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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b00177 • Publication Date (Web): 02 Feb 2018

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$Cu(OAc)_2$ Mediated Synthesis of 3-Sulfonyl Chromen-4-ones

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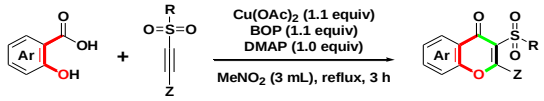
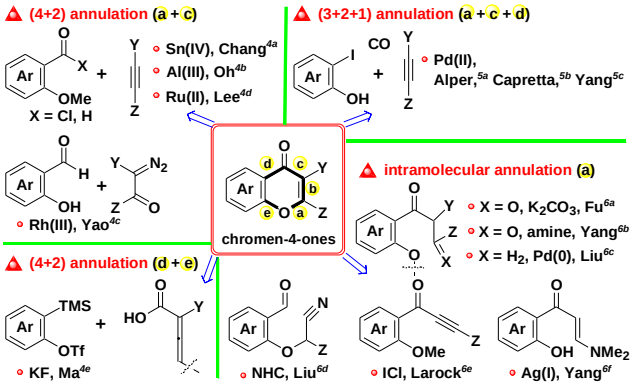


ABSTRACT: Copper acetate mediated (4+2) annulation of sulfonylacetylenes with salicyclic acids provides sulfonyl chromen-4-ones in the presence of BOP and DMAP in $MeNO_2$ at reflux for 3 h. The uses of various metal complexes and activating reagents are investigated for facile and efficient transformation. A plausible mechanism has been proposed.

Introduction

Functionalized chromen-4-ones (benzopyran-4-ones) are the key component of naturally occurring oxygen-containing heterocyclic compounds which possess various biological activities.[1-2] A large number of synthetic routes have been reported for this core structure along with their related derivatives, including common and classic Claisen condensation,[3a] the Baker-Venkatamaran rearrangement,[3b-c] the Kostanecki-Robinson reaction,[3d] the Simonis reaction,[3e] and the Ruhemann reaction[3f] under different metallic, basic, acidic, organocatalytic, solvent-free, or microwave-enchanced conditions. Recently, other efforts involving intermolecular (4+2)[4] or (3+2+1)[5] annulation and intramolecular annulation[6] were also demonstrated to provide more efficient synthetic pathways via "a~e" bond formations of a pyran-4-one motif (Scheme 1).

Scheme 1. Annulation Routes of Chromen-4-ones

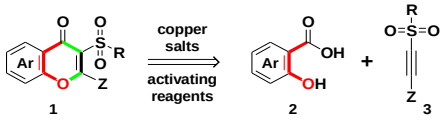


However, intermolecular annulations are also popular approaches to such chromen-4-ones among existing methods. Development of a new, single-vessel route for the simultaneous bond formation and ring-construction of diversified chromen-4-ones from readily available starting materials still represents a continuing need in the organic synthetic field. Although developed synthetic protocols have been extensively investigated for the functionalization of chromen-4-ones, most of these substituents (Y and Z groups of pyran-4-one) of reported molecules focused on alkyl and aryl groups (by a carbon-carbon bond linkage). Among the present scaffolds in the family, a core structure having a heteroatom-conjugated group (e.g., R_2N,[4a,6d] I,[6e] F_3CS,[6f] RSO_2[7]) is relatively rare, especially those with a sulfonyl substituent (Y = RSO_2). The traditional route for the involvement of a sulfonyl group requires additional two-step steps, including nucleophilic addition of chromen-4-ones with thiophenolate followed by oxidation of the corresponding sulfides.[7a-b] However, the direct introduction of a sulfonyl group into the chromen-4-ones skeleton had not been reported until recently. As a result of the recent findings, new methods for their preparation are needed.

Results and Discussion

Continuing our research on the synthesis of sulfonyl frameworks,[8] herein, we present various copper salts in a mediated synthesis of sulfonyl chromen-4-ones **1** via one-pot efficient (4+2) annulation of salicyclic acids **2** with sulfonylacetylenes **3** in the presence of activating reagents (Scheme 2).[9] On the basis of the facile preparation of **3**,[10] adopted by Zhang[10b] and Waser,[10c] skeleton **3** was obtained from an $AlCl_3$ mediated coupling reaction of RSO_2Cl and TMS-protected acetylenes. Skeleton **2** was afforded from Pinnick oxidation of commercially available 2-hydroxybenzaldehydes besides **2a** (Ar = Ph).

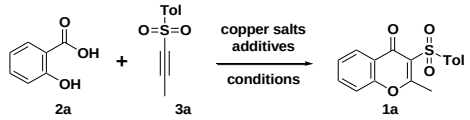
Scheme 2.Our Synthetic Route of **1**



The initial study commenced with treatment of model substrates **2a** (Ar = Ph, 0.5 mmol) and **3a** (R = Tol, Z = Me, 1.1

equiv) with a 0.3 equivalent of $Cu(OAc)_2$ in $MeNO_2$ at rt or 100 °C for 3 h. However, two conditions were unsuccessful. Following, a stoichiometric amount of $Cu(OAc)_2$ was increased to 1.1 equivalent, only an 18% yield of **1a** was provided under the refluxing $MeNO_2$ condition for 3 h. With the addition of DMAP (1.0 equiv), the yield was enhanced to 35%. The results prompted us to optimize the condition to improve the yield of **1a**. Gratifyingly, when BOP (1.1 equiv, benzotriazol-1-yloxy tri(dimethylamino)phosphonium hexafluorophosphate, Castro's reagent), and DMAP (1.0 equiv) were added to the reaction mixture, the yield of **1a** was enhanced 80%. Compared with 1.0 equivalent of DMAP, a catalytic amount of DMAP (0.2 equiv) was treated to $Cu(OAc)_2$ mediated reaction of **2a** and **3a** in the presence of BOP (1.1 equiv), however, **1a** was isolated in lower yield (51%).

Table 1. Reaction Conditions[a]

