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Efficient access to polysubstituted amidines, benzimidazoles and pyrimidines from amides

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ABSTRACT

Polysubstituted amidines, benzimidazoles and pyrimidines were synthesized via the electrophilic activation of amides with trifluoromethanesulfonic anhydride and 2-chloropyridine. The one-pot protocol is concise and efficient and the substrates are readily available.

1. Introduction

Amidines are an important class of compounds for their biological properties[1] and applications in heterocyclic synthesis.[2] Consequently, their synthesis has received much attention.[3] Conventional methods for the preparation of polysubstituted amidines include imidoylation of amines with imidoyl chlorides,[4] imidate fluoroborates,[5] iminium triflates,[6] iminium sulfonates,[7] or imidoylbenzotriazoles.[3b]

As previous reported, amide is attractive starting material due to their easily accessible. However, amide itself is seldom used in organic synthesis for its relative stable. The nitrogen atom of the amide donates its lone pair electrons to C–N bond, both nucleophilicity of nitrogen and electrophilicity of carbonyl are hence decreased. There are several ways to activate the amide functional group in the literature. Among those methods, combination of trifluoromethanesulfonic anhydride (Tf_2O) and pyridine or 2-chloropyridine (2-ClPy) is hitherto the most attractive and feasible way. In the presence of a suitable nucleophile, a variety of compounds such as piperidines,[8] carboxylic acid derivatives,[9] amines,[10] pyrimidines,[11] and pyridines[12] were thus constructed via this electrophilic activation of amide pathway. Recently, we also developed a one-pot domino synthesis of indoles from amides and diazoacetate through finely tuning the electrophilicity of the activated *N*-aryl amides using the combination of Tf_2O, 2-ClPy and 2,6-Cl_2Py in a certain ratio.[13] As the extension of these preliminary results, we considered the amide itself function as a weak nucleophile and tested the possibility of the self-dimerization of amides. We herein report the details of this effort.

2. Results and discussion

Initially, we chose to focus our attention on the reaction of *N*-phenylbenzamide (**1a**). As we expected, when the combination of Tf_2O and 2-ClPy was used as the activating reagent, the amidine **2a** was readily obtained (Scheme 1).

In order to obtain the optimized reaction conditions, several combinations of base additive were investigated (Table 1). When pyridine and its analogous (Py, 2-ClPy, and 2,6-Cl_2Py) were used as base additive (Table 1, entries 8, 7, and 4, respectively), dimerized product **2a** was isolated in moderate to good yield. Other base additives such as DMAP, triethylamine or DBU (Table 1, entries 9, 10 and 11, respectively) were found to be ineffective in this one-pot approach. 2-ClPy functioned as base additive was thereby screened for further investigation. By comparison, refluxing is necessary for reaction completeness (Table 1, entries 4, 5 and 6), whereas half hour is enough (Table 1, entries 2, 3 and 4). Dimerization may also occur using Tf_2O as the sole activating reagent but with relatively lower yield (Table 1, entries 1 and 2). The mechanism presented in Scheme 1 showed slightly difference between with or without the

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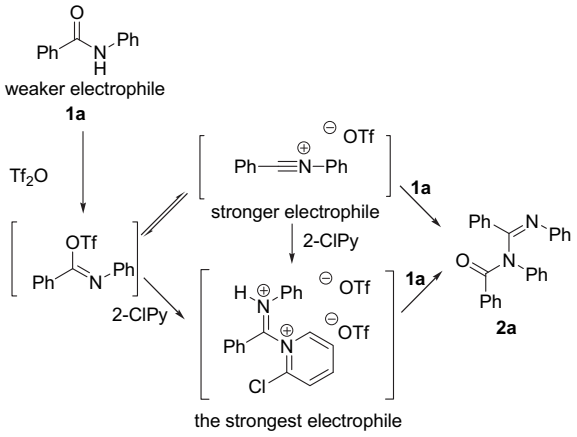
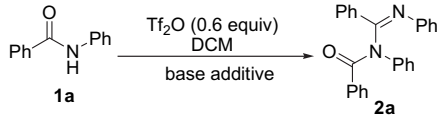


Scheme 1. Formation of amidine **2a**.

Table 1
Survey of reaction conditions for preparation of amidine **2a**



Entry	Base additive (equiv)	Temperature (°C)	Time (h)	Yield[a] (%)
1	none	−78 ~ reflux	8	50
2	2-ClPy (0.6)	−78 ~ reflux	8	88
3	2-ClPy (0.6)	−78 ~ reflux	3	86
4	2-ClPy (0.6)	−78 ~ reflux	0.5	85
5	2-ClPy (0.6)	−78 ~ rt.	0.5	75
6	2-ClPy (0.6)	−78	0.5	20
7	2,6-Cl_2Py (0.6)	−78 ~ reflux	0.5	78
8	Py (0.6)	−78 ~ reflux	0.5	80
9	DMAP (0.6)	−78 ~ reflux	0.5	trace
10	TEA (0.6)	−78 ~ reflux	0.5	trace
11	DBU (0.6)	−78 ~ reflux	0.5	trace

[a] Isolated yield refers to amide **1a**.

participation of 2-ClPy. In comparison with phosphoric anhydride[14] as activating reagent, our method is more general and efficient.

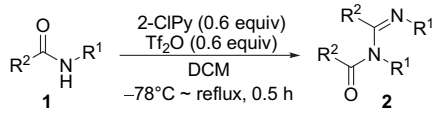
Using the optimized reaction condition, we explored the scope of the reaction with a variety of the accessible amides (Table 2). In all cases, amides **1** proceeded to furnish the corresponding substituted amidines **2**. Both the amides with an aromatic acyl (Table 2, entries 1–7) and the amides with an aliphatic acyl (Table 2, entry 8) gave good to excellent yields (79–90%). The amide with heterocycles such as furan or thiophene (Table 2, entries 9 and 10, respectively) could also undergo the reaction. Moreover, the inductive effects of the *N*-aryl side of amide on the reaction were insignificant (Table 2, entries 1, 3, 5 and 6).

When the amides **3a**–**3g**, derived from symmetric 1,2-diaminobenzenes, were used as the substrates, *N*-acyl benzimidazoles **4** were constructed in moderate yields (Table 3). Unsymmetrically substituted diamides **5** afforded a mixture of two isomers **6** and **7** (Table 4). The structure of **7c** was unambiguously determined by X-ray diffraction analysis.[15]

Since benzimidazoles are of wide applications as drugs with biological and pharmaceutical impact,[16] and as molecular precursors for the development of ligands,[17] dyes[18] and polymers,[19] our reaction provides a novel synthetic method leading to this important class of heterocyclic compounds.

