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Palladium-Catalyzed C-H Functionalization of Phenyl 2-Pyridylsulfonate

Bin Li, Dong-Dong Guo, Shi-Huan Guo, Gao-Fei Pan, Ya-Ru Gao, Yong-Qiang Wang*[a]

Abstract: A general and efficient palladium(II)-catalyzed intermolecular direct *ortho* alkenylation and acetoxylation of phenols have been developed. The reaction proceeded via a seven-membered cyclopalladated intermediate and showed complete regio- and diastereoselectivity. The approach also presented an efficient route for synthesis of corresponding coumarins and benzofurans.

Introduction

In the past decade, the direct functionalization of C-H bonds has revolutionized the field of organic synthesis due to its atom and step economy by eliminating the need for preactivation of the starting materials.[1] In this area, the transition-metal-catalyzed protocol has been greatly developed.[2] Because the palladium catalyst possesses remarkable reactivity, compatibility and selectivity, the palladium-catalyzed C-H activation and functionalization have been studied largely.[3] To date, direct C-H activation and functionalization via five or six-membered cyclopalladated intermediates have been well documented.[4] However, the more than six-membered, such as seven-membered cyclopalladated processes are fairly rare, which likely lie in the more instability of these palladacycles than the five- and six-membered ones.[5]

Phenol is ubiquitous structural motif in natural products, pharmaceuticals and organic materials.[6] Therefore, the functionalization of phenol and its derivatives have attracted intensive efforts from the community studying C−H activations and functionalizations. In this regard, *ortho*-C-H functionalizations of phenols are interesting subjects.[7] Despite of tremendous progress,[8] further development of efficient *ortho*-C-H functionalizations of phenols is still in demand because most of the systems reported suffered from following synthetic restrictions: harsh reaction conditions (e.g. high reaction temperature and highly acidic medium), the challenge with respect to the removal/transformation of undesired external directing group or a limited substrate scope. Moreover, most reactions required large excess of oxidants such as inorganic salts (AgOAc, $Cu(OAc)_2$, etc.), BQ, DDQ, IBX, and $PhI(OAc)_2$ to regenerate the catalyst, which produced at least stoichiometric amounts of the reduced external oxidant as waste.

Recently, Yu et al. reported the Pd-catalyzed C-H olefinations of 3-phenylpropionic acids via a seven-membered cyclopalladated pathway;[9] and 2-pyridyloxyl group was reported to be a powerful directing group for the selective *ortho* olefination of a variety of aromatic compounds.[10] Inspired by these pioneering studies, we envisioned that 2-pyridylsulfonyl group might serve as a promising removable and highly valuable directing and protecting group of phenols to achieve the palladium-catalyzed direct *ortho*-C-H functionalizations through the formation of a seven-membered cyclopalladated intermediate. If the activity of palladium catalyst was improved, oxygen could be employed as the ideal oxidant with water as reduced waste. Herein, we report progress toward achieving these goals.

Results and Discussion

Because *ortho*-alkenyl phenols are important building blocks for synthetic organic chemistry,[10,11] we initially aimed to develop *ortho*-C-H olefination of phenol derivatives. First, the reaction was carried out with phenyl 2-pyridylsulfonate (**1a**) and methyl acrylate (**2a**) as model substrates employing $Pd(OAc)_2$ (10 mol%) as the catalyst and oxygen as the oxidant in DCE (Table 1). It was found that the reaction proceeded much slowly (entry 1). Considering trifluoroacetic acid (TFA) and $Pd(OAc)_2$ can facilitate the generation of more electropositive $[Pd(II)O_2CCF_3]^+$ specie, which, compared with $[Pd(II)OAc]^+$, possesses higher activity for electrophilic substitution of C-H bonds to form σ-phenyl-Pd complex,[12] 1.0 equiv of TFA was added to the reaction system. To our delight, the reaction was accelerated greatly and afforded the alkenylation product in 52% yield with complete *ortho*-regioselectivity and *E* diastereoselectivity (entry 2). Next, the amount of TFA was investigated, and 2.0 equiv of TFA (with respect to the substrate) gave the best result (entries 3-5). Then the palladium source was examined (Table 1, entries 6, 7); $Pd(TFA)_2$ or $PdCl_2$ did not improve the yield of the desired product. In the absence of palladium catalyst, the reaction would not occur (entry 8). After careful solvent screening, hexafluoroisopropanol (HFIP) proved to be the best solvent to give excellent yield (Table 1, entries 9–10). Finally we checked the amount of the catalyst $Pd(OAc)_2$, and we found the conversion decreased remarkably when $Pd(OAc)_2$ was reduced to 5 mol% (Table 1, entry 11). Accordingly, the reaction conditions were optimized as follows: $Pd(OAc)_2$ (10% mol), TFA (2.0 equiv.) under oxygen atmosphere in the solvent HFIP at 60 ℃. Next, we wondered if the reaction would proceed through a seven-membered cyclopalladated intermediate. So under the optimized reaction conditions, the substrates **1b** and **1c** without pyridyl group were utilized in the transformation. The reactions

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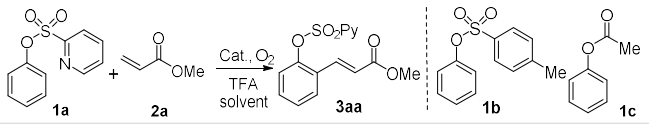
Table 1. Optimization of Reaction Conditions.[a]

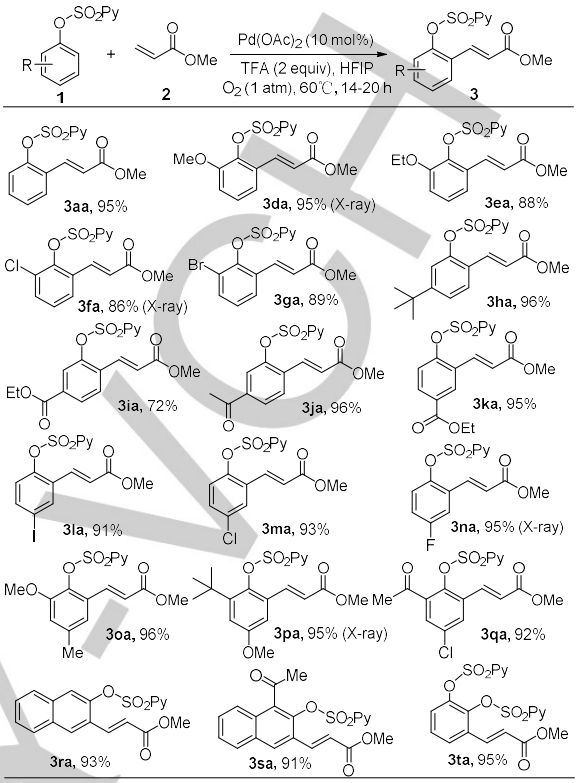


entry	Catalyst	solvent[j]	TFA(equiv)	yield (%)[b]
1	$Pd(OAc)_2$	DCE	-	15
2	$Pd(OAc)_2$	DCE	1.0	52
3	$Pd(OAc)_2$	DCE	2.0	76
4	$Pd(OAc)_2$	DCE	3.0	75
5	$Pd(OAc)_2$	DCE	5.0	65
6	$Pd(TFA)_2$	DCE	2.0	45
7	$PdCl_2$	DCE	2.0	<5
8	-	DCE	2.0	0
9	$Pd(OAc)_2$	solvents[c]	2.0	<20
10	$Pd(OAc)_2$	HFIP	2.0	95
11[d]	$Pd(OAc)_2$	HFIP	2.0	45
12[e]	$Pd(OAc)_2$	DCE	2.0	0

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (2.0 mmol), catalyst, O_2 (1 atm) and TFA in solvent (10 ml) for 16 h. [b] Isolated yield after purification by flash colum chromatography. [c] Solvents: toluene, AcOH, 1,4-Dioxane, DMSO, MeOH, CH_3CN, THF, DMA, *i*-PrOH, *t*-BuOH, 2,2,2-trifluoroethanol, CH_3NO_2. [d] 5% $Pd(OAc)_2$. [e] **1b** or **1c** used as substrate.

did not proceed, which demonstrated that the pyridyl group is absolutely necessary for the reaction. Based on these experiments and pioneering reports,[3e,10b] we considered that a seven-membered palladacycle including nitrogen atom of pyridyl group was likely a key intermediate.

Then, we moved on to explore the scope of the transformation. First, we studied the effect of electronic and structural variations on the phenol ring (Scheme 1). A broad range of substituent groups with diverse steric and electronic properties (ether, alkyl, halide, acetyl and ester groups) at *ortho*-, *meta*- or *para*-position of aryl rings all were compatible with this procedure, affording the corresponding olefinated products in 72-96% yields with complete regio- and diastereoselectivity. Halides (F, Cl, Br and I groups) survived under the reaction conditions. This is a synthetically interesting result as such substituents are versatile handles for further transformations. The high regiocontrol was observed in meta-substituted substrates, in favor of the C-H functionalization at the sterically less-hindered *ortho*-position (**3ha**-**3ja**). It is noteworthy that the regioselectivity of the reaction was highlighted again, alkenylation occurred only at the C-H ortho to the 2-pyridylsulfonate substituent, while no alkenylation

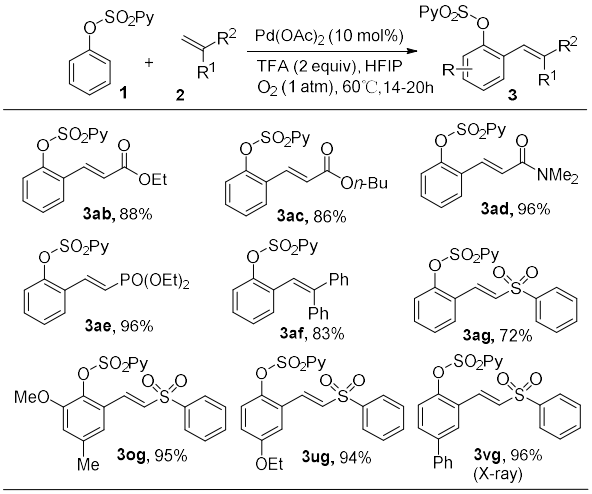


Scheme 1. Alkenylation of Phenol Derivatives.

was found at the position ortho to the CO_2Et or COMe in spite of them also being good directing groups for C-H bond activation reactions (**3ia**-**3ka**).[8c,13,14] Pleasingly, disubstituted substrates and naphthol derivatives were also amenable to the olefination reaction, which proceeded with high selectivity at the more accessible position (**3oa**-**3sa**). Interestingly, the substrate with two 2-pyridylsulfonate directing groups only provided monoalkenylated product in excellent yield under the standard reaction conditions (**3ta**).

As shown in Scheme 2, the present reaction protocol was successfully extended to other acrylates. Ethyl acrylate and *n*-butyl acrylate reacted efficiently with **1a** to give the corresponding products **3ab** and **3ac** in 88% and 86% yields, respectively. Acrylamide, vinyl phosphonate, 1,1-diphenylethylene and vinyl sulfone were also good partners for **1aa** in the olefination reaction, providing the desired products in excellent yields (**3ad**-**3ag**). The smooth reactions of vinyl sulfone with various phenyl 2-pyridylsulfonates possessing different steric and electronic property showed the generality of the olefination reaction (**3ag**, **3og**, **3ug** and **3vg**).

1,2-Disubstituted alkenes are particular substrates due to the few precedents and lower reactivity of this kind of olefin in oxidative alkenylation (Fujiwara-Moritani) reactions.[15] Delightedly, under the standard reaction conditions, dimethyl maleate reacted smoothly with various phenyl

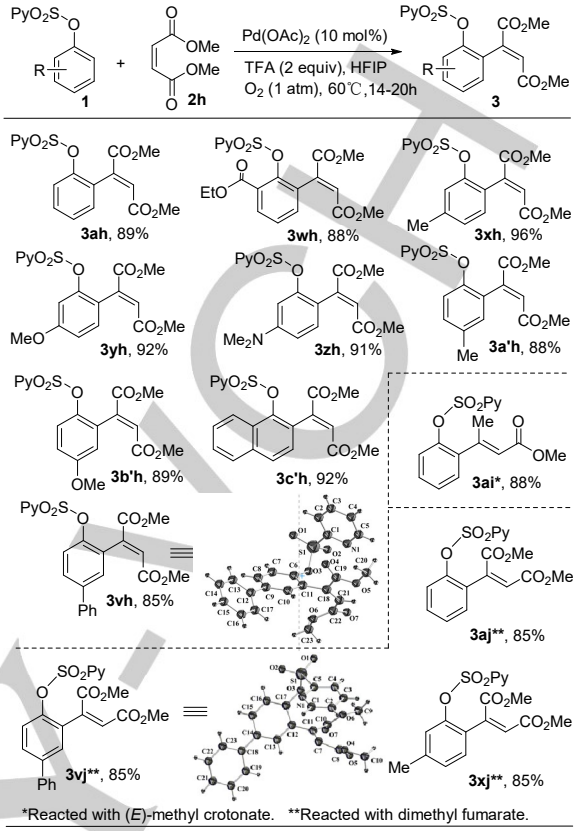


Scheme 2. Alkenylation of various alkenes.

