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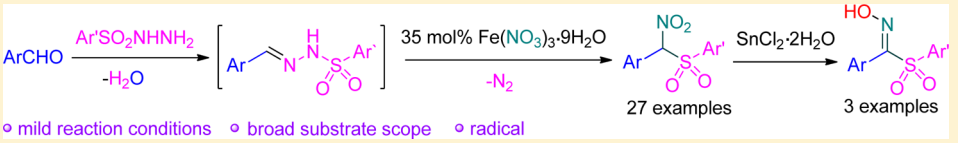
Iron(III)-Mediated Radical Nitration of Bisarylsulfonyl Hydrazones: Synthesis of Bisarylnitromethyl Sulfones

Dinabandhu Sar,[†] Raghunath Bag,[†] Debajyoti Bhattacharjee,[‡] Ramesh Chandra Deka,[‡] and Tharmalingam Punniyamurthy*[,†]

[†]Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati-781039, India

[‡]Department of Chemistry, Tezpur University, Tezpur-784028, India

Supporting Information

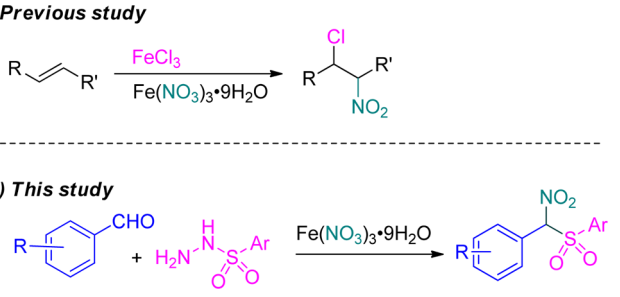


ABSTRACT: Iron(III)-mediated radical nitration of bisarylsulfonyl hydrazones is described. In this protocol, the nontoxic and inexpensive $Fe(NO_3)_3·9H_2O$ plays a dual role as catalyst as well as nitro source. The mild conditions, broad substrate scope, and the functional group compatibility are the significant features. The reaction pathway has been demonstrated using DFT calculations, and the products can be subsequently converted into oximes using $SnCl_2·2H_2O$ in high yields.

INTRODUCTION

Iron compounds have recently attracted significant interest in organic synthesis as nontoxic and inexpensive green elements.[1] Several studies have employed iron complexes as replacements for the expensive transition-metal catalysts such as Pd and Rh for the formation of carbon-heteroatom bonds.[2] In addition, $Fe(NO_3)_3·9H_2O$ is well-known to produce NO_2 radical on heating;[3,4] however, its application in synthetic chemistry is limited (Scheme 1a).[5] In continuation of our studies on bisarylhydrazones,[6] we report here an $Fe(NO_3)_3·9H_2O$-mediated radical nitration of bisarylsulfonyl hydrazones at moderate temperature (Scheme 1b). The broad substrate scope, use of nontoxic iron salt as the nitro source, and the readily accessible aryl aldehydes and arylsulfonyl hydrazides as the substrate precursors are the significant practical features. The reaction pathway is analyzed using density functional theory (DFT).

Scheme 1. Iron(III)-Mediated Radical Nitrations



The chemistry of nitroalkanes[7] and sulfones[8] continues to attract the attention of chemists as they comprise a synthetically important class of compounds for the generation of molecules of pharmaceutical relevance.[9] They are widely used in different efficient stereoselective carbon−carbon bond forming reactions and subsequent numerous functional group transformations. For examples, nitroalkanes are utilized in stereoselective Henry reaction[10] and Michael addition,[11] and for the generation of oximes, amines, and carbonyl compounds,[12] while aryl sulfones are substrate precursors for Julia olefination,[13] aldol reaction,[14] and Michael addition,[15] and for the generation of ketones and alkanes by desulfonylation.[16] Aryl nitroalkanes are demonstrated as key intermediates in the total synthesis of manzamine A[17] and (−)-nutlin-3.[18] Development of effective methods for the construction of nitromethane[19,20] with aryl and sulfonyl groups[21] would thus be valuable as they may serve as a precursor to an array of useful structural scaffolds (Scheme 2).[22]

RESULTS AND DISCUSSION

We commenced the optimization studies with aldehyde **1a** and *p*-toluenesulfonyl hydrazide **2a** as test substrates using a series of nitro sources in different solvents at varied temperature (Table 1). To our delight, the reaction occurred to give bisarylnitromethyl sulfone **3a** in 63% yield when the substrates **1a** and **2a** were stirred at 60 °C for 0.5 h in 1,2-dichloroethane (DCE) followed by at 80 °C for 1.5 h with $Fe(NO_3)_3·9H_2O$. In a set of nitro sources screened, $Fe(NO_3)_3·9H_2O$ gave **3a** in 51% yield, while $Cu(NO_3)_2·3H_2O$ afforded the target product in 38% yield (entries 1−2). In contrast, $Ca(NO_3)_2·4H_2O$, $Bi(NO_3)_3·5H_2O$, ^{t}BuONO, and $AgNO_3$ failed to react, and the formation of **3a** was not observed. DCE was found to be a solvent of choice, while CH_3CN, toluene and 1,4-dioxane gave

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Scheme 2. Some of the Possible Utilities of the Products

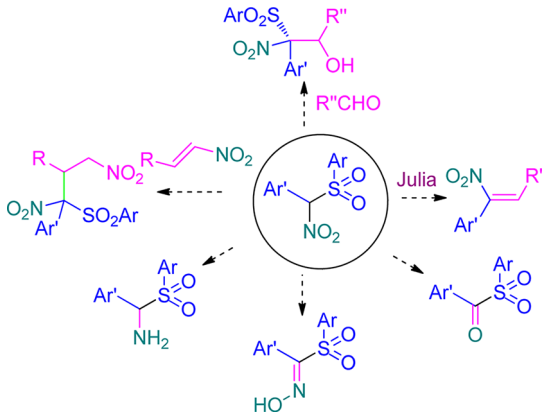
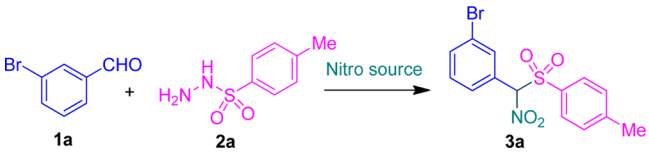


