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Palladium-Catalyzed Intramolecular Allylic Amidation via Decarboxylative Aromatization: Synthesis of *N*-Allyl-*N*-aryl Sulfonamides

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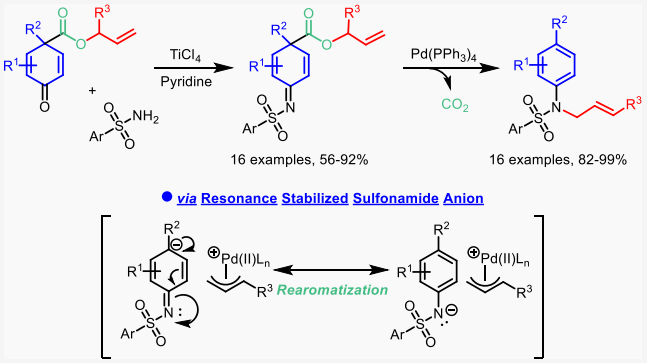
ABSTRACT: A protocol in the preparation of functionalized *N*-allyl-*N*-aryl sulfonamides via palladium-catalyzed intramolecular decarboxylative N-allylation reaction is presented. The alkylated 2,5-cyclohexadienyl ketoesters reacted with arylsulfonamides in the presence of titanium tetrachloride and pyridine, which allows the formation of alkylated 2,5-cyclohexadienyl sulfonyl iminoesters which then undergo a palladium-catalyzed intramolecular allylic amidation through decarboxylative aromatization to provide functionalized *N*-allyl-*N*-aryl sulfonamides. This allylation protocol proceeds with good regioselectivity. Moreover, we have also shown that *N*-allyl-*N*-aryl sulfonamide can be transformed into 4-aryl-1,2,3,4-tetrahydroquinoline and nitrogen-containing *β*-hydroxysulfide bioactives.



INTRODUCTION

Sulfonamides, since they were discovered as an antibacterial in 1932, have found widespread indications such as Alzheimer's disease and other central nervous system disorders, diabetes, and various cancers.[1] Bioisosteric replacement of the keto group in benzophenone by sulfonamide leads to development of a new series of *N*-phenylbenzenesulfonamide.[2] Sulfonamide analogues designed as anticancer agents were able to enhance sensitivity to radiation therapy.[3] N-Substituted biphenyl bissulfonamides have been shown to elicit anti Alzheimer activity by inhibiting acetyl- and butyrylcholinesterase.[4] Very recently, N-substituted sulfonamides were effective against dengue and Ebola virus infection (Scheme 1).[5]

Over the past decades, great efforts have been made in preparation of N-functionalized sulfonamides.[6] Among them, one of the most common methods to achieve *N*-aryl sulfonamides is the palladium- or copper-catalyzed cross-coupling reaction of primary sulfonamides with aryl halides,[7] pseudohalides,[8] arylboronic acids,[9] or sodium arylsulfinates.[10] Rhodium-catalyzed N-chelator-directed ortho C−H bond amidation of arenes with sulfonamides has recently been developed.[11] Moreover, a transition-metal-free procedure for N-arylation of sulfonamides by reaction with *o*-silylaryl triflates in the presence of cesium fluoride has also been reported (Scheme 2a).[12] For the synthesis of *N*-allyl sulfonamides, Cui and Yomamoto have reported the gold- or palladium-catalyzed intermolecular hydroamination of allenes with sulfonamides in high regio- and stereoselectivity.[13] Additionally, a gold- or palladium-catalyzed intramolecular decarboxylative amination of allylic *N*-tosylcarbamates via base-induced aza-Claisen rearrangement[14] or allylic substitution[15] has been developed. Furthermore, intermolecular allylic amidation of *β*,*γ*-unsaturated carboxylic acids or *α*,*α*-disubstituted alkenes mediated by metal catalysis,[16] hypervalent iodine(III) reagents,[17] or NBS-(P)/DBU combination strategy[18] have also been reported (Scheme 2b).

Transition metal-catalyzed intramolecular decarboxylative allylations are represented as a powerful strategy for the formation of carbon−carbon and carbon−heteroatom bonds.[19] Recently, we reported a palladium-catalyzed decarboxylative allylic etherification of cross-conjugated ketoesters in preparation of functionalized allyl aryl ethers via a resonance-stabilized aryl oxide intermediate.[20] Along this line, we envision that the strategy of C−O bond formation can be extended to C−N bond formation using cross-conjugated sulfonyl iminoesters. We assume that intramolecular decarboxylative N-allylation will also proceed via a stable amide anion intermediate. This amide anion can further undergo nucleophilic addition to the Pd-*π*-allyl electrophile to eventually realize C−N bond formation. As a result, various functionalized *N*-allyl-*N*-aryl sulfonamides can be readily synthesized (Scheme 2c). Herein,

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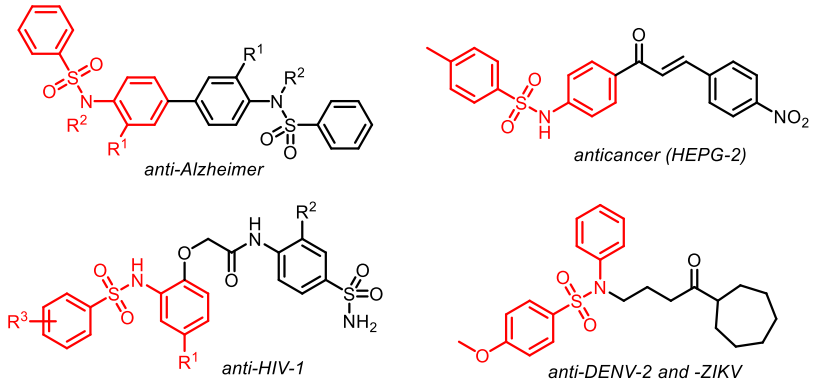
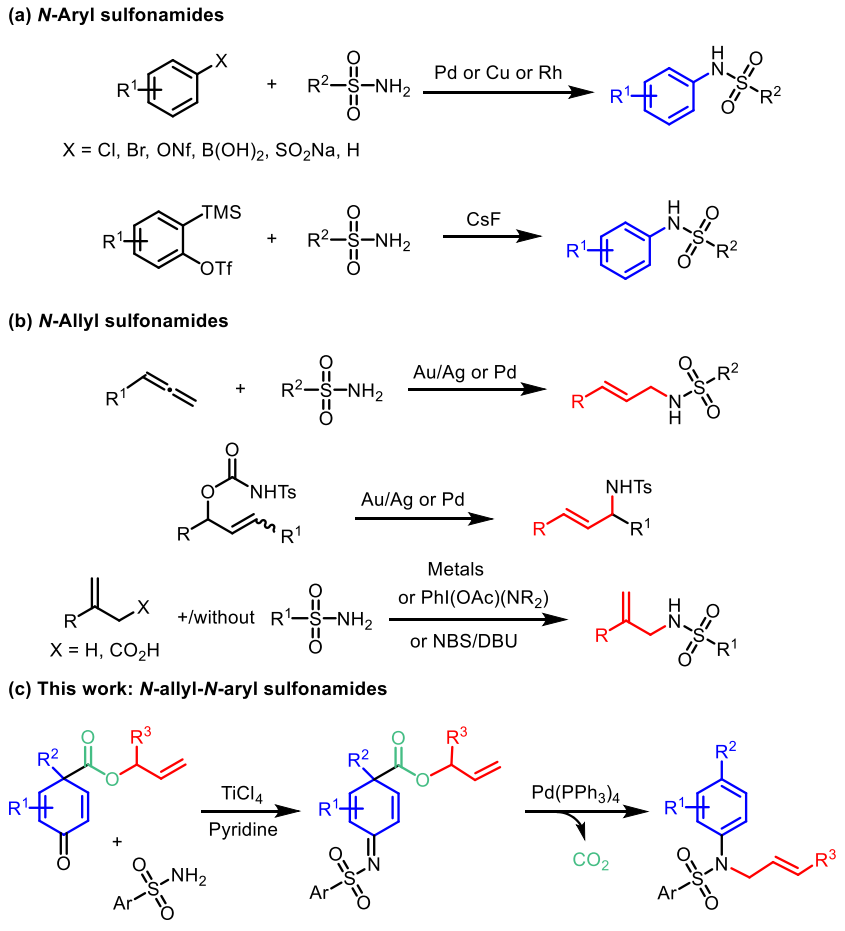
Scheme 1. Selected Examples of Biologically Active Sulfonamides



Scheme 2. Synthetic Methods for N-Functionalized Sulfonamides



we reported an intramolecular allylic amidation of cross-conjugated sulfonyl iminoesters in preparation of functionalized *N*-allyl-*N*-aryl sulfonamides via decarboxylative aromatization and its potential synthetic application.

RESULTS AND DISCUSSION

At the outset of our studies, we examined conditions for cross-conjugated sulfonyl iminoester formation (Table 1). The starting material cross-conjugated ketonester **1a** can be prepared according to our previous report.[20] Although the reaction conducted with **1a** and benzenesulfonamide **2a** in the presence of 3 equiv of titanium tetrachloride and 8 equiv of pyridine using tetrahydrofuran (THF) as a solvent at 0 °C was successful, it yielded only 22% product (entry 1). Next, yield was increased to 62% on elevating temperature to 80 °C (entry 2). We sought to evaluate the solvent effect. While replacing with dichloromethane yielded lower yield (52%, entry 3), the use of toluene had a detrimental effect on the reaction (entry 4). To our delight, the reaction yield was improved significantly in dioxane (92%, entry 5). Reducing the quantity of titanium tetrachloride on a 0.5 decremental basis marginally reduced the yield (entries 6−8). Control experiments indicated that titanium tetrachloride and pyridine were necessary ingredients (entries 9 and 10). Therefore, we used 3 equiv of titanium tetrachloride in dioxane at 80 °C as the

