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N-Sulfonylbenzotriazoles as Advantageous Reagents for *C*-Sulfonylation

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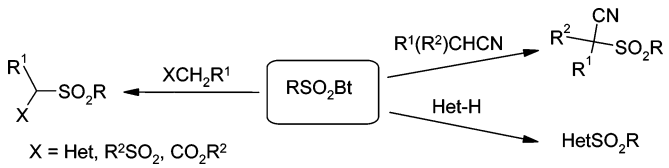

Reactions of readily available *N*-(alkyl-, aryl-, and heteroarylsulfonyl)benzotriazoles **3a**−**h** with diverse nitriles, reactive heteroaromatics, alkylheteroaromatics, sulfones, and esters produced α-cyanoalkyl sulfones **5a**−**i**, sulfonylheteroaromatics **7a**−**e**, α-(sulfonylalkyl)heterocycles **9a**−**f**, α-sulfonylalkyl sulfones **11a**−**g**, and esters of α-sulfonyl acids **14a**−**c**, respectively, in synthetically useful to excellent yields. The results represent the first examples of the successful application of sulfonylazoles for *C*-sulfonylation.

Introduction

Sulfones are important intermediates in organic synthesis[1] and additionally have a wide applicability in diverse fields including agrochemicals,[2] pharmaceuticals,[3] and polymers.[4] Sulfones are notable as "chemical chameleons"[5] due to the ability of the sulfonyl group to serve as a temporary transformer of chemical reactivity. The group RSO_2 can function as a nucleofuge producing a sulfinate anion[6] and powerfully stabilize adjacent carbanions.[7,8] Although lacking inherent asymmetry, the sulfonyl group can also function as a potential stereoinducer.[9]

N-Sulfonylbenzotriazoles **3** have been previously used in our group (i) to convert carboxylic acids into *N*-acylbenzotriazoles which are especially useful when the corresponding acid chlorides are difficult to obtain,[10] (ii) as intermediates for the benzotriazolylalkylation of aromatics,[11] and (iii) as effective reagents for the *N*-sulfonylation of amines and the *O*-sulfonylation of phenols to give the corresponding sulfonamides and sulfonates, respectively.[12] As a logical sequel, we now disclose *C*-sulfonylations by *N*-sulfonylbenzotriazoles **3** of nitriles, heterocycles, and active alkyl groups in heterocycles, sulfones, and esters leading to a wide variety of sulfones.

Results and Discussion

Preparation of *N*-Sulfonylbenzotriazoles. *N*-Sulfonylbenzotriazoles **3** were prepared following literature procedures either by the reaction of sulfonyl chloride **1** with benzotriazole in the presence of pyridine for alkyl- and arylsulfonylbenzotriazoles **3a**−**c**[10] or by the reaction of organolithium reagents **2** with sulfur dioxide at −78 °C to obtain sulfinic acid salts followed by the addition of *N*-chlorobenzotriazole for heteroarylsulfonylbenzotriazoles **3d**−**h**[12b] in good to excellent yields (Scheme 1).

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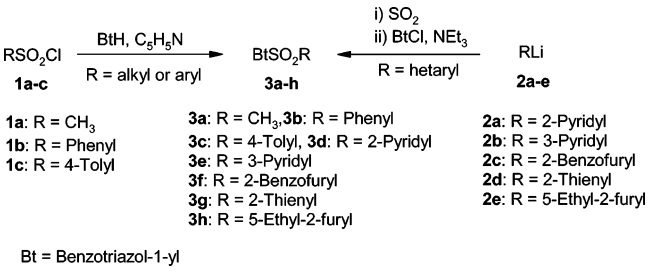
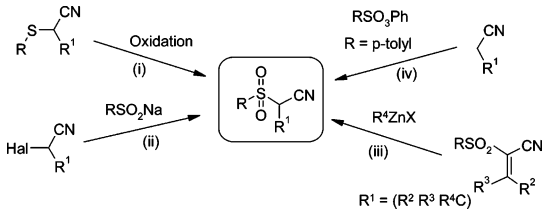
SCHEME 1



SCHEME 2

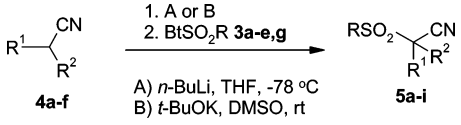


Synthesis of α-Cyanoalkyl Sulfones. α-Cyanoalkyl sulfones have extensive synthetic uses,[13] e.g., for the preparation of pyridones,[14] 4-aminopyrimidines,[15] 5,6-dihydro-4*H*-pyrans,[16] tetrahydrofurans,[17] cyclobutanes,[16] cyclopropanes,[18] and biologically active compounds such as *β*-amido sulfones[19] and L-indospicines.[20]

Published routes to α-cyano sulfones (Scheme 2) include (i) oxidation of the corresponding sulfides;[21] (ii) alkyation of benzenesulfinate salts with α-halo nitriles either under the conditions of anionic activation[22] or under solid−liquid phase-transfer catalysis without solvent;[23] (iii) Michael addition of Reformatsky reagents to geminal cyanosulfonylalkenes catalyzed by Cp_2TiCl_2;[24] and (iv) sulfonylation of nitriles with phenyl tosylate.[25] However, although these synthetic approaches have proven to be of great utility for specific classes of the title compounds, method (i) suffers from foul-smelling starting materials, (ii) and (iii) require the availability of α-halo nitriles and geminal cyanosulfonylalkenes, and (iv) is limited to the tosylation of arylacetonitriles. We herein report a general and efficient route to such α-cyano sulfones by reactions of nitriles **4** with 1-sulfonylbenzotriazoles **3** in the presence of either *n*-BuLi or *t*-BuOK (Scheme 3).

Initially, 4-bromophenyl acetonitrile (**4a**) was treated with 1.2 molar equiv of *n*-butyllithium at −78 °C in THF and reacted with 1-[(4-tolyl)sulfonyl]benzotriazole (**3c**).

SCHEME 3[a]



[a] For designation of R, R^1, and R^2 in **5**, see Table 1.

