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Reactivity of Functionalized *N*,*S*-Ketene Acetal: Regioselective Construction of Tetrahydrobenzo[*b*]pyran and Chromeno[2,3-*b*]quinoline Derivatives

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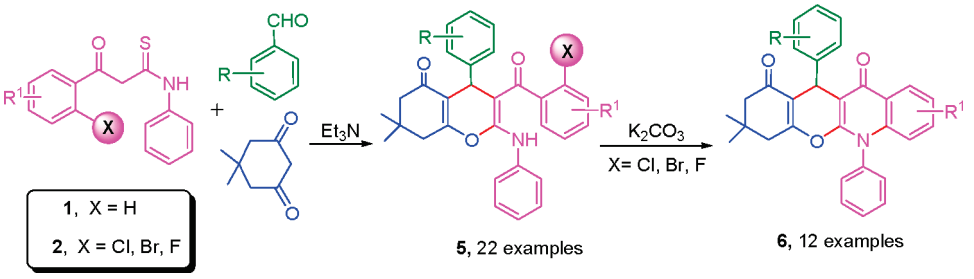

Regioselective synthesis of functionalized tetrahydrobenzo[*b*]pyrans has been developed by multicomponent reactions (MCRs) and tandem [3 + 3] annulations of *β*-benzoylthioacetanilides or *β*-(2-haloaroyl)thioacetanilides as valuable sources with aromatic aldehydes and 5,5-dimethyl-1,3-cyclohexanedione catalyzed by triethylamine. This MCR followed by a postcondensation cyclization via an intramolecular S_NAr in the presence of K_2CO_3 led to an unprecedented novel chromeno-[2,3-*b*]quinoline framework containing an important chromene moiety in good yields. The reactions were very mild, convenient, and *o*-selective to form new fused tetracyclic target molecules.

Introduction

A major challenge of modern drug discovery is the design of highly efficient chemical reaction sequences that provide maximum structural complexity and diversity with a minimum number of synthetic steps to assemble compounds with interesting properties.[1] Recently multicomponent reactions (MCRs) have emerged as a highly valuable tool in modern organic synthesis and modern drug discovery. The atom economy and convergent character,[2] the simplicity of a one-pot procedure, the possible structural variations, the accessible complexity of the molecules, and the very large number of accessible compounds are among the described advantages of a MCR.[3]

The exploration of privileged structures in drug discovery is a rapidly emerging theme in medicinal chemistry.[4] The chromene structural framework and heterofused analogues, as important privileged heterocyclic scaffolds,[5] appear in a plethora of natural products and in a variety of known inhibitors for a broad range of receptors.[6]

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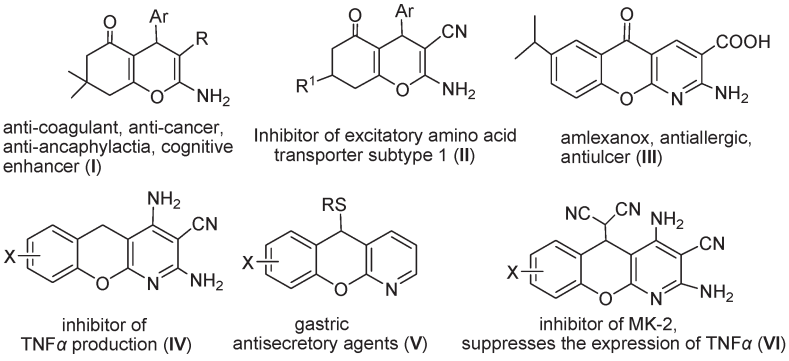

FIGURE 1. Selected examples of tetrahydrobenzo[*b*]pyrans and chromene-based heterocycles with biological and medicinal acitivities.

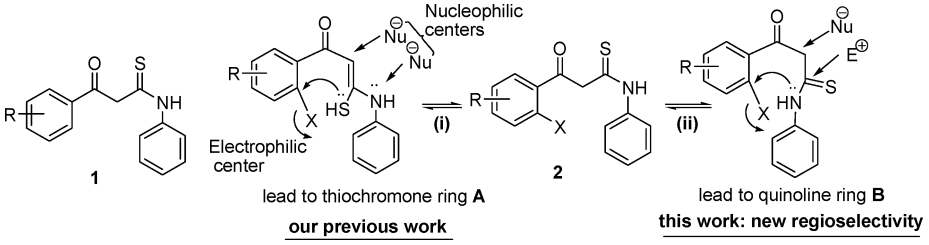

FIGURE 2. Reactivity profile of β-(2-haloaroyl)thioacetanilides **2**.

Among the different types of chromene systems (Figure 1), tetrahydrobenzo[*b*]pyrans (**I**) are of considerable interest because of their wide range of biological properties,[7] such as spasmolytic, diuretic, anticoagulant, anticancer, and antiancaphylactia activities.[8] They can also be used as cognitive enhancers not only for the treatment of schizophrenia and myoclonus but also for the treatment of neurodegenerative disease, including Alzheimer's disease, amyotrophic lateral sclerosis, Huntington's disease, Parkinson's disease, AIDS-associated dementia, and Down's syndrome.[9] Similar compounds (**II**), as the first class of compounds, have shown fully selective inhibition of the human excitatory amino acid transporter subtype 1 (EAAT 1).[10] Based on the chromene-based heterocycles framework, a typical example of an approved drug is amlexanox (**III**), which is a commonly prescribed antiallergic and typical antiulcer agent,[11] and many other compounds such as compound **IV**, **V**, and **VI** exemplify the wide therapeutic spectrum and active interest.[12]

In the course of studies on the chemistry of functionalized *N*,*S*-ketene acetal,[13] β-(2-haloaroyl)thioacetanilides **2** being novel building blocks with four active reaction sites show structural features of highly polarized push−pull interaction C=C double bond and Cl atom as leaving group (Figure 2). On the one hand, because of the conjugation effect of the electron-donating amino groups and electron-withdrawing carbonyl group, the nucleophilicity at the α carbon is greater than at the nitrogen atom. On the other hand, simply incorporating an *o*-halo group into the aryl ring of 2-benzoylthioacetanilides **1** would subject it to an intramolecular nucleophilic aryl substitution reaction (S_NAr). The S_NAr may occur by either (i) the *o*-chloro of the aryl group by attack of the mercapto group

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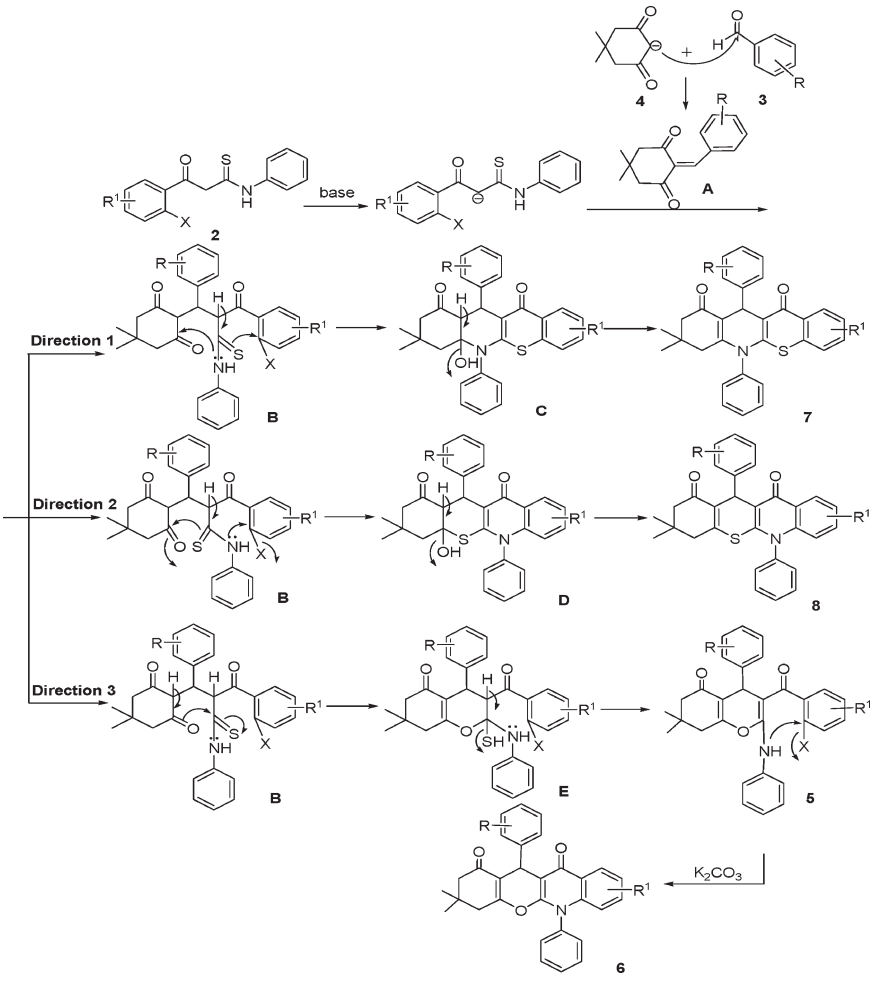
SCHEME 1



leading to thiochromone ring **A**[14] or (ii) the *o*-chloro of the aryl group by attack of the NH group to form quinoline ring **B** with chemo- and regioselectivity in this context.

