

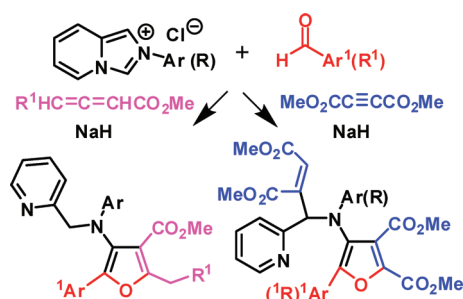
Multicomponent Reaction of Imidazo[1,5-*a*]pyridine Carbenes with Aldehydes and Dimethyl Acetylenedicarboxylate or Allenates: A Straightforward Approach to Fully Substituted Furans

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The facile three-component reactions of *N,N*-substituted imidazo[1,5-*a*]pyridine carbenes, namely imidazo[1,5-*a*]pyridin-3-ylidenes, with aldehydes and DMAD or allenates were disclosed. Both reactions proceeded via tandem nucleophilic addition, [3 + 2]-cycloaddition, and ring transformation to produce different 4-[(2-pyridyl)methyl]aminofuran derivatives generally in moderate yields. This work not only provided the first example of the application of imidazo[1,5-*a*]pyridin-3-ylidenes in organic synthesis but also developed a straightforward approach to fully substituted furans that are not easily accessible by other methods.

Introduction

Multicomponent reactions (MCRs) in which three or more reactants are connected sequentially in a one-pot reaction have attracted considerable attention owing to high synthetic efficiency, and, in many cases, the facile construction of complex organic compounds.¹ Nucleophilic carbenes are versatile and valuable intermediates not only as the

ligands in organometallics² but also organocatalysts³ and unique building blocks in organic synthesis.⁴ Although numerous studies on the reactivity and synthetic applications of nucleophilic carbenes, mainly *N*-heterocyclic carbenes, have been reported, the multicomponent reaction of carbenes remained largely unexplored until the 2000s. Since Nair and co-workers reported the first three-component reaction of dimethoxycarbene with dimethyl acetylenedicarboxylate (DMAD) and aldehydes or quinones in 2001,⁵ a series of multicomponent reactions of nucleophilic carbenes have appeared in the field of carbene chemistry.^{6,7} Most of the known MCRs participated by a carbene intermediate comprised of a nucleophilic carbene, an activated alkyne, and a carbonyl compound including aldehyde, ketone, anhydride, and ketene.^{5,6} These three-component reactions proceeded either via the nucleophilic addition of a carbene to the triple bond of the alkyne followed by cycloaddition of the zwitterions intermediate with the carbonyl group or

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TABLE 1. Reaction of 2-Phenylimidazo[1,5-*a*]pyridinium Salt **1a** with Benzaldehyde **3a** and Dimethyl Acetylenedicarboxylate **4** in the Presence of NaH under Different Conditions

entry	1a: 3a: 4: NaH	solvent	T (°C)	time (h)	yield (%)	
					5a	6a
1	1:1.1:1.2:1.5	THF	rt	12	10	12
2	1:1.5:2.2:1.5	THF	rt	12	26	32
3	1:1.5:2.2:1.5	THF	−20	12	42	11
4	1:1.5:2.2:1.5	THF	reflux	12	3	16
5	1:1.5:2.2:1.5	CH ₂ Cl ₂	−20	12	51	10
6	1:1.5:2.2:1.5	CICH ₂ CH ₂ Cl	−20	12	45	8
7	1:1.5:2.2:1.5	CH ₃ COCH ₃	−20	12	24	9
8	1:1.5:2.2:1.5	CH ₃ CN	−20	12	21	8
9	1:1.5:2.2:1.5	CH ₃ Ph	−20	12	4	3

through the nucleophilic addition of a carbene to the carbonyl group and then to the triple bond of the alkyne. Both reaction routes generally led to the formation of furan or furanone derivatives. Although the known three-component reactions of carbenes are successful, both types of carbenes and reactions of MCRs are still rather limited.

Our interest in nucleophilic carbenes and their applications in organic synthesis⁸ has led us to investigate multi-component reactions of *N*-heterocyclic carbenes.⁷ Our attention had been drawn to imidazo[1,5-*a*]pyridin-1-ylidenes and imidazo[1,5-*a*]pyridin-3-ylidenes, the carbon and nitrogen atom substituted and two nitrogen atom substituted imidazo[1,5-*a*]pyridine carbenes reported in 2005 by Lassaletta⁹ and Glorius.¹⁰ Both types of imidazo[1,5-*a*]pyridine carbenes have been shown to be strong C-ligands to Ag, Rh, Ir, and Pd cations and elemental Se,^{9,10} however, their reactions and applications as organic intermediates remain unexplored. Very recently, we studied the reaction of electron-deficient alkynes with the dipoles that were derived from the reaction

of imidazo[1,5-*a*]pyridin-1-ylidenes with aryl isothiocyanates.¹¹ After that, our attention was turned to the reactions of imidazo[1,5-*a*]pyridin-3-ylidenes. We envisioned that the multicomponent reactions of imidazo[1,5-*a*]pyridine carbenes might afford novel spiro-, fused, or monoheterocycles. We report herein our investigation on the three-component reactions of imidazo[1,5-*a*]pyridin-3-ylidenes with aldehydes and DMAD or allenates. The reactions provided a straightforward route to fully substituted furans.

Results and Discussion

We started the investigation with the reaction of 2-phenylimidazo[1,5-*a*]pyridin-3-ylidene **2a** with benzaldehyde **3a** and DMAD **4**. The 2-phenylimidazo[1,5-*a*]pyridin-3-ylidene **2a** was generated in situ from its precursor, 2-phenylimidazo[1,5-*a*]pyridinium salt **1a**, which was prepared from pyridine-2-carbaldehyde and aniline via a POCl₃-mediated cyclization of a formamide intermediate (see the Supporting Information).^{9,10} Initially, the reaction of 2-phenylimidazo[1,5-*a*]pyridinium salt **1a** with benzaldehyde **3a** and DMAD **4** in the presence of NaH (**1a**/**3a**/**4**/NaH = 1:1.1:1.2:1.5) was examined in dry THF at room temperature. After reaction for 12 h, a pair of isomeric products **5a** and **6a** were isolated in 10% and 12% yields, respectively (Table 1, entry 1). Having realized the products **5** and **6** were the 1 + 1 + 2 adducts of carbene **2a** with benzaldehyde **3a** and DMAD **4**, the reaction employing **1a**, **3a**, and **4** in a ratio of 1:1.5:2.2 was optimized by varying solvents and reaction temperature. As indicated in Table 1, the reaction at −20 °C in dry THF produced 42% yield of **5a** along with 11% yield of **6a**, while at ambient temperature the reaction gave total yields of **5a** and **6a** similar to those at −20 °C albeit with poor selectivity between **5a** and **6a**. The further increase of reaction temperature to around 60 °C led to diminished yields of **5a** and **6a**. The reaction was then examined at −20 °C in different solvents including dichloromethane, 1,2-dichloromethane, acetone, acetonitrile, and toluene. The best yield of **5a** (51%)

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TABLE 2. Reaction of Imidazo[1,5-*a*]pyridinium Salts **1** with Aldehydes **3** and Dimethyl Acetylenedicarboxylate **4** in the Presence of NaH under Optimized Conditions

entry	1	Ar (R)	3	Ar ¹	time (h)	yield (%)	
						5	6
1	1a	Ph	3a	Ph	12	5a : 51	6a : 10
2	1a	Ph	3b	<i>p</i> -CH ₃ OPh	10	5b : 26	6b : 12
3	1a	Ph	3c	<i>p</i> -BrPh	10	5c : 53	6c : 16
4	1a	Ph	3d	<i>p</i> -NO ₂ Ph	12	5d : 15	6d : 54
5	1a	Ph	3e	2-furyl	8	5e : 50	6e : 7
6	1a	Ph	3f	<i>p</i> -ClPh	10	5f : 55	6f : 14
7	1b	<i>p</i> -CH ₃ OPh	3f	<i>p</i> -ClPh	10	5g : 63	6g : 8
8	1c	<i>p</i> -ClPh	3f	<i>p</i> -ClPh	12	5h : 42	6h : 26
9	1d	<i>p</i> -CF ₃ Ph	3f	<i>p</i> -ClPh	12	5i : 45	<i>a</i>
10	1e	<i>i</i> -Pr	3f	<i>p</i> -ClPh	12	5j : 42	<i>a</i>
11	1f	Bn	3f	<i>p</i> -ClPh	12	5k : 47	6k : 6
12	1g	<i>p</i> -CH ₃ Ph	3e	2-furyl	8	5l : 66	6l : 10
13	1a	Ph	3g	<i>n</i> -Pr	12	<i>a</i>	6m : 42

^aA small amount of byproduct was detected by TLC without isolation.

was obtained from the reaction in dichloromethane, along with 10% yield of **6a**.

