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Sulphated tin oxide (STO)-catalyzed synthesis of arylated vinyl ethers

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The *C3* or *O*-alkylation of 4-hydroxycoumarin (formation of new C-C and C-O bond) is undoubtedly one of the most important and challenging reactions in synthetic chemistry due to its pharmaceutical utility. In this communication, we report sulfated tin oxide (STO)-catalyzed synthesis of arylated vinyl ethers in moderate to good isolated yields (68-93%) from the reaction of substituted phenyl acetylenes (terminal alkynes) with 4-hydroxy coumarin in polyethylene glycol (PEG 400) as solvent at 110 °C. The catalyst can be recycled up to 5 times without losing the significant yield.

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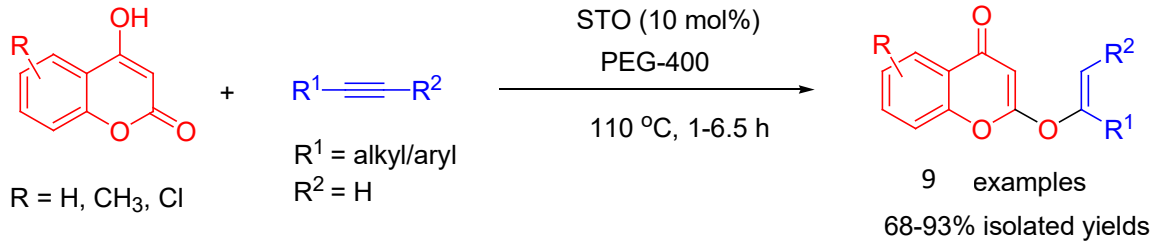

Graphical Abstract

1. Introduction

Coumarin and its derivatives are important heterocycles from a pharmacological standpoint. Because of their pharmacological and biological properties, including their anticoagulant, anti-HIV, and antifungal properties, coumarin and its derivatives are the subject of much research.[1-5] Coumarin is an essential ingredient in a number of natural products.[6-7] Furthermore, functionalized coumarin derivatives are widely employed as anticancer and antibacterial medications, which have a vast array of uses in biological science.[8] Many functionalized coumarin derivatives have been the focus of design and synthesis efforts in the realm of medicinal chemistry due to its unique physicochemical characteristics.[9-10]

4-Hydroxycoumarin is a significant member of the coumarin family due to its structure and chemical behavior, which have greatly influenced organic synthesis (**Fig. 1**).[11-16] Not only are they important synthetic endpoints, but they also form the structural core of many natural products, which has increased interest in them. Additionally, there are increasing reports

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on the investigation of 4-hydroxycoumarin derivatives as ligands of transition metals and rare earth element metal complexes that exhibit bioactivities of their own, such as fluorescence, etc.[17-19]

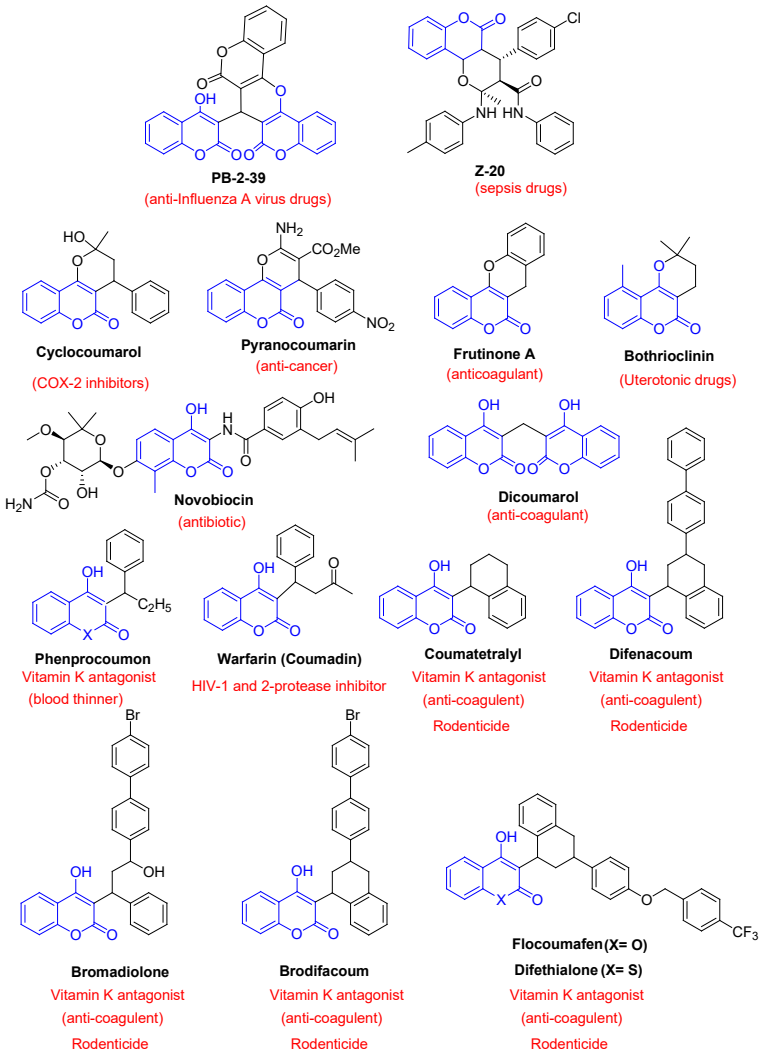


Fig. 1. Representative 4-hydroxycoumarins in market

The reactions involving 4-hydroxycoumarin based on the literature review show great regioselectivity, and their progression is readily regulated by altering the starting compounds' molecules' substituents and reaction conditions.[20] The three tautomeric structures of 4-hydroxy-2*H*-chromen-2-one (**Fig. 2**), which are the tautomeric keto-enol forms, 4-hydroxy-2-chromenone (I), 2,4-chromandione (II), and 2-hydroxy-4-chromenone (III), greatly regulate its reactivity. The phenomenon of proton shifting in the three tautomeric structures has been thoroughly studied using spectroscopic, thermochemical, computational, and other chemical reactivities. Both nucleophilic and electrophilic sites can be found in the structure of 4-hydroxycoumarin. Different kinds of nucleophiles can replace the carbon atom that is attached to the hydroxyl group, and this can result in a number of reactions, such as arylation, amination, and halogenations. The nucleophilicity of the carbon atom behind the carbonyl group is the most important component of the 4-hydroxycoumarin moiety.

