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Synthesis of Sulfones by Iron-Catalyzed Decomposition of Sulfonylhydrazones

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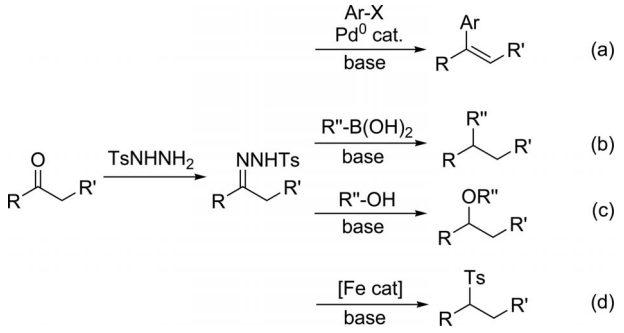
The Fe-catalyzed decomposition of sulfonylhydrazones gives rise to sulfones. The reaction is quite general and allows the preparation of sulfones from a variety of aryl, alkyl, and α,β-unsaturated aldehydes and ketones. Crossover experiments reveal that the reaction is an intermolecular process, which may proceed by nucleophilic attack of the sulfinate anion on an iron carbene complex.

Introduction

One of the main challenges of current organic chemistry is the development of new sustainable processes to achieve chemical transformations. Therefore, great efforts are being paid to the discover of new methodologies that improve the efficiency, selectivity, and availability of starting materials and the environmental sustainability of synthetic processes.[1] In this context, we have recently focused on tosylhydrazones[2] as valuable and readily available reagents in C–C and C–O bond-forming reactions through Pd-catalyzed[3] and metal-free processes[4] (Scheme 1, Equations a–c). Our group and others[5] have shown that the use of tosylhydrazones represents a very convenient methodology for the unconventional modification of carbonyl compounds.



Scheme 1. Equations a–c: recent applications of tosylhydrazones for the unconventional elaboration of carbonyl compounds; equation d: this work.

During our research, we observed that under certain reaction conditions sulfones could be obtained by the loss of nitrogen from tosylhydrazones (Scheme 1, Equation d). Taking into account the interest of sulfones both as synthetic intermediates[6] and as structural units in pharmaceuticals,[7] we optimized this background reaction and, thus, identified conditions to carry out this transformation through a Fe-catalyzed process. The formation of sulfones from tosylhydrazones had been previously reported by Che and co-workers by employing a Ru-based catalyst,[8] although the reaction showed a very limited scope. However, very recently, a similar transformation promoted by Cu salts was reported by Yu and co-workers.[9] This report prompted us to disclose our own results in this area.

The discovery of the Pd-catalyzed cross-coupling reaction between tosylhydrazones and aryl halides that allows the synthesis of polysubstituted olefins (Scheme 1, Equation a) triggered our interest in these types of reagents. Since our initial contribution, our group and others have developed different coupling reactions that employ tosylhydrazones and Pd catalysts. As a continuation of this study, we investigated whether or not this reaction could be carried out by employing other metal catalysts. Bolstered by the growing interest and applications of iron catalysts[10] and by the fact that iron is one of the most abundant, cheapest, and environmentally friendly metals,[11] we focused on iron-based catalysts for the latter transformation.

Results and Discussion

We first turned our attention to couplings involving $Fe(acac)_3$ as the catalyst (30 mol-%). When tosylhydrazone **1a** derived from 4-methylacetophenone was treated with 4-bromotoluene (**2**) in the presence of LiO*t*Bu in dioxane at 110 °C no cross-coupling reaction was observed (Scheme 2). The only products obtained were those derived from the evolution of the diazo compound generated from the hydrazone, Bamford–Stevens alkene **3**, and homocoupling products **4** and **5**.[12] Inclusion of $FeCl_3$ in the same reaction also failed to afford any cross-coupled product. However, under these reaction conditions a significant amount of sulfone **6a**

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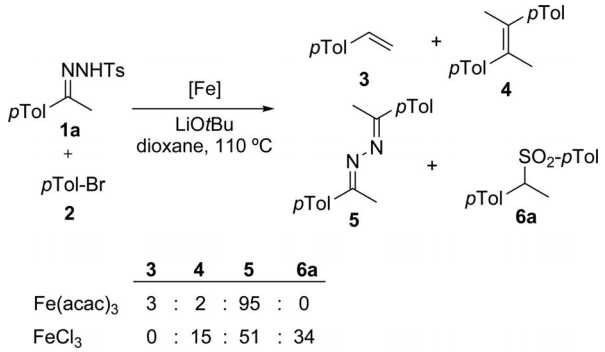
was isolated together with compounds **4** and **5**. These and numerous other failed reactions with an assortment of iron salts inspired us to rethink how best to accomplish our goal of developing an iron version of the previously developed Pd-catalyzed cross-couplings.



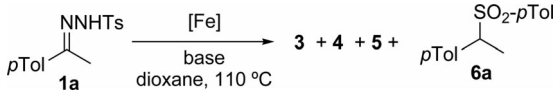
	3	4	5	6a
$Fe(acac)_3$	3	2	95	0
$FeCl_3$	0	15	51	34

Scheme 2. Unsuccessful attempts at an iron-catalyzed cross-coupling between tosylhydrazones and aryl halides.