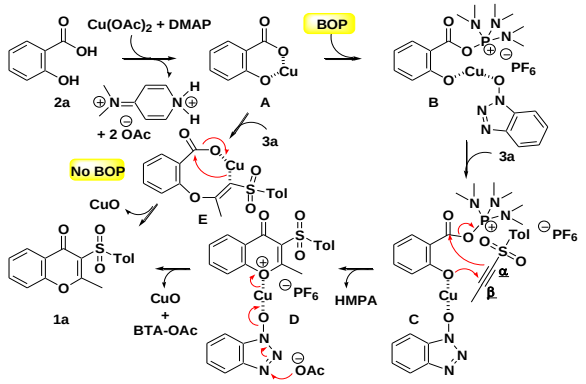


entry	copper salts (eq)	activators	solvent	time (h)	**1a** (%)[b]
1	$Cu(OAc)_2$ (1.1)	BOP	$MeNO_2$	3	80
2	$Cu(OAc)_2$ (1.1)	BOP	DMSO	3	—[c]
3	$Cu(OAc)_2$ (1.1)	BOP	DMF	3	55
4	$Cu(OAc)_2$ (1.1)	BOP	CH_2Cl_2	3	—[d]
5	$Cu(OAc)_2$ (1.1)	BOP	MeCN	3	<5
6	$Cu(OAc)_2$ (1.1)	BOP	THF	3	28
7	$Cu(OAc)_2$ (1.1)	BOP	toluene	3	—[d]
8	$Cu(OTf)_2$ (1.1)	BOP	$MeNO_2$	3	68
9	$CuSO_4$ (1.1)	BOP	$MeNO_2$	3	32
10	CuF_2 (1.1)	BOP	$MeNO_2$	3	14
11	CuI (1.1)	BOP	$MeNO_2$	3	—[d]
12	$Cu(OAc)_2$ (1.5)	BOP	$MeNO_2$	3	78
13	$Cu(OAc)_2$ (2.0)	BOP	$MeNO_2$	3	80
14	$Cu(OAc)_2$ (1.5)	HBTU	$MeNO_2$	3	30
15	$Cu(Oac)_2$ (2.0)	DCC	$MeNO_2$	3	11
16	$Cu(OAc)_2$ (1.1)	BOP	$MeNO_2$	6	71
17	$Cu(OAc)_2$ (1.1)	PyBOP	$MeNO_2$	3	70

[a]The reactions were run on a 0.5 mmol scale with **2a**, **3a** (1.1 equiv), DMAP (1.0 equiv), activators (1.1 equiv), solvent (3 mL), reflux. [b]Isolated yields. [c]Complex results. [d]No reaction.

Controlling DMAP as the base, we surveyed the effect of the additives on the reaction, revealing that activating reagents were indispensable for constructing a core structure of chromen-4-one, as shown in Table 1, entry 1. Furthermore, solvent screening was performed. It was obvious that the reaction was highly solvent-dependent with poor (28%; <5%) and moderate (58%) yields obtained in THF, MeCN, and DMF, respectively (entries 3, 5, 6), while no desired products were detected in DMSO, CH_2Cl_2, or toluene (Table 1, entries 2, 4, 7). Subsequently, some copper(II) complexes were studied, such as $Cu(OTf)_2$, $CuSO_4$, and CuF_2. However, none of them obtained higher yields of **1a** than $Cu(OAc)_2$ (entries 8-10). After changing $Cu(OAc)_2$ to CuI, no desired products were produced (entry 11). Next, other catalytic amounts (1.5 and 2.0 equiv) of $Cu(OAc)_2$ were examined; however, the isolated yields were similar (78% and 80%) (entries 12-13). By controlling $Cu(OAc)_2$ as the promoter, we found that other kinds of activating reagents, HBTU and DCC, were ineffective in the current reaction (entries 14-15). After elongating the reaction time (3 → 6 h), isolated yield (71%) was decreased (entry 16). To avoid the production of poison HMPA, BOP was changed to PyBOP. However, lower yield (70%) of **1a** were produced (entry 17). From these observations, we concluded that $Cu(OAc)_2$, BOP, and DMAP provided optimal conditions (refluxing $MeNO_2$ and 3 h) for one-pot (4+2) cyclization.

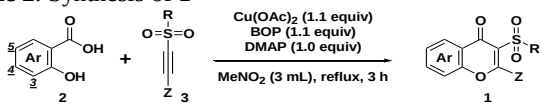
Scheme 3. Plausible Mechanism



On the basis of our experimental results, a plausible mechanism for the formation of **1a** is illustrated in Scheme 3. Initially, DMAP mediated complexation of $Cu(OAc)_2$ with hydroxyl and carboxylic acid groups of **2a** yields **A**. By intermolecular cross coupling of **A** and BOP, **B** should be afforded via the O-P bond cleavage of BOP. Following the involvement of **3a**, the oxy-copper arm of *in-situ* generated **C** attacks the β-position of **3a** via the O-C bond formation. Subsequently, the corresponding formed α-anion promotes the intramolecular C-C bond formation and the release of HMPA to produce **D**. Finally, the construction of **1a** furnished via the acetate anion mediated the removal of benzotriazoyl acetate (BTA-OAc) and copper oxide (CuO). The by-product BTA-OAc was isolated to confirm the mechanism pathway. On the other hand, when the $Cu(OAc)_2$ mediated reaction is not involved with BOP, cross coupling of **A** and **3a** provided **E** through a *syn*-addition. With the ring-contraction of **E** having an eight-membered ring and the elimination of CuO, **1a** is afforded. From the possible mechanism, we found that the stoichiometric amounts of $Cu(OAc)_2$, BOP, and DMAP required at least one equivalent, such that a one-pot reaction provided better yield (80%) of **1a**.

To study the scope and limitations of this approach, **2** and **3** were reacted with the combination of $Cu(OAc)_2$, BOP, and DMAP to afford diversified **1**, as shown in Table 2. With optimal conditions established (Table 1, entry 1) and a plausible mechanism proposed (Scheme 3), we found that this route allowed a direct (4+2) annulation under mild conditions in moderate to good yields (54%-86%). Among entries 1-38, efficient formation of **1a**-**1al** showed that the substituents (Ar, R, and Z) did not affect the yield. The structures of **1a**, **1f**, **1h**, and **1al** were determined by single-crystal X-ray crystallography.[11] For the electronic nature of aryl substituents (Ar) of **2**, not only electron-neutral but electron-withdrawing and electron-donating groups were appropriate. For the sulfonyl substituents (R) of **3**, both aliphatic and aromatic groups were well-tolerated. However, for the Z substituents of **3**, only aliphatic groups (Me, Et, CF_3, and CH_2Ar) could be well-applied.

Table 2. Synthesis of **1**[a]