Using optical diamide **8** as the substrate, derived from (1*R*,2*R*)-cyclohexane-1,2-diamine, chrial dihydroimidazoles **9** were obtained in excellent yields (Scheme 2).

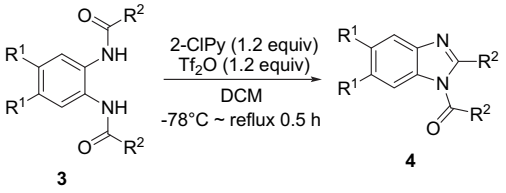
Table 2
Synthesis of amidines **2**[a]



Entry	R^1	R^2	Product	Yield[b] (%)
1	Ph	Ph	**2a**	85
2	Ph	2-ClC_6H_4	**2b**	85
3	4-$MeOC_6H_4$	Ph	**2c**	84
4	2-Me-4-MeO-C_6H_3	Ph	**2d**	80
5	4-MeC_6H_4	Ph	**2e**	79
6	4-BrC_6H_4	Ph	**2f**	83
7	2-MeC_6H_4	Ph	**2g**	90
8	Ph	*n*-C_5H_{11}	**2h**	89
9	Ph		**2i**	84
10	4-MeC_6H_4		**2j**	82

[a] All reactions were performed on 1 mmol of amide.
[b] Isolated yield refers to amide.

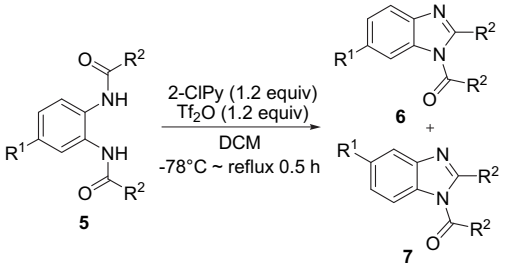
Table 3
Synthesis of 1-acyl-benzimidazoles **4**[a]



Entry	R^1	R^2	Product	Yield[b] (%)
1	H	Ph	**4a**	62
2	H	4-ClC_6H_4	**4b**	58
3	Cl	Ph	**4c**	60
4	Cl	4-MeC_6H_4	**4d**	66
5	CH_3	Ph	**4e**	55
6	CH_3	4-ClC_6H_4	**4f**	51
7	H	2-MeC_6H_4	**4g**	58

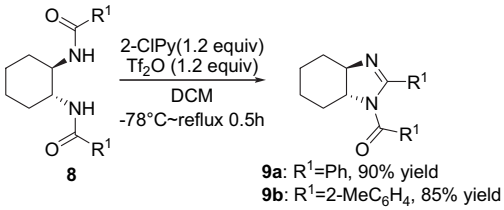
[a] All reactions were performed on 1 mmol of amide.
[b] Isolated yield refers to amide.

Table 4
Synthesis of 1-acyl-benzimidazoles **6** and **7**[a]



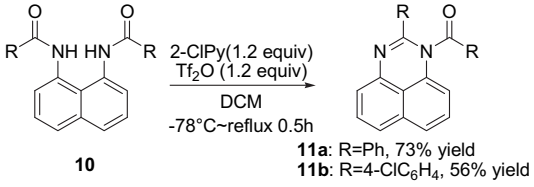
Entry	R^1	R^2	Product	Yield[c] (%)
1	Me	Ph	**6a**+**7a** (4:3)[b]	53
2	Cl	2-MeC_6H_4	**6b**	32
			7b	24
3	NO_2	Ph	**6c**	24
			7c	30

[a] All reactions were performed on 1 mmol of amide **5**.
[b] The ratio for **6a**/**7a** was determined by ^{1}H NMR spectra.
[c] Isolated yield refers to amide.

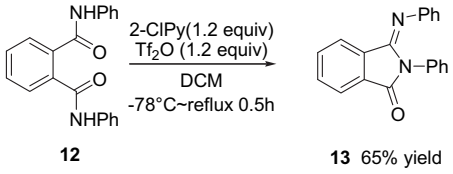


Scheme 2. Synthesis of dihydroimidazoles **9**.

Furthermore, when the amine part of amide was changed to 1,8-diaminonaphthlene, an intramolecular ring closure reaction also occurred and pyrimidine derivatives **11** were generated (Scheme 3). Similarly, when *N*,*N*′-diphenylphthalamide **12** was used as the substrate, we obtained isoindol-1-one **13** (Scheme 4).



Scheme 3. Synthesis of pyrimidines **11**.

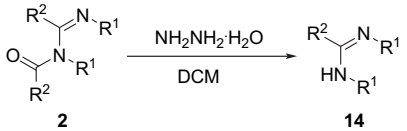


Scheme 4. Synthesis of isoindolone 1**3**.

As an expansion of this synthetic method, we could conveniently remove the acyl group of amidines **2** using excess hydrazine hydrate in DCM at room temperature (Table 5). The hydrazinolysis gave the corresponding amidines **14** in excellent yields.

Structure of benzamidine **2a** was determined by X-ray diffraction analysis (Fig. 1).[20] The C=N double bond adopted a *Z* configuration. Rotation of both N(1)–(25) and N(1)–C(26) resulted in four ultimate conformers **I**, **II**, **III** and **IV** (Fig. 2). Conformer **I** has the lowest energy and its structure is eventually consistent with the crystal structure which was shown in Figure 1. Energy differences for **II**, **III** and **IV** in comparison with **I**, respectively, were calculated to be 1.3, 2.3 and 0.7 kcal/mol higher. Inter-conversion among those four ultimate conformers led to the complexity of ^{1}H and ^{13}C NMR spectra at room temperature. This kind of complexity for *N*-acylamidines has also reported previously by Tebby.[14] Simplified NMR spectra could be expected either by raising the temperature in the case of **2b** (see Supplementary data) or by deacylation of amidines **2a**, **2e** and **2j** via hydrazinolysis as examples (Table 5). It is also noteworthy that **4**, **6**, **7**, **9**, **11** and **13** present neat ^{1}H and ^{13}C NMR spectra due to the rigidity of these heterocyclic structures.

Table 5
Synthesis of amidines **14**[a]



Entry	R^1	R^2	Product	Yield[b] (%)
1	Ph	Ph	**14a**	98
2	4-MeC_6H_4	Ph	**14b**	95
3	4-MeC_6H_4		**14c**	95

[a] All reactions were performed on 1 mmol of amide.
[b] Isolated yield refers to **2**.