In light of difficulties encountered when taking into account only the source of iron, we examined the impact of base upon the reaction. We were specifically interested in the use of Grignard reagents as bases, as their role in the formation of low-valent iron–magnesium catalysts was well established.[13] This preliminary survey showed that the catalytic systems being tested were not able to promote the desired cross-coupling reaction; instead, sulfone **6a** was again formed under the selected reaction conditions. Given the importance of sulfones as synthetic intermediates and also as members of a key structural motif in medicinal chemistry, we investigated the feasibility of this reaction as a synthetically useful transformation by which to obtain sulfones from sulfonylhydrazones.

Initial optimization efforts focused on the identification of the best iron source, base, solvent, and tosylhydrazone by using **1a** as the model substrate. We found that formation of sulfone **6a** took place to varying extents under a variety of reaction conditions; selected examples are included in Table 1. Using dioxane as solvent, $FeCl_3$ provided the best results and afforded product **6a** as the major component of a mixture (Table 1, Entry 2). Comparison of the results obtained with reactions using an assortment of bases indicated that ethylmagnesium bromide was the most effective reagent for this transformation (Table 1, Entries 2 and 4–6). A control experiment in the absence of base confirmed that the iron salt showed some catalytic ability, as **6a** was obtained in low yield (Table 1, Entry 11). However, in the absence of the iron salt, the reaction failed to provide appreciable amounts of sulfone (Table 1, Entry 12). The reaction was dependent on the nature of the solvent and on the temperature. Thus, better yields were achieved when the reaction was carried out in dioxane at 110 °C. The use of other solvents (THF, toluene; Table 1, Entries 14 and 15) as well as lower reaction temperatures (Table 1, Entry 13) provided poorer results. With respect to the catalyst loading, 10 mol-% of the iron salt was found to be optimal. When 5 mol-% of $FeCl_3$ was used, **6a** was formed in lower yield (Table 1, Entry 10).

Table 1. Influence of the reaction conditions in the Fe-catalyzed thermal decomposition of tosylhydrazone **1a**.[a]



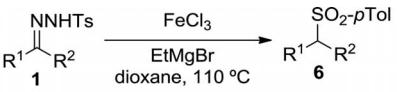
Entry	Fe source	Base	Product ratio [%][b]			
			3	4	5	6
1	$Fe(acac)_3$	EtMgBr	8	8	58	26
2	$FeCl_3$	EtMgBr	15	5	33	47
3	$Fe[Cp(CO)_2]Cl$	EtMgBr	4	16	68	12
4	$FeCl_3$	LiO*t*Bu	0	15	51	34
5	$FeCl_3$	K_2CO_3	14	31	35	20
6	$FeCl_3$	MeMgBr	0	21	71	8
7[c,f]	$FeCl_3$	EtMgBr	18	8	10	64
8[d,f]	$FeCl_3$	EtMgBr	17	4	10	69
9[e]	$FeCl_3$	EtMgBr	3	4	3	90
10[e,g]	$FeCl_3$	EtMgBr	0	23	29	48
11	$FeCl_3$	–	83	0	2	15
12	–	LiO*t*Bu	0	36	62	2
13[e,f,h]	$FeCl_3$	EtMgBr	29	18	34	19
14[e,f,i]	$FeCl_3$	EtMgBr	27	0	5	68
15[e,f,j]	$FeCl_3$	EtMgBr	7	8	66	19

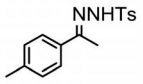
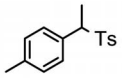
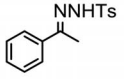
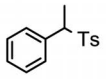
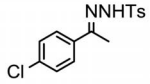
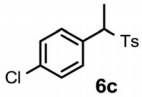
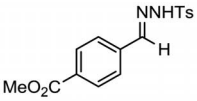
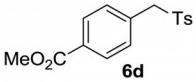
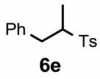
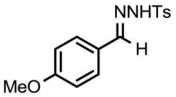
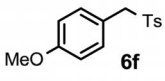
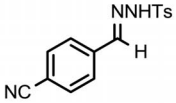
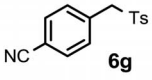
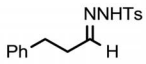
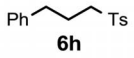
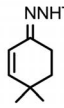
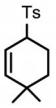
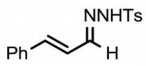
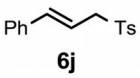
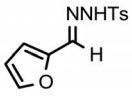
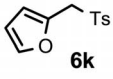
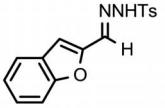
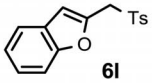
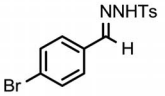
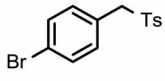
[a] Reaction conditions: **1a** (0.5 mmol), base (3 equiv.), Fe cat (30 mol-%), dioxane (2 mL). [b] Determined by GC–MS; total conversion of **1a** was observed in all cases. [c] Addition time of the tosylhydrazone: 2 h. [d] Addition time of the tosylhydrazone: 8 h. [e] Addition time of the tosylhydrazone: 4 h. [f] $FeCl_3$ (10 mol-%) was employed. [g] $FeCl_3$ (5 mol-%) was employed. [h] Carried out at 80 °C. [i] Carried out in refluxing THF. [j] Carried out in toluene at 90 °C.

