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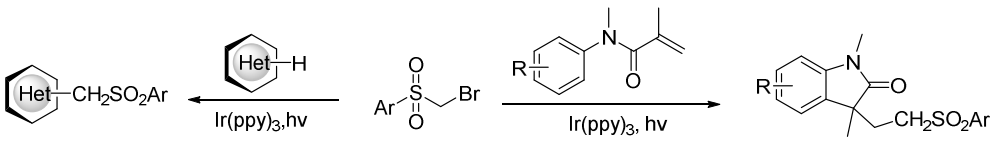
Visible-Light-Promoted (Phenylsulfonyl)methylation of Electron-Rich Heteroarenes and *N*-Arylacrylamides

Fei Liu and Pixu Li*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering, and Materials Science, Soochow University

199 RenAi Road, Suzhou, Jiangsu 215123, China

Tel: +86-512-65880826; E-mail: lipixu@suda.edu.cn



Abstract: Visible-light-promoted radical (phenylsulfonyl)methylation reactions of electron-rich heteroarenes and *N*-arylacrylamides have been developed starting from bromomethyl phenyl sulfone derivatives. This method provides a mild and efficient access to various (phenylsulfonyl)methylated compounds.

Introduction:

Methylation is a fundamental and ubiquitous reaction in organic synthesis and biological processes.[1-3] Traditional widely-used methylating reagents in organic synthesis include electrophilic iodomethane, dimethyl sulfate, dimethylcarbonate, and diazomethane. Recently, transition-metal catalyzed methylation reactions have attracted much attention.[4,5] Another important type of methylation reaction is the methyl radical addition to heteroarene.[6,7] Minisci reaction, in which the reactive species is the protonated heteroarene base, is a useful radical methylation reaction.[8,9] Recently, several interesting radical methylation of aromatic rings

using methyl radical derived from peroxide were reported.[10-13] While direct methylation of heteroarene is straight-forward and efficient, its major drawback is that the methylated product often is very difficult to be purified from the unreacted starting material because their structure and properties are so similar. Indirect methylation of heteroarene becomes one of the effective alternative methods to circumvent this problem. 2014, Baran group reported an elegant C-H methylation of heteroarenes.[14] Zinc bis(phenylsulfonylmethanelsulfinate) (PSMS) was prepared from the commercially available bromomethyl phenyl sulfone. PSMS reacted with heteroarene to afford (phenylsulfonyl)methylated heteroarene, which could be easily separated from the unreacted starting material and desulfonylated to give methylated heteroarene product. The reaction was reported to go through a phenylsulfonyl methyl radical addition pathway (Figure 1, equation 1).

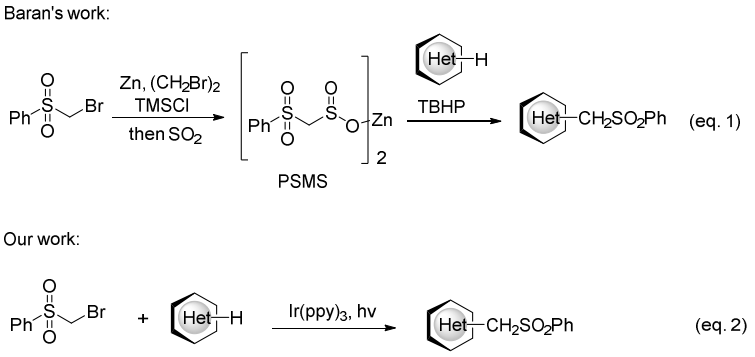
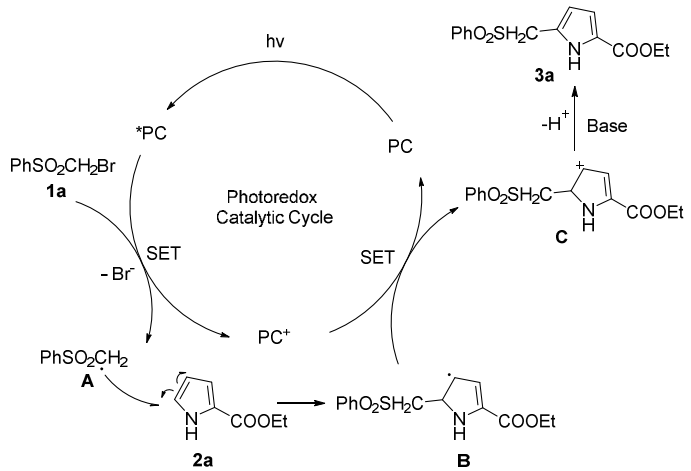


Figure 1. Radical benzenesulfonyl methylation reacitons

To the best of our knowledge, three reports on photoredox direct radical methylation reactions have been reported in the literature.[15-17] No indirect methylation by visible-light-promoted reaction has been disclosed. In continuation of our interest on the development of new visible-light-promoted C-H bond functionalization of arenes and heteroarenes,[18-21] we envisioned that the (phenylsulfonyl)methyl radical could be generated directly from

bromomethyl phenyl sulfone under photoredox conditions.[22] The resulting (phenylsulfonyl)methyl radical would react with electron-rich heteroarenes via electrophillic radical addition.[23] As shown in the proposed transformation (Scheme 1), the visible-light-exited photocatalyst reacts with bromomethyl phenyl sulfone via single electron transfer (SET) to generate a (phenylsulfonyl)methyl radical **A**. Radical addition of **A** to an electron-rich heteroarene would afford a radical species **B**. Oxidation of the radical intermediate **B** by the photocatalyst at high oxidation state completes the photocatalytic cycle and generates cation **C**. Upon giving up a proton, cation **C** rearomatizes and leads to the (phenylsulfonyl)methylated product **3a** (Scheme 1). Alternatively, radical **B** could be deprotonated to generate a radical anion species, followed by an oxidation to afford the product **3a**.