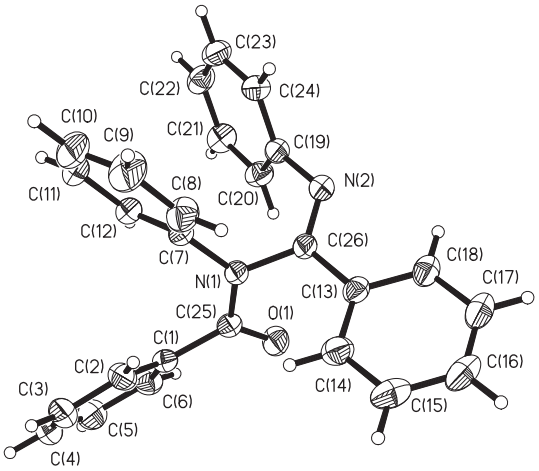


Figure 1. X-ray diffraction structure of **2a**.

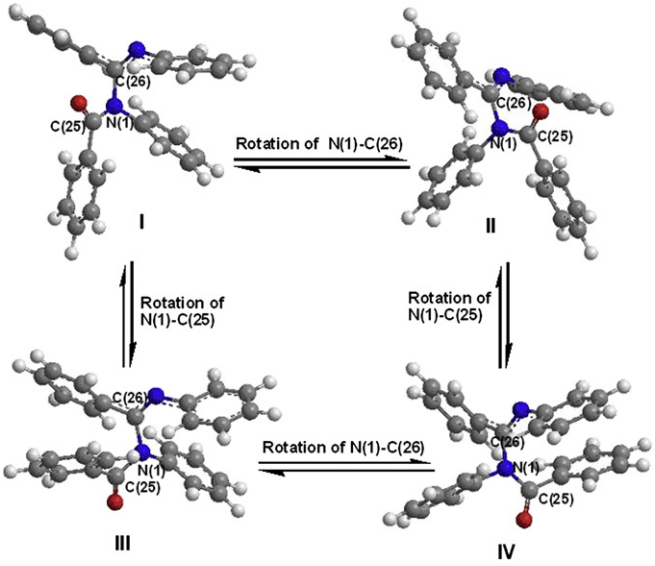


Figure 2. Four ultimate conformers calculated by B3LYP/6–31G (d) method. Grey, blue, red, and white balls represent C, N, O and H, respectively.

3. Conclusion

In conclusion, we have developed a one-pot approach to polysubstituted amidines, benzimidazoles and pyrimidines via the electrophilic activation of amides with trifluoromethanesulfonic anhydride and 2-chloropyridine. The present method is concise and efficient, and the reaction substrates are readily available.

4. Experimental

4.1. General

Infrared spectra were obtained on a FTIR spectrometer. ^{1}H NMR spectra were recorded on 500 MHz or 400 MHz spectrometer. The

chemical shifts were reported relative to internal standard TMS (0) in $CDCl_3$ or 2.5 in DMSO-d_6. The following abbreviations were used to describe peak patterns where appropriate: b=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. Coupling constants were reported in Hertz (Hz). ^{13}C NMR were recorded on 125 MHz or 100 MHz spectrometer, referred to the internal solvent signals (77.0 for $CDCl_3$ or 40.0 for DMSO-d_6). MS and HRMS were obtained using ESI ionization. Melting points were measured with micro melting point apparatus.

4.2. General Procedure for the synthesis of amidines 2

To a mixture of amide **1** (1 mmol) and 2-ClPy (0.6 mmol) in DCM (1.6 mL) was gradually added a solution of Tf_2O (0.6 mmol) in DCM (0.4 mL) via a syringe at −78 °C. The reaction mixture was kept at −78 °C for 5 min and at ambient temperature for additional 5 min and then refluxed for 0.5 h. The reaction mixture was diluted with DCM (25 mL). The organic layer was sequentially washed with the saturated aqueous $CuSO_4$ solution (10 mL), brine (15 mL×2), and water (10 mL). The organic layer was dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under vacuum and the residue was purified by silica gel column chromatography by using a mixture of ethyl acetate and petroleum ether as the eluent.

*4.2.1. N,N′-Diphenyl-N-benzoylbenzamidine (**2a**).* Ethyl acetate/Petroleum ether (1/6) was used as eluent. White solid; mp 174–175 °C; ^1H NMR (DMSO-d_6, 500 MHz) δ 8.04–7.77 (m, 2H), 7.51–6.49 (m, 18H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 172.8, 170.5, 158.2, 154.8, 149.0, 148.6, 141.3, 140.9, 136.8, 135.6, 134.1, 132.3, 131.9, 131.6, 130.5, 130.4, 129.6, 129.3, 128.8, 128.7, 128.5, 128.3, 127.3, 126.5, 126.1, 124.7, 123.6, 120.6, 119.7; IR (KBr) ν 3068, 3031, 1654, 1627, 1594, 1489, 1340, 1277, 765, 693 cm^{-1}; MS (ESI) m/z 399.4 ($[M+Na]^+$); HRMS (ESI) calcd for $C_{26}H_{20}N_2O$ ($[M+Na]^+$), 399.1468; found, 399.1484.

*4.2.2. N,N′-Diphenyl-N-(2-chlorobenzoyl)-2-chlorobenzamidine (**2b**).* Ethyl acetate/Petroleum ether (1/6) was used as eluent. White solid; mp 151–152 °C; ^1H NMR (DMSO-d_6, 500 MHz) δ 7.67–7.64 (m, 2H), 7.49 (d, J=7.5 Hz, 2H), 7.35–7.22 (m, 9H), 7.05–7.02 (m, 2H), 6.85–6.82 (m, 1H), 6.49 (d, J=7.5 Hz, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 168.6, 154.8, 147.7, 140.1, 136.6, 132.4, 132.1. 131.8, 131.6, 131.5, 131.4, 130.7, 130.4, 130.1, 129.7, 129.5, 129.2, 129.0, 128.8, 128.5, 127.8, 127.3, 127.2, 126.9, 124.7, 124.0, 120.8, 119.5; IR (KBr) ν 3061, 1677, 1645, 1590, 1492, 1327, 1294, 772, 695 cm^{-1}; MS (ESI) m/z 445.1 ($[M+H]^+$); HRMS (ESI) calcd for $C_{26}H_{18}Cl_2N_2O$ ($[M+H]^+$), 445.0869; found, 445.0883.