In order to minimize the formation of alkene and homocoupling products, the rate of addition of the tosylhydrazone was considered.[14] Delightfully, much better results were obtained when the tosylhydrazone was added slowly by using a syringe pump. Thus, when a solution of tosylhydrazone **1a** in dioxane was slowly added over the course of 4 h at 110 °C (at a rate of approximately 0.250 mL h^{-1}) to a solution of ethylmagnesium bromide (1 equiv.) and $FeCl_3$ (10 mol-%), sulfone **6a** was formed as the major product with only small amounts of other side products being detectable.

With this protocol in hand, we studied the scope of the reaction (Table 2). The transformation seems to be general, as tosylhydrazones derived from ketones or aldehydes were converted into corresponding compound **6** by using the above-mentioned conditions. Electron-rich aromatic systems (Table 2, Entries 1 and 6) as well as electron-poor derivatives (Table 2, Entries 3, 4 and 7) underwent the reaction. Moreover, esters and nitriles were unaffected by these conditions. Halogen substitution of the aromatic rings was also tolerated (Table 2, Entries 3 and 13), enabling further derivatization through metal-catalyzed cross-coupling techniques. The transformation was found to proceed in good yields when heterocyclic derivatives were used (Table 2, Entries 11 and 12). Importantly, unlike the Cu-catalyzed process, the reaction is not limited to tosylhydrazones derived

Table 2. Iron-catalyzed synthesis of tolyl sulfones from tosylhydrazones **1**.[a]

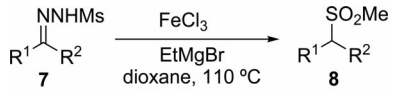


Entry	Hydrazone **1**	Rate of addition [mL/h]	Compound **6**	Yield [%][b]
1		0.250	 **6a**	62
2		0.250	 **6b**	62
3		0.125	 **6c**	75
4		0.500	 **6d**	40
5		0.143	 **6e**	58
6		0.250	 **6f**	76
7		0.250	 **6g**	72
8		0.143	 **6h**	65
9		0.250	 **6i**	50
10		0.143	 **6j**	67
11		0.250	 **6k**	61
12		0.250	 **6l**	70
13		0.250		57

[a] Reaction conditions: EtMgBr (1 equiv.), $FeCl_3$ (10 mol-%), dioxane. A solution of hydrazone **1** (0.5 mmol) in dioxane (1 mL) was added to the mixture of $FeCl_3$ and the base in dioxane (1 mL) at 110 °C over a period of 2 to 8 h. [b] Isolated yield after column chromatography.

from aromatic carbonyl compounds. Indeed, hydrazones derived from dialkyl ketones and alkyl aldehydes also participated successfully in the reaction (Table 2, Entries 5 and 8). Moreover, allyl sulfones, important synthetic intermediates,[15] could be prepared from α,β-unsaturated cyclic or acyclic tosylhydrazones (Table 2, Entries 9 and 10).

The reaction was also successfully conducted with mesylhydrazones, giving rise to dialkyl sulfones (Scheme 3). This is an interesting result, as the methyl sulfone group is found in many therapeutic agents.



8a, R^1 = p-Tol, R^2 = Me, 53 %
8b, R^1 = 3-ClC_6H_4, R^2 = Me, 57%
8c, R^1 = 4-$MeOC_6H_4$, R^2 = H, 75%
8d, R^1 = 3-BrC_6H_4, R^2 = Me, 73%
8e, R^1 = 2-benzofuryl, R^2 = H, 71%

Scheme 3. Iron-catalyzed synthesis of methyl sulfones **8** from mesylhydrazones **7**. Reaction conditions: EtMgBr (1 equiv.), $FeCl_3$ (10 mol-%), dioxane. A solution of hydrazone **7** (0.5 mmol) in dioxane (1 mL) was added to the mixture of $FeCl_3$ and the base in dioxane (1 mL) at 110 °C over 3–10 h. Yields are those obtained for the isolated product after column chromatography. For substrate **8b**, an additional amount of Li*O*t*Bu (2.4 equiv.) was needed to improve the yield.

It is well known that *N*-tosylhydrazones in the presence of base undergo thermal decomposition through the Bamford–Stevens reaction to generate diazo compounds, which may produce metal carbenes in the presence of a transition metal.[2] The mechanisms previously proposed by the groups of Che and Yu for the formation of sulfones from sulfonylhydrazones are based on this reaction and comprise the addition of the sulfinate, released upon decomposition of the sulfonylhydrazone, to the metal-stabilized carbene complex (Figure 1).