Table 1. Optimization of the Reaction Conditions[a]



entry	nitro source (mol %)	solvents	yield (%)
1	$Cu(NO_3)_2·3H_2O$ (50)	DCE	38
2	$Fe(NO_3)_3·9H_2O$ (35)	DCE	51
3	$Fe(NO_3)_3·9H_2O$ (35)	toluene	47
4	$Fe(NO_3)_3·9H_2O$ (35)	CH_3CN	38
5	$Fe(NO_3)_3·9H_2O$ (35)	dioxane	36
6	$Fe(NO_3)_3·9H_2O$ (35)	THF	trace
7	$Fe(NO_3)_3·9H_2O$ (35)	DMF	trace
8	$Fe(NO_3)_3·9H_2O$ (35)	DCE	36[b]
9	$Fe(NO_3)_3·9H_2O$ (35)	DCE	32[c]
10	$Fe(NO_3)_3·9H_2O$ (35)	DCE	63[d]

[a]Reaction conditions: aldehyde **1a** (1.0 mmol), sulfonyl hydrazide **2a** (1.2 mmol), DCE (3 mL), 60 °C, 0.5 h; $Fe(NO_3)_3·9H_2O$ (35 mol %), 80 °C, air, 1.5 h. [b]Temp. 60 °C. [c]Temp. 100 °C. [d]MS 4 Å (50 mg) used.

3a in 36−47% yields (entries 2−5). In contrast, THF and DMF yielded inferior results (entries 6−7). The optimum temperature was found to be 80 °C, and the addition of the molecular sieves of 4 Å led to an increase in the yield to 63% (entries 8−10).

With the optimal conditions, the scope of the protocol was explored for the reactions of a series of substituted aldehydes **1b−r** with *p*-toluenesulfonyl hydrazide **2a** as a standard substrate (Scheme 3). The reaction of benzaldehyde **1b** afforded bisarylnitromethyl sulfone **3b** in 66% yield. *o*-Tolualdehyde **1c** underwent the reaction to provide the target product **3c** in 57% yield. The reactions of the aldehydes **1d−g** with 3-chloro, 3-methyl, 3-nitro, and 3-trifluoromethyl substituents afforded the corresponding substituted bisarylnitromethyl sulfones **3d−g** in 51−61% yields. The aldehydes **1h−m** bearing 4-bromo, 4-chloro, 4-cyano, 4-fluoro, 4-methoxy, and 4-ester substituents underwent the reaction to produce the target products **3h−m** in 52−69% yields. In addition, the aldehyde **1n** with 2-methoxy and 3-bromo substituents produced the desired **3n** in 65% yield, while the reactions of the aldehydes **1o** and **1p** with 2,4,5-trimethoxy and 3,4,5-trimethoxy groups furnished **3o** and **3p** in 72% and 70% yields, respectively. Furthermore, 2-naphthaldehyde **1q** underwent the reaction to give **3q** in 73% yield. However, the reaction of aliphatic aldehyde **1r** was not successful due to the decomposition of the hydrazone generated from the aldehyde and sulfonyl hydrazide. Compound **3o** yielded single crystals in CH_3CN whose structure was determined by single crystal X-ray analysis (see the Supporting Information).

Next, the protocol was extended for the reaction of various arylsulfonyl hydrazides with the aldehydes **1i** and **1l** having 4-chloro and 4-methoxy substituents as the representative examples (Scheme 4). Arylsulfonyl hydrazide **2b** underwent the reaction to furnish the target bisarylnitromethyl sulfones **3s** and **3t** in 66% and 68% yields, respectively. Similarly, the reactions of the arylsulfonyl hydrazides **2c−e** bearing 4-chloro, 4-methoxy, and 4-nitro substituents occurred with 54−64% yields. Furthermore, arylsulfonyl hydrazide **2f** with 2,4,6-trimethyl substituents underwent the reaction with 66% and 64% yields, respectively. These results suggest that the protocol has broad substrate scope to afford an effective route for the construction of functionalized bisarylnitromethyl sulfones.

Finally, the reaction of the aldehyde **1a** and sulfonyl hydrazide **2a** was examined in gram-scale as representative examples (Scheme 5). The reaction readily took place to afford **3a** in good yields, which suggests that the protocol is scalable. Furthermore, the products can be readily converted into oximes in high yields (Scheme 6). For example, the Sn-mediated reaction of **3b**, **3h**, and **3l** afforded the corresponding oximes **4a−c** in high yields. The compound **4a** afforded single crystals in chloroform whose structure was determined by single crystal X-ray analysis (see the Supporting Information).

To gain insight into the mechanism, the reaction of bisarylsulfonyl hydrazone **5** was independently investigated (Scheme 7). As above, the nitration took place efficiently to afford **3a** in 64% yield, which suggests that the condensation of the aldehyde with sulfonyl hydrazide may first give bisarylsulfonyl hydrazone that may undergo nitration to afford the target products. Next, the reaction of the aldehyde **1b** and arylsulfonyl hydrazide **2a** was examined with $Fe(NO_3)_3·9H_2O$ as the representative examples in the presence of radical scavengers, 1,1-diphenylethyelene and *N*-*tert*-butyl-*α*-phenylnitrone (Scheme 8).[23] However, no reaction was observed, which suggests that the reaction may involve the radical intermediates. Furthermore, the substrates showed no nitration in the presence of base, which suggests that the reaction may not proceed via the carbene intermediate (Scheme 9).[24] In addition, *N*-benzyl bisarylsulfonyl hydrazone failed to react, and the substrate was isolated intact, which suggests that N−H is essential for the reaction (Scheme 10). Thus, the reaction of the aldehyde with arylsulfonyl hydrazide can give sulfonyl hydrazone ***a*** that can react with $Fe(NO_3)_3$ via single electron transfer to produce $Fe(NO_3)_2$, NO_3^-, and intermediate ***b*** (Scheme 11).[25] Isomerization of ***b*** can give ***c*** that can react with the NO_2 radical[3,4] to give ***d*** and the target products **3** via path ***a***. Alternatively, the intermediate ***c*** may give ***e*** via path **b**, which with the NO_2 radical can give the target product.[3,4] Oxidation of the Fe(II) species with HNO_3 can regenerate Fe(III) species to complete the catalytic cycle.

The optimized structures of different species involved in the reactions are shown in Figure 1.

