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Rhodium-catalyzed direct *ortho*-alkenylation of phenyl sulfones with alkynes utilizing sulfonyl function as modifiable directing group

Kazunori Nobushige [a], Koji Hirano [a], Tetsuya Satoh [a,b,*], Masahiro Miura [a,*]

[a] Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan
[b] JST, ACT-C, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

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ABSTRACT

The *ortho*-selective alkenylation of phenyl sulfones with alkynes proceeds effectively in the presence of a cationic Cp*-rhodium(III) catalyst together with an appropriate carboxylic acid involving regioselective C–H bond cleavage directed by the sulfonyl function. An (*ortho*-alkenylated phenyl) methyl sulfone prepared by this hydroarylation method undergoes palladium-catalyzed α-arylation and subsequent diastereoselective cyclization to directly produce the corresponding thiochromane 1,1-dioxide derivatives.

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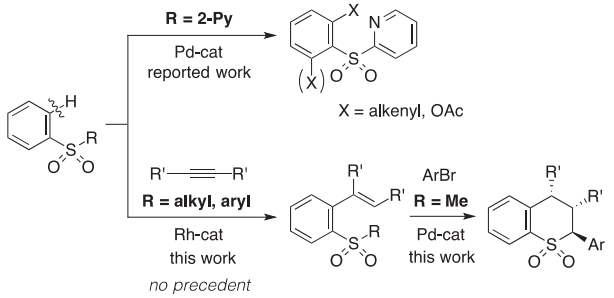
1. Introduction

Transition-metal-catalyzed direct C–H functionalization reactions of aromatic substrates have received much attention as environmentally-benign synthetic methods, because they provide atom- and step-economical routes from simple arenes to functionalized aromatic molecules.[1] Especially, the chelation-assisted version involving a C–H bond cleavage step with the assistance of a directing group, which leads to regioselective *ortho*-substitution, is highly useful in precise synthesis. As typical directing groups, oxygen- and nitrogen-containing groups have been utilized. Besides them, sulfur-containing functions are beginning to be employed as directing groups. Several examples for sulfide- and sulfoxide-directed C–H functionalization reactions have been recently reported by us[2] and others.[3] However, the utilization of sulfonyl groups, which can be readily introduced onto aromatic rings via electrophilic sulfonylation, has been less explored. So far, the palladium-catalyzed *ortho*-alkenylation[4] and –acetoxylation[5] employing a (2-pyridyl)sulfonyl group have been examined, the efficiency and selectivity being less acceptable. In these examples, coordination of the pyridyl function rather than the sulfonyl moiety seems to be the key for the *ortho*-functionalization. Other sulfonyl groups containing no pyridyl moiety have, to our knowledge, never been utilized as effective directing groups. During our continuous studies of rhodium-catalyzed C–H functionalization,[1t] we succeeded in finding that simple phenyl sulfones undergo direct alkenylation upon treatment with internal alkynes[2,6] in the presence of a rhodium catalyst through C–H bond cleavage directed by their sulfonyl group to produce *ortho*-alkenylated phenyl sulfones (Scheme 1). In these reactions, simple alkyl- and aryl sulfonyl functions without any pyridyl group could act as effective directing groups. Various *ortho*-substituted phenyl sulfone derivatives have recently drawn much attention because of their biological activities as well as their utilities as useful ligands for transition-metals.[7] Therefore, the present reaction provides a straightforward



Scheme 1. *ortho* C–H Functionalization of phenyl sulfones.

* Corresponding authors. E-mail addresses: satoh@chem.eng.osaka-u.ac.jp (T. Satoh), miura@chem.eng.osaka-u.ac.jp (M. Miura).

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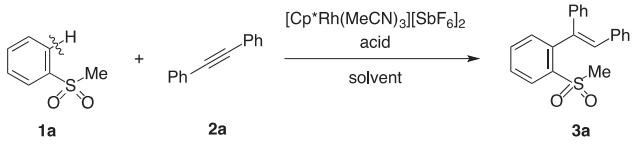
approach toward such an important class of compounds. Furthermore, the sulfonyl directing group was found to be readily modified after the *ortho*-alkenylation through palladium-catalyzed α-arylation[8,9] and subsequent diastereoselective cyclization to afford the corresponding 2-arylthiochromane 1,1-dioxide derivatives. These new findings are described herein.

2. Results and discussion

In an initial attempt, methyl phenyl sulfone (**1a**) (0.5 mmol) was treated with diphenylacetylene (**2a**) (0.25 mmol) in the presence of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.01 mmol) and PivOH (0.1 mmol, PivOH=pivalic acid) in chlorobenzene (1 mL) at 140 °C for 24 h under N_2. As a result, (*E*)-2-(1,2-diphenylethenyl)phenyl methyl sulfone (**3a**) was formed in 23% yield (entry 1 in Table 1). Increasing the amount of **1a** to 0.75 mmol somewhat improved the yield of **3a** to 42% (entry 2). It is conceivable that the addition of an excess amount of **1a** stands by the relatively low coordination ability of **1a**. While a similar result was obtained in $C_6H_5CF_3$ (entry 3), the reaction efficiencies were low in *o*-dichlorobenzene and diglyme (entries 4 and 5). The use of 1-$AdCO_2H$ (0.1 mmol, 1-$AdCO_2H$=1-adamantanecarboxylic acid) in place of PivOH significantly enhanced the yield of **3a** up to 66% (entry 6). In contrast, $C_6F_5CO_2H$ was less effective to decrease the reaction efficiency (entry 7). In the absence of any acids, the reaction hardly proceeded (entry 8). In addition, it was confirmed that a neutral rhodium complex, $[Cp^*RhCl_2]_2$, did not show any catalytic activity at all (entry 9).

