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# **Supporting Information**

# For

# Metal-free iminyl radical-mediated C–C single bond cleavage/functionalization of redox-active oxime esters

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# 1. General remarks

<sup>1</sup>H NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for <sup>13</sup>C NMR) agilent NMR spectrometer with CDCl<sub>3</sub> as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm,  $\delta$  scale) downfield from TMS at 0.00 ppm and referenced to the CDCl<sub>3</sub> at 7.26 ppm (for <sup>1</sup>H NMR) or 77.16 ppm (for <sup>13</sup>C NMR). HRMS was recorded on a GCT PremierTM (CI) Mass Spectrometer. Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR, v<sub>max</sub> in cm-1. All commercially available reagents and solvents were used as received unless otherwise specified.

# 2. Photochemical reaction setup

Household blue LED strips (22 W) were coiled around the inside of a 15 cm diameter glassware (see Figure S1a) or around the inside of a 8 cm diameter glassware (Figure S1b). Optimum yields were observed when the reactions were heated by the heat generated by the LEDs. Therefore, the LEDs and reactions were wrapped in aluminium foil to maintain a high reaction temperature. For the blue LED strips (Figure S1a), this resulted in a reaction temperature of approximately 35 °C; For the blue LED strips (Figure S1b), this resulted in a reaction temperature of approximately 55 °C.



Figure S1a: Reaction setup for GP2



Figure S1b: Reaction setup for GP3 and GP4

0 N-0 CF <sub>3</sub> <sup>+</sup> 1a	N 2a	Additive (20 mol%) HE (1.5 equiv), Solvent	N 3a
Entry <sup>a</sup>	Solvent	Additive	Yield (%) <sup>b</sup>
1	DCM	(PhO) <sub>2</sub> PO <sub>2</sub> H	80
2	DCE	(PhO)2PO2H	71
3	THF	(PhO)2PO2H	58
4	CH <sub>3</sub> CN	(PhO)2PO2H	37
5	Acetone	(PhO) <sub>2</sub> PO <sub>2</sub> H	50
6	DMSO	(PhO)2PO2H	34
8	PhCl	(PhO)2PO2H	53
9	DMF	(PhO) <sub>2</sub> PO <sub>2</sub> H	39
10	CHCl <sub>3</sub>	(PhO) <sub>2</sub> PO <sub>2</sub> H	51
11	DCM	TFA	31
12	DCM	CH <sub>3</sub> CO <sub>2</sub> H	13
13	DCM	CH <sub>3</sub> SO <sub>3</sub> H	36
14	DCM	CF <sub>3</sub> SO <sub>3</sub> H	55
15	DCM	<i>p</i> -TsOH	30
16 <sup>c</sup>	DCM	(PhO)2PO2H	65
$17^{d}$	DCE	(PhO) <sub>2</sub> PO <sub>2</sub> H	0
$18^e$	DCM	(PhO) <sub>2</sub> PO <sub>2</sub> H	0
19	DCM	_	0

# 3. Optimization of reaction conditions

<sup>*a*</sup>Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), HE (0.3 mmol) and acid (20% mmol) in solvent (2mL), 22 W household blue LEDs, 35 °C. <sup>*b*</sup>Isolated yield. <sup>*c*</sup>395 nm LEDs. <sup>*d*</sup>In the dark, reflux at 85 °C. <sup>*e*</sup>No HE.

	+ $SO_2Ph$ $\frac{HE (1.5 equiv}{22 W blue LE}$	/), Solvent Ds, 55 °C, 7f
Entry <sup>a</sup>	Solvent	Yield (%) <sup>b</sup>
1	CH <sub>3</sub> CN	38
2	DCE	65
3	THF	40
4	DMF	54
5	PhCl	46
6	DMSO	55
7	Dioxane	10
8	Toluene	30

<sup>*a*</sup>Reaction conditions: **11** (0.2 mmol), **6a** (0.3 mmol) and HE (0.3 mmol) in MeCN (2 mL), 22 W blue LEDs, 55 °C. <sup>*b*</sup>Isolated yield.

## 4. General procedures

#### General procedures 1A, 1B, 1C and 1D for preparation of cycloketone oxime esters

Cycloketone oxime esters were prepared by one of four procedures:



#### General procedure 1A (GP1A):

Cyclobutanone oxime esters were obtained from the corresponding cyclobutanones, which were commercial available or produced by the reduction of  $\alpha,\alpha$ -dichlorocyclobutanones synthesized from the corresponding alkenes by the reported procedure.<sup>[1]</sup> The following experimental procedure is typical: To a 50 mL three-necked flask under argon were added alkene derivative (5.0 mmol, 1.0 equiv), zinc-copper couple (960 mg, 15.0 mmol, 3.0 equiv), and anhydrous ether (10 mL). To the mixture was added a

solution of trichloroacetyl chloride (1.12 mL, 10.0 mmol, 2.0 equiv) and phosphorus oxychloride (0.51 mL, 5.5 mmol, 1.1 equiv) in ether (10 mL) over 1 h through an addition funnel. The suspension was stirred overnight at reflux. The resulting mixture was filtered through a pad of Celite and was washed with ether (20 mL). The organic solution was successively washed with water (30 mL), a saturated aqueous solution of NaHCO<sub>3</sub> (30 mL) and brine (30 mL), and dried over MgSO<sub>4</sub>. Then the solution was filtered, concentrated and used in the next step without further purification.

A mixture of 2,2-dichlorocyclobutanones (1.0 equiv) and zinc dust (4.0 equiv) in acetic acid (10 mL) was stirred at room temperature for 2 h and then heated at 80 °C for 5 h. The resulting mixture was allowed to cool to room temperature, followed by diluting with water (30 mL) and extracted with ether ( $3 \times 20$  mL). The organic phase was washed successively with a saturated solution of aqueous NaHCO<sub>3</sub> ( $3 \times 30$  mL), water (30 mL) and brine (30 mL), then dried over MgSO<sub>4</sub> and concentrated in vacuum. The residue was then purified by flash chromatography with a mixture of petroleum ether and ethyl acetate to afford various cyclobutanones.

To a stirred solution of cyclobutanones (1.0 equiv) in pyridine (0.5 M) was added hydroxylamine hydrochloride (2.0 equiv) at rt. After stirring for 2 h, pyridine was removed under reduced pressure. The residue was diluted with water and extracted with EtOAc. The aqueous layer was extracted with EtOAc and the combined organic extracts were washed with brine, dried over MgSO<sub>4</sub>, and evaporated under reduced pressure to give the crude material, which were used in the next step without further purification.

To a mixture of cyclobutanone oxime (1.0 equiv), triethylamine (2.0 equiv) and DCM (0.5 M) in a 30-mL two-necked flask was added 4-trifluoromethyl benzoyl chloride (1.5 equiv) at 0 °C. After 6 h, water was added to the above solution, and the mixture was diluted with diethyl ether. The organic layer was washed with water and dried over MgSO<sub>4</sub>. The solvent was removed under vacuum and the residue was subjected to column chromatography on SiO<sub>2</sub> with EtOAc–PE as an eluent to give cyclobutanone oxime esters.



#### General procedure 1B (GP1B):

To a mixture of hydroxylamine hydrochloride (18.0 mmol), sodium acetate (22.5 mmol), ethanol (10.5 mL) and water (4.5 mL) in a 30 mL two-necked flask was added

cyclobutanone (15 mmol) and the mixture was stirred at 100 °C for 12 h. The reaction mixture was cooled to room temperature and then ethanol was removed under reduced pressure and the resulting mixture was extracted with diethyl ether. The organic layer was washed with water and dried over MgSO<sub>4</sub>. The solvent was removed under vacuum and the residue was subjected to column chromatography to give cyclobutanone oxime as a white solid (1.0 g, 78%).

Cyclobutanone oxime (1.0 equiv) in absolute THF (0.5 M) was added *n*-BuLi (2.0 equiv) slowly at 0 °C, and the resulting mixture was stirred for another 15 min at this temperature for the formation of *syn* dianion. RX (1.0 equiv) was added dropwise at 0 °C and the mixture was warmed to RT for 2 h. Subsequently, the reaction was quenched by cold water, and the mixture was diluted with EA. The organic layer was washed with water and dried over MgSO<sub>4</sub>. The solvent was removed under vacuum and the residue was subjected to column chromatography on SiO<sub>2</sub> with EtOAc–PE as an eluent to give *a*-substituted oximes in quantitative yield.

#### General procedure 1C (GP1C):



A 50 mL flame-dried schlenk tube was filled with argon,  $Pd(OAc)_2$  (2.5% mmol),  $P(o-tol)_3$  (5% mmol), NaOAc (1.0 equiv), cyclopentanones (1.0 equiv), aryl bromides (1.3 equiv), pyrrolidine (0.3 equiv), 1,1,3,3-tetramethylbutylamine (0.3 equiv) and 1,4-dioxane (1 M). The tube was then sealed and heated at 110 °C under stirring for 12 hours, before cooled to room temperature. The mixture was filtered through a small plug of silica gel and eluted with ethyl acetate. The filtrate was then concentrated under *vacuo* and further purified by flash column chromatography to give the arylation product.

A mixture of NaH in DME (0.5 M) under argon atmosphere was cooled to 0 °C. Then, arylation product (1.0 equiv) was added slowly under stirring. After, the resulting mixture was maintained at 0 °C for 1 hours, MeI (1.0 equiv) was added dropwisely at 0 °C. The reaction was allowed to warm up to reflux, stirred 2 hours, and finally quenched with H<sub>2</sub>O. The resulting mixture was extracted with Et<sub>2</sub>O. The combined organic phases were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The resulting product.

#### General procedure 1D (GP1D):



A 100 mL flame-dried schlenk tube was filled with argon,  $Pd(OAc)_2$  (2.5% mmol), ligand (5% mmol), NaO'Bu (1.3 equiv), ketone (1.0 equiv), aryl bromides (1.3 equiv) and Toluene (1 M). The tube was then sealed and heated at 45 °C under stirring for 12 hours, and finally quenched with H<sub>2</sub>O. The resulting mixture was extracted with EA. The combined organic phases were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography to give the corresponding product.

#### General procedure 1E (GP1E): Preparation of allyl sulfones

Procedure for the synthesis of 6e-g.



