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Copper-Catalyzed Regio- and Stereoselective 1,6-Conjugate Addition of Aza-Heterocycles to 1-Sulfonyl-1,3-dienes

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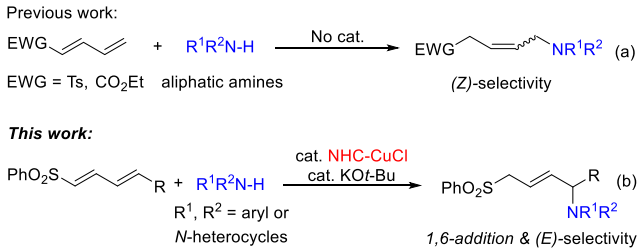
Abstract. An efficient and straightforward method for the synthesis of new and versatile sulfonyl-functionalized allylic amines through the selective copper-catalyzed aza-1,6-conjugate addition of heterocycles or arylamines to 1,4-disubstituted 1,3-dienyl sulfones has been developed. This catalytic process is promoted by a combination of an easily prepared and sterically demanding *N*-heterocyclic carbene-based copper complex and KO*t*-Bu under mild reaction conditions to provide a broad range of (*E*)-allylic amines with excellent regio- and stereoselectivities.

Keywords: Copper catalysis; aza-1,6-conjugate addition; regioselectivity; (*E*)-allylic amine; *N*-heterocyclic carbene

Introduction

The formation of carbon-nitrogen bonds is crucial in the construction of natural products, therapeutic agents and functional materials.[1] Therefore, the development of new and efficient synthetic methods for the synthesis of versatile amines has received substantial attention. Among the numerous reported approaches, the conjugate addition of nucleophilic amines to electron-deficient alkenes is a powerful and attractive tool because it is one of the most straightforward and atom economical processes for selectively constructing C-N bonds.[2] Despite great advances involving aza-1,4-conjugate addition reactions, aza-1,6-additions to electron-deficient dienes to generate allylic amines have rarely been studied due to the difficulty in controlling the regioselectivity (β- vs. δ-addition) and stereoselectivity (*E*- vs. *Z*-isomer product). For example, Back and coworkers showed that two allylic amines could be synthesized through a K_2CO_3-mediated 1,6-addition of iodoaniline derivatives to (*E*)-1-tosyl-1,3-butadiene in moderate yields with high (*E*)-selectivity.[3] Ukaji, Inomata and coworkers reported that secondary aliphatic amines could be selectively added at the δ-position of 1-sulfonyl-1,3-dienes or 2,4-dienoate, affording mainly the (*Z*)-selective 1,6-addition products in low reaction concentration at room temperature (Scheme 1a).[4] Although these reactions are highly regioselective, the scope of the dienes and amines for such 1,6-additions has been limited to terminal conjugated dienes and aliphatic amines, and controlling the stereoselectivity remains challenging. In recent studies, Jørgensen, Wang and coworkers developed organocatalyzed enantioselective aza-1,6-conjugate addition/cyclization cascade reactions of *N*-hydroxycarbamate derivatives with 2,4-dienals via iminium ion activation and applied this reaction in the synthesis of isoxazolidines and aziridines.[5] The selective addition of nucleophilic amines in a 1,6-conjugate mode remains a topic of great interest in organic synthesis.[6]

Allylic sulfones are important intermediates in many synthetic transformations[7] and valuable scaffolds in biologically active molecules.[8] Due to their synthetic and biological significance, we devised an efficient method for synthesizing new functionalized amine-substituted allylic sulfones through the 1,6-conjugate addition of aza-heterocycles or arylamines to sulfonyl-1,3-dienes, especially in a copper-catalyzed manner. Copper catalysts have the advantage of being easy to handle and inexpensive and have played crucial roles in controlling the selectivity and enhancing the reactivity of aza-Michael additions of amines under mild conditions.[9] To the best of our knowledge, the 1,6-conjugate addition of aza-heterocycles to electron-deficient dienes has not been reported. Herein, we describe an efficient and selective copper-catalyzed aza-1,6-conjugate addition of azoles or arylamines to 1,4-disubstituted-1,3-dienyl sulfones promoted by a sterically demanding *N*-heterocyclic carbene (NHC) ligand (Scheme 1b). A wide range of synthetically versatile functionalized allylic amines were synthesized in good to high yields with excellent regio- and (*E*)-stereoselectivities.

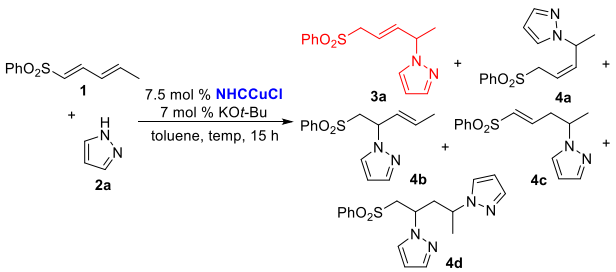


Scheme 1. Aza-1,6-conjugate additions of amines to dienes

Results and Discussion

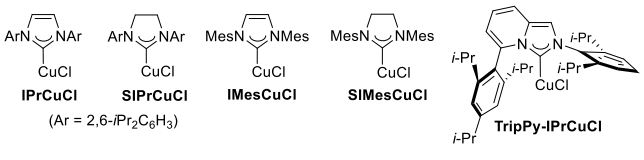
Our initial studies focused on optimizing the conditions for the 1,6-conjugate addition of pyrazole (**2a**) to 1-sulfonyl-1,3-diene **1**, as shown in Table 1. First, we attempted to examine copper catalysts based on 1,2-bis(diphenylphosphino)benzene (dppbz) and bis[(2-diphenylphosphino)phenyl] ether (DPEphos), which were highly effective in our previous studies involving Cu-catalyzed aza-1,4-conjugate additions of (hetero)arylamines to α,β-unsaturated carbonyls and α,β-unsaturated sulfones.[9a-b] However, these bidentate phosphine ligands in the presence of CuCl and KO*t*-Bu did not promote the aza-1,6-addition of **2a** to diene **1** to provide desired allylic amine product **3a** (<5% conv, <2% of **3a**). Therefore, we investigated the ability of NHC-based copper catalysts to promote the selective 1,6-conjugate addition reaction.[10] The strong electron-donating properties of NHC ligands were expected to be able to activate pyrazole for addition to diene **1** by enhancing its nucleophilicity.[11] To our delight, when the reaction was carried out in the presence of **IPrCuCl** and KO*t*-Bu at 70 °C for 15 h, pyrazole was added at the δ-position of diene **1**, affording desired (*E*)-selective allylic amine product **3a** in 50% yield with 86:14 regioselectivity (**3a**:**4b**), albeit with the generation of 5% of (*Z*)-isomer **4a**, 3% of vinyl sulfone **4c** and 17% of diaminated product **4d** as the main side product (entries 1 and 2). The structure of (*E*)-isomer **3a** and (*Z*)-isomer **4a** was confirmed by 2D NMR (NOESY) experiment. To improve the regioselectivity and stereoselectivity and suppress the diamination reaction, various NHC-CuCl catalysts were screened as illustrated in entries 3-7. Notably, a sterically demanding aryl-substituted **TripPy-IPrCuCl** catalyst[12] was found to be the most selective and efficient. When the 1,6-conjugate addition of pyrazole to **1** was carried out at 50 °C in the presence of **TripPy-IPrCuCl** and KO*t*-Bu, the (*E*)-allylic amine **3a** was obtained in 93% yield with >98:<2 regio- and stereoselectivities (entry 7). The addition of a second pyrazole, leading to diaminated side product **4d**, was retarded by the lower reaction temperature. Notably, the conjugate additions of **2a** with ligands (PPh_3 or 1,2-bis(diphenylphosphino)ethane (dppe)) that are relatively less sterically demanding and less electron-donating than NHC ligands preferentially generated 1,4-addition product **4b** (>88:<12 1,4-addition:1,6-addition, entries 8 and 9), albeit with less efficiency. In a similar context, the use of less bulky NHC-Cu catalysts such as **IMesCuCl** and **SIMesCuCl** compared to **TripPy-IPrCuCl**, provided certain amounts of 1,4-addition product **4b** (18-20% yield, entries 4 and 5), indicating that the regioselectivity was significantly influenced by the sterics of the ligand. The results summarized by entries 10-13 indicate that CuCl itself does not catalyze the aza-1,6-conjugate addition of **2a** (<2% conv), and an electron-donating NHC ligand and KO*t*-Bu are critical to the addition of pyrazole to sulfonyl diene **1**. It is postulated that the reaction of in situ-generated NHC-CuO*t*-Bu with pyrazole forms an NHC-copper-pyrazole complex as the main catalytic species, and this species selectively inserts into diene **1** to construct a C-N bond at the δ-position with concomitant generation of a C-Cu bond or O-Cu bond. Then, the copper intermediate reacts with pyrazole to release the protonated allylic amine product and regenerate the Cu-pyrazole species.[13]

Table 1. Optimization of the Cu-catalyzed 1,6-conjugate addition of pyrazole to sulfonyl diene **1**[a]



entry	NHC-CuCl	KO*t*-Bu (mol %)	temp (°C)	conv (%)[b]	**3a**:**4a**:**4b**:**4c**:**4d** (%)[b]
1[c]	**IPrCuCl**	7	70	77	50:5:7:3:6
2	**IPrCuCl**	7	70	>98	50:5:8:3:17
3	**SIPrCuCl**	7	70	>98	22:2:2:4:37
4	**IMesCuCl**	7	70	>98	20:2:18:<2:30
5	**SIMesCuCl**	7	70	79	28:5:20:3:13
6	**TripPy-IPrCuCl**	7	70	>98	62:5:<2:5:14
7	**TripPy-IPrCuCl**	7	50	>98	93:<2:<2:3:2
8	PPh_3 + CuCl	7	50	18	2:<2:14:<2:<2
9	dppe+ CuCl	7	50	74	7:<2:52:<2:7
10	CuCl	7	50	<2	<2
11	**TripPy-IPrCuCl**	0	50	<2	<2
12	no	7	50	<2	<2
13	no	0	50	<2	<2

[a]Reaction conditions: sulfonyl diene **1** (0.36 mmol), pyrazole (**2a**, 0.30 mmol), NHC-CuCl (7.5 mol %), KO*t*-Bu (7 mol %), toluene (1.0 M) under N_2. [b]Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c]The reaction time was 5 h.



