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# **Supporting Information**

Selective Synthesis of Enol Ethers by Nickel-Catalyzed Cross

Coupling of  $\alpha$ -oxy-Vinylsulfones with Alkylzinc Reagents

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### **1. General Information**

Flash column chromatography was performed using silica gel (300-400 mesh) purchased from Qindao Haiyang. Ni(OAc)<sub>2</sub>, 5-Me-bpy, DMA and THF were purchased from Energy Chemical and used as received. Unless otherwise noted, all reported yields of the reactions are isolated yields of purified products. NMR yields were determined by using 1,3,5-trimethoxybenzene as an internal standard. All new compounds were characterized by NMR spectroscopy, IR spectroscopy, high-resolution mass spectroscopy (HR-MS), and melting point (if solids). NMR spectra were recorded on a Bruker AMX 400 spectrometer and were calibrated using TMS (0.00 ppm) or residual deuterated solvent as an internal reference (CDCl<sub>3</sub>: 7.26 ppm for <sup>1</sup>H NMR and 77.16 ppm for <sup>13</sup>C NMR), and the tabulated data were reported in ppm. IR spectra were taken on Thermo Scientific Nicolet iS5 spectrometer (iD5 ATR, diamond). HR-MS spectra were recorded on a Waters Q-TOF Premier. Melting points (m.p.) were recorded on an INESA SGW X-4 melting point apparatus.

#### 2. General Procedure for the Ni-Catalyzed Cross-Coupling Reaction



Vinylsulfone **7** were weighed into a Schlenk tube containing a magnetic stir bar. The Schlenk tube was loosely capped and transferred into a nitrogen-filled glovebox. To the Schlenk tube was sequentially added Ni(OAc)<sub>2</sub>, 5-Me-bpy, and solvent (THF 0.1-0.2 M). The reaction mixture was stirred at glovebox for 1 min, and then added alkylzinc Reagents **8**. The Schlenk tube was screw capped and put into a preheated oil bath (50 or 70 °C). After stirring for 8 h, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with EtOAc and filtered with a pad of cellite. The filtrate was washed with brine. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. Then 1,3,5-trimethoxybenzene was added into the residue as internal standard and confirmed the *E/Z* ratios and NMR yield of the products in table **2** and **3** by analysis of the <sup>1</sup>H NMR spectra of the crude mixture. The crude mixture was purified with silica gel chromatography to give the pure product **9**.

# 3. Condition Optimization

## Table S1. Other Representative Conditions Not Listed in Table 1

0 	OMe		2	10 mmol% [M] C 0 mmol% Ligand		/le
	SO <sub>2</sub> Ph	+ NC	`ZnBr s	olvent, 50 °C, 8h	$\sim$	$\sim$
	0 10	11a			`О 12а	
entry	[M]	Ligand	Solvent	conversion of 10	yield of 12a	Z:E
1	Fe(OTf) <sub>3</sub>	Xantphos	THF	trace	0%	N.D.
2	FeCl <sub>2</sub>	Xantphos	THF	trace	0%	N.D.
3	PdCl <sub>2</sub>	Xantphos	THF	12%	0%	N.D.
4	Pd(OAc) <sub>2</sub>	Xantphos	THF	15%	0%	N.D.
5	Pd(PPh <sub>3</sub> ) <sub>4</sub>	Xantphos	THF	8%	0%	N.D.
6	Pd(PPh <sub>3</sub> ) <sub>4</sub>	N/A	THF	20%	0%	N.D.
7	Ni(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	N/A	THF	89%	25%	1:1
8	Ni(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	N/A	THF	93%	11%	1:1
9	Ni(OAc) <sub>2</sub>	L1	THF	92%	53%	5:1
10	Ni(OAc) <sub>2</sub>	L2	THF	>95%	68%	>19:1
11	Ni(OAc) <sub>2</sub>	L3	THF	64%	24%	10:1
12	Ni(OAc) <sub>2</sub>	L4	THF	70%	31%	4:1
13	Ni(OAc) <sub>2</sub>	L5	THF	46%	5%	N.D.
14	Ni(OAc) <sub>2</sub>	L6	THF	68%	49%	1:1
15	Ni(OAc) <sub>2</sub>	L7	THF	72%	5%	N.D.
16	Ni(OAc) <sub>2</sub>	L8	THF	86%	4%	N.D.
17	Ni(cod) <sub>2</sub>	L2	THF	>95%	61%	9:1
18	Ni(acac) <sub>2</sub>	L2	THF	>95%	39%	>19:1
19	NiCl <sub>2</sub>	L2	THF	46%	trace	N.D.
20	NiBr <sub>2</sub>	L2	THF	68%	30%	10:1
21	Ni(OTf) <sub>2</sub>	L2	THF	36%	trace	N.D.
22	Ni(OAc) <sub>2</sub>	L2	DCM	35%	trace	N.D.
23	Ni(OAc) <sub>2</sub>	L2	DCE	90%	55%	10:1
24	Ni(OAc) <sub>2</sub>	L2	CH <sub>3</sub> CN	>95%	53%	9:1
25	Ni(OAc) <sub>2</sub>	L2	toluene	>95%	63%	9:1
26	Ni(OAc) <sub>2</sub>	L2	Dioxane	>95%	57%	12:1
27	Ni(OAc) <sub>2</sub>	L2	EtOAc	>95%	60%	16:1



### 4. General Procedures for the Synthesis of Alkylzinc Reagents

### 4.1 Preparation of Alkylzinc Reagents<sup>1</sup>

A 25 mL of Schlenk tube was charged with zinc powder (295.0 mg, 4.5 mmol) and heated to 80 °C under vacuum for 30 min. After the tube was back-filled with argon and cooled to room temperature, iodine (38.0 mg, 0.15 mmol) and DMA (3.0 mL) were added. The resulting mixture was stirred until the brown color disappeared, then alkylbromide (3.0 mmol) was added. The reaction mixture was heated to 80 °C. After stirring for 10 h at 80 °C, the mixture was cooled to room temperature. The gray solution was filtered under an inert atmosphere by injection through a syringe filter and the filtrate was stored under argon in a Schlenk tube, the solution of the alkylzinc reagent was titrated with I<sub>2</sub> according to Knochel's method<sup>2</sup>. This alkylzinc solution can be stored at room temperature under argon for several weeks without deterioration.

### 4.2 Preparation of Starting Materials



The title compound was prepared according to literature procedure<sup>3</sup> from 2-(thiophen-3-yl)ethan-1-ol (10 mmol, 1.12 mL), affording 3-(2-bromoethyl)thiophene as a colorless liquid (1.24 g, 6.5 mmol, 65%). The analytical data is in full consistency with the data reported in the literature.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>) δ 7.29 (dd, *J* = 4.8, 3.2 Hz, 1H), 7.10 – 7.05 (m, 1H), 6.98 (d, *J* = 4.8 Hz, 1H), 3.57 (t, *J* = 7.6 Hz, 2H), 3.21 (t, *J* = 7.6 Hz, 2H).

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The title compound was prepared according to literature<sup>4</sup> procedure from 3 bromopropylammonium bromide (1.75 g, 8.0 mmol) affording 1-(3-bromopropyl)-2,5-dimethyl-1*H*-pyrrole as a colorless oil (1.27 g, 5.9 mmol, 73%). The analytical data is in full consistency with the data reported in the literature.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>) δ 5.77 (s, 2H), 3.89 (t, *J* = 7.2 Hz, 2H), 3.40 (t, *J* = 6.3 Hz, 2H), 2.23 (s, 6H), 2.17 (dt, *J* = 13.2, 6.4 Hz, 2H).

### 5. General Procedures for the Synthesis of Acyclic $\alpha$ -Oxy Vinylsulfones

MeOSO <sub>2</sub> Ph	+	R H	LDA, CIP(=O)(OEt) <sub>2</sub>	MeO R H
13-SM1a		13-SM2		13

### **5.1 Preparation of α-Methoxy Vinylsulfones**

The acyclic  $\alpha$ -methoxy vinyl sulfones were prepared according to literature procedures with slight modification.<sup>5</sup>

To a THF solution (15 mL) of [(methoxymethyl)sulfonyl]benzene<sup>6</sup> (**13-SM1a**, 3.3 mmol, 1.1 equiv) cooled at -78 °C was added LDA (9.0 mmol, 3.0 equiv, 2.0 M in THF) dropwise under nitrogen atmosphere. After 15 min, diethyl chlorophosphate (4.5 mmol, 1.5 equiv) was added dropwise over 10 min. The reaction mixture was stirred for 1 h, and a solution of aldehyde (**13-SM2** 3.0 mmol, 1.0 equiv) in THF (5 mL) was added over 5 min. The reaction was allowed to warm to room temperature and stirred overnight. Before being quenched with saturated aqueous NH4Cl at 0 °C. The mixture was extracted with ethyl acetate, and the combined organic layers were dried and concentrated in vacuo. The resulting residue was purified by flash chromatography to give **13** as a separable mixture of E/Z isomers.



Following **General Procedure**, 4-(1,3-dioxoisoindolin-2-yl)butanal **13-SM2a** (5.0 mmol, 1.086 g) and [(methoxymethyl)sulfonyl]benzene (**13-SM1a**, 5.5 mmol) were used. Compound **10** was isolated by silica gel chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 6/1) as a white solid (E/Z = 1:0.8, 1.4 g, 72% yield).

