Allyl 4-Chlorophenyl Sulfone as a Versatile 1,1-Synthon for Sequential α-Alkylation/Cobalt-Catalyzed Allylic Substitution

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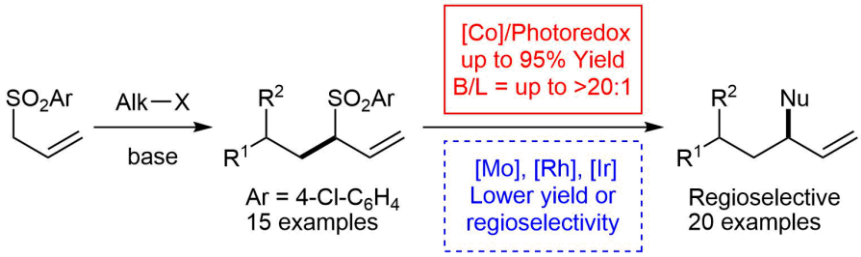

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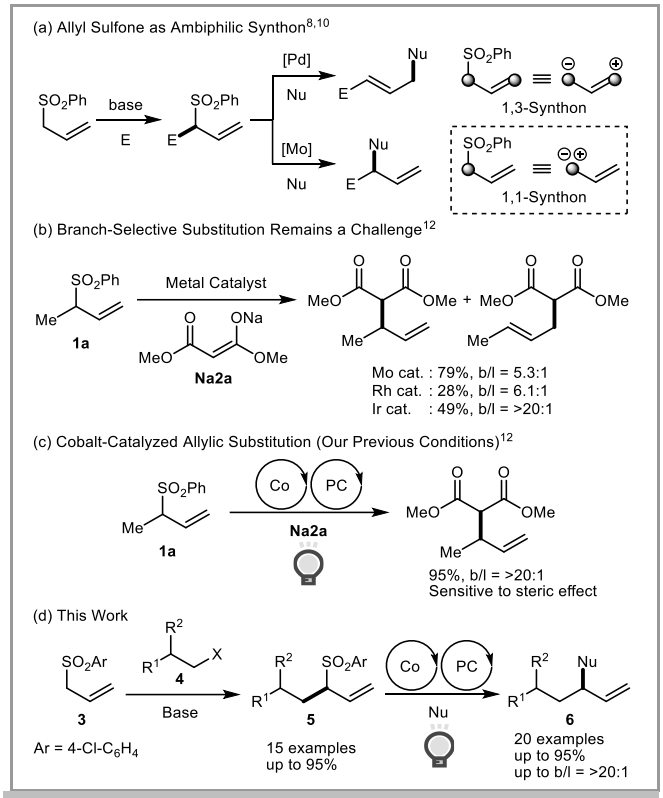
Abstract Despite their unique potential as rare 1,1-dipole synthons, allyl sulfones are rarely used in target-oriented syntheses, likely due to the lack of a general catalytic method for their branch-selective allylic substitution. Herein, we identified allyl 4-chlorophenyl sulfone as a versatile linchpin for both base-mediated α-derivatization and subsequent cobalt-catalyzed allylic substitution. The sequential transformations allow for highly regioselective access to branched allylic substitution products with a variety of aliphatic side chains. The photoredox-enabled cobalt catalysis was indispensable for achieving high yield and regioselectivity for the desulfonylative substitution in contrast to traditional metal-catalyzed protocols, which led to inferior outcomes in the respective transformations.

Key words Cobalt Catalysis; Photoredox Catalysis; Metallaphotoredox; Allylation; Sulfone; Regioselectivity

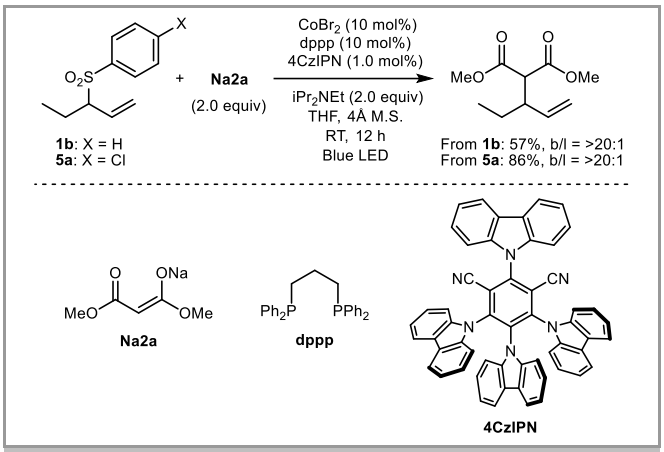
Metal-catalyzed regioselective allylic substitution reactions with soft carbon nucleophiles represent an integral research area in both organic synthesis and organometallic chemistry, and are supported by continuous progress in the development of palladium-,[1] ruthenium-,[2] rhodium-[3] and iridium-[4]based catalysts. Among a series of allylic electrophiles currently used in the catalytic method, allyl sulfones are especially unique due to their ambiphilic nature and potential in target-oriented synthesis.[5] Under basic conditions, an allyl sulfone is deprotonated to afford stabilized allyl anions and is readily alkylated when treated with an electrophile. This α-functionalization of allyl sulfones is particularly valuable because the resulting product with an aliphatic side chain is a potent electrophile for metal-catalyzed desulfonylative substitution.[6,7] Thus, sequential α-alkylation and palladium-catalyzed linear-selective allylic substitution allows for allyl sulfones to serve as 1,3-dipole synthons (Scheme 1a).[8] On the other hand, allyl sulfones serve as rare 1,1-dipole synthons[9] when α-alkylation is coupled with molybdenum-catalyzed branch-selective substitution (Scheme 1a).[10,11]

Despite these favorable features of allyl sulfones in synthetic chemistry, they have not been widely appreciated in complex molecule synthesis, presumably because of the limitations of the catalytic branch-selective substitution of allyl sulfones with regard to reactivity and regioselectivity. Our previous study[12] revealed that the molybdenum-catalyzed method,[10] as well as the established rhodium-[3c] and iridium-[4i]catalyzed protocols, produce unsatisfactory yields or branch selectivity for substitution of the simple allyl sulfone **1a** with sodium dimethyl malonate **Na2a** (Scheme 1b). Inspired by the recent progress in combining photoredox and cobalt catalysis,[13-15] we recently reported that the low valent cobalt catalyst generated *in situ* by photoredox catalysis (PC)[16] resulted in the allylic substitution of **1a** in excellent yield and branch selectivity (Scheme 1c).[12,17] The previous cobalt-catalyzed conditions, however, were not general in terms of the substrate scope. The cobalt-catalyzed method was sensitive to steric hindrance around the allylic C–S bond, and substitution of allyl sulfones with longer alkyl chains proceeded in modest yield even with higher catalyst loadings (see also Scheme 2, allylation using **1b**). To address this challenge, we herein report general, 2-step transformations of allyl sulfones for the unified synthesis of branched aliphatic allylic substitution products (Scheme 1d). Identification of allyl 4-chlorophenyl sulfone **3** as a new 1,1-dipole synthon was a key finding, and its application to α-alkylation and cobalt-catalyzed allylic substitution enabled the transformations of various allyl sulfones in high yield and regioselectivity (up to 95% yield, up to branch/linear = >20:1).



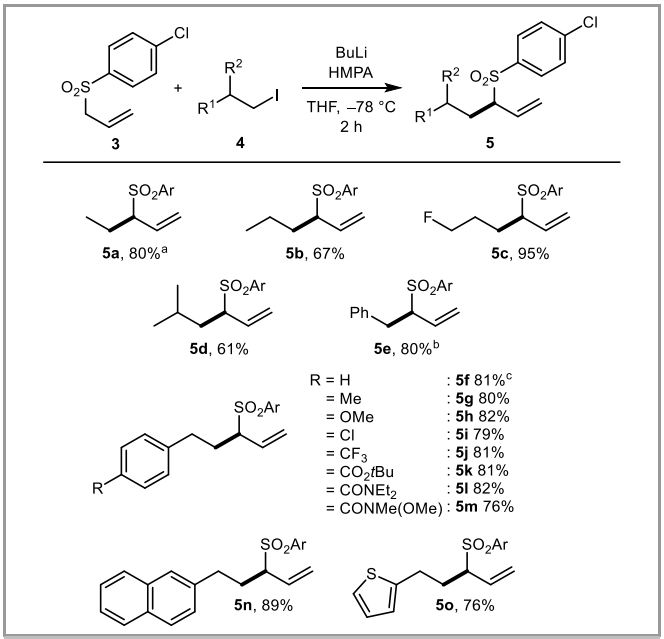
Scheme 1 Precedents of metal-catalyzed branch-selective substitution of allyl sulfones

To expand the generality of the desulfonylative allylic substitution, we hypothesized that allyl sulfones, which are equipped with a better leaving group than phenyl sulfinate, would facilitate the desired catalytic process. Considering both the leaving ability of the releasing sulfinate and the accessibility of the synthetic precursor, we turned our attention to allyl 4-chlorophenyl sulfone **3**. Our preliminary experiments revealed that, compared with **1b**, allyl sulfone **5a** derived from **3** afforded the substitution product in higher yield under the photoredox/cobalt-catalyzed conditions (Scheme 2).



Scheme 2 Evaluation of the leaving group

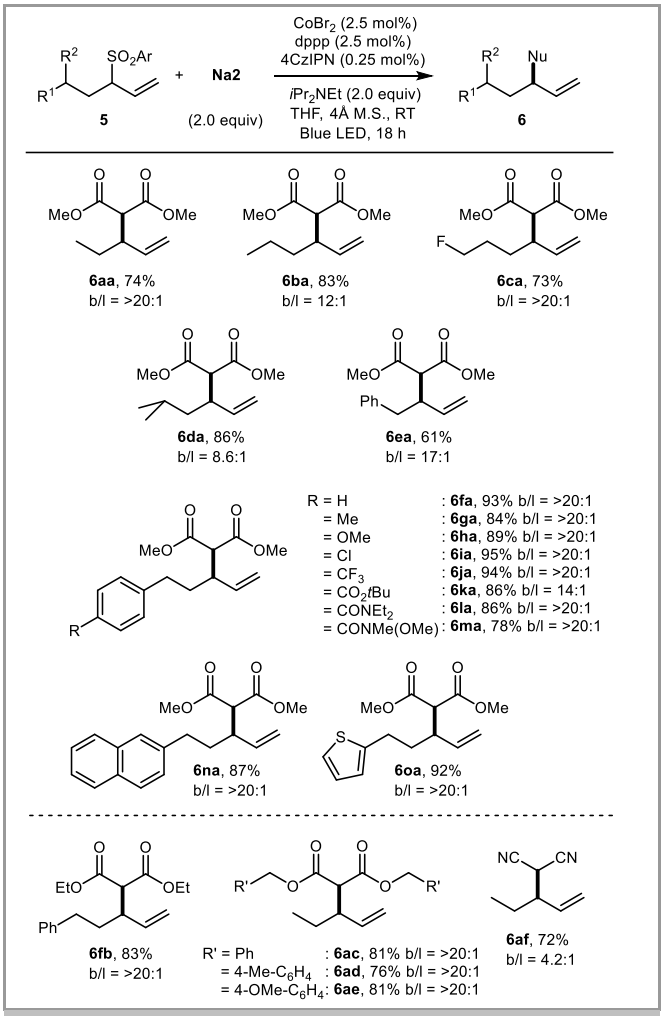
Encouraged by this result, we next investigated the conditions and substrate scope of base-mediated α-alkylation of **3**, which is also an indispensable transformation for its application as a 1,1-dipole synthon. To our delight, the desired α-alkylated products were obtained using **3**, *n*-butyllithium, hexamethylphosphoramide (HMPA), and readily available alkyl iodides. Note that quenching the reaction with acetic acid at a low temperature circumvents the isomerization to vinyl sulfone.[18] The substrate scope of the α-alkylation is summarized in Scheme 3. Ethylation of **3** proceeded smoothly in gram scale (**5a**). Other alkyl groups such as propyl (**5b**), 3-fluoropropyl (**5c**) and isobutyl (**5d**) can be readily installed by using the respective alkyl iodide. Benzylation of **3** was successfully performed with benzyl bromide (**5e**). Phenethyl iodide also afforded the desired product in 81% yield (**5f**). In terms of functional group tolerance, an electron-donating methyl (**5g**) or methoxy (**5h**) group on the aromatic ring of the phenethyl group did not affect product yield. Aryl chloride (**5i**) was also compatible with the organolithium-mediated α-alkylation. In terms of electron-withdrawing groups, not only a trifluoromethyl group (**5j**), but also ester (**5k**), amide (**5l**), and *N*-methoxy-*N*-methyl amide (**5m**) were compatible with the conditions, suggesting that the desired alkylation occurred chemoselectively in the presence of a carbonyl group. 2-Naphthyl- and 2-thiophenyl-substituted alkyl iodides can also be used, affording the corresponding products (**5n**, **5o**) in 89% and 76% yield, respectively.