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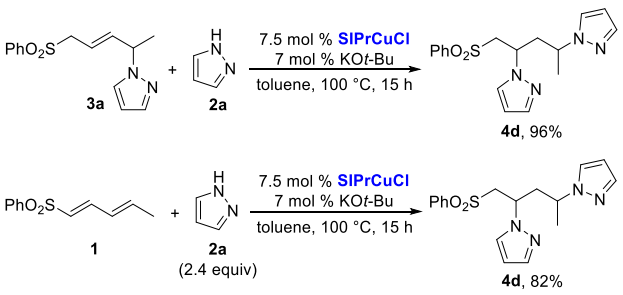
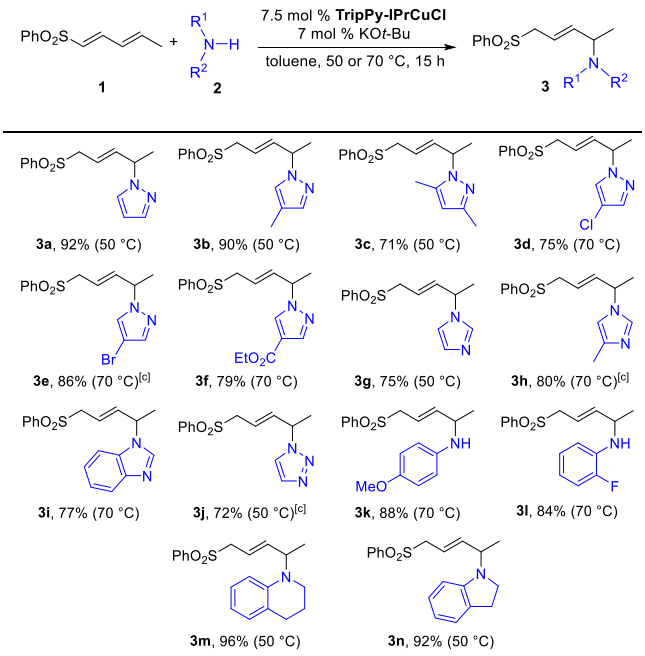


Scheme 2. One-pot Cu-catalyzed diamination with pyrazole

The generation of the diaminated side product **4d** is also indicated in Table 1. As illustrated in Scheme 2, when allylic amine **3a** was treated with pyrazole in the presence of **SIPrCuCl** and KO*t*-Bu at 100 °C, diamination product **4d** was synthesized in 96% yield,[14] indicating that the second amination proceeded via allylic amine **3a**. The reaction did not proceed in the absence of an NHC-Cu catalyst. It was assumed that allylic amine **3a** was isomerized to vinyl sulfone **4c** in the presence of **SIPrCuCl**, KO*t*-Bu and pyrazole and subsequently underwent a Cu-catalyzed 1,4-addition with pyrazole to afford diaminated product **4d**.[15] When 2.4 equiv of pyrazole was used in the presence of **SIPrCuCl**, the one-pot diamination with sulfonyl diene **1** successfully proceeded to give the desired product **4d** in 82% yield.

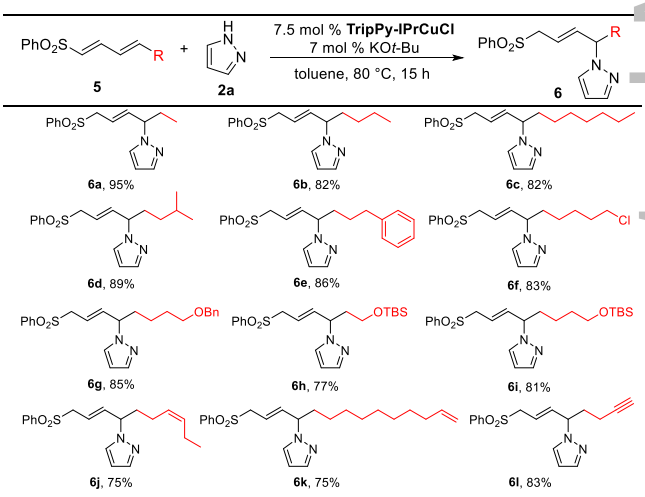
Table 2. Cu-catalyzed 1,6-conjugate addition of azoles and arylamines to sulfonyl diene **1**[a],[b]



[a]Reaction conditions: sulfonyl diene (0.36 mmol), amine (0.30 mmol), **TripPy-IPrCuCl** (7.5 mol %), KO*t*-Bu (7 mol %), toluene (1.0 M) under N_2. In all cases, >95:<5 regio- and stereoselectivities were achieved. [b]Yields of the isolated products. [c]Toluene (0.5 M).

After establishing the optimized reaction conditions, the scope of aza-heterocycles and arylamines was investigated as shown in Table 2. Pyrazoles are valuable building blocks for pharmaceutically active molecules and in heterocyclic synthesis.[16] Therefore, various pyrazole derivatives (**2a-2f**) were introduced in the 1,6-conjugate addition to sulfonyl-1,3-diene **1**. The catalytic reactions successfully afforded corresponding allylic amines **3a-3f** in 71-92% yields with excellent regio- and stereoselectivities (>95:<5). Pyrazoles **2d-2f** bearing chloro, bromo, or ester groups were well tolerated in this catalytic system. The Cu-catalyzed additions of azoles, including imidazole **2g**, methyl imidazole **2h**, benzimidazole **2i**, and triazole **2j**, worked well, providing sulfonyl-substituted (*E*)-amine products **3g-3j** in 72-80% yields. It was noted that the reaction of **1** with **2h** gave only 4-methylimidazole product **3h** regioselectively (vs. 5-methylimidazole product), presumably because of steric effects.[17] Arylamines such as anisidine **2k**, fluoro-aniline **2l**, tetrahydroquinoline **2m** and dihydroindole **2n** were efficiently and selectively transformed to the corresponding allylic amines (**3k-3n**) in 84-96% yields. However, the 1,6-addition of an indole to diene **1** was not effective under these catalytic reaction coniditions (<2% conv). Notably, higher reaction temperatures (70 °C vs. 50 °C) were required to improve the conversion and yield in reactions with heterocycles such as **2d-2f**, **2h-2i** and **2k-2l**.

Table 3. Cu-catalyzed 1,6-conjugate addition of pyrazole to various sulfonyl-1,3-dienes [a],[b]



[a]Reaction conditions: sulfonyl diene **5** (0.36 mmol), pyrazole (**2a**, 0.30 mmol), **TripPy-IPrCuCl** (7.5 mol %), KO*t*-Bu (7 mol %), toluene (1.0 M) under N_2. In all cases, >95:<5 regio- and stereoselectivities were achieved. [b]Yields of the isolated products.

Next, we explored the substrate scope of sulfonyl dienes. As depicted in Table 3, a range of 4-substituted-1-sulfonyl-1,3-dienes could be utilized in the Cu-catalyzed aza-1,6-addition of pyrazole, affording versatile and new sulfonyl-substituted (*E*)-

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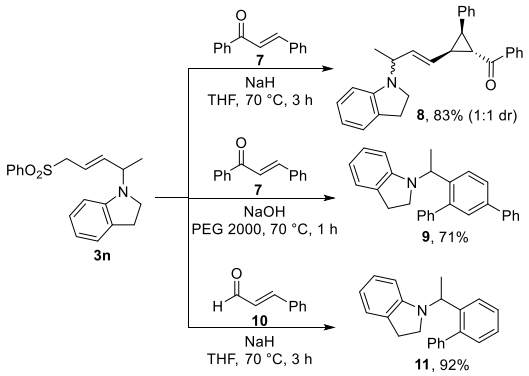
allylic amines in good to high yields. All the transformations were carried out in the presence of 7.5 mol % **TripPy-IPrCuCl** and 7 mol % KO*t*-Bu at 80 °C and showed excellent regio- and (*E*)-stereoselectivities (>95:<5). Dienes **5a**-**5e** substituted with alkyl functionalities such as ethyl, propyl, *n*-hexyl, isobutyl and phenethyl groups smoothly underwent aza-1,6-addition to give desired products **6a**-**6e** in 82-95% yields. With mild reaction conditions, this copper catalytic addition exhibited good compatibility with synthetically valuable functional groups such as a chloro, benzyl ether, silyl ether, alkene, and alkyne groups. New functionalized allylic amines **6f**-**6l** were obtained with high efficiencies and selectivities (75-85% yields).

To highlight the utility of our newly developed Cu-catalyzed aza-1,6-addition, we applied the sulfonyl-substituted allylic amine product to the synthesis of cyclopropane and polysubstituted phenyl motifs, as illustrated in Scheme 3.[18] When allylic sulfone **3n** bearing a dihydroindole group was treated with *trans*-chalcone (**7**) using NaH as a base, cyclopropane product **8** was selectively generated in 83% yield through the base-promoted 1,4-conjugate addition of sulfone **3n** to the chalcone, followed by S_N2 ring closure with the removal of a sulfonyl substituent.[19] On the other hand, the reaction of allylic sulfone **3n** with the same chalcone in the presence of NaOH and polyethylene glycol (PEG) 2000 provided terphenyl product **9** in 71% yield. When cinnamaldehyde was reacted with **3n** in the presence of NaH, cyclized biphenyl product **11** was efficiently and selectively obtained in 92% yield. In the case of two later reactions, the 1,2-additions of allylic sulfone **3n** to **7** or **10** were preferred under basic conditions. The one-pot syntheses of polysubstituted phenyl products **9** and **11** proceeded through tandem 1,2-addition/Julia olefination/electrocyclization/aromatization processes.



Scheme 3. Synthetic transformations

Conclusion

In summary, we have developed an efficient and highly regio- and stereoselective Cu-catalyzed aza-1,6-conjugate addition of heterocycles or arylamines with various 4-substituted-1-sulfonyl-1,3-dienes under mild reaction conditions. The key to controlling the selectivities is the use of a copper complex based on a sterically demanding NHC ligand. This catalytic system enables the synthesis of a wide range of new and versatile functionalized (*E*)-allylic amines bearing pyrazole, imidazole, triazole, and arylamine derivatives with excellent regio- and stereoselectivities. Sulfonyl-substituted allylic amines can be readily transformed to useful building blocks for the synthesis of more complex molecules. Further efforts are underway to expand the scope of diene substrates.

Experimental Section

General: Infrared (IR) spectra were recorded on a ABB MB3000 FT-IR spectrophotometer, νmax in cm^{-1}. Bands are characterized as strong (s), medium (m), and weak (w). ^1H NMR spectra were recorded a JEOL JNM-AL400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane, with the solvent resonance as the internal standard ($CDCl_3$: δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a JEOL JNM-AL400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.00 ppm). High-resolution mass spectra (HRMS) were performed at the Korea Basic Science Institute for technical assistance using an electrospray ionization (ESI) time-of-flight mass spectrometer. Unless otherwise noted, all reactions were carried out with distilled solvents under an atmosphere of dry N_2 in oven-dried (130 °C) glassware. Toluene and tetrahydrofuran were purified by distillation from sodium benzophenone ketyl immediately prior to use unless otherwise specified. Dichloromethane was purified by distillation from CaH_2 immediately prior to use. Copper(I) chloride was purchased from Sigma-Aldrich Corporation and used as received. Potassium *tert*-butoxide was purchased from Sigma-Aldrich Corporation and used as received. Sodium hydride was purchased from Sigma-Aldrich Corporation and used as received. All work-up and purification procedures were carried out with reagent grade solvents in air. NHC-CuCl complexes were synthesized according to reported experimental procedures.[20] A variety of 1-sulfonyl-1,3-dienes were prepared according to reported experimental procedures.[21]

Representative experimental procedure for the synthesis of 1-sulfonyl-1,3-diene

(((1*E*,3*E*)-Penta-1,3-dien-1-yl)sulfonyl)benzene (1). To a solution of (*E*)-1-(phenylsulfonyl)pent-3-en-2-ol (500 mg, 2.21 mmol) in CH_2Cl_2 (5 mL) was added Ac_2O (0.63 mL, 6.63 mmol) and DBU (1.32 mL, 8.84 mmol) at 0 °C. The mixture was allowed to stir at room temperature for 3 h. Then, the reaction was quenched by adding a saturated aqueous solution of $NaHCO_3$ (5 mL), and the mixture was washed with CH_2Cl_2 (5 x 3 mL). The organic layers were combined, dried over $MgSO_4$, filtered and concentrated. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5), affording desired diene product **1** (391 mg, 1.88 mmol, 85% yield) as a white solid. This compound has been previously reported, and its spectral data match the reported values.[22] **^1H NMR** ($CDCl_3$, 400 MHz): δ 7.90-7.88 (m, 2H), 7.61-7.59 (m, 1H), 7.55-7.52 (m, 2H), 7.29-7.23 (m, 1H), 6.29-6.23 (m, 2H), 6.16-6.13 (m, 1H), 1.88 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 142.8, 142.5, 141.0, 133.1, 129.2, 127.5, 127.4, 127.3, 18.8.