**HRMS** (**DART-TOF**) calculated for  $C_{20}H_{19}NNaO_5S^+[M+Na]^+ m/z 408.0876$ , found 408.0881.



(*E*)-2-(5-methoxy-5-(phenylsulfonyl)pent-4-en-1yl)isoindoline-1,3-dionee (*E*-10)

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 (d, J = 7.6 Hz, 2H), 7.84 (dd, J = 5.2, 3.2 Hz, 2H), 7.72 (dd, J = 5.6, 3.2 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 6.45 (t, J = 7.6 Hz, 1H), 3.82 (s, 3H), 3.70 (t, J = 7.2 Hz, 2H), 2.28 (dd, J = 15.6, 7.6 Hz, 2H), 1.84 (dt, J = 14.8, 7.6 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.4, 154.4, 139.1, 134.2, 133.7, 132.2, 129.2, 128.4, 125.5, 123.4, 63.3, 37.5, 27.7, 23.3. IR (thin film, cm<sup>-1</sup>): 2975, 2942, 1771, 1710, 1445, 1397, 1371, 1319, 1159, 1139, 1029, 956, 721, 648, 593 and 542 cm<sup>-1</sup>. m.p.: 108.5–111.5 °C



(Z)-2-(5-methoxy-5-(phenylsulfonyl)pent-4-en-1yl)isoindoline-1,3-dione (Z-10)

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.92 (d, J = 7.2 Hz, 2H), 7.84 (dd, J = 5.6, 3.2 Hz, 2H), 7.71 (dd, J = 5.6, 3.2 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 5.32 (t, J = 8.0 Hz, 1H), 3.75 (t, J = 7.2 Hz, 2H), 3.59 (s, 3H), 2.74 (dd, J = 15.2, 7.6 Hz, 2H), 1.94 – 1.81 (m, 2H). <sup>13</sup>**C NMR (101 MHz, CDCl<sub>3</sub>)** δ 168.5, 153.4, 139.8, 134.0, 133.7, 132.2, 129.1, 128.2, 123.3, 112.8, 58.4, 37.3, 29.1, 22.6. **IR (thin film, cm<sup>-1</sup>)**: 2936, 2853, 1770, 1710, 1446, 1397, 1322, 1275, 1145, 1085, 750, 690 and 608 cm<sup>-1</sup>. **m.p.**: 95.2–98.2 °C

#### TIPSO SO<sub>2</sub>Ph triisopropyl((5-methoxy-5-(phenylsulfonyl)pent-4-en-1yl)oxy)silane (13a)

Following **General Procedure**, 4-((triisopropylsilyl)oxy)butanal<sup>7</sup> **13-SM2b** (3.0 mmol, 733 mg) and [(methoxymethyl)sulfonyl]benzene **13-SM1a** (3.3 mmol) were used. Compound **13a** was isolated by silica gel chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 10/1) as a yellow oil (E/Z = 0.8:1, 453 mg, 37% yield).

TIPSO SO<sub>2</sub>Ph (*E*)-triisopropyl((5-methoxy-5-(phenylsulfonyl)pent-4-en-1-yl)oxy)silane (*E*-13a)

<sup>1</sup>**H NMR** (**400 MHz**, **CDCl**<sub>3</sub>) δ 7.91 (d, J = 7.2 Hz, 2H), 7.69 – 7.57 (m, 1H), 7.52 (t, J = 7.6 Hz, 2H), 6.47 (t, J = 7.6 Hz, 1H), 3.82 (s, 3H), 3.70 (t, J = 6.0 Hz, 2H), 2.34 (dd, J = 15.2, 7.6 Hz, 2H), 1.71 – 1.65 (m, 2H), 1.12 – 1.07 (m, 3H), 1.06 – 1.02 (m, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.9, 139.2, 133.5, 129.1, 128.3, 126.9, 63.2, 62.4, 31.9, 22.4, 18.1, 12.0. **IR** (thin film, cm<sup>-1</sup>): 2942, 2865, 1650, 1463, 1319, 1276, 1158, 1066, 883, 750, 686 and 594 cm<sup>-1</sup>. **HRMS (DART-TOF)** calculated for C<sub>21</sub>H<sub>36</sub>NaO<sub>4</sub>SSi<sup>+</sup> [M+Na]<sup>+</sup> m/z 435.1996, found 435.2001.

H (Z)-triisopropyl((5-methoxy-5-(phenylsulfonyl)pent-4-en-1-VI)OMe yl)oxy)silane (Z-13a) SO<sub>2</sub>Ph

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, J = 7.2 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 5.35 (t, J = 8.0 Hz, 1H), 3.75 (t, J = 6.4 Hz, 2H), 3.58 (s, 3H), 2.76 (dd, J = 15.2, 7.6 Hz, 2H), 1.71 (dd, J = 14.4, 6.8 Hz, 2H), 1.12 – 1.07 (m, 3H), 1.07 – 1.04 (m, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.7, 140.1, 133.6, 129.0, 128.2, 115.3, 62.9, 58.6, 33.5, 22.1, 18.1, 12.1. IR (thin film, cm<sup>-1</sup>): 2943, 2870, 1727, 1447, 1306, 1151, 1124, 995, 758, 730, 689 and 610 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>21</sub>H<sub>36</sub>NaO<sub>4</sub>SSi<sup>+</sup> [M+Na]<sup>+</sup> m/z 435.1996, found 435.1997.



## SO<sub>2</sub>Ph ((1-methoxydodeca-1,11-dien-1yl)sulfonyl)benzene (13b)

Following **General Procedure**, 10-undecenal **13-SM2c** (3.0 mmol, 601 uL) and [(methoxymethyl)sulfonyl]benzene **13-SM1a** (3.3 mmol) were used. Compound **13b** was isolated by silica gel chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 10/1) as a light yellow oil (E/Z = 1:0.92, 790 mg, 78% yield).



<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (d, J = 7.6 Hz, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 6.36 (t, J = 7.6 Hz, 1H), 5.77 – 5.67 (m, 1H), 4.91 (dd, J = 17.2, 1.4 Hz, 1H), 4.85 (d, J = 10.2 Hz, 1H), 3.73 (s, 3H), 2.13 (q, J = 7.6 Hz, 2H), 1.95 (q, J = 14.0, 7.0 Hz, 2H), 1.41 – 1.33 (m, 2H), 1.30 – 1.27 (m, 2H), 1.25 – 1.15 (m, 8H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.7, 139.3, 139.2, 133.5, 129.1, 128.3, 127.3, 114.2, 63.2, 33.8, 29.4, 29.3, 29.3, 29.1, 28.9, 28.5, 25.7. IR (thin film, cm<sup>-1</sup>): 3070, 2925, 2854, 1644, 1447, 1319, 1154, 1068, 909, 756, 688, 594 and 548 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>19</sub>H<sub>28</sub>NaO<sub>3</sub>S<sup>+</sup> [M+Na]<sup>+</sup> m/z 359.1651, found 359.1655.



# OMe (Z)-((1-methoxydodeca-1,11-dien-1yl)sulfonyl)benzene (Z-13b)

<sup>1</sup>**H NMR** (**400 MHz**, **CDCl**<sub>3</sub>) δ 7.93 (d, J = 7.2 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 5.86-5.76 (m, 1H), 5.28 (t, J = 8.0 Hz, 1H), 4.99 (d, J = 16.0, 1H), 4.93 (d, J = 8.0, 1H), 3.58 (s, 3H), 2.67 (dd, J = 15.2, 7.8 Hz, 2H), 2.04 (dd, J = 14.4, 6.8 Hz, 2H), 1.49 – 1.41 (m, 2H), 1.40 – 1.35 (m, 2H), 1.34 – 1.26 (m, 8H). IR (thin film, cm<sup>-1</sup>): 3071, 2926, 2855, 1730, 1639, 1447, 1307, 1187, 1145, 1085, 732, 688 and 591 cm<sup>-1</sup>. <sup>13</sup>C **NMR (101 MHz, CDCl**<sub>3</sub>) δ 152.6, 140.1, 139.3, 133.6, 129.0, 128.2, 115.9, 114.2, 58.7, 33.9, 30.3, 29.5, 29.5, 29.3, 29.2, 29.0, 25.3. **HRMS (DART-TOF)** calculated for C<sub>19</sub>H<sub>28</sub>NaO<sub>3</sub>S<sup>+</sup> [M+Na]<sup>+</sup> m/z 359.1651, found 359.1659.



((1-methoxy-4,8-dimethylnona-1,7-dien-1yl)sulfonyl)benzene (13c)

Following **General Procedure**, citronellal **13-SM2d** (3.0 mmol, 540 uL) and [(methoxymethyl)sulfonyl]benzene **13-SM1a** (3.3 mmol) were used. Compound **13c** was isolated by silica gel chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 10/1) as a yellow oil (E/Z = 1:0.61, 532 mg, 74% yield).



<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (d, J = 7.2 Hz, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 6.46 (t, J = 7.6 Hz, 1H), 5.04 (t, J = 7.2 Hz, 1H), 3.81 (s, 3H), 2.25 – 2.18 (m, 1H), 2.13 – 2.03 (m, 1H), 2.03 – 1.89 (m, 2H), 1.67 (s, 3H), 1.66 – 1.59 (m, 1H), 1.58 (s, 3H), 1.39 – 1.27 (m, 1H), 1.25 – 1.13 (m, 1H), 0.90 (d, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.1, 139.3, 133.5, 131.6, 129.1, 128.3, 126.3, 124.3, 63.1, 36.8, 32.7, 32.5, 25.8, 25.5, 19.7, 17.7. IR (thin film, cm<sup>-1</sup>): 2969, 2917, 2850, 1649, 1307, 1156, 1067, 751, 688, 595 and 546 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>18</sub>H<sub>26</sub>NaO<sub>3</sub>S<sup>+</sup> [M+Na]<sup>+</sup> m/z 345.1495, found 345.1500.