In continuation of our research interests regarding the development of the synthetic utility of *β*-aroylthioacetanilides as valuable sources,[14,15] we wish to report herein a simple and convenient protocol for chemo- and regioselective synthesis of tetrahydrobenzo[*b*]pyrans **5** via a one-pot three-component tandem [3 + 3] annulation of *β*-(aroyl)-thioacetanilides with aromatic aldehydes and 5,5-dimethyl-1,3- cyclohexanedione. This novel MCR followed by a post-condensation cyclization via an intramolecular S_NAr in the presence of K_2CO_3 leads to unprecedented new fused chromeno-[2,3-*b*]quinoline derivatives **6**. To the best of our knowledge, there have not been reports about the application of *β*-(aroyl)-thioacetanilides in the synthesis for chromene scaffold.

Results and Discussion

Reactions of *β*-(Aroyl)thioacetanilides with Aromatic Aldehydes and 5,5-Dimethyl-1,3-cyclohexanedione. Our approach toward the design and development of new domino and multicomponent procedures involves the use of building block **2** that contains a number of chemically distinct functionalities, which could be selectively reacted to generate diversity with aldehydes **3** and 5,5-dimethyl-1,3-cyclohexanedione **4**. Three directions of the reaction are outlined in Scheme 1.

In direction 1, the intermediate **B** undergoes the intramolecular *N*-cyclization and S_NAr of the mercapto group to give **7**, which follows the route of our recent studies.[15] In direction 2, the intermediate **B** undergoes the intramolecular *S*-cyclization and S_NAr of the amino group to give **8**. In direction 3, the intermediate **B** undergoes the intramolecular *O*-cyclization to give **5** and S_NAr of the amino group to give **6**. During our investigation, we did not trace **7** or **8**, and only **5** and **6** were obtained exclusively. Surprisingly, the reactions described show high regioselectivity.

In the initial experiment, the transformation of *β*-(2,4-dichlorobenzoyl)thioacetanilide **2a** with **3a** and **4** proceeded smoothly with Et_3N (1 equiv) in refluxing ethanol (15 mL), and at the end of the reaction (about 20 h later, monitored by TLC), the product was collected by filtration and recrystallized from ethanol, affording the nicely crystalline **5a** in good yield (68%, Table 1, entry 3). A variety of condition parameters were also investigated, and the results are collected in Table 1. There was no reaction with Et_3N (1 equiv)

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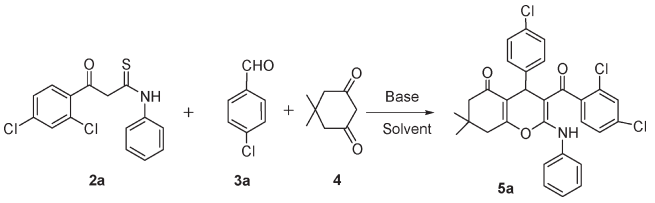
TABLE 1. Reaction of 2a with 3a and 4 under Different Conditions



entry	catalyst (equiv)	solvent	temp (°C)	time (h)[a]	yield (%)[b]
1	Et_3N (1.0)	EtOH	rt	20	*d*
2	*c*	EtOH	78	20	*d*
3	Et_3N (1.0)	EtOH	78	20	68
4	piperidine (1.0)	EtOH	78	20	34
5	pyridine (1.0)	EtOH	78	20	30
6	morpholine (1.0)	EtOH	78	20	31
7	KOH (1.0)	EtOH	78	20	26
8	K_2CO_3 (1.0)	EtOH	78	20	6
9	Na_2CO_3 (1.0)	EtOH	78	20	4
10	$CsCO_3$ (1.0)	EtOH	78	20	13
11	K_2CO_3 (1.0)	DMF	100	20	8[e]
12	NaH (1.0)	DMF	100	20	8
13	K_2CO_3 (1.0)/ $AgNO_3$ (1.0)	DMF	100	20	10
14	KOH (1.0)	DMF	100	20	30
15	Et_3N (1.0)	DMF	100	20	12
16	Et_3N (1.0)	CH_3CN	81	20	27
17	Et_3N (1.0)	CH_3OH	64	20	34
18	Et_3N (0.5)	EtOH	78	20	53
19	Et_3N (2.0)	EtOH	78	20	44

[a]Conventional heating. [b]Isolated yield. [c]No base. [d]No reaction.

in EtOH at room temperature (Table 1, entry 1) or in refluxing EtOH without Et_3N (Table 1, entry 2). In the presence of piperidine, pyridine, morpholine, KOH, K_2CO_3, Na_2CO_3, Cs_2CO_3, $K_2CO_3/AgNO_3$, NaH in EtOH or DMF, the reactions became sluggish (Table 1, entries 4−14). Different solvents were also tested in the presence of Et_3N as catalyst, for example, DMF, CH_3CN, and CH_3OH, but unfortunately they resulted in low yields (Table 1, entries 15−17). The yields of **5a** were not further improved with increased or decreased amount of the catalyst (Table 1, entries 18 and 19). Thus, it is clear from the experiments that the best condition for **5a** could be entry 3, employing Et_3N (1.0 equiv) as base and EtOH as solvent under refluxing conditions.

The tandem process described above represents a simple and efficient methodology for constructing tetrahydrobenzo[*b*]pyrans. To test the generality of this new reaction, the reactions of four *β*-*o*-chloroaroylthioamides **2a**−**d**, different aldehydes **3** and **4** were examined under the optimized conditions (Table 2). Initially, to test the scope of aldehyde substrates, *β*-(2,4-dichlorobenzoyl)thioacetanilide **2a** and **4** were used as model substrates to react with **3a**−**f** (Table 2, entries 1−6). The reactions showed remarkable flexibility, as the desired products were formed in moderate yields (53−68%) with various aromatic aldehydes selected to have either electron-withdrawing or electron-donating substitutes. Different substituents on thioamides **2** (Table 2, entries 7−11) did not show obvious differences in reactivity for the formation of **5**.

The versatility of the above MCR was further demonstrated by reaction of 2-benzoylthioacetanilides **1** with various aromatic aldehydes **3a**−**k** and **4** (Table 2, entries 12−22). Under the same experimental conditions, tetrahydrobenzo[*b*]pyrans **5l**−**v** were formed in better yields.

Although the yields are not high, these results certainly indicate the importance of our strategy for providing the tetrahydrobenzo[*b*]pyrans. Notably, it is found that the above reactions proceed in a highly regioselective manner. In this operationally simple three-component domino process, at least seven reactive distinct chemical sites participate in the chemical transformation that lead to the concomitant creation of three chemical bonds (two C−C bonds and one C−O bond).

S_NAr Reactions of Tetrahydrobenzo[*b*]pyrans 5 Leading to Tetracyclic Chromeno[2,3-*b*]quinoline Derivatives 6. On the basis of the results as described above and in continuation of our ongoing research toward the discovery of new reactions for the synthesis of heterocycles containing chromene-based frameworks, we designed a novel protocol by introducing an *o*-halo group into the aryl ring of 2-benzoylthioacetanilides for the preparation of tetracyclic chromeno[2,3-*b*]quinolines **6** from **5** through the intramolecular S_NAr (Scheme 2).