(((1*E*,3*E*)-Hexa-1,3-dien-1-yl)sulfonyl)benzene (5a). Compound **5a** was synthesized from (*E*)-1-(phenylsulfonyl)hex-3-en-2-ol (1.04 g, 4.33 mmol) in 75%

yield (722 mg, 3.25 mmol) as light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). **IR** (neat): 3055 (w), 2970 (w), 2878 (w), 1643 (m), 1589 (m), 1450 (m), 1304 (s), 1196 (w), 1142 (s), 1088 (m), 995 (s), 910 (m), 826 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.90-7.88 (m, 2H), 7.61-7.59 (m, 1H), 7.55-7.51 (m, 2H), 7.30-7.23 (m, 1H), 6.33-6.25 (m, 2H), 6.14-6.10 (m, 1H), 2.22 (qd, *J* = 7.2, 7.2 Hz, 2H), 1.05 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 149.1, 143.0, 141.1, 133.1, 129.2, 127.5, 127.4, 125.1, 26.1, 12.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{15}O_2S$ 223.0793, Found 223.0795.

(((1*E*,3*E*)-Octa-1,3-dien-1-yl)sulfonyl)benzene (5b). Compound **5b** was synthesized from (*E*)-1-(phenylsulfonyl)oct-3-en-2-ol (500 mg, 1.86 mmol) in 82% yield (382 mg, 1.53 mmol) as light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). **IR** (neat): 3055 (w), 2924 (m), 2854 (w), 1643 (m), 1589 (m), 1450 (m), 1311 (s), 1142 (s), 1088 (m), 995 (m), 825 (m), 756 (s), 717 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.90-7.88 (m, 2H), 7.60-7.59 (m, 1H), 7.55-7.51 (m, 2H), 7.25 (dd, *J* = 15.1, 10.5 Hz, 1H), 6.28-6.23 (m, 2H), 6.12 (dd, *J* = 15.1, 11.0 Hz, 1H), 2.18 (td, *J* = 7.2, 7.2 Hz, 2H), 1.43-1.31 (m, 4H), 0.90 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.9, 142.9, 141.0, 133.1, 129.2, 127.4, 127.3, 126.0, 32.7, 30.5, 22.2, 13.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{19}O_2S$ 251.1106, Found 251.1107.

(((1*E*,3*E*)-Undeca-1,3-dien-1-yl)sulfonyl)benzene (5c). Compound **5c** was synthesized from (*E*)-1-(phenylsulfonyl)undec-3-en-2-ol (400 mg, 1.29 mmol) in 89% yield (335 mg, 1.15 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). mp 58-59 °C; **IR** (neat): 3055 (w), 2924 (m), 2854 (w), 1643 (m), 1589 (m), 1450 (m), 1311 (s), 1142 (s), 1088 (m), 995 (m), 825 (m), 748 (s), 717 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.90-7.88 (m, 2H), 7.61-7.59 (m, 1H), 7.55-7.52 (m, 2H), 7.25 (dd, *J* = 14.6, 10.5 Hz, 1H), 6.30-6.22 (m, 2H), 6.10 (dd, *J* = 15.1, 11.0 Hz, 1H), 2.18 (td, *J* = 7.2, 7.2 Hz, 2H), 1.42 (quint, *J* = 7.1 Hz, 2H), 1.31-1.27 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.9, 143.0, 141.1, 133.1, 129.2, 127.5, 127.4, 126.0, 33.1, 31.7, 29.1, 29.0, 28.5, 22.6, 14.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{25}O_2S$ 293.1575, Found 293.1574.

(((1*E*,3*E*)-7-Methylocta-1,3-dien-1-yl)sulfonyl)benzene (5d). Compound **5d** was synthesized from (*E*)-7-methyl-1-(phenylsulfonyl)oct-3-en-2-ol (910 mg, 3.22 mmol) in 96% yield (815 mg, 3.08mol) as light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). **IR** (neat): 3055 (w), 2955 (w), 2870 (w), 2361 (m), 1736 (w), 1643 (m), 1589 (w), 1450 (w), 1311 (m), 1142 (s), 1088 (m), 995 (m), 825 (s), 748 (m), 717 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89 (d, *J* = 7.3 Hz, 2H), 7.62-7.58 (m, 1H), 7.55-7.51 (m, 2H), 7.25 (dd, *J* = 14.6, 10.5 Hz, 1H), 6.27-6.22 (m, 2H), 6.10 (dd, *J* = 15.1, 11.0 Hz, 1H), 2.18 (td, *J* = 7.3, 7.3 Hz, 2H), 1.58-1.52 (m, 1H), 1.30 (td, *J* = 7.5, 7.5 Hz, 2H), 0.89 (d, *J* = 6.4 Hz, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 148.0, 142.9, 141.1, 133.1, 129.2, 127.4, 127.4, 125.8, 37.5, 31.0, 27.5, 22.3; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{21}O_2S$ 265.1262, Found 265.1263.

(((1*E*,3*E*)-7-Phenylhepta-1,3-dien-1-yl)sulfonyl)benzene (5e). Compound **5e** was synthesized from (*E*)-7-phenyl-1-(phenylsulfonyl)hept-3-en-2-ol (580 mg, 1.76 mmol) in 57% yield (312 mg, 1.00 mmol) as light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). **IR** (neat): 3063 (w), 3032 (w), 2932 (w), 2862 (w), 2361 (s), 1643 (m), 1589 (m), 1450 (m), 1311 (m), 1142 (m), 1088 (m), 995 (m), 833 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.91-7.89 (m, 2H), 7.63-7.59 (m, 1H), 7.56-7.52 (m, 2H), 7.29-7.15 (m, 6H), 6.28-6.25 (m, 2H), 6.11 (dd, *J* = 15.5, 10.9 Hz, 1H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.22 (td, *J* = 7.3, 7.3 Hz, 2H), 1.77 (quint, *J* = 7.5 Hz, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.1, 142.7, 141.7, 141.0, 133.2, 129.2, 128.4, 128.4, 127.7, 127.5, 126.4, 125.9, 35.2, 32.5, 30.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{21}O_2S$ 313.1262, Found 313.1262.

(((1*E*,3*E*)-9-Chlorononа-1,3-dien-1-yl)sulfonyl)benzene (5f). Compound **5f** was synthesized from 6-phenylhex-3-yn-2-ol (400 mg, 1.26 mmol) in 82% yield (309 mg, 1.03 mmol) as light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). **IR** (neat): 3055 (w), 2932 (w), 2862 (w), 1736 (w), 1643 (m), 1589 (w), 1450 (m), 1311 (s), 1242 (w), 1196 (w), 1142 (s), 1088 (m), 995 (s), 825 (s), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.91-7.88 (m, 2H), 7.60-7.59 (m, 1H), 7.56-7.51 (m, 2H), 7.25 (dd, *J* = 14.6, 10.5 Hz, 1H), 6.29-6.21 (m, 2H), 6.11 (dd, *J* = 15.0, 10.5 Hz, 1H), 3.53 (t, *J* = 6.6 Hz, 2H), 2.22 (td, *J* = 6.9, 6.9 Hz, 2H), 1.80-1.76 (m, 2H), 1.50-1.44 (m, 4H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.0, 142.6, 141.0, 133.1, 129.2, 127.8, 127.5, 126.3, 44.8, 32.8, 32.3, 27.7, 26.3; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{20}ClO_2S$ 299.0873, Found 299.0873.

(((1*E*,3*E*)-8-(Benzyloxy)octa-1,3-dien-1-yl)sulfonyl)benzene (5g). Compound **5g** was synthesized from (*E*)-8-(benzyloxy)-1-(phenylsulfonyl)oct-3-en-2-ol (500 mg, 1.33 mmol) in 75% yield (346 mg, 0.970 mmol) as light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). **IR** (neat): 3055 (w), 2939 (w), 2862 (w), 1967 (w), 1898 (w), 1813 (w), 1736 (m), 1643 (m), 1589 (m), 1450 (m), 1366 (w), 1311 (m), 1142 (m), 1088 (m), 995 (m), 910 (w), 825 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.91-7.88 (m, 2H), 7.61-7.59 (m, 1H), 7.55-7.54 (m, 2H), 7.35-7.22 (m, 6H), 6.27-6.23 (m, 2H), 6.10 (dd, *J* = 15.1, 10.5 Hz, 1H), 4.50 (s, 2H), 3.47 (t, *J* = 6.4 Hz, 2H), 2.21 (td, *J* = 7.3, 7.3 Hz, 2H), 1.64-1.59 (m, 2H), 1.55-1.51 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.3, 142.7, 141.0, 138.5, 133.1, 129.2, 128.3, 127.7, 127.6, 127.5, 127.4, 126.3, 72.9, 69.9, 32.8, 29.2, 25.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{25}O_3S$ 357.1524, Found 357.1522.

***tert*-Butyldimethyl(((3*E*,5*E*)-6-(phenylsulfonyl)hexa-3,5-dien-1-yl)oxy)silane (5h)**. Compound **5h** was synthesized from (*E*)-6-((*tert*-butyldimethylsilyl)oxy)-1-(phenylsulfonyl)hex-3-en-2-ol (154 mg, 0.416 mmol) in 75% yield (110 mg, 0.312 mmol) as light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). **IR** (neat): 3055 (w), 2955 (w), 2854 (w), 1643 (m), 1589 (m), 1466 (m), 1389 (w), 1311 (m), 1250 (m), 1180 (w), 1142 (m), 1088 (m), 995 (s), 933 (m), 833 (s), 779 (m), 717 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89-7.87 (m, 2H), 7.60-7.58 (m, 1H), 7.54-7.52 (m, 2H), 7.25 (dd, *J* = 14.6, 10.5 Hz, 1H), 6.29-6.23 (m, 2H), 6.15 (dd, *J* = 15.1, 11.0 Hz, 1H), 3.68 (t, *J* = 6.4 Hz, 2H), 2.38 (td, *J* = 6.4, 6.4 Hz, 2H), 0.87 (s, 9H), 0.03 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 144.1, 142.6, 140.9, 133.1, 129.2, 127.9, 127.6, 127.4, 61.7, 36.4, 25.8, 18.2, -5.4; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{29}O_3SSi$ 353.1607, Found 353.1606.