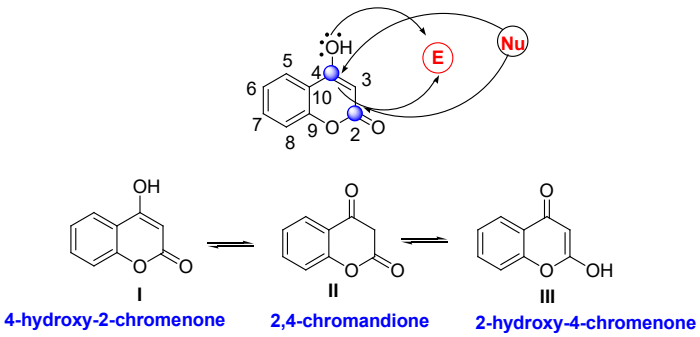


Fig. 2. Tautomeric and active centres of 4-hydroxycoumarin

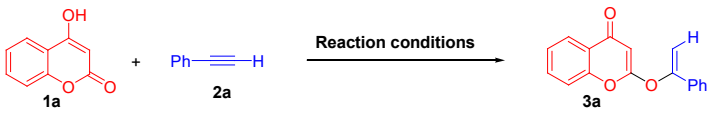
The carbonyl carbon is preferentially accessed by the comparatively mild nucleophiles. Several techniques have been documented where the hydroxyl group's oxygen atom functions as an excellent nucleophile and is targeted by acylating and alkylating chemicals. As previously indicated, the *C3* or *O*-alkylation of 4-hydroxycoumarin (creation of new C-C and C-O bonds) is unquestionably one of the most significant and difficult reactions in synthetic chemistry because of its potential for pharmacological applications. Therefore, a stronger catalyst that will activate the OH group of 4-hydroxycoumarin and increase their susceptibility to nucleophilic attack under mild circumstances is desperately needed. The ideal catalyst should be easily accessible, affordable, less hazardous, and capable of operating in an environmentally friendly way in order to meet the requirements of green chemistry. This will stimulate curiosity about the possible benefits and broad applications of the resultant target compounds.

In synthetic chemistry, solid heterogeneous catalysts are recognized to provide expected benefits such as easy regeneration, reduced corrosiveness, affordability, ease of handling, and efficient reusing.[21] Because of its huge surface area, high efficiency, non-corrosive nature, low cost, and wide surface area, sulfated tin oxide, commonly known as SO_4^{-2}/SnO_2, has gained popularity and efficiency as a catalyst. Composed of sulfated and sulfonic acid moieties on a range of heterogeneous solid bases, it is extensively used in chemical and industrial settings.[22-42] We have just now been able to successfully utilize STO's applications in the synthesis of β-amino alcohols and 4-aryl-NH-1,2,3-triazoles.[41-42] Following Majee and colleagues' initial discovery of this type of *O*-alkylation at the C2 atom of 4-HC, we describe here the effective synthesis of arylated vinyl ethers in keeping with our attempts to develop novel methodologies.[43]

The use of atom-efficient catalytic processes in the manufacturing of pharmaceuticals and fine chemicals has attracted attention as the pressing need for more sustainable, greener technologies becomes increasingly apparent. One such component that is receiving increasing attention is the use of alternative reaction media, which circumvents the problems associated with many of the traditional volatile organic solvents. Over time, a variety of suitable and eco-friendly alternative reaction media have been studied, such as supercritical fluids, ionic liquids, and polyethylene glycol.[44-46] According to this perspective, polyethylene glycol (PEG) functions as an environmentally friendly solvent and alternative reaction medium.[47-52] PEG has been studied as a solvent for chemical synthesis for more than 20 years. PEG is frequently used in chemical synthesis instead of hazardous organic solvents because of its biodegradable, biocompatible, non-toxic, and benign properties. PEG has reportedly been utilized as a solvent in a number of heterocyclic molecule synthesis processes, oxidations and reductions, heteroatom-heteroatom bond-forming events, and carbon-carbon and heteroatom-heteroatom bond-forming reactions.[53-62]

2. Results and Discussion

In continuation of our efforts in the development of C-C and C-heteroatom bond formation reactions,[41-42, 63] we have studied the reaction of 4-hydroxycoumarin (**1a**) and phenyl acetylene (**2a**) in a variety of solvents was the first step in the investigation (**Scheme 1**).