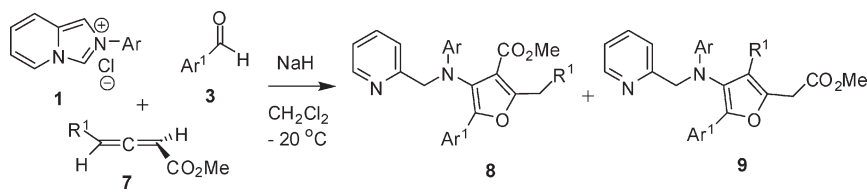
The generality of the reaction was studied under the optimized conditions using imidazo[1,5-*a*]pyridinium salts **1** and aldehydes **3** bearing different substituents. As shown in Table 2, the structures of aldehydes **3** strongly influenced the outcomes of the reactions. For example, when different aromatic aldehydes **3** reacted with 2-phenylimidazo[1,5-*a*]pyridin-3-ylidene **2a** and DMAD, 4-methoxybenzaldehyde **3b** afforded a much lower total yield of products **5b** and **6b** than other aromatic aldehydes including **3a** and **3c–f** (Table 2, entries 1–6). In addition, the reaction of carbene **2a** with DMAD and 4-nitrobenzaldehyde **3d**, or aliphatic *n*-butyraldehyde **3g**, produced isomer **6** rather than **5** as the major product (Table 2, entries 4 and 13). The lower reactivity of 4-methoxybenzaldehyde **3b** in the reaction can be explained by the electron-donating effect of the methoxy group that deactivates the aldehyde toward nucleophilic carbenes. On the other hand, the reaction of 4-nitrobenzaldehyde **3d** with carbene **2a** and DMAD produced **6d** instead of **5d** as the major product, probably because a strong electron-withdrawing substituent enhanced the acidity of allyl proton of **5** and promoted the isomerization of **5** to **6** (vide infra). The fact that the reaction of carbene **2a** with butyraldehyde **3g** and DMAD preferred to give isomer **6m** rather than **5m** is intriguing. Possibly, the unconjugated 5-alkylfuran is less stable than the aryl–aryl conjugated 5-arylfuran. Therefore, the isomerization of 5-propylfuran **5m** into more conjugated product **6m** probably took place much easier than that of 5-arylfurans **5a–l**. Being different from the influences of substituents of aldehydes, the *N*-substituents of carbene reactants showed small effects on the reaction. For instance, imidazo[1,5-*a*]pyridin-3-ylidenes **2** bearing either an alkyl including isopropyl and benzyl or a phenyl substituted by an electron-donating or electron-withdrawing group, reacted efficiently with 4-chlorobenzaldehyde **3f** and DMAD

TABLE 3. Reaction of Imidazo[1,5-*a*]pyridinium Salts **1** with Aromatic Aldehydes **3** and Dimethyl Acetylenedicarboxylate **4** in the Presence of NaH and DBU under Optimized Conditions

entry	1	Ar (R)	3	Ar ¹	time (h)	yield of 6 (%)
1	1a	Ph	3a	Ph	12	6a : 44
2	1a	Ph	3b	<i>p</i> -CH ₃ OPh	10	6b : 26
3	1a	Ph	3c	<i>p</i> -BrPh	10	6c : 52
4	1a	Ph	3d	<i>p</i> -NO ₂ Ph	12	6d : 73
5	1a	Ph	3e	2-furyl	8	6e : 59
6	1a	Ph	3f	<i>p</i> -ClPh	10	6f : 56
7	1b	<i>p</i> -CH ₃ OPh	3f	<i>p</i> -ClPh	10	6g : 40
8	1c	<i>p</i> -ClPh	3f	<i>p</i> -ClPh	12	6h : 48
9	1f	Bn	3f	<i>p</i> -ClPh	12	6k : 42
10	1g	<i>p</i> -CH ₃ Ph	3e	2-furyl	8	6l : 55

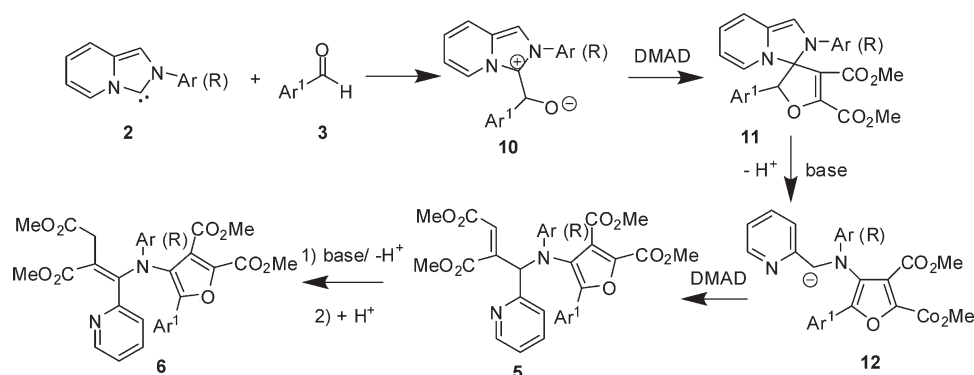
to produce **5** and **6** in 41–63% and 0–26% yields, respectively (Table 2, entries 6–11).

Having realized the compounds **6** were isomerized products of **5** by shifting the carbon–carbon double bond of maleate moiety of **5**, we considered that a base might promote the isomerization of **5** to **6** through deprotonation of the allyl proton of **5**. Thus, the reaction of imidazo[1,5-*a*]pyridinium salts **1** with aromatic aldehydes **3** and DMAD **4** was examined again in the presence of both NaH and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under the same conditions as those without DBU. To our delight, except the reaction of carbene **2a** with 4-methoxybenzaldehyde **3b** and DMAD that gave low yield of **6b**, all reactions afforded products **6** in moderate to good yields (Table 3), while none or a tiny amount of **5** were detected by TLC. The isomerization of

TABLE 4. Reaction of Imidazo[1,5-*a*]pyridinium Salts **1** with Aromatic Aldehydes **3** and Allenates **7** in the Presence of NaH


entry	1	Ar	3	Ar ¹	7	R ¹	time (h)	yield (%)	
								8	9
1	1a	Ph	3c	<i>p</i> -BrPh	7a	Me	10	8a : 45	<i>a</i>
2	1a	Ph	3c	<i>p</i> -BrPh	7b	Et	10	8b : 53	<i>a</i>
3	1a	Ph	3c	<i>p</i> -BrPh	7c	Bn	10	8c : 47	9c : 11
4	1a	Ph	3f	<i>p</i> -ClPh	7a	Me	11	8d : 42	<i>a</i>
5	1a	Ph	3f	<i>p</i> -ClPh	7c	Bn	10	8e : 54	9e : 6
6	1a	Ph	3g	<i>o</i> -FPh	7c	Bn	8	8f : 41	<i>a</i>
7	1b	<i>p</i> -CH ₃ OPh	3f	<i>p</i> -ClPh	7c	Bn	10	8g : 40	<i>a</i>
8	1g	<i>p</i> -CH ₃ Ph	3c	<i>p</i> -BrPh	7b	Et	10	8h : 44	<i>a</i>
9	1c	<i>p</i> -ClPh	3f	<i>p</i> -ClPh	7c	Bn	8	8i : 49	<i>a</i>

^aA small amount of byproduct was detected by TLC without isolation.

SCHEME 1. Proposed Mechanisms for the Reaction of Imidazo[1,5-*a*]pyridin-3-ylidenes **2** with Aldehydes **3** and Dimethyl Acetylenedicarboxylate **4** in the Presence of NaH or NaH and DBU

5 to **6** by the action of a base has also been confirmed through stirring the mixture of **5g** (0.2 mmol) with DBU (1 mmol) in CH₂Cl₂ (10 mL) at room temperature for 12 h, which afforded **6g** in 73% yield.

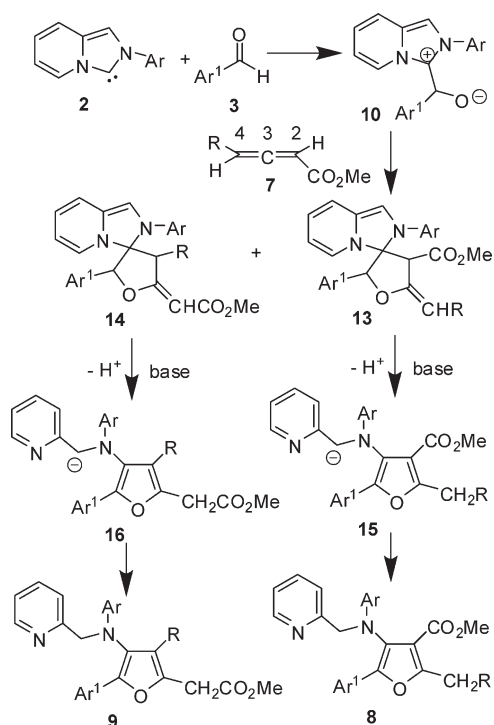
To further extend the application of imidazo[1,5-*a*]pyridine carbenes, we next explored the reaction of imidazo[1,5-*a*]pyridine carbenes **2** with aromatic aldehydes **3** and electron-deficient allenates **7**. Under the similar conditions as that of the reaction with DMAD, 2-arylimidazo[1,5-*a*]pyridin-3-ylidenes **2** reacted with aromatic aldehydes **3** and allenates **7**, both bearing different substituents, to produce products **8** in 40–54% yields along with a little amount of byproducts **9** (around 10% yields) (Table 4). Being different from compounds **5** and **6** that were 1 + 1 + 2 adducts of carbenes **2** with aldehyde **3** and DMAD, products **8** and **9** are constitutional isomers derived from addition of carbenes **2** to aldehyde **3** and allenates **7** in a ratio of 1:1:1 determined by the spectroscopic data.

The structures of all products **5**, **6**, **8**, and **9** were ascertained by spectroscopic methods, and the final proofs for the assigned structures of **6a** and **8e** were obtained by single-crystal X-ray analyses (see Figure S1 in the Supporting Information). The constitutional isomers **5** and **6** or **8** and **9** can be easily identified by the ¹H NMR spectra. For example, the methine

and vinyl protons of compounds **5** appeared as two singlet signals around 6.0 and 6.3 ppm, respectively, while the isomers **6** showed the allylic methylene protons as singlet signals at about 3.5 ppm. On the other hand, in the ¹H NMR spectra of **8**, only one singlet signal of CH₂ appeared at 4.6–4.8 ppm corresponding to the methylene protons adjacent to the pyridyl group, while isomers **9** have two singlet signals of CH₂ corresponding to the methylene protons adjacent to the pyridyl and carbonyl groups, respectively.

