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ORIGINAL PAPER

Ir-catalyzed C–S coupling of quinones with sulfonyl chloride

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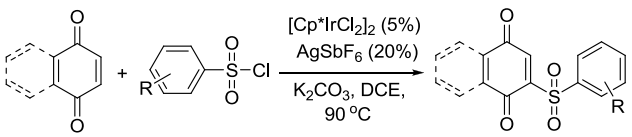
Abstract A concise, efficient method to sulfonyl quinones and sulfonyl-1,4-diols through Ir-catalyzed C–S coupling of quinones with sulfonyl chloride has been developed. Thus, this methodology proves its value as a versatile synthetic tool for a broad range of sulfonyl quinones, producing good to excellent yields.

Graphical Abstract



Keywords Ir-catalyzed · C–S coupling · Quinones · Sulfonyl chloride

Introduction

Transition metal-catalyzed carbon–heteroatom bond formation is a very useful reaction because it provides a convenient access to numerous medicines and pharmaceutical products.[1] Among these transformations, direct C–N, C–O, and C–S cross-coupling constitutes a powerful and efficient means of introducing a variety of substituents with diverse functional groups onto the heterocyclic scaffold.[2] Compared to methods developed for C–N and C–O coupling, transition metal-catalyzed C–S coupling remains relatively rare [26–29], because catalyst poisoning by sulfur species has been one of the serious limiting factors in this area [1, 7]. According to the literature, it has been reported that even very low concentrations of these sulfur species can rapidly, irreversibly deactivate the catalyst [30, 31]. Nowadays, scientists have paid great efforts to this area [32–41]. Several kinds of transition metals have proved to be effective for this transformation [42–48].

Sulfonyl-substituted quinones were important building blocks and convenient precursors for numerous biologically significant natural products and pharmaceuticals [49–51]. The direct C–S coupling was a nice method to the synthesis of these sulfonyl quinones (Scheme 1) [52, 53], since quinones were the very common materials. However, most of the transition metal-catalyzed couplings of quinones mainly focus on partners such as boron reagents,[3] indoles [61–64], and anilines [65, 66–79].

Recently, Wang et al. reported the Rh-catalyzed C–C coupling and Pd-catalyzed C–S coupling quinones. However, the yield is low to moderate and usually needs harsh terms [80–82]. Herein, we develop the Ir-catalyzed C–H functionalization of quinones with sulfonyl chloride through C–S coupling in moderate to good yields.

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[1] For some reviews, see [1–8].

[2] For some reviews and examples for C–S(N, O) cross-coupling, see [9–25].

[3] For the coupling of quinones with boron reagents, see [54–60].

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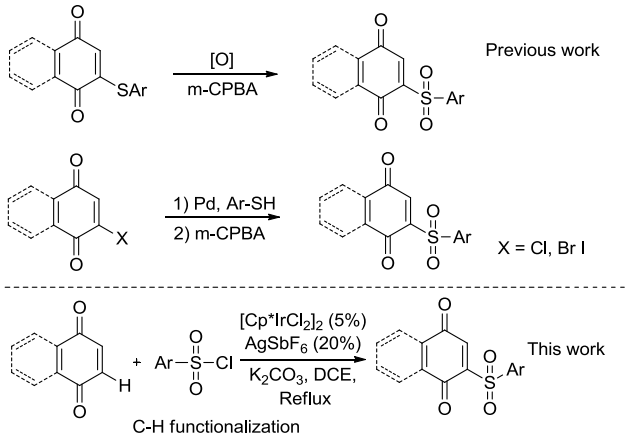


Scheme 1 C–S coupling reaction from quinones and naphthoquinones

First, various iridium catalysts were selected in order to test the reaction. Based on our experiments in this area, we set up the reaction of quinone with TsCl in the presence of Na_2CO_3 using the DCE solvent system under an air atmosphere. The result showed that 2-(toluene-4-sulfonyl)-[1,4]benzoquinone (**3a**) was obtained with 55 % yield (Table 1, entry 1). Other iridium catalysts gave significantly lower yields. Next, the screening of reaction conditions was carried forward to a high yield, and the results are shown in Table 1. When $[Cp^*IrCl_2]_2$ was used as a catalyst, K_2CO_3 was used as the base and $AgSbF_6$ as the additive in the DCE to give 81 % of the product (Table 1, entry 14). The solvent experiment showed this reaction to be highly solvent-dependent, and DCE gave the best result. Blank inspection showed that the reaction could not occur without an iridium catalyst (Table 1, entry 16).

