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Orthogonal Synthesis of Densely Functionalized Pyrroles and Thiophenes from the Reactions of Imidazo[1,5-*a*]pyridine Carbene-Derived Zwitterions with Electron-Deficient Alkynes

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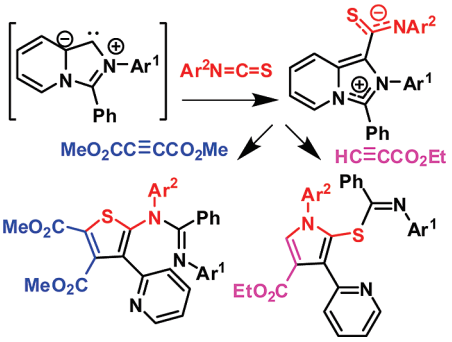

1-Thiocarbamoyl imidazo[1,5-*a*]pyridinium inner salts, which were obtained readily from the addition of *C*,*N*-substituted heterocyclic carbenes imidazo[1,5-*a*]pyridine-1-ylidenes to isothiocyanates, are powerful ambident nucleophilic zwitterions. They acted as nitrogen nucleophiles toward ethyl propiolate to produce polyfunctionalized pyrrole derivatives in high yields. When treated with dimethyl acetylenedicarboxylate, they behaved exclusively as sulfur nucleophiles to afford fully substituted thiophenes in excellent yields. This work provides highly efficient orthogonal synthesis of polyfunctionalized pyrroles and thiophenes that were not easily obtained by other chemical means.

Introduction

The studies of polyfunctionalized pyrroles and thiophenes continue to be an active field of research, spanning from natural product synthesis[1] through medicinal chemistry[2] and on to material science.[3] The pyrrole moiety is ubiquitous in natural products, and numerous natural and unnatural pyrrole derivatives possess remarkable biological and pharmacological activities.[4] For example, a series of chlorinated bisindole pyrroles, lynamicins A−E, show broad-spectrum activity against both Gram-positive and Gram-negative organisms,[5] while the pyrrole-amidine TAN 868A[6] and the chlorinated pyrrole LL-F42248[7] are antibiotics. The two analogous pyrrole-2-carboxylate alkaloids, Agelongine and Daminin, have antiserotonergic activity and neuroprotective properties, respectively.[8] A number of synthetic pyrrole derivatives were proven very active against both fungi and mycobacteria, and other pyrroles are COX-2 (cyclooxygenase) selective inhibitors.[2a] Similar to the pyrrole derivatives, many polyfunctional thiophenes have important

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bioactivities. For instance, some diarylthiophenes are inhibitors of tumor necrosis factor-α,[9] and a series of 2-amino-4-methylthiophenecarboxylate derivatives show good anti-inflammatory or analgesic activities.[10] In addition to the huge potentials in pharmacological applications, polyfunctional pyrroles and thiophenes are important precursors of organic functional materials. Polypyrrole- and polythiophene-based conducting polymers have various applications in microelectronics, electrode materials, sensors, and optoelectronics.[3,11] Because of the great importance of pyrrole and thiophene derivatives, the synthetic study remains undiminished.[12] The traditional Paal−Knorr,[13] Knorr,[14] and Hantzsch[15] reactions, along with the strategies of 1,3-dipolar cycloaddition,[16] metal-mediated synthesis,[17] carbenoid transfer reactions,[18] and ring contractions[19] have been well practised in the construction of pyrroles, and the Hinsberg[20] and Gewald[21] reactions are two of the most used methods for the preparation of thiophene derivatives. Although a number of methods for the construction of pyrroles and thiophenes have been established, the efficient synthesis of highly functionalized pyrroles and thiophenes remains challenging.

In 2006, we discovered that *N*-heterocyclic carbene-derived 2-thiocarbamoyl benzimidazolium and imidazolinium inner salts are unusual ambident 1,3-dipolar reagents.[22a] On the basis of the [3 + 2] cycloaddition reactions of novel 1,3-dipoles or dipolar intermediates readily available from the addition of *N*-heterocyclic carbenes to heterocumulenes such as isothiocyanates, isoselenocyanates and ketenimines, we have established and developed a powerful methodology for the construction of spiro- or fused pyrroles and thiophenes.[22] The diverse reaction pathways are regulated by the nature of both *N*-heterocyclic carbenes and 1,3-dipolarophiles. Our continued interest in the chemistry of *N*-heterocyclic carbenes led us to study the reactivity of novel dipolar adducts derived from various *N*-heterocyclic carbenes and heterocumulenes. Our attention was drawn then by imidazo[1,5-*a*]pyridine carbenes, which have been generated easily from the deprotonation of imidazo[1,5-*a*]pyridinium salts reported by Lassaletta[23] and Glorius[24] in 2005. Interestingly, depending on the position of a substituent on the imidazole ring, imidazo[1,5-*a*]pyridinium salts can be deprotonated at the 1- or 3-position to produce imidazo[1,5-*a*]pyridine-1-ylidenes or imidazo[1,5-*a*]pyridine-3-ylidenes that can be regarded as *C*,*N*-substituted and *N*,*N*-substituted carbenes, respectively. Both imidazo[1,5-*a*]pyridine-1-ylidenes and imidazo[1,5-*a*]pyridine-3-ylidenes have been shown to be strong C-ligands to Ag, Rh, Ir, and Pd cations and elemental Se. Surprisingly, their reactions with organic compounds either as reagents or as organocatalysts have never been explored. We envisioned that the addition of 3-arylimidazo[1,5-*a*]pyridine-1-ylidenes, the *C*,*N*-substituted carbenes, to aryl isothiocyanates would form 1-thiocarbamoylimidazo[1,5-*a*]pyridinium zwitterions. Being different from the 1,3-dipolar adducts derived from the addition of *N*,*N*- and *N*,*S*-substituted heterocyclic carbenes to heterocumulenes, the 1-thiocarbamoylimidazo[1,5-*a*]pyridinium zwitterions are not 1,3-dipoles because their cation and anion centers are separated by more than one atom. As a new bis-nucleophilic dipolar species, they might undergo unique reactions with electron-deficient alkynes. Herein we report highly efficient and orthogonal synthesis of polyfunctionalized pyrroles and thiophenes from the reaction of 1-thiocarbamoylimidazo[1,5-*a*]pyridinium inner salts with ethyl propiolate and dimethyl acetylenedicarboxylate.

