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Regiocontrolled Synthesis of α-Sulfonylmethyl *o*-Nitrostyrenes via ZnI_2-Mediated Sulfonylation and $AgNO_2/Pd(PPh_3)_4$-Promoted *o*-Nitration

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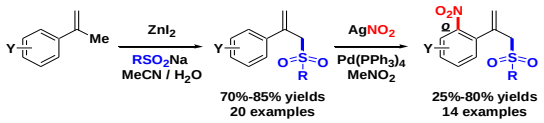
Supporting Information Placeholder

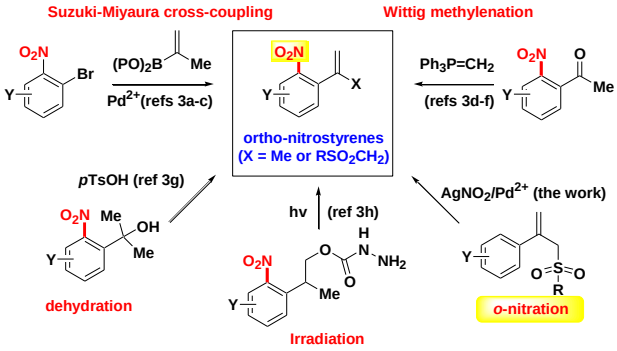


ABSTRACT: We report herein the $AgNO_2/Pd(PPh_3)_4$-promoted regiocontrolled *o*-nitration of α-sulfonylmethyl styrenes in $MeNO_2$ with good yields. The *o*-nitration process provides a series of sulfonyl *o*-nitrostyrenes. Substituted α-sulfonylmethyl styrenes were synthesized from ZnI_2-mediated sulfonylation of substituted α-methylstyrenes and sodium sulfinates (RSO_2Na) in MeCN with good to excellent yields. The structures of the key products were confirmed by X-ray crystallography. A plausible mechanism has been proposed herein.

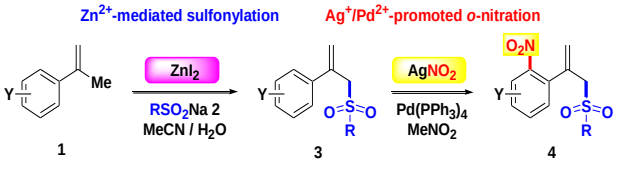
Introduction

Functionalized nitroarenes are important core structures in the preparation of dyes, plastics, perfumes, explosives and pharmaceuticals.[1] Numerous synthetic applications for such nitroarenes have been developed.[2] Apart from mixed-acid systems (HNO_3/H_2SO_4 or AcOH), nitrated salts ($NaNO_2$, NH_4NO_3, $AgNO_3$, $AgNO_2$, $Ce(NH_4)_2(NO_3)_6$, $Cu(NO_3)_2$, $Fe(NO_3)_3$, $Bi(NO_3)_3$) and nitration by means of metalation (mecuration, palladation, thallation, etc.) have been reported as efficient methods.[1b] Among them, nitronium ion-mediated electrophilic nitration of arenes, one of the most extensively used organic reactions, results in low regioselectivity owing to the formation of mixtures of isomeric nitrated products.[1c] However, there have been fewer report on the synthesis of *o*-nitrostyrenes (*o*-vinylnitroarenes) via a nitration route compared to common nitroarenes. As shown in Scheme 1, *o*-nitrostyrenes can be obtained easily by some synthetic routes, including Suzuki-Miyaura cross-coupling,[3a-c] Wittig olefination,[3d-f] Grignard double methylation followed by dehydration[3g] and photolytic irradiation.[3h] The major synthetic applications of the precursor of *o*-nitrostyrenes are focused on the formation of indole ring system via transition metal (Pd[4a], Fe/Ru/Rh[4b], Ti[4c], Rh[4d], Sn[4e], Co[4f]) and organodiborane catalyzed one-pot ring-closure,[4g] and electrolytic cyclization.[4h] The solid phase synthesis of benzothiazine skeleton from *o*-nitroarenes has been discussed.[4i] In continuation of our investigation into the synthetic applications of sulfonyl chemistry,[5] we introduce the styrenes **3** as the starting materials for synthesizing *o*-nitrostyrenes **4**. As shown in Scheme 2, the synthesis of **4** having the α-sulfonylmethyl group is well developed, and includes (1) ZnI_2-mediated sulfonylation of substituted α-methylstyrenes **1** and sodium sulfinates (**2**, RSO_2Na) in wet MeCN at reflux, and (2) $AgNO_2/Pd(PPh_3)_4$ promoted regiocontrolled *o*-nitration of **3** in $MeNO_2$ at reflux.

Scheme 1. Synthetic Routes of *o*-Nitrostyrenes



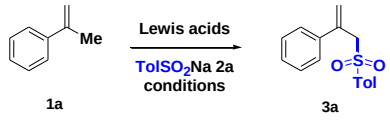
Scheme 2. Synthetic Route of α-Sulfonylmethyl *o*-Nitrostyrenes



Results and Discussions

Among these recent reports on the syntheses of α-sulfonylmethyl styrenes,[6] the one-pot strategy for the direct conjugation of carbon-sulfur (C-S) bond takes advantage of the tandem protocol that was established by Jiang (Cu^+/RSO_2NHNH_2),[6a] Zhou ($TBHP/RSO_2NHNH_2$),[6b] Liska (Cu^+/RSO_2Cl),[6c] Lei (Co^{2+}/RSO_2H),[6d] Kuhakarn (I_2/RSO_2Na),[6e] and Yallapragada (I_2/DMSO/TosMIC).[6f] Despite remarkable advances in the types of sulfonylative transformations, the continuing quest for a novel alternative route is still an important challenge. In comparison with the sulfonylating system, the combination of Zn^{2+}/RSO_2Na is applied to explore a new method for installing a sulfonyl group into the α-methyl group of **1**. Sodium sulfinates **2** have been widely used as sulfonylating reagents for the formation of carbon-sulfur and heteroatom-sulfur bonds.[7] Because of their ready availability, inexpensiveness, ease of operation and high air stability, sodium sulfinates are generally used as sulfonylating surrogates more than other sulfonyl synthons, such as sulfonyl chlorides, sulfonyl acids or sulfonyl hydrazines.[8] Substituted α-methylstyrenes **1** were easily prepared in high yields from Wittig methylenation (Ph_3PCH_3I, *t*-BuOK) of commercially available acetophenones (Y = H, 3,4-Cl_2, 4-CF_3, 3-F, 4-Cl, 4-NO_2 and 4-Ph or 2-naphthyl) under the standard protocols. With the starting materials **1** in hand, the next step was to find the optimal conditions for introducing the sulfonyl group of **2** on the α-methyl position of **3**.

Table 1. Optimal Conditions for **3a**[a]



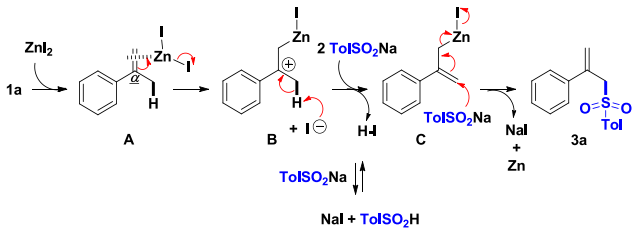
1a 3a

entry	Lewis acids	solvent	temp. (°C)	time (h)	**3a** (%)[b]
1	ZnI_2	MeCN	25	10	10
2	ZnI_2	MeCN	82	10	80
3	ZnI_2	MeCN	82	20	65
4	ZnI_2	CH_2Cl_2	40	10	—[c]
5	ZnI_2	DMF	82	10	58
6	ZnI_2	DMSO	82	10	61
7	$ZnCl_2$	MeCN	82	10	25
8	$Zn(OAc)_2$	MeCN	82	10	—[c]
9	$Zn(OTf)_2$	MeCN	82	10	—[c]
10	$ZnSO_4$	MeCN	82	10	—[c]
11	MgI_2	MeCN	82	10	57
12	AgI	MeCN	82	10	35
13	CuI	MeCN	82	10	50
14	KI	MeCN	82	10	—[c]
15	LiI	MeCN	82	10	—[c]
16	ZnI_2	MeCN	82	10	35[d]

[a]The reactions were run on a 1.0 mmol scale with **1a**, Lewis acids (1.2 quiv), $TolSO_2Na$ **2a** (2.2 equiv), solvent (9 mL) and H_2O (1 mL). [b]Isolated yields. [c]No reaction. [d]ZnI_2 (0.5 equiv) was added.

