilic substitution reactions by the addition of Et_3N. This switchable N−N and N−C bond formation process features mild reaction conditions, simple execution, high chemoselectivity and broad substrate scope. Further investigations on applying this methodology for preparation of other heterocycles are underway in our lab.

4. Experimental

4.1 General Methods

Synthetic reagents were purchased from Aladdin and used without further purification unless otherwise indicated. ***Caution!*** BTC will release phosgene in a moist environment, especially at elevated temperatures; it is highly not recommended to add BTC over 80°C. Analytical TLC (thin-layer chromatography) was performed with 0.25 mm silica gel G with a 254 nm fluorescent indicator. Melting points (m.p.) were obtained on a digital melting point apparatus and uncorrected. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Brüker (400 MHz & 101 MHz &

376 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$, DMSO-d_6 or tetramethylsilane as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. Infrared (IR) data were recorded as films on potassium bromide plates on a NICOLET iS50 FT-IR spectrometer. EI-MS were recorded on a ThermoFisher ITQ1100 Ion Trap Mass Spectrometer. High-resolution mass spectra (HRMS) were obtained on a Brüker mass spectrometer (ESI). Purification of products was accomplished by column chromatography on silica gel.

4.1.1 General Procedure for Aryl Amination

To a round-bottom flask equipped with a reflux condenser and a magnetic bar were added Aminoacetophenone (5 mmol, 1 eq.), the corresponding halide (7.5 mmol, 1.5 eq.), K_2CO_3 (6.25 mmol, 1.25 eq.), and Cu (15 mol%) were suspended in PhCl (8 mL) and heated to reflux for 24 h and then cooled to room temperature. Water (15 mL) was added and the reaction was extracted with EtOAc (15 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified via flash chromatography (0-5% EtOAc/hexanes).

1a–**1m** were prepared using known literture protocol and in agreement with the reported data.[14a]

Phenyl(2-(p-tolylamino)phenyl)methanone (1n) : yellow oil, (1.034 g, 71%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.68 (s, 1H), 7.67–7.56 (m, 3H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.45–7.37 (m, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.13 (t, *J* = 8.3 Hz, 4H), 6.77 (t, *J* = 7.5 Hz, 1H), 2.27 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 198.0, 147.0, 139.0, 137.8, 134.2, 133.9, 132.2, 131.6, 129.8, 129.0, 128.2, 121.5, 120.3, 117.1, 114.7, 20.4. **HRMS** (ESI) m/z $[M + H]^+$ calcd for $C_{20}H_{17}NO$ 288.1383, found 288.1391.

(5-Methyl-2-(p-tolylamino)phenyl)(phenyl)methanone (1o) : yellow oil, (1.170 g, 82%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.33 (s, 1H), 7.67–7.56 (m, 3H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.28–7.18 (m, 3H), 7.08 (q, *J* = 8.3 Hz, 4H), 2.25 (s, 3H), 2.18 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 197.8, 144.2, 138.8, 138.6, 134.9, 133.2, 131.7, 131.3, 129.8, 129.0, 128.3, 126.3, 121.4, 120.4, 115.8, 20.3, 20.0. **HRMS** (ESI): calcd for $C_{21}H_{19}NO$ $[M + H]^+$ 302.1539, found 302.1546.

***(5-Chloro-2-(p-tolylamino)phenyl)(phenyl)methanone (1p)*:** yellow oil, (0.917 g, 66%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.37 (s, 1H), 7.68–7.59 (m, 3H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.42 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.34 (d, *J* = 2.5 Hz, 1H), 7.21 (d, *J* = 9.0 Hz, 1H), 7.10 (q, *J* = 8.4 Hz, 4H), 2.26 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ

196.6, 145.4, 138.1, 137.8, 133.6, 132.4, 132.1, 132.05, 129.9, 129.0, 128.4, 122.3, 121.4, 120.5, 117.2, 20.4. **HRMS** (ESI): calcd for $C_{20}H_{16}ClNO$ $[M + H]^+$ 322.0993, found 322.0984.

***(4-Fluorophenyl)(2-(p-tolylamino)phenyl)methanone (1q)*:** yellow oil, (1.210 g, 85%).**^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.47 (s, 1H), 7.72 (dd, *J* = 8.3, 5.7 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.11 (q, *J* = 8.4 Hz, 4H), 6.80 (t, *J* = 7.5 Hz, 1H), 2.26 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 197.0, 164.6 (d, *J* = 250.1 Hz), 147.1, 138.6, 135.8 (d, *J* = 2.7 Hz), 134.6, 134.0, 132.5, 132.37 (d, *J* = 9.1 Hz), 130.3, 121.7, 121.3, 117.9, 115.8 (d, *J* = 21.9 Hz), 115.6, 20.9, **^{19}F NMR** (376 MHz, DMSO-d_6) δ -107.79 (m). **HRMS** (ESI): calcd for $C_{20}H_{16}FNO$ $[M + H]^+$ 306.1289, found 306.1297.

***1-(2-(p-Tolylamino)phenyl)propan-1-one (1r)*:** dark yellow oil, (0.910 g, 81%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.39 (s, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.21–7.09 (m, 5H), 6.76 (t, *J* = 7.5 Hz, 1H), 3.06 (q, *J* = 7.2 Hz, 2H), 2.28 (s, 3H), 1.10 (t, *J* = 7.2 Hz, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 203.8, 147.0, 137.4, 134.4, 132.8, 131.9, 129.9, 122.4, 118.4, 116.7, 113.7, 32.0, 20.4, 8.6. **HRMS** (ESI): calcd for $C_{16}H_{17}NO$ $[M + H]^+$ 240.1383, found 240.1397.

4.1.2 General Procedure for the Synthesis of Oximes

Method A. To a round-bottom flask equipped with a reflux condenser and a magnetic bar were added the ketone (1 mmol, 1 eq.), hydroxylamine hydrochloride (3 mmol, 3 eq.) and NaOH (6 mmol, 6 eq.), H_2O (3mL), EtOH (10 mL). The reaction was allowed to stir at 75 °C until complete consumption of the starting material was observed by TLC. The bulk of the ethanol was removed in vacuo and water was added. The crude product was extracted with EtOAc (3 × 15 mL), dried over Na_2SO_4 and concentrated. The crude oxime was purified via flash chromatography (0-20% EtOAc/hexanes).

Method B. To a round-bottom flask equipped with a reflux condenser and a magnetic bar were added the ketone (1 mmol, 1 eq.), hydroxylamine hydrochloride (3 mmol, 3 eq.) and pyridine (11 mmol, 11 eq.) were added to methanol (8 mL). The reaction was heated at reflux until complete consumption of the starting material was observed by TLC. The reaction was concentrated in vacuo, dissolved in EtOAc (10 mL), washed twice with water (2 × 20mL), dried over Na_2SO_4 and concentrated. The crude oxime was purified via flash chromatography (0-20% EtOAc/hexanes).

2a – **2m** were prepared using known literture protocol and in agreement with the reported data.[14a]

***(E)-Phenyl(2-(p-tolylamino)phenyl)methanone oxime (2n)*:** yellow oil, (0.330 g, 23%). **^{1}H NMR** (400 MHz,

DMSO-d_6) δ 11.68 (s, 1H), 7.45–7.39 (m, 2H), 7.36–7.24 (m, 5H), 7.04 (d, *J* = 7.4 Hz, 1H), 7.01–6.92 (m, 3H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.67 (s, 1H), 2.19 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 154.5, 141.6, 141.0, 136.4, 130.0, 129.5, 129.2, 128.9, 128.8, 128.2, 126.8, 124.6, 120.3, 117.9, 117.8, 20.2. **HRMS** (ESI): calcd for $C_{20}H_{18}N_2O$ $[M + H]^+$ 303.1492, found 303.1498.