***tert*-Butyldimethyl(((5*E*,7*E*)-8-(phenylsulfonyl)octa-5,7-dien-1-yl)oxy)silane (5i)**. Compound **5i** was synthesized from (*E*)-8-((*tert*-butyldimethylsilyl)oxy)-1-(phenylsulfonyl)oct-3-en-2-ol (475 mg, 1.19 mmol) in 82% yield (373 mg, 0.980 mmol) as light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). **IR** (neat): 3055 (w), 2955 (w), 2854 (w), 1643 (m), 1589 (m), 1466 (m), 1311 (m), 1250 (m), 1142 (m), 1088 (m), 995 (s), 933 (m), 833 (s), 779 (m), 717 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.91-7.89 (m, 2H), 7.61-7.59 (m, 1H), 7.55-7.54 (m, 2H), 7.25 (dd, *J* = 14.7, 10.5 Hz, 1H), 6.30-6.22 (m, 2H), 6.11 (dd, *J* = 14.6, 10.5 Hz, 1H), 3.61 (t, *J* = 6.0 Hz, 2H), 2.22 (td, *J* = 6.6, 6.6 Hz, 2H), 1.52-1.48 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.5, 142.8, 141.1, 133.1, 129.2, 127.6, 127.5, 126.2, 62.7, 32.8, 32.2, 25.9, 24.8, 18.3, -5.3; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{33}O_3SSi$ 381.1920, Found 381.1921.

(((1*E*,3*E*,7*Z*)-Deca-1,3,7-trien-1-yl)sulfonyl)benzene (5j). Compound **5j** was synthesized from (3*E*,7*Z*)-1-(phenylsulfonyl)deca-3,7-dien-2-ol (396 mg, 1.34 mmol) in 68% yield (250 mg, 0.906 mmol) as light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). **IR** (neat): 3055 (w), 3099 (w), 2962 (w), 2870 (w), 1643 (m), 1589 (m), 1450 (m), 1311 (s), 1142 (s), 1088 (m), 995 (s), 826 (s), 756 (s), 717 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.91-7.88 (m, 2H), 7.61-7.59 (m, 1H), 7.56-7.52 (m, 2H), 7.25 (dd, *J* = 14.6, 10.5 Hz, 1H), 6.28-6.24 (m, 2H), 6.12 (dd, *J* = 15.1, 10.5 Hz, 1H), 5.43-5.41 (m, 1H), 5.30-5.27 (m, 1H), 2.26-2.17 (m, 4H), 2.05-2.01 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.0, 142.7, 141.0, 133.1, 132.9, 129.2, 127.7, 127.5, 127.2, 126.3, 33.1, 26.0, 20.6, 14.2; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{21}O_2S$ 277.1262, Found 277.1262.

(((1*E*,3*E*)-Tetradeca-1,3,13-trien-1-yl)sulfonyl)benzene (5k). Compound **5k** was synthesized (*E*)-1-(phenylsulfonyl)tetradeca-3,13-dien-2-ol (570 mg, 1.63 mmol) in 94% yield (510 mg, 1.53 mmol) as a white solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). mp 38-39 °C; **IR** (neat): 3078 (m), 2924 (s), 2854 (m), 1643 (m), 1589 (m), 1450 (m), 1311 (s), 1142 (s), 1088 (m), 995 (s), 910 (m), 833 (s), 756 (m), 717 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.91-7.88 (m, 2H), 7.61-7.59 (m, 1H), 7.55-7.51 (m, 2H), 7.25 (dd, *J* = 14.6, 11.0 Hz, 1H), 6.29-6.22 (m, 2H), 6.09 (dd, *J* = 15.1, 11.0 Hz, 1H), 5.81 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 4.99 (dq, *J* = 17.2, 1.8 Hz, 1H), 4.93 (ddt, *J* = 10.2, 2.2, 1.1 Hz, 1H), 2.18 (td, *J* = 7.2, 7.2 Hz, 2H), 2.04-2.01 (m, 2H), 1.43-1.41 (m, 4H), 1.27 (s, 8H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 148.0, 142.9, 141.0, 139.2, 133.1, 129.2, 127.4, 127.3, 126.0, 114.1, 33.8, 33.0, 29.3, 29.3, 29.1, 29.0, 28.8, 28.4; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{29}O_2S$ 333.1888, Found 333.1889.

(((1*E*,3*E*)-Octa-1,3-dien-7-yn-1-yl)sulfonyl)benzene (5l). Compound **5l** was synthesized from (*E*)-1-(phenylsulfonyl)oct-3-en-7-yn-2-ol (1.10 g, 4.16 mmol) in 98% yield (1.00 g, 4.08 mmol) as light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). **IR** (neat): 3302 (w), 3055 (w), 2978 (w), 2916 (w), 2847 (w), 2114 (w), 1736 (m), 1643 (m), 1589 (m), 1443 (m), 1304 (s), 1142 (s), 1088 (m), 995 (s), 825 (s), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.90 (d, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 2H), 7.26 (dd, *J* = 14.6, 10.5 Hz, 1H), 6.37-6.27 (m, 2H), 6.20 (dd, *J* = 15.6, 11.0 Hz, 1H), 2.42-2.39 (m, 2H), 2.35-2.32 (m, 2H), 2.03 (s, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 144.3, 142.0, 140.7, 133.1, 129.1, 128.4, 127.3, 127.0, 82.6, 69.3, 31.4, 17.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{15}O_2S$ 247.0793, Found 247.0794.

Representative experimental procedure for the Cu-catalyzed 1,6-conjugate addition of heterocycles to sulfonyl dienes

TripPy-IPrCuCl (13.1 mg, 22.5 x 10^{-3} mmol), KO*t*-Bu (2.36 mg, 21.0 x 10^{-3} mmol), and 1*H*-pyrazole (**2a**, 20.4 mg, 0.300 mmol) were added to a vial (4 mL) charged with a magnetic bar in a glove box. The vial was sealed with a cap (phenolic open-top cap with gray PTFE/silicone) and was removed from the glove box. After the vial was purged with N_2 gas for 5 min, toluene (0.2 mL) was added to vial under N_2. The solution was allowed to premix for 20 min and then a solution of sulfonyl diene (**1**, 75.0 mg, 0.360 mmol) in toluene (0.1 mL) was added to the reaction vial using a syringe. Then, the mixture was allowed to stir at 50 °C for 15 h. After that time, the reaction solution was quenched by adding a saturated aqueous solution of NH_4Cl (1 mL), and the mixture was washed with CH_2Cl_2 (3 x 3 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1), affording desired (*E*)-allylic amine **3a** (76.3 mg, 0.276 mmol, 92% yield) as an ivory solid.

(*E*)-1-(5-(Phenylsulfonyl)pent-3-en-2-yl)-1*H*-pyrazole (3a). Compound **3a** was synthesized from 1*H*-pyrazole (**2a**, 20.4 mg, 0.300 mmol) and (((1*E*,3*E*)-penta-1,3-dien-1-yl)sulfonyl)benzene (**1**, 75.0 mg, 0.360 mmol) in 92% yield (76.3 mg, 0.276 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). mp 69-70 °C; **IR** (neat): 3140 (w), 1986 (w), 1520 (w), 1443 (m), 1396 (m), 1304 (s), 1142 (s), 1088 (s), 972 (s), 779 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.82 (d, *J* = 7.3 Hz, 2H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 2.1 Hz, 1H), 7.30 (d, *J* = 2.1 Hz, 1H), 6.24 (t, *J* = 2.1 Hz, 1H), 5.74 (dd, *J* = 15.3, 6.2 Hz, 1H), 5.51 (dtd, *J* = 15.4, 7.5, 1.1 Hz, 1H), 4.89 (quint, *J* = 6.7 Hz, 1H), 3.79 (d, *J* = 7.3 Hz, 2H), 1.54 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 140.7, 139.2, 137.9, 133.8, 129.1, 128.4, 127.2, 118.2, 105.5, 59.4, 58.4, 20.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{17}N_2O_2S$ 277.1011, Found 277.1010.

(*Z*)-1-(5-(Phenylsulfonyl)pent-3-en-2-yl)-1*H*-pyrazole (4a). The product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). **IR** (neat): 3070 (w), 2978 (w), 1651 (m), 1512 (w), 1304 (m), 1250 (s), 1142 (s), 1041 (m), 957 (m), 748 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.47 (s, 1H), 7.30 (s, 1H), 6.21 (d, *J* = 1.4 Hz, 1H), 5.98 (t, *J* = 9.2 Hz, 1H), 5.61-5.54 (m, 1H), 4.97 (quint, *J* = 7.4 Hz, 1H), 4.01 (dd, *J* = 14.3, 9.1 Hz, 1H), 3.82 (dd, *J* = 14.3, 7.1 Hz, 1H), 1.44 (dd, *J* = 6.9, 1.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.2, 138.7, 138.5, 133.9, 129.2, 128.3, 126.9, 117.5, 105.5, 54.9, 54.0, 20.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{17}N_2O_2S$ 277.1011, Found 277.1009.

(*E*)-1-(1-(Phenylsulfonyl)pent-3-en-2-yl)-1*H*-pyrazole (4b). The product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). **IR** (neat): 3001 (w), 2924 (w), 2854 (w), 1512 (w), 1450 (m), 1396 (m), 1288 (s), 1142 (s), 1080 (s), 964 (m), 810 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.45-7.41 (m, 2H), 7.35 (d, *J* = 2.1 Hz, 1H), 7.24 (d, *J* = 2.1 Hz, 1H), 6.1 (t, *J* = 2.1 Hz, 1H), 5.70-5.56 (m, 2H), 5.31-5.27 (m, 1H), 4.24 (dd, *J* = 14.6, 8.7 Hz, 1H), 3.58 (dd, *J* = 14.6, 4.6 Hz, 1H), 1.65 (d, *J* = 5.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.9, 139.3, 133.4, 130.3, 129.1, 128.9, 127.9, 127.6, 105.5, 59.6, 58.8, 17.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{17}N_2O_2S$ 277.1011, Found 277.1009.

(*E*)-1-(5-(Phenylsulfonyl)pent-4-en-2-yl)-1*H*-pyrazole (4c). The product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). **IR** (neat): 3005 (w), 2964 (w), 1641 (w), 1512 (w), 1450 (m), 1375 (m), 1243 (s), 1142 (s), 1080 (s), 910 (m), 805 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.76 (d, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.54-7.50 (m, 3H), 7.46 (s, 1H), 6.78 (dt, *J* = 15.0, 7.4 Hz, 1H), 6.19 (d, *J* = 15.0 Hz, 1H), 6.16 (s, 1H), 4.49-4.48 (m, 1H), 2.90-2.83 (m, 1H), 2.73-2.67 (m, 1H), 1.57 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 141.5, 140.1, 133.9, 133.3, 133.2, 129.2, 128.5, 127.6, 105.5, 58.0, 38.7, 20.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{17}N_2O_2S$ 277.1011, Found 277.1010.

