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Base-Promoted Direct Synthesis of Sulfinates from *N*-Sulfonylhydrazones under Metal-Free Conditions

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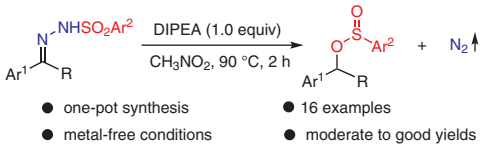

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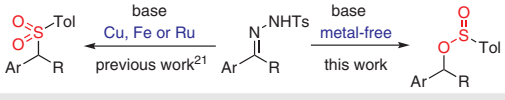
Abstract A base-promoted direct synthesis of sulfinates from *N*-sulfonylhydrazones is described. Various *N*-sulfonylhydrazones, derived from aldehydes and ketones, are converted into the corresponding sulfinates in moderate to good yields. This protocol possesses many advantages such as readily available and stable starting materials, broad substrate scope, and metal-free reaction conditions.

Key words sulfinates, hydrazones, DIPEA, carbonyl compounds, sulfonylhydrazines

Sulfinates are one class of the most versatile intermediates in organic synthesis.[1] They display a broad range of biological activities, such as stimulating the glucose uptake in muscle cells,[2] regulating the mitochondrial function of the Parkinsonism protein DJ-1,[3] employing as chemical probes in living cells,[4] etc.[5] In addition, sulfinates behave as both nucleophilic and electrophilic reagents, which provide convenient access to various sulfur compounds including sulfoxides,[6,7] sulfinamides,[8] sulfones,[9] and thioethers.[10]

In general, sulfinates could be produced by sulfination of sulfinyl cation $[ArS{=}O]^+$ or sulfinyl radical $[ArS{=}O]^\bullet$ with alcohols. The sulfinyl cation $[ArS{=}O]^+$ and radical $[ArS{=}O]^\bullet$ are in situ generated by activation of various different precursors, such as sulfinyl chloride,[11] sulfinic acids[12] (salts),[13] sulfonyl chlorides,[14] and sulfonylhydrazides,[15] or by oxidation of thiols[16] and disulfides.[17] In addition, other synthetic methods for sulfinates, such as substitution of benzyl alcohols with arylsulfonylmethyl isocyanides,[5b,18] are also described.[19]

On the other hand, *N*-tosylhydrazones, as precursors of diazo compounds, have been employed as building blocks for the construction of C–C, C–O, C–N, C–B, and C–Si bonds.[20] Usually, decomposition of *N*-tosylhydrazones generates the sulfones in the presence of suitable metal catalysts (e.g., copper, iron, and rhodium) and bases under heating conditions (Scheme 1).[21] However, the synthesis of sulfinates from *N*-tosylhydrazones is difficult, which has been accomplished by special strategies such as using the Wittig ylide in a polar aprotic solvent.[22] Despite these advances, general efficient methods to access sulfinates from *N*-tosylhydrazones under simple conditions remain in demand. Considering the importance of sulfinates in the area of chemical and biological sciences,[1–10] based on our recent work on the sulfinates[5b,13a,18c] and *N*-tosylhydrazones,[23] we would like to report here a base-promoted direct synthesis of sulfinates from *N*-tosylhydrazones under metal-free conditions (Scheme 1).



Scheme 1 Synthetic application of *N*-tosylhydrazones

4-Nitrobenzaldehyde *N*-tosylhydrazone (**1a**) was selected as a model substrate for optimizing the reaction conditions (Table 1). Reaction of **1a** with K_2CO_3 (1.0 equiv) at 90 °C for 2 hours afforded the desired sulfinate **2a** in 44% yield (Table 1, entry 1). The choice of bases was important for this reaction. The reaction was achieved in 12–50% yields with the use of various inorganic and organic bases, including Cs_2CO_3, KOH, DIPEA, Et_3N, DMAP, and DBU (entries 2–7). However, DIPEA was selected in our next investigations because it displayed the best efficiency (entries 1–7). Solvent played an important role in this transformation. With the use of various solvents including DCE, 1,4-dioxane, CH_3CN, DMSO, and DMF in comparison to CH_3NO_2, lower yields were found (entries 4 and 8–12). The effect of different temperatures was also investigated, and the reaction at 90 °C was found to give the sulfinate **2a** in higher yield (entries 4 and 13–16). Further parameter optimizations identified

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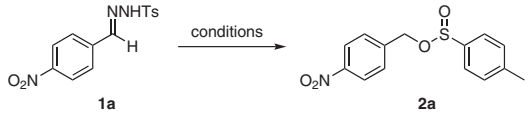
the most effective loading of DIPEA was 1.0 equivalent (entries 4 and 17–19). The reaction was also carried out under argon atmosphere, and the same yield was found, which indicated that oxygen atmosphere is not necessary for this reaction (entry 20). Furthermore, scaling up *N*-tosylhydrazone **1a** to 1.28 g, the reaction afforded the yield at a good level (entry 21).