Scheme 1. Proposed Transformation

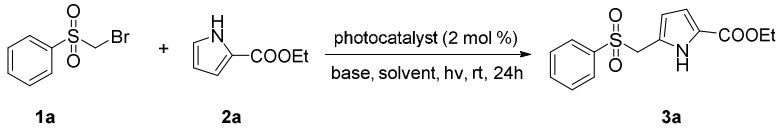


Results and Discussion:

Based on the above postulation, we started our investigation of this reaction using bromomethyl phenyl sulfone (**1a**) and ethyl 1H-pyrrole-2-carboxylate (**2a**) as the starting

materials and $Ir(ppy)_3$ as the photocatalyst. Because the reaction requires a base in the proposed mechanism, we screened several bases using DMSO as solvent. To our delight, the desired (phenylsulfonyl)methylated product **3a** was obtained (Table 1, entries 1-5). Among all of the bases screened, Li_2CO_3 was the most effective base (80%, Table 1, entries 5). Next, a series of photocatalysts, including other Ru or Ir-based polybipyridyl complexes and organic dyes, were screened. The highest yield was obtained in the reaction using $Ir(ppy)_3$ as the catalyst (Table 1, entries 5-11). The solvent effect was also checked. Commonly used solvents such as toluene, DMF, MeCN, MeOH, and THF were tested. However, none of the above solvents afforded higher yield than DMSO (Table 1, entries 12-16). When the reaction time was extended to 48 h, the yield of the desired product **3a** was boosted to 96% (Table 1, entry 17). To this end, a set of control experiments were carried out. No product **3a** was observed in the absence of either catalyst or visible-light irradiation (Table 1, entries 17−18). The results indicated that the catalyst and light irradiation were both critical to the reaction.

Table 1. Optimization of reaction conditions [a]



1a **2a** **3a**

Entry	Catalyst	Solvent	Base	LC Yield
1	$Ir(ppy)_3$	DMSO	NEt_3	20 %
2	$Ir(ppy)_3$	DMSO	DIEA	11 %
3	$Ir(ppy)_3$	DMSO	K_2CO_3	63 %
4	$Ir(ppy)_3$	DMSO	KOH	trace
5	$Ir(ppy)_3$	DMSO	Li_2CO_3	80 %

6	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	DMSO	Li_2CO_3	25 %
7	FIrpic	DMSO	Li_2CO_3	11 %
8	$Ir(dF(CF_3)ppy)(dtbbpy)PF_6$	DMSO	Li_2CO_3	16 %
9	$Ir(ppy)_2(dtbbpy)PF_6$	DMSO	Li_2CO_3	trace
10	Rose Bengal	DMSO	Li_2CO_3	N.R.
11	Eosin Yellowish	DMSO	Li_2CO_3	trace
12	$Ir(ppy)_3$	PhMe	Li_2CO_3	42 %
13	$Ir(ppy)_3$	DMF	Li_2CO_3	43 %
14	$Ir(ppy)_3$	MeCN	Li_2CO_3	75 %
15	$Ir(ppy)_3$	EtOH	Li_2CO_3	54 %
16	$Ir(ppy)_3$	THF	Li_2CO_3	20 %
17[b]	$Ir(ppy)_3$	DMSO	Li_2CO_3	96 % (83 %)[c]
18	—	DMSO	Li_2CO_3	N.R.
19	$Ir(ppy)_3$, no light	DMSO	Li_2CO_3	N.R.

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (0.5 mmol), photocatalyst (0.01 mmol, 2 mol %), base (1.0 mmol), solvent (1.25 mL) under N_2 atmosphere and a 14 W CFL irradiation. [b] reacted for 48 h. [c] Isolated yield.

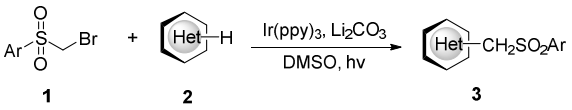
To verify the reaction was initiated by the formation of (phenylsulfonyl)methyl radical, a luminescence quenching reaction was carried out. The result clearly showed that bromomethyl phenyl sulfone was an effective quencher of excited $Ir(ppy)_3$. Moreover, the reaction was completely inhibited by the addition of 2 equivalents of TEMPO. And the adduct of (phenylsulfonyl)methyl radical and TEMPO was detected by LCMS.

With the optimized reaction conditions in hand, we then turned our attention to the generality of the reaction. The scope of bromomethyl aryl sulfone **1** and heteroarene **2** was investigated (Table 2). First, we investigated the scope of heteroarene. When substitution group on the pyrrole nitrogen was changed to methyl, ethyl, propyl, and Boc, the reactions afford 80%, 91%, 79%,

