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Synthetic Methods |*Hot Paper*|

One-Pot Synthesis of Allylic Sulfones, Ketosulfones, and Triflyl Allylic Alcohols from Domino Reactions of Allylic Alcohols with Sulfinic Acid under Metal-Free Conditions

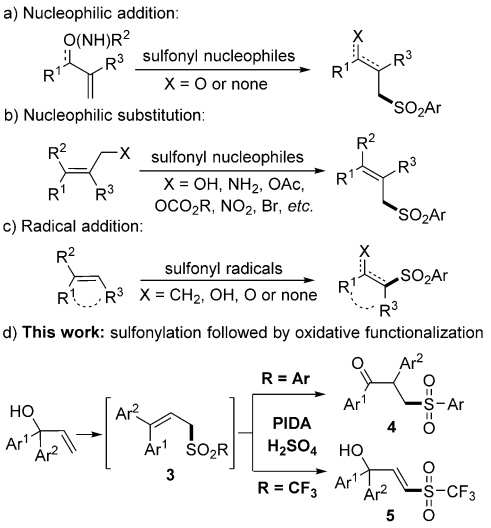
Xue-Qiang Chu, Hua Meng, Xiao-Ping Xu,* and Shun-Jun Ji*[a]

Abstract: A metal-free tandem procedure by using a sulfonylation reaction of aryl allylic alcohols followed by an iodobenzenediacetate (PIDA)-promoted oxidative functionalization has been established. Allylic sulfones, γ-ketosulfones, and triflyl allylic alcohols have been constructed in a single operation. The methodology incorporates the sulfonyl (both aryl and triflyl) functionality with a simple work-up procedure.

Introduction

The pluripotent sulfone-containing structure is arguably the most versatile skeleton available to agrochemical,[1] medicinal,[2] and material sciences;[3] for example, allylic sulfones[4] and ketosulfones[5] are useful pharmaceutically active molecules. Triflones[6] display unique chemical, physical, and biological properties through the interaction of the CF_3 group. Meanwhile, sulfone compounds are also important building blocks and intermediates in organic synthesis.[7,8] As such, considerable interest has been paid to exploring practical access to this framework (Scheme 1). The traditional preparation of arylalkylsulfones includes nucleophilic addition with various sulfonyl precursors (Scheme 1 a),[9] allylic substitution of allylic derivatives[10] (Scheme 1 b), the direct oxidation of the corresponding sulfoxides,[11] and transition-metal-catalyzed coupling reactions.[12] Nevertheless, these processes suffered from the need for external additives, prefunctionalization, narrow substrate scope, and residual catalysts. Critically, vinyltriflones are not widely available by direct C–S bond formation in these cases.[13,14] Recently, much effort has been devoted to expanding radical sulfonylation (Scheme 1 c).[15] However, further development of a cheaper, low-toxic, ecofriendly, and metal-free methodology to incorporate the sulfonyl functionality (both the aryl and triflyl groups) is still urgently required.

The functionalization of alkenes provides an attractive strategy for the efficient and rapid construction of complex molecules from simple raw materials.[16] In recent years, hypervalent iodine(III) reagents have fascinated chemists due to their environmentally benign and superior behavior in various transformations,[17] especially in the oxidative functionalization of alkenes.[18] Normally, the highly electrophilic hypervalent iodine(III) compounds add to C–C double bonds to give cationic intermediates, which can lead to rearrangement[19–22] (i.e., through oxidative ring expansion,[19] ring contraction,[20] aryl migration,[21] or rearrangement–cyclization)[22] or a direct reaction with nucleophiles. To the best of our knowledge, the $PhI(OAc)_2$-mediated functionalization of allylic sulfones has never previously been reported (Scheme 1 d). Herein, we present a novel metal-free transformation of allylic sulfones formed in situ into less accessible γ-ketosulfones and vinyltriflones. A $PhI(OAc)_2$-promoted intramolecular rearrangement or an addition–elimination sequence pathway have been suggested.



Scheme 1. Transformations of the sulfonyl functionality. PIDA = iodobenzenediacetate.

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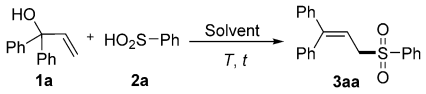
Results and Discussion

Although the direct sulfonylation of allylic alcohol has been well studied,[10] there is still room for improvement in this area. Initial efforts were focused on the synthesis of allylic sulfones without any additives (see Table 1 and Table S1 in the Supporting Information for more details). However, no reaction was observed between allylic alcohol **1a** and benzenesulfinic acid (**2a**) in acetonitrile at room temperature over 2 hours (Table 1, entry 1). To our delight, (3-tosylprop-1-ene-1,1-diyl)dibenzene (**3aa**) was afforded in 45% yield, as determined by means of liquid chromatography (LC), from the reaction at reflux temperature. The obtained γ-selectivity of the reaction probably arises from maximizing the conjugation and minimizing the steric hindrance[10f] (Table 1, entry 2). Further optimization of the amount of **2a** and the reaction temperature improved the yield, as determined by LC, of the desired product **3aa** to 65% (Table 1, entry 3). Solvent screening revealed that 1,2-dichloroethane was the best choice because less reaction efficiency was exhibited in toluene or 1,4-dioxane (Table 1, entries 4–6). Interestingly, the reaction proceeded rapidly[9] and went to completion within 5 minutes in a highly regioselective manner, with 95% yield of the isolated product (Table 1, entries 7–9).

Table 1. Initial discovery and optimization of reaction conditions.[a]

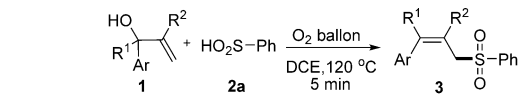


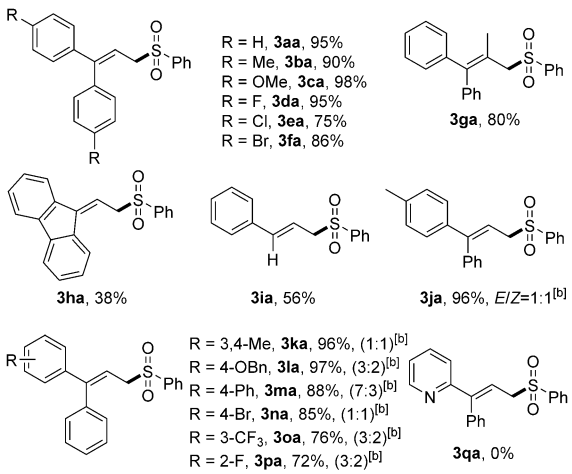
Entry	Solvent	*t* [min]	*T* [°C]	Yield [%][b]
1	MeCN	120	25	trace
2	MeCN	120	80	45
3	MeCN	90	reflux	65[c]
4	DCE	90	reflux	96[c]
5	toluene	90	reflux	91[c]
6	1,4-dioxane	90	reflux	53[c]
7	DCE	3	reflux	97[c]
8	DCE	5	reflux	99[c] (95)[c,d]
9	DCE	30	reflux	89[c]

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.51 mmol), solvent (2 mL), O_2 balloon. [b] Yields were determined by LC analysis with an internal standard. [c] **2a** (0.6 mmol) was heated at 120 °C in an oil bath. [d] Yield of the isolated product. DCE = 1,2-dichloroethane.

With the optimal conditions in hand, the scope of allylic alcohols as the subtrates was examined. All of the symmetrical electron-withdrawing groups (i.e., F, Cl, Br) on the aromatic ring were effectively converted into the corresponding products in moderate-to-good yields (75–98%; **3ba**–**fa**; Table 2). A methyl group rather than a hydrogen atom at the internal position of the double bond was also well tolerated (Table 2; **3ga**). However, a great drop in yield was observed when 9-vinyl-9*H*-fluoren-9-ol (**1h**) was introduced to react with **2a** (Table 2; **3ha**). The new C–S bond was formed exclusively at the terminal double bond of **1i**, and this mono-aryl-type substrate showed moderate reaction reactivity (Table 2; **3ia**). Meanwhile, the use of other unsymmetric alcohols **1j**–**p** provided products **3ja**–**pa** in 72–97% yield by using the current typical method (Table 2; **3ja**–**pa**). In contrast, heterocyclic substrate **1q** did not result in the desired product **3qa** possibly due to the relatively strong basicity that arises from the pyridine unit (Table 2; **3qa**).

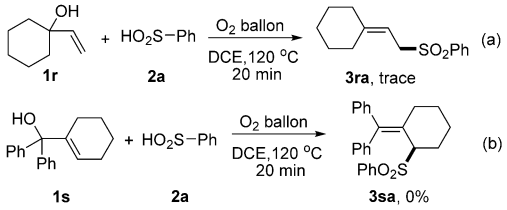
Table 2. Efficient sulfonylation of allylic alcohols **1** with benzenesulfinic acid (**2a**).[a]





[a] Yields of the isolated products under optimal conditions. [b] The *E*/*Z* ratio was determined by means of ^{1}H NMR spectroscopic analysis.

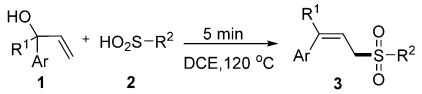
Alkyl allylic alcohol **1r** and cyclic allylic alcohol **1s** were not good candidates for this reaction with benzenesulfinic acid because no desired products were obtained under the standard conditions, albeit with a longer reation time (Scheme 2). We supposed that the conjugation and steric hindrance of the substrates affects the reaction to some extent.[9]

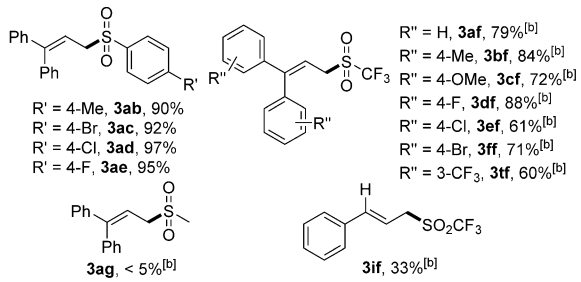


Scheme 2. Reactions of other allylic alcohols with **2a**.