***(E)-(5-Methyl-2-(p-tolylamino)phenyl)(phenyl)methanone oxime (2o)*:** yellow oil, (0.370 g, 30%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.64 (s, 1H), 7.41 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.34–7.28 (m, 3H), 7.19 (d, *J* = 8.3 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.87–6.78 (m, 3H), 6.53 (s, 1H), 2.24 (s, 3H), 2.17 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 154.6, 141.8, 139.0, 136.5, 130.1, 129.9, 129.7, 129.4, 128.8, 128.2, 128.1, 126.8, 125.5, 119.2, 116.9, 20.2. **HRMS** (ESI): calcd for $C_{21}H_{20}N_2O$ $[M + H]^+$ 317.1648, found 317.1654.

***(E)-(5-Chloro-2-(p-tolylamino)phenyl)(phenyl)methanone oxime (2p)*:** yellow oil, (0.280 g, 29%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.73 (s, 1H), 7.43–7.38 (m, 2H), 7.35–7.29 (m, 4H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.82 (s, 1H), 2.19 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 153.0, 140.9, 140.5, 135.7, 129.6, 129.4, 129.3, 129.1, 129.0, 128.3, 126.6, 125.7, 123.3, 119.2, 118.5, 20.3. **HRMS** (ESI): calcd for $C_{20}H_{17}ClN_2O$ $[M + H]^+$ 337.1102, found 337.1114.

***(E)-(4-Fluorophenyl)(2-(p-tolylamino)phenyl)methanone oxime (2q)*:** bright yellow oil, (0.320 g, 25%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.67 (s, 1H), 7.46–7.38 (m, 2H), 7.28 (dt, *J* = 16.0, 8.0 Hz, 2H), 7.14 (t, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 7.4 Hz, 1H), 7.01-6.92 (m, 3H), 6.85 (d, *J* = 8.2 Hz, 2H), 6.73 (s, 1H), 2.19 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 163.0 (d, *J* = 246.0 Hz), 154.0, 142.1, 141.5, 133.4 (d, *J* = 2.8 Hz), 130.6, 129.9, 129.9, 129.4, 129.3 (d, *J* = 8.4 Hz), 124.8, 120.8, 118.6, 118.4, 115.6 (d, *J* = 21.7 Hz), 20.7, **^{19}F NMR** (376 MHz, DMSO-d_6) δ -112.90 (m). **HRMS** (ESI): calcd for $C_{20}H_{17}FN_2O$ $[M + H]^+$ 321.1398, found 321.1405.

***(E)-1-(2-(p-Tolylamino)phenyl)propan-1-one oxime (2r)*:** yellow oil, (0.738 g, 76%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.20 (s, 1H), 9.28 (s, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.21-7.13 (m, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 6.86-6.80 (m, 1H), 2.76 (q, *J* = 7.5 Hz, 2H), 2.25 (s, 3H), 1.06 (t, *J* = 7.5 Hz, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 160.5, 142.9, 139.6, 130.5, 129.7, 129.1, 128.9, 120.8, 119.9, 118.4, 115.4, 20.3, 19.4, 11.0. **HRMS** (ESI): calcd for $C_{16}H_{18}N_2O$ $[M + H]^+$ 255.1492, found 255.1506.

***(E)-1-(2-(Benzylamino)phenyl)ethan-1-one oxime (2t)* :** yellow oil, (0.460 g, 69%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.12 (s, 1H), 8.18 (t, *J* = 5.5 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 4.3 Hz, 4H), 7.28-7.21 (m,

1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.66–6.57 (m, 2H), 4.42 (d, *J* = 5.8 Hz, 2H), 2.24 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.4, 146.4, 139.6, 129.2, 128.8, 128.5, 126.9, 126.8, 118.4, 115.0, 46.4, 12.3. **HRMS** (ESI): calcd for $C_{15}H_{16}N_2O$ $[M + H]^+$ 241.1335, found 241.1329.

***(E)-1-(2-((4-Methylbenzyl)amino)phenyl)ethan-1-one oxime (2u)*:** yellow oil, (0.370 g, 64%). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.09 (s, 1H), 8.12 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.64-6.57 (m, 2H), 4.35 (s, 2H), 2.27 (s, 3H), 2.23 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.9, 146.9, 137.0, 136.3, 129.7, 129.5, 129.2, 127.4, 118.8, 115.4, 111.4, 46.7, 21.1, 12.8. **HRMS** (ESI): calcd for $C_{16}H_{18}N_2O$ $[M + H]^+$ 255.1492, found 255.1505.

***(E)-1-(2-((4-(Trifluoromethyl)benzyl)amino)phenyl)ethan-1-one oxime (2v)*:** yellow oil, (0.360 g, 61%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.23–11.10 (m, 1H), 8.30 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.63 (t, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 8.3 Hz, 1H), 4.54 (s, 2H), 2.26 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 156.4, 146.2, 144.9, 129.2, 128.8, 127.5 (q, *J* = 31.31 Hz), 127.5, 125.3 (q, *J* = 3.03 Hz), 124.4 (q, *J* = 272.7 Hz), 118.6, 115.3, 110.9, 45.9, 12.3. **HRMS** (ESI): calcd for $C_{16}H_{15}F_3N_2O$ $[M + H]^+$ 309.1209, found 309.1221.

4.1.3 General Procedure for the Synthesis of N-ArylBenzimidazoles (Reaction conditions A)

To a round-bottom flask equipped with a reflux condenser and a magnetic bar were added the BTC (0.2 mmol, 0.4 eq.) PhCl (4 mL). The reaction was stirred at ambient temperature for 15 min, then a solution of Oxime 1 (0.5 mmol, 1 eq.) in PhCl (4 mL) was added slowly and the reaction was keep in ambient temperature for 3 h unless otherwise stated. Then, the mixture was quenched by saturated $NaHCO_3$ solution and extracted with CH_2Cl_2 (10 mL x 3). The combined organic phase was dried over Na_2SO_4 and filtered. After evaporation of the solvents, the residue was purified by silica gel chromatography (20% EtOAc/hexanes) to afford *N*-Arylbenzimidazole **3**.

2-Methyl-1-phenyl-1H-benzo[d]imidazole (3a) [25]**:** yellow solid, (0.098 g, 94%), m.p. 49.2~50.8°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 5.8 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 2.53 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6, 142.7, 136.6, 136.2, 130.0, 128.9, 127.2, 122.7, 122.5, 119.1, 110.0, 14.5. **HRMS** (ESI): calcd for $C_{14}H_{12}N_2$ $[M + H]^+$ 209.1073, found 209.1085.

2-Methyl-1-(p-tolyl)-1H-benzo[d]imidazole (3b) [26]**:** yellow solid, (0.105 g, 93%), m.p. 89.5~90.7°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.30-7.23 (m, 3H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.12

(d, *J* = 7.9 Hz, 1H), 2.51 (s, 3H), 2.48 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.6, 142.6, 138.8, 136.6, 133.4, 130.5, 126.8, 122.4, 122.2, 118.9, 109.9, 21.2, 14.4. **HRMS** (ESI): calcd for $C_{15}H_{14}N_2$ $[M + H]^+$ 223.1229, found 223.1235.

1-(4-Methoxyphenyl)-2-methyl-1H-benzo[d]imidazole (3c)[27]**:** tan solid, (0.111 g, 93%), m.p. 121.7~122.8°C.**^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.21-7.13 (m, 4H), 7.06 (d, *J* = 7.5 Hz, 1H), 3.85 (s, 3H), 2.39 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 159.2, 151.6, 142.3, 136.4, 128.2, 128.1, 122.1, 121.7, 118.4, 115.1, 109.7, 55.5, 14.0. **HRMS** (ESI): calcd for $C_{15}H_{14}N_2O$ $[M + H]^+$ 239.1178, found 239.1081.

1-(4-Chlorophenyl)-2-methyl-1H-benzo[d]imidazole (3d)[28]**:** yellow solid, (0.111 g, 91%), m.p. 99.3~100.5°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 2.47 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.4, 142.7, 136.4, 134.9, 134.7, 130.3, 128.5, 122.9, 122.7, 119.2, 109.8, 14.5. **HRMS** (ESI): calcd for $C_{14}H_{11}ClN_2$ $[M + H]^+$ 243.0683, found 243.0691.