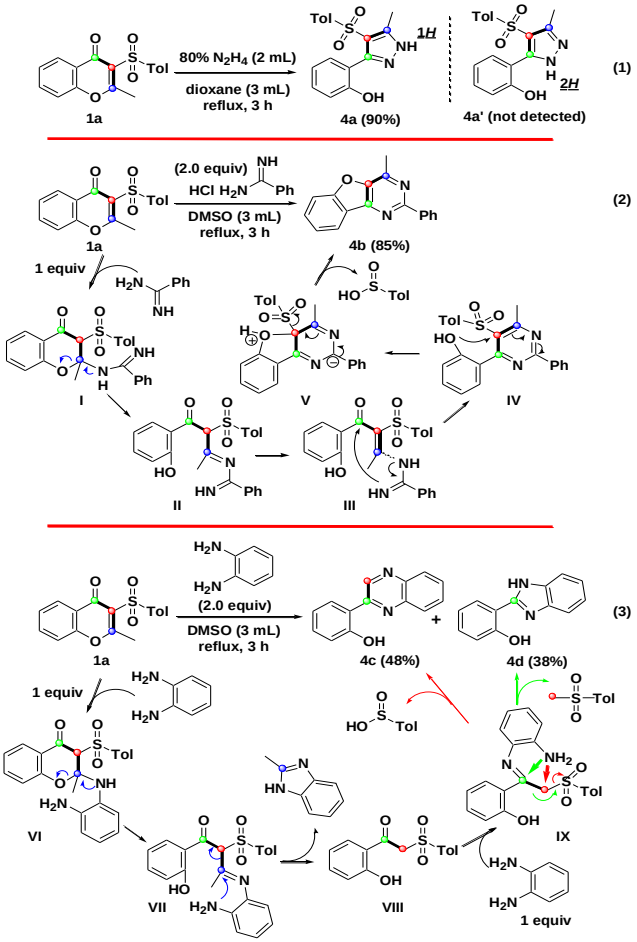


entry	**2**, Ar =	**3**, R =, Z =	**1**, (%)[b]
1	**2a**, Ph	**3a**, Tol, Me	**1a**, 80
2	**2a**, Ph	**3b**, Ph, Me	**1b**, 84
3	**2a**, Ph	**3c**, Me, Me	**1c**, 86
4	**2a**, Ph	**3d**, 4-FC_6H_4, Me	**1d**, 78
5	**2a**, Ph	**3e**, 4-$MeOC_6H_4$, Me	**1e**, 74
6	**2b**, 5-FC_6H_3	**3a**, Tol, Me	**1f**, 82
7	**2c**, 4-$MeOC_6H_3$	**3a**, Tol, Me	**1g**, 68
8	**2a**, Ph	**3f**, Tol, Et	**1h**, 80
9	**2a**, Ph	**3g**, Ph, Et	**1i**, 80
10	**2a**, Ph	**3h**, Me, Et	**1j**, 73
11	**2a**, Ph	**3i**, 4-FC_6H_4, Et	**1k**, 74
12	**2a**, Ph	**3j**, 4-$MeOC_6H_4$, Et	**1l**, 66
13	**2b**, 5-FC_6H_3	**3f**, Tol, Et	**1m**,84
14	**2c**, 4-$MeOC_6H_3$	**3f**, Tol, Et	**1n**, 68
15	**2a**, Ph	**3k**, Tol, CF_3	**1o**, 74
16	**2a**, Ph	**3l**, Ph, CF_3	**1p**, 73
17	**2a**, Ph	**3m**, Me, CF_3	**1q**, 64
18	**2a**, Ph	**3n**, 4-FC_6H_4, CF_3	**1r**, 60
19	**2b**, 5-FC_6H_3	**3k**, Tol, CF_3	**1s**, 66
20	**2c**, 4-$MeOC_6H_3$	**3k**, Tol, CF_3	**1t**, 54
21	**2a**, Ph	**3o**, Tol, CH_2Ph	**1u**, 73
22	**2a**, Ph	**3p**, Tol, CH_2-4-MeC_6H_4	**1v**, 78
23	**2a**, Ph	**3q**, Tol, CH_2-2-thienyl	**1w**, 72
24	**2a**, Ph	**3r**, Tol, CH_2-4-FC_6H_4	**1x**, 78
25	**2a**, Ph	**3s**, Tol, CH_2-4-$MeOC_6H_4$	**1y**, 78
26	**2a**, Ph	**3t**, Tol, CH_2-3,4-$(MeO)_2C_6H_4$	**1z**, 72
27	**2a**, Ph	**3u**, Tol, CH_2-1-naphthyl	**1aa**,70
28	**2a**, Ph	**3v**, 3-MeC_6H_4, Me	**1ab**, 80
29	**2a**, Ph	**3w**, 4-EtC_6H_4, Me	**1ac**, 82
30	**2a**, Ph	**3x**, 4-*i*PrC_6H_4, Me	**1ad**, 84
31	**2a**, Ph	**3y**, 4-*n*BuC_6H_4, Me	**1ae**, 80
32	**2a**, Ph	**3z**, 4-*t*BuC_6H_4, Me	**1af**, 83
33	**2a**, Ph	**3aa**, *n*Bu, Me	**1ag**, 76
34	**2d**, 5-BrC_6H_3	**3a**, Tol, Me	**1ah**, 70
35	**2e**, 5-ClC_6H_3	**3a**, Tol, Me	**1ai**, 71
36	**2f**, naphthyl	**3a**, Tol, Me	**1aj**, 73
37	**2g**, 5-Br-naphthyl	**3a**, Tol, Me	**1ak**, 73
38	**2h**, 3,5-$F_2C_6H_2$	**3a**, Tol, Me	**1al**, 63
39	**2a**, Ph	**3ab**, Tol, Ph	**1am**, —[c]
40	**2a**, Ph	**3ac**, Tol, Ac	**1an**, —[d]
41	**2a**, Ph	**3ad**, Tol, NMs_2	**1ao**, —[d]

[a]Reactions were run on a 0.5 mmol scale with **2**, **3** (1.1 equiv), $Cu(OAc)_2$ (1.1 equiv), BOP (1.1 equiv), DMAP (1.0 equiv), $MeNO_2$ (3 mL), 3 h, reflux. [b]Isolated yields. [c]No reaction. [d]Complex mixture.

Especially, **3k**-**3m** having both electron-withdrawing groups, sulfonyl and CF_3, could produce only one regioisomer (for **1o**-**1t**, entries 15-20). The possible reason should be sulfonyl group with bulkier steric hindrance inhibited oxy-copper arm of **C** to attack the α-position of **3** such that β-carbon position (conjugated a CF_3 group) with less-hindrance face could be installed regioselectively. Attempts to afford flavonoid **1am** (for **3ab**, Z = Ph) failed because the phenyl group could make the electron density of π-system more likely to inhibit the first step of (4+2) annulation (entry 38). However, for the $Cu(OAc)_2$/BOP mediated reactions of **2a** with **3ac** and **3ad**, complex results were observed and no desired **1an** and **1ao** was observed (entries 40-41). The results showed that β-aceto (Ac) and ditosylamino (NTs_2) could cause the electrophilic instability of the β-position of **3a**. In comparison with sulfonyl alkyne **3a**, $Cu(OAc)_2$ mediated reaction of **2a** with sulfoxide-substitutetd alkyne **3a'** (R = Tol, Z = Me)[12] was examined. In particular, complex mixture were observed and no **3a'** was recovered due to sulfoxide group was activated by BOP.[12b]

Scheme 4. One-step Synthesis of **4a-4d**



As an extension of one-pot annulations, the synthetic applications of **1a** with 1,2-, 1,3-, and 1,4-diamino synthons were investigated next (Scheme 4, equations 1-3). Treatment of **1a** with N_2H_4 provided only sole **4a** with a 1*H*-skeleton in a 90% yield via (3+2) annulation (equation 1). However, the reported 2*H*-skeleton of **4a'** was not observed on the framework having a sulfonyl substituent.[13] As shown in equation 2), changing hydrazine (1,2-N_2) to benzamidine (1,3-N_2),[6f] **4b** was pro-

duced in an 85% yield. The plausible mechanism could be that **I** was formed by the Michael addition of **1a** with benzamidine. Then, the ring-opening of **I** provided imine **II**. After tautomeization, the intramolecular ring-closure of **III** with enamino motif produced **IV**. Next, the S_NAr reaction of **IV** generated **4b** by removal of $TolSO_2H$. Furthermore, one-pot annulation of **1a** with *o*-diaminobenzene (1,4-N_2) was examined (equation 3). Unexpectedly, **4c** and **4d** were isolated in 48% and 38% yields, respectively. The initial event could be that **VI** was formed by the Michael addition of **1a** with one *o*-diaminobenzene (1 equiv). After removing the 2-methyl-1*H*-benzimidazole, **VII** was transformed to **VIII**. 2-Methyl-1*H*-benzimidazole could be isolated to confirm the reaction process. Next, condensation of **VIII** with another *o*-diaminobenzene (1 equiv) provided **4c** and **4d** by removal of the $TolSO_2H$ or $TolSO_2Me$ of **IX**, respectively. To the best of our knowledge, the transformations of equations 1-3 have not been explored to date. By the use of chromen-4-one as the model substrate, four kinds of pyrazole, pyrimidine, quinoxaline and benzimidazole were generated by a one-pot synthetic route. The structures of **4a-4d** were determined by single-crystal X-ray crystallography.[11]

