JOC Article

Application of β-(2-Chloroaroyl) Thioacetanilides in Synthesis: An Unusual and Highly Efficient Access to Thiochromeno[2,3-*b*]pyridine Derivatives

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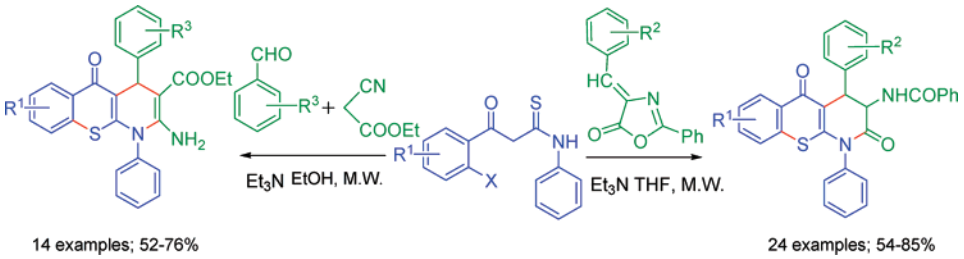

A series of unusual fused tricyclic thiochromeno[2,3-*b*]pyridines were successfully synthesized by tandem [3 + 3] annulation and S_NAr of β-(2-chloroaroyl) thioacetanilides with activated 4-arylidene-2-phenyloxazol-5(4*H*)-ones or aromatic aldehydes and ethyl 2-cyanoacetate under microwave irradiation, respectively. Because of the existence of the *o*-chloro atom of β-(2-chloroaroyl) thioacetanilides, these reactions were very mild, convenient, and ortho-selective to form new fused tricyclic target molecules. In the domino processes, at least seven reactive distinct chemical sites were involved and up to three new covalent bonds and one tricycle with only cis configuration were generated. A synthetic study and mechanistic proposal for these transformations are presented.

Introduction

In recent years, maximizing synthetic efficiency by designing a complexity-generating domino process is gaining more interest in organic synthesis and in drug discovery endeavors; therefore, the design and development of efficient synthetic strategies for the one-pot generation of multiple bonds is highly desirable.[1] In this context, domino reactions[2] and multicomponent reactions (MCRs)[3] have proven to be very effective and attractive; the notable feature of a domino process or multicomponent reactions is that bonds and new functionalities are constructed during the cascades, which, in turn, react further in subsequent steps under identical conditions to form new bonds and functionalities until termination leads to desirable molecules. These methodologies, which allow molecular complexity and diversity to be created by the facile formation of several new covalent bonds in a one-pot transformation, quite closely approach the concept of an ideal synthesis and are particularly well adapted for combinatorial chemistry. Hence, domino processes and multicomponent reactions, in an environmentally benign and atom-economic fashion, play important roles in organic synthesis, especially considering that certain complex compounds such as fused

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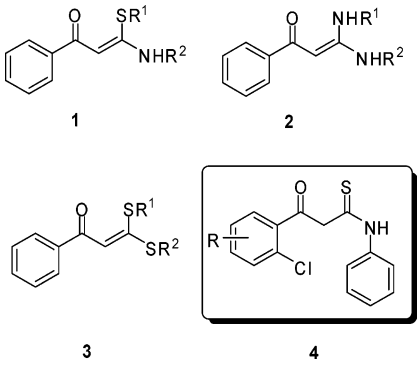

FIGURE 1. Functionalized ketene acetals.

polyheterocycles are of great significance. Continued efforts are being made to explore new domino processes and multicomponent reactions for developing popular organic reactions.

Functionalized thiochromones and their fused analogues, because of their interesting biological properties, represent an important class of heterocycles and have been tested and applied as drugs.[4] Although few known methods have been developed for thiochromone structural motifs, partly because they are difficult to access,[5] it is still challenging to explore new and efficient synthetic routes for this class of compounds, particularly those with wide general applicability to achieve more flexible substitution patterns.

Polarized ketene *N,S*-,[6] *N,N*-,[7] and *S,S*-acetals[8] with general structures **1**−**3** (Figure 1), as a class of highly versatile enamines, have proven to be important building blocks in the construction of heterocyclic systems. Reactions of these ketene acetals with 1,2- and 1,3- bis-acceptor substrates leading to five- and six-membered heterocycles have been reported repeatedly in the past decades.[6−8] *β*-(2-Chloroaroyl) thioacetanilides **4** (Figure 2), as *N,S*-ketene acetal precursors, show promising structural features as versatile building blocks for (1) two nucleophilic centers localized on the heteroatoms (sulfur and nitrogen); (2) a potential third nucleophilic center of the

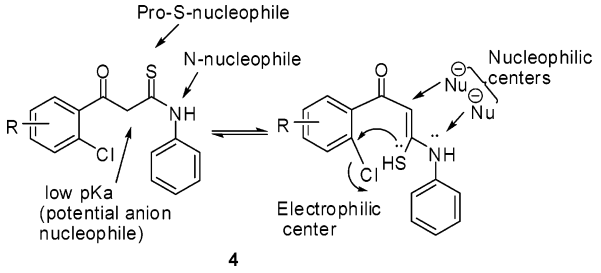

FIGURE 2. Reactivity profile of *β*-(2-chloroaroyl) thioacetanilides **4**.

α-carbon behaving as an Michael addition donor in base condition; and (3) a potential leaving halogen group on the aromatic ring, owing to the presence of an *o*-carbonyl group with an electron-withdrawing effect and subjected to an intramolecular nucleophilic aryl substitution (S_NAr) reaction by attack of mercapto group, which is a new methodology to form a thiapyran ring. Therefore, precursors **4** represent a class of polyfunctional scaffolds with four active reaction sites, which displayed a reactivity profile different than that of *β*-aroyl thioacetanilides **1** and could be used to develop a new strategy for the synthesis of an unusual series of thiochromeno[2,3-*b*]-pyridine derivatives.

Our approach toward the design and development of new domino and multicomponent procedures involves the use of building block **4** that contains a number of chemically distinct functionalities, which could be selectively reacted to generate diversity. As a logical extension of this work and in conjunction with our interests in the synthesis of thiochromone derivatives, herein we report two new kinds of rapid, unusual, and efficient methods to synthesize thiochromeno[2,3-*b*]pyridines in good yields by tandem [3 + 3] annulation and S_NAr of *β*-(2-chloroaroyl) thioacetanilides **4** with activated 4-arylidene-2-phenyloxazol-5(4*H*)-ones **5** or aromatic aldehydes **7** and ethyl 2-cyanoacetate **8** under microwave irradiation, respectively. In the domino processes, at least seven reactive distinct chemical sites are involved, and up to three new covalent bonds and one tricycle with only one diastereoisomer are generated. The results of our studies, which led to an unprecedented synthesis of thiochromeno[2,3-*b*]pyridines are presented herein. To the best of our knowledge, the thiochromeno[2,3-*b*]pyridines have not been reported before, and there are no obvious methods to synthesize them.

Results and Discussion

Reactions of *β*-(2-Chloroaroyl) Thioacetanilides with Activated 4-Arylidene-2-phenyloxazol-5(4*H*)-ones. Extremely simple reagents and conditions were used in the two-component domino reaction of **4a**−**c** with **5a**−**h**. In the initial experiment, the ring transformation of *β*-(2,4-dichlorobenzoyl) thioacetanilides **4a** with 4-(4-chlorobenzylidene)-2-phenyloxazol-5(4*H*)-one **5a** was examined, which proceeded smoothly with Et_3N (1 equiv) in refluxing THF under conventional heating. At the end

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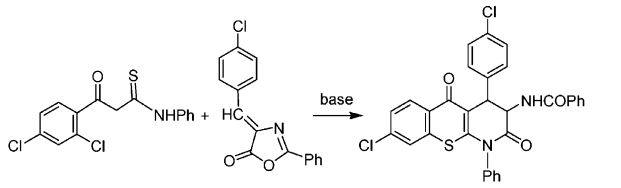
TABLE 1. Reaction of 4a with 5a under Different Conditions



4a 5a 6a

Entry	Base (equiv)	Solv.	Temp. (°C)	Time	Yield (%)[a]
1	Et_3N(1.0)	THF	66	22h[b]	54
2	Et_3N(1.0)	THF	66	30min[c]	73
3	Et_3N(1.0)	THF	rt	24h[b]	Nil[d]
4	-[e]	THF	66	40min[c]	Nil[d]
5	Et_3N(1.0)	EtOH	78	40min[c]	48
6	Et_3N(0.5)	THF	66	100min[c]	57
7	Et_3N(2.0)	THF	66	30min[c]	73
8	Et_3N(3.0)	THF	66	30min[c]	74
9	Et_3N(4.0)	THF	66	30min[c]	73
10	Et_3N(5.0)	THF	66	30min[c]	68
12	Et_3N(6.0)	THF	66	30min[c]	42
13	NaH(1.0)	THF	66	40min[c]	18
14	K_2CO_3(1.0)	THF	66	40min[c]	15
15	NaOH(1.0)	THF	66	40min[c]	10
16	piperidine(1.0)	THF	66	40min[c]	46
17	morpholine(1.0)	THF	66	40min[c]	42

[a] Isolated. [b] Conventional heating. [c] Microwave irradiation. [d] No reaction. [e] No base.

of the reaction (about 22 h later, monitored by TLC), the product was collected by filtration and recrystallized from THF−EtOH (1:4, v /v) to afford the nicely crystalline tricyclic thiochromeno-[2,3-*b*]pyridine **6a** in good yield (54%, Table 1, entry 1).