1-(4-Fluorophenyl)-2-methyl-1H-benzo[d]imidazole (3e)**:** tan solid, (0.099 g, 88%), m.p. 78.4~79.6°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.35-7.31 (m, 2H), 7.27–7.23 (m, 3H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 2.47 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 249.5 Hz), 151.6, 142.6, 136.6, 132.1 (d, *J* = 2.9 Hz), 129.0 (d, *J* = 8.7 Hz), 122.8, 122.6, 119.1, 117.0 (d, *J* = 22.9 Hz), 109.8, 14.4, **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.74 (m). HRMS (ESI): calcd for $C_{14}H_{11}FN_2$ $[M + H]^+$ 227.0979, found 227.0982.

2-Methyl-1-(4-nitrophenyl)-1H-benzo[d]imidazole (3f)**:** brown oil, (0.098 g, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 2.57 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.8, 147.5, 142.8, 141.8, 135.7, 127.7, 125.6, 123.5, 123.4, 119.6, 109.7, 14.8. **HRMS** (ESI): calcd for $C_{14}H_{11}N_3O_2$ $[M + H]^+$ 254.0924, found 254.0932.

2-Methyl-1-(4-(trifluoromethyl)phenyl)-1H-benzo[d]imidazole (3g)**:** colorless oil, (0.105g, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.29 (t, *J* = 6 Hz 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 2.53 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.1, 142.8, 139.4, 136.1, 131.0 (q, *J* = 33.4 Hz), 127.5,127.3 (q, *J* = 3.0 Hz) 123.7 (q, *J* = 272.7 Hz),123.1, 122.9, 119.4, 109.7, 14.6,

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.58. **HRMS** (ESI): calcd for $C_{15}H_{11}F_3N_2$ $[M + H]^+$ 277.0947, found 277.0952.

1-(3-Methoxyphenyl)-2-methyl-1H-benzo[d]imidazole (3h)[29]**:** yellow solid, (0.109g, 91%), m.p. 131.8~132.9°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 8.1 Hz, 1H), 7.37-7.33 (m, 1H), 7.31-7.24 (m, 2H), 7.15–7.13 (m, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 7.00-6.98 (m, 1H), 3.95 (s, 3H), 2.62 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.8, 151.5, 142.6, 137.2, 136.5, 130.7, 122.6, 122.4, 119.3, 119.0, 114.4, 113.0, 110.1, 55.6, 14.5. **HRMS** (ESI): calcd for $C_{15}H_{14}N_2O$ $[M + H]^+$ 239.1178, found 239.1186.

1-(3-Chlorophenyl)-2-methyl-1H-benzo[d]imidazole (3i)[26]**:** yellow solid, (0.113 g, 93%), m.p. 165.3-166.4°C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.74 (s, 1H), 7.69-7.62 (m, 3H), 7.54 (d, *J* = 6.8 Hz, 1H), 7.24–7.19 (m, 2H), 7.15 (t, *J* = 7.8 Hz, 1H), 2.44 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 151.2, 142.3, 137.0, 135.8, 134.1, 131.5, 128.8, 127.0, 125.9, 122.5, 122.1, 118.5, 109.7, 14.1. **HRMS** (ESI): calcd for $C_{14}H_{11}ClN_2$ $[M + H]^+$ 243.0683, found 243.0694.

1-(3-Fluorophenyl)-2-methyl-1H-benzo[d]imidazole (3j)**:** yellow solid, (0.104 g, 92%), m.p. 127.4~128.7°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.55 (q, *J* = 8.0 Hz, 1H), 7.29-7.17 (m, 4H), 7.16–7.09 (m, 2H), 2.52 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1 (d, *J* = 249.7 Hz), 151.2, 142.6, 137.5 (d, *J* = 9.7 Hz), 136.2, 131.2 (d, *J* = 9.1 Hz), 122.9, 122.9, 122.7, 119.2, 116.0 (d, *J* = 21.0 Hz), 114.6 (d, *J* = 23.0 Hz), 109.8, 14.4, **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.80 (m). **HRMS** (ESI): calcd for $C_{14}H_{11}FN_2$ $[M + H]^+$ 227.0979, found 227.0985.

1-(2-Methoxyphenyl)-2-methyl-1H-benzo[d]imidazole (3k)[26]**:** yellow solid, (0.109 g, 91%), m.p. 123.3~124.9°C.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.52–7.45 (m, 1H), 7.29 (d, *J* = 6.8 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.17-7.10 (m, 3H), 6.98 (d, *J* = 8.0 Hz, 1H), 3.73 (s, 3H), 2.41 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.3, 152.8, 142.8, 136.8, 130.7, 129.3, 124.5, 122.3, 122.1, 121.2, 118.9, 112.5, 110.0, 55.7, 14.0. **HRMS** (ESI): calcd for $C_{15}H_{14}N_2O$ $[M + H]^+$ 239.1179, found 239.1184.

1-(2-Chlorophenyl)-2-methyl-1H-benzo[d]imidazole (3l)[26]**:** yellow solid, (0.110 g, 90%),m.p. 72.8~73.6°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.68–7.61 (m, 1H), 7.54–7.44 (m, 2H), 7.42–7.36 (m, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 2.43 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 142.8, 136.3, 133.8, 133.3, 131.1, 130.9, 130.1, 128.3, 122.8, 122.6, 119.2, 109.9, 14.1. **HRMS** (ESI): calcd for $C_{14}H_{11}ClN_2$ $[M + H]^+$ 243.0683, found 243.0692

***1-(2-Fluorophenyl)-2-methyl-1H-benzo[d]imidazole (3m)*:** brown oil, (0.101 g, 89%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.54–7.49 (m, 1H), 7.42-7.38 (m, 1H), 7.36-7.32 (m, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 2.48 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.7 (d, *J* = 252.6 Hz), 152.0, 142.8, 136.3, 130.9 (d, *J* = 7.7 Hz), 129.4, 125.2 (d, *J* = 3.9 Hz), 123.8 (d, *J* = 13.0 Hz), 122.8, 122.5, 119.1, 117.3 (d, *J* = 19.6 Hz), 109.7, 13.9, **^{19}F NMR** (376 MHz, $CDCl_3$) δ -120.21(m). **HRMS** (ESI): calcd for $C_{14}H_{11}FN_2$ $[M + H]^+$ 227.0979, found 227.0984.

***2-Phenyl-1-(p-tolyl)-1H-benzo[d]imidazole (3n)*:** yellow oil, (0.126 g, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.0 Hz, 2H), 7.39-7.28 (m, 8H), 7.23 (d, *J* = 8.1 Hz, 2H), 2.48 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.5, 143.1, 138.7, 137.5, 134.5, 130.6, 130.2, 129.6, 129.5, 128.4, 127.3, 123.3, 123.0, 119.9, 110.6, 21.4. IR (neat) $\tilde{\nu}$ = 1608, 1514 cm^{-1}. **HRMS** (ESI): calcd for $C_{20}H_{16}N_2$ $[M + H]^+$ 285.1386, found 285.1391.

***5-Methyl-2-phenyl-1-(p-tolyl)-1H-benzo[d]imidazole (3o)*:** yellow solid, (0.130 g, 87%), m.p. 152.3~154.7°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.55 (d, *J* = 7.1 Hz, 2H), 7.32-7.28 (m, 2H), 7.25–7.22 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.06 (q, *J* = 8.3 Hz, 2H), 2.48 (s, 3H), 2.40 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.4, 143.4, 138.5, 135.6, 134.6, 132.7, 130.5, 130.3, 129.5, 129.4, 128.3, 127.2, 124.8, 119.6, 110.1, 21.7, 21.3. IR (neat) $\tilde{\nu}$ = 1616, 1515 cm^{-1}. **HRMS** (ESI): calcd for $C_{21}H_{18}N_2$ $[M + H]^+$ 299.1543, found 299.1547.