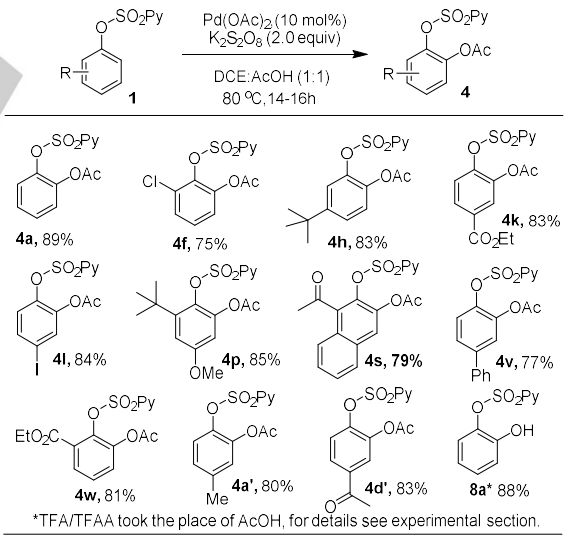
2-pyridylsulfonates regardless of their electronic and structural nature, affording the corresponding trisubstituted alkene products in excellent yields (Scheme 3, **3ah**, **3vh-3zh**, and **3a'h-3c'h**). And dimethyl fumarate possessing reversed configuration with dimethyl maleate was also suitable partner for the reaction to produce the desired trisubstituted alkenes in high yields (**3aj**, **3vj** and **3xj**). It is noteworthy that the configuration of two CO_2Me gruops were completely reversed in both above reactions, that is two CO_2Me gruops were *cis*-configuration in starting material but they were *trans*-configuration in the products, and vice versa, which were confirmed by single-crystal X-ray analyses of **3vh** and **3vj**. These stereochemical results indicated that the mechanism of the reaction probably was a *syn*-carbopalladation followed by a *syn*-dehydropalladation. (*E*)-methyl crotonate was also an amenable substrate to give the desired product **3ai** in 88% yield.

Encouraged by the success of *ortho*-C-H olefination of phenols via a seven-membered cyclopalladated intermediates, we next explored the acetoxylation reaction with the similar strategy. After optimizing the reaction conditions, we found that the acetoxylation reaction could proceed successfully in the presence of $Pd(OAc)_2$ (10 mol %), $K_2S_2O_8$ (2.0 equiv) in DCE / AcOH (1:1) at 80 ℃ for 14 - 16 h. The reaction could be applied to various substituted substrates, providing the desired products in 75-89% yields (Scheme 4). For *meta*-substituted substrate, the reaction also exhibited excellent regioselectivity (**4h**). Unfortunately, formic acid and benzoic acid did not work under the present reaction conditions. When TFA / TFAA took the place of AcOH, the reaction of **1a** afforded valueble catechol derivative (**8a**) in 88% yield.

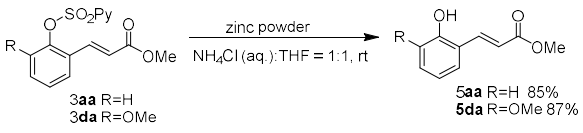
2-Pyridylsulfonyl group could be readily removed by zinc in NH_4Cl (aq.) / THF (1:1) at room temperature, with the olefin moiety untouched (Scheme 5). To further demonstrate the synthetic potential of this methodology, we sought to explore the possibility of the synthesis of coumarins and benzofurans from phenyl 2-pyridylsulfonates (Scheme 6). It is well known that coumarins and benzofurans are two kinds of valuable organic molecules with broad biological and pharmacological activities,



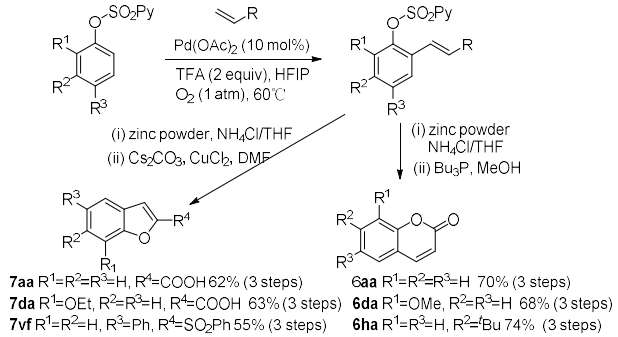
Scheme 3. Alkenylation of 1,2-Disubstituted Alkenes



Scheme 4. Acetoxylation of Phenol Derivatives



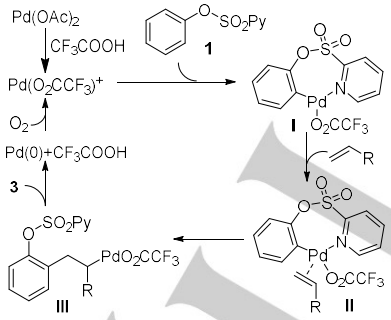
Scheme 5. Removal of 2-Pyridylsulfonyl Group.



Scheme 6. Synthesis of Coumarins and Benzofurans.

including antitumor,[16] anti-HIV,[17] antioxidant,[18] antibacterial,[19] and anti-inflammatory activities.[20] After the coupling reactions of phenyl 2-pyridylsulfonates and alkenes were complete, 2-pyridylsulfonyl directing group was removed with above conditions, then the resulting phenol products were treated with Bu_3P/MeOH to give coumarins (**6aa**, **6da** and **6ha**), alternatively treated with Cs_2CO_3/$CuCl_2$/DMF to provide benzofurans (**7aa**, **7da** and **7vf**). Both procedures proceeded very well to afford the desired products in good yields.

A plausible mechanism for the reaction is shown in scheme 7. $Pd(OAc)_2$ is treated with TFA to get active $Pd(O_2CCF_3)^+$,[12] which affords the seven-membered cyclopalladated intermediate (**I**) through the electronic attack of palladium(II) into phenyl 2-pyridylsulfonate. Then coordination of alkene (intermediate **II**) and insertion of C=C bond forms the palladium (II) complex **III**. The subsequent *β*–hydride elimination results in the product and librates Pd(0) which can be re-oxidized to $Pd(O_2CCF_3)^+$ by O_2 in the presence of TFA to complete the catalytic cycle.



Scheme 7. Plausible Mechanism for the Alkenylation.

Conclusions

In summary, we have successfully developed a simple and efficient palladium(II)-catalyzed *ortho*-C-H alkenylation and acetoxylation of phenyl 2-pyridylsulfonates via a seven-membered cyclopalladated intermediate. The reaction exhibited complete regio- and diastereoselectivity. 2-Pyridylsulfonyl group can be easily removed and the resulting phenol derivatives could be facilely utilized in the synthesis of valuable coumarins and benzofurans. The method might have many applications in organic and medical chemistry. Detailed mechanistic investigations and the extension of a similar reaction in other organic molecules are currently underway.

Experimental Section

General Comments. All commercial reagents and solvents were used as received without further purification. Reactions were followed with TLC (0.254 mm silica gel 60-F plates). Visualization was accomplished with UV light. Flash chromatographies were carried out on silica gel 200-300 mesh. Melting points (m. p.) were measured on electrothermal digital melting point apparatus and were uncorrected. ^{1}HNMR and ^{13}CNMR spectra were recorded at 400 MHz using $CDCl_3$ or $(CD_3)_2SO$ as solvent. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), $(CD_3)_2SO$ (δ 2.50 ppm) or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br. s = broad singlet. Infrared (IR) data were recorded as films on potassium bromide plates on a Bruker Tensor 27 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-QII mass spectrometer. X-ray crystal structure analyses were measured on Bruker Smart APEXIICCD instrument using Mo-Kα radiation. The structures were solved and refined using the SHELXTL software package.

General procedure for pyridine-2-sulfonyl chloride synthesis.

To a 500 mL round bottom flask were added 13.5 mmol (1.50 g) pyridine-2-thiol and 40 mL concerned H_2SO_4. Then 150 mL sodium hypochlorite solution was added dropwise to the solution under ice bath. The reaction mixture was left at 0 ℃ for 15 min, and finally extracted with 150 mL DCM for three times. The organic layer was combined, dried with Na_2SO_4 and evaporated in vacuum to remove the solvents to give the product. The product was used without further purification.

General procedure for phenyl pyridine-2-sulfonate synthesis.

To a solution of 10.6 mmol (1.00 g) of phenol dissolved in 50 mL DCM was added 20.0 mmol (2.76 mL) Et_3N. The mixture was stirred at room temperature for 15 min and 20.0 mmol (3.54 g) pyridine-2-sulfonyl chloride was added. Then the reaction was stirred overnight. The solvent was removed by distillation and the mixture was purified by column chromatography to give the product **1**.

Phenyl pyridine-2-sulfonate (1a) Prepared according to general procedure as a white solid (2.24 g, obtained from 10.6 mmol corresponding phenol, 90%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 94 - 95 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 3.6 Hz, 1H), 7.86 (d, *J* = 3.2 Hz, 2H), 7.54 (d, *J* = 4.0 Hz, 1H), 7.25 – 7.10 (m, 3H), 7.02 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 150.6, 149.6, 138.4, 129.8, 128.4, 127.3, 124.3, 122.2. HRMS (ESI) *m/z* calcd for $C_{11}H_9NO_3SNa$ 258.0195 $[M+Na]^+$; found 258.0188. IR (KBr): 3099, 1585, 1483, 1201, 1147, 1120, 796 cm^{-1}.

2-Methoxyphenyl pyridine-2-sulfonate (1d) Prepared according to general procedure as a colorless oil (488 mg, obtained from 2.0 mmol

corresponding phenol, 92%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 3.6 Hz, 1H), 7.95 (d, *J* = 3.2 Hz, 2H), 7.63 – 7.49 (m, 1H), 7.20 – 7.11 (m, 2H), 6.92 – 6.79 (m, 2H), 3.49 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 151.5, 150.2, 138.5, 138.2, 128.4, 128.0, 124.0, 123.9, 120.7, 112.7, 55.6. HRMS (ESI) *m/z* calcd for $C_{12}H_{11}NO_4SNa$ 288.0301 $[M+Na]^+$; found 288.0288. IR (KBr): 3091, 1585, 1506, 1486, 1374, 1203, 1160, 1108, 875, 792 cm^{-1}.

2-Ethoxyphenyl pyridine-2-sulfonate (1e) Prepared according to general procedure as a colorless oil (519 mg, obtained from 2.0 mmol corresponding phenol, 93%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 3.1 Hz, 1H), 8.06 – 7.86 (m, 2H), 7.65 – 7.56 (m, 1H), 7.29 – 7.12 (m, 2H), 6.93 – 6.75 (m, 2H), 3.83 (q, *J* = 8.0 Hz, 2H), 1.14 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 151.0, 150.17, 138.8, 138.0, 128.2, 127.8, 124.1, 123.8, 120.6, 113.8, 64.2, 14.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{13}NO_4SNa$ 302.0457 $[M+Na]^+$; found 302.0454. IR (KBr): 3094, 1581, 1487, 1468, 1372, 1202, 1156, 1109, 877, 798 cm^{-1}.

2-Chlorophenyl pyridine-2-sulfonate (1f) Prepared according to general procedure as a white solid (484 mg, obtained from 2.0 mmol corresponding phenol, 90%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 102 – 104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.0 Hz, 1H), 8.06 (d, *J* = 6.0 Hz, 1H), 8.00- 7.95 (m, 1H), 7.65 – 7.61 (m, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.39 – 7.33 (m, 1H), 7.32 – 7.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 150.5, 146.0, 138.4, 130.7, 128.2, 128.1, 128.0, 127.3, 124.5, 124.1. HRMS (ESI) *m/z* calcd for $C_{11}H_8ClNO_3SNa$ 291.9806 $[M+Na]^+$; found 291.9809. IR (KBr): 3102, 1585, 1486, 1164, 1089, 856, 792 cm^{-1}.

2-Bromophenyl pyridine-2-sulfonate (1g) Prepared according to general procedure as a white solid (556 mg, obtained from 2.0 mmol corresponding phenol, 89%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 104 – 105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.5 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 8.01 – 7.95 (m, 1H), 7.65 – 7.61 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.21 – 7.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8 , 150.6 , 147.3 , 138.5 , 133.8 , 128.8 , 128.5 , 128.4 , 124.2 , 124.2 . HRMS (ESI) *m/z* calcd for $C_{11}H_8BrNO_3SNa$ 335.9300 $[M+Na]^+$; found 335.9301. IR (KBr): 3099, 1585, 1486, 1203, 1197, 1122, 1045, 997, 867, 707 cm^{-1}.

3-*tert*-Butylphenyl pyridine-2-sulfonate (1h) Prepared according to general procedure as a white solid (518 mg, obtained from 2.0 mmol corresponding phenol, 89%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (5:1 v/v). m. p. = 111 – 112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.97 – 7.93 (m , 2H), 7.66 – 7.64 (m, 1H), 7.38 – 7.21 (m, 2H), 7.01 – 6.97 (m, 2H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4 , 150.6 , 149.6 , 138.1 , 129.3 , 128.0 , 124.5 , 124.2 , 119.5 , 119.3 , 34.7 , 31.1 . 55.5 . HRMS (ESI) *m/z* calcd for $C_{15}H_{17}NO_3SNa$ 314.0821 $[M+Na]^+$; found 314.0823. IR (KBr): 2969, 1587, 1432, 1373, 1268, 1203, 1162, 1120, 993, 931, 842, 786 cm^{-1}.

Ethyl 3-(pyridin-2-ylsulfonyloxy)benzoate (1i) Prepared according to general procedure as a colorless oil (560 mg, obtained from 2.0 mmol corresponding phenol, 91%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.0 Hz m, 1H), 8.08 – 7.88 (m, 3H), 7.76 (s, 1H), 7.68 – 7.59 (m, 1H), 7.47 – 7.32 (m, 2H), 4.36 (q, *J* = 8.0 Hz, 2H), 1.38 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 153.4, 150.7, 149.6, 138.4, 132.4, 129.8, 128.4, 128.3, 126.8, 124.3, 123.4, 61.5, 14.3. HRMS (ESI) *m/z* calcd for $C_{14}H_{13}NO_5SNa$ 330.0407 $[M+Na]^+$; found 330.0401. IR (KBr): 3081, 1585, 1485, 1385, 1203, 1197, 1141, 1124, 782 cm^{-1}.