Conducting a postcondensation reaction can generate more complicated molecules.[3d] During the course of our research toward the synthesis of novel chromeno[2,3-*b*]quinoline derivatives **6**, a variety of conditions were investigated by using **5a**. The results of the cyclization step from **5a** to **6a** in DMF under different conditions are summarized in the Table 3. In a preliminary experiment, first this reaction was tested in the presence of K_2CO_3 at different reaction times and temperatures (Table 3, entries 1−5). It was observed that **6a** could be obtained in 88% yield in the presence of K_2CO_3 (1.0 equiv) for 120 min at 100 °C (Table 3, entry 3). Next, this reaction was examined in the presence of $K_2CO_3/AgNO_3$ in different molar ratio, and **6a** could also be obtained in moderate yields but lower than that with K_2CO_3 as catalyst (Table 3, entries 6−10). Unfortunately, $AgNO_3$ (1.0 equiv) was utterly ineffective for this reaction (Table 3, entry 11). KOH gave only

SCHEME 2. Retrosynthetic Analysis for Chromeno[2,3-*b*]quinolines 6

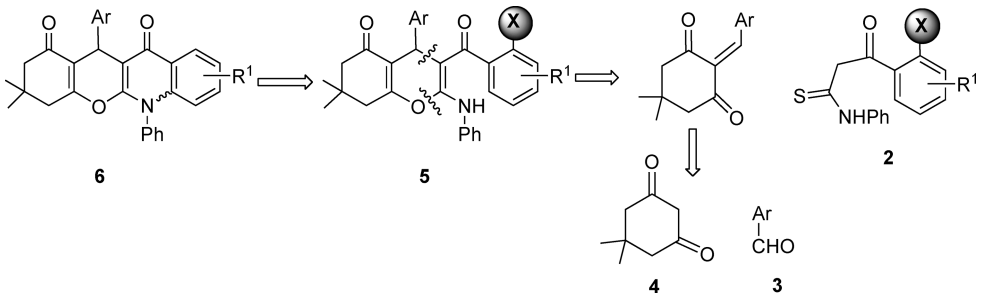
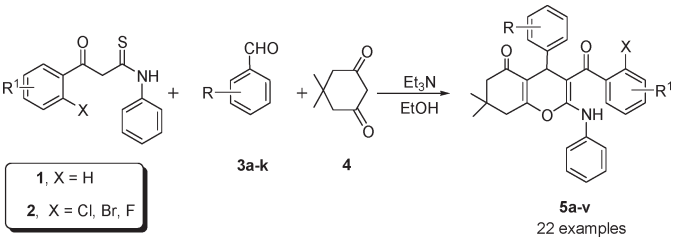
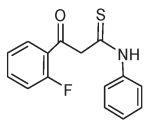
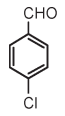
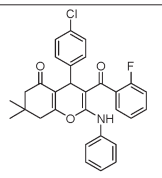
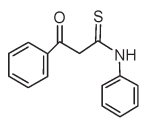
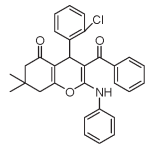
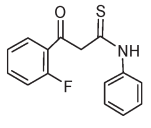
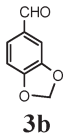
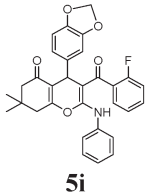
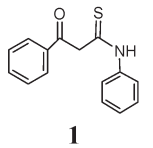
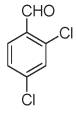
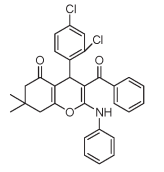
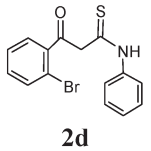
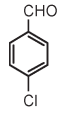
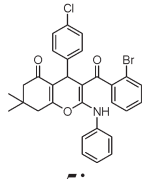
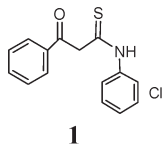
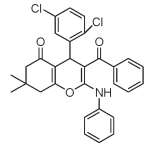
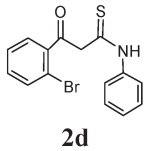
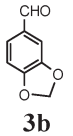
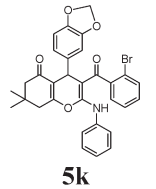
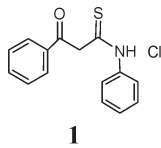
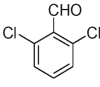
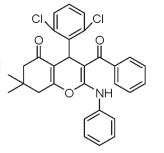


TABLE 2. Synthesis of Tetrahydrobenzo[*b*]pyrans 5a−v



Entry	Precursor 2	Precursor 3	Product 5	Yield (%)[a]	Entry	Precursor 1	Precursor 3	Product 5	Yield (%)[a]
1	2a	3a	5a	68	12	1	3a	5l	76
2	2a	3b	5b	52	13	1	3b	5m	66
3	2a	3c	5c	65	14	1	3c	5n	69
4	2a	3d	5d	55	15	1	3d	5o	64
5	2a	3e	5e	56	16	1	3e	5p	66
6	2a	3f	5f	53	17	1	3f	5q	62
7	2b	3a	5g	56	18	1	3g	5r	49

TABLE 2. Continued

Entry	Precursor 2	Precursor 3	Product 5	Yield (%)[a]	Entry	Precursor 1	Precursor 3	Product 5	Yield (%)[a]
8	 **2c**	 **3a**	 **5h**	47	19	 **1**	 **3h**	 **5s**	66
9	 **2c**	 **3b**	 **5i**	44	20	 **1**	 **3i**	 **5t**	61
10	 **2d**	 **3a**	 **5j**	51	21	 **1**	 **3j**	 **5u**	57
11	 **2d**	 **3b**	 **5k**	47	22	 **1**	 **3k**	 **5v**	46

[a]Isolated yield.

moderate yield (Table 3, entry 12). Thus, it was clear from the experiments that the best condition for this reaction is K_2CO_3 as a catalyst in DMF at 100 °C.

Then the broad tolerance for various R^1 and R substituents to S_NAr reaction was investigated (Table 4). The results showed that tetrahydrobenzo[*b*]pyrans **5** with either aryl groups bearing electron-donating or electron-withdrawing groups could afford the corresponding thiochromeno[2,3-*b*]quinolines **6** in good to excellent yields. It is noteworthy that the reaction is easy to perform, and all of the isolated products only need recrystallization rather than column chromatography. This ease of purification makes this methodology facile, practical, and rapid to execute.

The structural determination of all products **5a**−**v** and **6a**−**l** was achieved by ^{1}H NMR, ^{13}C NMR, IR, and HRMS and unequivocally established by the X-ray single crystal diffraction analysis of compounds **5u**[16] and **6g**.[17]

A plausible reaction scenario for the domino cyclocondensation is outlined in Scheme 3. First, compounds **3** proceed through Knoevenagel condensation with **4** under Et_3N as catalyst to give the intermediate [**A**]; **2** are mediated by Et_3N and deprotonate to form the anions of *β*-(haloaroyl)thioacetanilides, which trigger tandem [3 + 3] annulation involving Michael addition with [**A**] to generate the intermediate [**B**], which could probably undergo three directions of O-, N-, or S-cyclization (Scheme 1). 5,5-Dimethyl-1,3-cyclohexanedione with a very low pK_a value (pK_a = 5.32)[18] is highly acidic, indicating that proton transfer from the keto [**B**] to enol [**C**] undergoing a rapid keto−enol tautomerization would be easier. Then [**C**] is followed by the intramolecular regiospecific O-cyclization to give the intermediate [**D**], rather than the pathway of N-cyclization or S-cyclization. The [**D**] eliminates one molecule of H_2S to afford tetrahydrobenzo[*b*]pyrans **5**. Finally an intramolecular S_NAr of the *o*-halo of aryl group by attack of NH group in the presence of K_2CO_3 leads to new and highly functionalized chromeno[2,3-*b*]quinoline derivatives **6**.

Conclusion

In conclusion, we have developed a convenient and regioselective synthesis of functionalized tetrahydrobenzo[*b*]pyran and chromeno[2,3-*b*]quinoline frameworks containing a chromene moiety, thus demonstrating the applications of *β*-(2-haloaroyl) thioacetanilides. In this experimentally simple process, at least 10 different active sites are involved: two C−C bonds, two C−N bonds, and two new rings are constructed with all reactants efficiently utilized. The advantages of these methods, which include high regioselectivity, high bond-forming efficiency, and the

(16) For X-ray diffraction data for **5u**, see: Wen, L.-R.; Sun, J.-H.; Ji, C.; Xie, H.-Y. *Acta Crystallogr.* **2008**, *E64*, o407.

(17) X-ray diffraction data for **6g** has been deposited in the Cambridge Crystallographic Data Center with supplementary publication number 705397. Its CIF file is also available in the Supporting Information.

(18) Stankevich, É. I.; Grinshtein, É. É.; Dubur, G. Ya. *Chem. Heterocycl. Compd.* **1975**, *11*, 196–198.