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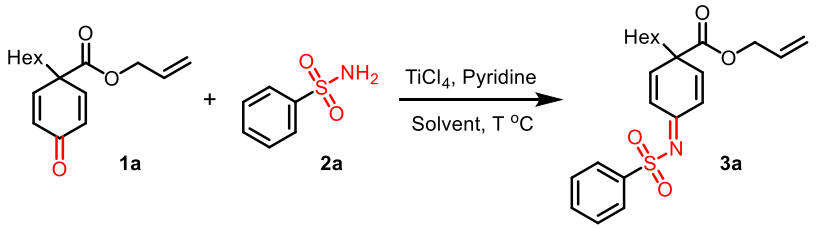
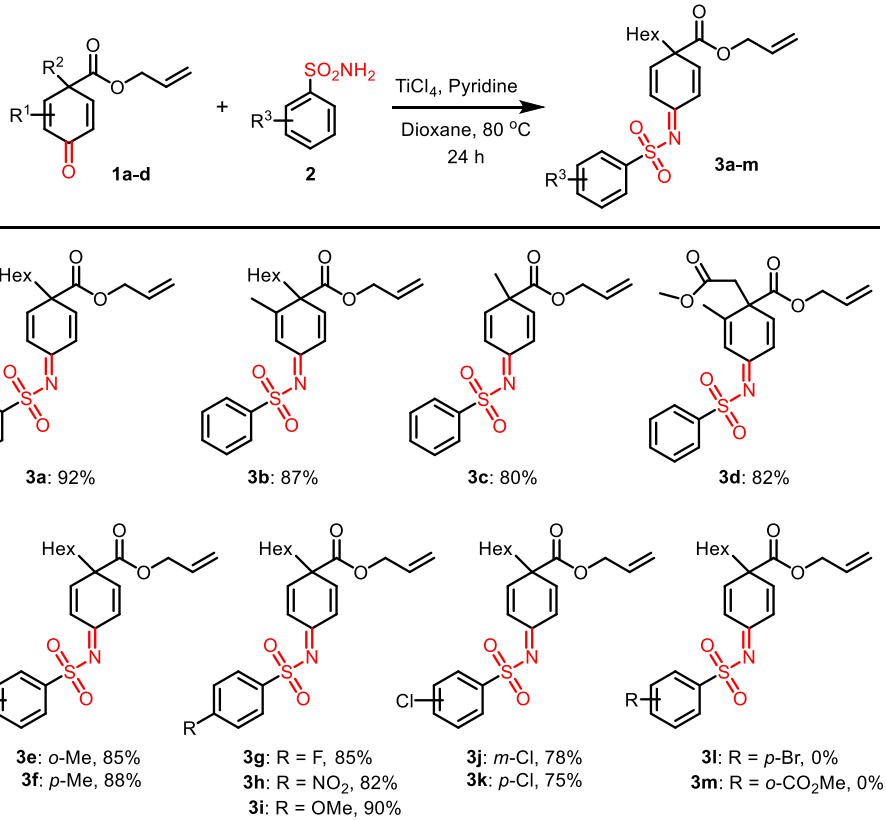
Table 1. Optimization of the Cross-Conjugated Sulfonyl Iminoester Formation[a]



entry	$TiCl_4$ (equiv)	solvent	T (°C)	yield (%)[b]
1	3	THF	0	22
2	3	THF	80	62
3	3	CH_2Cl_2	reflux	51
4	3	toluene	80	0
5	3	dioxane	80	95
6	2.5	dioxane	80	85
7	2	dioxane	80	80
8	1.5	dioxane	80	76
9		dioxane	80	0
10[c]	3	dioxane	80	0

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), and pyridine (0.8 mmol) in a 1.0 mL solvent under an argon atmosphere for 24 h. [b]Yield. [c]Without pyridine.

Scheme 3. Substrate Scope for *N*-Sulfonyl Imines[a]



[a]Reaction was performed with **1** (0.2−0.5 mmol) and 5 mol % of $Pd(PPh_3)_4$ in 1 mL of acetonitrile.

standard conditions in the following experiments for cross-conjugated sulfonyl iminoesters formation.

Having optimized the conditions for cross-conjugated sulfonyl iminoester formation, we looked to study the substrate scope by varying cross-conjugated ketoester's substituents (Scheme 3). Replacing the *n*-hexyl substituent with methyl (**3c**)- or C-2 methyl-substituted derivatives with C-1 *n*-hexyl (**3b**) and methylene methyl ester (**3d**) gave satisfactory yield. However, C-1 isopropyl-substituted derivatives gave no desired product, and the starting material was decomposed under these conditions. To document the scope and versatility with respect to the sulfonamide substituent, we used a variety of substrates by keeping *n*-hexyl as the cross-conjugated ketoester's substituent. Sulfonamides with electron-donating substituents

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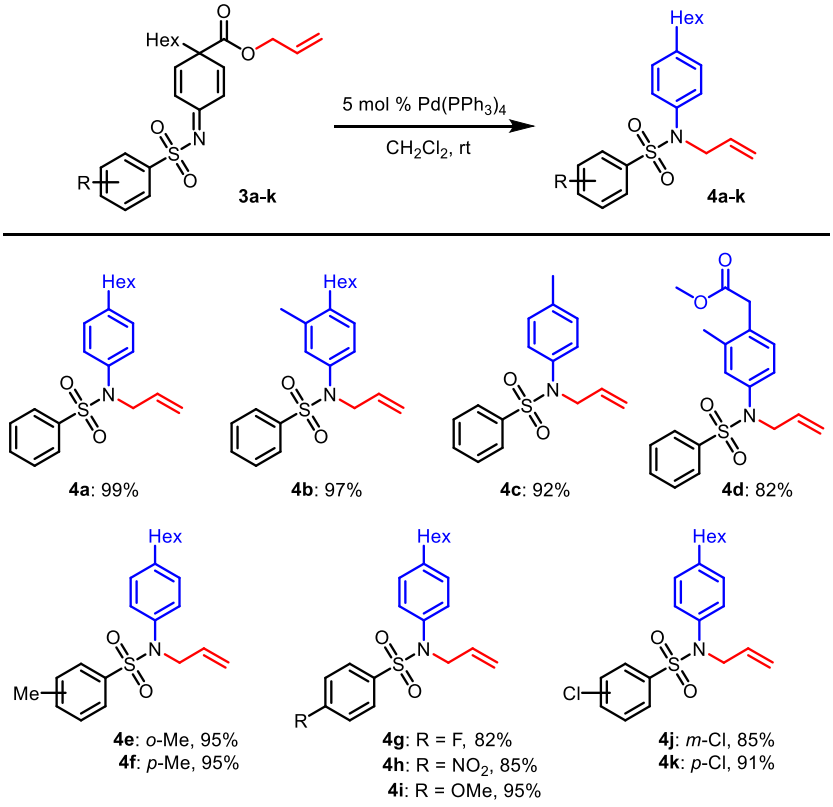
Scheme 4. Substrate Scope of Allylic Amidation[a]



[a]Reaction was performed with **3** (0.09−0.2 mmol) and 5 mol % $Pd(PPh_3)_4$ in CH_2Cl_2.

in ortho and para positions gave **3e**, **3f**, and **3i** in 85−90% yields. The presence of the electron-withdrawing group provided varying results, while **3h** with nitro at the para position was obtained in 82% yield. Halogenated sulfonamides produced varying results; their yield reduced with decreased electronegativity. Compound **3g**, with high electronegativity of the fluorine atom, was obtained in 85%, and those of meta- and para-chloroulfonamides were 75% (**3j**) and 78% (**3k**), respectively. The presence of ortho-ester and bromo-substituted sulfonamide was futile (**3m** and **3l**, 0%).

With the cross-conjugated sulfonyl iminoesters in hand, we next investigated feasibility of performing intramolecular decarboxylative N-allylation under $Pd(PPh_3)_4$ using dichloromethane as a solvent at room temperature and the resulting decarboxylative N-allylation products of **4** are shown in Scheme 4. Both electron-donating and -withdrawing sulfonamides were tolerated and provided **4a−k** in excellent yields (82−99% yields). Overall, neither cross-conjugated ketoester's substituents nor those of sulfonamides have detrimental ramification on decarboxylative N-allylation. Subsequently, the scope of allyl substituents and regioselectivity of N-allylation was also investigated. As shown in Scheme 5, the product obtained, **6a**, using the 1-methylallyl substrate was compatible with these conditions and resulted in 85% yield with moderate regioselectivity (linear/branched = 1.95:1, entry 1). Exclusively linear products (**6b−6d**) with excellent yields were obtained on employing prenyl, 3-alkyl substituted allyl, cinnamyl, and 1-phenylallyl substrates (entries 2−5). It is interesting to note that opposite regioselectivity was observed in the prenyl-substituted substrate of decarboxylative O-allylation. These results suggest that product formation is kinetically driven, which is consistent with our previous report.[20]

Based on our experiment results, we propose a plausible mechanism for this intramolecular decarboxylative allylic amidation reaction (Scheme 6). The substrate **5** is first ionized by the Pd(0) which leads to the formation of Pd-π-allyl species and carboxylate ion pair **A** followed by decarboxylation to give the sulfonyliminocyclohexadienyl anion and Pd-π-allyl species ion pair **B** which then rearomatized to generate a stable *N*-aryl sulfonamide anion intermediate **C**. Finally, the N-allylation of the *N*-aryl sulfonamide anion occurred with Pd-π-allyl species to afford *N*-allyl-*N*-aryl sulfonamides **6** as a kinetic product, and the Pd(0) was regenerated to complete the catalytic cycle.