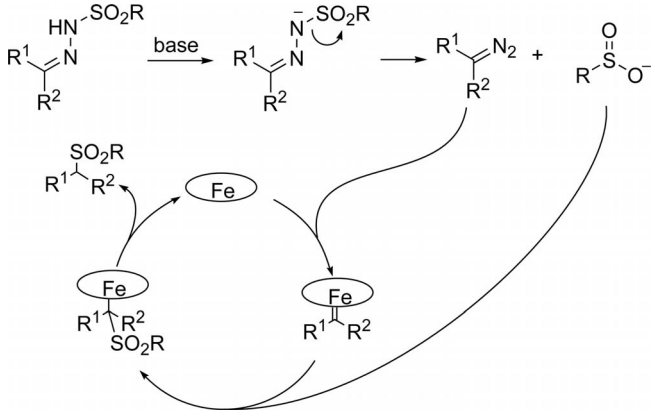
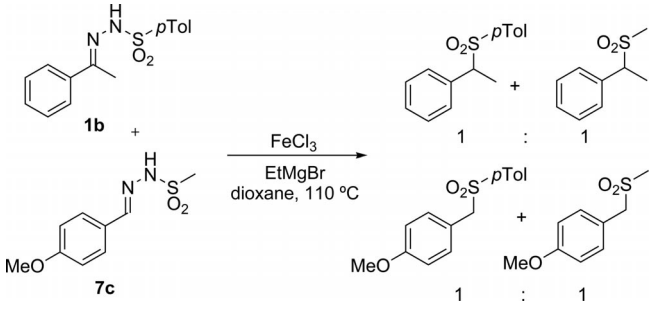


Figure 1. Proposed mechanism for the Fe-catalyzed C–S bond-forming reaction.

To find additional support for this mechanistic proposal and to eliminate the possibility of an intramolecular nitrogen extrusion reaction, we carried out a crossover experiment by employing two different sulfonylhydrazones. Thus, tosylhydrazone **1b**, derived from acetophenone, and mes-

ylhydrazone **7c**, derived from 4-methoxybenzaldehyde, were used in the established procedure (Scheme 4). The reaction afforded an equimolar mixture of the four different combinations of the carbonyl and sulfonyl fragments – two methyl sulfones and two tolyl sulfones – indicating that, indeed, the intermolecular pathway and not an intramolecular extrusion process takes place.



Scheme 4. Study of the pathway of the iron-promoted synthesis of sulfones through a crossover experiment.

Although mechanistic studies to shed light on this process and establish the role of the metal catalyst are currently underway, a plausible catalytic cycle involves an iron carbene (Figure 1). Attack of the sulfinate group upon the iron carbene[16] is envisioned to generate a metal–alkyl complex that, upon protonolysis, affords the sulfone.

Conclusions

In conclusion, we have developed a new iron-catalyzed C–S bond-forming reaction. This transformation, catalyzed by inexpensive and environmentally friendly $FeCl_3$, provides efficient access to a great variety of sulfones, which are highly useful organic products. Moreover, it is worth noting that these reactions meet the requirements of sustainable chemistry: (i) a nontoxic metal catalyst is employed and (ii) a carbonyl compound is transformed into a sulfone with H_2O and N_2 as the only byproducts. Furthermore, the importance of the process lies in its intermolecular nature. Thus, the reaction involves the introduction of a nucleophile, the sulfinate group, and an electrophile, the proton, in a sequential manner. Future work in this area will include detailed mechanistic studies and the extension of the reaction to other types of nucleophiles and electrophiles.

Experimental Section

General Methods: All reactions were carried out with a RR98030 12 place Carousel Reaction Station from Radleys Discovery Technologies, equipped with gas-tight threaded caps with a valve, cooling reflux head system, and digital temperature controller. Dioxane and dichloromethane were dried by standard procedures. Anhydrous $FeCl_3$ was purchased from Aldrich Chemical Co. and used without further purification and weighed in air. EtMgBr (1.0 M in THF) was purchased from Aldrich Chemical Co. All carbonyl compounds are commercially available from Aldrich Chemical Co., Acros Organics Chemical Co., and Alfa Aesar Chemical Co. and were used without further purification. *N*-Tosylhydrazones **1** and *N*-mesylhydrazones **7** derived from carbonyl compounds **4** were prepared following a procedure described in the literature.[17] NMR spectra were recorded at 400 or 300 MHz for ^1H and 100 or 75 MHz for ^{13}C, with the residual solvent signals as standard for ^1H and ^{13}C. The data are being as s = singlet, br. s = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, and m = multiplet or unresolved. Mass spectra were obtained by EI (70 eV) with a Finnigan Mat 95 spectrometer.

General Procedure for the Synthesis of Tolyl Sulfones from Tosylhydrazones 1: A reaction tube under a nitrogen atmosphere was charged with $FeCl_3$ (4.87 mg, 10 mol-%, 0.03 mmol). After 1 min, ethylmagnesium bromide (1.0 equiv.) and dioxane (1 mL) were added. The system was heated at 110 °C with stirring, and the corresponding tosylhydrazone 1 (0.3 mmol) dissolved in dioxane (1 mL) was added with a syringe pump over 2 to 8 h (0.500 to 0.125 mL/h). After addition, the reaction mixture was kept at 110 °C for an additional period of 24 h (GC–MS monitoring). When the reaction was complete, the crude reaction mixture was allowed to reach room temperature, the solvent was eliminated, and 1 M HCl and dichloromethane were added, and the layers were separated. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were washed with two portions of 1 M HCl and brine and then dried with $MgSO_4$ and filtered. Solvent was removed under reduced pressure. If necessary, the products were purified by chromatography on silica gel.