3-Acetylphenyl pyridine-2-sulfonate (1j) Prepared according to general procedure as a colorless oil (492 mg, obtained from 2.0 mmol corresponding phenol, 93%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.01 - 7.97 (m, 2H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.55 – 7.24 (m, 2H), 2.57 (s 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 153.3, 150.7, 149.9, 138.7, 138.4, 130.1, 128.4, 127.1, 126.9, 124.3, 122.0, 26.7. HRMS (ESI) *m/z* calcd for $C_{12}H_{11}NO_4SNa$ 288.0301 $[M+Na]^+$; found 288.0306. IR (KBr): 3083, 1756, 1585, 1486, 1345, 1199, 1132, 1020, 788 cm^{-1}.

Ethyl 4-(pyridin-2-ylsulfonyloxy)benzoate (1k) Prepared according to general procedure as a colorless oil (521 mg, obtained from 2.0 mmol corresponding phenol, 85%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 144 – 145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 – 8.69 (m, 1H), 8.01 – 7.79 (m, 4H), 7.71 – 7.55 (m, 1H), 7.35 – 7.03 (m, 2H), 4.36 (q, *J* = 8.0 Hz, 2H), 1.37 (t, *J* = 8.0 Hz,, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 153.2, 152.9, 150.7, 138.4, 131.3, 129.4, 128.3, 124.2, 122.2, 61.3, 14.2. HRMS (ESI) *m/z* calcd for $C_{14}H_{13}NO_5SNa$ 330.0407 $[M+Na]^+$; found 330.0398. IR (KBr): 3088, 1582, 1481, 1383, 1201, 1197, 1140, 1124, 784 cm^{-1}.

4-Iodophenyl pyridine-2-sulfonate (1l) Prepared according to general procedure as a colorless oil (671 mg, obtained from 2.0 mmol corresponding phenol, 93%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 144 – 145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.4 Hz, 1H), 7.96 (d, *J* = 5.6 Hz, 2H), 7.63 – 7.58 (m, 3H), 6.89 (d, *J* = 8.8 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 150.7, 149.5, 138.9, 138.5, 128.4, 124.4, 124.3, 92.0. HRMS (ESI) *m/z* calcd for $C_{11}H_8INO_3SNa$ 383.9162 $[M+Na]^+$; found 383.9167. IR (KBr): 3089, 1585, 1486, 1207, 1172, 842, 786 cm^{-1}.

4-Chlorophenyl pyridine-2-sulfonate (1m) Prepared according to general procedure as a white solid (500 mg, obtained from 2.0 mmol corresponding phenol, 93%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 114 – 115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.0 Hz, 1H), 7.98 (d, *J* = 4.0 Hz, 2H), 7.67 – 7.63 (m, 1H), 7.26 (d, *J* = 8.8

Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 150.7, 148.1, 138.5, 132.8, 129.8, 128.5, 124.3, 123.7. HRMS (ESI) *m/z* calcd for $C_{11}H_8ClNO_3SNa$ 291.9806 $[M+Na]^+$; found 291.9809. IR (KBr): 3099, 1585, 1486, 1203, 1164, 1141, 1089, 993, 871, 856 cm^{-1}.

4-Fluorophenyl pyridine-2-sulfonate (1n) Prepared according to general procedure as a coloelrss solid (471 mg, obtained from 2.0 mmol corresponding phenol, 93%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 144 – 145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.5 Hz, 1H), 7.97 (d, *J* = 4.0 Hz, 2H), 7.70 – 7.57 (m, 1H), 7.12 – 7.08 (m, 2H), 7.00 – 6.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (J_{C-F} = 245.2 Hz), 153.1, 150.7, 145.4 (J_{C-F} = 2.8 Hz), 138.4, 128.4, 124.4, 124.0 (J_{C-F} = 8.8 Hz), 116.5 (J_{C-F} = 23.8 Hz). HRMS (ESI) *m/z* calcd for $C_{11}H_8FNO_3SNa$ 276.0101 $[M+Na]^+$; found 276.0103. IR (KBr): 3099, 1585, 1486, 1203, 1147, 1120, 865, 796, 705 cm^{-1}.

2-Methoxy-4-methylphenyl pyridine-2-sulfonate (1o) Prepared according to general procedure as a colorless oil (531 mg, obtained from 2.0 mmol corresponding phenol, 95%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.86 – 8.71 (m, 1H), 8.11 – 7.88 (m, 2H), 7.73 – 7.56 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.70 – 6.66 (m, 2H), 3.51 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 154.4, 151.1, 150.2, 138.5, 138.0, 136.4, 127.8, 123.9, 123.6, 121.2, 113.5, 55.6, 21.5. HRMS (ESI) *m/z* calcd for $C_{13}H_{13}NO_4SNa$ 302.0457 $[M+Na]^+$; found 302.0452. IR (KBr): 3097,3083, 1581, 1371, 1190, 1111, 874, 792 cm^{-1}.

2-*tert*-Butyl-4-methoxyphenyl pyridine-2-sulfonate (1p) Prepared according to general procedure as a colorless oil (545 mg, obtained from 2.0 mmol corresponding phenol, 85%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.81 (d, *J* = 4.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 2H), 8.10 - 7.97 (m, 1H), 7.63 – 7.59 (m, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 6.92 (d, *J* = 3.2 Hz, 1H), 6.69 – 6.65 (m, 1H), 3.75 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (100MHz, $CDCl_3$) δ 157.3, 154.9, 150.6, 143.2, 142.9, 138.6, 128.1, 123.8, 122.3, 114.5, 110.6, 55.5, 34.8, 30.3. HRMS (ESI) *m/z* calcd for $C_{16}H_{19}NO_4SNa$ 344.0927 $[M+Na]^+$; found 344.0933. IR (KBr): 3091, 2969, 1587, 1429, 1373, 1203, 1162, 1120, 993, 931, 842, 774 cm^{-1}.

2-Acetyl-4-chlorophenyl pyridine-2-sulfonate (1q) Prepared according to general procedure as a white solid (528 mg from 2.0 mmol corresponding phenol, 85%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 132 – 133 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.89 – 8.68 (m, 1H), 8.12 – 7.97 (m, 2H), 7.79 – 7.55 (m, 2H), 7.36 – 7.30 (m, 1H), 7.49 – 7.23 (m, 1H), 2.60 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 196.6, 152.8, 150.8, 145.8, 138.6, 134.5, 133.2, 132.8, 130.0, 128.6, 124.8, 124.4, 30.6. HRMS (ESI) *m/z* calcd for $C_{13}H_{10}ClNO_4SNa$ 333.9911 $[M+Na]^+$; found 333.9909. IR (KBr): 3103, 3083, 1582, 1476, 1223, 1164, 1124, 1088, 993, 872, 848 cm^{-1}.

Naphthalen-2-yl pyridine-2-sulfonate (1r) Prepared according to general procedure as a white solid (525 mg, obtained from 2.0 mmol corresponding phenol, 92%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 239 – 240 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.78 (d, *J* = 4.0 Hz, 1H), 7.92 (d, *J* = 7.6Hz, 1H), 7.83 – 7.67 (m, 4H), 7.58 (s, 1H), 7.54 – 7.48 (m, 1H), 7.46 – 7.39 (m, 2H), 7.24 – 7.17 (m, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ 153.2, 150.7, 147.2, 138.4, 133.4, 131.9, 130.0, 128.3, 127.9, 127.8, 127.1, 126.6, 124.3, 120.9, 119.9. HRMS (ESI) *m/z* calcd for $C_{15}H_{11}NO_3SNa$ 308.0352 $[M+Na]^+$; found 308.0357. IR (KBr): 2957, 1574, 1433, 1265, 1195, 1121, 1072, 1043, 893, 789, 704 cm^{-1}.

1-Acetylnaphthalen-2-yl pyridine-2-sulfonate (1s) Prepared according to general procedure as a colorless solid (556 mg, obtained from 2.0 mmol corresponding phenol 85%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 103 – 104 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.77 (d, *J* = 4.4 Hz, 1H), 7.97 – 7.79 (m, 4H), 7.79 – 7.64 (m, 1H), 7.64 – 7.34 (m, 4H), 2.64 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 201.7, 152.9, 150.8, 143.5, 138.5, 132.1, 131.6, 131.3, 129.6, 128.5, 128.4, 128.1, 126.8, 124.8, 124.3, 120.9, 32.9. HRMS (ESI) *m/z* calcd for $C_{17}H_{13}NO_4SNa$ 350.0457 $[M+Na]^+$; found 350.0451. IR (KBr): 3085, 2955, 1774, 1574, 1433, 1265, 1174, 1072, 1043, 890, 789, 744 cm^{-1}.

1,2-Phenylene dipyridine-2-sulfonate (1t) Prepared according to general procedure as a colorless oil (666 mg, obtained from 2.0 mmol corresponding phenol, 85%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 136 – 138 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.4 Hz, 2H), 7.98 (d, *J* = 4.0 Hz, 4H), 7.67 – 7.54 (m, 1H), 7.37 - 7.24 (m, 4H). ^{13}C NMR (100MHz, $CDCl_3$) δ 153.2, 150.4, 141.4, 138.5, 128.4, 128.3, 124.6, 124.2. HRMS (ESI) *m/z* calcd for $C_{16}H_{12}N_2O_6S_2Na$ 415.0029 $[M+Na]^+$; found 415.0022. IR (KBr): 3085, 1585, 1485, 1203, 1148, 1123, 788 cm^{-1}.

4-Ethoxyphenyl pyridine-2-sulfonate (1u) Prepared according to general procedure as a colorless oil (519 mg, obtained from 2.0 mmol corresponding phenol, 93%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 – 8.79 (m, 1H), 7.94 – 7.90 (m, 2H), 7.62 – 7.58 (m, 1H), 7.08 – 6.93 (m, 2H), 6.79 – 6.71 (m, 2H), 3.95 (q, *J* = 8.0 Hz, 2H), 1.37 (t, *J* = 8.0 Hz,, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 153.4, 150.6, 142.9, 138.2, 128.1, 124.4, 123.2, 115.1, 63.8, 14.7.HRMS (ESI) *m/z* calcd for $C_{13}H_{13}NO_4SNa$ 302.0457 $[M+Na]^+$; found 302.0451. IR (KBr): 3097, 3085, 1581, 1489, 1474, 1374, 1203, 1156, 1108, 877, 792 cm^{-1}.

Biphenyl-4-yl pyridine-2-sulfonate (1v) Prepared according to general procedure as a white solid (578 mg, obtained from 2.0 mmol corresponding phenol, 93%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 137 – 138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 3.6 Hz, 1H), 8.08 – 7.92 (m, 1H), 7.70 – 7.60 (m, 1H), 7.58 – 7.51 (m, 4H), 7.49 – 7.34 (m, 3H), 7.21 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 150.7, 149.1, 140.4, 139.6, 138.4, 128.9, 128.4, 128.3, 127.8, 127.1, 124.4, 122.6. HRMS (ESI) *m/z* calcd for $C_{17}H_{13}NO_3SNa$

334.0508 $[M+Na]^+$; found 334.0515. IR (KBr): 3099, 1585, 1486, 1203, 1147, 1120, 1022, 873,796, 775 cm^{-1}.

Ethyl 2-(pyridin-2-ylsulfonyloxy)benzoate (1w) Prepared according to general procedure as a colorless oil (540 mg, obtained from 2.0 mmol corresponding phenol, 88%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). ^1H NMR δ 8.69(d, *J* = 4.0 Hz, 1H), 7.97 – 7.88 (m, 2H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.53 (m, 1H), 7.46 – 7.36 (m, 1H), 7.31 – 7.23 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 4.22 (q, *J* = 8.0 Hz,, 2H), 1.29 (t, *J* = 8.0 Hz,, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 153.7 , 150.4 , 148.2, 138.5, 133.4, 131.9, 128.2, 127.2, 125.6, 124.0, 123.7, 61.5, 14.0. HRMS (ESI) *m/z* calcd for $C_{14}H_{13}NO_5SNa$ 330.0407 $[M+Na]^+$; found 330.0391. IR (KBr): 3085, 1627, 1585, 1486, 1378, 1203, 1197, 1147, 1120, 782 cm^{-1}.

3-Methylphenyl pyridine-2-sulfonate (1x) Prepared according to general procedure as a colorless oil (448 mg, obtained from 2.0 mmol corresponding phenol, 90%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.0 Hz, 1H), 7.92 (d, *J* = 4.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.11 (m, 1H), 7.07 – 6.97 (m, 1H), 6.97 (s, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 2.3 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 150.6, 149.5, 140.2, 138.3, 129.4, 128.2, 128.1, 124.3, 122.8, 119.0, 21.3. HRMS (ESI) *m/z* calcd for $C_{12}H_{11}NO_3SNa$ 272.0352 $[M+Na]^+$; found 272.0342. IR (KBr): 3085, 1585, 1378, 1197, 1120, 782 cm^{-1}.