The vibrational frequencies of all of the optimized structures are found to be positive, confirming them to be at energy minima (see the Supporting Information).[26,27] To understand the feasibility of the reaction paths, we have calculated the standard reaction enthalpy (ΔH_r) and Gibbs free energy (ΔG_r)

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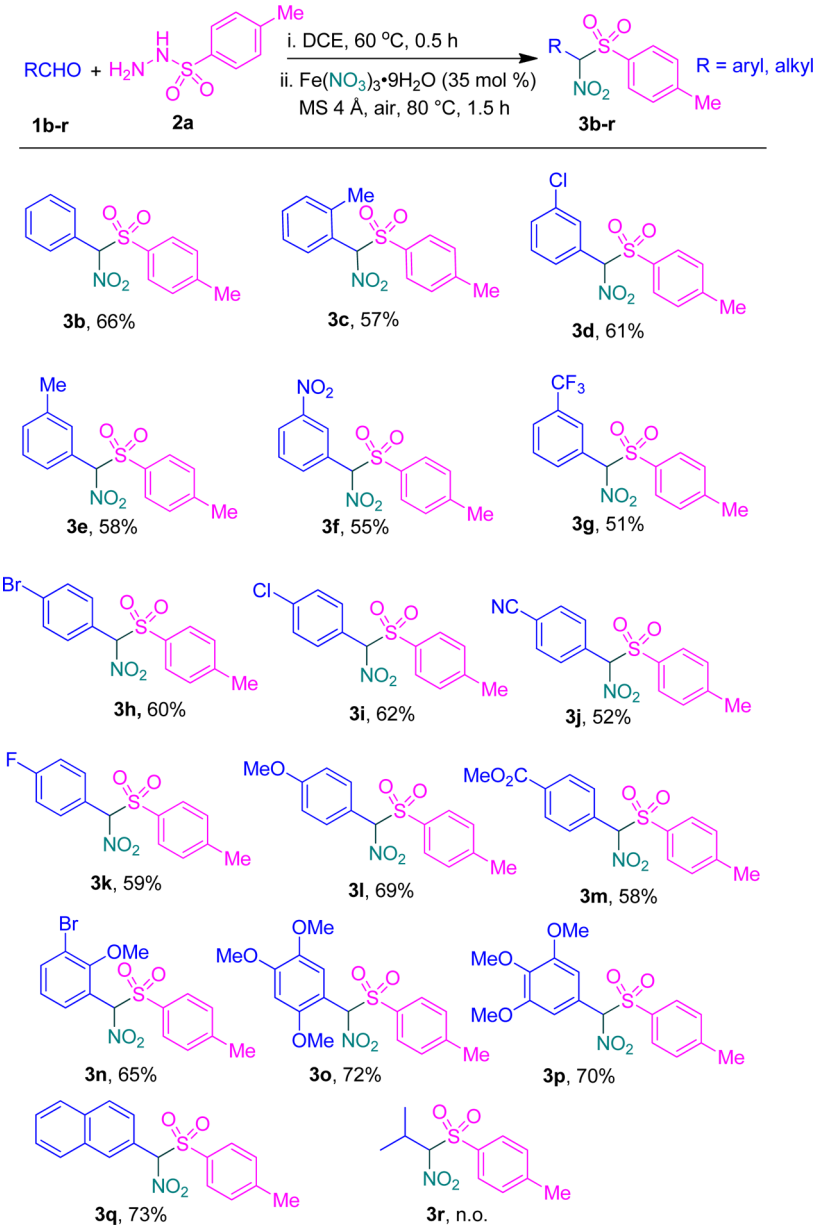
Scheme 3. Reaction of Various Aldehydes with *p*-Toluenesulfonyl Hydrazide[a]



[a]Reaction conditions: aldehyde (1.0 mmol), sulfonyl hydrazide **2a** (1.2 mmol), DCE (3 mL), 60 °C, 0.5 h; $Fe(NO_3)_3{\cdot}9H_2O$ (35 mol %), MS 4 Å (50 mg), air, 80 °C, 1.5 h. n.o. = not observed.

for both the paths including zero point correction. The ΔG_r value for path ***a*** is found to be −1.76 eV, which indicates that this path is feasible. The ΔH_r value is found also to be negative (−13.95 eV) indicating that the path is exothermic in nature. For path ***b***, both the thermochemical parameters ΔG_r and ΔH_r are found to be highly positive, which reveals that this pathway is not feasible. Hence, path ***a*** may be predominant in nature.

CONCLUSIONS

In summary, iron(III)-mediated radical nitration of bisarylsulfonyl hydrazones is reported at moderate temperature. The reaction is free from the use of additives and effective under neutral conditions. The mild reaction conditions, broad substrate scope, and the use of nontoxic iron salt as the nitro source are the important practical features. The products can be converted into oximes using $SnCl_2$ in high yields. The reaction pathway has been analyzed using DFT calculations.

EXPERIMENTAL SECTION

General Information. Arylsulfonyl chlorides, aryl aldehydes, hydrazine hydrate (99−100%), and $SnCl_2{\cdot}2H_2O$ (97%) were purchased from a commercial source and used as received. $Fe(NO_3)_3{\cdot}9H_2O$ (98%) was purchased from a chemical supplier and used as received. Sulfonyl hydrazides,[28] aryl aldehydes,[29] and sulfonyl hydrazones[30] were prepared according to a reported procedure. TLC analysis was performed on silica gel G/GF 254 plates. Silica gel (60−120 mesh) was used for column chromatography. NMR spectra were recorded on 400 and 600 MHz spectrometers using Me_4Si as an internal standard. Melting points were determined with a melting point apparatus and are uncorrected. FT-IR spectra were collected using an IR spectrometer. A Q-Tof ESI-MS instrument was used for recording high-resolution mass spectra (HRMS). Single crystal X-ray

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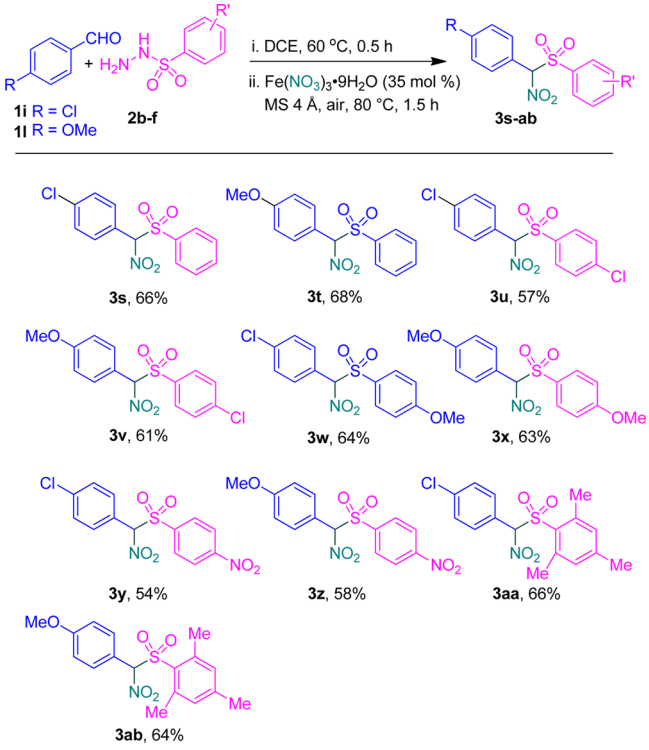
Scheme 4. Reaction of Different Sulfonyl Hydrazides with Aldehydes 1i and 1l[a]