To a solution of paraformaldehyde (3.98 g, 133.2 mmol) and ethylacrylate (10.8 mL, 100 mmol) in 80 mL of dioxane-water (1:1, v/v) was added DABCO (14.96 g, 133.2 mmol) and the reaction progress was monitored by TLC. Upon completion, the reaction mixture was partitioned with EtOAc (200 mL) and water (100 mL). The organic layer was separated and washed with brine (100 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give **B1** as a colorless oil (8.45 g, 65% yield).

To a solution of **B1** (8.45 g, 65 mmol) was added PBr<sub>3</sub> (2.15 ml, 22.6 mmol) in dry THF (65 mL) at -10 °C. The temperature was allowed to rise to rt and stirring was continued for 3 h. Water (20 mL) was then added and the mixture was extracted with petroleum ether (3 × 100 mL). The organic phase was washed with brine (100 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give **B2** as a colorless oil (10.36 g, 83% yield).

To a solution of **B2** (10.36 g, 54.0 mmol) in dry methanol (100 mL) was added sodium phenylsulfinate (10.63 g, 64.8 mmol). After 2 h of reflux, the mixture was concentrated under reduced pressure, the obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and the filtrate was evaporated and purified by chromatography to give **6e** as a viscous oil (11.11 g, 81% yield).<sup>[8]</sup>

Procedure for the synthesis of 6a-d.



A mixture of methyltriphenylphosphonium bromide (1.2 equiv) in dry THF (0.5 M) under argon atmosphere was cooled to 0 °C. Then, *n*-BuLi (2.5 M solution in hexane, 1.2 equiv) was added slowly under stirring. After, the resulting orange mixture was maintained at 0 °C for 1 h, a solution of the corresponding ketone (1.0 equiv) in dry THF was added dropwisely at 0 °C. The reaction was allowed to warm up to rt, stirred overnight, and finally quenched with a saturated aqueous solution of NaCl. The resulting mixture was extracted with DCM. The combined organic phases were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography to give the corresponding propene **S1**.

To a solution of NBS (1.05 equiv) and TsOH (0.1 equiv) in dry THF (0.5 M) under argon atmosphere. Then, **S1** (1.0 equiv) was added. The reaction solution was heated to 100 °C and stirred for 4 h, then cooled down to rt, quenched with water, and extracted with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography to afford the product **S2**.<sup>[9]</sup>

To a solution of **S2** (1.0 equiv) in dry methanol (0.5 M) was added sodium phenylsulfinate (1.2 equiv). After 2 h of reflux, the mixture was concentrated under reduced pressure, the obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and the filtrate was evaporated and purified by chromatography to give corresponding product.

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#### General procedure 2 (GP2):



To a mixture of cycloketone oxime ester (1, 0.2 mmol), 2 (0.3 mmol), HE (76 mg, 0.3 mmol), and (PhO)<sub>2</sub>PO<sub>2</sub>H (10.0 mg, 20 mol%) in a flame-dried Schlenk tube was added DCM (2.0 mL) under argon atmosphere. The resulting mixture was stirred at 35 °C upon irradiation with blue LEDs (22 W). After the reaction finished (monitored by TLC), the solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford **3** or **4**.

#### General procedure 3 (GP3):



To a mixture of cycloketone oxime ester (1, 0.2 mmol), 6 (0.3 mmol), and HE (76 mg, 0.3 mmol) in a flame-dried Schlenk tube was added DCE (2.0 mL) under argon atmosphere. The resulting mixture was stirred at 55 °C for 3-24 h upon irradiation with blue LEDs (22 W). After the reaction finished (monitored by TLC), the solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford 7.

General procedure 4 (GP4):



To a mixture of cyclobutanone oxime ester (11, 0.2 mmol), radical acceptor (0.3 mmol), and HE (76 mg, 0.3 mmol) in a flame-dried Schlenk tube was added DCE (2.0 mL) under argon atmosphere. The resulting mixture was stirred at 55  $^{\circ}$ C upon irradiation with blue LEDs (22 W). After the reaction finished (monitored by TLC), the solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

## 5. Mechanistic studies

#### 5.1 UV/Vis absorption spectroscopy

Figure S1 showed the UV/Vis absorption spectra of DMA solutions of **1a** and HE. No red-shift in absorbance was found, which indicated that no EDA complex was formed.



A) **1a** (0.1 M)

B) HE (0.15 M)

C) (PhO)<sub>2</sub>PO<sub>2</sub>H (0.02 M)

D) Mixture of 1a (0.1 M) and HE (0.15 M)

E) Mixture of 1a (0.1 M) and (PhO)<sub>2</sub>PO<sub>2</sub>H (0.02 M)

F) Mixture of **1a** (0.1 M), HE (0.15 M) and (PhO)<sub>2</sub>PO<sub>2</sub>H (0.02 M)



Figure S2. UV/Vis absorption spectra of 1a and HE

#### 5.2 Light/dark experiment.



Figure S3. Light/dark experiment.

Eight standard reaction mixtures in 10 mL glass vials were charged with cyclobutanone oxime ester (1a, 51.4 mg, 0.2 mmol), 2-vinylpyridine (2a, 32 µL, 0.3 mmol), HE (75.9 mg, 0.3 mmol), (PhO)<sub>2</sub>PO<sub>2</sub>H (10 mg, 20 mol%) and 2.0 mL of DCM under Ar. The mixtures were then stirred rapidly and irradiated with a 22 W blue LED at 35 °C. After 3 h, the light was turned off, and one vial was removed from the irradiation setup for analysis. The remaining seven vials were stirred in the absence of light for an additional 1h. Then, one vial was removed for analysis, and the blue LEDs were turned back on to irradiate the remaining six reaction mixtures. After an additional 3 h of irradiation, the blue LED was turned off, and one vial was removed for analysis. The remaining five vials were stirred in the absence of light for an additional 1 h. Then, a vial was removed for analysis, and the blue LED was turned back on to irradiate the remaining four reaction mixtures. After 3 h, the blue LED was turned off, and one vial was removed for analysis. The remaining three vials were stirred in the absence of light for an additional 1 h, then, a vial was removed for analysis and the blue LED was turned back on to irradiate the remaining two reaction mixtures. After 3 h, the blue LED was turned off, and one vial was removed for analysis. The last vial was stirred in the absence of light for an additional 1 h, and then it was analyzed. The yield was determined by <sup>1</sup>H NMR spectroscopy using dibromomethane as the internal standard. The results revealed that a radical chain process could not be the major reaction pathway, while it can't be completely ruled out at the current stage.

## **5.3 Radical trapping experiment**



When 2.0 equiv of TEMPO was added to the reaction of **1b** with **2a** under the standard conditions, the resulting mixture was stirred at 35 °C for 12 h, and the solvent was then removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE : EA = 20 : 1) to afford **5** as an oil (58% yield).

## 5.4 Stern-Volmer luminescence quenching studies



Figure S4. a) HE emission quenching by 1a. b) HE emission quenching by 2a

Emission intensities were recorded using LS55 Luminescence Spectrometer for all experiments. All HE solutions were excited at 390 nm. In a typical experiment, the DCE solution of HE (1  $\mu$ M) was added the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. After blowing with argon for 15 min, the emission spectra of the samples were collected. The results showed that **1a** quenched the photoexcited HE effectively, while the **2a** was not effective.

## 5.5 Gram-scale reaction



To a mixture of cyclobutanone oxime ester (**1a**, 1.03 g, 4.0 mmol), 2-vinylpyridine (**2a**, 640  $\mu$ L, 6.0 mmol), HE (1.52 g, 6.0 mmol), and (PhO)<sub>2</sub>PO<sub>2</sub>H (200 mg, 20 mol%) in a flame-dried Schlenk tube was added degassed DCM (20 mL) under Ar. The resulting mixture was stirred at 35 °C for 12 h, and the solvent was then removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE : EA = 4 : 1) to afford 0.530 g of **3a** as an oil (76% yield).

#### 6. Characterization of the substrates and products



**Cyclobutanone** *O*-(**4**-(**trifluoromethyl)benzoyl**) **oxime** (**1a**): <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 3.15 (t, *J* = 8.1 Hz, 4H), 2.13 (p, *J* = 8.1 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  170.1, 162.9, 134.8 (q, *J* = 32.7 Hz), 132.5, 130.1, 125.6 (q, *J* = 3.5 Hz), 123.7 (q, *J* = 272.8 Hz), 32.1, 32.0, 14.4.



**Cyclobutanone** *O***-benzoyl oxime (1aa):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.04 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 3.14 (t, *J* = 8.0 Hz, 4H), 2.11 (p, *J* = 8.1 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.4, 164.1, 133.2, 129.6, 129.1, 128.5, 31.9, 31.8, 14.3.



**Cyclobutanone** *O*-(4-fluorobenzoyl) oxime (1ab): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (dd, *J* = 7.6, 5.9 Hz, 2H), 7.12 (t, *J* = 8.4 Hz, 2H), 3.13 (t, *J* = 8.0 Hz, 4H), 2.12 (p, *J* = 8.0 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  169.5, 165.9 (d, *J* = 254.5 Hz), 163.2, 132.2 (d, *J* = 9.3 Hz), 125.4 (d, *J* = 2.8 Hz), 115.8 (d, *J* = 22.0 Hz), 32.0, 31.9, 14.4.



**Cyclobutanone** *O*-perfluorobenzoyl oxime (1ac): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.10 (dt, J = 21.8, 8.0 Hz, 4H), 2.11 (p, J = 8.1 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  171.3, 156.7, 146.7 – 146.1 (m), 144.8 – 144.5 (m), 144.5 – 144.1 (m), 142.9 – 142.2 (m), 138.9 – 138.4 (m), 137.3 – 136.6 (m), 32.2, 31.7, 14.2.



**3-Phenylcyclobutan-1-one** *O*-(**4**-(**trifluoromethyl)benzoyl**) **oxime** (**1b**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.18 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.26 (m, 3H), 3.84 – 3.48 (m, 3H), 3.41 – 3.18 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  166.9, 162.9, 142.9, 134.9 (q, *J* = 32.8 Hz), 132.4, 130.2, 128.9, 127.1, 126.4, 125.71 (q, *J* = 3.5 Hz), 123.67 (q, *J* = 272.7 Hz), 39.7, 39.6, 32.6.