First, **1a** and **2a** (equiv ratio = 1:2.2) were chosen as the model substrates for scanning the reaction conditions, as shown in Table 1. By controlling the ZnI_2 as the Lewis acid in wet MeCN, reaction temperature and time were examined. In entry 1, only a 10% yield of **3a** was isolated at 25 °C. After elevating the temperature (rt → reflux), the yield was increased to 80% (entry 2). However, by elongating the reaction time (10 → 20 h) the yield of **3a** was decreased to 65% (entry 3). Furthermore, the factor of the solvent was studied. In entries 4-6, after changing the solvents (from refluxing MeCN to refluxing CH_2Cl_2, warming DMF and DMSO), the results showed that no formation of **3a** was obtained in CH_2Cl_2, and DMF and DMSO provided **3a** in 58% and 61% yields, respectively. For the other shown zinc complex of entries 7-10, only $ZnCl_2$ provided **3a** in only 25% yield and no isolation of **3a** for $Zn(OAc)_2$, $Zn(OTf)_2$ and $ZnSO_4$. Next, other metal iodides were studied (entries 11-15). However, MgI_2 (57%), AgI (35%), CuI (50%), NaI (NR), and KI (NR) provided poorer yields of **3a** than ZnI_2 (80%) did under similar conditions. With these results in hand, we found that ZnI_2 belonged to the most reactive and used catalyst compared to other Lewis acids. After decreasing the amounts (1.1 → 0.5 equiv) of ZnI_2, entry 16 showed that lower yields (35%) of **3a** were detected. According to the results, the 1.1 equivalent of ZnI_2/wet MeCN/reflux/10 h condition would be an optimal combination for yielding **3a**. On the basis of the results, a plausible mechanism with a reasonable explanation is described in Scheme 3. Initially, the complexation of **1a** with ZnI_2 generates **A**. Next, **A** is converted to **B** having a coordinated Zn^{2+} complex along with the removal of an iodide ion. The releasing iodide ion promotes the deprotonation of **B** to yield **C** with an allylic ZnI side arm and HI. By the involvement of $TolSO_2Na$ **2a** (2 equiv), **3a** is produced by intermolecular nucleophilic substitution of **C** with one $TolSO_2Na$ **2a**. Among the process, NaI and Zn should be generated. Subsequently, the other $TolSO_2Na$ **2a** traps the *in situ* formed HI to afford the resulting NaI and $TolSO_2H$ under the equilibrium conditions.

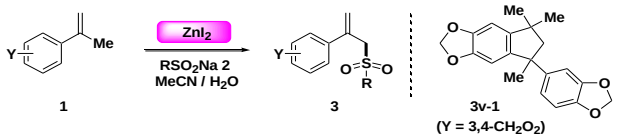
Scheme 3. Plausible Mechanism for **3a**



With the optimal condition (Table 1, entry 2), we further explored the substrate scope of the reaction; the results of α-sulfonylation are shown in Table 2. For the formation of α-sulfonylmethyl styrenes **3a-t** (entries 1-20), the diversified and well-tolerated Y and R substituents of **1a-h** and **2a-m**, including the electron-donating aryl group (**2f**, R = 4-$MeOC_6H_4$), electron-neutral aryl group (**2a-b**, R = Tol, Ph; **1g**, biphenyl, **1h**, 2-naphthyl) or aliphatic group (**2c-d**, R = Me, *n*Bu) and an electron-withdrawing aryl group (**1b-c**, Y = 3-F, 4-CF_3 and **1f**, Y = 4-NO_2) did not affect the distributed yields of **3a-t** (70%-85%) by ZnI_2-mediated allylic sulfonylation. However, the optimal condition was inappropriate for CF_3SO_2Na **2n**

(Langlois' reagent), and a complex mixture was observed (entry 21).[9] Especially, when reaction of **1i** (Y = 3,4-CH_2O_2) and **2a** was treated with 1.2 equivalents of ZnI_2, no desired **3v** was obtained, and only dimer **3v-1** was isolated in a 46% yield (entry 22).[10] From the results, we believed that self-dimerization of α-methylstyrenes having oxygenated aryl group was easier to initiate than sulfonylation route due to electron-donating group could stabilize the intermediate with the tertiary carbocation under ZnI_2 mediated conditions. Overall, for the electronic effect of Y substituent on the skeleton of α-methylstyrenes **1**, the electron-donating oxygenated group was inappropriate in the formation of **3**. For R substituent of sodium sulfinates **2**, both of electron-donating aromatic group and electron-withdrawing aromatic group could provide good yields of **3**, and no obvious electronic effect occurred under the ZnI_2-mediated sulfonylation reaction besides R = CF_3 group.

Table 2. Synthesis of **3**[a]



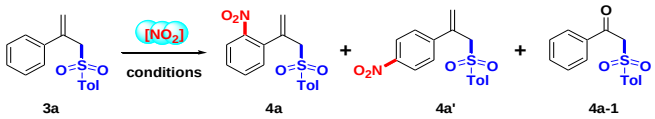
1 3 3v-1 (Y = 3,4-CH_2O_2)

entry	**1**, Y =	**2**, R =	**3**, (%)[b]
1	**1a**, H	**2a**, Tol	**3a**, 80
2	**1a**, H	**2b**, Ph	**3b**, 73
3	**1a**, H	**2c**, Me	**3c**, 70
4	**1a**, H	**2d**, *n*Bu	**3d**, 76
5	**1a**, H	**2e**, 4-FC_6H_4	**3e**, 82
6	**1a**, H	**2f**, 4-$MeOC_6H_4$	**3f**, 83
7	**1a**, H	**2g**, 3-MeC_6H_4	**3g**, 82
8	**1a**, H	**2h**, 4-EtC_6H_4	**3h**, 74
9	**1a**, H	**2i**, 4-*i*PrC_6H_4	**3i**, 76
10	**1a**, H	**2j**, 4-*n*BuC_6H_4	**3j**, 85
11	**1a**, H	**2k**, 4-*t*BuC_6H_4	**3k**, 80
12	**1a**, H	**2l**, 4-BrC_6H_4	**3l**, 80
13	**1a**, H	**2m**, 4-ClC_6H_4	**3m**, 72
14	**1b**, 3-F	**2a**, Tol	**3n**, 78
15	**1c**, 4-CF_3	**2a**, Tol	**3o**, 71
16	**1d**, 3,4-Cl_2	**2a**, Tol	**3p**, 70
17	**1e**, 4-Cl	**2a**, Tol	**3q**, 76
18	**1f**, 4-NO_2	**2a**, Tol	**3r**, 70
19	**1g**, 4-Ph	**2a**, Tol	**3s**, 78
20	**1h**, 2-naphthyl	**2a**, Tol	**3t**, 77
21	**1a**, Ph	**2n**, CF_3	**3u**, —[c]
22	**1i**, 3,4-CH_2O_2	**2a**, Tol	**3v**, —[d]

[a]The reactions were run on a 1.0 mmol scale with **1**, ZnI_2 (1.2 quiv), RSO_2Na (2.2 equiv), co-solvent of solvent (9 mL) and H_2O (1 mL), 10 h, 82 °C. [b]Isolated yields. [c]Complex mixture. [d]46% of **3v-1** was isolated.

With **3** in hand, the regiocontrolled nitration of α-sulfonylmethyl styrenes was examined next. The initial experiment was performed with **3a** and a common HNO_3/H_2SO_4 (0.5/1.0 mL) in CH_2Cl_2 at 25 °C under open-vessel condition, as shown in Table 3, entry 1.[11] However, an inseparated mixture of *o*- and *p*-nitrated products (**4a** and **4a'**) was provided in a 28% yield with a ratio of 1:1 along with the formation of a β-ketosulfone **4a-1** (46%). In entry 2, a combination of NH_4NO_3/TFAA (0.5/1.0 mL) provided a similar result (*o*-/*p*- = 6/4) with a 48% yield compared with entry 1.[12] Other transition metal nitrates were applied in this *o*-nitration, including Ag(I),[13] Ce(IV),[14] Pd(II),[15] Cu(II),[16] Fe(III),[17] and Bi(III)[18] salts. However, no regioselective nitration was observed for $AgNO_3$ (1.5 equiv)/CCl_4 combination in a 55% yield with a ratio of 2:1 (entry 3). For $Ce(NH_4)_2(NO_3)_6$ (2.0 equiv)/MeCN, only complex products were isolated (entry 4). When a 10 mol % of $Pd(OAc)_2$ was involved to the *t*-BuONO (1.5 equiv) mediated nitration, the ratio of *o*- and *p*-nitrated product was increased to 4:1 (entry 5).