*4.2.3. N,N′-Bis(4-methoxyphenyl)-N-benzoylbenzamidine (**2c**).* Ethyl acetate/Triethylamine/Petroleum ether (1/1/6) was used as eluent. Yellow solid; mp 154–155 °C; ^1H NMR (DMSO-d_6, 500 MHz) δ 8.04–7.78 (m, 2H), 7.51–7.12 (m, 9H), 6.91–6.42 (m, 7H), 3.68–3.60 (m, 6H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 172.8, 170.4, 158.2, 157.9, 157.6, 157.0, 155.8, 154.3, 140.5, 142.2, 141.7, 139.6, 137.1, 135.7, 134.4, 133.7, 133.5, 132.5, 131.5, 131.3, 130.5, 130.2, 129.4, 129.2, 128.7, 128.6, 128.2, 127.4, 123.1, 122.0, 121.2, 114.7, 114.6, 114.4, 55.7, 55.6, 55.5; IR (KBr) ν 3061, 2953, 1651, 1624, 1578, 1508, 1345, 1249, 829, 697 cm^{-1}; MS (ESI) m/z 437.4 ($[M+H]^+$); HRMS (ESI) calcd for $C_{28}H_{24}N_2O_3$ ($[M+H]^+$), 437.1860; found, 437.1880.

*4.2.4. N,N′-Bis(2-methyl-4-methoxyphenyl)-N-benzoylbenzamidine (**2d**).* Ethyl acetate/Petroleum ether (1/4) was used as eluent. Yellow solid; mp 179–180 °C; ^1H NMR (DMSO-d_6, 500 MHz) δ 7.78 (m, 2H), 7.40 (br s, 3H), 7.30–7.27 (m, 3H), 7.19 (br s, 2H), 6.78–6.55 (m, 4H), 6.32 (d, J=6 Hz, 1H), 5.88–5.76 (m, 1H), 3.71–3.57 (m, 6H), 2.33–2.12 (m, 6H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 172.5, 158.7, 158.1, 157.8, 155.8, 141.1, 137.6, 137.0, 136.2, 133.0, 132.7, 132.6, 132.1, 131.4, 130.7, 130.1, 130.0, 129.4, 129.2, 129.0, 128.9, 128.7, 128.7, 128.5, 127.9, 126.5, 119.8, 118.5, 117.7, 116.3, 115.8, 112.6, 112.2, 111.5, 111.0, 55.7, 55.6, 55.5, 55.4, 19.5, 18.7, 18.6, 17.7; IR (KBr) ν 3060, 2949, 1677, 1618, 1579, 1501, 1280, 1250, 695 cm^{-1}; MS (ESI) m/z 465.1 ($[M+H]^+$); HRMS (ESI) calcd for $C_{30}H_{28}N_2O_3$ ($[M+H]^+$), 465.2173; found, 465.2196.

*4.2.5. N,N′-Bis(4-methylphenyl)-N-benzoylbenzamidine (**2e**).* Ethyl acetate/Petroleum ether (1/6) was used as eluent. White solid; mp 127–128 °C; ^1H NMR (DMSO-d_6, 500 MHz) δ 8.01–7.77 (m, 2H), 7.50–6.37 (m, 16H), 2.21–2.12 (m, 6H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 172.7, 170.4, 157.9, 154.2, 146.5, 146.1, 138.6, 138.3, 137.0, 136.6, 135.8, 135.6, 134.4, 133.7, 132.4, 131.7, 131.4, 130.5, 130.3, 130.1, 129.8, 129.6, 129.2, 128.7, 128.5, 128.0, 125.9, 121.4, 120.6, 119.7, 21.0, 20.9, 20.8; IR (KBr) ν 3058, 2919, 1671, 1623, 1510, 1286, 817, 695 cm^{-1}; MS (ESI) m/z 405.1 ($[M+H]^+$); HRMS (ESI) calcd for $C_{28}H_{24}N_2O$ ($[M+H]^+$), 405.1961; found, 405.1966.

*4.2.6. N,N′-Bis(4-bromophenyl)-N-benzoylbenzamidine (**2f**).* Ethyl acetate/Petroleum ether (1/6) was used as eluent. White solid; mp 169–170 °C; ^1H NMR (DMSO-d_6, 500 MHz) δ 8.01–7.80 (m, 2H), 7.52–7.23 (m, 13H), 6.71–6.46 (m, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 172.6, 170.2, 158.5, 148.1, 140.5, 140.2, 136.3, 135.2, 133.5, 132.6, 132.3, 132.1, 132.0, 131.8, 130.8, 130.5, 129.4, 128.9, 128.7, 128.1, 122.9, 122.0, 120.3, 119.3, 117.2, 115.9; IR (KBr) ν 3064, 1653, 1631, 1484, 1326, 1281, 831, 715, 694 cm^{-1}; MS (ESI) m/z 555.0 ($[M+Na]^+$); HRMS (ESI) calcd for $C_{26}H_{18}Br_2N_2O$ ($[M+Na]^+$), 554.9678; found, 554.9705.

*4.2.7. N,N′-Bis(2-methylphenyl)-N-benzoylbenzamidine (**2g**).* Ethyl acetate/Petroleum ether (1/6) was used as eluent for column chromatography. White solid; mp 117–118 °C; ^1H NMR (DMSO-d_6, 500 MHz) δ 7.79–7.78 (m, 2H), 7.41–7.38 (m, 3H), 7.31–7.15 (m, 9H), 7.06–7.05 (m, 2H), 6.77–6.76 (m, 2H), 6.00–5.98 (m, 1H), 2.38 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 172.4, 157.8, 147.7, 140.1, 139.7, 136.7, 136.1, 132.8, 132.3, 131.6, 131.5, 130.4, 130.3, 129.3, 129.0, 128.8, 128.7, 128.6, 128.2, 127.4, 126.5, 124.4, 123.6, 118.8, 117.6, 18.5, 18.3, 17.4; IR (KBr) ν 3066, 2924, 1677, 1627, 1491, 1294, 1269, 757, 698 cm^{-1}; MS (ESI) m/z 405.1 ($[M+H]^+$); HRMS (ESI) calcd for $C_{28}H_{24}N_2O$ ($[M+H]^+$), 405.1961; found, 405.1959.