1-Methyl-4-[(1-*p*-tolylethyl)sulfonyl]benzene (6a): 4-Methyl-*N*′-(1-*p*-tolylethylidene)benzenesulfonohydrazide (90.7 mg, 0.3 mmol) afforded **6a** (51.0 mg, 62% yield) as a white solid (m.p. 131.0–140.3 °C). Compound **6a** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 4:1). R_f (hexanes/ethyl acetate, 4:1) = 0.31. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.71 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CHCH_3), 2.32 (s, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 4.18 (q, $^3J_{H,H}$ = 7.2 Hz, 1 H, CHCH$_3$), 7.01–7.10 (m, 4 H, CH_{arom}), 7.19 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, CH_{arom}), 7.43 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (CH_3), 21.1 (CH_3), 21.5 (CH_3), 65.6 (CH), 129.0 (2 CH), 129.2 (4 CH), 129.3 (2 CH), 130.7 (C), 134.0 (C), 138.5 (C), 144.3 (C) ppm. HRMS (EI): calcd. for $C_{16}H_{18}O_2S$ 274.1028; found 274.1021.

1-Methyl-4-[(1-phenylethyl)sulfonyl]benzene (6b):[18] 4-Methyl-*N*′-(1-phenylethylidene)benzenesulfonohydrazide (86.5 mg, 0.3 mmol) afforded **6b** (48.4 mg, 62% yield) as a yellow solid (m.p. 133.0–138.0 °C). Compound **6b** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 4:1). R_f (hexanes/ethyl acetate, 4:1) = 0.40. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.77 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CHCH_3), 2.41 (s, 3 H, CH_3), 4.23 (q, $^3J_{H,H}$ = 7.0 Hz, 1 H, CHCH$_3$), 7.12–7.34 (m, 7 H, CH_{arom}), 7.43 (d, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 21.5 (CH_3), 65.9 (CH), 128.2 (2 CH), 128.6 (CH), 129.0 (2 CH), 129.1 (2 CH), 129.3 (2 CH), 133.8 (2 C), 144.3 (C) ppm. HRMS (EI): calcd. for $C_{15}H_{16}O_2S$ 260.0871; found 266.0880.

1-Chloro-4-[(1-*p*-tolylethyl)sulfonyl]benzene (6c): *N*′-[1-(4-Chlorophenyl)ethylidene]-4-methylbenzenesulfonohydrazide (96.8 mg, 0.3 mmol) afforded **6c** (66.3 mg, 75% yield) as a yellow oil. Compound **6c** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 2:1). R_f (hexanes/ethyl acetate, 2:1) = 0.37. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.73 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CHCH_3), 2.42 (s, 3 H, CH_3), 4.20 (q, $^3J_{H,H}$ = 7.2 Hz, 1 H, CHCH$_3$), 7.08 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, CH_{arom}), 7.19–7.25 (m, 4 H, CH_{arom}), 7.43 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 (CH_3), 21.6 (CH_3), 65.3 (CH), 128.6 (2 CH), 129.2 (2 CH), 129.4 (2 CH), 130.7 (2 CH), 132.5 (C), 133.7

(C), 134.8 (C), 144.7 (C) ppm. HRMS (EI): calcd. for $C_{15}H_{15}ClO_2S$ 294.0481; found 294.0468.

Methyl 4-[(*p*-tolylsulfonyl)methyl]benzoate (6d):[19] Methyl 4-[(2-tosylhydrazono)methyl]benzoate (60.8 mg, 0.3 mmol) afforded **6d** (44.3 mg, 40% yield) as a yellow solid (m.p. 179.0–198.5 °C, decomposition). Compound **6d** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 3:1). R_f (hexanes/ethyl acetate, 3:1) = 0.53. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.21 (s, 3 H, CH_3), 3.46 (s, 3 H, CH_3), 3.82 (s, 2 H, CH_2), 6.18 (d, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH_{arom}), 6.24 (d, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH_{arom}), 6.45 (d, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH_{arom}), 6.81 (d, $^3J_{H,H}$ = 6.8 Hz, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5 (CH_3), 52.2 (CH_3), 62.6 (CH_2), 128.5 (2 CH), 129.5 (2 CH), 129.6 (2 CH), 130.3 (C), 130.7 (2 CH), 133.2 (C), 134.7 (C), 144.9 (C), 166.5 (C) ppm. HRMS (EI): calcd. for $C_{16}H_{16}O_4S$ 304.0769; found 304.0762.

1-Methyl-4-(1-phenylpropan-2-ylsulfonyl)benzene (6e): 4-Methyl-*N*′-(1-phenylpropan-2-ylidene)benzenesulfonohydrazide (90.7 mg, 0.3 mmol) afforded **6e** (47.7 mg, 58% yield) as a colorless oil. Compound **6e** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 3:1). R_f (hexanes/ethyl acetate, 3:1) = 0.34. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_2CHCH_3), 2.45–2.53 (m, 4 H, CH_3, CHHCHCH$_3$), 3.16–3.30 (m, 1 H, CH_2CHCH_3), 3.42 (dd, $^2J_{H,H}$ = 3.1, $^3J_{H,H}$ = 13.2 Hz, 1 H, CHHCHCH$_3$), 7.07–7.12 (m, 2 H, CH_{arom}), 7.20–7.30 (m, 3 H, CH_{arom}), 7.35–7.42 (m, 2 H, CH_{arom}), 7.81 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.6 (CH_3), 21.6 (CH_3), 35.3 (CH_2), 61.6 (CH), 126.8 (CH), 128.6 (2 CH), 128.9 (2 CH), 129.0 (2 CH), 129.7 (2 CH), 134.1 (C), 137.0(C), 144.6 (C) ppm. HRMS (EI): calcd. for $C_{15}H_{16}O_3S$ 276.0808; found 276.0802.