3-Methoxyphenyl pyridine-2-sulfonate (1y) Prepared according to general procedure as a colorless oil (493 mg, obtained from 2.0 mmol corresponding phenol, 93%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 3.6 Hz, 1H), 8.07 – 7.77 (m, 2H), 7.75 – 7.53 (m, 1H), 7.26 – 7.09 (m, 1H), 6.90 – 6.76 (m, 1H), 6.74 – 6.57 (m, 2H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5 , 153.4, 150.6 , 150.4 , 138.2, 130.0, 128.1, 124.4, 114.2, 113.2, 108.2, 55.5. HRMS (ESI) *m/z* calcd for $C_{12}H_{11}NO_4SNa$ 288.0301 $[M+Na]^+$; found 288.0299. IR (KBr): 3095, 1581, 1498, 1486, 1372, 1203, 1160, 1107, 872, 792 cm^{-1}.

3-(Dimethylamino)phenyl pyridine-2-sulfonate (1z) Prepared according to general procedure as a white solid (517 mg, obtained from 2.0 mmol corresponding phenol, 93%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 124 – 125 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.0 Hz, 1H), 8.11 – 7.85 (m, 2H), 7.67 – 7.50 (m, 1H), 7.11 – 6.99 (m, 1H), 6.66 – 6.44 (m, 1H), 6.41 – 6.11 (m, 2H), 2.79 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 151.5, 150.7, 150.5, 138.3, 129.8, 128.2, 124.4, 110.9, 109.0, 105.6, 40.1. HRMS (ESI) *m/z* calcd for $C_{13}H_{14}N_2O_3SNa$ 301.0617 $[M+Na]^+$; found 301.0619. IR (KBr): 3085, 2915,1585, 1486, 1203, 1147, 1120, 1087, 799 cm^{-1}.

4-Methylphenyl pyridine-2-sulfonate (1a') Prepared according to general procedure as a colorless oil (464 mg, obtained from 2.0 mmol corresponding phenol, 93%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.4 Hz, 1H), 8.08 – 7.90 (m, 2H), 7.55 – 7.42 (m, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.97 – 6.93 (m, 2H), 2.29 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5 , 150.6 , 147.5 , 138.2 , 137.2 , 130.2 , 128.0 , 124.3 , 122.0 , 20.9. HRMS (ESI) *m/z* calcd for $C_{12}H_{11}NO_3SNa$ 272.0352 $[M+Na]^+$; found 272.0354. IR (KBr): 3089, 1581, 1371, 1190, 1111, 879, 782 cm^{-1}.

4-Methoxyphenyl pyridine-2-sulfonate (1b') Prepared according to general procedure as a colorless oil (445 mg, obtained from 2.0 mmol corresponding phenol, 84%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 4.0 Hz, 1H), 7.94 (d, *J* = 3.2 Hz, 2H), 7.64 – 7.53 (m, 1H), 7.00 (d, *J* = 2.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 3H), 3.74 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 153.2, 150.6, 143.0, 138.3, 128.2, 124.4, 123.2, 116.1, 114.7, 114.6, 55.6. HRMS (ESI) *m/z* calcd for $C_{12}H_{11}NO_4SNa$ 288.0301 $[M+Na]^+$; found 288.0299. IR (KBr): 3097, 1581, 1489, 1474, 1374, 1203, 1156, 1108, 877, 792 cm^{-1}.

Naphthalen-1-yl pyridine-2-sulfonate (1c') Prepared according to general procedure as a colorless oil (524 mg, obtained from 2.0 mmol corresponding phenol 92%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.0 Hz, 1H), 8.08 – 8.02 (m, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.90 – 7.80 (m, 2H), 7.79 – 7.69 (m, 1H), 7.58 – 7.35 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ153.5, 150.7, 145.7, 138.3, 134.7, 128.2, 127.8, 127.4, 127.1, 126.9, 126.8, 125.3, 124.2, 121.6, 118.6. HRMS (ESI) *m/z* calcd for $C_{15}H_{11}NO_3SNa$ 308.0352 $[M+Na]^+$; found 308.0355. IR (KBr): 2956, 1585, 1436, 1265, 1195, 1120, 1072, 1043, 894, 798, 713 cm^{-1}.

4-Acetylphenyl pyridine-2-sulfonate (1d') Prepared according to general procedure as a colorless oil (514 mg, obtained from 2.0 mmol corresponding phenol, 93%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 8.85 - 8.80 (m, 1H), 8.02 - 7.90 (m 4H), 7.28 - 7.22 (m, 2H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 153.3, 153.1, 150.7, 138.4, 135.8, 130.2, 128.3, 124.2, 122.4, 26.7. HRMS (ESI) m/z calcd for $C_{13}H_{11}NO_4SNa$ 300.0301 $[M+Na]^+$; found 300.0304. IR (KBr): 3359, 3104, 2921, 1683, 1365, 1222, 1140, 796, 623 cm^{-1}.

General procedure for alkenylation of phenyl pyridine-2-sulfonate synthesis.

A round bottom flask containing the phenyl pyridine-2-sulfonate derivative **1** (2.0 mmol), $Pd(OAc)_2$ (120 mg, 10 mol%) was evacuated and filled with dioxygen gas using an oxygen containing balloon. Then, Hexafluoroisopropanol (10 mL), alkene **2** (4.0 mmol) and trifluoroacetic acid (TFA, 4 mmol) were sequentially added to the system under an oxygen atmosphere. (If alkene **2** is a solid, it can be charged with phenyl pyridine-2-sulfonate derivative **1** in the full oxygen round bottom flask.) The mixture was heated to 60 ºC for 12-16 h. It was allowed to reach room temperature and concentrated under reduced pressure. Purification

by flash chromatography afforded the alkenylated phenyl pyridine-2-sulfonate derivative **3**.

Methyl 3-(2-(pyridin-2-ylsulfonyloxy)phenyl)acrylate (3aa) Prepared according to general procedure as a colorless oil (30.3 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 95%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.74 (d, *J* = 4.4 Hz, 1H), 8.03 – 7.87 (m, 2H), 7.64 – 7.57 (m, 3H), 7.54 – 7.50 (m, 2H), 7.43 – 7.25 (m, 1H), 6.24 (d, *J* = 16.4 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.5, 153.0, 150.7, 148.0, 138.5, 137.3, 131.5, 128.3, 128.0, 127.7, 127.6, 124.2, 123.7, 120.1, 51.8. HRMS (ESI) *m/z* calcd for $C_{15}H_{13}NO_5SNa$ 342.0407 $[M+Na]^+$; found 342.0404. IR (KBr): 3083, 2960, 1722, 1643, 1488, 1326, 1205, 1087, 781 cm^{-1}.

Ethyl 3-(2-(pyridin-2-ylsulfonyloxy)phenyl)acrylate (3ab) Prepared according to general procedure as a colorless oil (29.3 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 88%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.77 – 8.71 (m, 1H), 8.10 – 7.89 (m, 2H), 7.65 - 7.51 (m, 3H), 7.43 - 7.39 (m, 2H), 7.33 - 7.27 (m, 1H), 6.22 (d, *J* = 16.0 Hz, 2H), 4.23 (q, *J* = 8.0 Hz, 2H), 1.33 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.1, 153.1, 150.7, 148.0, 138.5, 137.0, 131.4, 128.2, 128.1 , 127.7, 127.6, 124.2, 123.8, 120.6, 60.6, 14.4. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}NO_5SNa$ 356.0563 $[M+Na]^+$; found 356.0559. IR (KBr): 3072, 2989, 1714, 1641, 1585, 1484, 1376, 1201, 1087, 781, 698 cm^{-1}.

***n*-Butyl 3-(2-(pyridin-2-ylsulfonyloxy)phenyl)acrylate (3ac)** Prepared according to general procedure as a colorless oil (31.0 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 86%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.76 (d, *J* = 4.0 Hz, 1H), 8.11 – 7.90 (m, 2H), 7.70 – 7.54 (m, 3H), 7.49 – 7.41 (m, 2H), 7.38 - 7.32 (m, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 8.0 Hz,, 2H), 1.76 – 1.63 (m, 2H), 1.58 – 1.43 (m, 2H), 1.00 (t, *J* = 8.0 Hz,, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.2, 153.2, 150.6, 148.1, 138.3, 138.2, 137.1, 131.4, 129.7, 128.1, 127.6, 124.2, 123.8, 120.6, 64.5, 30.7, 19.2, 13.8. HRMS (ESI) *m/z* calcd for $C_{18}H_{19}NO_5SNa$ 384.0876 $[M+Na]^+$; found 384.0878. IR (KBr): 3069, 2992, 2987, 1718, 1641, 1585, 1488, 1376, 1201, 1087, 781, 698 cm^{-1}.

2-(3-(Dimethylamino)-3-oxoprop-1-enyl)phenyl pyridine-2-sulfonate (3ad) Prepared according to general procedure as a colorless oil (31.9 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 96%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.79 (d, *J* = 4.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.00 – 7.87 (m, 1H), 7.70 – 7.56 (m, 1H), 7.54 – 7.45 (m, 2H), 7.43 – 7.21 (m, 3H), 6.89 (d, *J* = 16.0 Hz, 1H), 3.24 – 3.15 (s, 3H), 3.11 – 3.00 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.1, 153.4, 150.5, 147.9, 138.4, 135.0, 130.4, 129.0, 128.8, 128.2, 127.4, 124.2, 123.4, 121.2, 37.5, 35.9. HRMS (ESI) *m/z* calcd for $C_{16}H_{16}N_2O_4Sna$ 355.0723 $[M+Na]^+$; found 355.0714. IR (KBr): 3099, 2940, 1725, 1656, 1617, 1496, 1384, 1270, 1201, 1176, 1085, 860, 715 cm^{-1}.

2-(2-(Diethoxyphosphoryl)vinyl)phenyl pyridine-2-sulfonate (3ae) Prepared according to general procedure as a yellow oil (38.1 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 96%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.94 – 8.73 (m, 1H), 8.03 – 7.99 (m, 2H), 7.69 – 7.48 (m, 3H), 7.42 – 7.25 (m, 3H), 6.28 – 6.24 (m, 1H), 4.14 (q, *J* = 8.0 Hz, 4H), 1.37 (t, *J* = 8.0 Hz, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ 153.1, 150.7, 147.7, 140.8, 140.7, 138.5, 131.2, 128.7, 128.5, 128.4, 127.6, 127.4, 124.1, 123.3, 118.1 ,116.2 ,62.1 ,62.0 ,16.4 ,16.3 . HRMS (ESI) *m/z* calcd for $C_{17}H_{20}NO_6PSNa$ 420.0641 $[M+Na]^+$; found 420.0642. IR (KBr): 2991, 1623, 1354, 1255, 1203, 1164, 1049, 973, 881, 781 cm^{-1}.

2-(2,2-Diphenylvinyl)phenyl pyridine-2-sulfonate (3af) Prepared according to general procedure as a colorless oil (34.3 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 83%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.0 Hz, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.76 – 7.68 (m, 1H), 7.38 – 7.26 (m, 9H), 7.24 – 7.14 (m, 3H), 7.08 – 7.00 (m, 2H), 6.91 (d, *J* = 6.8 Hz, 1H), 6.82 (s, 1H), 6.75 (d, *J* = 3.6Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 150.5, 148.4, 144.4, 142.6, 139.4, 137.9, 130.9, 130.7, 130.4, 127.9, 126.5, 123.8, 123.4, 121.3. HRMS (ESI) *m/z* calcd for $C_{25}H_{19}NO_3SNa$ 436.0978 $[M+Na]^+$; found 436.0983. IR (KBr): 3093, 3054 1581, 1489, 1313, 1203, 1147, 1120, 1021, 840, 796, 775, 578 cm^{-1}.

2-(2-(Phenylsulfonyl)vinyl)phenyl pyridine-2-sulfonate (3ag) Prepared according to general procedure as a colorless oil (28.8 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 72%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.78 (d, *J* = 4.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.02 – 7.95 (m, 1H), 7.91 (d, *J* = 7.2 Hz, 2H), 7.75 (d, *J* = 16.0 Hz, 1H), 7.68 – 7.59 (m, 2H), 7.56 – 7.52 (m, 2H), 7.47 – 7.44 (m, 3H), 7.34 – 7.25 (m, 1H), 6.86 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ153.0 ,151.0 ,148.3 ,140.2 ,138.8, 135.6, 133.6, 132.4, 129.8, 129.4, 128.7, 128.5, 127.8, 127.7, 126.1, 124.2, 123.9. HRMS (ESI) *m/z* calcd for $C_{19}H_{15}NO_5S_2Na$ 424.0284 $[M+Na]^+$; found 424.0286. IR (KBr): 3056, 1623, 1452, 1311, 1207, 1085, 877, 815, 808 cm^{-1}.

Dimethyl 2-(2-(pyridin-2-ylsulfonyloxy)phenyl)maleate (3ah) Prepared according to general procedure as a colorless oil (33.5 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 89%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.77 (d, *J* = 4.4 Hz, 1H), 7.95 – 7.90 (m, 2H), 7.61 – 7.55 (m, 1H), 7.40 – 7.15 (m, 4H), 7.02 (d, *J* = 3.6 Hz, 1H), 3.78 (s, 3H), 3.60 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 165.6, 164.7, 153.8, 150.5, 146.9, 139.9, 138.2, 131.1, 130.5, 130.1, 128.0, 127.9, 126.5, 124.1, 122.1, 53.1, 52.0. HRMS (ESI) *m/z* calcd for $C_{17}H_{15}NO_7SNa$ 400.0461 $[M+Na]^+$; found 400.0465.

IR (KBr): 3083, 3016, 2960, 1722, 1643, 1488, 1444, 1394, 1326, 1232, 1205, 1174, 831 cm^{-1}.