SCHEME 3. Plausible Reaction Scenario of 5 and 6

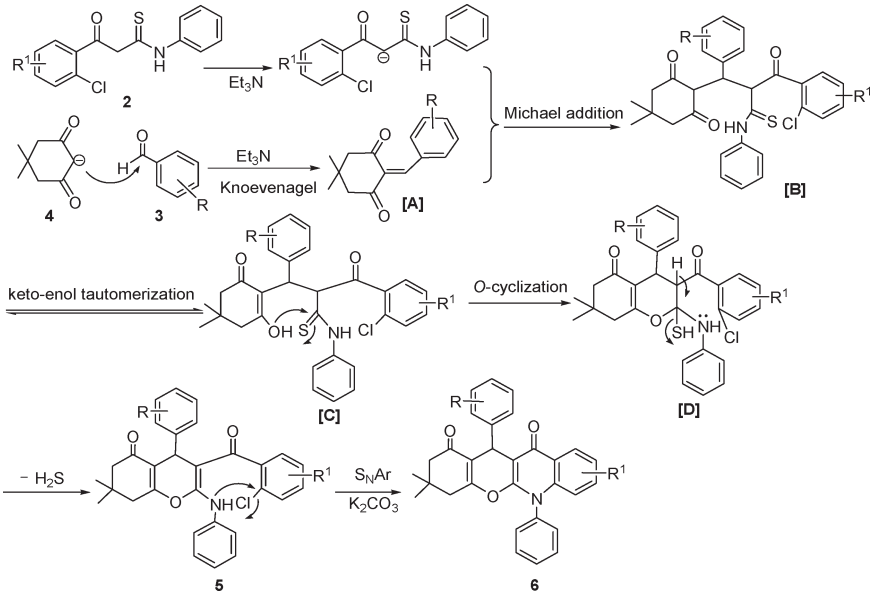
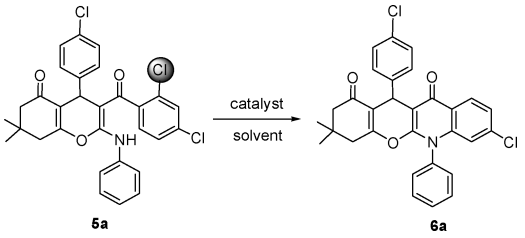


TABLE 3. Conversion 5a to 6a under Different Conditions



entry	catalyst (equiv)	solvent	temp (°C)	time (min)	yield (%)[a]
1	*b*	DMF	78	160	*c*
2	K_2CO_3 (1.0)	DMF	25	160	*c*
3	K_2CO_3 (1.0)	DMF	100	120	88
4	K_2CO_3 (0.5)	DMF	100	160	69
5	K_2CO_3 (1.2)	DMF	100	120	86
6	K_2CO_3 (1.0)/ $AgNO_3$ (1.0)	DMF	100	90	50
7	K_2CO_3 (1.0)/ $AgNO_3$ (0.25)	DMF	100	80	66
8	K_2CO_3 (0.5)/ $AgNO_3$ (1.0)	DMF	100	90	55
9	K_2CO_3 (0.5)/ $AgNO_3$ (0.5)	DMF	100	80	71
10	K_2CO_3 (0.5)/ $AgNO_3$ (0.25)	DMF	100	80	77
11	$AgNO_3$ (1.0)	DMF	100	120	*c*
12	KOH (1.0)	DMF	100	120	76

[a]Isolated yield. [b]No base. [c]No reaction.

ready availability of a wide range of substrates from cheap starting materials, make this new strategy highly attractive. The simplicity of the sequence, mild reaction conditions, lack of need for transition metals, and economy of the sequence indicate that this process could be capable of broad application for highly functionalized tetracyclic systems. Further investigations to expand the scope of β-(2-haloaroyl)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

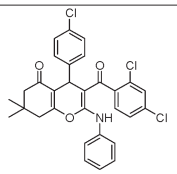
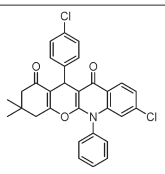
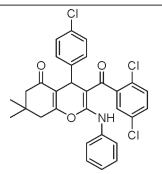
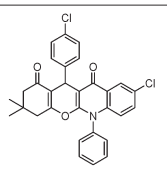
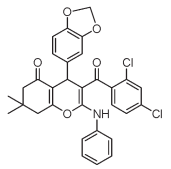
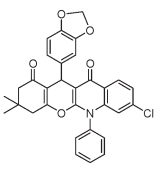
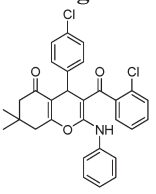
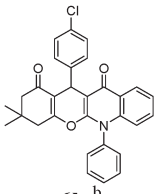
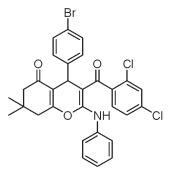
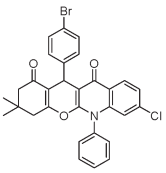
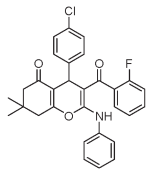
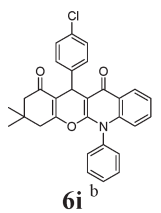
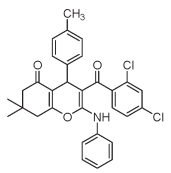
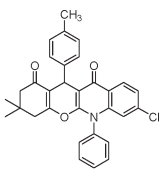
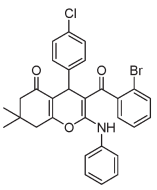
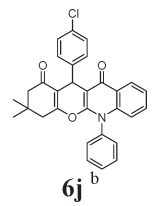
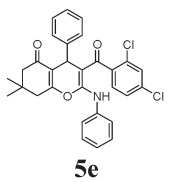
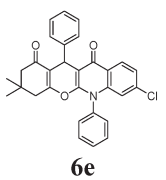
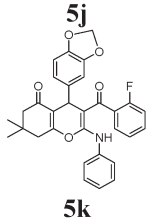
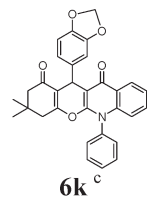
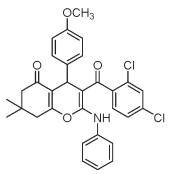
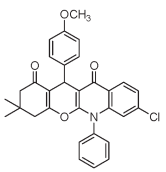
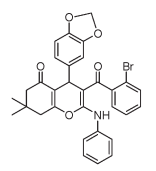
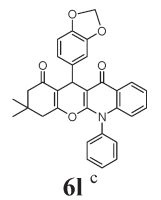
General Procedure for the Synthesis of 5 (5a). An equimolar mixture of β-(2,4-dichlorophenyl)thioacetanilide **2a** (0.324 g, 1 mmol), 4-chlorobenzaldehyde **3a** (0.140 g, 1 mmol), and 5,5-dimethyl-1,3-cyclohexanedione **4** (0.140 g, 1 mmol) was refluxed for 20 h in EtOH (15 mL) containing Et_3N (0.10 g, 1 mmol). 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, subsequently dried, and recrystallized from EtOH to give the pure product **5a**.

4-(4-Chlorophenyl)-3-(2,4-dichlorobenzoyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5a). Yellow powder; mp 186−188 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.82 (s, 3H), 1.05 (s, 3H), 2.08 (d, J = 16.0 Hz, 1H), 2.28 (d, J = 16.0 Hz, 1H), 2.50 (d, J = 18.0 Hz, 1H), 2.71 (d, J = 18.0 Hz, 1H), 4.36 (s, 1H), 6.71−7.66 (m, 12H), 12.78 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.7, 29.1, 32.4, 34.9, 50.4, 90.9, 116.3, 123.0, 125.7, 127.8, 128.3, 129.5, 129.9, 131.3, 134.7, 136.5, 138.4, 138.8, 144.1, 158.1, 161.7, 190.5, 196.0; IR (KBr, cm^{-1}) 1688, 1670, 1626, 1593, 1564, 1363, 1309, 828, 748; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{30}H_{25}Cl_3NO_3$ 552.0900, found 552.0912.