Results and Discussion

In this work, the carbene precursors, 3-arylimidazo[1,5-*a*]pyridinium salts **1**, were synthesized from pyridine-2-carbaldehyde and amines via a $POCl_3$-mediated cyclization of an amide intermediate according to literature methods.[23,24]

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SCHEME 1. Preparation of 1-Thiocarbamoyl Imidazo[1,5-*a*]pyridinium Inner Salts 4

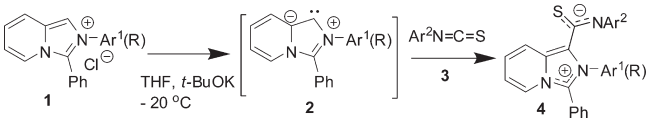


TABLE 1. Reaction of Imidazo[1,5-*a*]pyridinium Salts 1 with Aryl Isothiocyanates in the Presence of *t*-BuOK[a]

entry	1	Ar^1 or R	3	Ar^2	yield of 4 (%)[b]
1	**1a**	Ph	**3a**	Ph	**4a**: 84
2	**1b**	*p*-MeC_6H_4	**3a**	Ph	**4b**: 75
3	**1b**	*p*-MeC_6H_4	**3b**	*p*-BrC_6H_4	**4c**: 66
4	**1c**	*p*-$MeOC_6H_4$	**3a**	Ph	**4d**: 80
5	**1c**	*p*-$MeOC_6H_4$	**3b**	*p*-BrC_6H_4	**4e**: 59
6	**1d**	*p*-ClC_6H_4	**3a**	Ph	**4f**: 67
7	**1d**	*p*-ClC_6H_4	**3b**	*p*-BrC_6H_4	**4g**: 81
8	**1d**	*p*-ClC_6H_4	**3c**	*p*-ClC_6H_4	**4h**: 72
9	**1d**	*p*-ClC_6H_4	**3d**	*p*-$MeOC_6H_4$	**4i**: 67
10	**1f**	Et	**3a**	Ph	**4j**: 81
11	**1g**	*i*-Pr	**3b**	*p*-BrC_6H_4	**4k**: 74

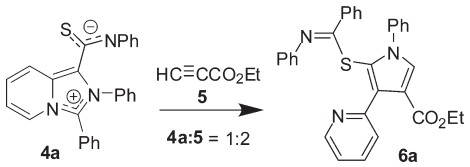
[a]Reaction conditions: THF, −20 °C, 8 h, **1**:**3** = 1:1.2. [b]Isolated yield.

The 3-aryl-1-thiocarbamoylimidazo[1,5-*a*]pyridinium zwitterions **4** were prepared from the reaction of 3-arylimidazo-[1,5-*a*]pyridine-1-ylidenes **2** with aryl isothiocyanates. Thus, the reaction of 3-arylimidazo[1,5-*a*]pyridinium salts **1** with aryl isothiocyanates **3** in the presence of *t*-BuOK took place at −20 °C for 8 h to afford yellow crystalline 1-thiocarbamoyl imidazo[1,5-*a*]pyridinium inner salts **4** in 59−84% yields (Scheme 1, Table 1).

With 1-thiocarbamoylimidazo[1,5-*a*]pyridinium zwitterions **4** in hand, we first studied their reaction with ethyl propiolate. The reaction of 1-(*N*-phenyl)thiocarbamoyl-2,3-diphenylimidazo[1,5-*a*]pyridinium inner salt **4a** with ethyl propiolate in THF proceeded smoothly at ambient temperature to give a new product. Instead of the formation of spiro or fused heterocyclic product that was anticipated on the basis of our previous investigations, the product was surprisingly a polyfunctionalized pyrrole derivative, (*Z*)-1-phenyl-5-[phenyl(phenylimino)methylthio]-4-(2-pyridinyl)pyrrole-3-carboxylate **6a**. The reaction conditions were optimized by varying solvents and reaction temperature in order to obtain high chemical yield. At room temperature, the reaction was found to proceed smoothly in both polar and nonpolar solvents including acetone, acetonitrile, 1,4-dioxane, THF, dichloromethane, and benzene. The highest yield of product **6a** (93%) was obtained when reaction was performed in 1,4-dioxane at room temperature. The increase of the temperature led to acceleration of the reaction but with a diminished chemical yield (Table 2, entries 6 and 7).

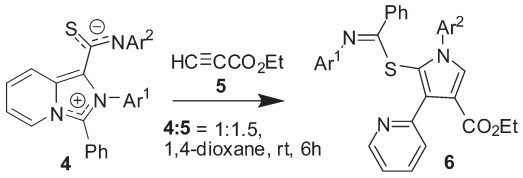
The generality of the reaction was studied under the optimized conditions using zwitterions **4** bearing different substituents. As summarized in Table 3, 1-arylthiocarbamoyl-2-aryl imidazo[1,5-*a*]pyridiniums **4** with a *p*-tolyl, *p*-anisyl, or *p*-halophenyl on the nitrogen atom of the imidazole ring or thiocarbamoyl group reacted efficiently with ethyl propiolate, furnishing (*Z*)-1-aryl-5-[aryl(arylimino)-methylthio]-4-(2-pyridinyl)pyrrole-3-carboxylates **6** in good to excellent yields. Varying 2-aryl to 2-alkyl, the reactions of 2-ethyl- and 2-isopropyl-substituted imidazo[1,5-*a*]pyridinium inner salts **4j** and **4k** with ethyl propiolate were also examined. Although these reactions proceeded equally efficiently,

TABLE 2. Reaction of 4a with Ethyl Propiolate under Different Conditions



	reaction conditions			
entry	solvent	temp	time	yield of **6a** (%)
1	THF	rt	6 h	77
2	acetone	rt	6 h	69
3	dichloromethane	rt	6 h	74
4	acetonitrile	rt	6 h	65
5	benzene	rt	6 h	76
6	1,4-dioxane	rt	6 h	93
7	1,4-dioxane	80 °C	20 min	68

TABLE 3. Reaction of 4 with Ethyl Propiolate under Optimized Conditions

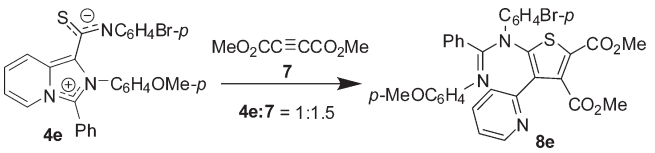


entry	4	Ar^1	Ar^2	yield of **6** (%)
1	**4a**	Ph	Ph	**6a**: 93
2	**4b**	*p*-MeC_6H_4	Ph	**6b**: 89
3	**4c**	*p*-MeC_6H_4	*p*-BrC_6H_4	**6c**: 93
4	**4d**	*p*-$MeOC_6H_4$	Ph	**6d**: 92
5	**4e**	*p*-$MeOC_6H_4$	*p*-BrC_6H_4	**6e**: 84
6	**4f**	*p*-ClC_6H_4	Ph	**6f**: 86
7	**4g**	*p*-ClC_6H_4	*p*-BrC_6H_4	**6g**: 85
8	**4h**	*p*-ClC_6H_4	*p*-ClC_6H_4	**6h**: 90

they afforded however a mixture of products that were most probably the *Z*- and *E*-isomers determined by ^{1}H NMR and microanalysis. These isomers could not been separated by column chromatography or recrystallization, and therefore pure products from 2-alkylimidazo[1,5-*a*]pyridinium inner salts **4** were not obtained.

