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Transition metal- and oxidant-free sulfonylation of 1-sulfonyl-1*H*-1,2,3-triazoles to enols for the synthesis of sulfonate derivatives

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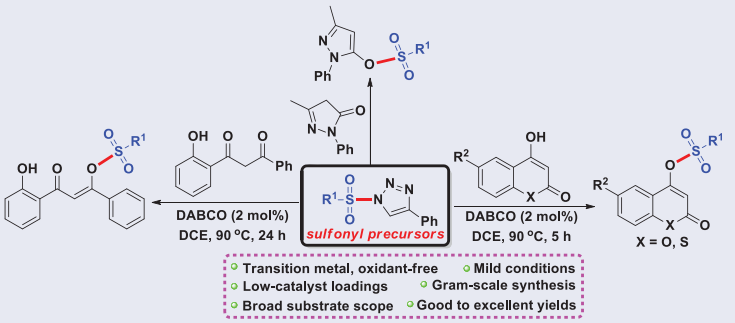
ABSTRACT

A novel and convenient protocol for the synthesis of sulfonate derivatives via DABCO-catalyzed direct sulfonylation of 1-sulfonyl-1,2,3-triazoles to different enols has been established. This synthetic route could effectively avoid the use of transition metal catalysts and extra oxidants, and the target products could be obtained in good to excellent yields (75–86%) with wide substrate scope under mild conditions at low-catalyst loadings, which would provide a facile and practical access to enol sulfonates. Furthermore, the use of the resulting enol sulfonates for the C–C bond formation has been demonstrated via Suzuki-Miyaura, Sonogashira, and Heck cross-coupling reaction.

GRAPHIC ABSTRACT



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1,4-Diazabicyclo[2.2.2]octane; 1-sulfonyl-1,2,3-triazoles; enols; sulfonates; sulfonylation

Introduction

Enol esters and their derivatives are valuable synthetic intermediates in organic synthesis.[1] Many natural products containing the enol ester moiety exhibit useful biological activities.[2] Among them, enol sulfonates play an important role in the fields of organic reactions,[3] especially in various cross-coupling reactions,[4] such as Suzuki–Miyaura,[5]

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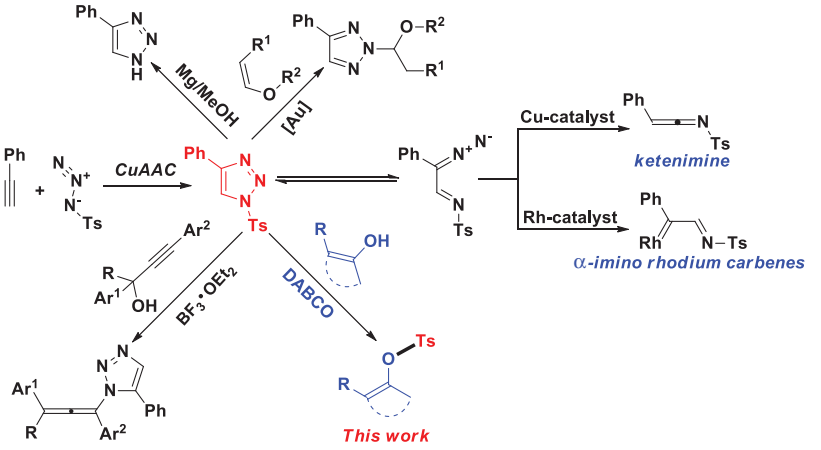


Scheme 1. Chemistry of *N*-tosyl-1,2,3-triazoles.