***5-Chloro-2-phenyl-1-(p-tolyl)-1H-benzo[d]imidazole (3p)*:** yellow solid, (0.138 g, 86%), m.p. 144.8~145.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89–7.85 (m, 1H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.40-7.29 (m, 5H), 7.24-7.13 (m, 4H), 2.47 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.7, 143.8, 139.0, 136.2, 134.1, 130.7, 129.8, 129.7, 129.5, 128.5, 128.5, 127.1, 123.7, 119.6, 111.4, 21.4. IR (neat) $\tilde{\nu}$ = 1611, 1506 cm^{-1}. **HRMS** (ESI): calcd for $C_{20}H_{15}ClN_2$ $[M + H]^+$ 319.0997, found 319.1024

***2-(4-Fluorophenyl)-1-(p-tolyl)-1H-benzo[d]imidazole (3q)*:** yellow oil, (0.127 g, 84%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0, Hz,1H), 7.58 (dd, *J* = 8.2, 5.6 Hz, 2H), 7.35-7.27 (m, 3H), 7.26–7.23 (m, 2H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.00 (t, *J* = 8.5 Hz, 2H), 2.45 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.4 (d, *J* = 250.4 Hz), 151.5, 142.9, 138.8, 137.4, 134.2, 131.4 (d, *J* = 8.4 Hz), 130.6, 127.2, 126.3 (d, *J* = 3.1 Hz), 123.3, 123.0, 119.8, 115.5 (d, *J* = 21.8 Hz), 110.5, 21.3, **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.86 (m). IR (neat) $\tilde{\nu}$ = 1608, 1507 cm^{-1}. **HRMS** (ESI): calcd for $C_{20}H_{15}FN_2$ $[M + H]^+$ 303.1292, found 303.1325

***2-Ethyl-1-(p-tolyl)-1H-benzo[d]imidazole (3r)*:** yellow oil, (0.104 g, 89%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.27-7.22 (m, 3H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 2.79 (q, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.34 (t, *J* = 7.5 Hz, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.5, 142.6, 139.0, 136.8, 133.5, 130.6, 127.2, 122.5, 122.3, 119.2, 110.0, 21.3, 12.2. IR (neat) $\tilde{\nu}$ = 1616, 1516 cm^{-1}. **HRMS** (ESI): calcd for $C_{16}H_{16}N_2$ $[M + H]^+$ 237.1386, found 237.1398

***2-Pentyl-1-(p-tolyl)-1H-benzo[d]imidazole (3s)*:** yellow oil, (0.114 g, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 6.8 Hz, 3H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 2.76 (t, *J* = 7.8 Hz, 2H), 2.47 (s, 3H), 1.74-1.82 (m, 2H), 1.26-1.31 (m, 4H), 0.84 (t, *J* = 6.9 Hz, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.6, 142.7, 139.0, 136.8, 133.5, 130.6, 127.2, 122.5, 122.3, 119.1, 110.0, 31.6, 27.8, 27.6, 22.4, 21.3, 14.0. IR (neat) $\tilde{\nu}$ = 1612, 1521 cm^{-1}. **HRMS** (ESI): calcd for $C_{19}H_{22}N_2$ $[M + H]^+$ 279.1856, found 279.1861

4.1.4 General Procedure for the Synthesis of Indazoles (Reaction conditions B)

To a round-bottom flask equipped with a reflux condenser and a magnetic bar were added the oxime (0.5 mmol, 1.0 eq.) and Et_3N (3 mmol, 6 eq.), DCM (4 mL). The reaction was stirred at ambient temperature for 15 min, then cooled to -5°C. A solution of BTC (0.375 mmol, 0.75 eq.) in DCM (6 mL) was added slowly and the reaction was keep in -5 °C for 3 h unless otherwise stated. Then, the mixture was quenched by saturated $NaHCO_3$ solution and extracted with CH_2Cl_2 (10 mL x 3). The combined organic phase was dried over Na_2SO_4 and filtered. After evaporation of the solvents, the residue was purified by silica gel chromatography (3% EtOAc/hexanes) to afford N-Arylindazole **4**.

***3-Methyl-1-phenyl-1H-indazole (4a)*[30]:** yellow solid, (0.093 g, 89%), m.p. 72.8~73.7°C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.81 (t, *J* = 9.2 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.9 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 2.58 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 144.1, 140.3, 139.2, 130.0, 128.0, 126.4, 125.0, 122.0, 121.5, 121.3, 110.8, 12.1. **HRMS** (ESI): calcd for $C_{14}H_{12}N_2$ $[M + H]^+$ 209.1073, found 209.1085.

***3-Methyl-1-(p-tolyl)-1H-indazole (4b)*:** yellow oil, (0.100 g, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 18.7, 8.3 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 2.67 (s, 3H), 2.43 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 139.7, 138.0, 136.1, 130.1, 127.1, 124.8, 122.6, 120.7, 120.7, 110.4, 21.2, 12.1. **HRMS** (ESI): calcd for $C_{15}H_{14}N_2$ $[M + H]^+$ 223.1229, found 223.1234.

1-(4-Methoxyphenyl)-3-methyl-1H-indazole (4c)[31]**:** yellow solid, (0.110 g, 92%), m.p. 48.7~49.9°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.64–7.57 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.66 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.2, 143.4, 139.8, 133.6, 127.0, 124.6, 124.3, 120.6, 114.7, 110.2, 55.7, 12.0. **HRMS** (ESI): calcd for $C_{15}H_{14}N_2O$ $[M + H]^+$ 239.1178, found 239.1083.

1-(4-Chlorophenyl)-3-methyl-1H-indazole (4d)**:** yellow oil, (0.088 g, 72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 3H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 2.65 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.6, 139.5, 139.0, 131.5, 129.6, 127.5, 125.2, 123.4, 121.2, 120.9, 110.2, 12.0. **HRMS** (ESI): calcd for $C_{14}H_{11}ClN_2$ $[M + H]^+$ 243.0683, found 243.0697.

1-(4-Fluorophenyl)-3-methyl-1H-indazole (4e)**:** pale yellow oil, (0.084 g, 74%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.69-7.60 (m, 3H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 8.2 Hz, 3H), 2.66 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.9 (d, J = 245.8 Hz), 144.1, 139.7, 136.6 (d, J = 2.4 Hz), 127.4, 124.91, 124.3 (d, J = 8.3 Hz), 121.0, 120.8, 116.3 (d, J = 22.9 Hz), 110.1, 12.0, **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.79 (m). **HRMS** (ESI): calcd for $C_{14}H_{11}FN_2$ $[M + H]^+$ 227.0979, found 227.0986.

3-Methyl-1-(4-nitrophenyl)-1H-indazole (4f)**:** yellow oil, (0.089 g, 35%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.9 Hz, 2H), 7.94 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 2.66 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 145.7, 144.6, 139.4, 128.4, 126.3, 125.4, 122.3, 121.3, 120.7, 110.7, 12.1. **HRMS** (ESI): calcd for $C_{14}H_{11}N_3O_2$ $[M + H]^+$ 254.0924, found 254.0936.

3-Methyl-1-(4-(trifluoromethyl)phenyl)-1H-indazole (4g)**:** yellow oil, (0.152 g, 55%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.74 (t, *J* = 9.0 Hz, 4H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 2.65 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.4, 143.2, 139.3, 127.7, 127.5 (q, *J* = 33.3 Hz),126.6 (q, *J* = 3.0 Hz), 125.6, 124.1 (q, *J* = 273.7 Hz), 121.5, 121.4, 120.9, 110.3, 11.9, **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.11. **HRMS** (ESI): calcd for $C_{15}H_{11}F_3N_2$ $[M + H]^+$ 277.0947, found 277.0956.

1-(3-Methoxyphenyl)-3-methyl-1H-indazole (4h)**:** yellow oil, (0.103 g, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (t, *J* = 8.9 Hz, 2H), 7.46-7.37 (m, 2H), 7.35–7.28 (m, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.91–6.85 (m, 1H), 3.89 (s, 3H), 2.67 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6, 144.1, 141.5, 139.6, 130.2, 127.3, 125.1, 121.0, 120.7, 114.5, 112.1, 110.6, 108.2, 55.6, 12.0. **HRMS** (ESI): calcd for $C_{15}H_{14}N_2O$ $[M + H]^+$ 239.1178, found 239.1191.