1,1'-(1-(Phenylsulfonyl)pentane-2,4-diyl)bis(1*H*-pyrazole) (4d) Compound **4d** was synthesized from 1*H*-pyrazole (**2a**, 24.5 mg, 0.360 mmol) and (*E*)-1-(5-(phenylsulfonyl)pent-3-en-2-yl)-1*H*-pyrazole (**3a**, 82.9 mg, 0.300 mmol) in 96% yield (99.2 mg, 0.288 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). mp 61-62 °C; **IR** (neat): 3109 (w), 2993 (w), 2932 (w), 1512 (w), 1396 (m), 1288 (s), 1142 (s), 1088 (m), 933 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz), a 1:1 mixture of diastereomers: δ 7.61-7.50 (m, 7H), 7.46 (d, *J* = 1.4 Hz, 1H), 7.41-7.37 (m, 4H), 7.32 (s, 1H), 7.28 (d, *J* = 2.3 Hz, 1H),

7.25 (s, 1H), 7.20 (d, *J* = 2.3 Hz, 1H), 7.18 (d, *J* = 2.3 Hz, 1H), 7.12 (d, *J* = 2.3 Hz, 1H), 6.25 (t, *J* = 1.8 Hz, 1H), 6.18 (t, *J* = 1.8 Hz, 1H), 6.05 (t, *J* = 1.8 Hz, 1H), 6.02 (t, *J* = 1.8 Hz, 1H), 4.70-4.63 (m, 1H), 4.32-4.25 (m, 1H), 4.12-4.03 (m, 1H), 3.97-3.88 (m, 2H), 3.66-3.58 (m, 1H), 3.43 (dd, *J* = 14.6, 3.7 Hz, 1H), 3.38 (dd, *J* = 14.9, 3.9 Hz, 1H), 2.60-2.30 (m, 4H), 1.43 (d, *J* = 6.9 Hz, 3H), 1.34 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz), a 1:1 mixture of diastereomers: δ 140.7, 140.3, 139.6, 139.3, 139.0, 139.0, 133.5, 133.5, 131.4, 129.8, 128.2, 127.6, 127.5, 127.5, 105.4, 105.3, 105.3, 104.8, 60.1, 59.4, 54.2, 54.2, 53.8, 53.8, 42.4, 41.6, 21.9, 20.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{21}N_4O_2S$ 345.1385, Found 345.1386.

(*E*)-4-Methyl-1-(5-(phenylsulfonyl)pent-3-en-2-yl)-1*H*-pyrazole (3b). Compound **3b** was synthesized from 4-methyl-1*H*-pyrazole (**2b**, 24.6 mg, 0.300 mmol) and (((1*E*,3*E*)-penta-1,3-dien-1-yl)sulfonyl)benzene (**1**, 75.0 mg, 0.360 mmol) in 90% yield (78.0 mg, 0.269 mmol) as light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). **IR** (neat): 3070 (w), 2978 (w), 1628 (m), 1450 (m), 1311 (s), 1149 (s), 980 (m), 910 (m), 733 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.54-7.50 (m, 2H), 7.26 (s, 1H), 7.02 (s, 1H), 5.69 (dd, *J* = 15.6, 6.4 Hz, 1H), 5.47 (dt, *J* = 15.6, 7.3 Hz, 1H), 4.77 (quint, *J* = 6.6 Hz, 1H), 3.77 (d, *J* = 7.3 Hz, 2H), 2.03 (s, 3H), 1.47 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 140.8, 139.4, 137.9, 133.7, 129.0, 128.4, 125.9, 117.9, 115.9, 59.3, 58.1, 19.9, 8.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2O_2S$ 291.1167, Found 291.1168.

(*E*)-3,5-Dimethyl-1-(5-(phenylsulfonyl)pent-3-en-2-yl)-1*H*-pyrazole (3c). Compound **3c** was synthesized from 3,5-dimethyl-1*H*-pyrazole (**2c**, 28.8 mg, 0.300 mmol) and (((1*E*,3*E*)-penta-1,3-dien-1-yl)sulfonyl)benzene (**1**, 75.0 mg, 0.360 mmol) in 71% yield (65.0 mg, 0.213 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). mp 91-92 °C; **IR** (neat): 2955 (w), 2878 (w), 1551 (w), 1443 (m), 1296 (s), 1142 (s), 1080 (m), 980 (m), 733 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.76 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.50-7.46 (m, 2H), 5.74 (s, 1H), 5.69 (dd, *J* = 15.6, 5.9 Hz, 1H), 5.31 (dt, *J* = 15.6, 7.6 Hz, 1H), 4.66 (quint, *J* = 6.7 Hz, 1H), 3.72 (d, *J* = 7.6 Hz, 2H), 2.15 (s, 3H), 2.14 (s, 3H), 1.46 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 147.2, 141.1, 138.2, 137.9, 133.6, 128.9, 128.3, 116.9, 105.1, 59.3, 54.4, 19.8, 13.5, 10.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{21}N_2O_2S$ 305.1324, Found 305.1324.

(*E*)-4-Chloro-1-(5-(phenylsulfonyl)pent-3-en-2-yl)-1*H*-pyrazole (3d). Compound **3d** was synthesized from 4-chloro-1*H*-pyrazole (**2d**, 30.8 mg, 0.300 mmol) and (((1*E*,3*E*)-penta-1,3-dien-1-yl)sulfonyl)benzene (**1**, 75.0 mg, 0.360 mmol) in 75% yield (70.0 mg, 0.225 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). mp 122-123 °C; **IR** (neat): 3124 (w), 2993 (w), 1443 (m), 1304 (s), 1142 (s), 972 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.80 (d, *J* = 7.3 Hz, 2H), 7.64 (t, *J* = 7.3 Hz, 1H), 7.55-7.51 (m, 2H), 7.36 (s, 1H), 7.19 (s, 1H), 5.66 (dd, *J* = 15.5, 6.4 Hz, 1H), 5.52 (dt, *J* = 15.5, 7.6 Hz, 1H), 4.78 (quint, *J* = 6.5 Hz, 1H), 3.78 (d, *J* = 7.3 Hz, 2H), 1.48 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.7, 137.8, 137.4, 133.9, 129.1, 128.3, 125.3, 119.0, 109.8, 59.2, 59.1, 19.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{16}ClN_2O_2S$ 311.0621, Found 311.0623.

(*E*)-4-Bromo-1-(5-(phenylsulfonyl)pent-3-en-2-yl)-1*H*-pyrazole (3e). Compound **3e** was synthesized from 4-bromo-1*H*-pyrazole (**2e**, 44.1 mg, 0.300 mmol) and (((1*E*,3*E*)-penta-1,3-dien-1-yl)sulfonyl)benzene (**1**, 75.0 mg, 0.360 mmol) in 86% yield (92.0 mg, 0.259 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). mp 121-122 °C; **IR** (neat): 3124 (w), 2986 (w), 1435 (m), 1304 (s), 1142 (s), 972 (s), 949 (s), 818 (m), 849 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.55-7.53 (m, 2H), 7.42 (s, 1H), 7.22 (s, 1H), 5.67 (dd, *J* = 15.5, 6.0 Hz, 1H), 5.54 (dd, *J* = 15.5, 7.3 Hz, 1H), 4.82 (quint, *J* = 6.6 Hz, 1H), 3.79 (d, *J* = 6.9 Hz, 2H), 1.51 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.7, 139.7, 137.8, 133.9, 129.2, 128.4, 127.4, 119.1, 93.1, 59.3, 59.1, 19.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{16}BrN_2O_2S$ 355.0116, Found 355.0119.

Ethyl (*E*)-1-(5-(phenylsulfonyl)pent-3-en-2-yl)-1*H*-pyrazole-4-carboxylate (3f). Compound **3f** was synthesized from 1*H*-pyrazole-4-carboxylate (**2f**, 40.0 mg, 0.300 mmol) and (((1*E*,3*E*)-penta-1,3-dien-1-yl)sulfonyl)benzene (**1**, 75.0 mg, 0.360 mmol) in 79% yield (82.6 mg, 0.237 mmol) as ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). mp 82-83 °C; **IR** (neat): 3124 (w), 2978 (w), 1705 (s), 1551 (m), 1443 (m), 1404 (m), 1304 (s), 1219 (s), 1180 (s), 1142 (s), 1026 (s), 980 (m), 771 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.85 (s, 1H), 7.80 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 5.69 (dd, *J* = 15.3, 6.4 Hz, 1H), 5.54 (dt, *J* = 15.3, 7.4 Hz, 1H), 4.85 (quint, *J* = 6.6 Hz, 1H), 4.28 (q, *J* = 6.9 Hz, 2H), 3.78 (d, *J* = 7.4 Hz, 2H), 1.51 (d, *J* = 6.9 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 162.8, 140.8, 139.4, 137.8, 133.9, 130.6, 129.1, 128.3, 119.2, 115.0, 60.1, 59.2, 59.0, 19.9, 14.3; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{21}N_2O_4S$ 349.1222, Found 349.1222.

(*E*)-1-(5-(Phenylsulfonyl)pent-3-en-2-yl)-1*H*-imidazole (3g). Compound **3g** was synthesized from 1*H*-imidazole (**2g**, 20.4 mg, 0.300 mmol) and (((1*E*,3*E*)-penta-1,3-dien-1-yl)sulfonyl)benzene (**1**, 75.0 mg, 0.360 mmol) in 75% yield (62.5 mg, 0.226 mmol) as yellow oil. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). **IR** (neat): 3078 (w), 2986 (w), 1643 (w), 1497 (m), 1304 (s), 1142 (s), 910 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.51-7.47 (m, 2H), 7.34 (s, 1H), 6.97 (s, 1H), 6.74 (s, 1H), 5.62 (dd, *J* = 15.3, 6.0 Hz, 1H), 5.44 (dt, *J* = 15.3, 7.4 Hz, 1H), 4.66 (quint, *J* = 6.6 Hz, 1H), 3.75 (d, *J* = 7.4 Hz, 2H), 1.44 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 140.1, 137.8, 135.2, 133.8, 129.1, 128.1, 127.3, 118.5, 116.9, 58.9, 53.7, 20.4; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{17}N_2O_2S$ 277.1011, Found 277.1012.

(*E*)-4-Methyl-1-(5-(phenylsulfonyl)pent-3-en-2-yl)-1*H*-imidazole (3h). Compound **3h** was synthesized from 4-methyl-1*H*-imidazole (**2h**, 24.6 mg, 0.300 mmol) and (((1*E*,3*E*)-penta-1,3-dien-1-yl)sulfonyl)benzene (**1**, 75.0 mg, 0.360 mmol) in 80% yield (70.0 mg, 0.241 mmol) as yellow oil. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). **IR** (neat): 3109 (w), 2978 (w), 1643 (m), 1450 (m), 1304 (s), 1149 (s), 910 (m), 733 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.21 (s, 1H), 6.43 (s, 1H), 5.69 (dd, *J* = 15.6, 5.9 Hz, 1H), 5.43 (dt, *J* = 15.6, 7.3 Hz, 1H), 4.56 (quint, *J* = 6.4 Hz, 1H), 3.77 (d, *J* = 7.3 Hz, 2H), 2.13 (s, 3H), 1.40 (d, *J* = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 140.3, 137.8, 134.3, 133.7, 129.0, 128.1, 127.3, 118.3, 113.4, 59.0, 53.5, 20.3, 13.6; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2O_2S$ 291.1167, Found 291.1169.