Table 1
Reaction of methyl phenyl sulfone (**1a**) with diphenylacetylene (**2a**)[a]



1a 2a 3a

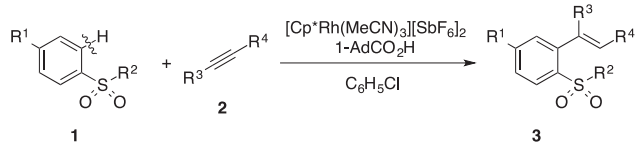
Entry	Acid	Solvent	Yield of **3a** (%)[b]
1[c]	PivOH[d]	C_6H_5Cl	23
2	PivOH	C_6H_5Cl	42
3	PivOH	$C_6H_5CF_3$	43
4	PivOH	*o*-$C_6H_4Cl_2$	21
5	PivOH	Diglyme	7
6	1-$AdCO_2H$[e]	C_6H_5Cl	66 (63)
7	$C_6F_5CO_2H$	C_6H_5Cl	14
8	—	C_6H_5Cl	5
9[f]	1-$AdCO_2H$	C_6H_5Cl	0

[a] Reaction conditions: **1a** (0.75 mmol), **2a** (0.25 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.01 mmol), acid (0.1 mmol), in solvent (1 mL) at 140 °C for 24 h under N_2, unless otherwise noted.
[b] GC yield based on the amount of **2a** used. Value in parentheses indicates yield after purification.
[c] Using **1a** (0.5 mmol).
[d] PivOH=pivalic acid.
[e] 1-$AdCO_2H$=1-adamantanecarboxylic acid.
[f] Using $[(Cp^*RhCl_2)_2]$ (0.005 mmol) in place of $[Cp^*Rh(MeCN)_3][SbF_6]_2$.

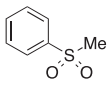
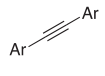
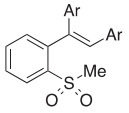
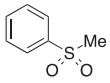
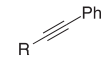
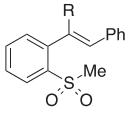
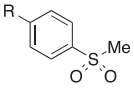
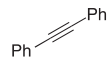
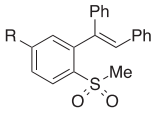
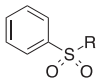
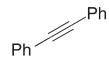
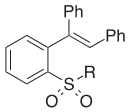
With the effective reaction conditions in hand, we next examined the substrate scope for the reaction of phenyl sulfones **1** with alkynes **2** (Table 2). The reactions of 4,4′-disubstituted diphenylacetylenes **2b**–**d** with **1a** gave the corresponding *ortho*-alkenylated phenyl sulfones **3b**–**d** in moderate to good yields (entries 1–3). Unsymmetrical alkynes, 1-phenyl-1-hexyne (**2e**) and 1-phenyl-1-propyne (**2f**), also reacted with **1a** to produce **3e** and **3f**, albeit with moderate to low yields (entries 4 and 5). Notably, no other regioisomers were detected by GC–MS at all in these cases. In contrast, treatment of ethyl 3-phenylpropiolate with **1a** did not give a desired coupling product at all.

The reactions using a series of 4-substituted phenyl sulfones **1b**–**e** with **2a** were also examined. Treatment of methyl (4-methylphenyl) sulfone (**1b**) with **2a** under standard conditions gave **3g** in 57% yield (entry 6). In contrast, the reactions of 4-methoxy- (**1c**), 4-phenoxy- (**1d**), and 4-chloro- (**1e**) substituted phenyl sulfones were somewhat sluggish. These reactions could be conducted more effectively by increasing the catalyst loading and reaction temperature in *o*-dichlorobenzene to produce **3h**–**j** in 38–59% yields (entries 7–9). Ethyl phenyl sulfone (**1f**) and diphenyl sulfone (**1g**) underwent *ortho*-alkenylation upon treatment with **2a** under standard conditions to afford **3k** and **3l** in 51 and 65% yields, respectively (entries 10 and 11).

Table 2
Reaction of phenyl sulfones **1** with alkynes **2**[a]



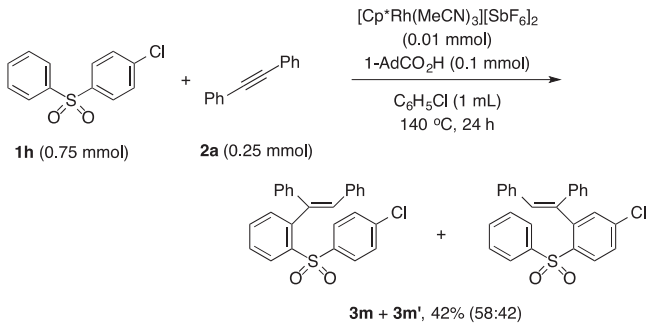
1 2 3

entry	1	2	product, % yield
			
1	**1a**	**2b**: Ar = 4-ClC_6H_4	**3b**: Ar = 4-ClC_6H_4, 77
2		**2c**: Ar = 4-$CF_3C_6H_4$	**3c**: Ar = 4-$CF_3C_6H_4$, 59
3		**2d**: Ar = 4-MeC_6H_4	**3d**: Ar = 4-MeC_6H_4, 46
			
4	**1a**	**2e**: R = ^{n}Bu	**3e**: R = ^{n}Bu, 47
5		**2f**: R = Me	**3f**: R =Me, 26
			
6	**1b**: R = Me	**2a**	**3g**: R = Me, 57
7[b]	**1c**: R = OMe		**3h**: R = OMe, 59
8[b]	**1d**: R = OPh		**3i**: R = OPh, 41
9[b]	**1e**: R = Cl		**3j**: R = Cl, 38
			
10	**1f**: R = Et	**2a**	**3k**: R = Et, 51
11	**1g**: R = Ph		**3l**: R = Ph, 65

[a] Reaction conditions: 1 (0.75 mmol), 2 (0.25 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.01 mmol), 1-$AdCO_2H$ (0.1 mmol), in C_6H_5Cl (1 mL) at 140 °C for 24 h under N_2, unless otherwise noted.
[b] Using $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (0.02 mmol) in o-$C_6H_4Cl_2$ (1 mL) at 150 °C.