To further demonstrate the synthetic utility of *N*-allyl-*N*-aryl sulfonamide products, two follow-up transformations were performed, as shown in Scheme 7. We first submitted *N*-allyl-*N*-aryl sulfonamide **4a** under the conditions of $PdCl_2$, Li_2CO_3, and CuBr, leading to the formation of 4-aryl-1,2,3,4-tetrahydroquinoline **7** which can be transformed into bioactives.[21,22] In addition, a bioactive nitrogen-containing β-hydroxysulfide **8** can also be readily obtained using **4a** and heating it with sulfonyl hydrazides in the presence of $FeBr_3$-bpy and $Na_2S_2O_8$.[23,24]

CONCLUSIONS

In summary, we have carried out the cross-conjugated sulfonyl iminoester formation and their synthesis for *N*-allyl-*N*-aryl sulfonamides through palladium-catalyzed decarboxylative N-allylation. This reaction proceeds well with good regioselectivity and gives diverse *N*-allyl-*N*-aryl sulfonamides, which are particularly important features of natural products and

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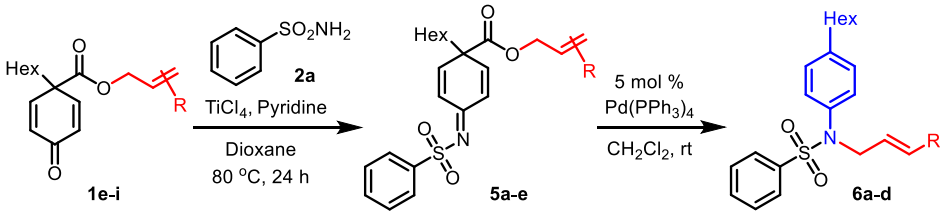
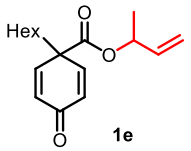
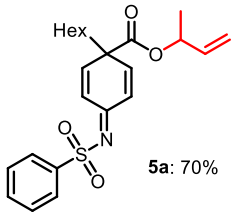
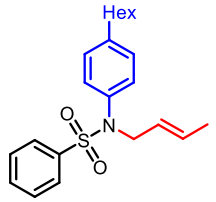
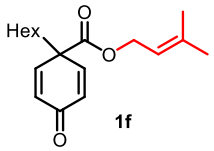
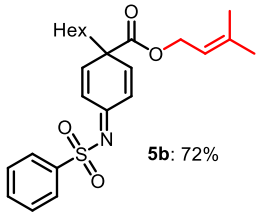
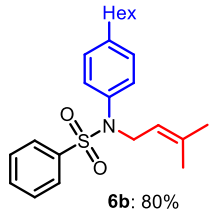
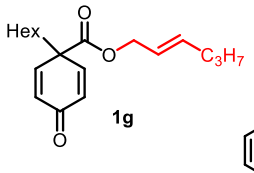
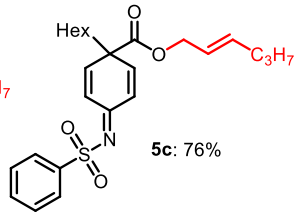
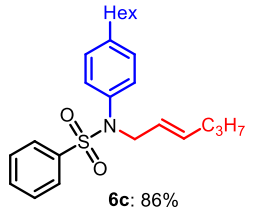
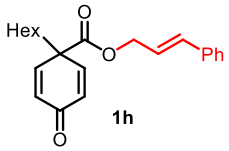
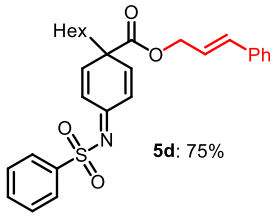
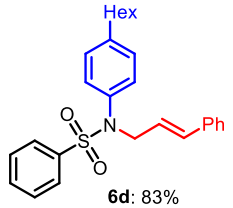
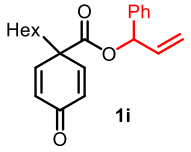
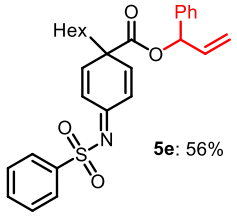
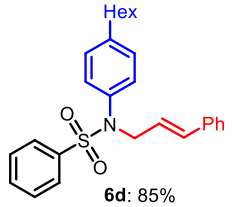
Scheme 5. Substrate Scope of Allyl Electrophiles[a,b]



entry	ketones	sulfonylimines	sulfonylamides
1	 **1e**	 **5a**: 70%	 **6a**: 85% (l:b = 1.95:1)[c]
2	 **1f**	 **5b**: 72%	 **6b**: 80%
3	 **1g**	 **5c**: 76%	 **6c**: 86%
4	 **1h**	 **5d**: 75%	 **6d**: 83%
5	 **1i**	 **5e**: 56%	 **6d**: 85%

[a]Reaction was performed with **1e−i** (1 equiv), sulfonamide (1 equiv), and pyridine (8 equiv) in dioxane. [b]Reaction was performed with **5** (0.1−0.2 mmol) and 5 mol % $Pd(PPh_3)_4$ in CH_2Cl_2. [c]Ratio was determined by ^1H NMR, l: linear and b: branched.

pharmaceuticals. Moreover, we have also shown that *N*-allyl-*N*-aryl sulfonamide can be transformed into 4-aryl-1,2,3,4-tetrahydroquinoline and nitrogen-containing *β*-hydroxysulfide bioactive compounds.

EXPERIMENTAL SECTION

General Information. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich, Fluka, Acros, or Lancaster. ^1H, ^{19}F, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian-Mercury-300 (300 MHz) spectrometer. Chemical shifts for protons are reported in parts per million (ppm) downfield from TMS and are referenced to the residual proton in the NMR solvent ($CDCl_3$ δ = 7.26 ppm and DMSO-d_6 δ = 2.49 ppm). $^{13}C\{^1H\}$ chemical shifts are reported in ppm downfield from TMS and were referenced to the carbon resonances of the solvent ($CDCl_3$ δ = 77.0 ppm and DMSO-d_6 δ = 39.50 ppm). NMR data are indicated as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), and coupling constants in Hertz (Hz). Thin-layer chromatography (TLC)

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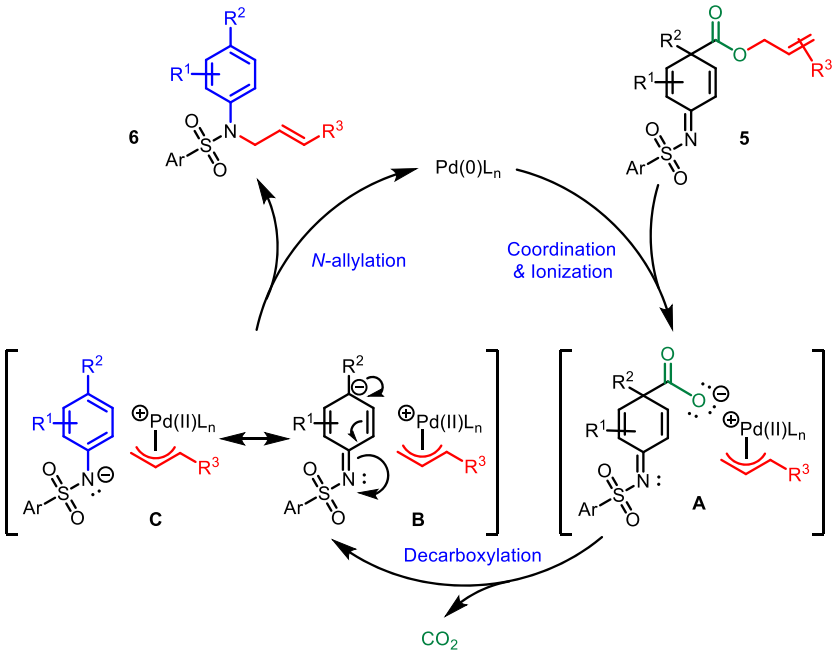
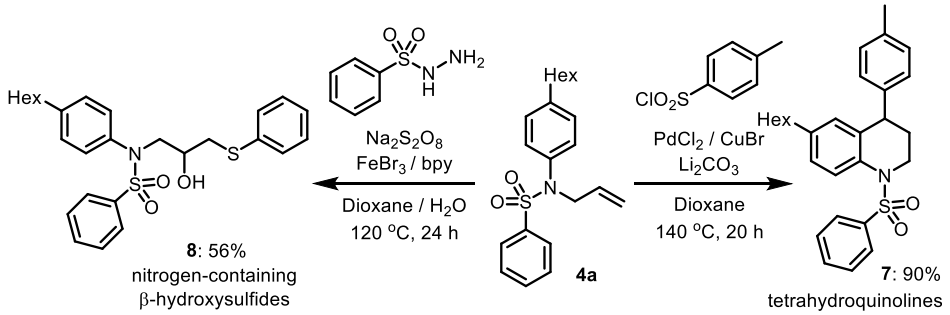
Scheme 6. Proposed Mechanism for the Intramolecular Allylic Amidation



Scheme 7. Product Derivatizations to Bioactive Compounds



was performed using Merck silica gel 60 F-254 plates, and detection of compounds with UV light or dipping into a solution of $KMnO_4$ followed by heating was carried out. Flash column chromatography was performed using Merck silica gel 60 (40−63 μm) applying a pressure of about 0.4 bar. The melting point apparatus was obtained using a Fargo MP-2D. The electron impact (EI) mass spectral data were obtained using a SHIMADZU QP2020 and JEOL AccuTOF GCx-plus. Compounds **1a−1d** and **1e−1i** were prepared according to the literature procedure.[20] Compound **2** was commercially available (see chemical structures in the Supporting Information).

General Procedure of *N*-Sulfonyl Imines Synthesis. Compounds **1a−1i** (1 equiv) were added into sulfonamide (1 equiv) and pyridine (8 equiv) in dioxane. Titanium tetrachloride ($TiCl_4$) (3 equiv) was added into the solution under Ar. The reaction mixture was refluxed for 24 h. The solution was extracted with diethyl ether. The organic phase was washed with 10% $NaHCO_{3(aq)}$ and saturated $NaCl_{(aq)}$ and then dried over $MgSO_4$. The solvent was removed using a rotary evaporator to give the crude mixture. The crude product was purified by column chromatography to afford the *N*-sulfonyl imines **3a−3k** or **5a−5e**.

General Procedure of the Pd-Catalyzed Allylic Amidation for *N*-Allyl-*N*-Aryl Sulfonamide Synthesis. Compounds **3a−3k** or **5a−5e** and $Pd(PPh_3)_4$ (5 mol %) were added into the reaction container. Dichloromethane (DCM) was added into the container under Ar gas. The reaction was traced by TLC, and after 1 h at room temperature, it showed full conversion of the reactant. The mixture was filtered with Celite, and the solvent was removed using a rotary evaporator to give the crude mixture. The crude product was purified by column chromatography to afford the *N*-allyl-*N*-aryl sulfonamides **4a−4k** or **6a−6d**.

