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Hypervalent Iodine(III) Mediated Tosyloxylation of 4-Hydroxycoumarins

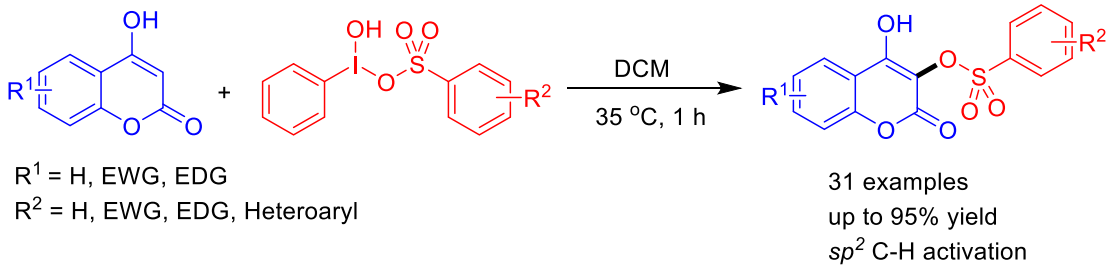
Bowen Xu,[†] Yiping Gao,[‡] Jianwei Han,*[†] Zejing Xing,[†] Sihan Zhao,[†] Ziyang Zhang,[†] Runlin Ren,[†] and Limin Wang*[†]

[†]Key Laboratory for Advanced Materials and Feringa Nobel Prize Scientist Joint Research Center, Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science & Technology, 130 Meilong Road, Shanghai, 200237, China

[‡] Shanghai Xuhui Central Hospital, Shanghai 200031, P. R. China

Email: Jianwei Han – jianweihan@ecust.edu.cn; Limin Wang – wanglimin@ecust.edu.cn

* Corresponding author



Abstract

An efficient approach was developed for synthesis of 3-tosyloxy-4-hydroxycoumarins under mild conditions by using Koser's reagents. The reaction tolerated various functional groups and the products served as useful aromatic building blocks. Additionally, a plausible mechanism via iodonium ylide was proposed and the oral anticoagulant Warfarin was synthesized in good yield.

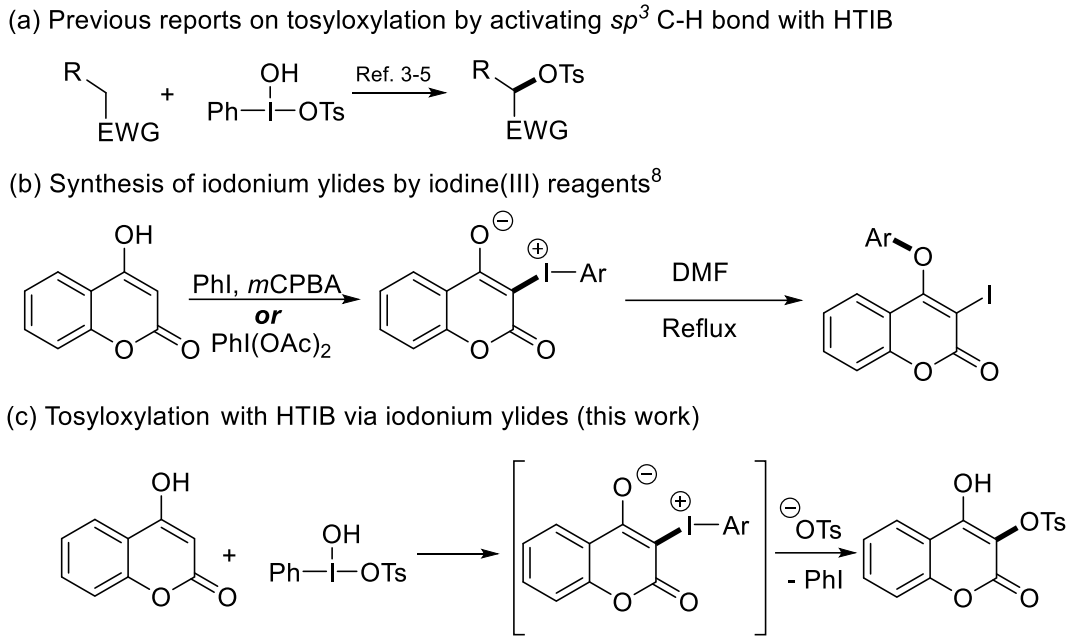
Key words: Tosyloxylation, HTIB, Synthetic methods, Hypervalent iodine, Ylide.

Introduction

Recent years have witnessed a rapid growth in the field of hypervalent iodine chemistry with exploring their novel reactivity in a diverse range of chemical transformations.[1] For example, hydroxy(tosyloxy)iodo]benzene (HTIB), which is known as Koser's reagent, is one of these useful reagents to perform α-functionalization of ketones such as tosyloxylation, hydroxylation, and acyloxylation.[2] Following the seminal report that Koser et al. used HTIB to produce corresponding α-tosyloxyketones from enolizable ketones and its first asymmetric version by Wirth,[3] much efforts were contributed to explore the activated aliphatic ketones as well as the catalytic and enantioselective version of these reactions (Scheme 1a).[4] Recently, Legault et al. reported an elegant study on the mechanistic insights of the α-tosyloxylation of ketones with computational method, in which HTIB formed a novel iodonium intermediates as Lewis acids to enhance the electrophilicity of carbonyl compounds.[5] An experimental evidence supported this mechanism in the α-tosyloxylation of enol esters by the same research group.[6] As such, HTIB involved tosyloxylations for transferring TsO-groups to the target products would be ideal. Considering that arylsulfonates can serve as excellent leaving groups for further coupling reactions, access to the aromatic compounds bearing OTs group is a topic of much interest. The tosyloxylations of aromatic substrates with HTIB is one highly desirable method. However, in sharp contrast, tosyloxylations of aromatics or heterocyclic rings of this type have rarely been

reported.[7] In fact, as early as 1978, Kappe et al. reported the reaction of 4-hydroxycoumarin with (diacetoxyiodo)benzenes (DIB) to afford iodonium ylides in good yields. Very recently, Panda et al. reported an efficient protocol for the synthesis of coumestans, in which the iodine(III) reagents generated from iodobenzene in situ by oxidants of *m*CPBA to afford the ylides.[8] The iodonium ylides, also called as zwitterionic iodonium compounds (ZICs),[9] were transformed into 4-aryloxy-3-iodocoumarins via a variation of Smiles rearrangement, which further gave coumestan derivatives (Scheme 1b).[10]

On the other hand, 4-hydroxycoumarins are important compounds in the synthesis of bioactive molecules such as warfarin, acenocoumarol and phenprocoumon, which are commonly prescribed as oral anticoagulants for prevention and treatment of thromboembolic disorders.[11] Additionally, sulfonyl group is a biologically active pharmacophore as a part of several clinically used drugs.[12] As a result, recently many researchers have shown interested in sulfonyl-containing coumarin derivatives. For examples, in 2016, Salar et al. reported a library of coumarin sulfonates by reacting hydroxycoumarin with different substituted sulfonyl chlorides, in which eleven compounds were demonstrated to have potential suppressive effect on production of reactive oxygen species. Later, coumarin derived sulfonyl esters were also found to be effective inhibitors of alkaline phosphatases.[13] However, to the best of our knowledge, there is no report concerning synthesis of 3-sulfonyl-4-hydroxycoumarins which might also be potentially bioactive.



Scheme 1. Tosyloxylation with HTIB.