***1-(3-Chlorophenyl)-3-methyl-1H-indazole (4i)*:** yellow oil, (0.083 g, 68%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.44 (q, *J* = 7.9, 7.2 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 2.65 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.9, 141.6, 139.5, 135.2, 130.5, 127.6, 126.0, 125.4, 122.3, 121.3, 120.9, 120.0, 110.4, 12.0. **HRMS** (ESI): calcd for $C_{14}H_{11}ClN_2$ $[M + H]^+$ 243.0683, found 243.0687.

***1-(3-Fluorophenyl)-3-methyl-1H-indazole (4j)*:** yellow oil, (0.074 g, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77–7.70 (m, 2H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.51–7.42 (m, 3H), 7.26–7.20 (m, 1H), 7.04–6.97 (m, 1H), 2.66 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.37 (d, *J* = 246.6 Hz), 144.8, 141.96 (d, *J* = 10.3 Hz), 139.5, 130.7 (d, *J* = 9.3 Hz), 127.6, 125.4, 121.3, 120.9, 117.4(d, *J* = 2.0 Hz), 112.8 (d, *J* = 21.1 Hz), 110.5, 109.6 (d, *J* = 25.1 Hz), 12.1, **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.05 (m). **HRMS** (ESI): calcd for $C_{14}H_{11}FN_2$ $[M + H]^+$ 227.0979, found 227.0988.

1-(2-Methoxyphenyl)-3-methyl-1H-indazole (4k): yellow oil, (0.101 g, 84%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.50–7.46 (m, 1H), 7.43-7.34 (m, 2H), 7.19 (dd, *J* = 17.0, 8.3 Hz, 2H), 7.12-7.08 (m, 2H), 3.79 (s, 3H), 2.68 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.3, 143.6, 141.4, 129.2, 128.63, 128.56,126.5, 123.9, 121.0, 120.2, 112.3, 111.1, 55.8, 12.1. **HRMS** (ESI): calcd for $C_{15}H_{14}N_2O$ $[M + H]^+$: 239.1179, found 239.1185.

***1-(2-Chlorophenyl)-3-methyl-1H-indazole (4l)*:** yellow oil, (0.088 g, 72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.60-7.58 (m, 1H), 7.54–7.49 (m, 1H), 7.44–7.36 (m, 3H), 7.23-7.20 (m, 2H), 2.68 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.4, 141.2, 137.4, 131.5, 130.7, 129.7, 129.6, 127.7, 127.0, 124.1, 120.7, 120.5, 110.7, 12.1. **HRMS** (ESI): calcd for $C_{14}H_{11}ClN_2$ $[M + H]^+$ 243.0683, found 243.0691.

***1-(2-Fluorophenyl)-3-methyl-1H-indazole (4m)*:** brown oil, (0.073 g, 64%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.45–7.40 (m, 1H), 7.39–7.33 (m, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 2.67 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.2 (d, *J* = 251.8 Hz), 144.9, 141.1, 128.9 (d, *J* = 7.6 Hz), 128.0, 127.8 (d, *J* = 11.6 Hz), 127.2, 125.0 (d, *J* = 3.4 Hz), 124.5, 120.9, 120.5, 117.0 (d, *J* = 19.7 Hz), 110.6 (d, *J* = 4.9 Hz), 12.1, **^{19}F NMR** (376 MHz, $CDCl_3$) δ -120.40 (m). **HRMS** (ESI): calcd for $C_{14}H_{11}FN_2$ $[M + H]^+$ 227.0979, found 227.0993.

***3-Phenyl-1-(p-tolyl)-1H-indazole (4n)*:** yellow solid, (0.120 g, 84%), m.p. 91.5~92.7°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13-8.03 (m, 3H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.49–7.42 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 2.46 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.9,

140.5, 137.8, 136.7, 133.5, 130.1, 128.9, 128.3, 127.9, 127.1, 123.2, 123.1, 121.9, 121.7, 110.8, 21.2. IR (neat) $\tilde{\nu}$ = 1603, 1511 cm^{-1}. **HRMS** (ESI): calcd for $C_{20}H_{16}N_2$ $[M + H]^+$ 285.1386, found 285.1396.

***5-Methyl-3-phenyl-1-(p-tolyl)-1H-indazole (4o)*:** yellow solid, (0.123 g, 82%), m.p. 99.8~101.2°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.7 Hz, 2H), 7.86 (s, 1H), 7.71–7.62 (m, 3H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 1H), 2.53 (s, 3H), 2.45 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.3, 139.2, 138.0, 136.5, 133.7, 131.4, 130.1, 129.1, 128.9, 128.2, 127.9, 123.5, 122.9, 120.7, 110.5, 21.6, 21.2. IR (neat) $\tilde{\nu}$ = 1616, 1508 cm^{-1}. **HRMS** (ESI): calcd for $C_{21}H_{18}N_2$ $[M + H]^+$ 299.1543, found 299.1568.

5-Chloro-3-phenyl-1-(p-tolyl)-1H-indazole (4p): yellow solid, (0.114 g, 71%), m.p. 90.5~91.8°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.99 (d, *J* = 7.4 Hz, 2H), 7.64 (t, *J* = 8.9 Hz, 3H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.41–7.33 (m, 3H), 2.45 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.4, 139.0, 137.4, 137.2, 132.9, 130.2, 129.1, 128.6, 127.8, 127.7, 127.6, 123.9, 123.2, 120.9, 111.9, 21.3. IR (neat) $\tilde{\nu}$ = 1613, 1508 cm^{-1}. **HRMS** (ESI): calcd for $C_{20}H_{15}ClN_2$ $[M + H]^+$: 319.0997, found 319.1028.

***3-(4-Fluorophenyl)-1-(p-tolyl)-1H-indazole (4q)*:** yellow solid, (0.117 g, 77%), m.p. 115.9~117.1°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00-7.97 (m, 3H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.27–7.17 (m, 3H), 2.41 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9 (d, *J* = 247.4 Hz), 144.8, 140.4, 137.6, 136.7, 130.1, 129.6 (d, *J* = 3.2 Hz), 129.4 (d, *J* = 8.1 Hz), 127.1, 123.0, 122.8, 121.9, 121.3, 115.8 (d, *J* = 21.5 Hz), 110.8, 21.1, **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.46 (m). IR (neat) $\tilde{\nu}$ = 1610, 1517 cm^{-1}. **HRMS** (ESI): calcd for $C_{20}H_{15}FN_2$ $[M + H]^+$ 303.1292, found 303.1312.

***3-Ethyl-1-(p-tolyl)-1H-indazole (4r)*:** yellow oil, (0.098 g, 83%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 3.10 (q, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 1.48 (t, *J* = 7.6 Hz, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.1, 139.8, 138.0, 136.0, 130.0, 127.0, 124.0, 122.6, 120.7, 120.6, 110.5, 21.2, 20.6, 13.8. IR (neat) $\tilde{\nu}$ = 1618, 1508 cm^{-1}. **HRMS** (ESI): calcd for $C_{16}H_{16}N_2$ $[M + H]^+$ 237.1386, found 237.1392.

3-Pentyl-1-(p-tolyl)-1H-indazole (4s): yellow oil, (0.110 g, 79%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 3.06 (t, *J* = 7.8 Hz, 2H), 2.43 (s, 3H), 1.95-1.85 (m, 2H), 1.53–1.35 (m, 4H), 0.94 (t, *J* = 7.0 Hz, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.1, 139.8, 138.0, 136.0, 130.0, 126.9, 124.3, 122.6, 120.8, 120.6, 110.5,

32.0, 29.2, 27.23, 22.6, 21.2, 14.2. IR (neat) $\tilde{\nu}$ = 1598, 1507 cm^{-1}. **HRMS** (ESI): calcd for $C_{19}H_{22}N_2$ $[M + H]^+$ 279.1856, found 279.1877.

