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Synthesis of Sulfones *via* Ru(II)-Catalyzed Sulfination of Boronic Acids

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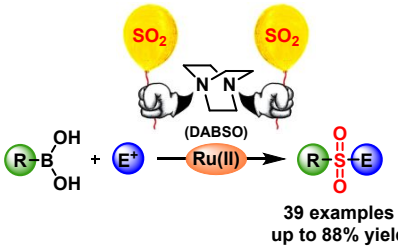


ABSTRACT: Ruthenium(II) complexes catalyze insertion of sulfur dioxide into (het)aryl and alkenyl boronic acids. The transmetalation-sulfination process proceeds with DABSO in the presence of 5 mol% $RuCl_2(PPh_3)_3$ in methanol at 100 °C. The intermediate sulfinate salt can be quenched with various electrophiles such alkyl halides, epoxides, Michael acceptors and λ^3-iodanes in moderate to good yields. The reported sulfone synthesis can be performed either as a direct one-pot or one-pot two-step procedure depending on the reactivity of the electrophile.

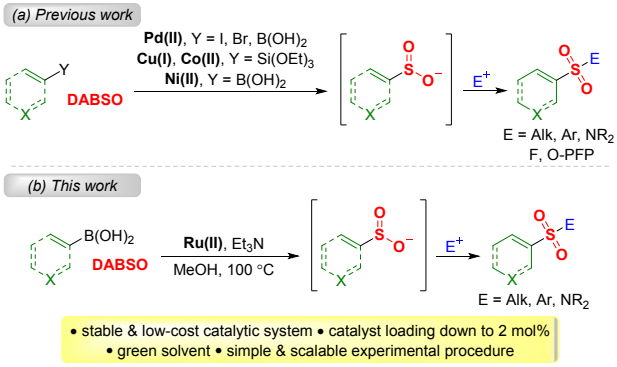
Sulfonyl group containing compounds, particularly sulfones and sulfonamides, are widely explored and applied in pharmacy[1], agrochemistry[2] and materials science[3]. During the last decade, one-pot multi-component procedures for the direct insertion of sulfur dioxide into small molecules under transition metal catalysis[4] have proved to be an attractive alternative to the traditional approaches[5] towards these valuable compounds.

It is known that gaseous SO_2 can be efficiently applied for the synthesis of various sulfonyl derived compounds *via* pericyclic reactions.[6] At the same time, large excess of SO_2 may poison catalytic species. Thus, application of gaseous SO_2 for transition metal catalyzed insertion reactions is limited.[7]

In 2010, based on analogy with aminocarbonylation[8] Willis group developed aminosulfonylation[9] of aryl halides with DABSO[10,11] - a SO_2 surrogate[12] that is compatible with the palladium catalyst. Since then, palladium catalyzed sulfonylation of (het)aryl/vinyl halides as well as boronic acids using DABSO has been applied for the synthesis of a variety of sulfonyl group containing compounds such as sulfonamides[9,13], sulfones[13e,14], sulfonyl fluorides[15] and activated sulfonate esters[16] (Scheme 1a). Additionally, transmetalation-sulfination approach by combination of boronic acids or aryl triethoxysilanes with DABSO has also proved to be successful in the presence of abundant metal (Cu[17], Co[18] or Ni[19]) catalysts. Nevertheless, these methods suffer from catalyst loading, base or catalyst stability, need for external ligand, highly polar and/or toxic reaction solvent or limited applications. Thus, there is still place for the development of more versatile, accessible and environment-friendly reaction conditions.

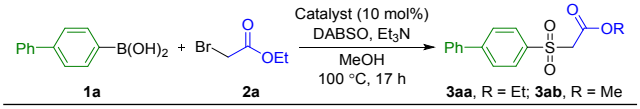
Unlike palladium, ruthenium has a wide scope of oxidation states that leads to diverse coordination geometries of metal complexes. Thus, ruthenium complexes are considered to have a great potential for a broad range of catalytic transformations.[20] Besides, also in terms of price ruthenium is superior to palladium. Hence, we were encouraged to explore sulfonylative cross-coupling reaction under ruthenium catalysis for the first time (Scheme 1b). We hypothesized that aryl-Ru(II) as organometallic species generated from aryl boronic acid[21] would undergo SO_2 insertion, similarly to its previously reported additions to C=O systems[21a-e]. The obtained sulfinate salts are known to be relatively stable reaction intermediates that can provide a wide variety of sulfonyl moiety containing products upon treatment with electrophiles.

Scheme 1. Synthesis of Sulfonyl Derived Compounds *via* Transition Metal Catalyzed Generation of Sulfinate Intermediate by Employing DABSO as a SO_2 Surrogate



We started our study by screening a catalytic activity of various Ru(II) complexes for the synthesis of sulfone **3aa** from biphenyl boronic acid **1a**, DABSO and ethyl bromoacetate (**2a**) in a one-pot process (Table 1). To our delight, almost all tested catalysts gave yields over 50% (Table 1, entries 2-8). The reactions were carried out in the presence of amine base in methanol solution. Therefore, it was no surprise to observe transesterification to methyl ester **3ab** in a trace amount. When corresponding potassium or tetrabutylammonium aryl tetrafluoroborate was used instead of boronic acid **1a** in the presence of $RuCl_2(PPh_3)_3$, desired sulfone **3aa** was isolated in 9% or 47% yield, respectively. Under selected screening conditions we have also demonstrated the first example of Rh(I)-catalyzed sulfonylative cross-coupling reaction (Table 1, entry 10). At the same time, previously reported Pd(II) catalysis (Table 1, entry 11) was less effective under these conditions. $RuCl_2(PPh_3)_3$ as a cheap, air stable complex (Table 1, entry 2) was selected for the subsequent research.

Table 1. Catalyst Screening[a]



entry	catalyst	isolated yield **3aa**+**3ab**, %[b]
1	without catalyst	NR
2	$RuCl_2(PPh_3)_3$	72 (3)
3[c]	$RuCl(PPh_3)_3OAc$	72 (2)
4[c]	$Ru(2\text{-methallyl})_2(COD)$	71 (4)
5	$RuCl_2(COD)$	63 (2)
6[c]	$[RuCl_2(mesitylene)]_2$	60 (<1)
7	$[RuCl_2(p\text{-cymene})]_2$	57 (<1)
8	$[RuCl_2(C_6H_6)]_2$	54 (<1)
9	$RuCp(PPh_3)_2Cl$	24 (<1)
10	$[RhCl(COD)]_2$	47 (<1)
11	$Pd(OAc)_2$	47 (<1)

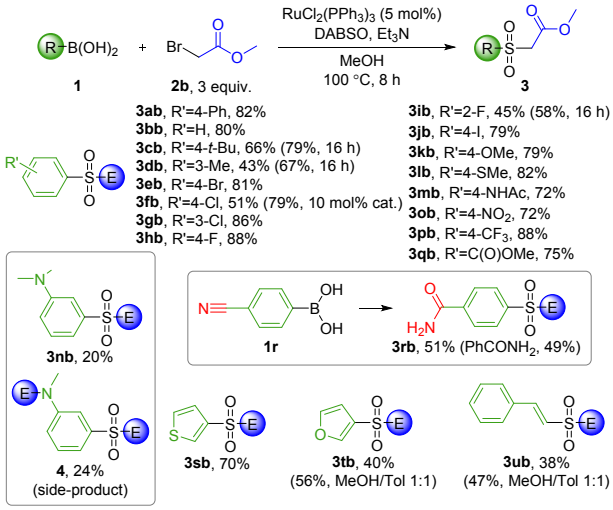
[a] Reaction conditions: **1a** (0.385 mmol, 1 equiv.), **2a** (3 equiv.), DABSO (1 equiv.), Et_3N (2 equiv.) and catalyst (10 mol%) in MeOH (2 mL) at 100 °C for 17 h. [b] In parenthesis yield (%) of transesterification product **3ab** determined by NMR analysis. [c] N_2 atmosphere.