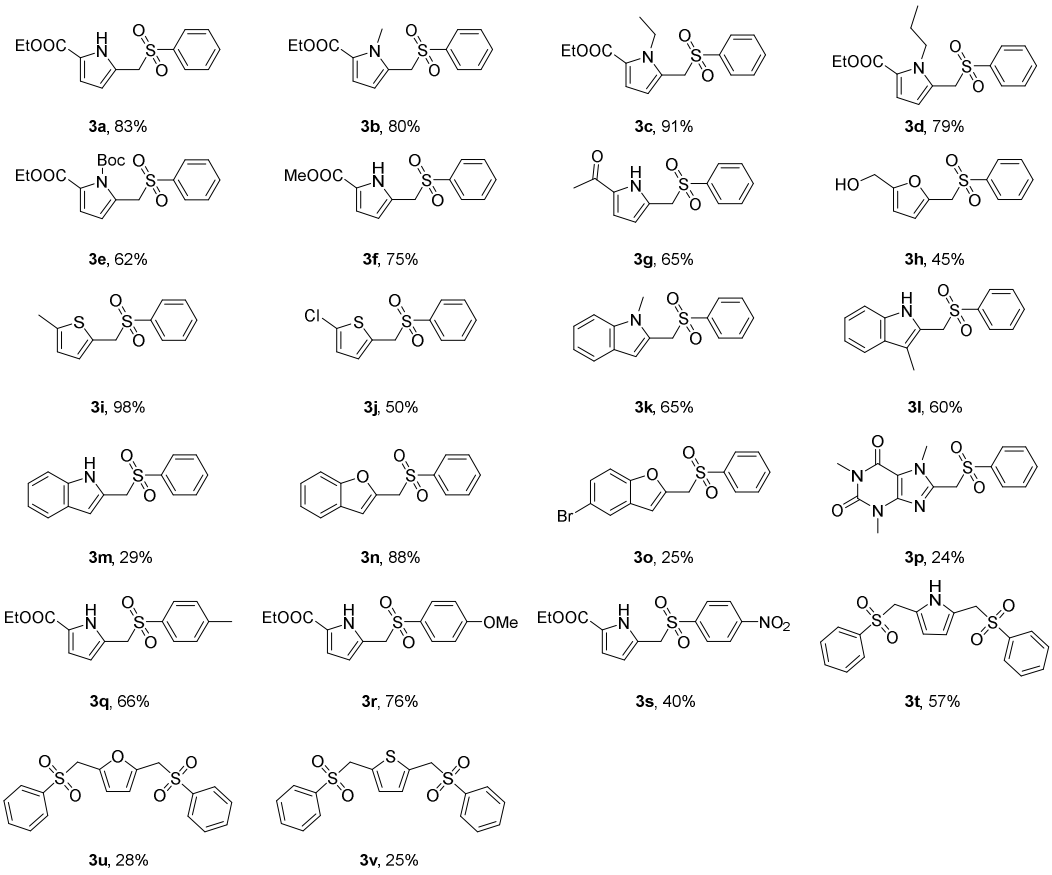
and 62% yields of the corresponding products, respectively (Table 2, **3b**-**3e**). Switching the ethyl ester group of **2a** to methyl ester (**2f)** or acyl group (**2g)** afforded the desired products in good yields too (75% and 65% respectively, Table 2, **3f**-**g**). Next, other 5-membered heteroarenes, such as furan and thiophene derivatives, were screened. The reactions of 2-hydroxymethylfuran (**2h**), 2-methylthiophene (**2i**), and 2-chlorothiophene (**2j**) proceeded smoothly and afforded the desired products in 45%, 98%, and 50% respectively (Table 2, **3h**-**j**). Particularly, 2-methyl-4-benzenesulfonylmethylthiophene (**3i**) was obtained in near quantitative isolated yield. Indoles are very important compounds both in pharmaceuticals and natural products. So we also investigated the reaction of indole derivatives. It was found that indoles also underwent the (phenylsulfonyl)methylation reaction regardless of the nitrogen was substituted or not (Table 2, **3k**-**3m**). However, they typically gave lower yields than those of pyrrole derivatives. Other bicyclic arenes, such as benzofuran and 5-bromo benzofuran, were examined as well. Good yield was obtained with benzofuran as the substrate (88%, Table 2, **3n**). On the contrary, 5-bromobenzofuran only afforded 25% yield of the corresponding product (Table 2, **3o**), suggesting that the substituent could significantly affect the radical addition reaction. To our surprise, caffeine only afforded the corresponding product in 24% under our conditions (Table 2, **3p)**. It is much lower than the 75% yield using Baran's conditions. It indicated that other factors in the reaction might have compound influence on the radical addition. We also investigated various substituents on the phenyl ring of the bromomethyl phenyl sulfone. Bromomethyl phenyl sulfones with electron-donating groups, such as methyl or methoxyl group, on the phenyl group afforded the corresponding products in good yields (66% and 76% respectively, Table 2, **3q** and **3r**). However, bromomethyl phenyl sulfone with an electron-withdrawing nitro group only gave

moderate yield of product (40%, Table 2, **3s**). When unsubstituted pyrrole, furan, and thiophene were employed as the substrates, bis(phenylsulfonyl)methylation occurred. Pyrrole gave 57% yield of the bis(phenylsulfonyl)methylated product, while furan and thiophene afforded 28% and 25% yields of the corresponding products, respectively (Table 2, **3t-3v**).

Table 2. Scope of substrates [a]



1 **2** **3**

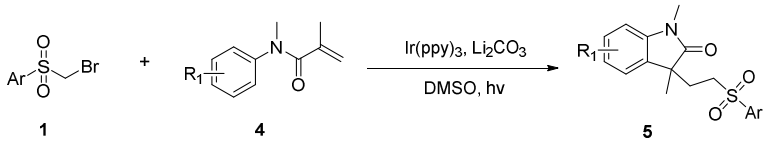


[a] Reaction conditions: **1** (1.0 mmol), **2** (0.5 mmol), $Ir(ppy)_3$ (0.01 mmol, 2 mol %), Li_2CO_3 (1.0 mmol), DMSO (1.25 mL) for 48 h under N_2 atmosphere and a 14 W CFL irradiation.

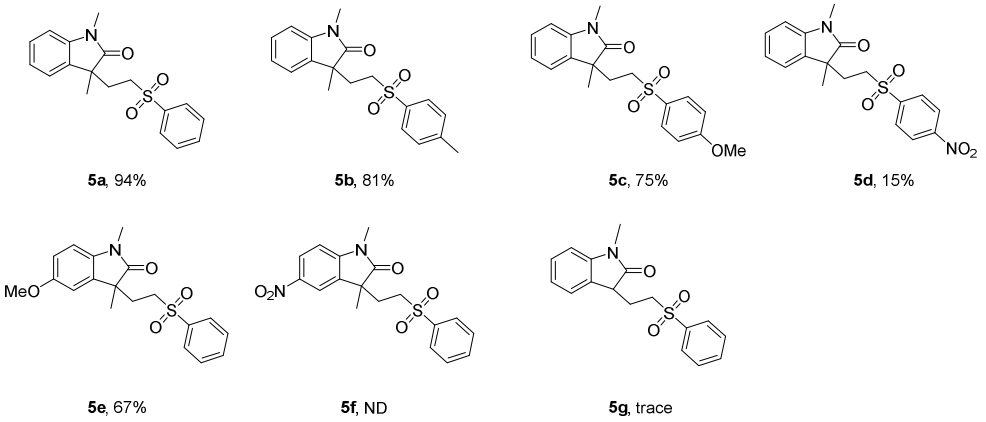
In addition to the (phenylsulfonyl)methylation of heteroarenes, we have also found that

(phenylsulfonyl)methyl radical reacted with *N*-arylacrylamide derivatives **4**.[24] A visible-light-promoted free radical addition/cyclization cascade reaction[17,25-27] occurred to produce a series of (phenylsulfonyl)methylated oxindoles **5**. The results were shown in Table 3. The reaction of bromomethyl phenyl sulfone (**1a**) and *N*-methyl-*N*-phenylmethacrylamide (**4a**) under our photoredox reaction conditions afforded oxindole **5a** in 94% yield (Table 3, **5a**). When the substituents on the phenyl ring of the bromomethyl phenyl sulfone were electron-donating groups, such as methyl and methoxy groups, the reactions proceeded smoothly and gave the corresponding products in good yields (81% and 75% respectively, Table 3, **5b** and **5c**). The bromomethyl phenyl sulfone bearing an electron-withdrawing nitro group only afforded 15% yield of the desired product (Table 3, **5d**). When substituent on the phenyl ring of *N*-arylacrylamide **4** was electron-donating methoxy group, good yield was obtained (67%, Table 3, **5e**). However, no desired product was formed when an electron-withdrawing nitro group was on the phenyl ring of *N*-arylacrylamide **4** (Table 3, **5f**). When *N*-methyl-*N*-phenylacrylamide (**4g**) was used as the reactant, only trace amount of **5g** was formed (Table 3, **5g**).