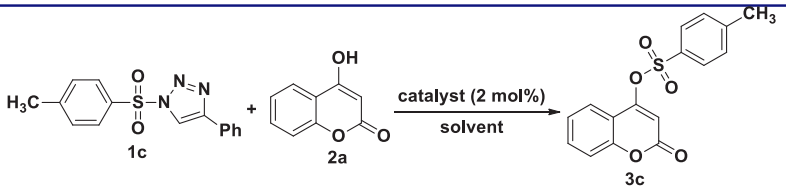
Negishi,[6] Stille,[7] Kumada,[8] and Buchwald–Hartwig couplings,[9] serving as effective equivalents of vinyl halides. The most conventional synthetic route to enol sulfonates is the sulfonylation of enols and sulfonyl halides. More recently, several sulfonyl precursors including sulfonyl halides,[10] sulfonyl hydrazides,[11] sodium sulfinates,[12] sulfinic acids,[13] sulfonyl azides,[14] sulfonyl isocyanides,[15] sulfoxides,[16] and DABCO·$(SO_2)_2$ (named: DABSO),[17] were employed in the sulfonylation reaction to access organosulfone compounds. Therefore, the development of general methods for the synthesis of enol sulfonates by utilizing new sulfonyl precursors is consequently an important goal in organic chemistry.

In recent years, the chemistry of 1-tosyl-4-aryl/alkyl-1,2,3-triazoles has attracted much attention from synthetic chemists since its initial discovery by the groups of Fokin and Gevorgyan. These compounds are highly useful building blocks and have been abundantly used as precursors of ketenimine and α-imino rhodium carbenes.[18] *N*-tosyl α-diazo imine could be converted into 1-tosyl ketenimine *via* denitrogenation and rearrangement and subsequently derived into various heterocycles and carbocycles.[19] On the other hand, these compounds are capable of acting as convenient precursors to generate reactive α-imino metal carbenoid species and undergo subsequent reactions, such as cyclization,[20] transannulation,[21] denitrogenative reaction,[22] cyclopropanation,[23] arylation,[24] and X–H insertions (X=C, N, O).[25] Beside of these two fates, other reactions were seldom reported based on the fragile 1-tosyl-1,2,3-triazole except for the direct desulfonylation by using magnesium in methanol,[26] the N2-selective alkylation in the presence of Au-catalyst or DABCO (1,4-diazabicyclo[2.2.2]octane),[27] and the nucleophilicity of 1-sulfonyl-1,2,3-triazoles in the presence of Lewis acid.[28] Here we would like to report an unprecedented and general approach to enol sulfonates through the direct sulfonylation of 1-sulfonyl-1,2,3-triazoles to enols in the presence of DABCO (Scheme 1).

Results and discussion

We initially started our investigation by choosing 4-phenyl-1-(tosylsulfonyl)-1*H*-1,2,3-triazole (**1c**) to react with 4-hydroxy-2*H*-chromen-2-one (**2a**) in the presence of

Table 1. Optimization of the reaction conditions for the model reaction.[a]

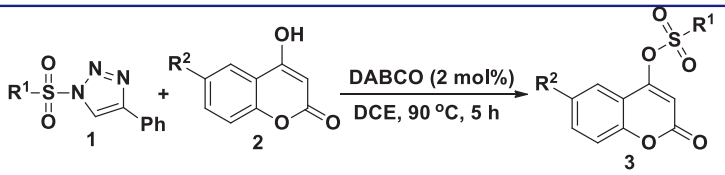


Entry	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
1	DBU	DCE	90	5	70
2	TEA[f]	DCE	90	5	60
3	DABCO	DCE	90	5	81
4	NaOH	DCE	90	5	Trace
5	$NaHCO_3$	DCE	90	5	Trace
6	$KHCO_3$	DCE	90	5	Trace
7	NaOAc	DCE	90	5	Trace
8	NH_4OAc	DCE	90	5	Trace
9	CsOAc	DCE	90	5	50
10	–	DCE	90	5	NR[g]
11[c]	DABCO	DCE	90	5	52
12[d]	DABCO	DCE	90	5	82
13[e]	DABCO	DCE	90	5	83
14	DABCO	Toluene	90	5	69
15	DABCO	DMF	90	5	NR[g]
16	DABCO	MeCN	90	5	72
17	DABCO	EtOH	90	5	70
18	DABCO	DMSO	90	5	NR[g]
19	DABCO	H_2O	90	5	NR[g]
20	DABCO	DCE	25	5	Trace
21	DABCO	DCE	50	5	Trace
22	DABCO	DCE	70	5	70
23	DABCO	DCE	110	5	83
24	DABCO	DCE	90	2	65
25	DABCO	DCE	90	7	82