Scheme 3 Preparation of allyl sulfones **5** from **3**. *Reagents and conditions:* **3** (1.1–1.3 mmol), alkyl iodide **4** (2.0 equiv), BuLi (1.0 equiv), HMPA (2.0 equiv) in THF (0.2 M) at −78 °C for 2 hours. [a]8.5 mmol of **3** was used. [b]Benzyl bromide was used as an electrophile. [c]The reaction was run for 6 hours. Ar = 4-Cl-C_6H_4.

Based on the robust protocol for the α-alkylation of **3**, the scope of the cobalt-catalyzed allylic substitution of allyl sulfones was studied, and the results are summarized in Scheme 4. In general, catalytic allylation proceeded smoothly with low catalyst loadings (2.5 mol% of the cobalt complex and 0.25 mol% of the photocatalyst). Allyl sulfones with an ethyl group was exclusively transformed to the respective branched product (**6aa**). Substitution products with longer alkyl side chains, including propyl (**6ba**) and 3-fluoropropyl (**6ca**) were obtained in high to excellent regioselectivity. More sterically demanding isobutyl- or benzyl-substituted products (**6da**, **6ea**) were obtained with moderate to high branch selectivity. Substitution

of the allyl sulfone with a phenethyl group (**6fa**) proceeded in high yield and with excellent regioselectivity. Functional group compatibility was next investigated, and methyl- or methoxy-substituted substrates were converted to the allylic substitution products in high yield with complete branch selectivity (**6ga**, **6ha**). In addition, a chloro (**6ia**) group was tolerated in the reaction conditions, suggesting its compatibility with the photoredox-induced low valent cobalt catalysis. Allyl sulfones with other electron-withdrawing functional groups, such as trifluoromethyl (**6ja**), ester (**6ka**), and amide (**6la**), successfully underwent allylic substitution with high to excellent regioselectivity. Synthetically useful Weinreb amide was also compatible with the reaction conditions and only minimal undesired reductive cleavage of the N–O bond occurred (**6ma**). Extended π-systems (**6na**) and a heteroaromatic (**6oa**) were also compatible with the branch-selective allylic substitution.

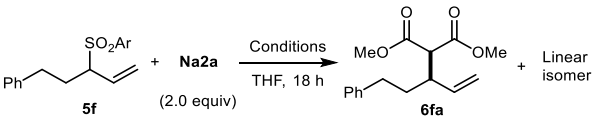


Scheme 4 Reaction scope of cobalt-catalyzed substitution of allyl sulfones. *Reagents and conditions:* **5** (0.30 mmol), **Na2** (2.0 equiv), $CoBr_2$ (2.5 mol%), dppp (2.5 mol%), 4CzIPN (0.25 mol%), iPr_2NEt (2.0 equiv), and 4Å molecular sieves (60 mg) in THF (0.2 M) under blue LED irradiation at room temperature for 18 hours. Ar = 4-Cl-C_6H_4.

With regard to the nucleophile scope, diethyl- and dibenzyl-malonate could be used, and the desired products were obtained in good yield with excellent regioselectivity (**6fb**, **6ac**). The substituents on the aryl ring of the dibenzyl malonate had a minimal effect, and 4-methylbenzyl malonate was allylated to afford **6ad** with excellent branch selectivity. The regioselective allylation of 4-methoxybenzyl malonate deserves attention because the 4-methoxybenzyl group can be removed under mild acidic or oxidative conditions to afford free carboxylic acid (**6ae**). When malononitrile was used as a nucleophile, the branched product was obtained in good yield, but with only modest regioselectivity (**6af**).

Finally, to confirm the superiority of cobalt catalysis for the branch-selective substitution of the allyl 4-chlorophenyl sulfone derivatives, we compared the catalytic conditions using **5f** as an electrophile (Table 1). The reported molybdenum-catalyzed protocol for the substitution of allyl sulfones[10] afforded the product in good yield but with lower regioselectivity (entry 2). **6fa** was obtained regioselectively by the representative rhodium[3c] (entry 3) or iridium[4i] (entry 4) catalysis, but in low to modest yield. In rhodium-catalyzed conditions, isomerization of **5f** to vinyl sulfone competed with the allylic substitution, and partially accounted for the low yield of **6fa**. Under iridium catalysis, slow consumption of **5f** rather than the isomerization was responsible for the modest yield of **6fa**. Thus, photoredox-enabled cobalt catalysis is particularly effective for the branch-selective substitution of the allyl 4-chlorophenyl sulfone derivatives and is indispensable for realizing the application of **3** as a practical 1,1-dipole synthon.

Table 1 Comparison of the reactivity for **5f**[a]



Entry	Conditions (mol%)	Yield [%][b]	b/l[b]
1	$CoBr_2$ (2.5), dppp (2.5), 4CzIPN (0.25), iPr_2NEt (200), 4Å M.S., Blue LED, THF, RT	93[c]	>20:1
2	$Mo(CO)_6$ (20), toluene, reflux	71	2.4:1
3	$Rh(PPh_3)_3Cl$ (2.5), $P(OPh)_3$ (10), THF, 30 °C	33	>20:1
4	$[Ir(cod)Cl]_2$ (1.25), $P(OPh)_3$ (5.0), THF, 30 °C	53	>20:1

[a]See the Supporting Information for experimental details. [b]Determined by ^1H NMR analysis. [c]Yield of the isolated product. Ar = 4-Cl-C_6H_4.

In conclusion, allyl 4-chlorophenyl sulfone **3** was newly identified as a practical 1,1-dipole synthon and successfully employed in successive base-mediated α-alkylation and cobalt-catalyzed allylic substitution.[19] The 2-step transformations provided access to synthetically versatile branched allylic substitution products with a variety of alkyl side chains. Implementation of the photoredox-enabled cobalt catalysis was essential for achieving a high yield and branch selectivity for the allylic substitution of allyl sulfones. Further studies on the catalytic substitution of allyl sulfones with other nucleophiles as well as an application to enantioselective reactions[20] are currently in progress in our group.

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Reactions were carried out under argon atmosphere unless otherwise noted. Reported melting points are uncorrected. Enantioselectivities were determined by high performance liquid chromatography (HPLC) analysis using 4.6 cm × 25 cm Daicel Chiralpak columns. NMR spectra were recorded on JEOL JNM-ECS400 spectrometers operating at 391.78 MHz for ^1H NMR and 98.52 MHz for ^{13}C NMR, JEOL JNM-ECX400 spectrometers operating at 396 MHz for ^1H NMR and 99.55 MHz for ^{13}C

NMR, and JNM-ECA500 spectrometers operating at 500.16 MHz for ^{1}H NMR and 125.77 MHz for ^{13}C NMR. Chemical shifts were reported in the scale relative to TMS (0.00 ppm for ^{1}H NMR in $CDCl_3$), $CHCl_3$ (7.26 ppm for ^{1}H NMR in $CDCl_3$), C_6H_6 (7.16 ppm for ^{1}H NMR in C_6D_6), $CDCl_3$ (77.00 ppm for ^{13}C NMR in $CDCl_3$), C_6D_6 (128.00 ppm for ^{13}C NMR in C_6D_6), $PhCF_3$ (–63.72 ppm for ^{19}F NMR in $CDCl_3$) as an internal reference, respectively. ESI mass spectra were measured on JEOL JMS-T100LCP spectrometer. Column chromatography was performed with silica gel Kanto Silica gel 60 N (40-50 mesh) or Yamazen YFLC AI-580 using Universal Column SiOH. All non-aqueous reactions were carried out in a flame-dried glassware under argon atmosphere unless otherwise noted or in an argon-filled glove box. Dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), diethyl ether (Et_2O), and toluene were purified by Glass Contour solvent purification system before use. Sodium hydride (NaH) was purchased as dispersion in mineral oil and was washed with hexane and stored under argon prior to use. The pronucleophile **2d** and the photocatalyst 4CzIPN were prepared as reported previously.[12] All other reagents were commercially available and used as received unless otherwise noted. Irradiation was performed with ISLM-150X150-BB447 (purchased from CCS Inc.) as photon source.

(Pent-1-en-3-ylsulfonyl)benzene (1b)

To a 30 mL flame dried flask with a balloon filled with argon, allyl phenyl sulfone (236 mg, 1.3 mmol), HMPA (450 µL, 2.6 mmol) and THF (6.5 mL) were added and cooled to −78 °C. Butyl lithium (1.6 M in hexane, 810 µL, 1.3 mmol) was added dropwise to the solution, and the mixture was stirred at −78 °C for 40 minutes. Then, ethyl iodide **4a** (130 µL, 1.6 mmol) was added, and the mixture was stirred at −78 °C for 2 hours. Then, saturated aqueous NH_4Cl was slowly added, and the reaction mixture was warmed to room temperature. The mixture was diluted with water and organic material was extracted with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the crude material with flash chromatography (silica gel, hexane/EtOAc) afforded **1b** (200 mg, 73%) as a white solid, mp 39-40 °C; R_f = 0.35 [hexane/EtOAc 3:1, UV, $KMnO_4$]. NMR spectra of the obtained product were consistent with the reported one.[21]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.85-7.83 (m, 2H), 7.67-7.60 (m, 1H), 7.56-7.52 (m, 2H), 5.61 (ddd, *J* = 18.4, 9.0, 8.1 Hz, 1H), 5.31 (d, *J* = 10.4 Hz, 1H), 5.06 (d, *J* = 17.1 Hz, 1H), 3.46-3.36 (m, 1H), 2.23-2.12 (m, 1H), 1.74-1.61 (m, 1H) , 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.3, 133.5, 129.9, 129.1, 128.7, 123.7, 71.3, 20.3, 11.1.

Bis(4-methoxybenzyl) malonate (2e)

To a solution of 4-methoxybenzyl alcohol (7.97 g, 57.7 mmol, 1.0 equiv) in CH_2Cl_2/DMF (10:1) (240 mL) under argon at 0 °C, malonic acid (3.00 g, 28.8 mmol) and DMAP (704 mg, 5.77 mmol) was added sequentially. After the reaction mixture was stirred for 5 minutes, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI· HCl) (26.5 g, 138 mmol) was added in one portion. The reaction mixture was stirred for 2.5 hours at room temperature. After the reaction, the volatiles were removed under reduced pressure, and the residue was partitioned between EtOAc and sat. aq. NH_4Cl. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography (hexane: EtOAc = 2:1) to afford **2e** as a colorless oil (2.73 g, 27%), R_f = 0.30 [hexane/EtOAc 2:1, UV, $KMnO_4$]. NMR spectra of the obtained product were consistent with the reported one.[22]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.26 (d, *J* = 8.5 Hz, 4H), 6.87 (d, *J* = 8.5 Hz, 4H), 5.10 (s, 4H), 3.81 (s, 6H), 3.42 (s, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 166.2, 159.6, 130.0, 127.2, 113.8, 66.9, 55.1, 41.5.

Allyl 4-Chlorophenyl sulfone (3)

3 was prepared according to the literature procedure.[23] To a 50 mL flame dried flask with a balloon filled with argon, sodium 4-chlorobenzenesulfinate (5.4 g, 27 mmol), ethanol (20 mL) and allyl bromide (2.5 mL, 30 mmol) were added. The mixture was heated to reflux and was stirred for 8 hours. After cooled to room temperature, the crude was filtered to remove white solids eluting with ethanol. The resulting mixture was concentrated under reduced pressure. Purification of the crude material with flash column chromatography (silica gel, hexane/EtOAc) afforded **3** (5.5 g, 92%) as a white solid, mp 32-33 °C; R_f = 0.21 [hexane/EtOAc 4:1, UV]. NMR spectra of the obtained product were consistent with the reported one.[24]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 5.85-5.74 (m, 1H), 5.36 (d, *J* = 10.3 Hz, 1H), 5.16 (d, *J* = 17.1 Hz, 1H), 3.81 (d, *J* = 7.2 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.5, 136.6, 130.0, 129.3, 125.0, 124.4, 60.8.