In summary, we have developed a $Cu(OAc)_2$ promoted one-pot (4+2) annulation of sulfonylacetylene **2** with salicyclic acid **3** in the presence of BOP and DMAP in $MeNO_2$ at reflux for 3 h in moderate to good yields. The one-pot process provides a series of sulfonyl chromen-4-ones **1** via a cascade pathway of C-O and then C-C bond formations. The related plausible mechanisms have been proposed. The structures of the key products were confirmed by X-ray crystallography. Further investigations regarding the synthetic application of copper salts will be conducted and published in due course.

Experimental Section

General. All reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400 and at 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (*J*) are given in Hertz. High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD).

*Representative synthetic procedure of skeleton **1** is as follows:* BOP (245 mg, 0.55 mmol, benzotriazo-1-yloxytri(dimethylamino)phosphonium hexafluorophosphate) was added to a solution of **2** (0.5 mmol) and $Cu(OAc)_2$ (100 mg, 0.55 mmol) in $MeNO_2$ (2 mL) at rt. The reaction mixture was stirred at rt for 5 min. DMAP (60 mg, 0.5 mmol, *p*-dimethylaminopyridine) was added to the reaction mixture. The reaction mixture was stirred at reflux for 2 h and then cooled to rt. Then, **3** (0.55 mmol) in $MeNO_2$ (1 mL) was added to the reaction mixture at rt. The reaction mixture was stirred at reflux for an additional 1 h. The reaction mixture was cooled to rt and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1~4/1) afforded **1**.

*2-Methyl-3-(toluene-4-sulfonyl)chromen-4-one (**1a**).* Yield = 80% (126 mg); Colorless solid; mp = 153-155 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{15}O_4S$ 315.0691, found 315.0698; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06-8.04 (m, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.68-7.64 (m, 1H), 7.43-7.40 (m, 1H), 7.38-7.34 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 3.03 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 171.6, 154.9, 144.3, 138.8, 134.5, 129.2 (2x), 128.3 (2x), 126.11, 126.05, 124.2, 123.5, 117.7, 21.6, 20.9. Single-crystal X-Ray diagram: crystal of compound **1a** was grown by slow diffusion of EtOAc into a solution of compound **1a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P - 1, *a* = 7.1482(5) Å , *b* = 10.6504(7) Å , *c* = 11.8975(8) Å , *V* = 825.16(10) Å ^{3}, *Z* = 2, d_{calcd} = 1.265 g/cm^3, *F*(000) = 328, 2θ range 1.870~26.403º, R indices (all data) R1 = 0.0347, wR2 = 0.0808.

*3-Benzenesulfonyl-2-methylchromen-4-one (**1b**).* Yield = 84% (126 mg); Colorless solid; mp = 91-93 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_{13}O_4S$ 301.0535, found 301.0533; ^1H NMR (400 MHz, $CDCl_3$): δ 8.09-8.06 (m, 2H), 7.95 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.62-7.57 (m, 1H), 7.54-7.50 (m, 1H), 7.47-7.43 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.30-7.264 (m, 1H), 2.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 171.8, 154.6, 141.4, 134.4, 133.2, 128.4 (2x), 128.0 (2x), 126.0, 125.6, 123.7, 123.2, 117.6, 20.7.

*3-Methanesulfonyl-2-methylchromen-4-one (**1c**).* Yield = 86% (102 mg); Colorless solid; mp = 132-134 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{11}H_{11}O_4S$ 239.0378, found 239.0377; ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.76-7.71 (m, 1H), 7.48-7.44 (m, 2H), 3.40 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 171.6, 155.0, 134.9, 126.4, 126.1, 123.7, 123.4, 117.8, 44.6, 20.5.

*3-(4-Fluorobenzenesulfonyl)-2-methylchromen-4-one (**1d**).* Yield = 78% (124 mg); Colorless solid; mp = 149-151 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_{12}FO_4S$ 319.0440, found 319.0442; ^1H NMR (400 MHz, $CDCl_3$): δ 8.18-8.13 (m, 2H), 8.05 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.70-7.66 (m, 1H), 7.43 (dd, *J* = 0.4, 8.4 Hz, 1H), 7.40-7.36 (m, 1H), 7.21-7.15 (m, 2H), 3.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 171.9, 165.6 (d, *J* = 254.0 Hz), 154.9, 137.6 (d, *J* = 3.0 Hz), 134.7, 131.4 (d, *J* = 9.1 Hz, 2x), 126.3, 126.0, 124.0, 123.4, 117.7, 115.8 (d, *J* = 22.0 Hz, 2x), 21.0.

*3-(4-Methoxybenzenesulfonyl)-2-methylchromen-4-one (**1e**).* Yield = 74% (122 mg); Colorless solid; mp = 118-120 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{15}O_5S$ 331.0640, found 331.0645; ^1H NMR (400 MHz, $CDCl_3$): δ 8.09-8.06 (m, 3H), 7.69-7.64 (m, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.39-7.35 (m, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 171.4, 163.5, 154.9, 134.5, 133.8,

130.8 (2x), 126.11, 126.09, 123.6, 117.7, 115.1, 113.8 (2x), 55.6, 21.0.

*6-Fluoro-2-methyl-3-(toluene-4-sulfonyl)chromen-4-one (**1f**).* Yield = 82% (136 mg); Colorless solid; mp = 134-136 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{14}FO_4S$ 333.0597, found 333.0602; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.54 (dd, *J* = 3.2, 8.0 Hz, 1H), 7.39 (dd, *J* = 4.0, 9.2 Hz, 1H), 7.32-7.27 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.95 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 171.4 (d, *J* = 2.2 Hz), 159.5 (d, *J* = 247.2 Hz), 150.8 (d, *J* = 1.6 Hz), 144.2, 138.2, 128.9 (2x), 128.0 (2x), 124.4 (d, *J* = 7.6 Hz), 123.3, 122.4 (d, *J* = 25.0 Hz), 120.0 (d, *J* = 8.3 Hz), 110.4 (d, *J* = 24.3 Hz), 21.2, 20.6. Single-crystal X-Ray diagram: crystal of compound **1f** was grown by slow diffusion of EtOAc into a solution of compound **1f** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/n, *a* = 9.1290(8) Å , *b* = 18.4090(16) Å , *c* = 9.3444(8) Å , *V* = 1470.8(2) Å^3, *Z* = 4, d_{calcd} = 1.501 g/cm^3, *F*(000) = 688, 2*θ* range 2.213~26.389°, R indices (all data) R1 = 0.0459, wR2 = 0.0872.