Table 3. Optimal Conditions for **4a** [a]



3a 4a 4a' 4a-1

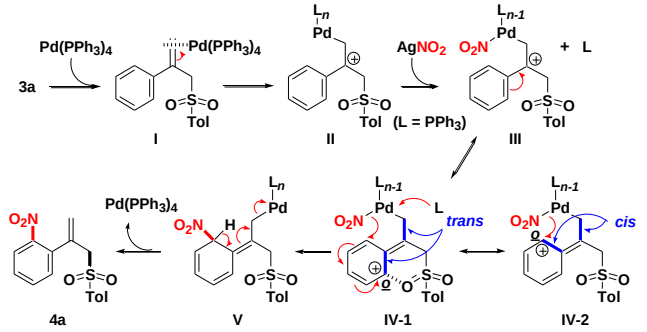
entry	reagents	solvent	temp (°C)	time (h)	ratio/yield (*o*/*p*, %)[b-c]
1	HNO_3/H_2SO_4 (0.5/1.0 mL)	CH_2Cl_2	25	10	1:1, 28
2	NH_4NO_3/TFAA (1.5/2.0 equiv)	CH_2Cl_2	25	10	6:4, 48
3	$AgNO_3$ (1.5 equiv)	CCl_4	25	10	2:1, 55
4	$Ce(NH_4)_2(NO_3)_6$ (2.0 equiv)	MeCN	25	10	—[d]
5	$Pd(PPh_3)_4$/*t*BuONO (10 mol%/1.5 equiv)	DME	25	10	4:1, 43
6	$Cu(NO_3)_2/K_2S_2O_8$ (1.2/1.2 equiv)	MeCN	25	10	1:1, 21
7	$Fe(NO_3)_3/K_2S_2O_8$ (1.2/1.2 equiv)	MeCN	25	10	1:1, 13
8	$Bi(NO_3)_3/K_2S_2O_8$ (1.2/1.2 equiv)	MeCN	25	10	1:1, 10
9	$AgNO_3/Pd(PPh_3)_4$ (1.5 equiv/10 mol %)	MeCN	25	10	5:1, 60
10	$AgNO_2/Pd(PPh_3)_4$ (1.5 equiv/10 mol %)	MeCN	25	10	>20:1, 51
11	$AgNO_2/Pd(PPh_3)_4$ (1.5 equiv/20 mol %)	MeCN	25	10	>20:1, 55
12	$AgNO_2/Pd(PPh_3)_4$ (1.5 equiv/20 mol %)	$MeNO_2$	25	10	>20:1, 62
13	$AgNO_2/Pd(PPh_3)_4$ (1.5 equiv/20 mol %)	$MeNO_2$	101	10	>20:1, 73
14	$AgNO_2/Pd(PPh_3)_4$ (1.5 equiv/20 mol %)	$MeNO_2$	101	20	>20:1, 63
15	$AgNO_2/Pd_2(dba)_3$ (1.5 equiv/20 mol %)	$MeNO_2$	101	10	>20:1, 50
16	$AgNO_2/Pd(OAc)_2$ (1.5 equiv/20 mol %)	$MeNO_2$	101	10	20:1, 28

[a]The reactions were run on a 0.5 mmol scale with **3a**, solvent (5 mL). [b]Determined by ^{1}H-NMR spectra. [c]Isolated yields. [d]Complex results.

Furthermore, three available commercial nitrated complexes, 1.2 equivalent of $Cu(NO_3)_2$, $Fe(NO_3)_3$ and $Bi(NO_3)_3$ were examined in the presence of $K_2S_2O_8$ (1.2 equiv). But, no obvious outcomes of *o*-nitrated product **4a** were detected, as shown in entries 6-8. By combining $AgNO_3$ (1.5 equiv) and $Pd(PPh_3)_4$ (10 mol %) of entries 3 and 5, the ratio of **4a** upgraded to 5:1 in a 60% yield (entry 9). After changing the source of nitronium ions from $AgNO_3$ to $AgNO_2$, **4a** was yielded as the dominant product (20:1) in a 51% yield (entry 10).[19] Thus, the combination of $AgNO_2/Pd(PPh_3)_4$ overcame the regioselective *o*-nitration issue. Next, it was necessary to increase the yield by optimizing the reaction conditions. In entry 11, the catalytic amounts of $Pd(PPh_3)_4$ were increased (10 → 20 mol%); however, the yield of **4a** increased slightly (51 → 55%). After replacing the solvent (MeCN → $MeNO_2$) and elevating the reaction temperature (25 → 101 °C), the yield was increased to 62% and 73%, respectively (entries 12-13). But, elongating the time (10 → 20 h) in entry 14 showed that the yield of **4a** was decreased. After changing the palladium catalyst from $Pd(PPh_3)_4$ to $Pd_2(dba)_3$ or $Pd(OAc)_2$ (entries 15-16), 50% and 28% yields of **4a** were observed, respectively. According to the above experimental results, the 1.5 equivalent of $AgNO_2$/20 mol % of $Pd(PPh_3)_4/MeNO_2$/reflux/10 h condition would be an optimal combination for yielding **4a**. To the best of our knowledge, the direct use of styrenes to synthesize *o*-nitrostyrenes via $AgNO_2/Pd(PPh_3)_4$-promoted regiocontrolled nitration has not been explored to date.[20] The structure of **4a** was determined by single-crystal X-ray crystallography.[21]

On the basis of the experimental results, a plausible mechanism for the formation of **4a** is described, as shown in Scheme 4.[22] Initially, complexation of $Pd(PPh_3)_4$ with olefin motif of **3a** yields **I**. Next, **I** is converted to **II** with a coordinated Pd^+ complex (PdL_n, L = PPh_3). Furthermore, **III** should be produced via an intermolecular cross-coupling of **II** with NO_2 group (in situ formed from $AgNO_2$).[23] Following the delocalized resonance of **III**, **IV-1** (a *trans*-form) and **IV-2** (a *cis*-form) having an *o*-carbocation should be generated more easily than *p*-carbocation due to the oxygen atom of sulfonyl group provides a stabilized six-membered coordination. By the involvement of a releasing ligand (L), the nitro group of palladium arm on **IV-1** could transfer to the ortho position of benzene ring by an intramolecular migration on the basis of a six-membered transition orientation. Subsequently, $Pd^0(PPh_3)_4$ is regenerated and **4a** is obtained via dehydrogenative aromatization. Finally, sulfonyl group induced regioselective *o*-nitration was furnished by the combination of $AgNO_2/Pd(PPh_3)_4$.

Scheme 4. Plausible Mechanism for **4a**



To explore the substrate scope, different R substituent of **3a-m** (for Y = H) in Table 2, entries 1-20, was first examined. As shown in Table 4 and entries 1-13, the treatment of **3a-m** afforded **4a-m** in a yield range of 60%-80% under the optimal conditions. The sulfonylarenes possessing the electron-donating group at the para position of sulfonyl, such as methyl (**4a**, 73%), methoxy (**4f**, 80%), ethyl (**4h**, 60%), isopropyl (**4i**, 66%), *n*-butyl (**4j**, 70%), and *t*-butyl (**4k**, 71%), and electron-neutral phenyl group (**4b**, 66%), were suitable for the current reaction, leading to the formation of desired products in moderate to good yields. The *meta*-tolylsulfonyl group of **3g** also generated a 71% yield of **4g**. The halophenyl group was compatible, including fluoro (**4e**, 70%), bromo (**4l**, 70%), and chloro (**4m**, 75%) for the synthesis of the resulting *o*-nitrated products. For the sulfonylaliphatic substituents, methyl (**4c**, 63%) and *n*-butyl (**4d**, 60%) groups were well tolerated, albeit with lower yields. For the isolated yields of **4a-m**, it should be noted that the strong electron-donating 4-methoxyphenyl group (for Y group) was a better partner for the present conversion. The structural frameworks of **4c** and **4f** were determined by single-crystal X-ray crystallography.[20] When Y = 3-F (for **3n**, entry 14), **4n** was isolated in only a 25% yield.