Table 1 Optimization of the Reaction Conditions[a]



1a **2a**

Entry	Base (equiv)[b]	Solvent	Temp (°C)	Yield (%)[c]
1	K_2CO_3 (1.0)	CH_3NO_2	90	44
2	Cs_2CO_3 (1.0)	CH_3NO_2	90	42
3	KOH (1.0)	CH_3NO_2	90	40
4	DIPEA (1.0)	CH_3NO_2	90	50
5	Et_3N (1.0)	CH_3NO_2	90	42
6	DMAP (1.0)	CH_3NO_2	90	12
7	DBU (1.0)	CH_3NO_2	90	15
8	DIPEA (1.0)	DCE	90	18
9	DIPEA (1.0)	1,4-dioxane	90	20
10	DIPEA (1.0)	CH_3CN	90	23
11	DIPEA (1.0)	DMSO	90	26
12	DIPEA (1.0)	DMF	90	45
13	DIPEA (1.0)	CH_3NO_2	30	30
14	DIPEA (1.0)	CH_3NO_2	50	40
15	DIPEA (1.0)	CH_3NO_2	70	45
16	DIPEA (1.0)	CH_3NO_2	110	48
17	DIPEA (0.5)	CH_3NO_2	90	26
18	DIPEA (2.0)	CH_3NO_2	90	48
19	DIPEA (3.0)	CH_3NO_2	90	45
20[d]	DIPEA (1.0)	CH_3NO_2	90	50
21[e]	DIPEA (1.0)	CH_3NO_2	90	48

[a] General conditions: **1a** (0.2 mmol) and base (0.1–0.6 mmol) in solvent (1.0 mL) at 30–110 °C for 2 h.
[b] DIPEA: *N*,*N*-Diisopropylethylamine; DMAP: 4-dimethylaminopyridine; DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene.
[c] Isolated yield.
[d] Under argon.
[e] Reaction was carried out on a 1.28 g scale of **1a** (4.0 mmol).

After the optimized reaction conditions in hand, the scope of the reaction with various sulfonylhydrazones was subsequently investigated (Table 2). Arylaldehyde-derived *N*-tosylhydrazones **1a–h**, with their aromatic rings bearing hydrogen atoms, electron-donating, and electron-withdrawing groups at the *ortho*-, *meta*-, and *para*-positions, reacted smoothly in the presence of DIPEA (1.0 equiv) at 90 °C to afford sulfinates **2a–h** in moderate to good yields within 2 hours (Table 2, entries 1–8). Arylketone-derived *N*-tosylhydrazones **1i–k** reacted well under the standard conditions to afford sulfinates **2i–k** in moderate to good yields (entries 9–11). Sulfonyl-derived hydrazones **1l–p** could afford the corresponding sulfinates **2l–p** in good yields (entries 12–16). No reaction took place on treatment of alkylaldehyde-derived *N*-tosylhydrazones **1q** under the standard conditions, and the starting material could be recovered (entry 17). *N*-Alkylated hydrazones **3b–e** and **3j–k** were observed as by-products in some of the above reactions (entries 2–5 and 10, 11). However, these compounds **3** containing nitro groups were not detected, which are consistent with the literature.[24]

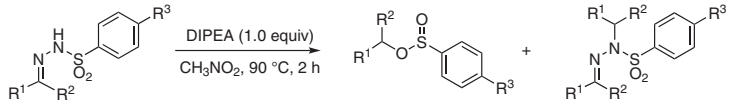
Sulfonylhydrazones can be readily prepared by mixing sulfonyl hydrazides with the corresponding carbonyl compounds. The one-pot synthesis of sulfinates **2** from carbonyl compounds **4** and sulfonyl hydrazines **5** without the isolation of arylsulfonylhydrazone intermediates was also investigated.

To our delight, after heating carbonyl compounds **4** and arylsulfonyl hydrazides **5** at 25 °C for 2 hours, followed by the addition of DIPEA, and stirring the mixture at 90 °C for another 2 hours, the desired sulfinates **2** were gained in similar yields, but without the need to isolate the arylsulfonylhydrazone intermediates **1** (Table 3).

To gain insight into the reaction mechanism, several control experiments were carried out (Scheme 2). The reaction of *N*-tosylhydrazone **1a** still proceeded, when the radical scavenger TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, Scheme 2a) or BHT (butylated hydroxytoluene, Scheme 2b) was added. These results ruled out the possibility of a radical process. By treating *N*-alkylated hydrazone **3d** in the presence of DIPEA (1.0 equiv) in CH_3NO_2 at 90 °C for 2 hours, no reaction took place and the starting material **3d** was recovered (Scheme 2c). These results indicated that the reactions probably underwent a cleavage of the N–H bond. The crossover experiment by employing two different arylsulfonylhydrazones was next investigated. The reaction of arylsulfonylhydrazones **1f** (1.0 equiv) and **1l** (1.0 equiv) under the standard conditions gave an equimolar mixture of sulfinates **2a**, **2f**, **2l**, and **2p** as indicated by ^{1}H NMR analysis (Scheme 2d). This result indicated that the reaction might involve an intermolecular pathway.