Methyl-3-(2-(pyridin-2-ylsulfonyloxy)phenyl)but-2-enoate (3ai) Prepared according to general procedure as a colorless oil (29.3 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 88%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.66 (d, *J* = 4.8 Hz, 1H), 7.87 – 7.32 (m, 2H), 7.56 – 7.45 (m, 1H), 7.39 – 7.14 (m, 4H), 7.08 (d, *J* = 7.6 Hz, 1H), 5.46 (s, 1H), 3.64 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 165.2, 152.6, 152.3, 149.5, 145.2, 137.1, 136.1, 128.7, 128.3, 126.9, 126.4, 123.0, 122.7, 121.3, 119.2, 50.1, 18.7. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}NO_5SNa$ 356.0563 $[M+Na]^+$; found 356.0553. IR (KBr): 3083, 3045, 2948, 1721, 1637, 1472, 1326, 1205, 1089, 789 cm^{-1}.

Dimethyl 2-(2-((pyridin-2-ylsulfonyl)oxy)phenyl)maleate (3aj) Prepared according to general procedure as a colorless oil (33.5 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 89%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 - 8.68 (m, 1H), 8.04 – 8.01 (m, 1H), 7.97 – 7.92 (m, 1H), 7.63 – 7.58 (m, 1H), 7.45 – 7.38 (m, 2H), 7.35 – 7.25 (m, 2H), 6.19 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 164.9, 153.3, 147.4, 138.3, 131.3, 130.4, 128.5, 128.3, 127.6, 124.6, 124.4, 123.3, 52.6, 52.1. HRMS (ESI) *m/z* calcd for $C_{17}H_{15}NO_7SNa$ 400.0461 $[M+Na]^+$; found 400.0462. IR (KBr): 3079, 3031, 2957, 2712, 1720, 1644, 1487, 1432, 1324, 1231, 1201, 1174, 831, 721 cm^{-1}.

Methyl 3-(3-methoxy-2-(pyridin-2-ylsulfonyloxy)phenyl)acrylate (3da) Prepared according to general procedure as a colorless solid (33.1 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 95%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). m. p. = 124 – 125 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.84 (d, *J* = 4.0 Hz, 1H), 8.18 – 7.91 (m, 2H), 7.81 – 7.50 (m, 2H), 7.34 – 7.12 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 3.76 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.5, 154.5 , 152.7 , 150.4 , 138.2, 137.8, 129.8, 127.8, 127.8, 123.7, 120.6, 118.8, 114.1, 56.1, 51.7. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}NO_6SNa$ 372.0512 $[M+Na]^+$; found 372.0514. IR (KBr): 3097, 1720, 1650, 1583, 1440, 1382, 1276, 1199, 1068, 1022, 875, 792 cm^{-1}. CCDC 1509677 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

(E)-Methyl 3-(3-ethoxy-2-(pyridin-2-ylsulfonyloxy)phenyl)acrylate (3ea) Prepared according to general procedure as a colorless oil (31.9 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 88%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.78 (d, *J* = 4.0 Hz, 1H), 8.11 – 7.93 (m, 2H), 7.73 (d, *J* = 16.0 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.27 – 7.11 (m, 2H), 6.98 – 7.93 (m, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 3.93 (q, *J* = 8.0 Hz, 2H), 3.73(s, 3H), 1.19 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.5, 154.5, 152.0, 150.4, 138.4, 137.9, 137.8, 129.6, 128.0, 127.8, 123.6, 120.4, 118.5, 115.1, 64.7, 51.7, 14.3. HRMS (ESI) *m/z* calcd for $C_{17}H_{17}NO_6SNa$ 386.0669 $[M+Na]^+$; found 386.0668. IR (KBr): 3079, 1718, 1638, 1472, 1382, 1321, 1208, 1081, 1022, 791, 698 cm^{-1}.

(E)-Methyl 3-(3-chloro-2-(pyridin-2-ylsulfonyloxy)phenyl)acrylate (3fa) Prepared according to general procedure as a white solid (30.3 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 86%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). m. p. = 112 – 113 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.80 (d, *J* = 4.0 Hz, 1H), 8.22 – 7.96 (m, 2H), 7.66 – 7.62 (m, 2H), 7.60 – 7.42 (m, 2H), 7.35 – 7.23 (m, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 3.75 (s, 3H).^{13}C NMR (100MHz, $CDCl_3$) δ 166.2, 153.8, 150.8, 144.7, 138.6, 137.4, 132.2, 131.1, 129.6, 128.4, 128.1, 126.0, 124.1, 121.2, 51.8. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}NO_5ClSNa$ 376.0017 $[M+Na]^+$; found 376.0012. IR (KBr): 3098, 1714, 1641, 1577, 1474, 1160, 1089, 825, 782, 711 cm^{-1}. CCDC 1509678 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Methyl 3-(3-chloro-2-(pyridin-2-ylsulfonyloxy)phenyl)acrylate (3ga) Prepared according to general procedure as a colorless oil (34.8 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 88%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.79 (d, *J* = 4.0 Hz, 1H), 8.19 – 7.91 (m, 2H), 7.63 – 7.60 (m, 4H), 7.21 – 7.17 (m, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.1, 153.8, 150.8, 145.9, 138.6, 137.6, 135.4, 131.1, 128.5, 128.5, 126.8, 124.2, 121.1, 118.7, 51.8. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}NO_5BrSNa$ 419.9512 $[M+Na]^+$; found 419.9498. IR (KBr): 3079, 1720, 1629, 1469, 1382, 1207, 1197, 1122, 1045, 997, 867, 707 cm^{-1}.

Methyl 3-(4-tert-butyl-2-(pyridin-2-ylsulfonyloxy)phenyl)acrylate (3ha Prepared according to general procedure as a colorless oil (36.0 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 96%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.81 (d, *J* = 4.0 Hz, 1H), 8.14 – 7.86 (m, 2H), 7.76 – 7.57 (m, 2H), 7.52 – 7.42 (m, 1H), 7.35 – 7.26 (m, 1H), 6.25 (d, *J* = 16.0 Hz, 1H), 3.76 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.7, 155.6, 153.2, 150.7, 147.9, 138.4, 137.4, 128.2, 127.2, 125.1, 124.8, 124.3, 120.9, 119.2, 51.7, 35.0, 30.9. HRMS (ESI) *m/z* calcd for $C_{19}H_{22}NO_5SNa$ 398.1033 $[M+Na]^+$; found 398.1030. IR (KBr): 3023, 2986, 1732, 1655, 1488, 1430, 1370, 1259, 1212, 1148, 985, 877, 825 cm^{-1}.

Ethyl 4-(3-methoxy-3-oxoprop-1-enyl)-3-(pyridin-2-ylsulfonyloxy) benzoate (3ia) Prepared according to general procedure as a colorless oil (28.2 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 72%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.82 (d, *J* = 4.0 Hz, 1H), 8.18 – 7.94 (m, 4H), 7.77 – 7.51 (m, 3H), 6.52 – 6.28 (m, 1H), 4.43 (q, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 1.44 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.2, 164.7, 153.2, 150.7, 147.8, 138.4, 136.5, 133.3, 132.3, 128.4,

128.3, 127.5, 124.9, 124.3, 122.2, 61.7, 51.9, 14.3. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}NO_8SNa$ 414.0618 $[M+Na]^+$; found 414.0622. IR (KBr): 3087, 2986, 1722, 1677, 1618, 1452, 1377, 1203, 1147, 857, 794 cm^{-1}.

Methyl 3-(4-acetyl-2-(pyridin-2-ylsulfonyloxy)phenyl)acrylate (3ja) Prepared according to general procedure as a colorless oil (34.6 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 96%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^1H NMR (400MHz, $CDCl_3$): δ 8.79 (d, *J* = 4.0 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.03 – 8.00 (m, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.75 – 7.55 (m, 3H), 6.39 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 195.9, 166.1, 153.1, 150.7, 148.1, 139.2, 138.5, 136.3, 132.4, 128.4, 127.8, 127.0, 124.3, 123.8, 122.4, 52.0, 26.7. HRMS (ESI) *m/z* calcd for $C_{17}H_{15}NO_6SNa$ 384.0512 $[M+Na]^+$; found 384.0508. IR (KBr): 3013, 1746, 1632, 1585, 1486, 1345, 1286, 1199, 1086, 878, 785 cm^{-1}.

Ethyl 3-(3-methoxy-3-oxoprop-1-enyl)-4-(pyridin-2-ylsulfonyloxy) benzoate (3ka) Prepared according to general procedure as a colorless oil (37.1 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 95%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^1H NMR (400MHz, $CDCl_3$): δ 8.75 (d, *J* = 4.0 Hz, 1H), 8.23 (d, *J* = 1.6 Hz, 1H), 8.11 – 7.93 (m, 3H), 7.70 – 7.57 (m, 2H), 7.52 (d, *J* = 8.4 Hz, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 4.39 (q, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 1.40 (t, *J* = 8.0 Hz,, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.2, 164.9, 152.9, 150.9, 150.7, 138.6, 136.4, 132.3, 129.7, 129.1, 128.5, 128.1, 124.2, 123.8, 121.3, 61.6, 51.8, 14.3. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}NO_7SNa$ 414.0618 $[M+Na]^+$; found 414.0624. IR (KBr): 3092, 2977, 1724, 1656, 1628, 1462, 1365, 1199, 1154, 861, 779 cm^{-1}.

Methyl 3-(5-iodo-2-(pyridin-2-ylsulfonyloxy)phenyl)acrylate (3la) Prepared according to general procedure as a white solid (40.4 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 91%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). m. p. = 111 – 112 °C. ^1H NMR (400MHz, $CDCl_3$): δ 8.82 (d, *J* = 4.0 Hz, 1H), 8.08 – 7.95 (m, 2H), 7.74 – 7.55 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.1, 153.0, 150.7, 147.9, 140.1, 138.5, 136.4, 135.9, 130.2, 128.3, 125.7, 124.2, 121.3, 92.2, 51.9. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}INO_5SNa$ 467.9373 $[M+Na]^+$; found 467.9369. IR (KBr): 3108, 2956, 1724, 1646, 1403, 1371, 1324, 1207, 1172, 1118, 985, 842, 786 cm^{-1}.

Methyl 3-(5-chloro-2-(pyridin-2-ylsulfonyloxy)phenyl)acrylate (3ma) Prepared according to general procedure as a colorless oil (32.7 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 93%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^1H NMR (400MHz, $CDCl_3$): δ 8.76 – 8.72 (m, 1H), 8.06 – 8.02 (m, H), 7.98 – 7.93 (m, 1H), 7.64 – 7.46 (m, 3H), 7.42 – 7.33 (m, 2H), 6.23 (d, *J* = 16.0 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.1, 153.0, 150.7, 146.4, 138.5, 136.1, 133.3, 131.2, 129.6, 128.4, 127.3, 125.2, 124.3, 121.3, 51.9 .HRMS (ESI) *m/z* calcd for $C_{15}H_{12}ClNO_5SNa$ 376.0017 $[M+Na]^+$; found 376.0012. IR (KBr): 3077, 2958, 1724,1641, 1587, 1438, 1380, 1317, 1261, 1187, 1116, 1079, 991, 852, 711 cm^{-1}.

Methyl 3-(5-fluoro-2-(pyridin-2-ylsulfonyloxy)phenyl)acrylate (3na) Prepared according to general procedure as a white solid (32.0 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 95%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). m. p. = 109 – 110 °C. ^1H NMR (400MHz, $CDCl_3$): δ 8.79 – 8.73 (m, 1H), 8.05 – 7.93 (m, 2H), 7.67 – 7.52 (m, 2H), 7.43 – 7.39 (m, 1H), 7.23 – 7.19 (m, 1H), 7.14 – 7.08 (m, 1H), 6.21 (d, *J* = 16.0 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.1, 160.9（$J_{C\text{-}F}$ = 246.3 Hz）, 152.9, 150.7, 143.9 ($J_{C\text{-}F}$ = 2.8 Hz), 138.6, 136.3 ($J_{C\text{-}F}$ = 1.9 Hz), 129.9 ($J_{C\text{-}F}$ = 8.2 Hz), 128.4, 125.5 ($J_{C\text{-}F}$ = 8.8 Hz), 124.3, 121.3, 118.2 ($J_{C\text{-}F}$ = 23.8 Hz), 113.7 ($J_{C\text{-}F}$ = 24.3 Hz), 51.9. HRMS (ESI) *m/z* calcd for $C_{15}H_{12}FNO_5SNa$ 360.0312 $[M+Na]^+$; found 360.0316. IR (KBr): 3021, 1721, 1638, 1430, 1384, 1288, 1205, 1146, 969, 868, 801 cm^{-1}. CCDC 1509679 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

(E)-Methyl 3-(3-methoxy-5-methyl-2-(pyridin-2-ylsulfonyloxy) phenyl) acrylate (3oa) Prepared according to general procedure as a colorless oil (34.8 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 96%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^1H NMR (400MHz, $CDCl_3$): δ 8.78 (d, *J* = 4.0 Hz, 1H), 8.02 – 7.93 (m, 2H), 7.73 – 7.54 (m, 2H), 6.95 (s, 1H), 6.76 (s, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 3.74 (s, 3H), 3.59 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.6, 154.5, 152.1, 150.4, 138.2, 138.1, 137.9, 135.6, 129.1, 127.9, 123.6, 120.3, 119.1, 115.1, 55.9, 51.7, 21.5. HRMS (ESI) *m/z* calcd for $C_{17}H_{17}NO_6SNa$ 386.0669 $[M+Na]^+$; found 386.0665. IR (KBr): 2940, 1589, 1471, 1380, 1311, 1147, 1083, 831, 773, 698 cm^{-1}.

