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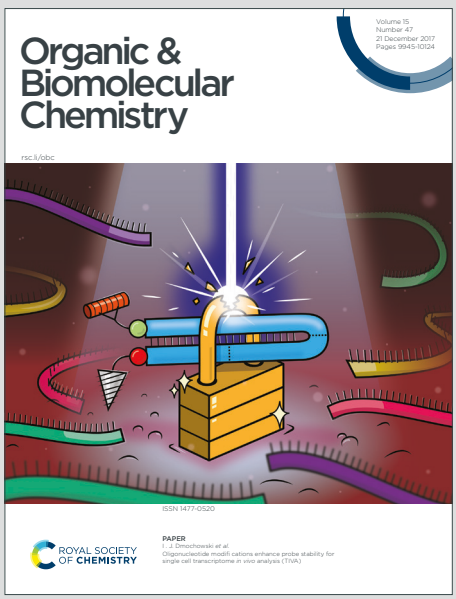

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ARTICLE

Visible-light-mediated difunctionalization of C–C bond for the synthesis of 1-sulfonylmethyl-3,4-dihydronaphthalenes

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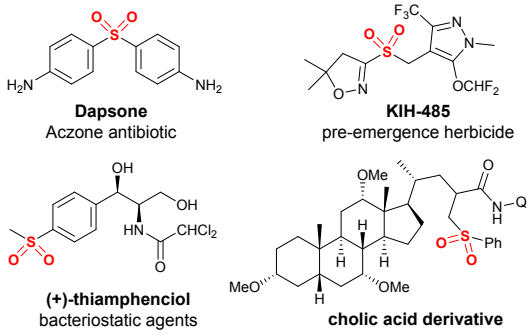
An efficient visible-light-mediated sulfonylation/arylation of C–C *σ*–bond in vinylcyclopropanes with sulfonyl chlorides to synthesize 1-sulfonylmethyl-substituted 3,4-dihydronaphalenes is developed. A radical-type pathway has been proved in this transformation. This difunctionalization procedure shows a series of advantages, such as using commercially and easily available sulfonyl chlorides, mild conditions and eco-friendly energy.

Introduction

Sulfones are extremely important organosulfur compounds in pharmaceutical industry and agriculture industry[1-2]. A great deal of attention has been paid to introduce sulfone skeletons into organic molecules, which displayed a unique application value in polymer materials, organic synthesis, medicinal chemistry, and agrochemical communities[3]. As shown in Scheme 1, **dapsone** (4,4′-diaminodiphenyl sulfone), an aryl sulfone, is widely used in the treatment of bacterial infections, especially in the killing of Mycobacterium leprae[3a].



Scheme 1 Selected drugs containing the sulfone moiety

Pyroxasulfone (**KIH-485**), a heteroaryl alkyl sulfone, is a novel pre-emergence herbicide with low toxicity and high efficiency[3b]. The (+)-thiamphenciol, an aryl alkyl sulfone, is a kind of bacteriostatic agent, especially in the aspect of Gram-negative and Gram-positive microorganisms. Additionally, (+)-thiamphenciol has a series of advantages, such as broad-spectrum antibacterial activity, excellent tissue distribution, the potential for oral administration, and low toxicity[3c]. The cholic acid derivative, an aryl alkyl sulfone, has a good application in the treatment of cholecystitis, bile deficiency and intestinal dyspepsia[3d]. However, based on all of the reported interesting structures and application of sulfones, efficient and convenient methods for accessing sulfone-containing compounds are urgent need.

In the past several decades, the introduction of sulfur-containing group, especially sulfonyl groups, into organic molecules has captured generous chemists' attentions[4,5]. Among the common sulfonyl sources, sulfonyl chlorides are a class of cheap, abundant and easily available sulfonyl sources, and have a wide application in organic chemical and pharmaceutical engineer. Sulfonyl chlorides could undergo sulfonylation reactions to afford sulfur–carbon bonds or sulfur–hetero bonds (Scheme 2)[6,7]. In 2018, our group[7a] reported the visible-light-mediated difunctionalization of active alkynes with sulfonyl chlorides under mild conditions (path I). In 2017, Ni's[7b] group presented a visible-light-catalyzed direct oxidative sulfonylation of alkenes with sulfonyl chlorides for the preparation of *β*-keto sulfones (path II). In 2013, Wu et al.[7c] reported a novel copper-catalyzed cross-coupling of quinolone *N*-oxides with sulfonyl chlorides for constructing sulfonylated quinolone *N*-oxides (path III). In 2016, Reiser and co-workers[7d] reported the hydroxylsulfonylation of styrenes with sulfonyl chlorides for the synthesis of *β*-hydroxysulfones by visible-light-catalysis (path IV). This transformation proceeded *via* an ATRA (atom transfer radical addition) process. This group[7e] also presented the visible-light-mediated sulfonylation of heterocyclic compounds with sulfonyl chlorides for constructing sulfonylated heterocyclic compounds (path V). Wu's group[7f] presented a mild and novel copper-catalyzed C5–H sulfonylation of 8-aminaquinoline amides with excellent functional tolerance (path VI). However, transition-metal catalysts, strong oxidants, bases and ligands are inevitably

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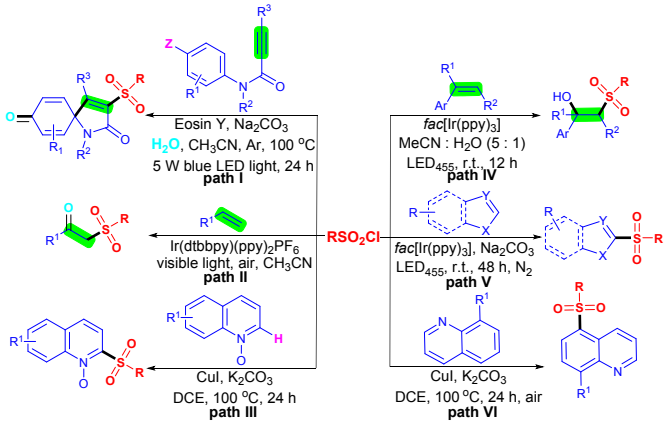
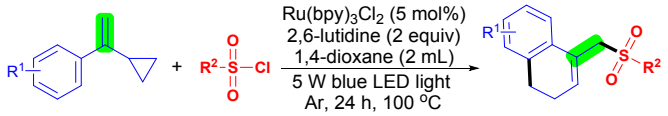
involved in most of these transformations. Thus, environmentally-friendly, safe, simple and mild sulfonylation methods are lacking.



Scheme 2 Selected sulfonylation reactions by using sulfonyl chlorides as sulfonyl sources

Recently, visible-light-catalysis has become an efficient and fascinating tool in organic transformations because of its environmentally benign sustainability, high efficiency and mild operating conditions[8]. Additionally, the methods for ring-opening and cyclization of vinylcyclopropanes were very few[9]. Therefore, based on our work in the aspect of sulfonylation reactions[10a-10c] and visible-light-catalysis reactions[10c-10i], we presented a visible-light-promoted sulfonylation/arylation of C–C *σ*–bond in vinylcyclopropanes with sulfonyl chlorides for the preparation of 1-sulfonylmethyl-3,4-dihydronaphalenes, which achieved by difunctionalization of C–C *σ*–bonds in cyclopropyl olefins with a sulfonyl radical and an aromatic carbon (Scheme 3).

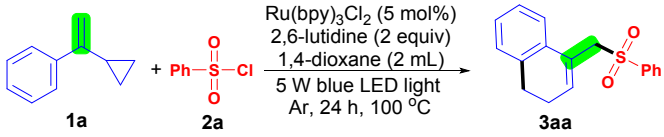


Scheme 3 Oxidative radical difunctionalization of C–C *σ*–bonds in vinylcyclopropanes

Results and discussion

In an initial attempt to clarify the optimal reaction conditions, we chose (1-cyclopropylvinyl)benzene **1a** and benzenesulfonyl chloride **2a** as model substrates. To our delight, the desired product 4-(phenylsulfonylmethyl)-1,2-dihydronaphthalene **3aa** was successfully obtained in 83% yield by using $Ru(bpy)_3Cl_2$ (5 mol%) as catalysts, 2,6-lutidine (2 equiv) as base in 1,4-dioxane (2 mL) at 100 °C under 5 W blue LED irradiation for 24 h. Encouraged by this result, a series of other visible-light catalysts, including $Ir(ppy)_3$, Eosin Y and Na_2-Eosin Y were examined (entries 2–4). Unfortunately, all of these catalysts could not increase the reaction yields obviously. Additionally, the reaction could not deliver the product **3aa** in the absence of catalyst or light irradiation (entries 5–6). Next, the amount of catalyst was investigated. The reaction performed with 10 mol% of $Ru(bpy)_3Cl_2$ gave similar yield with that using 5 mol% of $Ru(bpy)_3Cl_2$ and reducing the amount to 2 mol% led to a lower yield (entries 7–8). The yields of the reactions decreased when the reactions were conducted with other light sources, such as 36 W compact fluorescent light, 3 W blue LED light or 5 W green LED light (entries 9–11). The reaction employing 1 mol% $Ru(bpy)_3Cl_2$ and a 12 W blue LEDs only afforded the product **3aa** in 36% yield (entry 12). The effect of the base was examined. However, several other bases, such as K_2CO_3, Na_2CO_3, Cs_2CO_3, pyridine and Et_3N were less effective than 2,6-lutidine (entries 13–17). The reaction could deliver 63% yield in the presence of Na_2CO_3 (entry 14). No obvious improvement of yield was observed when a series of other solvents, including CH_3CN, THF, DMF, DMSO and toluene, were used in this transformation (entries 18–22). Using THF in the reaction afforded the product **3aa** in 74% yield (entry 19).

Table 1 Screening of optimal reaction conditions[a]



1a 2a 3aa

Entry	Variation from the standard conditions	Yield (%)[b]
1	none	83
2	$Ir(ppy)_3$ instead of $Ru(bpy)_3Cl_2$	78
3	Eosin Y instead of $Ru(bpy)_3Cl_2$	56
4	Na_2-Eosin Y instead of $Ru(bpy)_3Cl_2$	35
5	without $Ru(bpy)_3Cl_2$	0
6	without additional light	0
7	$Ru(bpy)_3Cl_2$ (10 mol%)	85
8	$Ru(bpy)_3Cl_2$ (2 mol%)	68
9[c]	none	33
10[d]	none	25
11[e]	none	31
12[f]	$Ru(bpy)_3Cl_2$ (1 mol%)	36
13	K_2CO_3 instead of 2,6-lutidine	47
14	Na_2CO_3 instead of 2,6-lutidine	63
15	Cs_2CO_3 instead of 2,6-lutidine	22
16	pyridine instead of 2,6-lutidine	39
17	Et_3N instead of 2,6-lutidine	26
18	CH_3CN instead of 1,4-dioxane	69
19	THF instead of 1,4-dioxane	74
20	DMF instead of 1,4-dioxane	22
21	DMSO instead of 1,4-dioxane	29
22	toluene instead of 1,4-dioxane	41
23	110 °C	71
24	90 °C	66
25	80 °C	57
26[g]	none	84
27[h]	none	72

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (2 equiv, 0.4 mmol), $Ru(bpy)_3Cl_2$ (5 mol%, 0.01 mmol), 2,6-lutidine (2 equiv, 0.4 mmol) in 1,4-dioxane (2 mL) at 100 °C under an argon atmosphere and 5 W blue LED light for 24 h. [b] isolated yield. [c] 36 W compact fluorescent light instead of 5 W blue LED light. [d] 3 W blue LED light instead of 5 W blue LED light. [e] 5 W green LED light instead of 5 W blue LED light. [f] 12 W blue LEDs. [g] 36 h instead of 24 h. [h] **1a** (1 g, 4.24 mmol) and solvent (10 mL) for 72 h.

Notably, the yield of the desired product **3aa** decreased to 71% when the oil bath temperature increased to 110 °C (entry 23), and the reaction carried out at 90 °C or 80 °C generated the desired

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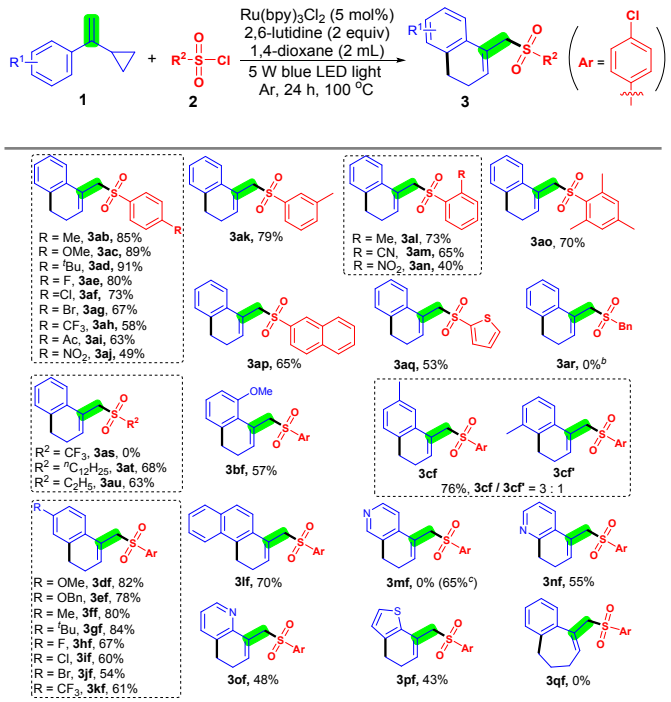
product **3aa** in low yields (entries 24–25). Additionally, the reaction yield did not increase obviously when the reaction was performed for a longer time (entry 26). To our delight, a scale-up reaction could successfully afford the product **3aa** in 72% yield (entry 27).

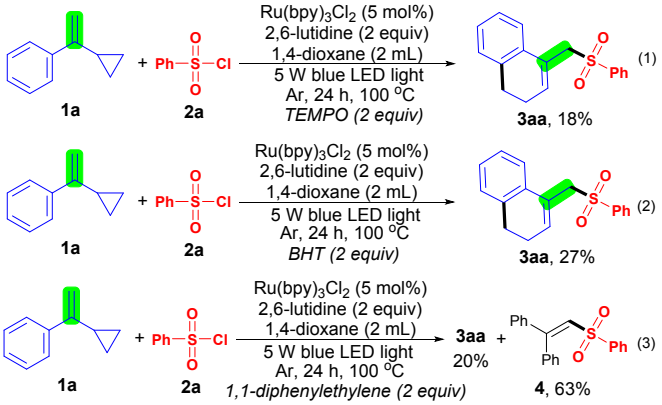
Table 2 Scope of cyclopropyl olefins (**1**) and sulfonyl chlorides (**2**)[a]



[a] Reaction conditions: **1** (0.2 mmol), **2** (2 equiv, 0.4 mmol), $Ru(bpy)_3Cl_2$ (5 mol%, 0.01 mmol), 2,6-lutidine (2 equiv, 0.4 mmol) at 100 °C under an argon atmosphere and 5 W blue LED light for 24 h. [b] No other product was detected and most of the starting materials was recovered. [c] The yield of (5-(((4-chlorophenyl)sulfonyl)methyl)isoquinoline **3mf'**.

Having the established conditions in hand, the scope of sulfonyl chlorides **2** were examined in the presence of (1-cyclopropylvinyl)benzene **1a** under the optimized conditions (Table 2). We were delighted to find that a series of arylsulfonyl chlorides, which connected with electron-withdrawing or electron-donating groups on the aromatic rings, could successfully deliver the target products in moderate to excellent yields (**3ab–ap**). The arylsulfonyl chlorides with electron-rich groups delivered higher yields than that with electron-deficient groups. Additionally, the steric effect also had significant influence on the reaction yields according to the experimental results, and the reactivity order for sulfonylation is *ortho* < *meta* < *para* (products **3ab**, **3ak**, and **3al**). Surprisingly, 4-nitrobenzene-1-sulfonyl chloride **2j** was suitable for this sulfonylation/arylation and delivered the target product 4-((4-nitrophenylsulfonyl)methyl)-1,2-dihydronaphthalene **3aj** in 49% yields. The 2,4,6-trimethylbenzene-1-sulfonyl chloride **2o** was also compatible for the standard conditions (product **3ao**). It should be noted that thiophene-2-sulfonyl chloride **2q** was employed as sulfonyl source in the present reaction systems and could lead to 1-sulfonylmethyl-substituted 3,4-dihydronaphalene **3aq** in 53% yield. Unfortunately, using benzylsulfonyl chloride **2r** as sulfonyl source under the standard conditions could not generate the target product (product **3ar**). Notably, several aliphatic sulfonyl chlorides, including dodecane-1-sulfonyl chloride **2t** and ethanesulfonyl chloride **2u** could afford the target product in good yields (products **3at** and **3au**).

Next, we turn our attention to investigate the scope of cyclopropyl olefins **1** in the presence of 4-chlorobenzene-1-sulfonyl chloride **2f**, $Ru(bpy)_3Cl_2$, 2,6-lutidine in 1,4-dioxane at 100 °C under 5 W blue LED irradiation for 24 h. A series of cyclopropyl olefins were examined and these reactions could proceed smoothly to deliver the sulfonylation/arylation products in moderate to good yields (products **3bf–pf**). However, the cyclopropyl olefins **1c** with an *meta*-substituted aryl group could undergo this difunctionalization smoothly and the products 4-(((4-chlorophenyl)sulfonyl)methyl)-6-methyl-1,2-dihydronaphthalene **3cf** and 4-(((4-chlorophenyl)sulfonyl)methyl)-8-methyl-1,2-dihydronaphthalene **3cf'** could be obtained in 76% yield (3 : 1). The cyclopropyl olefins with electron-donating substituted aryl groups afforded high yields than which with electron-withdrawing substituted aryl groups (products **3df–kf**). To our delight, 2-(1-cyclopropylvinyl)naphthalene **1l** was suitable for this reaction system and produced the major product **3lf** in 70% yield. The heteroaromatic substituted vinylcyclopropanes **1n–p** could successfully deliver the corresponding products **3nf–pf** in moderate yields. It's worth noting that the reaction of substrate **1n** (3-(1-cyclopropylvinyl)pyridine) only gave the product **3nf** as major product and another isomer was quite few. However, cyclopropyl olefins **1m** could not afford the target product **3mf** in this transformation. Another dehydrogenation product (5-(((4-chlorophenyl)sulfonyl)methyl)isoquinoline **3mf'** could be obtained in 65% yield. Additionally, vinylcyclobutane **1q** was not compatible with the standard conditions (product **3qf**).



Scheme 4 Control experiments.

To gain insights into the mechanism of this transformation, a series of control experiments were performed (Scheme 4). According to the previous literature, this difunctionalization of cyclopropyl olefins and sulfonyl chlorides proceeded *via* a radical process[9,10b-10c]. Several radical inhibitors such as TEMPO or BHT were added into the reaction between **1a** and **2a** under the optimal conditions (eqs 1–2, Scheme 4). Notably, all of these reactions were obviously inhibited. When 1,1-diphenylethylene was added into the reaction, the target difunctional product **3aa** was obtained only in

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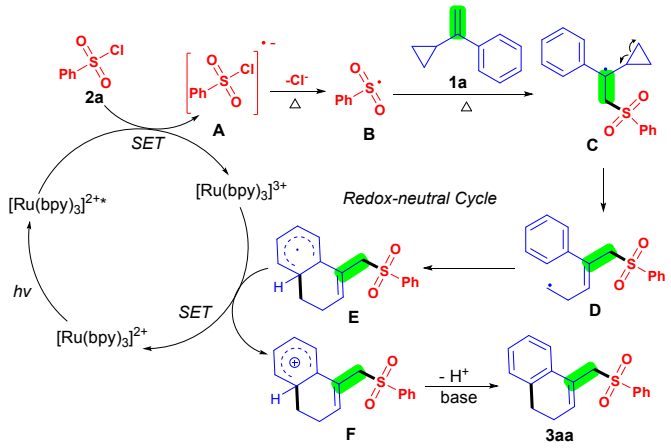
20% yield, along with delivering (2-(phenylsulfonyl)ethene-1,1-diyl)dibenzene **4** in 63% yield (eq 3, Scheme 4). The results demonstrated that a radical route was involved in this difunctionalization.

A plausible mechanism was displayed in Scheme 5 inspired by presented results and previous reports[6-11]. Initially, $[Ru(bpy)_3]^{2+}$ is photoexcited by visible light to form a strong reductant $[Ru(bpy)_3]^{2+*}$, which can undergo a quenching reductive cycle. The radical anion **A** is generated from benzenesulfonyl chloride **2a** under the action of $[Ru(bpy)_3]^{2+*}$ *via* a *SET* process[7a,7b,7d,7e,9]. The intermediate **A** performs decomposition to afford the sulfonyl radical **B**. The radical addition of radical **B** to the terminal carbon of double bond in vinylcyclopropane **1a** delivers the stable benzyl radical **C**. The experimental results of entries 23−25 in Table 1 suggested that the formation of benzyl radical **C** (including the formation of the sulfonyl radical and the addition of the sulfonyl radical to the double bond in vinylcyclopropanes) needed heating. Next, the intermediate **C** proceeds homolytic cleavage of C−C *σ*−bond in three-membered carbocyclic ring to generate the terminal alkyl radical **D**. Then, it undergoes cyclization with the intermolecular phenyl ring to give the aryl radical **E**, which is oxidized into the aryl cation **F** by $[Ru(bpy)_3]^{3+}$. Finally, the target product **3aa** is produced by deprotonation of the intermediate **F** under the action of base. Notably, quantum yield measurements of this difunctionalization process (Φ = 0.016) suggested that radical chain are not the major product-forming pathway in this transformation[11].



Scheme 5 Proposed mechanism.

Conclusion

In conclusion, a mild and facile visible-light-mediated sulfonylation/arylation of C−C *σ*−bond in cyclopropyl olefins with sulfonyl chlorides for accessing 1-sulfonylmethyl-substituted 3,4-dihydronaphalenes is developed. Our investigations show that this C−C *σ*−bond sulfonylation/arylation contains a radical pathway. This novel method has the advantages of using commercially and easily available sulfonyl chlorides, mild conditions, and eco-friendly energy. This C−C *σ*−bond sulfonylation/arylation involves a series of sulfonyl radical addition, radical rearrangement and C−C bond formation. A wide application of this new method in organic synthesis and medicinal chemical is ongoing in our laboratory.

Experimental

General methods

All reactions were carried out with magnetic stirring and in dried glassware. Standard syringe techniques were applied for transfer of dry solvents. All reagents and solvents were commercially available and used without any further purification unless specified. Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were recorded at 400 MHz and 100MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: TMS = 0.00 ppm, for ^{13}C NMR: $CDCl_3$ = 77.00 ppm. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet, and br = broad. Analytical TLC was performed on precoated silica gel plates. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

General procedure for the synthesis of 1-sulfonylmethyl-3,4-dihydronaphthalenes 3

To a Schlenk tube were added **1a** (0.2 mmol), **2a** (2 equiv, 0.4 mmol), $Ru(bpy)_3Cl_2$ (5 mol %, 0.01 mmol), 2,6-lutidine (2 equiv, 0.4 mmol) in 1,4-dioxane (2 mL). Then the mixture was stirred at 100 °C (oil bath temperature) in argon atmosphere (1 atm) under 5 W blue LED light for 24 h until complete consumption of starting material as monitored by TLC and GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 10 : 1 to 1 : 1) to afford the desired products **3**.

4-((Phenylsulfonyl)methyl)-1,2-dihydronaphthalene (3aa): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.13-7.08 (m, 4H), 5.93-5.90 (m, 1H), 4.23 (s, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.25-2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.3, 135.9, 135.0, 133.6, 128.8, 128.7, 128.7, 127.6, 127.4, 126.4, 125.8, 123.1, 60.0, 27.7, 23.3; HRMS (ESI-TOF) *m/z*: $C_{17}H_{17}O_2S$ $(M + H)^+$ calcd for 285.0944, found 285.0949.

4-(Tosylmethyl)-1,2-dihydronaphthalene (3ab): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.14-7.05 (m, 4H), 5.92-5.89 (m, 1H), 4.20 (s, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.25-2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.6, 135.8, 134.7, 132.6, 130.8, 129.8, 127.5, 127.2, 126.3, 126.0, 123.1, 113.9, 60.1, 55.6, 27.7, 23.3; HRMS (ESI-TOF) *m/z*: $C_{18}H_{19}O_2S$ $(M + H)^+$ calcd for 299.1100, found 299.1106.

4-(((4-Methoxyphenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3ac): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72-7.68 (m, 2H), 7.11-7.07 (m, 4H), 6.88-6.85 (m, 2H), 5.92-5.90 (m, 1H), 4.19 (s, 2H), 3.82 (s, 3H), 2.71-2.63 (m, 2H), 2.25-2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.7, 135.9, 134.8, 132.7, 130.9, 129.9, 127.6, 127.3,

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126.4, 126.1, 123.2, 114.0, 60.2, 55.7, 27.8, 23.3; HRMS (ESI-TOF) *m/z*: $C_{18}H_{19}O_3S$ (M + H)$^+$ calcd for 315.1049, found 315.1055.

4-(((4-(*tert*-Butyl)phenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3ad): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.05-7.04 (m, 2H), 7.00-6.98 (m, 2H), 6.03-6.01 (m, 1H), 4.20 (s, 2H), 2.69 (d, *J* = 8.0 Hz, 2H), 2.27-2.22 (m, 2H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.5, 135.8, 135.3, 134.8, 132.6, 128.5, 128.2, 127.5, 127.2, 126.2, 125.7, 122.9, 59.9, 35.1, 31.0, 27.7, 23.3; HRMS (ESI-TOF) *m/z*: $C_{21}H_{25}O_2S$ (M + H)$^+$ calcd for 341.1570, found 341.1575.

4-(((4-Fluorophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3ae): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72-7.69 (m, 2H), 7.20-7.18 (m, 2H), 7.13-7.11 (m, 2H), 7.01 (t, *J* = 8.8 Hz, 2H), 6.07 (t, *J* = 7.2 Hz, 1H), 4.39 (s, 2H), 3.63 (t, *J* = 6.8 Hz, 2H), 2.73-2.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.7 (d, *J* = 254.9 Hz, 1C), 140.2, 134.8 (d, *J* = 3.2 Hz, 1C), 133.9, 131.2 (d, *J* = 9.6 Hz, 1C), 130.9, 130.5, 128.4, 127.9, 127.6, 126.3, 116.2 (d, *J* = 22.5 Hz, 1C), 57.9, 43.6, 32.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ: -103.5 (s, 1F); HRMS (ESI-TOF) *m/z*: $C_{17}H_{16}{}^{19}FO_2S$ (M + H)$^+$ calcd for 303.0850, found 303.0855.

4-(((4-Chlorophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3af): 73%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.13-7.07 (m, 4H), 5.95-5.93 (m, 1H), 4.23 (s, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.26-2.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.3, 136.7, 135.9, 135.1, 132.3, 130.2, 129.0, 127.7, 127.5, 126.4, 125.7, 123.0, 60.1, 27.6, 23.3; HRMS (ESI-TOF) *m/z*: $C_{17}H_{16}{}^{35}ClO_2S$ (M + H)$^+$ calcd for 319.0554, found 319.0560.

4-(((4-Bromophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3ag): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.15-7.07 (m, 4H), 5.95-5.93 (m, 1H), 4.22 (s, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.27-2.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.4, 136.7, 135.9, 135.2, 132.3, 130.2, 129.1, 127.8, 127.6, 126.4, 125.7, 123.1, 60.1, 27.7, 23.3; HRMS (ESI-TOF) *m/z*: $C_{17}H_{16}{}^{79}BrO_2S$ (M + H)$^+$ calcd for 363.0049, found 363.0054.

4-(((4-(Trifluoromethyl)phenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3ah): yellow solid, mp 84.2-85.4 °C (uncorrected);^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.11-6.99 (m, 4H), 6.01-5.98 (m, 1H), 4.26 (m, 2H), 2.68 (t, *J* = 8.0 Hz, 2H), 2.27-2.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.7, 135.8, 135.4, 135.1, 132.1, 129.3 (2C), 127.7, 127.6, 126.4, 125.8 (t, *J* = 3.7 Hz, 1C), 125.4, 122.8, 59.9, 27.6, 23.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ: -63.3 (s, 3F); HRMS (ESI-TOF) *m/z*: $C_{18}H_{16}{}^{19}F_3O_2S$ (M + H)$^+$ calcd for 353.0818, found 353.0823.

1-(4-(((3,4-Dihydronaphthalen-1-yl)methyl)sulfonyl)phenyl)ethanone (3ai): white solid, mp 82.6-84.0 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.16-7.15 (m, 2H), 7.12-7.10 (m, 2H), 6.07 (t, *J* = 7.6 Hz, 1H), 4.42 (s, 2H), 3.64-3.61 (m, 2H), 2.73-2.66 (m, 2H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.7, 142.4, 140.5, 140.0, 134.2, 130.1, 129.1, 128.8, 128.5, 128.4, 128.3, 127.5, 126.4, 57.7, 43.6, 32.5, 26.9; HRMS (ESI-TOF) *m/z*: $C_{19}H_{19}O_3S$ (M + H)$^+$ calcd for 327.1049, found 327.1055.

4-(((4-Nitrophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3aj): yellow solid, mp 156.8-158.4 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.09-7.08 (m, 2H), 7.04-7.03 (m, 2H), 6.01-5.99 (m, 1H), 4.30 (m, 2H), 2.68 (t, *J* = 8.0 Hz, 2H), 2.27-2.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.7, 143.8, 135.9, 135.6, 132.0, 130.2, 127.9, 127.7, 126.4, 125.3, 123.8, 122.8, 60.0, 27.6, 23.3; HRMS (ESI-TOF) *m/z*: $C_{17}H_{16}NO_4S$ (M + H)$^+$ calcd for 330.0795, found 330.0800.

4-((*m*-Tolylsulfonyl)methyl)-1,2-dihydronaphthalene (3ak): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.48 (m, 2H), 7.25-7.19 (m, 2H), 7.06-6.97 (m, 4H), 5.88-5.86 (m, 1H), 4.14 (s, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 2.25 (s, 3H), 2.20-2.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.0, 138.1, 135.9, 134.8, 134.3, 132.6, 129.1, 128.6, 127.5, 127.3, 126.3, 125.8, 125.7, 123.0, 59.9, 27.7, 23.3, 21.1; HRMS (ESI-TOF) *m/z*: $C_{18}H_{19}O_2S$ (M + H)$^+$ calcd for 299.1100, found 299.1106.

4-((*o*-Tolylsulfonyl)methyl)-1,2-dihydronaphthalene (3al): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 7.6 Hz, 1H), 7.45-7.41 (m, 1H), 7.27-7.20 (m, 3H), 7.12-7.06 (m, 3H), 5.90-5.87 (m, 1H), 4.24 (s, 2H), 2.68-2.63 (m, 5H), 2.23-2.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.4, 136.5, 135.9, 134.7, 133.6, 132.7, 132.4, 130.9, 127.6, 127.4, 126.4, 126.3, 125.6, 123.1, 59.2, 27.6, 23.3, 20.7; HRMS (ESI-TOF) *m/z*: $C_{18}H_{19}O_2S$ (M + H)$^+$ calcd for 299.1100, found 299.1106.

2-(((3,4-Dihydronaphthalen-1-yl)methyl)sulfonyl)benzonitrile (3am): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, *J* = 8.0 Hz, 1H), 7.63-7.54 (m, 3H), 7.13-7.11 (m, 2H), 7.09-7.06 (m, 2H), 6.12-6.09 (m, 1H), 4.67 (m, 2H), 3.71 (t, *J* = 6.4 Hz, 2H), 2.92-2.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.0, 139.7, 135.2, 134.9, 133.5, 132.8, 130.8, 129.3, 128.3, 128.3, 127.7, 127.5, 126.3, 115.6, 111.5, 56.4, 43.7, 32.5; HRMS (ESI-TOF) *m/z*: $C_{18}H_{16}NO_2S$ (M + H)$^+$ calcd for 310.0896, found 310.0902.

4-(((2-Nitrophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3an): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 7.6 Hz, 1H), 7.68-7.62 (m, 2H), 7.57-7.53 (m, 1H), 7.26-7.24 (m, 2H), 7.17-7.15 (m, 2H), 6.16 (t, *J* = 7.2 Hz, 1H), 4.87 (s, 2H), 3.66 (t, *J* = 6.4 Hz, 2H), 2.85-2.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.7, 139.9, 134.8, 134.6, 132.8, 132.6, 132.2, 130.1. 128.8, 128.5, 128.3, 127.7, 126.6, 124.6, 57.5, 43.6, 32.5; HRMS (ESI-TOF) *m/z*: $C_{17}H_{16}NO_4S$ (M + H)$^+$ calcd for 330.0795, found 330.0800.

4-((Mesitylsulfonyl)methyl)-1,2-dihydronaphthalene (3ao): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24-7.21 (m, 1H), 7.15-7.06 (m, 3H), 6.87 (s, 2H), 5.83-5.80 (m, 1H), 4.21 (s, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.57 (s, 6H), 2.27 (s, 3H), 2.23-2.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.2, 140.5, 135.9, 134.5, 132.8, 132.3, 131.9, 127.6, 127.3, 126.4, 125.8, 123.3, 59.5, 27.6, 23.4, 23.2, 21.0; HRMS (ESI-TOF) *m/z*: $C_{20}H_{23}O_2S$ (M + H)$^+$ calcd for 327.1413, found 327.1419.

2-(((3,4-Dihydronaphthalen-1-yl)methyl)sulfonyl)naphthalene (3ap): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (s, 1H), 7.89-7.85 (m, 3H), 7.80-7.77(m, 1H), 7.66-7.55 (m, 2H), 7.18-7.17 (m, 1H), 7.02-7.00 (m, 3H), 5.88-5.85 (m, 1H), 4.29 (s, 2H), 2.64 (t, *J* = 8.0 Hz, 2H), 2.19-2.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.8, 135.2, 135.1, 134.9, 132.5, 131.8, 130.5, 129.2, 129.1, 128.9, 127.8, 127.5, 127.5, 127.3, 126.2, 125.8, 123.3, 123.1, 60.0, 27.6, 23.2; HRMS (ESI-TOF) *m/z*: $C_{21}H_{19}O_2S$ (M + H)$^+$ calcd for 335.1100, found 335.1106.

2-(((3,4-Dihydronaphthalen-1-yl)methyl)sulfonyl)thiophene (3aq): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81-7.78 (m, 2H), 7.11-7.07 (m, 5H), 5.96-5.93 (m, 1H), 4.23 (s, 2H), 2.72-2.67 (m, 2H), 2.27-2.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.3, 139.7, 135.1, 134.7, 134.3, 134.2, 134.1, 130.5, 128.3, 127.8, 127.6, 126.3, 59.0, 43.6, 32.4; HRMS (ESI-TOF) *m/z*: $C_{15}H_{15}O_2S_2$ (M + H)$^+$ calcd for 291.0508, found 291.0513.

4-((Dodecylsulfonyl)methyl)-1,2-dihydronaphthalene(3at): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 7.6 Hz, 1H), 7.26-7.15 (m, 3H), 6.32-6.30 (m, 1H), 4.12 (s, 2H), 2.91 (t, *J* = 8.0 Hz, 2H), 2.81 (t, *J* = 8.0 Hz, 2H), 2.41-2.38 (m, 2H), 1.82-1.78 (m, 2H), 1.30-1.24 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.2, 134.7, 132.6, 128.0, 127.8, 126.6, 125.6, 123.1, 56.5, 51.8, 31.9, 29.6, 29.5, 29.5, 29.3, 29.2, 29.0, 28.4, 27.8, 23.4, 22.7, 21.8, 14.1; HRMS (ESI-TOF) *m/z*: $C_{23}H_{37}O_2S$ (M + H)$^+$ calcd for 377.2509, found 377.2514.

4-((Ethylsulfonyl)methyl)-1,2-dihydronaphthalene (3au): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (d, *J* = 7.2 Hz, 1H), 7.27-7.16 (m, 3H), 6.33-6.30 (m, 1H), 4.14 (s, 2H), 2.99-2.93 (m, 2H), 2.81 (t, *J* = 8.0 Hz, 2H), 2.41-2.36 (m, 2H), 1.37 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.1, 134.8, 132.5, 128.0, 127.8, 126.6, 125.5, 123.0, 55.8, 46.0, 27.7, 23.4, 6.2; HRMS (ESI-TOF) *m/z*: $C_{13}H_{17}O_2S$ (M + H)$^+$ calcd for 237.0944, found 237.0949.

4-(((4-chlorophenyl)sulfonyl)methyl)-5-methoxy-1,2-dihydronaphthalene (3bf): white solid, mp 98.1-99.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.45 (d, *J* = 7.6 Hz, 1H),6.09 (t, *J* = 5.2 Hz, 1H), 4.69 (s, 2H), 3.64 (s, 3H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.15-2.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.2, 139.8, 139.2, 137.0, 136.5, 129.9, 128.2, 128.0, 125.5, 121.0, 120.3, 109.4, 62.6, 54.9, 28.9, 22.9; HRMS (ESI-TOF) *m/z*: $C_{18}H_{18}{}^{35}ClO_3S$ (M + H)$^+$ calcd for 349.0660, found 349.0665.