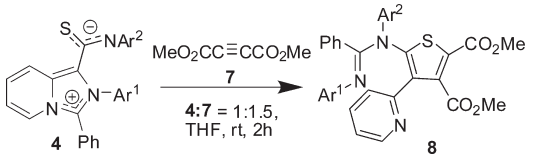
After the reaction of zwitterions **4** with propiolate, the interaction of **4** with dimethyl acetylenedicarboxylate (DMAD), a more electrophilic reagent, was studied. The reaction of 1-*N*-(*p*-bromophenyl)thiocarbamoyl-2-(*p*-methoxyphenyl)-3-phenylimidazo[1,5-*a*]pyridinium inner salt **4e** with DMAD took place more efficiently. In all reaction media including acetone, acetonitrile, 1,4-dioxane, THF, dichloromethane, and benzene, for example, the reaction went to completion within 2 h at room temperature to yield a single product in an excellent yield (Table 4). Interestingly, the reaction afforded a fully substituted thiophene compound, (*E*)-dimethyl 5-[*N*-(4-bromophenyl)-*N*′-(4-methoxyphenyl)benzimidamido]-4-(2-pyridinyl)thiophene-2,3-dicarboxylate **8e** rather than pyrrole product. Applying the optimized conditions such as using THF as the solvent, other 2-arylimidazo[1,5-*a*]pyridiniums **4**

TABLE 4. Reaction of 4e with DMAD under Different Conditions



	reaction conditions			
entry	solvent	temp	time	yield of **6a** (%)
1	THF	rt	2 h	94
2	acetone	rt	2 h	91
3	dichloromethane	rt	2 h	90
4	acetonitrile	rt	2 h	90
5	benzene	rt	2 h	88
6	1,4-dioxane	rt	2 h	90

TABLE 5. Reaction of 4 with DMAD under Optimized Conditions

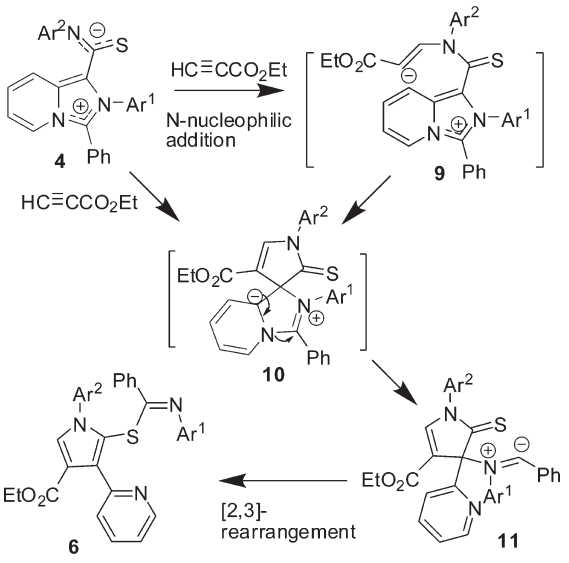


entry	**4**	Ar^1	Ar^2	yield of **8** (%)
1	**4a**	Ph	Ph	**8a**: 94
2	**4b**	*p*-MeC_6H_4	Ph	**8b**: 83
3	**4c**	*p*-MeC_6H_4	*p*-BrC_6H_4	**8c**: 90
4	**4d**	*p*-$MeOC_6H_4$	Ph	**8d**: 84
5	**4e**	*p*-$MeOC_6H_4$	*p*-BrC_6H_4	**8e**: 86
6	**4f**	*p*-ClC_6H_4	Ph	**8f**: 94
7	**4g**	*p*-ClC_6H_4	*p*-BrC_6H_4	**8g**: 94
8	**4i**	*p*-ClC_6H_4	*p*-$MeOC_6H_4$	**8i**: 93

bearing different substituents underwent reaction with DMAD very efficiently at ambient temperature to furnish 4-(2-pyridinyl)thiophene-2,3-dicarboxylates **8** in good to excellent yields (Table 5). Similar to the reaction of 2-alkylimidazo[1,5-*a*]-pyridinium zwitterions **4** with propiolate, the interaction of 2-isopropylimidazo[1,5-*a*]pyridinium inner salt **4k** with DMAD also gave most probably a mixture of *Z*- and *E*-configured amidino-substituted thiophene isomers, which could not be separated by column chromatography or recrystallization.

The structures of all products were fully characterized by spectroscopic data and microanalysis. The NMR spectra, mass data, and microanalysis indicated that the constitutions of all products **6** and **8** were the 1 + 1 adducts of two starting materials. Since the spectroscopic data did not allow full verification of the structures, to identify the products beyond doubt, the structures of **6g** and **8f** were determined unambiguously by single crystal X-ray diffraction analysis (see Figure S1 in Supporting Information). Interestingly, the imine double bonds of products **6** have a *Z*-configuration, whereas those of compounds **8** are *E*-configured. It is most likely that the reaction of zwitterions **4** with propiolate preferred to form *Z*-configured products **6**, since the *Z*-imine could avoid the steric repulsion between two aryl rings bearing the C=N bond. However, the predominate formation of *E*-configured thiophenes **8** was not expected. The

