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"One-pot" access to dihydrofurans *via* tandem oxidative difunctionalization and ring contraction of aminopyrans†

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An operationally simple and efficient protocol for the construction of dihydrofuran derivatives has been accomplished *via* a sequential addition of *N*-chlorosuccinimide and a base to 2-amino-4*H*-pyran derivatives in alcohol medium. The one-pot protocol proceeding *via* tandem oxidative difunctionalization and ring contraction provides an entirely new strategy for the construction of the dihydrofuran skeleton.

Introduction

Aminopyrans are attention worthy heterocyclic molecules due to their unique applications in the field of synthetic organic chemistry,[1] cosmetics,[2] agrochemicals[3] and medicinal chemistry.[4] They are allied with numerous types of biological activities such as antimicrobial,[5] anticancer,[6] anti-inflammatory,[7] fungicidal,[8] molluscicidal,[9] anticonvulsant,[10] inhibitors of human Chk1 kinase,[11] *etc.*, which sustains the interest in this class of molecules. In recent years though a great effort has gone into improvising synthetic procedures for easy access to aminopyrans, they are largely handicapped by the unusual reactivity and weak stability of the aminopyran ring towards many reagents. The pyran ring is known to open and recyclize in the presence of a variety of reagents such as strong acids, bases, nucleophiles, *etc.* From this perspective, our laboratory has been actively pursuing the synthesis and reactivity of these versatile substrates. Recently a mild method for oxidative difunctionalization of 2-amino-4*H*-pyrans has been developed by our group employing iodobenzene diacetate (IBD) and *N*-chlorosuccinimide (NCS) in an alcoholic medium.[12] Herein 2-amino-4*H*-pyrans are shown to undergo geminal dialkoxylation with an unusual 1,2-amino migration in the presence of iodobenzene diacetate and addition of chlorine and alkoxy groups takes place across the chromene double bond when NCS is employed.

Attention is now focused on the newly functionalized derivatives. It is envisioned that 2-amino-3-chloro-2-alkoxy-4-aryl-2,3-dihydro-4*H*-benzo[*h*]chromene-3-carbonitrile analogs might be good substrates for base catalyzed dehydrohalogenation. Since the chemical reactivity of the pyran ring towards strong bases such as alcoholic NaOH–KOH is well known[13] (*i.e.*, ring opening and recyclization to 2-alkoxypyridines), a deliberate usage of mild bases was envisaged for dehydrohalogenation.

Results and discussion

To begin with, the dehydrohalogenation was attempted on **2a** (2-amino-3-chloro-2-ethoxy-4-phenyl-2,3-dihydro-4*H*-benzo[*h*]-chromene-3-carbonitrile) with piperidine as a base in solvent methanol at room temperature. The reaction mixture turned to a clear brown colored solution, followed by the precipitation of product after 10 hours. The spectral data of the product showed some unusual features. In the ^{1}H-NMR spectra of starting material **2a**, the pyran (4*H*) proton which is observed as a singlet (δ = 4.91 ppm) is deshielded (δ = 5.17 ppm) for the product (Fig. 1). Similarly the $-OCH_2$ protons of the ethoxy group in **2a** appeared as two multiplets integrating for one proton each (δ = 4.10–4.01 and δ = 3.68–3.60 ppm, respectively), indicating that they are diastereotopic and attached to an sp^3 chiral carbon. However in the product the $-OCH_2$ protons of the ethoxy group appear only as a multiplet integrating for two protons (δ = 4.50–4.38 ppm). A new distinct singlet in the downfield region (δ = 8.17 ppm) is indicative of an –NH proton.

Mass spectrometry showed the molecular ion peak [M + H] at $m/z \sim 343$ and no [M + 2] peak indicating the loss of a chlorine atom in the form of HCl. Since the pyran (4*H*) proton is intact, it was concluded that a proton was lost from the $-NH_2$

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†Electronic supplementary information (ESI) available: Copies of ^{1}H and ^{13}C NMR spectra of all the new compounds and CIF files for the compounds **3h** and **6**. CCDC 938721 and 938722. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ob00324a

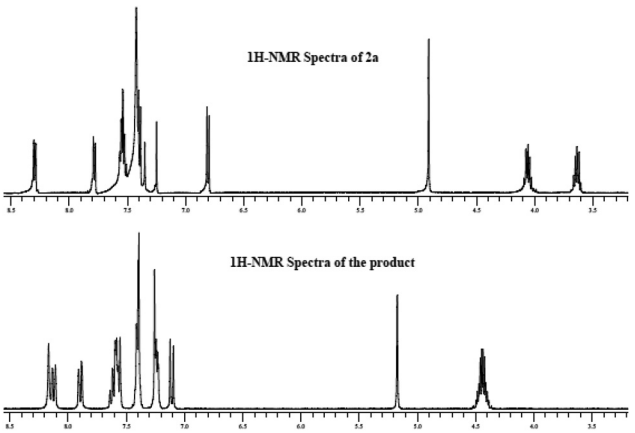


Fig. 1 Comparison of ^{1}H-NMR spectra of the product with the substrate.

group and therefore the product should either have structure A or structure B (Fig. 2).

Owing to the fact that the ethoxy group is still attached to one of the diastereomeric centres in structure A, the change in the $-OCH_2$ protons in ^{1}H-NMR pattern cannot be accounted for, thus ruling out structure A as the product. In structure B, the ethoxy group is directly attached to an sp^2 hybridized carbon, which indicates that only one signal should appear for the $-OCH_2$ protons. However, the appearance of a multiplet signal instead of a clear quartet in the ^{1}H-NMR spectrum indicates that the multiplicity of the $-OCH_2$ protons in structure B is probably due to the influence of the asymmetric quaternary carbon of the dihydrofuran system. Since structure B satisfies the ^{1}H-NMR spectral parameters, it is inferred that 2,3-dihydrofuran is indeed the product formed. Additional proof for the 2,3-dihydrofuran system was obtained from the X-ray crystallography data.

Encouraged by these results the standardization of the reaction protocol was carried out in an alcoholic medium by employing various organic and inorganic bases (Table 1). When pyridine and imidazole were used as the bases, the progress of reaction was negligible even after 48 hours. The reaction proceeded to completion in 12 hours when triethylamine was used as the base. In case of piperidine the reaction proceeds to completion in 10 hours with better yields. Inorganic bases especially carbonates did not facilitate the rearrangement. Even though the reaction was rapid in alcoholic potassium hydroxide, yields were comparatively poor due to the formation of side products.