***1-Benzyl-3-methyl-1H-indazole (4t)*:** yellow oil, (0.078 g, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 1H), 7.35–7.24 (m, 5H), 7.20 (d, *J* = 7.1 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 5.54 (s, 2H), 2.61 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 140.6, 137.4, 128.8, 127.7, 127.2, 126.5, 123.9, 120.6, 119.9, 109.3, 52.7, 12.1. IR (neat) $\tilde{\nu}$ = 1615, 1508 cm^{-1}. **HRMS** (ESI): calcd for $C_{15}H_{14}N_2$ $[M + H]^+$ 223.1230, found 223.1229.

***3-Methyl-1-(4-methylbenzyl)-1H-indazole (4u)*:** yellow oil, (0.090 g, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 1H), 7.37–7.28 (m, 2H), 7.17–7.09 (m, 5H), 5.52 (s, 2H), 2.64 (s, 3H), 2.33 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 140.5, 137.3, 134.3, 129.4, 127.2, 126.3, 123.8, 120.5, 119.8, 109.3, 52.5, 21.1, 12.0. IR (neat) $\tilde{\nu}$ = 1614, 1508 cm^{-1}. **HRMS** (ESI): calcd for $C_{16}H_{16}N_2$ $[M + H]^+$ 237.1386, found 237.1380.

***3-Methyl-1-(4-(trifluoromethyl)benzyl)-1H-indazole (4v)*:** yellow oil, (0.094 g, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.27–7.21 (m, 3H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.56 (s, 2H), 2.59 (s, 3H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.6, 141.4, 140.7, 130.1 (q, *J* = 32.7 Hz), 127.4, 126.8, 125.8 (q, *J* = 3.03 Hz), 124.2 (q, *J* = 272.7 Hz), 124.0, 120.7, 120.2, 108.9, 52.1, 12.1, **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.53. IR (neat) $\tilde{\nu}$ = 1617, 1509 cm^{-1}. **HRMS** (ESI): calcd for $C_{16}H_{13}F_3N_2$ $[M + H]^+$ 291.1104, found 291.1099.

4.1.5 General Procedure for the Control experiments a

The reaction was performed according to the reaction conditions A using 0.55 g (3.0 mmol, 1 eq.) of *N*-benzylaniline, 0.356 g (1.2 mmol, 0.4 eq.) of BTC to afford *N*-Arylbenzimidazole *N*-Benzyl-*N*-phenylcarbamoyl chloride **6**, the residue was purified by silica gel chromatography (5% EtOAc/hexanes) to afford the product.

***N-Benzyl-N-phenylcarbamoyl chloride (6)*[32]:** white solid, (0.132 g, 18%), m.p. 44.6~45.8°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.29 (m, 3H), 7.29–7.25 (m, 3H), 7.19 (br, 2H), 7.01 (br, 2H), 4.86 (s, 2H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.8, 141.6, 135.6, 129.4, 129.0, 128.7, 128.5, 128.2, 56.7.

4.1.6 General Procedure for the Control experiments b

The reaction was performed according to the reaction conditions A using 0.811 g (6.0 mmol, 1 eq.) of (*E*)-1-phenylethan-1-one oxime, 1.015 g (6 mmol, 1 eq.) of Diphenylamine, 0.712 g (2.4 mmol, 0.4 eq.) of BTC to afford (*E*)-1-Phenylethan-1-one-*O*-chlorocarbonyl oxime **9**, the residue was purified by silica gel chromatography

(5% EtOAc/hexanes) to afford 79% of the product (0.940 g, 4.75 mmol).

The reaction was performed according to the reaction conditions B using 0.811 g (6.0 mmol, 1 eq.) of (*E*)-1-phenylethan-1-one oxime, 1.015 g (6 mmol, 1 eq.) of Diphenylamine, 1.33 g (4.5mmol, 0.75 eq.) of BTC, 3.64 g (36mmol, 6 eq.) of Et_3N to afford (*E*)-1-Phenylethan-1-one-*O*-chlorocarbonyl oxime **9**, the residue was purified by silica gel chromatography (5% EtOAc/hexanes) to afford 76% of the product (0.904 g, 4.57 mmol).

(E)-1-Phenylethan-1-one-O-chlorocarbonyl oxime (9)[33]**:** yellow oil. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.79 (d, J = 7.0 Hz, 2H), 7.56-7.48 (m, 3H), 2.44 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 163.9, 151.3, 133.9, 130.9, 128.7, 126.9, 14.2. **EI-MS**: m/z 197 ($[M + H]^+$ for ^{35}Cl), 199 ($[M + H]^+$ for ^{37}Cl).

4.1.7 General Procedure for the Control experiments c

The reaction was performed according to the reaction conditions A using 0.159 g (0.80 mmol, 1 eq.) of (*E*)-1-Phenylethan-1-one-*O*-chlorocarbonyl oxime **9**, 0.095 g (0.32 mmol, 0.4 eq.) of BTC to afford Acetanilide **11**, the residue was purified by silica gel chromatography (20% EtOAc/hexanes) to afford 56% of the product (0.061 g, 0.45 mmol).

The reaction was performed according to the reaction conditions B using 0.159 g (0.80 mmol, 1 eq.) of (*E*)-1-Phenylethan-1-one-*O*-chlorocarbonyl oxime **9**, 0.179 g (0.60 mmol, 0.75 eq.) of BTC, 0.488 g (4.8 mmol, 6 eq.) of Et_3N.

Acetanilide (11)[34]**:** White solid; (0.061 g, 56 %), m.p. 112.6~114.7°C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.92 (s, 1H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 2.04 (s, 3H), **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.3, 139.3, 128.6, 123.0, 119.0, 24.0.

4.1.8 General Procedure for the Control experiments d

To a round-bottom flask equipped with a hydrochloric acid gas generator, reflux condenser and magnetic bar were added the BTC (0.2 mmol, 0.4 eq.) PhCl (4 mL). The reaction was stirred under HCl atmosphere at ambient temperature for 15 min, then a solution of Oxime 1 (0.5 mmol, 1 eq.) in PhCl (4 mL) was added slowly and the reaction was keep in ambient temperature for 3 h. Then, the mixture was quenched by saturated $NaHCO_3$ solution and extracted with CH_2Cl_2 (10 mL x 3). The combined organic phase was dried over Na_2SO_4 and filtered. After evaporation of the solvents, the residue was purified by silica gel chromatography (20% EtOAc/hexanes) to afford 54% of *N*-Arylbenzimidazole **3** (0.056 g, 0.27 mmol).

To a round-bottom flask equipped with a hydrochloric acid gas generator, reflux condenser and magnetic bar were added the BTC (0.2 mmol, 0.4 eq.) PhCl (4 mL). The reaction was stirred under HCl atmosphere at ambient temperature for 15 min, then a solution of Oxime 1 (0.5 mmol, 1 eq.) in PhCl (4 mL) was added slowly and the reaction was keep in ambient temperature for 5 h. Then, the mixture was quenched by saturated $NaHCO_3$ solution and extracted with CH_2Cl_2 (10 mL x 3). The combined organic phase was dried over Na_2SO_4 and filtered. After evaporation of the solvents, the residue was purified by silica gel chromatography (20% EtOAc/hexanes) to afford 92% of *N*-Arylbenzimidazole **3** (0.096 g, 0.46 mmol).

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Associated Content

Supporting Information

Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra of starting materials and all products.

References

[1] (a) Sabat, M.; VanRens, J. C.; Laufersweiler, M. J.; Brugel, T. A.; Maier, J.; Golebiowski, A.; De, B.; Easwaran, V.; Hsieh, L. C.; Walter, R. L.; Mekel, M. J.; Evdokimov, A.; Janusz, M. J. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 5973-5977;

(b) Xie, J.; Poda, G. I.; Hu, Y.; Chen, N. X.; Heier, R. F.; Wolfson, S. G.; Reding, M. T.; Lennon, P. J.; Kurumbail, R. G.; Selness, S. R.; Li, X.; Kishore, N. N.; Sommers, C. D.; Christine, L.; Bonar, S. L.; Venkatraman, N.; Mathialagan, S.; Brustkern, S. J.; Huang, H. C. *Bioorg. Med. Chem.* **2011**, *19*, 1242-1255.