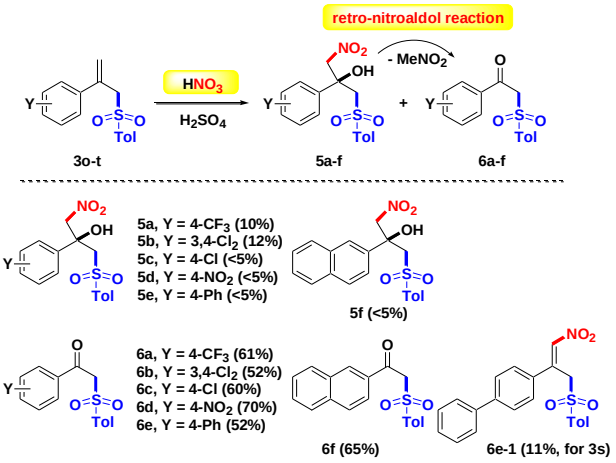
Table 4. Synthesis of **4**[a]

entry	**3**, R =, Y =	**4**, (%)[b]
1	**3a**, Tol, H	**4a**, 73
2	**3b**, Ph, H	**4b**, 66
3	**3c**, Me, H	**4c**, 63
4	**3d**, *n*Bu, H	**4d**, 60
5	**3e**, 4-FC_6H_4, H	**4e**, 70
6	**3f**, 4-$MeOC_6H_4$, H	**4f**, 80
7	**3g**, 3-MeC_6H_4, H	**4g**, 71
8	**3h**, 4-EtC_6H_4, H	**4h**, 60
9	**3i**, 4-*i*PrC_6H_4, H	**4i**, 66
10	**3j**, 4-*n*BuC_6H_4, H	**4j**, 70
11	**3k**, 4-*t*BuC_6H_4, H	**4k**, 71
12	**3l**, 4-BrC_6H_4, H	**4l**, 70
13	**3m**, 4-ClC_6H_4, H	**4m**, 75
14	**3n**, Tol, 3-F	**4n**, 25
15	**3o**, Tol, 4-CF_3	**4o**, —[c]
16	**3p**, Tol, 3,4-Cl_2	**4p**, —[c]
17	**3q**, Tol, 4-Cl	**4q**, —[c]
18	**3r**, Tol, 4-NO_2	**4r**, —[c-d]
19	**3s**, Tol, 4-Ph	**4s**, —[c]
20	**3t**,Tol, 2-naphthyl	**4t**, —[c]

[a]The reactions were run on a 0.5 mmol scale with **3**, $Pd(PPh_3)_4$ (23 mg, 0.2 mmol), $AgNO_2$ (115 mg, 1.5 equiv), $MeNO_2$ (5 mL), 10 h, 101 °C. [b]Isolated yields. [c]Complex mixture. [d]45% of **3r** was recovered.

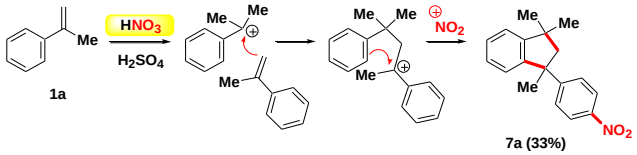
However, attempts to examine the *o*-nitration of **3o-q** with the *para*-aryl substituents (Y = 4-CF_3, 3,4-Cl_2, 4-Cl, entries 15-17) failed due to the electronic effect affecting the aryl π-system reactions' production of a complex mixture. When Y was a *para*-nitro group (entry 18), starting material **3r** was recovered at 45%. In entries 19-20, complex mixtures with different nitrated products were generated for biphenyl (for **3s**, Y = 4-Ph) and 2-naphthyl (for **3t**) group under the *o*-nitration conditions. In the other hand, **3u** and **3v** could be not obtained by ZnI_2 mediated reaction such that no available materials were examined next for $AgNO_2$/$Pd(PPh_3)_4$ mediated *o*-nitration. Overall, for the electronic effect of Y substituent on the skeleton of α-sulfonylmethyl styrenes **3**, the optimal condition was inappropriate for both of 4-trifluoromethylphenyl group and 4-nitrophenyl group due to their stronger electron-withdrawing nature. On the basis of unavailable starting materials (from Table 2, entry 22), no **3v** with an electron-donating oxygenated group was studied in the formation of **4**.

Scheme 5. Synthesis of **5** and **6**



Compared with the $AgNO_2$/$Pd(PPh_3)_4$ combination, treatment of **3o-t** (Y ≠ H) with the HNO_3 (0.5 mL)/H_2SO_4 (1 mL) system was examined next (Scheme 4). In Table 3 and entry 1, we observed that **3a** (Y = H) provided the mixture of *o*- and *p*-nitrated products (ratio 1:1). With these results in hand, nitration of **3o-t** was investigated. Unexpectedly, when *para*-Y is not a hydrogen atom, we found that β-ketosulfones was generated as major products and replaced the desired *o*-nitrated products. As shown in Scheme 5, the treatment of **3o-t** (Y = 4-CF_3, 3,4-Cl_2, 4-Cl, 4-NO_2, 4-Ph or 2-naphthyl) with the HNO_3/H_2SO_4 system converted it into β-ketosulfones **6a-f** (52%-70%) along with the trace amounts of vicinal nitroalcohols **5a-f** (5%-12%). Although the isolated yields of **6a-f** were not high, one-pot HNO_3/H_2SO_4 mediated double bond cleavage of 1,1-disubstituted olefins was first reported via the *in situ* formed retro-nitroaldol reaction of **5a-f** and removal of nitromathane. To the best of our knowledge, the present route is a novel nitration method for the transformation from α-sulfonylmethyl styrenes to α-sulfonyl ketones in the tandem and oxidant manner. For nitration of **6e**, however, dehydration of intermediate **5e** also provided an 11% yield of **6e-1**. For HNO_3/H_2SO_4 mediated nitration of α-sulfonylmethyl styrenes, the difference between Y = H and Y ≠ H should be the substituent effect and position. The structure of **6c** was determined by single-crystal X-ray crystallography.[21] In another way, HNO_3/H_2SO_4 mediated nitration of **1a** was also studied (Scheme 6). By the protocol, dimerization of **1a** provided nitrated indane **7a** with a 33% yield via two intermediates of the plausible *in situ* formed carbocations under acidic conditions.[21] The structure of **7a** was determined by single-crystal X-ray crystallography.[21]

Scheme 6. Synthesis of **7a**



In summary, we have developed two-step synthetic route for the synthesis of sulfonyl *o*-nitrostyrenes with moderate to good yields, including (1) ZnI_2-mediated sulfonylation of substituted α-methylstyrenes and sodium sulfinates (RSO_2Na) in wet MeCN at reflux for 10 h, and (2) $AgNO_2$/$Pd(PPh_3)_4$-promoted regiocontrolled *o*-nitration of α-sulfonylmethyl styrenes in $MeNO_2$ at reflux for 10 h. The structures of the key products were confirmed by X-ray crystallography. Further investigations regarding the synthetic application of sodium sulfinates will be conducted and published in due course.

Experimental Section

General Methods. All reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration *in vacuo*. Purity was determined by NMR and melting point. Melting points were determined with an SMP3 melting apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian spectrometer operating at 400 and 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm), and the coupling constants (*J*) are given in hertz. High resolution mass spectra (HRMS) were measured with a mass spectrometer microTOF-Q by ESI using a hybrid ion-trap. X-ray crystal structures were obtained with a diffractometer (CAD4, Kappa CCD).

*A representative synthetic procedure of compounds **3a-t** is as follows:* A solution of sodium sulfinates **2** (RSO_2Na, 2.2 mmol) in H_2O (1 mL) was added to a solution of substituted α-methylstyrenes **1** (1.0 mmol) in MeCN (9 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. ZnI_2 (380 mg, 1.2 mmol) was added to the reaction mixture at 25 °C. Then, the reaction mixture was stirred at 82 °C for 10 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1~4/1) afforded compounds **3a-t** and **3v-1**.