Based on the above results and related reports in the literature,[22] a possible reaction mechanism is illustrated in Scheme 3. First, hydrazone anions **6** are formed in the presence of base from hydrazones **1**. Tautomerization of hydrazone anions **6**, followed by protonation with the Base-H lead to intermediates **7**. Subsequently, the nucleophilic O-attack of the intermediates **7** onto another molecule of intermediates **7** generates the desired sulfinates **2** by releasing N_2. On the other hand, nucleophilic substitution reaction of the intermediates **7** with hydrazone anions **6** can form the *N*-alkylated hydrazones **3**.

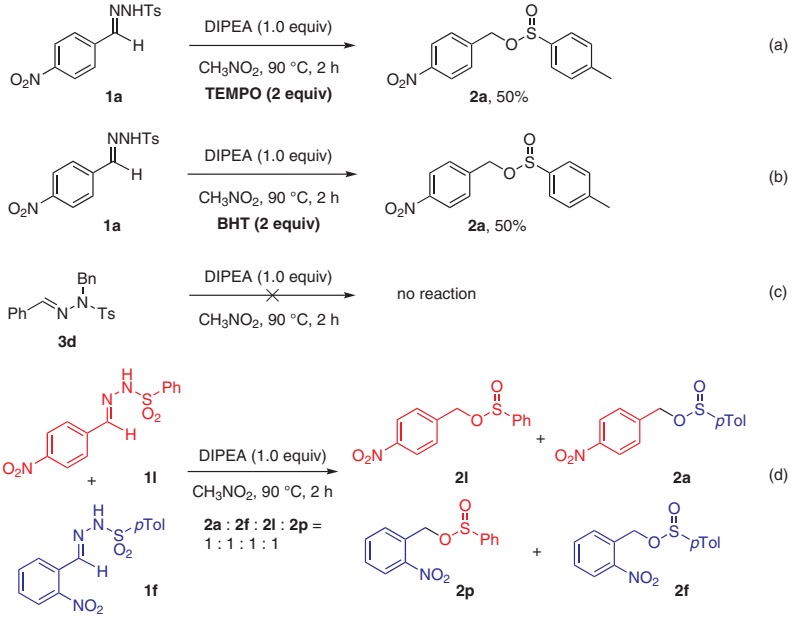
Table 2 Synthesis of Various Sulfinates[a]



1 2 3

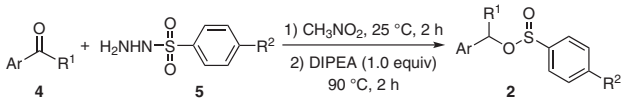
Entry	1	R^1	R^2	R^3	Yield (%)[b] of 2/3
1	**1a**	4-$NO_2C_6H_4$	H	CH_3	50/N.D.
2	**1b**	4-ClC_6H_4	H	CH_3	50/17
3	**1c**	4-$CF_3C_6H_4$	H	CH_3	45/10
4	**1d**	Ph	H	CH_3	53/15
5	**1e**	4-$CH_3C_6H_4$	H	CH_3	48/16
6	**1f**	2-$NO_2C_6H_4$	H	CH_3	52/N.D.
7	**1g**	2-NO_2-5-FC_6H_3	H	CH_3	54/N.D.
8	**1h**	2-NO_2-5-ClC_6H_3	H	CH_3	48/N.D.
9	**1i**	4-$NO_2C_6H_4$	CH_3	CH_3	46/N.D.
10	**1j**	4-$CF_3C_6H_4$	CH_3	CH_3	52/20
11	**1k**	4-$CF_3C_6H_4$	Et	CH_3	60/20
12	**1l**	4-$NO_2C_6H_4$	H	H	52/N.D.
13	**1m**	4-$NO_2C_6H_4$	H	OCH_3	54/N.D.
14	**1n**	4-$NO_2C_6H_4$	H	*t*-Bu	6/N.D.
15	**1o**	4-$NO_2C_6H_4$	H	Br	51/N.D.
16	**1p**	2-$NO_2C_6H_4$	H	H	51/N.D.
17	**1q**	*t*-Bu	H	CH_3	N.R.

[a] General conditions: **1** (0.5 mmol) and DIPEA (0.5 mmol) in CH_3NO_2 (2.0 mL) at 90 °C for 2 h.
[b] Isolated yield. N.R.: No reaction. N.D.: Not detected.



Scheme 2 Control experiments

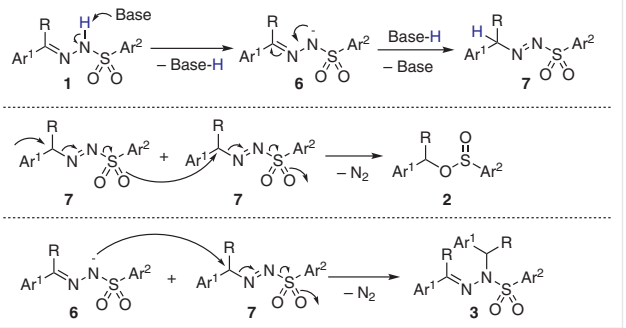
Table 3 Synthesis of Various Sulfinates from Carbonyl Compounds and Sulfonylhydrazines[a]