*7-Methoxy-2-methyl-3-(toluene-4-sulfonyl)chromen-4-one (**1g**).* Yield = 68% (117 mg); Colorless solid; mp = 92-94 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{17}O_5S$ 345.0797, found 345.0798; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 9.2 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.92 (dd, *J* = 2.4, 8.8 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 3.88 (s, 3H), 3.00 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 171.2, 164.7, 156.7, 144.2, 139.0, 129.2 (2x), 128.4 (2x), 127.5, 124.1, 117.3, 115.2, 100.1, 55.9, 21.6, 20.8.

*2-Ethyl-3-(toluene-4-sulfonyl)chromen-4-one (**1h**).* Yield = 80% (131 mg); Colorless solid; mp = 93-95 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{17}O_4S$ 329.0848, found 329.0851; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.88 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.56-7.52 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.38 (q, *J* = 7.6 Hz, 2H), 2.26 (s, 3H), 1.40 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 172.2, 154.5, 143.8, 138.4, 134.2, 128.7 (2x), 127.9 (2x), 125.6, 125.3, 123.0, 122.9, 117.3, 26.4, 21.1, 12.3. Single-crystal X-Ray diagram: crystal of compound **1h** was grown by slow diffusion of EtOAc into a solution of compound **1h** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P -1, *a* = 8.922(2) Å , *b* = 10.140(2) Å , *c* = 10.581(2) Å , *V* = 768.7(3) Å^3, *Z* = 2, d_{calcd} = 1.419 g/cm^3, *F*(000) = 344, 2*θ* range 2.204~26.563°, R indices (all data) R1 = 0.0457, wR2 = 0.0984.

*3-Benzenesulfonyl-2-ethylchromen-4-one (**1i**).* Yield = 80% (126 mg); Colorless solid; mp = 178-180 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{15}O_4S$ 315.0691, found 315.0699; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14-8.11 (m, 2H), 8.04 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.69-7.65 (m, 1H), 7.60-7.56 (m, 1H), 7.53-7.49 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.38-7.34 (m, 1H), 3.49 (q, *J* = 7.6 Hz, 2H), 1.51 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 172.7, 155.0, 141.7, 134.5, 133.3, 128.5 (2x), 128.2 (2x), 126.1, 126.0, 123.4, 123.3, 117.7, 26.9, 12.7.

*2-Ethyl-3-methanesulfonylchromen-4-one (**1j**).* Yield = 73% (92 mg); Colorless solid; mp = 71-73 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{13}O_4S$ 253.0535, found 253.0532; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.70-7.66 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.41-7.37 (m, 1H), 3.32 (s, 3H), 3.26 (q, *J* = 7.6 Hz, 2H), 1.34 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 173.6, 154.8, 134.7, 126.1, 125.7, 123.0, 122.8, 117.6, 44.4, 26.3, 12.3.

*2-Ethyl-3-(4-fluorobenzenesulfonyl)chromen-4-one (**1k**).* Yield = 74% (123 mg); Colorless solid; mp = 100-102 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{14}FO_4S$ 333.0597, found 333.0598; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15-8.10 (m, 2H), 8.00 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.68-7.64 (m, 1H), 7.42 (dd, *J* = 0.8, 8.4 Hz, 1H), 7.37-7.33 (m, 1H), 7.18-7.12 (m, 2H), 3.45 (q, *J* = 7.6 Hz, 2H), 1.48 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 172.6, 165.4 (d, *J* = 253.9 Hz), 154.9, 137.6 (d, *J* = 2.3 Hz), 134.6, 131.3 (d, *J* = 9.9 Hz, 2x), 126.1, 125.8, 123.23, 123.15, 117.6, 115.6 (d, *J* = 22.7 Hz, 2x), 26.0, 12.6.

*2-Ethyl-3-(4-methoxybenzenesulfonyl)chromen-4-one (**1l**).* Yield = 66% (114 mg); Colorless solid; mp = 75-77 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{17}O_5S$ 345.0797, found 345.0796; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-8.04 (m, 1H), 8.06 (d, *J* = 9.2 Hz, 2H), 7.68-7.63 (m, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.37-7.33 (m, 1H), 6.96 (d, *J* = 9.2 Hz, 2H), 3.83 (s, 3H), 3.47 (q, *J* = 7.6 Hz, 2H), 1.49 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 172.8, 163.4, 155.0, 140.0, 134.4, 130.7 (2x), 126.0 (2x), 123.5, 117.6, 113.7 (2x), 67.0, 55.5, 26.9, 12.6.

*2-Ethyl-6-fluoro-3-(toluene-4-sulfonyl)chromen-4-one (**1m**).* Yield = 84% (145 mg); Colorless solid; mp = 130-132 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{16}FO_4S$ 347.0753, found 347.0761; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.62 (dd, *J* = 2.8, 8.0 Hz, 1H), 7.44 (dd, *J* = 4.0, 9.2 Hz, 1H), 7.37-7.32 (m, 1H), 7.27 (d, *J* = 8.8 Hz, 2H), 3.45 (q, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 1.47 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 171.9, 159.7 (d, *J* = 247.1 Hz), 151.1 (d, *J* = 1.5 Hz), 144.3, 138.4, 129.1 (2x), 128.2 (2x), 124.5 (d, *J* = 7.5 Hz), 123.0, 122.6 (d, *J* = 25.8 Hz), 120.0 (d, *J* = 8.4 Hz), 110.7 (d, *J* = 24.3 Hz), 26.7, 21.4, 12.5.

*2-Ethyl-7-methoxy-3-(toluene-4-sulfonyl)chromen-4-one (**1n**).* Yield = 68% (122 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{19}O_5S$ 359.0953, found 359.0955; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.84 (dd, *J* = 2.4, 9.2 Hz, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 3.82 (s, 3H), 3.40 (q, *J* = 7.6 Hz, 2H), 2.33 (s, 3H), 1.44 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.3, 171.8, 164.5, 156.5, 143.9, 138.8, 128.9 (2x), 128.0 (2x), 127.0, 123.1, 116.8, 115.0, 99.8, 55.8, 26.5, 21.3, 12.5.

*3-(Toluene-4-sulfonyl)-2-trifluoromethylchromen-4-one (**1o**).* Yield = 74% (136 mg); Colorless solid; mp = 137-139 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{12}F_3O_4S$ 369.0408, found 369.0412; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-8.07 (m, 3H), 7.81-7.77 (m, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.51-7.47 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 172.5, 154.6 (q, *J* = 40.9 Hz), 153.8, 145.3, 137.2, 135.8, 129.4 (2x), 129.3 (2x), 128.4, 127.6, 126.2, 123.7, 118.4, 118.2 (q, *J* = 277.4 Hz), 21.6.

3-Benzenesulfonyl-2-trifluoromethylchromen-4-one ***(1p)***. Yield = 74% (131 mg); Colorless solid; mp = 196-198 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{10}F_3O_4S$ 355.0252, found 355.0254; ^1H NMR (400 MHz, $CDCl_3$): δ 8.23-8.20 (m, 2H), 8.09 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.82-7.78 (m, 1H), 7.66-7.62 (m, 1H), 7.58-7.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 154.9 (q, *J* = 40.9 Hz), 153.9, 140.2, 135.8, 134.1, 129.2 (2x), 128.8 (2x), 127.7, 126.9, 126.3, 123.8, 118.4, 118.2 (q, *J* = 277.4 Hz).