2-Methoxy-4-methyl-6-(2-(phenylsulfonyl)vinyl)phenyl pyridine-2-sulfonate (3og) Prepared according to general procedure as a white solid (42.3 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 95%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). m. p. = 127 – 129 °C. ^1H NMR (400MHz, $CDCl_3$): δ 8.95 – 8.80 (m, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.04 – 8.00 (m, 1H), 7.97 – 7.88 (m, 2H), 7.80 (d, *J* = 16.0 Hz, 1H), 7.72 – 7.49 (m, 4H), 6.85 – 6.80 (m, 3H), 3.65 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 154.4, 152.4, 150.8, 140.3, 138.3, 138.2, 136.4, 135.9, 133.4, 129.7, 129.3, 128.2, 127.8, 127.4, 123.7, 119.7, 115.9, 56.1, 21.5. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}NO_6S_2Na$ 468.0546 $[M+Na^+]$; found 468.0544. IR (KBr): 2940, 1631, 1588, 1471, 1380, 1311, 1147, 1083, 985, 858, 811, 773, 701 cm^{-1}.

Methyl 3-(3-tert-butyl-5-methoxy-2-(pyridin-2-ylsulfonyloxy) phenyl) acrylate (3pa) Prepared according to general procedure as a white solid (38.5 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 95%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). m. p. = 127 – 128 °C. ^1H NMR (400MHz, $CDCl_3$): δ 8.81 (d, *J* =

4.0 Hz, 1H), 7.98 – 7.94 (m, 2H), 7.61 – 7.57 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.08 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 3.67 (s, 3H), 1.51 (s, 9H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.3, 157.5, 154.3, 150.8, 146.4, 140.9, 139.9, 138.3, 130.6, 127.9, 124.0, 119.2, 118.1, 109.1, 55.5, 51.5, 36.0, 31.7. HRMS (ESI) *m/z* calcd for $C_{20}H_{23}NO_6SNa$ 428.1138 $[M+Na]^+$; found 428.1132. IR (KBr): 3099, 2942, 1724, 1628, 1593, 1486, 1384, 1270, 1201, 1147, 1083, 983, 860, 811, 794, 718 cm^{-1}. CCDC 1509680 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

(E)-Methyl 3-(3-acetyl-5-chloro-2-(pyridin-2-ylsulfonyloxy) phenyl) acrylate (3qa) Prepared according to general procedure as a colorless oil (36.2 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 92%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.0 Hz, 1H), 8.03 – 7.93 (m, 2H), 7.63 – 7.58 (m, 3H), 7.43 (d, *J* = 16.0 Hz, 1H), 6.15 (d, *J* = 16.0 Hz, 1H), 3.77 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 196.8, 165.7, 152.4, 150.8, 143.4, 138.7, 137.5, 135.7, 133.7, 131.5, 131.1, 129.8, 128.6, 124.5, 121.8, 51.9, 29.9. HRMS (ESI) *m/z* calcd for $C_{17}H_{14}ClNO_6SNa$ 418.0123 $[M+Na]^+$; found 418.0121. IR (KBr): 3103, 1685, 1584, 1479, 1443, 1368, 1302, 1246, 1178, 1124, 1071, 884, 853, 804 cm^{-1}.

Methyl 3-(3-(pyridin-2-ylsulfonyloxy)naphthalen-2-yl)acrylate (3ra) Prepared according to general procedure as a white solid (34.3 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 93%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). m. p. = 112 – 113 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.0 Hz, 1H), 8.04-7.96 (m, 2H), 7.93 – 7.89 (m, 1H), 7.87 – 7.69 (m, 4H), 7.63 – 7.47 (m, 3H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.6, 153.3, 150.6, 145.3, 138.4, 138.0, 134.1, 131.7, 128.4, 128.2, 128.0, 127.8, 127.2, 126.7, 124.2, 121.4, 120.3, 51.8. HRMS (ESI) *m/z* calcd for $C_{19}H_{15}NO_5SNa$ 392.0563 $[M+Na]^+$; found 392.0567. IR (KBr): 2986, 1721, 1655, 1585, 1436, 1358, 1265, 1195, 1120, 1043, 887, 789, 723 cm^{-1}.

Methyl 3-(4-acetyl-3-(pyridin-2-ylsulfonyloxy) naphthalen-2-yl) acrylate (3sa) Prepared according to general procedure as a colorless oil (37.3 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 91%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.78 (d, *J* = 4.0 Hz, 1H), 8.13 (s, 1H), 7.94 – 7.76 (m, 5H), 7.68 – 7.48 (m, 3H), 6.43 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 201.0, 166.4, 152.8, 150.9, 141.7, 138.5, 137.9, 133.5, 132.0, 130.4, 129.8, 129.0, 128.9, 128.6, 127.6, 127.5, 125.1, 124.5, 120.8, 51.8, 32.7. HRMS (ESI) *m/z* calcd for $C_{21}H_{17}NO_6SNa$ 434.0669 $[M+Na]^+$; found 434.0667. IR (KBr): 3103, 2986, 1799, 1697, 1585, 1431, 1368, 1283, 1195, 1120, 1074, 887, 804, 738 cm^{-1}.

Methyl (E)-3-(2,3-bis((pyridin-2-ylsulfonyl)oxy)phenyl)acrylate (3ta) Prepared according to general procedure as a colorless oil (45.2 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 95%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). m. p. = 251 – 252 °C. ^{1}H NMR (100MHz, d_6-DMSO): δ 8.77 (d, *J* = 4.0 Hz, 2H), 8.21 – 8.11 (m, 2H), 8.01 – 7.97 (m, 2H), 7.93 – 7.78 (m, 3H), 7.51 – 7.33 (m, 3H), 6.61 (d, *J* = 16.0 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (100MHz, d_6-DMSO) δ 166.2, 152.6, 152.5, 151.5, 151.2, 143.0, 140.1, 140.0, 139.9, 136.0, 130.7, 129.8, 129.0, 127.1, 126.2, 124.7, 124.6, 122.1, 52.2. HRMS (ESI) *m/z* calcd for $C_{20}H_{16}N_2O_8S_2Na$ 499.0240 $[M+Na]^+$; found 499.0237. IR (KBr): 3079, 2860, 1714, 1644, 1472, 1201, 1087,883, 774 cm^{-1}

4-Ethoxy-2-(2-(phenylsulfonyl)vinyl)phenyl pyridine-2-sulfonate (3ug Prepared according to general procedure as a colorless oil (41.7 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 94%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.83 (d, *J* = 4.0 Hz, 1H), 8.25 – 7.82 (m, 4H), 7.77 – 7.46 (m, 5H), 7.36 – 7.17 (m, 1H), 7.02 – 6.73 (m, 3H), 3.98 (q, *J* = 8.0 Hz, 2H), 1.36 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 157.7, 153.0, 150.9, 141.7, 140.2, 138.7, 135.7, 133.6, 129.8, 129.4, 128.6, 127.8, 126.9, 124.9, 124.2, 118.2, 113.1, 64.2, 14.7. HRMS (ESI) *m/z* calcd for $C_{21}H_{19}NO_6S_2Na$ 468.0546 $[M+Na]^+$; found 468.0543. IR (KBr): 3089, 1726, 1645, 1481, 1389, 1324, 1201, 1076, 1023, 801, 704 cm^{-1}.

3-(2-(Phenylsulfonyl)vinyl)biphenyl-4-yl pyridine-2-sulfonate (3vg) Prepared according to general procedure as a white solid (45.8 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 96%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). m. p. = 119 – 120 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.80 (d, *J* = 4.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.04 – 8.00 (m, 1H), 7.97 – 7.89 (m, 2H), 7.75 (d, *J* = 16.0 Hz, 1H), 7.67 – 7.58 (m, 4H), 7.57 – 7.40 (m, 7H), 7.40 – 7.35 (m, 1H), 6.89 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ 153.2, 151.0, 147.6, 141.0, 140.2, 138.9, 138.8, 135.7, 133.6, 131.0, 130.0, 129.4, 129.0, 128.6, 128.2, 127.8, 127.1, 127.0, 126.3, 124.3, 124.2. HRMS (ESI) *m/z* calcd for $C_{25}H_{19}NO_5S_2Na$ 500.0597 $[M+Na]^+$; found 500.0601. IR (KBr): 2954, 1603, 1583, 1434, 1382, 1238, 1186, 1110, 1022, 873, 815, 808, 765 cm^{-1}. CCDC 1509681 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Dimethyl 2-(4-(pyridin-2-ylsulfonyloxy)biphenyl-3-yl)maleate (3vh) Prepared according to general procedure as a colorless oil (38.6 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 85%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). m. p. = 126 – 127 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.83 (d, *J* = 4.0Hz, 1H), 8.12 – 7.90 (m, 2H), 7.70 – 7.43 (m, 8H), 7.42 – 7.35 (m, 1H), 7.31 (s, 1H), 7.10 (s, 1H), 3.86 – 3.83 (s, 3H), 3.68 – 3.63 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 165.6, 164.7, 153.8, 150.6, 150.6, 146.3, 139.7, 139.6, 139.5, 138.2, 130.7, 129.8, 129.0, 128.8, 128.7, 128.5, 128.1, 128.1, 128.0, 127.8, 127.2,

124.1, 122.6, 122.4, 53.1, 52.0. HRMS (ESI) *m/z* calcd for $C_{23}H_{19}NO_7SNa$ 476.0774 $[M+Na]^+$; found 476.0778. IR (KBr): 2954, 1720, 1583, 1434, 1382, 1238, 1186, 1110, 1022, 873, 775 cm^{-1}. CCDC 1509676 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Dimethyl 2-(4-((pyridin-2-ylsulfonyl)oxy)-[1,1'-biphenyl]-3-yl)fumarate (3vj) Prepared according to general procedure as a white solid (41.4 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 91%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). m. p. = 129 – 130 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.71 - 8.69 (m, 1H), 8.07 (d, *J* = 8.0Hz, 1H)), 7.97 – 7.93 (m, 1H), 7.63 – 7.59 (m, 2H), 7.53 – 7.50 (m, 4H), 7.45 – 7.41 (m, 2H), 7.39 – 7.36 (m, 1H), 3.80 (s, 3H), 3.80 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 164.9, 153.4, 150.4, 146.7, 142.1, 140.8, 139.0, 138.3, 129.0, 128.9, 128.8, 128.3, 128.1, 127.1, 125.0, 124.5, 123.7, 52.8, 52.2. HRMS (ESI) *m/z* calcd for $C_{23}H_{19}NO_7SNa$ 476.0774 $[M+Na]^+$; found 476.0777. IR (KBr): 2953, 1711, 1583, 1432, 1377, 1238, 1189, 1111, 1004, 875 cm^{-1}. CCDC 1515863 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Dimethyl 2-(3-(ethoxycarbonyl)-2-(pyridin-2-ylsulfonyloxy) phenyl) maleate (3wh) Prepared according to general procedure as a colorless oil (39.6 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 88%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^1H NMR (400MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.0 Hz, 1H), 8.05 – 7.85 (m, 3H), 7.68 – 7.56 (m, 1H), 7.45 – 7.35 (m, 2H), 6.83 (s, 1H), 4.32 (q, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 3.66 (s, 3H), 1.41 (t, *J* = 8.0 Hz, 3H).^{13}C NMR (100MHz, $CDCl_3$) δ 165.1, 164.9, 164.4, 154.2, 150.4, 145.3, 139.4, 137.9, 134.9, 132.7, 132.4, 130.7, 129.6, 128.0, 127.8, 126.8, 126.3, 123.8, 61.7, 53.1, 52.0, 14.0. HRMS (ESI) *m/z* calcd for $C_{20}H_{19}NO_9SNa$ 472.0673 $[M+Na]^+$; found 472.0663. IR (KBr): 3099, 2960, 1722, 1643, 1575, 1472, 1378, 1203, 1197, 1147, 1120, 869, 782 cm^{-1}.

Dimethyl 2-(4-methyl-2-(pyridin-2-ylsulfonyloxy)phenyl)maleate (3xh) Prepared according to general procedure as a colorless oil (37.5 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 96%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^1H NMR (400MHz, $CDCl_3$): δ 8.77 (d, *J* = 4.0 Hz, 1H), 8.04 – 7.86 (m, 2H), 7.65 – 7.51 (m, 1H), 7.16 (s, 2H), 6.95 (s, 1H), 3.75 (s, 3H), 3.60 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 165.7, 164.7, 153.6, 150.5, 146.7, 140.8, 139.9, 138.2, 130.8, 130.1, 128.1, 127.4, 124.7, 124.1, 122.7, 53.0, 52.0, 21.3. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}NO_7SNa$ 414.0618 $[M+Na]^+$; found 414.0604. IR (KBr): 3097,3021, 2919, 1723, 1628, 1378, 1208, 1188, 1069, 1035, 935, 837, 794 cm^{-1}.

Dimethyl 2-(4-methyl-2-((pyridin-2-ylsulfonyl)oxy)phenyl)maleate (3xj) Prepared according to general procedure as a colorless oil (34.0 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 87%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 8.71 - 8.66 (m, 1H), 8.05 – 8.01 (m, 1H), 7.96 – 7.90 (m, 1H), 7.61 – 7.56 (m, 1H), 7.30 – 7.27 (m, 1H), 7.20 – 7.15 (m, 1H), 7.12 – 7.08 (m, 1H), 6.14 (s, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 165.0, 153.4, 150.3, 147.2, 138.2, 129.9, 128.4, 128.1 125.3, 124.4, 124.1, 123.6，52.6, 52.0, 21.4. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}NO_7SNa$ 414.0618 $[M+Na]^+$; found 414.0615. IR (KBr): 3111,3032, 2934, 1726, 1635, 1384, 1218, 1199, 1067, 1033, 886, 794, 695 cm^{-1}.