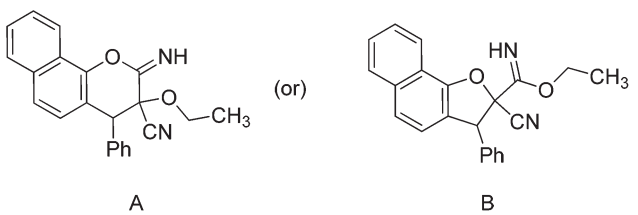
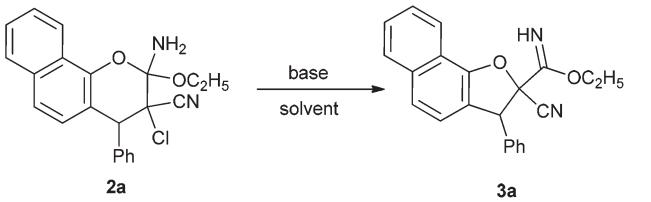


Fig. 2 Expected structures for the product.

Table 1 Optimization of reaction conditions[a] on highly functionalized pyran derivatives



2a 3a

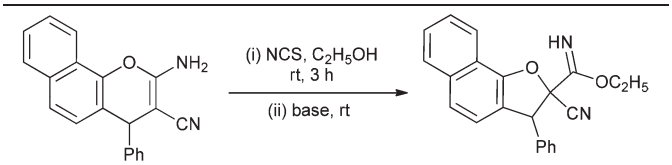
Entry	Base	Solvent	Time	Yield (%) of **3a**
1	Pyridine	MeOH	48 h	—
2	Imidazole	MeOH–EtOH	48 h	—
3	Triethylamine (TEA)	MeOH–EtOH	12 h	70
4	Piperidine	MeOH–EtOH	10 h	78
5	K_2CO_3	MeOH	24 h	—
6	Na_2CO_3	MeOH	24 h	—
7	$NaHCO_3$	MeOH	24 h	—
8	Alc. KOH[b]	—	20 min	62
9	Alc. KOH[c]	—	30 min	77

[a] Conditions: **2a** (1 mmol), base (1.1 mmol), rt. [b] 1 N methanolic KOH (1 mmol) was used. [c] 0.1 N methanolic KOH (1 mmol) was used.

Further, to simplify and broaden the optimization studies we have directed our focus on to the one-pot multicomponent protocol with 2-amino-4*H*-pyran analogs as starting materials. A sequential addition of NCS followed by the addition of piperidine in alcohol medium without isolating the 2-amino-3-chloro-2-alkoxy-benzo[*h*]chromene-3-carbonitrile analogs was attempted to check the feasibility of the one-pot approach. In congruence with the anticipation, the one-pot oxidative difunctionalization followed by the ring contraction was facile and aminopyran **1a** was transformed to dihydrofuran **3a** in high yield (Table 2).

Once the optimized reaction conditions were established (Table 2, entries 1 & 4), the scope of the one-pot protocol was scrutinized by varying the aryl substituent on the aminopyran

Table 2 Optimization of reaction conditions under one-pot conditions[a]



1a 3a

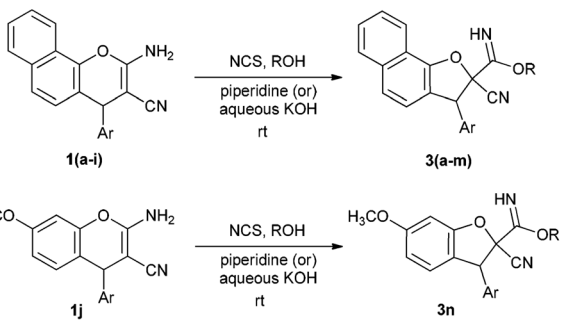
Entry	Base	Time[b]	Yield (%) of **3a**
1	Piperidine	5 h	77
2	Triethylamine (TEA)	6 h	70
3	Pyridine	24 h	—
4	Aqueous KOH[c]	5 h	76
5	Methanolic KOH[d]	6 h	Mixture of products

[a] Conditions: **1** (5 mmol), NCS (5.5 mmol), base (6 mmol), rt. [b] Reaction time for the base to carry out the transformation. [c] 1 N aqueous KOH (10 mmol) was used. [d] 1 N methanolic KOH (6 mmol) was used.

derivative employing piperidine as a base and an alcohol as the solvent. It is worth mentioning that a variety of aryl substitutions both electron rich and electron deficient are tolerated. Heteroaryl substituents like thiophen-2-yl and pyridin-3-yl also bestowed the desired products **3c**, **3f** and **3k**, respectively, in satisfactory yields (Scheme 1).

Furthermore, the versatility of this method was extended by carrying out a one-pot reaction on amino-1*H*-pyrans. Under optimized reaction conditions, a sequential addition of NCS followed by the addition of piperidine led to the formation of the dihydrofurans **5(a–d)** from **4(a–d)**, respectively, in satisfactory yields irrespective of the aryl ring substituent (Scheme 2).

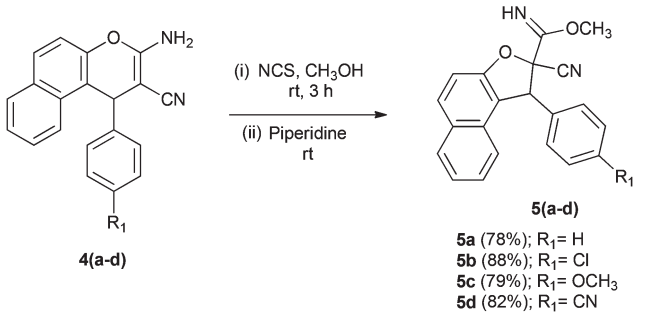
On the basis of the above experimental observations, a mechanistic rationale for the ring contraction of a pyran to a dihydrofuran has been arrived at (Scheme 3). Initially aminopyran undergoes oxidative difunctionalization with NCS in the presence of an alcohol solvent.[12] Subsequent addition of base to the aminopyran leads to proton abstraction from the amino group. This leads to a cascade pyran ring opening by the cleavage of the (C_2–O_1) bond, and ring closure of the (O_1–C_3) bond to dihydrofuran *via* elimination of HCl. The sequential elementary processes lead to formation of the ring contracted dihydrofuran carbimidate ester.