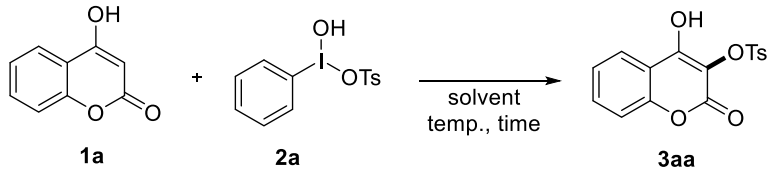
Given our continued interest in the hypervalent iodine chemistry,[14] we recently synthesized iodonium salts that incorporated vicinal groups for exploring their unique reactivity.[14a] When the reactivity pattern was attempted to prepare heterocyclic iodonium salts bearing vicinal OTf groups, the tosyloxylation of 4-hydroxycoumarins proceeded smoothly without phenyl migration by thermal rearrangement of iodonium ylides. Herein we reported the detailed results in the preparation of 3-sulfonyl substituted 4-hydroxycoumarins (Scheme 1c).

Results and Discussion

Preliminarily, treatment of 4-hydroxycoumarin (**1a**) with 0.4 equivalent HTIB (**2a**) as model reaction in dichloromethane (DCM) at room temperature gave 40% yield of **3aa** after 3 hours (Table 1, entry 1). In order to improve the yield of **3aa**, we found that the conversion of **1a** afforded **3aa** in 70% or 77% yield respectively when 1 or 1.2 equivalent HTIB was used. Further increasing the amount of **2a** did not result in a

better yield (Table 1, entries 2-4). Then, the effect of solvent was also examined and the results were shown in Table 1. Reaction with toluene or MeCN as solvent furnished lower yields at 46% and 52% respectively. Almost no reaction took place in DMF and the reaction mixture changed into dark color at the moment when the solvent was added (Table 1, entries 5-7). To our delight, the elevated temperature of 35 ^{o}C increased the yield to 85%, while higher temperature cannot result in a better result (Table 1, entries 8-9). An investigation of reaction time indicated that the reaction can finish in one hour (Table 1, entries 10-11).

Table 1. Reaction optimization[a]



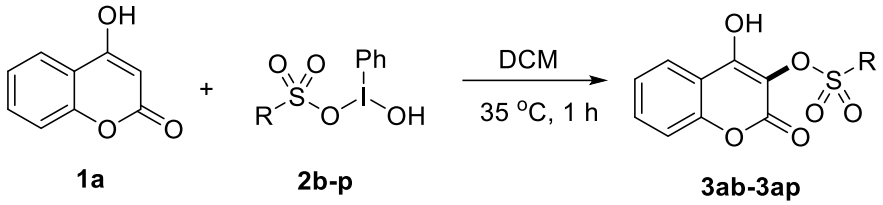
Entry	Eqv. of **2a**	Solvent	Temp.(^{o}C)	Time(h)	Yield (%)
1	0.4	DCM	r.t.	3	40
2	1	DCM	r.t.	3	70
3	1.2	DCM	r.t.	3	77
4	2	DCM	r.t.	3	77
5	1.2	Tol	r.t.	3	46
6	1.2	MeCN	r.t.	3	52
7	1.2	DMF	r.t.	3	-
8	1.2	DCM	35	3	85
9	1.2	DCM	reflux	3	86
10	1.2	DCM	35	1	85
11	1.2	DCM	35	0.5	36

[a] Reaction conditions: **1a** (0.3 mmol), **2a** and solvents (10 mL).

Next, the substrate scope of tosyloxylation of 4-hydroxycoumarin (**1a**) with various Koser's reagents was explored under the optimized conditions. As shown in Table 2,

the 3-position tosyloxylation of **1a** with Koser's reagents including meta- or para-halogen substituted aryl motifs afforded the corresponding products **3ab**-**3ae** in 71-72% yields by the transfer of arylsulfonyl groups (Table 2, entries 1-4). A moderate yield of 68% for **3af** was achieved with **2f** bearing phenyl group (Table 2, entry 5). Koser's reagent of **2g** with 2,4-dinitroaryl unit resulted in the desired product (**3ag**) in an acceptable yield of 46%. Regarding Koser's reagents of **2h-2k** contained electron-withdrawing groups such as nitro-, trifluoromethoxy, trifluoromethyl and nitrile groups, the reaction afforded **3ah**-**3ak** in 54-75% yields (Table 2, entries 6-10). Furthermore, when the Koser's reagents of **2l-2m** with electron-donating groups were used in this protocol, the corresponding products of **3al** and **3am** were isolated in excellent yields of 85% and 90% respectively, which suggested HTIBs bearing electron-donating group favor this reaction (Table 2, entries 11-12). Of note, the methylsulfonyl group can be transferred to give **3an** in 43% yield when **2n** was employed. Additionally, hydroxyl-(phenyl)-iodanyl naphthalene-1-sulfonate (**2l**) was also well tolerated in this reaction. It was worth to mention that **3ap** with a camphor sulfonate motif was afforded in 59% yield with this procedure (Table 2, entry 15).

Table 2. Scope of diverse HTIB in tosyloxylation[a]



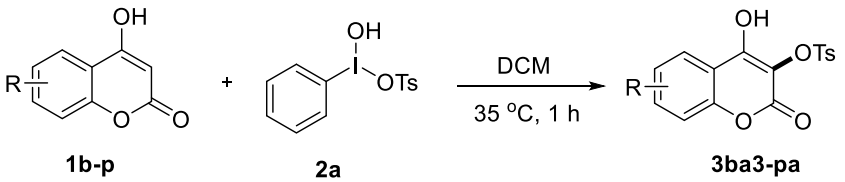
Entry	R	Product	Yield (%)
1	4-FC_6H_4	**3ab**	71
2	4-ClC_6H_4	**3ac**	72
3	4-BrC_6H_4	**3ad**	71
4	3-ClC_6H_4	**3ae**	72
5	C_6H_5	**3af**	68
6	2,4-di$NO_2C_6H_4$	**3ag**	46
7	4-$OCF_3C_6H_4$	**3ah**	54
8	4-$CF_3C_6H_4$	**3ai**	72
9	4-CNC_6H_4	**3aj**	75
10	4-$NO_2C_6H_4$	**3ak**	72
11	4-^{t}BuC_6H_4	**3al**	85
12	4-$OMeC_6H_4$	**3am**	90
13	Me	**3an**	43
14	2-Naphthalene	**3ao**	59
15	10-Camphor	**3ap**	55

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol) and DCM (10 mL) at 35 °C for 1 hour.

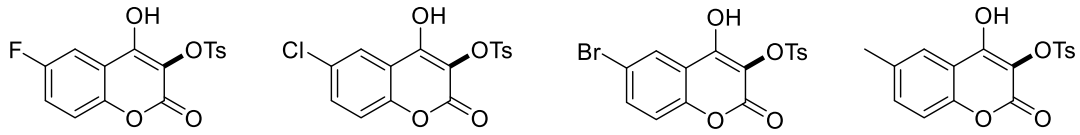
We successively examined the structural diversity of a variety of 4-hydroxycoumarin derivatives by changing the substituted groups on the molecular skeleton. As shown in Table 3, both 6- and 7- position substituted 4-hydroxycoumarins with halogens, methyl and methoxy groups were well tolerated in the tosyloxylation reaction, **3ba-3ja** were furnished in 38-82% yields. Of note, the reaction of 7-dimethylamine-4-hydroxycoumarin **1k** with HTIB afforded the product **3ka** in 64% yield. The compound of **3ka** emitted strong fluorescence by irradiation of ultraviolet light because of its D-π-A structure. Interestingly, methyl substituted derivatives **1l-1m** accomplished the tosyloxylated products in good yields of 77-80%.