[a]Reaction conditions: 4-phenyl-1-(tosylsulfonyl)-1*H*-1,2,3-triazole **1c** (0.5 mmol), 4-hydroxy-2*H*-chromen-2-one **2a** (0.5 mmol), solvent (2 mL), catalyst (2 mol%).
[b]Isolated yields.
[c]The amount of catalyst was 1 mol%.
[d]The amount of catalyst was 5 mol%.
[e]The amount of catalyst was 10 mol%.
[f]TEA = Triethylamine.
[g]No reaction.

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 1,2-dichloroethene (DCE) at 90 °C for 5 h, and to our delight the desired product **3c** was harvested in 70% yield as shown in Table 1 (entry 1). Subsequently, various bases such as organic (e.g., DBU, TEA, DABCO) and inorganic bases (e.g., NaOH, $NaHCO_3$, $KHCO_3$, NaOAc, NH_4OAc, CsOAc) were tested as the catalysts, organic bases were proved to be the best choice (Table 1, entries 1–3), and the target product **3c** was obtained in the highest yield (81%) when 1,4-diazabicyclo[2.2.2]octane (DABCO) was chosen as catalyst for this reaction (Table 1, entry 3). Also, among the solvents tested, DCE, toluene, MeCN, and EtOH were shown to be more effective than the others such as DMF (*N*,*N*-dimethylformamide), DMSO (dimethyl sulfoxide), and H_2O (Table 1, entries 14–19), and DCE was proved to be the best choice (Table 1, entry 3). Moreover, no conversion was observed when the reaction was performed in the absence of catalyst (Table 1, entry 10). In addition, the yield could not be obvious promoted by increasing or decreasing amount of catalyst (Table 1, entries 11–13). Furthermore, the effects of the temperature and

Table 2. DABCO-catalyzed direct O–H bond sulfonylation of *N*-sulfonyl-1,2,3-triazoles with 4-hydroxy-2*H*-chromen-2-ones.[a]