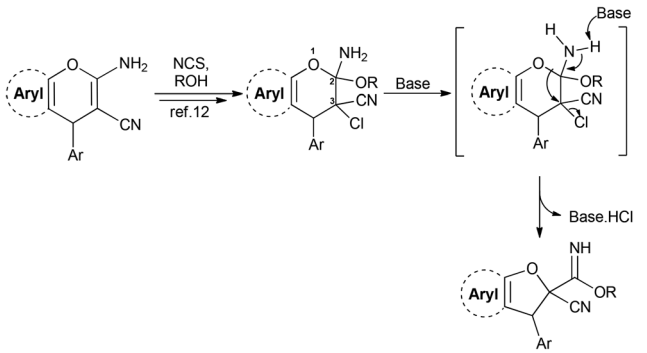
Substrate	Ar	R	Product	Yield (%)[a]	Yield (%)[b]
1a	C_6H_5	C_2H_5	**3a**	77	76
1b	4-ClC_6H_4	C_2H_5	**3b**	80	80
1c	thiophen-2-yl	C_2H_5	**3c**	83	81
1a	C_6H_5	$CH(CH_3)_2$	**3d**	79	75
1a	C_6H_5	CH_3	**3e**	81	79
1c	thiophen-2-yl	CH_3	**3f**	80	76
1d	4-$NO_2C_6H_4$	CH_3	**3g**	90	87
1b	4-ClC_6H_4	CH_3	**3h**	86	84
1e	4-$CH_3C_6H_4$	CH_3	**3i**	78	75
1f	4-BrC_6H_4	CH_3	**3j**	86	81
1g	pyridin-3-yl	CH_3	**3k**	83	78
1h	4-CNC_6H_4	CH_3	**3l**	85	72
1i	4-FC_6H_4	CH_3	**3m**	86	81
1j	4-ClC_6H_4	---	**3n**	69	68

Substrate in 5 mmol scale. [a] *Isolated yields of product with piperidine (6 mmol) as a base in corresponding alcohol solvent and rt stirring for 5 hours.* [b] *Isolated yields of product with 1N aqueous KOH (10 mmol) as a base and rt stirring for 5 hours*

Scheme 1 Synthesis of dihydrofurans from 4*H*-pyran derivatives.



Scheme 2 One-pot synthesis of dihydrofurans from amino-1*H*-pyran derivatives.

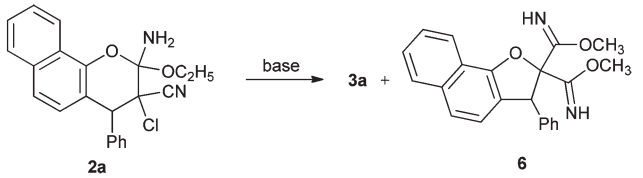


Scheme 3 Plausible mechanism for the formation of dihydrofurans.

Attention was focused on the alcoholic KOH reactions where the formation of more than one product was observed. The minor product was identified as the compound formed by partial hydrolysis of the cyanide group, probably due to the basicity of alcoholic KOH. A detailed study was attempted on the variation of the product ratios by varying both the number of equivalents and concentration of alcoholic KOH. It was found that 0.1 N methanolic KOH (Table 3, entry 3) was best suited for formation of product **3a** exclusively by restricting the cyanide hydrolysis. It was observed that when an excess amount of methanolic KOH was used as a base (Table 3, entry 5), ethyl 2-cyano-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-2-carbimidate (**3a**) formed initially (monitored by TLC) was completely converted into dimethyl 3-phenylnaphtho[1,2-*b*]furan-2,2(3*H*)-bis(carbimidate) (**6**). However, the methanolic KOH transformations were not extendable to one-pot tandem oxidative difunctionalization and ring contraction.

With the optimized conditions in hand, for alcoholic KOH ring contraction reactions, highly functionalized pyran derivative compounds like **2a**, **2b**, **2e** and **2f** were treated with 1 N methanolic KOH (3 mmol) to obtain the products **6**, **7**, **8** and **9**, respectively, in good yields. An additional feature observed

Table 3 Optimization of reaction under methanolic KOH conditions

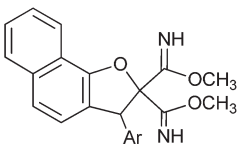


2a 6

Entry	Base	Time	Yield (%) of product 3a	6
1	Methanolic KOH[a]	20 min	62	20
2	Methanolic KOH[b]	30 min	70	14
3	**Methanolic KOH[c]**	**30 min**	77	Traces
4	Methanolic KOH[d]	45 min	70	Traces
5	**Methanolic KOH[e]**	**36 h**	–	**75**

Substrate (**2a**) in 1 mmol scale. [a] 1 N methanolic KOH (1 mmol) was used. [b] 0.5 N methanolic KOH (1 mmol) was used. [c] 0.1 N methanolic KOH (1 mmol) was used. [d] 0.05 N methanolic KOH (1 mmol) was used. [e] 1 N methanolic KOH (3 mmol) was used.

in these reactions was transesterifications which were prevalent whenever the alkoxy group of carbimidate ester and alcoholic solvent were different (Fig. 3).



(6-9)

6 (75%); Ar = C_6H_5
7 (72%); Ar = 4-ClC_6H_4
8 (70%); Ar = 4-$CH_3C_6H_4$
9 (73%); Ar = thiophen-2-yl

Fig. 3 Substrate scope of transesterified products.

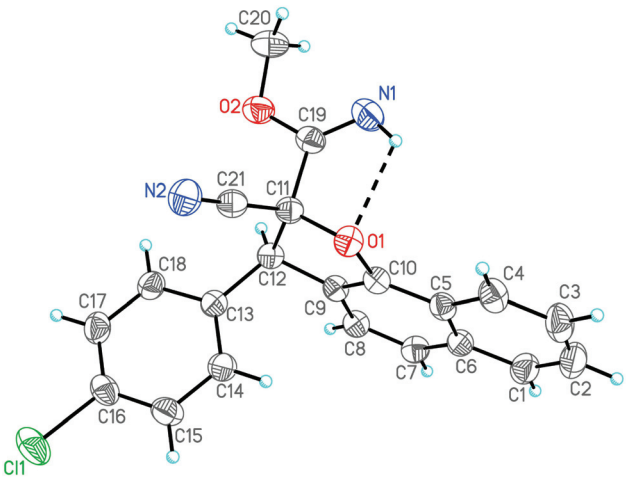


Fig. 4 The ORTEP diagram of **3h** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius. An intramolecular N–H···O hydrogen bond is indicated by dotted lines [bond distances N1–H1, H1N···O1, N1···O1 and angle ∠N1–H1N···O1 parameters are 0.90 Å, 2.22 Å, 2.720(2) Å and 114°, respectively].