4-(Benzo[*d*][1,3]dioxol-5-yl)-3-(2,4-dichlorobenzoyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5b). Yellow powder; mp 180−182 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.86 (s, 3H), 1.05 (s, 3H), 2.09 (d, J = 16.0 Hz, 1H), 2.28 (d, J = 16.0 Hz, 1H), 2.54 (d, J = 17.4 Hz, 1H), 2.68 (d, J = 17.4 Hz, 1H), 4.28 (s, 1H), 5.91 (bs, 1H), 5.93 (bs, 1H), 6.13−7.66 (m, 11H), 12.75 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.8, 29.1, 32.4, 34.9, 41.4, 50.4, 91.4, 101.2, 108.1, 108.4, 116.6, 121.3, 122.9, 125.6, 127.7, 129.4, 129.9, 134.5, 136.6, 138.5, 139.2, 146.0, 147.2, 158.0, 161.4, 190.6, 196.1; IR (KBr, cm^{-1}) 1670, 1627, 1594, 1561, 1363, 1309, 1204, 820, 750; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{31}H_{26}Cl_2NO_5$ 562.1188, found 562.1178.

4-(4-Bromophenyl)-3-(2,4-dichlorobenzoyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5c). Yellow powder; mp 232−235 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.80 (s, 3H), 1.03 (s, 3H), 2.05 (d, J = 16.5 Hz, 1H), 2.27 (d, J = 16.5 Hz, 1H), 2.51 (d, J = 20.0 Hz, 1H), 2.69 (d, J = 20.0 Hz, 1H), 4.31 (s, 1H), 6.61−7.67 (m, 12H), 12.77 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.7, 29.1, 32.4, 34.9, 50.3, 90.9, 116.3, 119.8, 123.0, 125.8, 127.8, 129.5, 129.9, 130.3, 131.0, 131.2, 134.7, 136.5, 138.4,

TABLE 4. Synthesis of Chromeno[2,3-*b*]quinolines 6a−l

Entry	Comp. **5**	Product **6**	Yield (%)[a]	Entry	Comp. **5**	Product **6**	Yield (%)[a]
1	 **5a**	 **6a**	88	7	 **5g**	 **6g**	80
2	 **5b**	 **6b**	86	8	 **5h**	 **6h**[b]	77
3	 **5c**	 **6c**	70	9	 **5i**	 **6i**[b]	81
4	 **5d**	 **6d**	82	10	 **5j**	 **6j**[b]	67
5	 **5e**	 **6e**	83	11	 **5k**	 **6k**[c]	83
6	 **5f**	 **6f**	90	12	 **5l**	 **6l**[c]	92

[a]Isolated yield. [b]**6h**, **6i**, and **6j** are the same. [c]**6k** is the same as **6l**.

144.5, 158.1, 161.8, 190.5, 196.1; IR (KBr, cm^{-1}) 1680, 1669, 1626, 1591, 1563, 1363, 1311, 1206, 829, 747; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{30}H_{25}BrCl_2NO_3$ 596.0395, found 596.0382.

3-(2,4-Dichlorobenzoyl)-7,7-dimethyl-2-(phenylamino)-4-*p*-tolyl-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5d). Yellow powder; mp 203−205 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.81 (s, 3H), 1.04 (s, 3H), 2.05 (d, J = 16.0 Hz, 1H), 2.18 (s, 3H), 2.28 (d, J = 16.0 Hz, 1H), 2.52 (d, J = 18.0 Hz, 1H), 2.70 (d, J = 18.0 Hz, 1H), 4.30 (s, 1H), 6.54−7.66 (m, 12H), 12.74 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 21.1, 26.6, 29.2, 32.4, 34.8, 50.4, 91.6, 117.0, 122.9, 125.7, 127.8, 127.9, 129.0, 129.5, 129.9, 134.6, 135.8, 136.6, 138.6, 142.3, 158.1, 161.5, 190.6, 196.1; IR (KBr, cm^{-1}) 1688, 1671, 1627, 1590, 1560, 1370, 1321, 827, 761; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{31}H_{28}Cl_2NO_3$ 532.1446, found 532.1437.

3-(2,4-Dichlorobenzoyl)-7,7-dimethyl-4-phenyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5e). Pale yellow powder; mp 188−189 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.81 (s, 3H), 1.04 (s, 3H), 2.06 (d, J = 16.0 Hz, 1H), 2.28 (d, J = 16.0 Hz, 1H), 2.52 (d, J = 17.5 Hz, 1H), 2.70 (d, J = 17.5 Hz, 1H), 4.35 (s, 1H), 6.67−7.80 (m, 13H), 12.76 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.6, 29.1, 32.4, 35.2, 50.4, 91.5, 116.8, 122.9, 125.6, 126.8, 127.7, 128.0, 128.4, 129.4, 129.9, 134.5, 136.6, 138.5, 145.2, 158.1, 161.5, 190.6, 196.0; IR (KBr, cm^{-1}) 1687, 1674, 1627, 1595, 1562, 1360, 745, 699; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{30}H_{26}Cl_2NO_3$ 518.1290, found 518.1295.

3-(2,4-Dichlorobenzoyl)-4-(4-methoxyphenyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5f). Yellow powder; mp 192−194 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.93

(s, 3H), 1.12 (s, 3H), 2.17 (d, J = 16.0 Hz, 1H), 2.26 (d, J = 16.0 Hz, 1H), 2.48 (d, J = 17.5 Hz, 1H), 2.55 (d, J = 17.5 Hz, 1H), 3.73 (s, 3H), 4.39 (s, 1H), 6.36−7.43 (m, 12H), 13.07 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.2, 29.3, 32.3, 35.10, 40.4, 50.8, 55.2, 91.5, 113.4, 117.9, 125.2, 126.8, 129.2, 129.6, 130.1, 130.8, 134.9, 136.7, 137.5, 138.2, 158.1, 158.2, 159.9, 191.5, 195.9; IR (KBr, cm^{-1}) 1684, 1668, 1626, 1591, 1559, 1368, 1256, 827, 775, 757, 690; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{31}H_{28}Cl_2NO_4$ 548.1395, found 548.1385.

4-(4-Chlorophenyl)-3-(2,5-dichlorobenzoyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5g). Pale yellow powder; mp 169−171 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.81 (s, 3H), 1.03 (s, 3H), 2.05 (d, J = 16.5 Hz, 1H), 2.27 (d, J = 16.5 Hz, 1H), 2.51 (d, J = 18.0 Hz, 1H), 2.68 (d, J = 18.0 Hz, 1H), 4.31 (s, 1H), 6.68−7.50 (m, 12H), 12.76 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.7, 29.1, 32.4, 35.0, 41.2, 50.4, 90.8, 116.1, 123.1, 125.8, 128.3, 129.9, 130.1, 130.7, 131.4, 131.7, 132.3, 136.5, 141.1, 144.2, 158.2, 161.6, 189.9, 196.1; IR (KBr, cm^{-1}) 1685, 1668, 1622, 1594, 1564, 1364, 1205, 822, 757, 691; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{30}H_{25}Cl_3NO_3$ 552.0900, found 552.0885.

4-(4-Chlorophenyl)-3-(2-fluorobenzoyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5h). Yellow powder; mp 232−234 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.93 (s, 3H), 1.13 (s, 3H), 2.16 (d, J = 16.0 Hz, 1H), 2.26 (d, J = 16.0 Hz, 1H), 2.47 (d, J = 17.5 Hz, 1H), 2.55 (d, J = 17.5 Hz, 1H), 4.60 (s, 1H), 6.69−7.44 (m, 13H), 13.13 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.1, 29.3, 32.3, 34.7, 40.4, 50.7, 91.2, 115.8, 116.0, 117.2, 122.6, 124.2, 125.2, 128.0, 128.6, 128.7, 129.2, 129.3, 130.8, 130.9, 131.9, 136.6, 143.6, 157.0, 157.8, 158.9, 160.4, 190.7, 195.8; IR (KBr, cm^{-1}) 1688, 1668, 1626, 1593, 1563, 1362, 769, 754; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{30}H_{26}ClFNO_3$ 502.1585, found 502.1581.

4-(Benzo[*d*][1,3]dioxol-5-yl)-3-(2-fluorobenzoyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5i). Yellow powder; mp 189−191 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.84 (s, 3H), 1.03 (s, 3H), 2.06 (d, J = 16.5 Hz, 1H), 2.26 (d, J = 16.0 Hz, 1H), 2.48 (d, J = 15.0 Hz, 1H), 2.67 (d, J = 15.0 Hz, 1H), 4.38 (s, 1H), 5.88 (bs, 1H), 5.91 (d, J = 1 Hz, 1H), 6.06−7.46 (m, 12H), 12.68 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.8, 29.2, 32.4, 34.7, 50.4, 92.1, 101.2, 108.1, 108.2, 116.7, 120.9, 122.9, 124.9, 125.5, 128.8, 129.0, 129.8, 131.7, 131.8, 136.7, 139.5, 145.9, 147.2, 157.6, 159.1, 161.7, 189.9, 196.2; IR (KBr, cm^{-1}) 1684, 1671, 1615, 1598, 1558, 1490, 1366, 1307, 758; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{31}H_{27}FNO_5$ 512.1873, found 512.1888.