Microwave irradiation is very attractive for chemical applications and has become a widely accepted nonconventional energy source for performing organic synthesis.[9] For comparison, we performed the synthesis of **6a** under both microwave irradiation and classical heating conditions in refluxing THF. Under conventional heating, the reaction time was 22 h and the yield of **6a** was 54% (Table 1, entry 1), while microwave irradiation could dramatically reduce the reaction time to around 30 min and improve the yield to 73% (Table 1, entry 2).

A variety of conditions (such as base, solvent, time, etc.) were also investigated, and the results are shown in Table 1. There was no reaction with Et_3N (1 equiv) in THF at room temperature (Table 1, entry 3) or without Et_3N in refluxing THF (Table 1, entry 4). The reaction gave a lower yield in the presence of Et_3N (1 equiv) in EtOH (48%, Table 1, entry 5). The transformation was very slow in a small amount of Et_3N (0.5 equiv, Table 1, entry 6) and took a long time (100 min). However, a large excess of Et_3N, 6 equiv, for example, would result in a low yield of **6a**, and the color of reaction system changed from brown to black (Table 1, entry 12). In the presence of NaH, K_2CO_3, or NaOH, the reaction became sluggish and the corresponding product was only obtained in 18%, 15%, 10% yields, respectively (Table 1, entries 13−15), even if the reaction time was prolonged to 100 min. In the presence of piperidine or morpholine, it gave moderate yield (Table 1, entries 16 and 17). Thus, it was clear from the experiments that the best conditions of **6a** could be entry 2, employing Et_3N as base and THF as solvent under microwave irradiation.

To extend the scope of this new procedure for the synthesis of the tricyclic thiochromeno[2,3-*b*]pyridines, three *β*-(2-chloroaroyl) thioacetanilides **4a**−**c** were then examined for their reactions with eight 4-arylidene-2-phenyloxazol-5(4*H*)-ones **5a**−**h** under the optimized conditions (Table 2). For precursors **5** bearing either electron-donating or electron-withdrawing substituents, the reaction proceeded very smoothly in all cases. However, for precursors **4** where the aromatic rings with electron-withdrawing substituents, the yields were higher. For example, the yields of **6a**−**p** were obviously higher than the corresponding ones of **6o**−**x**, respectively, presumably due to the lower electron density of the aryl of **6a**−**p** making the *o*-chlorine easy to leave. In these domino process, one C−C, one C−N, and one C−S bond and one tricycle were formed with the concomitant creation. Importantly, this reaction of **4** with **5** generates two chiral centers, but only the cis configuration was observed through ^{1}H NMR, ^{13}C NMR spectra, thin-layer chromatography, and X-ray diffraction analysis of monocrystal **6e**.

Reactions of *β*-(2-Chloroaroyl) Thioacetanilides with Aromatic Aldehydes and Ethyl 2-Cyanoacetate. Multicomponent reactions (MCRs)[3] constitute an especially attractive synthetic strategy for rapid and efficient library generation due to the fact that the products are formed in a single step and the diversity can be achieved simply by varying the reacting components. Although the reaction of *β*-aroyl thioacetanilides with various nucleophilic species[6] can react under classical two-component reactions, careful literature search shows that the reaction of substituted *β*-(2-chloroaroyl) thioacetanilides **4** with aromatic aldehydes and ethyl 2-cyanoacetate in a three-component reaction strategy has not been disclosed thus far. As a part of our endeavors to develop diversity-oriented syntheses[10] for the thiochromeno[2,3-*b*]pyridine motif with functionalized *β*-(2-chloroaroyl) thioacetanilides **4** as key precursors, we discovered a novel three-component reaction consisting of **4**, aromatic aldehydes **7**, and ethyl 2-cyanoacetate **8**.

The three-component reaction of **4a**, **7a**, and **8** proceeded smoothly with Et_3N (1 equiv) in refluxing EtOH under microwave irradiation. At the end of the reaction (about 45 min, mornitored by TLC), the product was collected by filtration and recrystallized from THF−EtOH (1:4, v /v) to afford fused tricyclic thiochromeno[2,3-*b*]pyridine **9a** in 68% yield. The reason we choose EtOH as solvent instead of THF is that the product is easier to isolate and the yield is higher in EtOH compared with THF. The scope of this reaction was examined by using seven *β*-(2-chloroaroyl) thioacetanilides **4** and eight aldehydes **7** as starting materials, as shown in Table 3. A series of compounds **7**, in which the aromatic ring bearing electron-withdrawing groups (such as halo or nitro) or electron-donating groups (such as alkoxy or alkyl), react with **4a** and **8** in the presence of Et_3N under microwave irradiation to give the corresponding products **9** in good yields. When precursors **4**, which contain an aromatic ring with more electron-withdrawing substituents or higher electronegativity, were used, the yields were higher. Significantly, in this operationally simple three-component domino process, at least seven reactive distinct

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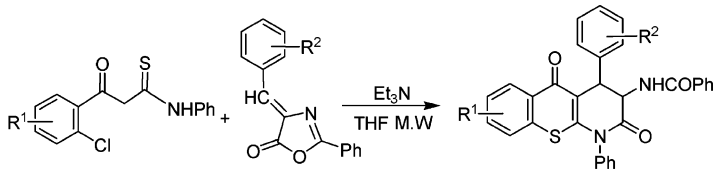
TABLE 2. Synthesis of Thiochromeno[2,3-*b*]pyridines 6a−x



4a-c **5a-h** **6a-x**

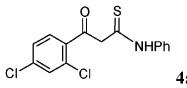
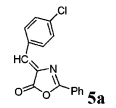
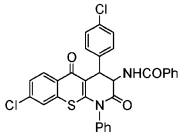
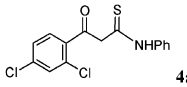
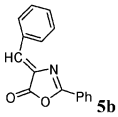
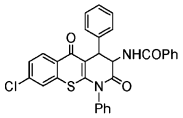
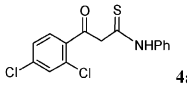
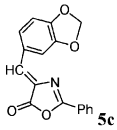
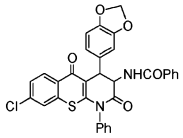
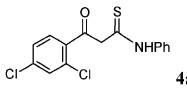
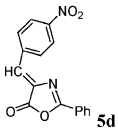
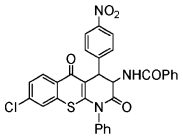
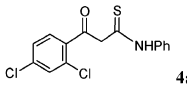
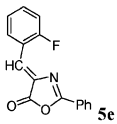
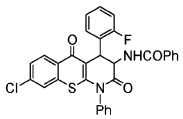
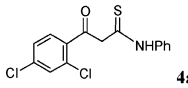
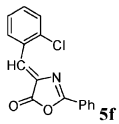
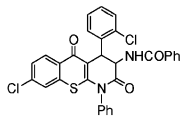
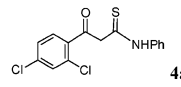
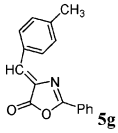
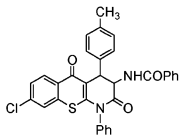
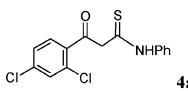
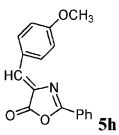
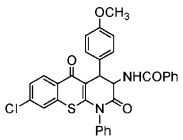
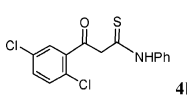
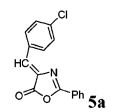
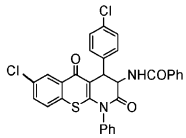
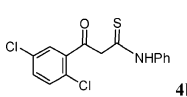
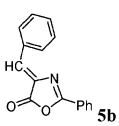
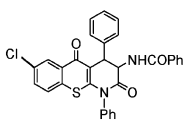
Entry	Precursors **4**	Precursors **5**	Products **6**	Time[b](min)	Yield[a] (%)
1	 **4a**	 **5a**	 **6a**	30	73
2	 **4a**	 **5b**	 **6b**	40	71
3	 **4a**	 **5c**	 **6c**	35	74
4	 **4a**	 **5d**	 **6d**	30	77
5	 **4a**	 **5e**	 **6e**	30	85
6	 **4a**	 **5f**	 **6f**	30	82
7	 **4a**	 **5g**	 **6g**	40	74
8	 **4a**	 **5h**	 **6h**	40	76
9	 **4b**	 **5a**	 **6i**	30	72
10	 **4b**	 **5b**	 **6j**	30	69

Table 2 (Continued)