Various bases and solvents were tested (see Supporting Information (SI), Table S1 and S2). All inorganic bases screened (K_2CO_3, K_3PO_4, NaOAc, Cs_2CO_3, KF) were inefficient, but amines showed good results with Et_3N being superior to others. We also noticed that the presence of methanol as a solvent is mandatory for the reaction to occur. For example, experiment in MeOH/Tol (1:1) resulted in 79% yield, while in pure toluene only 7% of sulfone **3aa** was isolated. Pure methanol gave the best relation between reaction yield and level of transesterification. To note, reaction outcome was significantly reduced when other alcohol such as ethanol (23%) or isopropanol (<5%) was used as a solvent.

Next, catalyst loading was optimized to 5 mol% without significant loss in yield, while temperature decrease seemed to be undesirable (SI, Table S3). Reduced amount of bromide **2a** (2 equiv.) or DABSO (0.6 equiv.) as well as increased amount of Et_3N (3 equiv.) instead of initial conditions did not bring any contribution. Also cationic system in the presence of AgOTf[21g] or bromide stabilization[13e] (Bu_4NBr additive) did not provide any improvement. Finally, other sources of SO_2 were tested. While $K_2S_2O_5$ and gaseous SO_2 did not provide desired product under our conditions, DMAP·SO_2[22], another bench stable amine-SO_2 complex, gave sulfone **3ab** in a moderate yield (51%). In conclusion, we decided to continue with initial conditions by employing 5 mol% of Ru(II) catalyst and for reduced reaction time.

Scope of boronic acids **1** tested for the novel Ru(II)-catalyzed one-step procedure towards sulfones **3** by employing bromoacetate **2b** as a coupling partner is summarized in Scheme 2. Phenyl boronic acids bearing either electron donating or electron-withdrawing *para*- or *meta*-substituents worked well under newly developed conditions. Pleasingly, sensitive functional groups such as thioether (**3lb**), amide (**3mb**) and ester (**3qb**) were compatible. Ruthenium(II) catalytic system is also suitable for iodo-substituted boronic acid **1j**. Such a substrate compatibility has been demonstrated only for a nickel catalyst so far.[19] Reports on Ru(II)-catalyzed hydration of nitriles[23] explain formation of amide **3rb** when CN group containing substrate **1r** was used. *meta*-Substituted dimethylamino phenyl boronic acid **3n** gave mixture of desired sulfone **3nb** and transalkylation side product **4** in a moderate combined yield. Among the tested *orto*-substituted boronic acids, only fluorine containing substrate **1i** led to the formation of target sulfone **3ib**. Apparently, bigger substituents such as Br, Me and OH sterically blocked active site and starting material was recovered. Thiophen-3-yl sulfone **3sb** and furan-3-yl sulfone **3tb** demonstrate application of our catalytic system for heteroaromatic substrates. While thiophen-3-yl boronic acid **1s** reacted smoothly under optimized reaction conditions, solvent modification was necessary to improve yield of furan derivative **3tb**. Also for alkenyl boronic acid **1u** solvent mixture MeOH/Tol (1:1) allowed to improve reaction outcome.

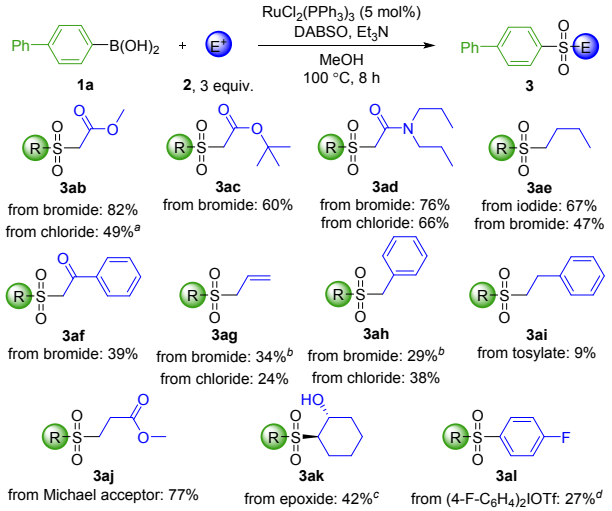
Scheme 2. Scope of Boronic Acids



Next, we screened reactivity of various *C*-electrophiles in the one-step process (Scheme 3). *α*-Bromoesters (**3ab** and **3ac**) and *α*-haloamides (**3ad**) as well as alkyl iodide (**3ae**) and methyl acrylate (**3aj**) as a Michael acceptor gave good yields under optimized reaction conditions. Due to the limited reports in the literature[12d], the latter example is a valuable complement to the sulfone synthesis *via* sulfonylative cross-coupling. Alkyl bromide (**3ae**) and *α*-bromoketone (**3af**) gave desired sulfones in modest yields. Unexpected low yields were observed when allyl (**3ag**) and benzyl (**3ah**) halides were used as electrophiles. We proposed that these halides readily react with Et_3N and DABCO forming quaternary ammonium salts. Apparently, the same problem occurred when NaI (1 equiv.) was used as an additive in order to increase reactivity of *α*-chloroacetate (**3ab**) by *in situ* halide exchange. When tosylate was used as a leaving group, sulfone **3ai** was isolated in only 9% yield. Opening of cyclohexene oxide led to *α*-hydroxyl sufone **3ak** in 42% yield. Finally, synthesis of diaryl sulfone **3al** was demonstrated by employing λ^3-iodane complex $(4\text{-F-}C_6H_4)_2IOTf$ as an electrophilic partner.

It is known that the alternative Pd-catalyzed sulfonylative cross-coupling reactions proceed *via* sulfinate intermediates that can be quenched by electrophiles in a one-pot two-step procedure.[13e,14b] By applying this concept we adapted other

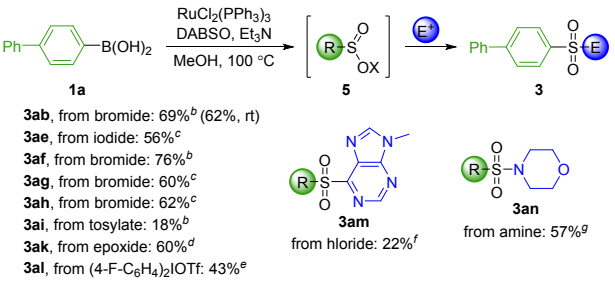
Scheme 3. Scope of *C*-Electrophiles



[a] 10 mol% Ru(II). [b] 17 h. [c] 5 equiv. E^+. [d] MeOH/Tol 1:1.

conditions for sulfinate derivatization step (Scheme 4) to improve the initial yields (Scheme 3). In the case of α-bromoacetate **2b** we demonstrated that elevated temperature is required for sulfinate **5** formation, while electrophile adds even at ambient temperature. It is important to note that the presence of Et_3N in the first step has beneficial effect on the course of reaction. Sulfone **3ab** was isolated with low 14% yield, when Et_3N was added only for the second step that was carried out at ambient temperature[13e]. Our two step procedure applying the initial catalytic conditions worked well for α-bromoketone (**3af**) increasing yield from 39% to 76%. By lowering temperature to 80 °C for the alkylation step, allyl and benzyl bromides gave sulfones **3ag** and **3ah** in 62% and 60% yield, respectively. Enhancement was also observed for sulfones **3ak** and **3al** when derivatization of the sulfinate **5** was performed in another solvent. Finally, this approach gave us opportunity to expend novel methodology. Diaryl sulfone **3am** was synthesized through S_NAr chemistry, while reaction between sulfinate **5** and *N*-chloromorpholine generated *in situ* by NaOCl[24] led to sulfonamide **3an**.