4 5 2

Entry	4	Ar	R^1	5	R^2	Yield (%)[b] of 2
1	**4a**	4-$NO_2C_6H_4$	H	**5a**	CH_3	**2a**, 48
2	**4d**	Ph	H	**5a**	CH_3	**2d**, 49
3	**4e**	4-$CH_3C_6H_4$	H	**5a**	CH_3	**2e**, 43
4	**4i**	4-$NO_2C_6H_4$	CH_3	**5a**	CH_3	**2i**, 42
5	**4l**	4-$NO_2C_6H_4$	H	**5b**	H	**2l**, 48

[a] General conditions: (1) **4** (0.5 mmol) and **5** (0.5 mmol) in CH_3NO_2 (2.0 mL) at 25 °C for 2 h; (2) DIPEA (0.5 mmol) was added and stirred at 90 °C for 2 h.
[b] Isolated yield.



Scheme 3 Proposed mechanism

As reported previously, the synthesis of sulfones from sulfonylhydrazones is usually performed under the metal reaction conditions.[21] The reaction of metal catalyst and sulfinate anions could generate an active 'M–SO_2Ar' species, which reacts with diazo cations to form the arylsulfonyl-metal-carbene species. A subsequent $ArSO_2$-migratory insertion and protonation deliver the final product.[20d,21b–d] In contrast with sulfone synthesis, our sulfinate synthesis were performed under metal-free conditions, in which hydrazones might not be decomposed to sulfinate anions and the nucleophile is still the sulfone function (Scheme 3). As the sulfur atom of a sulfone exhibits a partial positive charge, one of the oxygen atoms, exhibiting a partial negative charge, acts as the attacking atom and thus facilitates the formation of a sulfinate.[18c] Moreover, the tetrahedral-like sulfur atom is sterically crowded, which might prevent it to act as the attacking atom and thus obviates the formation of a sulfone.

In summary, we have developed a facile synthesis of sulfinates from *N*-sulfonylhydrazones by using base as a promoter. A wide variety of sulfinates were obtained in moderate to good yields. The reactions were performed under metal-free conditions, which offers attractive industrial prospects. Sulfinates were also provided from carbonyl compounds and sulfonylhydrazines without the isolation of arylsulfonylhydrazone intermediates. One drawback of the sulfinate synthesis is that some *N*-alkylated hydrazones were formed as by-products. Further applications of this method are ongoing in our laboratory.

All commercially available chemicals used were from commercial sources without any further purification. Melting points were gained on a Gongyi X-5 microscopy digital melting point apparatus and are uncorrected. High-resolution mass spectra (HRMS) were recorded on an Electrothemal LTQ-Orbitrap mass spectrometer. IR spectra were recorded on an Electrothemal Nicolet 380 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz NMRn spectrometer. All signals for protons are recorded in ppm using the residual NMR solvent signal as an internal reference ($CDCl_3$, 7.26 ppm). All signals for carbon resonances are recorded in ppm using the residual NMR solvent signal as an internal reference ($CDCl_3$, 77.0 ppm).

Sulfinates from *N*-Sulfonylhydrazones; General Procedure

A mixture of a *N*-sulfonylhydrazone **1** (0.5 mmol, 1 equiv) and DIPEA (65 mg, 0.5 mmol, 1 equiv) in CH_3NO_2 (2.0 mL) was stirred at 90 °C for 2 h. After completion of the reaction, H_2O (5 mL) and EtOAc (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed by brine, dried (anhyd Na_2SO_4), filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh, elution with 15% EtOAc in PE) to afford the desired sulfinates **2**. In addition, *N*-alkylated hydrazone products **3** were also formed in some examples.

4-Nitrobenzyl 4-Methylbenzenesulfinate (2a)

Yellow solid; yield: 72.7 mg (50%); mp 38–40 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 7.8 Hz, 2 H), 7.62 (d, *J* = 7.1 Hz, 2 H), 7.42 (d, *J* = 7.7 Hz, 2 H), 7.35 (d, *J* = 7.3 Hz, 2 H), 5.07 (d, *J* = 12.6 Hz, 1 H), 4.59 (d, *J* = 12.6 Hz, 1 H), 2.42 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.4, 143.2, 142.9, 140.8, 129.7, 128.4, 125.0, 123.4, 63.2, 21.3.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{14}NO_4S$ [M + H]$^+$: 292.0638; found: 292.0645.

4-Chlorobenzyl 4-Methylbenzenesulfinate (2b)

Yellow liquid; yield: 70.0 mg (50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.1 Hz, 2 H), 7.33 (d, *J* = 7.9 Hz, 2 H), 7.27 (d, *J* = 8.2 Hz, 2 H), 7.19 (d, *J* = 8.3 Hz, 2 H), 4.97 (d, *J* = 11.6 Hz, 1 H), 4.50 (d, *J* = 11.6 Hz, 1 H), 2.42 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7, 141.2, 134.0, 133.9, 129.6, 129.5, 128.4, 125.0, 64.2, 21.2.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{13}ClO_2SNa$ [M + Na]$^+$: 303.0217; found: 303.0223.