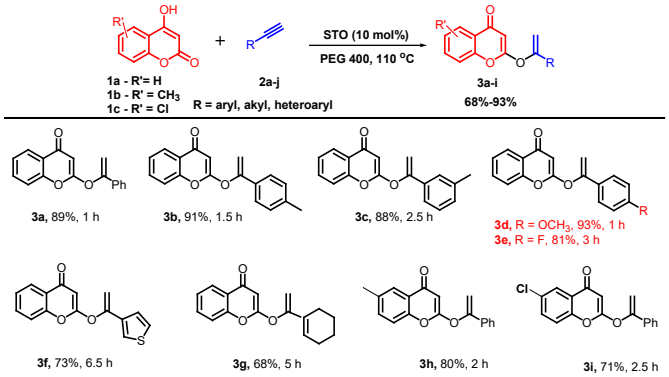


Entry	Catalyst (mol%)	Solvent	Temp (0 °C)	Yield (%)
1	SnO_2 (20 mol%)	CH_3CN	80	NR
2	STO (20 mol%)	CH_3CN	80	65
3	STO (20 mol%)	toluene	110	78
4	STO (20 mol%)	$CHCl_3$	reflux	38
5	STO (20 mol%)	THF	reflux	23
6	STO (20 mol%)	neat	110	17
7	STO (20 mol%)	PEG 400	110	90
8	**STO (10 mol%)**	**PEG 400**	**110**	**89**
9	STO (5 mol%)	PEG 400	110	56

Scheme 1. Optimization of the reaction conditions

In the target reaction, tin oxide was found to be ineffective (entry 1). The reaction was first conducted using 20 mol% STO in CH_3CN at 80 °C with ambient air. Fortunately, after a brief reaction period of one hour, the product, 2-((1-phenylvinyl)oxy)-4*H*-chromen-4one (**3a**), was obtained in good yield (65%) (entry 2). Motivated by this outcome, we conducted a number of reactions to improve the reaction circumstances; **Scheme 1** provides a summary of the outcomes. Common solvents including acetonitrile, THF, and $CHCl_3$ were initially used in the procedure, however the yields of the

intended products were lower (entries 2, 4, and 5). The intended product has a 78% isolated yield in toluene (entry 3). The reaction yield (entry 6) indicates that the reaction was ineffective when there was no solvent present. To our surprise, the yield of the intended product rose significantly (entry 8, 89%) when the reaction was carried out using 10 mol% STO in PEG 400. In contrast to the reaction condition from entry 8, altering the catalyst loading (entries 7 and 9) did not improve the reaction yield. The substrate scope of this protocol was examined when the optimal reaction conditions (10 mol% STO in PEG 400 at 110 °C in air) were determined. We concentrated on how different terminal alkynes interacted with 4-hydroxycoumarin (**1a**) (**Scheme 2**). Excellent yields of the required products (**3b-d**) were obtained by substituting electron-donating groups (CH_3, OCH_3) into phenyl acetylenes. With an electron-withdrawing substituent, phenol acetylene yielded the intended product **3e** in a high yield of 81%. Furthermore, at the ideal reaction circumstances, terminal alkyne replaced with a heterocyclic moiety also performed well (**3f**, 73%). Notably, aliphatic alkynes **2g** also reacted well with **1a**, yielding good yields (68%) of the corresponding products **3g**.



Scheme 2. Substrate scope of the reaction between 4-hydroxycoumarin and alkyne

In addition, we have exploited the utility of substituted 4-hydroxycoumarins (**1b** and **1c**) to establish the general applicability of the reaction conditions and the desired products were obtained in good yields (**3h**, 80%; **3i**, 71%). The mild reaction conditions prevent the products from breaking down or the starting materials from polymerizing. The recycling of the STO catalyst in the reaction between 4-HC (**1a**) and phenyl acetylene (**2**a) was then examined (**Fig. 3**). After the reaction was finished, the STO was cleaned with diethyl ether, and the solution was vacuum-filtered through a glass funnel that had been sintered. Immediately after drying, the recovered catalyst was used once more without requiring additional purification. The catalyst may be extracted and used up to five additional times without seeing a discernible decrease in its catalytic activity (85% isolated yield for **3a** after the fifth run).

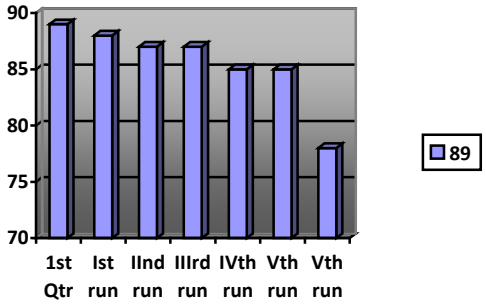


Fig. 3. Reusability chart of STO for the compound **3a**

In summary, using STO under mild reaction conditions has resulted in *O*-vinylation of 4-hydroxycoumarin from the reaction of 4-hydroxycoumarin and alkynes. Using this atom-efficient approach, a small library of 2-(vinyloxy)-4*H*-chromen-4-one derivatives (**3**) has been synthesized. PEG was determined to be the ideal solvent of choice to execute the reaction during optimization. Notable benefits of the current procedure include its rapid reaction time, recyclable heterogeneous catalyst and tolerance for a broad variety of functional groups.

3. Experimental procedure

A Bruker 400 (400 MHz) spectrometer was used to determine the ^1H and ^{13}C NMR spectra of solutions in $CDCl_3$. The signals are recorded as s (singlet), d (doublet), t (triplet), and m (multiplet), while the coupling constants J are supplied in Hz. Chemical shifts are indicated in parts per million (ppm, δ). A glass slide coated with silica gel (Merck, Silica gel G for TLC) was used for TLC. For column chromatography, silica gel (60-120 mesh) was utilized. Prior to usage, every solvent

was dried and distilled. All of the starting materials, including terminal alkynes **2** and 4-hydroxycoumarin **1a**, substituted 4-hydroxycoumarins (**1b** and **1c**), as well as other reagents, catalysts, and solvents, were acquired from commercial vendors such as Spectrochem Chemicals, Sigma-Aldrich, and Merck.