*But-3-en-2-yl 1-Hexyl-4-oxocyclohexa-2,5-diene-1-carboxylate (**1e**).* According to the general procedure,[20] oxalyl chloride (0.6 mL, 7.2 mmol), 1-hexylcyclohexa-2,5-diene-1-carboxylic acid (1.0 g, 4.8 mmol) in dry DCM (20.0 mL), *N*,*N*-dimethylformamide (DMF) (0.1 mL), 2-methyl-2-propen-1-ol (0.5 mL, 5.28 mmol), pyridine (0.5 mL, 5.76 mmol), and DMAP (catalytic amount) in DCM (20.0 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give but-3-en-2-yl 1-hexylcyclohexa-2,5-diene-1-carboxylate as a yellow liquid (1.07 g, 85%). Copper iodide (13 mg, 0.69 mmol) and but-3-en-2-yl 1-hexylcyclohexa-2,5-diene-1-carboxylate (600 mg, 2.29 mmol) in acetonitrile (9.5 mL) were added. *tert*-Butyl hydroperoxide (TBHP) (70%, 1.5 mL, 16 mmol) was added into the solution. The crude product was purified by flash column chromatography (EA/hexane) to give **1e** as a yellow liquid (556 mg, 88%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.05 (d, J = 12 Hz, 2H), 6.34 (d, J = 9 Hz, 2H), 5.86−5.75 (m, 1H), 5.38−5.34 (m, 1H), 5.26−5.14 (m, 2H), 1.96−1.90 (m, 2H), 1.33−1.23 (m, 11H), 0.84 (t, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 185.3, 169.6, 148.4, 136.7, 123.0, 116.7, 72.9, 52.6, 38.5, 31.4, 29.2, 24.2, 22.5, 19.8, 14.0. HRMS (EI) m/z: $[M]^+$ calcd for $C_{17}H_{24}O_3$, 276.1725; found, 276.1718.

*3-Methylbut-2-en-1-yl 1-Hexyl-4-oxocyclohexa-2,5-diene-1-carboxylate (**1f**).* According to the general procedure,[20] oxalyl chloride (0.6 mL, 7.2 mmol), 1-hexylcyclohexa-2,5-diene-1-carboxylic acid (1 g, 4.8 mmol) in dry DCM (17.8 mL), DMF (0.1 mL), substituted 3-methyl-2-buten-1-ol (0.5 mL, 5.28 mmol), pyridine (0.5 mL, 5.76 mmol), and DMAP (catalytic amount) in DCM (18.0 mL) were

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added. The crude product was purified by flash column chromatography (EA/hexane) to give 3-methylbut-2-en-1-yl 1-hexylcyclohexa-2,5-diene-1-carboxylate as a yellow liquid (1.034 g, 78%). Copper iodide (20 mg, 0.11 mmol) and 3-methylbut-2-en-1-yl 1-hexylcyclohexa-2,5-diene-1-carboxylate (970 mg, 3.5 mmol) in acetonitrile (14.6 mL) were added. TBHP (70%, 2.4 mL, 24.5 mmol) was added into the solution. The crude product was purified by flash column chromatography (EA/hexane) to give **1f** as a yellow liquid (823 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.04 (d, J = 9 Hz, 2H), 6.31 (d, J = 9 Hz, 2H), 5.31−5.28 (m, 1H), 4.60 (d, J = 9 Hz, 2H), 1.93−1.90 (m, 2H), 1.71 (d, J = 3 Hz, 6H), 1.21−1.20 (m, 8H), 0.83 (t, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 185.2, 170.3, 148.4, 140.1, 129.8, 117.7, 62.8, 52.5, 38.6, 31.4, 29.1, 25.7, 24.2, 22.4, 18.0, 13.9. HRMS (EI) m/z: [M]$^+$ calcd for $C_{18}H_{26}O_3$, 290.1882; found, 290.1873.

*(E)-Hex-2-en-1-yl 1-Hexyl-4-oxocyclohexa-2,5-diene-1-carboxylate (**1g**).* According to the general procedure,[20] oxalyl chloride (0.6 mL, 7.2 mmol), 1-hexylcyclohexa-2,5-diene-1-carboxylic acid (1 g, 4.8 mmol), in dry DCM (20.0 mL), DMF (0.1 mL), (*E*)-hex-2-en-1-ol (0.5 mL, 5.28 mmol), pyridine (0.5 mL, 5.76 mmol), and DMAP (catalytic amount) in dry DCM (20.0 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give (*E*)-hex-2-en-1-yl 1-hexyl-4-oxocyclohexa-2,5-diene-1-carboxylate as a yellow liquid (1.198 g, 86%). Copper iodide (21 mg, 0.11 mmol) was added into the solution containing (*E*)-hex-2-en-1-yl 1-hexyl-4-oxocyclohexa-2,5-diene-1-carboxylate (2 mg, 3.72 mmol) in acetonitrile (15.5 mL). TBHP (70%, 2.5 mL, 26.0 mmol) was added into the solution. The crude product was purified by flash column chromatography (EA/hexane) to give **1g** as a yellow liquid (939 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.03 (d, J = 9 Hz, 2H), 6.32 (d, J = 12 Hz, 2H), 5.81−5.71 (m, 1H), 5.56−5.46 (m, 1H), 4.55 (d, J = 6 Hz, 2H), 2.05−2.00 (m, 2H), 1.97−1.89 (m, 2H), 1.42−1.35 (m, 2H), 1.27−1.17 (m, 8H), 0.90−0.81 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 185.2, 170.1, 148.3, 137.5, 129.9, 123.0, 66.7, 52.5, 38.6, 34.2, 31.4, 29.1, 24.2, 22.4, 21.9, 13.9, 13.5. HRMS (EI) m/z: [M]$^+$ calcd for $C_{19}H_{28}O_3$, 304.2038; found, 304.2045.

*Cinnamyl 1-Hexyl-4-oxocyclohexa-2,5-dienecarboxylate (**1h**).* According to the general procedure,[20] oxalyl chloride (1.2 mL, 14.4 mmol) was added to a solution of 1-hexylcyclohexa-2,5-diene-1-carboxylic acid (2 g, 9.6 mmol) in DCM (40.0 mL), DMF (0.2 mL), (*E*)-3-phenylprop-2-en-1-ol (1.4 g, 10.56 mmol), pyridine (0.9 mL, 11.52 mmol), and DMAP (catalytic amount) in dry DCM (40.0 mL) The crude product was purified by flash column chromatography (EA/hexane) to give cinnamyl 1-hexylcyclohexa-2,5-diene-1-carboxylate as a yellow liquid (2.49 g, 80%). Copper iodide (32 mg, 0.17 mmol) was added into the solution containing cinnamyl 1-hexylcyclohexa-2,5-diene-1-carboxylate (1.82 g, 5.61 mmol) in acetonitrile (18.7 mL). TBHP (70%, 5.4 mL, 26.03 mmol) was added into the solution. The crude product was purified by flash column chromatography (EA/hexane) to give **1h** as a yellow liquid (1.89 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41−7.25 (m, 4H), 7.14−6.99 (m, 3H), 6.78−6.64 (m, 2H), 6.37 (d, J = 12.0 Hz, 1H), 6.32−6.19 (m, 1H), 4.90−4.77 (m, 2H), 2.56 (t, 2H), 199−1.94 (m, 2H), 1.30−1.23 (m, 6H), 0.87 (t, J = 9 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 185.3, 170.1, 148.5, 135.8, 135.3, 129.9, 129.2, 128.6, 128.3, 126.6, 121.9, 115.1, 77.6, 77.2, 76.8, 66.6, 52.6, 38.6, 31.4, 29.1, 24.2, 22.4, 14.0. HRMS (EI) m/z: [M]$^+$ calcd for $C_{22}H_{26}O_3$, 338.1876; found, 338.1878.

*1-Phenylallyl 1-Hexyl-4-oxocyclohexa-2,5-diene-1-carboxylate (**1i**).* According to the general procedure,[20] oxalyl chloride (1.2 mL, 14.4 mmol) was added to a solution of 1-hexylcyclohexa-2,5-diene-1-carboxylic acid (2 g, 9.6 mmol) in DCM (40.0 mL), DMF (0.2 mL), 1-phenylprop-2-en-1-ol (1.4 g, 10.56 mmol), pyridine (0.9 mL, 11.52 mmol), and DMAP (catalytic amount) in dry DCM (40.0 mL) The crude product was purified by flash column chromatography (EA/hexane) to give 1-phenylallyl 1-hexylcyclohexa-2,5-diene-1-carboxylate as a yellow liquid (1.38 g, 34%). Copper iodide (32 mg, 0.17 mmol) was added into the solution containing 1-phenylallyl 1-hexylcyclohexa-2,5-diene-1-carboxylate (1.82 g, 5.61 mmol) in acetonitrile (18.7 mL). TBHP (70%, 5.4 mL, 26.03 mmol) was added into the solution. The crude product was purified by flash column chromatography (EA/hexane) to give **1i** as a yellow liquid (911 mg, 48%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39−7.29 (m, 5H), 7.06 (d, J = 9 Hz, 2H), 6.36 (d, J = 12 Hz, 2H), 6.26 (d, J = 6.0 Hz, 1H), 6.03−5.92 (m, 1H), 5.31−5.24 (m, 2H), 1.95−1.90 (m, 2H), 1.25−1.14 (m, 8H), 0.84 (t, J = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 185.2, 169.2, 148.0, 148.0, 137.9, 135.34, 130.1, 130.0, 128.6, 128.5, 128.4, 126.9, 77.7, 77.4, 76.9, 76.5, 52.5, 38.5, 31.3, 29.1, 24.1, 22.4, 13.9. HRMS (EI) m/z: [M]$^+$ calcd for $C_{22}H_{26}O_3$, 338.1882; found, 338.1876.

*Allyl-1-hexyl-4-((phenylsulfonyl)imino)cyclohexa-2,5-diene-1-carboxylate (**3a**).* According to the general procedure, **1a** (150 mg, 0.57 mmol), titanium tetrachloride (1 M in toluene, 1.72 mL, 1.72 mmol), benzenesulfonamide (109 mg, 0.57 mmol), and pyridine (0.5 mL, 4.57 mmol) in dioxane (2.4 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **3a** as a yellow liquid (211 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, J = 6 Hz, 2H), 7.76−7.50 (m, 4H), 7.10−6.97 (m, 2H), 6.44 (d, J = 12 Hz, 1H), 5.95−5.82 (m, 1H), 5.35−5.26 (m, 2H), 4.62 (d, J = 9 Hz, 2H), 1.98−1.93 (m, 2H), 1.40−1.23 (m, 8H), 0.86 (t, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.5, 164.5, 149.2, 147.5, 141.2, 132.7, 131.1, 129.4, 128.8, 127.0, 123.3, 119.3, 66.6, 53.1, 38.9, 31.3, 29.1, 24.3, 22.4, 13.9. HRMS (EI) m/z: [M]$^+$ calcd for $C_{22}H_{27}NO_4S$, 401.1661; found, 401.1653.