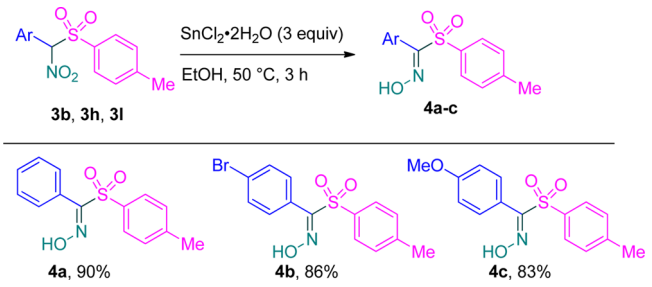
[a]Reaction conditions: aldehyde (1.0 mmol), sulfonyl hydrazide (1.2 mmol), DCE (3 mL), 60 °C, 0.5 h; $Fe(NO_3)_3·9H_2O$ (35 mol %), MS 4 Å (50 mg), air, 80 °C, 1.5 h.

data were collected using a CCD diffractometer, which is equipped with 1.75 kW sealed-tube Mo–Kα irradiation (λ = 0.71073 Å) at 298(2) K. The crystal structure was solved by a direct method using SHELXL-97 (Göttingen, Germany).

General Procedure for the Iron(III)-Mediated Nitration of Bisarylsulfonyl hydrazones. Aryl aldehyde **1** (1 mmol) and arylsulfonyl hydrazide **2** (1.2 mmol) were stirred in 1,2-dichloroethane (3 mL) for 0.5 h at 60 °C under air. The reaction mixture was cooled to room temperature and then treated with $Fe(NO_3)_3·9H_2O$ (35 mol %, 0.35 mmol, 141 mg) and molecular sieves (4 Å, 50 mg). The resultant mixture was stirred for 1.5 h at 80 °C under air. The progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. After completion, the reaction mixture was cooled to room temperature, and the solvent was evaporated under reduced pressure. The residue was treated with saturated $NaHCO_3$ (3 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic solution was successively washed with brine (1 × 10 mL) and water (1 × 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and ethyl acetate as eluent.

1-Bromo-3-(nitro(tosyl)methyl)benzene ***3a.*** Analytical TLC on silica gel, 1:3 ethyl acetate/hexane R_f = 0.41; white solid (231 mg, 63%); mp 79–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.56 (s, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.29 (t, J = 8.4 Hz, 1H), 6.40 (s, 1H), 2.48 (s, 3H); ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) δ 147.4, 135.0, 132.6, 130.7, 130.5, 130.1, 128.5, 127.1, 123.0, 103.0, 22.0; FT-IR (KBr) 2982, 1594, 1561, 1473, 1337, 1257, 1188, 1153, 1081, 1039, 1014, 661 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{14}H_{12}BrNO_4S$, 367.9598; found, 367.9591.

Scheme 6. Synthesis of Oximes



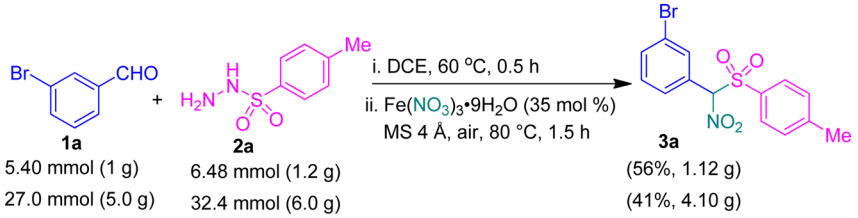
1-Methyl-4-(nitro(phenyl)methylsulfonyl)benzene ***3b.*** Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.52; white solid (192 mg, 66%); mp 163–164 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, J = 7.8 Hz, 2H), 7.51 (t, J = 7.8 Hz, 1H), 7.47 (d, J = 7.2 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.46 (s, 1H), 2.46 (s, 3H); ^{13}C {^{1}H}NMR (150 MHz, $CDCl_3$) δ 147.0, 131.8, 131.2, 130.7, 130.0, 129.7, 129.1, 125.3, 103.9, 22.0; FT-IR (KBr) 2984, 2359, 1592, 1559, 1488, 1454, 1333, 1303, 1184, 1155, 1083, 1030, 1016 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{14}H_{13}NO_4S$, 290.0493; found, 290.0486.

1-Methyl-2-(nitro(tosyl)methyl)benzene ***3c.*** Analytical TLC on silica gel, 1:3 ethyl acetate/hexane R_f = 0.38; white solid (173 mg, 57%); mp 198–199 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, J = 7.8 Hz, 2H), 7.54 (d, J = 7.8 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 8.4 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 6.81 (s, 1H), 2.47 (s, 3H), 2.39 (s, 3H); ^{13}C {^{1}H}NMR (150 MHz, $CDCl_3$) δ 147.0, 138.9, 131.8, 131.7, 131.2, 130.8, 130.0, 128.4, 126.8, 124.2, 99.2, 22.0, 19.8; FT-IR (KBr) 2999, 1689, 1595, 1557, 1491, 1456, 1406, 1355, 1331, 1292, 1264, 1153, 1084, 1037, 1018 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{15}H_{15}NO_4S$, 304.0649; found, 304.0658.

1-Chloro-3-(nitro(tosyl)methyl)benzene ***3d.*** Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.39; white solid (198 mg, 61%); mp 82–84 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, J = 7.8 Hz, 2H), 7.50 (d, J = 7.8 Hz, 1H), 7.45 (s, 1H), 7.40 (d, J = 7.8 Hz, 1H), 7.36–7.34 (m, 3H), 6.41 (s, 1H), 2.48 (s, 3H); ^{13}C {^{1}H}NMR (150 MHz, $CDCl_3$) δ 147.4, 135.2, 132.0, 130.9, 130.7, 130.3, 130.1, 129.8, 128.1, 127.0, 103.1, 22.0; FT-IR (KBr) 2990, 1597, 1562, 1477, 1408, 1384, 1340, 1261, 1187, 1157, 1083, 1017, 663 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{14}H_{12}ClNO_4S$, 324.0103; found, 324.0110.