General Procedure A for the preparation of alkyl iodides

To a solution of the corresponding alcohol (1.0 equiv) in dichloromethane (0.5 M), imidazole (1.2 equiv), PPh_3 (1.1 equiv) and iodine (1.1 equiv) was sequentially added at 0 °C. After completion of addition, the mixture was stirred at 0 ºC for 10 minutes. The resulting mixture was warmed to room temperature and was stirred for 1 hour. The reaction was quenched by saturated aqueous $Na_2S_2O_3$. The organic layer was separated and dried over anhydrous Na_2SO_4. After the solvent was removed *in vacuo*, the crude product was purified by flash column chromatography (silica gel, hexane/EtOAc) to give the corresponding alkyl iodides **4**.

1-(2-Iodoethyl)-4-methylbenzene (4g)

According to the general procedure A, **4g** was prepared from 2-(4-methylphenyl)ethan-1-ol (1.00 g, 7.34 mmol), iodine (2.05 g, 8.08 mmol), PPh_3 (2.12 g, 8.08 mmol) and imidazole (600 mg, 8.81 mmol). The crude product was purified by Yamazen YFLC AI-580 using Universal Column SiOH (hexane/EtOAc) to provide **4g** (1.75 g, 99%) as a colorless oil, R_f = 0.58 [hexane/EtOAc 19:1, UV]. NMR spectra of the obtained product were consistent with the reported one.[25]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.13 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 3.33 (t, *J* = 7.9 Hz, 2H), 3.14 (t, *J* = 7.9 Hz, 2H), 2.32 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.6, 136.4, 129.3, 128.1, 39.9, 21.1, 6.0.

1-(2-Iodoethyl)-4-methoxybenzene (4h)

According to the general procedure A, **4h** was prepared from 2-(4-methoxyphenyl)ethan-1-ol (1.5 g, 9.9 mmol), iodine (2.5 g, 9.9 mmol), PPh_3 (2.7 g, 10 mmol) and imidazole (705 mg, 10 mmol). The crude product was purified by Yamazen YFLC AI-580 using Universal Column SiOH (silica gel, hexane/EtOAc) to provide **4h** (1.8 g, 70%) as a colorless oil, R_f = 0.71 [hexane/EtOAc 3:1, UV]. NMR spectra of the obtained product were consistent with the reported one.[26]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.10 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 3.30 (t, *J* = 7.5 Hz, 2H), 3.11 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.4, 132.8, 129.3, 114.0, 55.2, 39.5, 6.3.

1-(2-Iodoethyl)-4-chlorobenzene (4i)

According to the general procedure A, **4i** was prepared from 2-(4-chlorophenyl)ethan-1-ol (1.86 mL, 14.0 mmol), iodine (3.91 g, 15.4 mmol), PPh_3 (4.04 g, 15.4 mmol) and imidazole (1.14 g, 16.8 mmol). The crude product was purified by Yamazen YFLC AI-580 using Universal Column SiOH (hexane/EtOAc) to provide **4i** (3.56 g, 96%) as a colorless oil, R_f = 0.57 [hexane/EtOAc 19:1, UV]. NMR spectra of the obtained product were consistent with the reported one.[27]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.29 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 3.32 (t, *J* = 7.7 Hz, 2H), 3.15 (t, *J* = 7.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 138.9, 132.6, 129.6, 128.7, 39.4, 5.2.

1-(2-Iodoethyl)-4-(trifluoromethyl)benzene (4j)

According to the general procedure A, **4j** was prepared from 2-(4-(trifluoromethyl)phenyl)ethan-1-ol (980 mg, 5.1 mmol), iodine (1.4 g, 5.7 mmol), PPh_3 (1.5 g, 5.7 mmol) and imidazole (420 mg, 6.2 mmol). The crude product was purified by Yamazen YFLC AI-580 using Universal Column SiOH (hexane/EtOAc) to provide **4j** (1.4 g, 93%) as a colorless oil, R_f = 0.50 [hexane/EtOAc 19:1, UV]. NMR spectra of the obtained product were consistent with the reported one.[28]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.57 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 7.7 Hz, 2H), 3.35 (t, *J* = 7.5 Hz, 2H), 3.23 (t, *J* = 7.5 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.3, 129.1 (q, $^2J_{CF}$ = 32.4 Hz), 128.7, 125.5 (q, $^3J_{CF}$ = 3.8 Hz), 124.1 (q, $^1J_{CF}$ = 272.8 Hz), 39.7, 4.4.

***tert*-Butyl 4-(2-iodoethyl)benzoate (4k)**

According to the general procedure A, **4k** was prepared from *tert*-butyl 4-(2-hydroxyethyl)benzoate (prepared according to the literature procedure,[29] 676 mg, 3.04 mmol), iodine (848 mg, 3.34 mmol), PPh_3 (787 mg, 3.34 mmol) and imidazole (249 mg, 3.65 mmol). The crude product was purified by Yamazen YFLC AI-580 using Universal Column SiOH (hexane/EtOAc) to provide **4k** (918 mg, 83%) as a white solid, mp 50-51 °C; R_f = 0.35 [hexane/EtOAc 9:1, UV].

IR (KBr): 2978, 1707, 1366, 1296, 1253, 1168, 1115, 850, 768 cm^{-1}.

^{1}H NMR (C_6D_6, 400 MHz): δ = 8.08 (d, *J* = 8.1 Hz, 2H), 6.70 (d, *J* = 8.5 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.62 (t, *J* = 7.4 Hz, 2H), 1.47 (s, 9H),.

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.4, 145.2, 131.2, 130.1, 128.4, 80.4, 39.9, 28.1, 4.5.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{13}H_{17}O_2INa$: 355.0165; found: 355.0172.

***N*,*N*-Diethyl-4-(2-iodoethyl)benzamide (4l)**

To a solution of *N*,*N*-diethyl-4-vinylbenzamide (prepared according to the literature procedure,[30] 1.92 g, 9.0 mmol) and $NaHCO_3$ (1.36 g, 16.2 mmol) in dichloromethane (45 mL), *m*CPBA (70%, 3.77 g, 15.3 mmol) was added portionwise at 0 °C. After 1 hour, the reaction mixture was warmed to room temperature and was stirred for 6 hours. Then, the reaction mixture was cooled to 0 °C and $NaHCO_3$ (1.36 g, 16.2 mmol) and *m*CPBA (70%, 3.77 g, 15.3 mmol) was added, and the mixture was stirred at 0 °C for 1 hour. Then, the reaction mixture was warmed to room temperature and was stirred for 1 hour. The reaction was then quenched with sat. aq. $Na_2S_2O_3$. The organic layer was separated and dried over Na_2SO_4. After the solvent was removed *in vacuo*, the crude was roughly purified by flash column chromatography (silica gel, hexane/EtOAc = 1/1, 2% Et_3N) to afford the crude styrene oxide as a colorless oil (1.64 g).

The crude styrene oxide (1.64 g) and Pd/C (51% water, 10% Pd on the dehydrous basis, 1.24 g, ca. 0.58 mmol) were dissolved in methanol (29 mL) and the resulting solution was subjected to 1 atm of H_2 at room temperature. After 8 hours, the reaction mixture was filtered through a celite pad with methanol and the solvent was removed under reduced pressure. The crude was then roughly purified by flash column chromatography (silica gel, $CHCl_3$/MeOH = 12/1) to afford the crude alcohol as a white solid (881 mg).

According to the general procedure A, the crude alcohol (881 mg) was treated with iodine (1.62 g, 6.40 mmol), PPh_3 (1.68 g, 6.40 mmol) and imidazole (475 mg, 6.98 mmol) in CH_2Cl_2 (11.6 mL) and **4l** was obtained as a colorless oil (1.21 g, 3.65 mmol, 41% for 3 steps), R_f = 0.58 [hexane/EtOAc 1:2, UV].

IR (NaCl): 2971, 2929, 2876, 1627, 1426, 1389, 1285, 1173, 1095, 629 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.33 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 3.34 (t, *J* = 7.6 Hz, 2H), 3.20 (t, *J* =7.9 Hz, 2H), 3.62-3.15 (m, 4H), 1.31-1.05 (m, 6H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 170.9, 141.4, 135.7, 128.2, 126.6, 43.1, 39.9, 39.1, 14.1, 12.8, 4.9.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{13}H_{18}ONINa$: 354.0325; found: 354.0330.

4-(2-Iodoethyl)-*N*-methoxy-*N*-methylbenzamide (4m)

To a solution of *N*-methoxy-*N*-methyl-4-vinylbenzamide (prepared according to the literature procedure,[30] 6.31 g, 33 mmol) and $NaHCO_3$ (9.98 g, 119 mmol) in dichloromethane (165 mL), *m*CPBA (70%, 21.2 g, 85.8 mmol) was added portionwise at 0 °C. After 1 hour the reaction was warmed to room temperature and was stirred for 5 hours. The reaction was quenched with sat. aq. $Na_2S_2O_3$. The organic layer was separated and dried over Na_2SO_4. After the solvent was removed *in vacuo*, the crude was roughly purified by flash column chromatography (silica gel, hexane/EtOAc = 1/2, 2% Et_3N) to give the crude styrene oxide as a pale yellow oil (3.7 g).

The crude styrene oxide (3.7 g) and Pd/C (51% water, 10% Pd on the dehydrous basis, 1.43 g, ca. 0.67 mmol) were dissolved in methanol (84 mL) and the resulting solution was subjected to 1 atm of H_2 at room temperature. After 13 hours, the reaction mixture was filtered through a celite pad with methanol and the solvent was removed under reduced pressure. The crude was then roughly purified by flash column chromatography (silica gel, CH_2Cl_2/MeOH = 12/1) to afford the crude alcohol (1.31 g) as a light yellow oil.

According to the general procedure A, the crude phenethyl alcohol (1.31 g) was treated with iodine (1.54 g, 6.05 mmol), PPh_3 (1.59 g, 6.05 mmol) and imidazole (449 mg, 6.60 mmol) in CH_2Cl_2 (11 mL) to afford **4m** as a colorless oil (1.34 g, 4.13 mmol, 13% for 3 steps), R_f = 0.38 [hexane/EtOAc 1:1, UV]

IR (NaCl): 2966, 2933, 1643, 1420, 1376, 1220, 1172, 979, 629 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.55 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 3.29-3.20 (m, 5H), 3.14 (s, 3H), 3.11 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 169.2, 142.8, 132.2, 128.2, 127.6, 60.7, 39.6, 33.5, 4.7.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{11}H_{14}O_2NINa$: 341.9961; found: 341.9965.

2-(2-Iodoethyl)naphthalene (4n)

2-Naphthylacetic acid (2.5 g, 13 mmol) in Et_2O (56 mL) was added slowly to lithium aluminium hydride (1.0 g, 27 mmol) in Et_2O (11 ml) and stirred for 15 minutes at room temperature. The crude reaction mixture was quenched by adding water (1 mL), 15% aqueous NaOH (1 mL) and water (3 mL) sequentially. The resulting white solid was removed by filtering through a celite pad eluting with EtOAc. The organic layer was separated and dried over Na_2SO_4. After removal of the solvent, the crude product was purified by Yamazen YFLC AI-580 using Universal Column SiOH (hexane/EtOAc) to afford crude 2-(2-naphthyl)ethan-1-ol (2.1 g) as a white solid.

According to the general procedure A, the crude alcohol (2.1 g, ca. 12 mmol) was treated with iodine (3.4 g, 13 mmol), PPh_3 (3.5 g, 13 mmol) and imidazole (990 mg, 15 mmol). The crude product was purified by Yamazen YFLC AI-580 using Universal Column SiOH (hexane/EtOAc) to provide **4n** (2.0 g, 6.9 mmol) as a white solid (52% for 2 steps), mp 71-72 °C; R_f = 0.50 [hexane/EtOAc 9:1, UV]. NMR spectra of the obtained product were consistent with the reported one.[31]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.83-7.78 (m, 3H), 7.65 (s, 1H), 7.49-7.44 (m, 2H), 7.32 (dd, *J* = 8.3, 1.6 Hz, 1H), 3.44 (t, *J* = 7.4 Hz, 2H), 3.34 (t, *J* = 7.4 Hz, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 138.0, 133.5, 132.3, 128.3, 127.7, 127.6, 126.9, 126.5, 126.2, 125.6, 40.4, 5.4.

2-(2-Iodoethyl)-thiophene (4o)

According to the general procedure A, **4o** was prepared from 2-(2-thienyl)ethan-1-ol (1.00 g, 7.80 mmol), iodine (2.18 g, 8.58 mmol), PPh_3 (2.25 g, 8.58 mmol) and imidazole (637 mg, 9.36 mmol). The crude product was purified by Yamazen YFLC AI-580 using Universal Column SiOH (hexane/EtOAc) to provide **4o** (1.79 g, 96%) as a colorless oil, R_f = 0.40 [hexane, UV]. NMR spectra of the obtained product were consistent with the reported one.[32]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.17-7.12 (m, 1H), 6.95-6.90 (m, 1H), 6.88-6.80 (m, 1H), 3.38-3.30 (m, 4H).