Table 3. (Phenylsulfonyl)methyl radical addition to *N*-arylacrylamide derivatives [a]



1 **4** **5**



[a] Reaction conditions: **1** (1.0 mmol), **4** (0.5 mmol), $Ir(ppy)_3$ (0.01 mmol, 2 mol %), Li_2CO_3 (1.0 mmol), DMSO (1.25 mL) for 24 h under an atmosphere of N_2 and a 14 W CFL irradiation.

In summary, we have developed a mild visible-light-promoted (phenylsulfonyl)methylation of electron-rich heteroarenes. In the reaction, (phenylsulfonyl)methyl radical was generated from bromomethyl phenyl sulfone via SET with photo sensitizer under visible light irradiation. It reacted with heteroarenes intermolecularly to afford various (phenylsulfonyl)methylated heteroarenes, which could be further desulfonylated to methylated heteroarenes. Inexpensive and easily accessible bromomethyl phenyl sulfone derivatives were used as the reagent. In addition, this (phenylsulfonyl)methylation reaction is applicable to the reaction with *N*-arylacrylamide derivatives to afford oxindoles.

Experimental Section:

General Information: All reactions were carried out in glassware under N_2 atmosphere. Starting materials, bromomethyl aryl sulfones and *N*-arylacrylamide derivatives, were synthesized according to the literature methods.[28,29] Chemicals without special descriptions were obtained from commercial sources, and were used without further purification. Column chromatography was generally performed on silica gel (300-400 mesh). Thin-layer

chromatography (TLC) was visualized using UV light. NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 400 MHz spectrometer. Chemical shifts were reported in parts per million (δ) relative to TMS (0.00 ppm) for ^{1}H NMR data and $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.52 ppm) for ^{13}C NMR data. The abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, m = multiplet, br.s = broad singlet, and br = broad signal. HRMS spectra were measured on a TOF mass spectrometer with electrospray ionization (ESI) as the ionization source. Melting points are uncorrected.

General procedure:

(Phenylsulfonyl)methylation of heteroarenes: To a solution of bromomethyl aryl sulfone **1** (1.0 mmol), heteroarene **2** (0.5 mmol), and Li_2CO_3 (74.0 mg, 1.0 mmol) in DMSO (1.25 mL) was added $Ir(ppy)_3$ (6.5 mg, 0.01 mmol, 2 mol %) under nitrogen atmosphere. The reaction mixture were placed at a distance of 5 cm from a 14 W compact fluorescent lamp and stirred at room temperature. After 48 h, the reaction mixture was poured into H_2O (15 mL) and extracted with EtOAc (3×15 mL). The combined organic layers were washed with water (2×30 mL) and brine (30 mL) and dried over anhydrous $MgSO_4$. The mixture was filtered and the filtrate was concentrated under reduced pressure. The crude material was purified by silica gel flash chromatography to give the desired product.

Radical cascade reactions of *N*-arylacrylamide derivatives: To a solution of bromomethyl aryl sulfone **1** (1.0 mmol), *N*-arylacrylamide **4** (0.5 mmol), and Li_2CO_3 (74 mg, 1.0 mmol) in DMSO (1.25 mL) was added $Ir(ppy)_3$ (6.5 mg, 0.01 mmol, 2 mol %) under nitrogen atmosphere. The reaction mixture were placed at a distance of 5 cm from a 14 W compact

fluorescent lamp and stirred at room temperature. After 24 h, the reaction mixture was poured into H_2O (15 mL) and extracted with EtOAc (3×15 mL). The combined organic layers were washed with water (2×30 mL) and brine (30 mL) and dried over anhydrous $MgSO_4$. The mixture was filtered and the filtrate was concentrated under reduced pressure. The crude material was purified by silica gel flash chromatography to give the desired product.

Ethyl 5-((phenylsulfonyl)methyl)-1H-pyrrole-2-carboxylate (3a)[14]: The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and ethyl 1H-pyrrole-2-carboxylate **2a** (69.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (1:2) as the eluent afforded **3a** (121.8 mg, 83%) as a white solid. mp = 144−146 °C (lit 105−107 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.71 – 7.58 (m, 3H), 7.53 – 7.43 (m, 2H), 6.80 – 6.68 (m, 1H), 5.89 – 5.81 (m, 1H), 4.40 – 4.29 (m, 4H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 137.6, 134.2, 129.2, 128.5, 124.8, 123.2, 115.6, 113.1, 60.8, 55.7, 14.5. IR (neat): 3282, 3140, 2989, 2922, 1679, 1488, 1228, 764 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{14}H_{16}NO_4S^+$ $[M+H]^+$ 294.0795, found 294.0808.

Ethyl 1-methyl-5-((phenylsulfonyl)methyl)-1H-pyrrole-2-carboxylate (3b): The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and ethyl 1-methyl-1H-pyrrole-2-carboxylate **2b** (76.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (1:4) as the eluent afforded **3b** (123.0 mg, 80%) as a white solid. mp = 58−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.62

(m, 3H), 7.54 – 7.46 (m, 2H), 6.83 (d, J = 4.0 Hz, 1H), 5.80 (d, J = 4.0 Hz, 1H), 4.40 (s, 2H), 4.27 (q, J = 7.2 Hz, 2H), 3.77 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 137.8, 134.2, 129.2, 128.7, 126.3, 124.9, 117.1, 112.4, 60.1, 54.6, 32.9, 14.5. IR (neat): 3071, 2980, 2934, 2908, 1698, 1317, 1246, 1149, 743 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{15}H_{18}NO_4S^+$ $[M+H]^+$ 308.0951, found 308.0948.