N-(4-Chlorobenzyl)-*N*′-(4-chlorobenzylidene)-4-methylbenzenesulfonohydrazide (3b)

White solid; yield: 36.7 mg (17%); mp 146–148 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.3 Hz, 2 H), 7.54 (s, 1 H), 7.45 (d, *J* = 8.5 Hz, 2 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 7.29–7.27 (m, 2 H), 7.31–7.24 (m, 6 H), 4.82 (s, 2 H), 2.42 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.2, 144.3, 136.0, 134.2, 133.7, 133.4, 132.2, 129.6, 129.0, 128.8, 128.4, 128.2, 128.0, 51.3, 21.5.

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{19}Cl_2N_2O_2S$ [M + H]$^+$: 433.0539; found: 433.0546.

4-(Trifluoromethyl)benzyl 4-Methylbenzenesulfinate (2c)

Yellow liquid; yield: 70.6 mg (45%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.1 Hz, 2 H), 7.56 (d, *J* = 8.1 Hz, 2 H), 7.37 (d, *J* = 8.1 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 5.05 (d, *J* = 12.1 Hz, 1 H), 4.58 (d, *J* = 12.1 Hz, 1 H), 2.41 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.1, 141.2, 139.7, 130.3 (q, $J_{C,F}$ = 32.4 Hz), 129.7, 128.3, 125.3 (q, $J_{C,F}$ = 3.7 Hz), 125.2, 123.9 (q, $J_{C,F}$ = 272.1 Hz), 64.0, 21.3.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{13}F_3O_2SNa$ [M + Na]$^+$: 337.0481; found: 337.0487.

4-Methyl-*N*-[4-(trifluoromethyl)benzyl]-*N*′-[4-(trifluoromethyl)-benzylidene]benzenesulfonohydrazide (3c)

White liquid; yield: 25 mg (10%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.1 Hz, 2 H), 7.63–7.55 (m, 6 H), 7.51 (s, 1 H), 7.46 (d, *J* = 8.0 Hz, 2 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 5.00 (s, 2 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6, 143.0, 139.1, 137.0, 134.3, 131.6 (q, $J_{C,F}$ = 32.6 Hz), 130.2 (q, $J_{C,F}$ = 32.4 Hz), 129.7, 128.1, 127.4, 126.9, 126.0 (q, $J_{C,F}$ = 3.5 Hz), 125.5 (q, $J_{C,F}$ = 3.7 Hz), 123.9 (q, $J_{C,F}$ = 272.2 Hz), 123.8 (q, $J_{C,F}$ = 272.2 Hz), 51.0, 21.5.

HRMS (ESI): *m*/*z* calcd for $C_{23}H_{19}F_6N_2O_2S$ [M + H]$^+$: 501.1066; found: 501.1069.

Benzyl 4-Methylbenzenesulfinate (2d)

Pale yellow liquid; yield: 65.1 mg (53%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.6 Hz, 2 H), 7.34–7.29 (m, 7 H), 5.05 (d, *J* = 11.4 Hz, 1 H), 4.57 (d, *J* = 11.4 Hz, 1 H), 2.41 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.4, 141.3, 135.2, 129.4, 128.1, 128.0, 124.9, 65.1, 21.1.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{14}O_2SNa$ [M + Na]$^+$: 269.0607; found: 269.0613.

***N*-Benzyl-*N*′-benzylidene-4-methylbenzenesulfonohydrazide (3d)**

Yellow solid; yield: 27.3 mg (15%); mp 108–110 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.2 Hz, 2 H), 7.64 (s, 1 H), 7.54–7.52 (m, 2 H), 7.40–7.26 (m, 10 H), 4.90 (s, 2 H), 2.42 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.1, 143.9, 135.2, 134.4, 133.8, 129.9, 129.4, 128.7, 128.3, 128.0, 127.5, 127.1, 126.6, 51.7, 21.3.

HRMS (ESI): *m*/*z* calcd for $C_{21}H_{21}N_2O_2S$ [M + H]$^+$: 365.1318; found: 365.1324.

4-Methylbenzyl 4-Methylbenzenesulfinate (2e)

Yellow liquid; yield: 62.4 mg (48%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 7.9 Hz, 2 H), 7.17 (d, *J* = 7.9 Hz, 2 H), 7.12 (d, *J* = 7.9 Hz, 2 H), 5.00 (d, *J* = 11.2 Hz, 1 H), 4.52 (d, *J* = 11.2 Hz, 1 H), 2.40 (s, 3 H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.3, 141.3, 137.8, 132.1, 129.3, 128.8, 128.3, 124.9, 65.2, 21.0, 20.8.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{16}O_2SNa$ [M + Na]$^+$: 283.0763; found: 283.0772.