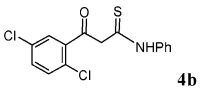
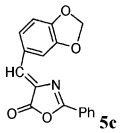
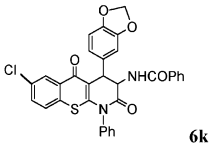
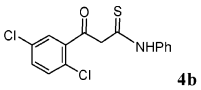
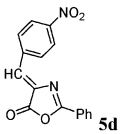
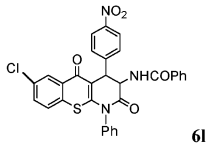
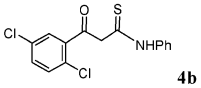
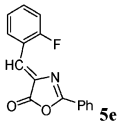
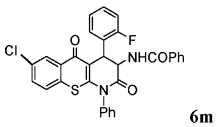
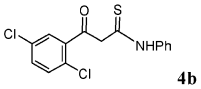
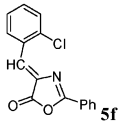
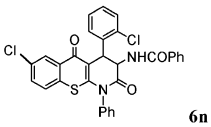
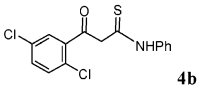
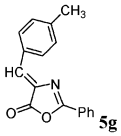
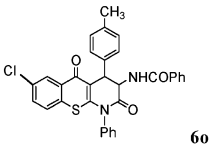
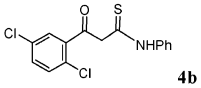
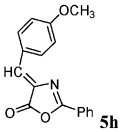
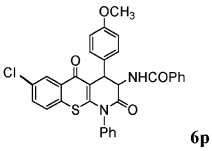
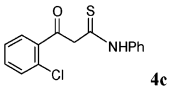
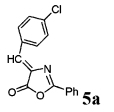
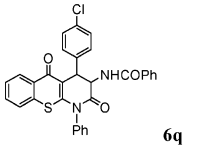
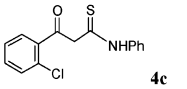
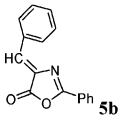
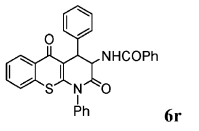
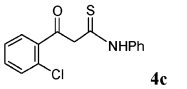
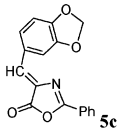
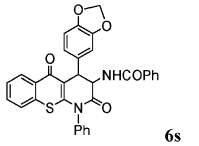
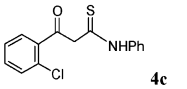
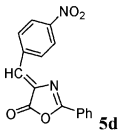
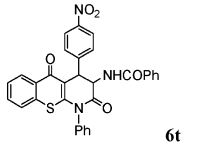
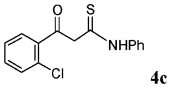
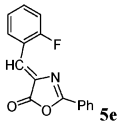
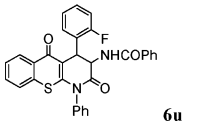
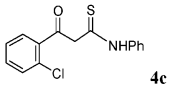
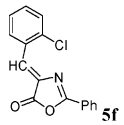
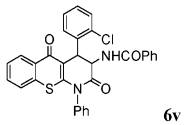
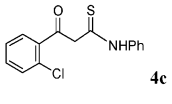
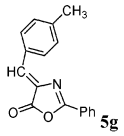
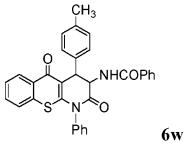
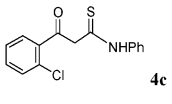
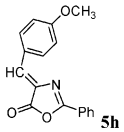
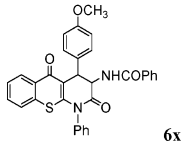
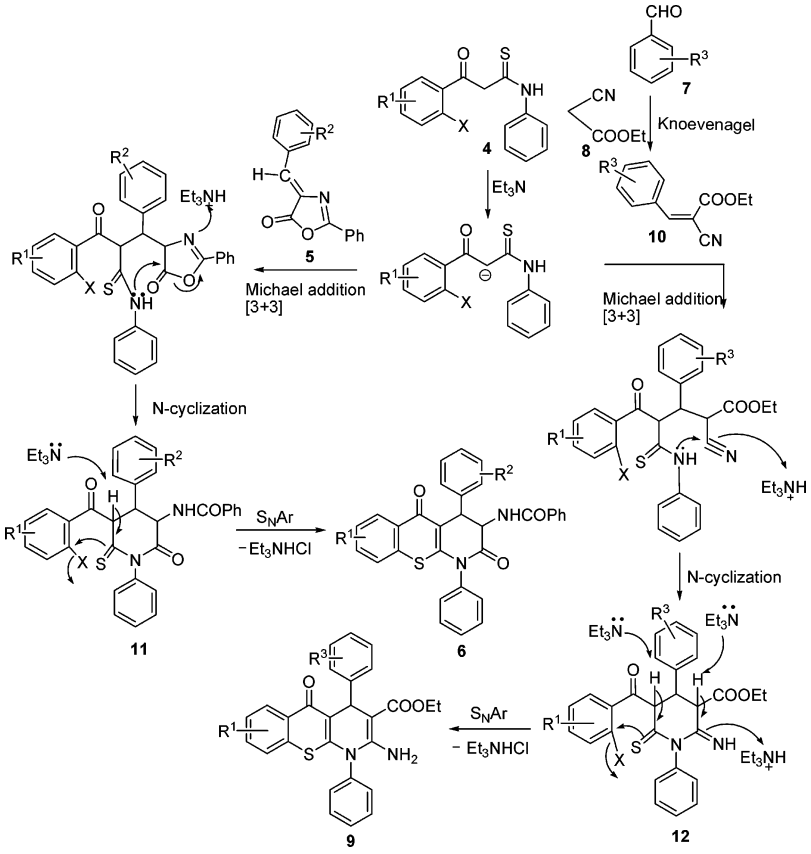
Entry	Precursors **4**	Precursors **5**	Products **6**	Time[b](min)	Yield[a] (%)
11	 **4b**	 **5c**	 **6k**	35	76
12	 **4b**	 **5d**	 **6l**	30	74
13	 **4b**	 **5e**	 **6m**	30	80
14	 **4b**	 **5f**	 **6n**	30	75
15	 **4b**	 **5g**	 **6o**	35	71
16	 **4b**	 **5h**	 **6p**	40	74
17	 **4c**	 **5a**	 **6q**	35	64
18	 **4c**	 **5b**	 **6r**	40	62
19	 **4c**	 **5c**	 **6s**	35	58
20	 **4c**	 **5d**	 **6t**	35	68
21	 **4c**	 **5e**	 **6u**	30	71

Table 2 (Continued)

Entry	Precursors **4**	Precursors **5**	Products **6**	Time[b](min)	Yield[a] (%)
24	 **4c**	 **5f**	 **6v**	30	65
23	 **4c**	 **5g**	 **6w**	35	54
24	 **4c**	 **5h**	 **6x**	35	55

[a] Isolated. [b] Microwave irradiation.

SCHEME 1. Plausible Reaction Scenario of 6 and 9



chemical sites participated in the chemical transformation that led to the concomitant creation of four chemical bonds (two C−C, one C−N, and one C−S bonds) and one tricycle.

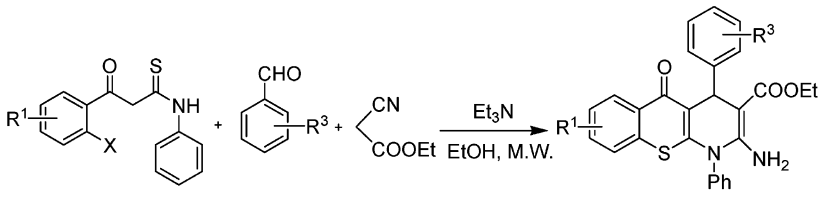
The structural determination of all products **6a**−**x** and **9a**−**n** were achieved following their analytical and spectral data and unequivocally established by the X-ray diffraction analysis of monocrystals **6e** and **9b**.[11]

It is worthy of noting that all the isolated products only need recrystallization rather than column chromatography. This ease of purification makes this methodology facile, practical, and rapid to execute.

A plausible reaction scenario for these two domino cyclocondensation is outlined in Scheme 1. First, compound **7** proceeds through Knoevenagel condensation with **8** to give

(11) X-ray diffraction data for **6e** and **9b** have been deposited with the Cambridge Crystallographic Data Centre with supplementary publication numbers of CCDC 661240 (**6e**) and 661241 (**9b**). The CIF files are also available in the Supporting Information.