3-Methanesulfonyl-2-trifluoromethylchromen-4-one ***(1q)***. Yield = 64% (93 mg); Colorless solid; mp = 158-160 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{11}H_8F_3O_4S$ 293.0095, found 293.0094; ^1H NMR (400 MHz, $CDCl_3$): δ 8.22 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.89-7.84 (m, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.61-7.57 (m, 1H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 154.9 (d, *J* = 41.7 Hz), 154.0, 136.1, 127.9, 126.3, 126.2, 123.6, 118.5, 118.0 (q, *J* = 277.4 Hz), 44.8.

3-(4-Fluorobenzenesulfonyl)-2-trifluoromethylchromen-4-one ***(1r)***. Yield = 60% (112 mg); Colorless solid; mp = 193-195 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_9F_4O_4S$ 373.0158, found 373.0155; ^1H NMR (400 MHz, $CDCl_3$): δ 8.27-8.22 (m, 2H), 8.10 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.83-7.79 (m, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.54-7.50 (m, 1H), 7.24-7.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 166.1 (d, *J* = 255.5 Hz), 154.9 (q, *J* = 41.0 Hz), 153.9, 136.1 (d, *J* = 3.0 Hz), 135.9, 132.5 (d, *J* = 9.9 Hz, 2x), 127.8, 126.8, 126.2, 123.7, 118.5, 118.2 (q, *J* = 277.5 Hz), 116.2 (d, *J* = 22.7 Hz, 2x).

6-Fluoro-3-(toluene-4-sulfonyl)-2-trifluoromethylchromen-4-one ***(1s)***. Yield = 66% (127 mg); Colorless solid; mp = 179-181 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{11}F_4O_4S$ 387.0314, found 387.0312; ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.73 (dd, *J* = 3.2, 7.6 Hz, 1H), 7.61 (dd, *J* = 4.0, 9.2 Hz, 1H), 7.54-7.49 (m, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9 (d, *J* = 22.0 Hz), 161.9, 159.4, 154.7 (q, *J* = 40.9 Hz), 150.1, 145.5, 137.0, 129.5 (2x), 129.4 (2x), 125.2 (d, *J* = 7.6 Hz), 124.1 (d, *J* = 25.7 Hz), 120.9 (d, *J* = 8.3 Hz), 118.2 (q, *J* = 277.4 Hz), 111.4 (d, *J* = 24.3 Hz), 21.7.

7-Methoxy-3-(toluene-4-sulfonyl)-2-trifluoromethylchromen-4-one ***(1t)***. Yield = 54% (107 mg); Colorless solid; mp = 140-142 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{14}F_3O_5S$ 399.0514, found 399.0511; ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 9.2 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.03 (dd, *J* = 2.4, 9.2 Hz, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 3.92 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 165.6 (2x), 155.5 (d, *J* = 42.0 Hz), 145.3, 137.3, 129.4 (2x), 129.3 (2x), 127.7, 119.7, 118.3 (q, *J* = 276.7 Hz), 117.5, 117.1, 100.3, 56.2, 21.7.

2-Benzyl-3-(toluene-4-sulfonyl)chromen-4-one ***(1u)***. Yield = 73% (142 mg); Colorless solid; mp = 180-182 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{19}O_4S$ 391.1004, found 391.1002; ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.61-7.56 (m, 1H), 7.41-7.31 (m, 7H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.04-7.01 (m, 2H), 4.62 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 152.9, 145.3, 138.4, 136.1, 132.7, 132.0, 131.9, 129.9 (2x), 129.6, 128.6 (2x), 128.5 (2x), 128.1 (2x), 127.1, 124.3, 118.5, 116.8, 56.5, 21.6.

2-(4-Methylbenzyl)-3-(toluene-4-sulfonyl)chromen-4-one ***(1v)***. Yield = 78% (158 mg); Colorless solid; mp = 199-201 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{21}O_4S$ 405.1161, found 405.1161; ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.60-7.56 (m, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.40-7.33 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 4.64 (s, 2H), 2.45 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 152.8, 145.3, 138.5, 138.3, 136.1, 132.0, 131.9, 129.9 (2x), 129.7, 129.5 (2x), 129.2 (2x), 128.2 (2x), 127.0, 124.3, 118.6, 116.8, 56.6, 21.6, 21.3.

2-Thiophen-2-ylmethyl-3-(toluene-4-sulfonyl)chromen-4-one ***(1w)***. Yield = 72% (143 mg); Colorless solid; mp = 191-193 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{17}O_4S_2$ 397.0568, found 397.0566; ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.61-7.57 (m, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.44 (dd, *J* = 1.2, 4.8 Hz, 1H), 7.39-7.32 (m, 2H), 7.263 (d, *J* = 8.4 Hz, 2H), 7.05-7.00 (m, 2H), 4.78 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 152.8, 145.5, 140.2, 136.1, 132.6, 132.4, 130.4, 130.0 (2x), 128.3, 128.1 (2x), 127.3, 126.9, 125.2, 124.5, 118.4, 116.9, 56.8, 21.6.

2-(4-Fluorobenzyl)-3-(toluene-4-sulfonyl)chromen-4-one ***(1x)***. Yield = 78% (159 mg); Colorless solid; mp = 183-185 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{18}FO_4S$ 409.0910, found 409.0912; ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.63-7.58 (m, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.39-7.35 (m, 1H), 7.262 (d, *J* = 8.0 Hz, 2H), 7.05 (br s, 2H), 7.03 (br s, 2H), 4.59 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (d, *J* = 247.1 Hz), 160.3, 152.9, 145.6, 138.8, 136.2, 132.3, 131.7 (d, *J* = 7.5 Hz, 2x), 131.0, 130.1 (2x), 128.6 (d, *J* = 3.7 Hz), 128.1 (2x), 127.1, 124.5, 118.4, 117.0, 115.7 (d, *J* = 21.3 Hz, 2x), 56.6, 21.7.

2-(4-Methoxybenzyl)-3-(toluene-4-sulfonyl)chromen-4-one ***(1y)***. Yield = 78% (164 mg); Colorless solid; mp = 188-190 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{21}O_5S$ 421.1110, found 421.1112; ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.59-7.55 (m, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.34-7.32 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.65 (s, 2H), 3.84 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 159.7, 152.7, 145.3, 138.2, 136.1, 131.8, 131.7, 131.0, 129.9 (2x), 128.1 (2x), 127.0 (2x), 124.8, 124.3, 118.6, 116.8, 113.9 (2x), 56.5, 55.3, 21.6.

2-(3,4-Dimethoxybenzyl)-3-(toluene-4-sulfonyl)chromen-4-one ***(1z)***. Yield = 72% (162 mg); Colorless solid; mp = 137-139 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{23}O_6S$ 451.1215, found 451.1218; ^1H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.57-7.53 (m, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.36

(d, *J* = 8.0 Hz, 1H), 7.33-7.29 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.72 (br s, 1H), 6.66 (dd, *J* = 2.0, 8.4 Hz, 1H), 4.66 (br s, 2H), 3.90 (s, 3H), 3.83 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 152.7, 149.3, 148.8, 145.3, 138.4, 136.4, 131.84, 131.78, 129.9 (2x), 127.9 (2x), 126.9, 125.1, 124.2, 122.1, 118.5, 116.8, 113.2, 111.0, 56.6, 55.91, 55.86, 21.6.