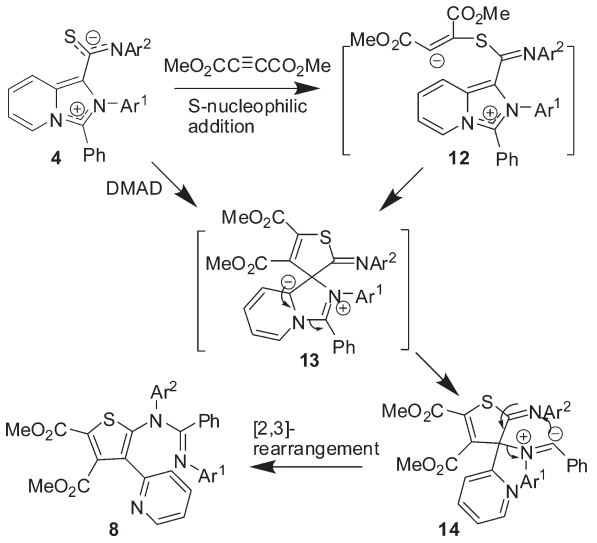
SCHEME 2. Proposed Mechanism for the Formation of 4-Pyridinylpyrroles 6



single crystal structure of **8f** indicated that a *E*-configured C=N bond could reduce the steric repulsion between *N*-aryl and pyridinyl groups substituted to the imine and thiophene moiety, respectively. Therefore, the stereoselectivity of the reaction between **4** and DMAD was probably controlled by the steric hindrance between *N*-aryl and pyridinyl groups of products **8**. As aforementioned, the reaction of 2-ethyl- or 2-isopropylimidazo[1,5-*a*]pyridinium inner salt **4j** or **4k** with both propiolate and DMAD had stereoselectivity lower than that of 2-arylimidazo[1,5-*a*]pyridinium inner salts **4a**−**4i**, producing a mixture of isomeric products. Apparently, it is the steric effect of substituents connected to the imine moiety that controlled the stereoselectivity, because the steric repulsion between an ethyl or an isopropyl and an aryl group is less than the repulsion between two aryl groups.

Our previous studies have shown that the 1,3-dipolar adducts derived from *N*-heterocyclic carbenes and isothiocyanates are ambident C^+-C-S^- and C^+-C-N^- 1,3-dipoles reacting with electron-deficient alkenes, alkynes, ketenes, and allenes to afford either spiro- or fused-pyrrole and spiro- or fused-thiophene derivatives.[22a−f] The respective formation of 5-aryliminomethylthio-4-pyridinylpyrroles **6** and 5-benzimidamido-4-pyridinylthiophenes **8** from the reactions of zwitterions **4** with propiolate and dimethyl acetylenedicarboxylate is however intriguing. The pyrrole-3-carboxylate moiety in **6** and thiophene-2,3-dicarboxylate moiety in **8** indicated that the overall reactions involved an annulation of the C−C−N or C−C−S species of zwitterions **4** with the carbon−carbon triple bond of alkynes. To account for the formations of 4-pyridinylpyrroles **6** and 4-pyridinylthiophenes **8**, two different tandem chemo-specific cyclizations and the subsequent [2,3]-sigmatropic rearrangements were proposed. As depicted in Scheme 2, imidazo[1,5-*a*]pyridinium inner salts **4** behaved as a nitrogen nucleophile to undergo a nucleophilic addition and intramolecular cyclization (or a formal [3 + 2] cycloaddition) with propiolate to form spiro-pyrrole intermediate **10**. Aromatization of the dihydropyridine anion of **10** led to the ring opening of imidazole forming a 3-iminium ylide substituted pyrrole-2-thione

SCHEME 3. Proposed Mechanism for the Formation of 4-Pyridinylthiophenes 8



intermediate **11**. Most likely, an [2,3]-sigmatropic rearrangement of S=C−C−N$^+$=C$^-$ to N=C−S−C=C furnished 5-aryliminomethylthio-4-pyridinylpyrroles **6** (Scheme 2). When treated with DMAD, the ambident zwitterions **4** acted as a sulfur nucleophile to cyclize with the triple bond of DMAD to form spiro-thiophene intermediate **13**. Aromatization of the dihydropyridine anion of **13** produced an 3-iminium ylide substituted 2-aryliminothiophene intermediate **14**. The [2,3]-sigmatropic rearrangement from N=C−C−N$^+$=C$^-$ to N=C−N−C=C moiety of **14** afforded the final 5-benzimidamido-4-pyridinylthiophenes **8** (Scheme 3). It should be noted that the chemoselectivity of the reactions of 1-thiocarbamoyl imidazo[1,5-*a*]pyridinium zwitterions **4** with propiolate and with DMAD was in good agreement with our previous observations on the reactions of 1,3-dipoles derived from *N*,*N*- and *N*,*S*-substituted heterocyclic carbenes. On the basis of our theoretical study, it is the electronic and steric effects of dipolarophile that controlled the chemoselectivity of the dipoles derived from *N*-heterocyclic carbenes and isothiocyanates.[22b−d] It is also worth addressing that all documented [2,3]-sigmatropic rearrangements generally involve either the transformation of C=C−C−X$^+$−Y$^-$ to X−Y−C−C=C or the conversion of C≡C−C−X$^+$−Y$^-$ to X−Y−C=C=C, the transposition of the double bond of an allyl or propargyl group with the migration to its vicinal anion center.[25,26] In the current work, however, the reactions most probably proceeded via two new versions of [2,3]-sigmatropic rearrangements. One of them involves the conversion of S=C−C−N$^+$=C$^-$ to C=C−S−C=N, while the other is the transformation of N=C−C−N$^+$=C$^-$ to C=C−N−C=N. The driving force of the unusual [2,3]-sigmatropic rearrangements was probably attributed to the stabilization energy gained from aromatization, the formation of polyconjugated pyrroles and thiophenes.

Conclusion

In summary, we have shown that 1-thiocarbamoyl imidazo[1,5-*a*]pyridinium inner salts, which were derived readily from addition of imidazo[1,5-*a*]pyridine-1-ylidenes with aryl isothiocyanates, were powerful ambident nucleophilic zwitterions. Under very mild conditions, they acted exclusively as nitrogen or sulfur nucleophiles toward ethyl propiolate or dimethyl acetylenedicarboxylate to produce 4-pyridinylpyrrole or 4-pyridinylthiophene derivatives, respectively, in good to excellent yields. Two different tandem chemo-specific cyclizations and subsequent novel [2,3]-sigmatropic rearrangements were proposed for the formations of products. The reactions provide highly efficient orthogonal synthesis of polyfunctionalized pyrroles and thiophenes that were not easily obtained by other chemical means.

Experimental Section

General Procedure for the Reaction of 1-Thiocarbamoyl Imidazo[1,5-*a*]pyridinium Inner Salts 4 with Ethyl Propiolate. At ambient temperature (summer time, around 25 °C), the ethyl propiolate (1.1 mmol) was added dropwise to the 1-thiocarbamoyl imidazo[1,5-*a*]pyridinium salts **4** (0.6 mmol) in 1,4-dioxane (30 mL). The reaction mixture was stirred at room temperature for about 6 h. After removal of solvent under vacuum, the products, (*Z*)-1-aryl-5-[aryl(arylimino)methylthio]-4-(2-pyridinyl)-pyrrole-3-carboxylates **6**, were isolated in 84−93% yields by chromatography on a silica gel column eluting with a mixture of ethyl acetate and petroleum ether (30−60 °C) (1:2).