*4.2.8. N-Phenyl-N-(1-(phenylimino)hexyl)hexanamide (**2h**).* Ethyl acetate/Petroleum ether (1/6) was used as eluent. Yellow oil; ^1H NMR (DMSO-d_6, 500 MHz) δ 7.48–6.90 (m, 8H), 6.72–6.70 (m, 2H), 2.58–2.33 (m, 3H), 1.94–1.46 (m, 4H), 1.29–1.23 (m, 5H), 1.06–0.97 (m, 4H), 0.86–0.83 (m, 3H), 0.76–0.71 (m, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 174.6, 173.0, 162.1, 148.8, 140.7, 139.3, 129.8, 129.5, 129.1, 128.8, 128.1, 127.7, 124.2, 123.8, 119.8, 119.6, 36.8, 36.5, 34.1, 31.3, 31.1, 30.9, 30.3, 26.0, 25.7, 25.2, 24.7, 22.4, 22.3, 22.2, 21.8, 14.4, 14.3, 14.1, 14.0; IR (KBr) ν 3062, 2956, 2860, 1687, 1655, 1594, 1492, 1289, 1249, 758, 697 cm^{-1}; MS (ESI) m/z 387.3 ($[M+Na]^+$); HRMS (ESI) calcd for $C_{24}H_{32}N_2O$ ($[M+Na]^+$), 387.2407; found, 387.2425.

*4.2.9. N-(Furan-2-yl(phenylimino)methyl)-N-phenylfuran-2-carboxamide (**2i**).* Ethyl acetate/Petroleum ether (1/4) was used as eluent. White solid; mp 149–150 °C; ^1H NMR (DMSO-d_6, 500 MHz) δ 7.93–7.80 (m, 1H), 7.70 (s, 1H), 7.43–7.17 (m, 6H), 7.07–7.01 (m, 2H), 6.78–6.37 (m, 6H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 160.8, 159.4, 150.1, 149.2, 148.0, 147.6, 147.1, 147.0, 146.8, 146.0, 145.2, 144.6, 140.6, 139.9, 129.8, 129.5, 129.4, 129.2, 127.5, 127.3, 127.0, 126.3, 125.1, 124.3, 120.3, 119.5, 118.8, 118.6, 118.3, 116.5, 113.2, 112.7, 112.6; IR (KBr) ν 3137, 3123, 1673, 1645, 1592, 1461, 1323, 1304, 1179, 753,

693 cm^{-1}; MS (ESI) *m/z* 357.0 ($[M+H]^+$); HRMS (ESI) calcd for $C_{22}H_{16}N_2O_3$ ($[M+H]^+$), 357.1234; found, 357.1238.

*4.2.10. N-(Thiophen-2-yl(p-tolylimino)methyl)-N-p-tolylthiophene-2-carboxamide (**2j**).* Ethyl acetate/Petroleum ether (1/3) was used as eluent for column chromatography. Yellow solid; mp 173–174 °C; ^1H NMR (DMSO-d_6, 500 MHz) δ 7.82–6.55 (m, 14H), 2.28–2.23 (m, 6H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 165.3, 163.4, 152.1, 149.1, 146.6, 144.8, 141.4, 139.1, 138.9, 137.4, 137.0, 134.6, 134.3, 133.8, 133.5, 133.0, 132.7, 132.5, 132.2, 131.7, 130.3, 130.2, 130.1, 129.8, 128.8, 128.1, 127.9, 127.5, 127.2, 125.4, 120.4, 119.3, 21.2, 21.0; IR (KBr) *v* 3094, 3073, 3018, 2922, 1647, 1624, 1510, 1412, 1355, 1238, 1110, 854, 817, 754, 745, 716 cm^{-1}; MS (ESI) *m/z* 416.8 ($[M+H]^+$); HRMS (ESI) calcd for $C_{24}H_{20}N_2OS_2$ ($[M+H]^+$), 417.1090; found, 417.1086.

4.3. Procedure for the synthesis of 4, 6, 7, 9, 11 and 13

A solution of Tf_2O (1.2 mmol) in DCM (0.4 mL) was added into a mixture of amide (1 mmol) and 2-ClPy (1.2 mmol) in DCM (1.6 mL) via a syringe at −78 °C. The reaction temperature was firstly kept at −78 °C for 5 min and raised to ambient temperature for 5 min. After the mixture was refluxed for 0.5 h, the reaction mixture was diluted with DCM (25 mL). Organic layer was then sequentially washed with saturated aqueous $CuSO_4$ solution (10 mL), water (10 mL) and brine (15 mL×2). Then dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography.

*4.3.1. N-Benzoyl-2-phenylbenzimidazole (**4a**).* Ethyl acetate/Petroleum ether (1/4) was used as eluent. White solid; mp 150–151 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.88 (d, *J*=7.6 Hz, 1H), 7.70 (d, *J*=8 Hz, 2H), 7.60 (m, 2H), 7.51 (t, *J*=7.6 Hz, 1H), 7.46 (d, *J*=8 Hz, 1H), 7.41–7.26 (m, 7H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.1, 154.0, 142.9, 134.9, 134.0, 133.1, 130.5, 130.4, 129.8, 129.2, 128.7, 128.3, 124.6, 124.5, 120.2, 113.1; IR (KBr) *v* 3058, 1702, 1598, 1451, 1334, 1286, 1226, 751 cm^{-1}; MS (ESI) *m/z* 299.1 ($[M+H]^+$); HRMS (ESI) calcd for $C_{20}H_{14}N_2O$ ($[M+H]^+$), 299.1179; found, 299.1190.

*4.3.2. N-(4-Chlorobenzoyl)-2-(4-chlorophenyl)benzimidazole (**4b**).* Ethyl acetate/Petroleum ether (1/3) was used as eluent. White solid; mp 185–186 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.87 (d, *J*=7.6 Hz, 1H), 7.67 (d, *J*=8 Hz, 2H), 7.55 (d, *J*=8 Hz, 2H), 7.40 (m, 4H), 7.32 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.8, 152.7, 142.9, 141.1, 136.3, 134.7, 131.9, 131.2, 130.4, 129.3, 128.8, 128.7, 125.0, 124.8, 120.4, 113.0; IR (KBr) *v* 3089, 3056, 1705, 1587, 1449, 1328, 1288, 1224, 758 cm^{-1}; MS (ESI) *m/z* 367.2 ($[M+H]^+$); HRMS (ESI) calcd for $C_{20}H_{12}Cl_2N_2O$ ($[M+H]^+$), 367.0398; found, 367.0415.