Moreover, the tosyloxylated benzo-4-hydroxycoumarin derivative **3na** was synthesized in 78% yield under the standard conditions with this protocol. Furthermore, 4-hydroxy-1-methylquinolinone and 4-hydroxy-6-methyl-pyranone were adopted in this reaction, the corresponding products of **3oa** and **3pa**[15] were obtained in 72% and 95% yields, respectively.

Table 3. Scope of 4-hydroxycoumarin derivatives in 3-position tosyloxylation[a]



1b-p **2a** **3ba3-pa**

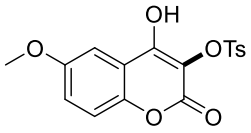


3ba, yield 57%

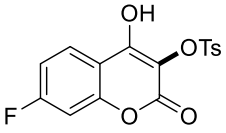
3ca, yield 68%

3da, yield 65%

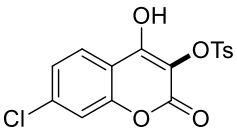
3ea, yield 82%



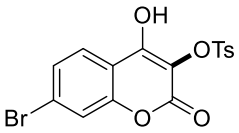
3fa, yield 50%



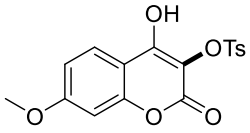
3ga, yield 38%



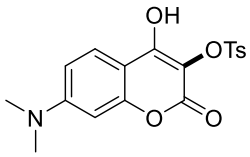
3ha, yield 53%



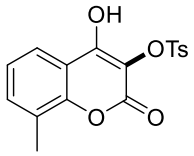
3ia, yield 61%



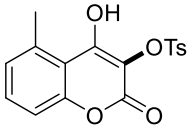
3ja, yield 70%



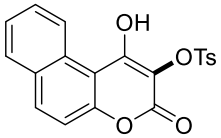
3ka, yield 64%



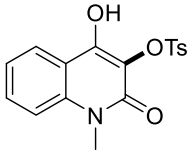
3la, yield 77%



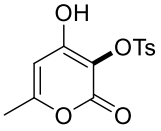
3ma, yield 80%



3na, yield 78%



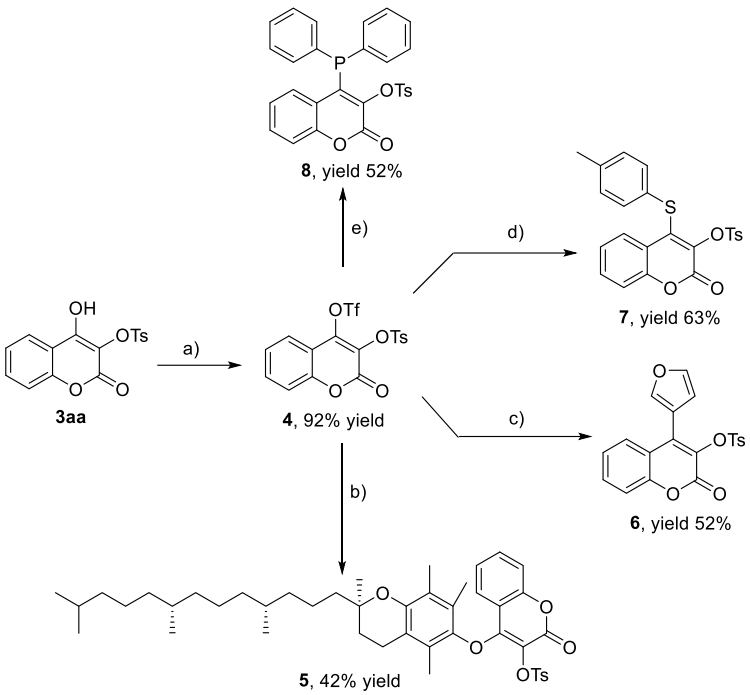
3oa, yield 72%



3pa, yield 95%[b]

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol) and DCM (10 mL) at 35 °C for 1 hour. [b] DCM (3 mL) was used.

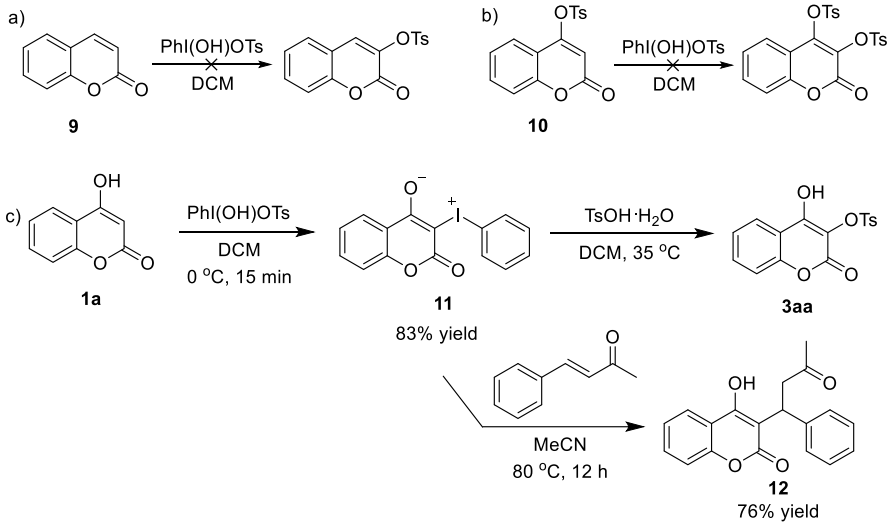
Next, to show the potential utility of target products, an attempt to convert the tosyloxylation products into aromatic building blocks was described in Scheme 2. In consideration of the benzenesulfonyl group as an excellent leaving group (LG), **3aa** was tried in the coupling reactions, however, **3aa** did not exhibit any reactivity due to the existence of ortho-carbonyl and hydroxyl groups. An alternative strategy to protect the hydroxyl with trifluoromethanesulfonic anhydride (Tf_2O) was employed to give product **4** in 92% yield. Taking advantage of the leaving group of OTf, several synthetic manipulations to transform **4** into functional molecules **5-8** were carried out. Of note, biologically interesting molecule of vitamin E was directly coupled with **4** in the presence of K_2CO_3 as base; the corresponding conjugated compound **5** was formed in 42% yield. Additionally, the transition metal free coupling reaction of **4** under strong basic conditions using LiHMDS was attempted with diphenylphophane, para-toluenethiol and furan, respectively, the corresponding products **6-8** were obtained in 52-63% yields, which suggested **4** was an excellent coumarin-based motif to prepare the related target molecules. For newly-formed benzenesulfonyl group as leaving group (LG), further transformation of **6-8** with general coupling reactions of Suzuki coupling and others, unfortunately, no positive result was achieved so far, which may be due to the steric hindrance in the ortho-positions.