2-Naphthalen-1-ylmethyl-3-(toluene-4-sulfonyl)chromen-4-one ***(1aa)***. Yield = 70% (154 mg); Colorless solid; mp = 167-169 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{27}H_{21}O_4S$ 441.1161, found 441.1166; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.91-7.88 (m, 2H), 7.67-7.63 (m, 1H), 7.50-7.37 (m, 6H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17-7.12 (m, 3H), 4.64 (d, *J* = 14.0 Hz, 1H), 4.19 (d, *J* = 13.6 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 153.3, 145.3, 140.6, 136.4, 133.5, 132.3, 131.0, 130.3, 129.9 (2x), 129.4, 128.8, 128.7, 128.0, 127.9 (2x), 127.3, 127.0, 126.2, 125.3, 124.5, 124.2, 118.5, 117.0, 57.3, 21.6.

2-Methyl-3-(toluene-3-sulfonyl)chromen-4-one ***(1ab)***. Yield = 80% (126 mg); Colorless solid; mp = 123-125 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{17}H_{15}O_4S$ 315.0691, found 315.0693; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.93-7.90 (m, 2H), 7.67 (dt, *J* = 1.6, 8.8 Hz, 1H), 7.43-7.35 (m, 4H), 3.04 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 171.8, 155.0, 141.6, 138.7, 134.5, 134.2, 128.4, 128.3, 126.2, 126.1, 125.4, 124.1, 123.6, 117.7, 21.3, 20.9.

3-(4-Ethylbenzenesulfonyl)-2-methylchromen-4-one ***(1ac)***. Yield = 82% (134 mg); Colorless solid; mp = 155-157 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{18}H_{17}O_4S$ 329.0848, found 329.0852; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.68-7.64 (m, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 7.38-7.35 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 3.04 (s, 3H), 2.69 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 171.6, 154.9, 150.4, 139.0, 134.5, 128.4 (2x), 128.1 (2x), 126.11, 126.06, 124.3, 123.6, 117.7, 28.8, 20.9, 14.9.

3-(4-Isopropylbenzenesulfonyl)-2-methylchromen-4-one ***(1ad)***. Yield = 84% (144 mg); Colorless solid; mp = 157-159 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{19}H_{19}O_4S$ 343.1004, found 343.1002; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-8.06 (m, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.68-7.64 (m, 1H), 7.43-7.39 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 3.04 (s, 3H), 2.99-2.92 (m, 1H), 1.24 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 171.6, 154.9 (2x), 139.0 134.5, 128.5 (2x), 126.7 (2x), 126.14, 126.07, 124.2, 123.6, 117.7, 34.2, 23.5 (2x), 21.0.

3-(4-n-Butylbenzenesulfonyl)-2-methylchromen-4-one ***(1ae)***. Yield = 80% (142 mg); Colorless solid; mp = 112-114 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{20}H_{21}O_4S$ 357.1161, found 357.1163; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (dd, *J* = 1.6, 8.0 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.66 (dt, *J* = 1.6, 8.4 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.37 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 3.04 (s, 3H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.63-1.55 (m, 2H), 1.38-1.29 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 171.6, 155.0, 149.2, 138.9, 134.5, 128.6 (2x), 128.4 (2x), 126.13, 126.11, 124.3, 123.6, 117.7, 35.6, 33.0, 22.3, 21.0, 13.8.

3-(4-t-Butylbenzenesulfonyl)-2-methylchromen-4-one ***(1af)***. Yield = 83% (148 mg); Colorless solid; mp > 220 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{20}H_{21}O_4S$ 357.1161, found 357.1163; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-8.04 (m, 3H), 7.66 (dt, *J* = 1.6, 8.8 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.42 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.37 (dt, *J* = 1.2, 8.0 Hz, 1H), 3.04 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 171.6, 157.2, 155.0, 138.7, 134.5, 128.2 (2x), 126.14, 126.10, 125.6 (2x), 124.3, 123.7, 117.7, 35.2, 31.0 (3x), 21.0.

3-(n-Butane-1-sulfonyl)-2-methylchromen-4-one ***(1ag)***. Yield = 76% (106 mg); Colorless gum; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{14}H_{17}O_4S$ 281.0848, found 281.0843; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.65-7.60 (m, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 3.45-3.41 (m, 2H), 2.76 (s, 3H), 1.65-1.57 (m, 2H), 1.36-1.27 (m, 2H), 0.79 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 172.0, 154.5, 134.6, 126.0, 125.5, 122.8, 121.5, 117.5, 54.9, 23.9, 21.09, 20.06, 13.2.

6-Bromo-2-methyl-3-(toluene-4-sulfonyl)chromen-4-one ***(1ah)***. Yield = 70% (137 mg); Colorless solid; mp = 121-123 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{17}H_{14}BrO_4S$ 392.9796, found 392.9795; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 2.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.73 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.33-7.29 (m, 3H), 3.03 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 171.3, 153.7, 144.6, 138.4, 137.5, 129.2 (2x), 128.7, 128.4 (2x), 124.8, 124.5, 119.6, 31.5, 21.6, 21.0.

6-Chloro-2-methyl-3-(toluene-4-sulfonyl)-chromen-4-one ***(1ai)***. Yield = 71% (124 mg); Colorless solid; mp = 204-206 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{17}H_{14}ClO_4S$ 349.0301, found 349.0308; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 2.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.59 (dd, *J* = 2.8, 8.8 Hz, 1H), 7.38 (d, *J* = 9.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.03 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 171.4, 153.3, 144.6, 138.5, 134.7, 132.2, 129.2 (2x), 128.5 (2x), 125.5, 124.5, 124.4, 119.5, 21.6, 20.9.

2-Methyl-3-(toluene-4-sulfonyl)benzo[h]chromen-4-one ***(1aj)***. Yield = 73% (133 mg); Colorless solid; mp > 245 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{21}H_{17}O_4S$ 365.0848, found 365.0849; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, *J* = 7.2 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.74-7.68 (m, 3H), 7.33 (d, *J* = 7.6 Hz, 2H), 3.19 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 152.5, 144.4, 138.7, 136.1, 131.0, 129.8, 129.3 (2x), 128.6, 128.5 (2x), 128.0, 127.6, 126.3, 124.0, 122.3, 122.0, 120.5, 21.7, 20.8.

6-Bromo-2-methyl-3-(toluene-4-sulfonyl)-benzo[h]chromen-4-one ***(1ak)***. Yield = 73% (161 mg); Colorless solid; mp = 225-227 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{21}H_{16}BrO_4S$ 442.9953, found 442.9956; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, *J* = 8.0 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 8.25 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.83-7.73 (m, 2H), 7.33

(d, *J* = 8.0 Hz, 2H), 3.18 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 170.6, 151.7, 144.7, 138.4, 134.2, 131.0, 129.3 (2x), 128.6 (2x), 128.5, 128.4, 127.9, 124.1, 124.0, 122.3, 120.7, 120.5, 21.7, 20.8.

