Supporting information

Visible-Light Photoredox-Catalyzed Aryl Radical *in situ* SO₂-capture Reactions

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1. General Information

Unless otherwise mentioned, all commercial reagents and solvents were used without further purification. Thin layer chromatography (TLC) was performed on pre-coated silica gel GF254 plates. Visualization of TLC was achieved by the use of UV light (254 nm). Column chromatography was performed on silica gel (300-400 mesh) using a proper eluent. ¹H NMR was recorded on FT AM 400 (400 MHz). Chemical shifts were reported in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane or chloroform-d (CDCl₃) at 7.26 ppm. The following abbreviations were used to describe peak splitting patterns: brs = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, td = triplet of doublet, ddd = doublet of doublet of doublet, m = multiplet. Coupling constants, *J*, were reported in hertz (Hz). The fully decoupled ¹³C NMR was recorded on FT AM 400 (101 MHz). Chemical shifts were reported in ppm referenced to the center of a triplet at 77.36 ppm of chloroform-d. Infrared (IR) spectra were recorded neat in KBr cell. Frequencies are given in centimeter inverse (cm⁻¹) and only selected absorbance is reported. High resolution mass spectra were obtained by using the UHD Accurate-Mass Q-TOF. Vinyl triflates^[1], arenediazonium salts^[2], propylene triflones^[3], acetylenic triflones^[4] were prepared from the corresponding materials according to previously reported methods.

2. Detailed Optimization of Reaction Conditions

		o ^{,SO₂CF₃} + N ₂ BF ₄ whi	bhotocatalyst(1 mol%) ite LEDs, rt, 1.5h,solver		
		2a 1a		° ° 3a	·
Entry	1a:2a	photocatalyst	solvent	c/mol.L ⁻¹	yield
1	1:1	Ir(ppy)2(dtbbpy)PF6	DMF	0.05	10%
2	1:1	Ru(bpy)3	DMF	0.05	15%
3	1:1	Ru(bpy) ₃ Cl ₂	DMF	0.05	26%
4	1:1	Acridine•HCl	DMF	0.05	0%
5	1:1	Ir(dFMeppy) ₂ (bpy)•PF ₆	DMF	0.05	15%
6	1:1	Ir(ppy)3	DMF	0.05	0%
7	1:1.5	Ru(bpy) ₃ Cl ₂	1,4-dioxane	0.05	38%
8	1:1.5	Ru(bpy) ₃ Cl ₂	1,4-dioxane	0.10	63%
9	1:1.5	Ru(bpy) ₃ Cl ₂	1,4-dioxane	0.20	59%
10 ^b	1:2.0	Ru(bpy)3Cl2	1,4-dioxane	0.10	75%
11	1:2.0	Ru(bpy) ₃ Cl ₂ (0.5 mol%)	1,4-dioxane	0.20	61%
12	1:2.0		1,4-dioxane	0.20	18%
13 ^c	1:2.0	Ru(bpy) ₃ Cl ₂	1,4-dioxane	0.20	trace

2.1 Table S1: Screen of the reaction condition for synthesis of 3a

[a] A 10 mL Schlenk tube filled with argon, 1a(0.2 mmol), 4a(0.4 mmol), photocatalyst(1 mol%) and solvent were added under argon atmosphere. Irradiated by white LEDs(24 W) and stirred for 1 hour. Isolated yield.[b] With 1a(0.4 mmol), 4a(0.8 mmol). [c] The reaction was stirred in dark.

As shown in Table S1, among the conditions tested, when under the **condition** A (entry 10), the reaction gave the best result, and we confirmed the condition for the further substrates scope exploration.

22	Tabla S'	2. 50	roon o	ftha	roaction	condition	for	syntha	sic of	7.
L. L	Table S.	2. SU	I CEII U	I UIE	reaction	conunion	101	Synthes	315 UI	/ a

		PhN ₂ BF ₄ 1a	+ CF ₃ Ph 6a	Ph	Ph 7a	
Entry	1a:6a	photocatalyst	solvent	Additive1	Additive2	yield
1	1:1.5	Ru(bpy) ₃ Cl ₂	dioxane			21%
2	1:1.5	Ru(bpy) ₃ Cl ₂	DMF			11%
3	1:1	Ru(bpy) ₃ Cl ₂	dioxane	Mesitylene(0.5 eq.)		31%
4	1:1	Ru(bpy) ₃ Cl ₂	dioxane	Mesitylene(1.0 eq.)		30%
5	1:1	Ru(bpy) ₃ Cl ₂	dioxane	Mesitylene(2.0 eq.)		32%
6	1:1	Ru(bpy) ₃ Cl ₂	dioxane	Mesitylene(4.0 eq.)		36%
7	1.5	Ru(bpy) ₃ Cl ₂	dioxane	Mesitylene(8.0 eq.)		35%
8	1.5	Ru(bpy) ₃ Cl ₂	DMF	Mesitylene(4.0 eq.)		30%
9	1.5	Ru(bpy) ₃ Cl ₂	MeCN	Mesitylene(4.0 eq.)		trace
10	1.5	Ru(bpy) ₃ Cl ₂	DMSO	Mesitylene(4.0 eq.)		
11	1.5	Ru(bpy) ₃ Cl ₂	dioxane	Ar1(4.0 eq.)		mess
12	1.5	Ru(bpy) ₃ Cl ₂	dioxane	Ar2(4.0 eq.)		mess
13	1:1.5	Ru(bpy) ₃ Cl ₂	dioxane	Mesitylene(4.0 eq.)	MS4Å	39%
14	1:2.0	Ru(bpy) ₃ Cl ₂	dioxane	Mesitylene(4.0 eq.)	MS4Å	43%
15 ^c	1:2.0	Ru(bpy) ₃ Cl ₂	dioxane	Mesitylene(4.0 eq.)	MS4Å	47%
		o k	Me			

02 02 condition



[a] A 10 mL Schlenk tube filled with argon, 1a, 6a, photocatalyst(1 mol%), additive, solvent were added under argon atmosphere. Irradiated by white LEDs(24 W) and stirred for 2 hours. Isolated yield. [b] With activated MS4Å (100 mg) [c] With 0.5 mol% Ru(bpy)_3Cl_2, and stirred for 12 h.

As shown in Table S2, among the conditions tested, when under the condition (entry 15), the reaction gave the best result, and we confirmed the condition for the further substrates scope exploration.

3. General Procedures for in situ SO2 Capture Reaction

3.1 General procedures for synthesis β -ketone sulfones 3



Condition A: Under Argon atmosphere, 1(0.4 mmol), 2(0.8 mmol), $\text{Ru}(\text{bpy})_3\text{Cl}_2(1 \text{ mol}\%)$ were dissolved in 1,4-dioxane (4 mL). After that, the solution was stirred under irritation of white LEDs for 1 hour. The crude products were purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1~2:1) to afford the aim products.