**3-(4-Fluorophenyl)cyclobutan-1-one** *O*-(**4**-(trifluoromethyl)benzoyl) oxime (1c): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.17 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.24 (m, 2H), 7.05 (t, J = 8.4 Hz, 2H), 3.85 – 3.48 (m, 3H), 3.28 – 3.17 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.5, 163.0, 161.9 (d, J = 245.6 Hz), 138.6 (d, J = 3.0 Hz), 134.9 (q, J = 32.8 Hz), 132.3, 130.2, 128.0 (d, J = 8.0 Hz), 125.7 (q, J = 3.7 Hz), 123.6 (q, J = 272.7 Hz), 115.7 (d, J = 21.3 Hz), 39.9, 39.8, 32.1.



3-(P-tolyl)cyclobutan-1-one O-(4-(trifluoromethyl)benzoyl) oxime (1d): <sup>1</sup>H NMR (400

MHz, CDCl<sub>3</sub>)  $\delta$  8.17 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.18 (m, 4H), 3.83 – 3.44 (m, 3H), 3.34 – 3.14 (m, 2H), 2.35 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  167.1, 162.9, 139.9, 136.7, 134.8 (q, J = 32.8 Hz), 132.4, 130.1, 129.5, 126.3, 125.6 (q, J = 3.7 Hz), 123.6 (q, J = 272.8 Hz), 39.7, 39.6, 32.3, 21.1.



**3-(4-(***tert***-Butyl)phenyl)cyclobutan-1-one** *O*-(**4-(trifluoromethyl)benzoyl)** oxime (1e): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.19 (d, *J* = 7.9 Hz, 2H), 7.74 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 3.65 (m, 3H), 3.34 – 3.21 (m, 2H), 1.34 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  167.1, 162.9, 150.1, 139.9, 134.8 (q, *J* = 32.7 Hz), 132.4, 130.1, 126.1, 125.8, 125.6 (q, *J* = 3.2 Hz), 123.6 (q, *J* = 272.7 Hz), 39.7, 39.6, 34.6, 32.2, 31.4.



**3-Methyl-3-phenylcyclobutan-1-one** *O*-(**4**-(trifluoromethyl)benzoyl) oxime (1f): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.20 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.32 – 7.26 (m, 3H), 3.50 (t, J = 15.3 Hz, 2H), 3.34 – 3.20 (m, 2H), 1.62 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  166.1, 162.9, 147.9, 134.9 (q, J = 32.7 Hz), 132.4, 130.2, 128.8, 126.6, 125.6 (q, J = 3.3 Hz), 125.2, 123.6 (q, J = 272.7 Hz), 44.9, 44.8, 38.1, 30.9.



**Methyl 3-**(((4-(trifluoromethyl)benzoyl)oxy)imino)cyclobutane-1-carboxylate (1g): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.13 (d, J = 8.1 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 3.75 (s, 3H), 3.49 – 3.38 (m, 4H), 3.36 – 3.24 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  173.6, 165.2, 162.6, 134.9 (q, J = 32.7 Hz), 132.1, 130.1, 125.7 (q, J = 3.6 Hz), 123.6 (q, J = 272.7 Hz), 52.5, 35.8, 35.7, 30.9.



*tert*-Butyl-3-(((4-(trifluoromethyl)benzoyl)oxy)imino)cyclobutane-1-carboxylate (1h): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 3.35 (d, J= 7.8 Hz, 4H), 3.26 – 3.07 (m, 1H), 1.48 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  172.4, 165.7, 162.7, 134.9 (q, J = 32.8 Hz), 130.1, 125.7 (q, J = 3.3 Hz), 123.63 (q, J = 272.7 Hz), 81.8, 35.8, 35.6, 32.1, 28.1.



**3-(Benzyloxy)cyclobutan-1-one** *O*-(**4**-(**trifluoromethyl)benzoyl**) **oxime** (**1i**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 (d, *J* = 7.9 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.37 (m, 5H), 4.64 – 4.45 (m, 2H), 4.36 – 4.21 (m, 1H), 3.47 – 3.33 (m, 2H), 3.21 – 3.07 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  164.0, 162.8, 137.2, 134.9 (q, *J* = 32.9 Hz), 132.3, 130.1, 128.7, 128.2, 128.0, 125.6 (q, *J* = 3.4 Hz), 123.6 (q, *J* = 272.8 Hz), 71.3, 66.6, 40.5, 40.4.



*tert*-Butyl 3-(((4-(trifluoromethyl)benzoyl)oxy)imino)azetidine-1-carboxylate (1j): <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.14 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 4.84 (s, 2H), 4.83 (s, 2H), 1.49 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  162.2, 159.5, 156.0, 135.3 (q, J = 32.8 Hz), 131.5, 130.3, 125.9 (q, J = 3.6 Hz), 123.5 (q, J = 272.8 Hz), 81.5, 58.4, 28.4.



**Oxetan-3-one** *O*-(**4**-(**trifluoromethyl**)**benzoyl**) **oxime** (**1k**): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.09 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 5.46 (s, 2H), 5.44 (s, 2H); <sup>13</sup>C NMR

(150 MHz, CDCl<sub>3</sub>) δ 163.9, 162.1, 135.1 (q, *J* = 32.8 Hz), 131.4, 130.1, 125.7 (q, *J* = 3.4 Hz), 123.5 (q, *J* = 272.7 Hz), 78.3.



**2-Methylcyclobutan-1-one** *O*-(**4**-(**trifluoromethyl)benzoyl**) **oxime** (**11**): *Z/E* mixture; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 (d, *J* = 7.9 Hz, 2H), 7.76 – 7.65 (m, 2H), 3.62 – 3.41 (m, 1H), 3.23 – 2.94 (m, 2H), 2.35 – 2.23 (m, 1H), 1.76 – 1.67 (m, 1H), 1.44 (d, *J* = 7.2 Hz, 1.4H)/1.38 (d, *J* = 7.1 Hz, 1.6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 173.9/173.3, 163.1/163.0, 134.8 (q, *J* = 32.8 Hz)/134.7 (q, *J* = 32.7 Hz), 132.6/132.5, 130.1/130.0, 125.7/125.6 (q, *J* = 4.1 Hz), 123.7 (q, *J* = 272.7 Hz)/123.6 (q, *J* = 273.0 Hz), 41.2/40.7, 29.3/28.6, 22.9/22.0, 17.6/17.5.



**2-Benzylcyclobutan-1-one** *O*-(**4**-(**trifluoromethyl**)**benzoyl**) **oxime** (**1m**): *Z/E* mixture; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (d, *J* = 8.0 Hz, 1.3H)/8.01 (d, *J* = 8.0 Hz, 0.7H), 7.73 (d, *J* = 8.1 Hz, 1.3H)/7.69 (d, *J* = 8.1 Hz, 0.7H), 7.45 – 7.27 (m, 2H), 7.25 – 7.11 (m, 3H), 3.82 – 3.66 (m, 1H), 3.33 – 3.20 (m, 1H), 3.08 – 2.92 (m, 3H), 2.26 – 2.10 (m, 1H), 1.94 – 1.78 (m, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 172.5/171.3, 163.0/163.0, 138.6/138.3, 134.9 (q, *J* = 32.6 Hz)/134.8 (q, *J* = 32.5 Hz), 132.5/132.3, 130.1/130.0, 129.0/128.9, 128.8/128.7, 126.8/126.6, 125.8 – 125.6 (m), 123.7 (q, *J* = 272.7 Hz)/123.6 (q, *J* = 271.2 Hz), 47.3/46.6, 38.0/37.6, 29.2/29.1, 20.7/19.9.



(*E*)-2-Phenylcyclopentan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1n): <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  8.17 (d, J = 7.9 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.39 – 7.30 (m, 4H), 7.27 – 7.21 (m, 1H), 4.07 (t, J = 7.2 Hz, 1H), 3.04 – 2.90 (m, 1H), 2.87 – 2.74 (m, 1H), 2.39 – 2.24 (m, 1H), 2.15 – 1.96 (m, 2H), 1.95 – 1.77 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  178.3, 162.8, 140.3, 134.8 (q, J = 35.1 Hz), 132.7, 130.1, 128.8, 128.0, 127.1, 125.7 (q, J = 3.7 Hz), 123.7 (q, J = 269.6 Hz), 49.4, 34.8, 30.2, 22.6.



(*E*)-2-Phenylcyclohexan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1o): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.19 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.33 (m, 4H), 7.32 – 7.22 (m, 1H), 4.02 (t, *J* = 5.0 Hz, 1H), 3.02 – 2.90 (m, 1H), 2.57 – 2.45 (m, 1H), 2.42 – 2.28 (m, 1H), 2.17 – 2.03 (m, 1H), 1.91 – 1.77 (m, 2H), 1.77 – 1.65 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  172.2, 163.2, 138.9, 134.7 (q, *J* = 32.8 Hz), 132.9, 130.1, 128.8, 127.8, 126.9, 125.7 (q, *J* = 3.6 Hz), 123.7 (q, *J* = 272.9 Hz), 45.7, 31.2, 26.5, 25.6, 22.3.



(*E*)-2-Phenylcycloheptan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1p): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.18 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.39 – 7.31 (m, 4H), 7.29 – 7.20 (m, 1H), 4.13 (dd, J = 10.8, 6.7 Hz, 1H), 3.18 – 3.05 (m, 1H), 2.46 – 2.28 (m, 1H), 2.20 – 2.09 (m, 1H), 2.03 – 1.86 (m, 4H), 1.64 – 1.51 (m, 1H), 1.52 – 1.35 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  173.9, 162.9, 140.8, 134.8 (q, J = 32.7 Hz), 132.8, 130.1, 128.8, 127.4, 127.1, 125.7 (q, J = 3.3 Hz), 123.7 (q, J = 272.8 Hz), 48.6, 31.2, 30.9, 27.8, 26.4, 25.6.