Scheme 4. One-Pot Two-Step Synthesis of Sulfones *via* Ru(II)-Catalyzed Generation of Sulfinate[a]



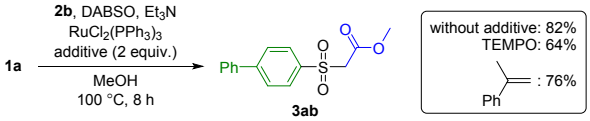
[a] **1a** → **5**: **1a** (0.385 mmol, 1 equiv.), DABSO (1 equiv.), Et_3N (2 equiv.) and $RuCl_2(PPh_3)_3$ (5 mol%) in MeOH (2 mL) at 100 °C for 2 h. **5** → **3**: [b] E^+ (3 equiv.), 100 °C, 8 h. [c] E^+ (3 equiv.), 80 °C, 8 h. [d] E^+ (5 equiv.), H_2O, 90 °C, 12 h. [e] E^+ (3 equiv.), DMF, 90 °C, 12 h. [f] E^+ (3 equiv.), DMSO, 100 °C, 12 h. [g] morpholine (5 equiv.), NaOCl (3 equiv.), H_2O, rt, 12 h.

Next, we turned our attention to the reaction mechanism. When synthesis of sulfone **3ab** was carried out under optimized reaction conditions in the presence of radical trapping agent such as TEMPO or 1-methyl styrene, no significant inhibition of reaction was observed (Scheme 5a). Thus, radical pathway was excluded.

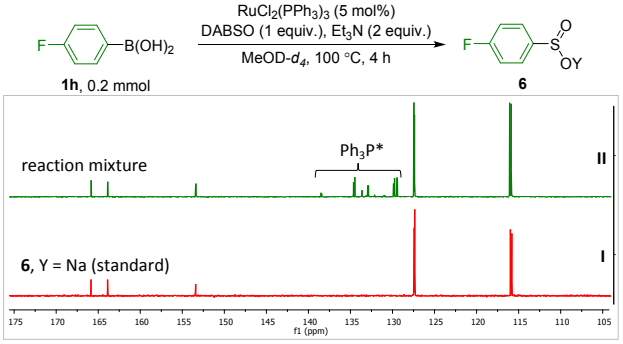
Formation of sulfinate intermediate **6** was detected by ^{13}C NMR spectroscopy (Scheme 5b). 4-Fluorophenyl boronic acid (**1h**) was subjected to the conditions of sulfinate generation step. Corresponding sodium aryl sulfinate **6** (Y = Na) was used as a standard. Full consumption of boronic acid **1h** and formation of sulfinate salt **6** were observed. To note, without the amine only partial conversion of boronic acid **1h** was detected (see SI).

Scheme 5. Mechanistic Studies

(a) Control experiments with radical traps



(b) $^{13}C\{^1H\}$ NMR (126 MHz, MeOD-d_4) studies



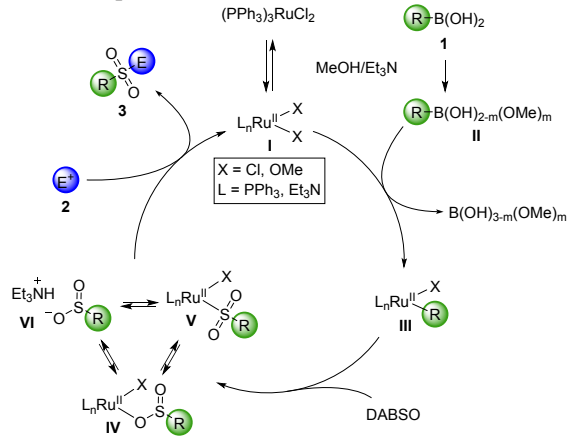
* free and coordinated

Referring to the studies on palladium-centered transmetalation of boronic acids[25], formation of more basic alkoxy-Ru(II)[26] species that favors coordination with highly oxophilic boron center of *in situ* formed $ArB(OH)_{2-m}(OMe)_m$ is the most feasible scenario. In that case, formation of boric acid esters $B(OH)_{3-m}(OMe)_m$ should be detected. Indeed, both GC-FID and ^{11}B NMR analysis of the reaction mixture after generation of sulfinate salt **6** confirmed release of $B(OMe)_3$ (see SI).

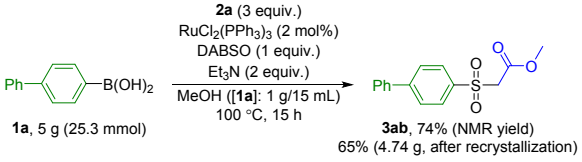
Based on the aforementioned observations, herein we propose redox neutral mechanism for Ru(II)-catalyzed sulfonylative cross-coupling reaction (Scheme 6). The catalytic cycle starts with transmetalation between alkoxy-Ru(II) complex **I** and organoboron species **II** leading to the aryl-Ru(II) intermediate **III** and release of methyl borate. Next, DABSO delivers SO_2 molecule that inserts into Ru(II)-carbon bond. Although formation of Ru-S bond (**V**) is more likely[27], equilibrium to sulfinates **IV** and **VI** is also possible. Nevertheless, either of intermediates **IV**-**VI** can provide sulfone **3** when trapped with electrophile **2**.

Finally, we have demonstrated the application of this newly developed Ru(II)-catalyzed one-pot multi-component sulfone synthesis on a gram-scale. Using 2 mol% catalyst loading and substrate **1a** / solvent ratio 1:15 (g/mL), the sulfone **3ab** was isolated in 65% after simple recrystallization (Scheme 7).

Scheme 6. Proposed Reaction Mechanism



Scheme 7. Gram-Scale Synthesis of the Sulfone 3ab



In summary, we have developed the first Ru(II)-catalyzed sulfonylative cross-coupling reaction. A series of sulfones have been synthesized from boronic acids, DABSO and various electrophiles in moderate to good yields and good functional group tolerance. This method is relatively cheap and offers simple and scalable experimental procedure with MeOH as a green reaction solvent. Depending on the nature of electrophile, one-step or two-step one-pot procedure can be adapted. Reaction mechanism through redox neutral Ru(II)-catalyzed formation of sulfinate species has been proposed. The overall transformation discloses application of Ru-catalysis for direct insertion of SO_2 into various types of bonds as a novel area to be investigated.

EXPERIMENTAL SECTION

Unless otherwise stated, all reactions were carried out in glass pressure tubes sealed with PTFE screw caps and no inert atmosphere as well as anhydrous conditions were provided. All commercially available reagents were used as received. Phenethyl 4-methylbenzenesulfonate[28] (for **3ai**), $[(4\text{-F-}C_6H_4)_2IOTf]$[29] (for **3al**), 6-chloro-9-methyl-9*H*-purine[30] (for **3am**) and DABSO[9] were synthesized according to the reported procedures. Reaction mixture and chromatographic purification were monitored by thin-layer chromatography (TLC) on E. Merck Kieselgel 60 F254, with detection by UV light (254 nm) or iodine as a visualizing agent. Column chromatography was performed on ROCC (60 Å, 40–60 µm) or LiChroprep RP-18 (25–40 µm) silica gel. ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker spectrometer at 500 MHz and 126 MHz, respectively. The chemical shifts (δ) are reported in ppm. The residual solvent peak is used as an internal reference (for ^{1}H NMR: 7.26 ($CDCl_3$), 2.50 (DMSO-d_6), 3.31 (MeOD-d_6) ppm; for $^{13}C\{^1H\}$ NMR: 77.16 ($CDCl_3$), 39.52 (DMSO-d_6), 49.00 (MeOD-d_4)). The coupling constants (J) are given in Hz and reported with the following abbreviations: s (singlet), d (doublet), dd (double doublet), ddd (double doublet of doublets), t (triplet), dt (double triplet), q (quartet), m (multiplet), br (broad). For quantitative ^{1}H NMR relaxation time was increased (d1 = 10). ^{11}B NMR spectra were recorded on a Bruker spectrometer at 160 MHz with the automatic internal calibration system for the chemical shift values. High-resolution mass (HRMS) (electrospray ionization (ESI)) were recorded with an Agilent 1290 Infinity series ultra-high pressure liquid chromatography connected to an Agilent 6230 time-of-flight mass spectrometer. Gas chromatography was performed on Agilent 6890N Network Gas Chromatograph equipped with flame ionization detector (FID). Fourier transform infrared (FT-IR, Varian 800 FT-IR, Scimitar Series, USA) spectra were recorded in the Attenuated Total Reflectance (ATR, GladiATRTM, Pike technologies, USA) mode with an internal range from 400 cm^{-1} to 4000 cm^{-1}. Melting point for compound **3ab** was determined using STUART melting point SMP110 apparatus.