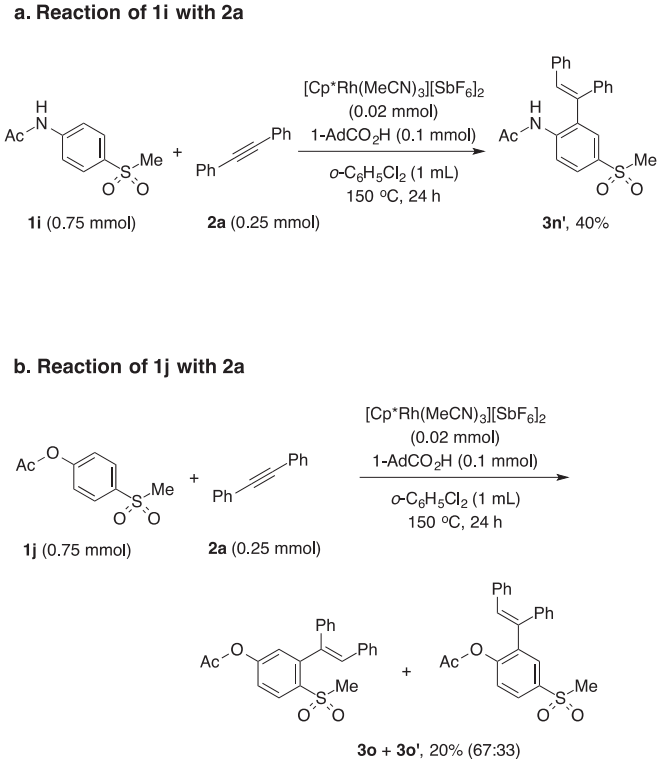
As described above, 4-chloro-substituted phenyl sulfone **1e** showed significantly lower reactivity than that of unsubstituted **1a** (entry 9 in Table 2). Therefore, we expected that unsymmetrically substituted (4-chlorophenyl) phenyl sulfone (**1h**) would react with **2a** selectively on the more reactive unsubstituted phenyl ring. However, unexpectedly, treatment of **1h** with **2a** under standard conditions gave an almost 1:1 mixture of possible alkenylated products **3m** and **3m′** (Scheme 2).

The reaction of (4-acetylaminophenyl) methyl sulfone (**1i**) with **2a** exclusively gave (4-acetylamino-3-alkenylphenyl) methyl sulfone (**3n′**). Thus, the hydrogen at the *ortho*-position of the acetylamino function[10] in **1i** is highly reactive compared to that at the



Scheme 2. Reaction of **1h** with **2a**.

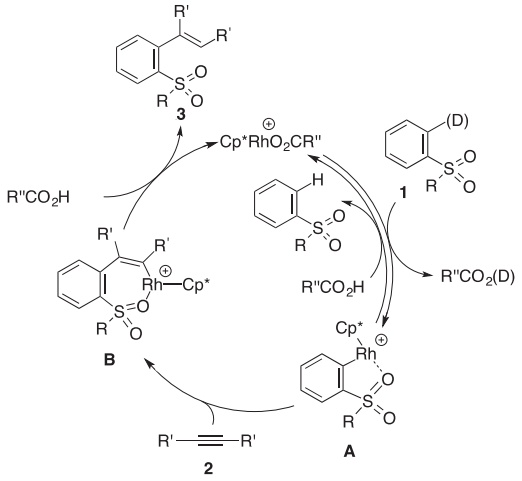
ortho-position of the sulfonyl group (Scheme 3a). On the other hand, the sulfonyl group-directed alkenylation took place predominantly upon treatment of sulfonyl(4-acetoxyphenyl) methyl sulfone (**1j**) with **2a** to form **3o** in preference to acetoxy-directed[11] alkenylation (Scheme 3b).



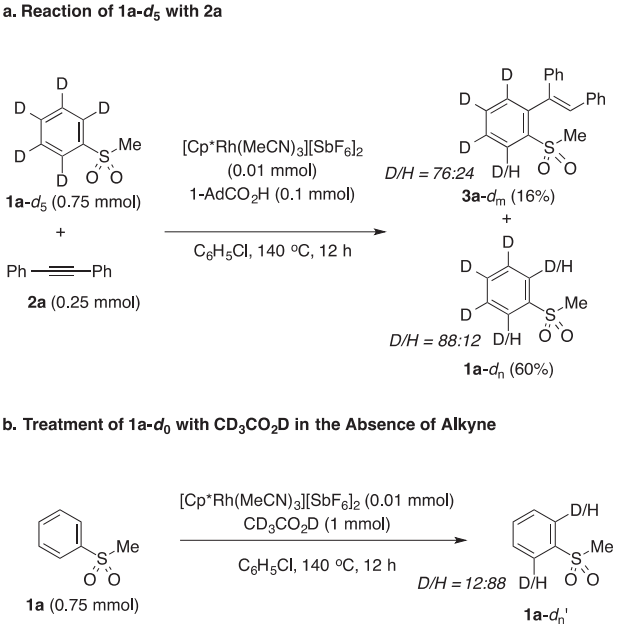
Scheme 3. Reactions of *p*-substituted phenyl sulfones.