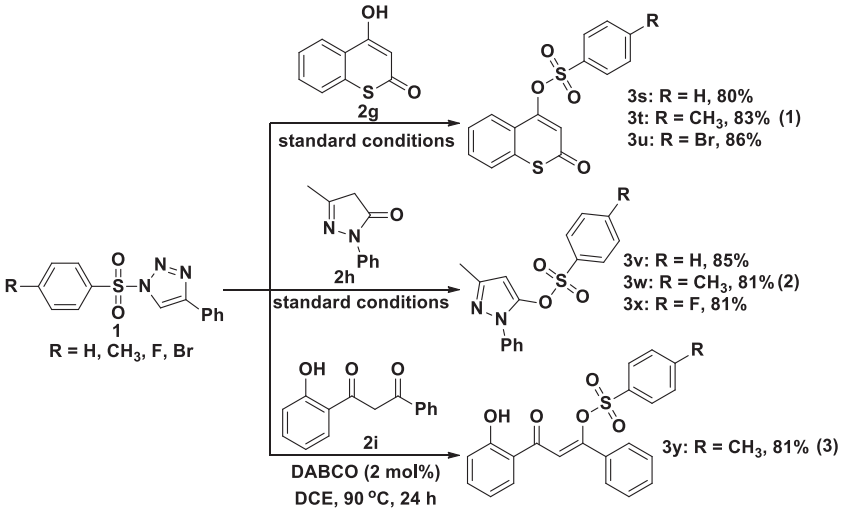


Entry	R^1	R^2	Product	Yield (%)[b]
1	CH_3 (**1a**)	H (**2a**)	**3a**	80
2	C_6H_5 (**1b**)	**2a**	**3b**	80
3	4-$CH_3C_6H_4$ (**1c**)	**2a**	**3c**	83
4	4-FC_6H_4 (**1d**)	**2a**	**3d**	80
5	4-BrC_6H_4 (**1e**)	**2a**	**3e**	80
6	2,4,6-^{i}PrC_6H_2 (**1f**)	**2a**	**3f**	81
7	4-$CH_3OC_6H_4$ (**1g**)	**2a**	-	NR[c]
8	4-$CH_3CONHC_6H_4$ (**1h**)	**2a**	-	NR[c]
9	CH_3 (**1a**)	CH_3 (**2b**)	**3g**	81
10	C_6H_5 (**1b**)	**2b**	**3h**	83
11	4-$CH_3C_6H_5$ (**1c**)	**2b**	**3i**	85
12	4-FC_6H_5 (**1d**)	**2b**	**3j**	78
13	4-BrC_6H_5 (**1e**)	**2b**	**3k**	81
14	2,4,6-^{i}PrC_6H_2 (**1f**)	**2b**	**3l**	83
15	CH_3 (**1a**)	CH_3O (**2c**)	**3m**	83
16	4-FC_6H_5 (**1d**)	**2c**	**3n**	77
17	2,4,6-^{i}PrC_6H_2 (**1f**)	**2c**	**3o**	80
18	2,4,6-^{i}PrC_6H_2 (**1f**)	F (**2d**)	**3p**	80
19	2,4,6-^{i}PrC_6H_2 (**1f**)	Cl (**2e**)	**3q**	78
20	2,4,6-^{i}PrC_6H_2 (**1f**)	Br (**2f**)	**3r**	75

[a]Reaction conditions: 4-phenyl-1-sulfonyl-1*H*-1,2,3-triazole **1** (0.5 mmol), 4-hydroxy-2*H*-chromen-2-one **2** (0.5 mmol), DCE (2 mL), DABCO (2 mol%), 90 °C for 5 h.
[b]Isolated yields.
[c]No reaction.

reaction time were also investigated (Table 1, entries 20–25). It was found that neither decreasing nor increasing the reaction temperature or time could improve the yield. Therefore, the optimal reaction conditions were found to be 2 mol% DABCO as catalyst with DCE as the solvent at 90 °C for 5 h (Table 1, entry 3).

Having identified this acceptable optimization, we then turned to evaluate the scope of the DABCO-catalyzed direct sulfonylation by utilizing different *N*-sulfonyl-1,2,3-triazoles and 4-hydroxy-2*H*-chromen-2-ones, and the results are summarized in Table 2. A series of 2-oxo-2*H*-chromen-4-yl-4-sulfonate derivatives were obtained in good yields (75–85%). For *N*-sulfonyl-1,2,3-triazoles **1**, a set of substrates with aliphatic or aromatic sulfonyl group could be efficiently sulfonated with 4-hydroxy-2*H*-chromen-2-one (**2a**) to deliver the desired products **3a–3f** in good yields (80–83%). Reactions of 4-phenyl-1-arylsulfonyl-1*H*-1,2,3-triazoles, which bearing with electron-donating (e.g. $-CH_3$) or electron-withdrawing groups (e.g. –F, –Br) on the aromatic ring of aryl group (Table 2, entries 3–5), proceeded well, and almost equal yields were achieved. Notably, substrate bearing with three sterically demanding isopropyl groups at the 2,4,6-positions of the benzene ring (**1f**) was also tolerated to give the corresponding products in 75–83% yields (Table 2, entries 6, 14, 17–20), the results showed that the steric hindrance did not influence this reaction obviously. When 4-phenyl-1-arylsulfonyl-1*H*-1,2,3-triazoles with a strong electron-donating group (e.g. $-OCH_3$, $-NHCOCH_3$) were subjected to