Dimethyl 2-(4-methoxy-2-(pyridin-2-ylsulfonyloxy)phenyl)maleate (3yh) Prepared according to general procedure as a yellow oil (37.3 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 92%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^1H NMR (400MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.0 Hz, 1H), 7.99 – 7.84 (m, 2H), 7.64 – 7.51 (m, 1H) , 7.12 (d, *J* = 8.8 Hz, 1H), 6.98 – 6.84 (m, 2H), 6.84 – 6.70 (m, 1H), 3.73 (s, 6H) 3.58 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 165.8, 164.8, 160.7, 153.4, 150.5, 147.6, 139.6, 138.4, 131.8, 129.8, 128.2, 124.1, 119.6, 112.3, 108.1, 55.5, 53.0, 51.9. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}NO_8SNa$ 430.0567 $[M+Na]^+$; found 430.0554. IR (KBr): 3083, 1711, 1635, 1581, 1470, 1362, 1143, 1093, 1032, 843, 783 cm-1. cm^{-1}.

Dimethyl 2-(4-(dimethylamino)-2-(pyridin-2-ylsulfonyloxy) phenyl) maleate (3zh) Prepared according to general procedure as a white solid (38.2 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 91%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). m. p. = 136 – 137 °C. ^1H NMR (400MHz, $CDCl_3$): δ 8.73 (d, *J* = 4.0 Hz, 1H), 8.01 – 7.82 (m, 2H), 7.63 – 7.46 (m, 1H), 7.12 – 7.01 (m, 1H), 6.78 (s, 1H), 6.60 – 6.51 (m, 2H), 3.76 (s, 3H), 3.64 (s, 3H), 2.92 (s, 6H). ^{13}C NMR (100MHz, $CDCl_3$) δ 166.6, 165.2, 153.6, 151.6, 150.4, 148.0, 140.1, 138.1, 131.8, 128.1, 127.9, 124.3, 113.9, 109.7, 105.4, 52.9, 51.8, 40.0. HRMS (ESI) *m/z* calcd for $C_{19}H_{20}N_2O_7SNa$ 443.0883 $[M+Na]^+$; found 443.0889. IR (KBr): 2915, 1725, 1623, 1535, 1440, 1380, 1263, 1172, 1087, 1027, 910, 802 cm^{-1}.

Dimethyl 2-(5-methyl-2-(pyridin-2-ylsulfonyloxy)phenyl) maleate (3a'h) Prepared according to general procedure as a colorless oil (34.3 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 88%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). ^1H NMR (400MHz, $CDCl_3$): δ 8.75 (d, *J* = 4.0 Hz, 1H), 7.98 – 7.83 (m, 2H), 7.59 – 7.55 (m, 1H), 7.16 – 7.12 (m, 2H), 7.05 – 6.92 (m, 2H), 3.77 (s, 3H), 3.60 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 165.6, 164.7, 153.7, 150.5, 144.8, 139.9, 138.2, 136.4, 131.4, 130.7, 130.3, 128.0, 127.5, 124.1, 121.8, 53.0, 51.9, 20.9. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}NO_8SNa$ 414.0618 $[M+Na]^+$; found 414.0622. IR (KBr): 3087, 3005, 2929, 1721, 1617, 1385, 1212, 1199, 1059, 1031, 917, 847, 801 cm^{-1}.

Dimethyl 2-(5-methoxy-2-(pyridin-2-ylsulfonyloxy)phenyl)maleate (3b'h) Prepared according to general procedure as a colorless oil (36.0 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 89%) after purification by flash column chromatography using a mixture

of petroleum ether and ethyl acetate (3:1 v/v). ^{1}H NMR (400MHz, $CDCl_3$): δ 8.76 (d, *J* = 4.0Hz, 1H), 7.92 (s, 2H), 7.59 (s, 1H), 7.31 (s, 1H), 7.20 (d, *J* = 8.8 Hz, 1H), 7.01 (s, 1H), 6.87 – 6.70 (m, 2H), 3.83 – 3.70 (m, 6H), 3.62 (s, 3H).^{13}C NMR (100MHz, $CDCl_3$) δ 165.4, 164.5, 157.4, 153.6, 150.6, 150.5, 140.3, 139.5, 138.2, 130.6, 128.8, 128.0, 124.3, 123.2, 116.2, 114.8, 55.6, 53.1, 52.0. HRMS (ESI) *m/z* calcd for $C_{18}H_{17}NO_8SNa$ 430.0567 $[M+Na]^+$; found 430.0563. IR (KBr): 3087, 1715, 1644，1585, 1506, 1488, 1374,, 1160, 1089, 845, 789 cm^{-1}.

Dimethyl 2-(1-(pyridin-2-ylsulfonyloxy)naphthalen-2-yl)maleate (3c'h) Prepared according to general procedure as a colorless oil (43.7 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 92%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). m. p. = 115 – 116 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.87 (d, *J* = 4.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.96 – 7.71 (m, 4H), 7.73 – 7.45 (m, 3H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.03 (s, 1H), 3.82 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 165.7, 165.6, 164.6, 154.0, 150.6, 144.9, 144.1, 142.8, 140.5, 138.1, 134.7, 134.3, 132.0, 130.7, 128.1, 127.7, 127.4, 127.3, 127.2, 127.1, 126.6, 125.3, 125.2, 123.9, 122.9, 120.3, 53.1, 52.0. HRMS (ESI) *m/z* calcd for $C_{21}H_{17}NO_7SNa$ 500.0597 $[M+Na]^+$; found 500.0601. IR (KBr): 2956, 1729, 1650, 1585, 1378, 1265, 1195, 1120, 1072, 894, 798, 713 cm^{-1}.

General procedure for acetoxylation of phenyl pyridine-2-sulfonate synthesis:

DCE (2 ml) and AcOH (2 ml) were added to a round bottom flask containing the phenyl pyridine-2-sulfonate derivative **1** (1.0 mmol), $Pd(OAc)_2$ (10 mol%) and potassium persulfate (2.0 mmol). Then the mixture was heated to 80 °C for 12 - 24 h. It was allowed to reach room temperature and concentrated under reduced pressure. Purification by flash chromatography afforded the acetoxylated phenyl pyridine-2-sulfonate derivative **4**.

2-((Pyridin-2-ylsulfonyl)oxy)phenyl acetate (4a) Prepared according to general procedure as a colorless oil (26.1 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 89%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (2:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 4.8 Hz, 1H), 8.03 – 7.85 (m, 2H), 7.62-7.57 (m, 1H), 7.35 – 7.25 (m, 2H), 7.25 – 7.15 (m, 1H), 7.12 – 7.09 (m, 1H), 2.18 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 168.2, 153.4, 150.7, 142.9, 141.2, 138.5, 128.5, 128.1, 126.9, 124.1, 124.1, 123.9, 20.6. HRMS (ESI) *m/z* calcd for $C_{13}H_{11}NO_5SNa$ 316.0250 $[M+Na]^+$; found 316.0259. IR (KBr): 3070, 1772, 1581, 1493, 1381, 1200, 1159, 1005, 879, 773 cm^{-1}.

3-Chloro-2-((pyridin-2-ylsulfonyl)oxy)phenyl acetate (4f) Prepared according to general procedure as a colorless oil (24.3 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 75%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (2:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 – 8.79 (m, 1H), 8.08 – 8.05 (m, 1H), 8.02 – 7.97 (m, 1H), 7.67 – 7.62 (m, 1H), 7.29 – 7.15 (m, 3H), 2.25 (s, 3H) ^{13}C NMR (100MHz, $CDCl_3$) δ 168.1, 154.3, 150.5, 145.0, 138.8, 138.4, 128.8, 128.4, 127.82, 127.81, 123.8, 122.8, 20.7. HRMS (ESI) *m/z* calcd for $C_{13}H_{10}ClNO_5SNa$ 349.9860 $[M+Na]^+$; found 349.9866. IR (KBr): 3089, 1776, 1585, 1385, 1196, 1012, 862, 754 cm^{-1}.

4-(*tert*-Butyl)-2-((pyridin-2-ylsulfonyl)oxy)phenyl acetate (4h) Prepared according to general procedure as a colorless oil (29.0 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 83%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (2:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 4.8 Hz, 1H), 7.94 (d, *J* = 4.0 Hz, 2H), 7.73 – 7.59 (m, 1H), 7.35 – 7.24 (m, 1H), 7.14 (d, *J* = 2.0 Hz, 1H), 7.05 (d, *J* = 8.8 Hz, 1H), 2.2(s, 3H), 1.2 (s, 9H). ^{13}C NMR (100MHz, $CDCl_3$) δ 168.5, 153.6, 150.6, 150.3, 140.5, 140.3, 138.3, 128.3, 124.9, 124.3, 123.3, 121.1, 34.6, 31.1, 20.7. HRMS (ESI) *m/z* calcd for $C_{17}H_{19}NO_5SNa$ 372.0876 $[M+Na]^+$; found 372.0871. IR (KBr): 3394, 1705, 1612, 1427, 1365, 1281, 1165, 945, 856 762 cm^{-1}.

Ethyl 3-acetoxy-4-((pyridin-2-ylsulfonyl)oxy)benzoate (4k) Prepared according to general procedure as a colorless oil (30.3 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 83%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (2:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 - 8.78 (m, 1H), 8.01 - 7.92 (m, 3H), 7.82 (d, *J* = 2.0 Hz, 1H), 7.66 – 7.63 (m, 1H) 7.45 (d, *J* = 8.4 Hz, 1H), 4.37 (q, *J* = 8.0 Hz, 2H), 2.24 (s, 1H), 1.37 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 164.7, 153.5, 150.7, 144.7, 142.7, 138.4, 130.3, 128.4, 128.2, 125.4, 124.1, 123.8, 61.6, 20.6, 14.3. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}NO_7SNa$ 388.0461 $[M+Na]^+$; found 388.0463. IR (KBr): 2985, 1720, 1588, 1379, 1265, 1093, 933, 769 cm^{-1}.

5-Iodo-2-((pyridin-2-ylsulfonyl)oxy)phenyl acetate (4l) Prepared according to general procedure as a colorless oil (33.2 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 84%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (2:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 – 8.77 (m, 1H), 8.04 – 7.91 (m, 2H), 7.69 – 7.61 (m, 1H), 7.56 – 7.51 (m, 1H), 7.48 (s, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 2.2 (s, 3H).^{13}C NMR (100MHz, $CDCl_3$) δ 167.9, 153.4, 150.7, 143.4, 141.4, 138.5, 136.0, 133.1 128.5, 125.5, 124.1, 91.1, 20.6. HRMS (ESI) *m/z* calcd for $C_{13}H_{10}INO_5SNa$ 418.9324 $[M+Na]^+$; found 418.9319. IR (KBr): 2960, 1722, 1579, 1427, 1367, 1196, 924, 781, cm^{-1}.

3-(*t*-Butyl)-5-methoxy-2-((pyridin-2-ylsulfonyl)oxy)phenyl acetate (4p) Prepared according to general procedure as a colorless oil (32.2 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 85%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (2:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 - 8.82 (m, 1H), 8.08 - 8.06 (m, 1H), 8.01 - 7.977.54 (m, 1H), 7.64 – 7.60 (m, 1H), 6.83 (d, *J* = 4.0 Hz, 1H), 6.58 (d, *J* = 4.0 Hz, 1H), 3.76 (s, 3H), 2.01 (s, 3H), 1.24 (s, 9H) . ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 157.2, 155.7, 150.4, 144.8, 143.9, 138.3, 134.9, 127.9, 123.0, 112.1, 106.3, 55.6, 35.2, 30.5, 20.7. HRMS (ESI) *m/z* calcd for $C_{18}H_{21}NO_6SNa$ 402.0982 $[M+Na]^+$; found 402.0987. IR (KBr): 2962, 1774, 1587, 1371, 1198, 1020, 850, 611 cm^{-1}.

4-Acetyl-3-((pyridin-2-ylsulfonyl)oxy)naphthalen-2-yl acetate (4s) Prepared according to general procedure as a colorless oil (30.3 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 79%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (2:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 - 8.79 (m, 1H), 7.98 - 7.89 (m, 2H), 7.82 - 7.78 (m, 2H), 7.70 - 7.61 (m, 2H), 7.55 - 7.45 (m, 2H), 2.47 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 168.7, 153.3, 150.8, 140.9, 138.5, 136.7, 133.4, 132.4, 128.6, 128.1, 127.8, 127.6, 127.4, 124.8, 124.2, 123.5, 32.7, 20.9. HRMS (ESI) *m/z* calcd for $C_{19}H_{15}NO_6SNa$ 408.0512 $[M+Na]^+$; found 408.0514. IR (KBr): 3373, 3062, 1697, 1427, 1363, 1209, 922, 804 cm^{-1}.

4-((Pyridin-2-ylsulfonyl)oxy)-[1,1'-biphenyl]-3-yl acetate (4v) Prepared according to general procedure as a colorless oil (28.4 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 77%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (2:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 – 8.81 (m, 1H), 8.09 – 7.91 (m, 2H), 7.66 – 7.59 (m, 1H), 7.54 – 7.48 (m, 2H), 7.45 – 7.32 (m, 6H), 2.24 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 168.3, 153.8, 150.7, 143.0, 141.5, 140.4, 139.1, 138.3, 128.9, 128.3, 128.0, 127.2, 125.4, 124.2, 124.1, 122.6, 20.7. HRMS (ESI) *m/z* calcd for $C_{19}H_{15}NO_5SNa$ 392.0563 $[M+Na]^+$; found 392.0558. IR (KBr): 3069, 2927, 1772, 1579, 1485, 1379, 1198, 833, 769 cm^{-1}.