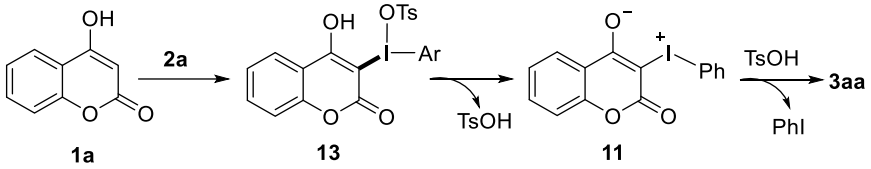
Scheme 2. Versatility of **3aa** in further transformations. a) Tf_2O, Et_3N, DCM. b) K_2CO_3, Vitamin E, DMF, 100 °C. c) Furan, LiHDMs, Tol, r.t.. d) 4-Methylbenzenethiol, LiHDMs, Tol, 110 °C. e) Ph_2PH, LiHDMs, Tol, 110 °C. DMF = *N*,*N*-dimethylformamide, LiHDMs = Lithium bis(trimethylsilyl)amide, Tol = toluene.

Control experiments were also performed to clarify the mechanism of this transformation. Coumarin (**9**) and 4-tosyl substituted coumarin (**10**) were unable to form the corresponding products under the standard conditions (Scheme 3a & 3b). A low temperature reaction afforded the intermediate **11** in 83% isolated yield, which was isolated and determined by NMR and HRMS.[9] Furthermore, the iodonium ylide **11** can afford **3aa** in 80% yield in the presence of TsOH (Scheme 3c). Interestingly, the oral anticoagulant Warfarin was synthesized by using the intermediate of **11**. Warfarin **12** was synthesized in one step with 76% yield, which provides an alternative way to afford this bioactive molecule without catalyst or addtional promotors.

As such, a plausible mechanism was proposed in scheme 4, of 4-hydroxycoumarin in enol-keto tautomerism attacked the positive iodine center of Koser's reagent to give **13**, which formed iodonium ylide **11** by leaving of TsOH. **11** was easily transformed into **3aa** with the anion of OTs in the solvent.



Scheme 3 Control experiments and synthesis of warfarin



Scheme 4 Plausible mechanism

Conclusion

In summary, we have developed an alternative method for 3-position tosyloxylation of 4-hydroxycoumarin derivatives via sp^2 C-H bond activation. The current approach can tolerate various substrates under mild reaction condition without using transition-metal catalyst. Furthermore, the oral anticoagulant Warfarin was synthesized with this procedure, which demonstrated the potential applications of this method in organic synthesis.

Experimental Section

General Information. (a) Methods: ^{1}H, ^{13}C spectra were recorded on a Bruker AVANCE 400 spectrometer, operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR respectively. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; Mass spectra were in general recorded on a Waters LCT Premier XE spectrometer; Column chromatography was performed with silica gel (200-300 mesh ASTM). All solvents were dried and/or distilled by standard methods. **(b) Materials:** All solvents were dried and/or distilled by standard methods. All reagents were purchased from commercial sources and used without further purification. The [hydroxy(sulfonyloxy)iodo]arenes and the substituted 4-hydroxy-2*H*-chromen-2-one were synthesized according to the literature procedures [16-18,4c] or commercially available and were used as recevied. The preparation of all other materials is described in detail below.

Procedure for Synthesis of 3-tosylated 4-hydroxy-2*H*-chromen-2-one:

To a 50 ml round-bottomed flask was added the substituted 4-hydroxy-2*H*-chromen-2-one **1** (0.3 mmol) and [hydroxy(sulfonyloxy)iodo]arenes **2** (0.36 mmol). DCM (10 ml) was added and the mixture was stirred at 35 ^{o}C under oil bath for 1 hour. Then the solvent was evaporated under vacuum. The crude products were purified using flash column chromatography on silica gel to afford the desired product.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate (3aa). Following the general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2a** (141 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 85 mg (85%) of **3aa** as white solid. For a gram-scale experiment, following the general procedure, the reaction of **1a** (1.62 g, 10 mmol), **2a** (4.7 g, 12 mmol) and DCM (100 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 2.72 g (82%) of **3aa** as white solid. M.P.: 155-156 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.72 (t, J = 7.8 Hz, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.49 – 7.42 (m, 2H), 2.49 (s, 3H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 157.8, 157.6, 151.0, 145.5, 132.8, 129.8, 128.4, 124.5, 124.0, 116.6, 116.5, 116.4, 21.2. HRMS m/z (ESI-TOF): calculated for $C_{16}H_{12}NaO_6S$ $[M+Na]^+$ 355.0252, found 355.0253.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl 4-fluorobenzenesulfonate (3ab). Following the general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2b** (143 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 72 mg (71%) of **3ab** as white solid. M.P.: 95-96 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 – 8.08 (m, 2H), 7.93 (dd, J = 7.7, 1.2 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.55 – 7.44 (m, 2H), 7.35 (t, J = 8.0 Hz, 2H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.3(d, J_{C-F} = 252 Hz), 160.5, 158.3, 151.4, 132.9, 132.1, 131.6(d, J_{C-F} = 10 Hz), 124.4, 123.8, 118.6, 116.6, 116.4(d, J_{C-F} = 23 Hz), 116.2. HRMS m/z (ESI-TOF): calculated for $C_{15}H_8O_6SF$ $[M-H]^-$ 335.0026, found 335.0024.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl 4-chlorobenzenesulfonate (3ac). Following the

general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2c** (148 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 76 mg (72%) of **3ac** as white solid. M.P.: 143-145 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 – 7.97 (m, 2H), 7.94 (dd, J = 8.2, 1.3 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.70 – 7.62 (m, 1H), 7.39 (t, J = 7.6 Hz, 2H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 158.8, 157.8, 151.1, 139.6, 134.9, 132.6, 130.3, 129.5, 124.3, 124.2, 117.1, 116.7, 116.4. HRMS m/z (ESI-TOF): calculated for $C_{15}H_8O_6SCl$ [M-H]$^-$ 350.9730, found 350.9736.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl 4-bromobenzenesulfonate (3ad). Following the general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2d** (164 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 84 mg (71%) of **3ad** as white solid. M.P.: 154-155 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (t, J = 8.3 Hz, 3H), 7.85 (d, J = 8.3 Hz, 2H), 7.60 (t, J = 7.7 Hz, 1H), 7.39 – 7.28 (m, 2H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 160.3, 158.2, 151.3, 135.9, 132.3, 130.2, 128.5, 126.7, 124.3, 123.9, 118.4, 116.6, 116.3. HRMS m/z (ESI-TOF): calculated for $C_{15}H_8O_6SBr$ [M-H]$^-$ 394.9225, found 394.9233.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl 3-chlorobenzenesulfonate (3ae). Following the general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2e** (148 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 76 mg (72%) of **3ae** as white solid. M.P.: 147-148 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05 (s, 1H), 7.95 (dd, J = 6.3, 2.1 Hz, 2H), 7.90 (dd, J = 8.1, 1.1 Hz, 1H), 7.68 (dd, J