<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, J = 7.2 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 5.30 (t, J = 8.0 Hz, 1H), 5.09 (t, J = 7.2 Hz, 1H), 3.60 (s, 3H), 2.71 – 2.64 (m, 1H), 2.63 – 2.53 (m, 1H), 2.10 – 1.90 (m, 2H), 1.69 (s, 3H), 1.60 (s, 3H), 1.59 – 1.51 (m, 1H), 1.47 – 1.32 (m, 1H), 1.29 – 1.16 (m, 1H), 0.93 (d, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.0, 140.1, 133.6, 131.5, 129.0, 128.2, 124.6, 114.9, 58.8, 36.7, 33.7, 32.2, 25.8, 25.7, 19.4, 17.8. IR (thin film, cm<sup>-1</sup>): 2975, 2952, 2850, 1707, 1447, 1322, 1307, 1275, 1259, 1143, 1084, 974, 763, 750, and 688 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>18</sub>H<sub>26</sub>NaO<sub>3</sub>S<sup>+</sup> [M+Na]<sup>+</sup> m/z 345.1495, found 345.1498.

# OMe ethyl 3-methoxy-3-(phenylsulfonyl)acrylate (13d) EtOOC

Following General Procedure, ethyl glyoxalate 13-SM2e (6.0 mmol, 595 uL) and [(methoxymethyl)sulfonyl]benzene 13-SM1a (4.0 mmol) were used. Compound 13d was isolated by silica gel chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 10/1) as a yellow oil (E/Z = 0.64:1, 433 mg, 40% yield).

# OMe ethyl (E)-3-methoxy-3-(phenylsulfonyl)acrylate (E-13d)

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, J = 8.0 Hz, 2H), 7.68 (t, J = 7.6 Hz, 1H), 7.57 (t, J = 7.6 Hz, 2H), 6.54 (s, 1H), 4.22 (q, J = 7.2 Hz, 2H), 4.00 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.5, 163.2, 137.3, 134.5, 129.4, 129.2, 107.2, 64.6, 61.5, 14.2. IR (thin film, cm<sup>-1</sup>): 3067, 2984, 2946, 2843, 1719, 1641, 1447, 1322, 1190, 1158, 1107, 1074, 1027, 977, 877, 759, 734, 688, 581 and 537 cm<sup>-1</sup>.HRMS (DART-TOF) calculated for  $C_{12}H_{14}NaO_5S^+$ [M+Na]<sup>+</sup> m/z 293.0454, found 293.0460.



<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (d, J = 7.2 Hz, 2H), 7.67 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 2H), 5.52 (s, 1H), 4.32 (q, J = 7.2 Hz, 2H), 3.64 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.4, 159.9, 138.1, 134.3, 129.2, 129.2, 100.5, 62.0, 58.0, 14.1. IR (thin film, cm<sup>-1</sup>): 3055, 2984, 2942, 2896, 1742, 1639, 1448, 1332, 1192, 1149, 1084, 1030, 965, 749, 688, 619, 597 and 546 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>20</sub>H<sub>19</sub>NNaO<sub>5</sub>S<sup>+</sup> [M+Na]<sup>+</sup> m/z 293.0454, found 293.0458.

# Me SO<sub>2</sub>Ph ((1-methoxy-3-phenylbut-1-en-1-yl)sulfonyl)benzene (13e)

Following **General Procedure**, 2-phenylpropionaldehyde **13-SM2f** (3.0 mmol, 395 uL) and [(methoxymethyl)sulfonyl]benzene **13-SM1a** (3.3 mmol) were used. Compound **13e** was isolated by silica gel chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 10/1) as a yellow oil (E/Z = 0.76:1, 580 mg, 64% yield).

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<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (d, J = 7.2 Hz, 2H), 7.64 – 7.56 (m, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.22 (dd, J = 9.8, 4.4 Hz, 3H), 6.62 (d, J = 10.4 Hz, 1H), 3.92 – 3.84 (m, 1H), 3.81 (s, 3H), 1.41 (d, J = 7.2 Hz, 3H). <sup>13</sup>**C** NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.5, 143.5, 139.1, 133.6, 130.9, 129.2, 128.9, 128.3, 126.9, 63.5, 36.3, 21.8. IR (thin film, cm<sup>-1</sup>): 3064, 3028, 2969, 2936, 1646, 1448, 1307, 1161, 1135, 1094, 1064, 951, 688, 604 and 550 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>17</sub>H<sub>18</sub>NaO<sub>3</sub>S<sup>+</sup> [M+Na]<sup>+</sup> m/z 325.0869, found 325.0870.

$$\begin{array}{ccc} & \mathsf{Me} & \mathsf{SO}_2\mathsf{Ph} & (Z)-((1-\mathsf{methoxy-3-phenylbut-1-en-1-yl})\mathsf{sulfonyl})\mathsf{benzene} & (Z-13e) \\ & \mathsf{Ph} & & \\ & \mathsf{H} & \\ & \mathsf{H} & \end{array}$$

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.88 (d, J = 7.2 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.34 – 7.26 (m, 4H), 7.24 – 7.18 (m, 1H), 5.33 (d, J = 10.8 Hz, 1H), 5.02 – 4.88 (m, 1H), 3.55 (s, 3H), 1.44 (d, J = 6.8 Hz, 3H). <sup>13</sup>**C NMR** (101 MHz, CDCl<sub>3</sub>) δ 151.6, 145.1, 139.8, 133.7, 129.1, 128.7, 128.3, 127.0, 126.6, 119.5, 58.4, 34.8, 22.5. **IR** (thin film, cm<sup>-1</sup>): 3068, 3038, 2966, 2932, 1631, 1448, 1324, 1143, 1082, 777, 735, 700, 608 and 582 cm<sup>-1</sup>. **HRMS** (DART-TOF) calculated for C<sub>17</sub>H<sub>18</sub>NaO<sub>3</sub>S<sup>+</sup> [M+Na]<sup>+</sup> m/z 325.0869, found 325.0873.

# MeO SO<sub>2</sub>Ph ((1-methoxy-3,3-dimethylbut-1-en-1-yl)sulfonyl)benzene (13f)

Following **General Procedure**, pivaldehyde **13-SM2g** (3.0 mmol, 326 uL) and [(methoxymethyl)sulfonyl]benzene **13-SM1a** (3.3 mmol) were used. Compound **13f** was isolated by silica gel chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 10/1) as a yellow oil (E/Z = 0.81:1, 220 mg, 29% yield).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (dd, J = 17.6, 7.6 Hz, 3.4H, 2H<sub>*E*</sub>, 1.4 H<sub>*z*</sub>), 7.88 (t, J = 7.6 Hz, 1.7H, 1H<sub>*E*</sub>, 0.7 H<sub>*z*</sub>), 7.56 – 7.49 (m, 3.4H, 2H<sub>*E*</sub>, 1.4H<sub>*z*</sub>), 6.38 (s, 1H, H<sub>*E*</sub>), 5.44 (s, 0.7H, H<sub>*z*</sub>), 3.87 (s, 3H, H<sub>*E*</sub>), 3.52 (s, 2.1H, H<sub>*z*</sub>), 1.39 (s, 6.3H, H<sub>*z*</sub>), 1.16 (s, 9H, H<sub>*E*</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.5 (C<sub>*Z*</sub>), 151.8 (C<sub>*E*</sub>), 140.0 (C<sub>*Z*</sub>), 139.6 (C<sub>*E*</sub>), 135.4 (C<sub>*E*</sub>), 133.5 (C<sub>*E*</sub>), 133.4 (C<sub>*Z*</sub>), 129.2 (C<sub>*E*</sub>), 128.9 (C<sub>*Z*</sub>), 128.6 (C<sub>*Z*</sub>), 128.1 (C<sub>*E*</sub>), 127.8 (C<sub>*Z*</sub>), 63.5 (C<sub>*E*</sub>), 59.6 (C<sub>*Z*</sub>), 33.1 (C<sub>*E*</sub>), 31.8 (C<sub>*Z*</sub>), 31.7 (C<sub>*Z*</sub>), 29.7 (C<sub>*E*</sub>). IR (thin film, cm<sup>-1</sup>): 2960, 2866, 1447, 1306, 1154, 1067, 752, 688, 659, 597 and 555 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>13</sub>H<sub>18</sub>NaO<sub>3</sub>S<sup>+</sup> [M+Na]<sup>+</sup> m/z 277.0869, found 277.0870.

# PhO<sub>2</sub>S OMe (Z)-((1-methoxy-3,3-dimethylbut-1-en-1-yl)sulfonyl)benzene (Z-13f)

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 5.44 (s, 1H), 3.52 (s, 3H), 1.39 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.5, 140.0, 133.5, 128.9, 128.6, 127.9, 59.6, 31.9, 31.7. IR (thin film, cm<sup>-1</sup>): 2958, 2869, 1614, 1447, 1320, 1156, 1130, 1081, 1035, 961, 828, 756, 728, 687, 658, 565, 514 and 458 cm<sup>-1</sup>.