(*Z*)-Ethyl 1-Phenyl-5-[phenyl(phenylimino)methylthio]-4-(2-pyridinyl)pyrrole-3-carboxylate 6a. Yield 93%, mp 146−147 °C; IR ν (cm^{-1}) 1714, 1612, 1591, 1509; ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C) δ (ppm) 8.67 (d, J = 4.3 Hz, 1H), 7.85 (dt, J = 7.7, 1.6 Hz, 1H), 7.65 (br, 1H), 7.54−7.58 (m, 3H), 7.34−7.41 (m, 4H), 7.22−7.26 (m, 5H), 7.00−7.04 (m, 3H), 6.43 (d, J = 7.4 Hz, 2H), 4.03 (q, J = 7.1 Hz, 2H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 162.6, 161.5, 152.6, 149.3, 148.6, 137.2, 136.1, 135.4, 133.2, 130.6, 130.1, 129.1, 128.8, 128.4, 127.5, 126.4, 126.0, 124.1, 122.0, 120.2, 118.9, 118.6, 115.1, 59.3, 13.8; MS (ESI) 504 (M + 1), 526 (M + Na$^+$). Anal. Calcd for $C_{31}H_{25}N_3O_2S$: C 73.93, H 5.00, N 8.34. Found: C 73.64, H 5.38, N 8.31.

(*Z*)-Ethyl 1-Phenyl-5-[phenyl(*p*-tolylimino)methylthio]-4-(2-pyridinyl)pyrrole-3-carboxylate 6b. Yield 89%, mp 120−121 °C; IR ν (cm^{-1}) 1713, 1611, 1589, 1506; ^{1}H NMR (400 MHz, DMSO-d_6, 70 °C) δ (ppm) 8.64 (d, J = 4.1 Hz, 1H), 7.83 (dt, J = 7.7, 1.8 Hz, 1H), 7.61 (br, 1H), 7.52−7.54 (m, 3H), 7.31−7.37 (m, 3H), 7.23 (d, J = 7.7 Hz, 4H), 7.03 (d, J = 6.8 Hz, 2H), 6.97 (d, J = 6.4 Hz, 2H), 6.31 (d, J = 8.2 Hz, 2H), 4.01 (q, J = 7.1 Hz, 2H), 2.23 (s, 3H), 1.03 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 163.5, 162.0, 153.2, 149.0, 147.0, 137.9, 136.8, 135.3, 134.0, 133.6, 130.5, 130.0, 129.2, 129.1, 128.8, 128.3, 127.6, 126.6, 126.3, 122.0, 120.8, 119.7, 115.7, 59.8, 21.0, 14.1; MS (ESI) 518 (M + 1), 540 (M + Na$^+$).

(25) Some reviews for the [2,3]-sigmatropic rearrangements, see: (a) Nakai, T.; Mikami, K. *Chem. Rev.* **1986**, *86*, 885–902. (b) Somfai, P.; Panknin, O. *Synlett* **2007**, 1190–1202. (c) Braverman, S.; Cherkinsky, M. *Top. Curr. Chem.* **2007**, *275*, 67–101. (d) Reggelin, M. *Top. Curr. Chem.* **2007**, *275*, 1–65.

(26) For some examples for the [2,3]-sigmatropic rearrangements, see: (a) Hodgson, D. M.; Angrish, D.; Erickson, S. P.; Kloesges, J.; Lee, C. H. *Org. Lett.* **2008**, *10*, 5553–5556. (b) Armstrong, A.; Emmerson, D. P. G. *Org. Lett.* **2009**, *11*, 1547–1550. (c) Armstrong, A.; Challinor, L.; Cooke, R. S.; Moir, J. H.; Treweeke, N. R. *J. Org. Chem.* **2006**, *71*, 4028–4030. (d) Blid, J.; Panknin, O.; Somfai, P. *J. Am. Chem. Soc.* **2005**, *127*, 9352–9353. (e) Roberts, E.; Sancon, J. P.; Sweeney, J. B. *Org. Lett.* **2005**, *7*, 2075–2078. (f) Workman, J. A.; Garrido, N. P.; Sancon, J.; Roberts, E.; Wessel, H. P.; Sweeney, J. B. *J. Am. Chem. Soc.* **2005**, *127*, 1066–1067. (g) Crich, D.; Zou, Y.; Brebion, F. *J. Org. Chem.* **2006**, *71*, 9172–9177. (h) Ma, M.; Peng, L.-L.; Li, C.-K.; Zhang, X.; Wang, J.-B. *J. Am. Chem. Soc.* **2005**, *127*, 15016–15017. (i) Cere, V.; Paolucci, C.; Pollicino, S.; Sandri, E.; Fava, A. *J. Org. Chem.* **1979**, *44*, 4128–4135. (j) Blid, J.; Panknin, O.; Tuzina, P.; Somfai, P. *J. Org. Chem.* **2007**, *72*, 1294–1300. (k) Crich, D.; Krishnamurthy, V.; Hutton, T. K. *J. Am. Chem. Soc.* **2006**, *128*, 2544–2545. (l) Reich, H. J.; Yelm, K. E. *J. Org. Chem.* **1991**, *56*, 5672–5679.

Anal. Calcd for $C_{32}H_{27}N_3O_2S$: C 74.25, H 5.26, N 8.12. Found: C 73.96, H 5.62, N 8.09.

(*Z*)-Ethyl 1-(*p*-Bromophenyl)-5-[phenyl(*p*-tolylimino)methylthio]-4-(2-pyridinyl)pyrrole-3-carboxylate 6c. Yield 93%, mp 130−131 °C; IR ν (cm^{-1}) 1704, 1607, 1590, 1504, 1493; ^1H NMR (400 MHz, DMSO-d_6, 70 °C) δ (ppm) 8.66 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 7.85 (dt, J = 7.7, 1.8 Hz, 1H), 7.72 (d, J = 8.6 Hz, 2H), 7.67 (brs, 1H), 7.32−7.37 (m, 3H), 7.24 (t, J = 7.8 Hz, 2H), 7.23 (br, 2H), 7.05 (d, J = 7.1 Hz, 2H), 7.01 (d, J = 7.3 Hz, 2H), 6.35 (d, J = 8.2 Hz, 2H), 4.02 (q, J = 7.1 Hz, 2H), 2.25 (s, 3H), 1.04 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 163.4, 161.2, 152.9, 149.0, 146.7, 136.8, 135.4, 134.3, 133.8, 132.2, 130.1, 129.3, 128.8, 128.1, 127.7, 126.3, 122.1, 120.7, 119.9, 116.0, 59.9, 21.0, 14.1; MS (ESI) 596 (M + 1), 618 (M + Na^+). Anal. Calcd for $C_{32}H_{26}BrN_3O_2S$: C 64.43, H 4.39, N 7.04. Found: C 64.21, H 4.72, N 7.02.