TABLE 1. Preparation of α-Cyanoalkyl Sulfones 5a−i

compd	R of $BtSO_2R$ **3**	R^1 of nitrile **4**	R^2 of nitrile **4**	method	yield (%) of **5**
5a	CH_3	4-BrC_6H_4	H	B	82
5b	CH_3	2,4-$Cl_2C_6H_3$	H	B	87
5c	4-tolyl	4-BrC_6H_4	H	A	93
5d	4-tolyl	2,4-$Cl_2C_6H_3$	H	B	97
5e	Ph	Ph	H	A	76
5f	Ph	H	H	A	50
5g	2-thienyl	2,4-$Cl_2C_6H_3$	H	A	90
5h	2-pyridyl	*n*-C_6H_{13}	H	A	54
5i	3-pyridyl	Ph	CH_3	A	73

After the addition of **3c**, the reaction mixture was stirred overnight; aqueous workup yielded the 4-bromophenyl-(toluene-4-sulfonyl)acetonitrile (**5c**) in 43% yield with recovery of about 50% of the starting nitrile **4a**. The yield of **5c** was improved to 93% by using 2 molar equiv of *n*-butyllithium. To simplify the procedure, the reaction of nitrile **4a** with **3c** was next examined in the presence of 2 molar equiv of *t*-BuOK in DMSO at room temperature and provided α-cyano sulfone **5c** in 88% yield. The use of 2 molar equiv of either *n*-butyllithium in THF at −78 °C or *t*-BuOK in DMSO at room temperature proved to be appropriate for the sulfonylation of nitriles.

After this optimization of the conditions, we investigated the reactions of 1-sulfonylbenzotriazoles **3a**−**e**,**g** with nitriles **4a**−**f**. In every case, the reaction proceeded smoothly giving the corresponding α-cyano sulfones **5a**−**i** (Scheme 3 and Table 1). Success with a wide range of 1-sulfonylbenzotriazoles and nitriles demonstrates the general applicability of this procedure. It can be used with alkylsulfonylbenzotriazoles to give α-cyanoalkyl sulfones **5a**,**b** in 82% and 87% yields, respectively. Arylsulfonylbenzotriazoles were also used to convert acetonitrile itself and arylacetonitriles into the corresponding sulfonylated products **5c**−**f** in 50-97% yields. As heterocyclic sulfonylating reagent examples, 1-(2-pyridyl-, 3-pyridyl-, or 2-thienyl)sulfonylbenzotriazoles **3d**,**e**,**g** reacted with a range of nitriles to give the desired products **5g**−**i** in 54−90% yield.

The structures of compounds **5a**−**i** were supported by NMR spectral data and elemental analyses. The ^{13}C NMR and ^1H NMR spectra of α-cyano sulfones **5a**−**i** showed characteristic signals in the regions 45.7−62.5 and 4.10−5.85 ppm which were assigned to the carbon and proton α to the cyano group.

Synthesis of Sulfonylheterocycles. Sufonylheterocycles are important in medicinal chemistry: recent examples include HIV-1 non-nucleosides,[26] nucleoside reverse transcriptases,[27] integrase inhibitors,[28] potential cardiovascular agents,[29] and anti-ulcer agents.[30] Previous preparations of sulfonylheterocycles directly from the

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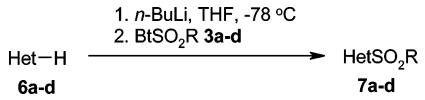
SCHEME 4[a]



[a] For designation of Het and R in **7**, see Table 2.

TABLE 2. Preparation of Sulfonylheterocycles 7a−d

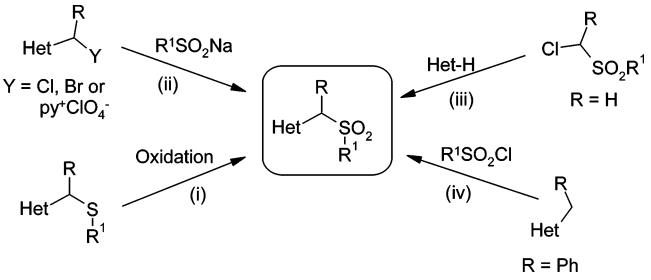
compd	Het	R	yield (%)	lit. yield (%)
7a	2-thienyl	Me	47	
7b	2-ethyl-5-furyl	Ph	80	
7c	2-benzofuryl	4-MeC_6H_4	73	30[35]
7d	1-methylpyrrole	2-pyridyl	54	

parent heterocycles include the following: (i) oxidation of sulfides;[31] (ii) metal-mediated cross-coupling of either sulfinic acid salts with heteroaryl halides[32] or sulfonyl chlorides with heteroaryl boronic acids;[33] and (iii) Friedel−Crafts-type sulfonylation of heterocycles with sulfonyl chloride and diverse catalysts.[34] However, method (i) is unattractive because of the obnoxious smell of the starting material, (ii) is limited by the availability of heteroaryl halides or heteroaryl boronic acids, and (iii) utilizes sulfonyl chlorides which are often liquids that are difficult to store and handle. We now report a new method for the synthesis of sulfonyl heteroaromatics by reactions of readily available and odorless 1-sulfonylbenzotriazoles **3** with the metalated heterocyles (Scheme 4).

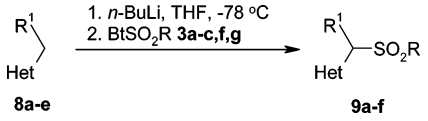
Reactions of heterocyclic lithio derivatives **6a−d** (generated by lithiation of the parent heterocycle) in dry THF at −78 °C with the appropriate 1-sulfonylbenzotriazoles **3a−d** provided the corresponding *C*-sulfonylated heterocycles **7a−d**. The TLC and NMR of the crude products show that the reactions are clean (usually benzotriazole is the only byproduct, but occasionally, small amounts of unreacted starting materials are detected). This approach improved the previously reported yield[35] of compound **7c** from 30% to 73% and afforded novel sulfonylheterocycles **7a**,**b**,**d** in 47−80% yields (Scheme 4, Table 2). The NMR spectra of the sulfonylated products **7a−d** clearly showed the disappearance of the benzotriazolyl signals; the NMR data for the known compound **7c**[35] are consistent with those in the literature.

Synthesis of α-(Sulfonylalkyl)heterocycles. *C*-(α-Sulfonylalkyl)heterocycles are useful synthons for indoles[36] and quinolines,[37] are antiinflammatory agents,[38]

SCHEME 5



SCHEME 6[a]



[a] For designation of Het, R, and R^1 in **9**, see Table 3.

possess antibacterial activity,[39] are inhibitors of polymerase,[40] and are (PPAR) γ agonists.[41]

α-(Sulfonylalkyl)heterocycles were previously synthesized (Scheme 5) by (i) oxidation of sulfides,[42] (ii) reactions arenesulfinate salts with either α-(haloalkyl)heterocycles[43] or heteroalkylpyridinium salts,[44] (iii) vicarious nucleophilic substitution,[45] (iv) direct sulfonylation of alkylheterocycles with arylsulfonyl chlorides, and (v) diverse ring syntheses, e.g., ref 47. We now report the use of *N*-sulfonylbenzotriazoles in a convenient synthesis of α-(sulfonylalkyl)heterocycles **9** (Scheme 6).