3-(2-Bromobenzoyl)-4-(4-chlorophenyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5j). Yellow powder; mp 197−200 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.79 (s, 3H), 1.02 (s, 3H), 2.03 (d, J = 16.0 Hz, 1H), 2.27 (d, J = 16.5 Hz, 1H), 2.50 (d, J = 18.0 Hz, 1H), 2.70 (d, J = 18.0 Hz, 1H), 4.35 (s, 1H), 6.59−7.59 (m, 13H), 12.81 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.8, 29.4, 32.7, 35.3, 50.6, 90.8, 114.9, 116.6, 123.1, 125.9, 128.3, 128.5, 129.0, 130.2, 131.4, 131.5, 133.2, 136.8, 141.6, 144.4, 158.3, 162.1, 188.1, 192.86, 196.53; IR (KBr, cm^{-1}) 1669, 1627, 1596, 1565, 1364, 1306, 752, 690; HRMS (ESI-TOF, $[M+H]^+$) calcd for $C_{30}H_{26}BrClNO_3$ 562.0785, found 562.0796.

4-(Benzo[*d*][1,3]dioxol-5-yl)-3-(2-bromobenzoyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5k). Yellow powder; mp 176−179 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.84 (s, 3H), 1.04 (s, 3H), 2.07 (d, J = 16.0 Hz, 1H), 2.27 (d, J = 16.0 Hz, 1H), 2.53 (d, J = 17.5 Hz, 1H), 2.68 (d, J = 17.5 Hz, 1H), 4.28 (s, 1H), 5.89 (bs, 1H), 5.91 (d, J = 1 Hz, 1H), 6.10−7.62 (m, 12H), 12.79 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.7, 29.0, 32.4, 35.0, 50.3, 91.1, 101.1, 108.0, 108.5, 116.8, 121.2, 122.7, 125.4, 127.8, 128.6, 129.8, 130.8, 132.8, 136.6, 139.3, 141.5, 145.8, 147.1, 157.8, 161.4, 192.6, 196.0; IR (KBr, cm^{-1}) 1682, 1672, 1627, 1597, 1561, 1361, 1297, 1248, 751; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{31}H_{27}BrNO_5$ 572.1073, found 572.1091.

3-Benzoyl-4-(4-chlorophenyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5l). Pale yellow powder; mp 254−255 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.93 (s, 3H), 1.13 (s, 3H), 2.18 (d, J = 16.1 Hz, 1H), 2.26 (d, J = 16.1 Hz, 1H), 2.47 (d, J = 18.0 Hz, 1H), 2.54 (d, J = 18.0 Hz, 1H), 4.81 (s, 1H), 6.71−7.39 (m, 14H), 13.17 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.8, 29.2, 32.5, 34.9, 41.7, 50.5, 91.2, 100.0, 116.5, 122.4, 125.1, 127.0, 128.5, 128.7, 129.6, 129.8, 130.2, 131.2, 137.4, 138.0, 140.9, 144.8, 157.6, 162.4, 194.6, 196.3; IR (KBr, cm^{-1}) 1687, 1667, 1624, 1593, 1561, 1362, 1318, 841, 753, 706; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{30}H_{27}ClNO_3$ 484.1679, found 484.1682.

4-(Benzo[*d*][1,3]dioxol-5-yl)-3-benzoyl-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5m). Pale yellow powder; mp 210−212 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.94 (s, 3H), 1.11 (s, 3H), 2.18 (d, J = 16.0 Hz, 1H), 2.25 (d, J = 16.0 Hz, 1H), 2.47 (d, J = 17.5 Hz, 1H), 2.51 (d, J = 17.5 Hz, 1H), 4.75 (s, 1H), 5.84 (d, J = 1 Hz, 1H), 5.85 (d, J = 1 Hz, 1H), 6.22−7.40 (m, 13H), 13.13 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.9, 29.2, 32.5, 34.8, 41.5, 50.6, 91.7, 101.3, 108.0, 108.3, 117.0, 120.7, 122.3, 125.0, 127.0, 128.6, 129.8, 130.2, 137.4, 139.8, 141.0, 145.9, 147.4, 157.5, 162.2, 194.6, 196.4; IR (KBr, cm^{-1}) 1685, 1669, 1625, 1596, 1560, 1361, 1248, 753, 700; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{31}H_{28}NO_5$ 494.1967, found 494.1965.

3-Benzoyl-4-(4-bromophenyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5n). Pale yellow powder; mp 248−250 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.96 (s, 3H), 1.14 (s, 3H), 2.18 (d, J = 16.0 Hz, 1H), 2.28 (d, J = 16.0 Hz, 1H), 2.49 (d, J = 17.5 Hz, 1H), 2.56 (d, J = 17.5 Hz, 1H), 4.82 (s, 1H), 6.67−7.43 (m, 14H), 13.17 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.2, 29.3, 32.4, 34.9, 40.5, 50.8, 90.0, 117.4, 120.1, 122.5, 125.0, 126.3, 128.3, 129.3, 129.5, 129.6, 131.1, 137.0, 140.7, 144.3, 158.0, 160.9, 195.5, 195.9; IR (KBr, cm^{-1}) 1688, 1669, 1626, 1592, 1560, 1362, 1318, 1050, 839, 753, 706; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{30}H_{27}BrNO_3$ 528.1174, found 528.1179.

3-Benzoyl-7,7-dimethyl-2-(phenylamino)-4-*p*-tolyl-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5o). Yellow powder; mp 197−199 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.81 (s, 3H), 1.03 (s, 3H), 2.03 (d, J = 17.5 Hz, 1H), 2.13 (s, 3H), 2.25 (d, J = 17.5 Hz, 1H), 2.47 (d, J = 17.5 Hz, 1H), 2.67 (d, J = 17.5 Hz, 1H), 4.66 (s, 1H), 6.56−7.42 (m, 14H), 12.41 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 21.0, 26.7, 29.2, 32.4, 34.6, 41.2, 50.5, 91.7, 117.1, 122.2, 124.9, 127.0, 127.4, 128.5, 129.1, 129.8, 130.1, 135.6, 137.3, 140.9, 142.8, 157.6, 162.2, 194.5, 196.2; IR (KBr, cm^{-1}) 1688, 1671, 1625, 1596, 1560, 1361, 1305, 1211, 897, 755, 703; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{31}H_{30}NO_3$ 464.2226, found 464.2236.

3-Benzoyl-7,7-dimethyl-4-phenyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5p). Pale yellow powder; mp 166−168 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.95 (s, 3H), 1.14 (s, 3H), 2.19 (d, J = 16.5 Hz, 1H), 2.28 (d, J = 16.5 Hz, 1H), 2.50 (d, J = 17.5 Hz, 1H), 2.56 (d, J = 17.5 Hz, 1H), 4.86 (s, 1H), 6.82−7.44 (m, 15H), 13.21 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.8, 29.3, 32.5, 35.2, 50.6, 91.7, 117.0, 122.3, 125.0, 126.7, 127.1, 127.6, 128.6, 128.6, 129.8, 130.2, 137.4, 141.0, 145.8, 157.7, 162.36, 194.6, 196.2; IR (KBr, cm^{-1}) 1686, 1668, 1625, 1594, 1561, 1362, 755, 695; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{30}H_{28}NO_3$ 450.2069, found 450.2074.

3-Benzoyl-4-(4-methoxyphenyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5q). Pale yellow powder; mp 172−174 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.81 (s, 3H), 1.03 (s, 3H), 2.06 (d, J = 16.0 Hz, 1H), 2.24 (d, J = 16.0 Hz, 1H), 2.48 (d, J = 17.5 Hz, 1H), 2.67 (d, J = 17.5 Hz, 1H), 3.60 (s, 3H), 4.64 (s, 1H), 6.59−7.42 (m, 14H), 12.41 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.7, 29.2, 32.4, 34.2, 50.5, 55.3, 91.8, 113.8, 117.2, 122.2, 124.9, 127.0, 128.5, 128.6, 129.8, 130.1, 137.3, 137.8, 140.9, 157.5, 157.9, 162.0, 194.6, 196.2; IR (KBr, cm^{-1}) 1688, 1670, 1624, 1596, 1559, 1361, 1241, 834, 753, 702; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{31}H_{30}NO_4$ 480.2175, found 480.2164.