(*Z*)-Ethyl 1-Phenyl-5-[phenyl(*p*-methoxyphenylimino)methylthio]-4-(2-pyridinyl)pyrrole-3-carboxylate 6d. Yield 92%, mp 104−105 °C; IR ν (cm^{-1}) 1717, 1614, 1590, 1501; ^1H NMR (400 MHz, DMSO-d_6, 70 °C) δ (ppm) 8.66 (d, J = 4.1 Hz, 1H), 7.84 (dt, J = 7.7, 1.8 Hz, 1H), 7.63 (br, 1H), 7.53−7.54 (m, 3H), 7.34−7.37 (m, 4H), 7.24 (t, J = 7.4 Hz, 3H), 7.00 (brs, 2H), 6.82 (d, J = 6.7 Hz, 2H), 6.41 (d, J = 8.6 Hz, 2H), 4.02 (q, J = 7.1 Hz, 2H), 3.73 (s, 3H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 162.6, 160.8, 156.2, 152.6, 148.6, 142.3, 137.2, 136.3, 135.4, 133.0, 130.4, 130.0, 129.1, 128.4, 127.5, 126.4, 125.9, 122.0, 121.6, 120.5, 119.0, 115.1, 114.0, 59.3, 55.1, 13.8; MS (ESI) 534 (M + 1), 556 (M + Na^+). Anal. Calcd for $C_{32}H_{27}N_3O_3S$: C 72.02, H 5.10, N 7.87. Found: C 71.75, H 5.46, N 7.84.

(*Z*)-Ethyl 1-(*p*-Bromophenyl)-5-[phenyl(*p*-methoxyphenylimino)-methylthio]-4-(2-pyridinyl)pyrrole-3-carboxylate 6e. Yield 84%, mp 138−139 °C; IR ν (cm^{-1}) 1712, 1621, 1590, 1501; ^1H NMR (400 MHz, DMSO-d_6, 70 °C) δ (ppm) 8.64 (d, J = 4.0 Hz, 1H), 7.83 (dt, J = 7.7, 1.7 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.63 (br, 1H), 7.31−7.37 (m, 3H), 7.23 (t, J = 7.4 Hz, 3H), 7.20 (br, 1H), 6.99 (d, J = 6.4 Hz, 2H), 6.82 (d, J = 6.0 Hz, 2H), 6.41 (d, J = 8.6 Hz, 2H), 4.01 (q, J = 7.1 Hz, 2H), 3.72 (s, 3H), 1.03 (t, J = 7.1 Hz, 3H); ^{13}C NMR (400 MHz, DMSO-d_6) δ (ppm) 162.6, 160.4, 156.4, 152.4, 148.7, 142.0, 136.3, 135.4, 133.2, 132.0, 130.3, 130.0, 128.4, 128.3, 127.6, 125.9, 122.0, 121.4, 120.6, 119.1, 115.3, 113.9, 59.4, 55.1, 13.8; MS (ESI) 612 (M + 1), 623 (M + Na^+). Anal. Calcd for $C_{32}H_{26}BrN_3O_3S$: C 62.75, H 4.28, N 6.86. Found: C 62.64, H 4.32, N 6.86.

(*Z*)-Ethyl 1-Phenyl-5-[phenyl(*p*-chlorophenylimino)methylthio]-4-(2-pyridinyl)pyrrole-3-carboxylate 6f. Yield 86%, mp 156−157 °C; IR ν (cm^{-1}) 1716, 1610, 1589, 1507; ^1H NMR (400 MHz, DMSO-d_6, 70 °C) δ (ppm) 8.64 (ddd, J = 4.8, 1.7, 1.0 Hz, 1H), 7.84 (dt, J = 7.7, 1.8 Hz, 1H), 7.64 (brs, 1H), 7.52−7.58 (m, 3H), 7.33−7.38 (m, 3H), 7.23−7.26 (m, 6H), 6.98 (d, J = 7.3 Hz, 2H), 6.41 (d, J = 8.6 Hz, 2H), 4.02 (q, J = 7.1 Hz, 2H), 1.04 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.4, 153.2, 149.0, 148.0, 137.9, 136.6, 135.2, 133.9, 130.6, 130.2, 129.6, 129.0, 128.7, 128.4, 127.7, 126.6, 126.3, 122.0, 121.1, 119.3, 115.8, 59.8, 14.0; MS (ESI) 538 (M + 1), 560 (M + Na^+). Anal. Calcd for $C_{31}H_{24}ClN_3O_2S$: C 69.20, H 4.50, N 7.81. Found: C 68.94, H 4.85, N 7.78.

(*Z*)-Ethyl 1-(*p*-Bromophenyl)-5-[phenyl(*p*-chlorophenylimino)-methylthio]-4-(2-pyridinyl)pyrrole-3-carboxylate 6g. Yield 85%, mp 119−120 °C; IR ν (cm^{-1}) 1712, 1609, 1589, 1536, 1508, 1493; ^1H NMR (400 MHz, DMSO-d_6, 70 °C) δ (ppm) 8.67 (ddd, J = 4.8, 1.6, 0.9 Hz, 1H), 7.85 (dt, J = 7.7, 1.8 Hz, 1H), 7.74 (d, J = 8.6 Hz, 2H), 7.70 (br, 1H), 7.34−7.40 (m, 3H), 7.24−7.28 (m, 6H), 7.03 (d, J = 7.4 Hz, 2H), 6.46 (d, J = 8.6 Hz, 2H), 4.03 (q, J = 7.1 Hz, 2H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 163.3, 162.6, 152.8, 149.0, 147.6, 136.8, 136.5, 135.3, 134.0, 132.3, 130.4, 130.3, 130.0, 128.8, 127.8, 126.3, 122.4, 122.2, 121.3, 119.5, 116.1, 60.0, 14.1; MS (ESI) 617 (M + 2), 638 (M + Na^+). Anal. Calcd for $C_{31}H_{23}BrClN_3O_2S$: C 60.35, H 3.76, N 6.81. Found: C 60.15, H 4.07, N 6.79.