TABLE 3. Synthesis of Thiochromeno[2,3-*b*]pyridines 9a−n



4a-g 7a-h 8 9

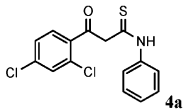
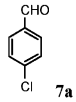
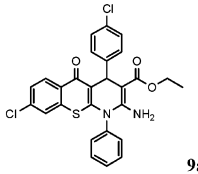
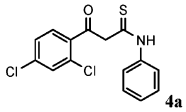
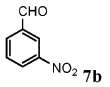
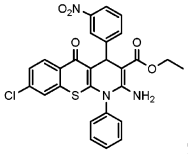
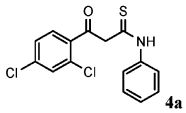
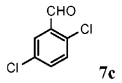
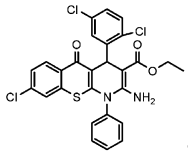
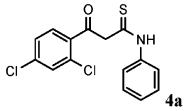
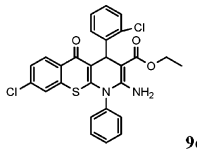
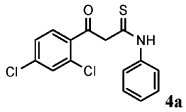
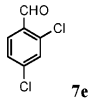
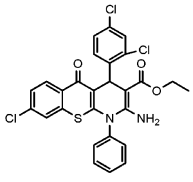
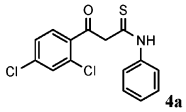
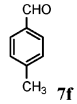
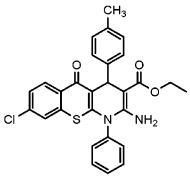
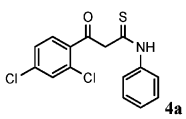
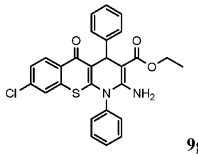
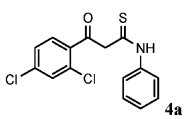
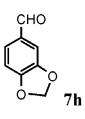
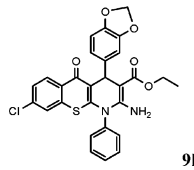
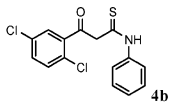
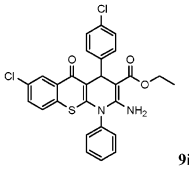
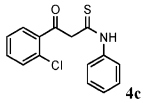
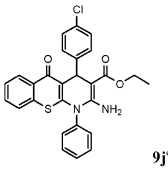
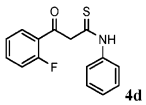
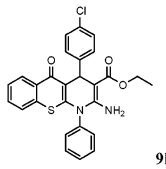
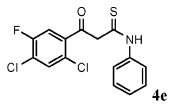
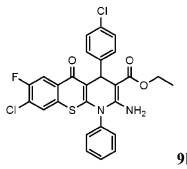
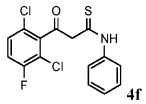
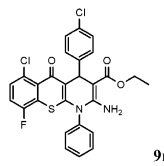
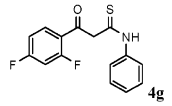
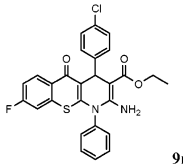
Entry	Precursors **2**	Precursors **6**	Products **9**	Time[b] (min)	Yield[a] (%)
1	 **4a**	 **7a**	 **9a**	45	68
2	 **4a**	 **7b**	 **9b**	50	74
3	 **4a**	 **7c**	 **9c**	45	76
4	 **4a**	 **7d**	 **9d**	45	55
5	 **4a**	 **7e**	 **9e**	45	63
6	 **4a**	 **7f**	 **9f**	45	54
7	 **4a**	 **7g**	 **9g**	50	65
8	 **4a**	 **7h**	 **9h**	55	53

Table 3 (Continued)

Entry	Precursors **2**	Precursors **6**	Products **9**	Time[b] (min)	Yield[a] (%)
9	 **4b**	 **7a**	 **9i**	45	72
10	 **4c**	 **7a**	 **9j**[c]	60	52
11	 **4d**	 **7a**	 **9k**[c]	60	58
12	 **4e**	 **7a**	 **9l**	40	76
13	 **4f**	 **7a**	 **9m**	40	74
14	 **4g**	 **7a**	 **9n**	45	65

[a] Isolated. [b] Microwave irradiation. [c] **9j** is the same as **9k**.

intermediate **10**. Second, **4** undergoes expected tandem [3 + 3] annulation involving Michael addition to **5** or **10** followed by the intramolecular N-cyclization to give intermediates **11** or **12**. Finally, an intramolecular nucleophilic aryl substitution of the *o*-chloro of aryl group (S_NAr) by attack of mercapto group leads to new and highly functionalized thiochromenopyridine derivatives **6a**−**x** or **9a**−**n** with elimination of HCl.

Conclusion

These studies highlighted the concept of a substrate-design approach to the development of novel domino and multicomponent reactions. By simply incorporating an *o*-halo group into the aryl ring of *β*-aroylthioacetanilides, we have obtained *β*-(2-chloroaroyl) thioacetanilides **4**, which displayed a completely different reactivity profile to to that of *β*-aroyl thioacetanilides, and developed a new strategy for the synthesis of two unusual series of tricyclic thiochromeno[2,3-*b*]pyridine derivatives. The advantages of these methods, which include high chemo- and regioselectivity, high bond-forming efficiency, and the ready availability of a wide range of substrates from cheap starting materials, make this new strategy highly attractive in diversity-oriented synthesis. The simplicity of the sequence, mild reaction conditions and economy of the sequence indicate that this process could be capable of broad application for elaboration of more complex and highly functionalized tricyclic systems. Further investigations to expand the scope of the diversity-oriented synthesis of *β*-(2-chloroaroyl) thioacetanilides as versatile building blocks by the combined use of domino and MCRs are in progress and will be reported elsewhere in due course.

Experimental Section

General Procedure for Synthesis of Product 6 (e.g., 6a). Method A. An equimolar mixture of *β*-(2,4-dichlorophenyl) thioacetanilides **4a** (1 mmol) and 4-(4-chlorobenzylidene)-2-phe-

nyloxazol-5(4*H*)-one **5a** (1 mmol) refluxed for 22 h in THF (15 mL) containing Et_3N (0.10 g, 1 mmol) under conventional heating. After completion of the reaction as indicated by TLC (petroleum−EtOAc, 8:2, v /v), the mixture was cooled to room temperature, and the solid product was filtered, washed with water, and subsequently dried and recrystallized from THF−EtOH (1:4, v /v) to give the pure product **6a**.

Method B. An equimolar mixture of *β*-(2,4-dichlorophenyl) thioacetanilides **4a** (1 mmol) and 4-(4-chlorobenzylidene)-2-phenyloxazol-5(4*H*)-one **5a** (1 mmol) refluxed for 30 min in THF (15 mL) containing Et_3N (0.10 g, 1 mmol) under microwave irradiation (600 W). After completion of the reaction as indicated by TLC (petroleum−EtOAc, 8:2, v/v), the mixture was cooled to room temperature, and the solid product was filtered, washed with water, and subsequently dried and recrystallized from THF−EtOH (1:4, v /v) to give the pure product **6a**.

6a: yellow crystal; yield 73% (microwave irradiation), 54% (conventional heating); mp 252−254 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.05 (d, J = 7.45 Hz, 1H, 4-H), 5.77 (t, J = 7.35, 7.35 Hz, 1H, 3-H), 7.25−8.26 (m, 17H, Ar-H), 8.39 (d, J = 7.00 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 39.40, 53.91, 116.85, 126.89, 128.18, 128.79, 129.00, 129.18, 130.31, 130.79, 132.10, 132.65, 134.10, 135.52, 135.70, 136.22, 137.55, 151.68, 167.37, 167.90, 176.94; IR (KBr) ν 3421, 3059, 1714, 1640, 1625, 1240, 777, 743, 695 cm^{-1}; MS (ESI) *m/z* 571.4 [M + H]$^+$. Anal. Calcd for $C_{31}H_{20}Cl_2N_2O_3S$: C, 65.15; H, 3.53; N, 4.90. Found: C, 65.10; H, 3.55; N, 4.94.

6b: yellow crystal; yield 71%; mp 256−258 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.13 (d, J = 7.45 Hz, 1H, 4-H), 5.75 (t, J = 7.20, 7.20 Hz, 1H, 3-H), 7.26−8.21 (m, 18H, Ar-H), 8.24 (d, J = 9.00 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 39.53, 54.11, 117.43, 126.88, 127.36, 128.06, 128.81, 129.20, 129.64, 130.33, 130.81, 132.06, 134.22, 135.51, 136.31, 136.69, 137.49, 151.30, 167.27, 168.09, 176.97; IR (KBr) ν 3418, 3053, 3028, 1717, 1697, 1661, 1615, 1239, 835, 741, 694 cm^{-1}; MS (ESI) *m/z* 537.1-[M + H]$^+$. Anal. Calcd for $C_{31}H_{21}ClN_2O_3S$: C, 69.33; H, 3.94; N, 5.22. Found: C, 69.44; H, 3.88; N, 5.25.

6c: yellow crystal; yield 74%; mp 222−224 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.01 (d, J = 7.40 Hz, 1H, 4-H), 5.71 (t, J = 7.25, 7.30 Hz, 1H, 3-H), 5.98 (s, 2H, OCH_2O), 6.74−8.27 (m, 16H, Ar-H), 8.28 (d, J = 7.15 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 54.14, 101.44, 108.92, 109.18, 117.51, 121.96, 126.88, 127.34, 128.14, 128.79, 130.35, 130.80, 132.06, 134.21, 135.53, 136.29, 137.45, 147.15, 147.92, 151.20, 167.27, 168.14, 176.94; IR (KBr) ν 3414, 3059, 1714, 1665, 1641, 1621, 1237, 835, 745, 693 cm^{-1}; MS (ESI) *m/z* 581.3 [M + H]$^+$. Anal. Calcd for $C_{32}H_{21}ClN_2O_5S$: C, 66.15; H, 3.64; N, 4.82. Found: C, 66.11; H, 3.67; N, 4.89.