General Procedures for Ru(II)-Catalyzed Synthesis of Sulfones:

*(A) One-Step Procedure (**3aa**, Scheme 2, Scheme 3).* Boronic acid **1** (0.385 mmol, 1 equiv.), DABSO (1 equiv.) and $RuCl_2(PPh_3)_3$ (5 mol%) were placed into a glass pressure tube (15 or 20 mL) equipped with a magnetic stirring bar. Then MeOH (2 mL) was added followed by Et_3N (2 equiv.) and electrophile **2** (3 equiv.). The resulting mixture was stirred at 100 °C (oil bath) for 8 h. After cooling to room temperature, reaction mixture was filtered through a pad of silica gel using EtOAc. The filtrate was evaporated under reduced pressure and the residue purified by column chromatography (hexanes/EtOAc) to afford sulfone **3**.

(B) One-Pot Two-Step Procedure (Scheme 4). 4-Biphenylboronic acid (**1a**, 0.385 mmol, 1 equiv.), DABSO (1 equiv.) and $RuCl_2(PPh_3)_3$ (5 mol%) were placed into a glass pressure tube (15 or 20 mL) equipped with a magnetic stirring bar. Then MeOH (2 ml) was added followed by Et_3N (2 equiv.). The resulting mixture was stirred at 100 °C (oil bath) for 2 h. After cooling to room temperature: *for **3ab**, **3af**, **3ai:*** electrophile (3 equiv.) was added and the reaction mixture was stirred at 100 °C (oil bath) for 8 h. Reaction mixture was then cooled to room temperature and filtered through a pad of silica gel using EtOAc. Filtrate was evaporated under reduced pressure and the residue purified by column chromatography (hexanes/EtOAc); *for **3ae**, **3ag**, **3ah:*** electrophile (3 equiv.) was added and the reaction mixture was stirred at 80 °C (oil bath) for 8 h. Reaction mixture was then cooled to room temperature and filtered through a pad of silica gel using EtOAc. Filtrate was evaporated under reduced pressure and the residue purified by column chromatography (hexanes/EtOAc); *for **3ak***[14b]: reaction mixture was concentrated in *vacuo*. To the residue H_2O (2 mL) and cyclohexene oxide (5 equiv.) were added. The resulting suspension was stirred at 90 °C (oil bath) for 12 h. The reaction mixture was then cooled to room temperature, poured into $NH_4Cl_{(aq)}$ (25 mL) and extracted with DCM (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc); *for **3al***[14b]: reaction mixture was concentrated in *vacuo*. To the residue DMF (2 mL) and $(4\text{-F-}C_6H_4)_2IOTf$ (3 equiv.) were added. The resulting suspension was stirred at 90 °C (oil bath) for 12 h. The reaction mixture was then cooled to room temperature, poured into H_2O (25 mL) and extracted with Et_2O (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and

evaporated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc); *for* ***3am***[14b]: reaction mixture was concentrated in *vacuo*. To the residue DMSO (2 mL) and 6-chloro-9-methyl-9*H*-purine (3 equiv.) were added. The resulting mixture was stirred at 100 °C (oil bath) for 12 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc (40 mL) and washed with brine (4 × 15 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc) followed by reverse-phase column chromatography (MeOH/H_2O); *for* ***3an***[13e]: reaction mixture was concentrated in *vacuo*. To the residue H_2O (2 mL), morpholine (5 equiv.) were added. $NaOCl_{(aq)}$ (14% solution, 3 equiv.) was added at 0 °C and the reaction mixture was allowed to warm and stir at room temperature for 12 h. $Na_2S_2O_{3(aq)}$ (0.5M, 15 mL) was then added and the resultant mixture was stirred for additional 30 min. The aqueous solution was extracted with DCM (3 × 20 mL) and the combined organic layers were washed with $HCl_{(aq)}$ (1M, 1 × 40 mL). The organic fraction was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (hexanes/EtOAc).

Gram-Scale Synthesis of the Sulfone 3ab (Scheme 7):

4-Biphenylboronic acid (**1a**, 5 g, 25.3 mmol, 1 equiv.), DABSO (1 equiv.) and $RuCl_2(PPh_3)_3$ (2 mol%) were placed into a glass pressure tube (150 mL) equipped with a magnetic stirring bar. Then MeOH (75 mL) was added followed by Et_3N (2 equiv.) and ethyl 2-bromoacetate (3 equiv.). The resulting mixture was stirred at 100 °C (oil bath) for 15 h. After cooling to room temperature, reaction mixture was filtered through a glass filter and filtrate evaporated under reduced pressure. The solid residue was mixed with H_2O (150 mL) and EtOAc (80 mL). Organic layer was separated. The aqueous layer was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The solid residue was dissolved in DCM, filtered through a pad of silica gel (50 g) and continued by washing with DCM. Then the filtrate was evaporated under reduced pressure to obtain crude product (NMR yield **3ab** 74%, 6.65 g with purity 82%). After recrystallization from *n*-octane/EtOAc (1:1) pure sulfone **3ab** was isolated in 65% yield (4.74 g; mp 112–114 °C).

*Ethyl 2-([1,1'-biphenyl]-4-ylsulfonyl)acetate (**3aa**).*[31] Prepared according to the general procedure A from 4-biphenylboronic acid and ethyl 2-bromoacetate; yield 67% (78.9 mg). White solid. R_f = 0.39 (EtOAc/hexanes 3:7). Note: formation of transesterification product **3ab** in 2% yield was observed. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04–7.99 (m, 2H), 7.82–7.76 (m, 2H), 7.65–7.59 (m, 2H), 7.53–7.47 (m, 2H), 7.47–7.42 (m, 1H), 4.17 (q, J = 7.1 Hz, 2H), 4.15 (s, 2H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 162.6, 147.4, 139.1, 137.4, 129.3 (2C), 128.9, 127.9, 127.6, 62.6, 61.3, 14.0.

*Methyl 2-([1,1'-biphenyl]-4-ylsulfonyl)acetate (**3ab**).* Prepared according to the general procedure A from 4-biphenylboronic acid and methyl 2-haloacetate; yield 82% (92.0 mg) from methyl 2-bromoacetate; yield 49% (54.6 mg) from methyl 2-chloroacetate (in the presence of 10 mol% $RuCl_2(PPh_3)_3$). Prepared also according to the general procedure B from methyl 2-bromoacetate; yield 69% (76.9 mg). White solid. R_f = 0.30 (EtOAc/hexanes 3:7). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04–7.98 (m, 2H), 7.81–7.76 (m, 2H), 7.65–7.59 (m, 2H), 7.52–7.47 (m, 2H), 7.47–7.41 (m, 1H), 4.17 (s, 2H), 3.74 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.1, 147.4, 139.1, 137.3, 129.2 (2C), 128.9, 128.0, 127.6, 61.0, 53.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{15}O_4S$ 291.0686; Found 291.0710. IR (neat, cm^{-1}): 2933, 1731 (C=O), 1592, 1434, 1392, 1325 (SO_2), 1280, 1258, 1160 (SO_2), 1122, 1090.