Having established the optimal conditions of $[Cp^*IrCl_2]_2$ (5 %), K_2CO_3 as the base, and $AgSbF_6$ as the additive in DCE, various substrates were applied to the standard conditions in order to determine the scope and limitations of the present methodology. Generally, all the substrates reacted successfully to generate the desired products. The results are summarized in Table 2. The results showed that substrates with electron-donating groups such as Me, OMe, and ^{t}Bu could achieve high yields.

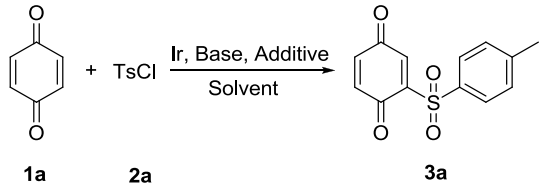
Next, we evaluated the reactivity of this transformation with benzoquinone substrates and sulfonyl chloride (Table 2). As illustrated in Table 2, full conversions were achieved with all the substrates. In the majority of cases, the corresponding aryl-substituted sulfonyl quinones were separated in good to excellent yields. However, in the case of substrates with a strong electron-withdrawing group, this methodology produced a disappointing result.

2-Tosylbenzene-1,4-diol and naphthalene-1,4 diol/quinones are potent inhibitors of *β-Ketoacyl-ACP-synthase III* (FabH) [49], a key condensing enzyme for bacterial fatty acid biosynthesis [50–52, 83]. Reynolds et al. [84] conducted a detailed study on activity tests of quinone derivatives against FabHs. Two typical models were shown in Scheme 2, and compound **A** could be easily synthesized with 77 % yield with this methodology (Table 2, **3i**). Consequently, 2-tosylbenzene-1,4-diol (**B**) was obtained only by one more step reduction under conditions of sodium borohydride in good yield with Wang's method [80–82] (Scheme 3).

A possible mechanism for the Ir-catalyzed C–S bond formation reaction can be proposed (Scheme 4). (1) The oxidation addition of Ir(I) with sulfonyl chloride to get species **5**; (2) followed with carboiridation, whereby intermediate **6** was formed; (3) intermediate **6** released the Ir(III) **7** via β-H elimination to produce the coupling product **3**; (4) the reductive elimination of Ir(III) **7** to regenerate the Ir(I) **4**, which enters a new catalytic cycle.

In summary, a concise, efficient method to sulfonyl quinones and sulfonyl-1,4-diols through Ir-catalyzed C–S coupling of quinones with sulfonyl chloride has been developed. Accordingly, this methodology proves its value as a