*6,8-Difluoro-2-methyl-3-(toluene-4-sulfonyl)chromen-4-one (**1al**).* Yield = 63% (110 mg); Colorless solid; mp = 179-181 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{13}F_2O_4S$ 351.0503, found 351.0509; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.49-7.46 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.24-7.19 (m, 1H), 3.06 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 170.7 (d, *J* = 6.1 Hz), 160.0 (d, *J* = 9.1 Hz), 157.5 (d, *J* = 9.8 Hz), 152.1 (d, *J* = 11.4 Hz), 149.6 (d, *J* = 12.1 Hz), 144.7 (2x), 140.5 (d, *J* = 11.3 Hz), 138.2 (2x), 110.0 (d, *J* = 20.5 Hz), 109.7 (d, *J* = 19.7 Hz), 106.4 (d, *J* = 23.5 Hz), 106.4 (d, *J* = 24.2 Hz), 21.6, 20.8. Single-crystal X-Ray diagram: crystal of compound **1al** was grown by slow diffusion of EtOAc into a solution of compound **1al** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P -1, *a* = 10.374(3) Å, *b* = 11.581(3) Å, *c* = 19.365(5) Å, *V* = 2261.4(9) Å^3, *Z* = 6, d_{calcd} = 1.543 g/cm^3, *F*(000) = 1080, 2θ range 1.071~26.549°, R indices (all data) R1 = 0.0759, wR2 = 0.1405.

*2-[5-Methyl-4-(toluene-4-sulfonyl)-2H-pyrazol-3-yl]-phenol (**4a**).* 80% $N_2H_{4(aq)}$ (2 mL) was added to a solution of **1a** (95 mg, 0.3 mmol) in dioxane (3 mL) at rt. The reaction mixture was stirred at reflux for 3 h. The reaction mixture was cooled to rt and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1~4/1) afforded **4a**. Yield = 90% (89 mg); Colorless solid; mp = 144-146 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{17}N_2O_3S$ 329.0960, found 329.0962; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 (br s, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.30 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.14-7.09 (m, 3H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 147.3, 145.9, 144.0, 139.1, 131.0, 130.8, 129.4 (2x), 126.5 (2x), 119.6, 117.5, 116.6, 116.5, 21.3, 11.4. Single-crystal X-Ray diagram: crystal of compound **4a** was grown by slow diffusion of EtOAc into a solution of compound **4a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, *a* = 29.6762(12) Å, *b* = 13.3274(5) Å, *c* = 8.2384(3) Å, *V* = 3232.7(2) Å^3, *Z* = 8, d_{calcd} = 1.349 g/cm^3, *F*(000) = 1376, 2θ range 0.692~26.425°, R indices (all data) R1 = 0.0637, wR2 = 0.1233.

*4-Methyl-2-phenylbenzo[4,5]furo[3,2-d]pyrimidine (**4b**).* Benzamidine-HCl (93 mg, 0.6 mmol) was added to a solution of **1a** (95 mg, 0.3 mmol) in DMSO (3 mL) at rt. The reaction mixture was stirred at reflux for 3 h. The reaction mixture was cooled to rt and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 4/1~1/1) afforded **4b**. Yield = 85% (66 mg); Colorless solid; mp = 124-126 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{13}N_2O$ 261.1028, found 261.1030; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57-8.54 (m, 2H), 8.25 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.63-7.40 (m, 6H), 2.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 157.8, 149.9, 149.4, 145.6, 138.1, 131.1, 129.8, 128.4 (2x), 128.1 (2x), 123.7, 122.4, 122.1, 112.5, 18.6. Single-crystal X-Ray diagram: crystal of compound **4b** was grown by slow diffusion of EtOAc into a solution of compound **4b** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the orthorhombic crystal system, space group P b c a, *a* = 13.4110(6) Å, *b* = 10.1144(4) Å, *c* = 18.3473(10) Å, *V* = 2488.7(2) Å^3, *Z* = 8, d_{calcd} = 1.389 g/cm^3, *F*(000) = 1088, 2θ range 2.220~26.392°, R indices (all data) R1 = 0.1095, wR2 = 0.2093.

*2-Quinoxalin-2-ylphenol (**4c**)* and *2-(1H-Benzoimidazol-2-yl)phenol (**4d**).* 1,2-Diaminobenzene (65 mg, 0.6 mmol) was added to a solution of **1a** (95 mg, 0.3 mmol) in DMSO (3 mL) at rt. The reaction mixture was stirred at reflux for 3 h. The reaction mixture was cooled to rt and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 4/1~1/2) afforded **4c** and **4d**. For **4c**: Yield = 48% (32 mg); Colorless solid; mp = 190-192 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{11}N_2O$ 223.0871, found 223.0877; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.54 (s, 1H), 8.19 (dd, *J* = 1.2, 8.0 Hz, 1H), 8.09-8.05 (m, 2H), 7.86-7.78 (m, 2H), 7.44 (dt, *J* = 1.2, 8.4 Hz, 1H), 7.13 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.04 (dt, *J* = 1.2, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 152.1, 141.8, 139.7, 138.7, 133.2, 131.5, 130.1, 128.7, 127.6, 126.8, 119.6, 118.9, 117.1. Single-crystal X-Ray diagram: crystal of compound **4c** was grown by slow diffusion of EtOAc into a solution of compound **4c** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/n, *a* = 5.9308(11) Å, *b* = 15.169(3) Å, *c* = 17.477(3) Å, *V* = 1564.7(5) Å^3, *Z* = 2, d_{calcd} = 1.415 g/cm^3, *F*(000) = 696, 2θ range 1.781~26.429°, R indices (all data) R1 = 0.0741, wR2 = 0.1118. For **4d**: Yield = 38% (24 mg); Colorless solid; mp = 226-228 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{11}N_2O$ 211.0871, found 211.0872; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.20 (br s, 2H), 8.02 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.66-7.64 (m, 2H), 7.37 (dt, *J* = 1.6, 8.4 Hz, 1H), 7.28 (t, *J* = 6.8 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 7.03 (dd, *J* = 0.8, 6.8 Hz, 1H), 7.00 (dd, *J* = 1.2, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.2 (2x), 151.9, 132.1 (2x), 126.5 (2x), 123.2, 119.6 (2x), 117.5 (2x), 112.9. Single-crystal X-Ray diagram: crystal of compound **4d** was grown by slow diffusion of EtOAc into a solution of compound **4d** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21, *a* = 3.7669(4) Å, *b* = 22.031(2) Å, *c* = 5.8049(6) Å, *V* = 480.22(8) Å^3, *Z* = 2, d_{calcd} = 1.454 g/cm^3, *F*(000) = 220, 2θ range 1.849~26.366°, R indices (all data) R1 = 0.0338, wR2 = 0.0929.

ASSOCIATED CONTENT

Supporting Information

Scanned photocopies of NMR spectral data for all compounds and X-ray analysis data of **1a**, **1f**, **1h**, **1al** and **4a**-**4d**. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The authors would like to thank the Ministry of Science and Technology of the Republic of China for financial support (MOST 106-2628-M-037-001-MY3).

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