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Annulation

Thermally Induced Denitrogenative Annulation for the Synthesis of Dihydroquinolinimines and Chroman-4-imines

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Abstract: A rapid growth in synthetic methods for the preparation of diverse organic molecules using *N*-sulfonyl-1,2,3-triazoles is of great interest in organic synthesis. Transition metals are generally used to activate the α-imino diazo intermediates. Metal-free methods have not been studied in detail, but can be a good complement to transition metal catalysis in the mild reaction conditions. We herein report a novel method for the preparation of 2,3-dihydroquinolin-4-imine and chroman-4-imine analogs from their corresponding *N*-sulfonyl-1,2,3-triazoles in the absence of metal catalysts. To achieve intramolecular annulation, the introduction of an electron-donating group is required at the *meta* position of *N*-sulfonyl-1,2,3-triazole methyl anilines. The inclusion of tailored substituents on the aniline moieties and nitrogen atoms enhances the nucleophilicity of the phenyl π-electrons, thus allowing them to undergo a Friedel–Crafts-type reaction with the highly electrophilic ketenimines. This metal-free method was carefully optimized to generate a variety of dihydroquinolin-4-imines and chroman-4-imines in moderate-to-good yields.

Introduction

Diazo compounds are popular precursors for the generation of carbene intermediates,[1–5] and transition metal catalysis is commonly used in the preparation of carbenoids from these precursors, including dirhodium,[6–13] copper,[14–17] ruthenium,[18–21] and iron complexes.[22,23] The reactivity of these intermediate metal carbenoids, which are used in a variety of reactions to synthesize important building blocks, is highly dependent on their chemical stability, which is defined by the electronic properties of the substituent groups. Electron-withdrawing groups (EWGs) on the carbenoid moiety can accelerate the transformation of diazo compounds into carbenoids. However, EWGs can also render the carbenoids extremely reactive, resulting in lower selectivity, thereby leading to undesired side reactions. Thus, the presence of both EWGs and electron-donating groups (EDGs) on diazo compounds can trigger the formation of stable carbenoids for use in the synthesis of complex targets.[24,25] This substituent-stabilized carbenoid is known as a donor/acceptor carbenoid and shows better selectivity than carbenoids lacking EDGs.

Although donor/acceptor carbenoids have been widely used in organic synthesis,[26–28] their preparation usually involves hazardous α-nitrodiazo compounds[29,30] or the rearrangement of dicarbonyl diazo compounds.[31–34] The limited number of methods and the hazardous materials used for the generation of donor/acceptor carbenes necessitates the development of new reactions to expand the scope of these important intermediates. In 2011, Davies and co-workers reported thermally inducible cycloaddition of aryldiazoacetates and alkenes to generate cyclopropanes in good yield and good diastereoselectivity (up to 19:1).[35] In these reactions, the electronic properties of the aryl groups dominated both the chemical reactivity and stereoselectivity. The traditional carbene precursor, ethyl diazoacetate, was heated to generate the acceptor carbene, affording the cyclopropane in good yield, but with poor diastereoselectivity. This highly stereoselective cyclopropanation can be observed with electron-rich aryl substituents on aryldiazoacetates. Electron-rich substituents such as the *p*-methoxy (*p*-OMe) group are believed to favor a singlet ground state, and therefore, they undergo subsequent cyclopropanation with high diastereoselectivity.[36] Gevorgyan et al. were the first to report the preparation of indolizines and imidazopyridines via the Rh-catalyzed transannulation of pyridotriazoles using alkynes and nitriles.[37] During this transformation, the imino diazo intermediate is in equilibrium with pyridotriazole until the addition of a catalytic amount of rhodium(II) acetate, which causes immediate conversion of the α-imino diazo intermediate to a Rh carbenoid. Fokin[38] and Murakami[39] later demonstrated the use of *N*-sulfonyltriazoles as efficient precur-

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sors to Rh- and Ni-carbenoid intermediates for the preparation of imidazole and pyrroles. Sulfonyl triazoles, prepared from *N*-propargylanilines and tosyl azides, have been used as precursors in the metal-catalyzed denitrogenative intramolecular cyclization for heterocycle synthesis.[40–42] Accordingly, Cu^{I}-catalyzed denitrogenative annulation of substituted dihydropyrimidin-4-ones has been successfully developed by our group.[43] Indeed, we recently reported a Cu/Rh-catalyzed annulation reaction for the preparation of 3-indolylimines from *N*-propargylanilines.[44]

Metal catalysis is conventionally used in the preparation of such metal carbenoids, with photochemical processes having been reported as an alternative method.[45] However, thermally induced synthesis of carbenes from diazo compounds has not yet been addressed in detail. In 2012, Davies et al. reported the use of *N*-phthalimido-1,2,3-triazoles as ideal precursors for the preparation of 1-cyclopropane α-amino acids. Remarkably, *N*-phthalimido-1,2,3-triazoles were elegantly transformed into amino-functionalized donor/acceptor carbenoids at 55 °C in the absence of catalysts, before immediately forming the corresponding cyclopropanes via Cy–H insertion (Scheme 1 b).[46] More recently, various 4-alkoxy-1-sulfonyl triazoles, prepared from sulfonyl azides and ynol ethers, have been used to trigger a metal-free thermal denitrogenative reaction under microwave irradiation. The resulting carbenoid intermediates are resonance-stabilized and undergo sequential transformations during the aminoacylation of indoles and pyrroles (Scheme 1 c).[47] In this metal-free strategy, the remarkable stabilization of the π-donating amino and alkoxy groups is the driving force behind the rapid transformation of α-imino diazo compound into carbene **1** (Scheme 1 a, step (i)). The resonance structures contribute stabilization energy and allow the resulting carbenoid intermediates to take part in subsequent transformations, such as those shown in Figure 1 b and 1 c. Thus, the presence of a weak EDG such as alkyl groups on sulfonyl triazole may partially stabilize the formation of carbenes, but results in immediate conversion into ketenimine intermediate **2** via a Wolff-type rearrangement (Scheme 1 a, step (ii)).