Table 1 Screening of reaction conditions

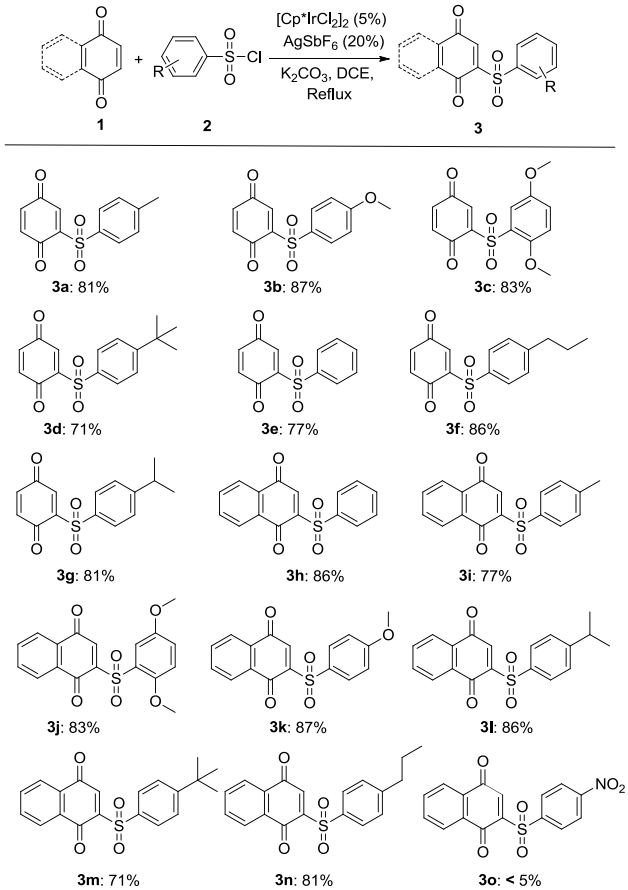


Entry	Catalyst	Base	Solvent	Yield [%]
1	$[Cp^*IrCl_2]_2$	Cs_2CO_3	DCE	55
2	$IrCl_3$	Cs_2CO_3	DCE	<5
3	$[(COD)IrCl]_2$	Cs_2CO_3	DCE	23
4	$[Cp^*IrCl_2]_2$	Cs_2CO_3	DMF	16
5	$[Cp^*IrCl_2]_2$	Cs_2CO_3	Benzene	<5
6	$[Cp^*IrCl_2]_2$	Cs_2CO_3	THF	12
7	$[Cp^*IrCl_2]_2$	Cs_2CO_3	Toluene	<5
8	$[Cp^*IrCl_2]_2$	Cs_2CO_3	Dioxane	10
9	$[Cp^*IrCl_2]_2$	$KHCO_3$	DCE	34
10	$[Cp^*IrCl_2]_2$	NaOH	DCE	22
11	$[Cp^*IrCl_2]_2$	^{t}BuONa	DCE	33
12	$[Cp^*IrCl_2]_2$	Na_2CO_3	DCE	41
13	$[Cp^*IrCl_2]_2$	K_2CO_3	DCE	73
14	$[Cp^*IrCl_2]_2/AgSbF_6$	K_2CO_3	DCE	81
15	$[Cp^*IrCl_2]_2/CuCl$	K_2CO_3	DCE	66
16	–	K_2CO_3	DCE	<5

Conditions: **1a** (0.5 mmol, 1.0 equiv.), **2a** (1.5 equiv.), [Ir] (5 mol%), base (1.5 equiv.), solvent, 12 h, reflux

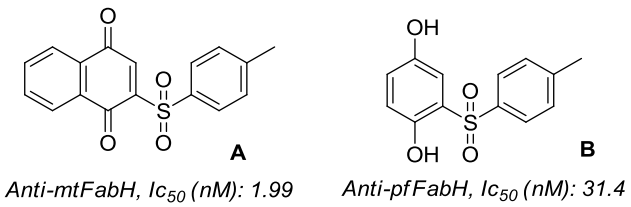
Isolated yields based on **1a**

Table 2 Substrate expansion of quinones



Conditions: **1a** (0.5 mmol, 1.0 equiv.), **2** (1.5 equiv.), $[Cp^*IrCl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%), K_2CO_3 (1.5 equiv.), DCE (3 mL), 12 h, reflux

Isolated yields based on **1a**

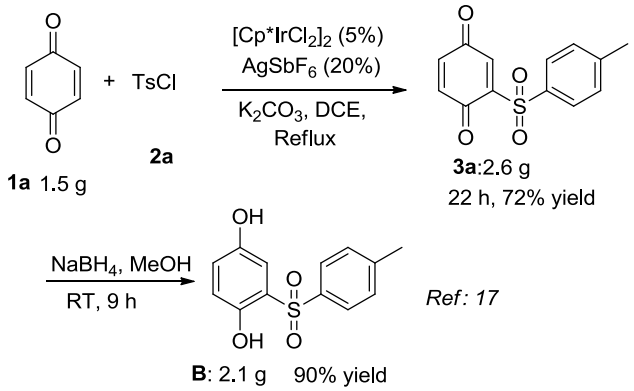


Scheme 2 Two typical FabH inhibitors

versatile synthetic tool for a broad range of sulfonyl quinones, producing good to excellent yields.

General procedure for the synthesis of pyrazol-chromeno[2,3-d]pyrimidine-ones (3a–3n)

A mixture of 1,4-quinone(**1a**) (54.0 mg, 0.50 mmol), TsCl(**2a**) (145.0 mg, 0.75 mmol), $[Cp^*IrCl_2]_2$ (19.9 mg, 5 mol%), $AgSbF_6$ (34.4 mg, 20 mol%), and K_2CO_3 (37.4 mg, 1.5 equiv.) in DCE (2.0 mL) was stirred at 90 °C under air for 12 h. Upon completion, the reaction mixture was evaporated to give the residue. The residue was then purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:10) to provide the corresponding product.