To account for the formation of [(2-pyridyl)methyl]-aminofuran derivatives **5** and **6** or **8** and **9** from the reaction of imidazo[1,5-*a*]pyridin-3-ylidenes **2** with aldehydes **3** and DMAD or allenates **7**, two tandem reaction mechanisms comprising nucleophilic addition of imidazo[1,5-*a*]pyridine carbene, [3 + 2]-cycloaddition, and ring transformation were proposed. As depicted in Scheme 1, imidazo[1,5-*a*]pyridin-3-ylidenes **2** undergo a nucleophilic addition to aldehydes **3** to form dipolar intermediates **10**. The consecutive [3 + 2] cycloaddition of dipoles **10** with DMAD **4** produces the spiro-dihydrofuran intermediates **11**. Deaminative aromatization of the dihydrofuran intermediates **11** gives rise to the opening of the imidazole ring to form carbanions **12**. The nucleophilic addition of carbanions **12** to DMAD affords products **5**. The isomerization of compounds **5** to **6** took

SCHEME 2. Proposed Mechanisms for the Reaction of Imidazo[1,5-*a*]pyridin-3-ylidenes **2** with Aromatic Aldehydes **3** and Allenates **7** in the Presence of NaH



place most likely through deprotonation of the acidic proton adjacent to the carbonyl and pyridyl groups of **5** by a base, followed by shifting of the carbon–carbon double bonds and reprotonation of allyl anions. In the reaction of carbenes **2** with aldehydes **3** and allenates **7**, dipoles **10** undergo [3 + 2]-cycloaddition with either the C2–C3 double bond or C3–C4 double bond of allenates **7** to form spiro-tetrahydrofuran intermediates **13** or **14**, respectively. In the presence of a base, the transformations of spiro-tetrahydrofurans **13** and **14** to furan carbanions **15** and **16**, respectively, were furnished by aromatization of tetrahydrofuran moieties of **13** and **14** through deamination and rearrangement of the exocyclic carbon–carbon double bonds to the endocyclic double bonds (Scheme 2). Being different from the carbanions **12** that undergo a nucleophilic addition to DMAD (Scheme 1), the carbanions **15** and **16** did not attack the allenates **7**, probably because allenates are less reactive and more stereo-hindered than DMAD. In results, the protonation of carbanions **15** and **16** led to the formation of products **8** and **9**, respectively. The predominant formation of products **8** rather than **9** was most probably because the ester carbonyl substituted C2–C3 double bond is more active than alkyl substituted C3–C4 double bond toward nucleophilic addition of dipoles **10**.

Conclusion

In summary, we have studied two three-component reactions of imidazo[1,5-*a*]pyridine carbenes. In the absence or presence of DBU, the reaction of imidazo[1,5-*a*]pyridin-3-ylidenes with aldehydes and DMAD produced 4-(2,3-dimethoxycarbonyl-1-(2-pyridyl)allyl)aminofuran-2,3-dicarboxylates or 4-(2,3-dimethoxycarbonyl-1-(2-pyridyl)prop-1-enyl)amino-

furan-2,3-dicarboxylates, respectively, as major products generally in moderate to good yields. While reacting with aldehydes and allenates, imidazo[1,5-*a*]pyridin-3-ylidenes produced 4-(2-pyridylmethyl)aminofuran-3-carboxylates in moderate yields. Two tandem nucleophilic addition, [3 + 2]-cycloaddition and ring transformation mechanisms, were proposed for the formation of products. This work not only provided the first example of the synthetic application of imidazo[1,5-*a*]pyridin-3-ylidenes but also developed a straightforward approach to fully substituted furans that are not easily accessible by other methods and are potentially amenable to further transformations.

Experimental Section

General Procedure for the Reaction of 2-Aryl(2-alkyl)imidazo[1,5-*a*]pyridinium Salts **1 and Aldehydes **3** with DMAD **4** in the Presence of NaH (Method A).** Under nitrogen atmosphere and at $-20\text{ }^{\circ}\text{C}$, imidazo[1,5-*a*]pyridinium salts **1** (1.0 mmol), aldehydes **3** (1.5 mmol), and DMAD (2.2 mmol) were mixed in dry dichloromethane (60 mL). To this mixture was added NaH (1.5 mmol), and the reaction mixture was then stirred at $-20\text{ }^{\circ}\text{C}$ for 8–12 h. After removal of the excess NaH and NaCl by filtration and evaporation of the solvent under vacuum, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether ($30\text{--}60\text{ }^{\circ}\text{C}$) and ethyl acetate (5:1–2:1) to afford white crystallines **5** and **6**.

General Procedure for the Reaction of Imidazo[1,5-*a*]pyridinium Salts **1 and Aromatic Aldehydes **3** with DMAD **4** in the Presence of NaH and DBU (Method B).** Under nitrogen atmosphere and at $-20\text{ }^{\circ}\text{C}$, imidazo[1,5-*a*]pyridinium salts **1** (1.0 mmol), aromatic aldehydes **3** (1.5 mmol), and DMAD (2.2 mmol) were mixed in dry dichloromethane (60 mL), and then NaH (1.5 mmol) and DBU (1.5 mmol) were added. The reaction mixture was stirred at $-20\text{ }^{\circ}\text{C}$ for 8–12 h. After removal of the excess NaH and NaCl by filtration and evaporation of the solvent under vacuum, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether ($30\text{--}60\text{ }^{\circ}\text{C}$) and ethyl acetate (5:1–2:1) to afford products **6**.

(Z)-Dimethyl 4-(N-(2,3-dimethoxycarbonyl-1-(2-pyridyl)allyl)-N-phenylamino)-5-phenylfuran-2,3-dicarboxylate (5a**):** 51% (method A); white crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp $127\text{--}128\text{ }^{\circ}\text{C}$; $\nu_{\text{max}}/\text{cm}^{-1}$ 1729, 1656, 1598; δ_{H} (400 MHz, CDCl_3) 8.13 (dd, $J = 4.0, 0.7\text{ Hz}$, 1H), 7.46 (dd, $J = 7.8, 2.0\text{ Hz}$, 2H), 7.32 (dt, $J = 7.7, 1.8\text{ Hz}$, 1H), 7.24–7.28 (m, 3H), 7.16 (dd, $J = 7.3, 1.5\text{ Hz}$, 2H), 7.03 (d, $J = 7.8\text{ Hz}$, 1H), 6.92 (ddd, $J = 7.4, 4.8, 0.8\text{ Hz}$, 1H), 6.80–6.85 (m, 3H), 6.22 (s, 1H), 5.92 (s, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 3.60 (s, 1H), 3.49 (s, 3H); δ_{C} (100 MHz, CDCl_3) 167.3, 165.5, 163.0, 157.9, 154.3, 154.0, 149.1, 146.8, 145.1, 139.7, 135.9, 129.7, 129.1, 128.5, 128.2, 127.9, 126.6, 126.1, 125.0, 123.6, 123.0, 120.1, 115.9, 68.5, 52.7, 52.4 (2 C), 51.9; MS (EI) 175 (87), 204 (100), 351 (90), 584 (M^+ , 10). Anal. Calcd for $\text{C}_{32}\text{H}_{28}\text{N}_2\text{O}_9$: C, 65.75; H, 4.83; N, 4.79. Found: C, 65.62; H, 4.59; N, 4.74.

(E)-Dimethyl 4-(N-(2,3-dimethoxycarbonyl-1-(2-pyridyl)prop-1-enyl)-N-phenylamino)-5-phenylfuran-2,3-dicarboxylate (6a**):** 10% (method A); 44% (method B), white crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp $165\text{--}167\text{ }^{\circ}\text{C}$; $\nu_{\text{max}}/\text{cm}^{-1}$ 1740, 1715, 1612, 1594; δ_{H} (400 MHz, CDCl_3) 8.41 (dd, $J = 3.9, 0.7\text{ Hz}$, 1H), 7.69 (dd, $J = 6.1, 3.6\text{ Hz}$, 2H), 7.46 (dt, $J = 7.7, 1.7\text{ Hz}$, 1H), 7.29–7.31 (m, 4H), 7.03–7.18 (m, 5H), 6.90–6.94 (m, 1H), 3.88 (s, 3H), 3.68 (s, 3H), 3.52 (s, 2H), 3.43 (s, 3H), 3.37 (s, 3H); δ_{C} (100 MHz, CDCl_3) 170.2, 169.8, 162.7, 157.8, 155.1, 150.7, 150.3, 148.8, 145.7, 139.2, 135.5, 129.5, 129.2, 128.2, 127.4, 126.7, 126.3, 126.0, 124.6, 123.6, 123.2, 122.3, 116.5, 52.7, 52.4, 51.7, 51.5, 35.9; MS (ESI) 585 ($\text{M} + 1$), 607 ($\text{M} + \text{Na}^+$). Anal. Calcd for $\text{C}_{32}\text{H}_{28}\text{N}_2\text{O}_9$: C, 65.75; H, 4.83; N, 4.79. Found: C, 65.41; H, 5.10; N, 4.53.

(Z)-Dimethyl 4-(N-(2,3-dimethoxycarbonyl-1-(2-pyridyl)allyl)-N-phenylamino)-5-(p-methoxyphenyl)furan-2,3-dicarboxylate (5b): 26% (method A); white crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 174–176 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1721, 1608, 1597; δ_{H} (400 MHz, CDCl_3) 8.15 (d, $J = 3.9$ Hz, 1H), 7.38 (d, $J = 8.3$ Hz, 3H), 7.15 (d, $J = 7.9$ Hz, 2H), 7.11 (br, 1H), 6.96 (br, 1H), 6.76–6.82 (m, 5H), 6.23 (s, 1H), 5.95 (s, 1H), 3.80 (s, 3H), 3.73 (s, 6H), 3.59 (s, 3H), 3.48 (s, 3H); δ_{C} (100 MHz, CDCl_3) 167.3, 165.5, 163.1, 160.7, 158.0, 154.3, 148.9, 146.8, 145.0, 138.9, 136.0, 129.1, 128.4, 128.2, 125.1, 124.6, 123.6, 123.1, 120.5, 120.0, 115.8, 114.0, 68.5, 55.3, 52.7, 52.4, 52.3, 51.9; HRMS (ESI) 615.1982 ($M + 1$), calcd for $\text{C}_{33}\text{H}_{31}\text{N}_2\text{O}_{10}$ 615.1979 ($M + 1$).