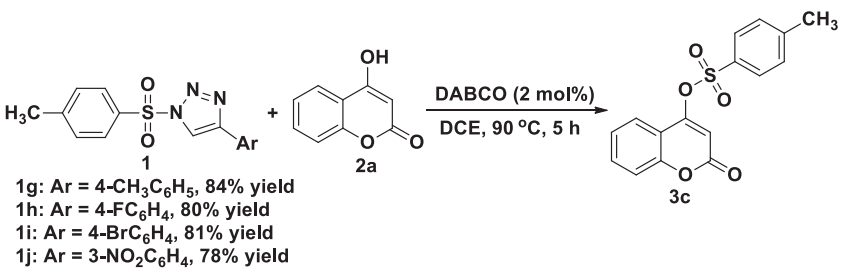


Scheme 2. DABCO-catalyzed sulfonylation of 4-phenyl-1-sulfonyl-1*H*-1,2,3-triazole with other enols.

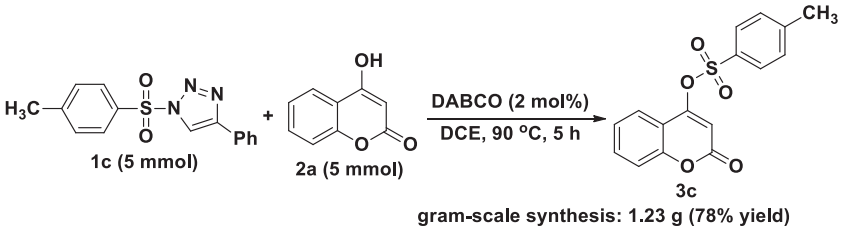
this reaction, the corresponding products were not obtained (Table 2, entries 7, 8). 4-Hydroxy-2*H*-chromen-2-ones possessing either electorn-donating (**2b**, **2c**) or electron-withdrawing substituents (**2d–2f**) were well tolerated in this sulfonylation (Table 2, entries 9–20), affording the desired products in good yields (75–85%). This protocol was tolerant of synthetically valuable functional groups on the phenyl moiety (e.g., methoxyl, fluoro, chloro, and bromo groups), which could allow an opportunity for further transformations. In addition, all of the products were characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy and HRMS analysis, and the structures of products **3c** was also unambiguously confirmed by X-ray crystallographic analysis (see Supporting Information, Figure S1).

Next, to further demonstrate the utility of this newly developed protocol, different enols and ketones containing active methylene were examined (Scheme 2). Gratifyingly, the reaction worked well with 4-hydroxy-2*H*-thiochromen-2-one (**2g**) to provide the corresponding products **3 s**, **3t**, and **3 u** in 80%, 83%, and 86% yields, respectively (Scheme 2, Eq (1)). Likewise, reaction of 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (**2h**) with different 4-phenyl-1-sulfonyl-1*H*-1,2,3-triazoles were also compatible and gave the desired products **3v**, **3w**, and **3x** in 85%, 81%, and 81% yields, respectively (Scheme 2, Eq (2)). It is worth noting that the reaction using 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione (**2i**) with 4-phenyl-1-tosyl-1*H*-1,2,3-triazole (**1c**) proceeded well and gave the desired enol sulfonate product **3y** in 78% yield after prolonging the reaction time to 24 h (Scheme 2, Eq (3)). These results suggested that this direct sulfonylation would provide a convenient and practical method for the synthesis of a series of enol sulfonate derivatives by using 4-phenyl-1-sulfonyl-1*H*-1,2,3-triazoles as sulfonyl precursors.