General procedure for the synthesis of 3a-i

A mixture of 4-hydroxycoumarin, **1a** or substituted 4-hydroxycoumarins, **1b-c** (1 mmol), terminal alkyne **2** (1 mmol) and STO (10 mol%) in PEG-400, stirred at 110 °C for the time specified. Following the conclusion of the reaction, which was observed by thin-layer chromatography, the mixture was diluted with anhydrous diethyl ether and allowed to stir for fifteen minutes. Subsequently, the layers were allowed to separate and the ether layer was decanted. The mother liquor (PEG) was set aside for subsequent runs, and this procedure was performed twice to provide the crude products in diethyl ether. Following solvent evaporation, the crude product was refined using column chromatography on silica gel with 1:1 petroleum ether/ethyl acetate to produce the pure corresponding products (**3a-i**).

Spectral data for the synthesized compounds

2-((1-Phenylvinyl)oxy)-4*H*-chromen-4-one (3a): 89%, light yellow solid; mp. 59-61 °C. IR (KBr): 1680 (-C=O), 1221 (-C-O) 832, 751 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.13-8.15 (m, 1 H, Ar), 7.63-7.67 (m, 1 H, Ar), 7.53-7.56 (m, 2 H, Ar), 7.35-7.46 (m, 5 H, Ar), 5.70 (s, 1 H, -C<u>H</u>=), 5.55 (d, *J* = 2.8 Hz, 1 H, -C<u>H</u>$_2$), 5.21 (d, *J* = 2.8 Hz, 1 H, C<u>H</u>$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.40 (-<u>C</u>=O), 166.37, 154.29, 153.89, 133.57, 132.43, 129.96, 129.02, 125.95, 125.60, 125.34, 123.05, 117.50, 102.39 (-<u>C</u>H$_2$=), 91.06 (-<u>C</u>H=).
2-((1-(*p*-Tolyl)vinyl)oxy)-4*H*-chromen-4-one (3b): 91%, yellow gum. IR (KBr): 1637, 1373, 1060, 616 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.15–8.12 (m, 1 H), 7.67–7.62 (m, 1 H), 7.45–7.37 (m, 4 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 5.69 (s, 1 H), 5.49 (d, *J* = 2.8 Hz, 1 H), 5.14 (d, *J* = 2.8 Hz, 1 H), 2.34 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.37 (-<u>C</u>=O), 166.45, 154.41, 153.90, 140.16, 133.51, 129.69, 129.63, 125.94, 125.55, 125.29, 123.08, 117.49, 101.47 (-<u>C</u>H$_2$=), 91.01 (-<u>C</u>H=), 21.41 (CH_3).
2-((1-(*m*-Tolyl)vinyl)oxy)-4*H*-chromen-4-one (3c): 88%, yellow gum. IR (KBr): 1684, 1274, 816, 768 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.15–8.13 (m, 1 H), 7.67–7.63 (m, 1 H), 7.46–7.34 (m, 4 H), 7.27–7.23 (m, 1 H), 7.18 (d, *J* = 7.6 Hz, 1 H), 5.70 (s, 1 H), 5.52 (d, *J* = 2.8 Hz, 1 H), 5.17 (d, *J* = 2.8 Hz, 1 H), 2.35 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.39 (-<u>C</u>=O), 166.44, 154.49, 153.91, 138.76, 133.53, 132.42, 130.78, 128.90, 125.99, 125.94, 125.56, 123.10, 122.52, 117.50, 102.23, 91.01, 21.57 (CH_3).