(*E*)-2-Phenylcyclooctan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1q): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.20 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 7.5 Hz, 2H), 7.27-7.21 (m, 1H), 4.04 (dd, J = 12.6, 3.1 Hz, 1H), 2.94 – 2.78 (m, 1H), 2.47 – 2.33 (m, 1H), 2.24 – 2.02 (m, 2H), 2.02 – 1.88 (m, 2H), 1.87 – 1.72 (m, 4H), 1.59 – 1.39 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  174.8, 162.8, 140.5, 134.7 (q,

*J* = 32.7 Hz), 132.7, 130.0, 128.7, 127.5, 127.2, 125.7 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.9 Hz), 48.7, 27.1, 26.9, 26.7, 26.4, 25.0, 24.9.



**Bicyclo[3.2.0]hept-2-en-6-one** *O*-(4-(trifluoromethyl)benzoyl) oxime (1r): *Z/E* mixture; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (d, *J* = 8.2 Hz, 0.8H)/8.13 (d, *J* = 8.2 Hz, 1.2H), 7.73 (d, *J* = 8.2 Hz, 0.8H)/7.70 (d, *J* = 8.2 Hz, 1.2H), 5.90 – 5.77 (m, 2H), 4.00 – 3.89 (m, 1H), 3.51 – 3.42 (m, 1H), 3.36 – 3.23 (m, 1H), 2.94 – 2.66 (m, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  173.9/172.6, 162.9/162.7, 134.9 (q, *J* = 32.7 Hz)/ 134.8 (q, *J* = 32.7 Hz), 132.7/132.2, 132.5/132.4, 132.1/131.7, 130.1/130.0, 125.7 (q, *J* = 3.5 Hz)/125.6 (q, *J* = 3.5 Hz), 123.7 (q, *J* = 272.9 Hz), 47.1/47.0, 40.9/40.1, 39.1/39.0, 37.8/35.9.



**2,2a,7,7a-Tetrahydro**-*1H*-cyclobuta[a]inden-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1s): *Z/E* mixture; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.20 (d, *J* = 8.0 Hz, 0.6H)/8.09 (d, *J* = 8.1 Hz, 1.4H), 7.77 (d, *J* = 8.1 Hz, 0.6H)/7.68 (d, *J* = 8.1 Hz, 1.4H), 7.32 – 7.20 (m, 4H), 4.24 – 4.12 (m, 1H), 4.09 – 3.98 (m, 1H), 3.69 – 3.27 (m, 3H), 3.12 – 2.88 (m, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  172.7/171.7, 162.7/162.6, 144.0, 143.1, 142.4, 134.9 (q, *J* = 32.8 Hz)/134.7 (q, *J* = 32.7 Hz), 132.3, 130.5, 130.1, 130.0, 127.7, 127.6, 127.5, 125.7 (q, *J* = 3.1 Hz)/125.5 (q, *J* = 3.3 Hz), 125.4, 125.1, 125.0, 124.9, 123.7 (q, *J* = 272.8 Hz)/123.6 (q, *J* = 272.8 Hz), 48.0, 40.5, 40.2, 39.9, 39.7, 37.0, 35.3.



**2,2,4,4-Tetramethyl-3-**(((4-(trifluoromethyl)benzoyl)oxy)imino)cyclobutan-1-one (1t): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 1.59 (s,

6H), 1.53 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 213.3, 174.9, 162.6, 135.1 (q, *J* = 32.8 Hz), 132.1, 130.0, 125.9 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.9 Hz), 65.8, 63.3, 21.5, 20.4.



(*E*)-2-Methyl-2-phenylcyclopentan-1-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1u): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.20 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 2.94 – 2.80 (m, 1H), 2.81 – 2.64 (m, 1H), 2.59 – 2.43 (m, 1H), 2.02 – 1.88 (m, 1H), 1.86 – 1.77 (m, 1H), 1.75 – 1.55 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  179.8, 162.8, 143.7, 134.6 (q, *J* = 32.7 Hz), 132.8, 130.0, 128.7, 126.8, 126.3, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.7 Hz), 52.1, 40.6, 29.2, 27.3, 20.5.



(*E*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one *O*-(4-(trifluoromethyl)benzoyl) oxime (1v): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 2.81 – 2.69 (m, 1H), 2.27 (d, *J* = 18.1 Hz, 1H), 1.99 (t, *J* = 4.3 Hz, 1H), 1.95 – 1.86 (m, 1H), 1.86 – 1.77 (m, 1H), 1.66 – 1.55 (m, 1H), 1.35 – 1.23 (m, 1H), 1.19 (s, 3H), 0.97 (s, 3H), 0.88 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  179.6, 163.0, 134.6 (q, *J* = 32.7 Hz), 133.0, 130.0, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.7 Hz), 53.6, 48.9, 43.6, 35.1, 32.6, 27.2, 19.7, 18.6, 11.1.



**6-(Pyridin-2-yl)hexanenitrile (3a):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 4:1) to give a colorless oil; 80% yield (28 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.50 (d, *J* = 4.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.15 – 7.06 (m, 2H), 2.78 (t, *J* = 7.7 Hz, 2H), 2.32 (t, *J* = 7.1 Hz, 2H), 1.83 – 1.72 (m, 2H), 1.72 – 1.64 (m, 2H), 1.54 – 1.46 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  161.6, 149.3, 136.5, 122.9, 121.2, 119.8, 38.0, 29.0, 28.4, 25.3, 17.2; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2920, 2852, 2242, 1435, 1129; HRMS (CI) calcd C<sub>11</sub>H<sub>15</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 175.1235, found: 175.1231.



**3-Phenyl-6-(pyridin-2-yl)hexanenitrile** (**3b**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 4:1) to give a colorless oil; 80% yield (40 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (d, *J* = 4.1 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.14 – 7.06 (m, 2H), 3.03 – 2.94 (m, 1H), 2.84 – 2.73 (m, 2H), 2.60 (d, *J* = 6.9 Hz, 2H), 1.94 – 1.87 (m, 1H), 1.86 – 1.79 (m, 1H), 1.75 – 1.58 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  161.5, 149.3, 141.7, 136.5, 129.0, 127.6, 127.3, 122.9, 121.26, 118.6, 42.3, 38.0, 34.6, 27.5, 25.3; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2923, 2858, 2239, 1584, 1429; HRMS (CI) calcd C<sub>17</sub>H<sub>19</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 251.1548, found: 251.1548.



**3-(4-Fluorophenyl)-6-(pyridin-2-yl)hexanenitrile (3c):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 2:1) to give a colorless oil; 71% yield (38 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.49 (d, *J* = 4.5 Hz, 1H), 7.58 (td, *J* = 7.7, 1.6 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.13 – 7.05 (m, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 3.01 – 2.91 (m, 1H), 2.83 – 2.70 (m, 2H), 2.62 – 2.50 (m, 2H), 1.92 – 1.73 (m, 2H), 1.72 – 1.54 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.1 (d, *J* = 245.8 Hz), 161.3, 149.2, 137.3 (d, *J* = 3.0 Hz), 136.7, 128.8 (d, *J* = 8.0 Hz), 123.0, 121.4, 118.4, 115.9 (d, *J* = 21.5 Hz), 41.6, 37.9, 34.7, 27.4, 25.4; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2923, 2245, 1472, 1050, 770; HRMS (CI) calcd C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>F [M + H]<sup>+</sup>: 269.1454, found: 269.1450.



**6-(Pyridin-2-yl)-3-(p-tolyl)hexanenitrile** (3d): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 2:1) to give a colorless oil; 78% yield (41 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.49 (d, J = 3.8 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.21 – 7.00 (m, 6H), 2.98 – 2.87 (m, 1H), 2.85 – 2.69 (m, 2H), 2.56 (d, J = 6.9 Hz, 2H), 2.32 (s, 3H), 1.92 – 1.73 (m, 2H), 1.71 – 1.54 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)

δ 161.6, 149.3, 138.6, 137.1, 136.5, 129.7, 127.1, 122.9, 121.2, 118.7, 41.9, 38.0, 34.6, 27.5, 25.4, 21.2; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2929, 2246, 1437, 1044, 809; HRMS (CI) calcd C<sub>18</sub>H<sub>21</sub>N<sub>2</sub> [M + H]<sup>+</sup> 265.1705:, found: 265.1707.



**3-(4-(***tert***-Butyl)phenyl)-6-(pyridin-2-yl)hexanenitrile (3e):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 2:1) to give a colorless oil; 73% yield (45 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.49 (d, *J* = 3.9 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.14 – 7.04 (m, 4H), 2.99 – 2.88 (m, 1H), 2.82 – 2.69 (m, 2H), 2.57 (d, *J* = 6.8 Hz, 2H), 1.92 – 1.75 (m, 2H), 1.72 – 1.59 (m, 2H), 1.30 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.6, 150.3, 149.3, 138.6, 136.5, 126.9, 125.8, 122.9, 121.2, 118.8, 41.7, 38.1, 34.6, 31.4, 27.5, 25.3; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2955, 2240, 1470, 1109, 825; HRMS (CI) calcd C<sub>21</sub>H<sub>27</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 307.2174, found: 307.2169.



**3-Methyl-3-phenyl-6-(pyridin-2-yl)hexanenitrile (3f):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 2:1) to give a colorless oil; 56% yield (30 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.49 (d, J = 4.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.33 (t, J = 7.6 Hz, 2H), 7.28 – 7.25 (m, 3H), 7.23 (t, J = 7.3 Hz, 1H), 7.11 – 7.07 (m, 1H), 7.05 (d, J = 7.8 Hz, 1H), 2.73 (t, J = 7.6 Hz, 2H), 2.67 – 2.58 (m, 2H), 1.98 – 1.89 (m, 1H), 1.85 – 1.76 (m, 1H), 1.65 – 1.54 (m, 1H), 1.51 (s, 3H), 1.50 – 1.40 (m, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  161.5, 149.3, 144.1, 136.5, 128.8, 126.9, 125.8, 122.9, 121.3, 118.2, 41.3, 40.2, 38.5, 31.7, 25.1, 24.6; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2919, 2243, 1428, 1144, 761; HRMS (CI) calcd C<sub>18</sub>H<sub>21</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 265.1705, found: 265.1697.