[2] Beaulieu, C.; Wang, Z.; Denis, D.; Greig, G.; Lamontagne, S.; O'Neill, G.; Slipetz, D.; Wang, J. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 3195-3199.

[3] (a) Solanki, S.; Innocenti, P.; Mas-Droux, C.; Boxall, K.; Barillari, C.; van Montfort, R. L.; Aherne, G. W.; Bayliss, R.; Hoelder, S. *J. Med. Chem.* **2011**, *54*, 1626-1639;

(b) Liu, M.; Xu, Q.; Guo, S.; Zuo, R.; Hong, Y.; Luo, Y.; Li, Y.; Gong, P.; Liu, Y. *Bioorg. Med. Chem.* **2018**, *26*, 2621-2631;

(c) Baudy, R. B.; Yardley, J. P.; Zaleska, M. M.; Bramlett, D. R.; Tasse, R. P.; Kowal, D. M.; Katz, A. H.; Moyer, J. A.; Abou-Gharbia, M. *J. Med. Chem.* **2001**, *44*, 1516-1529.

[4] (a) Carvalho, L. C.; Fernandes, E.; Marques, M. M. *Chem. Eur. J.* **2011**, *17*, 12544-12555;

(b) Cao, H.; Sun, H.; Yin, Y.; Wen, X.; Shan, G.; Su, Z.; Zhong, R.; Xie, W.; Li, P.; Zhu, D. *J. Mater. Chem. C* **2014**, *2*, 2150-2159;

(c) Wang, F.; Hu, J.; Cao, X.; Yang, T.; Tao, Y.; Mei, L.; Zhang, X.; Huang, W. *J. Mater. Chem. C* **2015**, *3*, 5533-5540;

(d) Bodedla, G. B.; Thomas, K. R. J.; Li, C.-T.; Ho, K.-C. *RSC Adv.* **2014**, *4*, 53588-53601.

[5] (a) Ganotra, G. K.; Wade, R. C. *ACS Med. Chem. Lett.* **2018**, *9*, 1134-1139;

(b) Blaquiere, N.; Castanedo, G. M.; Burch, J. D.; Berezhkovskiy, L. M.; Brightbill, H.; Brown, S.; Chan, C.; Chiang, P. C.; Crawford, J. J.; Dong, T.; Fan, P.; Feng, J.; Ghilardi, N.; Godemann, R.; Gogol, E.; Grabbe, A.; Hole, A. J.; Hu, B.; Hymowitz, S. G.; Alaoui Ismaili, M. H.; Le, H.; Lee, P.; Lee, W.; Lin, X.; Liu, N.; McEwan, P. A.; McKenzie, B.; Silvestre, H. L.; Suto, E.; Sujatha-Bhaskar, S.; Wu, G.; Wu, L. C.; Zhang, Y.; Zhong, Z.; Staben, S. T. *J. Med. Chem.* **2018**, *61*, 6801-6813;

(c) McCoull, W.; Bailey, A.; Barton, P.; Birch, A. M.; Brown, A. J.; Butler, H. S.; Boyd, S.; Butlin, R. J.;

Chappell, B.; Clarkson, P.; Collins, S.; Davies, R. M.; Ertan, A.; Hammond, C. D.; Holmes, J. L.; Lenaghan, C.; Midha, A.; Morentin-Gutierrez, P.; Moore, J. E.; Raubo, P.; Robb, G. *J. Med. Chem.* **2017**, *60*, 3187-3197;
(d) Uno, T.; Kawai, Y.; Yamashita, S.; Oshiumi, H.; Yoshimura, C.; Mizutani, T.; Suzuki, T.; Chong, K. T.; Shigeno, K.; Ohkubo, M.; Kodama, Y.; Muraoka, H.; Funabashi, K.; Takahashi, K.; Ohkubo, S.; Kitade, M. *J. Med. Chem.* **2019**, *62*, 531-551.

[6] (a) Jui, N. T.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2013**, *52*, 11624-11627;
(b) Nagao, I.; Ishizaka, T.; Kawanami, H. *Green Chem.* **2016**, *18*, 3494-3498;
(c) Youn, S. W.; Lee, E. M. *Org. Lett.* **2016**, *18*, 5728-5731;
(d) Lee, Y.-S.; Cho, Y.-H.; Lee, S.; Bin, J.-K.; Yang, J.; Chae, G.; Cheon, C.-H. *Tetrahedron* **2015**, *71*, 532-538.

[7] (a) De Luca, L.; Porcheddu, A. *Eur. J. Org. Chem.* **2011**, 5791-5795;
(b) Zhang, R.; Qin, Y.; Zhang, L.; Luo, S. *Org. Lett.* **2017**, *19*, 5629-5632.

[8] (a) Selvam, K.; Swaminathan, M. *Tetrahedron Lett.* **2011**, *52*, 3386-3392;
(b) Das, S.; Mallick, S.; De Sarkar, S. *J. Org. Chem.* **2019**, *84*, 12111-12119.

[9] (a) Lin, J. P.; Zhang, F. H.; Long, Y. Q. *Org. Lett.* **2014**, *16*, 2822-2825;
(b) Li, J.; Benard, S.; Neuville, L.; Zhu, J. *Org. Lett.* **2012**, *14*, 5980-5983;
(c) Baars, H.; Beyer, A.; Kohlhepp, S. V.; Bolm, C. *Org. Lett.* **2014**, *16*, 536-539;
(d) Deng, X.; Mani, N. S. *Eur. J. Org. Chem.* **2010**, *2010*, 680-686.

[10] (a) Cho, C. S.; Lim, D. K.; Heo, N. H.; Kim, T. J.; Shim, S. C. *Chem. Commun.* **2004**, 104-105;
(b) Annor-Gyamfi, J. K.; Gnanasekaran, K. K.; Bunce, R. A. *Molecules* **2018**, *23*;
(c) Wiethan, C.; Lavoie, C. M.; Borzenko, A.; Clark, J. S. K.; Bonacorso, H. G.; Stradiotto, M. *Org. Biomol. Chem.* **2017**, *15*, 5062-5069;
(d) Xiong, X.; Jiang, Y.; Ma, D. *Org. Lett.* **2012**, *14*, 2552-2555.

[11] (a) Li, P.; Wu, C.; Zhao, J.; Rogness, D. C.; Shi, F. *J. Org. Chem.* **2012**, *77*, 3149-3158;
(b) Spiteri, C.; Keeling, S.; Moses, J. E. *Org. Lett.* **2010**, *12*, 3368-3371.

[12] (a) Tang, L.; Ma, M.; Zhang, Q.; Luo, H.; Wang, T.; Chai, Y. *Adv. Synth. Catal.* **2017**, *359*, 2610-2620;
(b) Wei, W.; Wang, Z.; Yang, X.; Yu, W.; Chang, J. *Adv. Synth. Catal.* **2017**, *359*, 3378-3387;
(c) Xu, P.; Wang, G.; Wu, Z.; Li, S.; Zhu, C. *Chem. Sci.* **2017**, *8*, 1303-1308;
(d) Li, X.; He, L.; Chen, H.; Wu, W.; Jiang, H. *J. Org. Chem.* **2013**, *78*, 3636-3646.

[13] (a) Yu, S.; Tang, G.; Li, Y.; Zhou, X.; Lan, Y.; Li, X. *Angew. Chem. Int. Ed.* **2016**, *55*, 8696-8700;
(b) Chen, C.-y.; He, F.; Tang, G.; Ding, H.; Wang, Z.; Li, D.; Deng, L.; Faessler, R. *Eur. J. Org. Chem.* **2017**, 6604-6608;
(c) Chen, C. Y.; Tang, G.; He, F.; Wang, Z.; Jing, H.; Faessler, R. *Org. Lett.* **2016**, *18*, 1690-1693;
(d) Wang, Q.; Li, X. *Org. Lett.* **2016**, *18*, 2102-2105.