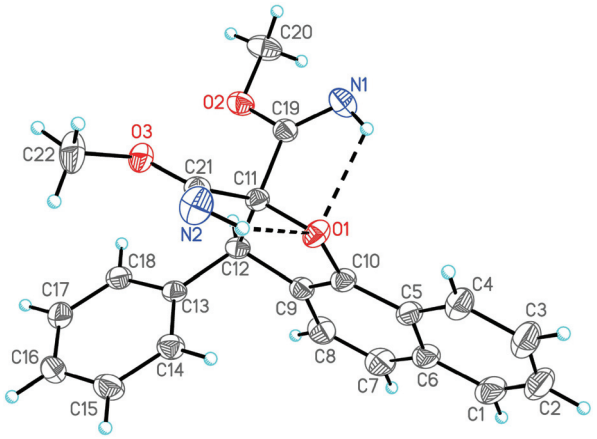
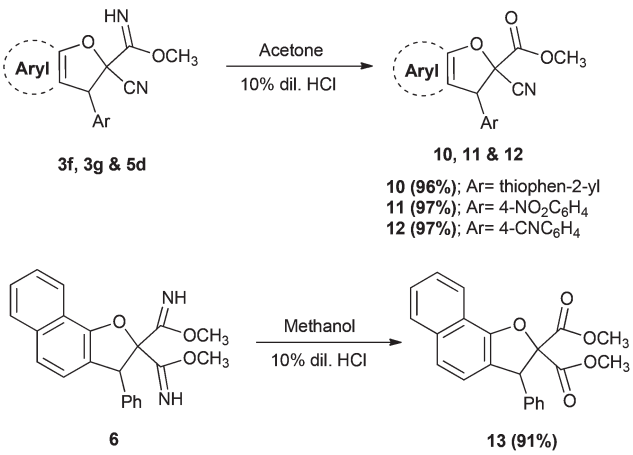


Fig. 5 The ORTEP diagram of **6** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius. The two intramolecular N–H···O hydrogen bonds are indicated by dotted lines [bond distances N–H, H···O, N···O and angle ∠N–H···O parameters are 0.87 Å, 2.26 Å, 2.722(2) Å, 116° for N1–H1N···O1 and 0.91 Å, 2.21 Å, 2.707(2) Å, 114° for N2–H2N···O1, respectively].

Arene ring fused furans or dihydrofurans are found in a wide range of natural products and as a key structural unit in many of the biologically and pharmaceutically active organic molecules.[14–16] Many approaches for the construction of this class of compounds are available in literature.[17] However, the construction of a dihydrofuran ring by contraction of pyran ring has no precedence in the literature. Even more unusual is the presence of a stable carbimidate ester, which is due to the hydrogen bonding between the proton of the carbimidate (–NH) and the oxygen of the dihydrofuran ring. Further, conclusive proof for the carbimidate ester of dihydrofuran and a transesterified product was obtained from X-ray crystallography data of **3h** and **6**, respectively (Fig. 4 and 5).

The carbimidate ester could be cleaved to a simple ester in a facile manner with 10% dil. HCl in acetone or methanol solvent (Scheme 4).



Scheme 4 Hydrolysis of carbimidate ester.

Conclusions

In summary, a novel and efficient methodology for the construction of dihydrofuran derivatives has been achieved by tandem oxidative difunctionalization and ring contraction of aminopyran analogs. The protocol illustrates the atypical reactivity of 4*H*-pyrans with *N*-chlorosuccinimide and base under one-pot conditions. In depth investigation of the methodology focussed on various basic media led to the accomplishment of some unusual dihydrofuran frameworks.

Experimental

General consideration

All reactions were performed under RT conditions and open to air. Melting points were determined in open capillary tubes and are uncorrected. ^{1}H NMR (300 MHz, 500 MHz) and ^{13}C NMR (75 MHz, 125 MHz) spectra were recorded in $CDCl_3$. Chemical shifts are given in δ values referenced to the solvent. All the yields mentioned in the data are that of isolated crude products unless otherwise mentioned. However the recrystallizations of the products were carried out from methanol or ethanol.

General procedure for preparation of starting materials [1(a–j)]. All the substrates **1(a–i)** were prepared according to our reported procedure.[12] Compound **1j** was prepared according to the procedure reported in literature.[18]

General procedure for the synthesis of compounds 3(a–n). *With piperidine as a base*: to a suspension of the 2-amino-4*H*-pyran analog (5 mmol) in alcohol (10 mL), *N*-chlorosuccinimide (5.5 mmol) was added at room temperature. After 3 hours of stirring, piperidine (6 mmol) was added and stirred at the same temperature for 5–6 hours, till the product is completely precipitated out. The reaction mixture was filtered, and washed with ethanol to separate the desired product (or) recrystallized from ethanol to afford the pure product [**3(a–n)**].

With aqueous KOH as a base: to a suspension of the 2-amino-4*H*-pyran analog (5 mmol) in alcohol (10 mL), *N*-chlorosuccinimide (5.5 mmol) was added at room temperature. After 3 hours of stirring, 1 N aqueous KOH (10 mmol) solution was added and the resulting mixture was stirred at the same temperature for 6 hours. After the completion of the reaction as indicated by TLC, 10 mL of water was added to the reaction mixture. The solid product was filtered, and washed with ethanol to give the desired product (or) recrystallized from ethanol to afford the pure product [**3(a–n)**].

From highly functionalized pyran derivatives: to the highly functionalized pyran analog[12] [5 mmol], in ethanol (10 mL), piperidine (6 mmol) was added at room temperature. The reaction mixture was stirred at room temperature, till the product is completely precipitated out. The reaction mixture was filtered and recrystallized from ethanol to afford the pure product.

*Ethyl 2-cyano-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-2-carbimidate (**3a**).* Yield: 1.32 g (77%); mp 164–166 °C; IR (neat, cm^{-1}) 3318, 2983, 1968, 1675, 1375, 858; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.17 (s, 1H), 8.12 (d, J = 7.5 Hz, 1H), 7.89 (d, J = 8.3 Hz, 1H), 7.65–7.53 (m, 3H), 7.43–7.36 (m, 3H), 7.27–7.21 (m, 2H), 7.11 (d, J = 8.3 Hz, 1H), 5.17 (s, 1H), 4.50–4.38 (m, 2H), 1.45 (t, J = 7.5 & 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 164.4, 152.6, 137.1, 134.5, 129.3, 128.9, 128.8, 127.0, 126.7, 123.7, 122.0, 121.0, 120.1, 119.6, 114.3, 85.1, 64.0, 58.9, 14.0; MS (ESI): m/z 343 $(M + H)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{22}H_{19}N_2O_2$ $(M + H)^+$ 343.1441, found 343.1431.