4-(((4-chlorophenyl)sulfonyl)methyl)-6-methyl-1,2-dihydronaphthalene (3cf) and **4-(((4-chlorophenyl)sulfonyl)methyl)-8-methyl-1,2-dihydronaphthalene (3cf'):** yellow solid, mp 111.2-113.5 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, *J* = 8.8 Hz, 1.5H), 7.59 (d, *J* = 8.8 Hz, 0.5H), 7.37 (d, *J* = 8.4 Hz, 1.5H), 7.27 (d, *J* = 9.2 Hz, 0.5H), 7.07 (t, *J* = 7.6 Hz, 0.3H), 7.02-6.95 (m, 2.4H), 6.91 (d, *J* = 6.0 Hz, 0.3H), 6.03 (t, *J* = 7.6 Hz, 0.25H), 5.93-5.91 (m, 0.75H), 4.37 (s, 0.5H), 4.22 (s, 1.5H), 3.63 (t, *J* = 6.8 Hz, 0.5H), 2.74-2.68 (m, 0.5H), 2.62 (t, *J* = 8.4 Hz, 1.5H), 2.24-2.19 (m, 4.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.2, 140.0, 137.9, 137.1, 136.7, 135.0, 134.5, 134.2, 133.6, 132.1, 130.5, 130.1, 129.8, 129.6, 128.9, 128.9, 128.2, 128.2, 127.2, 125.8, 125.6, 123.4, 121.1, 60.3, 57.9, 43.6, 32.4, 23.3, 22.9, 21.2, 19.7; HRMS (ESI-TOF) *m/z*: $C_{18}H_{18}{}^{35}ClO_2S$ (M + H)$^+$ calcd for 333.0711, found 333.0716.

4-(((4-Chlorophenyl)sulfonyl)methyl)-7-methoxy-1,2-dihydronaphthalene (3df): yellow solid, mp 88.9-90.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.74-6.71 (m, 1H), 5.98 (t, *J* = 7.6 Hz, 1H), 4.35 (s, 2H), 3.78 (s, 3H), 3.62 (d, *J* = 6.4 Hz, 2H), 2.69-2.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.2, 140.3, 137.2, 132.5, 132.3, 130.2, 129.8, 129.8, 129.1, 129.0, 127.5, 113.7, 58.0, 55.3, 43.7, 32.4; HRMS (ESI-TOF) *m/z*: $C_{18}H_{18}{}^{35}ClO_3S$ (M + H)$^+$ calcd for 349.0660, found 349.0665.

7-(benzyloxy)-4-(((4-chlorophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3ef): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 8.8 Hz, 2H), 7.43-7.38 (m, 4H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 5.98 (t, *J* = 7.2 Hz, 1H), 5.03 (s, 2H), 4.34 (s, 2H), 3.60 (d, *J* = 6.8 Hz, 2H), 2.69-2.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 140.3, 137.2, 136.7, 132.7, 132.4, 130.2, 129.8, 129.7, 129.1, 128.6, 128.6, 128.0, 127.5, 127.4, 114.6, 70.0, 57.9, 43.7, 32.4; HRMS (ESI-TOF) *m/z*: $C_{24}H_{22}{}^{35}ClO_3S$ (M + H)$^+$ calcd for 425.0973, found 425.0978.

4-(((4-chlorophenyl)sulfonyl)methyl)-7-methyl-1,2-dihydronaphthalene (3ff): white solid, mp 103.8-104.9 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71-7.70 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.85-5.82 (m, 1H), 4.20 (s, 2H), 2.64 (t, *J* = 8.0 Hz, 2H), 2.28 (s, 3H), 2.22-2.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.3, 137.4, 136.6, 135.8, 133.9, 130.1, 129.6, 129.0, 128.5, 126.9, 125.6, 123.0, 60.1, 27.7, 23.3, 21.0; HRMS (ESI-TOF) *m/z*: $C_{18}H_{18}{}^{35}ClO_2S$ (M + H)$^+$ calcd for 333.0711, found 333.0716.

7-(*tert*-butyl)-4-(((4-chlorophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3gf): white solid, mp 100.7-102.0 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.09-7.04 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 1H), 5.92-5.90 (m, 1H), 4.21 (s, 2H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.27-2.22 (m, 2H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.6, 140.2, 136.7, 135.4, 134.2, 130.2, 129.6, 128.9, 125.5, 124.8, 123.1, 122.7, 60.1, 34.4, 31.2, 28.0, 23.4; HRMS (ESI-TOF) *m/z*: $C_{21}H_{24}{}^{35}ClO_2S$ (M + H)$^+$ calcd for 375.1180, found 375.1186.

4-(((4-Chlorophenyl)sulfonyl)methyl)-7-fluoro-1,2-dihydronaphthalene (3hf): white solid, mp 85.0-86.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74-7.71 (m, 2H), 7.44-7.42 (m, 2H), 7.15-7.11 (m, 1H), 6.83-6.78 (m, 2H), 5.86-5.83 (m, 1H), 4.21 (s, 2H), 2.68 (t, *J* = 8.0 Hz, 2H), 2.25-2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.8 (d, *J* = 246.2 Hz, 1C), 140.5, 138.5 (d, *J* = 7.6 Hz, 1C), 136.5, 134.3 (d, *J* = 2.1 Hz, 1C), 130.1, 129.1, 128.5, 124.9 (t, *J* = 6.2 Hz, 1C), 114.8 (d, *J* = 21.2 Hz, 1C), 112.8 (d, *J* = 21.2 Hz, 1C), 60.1, 27.8, 27.8, 23.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ: -114.1 (s, 1F); HRMS (ESI-TOF) *m/z*: $C_{17}H_{15}{}^{35}Cl^{19}FO_2S$ (M + H)$^+$ calcd for 337.0460, found 337.0465.

7-Chloro-4-(((4-chlorophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3if): yellow solid, mp 96.5-98.1 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74-7.71 (m, 2H), 7.45-7.43 (m, 2H), 7.09 (s, 3H), 5.90-5.88 (m, 1H), 4.20 (s, 2H), 2.67 (t, *J* = 8.0 Hz, 2H), 2.26-2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.6, 137.7, 136.4, 135.4, 132.9, 130.8, 130.1, 129.2, 127.7, 126.4, 125.0, 124.5, 59.9, 27.5, 23.0; HRMS (ESI-TOF) *m/z*: $C_{17}H_{15}{}^{35}Cl_2O_2S$ (M + H)$^+$ calcd for 353.0164, found 353.0170.

7-Bromo-4-(((4-chlorophenyl)sulfonyl)methyl)-1,2-dihydronaphthalene (3jf): white solid, mp 144.3-145.9 °C (uncorrected);^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.26-7.23 (m, 2H), 7.03-7.01 (m, 1H), 5.92-5.91 (m, 1H), 4.19 (s, 2H), 2.67 (t, *J* = 8.0 Hz, 2H), 2.25-2.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.7, 138.1, 136.5, 135.7, 131.4, 130.7, 130.2, 129.4, 129.2, 125.1, 124.8, 121.3, 60.0, 27.5, 23.2; HRMS (ESI-TOF) *m/z*: $C_{17}H_{15}{}^{79}Br^{35}ClO_2S$ (M + H)$^+$ calcd for 396.9659, found 396.9665.