Scheme 3 Synthesis of the tosylbenzene-1,4-diol inhibitor

2-(Toluene-4-sulfonyl)-[1,4]benzoquinone (3a)

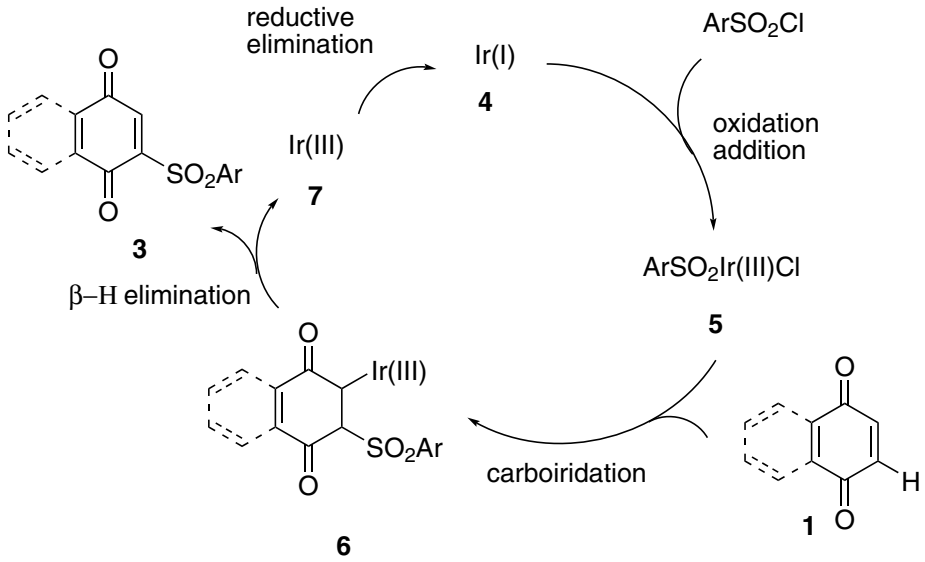
Light yellow solid (81 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.0 Hz, 2H), 7.25–7.14 (m, 2H), 6.85–6.67 (m, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7 (s), 186.8 (s), 145.8 (s), 140.6 (s), 137.0 (s), 136.2 (s), 132.0 (s), 129.8 (s), 129.3 (s), 129.2 (s), 21.4 (s). Anal. Calcd for $C_{13}H_{10}O_4S$: C, 59.53; H, 3.84; O, 24.40; S, 12.23. Found: C, 59.37; H, 3.93; O, 24.27; S, 12.41.

2-(4-Methoxy-benzenesulfonyl)-[1,4]benzoquinone (3b)

Light yellow solid (87 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.87–6.75 (m, 3H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7 (s), 187.1 (s), 161.4 (s), 145.2 (s), 137.0 (s), 136.2 (s), 131.1 (s), 130.9 (s), 125.0 (s), 114.1 (s), 55.4 (s). Anal. Calcd for $C_{13}H_{10}O_5S$: C, 56.11; H, 3.62; O, 28.75; S, 11.52. Found: C, 56.24; H, 3.55; O, 28.89; S, 11.42.

2-(2,5-Dimethoxy-benzenesulfonyl)-[1,4]benzoquinone (3c)

Light yellow solid (83 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98–6.92 (m, 1H), 6.92–6.84 (m, 2H), 6.83–6.77 (m, 2H), 6.73 (d, J = 2.8 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7 (s), 185.5 (s), 153.4 (s), 151.3 (s), 145.8 (s), 137.1 (s), 136.1 (s), 134.4 (s), 123.2 (s), 116.1 (s), 116.0 (s), 112.5 (s), 56.3 (s), 55.8 (s). Anal. Calcd for $C_{14}H_{12}O_6S$: C, 54.54; H, 3.92; O, 31.14; S, 10.40. Found: C, 54.66; H, 3.83; O, 31.23; S, 10.26.



Scheme 4 A possible mechanism for the Ir-catalyzed C–S coupling reaction

2-(4-tert-Butyl-benzenesulfonyl)-[1,4]benzoquinone (3d)

Light yellow solid (71 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.43 (m, 4H), 6.89–6.83 (m, 3H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7 (s), 186.9 (s), 153.6 (s), 145.7 (s), 137.0 (s), 136.2 (s), 132.1 (s), 129.7 (s), 129.0 (s), 125.6 (s), 34.8 (s), 31.1 (s). Anal. Calcd for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30; O, 21.03; S, 10.54. Found: C, 63.22; H, 5.23; O, 21.10; S, 10.46.