Arenesulfinic acids bearing functional groups also worked well (Table 3; **3ab**–**ae**). Apart from arylallylic sulfones, the valuable trifluoromethanesulfonyl (triflyl) relevant derivatives were synthesized by this direct C–S bond-forming reaction,[13] with a slight modification (Table 3; **3af**–**ff** and **3tf**). A large-scale (3 mmol) synthesis of **3ff** based on the present protocol led to the isolation of 1.1 grams (78% yield) of the desired product, which proved the practicality of this methodology

Table 3. The reaction of allylic alcohols **1** with aryl- or trifluoromethylsulfinic acids **2**.[a]





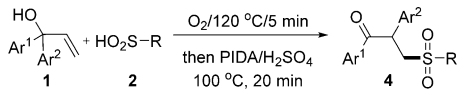
[a] Yields of the isolated products under optimal conditions. [b] Sulfinic acids were generated in situ by using sodium sulfinate (2 equiv) and conc. HCl (wt%: 37%, 3 equiv).

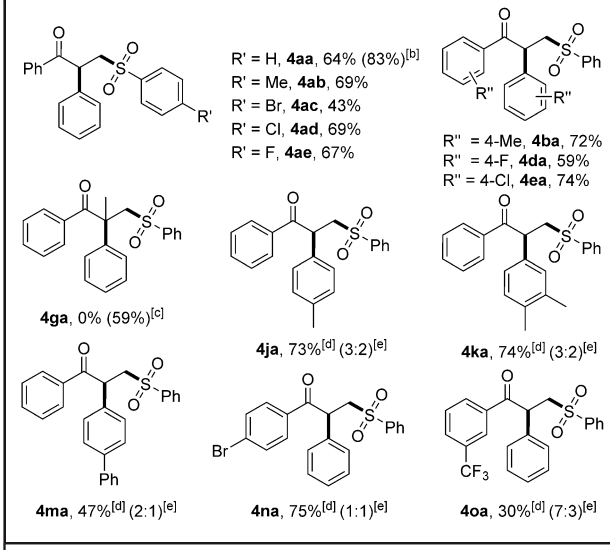
(see the Supporting Information for details). In contrast, the fact that aliphatic sulfinic acid **3ag** was almost inert could be attributable to its low electrophilic reactivity. Mono-aryl-type **3if** was formed in a lower yield (33% yield).

Our interest in the functionalization of alkenes[23] led us to explore whether this efficient sulfonylation reaction could be combined with a second rearrangement reaction in a single operation. If this approach works, useful frameworks with a sulfonlyl group can be constructed in a step-economical and "greener" fashion. We chose to explore this idea through hypervalent iodine(III)-promoted oxidative functionalization by using allylic sulfones **3** generated in situ (the results are summarized in Table 4 and see Table S2 in the Supporting Information for more details). We were pleased to find that the tandem sulfonylation/migration process was productive for a diverse sets of allylic alcohols **1** and sulfinic acid **2** with PIDA in the presence of concentrated sulfuric acid, thus leading to the expected γ-ketosulfones in 30–75% yield (Table 4; **4aa**–**ae**, **4ba**–**ea**, and **4ja**–**oa**). It was realized that steric hindrance had dramatic detrimental effect on aryl migration because ketone **4ga** containing an α-quaternary center[14c] was not obtained (Table 4; **4ga**). During the use of unsymmetric alcohols, it was observed that more electron-rich aryl rings preferentially migrated, thus suggesting that the reaction might go through a carbocation pathway.[21]

To our surprise, triflylated allylic alcohols rather than migrated products were constructed when we further expanded the generality of this metal-free tandem oxidative reaction to sodium trifluoromethanesulfinate with **1** (Table 5). We supposed that the reaction, after the electrophilic addition of PIDA to allylic sulfones **3**, was more prone to direct oxidation/eliminatation than oxidation/migration because of the strong electron-withdrawing power of the triflyl (CF_3SO_2) group.[6e,f] Notably, this chemistry provided a convenient platform to prepare various disubstituted vinyltriflones that feature exclusive *E* selectivity (the results are shown in Table 5).

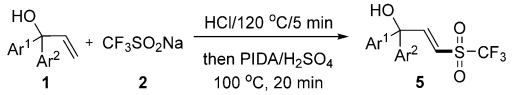
Table 4. One-pot synthesis of γ-ketosulfones.[a]

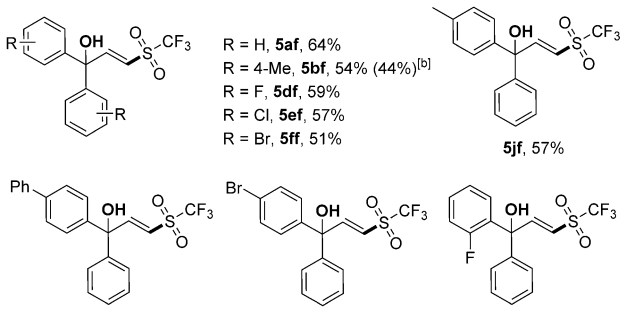




[a] Reaction conditions: **1** (0.3 mmol) and **2** (0.6 mmol) in DCE (2 mL) were heated at 120 °C for 5 min; (diacetoxyiodo)benzene (0.9 mmol) and conc. H_2SO_4 (wt%: 98%, 0.6 mmol) were added to the reaction mixture, which was heated for a further 20 min at 100 °C; yields of isolated products are given. [b] Compound **3aa** (0.3 mmol) was used as a starting material. [c] Yield of **3ga**. [d] Yields of **3** and its isomer; only major products were shown. [e] Determined by means of ^{1}H NMR spectroscopic analysis of the isolated products.

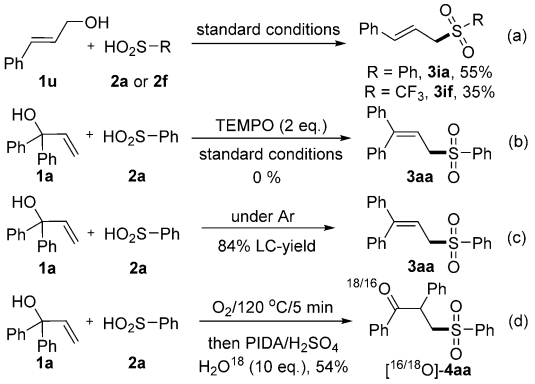
Table 5. One-pot synthesis of triflyl allylic alcohols.[a]





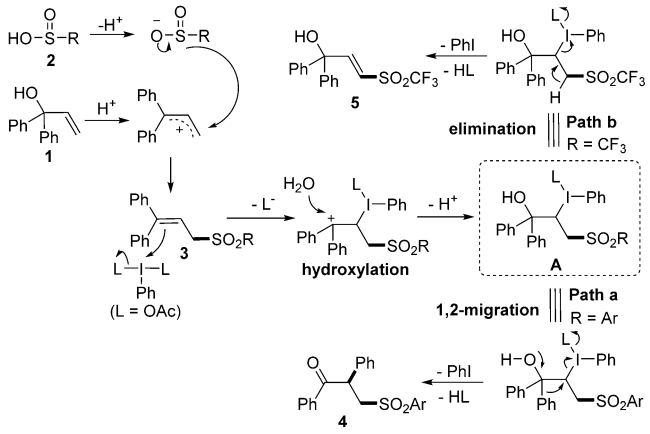
[a] Reaction conditions: **1** (0.3 mmol), **2** (0.6 mmol), and conc. HCl (wt%: 37%, 0.9 mmol) in DCE (2 mL) were heated at 120 °C for 5 min; then (diacetoxyiodo)benzene (0.9 mmol) and conc. H_2SO_4 (wt%: 98%, 0.6 mmol) were added to the reaction mixture, which was heated for a further 20 min at 100 °C; yields of the isolated products are given. [b] Yield of **3bf**.

Some control experiments were carried out to understand the details of the mechanism. When cinnamyl alcohol (**1u**) was employed under standard conditions, the reactions afforded unbranched derivatives **3ia** and **3if** in 55 and 35% yield, respectively (Scheme 3a). The generation of a π-allylic intermediate could provide a rationale for this regioselectivity.[10] Although the use of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO; 2 equiv) completely suppressed the reaction (Scheme 3b), this inhibition did not proceed in absence of oxygen (Scheme 3c). This outcome further implies that the reaction more likely proceeds through a traditional π-allylic substitution[9,10] than a free-radical pathway (although easily initiated by O_2).[15] To verify whether the oxygen atoms in products **4** and **5** were from water, we conducted an ^{18}O-labeling experiment (Scheme 3d; see the Supporting Information for further details). The ^{18}O atoms were incorporated into the carbonyl group in the presence of $H_2{}^{18}O$ (10 equiv).



Scheme 3. Control experiments.

On the basis of the above results and previous precedents, we propose a plausible mechanism (Scheme 4). Initially, the nucleophilic attack on a π-allylic carbocation by a sulfinyl anion from **2** led to the formation of an allylsulfone **3**,[9] which underwent electrophilic addition with a hypervalent iodine species (i.e., PIDA). The capture of a benzylic carbocation by water afforded the key intermediate **A**.[18] When the R group was an aryl moiety, an oxocarbenium-assisted 1,2-phenyl migration[21d] was allowed, with the release of phenyl iodide and an acetate ion (Scheme 4, path a). Alternatively, when the R group was a trifluoromethyl species, a concerted proton elimination and cleavage of the C–I bond occurred to convert **A** into the desired triflylated allylic alcohols **5** (Scheme 4, path b).[22e] It should be noted that the two aryl groups were essential for our rearrangement reaction probably due to the formation of stable **A**.