1-Methoxy-4-[(*p*-tolylsulfonyl)methyl]benzene (6f):[20] *N*′-(4-Methoxybenzylidene)-4-methylbenzenesulfonohydrazide (91.3 mg, 0.3 mmol) afforded **6f** (63.0 mg, 76% yield) as a white solid (m.p. 115.0–124.0 °C). Compound **6f** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 4:1). R_f (hexanes/ethyl acetate, 4:1) = 0.32. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, CH_3), 3.80 (s, 3 H, CH_3), 4.24 (s, 2 H, CH_2), 6.80 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, CH_{arom}), 7.02 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, CH_{arom}), 7.25 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, CH_{arom}), 7. 52 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5 (CH_3), 55.1 (CH_3), 62.1 (CH_2), 113.9 (2 CH), 120.0 (C), 128.5 (2 CH), 129.4 (2 CH), 131.9 (2 CH), 135.0 (C), 144.4 (C), 159.8 (C) ppm. HRMS (EI): calcd. for $C_{15}H_{16}O_3S$ 276.0808; found 276.0802.

4-[(*p*-Tolylsulfonyl)methyl]benzonitrile (6g): *N*′-(4-Cyanobenzylidene)-4-methylbenzenesulfonohydrazide (89.8 mg, 0.3 mmol) afforded **6g** (58.6 mg, 72% yield) as a yellow solid (m.p. 198.5–208.0 °C, decomposition). Compound **6g** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 20:1). R_f (hexanes/ethyl acetate, 20:1) = 0.47. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, CH_3), 4.33 (s, 2 H, CH_2), 7.23 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, CH_{arom}), 7.27 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H), 7.51 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, CH_{arom}), 7.57 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH_3), 62.5 (CH_2), 112.7 (C), 118.1 (C), 128.4 (2 CH), 129.7 (2 CH), 131.4 (2 CH), 132.2 (2 CH), 133.5 (C), 134.6 (C), 145.3 (C) ppm. HRMS (EI): calcd. for $C_{15}H_{13}NO_2S$ 271.0667; found 271.0673.

1-Methyl-4-[(3-phenylpropyl)sulfonyl]benzene (6h):[21] 4-Methyl-*N*′-(3-phenylpropylidene)benzenesulfonohydrazide (90.7 mg, 0.3 mmol) afforded **6h** (53.5 mg, 65% yield) as a yellow oil. Compound **6h** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 3:1). R_f (hexanes/ethyl acetate, 3:1) = 0.41. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.97–2.12 (m, 2 H, $CH_2CH_2CH_2$), 2.47 (s, 3 H, CH_3), 2.71 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H, $CH_2CH_2CH_2$), 3.03–3.12 (m, 2 H, $CH_2CH_2CH_2$), 7.12 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_{arom}), 7.18–7.28 (m, 3 H, CH_{arom}), 7.37 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, CH_{arom}), 7.79 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH_3), 24.2 (CH_2), 34.1 (CH_2), 55.5 (CH_2), 126.3 (CH), 128.0 (2 CH), 128.3 (2 CH), 128.5 (2 CH), 129.8 (2 CH), 136.1 (C), 139.9 (C), 144.6 (C) ppm. HRMS (EI): calcd. for $C_{16}H_{18}O_2S$ 274.1028; found 274.1021.

1-(4,4-Dimethylcyclohex-2-enylsulfonyl)-4-methylbenzene (6i): *N*′-(4,4-Dimethylcyclohex-2-enylidene)-4-methylbenzenesulfonohydrazide (87.7 mg, 0.3 mmol) afforded **6i** (39.7 mg, 50% yield) as a yellow oil. Compound **6i** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 3:1). R_f (hexanes/ethyl acetate, 3:1) = 0.50. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (s, 3 H, CH_3), 0.93 (s, 3 H, CH_3), 1.23–1.36 (m, 1 H, CCHHCH$_2$), 1.42–1.52 (m, 1 H, CCHHCH$_2$), 1.85–2.01 (m, 2 H, CCH_2CH_2), 2.44 (s, 3 H, CH_3), 3.64–3.71 (m, 1 H, CH), 5.65 (dd, $^3J_{H,H}$ = 3.0, 10.1 Hz, 1 H, CH=CH), 5.77 (d, $^3J_{H,H}$ = 10.1 Hz, 1 H, CH=CH), 7.33 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, CH_{arom}), 7.74 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.8 (CH_2), 21.6 (CH_3), 28.2 (CH_3), 29.3 (CH_3), 31.3 (C), 33.9 (CH_2), 61.9 (CH), 116.2 (CH), 129.2 (2 CH), 129.4 (2 CH), 134.2 (C), 144.5 (C), 144.9 (CH) ppm. HRMS (EI): calcd. for $C_{15}H_{20}O_2S$ 264.1184; found 264.1181.