1-Methyl-3-(nitro(tosyl)methyl)benzene ***3e.*** Analytical TLC on silica gel, 1:6 ethyl acetate/hexane R_f = 0.49; white solid (177 mg, 58%); mp 116–117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61(d, J = 7.6 Hz, 2H), 7.32 (d, J = 7.6 Hz, 2H), 7.26–7.23 (m, 4H), 6.42 (s, 1H), 2.47 (s, 3H), 2.33 (s, 3H); ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) δ

Scheme 5. Gram-Scale Synthesis



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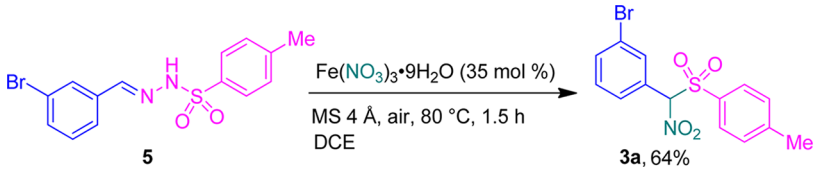
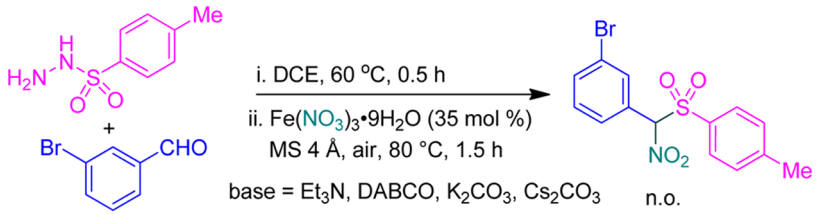
Scheme 7. Nitration of Bisarylsulfonyl Hydrazone

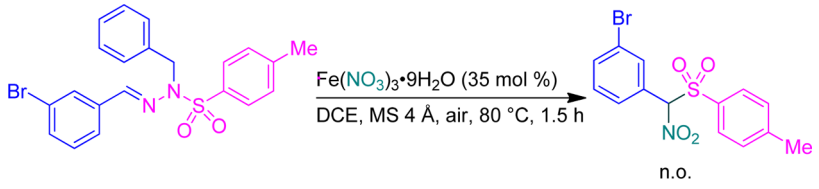


Scheme 8. Effect of Radical Scavengers

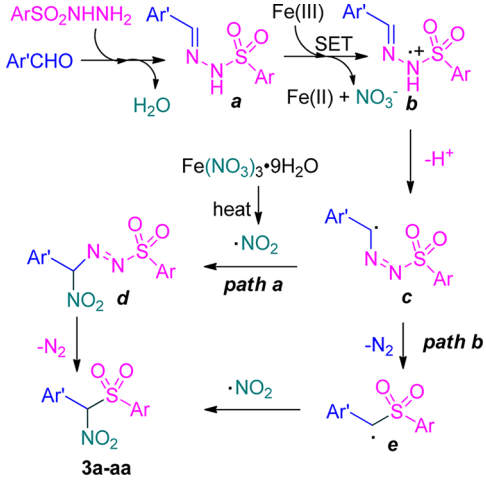
Scheme 9. Effect of Base



Scheme 10. Effect of *N*-Protecting Group



Scheme 11. Proposed Reaction Pathway



146.9, 139.1, 132.6, 131.2, 130.8, 130.2, 129.9, 128.9, 126.8, 125.1, 103.9, 22.0, 21.4; FT-IR (KBr) 2983, 1633, 1592, 1554, 1484, 1333, 1305, 1155, 1083, 1039, 1017 cm^{-1}; HRMS (APCI) m/z $[M - H]^-$ calcd for $C_{15}H_{15}NO_4S$, 304.0649; found, 304.0641.

1-Nitro-3-(nitro(tosyl)methyl)benzene ***3f***. Analytical TLC on silica gel, 1:3 ethyl acetate/hexane R_f = 0.28; yellow solid (184 mg, 55%); mp 132−133 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 8.4 Hz, 1H), 8.33 (s, 1H), 8.00 (d, J = 7.2 Hz, 1H), 7.70−7.66 (m, 3H), 7.39 (d, J = 7.6 Hz, 2H), 6.59 (s, 1H), 2.49 (s, 3H); ^{13}C {^1H}NMR (100 MHz, $CDCl_3$) δ 148.3, 147.9, 135.9, 130.5, 130.4, 130.3, 127.0, 126.6, 125.2, 102.3, 22.0; FT-IR (KBr) 2925, 1707, 1618, 1533, 1481, 1446, 1352, 1291, 1158, 1124, 1035, 1010, 815, 720, 668 cm^{-1}; HRMS (APCI) m/z $[M - H]^-$ calcd for $C_{14}H_{12}N_2O_6S$, 335.0343; found, 335.0349.

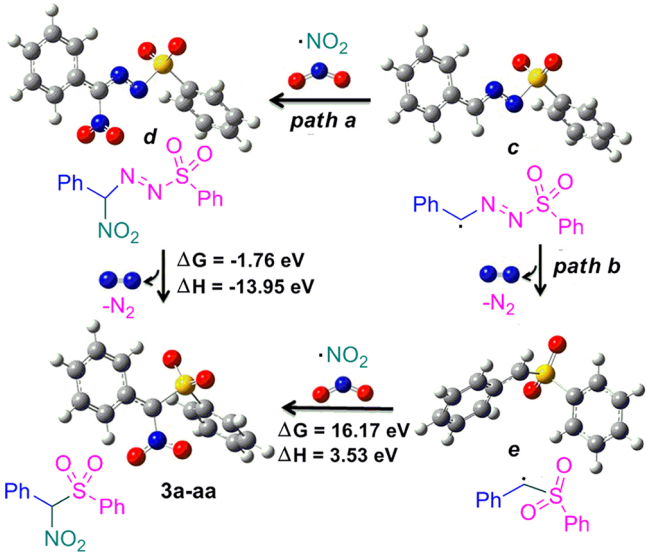


Figure 1. Optimized structures of organic species (white, hydrogen; gray, carbon; yellow, sulfur; red, oxygen; and blue, nitrogen).

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1-(Nitro(tosyl)methyl)-3-(trifluoromethyl)benzene **3g**. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.29; yellow liquid (183 mg, 51%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, J = 7.8 Hz, 2H), 7.60−7.58 (m, 4H), 7.34 (d, J = 8.4 Hz, 2H), 6.51 (s, 1H), 2.47 (s, 3H); ^{13}C {^{1}H}NMR (150 MHz, $CDCl_3$) δ 147.6, 133.5, 133.3, 130.7, 130.2, 129.8, 129.4, 128.6, 127.3, 126.6, 126.3, 103.1, 22.0; FT-IR (neat) 2926, 1596, 1566, 1452, 1384, 1332, 1261, 1159, 1133, 1101, 1081, 814, 703, 659 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{15}H_{12}F_3NO_4S$, 358.0361; found, 358.0367.