Methyl 2-(cyanomethyl)-5-(pyridin-2-yl)pentanoate (3g): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 1:1) to give a colorless oil; 60% yield (28 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.50 (d, *J* = 4.7 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.13 – 7.07 (m, 2H), 3.71 (s, 3H), 2.82 – 2.71 (m, 3H), 2.63 (dd, *J* = 16.9, 7.0 Hz,

1H), 2.55 (dd, J = 16.9, 6.6 Hz, 1H), 1.85 – 1.69 (m, 4H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  173.1, 161.0, 149.4, 136.6, 122.9, 121.4, 117.8, 52.5, 41.5, 37.7, 30.96, 26.7, 19.4; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2926, 2246, 1731, 1431, 751; HRMS (CI) calcd C<sub>13</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 233.1290, found: 233.1291.



*tert*-Butyl 2-(cyanomethyl)-5-(pyridin-2-yl)pentanoate (3h): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 1:1) to give a colorless oil; 61% yield (33 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.50 (d, *J* = 4.3 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.15 – 7.06 (m, 2H), 2.80 (t, *J* = 6.9 Hz, 2H), 2.66 – 2.61 (m, 1H), 2.57 (dd, *J* = 16.7, 7.2 Hz, 1H), 2.48 (dd, *J* = 16.7, 6.5 Hz, 1H), 1.82 – 1.73 (m, 3H), 1.70 – 1.62 (m, 1H), 1.44 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  171.8, 161.2, 149.4, 136.5, 122.9, 121.3, 118.0, 82.1, 42.3, 37.8, 31.0, 28.1, 26.6, 19.5; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2932, 2858, 2246, 1724, 1151; HRMS (ESI) calcd C<sub>16</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 275.1754, found: 275.1757.



**3-(Benzyloxy)-6-(pyridin-2-yl)hexanenitrile** (3i): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 1:1) to give a colorless oil; 71% yield (40 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.53 (d, *J* = 3.9 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.36 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 7.14 – 7.09 (m, 2H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 3.75 – 3.68 (m, 1H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.59 – 2.50 (m, 2H), 1.92 – 1.86 (m, 1H), 1.83 – 1.75 (m, 2H), 1.72 – 1.63 (m, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  161.4, 149.4, 137.7, 136.6, 128.6, 128.1, 128.0, 123.0, 121.4, 117.7, 74.5, 72.0, 37.9, 33.9, 25.2, 23.1; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2935, 2243, 1592, 1090, 745; HRMS (CI) calcd C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>O [M + H]<sup>+</sup>: 281.1654, found: 281.1653.



*tert*-Butyl (cyanomethyl)(3-(pyridin-2-yl)propyl)carbamate (3j): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 1:1) to give the colorless oil; 73% yield (40 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.50 (d, *J* = 3.4 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.11 (t, 1H), 4.25 – 4.03 (m, 2H), 3.38 (t, *J* = 6.5 Hz, 2H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.05 – 1.97 (m, 2H), 1.44 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  160.8, 154.9/154.1, 149.3, 136.7, 123.0, 121.4, 116.3, 81.6, 47.3, 35.9, 35.1, 28.3, 27.8; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2926, 2249, 1695, 1157, 771; HRMS (CI) calcd C<sub>15</sub>H<sub>22</sub>N<sub>3</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 276.1712, found: 276.1716.



**2-(3-(Pyridin-2-yl)propoxy)acetonitrile** (**3k**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 1:1) to give a colorless oil; 70% yield (25 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (d, *J* = 3.4 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.19 – 7.07 (m, 2H), 4.23 (s, 2H), 3.61 (t, *J* = 6.2 Hz, 2H), 2.86 (t, *J* = 7.5 Hz, 2H), 2.12 – 2.00 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.0, 149.4, 136.6, 123.1, 121.4, 116.2, 71.1, 56.4, 34.4, 29.1; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2919, 2249, 1437, 1109, 771; HRMS (CI) calcd C<sub>10</sub>H<sub>13</sub>N<sub>2</sub>O [M + H]<sup>+</sup>: 177.1028, found: 177.1022.

**4-Methyl-6-(pyridin-2-yl)hexanenitrile** (**3l):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 2:1) to give a colorless oil; 56% yield (21 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (d, *J* = 4.5 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.11 – 7.07 (m, 1H), 2.88 – 2.80 (m, 1H), 2.79 – 2.71 (m, 1H), 2.39 – 2.28 (m, 2H), 1.81 – 1.72 (m, 2H), 1.69 – 1.56 (m, 2H), 1.56 – 1.48 (m, 1H), 0.99 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  161.9, 149.4, 136.5, 122.8, 121.2, 120.0, 36.3, 35.7, 32.3, 32.0, 18.9, 15.0; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2922, 2246, 1582, 1428, 751; HRMS (CI) calcd C<sub>12</sub>H<sub>17</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 189.1392, found: 189.1388.



**4-Benzyl-6-(pyridin-2-yl)hexanenitrile (3m):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 2:1) to give a colorless oil; 45% yield (24 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.52 (d, *J* = 4.1 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.12 – 7.08 (m, 2H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.77 (dd, *J* = 13.8, 6.3 Hz, 1H), 2.54 (dd, *J* = 13.7, 7.8 Hz, 1H), 2.35 – 2.24 (m, 2H), 1.91 – 1.83 (m, 1H), 1.83 – 1.72 (m, 2H), 1.72 – 1.61 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  161.6, 149.4, 139.9, 136.6, 129.2, 128.6, 126.4, 122.9, 121.3, 119.9, 40.1, 38.7, 35.3, 33.0, 29.0, 14.9; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2923, 2861, 2245, 1587, 1429; HRMS (CI) calcd C<sub>18</sub>H<sub>21</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 265.1705, found: 265.1700.



**5-Phenyl-7-(pyridin-2-yl)heptanenitrile** (**3n**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 4:1) to give a colorless oil; 57% yield (30 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (d, *J* = 4.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.08 (dd, *J* = 7.0, 5.3 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 2.69 – 2.59 (m, 2H), 2.59 – 2.52 (m, 1H), 2.22 (t, *J* = 7.3 Hz, 2H), 2.18 – 2.11 (m, 1H), 2.06 – 1.96 (m, 1H), 1.89 – 1.80 (m, 1H), 1.78 – 1.67 (m, 1H), 1.57 – 1.40 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  161.8, 149.2, 144.1, 136.5, 128.8, 127.7, 126.7, 123.0, 121.2, 119.7, 45.3, 36.7, 36.2, 35.8, 23.6, 17.2; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2919, 2249, 1473, 1051, 703; HRMS (CI) calcd C<sub>18</sub>H<sub>21</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 265.1705, found: 265.1710.



**6-Phenyl-8-(pyridin-2-yl)octanenitrile** (**3o**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 4:1) to give a colorless oil; 46% yield (26 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (d, *J* = 3.3 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 2H), 7.11 – 7.05 (m, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 2.61 (t, *J* = 7.4 Hz, 2H), 2.57 – 2.48 (m, 1H), 2.30 – 2.19 (m, 2H), 2.18 – 2.06 (m, 1H), 2.05 – 1.92 (m, 1H), 1.77 – 1.67 (m, 1H), 1.67 – 1.47 (m, 3H), 1.42 – 1.22 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.1, 149.4, 144.8, 136.4, 128.7, 127.8, 126.5, 123.0, 121.1, 119.8, 45.7, 36.8, 36.4, 36.2, 26.9, 25.6, 17.2; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2935, 2245, 1474, 1052, 695; HRMS (ESI) calcd C<sub>19</sub>H<sub>23</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 279.1856, found: 279.1857.



**7-Phenyl-9-(pyridin-2-yl)nonanenitrile** (**3p**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 4:1) to give a colorless oil; 54% yield (31 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.50 (d, *J* = 3.8 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.23 – 7.12 (m, 3H), 7.10 – 7.04 (m, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 2.69 – 2.58 (m, 2H), 2.57 – 2.50 (m, 1H), 2.24 (t, *J* = 7.0 Hz, 2H), 2.17 – 2.05 (m,

1H), 2.03 – 1.89 (m, 1H), 1.73 – 1.64 (m, 1H), 1.63 – 1.51 (m, 2H), 1.44 – 1.29 (m, 3H), 1.26 – 1.08 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.2, 149.3, 145.2, 136.4, 128.5, 127.8, 126.3, 122.9, 121.0, 119.9, 45.8, 36.8, 36.6, 36.4, 28.7, 26.8, 25.3, 17.1; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2929, 2242, 1462, 1078, 698; HRMS (ESI) calcd C<sub>20</sub>H<sub>25</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 293.2012, found: 293.2015.



**8-Phenyl-10-(pyridin-2-yl)decanenitrile** (**3q**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 4:1) to give a colorless oil; 33% yield (20 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.50 (d, J = 4.2 Hz, 1H), 7.53 (td, J = 7.7, 1.8 Hz, 1H), 7.30 (t, J = 7.4 Hz, 2H), 7.22 – 7.18 (m, 1H), 7.18 – 7.13 (m, 2H), 7.07 (dd, J = 6.7, 5.1 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H), 2.68 – 2.58 (m, 2H), 2.58 – 2.49 (m, 1H), 2.26 (t, J = 7.1 Hz, 2H), 2.16 – 2.06 (m, 1H), 2.01 – 1.91 (m, 1H), 1.72 – 1.63 (m, 1H), 1.62 – 1.52 (m, 3H), 1.39 – 1.31 (m, 2H), 1.30 – 1.10 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.3, 149.3, 145.4, 136.3, 128.5, 127.8, 126.2, 122.3, 121.0, 119.9, 45.9, 36.9, 36.5, 28.9, 28.6, 27.3, 25.4, 17.2; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2932, 2239, 1423, 1058, 703; HRMS (ESI) calcd C<sub>21</sub>H<sub>27</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 307.2169, found: 307.2172.



**2-(5-(2-(Pyridin-2-yl)ethyl)cyclopent-2-en-1-yl)acetonitrile (3r):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 2:1) to give a colorless oil; 58% yield (25 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (d, *J* = 4.4 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.11 – 7.05 (m, 1H), 5.87 – 5.80 (m, 1H), 5.65 – 5.59 (m, 1H), 2.89 – 2.75 (m, 2H), 2.74 – 2.64 (m, 2H), 2.45 (dd, *J* = 16.7, 5.8 Hz, 1H), 2.36 (dd, *J* = 16.7, 6.9 Hz, 1H), 2.15 – 2.08 (m, 1H), 2.04 – 1.93 (m, 2H), 1.83 – 1.74 (m, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  161.7, 149.3, 136.6, 132.7, 130.9, 122.8, 121.3, 118.9, 48.3, 43.4, 38.9, 36.7, 35.5, 22.9; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2916, 2243, 1589, 1147, 751; HRMS (CI) calcd C<sub>14</sub>H<sub>17</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 213.1392, found: 213.1390.