A plausible mechanism for the reaction of phenyl sulfone **1** with alkyne **2** is illustrated in Scheme 4. Coordination of the sulfonyl group[7b] of **1** to a cationic Rh^{III} center and subsequent *ortho*-rhodation would take place to form a five-membered rhodacycle intermediate **A**. Then, alkyne insertion into the resulting Rh–C bond to form **B** and subsequent protonolysis may occur to produce **3**. The added acid may promote the last protonolysis step.[12]

For obtaining further mechanistic information, a deuterated substrate, methyl d_5-phenyl sulfone (**1a**-d_5), was treated with **2a** under standard conditions (Scheme 5a). In the early stage, considerable contamination by hydrogens at the 6-position of produced **3a**-d_n as well as at the *ortho* positions of recovered **1a**-d_n was observed. Similar H/D exchange at the *ortho* positions of **1a**-d_0 was also observed during treatment with CD_3CO_2D without **2a** (Scheme 5b). These results indicate that the C–H(D) bond cleavage step to form **A** is likely reversible.

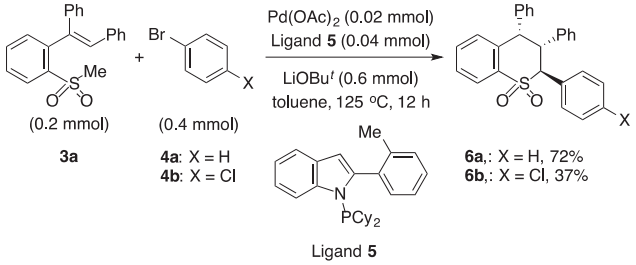


Scheme 4. Plausible mechanism for the reaction of **1** with **2**.



Scheme 5. Investigation for mechanistic insights.

Recently, elegant work on the palladium-catalyzed α-arylation of methyl sulfones with aryl bromides has been disclosed by Walsh and co-workers.[8] We applied their arylation method to our (*ortho*-alkenylated phenyl) methyl sulfone **3a** for further functionalization. Thus, **3a** (0.2 mmol) was treated with bromobenzene (**4a**) (0.4 mmol) in the presence of $Pd(OAc)_2$ (0.02 mmol), **5** (0.04 mmol), and $LiOBu^t$ (0.6 mmol) as catalyst, ligand, and base, respectively, in toluene (1 mL) at 125 °C for 12 h (Scheme 6). Unexpectedly, the α-phenylation was followed by successive cyclization to produce the



Scheme 6. Further functionalization of **3a**.

corresponding 2-phenylthiochromane 1,1-dioxide derivative **6a** in 72% yield. The X-ray crystal analysis of **6a** indicates that the cyclization proceeds in a diastereoselective manner. Similar arylation/cyclization product **6b** could also be obtained upon treatment of **3a** with 4-chloro-1-bromobenzene (**4b**). It should be noted that such thiochromane 1,1-dioxide frameworks can be seen in a wide range of biologically active molecules including meticrane.[13]

3. Conclusions

We have demonstrated that the rhodium-catalyzed *ortho*-alkenylation of phenyl sulfones occurs efficiently via unprecedented sulfonyl group directed C–H bond cleavage. Thus obtained (*ortho*-alkenylated phenyl) methyl sulfone can be readily transformed to the corresponding thiochromane 1,1-dioxide derivatives.

4. Experimental section

4.1. General

^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz for $CDCl_3$ solutions. HRMS data were obtained by CI using a TOF mass spectrometer, unless noted. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm1.5 m). GC–MS analysis was carried out using a CBP-1 capillary column (i. d. 0.25 mm×25 m). The structures of all products listed below were unambiguously determined by ^{1}H and ^{13}C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

Phenyl Sulfones **1b**,**c**,**e**,**f**,[14] **1d**,[15] **1i**,[16] and **1j**[17] and alkynes **2b**–**d**[18] were prepared according to published procedures. All starting materials and reagents were commercially available.

4.2. Preparation of methyl phenyl sulfones 1

Synthesis of **1b** is representative. To a 20 mL two-necked flask with a rubber cup were added 4-(methylthio)toluene (1 mmol, 138 mg), oxone (1.5 mmol, 922 mg) and H_2O (5 mL). Then, the resulting mixture was stirred under air at 60 °C for 12 h. After reaction, the reaction mixture was diluted with ethyl acetate (40 mL) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, sulfone **1b** (143 mg, 84%) was obtained.

4.3. Preparation of 1-(methylsulfonyl)-4-phenoxybenzene (1d)

To a 100 mL two-necked flask with a rubber cup were added 4-(methylsulfonyl)phenol (10 mmol, 1.72 g), phenylboronic acid (10 mmol, 2.42 g), $Cu(OAc)_2$ (10 mmol, 1.81 g), Et_3N (20 mmol, 2.04 g) and CH_2Cl_2 (40 mL). Then, the resulting mixture was stirred under air at rt for 5 days. After the reaction, the mixture was diluted with CH_2Cl_2 (40 mL) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, sulfone **1d** (258 mg, 10%) was isolated by column chromatography on silica gel using hexane/ethyl acetate (3:1, v/v) as eluent.