*Allyl(Z)-1-hexyl-2-methyl-4-((phenylsulfonyl)imino)cyclohexa-2,5-diene-1-carboxylate (**3b**).* According to the general procedure, **1b** (150 mg, 0.54 mmol), titanium tetrachloride (1 M in toluene, 2.2 mL, 2.168 mmol), benzenesulfonamide (85 mg, 0.54 mmol), and pyridine (0.4 mL, 4.34 mmol) in dioxane (2.2 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **3b** as a yellow liquid (196 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, J = 9 Hz, 2H), 7.69−7.47 (m, 4H), 6.79−6.66 (m, 1H), 6.44−6.26 (m, 1H), 5.86−5.77 (m, 1H), 5.28−5.20 (m, 2H), 4.61−4.48 (m, 2H), 2.16−2.01 (m, 3H), 1.96 (s, 2H), 1.32−1.21 (m, 8H), 0.84 (t, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.1, 168.9, 165.6, 165.4, 158.6, 156.4, 149.1, 147.3, 141.4, 132.4, 130.8, 129.7, 128.9, 128.6, 126.7, 123.5, 123.2, 119.1, 66.4, 56.4, 35.1, 31.1, 28.9, 23.1, 23.1, 22.3, 21.1, 20.2, 13.7. HRMS (EI) m/z: [M]$^+$ calcd for $C_{23}H_{29}NO_4S$, 415.1817; found, 415.1810.

*Allyl-1-methyl-4-((phenylsulfonyl)imino)cyclohexa-2,5-diene-1-carboxylate (**3c**).* According to the general procedure, **1c** (200 mg, 1.04 mmol), titanium tetrachloride (1 M in toluene, 3.1 mL, 3.12 mmol), benzenesulfonamide (163 mg, 1.04 mmol), and pyridine (0.7 mL, 8.32 mmol) in dioxane (4.2 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **3c** as a yellow liquid (276 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02−7.98 (m, 2H), 7.64−7.50 (m, 4H), 7.09−7.67 (m, 2H), 6.38 (d, J = 12 Hz, 1H), 5.95−5.82 (m, 1H), 5.34−5.26 (m, 2H), 4.64−4.62 (m, 2H), 1.57 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.8, 164.3, 149.6, 148.1, 141.2, 132.8, 131.0, 128.9, 128.5, 127.1, 122.3, 119.3, 66.8, 48.7, 24.7. HRMS (EI) m/z: [M]$^+$ calcd for $C_{17}H_{17}NO_4S$, 331.0878; found, 331.0876.

*Allyl-(Z)-1-(2-methoxy-2-oxoethyl)-2-methyl-4-((phenylsulfonyl)-imino)cyclohexa-2,5-diene-1-carboxylate (**3d**).* According to the general procedure, **1d** (200 mg, 0.8 mmol), titanium tetrachloride (1 M in toluene, 2.5 mL, 2.5 mmol), benzenesulfonamide (126 mg, 0.8 mmol), and pyridine (0.5 mL, 6.4 mmol) in dioxane (3.2 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **3d** as a colorless liquid (265 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, J = 9 Hz, 2H), 7.68−7.48 (m, 4H), 7.17−7.07 (m, 1H), 6.44−6.31 (m, 1H), 5.88−5.75 (m, 1H), 5.29−5.21 (m, J = 9 Hz, 2H), 4.59 (d, J = 9 Hz, 2H), 3.63 (s, 3H), 3.27 (d, J = 15 Hz, 1H), 2.66 (d, J = 15 Hz, 1H), 2.05 (d, J = 45 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.4, 168.1, 164.7, 156.1, 154.1, 147.5, 145.8, 141.3, 132.6, 130.7, 129.3, 129.1, 128.8, 126.9, 123.3, 123.1, 119.4, 67.1, 53.3, 52.1, 39.9, 39.8, 20.9, 20.2. HRMS (EI) m/z: [M]$^+$ calcd for $C_{20}H_{21}NO_6S$, 403.1090; found, 403.1085.

*Allyl-1-hexyl-4-((o-tolylsulfonyl)imino)cyclohexa-2,5-diene-1-carboxylate (**3e**).* According to the general procedure, **1a** (150 mg, 0.57 mmol), 2-methylbenzenesulfonamide (77 mg, 0.57 mmol),

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titanium tetrachloride (1 M in toluene, 1.7 mL, 1.72 mmol), and pyridine (0.4 mL, 4.57 mmol) in dioxane (2.3 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **3e** as a yellow liquid (202 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (d, J = 9 Hz, 1H), 7.64−7.60 (m, 1H), 7.49−7.43 (m, 1H), 7.35−7.30 (m, 2H), 7.08−6.96 (m, 2H), 6.43−6.39 (m, 1H), 5.95−5.82 (m, 1H), 5.35−5.25 (m, 2H), 4.63−4.60 (m, 2H), 2.66 (s, 3H).1.98−1.92 (m, 2H), 1.33−1.23 (m, 8H), 0.86 (t, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.5, 164.7, 148.8, 147.4, 139.3, 137.8, 132.8, 132.1, 131.0, 129.4, 127.9, 125.9, 123.5, 119.3, 66.6, 53.1, 38.9, 31.2, 29.1, 24.2, 22.4, 20.5, 13.9. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{29}NO_4S$, 415.1817; found, 415.1810.

*Allyl-1-hexyl-4-(tosylimino)cyclohexa-2,5-diene-1-carboxylate (**3f**).* According to the general procedure, **1a** (200 mg, 0.76 mmol), 4-methylbenzenesulfonamide (130 mg, 0.76 mmol), titanium tetrachloride (1 M in toluene, 2.3 mL, 2.29 mmol), and pyridine (0.5 mL, 6.1 mmol) in dioxane (3 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **3f** as a yellow liquid (279 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86 (d, J = 9 Hz, 2H), 7.66−7.62 (m, 1H), 7.30 (d, J = 9 Hz, 2H), 7.07−6.94 (m, 2H), 6.41−6.37 (m, 1H), 5.94−5.81 (m, 1H), 5.33−5.24 (m, 2H), 4.60 (d, J = 6 Hz, 2H), 2.41 (s, 3H), 1.96−1.91 (m, 2H), 1.24−1.22 (m, 8H), 0.85 (t, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.5, 164.3, 148.9, 147.3, 143.5, 138.3, 131.0, 129.4, 129.4, 127.0, 123.2, 119.3, 66.6, 53.0, 38.8, 31.3, 29.1, 24.1, 22.4, 21.5, 13.9. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{29}NO_4S$, 415.1817; found, 415.1812.

*Allyl-4-(((4-fluorophenyl)sulfonyl)imino)-1-hexylcyclohexa-2,5-diene-1-carboxylate (**3g**).* According to the general procedure, **1a** (150 mg, 0.57 mmol), 4-fluorobenzenesulfonamide (100 mg, 0.57 mmol), titanium tetrachloride (1 M in toluene, 1.7 mL, 1.72 mmol), and pyridine (0.4 mL, 4.57 mmol) in dioxane (2.28 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **3g** as a yellow liquid (204 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04−7.98 (m, 2H), 7.63−7.59 (m, 1H), 7.23−7.16 (m, 2H), 7.11−6.88 (m, 2H), 6.42−6.43 (m, 1H), 5.95−5.82 (m, 1H), 5.35−5.25 (m, 2H), 4.63−4.60 (m, 2H), 1.98−1.93 (m, 2H), 1.33−1.23 (m, 8H), 0.86 (t, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.4, 166.8, 164.6, 163.4, 149.5, 147.8, 137.4, 131.0, 129.9, 129.3, 123.2, 119.4, 116.2, 115.9, 66.7, 53.2, 38.9, 31.3, 29.1, 24.3, 22.4, 13.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ −105.3. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{26}FNO_4S$, 419.1567; found, 419.1558.

*Allyl-1-hexyl-4-(((4-nitrophenyl)sulfonyl)imino)cyclohexa-2,5-diene-1-carboxylate (**3h**).* According to the general procedure, **1a** (100 mg, 0.38 mmol), 4-nitrobenzenesulfonamide (77 mg, 0.38 mmol), titanium tetrachloride (1 M in toluene, 1.0 mL, 0.95 mmol), and pyridine (0.2 mL, 3.05 mmol) in dioxane (1.5 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **3h** as a yellow liquid (140 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (d, J = 9 Hz, 2H), 8.15 (d, J = 9 Hz, 2H), 7.54 (d, J = 9 Hz, 1H), 7.16−7.05 (m, 2H), 6.39 (d, J = 12 Hz, 1H), 5.93−5.80 (m, 1H), 5.32−5.23 (m, 2H), 4.61 (d, J = 6 Hz, 2H), 1.99−1.94 (m, 2H), 1.28−1.21 (m, 8H), 0.82 (t, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.0, 165.3, 150.5, 149.9, 148.9, 148.1, 146.7, 130.9, 129.9, 128.9, 128.3, 124.0, 123.2, 119.3, 66.7, 53.4, 38.8, 31.2, 29.0, 24.2, 22.3, 13.8. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{26}N_2O_6S$, 446.1512; found, 446.1505.

*Allyl-1-hexyl-4-(((4-methoxyphenyl)sulfonyl)imino)cyclohexa-2,5-diene-1-carboxylate (**3i**).* According to the general procedure, **1a** (200 mg, 0.76 mmol), 4-methoxybenzenesulfonamide (143 mg, 0.76 mmol), titanium tetrachloride (1 M in toluene, 2.3 mL, 2.29 mmol), and pyridine (0.5 mL, 6.1 mmol) in dioxane (3 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **3i** as a yellow liquid (296 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 6 Hz, 2H), 7.66−7.62 (m, 1H), 7.06−6.93 (m, 4H), 6.41−6.37 (m, 1H), 5.94−5.81 (m, 1H), 5.33−5.24 (m, 2H), 4.60 (d, J = 6 Hz, 2H), 3.85 (s, 3H), 1.96−1.91 (m, 2H), 1.27−1.21 (m, 8H), 0.85 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.5, 164.0, 162.9, 148.8, 147.2, 133.0, 131.0, 129.5, 129.2, 123.1, 119.3, 114.0, 66.6, 55.5, 53.0, 39.0, 31.3, 29.1, 24.2, 22.4, 13.9. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{29}NO_5S$, 431.1766; found, 431.1758.

*Allyl-4-(((3-chlorophenyl)sulfonyl)imino)-1-hexylcyclohexa-2,5-diene-1-carboxylate (**3j**).* According to the general procedure, compound **1a** (150 mg, 0.57 mmol), 3-chlorobenzenesulfonamide (109 mg, 0.57 mmol), titanium tetrachloride (1 M in toluene, 1.7 mL, 1.72 mmol), and pyridine (0.4 mL, 4.57 mmol) in dioxane (2.4 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **3j** as a yellow liquid (195 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99−7.98 (m, 1H), 7.90−7.86 (m, 1H), 7.66−7.44 (m, 3H), 7.12−7.01 (m, 2H), 6.44−6.34 (m, 1H), 5.96−5.83 (m, 1H), 5.36−5.26 (m, 2H), 4.64−4.61 (m, 2H), 2.00−1.94 (m, 2H), 1.33−1.18 (m, 8H), 0.86 (t, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.4, 165.0, 149.8, 148.1, 143.0, 135.0, 132.8, 131.1, 130.1, 129.3, 127.3, 125.2, 123.4, 119.5, 66.7, 53.3, 39.0, 31.3, 29.2, 24.3, 22.5, 14.0. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{26}ClNO_4S$, 435.1271; found, 435.1263.

*Allyl-4-(((4-chlorophenyl)sulfonyl)imino)-1-hexylcyclohexa-2,5-diene-1-carboxylate (**3k**).* According to the general procedure, **1a** (200 mg, 0.76 mmol), 4-chlorobenzenesulfonamide (146 mg, 0.76 mmol), titanium tetrachloride (1 M in toluene, 2.3 mL, 2.29 mmol), and pyridine (0.5 mL, 6.10 mmol) in dioxane (3.0 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **3k** as a yellow liquid (249 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91−7.86 (m, 2H), 7.59−7.42 (m, 3H), 7.09−6.96 (m, 2H), 6.38−6.29 (m, 1H), 5.90−5.77 (m, 1H), 5.30−5.19 (m, 2H), 4.60−4.56 (m, 2H), 1.95−1.90 (m, 2H), 1.23−1.18 (m, 8H), 0.81 (t, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.2, 164.6, 149.5, 148.0, 147.9, 130.9, 129.9, 129.1, 128.9, 128.4, 123.1, 119.2, 66.5, 53.1, 38.7, 31.1, 28.9, 24.1, 22.3, 13.8. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{26}ClNO_4S$, 435.1271; found, 435.1263.

*N-Allyl-N-(4-hexylphenyl)benzenesulfonamide (**4a**).* According to the general procedure, **3a** (40 mg, 0.1 mmol) and $Pd(PPh_3)_4$ (6 mg, 0.005 mmol) in DCM (1.0 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **4a** as a yellow liquid (35 mg, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63−7.43 (m, 5H), 7.08 (d, J = 6 Hz, 2H), 6.92 (d, J = 9 Hz, 2H), 5.12−5.68 (m, 1H), 5.15−5.05 (m, 2H), 4.18−4.15 (m, 2H), 2.60−2.54 (m, 2H), 1.61−1.59 (m, 2H), 1.34−1.26 (m, 6H), 0.88 (t, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 142.8, 138.5, 136.4, 132.8, 132.5, 128.8, 128.7, 128.6, 127.6, 118.3, 53.7, 35.5, 31.6, 31.1, 28.9, 22.3, 14.0. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{27}NO_2S$, 357.1762; found, 357.1757.

*N-Allyl-N-(4-hexyl-3-methylphenyl)benzenesulfonamide (**4b**).* According to the general procedure, **3b** (60 mg, 0.14 mmol) and $Pd(PPh_3)_4$ (8 mg, 0.007 mmol) in DCM (1.5 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **4b** as a yellow liquid (52 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65−7.54 (m, 3H), 7.48−7.42 (m, 2H), 7.01 (d, J = 9 Hz, 1H), 6.83 (s, 1H), 6.70 (d, J = 6 Hz, 1H), 5.81−5.67 (m, 1H), 5.12−5.02 (m, 2H), 4.16−4.13 (m, 2H), 2.56−2.51 (m, 2H), 1.56−1.51 (s, 3H), 1.37−1.26 (m, 2H), 1.38−1.23 (m, 6H), 0.91−0.87 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 140.9, 138.6, 136.6, 136.3, 132.9, 132.4, 130.5, 128.9, 128.6, 127.6, 125.6, 118.4, 53.7, 32.8, 31.6, 29.8, 29.2, 22.2, 19.2, 14.0. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{29}NO_2S$, 371.1919; found, 371.1910.

*N-Allyl-N-(p-tolyl)benzenesulfonamide (**4c**).* According to the general procedure, **3c** (40 mg, 0.12 mmol) and $Pd(PPh_3)_4$ (7 mg, 0.006 mmol) in DCM (1.2 mL) were added. The crude product was purified by column chromatography (EA/hexane) to give **4c** as a yellow liquid (32 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64−7.43 (m, 5H), 7.10−7.07 (m, 2H), 6.93−6.88 (m, 2H), 5.80−5.67 (m, 1H), 5.11−5.02 (m, 2H), 4.18−4.15 (m, 2H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 138.4, 137.8, 136.2, 132.8, 132.5, 129.5, 128.7, 128.6, 127.6, 118.7, 53.6, 21.0. HRMS (EI) m/z: $[M]^+$ calcd for $C_{16}H_{17}NO_2S$, 287.0980; found, 287.0972.

*Methyl-2-(4-(N-allylphenylsulfonamido)phenyl)acetate (**4d**).* According to the general procedure, **3d** (60 mg, 0.15 mmol) and $Pd(PPh_3)_4$ (7 mg, 0.007 mmol) in DCM (1.5 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **4d** as a colorless liquid (44 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64−7.55 (m, 3H), 7.49−7.44 (m, 2H), 7.09 (d, J =

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9 Hz, 1H), 6.91 (s, 1H), 6.75 (d, J = 6 Hz, 1H), 5.80−5.66 (m, 1H), 5.12−5.03 (m, 2H), 4.16−4.13 (m, 2H), 3.69 (s, 3H), 3.60 (s, 2H), 2.24 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 171.6, 138.5, 138.0, 137.8, 132.8, 132.6, 132.5, 131.0, 130.5, 128.8, 127.7, 125.9, 118.8, 53.7, 52.1, 38.6, 19.7. HRMS (EI) m/z: $[M]^+$ calcd for $C_{19}H_{21}NO_4S$, 359.1191; found, 359.1184.

*N-Allyl-N-(4-hexylphenyl)-2-methylbenzenesulfonamide (**4e**).* According to the general procedure, **3e** (85 mg, 0.2 mmol) and $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) in DCM (2 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **4e** as a yellow liquid (71 mg, 95%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.82−7.79 (m, 1H), 7.44−7.39 (m, 1H), 7.27−7.23 (m, 2H), 7.0.8−6.98 (m, 4H), 5.82−5.73 (m, 1H), 5.10−5.04 (m, 2H), 4.24−4.21 (m, 2H), 2.58−2.53 (m, 2H), 2.35 (s, 3H), 1.63−1.54 (m, 2H), 1.28 (m, 6H), 0.87 (t, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 142.7, 138.1, 136.9, 136.2, 133.0, 132.6, 132.5, 130.2, 128.9, 128.7, 126.0, 118.7, 53.8, 35.4, 31.6, 31.1, 28.8, 22.6, 20.7, 14.0. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{29}NO_2S$, 371.1919; found, 371.1916.

*N-Allyl-N-(4-hexylphenyl)-4-methylbenzenesulfonamide (**4f**).* According to the general procedure, **3f** (140 mg, 0.34 mmol) and $Pd(PPh_3)_4$ (19 mg, 0.02 mmol) in DCM (3.3 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **4f** as a yellow liquid (119 mg, 95%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.52 (d, J = 9 Hz, 2H), 7.29−7.26 (m, 2H), 7.11 (d, J = 6 Hz, 2H), 6.95 (d, J = 12 Hz, 2H), 5.83−5.70 (m, 1H), 5.14−5.04 (m, 2H), 4.19−4.16 (m, 2H), 2.62−2.57 (m, 2H), 2.45 (s, 3H), 1.67−1.59 (m, 2H), 1.37−1.29 (m, 6H), 0.91 (t, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 143.2, 142.6, 136.4, 135.4, 132.8, 129.3, 128.7, 128.5, 127.6, 118.5, 53.5, 35.4, 31.6, 31.0, 28.9, 22.5, 21.5, 14.0 HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{29}NO_2S$, 371.1919; found, 371.1914.

*N-Allyl-4-fluoro-N-(4-hexylphenyl)benzenesulfonamide (**4g**).* According to the general procedure, **3g** (55 mg, 0.13 mmol) and $Pd(PPh_3)_4$ (7.6 mg, 0.007 mmol) in DCM (1.3 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **4g** as a yellow liquid (40 mg, 82%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.64−7.58 (m, 2H), 7.15−7.07 (m, 4H), 6.93−6.90 (m, 2H), 5.78−5.37 (m, 1H), 5.12−5.04 (m, 2H), 4.16−4.14 (m, 2H), 2.60−2.54 (m, 2H), 1.61−1.56 (m, 2H), 1.30−1.29 (m, 6H), 0.88 (t, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 166.7, 163.3, 143.0, 136.2, 134.7, 132.7, 130.4, 130.3, 128.9, 128.6, 118.8, 116.1, 115.8, 53.7, 35.5, 31.6, 31.1, 28.9, 22.6, 14.0. ^{19}F NMR (282 MHz, $CDCl_3$): δ −105.4. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{26}FNO_2S$, 375.1668; found, 375.1666.