(*Z*)-Ethyl 1-(*p*-Chlorophenyl)-5-[phenyl(*p*-chlorophenylimino)-methylthio]-4-(2-pyridinyl)pyrrole-3-carboxylate 6h. Yield 90%, mp 133−134 °C; IR ν (cm^{-1}) 1704, 1602, 1590, 1511, 1496; ^1H NMR (400 MHz, DMSO-d_6, 70 °C) δ (ppm) 8.64 (d, J = 4.0 Hz, 1H), 7.84 (dt, J = 7.7 1.8 Hz, 1H), 7.68 (brs, 1H), 7.59 (d, J = 8.7 Hz, 2H), 7.34−7.38 (m, 3H), 7.24−7.27 (m, 6H), 7.00 (d, J = 7.5 Hz, 2H), 6.45 (d, J = 8.6 Hz, 2H), 4.02 (q, J = 7.1 Hz, 2H), 1.04 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 163.3, 162.6, 152.9, 149.0, 147.8, 136.4, 135.3, 134.4, 134.1, 130.4, 129.9, 129.2, 129.0, 128.8, 127.8, 126.2, 122.1, 121.5, 121.3, 119.4, 116.1, 59.9, 14.0; MS (ESI) 572 (M + 1). Anal. Calcd for $C_{31}H_{23}Cl_2N_3O_2S$: C 65.04, H 4.05, N 7.34. Found: C 64.92, H 4.32, N 7.16.

General Procedure for the Reaction of 1-Thiocarbamoyl Imidazo[1,5-*a*]pyridinium Inner Salts 4 with Dimethyl Acetylenedicarboxylate. At ambient temperature (winter time, around 15 °C), DMAD (1.0 mmol) was added dropwise to the 1-thiocarbamoyl imidazo[1,5-*a*]pyridinium salts **4** (0.6 mmol) in THF (30 mL). The reaction mixture was stirred at room temperature for about 2 h. After removal of solvent under vacuum, the residue was chromatographied on a silica gel column (ethyl acetate/petroleum ether (30−60 °C) = 1:2) to afford (*E*)-dimethyl 5-(*N*-aryl-*N*′-arylbenzimidamido)-4-(2-pyridinyl)thiophene-2,3-dicarboxylates **8** in 83−94% yields.

(*E*)-Dimethyl 5-(*N*,*N*′-Diphenylbenzimidamido)-4-(2-pyridinyl)-thiophene-2,3-dicarboxylate 8a. Yield 93%, mp 182−181 °C; IR ν (cm^{-1}) 1725, 1717, 1635, 1590, 1491; ^1H NMR (400 MHz, CD_3COCD_3) δ (ppm) 8.66 (ddd, J = 4.8, 1.7, 0.9 Hz, 1H), 7.89 (dt, J = 7.8, 1.8 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.34−7.38 (m, 3H), 7.24 (dt, J = 8.2, 2.1 Hz, 2H), 7.02−7.13 (m, 6H), 6.94 (dt, J = 8.4, 1.6 Hz, 2H), 6.75 (dt, J = 7.2, 1.2 Hz, 1H), 6.19 (dt, J = 8.4, 1.1 Hz, 2H), 3.82 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.8, 161.4, 157.6, 151.7, 151.5, 149.4, 149.2, 144.4, 139.1, 136.3, 131.6, 130.1, 129.1, 128.9, 128.3, 128.1, 127.7, 126.6, 125.9, 125.1, 123.9, 122.6, 122.1, 121.6, 52.7, 52.5; MS (ESI) 548 (M + 1), 570 (M + Na^+). Anal. Calcd for $C_{32}H_{25}N_3O_4S$: C 70.18, H 4.60, N 7.67. Found: C 70.10, H 4.83, N 7.63.

(*E*)-Dimethyl 5-[*N*-Phenyl-*N*′-(*p*-tolyl)benzimidamido]-4-(2-pyridinyl)thiophene-2,3-dicarboxylate 8b. Yield 83%, mp 148−149 °C; IR ν (cm^{-1}) 1732, 1715, 1626, 1591, 1490; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.58 (d, J = 4.5 Hz, 1H), 7.61 (dt, J = 7.8, 1.8 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.08−7.17 (m, 5H), 6.93−7.03 (m, 5H), 6.89 (d, J = 7.3 Hz, 2H), 6.73 (d, J = 8.1 Hz, 2H), 6.09 (d, J = 8.2 Hz, 2H), 3.78 (s, 3H), 3.74 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.8, 161.2, 157.5, 151.8, 151.6, 149.4, 146.5, 144.4, 139.1, 136.2, 134.9, 131.7, 131.4, 130.1, 129.0, 128.9, 128.8, 127.7, 126.5, 125.8, 125.0, 124.0, 122.6, 121.5, 52.6, 52.1, 20.7; MS (ESI) 562 (M + 1), 584 (M + Na^+). Anal. Calcd for $C_{33}H_{27}N_3O_4S$: C 70.57, H 4.85, N 7.48. Found: C 70.52, H 5.17, N 7.48.

(*E*)-Dimethyl 5-[*N*-(*p*-Bromophenyl)-*N*′-(*p*-tolyl)benzimidamido]-4-(2-pyridinyl)thiophene-2,3-dicarboxylate 8c. Yield 90%, mp 168−169 °C; IR ν (cm^{-1}) 1724, 1634, 1586, 1486; ^1H NMR (400 MHz, CD_3COCD_3) δ (ppm) 8.52 (d, J = 4.2 Hz, 1H), 7.72 (dt, J = 7.8, 1.7 Hz, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.25 (d, J = 8.8 Hz, 2H), 7.20−7.23 (m, 1H), 7.14 (d, J = 8.8 Hz, 2H), 6.3−7.00 (m, 5H), 6.63 (d, J = 8.1 Hz, 2H), 5.98 (d, J = 8.2 Hz, 2H), 3.69 (s, 3H), 3.59 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 165.7, 161.4, 158.1, 152.3, 151.7, 150.4, 147.7, 144.9, 140.3, 137.5, 136.4, 132.8, 132.6, 132.0, 131.1, 130.1, 129.6, 129.5, 128.6, 125.9, 124.5, 123.9, 122.0, 119.6, 52.9, 52.7, 20.7; MS (ESI) 640 (M + 1), 664 (M + Na^+). Anal. Calcd for $C_{33}H_{26}BrN_3O_4S$: C 61.88, H 4.09, N 6.56. Found: C 61.51, H 3.80, N 6.45.