4.4. Preparation of *N*-(4-(methylsulfonyl)phenyl)acetamide (1i)

To a 20 mL two-necked flask with a rubber cup were added 4-(methylsulfonyl)aniline (10 mmol, 1.74 g), pyridine (20 mmol, 0.8 mL) and Ac_2O (12 mmol, 2.29 g). Then, the resulting mixture was stirred under N_2 at 120 °C for 12 h. After the reaction, the mixture was diluted with ethyl acetate (40 mL) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, sulfone **1i** (214 mg, 10%) was isolated by column chromatography on silica gel using hexane/ethyl acetate (3:1, v/v) as eluent.

4.5. Preparation of 4-(methylsulfonyl)phenyl acetate (1j)

To a 20 mL two-necked flask with a rubber cup were added 4-(methylsulfonyl)phenol (2 mmol, 345 mg), Ac_2O (2.4 mmol, 253 mg) and DABCO (2 mmol, 232 mg). Then, the resulting mixture was stirred under N_2 at 60 °C for 12 h. After the reaction, the mixture was diluted with ethyl acetate (40 mL) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, sulfone **1j** (411 mg, 96%) was obtained.

4.6. Reaction of methyl phenyl sulfones 1 with alkynes 2

To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added methyl phenyl sulfone **1** (0.75 mmol), alkyne **2** (0.25 mmol), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (0.01 mmol, 8.3 mg), 1-AdCOOH (0.1 mmol, 18 mg), 1-methylnaphlene (ca. 30 mg) as internal standard, and PhCl (1 mL). Then, the resulting mixture was stirred under nitrogen at 140 °C for 24 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL). The organic layer was washed by aqueous $NaHCO_3$ (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, product **3** was isolated by column chromatography on silica gel using hexane/ethyl acetate as eluent. Further purification by gel permeation chromatography (GPC) was performed, if needed.

4.7. Further functionalization of 3a

Synthesis of **6a** is representative. To a 10 mL Schlenk flask with a rubber cup were added $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), ligand **5** (0.04 mmol, 16.1 mg), LiO^tBu (0.60 mmol, 48 mg), and dry toluene (1 mL). The resulting mixture was stirred for 30 min at rt. Then, sulfone **3a** (0.2 mmol, 67 mg) and bromobenzene (0.4 mmol, 42.4 μL) were added to the mixture. The resulting mixture was stirred under nitrogen atmosphere at 125 °C for 12 h. After the reaction, the mixture was diluted with ethyl acetate (40 mL) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, product **6a** (59 mg, 72%) was isolated by column chromatography on silica gel using hexane/ethyl acetate (3:1, v/v) as eluent and subsequent gel permeation chromatography (GPC).

4.8. Reaction of deuterated substrate 1a-d_5 with 2a

To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added sulfone **1a**-d_5 (0.75 mmol, 117 mg), diphenylacetylene (**2a**) (0.25 mmol, 45 mg), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (0.02 mmol, 16.6 mg), 1-AdCOOH (0.1 mmol, 18 mg) and PhCl (1 mL). Then, the resulting mixture was stirred under nitrogen at 140 °C for 12 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL). The organic layer was washed by aqueous $NaHCO_3$ (100 mL, three times), and dried over Na_2SO_4. After evaporation of the solvents under vacuum, product **3a**-d_5 (14 mg, 16%) and **1a**-d_n (72 mg, 60%) were isolated by column chromatography on silica gel using hexane/ethyl acetate (3:1, v/v) as eluent and subsequent GPC.

4.9. Treatment of 1a-d_0 with CD_3CO_2D in the absence of alkyne

To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added sulfone **1a**-d_0 (0.75 mmol, 117 mg), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (0.02 mmol, 16.6 mg), CD_3CO_2D (1 mmol, 62 mg) and PhCl (1 mL). Then, the resulting mixture was stirred under nitrogen at 140 °C for 12 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL). The organic layer was washed by aqueous $NaHCO_3$ (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, **1a**-$d_{n'}$ was completely recovered (117 mg, 100%).

4.10. (*E*)-1-(2-(Methylsulfonyl)phenyl)-1,2-diphenylethene (3a)

Mp 118–119 °C (yellow powder), 53 mg (64%), isolated by column chromatography using hexane/ethyl acetate (3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 3H), 6.71 (s, 1H), 7.17–7.25 (m, 10H), 7.46 (dd, J=1.3, 7.5 Hz, 1H), 7.52 (dt, J=1.4, 7.7 Hz, 1H), 7.64 (dt, J=1.4, 7.5 Hz, 1H), 8.13 (dd, J=1.2, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 120.9, 123.3, 127.9, 128.0, 128.3, 128.5, 128.8, 129.1, 129.4, 129.6, 131.1, 132.3, 134.1, 134.4, 144.1, 149.1; HRMS (APCI) m/z calcd for $C_{21}H_{19}O_2S$ ($M+H^+$) 335.1100, found 335.1122.

4.11. (*E*)-1,2-Bis(4-chlorophenyl)-1-(2-(methylsulfonyl)phenyl)ethene (3b)

Mp 46–48 °C (white powder), 77 mg (77%), isolated by column chromatography using hexane/ethyl acetate (3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.64 (s, 3H), 6.63 (s, 1H), 7.10 (d, J=8.4 Hz, 2H), 7.15 (d, J=8.7 Hz, 2H), 7.17–7.22 (m, 4H), 7.41 (dd, J=1.3, 7.6 Hz, 1H), 7.54 (dt, J=1.4, 7.9 Hz, 1H), 7.64 (dt, J=1.4, 7.5 Hz, 1H), 8.12 (dd, J=1.3, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.7, 128.5, 128.60, 128.63, 130.2, 130.4, 130.6, 132.1, 132.8, 133.3, 133.6, 133.9, 134.8, 137.1, 139.1, 139.6, 143.3; HRMS (APCI) m/z calcd for $C_{21}H_{17}Cl_2O_2S$ ($M+H^+$) 403.0321, found 403.0321.