*1-Methyl-4-(2-phenylallylsulfonyl)benzene (**3a**).*[6d] Yield = 80% (218 mg); Colorless solid; mp = 96-97 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{17}O_2S$ 273.0949; Found 273.0948; ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.28-7.20 (m, 7H), 5.59 (s, 1H), 5.21 (s, 1H), 4.25 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 138.8, 136.6, 135.4, 129.5 (2x), 128.6 (2x), 128.3 (2x), 127.9, 126.2 (2x), 121.7, 62.1, 21.5.

*(2-Phenylallylsulfonyl)benzene (**3b**).*[6d] Yield = 73% (188 mg); Colorless solid; mp = 61-62 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{15}O_2S$ 259.0793; Found 259.0796; ^1H NMR (400 MHz, $CDCl_3$): δ 7.80-7.77 (m, 2H), 7.57-7.52 (m, 1H), 7.45-7.40 (m, 2H), 7.28-7.21 (m, 5H), 5.59 (s, 1H), 5.22 (s, 1H), 4.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 138.3, 136.4, 133.6, 128.8 (2x), 128.6 (2x), 128.3 (2x), 128.0 (2x), 126.1, 121.8, 62.0.

*(3-Methylsulfonylprop-1-en-2-yl)benzene (**3c**).*[6d] Yield = 70% (137 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{13}O_2S$ 197.0636; Found 197.0633; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48-7.44 (m, 2H), 7.38-7.29 (m, 3H), 5.73 (s, 1H), 5.53 (s, 1H), 4.17 (s, 2H), 2.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 136.4, 128.5 (2x), 128.2, 126.1 (2x), 121.8, 60.2, 40.0.

*3-(n-Butylsulfonylprop-1-en-2-yl)benzene (**3d**).* Yield = 76% (181 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{19}O_2S$ 239.1106; Found 239.1102; ^1H NMR (400 MHz, $CDCl_3$): δ 7.47-7.44 (m, 2H), 7.39-7.32 (m, 3H), 5.73 (s, 1H), 5.55 (s, 1H), 4.13 (s, 2H), 2.80-2.76 (m, 2H), 1.72-1.65 (m, 2H), 1.33-1.24 (m, 2H), 0.83 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 136.4, 128.7 (2x), 128.4, 126.3 (2x), 122.0, 58.6, 51.9, 23.7, 21.5, 13.3.

*1-Fluoro-4-(2-phenylallylsulfonyl)benzene (**3e**).* Yield = 82% (226 mg); Colorless solid; mp = 84-86 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{14}FO_2S$ 277.0699; Found 277.0702; ^1H NMR (400 MHz, $CDCl_3$): δ 7.77-7.72 (m, 2H), 7.25-7.19 (m, 5H), 7.06-7.01 (m, 2H), 5.57 (s, 1H), 5.22 (s, 1H), 4.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4 (d, *J* = 254.7 Hz), 138.3, 136.3, 134.2 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 9.1 Hz, 2x), 128.2 (2x), 127.8, 125.9 (2x), 121.7, 115.9 (d, *J* = 22.0 Hz, 2x), 61.8.

*1-Methoxy-4-(2-phenylallylsulfonyl)benzene (**3f**).*[6d] Yield = 83% (239 mg); Colorless solid; mp = 84-85 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{17}O_3S$ 289.0899; Found 289.0901; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.28-7.21 (m, 5H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.58 (s, 1H), 5.21 (s, 1H), 4.25 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 138.8, 136.8, 130.8 (2x), 130.0, 128.3 (2x), 127.9, 126.2 (2x), 121.6, 114.0 (2x), 62.3, 55.6.

*1-Methyl-3-(2-phenylallylsulfonyl)benzene (**3g**).* Yield = 82% (223 mg); Colorless solid; mp = 60-61 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{17}O_2S$ 273.0949; Found 273.0953; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60-7.57 (m, 1H), 7.54 (br s, 1H), 7.32-7.19 (m, 7H), 5.58 (s, 1H), 5.24 (s, 1H), 4.26 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 138.6, 138.1, 136.3, 134.2, 128.7, 128.6, 128.1 (2x), 127.8, 126.0 (2x), 125.4, 121.6, 61.8, 21.0.

*1-Ethyl-4-(2-phenylallylsulfonyl)benzene (**3h**).* Yield = 74% (212 mg); Colorless solid; mp = 79-80 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{19}O_2S$ 287.1106; Found 287.1112; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.24-7.19 (m, 7H), 5.59 (s, 1H), 5.25 (s, 1H), 4.25 (s, 2H), 2.66 (q, *J* = 8.0 Hz, 2H), 1.21 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 138.8, 136.5, 135.6, 128.7 (4x), 128.3 (2x), 127.8, 126.1 (2x), 121.7, 62.0, 28.8, 15.1.

*1-Isopropyl-4-(2-phenylallylsulfonyl)benzene (**3i**).* Yield = 76% (228 mg); Colorless solid; mp = 66-68 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{21}O_2S$ 301.1262; Found 301.1257; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.21-7.17 (m, 5H), 5.60 (s, 1H), 5.29 (s, 1H), 4.26 (s, 2H), 2.94-2.87 (m, 1H), 1.21 (d, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 138.7, 136.5, 135.7, 128.7 (2x), 128.2 (2x), 127.8, 126.8 (2x), 126.0 (2x), 121.7, 61.9, 34.1, 23.5 (2x).

*1-n-Butyl-4-(2-phenylallylsulfonyl)benzene (**3j**).* Yield = 85% (267 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{23}O_2S$ 315.1419; Found 315.1423; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.25-7.19 (m, 7H), 5.60 (d, *J* = 0.8 Hz, 1H), 5.26 (d, *J* = 0.8 Hz, 1H), 4.25 (s, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.60-1.53 (m, 2H), 1.37-1.26 (m, 2H), 0.93 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 138.9, 136.6, 135.6, 128.8 (2x), 128.7 (2x), 128.3 (2x), 127.9, 126.1 (2x), 121.7, 62.1, 35.5, 33.1, 22.2, 13.8.

*1-t-Butyl-4-(2-phenylallylsulfonyl)benzene (**3k**).* Yield = 80% (251 mg); Colorless solid; mp = 82-84 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{23}O_2S$ 315.1419; Found 315.1423; ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.21-7.16 (m, 5H), 5.60 (s, 1H), 5.31 (s, 1H), 4.26 (s, 2H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 138.7, 136.5, 135.3, 128.4 (2x), 128.2 (2x), 127.8, 126.0 (2x), 125.7 (2x), 121.7, 61.9, 35.0, 30.9 (3x).

*1-Bromo-4-(2-phenylallylsulfonyl)benzene (**3l**).*[6d] Yield = 80% (269 mg); Colorless solid; mp = 127-129 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{14}BrO_2S$ 336.9898; Found 336.9903; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.259-7.20 (m, 5H), 5.60 (s, 1H), 5.25 (s, 1H), 4.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 137.3, 136.4, 132.1 (2x), 130.2 (2x), 129.0, 128.4 (2x), 128.1, 126.2 (2x), 122.1, 62.2.

*1-Chloro-4-(2-phenylallylsulfonyl)benzene (**3m**).*[6d] Yield = 72% (210 mg); Colorless solid; mp = 114-116 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{14}ClO_2S$ 293.0403; Found 293.0405; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.255-7.21 (m, 5H), 5.60 (s, 1H), 5.25 (s, 1H), 4.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 138.4, 136.8, 136.4, 130.1 (2x), 129.1 (2x), 128.4 (2x), 128.1, 126.1 (2x), 122.1, 62.2.

*1-Methyl-4-((2-(3-fluorophenylallyl)sulfonyl)benzene (**3n**).* Yield = 78% (226 mg); Colorless solid; mp = 75-77 °C (re-

crystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{16}FO_2S$ 291.0855; Found 291.0854; ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.21-7.17 (m, 1H), 7.07-7.05 (m, 1H), 6.94-6.89 (m, 2H), 5.59 (s, 1H), 5.25 (s, 1H), 4.21 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6 (d, *J* = 244.1 Hz), 144.8, 141.1 (d, *J* = 7.5 Hz), 135.6 (d, *J* = 2.3 Hz), 135.2, 129.8 (d, *J* = 8.3 Hz), 129.5 (2x), 128.6 (2x), 122.7, 121.9 (d, *J* = 3.0 Hz), 114.7 (d, *J* = 21.2 Hz), 113.2 (d, *J* = 22.8 Hz), 61.9, 21.5.