(E)-Dimethyl 4-(N-(2,3-dimethoxycarbonyl-1-(2-pyridyl)prop-1-enyl)-N-phenylamino)-5-(p-methoxyphenyl)furan-2,3-dicarboxylate (6b): 26% (method B), 12% (method A); white crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 158–159 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1736, 1713, 1608; δ_{H} (400 MHz, CDCl_3) 8.42 (d, $J = 4.4$ Hz, 1H), 7.66 (d, $J = 8.9$ Hz, 2H), 7.48 (t, $J = 7.6$ Hz, 1H), 7.31 (d, $J = 7.9$ Hz, 1H), 7.17 (brs, 2H), 7.06–7.14 (m, 2H), 7.01 (d, $J = 7.1$ Hz, 1H), 6.89–6.93 (m, 1H), 6.82 (d, $J = 8.9$ Hz, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 3.70 (s, 3H), 3.51 (s, 2H), 3.44 (s, 3H), 3.39 (s, 3H); δ_{C} (125 MHz, CD_3COCD_3) 169.6, 169.1, 162.6, 160.7, 157.3, 155.4, 150.2, 150.1, 148.7, 146.0, 138.3, 135.5, 129.1, 128.5, 126.6, 124.8, 123.3, 123.1, 122.0, 121.5, 120.2, 117.3, 113.7, 54.8, 52.1, 51.7, 50.9, 50.6, 35.6; MS (ESI) 615 ($M + 1$). Anal. Calcd for $\text{C}_{33}\text{H}_{30}\text{N}_2\text{O}_{10}$: C, 64.49; H, 4.92; N, 4.56. Found: C, 64.14; H, 4.85; N, 4.18.

(Z)-Dimethyl 5-(p-bromophenyl)-4-(N-(2,3-dimethoxycarbonyl-1-(2-pyridyl)allyl)-N-phenylamino)furan-2,3-dicarboxylate (5c): 53% (method A), white crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 151–153 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1727, 1657, 1589; δ_{H} (400 MHz, CDCl_3) 8.22 (s, 1H), 7.44–7.49 (m, 5H), 7.23 (d, $J = 7.4$ Hz, 2H), 7.22 (brs, 1H), 7.05 (brs, 1H), 6.91 (d, $J = 7.4$ Hz, 1H), 6.88 (d, $J = 8.2$ Hz, 2H), 6.29 (s, 1H), 6.04 (s, 1H), 3.89 (s, 3H), 3.80 (s, 3H), 3.69 (s, 3H), 3.58 (s, 3H); δ_{C} (100 MHz, CDCl_3) 167.2, 165.4, 162.9, 157.8, 154.2, 152.9, 149.1, 146.5, 144.7, 139.7, 136.1, 131.8, 129.2, 128.3, 128.0, 126.7, 126.5, 125.0, 124.2, 123.8, 123.2, 120.4, 115.9, 68.2, 52.8, 52.5, 52.4, 52.0; MS (ESI) 663 ($M + 1$), 685 ($M + \text{Na}^+$). Anal. Calcd for $\text{C}_{32}\text{H}_{27}\text{BrN}_2\text{O}_9$: C, 57.93; H, 4.10; N, 4.22. Found: C, 57.79; H, 3.78; N, 4.19.

(E)-Dimethyl 5-(p-bromophenyl)-4-(N-(2,3-dimethoxycarbonyl-1-(2-pyridyl)prop-1-enyl)-N-phenylamino)furan-2,3-dicarboxylate (6c): 52% (method B), 16% (method A); white crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 147–149 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1729, 1705, 1590; δ_{H} (400 MHz, CDCl_3) 8.38 (d, $J = 4.4$ Hz, 1H), 7.61 (d, $J = 8.6$ Hz, 2H), 7.50 (t, $J = 6.2$ Hz, 1H), 7.39 (d, $J = 8.6$ Hz, 2H), 7.31 (d, $J = 7.1$ Hz, 1H), 7.15 (brs, 2H), 7.08 (t, $J = 7.4$ Hz, 2H), 6.96 (d, $J = 8.1$ Hz, 1H), 6.90 (t, $J = 8.0$ Hz, 1H), 3.85 (s, 3H), 3.69 (s, 3H), 3.48 (s, 2H), 3.41 (s, 3H), 3.38 (s, 3H); δ_{C} (125 MHz, CD_3COCD_3) 169.5, 169.0, 162.3, 157.2, 155.2, 149.8, 148.8, 148.2, 145.6, 139.3, 135.7, 131.3, 129.2, 129.1, 128.5, 126.9, 126.7, 126.2, 125.0, 123.5, 123.4, 123.1, 122.4, 121.6, 117.9, 52.2, 51.9, 51.0, 50.7, 35.6; MS (ESI) 663 ($M + 1$), 685 ($M + \text{Na}^+$). Anal. Calcd for $\text{C}_{32}\text{H}_{27}\text{BrN}_2\text{O}_9$: C, 57.93; H, 4.10; N, 4.22. Found: C, 57.98; H, 4.01; N, 3.92.

(Z)-Dimethyl 4-(N-(2,3-dimethoxycarbonyl-1-(2-pyridyl)allyl)-N-phenylamino)-5-(p-nitrophenyl)furan-2,3-dicarboxylate (5d): 15% (method A), yellow crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 179–181 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1728, 1657, 1599; δ_{H} (400 MHz, CDCl_3) 8.21 (d, $J = 8.9$ Hz, 2H), 8.17 (d, $J = 4.6$ Hz, 1H), 7.85 (d, $J = 8.8$ Hz, 2H), 7.50 (t, $J = 7.6$ Hz, 1H), 7.24–7.30 (m, 3H), 7.06 (t, $J = 6.8$ Hz, 1H), 6.93 (d, $J = 7.4$ Hz, 1H), 6.90 (d, $J = 8.0$ Hz, 2H), 6.29 (s, 1H), 6.10 (s, 1H), 3.91 (s, 3H), 3.79 (s, 3H), 3.69 (s, 3H), 3.59 (s, 3H); δ_{C} (100 MHz, CDCl_3) 167.1, 165.3, 162.6, 157.5, 154.2, 151.2, 149.2, 147.8, 146.1, 144.3, 140.9, 136.4, 133.4, 129.3, 129.0, 128.1, 127.2, 125.0, 124.2, 123.7, 123.4, 120.9, 116.3, 68.0, 52.9, 52.6, 52.5, 52.0; MS (EI) 93 (100), 181 (25), 629 (M^+ , 1). Anal. Calcd

for $\text{C}_{32}\text{H}_{27}\text{N}_3\text{O}_{11}$: C, 61.05; H, 4.32; N, 6.67. Found: C, 60.90; H, 4.14; N, 6.42.

(E)-Dimethyl 4-(N-(2,3-dimethoxycarbonyl-1-(2-pyridyl)prop-1-enyl)-N-phenylamino)-5-(p-nitrophenyl)furan-2,3-dicarboxylate (6d): 54% (method A), 73% (method B); yellow crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 165–167 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1738, 1730, 1714, 1597; δ_{H} (400 MHz, CDCl_3) 8.39 (d, $J = 4.6$ Hz, 1H), 8.14 (d, $J = 9.0$ Hz, 2H), 7.99 (d, $J = 8.9$ Hz, 2H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.40 (d, $J = 6.5$ Hz, 1H), 7.10–7.23 (m, 4H), 7.00 (d, $J = 7.8$ Hz, 1H), 6.93 (t, $J = 7.2$ Hz, 1H), 3.90 (s, 3H), 3.73 (s, 3H), 3.54 (s, 2H), 3.44 (s, 3H), 3.41 (s, 3H); δ_{C} (100 MHz, CDCl_3) 169.9, 169.4, 162.2, 157.4, 154.7, 149.8, 148.9, 147.5, 146.8, 145.2, 140.5, 135.9, 132.9, 129.4, 129.3, 129.0, 127.2, 126.0, 125.1, 124.1, 123.6, 123.4, 122.7, 122.1, 117.9, 52.9, 52.6, 51.8, 51.7, 35.9; MS (ESI) 630 ($M + 1$), 652 ($M + \text{Na}^+$). Anal. Calcd for $\text{C}_{32}\text{H}_{27}\text{N}_3\text{O}_{11}$: C, 61.05; H, 4.32; N 6.67. Found: C, 61.26; H, 4.30; N, 6.60.

(Z)-Dimethyl 4-(N-(2,3-dimethoxycarbonyl-1-(2-pyridyl)allyl)-N-phenylamino)-5-(2-furyl)furan-2,3-dicarboxylate (5e): 50% (method A), pale yellow crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 165–166 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1725, 1657, 1596; δ_{H} (400 MHz, CDCl_3) 8.26 (d, $J = 4.2$ Hz, 1H), 7.40 (s, 2H), 7.20 (br, 1H), 7.11 (t, $J = 8.9$ Hz, 2H), 7.00 (br, 1H), 6.78 (d, $J = 8.0$ Hz, 2H), 6.77 (t, $J = 7.8$ Hz, 1H), 6.52 (d, $J = 2.8$ Hz, 1H), 6.45 (s, 1H), 6.36 (dd, $J = 3.4, 1.6$ Hz, 1H), 6.07 (br, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 3.61 (s, 3H), 3.52 (s, 3H); δ_{C} (100 MHz, CDCl_3) 167.4, 165.7, 162.6, 157.7, 154.5, 149.1, 146.7, 146.4, 144.8, 144.0, 142.8, 139.4, 136.2, 128.9, 128.0, 125.7, 125.0, 123.9, 123.2, 120.1, 116.2, 111.8, 111.5, 68.1, 52.8, 52.41, 52.39, 51.9; MS (EI) 341 (100), 574 (M^+ , 5). Anal. Calcd for $\text{C}_{30}\text{H}_{26}\text{N}_2\text{O}_{10}$: C, 62.72; H, 4.56; N, 4.88. Found: C, 62.62; H, 4.32; N, 4.63.