1-Bromo-4-(nitro(tosyl)methyl)benzene **3h**. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.40; white solid (222 mg, 60%); mp 129−130 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.37−7.33 (m, 4H), 6.41 (s, 1H), 2.47 (s, 3H); ^{13}C {^{1}H}NMR (150 MHz, $CDCl_3$) δ 147.3, 132.5, 131.3, 131.0, 130.7, 130.2, 126.8, 124.2, 103.2, 22.0; FT-IR (KBr) 2923, 1626, 1562, 1488, 1408, 1384, 1340, 1155, 1075, 1012, 707, 658 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{14}H_{12}BrNO_4S$, 367.9598; found, 367.9591.

1-Chloro-4-(nitro(tosyl)methyl)benzene **3i**. Analytical TLC on silica gel, 1:3 ethyl acetate/hexane R_f = 0.50; white solid (201 mg, 62%); mp 128−129 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, J = 7.8 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 6.43 (s, 1H), 2.47 (s, 3H); ^{13}C {^{1}H}NMR (150 MHz, $CDCl_3$) δ 147.3, 138.5, 131.2, 131.0, 130.6, 130.2, 129.5, 123.7, 103.1, 22.0; FT-IR (KBr) 2979, 1665, 1594, 1568, 1494, 1413, 1340, 1310, 1291, 1177, 1152, 1082, 1018, 818, 662 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{14}H_{12}ClNO_4S$, 324.0103; found, 324.0108.

4-(Nitro(tosyl)methyl)benzonitrile **3j**. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.40; white solid (164 mg, 52%); mp 125−126 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2 H), 6.49 (s, 1H), 2.48 (s, 3H); ^{13}C {^{1}H}NMR (150 MHz, $CDCl_3$) δ 147.8, 132.8, 130.8, 130.7, 130.4, 129.7, 117.7, 115.9, 102.9, 22.1; FT-IR (KBr) 2924, 2853, 2231, 1741, 1628, 1563, 1462, 1338, 1152, 1081, 1017, 812 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{15}H_{12}N_2O_4S$, 315.0445; found, 315.0451.

1-Fluoro-4-(nitro(tosyl)methyl)benzene **3k**. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.56; yellow solid (182 mg, 59%); mp 107−108 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, J = 7.8 Hz, 2H), 7.52−7.49 (m, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.10 (t, J = 8.4 Hz, 2H), 6.44 (s, 1H), 2.47 (s, 3H); ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) δ 166.1 (J_{C-F} = 251.7 Hz), 147.2, 132.2 (J_{C-F} = 9.2 Hz), 131.0, 130.6, 130.1, 121.2 (J_{C-F} =3.8 Hz), 116.5 (J_{C-F} = 22.1 Hz), 103.0, 22.0; FT-IR (KBr) 2979, 1605, 1566, 1512, 1406, 1384, 1339, 1233, 1154, 1083, 1016, 820, 665 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{14}H_{12}FNO_4S$, 308.0398; found, 308.0396.

1-Methoxy-4-(nitro(tosyl)methyl)benzene **3l**. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.51; yellow solid (221 mg, 69%); mp 126−127 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 6.40 (s, 1H), 3.83 (s, 3H), 2.46 (s, 3H); ^{13}C {^{1}H}NMR (150 MHz, $CDCl_3$) δ 162.4, 146.9, 131.5, 131.4, 130.7, 130.0, 117.0, 114.5, 103.6, 55.6, 22.0; FT-IR (KBr) 2995, 1609, 1596, 1552, 1515, 1460, 1341, 1309, 1278, 1263, 1182, 1157, 1085, 1019 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{15}H_{15}NO_5S$, 320.0598; found, 320.0599.

Methyl-4-(nitro(tosyl)methyl)benzoate **3m**. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.22; white solid (202 mg, 58%); mp 110−111 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 2H), 7.59−7.54 (m, 4H), 7.32 (d, J = 8.4 Hz, 2H), 6.52 (s, 1H), 3.94 (s, 3H), 2.46 (s, 3H); ^{13}C {^{1}H}NMR (150 MHz, $CDCl_3$) δ 166.1, 147.4, 133.2, 130.9, 130.7, 130.2, 130.1, 129.8, 129.5, 103.4, 52.7, 22.0; FT-IR (KBr) 2995, 1714, 1593, 1555, 1432, 1341, 1291, 1187, 1154, 1114, 1083, 1018 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{16}H_{15}NO_6S$, 348.0547; found, 348.0541.

1-Bromo-2-methoxy-3-(nitro(tosyl)methyl)benzene **3n**. Analytical TLC on silica gel, 1:3 ethyl acetate/hexane R_f = 0.35; white solid (260 mg, 65%); mp 153−154 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 2.4 Hz, 1H); 7.69 (d, J = 7.8 Hz, 2H), 7.56 (dd, J = 9.0, 2.4 Hz, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.12 (s, 1H), 6.80 (d, J = 9.0 Hz, 1H), 3.76 (s, 3H), 2.48 (s, 3H); ^{13}C {^{1}H}NMR (150 MHz, $CDCl_3$) δ 157.0, 147.0, 136.0, 132.9, 131.8, 130.5, 130.0, 115.7, 113.3, 112.9, 95.1, 56.5, 22.0; FT-IR (KBr) 2981, 1595, 1556, 1487, 1462, 1441, 1403, 1352, 1329, 1305, 1282, 1260, 1213, 1186, 1155, 1116, 1085, 1019, 820, 647 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{15}H_{14}BrNO_5S$, 397.9703; found, 397.9710.

1,2,4-Trimethoxy-5-(nitro(tosyl)methyl)benzene **3o**. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.64; yellow solid (274 mg, 72%); mp 148−149 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.15 (s, 1H), 7.11 (s, 1H), 6.46 (s, 1H), 3.91 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H), 2.46 (s, 3H); ^{13}C {^{1}H}NMR (150 MHz, $CDCl_3$) δ 153.5, 153.0, 146.5, 143.4, 132.4, 130.5, 129.9, 112.1, 104.4, 96.6, 95.9, 56.9, 56.4, 56.2, 21.9; FT-IR (KBr) 2977, 1599, 1525, 1406, 1384, 1332, 1305, 1232, 1214, 1153, 1112, 1083, 1039, 1027 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{17}H_{19}NO_7S$, 380.0809; found, 380.0807.