# OMe ((2-cyclopropyl-1-methoxyvinyl)sulfonyl)benzene (13g)

Following **General Procedure**, cyclopropanecarboxaldehyde **13-SM2h** (5.0 mmol, 374 uL) and [(methoxymethyl)sulfonyl]benzene **13-SM1a** (5.5 mmol) were used. Compound **13g** was isolated by silica gel chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 10/1) as a yellow oil (E/Z = 0.82:1, 1.082 g, 91% yield).

# OMe (E)-((2-cyclopropyl-1-methoxyvinyl)sulfonyl)benzene (E-13g)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 (d, J = 7.6 Hz, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 5.88 (d, J = 10.6 Hz, 1H), 3.87 (s, 3H), 1.74 – 1.63 (m, 1H), 1.01 – 0.92 (m, 2H), 0.68 – 0.61 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.6, 139.3, 133.4, 132.4, 129.1, 128.2, 63.2, 9.0, 8.4. IR (thin film, cm<sup>-1</sup>): 3065, 3008, 2943, 2843, 1644, 1446, 1372, 1308, 1148,

1096, 1063, 954, 852, 753, 714, 689, 649, 590 and 551 cm<sup>-1</sup>. **HRMS (DART-TOF)** calculated for  $C_{12}H_{14}NaO_3S^+$  [M+Na]<sup>+</sup> m/z 261.0556, found 261.0559.



<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 (d, J = 7.2 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 4.74 (d, J = 10.6 Hz, 1H), 3.57 (s, 3H), 2.78 – 2.70 (m, 1H), 1.05 – 0.87 (m, 2H), 0.48 – 0.35 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 151.8, 140.2, 133.6, 129.1, 128.1, 124.0, 59.8, 8.6, 8.1. **IR** (thin film, cm<sup>-1</sup>): 3074, 3007, 2942, 2837, 1636, 1448, 1322, 1306, 1193, 1150, 1132, 1082, 975, 758, 734, 689, 602 and 572 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for  $C_{12}H_{14}NaO_3S^+$  [M+Na]<sup>+</sup> m/z 261.0556, found 261.0558.

# OMe ((2-cyclohexyl-1-methoxyvinyl)sulfonyl)benzene (13h)

Following **General Procedure**, cyclohexanecarboxaldehyde **13-SM2i** (3.0 mmol, 363 uL) and [(methoxymethyl)sulfonyl]benzene **13-SM1a** (3.3 mmol) were used. Compound **13h** was isolated by silica gel chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 10/1) as a yellow oil (E/Z = 0.91:1, 777 mg, 92% yield).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 – 7.83 (m, 2.42H, 2H<sub>E</sub>, 0.42H<sub>Z</sub>), 7.60 (t, *J* = 7.6 Hz, 1.21H, 1H<sub>E</sub>, 0.21H<sub>Z</sub>), 7.52 (t, *J* = 7.6 Hz, 2.42H, 2H<sub>E</sub>, 0.42H<sub>Z</sub>), 6.31 (d, *J* = 10.2 Hz, 1H, H<sub>E</sub>), 5.10 (d, *J* = 10.2 Hz, 0.21H, H<sub>Z</sub>), 3.81 (s, 3H, H<sub>E</sub>), 3.55 (s, 0.64H, H<sub>Z</sub>), 3.39 – 3.28 (m, 0.21H, H<sub>Z</sub>), 2.49 – 2.37 (m, 1H, H<sub>E</sub>), 1.82 – 1.70 (m, 3H, 2.5H<sub>E</sub>, 0.5H<sub>Z</sub>), 1.69 – 1.58 (m, 3H, 2.5H<sub>E</sub>, 0.5H<sub>Z</sub>), 1.43 – 1.04 (m, 6.05H, 5H<sub>E</sub>, 1.05H<sub>Z</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.2 (C<sub>E</sub>), 151.5 (C<sub>Z</sub>), 140.1 (C<sub>Z</sub>), 139.2 (C<sub>E</sub>), 133.5 (C<sub>Z</sub>), 133.4 (C<sub>E</sub>), 132.0 (C<sub>E</sub>), 129.1 (C<sub>E</sub>), 128.9 (C<sub>Z</sub>), 128.2 (C<sub>E</sub>), 128.1 (C<sub>Z</sub>), 120.9 (C<sub>Z</sub>), 63.7 (C<sub>E</sub>), 58.5 (C<sub>Z</sub>), 35.3 (C<sub>E</sub>), 34.2(C<sub>Z</sub>), 33.9 (C<sub>Z</sub>), 32.2 (C<sub>E</sub>), 25.8 (C<sub>Z</sub>), 25.7 (C<sub>E</sub>), 25.6 (C<sub>Z</sub>), 25.4 (C<sub>E</sub>). IR (thin film, cm<sup>-1</sup>): 2925, 2851, 1633, 1447, 1322, 1145, 1128, 1081, 1063, 973, 894, 844, 740, 688, 599, 562 and 540 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>15</sub>H<sub>20</sub>NNaO<sub>3</sub>S<sup>+</sup> [M+Na]<sup>+</sup> m/z 303.1025, found 303.1027.



<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 5.10 (d, *J* = 10.4 Hz, 1H), 3.55 (s, 3H), 3.39 – 3.29 (m, 1H), 1.76 – 1.66 (m, 5H), 1.46 – 1.30 (m, 2H), 1.22 – 1.00 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.5, 140.1, 133.5, 129.0, 128.1, 120.9, 58.5, 34.2, 33.9, 25.8, 25.6. IR (thin film, cm<sup>-1</sup>): 2924, 2850, 1633, 1447, 1322, 1292, 1146, 1127, 1081, 973, 894, 740, 688, 609, 592, 540 and 520 cm<sup>-1</sup>.

# Boc SO<sub>2</sub>Ph tert-butyl 4-(2-methoxy-2-(phenylsulfonyl)vinyl)piperidine-1-OMe carboxylate (13i)

Following **General Procedure**, 1-tert-Butoxycarbonyl-4-piperidinecarboxaldehyde **13-SM2j** (3.0 mmol, 640 mg) and [(methoxymethyl)sulfonyl]benzene **13-SM1a** (3.3 mmol) were used. Compound **13i** was isolated by silica gel chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 6/1) as a light yellow oil (E/Z = 0.7:1, 626 mg, 64% yield).



<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (d, J = 7.2 Hz, 2H), 7.63 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 6.28 (d, J = 9.8 Hz, 1H), 4.24 – 3.99 (m, 2H), 3.85 (s, 3H), 2.77 (t, J = 12.0 Hz, 2H), 2.66 – 2.50 (m, 1H), 1.67 – 1.57 (m, 2H), 1.46 (s, 9H), 1.45 – 1.34 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.8, 153.4, 139.0, 133.7, 129.7, 129.2, 128.3, 79.7, 63.7, 43.2, 33.6, 31.1, 28.5. IR (thin film, cm<sup>-1</sup>): 2982, 2934, 2857, 1688, 1423, 1143, 1162, 972, 779, 689 and 603 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>19</sub>H<sub>27</sub>NNaO<sub>5</sub>S<sup>+</sup> [M+Na]<sup>+</sup> m/z 404.1502, found 404.1507.



# tert-butyl (Z)-4-(2-methoxy-2-(phenylsulfonyl)vinyl)piperidine-1-carboxylate (Z-13i)

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (d, J = 7.2 Hz, 2H), 7.64 (t, J = 7.6 Hz, 1H), 7.55 (t, J = 7.6 Hz, 2H), 5.01 (d, J = 10.2 Hz, 1H), 4.18 – 4.02 (m, 2H), 3.56 (s, 3H), 3.51 (m, 1H), 2.82 (t, J = 11.6 Hz, 2H), 1.79 – 1.68 (m, 2H), 1.47 (s, 9H), 1.34 – 1.21 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.8, 152.5, 139.6, 133.7, 129.0, 128.2, 117.5, 79.4, 58.2, 43.3, 32.8, 32.6, 28.5. IR (thin film, cm<sup>-1</sup>): 2975, 2933, 2852, 1686, 1424, 1325, 1146, 1082, 975 and 613 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>19</sub>H<sub>27</sub>NNaO<sub>5</sub>S<sup>+</sup> [M+Na]<sup>+</sup> m/z 404.1502, found 404.1510.

5.2	preparati	ion of α-	Benzyloxy	y VinylSı	ılfones
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≪∽+	Bn <sub>o</sub> ci	Nao <sup>t</sup> Bu DMF, 0 °C to rt	BnOSPh	<i>m</i> -CPBA DCM, 0 °C to rt	BnOSO₂Ph
13-SM1ba	13-SM1k	ob	13-SM1bc		13-SM1b

To a DMF solution (30 mL) of NaO'Bu (9.6 mmol, 1.2 equiv) cooled at 0  $\,^{\circ}$ C was added thiophenol **13-SM1ba** (8.0 mmol, 1.0 equiv) dropwise under nitrogen atmosphere. After 30 min, benzylchloromethyl ether **13-SM1bb** (8.8 mmol, 1.1 equiv) was added dropwise over 10 min. The reaction was allowed to warm to room temperature and stirred overnight, before being quenched with brine at 0  $\,^{\circ}$ C. The mixture was extracted with ethyl acetate, and the combined organic layers were dried and concentrated in vacuo. The resulting residue was purified by flash chromatography of petroleum ether to give **13-SM1bc** as a colorless oil (1.84g, 99% yield).

To a DCM solution (30 mL) of **13-SM1bc** (7.5 mmol, 1.0 equiv) cooled at 0  $^{\circ}$ C was added *m*-CPBA (18.0 mmol, 2.4 equiv) dropwise over 10 min. The reaction was allowed to warm to room temperature and stirred for another 2h, and then diluted by addition of DCM. The mixture washed by sat. aq. NaHCO<sub>3</sub> (×2), and brine (×1). The mixture was extracted with ethyl acetate, and the combined organic layers were dried and concentrated in vacuo. The resulting residue was purified by flash chromatography (petroleum ether/ethyl acetate = 6/1) to give **13-SM1b** as a white solid (0.9g, 64% yield).

## Ph<sup>O</sup>SO<sub>2</sub>Ph ((benzyloxy)methyl)sulfonyl)benzene (13-SM1b)<sup>8</sup>

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (d, J = 7.2 Hz, 2H), 7.68 (t, J = 7.2 Hz, 1H), 7.57 (t, J = 8.0 Hz, 2H), 7.41 – 7.30 (m, 3H), 7.29 – 7.24 (m, 2H), 4.90 (s, 2H), 4.57 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  137.3, 135.8, 134.1, 129.2, 128.7, 128.6, 128.38, 128.2, 84.7, 74.5.



To a THF solution (15 mL) of (((benzyloxy)methyl)sulfonyl)benzene (**13-SM1b**, 3.3 mmol, 1.1 equiv) cooled at -78  $^{\circ}$ C was added LDA (9.0 mmol, 3.0 equiv, 2.0 M in THF) dropwise under nitrogen atmosphere. After 15 min, diethyl chlorophosphate (4.5 mmol, 1.5 equiv) was added dropwise over 10 min. The reaction mixture was stirred for 1 h, and a solution of aldehyde (**13-SM2a**, 3.0 mmol, 1.0 equiv) in THF (5 mL) was added over 5 min. The reaction was allowed to warm to room temperature and stirred overnight, before being quenched with saturated aqueous NH4Cl at 0  $^{\circ}$ C. The mixture was extracted with ethyl acetate, and the combined organic layers were dried and concentrated in vacuo. The resulting residue was purified by flash chromatography to give **13j** as a separable mixture of *E*/*Z* isomers.

#### O SO<sub>2</sub>Ph SO<sub>2</sub>Ph OBn H OBn H

Following General Procedure, 4-(1,3-dioxoisoindolin-2-yl)butanal 13-SM2a (5.0 mmol, 1.086 g) and (((benzyloxy)methyl)sulfonyl)benzene 13-SM1b (5.5 mmol) were used. Compound 13j was isolated by silica gel chromatography (SiO<sub>2</sub>, petroleum ether/ethyl acetate = 6/1) as a yellow oil (E/Z = 1:0.73, 1.98 g, 86% yield).

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (dd, J = 7.2, 1.5 Hz, 3.36H, 1.36H<sub>E</sub>, 2H<sub>Z</sub>), 7.78 – 7.70 (m, 3.36H, 1.36H<sub>E</sub>, 2H<sub>Z</sub>), 7.65 – 7.58 (m, 3.36H, 1.36H<sub>E</sub>, 2H<sub>Z</sub>), 7.58 – 7.47 (m, 1.68H, 0.68H<sub>E</sub>, 1H<sub>Z</sub>), 7.43 (t, J = 7.6 Hz, 3.37H, 0.68H<sub>E</sub>, 1H<sub>Z</sub>), 7.26 – 7.15 (m, 6.63H, 2.63H<sub>E</sub>, 4H<sub>Z</sub>), 7.10 – 7.03 (m, 1.7H, 0.7H<sub>E</sub>, 1H<sub>Z</sub>), 6.40 (t, J = 7.6 Hz, 0.68H, H<sub>E</sub>), 5.34 (t, J = 8.0 Hz, 1H, H<sub>Z</sub>), 4.99 (s, 1.37H, H<sub>E</sub>), 4.75 (s, 2H, H<sub>Z</sub>), 3.62 (t, J = 7.2 Hz, 2H, H<sub>Z</sub>), 3.49 (t, J = 7.2 Hz, 1.39H, H<sub>E</sub>), 2.65 (dd, J = 15.2, 7.6 Hz, 2H, H<sub>Z</sub>), 1.96 (dd, J = 15.6, 7.6 Hz, 1.4H, H<sub>E</sub>), 1.82 – 1.68 (m, 2H, H<sub>Z</sub>), 1.63 – 1.50 (m, 1.38H, H<sub>E</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.4 (C<sub>Z</sub>), 168.2 (C<sub>E</sub>), 152.3 (C<sub>E</sub>), 151.9 (C<sub>Z</sub>), 139.6 (C<sub>Z</sub>), 139.1 (C<sub>E</sub>), 135.6 (C<sub>E</sub>), 135.4 (C<sub>Z</sub>), 134.1 (C<sub>E</sub>), 134.0 (C<sub>Z</sub>), 133.7 (C<sub>Z</sub>), 133.6 (C<sub>E</sub>), 132.2 (C<sub>Z</sub>), 132.1 (C<sub>E</sub>), 129.2, 129.1 (C<sub>E</sub>), 129.0 (C<sub>Z</sub>), 128.8, 128.6 (C<sub>Z</sub>), 128.5 (C<sub>E</sub>), 128.5 (C<sub>Z</sub>), 128.4(C<sub>E</sub>), 127.8, 127.1 (C<sub>E</sub>), 23.4 (C<sub>E</sub>), 22.7 (C<sub>Z</sub>). **IR (thin film, cm<sup>-1</sup>)**: 3064, 3038, 2930, 2863, 1770, 1708, 1445, 1396, 1329, 2240, 2084, 1025, 892, 797, 719, 689, 623, 596 and 531 cm<sup>-1</sup>. **HRMS (DART-TOF)** calculated for C<sub>26</sub>H<sub>23</sub>NNaO<sub>5</sub>S<sup>+</sup> [M+Na]<sup>+</sup> m/z 484.1189, found 484.1184.

### 6. Characterization Data for Products in Table 2



(Z)-9-(1,3-dioxoisoindolin-2-yl)-5-methoxynon-5enenitrile (12a)

The product **12a** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (40.3 mg, 0.13 mmol, 64%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 – 7.83 (m, 2H), 7.76 – 7.61 (m, 2H), 4.63 (t, J = 7.2 Hz, 1H), 3.68 (t, J = 7.6 Hz, 2H), 3.50 (s, 3H), 2.37 (t, J = 7.2 Hz, 2H), 2.26 (t, J = 7.2 Hz, 2H), 2.13 (q, J = 7.2 Hz, 2H), 1.82 – 1.75 (m, 2H), 1.75 – 1.68 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.5, 153.5, 134.0, 132.3, 123.3, 119.7, 111.0, 56.7, 37.8, 30.0, 28.7, 22.9, 22.3, 16.3. IR (thin film, cm<sup>-1</sup>): 2943, 2876, 1705, 1466, 1396, 1370, 1174, 1033, 945, 862, 795, 719, 622 and 530 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>3</sub><sup>+</sup> [M+Na]<sup>+</sup> m/z 335.1366, found 335.1371.



The product **12b** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a yellow oil (36.6 mg, 0.12 mmol, 58%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (dd, J = 5.6, 3.2 Hz, 2H), 7.70 (dd, J = 5.6, 3.2 Hz, 2H), 5.88 – 5.70 (m, 1H), 5.01 (ddd, J = 17.2, 3.2, 1.6 Hz, 1H), 4.98 – 4.92 (m, 1H), 4.51 (t, J = 7.2 Hz, 1H), 3.69 (t, J = 7.6 Hz, 2H), 3.50 (s, 3H), 2.14 – 2.02 (m, 6H), 1.74 – 1.67 (m, 2H), 1.55 – 1.47 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.5, 155.6, 138.6, 133.9, 132.4, 123.2, 123.2, 114.9, 108.3, 56.2, 37.9, 33.2, 30.6, 28.8, 26.4, 22.3. IR (thin film, cm<sup>-1</sup>): 2936, 2860, 1707, 1437, 1395, 1368, 1188, 1112, 1041, 912, 794, 719, 623 and 530 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>19</sub>H<sub>23</sub>NNaO<sub>3</sub><sup>+</sup> [M+Na]<sup>+</sup> m/z 336.1570, found 336.1574.



The product **12c** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a yellow oil (54.6 mg, 0.15 mmol, 76%).

<sup>1</sup>**H NMR** (**400 MHz, CDCl**<sub>3</sub>) δ 7.83 (dd, J = 5.6, 3.2 Hz, 2H), 7.71 (dd, J = 5.6, 3.2 Hz, 2H), 4.53 (t, J = 7.2 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 3.68 (t, J = 7.6 Hz, 2H), 3.51 (s, 3H), 2.32 (t, J = 7.6 Hz, 2H), 2.18 – 2.07 (m, 4H), 1.73 (tt, J = 14.8, 7.6 Hz, 4H), 1.25 (t, J = 7.2 Hz, 3H). <sup>13</sup>**C NMR** (**101 MHz, CDCl**<sub>3</sub>) δ 173.5, 168.4, 154.7, 133.8, 132.3, 123.1, 109.0, 60.3, 56.3, 37.9, 33.4, 30.5, 28.7, 22.4, 22.2, 14.3. **IR** (**thin film, cm**<sup>-1</sup>): 2938, 2847, 1707, 1437, 1395, 1369, 1186, 1038, 888, 794, 719, 623 and 530 cm<sup>-1</sup>.**HRMS** (**DART-TOF**) calculated for C<sub>20</sub>H<sub>25</sub>NNaO<sub>5</sub><sup>+</sup> [M+Na]<sup>+</sup> m/z 382.1625, found 382.1630.