(E)-Dimethyl 4-(N-(2,3-dimethoxycarbonyl-1-(2-pyridyl)prop-1-enyl)-N-phenylamino)-5-(2-furyl)furan-2,3-dicarboxylate (6e): 59% (method B), 7% (method A); pale yellow crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 151–153 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1749, 1732, 1703, 1596; δ_{H} (400 MHz, CDCl_3) 8.41 (d, $J = 4.7$ Hz, 1H), 7.71 (d, $J = 8.6$ Hz, 2H), 7.51 (t, $J = 7.8$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.25 (s, 1H), 7.18 (d, $J = 4.0$ Hz, 2H), 7.11 (t, $J = 7.4$ Hz, 2H), 6.98 (d, $J = 8.1$ Hz, 1H), 6.91–6.94 (m, 1H), 3.88 (s, 3H), 3.72 (s, 3H), 3.51 (s, 2H), 3.43 (s, 3H), 3.40 (s, 3H); δ_{C} (100 MHz, CDCl_3) 170.1, 169.5, 162.6, 157.6, 154.9, 150.3, 148.6, 145.4, 139.3, 136.1, 135.5, 129.3, 128.5, 128.0, 126.5, 126.2, 125.7, 125.0, 123.8, 123.4, 122.4, 122.1, 117.0, 52.8, 52.4, 51.7, 51.6, 35.8; HRMS (ESI) 575.1642 ($M + 1$), calcd for $\text{C}_{30}\text{H}_{27}\text{N}_2\text{O}_{10}$ 575.1666 ($M + 1$).

(Z)-Dimethyl 5-(p-chlorophenyl)-4-(N-(2,3-dimethoxycarbonyl-1-(2-pyridyl)allyl)-N-phenylamino)furan-2,3-dicarboxylate (5f): 55% (method A), white crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 146–148 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1727, 1594; δ_{H} (400 MHz, CDCl_3) 8.16 (d, $J = 4.3$ Hz, 1H), 7.44 (d, $J = 8.5$ Hz, 3H), 7.43 (brs, 1H), 7.24 (d, $J = 8.6$ Hz, 2H), 7.15 (d, $J = 7.4$ Hz, 2H), 7.01 (brs, 1H), 6.82 (d, $J = 7.3$ Hz, 1H), 6.79 (d, $J = 8.3$ Hz, 2H), 6.25 (s, 1H), 6.03 (s, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 3.60 (s, 3H), 3.48 (s, 3H); δ_{C} (100 MHz, CDCl_3) 167.2, 165.4, 162.9, 157.8, 154.2, 152.9, 148.9, 146.4, 144.6, 139.7, 136.3, 135.8, 129.2, 128.8, 128.2, 127.8, 126.4, 126.2, 125.1, 124.0, 123.2, 120.4, 115.9, 68.2, 52.8, 52.5, 52.4, 52.0; MS (EI) 93 (99), 181 (100), 618 (M^+ , 5). Anal. Calcd for $\text{C}_{32}\text{H}_{27}\text{ClN}_2\text{O}_9$: C, 62.09; H, 4.40; N, 4.53. Found: C, 61.99; H, 4.09; N, 4.44.

(E)-Dimethyl 5-(p-chlorophenyl)-4-(N-(2,3-dimethoxycarbonyl-1-(2-pyridyl)prop-1-enyl)-N-phenylamino)furan-2,3-dicarboxylate (6f): 52% (method B), 14% (method A); white crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 153–154 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1730, 1706, 1593; δ_{H} (400 MHz, CDCl_3) 8.41 (d, $J = 4.3$ Hz, 1H), 7.71 (d, $J = 8.7$ Hz, 2H), 7.52 (t, $J = 7.1$ Hz, 1H), 7.33 (d, $J = 7.7$ Hz, 1H), 7.26 (d, $J = 8.6$ Hz, 2H), 7.18 (brs, 2H), 7.09–7.11 (m, 2H), 6.99 (d, $J = 7.9$ Hz, 1H), 6.90–6.94 (m, 1H), 3.88 (s, 3H), 3.72 (s, 3H), 3.51 (s, 2H), 3.44 (s, 3H), 3.40 (s, 3H);

δ_{C} (125 MHz, CD_3COCD_3) 169.6, 169.1, 162.4, 157.2, 155.2, 149.8, 148.8, 148.2, 145.7, 139.3, 135.7, 134.7, 129.2, 129.1, 128.3, 126.8, 126.4, 126.1, 125.0, 123.5, 123.4, 123.3, 122.3, 121.6, 117.9, 52.2, 51.8, 51.0, 50.7, 35.7; MS (EI) 181 (100), 618 (M^+ , 5). Anal. Calcd for $\text{C}_{32}\text{H}_{27}\text{ClN}_2\text{O}_9$: C, 62.09; H, 4.40; N, 4.53. Found: C, 62.05; H, 4.16; N, 4.30.

(Z)-Dimethyl 5-(*p*-chlorophenyl)-4-(*N*-(2,3-dimethoxycarbonyl-1-(2-pyridyl)allyl)-*N*-(*p*-methoxyphenyl)amino)furan-2,3-dicarboxylate (5g): 63% (method A); white crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 106–107 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1727, 1667, 1588; δ_{H} (400 MHz, CDCl_3) 8.25 (s, 1H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.51 (br, 1H), 7.35 (d, $J = 8.5$ Hz, 2H), 7.28 (br, 1H), 7.09 (br, 1H), 6.84 (d, $J = 9.2$ Hz, 2H), 6.79 (d, $J = 9.2$ Hz, 2H), 6.35 (br, 1H), 6.06 (br, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 3.75 (s, 3H), 3.68 (s, 3H), 3.56 (s, 3H); δ_{C} (100 MHz, CDCl_3) 167.3, 165.4, 163.1, 157.8, 154.5, 153.8, 152.6, 149.0, 145.0, 140.2, 139.6, 136.2, 135.7, 128.8, 128.1, 127.8, 127.5, 126.4, 125.0, 123.9, 123.2, 117.7, 114.5, 68.3, 55.5, 53.4, 52.7, 52.4, 51.9; MS (ESI) 649 ($\text{M} + 1$). Anal. Calcd for $\text{C}_{33}\text{H}_{29}\text{ClN}_2\text{O}_{10}$: C, 61.07; H, 4.50; N, 4.32. Found: C, 61.15; H, 4.53; N, 4.06.

(E)-Dimethyl 5-(*p*-chlorophenyl)-4-(*N*-(2,3-dimethoxycarbonyl-1-(2-pyridyl)prop-1-enyl)-*N*-(*p*-methoxyphenyl)amino)furan-2,3-dicarboxylate (6g): 40% (method B), 8% (method A); white crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 142–143 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1732, 1713, 1608, 1596, 1579; δ_{H} (400 MHz, CDCl_3) 8.42 (d, $J = 4.4$ Hz, 1H), 7.74 (d, $J = 8.7$ Hz, 2H), 7.50 (t, $J = 9.2$ Hz, 1H), 7.32 (br, 1H), 7.29 (d, $J = 8.6$ Hz, 2H), 7.09 (d, $J = 6.4$ Hz, 2H), 6.96 (d, $J = 7.5$ Hz, 1H), 6.68 (d, $J = 9.2$ Hz, 1H), 6.65 (d, $J = 9.0$ Hz, 1H), 3.88 (s, 3H), 3.71 (s, 3H), 3.70 (s, 3H), 3.51 (s, 2H), 3.44 (s, 3H), 3.37 (s, 3H); δ_{C} (125 MHz, CD_3COCD_3) 169.8, 169.2, 162.4, 157.2, 156.3, 155.4, 150.8, 148.7, 147.8, 139.2, 138.7, 135.6, 134.6, 128.4, 127.6, 126.4, 126.0, 125.1, 124.6, 124.1, 123.3, 115.9, 114.3, 114.1, 54.9, 52.1, 51.8, 50.9, 50.5, 35.3; MS (ESI) 649 ($\text{M} + 1$). Anal. Calcd for $\text{C}_{33}\text{H}_{29}\text{ClN}_2\text{O}_{10}$: C, 61.07; H, 4.50; N, 4.32. Found: C, 60.74; H, 4.40; N, 4.11.

(Z)-Dimethyl 5-(*p*-chlorophenyl)-4-(*N*-(*p*-chlorophenyl)-*N*-(2,3-dimethoxycarbonyl-1-(2-pyridyl)allyl)amino)furan-2,3-dicarboxylate (5h): 41% (method A); white crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 139–140 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1727, 1657, 1593; δ_{H} (400 MHz, CDCl_3) 8.22 (d, $J = 3.5$ Hz, 1H), 7.52 (d, $J = 8.3$ Hz, 2H), 7.48 (brs, 1H), 7.32 (d, $J = 8.6$ Hz, 2H), 7.23 (d, $J = 7.5$ Hz, 2H), 7.05 (brs, 1H), 6.91 (d, $J = 7.5$ Hz, 1H), 6.88 (d, $J = 8.3$ Hz, 2H), 6.30 (s, 1H), 6.05 (s, 1H), 3.89 (s, 3H), 3.80 (s, 3H), 3.69 (s, 3H), 3.58 (s, 3H); δ_{C} (100 MHz, CDCl_3) 167.2, 165.4, 162.9, 157.8, 154.2, 152.9, 149.2, 146.5, 144.8, 139.7, 136.1, 135.8, 129.2, 128.8, 128.2, 127.8, 126.4, 126.2, 125.0, 123.7, 123.2, 120.3, 115.9, 68.3, 52.8, 52.4 (2C), 52.0; MS (ESI) 653 ($\text{M} + 1$). Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{Cl}_2\text{N}_2\text{O}_9$: C, 58.82; H, 4.01; N, 4.29. Found: C, 58.47; H, 4.27; N, 4.18.

(E)-Dimethyl 5-(*p*-chlorophenyl)-4-(*N*-(*p*-chlorophenyl)-*N*-(2,3-dimethoxycarbonyl-1-(2-pyridyl)prop-1-enyl)amino)furan-2,3-dicarboxylate (6h): 48% (method B), 26% (method A); white crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 154–155 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1729, 1706, 1592; δ_{H} (400 MHz, CDCl_3) 8.43 (d, $J = 4.4$ Hz, 1H), 7.70 (d, $J = 8.6$ Hz, 2H), 7.57 (brs, 1H), 7.38 (brs, 1H), 7.28 (d, $J = 7.2$ Hz, 2H), 7.10–7.18 (m, 3H), 7.01 (d, $J = 5.8$ Hz, 1H), 6.92 (t, $J = 6.5$ Hz, 1H), 3.89 (s, 3H), 3.72 (s, 3H), 3.52 (s, 2H), 3.44 (s, 3H), 3.42 (s, 3H); δ_{C} (100 MHz, CDCl_3) 170.4, 169.9, 163.2, 158.1, 156.1, 150.7, 149.7, 149.1, 146.6, 140.2, 136.6, 135.6, 130.0, 130.04, 129.97, 129.3, 129.2, 127.7, 127.3, 127.0, 125.9, 124.34, 124.26, 123.3, 122.5, 118.8, 53.1, 52.7, 51.9, 51.5, 36.5; HRMS (ESI) 653.1088 ($\text{M} + 1$), $\text{C}_{32}\text{H}_{27}\text{Cl}_2\text{N}_2\text{O}_9$ requires 653.1094 ($\text{M} + 1$). Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{Cl}_2\text{N}_2\text{O}_9$: C, 58.82; H, 4.01; N, 4.29. Found: C, 58.41; H, 4.05; N, 4.07.