4.12. (*E*)-1-(2-(Methylsulfonyl)phenyl)-1,2-bis(4-trifluoromethylphenyl)ethene (3c)

Mp 50–52 °C (white powder), 70 mg (59%), isolated by column chromatography using hexane/ethyl acetate (3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 (s, 3H), 6.78 (s, 1H), 7.28 (d, J=8.3 Hz, 2H), 7.35 (d, J=8.1 Hz, 2H), 7.43 (dd, J=1.3, 7.6 Hz, 1H), 7.47–7.49 (m, 4H), 7.58 (dt, J=1.4, 7.8 Hz, 1H), 7.68 (dt, J=1.4, 7.5 Hz, 1H), 8.14 (dd, J=1.3, 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.9, 123.9 (q, J=270.6 Hz), 124.0 (q, J=270.3 Hz), 125.2 (q, J=3.7 Hz), 125.4 (q, J=3.6 Hz), 129.0, 129.5 (q, J=32.2 Hz), 129.6, 130.0 (q, J=32.5 Hz), 130.3, 131.0, 131.1, 132.6, 133.7, 139.2, 139.6, 141.0, 142.0, 142.6; HRMS (APCI) m/z calcd for $C_{23}H_{17}F_6O_2S$ ($M+H^+$) 471.0848, found 471.0850.

4.13. (*E*)-1-(2-(Methylsulfonyl)phenyl)-1,2-bis(4-methylphenyl)ethene (3d)

Mp 70–73 °C (white powder), 42 mg (46%), isolated by column chromatography using hexane/ethyl acetate (3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 6H), 2.61 (s, 3H), 6.63 (s, 1H), 7.00–7.03 (m, 4H), 7.08–7.13 (m, 4H), 7.42 (dd, J=1.2, 7.6 Hz, 1H), 7.49 (dt, J=1.3, 7.9 Hz, 1H), 7.60 (dt, J=1.4, 7.4 Hz, 1H), 8.12 (dd, J=1.2, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 22.7, 44.3, 128.0, 128.85, 128.89, 129.3, 129.9, 130.7, 131.09, 133.0, 133.3, 133.9, 136.3, 137.1, 137.5, 138.9, 139.2, 144.6; HRMS (APCI) m/z calcd for $C_{23}H_{23}O_2S$ ($M+H^+$) 363.1413, found 363.1414.

4.14. (*E*)-1-(Methylsulfonyl)-2-(1-phenylhex-1-en-2-yl)benzene (3e)

Oil, 37 mg (47%), isolated by column chromatography using hexane/ethyl acetate (3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, J=7.1 Hz, 3H), 1.25–1.33 (m, 4H), 2.79 (t, J=7.3 Hz, 2H), 3.12 (s, 3H), 6.39 (s, 1H), 7.29–7.30 (m, 1H), 7.34 (dd, J=1.3, 7.6 Hz, 1H), 7.36–7.40 (m, 4H), 7.51 (dt, J=1.4, 7.7 Hz, 1H), 7.62 (dt, J=1.4, 7.5 Hz, 1H), 8.14 (dd, J=1.3, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 22.8, 30.3, 33.2, 44.9, 127.1, 127.7, 128.4, 128.8, 129.4, 130.0, 131.8, 133.1, 136.8, 138.6, 143.5, 144.2; HRMS (APCI) m/z calcd for $C_{19}H_{23}O_2S$ ($M+H^+$) 315.1413, found 315.1413.

4.15. (*E*)-1-(Methylsulfonyl)-2-(1-phenylprop-1-en-2-yl)benzene (3f)

Mp 123–125 °C (yellow powder), 18 mg (26%), isolated by column chromatography using hexane/ethyl acetate (3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (d, J=1.6 Hz, 3H), 3.13 (s, 3H), 6.42 (d, J=1.4 Hz, 1H), 7.28–7.31 (m, 1H), 7.37 (dd, J=1.1, 7.5 Hz, 1H), 7.40–7.41 (m, 4H), 7.49 (dt, J=1.4, 7.7 Hz, 1H), 7.64 (dt, J=1.4, 7.5 Hz, 1H), 8.12 (dd, J=1.1, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 45.0, 127.2, 127.7, 128.4, 129.0, 129.2, 130.1, 130.7, 133.6, 136.8, 138.2, 138.5, 145.9; HRMS (APCI) m/z calcd for $C_{16}H_{17}O_2S$ ($M+H^+$) 273.0944, found 273.0951.

4.16. (*E*)-1-(5-Methyl-2-(methylsulfonyl)phenyl)-1,2-diphenylethene (3g)

Mp 169–171 °C (yellow powder), 50 mg (57%), isolated by column chromatography using hexane/ethyl acetate (3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44, (s, 3H), 2.51 (s, 3H), 6.68 (s, 1H), 7.18–7.26 (m, 11H), 7.31 (d, J=8.1 Hz, 1H), 7.99 (d, J=8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 44.4, 127.2, 127.7, 128.1, 128.2, 128.8, 129.4, 130.2, 130.9, 131.2, 133.6, 136.3, 136.7, 139.1, 140.1, 144.1, 144.3; HRMS (APCI) m/z calcd for $C_{22}H_{21}O_2S$ ($M+H^+$) 349.1257, found 349.1266.