2-((1-(4-Methoxyphenyl)vinyl)oxy)-4*H*-chromen-4-one (3d): 93%, yellow gum. IR (KBr): 1685, 1260, 832, 763 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.15–8.13 (m, 1 H), 7.67–7.62 (m, 1 H), 7.49–7.37 (m, 4 H), 6.89–6.87 (m, 2 H), 5.71 (s, 1 H), 5.41 (d, *J* = 2.4 Hz, 1 H), 5.08 (d, *J* = 2.8 Hz, 1 H), 3.81 (s, 3 H, -OC<u>H</u>$_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.40 (-<u>C</u>=O), 166.51, 160.92, 154.18, 153.93, 133.52, 126.89, 125.96, 125.56, 124.97, 123.10, 117.49, 114.39, 100.38, 91.02, 55.50 (O<u>C</u>H$_3$).
2-((1-(4-Fluorophenyl)vinyl)oxy)-4*H*-chromen-4-one (3e): 81%, yellow gum. IR (KBr): 1685, 1229, 833, 753 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.15–8.13 (m, 1 H), 7.67–7.63 (m, 1 H), 7.56–7.52 (m, 2 H), 7.44–7.38 (m, 2 H), 7.08–7.04 (m, 2 H), 5.70 (s, 1 H), 5.48 (d, *J* = 2.8 Hz, 1 H), 5.17 (d, *J* = 2.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.33 (-<u>C</u>=O), 166.13, 164.90, 162.41, 153.90, 153.46, 133.64, 128.72, 127.40, 125.97, 125.67, 123.04, 117.48, 116.14, 102.0, 91.18.
2-((1-(Thiophen-3-yl)vinyl)oxy)-4*H*-chromen-4-one (3f): 73%, brown gum. IR (KBr): 1695, 1275, 949, 747 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.17–8.14 (m, 1 H), 7.68–7.64 (m, 1 H), 7.46–7.39 (m, 3 H), 7.35–7.33 (m, 1 H), 7.24–7.22 (m, 1 H), 5.77 (s, 1 H), 5.42 (d, *J* = 2.8 Hz, 1 H), 5.11 (d, *J* = 2.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.46 (-<u>C</u>=O), 166.42, 153.91, 150.60, 134.58, 133.61, 127.32, 125.97, 125.65, 124.95, 123.35, 123.08, 117.52, 101.35, 90.84.
2-((1-(Cyclohex-1-en-1-yl)vinyl)oxy)-4*H*-chromen-4-one (3g): 68%, yellow gum. IR (KBr): 1680, 1220, 828, 753 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.16–8.14 (m, 1 H), 7.65–7.61 (m, 1 H), 7.43-7.36 (m, 2 H), 6.12 (t, *J* = 8.4 Hz, 1 H), 5.67 (s, 1 H), 5.03 (d, *J* = 2.4 Hz, 1 H), 4.9 (d, *J* = 2.4 Hz, 1 H), 2.19–2.16 (m, 2 H), 2.12–2.08 (m, 2 H), 1.73–1.67 (m, 2 H), 1.60–1.54 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.60 (-<u>C</u>=O), 167.27, 155.13, 153.84, 133.41, 128.78, 128.00, 125.86, 125.45, 123.07, 117.44, 100.56, 89.65, 25.40, 24.85, 22.22, 21.71.
6-Methyl-2-((1-phenylvinyl)oxy)-4*H*-chromen-4-one (3h): 80%, yellow gum. IR (KBr): 1681, 1275, 815, 772 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.92 (d, *J* = 1.6 Hz, 1 H), 7.56–7.53 (m, 2 H), 7.46–7.43 (m, 1 H), 7.37–7.32 (m, 4 H), 5.69 (s, 1 H), 5.54 (d, *J* = 2.4 Hz, 1 H), 5.18 (d, *J* = 2.8 Hz, 1 H), 2.43 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.56 (-<u>C</u>=O), 166.32, 154.38, 152.13, 135.58, 134.65, 132.54, 129.94, 129.00, 125.40 (2C), 122.72, 117.22, 102.22, 91.04, 21.00 (CH_3).
6-Chloro-2-((1-phenylvinyl)oxy)-4*H*-chromen-4-one (3i): 71%, yellow gum. IR (KBr): 1682, 1261, 817, 771 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.10 (d, *J* = 2.4 Hz, 1 H), 7.60–7.57 (m, 1 H), 7.55–7.52 (m, 2 H), 7.41–7.36 (m, 4 H), 5.71 (s, 1 H), 5.56 (d, *J* = 2.8 Hz, 1 H), 5.20 (d, *J* = 2.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 178.06 (-<u>C</u>=O), 166.52, 154.38, 152.18, 133.69, 132.34, 131.66, 130.10, 129.09, 125.56, 125.36, 124.22, 119.15, 102.48, 91.09.