*Ethyl 2-cyano-3-(4-chlorophenyl)-2,3-dihydronaphtho[1,2-*b*]-furan-2-carbimidate (**3b**).* Yield: 1.50 g (80%); mp 101–103 °C; IR (neat, cm^{-1}) 3315, 2989, 1908, 1665, 1386, 859; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.19 (s, 1H), 8.11 (d, J = 7.5 Hz, 1H), 7.90 (d, J = 7.1 Hz, 1H), 7.65–7.54 (m, 3H), 7.38 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.3 Hz, 1H), 5.15 (s, 1H), 4.44 (qd, J = 7.2 & 2.2 Hz, 2H), 1.45 (t, J = 7.2 & 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.1, 152.7, 135.6, 134.9, 134.7, 130.6, 129.1, 128.1, 127.2, 126.8, 124.0, 121.7, 121.0, 120.1, 119.1, 114.2, 84.8, 64.0, 58.3, 14.0; MS (ESI): m/z 377 $(M + H)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{22}H_{18}N_2O_2Cl$ $(M + H)^+$ 377.1051, found 377.1048.

*Ethyl 2-cyano-3-(thiophen-2-yl)-2,3-dihydronaphtho[1,2-*b*]-furan-2-carbimidate (**3c**).* Yield: 1.44 g (83%); mp 153–155 °C; IR (neat, cm^{-1}) 3317, 2983, 1677, 1376, 853; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.17 (s, 1H), 8.11 (d, J = 8.7 Hz, 1H), 7.90 (d, J = 8.7 Hz, 1H), 7.63–7.56 (m, 3H), 7.37 (dd, J = 5.0 & 1.4 Hz, 1H), 7.27–7.24 (m, 1H), 7.09–7.05 (m, 2H), 5.45 (s, 1H), 4.45 (m, J = 7.2 & 4.2 Hz, 2H), 1.48 (t, J = 7.2 & 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.0, 152.4, 139.7, 134.8, 128.2, 128.1, 127.3, 127.2, 126.8, 126.7, 123.7, 121.9, 121.1, 120.1, 119.0, 114.0, 85.1, 64.1, 53.9, 14.0; MS (ESI): m/z 349 $(M + H)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{20}H_{17}N_2O_2S$ $(M + H)^+$ 349.1005, found 349.0997.

*Isopropyl 2-cyano-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-2-carbimidate (**3d**).* Yield: 1.40 g (79%); mp 170–172 °C; IR (neat, cm^{-1}) 3322, 2980, 1970, 1669, 1338, 846; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.15 (s, 1H), 8.12 (d, J = 7.9 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.63–7.54 (m, 3H), 7.43–7.38 (m, 3H), 7.26–7.21 (m, 2H), 7.10 (d, J = 8.4 Hz, 1H), 5.30 (sep, J = 6.2 Hz, 1H), 5.14 (s, 1H), 1.46 (d, J = 6.2 Hz, 3H), 1.40 (d, J = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 163.8, 152.7, 137.2, 134.6, 129.3, 128.9, 128.8, 128.1, 127.0, 126.7, 123.7, 122.1, 121.1, 120.2, 119.6, 114.4, 85.2, 71.2, 58.9, 21.6, 21.2; MS (ESI): m/z 357 $(M + H)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{23}H_{21}N_2O_2$ $(M + H)^+$ 357.1598, found 357.1588.

*Methyl 2-cyano-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-2-carbimidate (**3e**).* Yield: 1.33 g (81%); mp 154–155 °C; IR (neat, cm^{-1}) 3300, 2995, 1960, 1675, 1381, 722; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.21 (s, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.63–7.54 (m, 3H), 7.41–7.36 (m, 3H), 7.25–7.20 (m, 2H), 7.10 (d, J = 8.1 Hz, 1H), 5.16 (s, 1H), 4.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.0, 152.5, 137.0, 134.5, 129.2, 128.8, 128.0, 127.0, 126.7, 123.8, 121.9, 120.9, 120.0, 119.6, 114.2, 85.0, 58.8, 55.1; MS (ESI): m/z 329 $(M + H)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{21}H_{17}N_2O_2$ $(M + H)^+$ 329.1284, found 329.1284.

*Methyl 2-cyano-3-(thiophen-2-yl)-2,3-dihydronaphtho[1,2-b]furan-2-carbimidate (**3f**).* Yield: 1.33 g (80%); mp 176–178 °C; IR (neat, cm^{-1}) 3316, 2952, 1901, 1670, 1342, 865; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.22 (s, 1H), 8.11 (d, J = 7.1 Hz, 1H), 7.90 (d, J = 7.1 Hz, 1H), 7.65–7.54 (m, 3H), 7.39–7.34 (m, 1H), 7.28–7.22 (m, 1H), 7.10–7.05 (m, 2H), 5.45 (s, 1H), 4.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.7, 152.4, 139.6, 134.8, 128.2, 128.1, 127.4, 127.2, 126.8, 126.7, 123.8, 121.9, 121.1, 120.1, 119.1, 113.9, 85.1, 55.1, 53.8; MS (ESI): m/z 335 $(M + H)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{19}H_{15}N_2O_2S$ $(M + H)^+$ 335.0848, found 335.0844.

*Methyl 2-cyano-3-(4-nitrophenyl)-2,3-dihydronaphtho[1,2-b]furan-2-carbimidate (**3g**).* Yield: 1.68 g (90%); mp 185–187 °C; IR (neat, cm^{-1}) 3325, 2946, 1960, 1670, 1379, 817; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.30 (s, 1H), 8.27 (d, J = 8.3 Hz, 2H), 8.13 (d, J = 8.3 Hz, 1H), 7.92 (d, J = 6.8 Hz, 1H), 7.68–7.57 (m, 3H), 7.44 (d, J = 8.3 Hz, 2H), 7.06 (d, J = 8.3 Hz, 1H), 5.29 (s, 1H), 4.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.1, 152.8, 148.1, 144.1, 134.8, 130.3, 128.1, 127.5, 127.1, 124.4, 124.0, 121.3, 121.0, 120.1, 118.3, 113.9, 84.3, 58.2, 55.3; MS (ESI): m/z 374 $(M + H)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{21}H_{16}N_3O_4$ $(M + H)^+$ 374.1135, found 374.1136.

*Methyl 3-(4-chlorophenyl)-2-cyano-2,3-dihydronaphtho[1,2-b]furan-2-carbimidate (**3h**).* Yield: 1.55 g (86%); mp 150–152 °C; IR (neat, cm^{-1}) 3330, 2950, 1993, 1669, 1327, 816; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.23 (s, 1H), 8.11 (d, J = 7.5 Hz, 1H), 7.90 (d, J = 7.5 Hz, 1H), 7.66–7.55 (m, 3H), 7.38 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.3 Hz, 1H), 5.14 (s, 1H), 4.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.8, 152.6, 135.5, 135.0, 134.7, 130.6, 129.2, 128.1, 127.2, 126.8, 124.0, 121.7, 121.0, 120.1, 119.1, 114.1, 84.8, 58.2, 55.2; MS (ESI): m/z 363 $(M + H)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{21}H_{16}N_2O_2Cl$ $(M + H)^+$ 363.0894, found 363.0901.