4-Methyl-*N*-(4-methylbenzyl)-*N*′-(4-methylbenzylidene)benzene-sulfonohydrazide (3e)

White solid; yield: 31.3 mg (16%); mp 150–152 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (dd, *J* = 8.2, 1.6 Hz, 2 H), 7.69 (s, 1 H), 7.46 (d, *J* = 7.8 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.29–7.27 (m, 2 H), 7.16–7.13 (m, 4 H), 4.82 (s, 2 H), 2.42 (s, 3 H), 2.34 (s, 3 H), 2.33 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.4, 143.8, 140.2, 137.0, 134.4, 132.3, 131.1, 129.3, 129.0, 128.0, 127.2, 126.7, 51.8, 21.3, 21.2, 20.8.

HRMS (ESI): *m*/*z* calcd for $C_{23}H_{25}N_2O_2S$ [M + H]$^+$: 393.1631; found: 393.1634.

2-Nitrobenzyl 4-Methylbenzenesulfinate (2f)

Yellow solid; yield: 75.6 mg (52%); mp 30–32 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.2 Hz, 1 H), 7.67–7.57 (m, 4 H), 7.42 (t, *J* = 7.7 Hz, 1 H), 7.32 (d, *J* = 7.9 Hz, 2 H), 5.41 (d, *J* = 14.5 Hz, 1 H), 5.01 (d, *J* = 14.5 Hz, 1 H), 2.40 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.0, 143.1, 141.0, 133.6, 132.2, 129.7, 129.3, 128.6, 124.9, 124.6, 62.3, 21.3.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{13}NO_4SNa$ [M + Na]$^+$: 314.0457; found: 314.0464.

5-Fluoro-2-nitrobenzyl 4-Methylbenzenesulfinate (2g)

Yellow solid; yield: 83.4 mg (54%); mp 36–38 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (dd, *J* = 9.0, 5.0 Hz, 1 H), 7.66 (d, *J* = 8.0 Hz, 2 H), 7.46 (dd, *J* = 9.3, 1.9 Hz, 1 H), 7.37 (d, *J* = 7.9 Hz, 2 H), 7.14–7.09 (m, 1 H), 5.45 (d, *J* = 15.6 Hz, 1 H), 5.03 (d, *J* = 15.6 Hz, 1 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4 (d, $J_{C,F}$ = 257.8 Hz), 143.5, 142.8 (d, $J_{C,F}$ = 3.2 Hz), 140.9, 137.0 (d, $J_{C,F}$ = 9.2 Hz), 129.9, 127.9 (d, $J_{C,F}$ = 9.9 Hz), 125.1, 116.2 (d, $J_{C,F}$ = 25.8 Hz), 115.4 (d, $J_{C,F}$ = 23.5 Hz), 61.8, 21.5.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{13}FNO_4S$ [M + H]$^+$: 310.0544; found: 310.0550.

5-Chloro-2-nitrobenzyl 4-Methylbenzenesulfinate (2h)

Pale yellow liquid; yield: 78.0 mg (48%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.7 Hz, 1 H), 7.70 (d, *J* = 2.1 Hz, 1 H), 7.65 (d, *J* = 8.2 Hz, 2 H), 7.41 (dd, *J* = 8.8, 2.3 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 5.41 (d, *J* = 15.2 Hz, 1 H), 4.98 (d, *J* = 15.2 Hz, 1 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 143.5, 140.8, 140.6, 134.8, 129.9, 129.3, 128.6, 126.3, 125.1, 61.3, 21.5.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{13}ClNO_4S$ [M + H]$^+$: 326.0248; found: 326.0253.

1-(4-Nitrophenyl)ethyl 4-Methylbenzenesulfinate (2i)

The product was obtained as a 1:1 mixture of diastereomers; yellow solid; yield: 70.1 mg (46%); mp 41–43 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 8.6 Hz, 1 H), 8.06 (d, *J* = 8.6 Hz, 1 H), 7.59 (d, *J* = 8.1 Hz, 1 H), 7.52 (d, *J* = 8.6 Hz, 1 H), 7.49 (d, *J* = 8.1 Hz, 1 H), 7.35 (d, *J* = 7.9 Hz, 1 H), 7.28 (d, *J* = 8.6 Hz, 1 H), 7.20 (d, *J* = 7.9 Hz, 1 H),

5.48–5.42 (m, 1 H), 2.44 (s, 1.5 H), 2.36 (s, 1.5 H), 1.64 (d, *J* = 6.6 Hz, 1.5 H), 1.50 (d, *J* = 6.6 Hz, 1.5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 148.8, 147.5, 147.2, 143.2, 143.1, 141.9, 141.5, 129.7, 129.4, 127.0, 126.9, 125.1, 124.9, 123.8, 123.4, 74.4, 73.1, 24.4, 24.0, 21.5, 21.4.

HRMS (ESI): *m*/*z* calcd for $C_{15}H_{15}NO_4SNa$ [M + Na]$^+$: 328.0614; found: 328.0619.