1,2,3-Trimethoxy-5-(nitro(tosyl)methyl)benzene **3p**. Analytical TLC on silica gel, 1:2 ethyl acetate/hexane R_f = 0.59; yellow solid (267 mg, 70%); mp 150−151 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 6.63 (s, 2H), 6.37 (s, 1H), 3.86 (s, 3H), 3.75 (s, 6H), 2.46 (s, 3H); ^{13}C {^{1}H}NMR (150 MHz, $CDCl_3$) δ 153.4, 147.0, 140.9, 131.1, 130.8, 129.9, 120.1, 107.0, 103.8, 61.1, 56.3, 21.9; FT-IR (KBr) 2945, 1593, 1557, 1509, 1465, 1424, 1336, 1277, 1244, 1230, 1155, 1129, 1079, 1018 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{17}H_{19}NO_7S$, 380.0809; found, 380.0815.

2-(Nitro(tosyl)methyl)naphthalene **3q**. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.71; white solid (249 mg, 73%); mp 175−176 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.86 (t, J = 9.0 Hz, 2H), 7.82 (d, J = 7.8 Hz, 1H), 7.61−7.52 (m, 5H), 7.29 (d, J = 8.4 Hz, 2H), 6.63 (s, 1H), 2.45 (s, 3H); ^{13}C {^{1}H}NMR (150 MHz, $CDCl_3$) δ 147.0, 134.6, 132.7, 131.3, 130.9, 130.7, 130.0, 129.0, 128.8, 128.4, 127.9, 127.3, 125.3, 122.5, 104.2, 22.0; FT-IR (KBr) 2987, 1593, 1559, 1507, 1338, 1306, 1211, 1156, 1125, 1083, 1018, 818, 665 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{18}H_{15}NO_4S$, 340.0649; found, 340.0653.

1-Chloro-4-(nitro(phenylsulfonyl)methyl)benzene **3s**. Analytical TLC on silica gel, 1:6 ethyl acetate/hexane R_f = 0.29; white solid (205 mg, 66%); mp 117−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76−7.74 (m, 3H), 7.56 (t, J = 7.6 Hz, 2H), 7.44−7.38 (m, 4H), 6.46 (s, 1H); ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) δ 138.6, 135.7, 134.0, 131.1, 130.6, 129.6, 129.5, 123.5, 103.0; FT-IR (KBr) 2979, 1565, 1488, 1448, 1411, 1355, 1337, 1289, 1180, 1154, 1080, 1012, 770, 728 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{13}H_{10}ClNO_4S$, 309.9941; found, 309.9943

1-Methoxy-4-(nitro(phenylsulfonyl)methyl)benzene **3t**. Analytical TLC on silica gel, 1:6 ethyl acetate/hexane R_f = 0.31; white solid (209 mg, 68%); mp 143−144 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 6.43 (s, 1H), 3.82 (s, 3H); ^{13}C {^{1}H}NMR (150 MHz, $CDCl_3$) δ 162.4, 135.4, 134.4, 131.4, 130.6, 129.3, 116.8, 114.5, 103.5, 55.6; FT-IR (KBr) 2990, 1607, 1578, 1554, 1513, 1460, 1445, 1338, 1309, 1276, 1262, 1181, 1160, 1113, 1084, 1018 cm^{-1}; HRMS (APCI) m/z [M − H]$^-$ calcd for $C_{14}H_{13}NO_5S$, 306.0442; found, 306.0448.

1-Chloro-4-(((4-chlorophenyl)(nitro)methyl)sulfonyl)benzene **3u**. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.45; white solid (197 mg, 57%); mp 117−118 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J = 9.0 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.41 (s, 4H), 6.44 (s, 1H); ^{13}C {^{1}H}NMR (150 MHz, $CDCl_3$) δ 143.0, 138.8, 132.4, 132.1, 131.0, 129.9, 129.7, 123.3, 103.1; FT-IR (KBr) 2901, 2072, 1639, 1430, 1372, 1339, 1319, 1282, 1205, 1163, 1059, 1032, 896, 707 cm^{-1}; HRMS (APCI) jkm/z [M − H]$^-$ calcd for $C_{13}H_9Cl_2NO_4S$, 343.9557; found, 343.9550.

1-Chloro-4-(((4-methoxyphenyl)(nitro)methyl)sulfonyl)benzene **3v**. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.40; yellow solid (208 mg, 61%); mp 113−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 6.39 (s, 1H), 3.82 (s, 3H); ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$) δ 162.5, 142.5, 132.7, 132.1, 131.3,

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129.6, 116.6, 114.7, 103.6, 55.6; FT-IR (KBr) 2958, 1608, 1579, 1556, 1513, 1469, 1447, 1427, 1395, 1356, 1339, 1310, 1182, 1152, 1142, 1116, 1090, 1077, 1028, 657 cm^{-1}; HRMS (APCI) m/z $[M - H]^-$ calcd for $C_{14}H_{12}ClNO_5S$, 340.0052; found, 340.0057.

1-Chloro-4-((4-methoxyphenylsulfonyl)(nitro)methyl)benzene ***3w***. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.34; yellow solid (218 mg, 64%); mp 112−113 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, J = 9.0 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 9.0 Hz, 2H), 6.42 (s, 1H), 3.91 (s, 3H); ^{13}C $\{^1H\}$NMR (150 MHz, $CDCl_3$) δ 165.5, 138.4, 133.1, 131.1, 129.5, 124.9, 123.9, 114.7, 103.2, 56.1; FT-IR (KBr) 2992, 1594, 1562, 1496, 1461, 1409, 1332, 1316, 1263, 1150, 1083, 1019, 830, 663 cm^{-1}; HRMS (APCI) m/z $[M - H]^-$ calcd for $C_{14}H_{12}ClNO_5S$, 340.0052; found, 340.0057.

1-Methoxy-4-((4-methoxyphenyl)(nitro)methylsulfonyl)benzene ***3x***. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.50; yellow solid (212 mg, 63%); mp 118−119 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 6.8 Hz, 2H), 7.39 (d, J = 7.2 Hz, 2H), 6.96 (d, J = 6.8 Hz, 2H), 6.88 (d, J = 6.8 Hz, 2H), 6.41(s, 1H), 3.88 (s, 3H), 3.81 (s, 3H); ^{13}C $\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 165.2, 162.3, 133.0, 131.3, 125.3, 117.2, 114.5, 114.4, 103.7, 55.9, 55.6; FT-IR (KBr) 2993, 2389, 1609, 1592, 1561, 1513, 1499, 1461, 1441, 1330, 1310, 1267, 1179, 1148, 1084, 1023 cm^{-1}; HRMS (APCI) m/z $[M - H]^-$ calcd for $C_{15}H_{15}NO_6S$, 336.0547; found, 336.0542.