^{13}C NMR ($CDCl_3$, 100 MHz,): δ = 142.8, 126.8, 125.1, 123.9, 34.1, 5.1.

General procedure B for α-alkylation of allyl 4-chlorophenyl sulfone 3: To a 30 mL flame dried flask with a balloon filled with argon, **3** (282 mg, 1.3 mmol), HMPA (452 μL, 2.6 mmol) and THF (6.5 mL) were added and cooled to −78 °C. *n*-Butyllithium (1.6 M in hexane, 834 μL, 1.3 mmol) was added dropwise to the solution, and the mixture was stirred at −78 °C for 30 minutes. Then, alkyl iodide **4** (2.6 mmol) was added, and the mixture was stirred at −78 °C for 2 hours. Then, acetic acid in THF (1 M, 1.3 mL) was slowly added via syringe, and the reaction mixture was warmed to room temperature. The mixture was concentrated under reduced pressure and the obtained crude material was purified by flash column chromatography (silica gel, hexane/EtOAc) to afford the α-alkylated product **5**.

1-Chloro-4-(pent-1-en-3-ylsulfonyl)benzene (5a)

According to the general procedure B, **5a** was prepared using **3** (1.84 g, 8.5 mmol), ethyl iodide **4a** (1.36 mL, 17 mmol), BuLi (1.6 M in hexane, 5.47 mL, 8.5 mmol) and HMPA (2.95 mL, 17 mmol) in THF (37 mL). **5a** was isolated as a white solid (1.67 g, 80%), mp 44-45 °C; R_f = 0.30 [hexane/EtOAc 4:1, UV, $KMnO_4$].

IR (KBr): 2971, 2926, 2874, 1912, 1638, 1583, 1476, 1394, 1316, 1290, 1276, 1146, 1087, 1012, 990, 953, 824, 754, 639 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.77 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 5.60 (ddd, *J* = 17.2, 10.0, 10.0 Hz, 1H), 5.33 (d, *J* = 10.4 Hz, 1H), 5.06 (d, *J* = 17.6 Hz, 1H), 3.44-3.35 (m, 1H), 2.24-2.10 (m, 1H), 1.74-1.60 (m, 1H), 0.96 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.3, 135.9, 130.7, 129.9, 129.1, 124.1, 71.6, 20.3, 11.1.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{11}H_{13}O_2ClNaS$: 267.0217; found: 267.0222.

1-Chloro-4-(hex-1-en-3-ylsulfonyl)benzene (5b)

According to the general procedure B, **5b** was prepared from **3** (282 mg, 1.3 mmol) and propyl iodide **4b** (0.77 mL, 2.6 mmol). **5b** was isolated as a colorless oil (227 mg, 67%), R_f = 0.56 [hexane/EtOAc 3:1, UV, $KMnO_4$].

IR (NaCl): 2961, 2873, 1582, 1476, 1318, 1147, 1088, 1013, 754, 637 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.77 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 9.2 Hz, 2H), 5.60 (ddd, *J* = 17.6, 10.4, 9.6 Hz, 1H), 5.30 (d, *J* = 10.0 Hz, 1H), 5.04 (d, *J* = 18.0 Hz, 1H), 3.54-3.44 (m, 1H), 2.11-2.01 (m, 1H), 1.72-1.59 (m, 1H), 1.52-1.37 (m, 1H), 1.33-1.18 (m, 1H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.2, 135.7, 130.6, 130.1, 129.0, 123.8, 69.7, 28.5, 19.6, 13.4.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{12}H_{15}O_2ClNaS$: 281.0374; found: 281.0378.

1-Chloro-4-((6-fluorohex-1-en-3-yl)sulfonyl)benzene (5c)

According to the general procedure B, **5c** was prepared from **3** (282 mg, 1.3 mmol) and 3-iodo-1-fluoropropane **4c** (253 μL, 2.6 mmol). **5c** was isolated as a white solid (341 mg, 95%), mp 43-44 °C; R_f = 0.38 [hexane/EtOAc 3:1, UV, $KMnO_4$].

IR (KBr): 2935, 1583, 1476, 1391, 1325, 1308, 1149, 1085, 1149, 1085, 934, 628 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.77 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 5.63 (ddd, *J* = 17.2, 10.0, 9.7 Hz, 1H), 5.34 (d, *J* = 10.0 Hz, 1H), 5.08 (d, *J* = 17.2 Hz, 1H), 4.52 (t, *J* = 5.4 Hz, 1H), 4.40 (t, *J* = 5.7 Hz, 1H), 3.54 (td, *J* = 9.7, 3.5 Hz, 1H), 2.32-2.20 (m, 1H), 1.86-1.60 (m, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.5, 135.6, 130.7, 129.8, 129.2, 124.4, 83.2 (d, $^1J_{CF}$ = 165.4 Hz), 69.5, 27.4 (d, $^2J_{CF}$ = 20.7 Hz), 23.2 (d, $^3J_{CF}$ = 4.6 Hz).

^{19}F NMR ($CDCl_3$, 372 MHz): δ = −220.1-−220.5 (m).

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{12}H_{14}O_2ClFNaS$: 299.0279; found: 299.0284.

1-Chloro-4-((5-methylhex-1-en-3-yl)sulfonyl)benzene (5d)

According to the general procedure B, **5d** was prepared from **3** (238 mg, 1.1 mmol), isobutyl iodide **4d** (255 μL, 2.2 mmol), BuLi (1.6 M in hexane, 710 μL, 1.1 mmol) and HMPA (383 μL, 2.2 mmol) in THF (5.5 mL). **5d** was isolated as a white solid (182 mg, 61%), mp 63-64 °C; R_f = 0.46 [hexane/EtOAc 4:1, UV, $KMnO_4$].

IR (KBr): 3456, 3015, 2970, 2359, 1739, 1437, 1366, 1217, 1092, 898, 649cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.76 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 5.58 (ddd, *J* = 17.2, 9.6, 9.6 Hz, 1H), 5.29 (d, *J* = 10.8 Hz, 1H), 5.04 (d, *J* = 17.2 Hz, 1H), 3.59-3.53 (m, 1H), 1.88-1.77 (m, 1H), 1.74-1.55 (m, 2H), 0.96 (d, *J* = 6.3 Hz, 3H), 0.83 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.2, 135.7, 130.6, 130.2, 129.0, 123.7, 68.6, 35.0, 25.0, 23.5, 20.5.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{13}H_{17}O_2ClNaS$: 295.0530; found: 259.0535.

1-Chloro-4-((1-phenylbut-3-en-2-yl)sulfonyl)benzene (5e)

According to the general procedure B, **5e** was prepared from **3** (282 mg, 1.3 mmol) and benzyl bromide **4e** (309 μL, 2.6 mmol). **5e** was isolated as a white solid (320 mg, 80%), mp 68-69 °C; R_f = 0.50 [hexane/EtOAc 3:1, UV, $KMnO_4$].

IR (KBr): 3016, 2967, 2946, 2137, 1740, 1437, 1366, 1216, 1145, 1091, 899, 634 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.30-7.16 (m, 3H), 7.14-7.08 (m, 2H), 5.65 (ddd, *J* = 16.8, 10.0, 10.0 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 4.80 (d, *J* = 17.6 Hz, 1H), 3.78-3.67 (m, 1H), 3.56 (dd, *J* = 14.0, 3.2 Hz, 1H), 2.90 (dd, *J* = 14.4, 11.6 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.3, 136.1, 135.5, 130.5, 129.2, 129.0, 128.4, 126.7, 124.5, 71.1, 33.0 (One aromatic carbon is overlapped).

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{22}H_{25}O_4ClNaS$: 329.0374; found: 329.0380.

1-Chloro-4-((5-phenylpent-1-en-3-yl)sulfonyl)benzene (5f)

According to the general procedure B, **5f** was prepared by treating **3** (282 mg, 1.3 mmol) with phenethyl iodide **4f** (370 μL, 2.6 mmol) for 6 h. **5f** was isolated as a white solid (339 mg, 81%), mp 60-61 °C; R_f = 0.31 [hexane/EtOAc 4:1, UV, $KMnO_4$].

IR (KBr): 1581, 1477, 1457, 1394, 1012, 948, 833, 786, 748, 559 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.31-7.20 (m, 3H), 7.13 (d, *J* = 7.2 Hz, 2H), 5.67 (ddd, *J* = 18.8, 8.5, 8.5 Hz, 1H), 5.39 (d, *J* = 10.3 Hz, 1H), 5.08 (d, *J* = 17.1 Hz, 1H), 3.52-3.43 (m, 1H), 2.84-2.75 (m, 1H), 2.59-2.49 (m, 1H), 2.49-2.40 (m, 1H), 2.04-1.92 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.4, 139.8, 135.7, 130.7, 129.9, 129.1, 128.6, 128.4, 126.4, 124.5, 69.0, 32.2, 28.2.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{17}H_{17}O_2ClNaS$: 343.0530; found: 343.0536.

1-Chloro-4-((5-(p-tolyl)pent-1-en-3-yl)sulfonyl)benzene (5g)

According to the general procedure B, **5g** was prepared from **3** (282 mg, 1.3 mmol) and **4g** (619 mg, 2.6 mmol). **5g** was isolated as a white solid (350 mg, 80%), mp 87-88 °C; R_f = 0.37 [hexane/EtOAc 4:1, UV, $KMnO_4$].

IR (KBr): 1299, 1273, 1149, 1087, 814, 756, 645 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.72 (d, *J* = 9.0 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 5.66 (ddd, *J* = 18.5, 8.5, 8.5 Hz, 1H), 5.38 (d, *J* = 9.9 Hz, 1H), 5.08 (d, *J* = 17.1 Hz, 1H), 3.51-3.42 (m, 1H), 2.80-2.70 (m, 1H), 2.55-2.36 (m, 2H), 2.32 (s, 3H), 2.00-1.89 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.1, 136.6, 135.6, 135.6, 130.5, 129.7, 129.1, 128.9, 128.1, 124.3, 68.8, 31.6, 28.2, 20.8.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{18}H_{19}O_2ClNaS$: 357.0687; found: 357.0694.

1-Chloro-4-((5-(4-methoxyphenyl)pent-1-en-3-yl)sulfonyl)benzene (5h)

According to the general procedure B, **5h** was prepared from **3** (282 mg, 1.3 mmol) and **4h** (681 mg, 2.6 mmol). **5h** was isolated as a white solid (374 mg, 82%), mp 68-69 °C; R_f = 0.55 [hexane/EtOAc 2:1, UV, $KMnO_4$].

IR (KBr): 2924, 1611, 1513, 1476, 1321, 1246, 1147, 1088, 951, 829, 815, 757, 709, 643 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.72 (d, *J* = 9.0 Hz, 2H), 7.49 (d, *J* = 9.0 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.65 (ddd, *J* = 18.5, 8.5, 8.5 Hz, 1H), 5.38 (d, *J* = 10.3 Hz, 1H), 5.07 (d, *J* = 17.5 Hz, 1H), 3.79 (s, 3H), 3.49-3.40 (m, 1H), 2.80-2.70 (m, 1H), 2.53-2.35 (m, 2H), 2.00-1.88 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.0, 140.2, 135.6, 131.7, 130.5, 129.8, 129.2, 129.0, 124.4, 113.8, 68.8, 55.1, 31.2, 28.3.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{18}H_{19}O_3ClNaS$: 373.0636; found: 373.0641.

1-Chloro-4-((5-(4-chlorophenyl)pent-1-en-3-yl)sulfonyl)benzene (5i)

According to the general procedure B, **5i** was prepared from **3** (282 mg, 1.3 mmol) and **4i** (693 mg, 2.6 mmol). **5i** was isolated as a white solid (364 mg, 79%), mp 58-59 °C; R_f = 0.56 [hexane/EtOAc 2:1, UV, $KMnO_4$].

IR (KBr): 3457, 3015, 2970, 1738, 1436, 1366, 1216, 1146, 1092, 898, 828, 763 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.72 (d, J = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 5.64 (ddd, *J* = 18.6, 8.6, 8.6 Hz, 1H), 5.37 (d, *J* = 10.4 Hz, 1H), 5.04 (d, *J* = 16.8 Hz, 1H), 3.47-3.38 (m, 1H), 2.82-2.71 (m, 1H), 2.58-2.47 (m, 1H), 2.47-2.37 (m, 1H), 2.02-1.91 (m, 1H),.

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.4, 138.3, 135.5, 132.1, 130.6, 129.8, 129.7, 129.2, 128.7, 124.6, 68.9, 31.6, 28.0.