Ethyl 1-ethyl-5-((phenylsulfonyl)methyl)-1H-pyrrole-2-carboxylate (3c): The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and ethyl 1-ethyl-1H-pyrrole-2-carboxylate **2c** (83.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (1:4) as the eluent afforded **3c** (142.6 mg, 91%) as a white solid. mp = 65−67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 2H), 7.67 – 7.61 (m, 1H), 7.53 – 7.46 (m, 2H), 6.83 (d, J = 4.0 Hz, 1H), 5.79 (d, J = 4.0 Hz, 1H), 4.40 (s, 2H), 4.35 – 4.23 (m, 4H), 1.34 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 137.7, 134.1, 129.1, 128.7, 125.3, 123.6, 117.4, 112.5, 60.0, 54.3, 40.1, 16.4, 14.3. IR (neat): 3064, 2989, 2938, 2873, 1706, 1249, 1148, 741 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{16}H_{20}NO_4S^+$ $[M+H]^+$ 322.1108, found 322.1110.

Ethyl 5-((phenylsulfonyl)methyl)-1-propyl-1H-pyrrole-2-carboxylate (3d): The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and ethyl 1-propyl-1H-pyrrole-2-carboxylate **2d** (90.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (1:5) as the eluent afforded **3d** (132.5 mg, 79%) as a white solid. mp = 77−80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.60

(m, 3H), 7.55 – 7.46 (m, 2H), 6.83 (d, J = 4.0 Hz, 1H), 5.79 (d, J = 4.0 Hz, 1H), 4.39 (s, 2H), 4.27 (q, J = 7.1 Hz, 2H), 4.22 – 4.14 (m, 2H), 1.66 – 1.55 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 137.8, 134.2, 129.2, 128.8, 125.8, 124.1, 117.5, 112.5, 60.1, 54.7, 46.7, 24.8, 14.5, 11.2. IR (neat): 3020, 2985, 2960, 2876, 1703, 1319, 1144, 1082, 739 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{17}H_{22}NO_4S^+$ $[M+H]^+$ 336.1264, found 336.1270.

1-(*tert*-Butyl) 2-ethyl 5-((phenylsulfonyl)methyl)-1H-pyrrole-1,2-dicarboxylate (3e): The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and 1-(tert-butyl) 2-ethyl 1H-pyrrole-1,2-dicarboxylate **2e** (119.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using DCM/PE (5:2) as the eluent afforded **3e** (122.3 mg, 62%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.76 – 7.71 (m, 2H), 7.66 – 7.60 (m, 1H), 7.55 – 7.47 (m, 2H), 6.69 (d, J = 3.6 Hz, 1H), 5.94 (d, J = 3.6 Hz, 1H), 4.75 (s, 2H), 4.29 (q, J = 7.2 Hz, 2H), 1.58 (s, 9H), 1.35 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 148.7, 138.3, 134.0, 129.1, 128.6, 127.9, 125.8, 118.0, 114.5, 86.0, 61.0, 54.4, 27.5, 14.4. IR (neat): 3065, 2982, 2937, 2907, 1717, 1307, 1221, 1135, 745 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{19}H_{23}NO_6SNa^+$ $[M+Na]^+$ 416.1138, found 416.1152.

Methyl 5-((phenylsulfonyl)methyl)-1H-pyrrole-2-carboxylate (3f): The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and methyl 1H-pyrrole-2-carboxylate **2f** (62.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (1:2.5) as the eluent afforded **3f** (105.0 mg, 75%) as

a white solid. mp = 144−146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.70 – 7.64 (m, 2H), 7.63 – 7.55 (m, 1H), 7.50 – 7.42 (m, 2H), 6.80 – 6.73 (m, 1H), 5.92 – 5.86 (m, 1H), 4.44 (s, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 137.5, 134.1, 129.1, 128.5, 124.2, 123.6, 115.8, 113.0, 55.7, 51.8. IR (neat): 3278, 3144, 2985, 2950, 2920, 2844, 1686, 1490, 1229, 1124, 753 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{13}H_{14}NO_4S^+$ $[M+H]^+$ 280.0638, found 280.0639.

1-(5-((Phenylsulfonyl)methyl)-1H-pyrrol-2-yl)ethan-1-one (3g): The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and 1-(1H-pyrrol-2-yl)ethan-1-one **2g** (54.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (1:3) as the eluent afforded **3g** (85.8 mg, 65%) as a white solid. mp = 161−163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.73 – 7.66 (m, 2H), 7.61 – 7.53 (m, 1H), 7.50 – 7.40 (m, 2H), 6.84 – 6.75 (m, 1H), 6.09 – 5.98 (m, 1H), 4.49 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.3, 137.8, 134.1, 133.2, 129.1, 128.5, 125.8, 117.5, 113.2, 55.6, 25.6. IR (neat): 3235, 3127, 2982, 2916, 1638, 1488, 1153, 796 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{13}H_{14}NO_3S^+$ $[M+H]^+$ 264.0689, found 264.0686.

(5-((Phenylsulfonyl)methyl)furan-2-yl)methanol (3h): The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and furan-2-ylmethanol **2h** (49.0 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (1:2.5) as the eluent afforded **3h** (57.0 mg, 45%) as a white solid. mp = 73−75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.67 – 7.61 (m, 1H), 7.54 – 7.47 (m, 2H),

6.22 (s, 2H), 4.44 (s, 2H), 4.40 (s, 2H), 2.40 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 142.1, 138.2, 134.1, 129.2, 128.6, 113.1, 109.2, 57.2, 56.1. IR (neat): 3494, 3134 2975, 2923, 2855, 1445, 1150, 1020, 765 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{12}H_{12}O_4SNa^+$ $[M+Na]^+$ 275.0349, found 275.0362.