References

1. Cao D., Liu Z., Verwilst P., Koo S., Jangjili P., Kim J. S., and LinW. **(2019)** Coumarin-based small-molecule fluorescent chemosensors. *Chem. Rev.*, 119(18) 10403-10519. https://doi.org/10.1021/acs.chemrev.9b00145
2. Citarella A., Vittorio, S., Dank, C., and Ielo L. (**2024**) Syntheses, reactivity, and biological applications of coumarins. *Front Chem*., 12 1362992. DOI: 10.3389/fchem.2024.1362992
3. Annunziata F., Pinna C., Dallavalle S., Tamborini L., and Pinto A. (**2020**) An overview of coumarin as a versatile and readily accessible scaffold with broad-ranging biological activities. *Int. J. Mol. Sci.,* 214618. https://doi.org/10.3390/ijms21134618
4. Srikrishna D., Godugu C., and Dubey P. K. (**2018**) A review on pharmacological properties of coumarins. *Mini Rev. Med. Chem.,* 18 113-141. 10.2174/1389557516666160801094919
5. Balewski Ł., Szulta S., Jalińska A., and Kornicka A. (**2021**) A mini-review: Recent advances in coumarin-metal complexes with biological properties. *Front. Chem*., 9781779. 10.3389/fchem.2021.781779
6. Wu Y, Xu J, Liu Y, Zeng Y and Wu G (**2020**) A review on anti-tumor mechanisms of coumarins. *Front. Oncol*., 10 592853. DOI: 10.3389/fonc.2020.592853
7. Bouhaoui A., Eddahmi M., Dib M., Khouili M., Aires A., Catto M., and Bouissane L. (**2021**) Synthesis and biological properties of coumarin derivatives. A review. *ChemistrySelect* 16(24) 5848-5870. https://doi.org/10.1002/slct.202101346
8. Gouda M A., Salem M A., and Helal M H. (**2020**) A review on synthesis and pharmacological activity of coumarins and their analogs. *Curr. Bioactive Comp.,* 16(6) 818-836. https://doi.org/10.2174/1573407215666190405154406
9. Safavi-Mirmahalleh S-A., Golshan M., Gheitarani B., Hosseini M S., and Salami-Kalajahi M. (**2023**) A review on applications of coumarin and its derivatives in preparation of photo-responsive polymers. *Eur. Poly. J*., 198 112430. https://doi.org/10.1016/j.eurpolymj.2023.112430
10. Tolba M S., ul-Malik M A A., El-Dean A M K., Geies A A., Radwan S M., Zakic R M., Sayed M., Mohamed S K., and AbdelRaheem S A A. An overview on synthesis and reactions of coumarin based compounds. (**2022**) *Curr. Chem. Lett.,* 11 29-42; DOI: 10.5267/j.ccl.2021.009.007
11. Pulagam M., and Bollikolla H. (**2025**) PEG 400-Catalyzed C3 and O-alkylation reactions of 4-hydroxycoumarin-A study. *Curr. Chem. Lett*., 14(1) 129-138. DOI: 10.5267/j.ccl.2024.8.004
12. Borah B., Dwivedi K D., and Chowhan L R. (**2021**) 4-Hydroxycoumarin: A versatile substrate for transition-metal-free multicomponent synthesis of bioactive heterocycles. *Asian J. Org. Chem.,* 10(12) 3101-3126. https://doi.org/10.1002/ajoc.202100550
13. Jung J-C., and Park O-S. (**2009**) Synthetic approaches and biological activities of 4-hydroxycoumarin derivatives. *Molecules.* 14(11) 4790-4803. DOI: 10.3390/molecules14114790
14. Romal J R A., and Ong S K. (**2023**) Extending the library of 4-hydroxycoumarin derivatives with potential pharmacological activity by a catalyst-free and purification-free method. *ChemistrySelect.* 8(10) e202300519. https://doi.org/10.1002/slct.202300519
15. Ziarani G M., Moradi R., Ahmadi T., and Gholamzadeh P. (**2019**) The molecular diversity scope of 4-hydroxycoumarin in the synthesis of heterocyclic compounds *via* multicomponent reactions. *Mol. Divers.,* 23 1029-1064. https://doi.org/10.1007/s11030-019-09918-7
16. Abdou M M., El-Saeed R A., and Bondock S. (**2019**) Recent advances in 4-hydroxycoumarin chemistry. Part 1: Synthesis and reactions. *Arabian J. Chem*., 12(1) 88-121. https://doi.org/10.1016/j.arabjc.2015.06.012
17. Abdou M M., El-Saeed R A., and Bondock S. (**2019**) Recent advances in 4-hydroxycoumarin chemistry. Part 2: Synthesis and reactions. *Arabian J. Chem*., 12(7) 974-1003. https://doi.org/10.1016/j.arabjc.2015.06.029
18. Su Q., Qian H., Li Z., Sun X., and Wang Z. (**2017**) Lewis-base-catalyzed alkylation reaction of 4-hydroxycoumarins with allenoates: Regioselective synthesis of 2*H*-[3,2-*c*] furocoumarins and 4-hydroxycoumarin vinyl ether derivatives. *Asian J. Org. Chem.,* 6(5) 512-515. https://doi.org/10.1002/ajoc.201600631
19. (a) Bandaru S K., and Risi M C. (**2022**) $Zn(OAc)_2.2H_2O$-Catalyzed C3-alkylation and *O*-alkylation of 4-hydroxycoumarin derivatives. *Caribbean J. Sci. Tech.*, 10(2) 10-16. DOI: 10.55434/CBI.2022.2010 and references cited therein. (b) Sharapov A D., Fatykhov R F., and Khalymbadzha I A. (**2024**) Synthesis of fluorophores based on benzo[*g*]coumarin framework (microreview). *Chem. Heterocycl. Comp.,* 60 26-28. https://doi.org/10.1007/s10593-024-03286-3
20. Chatterjee R., Mukherjee A., Zyryanov G. V., and Majee A. (**2020**) Metal and solvent free direct C3-alkylation of 4-hydroxycoumarins with styrene. *AIP Conf. Proc.,* 2280 040011. https://doi.org/10.1063/5.0018529
21. Vogt C., and Weckhuysen, B.M. (**2022**) The concept of active site in heterogeneous catalysis. *Nat. Rev. Chem.,* 6 89-111. https://doi.org/10.1038/s41570-021-00340-y
22. Narayana V R., Pudukulathan Z., and Varala R. (**2013**) SO_4^{2-}/SnO_2-Catalyzed efficient one-pot synthesis of 7,8-dihydro-2*H*-Chromen-5-ones by formal [3+3] cycloaddition and 1,8-dioxo-octahydroxanthenes via a Knoevenagel condensation. *Org. Commun*., 6(3) 110-119.
23. Koduri R G., Boodida S., Varala R., Pagadala R., and Damera T. (**2024**) Ultrasound-assisted multicomponent reaction catalyzed by SO_4^{2-}/SnO_2 for the synthesis of tetraaryl imidazoles: Computational study against 1O75 protein of syphilis bacteria. *Russ. J. Gen. Chem*., 94(5) 1159-1166. DOI: https://doi.org/10.1134/S1070363224050141