= 15.4, 7.5 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H). A signal for OH-proton is not visible. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 158.6, 157.8, 151.1, 137.8, 134.6, 133.8, 132.7, 131.3, 127.8, 127.1, 124.3, 124.2, 116.7, 116.5. HRMS m/z (ESI-TOF): calculated for $C_{15}H_8O_6SCl$ $[M-H]^-$ 350.9730, found 350.9736.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl benzenesulfonate (3af). Following the general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2f** (136 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 65 mg (68%) of **3af** as white solid. M.P.: 139-140 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 – 7.97 (m, 2H), 7.96 – 7.91 (m, 1H), 7.80 (t, *J* = 7.5 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 3H), 7.39 (t, *J* = 8.1 Hz, 2H). A signal for OH-proton is not visible. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 158.1, 157.7, 151.1, 136.0, 134.6, 132.7, 129.3, 128.3, 124.3, 124.1, 116.7, 116.4. HRMS m/z (ESI-TOF): calculated for $C_{15}H_9O_6S$ $[M-H]^-$ 317.0120, found 317.0120.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl 2,4-dinitrobenzenesulfonate (3ag). Following the general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2g** (140 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 56 mg (46%) of **3ag** as colourless oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.77 (d, *J* = 2.8 Hz, 1H), 8.34 (dd, *J* = 9.4, 2.8 Hz, 1H), 7.83 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.22 (dd, *J* = 8.3, 6.7 Hz, 3H). A signal for OH-proton is not visible. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 159.1, 157.3, 152.3, 139.6, 137.7, 130.4, 129.0, 124.6, 122.5, 121.3, 117.5, 117.4, 115.9. HRMS m/z (ESI-TOF): calculated for $C_{15}H_7N_2O_{10}S$ $[M-H]^-$ 406.9821, found 406.9821.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl 4-(trifluoromethoxy)benzenesulfonate (3ah). Following the general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2h** (167 mg, 0.36 mmol) and DCM (10 mL) at 35 ºC for 1 h, after column chromatography on silica gel afforded 65 mg (54%) of **3ah** as white solid. M.P.: 171-172 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 – 8.10 (m, 2H), 7.95 (dd, J = 8.2, 1.5 Hz, 1H), 7.73 – 7.60 (m, 3H), 7.44 – 7.38 (m, 2H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 158.4, 157.7, 152.4, 151.1, 134.7, 132.8, 131.3, 124.4, 124.1, 121.2, 119.8(q, J_{C-F} = 257 Hz), 116.7, 116.7, 116.5. HRMS m/z (ESI-TOF): calculated for $C_{16}H_9O_7SF_3K$ $[M+K]^+$ 440.9659, found 440.9658.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl 4-(trifluoromethyl)benzenesulfonate (3ai). Following the general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2h** (161 mg, 0.36 mmol) and DCM (10 mL) at 35 ºC for 1 h, after column chromatography on silica gel afforded 83 mg (72%) of **3ai** as white solid. M.P.: 186-187 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.24 (d, J = 8.3 Hz, 2H), 8.04 (d, J = 8.4 Hz, 2H), 7.91 (dd, J = 7.8, 1.3 Hz, 1H), 7.66 – 7.55 (m, 1H), 7.34 (t, J = 8.3 Hz, 2H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 160.6, 158.2, 151.4, 140.8, 133.58(d, J_{C-F} = 32 Hz), 132.1, 129.3, 126.3(q, J_{C-F} = 4 Hz), 124.4, 123.8, 123.4(d, J_{C-F} = 272 Hz), 118.7, 116.7, 116.3. HRMS m/z (ESI-TOF): calculated for $C_{16}H_9O_6SF_3Na$ $[M+Na]^+$ 408.9970, found 408.9980.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl 4-cyanobenzenesulfonate (3aj). Following the general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2j** (145 mg, 0.36 mmol) and DCM (10 mL) at 35 ºC for 1 h, after column chromatography on silica gel afforded 77

mg (75%) of **3aj** as white solid. M.P.: 167-168 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 – 8.09 (m, 4H), 8.00 – 7.89 (m, 1H), 7.71 – 7.59 (m, 1H), 7.37 (t, J = 8.1 Hz, 2H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 159.2, 157.9, 151.2, 140.3, 133.3, 132.6, 129.1, 124.2, 124.2, 117.5, 117.3, 116.8, 116.7, 116.4. HRMS m/z (ESI-TOF): calculated for $C_{16}H_8NO_6S$ $[M-H]^-$ 342.0072, found 342.0077.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl 4-nitrobenzenesulfonate (3ak). Following the general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2k** (152 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 78 mg (72%) of **3ak** as white solid. M.P.: 132-133 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.44 (d, J = 8.9 Hz, 2H), 8.30 (d, J = 8.8 Hz, 2H), 7.91 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 8.8 Hz, 2H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 161.1, 158.3, 151.5, 150.5, 142.4, 132.0, 130.0, 124.4, 124.3, 123.7, 119.0, 116.7, 116.2. HRMS m/z (ESI-TOF): calculated for $C_{15}H_8NO_8S$ $[M-H]^-$ 361.9971, found 361.9978.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl 4-(tert-butyl)benzenesulfonate (3al). Following the general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2l** (156 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 95 mg (85%) of **3al** as white solid. M.P.: 75-77 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (dd, J = 12.4, 5.1 Hz, 3H), 7.60 (dd, J = 10.9, 5.0 Hz, 3H), 7.39 – 7.20 (m, 2H), 1.25 (s, 9H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 157.9, 157.6, 157.6, 151.0, 133.0, 132.8, 128.3, 126.2,

124.5, 124.0, 116.8, 116.5, 116.2, 35.1, 30.6. HRMS m/z (ESI-TOF): calculated for $C_{19}H_{18}O_6SNa$ $[M+Na]^+$ 397.0722, found 397.0732.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl 4-methoxybenzenesulfonate (3am). Following the general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2m** (147 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 94 mg (90%) of **3am** as white solid. M.P.: 153-155 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 – 7.81 (m, 3H), 7.72 – 7.61 (m, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.25 – 7.10 (m, 2H), 3.88 (s, 3H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 163.9, 157.7, 157.6, 151.0, 132.7, 130.9, 126.9, 124.4, 124.0, 116.6, 116.4, 114.5, 55.9. HRMS m/z (ESI-TOF): calculated for $C_{16}H_{11}O_7S$ $[M-H]^-$ 347.0225, found 347.0229.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl methanesulfonate (3an). Following the general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2n** (114 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 33 mg (43%) of **3an** as white solid. M.P.: 153-155 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 (dd, J = 7.9, 1.2 Hz, 1H), 7.72 – 7.65 (m, 1H), 7.42 (dd, J = 12.0, 4.3 Hz, 2H), 3.48 (s, 3H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 158.5, 158.1, 151.0, 132.6, 124.3, 124.1, 117.2, 117.0, 116.4, 39.7. HRMS m/z (ESI-TOF): calculated for $C_{10}H_7O_6S$ $[M-H]^-$ 254.9963, found 254.9963.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl naphthalene-2-sulfonate (3ao). Following the general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2o** (154 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 65

mg (59%) of **3ao** as white solid. M.P.: 116-117 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (s, 1H), 8.24 – 8.14 (m, 3H), 8.12 – 8.04 (m, 1H), 7.82 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.71 – 7.64 (m, 1H), 7.46 – 7.37 (m, 1H), 7.20 – 7.12 (m, 2H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.7, 159.6, 152.1, 135.7, 134.6, 131.4, 130.4, 129.4, 129.0, 128.9, 128.6, 127.8, 127.3, 124.8, 123.7, 123.4, 122.3, 116.4, 115.7. HRMS m/z (ESI-TOF): calculated for $C_{19}H_{11}O_6S$ [M-H]$^-$ 367.0276, found 367.0276.