1-[4-(Trifluoromethyl)phenyl]ethyl 4-Methylbenzenesulfinate (2j)

First eluted fraction: Yellow solid; yield: 42.6 mg (26%); mp 37–39 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.1 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.1 Hz, 2 H), 7.14 (d, *J* = 7.9 Hz, 2 H), 5.41 (q, *J* = 6.7 Hz, 1 H), 2.32 (s, 3 H), 1.62 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.5, 142.7, 141.5, 129.6 (q, $J_{C,F}$ = 32.4 Hz), 129.2, 126.3, 125.1, 125.0 (q, $J_{C,F}$ = 3.8 Hz), 123.9 (q, $J_{C,F}$ = 272.1 Hz), 73.4, 24.1, 21.1.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{15}F_3O_2SNa$ [M + Na]$^+$: 351.0637; found: 351.0639.

Second eluted fraction; Yellow solid; yield: 42.6 mg (26%); mp 31–33 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.2 Hz, 2 H), 7.59 (d, *J* = 8.2 Hz, 2 H), 7.49 (d, *J* = 8.2 Hz, 2 H), 7.33 (d, *J* = 8.2 Hz, 2 H), 5.46 (q, *J* = 6.6 Hz, 1 H), 2.42 (s, 3 H), 1.52 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.8, 142.9, 142.2, 130.2 (q, $J_{C,F}$ = 32.4 Hz), 129.6, 126.5, 125.5 (q, $J_{C,F}$ = 3.7 Hz), 124.8, 123.9 (q, $J_{C,F}$ = 272.1 Hz), 75.2, 23.9, 21.3.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{15}F_3O_2SNa$ [M + Na]$^+$: 351.0637; found: 351.0641.

4-Methyl-*N*-{1-[4-(trifluoromethyl)phenyl]ethyl}-*N*′-{1-[4-(trifluoromethyl)phenyl]ethylidene}benzenesulfonohydrazide (3j)

Pale yellow solid; yield: 52.8 mg (20%); mp 128–130 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.2 Hz, 2 H), 7.72 (d, *J* = 8.2 Hz, 2 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 7.43–7.38 (m, 4 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 5.29 (q, *J* = 7.0 Hz, 1 H), 2.39 (s, 3 H), 2.39 (s, 3 H), 1.27 (d, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.7, 144.3, 143.9, 140.2, 134.4, 132.8 (q, $J_{C,F}$ = 32.6 Hz), 129.6 (q, $J_{C,F}$ = 32.4 Hz), 129.1, 128.3, 128.2, 127.5, 125.5 (q, $J_{C,F}$ = 3.7 Hz), 124.9 (q, $J_{C,F}$ = 3.6 Hz), 124.0 (q, $J_{C,F}$ = 272.1 Hz), 123.8 (q, $J_{C,F}$ = 272.3 Hz), 60.2, 21.3, 17.8.

HRMS (ESI): *m*/*z* calcd for $C_{25}H_{23}F_6N_2O_2S$ [M + H]$^+$: 529.1379; found: 529.1384.

1-[4-(Trifluoromethyl)phenyl]propyl 4-Methylbenzenesulfinate (2k)

First eluted fraction: Yellow solid; yield: 51.3 mg (30%); mp 28–30 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (t, *J* = 8.4 Hz, 4 H), 7.13 (d, *J* = 8.1 Hz, 2 H), 7.08 (d, *J* = 7.8 Hz, 2 H), 5.16 (t, *J* = 6.8 Hz, 1 H), 2.30 (s, 3 H), 1.98–1.77 (m, 2 H), 0.89 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6, 142.6, 141.4, 129.4 (q, $J_{C,F}$ = 32.3 Hz), 129.1, 126.7, 125.0, 124.8 (q, $J_{C,F}$ = 3.7 Hz), 123.9 (q, $J_{C,F}$ = 272.1 Hz), 78.0, 30.9, 21.1, 9.6.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{17}F_3O_2SNa$ [M + Na]$^+$: 365.0794; found: 365.0798.

Second eluted fraction: Yellow solid; yield: 51.3 mg (30%); mp 59–61 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.2 Hz, 2 H), 7.56 (d, *J* = 8.2 Hz, 2 H), 7.45 (d, *J* = 8.2 Hz, 2 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 5.21 (t, *J* = 6.7 Hz, 1 H), 2.40 (s, 3 H), 1.96–1.74 (m, 2 H), 0.85 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.7, 142.8, 142.3, 130.1 (q, $J_{C,F}$ = 32.4 Hz), 129.5, 126.9, 125.4 (q, $J_{C,F}$ = 3.7 Hz), 124.6, 123.9 (q, $J_{C,F}$ = 272.1 Hz), 80.8, 30.7, 21.2, 9.4.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{17}F_3O_2SNa$ [M + Na]$^+$: 365.0794; found: 365.0801.