2-Picoline was treated with 2 molar equiv of LDA to give 2-$LiCH_2$Py **8a** in situ which on treatment with 1-(phenylsulfonyl)-benzotriazole (**3b**) at −78 °C in THF and aqueous workup afforded 59% of 2-(phenylsulfonylmethyl)pyridine (**9a**). Two equivalents of LDA could be replaced by 1 equiv of *n*-BuLi; use of 2 molar equiv of *n*-butyllithium under the same reaction conditions did not improve the yield. Lithio derivatives **8a−e** (generated in situ by treating the corresponding alkylated heterocycles with 1 equiv of *n*-BuLi) reacted with the appropriate 1-sulfonylbenzotriazoles **3** to afford the corresponding α-(sulfonylalkyl)heterocycles **9b−f**. Our approach provided previously unreported *C*-sulfonylated alkylheterocycles **9b−f** in 43−94% yields (Scheme 6 and Table 3). Assigned structures of **9a−f** were supported by NMR spectral data in agreement with the published data in

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TABLE 3. (α-Sulfonylalkyl)heterocycles 9a−f

compd	Het	R	R^1	yield (%)
9a	2-pyridyl	Ph	H	59
9b	2-pyridyl	Ph	Ph	94
9c	4-pyridyl	CH_3	Ph	53
9d	2-pyridyl	4-MeC_6H_4	CH_3	43
9e	2-(1-methylbenzimidazolyl)	2-thienyl	H	61
9f	2-benzothiazolyl	2-benzofuryl	H	76

the case of **9a**.[48] The ^{13}C NMR and ^1H NMR spectra of **9a−f** showed characteristic signals in the regions 56.6−73.6 and 3.90−5.66 ppm, which were assigned to the carbon and the proton α to the hetero group.

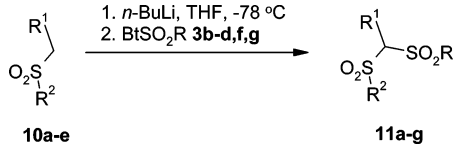
Our synthetic sequence for the synthesis of α-(sulfonylalkyl)heterocycles **9** provides a general and efficient approach. The closest literature analogy is the direct sulfonylation of alkylheterocyles with sulfonyl chloride[46] (Scheme 3, iv) but this method is limited to three examples of the tosylation of 4-alkylpyridines and utilizes 3.6 molar equiv of the sulfonyl chloride to give products of type **9**. The quoted yields of 40−79% (average 60%) are based on the amount of alkylheterocycles used, whereas recalculation based on the sulfonyl chloride used gives yields of only 11−23% (average 17%). Our method uses alkylated heterocycles and readily available *N*-sulfonylbenzotriazoles in a 1:1 ratio and affords yields that range from 43% to 94% (average 69%).

Synthesis of α-Sulfonylalkyl Sulfones. α-Sulfonylalkyl sulfones are valuable intermediates for a number of carbocycles[49] and heterocycles,[50] reactive synthons for Ramberg−Backlund olefinations[51] and metal-catalyzed cross-coupling reactions[52] and useful for the synthesis of α-aryl propanoic acid ibuprofen analogues.[53]

The only well-known routes to α-sulfonylalkyl sulfones involve the oxidation of the corresponding bis-sulfides[54] or α-sulfonylalkyl sulfides.[55] Prompted by the lack of available methods and in order to study the generality of our *C*-sulfonylation methodology, we developed a robust, high-yielding, and general method to a diverse range of target molecules.

Treatment of the lithio derivatives of sulfones **10a−e** (generated in situ by the lithiation of the sulfones with *n*-BuLi) at −78 °C with 1-sulfonylbenzotriazoles **3b−d**,**f**,**g** gave the corresponding α-sulfonylalkyl sulfones **11a−g** in moderate to excellent yields (Scheme 7 and Table 4). For optimum yields, the reactions of 1-sulfonylbenzotriazoles with sulfones required 2 molar equivalents of *n*-BuLi, since the α-sulfonylalkyl sulfones formed would

SCHEME 7[a]

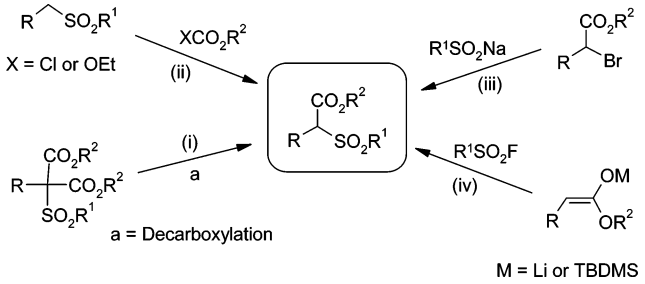


[a] For designation of R, R^1, and R^2 in **11**, see Table 4.

TABLE 4. Preparation of α-Sulfonyl Sulfones 11a−g

compd	R of $BtSO_2R$ **3**	R^1 of sulfone **10**	R^2 of sulfone **10**	yield (%) of **11**
11a	4-tolyl	C_6H_5	C_6H_5	96
11b	4-tolyl	H	C_6H_5	87
11c	4-tolyl	$(-CH_2-)_3$		78
11d	phenyl	CH_3	C_2H_5	91
11e	2-pyridinyl	CH_3	C_2H_5	87
11f	2-benzenefuryl	$(-CH_2-)_3$		67
11g	2-thienyl	CH_3	C_2H_5	71

SCHEME 8



rapidly be deprotonated by unreacted carbanion; this was suggested by our previous study of the acylation of sulfones with *N*-acylbenzotriazoles.[56] Products **11a−g** were identified on the basis of their ^1H and ^{13}C NMR spectra together with elemental analyses.

This new synthetic procedure for the synthesis of α-sulfonylalkyl sulfones is tolerant of structural diversity of both sulfonylating reagent and sulfone: aryl- and heteroarylsulfonylbenzotriazoles convert both acyclic and alicyclic sulfones into the corresponding bis-sulfones.

Synthesis of Esters of α-Sulfonyl Carboxylic Acids. Esters of α-sulfonyl carboxylic acids are useful for the synthesis of metalloproteinase inhibitors α-sulfonylhydroxamic acids[57] and synthons for paramagnetic heterocycles.[58] α-Sulfonyl esters have been prepared (Scheme 8) (i) by decarboxylation of α-sulfonyl malonic esters,[59] (ii) by alkoxycarboxylation of arylmethyl sulfones,[60] (iii) from benzenesulfinate salts and α-halo esters,[61] and (iv) by direct sulfonylation of ester lithium enolates or silyl ketene acetals.[62] We now use our *C*-sulfonylation methodology in a new and general method providing a range of these target molecules.