3.2 General procedures for synthesis allyl sulfones 5

$$Ar - N_2BF_4 + R^{\uparrow} \xrightarrow{Ph} \underbrace{Ru(bpy)_3CI_2(2 \text{ mol}\%)}_{1,4-\text{dioxane, Ar, rt., 2h}} R^{\uparrow} \xrightarrow{Ph} O_2 \\ R^{\uparrow} \xrightarrow{SO_2CF_3} \underbrace{white \text{ LEDs}}_{white \text{ LEDs}} S^{\bullet} \xrightarrow{Ar}$$

Condition B: Under Argon atmosphere, 1(0.4 mmol), 4(0.8 mmol), $\text{Ru}(\text{bpy})_3\text{Cl}_2(1 \text{ mol}\%)$ were dissolved in 1,4-dioxane (4 mL). After that, the solution was stirred under irritation of white LEDs for 2 hours. The crude products were purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1~2:1) to afford the aim products 5.

3.3 General procedures for synthesis alkynyl sulfones 7



Condition C: Under Argon atmosphere, 1(0.2 mmol), 6(0.4 mmol), Mesitylene(0.8 mmol), activated MS4Å(100 mg), (Ru(bpy)₃Cl₂(0.5 mol%) were dissolved in 1,4-dioxane (1 mL). After that, the solution was stirred under irritation of white LEDs(24 W) for 12 hours. The crude products were purified by flash chromatography on silica gel (petroleum ether/DCM 2:1~1:1) to afford the aim products 7.

3.4 Synthesis of 2e



To a solution of 1-(*p*-tolyl)ethan-1-one (10 mmol, 1.34 g) and Na₂CO₃ (20 mmol, 2.12g) in DCM (15 ml) was cooled to 0 °C, Tf₂O(15 mmol, 4.23g, dissolved in 10 mL DCM) was added dropwise to the solution. The mixture was warmed to room temperature and stirred for another 12 h. NaHCO₃(sat. 50 mL) NaHCO₃ (sat. 50 mL) was poured to the solution, and petroleum(100 mL) was added. The organic layer was separate and washed with more NaHCO₃ (sat. aq. 50 mL), brine (sat. 50 mL), and dried over Na2SO4, the solvent was removed under reduced pressure and afford the crude product 2j (mix with1-(*p*-tolyl)ethan-1-one, 4:8, about 50 wt.%). The mixture was used in the synthesis of beta-ketone sulfone reaction without further purification.

Crude ¹H NMR for the mixture.



3.5 General procedures for control experiments



Under the standard condition, TEMPO(2.0 eq.) was added to the reaction, TLC and ¹H NMR spectrum showed that the generation of **3aa** was inhabited completely, and the phenyl-TEMPO adduct could be detected by HRMS analysis, this result suggested that the phenyl radical was generated in the reaction.



Under the standard condition, silyl enol ether 2a'(2.0 eq.) was added to the reaction. Besides the product **3a** was detected in 48% yield and the product **3d** could also be detected in 16% yield by ¹H NMR (use CH₂Br₂ as internal standard), this result suggested that the product is generate via intermolecular addition other than an intramolecular sulforyl shift process.



Under the standard condition, besides the product 3j was obtained in 76% yield and the byproduct 3j' could also be isolated in 37% yield, this result suggested that part of enol triflates could serve as SO₂ source in the reaction.



Under the standard condition, 2j could transform into 3j directly under standard condition, which reveal how the iniatial SO₂ come into being.



Under the standard condition, applied aryl diazo compound **8** (0.2 mmol) and enol triflate **2a** (0.4 mmol) as substrates, the product **9** could isolated in 45% yield. This result indicated that initiate from the aryl diazo compound.



Under initial condition of de-CF₃ arylation reaction, the side product **10** could be isolated in 32% yield, this result suggested that solvent have a great influence in target product yield.



Under standard condition of de-CF₃ arylation reaction, the side product Mes-CF₃ could be detected in 0.106 mmol(27%, based on **1a**, determined by ¹⁹F NMR), this result suggested that the mesitylene could combine with trifluoromethyl radical to complete the catalytic cycle.



4. Proposed Mechanism for Synthesis of alkynyl arylsulfones



5. Spectroscopic Data

2-(phenylsulfonyl)-3,4-dihydronaphthalen-1(2H)-one (3a)^[5]



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 85.7 mg, yield: 75%.

¹H NMR (400 MHz, CDCl₃) δ 8.03 – 7.90 (m, 3H), 7.68 (dd, J = 9.1, 5.7 Hz, 1H), 7.63 – 7.48 (m, 3H), 7.37 – 7.24 (m, 2H), 4.14 (t, J = 5.8 Hz, 1H), 3.50 (ddt, J = 16.5, 10.6, 5.6 Hz, 1H), 3.01 (dt, J = 17.1, 5.3 Hz, 1H), 2.91 – 2.79 (m, 1H), 2.67 (ddt, J = 14.3, 9.7, 4.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 188.6, 143.6, 139.0, 134.5, 134.0, 131.7, 129.1, 129.0, 129.0, 127.9, 127.9, 127.1, 69.6, 26.6, 23.6. Spectroscopic data matched with the reported data in the literature.

3-(phenylsulfonyl)chroman-4-one (3b)



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 4:1); white solid, 98.2 mg, yield: 85%; M.p. = $155\sim157$ °C.

¹**H** NMR (400 MHz, CDCl₃) δ 7.84 (dd, J = 12.4, 7.9 Hz, 3H), 7.59 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.2 Hz, 3H), 7.01 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 5.29 (dd, J = 12.9, 2.6 Hz, 1H), 4.73 (dd, J = 12.9, 4.1 Hz, 1H), 4.06 (d, J = 3.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 182.5, 160.8, 137.9, 137.0, 134.4, 129.3, 128.9, 127.5, 122.1, 120.5, 118.1, 68.7, 66.0. IR (KBr, cm⁻¹): 1686, 1605, 1477, 1465, 1308, 1275, 1148, 751, 725, 686, 590, 504. HRMS m/z (ESI) calcd. for C₁₅H₁₂NaO₄S⁺ (M + Na)⁺ 311.0349, found 311.0351.

2-(phenylsulfonyl)-2,3-dihydro-1H-inden-1-one (3c)^[6]



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 82.6 mg, yield: 76%. ¹H NMR (400 MHz, CDCl₃) δ 7.92 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.71 – 7.52 (m, 5H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 4.31 (dd, *J* = 8.4, 3.4 Hz, 1H), 3.79 (dd, *J* =

18.3, 3.4 Hz, 1H), 3.53 (dd, *J* = 18.3, 8.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 194.5, 151.9, 137.6, 136.0, 135.8, 134.2, 129.2, 129.1, 128.2, 126.5, 124.8, 68.7, 28.2. Spectroscopic data matched with the reported data in the literature.