6d: yellow crystal; yield 77%; mp 254−256 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.16 (d, J = 7.80 Hz, 1H, 4-H), 5.89 (t, J = 7.35, 7.60 Hz, 1H, 3-H), 7.45−8.26 (m, 17H, Ar-H), 8.46 (d, J = 7.25 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 39.45, 53.64, 116.14, 124.35, 126.92, 127.22, 128.21, 128.77, 129.05, 130.43, 130.93, 132.12, 134.05, 135.53, 136.20, 137.63, 144.95, 147.52, 152.17, 167.43, 167.68, 176.94; IR (KBr) ν 3398, 3064, 1716, 1659, 1617, 1246, 833, 742, 692 cm^{-1}; MS (ESI) *m/z* 582.3 [M + H]$^+$. Anal. Calcd for $C_{31}H_{20}ClN_3O_5S$: C, 63.97; H, 3.46; N, 7.22. Found: C, 64.01; H, 3.42; N, 7.26.

6e: yellow crystal; yield 85%; mp 283−285 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.40 (d, J = 7.85 Hz, 1H, 4-H), 5.85 (t, J = 7.75, 7.60 Hz, 1H, 3-H), 7.14−8.24 (m, 17H, Ar-H), 8.55(d, J = 7.45 Hz, 1H, N−H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 34.94, 53.54, 116.06, 116.26, 123.99, 124.11, 125.32, 126.89, 127.27, 128.16, 128.64, 128.97, 129.79, 129.88, 129.91, 129.99, 130.06, 130.28, 130.41, 130.66, 130.85, 130.97, 131.86, 134.46, 135.55, 136.39, 137.54, 152.20, 160.77, 162.72, 167.52, 167.86, 176.92; IR (KBr) ν 3415, 3055, 1721, 1706, 1666, 1613, 1240, 834, 748, 693 cm^{-1}; MS (ESI) *m/z* 555.0 [M + H]$^+$. Anal. Calcd for $C_{31}H_{20}ClFN_2O_3S$: C, 67.08; H, 3.63; N, 5.05. Found: C, 67.01; H, 3.61; N, 5.02.

6f: yellow solid; yield 82%; mp 281−283 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.55 (d, J = 7.85 Hz, 1H, 4-H), 5.96 (t, J = 7.95, 8.00 Hz, 1H, 3-H), 7.28−8.23 (m, 17H, Ar-H), 8.56 (d, J = 8.05 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 37.80, 46.08, 53.56, 117.39, 126.85, 127.27, 128.29, 128.40, 128.53, 128.94, 129.17, 129.56, 129.84, 130.25, 130.40, 130.62, 130.84, 131.71, 134.68, 135.14, 135.54, 136.38, 137.51, 152.03, 167.72, 167.93, 176.89; IR (KBr) ν 3415, 3065, 1719, 1663, 1618, 1240, 832, 737, 692 cm^{-1}; MS (ESI) *m/z* 571.2 [M + H]$^+$. Anal. Calcd for $C_{31}H_{20}Cl_2N_2O_3S$: C, 65.15; H, 3.53; N, 4.90. Found: C, 65.17; H, 3.49; N, 4.95.

6g: yellow crystal; yield 74%; mp 225−226 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 2.08 (s,3H,CH_3), 5.57 (d, J = 8.00 Hz, 1H, 4-H), 5.99 (t, J = 7.90, 8.00 Hz, 1H, 3-H), 7.29−8.19 (m, 17H, Ar-H), 8.55 (d, J = 7.85 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 31.18, 37.85, 53.55, 117.24, 128.32, 128.41, 128.64, 129.19, 129.58, 129.92, 130.26, 130.88, 131.73, 132.53, 132.56, 134.68, 135.15, 135.57, 136.43, 152.62, 167.75, 167.96, 176.47; IR (KBr) υ 3412, 3057, 2920, 1709, 1663, 1618, 1581, 1364, 1245, 745, 694 cm^{-1}; MS (ESI) *m/z* 551.2 [M + H]$^+$. Anal. Calcd for $C_{32}H_{23}ClN_2O_3S$: C, 69.75; H, 4.21; N, 5.08. Found: C, 69.64, H 4.22; N, 5.05.

6h: yellow crystal; yield 76%; mp 203−205 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 3.70 (s,3H,OCH_3), 5.04 (d, J = 7.20 Hz, 1H, 4-H), 5.67 (t, J = 6.85, 7.15 Hz, 1H, 3-H), 6.88−8.16(m, 17H, Ar-H), 8.23 (d, J = 8.75 Hz, 1H, N−H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 39.42, 54.23, 55.44, 114.57, 117.72, 126.83, 127.30, 128.05, 128.33, 128.78, 128.87, 129.62 129.91, 130.27, 130.63, 130.76, 130.89, 132.02, 134.18, 135.45, 136.28, 137.41, 151.01, 159.08, 167.20, 168.12, 176.87; IR (KBr) ν 3410, 3059, 2931, 1709, 1666, 1612, 1579, 1361, 1245, 747, 696 cm^{-1}; MS (ESI) *m/z* 567.2 [M + H]$^+$. Anal. Calcd for $C_{32}H_{23}ClN_2O_4S$: C, 67.78; H, 4.09; N, 4.94. Found: C, 67.68; H, 4.08; N, 4.92.

6i: yellow crystal; yield 72%; mp 206−208 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.07 (d, J = 7.45 Hz, 1H, 4-H), 5.79 (t, J = 7.15, 7.50 Hz, 1H, 3-H), 7.26−8.21 (m, 17H, Ar-H), 8.42 (d, J = 7.20 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 40.58, 53.92, 116.74, 127.41, 128.22, 128.78, 129.19, 130.83, 130.90, 132.09, 132.52, 133.61, 134.15, 135.72, 136.30, 152.25, 167.37, 167.94, 176.51; IR (KBr) υ 3423, 3059, 2971, 1722, 1639, 1616, 1577, 1363, 1237, 734, 694 cm^{-1}; MS (ESI) *m/z*: 571.2 [M + H]$^+$. Anal. Calcd for $C_{31}H_{20}Cl_2N_2O_3S$: C, 65.15; H, 3.53; N, 4.90. Found: C, 65.24; H, 3.49; N, 4.88.

6j: yellow crystal; yield 69%; mp 184−185 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.08 (d, J = 7.50 Hz, 1H, 4-H), 5.71 (t, J = 6.70, 7.20 Hz, 1H, 3-H), 7.21−8.18 (m, 18H, Ar-H), 8.19 (d, J = 6.95 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 40.16, 53.59, 116.74, 126.91, 127.50, 127.59, 128.30, 128.40, 128.71, 129.41, 129.50, 130.35, 132.00, 133.06, 133.70, 135.84, 136.16, 151.43, 166.79, 167.60, 176.05; IR (KBr) ν 3416, 3086, 3064, 1708, 1662, 1617, 1240, 825, 732, 695 cm^{-1}; MS (ESI) *m/z* 559.1 [M + Na]$^+$. Anal. Calcd for $C_{31}H_{21}ClN_2O_3S$: C, 69.33; H, 3.95; N, 5.22. Found: C, 69.44; H, 3.88; N, 5.17.

6k: yellow crystal; yield 76%; mp 250−253 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.02 (d, J = 7.45 Hz, 1H, 4-H), 5.71 (t, J = 7.30, 7.35 Hz, 1H, 3-H), 5.91(s, 2H, CH_2) 7.44−8.21 (m, 16H, Ar-H), 8.31 (d, J = 7.20 Hz, 1H, N−H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 41.37, 54.17, 117.41, 122.02, 127.44, 128.20, 128.83, 129.54, 129.94, 130.05, 130.39, 130.47, 130.76, 130.87, 132.11, 132.49, 132.58, 133.57, 134.26, 136.38, 147.21, 147.98, 151.83, 167.32, 168.18, 176.57; IR (KBr) ν 3439, 3070, 1714, 1697, 1662, 1615, 1229, 827, 734, 690 cm^{-1}; MS (ESI) *m/z* 581.3 [M + H]$^+$. Anal. Calcd for $C_{32}H_{21}ClN_2O_5S$: C, 66.15; H, 3.64; N, 4.82. Found: C, 66.21; H, 3.67; N, 4.79.

6l: yellow crystal; yield 74%; mp 196−197 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.12 (d, J = 7.70 Hz, 1H, 4-H), 5.86 (t,

J = 7.45, 7.60 Hz, 1H, 3-H), 7.40−8.28 (m, 17H, Ar-H), 8.43 (d, J = 7.45 Hz, 1H, N−H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 41.19, 53.58, 115.94, 124.32 127.34, 128.19, 128.73, 129.83, 129.89, 130.42, 130.65, 130.81, 132.08, 132.49, 132.56, 133.63, 134.00, 136.19, 144.86, 144.48, 152.72, 167.38, 167.66, 176.48; IR (KBr) ν 3411, 3062, 1712, 1697, 1638, 1620, 1223, 817, 732, 697 cm^{-1}; MS (ESI) *m/z* 582.4 [M + H]$^+$. Anal. Calcd for $C_{31}H_{20}ClN_3O_5S$: C, 63.97; H, 3.46; N, 7.22. Found: C, 64.04; H, 3.42; N, 7.19.