Scheme 4. Proposed mechanism.

Conclusion

We have described a novel metal-free approach to the assembly of the important sulfonyl skeleton from widely available allylic alcohols and sulfinic acids in a single operation. A variety of allylic sulfones, γ-ketosulfones, and triflyl allylic alcohols were prepared. In particular, direct C_{allyl}–$S_{triflyl}$ bond formation and iodine(III)-promoted oxidative functionalization offer attractive methods for the synthesis of CF_3SO_2-containing compounds. Further investigation of the reaction mechanism and the application of this method in organic synthesis are underway in our laboratory.

Experimental Section

General: Unless otherwise stated, all the reagents were purchased from commercial suppliers and used without further purification. All the reactions were carried out in air and in an undistilled solvent, without the need of precautions to exclude air and moisture, unless otherwise noted. Melting points were recorded on an Electrothermal digital melting-point apparatus; IR spectra were recorded on a FTIR spectrophotometer with KBr optics. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on 400 MHz spectometers. TMS served as an internal standard for the ^1H and ^{13}C NMR spectra. High-resolution mass spectra were obtained on a commercial apparatus (ESI or EI source).

General procedure for direct sulfonylation of allylic alcohols with arenesulfinic acids: Allylic alcohol **1** (0.3 mmol) and arenesulfinic acid **2** (0.6 mmol) in dichloroethane (2 mL) were stirred at 120 °C with an O_2 balloon for 5 min. Upon completion of the reaction (as indicated by TLC analysis), the solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel with petroleum/ethyl acetate as the eluent to afford pure product **3**.

General procedure for direct sulfonylation of allylic alcohols with sodium trifluoromethanesulfinate: Allylic alcohol **1** (0.3 mmol), sodium trifluoromethanesulfinate **2** (0.6 mmol), and conc. HCl (wt%: 37%, 0.9 mmol) in dichloroethane (2 mL) were stirred at 120 °C in air for 5 min. Upon completion of the reaction (as indicated by TLC analysis), the solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel with petroleum/ethyl acetate as the eluent to afford pure product **3**.

General procedure for the synthesis of 4 in a single operation: Allylic alcohol **1** (0.3 mmol) and arenesulfinic acid **2** (0.6 mmol) in dichloroethane (2 mL) were stirred at 120 °C with an O_2 ballon for 5 min. (Diacetoxyiodo)benzene (0.9 mmol), conc. H_2SO_4 (wt%: 98%, 0.6 mmol), and dichloroethane (2 mL) were added to the reaction mixture at 100 °C for another 20 min. Upon completion of the reac-

tion (as indicated by TLC analysis), the solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel to afford pure product **4**.

General procedure for the synthesis of 5 in a single operation: Allylic alcohol **1** (0.3 mmol), sodium trifluoromethanesulfinate **2** (0.6 mmol), and conc. HCl (wt%: 37%, 0.9 mmol) in dichloroethane (2 mL) were stirred at 120 °C in air for 5 min. (Diacetoxyiodo)benzene (0.9 mmol), conc. H_2SO_4 (wt%: 98%, 0.6 mmol), and dichloroethane (2 mL) were added to the reaction mixture at 100 °C for another 20 min. Upon completion of the reaction (as indicated by TLC analysis), the solvent was removed in vacuo and the residue was purified by flash column chromatograpy on silica gel with petroleum/ethyl acetate as the eluent to afford pure product **5**.

Large-scale synthesis of 3 ff: Allylic alcohol **1** (3 mmol), sodium trifluoromethanesulfinate **2** (6 mmol), and conc. HCl (wt%: 37%, 9 mmol) in dichloroethane (10 mL) were stirred at 120 °C in air for 10 min. Upon completion of the reaction (as indicated by TLC analysis), the solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel with petroleum/ethyl acetate as the eluentto afford pure product **3 ff**.

[3-(Phenylsulfonyl)prop-1-ene-1,1-diyl]dibenzene (3 aa): Yield = 95%; white soild; m.p. 77–79 °C; IR (KBr): $\tilde{\nu}$ = 2919, 1447, 1138, 1086, 743, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.75 (m, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.28–7.20 (m, 6H), 7.18–7.12 (m, 2H), 6.67 (dd, J = 7.9, 1.3 Hz, 2H), 6.14 (t, J = 7.9 Hz, 1H), 3.91 ppm (d, J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0, 140.9, 138.9, 138.06, 133.8, 129.4, 129.3, 128.7, 128.6, 128.5, 128.5, 128.0, 127.6, 114.2, 57.7 ppm; HRMS *m/z*: calcd for $C_{21}H_{18}NaO_2S$: 357.0925 $[M+Na]^+$; found: 357.0925.

4,4′-[3-(Phenylsulfonyl)prop-1-ene-1,1-diyl]bis(methylbenzene) (3 ba): Yield = 90%; white soild; m.p. 140–142 °C; IR (KBr): $\tilde{\nu}$ = 2919, 1446, 1304, 1145, 1083, 818, 727, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 7.7 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.12–6.97 (m, 6H), 6.54 (d, J = 7.8 Hz, 2H), 6.06 (t, J = 7.9 Hz, 1H), 3.91 (d, J = 7.9 Hz, 2H), 2.33 (s, 3H), 2.31 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.8, 138.9, 138.4, 137.6, 135.1, 133.8, 129.3, 129.2, 129.2, 129.2, 128.7, 127.5, 113.1, 57.8, 21.4, 21.3 ppm; HRMS *m/z*: calcd for $C_{23}H_{22}NaO_2S$: 385.1233 $[M+Na]^+$; found: 385.1239.

4,4′-[3-(Phenylsulfonyl)prop-1-ene-1,1-diyl]bis(methoxybenzene) (3 ca): Yield = 98%; white soild; m.p. 82–84 °C; IR (KBr): $\tilde{\nu}$ = 2924, 1602, 1509, 1304, 1144, 1027, 831, 727 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, J = 7.7 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.08 (d, J = 8.7 Hz, 2H), 6.82–6.73 (m, 4H), 6.61 (d, J = 8.5 Hz, 2H), 5.98 (t, J = 7.9 Hz, 1H), 3.92 (d, J = 7.9 Hz, 2H), 3.81 (s, 3H), 3.78 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 159.3, 149.2, 139.0, 134.0, 133.7, 130.7, 130.4, 129.2, 128.9, 128.7, 113.9, 113.8, 111.9, 57.8, 55.5, 55.4 ppm; HRMS *m/z*: calcd for $C_{23}H_{22}NaO_4S$: 417.1131 $[M+Na]^+$; found: 417.1137.

4,4′-[3-(Phenylsulfonyl)prop-1-ene-1,1-diyl]bis(fluorobenzene) (3 da): Yield = 95%; white soild; m.p. 106–108 °C; IR (KBr): $\tilde{\nu}$ = 2925, 1508, 1307, 1219, 1138, 831, 745, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.75 (m, 2H), 7.65 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.16–7.06 (m, 2H), 7.02–6.91 (m, 4H), 6.76–6.66 (m, 2H), 6.07 (t, J = 8.0 Hz, 1H), 3.88 ppm (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 163.8, 161.8, 161.3, 148.0, 139.0, 137.0, 137.0, 134.0, 133.7, 133.7, 131.2, 131.1, 129.4, 129.3, 129.3, 128.6, 115.8, 115.6, 115.4, 114.4, 57.7 ppm; HRMS *m/z*: calcd for $C_{21}H_{16}F_2NaO_2S$: 393.0731 $[M+Na]^+$; found: 393.0733.

4,4′-[3-(Phenylsulfonyl)prop-1-ene-1,1-diyl]bis(chlorobenzene) (3 ea): Yield = 75%; white soild; m.p. 136–138 °C; IR (KBr): $\tilde{\nu}$ = 2927, 1489, 1288, 1145, 1084, 1012, 825, 729, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.75 (m, 2H), 7.69–7.62 (m, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.26–7.22 (m, 4H), 7.10–7.03 (m, 2H), 6.71–6.62 (m, 2H), 6.13 (t, J = 8.0 Hz, 1H), 3.87 ppm (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 139.0, 138.9, 135.9, 134.7, 134.4, 134.0, 130.8, 129.4, 129.0, 128.8, 128.6, 115.2, 57.7 ppm; HRMS *m/z*: calcd for $C_{21}H_{16}Cl_2NaO_2S$: 425.0140 $[M+Na]^+$; found: 425.0143.

4,4′-[3-(Phenylsulfonyl)prop-1-ene-1,1-diyl]bis(bromobenzene) (3 fa): Yield = 86%; white soild; m.p. 143–145 °C; IR (KBr): $\tilde{\nu}$ = 2925, 1487, 1312, 1145, 1008, 823, 731, 673 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.76 (m, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.8 Hz, 2H), 7.43–7.36 (m, 4H), 7.00 (d, J = 8.6 Hz, 2H), 6.60 (d, J = 8.3 Hz, 2H), 6.14 (t, J = 8.0 Hz, 1H), 3.87 ppm (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 139.4, 138.9, 136.32, 134.05, 132.0, 131.8, 131.1, 129.4, 129.1, 128.6, 123.0, 122.6, 115.2, 57.7 ppm; HRMS *m/z*: calcd for $C_{21}H_{16}{}^{79}Br^{81}BrNaO_2S$: 514.9110 $[M+Na]^+$; found: 514.9119.

[2-Methyl-3-(phenylsulfonyl)prop-1-ene-1,1-diyl]dibenzene (3 ga): Yield = 80%; white soild; m.p. 124–126 °C; IR (KBr): $\tilde{\nu}$ = 2916, 1445, 1301, 1149, 1083, 765, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, J = 7.3 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.26 (t, J = 7.3 Hz, 2H), 7.22–7.10 (m, 4H), 6.99 (d, J = 7.0 Hz, 2H), 6.68–6.59 (m, 2H), 4.06 (s, 2H), 2.06 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.7, 141.8, 141.1, 139.3, 133.7, 129.3, 129.1, 128.5, 128.4, 128.3, 127.3, 127.1, 122.7, 62.6, 20.6 ppm; HRMS *m/z*: calcd for $C_{22}H_{20}NaO_2S$: 371.1076 $[M+Na]^+$; found: 371.1081.!

9-[2-(Phenylsulfonyl)ethylidene]-9*H*-fluorene (3 ha): Yield = 38%; white soild; m.p. 74–75 °C; IR (KBr): $\tilde{\nu}$ = 2924, 1446, 1297, 1137, 1079, 771, 727 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.99–7.93 (m, 2H), 7.65 (t, J = 7.3 Hz, 3H), 7.58–7.46 (m, 4H), 7.40–7.30 (m, 3H), 7.21–7.15 (m, 1H), 6.58 (t, J = 8.3 Hz, 1H), 4.62 ppm (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.0, 141.8, 139.4, 138.8, 138.6, 135.9, 134.2, 129.4, 129.4, 129.2, 128.6, 127.6, 127.3, 124.6, 120.7, 120.2, 119.8, 112.9, 77.6, 77.2, 76.9, 57.0 ppm; HRMS *m/z*: calcd for $C_{21}H_{16}NaO_2S$: 355.0763 $[M+Na]^+$; found: 355.0764.

Cinnamylsulfonylbenzene (3 ia): Yield = 56%. Yellow oil; IR (KBr): $\tilde{\nu}$ = 2925, 1447, 1305, 1140, 746, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.86 (m, 2H), 7.67–7.62 (m, 1H), 7.57–7.51 (m, 2H), 7.32–7.26 (m, 5H), 6.37 (d, J = 15.9 Hz, 1H), 6.16–6.05 (m, 1H), 3.95 ppm (dd, J = 7.6, 1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.4, 138.6, 136.0, 134.0, 129.3, 128.9, 128.8, 126.8, 115.3, 60.7 ppm; HRMS *m/z*: calcd for $C_{15}H_{14}NaO_2S$: 281.0607 $[M+Na]^+$; found: 281.0610.

(*E*,*Z*)-1-Methyl-4-[1-phenyl-3-(phenylsulfonyl)prop-1-enyl]benzene (3 ja): Yield = 96% (*E*/*Z* = 1:1); white soild; m.p. 112–114 °C; IR (KBr): $\tilde{\nu}$ = 2917, 1446, 1143, 819, 727, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.75 (m, 2H), 7.67–7.60 (m, 1H), 7.54–7.46 (m, 2H), 7.27–7.14 (m, 4H), 7.09–7.02 (m, 3H), 6.69–6.53 (m, 2H), 6.13–6.07 (m, 1H), 3.95–3.88 (m, 2H), 2.33 ppm (d, J = 8.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0, 149.8, 141.2, 138.8, 138.8, 138.4, 138.1, 138.1, 137.7, 135.0, 133.8, 129.4, 129.3, 129.2, 129.2, 129.2, 128.7, 128.7, 128.5, 128.4, 128.4, 127.9, 127.6, 127.5, 114.0, 113.2, 57.8, 57.7, 21.4, 21.3 ppm; HRMS *m/z*: calcd for $C_{22}H_{20}NaO_2S$: 371.1076 $[M+Na]^+$; found: 371.1084.

(*E*,*Z*)-1,2-Dimethyl-4-[1-phenyl-3-(phenylsulfonyl)prop-1-enyl]benzene (3 ka): Yield = 96% (*E*/*Z* = 1:1); white soild; m.p. 69–71 °C; IR (KBr): $\tilde{\nu}$ = 2917, 1444, 1300, 767, 741, 687 $cm^{-1;}$ ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (t, J = 6.7 Hz, 2H), 7.66–7.59 (m, 1H), 7.53–7.46 (m, 2H), 7.28–7.14 (m, 4H), 7.05–6.92 (m, 1.6H), 6.86 (d, J = 7.8 Hz, 0.6H), 6.64 (d, J = 6.8 Hz, 1H), 6.41 (d, J = 7.6 Hz, 0.4H), 6.34 (s, 0.4H), 6.10 (t, J = 7.9 Hz, 1H), 3.93 (d, J = 7.9 Hz, 1H), 3.89 (d, J = 7.9 Hz, 1H), 2.24 (s, 1.5H), 2.23 (s, 1.5H), 2.19 (s, 1.5H), 2.13 ppm (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.0, 149.9,

141.2, 138.8, 138.8, 138.6, 138.1, 137.2, 136.7, 136.3, 135.4, 133.8, 133.7, 130.3, 129.7, 129.7, 129.3, 129.2, 129.2, 128.7, 128.7, 128.6, 128.5, 128.4, 128.3, 127.8, 127.6, 126.8, 125.1, 113.9, 113.1, 57.8, 57.7, 20.0, 19.9, 19.7, 19.7 ppm; HRMS *m/z*: calcd for $C_{23}H_{22}NaO_2S$: 385.1233 $[M+Na]^+$; found: 385.1246.

(*E*,*Z*)-1-(Benzyloxy)-4-[1-phenyl-3-(phenylsulfonyl)prop-1-enyl]-benzene (3 la): Yield = 97% (*E*/*Z* = 3:2); colorless oil; IR (KBr): $\tilde{\nu}$ = 2929, 1681, 1584, 1446, 1305, 1137, 1010, 739, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.78 (m, 2H), 7.68–7.60 (m, 1H), 7.55–7.34 (m, 7H), 7.32–7.17 (m, 4H), 7.14–7.09 (m, 1H), 6.93–6.84 (m, 2H), 6.70–6.63 (m, 2H), 6.09 (dd, *J* = 17.0, 8.0 Hz, 1H), 5.09 (s, 0.8H), 5.07 (s, 1.2H), 3.98 (d, *J* = 7.9 Hz, 0.8H), 3.91 ppm (d, *J* = 7.9 Hz, 1.2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 158.5, 149.7, 149.4, 141.4, 138.9, 138.8, 138.1, 136.9, 136.9, 133.8, 133.7, 130.7, 130.5, 129.4, 129.3, 128.8, 128.8, 128.8, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 127.9, 127.7, 127.7, 127.6, 114.8, 114.7, 113.9, 112.3, 70.2, 57.8, 57.7 ppm; HRMS *m/z*: calcd for $C_{28}H_{24}NaO_3S$: 463.1338 $[M+Na]^+$; found: 463.1348.

(*E*,*Z*)-4-[1-Phenyl-3-(phenylsulfonyl)prop-1-enyl]biphenyl (3 ma): Yield = 88% (*E*/*Z* = 7:3); white soild; m.p. 46–48 °C; IR (KBr): $\tilde{\nu}$ = 3029, 1486, 1446, 1306, 1138, 835, 762, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.76 (m, 2H), 7.66–7.53 (m, 4H), 7.52–7.42 (m, 6H), 7.38–7.33 (m, 1H), 7.29–7.21 (m, 4H), 6.77 (d, *J* = 8.2 Hz, 0.6H), 6.73–6.67 (m, 1.4H), 6.23–6.11 (m, 1H), 3.98 (d, *J* = 7.9 Hz, 0.6H), 3.93 ppm (d, *J* = 7.9 Hz, 1.4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.7, 149.5, 141.3, 141.0, 140.8, 140.6, 140.5, 139.8, 138.9, 138.8, 137.9, 136.9, 133.9, 130.9, 130.2, 129.9, 129.4, 129.3, 129.1, 129.0, 128.7, 128.6, 128.5, 128.0, 128.0, 127.8, 127.7, 127.7, 127.2, 127.2, 114.3, 114.1, 57.8 ppm; HRMS *m/z*: calcd for $C_{27}H_{22}NaO_2S$: 433.1233 $[M+Na]^+$; found: 433.1231.

(*E*,*Z*)-1-Bromo-4-[1-phenyl-3-(phenylsulfonyl)prop-1-enyl]benzene (3 na): Yield = 85% (*E*/*Z* = 1:1); white soild; m.p. 51–53 °C; IR (KBr): $\tilde{\nu}$ = 2921, 1484, 1446, 1139, 1009, 825, 686 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.74 (m, 2H), 7.67–7.61 (m, 1H), 7.55–7.48 (m, 2H), 7.41–7.36 (m, 2H), 7.29–7.21 (m, 3H), 7.15–7.10 (m, 1H), 7.05–6.99 (m, 1H), 6.71–6.64 (m, 1H), 6.60 (d, *J* = 8.3 Hz, 1H), 6.13 (q, *J* = 7.8 Hz, 1H), 3.89 ppm (dd, *J* = 7.9, 5.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9, 148.9, 140.5, 139.9, 138.9, 138.8, 137.4, 136.9, 134.0, 133.9, 131.8, 131.7, 131.1, 129.4, 129.3, 129.1, 128.7, 128.7, 128.6, 128.2, 127.6, 122.7, 122.3, 114.7, 114.7, 57.7 ppm; HRMS *m/z*: calcd for $C_{21}H_{17}{}^{79}BrNaO_2S$ $[M+Na]^+$ 435.0025; found: 435.0027.

(*E*,*Z*)-1-[1-Phenyl-3-(phenylsulfonyl)prop-1-enyl]-3-(trifluoromethyl)benzene (3 oa): Yield = 76% (*E*/*Z* = 3:2); colorless oil; IR (KBr): $\tilde{\nu}$ = 2920, 1446, 1306, 1121, 1073, 742, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.75 (m, 2H), 7.68–7.61 (m 1H), 7.58–7.47 (m, 3H), 7.43–7.35 (m, 1H), 7.34–7.24 (m, 4H), 7.16–7.09 (m, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.90 (s, 1H), 6.71 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.25–6.14 (m, 1H), 3.94 (d, *J* = 7.9 Hz, 2H), 3.87 ppm (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.8, 148.6, 141.8, 140.2, 138.8, 138.8, 138.6, 137.1, 134.1, 134.0, 133.0, 133.0, 131.0, 130.9, 129.4, 129.3, 129.2, 129.0, 128.8, 128.7, 128.6, 128.6, 128.4, 127.5, 126.0 (m), 125.0 (m) 124.2, 124.1, 116.0, 115.5, 57.7, 57.6 ppm; HRMS *m/z*: calcd for $C_{22}H_{17}F_3NaO_2S$: 425.0794 $[M+Na]^+$; found: 425.0798.

(*E*,*Z*)-1-Fluoro-2-[1-phenyl-3-(phenylsulfonyl)prop-1-enyl]benzene (3 pa): Yield = 72% (*E*/*Z* = 3:2); white soild; m.p. 63–65 °C; IR (KBr): $\tilde{\nu}$ = 2918, 1448, 1213, 1140, 776, 742, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.74 (m, 2H), 7.68–7.59 (m, 1H), 7.54–7.46 (m, 2H), 7.34–7.12 (m, 5.6H), 7.00–6.96 (m, 2.4H), 6.76–6.71 (m, 0.6H), 6.54 (m, 0.6H), 6.25 (t, *J* = 7.9 Hz, 0.6H), 6.10 (t, *J* = 7.9 Hz, 0.4H), 3.98 (d, *J* = 7.9 Hz, 0.8H), 3.87 ppm (d, *J* = 7.9 Hz, 1.2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4, 160.9, 158.9, 158.4, 144.6, 143.4, 139.9, 138.8, 138.7, 137.9, 133.9, 133.9, 131.5, 131.5, 131.1, 131.0, 130.3, 130.2, 129.9, 129.8, 129.3, 129.3, 128.9, 128.7, 128.6, 128.6, 128.5, 128.5, 128.o, 127.0, 125.2, 125.1, 124.3, 124.3, 124.1, 124.1, 118.7, 118.6, 116.6, 116.4, 116.1, 115.9, 57.8, 57.4 ppm; HRMS *m/z*: calcd for $C_{21}H_{17}FNaO_2S$: 375.0826 $[M+Na]^+$; found: 375.0829.

(3-Tosylprop-1-ene-1,1-diyl)dibenzene (3 ab): Yield = 90%; white soild; m.p. 113–115 °C; IR (KBr): $\tilde{\nu}$ = 2922, 1444, 1312, 1132, 1083, 772, 748, 707, 638 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.2 Hz, 2H), 7.30–7.20 (m, 8H), 7.18–7.13 (m, 2H), 6.70 (d, *J* = 6.7 Hz, 2H), 6.12 (t, *J* = 7.9 Hz, 1H), 3.90 (d, *J* = 7.9 Hz, 2H), 2.44 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.8, 144.8, 141.1, 138.0, 136.0, 129.9, 129.4, 128.7, 128.5, 128.5, 128.4, 127.9, 127.6, 114.4, 57.8, 21.8 ppm; HRMS *m/z*: calcd for $C_{22}H_{20}NaO_2S$: 371.1076 $[M+Na]^+$; found: 371.1083.

{3-(4-Bromophenylsulfonyl)prop-1-ene-1,1-diyl]dibenzene (3 ac): Yield = 92%; white soild; m.p. 113–115 °C; IR (KBr): $\tilde{\nu}$ = 2959, 1574, 1318, 1132, 1010, 820, 758, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.59 (m, 4H), 7.30–7.23 (m, 6H), 7.18–7.14 (m, 2H), 6.72–6.68 (m, 2H), 6.11 (t, *J* = 8.0 Hz, 1H), 3.94 ppm (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.4, 140.9, 137.8, 137.8, 132.6, 130.2, 129.3, 129.2, 128.6, 128.6, 128.6, 128.1, 127.6, 113.8, 57.5 ppm; HRMS *m/z*: calcd for $C_{21}H_{17}BrNaO_2S$: 435.0025 $[M+Na]^+$; found: 435.0029.

[3-(4-Chlorophenylsulfonyl)prop-1-ene-1,1-diyl]dibenzene (3 ad): Yield = 97%; white soild; m.p. 116–118 °C; IR (KBr): $\tilde{\nu}$ = 1584, 1318, 1134, 1087, 824, 765, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.30–7.24 (m, 6H), 7.18–7.13 (m, 2H), 6.73–6.68 (m, 2H), 6.11 (t, *J* = 8.0 Hz, 1H), 3.94 ppm (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.3, 140.9, 140.7, 137.8, 137.3, 130.2, 129.6, 129.3, 128.6, 128.6, 128.6, 128.1, 127.6, 113.8, 57.6 ppm; HRMS *m/z*: calcd for $C_{21}H_{17}ClNaO_2S$: 391.0530 $[M+Na]^+$; found: 391.0530.

[3-(4-Fluorophenylsulfonyl)prop-1-ene-1,1-diyl]dibenzene (3 ae): Yield = 95%; white soild; m.p. 80–82 °C; IR (KBr): $\tilde{\nu}$ = 3053, 1591, 1491, 1318, 1137, 833, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.70 (m, 2H), 7.32–7.22 (m, 6H), 7.20–7.10 (m, 4H), 6.71 (d, *J* = 6.4 Hz, 2H), 6.12 (t, *J* = 7.9 Hz, 1H), 3.93 ppm (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 164.8, 150.2, 140.8, 137.6, 134.9, 131.5, 131.5, 129.3, 128.6, 128.6, 128.1, 127.6, 116.7, 116.4, 114.0, 57.7 ppm; HRMS *m/z*: calcd for $C_{21}H_{17}FNaO_2S$: 375.0826 $[M+Na]^+$; found: 375.0823.

[3-(Trifluoromethylsulfonyl)prop-1-ene-1,1-diyl]dibenzene (3 af): Yield = 79%; colorless oil; IR (KBr): $\tilde{\nu}$ = 1494, 1354, 1194, 1117, 761, 698 $cm^{-1;}$ ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.39 (m, 3H), 7.35–7.29 (m, 3H), 7.28–7.24 (m, 2H), 7.23–7.18 (m, 2H), 6.12 (t, *J* = 7.8 Hz, 1H), 4.09 ppm (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.88, 140.55, 137.55, 129.63, 129.05, 129.01, 128.75, 128.66, 127.89, 119.8 (q, *J* = 326.4 Hz), 109.15, 52.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −77.0 ppm; HRMS *m/z*: calcd for $C_{16}H_{13}F_3NaO_2S$: 349.0481 $[M+Na]^+$; found: 349.0482.

4,4′-[3-(Trifluoromethylsulfonyl)prop-1-ene-1,1-diyl]bis(methylbenzene) (3 bf): Yield = 84%; white soild; m.p. 62–64 °C; IR (KBr): $\tilde{\nu}$ = 2956, 1351, 1207, 1114, 815, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.21 (m, 2H), 7.17–7.05 (m, 6H), 6.04 (t, *J* = 7.7 Hz, 1H), 4.09 (d, *J* = 7.7 Hz, 2H), 2.40 (s, 3H), 2.34 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 139.1, 138.6, 138.0, 134.7, 129.6, 129.6, 129.3, 127.8, 119.8 (q, *J* = 326.5 Hz), 107.9, 52.2, 21.5, 21.4 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −77.0 ppm; HRMS *m/z*: calcd for $C_{18}H_{17}F_3NaO_2S$: 377.0794 $[M+Na]^+$; found: 377.0797.

4,4′-[3-(Trifluoromethylsulfonyl)prop-1-ene-1,1-diyl]bis(methoxybenzene) (3 cf): Yield = 72%; white soild; m.p. 82–84 °C; IR (KBr): $\tilde{\nu}$ = 2957, 1603, 1508, 1354, 1251, 1194, 1114, 1030, 831 cm^{-1};

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 5.96 (t, J = 7.7 Hz, 1H), 4.10 (d, J = 7.8 Hz, 2H), 3.85 (s, 3H), 3.80 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3, 159.9, 152.1, 133.6, 131.0, 129.9, 129.3, 119.8 (q, J = 326.7 Hz), 114.3, 113.9, 106.6, 55.5, 55.5, 52.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −77.0 ppm; HRMS m/z: calcd for $C_{18}H_{17}F_3NaO_4S$: 409.0692 $[M+Na]^+$; found: 409.0687.

4,4′-[3-(Trifluoromethylsulfonyl)prop-1-ene-1,1-diyl]bis(fluorobenzene) (3df): Yield = 88%; white soild; m.p. 66–67 °C; IR (KBr): $\tilde{\nu}$ = 2927, 1628, 1508, 1349, 1199, 1119, 837, 718 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.23 (m, 4H), 7.20 (t, J = 8.6 Hz, 2H), 7.07 (t, J = 8.6 Hz, 2H), 6.12 (t, J = 7.8 Hz, 1H), 4.12 ppm (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5 (d, J = 36.5 Hz), 162.0 (d, J = 36.0 Hz), 151.0, 136.6 (d, J = 3.3 Hz), 133.2 (d, J = 3.5 Hz), 131.5 (d, J = 8.1 Hz), 129.7 (d, J = 8.2 Hz), 119.8 (q, J = 326.3 Hz), 116.3 (d, J = 21.5 Hz), 115.7 (d, J = 21.6 Hz), 109.3, 51.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −77.1, −112.2, −112.3 ppm; HRMS m/z: calcd for $C_{16}H_{11}F_5NaO_2S$: 385.0292 $[M+Na]^+$; found: 385.0293.

4,4′-[3-(Trifluoromethylsulfonyl)prop-1-ene-1,1-diyl]bis(chlorobenzene) (3ef): Yield = 61%; white soild; m.p. 77–79 °C; IR (KBr): $\tilde{\nu}$ = 2914, 1493, 1354, 1217, 1198, 1112, 1091, 1013, 811, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.41 (m, 2H), 7.33–7.27 (m, 2H), 7.20–7.12 (m, 4H), 6.11 (t, J = 7.8 Hz, 1H), 4.06 ppm (d, J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.8, 138.6, 135.4, 135.4, 135.2, 131.0, 129.5, 129.1, 129.0, 119.7 (q, J = 326.3 Hz), 110.1, 51.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −77.1 ppm; HRMS m/z: calcd for $C_{16}H_{11}Cl_2F_3NaO_2S$: 416.9701 $[M+Na]^+$; found: 416.9700.

4,4′-[3-(Trifluoromethylsulfonyl)prop-1-ene-1,1-diyl]bis(bromobenzene) (3ff): Yield = 71%; white soild; m.p. 90–92 °C; IR (KBr): $\tilde{\nu}$ = 2911, 1587, 1488, 1353, 1216, 1111, 1008, 828, 809 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.54 (m, 2H), 7.51–7.41 (m, 2H), 7.14–7.03 (m, 4H), 6.12 (t, J = 7.8 Hz, 1H), 4.05 ppm (d, J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.9, 139.0, 135.8, 132.5, 132.0, 131.3, 129.4, 123.7, 123.4, 110.1, 119.7 (q, J = 326.3 Hz), 51.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −77.0 ppm; HRMS m/z: calcd for $C_{16}H_{11}Br_2F_3NaO_2S$: 504.8691 $[M+Na]^+$; found: 504.8696.

(*E*)-[3-(Trifluoromethylsulfonyl)prop-1-enyl]benzene (3if): Yield = 33%; colorless oil; IR (KBr) = 2911, 1360, 1190, 1118, 971, 757, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.40 (m, 2H), 7.39–7.33 (m, 3H), 6.82 (d, J = 15.8 Hz, 1H), 6.19–6.09 (m, 1H), 4.14 ppm (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.9, 135.2, 129.5, 129.1, 127.2, 119.9 (q, J = 326.3 Hz), 110.4, 54.7 ppm; 19F NMR (376 MHz, $CDCl_3$): δ = −78.2 ppm; HRMS m/z: calcd for $C_{10}H_9F_3NaO_2S$: 273.0168 $[M+Na]^+$; found: 273.0170.

3,3′-[3-(Trifluoromethylsulfonyl)prop-1-ene-1,1-diyl]bis[(trifluoromethyl)benzene] (3tf): Yield = 60%; white soild; m.p. 75–77 °C; IR (KBr): $\tilde{\nu}$ = 2919, 1359, 1314, 1193, 1113, 1074, 804, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, J = 7.8 Hz, 1H), 7.66–7.59 (m, 2H), 7.48 (m, 4H), 7.39 (d, J = 7.9 Hz, 1H), 6.25 (t, J = 7.9 Hz, 1H), 4.05 ppm (d, J = 7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.4, 140.6, 137.5, 133.0, 132.1, 131.8, 131.7, 131.4, 131.2, 131.2, 130.0, 129.5, 126.2 (m), 125.3, 125.2, 124.3 (m), 122.6, 122.5, 121.3, 118.1, 112.2, 51.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −62.8, −62.8, −77.2 ppm; HRMS m/z: calcd for $C_{18}H_{11}F_9NaO_2S$: 485.0228 $[M+Na]^+$; found: 485.0216.

1,2-Diphenyl-3-(phenylsulfonyl)propan-1-one (4aa): Yield = 64%; white soild; m.p. 106–108 °C; IR (KBr): $\tilde{\nu}$ = 2934, 1679, 1446, 129.6, 1135, 912, 752, 686 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (m, 2H), 7.85–7.80 (m, 2H), 7.57 (m, 1H), 7.48 (m, 3H), 7.39 (t, J = 7.7 Hz, 2H), 7.25 (m, 4H), 7.21–7.17 (m, 1H), 5.30 (m, 1H), 4.46–4.39 (m, 1H), 3.48–3.42 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.0, 139.6, 136.6, 135.6, 133.9, 133.7, 129.6, 129.4, 129.1, 128.8, 128.3, 128.2, 59.4, 47.7 ppm; HRMS m/z: calcd for $C_{21}H_{18}NaO_3S$: 373.0869 $[M+Na]^+$; found: 373.0874.

1,2-Diphenyl-3-tosylpropan-1-one (4ab): Yield = 69%; colorless oil; IR (KBr): $\tilde{\nu}$ = 2926, 1680, 1448, 1300, 1135, 1085, 761, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, J = 7.3 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.7 Hz, 2H), 7.31 (m, 1H), 7.25–7.18 (m, 6H), 5.31–5.25 (m, 1H), 4.46–4.36 (m, 1H), 3.45–3.39 (m, 1H), 2.38 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.1, 144.9, 136.7, 136.6, 135.7, 133.6, 130.0, 129.6, 129.1, 128.8, 128.3, 128.3, 128.1, 77.6, 77.2, 76.9, 59.5, 47.7, 21.8 ppm; HRMS m/z: calcd for $C_{22}H_{20}NaO_3S$: 387.1025 $[M+Na]^+$; found: 387.1029.

3-(4-Bromophenylsulfonyl)-1,2-diphenylpropan-1-one (4ac): Yield = 43%; white soild; m.p. 103–105 °C; IR (KBr): $\tilde{\nu}$ = 2930, 1674, 1574, 1310, 1262, 1138, 1010, 757, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.86 (m, 2H), 7.67–7.63 (m, 2H), 7.58–7.48 (m, 3H), 7.39 (t, J = 7.7 Hz, 2H), 7.28–7.18 (m, 5H), 5.30–7.24 (m, 1H), 4.44–4.35 (m, 1H), 3.51–3.44 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.9, 138.6, 136.3, 135.5, 133.8, 132.6, 129.8, 129.7, 129.3, 129.0, 128.9, 128.3, 128.3, 59.5, 47.8 ppm; HRMS m/z: calcd for $C_{21}H_{17}{}^{79}BrNaO_3S$: 450.9974 $[M+Na]^+$; found: 450.9977.

3-(4-Chlorophenylsulfonyl)-1,2-diphenylpropan-1-one (4ad): Yield = 69%; white soild; m.p. 92–94 °C; IR (KBr): $\tilde{\nu}$ = 2929, 1677, 1578, 1306, 1138, 1086, 911, 772, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.87 (m, 2H), 7.76–7.69 (m, 2H), 7.53–7.48 (m, 1H), 7.42–7.36 (m, 4H), 7.27–7.19 (m, 5H), 5.31–5.25 (m, 1H), 4.44–4.36 (m, 1H), 3.51–3.44 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.9, 140.6, 138.0, 136.3, 135.5, 133.8, 129.7, 129.6, 129.0, 128.9, 128.3, 128.3, 59.5, 47.8 ppm; HRMS m/z: calcd for $C_{21}H_{17}ClNaO_3S$: 407.0479 $[M+Na]^+$; found: 407.0485.

3-(4-Fluorophenylsulfonyl)-1,2-diphenylpropan-1-one (4ae): Yield = 67%; colorless oil; IR (KBr): $\tilde{\nu}$ = 3065, 1680, 1590, 1492, 1287, 1142, 1085, 839, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91–7.80 (m, 4H), 7.51 (t, J = 7.3 Hz, 1H), 7.42–7.28 (m, 4H), 7.22–7.15 (m, 3H), 7.10 (t, J = 8.5 Hz, 2H), 5.32–5.26 (m, 1H), 4.45–4.36 (m, 1H), 3.53–3.42 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.0, 136.4, 135.5, 133.8, 131.8, 131.7, 131.2, 131.1, 129.6, 129.4, 129.2, 129.1, 128.9, 128.3, 128.3, 128.1, 116.8, 116.5, 59.6, 47.8 ppm; HRMS m/z: calcd for $C_{21}H_{17}FNaO_3S$: 391.0775 $[M+Na]^+$; found: 391.0781.

3-(Phenylsulfonyl)-1,2-dip-tolylpropan-1-one (4ba): Yield = 72%; white soild; m.p. 108–110 °C; IR (KBr): $\tilde{\nu}$ = 2920, 1672, 1290, 1144, 970, 814, 703, 688 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.77 (m, 4H), 7.57 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 5.26–5.21 (m, 1H), 4.42–4.33 (m, 1H), 3.46–3.39 (m, 1H), 2.35 (s, 3H), 2.24 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.6, 144.5, 139.7, 137.9, 133.8, 133.8, 133.1, 130.2, 129.5, 129.3, 129.2, 128.2, 128.2, 59.4, 47.2, 21.8, 21.2 ppm; HRMS m/z: calcd for $C_{23}H_{22}NaO_3S$: 401.1182 $[M+Na]^+$; found: 401.1187.