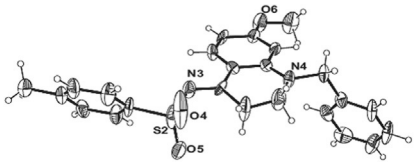
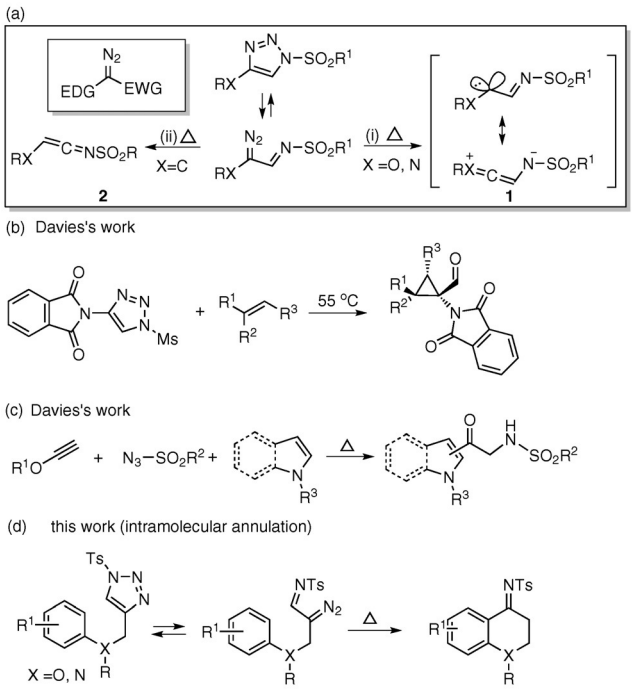


Figure 1. X-ray ORTEP structure of compound **4 a**.[50]

Based on the above studies, we aim to use (1-tosyl-1,2,3-triazol-4-yl)methyl)aniline (X = N, Scheme 1 d) to direct the formation of dihydroquinolines by intramolecular annulation via the formation of ketenimine intermediates. The alkyl substituent is expected to drive the formation of carbenes in the equilibrium of triazole and α-imino diazo intermediates upon heating. We predict that the lack of resonance hybrid forms will result in the immediate conversion of carbenes into electrophilic ketenimine intermediates, which will be subjected to nucleophilic reactions. In light of our continued interest in developing novel methodologies, we report studies on an annulation reaction yielding 2,3-dihydroquinolinimine and chroman-4-imine analogs from the corresponding *N*-sulfonyl-1,2,3-traizoles via denitrogenative annulation under metal-free thermal conditions.



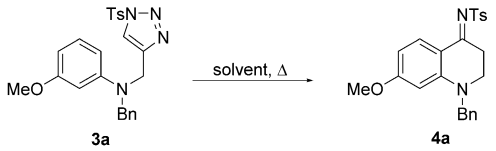
Scheme 1. (a) Two plausible transformations of a donor/acceptor carbenoid upon heating, bearing (i) an alkyl substituent, and (ii) a π-donating substituent. Two reactions reported by the research group of Davies are shown in parts (b) and (c).[46] (d) Intramolecular annulation proposed in this study.

Results and Discussion

Development of Conditions for Intramolecular Annulation of *N*-Tethered *N*-Sulfonyl-1,2,3-Triazole.

Table 1 lists the starting reagents and reaction conditions used throughout this study. *N*-Benzyl-3-methoxy-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)aniline (**3 a**) was selected as the initial screening model for the optimization of solvent and reaction temperature (Table 1). Compound **3 a** was dissolved in toluene and heated at reflux (120 °C) for 24 h to give the desired product **4 a** in 34 % yield, with traces of unreacted starting material remaining (Table 1, entry 1). Several commonly used solvents including 1,2-dichloroethane (DCE), tetrahydrofuran, acetonitrile, and 1,4-dioxane were evaluated, but all, except for DCE, yielded multiple products or poor efficiency (Table 1). Using DCE gave comparable yields to toluene (Table 1, entry 4). However, the use of *N*,*N*-dimethylformamide (DMF) gave an optimized isolated yield of 89 % at 120 °C in only 2.5 h (Table 1, entry 2). This reaction was completely retarded at lower temperatures, with only unreacted starting materials remaining after 12 h at 60 °C (Table 1, entry 3). In all cases where the reaction proceeded, it was carefully monitored until all starting ma-

Table 1. Optimization of reaction conditions.



3a 4a

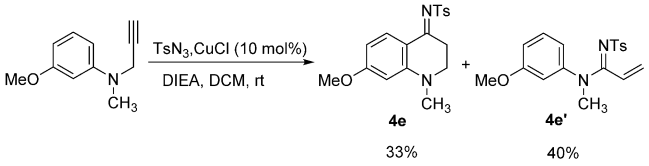
Entry	Solvent	*T* [°C]	*t* [h]	Yield [%]
1	toluene	120	24	34
2	*N,N*-dimethylformamide	120	2.5	89
3	*N,N*-dimethylformamide	60	12	–[a]
4	1,2-dichloroethane	85	24	36
5	tetrahydrofuran	60	24	trace[a]
6	acetonitrile	80	12	–[b]
7	1,4-dioxane	90	12	–[b]

[a] Starting material recovered; [b] Formation of the multiple products.

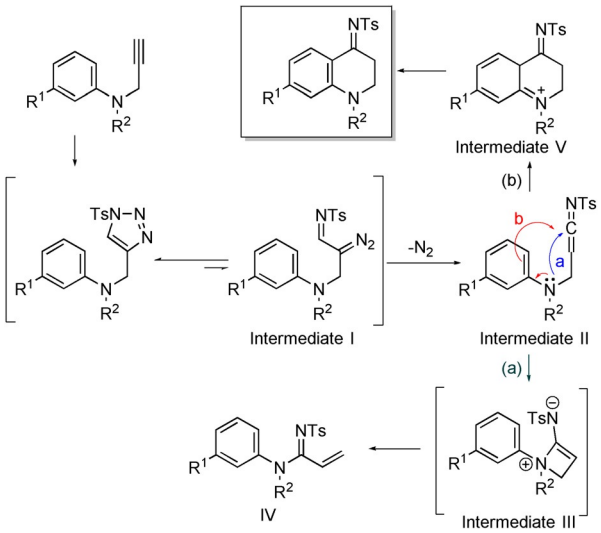
terials were consumed, after which time it was quenched immediately. Without rapid quenching, undesired byproducts were formed, which were difficult to separate from the desired products.

The X-ray ORTEP (Oak Ridge Thermal Ellipsoid Plot) of the isolated product **4a** confirmed the formation of the desired 2,3-dihydroquinolin-4(1*H*)-imine analog (Figure 1). Interestingly, previous studies have shown that the reaction of *N,N*-substituted propargylanilines with tosyl azide in the presence of CuCl results in the formation of acrylamidines.[48] In this research, the heating process without the use of catalysts may trigger the Friedel–Crafts reaction to dominate the formation of thermodynamically stable six-membraned ring intermediate, which subsequently can transform into the corresponding dihydroquinolin-4-imine after aromatization.

In terms of plausible reaction mechanisms, the electron-withdrawing properties of the sulfonyl group result in an equilibrium between the sulfonyl triazole and the ring-opened imino diazo intermediate I (Scheme 2) The α-imino diazo compound could then be converted into ketenimine II by the release of nitrogen gas and accompanying 1,2-rearrangement either by heating or Cu^{I} catalysis. The reactive ketenimine II can then undergo two possible intramolecular reactions: path (a) and path (b). In path (a), when a Cu^{I} catalyst is used, the reaction is under kinetic control, with the formation of a relatively unstable four-membered ring intermediate III (Scheme 2, path a) followed by a ring-opening rearrangement to form acrylamidine IV.[48] To further support this pathway, 3-methoxy-*N*-methyl-*N*-(prop-2-ynyl)benzenamine was treated with tosyl azide in the presence CuCl and *N,N*-diisopropylethylamine (DIPEA), as shown in Scheme 3. The sequential transformation allows to obtain the corresponding acrylamidine **4e′** as the major product along with the minor product dihydroquinolin-4-imine analogue **4e** in a 40:33 ratio. The result clearly indicates that Cu^{I} catalyst can trigger the transformation to ketenimine intermediate but also results in the formation of mixtures **4e** and **4e′**.