**2-(2-(Pyridin-2-yl)ethyl)-2,3-dihydro-1H-inden-1-yl)acetonitrile (3s):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 2:1) to give a colorless oil; 81% yield (43 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.52 (d, *J* = 3.9 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.33 – 7.27 (m, 1H), 7.25 – 7.15 (m, 4H), 7.15 – 7.07 (m, 1H), 3.27 – 3.15 (m, 2H), 3.01 – 2.90 (m, 1H), 2.90 – 2.80 (m, 1H), 2.74 – 2.61 (m, 3H), 2.29 – 2.21 (m, 1H), 2.19 – 2.11 (m, 1H), 1.93 – 1.80 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.5, 149.4, 142.8, 142.6, 136.6, 127.8, 126.9, 125.0, 123.6, 122.9, 121.3, 118.8, 47.0, 45.5, 37.6, 36.6, 34.5, 21.9; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2919, 2249, 1479, 1051, 742; HRMS (CI) calcd C<sub>18</sub>H<sub>19</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 263.1548, found: 263.1548.



**2,2,4,4-Tetramethyl-3-oxo-6-(pyridin-2-yl)hexanenitrile** (**3t**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 1:1) to give a colorless oil; 41% yield (20 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (d, *J* = 4.3 Hz, 1H), 7.59 (td, *J* = 7.7, 1.8 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.10 (dd, *J* = 7.0, 5.3 Hz, 1H), 2.71 – 2.65 (m, 2H), 2.24 – 2.13 (m, 2H), 1.56 (s, 6H), 1.47 (s, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  208.2, 161.4, 149.4, 136.6, 123.5, 122.8, 121.4, 50.0, 40.2, 39.6, 34.0, 27.0, 24.5; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2938, 2230, 1448, 1037, 7455; HRMS (CI) calcd C<sub>15</sub>H<sub>21</sub>N<sub>2</sub>O [M + H]<sup>+</sup>: 245.1654, found: 245.1654.



**5-Methyl-5-phenyl-7-(pyridin-2-yl)heptanenitrile (3u):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 2:1) to give a colorless oil; 47% yield (26 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.49 (s, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.30 (m, 4H), 7.24 – 7.16 (m, 1H), 7.11 – 7.04 (m, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 2.66 (td, *J* = 13.0, 4.6 Hz, 1H), 2.43 (td, *J* = 13.0, 4.1 Hz, 1H), 2.27 – 2.09 (m, 3H), 2.03 – 1.86 (m, 2H), 1.73 (td, *J* = 12.8, 4.2 Hz, 1H), 1.61 – 1.48 (m, 1H), 1.42 (s, 3H), 1.36 – 1.29 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.4, 149.3, 146.2, 136.5, 128.6, 126.4, 126.1, 122.8, 121.1, 119.7, 43.4, 42.7, 40.9, 33.4, 24.0, 20.8, 17.8; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2923, 2239, 1477, 1123, 698; HRMS (ESI) calcd C<sub>19</sub>H<sub>23</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 279.1856, found: 279.1858.



**2,2,3-Trimethyl-3-(2-(pyridin-2-yl)ethyl)cyclopentyl)acetonitrile (3v):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 2:1) to give a colorless oil; 54% yield (28 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (d, *J* = 4.5 Hz, 1H), 7.58 (td, *J* = 7.7, 1.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.11 – 7.06 (m, 1H), 2.80 – 2.65 (m, 2H), 2.36 – 2.29 (m, 1H), 2.27 – 2.12 (m, 2H), 2.11 – 1.96 (m, 1H), 1.85 – 1.75 (m, 1H), 1.67 – 1.55 (m, 2H), 1.53 – 1.42 (m, 1H), 1.43 – 1.32 (m, 1H), 0.94 (s, 3H), 0.87 (s, 3H), 0.75 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  163.0, 149.4, 136.6, 122.8, 121.1, 120.1, 47.3, 45.7, 44.2, 36.5, 34.4, 32.6, 27.9, 22.0, 20.0, 19.4, 19.1; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2951, 2240, 1473, 1151, 745; HRMS (CI) calcd C<sub>17H25</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 257.2018, found: 257.2015.

<sup>≷</sup>N *⊳*N

**6-(4-Methylpyridin-2-yl)hexanenitrile** (**4a):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 4:1) to give a colorless oil; 58% yield (22 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (d, *J* = 4.9 Hz, 1H), 6.96 (s, 1H), 6.94 (d, *J* = 4.9 Hz, 1H), 2.75 (t, *J* = 7.7 Hz, 2H), 2.33 (t, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 1.80 - 1.73 (m, 2H), 1.73 - 1.66 (m, 2H), 1.55 - 1.47 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  161.4, 149.1, 147.7, 123.9, 122.3, 119.9, 37.8, 29.0, 28.5, 25.4, 21.1, 17.2; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2926, 2246, 1602, 1457, 812; HRMS (CI) calcd C<sub>12</sub>H<sub>17</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 189.1392, found: 189.1386.

<sup>≷</sup>N .N

**6-(5-Methylpyridin-2-yl)hexanenitrile** (**4b**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 4:1) to give a colorless oil; 56% yield (21 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.34 (s, 1H), 7.40 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 2.80 – 2.71 (m, 2H), 2.32 (t, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 1.80 – 1.72 (m, 2H), 1.71 – 1.62 (m, 2H), 1.54 – 1.44 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.6, 149.6, 137.2, 130.5, 122.4, 119.9, 37.5, 29.1, 28.4, 25.4, 18.2, 17.2; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2932, 2858, 2245, 1486, 1027; HRMS (CI) calcd C<sub>12</sub>H<sub>17</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 189.1392, found: 189.1389.



**6-Phenyl-6-(pyridin-2-yl)hexanenitrile** (**4c**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 5:1) to give a colorless oil; 40% yield (20 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.60 – 8.53 (m, 1H), 7.55 (td, *J* = 7.7, 1.8 Hz, 1H), 7.35 – 7.26 (m, 4H), 7.23 – 7.16 (m, 1H), 7.16 – 7.05 (m, 2H), 4.03 (t, *J* = 7.7 Hz, 1H), 2.37 – 2.24 (m, 3H), 2.14 – 2.03 (m, 1H), 1.74 – 1.64 (m, 2H), 1.46 – 1.36 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  163.5, 149.4, 143.5, 136.6, 128.7, 128.0, 126.7, 123.0, 121.5, 119.8, 53.5, 34.2, 27.2, 25.5, 17.1; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2941, 2245, 1432, 994, 700; HRMS (CI) calcd C<sub>17</sub>H<sub>19</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 251.1548, found: 251.1544.



**6-(4-Chlorophenyl)-6-(pyridin-2-yl)hexanenitrile (4d):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 20:1 to 5:1) to give a colorless oil; 42% yield (24 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.57 (dd, J = 5.2, 1.8 Hz, 1H), 7.57 (td, J = 7.7, 1.8 Hz, 1H), 7.29 – 7.23 (m, 4H), 7.14 – 7.07 (m, 2H), 4.00 (t, J = 7.7 Hz, 1H), 2.34 – 2.23 (m, 3H), 2.13 – 1.95 (m, 1H), 1.73 – 1.63 (m, 2H), 1.44 – 1.33 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.9, 149.5, 142.0, 136.7, 132.5, 129.4, 128.8, 123.0, 121.8, 119.7, 52.9, 34.3, 27.2, 25.5, 17.2; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2935, 2240, 1492, 1012, 748; HRMS (ESI) calcd C<sub>17</sub>H<sub>18</sub><sup>35</sup>ClN<sub>2</sub>[M + H]<sup>+</sup>: 285.1153, found: 285.1156.



**6-(Pyridin-2-yl)-5-(p-tolyl)hexanenitrile** (**4e**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 4:1) to give a colorless oil; 33% yield (18 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.53 (d, *J* = 4.4 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.14 – 7.08 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 7.7 Hz, 1H), 3.17 – 3.07 (m, 2H), 3.08 – 2.99 (m, 1H), 2.29 (s, 3H), 2.22 (t, *J* = 7.2 Hz, 2H), 1.83 – 1.75 (m, 2H), 1.53 – 1.45 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  159.8, 148.7, 140.4, 136.9, 136.2, 129.4, 127.5, 124.2, 121.6, 119.7, 45.6, 45.4, 34.8, 23.6, 21.2, 17.2; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2926, 2248, 1477, 1052, 745; HRMS (ESI) calcd C<sub>18</sub>H<sub>21</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 265.1699, found: 265.1698.



**6-(Pyridin-4-yl)hexanenitrile (4f):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 4:1) to give a colorless oil; 75% yield (26 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.49 (d, *J* = 5.9 Hz, 2H), 7.11 (d, *J* = 4.6, 1.5 Hz, 2H), 2.65 – 2.59 (m, 2H), 2.33 (t, *J* = 7.1 Hz, 2H), 1.72 – 1.61 (m, 4H), 1.54 – 1.44 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  151.4, 149.7, 124.1, 119.6, 35.0, 29.5, 28.3, 25.3, 17.2; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2935, 2861, 2242, 1602, 1415; HRMS (CI) calcd C<sub>11</sub>H<sub>15</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 175.1235, found: 175.1229.



**6-(2-Methylpyridin-4-yl)hexanenitrile** (**4g**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 4:1) to give a colorless oil; 52% yield (20 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.38 (d, *J* = 5.1 Hz, 1H), 6.97 (s, 1H), 6.91 (d, *J* = 5.0 Hz, 1H), 2.62 – 2.56 (m, 2H), 2.52 (s, 3H), 2.34 (t, *J* = 7.1 Hz, 2H), 1.72 – 1.61 (m, 4H), 1.54 – 1.44 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.4, 151.4, 149.1, 123.5, 121.1, 119.7, 35.0, 29.6, 28.4, 25.3, 24.4, 17.2; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2919, 2240, 1608, 1125, 835; HRMS (CI) calcd C<sub>12</sub>H<sub>17</sub>N<sub>2</sub> [M + H]<sup>+</sup>: 189.1392, found: 189.1388.