1-phenyl-2-(phenylsulfonyl)ethan-1-one (3d)^[7]



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); White solid, 82.4 mg, yield: 79%. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (t, *J* = 8.3 Hz, 4H), 7.62 (dt, *J* = 18.1, 7.4 Hz, 2H), 7.49 (dt, *J* = 29.1, 7.7 Hz, 4H), 4.77 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 188.1,

138.8, 135.7, 134.4, 134.2, 129.3, 129.2, 128.9, 128.5, 63.4. Spectroscopic data matched with the reported data in the literature.

2-(phenylsulfonyl)-1-(p-tolyl)ethan-1-one (3e)^[8]



Due to the purification of enol triflates 2e was failed(decomposed both in silica gel and Al_2O_3 column), we used a mixture of ketone and enol triflate **2e** (about 8:4, 50 wt%)(425 mg) as the substrate. According to the condition A, purification of the

reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); White solid, 50.6 mg, yield: 46%.

¹**H NMR** (400 MHz, Chloroform-*d*) δ 7.98 – 7.78 (m, 4H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.74 (s, 2H), 2.42 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 187.55, 145.64, 138.76, 134.22, 133.28, 129.58, 129.46, 129.21, 128.56, 63.33, 21.82.

Spectroscopic data matched with the reported data in the literature.

methyl 4-(2-(phenylsulfonyl)acetyl)benzoate (3f)^[8]



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 88.6 mg, yield: 69%.

¹H NMR (400 MHz, CDCl₃) δ 8.16 – 8.09 (m, 2H), 8.03 – 7.96 (m, 2H), 7.94 – 7.86 (m, 2H), 7.73 – 7.64 (m, 1H), 7.56 (dd, J = 8.4, 7.2 Hz, 2H), 4.79 (s, 2H), 3.96 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 187.7, 165.9, 138.7, 138.6, 134.9, 134.4, 130.0, 129.3, 129.2, 128.5, 63.7, 52.6. Spectroscopic data matched with the reported data in the literature.

1-(4-iodophenyl)-2-(phenylsulfonyl)ethan-1-one (3g)^[9]



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 121.4 mg, yield: 79%.

¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.83 (m, 4H), 7.72 – 7.64 (m, 3H), 7.57 (t, *J* = 7.7 Hz, 2H), 4.71 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 187.4, 138.6, 138.2, 135.0, 134.4, 130.5, 129.3, 128.5, 103.1, 63.5. Spectroscopic data matched with the reported data in the literature.

1-(4-bromophenyl)-2-(phenylsulfonyl)ethan-1-one (3h)^[9]

According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 88.4 mg, yield: 67%.



¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.85 (m, 2H), 7.82 (d, J = 8.6 Hz, 2H), 7.73 – 7.52 (m, 5H), 4.73 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 187.1, 138.6, 134.5, 134.4, 132.2, 130.8, 130.0, 129.3, 128.5, 63.5. Spectroscopic data matched with the

reported data in the literature.

1-(2-fluorophenyl)-2-(phenylsulfonyl)ethan-1-one (3i)^[10]



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 83.2 mg, yield: 74%. ¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.86 (m, 2H), 7.79 (td, *J* = 7.7, 1.9 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.53 (q, *J* = 8.0 Hz, 3H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.09 (dd, *J* = 11.6,

8.3 Hz, 1H), 4.81 (s, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 185.9 (d, J = 3.1 Hz), 161.8 (d, J = 255.3 Hz), 139.1, 136.1 (d, J = 9.5 Hz), 134.1, 131.1 (d, J = 1.6 Hz), 129.2, 128.5, 124.8 (d, J = 3.4 Hz), 124.5 (d, J = 11.0 Hz), 116.8 (d, J = 23.6 Hz), 67.0 (d, J = 8.7 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ - 108.65. Spectroscopic data matched with the reported data in the literature.

1-(3-chlorophenyl)-2-(phenylsulfonyl)ethan-1-one (3j)^[11]



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 95.0 mg, yield: 82%.

¹**H** NMR (400 MHz, CDCl₃) δ 7.94 – 7.81 (m, 4H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.57 (q, *J* = 8.1, 6.3 Hz, 3H), 7.43 (t, *J* = 7.9 Hz, 1H), 4.74 (s, 2H). ¹³**C** NMR (101 MHz, CDCl₃) δ 187.0, 138.6, 137.2, 135.2, 134.4, 134.3, 130.2, 129.3, 129.1, 128.5, 127.5, 63.5. Spectroscopic data matched with the reported data in the literature.

1-(3-bromo-4-fluorophenyl)-2-(phenylsulfonyl)ethan-1-one (3k)



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 92.4 mg, yield: 65%; M.p. = $138 \sim 140$ °C.

¹**H** NMR (400 MHz, CDCl₃) δ 8.15 (dd, J = 6.5, 2.3 Hz, 1H), 7.95 (ddd, J = 8.6, 4.6, 2.3 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.72 – 7.65 (m, 1H), 7.57 (t, J = 7.8 Hz, 2H), 7.22 (t, J = 8.3 Hz, 1H), 4.73 (s, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 185.6, 162.7 (d, J = 258.1 Hz), 138.5, 135.2 (d, J = 2.1 Hz), 134.5, 133.2 (d, J = 3.5 Hz), 130.9 (d, J = 8.9 Hz), 129.4, 128.5, 117.0 (d, J = 23.2 Hz), 110.2 (d, J = 21.9 Hz), 63.5. **IR** (KBr, cm⁻¹): 1681, 1587, 1489, 1322, 1275, 1261, 1154, 1084, 763, 749, 686, 556. **HRMS** m/z (ESI) calcd. for C₁₄H₁₀BrFNaO₃S⁺ (M + Na)⁺ 378.9410, found 378.9408.

1-(3,4-dichlorophenyl)-2-(phenylsulfonyl)ethan-1-one (31)^[12]



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 99.6 mg, yield: 68%.

¹**H** NMR (400 MHz, CDCl₃) δ 8.01 (d, J = 2.2 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.82 (dd, J = 8.4, 2.2 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.59 (dt, J = 7.8, 3.5 Hz, 3H), 4.71 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 186.0, 139.3, 138.5, 135.2, 134.5, 133.7, 131.1, 131.0, 129.4, 128.5, 128.4, 63.6. Spectroscopic data matched with the reported data in the literature.

2-tosyl-3,4-dihydronaphthalen-1(2H)-one (3n)^[13]



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 98.4 mg, yield: 82%.

¹**H** NMR (400 MHz, CDCl₃) δ 8.00 (dd, J = 7.9, 1.4 Hz, 1H), 7.85 – 7.77 (m, 2H), 7.53 (td, J = 7.5, 1.4 Hz, 1H), 7.41 – 7.25 (m, 4H), 4.11 (t, J = 5.7 Hz, 1H), 3.53 (ddd, J = 17.0, 9.7, 4.7 Hz, 1H), 3.00 (dt, J = 17.0, 5.5 Hz, 1H), 2.87 (dq, J = 17.0, 5.6 Hz, 1H), 2.67 (dq, J = 9.5, 4.8 Hz, 1H), 2.47 (s, 3H). ¹³**C** NMR (101 MHz, CDCl₃) δ 188.8, 145.1, 143.6, 136.0, 134.5, 131.8, 129.7, 129.1, 128.9, 127.9, 127.0, 69.7, 26.6, 23.7, 21.7. Spectroscopic data matched with the reported data in the literature.