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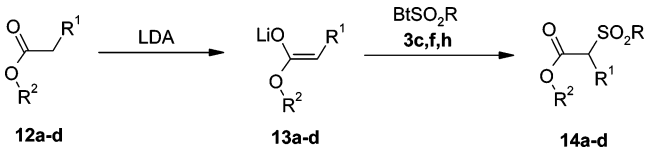
SCHEME 9[a]



[a] For designation of R, R^1, and R^2 in **14**, see Table 5.

TABLE 5. Preparation of Ester α-Sulfonyl Carboxylic Acids 14a−d

compd	R	R^1	R^2	yield (%)	lit. yield (%)
14a	4-MeC_6H_4	Ph	Et	60	36[62]
14b	4-MeC_6H_4	1-naphthyl	Me	62	
14c	2-benzofuryl	Bz	Et	71	
14d	5-ethyl-2-furyl	Et	Me	47	

Ester enolates **13a−d** (prepared by treating the corresponding ester **12** with LDA in THF at rt for **13a**,**b**,**d** or at −78 °C for **13c**) were treated with *N*-sulfonylbenzotriazole **3c**,**f**,**h** in THF at −78 °C. The reaction mixture was allowed to warm to room temperature while stirring overnight and afforded, after workup, α-sulfonyl esters **14a−d** in 60−71% isolated yields (Scheme 9 and Table 5).

C-Sulfonylation of esters with *N*-sulfonylbenzotriazoles provides a convenient synthetic methodology for the synthesis of α-sulfonyl esters **14** in comparison with reported direct sulfonylation of esters (Scheme 8, iv), which is limited to tosylation and requires the use of moisture-sensitive *p*-tolylsulfonyl fluoride[62] since the use of *p*-tolylsulfonyl chloride gave α-chloro esters with no sulfonylation.

In summary, novel and advantageous methods for the syntheses of several classes of *C*-sulfonylated products have been developed using 1-sulfonylbenzotriazoles. These approaches broaden the range of available sulfone derivatives, which are compounds of major synthetic, biological, and medicinal importance. Advantages of our procedures include the following: (i) the use of sulfonyl chloride and foul-smelling sulfides is avoided; (ii) 1-sulfonylbenzotriazoles are neutral and odorless crystalline compounds, easily accessible, and stable to storage over years; and (iii) the *C*-sulfonylated products are generally obtained in synthetically useful yields. Our results represent the first examples of the successful use of sulfonamides as *C*-sulfonylating reagents and suggest that few limitations are to be expected for the sulfonylation of nitriles, heterocycles, alkylated heterocycles, sulfones, and esters using benzotriazole methodology. The present procedures require only simple manipulations and low-priced reagents; thus, they should be appropriate for providing highly demanded sulfone derivatives. The present work provides additional evidence for the good leaving ability of a benzotriazole group.

Experimental Section

Melting points were uncorrected. NMR spectra were recorded in $CDCl_3$ with tetramethylsilanes as internal standard for ^1H (300 MHz) or solvent as the internal standard for ^{13}C (75 MHz). Microanalyses were performed on an elemental analyzer. THF was distilled from sodium benzophenone ketyl, and DMSO was dried over molecular sieves prior to use. Column chromatography was performed on silica gel 200−245 mesh.

N-Sulfonylbenzotriazoles **3** were prepared according to previously published procedures.[10,12b]

General Procedure for Preparation of 3f,h. A solution of benzofuran (4.1 g, 35 mmol) in anhydrous THF (120 mL) was cooled to −78 °C under nitrogen and then treated dropwise with *n*-BuLi (21.8 mL of 1.6 M in hexane, 35 mmol) and stirred at this temperature for 15 min and then at room temperature for 1.0 h. Sulfur dioxide was bubbled into the reaction mixture at −78 °C and stirred at that temperature for 15 min and then at room temperature for 1 h. *N*-Chlorobenzotriazole (5.4 g, 35 mmol) was added in one portion at room temperature, and the mixture was then stirred for 2 h. Triethylamine (5.3 mL, 40 mmol) was added followed by stirring at room temperature for 10 h. Water (300 mL) was added to the reaction mixture, and the product was extracted with ethyl acetate (3 × 300 mL). The combined organic layers were washed with water and brine and dried over $MgSO_4$. After evaporation, the residue was recrystallized from ethyl acetate to give pure products **3f**,**h**.

1-(Benzofuran-2-ylsulfonyl)-1*H*-1,2,3-benzotriazole (3f): colorless microcrystals (81%); mp 147−148 °C; ^1H NMR δ 8.16 (d, J = 8.4 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.86 (s, 1H), 7.70−7.75 (m, 2H), 7.46−7.56 (m, 3H), 7.32−7.38 (m, 1H); ^{13}C NMR δ 156.5, 145.5, 131.6, 130.7, 129.4, 126.2, 125.2, 124.9, 123.6, 120.7, 116.9, 112.7, 112.2. Anal. Calcd for $C_{14}H_9N_3O_3S$: C, 56.18; H, 3.03; N, 14.04. Found: C, 56.4; H, 2.83; N, 14.12.

1-(5-Ethylfuran-2-yl-sulfonyl)-1*H*-1,2,3-benzotriazole (3h): colorless prisms (66%); mp 147−148 °C; ^1H NMR δ 8.09 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.66−7.72 (m, 1H), 7.49−7.54 (m, 1H), 7.43 (d, J = 3.7 Hz, 1H), 6.20 (d, J = 3.7 Hz, 1H), 2.64 (q, J = 7.6 Hz, 2H), 1.18 (t, J = 7.6 Hz, 3H); ^{13}C NMR δ 166.2, 145.5, 142.5, 131.6, 130.3, 126.0, 122.8, 120.6, 112.2, 107.5, 21.7, 21.7, 11.2. Anal. Calcd for $C_{12}H_{11}N_3O_3S$: C, 51.98; H, 4.00; N, 15.15. Found: C, 52.19; H, 3.83; N, 15.22.

General Procedures for the Preparation of α-Cyano Sulfones 5a−i. Method A. A solution of the nitrile **4** (2 mmol) in anhydrous THF (15 mL) was cooled to −78 °C under nitrogen and then treated dropwise with *n*-BuLi (2.6 mL of 1.55 M in hexane 4 mmol) to afford a clear solution, which was stirred at this temperature for 1 h. *N*-Sulfonylbenzotriazole **3** (dissolved in 10 mL of anhydrous THF) was then added dropwise. The reaction mixture was allowed to warm to room temperature while stirring overnight. After the reaction was quenched by addition of saturated NH_4Cl, the mixture was extracted with EtOAc. The organic extracts were combined, washed with aqueous Na_2CO_3 10% solution and brine, and dried over $MgSO_4$. After evaporation under vacuum, the residue was purified by flash chromatography (hexanes/EtOAc, 5:1) to afford the pure **5**.