*4.3.3. N-Benzoyl-2-phenyl-5,6-dichlorobenzimidazole (**4c**).* Ethyl acetate/Petroleum ether (1/6) was used as eluent. White solid; mp 131–132 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.94 (s, 1H), 7.69 (s, 1H), 7.63 (m, 2H), 7.55 (m, 2H), 7.50 (m, 1H), 7.35–7.24 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.5, 155.5, 142.1, 134.4, 134.0, 132.3, 130.5, 130.3, 129.6, 129.2, 128.8, 128.7, 128.6. 128.5, 121.3, 114.6; IR (KBr) *v* 3102, 3062, 1695, 1599, 1438, 1323, 1297, 1280, 1224, 718, 693 cm^{-1}; MS (ESI) *m/z* 389.0 ($[M+Na]^+$); HRMS (ESI) calcd for $C_{20}H_{12}Cl_2N_2O$ ($[M+Na]^{+)}$, 389.0219; found, 389.0230.

*4.3.4. N-(4-Methylbenzoyl)-2-(4-methylphenyl)-5,6-dichlorobenzimidazole (**4d**).* Ethyl acetate/Petroleum ether (1/6) was used as eluent. White solid; mp 184–185 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.92 (s, 1H), 7.59 (d, *J*=8.4 Hz, 2H), 7.52 (s, 1H), 7.48 (d, *J*=8 Hz, 2H), 7.17 (d, *J*=8 Hz, 2H), 7.10 (d, *J*=7.6 Hz, 2H), 2.38 (s, 3H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.3, 155.8, 146.0, 142.3, 140.7, 134.1, 130.8, 129.6, 129.4, 129.2, 129.0, 128.2, 126.7, 121.1, 114.2, 21.8, 21.4; IR (KBr) *v* 3033, 1711, 1605, 1438, 1314, 1271, 1228, 1178, 828 cm^{-1}; MS (ESI) *m/z* 394.9 ($[M+H]^+$); HRMS (ESI) calcd for $C_{22}H_{16}Cl_2N_2O$ ($[M+H]^+$), 395.0712; found, 395.0715.

*4.3.5. N-Benzoyl-2-phenyl-5,6-dimethylbenzimidazole (**4e**).* Ethyl acetate/Petroleum ether (1/6) was used as eluent. White solid; mp 125–126 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.65 (m, 2H), 7.62 (s, 1H), 7.55 (m, 2H), 7.47 (t, *J*=7.6 Hz, 1H), 7.30 (t, *J*=8 Hz, 3H), 7.24 (m, 3H), 2.39 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.2, 153.1, 141.4, 134.0, 133.8, 133.4, 133.4, 133.3, 130.7, 130.4, 129.5, 129.1, 128.5, 128.2, 120.2, 113.4, 20.6, 20.3; IR (KBr) *v* 3061, 1697, 1598, 1448, 1325, 1281, 1226, 1176, 700 cm^{-1}; MS (ESI) *m/z* 327.0 ($[M+H]^+$); HRMS (ESI) calcd for $C_{22}H_{18}N_2O$ ($[M+H]^+$), 327.1492; found, 327.1489.

*4.3.6. N-(4-Chlorobenzoyl)-2-(4-chlorophenyl)-5,6-dimethylbenzimidazole (**4f**).* Ethyl acetate/Petroleum ether (1/6) was used as eluent. White solid; mp 213–214 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.64 (s, 1H), 7.61 (d, *J*=3.6 Hz, 2H), 7.50 (d, *J*=8.4 Hz, 2H), 7.35 (d, *J*=8.4 Hz, 2H), 7.27 (d, *J*=8.0 Hz, 2H), 7.21 (s, 1H), 2.39 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.0, 151.8, 141.3, 140.8, 135.9, 134.5, 133.8, 133.2, 131.8, 131.4, 130.3, 129.2, 129.0, 128.7, 130.4, 113.2, 20.6, 20.3; IR (KBr) *v* 3090, 3060, 1698, 1588, 1460, 1322, 1278, 1225, 1174, 1090, 845 cm^{-1}; MS (ESI) *m/z* 395.1 ($[M+H]^+$); HRMS (ESI) calcd for $C_{22}H_{16}Cl_2N_2O$ ($[M+H]^+$), 395.0712; found, 395.0713.

*4.3.7. N-(2-Methylbenzoyl)-2-(2-methylphenyl)benzimidazole (**4g**).* Ethyl acetate/Petroleum ether (1/3) was used as eluent. White solid; mp 113–114 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.85 (d, *J*=8 Hz, 1H), 7.49 (d, *J*=8 Hz, 1H), 7.42–7.39 (m, 1H), 7.34–7.31 (m, 1H), 7.27–7.22 (m, 2H), 7.19–7.02 (m, 6H), 2.36 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.8, 153.4, 142.8, 138.2, 136.9, 133.7, 133.7, 131.9, 131.2, 131.0, 130.2, 129.7, 129.5, 129.0, 125.4, 125.2, 124.9, 124.6, 120.2, 113.7, 20.0, 19.7; IR (KBr) *v* 3056, 2956, 1704, 1537, 1452, 1329, 1308, 1220, 1146, 934, 891, 764, 750 cm^{-1}; MS (ESI) *m/z* 327.1 ($[M+H]^+$); HRMS (ESI) calcd for $C_{22}H_{18}N_2O$ ($[M+H]^+$), 327.1492; found, 327.1489.

*4.3.8. N-Benzoyl-2-phenyl-6-methylbenzimidazole (**6a**) and N-Benzoyl-2-phenyl-5-methylbenzimidazole (**7a**).* Ethyl acetate/Petroleum ether (1/3) was used as eluent. White solid; mp 115–116 °C; ^1H NMR ($CDCl_3$, 400 MHz) (**6a**:**7a**=4:3, total 37H) δ 7.76–7.12 (m, 31H), 2.50 (s, 3H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.2, 169.1, 154.0, 153.4, 143.2, 141.0, 135.2, 134.9, 134.3, 133.8, 133.2, 133.2, 133.0, 130.6, 130.6, 130.5, 129.6, 129.6, 129.2, 129.1, 128.6, 128.6, 128.2, 126.0, 125.9, 120.0, 119.7, 113.0, 112.7, 21.8, 21.5; IR (KBr) *v* 3059, 3030, 2924, 2864, 1709, 1598, 1478, 1450, 1327, 1308, 1288, 1225, 1178, 906, 768, 698 cm^{-1}; MS (ESI) *m/z* 313.1 ($[M+H]^+$); HRMS (ESI) calcd for $C_{21}H_{16}N_2O$ ($[M+H]^+$), 313.1335; found, 313.1331.