24. Koduri R G., Varala R., Boodida S., Damera T., and Pagadala R. (**2024**) A solvent free green approach for the construction of 1,3,5-triaryl benzene derivatives under sulphated tin oxide catalyst. *Rasayan J. Chem*., 17(3) 1258-1264. DOI: http://doi.org/10.31788/RJC.2024.1738905
25. Koduri R G., Varala R., Boodida S., Pagadala R., and Damera T. (**2024**) Ultrasound assisted and SO_4^{2-}/SnO_2 catalyzed one-pot multicomponent reaction for the synthesis of 1,2,3,4,6-pentasubstituted piperidines. *Ind. J. Heterocyclic Chem.,* 34(2) 211-217. DOI: 10.59467/IJHC.2024.34.211
26. Chennuboyina S., Pallapati R K., Saradhi Ch V., Varala R., and Bollikolla H B. (**2023**) Sulfated tin oxide (STO)-catalyzed efficient synthesis of β-enaminoesters. *Caribbean J. Sci. Tech.,* 11(2) 21-23. DOI: 10.55434/CBI.2023.20104
27. Totawar P R., Varala R., Kotra V., and Pulle J S. (**2023**) Synthesis of phthalimide and naphthalimide derived Biginelli compounds and evaluation of their anti-inflammatory and anti-oxidant activities. *Curr. Chem. Lett.,* 12 249-256. DOI: https://doi.org/10.5267/j.ccl.2023.1.004
28. Koduri R G., Pagadala R., Varala R., and Boodida S. (**2021**) An effective process for the synthesis of dihydropyridines *via* SO_4^{-2}/SnO_2-catalyzed Hantzsch reaction. *J. Chin. Chem. Soc.,* 68(2) 333-337; DOI: https://doi.org/10.1002/jccs.202000264
29. Koduri R G., Pagadala R., Boodida S., and Varala R. (**2020**) SO_4^{-2}/SnO_2-catalyzed cyclocondensation for the synthesis of fully functionalized pyridines. *J. Heterocycl. Chem.,* 57(2) 923-928. DOI: https://doi.org/10.1002/jhet.3806
30. Pol U N., Niwadange S N., Mathapati S R., and Kagne R P. (**2023**) Synthesis of bioactive polyhydroquinolines using sulfated tin oxide as an efficient solid superacid catalyst. *Rasayan J. Chem*., 16(2) 752-759. http://doi.org/10.31788/RJC.2023.1628183
31. Kim Y., Kim J., Kim H. W., Kim T-W., Kim H. J., Chang H., Park M. B., and Chae H-J. (**2019**) Sulfated tin oxide as highly selective catalyst for the chlorination of methane to methyl chloride. *ACS Catal.,* 9(10) 9398-9410. https://doi.org/10.1021/acscatal.9b02645
32. Cho S. -M., Hong C. -Y., Park S. -Y., Lee D. -S., Choi J. -H., Koo B., and Choi I. -G. (**2019**) Application of sulfated tin (IV) oxide solid superacid catalyst to partial coupling reaction of α-pinene to produce less viscous high-density fuel. *Energies* 12(10), 1905. https://doi.org/10.3390/en12101905
33. Kaminwar N S., Tekale S U., Nakkalwar S L., and Pawar, R P. (**2021**) Sulfated tin oxide: A convenient heterogeneous catalyst for the synthesis of 4-arylmethylidene-3-substituted-isoxazol-5(4*H*)-ones. *Lett. Org. Chem.,* 18(12) 945-949. DOI: 10.2174/1570178618666210729114845
34. Dubasi N., and Varala R. (**2022**) Applications of sulfated tin oxide (STO) in organic synthesis-From 2016 to 2021. *Heterocycles* 104(5) 843-853. DOI: https://doi.org/10.3987/REV-22-978
35. Varala R., Narayana V. R., Kulakarni S. R., Khan M., Alwarthan A., and Adil S. F. (**2016**) Sulfated tin oxide (STO)-Structural properties and application in catalysis: A review. *Arabian J. Chem.,* 9(4) 550-573. DOI: https://doi.org/10.1016/j.arabjc.2016.02.015
36. Koduri R G., Pagadala R., Boodida S., and Varala R. (**2022**) Ultrasound promoted synthesis of 2-amino-4-*H*-pyranoquinolines using sulphated tin oxide as a catalyst. *Polycycl. Aromat. Compd.,* 42(10) 6908-6916. DOI: https://doi.org/10.1080/10406638.2021.1992456
37. Chandane W., Gajare S., Kagne R., Kukade M., Pawar A., Rashinkar G., and Tamhankar B. (**2022**) Sulfated tin oxide (SO_4^{-2}/SnO_2): an efficient heterogeneous solid superacid catalyst for the facile synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones. *Res. Chem. Intermed.*, 48 1439-1456. DOI: https://doi.org/10.1007/s11164-022-04670-4
38. Ashine F., Balakrishnan S., Kiflie Z., and Tizazu B. Z. (**2023**) Epoxidation of *Argemone mexicana* oil with peroxyacetic acid formed *in-situ* using sulfated tin (IV) oxide catalyst: Characterization; kinetic and thermodynamic analysis. *Heliyon* 9(1) e12817. DOI: https://doi.org/10.1016/j.heliyon.2023.e12817
39. Kagne R., Niwadange S., Kalalawe V., Khansole G., and Munde D. (**2021**) Synthesis of bioactive 1,4-DHPs using sulfated tin oxide as an efficient solid superacid catalyst. 400(1) 2100056, Special Issue:International Conference on Advances in Materials Science - ICAMS 2021. https://doi.org/10.1002/masy.202100056
40. Narayana V., Varala R., and Zubaidha P. K. (**2012**) SO_4^{2-}/SnO_2-Catalyzed C3-alkylation of 4- hydroxycoumarin with secondary benzyl alcohols and *O*-alkylation with *O*- acetyl compounds. *Int. J. Org. Chem.*, 2 (3A) 287-294. DOI: 10.4236/ijoc.2012.223039
41. Chinta B., Chintalapudi R., and Satyadev T. (**2024**) Sulfated tin oxide (STO)-catalyzed efficient synthesis of 4-aryl-NH-1,2,3-triazoles. *Curr. Chem. Lett.*, 13(4) 669-676. DOI: 10.5267/j.ccl.2024.5.004
42. Krishna C., Seetharam K., and Satyadev T. (**2024**) Synthesis of β-amino alcohols by ring opening of epoxides with amines catalyzed by sulfated tin oxide under mild and solvent-free conditions. *Curr. Chem. Lett.*, 13(2) 343-350. DOI: 10.5267/j.ccl.2023.11.004
43. Chatterjee R., Santra S., Zyryanov G V., and Majee A. (**2019**) Vinylation of carbonyl oxygen in 4-hydroxycoumarin: Synthesis of heteroarylated vinyl ethers. *Synthesis* 51(11) 2371-2378. DOI: 10.1055/s-0037-1610696
44. Andrade C. K. Z., and Alves L. M. (**2005**) Environmentally benign solvents in organic synthesis: current topics. *Curr. Org. Chem.,* 9 195-218. https://doi.org/10.2174/1385272053369178
45. Winterton N. (**2021**) The green solvent: a critical perspective. *Clean Technol. Environ. Policy.,* 23(9) 2499-2522. DOI: 10.1007/s10098-021-02188-8