Method B. A mixture of nitrile **4** (2 mmol) and potassium *tert*-butoxide (0.45 g, 4 mmol) in DMSO (10 mL) was stirrred below 10 °C for 10 min. After addition of 1-sulfonylbenzotriazole **3** (2 mmol) in DMSO (5 mL), the mixture was allowed to warm to room temperature and stirred for 8 h. The mixture was poured into water (40 mL), acidified with ammonium chloride, and then extracted with ethyl acetate (3 × 30). The extracts were washed with water and dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column using hexanes/EtOAc 10:1 as elutent to give the pure product **5**.

4-Bromophenylmethanesulfonylacetonitrile (5a): colorless plates (82%); mp 111−113 °C; ^1H NMR δ 7.64 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 7.7 Hz, 2H), 5.07 (s, 1H), 3.07 (s, 3H); ^{13}C NMR δ 132.8, 131.1, 125.7, 123.4, 113.0, 60.5, 38.1. Anal. Calcd for $C_9H_8BrNO_2S$: C, 39.43; H, 2.94; N, 5.11. Found: C, 39.60; H, 2.84; N, 5.00.

2,4-Dichlorophenylmethanesulfonylacetonitrile (5b): colorless prisms (87%); mp 155−157 °C; ^1H NMR δ 7.73 (d, J = 8.5 Hz, 1H), 7.55 (d, J = 1.9 Hz, 1H), 7.45 (dd, J = 8.5, 1,9 Hz, 1H), 5.75 (s, 1H), 3.17 (s, 3H); ^{13}C NMR δ 138.2, 135.4, 132.0, 130.4, 128.6, 121.7, 112.7, 56.6, 39.5. Anal. Calcd for

$C_9H_7Cl_2NO_2S$: C, 40.93; H, 2.67; N, 5.30. Found: C, 41.01; H, 2.56; N, 5.11.

4-Bromophenyltoluene-4-sulfonylacetonitrile (5c): colorless microcrystals (93%); mp 138−139 °C; ^{1}H NMR δ 7.62 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 5.06 (s, 1H), 2.48 (s, 3H); ^{13}C NMR δ 147.0, 132.3, 131.2, 131.1, 130.1, 130.0, 125.2, 124.5, 113.2, 62.5, 21.8. Anal. Calcd for $C_{15}H_{12}BrNO_2S$: C, 51.44; H, 3.45; N, 4.00. Found: C, 51.56; H, 3.35; N, 3.92.

2,4-Dichlorophenyltoluene-4-sulfonylacetonitrile (5d): colorless prisms (97%); mp 126−128 °C; ^{1}H NMR δ 7.75 (d, J = 8.0 Hz, 2H), 7.48−7.33 (m, 5H), 5.70 (s, 1H), 2.50 (s, 3H); ^{13}C NMR δ 147.2, 137.7, 135.8, 132.0, 131.9, 130.2, 130.0, 129.9, 128.1, 122.8, 113.0, 58.4, 21.9. Anal. Calcd. for $C_{15}H_{11}Cl_2NO_2S$: C, 52.95; H, 3.26; N, 4.12. Found: C, 52.90; H, 3.16; N, 4.04.

Benzenesulfonylphenylacetonitrile (5e): colorless crystals (76%); mp 148−150 °C (lit.[63] mp 147.0−148 °C); ^{1}H NMR δ 7.73−7.70 (m, 3H), 7.55−7.26 (m, 7H), 5.14 (s, 1H); ^{13}C NMR δ 135.2, 134.3, 130.5, 130.1, 129.7, 129.2, 129.0, 125.3, 113.4, 63.1. Anal. Calcd for $C_{14}H_{11}NO_2S$: N, 5.44. Found: N, 5.71.

Benzenesulfonylacetonitrile (5f): colorless crystals (50%); mp 87−88 °C (lit.[64] mp 88 °C); ^{1}H NMR δ 8.06−8.02 (m, 2H), 7.82−7.77 (m, 1H), 7.69−7.64 (m, 2H), 4.10 (s, 2H); ^{13}C NMR δ 136.6, 135.4, 129.8, 128.8, 110.4, 45.7. Anal. Calcd. for $C_8H_7NO_2S$: C, 53.03; H, 3.89; N, 7.73. Found: C, 53.09; H, 3.81; N, 7.62.

2,4-Dichlorophenyl(thiophene-2-sulfonyl)acetonitrile (5g): pale yellow plates (90%); mp 142−144 °C; ^{1}H NMR δ 7.91 (d, J = 4.9 Hz, 1H), 7.73 (d, J = 3.8 Hz, 1H), 7.48 (d, J = 8.5 Hz, 1H), 7.46 (d, J = 1.9 Hz, 1H), 7.36 (dd, J = 8.4, 1.9 Hz, 1H), 7.25 (dd, J = 4.9, 3.3 Hz, 1H), 5.85 (s, 1H). ^{13}C NMR δ 137.9, 137.8, 137.5, 135.9, 134.6, 131.8, 130.1, 128.6, 128.1, 122.7, 112.8, 59.4. Anal. Calcd for $C_{12}H_7Cl_2NO_2S$: C, 43.38; H, 2.12; N, 4.22. Found: C, 43.43; H, 2.01; N, 4.07.

2-Methyl-2-(2-pyridinylsulfonyl)hexanenitrile (5h): red oil (54%); ^{1}H NMR δ 8.82−8.80 (m, 1H), 8.19 (d, J = 7.8 Hz, 1H), 8.06 (td, J = 7.8, 1.6 Hz, 1H), 7.67(dd, J = 7.7, 4.8 Hz, 1H), 4.64 (dd, J = 10.2, 5.0 Hz, 1H), 2.25−2.13 (m, 2H), 1.76−1.50 (m, 2H), 1.45−1.21 (m, 6H), 0.90 (t, J = 6.6 Hz, 3H); ^{13}C NMR δ 154.5, 150.5, 138.6, 128.5, 123.6, 113.4, 63.1, 31.0, 28.2, 26.4, 25.0, 22.2, 13.8. Anal. Calcd for $C_{13}H_{18}N_2O_2S$: C, 58.62; H, 6.81; N, 10.52. Found: C, 59.39; H, 7.13; N, 10.48.

2-Phenyl-2-(3-pyridinylsulfonyl)propanenitrile (5i): colorless microcrystals (73%); mp 121−122 °C; ^{1}H NMR δ 8.85 (dd, J = 4.9, 1.7 Hz, 1H), 8.57 (d, J = 2.2 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.46−7.37 (m, 6H), 2.28 (s, 3H); ^{13}C NMR δ 155.1, 150.8, 138.3, 130.6, 130.1, 129.5, 129.0, 128.1, 123.4, 116.8, 67.2, 19.2. Anal. Calcd for $C_{14}H_{12}N_2O_2S$: C, 61.75; H, 4.44; N, 10.29. Found: C, 61.77; H, 4.44; N, 10.05.