*4.3.9. N-(2-Methylbenzoyl)-2-(2-methylphenyl)-5-chlorobenzimidazole (**6b**).* Ethyl acetate/Petroleum ether (1/6) was used as eluent. White solid; mp 109–110 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, *J*=8.8 Hz, 1H), 7.64 (s, 1H), 7.38 (d, *J*=8.8 Hz, 1H), 7.26–7.02 (m, 8H), 2.36 (s, 3H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.7, 154.0, 141.4, 138.3, 136.9, 134.3, 133.3, 132.1, 131.3, 130.8, 130.5, 130.3, 129.8, 129.7, 128.9, 125.4, 125.3, 125.2, 121.0, 114.1, 20.0, 19.7; IR (KBr) *v* 3087, 3021, 2959, 2927, 1705, 1600, 1484, 1457, 1308, 1257, 1217, 1150, 1079, 943, 903, 771, 735 cm^{-1}; MS (ESI) *m/z* 361.2 ($[M+H]^+$); HRMS (ESI) calcd for $C_{22}H_{17}ClN_2O$ ($[M+H]^+$), 361.1102; found, 361.1097.

*4.3.10. N-(2-Methylbenzoyl)-2-(2-methylphenyl)-6-chlorobenzimidazole (**7b**).* Ethyl acetate/Petroleum ether (1/6) was used

as eluent. White solid; mp 115–116 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, J=1.6 Hz, 1H), 7.47 (d, J=8.8 Hz, 1H), 7.31 (dd, J_1=1.6 Hz, J_2=8.8 Hz, 1H), 7.29–7.03 (m, 8H), 2.35 (s, 3H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.6, 154.6, 143.6, 138.3, 136.9, 133.4, 132.3, 132.1, 131.3, 130.5, 130.3, 130.2, 129.7, 128.9, 125.5, 125.2, 120.1, 114.6, 20.0, 19.6; IR (KBr) ν 3088, 3014, 2926, 1707, 1602, 1488, 1454, 1326, 1308, 1276, 1220, 1149, 906, 767, 739 cm^{-1}; MS (ESI) m/z 361.2 ([M+H]$^+$); HRMS (ESI) calcd for $C_{22}H_{17}ClN_2O$ ([M+H]$^+$), 361.1102; found, 361.1097.

*4.3.11. N-Benzoyl-2-phenyl-6-nitrobenzimidazole (**6c**).* Ethyl acetate/Petroleum ether (1/3) was used as eluent. White solid; mp 137–138 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.45 (s, 1H), 8.32 (d, J=8.8 Hz, 1H), 7.94 (d, J=8.8 Hz, 1H), 7.68 (d, J=8 Hz, 2H), 7.63 (d, J=8 Hz, 2H), 7.55 (t, J=7.6 Hz, 1H), 7.39–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.2, 158.2, 147.1, 144.7, 134.8, 134.4, 132.0, 130.8, 130.6, 139.4, 129.3, 129.0, 128.6, 120.3, 120.2, 109.8; IR (KBr) ν 3111, 2924, 2852, 1713, 1527, 1515, 1342, 1279, 1221, 902, 779, 734, 721 cm^{-1}; MS (ESI) m/z 344.4 ([M+H]$^+$); HRMS (ESI) calcd for $C_{20}H_{13}N_3O_3$ ([M+H]$^+$), 344.1030; found, 344.1022.

*4.3.12. N-Benzoyl-2-phenyl-5-nitrobenzimidazole (**7c**).* Ethyl acetate/Petroleum ether (1/3) was used as eluent. White solid; mp 146–147 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.76 (d, J=1.6 Hz, 1H), 8.24 (dd, J_1=2 Hz, J_2=8.8 Hz, 1H), 7.69 (d, J=8 Hz, 2H), 7.63–7.54 (m, 4H), 7.39–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.4, 156.9, 145.1, 142.6, 138.9, 134.8, 132.1, 130.7, 130.6, 129.3, 129.2, 129.0, 128.6, 120.0, 116.5, 113.0; IR (KBr) ν 3095, 3076, 2924, 2854, 1715, 1519, 1349, 1310, 1220, 1144, 928, 825, 742, 694 cm^{-1}; MS (ESI) m/z 344.3 ([M+H]$^+$); HRMS (ESI) calcd for $C_{20}H_{13}N_3O_3$ ([M+H]$^+$), 344.1030; found, 344.1022.

*4.3.13. (3aR,7aR)-1-Benzoyl-2-phenylhexahydrobenzimidazole (**9a**).* Ethyl acetate/Petroleum ether (1/2) was used as eluent. White solid; $[\alpha]_D^{20}$ +160.44 (c 1.0, DMF); mp 116–117 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.47–7.45 (m, 2H), 7.34–7.32 (m, 2H), 7.25–7.23 (m, 1H), 7.17–7.08 (m, 5H), 3.78–3.73 (m, 1H),3.52–3.46 (m, 1H), 2.60–2.57 (m, 1H), 2.47–2.44 (m, 1H), 1.95–1.86 (m, 2H), 1.62–1.39 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.4, 161.7, 135.4, 131.7, 131.2, 130.0, 129.1, 128.5, 128.0, 127.8, 126.9, 72.6, 70.4, 30.4, 29.2, 25.6, 24.4; IR (KBr) ν 3072, 2966, 2935, 2860, 1650, 1596, 1448, 1396, 1332, 1298, 1076, 782, 729, 695, 661 cm^{-1}; MS (ESI) m/z 305.1 ([M+H]$^+$); HRMS (ESI) calcd for $C_{20}H_{20}N_2O$ ([M+H]$^+$), 305.1648; found, 305.1644.

*4.3.14. (3aR,7aR)-1-(2-Methylbenzoyl)-2-(2-methylphenyl)hexahydrobenzimidazole (**9b**).* Ethyl acetate/Petroleum ether (1/3) was used as eluent. White solid; $[\alpha]_D^{20}$ +121.46 (c 1.0, DMF). Mp 260–261 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.12–6.84 (m, 8H), 3.69–3.64 (m, 1H), 3.51–3.45 (m, 1H), 2.72–2.41 (m, 2H), 2.27–2.24 (m, 6H), 1.95–1.88 (m, 2H), 1.63–1.44 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.0, 160.6, 136.1, 135.6, 135.4, 131.6, 130.4, 130.0, 129.6, 129.1, 128.0, 124.9, 124.8, 72.1, 68.9, 30.4, 29.1, 25.5, 24.4, 19.4, 19.3; IR (KBr) ν 3278, 3062, 3022, 2924, 2856, 1633, 1533, 1330, 1307, 743, 724, 688 cm^{-1}; MS (ESI) m/z 333.0 ([M+H]$^+$); HRMS (ESI) calcd for $C_{20}H_{24}N_2O$ ([M+H]$^+$), 333.1961; found, 333.1954.