Scheme 3. Cu^{I}-catalyzed transformations of 3-methoxy-*N*-methyl-*N*-(prop-2-ynyl)benzenamine with tosyl azide and CuCl.



Scheme 2. Plausible reaction pathways.

In path (b), the direct nucleophilic attack by π electrons of the phenyl ring results in a thermodynamically controlled process that generates intermediate V. In the absence of a Cu^{I} catalyst, the external energy provided by heating facilitates the intramolecular annulation, yielding 2,3-dihydroquinolin-4-imine analogs after regaining aromaticity. To further support the proposed mechanism, when the sulfonyl triazole proton was displaced by deuterium (50% incorporation), deuterium was found to rearrange to the α-carbon of the dihydroquinolinimine product (confirmed by ^{1}H NMR spectroscopy).[49] This result supports the proposed formation of ketenimine V via 1,2-H migration, and therefore indicates that the production of carbenoid intermediates can be triggered by a thermal process.

Scope of Intramolecular Annulation of *N*-Tethered Substrates

In the proposed mechanism, the key step in the cyclization involves electrophilic aromatic substitution, which depends on both the electrophile and the activating groups present on the phenyl ring. As the ketenimine intermediate is a good electrophile, the phenyl group could compete with the amino group in the subsequent nucleophilic attack. Table 2 shows the results of substrate screening under optimized conditions for each substrate. The R^{1} substituent can either accelerate or impede the reaction depending on its electron-donating or electron-withdrawing properties. The absence of substituents

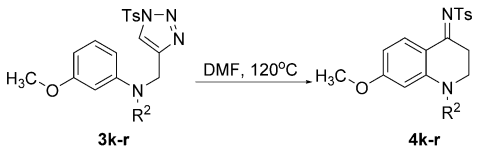
Table 2. Scope of R^1 and R^2 substituent groups.

3a-j 4a-j

Entry	R^1	R^2	Solvent	*t* [%]	Yield [%]
1	OMe	Bn	DMF	2.5	89 (**4a**)
2	H	Me	toluene[a]	18	26 (**4b**)
3	H	Et	toluene	18	45 (**4c**)
4	H	*n*Bu	toluene	18	45 (**4d**)
5	OMe	Me	DMF	0.5	86 (**4e**)
6	OBn	Me	DMF	0.5	90 (**4f**)
7[b]	OTBS	Me	DMF	0.5	72[c] (**4g**)
8	OAc	Me	DMF	0.5	–[d] (**4h**)
9	Me	Me	DMF	0.5	–[d] (**4i**)
10	Cl	Me	DMF	0.5	–[d] (**4j**)

[a] When DMF was used as solvent, multiple products were found. [b] 40% of desillyl cyclized product. [c] TBS (R^1 group) is removed from the product. [d] Formation of multiple spots.

Table 3. Scope of R^2 substituent groups.



3k-r 4k-r

Entry	R^2	*t* [h]	Yield [%]
1	Et	0.5	73 (**4k**)
2	*n*-propyl	0.5	70 (**4l**)
3	*n*-butyl	2.5	71 (**4m**)
4	*n*-hexyl	3.0	83 (**4n**)
5	allyl	2.5	86 (**4o**)
6	acetyl	3.0	–[a] (**4p**)
7	phenyl	5.0	–[a] (**4q**)
8	anisole	5.0	–[a] (**4r**)

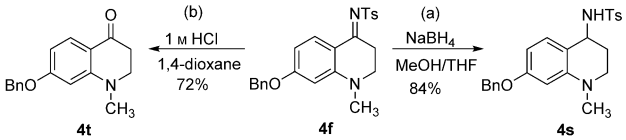
[a] Staring material recovered.

on the aromatic ring resulted in decomposition of the products in DMF at 120 °C. (Table 2, footnote a) However, the use of toluene (Table 2, entries 2–4) resulted in the formation of the desired annulation products in low-to-moderate yields, although a large amount of starting material remained. When the aniline *meta* substituent was a π-donating group such as OMe and OBn, the resonance effect accelerated the annulation reaction to give excellent yields (86% and 90%, respectively, Table 2, entries 5 and 6). To facilitate expansion of the structural complexity of the R^1 substituent, a hydroxyl substituent was included in the core for further functionalization. However, the presence of a hydroxyl group on aniline led to the failed synthesis of triazole compounds. Therefore, a *tert*-butyldimethylsilyl ether (TBS-O) group was used as a hydroxyl protecting group, resulting in successful transformation to triazole **3g**. TBS-protected **3g** was then subjected to heat-induced annulation followed by deprotection to give the desired **4g** in 72% yield (Table 2, entry 7). The presence of EWGs such as OAc and Cl (Table 2, entries 8 and 10, respectively) resulted in the formation of unstable arenium ion intermediates during the first step of the electrophilic substitution, thus yielding multiple undesired products.

Although low yields were obtained with non-activating R^1 substituents (Table 2, entry 2), longer alkyl R^2 substituents were found to improve the yield (Table 2, entries 3 and 4). Therefore, the use of amino group substituents to help direct the annulation reaction was explored further by maintaining OMe as the R^1 substituent, and altering the R^2 functional groups (Table 3). Alkyl substituents such as ethyl, *n*-propyl, *n*-butyl, and n-hexyl afforded reasonably good yields (73–83%, Table 3, entries 1–4), while allyl and benzyl groups provided higher yields of 86% (Table 3, entry 5) and 89% (Table 2, entry 1), respectively. In contrast, the electron-withdrawing acetyl substituents appeared to weaken the nucleophilicity through delocalization of the non-bonding nitrogen electron pair onto the carbonyl groups. In the absence of an appropriate nucleophile, the reactive ketenimine intermediates converted to multiple byproducts. Similarly, phenyl and anisole nitrogen substituents induced delocalization of the electrons to the aromatic ring, thus inhibiting the formation of the desired annulation products (Table 3, entries 7 and 8).

Further Application of the Tosyl Imine Group

The tosyl imine group of the obtained dihydroquinonlin-4-imines is of great interest from the viewpoint of structural evolution. The imine group was subjected to reduction by sodium borohydride ($NaBH_4$) to generate dihydroquinonlin-4-amine (**4s**) in 84% isolated yield (Scheme 4, reaction path (a)). The resulting amine group is therefore readily available for further functionalization. Furthermore, the acidic hydrolysis of dihydroquinonlin-4-imines yielded dihydroquinolinones, which are important heterocyclic scaffolds. As shown in Scheme 4 (reaction path (b)), compound **4t** was obtained in 72% yield by treatment of **4f** with 1 M HCl in 1,4-dioxane. Thus, the thermally induced annulation developed in this study can elegantly transform sulfonyl triazoles into dihydroquinolin-4-imines, which can be subsequently converted into organic scaffolds such as dihydroquinolin-4-amines and dihydroquinolin-4-ones.



Scheme 4. Transformation of dihydroquinonlin-4-imine (**4f**) to (a) dihydroquinonlin-4-amine (**4s**) and (b) dihydroquinonlin-4-one (**4t**).

Development of Conditions for the Intramolecular Annulation of O-Tethered *N*-Sulfonyl-1,2,3-triazole

We investigated the use of 4-(phenoxymethyl)-1-tosyl-1*H*-1,2,3-triazole substrates (**6**) to facilitate the synthesis of chroma-4-imines and chromanones. We expected that the optimized

conditions for the aniline analogs would be suitable for the preparation of phenoxymethyl sulfonyl triazole analogs.

However, using DMF at 120 °C resulted in the formation of multiple products. After solvent screening using toluene, 1,4-dioxane, acetonitrile (ACN), and tetrahydrofuran (THF), toluene was found to give reasonably good conversions (60%, **7a**), with only 8% of the starting compound **6a** being recovered (Table 4, entry 3). The structure of **7a** was also confirmed by X-ray diffraction, as shown in Figure 2. Notably, the reaction

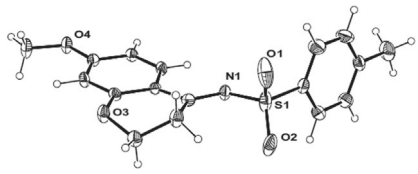


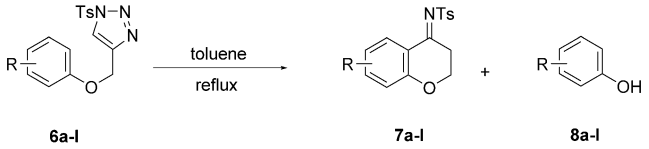
Figure 2. X-ray ORTEP structure of compound **7a**.[50]

times for the phenoxymethyl sulfonyl triazole analogs were longer than for the aniline analogs. Moreover, undesired by-products from hydrolysis and fission side reactions were observed. The weaker nucleophilicity of the oxygen atom compared to the nitrogen atom, in addition to the instability of the oxonium intermediate compared to the ammonium intermediate, rendered the annulation reactions problematic.

Scope of Intramolecular Annulation of O-Tethered Substrates

Under optimal conditions (i.e., refluxing in toluene), a variety of substituted 4-(phenoxymethyl)-1-tosyl-1*H*-1,2,3-triazole analogs was prepared from corresponding propargyl aryl ethers (5) and used to generate the corresponding chroman-4-imines. The analog bearing a phenyl ring alone did not yield the desired product, likely due to the absence of an activating group. An electron-donating substituent such as 3-OMe (**6a**) at the phenyl meta position was vital for the annulation reaction (Table 5, entry 1). In contrast, 2- and 4-OMe (*ortho* and para) substituents did not yield the chroman-4-imines of interest, but instead gave a mixture of products. The resonance effect and directing ability of the OMe group at the *meta* position facilitates the annulation, giving chroman-4-imine **7a**, whereas these effects were not present in the *ortho* and *para* OMe substituents, thus accounting for the complex product mixtures. Several 3-substituted phenols including 1-naphthol, 2-naphthol, 3-OBn, and sesamol (Table 5, entries 5, 6, 10, and 12) were transformed into substituted 4-(phenoxymethyl)-1-tosyl-1*H*-1,2,3-triazoles in moderate-to-good yields via the thermally promoted annulation reaction (42–70%). Notably, some substituents (e.g., 3-OBz) yielded phenols as undesired byproducts. A mechanism for this side-reaction is proposed in Scheme 5. The initial expulsion of nitrogen from the imino diazo intermediate leads to the formation of the ketenimine intermediate. Attack on the ketenimine intermediate by the oxygen atom followed by collapse of the resulting four-membered ring gives Intermediate IV. Removal of the allylnitrile moiety and subsequent hydrolysis then gives the phenol byproducts.

Table 5. Substituent scope in the preparation of chroman-4-imines

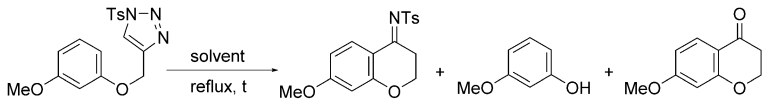


6a-l **7a-l** **8a-l**

Entry	R	*t* [h]	Yield of **7** [%]	Yield of **8** [%]
1	3-OMe (**6a**)	30	60 (**7a**)	trace (**8a**)
2	H (**6b**)	24	–[a] (**7b**)	–[a] (**8b**)
3	2-OMe (**6c**)	40	–[a] (**7c**)	–[a] (**8c**)
4	4-OMe (**6c**)	40	–[a] (**7d**)	–[a] (**8d**)
5[b]	1-naphtol (**6e**)	20	70 (**7e**)	– (**8e**)
6[c]	2-naphtol (**6f**)	20	42 (**7f**)	16 (**8f**)
7	3-phenyl (**6g**)	50	– (**7g**)	52 (**8g**)
8	3-Me (**6h**)	43	–[a] (**7h**)	–[a] (**8h**)
9	3-^{t}Bu (**6i**)	43	–[a] (**7i**)	–[a] (**8i**)
10	3-OBn (**6j**)	19	63 (**7j**)	24 (**8j**)
11	3-OBz (**6k**)	24	– (**7k**)	82 (**8k**)
12	sesamol (**6l**)	25	54 (**7l**)	– (**8l**)

[a] Multiple spots; [b] 29% of **6e**; [c] 19% of **9f**.

Table 4. Reaction optimization for the synthesis of chroman-4-imine analogs.



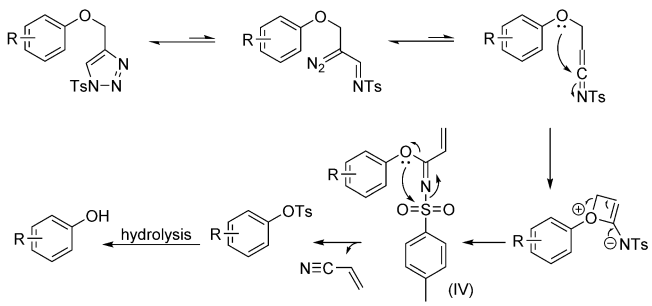
6a **7a** **8a** **9a**

Entry	Solvent	*t* [h]	Yield of **7a** [%]	Yield of **8a** [%]	Yield of **9a** [%]
1	DMF	2	–[a]	–[a]	–[a]
2	toluene	50	48	11	–[b]
3[c]	toluene	30	60	trace	–[b]
4	toluene[d]	21	25	17	38
5[e]	1,4-dioxane	44	48	11	–[b]
6	DCE	overnight	NR	–	–
7	ACN	overnight	NR	–	–
8	THF	overnight	NR	–	–

[a] Multiple spots; [b] no product formed; [c] 8% of **6a**; [d] at high pressure; [e] trace **6a**.

Conclusions

In summary, we have developed a new method employing the denitrogenative properties of *N*-sulfonyl-1,2,3-triazoles for the preparation of 2,3-dihydroquinolin-4(1H)-imine and chroman-4-imine analogs. Variation in the electronic properties of the substituents was demonstrated to control the formation of thermodynamic products rather than the kinetic acrylamidines and phenols. A metal-free denitrogenative annulation was performed through the introduction of an activating group onto the phenyl ring and promotion of the reaction via heating. This reaction was



Scheme 5. Proposed mechanism for the formation of phenol byproducts.

facile, environmentally friendly, and cost-effective, as it could be carried out in the absence of a metal catalyst. We believe the use of a thermally directed transformation of *N*-sulfonyl-1,2,3-triazoles will attract interest of the synthetic organic chemistry community and will lead to further developments in this promising field.

Experimental Section

General Considerations: All reactions were performed under an atmosphere of nitrogen and the workups were carried out in air. All the solvents used for the optimization of reaction conditions were dried using reported procedures. Especially, *N*,*N*-dimethylformamide should be freshly prepared. Unless noted, all materials were purchased from commercial suppliers and used as received. Tosyl azide was prepared in house by using conventional procedures. Cuprisorb resin was purchased from Seachem Laboratory (Madison, GA, USA) and dried in high vacuum before use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Ultrashield TM 300 and 75 MHz spectrometer, respectively. NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz). Solvent residual peaks calibrations: for 1H NMR: $CDCl_3$:7.26 ppm and for ^{13}C NMR: $CDCl_3$:77.23 ppm. Melting points of the products were calculated in open capillary tubes using Fargo Melting Point Apparatus MP-2D. Infra-Red spectra were recorded using PerkinElmer 100 FTIR Spectrometer. High Resolution Mass Spectra (HRMS) were performed on an Electronspray Ionization Time-of-Flight (ESI-TOF), Fast Atom Bombardment (FAB), Electron Ionization (EI), and Atmospheric-pressure chemical ionization Time-of-Flight (APCI-TOF) mass spectrometers. Flash chromatography was performed using silica gel (43–60 mm, Merck).

Representative Procedure for the Preparation of Dihydroquinolinimines (**4a–4g**, **4k–4o**): Preparation of (*E*)-*N*-(1-benzyl-7-methoxy-2,3-dihydroquinolin-4(1*H*)-ylidene)-4-methylbenzenesulfonamide (**4a**). A solution of *N*-benzyl-3-methoxy-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)aniline (50 mg, 0.11 mmol) in DMF (6.72 mL) was allowed to react at 120 °C for 2 h. Then, the solvent was removed under reduced pressure to afford the crude product, which was purified by silica-gel flash column chromatography on using 5% ethyl acetate in hexane as a solvent system to obtain the desired product **4a** (42 mg, 89%).

(*E*)-*N*-(1-benzyl-7-methoxy-2,3-dihydroquinolin-4(*1H*)-ylidene)-4-methylbenzenesulfonamide (4a): Yellow solid (42 mg, 0.10 mmol, 89%); m.p. 110–114 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, J = 9.0 Hz, 1H), 7.91 (d, J = 8.2 Hz, 2H), 7.40–7.27 (m, 7H), 6.24 (dd, J = 9.1, 2.2 Hz, 1H), 6.06 (d, J = 2.0 Hz, 1H), 4.54 (s, 2H), 3.69 (s, 3H), 3.54–3.40 (m, 4H), 2.43 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.5, 166.6, 153.8, 143.0, 140.0, 137.0, 131.4, 129.5, 129.2, 127.8, 127.0, 126.9, 112.9, 106.2, 96.9, 55.6, 55.5, 48.4, 31.9, 21.8 ppm; IR (KBr): $\tilde{\nu}$ = 2922, 2092, 1622 cm^{-1}; HRMS (MALDI) calcd for $C_{24}H_{24}N_2O_3S$ $[M]^+$ 420.1508, found 420.1510.

(*E*)-4-methyl-*N*-(1-methyl-2,3-dihydroquinolin-4(*1H*)-ylidene)benzenesulfonamide (4b): Orange solid (12 mg, 0.038 mmol, 26%); m.p. 140–146 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (dd, J = 8.1, 1.5 Hz, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.41–7.36 (m, 1H), 7.32 (d, J = 8.4 Hz, 2H), 6.71–6.61 (m, 2H), 3.52–3.45 (m, 2H), 3.42–3.35 (m, 2H), 2.99 (s, 3H), 2.44 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.8, 152.9, 143.3, 139.6, 136.3, 129.6, 128.8, 127.1, 118.9, 117.5, 113.4, 50.1, 39.5, 32.3, 21.8 ppm; IR (KBr): $\tilde{\nu}$ = 2087, 1644, 1458, 1278 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{19}N_2O_2S$ $[M+H]^+$ 315.1162, found 315.1159.

(*E*)-*N*-(1-ethyl-2,3-dihydroquinolin-4(*1H*)-ylidene)-4-methylbenzenesulfonamide (4c): Yellow solid (21 mg, 0.063 mmol, 45%); mp 113–116 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (dd, J = 8.1, 1.5 Hz, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 7.2 Hz, 2H), 6.70 (d, J = 8.4 Hz, 1H), 6.63–6.55 (m, 1H), 3.51–3.37 (m, 6H), 2.43 (s, 3H), 1.18 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.8, 151.4, 143.2, 139.7, 136.3, 129.6, 129.2, 127.1, 118.7, 116.8, 113.2, 47.0, 45.9, 32.0, 21.8, 11.1 ppm; IR (KBr): $\tilde{\nu}$ = 2087, 1644, 1462, 1260, 1193 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{21}N_2O_2S$ $[M+H]^+$ 329.1324, found 329.1326.

(*E*)-*N*-(1-butyl-2,3-dihydroquinolin-4(*1H*)-ylidene)-4-methylbenzenesulfonamide (4d). Yellow solid (21 mg, 0.059 mmol, 45%); m.p. 180–184 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (dd, J = 8.1, 1.5 Hz, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.35–7.28 (m, 3H), 6.68 (d, J = 8.4 Hz, 1H), 6.58 (t, J = 7.2 Hz, 1H), 3.43 (s, 4H), 3.35 (t, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.66–1.58 (m, 2H), 1.44–1.34 (m, 2H), 0.97 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.7, 151.6, 143.2, 139.7, 136.2, 129.6, 129.1, 127.1, 118.4, 116.7, 113.1, 51.5, 47.8, 32.0, 28.8, 21.8, 20.5, 14.1 ppm; IR (KBr): $\tilde{\nu}$ = 2068, 1642, 1505, 1460 cm^{-1}; HRMS (MALDI) calcd for $C_{20}H_{24}N_2O_2S$ $[M]^+$ 356.1558, found 356.1545.

(*E*)-*N*-(7-methoxy-1-methyl-2,3-dihydroquinolin-4(*1H*)-ylidene)-4-methylbenzenesulfonamide (4e): Yellow solid (40 mg, 0.12 mmol, 86%); m.p. 175–178 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, J = 9.0 Hz, 1H), 7.89 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 6.26 (dd, J = 9.0, 2.0 Hz, 1H), 6.06 (d, J = 1.7 Hz, 1H), 3.83 (s, 3H), 3.48–3.31 (m, 4H), 2.97 (s, 3H), 2.43 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.7, 166.7, 154.8, 143.0, 140.0, 131.3, 129.5, 127.0, 113.0, 106.0, 96.6, 55.6, 50.2, 39.5, 32.0, 21.7 ppm; IR (KBr): $\tilde{\nu}$ = 2925, 2087, 1618 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{21}N_2O_3S$ $[M+H]^+$, 345.1273, found 345.1281.

(*E*)-*N*-(3-methoxyphenyl)-*N*-methyl-*N*′-tosylacrylimidamide (4e′): Yellow oil (47 mg, 0.14 mmol, 40%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.1 Hz, 2H), 7.29–7.27 (m, 1H), 7.25–7.22 (m, 1H), 6.83 (dd, J = 8.1, 2.1 Hz, 1H), 6.68 (dd, J = 7.5, 1.2 Hz, 1H), 6.62 (t, J = 2.1 Hz, 1H), 6.44 (dd, J = 18, 12 Hz, 1H), 5.62–5.46 (m, 2H), 3.77 (s, 3H), 3.35 (s, 3H), 2.40 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.2, 160.7, 144.9, 142.2, 141.3, 130.6, 129.2, 129.0, 127.0, 126.7, 119.4, 113.7, 113.2, 55.7, 40.8, 21.6 ppm; IR (KBr): $\tilde{\nu}$ = 2918, 2850, 1603, 1520 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{20}N_2O_3SNa$ $[M+Na]^+$, 367.1092, found 367.1089.

(*E*)-*N*-(7-(benzyloxy)-1-methyl-2,3-dihydroquinolin-4(*1H*)-ylidene)-4-methylbenzenesulfonamide (4f): Yellow solid (42 mg, 0.10 mmol, 90%); m.p. 135–138 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, J = 9.0 Hz, 1H), 7.90 (d, J = 8.1 Hz, 2H), 7.47–7.33 (m, 5H), 7.30 (d, J = 8.1 Hz, 2H), 6.33 (dd, J = 9.0, 2.1 Hz, 1H), 6.15 (d, J = 2.1 Hz, 1H), 5.09 (s, 2H), 3.58–3.31 (m, 4H), 2.94 (s, 3H), 2.43 ppm

(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.7, 165.8, 154.7, 143.0, 140.0, 136.3, 131.3, 129.5, 128.9, 128.5, 127.7, 127.0, 113.2, 106.4, 97.8, 70.3, 50.1, 39.5, 32.0, 21.7 ppm; IR (KBr): $\tilde{\nu}$ = 2919, 2067, 1620 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}N_2O_3SNa$ [*M*+Na]$^+$, 443.1405, found 443.1409.

(*E*)-*N*-(7-((*tert*-butyldimethylsilyl)oxy)-1-methyl-2,3-dihydroquinolin-4(1*H*)-ylidene)-4-methylbenzenesulfonamide (4g): Yellow oil (11 mg, 0.025 mmol, 24%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 8.7 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.17 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.06 (d, *J* = 2.1 Hz, 1H), 3.44–3.34 (m, 4H), 2.93 (s, 3H), 2.42 (s, 3H), 0.97 (s, 9H), 0.22 ppm (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.8, 163.5, 154.8, 143.0, 140.0, 131.1, 129.5, 127.0, 113.5, 111.3, 103.4, 50.1, 39.5, 32.0, 25.8, 21.7, 18.5, −4.0 ppm; IR (KBr): $\tilde{\nu}$ = 2927, 2067, 1614, 1547, 1497 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{33}N_2O_3SSi$ [*M*+H]$^+$, 445.1981, found 445.1988.

Synthesis of *N*-(7-*h*ydroxy-1-methyl-2,3-dihydroquinolin-4(1H)-ylidene)-4-methylbenzenesulfonamide (4g′): To a stirred solution of 3-((*tert*-butyldimethylsilyl)oxy)-*N*-methyl-*N*-((1-tosyl- 1*H*-1,2,3-triazol-4-yl)methyl)aniline (55 mg, 0.12 mmol) in DMF (6.00 mL) and the resultant mixture was stirred for 20 minutes at 120 °C. The reaction mixture was concentrated to afford the crude product, then quenched with a solution of NH_4Cl, washed with ethyl acetate, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford the crude product, which was purified by silica-gel column chromatography to afford the desired product (28 mg, 72%) as a yellow solid.

***N*-(7-hydroxy-1-methyl-2,3-dihydroquinolin-4(1*H*)-ylidene)-4-methylbenzenesulfonamide (4g′):** Yellow solid (18 mg, 0.054 mmol, 51%); m.p. 165–168 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (m, 3H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.16 (d, *J* = 7.5 Hz, 1H), 6.07 (s, 1H), 3.44–3.30 (m, 4H), 2.93 (s, 3H), 2.43 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.8, 163.5, 155.1, 143.1, 139.9, 131.7, 129.6, 127.0, 113.0, 107.4, 98.5, 50.0, 39.5, 31.9, 21.8 ppm; IR (KBr): $\tilde{\nu}$ = 3432, 1621, 1556, 1498 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{17}N_2O_3S$ [*M*−H]$^-$ 329.0960, found 329.0959.

(*E*)-*N*-(1-ethyl-7-methoxy-2,3-dihydroquinolin-4(1*H*)-ylidene)-4-methylbenzenesulfonamide (4k): Yellow solid (77 mg, 0.22 mmol, 73%); m.p. 189–192 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.22 (dd, *J* = 9.0, 2.2 Hz, 1H), 6.09 (d, *J* = 2.1 Hz, 1H), 3.82 (s, 3H), 3.43 (q, *J* = 7.1 Hz, 2H), 3.39 (s, 4H), 2.43 (s, 3H), 1.19 ppm (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.7, 166.7, 153.2, 142.9, 140.1, 131.7, 129.5, 127.0, 113.0, 105.5, 96.3, 55.6, 47.2, 46.0, 31.7 (grease), 21.8, 14.3, 11.1 ppm; IR (KBr): $\tilde{\nu}$ = 2075, 1644, 1496 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{22}N_2O_3SNa$ [*M*+Na]$^+$ 381.1249, found, 381.1259.

(*E*)-*N*-(7-methoxy-1-propyl-2,3-dihydroquinolin-4(1*H*)-ylidene)-4-methylbenzenesulfonamide (4l): Yellow solid (77 mg, 0.21 mmol, 70%); m.p. 141–147 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.30(d, *J* = 8.1 Hz, 2H), 6.22 (dd, *J* = 9.0, 2.0 Hz, 1H), 6.06 (d, *J* = 2.0 Hz, 1H), 3.82 (s, 3H), 3.50–3.33 (m, 4H), 3.28 (t, *J* = 7.4 Hz, 2H), 2.43 (s, 3H), 1.7–1.5 (m, 2H), 0.98 ppm (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.7, 166.6, 153.5, 142.9, 140.1, 131.6, 129.5, 127.0, 112.8, 105.3, 96.3, 55.5, 53.5, 48.0, 31.6, 21.8, 19.9, 11.7 ppm; IR (KBr): $\tilde{\nu}$ = 2924, 2084, 1638 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{25}N_2O_3S$ [*M*+H]$^+$, 373.1586, found, 373.1579.

(*E*)-*N*-(1-butyl-7-methoxy-2,3-dihydroquinolin-4(1*H*)-ylidene)-4-methylbenzenesulfonamide (4m): Yellow solid (33.1 mg, 0.086 mmol, 71%); m.p. 148–152 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 9.2 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 6.21 (dd, *J* = 9.1, 2.4 Hz, 1H), 6.06 (s, 1H), 3.82 (s, 3H), 3.39 (s,4H), 3.32, (t, *J* = 7.3 Hz, 2H), 2.42 (s, 3H), 1.66–1.57 (m, 2H), 1.46–1.33 (m, 2H), 0.97 ppm (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.7, 166.6, 153.5, 142.9, 140.1, 131.6, 129.5, 127.0, 112.8, 105.4, 96.2, 55.5, 51.5, 48.0, 31.7, 28.7, 21.7, 20.5, 14.1 ppm; IR (KBr): $\tilde{\nu}$ = 2925, 2854, 2067, 1621, 1456 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{27}N_2O_3S$ [*M*+H]$^+$ 387.1737, found 387.1736.

(*E*)-*N*-(1-hexyl-7-methoxy-2,3-dihydroquinolin-4(1*H*)-ylidene)-4-methylbenzenesulfonamide (4n): Yellow solid (40.7 mg, 0.098 mmol, 87%); m.p. 118–120 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 9.1 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.21 (dd, *J* = 9.0, 1.7 Hz, 1H), 6.06 (d, *J* = 1.7 Hz, 1H), 3.82 (s, 3H), 3.39 (s, 4H), 3.31 (t, *J* = 7.4 Hz, 2H), 2.43 (s, 3H), 1.64–1.58 (m, 2H), 1.38–1.30 (m, 6H), 0.90 ppm (t, *J* = 5.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.6, 166.6, 153.5, 142.9, 140.1, 131.6, 129.5, 127.0, 112.8, 105.4, 96.2, 55.5, 51.8, 48.0, 31.8, 31.7, 27.0, 26.5, 22.8, 21.7, 14.2 ppm; IR (KBr): $\tilde{\nu}$ = 2925, 2854, 1705, 1621, 1461 cm^{-1}; HRMS (APCI) calcd for $C_{23}H_{31}N_2O_3S$ [*M*+H]$^+$ 415.2055, found 415.2065

(*E*)-*N*-(1-allyl-7-methoxy-2,3-dihydroquinolin-4(1*H*)-ylidene)-4-methylbenzenesulfonamide (4o): Yellow solid (40 mg, 0.108 mmol, 86%); m.p. 138–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 4.5 Hz, 1H), 7.90 (d, *J* = 4.1 Hz, 2H), 7.31 (d, *J* = 4.0 Hz, 2H), 6.24 (dd, *J* = 9.2, 2.3 Hz, 1H), 6.09 (d, *J* = 1.1 Hz, 1H), 5.90–5.76 (m, 1H), 5.28–5.20 (m, 2H), 3.96 (d, *J* = 5.1 Hz, 2H), 3.80 (s, 3H), 3.42 (s, 4H), 2.43 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.6, 166.6, 153.6, 143.0, 140.0, 132.1, 131.4, 129.5, 127.0, 117.9, 112.9, 106.0, 96.8, 55.6, 54.3, 48.0, 31.8, 31.1 (grease), 21.8 ppm; IR (KBr): $\tilde{\nu}$ = 2923, 2852, 1619, 1544, 1456 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{23}N_2O_3S$ [*M*+H]$^+$ 371.1429, found 371.1432.

Synthesis of *N*-(7-(benzyloxy)-1-methyl-1,2,3,4-tetrahydroquinolin-4-yl)-4- methylbenzenesulfonamide (4s): To a stirred solution of *N*-(7-(benzyloxy)-1-methyl-2,3-dihydroquinolin-4(1*H*)-ylidene)-4-methylbenzenesulfonamide (90 mg, 0.21 mmol) in THF (10 mL) was added $NaBH_4$ (10 mg, 0.26 mmol) and MeOH (1 mL) at 0 °C, the resultant mixture was stirred at room temperature for 1 h. The reaction was evaporated under reduced pressure. The resultant residue was dissolved in ethyl acetate, washed with H_2O, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford the desired product (76 mg, 84%) as an off white solid.

***N*-(7-(benzyloxy)-1-methyl-1,2,3,4-tetrahydroquinolin-4-yl)-4-methylbenzenesulfonamide (4s):** Colorless oil (76 mg, 0.179 mmol, 84%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 9.0 Hz, 2H), 7.40–7.24 (m, 7H), 6.43 (d, *J* = 6.0 Hz, 1H), 6.18 (d, *J* = 3.0 Hz, 1H), 6.12 (dd, *J* = 3.0 Hz, 1H), 4.99 (s, 2H), 4.45 (d, *J* = 6.0 Hz, 1H), 4.25–4.27 (m, 1H), 3.35–3.25 (m, 1H), 3.13–3.09 (m, 1H), 2.85 (s, 3H), 2.47 (s, 3H), 2.18–2.08 (m, 1H), 1.94–1.85 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.3, 147.7, 143.7, 138.0, 137.3, 130.3, 130.0, 128.8, 128.1, 127.7, 127.5, 113.7, 102.4, 98.8, 70.1, 50.1, 46.2, 39.2, 29.4, 21.8 ppm; IR (KBr): $\tilde{\nu}$ = 1616, 1572, 1510, 1454 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}N_2O_3SNa$ [*M*+Na]$^+$ 445.1562, found 445.1559.

Synthesis of 7-(benzyloxy)-1-methyl-2,3-dihydroquinolin-4(1*H*)-one (4t): A mixture of 1 M HCl (2 mL) and 1,4-dioxane (8 mL) was added to *N*-(7-(benzyloxy)-1-methyl-2,3-dihydroquinolin-4(1*H*)-ylidene)-4-methylbenzenesulfonamide (50 mg, 0.12 mmol) and heated to 100 °C for 2 h. The solution mixture was evaporated under reduce pressure and diluted with H_2O, extracted with ethyl acetate, dried over $MgSO_4$, filled, and concentrated under reduced pressure to afford the crude product, which was purified by silica-gel column chromatography to afford the desired product (23 mg, 72%) as a colorless oil.

7-(benzyloxy)-1-methyl-2,3-dihydroquinolin-4(1*H*)-one (4t): colorless oil (23 mg, 0.085 mmol, 72%); ^{1}H NMR (300 MHz, $CDCl_3$): δ =

7.87 (d, J=9.0 Hz, 1H), 7.45–7.33 (m, 6H), 6.71 (d, J=9.0 Hz, 1H), 5.22 (s, 2H), 3.58 (t, J=6.0 Hz, 2H), 3.13 (s, 3H), 2.69 ppm (t, J=6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=194.0, 160.1, 153.4, 136.1, 128.9, 128.4, 127.6, 127.2, 121.2, 115.4, 107.6, 71.1, 51.1, 41.0, 33.2 ppm; IR (KBr): $\tilde{\nu}$=1679, 1588, 1550, 1498 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{16}NO_2$ $[M-H]^+$ 266.1181, found 266.1187.

Representative Procedure for the Preparation of Chroman-4-imines (**7a**, **7e**, **7f**, **7j**, **7l**): Preparation of *N*-(7-*m*ethoxychroman-4-ylidene)-4-methylbenzenesulfonamide (**7a**). A solution of 4-((3-methoxyphenoxy)methyl)-1-tosyl-1*H*-1,2,3-triazole (100.0 mg, 0.28 mmol) in toluene (14 mL) was allowed to react at 120 °C for 30 h. Then, the solvent was removed under reduced pressure to afford the crude product, which was purified by silica-gel flash column chromatography using 20% ethyl acetate in hexane as a solvent system to afford the desired product **7a** (51 mg, 60%).

***N*-(7-methoxychroman-4-ylidene)-4-methylbenzene sulfonamide (7a):** Pale yellow solid (51 mg, 0.15 mmol, 60%); m.p. 108–113 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.94–7.85 (m, 3H), 7.33 (d, J=8.1 Hz, 2H), 6.50 (dd, J=9.2, 2.3 Hz, 1H), 6.36 (d, J=2.3 Hz, 1H), 4.39 (t, J=6.3 Hz, 2H), 3.82 (s, 3H), 3.51 (t, J=6.3 Hz, 2H), 2.44 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=172.5, 166.8, 163.5, 143.5, 139.2, 129.6, 127.2, 113.6, 110.9, 100.9, 65.7, 55.9, 31.5, 21.8 ppm; IR (KBr): $\tilde{\nu}$=2921, 1619, 1556 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{17}NO_4SNa$ $[M+Na]^+$ 354.0776, found 354.0770.

(*E*)-*N*-(2H-benzo[*h*]chromen-4(3*H*)-ylidene)-4-methylbenzene sulfonamide (7e): Pale yellow solid (65 mg, 0.19 mmol, 70%); m.p. 154–158 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=8.25 (d, J=8.3 Hz, 1H), 7.96 (d, J=8.1 Hz, 2H), 7.88 (d, J=8.9 Hz, 1H), 7.74 (d, J=8.1 Hz, 1H), 7.60 (td, J=7.4, 0.8 Hz, 1H), 7.51 (td, J=7.4, 0.8 Hz, 1H), 7.36(d, J=8.1 Hz, 2H), 7.30 (d, J=8.9 Hz, 1H), 4.63 (t, J=6.6 Hz, 2H), 3.66 (t, J=6.6 Hz, 2H), 2.46 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=172.7, 160.0, 143.7, 139.0, 137.7, 130.2, 129.7, 128.0, 127.3, 126.6, 125.0, 123.7, 122.4, 121.3, 114.7, 66.2, 31.3, 21.8 ppm; IR (KBr): $\tilde{\nu}$=1628, 1574, 1459, 1089 cm^{-1}; HRMS (ESI): calcd for $C_{20}H_{17}NO_3SNa$ $[M+Na]^+$ 374.0827, found 374.0818.

(*E*)-*N*-(2,3-dihydro-1*H*-benzo[*f*]chromen-1-ylidene)-4-methyl benzenesulfonamide (7f): Brick red solid (39 mg, 0.11 mol, 42%); m.p. 155–160 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=9.15 (d, J=8.5 Hz, 1H), 7.97 (d, J=8.3 Hz, 2H), 7.88 (d, J=9.0 Hz, 1H), 7.72 (dd, J=7.9, 1.3 Hz, 1H), 7.48–7.33 (m, 4H), 7.07 (d, J=9.1 Hz, 1H), 4.48 (t, J=6.5 Hz, 2H), 3.73 (t, J=6.5 Hz, 2H), 2.47 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=173.4, 164.1, 143.6, 139.5, 138.4, 131.6, 129.9, 192.7, 129.5, 129.1, 127.1, 127.0, 125.1, 119.0, 112.7, 65.2, 33.1, 21.8 ppm; IR (KBr): $\tilde{\nu}$=1644, 1433, 1150 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{18}NO_3S$ $[M+H]^+$ 352.1007, found 352.1006.

(*E*)-*N*-(7-(benzyloxy)chroman-4-ylidene)-4-methylbenzene sulfonamide (7j): Pale yellow solid (59 mg, 0.14 mmol, 63%); m.p. 134–132 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.95–7.85 (m, 3H), 7.46–7.28 (m, 7H), 6.58 (dd, J=9.1, 2.3 Hz, 1H), 6.44 (d, J=2.2 Hz, 1H), 5.07(s, 2H), 4.38 (t, J=6.4 Hz, 2H), 3.51 (t, J=6.4 Hz, 2H), 2.44 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=172.4, 165.9, 163.4, 143.5, 139.2, 135.9, 129.6, 128.9, 128.6, 127.7, 127.2, 113.8, 111.4, 102.0, 70.6, 65.8, 31.5, 21.8 ppm; IR (KBr): $\tilde{\nu}$=1626, 1574, 1458, 1367 cm^{-1}; HRMS (MALDI) calcd for $C_{23}H_{22}NO_4S$ $[M+H]^+$ 408.1270, found 408.1257.

(*E*)-*N*-(6H-[1,3]dioxolo[4,5*g*]chromen-8(7*H*)-ylidene)-4-methylbenzenesulfonamide (7l): Orange solid (50 mg, 0.15 mmol, 54%); m.p. 154–160 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.89 (d, J=8.3 Hz, 2H), 7.33 (d, J=8.3 Hz, 2H), 7.30 (s, 1H), 6.38 (s, 1H), 5.96 (s, 2H), 4.35 (t, J=6.5 Hz, 2H), 3.48 (t, J=6.5 Hz, 2H), 2.44 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=172.2, 160.0, 155.2, 143.6, 143.5, 139.2, 129.6, 127.2, 113.5, 104.4, 102.4, 98.6, 66.0, 31.3, 21.8 ppm; IR (KBr): $\tilde{\nu}$=1637, 1560, 1475, 1449 cm^{-1}; HRMS (APCI) calcd for $C_{17}H_{16}NO_5S$ $[M+H]^+$ 346.0749, found 346.0756.

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[49] See the Supporting Information.
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