*Methyl 2-(phenylsulfonyl)acetate (**3bb**).*[32] Prepared according to the general procedure A from phenylboronic acid and methyl 2-bromoacetate; yield 80% (66.2 mg). Colorless oil. R_f = 0.32 (EtOAc/hexanes 3:7). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99–7.91 (m, 2H), 7.72–7.67 (m, 1H), 7.62–7.56 (m, 2H), 4.13 (s, 2H), 3.70 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.0, 138.8, 134.5, 129.4, 128.6, 61.0, 53.2.

*Methyl 2-((4-(tert-butyl)phenyl)sulfonyl)acetate (**3cb**).* Prepared according to the general procedure A from (4-(*tert*-butyl)phenyl)boronic acid and methyl 2-bromoacetate; reaction time 16 h; yield 79% (82.5 mg). Yellowish oil. R_f = 0.42 (EtOAc/hexanes 3:7). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90–7.82 (m, 2H), 7.62–7.54 (m, 2H), 4.11 (s, 2H), 3.72 (s, 3H), 1.35 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.1, 158.5, 135.8, 128.5, 126.4, 61.0, 53.2, 35.5, 31.5 HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{19}O_4S$ 271.0999; Found 271.0989. IR (neat, cm^{-1}): 2958, 1742 (C=O), 1593, 1436, 1397, 1324 (SO_2), 1278, 1152 (SO_2), 1106, 1082.

*Methyl 2-(meta-tolylsulfonyl)acetate (**3db**).* Prepared according to the general procedure A from *meta*-tolylboronic acid and methyl 2-bromoacetate; reaction time 16 h; yield 67% (58.6 mg). Colorless oil. R_f = 0.33 (EtOAc/hexanse 3:7). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78–7.71 (m, 2H), 7.51–7.43 (m, 2H), 4.11 (s, 2H), 3.71 (s, 3H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.0, 139.8, 138.7, 135.3, 129.2, 128.8, 125.7, 61.0, 53.2, 21.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{13}O_4S$ 229.0529; Found 229.0511. IR (neat, cm^{-1}): 3006, 2953, 1740 (C=O), 1436, 1324 (SO_2), 1303, 1279, 1219, 1142 (SO_2), 1082.

*Methyl 2-((4-bromophenyl)sulfonyl)acetate (**3eb**).*[31] Prepared according to the general procedure A from (4-bromophenyl)boronic acid and methyl 2-bromoacetate; yield 81% (91.9 mg). White solid. R_f = 0.48 (EtOAc/hexanes 2:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84–7.78 (m, 2H), 7.75–7.70 (m, 2H), 4.12 (s, 2H), 3.72 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 162.8, 137.7, 132.7, 130.3, 130.0, 60.8, 53.3.

*Methyl 2-((4-chlorophenyl)sulfonyl)acetate (**3fb**).* Prepared according to the general procedure A from (4-chlorophenyl)boronic acid and methyl 2-bromoacetate; in the presence of 10 mol% $RuCl_2(PPh_3)_3$); yield 79% (75.7 mg). White solid. R_f = 0.39 (EtOAc/hexanes 3:7). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92–7.85 (m, 2H), 7.59–7.52 (m, 2H), 4.13 (s, 2H), 3.71 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 162.9, 141.4, 137.2, 130.2, 129.7, 60.8, 53.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_{10}ClO_4S$ 248.9983; Found 248.9974. IR (neat, cm^{-1}): 2985, 2933, 1733 (C=O), 1576, 1475, 1442, 1397, 1316 (SO_2), 1217, 1158 (SO_2), 1116, 1080.

*Methyl 2-((3-chlorophenyl)sulfonyl)acetate (**3gb**).* Prepared according to the general procedure A from (3-chlorophenyl)boronic acid and methyl 2-bromoacetate; yield 86% (85.6 mg). Yellowish oil. R_f = 0.36 (EtOAc/hexane 3:7). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (dd, J = 2.0, 1.7 Hz, 1H),

7.84 (ddd, J = 7.9, 1.7, 1.0 Hz, 1H), 7.66 (ddd, J = 7.9, 2.0, 1.0 Hz, 1H), 7.54 (t, J = 7.9 Hz, 1H), 4.14 (s, 2H), 3.73 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 162.7, 140.4, 135.7, 134.7, 130.7, 128.8, 126.9, 60.8, 53.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_{10}ClO_4S$ 248.9983; Found 248.9996. IR (neat, cm^{-1}): 3005, 2952, 1740 (C=O), 1579, 1436, 1327 (SO_2), 1295, 1279, 1151 (SO_2), 1103, 1076.

Methyl 2-((4-fluorophenyl)sulfonyl)acetate ***(3hb)***. Prepared according to the general procedure A from (4-fluorophenyl)boronic acid and methyl 2-bromoacetate; yield 88% (78.4 mg). Yellowish oil. R_f = 0.25 (EtOAc/hexanes 3:7). ^1H NMR (500 MHz, $CDCl_3$): δ 8.04–7.92 (m, 2H), 7.32–7.20 (m, 2H), 4.13 (s, 2H), 3.72 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 166.3 (d, J = 259 Hz), 162.9, 134.8 (d, J = 3 Hz), 131.7 (d, J = 10 Hz), 116.7 (d, J = 23 Hz), 60.9, 53.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_{10}FO_4S$ 233.0278; Found 233.0285. IR (neat, cm^{-1}): 2958, 1737 (C=O), 1590, 1494, 1437, 1324 (SO_2), 1292, 1271, 1229, 1146 (SO_2), 1084.

Methyl 2-((2-fluorophenyl)sulfonyl)acetate ***(3ib)***. Prepared according to the general procedure A from (2-fluorophenyl)boronic acid and methyl 2-bromoacetate; reaction time 16 h; yield 58% (51.5 mg). Yellowish oil. R_f = 0.41 (EtOAc/hexanes 2:3). ^1H NMR (500 MHz, $CDCl_3$): δ 7.95 (dt, J = 8.1, 1.7 Hz, 1H), 7.74–7.65 (m, 1H), 7.36 (dt, J = 7.8, 1.2 Hz, 1H), 7.27 (ddd, J = 10.1, 8.2, 1.2 Hz, 1H), 4.31 (s, 2H), 3.69 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 162.7, 159.7 (d, J = 256 Hz), 136.9 (d, J = 9 Hz), 131.0, 126.7 (d, J = 14 Hz), 124.9 (d, J = 4 Hz), 117.3 (d, J = 21 Hz), 60.0 (d, J = 3 Hz), 53.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_{10}FO_4S$ 233.0278; Found 233.0260. IR (neat, cm^{-1}): 2955, 1741 (C=O), 1599, 1474, 1437, 1330 (SO_2), 1265, 1149 (SO_2), 1119, 1070.

Methyl 2-((4-iodophenyl)sulfonyl)acetate ***(3jb)***. Prepared according to the general procedure A from (4-iodophenyl)boronic acid and methyl 2-bromoacetate; yield 79% (103 mg). White amorphous solid. R_f = 0.52 (EtOAc/hexanes 2:3). ^1H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 4.11 (s, 2H), 3.72 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 162.8, 138.7, 138.4, 130.0, 102.8, 60.8, 53.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_9H_{10}IO_4S$ 340.9339; Found 340.9353. IR (neat, cm^{-1}): 2941, 1735 (C=O), 1564, 1430, 1380, 1318 (SO_2), 1271, 1146 (SO_2), 1126, 1079.