(*E*)-1-(5-(Phenylsulfonyl)pent-3-en-2-yl)-1*H*-benzo[*d*]imidazole (3i). Compound **3i** was synthesized from 1*H*-benzo[*d*]imidazole (**2i**, 35.4 mg, 0.300 mmol) and (((1*E*,3*E*)-penta-1,3-dien-1-yl)sulfonyl)benzene (**1**, 75.0 mg, 0.360 mmol) in 77% yield (75.6 mg, 0.232 mmol) as ivory oil. The crude product was purified using silica gel column chromatography (10% MeOH in EtOAc). **IR** (neat): 3094 (w), 2986 (w), 1620 (w), 1489 (m), 1311 (s), 1227 (m), 1149 (s), 1088 (m), 910 (s), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.83-7.80 (m, 1H), 7.77 (s, 1H), 7.68 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.38 (t, *J* =7.8 Hz, 2H), 7.31-7.30 (m, 3H), 5.77 (dd, *J* = 15.6, 5.9 Hz, 1H), 5.53 (dtd, *J* = 15.6, 7.3, 1.4 Hz, 1H), 5.01 (quint, *J* = 6.5 Hz, 1H), 3.78 (d, *J* = 7.3 Hz, 2H), 1.67 (d, *J* = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 144.0, 140.4, 139.4, 137.8, 133.9, 129.1, 128.2,

123.0, 122.4, 120.6, 119.1, 110.2, 59.2, 52.4, 19.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{19}N_2O_2S$ 327.1167, Found 327.1169.

(*E*)-1-(5-(Phenylsulfonyl)pent-3-en-2-yl)-1*H*-1,2,3-triazole (3j). Compound **3j** was synthesized from 1*H*-1,2,3-triazole (**2j**, 17.4 μL, 0.300 mmol) and (((1*E*,3*E*)-penta-1,3-dien-1-yl)sulfonyl)benzene (**1**, 75.0 mg, 0.360 mmol) in 72% yield (60.0 mg, 0.216 mmol) as ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). mp 46-47 °C; **IR** (neat): 3063 (w), 2986 (w), 1450 (m), 1420 (w), 1304 (s), 1142 (s), 1080 (m), 964 (m), 818 (s), 741 (s), 710 (m) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.57 (s, 2H), 7.53-7.49 (m, 2H), 5.74 (dd, *J* = 15.5, 6.9 Hz, 1H), 5.55 (dt, *J* = 15.5, 7.4 Hz, 1H), 5.21 (quint, *J* = 6.7 Hz, 1H), 3.77 (d, *J* = 7.3 Hz, 2H), 1.57 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 141.2, 139.2, 137.8, 133.9, 133.7, 129.0, 128.5, 119.0, 61.6, 59.3, 19.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{16}N_3O_2S$ 278.0963, Found 278.0965.

(*E*)-4-Methoxy-*N*-(5-(phenylsulfonyl)pent-3-en-2-yl)aniline (3k). Compound **3k** was synthesized from 4-methoxyaniline (**2k**, 36.9 mg, 0.300 mmol) and (((1*E*,3*E*)-penta-1,3-dien-1-yl)sulfonyl)benzene (**1**, 75.0 mg, 0.360 mmol) in 88% yield (87.6 mg, 0.264 mmol) as orange oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). **IR** (neat): 3001 (w), 2908 (w), 1512 (s), 1443 (w), 1296 (m), 1234 (s), 1142 (m), 1034 (m), 972 (m), 910 (m), 818 (m), 733 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.76 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.49 (d, *J* = 8.9 Hz, 2H), 5.59 (dt, *J* = 15.5, 7.3 Hz, 1H), 5.50 (dd, *J* = 15.5, 5.5 Hz, 1H), 3.84 (quint, *J* = 6.3 Hz, 1H), 3.76-3.73 (m, 5H), 3.21 (br s, 1H), 1.17 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 152.1, 143.9, 140.9, 138.0, 133.5, 128.9, 128.4, 115.9, 114.7, 114.6, 59.5, 55.7, 50.8, 21.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{22}NO_3S$ 332.1320, Found 332.1320.

(*E*)-2-Fluoro-*N*-(5-(phenylsulfonyl)pent-3-en-2-yl)aniline (3l). Compound **3l** was synthesized from 2-fluoroaniline (**2l**, 29.0 μL, 0.300 mmol) and (((1*E*,3*E*)-penta-1,3-dien-1-yl)sulfonyl)benzene (**1**, 75.0 mg, 0.360 mmol) in 84% yield (80.5 mg, 0.252 mmol) as ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:5). mp 49-50 °C; **IR** (neat): 3371 (br), 3124 (w), 2962 (w), 1620 (w), 1512 (m), 1296 (s), 1142 (s), 1080 (m), 980 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.75 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.00-6.95 (m, 2H), 6.67-6.63 (m, 1H), 6.57 (t, *J* = 8.5 Hz, 1H), 5.61 (dt, *J* = 15.1, 7.3 Hz, 1H), 5.50 (dd, *J* = 15.1, 5.5 Hz, 1H), 3.94 (quint, *J* = 6.1 Hz, 1H), 3.78-3.77 (m, 3H), 1.24 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 151.3 (J_{C-F} = 23.9 Hz), 143.1, 137.9, 135.2 (J_{C-F} = 10.6 Hz), 133.7, 128.9, 128.5, 124.5 (J_{C-F} = 3.9 Hz), 116.8 (J_{C-F} = 6.7 Hz), 116.3, 114.4 (J_{C-F} = 18.3 Hz), 112.9 (J_{C-F} = 3.9 Hz), 59.5, 49.8, 21.4; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{19}FNO_2S$ 320.1121, Found 320.1123.

(*E*)-1-(5-(Phenylsulfonyl)pent-3-en-2-yl)-1,2,3,4-tetrahydroquinoline (3m). Compound **3m** was synthesized from 1,2,3,4-tetrahydroquinoline (**2m**, 37.7 μL, 0.300 mmol) and (((1*E*,3*E*)-penta-1,3-dien-1-yl)sulfonyl)benzene (**1**, 75.0 mg, 0.360 mmol) in 96% yield (98.0 mg, 0.287 mmol) as light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). **IR** (neat): 2908 (w), 2808 (w), 1450 (w), 1304 (s), 1142 (s), 1080 (m), 910 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.87 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.54-7.50 (m, 2H), 7.13-7.05 (m, 3H), 6.98-6.96 (m, 1H), 5.64-5.55 (m, 2H), 3.89-3.80 (m, 2H), 3.62 (d, *J* = 15.0 Hz, 1H), 3.53 (d, *J* = 15.0 Hz, 1H), 3.12 (quint, *J* = 6.4 Hz, 1H), 2.85-2.73 (m, 2H), 2.66 (dt, *J* = 11.6, 5.5 Hz, 1H), 2.49 (dt, *J* = 11.6, 5.9 Hz, 1H), 1.14 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 142.9, 138.1, 134.5, 134.1, 133.6, 129.0, 128.6, 128.3, 126.6, 126.1, 125.5, 117.6, 60.9, 59.8, 52.4, 46.8, 29.1, 17.0; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{24}NO_2S$ 342.1528, Found 342.1530.

(*E*)-1-(5-(Phenylsulfonyl)pent-3-en-2-yl)indoline (3n). Compound **3n** was synthesized from indoline (**2n**, 33.7 μL, 0.300 mmol) and (((1*E*,3*E*)-penta-1,3-dien-1-yl)sulfonyl)benzene (**1**, 75.0 mg, 0.360 mmol) in 92% yield (90.4 mg, 0.276 mmol) as ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). mp 88-89 °C; **IR** (neat): 3016 (w), 2970 (w), 1605 (m), 1489 (m), 1389 (m), 1296 (s), 1142 (s), 1011 (m), 987 (m), 872 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.06-7.02 (m, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 1H), 5.66-5.55 (m, 2H), 4.17-4.11 (m, 1H), 3.79 (d, *J* = 5.9 Hz, 2H), 3.32-3.26 (m, 1H), 3.07-3.00 (m, 1H), 2.95-2.81 (m, 2H), 1.24 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 150.5, 140.8, 138.0, 133.5, 130.0, 129.0, 128.4, 127.2, 124.5, 117.6, 117.4, 107.3, 59.8, 51.5, 46.8, 28.0, 16.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{22}NO_2S$ 328.1371, Found 328.1373.

(*E*)-1-(6-(Phenylsulfonyl)hex-4-en-3-yl)-1*H*-pyrazole (6a). Compound **6a** was synthesized from 1*H*-pyrazole (**2a**, 20.4 mg, 0.300 mmol) and (((1*E*,3*E*)-hexa-1,3-dien-1-yl)sulfonyl)benzene (**5a**, 80.0 mg, 0.360 mmol) in 95% yield (82.8 mg, 0.285 mmol) as ivory oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). **IR** (neat): 2978 (w), 1512 (w), 1450 (w), 1396 (m), 1304 (s), 1142 (s), 1088 (s), 972 (s), 910 (m), 733 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.51-7.47 (m, 3H), 7.28 (d, *J* = 1.8 Hz, 1H), 6.22 (t, *J* = 1.8 Hz, 1H), 5.74 (dd, *J* = 15.6, 6.9 Hz, 1H), 5.49 (dt, *J* = 15.6, 7.4 Hz, 1H), 4.55 (q, *J* = 7.2 Hz, 1H), 3.77 (d, *J* = 7.4 Hz, 2H), 1.94 (dquint, *J* = 14.0, 7.8 Hz, 1H), 1.77 (dquint, *J* = 14.0, 7.0 Hz, 1H), 0.75 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.6, 139.1, 137.9, 133.7, 129.0, 128.3, 127.8, 118.8, 105.2, 64,9, 59.3, 27.6, 10.3; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2O_2S$ 291.1167, Found 291.1169.

(*E*)-1-(1-(Phenylsulfonyl)oct-2-en-4-yl)-1*H*-pyrazole (6b). Compound **6b** was synthesized from 1*H*-pyrazole (**2a**, 20.4 mg, 0.300 mmol) and (((1*E*,3*E*)-octa-1,3-dien-1-yl)sulfonyl)benzene (**5b**, 90.1 mg, 0.360 mmol) in 82% yield (78.0 mg, 0.245 mmol) as light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). **IR** (neat): 2932 (w), 2862 (w), 1512 (w), 1450 (w), 1304 (s), 1234 (w), 1142 (s), 1088 (m), 972 (s), 918 (w), 733 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 7.8 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.53-7.49 (m, 3H), 7.29 (s, 1H), 6.23 (s, 1H), 5.74 (dd, *J* = 15.6, 6.9 Hz, 1H), 5.49 (dt, , *J* = 15.6, 7.4 Hz, 1H), 4.63 (q, *J* = 7.3 Hz, 1H), 3.77 (d, *J* = 7.4 Hz, 2H), 1.97-1.88 (m, 1H), 1.77-1.69 (m, 1H), 1.30-1.15 (m, 2H), 1.17-1.02 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.9, 139.2, 137.9, 133.7, 129.0, 128.4, 127.8, 118.7, 105.3, 63.4, 59.4, 34.1, 27.8, 22.1, 13.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{23}N_2O_2S$ 319.1480, Found 319.1482.