General Procedure for the Preparation of Sulfonylheterocycles 7a−d. A solution of the appropriate heterocycle (3 mmol) in anhydrous THF (20 mL) was cooled to −78 °C under nitrogen and then treated dropwise with n-BuLi (1.91 mL of 1.6 M in hexane, 3.05 mmol). The mixture was stirred at −78 °C for 15 min and then at room temperature for 1.0 h. After the mixture was cooled to −78 °C, a solution of N-sulfonylbenzotriazoles **3** (3.05 mmol) in THF (10 mL) was added slowly to the reaction mixture at −78 °C. The reaction mixture was allowed to warm to room temperature while stirring overnight, quenched by the addition of saturated NH_4Cl, and extracted with EtOAc. The organic extracts were combined, washed with brine, and dried over $MgSO_4$. After evaporation under vacuum, the residue was chromatographed on a silica gel eluted with hexanes/EtOAc 4:1 to give **7a−d**.

2-(Methylsulfonyl)thiophene (7a): colorless oil (47%); ^{1}H NMR δ 7.71−7.74 (m, 2H), 7.12 (dd, J = 4.8, 3.8 Hz, 1H), 3.2 (s, 3H); ^{13}C NMR δ 141.7, 133.7, 133.4, 127.9, 46.1. Anal. Calcd for $C_5H_6O_2S_2$: C, 37.02; H, 3.73. Found: C, 37.12; H, 3.66.

2-Ethyl-5-(phenylsulfonyl)furan (7b): yellowish oil (80%); ^{1}H NMR δ 7.97−8.00 (m, 2H), 7.50−7.63 (m, 3H), 1.21 (t, J = 7.6 Hz, 3H), 7.12 (d, J = 3.4 Hz, 1H), 6.12 (d, J = 3.4 Hz, 1H), 2.66 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H); ^{13}C NMR δ 164.1, 147.4, 140.4, 133.4, 133.4, 129.2, 127.6, 118.8, 106.5, 21.6, 11.5. Anal. Calcd For $C_{12}H_{12}O_3S$: C, 61.00; H, 5.12. Found: 61.03; H, 5.17.

2-[(4-Methylphenyl)sulfonyl]benzofuran (7c): colorless microcrystals (73%); mp 95−96 °C (lit.[35] mp 95−95 °C); ^{1}H NMR δ 7.96 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 0.6 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.42 (td, J = 7.0 Hz, J = 1.1 Hz, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.29 (dd, J = 8.0, 1.0 Hz, 1H), 2.42 (s, 3H).^{13}C NMR δ 151.9, 145.3, 136.3, 130.0, 128.3, 127.9, 125.9, 124.2, 123.1, 112.8, 112.4, 21.6. Anal. Calcd for $C_{15}H_{12}O_3S$: C, 66.16; H, 4.44. Found: C, 65.97; H, 4.33.

2-(Methyl-1*H*-pyrrole-2-sulfonyl)pyridine (7d): pink prisms (54%); mp 62−63 °C; ^{1}H NMR δ 8.67 (br d, J = 4.7 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.92 (td, J = 7.7, 1.6 Hz, 1H), 7.46 (ddd, J = 7.7, 4.8, 1.0 Hz, 1H), 7.03 (dd, J = 4.1, 1.9 Hz, 1H), 6.85 (t, J = 2.1 Hz, 1H), 6.18 (dd, J = 4.1, 2.6 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR δ 159.8, 150.1, 138.1, 130.6, 126.7, 121.2, 120.1, 108.5, 36.5. Anal. Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.04; H, 4.53; N, 12.60. Found: C, 54.42; H, 4.58; N, 12.56.

General Procedure for the Preparation of (α-Sulfonylalkyl)heterocycles 9a−f. A solution of the appropriate alkylheterocycles **8** (3 mmol) in THF (20 mL) was cooled to −78 °C under nitrogen and treated with n-BuLi (2.0 mL of 1.6 M in hexane, 3.15 mmol) or LDA (2.25 mL of 2.0 M in heptane/THF/ethylbenzene, 4.5 mmol) for **9b**,**c**. The reaction mixture was stirred at −78 °C for 1.5−2.5 h and N-sulfonylbenzotriazole **3** (3.15 mmol) in THF (10 mL) was added slowly. The mixture was allowed to warm to room temperature while stirring overnight, quenched with saturated NH_4Cl, and extracted with EtOAc. The combined extracts were washed with brine and dried over $MgSO_4$. After evaporation under vacuum, the residue was chromatographed or recrystalized from an appropriate solvent to give the pure products **9a−f**.

2-[(Phenylsulfonyl)methyl]pyridine (9a): colorless microcrystals (59%); mp 110−111 °C (lit.[48] mp 111−112 °C); ^{1}H NMR δ 8.42 (br d, J = 4.3 Hz, 1H), 7.59−7.78 (m, 4H), 7.44−7.49 (m, 3H), 7.21−7.25 (m, 1H), 4.56 (s, 2H); ^{13}C NMR δ 149.7, 149.0, 136.7, 133.7, 129.4, 129.0, 128.4, 125.7, 123.3, 64.7. Anal. Calcd for $C_{12}H_{11}NO_2S$: C, 61.78; H, 4.75; N, 6.00. Found: C, 61.59; H, 4.72; N, 5.60.

2-[Phenyl(phenylsulfonyl)methyl]pyridine (9b): colorless needless (94%); mp 163−164 °C; ^{1}H NMR δ 8.53 (br d, J = 4.7 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.71 (td, J = 7.7, 1.7 Hz, 1H), 7.50−7.61 (m, 5H), 7.28−7.39 (m, 5H), 7.21−7.25 (m, 1H), 5.58 (s, 1H); ^{13}C NMR δ 153.1, 149.6, 138.0, 136.9, 133.6, 131.8, 130.4, 129.2, 128.9, 128.6, 128.6, 124.8, 123.3, 78.1. Anal. Calcd for $C_{18}H_{15}NO_2S$: C, 69.88; H, 4.89; N, 4.53. Found: C, 69.83; H, 4.80; N, 4.50.

4-[(Methylsulfonyl)(phenyl)methyl]pyridine (9c): colorless prisms (53%); mp 86−87 °C; ^{1}H NMR δ 8.66 (d, J = 5.8 Hz, 2H), 7.61−7.64 (m, 2H), 7.57 (d, J = 5.8 Hz, 2H), 7.44−7.47 (m, 3H), 5.30 (s, 1H), 2.81 (s, 3H); ^{13}C NMR δ 150.4, 141.1, 131.6, 129.6, 129.58, 129.4, 124.4, 73.6, 40.1. Anal. Calcd for $C_{13}H_{13}NO_2S$: C, 63.13; H, 5.30; N, 5.66. Found: C, 63.18; H, 5.34; N, 5.61.