1,2-Bis(4-fluorophenyl)-3-(phenylsulfonyl)propan-1-one (4da): Yield = 59%; colorless oil; IR (KBr): $\tilde{\nu}$ = 2928, 2681, 1595, 1506, 1305, 1227, 1152, 1084, 836, 748, 687 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01–7.91 (m, 2H), 7.87–7.81 (m, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.26–7.19 (m, 2H), 7.12–7.06 (m, 2H), 7.00–6.93 (m, 2H), 5.31–5.26 (m, 1H), 4.40–4.33 (m, 1H), 3.50–3.43 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.5, 167.4, 164.8, 163.8, 161.3, 139.5, 134.0, 131.8, 131.7, 130.0, 130.0, 129.4, 128.14, 116.7, 116.5, 116.2, 116.0, 59.3, 46.8 ppm; HRMS m/z: calcd for $C_{21}H_{16}F_2NaO_3S$: 409.0680 $[M+Na]^+$; found: 409.0682.

1,2-Bis(4-chlorophenyl)-3-(phenylsulfonyl)propan-1-one (4ea): Yield = 74%; white soild; m.p. 41–43 °C; IR (KBr): $\tilde{\nu}$ = 2920, 1681, 1588, 1308, 1138, 1086, 1012, 823, 769, 687 cm^{-1}; ^{1}H NMR

(400 MHz, $CDCl_3$): $\delta = 7.87–7.81$ (m, 3H), 7.65–7.59 (m, 1H), 7.50 (t, $J = 7.8$ Hz, 2H), 7.40 (d, $J = 8.6$ Hz, 2H), 7.31–7.22 (m, 3H), 7.18 (d, $J = 8.5$ Hz, 2H), 5.28–5.23 (m, 1H), 4.40–4.21 (m, 1H), 3.50–3.42 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 194.7$, 140.4, 139.5, 134.6, 134.5, 134.0, 133.7, 130.4, 129.8, 129.7, 129.5, 129.3, 128.1, 59.1, 47.0 ppm; HRMS *m/z*: calcd for $C_{21}H_{16}Cl_2NaO_3S$: 441.0089 $[M+Na]^+$; found: 441.0094.

1-Phenyl-3-(phenylsulfonyl)-2-*para*-tolylpropan-1-one (4ja) and **2-phenyl-3-(phenylsulfonyl)-1-*para*-tolylpropan-1-one (4ja′)**: Yield = 73% (3:2); white soild; IR (KBr): $\tilde{\nu} = 2921$, 1679, 1446, 1304, 1136, 1085, 922, 739, 686 cm^{-1}; the ^1H NMR spectrum of the isolated product showed a 3:2 mixture of **4ja** and its isomer **4ja′**; ^1H NMR (400 MHz, $CDCl_3$) **4ja**/**4ja′**: $\delta = 7.92–7.87$ (m, 1.2H), 7.85–7.78 (m, 2.7H), 7.60–7.54 (m, 1.1H), 7.52–7.41 (m, 2.7H), 7.38 (t, $J = 7.7$ Hz, 1.2H), 7.25–7.15 (m, 2.8H), 7.11 (d, $J = 8.1$ Hz, 1.1H), 7.04 (d, $J = 8.0$ Hz, 1.2H), 5.31–5.22 (m, 1H), 4.45–4.35 (m, 1H), 3.48–3.39 (m, 1H), 2.35 (s, 1.2H), 2.24 ppm (s, 1.8H); ^{13}C NMR (100 MHz, $CDCl_3$) **4ja**/**4ja′**: $\delta = 196.1$, 195.5, 144.6, 139.7, 139.6, 138.0, 136.8, 135.7, 133.8, 133.8, 133.6, 133.5, 133.1, 130.3, 129.5, 129.3, 129.2, 129.1, 128.8, 128.3, 128.2, 128.2, 128.1, 59.4, 59.3, 47.6, 47.4, 21.8, 21.2 ppm; HRMS *m/z*: calcd for $C_{22}H_{20}NaO_3S$: 387.1025 $[M+Na]^+$; found: 387.1033.

2-(3,4-Dimethylphenyl)-1-phenyl-3-(phenylsulfonyl)propan-1-one (4ka) and 1-(3,4-dimethylphenyl)-2-phenyl-3-(phenylsulfonyl)propan-1-one (4ka′): Yield = 74% (3:2); colorless oil; IR (KBr): $\tilde{\nu} = 2922$, 1678, 1446, 1305, 1149, 1085, 735, 686 cm^{-1}; the ^1H NMR spectrum of the isolated product showed a 3:2 mixture of **4ka** and its isomer **4ka′**; ^1H NMR (400 MHz, $CDCl_3$) **4ka**/**4ka′**: $\delta = 7.93–7.88$ (m, 1H), 7.86–7.79 (m, 2H), 7.69–7.62 (m, 1H), 7.58–7.53 (m, 1H), 7.50–7.30 (m, 4H), 7.23 (d, $J = 4.4$ Hz, 1.5H), 7.21–7.07 (m, 1.5H), 7.01–6.88 (m, 2H), 5.31–5.19 (m, 1H), 4.44–4.36 (m, 1H), 3.48–3.40 (m, 1H), 2.25 (s, 2H), 2.22 (d, $J = 4.7$ Hz, 1H), 2.14 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) **4ka**/**4ka′**: $\delta = 196.1$, 195.8, 143.4, 139.7, 139.7, 137.9, 137.2, 136.9, 136.7, 135.7, 133.8, 133.8, 133.7, 133.5, 133.5, 130.7, 130.2, 130.0, 129.5, 129.3, 129.3, 129.3, 129.1, 128.8, 128.3, 128.2, 126.9, 126.8, 125.8, 59.5, 59.4, 47.5, 47.4, 20.2, 20.0, 19.9, 19.5 ppm; HRMS *m/z*: calcd for $C_{23}H_{22}Na\,O_3S$: 401.1182 $[M+Na]^+$; found: 401.1191.

2-(Biphenyl-4-yl)-1-phenyl-3-(phenylsulfonyl)propan-1-one (4ma) and 1-(biphenyl-4-yl)-2-phenyl-3-(phenylsulfonyl)propan-1-one (4ma′): Yield = 47% (2:1); white soild; IR (KBr): $\tilde{\nu} = 2932$, 1674, 1446, 1301, 1136, 762, 686 cm^{-1}; the ^1H NMR spectrum of the isolated product showed a 2:1 mixture of **4ma** and its isomer **4ma′**; ^1H NMR (400 MHz, $CDCl_3$) **4ma**/**4ma′**: $\delta = 8.01–7.91$ (m, 2H), 7.83 (t, $J = 7.9$ Hz, 2H), 7.63–7.53 (m, 4H), 7.50–7.37 (m, 7H), 7.31–7.22 (m, 4H), 5.38–5.31 (m, 1H), 4.49–4.38 (m, 1H), 3.58–3.42 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) **4ma**/**4ma′**: $\delta = 196.0$, 195.5, 146.3, 141.1, 140.3, 139.8, 139.6, 139.6, 136.7, 135.6, 135.4, 134.3, 133.9, 133.8, 133.7, 129.7, 129.6, 129.4, 129.4, 129.1, 129.1, 129.0, 128.9, 128.8, 128.5, 128.4, 128.2, 127.8, 127.5, 127.4, 127.2, 59.4, 59.4, 47.7, 47.4 ppm; HRMS *m/z*: calcd for $C_{27}H_{22}NaO_3S$: 449.1182 $[M+Na]^+$; found: 449.1186.

1-(4-Bromophenyl)-2-phenyl-3-(phenylsulfonyl)propan-1-one (4na) and 2-(4-bromophenyl)-1-phenyl-3-(phenylsulfonyl)propan-1-one (4na′): Yield = 75% (1:1); white soild; IR (KBr): $\tilde{\nu} = 2928$, 1681, 1583, 1446, 1305, 1137, 1010, 739, 686 cm^{-1}; the ^1H NMR spectrum of the isolated product showed a 1:1 mixture of **4na** and its isomer **4na′**; ^1H NMR (400 MHz, $CDCl_3$) **4na**/**4na′**: $\delta = 7.91–7.74$ (m, 4H), 7.63–7.34 (m, 7H), 7.28–7.18 (m, 3H), 7.14–7.03 (m, 1H), 5.31–5.20 (m, 1H), 4.45–4.19 (m, 1H), 3.50–3.40 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) **4na**/**4na′**: $\delta = 195.7$, 195.1, 139.6, 139.5, 136.2, 135.5, 135.3, 134.4, 134.0, 133.9, 132.7, 132.2, 132.1, 131.0, 130.6, 130.1, 129.7, 129.4, 129.1, 128.9, 128.4, 128.3, 128.2, 128.2, 59.3, 59.1, 47.7, 47.1 ppm; HRMS *m/z*: calcd for $C_{21}H_{17}{}^{79}BrNaO_3S$: 450.9974 $[M+Na]^+$; found: 450.9979.

2-Phenyl-3-(phenylsulfonyl)-1-[3-(Trifluoromethyl)phenyl]propan-1-one (4oa) and 1-phenyl-3-(phenylsulfonyl)-2-[3-(Trifluoromethyl)phenyl)propan-1-one (4oa′): Yield = 30% (7:3); colorless oil; IR (KBr): $\tilde{\nu} = 2929$, 1688, 1447, 1326, 124, 1072, 788, 687 cm^{-1}. The ^1H NMR spectrum of the isolated product showed a 7:3 mixture of **4na** and its isomer **4na′**; ^1H NMR (400 MHz, $CDCl_3$) **4oa**/**4oa′**: $\delta = 8.16–8.08$ (m, 1H), 7.93–7.75 (m, 3H), 7.60–7.39 (m, 6H), 7.31–7.20 (m, 4H), 5.42–5.25 (m, 1H), 4.47–4.30 (m, 1H), 3.56–3.41 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) **4oa**/**4oa′**: $\delta = 195.7$, 194.9, 139.5, 139.4, 137.6, 137.4, 136.2, 136.2, 135.8, 135.2, 134.1, 132.1, 131.9, 130.1, 130.0, 129.8, 129.5, 129.5, 129.5, 129.1, 129.0, 128.6, 128.3, 128.2, 128.2, 125.9 (m), 125.2 (m), 59.3, 59.2, 47.9, 47.3 ppm; HRMS *m/z*: calcd for $C_{22}H_{17}F_3NaO_3S$: 441.0743 $[M+Na]^+$; found: 441.0750.