4-Methyl-*N*-{1-[4-(trifluoromethyl)phenyl]propyl}-*N*′-{1-[4-(trifluoromethyl)phenyl]propylidene}benzenesulfonohydrazide (3k)

Yellow liquid; yield: 55.6 mg (20%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.2 Hz, 2 H), 7.74 (d, *J* = 8.3 Hz, 2 H), 7.37–7.31 (m, 6 H), 7.04 (d, *J* = 7.9 Hz, 2 H), 4.94 (dd, *J* = 10.0, 5.3 Hz, 1 H), 3.08–3.05 (m, 2 H), 2.33 (s, 3 H), 1.78–1.62 (m, 2 H), 0.94 (t, *J* = 7.6 Hz, 3 H), 0.70 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.8, 143.6, 141.9, 139.4, 134.6, 132.5 (q, $J_{C,F}$ = 32.6 Hz), 129.6 (q, $J_{C,F}$ = 32.2 Hz), 129.2, 128.8, 128.1, 128.0, 125.6 (q, $J_{C,F}$ = 3.6 Hz), 124.7 (q, $J_{C,F}$ = 3.6 Hz), 124.0 (q, $J_{C,F}$ = 272.0 Hz), 123.9 (q, $J_{C,F}$ = 272.4 Hz), 66.8, 23.6, 21.3, 11.3, 10.8.

HRMS (ESI): *m*/*z* calcd for $C_{27}H_{27}F_6N_2O_2S$ [M + H]$^+$: 557.1692; found: 557.1697.

4-Nitrobenzyl Benzenesulfinate (2l)

Yellow liquid; yield: 72.0 mg (52%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.1 Hz, 2 H), 7.72 (d, *J* = 7.1 Hz, 2 H), 7.57–7.50 (m, 3 H), 7.40 (d, *J* = 8.4 Hz, 2 H), 5.07 (d, *J* = 12.7 Hz, 1 H), 4.61 (d, *J* = 12.7 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.5, 143.6, 142.7, 132.5, 129.1, 128.4, 125.0, 123.4, 63.7.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{12}NO_4S$ [M + H]$^+$: 278.0482; found: 278.0487.

4-Nitrobenzyl 4-Methoxybenzenesulfinate (2m)

Yellow liquid; yield: 82.9 mg (54%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, *J* = 8.0 Hz, 2 H), 7.66 (d, *J* = 8.6 Hz, 2 H), 7.42 (d, *J* = 8.5 Hz, 2 H), 7.02 (d, *J* = 8.7 Hz, 2 H), 5.06 (d, *J* = 12.7 Hz, 1 H), 4.60 (d, *J* = 12.7 Hz, 1 H), 3.85 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9, 147.6, 143.1, 135.4, 128.5, 127.0, 123.5, 114.5, 63.1, 55.5.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{14}NO_5S$ [M + H]$^+$: 308.0587; found: 308.0591.

4-Nitrobenzyl 4-Methoxybenzenesulfinate (2n)

Yellow liquid; yield: 93.2 mg (56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.7 Hz, 2 H), 7.66 (d, *J* = 8.5 Hz, 2 H), 7.56 (d, *J* = 8.5 Hz, 2 H), 7.43 (d, *J* = 8.6 Hz, 2 H), 5.09 (d, *J* = 12.7 Hz, 1 H), 4.65 (d, *J* = 12.7 Hz, 1 H), 1.34 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.4, 147.7, 143.1, 140.9, 128.7, 126.2, 125.1, 123.6, 63.5, 35.1, 31.1.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{20}NO_4S$ [M + H]$^+$: 334.1108; found: 334.1112.

4-Nitrobenzyl 4-Bromobenzenesulfinate (2o)

Yellow liquid; yield: 90.4 mg (51%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.6 Hz, 2 H), 7.70 (d, *J* = 8.4 Hz, 2 H), 7.61 (d, *J* = 8.4 Hz, 2 H), 7.43 (d, *J* = 8.5 Hz, 2 H), 5.10 (d, *J* = 12.6 Hz, 1 H), 4.61 (d, *J* = 12.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.7, 143.0, 142.5, 132.5, 128.6, 127.5, 126.8, 123.7, 63.9.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{11}BrNO_4S$ [M + H]$^+$: 355.9587, found: 355.9591.

2-Nitrobenzyl Benzenesulfinate (2p)

Yellow liquid; yield: 70.6 mg (51%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.1 Hz, 1 H), 7.78–7.75 (m, 2 H), 7.70–7.55 (m, 5 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 5.46 (d, *J* = 14.4 Hz, 1 H), 5.05 (d, *J* = 14.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.2, 144.0, 133.7, 132.5, 132.2, 129.5, 129.1, 128.8, 125.1, 124.8, 62.7.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{12}NO_4S$ [M + H]$^+$: 278.0482; found: 278.0489.

One-Pot Synthesis of Sulfinates from Carbonyl Compounds and Sulfonylhydrazides; General Procedure

A solution of the carbonyl compound **4** (0.5 mmol, 1 equiv) and sulfonyl hydrazide **5** (65 mg, 0.5 mmol, 1 equiv) in $MeNO_2$ (2.0 mL) was stirred at 25 °C for 2 h. Then DIPEA (0.5 mmol, 1 equiv) was added to the reaction mixture. The mixture was stirred at 90 °C for another 2 h. After completion of the reaction, H_2O (5 mL) and EtOAc (10 mL) were added. The two layers were separated, and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed by brine, dried (anhyd Na_2SO_4), filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh, elution with 15% EtOAc in PE) to afford the desired sulfinates **2**.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690754.

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