4-Hydroxy-2-oxo-2*H*-chromen-3-yl((1R,2S,4R)-7,7-dimethyl-6-oxobicyclo[2.2.1]heptan-2-yl) methanesulfonate (3ap). Following the general procedure, the reaction of **1a** (49 mg, 0.3 mmol), **2p** (163 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 65 mg (55%) of **3ap** as white solid. M.P.: 156-157 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.71 – 7.54 (m, 1H), 7.45 – 7.28 (m, 2H), 3.89 (q, *J* = 15.1 Hz, 2H), 2.47 – 2.28 (m, 2H), 2.10 (t, *J* = 4.4 Hz, 1H), 1.98 (d, *J* = 18.4 Hz, 2H), 1.61 (ddd, *J* = 13.6, 9.4, 4.6 Hz, 1H), 1.51 – 1.38 (m, 1H), 1.08 (s, 3H), 0.87 (s, 3H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 213.6, 160.5, 159.0, 151.3, 131.9, 124.4, 123.8, 118.9, 117.3, 116.2, 57.8, 54.9, 49.8, 47.7, 42.2, 41.9, 26.2, 24.9, 19.2. HRMS m/z (ESI-TOF): calculated for $C_{19}H_{19}O_7S$ [M-H]$^-$ 391.0860, found 391.0852.

6-Fluoro-4-hydroxy-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate (3ba). Following the general procedure, the reaction of **1b** (54 mg, 0.3 mmol), **2a** (141 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 60 mg (57%) of **3ba** as white solid. M.P.: 89-90 °C. ^{1}H NMR (400

MHz, DMSO-d_6) δ 7.87 (d, J = 8.3 Hz, 2H), 7.45 (dd, J = 9.0, 3.1 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.29 – 7.20 (m, 1H), 7.16 (dd, J = 8.9, 4.4 Hz, 1H), 2.34 (s, 3H). A signal for OH-proton is not visible. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 163.7, 159.2, 157.7(d, J_{C-F} = 237 Hz), 148.2, 143.8, 135.3, 129.2, 128.1, 117.8(d, J_{C-F} = 6 Hz), 116.5, 109.8(d, J_{C-F} = 24 Hz), 21.1. HRMS m/z (ESI-TOF): calculated for $C_{16}H_{10}O_6SF$ $[M-H]^-$ 349.0182, found 349.0178.

6-Chloro-4-hydroxy-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate (3ca). Following the general procedure, the reaction of **1c** (59 mg, 0.3 mmol), **2a** (141 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 75 mg (68%) of **3ca** as white solid. M.P.: 97-98 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 7.87 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 2.7 Hz, 1H), 7.39 (dd, J = 8.7, 2.7 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.7 Hz, 1H), 2.34 (s, 3H). A signal for OH-proton is not visible. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 164.2, 159.2, 150.7, 143.7, 135.5, 130.0, 129.1, 128.0, 126.7, 125.1, 123.9, 117.9, 116.3, 21.1. HRMS m/z (ESI-TOF): calculated for $C_{16}H_{10}O_6SCl$ $[M-H]^-$ 364.9887, found 364.9895.

6-Bromo-4-hydroxy-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate (3da). Following the general procedure, the reaction of **1d** (72 mg, 0.3 mmol), **2a** (141 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 80 mg (65%) of **3da** as white solid. M.P.: 105-106 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, J = 2.5 Hz, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.65 (dd, J = 8.7, 2.5 Hz, 1H), 7.41 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.7 Hz, 1H), 2.42 (s, 3H). A

signal for OH-proton is not visible. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 158.7, 150.8, 144.2, 134.8, 133.5, 129.3, 128.1, 126.8, 118.4, 116.5, 115.0, 21.1. HRMS m/z (ESI-TOF): calculated for $C_{16}H_{10}O_6SBr$ $[M-H]^-$ 408.9381, found 408.9385.

4-Hydroxy-6-methyl-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate (3ea). Following the general procedure, the reaction of **1e** (53 mg, 0.3 mmol), **2a** (141 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 85 mg (82%) of **3ea** as white solid. M.P.: 145-146 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 (d, J = 8.3 Hz, 2H), 7.77 (s, 1H), 7.50 (d, J = 8.1 Hz, 3H), 7.33 (d, J = 8.4 Hz, 1H), 2.48 (s, 3H), 2.43 (s, 3H). A signal for OH-proton is not visible. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 158.1, 157.8, 149.2, 145.3, 133.7, 133.4, 133.1, 129.7, 128.4, 123.7, 116.7, 116.5, 116.2, 21.2, 20.3. HRMS m/z (ESI-TOF): calculated for $C_{17}H_{13}O_6S$ $[M-H]^-$ 345.0433, found 345.0428.

4-Hydroxy-6-methoxy-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate (3fa). Following the general procedure, the reaction of **1f** (58 mg, 0.3 mmol), **2a** (141 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 54 mg (50%) of **3fa** as white solid. M.P.: 144-145 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.89 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 3.0 Hz, 1H), 7.26 (d, J = 9.0 Hz, 1H), 7.17 (dd, J = 9.0, 3.0 Hz, 1H), 3.80 (s, 3H), 2.42 (s, 3H). A signal for OH-proton is not visible. $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 158.4, 155.3, 145.6, 144.7, 134.0, 129.5, 128.3, 119.6, 117.5, 116.9, 106.2, 55.6, 21.1. HRMS m/z (ESI-TOF): calculated for $C_{17}H_{13}O_7S$ $[M-H]^-$ 361.0382, found 361.0383.

7-Fluoro-4-hydroxy-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate (3ga). Following the general procedure, the reaction of **1g** (54 mg, 0.3 mmol), **2a** (141 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 40 mg (38%) of **3ga** as white solid. M.P.: 90-91 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 (dd, J = 8.9, 6.2 Hz, 1H), 7.87 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.37 (dd, J = 9.6, 2.4 Hz, 1H), 7.28 (td, J = 8.7, 2.5 Hz, 1H), 2.43 (s, 3H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 164.1(d, J_{C-F} = 249 Hz), 158.4, 157.7, 152.3(d, J_{C-F} = 13 Hz), 145.2, 133.1, 129.7, 128.4, 126.4(d, J_{C-F} = 11 Hz), 116.0, 114.14, 112.2(d, J_{C-F} = 23 Hz), 104.0(d, J_{C-F} = 26 Hz), 21.2. HRMS m/z (ESI-TOF): calculated for $C_{16}H_{10}O_6SF$ $[M-H]^-$ 349.0182, found 349.0175.

7-Chloro-4-hydroxy-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate (3ha). Following the general procedure, the reaction of **1h** (59 mg, 0.3 mmol), **2a** (141 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 58 mg (53%) of **3ha** as white solid. M.P.: 85-86 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (t, J = 9.3 Hz, 3H), 7.52 (s, 1H), 7.42 (t, J = 9.1 Hz, 3H), 2.41 (s, 3H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 158.9, 157.6, 151.6, 145.1, 136.5, 133.4, 129.6, 128.3, 125.8, 124.3, 117.0, 116.5, 116.4, 21.1. HRMS m/z (ESI-TOF): calculated for $C_{16}H_{10}O_6SCl$ $[M-H]^-$ 364.9887, found 364.9887.

7-Bromo-4-hydroxy-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate (3ia). Following the general procedure, the reaction of **1i** (72 mg, 0.3 mmol), **2a** (141 mg,

0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 75 mg (61%) of **3ia** as white solid. M.P.: 95-96 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (d, J = 2.5 Hz, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.65 (dd, J = 8.7, 2.5 Hz, 1H), 7.41 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.7 Hz, 1H), 2.42 (s, 3H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 159.6, 157.8, 151.6, 145.0, 133.5, 129.6, 128.3, 126.9, 126.0, 124.8, 119.1, 117.8, 116.6, 21.1. HRMS m/z (ESI-TOF): calculated for $C_{16}H_{10}O_6SBr$ $[M-H]^-$ 408.9381, found 408.9384.