1-Chloro-4-(nitro((4-nitrophenyl)sulfonyl)methyl)benzene ***3y***. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.29; yellow solid (192 mg, 54%); mp 198−199 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, J = 9.0 Hz, 2H), 7.95 (d, J = 9.0 Hz, 2H), 7.44−7.40 (m, 4H), 6.51 (s, 1H); ^{13}C $\{^1H\}$NMR (150 MHz, $CDCl_3$) δ 152.0, 139.7, 139.2, 132.3, 130.9, 129.9, 124.4, 122.7, 103.1; FT-IR (KBr) 2989, 1639, 1593, 1554, 1533, 1491, 1412, 1341, 1315, 1290, 1157, 1108, 1093, 1080, 1030, 740 cm^{-1}; HRMS (APCI) m/z $[M - H]^-$ calcd for $C_{13}H_9ClN_2O_6S$, 354.9792; found, 354.9799.

1-Methoxy-4-(nitro((4-nitrophenyl)sulfonyl)methyl)benzene ***3z***. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.28; white solid (204 mg, 58%); mp 172−173 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 8.35 (d, J = 9.0 Hz, 2H), 7.92 (d, J = 9.0 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 6.48 (s, 1H), 3.84 (s, 3H); ^{13}C $\{^1H\}$NMR (150 MHz, $CDCl_3$) δ 162.8, 151.8, 140.0, 132.4, 131.2, 124.2, 116.0, 114.9, 103.6, 55.7; FT-IR (KBr) 2959, 1610, 1582, 1556, 1526, 1513, 1402, 1344, 1307, 1252, 1179, 1144, 1111, 1079, 1026 cm^{-1}; HRMS (APCI) m/z $[M - H]^-$ calcd for $C_{14}H_{12}N_2O_7S$, 351.0292; found, 351.0289.

2-((4-Chlorophenyl)(nitro)methylsulfonyl)-1,3,5-trimethylbenzene ***3aa***. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.36; white solid (233 mg, 66%); mp 164−165 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, J = 9.0 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.00 (s, 2H), 6.43 (s, 1H), 2.53 (s, 6H), 2.33 (s, 3H); ^{13}C $\{^1H\}$NMR (150 MHz, $CDCl_3$) δ 145.8, 142.1, 138.5, 132.9, 132.1, 129.4, 129.2, 123.3, 102.5, 23.2, 21.4; FT-IR (KBr) 2997, 1598, 1567, 1489, 1443, 1411, 1350, 1322, 1288, 1144, 1089, 714, 651 cm^{-1}; HRMS (APCI) m/z $[M - H]^-$ calcd for $C_{16}H_{16}ClNO_4S$, 352.0416; found, 352.0420.

2-((4-Methoxyphenyl)(nitro)methylsulfonyl)-1,3,5-trimethylbenzene ***3ab***. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.54; yellow solid (223 mg, 64%); mp 134−135 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, J = 9.0 Hz, 2H), 6.98 (s, 2H), 6.95 (d, J = 9.0 Hz, 2H), 6.40 (s, 1H), 3.84 (s, 3H), 2.52 (s, 6H), 2.32 (s, 3H); ^{13}C $\{^1H\}$NMR (150 MHz, $CDCl_3$) δ 162.5, 145.4, 142.0, 132.8, 132.3, 129.6, 116.7, 114.5, 103.1, 55.6, 23.2, 21.3; FT-IR (KBr) 2979, 1608, 1556, 1515, 1443, 1410, 1384, 1357, 1329, 1267, 1176, 1153, 1025 cm^{-1}; HRMS (APCI) m/z $[M - H]^-$ calcd for $C_{17}H_{19}NO_5S$, 348.0911; found, 348.0905.

General Procedure for the Synthesis of Oximes. To a solution of bisarylnitromethyl sulfone (0.25 mmol) in ethanol (1 mL) was added $SnCl_2{\cdot}2H_2O$ (0.75 mmol, 169 mg). The reaction mixture was stirred for 3 h at 50 °C under air. The progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. After completion, the reaction mixture was cooled to room temperature, and the solvent was evaporated under reduced pressure. The residue was treated with saturated $NaHCO_3$ (3 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic solution was successively washed with brine (1 × 10 mL) and water (1 × 10 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by column chromatography using hexane and ethyl acetate as eluent.

(E)-Phenyl(tosyl)methanone Oxime ***4a***. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.49; white solid (61 mg, 90%); mp 145−146 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.67 (d, J = 7.8 Hz, 2H), 7.46−7.44 (m, 1H), 7.41−7.40 (m, 4H), 7.27 (d, J = 7.8 Hz, 2H), 2.41 (s, 3H); ^{13}C $\{^1H\}$NMR (150 MHz, $CDCl_3$) δ 158.6, 145.6, 134.7, 130.9, 130.0, 129.6, 129.3, 128.6, 125.7, 21.9; FT-IR (KBr) 3373, 2922, 2854, 1593, 1443, 1385, 1289, 1145, 1086, 1014, 970 cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{13}NO_3S$, 276.0694; found, 276.0698.

(E)-(4-Bromophenyl)(tosyl)methanone Oxime ***4b***. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.42; white solid (76 mg, 86%); mp 160−161 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H); ^{13}C $\{^1H\}$NMR (150 MHz, $CDCl_3$) δ 158.5, 145.8, 134.5, 132.0, 131.2, 130.1, 129.4, 125.8, 124.4, 21.9; FT-IR (KBr) 3325, 2921, 2851, 1594, 1586, 1484, 1315, 1215, 1147, 1073, 1019, 998, 810, 674 cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{12}BrNO_3S$, 353.9800; found, 353.9796.

(E)-(4-Methoxyphenyl)(tosyl)methanone Oxime ***4c***. Analytical TLC on silica gel, 1:4 ethyl acetate/hexane R_f = 0.48; white solid (63 mg, 83%); mp 143−144 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 9.0 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 6.92 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H), 2.41 (s, 3H); ^{13}C $\{^1H\}$NMR (150 MHz, $CDCl_3$) δ 161.5, 158.5, 145.4, 135.0, 131.4, 129.9, 129.2, 117.5, 114.1, 55.5, 21.9; FT-IR (KBr) 3448, 2961, 2924, 2854, 1604, 1507, 1455, 1314, 1293, 1258, 1173, 1149, 1088, 1019, 969, 835 cm^{-1}; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{15}NO_4S$, 306.0800; found, 306.0800.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystal data and structures of **3o** and **4a**, computational details, and NMR spectra (^1H and ^{13}C) of the products **3a−q**, **3s-ab**, and **4a−c**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00820.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tpunni@iitg.ernet.in.

Notes

The authors declare no competing financial interest.

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