(Z)-Dimethyl 5-(*p*-chlorophenyl)-4-(*N*-(2,3-dimethoxycarbonyl-1-(2-pyridyl)allyl)-*N*-(*p*-trifluoromethylphenyl)amino)furan-2,3-dicarboxylate (5i): 45% (method A); white crystals (CH_2Cl_2 ,

petroleum ether, ethyl acetate); mp 167–169 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1729, 1660, 1616, 1586; δ_{H} (400 MHz, CDCl_3) 8.23 (s, 1H), 7.50 (d, $J = 8.3$ Hz, 2H), 7.47 (br, 1H), 7.43 (d, $J = 6.6$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.17 (brs, 1H), 7.08 (brs, 1H), 6.93 (d, $J = 8.7$ Hz, 2H), 6.24 (s, 1H), 6.06 (s, 1H), 3.91 (s, 3H), 3.84 (s, 3H), 3.70 (s, 3H), 3.58 (s, 3H); δ_{C} (100 MHz, CDCl_3) 166.8, 165.2, 162.7, 157.7, 153.6, 153.0, 149.2, 148.9, 143.4, 140.3, 136.6, 136.2, 129.0, 127.7, 126.6, 126.5, 125.9, 125.8, 125.1, 123.5, 123.1, 122.6, 122.2, 121.9, 115.2, 68.1, 52.9, 52.5, 52.1; HRMS (ESI) 687.1349 ($\text{M} + 1$), $\text{C}_{33}\text{H}_{27}\text{ClF}_3\text{N}_2\text{O}_9$ required 687.1345 ($\text{M} + 1$).

(Z)-Dimethyl 5-(*p*-chlorophenyl)-4-(*N*-isopropyl-*N*-(2,3-dimethoxycarbonyl-1-(2-pyridyl)allylamino)furan-2,3-dicarboxylate (5j): 42% (method A); colorless crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 141–142 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1748, 1732, 1646, 1589; δ_{H} (400 MHz, CD_3COCD_3) 8.53 (d, $J = 8.7$ Hz, 2H), 8.33 (brs, 1H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.53 (d, $J = 8.8$ Hz, 3H), 7.13 (brs, 1H), 6.62 (s, 1H), 5.66 (s, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 3.80 (br, 1H), 3.65 (s, 6H), 1.02 (d, $J = 6.2$ Hz, 3H), 0.89 (d, $J = 6.6$ Hz, 3H); δ_{C} (100 MHz, CD_3COCD_3) 167.6, 165.6, 165.5, 158.4, 158.1, 153.1, 149.7, 149.4, 140.8, 137.0, 135.2, 129.9, 129.3, 129.2, 129.0, 127.4, 125.5, 124.8, 123.7, 70.7, 53.0, 52.6, 52.5, 52.2, 52.1, 20.7, 18.5; HRMS (TOF-ESI) 585.1634 ($\text{M} + 1$), $\text{C}_{29}\text{H}_{30}\text{ClN}_2\text{O}_9$ required 585.1640 ($\text{M} + 1$).

(Z)-Dimethyl 4-(*N*-benzyl-*N*-(2,3-dimethoxycarbonyl-1-(2-pyridyl)allylamino)-5-(*p*-chlorophenyl)furan-2,3-dicarboxylate (5k): 47% (method A); white crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 141–142 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1728, 1587; δ_{H} (400 MHz, CDCl_3) 8.31 (d, $J = 4.4$ Hz, 1H), 7.50 (d, $J = 8.6$ Hz, 2H), 7.45 (br, 1H), 7.24 (br, 1H), 7.13 (d, $J = 8.6$ Hz, 2H), 7.04 (br, 1H), 6.93 (s, 5H), 6.52 (br, 1H), 5.34 (br, 1H), 4.23 (d, $J = 12.5$ Hz, 1H), 4.05 (d, $J = 12.5$ Hz, 1H), 3.91 (s, 3H), 3.74 (s, 3H), 3.62 (s, 3H), 3.60 (s, 3H); δ_{C} (100 MHz, CDCl_3) 167.2, 165.2, 164.7, 158.0, 156.1, 151.2, 149.3, 147.8, 139.5, 136.2, 135.9, 134.8, 129.9, 129.0, 128.4, 127.9, 127.8, 127.4, 127.0, 126.2, 124.2, 124.1, 123.1, 72.3, 57.0, 52.9, 52.3, 52.0; MS (ESI) 633 ($\text{M} + 1$). Anal. Calcd for $\text{C}_{33}\text{H}_{29}\text{ClN}_2\text{O}_9$: C, 62.61; H, 4.62; N, 4.43. Found: C, 62.47; H, 4.42; N, 4.30.

(E)-Dimethyl 4-(*N*-benzyl-*N*-(2,3-dimethoxycarbonyl-1-(2-pyridyl)prop-1-enyl)amino)-5-(*p*-chlorophenyl)furan-2,3-dicarboxylate (6k): 42% (method B), 6% (method A); white crystals (CH_2Cl_2 , petroleum ether, ethyl acetate); mp 116–118 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1730, 1689, 1597, 1564; δ_{H} (400 MHz, CDCl_3) 8.66 (d, $J = 4.2$ Hz, 1H), 7.99 (d, $J = 8.6$ Hz, 2H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.38 (d, $J = 8.6$ Hz, 2H), 7.21 (t, $J = 6.9$ Hz, 2H), 7.03–7.09 (m, 3H), 6.98 (d, $J = 5.8$ Hz, 2H), 4.52 (s, 2H), 3.90 (s, 3H), 3.87 (s, 3H), 3.63 (s, 2H), 3.44 (s, 3H), 3.25 (s, 3H); δ_{C} (125 MHz, CD_3COCD_3) 170.4, 169.3, 163.2, 157.3, 155.8, 155.0, 148.9, 147.8, 139.7, 136.7, 135.9, 134.7, 129.0, 128.6, 128.4, 127.9, 127.5, 127.2, 126.9, 126.2, 125.2, 123.6, 109.1, 56.2, 52.5, 51.9, 50.8, 50.3, 34.8; HRMS (TOF-ESI) 633.1620 ($\text{M} + 1$), $\text{C}_{33}\text{H}_{30}\text{ClN}_2\text{O}_9$ requires 633.1640 ($\text{M} + 1$).

(Z)-Dimethyl 4-(*N*-(2,3-dimethoxycarbonyl-1-(2-pyridyl)allyl)-*N*-(*p*-methylphenyl)amino)-5-(2-furyl)furan-2,3-dicarboxylate (5l): 66% (method A); mp 153–155 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1720, 1652, 1576; δ_{H} (400 MHz, CDCl_3) 8.33 (d, $J = 4.4$ Hz, 1H), 7.48 (s, 2H), 7.27 (br, 1H), 7.05 (br, 1H), 7.00 (d, $J = 8.4$ Hz, 2H), 6.77 (d, $J = 8.6$ Hz, 2H), 6.61 (d, $J = 3.4$ Hz, 1H), 6.51 (s, 1H), 6.44 (dd, $J = 3.4$, 1.7 Hz, 1H), 6.09 (brs, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.69 (s, 3H), 3.60 (s, 3H), 2.23 (s, 3H); δ_{C} (100 MHz, CDCl_3) 167.4, 165.7, 162.6, 157.7, 154.6, 149.1, 146.3, 145.1, 144.3, 144.0, 142.8, 139.3, 136.1, 129.5, 129.3, 128.0, 126.0, 124.9, 123.8, 123.1, 116.2, 111.8, 111.5, 68.1, 52.8, 52.4, 51.93, 51.89, 20.4; MS (ESI) 589 ($\text{M} + 1$). Anal. Calcd for $\text{C}_{31}\text{H}_{28}\text{N}_2\text{O}_{10}$: C, 63.26; H, 4.80; N, 4.76. Found: C, 63.10; H, 5.03; N, 4.70.

(E)-Dimethyl 4-(*N*-(2,3-dimethoxycarbonyl-1-(2-pyridyl)prop-1-enyl)-*N*-(*p*-methylphenyl)amino)-5-(2-furyl)furan-2,3-dicarboxylate (6l): 55% (method B), 10% (method A); mp 183–184 °C;

$\nu_{\text{max}}/\text{cm}^{-1}$ 1735, 1725, 1692; δ_{H} (400 MHz, CDCl_3) 8.39 (d, $J = 4.3$ Hz, 1H), 7.45 (br, 1H), 7.38 (br, 1H), 7.36 (s, 1H), 7.03 (br, 1H), 6.83–6.88 (m, 4H), 6.60 (d, $J = 2.5$ Hz, 1H), 6.36 (dd, $J = 3.4, 1.6$ Hz, 1H), 3.81 (s, 3H), 3.53 (s, 2H), 3.49 (s, 3H), 3.35 (s, 3H), 3.32 (s, 3H), 2.14 (s, 3H); δ_{C} (100 MHz, CDCl_3) 170.3, 170.0, 162.3, 157.6, 154.7, 150.7, 148.6, 143.8, 142.6, 142.3, 139.2, 135.9, 133.5, 129.63, 129.57, 126.0, 124.9, 124.6, 123.4, 122.8, 116.9, 111.9, 111.5, 52.6, 52.4, 51.6, 35.8, 20.7; MS (ESI) 589 ($M + 1$). Anal. Calcd for $\text{C}_{31}\text{H}_{28}\text{N}_2\text{O}_{10}$: C, 63.26; H, 4.80; N, 4.76. Found: C, 63.09; H, 4.87; N, 4.70.