2-((4-(tert-butyl)phenyl)sulfonyl)-3,4-dihydronaphthalen-1(2H)-one (30)



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 83.4 mg, yield: 71%; M.p. = $122\sim124^{\circ}$ C.

¹**H NMR** (400 MHz, CDCl₃) δ 7.99 (dd, J = 7.9, 1.4 Hz, 1H), 7.91 – 7.79 (m, 2H), 7.62 – 7.46 (m, 3H), 7.28 (dt, J = 14.6, 7.9 Hz, 2H), 4.13 (dd, J = 6.3, 5.3 Hz, 1H), 3.48 (ddd, J = 16.9, 9.5, 4.7 Hz, 1H), 2.98 (dt, J = 17.0, 5.5 Hz, 1H), 2.82 (dtd, J = 14.1, 6.2, 4.7 Hz, 1H), 2.64 (ddt, J = 14.4, 9.9, 5.1 Hz, 1H), 1.36 (s, 9H). ¹³**C NMR** (101 MHz, CDCl₃) δ 188.8, 157.9, 143.6, 136.0, 134.4, 131.8, 129.0, 128.9, 127.9, 127.0, 126.0, 69.7, 35.3, 31.1, 26.6, 23.8. **IR** (KBr, cm⁻¹): 1681, 1595, 1455, 1399, 1316, 1274, 1107, 764, 659, 577,557, 486. **HRMS** m/z (ESI) calcd. for C₂₀H₂₂NaO₃S⁺ (M + Na)⁺ 365.1182, found 365.1190.

2-((4-methoxyphenyl)sulfonyl)-3,4-dihydronaphthalen-1(2H)-one (3p)

According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); yellow solid, 55.8 mg, yield: 44%; M.p. = 133~135°C.



¹**H NMR** (400 MHz, CDCl₃) δ 7.99 (d, J = 7.9 Hz, 1H), 7.84 (d, J = 8.6 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.34 – 7.24 (m, 2H), 7.02 (d, J = 8.6 Hz, 2H), 4.09 (t, J= 5.8 Hz, 1H), 3.88 (s, 3H), 3.56 – 3.43 (m, 1H), 2.98 (dt, J = 17.1, 5.6 Hz, 1H), 2.83 (dq, J = 17.3, 5.6 Hz, 1H), 2.65 (tt, J = 9.6, 5.1 Hz, 1H). ¹³**C NMR** (101

MHz, CDCl₃) δ 189.0, 164.0, 143.6, 134.4, 131.8, 131.4, 130.4, 129.0, 127.9, 127.0, 114.2, 69.9, 55.7, 26.6, 23.8. **IR** (KBr, cm⁻¹): 1681, 1594, 1578, 1497, 1298, 1262, 1113, 748, 679, 581, 536. **HRMS** m/z (ESI) calcd. for C₁₇H₁₆NaO₄S⁺ (M + Na)⁺ 339.0662, found 339.0666.

2-((4-chlorophenyl)sulfonyl)-3,4-dihydronaphthalen-1(2H)-one (3q)



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 70.8 mg, yield: 55%; M.p. = $123\sim125^{\circ}$ C.

¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, J = 7.9 Hz, 1H), 7.87 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.0 Hz, 3H), 7.35 – 7.26 (m, 2H), 4.13 (t, J = 6.1 Hz, 1H), 3.46 (ddd, J = 17.0, 9.1, 4.7 Hz, 1H), 3.01 (dt, J = 17.1, 5.8 Hz, 1H), 2.88 – 2.76 (m, 1H), 2.68 (ddt, J = 14.2, 9.8, 5.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 188.6, 143.5, 140.8, 137.5, 134.7, 131.6, 130.7, 129.3, 129.0, 127.9, 127.1, 69.7, 26.7, 23.5. IR (KBr, cm⁻¹): 1682, 1598, 1476, 1316, 1145, 1086, 1047, 1024, 758, 627, 539, 485. HRMS m/z (ESI) calcd. for C₁₆H₁₃ClNaO₃S⁺ (M + Na)⁺ 343.0166, found 343.0165.

2-((4-bromophenyl)sulfonyl)-3,4-dihydronaphthalen-1(2H)-one(3r)



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 76.0 mg, yield: 52%; M.p. = $130 \sim 132$ °C.

¹**H** NMR (400 MHz, CDCl₃) δ 7.98 (dd, J = 7.9, 1.4 Hz, 1H), 7.84 – 7.77 (m, 2H), 7.75 – 7.67 (m, 2H), 7.54 (td, J = 7.5, 1.5 Hz, 1H), 7.37 – 7.27 (m, 2H), 4.12 (dd, J = 6.7, 5.3 Hz, 1H), 3.47 (ddd, J = 17.0, 9.1, 4.7 Hz, 1H), 3.02 (dt, J = 17.0, 5.7 Hz, 1H), 2.84 (dtd, J = 13.5, 6.6, 4.7 Hz, 1H), 2.69 (ddt, J = 14.2, 9.1, 5.1 Hz, 1H). ¹³**C** NMR (101 MHz, CDCl₃) δ 188.5, 143.5, 138.0, 134.6, 132.3, 131.6, 130.7, 129.5, 129.0, 127.9, 127.2, 69.7, 26.7, 23.5. IR (KBr, cm⁻¹): 1681, 1598, 1573, 1316, 1143, 1082, 1023, 743, 650, 553. HRMS m/z (ESI) calcd. for C₁₆H₁₃BrNaO₃S⁺ (M + Na)⁺ 386.9661, found 386.9663.

2-((3-chlorophenyl)sulfonyl)-3,4-dihydronaphthalen-1(2H)-one(3s)



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 72.0 mg, yield: 56%; M.p. = $123 \sim 125^{\circ}$ C.

¹**H NMR** (400 MHz, CDCl₃) δ 8.04 – 7.91 (m, 2H), 7.84 (dt, J = 7.9, 1.4 Hz, 1H), 7.65 (ddd, J = 8.1, 2.0, 1.0 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.37 – 7.28 (m, 2H), 4.16 (dd, J = 6.7, 5.3 Hz, 1H), 3.48 (ddd, J = 17.0, 9.1, 4.7 Hz, 1H), 3.03 (dt, J = 17.0, 5.7 Hz, 1H), 2.85 (dtd, J = 13.6, 6.7, 4.7 Hz, 1H), 2.70 (ddt, J = 14.2, 9.1, 5.1 Hz, 1H). ¹³**C NMR** (101 MHz, CDCl₃) δ 188.4, 143.5, 140.8, 135.2, 134.7, 134.1, 131.6, 130.3, 129.1, 129.0, 128.0, 127.4, 127.2, 69.7, 26.7, 23.5. **IR** (KBr, cm⁻¹): 1682, 1599, 1456, 1297, 1110, 1077, 681, 595, 561, 489, 444. **HRMS** m/z (ESI) calcd. for C₁₆H₁₃ClNaO₃S⁺ (M + Na)⁺ 343.0166, found 343.0168.

2-((3-bromophenyl)sulfonyl)-3,4-dihydronaphthalen-1(2H)-one (3t)



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 93.4 mg, yield: 64%; M.p. = $128\sim130$ °C.

¹**H NMR** (400 MHz, CDCl₃) δ 8.08 (s, 1H), 7.98 (d, J = 7.9 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.9 Hz, 1H), 7.36 – 7.27 (m, 2H), 4.16 (t, J = 6.1 Hz, 1H), 3.46 (ddd, J = 17.0, 9.0, 4.7 Hz, 1H), 3.02 (dt, J = 17.1, 5.8 Hz, 1H), 2.83 (dtd, J = 13.6, 6.7, 4.6 Hz, 1H), 2.69 (ddt, J = 14.2, 9.7, 5.1 Hz, 1H). ¹³**C NMR** (101 MHz, CDCl₃) δ 188.4, 143.5, 140.9, 137.0, 134.6, 131.8, 131.6, 130.5, 129.0, 128.0, 127.9, 127.2, 122.9, 69.7, 26.7, 23.5. **IR** (KBr, cm⁻¹): 1703, 1646, 1569, 1354, 1145, 1081, 1023, 764, 594, 561, 484. **HRMS** m/z (ESI) calcd. for C₁₆H₁₃BrNaO₃S⁺ (M + Na)⁺ 386.9661, found 386.9662.

Product 3u



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 125.4 mg, yield: 67%, 1:1 d.r.; $M.p = 75 \sim 78$ °C.

¹**H NMR** (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.2 Hz, 2H), 7.99 (ddd, *J* = 11.6, 8.2, 1.6 Hz, 3H), 7.54 (td, *J* = 7.5, 1.4 Hz, 1H), 7.36 – 7.28 (m, 2H), 4.99

(td, J = 10.9, 4.4 Hz, 1H), 4.17 (ddd, J = 7.1, 5.5, 2.4 Hz, 1H), 3.50 (ddd, J = 16.8, 9.2, 4.7 Hz, 1H), 3.03 (dt, J = 17.1, 5.7 Hz, 1H), 2.88 (ddd, J = 14.2, 6.8, 5.0 Hz, 1H), 2.78 – 2.66 (m, 1H), 2.14 (dd, J = 12.1, 4.1 Hz, 1H), 1.96 (ddq, J = 13.5, 6.8, 3.5, 2.9 Hz, 1H), 1.79 – 1.72 (m, 2H), 1.66 – 1.54 (m, 2H), 1.21 – 1.10 (m, 2H), 1.00 – 0.90 (m, 7H), 0.81 (dd, J = 7.0, 1.3 Hz, 3H).¹³**C NMR** (101 MHz, CDCl₃) δ 188.5, 188.4, 164.5, 164.5, 143.5, 142.7, 142.6, 135.7, 134.7, 131.6, 130.1, 129.2, 129.0, 128.0, 127.2, 75.9, 69.6, 47.2, 40.9, 40.9, 34.2, 31.5, 26.7, 26.7, 26.5, 26.4, 23.6, 23.5, 23.4, 22.0, 20.8, 20.8, 16.5, 16.4. **IR** (KBr, cm⁻¹):2955, 1715, 1682, 1485, 1270, 1240, 1115, 738, 619, 538. **HRMS** m/z (ESI) calcd. for C₂₇H₃₂NaO₅S⁺ (M + Na)⁺ 491.1863, found 491.1861.

2-((2-iodophenyl)sulfonyl)-3,4-dihydronaphthalen-1(2H)-one (3v)



According to the condition A, purification of the reaction mixture using column chromatography (petroleum ether/ethyl acetate = 5:1); white solid, 40.9 mg, yield: 25%; M.p. = $132 \sim 136^{\circ}$ C.

¹**H NMR** (400 MHz, CDCl₃) δ 8.15 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.97 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.64 – 7.52 (m, 2H), 7.38 – 7.30 (m, 3H), 4.83 (t, *J* = 5.8 Hz, 1H), 3.51 (ddt, *J* = 17.5, 7.8, 4.7

Hz, 1H), 3.11 – 2.95 (m, 2H), 2.82 – 2.70 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 188.5, 143.6, 142.5, 141.6, 134.6, 134.6, 132.9, 131.7, 129.0, 128.6, 127.9, 127.1, 92.9, 66.2, 26.8, 22.7. IR (KBr, cm⁻¹): 1679, 1599, 1454, 1315, 1275, 1260, 1146, 1120, 1010, 755, 591, 488, 446. HRMS m/z (ESI) calcd. for C¹⁶H¹³INaO³S⁺ (M + Na)⁺ 434.9522, found 434.9525.

methyl (E)-5-phenyl-6-(phenylsulfonyl)hex-4-enoate (5a)

Ph <mark>O</mark>2

MeOOC.

Under Argon atmosphere, 1(0.4 mmol), 4(0.8 mmol), Ru(bpy)₃Cl₂(1 mol%) were dissolved in 1,4-dioxane(4 mL). After that, the solution was stirred under irritation of white LEDs for **2 hours**. The crude products were purified by flash

chromatography on silica gel (petroleum ether/ethyl acetate $5:1\sim2:1$) to afford the aim products **5aa**. Colorless oil, 84.2 mg, yield: 61%, E/Z > 20:1.

¹**H NMR** (400 MHz, CDCl₃) δ 7.84 – 7.72 (m, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.16 (m, 5H), 6.03 – 5.94 (m, 1H), 4.43 (s, 2H), 3.69 (s, 3H), 2.51 – 2.39 (m, 4H). ¹³**C NMR** (101 MHz, CDCl₃) δ 173.1, 140.6, 139.1, 136.1, 133.5, 129.3, 128.9, 128.4, 128.3, 127.4, 126.4, 57.6, 51.7, 33.2, 24.8. **IR** (KBr, cm⁻¹): 1732, 1446, 1307, 1276, 1163, 1136, 1084, 1024, 906, 764, 688, 530. **HRMS** m/z (ESI) calcd. for C₁₉H₂₀NaO₄S⁺ (M + Na)⁺ 367.0975, found 369.0977. The *E*-conformation was assigned by 2D NOE experiment.

(E)-7-phenyl-8-(phenylsulfonyl)oct-6-en-3-one (5b)



¹**H NMR** (400 MHz, CDCl₃) δ 7.82 – 7.74 (m, 2H), 7.58 – 7.49 (m, 1H), 7.42 (dd, J = 8.4, 7.1 Hz, 2H), 7.26 – 7.14 (m, 5H), 5.96 (t, J = 7.6 Hz, 1H), 4.44 (s, 2H), 2.55 (t, J = 7.0 Hz, 2H), 2.42 (dt, J = 14.7, 7.3 Hz, 4H), 1.07 (t, J = 7.3 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 173.1, 140.6, 139.1, 136.1, 133.5, 129.3, 128.9, 128.4, 128.3, 127.4, 126.4, 57.6, 51.7, 33.2, 24.8. **IR** (KBr, cm⁻¹): 2977, 1712, 1446, 1306, 1135, 1804, 912, 764, 748, 688, 590, 530. **HRMS** m/z (ESI) calcd. for C₂₀H₂₂NaO₃S⁺ (M + Na)⁺ 365.1182, found 365.1185. The *E*-conformation was assigned by 2D NOE experiment.

(E)-3-(2-phenyl-3-(phenylsulfonyl)prop-1-en-1-yl)cyclohexan-1-one (5c)

$$0 = \underbrace{\begin{array}{c} Ph & \mathbf{0}_2 \\ \mathbf{S}, Ph \\ \mathbf{5c} \end{array}}_{\mathbf{5c}}$$

Under Argon atmosphere, 1(0.4 mmol), 4(0.8 mmol), $\text{Ru}(\text{bpy})_3\text{Cl}_2(1 \text{ mol}\%)$ were dissolved in 1,4-dioxane(4 mL). After that, the solution was stirred under irritation of white LEDs for **2 hours**. The crude products were purified by flash

chromatography on silica gel (petroleum ether/ethyl acetate $5:1\sim2:1$) to afford the aim products **5ac**. Yellow oil, 99.2 mg, yield: 73%, E/Z > 20:1.

¹**H NMR** (400 MHz, CDCl₃) δ 7.72 (d, *J* = 7.7 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.22 – 7.10 (m, 5H), 5.89 (d, *J* = 10.1 Hz, 1H), 4.40 (s, 2H), 3.17 (dddd, *J* = 16.8, 13.1, 8.5, 5.1 Hz, 1H), 2.42 – 2.16 (m, 4H), 1.95 (dd, *J* = 18.3, 10.5 Hz, 1H), 1.84 – 1.64 (m, 1H). ¹³**C NMR** (101 MHz, CDCl₃) δ 217.9, 140.4, 140.3, 139.0, 133.7, 128.9, 128.5, 128.4, 128.3, 127.5, 126.4, 57.8, 44.8, 38.1, 37.4, 29.8. **IR** (KBr, cm⁻¹): 3058, 2932, 1740, 1446, 1307, 1135, 1084, 914, 743, 688, 610, 528. **HRMS** m/z (ESI) calcd. for C₂₀H₂₀NaO₃S⁺ (M + Na)⁺ 363.1025, found 363.1026. The *E*-conformation was assigned by 2D

NOE experiment.

(E)-3-(2-phenyl-3-(phenylsulfonyl)prop-1-en-1-yl)cyclohexan-1-one (5d)

Under Argon atmosphere, 1(0.4 mmol), 4(0.8 mmol), Ru(bpy)₃Cl₂(1 mol%) were dissolved in 1,4-dioxane(4 mL). After that, the solution was stirred under irritation of white LEDs for **2 hours**. The crude products were purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1~2:1) to afford the aim products **5ad**. Yellow oil, 106.1 mg, yield: 75%, E/Z > 20:1.

¹**H** NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.14 (m, 5H), 5.82 (d, *J* = 10.1 Hz, 1H), 4.36 (d, *J* = 3.0 Hz, 2H), 2.77 (qt, *J* = 10.6, 4.0 Hz, 1H), 2.45 – 2.34 (m, 1H), 2.34 – 2.21 (m, 2H), 2.20 – 2.02 (m, 2H), 1.86 – 1.66 (m, 2H), 1.52 (dtd, *J* = 13.4, 11.3, 3.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 209.8, 140.3, 140.1, 139.0, 133.7, 129.0, 128.4, 127.7, 127.6, 126.6, 57.5, 46.8, 41.1, 39.3, 31.0, 25.1. IR (KBr, cm⁻¹): 3032, 2930, 1741, 1442, 1280, 1130, 880, 721, 671, 586. HRMS m/z (ESI) calcd. for C₂₁H₂₂NaO₃S⁺ (M + Na)⁺ 377.1182, found 377.1184. The *E*-conformation was assigned by 2D NOE experiment.

(E)-3-(3-((4-methoxyphenyl)sulfonyl)-2-phenylprop-1-en-1-yl)cyclohexan-1-one (5e)



Under Argon atmosphere, 1(0.4 mmol), 4(0.8 mmol), $\text{Ru}(\text{bpy})_3\text{Cl}_2(1 \text{ mol}\%)$ were dissolved in 1,4-dioxane(4 mL). After that, the solution was stirred under irritation of white LEDs for **4 hours**. The crude products were purified by flash chromatography on silica gel (petroleum ether/ethyl

acetate 5:1~2:1) to afford the aim products **5bd**. Yellow oil, 93.6 mg, yield: 61%, E/Z > 20:1. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 8.6 Hz, 2H), 7.27 – 7.12 (m, 5H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.80 (d, *J* = 10.1 Hz, 1H), 4.33 (d, *J* = 3.2 Hz, 2H), 3.84 (s, 3H), 2.74 (qt, *J* = 10.7, 4.1 Hz, 1H), 2.47 – 2.35 (m, 1H), 2.26 (ddd, *J* = 21.9, 8.8, 4.2 Hz, 2H), 2.17 – 2.02 (m, 2H), 1.84 (dd, *J* = 13.3, 4.2 Hz, 1H), 1.70 (tt, *J* = 12.8, 4.2 Hz, 1H), 1.51 (dtd, *J* = 13.5, 11.4, 3.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 209.9, 163.7, 140.4, 139.8, 130.5, 130.3, 128.3, 128.1, 127.5, 126.6, 114.2, 57.7, 55.7, 46.9, 41.1, 39.3, 31.0, 25.1. **IR** (KBr, cm⁻¹): 2709, 1564, 1545, 1423, 1376, 1115, 1083, 949, 761, 669, 625, 556. **HRMS** m/z (ESI) calcd. for C₂₂H₂₄NaO₄S⁺ (M + Na)⁺ 407.1288, found 407.1288. The *E*-conformation was assigned by 2D NOE experiment.

(E)-3-(3-((4-chlorophenyl)sulfonyl)-2-phenylprop-1-en-1-yl)cyclohexan-1-one (5f)

Under Argon atmosphere, 1(0.4 mmol), 4(0.8 mmol), $\text{Ru}(\text{bpy})_3\text{Cl}_2(1 \text{ mol}\%)$ were dissolved in 1,4-dioxane(4 mL). After that, the solution was stirred under irritation of white LEDs for **2 hours**. The crude products were purified

by flash chromatography on silica gel (petroleum ether/ethyl acetate $5:1\sim2:1$) to afford the aim products **5g**. Yellow oil, 71.6 mg, yield: 46%, E/Z > 20:1.