(*E*)-1,1-Diphenyl-3-(trifluoromethylsulfonyl)prop-2-en-1-ol (5af): Yield = 64%; white soild; m.p. 91–93 °C; IR (KBr): $\tilde{\nu} = 3524$, 3060, 1612, 1449, 1359, 1205, 1110, 845, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.78$ (d, $J = 14.8$ Hz, 1H), 7.43–7.33 (m, 6H), 7.30 (dd, $J = 7.7$, 1.6 Hz, 4H), 6.91 (d, $J = 14.8$ Hz, 1H), 2.58 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 161.8$, 142.4, 129.2, 129.0, 127.0, 120.0, 119.8 (q, $J = 323.3$ Hz), 79.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -78.6$ ppm; HRMS *m/z*: calcd for $C_{16}H_{13}F_3NaO_3S$: 365.0430 $[M+Na]^+$; found: 365.0420.

(*E*)-1,1-Di-*para*-tolyl-3-(trifluoromethylsulfonyl)prop-2-en-1-ol (5bf): Yield = 54%; white soild; m.p. 74–76 °C; IR (KBr): $\tilde{\nu} = 3500$, 2922, 1350, 1199, 1111, 854, 807, 770 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.75$ (d, $J = 14.8$ Hz, 1H), 7.24–7.13 (m, 8H), 6.88 (d, $J = 14.8$ Hz, 1H), 2.38 (s, 1H), 2.37 ppm (d, $J = 7.7$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 162.2$, 139.5, 138.9, 129.8, 126.9, 119.8 (q, $J = 323.3$ Hz), 119.5, 79.6, 21.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -78.7$ ppm; HRMS *m/z*: calcd for $C_{18}H_{17}F_3NaO_3S$: 393.0743 $[M+Na]^+$; found: 393.0738.

(*E*)-1,1-Bis(4-fluorophenyl)-3-(trifluoromethylsulfonyl)prop-2-en-1-ol (5df): Yield = 59%; white soild; m.p. 104–106 °C; IR (KBr): $\tilde{\nu} = 3498$, 3061, 1613, 1505, 1359, 1218, 1111, 1003, 836 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.70$ (d, $J = 14.8$ Hz, 1H), 7.31–7.25 (m, 4H), 7.09 (t, $J = 8.5$ Hz, 4H), 6.91 (d, $J = 14.8$ Hz, 1H), 2.55 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 163.0$ (d, $J = 247.9$ Hz), 161.0, 138.0 (d, $J = 3.2$ Hz), 128.9 (d, $J = 8.3$ Hz), 120.4, 119.8 (q, $J = 323.3$ Hz), 116.3 (d, $J = 21.7$ Hz), 79.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -78.5$, -112.2 ppm; HRMS *m/z*: calcd for $C_{16}H_{11}F_5NaO_3S$: 401.0242 $[M+H]^+$; found: 401.0234.

(*E*)-1,1-Bis(4-chlorophenyl)-3-(trifluoromethylsulfonyl)prop-2-en-1-ol (5ef): Yield = 57%; white soild; m.p. 122–124 °C; IR (KBr): $\tilde{\nu} = 3492$, 3066, 1614, 1489, 1351, 1202, 1094, 1012, 821 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.68$ (d, $J = 14.8$ Hz, 1H), 7.40–7.34 (m, 4H), 7.25–7.20 (m, 4H), 6.91 (d, $J = 14.8$ Hz, 1H), 2.55 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 160.4$, 140.4, 135.4, 129.5, 128.3, 120.9, 119.7 (q, $J = 323.2$ Hz), 79.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -78.4$ ppm; HRMS *m/z*: calcd for $C_{16}H_{11}Cl_2F_3NaO_3S$: 432.9650 $[M+Na]^+$; found: 432.9645.

(*E*)-1,1-Bis(4-bromophenyl)-3-(trifluoromethylsulfonyl)prop-2-en-1-ol (5ff): Yield = 51%; white soild; m.p. 122–124 °C; IR (KBr): $\tilde{\nu} = 3491$, 3067, 1613, 1485, 1351, 1184, 1112, 1010, 818 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.67$ (d, $J = 14.8$ Hz, 1H), 7.57–7.49 (m, 4H), 7.21–7.12 (m, 4H), 6.91 (d, $J = 14.8$ Hz, 1H), 2.54 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 160.2$, 140.9, 132.5, 128.6, 123.6, 121.0, 119.7 (q, $J = 323.3$ Hz), 79.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -78.4$ ppm; HRMS *m/z*: calcd for $C_{16}H_{11}Br_2F_3NaO_3S$: 522.8620 $[M+Na]^+$; found: 522.8619.

(*E*)-1-Phenyl-1-*para*-tolyl-3-(trifluoromethylsulfonyl)prop-2-en-1-ol (5jf): Yield = 57% (*E*/*Z* = 1:1); white soild; m.p. 62–64 °C; IR (KBr): $\tilde{\nu}$ = 3511, 3066, 1613, 1358, 1197, 1112, 849, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.69 (m, 1H), 7.40–7.23 (m, 6H), 7.23–7.04 (m, 3H), 6.89 (dd, *J* = 14.7, 4.1 Hz, 1H), 2.56 (s, 1H), 2.37 ppm (d, *J* = 8.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1, 161.2, 142.4, 142.1, 141.5, 139.5, 139.0, 137.0, 135.2, 131.6, 129.8, 129.3, 129.2, 129.1, 128.9, 127.5, 126.9, 126.9, 125.2, 120.4, 119.7, 119.8 (q, *J* = 323.3 Hz), 119.8 (q, *J* = 323.3 Hz), 79.7, 79.3, 21.3, 20.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −78.5, −78.6 ppm; HRMS *m*/*z*: calcd for $C_{17}H_{15}F_3NaO_3S$: 379.0587 $[M+Na]^+$; found: 379.0577.

(*E*)-1-(Biphenyl-4-yl)-1-phenyl-3-(trifluoromethylsulfonyl)prop-2-en-1-ol (5mf): Yield = 64%; white soild; m.p. 121–123 °C; IR (KBr): $\tilde{\nu}$ = 3497, 3064, 1613, 1488, 1355, 1200, 1114, 825, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 14.8 Hz, 1H), 7.63–7.54 (m, 4H), 7.46–7.33 (m, 10H), 6.95 (d, *J* = 14.8 Hz, 1H), 2.58 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 142.3, 141.9, 141.2, 140.3, 129.3, 129.1, 129.1, 128.0, 127.9, 127.4, 127.3, 127.0, 120.1, 119.8 (q, *J* = 323.3 Hz), 79.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −78.5 ppm; HRMS *m*/*z*: calcd for $C_{22}H_{17}F_3NaO_3S$: 441.0743 $[M+Na]^+$; found: 441.0752.

(*E*)-1-(4-Bromophenyl)-1-phenyl-3-(trifluoromethylsulfonyl)prop-2-en-1-ol (5nf): Yield = 55%; white soild; m.p. 109–111 °C; IR (KBr): $\tilde{\nu}$ = 3498, 3062, 1613, 1448, 1351, 1204, 1110, 824, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 14.8 Hz, 1H), 7.55–7.50 (m, 2H), 7.42–7.37 (m, 3H), 7.28–7.25 (m, 2H), 7.23–7.18 (m, 2H), 6.92 (d, *J* = 14.8 Hz, 1H), 2.55 ppm (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0, 142.1, 141.2, 132.3, 129.4, 129.4, 128.7, 126.9, 123.2, 120.6, 119.8 (q, *J* = 323.2 Hz), 79.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −78.5 ppm; HRMS *m*/*z*: calcd for $C_{16}H_{12}{}^{81}BrF_3NaO_3S$: 444.9515 $[M+Na]^+$; found: 444.9512.

(*E*)-1-(2-Fluorophenyl)-1-phenyl-3-(trifluoromethylsulfonyl)prop-2-en-1-ol (5pf): Yield = 68%; white soild; m.p. 62–64 °C; IR (KBr): $\tilde{\nu}$ = 3499, 3068, 1613, 1489, 1344, 1112, 853, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 14.8 Hz, 1H), 7.56–7.50 (m, 1H), 7.44–7.36 (m, 4H), 7.27–7.22 (m, 3H), 7.12–7.05 (m, 1H), 6.96 (d, *J* = 14.8 Hz, 1H), 2.82 ppm (d, *J* = 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8 (d, *J* = 246.0 Hz), 158.7 (d, *J* = 3.0 Hz), 141.8, 131.2 (d, *J* = 8.6 Hz), 129.4, 129.3, 129.1 (d, *J* = 11.2 Hz), 128.1 (d, *J* = 3.0 Hz), 126.2, 125.0 (d, *J* = 3.4 Hz), 120.9, 119.8 (d, *J* = 323.1 Hz), 116.8 (d, *J* = 21.9 Hz), 78.0 ppm (d, *J* = 1.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ = −78.6, −110.1 ppm; HRMS *m*/*z*: calcd for $C_{16}H_{12}F_4NaO_3S$: 383.0336 $[M+Na]^+$; found: 383.0337.

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