*4.3.15. N-Benzoyl-2-phenylpyrimidine (**11a**).* Ethyl acetate/Petroleum ether (1/4) was used as eluent. Yellow solid; mp 151–152 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58 (d, J=7.6 Hz, 2H), 7.51 (d, J=8 Hz, 1H), 7.42 (m, 5H), 7.35 (t, J=7.2 Hz, 1H), 7.29 (t, J=8 Hz, 1H), 7.22–7.14 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.0, 154.0, 140.6, 137.4, 135.9, 135.6, 134.6, 133.0, 130.0, 129.2, 128.5, 128.4, 128.2, 128.0, 127.5, 123.2, 121.8, 121.0, 118.9, 107.7; IR (KBr) ν 3057, 1710,1626, 1582, 1450, 1328, 1244, 1180, 1145, 1090, 769 cm^{-1}; MS (ESI) m/z 349.2 ([M+H]$^+$); HRMS (ESI) calcd for $C_{24}H_{16}N_2O$ ([M+H]$^+$), 349.1335; found, 349.1340.

*4.3.16. N-(4-Chlorobenzoyl)-2-(4-chlorophenyl) pyrimidine (**11b**).* Ethyl acetate/Petroleum ether (1/4) was used as eluent. Yellow solid; mp 156–157 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53 (m, 3H), 7.48–7.40 (m, 5H), 7.30 (t, J=8 Hz, 1H), 7.22 (m, 4H), 7.18 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.7, 152.6, 140.1, 139.7, 136.5, 135.8, 135.5, 134.5, 133.8, 130.6, 129.3, 129.1, 128.9, 128.3, 127.5, 123.8, 122.2, 120.9, 119.4, 108.3; IR (KBr) ν 3057, 1680,1625, 1579, 1489, 1323, 1255, 1088, 824 cm^{-1}; MS (ESI) m/z 417.0 ([M+H]$^+$); HRMS (ESI) calcd for $C_{24}H_{14}Cl_2N_2O$ ([M+H]$^+$), 417.0556; found, 417.0571.

*4.3.17. 2-Phenyl-3-(phenylimino)isoindol-1-one (**13**).* Ethyl acetate/Triethylamine/Petroleum ether (1/1/6) was used as eluent for column chromatography. Yellow solid; mp 150–151 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, J=7.6 Hz, 1H), 7.59 (t, J=7.2 Hz, 1H), 7.53 (m, 4H), 7.38 (m, 4H), 7.19 (t, J=7.2 Hz, 1H), 6.97 (d, J=7.2 Hz, 2H), 6.67 (d, J=7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.1, 151.2, 148.7, 133.3, 133.0, 132.2, 132.1, 129.4, 129.3, 128.9, 128.0, 127.9, 125.8, 124.1, 123.8, 119.6; IR (KBr) ν 3059, 1741,1679, 1597, 1492, 1384, 1184, 1127, 707 cm^{-1}; MS (ESI) m/z 321.2 ([M+Na]$^+$); HRMS (ESI) calcd for $C_{20}H_{14}N_2O$ ([M+Na]$^+$), 321.0998; found, 321.0999.

4.4. Procedure for the synthesis of 14

The mixture of amidine **2** (1 mmol) in DCM (10 mL) and excess hydrazine hydrate was stirred over night and then diluted with DCM (10 mL). The solution was washed with water (20 mL) and the aqueous layer was extracted with DCM (10 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, concentrated under reduced pressure, and subjected to flash chromatography using ethyl acetate/petroleum ether (1/4) as eluent.

*4.4.1. N,N′-Diphenylbenzamidine (**14a**).* White solid; mp 150–151 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 9.25 (s, 1H), 7.92 (d, J=7.5 Hz, 2H), 7.31 (s, 7H), 7.03 (d, J=6.5 Hz, 2H), 6.99 (d, J=6.0 Hz, 1H), 6.76 (d, J=6.0 Hz, 1H), 6.60 (d, J=6.5 Hz, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 155.2, 151.1, 141.9, 135.3, 129.4, 128.8, 128.5, 122.8, 122.4, 121.4, 120.0; IR (KBr) ν 3301, 3055, 1626, 1588, 1536, 1486, 1441, 1333, 1223, 758, 699 cm^{-1}; MS (ESI) m/z 273.3 ([M+H]$^+$); HRMS (ESI) calcd for $C_{19}H_{16}N_2$ ([M+H]$^+$), 273.1386; found, 273.1374.

*4.4.2. N,N′-Bis(4-methyl)phenylbenzamidine (**14b**).* White solid; mp 134–135 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 9.05 (s, 1H), 7.77 (d, J=7.5 Hz, 2H), 7.30 (d, J=3.5 Hz, 3H), 7.27 (d, J=4.5 Hz, 2H), 7.08 (d, J=7.5 Hz, 2H), 6.83 (d, J=7.5 Hz, 2H), 6.46 (d, J=7.5 Hz, 2H) 2.25 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 155.1, 148.6, 139.5, 135.5, 131.0, 129.7, 129.4, 129.3, 129.2, 128.5, 122.6, 120.0, 21.0, 20.8; IR (KBr) ν 3367, 3022, 2922, 1625, 1592, 1526, 1505, 1335, 1218, 1101, 821, 701 cm^{-1}; MS (ESI) m/z 300.9 ([M+H]$^+$); HRMS (ESI) calcd for $C_{21}H_{20}N_2$ ([M+H]$^+$), 301.1699; found, 301.1695.

*4.4.3. N,N′-Bis(4-methylphenyl)thiophene-2-carboximidamide (**14c**).* Yellow solid; mp 118–119 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 9.04 (s, 1H), 7.66–6.54 (m, 11H), 2.21 (s, 6H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 148.6, 148.1, 139.1, 134.8, 131.3, 130.4, 129.5, 129.3, 126.9, 122.0, 120.4, 20.9; IR (KBr) ν 3281, 3090, 3025, 2919, 2863, 1590, 1518, 1421, 1318, 1241, 1219, 852, 817, 712 cm^{-1}; MS (ESI) m/z 307.0

($[M+H]^+$); HRMS (ESI) calcd for $C_{19}H_{18}N_2S$ ($[M+H]^+$), 307.1263; found, 307.1254.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2009.12.034.

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