4-(((4-chlorophenyl)sulfonyl)methyl)-7-(trifluoromethyl)-1,2-dihydronaphthalene (3kf): white solid, mp 103.4-134.8 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.06-6.03 (m, 1H), 4.23 (s, 2H), 2.76 (t, *J* = 8.0 Hz, 2H), 2.31-2.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.7, 137.6, 136.5 (d, *J* = 7.5 Hz, 1C), 135.6, 130.1, 129.2, 129.1 (d, *J* = 32.2 Hz, 1C), 125.1, 124.4 (q, *J* = 3.7 Hz, 1C), 124.0 (d, *J* = 270.5 Hz, 1C), 123.4 (q, *J* = 4.0 Hz, 1C), 123.3, 122.6, 59.8, 27.4, 23.0; ^{19}F NMR (282 MHz, $CDCl_3$): δ: -62.6 (s, 3F); HRMS (ESI-TOF) *m/z*: $C_{18}H_{15}{}^{35}Cl^{19}F_3O_2S$ (M + H)$^+$ calcd for 387.0428, found 387.0433.

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1-(((4-chlorophenyl)sulfonyl)methyl)-3,4-dihydrophenanthrene (3lf): white solid, mp 86.5-87.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.51-7.48 (m, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.30-7.28 (m, 3H), 6.00-5.98 (m, 1H), 4.31 (s, 2H), 3.10 (t, *J* = 8.4 Hz, 2H), 2.37-2.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.3, 136.5, 134.6, 132.9, 131.6, 131.0, 130.1, 129.4, 129.0, 129.0, 128.5, 126.2, 126.2, 125.5, 123.5, 121.5, 60.4, 22.9, 22.6; HRMS (ESI-TOF) *m/z*: $C_{21}H_{18}{}^{35}ClO_2S$ $(M + H)^+$ calcd for 369.0771, found 369.0716.

5-(((4-chlorophenyl)sulfonyl)methyl)isoquinoline (3mf'): white solid, mp 91.9-93.1 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.25 (s, 1H), 8.50 (d, *J* = 6.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 6.0 Hz, 1H), 7.56-7.52 (m, 3H), 7.46 (d, *J* = 6.4 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 4.79 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.2, 143.8, 140.9, 136.1, 134.7, 134.6, 130.0, 129.5, 129.4, 128.7, 126.6, 123.6, 116.3, 59.0; HRMS (ESI-TOF) *m/z*: $C_{16}H_{13}{}^{35}ClNO_2S$ $(M + H)^+$ calcd for 318.0350, found 318.0356.

5-(((4-chlorophenyl)sulfonyl)methyl)-7,8-dihydroquinoline (3nf): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32-8.30 (m, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.49-7.45 (m, 3H), 7.09-7.06 (m, 1H), 5.92-5.90 (m, 1H), 4.19 (s, 2H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.42-2.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.6, 147.5, 140.7, 136.3, 136.2, 130.1, 130.1, 129.3, 127.9, 124.4, 121.6, 59.5, 30.1, 23.1; HRMS (ESI-TOF) *m/z*: $C_{16}H_{15}{}^{35}ClNO_2S$ $(M + H)^+$ calcd for 320.0507, found 320.0512.

5-(((4-chlorophenyl)sulfonyl)methyl)-7,8-dihydroquinoline (3nf): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32-8.30 (m, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.49-7.45 (m, 3H), 7.09-7.06 (m, 1H), 5.92-5.90 (m, 1H), 4.19 (s, 2H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.42-2.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.6, 147.5, 140.7, 136.3, 136.2, 130.1, 130.1, 129.3, 127.9, 124.4, 121.6, 59.5, 30.1, 23.1; HRMS (ESI-TOF) *m/z*: $C_{16}H_{15}{}^{35}ClNO_2S$ $(M + H)^+$ calcd for 320.0507, found 320.0512.

7-(((4-Chlorophenyl)sulfonyl)methyl)-4,5-dihydrobenzo[b]thiophene (3pf): yellow solid, mp 69.4-71.2°C (uncorrected);^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.09 (s, 2H), 5.90-5.88 (m, 1H), 4.20 (s, 2H), 2.67 (t, *J* = 8.0 Hz, 2H), 2.26-2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.7, 140.7, 137.1, 131.9, 130.1, 1293, 127.5, 124.8, 124.3, 124.2, 58.2, 43.4, 32.3; HRMS (ESI-TOF) *m/z*: $C_{15}H_{14}{}^{35}ClO_2S_2$ $(M + H)^+$ calcd for 325.0118, found 325.0124.

(2-(phenylsulfonyl)ethene-1,1-diyl)dibenzene (4): white oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.27-7.15 (m, 8H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.3, 141.4, 139.1, 135.5, 133.0, 130.4, 129.8, 129.0, 128.8, 128.7, 128.3, 128.3, 127.9, 127.6; HRMS (ESI-TOF) *m/z*: $C_{20}H_{17}O_2S$ $(M + H)^+$ calcd for 321.0944, found 321.0949.

Conflicts of interest

There are no conflicts to declare.

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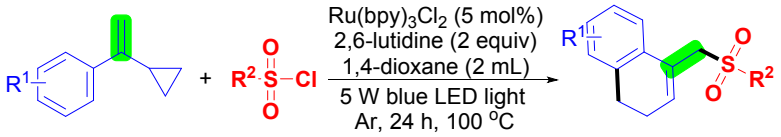
Table of Contents

Visible-light-mediated C−C σ–bond sulfonylation/arylation of vinylcyclopropanes with sulfonyl chlorides for the synthesis of 1-sulfonylmethyl-3,4-dihydronaphthalenes

Qiao-Lin Wang,† Wen-Zheng Zhang,† Quan-Zhou, Cong-Shan Zhou, Bi-QuanXiong, Ke-Wen Tang, Yu Liu*



- ***visible-light-catalysis***
- ***readily available substrates***
- ***good functional group tolerance***
- ***33 examples up to 91% yield***

An efficient visible-light-mediated sulfonylation/arylation of C−C *σ*–bond in vinylcyclopropanes with sulfonyl chlorides to synthesize 1-sulfonylmethyl-substituted 3,4-dihydronaphalenes is developed.