1-(Cinnamylsulfonyl)-4-methylbenzene (6j):[22] 4-Methyl-*N*′-[(*E*)-3-phenylallylidene]benzenesulfonohydrazide (90.1 mg, 0.3 mmol) afforded **6j** (54.7 mg, 67% yield) as a white solid. Compound **6j** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 3:1). R_f (hexanes/ethyl acetate, 3:1) = 0.63. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, CH_3), 3.93 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, CH=CHCH_2), 6.10 (dt, $^3J_{H,H}$ = 7.6, 16.1 Hz, 1 H, CH=CHCH$_2$), 6.39 (d, $^3J_{H,H}$ = 16.1 Hz, 1 H, CH=CHCH$_2$), 7.27–7.35 (m, 7 H, CH_{arom}), 7.76 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5 (CH_3), 60.5 (CH_2), 115.3 (CH), 126.5 (CH), 128.3 (CH), 128.4 (2 CH), 128.6 (2 CH), 129.6 (2 CH), 135.5 (C), 135.7 (C), 138.9 (CH), 144.7 (C) ppm. HRMS (EI): calcd. for $C_{16}H_{16}O_2S$ 272.00873; found 272.0871.

2-[(*p*-Tolylsulfonyl)methyl]furan (6k):[23] *N*′-(Furan-2-ylmethylene)-4-methylbenzenesulfonohydrazide (79.3 mg, 0.3 mmol) afforded **6k** (43.2 mg, 61% yield) as a yellow oil. Compound **6k** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 2:1). R_f (hexanes/ethyl acetate, 8:1) = 0.30. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, CH_3), 4.18 (s, 2 H, CH_2), 6.29–6.34 (br. s, 1 H, CH_{arom}), 7.21–7.25 (m, 1 H, CH_{arom}), 7.29 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, CH_{arom}), 7.36–7.38 (m, 1 H, CH_{arom}), 7.63 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH_3), 53.4 (CH_2), 112.5 (CH), 112.8 (C), 128.6 (2 CH), 129.6 (2 CH), 134.9 (C), 142.8 (CH), 143.4 (CH), 144.8 (C) ppm. HRMS (EI): calcd. for $C_{12}H_{12}O_3S$ 236.0507; found 236.0496.

2-[(*p*-Tolylsulfonyl)methyl]benzofuran (6l): *N*′-(Benzofuran-2-ylmethylene)-4-methylbenzenesulfonohydrazide (94.3 mg, 0.3 mmol) afforded **6l** (60.1 mg, 70% yield) as a pale brown solid (m.p. 202.0–205.8 °C, decomposition). Compound **6l** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 3:1). R_f (hexanes/ethyl acetate, 3:1) = 0.43. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, CH_3), 4.55 (s, 2 H, CH_2), 6.69 (s, 1 H, CH_{arom}), 7.20–7.34 (m, 4 H, CH_{arom}), 7.39 (d, $^3J_{H,H}$ = 7.4 Hz, 1 H, CH_{arom}), 7.55 (d, $^3J_{H,H}$ = 7.4 Hz, 1 H, CH_{arom}), 7.67 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH_3), 53.4 (CH_2), 108.8 (CH), 111.2 (CH), 121.1 (CH), 123.0 (CH), 124.8 (CH), 127.8 (C), 128.4 (2 CH), 129.7 (2 CH), 135.2 (C), 145.0 (C), 145.2 (C), 155.2 (C) ppm. HRMS (EI): calcd. for $C_{16}H_{14}O_3S$ 286.0700; found 286.0664.

1-Bromo-4-(*p*-tolylsulfonylmethyl)benzene (6m): *N*′-(4-Bromobenzylidene)-4-methylbenzenesulfonohydrazide (106.0 mg, 0.3 mmol) afforded **6m** (55.4 mg, 57% yield) as a yellow solid (m.p. 162.0–180.0 °C). Compound **6m** was purified by flash chromatography on alumina (hexanes/ethyl acetate, 2:1). R_f (hexanes/ethyl acetate, 2:1) = 0.20. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, CH_3), 4.25 (s, 2 H, CH_2), 6.98 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, CH_{arom}), 7.28 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, CH_{arom}), 7.42 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, CH_{arom}), 7.53 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH_2), 62.1 (CH_3), 123.1 (C), 127.3 (C), 128.5 (2 CH), 129.6 (2 CH), 131.7 (2 CH), 132.3 (2 CH), 134.7 (C), 144.9 (C) ppm. HRMS (EI): calcd. for $C_{14}H_{13}BrO_2S$ 323.9820; found 323.9814.

General Procedure for the Synthesis of Methyl Sulfones from Mesylhydrazones 7: A reaction tube under nitrogen atmosphere was charged with $FeCl_3$ (4.87 mg, 10 mol-%, 0.03 mmol). After 1 min, ethylmagnesium bromide (1.0 equiv.) and dioxane (1 mL) were added. The system was heated at 110 °C with stirring, and the corresponding mesylhydrazone **7** (0.3 mmol) dissolved in dioxane (1 mL) was added with a syringe pump over 3 to 10 h (0.333 to 0.100 mL/h). After addition, the reaction mixture was kept at 110 °C for an additional 24 h (GC–MS monitoring). When the reaction was complete, the crude reaction mixture was allowed to reach room temperature, the solvent was eliminated, and 1 M HCl and dichloromethane were added, and the layers were separated. The aqueous phase was extracted three times with dichloromethane. The combined organic layers were washed with two portions of 1 M HCl and brine and then dried with $MgSO_4$, and filtered. The solvent was removed under reduced pressure. If necessary, the products were purified by chromatography on silica gel.