6m: yellow crystal; yield 80%; mp 180−182 °C; ^{1}H NMR (DMSO-d_6, 600 MHz) δ 5.40 (d, J = 7.80 Hz, 1H, 4-H), 5.86 (t, J = 7.80, 7.80 Hz, 1H, 3-H), 7.44−8.58 (m, 17H, Ar-H), 8.59 (d, J = 7.32 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ 34.67, 53.11, 115.57, 123.57, 123.67, 125.02, 127.06, 127.80, 128.38, 129.45, 129.53, 129.56, 129.77, 129.82, 130.12, 130.41, 130.57, 130.61, 131.64, 132.18, 132.22, 133.30, 134.00, 136.03, 152.48, 162.20, 167.50, 176.24; IR (KBr) ν 3426, 3063, 1726, 1697, 1654, 1617, 1229, 848, 737, 698 cm^{-1}; MS (ESI) *m/z* 555.2 [M + H]$^+$. Anal. Calcd for $C_{31}H_{20}ClFN_2O_3S$: C, 67.08; H, 3.63; N, 5.05. Found: C, 67.01; H, 3.64; N, 5.02

6n: yellow crystal; yield 75%; mp 195−198 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.09 (d, J = 7.35 Hz, 1H, 4-H), 5.71 (t, J = 7.05, 7.15 Hz, 1H, 3-H), 7.15−8.18 (m, 17H, Ar-H), 8.23 (d, J = 8.10 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 40.48, 54.18, 117.61, 126.88, 127.35, 128.08, 128.77, 128.82, 128.91, 129.62, 129.78, 130.32, 130.68, 130.80, 130.93, 132.07, 133.50, 134.20, 135.49, 136.32, 136.69, 137.08, 137.46, 151.16, 167.23, 168.14, 176.22; IR (KBr) ν 3427, 3074, 1721, 1655, 1622, 1600, 1528, 1267, 832, 737, 692 cm^{-1}; MS (ESI) *m/z* 571.2 [M + H]$^+$. Anal. Calcd for $C_{31}H_{20}Cl_2N_2O_3S$: C, 65.15; H, 3.53; N, 4.90. Found: C, 65.17; H, 3.54; N, 4.87.

6o: yellow crystal; yield 71%; mp 244−245 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 2.26 (s, 3H, CH_3), 5.10 (d, J = 7.25 Hz, 1H, 4-H), 5.74 (t, J = 7.05, 7.20 Hz, 1H, 3-H), 7.14−8.19 (m, 17H, Ar-H), 8.20 (d, J = 7.10 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 21.09, 40.70, 54.12, 117.41, 127.36, 128.06, 128.74, 128.78, 129.59, 129.84, 129.96, 130.03, 130.79, 130.87, 130.98, 132.04, 132.39, 132.43, 133.50, 134.15, 136.32, 137.06, 151.72, 167.21, 168.11, 176.46; IR (KBr) ν 3435, 3062, 3030, 1721, 1662, 1604, 1568, 1356, 1225, 735, 692 cm^{-1}; MS (ESI) *m/z* 551.5 [M + H]$^+$. Anal. Calcd for $C_{32}H_{23}ClN_2O_3S$: C, 69.75; H, 4.21; N, 5.08. Found: C, 69.67, H 4.13; N, 5.16.

6p: yellow crystal; yield 74%; mp 200−202 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 3.71 (s, 3H, OCH_3), 5.06 (d, J = 7.30 Hz, 1H, 4-H), 5.71 (t, J = 7.10, 7.15 Hz, 1H, 3-H), 6.89−8.19 (m, 17H, Ar-H), 8.20 (d, J = 7.55 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 39.48, 54.26, 55.48, 114.61, 117.61, 127.40, 128.11, 128.37, 128.11, 128.37, 128.81, 129.90, 129.96, 130.01, 130.83, 132.06, 132.44, 132.49, 133.53, 134.15, 136.37, 151.65, 159.13, 167.25, 168.18, 176.50; IR (KBr) ν 3400, 3068, 2964, 1723, 1670, 1613, 1512, 1355, 1233, 738, 694 cm^{-1}; MS (ESI) *m/z* 567.4 [M + H]$^+$. Anal. Calcd for $C_{32}H_{23}ClN_2O_4S$: C, 67.78; H, 4.09; N, 4.94. Found: C, 67.69, H 4.08; N, 4.93.

6q: yellow crystal; yield 64%; mp 247−248 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.08 (d, J = 7.45 Hz, 1H, 4-H), 5.77 (t, J = 7.30, 7.30 Hz, 1H, 3-H), 7.26−8.28 (m, 18H, Ar-H), 8.40 (d, J = 7.15 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 40.85, 54.04, 116.86, 127.65, 128.26, 128.38, 128.63, 128.68, 128.84, 129.22, 129.87, 130.38, 130.88, 132.15, 132.64, 133.81, 134.22, 135.97, 136.47, 151.73, 167.38, 168.01, 177.64; IR (KBr) ν 3426, 3065, 2957, 1717, 1657, 1615,1580, 1365, 1238, 796, 718, 693 cm^{-1}; MS (ESI) *m/z* 537.1 [M + H]$^+$. Anal. Calcd for $C_{31}H_{21}ClN_2O_3S$: C, 69.33; H, 3.94; N, 5.22. Found: C, 69.44; H, 3.90; N, 5.25.

6r: yellow crystal; yield 62%; mp 266−269 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.10 (d, J = 7.40 Hz, 1H, 4-H), 5.69 (t, J = 7.15, 7.10 Hz, 1H, 3-H), 7.21−8.16 (m, 19H, Ar-H), 8.23 (d, J = 8.00 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 41.39, 53.67, 116.80, 127.09, 127.44, 127.58, 127.83, 128.12, 128.31, 128.41, 128.69, 130.24, 131.57, 132.03, 133.23, 133.72, 135.95 136.34, 150.86 166.76, 167.62, 177.13; IR (KBr) ν 3412, 3059, 3030, 1702, 1664, 1616, 1578, 1365, 751, 721, 694 cm^{-1}; MS (ESI) *m/z* 503.2 [M + H]$^+$. Anal. Calcd for $C_{31}H_{22}N_2O_3S$: C, 74.08; H, 4.41; N, 5.57. Found: C, 73.99, H, 4.39; N, 5.25.

6s: yellow crystal; yield 58%; mp 198−200 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.03 (d, J = 7.40 Hz, 1H, 4-H), 5.71 (t, J = 7.30, 7.30 Hz, 1H, 3-H), 6.73−7.86 (m, 17H, Ar-H), 8.28 (d, J = 6.70 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 39.96, 53.70, 116.97, 121.44, 123.58, 127.08, 127.63, 127.83, 128.14, 128.30, 130.05, 130.22, 131.55, 132.00, 133.75, 135.96, 146.62, 147.42, 150.67, 166.74, 167.65, 177.10; IR (KBr) ν 3425, 3066, 1705, 1661, 1616, 1590, 1235, 758, 723, 695 cm^{-1}; MS (ESI) *m/z* 547.3 [M + H]$^+$. Anal. Calcd for $C_{32}H_{22}N_2O_5S$: C, 70.32; H, 4.06; N, 5.13. Found: C, 70.39; H, 4.08; N, 5.15.

6t: yellow crystal; yield 68%; mp 208−210 °C; ^{1}H NMR (DMSO-d_6, 600 MHz) δ 5.17 (d, J = 7.80 Hz, 1H, 4-H), 5.88 (t, J = 7.32, 7.80 Hz, 1H, 3-H), 7.46−8.26 (m, 18H, Ar-H), 8.46 (d, J = 7.38 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ 39.63, 53.24, 115.68, 124.00, 127.81, 127.93, 128.11, 128.44, 130.04, 133.38, 133.61, 135.94, 144.75, 147.13, 151.86, 167.31, 168.09, 177.28; IR (KBr) ν 3424, 3066, 1713, 1643, 1608, 1578, 1239, 746, 720, 691 cm^{-1}; MS (ESI) *m/z* 570.6 [M + Na]$^+$. Anal. Calcd for $C_{31}H_{21}N_3O_5S$: C, 68.00; H, 3.87; N, 7.67. Found: C, 68.08; H, 3.89; N, 7.65.

6u: yellow crystal; yield 71%; mp 253−255 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.42 (d, J = 7.85 Hz, 1H, 4-H), 5.86 (t, J = 7.65, 7.70 Hz, 1H, 3-H), 7.13−8.26 (m, 18H, Ar-H), 8.53 (d, J = 7.50 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 35.16, 53.86, 116.24, 124.40, 124.53, 125.57, 127.83, 128.42, 128.54, 128.80, 128.89, 130.09, 131.02, 132.10, 132.82, 134.04, 134.74, 136.79, 152.48, 167.76, 168.16, 177.83; IR (KBr) ν 3415, 3060, 1707, 1669, 1615, 1589, 1578, 1546, 1514, 1487, 1362, 1244, 760, 721, 694 cm^{-1}; MS (ESI) *m/z* 521.2 [M + H]$^+$. Anal. Calcd for $C_{31}H_{21}FN_2O_3S$: C, 71.52; H, 4.07; N, 5.38. Found: C 71.59, H 4.11; N, 5.35.