[14] (a) Wray, B. C.; Stambuli, J. P. *Org. Lett.* **2010**, *12*, 4576-4579;
(b) Tang, X.; Gao, H.; Yang, J.; Wu, W.; Jiang, H. *Org. Chem. Front.* **2014**, *1*, 1295-1298;
(c) Conlon, I. L.; Konsein, K.; Morel, Y.; Chan, A.; Fletcher, S. *Tetrahedron Lett.* **2019**, *60*, 150929.
(d) Paul, S.; Panda, S.; Manna, D. *Tetrahedron Lett.* **2014**, 55, 2480-2483.

[15] (a) Zhang, X.; Chen, D.; Zhao, M.; Zhao, J.; Jia, A.; Li, X. *Adv. Synth. Catal.* **2011**, *353*, 719-723;
(b) Zhang, Z. W.; Lin, A.; Yang, J. *J. Org. Chem.* **2014**, *79*, 7041-7050;
(c) Too, P. C.; Wang, Y. F.; Chiba, S. *Org. Lett.* **2010**, *12*, 5688-5691;
(d) Yu, L.; Li, H.; Zhang, X.; Ye, J.; Liu, J.; Xu, Q.; Lautens, M. *Org. Lett.* **2014**, *16*, 1346-1349.

[16] (a) Srivastava, V. P.; Patel, R.; Garima; Yadav, L. D. *Chem. Commun.* **2010**, *46*, 5808-5810;
(b) Vanos, C. M.; Lambert, T. H. *Chemical Science* **2010**, *1*, 705;

(c) Yang, S. H.; Chang, S. *Org. Lett.* **2001**, *3*, 4209-4211.

[17] (a) Tanaka, K.; Mori, Y.; Narasaka, K. *Chem. Lett.* **2004**, *33*, 26-27;
(b) Counceller, C. M.; Eichman, C. C.; Wray, B. C.; Stambuli, J. P. *Org. Lett.* **2008**, *10*, 1021-1023.

[18] (a) Tang, X.; Yang, J.; Zhu, Z.; Zheng, M.; Wu, W.; Jiang, H. *J. Org. Chem.* **2016**, *81*, 11461-11466;
(b) Tang, X.; Zhu, Z.; Qi, C.; Wu, W.; Jiang, H. *Org. Lett.* **2016**, *18*, 180-183;
(c) Zhu, Z.; Tang, X.; Li, J.; Li, X.; Wu, W.; Deng, G.; Jiang, H. *Org. Lett.* **2017**, *19*, 1370-1373;
(d) Huang, H.; Qu, Z.; Ji, X.; Deng, G.-J. *Org. Chem. Front.* **2019**, *6*, 1146-1150;
(e) Ren, Z.-H.; Zhao, M.-N.; Guan, Z.-H. *RSC Adv.* **2016**, *6*, 16516-16519.

[19] (a) Ke, J.; Tang, Y.; Yi, H.; Li, Y.; Cheng, Y.; Liu, C.; Lei, A. *Angew. Chem. Int. Ed.* **2015**, *54*, 6604-6607;
(b) Hong, W. P.; Iosub, A. V.; Stahl, S. S. *J. Am. Chem. Soc.* **2013**, *135*, 13664-13667;
(c) Zhao, M. N.; Hui, R. R.; Ren, Z. H.; Wang, Y. Y.; Guan, Z. H. *Org. Lett.* **2014**, *16*, 3082-3085;
(d) John, A.; Nicholas, K. M. *Organometallics* **2012**, *31*, 7914-7920.

[20] Cotarca, L.; Geller, T.; Répási, J. *Org. Process Res. Dev.* **2017**, *21*, 1439-1446.

[21] (a) Saputra, M. A.; Ngo, L.; Kartika, R. *J. Org. Chem.* **2015**, *80*, 8815-8820;
(b) Villalpando, A.; Ayala, C. E.; Watson, C. B.; Kartika, R. *J. Org. Chem.* **2013**, *78*, 3989-3996;
(c) Su, W.; Zhong, W.; Bian, G.; Shi, X.; Zhang, J. *Org. Prep. Proced. Int.* **2004**, *36*, 499-547;
(d) Su, W. K.; Zhu, X. Y.; Li, Z. H. *Org. Prep. Proced. Int.* **2009**, *41*, 69-75;
(e) Su, W. K.; Zhang, Y.; Li, J. J.; Li, P. *Org. Prep. Proced. Int.* **2008**, *40*, 543-550.
(f) Ayala, C. E., Villalpando, A., Nguyen, A. L., McCandless, G. T., Kartika, R. *Org. Lett.* **2012**, *14*, 3676-3679.

[22] (a) Li, Z. H.; Jiang, Z. J.; Shao, Q. L.; Qin, J. J.; Shu, Q. F.; Lu, W. H.; Su, W. K. *J. Org. Chem.* **2018**, *83*, 6423-6431;
(b) Zhong, W.; Wu, D.; Li, Z. *Heterocycles* **2012**, *85*, 1417;
(c) Su, W. K.; Li, Z. H.; Zhao, L. Y. *Org. Prep. Proced. Int.* **2007**, *39*, 495-502;
(d) Zou, Y.; Li, Z.; Su, W. *J. Chem. Res.* **2014**, *38*, 143-146.

[23] Please refer to the Supporting Information.

[24] (a) Zheng, W.; Yang, W.; Luo, D.; Min, L.; Wang, X.; Hu, Y. *Adv. Synth. Catal.* **2019**, *361*, 1995-1999;
(b) Zhu, Z.; Cen, J.; Tang, X.; Li, J.; Wu, W.; Jiang, H. *Adv. Synth. Catal.* **2018**, *360*, 2020-2031;
(c) Kalkhambkar, R. G.; Savanur, H. M. *RSC Adv.* **2015**, *5*, 60106-60113;
(d) Raju, G.; Guguloth, V.; Satyanarayana, B. *RSC Adv.* **2016**, *6*, 45036-45040.

[25] Brain, C. T.; Steer, J. T. *J. Org. Chem.* **2003**, *68*, 6814-6816.

[26] Zheng, N.; Anderson, K. W.; Huang, X.; Nguyen, H. N.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2007**, *46*, 7509-7512.

[27] Alonso, J.; Halland, N.; Nazaré, M.; R'Kyek, O.; Urmann, M.; Lindenschmidt, A. *Eur. J. Org. Chem.* **2011**, 234-237.

[28] Yang, D.; Fu, H.; Hu, L.; Jiang, Y.; Zhao, Y. *J. Org. Chem.* **2008**, *73*, 7841-7844.

[29] Altman, R. A.; Koval, E. D.; Buchwald, S. L. *J. Org. Chem.* **2007**, *72*, 6190-6199.

[30] Gao, M.; Liu, X.; Wang, X.; Cai, Q.; Ding, K. *Chin. J. Chem* . **2011**, *29*, 1199-1204.

[31] Lebedev, A. Y.; Khartulyari, A. S.; Voskoboynikov, A. Z. *J. Org. Chem.* **2005**, *70*, 596-602.

[32] Iwai, T.; Fujihara, T.; Terao, J.; Tsuji, Y. *J. Am. Chem. Soc.* **2010**, *132*, 9602-9603.

[33] (a) Paryzek, Z.; Koenig, H. *Synthesis Commun.* **2003**, *33*, 3405-3410;
(b) Kolano, C.; Bucher, G.; Schade, O.; Grote, D.; Sander, W. *J. Org. Chem.* **2005**, *70*, 6609-6615.

[34] Kang, Y.-J.; Chung, H.-A.; Kim, J.-J.; Yoon, Y.-J. *Synthesis* **2002**, 733-738.

Highlights

- A divergent synthesis of *N*-arylbenzimidazoles and *N*-arylindazoles from arylamino oximes based on reaction conditions selection was developed.

- This switchable hectorcycle formation process features mild reaction conditions, simple execution, high chemoselectivity and broad substrate scope.

- The chemoselectiyity of this synthesis was regulated by the amount of Et_3N.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: