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Base-Promoted Denitrogenative/Deoxygenative/Deformylative Benzannulation of *N*-Tosylhydrazones with 3-Formylchromones for Diverse and Polyfunctionalized Xanthones

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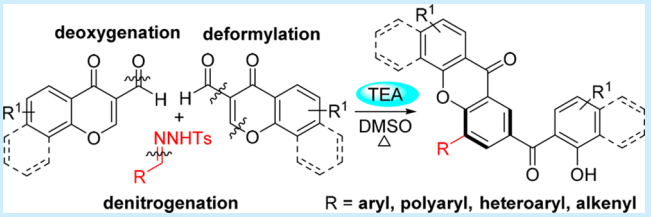
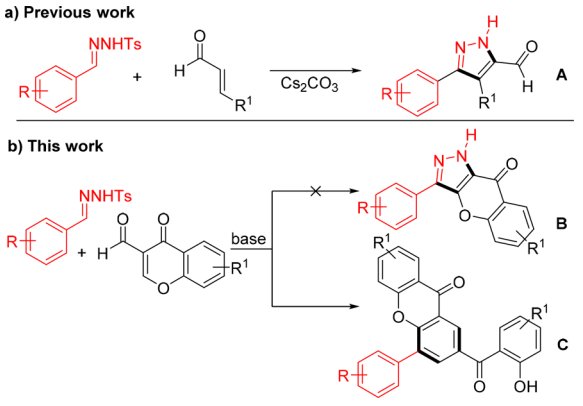
Supporting Information

ABSTRACT: A simple and efficient base-promoted denitrogenative/deoxygenative/deformylative benzannulation is developed for the construction of biologically interesting polyfunctionalized xanthones starting from *N*-tosylhydrazones and two molecules of 3-formylchromones. This unprecedented protocol proceeds via a cascade diazo formation/Michael addition/denitrogenation/[4 + 2] cycloaddition/elimination/ring opening. The synthesized xanthones possess potent UV-filter, fluorescent sensor, and antioxidant properties.



Over the past decade, *N*-tosylhydrazones have been widely used as precursors or sources of diazo compounds.[1] They have also been employed as versatile starting materials and powerful building blocks in organic synthesis.[2] In pioneering work, Barluenga,[3] Valdés,[3,4] and Wang[5] developed new methodologies for the formation of C−C, C−O, C−N, C−B, and C−Si bonds starting from *N*-tosylhydrazones. Subsequently, a number of transition-metal-catalyzed and transition-metal-free transformations of *N*-tosylhydrazones via cyclopropanation,[6] C−H insertion,[7] ring expansion,[8] coupling reactions,[9] and construction of heterocycles[10] have been demonstrated. In addition, cycloaddition reactions between *N*-tosylhydrazones and electron-deficient alkenes or alkynes have been well reported;[11] for example, the reaction of *N*-tosylhydrazones and α,β-unsaturated carbonyl compounds, such as cinnamaldehydes, in the presence of base provides pyrazoles **A** (Scheme 1).[12] Despite remarkable and excellent developments of novel protocols using *N*-tosylhydrazones in organic synthesis, there are no reports on the reaction of *N*-tosylhydrazones with 3-formylchromones so far. In this regard, the reaction of *N*-tosylhydrazones with 3-formylchromones in the presence of base was examined aiming to synthesize fused pyrazoles **B** (Scheme 1). However, the first attempt in the presence of a mild base leads to unexpected xanthones **C** (Scheme 1).

Scheme 1. Base-Promoted Benzannulation between *N*-Tosylhydrazones and α,β-Unsaturated Carbonyls



Xanthones are important oxygenated heterocycles found in many natural products exhibiting prominent biological and pharmacological activities.[13] Molecules bearing a xanthone moiety exhibit potent anticancer,[14] antimicrobial,[15] antimalarial,[16] anticonvulsant,[17] anticholinesterase,[18] anti-HIV,[19] antioxidant,[20] antiangiogenesis,[21] anti-inflammatory,[22] antialzheimer,[23] and cholesterol acyltransferase inhibitory activities.[24] In addition, some of these compounds are evaluated and utilized as major drug candidates.[25] Owing to their importance and effectiveness, various biosynthetic pathways[26] and synthetic approaches[27] for xanthones have been demonstrated. Although several approaches for the synthesis of xanthones have been described, more facile and efficient protocols for diverse and functionalized xanthones are still highly desirable.

This paper reports the construction of diverse and polyfunctionalized xanthones bearing a 2-hydroxybenzoyl group by mild base-promoted condensation reactions of *N*-tosylhydrazones with 4-oxo-4*H*-chromene-3-carbaldehydes (Scheme 2). To the best of our knowledge, this is the first example for the construction of substituted xanthones by decomposition of *N*-tosylhydrazones under mild base conditions.

The study was initiated by the optimization of the reaction between (*E*)-*N*′-benzylidene-4-methylbenzenesulfonohydra-

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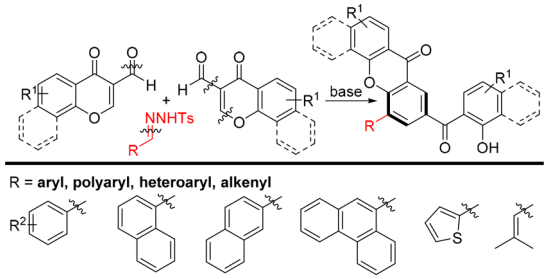
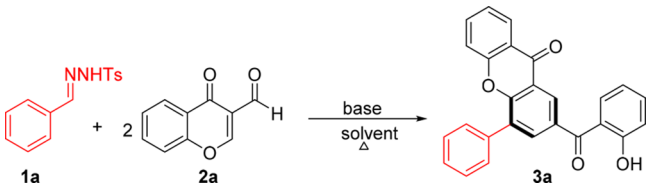
Scheme 2. Novel Strategy for Diverse and Polyfunctionalized Xanthones from *N*-Tosylhydrazones



zide (**1a**) and 2 equiv of 4-oxo-4*H*-chromene-3-carbaldehyde (**2a**) with different bases and solvents (Table 1). The initial

Table 1. Optimization of the Reaction Conditions[a]



entry	base (equiv)	solvent	temp (°C)	time (h)	yield (%)[b]
1	K_2CO_3 (1)	DMSO	90	5	62
2	Cs_2CO_3 (1)	DMSO	90	5	68
3	KOH (1)	DMSO	90	5	64
4	TEA (1)	DMSO	90	3	83
5	TEA (0.5)	DMSO	90	3	61
6	TEA (2)	DMSO	90	3	72
7	DBU (1)	DMSO	90	3	73
8	DABCO (1)	DMSO	90	5	68
9	TEA (1)	toluene	90	10	31
10	TEA (1)	THF	reflux	10	55
11	TEA (1)	DMF	90	8	62
12	TEA (1)	ethanol	reflux	10	43
13	TEA (1)	DMSO	50	6	68
14	TEA (1)	DMSO	120	3	76
15	TEA (1)	DMSO	90	3	83[c]

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1 mmol) in solvent (5 mL). [b]Isolated yields after column chromatography. [c]3 mL of DMSO was used.

attempt with the inorganic bases K_2CO_3 (1 equiv) and Cs_2CO_3 (1 equiv) in DMSO at 90 °C for 5 h provided product **3a** in 62 and 68% yield, respectively (entries 1−2). With a stronger base, KOH (1 equiv), the yield of **3a** did not significantly change (64%, entry 3). In an attempt to increase the yield, other organic bases were next screened. With 1 equiv of TEA in DMSO at 90 °C for 3 h, **3a** was produced in 83% yield (entry 4). Decreasing the loading of TEA to 0.5 equiv or increasing it to 2 equiv did not improve the yield (entries 5−6). Further attempts to increase the yield of **3a** by using other stronger organic bases such as DBU (1 equiv) and DABCO (1 equiv) were not successful (entries 7−8). Using other nonpolar and polar solvents such as toluene, THF, DMF, and ethanol provided **3a** in 31, 55, 62, and 43% yields, respectively (entries 9−12). In addition, when the reaction was carried out at lower (50 °C) or higher (120 °C) temperatures, the yield of **3a** did not improve (entries 13−14). Decreasing the amount of DMSO to 3 mL provided **3a** in the same yield (83%, entry 15). The structure of **3a** was identified by the analysis of its spectral data. The ^{1}H NMR spectrum of **3a** revealed the characteristic OH peak at δ 11.86 ppm as a broad singlet and two aromatic protons on the new-made benzene ring at δ 8.66 (d, J = 2.2 Hz) and 8.11 ppm (d, J = 2.2 Hz), which appeared as doublets due to long-range couplings. The ^{13}C NMR spectrum showed two carbonyl and one hydroxyl-containing carbon peaks at δ 199.5, 176.7, and 163.3 ppm, respectively. The structure of **3a** was further confirmed by the single-crystal X-ray crystallographic analysis of structurally related compound **3k** (Figure 1).

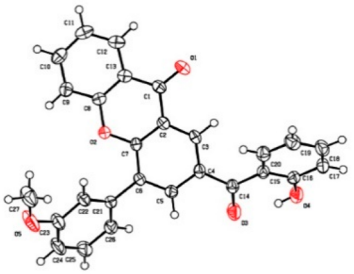


Figure 1. X-ray structure of compound **3k**.

With the optimized conditions in hand, the generality of the reaction was further investigated by employing different *N*-tosylhydrazones **1a−1g** with diverse 4-oxo-4*H*-chromene-3-carbaldehydes **2a−2h** to afford a variety of xanthone derivatives (Table 2). The reaction of **1a** with **2b−2d** bearing electron-donating groups such as 6-methyl, 6-isopropyl, and 6-methoxy provided products **3b−3d** in 85, 84, and 87% yields, respectively (entries 1−3). Furthermore, the combination of **1a** with **2e−2g** bearing the electron-withdrawing groups 6-bromo, 6-chloro, and 6-fluoro afforded products **3e−3g** in 67−74% yields (entries 4−6). In addition, the reaction of **1a** with **2h** bearing both an electron-donating and electron-withdrawing group provided desired product **3h** in 79% yield (entry 7). These results show that 4-oxo-4*H*-chromene-3-carbaldehydes **2b−2d** bearing electron-donating groups provide the desired products in slightly higher yields than substrates **2e−2g** bearing electron-withdrawing groups while maintaining a remarkable functional group tolerance. Moreover, the reactions of **2a** with **1b−1e** bearing electron-donating groups such as 4-methyl, 2,5-dimethyl, 3-methoxy, and 3,5-dimethoxy on the benzene ring of the benzylidene-4-methylbenzenesulfonohydrazide for 3−4 h produced desired products **3i−3l** in the range 76−82% yields (entries 8−11). Treatment of **2a** with **1f−1g** bearing an electron-withdrawing group such as 2-bromo and 2-chloro on the benzene ring successfully afforded products **3m** and **3n** in 75 and 71% yields, respectively (entries 12−13). This protocol provides a rapid synthetic route to diverse xanthone derivatives bearing various electron-donating or electron-withdrawing substituents on the benzene ring of the xanthone moiety.

To demonstrate the versatility of this reaction, further reactions between a variety of *N*-tosylhydrazones bearing polyaromatic or heteroaromatic rings and 3-formylchromones with or without polyaromatic rings were next examined (Scheme 3). Reactions of (*Z*)-4-methyl-*N*′-(naphthalen-1-ylmethylene) benzenesulfonohydrazide (**1h**) with **2a**, **2b**, **2d**, or **2f** provided the products **4a−4d** in 68, 78, 81, and 74% yields, respectively. Similarly, treatment of (*Z*)-4-methyl-*N*′-(naphthalen-2-ylmethylene) benzenesulfonohydrazide (**1i**)

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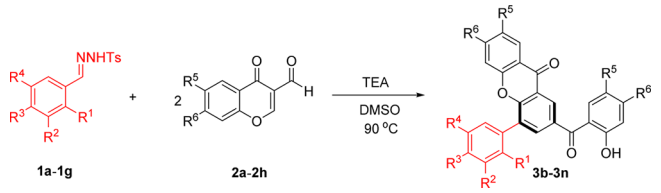
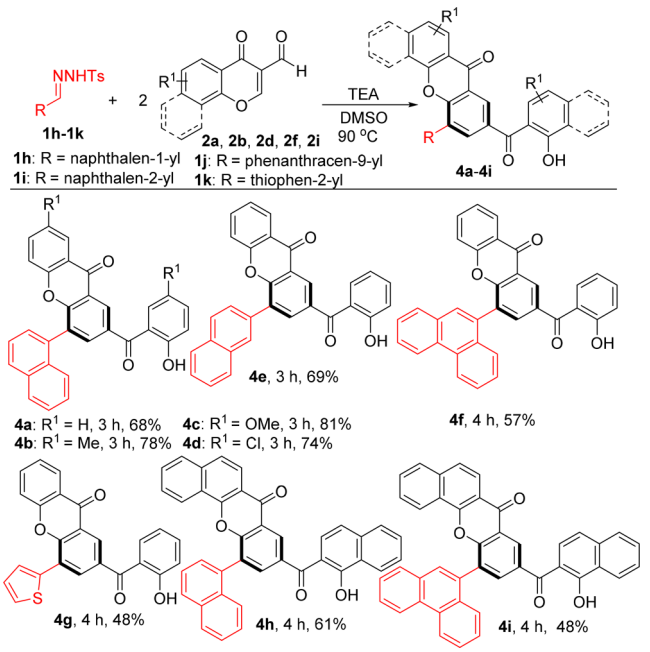
Table 2. Synthesis of Various Xanthone Derivatives 3b−3n by Reaction of 1a−1g with 2a−2h

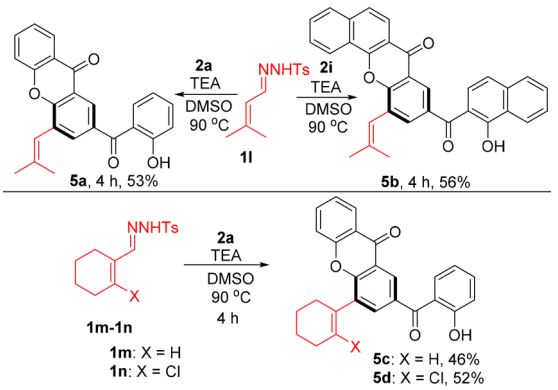


entry	1	2	time (h)	product (3)	yield (%)
1	**1a**: $R^1 = R^2 = R^3 = R^4 = H$	**2b**: R^5 = Me, R^6 = H	3	**3b**	85
2	**1a**: $R^1 = R^2 = R^3 = R^4 = H$	**2c**: R^5 = *i*-Pr, R^6 = H	3	**3c**	84
3	**1a**: $R^1 = R^2 = R^3 = R^4 = H$	**2d**: R^5 = OMe, R^6 = H	3	**3d**	87
4	**1a**: $R^1 = R^2 = R^3 = R^4 = H$	**2e**: R^5 = Br, R^6 = H	3	**3e**	74
5	**1a**: $R^1 = R^2 = R^3 = R^4 = H$	**2f**: R^5 = Cl, R^6 = H	3	**3f**	69
6	**1a**: $R^1 = R^2 = R^3 = R^4 = H$	**2g**: R^5 = F, R^6 = H	3	**3g**	67
7	**1a**: $R^1 = R^2 = R^3 = R^4 = H$	**2h**: R^5 = Cl, R^6 = Me	3	**3h**	79
8	**1b**: $R^1 = R^2$ = H, R^3 = Me, R^4 = H	**2a**: $R^5 = R^6 = H$	3	**3i**	82
9	**1c**: R^1 = Me, $R^2 = R^3$ = H, R^4 = Me	**2a**: $R^5 = R^6 = H$	4	**3j**	76
10	**1d**: R^1 = H, R^2 = OMe, $R^3 = R^4 = H$	**2a**: $R^5 = R^6 = H$	3	**3k**	78
11	**1e**: R^1 = H, R^2 = OMe, R^3 = H, R^4 = OMe	**2a**: $R^5 = R^6 = H$	4	**3l**	77
12	**1f**: R^1 = Br, $R^2 = R^3 = R^4 = H$	**2a**: $R^5 = R^6 = H$	4	**3m**	75
13	**1g**: R^1 = Cl, $R^2 = R^3 = R^4 = H$	**2a**: $R^5 = R^6 = H$	4	**3n**	71

Scheme 3. Synthesis of Diverse Xanthone Derivatives 4a−4i by the Reaction of 1h−1k with 2a, 2b, 2d, 2f, or 2i



Scheme 4. Synthesis of Xanthone Derivatives 5a−5d by the Reaction of 1l−1n with 2i or 2a



with **2a** provided the product **4e** in 69% yield. In addition, a combination of (*Z*)-4-methyl-*N*′-(phenanthren-9-ylmethylene) benzenesulfonohydrazide (**1j**) with **2a** afforded the desired product **4f** in 57% yield, and that of (*Z*)-4-methyl-*N*′-(thiophen-2-ylmethylene) benzenesulfonohydrazide (**1k**) with **2a** afforded **4g** in 48% yield. Further reactions of **1h** or **1j** with 4-oxo-4*H*-benzo[*h*]chromene-3-carbaldehyde (**2i**) afforded the products **4h** and **4i** in 61 and 48% yields, respectively. These reactions provide a rapid synthetic route to diverse xanthone derivatives bearing polyaromatics and heteroaromatics on the benzene ring of the xanthone moiety.

Importantly, this benzannulation protocol is not restricted to *N*-tosylhydrazones bearing aryl and heteroaryl groups. As shown in Scheme 4, the reaction of **1l** bearing an alkenyl group with **2a** proceeded successfully to afford **5a** in 53% yield, and that with **2i** provided **5b** in 56% yield. Similarly, treatment of **1m**, bearing a 1-cyclohexenyl group, with **2a** afforded desired product **5c** in 46% yield. Moreover, a reaction of **1n** bearing an alkenyl and electron-withdrawing chloro group on the cyclohexene ring with **2a** provided the product **5d** in 52% yield.

To understand the substitution effect, the competing reaction of **1a** with two different 4-oxo-4*H*-chromene-3-carbaldehydes, **2d** and **2g** bearing an electron-donating and electron-withdrawing group, respectively, was examined (Scheme 5). Thus, treatment of **1a** (0.5 mmol) with **2d** (1 mmol) and **2g** (1 mmol) afforded products **3d** (19%) and **3g** (31%), along with crossed products **3o** (9%) and **3p** (20%). This result indicates that the electron-withdrawing fluoro group on the 4-oxo-4*H*-chromene-3-carbaldehyde renders good Michael acceptor properties to the substrate and hence favors the formation of products compared to the 4-oxo-4*H*-chromene-3-carbaldehyde containing the electron-donating methoxy group.

Based on the experimental results and literature precedent, the plausible mechanism for the formation of **3a** is depicted in Scheme 6. Under basic conditions, *N*-tosylhydrazone **1a** gives

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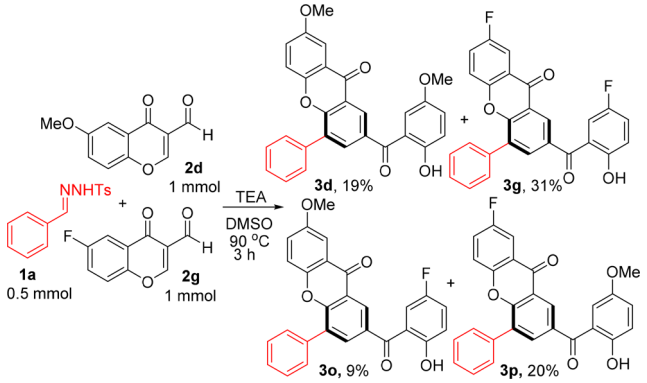
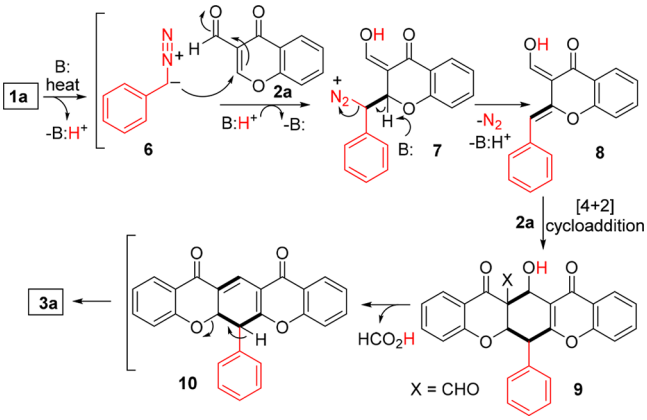
Scheme 5. Further Reaction for the Competition of Two Different 4-Oxo-4*H*-chromene-3-cabaldehydes 2d and 2g



Scheme 6. Plausible Mechanism for the Formation of 3a



diazo compound **6**,[1] which undergoes Michael addition with **2a** to give diene intermediate **8** via elimination of the nitrogen molecule from **7**. The facile Diels–Alder reaction of in situ generated diene **8** with dienophile **2a** generates [4 + 2] cycloadduct **9**.[28] Finally, the adduct **9** undergoes elimination of formic acid followed by aromatization and ring opening to furnish product **3a**. The detection of formic acid by GC-MS in the crude reaction mixture supports the suggested reaction mechanism (Supporting Information (SI), Figures S4–S6). As an application of this protocol, synthesized compounds were evaluated for their UV-filter, fluorescent sensor, and antioxidant properties (see the SI).

In conclusion, we have developed a novel methodology for the regiospecific construction of biologically interesting and polyfunctionalized xanthones via a mild-base-promoted condensation reaction of *N*-tosylhydrazones and 4-oxo-4*H*-chromene-3-carbaldehydes. This protocol has several advantages, such as transition-metal-free one-pot procedure, mild reaction conditions, and tolerance of various functional groups. The synthesized compounds showed potent UV-filter properties compared to common sunscreen agents, excellent turn-off fluorescence sensing properties for Fe^{3+} ions, and antioxidant activities comparable to standard BHT.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03106.

Detailed experimental procedures, characterization data, GC-Mass and HRMS spectra, fluorescence spectra, and photophysical data (PDF)

Accession Codes

CCDC 1822370 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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