Methyl 2-((4-methoxyphenyl)sulfonyl)acetate ***(3kb)***. Prepared according to the general procedure A from (4-methoxyphenyl)boronic acid and methyl 2-bromoacetate; yield 79% (74.0 mg). Yellowish oil. R_f = 0.35 (EtOAc/hexanes 2:3). ^1H NMR (500 MHz, $CDCl_3$): δ 7.89–7.82 (m, 2H), 7.05–6.99 (m, 2H), 4.09 (s, 2H), 3.88 (s, 3H), 3.70 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 164.4, 163.2, 130.9, 130.2, 114.5, 61.2, 55.9, 53.2. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{13}O_5S$ 245.0478; Found 245.0475. IR (neat, cm^{-1}): 2950, 1739 (C=O), 1593, 1497, 1437, 1324 (SO_2), 1299, 1258, 1141 (SO_2), 1084.

Methyl 2-((4-(methylthio)phenyl)sulfonyl)acetate ***(3lb)***. Prepared according to the general procedure A from (4-(methylthio)phenyl)boronic acid and methyl 2-bromoacetate; yield 82% (82.1 mg). Yellowish oil. R_f = 0.41 (EtOAc/hexanes 2:3). ^1H NMR (500 MHz, $CDCl_3$): δ 7.87–7.74 (m, 2H), 7.39–7.29 (m, 2H), 4.10 (s, 2H), 3.71 (s, 3H), 2.52 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.1, 148.4, 134.2, 128.9, 125.3, 61.0, 53.2, 14.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{13}O_4S_2$ 261.0250; Found 261.0225. IR (neat, cm^{-1}): 2925, 1738 (C=O), 1577, 1434, 1396, 1318 (SO_2), 1277, 1149 (SO_2), 1094, 1076.

Methyl 2-((4-acetamidophenyl)sulfonyl)acetate ***(3mb)***. Prepared according to the general procedure A from (4-acetamidophenyl)boronic acid and methyl 2-bromoacetate; yield 72% (75.6 mg). Recrystallized from $CHCl_3$. Yellowish solid. R_f = 0.46 (EtOAc). ^1H NMR (500 MHz, DMSO-d_6): δ 10.43 (br s, 1H), 7.94–7.69 (m, 4H), 4.55 (s, 2H), 3.59 (s, 3H), 2.10 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 169.2, 163.3, 144.3, 132.2, 129.4, 118.5, 59.9, 52.6, 24.2. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{14}NO_5S$ 272.0587; Found 272.0574. IR (neat, cm^{-1}): 3373 (NH), 2933, 1738 ((OMe)C=O), 1693 ((NH)C=O), 1587, 1524, 1435, 1400, 1371, 1311 (SO_2), 1286, 1248, 1146 (SO_2), 1084.

Methyl 2-((3-(dimethylamino)phenyl)sulfonyl)acetate ***(3nb)***. Prepared according to the general procedure A from 3-(dimethylamino)phenylboronic acid and methyl 2-bromoacetate; yield 20% (19.8 mg). Ruby red oil. R_f = 0.39 (EtOAc/hexanes 2:3). ^1H NMR (500 MHz, $CDCl_3$): δ 7.38 (dd, J = 8.5, 7.6 Hz, 1H), 7.20 (ddd, J = 7.6, 1.8, 0.8 Hz, 1H), 7.16 (dd, J = 2.7, 1.8 Hz, 1H), 6.93 (ddd, 8.5, 2.7, 0.8 Hz, 1H), 4.10 (s, 2H), 3.72 (s, 3H), 3.01 (s, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.1, 150.7, 139.5, 130.0, 117.4, 115.2, 110.8, 61.1, 53.2, 40.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{16}NO_4S$ 258.0795; Found 258.0800. IR (neat, cm^{-1}): 2950, 1739 (C=O), 1597, 1499, 1433, 1312 (SO_2), 1278, 1144 (SO_2), 1092.

Methyl 2-((3-((2-methoxy-2-oxoethyl)(methyl)amino)phenyl) sulfonyl)acetate ***(4)***. Isolated as a side-product of target compound **3mb** that was prepared according to the general procedure A from 3-(dimethylamino)phenylboronic acid and methyl 2-bromoacetate; yield 24% (29.4 mg). Ruby red oil. R_f = 0.21 (EtOAc/hexanes 2:3). ^1H NMR (500 MHz, $CDCl_3$): δ 7.39 (dt, J = 8.4, 7.8 Hz, 1H), 7.26 (ddd, J = 7.8, 1.8, 0.9 Hz, 1H), 7.16 (dd, J = 2.8, 1.8 Hz, 1H), 6.90 (ddd, J = 8.4, 2.8, 0.9 Hz, 1H), 4.12 (s, 2H), 4.09 (s, 2H), 3.73 (s, 3H), 3.71 (s, 3H), 3.10 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 170.6, 163.0, 149.4, 139.7, 130.2, 117.4, 116.5, 111.3, 61.0, 54.0, 53.2, 52.3, 39.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{18}NO_6S$ 316.0849; Found 316.0824. IR (neat, cm^{-1}): 2953, 1737 (C=O), 1597, 1496, 1434, 1368, 1311 (SO_2), 1278, 1203, 1146 (SO_2), 1094.

Methyl 2-((4-nitrophenyl)sulfonyl)acetate ***(3ob)***.[33] Prepared according to the general procedure A from (4-nitrophenyl)boronic acid and methyl 2-bromoacetate; yield 72% (72.1 mg). Yellowish solid. R_f = 0.44 (EtOAc/hexanes 2:3). ^1H NMR (500 MHz, $CDCl_3$): δ 8.47–8.39 (m, 2H), 8.21–8.13 (m, 2H), 4.20 (s, 2H), 3.73 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 162.6, 151.3, 144.1, 130.4, 124.5, 60.5, 53.5.

Methyl 2-((4-(trifluoromethyl)phenyl)sulfonyl)acetate ***(3pb)***. Prepared according to the general procedure A from (4-(trifluoromethyl)phenyl)boronic acid and methyl 2-bromoacetate; yield 88% (95.5 mg). White solid. R_f = 0.61 (EtOAc/hexanes 2:3). ^1H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 4.17 (s, 2H), 3.73 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 162.7, 142.2, 136.1 (q, J = 33 Hz), 129.5, 126.5 (q, J = 4 Hz), 123.2 (q, J = 272 Hz), 60.6, 53.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{10}F_3O_4S$ 283.0246; Found 283.0266. IR (neat, cm^{-1}): 2980, 2935, 1742

(C=O), 1435, 1402, 1316 (SO_2), 1197, 1152 (SO_2), 1122, 1087, 1060.

Methyl 4-((2-methoxy-2-oxoethyl)sulfonyl)benzoate ***(3qb)***. Prepared according to the general procedure A from (4-(methoxycarbonyl)phenyl)boronic acid and methyl 2-bromoacetate; yield 75% (79.0 mg). White amorphous solid. R_f = 0.29 (EtOAc/hexanes 2:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33–8.19 (m, 2H), 8.10–7.97 (m, 2H), 4.15 (s, 2H), 3.96 (s, 3H), 3.70 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 165.5, 162.7, 142.4, 135.5, 130.5, 128.8, 60.7, 53.3, 52.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{13}O_6S$ 273.0427; Found 273.0400. IR (neat, cm^{-1}): 2999, 2945, 1735 (C=O), 1717 (C=O), 1431, 1397, 1325 (SO_2), 1272, 1228, 1159 (SO_2), 1113, 1083.