¹**H NMR** (400 MHz, CDCl₃) δ 7.67 – 7.54 (m, 2H), 7.33 – 7.27 (m, 2H), 7.18 (dd, J = 5.0, 2.0 Hz, 3H), 7.13 – 7.04 (m, 2H), 5.83 (d, J = 10.1 Hz, 1H), 4.35 (d, J = 2.6 Hz, 2H), 2.84 (qt, J = 10.6, 4.0 Hz, 1H), 2.46 – 2.23 (m, 3H), 2.23 – 2.06 (m, 2H), 1.94 – 1.83 (m, 1H), 1.82 – 1.70 (m, 1H), 1.62 – 1.53 (m, 1H). ¹³**C NMR** (101 MHz, CDCl₃) δ 209.7, 140.4, 140.3, 140.1, 137.3, 129.9, 129.7, 128.4, 127.6, 127.5, 126.5, 57.7, 46.9, 41.1, 39.3, 31.0, 25.0. **IR** (KBr, cm⁻¹): 1709, 1507, 1445, 1323, 1276, 1135, 1083, 909, 764, 699, 615, 555. **HRMS** m/z (ESI) calcd. for $C_{21}H_{21}CINaO_3S^+$ (M + Na)⁺ 411.0792, found 411.0796. The *E*-conformation was assigned by 2D NOE experiment.

((2-phenylallyl)sulfonyl)benzene(5g)

Ph O₂ S, Pr Under Argon atmosphere, 1(0.4 mmol), 4(0.8 mmol), Ru(bpy)₃Cl₂(1 mol%) were dissolved in 1,4-dioxane(4 mL). After that, the solution was stirred under irritation of white LEDs for 4 hours. The crude products were purified by flash chromatography on silica gel (petroleum

ether/ethyl acetate 5:1~2:1) to afford the aim products **5e**. Yellow oil, 42.4 mg, yield: 41%. ¹**H NMR** (400 MHz, Chloroform-*d*) δ 7.86 – 7.76 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.23 (m, 5H), 5.62 (s, 1H), 5.25 (s, 1H), 4.30 (s, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 138.8, 138.4, 136.5, 133.6, 128.9, 128.7, 128.4, 128.1, 126.2, 121.9, 62.1. Spectroscopic data matched with the reported data in the literature.

((phenylethynyl)sulfonyl)benzene(7a)



Under Argon atmosphere, 1(0.2 mmol), 6(0.4 mmol), mesitylene(0.8 mmol), activated MS4Å(100 mg), Ru(bpy)₃Cl₂ (0.5 mol%) were dissolved in 1,4-dioxane(1 mL). After that, the solution was stirred under irritation of white LEDs at room temperature for 12 hours. The crude products were purified by flash chromatography on silica gel

(petroleum ether/ethyl acetate 10:1) to afford the aim products **7a**. Light yellow oil, 21.4 mg, yield: 43%. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.19 – 8.08 (m, 2H), 7.76 – 7.69 (m, 1H), 7.63 (t, *J* = 7.7 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.53 – 7.46 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 141.81, 134.18, 132.77, 131.60, 129.39, 128.71, 127.42, 117.88, 93.51, 85.34. Spectroscopic data matched with the reported data in the literature.

1-methyl-4-((phenylethynyl)sulfonyl)benzene(7b)^[14]



Under Argon atmosphere, 1(0.2 mmol), 6(0.4 mmol), mesitylene(0.8 mmol), activated MS4Å(100 mg), Ru(bpy)₃Cl₂(0.5 mol%) were dissolved in 1,4-dioxane(1 mL). After that, the solution was stirred under irritation of white LEDs at room temperature for 12 hours. The crude products were purified by flash

chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to afford the aim products **7b**. Yellow soild, 21.1 mg, yield: 41%.

¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.06 – 7.95 (m, 2H), 7.58 – 7.46 (m, 3H), 7.40 (dt, *J* = 8.5, 7.1 Hz, 4H), 2.49 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 145.4, 139.0, 132.7, 131.4, 130.0, 128.7, 127.5, 118.04, 93.0, 85.6, 21.7. Spectroscopic data matched with the reported data in the literature.

1-(tert-butyl)-4-((phenylethynyl)sulfonyl)benzene(7c)^[14]



Under Argon atmosphere, 1(0.2 mmol), 6(0.4 mmol), mesitylene(0.8 mmol), activated MS4Å(100 mg), Ru(bpy)₃Cl₂ (0.5 mol%) were dissolved in 1,4-dioxane(1 mL). After that, the solution was stirred under irritation of white LEDs at room temperature for 12 hours. The crude products were purified by flash

chromatography on silica gel (petroleum ether/DCM 1:1) to afford the aim products 7c. Yellow soild, 30.4 mg, yield: 51%.

¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.05 – 7.98 (m, 2H), 7.63 (d, J = 1.9 Hz, 1H), 7.62 – 7.44 (m, 4H), 7.43 – 7.34 (m, 2H), 1.39 (s, 9H). ¹³**C NMR** (101 MHz, CDCl₃) δ 158.3, 138.8, 132.8, 131.4, 128.7,

127.3, 126.4, 118.1, 93.0, 85.6, 35.4, 31.0. Spectroscopic data matched with the reported data in the literature.

1-chloro-4-((phenylethynyl)sulfonyl)benzene(7d)^[14]



Under Argon atmosphere, 1(0.2 mmol), 6(0.4 mmol), mesitylene(0.8 mmol), activated MS4Å(100 mg), Ru(bpy)₃Cl₂(0.5 mol%) were dissolved in 1,4-dioxane(1 mL). After that, the solution was stirred under irritation of white LEDs at room temperature for 12 hours. The crude products were purified by flash

chromatography on silica gel (petroleum ether/DCM 1:1) to afford the aim products 7c. Yellow soild, 27.6 mg, yield: 50%.

¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.15 – 8.07 (m, 2H), 7.75 – 7.68 (m, 1H), 7.66 – 7.59 (m, 2H), 7.57 – 7.53 (m, 2H), 7.53 – 7.45 (m, 1H), 7.40 (t, *J* = 7.5 Hz, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 141.9, 134.1, 132.8, 131.6, 129.4, 128.7, 127.4, 117.9, 93.5, 85.4. Spectroscopic data matched with the reported data in the literature.

1-bromo-4-((phenylethynyl)sulfonyl)benzene(7e)^[14]



Under Argon atmosphere, 1(0.2 mmol), 6(0.4 mmol), mesitylene(0.8 mmol), activated MS4Å(100 mg), Ru(bpy)₃Cl₂ (0.5 mol%) were dissolved in 1,4-dioxane(1 mL). After that, the solution was stirred under irritation of white LEDs at room temperature for 12 hours. The crude products were purified by flash

chromatography on silica gel (petroleum ether/DCM 1:1) to afford the aim products 7e. Yellow soild, 36.0 mg, yield: 50%. Spectroscopic data matched with the reported data in the literature.

¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.08 – 8.00 (m, 2H), 7.64 – 7.57 (m, 2H), 7.57 – 7.47 (m, 3H), 7.45 – 7.36 (m, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 141.0, 140.3, 132.8, 131.7, 129.7, 128.9, 128.7, 117.7, 94.0, 85.1.

1-bromo-3-((phenylethynyl)sulfonyl)benzene(7f)^[14]



Under Argon atmosphere, 1(0.2 mmol), 6(0.4 mmol), mesitylene(0.8 mmol), activated MS4Å(100 mg), Ru(bpy)₃Cl₂ (0.5 mol%) were dissolved in 1,4-dioxane(1 mL). After that, the solution was stirred under irritation of white LEDs at room temperature for 12 hours. The crude products were purified by flash

chromatography on silica gel (petroleum ether/DCM 1:1) to afford the aim products **7f**. Yellow soild, 19.3 mg, yield: 30%. Spectroscopic data matched with the reported data in the literature.

¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.24 (t, J = 1.9 Hz, 1H), 8.04 (ddd, J = 7.9, 1.8, 1.0 Hz, 1H), 7.83 (ddd, J = 8.1, 2.0, 1.0 Hz, 1H), 7.62 – 7.46 (m, 4H), 7.42 (dd, J = 8.2, 6.9 Hz, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 143.6, 137.2, 132.9, 131.8, 130.9, 130.3, 128.8, 126.0, 123.3, 117.6, 94.4, 84.9.

Compound 9



Under Argon atmosphere, 8(0.2 mmol), 1(0.4 mmol), $\text{Ru}(\text{bpy})_3\text{Cl}_2(1 \text{ mol}\%)$ were dissolved in 1,4-dioxane(1 mL). After that, the solution was stirred under irritation of white LEDs at room temperature for **2 hours**. The crude products were purified by flash chromatography on silica gel (petroleum ether/ethyl

acetate 5:1~2:1) to afford the aim products 9. Yellow oil, 35.8 mg, yield: 45%, 1:1 d.r..

¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.09 (dd, J = 8.4, 3.0 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.39 (t, J =7.7 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.21 (td, J = 8.0, 2.6 Hz, 1H), 6.94 (td, J = 7.5, 2.6 Hz, 1H), 6.86 (dd, J = 8.0, 2.1 Hz, 1H), 4.79 (q, J = 9.5 Hz, 1H), 4.61 (ddd, J = 16.1, 9.7, 6.3 Hz, 1H), 4.26 - 4.13 (m, 1H), 4.13 – 4.02 (m, 1H), 3.98 (dd, J = 7.2, 5.5 Hz, 1H), 3.82 – 3.73 (m, 1H), 3.42 (ddd, J = 13.6, 9.7, 4.5 Hz, 2H), 3.02 (ddd, J = 17.0, 7.1, 4.9 Hz, 1H), 2.85 (ddtd, J = 11.6, 8.9, 7.1, 4.5 Hz, 1H), 2.69 (tt, J = 14.1, 5.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 189.6, 189.5, 159.8, 159.7, 143.8, 135.0, 131.4, 129.4, 129.3, 129.0, 128.2, 127.3, 127.0, 126.9, 124.6, 124.4, 121.0, 120.9, 110.1, 110.0, 76.0, 76.0, 68.1, 66.8, 58.4, 58.0, 36.2, 35.8, 26.8, 26.72, 22.0, 21.8. IR (KBr, cm⁻¹): 1678, 1598, 1482, 1458, 1304, 1235, 1129, 1017, 966, 913, 748. HRMS m/z (ESI) calcd. for C19H18NaO4S⁺ (M + Na)⁺ 365.0818, found 365.0816.

1-(3-chlorophenyl)-3,3,3-trifluoropropan-1-one^[15]

Under Argon atmosphere, 3i (0.8 mmol), Ru(bpy)₃Cl₂ (2.56 mg) were dissolved in 1,4-dioxane (4 mL). After that, the solution was stirred under irritation of white LEDs at room temperature for 1 hour. The crude products were purified by flash

chromatography on silica gel (petroleum ether/EA 20:1) to afford the aim products 3i'. Colorless oil, 65.7 mg, yield: 37%.

¹**H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (t, *J* = 1.9 Hz, 1H), 7.82 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.62 (ddd, J = 8.0, 2.1, 1.0 Hz, 1H), 7.48 (t, J = 7.9 Hz, 1H), 3.81 (q, J = 9.9 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 188.6, 188.6, 134.2, 130.3, 128.4, 126.4, 123.8 (q, J = 277.0 Hz), 42.2 (q, J = 28.5 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.09.

Compound 10^[16]



Under Argon atmosphere, 1(0.2 mmol), 6(0.4 mmol), Ru(bpy)₃Cl₂ (2 mol%) were dissolved in 1,4-dioxane(1 mL). After that, the solution was stirred under irritation of white LEDs at room temperature for 2 hours. The crude products were purified by flash chromatography on silica gel (petroleum ether/EA 20:1) to afford the aim products 10. Colorless oil, 24 mg, yield: 32%.

¹**H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (dd, *J* = 7.4, 2.1 Hz, 2H), 7.33 (d, *J* = 6.6 Hz, 3H), 4.59 (dd, J = 8.5, 2.9 Hz, 1H), 3.96 (dt, J = 11.5, 3.4 Hz, 2H), 3.80 - 3.68 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 131.9, 128.7, 128.3, 122.1, 86.6, 84.3, 70.4, 66.5, 66.4, 65.8. Spectroscopic data matched with the reported data in the literature.

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7. Copies of NMR spectra





3-(phenylsulfonyl)chroman-4-one (3b)























S30



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)







10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)









 $\label{eq:linear} 2-((4-chlorophenyl) sulfonyl)-3, 4-dihydronaphthalen-1(2H)-one~(3q)$

















S45

















(E)-3-(3-((4-methoxyphenyl)sulfonyl)-2-phenylprop-1-en-1-yl)cyclohexan-1-one (5e)







(E)-3-(3-((4-chlorophenyl)sulfonyl)-2-phenylprop-1-en-1-yl)cyclohexan-1-one (5f)





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

1-chloro-4-((phenylethynyl)sulfonyl)benzene(7d)







1-bromo-3-((phenylethynyl)sulfonyl)benzene(7f)

8.2459 8.2411 8.2364 8.0539 8.0515 8.0515 8.0497 8.0497 8.0318 8.0318 8.0318	8.0298 8.0272 7.8460 7.8460 7.8461 7.8411 7.8210 7.8236 7.8236 7.8236 7.5906 7.5828	7,506 7,576 566 7,5706 7,5706 7,546 7,546 7,546 7,548 7,548 7,548 7,538 7,501 3,750 486 7,501 3,750 486 7,501 3,750 486 7,501 3,750 486 7,501 3,750 501 3,750 501 3,750 501 3,750 500 500 7,500 500 500 500 500 500 500 500 500 500
		<u>, , , , , , , , , , , , , , , , , , , </u>









10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)