*1-Methyl-4-((2-(4-trifluoromethylphenyl)allyl)sulfonyl)benzene (**3o**).*[6d] Yield = 71% (241 mg); Colorless solid; mp = 128-130 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{16}F_3O_2S$ 341.0823; Found 341.0830; ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.65 (s, 1H), 5.33 (s, 1H), 4.25 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 142.3, 135.7, 135.2, 129.9, 129.5 (2x), 128.5 (2x), 126.6 (2x), 125.2 (q, *J* = 3.1 Hz, 2x), 123.7, 122.6, 62.0, 21.4.

*1-Methyl-4-((2-(3,4-dichlorophenyl)allyl)sulfonyl)benzene (**3p**).* Yield = 70% (238 mg); Colorless solid; mp = 87-89 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{15}Cl_2O_2S$ 341.0170; Found 341.0178; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.21-7.18 (m, 2H), 7.10 (dd, *J* = 2.0, 8.4 Hz, 1H), 5.56 (s, 1H), 5.25 (s, 1H), 4.16 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 138.7, 135.0, 134.7, 132.3, 131.8, 130.1, 129.5 (2x), 128.4 (2x), 128.1, 125.6, 123.2, 61.8, 21.4.

*1-Methyl-4-((2-(4-chlorophenylallyl)sulfonyl)benzene (**3q**).*[6d] Yield = 76% (233 mg); Colorless solid; mp = 120-22 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{16}ClO_2S$ 307.0560; Found 307.0563; ^1H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.20 (br s, 4H), 5.57 (s, 1H), 5.21 (s, 1H), 4.21 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 137.3, 135.6, 135.3, 133.9, 129.5 (2x), 128.6 (2x), 128.5 (2x), 127.6 (2x), 122.2, 62.1, 21.5.

*1-Methyl-4-((2-(4-nitrophenylallyl)sulfonyl)benzene (**3r**).* Yield = 70% (222 mg); Colorless solid; mp = 135-137 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{16}NO_4S$ 318.0800; Found 318.0805; ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 9.2 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 5.72 (s, 1H), 5.37 (s, 1H), 4.25 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 145.2, 145.1, 135.1, 129.74, 129.69 (2x), 128.5 (2x), 127.2 (2x), 125.1, 123.6 (2x), 61.7, 21.5.

*4-(3-Tosylprop-1-en-2-yl)-1,1'-biphenyl (**3s**).*[6d] Yield = 78% (271 mg); Colorless solid; mp = 112-114 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{21}O_2S$ 349.1262; Found 349.1263; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.57-7.50 (m, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.38-7.34 (m, 3H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.65 (s, 1H), 5.23 (s, 1H), 4.29 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 140.8, 140.4, 137.6, 136.2, 135.5, 129.5 (2x), 128.8 (2x), 128.7 (2x), 127.5, 127.0 (2x), 126.9 (2x), 126.6 (2x), 121.6, 62.1, 21.6.

*4-(3-Tosylprop-1-en-2-yl)-2-naphthalene (**3t**).*[6d] Yield = 77% (248 mg); Colorless solid; mp = 114-116 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{19}O_2S$ 323.1106; Found 323.1112; ^1H NMR (400 MHz, $CDCl_3$): δ 7.78-7.76 (m, 1H), 7.71-7.69 (m, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.47-7.44 (m, 2H), 7.41 (dd, *J* = 2.0, 8.8 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 5.73 (s, 1H), 5.34 (s, 1H), 4.37 (s, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 136.5, 135.8, 135.4, 132.9, 132.7, 129.3 (2x), 128.5 (2x), 128.2, 128.0, 127.4, 126.20, 126.17, 125.4, 124.0, 122.0, 62.2, 21.3.

*5-Benzo[1,3]dioxol-5-yl-5,7,7-trimethyl-6,7-dihydro-5H-indeno[5,6-d][1,3]dioxole (**3v-1**).* Yield = 46% (75 mg); Colorless oil; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{21}O_4$ 325.1440; Found 325.1438; ^1H NMR (400 MHz, $CDCl_3$): δ 6.71-6.62 (m, 4H), 6.53 (s, 1H), 5.96 (d, *J* = 1.6 Hz, 1H), 5.95 (d, *J* = 1.2 Hz, 1H), 5.91 (d, *J* = 2.0 Hz, 1H), 5.91 (d, *J* = 1.6 Hz, 1H), 2.34 (d, *J* = 13.2 Hz, 1H), 2.16 (d, *J* = 12.8 Hz, 1H), 1.61 (s, 3H), 1.29 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 147.2, 146.7, 145.3, 145.2 (2x), 141.5, 119.4, 107.6, 107.4, 104.9, 102.8, 101.0, 100.8, 59.7, 50.3, 42.6, 30.93, 30.87, 30.4.

*A representative synthetic procedure of compounds **4a-n** is as follows:* $Pd(PPh_3)_4$ (116 mg, 0.1 mmol) was added to a solution of substituted α-sulfonylmethylstyrenes **3a-n** (0.5 mmol) in $MeNO_2$ (5 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 5 min. $AgNO_2$ (115 mg, 0.75 mmol) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 101 °C for 10 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1~4/1) afforded compounds **4a-n**.

*1-Methyl-4-((2-(2-nitrophenyl)allyl)sulfonyl)benzene (**4a**).* Yield = 73% (116 mg); Colorless solid; mp = 103-105 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{16}NO_4S$ 318.0800; Found 318.0812; ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.57 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.48-7.41 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.43 (s, 1H), 5.37 (s, 1H), 4.14 (d, *J* = 0.8 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 136.2, 135.9, 135.0, 133.6, 132.7, 129.8 (2x), 129.0 (2x), 128.2 (2x), 124.4, 124.3, 62.7, 21.5. Single-crystal X-Ray diagram: crystal of compound **4a** was grown by slow diffusion of EtOAc into a solution of compound **4a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, *a* = 8.8147(15) Å, *b* = 8.1358(14) Å, *c* = 20.421(4) Å, *V* = 1463.8(4) $Å^3$, *Z* = 4, d_{calcd} = 1.440 g/cm^3, *F*(000) = 664, 2θ range 1.995~26.522°, R indices (all data) R1 = 0.0915, wR2 = 0.2397.

*4-((2-(2-Nitrophenylallyl)sulfonyl)benzene (**4b**).* Yield = 66% (100 mg); Colorless solid; mp = 119-121 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M +

H]$^+$ Calcd for $C_{15}H_{14}NO_4S$ 304.0644; Found 304.0648; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.84-7.81 (m, 2H), 7.64-7.60 (m, 1H), 7.58 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.50-7.40 (m, 2H), 5.46 (s, 1H), 5.39 (s, 1H), 4.17 (d, *J* = 0.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.94, 138.9, 136.1, 134.9, 133.8, 133.6, 132.7, 129.2 (2x), 129.1, 128.2 (2x), 124.48, 124.47, 62.6.

1-Nitro-2-(3-methylsulfonylprop-1-en-2-yl)benzene ***(4c)***. Yield = 63% (76 mg); Colorless solid; mp = 117-119 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ Calcd for $C_{10}H_{12}NO_4S$ 242.0487; Found 242.0486; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.66-7.62 (m, 1H), 7.54-7.49 (m, 2H), 5.70 (s, 1H), 5.48 (s, 1H), 4.11 (s, 2H), 2.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.8, 135.0, 133.7, 132.6 (2x), 129.3, 124.7, 124.3, 61.3, 40.6. Single-crystal X-Ray diagram: crystal of compound **4c** was grown by slow diffusion of EtOAc into a solution of compound **4c** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P -1, *a* = 7.1934(7) Å, *b* = 7.9479(7) Å, *c* = 9.7888(9) Å, *V* = 540.42(9) Å^3, *Z* = 2, d_{calcd} = 1.483 g/cm^3, *F*(000) = 252, 2θ range 2.889~26.442°, R indices (all data) R1 = 0.287, wR2 = 0.0674.