4.17. (*E*)-1-(5-methoxy-2-(methylsulfonyl)phenyl)-1,2-diphenylethene (3h)

Mp 130–131 °C (yellow powder), 53 mg (59%), isolated by column chromatography using hexane/ethyl acetate (3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.89 (s, 3H), 6.70 (s, 1H), 6.95–6.99 (m, 2H), 7.18–7.26 (m, 10H), 8.04 (d, J=8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.4, 55.6, 112.8, 118.5, 127.3, 127.8, 128.1, 128.2, 129.4, 130.9, 131.0, 131.1, 132.6, 136.6, 138.8, 140.0, 146.3, 163.1; HRMS (APCI) m/z calcd for $C_{22}H_{21}O_3S$ ($M+H^+$) 365.1206, found 365.1223.

4.18. (*E*)-1-(5-Phenoxy-2-(methylsulfonyl)phenyl)-1,2-diphenylethene (3i)

Mp 58–60 °C, 44 mg (41%), isolated by column chromatography using hexane/ethyl acetate (3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 6.71 (s, 1H), 6.97 (dd, J=8.8, 2.6 Hz, 1H), 7.08–7.12 (m, 3H), 7.17–7.18 (m, 5H), 7.21–7.26 (m, 6H), 7.42 (dd, J=7.4, 6.6 Hz, 2H) 8.03 (d, J=8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.3, 116.0, 120.3, 121.7, 125.1, 127.4, 127.9, 128.1 (overlapped), 129.4, 130.2, 130.9, 131.4, 132.6, 132.8, 136.5, 138.7, 139.6, 146.6, 154.9, 161.7; HRMS (APCI) m/z calcd for $C_{27}H_{23}O_3S$ ($M+H^+$) 427.1362, found 427.1380.

4.19. (*E*)-1-(5-Chloro-2-(methylsulfonyl)phenyl)-1,2-diphenylethene (3j)

Mp 157–159 °C (yellow powder), 35 mg (38%), isolated by column chromatography using hexane/ethyl acetate (3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (s, 3H), 6.71 (s, 1H), 7.12–7.23 (m, 10H), 7.46 (d, J=2.0 Hz, 1H), 7.49 (dd, J=2.2, 8.5 Hz, 1H), 8.06 (d, J=8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.2, 127.6, 128.1, 128.2, 128.3, 128.4, 129.4, 130.9, 131.7, 132.1, 132.8, 136.2, 137.7, 138.4, 138.7, 139.8, 145.9; HRMS (APCI) m/z calcd for $C_{21}H_{18}ClO_2S$ ($M+H^+$) 369.0711, found 369.0710.

4.20. (*E*)-1-(2-(Ethylsulfonyl)phenyl)-1,2-diphenylethene (3k)

Mp 115–117 °C (yellow powder), 45 mg (51%), isolated by column chromatography using hexane/ethyl acetate (3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, J=7.2 Hz, 3H), 2.49 (q, J=7.6 Hz, 2H), 6.66 (s, 1H), 7.18–7.21 (m, 10H), 7.47 (dd, J=1.1, 7.6 Hz, 1H), 7.51 (dt, J=1.3, 7.8 Hz, 1H), 7.63 (dt, J=1.4, 7.5 Hz, 1H), 8.07 (dd, J=1.1, 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.2, 50.1, 127.3, 127.7, 127.9, 128.0, 128.2, 129.4,

130.8, 131.2, 131.4, 133.1, 133.2, 136.7, 137.0, 139.1, 140.1, 144.6; HRMS (APCI) m/z calcd for $C_{22}H_{21}O_2S$ ($M+H^+$) 349.1257, found 349.1246.

4.21. (*E*)-1,2-Diphenyl-1-(2-(phenylsulfonyl)phenyl)ethene (3l)

Mp 111–113 °C (white powder), 65 mg (65%), isolated by column chromatography using hexane/ethyl acetate (5:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (s, 1H), 6.96–7.00 (m, 4H), 7.10–7.18 (m, 7H), 7.26–7.31 (m, 2H), 7.44–7.52 (m, 3H), 7.71–7.74 (m, 2H), 8.40–8.42 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.2, 127.5, 127.6, 128.0, 128.05, 128.11, 128.8, 129.6, 130.1, 130.3, 132.7, 132.8, 132.9, 133.0, 136.5, 138.2, 139.5, 139.6, 142.5, 144.5; HRMS (APCI) m/z calcd for $C_{26}H_{21}O_2S$ ($M+H^+$) 397.1257, found 397.1274.

4.22. (*E*)-1-{2-[(4-Chlorophenyl)sulfonyl]phenyl}-1,2-diphenylethene+(*E*)-1-[5-chloro-2-(phenylsulfonyl)phenyl]-1,2-diphenylethene (42:58) (3m+3m′)

Mp 53–56 °C (white powder), 45 mg (42%), isolated by column chromatography using hexane/ethyl acetate (5:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.13 (s, 1H, 3m), 6.16 (s, 1H, 3m′), 6.93–6.99 (m, 4H, 3m′), 6.99–7.02 (m, 4H, 3m), 7.12–7.15 (m, 3H, 3m), 7.16–7.19 (m, 9H), 7.20–7.23 (m, 2H, 3m), 7.28–7.32 (m, 2H, 3m′), 7.45–7.48 (m, 2H, 3m′), 7.50–7.54 (m, 2H, 3m), 7.60–7.63 (m, 2H, 3m′), 7.69–7.72 (m, 2H, 3m), 8.34–8.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.4, 127.5 (overlapped), 127.6, 127.75, 127.79, 128.1 (overlapped), 128.15, 128.17, 128.3, 128.9, 129.0, 129.4, 129.5, 129.6, 130.1, 130.21 (overlapped), 130.24, 131.6, 132.7, 132.8, 133.0, 133.3, 133.6, 136.1, 136.4, 137.0, 138.2, 138.3, 138.8, 139.20, 139.25, 139.4, 139.5, 141.0, 142.1, 144.5, 146.2; HRMS (APCI) m/z calcd for $C_{26}H_{20}ClO_2S$ ($M+H^+$) 431.0867, found 431.0867.