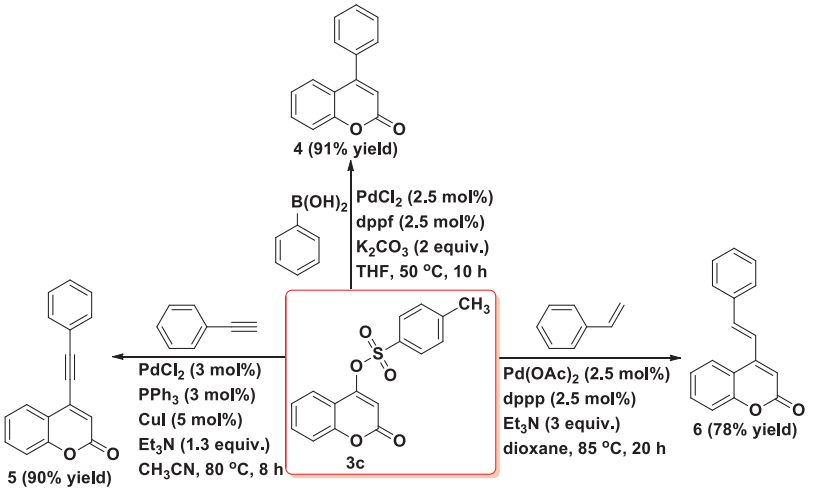
Moreover, the sulfonylation process also occurred well with 4-aryl-1-(tosylsulfonyl)-1*H*-1,2,3-triazoles (**1g–1j**) and 4-hydroxy-2*H*-chromen-2-one (**2a**), affording the desired products **3c** in 84%, 80%, 81%, and 78% yields, respectively (Scheme 3). It should be noted that the electronic and steric nature of the Ar group did not show obvious effects on the yields of product **3c**.



Scheme 3. DABCO-catalyzed Sulfonylation of 4-Aryl-1-(tosylsulfonyl)-1*H*-1,2,3-triazoles and 4-Hydroxy-2*H*-chromen-2-one.



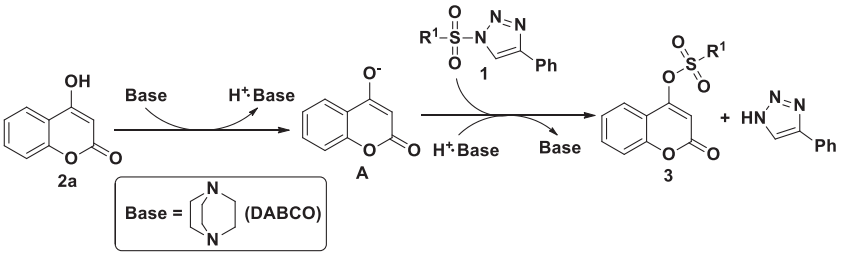
Scheme 4. Gram-scale synthesis of this method.



Scheme 5. The cross-coupling transformation of 2-oxo-2*H*-chromen-4-yl 4-methylbenzenesulfonate **3c**.

In addition, we carried out a gram-scale reaction of 4-phenyl-1-(tosylsulfonyl)-1*H*-1,2,3-triazole (**1c**, 5 mmol) to react with 4-hydroxy-2*H*-chromen-2-one (**2a**, 5 mmol) under the standard conditions, and the product **3c** was isolated in 80% (1.52 g) yield (Scheme 4), which showed promise for this synthetic method as a useful tool in practical synthetic contexts.

Having demonstrated the preparation of the 2-oxo-2*H*-chromen-4-yl-4-sulfonate compounds, their reactivity of Pd-catalyzed cross-coupling reactions was then investigated, such as Suzuki-Miyaura, Sonogashira, and Heck coupling reaction. As revealed from the results depicted in Scheme 5, the generated 2-oxo-2*H*-chromen-4-yl 4-methylbenzenesulfonate (**3c**) smoothly reacted with phenylboronic acid, phenylacetylene, and



Scheme 6. Proposed mechanism for the synthesis of enol sulfonate derivatives **3**.

styrene to obtain the corresponding products in 91%, 90%, and 78% yield, respectively. Therefore, the generated 2-oxo-2*H*-chromen-4-yl-4-arylsulfonate compounds from 4-aryl-1-(tosylsulfonyl)-1*H*-1,2,3-triazoles and 4-hydroxy-2*H*-chromen-2-one would be of profound interest for C–C bond formation, leading to numerous applications in organic chemistry.