2-Methyl-5-((phenylsulfonyl)methyl)thiophene (3i)[30]: The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and 2-methylthiophene **2i** (49.0 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using DCM/PE (2:1) as the eluent afforded **3i** (123.5 mg, 98%) as a white solid. mp = 132−134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.78 – 7.71 (m, 2H), 7.66 – 7.60 (m, 1H), 7.53 – 7.46 (m, 2H), 6.61 – 6.54 (m, 2H), 4.43 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 137.7, 133.9, 130.4, 129.1, 128.8, 125.9, 125.5, 57.6, 15.4. IR (neat): 3092, 3059, 2965, 2920, 1445, 1301, 1141, 728 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{12}H_{12}O_2S_2Na^+$ $[M+Na]^+$ 275.0171, found 275.0178.

2-Chloro-5-((phenylsulfonyl)methyl)thiophene (3j): The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and 2-chlorothiophene **2j** (59.0 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using DCM/PE (3:1) as the eluent afforded **3j** (68.3mg, 50%) as a white solid. mp = 131−134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.69 – 7.63 (m, 1H), 7.56 – 7.49 (m, 2H), 6.74 (d, J = 4.0 Hz, 1H), 6.60 (d, J = 4.0 Hz, 1H), 4.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 134.3, 132.1, 129.9, 129.3, 128.8, 127.4, 126.4, 57.6. IR (neat): 3054, 2990, 2966,

2920, 1476, 1299, 1143, 728 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{11}H_9ClO_2S_2Na^+$ $[M+Na]^+$ 294.9625, found 294.9624.

1-Methyl-2-((phenylsulfonyl)methyl)-1H-indole (3k)[31]: The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and 1-methyl-1H-indole **2k** (65.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using DCM/PE (2:1) as the eluent afforded **3k** (92.9 mg, 65%) as a white solid. mp = 177−179 °C (lit 177 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.59 (m, 3H), 7.51 – 7.41 (m, 3H), 7.32 – 7.21 (m, 2H), 7.12 – 7.05 (m, 1H), 6.11 (s, 1H), 4.55 (s, 2H), 3.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 137.8, 134.1, 129.1, 128.8, 127.1, 126.4, 122.6, 120.9, 120.0, 109.7, 105.7, 55.1, 30.2. IR (neat): 3023, 2946, 2896, 2839, 1592, 1496, 1260, 1150, 833, 759 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{16}H_{15}NO_2SNa^+$ $[M+Na]^+$ 308.0716, found 308.0726.

3-Methyl-2-((phenylsulfonyl)methyl)-1H-indole (3l)[32]: The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and 3-methyl-1H-indole **2l** (65.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (1:4) as the eluent afforded **3l** (85.5 mg, 60%) as a colorless solid. mp = 176−178 °C (lit 183−185 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.62 – 7.56 (m, 3H), 7.44 – 7.33 (m, 4H), 7.24 – 7.19 (m, 1H), 7.12 – 7.06 (m, 1H), 4.49 (s, 2H), 1.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 136.6, 134.1, 129.2, 128.4, 128.1, 123.2, 121.1, 119.6,

119.1, 113.4, 111.2, 54.5, 7.8. IR (neat): 3363, 2954, 2924, 2854, 1450, 1288, 1139, 1082, 738 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{16}H_{16}NO_2S^+$ $[M+H]^+$ 286.0896, found 286.0888.

2-((Phenylsulfonyl)methyl)-1H-indole (3m)[31]: The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and 1H-indole **2n** (58.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using DCM/PE (5:2) as the eluent afforded **3n** (39.6 mg, 29%) as a white solid. mp = 189−190 °C (lit 190 °C). ^{1}H NMR (400 MHz, DMSO) δ 11.13 (s, 1H), 7.81 – 7.68 (m, 3H), 7.66 – 7.55 (m, 2H), 7.45 – 7.40 (m, 1H), 7.40 – 7.34 (m, 1H), 7.12 – 7.01 (m, 1H), 7.00 – 6.90 (m, 1H), 6.11 (s, 1H), 4.83 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 138.5, 136.6, 134.0, 129.3, 128.0, 127.6, 125.7, 121.6, 120.0, 119.2, 111.5, 103.8, 55.0. IR (neat): 3324, 3056, 2992, 2918, 2849, 1734, 1292, 1082, 801, 710 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{15}H_{13}NO_2SNa^+$ $[M+Na]^+$ 294.0559, found 294.0557.

2-((Phenylsulfonyl)methyl)benzofuran (3n)[33]: The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and benzofuran **2o** (59.0 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using DCM/PE (2:1) as the eluent afforded **3o** (120.0 mg, 88%) as a white solid. mp = 166−168 °C (lit 166−168 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.86 – 7.71 (m, 2H), 7.68 – 7.59 (m, 1H), 7.56 – 7.42 (m, 3H), 7.39 – 7.31 (m, 1H), 7.30 – 7.18 (m, 2H), 6.67 (s, 1H), 4.55 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 145.2, 138.3, 134.2, 129.3, 128.6, 128.0, 125.1, 123.3, 121.4, 111.4, 109.1, 56.6. IR (neat): 3120, 3064, 2991, 2937, 1445, 1306, 1146, 740 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{15}H_{12}O_3SNa^+$ $[M+Na]^+$ 295.0399, found 295.0397.

5-Bromo-2-((phenylsulfonyl)methyl)benzofuran (3o): The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and 5-bromobenzofuran **2p** (98.0 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using DCM/PE (3:2) as the eluent afforded **3p.** (43.9 mg, 25%) as a white solid. mp = 193−195 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.83 – 7.71 (m, 2H), 7.69 – 7.61 (m, 2H), 7.54 – 7.45 (m, 2H), 7.42 – 7.33 (m, 1H), 7.24 – 7.18 (m, 1H), 6.61 (s, 1H), 4.54 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 146.7, 138.1, 134.3, 129.9, 129.4, 128.6, 128.2, 124.0, 116.4, 112.9, 108.5, 56.5. IR (neat): 3109, 2989, 2962, 2920, 2849, 1719, 1443, 1152, 805 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{15}H_{11}BrO_3SNa^+$ $[M+Na]^+$ 372.9504, found 372.9501.