4.23. (*E*)-*N*-[2-(1,2-Diphenylethenyl)-4-(methylsulfonyl)phenyl]acetamide (3n′)

Mp 215–218 °C, 39 mg (40%), isolated by column chromatography using hexane/ethyl acetate (3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3H), 2.91 (s, 3H), 6.98–7.00 (m, 2H), 7.17–7.19 (m, 3H), 7.27 (s, 1H), 7.29–7.32 (m, 2H), 7.37–7.40 (m, 4H), 7.73 (d, J=2.2 Hz, 1H), 7.93 (dd, J=2.2, 8.7 Hz, 1H), 8.58 (d, J=8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6, 44.7, 121.0, 126.8, 128.3, 128.5, 128.7, 128.8, 128.9, 129.1, 129.8, 130.6, 132.1, 135.4, 135.6, 136.0, 140.45, 140.54, 168.4; HRMS (APCI) m/z calcd for $C_{23}H_{22}NO_3S$ ($M+H^+$) 392.1315, found 392.1315.

4.24. (*E*)-3-(1,2-Diphenylethenyl)-4-(methylsulfonyl)phenyl acetate+(*E*)-2-(1,2-diphenylethenyl)-4-(methylsulfonyl)phenyl acetate (2:1) (3o+3o′)

Mp 57–59 °C, 20 mg (20%), isolated by column chromatography using hexane/ethyl acetate (3:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83 (s, 3H, 3o′), 2.33 (s, 3H, 3o), 2.51 (s, 3H, 3o), 3.10 (s, 3H, 3o′), 6.72 (s, 1H, 3o), 6.83 (s, 1H, 3o′), 7.07–7.25 (m, 16H), 7.26–7.29 (m, 3H, 3o′), 7.92 (dd, J=2.4, 8.5 Hz, 1H, 3o′), 8.02 (d, J=2.3 Hz, 1H, 3o′), 8.15 (d, J=8.7 Hz, 1H, 3o); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 21.1, 44.3, 44.7, 121.3, 124.5, 126.0, 127.5, 127.6, 127.8, 127.87, 127.93, 128.16, 128.19, 128.23, 128.6, 129.4, 129.6, 129.7, 130.6, 130.9, 131.9, 132.0, 133.0, 136.3, 136.37, 136.40, 137.4, 138.1, 138.3, 138.6, 138.8, 139.1, 146.1, 152.4, 154.1, 168.4, 168.6; HRMS (APCI) m/z calcd for $C_{23}H_{21}O_4S$ ($M+H^+$) 393.1155, found 393.1174.

4.25. (2*S*,3*R*,4*S*)-2,3,4-Triphenylthiochromane-1,1-dioxide (6a)

Mp 207–210 °C, 59 mg (72%), isolated by column chromatography using hexane/ethyl acetate (5:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.63 (d, J=4.4 Hz, 1H), 4.76 (dd, J=4.4, 12.8 Hz, 1H), 5.15 (s, J=12.8 Hz, 1H), 6.52 (d, J=7.2 Hz, 3H), 6.97–7.03 (m, 3H), 7.09–7.13 (m, 3H), 7.15–7.19 (m, 4H), 7.26–7.29 (m, 3H), 7.46 (ddd, J=1.5, 7.4, 7.7 Hz, 1H), 7.52 (ddd, J=1.3, 7.5 Hz, 7.8 Hz, 1H), 8.10 (dd, J=1.4, 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.7, 53.0, 64.4, 124.4, 126.8, 127.1, 127.3, 127.7, 127.9, 128.1, 128.5, 128.8, 129.6, 130.6, 130.8, 131.9, 132.6, 137.8 (overlapped), 138.3, 139.3; HRMS (APCI) m/z calcd for $C_{27}H_{23}O_2S$ ($M+H^+$) 411.1413, found 411.1414.

4.26. (2*S*,3*R*,4*S*)-2-(4-Chlorophenyl)-3,4-diphenylthiochromane-1,1-dioxide (6b)

Mp 265–268 °C, 33 mg (37%), isolated by column chromatography using hexane/ethyl acetate (5:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.62 (d, J=4.4 Hz, 1H), 4.71 (dd, J=4.4, 12.8 Hz, 1H), 5.12 (d, J=12.8 Hz, 1H), 6.51 (d, J=7.2 Hz, 3H), 7.01–7.19 (m, 12H), 7.47 (ddd, J=1.5, 7.7, 7.4 Hz, 1H), 7.53 (ddd, J=1.3, 7.5, 7.7 Hz, 1H), 8.10 (dd, J=1.4, 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.6, 52.9, 63.7, 124.4, 125.7, 127.1, 127.4, 127.9, 128.0, 128.46, 128.54, 129.5, 130.6, 130.8, 132.8, 133.1, 135.0, 137.4, 127.7, 138.2, 139.0; HRMS (APCI) m/z calcd for $C_{27}H_{22}ClO_2S$ ($M+H^+$) 445.1024, found 445.1037.

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Supplementary data

Supplementary data (cocopies of ^{1}H- and ^{13}C NMR spectra of products) related to this article can be found at http://dx.doi.org/10.1016/j.tet.2015.03.046.

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