**3-Phenyl-4-**((**2,2,6,6-tetramethylpiperidin-1-yl)oxy)butanenitrile** (**5**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 10:1) to give a colorless oil; 58% yield (35 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 – 7.23 (m, 5H), 3.99 (d, *J* = 6.4 Hz, 2H), 3.28 – 3.18 (m, 1H), 2.91 (dd, *J* = 16.7, 5.9 Hz, 1H), 2.74 (dd, *J* = 16.7, 8.0 Hz, 1H), 1.60 – 1.48 (m, 1H), 1.48 – 1.39 (m, 4H), 1.35 – 1.29 (m, 1H), 1.16 – 1.01 (m, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.4, 128.9, 127.8, 127.7, 118.8, 78.3, 60.1, 42.1, 39.8, 39.8, 33.1, 21.2, 20.4, 20.3, 17.1; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2931, 2250, 1455, 1041, 757; HRMS (ESI) calcd C<sub>19</sub>H<sub>28</sub>N<sub>2</sub>O [M + H]<sup>+</sup>: 301.2274, found: 301.2272.



((2-Phenylallyl)sulfonyl)benzene (6a): <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 (d, J = 7.9 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.28 – 7.18 (m, 5H), 5.58 (s, 1H), 5.20 (s, 1H), 4.27 (s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  138.7, 138.3, 136.4, 133.7, 128.9, 128.6, 128.4, 128.0, 126.2, 121.9, 62.0.



**2-(3-(Phenylsulfonyl)prop-1-en-2-yl)naphthalene** (**6b**) <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (d, J = 7.9 Hz, 2H), 7.79 – 7.75 (m, 1H), 7.75 – 7.69 (m, 2H), 7.64 (s, 1H), 7.49 – 7.43 (m, 3H), 7.41 (d, J = 8.2 Hz, 1H), 7.36 (t, J = 15.1, 7.3 Hz, 2H), 5.74 (s, 1H), 5.33 (s, 1H), 4.39 (s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  138.6, 136.5, 136.0, 133.7, 133.2, 133.0, 129.0, 128.8, 128.4, 128.3, 127.6, 126.5, 125.6, 124.2, 122.3, 62.3.



**1-Chloro-4-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene (6c):** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.21 (s, 4H), 5.58 (s, 1H), 5.21 (s, 1H), 4.23 (s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 138.4, 137.3, 135.6, 134.2, 133.9, 129.1, 128.7, 128.7, 127.7, 122.5, 62.1.



**1-Bromo-4-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene** (6d): <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 (d, J = 7.3 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 5.57 (s, 1H), 5.20 (s, 1H), 4.22 (s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  138.3, 137.7, 135.6, 133.8, 131.5, 129.1, 128.6, 127.9, 122.5, 122.2, 62.0.

CO<sub>2</sub>Et

**Ethyl 2-((phenylsulfonyl)methyl)acrylate (6e):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 6.48 (s, 1H), 5.88 (s, 1H), 4.14 (s, 2H), 3.98 (q, *J* = 6.9 Hz, 2H), 1.14 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  164.8, 138.4, 133.9, 133.4, 129.2, 129.1, 128.8, 61.5, 57.6, 14.0.

*tert*-Butyl 2-((phenylsulfonyl)methyl)acrylate (6f): <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.84 (d, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 6.42 (s, 1H), 5.87 (s, 1H), 4.12 (s, 2H), 1.31 (s, 9H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 163.8, 138.6, 133.9, 132.8, 130.4, 129.1, 128.9, 81.9, 57.5, 27.8.

CO<sub>2</sub>Bn

**Benzyl 2-((phenylsulfonyl)methyl)acrylate (6g):** <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (d, J = 7.9 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.38 – 7.30 (m, 3H), 7.26 (d, J = 7.3 Hz, 2H), 6.53 (s, 1H), 5.92 (s, 1H), 5.00 (s, 2H), 4.17 (s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  164.6, 138.2, 135.3, 133.9, 133.8, 129.0, 128.8, 128.6, 128.5, 128.4, 128.2, 67.1, 57.4.

N

**6-Phenylhept-6-enenitrile (7a):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 10:1) to give a colorless oil; 57% yield (21 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 – 7.20 (m, 5H), 5.29 (s, 1H), 5.07 (s, 1H), 2.56 (t, *J* = 6.6 Hz, 2H), 2.31 (t, *J* = 6.6 Hz, 2H), 1.76 – 1.57 (m, 4H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  147.6, 140.9, 128.5, 127.7, 126.2, 119.8, 113.1, 34.6, 27.2, 25.0, 17.1; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2947, 2242, 1492, 1075, 706; HRMS (ESI) calcd C<sub>13</sub>H<sub>16</sub>N [M + H]<sup>+</sup>: 186.1277, found: 186.1275.



**3,6-Diphenylhept-6-enenitrile** (**7b**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 15:1) to give a colorless oil; 43% yield (22 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 – 7.17 (m, 10H), 5.27 (s, 1H), 5.00 (s, 1H), 3.07 – 2.86 (m, 1H), 2.56 (d, *J* = 6.8 Hz, 2H), 2.45 – 2.31 (m, 2H), 2.01 – 1.83 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  147.6, 141.4, 140.8, 129.1, 128.5, 127.7, 127.4, 126.2, 118.5, 113.2, 41.8, 33.5, 33.0, 25.3; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 3028, 2350, 1628, 1031, 777; HRMS (ESI) calcd C<sub>19</sub>H<sub>19</sub>NNa [M + Na]<sup>+</sup>: 284.1410, found: 284.1408.



**6-Phenyl-3-(p-tolyl)hept-6-enenitrile (7c):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 15:1) to give a colorless oil; 41% yield (23 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 – 7.23 (m, 5H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.11 – 7.06 (m, 2H), 5.26 (d, *J* = 1.2 Hz, 1H), 5.00 (d, *J* = 1.3 Hz, 1H), 3.01 – 2.88 (m, 1H), 2.54 (d, *J* = 6.9 Hz, 2H), 2.43 – 2.35 (m, 2H), 2.34 (s, 3H), 1.99 – 1.80 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  147.6, 140.8, 138.4, 137.3, 129.7, 128.5, 127.7, 127.3, 126.2, 118.7, 113.1, 41.5, 33.5, 33.0, 25.5, 21.2; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2920, 2242, 1629, 1447, 1028; HRMS (ESI) calcd C<sub>20</sub>H<sub>22</sub>N [M + H]<sup>+</sup>: 276.1747, found: 276.1748.



**3-Methyl-3,6-diphenylhept-6-enenitrile** (7d): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 10:1) to give a colorless oil; 31% yield (17 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 – 7.35 (m, 2H), 7.32 – 7.24 (m, 6H), 7.24 – 7.20 (m, 2H), 5.23 (d, *J* = 1.2 Hz, 1H), 5.00 (d, *J* = 1.2 Hz, 1H), 2.70 – 2.58 (m, 2H), 2.36 – 2.27 (m, 1H), 2.22 – 2.13 (m, 1H), 2.04 – 1.96 (m, 1H), 1.90 – 1.80 (m, 1H), 1.57 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  148.0, 143.8, 140.7, 128.9, 128.5, 127.7, 127.1, 126.1, 125.9, 118.1, 112.8, 40.7, 40.3, 31.8, 30.4, 24.9; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2923, 2248, 1492, 1025, 701; HRMS (ESI) calcd C<sub>20</sub>H<sub>22</sub>N [M + H]<sup>+</sup>: 276.1747, found: 276.1743.



**2-((3-Phenylbut-3-en-1-yl)oxy)acetonitrile (7e):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 20:1) to give a colorless oil; 51% yield (19 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 – 7.26 (m, 5H), 5.37 (s, 1H), 5.15 (d, *J* = 1.2 Hz, 1H), 4.21 (s, 2H), 3.70 (t, *J* = 6.9 Hz, 2H), 2.84 (t, *J* = 6.9 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  144.4, 140.5, 128.6, 127.9, 126.2, 116.1, 114.6, 70.5, 56.4, 35.3; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2936, 2159, 1588, 1090, 749; HRMS (ESI) calcd C<sub>12</sub>H<sub>14</sub>NO [M + H]<sup>+</sup>: 188.1070, found: 188.1062.



**4-Methyl-6-phenylhept-6-enenitrile (7f):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 20:1) to give a colorless oil; 65% yield (26 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 – 7.15 (m, 5H), 5.23 (s, 1H), 4.98 (s, 1H), 2.46 (dd, J = 14.0, 6.5 Hz, 1H), 2.35 – 2.11 (m, 3H), 1.76 – 1.53 (m, 2H), 1.45 – 1.31 (m, 1H), 0.82 (d, J = 6.5 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  146.7, 140.9, 128.5, 127.7, 126.3, 120.0, 114.6, 42.9, 32.1, 30.7, 18.9, 15.0; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2926, 2246, 1489, 1064, 780; HRMS (CI) calcd C<sub>14</sub>H<sub>18</sub>N [M + H]<sup>+</sup>: 200.1439, found: 200.1441.



**4-Benzyl-6-phenylhept-6-enenitrile (7g):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 10:1) to give a colorless oil; 73% yield (40 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 – 7.17 (m, 8H), 7.08 – 7.01 (m, 2H), 5.33 (d, J = 1.5 Hz, 1H), 5.10 (d, J = 1.2 Hz, 1H), 2.69 – 2.47 (m, 3H), 2.46 – 2.37 (m, 1H), 2.24 (t, J = 7.7 Hz, 2H), 1.90 – 1.76 (m, 1H), 1.73 – 1.58 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  146.8, 140.6, 139.9, 129.2, 128.6, 128.5, 127.8, 126.4, 126.4, 119.8, 115.0, 40.2, 39.8, 37.5, 29.2, 14.9; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2929, 2245, 1456, 1016, 701; HRMS (ESI) calcd C<sub>20</sub>H<sub>22</sub>N [M + H]<sup>+</sup>: 276.1747, found: 276.1748.