1,3,7-Trimethyl-8-((phenylsulfonyl)methyl)-3,7-dihydro-1H-purine-2,6-dione (3p)[14]: The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and 1,3,7-trimethyl-3,7-dihydro-1H-purine-2,6-dione **2q** (97.0 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (2:1) as the eluent afforded **3q.** (42.0 mg, 24%) as a white solid. mp = 244−245 °C (lit 243−245 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H), 7.74 – 7.67 (m, 1H), 7.60 – 7.52 (m, 2H), 4.56 (s, 2H), 4.06 (s, 3H), 3.40 (s, 3H), 3.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 151.6, 147.7, 141.3, 137.9, 134.7, 129.4, 128.8, 109.1, 54.8, 33.0, 29.7, 28.2. IR (neat): 3356, 2971, 2918, 2849, 1703, 1661, 1149, 755 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{15}H_{17}N_4O_4S^+$ $[M+H]^+$ 349.0965, found 349.0964.

Ethyl 5-(tosylmethyl)-1H-pyrrole-2-carboxylate (3q): The general procedure was followed using 1-((bromomethyl)sulfonyl)-4-methylbenzene **1b** (248.0 mg, 1.0 mmol) and ethyl 1H-pyrrole-2-carboxylate **2a** (69.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (1:2) as the eluent afforded **3r** (101.5 mg, 66%) as a white solid. mp = 177−179 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.56 – 7.50 (m, 2H), 7.29 – 7.23 (m, 2H), 6.78 – 6.74 (m, 1H), 5.90 – 5.86 (m, 1H), 4.38 (s, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 2.40 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 145.3, 134.7, 129.8, 128.5, 124.7, 123.5, 115.6, 113.1, 60.7, 55.7, 21.8, 14.5. IR (neat): 3269, 3141, 3004, 2986, 1683, 1489, 1279, 767 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{15}H_{17}NO_4SNa^+$ $[M+Na]^+$ 330.0770, found 330.0773.

Ethyl 5-(((4-methoxyphenyl)sulfonyl)methyl)-1H-pyrrole-2-carboxylate (3r): The general procedure was followed using 1-((bromomethyl)sulfonyl)-4-methoxybenzene **1c** (264.0 mg, 1.0 mmol) and ethyl 1H-pyrrole-2-carboxylate **2a** (69.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (1:3) as the eluent afforded **3s** (123.1 mg, 76%) as a white solid. mp = 168−169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.64 – 7.49 (m, 2H), 7.00 – 6.85 (m, 2H), 6.82 – 6.71 (m, 1H), 5.93 – 5.82 (m, 1H), 4.37 (s, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 160.9, 130.7, 129.0, 124.6, 123.7, 115.6, 114.3, 113.0, 60.7, 55.9, 55.8, 14.5. IR (neat): 3270, 3021, 2970, 2881, 1680, 1488, 1298, 765 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{15}H_{17}NO_5SNa^+$ $[M+Na]^+$ 346.0720, found 346.0726.

Ethyl 5-(((4-nitrophenyl)sulfonyl)methyl)-1H-pyrrole-2-carboxylate (3s): The general procedure was followed using 1-((bromomethyl)sulfonyl)-4-nitrobenzene **1d** (279.0 mg, 1.0 mmol) and ethyl 1H-pyrrole-2-carboxylate **2a** (69.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (1:2.5) as the eluent afforded **3t** (67.9 mg, 40%) as a white solid. mp = 184−186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 8.35 – 8.25 (m, 2H), 7.89 – 7.77 (m, 2H), 6.79 – 6.71 (m, 1H), 5.88 – 5.82 (m, 1H), 4.47 (s, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 151.1, 143.0, 130.1, 125.4, 124.3, 122.1, 115.6, 113.5, 61.1, 55.8, 14.5. IR (neat): 3273, 3124, 2917, 2849, 1673, 1521, 1275, 765 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{14}H_{14}N_2O_6SNa^+$ $[M+Na]^+$ 361.0465, found 361.0466.

2,5-Bis((phenylsulfonyl)methyl)-1H-pyrrole (3t): The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and ethyl 1H-pyrrole **2r** (69.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (2:3) as the eluent afforded **3u** (107.0 mg, 57%) as a white solid. mp = 154−156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.78 – 7.68 (m, 4H), 7.67 – 7.58 (m, 2H), 7.54 – 7.44 (m, 4H), 5.76 – 5.66 (m, 2H), 4.38 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 134.0, 129.1, 128.6, 120.1, 112.1, 55.9. IR (neat): 3357, 3187, 2958, 2849, 1646, 1289, 1147, 800, 686 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{18}H_{17}NO_4S_2Na^+$ $[M+Na]^+$ 398.0491, found 398.0487.

2,5-Bis((phenylsulfonyl)methyl)furan (3u): The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and furan **2s** (34.0 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (2:3) as the eluent afforded **3v** (52.7 mg, 28%) as a white solid. mp = 125−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 4H), 7.69 – 7.63 (m, 2H), 7.56 – 7.49 (m, 4H), 6.21 (s, 2H), 4.30 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 138.2, 134.2, 129.3, 128.6, 113.7, 55.8. IR (neat): 3061, 2976, 2930, 2849, 1304, 1143, 1083, 810, 685 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{18}H_{16}O_5S_2Na^+$ $[M+Na]^+$ 399.0331, found 399.0343.

2,5-Bis((phenylsulfonyl)methyl)thiophene (3v): The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and thiophene **2t** (42.0 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using DCM as the eluent afforded **3w** (49.3 mg, 25%) as a white solid. mp = 209−211 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.78 – 7.69 (m, 6H), 7.65 – 7.55 (m, 4H), 6.63 (s, 2H), 4.93 (s, 4H). ^{13}C NMR (101 MHz, DMSO) δ 137.9, 134.1, 131.2, 130.0, 129.2, 128.1, 55.6. IR (neat): 3068, 2978, 2922, 2850, 1300, 1144, 756, 683 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{18}H_{16}O_4S_3Na^+$ $[M+Na]^+$ 415.0103, found 415.0103.

1,3-Dimethyl-3-(2-(phenylsulfonyl)ethyl)indolin-2-one (5a): The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and *N*-methyl-*N*-phenylmethacrylamide **4a** (87.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (2:3) as the eluent afforded **5a**

(155.1 mg, 94%) as a white solid. mp = 112−114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 2H), 7.68 – 7.61 (m, 1H), 7.59 – 7.51 (m, 2H), 7.32 – 7.25 (m, 1H), 7.12 – 7.02 (m, 2H), 6.88 – 6.81 (m, 1H), 3.17 (s, 3H), 2.97 – 2.87 (m, 1H), 2.79– 2.69 (m, 1H), 2.23 (td, *J* = 13.0, 4.8 Hz, 1H), 2.11 (td, *J* = 13.1, 3.6 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 143.0, 138.7, 133.9, 132.1, 129.4, 128.6, 128.1, 123.2, 122.6, 108.5, 51.8, 46.8, 30.7, 26.4, 23.4. IR (neat): 3065, 2989, 2943, 2917, 1702, 1608, 1492, 1146, 750 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{18}H_{20}NO_3S^+$ $[M+H]^+$ 330.1158, found 330.1161.