HRMS (ESI): m/z calcd for $C_{17}H_{16}O_2Cl_2NaS$ [M+Na]$^+$: 377.0140; found:377.0147.

1-Chloro-4-((5-(4-(trifluoromethyl)phenyl)pent-1-en-3-yl)sulfonyl)benzene (5j)

According to the general procedure B, **5j** was prepared from **3** (282 mg, 1.3 mmol) and **4j** (780 mg, 2.6 mmol). **5j** was isolated as a white solid (407 mg, 81%), mp 50-51 °C; R_f = 0.32 [hexane/EtOAc 4:1, UV, $KMnO_4$].

IR (KBr): 2970, 1734, 1436, 1366, 1228, 1217, 1092, 900, 630 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73 (d, *J* = 9.1 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 9.1 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 5.67 (ddd, *J* = 18.7, 8.6, 8.6 Hz, 1H), 5.39 (d, *J* = 10.4 Hz, 1H), 5.06 (d, *J* = 17.2 Hz, 1H), 3.44 (td, *J* = 10.1, 3.3 Hz, 1H), 2.91-2.81 (m, 1H), 2.68-2.58 (m, 1H), 2.53-2.42 (m, 1H), 2.07-1.95 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.0, 140.3, 135.4, 130.5, 129.6, 129.1 (q, $^2J_{CF}$ = 57.2 Hz), 129.0, 128.6, 125.3 (q, $^3J_{CF}$ = 3.8 Hz), 124.5, 124.1 (q, $^1J_{CF}$ = 276.6 Hz), 68.8, 31.9, 27.8.

^{19}F NMR (372 MHz, $CDCl_3$): δ = –64.0 (s).

HRMS (ESI): m/z [M–H]$^-$ calcd for $C_{18}H_{15}O_2ClF_3S$: 387.0439; found: 387.0442.

***tert*-Butyl 4-(3-((4-chlorophenyl)sulfonyl)pent-4-en-1-yl)benzoate (5k)**

According to the general procedure B, **5k** was prepared from **3** (282 mg, 1.3 mmol) and **4k** (864 mg, 2.6 mmol). **5k** was isolated as a white solid (442 mg, 81%), mp 65-66 °C; R_f = 0.31 [hexane/EtOAc 4:1, UV, $KMnO_4$].

IR (KBr): 2980, 1699, 1582, 1475, 1392, 1367, 1296, 1177, 1141, 1085, 1013, 928, 824, 756, 631 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ = 8.12 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 5.37 (ddd, *J* = 18.5, 8.6, 8.6 Hz, 1H), 4.85 (d, *J* = 10.3 Hz, 1H), 4.55 (d, *J* = 17.1 Hz, 1H), 3.19-3.10 (m, 1H), 2.49-2.37 (m, 2H), 2.24-2.10 (m, 1H), 1.89-1.76 (m, 1H), 1.48 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ = 165.5, 144.6, 140.4, 135.5, 130.6, 130.2, 129.8, 129.7, 129.1, 128.2, 124.6, 80.9, 68.9, 32.1, 28.1, 27.8.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{22}H_{25}O_4ClNaS$: 443.1054; found: 443.1065.

4-(3-((4-Chlorophenyl)sulfonyl)pent-4-en-1-yl)-*N*,*N*-diethylbenzamide (5l)

According to the general procedure B, **5l** was prepared from **3** (282 mg, 1.3 mmol) and **4l** (861 mg, 2.6 mmol). **5l** was isolated as a white solid (445 mg, 82%), mp 85-86 °C; R_f = 0.37 [hexane/EtOAc 1:2, UV, $KMnO_4$].

IR (KBr): 2973, 1631, 1582, 1427, 1291, 1146, 1090, 1016, 827, 754, 638 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 5.66 (ddd, *J* = 18.4, 8.4, 8.4 Hz, 1H), 5.37 (d, *J* = 10.4 Hz, 1H), 5.03 (d, *J* = 17.2 Hz, 1H), 3.49-3.41 (m, 1H), 3.64-3.17 (m, 4H), 2.88-2.79 (m, 1H), 2.63-2.51 (m, 2H), 2.08-1.94 (m, 1H), 1.33-1.03 (m, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.1, 140.9, 140.5, 135.5, 135.4, 130.6, 129.9, 129.1, 128.4, 126.7, 124.6, 68.9, 43.2, 39.2, 31.9, 27.9, 14.2, 12.9.

HRMS (ESI): m/z calcd for $C_{22}H_{26}O_3NClNaS$ [M+Na]$^+$: 442.1214, found: 442.1222.

4-(3-((4-Chlorophenyl)sulfonyl)pent-4-en-1-yl)-*N*-methoxy-*N*-methylbenzamide (5m)

According to the general procedure B, **5m** was prepared from **3** (282 mg, 1.3 mmol) and **4m** (830 mg, 2.6 mmol). **5m** was isolated as a white solid (411 mg, 76%), mp 71-72 °C; R_f = 0.50 [hexane/EtOAc 1:2, UV, $KMnO_4$].

IR (KBr): 2934, 1628, 1393, 1311, 1146, 1087, 977, 945, 751, 636 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.73 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.66 (ddd, *J* = 18.5, 8.6, 8.6 Hz, 1H), 5.37 (d, *J* = 10.3 Hz, 1H), 5.06 (d, *J* = 17.2 Hz, 1H), 3.56 (s, 3H), 3.52-3.45 (m, 1H), 3.35 (s, 3H), 2.88-2.79 (m, 1H), 2.64-2.55 (m, 1H), 2.52-2.41 (m, 1H), 2.05-1.96 (m, 1H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 169.4, 142.5, 140.1, 135.3, 131.9, 130.4, 129.6, 128.9, 128.3, 127.8, 124.4, 68.6, 60.8, 33.5, 31.8, 27.6.

HRMS (ESI): m/z calcd for $C_{20}H_{22}O_4NClNaS$ [M+Na]$^+$: 430.0850, found: 430.0858.

2-(3-((4-Chlorophenyl)sulfonyl)pent-4-en-1-yl)naphthalene (5n)

According to the general procedure B, **5n** was prepared from **3** (282 mg, 1.3 mmol) and **4n** (734 mg, 2.6 mmol). **5n** was isolated as a white solid (427 mg, 89%), mp 71-72 °C; R_f = 0.36 [hexane/EtOAc 4:1, UV, $KMnO_4$].

IR (KBr): 3053, 2919, 1581, 1474, 1324, 1276, 1146, 1087, 1012, 939, 824, 754, 641 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.83-7.68 (m, 5H), 7.55 (s, 1H), 7.49-7.42 (m, 4H), 7.27-7.24 (m, 1H), 5.75-5.66 (m, 1H), 5.41 (d, *J* = 9.4 Hz, 1H), 5.08 (d, *J* = 17.1 Hz, 1H), 3.52-3.46 (m, 1H), 3.01-2.94 (m, 1H), 2.71 (dt, *J* = 15.7, 7.0 Hz, 1H), 2.60-2.50 (m, 1H), 2.13-2.02 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.3, 137.2, 135.6, 133.4, 132.1, 130.6, 129.9, 129.1, 128.3, 127.6, 127.4, 126.8, 126.7, 126.1, 125.5, 124.5, 68.9, 32.3, 28.0.

HRMS (ESI): m/z calcd for $[M+Na]^+$ $C_{21}H_{19}O_2ClNaS$: 393.0687; found: 393.0696.

2-(3-((4-Chlorophenyl)sulfonyl)pent-4-en-1-yl)thiophene (5o)

According to the general procedure B, **5o** was prepared from **3** (282 mg, 1.3 mmol) and **4o** (619 mg, 2.6 mmol). **5o** was isolated as a white solid (322 mg, 76%), mp 67-68 °C; R_f = 0.44 [hexane/EtOAc 4:1, UV, $KMnO_4$].

IR (KBr): 3106, 2956, 1580, 1478, 1314, 1278, 1145, 1088, 1012, 945, 831, 752, 708, 632, 562 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.75 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.13 (dd, *J* = 5.0, 1.4 Hz, 1H), 6.92 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.77 (dd, *J* = 3.6, 0.9 Hz, 1H), 5.65 (ddd, *J* = 18.6, 8.6, 8.6 Hz, 1H), 5.38 (d, *J* = 9.5 Hz, 1H), 5.09 (d, *J* = 17.2 Hz, 1H), 3.56-3.47 (m, 1H), 3.04-2.95 (m, 1H), 2.86-2.75 (m, 1H), 2.53-2.41 (m, 1H), 2.10-1.97 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 142.2, 140.2, 135.5, 130.5, 129.4, 129.0, 126.8, 124.7, 124.6, 123.5, 68.5, 28.4, 26.2.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{15}H_{15}O_2ClNaS$: 349.0094; found: 349.0101.

General procedure C for photoredox/cobalt-catalyzed allylic substitution of the sulfones derived from 3: A pronucleophile **2** (0.66 mmol, 2.2 equiv) was added dropwise over ca. 5 min to a slurry of sodium hydride (0.6 mmol, 2.0 equiv) in anhydrous THF (1.0 mL), resulting in the evolution of H_2 gas. In an argon-filled glovebox, a dry screw cap vial was charged with an allyl sulfone **5** (0.30 mmol, 1.0 equiv), $CoBr_2$ (7.5 μmol, 2.5 mol%), dppp (7.5 μmol, 2.5 mol%), 4CzIPN (0.75 μmol, 0.25 mol%), *i*Pr_2NEt (0.60 mmol, 2.0 equiv), activated 4Å molecular sieves (60 mg), and THF (0.5 mL). Then, the nucleophile solution was added to this solution. The vial was capped, and then removed from the glove box, and placed in front of the light source (4–5 cm from blue LED). After the mixture was stirred at room temperature for 18 h, the reaction was quenched with H_2O and poured into EtOAc. The organic layer was separated and dried over anhydrous Na_2SO_4. After the solvent was removed *in vacuo*, the crude was analyzed by ^1H NMR to determine the ratio of branched/linear product. The crude was purified by flash column chromatography (silica gel, hexane/EtOAc) to afford the allylic substitution product **6**.

Dimethyl 2-(pent-1-en-3-yl)malonate (6aa)

According to the general procedure C, **6aa** was prepared from **5a** (73 mg, 0.30 mmol) and **2a** (87 mg, 0.66 mmol). **6aa** was isolated as a colorless oil (45 mg, 74%), R_f = 0.29 [hexane/EtOAc 5:1, UV, $KMnO_4$].

IR (NaCl): 3080, 2958, 2877, 1739, 1641, 1436, 1263, 1197, 1147, 1025, 923, 773, 678 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 5.67-5.57 (m, 1H), 5.13-5.06 (m, 2H), 3.74 (s, 3H), 3.69 (s, 3H), 3.40 (d, *J* = 9.2 Hz, 1H), 2.68 (ddd, *J* = 18.9, 9.3, 3.7 Hz, 1H), 1.58-1.46 (m, 1H), 1.37-1.24 (m, 1H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.8, 168.6, 137.7, 117.6, 56.6, 52.4, 52.2, 45.8, 25.2, 11.5.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{10}H_{16}O_4Na$: 223.0941; found: 223.0946.

Dimethyl 2-(hex-1-en-3-yl)malonate (6ba)

According to the general procedure C, **6ba** was prepared from **5b** (78 mg, 0.30 mmol) and **2a** (87 mg, 0.66 mmol). **6ba** was isolated as a colorless oil (53 mg, 83%), R_f = 0.27 [hexane/EtOAc 8:1, UV, $KMnO_4$]. NMR spectra of the obtained product were consistent with the reported one.[33]

^1H NMR ($CDCl_3$, 400 MHz,): δ = 5.63 (ddd, *J* = 18.8, 8.5, 8.5 Hz, 1H), 5.12-5.05 (m, 2H), 3.74 (s, 3H), 3.69 (s, 3H), 3.38 (d, *J* = 9.0 Hz, 1H), 2.78 (ddd, *J* = 18.5, 9.3, 3.3 Hz, 1H), 1.45-1.18 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.8, 168.6, 138.1, 117.3, 56.9, 52.3, 52.2, 44.0, 34.4, 20.1, 13.8.

Dimethyl 2-(6-fluorohex-1-en-3-yl)malonate (6ca)

According to the general procedure C, **6ca** was prepared from **5c** (83 mg, 0.30 mmol) and **2a** (87 mg, 0.66 mmol). **6ca** was isolated as a colorless oil (51 mg, 73%), R_f = 0.30 [hexane/EtOAc 5:1, UV, $KMnO_4$].

IR (NaCl): 2956, 1738, 1641, 1436, 1242, 1160, 1018, 927, 678 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 5.68-5.59 (m, 1H), 5.14-5.10 (m, 2H), 4.48 (t, *J* = 5.9 Hz, 1H), 4.36 (t, *J* = 5.9 Hz, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 3.40 (d, *J* = 9.1 Hz, 1H), 2.83-2.76 (m, 1H), 1.83-1.55 (m, 3H), 1.45-1.36 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.5, 168.4, 137.4, 118.1, 83.6 (d, $^1J_{CF}$ = 165.0 Hz), 56.8, 52.5, 52.3, 43.9, 28.0 (d, $^2J_{CF}$ = 20.0 Hz), 27.9 (d, $^3J_{CF}$ =5.7 Hz).

^{19}F NMR ($CDCl_3$, 372 MHz): δ = −219.4-−219.9 (m).

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{11}H_{18}O_4F$: 233.1184; found: 233.1190.

Dimethyl 2-(5-methylhex-1-en-3-yl)malonate (6da)

According to the general procedure C, **6da** was prepared from **6d** (82 mg, 0.30 mmol) and **2a** (87 mg, 0.6 mmol). **6da** was isolated as a colorless oil (59 mg, 86%), R_f = 0.29 [hexane/EtOAc 8:1, UV, $KMnO_4$]. NMR spectra of the obtained product were consistent with the reported one.[12]

^1H NMR ($CDCl_3$, 400 MHz): δ = 5.61 (ddd, *J* = 18.5, 8.5, 8.5 Hz, 1H), 5.13-5.03 (m, 2H), 3.74 (s, 3H), 3.69 (s, 3H), 3.35 (d, *J* = 9.0 Hz, 1H), 2.87 (ddd, *J* = 20.0, 9.2, 3.6 Hz, 1H), 1.36-1.23 (m, 1H), 1.63-1.51 (m, 1H), 1.18-1.09 (m, 1H), 0.90-0.85 (m, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.7, 168.5, 138.1, 117.3, 57.3, 52.3, 52.1, 42.3, 41.5, 25.2, 23.7, 20.9.

Dimethyl 2-(1-phenylbut-3-en-2-yl)malonate (6ea)

According to the general procedure C, **6ea** was prepared from **5e** (92 mg, 0.30 mmol) and **2a** (87 mg, 0.66 mmol). **6ea** was isolated as a colorless oil (48 mg, 61%), R_f = 0.30 [hexane/EtOAc 4:1, UV, $KMnO_4$].

IR (NaCl): 3084, 3028, 2953, 2846, 1737, 1641, 1604, 1496, 1454, 1436, 1257, 1157, 999, 923, 802, 746, 702, 679, 582 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.30-7.24 (m, 2H), 7.22-7.13 (m, 3H), 5.74 (ddd, *J* = 17.7, 9.8, 7.9 Hz, 1H), 5.00 (d, *J* = 9.8 Hz, 1H), 4.94 (d, *J* = 17.7 Hz, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.46 (d, *J* = 8.2 Hz, 1H), 3.15-3.06 (m, 1H), 2.86 (dd, *J* = 13.5, 5.4 Hz, 1H), 2.65 (dd, *J* = 13.5, 8.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.8, 168.5, 138.9, 137.2, 129.3, 128.2, 126.3, 117.6, 55.7, 52.5, 52.3, 45.6, 38.8.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{15}H_{18}O_4Na$: 285.1097; found: 285.1101.

Dimethyl 2-(5-phenylpent-1-en-3-yl)malonate (6fa)

According to the general procedure C, **6fa** was prepared from **5f** (96 mg, 0.30 mmol) and **2a** (87 mg, 0.66 mmol). **6fa** was isolated as a colorless

oil (77 mg, 93%), R_f = 0.31 [hexane/EtOAc 6:1, UV, $KMnO_4$]. NMR spectra of the obtained product were consistent with the reported one.[34]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.30-7.25 (m, 2H), 7.20-7.14 (m, 3H), 5.71 (ddd, *J* = 18.0, 10.4, 8.4 Hz, 1H), 5.16 (d, *J* = 10.4 Hz, 1H), 5.14 (d, *J* = 18.0 Hz, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 3.42 (d, *J* = 9.0 Hz, 1H), 2.82 (m, 1H), 2.72-2.66 (m, 1H), 2.54-2.48 (m, 1H), 1.84-1.77 (m, 1H), 1.63 (ddt, *J* = 18.2, 10.5, 3.9 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.6, 168.4, 141.7, 137.6, 128.3, 128.3, 125.8, 118.1, 56.8, 52.4, 52.2, 43.9, 34.0, 33.3,.

Dimethyl 2-(5-(p-tolyl)pent-1-en-3-yl)malonate (6ga)

According to the general procedure C, **6ga** was prepared from **5g** (101 mg, 0.30 mmol) and **2a** (87 mg, 0.66 mmol). **6ga** was isolated as a colorless oil (73 mg, 84%), R_f = 0.28 [hexane/EtOAc 6:1, UV, $KMnO_4$].

IR (NaCl): 3471, 3079, 3004, 2952, 2860, 2360, 1737, 1642, 1515, 1435, 1246, 1153, 1021, 923, 808, 756, 735, 679 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.08 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 5.70 (ddd, *J* = 18.2, 8.8, 7.9 Hz, 1H), 5.18-5.10 (m, 2H), 3.71 (s, 3H), 3.68 (s, 3H), 3.41 (d, *J* = 8.5 Hz, 1H), 2.81 (ddd, *J* = 19.0, 9.5, 3.3 Hz, 1H), 2.88-2.76 (m, 1H), 2.70-2.61 (m, 1H), 2.52-2.42 (m, 1H), 2.31 (s, 3H), 1.83-1.72 (m, 1H), 1.65-1.53 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.6, 168.4, 20.9, 32.8, 34.1, 43.9, 52.2, 52.4, 56.8, 118.1, 128.2, 129.0, 135.2, 137.6, 138.5,.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{17}H_{22}O_4Na$: 313.1410; found: 313.1408.

Dimethyl 2-(5-(4-methoxylphenyl)pent-1-en-3-yl)malonate (6ha)

According to the general procedure C, **6ha** was prepared from **5h** (105 mg, 0.30 mmol) and **2a** (87 mg, 0.66 mmol). **6ha** was isolated as a colorless oil (82 mg, 89%), R_f = 0.27 [hexane/EtOAc 3:1, UV, $KMnO_4$].

IR (NaCl): 3000, 2952, 2838, 1737, 1641, 1612, 1583, 1513, 1436, 1246, 1154, 1246, 1154, 1035, 924, 679, 747 679 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.13 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.71 (m, 1H), 5.17-5.09 (m, 2H), 3.77 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 3.41 (d, *J* = 8.6 Hz, 1H), 2.81 (ddd, *J* = 19.1, 9.4, 3.3 Hz, 1H), 2.69-2.58 (m, 1H), 2.51-2.40 (m, 1H), 1.83-1.70 (m, 1H), 1.64-1.54 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.6, 168.4, 157.7, 137.6, 133.6, 129.2, 118.0, 113.7, 56.7, 55.1, 52.4, 52.2, 43.8, 34.2, 32.3.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{17}H_{22}O_5Na$: 329.1359; found: 329.1358.

Dimethyl 2-(5-(4-chlorophenyl)pent-1-en-3-yl)malonate (6ia)

According to the general procedure C, **6ia** was prepared from **5i** (107 mg, 0.30 mmol) and **2a** (87 mg, 0.66 mmol). **6ia** was isolated as a colorless oil (89 mg, 95%), R_f = 0.30 [hexane/EtOAc 6:1, UV, $KMnO_4$].

IR (NaCl): 3080, 2952, 2861, 2359, 1738, 1642, 1493, 1435, 1245, 1154, 1092, 1015, 925, 807, 680 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.23 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 5.69 (ddd, *J* = 18.7, 8.5, 8.5 Hz, 1H), 5.18-5.09 (m, 2H), 3.71 (s, 3H), 3.68 (s, 3H), 3.41 (d, *J* = 8.5 Hz, 1H), 2.79 (ddd, *J* = 19.3, 9.4, 3.1 Hz, 1H), 2.70-2.61 (m, 1H), 2.54-2.43 (m, 1H), 1.84-1.73 (m, 1H), 1.65-1.54 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.5, 168.3, 140.0, 137.4, 131.5, 129.7, 128.4, 118.3, 56.7, 52.4, 52.3, 43.6, 33.7, 32.6.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{16}H_{19}O_4ClNa$: 333.0864; found: 333.0863.

Dimethyl 2-(5-(4-trifluoromethylphenyl)pent-1-en-3-yl)malonate (6ja)

According to the general procedure C, **6ja** was prepared from **5j** (117 mg, 0.30 mmol) and **2a** (87 mg, 0.66 mmol). **6ja** was isolated as a colorless oil (97 mg, 94%), R_f = 0.48 [hexane/EtOAc 3:1, UV, $KMnO_4$].

IR (NaCl): 2954, 2361, 1738, 1618, 1436, 1326, 1247, 1121, 1067, 1018, 926, 823, 680, 598 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.52 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 5.70 (ddd, *J* = 18.9, 8.5, 8.5 Hz, 1H), 5.20-5.11 (m, 2H), 3.71 (s, 3H), 3.69 (s, 3H), 3.42 (d, *J* = 8.6 Hz, 1H), 2.86-2.70 (m, 2H), 2.62-2.53 (m, 1H), 1.88-1.78 (m, 1H), 1.70-1.57 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.5, 168.3, 145.7, 137.4, 128.7, 128.2 (q, $^2J_{CF}$ = 32.6 Hz), 125.2 (q, $^3J_{CF}$ = 3.8 Hz), 121.9 (q, $^1J_{CF}$ = 211.7 Hz), 118.4, 56.7, 52.4, 52.3, 43.7, 33.5, 33.1.

^{19}F NMR ($CDCl_3$, 372 MHz): δ = –64.1 (s).

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{17}H_{19}O_4F_3Na$: 367.1128; found: 367.1124.

Dimethyl 2-(5-(4-*tert*-butoxycarbonylphenyl)pent-1-en-3-yl)malonate (6ka)

According to the general procedure C, **6ka** was prepared from **5k** (126 mg, 0.30 mmol) and **2a** (87 mg, 0.66 mmol). **6ka** was isolated as a colorless oil (97 mg, 86%), R_f = 0.30 [hexane/EtOAc 4:1, UV, $KMnO_4$].

IR (NaCl): 2952, 1739, 1711, 1611, 1435, 1392, 1368, 1292, 1165, 1117, 1019, 925, 850, 769, 705 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.90 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 5.70 (ddd, *J* = 18.5, 8.4, 8.4 Hz, 1H), 5.19-5.10 (m, 2H), 3.72 (s, 3H), 3.68 (s, 3H), 3.41 (d, *J* = 9.0 Hz, 1H), 2.84-2.69 (m, 2H), 2.61-2.51 (m, 1H), 1.88-1.76 (m, 1H), 1.59 (s, 9H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.5, 168.3, 165.7, 146.5, 137.4, 129.7, 129.5, 128.2, 118.4, 80.7, 56.7, 52.4, 52.3, 43.7, 33.5, 33.2, 28.1.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{21}H_{28}O_6Na$: 399.1778; found: 399.1773.

Dimethyl 2-(5-(4-(diethylcarbamoyl)phenyl)pent-1-en-3-yl)malonate (6la)

According to the general procedure C, **6la** was prepared from **5l** (126 mg, 0.30 mmol) and **2a** (87 mg, 0.66 mmol). **6la** was isolated as a colorless oil (97 mg, 86%), R_f = 0.29 [hexane/EtOAc 1:2, UV, $KMnO_4$].

IR (NaCl): 3472, 2951, 2236, 1737, 1630, 1432, 1381, 1363, 1347, 1287, 1154, 1095, 1020, 923, 840, 732, 571 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.29 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.71 (ddd, *J* = 18.7, 8.4, 8.4 Hz, 1H), 5.19-5.11 (m, 2H), 3.72 (s, 3H), 3.69 (s, 3H), 3.42 (d, *J* = 8.6 Hz, 1H), 3.59-3.20 (m, 4H), 2.81 (ddd, *J* = 19.0, 9.3, 3.0 Hz, 1H), 2.75-2.66 (m, 1H), 2.58-2.49 (m, 1H), 1.86-1.76 (m, 1H), 1.67-1.57 (m, 1H), 1.29-1.05 (m, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 171.2, 168.4, 168.2, 142.7, 137.4, 134.7, 128.2, 126.3, 118.1, 56.5, 52.3, 52.1, 43.6, 43.1, 39.0, 33.6, 33.0, 14.0, 12.8.