46. Sheldon R A. (**2005**) Green solvents for sustainable organic synthesis: state of the art. *Green Chem.,* 7267-278. https://doi.org/10.1039/B418069K
47. Raithak P V., Dhabe A S., Atkore S T., Alam M M., Kotra V., Varala R. (**2022**) Synergetic catalytic bleaching earth clay and PEG-400 for rapid synthesis of polyhydroquinoline derivatives and their DPPH radical scavenging activity. *Ind. J. Heterocyclic Chem.,* **2022**, *32(1)*, 85-90; https://connectjournals.com/01951.2022.32.85
48. Atkore S T., Bondle G M., Raithak P V., Kamble V T., Varala R., Kuniyil M., Hatshan M R., Shaik B., Adil S F., and Hussain M A. (**2021**) Synthesis of 14-substituted-14*H*-dibenzo[a,j]xanthene derivatives in presence of effective synergetic catalytic system bleaching earth clay and PEG-600. *Catalysts 11(11)*, 1294; https://doi.org/10.3390/catal11111294
49. Soni J. P., Nusrat S., Sethiya A., and Agarwal S. **(2020**) Polyethylene glycol: A promising approach for sustainable organic synthesis. *J. Mol. Liq.,* 315, 113766. https://doi.org/10.1016/j.molliq.2020.113766
50. Hoffmann M. M. Polyethylene glycol as a green chemical solvent. (**2022**) *Curr. Opin. Colloid In.,* 57 101537. https://doi.org/10.1016/j.cocis.2021.101537
51. Liwei X., Fucai D., Zheng L., Xuemin J., Jie K., and Guangxian L. (**2019**) Polyethylene glycol: A new medium for green organic synthesis[J]. *Chin. J. Org. Chem*., 39(3) 648-660. https://doi.org/10.6023/cjoc201807056
52. Kardooni R., and Kiasat A. R. (**2020**) Polyethylene glycol as a green and biocompatible reaction media for the catalyst free synthesis of organic compounds. *Curr. Org. Chem*., 24 1275-1314. 10.2174/1385272824999200605161840
53. Chen J., Spear S. K., Huddleston J. G., and Rogers R. D. (**2005**) Polyethylene glycol and solutions of polyethylene glycol as green reaction media. *Green Chem*., 7 64-82. https://doi.org/10.1039/B413546F
54. Qadir M., Yaseen A., and Shah W. A. (**2023**) PEG-400 catalysed selective C-Se cross dehydrogenative coupling: An ultrasonication-assisted green strategy. *Results Chem.,* 5 100944. https://doi.org/10.1016/j.rechem.2023.100944
55. Yaseen A., Waseem M. A., Qadir M., Dar P. A., Hijazi S., Hussain M. A., and Shah W. A. (**2022**). PEG-400 catalyzed N-C, O-C & C-S bond formations: A robust sonication promoted synthesis of benzo[*d*]oxazole-2(3*H*)-thione & benzo[*d*]thiazole-2(3*H*)-thione hybrids. *Analytical Chem. Lett.*, 12(3) 302-309. https://doi.org/10.1080/22297928.2022.2068376
56. Hari Babu B., Vijay K., Krishna K. B. M., Sharmila N., and Baby Ramana M. (**2016**) An efficient PEG-400 mediated catalyst free green synthesis of 2-amino-thiazoles from α-diazoketones and thiourea. *J. Chem. Sci.,* 128(9) 1475-1478. https://doi.org/10.1007/s12039-016-1130-0
57. Mekala R S., Balam S K., Harinath J P S., Gajjal R R., Cirandur S R., and Weaver G. (**2015**). Polyethylene glycol (PEG-400): An efficient medium for the synthesis of 1,2-disubstituted benzimidazoles. *Cogent Chemistry* 1(1) 1049932. https://doi.org/10.1080/23312009.2015.1049932
58. Nagaraju K., Gummidi L., Maddila S., and Jonnalagadda S B. (**2020**) Polyethylene glycol (PEG-400) mediated one-pot green synthesis of 4,7-dihydro-2*H*-pyrazolo[3,4-*b*]pyridines under catalyst-free conditions. *ChemistrySelect* 5(40), 12407-12410. https://doi.org/10.1002/slct.202002538
59. Patnala H., Abbo H S., Potla K M., Titinchi S J J., and Chinnam S. (**2019**) Polyethylene glycol (PEG-400): An efficient one-pot green synthesis and anti-viral activity of novel α-diaminophosphonates, *Phosphorus, Sulfur, and Silicon and the Relat. Elem.*, 194(11) 1035-1039. https://doi.org/10.1080/10426507.2019.1597365
60. Hasaninejad A., and Beyrati M. (**2018**) Eco-friendly polyethylene glycol (PEG-400): a green reaction medium for one-pot, four-component synthesis of novel asymmetrical bis-spirooxindole derivatives at room temperature. *RSC Adv.,* 8(4) 1934-1939. https://doi.org/10.1039/c7ra13133j
61. Lim H Y., and Dolzhenko A V. (**2023**) Polyethylene glycol as a green medium for the microwave-assisted synthesis of guanamines. *ChemistrySelect* 8(29) e202302106. https://doi.org/10.1002/slct.202302106
62. Ponduri R., Kumar P., and Vadali L. R. (**2018**) PEG-400 promoted a simple, efficient, and recyclable catalyst for the one-pot eco-friendly synthesis of functionalized isoxazole substituted pyrroles in aqueous medium. *Synth.Commun.*, 48(24) 3113-3122. https://doi.org/10.1080/00397911.2018.1535078
63. Chinta B., Satyadev T., and Adilakshmi A. (**2023**) $Zn(OAc)_2 \bullet 2H_2O$-catalyzed one-pot synthesis of divergently substituted imidazoles. *Curr. Chem. Lett.*, 12(1) 175-184. DOI: 10.5267/j.ccl.2022.8.007

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