(E)-Dimethyl 4-(N-(2,3-dimethoxycarbonyl-1-(2-pyridyl)prop-1-enyl)-N-(*p*-methylphenyl)amino)-5-(*n*-propyl)furan-2,3-dicarboxylate (6m): 42% (method A); $\nu_{\text{max}}/\text{cm}^{-1}$ 1735, 1594, 1584, 1564; δ_{H} (400 MHz, CD_3COCD_3) 8.50 (d, $J = 4.1$ Hz, 1H), 7.66 (dt, $J = 7.8, 1.7$ Hz, 1H), 7.53 (d, $J = 7.9$ Hz, 1H), 7.20–7.24 (m, 1H), 7.18 (br, 2H), 7.00 (br, 2H), 6.94 (t, $J = 7.4$ Hz, 1H), 3.81 (s, 3H), 3.58 (s, 2H), 3.46 (s, 3H), 3.38 (s, 3H), 3.33 (s, 3H), 2.63 (t, $J = 7.3$ Hz, 2H), 1.62–1.69 (m, 2H), 0.93 (t, $J = 7.4$ Hz, 3H); δ_{C} (100 MHz, CD_3COCD_3) 170.8, 170.2, 163.3, 158.2, 156.3, 155.5, 151.4, 149.7, 146.5, 140.2, 136.7, 129.8, 128.0, 125.6, 124.3, 123.9, 123.1, 122.5, 118.8, 52.43, 52.36, 51.8, 51.4, 36.3, 28.6, 21.0, 14.1; HRMS (TOF-ESI) 551.2022 ($M + 1$), $\text{C}_{29}\text{H}_{31}\text{N}_2\text{O}_9$ requires 551.2030 ($M + 1$).

General Procedure for the Reaction of Imidazo[1,5-*a*]pyridinium Salts 1 and Aromatic Aldehydes 3 with Allenates 7 in the Presence of NaH. Imidazo[1,5-*a*]pyridinium salts 1 (1.0 mmol), aromatic aldehydes 3 (1.5 mmol), and allenates 7 (1.5 mmol) were mixed in dry dichloromethane (60 mL) at room temperature. Under nitrogen atmosphere and at -20°C , NaH (1.5 mmol) was added to the reaction mixture, and the mixture was then stirred at -20°C for 8–12 h. After removal of the excess NaH and NaCl by filtration and evaporation of the solvent under vacuum, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether (30–60 $^\circ\text{C}$) and ethyl acetate (8:1–5:1) to afford colorless, crystalline 8 and 9.

Methyl 5-(*p*-bromophenyl)-2-ethyl-4-(*N*-phenyl-*N*-(2-pyridylmethyl)amino)furan-3-carboxylate (8a): 45%; white crystals (CH_2Cl_2 , petroleum ether); mp 151–153 $^\circ\text{C}$; $\nu_{\text{max}}/\text{cm}^{-1}$ 1717, 1594, 1571; δ_{H} (400 MHz, CDCl_3) 8.47 (d, $J = 4.7$ Hz, 1H), 7.49 (d, $J = 8.2$ Hz, 2H), 7.45 (t, $J = 7.8$ Hz, 1H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.26 (brs, 1H), 7.20 (t, $J = 7.6$ Hz, 2H), 7.09 (t, $J = 5.6$ Hz, 1H), 6.80 (t, $J = 6.8$ Hz, 3H), 4.82 (br, 2H), 3.62 (s, 3H), 3.09 (q, $J = 7.5$ Hz, 2H), 1.35 (t, $J = 7.5$ Hz, 3H); δ_{C} (100 MHz, CDCl_3) 164.4, 163.3, 158.5, 148.9, 148.4, 146.6, 136.4, 131.6, 129.1, 128.0, 127.9, 126.9, 122.5, 122.0, 121.9, 118.5, 113.8, 111.9, 59.5, 51.2, 22.1, 12.1; MS (ESI) 490 ($M + 1$). Anal. Calcd for $\text{C}_{26}\text{H}_{23}\text{BrN}_2\text{O}_3$: C, 63.55; H, 4.72; N, 5.70. Found: C, 63.37; H, 4.79; N, 5.52.

Methyl 5-(*p*-bromophenyl)-4-(*N*-phenyl-*N*-(2-pyridylmethyl)amino)-2-propylfuran-3-carboxylate (8b): 53%; white crystals (CH_2Cl_2 , petroleum ether); mp 142–144 $^\circ\text{C}$; $\nu_{\text{max}}/\text{cm}^{-1}$ 1716, 1591, 1571; δ_{H} (400 MHz, CDCl_3) 8.47 (d, $J = 4.4$ Hz, 1H), 7.44–7.50 (m, 3H), 7.40 (d, $J = 8.3$ Hz, 2H), 7.25 (br, 1H), 7.20 (t, $J = 7.8$ Hz, 2H), 7.08–7.11 (m, 1H), 6.78–6.82 (m, 3H), 4.85 (br, 2H), 3.62 (s, 3H), 3.04 (t, $J = 7.5$ Hz, 2H), 1.80 (sextet, $J = 7.4$ Hz, 2H), 1.03 (t, $J = 7.4$ Hz, 3H); δ_{C} (100 MHz, CDCl_3) 163.4, 163.3, 158.5, 149.0, 148.5, 146.7, 136.2, 131.6, 129.1, 128.0, 127.8, 126.9, 122.5, 122.0, 118.4, 113.8, 112.5, 59.5, 51.2, 30.3, 21.3, 13.8; MS (ESI) 505 ($M + 1$). Anal. Calcd for $\text{C}_{27}\text{H}_{25}\text{BrN}_2\text{O}_3$: C, 64.16; H, 4.99; N, 5.54. Found: C, 64.12; H, 5.35; N, 5.35.

Methyl 5-(*p*-bromophenyl)-2-phenethyl-4-(*N*-phenyl-*N*-(2-pyridylmethyl)amino)furan-3-carboxylate (8c): 47%; white crystals (CH_2Cl_2 , petroleum ether); mp 140–141 $^\circ\text{C}$; $\nu_{\text{max}}/\text{cm}^{-1}$ 1705, 1622, 1594, 1572; δ_{H} (400 MHz, CDCl_3) 8.47 (d, $J = 4.5$ Hz, 1H), 7.38–7.48 (m, 5H), 7.30 (t, $J = 8.0$ Hz, 2H), 7.18–7.25 (m, 6H), 7.10 (t, $J = 5.5$ Hz, 1H), 6.80 (t, $J = 7.2$ Hz, 1H), 6.77 (d, $J = 8.2$ Hz, 2H), 4.83 (br, 2H), 3.59 (s, 3H), 3.38 (t, $J = 7.4$ Hz, 2H), 3.08

(t, $J = 8.1$ Hz, 2H); δ_{C} (100 MHz, CDCl_3) 163.1, 162.1, 158.4, 148.9, 148.4, 146.9, 140.5, 136.4, 131.6, 129.1, 128.5, 128.4, 127.9, 127.8, 127.0, 126.3, 122.6, 122.0, 118.5, 113.9, 113.0, 59.4, 51.2, 34.2, 30.4; HRMS (ESI) 567.1266 ($M + 1$), $\text{C}_{32}\text{H}_{28}\text{BrN}_2\text{O}_3$ requires 567.1283 ($M + 1$). Anal. Calcd for $\text{C}_{32}\text{H}_{27}\text{BrN}_2\text{O}_3$: C, 67.73; H, 4.80; N, 4.94. Found: C, 67.32; H, 4.96; N, 4.74.

Methyl 2-(3-benzyl-5-(*p*-bromophenyl)-4-(*N*-phenyl-*N*-(2-pyridylmethyl)amino)(2-furyl)acetate (9c): 11%; oil; $\nu_{\text{max}}/\text{cm}^{-1}$ 1743, 1596; δ_{H} (400 MHz, CDCl_3) 8.37 (d, $J = 4.5$ Hz, 1H), 7.34 (d, $J = 8.7$ Hz, 2H), 7.29 (d, $J = 8.7$ Hz, 2H), 7.11 (d, $J = 8.6$ Hz, 2H), 7.07 (d, $J = 7.3$ Hz, 2H), 7.02–7.06 (m, 4H), 6.93 (d, $J = 7.0$ Hz, 2H), 6.72 (t, $J = 7.8$ Hz, 1H), 6.71 (d, $J = 8.6$ Hz, 2H), 4.62 (s, 2H), 3.61 (s, 3H), 3.53 (s, 2H), 3.43 (s, 2H); δ_{C} (100 MHz, CDCl_3) 169.5, 158.1, 148.7, 147.5, 146.3, 144.5, 138.6, 136.7, 131.6, 129.8, 129.3, 128.6, 128.5, 128.4, 126.5, 126.3, 122.5, 122.3, 122.1, 121.4, 118.5, 113.7, 58.3, 52.3, 33.0, 29.1; HRMS (TOF-ESI): 567.1286 ($M + 1$), $\text{C}_{32}\text{H}_{28}\text{BrN}_2\text{O}_3$ requires 567.1283 ($M + 1$).

Methyl 5-(*p*-chlorophenyl)-2-ethyl-4-(*N*-phenyl-*N*-(2-pyridylmethyl)amino)furan-3-carboxylate (8d): 42%; white crystals (CH_2Cl_2 , petroleum ether); mp 147–148 $^\circ\text{C}$; $\nu_{\text{max}}/\text{cm}^{-1}$ 1719, 1594, 1568; δ_{H} (400 MHz, CDCl_3) 8.29 (d, $J = 4.2$ Hz, 1H), 7.38 (d, $J = 8.6$ Hz, 2H), 7.26 (dt, $J = 7.7, 1.7$ Hz, 1H), 7.05–7.08 (m, 2H), 7.02 (t, $J = 8.0$ Hz, 2H), 6.90 (dd, $J = 7.0, 5.3$ Hz, 1H), 6.63 (d, $J = 7.3$ Hz, 1H), 6.61 (d, $J = 8.2$ Hz, 3H), 4.64 (br, 2H), 3.44 (s, 3H), 2.91 (q, $J = 7.6$ Hz, 2H), 1.18 (t, $J = 7.6$ Hz, 3H); δ_{C} (100 MHz, CDCl_3) 164.3, 163.3, 158.6, 149.0, 148.5, 146.6, 136.2, 133.7, 129.1, 128.6, 127.8, 127.6, 122.4, 122.0, 118.4, 113.8, 111.9, 59.7, 51.2, 22.0, 12.1; MS (ESI) 447 ($M + 1$). Anal. Calcd for $\text{C}_{26}\text{H}_{23}\text{ClN}_2\text{O}_3$: C, 69.87; H, 5.19; N, 6.27. Found: C, 69.77; H, 5.43; N, 6.18.