2-Benzenesulfonyl-[1,4]benzoquinone (3e)

Light yellow solid (77 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.14 (m, 5H), 6.83–6.76 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5 (s), 186.6 (s), 145.6 (s), 140.4 (s), 136.8 (s), 136.0 (s), 131.8 (s), 129.6 (s), 129.1 (s), 129.0 (s). Anal. Calcd for $C_{12}H_8O_4S$: C, 58.06; H, 3.25; O, 25.78; S, 12.92. Found: C, 58.21; H, 3.13; O, 25.92; S, 12.77.

2-(4-Propyl-benzenesulfonyl)-[1,4]benzoquinone (3f)

Light yellow solid (86 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.4 Hz, 2H), 7.19 (t, J = 4.0 Hz, 2H), 6.81–6.73 (m, 3H), 2.56 (t, J = 7.9 Hz, 2H), 1.66–1.53 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7 (s), 186.9 (s), 145.8 (s), 145.3 (s), 137.0 (s), 136.2 (s), 132.0 (s), 130.0 (s), 129.2 (s), 128.7 (s), 37.8 (s), 24.3 (s), 13.8 (s). Anal. Calcd for $C_{15}H_{14}O_4S$: C, 62.05; H, 4.86; O, 22.04; S, 11.04. Found: C, 62.13; H, 4.79; O, 22.13; S, 10.88.

2-(4-Isopropyl-benzenesulfonyl)-[1,4]benzoquinone (3g)

Light yellow solid (81 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.93–6.75 (m, 3H), 3.01–2.91 (m, 1H), 1.28 (d, J = 7.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7 (s), 186.9 (s), 151.4 (s), 145.9 (s), 137.1 (s), 136.2 (s), 132.1 (s), 130.1 (s), 129.3 (s), 126.7 (s), 34.0 (s), 23.8 (s). Anal. Calcd for $C_{15}H_{14}O_4S$: C, 62.05; H, 4.86; O, 22.04; S, 11.04. Found: C, 62.17; H, 4.76; O, 22.13; S, 10.86.

2-Benzenesulfonyl-[1,4]naphthoquinone (3h)

Light yellow solid (86 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–7.97 (m, 2H), 7.77–7.64 (m, 2H), 7.46–6.96 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.0 (s), 184.4 (s), 147.8 (s), 140.2 (s), 134.4 (s), 133.6 (s), 133.5 (s), 132.3 (s), 131.9 (s), 130.3 (s), 129.2 (s), 129.0 (s), 126.8 (s), 125.7 (s). Anal. Calcd for $C_{16}H_{10}O_4S$: C, 64.42; H, 3.38; O, 21.45; S, 10.75. Found: C, 64.53; H, 3.24; O, 21.56; S, 10.53.

2-(Toluene-4-sulfonyl)-[1,4]naphthoquinone (3i)

Light yellow solid (77 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.07 (m, 2H), 7.83–7.72 (m, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.07 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2 (s), 184.6 (s), 148.0 (s), 140.4 (s), 134.6 (s), 133.8 (s), 133.7 (s), 132.5 (s), 132.1 (s), 130.5 (s), 129.4 (s), 129.2 (s), 127.0 (s), 125.9 (s), 21.4 (s). Anal. Calcd for $C_{17}H_{12}O_4S$: C, 65.37; H, 3.87; O, 20.49; S, 10.27. Found: C, 65.50; H, 3.69; O, 20.62; S, 10.05.

2-(2,5-Dimethoxy-benzenesulfonyl)-[1,4] naphthoquinone (3j)

Light yellow solid (83 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.08 (m, 2H), 7.80–7.72 (m, 2H), 7.02 (s, 1H), 6.98–6.90 (m, 2H), 6.82 (d, J = 2.8 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2 (s), 183.4 (s), 153.4 (s), 151.4 (s), 147.9 (s), 136.8 (s), 133.8 (s), 133.6 (s), 132.5 (s), 132.1 (s), 127.0 (s), 126.0 (s), 124.0 (s), 116.1 (s), 115.8 (s), 112.5 (s), 56.3 (s), 55.8 (s). Anal. Calcd for $C_{18}H_{14}O_6S$: C, 60.33; H, 3.94; O, 26.79; S, 8.95. Found: C, 60.55; H, 3.87; O, 26.85; S, 8.84.