2-{1-[(4-Methylphenyl)sulfonyl]ethyl}pyridine (9d): yellowish prisms (43%); mp 69−70 °C; ^{1}H NMR δ 8.40 (br d, J = 4.8 Hz, 1H), 7.68 (td, J = 7.7, 1.6 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.2 Hz, 2H), 7.20−7.22 (m, 3H), 4.49 (q, J = 7.1 Hz, 1H),), 2.40 (s, 3H), 1.78 (d, J = 7.1 Hz, 3H); ^{13}C NMR δ 153.7, 149.1, 144.6, 136.5, 133.9, 129.4, 129.0, 124.6, 123.3, 67.7, 21.6, 13.5. Anal. Calcd for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.79; N, 5.36. Found: 64.62; H, 5.96; N, 5.41.

1-Methyl-2-[(2-thienylsulfonyl)methyl]-1*H*-benzimidazole (9e): yellowish prisms (64%); mp 185−187 °C; ^{1}H NMR δ 7.69 (d, J = 4.9 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 2.7 Hz, 1H), 7.34−7.40 (m, 2H), 7.25−7.31 (m, 1H), 7.08−

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7.11 (m, 1H), 4.84 (s, 2H), 3.90 (s, 3H); ^{13}C NMR δ 142.4, 142.3, 138.0, 136.1, 135.4, 135.2, 128.0, 123.6, 122.6, 120.0, 109.8, 56.6, 30.8. Anal. Calcd for $C_{13}H_{12}N_2O_2S_2$: C, 53.40; H, 4.14; N, 9.58. Found: C, 53.44; H, 4.00; N, 9.50.

2-[(1-Benzofuran-2-ylsulfonyl)methyl]-1,3-benzothiazole (9f: yellowish microcrystals (67%); mp 176−177 °C; ^{1}H NMR δ 8.12−8.15 (m, 1H), 7.75−7.90 (m, 4H), 7.59−7.64 (m, 2H), 7.42−7.54 (m, 3H), 5.66 (s, 2H); ^{13}C NMR δ 156.9, 155.7, 152.3, 148.5, 135.7, 128.8, 126.5, 125.9, 125.6, 124.7, 123.8, 122.9, 122.4, 116.0, 112.4, 58.2. Anal. Calcd for $C_{16}H_{11}NO_3S_2$: C, 58.34; H, 3.37; N, 4.25. Found: C, 57.98; H, 3.20; N, 4.29.

General Procedures for the Preparation of α-Sulfonyl Sulfones 11a−g. To a solution of sulfone **10** (2 mmol) in dry THF (10 mL) was added *n*-BuLi (2.6 mL, 1.55 M in pentane, 4 mmol) at −78 °C. The solution was stirred at −78 °C for 1 h and a solution of 1-sulfonylbenzotriazole **3** (2 mmol) in THF (10 mL) was added. The reaction mixture was stirred for 10 h while the temperature was allowed to rise to 20 °C. After quenching with water (15 mL) and extraction with EtOAc (3 × 20 mL), the combined organic layers were washed with water (25 mL) and dried over $MgSO_4$, and the solvent was removed in vacuo. The resulted oil was subjected to column chromatography (eluent: ethyl acetate/hexanes = 1:10 then 1: 5) to give the pure **11**.

1-(Benzenesulfonylphenylsulfonyl)-4-methylbenzene (11a): colorless prisms (96%); mp 188−189 °C; ^{1}H NMR δ 7.75 (d, J = 8.0 Hz, 2H), 7.65−7.58 (m, 3H), 7.47−7.41 (m, 2H), 7.38−7.33 (m, 2H), 7.28−7.18 (m, 5H), 5.41 (s, 1H), 2.41 (s, 3H); ^{13}C NMR δ 145.7, 138.0, 135.0, 134.4, 130.3, 129.7, 129.6, 129.4, 128.8, 128.6, 125.8, 88.4, 21.7. Anal. Calcd for $C_{20}H_{18}O_4S_2$: C, 62.15; H, 4.64. Found: C, 61.96; H, 4.64.

1-Benzenesulfonylmethanesulfonyl-4-methylbenzene (11b): colorless prisms (87%); mp 93−94 °C; ^{1}H NMR δ 8.00−7.98 (m, 2H), 7.87 (d, J = 8.2 Hz, 2H), 7.77−7.72 (m, 1H), 7.64−7.56 (m, 2H), 7.41 (d, J = 8.0 Hz, 2H), 4.75 (s, 2H), 2.50 (s, 3H). ^{13}C NMR δ 146.1, 138.4, 135.4, 134.7, 129.9, 129.3, 128.8, 128.7, 74.5, 21.7. Anal. Calcd for $C_{14}H_{14}O_4S_2$: C, 54.18; H, 4.55. Found: C, 54.25; H, 4.45.

2-(Toluene-4-sulfonyl)tetrahydrothiophene-1,1-dione (11c): colorless plates (78%); mp 104−105 °C; ^{1}H NMR δ 7.89 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 4.32 (t, J = 8.0 Hz, 1H), 3.30−3.11 (m, 2H), 2.82−2.60 (m, 2H), 2.47 (s, 3H), 2.43−2.34 (m, 1H), 2.21−2.11 (m, 1H); ^{13}C NMR δ 146.1, 134.2, 129.9, 129.5, 77.3, 51.2, 24.3, 21.7, 18.9. Anal. Calcd for $C_{11}H_{14}O_4S_2$: C, 48.16; H, 5.14. Found: C, 48.38; H, 5.20.

(1-Ethanesulfonylethanesulfonyl)benzene (11d): colorless crystals (91%); mp 96−97 °C (lit.[65] mp 93−94 °C); ^{1}H NMR δ 7.97 (d, J = 7.4 Hz, 2H), 7.76−7.71 (m, 1H), 7.63−7.58 (m, 2H), 4.38 (q, J = 7.4 Hz, 1H), 3.67−3.47 (m, 2H), 1.69 (d, J = 7.3 Hz, 3H), 1.49 (t, J = 7.4 Hz, 3H); ^{13}C NMR δ 135.7, 134.9, 130.1, 129.1, 76.0, 48.2, 9.5, 6.2. Anal. Calcd for $C_{10}H_{14}O_4S_2$: C, 45.78; H, 5.38. Found: C, 45.73; H, 5.37.