*Methyl 2-cyano-3-(4-methylphenyl)-2,3-dihydronaphtho[1,2-b]furan-2-carbimidate (**3i**).* Yield: 1.33 g (78%); mp 118–120 °C; IR (neat, cm^{-1}) 3330, 2949, 1907, 1668, 1380, 861; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.20 (s, 1H), 8.11 (d, J = 7.7 Hz, 1H), 7.88 (d, J = 7.3 Hz, 1H), 7.65–7.52 (m, 3H), 7.25–7.06 (m, 5H), 5.13 (s, 1H), 4.00 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.1, 152.5, 138.7, 134.5, 134.0, 129.6, 129.1, 128.1, 127.0, 126.7, 123.7, 122.0, 121.0, 120.1, 119.8, 114.3, 85.2, 58.6, 55.1, 21.2; MS (ESI): m/z 343 $(M + H)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{22}H_{19}N_2O_2$ $(M + H)^+$ 343.1441, found 343.1445.

*Methyl 3-(4-bromophenyl)-2-cyano-2,3-dihydronaphtho[1,2-b]furan-2-carbimidate (**3j**).* Yield: 1.74 g (86%); mp 136–138 °C; IR (neat, cm^{-1}) 3318, 2952, 1678, 1381, 816; ^1H NMR (500 MHz, $CDCl_3$) δ: 8.23 (s, 1H), 8.11 (d, J = 7.7 Hz, 1H), 7.89 (d, J = 7.7 Hz, 1H), 7.64–7.56 (m, 3H), 7.53 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 7.7 Hz, 1H), 5.13 (s, 1H), 4.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.7, 152.6, 136.0, 134.7, 132.1, 130.9, 128.1, 127.2, 126.8, 124.0, 123.2, 121.7, 121.0, 120.1, 119.1, 114.1, 84.7, 58.2, 55.2; MS (ESI): m/z 407 $(M + H)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{21}H_{16}N_2O_2Br$ $(M + H)^+$ 407.0389, found 407.0392.

*Methyl 2-cyano-3-(pyridin-3-yl)-2,3-dihydronaphtho[1,2-b]furan-2-carbimidate (**3k**).* Yield: 1.36 g (83%); mp 141–143 °C; IR (neat, cm^{-1}) 3305, 2956, 1669, 1385, 812; ^1H NMR (500 MHz, $CDCl_3$) δ: 8.66 (d, J = 5.0 Hz, 1H), 8.61 (d, J = 2.0 Hz, 1H), 8.28 (s, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.65–7.57 (m, 3H), 7.54–7.51 (m, 1H), 7.36–7.32 (m, 1H), 7.06 (d, J = 8.0 Hz, 1H), 5.20 (s, 1H), 4.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.4, 152.7, 150.6, 150.3, 136.6, 134.7, 132.8, 128.1, 127.3, 126.9, 124.2, 123.7, 121.3, 121.0, 120.1, 118.4, 114.1, 84.7, 56.8, 55.2; MS (ESI): m/z 330 $(M + H)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{20}H_{16}N_3O_2$ $(M + H)^+$ 330.1237, found 330.1239.

*Methyl 2-cyano-3-(4-cyanophenyl)-2,3-dihydronaphtho[1,2-b]furan-2-carbimidate (**3l**).* Yield: 1.50 g (85%); mp 189–191 °C; IR (neat, cm^{-1}) 3305, 2947, 2225, 1676, 1382, 814; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.28 (s, 1H), 8.12 (d, J = 7.4 Hz, 1H), 7.91 (d, J = 7.2 Hz, 1H), 7.75–7.57 (m, 5H), 7.37 (d, J = 8.1 Hz, 2H), 7.05 (d, J = 8.3 Hz, 1H), 5.23 (s, 1H), 4.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.2, 152.8, 142.2, 134.8, 132.7, 130.1, 128.1, 127.4, 127.0, 124.3, 121.4, 121.0, 120.1, 118.3, 118.2, 113.9, 113.0, 84.4, 58.5, 55.3; MS (ESI): m/z 354 $(M + H)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{22}H_{16}N_3O_2$ $(M + H)^+$ 354.1237, found 354.1235.

*Methyl 2-cyano-3-(4-fluorophenyl)-2,3-dihydronaphtho[1,2-b]furan-2-carbimidate (**3m**).* Yield: 1.49 g (86%); mp 131–133 °C; IR (neat, cm^{-1}) 3317, 2942, 1892, 1674, 1383, 862; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.22 (s, 1H), 8.12 (d, J = 7.5 Hz, 1H), 7.90 (d, J = 7.3 Hz, 1H), 7.66–7.54 (m, 3H), 7.25–7.18 (m, 2H), 7.14–7.04 (m, 3H), 5.16 (s, 1H), 4.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.9, 163.9, 162.0, 152.6, 134.7, 132.9, 131.0, 130.9, 128.1, 127.1, 126.8, 124.0, 121.8, 121.1, 120.1, 119.3, 116.0, 115.6, 114.2, 85.0, 58.1, 55.2; MS (ESI): m/z 347 $(M + H)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{21}H_{16}N_2O_2F$ $(M + H)^+$ 347.1190, found 347.1184.

*Methyl 3-(4-chlorophenyl)-2-cyano-6-methoxy-2,3-dihydrobenzofuran-2-carbimidate (**3n**).* Yield: 1.18 g (69%); mp 111–112 °C; IR (neat, cm^{-1}) 3292, 2947, 1663, 1500, 1327, 823; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.12 (s, 1H), 7.37 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.3 Hz, 1H), 6.66–6.58 (m, 2H), 4.88 (s, 1H), 3.97 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.8, 161.7, 135.7, 134.9, 130.6, 129.1, 125.8, 117.5, 97.0, 56.9, 55.7, 55.1; MS (ESI): m/z 343 $(M + H)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{18}H_{16}N_2O_3Cl$ $(M + H)^+$ 343.0844, found 343.0842.

General procedure for the synthesis of compounds 5(a–d). Compounds **4(a–d)** were prepared according to the procedure reported in the literature.[19] To a suspension of 3-amino-1-aryl-1*H*-benzo[*f*]chromene-2-carbonitrile analog [**4(a–d)**, 3 mmol] in methanol (5 mL), *N*-chlorosuccinimide (3 mmol) was added. After stirring for half an hour at room temperature, piperidine (3.6 mmol) was added to the reaction mixture. The resulting mixture was stirred at room temperature, till the product is precipitated out. The solid precipitate was filtered and washed with cold methanol or ethanol to afford the pure product **5(a–d)**.