1-Methyl-4-[1-(methylsulfonyl)ethyl]benzene (8a): *N*′-(1-*p*-Tolylethylidene)methanesulfonohydrazide (67.9 mg, 0.3 mmol) afforded **8a** (31.5 mg, 53% yield) as a yellow solid (m.p. 80.6–83.6 °C). Compound **8a** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 1:1.5). R_f (hexanes/ethyl acetate, 1:1.5) = 0.13. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.79 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CHCH_3), 2.38 (s, 3 H, CH_3), 2.65 (s, 3 H, CH_3), 4.18 (q, $^3J_{H,H}$ = 7.2 Hz, 1 H, CHCH$_3$), 7.22 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, CH_{arom}), 7.34 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5 (CH_3), 21.0 (CH_3), 37.6 (CH_3), 64.4 (CH), 128.7 (2 CH), 129.6 (2 CH), 131.3 (C), 139.1 (C) ppm. HRMS (EI): calcd. for $C_{10}H_{14}O_2S$ 198.0715; found 198.0715.

1-Chloro-3-[1-(methylsulfonyl)ethyl]benzene (8b): *N*′-[1-(3-Chlorophenyl)ethylidene]methanesulfonohydrazide (74.0 mg, 0.3 mmol) afforded **8b** (37.4 mg, 57% yield) as a yellow oil. Compound **8b** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 1:1). R_f (hexanes/ethyl acetate, 1:1) = 0.43. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.77 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CHCH_3), 2.68 (s, 3 H, CH_3), 4.15 (q, $^3J_{H,H}$ = 7.2 Hz, 1 H, CHCH$_3$), 7.30–7.39 (m, 3 H, CH_{arom}), 7.42–7.48 (m, 1 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 (CH_3), 37.9 (CH_3), 64.1 (CH), 127.1 (CH), 128.9 (CH), 129.3 (CH), 130.2 (CH), 134.9 (C), 136.3 (C) ppm. HRMS (EI): calcd. for $C_9H_{11}ClO_2S$ 218.0168; found 218.0168.

1-Methoxy-4-[(methylsulfonyl)methyl]benzene (8c):[24] *N*′-(4-Methoxybenzylidene)methanesulfonohydrazide (68.5 mg, 0.3 mmol) afforded **8c** (45.1 mg, 75% yield) as a white solid (m.p. 108.0–122.0 °C). Compound **8c** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 1:1.5). R_f (hexanes/ethyl acetate, 1:1.5) = 0.10. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.76 (s, 3 H, CH_3), 3.84 (s, 3 H, CH_3), 4.19–4.22 (br. s, 2 H, CH_2), 6.95 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, CH_{arom}), 7.35 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.7 (CH_3), 55.3 (CH_3), 60.6 (CH_2), 114.5 (2 CH), 120.0 (C), 131.6 (2 CH), 160.2 (C) ppm. HRMS (EI): calcd. for $C_9H_{12}O_3S$ 200.0507; found 200.0509.

1-Bromo-3-[(methylsulfonyl)methyl]benzene (8d): *N*′-(3-Bromobenzylidene)methanesulfonohydrazide (83.1 mg, 0.3 mmol) afforded **8d** (54.6 mg, 73% yield) as a yellow solid (m.p. 88.0–103.0 °C). Compound **8d** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 1:1). R_f (hexanes/ethyl acetate, 1:1) = 0.57. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.54 (s, 3 H, CH_3), 3.71 (s, 2 H, CH_2), 6.24–6.31 (m, 1 H, CH_{arom}), 6.33–6.37 (m, 1 H, CH_{arom}), 6.46–6.54 (m, 2 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.3 (CH_3), 60.5 (CH_2), 123.0 (C), 129.1 (CH), 130.2 (C), 130.6 (CH), 132.3 (CH), 133.3 (CH) ppm. HRMS (EI): calcd. for $C_8H_9BrO_2S$ 249.9486; found 249.9501.

2-[(Methylsulfonyl)methyl]benzofuran (8e): *N*′-(Benzofuran-2-ylmethylene)methanesulfonohydrazide (94.3 mg, 0.3 mmol) afforded **8e** (44.8 mg, 71% yield) as a pale brown solid (m.p. 131.5–138.5 °C). Compound **8e** was purified by flash chromatography on silica gel (hexanes/ethyl acetate, 1:1.5). R_f (hexanes/ethyl acetate, 1:1.5) = 0.10. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.67 (s, 3 H, CH_3), 3.93 (s, 2 H, CH_2), 5.95–5.98 (m, 1 H, CH_{arom}), 6.23–6.35 (m, 2 H, CH_{arom}), 6.45 (d, $^3J_{H,H}$ = 6.7 Hz, 1 H, CH_{arom}), 6.54 (d, $^3J_{H,H}$ = 6.7 Hz, 1 H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.3 (CH_3), 54.8 (CH_2), 109.1 (CH), 111.3 (CH), 121.4 (CH), 123.4 (CH), 125.2 (CH), 127.9 (C), 145.1 (C), 155.3 (C) ppm. HRMS (EI): calcd. for $C_{10}H_{10}O_3S$ 210.0351; found 210.0359.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H and ^{13}C NMR spectra of compounds **6** and **8**.

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