The product **12d** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (34.0 mg, 0.12 mmol, 58%).

<sup>1</sup>**H NMR** (**400 MHz, CDCl**<sub>3</sub>) δ 7.83 (dd, J = 5.4, 3.1 Hz, 2H), 7.70 (dd, J = 5.4, 3.0 Hz, 2H), 4.55 – 4.46 (m, 2H), 4.38 (t, J = 6.2 Hz, 1H), 3.68 (t, J = 7.6 Hz, 2H), 3.50 (s, 3H), 2.11 (dt, J = 13.8, 7.1 Hz, 4H), 1.78 – 1.65 (m, 4H), 1.52 – 1.34 (m, 4H). <sup>13</sup>**C NMR** (**101 MHz, CDCl**<sub>3</sub>) δ 168.5, 155.6, 133.9, 132.4, 123.2, 108.4, 84.2 (d, J = 163.3 Hz), 56.3, 38.0, 31.1, 30.4 (d, J = 19.4Hz), 28.8, 26.9, 24.8 (d, J = 5.5 Hz), 22.3. **IR** (**thin film, cm**<sup>-1</sup>): 2937, 2861, 1706, 1436, 1367, 1171, 1111, 1639, 887, 794, 718, 622 and 530 cm<sup>-1</sup>. **HRMS** (**DART-TOF**) calculated for C<sub>19</sub>H<sub>24</sub>FNNaO<sub>3</sub><sup>+</sup> [M+Na]<sup>+</sup> m/z 356.1632, found 356.1626.



The product **12e** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (36.0 mg, 0.12 mmol, 58%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (dd, J = 5.6, 3.2 Hz, 2H), 7.70 (dd, J = 5.6, 3.2 Hz, 2H), 4.51 (t, J = 7.2 Hz, 1H), 3.68 (t, J = 7.6 Hz, 2H), 3.53 (t, J = 6.8 Hz, 2H), 3.50 (s, 3H), 2.15 – 2.09 (m, 4H), 1.82 – 1.69 (m, 4H), 1.44 (dt, J = 7.2, 3.6 Hz, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.5, 155.5, 133.9, 132.4, 123.2, 108.5, 56.3, 45.1, 38.0, 32.6, 31.1, 28.8, 26.5, 26.5, 22.3. IR (thin film, cm<sup>-1</sup>): 2933, 2857, 1708, 1437, 1395, 1367, 1188, 1107, 1041, 887, 793, 719, 649 and 530 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>19</sub>H<sub>24</sub>ClNNaO<sub>3</sub><sup>+</sup> [M+Na]<sup>+</sup> m/z 372.1337, found 372.1350.



The product **12f** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (56.8 mg, 0.14 mmol, 68%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.80 (dd, J = 5.2, 3.2 Hz, 2H), 7.67 (dd, J = 5.6, 3.2 Hz, 2H), 4.49 (t, J = 7.2 Hz, 1H), 3.66 (t, J = 7.6 Hz, 2H), 3.59 (t, J = 6.0 Hz, 2H), 3.48 (s, 3H), 2.10 (dt, J = 15.2, 7.8 Hz, 4H), 1.74 – 1.65 (m, 2H), 1.63 – 1.56 (m, 2H), 0.86 (s, 9H), 0.02 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.4, 155.5, 133.9, 132.3, 123.2, 108.0, 62.4, 56.1, 37.9, 30.5, 28.8, 27.5, 26.0, 22.2, 18.4, -5.2. IR (thin film, cm<sup>-1</sup>): 2930, 2856, 1711, 1437, 1394, 1256, 1099, 835, 775, 720, 529, 480, 432 and 407 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>23</sub>H<sub>35</sub>NNaO<sub>4</sub>Si<sup>+</sup> [M+Na]<sup>+</sup> m/z 440.2228, found 440.2225.



The product **12g** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 1:1) afforded the title product as a colorless oil (55.1 mg, 0.13 mmol, 64%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (dd, J = 5.6, 3.2 Hz, 2H), 7.74 – 7.68 (m, 2H), 4.55 (t, J = 7.2 Hz, 1H), 4.17 – 4.01 (m, 4H), 3.68 (t, J = 7.6 Hz, 2H), 3.50 (s, 3H), 2.18 (t, J = 6.4 Hz, 2H), 2.15 – 2.07 (m, 2H), 1.79 – 1.66 (m, 6H), 1.32 (t, J = 7.2 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 154.4, 133.9, 132.3, 123.2, 109.5, 61.5 (d, J = 6.4 Hz), 56.4, 37.8, 31.8 (d, J = 16.5 Hz), 28.7, 24.7 (d, J = 140.2 Hz), 22.2, 20.1 (d, J = 4.7 Hz), 16.5 (d, J = 6.0 Hz). IR (thin film, cm<sup>-1</sup>): 2985, 2943, 2909, 1707, 1438, 1396, 1368, 1234, 1165, 1022, 957, 794, 720, 604, and 530 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>21</sub>H<sub>30</sub>NNaO<sub>6</sub>P<sup>+</sup> [M+Na]<sup>+</sup> m/z 446.1703, found 446.1705.



The product **12h** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a yellow oil (48.9 mg, 0.14 mmol, 71%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (dd, J = 5.6, 3.2 Hz, 2H), 7.70 (dd, J = 5.6, 3.2 Hz, 2H), 4.89 (t, J = 4.8 Hz, 1H), 4.55 (t, J = 7.2 Hz, 1H), 4.01 – 3.93 (m, 2H), 3.89 – 3.82 (m, 2H), 3.68 (t, J = 7.6 Hz, 2H), 3.51 (s, 3H), 2.26 – 2.17 (m, 2H), 2.12 (q, J = 7.2 Hz, 2H), 1.82 – 1.75 (m,

2H), 1.75 - 1.67 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.4, 155.1, 133.9, 132.3, 123.2, 108.4, 103.9, 65.0, 56.3, 37.9, 31.6, 28.7, 25.6, 22.2. IR (thin film, cm<sup>-1</sup>): 2942, 2870, 1703, 1437, 1396, 1363, 1129, 1041, 947, 749, 719, 621 and 530 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>19</sub>H<sub>23</sub>NNaO<sub>5</sub><sup>+</sup> [M+Na]<sup>+</sup> m/z 368.1468, found 368.1465.



(Z)-2-(5-methoxy-8-morpholinooct-4-en-1yl)isoindoline-1,3-dione (12i)

The product **12i** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 1:1) afforded the title product as a colorless oil (48.4 mg, 0.13 mmol, 66%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (dd, J = 5.6, 3.2 Hz, 2H), 7.74 – 7.66 (m, 2H), 4.53 (t, J = 7.2 Hz, 1H), 3.73 – 3.65 (m, 6H), 3.50 (s, 3H), 2.43 (t, J = 4.4 Hz, 4H), 2.34 (t, J = 7.6 Hz, 2H), 2.14 – 2.09 (m, 4H), 1.77 – 1.66 (m, 2H), 1.66 – 1.55 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.5, 155.4, 133.9, 132.3, 123.2, 108.5, 67.1, 58.4, 56.3, 53.8, 37.9, 29.0, 28.8, 24.2, 22.2. IR (thin film, cm<sup>-1</sup>): 2942, 2854, 2808, 1707, 1438, 1396, 1367, 1188, 1116, 1069, 958, 916, 864, 720, 625 and 530 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>21</sub>H<sub>29</sub>N<sub>2</sub>O<sub>4</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 373.2122, found 373.2122.



(Z)-2-(5-methoxy-7-(thiophen-3-yl)hept-4-en-1yl)isoindoline-1,3-dione (12j)

The product **12j** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a yellow oil (32.1 mg, 0.09 mmol, 45%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (dd, J = 5.2, 3.2 Hz, 2H), 7.70 (dd, J = 5.2, 3.2 Hz, 2H), 7.23 (dd, J = 4.8, 3.2 Hz, 1H), 6.94 (t, J = 4.4 Hz, 2H), 4.54 (t, J = 7.2 Hz, 1H), 3.66 (t, J = 7.6 Hz, 2H), 3.53 (s, 3H), 2.80 – 2.70 (m, 2H), 2.43 – 2.35 (m, 2H), 2.12 (q, J = 7.2 Hz, 2H), 1.74 – 1.67 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.5, 155.1, 142.0, 133.9, 132.3, 128.3, 125.4, 123.2, 120.3, 108.9, 56.5, 37.9, 32.4, 28.7, 28.2, 22.3. IR (thin film, cm<sup>-1</sup>): 2933, 2854, 1707, 1436, 1395, 1367, 1188, 1112, 1063, 860, 887, 751, 719, 635 and 530 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>20</sub>H<sub>22</sub>NO<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup> m/z 356.1315, found 356.1315.