2-(4-Methoxy-benzenesulfonyl)-[1,4]naphthoquinone (3k)

Light yellow solid (87 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.08 (m, 2H), 7.81–7.74 (m, 2H), 7.59 (d, J = 8.8 Hz,, 2H), 7.05 (s, 1H), 7.00 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2 (s), 184.8 (s), 161.3 (s), 147.4 (s), 133.7 (s), 133.7 (s), 132.1 (s), 131.1 (s), 127.0 (s), 125.9 (s), 125.7 (s), 114.0 (s), 55.4 (s). Anal. Calcd for $C_{17}H_{12}O_5S$: C, 62.19; H, 3.68; O, 24.36; S, 9.77. Found: C, 62.33; H, 3.66; O, 24.40; S, 9.62.

2-(4-Isopropyl-benzenesulfonyl)-[1,4]naphthoquinone (3l)

Light yellow solid (86 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25–8.06 (m, 2H), 7.83–7.72 (m, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.07 (s, 1H), 3.03–2.93 (m, 1H), 1.29 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2 (s), 184.6 (s), 151.3 (s), 148.0 (s), 134.6 (s), 133.8 (s), 133.7 (s), 132.6 (s), 132.1 (s), 130.8 (s), 129.5 (s), 127.7 (s), 127.2 (s), 127.0 (s), 126.7 (s), 125.9 (s), 34.1 (s), 23.8 (s). Anal. Calcd for $C_{19}H_{16}O_4S$: C, 67.04; H, 4.74; O, 18.80; S, 9.42. Found: C, 67.13; H, 4.62; O, 18.95; S, 9.39.

2-(4-tert-Butyl-benzenesulfonyl)-[1,4]naphthoquinone (3m)

Light yellow solid (71 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.08 (m, 2H), 7.81–7.74 (m, 2H), 7.57–7.45 (m, 4H), 7.08 (s, 1H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2 (s), 184.6 (s), 153.5 (s), 148.0 (s), 134.7 (s), 133.8 (s), 133.7 (s), 132.6 (s), 132.1 (s), 130.5 (s), 129.2 (s), 127.0 (s), 125.9 (s), 125.5 (s), 34.8 (s), 31.2 (s). Anal. Calcd for $C_{20}H_{18}O_4S$: C, 67.78; H, 5.12; O, 18.06; S, 9.05. Found: C, 67.90; H, 5.01; O, 18.17; S, 9.00.

2-(4-Propyl-benzenesulfonyl)-[1,4]naphthoquinone (3n)

Light yellow solid (81 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.08 (m, 2H), 7.82–7.73 (m, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.08 (s, 1H), 2.65 (t, J = 7.6 Hz, 2H), 1.75–1.62 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2 (s), 184.6 (s), 148.0 (s), 145.2 (s), 134.6 (s), 133.8 (s), 133.7 (s), 132.5 (s), 132.1 (s), 130.7 (s), 129.4 (s), 128.6 (s), 127.0 (s), 125.9 (s), 37.9 (s), 24.3 (s), 13.8 (s). Anal. Calcd for $C_{19}H_{16}O_4S$: C, 67.04; H, 4.74; O, 18.80; S, 9.42. Found: C, 67.20; H, 4.66; O, 18.87; S, 9.33.

General procedure for the synthesis of pyrazol-chromeno[2,3-d]pyrimidine-ones (B)

The substrate **3a** (0.1 mmol) was dissolved in dry MeOH (2.0 mL), and $NaBH_4$ (0.4 mmol) was added by stirring for at least 0.5 h. The reaction mixture was stirred at room temperature for about 1 h. The reaction was terminated by careful dropwise addition of water. The layers were separated, the organic phase was washed with H_2O, and the combined aqueous layers were evaporated to dryness. The residue was separated by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:5) to give light yellow solids.

2-(Toluene-4-sulfonyl)-benzene-1,4-diol (B)

Light yellow solid (90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.88–6.81 (m, 1H), 6.76–6.68 (m, 2H), 4.92 (s, 1H), 4.75 (s, 1H), 2.40 (s, 3H).

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