4-Hydroxy-7-methoxy-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate (3ja). Following the general procedure, the reaction of **1j** (58 mg, 0.3 mmol), **2a** (141 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 76 mg (70%) of **3ja** as white solid. M.P.: 134-135 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.8 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 6.83 (dd, J = 8.8, 2.4 Hz, 1H), 6.78 (d, J = 2.4 Hz, 1H), 3.76 (s, 3H), 2.35 (s, 3H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 162.2, 158.7, 153.1, 144.5, 134.2, 129.4, 128.2, 125.5, 115.2, 111.4, 100.3, 55.8, 21.1. HRMS m/z (ESI-TOF): calculated for $C_{17}H_{13}O_7S$ $[M-H]^-$ 361.0382, found 361.0376.

7-(Dimethylamino)-4-hydroxy-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate (3ka). Following the general procedure, the reaction of **1k** (62 mg, 0.3 mmol), **2a** (141 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 72 mg (64%) of **3ka** as grey solid. M.P.:

168-169 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 9.0 Hz, 1H), 7.45 (d, J = 8.1 Hz, 2H), 6.77 (dd, J = 9.1, 2.4 Hz, 1H), 6.52 (d, J = 2.3 Hz, 1H), 3.02 (s, 6H), 2.43 (s, 3H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 158.4, 158.1, 153.3, 153.2, 145.2, 133.1, 129.7, 128.4, 124.6, 113.6, 109.3, 103.4, 97.2, 38.9, 21.2. HRMS m/z (ESI-TOF): calculated for $C_{18}H_{16}NO_6S$ $[M-H]^-$ 374.0698, found 374.0698.

4-Hydroxy-8-methyl-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate (3la). Following the general procedure, the reaction of **1l** (53 mg, 0.3 mmol), **2a** (141 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 80 mg (77%) of **3la** as white solid. M.P.: 146-147 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 7.0 Hz, 1H), 7.52 (d, J = 7.3 Hz, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.28 (t, J = 7.7 Hz, 1H), 2.44 (s, 3H), 2.34 (s,3H). A signal for OH-proton is not visible. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 158.5, 157.7, 149.4, 145.2, 133.6, 133.2, 129.7, 128.4, 125.3, 123.9, 121.8, 116.7, 116.6, 21.2, 15.2. HRMS m/z (ESI-TOF): calculated for $C_{17}H_{13}O_6S$ $[M-H]^-$ 345.0433, found 345.0440.

4-Hydroxy-5-methyl-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate (3ma). Following the general procedure, the reaction of **1m** (53 mg, 0.3 mmol), **2a** (141 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 83 mg (80%) of **3ma** as white solid. M.P.: 96-97 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86 (d, J = 8.3 Hz, 2H), 7.81 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.26 – 7.18 (m, 2H), 2.43 (s, 3H), 2.41 (s, 3H). A signal for OH-proton is not

visible. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 158.3, 157.8, 151.1, 145.3, 143.5, 133.0, 129.7, 128.4, 125.4, 123.8, 116.4, 116.1, 114.1, 21.2, 21.0. HRMS m/z (ESI-TOF): calculated for $C_{17}H_{13}O_6S$ $[M-H]^-$ 345.0433, found 345.0433.

1-Hydroxy-3-oxo-3*H*-benzo[f]chromen-2-yl 4-methylbenzenesulfonate (3na). Following the general procedure, the reaction of **1n** (64 mg, 0.3 mmol), **2a** (141 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 89 mg (78%) of **3na** as white solid. M.P.: 208-209 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 9.42 (d, J = 8.7 Hz, 1H), 8.23 (d, J = 9.0 Hz, 1H), 8.09 (d, J = 7.3 Hz, 1H), 7.95 (d, J = 8.3 Hz, 2H), 7.78 – 7.72 (m, 1H), 7.68 – 7.62 (m, 1H), 7.55 (d, J = 9.0 Hz, 1H), 7.50 (d, J = 8.1 Hz, 2H), 2.48 (s, 3H). A signal for OH-proton is not visible. $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 157.1, 152.2, 145.2, 134.0, 132.9, 130.3, 129.6, 129.4, 128.9, 128.6, 128.3, 125.7, 117.6, 117.0, 21.2. HRMS m/z (ESI-TOF): calculated for $C_{20}H_{13}O_6S$ $[M-H]^-$ 381.0433, found 381.0442.

4-Hydroxy-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl 4-methylbenzenesulfonate (3oa). Following the general procedure, the reaction of **1o** (53 mg, 0.3 mmol), **2a** (141 mg, 0.36 mmol) and DCM (10 mL) at 35 °C for 1 h, after column chromatography on silica gel afforded 75 mg (72%) of **3oa** as white solid. M.P.: 111-112 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 11.63 (s, 1H), 8.02 (dd, J = 8.0, 1.3 Hz, 1H), 7.93 (d, J = 8.3 Hz, 2H), 7.72 – 7.63 (m, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.37 – 7.29 (m, 1H), 3.55 (s, 3H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 157.9, 152.9, 144.9, 137.7, 133.8, 131.5, 129.5, 128.3, 123.7, 122.3, 122.0, 115.4, 114.8, 29.2, 21.1. HRMS m/z (ESI-TOF): calculated for $C_{17}H_{14}NO_5S$ $[M-H]^-$

344.0593, found 344.0586.

4-Hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl 4-methylbenzenesulfonate (3pa). Following the general procedure, the reaction of **1p** (38 mg, 0.3 mmol), **2a** (141 mg, 0.36 mmol) and DCM (3 mL) at 35 ºC for 1 h, after column chromatography on silica gel afforded 79 mg (95%) of **3pa** as white solid. M.P.: 117-118 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.37 (s, 1H), 7.84 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 6.04 (s, 1H), 2.43 (s, 3H), 2.18 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 161.9, 161.2, 159.4, 145.0, 133.6, 129.7, 128.1, 115.2, 99.8, 21.1, 19.2. HRMS m/z (ESI-TOF): calculated for $C_{13}H_{12}O_6SNa$ $[M+Na]^+$ 319.0252, found 319.0243.

2-Oxo-4-(((trifluoromethyl)sulfonyl)oxy)-2*H*-chromen-3-yl 4-methylbenzenesulfo-nate (4). To a 250 ml round-bottomed flask was added 4-hydroxy-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate **3aa** (5 mmol, 1.66 g) and Tf_2O (10 mmol, 2.82 g). DCM (20 ml) was added and Et_3N (0.5 mL) was slowly dropped to the solution. Then the mixture was stirred at room temperature for 3 hours. After TLC, the solvent was evaporated under vacuum. The crude products were purified using flash column chromatography on silica gel to afford 2.13 g (92%) of the desired product **4** as white solid. M.P.: 156-157 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2H), 7.78 – 7.66 (m, 2H), 7.55 – 7.37 (m, 4H), 2.50 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.1, 145.5, 143.0, 141.4, 128.6, 127.2, 124.7, 123.7, 119.4(q, J_{C-F} = 220 Hz), 112.1, 109.5, 16.6. HRMS m/z (ESI-TOF): calculated for $C_{17}H_{12}O_8S_2F_3$ $[M+H]^+$ 464.9926, found 464.9927.