On the basis of the experimental results obtained above, a plausible mechanism was proposed and described in Scheme 6. Initially, DABCO as a base obtained a proton from 4-hydroxy-2*H*-chromen-2-one (**2a**) to form the intermediate **A**. Subsequently, the desired products **3** resulted from nucleophilic substitution of intermediate **A** as a nucleophile with *N*-sulfonyl-1,2,3-triazoles **1**. Meanwhile, 4-phenyl-1,2,3-triazole was released as the byproduct.

Experimental section

General procedure for the synthesis of 2-oxo-2H-chromen-4-yl-4-sulfonates 3

To a stirred solution of *N*-sulfonyl-1,2,3-triazoles **1** (0.5 mmol), 4-hydroxy-2*H*-chromen-2-one **2** (0.5 mmol) in DCE (2 mL), DABCO (0.01 mmol) was added. The reaction mixture was heated in an oil bath at 90 °C for 5 h. After the reaction completed, the mixture was cooled to room temperature, extracted with CH_2Cl_2 (3 × 10 mL), and washed with water. The organic layers were combined, dried over Na_2SO_4, filtered, and evaporated under vacuum. The residue was further purified by flash column chromatography on silica gel (200-300 mesh) with ethyl acetate and petroleum ether (1:4/1:6, v/v) as the elution solvent to give the desired product **3**.

2 -Oxo-2H-chromen-4-yl methanesulfonate (3a)

This compound was purified by column chromatography (ethyl acetate/petroleum ether = 1:6) to afford a white solid in 80% yield; mp 98–99 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.2 Hz, 1H), 7.40–7.33 (m, 2H), 6.54 (s, 1H), 3.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.5, 157.2, 153.5, 133.5, 124.7, 122.9, 117.1, 114.6, 103.4, 39.1; IR (KBr) ν 3070, 3034, 1729, 1629, 1606, 1372, 1187, 1175, 1065, 898, 870, 796, 772, 746, 718 cm^{-1}; HRMS (ESI) Calcd for $[C_{10}H_8O_5S + H]^+$ 241.0165, Found 241.0165.

General procedure for the synthesis of 4-Phenyl-2H-chromen-2-one 4

To a solution of phenylboronic acid (0.6 mmol), 2-oxo-2*H*-chromen-4-yl 4-methylbenzenesulfonate (0.5 mmol), and potassium carbonate (1 mmol) in degassed THF (4 mL) was added freshly prepared degassed aqueous solution of $PdCl_2$ (2.5 mol%) and 1,1′-bis(diphenylphosphino)ferrocene (dppf) (2.5 mol%). The mixture was stirred at 50 °C under nitrogen atmosphere for 10 h. Upon completion of the reaction, the mixture was cooled to room temperature, and solvent was removed under reduced pressure. Water (10 mL) was added to the mixture, and extracted with EtOAc (3 × 10 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and the solvent was concentrated in vacuum. The crude residue was purified by chromatography on silica gel (*n*-Hexane/Ethyl Acetate: 9/1) to afford the corresponding product 4 in 91% yield.

4 -Phenyl-2H-chromen-2-one (4)[29]

White solid; mp 99–100 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56–7.52 (m, 4H), 7.50 (d, J = 7.5 Hz, 1H), 7.46–7.45 (m, 2H), 7.42 (d, J = 10.5 Hz, 1H), 7.23 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 155.8, 154.3, 135.3, 132.0, 129.8, 129.0, 128.5, 127.1, 124.3, 119.1, 117.4, 115.3; HRMS (APCI): $[M + H]^+$ Calcd for $C_{15}H_{11}O_2$ 223.0759; Found 223.0760.