(*E*)-1-(1-(Phenylsulfonyl)undec-2-en-4-yl)-1*H*-pyrazole (6c). Compound **6c** was synthesized from 1*H*-pyrazole (**2a**, 20.4 mg, 0.300 mmol) and (((1*E*,3*E*)-undeca-1,3-dien-1-yl)sulfonyl)benzene (**5c**, 105 mg, 0.360 mmol) in 82% yield (88.7 mg, 0.246 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). mp 54-55 °C; **IR** (neat): 3109 (w), 2924 (w), 1443 (w), 1396 (w), 1304 (s), 1142 (s), 1088 (s), 972 (m), 895 (w), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.52-7.48 (m, 3H), 7.29 (s, 1H), 6.23 (s, 1H), 5.74 (dd, *J* = 15.6, 6.9 Hz, 1H), 5.49 (dt, *J* = 15.6, 7.3 Hz, 1H), 4.63 (q, *J* = 6.9 Hz, 1H), 3.77 (d, *J* = 7.3 Hz, 2H), 1.97-1.87 (m, 1H), 1.76-1.69 (m, 1H), 1.29-1.21 (m, 8H), 1.16-1.03 (m, 2H), 0.86 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.9, 139.2, 137.9, 133.7, 129.0, 128.4, 127.8, 118.6, 105.3, 63.4, 59.4,

34.4, 31.6, 29.0, 25.7, 22.5, 14.0; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{29}N_2O_2S$ 361.1950, Found 361.1950.

(*E*)-1-(7-Methyl-1-(phenylsulfonyl)oct-2-en-4-yl)-1*H*-pyrazole (6d). Compound **6d** was synthesized from 1*H*-pyrazole (**2a**, 20.4 mg, 0.300 mmol) and (((1*E*,3*E*)-7-methylocta-1,3-dien-1-yl)sulfonyl)benzene (**5d**, 95.2 mg, 0.360 mmol) in 89% yield (89.0 mg, 0.268 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). mp 53-54 °C; **IR** (neat): 3101 (w), 2955 (w), 1443 (w), 1304 (s), 1242 (w), 1142 (s), 1088 (m), 1057 (w), 972 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.52-7.48 (m, 3H), 7.28 (d, *J* = 1.8 Hz, 1H), 6.22 (t, *J* = 1.8 Hz, 1H), 5.74 (dd, *J* = 15.6, 6.9 Hz, 1H), 5.48 (dt, *J* = 15.6, 7.3 Hz, 1H), 4.59 (q, *J* = 6.9 Hz, 1H), 3.77 (d, *J* = 7.3 Hz, 2H), 1.96-1.86 (m, 1H), 1.77-1.68 (m, 1H), 1.54-1.44 (m, 1H), 1.10-1.01 (m, 1H), 0.97-0.88 (m, 1H), 0.83 (d, *J* = 6.4 Hz, 3H), 0.82 (d, *J* = 6.4 Hz, 3H);**^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.9, 139.2, 137.9, 133.7, 129.0, 128.3, 127.7, 118.7, 105.2, 63.7, 59.3, 34.7, 32.3, 27.6, 22.4, 22.3; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{25}N_2O_2S$ 333.1637, Found 333.1639.

(*E*)-1-(7-Phenyl-1-(phenylsulfonyl)hept-2-en-4-yl)-1*H*-pyrazole (6e). Compound **6e** was synthesized from 1*H*-pyrazole (**2a**, 20.4 mg, 0.300 mmol) and (((1*E*,3*E*)-7-phenylhepta-1,3-dien-1-yl)sulfonyl)benzene (**5e**, 112.0 mg, 0.360 mmol) in 86% yield (98.0 mg, 0.258 mmol) as an ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). mp 78-79 °C; **IR** (neat): 3109 (w), 2970 (w), 1589 (w), 1497 (w), 1450 (w), 1304 (s), 1142 (s), 1088 (m), 972 (s), 895 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.77 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.50 (s, 1H), 7.47-7.43 (m, 2H), 7.31-7.27 (m, 3H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 7.3 Hz, 2H), 6.24 (s, 1H), 5.73 (dd, *J* = 15.6, 6.9 Hz, 1H), 5.49 (dt, *J* = 15.6, 7.3 Hz, 1H), 4.65 (q, *J* = 6.9 Hz, 1H), 3.77 (d, *J* = 7.3 Hz, 2H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.03-1.93 (m, 1H), 1.81-1.73 (m, 1H), 1.56-1.36 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 141.5, 139.6, 139.2, 137.8, 133.7, 129.0, 128.3, 128.3, 127.8, 125.9, 118.9, 105.3, 63.3, 59.3, 35.2, 33.8, 27.4; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{25}N_2O_2S$ 381.1637, Found 381.1636.

(*E*)-1-(9-Chloro-1-(phenylsulfonyl)non-2-en-4-yl)-1*H*-pyrazole (6f). Compound **6f** was synthesized from 1*H*-pyrazole (**2a**, 20.4 mg, 0.300 mmol) and (((1*E*,3*E*)-9-chlorononona-1,3-dien-1-yl)sulfonyl)benzene (**5f**, 108 mg, 0.360 mmol) in 83% yield (91.4mg, 0.249 mmol) as light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). **IR** (neat): 2924 (w), 2870 (w), 1512 (w), 1443 (w), 1396 (w), 1311 (s), 1142 (s), 1088 (m), 972 (m), 733 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.52-7.48 (m, 3H), 7.28 (d, *J* = 1.4 Hz, 1H), 6.23 (s, 1H), 5.75 (dd, *J* = 15.6, 6.9 Hz, 1H), 5.50 (dt, *J* = 15.6, 7.4 Hz, 1H), 4.64 (q, *J* = 6.9 Hz, 1H), 3.77 (d, *J* = 7.4 Hz, 2H), 3.47 (t, *J* = 6.6 Hz, 2H), 2.00-1.91 (m, 1H), 1.78-1.66 (m, 3H), 1.47-1.32 (m, 2H), 1.22-1.15 (m, 1H), 1.13-1.06 (m,1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.6, 139.2, 138.0, 133.7, 129.1, 128.3, 127.8, 118.8, 105.3, 63.2, 59.3, 44.7, 34.2, 32.1, 26.2, 24.9; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{24}ClN_2O_2S$ 367.1247, Found 367.1247.

(*E*)-1-(8-(Benzyloxy)-1-(phenylsulfonyl)oct-2-en-4-yl)-1*H*-pyrazole (6g). Compound **6g** was synthesized from 1*H*-pyrazole (**2a**, 20.4 mg, 0.300 mmol) and (((1*E*,3*E*)-8-(benzyloxy)octa-1,3-dien-1-yl)sulfonyl)benzene (**5g**, 128 mg, 0.360 mmol) in 85% yield (108 mg, 0.254mmol) as light yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). **IR** (neat): 2947 (w), 2854 (w), 1450 (w), 1396 (w), 1304 (m), 1142 (m), 1088 (m), 972 (w), 733 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.76 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.48-7.44 (m, 3H), 7.34-7.24 (m, 6H), 6.21 (s, 1H), 5.71 (dd, *J* = 15.6, 6.9 Hz, 1H), 5.46 (dt, *J* = 15.6, 7.4 Hz, 1H), 4.62 (q, *J* = 7.2 Hz, 1H), 4.44 (s, 2H), 3.74 (d, *J* = 7.4 Hz, 2H), 3.39 (t, *J* = 6.4 Hz 2H), 1.99-1.89 (m, 1H), 1.78-1.69 (m, 1H), 1.60-1.52 (m, 2H), 1.30-1.21 (m, 1H), 1.19-1.10 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.7, 139.2, 138.4, 137.9, 133.7, 129.0, 128.3, 128.3, 127.9, 127.6, 127.5, 118.8, 105.3, 72.8, 69.8, 63.3, 59.3, 34.2, 29.1, 22.5; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{29}N_2O_3S$ 425.1899, Found 425.1898.

(*E*)-1-(1-((*tert*-Butyldimethylsilyl)oxy)-6-(phenylsulfonyl)hex-4-en-3-yl)-1*H*-pyrazole (6h). Compound **6h** was synthesized from 1*H*-pyrazole (**2a**, 20.4 mg, 0.300 mmol) and *tert*-butyldimethyl(((3*E*,5*E*)-6-(phenylsulfonyl)hexa-3,5-dien-1-yl)oxy)silane (**5h**, 127 mg, 0.360 mmol) in 77% yield (97.0 mg, 0.231 mmol) as yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). **IR** (neat): 2955 (w), 2862 (w), 1466 (w), 1396 (w), 1311 (m), 1250 (m), 1142 (m), 1068 (s), 833 (s), 779 (s), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.51-7.47 (m, 3H), 7.31 (d, *J* = 1.8 Hz, 1H), 6.22 (s, 1H), 5.77 (dd, *J* = 15.6, 6.9 Hz, 1H), 5.47 (dt, *J* = 15.6, 7.4 Hz, 1H), 4.93 (q, *J* = 6.5 Hz, 1H), 3.75 (d, *J* = 7.4 Hz, 2H), 3.51 (dt, *J* = 10.3, 4.9 Hz, 1H), 3.29-3.23 (m, 1H), 2.19-2.11 (m, 1H), 1.95-1.87 (m, 1H), 0.87 (s, 9H), -0.01 (s, 3H), -0.03 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.9, 139.5, 137.9, 133.7, 129.0, 128.9, 128.4, 118.4, 105.0, 59.5, 59.4, 58.5, 37.0, 25.8, 18.1, -5.6,; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{21}H_{33}N_2O_3SSi$ 421.1981, Found 421.1980.

(*E*)-1-(8-((*tert*-Butyldimethylsilyl)oxy)-1-(phenylsulfonyl)oct-2-en-4-yl)-1*H*-pyrazole (6i). Compound **6i** was synthesized from 1*H*-pyrazole (**2a**, 20.4 mg, 0.300 mmol) and *tert*-butyldimethyl(((5*E*,7*E*)-8-(phenylsulfonyl)octa-5,7-dien-1-yl)oxy)silane (**5i**, 137 mg, 0.360 mmol) in 81% yield (109 mg, 0.243 mmol) as yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). **IR** (neat): 2947 (w), 2862 (w), 1450 (w), 1396 (w), 1311 (m), 1257 (m), 1142 (m), 1095 (s), 972 (w), 841 (s), 771 (s), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.51-7.47 (m, 3H), 7.27 (s, 1H), 6.21 (s, 1H), 5.73 (dd, *J* = 15.6, 6.9 Hz, 1H), 5.48 (dt, *J* = 15.6 7.4 Hz, 1H), 4.63 (q, *J* = 6.9 Hz, 1H), 3.76 (d, *J* = 7.4 Hz, 2H), 3.53 (t, *J* = 6.4 Hz, 2H), 1.99-1.90 (m, 1H), 1.77-1.71 (m, 1H), 1.50-1.42 (m, 2H), 1.24-1.16 (m, 1H), 1.14-1.09 (m, 1H), 0.85 (s, 9H), 0.00 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.8, 139.2, 138.0, 133.7, 129.0, 128.4, 127.8, 118.7, 105.3, 63.4, 62.6, 59.4, 34.2, 32.1, 25.9, 22.1, 18.2, -5.4; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{37}N_2O_3SSi$ 449.2294, Found 449.2294.