3-Benzoyl-7,7-dimethyl-4-(4-nitrophenyl)-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5r). Pale yellow powder; mp 262−264 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 0.92 (s, 3H), 1.14 (s, 3H), 2.17 (d, J = 16.5 Hz, 1H), 2.28 (d, J = 16.5 Hz, 1H), 2.50

(d, J = 16.8 Hz, 1H), 2.58 (d, J = 16.8 Hz, 1H), 4.97 (s, 1H), 6.91−7.93 (m, 14H), 13.21 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.9, 29.2, 32.5, 35.8, 50.4, 90.7, 100.0, 115.7, 122.4, 123.8, 125.1, 127.0, 128.7, 129.2, 129.8, 130.3, 137.3, 140.8, 146.3, 153.3, 157.5, 162.9, 194.5, 196.3; IR (KBr, cm^{-1}) 1685, 1665, 1625, 1594, 1560, 1518, 1362, 1346, 752, 702; HRMS (ESI-TOF, [M + H]$^+$) calcd for $C_{30}H_{27}N_2O_5$ 495.1920, found 495.1905.

3-Benzoyl-4-(2-chlorophenyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5s). Pale yellow powder; mp 168−170 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.90 (s, 3H), 1.08 (s, 3H), 2.06 (d, J = 16.0 Hz, 1H), 2.29 (d, J = 16.0 Hz, 1H), 2.71 (d, J = 17.5 Hz, 1H), 5.06 (s, 1H), 6.52−7.45 (m, 14H), 12.44 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.8, 29.2, 32.3, 35.2, 50.6, 90.1, 100.0, 114.6, 114.8, 122.3, 124.9, 126.6, 126.9, 128.35, 128.7, 129.8, 132.5, 132.6, 137.4, 141.0, 141.2, 157.3, 161.8, 194.6, 196.1; IR (KBr, cm^{-1}) 1683, 1660, 1619, 1595, 1553, 1362, 751, 701; HRMS (ESI-TOF, [M + H]$^+$) calcd for $C_{30}H_{27}ClNO_3$ 484.1679, found 484.1670.

3-Benzoyl-4-(2,4-dichlorophenyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5t). Pale yellow powder; mp 218−220 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.00 (s, 3H), 1.13 (s, 3H), 2.15 (d, J = 16.5 Hz, 1H), 2.23 (d, J = 16.5 Hz, 1H), 2.47 (d, J = 17.5 Hz, 1H), 2.53 (d, J = 17.5 Hz, 1H), 5.05 (s, 1H), 6.29−7.42 (m, 13H), 13.22 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 27.4, 29.2, 32.1, 35.6, 40.4, 50.7, 88.2, 114.0, 122.8, 125.0, 126.0, 126.1, 128.5, 129.2, 129.3, 129.9, 132.6, 133.8, 134.0, 136.9, 138.7, 141.0, 158.0, 161.4, 195.2, 196.2; IR (KBr, cm^{-1}) 1688, 1669, 1623, 1594, 1562, 1361, 837, 753, 702; HRMS (ESI-TOF, [M + H]$^+$) calcd for $C_{30}H_{26}Cl_2NO_3$ 518.1290, found 518.1297.

3-Benzoyl-4-(2,5-dichlorophenyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5u). Yellow powder; mp 194−196 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.91 (s, 3H), 1.07 (s, 3H), 2.08 (d, J = 16.1 Hz, 1H), 2.28 (d, J = 16.1 Hz, 1H), 2.70 (d, J = 17.6 Hz, 1H), 4.92 (s, 1H), 6.22−7.47 (m, 13H), 12.66 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.7, 29.2, 32.2, 36.3, 50.5, 88.6, 100.0, 112.8, 122.5, 125.2, 126.6, 128.3, 128.8, 129.9, 130.0, 131.0, 131.6, 132.0, 132.7, 137.1, 140.9, 142.3, 157.5, 162.7, 194.5, 196.3; IR (KBr, cm^{-1}) 1679, 1663, 1620, 1596, 1562, 1367, 1204, 753, 700; HRMS (ESI-TOF, [M + H]$^+$) calcd for $C_{30}H_{26}Cl_2NO_3$ 518.1290, found 518.1279.

3-Benzoyl-4-(2,6-dichlorophenyl)-7,7-dimethyl-2-(phenylamino)-7,8-dihydro-4*H*-chromen-5(6*H*)-one (5v). Pale yellow powder; mp 186−188 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.94 (s, 3H), 1.08 (s, 3H), 2.04 (d, J = 16.0 Hz, 1H), 2.29 (d, J = 16.0 Hz, 1H), 2.43 (d, J = 17.7 Hz, 1H), 2.68 (d, J = 17.7 Hz, 1H), 5.51 (s, 1H), 7.06−7.37 (m, 13H), 11.45 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.3, 28.8, 31.6, 32.9, 50.3, 89.9, 99.5, 111.6, 120.7, 123.6, 127.0, 128.1, 128.4, 129.2, 129.9, 137.2, 137.8, 140.3, 155.9, 162.9, 194.5, 195.7; IR (KBr, cm^{-1}) 1671, 1624, 1597, 1558, 1361, 1210, 764, 747, 699; HRMS (ESI-TOF, [M + H]$^+$) calcd for $C_{30}H_{26}Cl_2NO_3$ 518.1290, found 518.1279.

General Procedure for Synthesis of Chromeno[2,3-*b*]quinolines 6 (6a). A mixture of corresponding **5a** (1.158 g, 1.0 mmol) and K_2CO_3 (0.138 g, 1 mmol) was heated to 100 °C in DMF (15 mL). After completion of the reaction as indicated by TLC (about 40 min, petroleum−EtOAc, 8:2 v/v), the mixture was cooled to room temperature and was added to an amount of ice−water to precipitate the product, which was then collected by filtration and washed with cool water to afford pure **6a**.

8-Chloro-12-(4-chlorophenyl)-3,3-dimethyl-6-phenyl-3,4,6,12-tetrahydro-1*H*-chromeno[2,3-*b*]quinoline-1,11(2*H*)-dione (6a). Yellow powder; mp 280−282 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.85 (s, 3H), 0.98 (s, 3H), 2.10 (d, J = 16.0 Hz, 1H), 2.20 (d, J = 17.5 Hz, 1H), 2.27 (d, J = 16.0 Hz, 1H), 2.32 (d, J = 17.5 Hz, 1H), 4.99 (s, 1H), 6.64−8.11 (m, 12H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.8, 29.0, 32.3, 32.7, 50.4, 102.3, 115.0, 116.8, 123.2, 124.4, 128.0, 128.3, 129.6, 130.0, 130.6, 130.8, 130.9, 131.3, 135.4, 137.5, 140.9, 143.4, 151.8, 163.2, 174.8, 196.4; IR (KBr, cm^{-1}) 1668, 1619, 1591, 1544, 1361, 830, 711; HRMS (ESI-TOF, [M + H]$^+$) calcd for $C_{30}H_{24}Cl_2NO_3$ 516.1133, found 516.1147.

12-(Benzo[*d*][1,3]dioxol-5-yl)-8-chloro-3,3-dimethyl-6-phenyl-3,4,6,12-tetrahydro-1*H*-chromeno[2,3-*b*]quinoline-1,11(2*H*)-dione (6b). Yellow powder; mp 289−292 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.87 (s, 3H), 0.98 (s, 3H), 2.11−2.36 (m, 4H), 4.95 (s, 1H), 5.91 (bs, 1H), 5.93 (bs, 1H), 6.64−8.13 (m, 11H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.9, 29.0, 32.3, 32.6, 50.5, 101.2, 102.8, 108.2, 109.4, 115.5, 116.8, 121.7, 123.2, 124.2, 128.1, 129.6, 130.0, 130.7, 130.8, 130.9, 135.5, 137.4, 138.4, 140.9, 146.1, 147.3, 151.8, 163.0, 174.8, 196.4; IR (KBr, cm^{-1}) 1680, 1660, 1616, 1590, 1543, 1370, 1358, 1312, 1209, 794, 698; HRMS (ESI-TOF, [M + H]$^+$) calcd for $C_{31}H_{25}ClNO_5$ 526.1421, found 526.1423.