(*E*)-Dimethyl 5-[*N*′-(*p*-Methoxyphenyl)-*N*-phenylbenzimidamido]-4-(2-pyridinyl)thiophene-2,3-dicarboxylate 8d. Yield 84%, mp

178−179 °C; IR ν (cm^{-1}) 1737, 1721, 1615, 1592, 1456; ^1H NMR (400 MHz, CD_3COCD_3) δ (ppm) 8.63−8.65 (ddd, J = 4.8, 1.7, 1.0 Hz, 1H), 7.86 (dt, J = 7.8, 1.8 Hz, 1H), 7.69 (dt, J = 7.9, 1.0 Hz, 1H), 7.30−7.36 (m, 3H), 7.22 (dt, J = 8.3, 1.8 Hz, 2H), 7.05−7.10 (m, 6H), 6.53 (dd, J = 6.7, 2.0 Hz, 2H), 6.13 (dd, J = 6.7, 2.0 Hz, 2H), 3.83 (s, 3H), 3.73 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm) 165.2, 160.7, 157.7, 155.0, 151.8, 151.2, 149.9, 144.5, 142.6, 139.5, 137.4, 134.7, 131.9, 130.3, 129.6, 128.2, 127.2, 126.8, 124.1, 123.7, 123.6, 122.3, 121.7, 114.0, 55.4, 53.2, 52.9; MS (ESI) 578 (M + 1), 600 (M + Na^+). Anal. Calcd for $C_{33}H_{27}N_3O_5S$: C 68.61, H 4.71, N 7.27. Found: C 68.32, H 4.75, N 6.91.

(*E*)-Dimethyl 5-[*N*-(*p*-Bromophenyl)-*N*′-(*p*-methoxyphenyl)-benzimidamido]-4-(2-pyridinyl)thiophene-2,3-dicarboxylate 8e. Yield 86%, mp 158−159 °C; IR ν (cm^{-1}) 1737, 1725, 1618, 1487; ^1H NMR (400 MHz, CD_3COCD_3) δ (ppm) 8.52 (d, J = 4.2 Hz, 1H), 7.72 (dt, J = 7.8, 1.8 Hz, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.26 (dd, J = 6.8, 1.9 Hz, 2H), 7.20−7.23 (m, 1H), 7.14 (d, J = 6.8, 1.9 Hz, 2H), 6.98−7.02 (m, 1H), 6.94−7.06 (m, 4H), 6.41 (d, J = 8.8 Hz, 2H), 6.03 (d, J = 8.8 Hz, 2H), 3.70 (s, 3H), 3.60 (s, 3H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 165.7, 161.4, 158.2, 156.2, 152.4, 151.8, 150.4, 144.9, 143.4, 140.3, 137.5, 136.3, 132.8, 132.6, 131.2, 130.1, 129.4, 128.7, 125.8, 124.5, 123.8, 123.1, 119.5, 114.4, 55.4, 52.9, 52.7; MS (ESI) 656 (M + 1), 678 (M + Na^+). Anal. Calcd for $C_{33}H_{26}BrN_3O_5S$: C 60.37, H 3.99, N 6.40. Found: C 60.34, H 3.86, N 6.28.

(*E*)-Dimethyl 5-[*N*′-(*p*-Chlorophenyl)-*N*-phenylbenzimidamido]-4-(2-pyridinyl)thiophene-2,3-dicarboxylate 8f. Yield 94%, mp 181−182 °C; IR ν (cm^{-1}) 1736, 1709, 1625, 1587, 1488; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.65 (d, J = 4.3 Hz, 1H), 7.65 (dt, J = 7.8, 1.7 Hz, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.21−7.23 (m, 3H), 7.16 (t, J = 8.4 Hz, 2H), 7.05−7.10 (m, 2H), 7.01 (t, J = 7.2 Hz, 2H), 6.94 (d, J = 7.2 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 6.07 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.7, 161.1, 158.1, 151.8, 151.4, 149.4, 147.7, 144.1, 139.0, 136.5, 131.2, 130.1, 129.3, 129.0, 128.3, 128.2, 127.9, 127.3, 126.8, 126.2, 125.1, 123.9, 123.0, 122.7, 52.7, 52.5; MS (ESI) 582 (M + 1), 604 (M + Na^+). Anal. Calcd for $C_{32}H_{24}ClN_3O_4S$: C 66.03, H 4.16, N 7.22. Found: C 66.09, H 4.36, N 7.17.

(*E*)-Dimethyl 5-[*N*-(*p*-Bromophenyl)-*N*′-(*p*-chlorophenyl)-benzimidamido]-4-(2-pyridinyl)thiophene-2,3-dicarboxylate 8g. Yield 94%, mp 175−176 °C; IR ν (cm^{-1}) 1725, 1631, 1484; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.67 (d, J = 4.4 Hz, 1H), 7.67 (t, J = 7.7 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.24−7.29 (m, 3H), 7.10−7.13 (m, 3H), 7.04 (t, J = 7.2 Hz, 2H), 6.94−6.95 (m, 2H), 6.90 (d, J = 8.8 Hz, 2H), 6.06 (d, J = 8.6 Hz, 2H), 3.84 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) 165.6, 161.0, 157.7, 151.6, 150.6, 149.5, 147.6, 143.3, 138.9, 136.5, 135.2, 132.1, 130.9, 130.0, 129.6, 128.2, 128.1, 127.5, 125.6, 123.8, 122.8, 122.0, 119.5, 52.8, 52.6; MS (ESI) 662 (M + 1), 684 (M + Na^+). Anal. Calcd for $C_{32}H_{23}BrClN_3O_4S$: C 58.15, H 3.51, N 6.36. Found: C 58.05, H 3781, N 6.25.

(*E*)-Dimethyl 5-[*N*′-(*p*-Chlorophenyl)-*N*-(*p*-methoxyphenyl)-benzimidamido]-4-(2-pyridinyl)thiophene-2,3-dicarboxylate 8i. Yield 93%, mp 171−172 °C; IR ν (cm^{-1}) 1723, 1625, 1587, 1509; ^1H NMR (400 MHz, CD_3COCD_3) δ (ppm) 8.54 (d, J = 4.6 Hz, 1H), 7.73 (dt, J = 7.8, 1.4 Hz, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.22 (dd, J = 7.3, 5.1 Hz, 1H), 7.16 (d, J = 8.8 Hz, 2H), 6.91−6.97 (m, 5H), 6.77 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 8.9 Hz, 2H), 5.95 (d, J = 8.6 Hz, 2H), 3.68 (s, 3H), 3.59 (s, 3H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.8, 161.2, 158.0, 157.9, 152.1, 152.0, 149.4, 147.8, 139.0, 137.2, 136.4, 134.0, 131.4, 130.0, 129.1, 128.3, 128.1, 127.8, 127.1, 124.6, 123.8, 123.0, 122.6, 114.3, 55.3, 52.7, 52.4; HRMS (ESI) 612.1368 (M + 1). Anal. Calcd for $C_{33}H_{27}ClN_3O_5S$: 612.1360 (M + 1).

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Supporting Information Available: General procedure for the preparation of 1-thiocarbamoyl imidazo[1,5-*a*]pyridinium inner salts **4** and full characterization for **4**, copies of ^1H NMR and ^{13}C NMR spectra of products **4**, **6** and **8**, as well as single crystal data of **6g** and **8f** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.