*N-Allyl-N-(4-hexylphenyl)-4-nitrobenzenesulfonamide (**4h**).* According to the general procedure, **3h** (75 mg, 0.17 mmol) and $Pd(PPh_3)_4$ (10 mg, 0.008 mmol) in DCM (1.7 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **4h** as a white solid (57 mg, 85%). Melting point: 83−84 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 8.30 (d, J = 9 Hz, 2H), 7.78 (d, J = 9 Hz, 2H), 7.11 (d, J = 9.0 Hz, 2H), 6.91 (d, J = 6 Hz, 2H), 5.81−5.68 (m, 1H), 5.15−5.08 (m, 2H), 4.20 (d, J = 6 Hz, 2H), 2.58 (t, 2H), 1.61−1.59 (m, 2H), 1.30−1.25 (m, 6H), 0.87 (t, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 149.9, 144.4, 143.5, 135.6, 132.2, 129.2, 128.8, 128.5, 124.0, 119.4, 54.1, 35.5, 31.6, 31.1, 28.9, 22.6, 14.1. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{26}N_2O_4S$, 402.1613; found, 402.1606.

*N-Allyl-N-(4-hexylphenyl)-4-methoxybenzenesulfonamide (**4i**).* According to the general procedure, **3i** (90 mg, 0.2 mmol) and $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) in DCM (2.0 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **4i** as a white solid (74 mg, 95%). Melting point: 48−49 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.56−7.51 (m, 2H), 7.09−7.07 (m, 2H), 6.95−6.89 (m, 4H) 5.80−5.67 (m, 1H), 5.10−5.02 (m, 2H), 4.15−4.12 (m, 2H), 3.86 (s, 3H), 2.59−2.54 (m, 2H), 1.62−1.56 (m, 2H), 1.33−1.25 (m, 6H), 0.88 (t, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 162.7, 142.5, 136.5, 132.8, 129.9, 129.6, 128.6, 128.5, 118.4, 113.7, 55.4, 53.4, 35.4, 31.6, 30.9, 28.8, 22.5, 14.0. HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{29}NO_3S$, 387.1868; found, 387.1861.

*N-Allyl-3-chloro-N-(4-hexylphenyl)benzenesulfonamide (**4j**).* According to the general procedure, **3j** (40 mg, 0.09 mmol) and $Pd(PPh_3)_4$ (5 mg, 0.005 mmol) in DCM (0.9 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **4j** as a yellow liquid (30 mg, 85%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.61−7.36 (m, 4H), 7.10 (d, J = 12 Hz, 2H), 6.92 (d, J = 12 Hz, 2H), 5.81−5.68 (m, 1H), 5.13−5.05 (m, 2H), 4.16 (d, J = 6 Hz, 2H), 2.61−2.55 (m, 2H), 1.59−1.54 (m, 2H), 1.33−1.26 (m, 6H), 0.88 (t, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 143.1, 140.3, 136.0, 135.0, 132.6, 132.5, 130.0, 129.0, 128.6, 127.7, 125.7, 119.0, 53.9, 35.5, 31.6, 31.1, 28.9, 22.6, 14.1. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{26}ClNO_2S$, 391.1373; found, 391.1364.

*N-Allyl-4-chloro-N-(4-hexylphenyl)benzenesulfonamide (**4k**).* According to the general procedure, **3k** (60 mg, 0.14 mmol) and $Pd(PPh_3)_4$ (8 mg, 0.007 mmol) in DCM (1.4 mL) were added. The crude product was purified by flash column chromatography (EA/hexane) to give **4k** as a yellow liquid (49 mg, 91%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.56−7.52 (m, 2H), 7.44−7.41 (m, 2H), 7.10 (d, J = 9 Hz, 2H), 6.93−6.91 (m, 2H), 5.78−5.67 (m, 1H), 5.13−5.04 (m, 2H), 4.17−4.14 (m, 2H), 2.60−2.55 (m, 2H), 1.62−1.54 (m, 2H), 1.34−1.26 (m, 6H), 0.88 (t, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 169.2, 164.6, 149.5, 148.0, 147.9, 130.9, 129.9, 129.1, 128.9, 128.4, 123.7, 119.2, 66.5, 53.1, 38.7, 31.1, 28.9, 24.1, 22.3, 13.8. HRMS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{26}ClNO_2S$, 391.1373; found, 391.1367.

*But-3-en-2-yl-1-hexyl-4-((phenylsulfonyl)imino)cyclohexa-2,5-diene-1-carboxylate (**5a**).* According to the general procedure, **1e** (100 mg, 0.36 mmol) was added into **2a** (57 mg, 0.36 mmol) and pyridine (0.3 mL, 2.88 mmol) in dioxane (1.4 mL). Titanium tetrachloride (1 M in toluene, 0.9 mL, 0.9 mmol) was added into the solution under Ar. The crude product was purified by flash column chromatography (EA/hexane) to give **5a** as a yellow liquid (104 mg, 70%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.02−7.98 (m, 2H), 7.58−7.51 (m, 4H), 7.10−6.97 (m, 2H), 6.40 (d, 1H) 5.85−5.74 (m, 1H), 5.38−5.33 (m, 1H), 5.26−5.15 (m, 2H), 1.95−1.90 (m, 2H), 1.33−1.22 (m, 11H), 0.85 (t, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 169.0, 164.6, 149.5, 147.8, 141.2, 136.5, 132.7, 129.3, 128.8, 127.0, 123.2, 116.9, 73.2, 53.2, 39.0, 31.3, 29.1, 24.3, 22.4, 19.7, 13.9. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{29}NO_4S$, 415.1817; found, 415.1814.

*3-Methylbut-2-en-1-yl-1-hexyl-4-((phenylsulfonyl)imino)-cyclohexa-2,5-diene-1-carboxylate (**5b**).* According to the general procedure, **1f** (200 mg, 0.69 mmol) was added into **2a** (108 mg, 0.69 mmol) and pyridine (0.5 mL, 5.51 mmol) in dioxane (2.8 mL). Titanium tetrachloride (1 M in toluene, 2.1 mL, 2.07 mmol) was added into the solution under Ar. The crude product was purified by flash column chromatography (EA/hexane) to give **5b** as a yellow liquid (213 mg, 72%). ^1H NMR (300 MHz, DMSO-d_6): δ 7.93−7.89 (m, 2H), 7.71−7.60 (m, 3H), 7.45 (d, J = 9 Hz, 1H), 7.28 (d, J = 9 Hz, 1H), 7.13 (d, J = 9 Hz, 1H), 6.45 (d, J = 9 Hz, 1H), 5.31−5.25 (m, 1H), 4.61 (d, J = 6 Hz, 2H), 1.99−1.91 (m, 2H), 1.69 (d, J = 15 Hz, 6H), 1.23−1.17 (m, 8H), 0.83 (t, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): δ 169.5, 165.2, 151.8, 149.9, 141.4, 134.0, 133.6, 129.8, 129.1, 127.0, 122.8, 118.4, 63.1, 53.7, 37.9, 31.3, 29.0, 25.9, 24.2, 22.4, 18.3, 14.3. HRMS (EI) m/z: $[M]^+$ calcd for $C_{24}H_{31}NO_4S$, 429.1974; found, 429.1967.

*(E)-Hex-2-en-1-yl-1-hexyl-4-((phenylsulfonyl)imino)cyclohexa-2,5-diene-1-carboxylate (**5c**).* According to the general procedure, **1g** (100 mg, 0.33 mmol) was added into **2a** (52 mg, 0.33 mmol) and pyridine (0.2 mL, 2.63 mmol) in dioxane (1.3 mL). Titanium tetrachloride (1 M in toluene, 1.0 mL, 0.99 mmol) was added into the solution under Ar. The crude product was purified by flash column chromatography (EA/hexane) to give **5c** as a yellow liquid (110 mg, 76%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.02−7.98 (m, 2H), 7.65−7.49 (m, 4H), 7.10−6.98 (m, 2H), 6.41 (d, J = 6 Hz, 1H), 5.83−5.74 (m, 1H), 5.57−5.48 (m, 1H), 4.57 (d, J = 6 Hz, 2H), 2.08−2.00 (m, 2H), 1.95 (d, J = 9 Hz, 2H), 1.45−1.35 (m, 2H), 1.23 (s, 8H), 0.93−0.84 (m, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 169.7, 164.7, 149.5, 147.9, 141.4, 137.8, 132.7, 129.4, 128.8, 127.1, 123.2, 122.9,

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67.0, 53.2, 39.0, 34.2, 31.4, 29.2, 24.4, 22.5, 21.9, 14.0, 13.6. HRMS (EI) m/z: $[M]^+$ calcd for $C_{25}H_{33}NO_4S$, 443.2130; found, 443.2123.

*Cinnamyl-1-hexyl-4-((phenylsulfonyl)imino)cyclohexa-2,5-diene-1-carboxylate (**5d**).* According to the general procedure, **1h** (400 mg, 1.18 mmol) was added into **2a** (183 mg, 1.18 mmol) and pyridine (0.8 mL, 9.45 mmol) in dioxane (4.7 mL). Titanium tetrachloride (1 M in toluene, 3.5 mL, 3.55 mmol) was added into the solution under Ar. The crude product was purified by flash column chromatography (EA/hexane) to give **5d** as a yellow liquid (423 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02−7.99 (m, 2H), 7.68−7.49 (m, 5H), 7.42−7.28 (m, 6H), 7.11−6.99 (m, 3H), 6.66 (d, J = 15 Hz, 1H), 6.43 (d, J = 9 Hz, 1H), 6.30−6.20 (m, 1H), 4.78 (d, J = 6 Hz, 2H), 1.98 (d, J = 9 Hz, 2H), 1.23 (s, 8H), 0.85 (t, J = 12 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.7, 164.6, 149.3, 147.7, 141.3, 135.8, 135.6, 132.7, 129.4, 128.8, 127.0, 126.6, 123.4, 123.3, 121.9, 121.8, 66.8, 53.2, 39.0, 31.4, 29.2, 24.4, 22.5, 14.0. HRMS (EI) m/z: $[M]^+$ calcd for $C_{28}H_{31}NO_4S$, 477.1974; found, 477.1966.