Methyl 2-((4-carbamoylphenyl)sulfonyl)acetate ***(3rb)***. Prepared according to the general procedure A from (4-cyanophenyl)boronic acid and 2-bromoacetate; yield 51% (50.7 mg). Purified by column chromatography with MeOH/DCM as an eluent. Yellowish solid. R_f = 0.57 (MeOH/DCM 1:9). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.23 (br s, 1H), 8.12–8.06 (m, 2H), 8.03–7.97 (m, 2H), 7.68 (br s, 1H), 4.73 (s, 2H), 3.59 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6): δ 166.6, 163.2, 141.1, 139.3, 128.3, 128.2, 59.3, 52.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{12}NO_5S$ 258.0431; Found 258.0434. IR (neat, cm^{-1}): 3449 (NH_2), 3159, 2924, 1735 ((MeO)C=O), 1674 ((NH_2)C=O), 1570, 1444, 1387, 1323 (SO_2), 1287, 1261, 1174, 1126 (SO_2), 1085.

Methyl 2-(thiophen-3-ylsulfonyl)acetate ***(3sb)***. Prepared according to the general procedure A from thiophen-3-ylboronic acid and methyl 2-bromoacetate; yield 70% (58.9 mg). Yellowish oil. R_f = 0.36 (EtOAc/hexanes 2:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (dd, J = 3.1, 1.3 Hz, 1H), 7.47 (dd, J = 5.2, 3.1 Hz, 1H), 7.43 (dd, J = 5.2, 1.3 Hz, 1H), 4.14 (s, 2H), 3.73 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.0, 139.1, 134.1, 128.3, 126.5, 61.1, 53.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_7H_9O_4S_2$ 220.9937; Found 220.9933. IR (neat, cm^{-1}): 3108, 2952, 1737 (C=O), 1494, 1436, 1403, 1316 (SO_2), 1278, 1207, 1143 (SO_2), 1094, 1074.

Methyl 2-(furan-3-ylsulfonyl)acetate ***(3tb)***. Prepared according to the general procedure A from furan-3-ylboronic acid and methyl 2-bromoacetate; reaction solvent MeOH/Tol 1:1; yield 56% (43.6 mg). Yellow oil. R_f = 0.33 (EtOAc/hexanes 2:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (dd, J = 1.6, 0.8 Hz, 1H), 7.54 (dd, J = 2.0, 1.8 Hz, 1H), 6.75 (dd, J = 2.0, 0.8 Hz, 1H), 4.15 (s, 2H), 3.77 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.0, 148.2, 145.0, 126.9, 109.3, 61.2, 53.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_7H_9O_5S$ 205.0165; Found 205.0147. IR (neat, cm^{-1}): 3143, 2955, 1738 (C=O), 1547, 1498, 1437, 1322 (SO_2), 1280, 1225, 1150 (SO_2), 1118, 1082.

Methyl (E)-2-(styrylsulfonyl)acetate ***(3ub)***.[34] Prepared according to the general procedure A from (*E*)-styrylboronic acid and methyl 2-bromoacetate; reaction solvent MeOH/Tol 1:1; yield 47% (43.7 mg). Light brown amorphous solid. R_f = 0.46 (EtOAc/hexanes 2:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, J = 15.5 Hz, 1H), 7.57–7.52 (m, 2H), 7.50–7.40 (m, 3H), 7.07 (d, J = 15.5 Hz, 1H), 4.10 (s, 2H), 3.81 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 163.6, 145.9, 132.1, 131.8, 129.3, 129.0, 124.7, 60.0, 53.4.

tert-Butyl 2-([1,1'-biphenyl]-4-ylsulfonyl)acetate ***(3ac)***.[12b] Prepared according to the general procedure A from 4-biphenylboronic acid and *tert*-butyl 2-bromoacetate; yield 60% (76.1 mg). White amorphous solid. R_f = 0.58 (EtOAc/hexanes 3:7). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04–7.98 (m, 2H), 7.81–7.76 (m, 2H), 7.64–7.59 (m, 2H), 7.52–7.46 (m, 2H), 7.46–7.41 (m, 1H), 4.08 (s, 2H), 1.39 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 161.5, 147.2, 139.2, 137.6, 129.2 (2C), 128.9, 127.8, 127.5, 83.8, 62.3, 27.8.

2-([1,1'-Biphenyl]-4-ylsulfonyl)-N,N-dipropylacetamide ***(3ad)***. Prepared according to the general procedure A from 4-biphenylboronic acid and 2-halo-*N*,*N*-dipropylacetamide; yield 76% (105 mg) from 2-bromo-*N*,*N*-dipropylacetamide; yield 66% (91.8 mg) from 2-chloro-*N*,*N*-dipropylacetamide. White solid. R_f = 0.38 (EtOAc/hexanes 2:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02–7.94 (m, 2H), 7.80–7.72 (m, 2H), 7.65–7.58 (m, 2H), 7.50–7.45 (m, 2H), 7.45–7.38 (m, 1H), 4.25 (s, 2H), 3.43–3.36 (m, 2H), 3.30–3.23 (m, 2H), 1.63 (sextet, J = 7.5 Hz, 2H), 1.56 (sextet, J = 7.5 Hz, 2H), 0.95 (t, J = 7.5 Hz, 3H), 0.90 (t, J = 7.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 161.2, 147.1, 139.4, 137.6, 129.3, 129.2, 128.7, 127.8, 127.6, 60.0, 50.8, 48.3, 22.4, 20.8, 11.4, 11.3. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{26}NO_3S$ 360.1628; Found 360.1634. IR (neat, cm^{-1}): 2964, 1634 (C=O), 1593, 1454, 1316 (SO_2), 1238, 1149 (SO_2), 1087.

4-(Butylsulfonyl)-1,1'-biphenyl ***(3ae)***. Prepared according to the general procedure A from 4-biphenylboronic acid and butyl halide; yield 67% (70.2 mg) from butyl iodide; yield 47% (49.4 mg) from butyl bromide. Prepared also according to the general procedure B from butyl iodide; yield 56% (59.0 mg). White amorphous solid. R_f = 0.41 (EtOAc/hexanes 1:4). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00–7.94 (m, 2H), 7.80–7.74 (m, 2H), 7.65–7.59 (m, 2H), 7.52–7.46 (m, 2H), 7.46–7.40 (m, 1H), 3.18–3.08 (m, 2H), 1.79–1.68 (m, 2H), 1.41 (sextet, J = 7.3 Hz, 2H), 0.91 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 146.7, 139.3, 137.9, 129.2, 128.8, 128.7, 128.0, 127.5, 56.3, 24.8, 21.7, 13.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{19}O_2S$ 275.1100; Found 275.1085. IR (neat, cm^{-1}): 2960, 2925, 1593, 1464, 1287 (SO_2), 1234, 1140 (SO_2), 1087.

2-([1,1'-Biphenyl]-4-ylsulfonyl)-1-phenylethan-1-one ***(3af)***.[35] Prepared according to the general procedure A from 4-biphenylboronic acid and 2-bromo-1-phenylethan-1-one; yield 39% (50.5 mg). Prepared also according to the general procedure B from 2-bromo-1-phenylethan-1-one; yield 76% (98.9 mg). Pale yellow solid. R_f = 0.33 (EtOAc/hexanes 3:7). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00–7.92 (m, 4H), 7.77–7.71 (m, 2H), 7.65–7.58 (m, 3H), 7.52–7.46 (m, 4H), 7.46–7.41 (m, 1H), 4.78 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 188.2, 147.3, 139.2, 137.4, 135.9, 134.5, 129.4, 129.3, 129.2, 129.0, 128.9, 127.9, 127.6, 63.7.