HRMS (ESI): m/z [M+Na]$^+$ calcd for $C_{21}H_{29}O_5NNa$: 398.1938; found: 398.1932.

Dimethyl 2-(5-(4-(methoxy(methyl)carbamoyl)phenyl)pent-1-en-3-yl)malonate (6ma)

According to the general procedure C, **6ma** was prepared from **5m** (122 mg, 0.30 mmol) and **2a** (87 mg, 0.66 mmol). **6ma** was isolated as a colorless oil (85 mg, 78%), R_f = 0.28 [hexane/EtOAc 1:1, UV, $KMnO_4$].

IR (NaCl): 2952, 2245, 1737, 1642, 1567, 1435, 1375, 1246, 1154, 1065, 998, 923, 889, 848, 756, 733, 677, 618, 568 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.61 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.71 (ddd, *J* = 18.7, 8.5, 8.5 Hz, 1H), 5.19-5.11 (m, 2H), 3.72 (s, 3H), 3.69 (s, 3H), 3.57 (s, 3H), 3.42 (d, *J* = 8.6 Hz, 1H), 3.35 (s, 3H), 2.88-2.68 (m, 2H), 2.60-2.49 (m, 1H), 1.90-1.77 (m, 1H), 1.70-1.58 (m, 1H),.

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 169.8, 168.5, 168.3, 144.5, 137.4, 131.6, 128.3, 127.9, 118.3, 60.9, 56.7, 52.4, 52.2, 43.7, 33.5, 33.2 (One aliphatic carbon is overlapped).

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{25}O_6NNa$: 386.1574; found: 386.1567.

Dimethyl 2-(5-(naphthalen-2-yl)pent-1-en-3-yl)malonate (6na)

According to the general procedure C, **6na** was prepared from **5n** (111 mg, 0.30 mmol) and **2a** (87 mg, 0.66 mmol). **6na** was isolated as a colorless oil (86 mg, 87%), R_f = 0.32 [hexane/EtOAc 4:1, UV, $KMnO_4$].

IR (NaCl): 2952, 1737, 1435, 1244, 1151, 997, 923, 811, 747 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.71-7.66 (m, 3H), 7.50 (s, 1H), 7.37-7.30 (m, 2H), 7.22-7.18 (m, 1H), 5.66 (ddd *J* = 18.7, 8.5, 8.5 Hz, 1H), 5.12-5.06 (m, 2H), 3.61 (s, 3H), 3.59 (s, 3H), 3.36 (d, *J* = 8.6 Hz, 1H), 2.83-2.71 (m, 2H), 2.59 (ddd, *J* = 15.4, 8.6, 5.4 Hz, 1H), 1.86-1.77 (m, 1H), 1.67-1.57 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.5, 168.4, 139.1, 137.6, 133.5, 132.0, 127.9, 127.5, 127.3, 127.2, 126.3, 125.8, 125.1, 118.2, 56.8, 52.4, 52.2, 43.9, 33.8, 33.4.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{20}H_{22}O_4Na$: 349.1410; found: 349.1418.

Dimethyl 2-(5-(thiophen-2-yl)pent-1-en-3-yl)malonate (6oa)

According to the general procedure C, **6oa** was prepared from **5o** (98 mg, 0.30 mmol) and **2a** (87 mg, 0.66 mmol). **6oa** was isolated as a colorless oil (78 mg, 92%), R_f = 0.30 [hexane/EtOAc 6:1, UV, $KMnO_4$].

IR (NaCl): 2952, 2850, 1738, 1641, 1435, 1251, 1152, 1001, 925, 849, 698 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.10 (dd, *J* = 5.2, 1.1 Hz, 1H), 6.90 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.77 (dd, *J* = 3.5, 1.0 Hz, 1H), 5.68 (ddd, *J* = 18.5, 8.4, 8.4 Hz, 1H), 5.17-5.11 (m, 2H), 3.72 (s, 3H), 3.69 (s, 3H), 3.42 (d, *J* = 8.6 Hz, 1H), 2.93-2.70 (m, 3H), 1.91-1.82 (m, 1H), 1.74-1.65 (m, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.5, 168.3, 144.3, 137.3, 126.7, 124.2, 123.0, 118.4, 56.7, 52.4, 52.2, 43.5, 34.0, 27.3.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{14}H_{18}O_4NaS$: 305.0818; found: 305.0816.

Diethyl 2-(5-phenylpent-1-en-3-yl)malonate (6fb)

According to the general procedure C, **6fb** was prepared from **6f** (96 mg, 0.30 mmol) and diethyl malonate **2b** (106 mg, 0.66 mmol). **6fb** was isolated as a colorless oil (76 mg, 83%), R_f = 0.28 [hexane/EtOAc 9:1, UV, $KMnO_4$]. NMR spectra of the obtained product were consistent with the reported one.[35]

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.29-7.23 (m, 2H), 7.19-7.13 (m, 3H), 5.73 (ddd, *J* = 18.3, 9.1, 7.7 Hz, 1H), 5.17-5.11 (m, 2H), 4.21-4.11 (m, 4H), 3.37 (d, *J* = 8.6 Hz, 1H), 2.82 (ddd, *J* = 19.0, 9.3, 3.4 Hz, 1H), 2.75-2.64 (m, 1H), 2.56-2.47 (m, 1H), 1.88-1.77 (m, 1H), 1.68-1.57 (m, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.2, 168.1, 141.8, 137.8, 128.3, 128.3, 125.8, 118.0, 61.3, 61.1, 56.9, 43.7, 34.0, 33.3, 14.0 (One aliphatic carbon is overlapped).

Dibenzyl 2-(pent-1-en-3-yl)malonate (6ac)

According to the general procedure C, **6ac** was prepared from **5a** (73 mg, 0.30 mmol) and dibenzyl malonate **2c** (188 mg, 0.66 mmol). **6ac** was isolated as a colorless oil (86 mg, 81%), R_f = 0.29 [hexane/EtOAc 9:1, UV, $KMnO_4$].

IR (NaCl): 3067, 3033, 2964, 2875, 2359, 1735, 1456, 1378, 1261, 1218, 1142, 1001, 922, 750, 697, 597 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.33-7.26 (m, 10H), 5.66-5.57 (m, 1H), 5.14 (s, 2H), 5.09 (s, 2H), 5.05-4.98 (m, 2H), 3.48 (d, *J* = 8.8 Hz, 1H), 2.71 (ddd, *J* = 18.7, 9.2, 3.7 Hz, 1H), 1.55-1.44 (m, 1H), 1.35-1.22 (m, 1H), 0.84 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.1, 167.9, 137.6, 135.4, 135.3, 128.5, 128.4, 128.3, 128.2, 128.2, 128.2, 117.6, 67.0, 66.9, 56.7, 45.7, 25.2, 11.4.

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{22}H_{24}O_4Na$: 375.1567; found: 375.1562.

Bis(4-methylbenzyl) 2-(pent-1-en-3-yl)malonate (6ad)

According to the general procedure C, **6ad** was prepared from **5a** (73 mg, 0.30 mmol) and bis(4-methylbenzyl) malonate **2d** (206 mg, 0.66 mmol). **6ad** was isolated as a colorless oil (87 mg, 76%), R_f = 0.32 [hexane/EtOAc 8:1, UV, $KMnO_4$].

IR (NaCl): 2964, 1735, 1519, 1455, 1377, 1142, 995, 805 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.20-7.10 (m, 8H), 5.65-5.55 (m, 1H), 5.10-4.98 (m, 6H), 3.45 (d, *J* = 8.5 Hz, 1H), 2.74-2.64 (m, 1H), 2.34 (s, 6H), 1.55-1.43 (m, 1H), 1.33-1.22 (m, 1H), 0.83 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.1, 167.9, 138.0, 138.0, 137.6, 132.3, 132.3, 129.1, 129.1, 128.4, 128.3, 117.6, 66.9, 66.8, 56.7, 45.7, 25.2, 21.1, 11.4 (One aliphatic carbon is overlapped).

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{24}H_{28}O_4Na$: 403.1880; found: 403.1888.

Bis(4-methoxybenzyl) 2-(pent-1-en-3-yl)malonate (6ae)

According to the general procedure C, **6ae** was prepared from **5a** (73 mg, 0.30 mmol) and bis(4-methoxybenzyl) malonate **2e** (227 mg, 0.66 mmol). **6ae** was isolated as a colorless oil (100 mg, 81%), R_f = 0.31 [hexane/EtOAc 4:1, UV, $KMnO_4$].

IR (NaCl): 2962, 2837, 2060, 1732, 1613, 1516, 1463, 1377, 1303, 1250, 1175, 1142, 1034, 823, 567 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.24-7.18 (m, 4H), 6.87-6.82 (m, 4H), 5.64-5.54 (m, 1H), 5.06 (s, 2H), 5.02 (s, 2H), 5.03-4.97 (m, 2H), 3.79 (s, 6H), 3.42 (d, *J* = 9.0 Hz, 1H), 2.68 (ddd, *J* = 18.5, 9.3, 3.7 Hz, 1H), 1.54-1.43 (m, 1H), 1.33-1.20 (m, 1H), 0.83 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.1, 168.0, 159.6, 137.6, 130.1, 130.0, 127.5, 127.5, 113.8, 113.8, 117.5, 66.8, 66.7, 56.7, 55.2, 45.7, 25.2, 11.4 (One aliphatic and one aromatic carbons are overlapped).

HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{24}H_{28}O_6Na$: 435.1778; found: 435.1781.

2-(Pent-1-en-3-yl)malononitrile (6af)

According to the general procedure C, **6af** was prepared from **5a** (73 mg, 0.30 mmol) and malononitrile **2f** (44 mg, 0.66 mmol). **6af** was isolated as a colorless oil (29 mg, 72%), R_f = 0.30 [hexane/CH_2Cl_2 1:2, UV, $KMnO_4$].

IR (NaCl): 3087, 2970, 2933, 2880, 2256, 1725, 1643, 1462, 1424, 1384, 1297, 1220, 1120, 992, 936, 888, 771, 672 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.85 (m, 1H, linear isomer), 5.68 (ddd, *J* = 18.0, 8.9, 7.8 Hz, 1H), 5.47-5.35 (m, 2H, two isomers overlapped), 3.73 (m, 1H, two isomers overlapped), 2.69 (t, *J* = 7.0 Hz, 1H, linear isomer), 2.56 (m, 1H), 2.11 (t, *J* = 7.2 Hz, 1H, linear isomer), 1.85-1.55 (m, 2H, two isomers overlapped), 1.01-0.97 (m, 3H, two isomers overlapped).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.7 (linear isomer), 133.7, 121.6, 119.5 (linear isomer), 112.2 (linear isomer), 111.8, 111.6, 46.6, 33.8 (linear isomer), 28.3, 25.4 (linear isomer), 24.8, 23.4 (linear isomer), 13.1 (linear isomer), 11.2.

HRMS (ESI): m/z $[M-H]^-$ calcd for $C_8H_9N_2$: 133.0771; found: 133.0767.

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO (this text will be deleted prior to publication)

References

(1) Selected reviews on palladium-catalyzed Tsuji–Trost reaction: (a) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (b) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921. (c) Graening, T.; Schmalz, H.-G. *Angew. Chem. Int. Ed.* **2003**, *42*, 2580. (d) Trost, B. M. *J. Org. Chem.* **2004**, *69*, 5813. (e) Lu, Z.; Ma, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 258. (f) Trost, B. M.; Zhang, T.; Sieber, J. D. *Chem. Sci.* **2010**, *1*, 427. (g) Oliver, S.; Evans, P. A. *Synthesis* **2013**, *45*, 3179. (h) Butt, N. A.; Zhang, W. *Chem. Soc. Rev.* **2015**, *44*, 7929. (i) Trost, B. M. *Tetrahedron* **2015**, *71*, 5708.

(2) A selected review on ruthenium-catalyzed allylic substitution: Kitamura, M.; Miyata, K.; Seki, T.; Vatmurge, N.; Tanaka, S. *Pure Appl. Chem.* **2013**, *85*, 1121.

(3) Selected reviews on rhodium-catalyzed allylic substitution: (a) Turnbull, B. W. H.; Evans, P. A. *J. Org. Chem.* **2018**, *83*, 11463. (b) Thoke, M. B.; Kang, Q. *Synthesis* **2019**, *51*, 2585. Selected examples: (c) Evans, P. A.; Nelson, J. D. *J. Am. Chem. Soc.* **1998**, *120*, 5581. (d) Li, C.; Breit, B. *Chem. – Eur. J.* **2016**, *22*, 14655. (e) Tang, S.-B.; Zhang, X.; Tu, H.-F.; You, S.-L. *J. Am. Chem. Soc.* **2018**, *140*, 7737.