1-((2*E*,7*Z*)-1-(Phenylsulfonyl)deca-2,7-dien-4-yl)-1*H*-pyrazole (6j). Compound **6j** was synthesized from 1*H*-pyrazole (**2a**, 20.4 mg, 0.300 mmol) and (((1*E*,3*E*,7*Z*)-deca-1,3,7-trien-1-yl)sulfonyl)benzene (**5j**, 99.5 mg, 0.360 mmol) in 75% yield (77.6 mg, 0.225 mmol) as yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). **IR** (neat): 2962 (w), 2870 (w), 1450 (w), 1404 (w), 1311 (s), 1142 (s), 1088 (m), 972 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.50-7.46 (m, 3H), 7.27 (s, 1H), 6.22 (s, 1H), 5.73 (dd, *J* = 15.6, 6.9 Hz, 1H), 5.46 (dt, *J* = 15.6, 7.5 Hz, 1H), 5.40-5.34 (m, 1H), 5.24-5.18 (m, 1H), 4.65 (q, *J* = 6.9 Hz, 1H), 3.75 (d, *J* = 7.5 Hz, 2H), 2.06-1.95 (m, 1H), 1.91-1.81 (m, 4H), 1.78-1.70 (m, 1H), 0.89 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.8, 139.2, 137.9, 133.7, 133.2, 129.0, 128.3, 128.0, 126.7, 118.6, 105.2, 62.5, 59.3, 34.2, 23.1, 20.3, 14.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{25}N_2O_2S$ 345.1637, Found 345.1639.

(*E*)-1-(1-(Phenylsulfonyl)trideca-2,12-dien-4-yl)-1*H*-pyrazole (6k). Compound **6k** was synthesized from 1*H*-pyrazole (**2a**, 20.4 mg, 0.300 mmol) and (((1*E*,3*E*)-tetradeca-1,3,13-trien-1-yl)sulfonyl)benzene (**5k**, 120 mg, 0.360 mmol) in 75% yield (90.0 mg, 0.225 mmol) as ivory solid. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). mp 41-42 °C; **IR**

(neat): 3109 (w), 3078 (w), 2916 (m), 1643 (w), 1443 (w), 1396 (w), 1304 (s), 1142 (s), 1088 (m), 972 (m), 910 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.52-7.48 (m, 3H), 7.28 (s, 1H), 6.23 (s, 1H), 5.85-5.71 (m, 2H), 5.49 (dt, *J* = 15.2, 7.3 Hz, 1H), 5.01-4.91 (m, 2H), 4.63 (q, *J* = 6.9 Hz, 1H), 3.77 (d, *J* = 7.3 Hz, 2H), 2.02 (q, *J* = 6.9 Hz, 2H), 1.97-1.88 (m, 1H), 1.76-1.68 (m, 1H), 1.35 (quint, *J* = 6.9 Hz, 2H), 1.27-1.23 (m, 8H), 1.17-1.11 (m, 1H), 1.09-1.05 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.9, 139.2, 139.1, 138.0, 133.7, 129.0, 128.4, 127.8, 118.6, 114.1, 105.3, 63.4, 59.4, 34.4, 33.7, 29.3, 29.2, 29.0, 29.0, 28.8, 25.7; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{33}N_2O_2S$ 401.2263, Found 401.2262.

(*E*)-1-(1-(Phenylsulfonyl)oct-2-en-7-yn-4-yl)-1*H*-pyrazole (6l). Compound **6l** was synthesized from 1*H*-pyrazole (**2a**, 20.4 mg, 0.300 mmol) and (((1*E*,3*E*)-octa-1,3-dien-7-yn-1-yl)sulfonyl)benzene (**5l**, 88.7 mg, 0.360 mmol) in 83% yield (78.0 mg, 0.248 mmol) as yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:1). **IR** (neat): 3279 (w), 2955 (w), 2353 (w), 2322 (w), 1512 (w), 1443 (w), 1311 (m), 1142 (s), 1088 (m), 975 (m), 741 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.76 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.49-7.45 (m, 3H), 7.31 (s, 1H), 6.19 (s, 1H), 5.74 (dd, *J* = 15.6, 6.9 Hz, 1H), 5.53 (dt, *J* = 15.6, 7.4 Hz, 1H), 4.85 (q, *J* = 7.0 Hz, 1H), 3.74 (d, *J* = 7.4 Hz, 2H), 2.18-2.11 (m, 1H), 2.08-1.98 (m, 2H), 1.92-1.83 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 139.6, 138.8, 137.8, 133.7, 129.0, 128.7, 128.3, 119.4, 105.2, 82.3, 69.7, 61.5, 59.3, 32.7, 14.8; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{19}N_2O_2S$ 315.1167, Found 315.1165.

Experimental procedures for the synthesis of 8, 9 and 11

2-((*E*)-3-(Indolin-1-yl)but-1-en-1-yl)-3-phenylcyclopropyl)(phenyl)methanone (8). To a solution of compound **3n** (65.5 mg, 0.200 mmol) in THF (2 mL) was added NaH (60% in mineral oil, 20.0 mg, 0.500 mmol) at room temperature. And then a solution of *trans*-chalcone (**7**, 41.7 mg, 0.200 mmol) in THF (2 mL) was added to the reaction mixture. The reaction was heated at 70 °C and stirred for 3 h. After that time, the mixture was allowed to cool to room temperature, quenched with water (3 mL) and washed with EtOAc (3 x 2 mL). The organic layers were dried over $MgSO_4$, filtered and concentrated. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20), affording desired product **8** (65.0 mg, 0.165 mmol, 83%) as a yellow oil. **IR** (neat): 3055 (w), 2986 (w), 2839 (w), 1736 (m), 1666 (m), 1605 (m), 1489 (w), 1257 (m), 1018 (w), 972 (w), 910 (m), 872 (w), 733 (s), 702 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$), a 1:1 mixture of diastereomers: δ 8.08 (d, *J* = 7.3 Hz, 2H), 8.03 (d, *J* = 7.3 Hz, 2H), 7.64-7.59 (m, 2H), 7.55-7.49 (m, 4H), 7.37-7.33 (m, 4H), 7.30-7.27 (m, 6H), 7.07-6.99 (m, 4H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.40 (d, *J* = 7.8 Hz, 1H), 6.31 (d, *J* = 7.8 Hz, 1H), 5.82 (dd, *J* = 15.6, 5.9 Hz, 1H), 5.75 (dd, *J* = 15.3, 5.7 Hz, 1H), 5.22-5.15 (m, 2H), 4.11 (quint, *J* = 6.5 Hz, 2H), 3.34-3.11 (m, 8H), 2.94-2.83 (m, 4H), 2.69-2.62 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$), a 1:1 mixture of diastereomers: δ 198.0, 151.0, 150.9, 137.7, 136.4, 133.0, 132.9, 132.9, 132.4, 130.3, 130.1, 129.1, 129.1, 128.6, 128.6, 128.3, 128.1, 127.9, 127.8, 127.0, 127.0, 126.7, 124.4, 124.3, 117.1, 117.0, 107.6, 107.5, 52.0, 51.9, 46.9, 46.7, 34.8, 34.6, 34.6, 34.4, 32.2, 31.8, 28.1, 28.0, 16.7, 16.1; **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{28}NO$ 394.2171, Found 394.2172.

1-(1-([1,1':3',1''-Terphenyl]-4'-yl)ethyl)indoline (9). Allylic sulfone **3n** (65.5 mg, 0.200 mmol), *trans*-chalcone (**7**, 41.7 mg, 0.200 mmol), NaOH (32.0 mg, 0.800 mmol), and PEG 2000 (160 mg, 0.0800 mmol) were added to a vial (4 mL), which was sealed with a cap (phenolic open-top cap with gray PTFE/silicone). The reaction mixture was heated at 70 °C. After stirring for 1 h, the reaction was quenched by adding a saturated aqueous solution of NH_4Cl (2 mL), and the mixture was washed with EtOAc (3 × 1 mL). The organic layers were dried over $MgSO_4$, filtered and concentrated. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20), affording desired product **9** (53.0 mg, 0.141 mmol, 71%) as a light-yellow oil. **IR** (neat): 3032 (w), 2970 (w), 2847 (w), 1605 (m), 1481 (m), 1389 (w), 1257 (m), 1180 (w), 1026 (w), 910 (s), 733 (s), 702 (s) cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.69-7.61 (m, 4H), 7.55 (d, *J* = 1.8 Hz, 1H), 7.47-7.43 (m, 4H), 7.42-7.34 (m, 4H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.91 (t, *J* = 7.3 Hz, 1H), 6.59 (t, *J* = 7.3 Hz, 1H), 6.05 (d, *J* = 7.3 Hz, 1H), 4.76 (q, *J* = 6.9 Hz, 1H), 3.53-3.48 (m, 1H), 3.45-3.38 (m, 1H), 2.94 (dd, *J* = 9.6, 6.9 Hz, 2H), 1.41 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.9, 142.1, 141.2, 140.6, 139.7, 139.5, 130.2, 129.4, 129.2, 128.8, 128.2, 127.3, 127.1, 127.0, 126.0, 124.1, 116.9, 107.5, 51.8, 48.5, 28.2, 16.7; **HRMS** (ESI) *m/z*: $[M]^+$ Calcd for $C_{28}H_{25}N$ 375.1987, Found 375.1989.

1-(1-([1,1'-Biphenyl]-2-yl)ethyl)indoline (11). Compound **11** was synthesized from (*E*)-1-(5-(phenylsulfonyl)pent-3-en-2-yl)indoline (**3n**, 65.5 mg, 0.200 mmol) and cinnamaldehyde **10** (25.2 µL, 0.200 mmol) in 92% yield (55.0 mg, 0.184 mmol) as yellow oil. The crude product was purified using silica gel column chromatography (EtOAc:hexanes = 1:20). **IR** (neat): 3047 (w), 2986 (w), 1605 (m), 1481 (s), 1389 (w), 1257 (m), 1157 (w), 910 (m), 841 (m), 733 (s) cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.64-7.59 (m, 4H), 7.52-7.45 (m, 4H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 6.9 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.44 (d, *J* = 7.8 Hz, 1H), 4.80 (q, *J* = 6.9 Hz, 1H), 3.49-3.37 (m, 2H), 3.00 (t, *J* = 8.5 Hz, 2H), 1.60 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 151.3, 141.9, 140.8, 139.8, 130.1, 128.7, 127.5, 127.2, 127.1, 127.0, 124.4, 117.0, 107.2, 54.2, 47.9, 28.2, 16.5; **HRMS** (ESI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{21}N$ 299.1674, Found 299.1673.

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[15] When allylic sulfone **3a** was treated with 7.5 mol % **SIPrCuCl** and 7 mol % KO*t*-Bu in the absence of pyrazole, vinyl sulfone product **4c** was not observed. It was postulated that pyrazole was required for isomerization of **3a** to **4c**, although vinyl sulfone intermediate **4c** could not be detected by ^{1}H NMR analysis during the catalytic reaction of **3a** with pyrazole.

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FULL PAPER

Copper-Catalyzed Regio- and Stereoselective 1,6-Conjugate Addition of Aza-Heterocycles to 1-Sulfonyl-1,3-dienes

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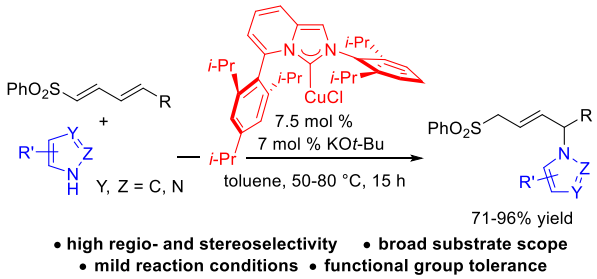

- high regio- and stereoselectivity
- broad substrate scope
- mild reaction conditions
- functional group tolerance