The product **12k** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a yellow oil (41.8 mg, 0.11 mmol, 55%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 – 7.82 (m, 2H), 7.71 – 7.69 (m, 2H), 5.75 (s, 2H), 4.56 (t, J = 6.8 Hz, 1H), 3.78 – 3.61 (m, 4H), 3.48 (s, 3H), 2.20 (s, 6H), 2.16 – 2.08 (m, 4H), 1.79 – 1.66 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.5, 154.6, 133.9, 132.3, 127.4, 123.2, 109.1, 105.2, 56.4, 43.0, 37.9, 28.8, 28.6, 28.2, 22.3, 12.6. IR (thin film, cm<sup>-1</sup>): 2924, 2853, 2246, 1676, 1641, 1456, 1262, 1206, 1115, 1053, 994, 909, 805, 748 and 637 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>23</sub>H<sub>29</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup> m/z 381.2173, found 381.2173.



The product **12l** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (20.7 mg, 0.08 mmol, 43%). (We noted this compound tend to undergo E/Z isomerization on column at high temperature.)

<sup>1</sup>**H NMR** (**400 MHz**, **CDCl**<sub>3</sub>) δ 7.83 (dd, J = 5.2, 3.2 Hz, 2H), 7.70 (dd, J = 5.2, 3.2 Hz, 2H), 4.41 (t, J = 7.2 Hz, 1H), 3.68 (t, J = 7.6 Hz, 2H), 3.52 (s, 3H), 2.17 – 2.02 (m, 2H), 1.79 (s, 3H), 1.74 – 1.68 (m, 2H). <sup>13</sup>**C NMR** (**101 MHz**, **CDCl**<sub>3</sub>) δ 168.5, 151.7, 133.9, 132.4, 123.2, 106.7, 55.5, 37.9, 28.7, 22.1, 17.4. **IR** (**thin film, cm**<sup>-1</sup>): 2940, 2860, 1707, 1437, 1396, 1367, 1170, 1121, 1048, 888, 795, 719, 625 and 530 cm<sup>-1</sup>. **HRMS** (**DART-TOF**) calculated for C<sub>15</sub>H<sub>17</sub>NNaO<sub>3</sub><sup>+</sup> [M+Na]<sup>+</sup> m/z 282.1101, found 282.1106.

### 7. Characterization Data for Products in Table 3



The product **14a** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (39.3 mg, 0.12 mmol, 58%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.64 (t, J = 7.2 Hz, 1H), 3.68 (t, J = 6.4 Hz, 2H), 3.52 (s, 3H), 2.35 (t, J = 7.2 Hz, 2H), 2.26 (t, J = 7.2 Hz, 2H), 2.14 (dd, J = 14.8, 7.6 Hz, 2H), 1.79 (p, J = 7.2 Hz, 2H), 1.61 – 1.55 (m, 2H), 1.08 – 1.04 (m, 21H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.8, 119.7, 112.6, 63.2, 57.0, 33.4, 30.3, 22.9, 21.4, 18.2, 16.3, 12.2. IR (thin film, cm<sup>-1</sup>): 2942, 2866, 2246, 1676, 1462, 1260, 1104, 1070, 883, 750 and 682 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>19</sub>H<sub>37</sub>NNaO<sub>2</sub>Si<sup>+</sup>[M+Na]<sup>+</sup> m/z 362.2486, found 362.2489.



The product **14b** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a yellow oil (31.6 mg, 0.12 mmol, 60%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 5.81 (ddt, J = 16.8, 10.4, 6.8 Hz, 1H), 4.99 (dd, J = 17.2, 1.6 Hz, 1H), 4.93 (dd, J = 10.0, 0.8 Hz, 1H), 4.61 (t, J = 7.2 Hz, 1H), 3.51 (s, 3H), 2.36 (t, J = 7.2 Hz, 2H), 2.26 (t, J = 7.2 Hz, 2H), 2.09 – 2.02 (m, 4H), 1.79 (p, J = 7.2 Hz, 2H), 1.43 – 1.34 (m, 2H), 1.28 (s, 10H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.4, 139.4, 119.7, 114.2, 113.3, 57.0, 33.9, 30.2, 30.0, 29.6, 29.5, 29.5, 29.2, 29.0, 24.9, 22.9, 16.3. IR (thin film, cm<sup>-1</sup>): 2925, 2853, 2246, 1676, 1641, 1457, 1262, 1115, 1075, 994 and 751 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>17</sub>H<sub>29</sub>NNaO<sup>+</sup> [M+Na]<sup>+</sup> m/z 286.2141, found 286.2144.



The product **14c** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (21.4 mg, 0.09 mmol, 43%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.09 (t, J = 7.2 Hz, 1H), 4.62 (t, J = 7.2 Hz, 1H), 3.50 (s, 3H), 2.36 (t, J = 7.2 Hz, 2H), 2.28 (t, J = 7.2 Hz, 2H), 2.11 – 1.88 (m, 4H), 1.80 (p, J = 7.2 Hz, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.44 (td, J = 13.2, 6.8 Hz, 1H), 1.38 – 1.30 (m, 1H), 1.15 (td, J = 13.6, 7.6 Hz, 1H), 0.87 (d, J = 6.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.0, 131.2, 125.0, 119.7, 111.7, 56.8, 36.9, 33.1, 32.0, 30.2, 25.9, 25.8, 23.0, 19.7, 17.8, 16.3. IR (thin film, cm<sup>-1</sup>): 2959, 2925, 2853, 2246, 1675, 1454, 1377, 1204, 1075, 1050, 827, 750 and 735 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>16</sub>H<sub>27</sub>NNaO<sup>+</sup> [M+Na]<sup>+</sup> m/z 272.1985, found 272.1989.



The product **14d** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (22.7 mg, 0.11 mmol, 57%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 5.06 (s, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.65 (s, 3H), 2.88 (t, J = 7.2 Hz, 2H), 2.38 (t, J = 7.6 Hz, 2H), 1.95 (dd, J = 14.8, 7.6 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 173.9, 167.5, 119.6, 92.0, 59.7, 55.7, 30.9, 23.5, 16.8, 14.5. IR (thin film, cm<sup>-1</sup>): 2975, 2938, 2853, 2247, 1705, 1621, 1440, 1380, 1262, 1172, 1134, 1053, 969, 823 and 750 cm<sup>-1</sup>.HRMS (DART-TOF) calculated for  $C_{10}H_{15}NNaO_3^+$  [M+Na]<sup>+</sup> m/z 220.0944, found 220.0941.



The product **14e** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (26.9 mg, 0.12 mmol, 58%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 – 7.21 (m, 4H), 7.20 – 7.13 (m, 1H), 4.80 (d, J = 9.6 Hz, 1H), 3.95 (dq, J = 14.4, 7.2 Hz, 1H), 3.51 (s, 3H), 2.29 (dt, J = 7.2, 6.4 Hz, 4H), 1.79 (p, J = 7.2 Hz, 2H), 1.31 (d, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 151.3, 147.1, 128.5, 126.8, 125.9, 119.6, 118.3, 56.7, 35.2, 29.8, 22.8, 22.6, 16.2. IR (thin film, cm<sup>-1</sup>): 3026, 2960, 2839, 2246, 1672, 1601, 1492, 1451, 1329, 1263, 1120 1085, 1062, 911, 801, 759, 736, 700 and 539 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>15</sub>H<sub>19</sub>NNaO<sup>+</sup> [M+Na]<sup>+</sup> m/z 252.1359, found 252.1361.



The product **14f** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (14.7 mg, 0.08 mmol, 39%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.56 (s, 1H), 3.47 (s, 3H), 2.35 (t, *J* = 7.2 Hz, 2H), 2.23 (t, *J* = 7.2 Hz, 2H), 1.77 (p, *J* = 7.2 Hz, 2H), 1.09 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ 151.0, 123.0, 119.8, 55.8, 31.6, 30.8, 30.0, 22.9, 16.1. IR (thin film, cm<sup>-1</sup>): 2953, 2870, 2246, 1667, 1459, 1228, 1131, 1062, 801 and 750 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>11</sub>H<sub>19</sub>NNaO<sup>+</sup> [M+Na]<sup>+</sup> m/z 204.1359, found 204.1359.



The product **14g** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (18.2 mg, 0.11 mmol, 55%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 4.10 (d, J = 9.2 Hz, 1H), 3.62 (s, 3H), 2.36 (t, J = 7.2 Hz, 2H), 2.24 (t, J = 7.2 Hz, 2H), 1.79 (p, J = 7.2 Hz, 2H), 1.72 – 1.62 (m, 1H), 0.75 – 0.66 (m, 2H), 0.32 – 0.23 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.7, 119.7, 116.9, 57.3, 30.5, 23.0, 16.4, 7.7, 6.9. IR (thin film, cm<sup>-1</sup>): 3005, 2946, 2247, 1713, 1425, 1168, 1025, 750 and 549 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>10</sub>H<sub>15</sub>NNaO<sup>+</sup> [M+Na]<sup>+</sup> m/z 188.1046, found 188.1048.