(4) Selected reviews on iridium-catalyzed allylic substitution: (a) Helmchen, G.; Dahnz, A.; Dübon, P.; Schelwies, M.; Weihofen, R. *Chem. Commun.* **2007**, 675. (b) Takeuchi, R.; Kezuka, S. *Synthesis* **2006**, 3349. (c) Hartwig, J. F.; Stanley, L. M. *Acc. Chem. Res.* **2010**, *43*, 1461. (d) Hethcox, J. C.; Shockley, S. E.; Stoltz, B. M. *ACS Catal.* **2016**, *6*, 6207. (e) Qu, J.; Helmchen, G. *Acc. Chem. Res.* **2017**, *50*, 2539. (f) Shockley, S. E.; Hethcox, J. C.; Stoltz, B. M. *Synlett* **2018**, *29*, 2481. (g) Cheng, Q.; Tu, H.-F.; Zheng, C.; Qu, J.-P.; Helmchen, G.; You, S.-L. *Chem. Rev.* **2019**, *119*, 1855. (h) Rössler, S. L.; Petrone, D. A.; Carreira, E. M. *Acc. Chem. Res.* **2019**, *52*, 2657. Selected examples: (i) Takeuchi, R.; Kashio, M. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 263. (j) Janssen, J. P.; Helmchen, G. *Tetrahedron Lett.* **1997**, *38*, 8025. (k) Ohmura, T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 15164. (l) Tissot-Croset, K.; Polet, D.; Alexakis, A. *Angew. Chem. Int. Ed.* **2004**, *43*, 2426. (m) Defieber, C.; Ariger, M. A.; Moriel, P.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2007**, *46*, 3139. (n) Liu, W.-B.; Zheng, C.; Zhuo, C.-X.; Dai, L.-X.; You, S.-L. *J. Am. Chem. Soc.* **2012**, *134*, 4812. (o) Liu, W.-B.; Reeves, C. M.; Virgil, S. C.; Stoltz, B. M. *J. Am. Chem. Soc.* **2013**, *135*, 10626. (p) Meza, A. T.; Wurm, T.; Smith, L.; Kim, S. W.; Zbieg, J. R.; Stivala, C. E.; Krische, M. J. *J. Am. Chem. Soc.* **2018**, *140*, 1275.

(5) Trost, B. M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 107.

(6) A selected review on the successive transformations of organosulfones: Trost, B. M.; Kalnmals, C. A. *Chem. – Eur. J.* **2019**, *25*, 11193.

(7) Selected recent examples of desulfonylative cross-coupling: (a) Merchant, R. R.; Edwards, J. T.; Qin, T.; Kruszyk, M. M.; Bi, C.; Che, G.; Bao, D.-H.; Qiao, W.; Sun, L.; Collins, M. R.; Fadeyi, O. O.; Gallego, G. M.; Mousseau, J. J.; Nuhant, P.; Baran, P. S. *Science* **2018**, *360*, 75. (b) Nambo, M.; Yim, J. C.-H.; Freitas, L. B. O.; Tahara, Y.; Ariki, Z. T.; Maekawa, Y.; Yokogawa, D.; Crudden, C. M. *Nat. Commun.* **2019**, *10*, Article number 4528.

(8) Trost, B. M.; Schmuff, N. R.; Miller, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 5979.

(9) For examples of 1,1-dipole synthon in multistep synthesis: (a) Trost, B. M.; Quayle, P. *J. Am. Chem. Soc.* **1984**, *106*, 2469. (b) Trost, B. M.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 7260. (c) Sato, T.; Okura, S.; Otera, J.; Nozaki, H. *Tetrahedron Lett.* **1987**, *28*, 6299. (d) Katritzky, A. R.; Wang, X.; Xie, L.; Toader, D. *J. Org. Chem.* **1998**, *63*, 3445. (e) Katritzky, A. R.; Luo, Z.; Fang, Y.; Steel, P. J. *J. Org. Chem.* **2001**, *66*, 2858.

(10) Trost, B. M.; Merlic, C. A. *J. Org. Chem.* **1990**, *55*, 1127.

(11) A selected review on molybdenum-catalyzed allylic substitution: (a) Belda, O.; Moberg, C. *Acc. Chem. Res.* **2004**, *37*, 159. Selected examples: (b) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543. (c) Trost, B. M.; Hachiya, I. *J. Am. Chem. Soc.* **1998**, *120*, 1104. (d) Glorius, F.; Pfaltz, A. *Org. Lett.* **1999**, *1*, 141. (e) Malkov, A. V.; Gouriou, L.; Lloyd-Jones, G. C.; Starý, I.; Langer, V.; Spoor, P.; Vinader, V.; Kočovský, P. *Chem. – Eur. J.* **2006**, *12*, 6910.

(12) Takizawa, K.; Sekino, T.; Sato, S.; Yoshino, T.; Kojima, M.; Matsunaga, S. *Angew. Chem. Int. Ed.* **2019**, *58*, 9199.

(13) Selected reviews on photoredox/transition metal dual catalysis: (a) Skubi, K. L.; Blum, T. R.; Yoon, T. P. *Chem. Rev.* **2016**, *116*, 10035. (b) Tellis, J. C.; Kelly, C. B.; Primer, D. N.; Jouffroy, M.; Patel, N. R.; Molander, G. A. *Acc. Chem. Res.* **2016**, *49*, 1429. (c) Hopkinson, M. N.; Tlahuext-Aca, A.; Glorius, F. *Acc. Chem. Res.* **2016**, *49*, 2261. (d) Twilton, J.; Le, C.; Zhang, P.; Shaw, M. H.; Evans, R. W.; MacMillan, D. W. C. *Nat. Rev. Chem.* **2017**, *1*, Article Number 0052.

(14) Selected reviews on the merger of photoredox and cobalt catalysis: (a) Cartwright, K. C.; Davies, A. M.; Tunge, J. A. *Eur. J. Org. Chem.* **2020**, 1245. (b) Kojima, M.; Matsunaga, S. *Trends Chem.* **2020**, *in press.* DOI:10.1016/j.trechm.2020.01.004. Selected examples: (c) Ruhl, K. E.; Rovis, T. *J. Am. Chem. Soc.* **2016**, *138*, 15527. (d) Thullen, S. M.; Rovis, T. *J. Am. Chem. Soc.* **2017**, *139*, 15504. (e) Call, A.; Casadevall, C.; Acuña-Parés, F.; Casitas, A.; Lloret-Fillol, J. *Chem. Sci.* **2017**, *8*, 4739. (f) Hou, J.; Ee, A.; Feng, W.; Xu, J.-H.; Zhao, Y.; Wu, J. *J. Am. Chem. Soc.* **2018**, *140*, 5257. (g) Hu, X.; Zhang, G.; Bu, F.; Lei, A. *Angew. Chem. Int. Ed.* **2018**, *57*, 1286. (h) Sun, X.; Chen, J.; Ritter, T. *Nat. Chem.* **2018**, *10*, 1229. (i) Cartwright, K. C.; Tunge, J. A. *ACS Catal.* **2018**, *8*, 11801. (j) Kalsi, D.; Dutta, S.; Barsu, N.; Rueping, M.; Sundararaju, B. *ACS Catal.* **2018**, *8*, 8115. (k) Ravetz, B. D.; Wang, J. Y.; Ruhl, K. E.; Rovis, T. *ACS Catal.* **2019**, *9*, 200. (l) Meng, Q.-Y.; Schirmer, T. E.; Katou, K.; König, B. *Angew. Chem. Int. Ed.* **2019**, *58*, 5723.

(15) Selected examples of metallaphotoredox-catalyzed allylation: (a) Lang, S. B.; O'Nele, K. M.; Tunge, J. A. *J. Am. Chem. Soc.* **2014**, *136*, 13606. (b) Lang, S. B.; O'Nele, K. M.; Douglas, J. T.; Tunge, J. A. *Chem. – Eur. J.* **2015**, *21*, 18589. (c) Xuan, J.; Zeng, T.-T.; Feng, Z.-J.; Deng, Q.-H.; Chen, J.-R.; Lu, L.-Q.; Xiao, W.-J.; Alper, H. *Angew. Chem. Int. Ed.* **2015**, *54*, 1625. (d) Matsui, J. K.; Gutiérrez-Bonet, Á.; Rotella, M.; Alam, R.; Gutierrez, O.; Molander, G. A. *Angew. Chem. Int. Ed.* **2018**, *57*, 15847. (e) Zhang, H.-H.; Zhao, J.-J.; Yu, S. *J. Am. Chem. Soc.* **2018**, *140*, 16914. (f) Zheng, J.; Breit, B. *Angew. Chem. Int. Ed.* **2019,** *58*, 3392.

(16) Selected reviews on photoredox catalysis: (a) Narayanam, J. M. R.; Stephenson, C. R. J. *Chem. Soc. Rev.* **2011**, *40*, 102. (b) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322. (c) Schultz, D. M.; Yoon, T. P. *Science* **2014**, *343*, 1239176. (d) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, *116*, 10075. (e) Xie, J.; Jin, H.; Hashmi, A. S. K. *Chem. Soc. Rev.* **2017**, *46*, 5193.

(17) Selected examples of cobalt-catalyzed allylic substitution: (a) Roustan, J. L.; Mérour, J. Y.; Houlihan, F. *Tetrahedron Lett.* **1979**, *20*, 3721. (b) Bhatia, B.; Reddy, M. M.; Iqbal, J. *Tetrahedron Lett.* **1993**, *34*, 6301. (c) Sun, M.; Chen, J.-F.; Chen, S.; Li, C. *Org. Lett.* **2019**, *21*, 1278. (d) Ghorai, S.; Chirke, S. S.; Xu, W.-B.; Chen, J.-F.; Li, C. *J. Am. Chem. Soc.* **2019**, *141*, 11430.

(18) Isomerization of the product **5** to vinyl sulfone was observed when the reaction was quenched with aqueous NH_4Cl. See the Supporting Information for details.

(19) It was confirmed in the control experiments that all the catalyst components (cobalt salt, photocatalyst, *i*Pr_2NEt) and visible light

irradiation were necessary for the allylic substitution of **5**. See the Supporting Information for details.
(20) Our preliminary study revealed that (*S*)-**6fa** was obtained in 90% ee when (*S*,*S*)-BDPP was used instead of dppp. See the Supporting Information for details.
(21) Tamura, R.; Kai, Y.; Kakihana, M.; Hayashi, K.; Tsuji, M.; Nakamura, T.; Oda, D. *J. Org. Chem.* **1986**, *51*, 4375.
(22) Babu, K. N.; Roy, A.; Singh, M.; Bisai, A. *Org. Lett.* **2018**, *20*, 6327.
(23) Du, Y.; Yu, A.; Jia, J.; Zhang, Y.; Meng, X. *Chem. Commun.* **2017**, *53*, 1684
(24) Tsui, G. C.; Lautens, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 8938.
(25) Ellwood, A. R.; Porter, M. J. *J. Org. Chem.* **2009**, *74*, 7982.
(26) Nisnevich, G.; Kulbitski, K.; Gandelman, M. PCT Int. Appl. WO 2015068159 A2, **2015**.
(27) Moriya, T.; Yoneda, S.; Kawana, K.; Ikeda, R.; Konakahara, T.; Sakai, N. *J. Org. Chem.* **2013**, *78*, 10642.
(28) Avery, M. A.; Alvim-Gaston, M.; Vroman, J. A.; Wu, B.; Ager, A.; Peters, W.; Robinson, B. L.; Charman, W. *J. Med. Chem.* **2002**, *45*, 4321.
(29) Kotake, Y.; Iijima, A.; Yoshimatsu, K.; Tamai, N.; Ozawa, Y.; Koyanagi, N.; Kitoh, K.; Nomura, H. *J. Med. Chem.* **1994**, *37*, 1616.
(30) Kawashima, S.; Aikawa, K.; Mikami, K. *Eur. J. Org. Chem.* **2016**, 3166.
(31) Newcomb, L. F.; Haque, T. S.; Gellman, S. H. *J. Am. Chem. Soc.* **1995**, *117*, 6509.
(32) Frøyen, P.; Juvvik, P. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1996**, *116*, 217.
(33) Blacker, A. J.; Clarke, M. L.; Loft, M. S.; Mahon, M. F.; Humphries, M. E.; Williams, J. M. J. *Chem. – Eur. J.* **2000**, *6*, 353.
(34) Stanley, L. M.; Bai, C.; Ueda, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 8918.
(35) Devine, S. K. J.; Van Vranken, D. L. *Org. Lett.* **2008**, *10*, 1909.