*1-Phenylallyl 1-Hexyl-4-((phenylsulfonyl)imino)cyclohexa-2,5-diene-1-carboxylate (**5e**).* According to the general procedure, **1i** (230 mg, 0.68 mmol) was added into **2a** (160 mg, 1.02 mmol) and pyridine (0.5 mL, 9.45 mmol) in dioxane (2.04 mL). Titanium tetrachloride (1 M in toluene, 2.0 mL, 2.04 mmol) was added into the solution under Ar. The crude product was purified by flash column chromatography (EA/hexane) to give **5e** as a yellow liquid (181 mg, 56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01 (d, J = 9.0 Hz, 2H), 7.65 (d, J = 11.8 Hz, 1H), 7.58−7.51 (m, 2H), 7.33−7.26 (m, 5H), 7.12−7.0 (m, 2H), 6.34 (dd, J = 6, 9 Hz, 2H), 6.04−5.93 (m, 1H), 5.40−5.25 (m, 2H), 1.90−1.94 (m, 2H), 1.25−1.18 (m, 8H), 0.85 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 168.6, 164.5, 149.1, 147.5, 141.2, 137.8, 135.2, 132.7, 129.4, 128.8, 127.0 126.9, 123.3, 117.9, 78.0, 77.4, 76.9, 76.5, 53.2, 39.0, 31.3, 29.1, 24.3, 22.4, 13.9. HRMS (EI) m/z: $[M]^+$ calcd for $C_{28}H_{31}NO_4S$, 477.1974; found, 477.1968.

*(E)-N-(But-2-en-1-yl)-N-(4-hexylphenyl)benzenesulfonamide (**6a**), N-(But-3-en-2-yl)-N-(4-hexylphenyl)benzenesulfonamide (**6a′**) (**6a**:**6a′** = 1.95:1).* According to the general procedure, **5a** (100 mg, 0.24 mmol) and $Pd(PPh_3)_4$ (14 mg, 0.012 mmol) were added into the reaction container. DCM (2.4 mL) was added into the container under Ar gas. The crude product was purified by flash column chromatography (EA/hexane) to give **6a** and **6a′** (mixture) as a yellow liquid (89 mg, 85%, **6a**:**6a′** = 1.95:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74−7.71 (m, 1H), 7.66−7.50 (m, 2H), 7.44 (m, 2H), 7.17−7.02 (m, 2H), 6.93−6.89 (m, 2H), 5.77−5.66 (m, 1H), 5.53−5.33 (m, 1H), 5.08−4.96 (m, 1H), 4.40−4.48 (m, **6a′**, 1H), 4.09 (d, J = 6 Hz, **6a**, 1H), 2.61−2.54 (m, 2H), 1.58 (m, 3H), 1.33−1.14 (m, 8H), 0.88 (m, 3H). HRMS (EI) m/z: $[M]^+$ calcd for $C_{22}H_{29}NO_2S$, 371.1913; found, 371.1911.

*N-(4-Hexylphenyl)-N-(3-methylbut-2-en-1-yl)-benzenesulfonamide (**6b**).* According to the general procedure, **5b** (72 mg, 0.18 mmol) and $Pd(PPh_3)_4$ (10 mg, 0.009 mmol) were added into the reaction container. DCM (1.8 mL) was added into the container under Ar gas. The crude product was purified by flash column chromatography (EA/hexane) to give **6b** as a yellow liquid (55 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01−7.98 (m, 2H), 7.64−7.49 (m, 4H), 7.09−6.98 (m, 2H), 6.40 (d, J = 9 Hz, 1H), 5.33−5.28 (m, 1H), 4.62 (d, J = 9 Hz, 2H), 1.94 (d, J = 9 Hz, 2H), 1.74 (d, J = 15 Hz, 6H), 1.24 (d, J = 6 Hz, 8H), 0.88−0.84 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 169.8, 164.8, 149.7, 148.0, 141.3, 140.4, 132.7, 129.3, 128.8, 127.0, 123.2, 117.6, 63.1, 53.2, 39.0, 31.4, 29.2, 25.8, 24.3, 22.5, 18.1, 14.0. HRMS (EI) m/z: $[M]^+$ calcd for $C_{23}H_{31}NO_2S$, 385.2075; found, 385.2073.

*(E)-N-(Hex-2-en-1-yl)-N-(4-hexylphenyl)benzenesulfonamide (**6c**).* According to the general procedure, **5c** (72 mg, 0.16 mmol) and $Pd(PPh_3)_4$ (9 mg, 0.008 mmol) were added into the reaction container. DCM (1.6 mL) was added into the container under Ar gas. The crude product was purified by flash column chromatography (EA/hexane) to give **6c** as a yellow liquid (55 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63−7.53 (m, 3H), 7.47−7.42 (m, 2H), 7.07 (d, J = 9 Hz, 2H), 6.89 (d, J = 6 Hz, 2H), 5.46−5.27 (m, 2H), 4.10 (d, J = 9 Hz, 2H), 2.59−2.54 (m, 2H), 1.89−1.82 (m, 2H), 1.64−1.53 (m, 2H), 1.29−1.26 (m, 6H), 1.24−1.16 (m, 2H), 0.9−0.86 (m, 3H), 0.75−0.67 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 142.5, 138.7, 136.3, 135.6, 132.3, 128.7, 128.6, 128.6, 127.6, 124.2, 53.1, 35.4, 34.0, 31.6, 31.1, 28.8, 22.5, 21.9, 14.0, 13.2. HRMS (EI) m/z: $[M]^+$ calcd for $C_{24}H_{33}NO_2S$, 399.2232; found, 399.2223.

*N-Cinnamyl-N-(4-hexylphenyl)benzenesulfonamide (**6d**).* According to the general procedure, **5d** or **5e** (35 mg, 0.07 mmol) and $Pd(PPh_3)_4$ (4 mg, 0.004 mmol) were added into the reaction container. DCM (0.7 mL) was added into the container under Ar gas. The crude product was purified by flash column chromatography (EA/hexane) to give **6d** as a yellow liquid (26 mg, 83% from **5d**; 27 mg, 85% from **5e**). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66−7.64 (m, 2H), 7.61−7.55 (m, 1H), 7.49−7.44 (m, 2H), 7.29−7.18 (m, 5H), 7.08 (d, J = 9 Hz, 2H), 6.96 (d, J = 9 Hz, 2H), 6.39 (d, J = 15 Hz, 1H), 6.16−6.06 (m, 1H), 4.33 (d, J = 3 Hz, 2H), 2.59−2.54 (m, 2H), 1.60−1.55 (m, 2H), 1.29 (s, 6H), 0.9−0.85 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 142.7, 138.6, 136.4, 136.2, 133.5, 132.5, 132.4, 128.8, 128.7, 128.5, 128.4, 127.6, 127.5, 126.3, 124.1, 124.0, 53.4, 35.4, 31.5, 31.0, 28.8, 22.4, 13.9. HRMS (EI) m/z: $[M]^+$ calcd for $C_{27}H_{31}NO_2S$, 433.2075; found, 433.2069.

*6-Hexyl-1-(phenylsulfonyl)-4-(p-tolyl)-1,2,3,4-tetrahydroquinoline (**7**).* In an oven-dried 25 mL Schlenk tube under argon were successively placed **4a** (102 mg, 0.29 mmol), 4-methylbenzenesulfonyl chloride (109 mg, 0.59 mmol), $PdCl_2$ (3 mg, 0.01 mmol), CuBr (20 mg, 0.14 mmol), Li_2CO_3 (63 mg, 0.86 mmol), and 1,4-dioxane (0.9 mL). Then, the reaction mixture was settled in a preheated (140 °C) oil bath for 20 h with stirring. The crude product was purified by flash column chromatography (EA/hexane) to give **7** as a yellow liquid (114 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, J = 9 Hz, 1H), 7.65 (d, J = 9 Hz, 2H), 7.60−7.55 (m, 1H), 7.42 (t, 2H), 7.06−7.03 (m, 1H), 6.96 (d, J = 6 Hz, 2H), 6.55−6.49 (m, 3H), 4.12−4.03 (m, 1H), 3.80−3.68 (m, 2H), 2.45−2.39 (m, 2H), 2.29 (s, 3H), 1.91−1.85 (m, 1H), 1.65−1.58 (m, 1H), 1.48 (d, J = 6 Hz, 2H), 1.25 (d, J = 12 Hz, 6H), 0.89−0.83 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 142.1, 139.8, 139.7, 135.9, 134.5, 132.5, 130.0, 130.1, 129.0, 128.0, 127.3, 127.0, 124.6, 124.5, 45.4, 42.8, 35.1, 31.6, 31.2, 30.5, 28.7, 22.9, 21.0, 14.1. HRMS (EI) m/z: $[M]^+$ calcd for $C_{28}H_{33}NO_2S$, 447.2232; found, 447.2224.

*N-(4-Hexylphenyl)-N-(2-hydroxy-3-(phenylthio)propyl)-benzenesulfonamide (**8**).* A 35 mL Schlenk-type tube equipped with a magnetic stir bar was charged with **4a** (200 mg, 0.56 mmol) and benzenesulfonyl hydrazide (191 mg, 1.12 mmol). Then, $FeBr_3$(33 mg, 0.11 mmol), 2,2′-dipyridyl (18 mg, 0.11 mmol), $Na_2S_2O_8$ (533 mg, 2.24 mmol), 1,4-dioxane (2.2 mL), and H_2O (0.22 mL) were added to this system. The tube was then sealed and placed in an oil bath at 120 °C. After the reaction mixture was stirred for 24 h, it was allowed to cool to ambient temperature. The reaction mixture was filtered, and the solvent was removed to give the crude product. The residue was purified by column chromatography (EA/hexane) to afford **8** as a brown liquid (151 mg, 56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60−7.56 (m, 3H), 7.45 (t, J = 9 Hz, 2H), 7.27−7.06 (m, 7H), 6.91−6.87 (m, 2H), 3.75−3.64 (m, 3H), 3.21 (dd, J = 14.0, 4.6 Hz, 1H), 2.97 (dd, J = 14.0, 7.0 Hz, 1H), 2.78 (s, 1H), 2.61−2.53 (m, 2H), 1.35−1.24 (m, 8H), 0.89 (d, J = 6.2 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.2, 137.6, 136.8, 134.9, 132.8, 130.0, 129.1, 128.9, 128.8, 128.2, 127.7, 126.6, 77.4, 76.9, 76.5, 67.8, 55.5, 38.9, 35.4, 31.6, 31.1, 28.9, 22.5, 14.0. HRMS (EI) m/z: $[M]^+$ calcd for $C_{27}H_{33}NO_3S_2$, 483.1902; found, 483.1862.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c01065.

Chemical structures of **1** and **2** and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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