The product **14h** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (29.0 mg, 0.14 mmol, 71%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.48 (d, J = 9.2 Hz, 1H), 3.51 (s, 3H), 2.46 – 2.38 (m, 1H), 2.35 (t, J = 7.2 Hz, 2H), 2.24 (t, J = 7.2 Hz, 2H), 1.78 (p, J = 7.2 Hz, 2H), 1.72 – 1.56 (m, 5H), 1.37 – 1.23 (m, 2H), 1.21 – 1.12 (m, 1H), 1.08 – 0.96 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  150.9, 119.7, 119.6, 57.1, 34.3, 33.8, 30.0, 26.2, 26.1, 22.9, 16.2. IR (thin film, cm<sup>-1</sup>): 2922, 2848, 2246, 1673, 1338, 1333, 1200, 1116, 1051, 967, 891, 795 and 602 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>13</sub>H<sub>21</sub>NNaO<sup>+</sup> [M+Na]<sup>+</sup> m/z 230.1515, found 230.1519.



The product **14i** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 6:1) afforded the title product as a colorless oil (41.5 mg, 0.13 mmol, 67%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.45 (d, J = 8.8 Hz, 1H), 4.12 – 3.92 (m, 2H), 3.53 (s, 3H), 2.76 (t, J = 12.0 Hz, 2H), 2.64 – 2.49 (m, 1H), 2.35 (t, J = 7.2 Hz, 2H), 2.27 (t, J = 7.2 Hz, 2H), 1.83 – 1.75 (m, 2H), 1.63 – 1.53 (m, 2H), 1.46 (s, 9H), 1.26 – 1.16 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ 155.0, 152.1, 119.5, 116.8, 79.3, 56.8, 43.9, 32.5, 29.8, 28.6, 22.8, 16.2. IR (thin film, cm<sup>-1</sup>):2932, 2849, 2245, 1683, 1422, 1365, 1234, 1162, 1121, 1047, 972, 813, 766, 603, 527 and 461 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>17</sub>H<sub>28</sub>N<sub>2</sub>NaO<sub>3</sub><sup>+</sup> [M+Na]<sup>+</sup> m/z 331.1992, found 331.1996.



The product **14j** was prepared following **General Procedure** at 0.2 mmol scale, purification by flash chromatography (SiO<sub>2</sub>, petroleum ether: EtOAc = 1:0 to 10:1) afforded the title product as a colorless oil (48.2 mg, 0.12 mmol, 62%). The chemical shift of vinylic proton is close to that of benzylic protons. It is therefore difficult to determine the configuration of this compound by NOE experiments. The stereochemistry is tentatively assigned by analogy to other products.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (dd, J = 5.6, 3.2 Hz, 2H), 7.70 (dd, J = 5.6, 3.2 Hz, 2H), 7.38 – 7.27 (m, 5H), 4.72 (t, J = 7.2 Hz, 1H), 4.69 (s, 2H), 3.66 (t, J = 7.6 Hz, 2H), 2.37 (t, J =7.2 Hz, 2H), 2.31 (t, J = 7.2 Hz, 2H), 2.13 (dd, J = 14.8, 7.2 Hz, 2H), 1.81 (p, J = 7.2 Hz, 2H), 1.69 (dd, J = 14.8, 7.6 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.5, 152.2, 137.5, 134.0, 132.3, 128.6, 128.0, 127.8, 123.2, 119.7, 112.6, 71.0, 37.7, 30.6, 28.6, 22.9, 22.5, 16.3. IR (thin film, cm<sup>-1</sup>): 3464, 2941, 2876, 2247, 1710, 1704, 1667, 1437, 1397, 1371, 1265, 1188, 1041, 907, 797, 721, 529, 449 and 424 cm<sup>-1</sup>. HRMS (DART-TOF) calculated for C<sub>24</sub>H<sub>24</sub>N<sub>2</sub>NaO<sub>3</sub><sup>+</sup> [M+Na]<sup>+</sup> m/z 411.1679, found 411.1683.

### 8. The E/Z Ratios of the Products in Table 2 and 3

We confirmed the E/Z ratios of the products in table 2 and 3 by analysis of the <sup>1</sup>H NMR spectra of the crude mixture:



Crude <sup>1</sup>H NMR Spectrum of **12b** 







Crude <sup>1</sup>H NMR Spectrum of **12d** 







Crude <sup>1</sup>H NMR Spectrum of **12f** 







Crude <sup>1</sup>H NMR Spectrum of **12h** 







Crude <sup>1</sup>H NMR Spectrum of **12j** 







Crude <sup>1</sup>H NMR Spectrum of **12**l























Crude <sup>1</sup>H NMR Spectrum of **14f** 







Crude <sup>1</sup>H NMR Spectrum of 14h







Crude <sup>1</sup>H NMR Spectrum of **14j** 

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### 10. NMR Spectra

Ph<sup>O</sup>SO<sub>2</sub>Ph

13-SM1b



<sup>1</sup>H NMR Spectrum of *13-SM1b* 

### CDCI3, 100.62 MHz



SO₂Ph Ph O

13-SM1b



- 84.70

— 74.49

<sup>13</sup>C NMR Spectrum of *13-SM1b* 



<sup>1</sup>H NMR Spectrum of *E*-10



## CDCI3, 400.13 MHz





*E*-10





<sup>1</sup>H NMR Spectrum of **Z-10** 

f1 (ppm)





-- 3.59





<sup>1</sup>H NMR Spectrum of *E*-13a



<sup>13</sup>C NMR Spectrum of *E*-13a









<sup>1</sup>H NMR Spectrum of **Z-13a** 



<sup>13</sup>C NMR Spectrum of **Z-13a** 



1D-NOE Spectrum of Z-13a



<sup>1</sup>H NMR Spectrum of *E*-13b









<sup>1</sup>H NMR Spectrum of **Z-13b** 









<sup>1</sup>H NMR Spectrum of *E*-13c

CDCI3, 400 MHz









1D-NOE Spectrum of *E*-13c

0



9.0

8.5

8.0

7.5

7.0

6.5

6.0

5.5

5.0



<sup>1</sup>H NMR Spectrum of **Z-13c** 

4.5 4.0 f1 (ppm)

3.5

3.0

2.5

2.0

1.5

1.0

0.5

0.0

-0.5









<sup>1</sup>H NMR Spectrum of *E*-13d



## CDCI3, 400.13 MHz



*E*-13d





14 12 10 8 6 4 2 0 f1 (ppm) 1D-NOE Spectrum of **E-13d** 



SO₂Ph

`OMe

EtOOC.

H Z-13d



— 3.64

- 0.00



<sup>1</sup>H NMR Spectrum of **Z-13d** 



<sup>13</sup>C NMR Spectrum of **Z-13d** 





<sup>1</sup>H NMR Spectrum of *E*-13e



# CDCI3, 400.13 MHz



6.63
6.60


<sup>&</sup>lt;sup>1</sup>H NMR Spectrum of **Z-13e** 



<sup>13</sup>C NMR Spectrum of **Z-13e** 





<sup>1</sup>H NMR Spectrum **13f** 







<sup>&</sup>lt;sup>1</sup>H NMR Spectrum **Z-13f** 



16







- 3.87



*E*-13g



<sup>1</sup>H NMR Spectrum of *E*-13g





5.89 5.87





SO₂Ph `OMe Ĥ. Z-13g



<sup>1</sup>H NMR Spectrum of **Z-13g** 









<sup>1</sup>H NMR Spectrum of **Z-13h** 







<sup>1</sup>H NMR Spectrum of **13h** 











- 3.85

----0.00





<sup>1</sup>H NMR Spectrum of *E*-13i









3.56





<sup>1</sup>H NMR Spectrum of **Z-13i** 



9



1D-NOE Spectrum of Z-13i



<sup>&</sup>lt;sup>1</sup>H NMR Spectrum of **13j** 



## CDCI3, 400.13 MHz













1D-NOE Spectrum of **Z-13j** 







<sup>1</sup>H NMR Spectrum of **12a** 







CDCI3, 400.13 MHz









<sup>1</sup>H NMR Spectrum of **12b** 




O OMe N Ha







- 3.51





<sup>&</sup>lt;sup>1</sup>H NMR Spectrum of **12c** 



















<sup>1</sup>H NMR Spectrum of **12d** 











3.50







<sup>1</sup>H NMR Spectrum of **12e** 















<sup>1</sup>H NMR Spectrum of **12f** 









- 3.50







<sup>1</sup>H NMR Spectrum of **12g** 













<sup>1</sup>H NMR Spectrum of **12h** 







На









<sup>1</sup>H NMR Spectrum of **12i** 









3.53







<sup>1</sup>H NMR Spectrum of **12j** 







CDCI3, 400.13 MHz



- 3.48







<sup>1</sup>H NMR Spectrum of **12k** 













<sup>1</sup>H NMR Spectrum of **12l** 









<sup>1</sup>H NMR Spectrum of **14a** 



## CDCI3, 400.13 MHz






<sup>1</sup>H NMR Spectrum of **14b** 

f1 (ppm)

-1



<sup>13</sup>C NMR Spectrum of **14b** 











14c



- 3.50

4.64 4.62 4.60

<sup>1</sup>H NMR Spectrum of **14c** 









- 5.06

- 3.65

---0.00





<sup>1</sup>H NMR Spectrum of **14d** 







<sup>1</sup>H NMR Spectrum of **14e** 









<sup>1</sup>H NMR Spectrum of 14f

f1 (ppm)


-- 3.47







OMe CN H 14g



<sup>1</sup>H NMR Spectrum of **14g** 









<sup>1</sup>H NMR Spectrum of **14h** 







1D-NOE Spectrum of 14h



8



<sup>&</sup>lt;sup>1</sup>H NMR Spectrum of **14i** 













<sup>1</sup>H NMR Spectrum of 14j

f1 (ppm)