2-Oxo-4-((2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl)oxy)-2*H*-

chromen-3-yl 4-methylbenzenesulfonate (5). To a solution of **4** (0.2 mmol, 97 mg) in DMF (2 ml), Vitamin E (0.24 mmol, 103 mg) and K_2CO_3 (0.4 mmol, 55 mg) was added. Then the mixture was stirred at 100 ºC under oil bath for 12 hours. After TLC, water (20 mL) was added, and the mixture was firstly extracted with DCM and then dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude compound was purified by column chromatography on silica gel to afford 63 mg (42%) of desired product **5** as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (t, *J* = 7.0 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 6.9 Hz, 2H), 7.29 – 7.22 (m, 2H), 2.63 (s, 2H), 2.42 (s, 3H), 2.14 (s, 3H), 2.08 (s, 6H), 1.92 – 1.78 (m, 2H), 1.60 (s, 2H), 1.57 – 1.47 (m, 2H), 1.40 (d, *J* = 20.1 Hz, 4H), 1.34 – 1.19 (m, 10H), 1.13 (dd, *J* = 11.7, 7.1 Hz, 3H), 1.06 (dd, *J* = 7.6, 4.7 Hz, 3H), 0.90 – 0.80 (m, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.7, 154.7, 150.9, 149.5, 144.8, 134.5, 132.4, 129.3, 128.4 126.0, 124.7, 124.5, 124.3, 123.3, 118.0, 116.8, 116.4, 75.2, 39.4, 37.4, 32.8, 28.0, 27.0, 24.9, 24.5, 22. 8, 22.7, 20. 8, 13.3, 12.0. HRMS m/z (ESI-TOF): calculated for $C_{45}H_{60}NaO_7S$ $[M+Na]^+$ 767.3957, found 767.3956.

4-(Furan-3-yl)-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate (6). To a solution of **4** (0.2 mmol, 97 mg) in toluene (2 ml), furan (1 mmol, 68 mg) was added under argon atmosphere at 0 ºC. Then LiHDMs (0.2 mmol) was also slowly added at the same temperature and the mixture was stirred for additional 12 h. After TLC, water (20 mL) was added, and the mixture was firstly extracted with DCM and then dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude compound was purified by column chromatography on silica gel to afford 40 mg (52%) of desired

product **6** as white solid. M.P.: 191-192 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 – 7.88 (m, 3H), 7.62 (s, 1H), 7.56 (d, J = 8.1 Hz, 2H), 7.29 – 7.14 (m, 2H), 6.94 (td, J = 7.6, 1.0 Hz, 1H), 6.86 – 6.81 (m, 1H), 6.60 (d, J = 2.6 Hz, 1H), 2.47 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 162.8, 154.1, 151.3, 146.3, 138.5, 130.8, 130.4, 130.3, 128.5, 128.4, 122.6, 121.9, 120.2, 118.5, 102.4, 79.9, 76.7, 21.2. HRMS m/z (EI-TOF): calculated for $C_{20}H_{14}O_6S$ $[M]^+$ 382.0511, found 382.0513.

2-Oxo-4-(p-tolylthio)-2*H*-chromen-3-yl 4-methylbenzenesulfonate (7). To a solution of **4** (0.2 mmol, 97 mg) in toluene (2 ml), 4-methylbenzenethiol (0.24 mmol, 30 mg) was added under argon atmosphere at 0 °C. Then LiHDMs (0.2 mmol) was also slowly added at the same temperature and the mixture was stirred at 110 °C under oil bath for additional 12 h. After TLC, water (20 mL) was added, and the mixture was firstly extracted with DCM and then dried over anhydrous Na_2SO_4 and concentrated in vaccum. The crude compound was purified by column chromatography on silica gel to afford 55 mg (63%) of desired product **7** as white solid. M.P.: 142-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.3 Hz, 2H), 7.76 (dd, J = 8.1, 1.2 Hz, 1H), 7.47 – 7.37 (m, 1H), 7.31 – 7.22 (m, 3H), 7.13 (td, J = 8.3, 1.5 Hz, 3H), 6.99 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H), 2.23 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.6, 151.1, 145.7, 143.7, 138.2, 136.0, 133.7, 131.9, 130.9, 130.3, 129.7, 128.8, 128.7, 128.0, 124.8, 119.0, 117.0, 21.8, 21.1. HRMS m/z (ESI-TOF): calculated for $C_{23}H_{19}O_5S_2$ $[M+H]^+$ 439.0674, found 439.0675.

4-(Diphenylphosphanyl)-2-oxo-2*H*-chromen-3-yl 4-methylbenzenesulfonate (8). To a solution of **4** (0.2 mmol, 97 mg) in toluene (2 ml), diphenylphosphane (0.24

mmol, 45 mg) was added under argon atmosphere at 0 °C. Then LiHDMs (0.2 mmol) was also slowly added at the same temperature and the mixture was stirred at 110 °C under oil bath for additional 12 h. After TLC, water (20 mL) was added, and the mixture was firstly extracted with DCM and then dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude compound was purified by column chromatography on silica gel to afford 52 mg (52%) of desired product **8** as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.76 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.47 – 7.37 (m, 1H), 7.31 – 7.22 (m, 3H), 7.13 (td, *J* = 8.3, 1.5 Hz, 3H), 6.99 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 2.23 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.6, 151.1, 145.7, 143.7, 138.2, 136.0, 133.7, 131.9, 130.9, 130.3, 129.7, 128.8, 128.7, 128.0, 124.8, 119.0, 117.0, 21.8, 21.1. HRMS m/z (ESI-TOF): calculated for $C_{28}H_{22}O_5PS$ $[M+H]^+$ 501.0926, found 501.0927.

2-Oxo-3-(phenyliodonio)-2*H*-chromen-4-olate (11). To a 50 ml round-bottomed flask was added 4-hydroxy-2*H*-chromen-2-one **1a** (1 mmol) and DCM (20 ml). Then the temperature was cooled to 0 °C and [hydroxy(sulfonyloxy)iodo]arenes **2** (1 mmol) was added slowly. After stirring for 15 minutes, the solvent was evaporated under vacuum. The crude products were purified using flash column chromatography on silica gel to afford 302 mg (83%) of the desired product **11** as pale yellow solid. M.P.: 136-137 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.61 – 7.50 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.21 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 172.5, 161.0, 153.9, 133.1, 132.8, 131.1, 130.7, 125.6, 123.4, 119.8, 116.3, 115.0, 82.0. HRMS m/z (EI-TOF): calculated for

$C_{15}H_9IO_3$ $[M]^+$ 363.9596, found 363.9599.

Warfarin (12). To a 50 ml round-bottomed flask was added ZICs **11** (0.5 mmol) and (*E*)-4-phenylbut-3-en-2-one (0.5 mmol). MeCN (20 ml) was added and the mixture was stirred at 80 ºC under oil bath for 12 hours. Then the solvent was evaporated under vacuum. The crude products were purified using flash column chromatography on silica gel to afford 117 mg (76%) of the desired product **12** as white solid. M.P.: 161-162 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.8 Hz, 0.50H), 7.80 (d, J = 7.7 Hz, 0.53H), 7.56 (t, J = 7.8 Hz, 0.44H), 7.48 (t, J = 7.8 Hz, 0.71H), 7.34 – 7.15 (m, 7.42H), 4.27 (d, J = 3.0 Hz, 0.44H), 4.16 (dd, J = 11.0, 6.8 Hz, 0.53H), 2.62 – 2.33 (m, 1.44H), 1.98 (t, J = 12.7 Hz, 0.56H), 1.69 (s, 1.59H), 1.66 (s, 1.40H). Analytical data are in agreement with the reported ones [19].

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Supporting Information

The characterization data and copies of ^{1}H, ^{13}C NMR spectra for all products. The Supporting Information is available free of charge via the internet at http://pubs.acs.org.

Conflict of interest

The author declare no conflict of interest.

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