General procedure for the synthesis of 4-(phenylethynyl)-2H-chromen-2-one 5

To a solution of phenylacetylene (0.6 mmol), 2-oxo-2*H*-chromen-4-yl 4-methylbenzenesulfonate (0.5 mmol), CuI (5 mol%) and triethylamine (0.75 mmol) in degassed acetonitrile (4 mL) was added freshly prepared degassed aqueous solution of $PdCl_2$ (3 mol%) and triphenylphosphine (3 mol%) under nitrogen atmosphere. The mixture was stirred at 80 °C under nitrogen atmosphere for 8 h. Upon completion of the reaction, the mixture was cooled to room temperature, and solvent was removed under reduced pressure. Water (10 mL) was added to the mixture, and extracted with EtOAc (3 × 10 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and the solvent was concentrated in vacuum. The crude residue was purified by chromatography on silica gel (*n*-Hexane/Ethyl Acetate: 10/1) to afford the corresponding product **5** in 90% yield.

4 -(Phenylethynyl)-2H-chromen-2-one (5)[30]

White solid; mp 132–133 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 8.0 Hz, 1H), 7.47–7.42 (m, 3H), 7.36 (t, J = 7.5 Hz, 2H), 6.63 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 153.7, 137.4, 132.4, 130.3, 128.8, 126.8, 124.6, 121.3, 118.5, 117.2, 102.3, 82.9; HRMS (APCI): $[M + H]^+$ Calcd for $C_{17}H_{11}O_2$ 247.0754; Found 247.0756.

General procedure for the synthesis of (E)-4-styryl-2H-chromen-2-one 6

To a solution of styrene (1.5 mmol), 2-oxo-2*H*-chromen-4-yl 4-methylbenzenesulfonate (0.5 mmol), and triethylamine (0.75 mmol) in degassed 1,4-dioxane (4 mL) was added freshly prepared degassed aqueous solution of $Pd(OAc)_2$ (2.5 mol%) and 1,3-bis(diphenylphosphino) propane (dppp) (2.5 mol%) under nitrogen atmosphere. The mixture was stirred at 85 °C under nitrogen atmosphere for 20 h. Upon completion of the reaction, the mixture was cooled to room temperature, and solvent was removed under reduced pressure. Water (10 mL) was added to the mixture, and extracted with EtOAc (3 × 10 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and the solvent was concentrated in vacuum. The crude residue was purified by chromatography on silica gel (*n*-Hexane/Ethyl Acetate: 10/1) to afford the corresponding product **6** in 78% yield.

(E)-4-Styryl-2H-chromen-2-one (6)[31]

White solid; mp 89–90 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 7.0 Hz, 2H), 7.56 (t, J = 8.0 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 8.0 Hz, 1H), 6.60 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 153.9, 150.4, 137.8, 135.6, 131.9, 129.6, 129.0, 127.5, 124.4, 124.2, 120.3, 118.7, 117.5, 110.5; HRMS (APCI): $[M + H]^+$ Calcd for $C_{17}H_{13}O_2$ 249.0916; Found 249.0918.

Conclusions

In conclusion, a novel and efficient base-catalyzed sulfonylation of *N*-sulfonyl-1,2,3-triazoles and 4-hydroxy-2*H*-chromen-2-ones for the synthesis of 2-oxo-2*H*-chromen-4-yl-4-arylsulfonates in good yields has been developed. Notably, this is the first example of the sulfonylation utilizing *N*-sulfonyl-1,2,3-triazoles as sulfonyl precursors. This metal and oxidant-free synthetic process works well with a wide range of substrates and can be safely conducted on a gram scale. The features such as generality, high efficiency (low catalyst loading), and mild reaction conditions make this method an attractive alternative for the preparation of organosulfone compounds. Furthermore, this new reaction can enrich the chemistry of *N*-sulfonyl-1,2,3-triazole compounds.

Full experimental detail, ^{1}H and ^{13}C NMR spectra. This material can be found via the "Supplementary Content" section of this article's webpage.

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