2-(1-Ethanesulfonylethanesulfonyl)pyridine (11e): red microcrystals (87%); mp 118−120 °C; ^{1}H NMR δ 8.77 (br d, J = 4.5 Hz, 1H), 8.14 (d, J = 7.8 Hz, 1H), 8.04−7.99 (m, 1H), 7.64−7.60 (m, 1H), 5.14 (q, J = 7.6 Hz, 1H), 3.60−3.33 (m, 2H), 1.86 (d, J = 7.5 Hz, 3H), 1.45 (t, J = 7.6 Hz, 3H); ^{13}C NMR δ 155.8, 150.2, 138.3, 128.0, 123.4, 72.4, 46.7, 8.8, 5.5. Anal. Calcd for $C_9H_{13}NO_4S_2$: C, 41.05; H, 4.98; N, 5.32. Found: C, 41.20; H, 4.94; N, 5.17.

2-(1-Benzofuran-2-ylsulfonyl)tetrahydrothiophene-1,1-dione (11f): colorless crystals (67%); mp 147−148 °C; ^{1}H NMR δ 7.97 (s, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 5.42 (t, J = 8.5 Hz, 1H), 3.42−3.35 (m, 1H), 3.28−3.18 (m, 1H), 2.54−2.46 (m, 2H), 2.25−2.17 (m, 1H), 2.07−1.99 (m, 1H); ^{13}C NMR δ 155.8, 148.3, 129.1, 125.6, 124.0, 117.1, 112.6, 76.7, 52.4, 25.3, 19.0. Anal. Calcd for $C_{12}H_{12}O_5S_2$: C, 47.99; H, 4.03. Found: C, 47.58; H, 4.15.

Ethyl 1-(2-thienylsulfonyl)ethyl sulfone (11g): yellow oil (71%); ^{1}H NMR δ 7.87 (dd, J = 4.9, 1.2 Hz, 1H), 7.83 (dd, J = 3.8, 1.2 Hz, 1H), 7.22 (dd, J = 4.8, 4.0 Hz, 1H), 4.50 (q, J = 7.3 Hz, 1H), 3.62−3.46 (m, 2H), 1.75 (d, J = 7.3 Hz, 3H), 1.47 (t, J = 7.4 Hz, 3H); ^{13}C NMR δ 137.4, 136.4, 135.5, 128.0, 76.1, 48.3, 9.5, 6.0. Anal. Calcd for $C_8H_{12}O_4S_3$: C, 35.80; H, 4.51. Found: C, 35.95; H, 4.37.

General Procedure for the Preparation of α-Sulfonyl Esters 14a−d. A solution of esters **12a−d** (3 mmol) in anhydrous THF (20 mL) was cooled to −78 °C under nitrogen and then treated dropwise with LDA (3 mL, 2.0 M in heptane/THF/ethylbenzene, 6 mmol). The mixture was stirred for 2.0 h at rt (for **13a**,**b**,**d**) or at −78 °C (for **13c**), and *N*-sulfonylbenzotriazoles **3c**,**f**,**h** (3.15 mmol) in THF (10 mL) were slowly added at −78 °C. The reaction mixture was stirred overnight while the temperature was allowed to rise to room temperature, quenched with saturated NH_4Cl, and extracted with EtOAc. The organic extracts were washed with a saturated solution of Na_2CO_3 and dried over $MgSO_4$. The solvent was evaporated and the resultant oil was chromatographed to give the pure product **14a−d**.

Ethyl 2-[(4-methylphenyl)sulfonyl]-2-phenylacetate (14a): colorless prisms (60%); mp 112−113 °C (lit.[62] mp 112−113 °C); ^{1}H NMR δ 7.48 (d, J = 8.2 Hz, 2H), 7.29−7.38 (m, 5H), 7.22 (d, J = 8.2 Hz, 2H), 5.08 (s, 1H), 4.13−4.30 (m, 2H), 2.41 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 164.9 145.3, 133.4, 130.3, 130.0, 129.6, 129.2, 128.6, 128.0, 75.3, 62.5, 21.7, 13.9. Anal. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70. Found: C, 64.22; H, 5.75.

Methyl 2-[(4-methylphenyl)sulfonyl]-2-(1-naphthyl)-acetate (14b): yellowish oil (62%); ^{1}H NMR δ 8.00−7.88 (m, 3H), 7.78 (dd, J = 7.4, 1.0 Hz, 1H), 7.56−7.51(m, 4H), 7.44 (t, J = 8.0 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 6.13 (s, 1H), 3.81 (s, 3H), 2.42 (s, 3H); ^{13}C NMR δ 165.9, 145.3, 133.7, 133.3, 131.8, 130.3, 130.0, 129.1, 129.0, 128.6, 127.1, 125.9, 124.9, 123.9, 122.4, 69.1, 53.2, 21.6; HRMS calcd for $C_{20}H_{18}O_4S$ 354.4265, found 354.0925. Anal. Calcd for $C_{20}H_{18}O_4S$: C, 67.78; H, 5.12. Found: C, 67.42; H, 5.26.

2-(Benzofuran-2-sulfonyl)-3-phenylpropionic acid ethyl ester (14c): colorless prisms (71%); mp 77−78 °C; ^{1}H NMR δ 7.74 (d, J = 7.8 Hz, 1H), 7.58−7.639 (m, 2H), 7.54 (td, J = 7.1, 1.2 Hz, 1H), 7.36−7.41 (m, 1H), 7.16−7.29 (m, 5H), 4.42 (dd, J = 11.5, 3.9 Hz, 1H), 4.03 (q, J = 7.1 Hz, 2H), 3.37−3.56 (m, 2H), 0.96 (t, J = 7.1 Hz, 1H); ^{13}C NMR δ 164.4, 156.5, 148.0, 135.2, 128.9, 128.8, 128.7, 127.3, 125.7, 125.7, 124.6, 123.4, 116.5, 112.6, 71.3, 62.4, 31.9, 13.6. Anal. Calcdfor $C_{19}H_{18}O_5S$: C, 63.67; H, 5.06. Found: C, 63.64; H, 5.01.

2-(5-Ethylfuran-2-sulfonyl)butyric acid methyl ester (14d): yellowish oil (47%); ^{1}H NMR δ 7.11 (d, J = 3.4 Hz, 1H), 6.21 (d, J = 3.4 Hz, 1H), 3.95 (dd, J = 10.6, 4.5 Hz, 1H), 3.76 (s, 1H), 2.75 (q, J = 7.6 Hz, 2H), 2.05−2.18 (m, 2H), 1.29 (t, J = 7.6 Hz, 3H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR δ 165.8, 164.8, 144.0, 121.8, 106.8, 71.6, 53.0, 21.7, 20.1, 11.6, 11.4. Anal. Calcd for $C_{10}H_{16}O_5S$: C, 50.76; H, 6.20. Found: C, 50.40; H, 6.25.

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