*Methyl 2-cyano-1-phenyl-1,2-dihydronaphtho[2,1-b]furan-2-carbimidate (**5a**).* Yield: 0.767 g (78%); mp 160–162 °C; IR (neat, cm^{-1}) 3317, 2951, 2230, 1961, 1669, 1379, 812; ^1H NMR

(300 MHz, $CDCl_3$) δ: 8.15 (s, 1H), 7.92–7.83 (m, 2H), 7.41–7.17 (m, 9H), 5.32 (s, 1H), 4.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.0, 154.8, 137.0, 131.5, 130.8, 129.6, 129.0, 128.9, 128.8, 128.7, 127.5, 124.4, 122.9, 117.6, 114.1, 111.4, 84.8, 57.5, 55.3; MS (ESI): *m/z* 329 $(M + H)^+$; HRMS ESI $(M + H)^+$ *m/z* calcd for $C_{21}H_{17}N_2O_2$ $(M + H)^+$ 329.1284, found 329.1276.

*Methyl 1-(4-chlorophenyl)-2-cyano-1,2-dihydronaphtho[2,1-*b*]furan-2-carbimidate (**5b**).* Yield: 0.955 g (88%); mp 167–169 °C; IR (neat, cm^{-1}) 3322, 2960, 1908, 1683, 1312, 821; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.18 (s, 1H), 7.92–7.83 (m, 2H), 7.39–7.30 (m, 5H), 7.19–7.11 (m, 3H), 5.30 (s, 1H), 4.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.6, 154.8, 135.4, 134.8, 131.8, 130.8, 130.1, 129.4, 129.3, 129.0, 127.7, 124.5, 122.7, 117.0, 114.0, 111.4, 84.5, 56.8, 55.3; MS (ESI): *m/z* 363 $(M + H)^+$; HRMS ESI $(M + H)^+$ *m/z* calcd for $C_{21}H_{16}N_2O_2Cl$ $(M + H)^+$ 363.0894, found 363.0892.

*Methyl 2-cyano-1-(4-methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-carbimidate (**5c**).* Yield: 0.848 g (79%); mp 140–142 °C; IR (neat, cm^{-1}) 3319, 2941, 1892, 1677, 1381, 862; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.13 (s, 1H), 7.90–7.82 (m, 2H), 7.39–7.06 (m, 6H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.29 (s, 1H), 4.00 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.1, 159.8, 154.7, 131.4, 130.8, 129.9, 129.7, 128.9, 127.5, 124.3, 123.0, 117.8, 114.4, 114.2, 111.5, 85.1, 57.0, 55.1; MS (ESI): *m/z* 359 $(M + H)^+$; HRMS ESI $(M + H)^+$ *m/z* calcd for $C_{22}H_{19}N_2O_3$ $(M + H)^+$ 359.1390, found 359.1384.

*Methyl 2-cyano-1-(4-cyanophenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-carbimidate (**5d**).* Yield: 0.868 g (82%); mp 188–190 °C; IR (neat, cm^{-1}) 3316, 2960, 2230, 1955, 1683, 1314, 821; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.23 (s, 1H), 7.96–7.86 (m, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.42–7.30 (m, 5H), 7.07 (d, *J* = 7.5 Hz, 1H), 5.38 (s, 1H), 4.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.1, 155.0, 142.0, 132.7, 132.1, 130.8, 129.6, 129.1, 127.8, 124.6, 122.4, 118.1, 116.2, 113.7, 112.8, 111.4, 84.1, 57.0, 55.3; MS (ESI): *m/z* 354 $(M + H)^+$; HRMS ESI $(M + H)^+$ *m/z* calcd for $C_{22}H_{16}N_3O_2$ $(M + H)^+$ 354.1237, found 354.1230.

General procedure for the synthesis of biscarbimidate esters (6–9). To the highly functionalized pyran analog [1 mmol], 1 N solution of methanolic KOH (3 mmol) was added and the resulting mixture was stirred at room temperature for 36 hours. The resultant reaction mixture was concentrated, 20 mL of $CHCl_3$ was added and filtered to remove KOH residue. The filtrate was concentrated and recrystallized from methanol or ethanol to give the pure product (**6–9**).

*Dimethyl 3-phenylnaphtho[1,2-*b*]furan-2,2(3*H*)-bis(carbimidate) (**6**).* Yield: 0.270 g (75%); mp 186–188 °C; IR (neat, cm^{-1}) 3325, 2945, 2843, 1667, 1434, 1082, 938; ^1H NMR (500 MHz, $CDCl_3$) δ: 8.19 (d, *J* = 8.2 Hz, 1H), 8.13 (s, 1H), 7.98 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.62–7.47 (m, 3H), 7.24–7.20 (m, 3H), 7.11–6.99 (m, 3H), 5.34 (s, 1H), 3.90 (s, 3H), 3.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.7, 166.0, 152.2, 138.5, 134.3, 129.6, 129.1, 128.1, 128.0, 127.6, 126.5, 126.2, 123.0, 122.6, 122.0, 121.0, 120.3, 92.7, 54.7, 54.6, 53.2; MS (ESI): *m/z* 383 $(M + Na)^+$; HRMS ESI $(M + H)^+$ *m/z* calcd for $C_{22}H_{20}N_2O_3Na$ $(M + Na)^+$ 383.1366, found 383.1352.

*Dimethyl 3-(4-chlorophenyl)naphtho[1,2-*b*]furan-2,2(3*H*)-bis-(carbimidate) (**7**).* Yield: 0.283 g (72%); mp 132–134 °C; IR (neat, cm^{-1}) 3237, 2941, 2849, 1664, 1348, 1099, 940; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.18 (d, *J* = 7.9 Hz, 1H), 8.13 (s, 1H), 7.99 (s, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.64–7.47 (m, 3H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.95 (d, *J* = 8.3 Hz, 2H), 5.33 (s, 1H), 3.90 (s, 3H), 3.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 168.4, 165.8, 152.3, 137.2, 134.4, 133.5, 130.5, 128.2, 126.7, 126.4, 123.3, 122.3, 121.6, 121.1, 120.3, 92.6, 54.7, 54.0, 53.3; MS (ESI): *m/z* 395 $(M + H)^+$; HRMS ESI $(M + H)^+$ *m/z* calcd for $C_{22}H_{20}N_2O_3Cl$ $(M + H)^+$ 395.1157, found 395.1138.