12-(4-Bromophenyl)-8-chloro-3,3-dimethyl-6-phenyl-3,4,6,12-tetrahydro-1*H*-chromeno[2,3-*b*]quinoline-1,11(2*H*)-dione (6c). Yellow powder; mp 288−290 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.86 (s, 3H), 0.98 (s, 3H), 2.10 (d, J = 16.0 Hz, 1H), 2.20 (d, J = 17.0 Hz, 1H), 2.27 (d, J = 16.0 Hz, 1H), 2.32 (d, J = 17.0 Hz, 1H), 4.97 (s, 1H), 6.64−8.11 (m, 12H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.8, 29.0, 32.3, 32.8, 50.4, 102.2, 114.9, 116.8, 119.8, 123.2, 124.3, 128.0, 129.6, 129.9, 130.7, 130.8, 130.89, 131.0, 131.2, 135.4, 137.4, 140.9, 143.8, 151.8, 163.2, 174.8, 196.4; IR (KBr, cm^{-1}) 1668, 1617, 1590, 1544, 1361, 1207, 722, 704; HRMS (ESI-TOF, [M + H]$^+$) calcd for $C_{30}H_{24}BrClNO_3$ 560.0628, found 560.0638.

8-Chloro-3,3-dimethyl-6-phenyl-12-(*p*-tolyl)-3,4,6,12-tetrahydro-1*H*-chromeno[2,3-*b*]quinoline-1,11(2*H*)-dione (6d). Yellow powder; mp 249−252 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.83 (s, 3H), 0.96 (s, 3H), 2.08 (d, J = 16.0 Hz, 1H), 2.18 (d, J = 17.5 Hz, 1H), 2.20 (s, 3H), 2.25 (d, J = 16.0 Hz, 1H), 2.30 (d, J = 17.5 Hz, 1H), 4.96 (s, 1H), 6.62−8.10 (m, 12H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 21.1, 26.8, 29.1, 32.3, 32.5, 50.5, 103.0, 115.6, 116.7, 123.2, 124.2, 128.1, 128.6, 129.0, 129.6, 129.9, 130.7, 130.8, 130.9, 135.5, 135.8, 137.4, 140.9, 141.5, 151.7, 163.0, 174.8, 196.3; IR (KBr, cm^{-1}) 1666, 1614, 1591, 1534, 1366, 1203, 721, 700; HRMS (ESI-TOF, [M + H]$^+$) calcd for $C_{31}H_{27}ClNO_3$ 496.1679, found 496.1681.

8-Chloro-3,3-dimethyl-6,12-diphenyl-3,4,6,12-tetrahydro-1*H*-chromeno[2,3-*b*]quinoline-1,11(2*H*)-dione (6e). Yellow powder; mp 292−294 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.85 (s, 3H), 0.98 (s, 3H), 2.10 (d, J = 16.0 Hz, 1H), 2.22 (d, J = 17.5 Hz, 1H), 2.28 (d, J = 16.0 Hz, 1H), 2.32 (d, J = 17.5 Hz, 1H), 5.03 (s, 1H), 6.65−8.12 (m, 13H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.7, 29.0, 32.3, 32.9, 50.4, 102.8, 115.5, 116.7, 123.2, 124.2, 126.7, 128.0, 128.4, 128.6, 129.5, 129.9, 130.6, 130.8, 130.9, 135.4, 137.3, 140.8, 144.3, 151.8, 163.1, 174.8, 196.3; IR (KBr, cm^{-1}) 1669, 1618, 1591, 1541, 1366, 1202, 701; HRMS (ESI-TOF, [M + H]$^+$) calcd for $C_{30}H_{25}ClNO_3$ 482.1523, found 482.1531.

8-Chloro-12-(4-methoxyphenyl)-3,3-dimethyl-6-phenyl-3,4,6,12-tetrahydro-1*H*-chromeno[2,3-*b*]quinoline-1,11(2*H*)-dione (6f). Yellow powder; mp 263−264 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.86 (s, 3H), 0.98 (s, 3H), 2.09 (d, J = 16.0 Hz, 1H), 2.20 (d, J = 17.5 Hz, 1H), 2.26 (d, J = 16.0 Hz, 1H), 2.31 (d, J = 17.5 Hz, 1H), 3.67 (s, 3H), 4.97 (s, 1H), 6.64−8.12 (m, 13H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.8, 29.1, 32.0, 32.3, 50.5, 55.5, 103.1, 115.7, 116.7, 123.2, 124.2, 128.0, 129.6, 129.9, 130.7, 130.8, 130.9, 135.5, 136.6, 137.3, 140.87, 151.7, 162.9, 174.8, 196.4; IR (KBr, cm^{-1}) 1670, 1662, 1613, 1591, 1544, 1364, 1312, 1254, 1209, 825, 720, 698; HRMS (ESI-TOF, [M + H]$^+$) calcd for $C_{31}H_{27}ClNO_4$ 512.1629, found 512.1618.

9-Chloro-12-(4-chlorophenyl)-3,3-dimethyl-6-phenyl-3,4,6,12-tetrahydro-1*H*-chromeno[2,3-*b*]quinoline-1,11(2*H*)-dione (6g). Pale yellow powder; mp 293−295 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.86 (s, 3H), 0.98 (s, 3H), 2.12−2.30 (m, 4H), 5.00 (s, 1H), 6.76−8.03 (m, 12H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.8, 29.0, 32.3, 32.8, 50.4, 102.2, 115.0, 120.2, 124.6, 125.6, 128.3, 128.8, 129.6, 129.9, 130.6, 130.6, 130.8, 131.3, 132.8, 135.6, 138.8, 143.4, 151.7, 163.2, 174.3, 196.4; IR (KBr, cm^{-1}) 1664, 1618, 1590, 1549, 1363, 1206, 830, 767, 698; HRMS (ESI-TOF, [M + H]$^+$) calcd for $C_{30}H_{24}Cl_2NO_3$ 516.1133, found 516.1152.

12-(4-Chlorophenyl)-3,3-dimethyl-6-phenyl-3,4,6,12-tetrahydro-1*H*-chromeno[2,3-*b*]quinoline-1,11(2*H*)-dione (6h, 6i, and 6j). Pale yellow powder; mp 266−268 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.86 (s, 3H), 0.98 (s, 3H), 2.10 (d, J = 16.0 Hz, 1H), 2.20 (d, J = 17.5 Hz, 1H), 2.27 (d, J = 16.0 Hz, 1H), 2.34 (d, J = 17.5 Hz, 1H), 5.02 (s, 1H), 6.73−8.11 (m, 13H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.8, 29.1, 32.3, 32.7, 50.4, 101.7, 115.1, 117.6, 124.0, 124.4, 125.7, 128.3, 129.6, 130.0, 130.4, 130.6, 130.7, 131.2, 132.9, 135.9, 140.1, 143.6, 151.4, 163.3, 175.4, 196.4; IR (KBr, cm^{-1}) 1668, 1616, 1591, 1555, 1366, 1209, 757, 703; HRMS (ESI-TOF, $[M + H]^+$) calcd for $C_{30}H_{25}ClNO_3$ 482.1523, found 482.1542.

12-(Benzo[*d*][1,3]dioxol-5-yl)-3,3-dimethyl-6-phenyl-3,4,6,12-tetrahydro-1*H*-chromeno[2,3-*b*]quinoline-1,11(2*H*)-dione (6k and 6l). Yellow powder; mp 252−254 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 0.81 (s, 3H), 0.92 (s, 3H), 2.05 (d, J = 16.0 Hz, 1H), 2.13 (d, J = 18.0 Hz, 1H), 2.21 (d, J = 16.0 Hz, 1H), 2.25 (d, J = 18.0 Hz, 1H), 4.91 (s, 1H), 5.97 (d, J = 1 Hz, 1H), 5.98 (d, J = 1 Hz, 1H), 6.67−8.22 (m, 12H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 26.8, 32.3, 32.5, 50.4, 101.2, 102.3, 108.2, 109.3, 115.5, 117.6, 121.5, 124.0, 124.4, 125.7, 129.5, 130.0, 130.3, 130.6, 130.7, 132.8, 135.8, 140.0, 146.0, 147.2, 151.4, 163.1, 175.5, 196.6; IR (KBr, cm^{-1}) 1665, 1616, 1591, 1553, 1371, 1232, 1207, 761, 699; HRMS (ESI-TOF, $[M+H]^+$) calcd for $C_{31}H_{26}NO_5$ 492.1811, found 492.1808.

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Supporting Information Available: Copies of ^{1}H NMR, ^{13}C NMR and HRMS spectra of all new compounds, and X-ray data for compound **6g** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.