1-Nitro-2-(3-n-butylsulfonylprop-1-en-2-yl)benzene ***(4d)***. Yield = 60% (85 mg); Colorless gum; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ Calcd for $C_{13}H_{18}NO_4S$ 284.0957; Found 284.0961; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.63 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.54 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.49 (dt, *J* = 1.2, 8.0 Hz, 1H), 5.67 (s, 1H), 5.46 (s, 1H), 4.04 (s, 2H), 2.94 (t, *J* = 8.0 Hz, 2H), 1.79-1.71 (m, 2H), 1.45-1.36 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 136.0, 134.6, 133.6, 132.6, 129.1, 124.5, 124.3, 59.1, 52.6, 23.8, 21.5, 13.4.

1-Fluoro-4-((2-(2-nitrophenyl)allyl)sulfonyl)benzene ***(4e)***. Yield = 70% (112 mg); Colorless solid; mp = 107-109 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ Calcd for $C_{15}H_{13}FNO_4S$ 322.0549; Found 322.0545; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.86-7.81 (m, 2H), 7.61-7.57 (m, 1H), 7.49-7.44 (m, 1H), 7.41 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.21-7.15 (m, 2H), 5.46 (s, 1H), 5.40 (s, 1H), 4.17 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8 (d, *J* = 254.7 Hz), 146.9, 135.9, 134.9 (d, *J* = 3.1 Hz), 134.8, 133.6, 132.7, 131.1 (d, *J* = 9.9 Hz, 2x), 129.2, 124.6, 124.5, 116.5 (d, *J* = 22.8 Hz, 2x), 62.7.

1-Methoxy-4-((2-(2-nitrophenyl)allyl)sulfonyl)benzene ***(4f)***. Yield = 80% (133 mg); Colorless solid; mp = 107-108 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ Calcd for $C_{16}H_{16}NO_5S$ 334.0749; Found 334.0753; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.73 (d, *J* = 9.2 Hz, 2H), 7.60-7.56 (m, 1H), 7.48-7.42 (m, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 5.43 (s, 1H), 5.37 (s, 1H), 4.13 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 136.3, 135.2, 133.5, 132.8, 130.4 (2x), 129.0, 124.5 (2x), 124.3 (2x), 114.3 (2x), 62.9, 55.7. Single-crystal X-Ray diagram: crystal of compound **4f** was grown by slow diffusion of EtOAc into a solution of compound **4f** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P 21/c, *a* = 10.958(3) Å, *b* = 7.579(2) Å, *c* = 18.911(5) Å, *V* = 1508.8(6) Å^3, *Z* = 4, d_{calcd} = 1.467 g/cm^3, *F*(000) = 696, 2θ range 1.935~27.104°, R indices (all data) R1 = 0.1205, wR2 = 0.2805.

1-Methyl-3-((2-(2-nitrophenyl)allyl)sulfonyl)benzene ***(4g)***. Yield = 71% (113 mg); Colorless gum; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ Calcd for $C_{16}H_{16}NO_4S$ 318.0800; Found 318.0802; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.60-7.54 (m, 3H), 7.46-7.32 (m, 4H), 5.46 (s, 1H), 5.38 (s, 1H), 4.15 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 139.4, 138.6, 136.0, 134.9, 134.4, 133.5, 132.7, 129.0 (2x), 128.3, 125.2, 124.4 (2x), 62.5, 21.1.

1-Ethyl-4-((2-(2-nitrophenyl)allyl)sulfonyl)benzene ***(4h)***. Yield = 60% (99 mg); Colorless gum; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ Calcd for $C_{17}H_{18}NO_4S$ 332.0957; Found 332.0961; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.56 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.44 (dt, *J* = 1.6, 8.4 Hz, 1H), 7.40 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 5.46 (s, 1H), 5.37 (s, 1H), 4.15 (s, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9, 146.9, 136.2, 136.1, 135.0, 133.5, 132.7, 129.0, 128.6 (2x), 128.3 (2x), 124.4, 124.3, 62.6, 28.8, 15.1.

1-Isopropyl-4-((2-(2-nitrophenyl)allyl)sulfonyl)benzene ***(4i)***. Yield = 66% (114 mg); Colorless solid; mp = 94-96 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ Calcd for $C_{18}H_{20}NO_4S$ 346.1113; Found 346.1118; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.51 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.39 (dt, *J* = 0.8, 7.6 Hz, 1H), 7.34-7.29 (m, 3H), 5.45 (s, 1H), 5.35 (s, 1H), 4.14 (s, 2H), 2.96-2.89 (m, 1H), 1.21 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 146.7, 135.95, 135.9, 135.0, 133.4, 132.5, 128.8, 128.2 (2x), 127.1 (2x), 124.3, 124.2, 62.4, 34.0, 23.4 (2x).

1-n-Butyl-4-((2-(2-nitrophenyl)allyl)sulfonyl)benzene ***(4j)***. Yield = 70% (126 mg); Colorless gum; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ Calcd for $C_{19}H_{22}NO_4S$ 360.1270; Found 360.1276; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.58-7.54 (m, 1H), 7.48-7.40 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.47 (s, 1H), 5.38 (s, 1H), 4.15 (s, 2H), 2.67 (t, *J* = 8.0 Hz, 2H), 1.64-1.56 (m, 2H), 1.39-1.30 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 146.9, 136.2, 136.1, 135.0, 133.5, 132.8, 129.2 (2x), 129.0, 128.2 (2x), 124.4, 124.3, 62.7, 35.5, 33.1, 22.2, 13.8.

1-t-Butyl-4-((2-(2-nitrophenyl)allyl)sulfonyl)benzene ***(4k)***. Yield = 71% (127 mg); Colorless gum; HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ Calcd for $C_{19}H_{22}NO_4S$ 360.1270; Found 360.1274; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.70 (dd, *J* = 8.4 Hz, 2H), 7.53 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.42 (dt, *J* = 1.6, 8.0 Hz, 1H), 7.35 (dd, *J* = 1.6, 7.6 Hz, 1H), 5.49 (s, 1H), 5.38 (s, 1H), 4.15 (s, 2H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 146.8, 139.5, 136.1, 135.8, 135.0, 133.5, 132.7, 128.9, 127.9 (2x), 126.1 (2x), 124.4, 124.3, 62.5, 35.1, 30.9 (3x).

1-Bromo-4-((2-(2-nitrophenyl)allyl)sulfonyl)benzene ***(4l)***. Yield = 70% (133 mg); Colorless solid; mp = 105-107 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ Calcd for $C_{15}H_{13}BrNO_4S$ 381.9749; Found 381.9753; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.68-7.62 (m, 4H), 7.60-7.56 (m, 1H), 7.46-7.45 (m, 1H), 7.40-7.38 (m, 1H), 5.46 (s, 1H), 5.40 (s, 1H), 4.16 (s, 2H); ^{13}C

NMR (100 MHz, $CDCl_3$): δ 146.9, 139.6, 137.7, 135.8, 134.6, 133.6, 132.6, 132.4 (2x), 129.7 (2x), 129.1, 124.7, 124.5, 62.6.

*1-Chloro-4-((2-(2-nitrophenyl)allyl)sulfonyl)benzene (**4m**).* Yield = 75% (126 mg); Colorless solid; mp = 78-80 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{13}ClNO_4S$ 338.0254; Found 338.0255; ^1H NMR (400 MHz, $CDCl_3$): δ 8.01 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.62-7.58 (m, 1H), 7.50-7.46 (m, 3H), 7.41 (dd, *J* = 1.6, 7.6 Hz, 1H), 5.47 (s, 1H), 5.41 (s, 1H), 4.17 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 140.6, 137.3, 135.9, 134.7, 133.6, 132.7, 129.7 (2x), 129.5 (2x), 129.2, 124.8, 124.6, 62.7.

*1-Methyl-4-((2-(3-fluoro-2-nitrophenyl)allyl)sulfonyl)benzene (**4n**).* Yield = 25% (42 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{15}FNO_4S$ 336.0706; Found 336.0712; ^1H NMR (400 MHz, $CDCl_3$): δ 8.10-8.06 (m, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.15-7.10 (m, 1H), 7.03 (dd, *J* = 2.8, 8.8 Hz, 1H), 5.47 (s, 1H), 5.39 (s, 1H), 4.13 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6 (d, *J* = 257.8 Hz), 145.1, 139.6 139.5 (d, *J* = 9.1 Hz), 135.8, 134.4, 129.9 (2x), 128.3 (2x), 127.4 (d, *J* = 9.8 Hz), 124.7, 119.8 (d, *J* = 23.5 Hz), 116.0 (d, *J* = 23.5 Hz), 62.5, 21.6.