*Dimethyl 3-(4-methylphenyl)naphtho[1,2-*b*]furan-2,2(3*H*)-bis-(carbimidate) (**8**).* Yield: 0.282 g (79%); mp 136–138 °C; IR (neat, cm^{-1}) 3320, 2941, 1902, 1662, 1435, 1099, 934; ^1H NMR (500 MHz, $CDCl_3$) δ: 8.17 (d, *J* = 8.2 Hz, 1H), 8.13 (s, 1H), 7.96 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.60–7.45 (m, 3H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.88 (d, *J* = 7.6 Hz, 2H), 5.31 (s, 1H), 3.89 (s, 3H), 3.27 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.8, 166.1, 152.2, 137.2, 135.5, 134.3, 129.0, 128.7, 128.1, 126.4, 126.2, 123.0, 122.6, 122.2, 121.1, 120.3, 92.8, 54.6, 54.4, 53.3, 21.0; MS (ESI): *m/z* 375 $(M + H)^+$; HRMS ESI $(M + H)^+$ *m/z* calcd for $C_{23}H_{23}N_2O_3$ $(M + H)^+$ 375.1703, found 375.1704.

*Dimethyl 3-(thiophen-2-yl)naphtho[1,2-*b*]furan-2,2(3*H*)-bis(carbimidate) (**9**).* Yield: 0.267 g (73%); mp 134–136 °C; IR (neat, cm^{-1}) 3319, 2944, 2841, 2230, 1663, 1433, 1081, 936; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.17 (d, *J* = 7.9 Hz, 1H), 8.12 (s, 1H), 7.96 (s, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.63–7.48 (m, 3H), 7.25–7.15 (m, 2H), 6.93–6.87 (m, 1H), 6.73 (d, *J* = 3.0 Hz, 1H), 5.64 (s, 1H), 3.89 (s, 3H), 3.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.3, 165.7, 152.1, 141.4, 134.5, 128.1, 127.1, 126.7, 126.5, 126.3, 125.4, 123.1, 122.5, 121.7, 121.1, 120.4, 92.5, 54.6, 53.5, 49.5; MS (ESI): *m/z* 367 $(M + H)^+$; HRMS ESI $(M + H)^+$ *m/z* calcd for $C_{20}H_{19}N_2O_3S$ $(M + H)^+$ 367.1110, found 367.1108.

General procedure for the hydrolysis of carbimidate esters, synthesis of compounds (10–12). 10% Dilute HCl (5 mL) was added to a carbimidate analog [1 mmol] in acetone (5 mL), and stirred at room temperature for 20–30 minutes. The resultant mixture was filtered and washed with cold methanol or recrystallized from methanol to afford the pure product [**10–12**].

*Methyl 2-cyano-3-(thiophen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-2-carboxylate (**10**).* Yield: 0.321 g (96%); mp 176–178 °C; IR (neat, cm^{-1}) 2956, 1770, 1252, 1095, 709; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.09–8.04 (m, 1H), 7.90–7.86 (m, 1H), 7.61–7.53 (m, 3H), 7.39–7.34 (m, 1H), 7.29–7.26 (m, 1H), 7.10–7.05 (m, 2H), 5.66 (s, 1H), 4.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.3, 153.0, 138.7, 134.8, 128.2, 128.0, 127.5, 127.1, 126.9, 126.6, 123.5, 121.6, 121.4, 120.2, 118.9, 113.4, 86.2, 54.6, 53.4; MS (ESI): *m/z* 358 $(M + Na)^+$; HRMS ESI $(M + H)^+$ *m/z* calcd for $C_{19}H_{13}NO_3SNa$ $(M + Na)^+$ 358.0508, found 358.0501.

*Methyl 2-cyano-3-(4-nitrophenyl)-2,3-dihydronaphtho[1,2-*b*]furan-2-carboxylate (**11**).* Yield: 0.362 g (97%); mp 185–187 °C; IR (neat, cm^{-1}) 2958, 1768, 1251, 1047, 806; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.27 (d, *J* = 9.0 Hz, 2H), 8.12–8.07 (m, 1H), 7.92–7.88 (m, 1H), 7.64–7.55 (m, 3H), 7.45 (d, *J* = 9.0 Hz, 2H),

7.09 (d, J = 8.3 Hz, 1H), 5.50 (s, 1H), 4.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 165.2, 153.4, 148.3, 143.4, 134.9, 130.3, 128.0, 127.4, 126.9, 124.2, 124.0, 121.4, 121.1, 120.2, 118.1, 113.5, 85.4, 57.7, 54.8; MS (ESI): m/z 397 $(M + Na)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{21}H_{14}N_2O_5Na$ $(M + Na)^+$ 397.0795, found 397.0790.

*Methyl 2-cyano-1-(4-cyanophenyl)-1,2-dihydronaphtho[2,1-b]furan-2-carboxylate (**12**).* Yield: 0.343 g (97%); mp 188–190 °C; IR (neat, cm^{-1}) 2957, 2228, 1767, 1251, 1051, 751; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.92 (d, J = 9.0 Hz, 1H), 7.90–7.87 (m, 1H), 7.68 (d, J = 8.5 Hz, 2H), 7.40–7.32 (m, 5H), 7.10 (d, J = 7.4 Hz, 1H), 5.52 (s, 1H), 3.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.4, 155.7, 141.5, 132.9, 132.2, 130.7, 129.6, 129.2, 127.9, 124.5, 122.4, 118.2, 116.1, 113.3, 113.1, 111.7, 84.1, 57.0, 54.9; MS (ESI): m/z 377 $(M + Na)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{22}H_{16}N_3O_2$ $(M + Na)^+$ 377.0902, found 377.0900.

Acidic hydrolysis of 6a

*Dimethyl 3-phenylnaphtho[1,2-b]furan-2,2(3H)-dicarboxylate (**13**).* 10% Dilute HCl (5 mL) was added to the biscarbimidate analog [**5a**, 1 mmol] in methanol (5 mL), and stirred at room temperature for 20 minutes. The resultant mixture was filtered and washed with cold methanol to give the pure product [**13**]. Yield: 0.330 g (91%); mp 133–135 °C; IR (neat, cm^{-1}) 2952, 1745, 1300, 1278, 1100, 1053, 746; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.17 (d, J = 7.9 Hz, 1H), 7.84 (d, J = 8.7 Hz, 1H), 7.55–7.46 (m, 3H), 7.29–7.23 (m, 3H), 7.18–7.12 (m, 3H), 5.75 (s, 1H), 3.89 (s, 3H), 3.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.1, 166.2, 153.6, 137.8, 134.4, 129.4, 128.2, 127.9, 127.8, 126.4, 125.9, 122.4, 122.3, 121.7, 120.9, 120.2, 94.2, 55.1, 53.7, 52.3; MS (ESI): m/z 385 $(M + Na)^+$; HRMS ESI $(M + H)^+$ m/z calcd for $C_{22}H_{18}O_5Na$ $(M + Na)^+$ 385.1046, found 385.1045.

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