4-(Allylsulfonyl)-1,1'-biphenyl ***(3ag)***.[36] Prepared according to the general procedure A from 4-biphenylboronic acid and allyl halide; yield 34% (33.9 mg) from allyl bromide (reaction time 17 h); yield 24% (24.0 mg) from allyl chloride. Prepared also according to the general procedure B from allyl bromide; yield 60% (59.2 mg). White solid. R_f = 0.33 (EtOAc/hexanes 1:4). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00–7.89 (m, 2H), 7.82–7.72 (m, 2H), 7.68–7.58 (m, 2H), 7.52–7.46 (m, 2H), 7.46–7.41 (m, 1H), 5.92–5.75 (m, 1H), 5.41–5.33 (m, 1H), 5.25–5.16 (m, 1H), 3.85 (d, J = 7.4 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 146.8, 139.2, 137.0, 129.2 (2C), 128.8, 127.8, 127.5, 124.9, 124.8, 61.1.

4-(Benzylsulfonyl)-1,1'-biphenyl ***(3ah)***.[14a] Prepared according to the general procedure A from 4-biphenylboronic acid and benzyl

halide; yield 29% (34.3 mg) from benzyl bromide (reaction time 17 h); yield 38% (45.1 mg) from benzyl chloride. Prepared also according to the general procedure B from benzyl bromide; yield 62% (73.7 mg). White solid. R_f = 0.41 (EtOAc/hexanes 1:4). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71–7.64 (m, 4H), 7.63–7.58 (m, 2H), 7.51–7.46 (m, 2H), 7.46–7.41 (m, 1H), 7.36–7.31 (m, 1H), 7.30–7.25 (m, 2H), 7.18–7.09 (m, 2H), 4.35 (s, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 146.7, 139.2, 136.6, 131.0, 129.3, 129.2, 128.9, 128.8 (2C), 128.3, 127.6, 127.5, 63.1.

4-(Phenethylsulfonyl)-1,1'-biphenyl ***(3ai)***.[37] Prepared according to the general procedure A from 4-biphenylboronic acid and phenethyl 4-methylbenzenesulfonate; yield 9% (10.6 mg). Prepared also according to the general procedure B from phenethyl 4-methylbenzenesulfonate; yield 18% (22.3 mg). Yellowish solid. R_f = 0.56 (EtOAc/hexanes 1:4). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03–7.97 (m, 2H), 7.80–7.75 (m, 2H), 7.65–7.60 (m, 2H), 7.53–7.48 (m, 2H), 7.48–7.42 (m, 1H), 7.30–7.24 (m, 2H), 7.24–7.18 (m, 1H), 7.17–7.11 (m, 2H), 3.45–3.38 (m, 2H), 3.13–3.06 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 146.9, 139.3, 137.7, 137.6, 129.3, 129.0, 128.9, 128.8, 128.5, 128.1, 127.6, 127.1, 57.8, 28.9.

Methyl 3-([1,1'-biphenyl]-4-ylsulfonyl)propanoate ***(3aj)***. Prepared according to the general procedure A from 4-biphenylboronic acid and methyl acrylate; yield 77% (89.9 mg). White solid. R_f = 0.52 (EtOAc/hexanes 2:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00–7.94 (m, 2H), 7.81–7.75 (m, 2H), 7.64–7.59 (m, 2H), 7.53–7.47 (m, 2H), 7.47–7.41 (m, 1H), 3.65 (s, 3H), 3.51–3.44 (m, 2H), 2.85–2.76 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 170.6, 147.2, 139.1, 137.1, 129.3, 128.9 (2C), 128.2, 127.5, 52.5, 51.7, 27.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{17}O_4S$ 305.0842; Found 305.0842. IR (neat, cm^{-1}): 2937, 1721 (C=O), 1593, 1479, 1437, 1371, 1306 (SO_2), 1262, 1197, 1148, 1135 (SO_2), 1093.

trans-2-([1,1'-Biphenyl]-4-ylsulfonyl)cyclohexan-1-ol ***(3ak)***. Prepared according to the general procedure A from 4-biphenylboronic acid and cyclohexene oxide (5 equiv.); yield 42% (50.8 mg). Prepared also according to the general procedure B; yield 60% (73.3 mg). White solid. R_f = 0.36 (EtOAc/hexanes 2:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01–7.92 (m, 2H), 7.84–7.76 (m, 2H), 7.67–7.60 (m, 2H), 7.54–7.48 (m, 2H), 7.48–7.41 (m, 1H), 4.33 (s, 1H), 3.95 (dt, J = 10.2, 4.9 Hz, 1H), 3.02 (ddd, J = 12.6, 10.0, 3.9 Hz, 1H), 2.20–2.11 (m, 1H), 2.01–1.93 (m, 1H), 1.79–1.68 (m, 2H), 1.43–1.13 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 147.2, 139.1, 135.4, 129.7, 129.3, 129.0, 128.0, 127.5, 69.2, 68.4, 34.3, 25.9, 24.7, 23.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{21}O_3S$ 317.1206; Found 317.1197. IR (neat, cm^{-1}): 3460 (OH), 2929, 2860, 1592, 1449, 1291, 1278 (SO_2), 1137 (SO_2), 1090.

4-((4-Fluorophenyl)sulfonyl)-1,1'-biphenyl ***(3al)***. Prepared according to the general procedure A from 4-biphenylboronic acid and (4-F-C_6H_4)$_2$IOTf; reaction solvent MeOH/Tol 1:1; yield 27% (30.6 mg). Prepared also according to the general procedure B; yield 43% (48.7 mg). White solid. R_f = 0.49 (EtOAc/hexanes 1:4). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04–7.96 (m, 4H), 7.74–7.68 (m, 2H), 7.60–7.54 (m, 2H), 7.50–7.44 (m, 2H), 7.44–7.38 (m, 1H), 7.23–7.16 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 165.6 (d, J = 256 Hz), 146.5, 140.1, 139.2, 138.0 (d, J = 3 Hz), 130.6 (d, J = 10 Hz), 129.2, 128.8, 128.3, 128.2, 127.5, 116.8 (d, J = 22 Hz). HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{14}FO_2S$ 313.0693; Found 313.0696. IR (neat, cm^{-1}): 2915, 2848, 1586, 1492, 1322 (SO_2), 1292, 1231, 1165, 1149 (SO_2), 1107, 1072.

6-([1,1'-Biphenyl]-4-ylsulfonyl)-9-methyl-9H-purine ***(3am)***. Prepared according to the general procedure B; yield 22% (29.3 mg). White solid. R_f = 0.63 (EtOAc/hexanes 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.06 (s, 1H), 8.38–8.26 (m, 3H), 7.78–7.70 (m, 2H), 7.61–7.52 (m, 2H), 7.48–7.42 (m, 2H), 7.42–7.37 (m, 1H), 3.96 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 155.2, 154.7, 151.9, 148.6, 147.4, 139.2, 137.2, 130.2, 129.8, 129.2, 128.8, 127.9, 127.5, 30.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{15}N_4O_2S$ 351.0910; Found 351.0911. IR (neat, cm^{-1}): 2919, 2850, 1590, 1558, 1498, 1387, 1328 (SO_2), 1212, 1158, 1137 (SO_2), 1081.

4-([1,1'-Biphenyl]-4-ylsulfonyl)morpholine ***(3an)***. Prepared according to the general procedure B; yield 57% (66.3 mg). White solid. R_f = 0.56 (EtOAc/hexanes 2:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88–7.80 (m, 2H), 7.79–7.70 (m, 2H), 7.66–7.57 (m, 2H), 7.55–7.47 (m, 2H), 7.46–7.40 (m, 1H), 3.85–3.71 (m, 4H), 3.13–2.99 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 146.2, 139.3, 133.8, 129.2, 128.7, 128.5, 127.9, 127.5, 66.3, 46.2. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{18}NO_3S$ 304.1002; Found 304.0993. IR (neat, cm^{-1}): 2920, 2863, 1592, 1450, 1345 (SO_2), 1330, 1261, 1161 (SO_2), 1107, 1068.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI:

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