Ethyl 3-acetoxy-2-((pyridin-2-ylsulfonyl)oxy)benzoate (4w) Prepared according to general procedure as a colorless oil (29.5 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 81%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (2:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 - 8.76 (m, 1H), 7.99 - 7.96 (m, 2H), 7.83 - 7.78 (m, 1H), 7.65 - 7.61 (m, 1H), 7.37 - 7.28 (m, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.09 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 164.3, 154.4, 150.5, 143.7, 138.3, 129.0, 128.1, 127.7, 127.6, 127.4, 123.8, 61.7, 20.5, 14.0. HRMS (ESI) *m/z* calcd for $C_{16}H_{15}NO_7SNa$ 388.0461 $[M+Na]^+$; found 388.0463. IR (KBr): 3413, 2960, 1722, 1382, 1292, 1120, 565 cm^{-1}.

5-Methyl-2-((pyridin-2-ylsulfonyl)oxy)phenyl acetate (4a') Prepared according to general procedure as a colorless oil (24.6 mg, obtained from 0.1 mmol corresponding phenyl 2-pyridinesulfonate, 80%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (2:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 - 8.79 (m, 1H), 7.99 - 7.90 (m, 2H), 7.65 - 7.59 (m, 1H), 7.19 - 7.15 (m, 1H), 7.03 - 6.97 (m, 1H), 6.95 - 6.92 (m, 1H), 2.32 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 153.8, 150.6, 138.2, 128.1, 127.4, 124.4, 124.1, 123.5, 21.0, 20.7. HRMS (ESI) *m/z* calcd for $C_{14}H_{13}NO_5SNa$ 330.0407 $[M+Na]^+$; found 330.0404. IR (KBr): 3425, 3076, 2920, 2555, 1955, 1579, 1373, 1192, 822, 592 cm^{-1}.

5-acetyl-2-((pyridin-2-ylsulfonyl)oxy)phenyl acetate (4d') Prepared according to general procedure as a colorless oil (27.8 mg from 0.1 mmol corresponding phenyl pyridine-2-sulfonate, 83%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (2:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 - 8.79 (m, 1H), 8.04 - 7.96 (m, 2H), 7.84 - 7.81 (m, 1H), 7.75 - 7.70 (m, 1H), 7.67 - 7.63 (m, 1H), 7.51 - 7.48 (m, 1H), 2.58 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 168.1, 153.6, 150.7, 143.0, 136.5, 128.4, 127.0, 124.12, 124.07, 124.05, 26.6, 20.6. HRMS (ESI) *m/z* calcd for $C_{15}H_{13}NO_6SNa$ 358.0356 $[M+Na]^+$; found 358.0353. IR (KBr): 3435, 3084, 2920, 1782, 1683, 1365, 1198, 1149, 850, 621 cm^{-1}.

Removing the directing group.

A suspension of alkenylated phenyl pyridine-2-sulfonate derivative (0.1 mmol) and activated Zn powder (327 mg, 5.0 mmol) in a 1:1 mixture of THF and saturated NH_4Cl solution in water (5 mL) was stirred at room temperature until consumption of the starting material (monitored by TLC). The mixture was filtered over a pad of celite to remove the Zn. The filtrate was extracted with EtOAc (15 mL) and washed with a saturated aqueous solution of ammonium chloride and brine. The combined organic phase was dried over $MgSO_4$ and concentrated to dryness. The residue was purified by flash chromatography to afford the corresponding alkenylated phenol derivatives **5**.

(E)-Methyl 3-(2-hydroxyphenyl)acrylate (5aa)[21] Prepared according to general procedure as a white solid (15.1 mg, obtained from 0.1 mmol corresponding alkenlated phenyl 2-pyridinesulfonate, 85%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 241 – 242 °C. ^{1}H NMR (400MHz $CDCl_3$): δ 10.27 (s, 1H), 7.90 (d, *J* = 16.0 Hz, 1H), 7.66 – 7.52 (m, 1H), 7.31 – 7.11 (m, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.89 – 6.85 (m, 1H), 6.62 (d *J* = 16.0 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 167.6, 157.3, 140.6, 132.2, 129.3, 121.1, 119.9, 117.3, 116.6, 51.8. HRMS (ESI) *m/z* calcd for $C_{10}H_{10}O_3Na$ 201.0522 $[M+Na]^+$; found 201.0518. IR (KBr): 3046, 2958, 1695, 1627, 1457, 1174,
995, 869, 760, 622 cm^{-1}.

(E)-Methyl 3-(2-hydroxy-3-methoxyphenyl)acrylate (5da)[22] Prepared according to general procedure as a white solid (15.5 mg, obtained from 0.1 mmol corresponding alkenlated phenyl 2-pyridinesulfonate, 87%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 247 – 248 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.96 (d, *J* = 16.0 Hz, 1H), 7.10 – 7.06 (m, 1H), 6.90 – 6.78 (m, 2H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.22 (s, 1H), 3.90 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 146.8, 145.4, 139.8, 120.9, 120.8, 119.7, 118.8, 111.8, 77.4, 77.1, 76.7, 56.2, 51.6. HRMS (ESI) *m/z* calcd for $C_{10}H_{10}O_3Na$ 201.0522 $[M+Na]^+$; found 201.0518. IR (KBr): 1714, 1635, 1492, 1457, 1324, 1272, 1238, 1184, 1089, 985, 917, 788 cm^{-1}.

General procedure for coumarin synthesis:

To a solution of 1.0 mmol methyl 2-hydroxycinnamat with different substituent groups in 10mL methanol was added 2.0 mmol Bu_3P. The mixture was stirred at 60℃ overnight. The solvent was removed by distillation and the mixture was purified by column chromatography to give the product **6** as white solid.

2H-Chromen-2-one (6aa)[23] Prepared according to general procedure as a white solid (10.7 mg, obtained from 0.1 mmol corresponding alkenlated phenyl 2-pyridinesulfonate, 70%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl

acetate (4:1 v/v). m. p. = 69–70 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.76 - 7.70 (d, *J* = 9.6 Hz, 1H), 7.57 - 7.47 (m, 2H), 7.35 - 7.25 (m, 2H), 6.42 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 154.0, 143.5, 131.9, 127.9, 124.5, 118.8, 116.8, 116.6, HRMS (ESI) *m/z* calcd for $C_9H_6O_2Na$ 169.0260 $[M+Na]^+$; found 169.0256. IR (KBr): 1729, 1617, 1457, 1403, 1267, 1184, 1122, 937, 835, 763 cm^{-1}.

8-Methoxy-2H-chromen-2-one (6da)[24] Prepared according to general procedure as a white solid (12.8 mg, obtained from 0.1 mmol corresponding alkenlated phenyl 2-pyridinesulfonate, 68%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 114 – 115 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.70 (d, *J* = 9.6 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.10 – 7.06 (m, 2H), 6.43 (d, *J* = 9.6 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 147.2, 143.7, 143.7, 124.3, 119.5, 119.5, 116.9, 113.7, 56.2. HRMS (ESI) *m/z* calcd for $C_{11}H_9O_3Na$ 212.1766 $[M+Na]^+$; found 212.1764. IR (KBr): 3246, 1726, 1619, 1452, 1418, 1267, 1184, 1120, 935, 835, 763cm^{-1}.

7-*tert*-Butyl-2H-chromen-2-one (6ha)[25] Prepared according to general procedure as a white solid (14.9 mg, obtained from 0.1 mmol corresponding alkenlated phenyl 2-pyridinesulfonate, 74%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 129 – 130 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.70 (d, *J* = 9.6 Hz, 1H), 7.45 -7.41 (m, 1H), 7.34- 7.29 (m, 2H), 6.36 (d, *J* = 9.6 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 156.3, 154.1, 143.3, 127.4, 122.0, 116.4, 115.6, 113.6, 35.2, 31.0. HRMS (ESI) *m/z* calcd for $C_{13}H_{14}O_2Na$ 225.0886 $[M+Na]^+$; found 225.0884. IR (KBr): 3258, 1721, 1618, 1458, 1399, 1267, 1179, 1123, 934, 831, 763 cm^{-1}.

General procedure for benzofuran synthesis.

To a solution of 1.0 mmol methyl 2-hydroxycinnamat or 2-(phenylsulfonylvinyl)phenol with different substituent groups in 10mL DMF was added 1.5 mmol Cesium carbonate and 0.5 mmol dihydrated copper (II) chloride. The mixture was stirred at 100℃ overnight. The mixture was poured into water, extracted with EtOAc and washed with brine. The combined organic phase was dried over $MgSO_4$ and concentrated to dryness. The residue was purified by flash chromatography to afford the corresponding benzofuran derivatives **7**

Benzofuran-2-carboxylic acid (7aa)[26] Prepared according to general procedure as a white solid (10.1 mg, obtained from 0.1 mmol corresponding alkenlated phenyl 2-pyridinesulfonate, 62%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (3:1 v/v). m. p. = 191 – 192 °C. ^{1}H NMR (400MHz, d_6-DMSO): δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.76 – 7.64 (m, 2H), 7.52 – 7.47 (m, 1H), 7.37 – 7.34 (m, 1H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 160.6, 155.4, 146.7, 128.0, 127.3, 124.3, 123.6, 113.9, 112.5. HRMS (ESI) *m/z* calcd for $C_9H_6O_3Na$ 185.0209 $[M+Na]^+$; found 185.0212. IR (KBr): 3457, 1695, 1581, 1430, 1301, 1232, 1187, 944, 819, 748 cm^{-1}.

7-Ethoxybenzofuran-2-carboxylic acid (7da)[26] Prepared according to general procedure as a white solid (12.9 mg, obtained from 0.1 mmol corresponding alkenlated phenyl 2-pyridinesulfonate, 63%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 203 – 204 °C. ^{1}H NMR (400MHz, d_6-DMSO): δ 7.64 (s, 1H), 7.33 – 7.27 (m, 1H), 7.26 -7.21 (m, 1H), 7.08 – 7.04 (m, 1H), 4.23 (q, *J* = 8.0 Hz, 2H), 1.42 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 160.5, 146.6, 145.1, 145.0, 128.9, 125.1, 115.0, 114.2, 110.3, 64.5, 15.1. HRMS (ESI) *m/z* calcd for $C_{11}H_{10}O_4Na$ 229.0471 $[M+Na]^+$; found 229.0467. IR (KBr): 3484, 2991, 2940. 1702, 1592, 1494, 1433, 1328, 1270, 1203, 1089, 1020, 941, 904, 652, 779, 730cm^{-1}.

7-Phenyl-2-(phenylsulfonyl)benzofuran (7vf)[26] Prepared according to general procedure as a white solid (18.4 mg, obtained from 0.1 mmol corresponding alkenlated phenyl 2-pyridinesulfonate, 55%) after purification by flash column chromatography using a mixture of petroleum ether and ethyl acetate (4:1 v/v). m. p. = 240 – 241 °C. ^{1}H NMR (400MHz $CDCl_3$): δ 8.13 - 8.08 (m, 2H), 7.86 - 7.83 (m, 1H), 7.68 - 7.56 (m, 8H), 7.48 - 7.44 (m, 2H). 7.38 - 7.33 (m, 1H),^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 152.2, 140.5, 139.3, 138.1, 134.3, 129.6, 129.0, 128.3, 127.9, 127.6, 127.4, 126.6, 121.4, 113.7, 112.6. HRMS (ESI) *m/z* calcd for $C_{20}H_{14}O_3SNa$ 357.0556 $[M+Na]^+$; found 357.0554. IR (KBr): 1546, 1452, 1338, 1164, 1097, 937, 894, 815, 761, 725, 692, 622cm^{-1}.

2-Hydroxyphenyl pyridine-2-sulfonate (8a) DCE (2 ml), TFA (1 ml) and trifluoroacetic anhydride (1 ml) were added to a round bottom flask containing the phenyl pyridine-2-sulfonate **1** (0.1 mmol), $Pd(OAc)_2$ (10 mol%) and potassium persulfate (0.2 mmol). Then the mixture was heated to 80 ºC for 15 h. It was allowed to reach room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether : ethyl acetate, 3:1 v/v) to afford the hydroxylated phenyl 2-pyridinesulfonate (**8a,** 22.1 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 8.70 - 8.65 (m, 1H), 8.09 - 8.04 (m, 1H), 7.98 - 7.93 (m, 1H), 7.61 - 7.56 (m, 1H), 7.30 - 7.25 (m, 1H), 7.19 - 7.14 (m, 1H), 7.03 - 6.98 (m, 1H), 6.87 - 6.81 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 149.5, 149.2, 139.6, 137.0, 129.0, 128.7, 124.1, 123.8, 120.3, 118.9. HRMS (ESI) *m/z* calcd for $C_{11}H_9NO_4SNa$ 274.0144 $[M+Na]^+$; found 274.0141. IR (KBr): 3445, 3082, 1577, 1495, 1199, 1157, 1120, 781, 675 cm^{-1}.

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Keywords: phenol · regioselectivity · C-H activation · olefination · acetoxylation

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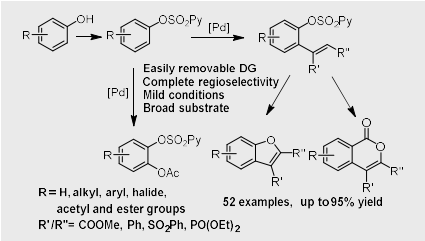

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Page No. – Page No.

Palladium-Catalyzed C-H Functionalization of Phenyl 2-Pyridylsulfonate