*A representative synthetic procedure of compounds **5a-b**, **6a-6f** and **6e-1** is as follows:* HNO_3 (97%, 0.5 mL) was added to a solution of **3o**-**t** (0.5 mmol) in CH_2Cl_2 (5 mL) at 25 °C. Then, H_2SO_4 (98%, 1 mL) was added to the reaction mixture. The reaction mixture was stirred at 25 °C for 10 h. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1~4/1) afforded compounds **5a-b**, **6a-6f** and **6e-1**.

*1-Nitro-3-(toluene-4-sulfonyl)-2-(4-trifluoromethylphenyl)propan-2-ol (**5a**).* Yield = 10% (20 mg); Colorless solid; mp = 190-192 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{17}F_3NO_5S$ 404.0780; Found 404.0775; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46-7.43 (m, 4H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 5.20 (br s, 1H), 4.85 (d, *J* = 12.4 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 3.95 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 142.2, 136.3, 129.9 (2x), 127.6 (2x), 125.72 (2x), 125.67 (q, *J* = 3.8 Hz, 2x), 125.66, 125.62, 83.0, 73.6, 62.2, 21.5.

*2-(3,4-Dichlorophenyl)-1-nitro-3-(toluene-4-sulfonyl)propan-2-ol (**5b**).* Yield = 12% (24 mg); Colorless solid; mp = 160-162 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{16}Cl_2NO_5S$ 404.0126; Found 404.0130; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.16 (dd, *J* = 2.0, 8.4 Hz, 1H), 5.19 (br s, 1H), 4.79 (d, *J* = 12.4 Hz, 1H), 4.74 (d, *J* = 12.4 Hz, 1H), 3.92 (d, *J* = 14.8 Hz, 1H), 3.88 (d, *J* = 15.2 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 138.4, 136.1, 130.7, 133.3, 133.1, 129.9 (2x), 127.59 (2x), 127.57, 124.6, 82.9, 73.2, 62.0, 21.6.

*2-(Toluene-4-sulfonyl)-1-(4-trifluoromethylphenyl)ethanone (**6a**).* Yield = 61% (104 mg); Colorless solid; mp = 140-142 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{14}F_3O_3S$ 343.0616; Found 343.06155; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 4H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.74 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.5, 145.7, 138.3, 135.5, 135.4, 135.2, 129.9 (2x), 129.7 (2x), 128.5 (2x), 125.8 (q, *J* = 3.8 Hz, 2x), 63.8, 21.7.

*1-(3,4-Dichlorophenyl)-2-(toluene-4-sulfonyl)ethanone (**6b**).* Yield = 52% (89 mg); Colorless solid; mp = 172-174 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{13}Cl_2O_3S$ 342.9963; Found 342.9966; ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 1.6 Hz, 1H), 7.82 (d, *J* = 1.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.66 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 145.8, 139.2, 135.3, 135.2, 133.7, 131.1, 130.9, 130.0 (2x), 128.5 (2x), 128.4, 63.8, 21.6.

*1-(4-Chlorophenyl)-2-(toluene-4-sulfonyl)ethanone (**6c**).* Yield = 60% (92 mg); Colorless solid; mp = 139-141 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{14}ClO_3S$ 309.0352; Found 309.0356; ^1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.68 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.0, 145.5, 141.0, 135.6, 134.0, 130.7 (2x), 129.8 (2x), 129.1 (2x), 128.5 (2x), 63.6, 21.6. Single-crystal X-Ray diagram: crystal of compound **6c** was grown by slow diffusion of EtOAc into a solution of compound **6c** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/n, *a* = 5.676(2) Å, *b* = 9.256(4) Å, *c* = 27.339(12) Å, *V* = 1436.2(10) Å^3, *Z* = 4, d_{calcd} = 1.428 g/cm^3, *F*(000) = 640, 2θ range 2.323~26.533°, R indices (all data) R1 = 0.1330, wR2 = 0.1640.

*1-(4-Nitrophenyl)-2-(toluene-4-sulfonyl)ethanone (**6d**).* Yield = 70% (112 mg); Colorless solid; mp = 144-146 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{14}NO_5S$ 320.0593; Found 320.0596; ^1H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 4.75 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.0, 151.0, 145.9, 139.9, 135.3, 130.5 (2x), 130.0 (2x), 128.5 (2x), 124.0 (2x), 64.1, 21.7.

*1-Biphenyl-4-yl-2-(toluene-4-sulfonyl)ethanone (**6e**).* Yield = 52% (91 mg); Colorless solid; mp = 118-120 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{19}O_3S$ 351.1055; Found 351.1058; ^1H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 9.2 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.79-7.73 (m, 7H), 7.36 (d, *J* = 8.4 Hz, 2H), 4.75 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.5, 146.0, 145.7, 144.3, 135.72, 135.67, 130.3 (2x), 129.9 (2x), 128.6 (2x), 128.2 (2x), 127.8 (3x), 124.3 (2x), 63.8, 21.7.

*4-[2-Nitro-1-(toluene-4-sulfonylmethyl)vinyl]biphenyl (**6e-1**).* Yield = 11% (22 mg); Colorless solid; mp = 196-198 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{20}NO_4S$ 394.1113; Found 394.1115; ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.68-7.65 (m, 2H), 7.62-7.58 (m, 4H), 7.50-7.46 (m, 2H), 7.43-7.40 (m, 1H), 7.40 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.15 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8,

144.1, 139.5, 139.2, 138.7, 135.8, 133.6, 129.9 (2x), 129.0 (2x), 128.4 (2x), 128.3, 128.2 (2x), 127.9 (2x), 127.1 (2x), 56.6, 21.7.

*1-Naphthalen-2-yl-2-(toluene-4-sulfonyl)ethanone (**6f**).* Yield = 65% (105 mg); Colorless solid; mp = 145-147 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{17}O_3S$ 325.0899; Found 325.0903; ^1H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, *J* = 1.2 Hz, 1H), 7.97-7.95 (m, 2H), 7.89-7.86 (m, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.66-7.62 (m, 1H), 7.59-7.55 (m, 1H), 7.31 (d, *J* = 8.8 Hz, 2H), 4.84 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.0, 145.4, 136.0, 135.7, 133.1, 132.24, 132.16, 130.0, 129.8 (2x), 129.3, 128.8, 128.6 (2x), 127.8, 127.1, 123.9, 63.8, 21.6.

*1,1,3-Trimethyl-3-(4-nitrophenyl)indan (**7a**).* HNO_3 (97%, 0.5 mL) was added to a solution of **1a** (118 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) at 25 °C. Then, H_2SO_4 (98%, 1 mL) was added to the reaction mixture. The reaction mixture was stirred at 25 °C for 10 h. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 20/1~4/1) afforded compounds **7a**. Yield = 33% (46 mg); Colorless solid; mp = 177-179 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{18}H_{20}NO_2$ 282.1494; Found 282.1499; ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.33-7.28 (m, 2H), 7.26-7.23 (m, 1H), 7.13-7.11 (m, 1H), 2.41 (d, *J* = 13.2 Hz, 1H), 2.28 (d, *J* = 13.2 Hz, 1H), 1.74 (s, 3H), 1.38 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 152.1, 147.1, 145.9, 127.8, 127.6 (2x), 127.0, 124.7, 123.3 (2x), 122.8, 59.1, 51.2, 43.0, 30.52, 30.48, 30.3. Single-crystal X-Ray diagram: crystal of compound **7a** was grown by slow diffusion of EtOAc into a solution of compound **7a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, a = 11.1208(9) Å , b = 11.5061(10) Å , c = 11.8471(10) Å , V = 1479.7(2) Å ^{3}, Z = 4, d_{calcd} = 1.263 g/cm^3, F(000) = 600, 2θ range 1.876~26.527°, R indices (all data) R1 = 0.0535, wR2 = 0.1143.

ASSOCIATED CONTENT

Supporting Information

Scanned photocopies of NMR ($CDCl_3$) spectral data for all compounds and X-ray analysis data of **4a**, **4c**, **4f**, **6c** and **7a** were supported. This information is available free of charge via the Internet at http: //pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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