6v: yellow crystal; yield 65%; mp 276−280 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 5.60 (d, J = 7.25 Hz, 1H, 4-H), 5.98 (t, J = 7.20, 7.20 Hz, 1H, 3-H), 7.31−8.28 (m, 18H, Ar-H), 8.47 (d, J = 7.25 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 37.94, 53.68, 117.39, 127.52, 128.28, 128.38, 128.56, 128.62, 129.19, 129.53, 130.27, 130.76, 131.72, 132.53, 133.78, 134.74, 136.55, 152.01 167.73, 167.97, 177.57; IR (KBr) ν 3421, 3060, 1715, 1670, 1614, 1589, 1241, 777, 722, 693 cm^{-1}; MS (ESI) *m/z* 537.2 [M + H]$^+$. Anal. Calcd for $C_{31}H_{21}ClN_2O_3S$: C, 69.33; H, 3.94; N, 5.22. Found: C, 69.39; H, 3.98; N, 5.25.

6w: yellow crystal; yield 54%; mp 248−250 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 2.25 (s, 3H, CH_3), 5.12 (d, J = 7.80 Hz, 1H, 4-H), 5.72(t, J = 7.20, 7.20 Hz, 1H, 3-H), 7.14−8.16 (m, 18H, Ar-H), 8.27 (d, J = 7.20 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 21.73, 39.48, 54.85, 118.14, 128.18, 128.68, 128.95, 129.16, 129.27, 129.39, 129.44, 130.24, 130.36, 130.92, 131.26, 131.33, 131.55, 132.68, 133.10, 134.28, 134.33, 134.84, 137.09, 137.63, 151.78, 167.82, 168.78, 178.20; IR (KBr) ν 3419, 3039, 1719, 1652, 1618, 1576,1545, 1361, 1235, 751, 694 cm^{-1}; MS (ESI) *m/z* 517.2 [M + H]$^+$. Anal. Calcd for $C_{32}H_{24}N_2O_3S$: C, 74.40; H, 4.68; N, 5.42. Found: C, 74.31; H, 4.64; N, 5.45.

6x: yellow crystal; yield 55%; mp 240−242 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 3.71(s,3H,OCH_3), 5.08 (d, J = 7.45 Hz, 1H, 4-H), 5.68 (t, J = 7.20, 7.20 Hz, 1H, 3-H), 6.89−8.17 (m, 18H, Ar-H), 8.27 (d, J = 9.00 Hz, 1H, N-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 39.49, 54.36, 55.49, 114.60, 127.59, 128.11, 128.34, 128.57, 128.64, 129.98, 130.73, 132.07, 132.50, 133.73, 134.27, 136.55, 151.07, 159.11, 167.23, 168.22, 177.59; IR (KBr) ν 3427, 3033, 1707, 1666, 1616, 1578, 1548, 1357, 1237, 755, 722, 693 cm^{-1}; MS (ESI) *m/z* 533.2 [M + H]$^+$. Anal. Calcd for $C_{32}H_{24}N_2O_4S$: C, 72.16; H, 4.54; N, 5.26. Found: C 72.24, H 4.58; N, 5.23.

General Procedure for One-Pot Synthesis of Product 9 under Microwave Irradiation (e.g., 9a). An equimolar mixture of β-(2,4-

dichlorophenyl) thioacetanilides **4a** (1 mmol), 4-chlorobenzaldehyde **7a** (1mmol), and ethyl 2-cyanoacetate **8** (1 mmol) refluxed for 45 min in EtOH (15 mL) containing Et_3N (0.10 g, 1 mmol) under microwave irradiation (600 W). After completion of the reaction as indicated by TLC (petroleum−EtOAc, 8:2, v /v), the mixture was cooled to room temperature, and the solid product was filtered, washed with water, and subsequently dried and recrystallized from THF−EtOH (1:4, v /v) to give the pure product **9a**.

9a: yellow crystal; yield 68%; mp 263−265 °C; ^{1}H NMR (DMSO-d_6, 600 MHz) δ 1.15 (t, 3H, CH_2CH_3, J = 6.90, 7.32 Hz), 4.03 (m, 2H, CH_2CH_3), 5.46 (s, 1H, 4-H), 6.91 (br s, 2H, NH_2), 7.30−8.17 (m, 12H, Ar-H); ^{13}C NMR (DMSO-d_6, 150 MHz) δ 14.53, 35.54, 58.93, 78.48, 115.64, 126.11, 128.13, 129.39, 129.81, 130.58, 130.91, 130.95, 134.55, 146.12, 148.56, 151.88, 168.46, 176.52; IR (KBr) ν 3490, 3291, 3042, 2972 1662, 1630, 1601, 1486, 1387, 1279, 1200, 829, 781, 702 cm^{-1}; MS (ESI) *m/z* 523.2 [M + H]$^+$. Anal. Calcd for $C_{27}H_{20}Cl_2N_2O_3S$: C, 61.95; H, 3.85; N, 5.35. Found: C, 61.93; H, 3.84; N, 5.42.

9b: yellow crystal; yield 74%; mp 263−265 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.15 (t, 3H, CH_2CH_3, J = 7.00 Hz, 7.50 Hz), 3.58 (m, 2H, CH_2CH_3), 5.55 (s, 1H, 4-H), 6.94 (br s, 2H, NH_2), 7.52−8.16 (m, 12H, Ar-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 14.73, 36.69, 59.31, 78.44, 115.39, 121.56, 122.57, 126.52, 127.35, 128.52, 130.10, 130.23, 131.22, 131.34, 131.88, 134.55, 134.76, 134.93, 137.16, 147.86, 149.53, 149.65, 152.43, 168.59, 176.78; IR (KBr) ν 3492, 3285, 3064, 1665, 1628, 1601, 1579, 1528, 1487, 1350, 1277, 1203, 834, 740, 703 cm^{-1}; MS (ESI) *m/z* 557.2 [M + H + Na]$^+$. Anal. Calcd for $C_{27}H_{20}ClN_3O_5S$: C, 60.73; H, 3.78; N, 7.87. Found: C, 60.79; H, 3.76; N, 7.83.

9c: yellow crystal; yield 76%; mp 278−280 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.10 (t, 3H, CH_2CH_3, J = 7.00, 7.50 Hz), 3.58 (m, 2H, CH_2CH_3), 5.54 (s, 1H, 4-H), 6.99(br s, 2H, NH_2), 7.29−8.11(m, 11H, Ar-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 14.10, 39.24, 58.65, 75.74, 112.36, 125.78, 126.73, 127.22, 127.91, 129.49, 130.34, 130.87, 131.28, 131.42, 133.32, 134.10, 136.51, 144.91, 149.69, 152.02, 168.44, 176.30; IR (KBr) ν 3490, 3267, 3053, 1658, 1625, 1601, 1583, 1542, 1487, 1349, 1273, 834, 791, 735, 699 cm^{-1}; MS (ESI) *m/z* 557.2 [M + H]$^+$. Anal. Calcd for $C_{27}H_{19}Cl_3N_2O_3S$: C 58.13; H, 3.43; N, 5.02. Found: C, 58.10; H, 3.46; N, 5.04.

9d: yellow crystal; yield 55%; mp 246−248 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.10 (t, 3H, CH_2CH_3, J = 7.00, 7.00 Hz), 3.99 (m, 2H, CH_2CH_3), 5.67 (s, 1H, 4-H), 6.95(br s, 2H, NH_2), 7.11−8.10 (m, 12H, Ar-H); ^{13}C NMR (DMSO-d_6,125 MHz) δ 14.40, 36.10, 58.63, 77.47, 114.17, 125.81, 126.55, 126.98, 127.44, 127.90, 129.40, 129.60, 130.85, 131.12, 131.41, 132.53, 132.72, 134.20, 134.42, 136.50, 144.11, 148.93, 151.86, 168.79, 176.38; IR (KBr) ν 3452, 3259, 3058, 1661, 1625, 1584, 1543, 1488, 1348, 1271, 1203, 833, 782, 753, 702 cm^{-1}; MS (ESI) *m/z* 523.4 [M + H]$^+$. Anal. Calcd for $C_{27}H_{20}Cl_2N_2O_3S$: C, 61.95; H, 3.85; N, 5.35. Found: C, 61.90; H, 3.83; N, 5.40.

9e: yellow crystal; yield 63%; mp 243−245 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.10 (t, 3H, CH_2CH_3, J = 7.00, 7.50 Hz), 3.96 (m, 2H, CH_2CH_3), 5.62 (s, 1H, 4-H), 6.97 (br s, 2H, NH_2), 7.32−8.10 (m, 11H, Ar-H); ^{13}C NMR (DMSO-d_6,125 MHz) δ 14.42, 36.00, 58.70, 76.89, 113.65, 125.85, 126.72, 126.87, 127.98, 128.57, 129.58, 130.89, 131.16, 131.48, 133.45, 134.07, 134.20, 134.28, 136.57, 143.23, 149.28, 151.94, 168.65, 176.38; IR (KBr) ν 3491, 3267, 3045, 1666, 1629, 1602 ,1582, 1542, 1486, 1349, 1276, 1202, 834, 786, 703 cm^{-1}; MS (ESI) *m/z* 557.4 [M + H]$^+$. Anal. Calcd for $C_{27}H_{19}Cl_3N_2O_3S$: C, 58.13; H, 3.43; N, 5.02. Found: C, 58.19; H, 3.46; N, 5.06.