Methyl 5-(*p*-chlorophenyl)-2-phenethyl-4-(*N*-phenyl-*N*-(2-pyridylmethyl)amino)furan-3-carboxylate (8e): 54%; white crystals (CH_2Cl_2 , petroleum ether); mp 145–146 $^\circ\text{C}$; $\nu_{\text{max}}/\text{cm}^{-1}$ 1716, 1592, 1568; δ_{H} (400 MHz, CDCl_3) 8.40 (d, $J = 4.7$ Hz, 1H), 7.41 (d, $J = 8.6$ Hz, 2H), 7.38 (br, 1H), 7.10–7.23 (m, 10H), 7.02 (br, 1H), 6.73 (t, $J = 7.2$ Hz, 1H), 6.69 (d, $J = 8.3$ Hz, 2H), 4.76 (br, 2H), 3.51 (s, 3H), 3.30 (t, $J = 8.2$ Hz, 2H), 3.00 (t, $J = 8.1$ Hz, 2H); δ_{C} (100 MHz, CDCl_3) 163.1, 162.0, 158.5, 149.0, 148.5, 146.9, 140.6, 136.3, 133.8, 129.1, 128.6, 128.5, 128.4, 127.6, 127.4, 126.7, 126.3, 122.5, 122.0, 118.5, 113.9, 113.0, 59.5, 51.2, 34.3, 30.4; MS (ESI) 523 ($M + 1$), 545 ($M + \text{Na}^+$). Anal. Calcd for $\text{C}_{32}\text{H}_{27}\text{ClN}_2\text{O}_3$: C, 73.49; H, 5.20; N, 5.36. Found: C, 73.35; H, 4.89; N, 5.34.

Methyl 2-(3-benzyl-5-(*p*-chlorophenyl)-4-(*N*-phenyl-*N*-(2-pyridylmethyl)amino)(2-furyl)acetate (9e): 6%; oil; $\nu_{\text{max}}/\text{cm}^{-1}$ 1743, 1596; δ_{H} (400 MHz, CDCl_3) 8.36 (d, $J = 4.7$ Hz, 1H), 7.40 (d, $J = 8.5$ Hz, 2H), 7.32 (d, $J = 7.6$ Hz, 1H), 6.99–7.15 (m, 9H), 6.94 (d, $J = 7.4$ Hz, 2H), 6.72 (t, $J = 5.2$ Hz, 1H), 6.71 (d, $J = 8.1$ Hz, 2H), 4.62 (s, 2H), 3.61 (s, 3H), 3.53 (s, 2H), 3.43 (s, 2H); δ_{C} (100 MHz, CDCl_3) 169.4, 158.1, 148.5, 147.6, 146.3, 144.4, 138.6, 136.7, 133.2, 129.7, 129.3, 128.6, 128.5, 128.3, 128.2, 126.3, 126.2, 122.4, 122.3, 122.1, 118.5, 113.7, 58.2, 52.2, 33.0, 29.1; HRMS (TOF-ESI) 523.1796 ($M + 1$), $\text{C}_{32}\text{H}_{28}\text{ClN}_2\text{O}_3$ required 523.1788 ($M + 1$).

Methyl 5-(*o*-fluorophenyl)-2-phenethyl-4-(*N*-phenyl-*N*-(2-pyridylmethyl)amino)furan-3-carboxylate (8f): 41%; white crystals (CH_2Cl_2 , petroleum ether); mp 100–102 $^\circ\text{C}$; $\nu_{\text{max}}/\text{cm}^{-1}$ 1700, 1599, 1581, 1495; δ_{H} (400 MHz, CDCl_3) 8.39 (d, $J = 4.4$ Hz, 1H), 7.20–7.29 (m, 5H), 7.13–7.16 (m, 3H), 7.07–7.11 (m, 3H), 6.96–7.00 (m, 3H), 6.70 (t, $J = 7.3$ Hz, 1H), 6.60 (d, $J = 8.2$ Hz, 2H), 4.71 (br, 2H), 3.46 (s, 3H), 3.30 (t, $J = 8.2$ Hz, 2H), 3.00 (t, $J = 8.2$ Hz, 2H); δ_{C} (100 MHz, CDCl_3) 162.8, 161.0, 158.8, 158.5, 149.0, 148.8, 143.8, 140.6, 136.3, 130.64, 130.56, 130.3, 130.2, 129.8, 128.8, 128.5, 128.4, 126.2, 124.02, 123.98, 121.8, 121.7, 118.3, 117.5, 117.3, 116.2, 116.0, 114.0, 112.3, 59.5, 51.1, 34.1, 30.4; MS (EI) 123 (100), 506 (M^+ , 80). Anal. Calcd for $\text{C}_{32}\text{H}_{27}\text{FN}_2\text{O}_3$: C, 75.87; H, 5.37; N, 5.53. Found: C, 75.56; H, 5.20; N, 5.20.

Methyl 5-(*p*-chlorophenyl)-4-(*N*-(*p*-methoxyphenyl)-*N*-(2-pyridylmethyl)amino)-2-phenethylfuran-3-carboxylate (8g): 40%; white crystals (CH₂Cl₂, petroleum ether); mp 97–98 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1708, 1623, 1594; δ_{H} (400 MHz, CDCl₃) 8.49 (d, J = 4.8 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.21–7.32 (m, 8H), 7.09 (t, J = 6.9 Hz, 1H), 6.77 (d, J = 9.2 Hz, 2H), 6.69 (d, J = 8.9 Hz, 2H), 4.78 (br, 2H), 3.75 (s, 3H), 3.61 (s, 3H), 3.36 (t, J = 8.1 Hz, 2H), 3.07 (t, J = 8.2 Hz, 2H); δ_{C} (100 MHz, CDCl₃) 163.2, 162.0, 158.8, 152.5, 149.0, 146.8, 142.6, 140.6, 136.3, 133.7, 128.6, 128.5, 128.4, 128.3, 127.5, 126.7, 126.3, 122.4, 122.0, 114.9, 114.5, 113.0, 59.9, 55.6, 51.3, 34.3, 30.5; HRMS (TOF-ESI) 553.1881 ($M + 1$), C₃₃H₃₀ClN₂O₄ requires 553.1894 ($M + 1$).

Methyl 5-(*p*-bromophenyl)-2-propyl-4-(*N*-(2-pyridylmethyl)-*N*-(*p*-tolyl)amino)furan-3-carboxylate (8h): 44%; white crystals (CH₂Cl₂, petroleum ether); mp 151–153 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1707, 1626, 1611, 1593; δ_{H} (400 MHz, CDCl₃) 8.47 (d, J = 4.8 Hz, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.44 (t, J = 7.6 Hz, 1H), 7.40 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 6.8 Hz, 1H), 7.07 (t, J = 6.7 Hz, 1H), 6.99 (d, J = 8.2 Hz, 2H), 6.68 (d, J = 8.2 Hz, 2H), 4.81 (br, 2H), 3.63 (s, 3H), 3.02 (t, J = 7.5 Hz, 2H), 2.24 (s, 3H), 1.80 (sextet, J = 7.4 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H); δ_{C} (100 MHz, CDCl₃) 163.4, 163.3, 158.7, 148.8, 146.6, 146.1, 136.4, 131.5, 129.7, 128.1, 128.05, 127.5, 126.9, 122.6, 122.0, 121.9, 113.8, 112.6, 59.5, 51.2, 30.3, 21.3, 20.4, 13.8; MS (ESI) 519 ($M + 1$). Anal. Calcd for C₂₈H₂₇BrN₂O₃: C, 64.74; H, 5.24; N, 5.39. Found: C, 64.76; H, 5.57; N, 5.23.

Methyl 5-(*p*-chlorophenyl)-4-(*N*-(*p*-chlorophenyl)-*N*-(2-pyridylmethyl)amino)-2-phenethylfuran-3-carboxylate (8i): 49%; white crystals (CH₂Cl₂, petroleum ether); mp 109–110 °C; $\nu_{\text{max}}/\text{cm}^{-1}$ 1709, 1592, 1569, 1493; δ_{H} (400 MHz, CDCl₃) 8.48 (d, J = 4.8 Hz, 1H), 7.46 (dd, J = 6.8, 1.8 Hz, 2H), 7.45–7.50 (m, 1H), 7.19–7.32 (m, 8H), 7.13 (dd, J = 9.0, 2.0 Hz, 2H), 7.12–7.15 (m, 1H), 6.70 (dd, J = 7.0, 2.1 Hz, 2H), 4.8 (br, 2H), 3.61 (s, 3H), 3.38 (t, J = 8.0 Hz, 2H), 3.08 (t, J = 7.4 Hz, 2H); δ_{C} (100 MHz, CDCl₃) 162.9, 162.1, 157.9, 149.0, 147.1, 147.0, 140.4, 136.4, 134.0, 129.0, 128.7, 128.5, 128.4, 127.22, 127.18, 126.6, 126.3, 123.4, 122.6, 122.2, 115.0, 112.8, 59.5, 51.3, 34.2, 30.4; HRMS (TOF-ESI) 557.1396 ($M + 1$), C₃₂H₂₇Cl₂N₂O₃ requires 557.1399 ($M + 1$).

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Supporting Information Available: General procedure for the preparation of 2-aryl (alkyl)imidazo[1,5-*a*]pyridinium salts **1**, copies of ¹H NMR and ¹³C NMR spectra of products **5**, **6**, **8**, and **9** excluding those byproducts without full characterization, as well as single-crystal data of **6a** and **8e** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.