1,3-Dimethyl-3-(2-tosylethyl)indolin-2-one (5b): The general procedure was followed using 1-((bromomethyl)sulfonyl)-4-methylbenzene **1b** (248.0 mg, 1.0 mmol) and *N*-methyl-*N*-phenylmethacrylamide **4a** (87.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (1:2) as the eluent afforded **5b** (139.6 mg, 81%) as a white solid. mp = 151−152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.63 (m, 2H), 7.37 – 7.31 (m, 2H), 7.31 – 7.25 (m, 1H), 7.15 – 7.01 (m, 2H), 6.88 – 6.80 (m, 1H), 3.17 (s, 3H), 2.88 (td, *J* = 13.2, 5.2 Hz, 1H), 2.71 (td, *J* = 13.2, 3.6 Hz, 1H), 2.44 (s, 3H), 2.20 (td, *J* = 13.0, 5.2 Hz, 1H), 2.10 (td, *J* = 13.0, 3.6 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 144.8, 142.9, 135.6, 132.0, 130.0, 128.5, 128.0, 123.0, 122.5, 108.4, 51.8, 46.8, 30.7, 26.3, 23.3, 21.6. IR (neat): 3033, 2975, 2936, 2873, 1696, 1611, 1302, 1143, 757 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{19}H_{22}NO_3S^+$ $[M+H]^+$ 344.1315, found 344.1322.

3-(2-((4-Methoxyphenyl)sulfonyl)ethyl)-1,3-dimethylindolin-2-one (5c): The general procedure was followed using 1-((bromomethyl)sulfonyl)-4-methoxybenzene **1c** (264.0 mg,

1.0 mmol) and *N*-methyl-*N*-phenylmethacrylamide **4a** (87.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (1.15:1) as the eluent afforded **5c** (135.0 mg, 75%) as a white solid. mp = 142−144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.22 – 7.16 (m, 1H), 7.05 – 6.94 (m, 2H), 6.93 – 6.88 (m, 2H), 6.79 – 6.73 (m, 1H), 3.78 (s, 3H), 3.08 (s, 3H), 2.79 (td, *J* = 13.0, 5.0 Hz, 1H), 2.66 – 2.56 (m, 1H), 2.12 (td, *J* = 13.0, 5.0 Hz, 1H), 2.01 (td, *J* = 13.0, 4.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9, 163.8, 142.9, 132.1, 130.2, 130.1, 128.5, 123.0, 122.5, 114.5, 108.4, 55.7, 51.9, 46.7, 30.8, 26.2, 23.3. IR (neat): 2981, 2929, 2872, 2840, 1693, 1593, 1493, 1139, 757 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{19}H_{21}NO_4SNa^+$ $[M+Na]^+$ 382.1083, found 382.1097.

1,3-Dimethyl-3-(2-((4-nitrophenyl)sulfonyl)ethyl)indolin-2-one (5d): The general procedure was followed using 1-((bromomethyl)sulfonyl)-4-nitrobenzene **1d** (279.0 mg, 1.0 mmol) and *N*-methyl-*N*-phenylmethacrylamide **4a** (87.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (1:2) as the eluent afforded **5d** (28.4 mg, 15%) as a light yellow solid. mp = 143−145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.35 (m, 2H), 8.08 – 7.99 (m, 2H), 7.35 – 7.28 (m, 1H), 7.18 – 7.04 (m, 2H), 6.90 – 6.81 (m, 1H), 3.18 (s, 3H), 3.01 – 2.90 (m, 1H), 2.90 – 2.80 (m, 1H), 2.27 – 2.18 (m, 1H), 2.16 – 2.07 (m, 1H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.8, 151.1, 144.4, 143.0, 132.0, 129.7, 128.9, 124.7, 123.4, 122.6, 108.7, 51.8, 46.8, 30.5, 26.5, 23.5. IR (neat): 3099, 2957, 2919, 2849, 1692, 1492, 1149, 738 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{18}H_{18}N_2O_5SNa^+$ $[M+Na]^+$ 397.0829, found 397.0833.

5-Methoxy-1,3-dimethyl-3-(2-(phenylsulfonyl)ethyl)indolin-2-one (5e): The general procedure was followed using bromomethyl phenyl sulfone **1a** (234.0 mg, 1.0 mmol) and *N*-(4-methoxyphenyl)-*N*-methylmethacrylamide **4b** (102.5 mg, 0.5 mmol) as the starting materials. Purification by column chromatography using EtOAc/PE (2:3) as the eluent afforded **5e** (120.5 mg, 67%) as a colorless solid. mp = 109−111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.86 – 7.80 (m, 2H), 7.68 – 7.62 (m, 1H), 7.58 – 7.51 (m, 2H), 6.83 – 6.69 (m, 3H), 3.77 (s, 3H), 3.14 (s, 3H), 2.92 (td, *J* = 13.3, 4.8 Hz, 1H), 2.76 (td, *J* = 13.3, 4.8 Hz, 1H), 2.22 (td, *J* = 13.0, 4.8 Hz, 1H), 2.08 (td, *J* = 13.1, 4.8 Hz, 1H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.4, 156.3, 138.5, 136.3, 133.8, 133.3, 129.3, 127.9, 112.6, 110.0, 108.7, 55.7, 51.6, 47.1, 30.6, 26.3, 23.3. IR (neat): 2996, 2967, 2934, 2832, 1694, 1594, 1490, 1149, 745 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{19}H_{22}NO_4S^+$ $[M+H]^+$ 360.1264, found 360.1264.

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Supporting information: ^{1}H and ^{13}C NMR spectra of all products. Mechanistic experiments and results. This material is available free of charge via the Internet at http://pubs.acs.org/.

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