9f: yellow crystal; yield 54%; mp 228−231 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.16 (t, 3H, CH_2CH_3, J = 7.0, 7.50 Hz), 2.21 (s, 3H, C_6H_4-CH_3), 3.97 (m, 2H, CH_2CH_3), 5.47 (s, 1H, 4-H), 6.85 (br s, 2H, NH_2), 7.04−8.18 (m, 12H, Ar-H); ^{13}C NMR (DMSO-d_6,125 MHz) δ 15.00, 21.14, 35.68, 59.24, 79.50, 116.81, 126.53, 127.72, 128.43, 129.16, 130.24, 131.31, 131.35, 131.76, 134.98, 135.23, 135.44, 137.04, 144.66, 148.42, 152.44, 169.09, 176.96; IR (KBr) ν 3491, 3288, 3043, 1663, 1627, 1580, 1541, 1486, 1348, 1277, 1202, 831, 780, 756, 703 cm^{-1}; MS (ESI) *m/z* 503.2 [M + H]$^+$. Anal. Calcd for $C_{28}H_{23}ClN_2O_3S$: C, 66.86; H, 4.61; N, 5.57. Found: C, 66.79; H, 4.56; N, 5.51.

9g: yellow crystal; yield 65%; mp 245−248 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.15 (t, 3H, CH_2CH_3, J = 7.0, 7.00 Hz), 4.03 (m, 2H, CH_2CH_3), 5.48 (s, 1H, 4-H), 6.83 (br s, 2H, NH_2), 7.24−8.18 (m, 13H, Ar-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 14.60, 35.89, 59.01, 79.24, 116.30, 126.12, 126.25, 126.80, 127.32, 127.51, 128.18, 128.29, 129.94, 130.88, 131.06, 131.51, 134.62, 134.77, 136.84, 147.20, 148.39, 152.07, 168.76, 176.73; IR (KBr) ν 3494, 3296, 3060, 1661, 1629, 1604, 1579, 1539, 1485, 1348, 1280, 1202, 857, 825, 696 cm^{-1}; MS (ESI) *m/z* 489.2 [M + H]$^+$. Anal. Calcd for $C_{27}H_{21}ClN_2O_3S$: C, 66.32; H, 4.33; N, 5.73. Found: C, 66.40; H 4.30; N, 5.75.

9h: yellow crystal; yield 53%; mp 177−179 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.15 (t, 3H, CH_2CH_3, J = 7.00, 7.50 Hz), 4.02 (m, 2H, CH_2CH_3), 5.42 (s, 1H, 4-H), 5.90 (s, 2H, CH_2), 6.82 (br s, 2H, NH_2), 7.00−8.19 (m, 11H, Ar-H); ^{13}C NMR (DMSO-d_6,125 MHz) δ14.90, 35.70, 59.16, 79.27, 101.06, 108.36, 116.56, 120.41, 126.44, 127.56, 128.37, 130.16, 131.15, 131.26, 131.69, 134.87, 135.01, 136.97, 141.62, 145.78, 147.20, 148.36, 152.30, 168.93, 176.90; IR (KBr) ν 3495, 3287, 2974, 1667, 1626, 1603, 1579, 1542, 1486, 1278, 1201, 915, 798, 703 cm^{-1}; MS (ESI) *m/z* 533.1 [M + H]$^+$. Anal. Calcd for $C_{28}H_{21}ClN_2O_5S$: C, 63.10; H, 3.97; N, 5.26. Found: C, 63.11; H, 3.94; N, 5.27.

9i: yellow crystal; yield 72%; mp 128−130 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.18 (t, 3H, CH_2CH_3,J = 7.00, 7.00 Hz), 4.01 (m, 2H, CH_2CH_3 J = 7.00 Hz), 5.47 (s, 1H, 4-H), 6.92 (br s, 2H, NH_2), 7.31−8.14 (m, 12H, Ar-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 14.86, 35.02, 59.22, 78.76, 115.88, 128.43, 129.72, 130.14, 130.89, 131.26, 131.84, 133.10, 134.93, 146.42, 149.44, 152.34, 168.80, 176.37; IR (KBr) ν 3400, 3291, 3042, 2973, 1648, 1629, 1608, 1579, 1544, 1486, 1347, 1279, 1205, 827, 729, 698 cm^{-1}; MS (ESI) *m/z* 523.1 [M + H]$^+$. Anal. Calcd for $C_{27}H_{20}Cl_2N_2O_3S$: C, 61.95; H, 3.85; N, 5.35. Found: C, 61.87; H, 3.80; N, 5.36.

9j and 9k: orange crystal; yield 52% (from precursor **1c**), 58% (from precursor **1d**); mp 220−221 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.17 (t, 3H, CH_2CH_3, J = 7.00, 7.50 Hz), 4.01 (m, 2H, CH_2CH_3), 5.50 (s, 1H, 4-H), 6.89 (br s, 2H, NH_2), 7.30−7.63 (m, 13H, Ar-H); ^{13}C NMR (DMSO-d_6,125 MHz) δ 14.66, 35.64, 58.95, 78.57, 115.75, 126.91, 127.82, 127.94, 128.18, 128.57, 129.48, 130.95, 131.08, 131.43, 131.85, 132.89, 134.85, 146.43, 148.60, 152.23, 168.64, 177.30; IR (KBr) ν 3478, 3290, 3028, 1663, 1632, 1606, 1589, 1546, 1448, 1360, 1281, 1201, 827, 743, 704 cm^{-1}; MS (ESI) *m/z* 489.1 [M + H]$^+$. Anal. Calcd for $C_{27}H_{21}ClN_2O_3S$: C, 66.32; H, 4.32; N, 5.73. Found: C, 66.22; H, 4.30; N, 5.78.

9l: yellow crystal; yield 76%; mp 245−248 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.15 (t, 3H, CH_2CH_3, J = 7.00, 7.00 Hz), 4.02 (m, 2H, CH_2CH_3), 5.46 (s, 1H, 4-H), 6.90 (br s, 2H, NH_2) 7.30−8.24 (m, 11H, Ar-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 14.41, 35.38, 58.74, 78.34, 115.30, 125.27, 127.97, 129.24, 130.41, 130.79, 134.47, 146.07, 148.20, 151.92, 168.37, 176.28; IR (KBr) ν 3484, 3293, 3045, 1663, 1631, 1591, 1486, 1347, 1281, 1199, 840, 786, 702 cm^{-1}; MS (ESI) *m/z* 541.1 [M + H]$^+$. Anal. Calcd for $C_{27}H_{19}Cl_2FN_2O_3S$: C, 59.90; H, 3.54; N, 5.17. Found: C, 59.85; H, 3.50; N, 5.13.

9m: yellow crystal; yield 74%; mp 234−236 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.17 (t, 3H, CH_2CH_3, J = 7.00, 7.00 Hz), 4.03 (m, 2H, CH_2CH_3 J = 6.5 Hz), 5.44 (s, 1H, 4-H), 6.91 (br s, 2H, NH_2); 7.32−7.74 (m, 11H, Ar-H); ^{13}C NMR (DMSO-d_6,125 MHz) δ 14.83, 36.09, 59.24, 78.88, 116.98, 126.01, 128.50, 129.65, 130.12, 130.95, 131.24, 131.36, 131.91, 132.01, 134.61, 145.42, 146.35, 152.15, 168.76, 176.43; IR (KBr) ν 3494, 3296, 3060, 1661, 1629, 1604, 1579, 1539, 1348, 1280, 825, 748, 696 cm^{-1}; MS (ESI) *m/z* 541.4 [M + H]$^+$. Anal. Calcd for $C_{27}H_{19}Cl_2FN_2O_3S$: C, 59.90; H, 3.54; N, 5.17. Found: C, 59.85; H, 3.50; N, 5.12.

9n: yellow crystal; yield 65%; mp 251−252 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.25 (t, 3H, CH_2CH_3, J = 6.50, 8.00 Hz),

4.11 (m, 2H, CH_2CH_3), 5.65 (s, 1H, 4-H), 6.37 (br s, 2H, NH_2), 6.95−8.45 (m, 12H, Ar-H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 14.95, 35.95, 59.29, 78.88, 113.27, 113.47, 115.83, 116.38, 116.56, 125.80, 128.51, 129.81, 130.95, 131.33, 131.41, 131.51, 131.83, 135.02, 135.45, 135.53, 146.64, 148.72, 152.45, 162.68, 164.69, 168.92, 176.80; IR (KBr) ν 3448, 3290, 3067, 1662, 1629, 1592, 1551, 1488, 1353, 1281, 1201, 792, 703 cm^{-1}; MS (ESI) *m/z* 507.1 $[M + H]^+$. Anal. Calcd for $C_{27}H_{20}ClFN_2O_3S$: C, 63.97; H, 3.98; N, 5.53. Found: C, 64.06; H 3.90; N, 5.58.

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Supporting Information Available: Experimental procedures and characterization data for all new compounds and X-ray data for compounds **6e** and **9b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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