**5,7-Diphenyloct-7-enenitrile (7h):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 25:1) to give a colorless oil; 63% yield (35 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 – 7.25 (m, 7H), 7.22 – 7.17 (m, 1H), 7.09 – 7.03 (m, 2H), 5.18 (d, *J* = 1.5 Hz, 1H), 4.92 (d, *J* = 1.3 Hz, 1H), 2.81 (d, *J* = 7.2 Hz, 2H), 2.66 – 2.57 (m, 1H), 2.16 (t, *J* = 7.1 Hz, 2H), 1.92 – 1.80 (m, 1H), 1.73 – 1.63 (m, 1H), 1.45 – 1.35 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  146.5, 144.2, 141.0, 128.6, 128.5, 127.6, 126.6, 126.5, 119.7, 114.9, 43.6, 43.5, 34.6, 23.5, 17.2; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2915, 2243, 1625, 1492, 897; HRMS (ESI) calcd C<sub>20</sub>H<sub>22</sub>N [M + H]<sup>+</sup>: 276.1747, found: 276.1752.



**6,8-Diphenylnon-8-enenitrile (7i):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 25:1) to give a colorless oil; 60% yield (35 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 – 7.29 (m, 4H), 7.29 – 7.22 (m, 3H), 7.19 – 7.11 (m, 1H), 7.04 (d, *J* = 7.3 Hz, 2H), 5.15 (s, 1H), 4.89 (s, 1H), 2.78 (d, *J* = 7.3 Hz, 2H), 2.64 – 2.55 (m, 1H), 2.20 – 2.07 (m, 2H), 1.75 – 1.64 (m, 1H), 1.61 – 1.56 (m, 1H), 1.54 – 1.38 (m, 2H), 1.21 – 1.12 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  146.8, 144.8, 141.1, 128.5, 127.7, 127.6, 126.5, 126.4, 119.8, 114.6, 43.8, 43.5, 34.8, 26.7, 25.5, 17.1; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2934, 2248, 1626, 1456, 897; HRMS (ESI) calcd C<sub>21</sub>H<sub>23</sub>NNa [M + Na]<sup>+</sup>: 312.1723, found: 312.1724.



**7,9-Ddiphenyldec-9-enenitrile** (**7j**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 25:1) to give a colorless oil; 58% yield (38 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 – 7.31 (m, 4H), 7.30 – 7.23 (m, 3H), 7.21 – 7.15 (m, 1H), 7.06 (d, *J* = 7.3 Hz, 2H), 5.16 (s, 1H), 4.90 (s, 1H), 2.78 (d, *J* = 7.3 Hz, 2H), 2.66 – 2.54 (m, 1H), 2.20 (t, *J* = 7.1 Hz, 2H), 1.76 – 1.64 (m, 1H), 1.61 – 1.56 (m, 1H), 1.53 – 1.46 (m, 2H), 1.38 – 1.28 (m, 2H), 1.15 – 1.02 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  146.9, 145.2, 141.2, 128.5, 128.4, 127.7, 127.5, 126.5, 126.2, 119.9, 114.5, 43.9, 43.6, 35.3, 28.7, 26.6, 25.3, 17.1; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2931, 2243, 1592, 1445, 780; HRMS (ESI) calcd C<sub>22H25</sub>NNa [M + Na]<sup>+</sup>: 326.1879, found: 326.1889.



**10-(Naphthalen-2-yl)-8-phenylundec-10-enenitrile (7k):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 20:1) to give a colorless oil; 42% yield (31 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 – 7.80 (m, 3H), 7.78 (s, 1H), 7.55 – 7.45 (m, 3H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 7.20 (t, J = 7

2H), 5.32 (s, 1H), 5.02 (s, 1H), 2.98 – 2.86 (m, 2H), 2.72 – 2.63 (m, 1H), 2.20 (t, J = 7.2 Hz, 2H), 1.77 – 1.69 (m, 1H), 1.63 – 1.58 (m, 1H), 1.53 – 1.48 (m, 2H), 1.31 – 1.26 (m, 2H), 1.25 – 1.13 (m, 2H), 1.12 – 1.05 (m, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  146.8, 145.4, 138.5, 133.5, 132.9, 128.4, 128.3, 128.0, 127.8, 127.7, 126.3, 126.2, 125.9, 125.1, 125.1, 119.9, 115.1, 44.1, 43.6, 35.5, 28.7, 28.5, 27.1, 25.3, 17.1; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2921, 2250, 1739, 1448, 750; HRMS (ESI) calcd C<sub>27</sub>H<sub>30</sub>N [M + H]<sup>+</sup>: 368.2373, found: 368.2380.



**2-(2-(2-Phenylallyl)-2,3-dihydro-1H-inden-1-yl)acetonitrile** (7I): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 10:1) to give a colorless oil; 65% yield (36 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 5.38 (s, 1H), 5.15 (s, 1H), 3.23 (q, *J* = 6.1 Hz, 1H), 3.08 (dd, *J* = 16.3, 8.0 Hz, 1H), 2.90 (dd, *J* = 14.2, 6.5 Hz, 1H), 2.72 – 2.63 (m, 2H), 2.56 (d, *J* = 6.5 Hz, 2H), 2.41 – 2.30 (m, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  146.8, 142.8, 142.4, 140.7, 128.7, 127.88, 127.83, 126.9, 126.4, 125.1, 123.9, 118.8, 114.6, 46.8, 43.6, 40.9, 37.4, 22.5; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2923, 2236, 1483, 1025, 701; HRMS (ESI) calcd C<sub>20</sub>H<sub>20</sub>N [M + H]<sup>+</sup>: 274.1590, found: 274.1594.



**5-Methyl-5,7-diphenyloct-7-enenitrile** (7m): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 15:1) to give a colorless oil; 42% yield (24 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 – 7.16 (m, 9H), 7.14 – 7.10 (m, 1H), 5.13 (d, *J* = 1.7 Hz, 1H), 4.78 (s, 1H), 2.92 – 2.81 (m, 2H), 2.08 – 2.03 (m, 2H), 1.85 (td, *J* = 13.0, 4.2 Hz, 1H) 1.66 – 1.58 (m, 1H), 1.43 – 1.35 (m, 1H), 1.24 – 1.20 (m, 1H), 1.19 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  146.4, 146.2, 143.5, 128.22, 128.20, 127.1, 126.6, 126.4, 125.9, 119.7, 117.7, 48.9, 41.8, 41.3, 24.3, 20.8, 17.6; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2935, 2251, 1438, 1025, 698; HRMS (ESI) calcd C<sub>21</sub>H<sub>24</sub>N [M + H]<sup>+</sup>: 290.1903, found: 290.1901.


**2,2,4,4-Tetramethyl-3-oxo-6-phenylhept-6-enenitrile** (**7n**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 15:1) to give a colorless oil; 35% yield (18 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 – 7.33 (m, 2H), 7.33 – 7.29 (m, 2H), 7.26 – 7.23 (m, 1H), 5.27 (d, *J* = 1.5 Hz, 1H), 5.12 (s, 1H), 3.06 (s, 2H), 1.34 (s, 6H), 1.29 (s, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  207.7, 145.7, 142.5, 128.5, 127.6, 127.1, 123.6, 118.3, 50.45, 44.5, 40.4, 26.6, 25.3; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2929, 2159, 1729, 1591, 1097, 751; HRMS (ESI) calcd C<sub>17</sub>H<sub>21</sub>NONa [M + Na]<sup>+</sup>: 278.1515, found: 278.1511.



**2,2,3-Trimethyl-3-(2-(naphthalen-2-yl)allyl)cyclopentyl)acetonitrile** (**70**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 25:1) to give a colorless oil; 49% yield (31 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.86 – 7.76 (m, 4H), 7.53 – 7.42 (m, 3H), 5.43 (d, *J* = 1.7 Hz, 1H), 5.13 (s, 1H), 2.63 (d, *J* = 13.3 Hz, 1H), 2.49 (d, *J* = 13.3 Hz, 1H), 2.38 – 2.30 (m, 2H), 2.22 – 2.14 (m, 1H), 1.87 – 1.80 (m, 1H), 1.62 – 1.57 (m, 1H), 1.22 – 1.12 (m, 2H), 1.00 (s, 3H), 0.72 (d, *J* = 6.1 Hz, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  147.6, 141.4, 133.5, 132.8, 128.2, 128.0, 127.7, 126.3, 125.9, 125.1, 124.9, 120.2, 118.4, 48.4, 46.1, 44.3, 40.6, 32.3, 27.9, 22.0, 21.0, 19.43, 19.36; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2915, 2238, 1623, 1375, 858; HRMS (ESI) calcd C<sub>23</sub>H<sub>28</sub>N [M + H]<sup>+</sup>: 318.2216, found: 318.2216.



**6-(4-Chlorophenyl)-4-methylhept-6-enenitrile** (**7p**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 20:1) to give a colorless oil; 58% yield (27 mg); <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$  7.32 – 7.27 (m, 4H), 5.29 (d, *J* = 1.3 Hz, 1H), 5.07 (d, *J* = 1.2 Hz, 1H), 2.56 – 2.46 (m, 1H), 2.40 – 2.20 (m, 3H), 1.80 – 1.69 (m, 1H), 1.69 – 1.61 (m, 1H), 1.52 – 1.39 (m, 1H), 0.88 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  145.6, 139.3, 133.5, 128.7, 127.6, 119.8, 115.2, 42.7, 32.0, 30.6, 18.8, 15.0; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2932, 2251, 1486, 1007, 834; HRMS (ESI) calcd C<sub>14</sub>H<sub>17</sub><sup>35</sup>ClN [M + H]+: 234.1044, found: 234.1043.



**6-(4-Bromophenyl)-4-methylhept-6-enenitrile (7q):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 20:1) to give a colorless oil; 54% yield (30 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.45 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 5.30 (s, 1H), 5.08 (s, 1H), 2.51 (dd, *J* = 14.2, 6.6 Hz, 1H), 2.38 – 2.22 (m, 3H), 1.77 – 1.69 (m, 1H), 1.69 – 1.62 (m, 1H), 1.49 – 1.41 (m, 1H), 0.88 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  145.7, 139.8, 131.7, 128.0, 121.6, 119.8, 115.2, 42.7, 32.0, 30.6, 18.8, 15.0; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2923, 2245, 1483, 1010, 837; HRMS (ESI) calcd C<sub>14</sub>H<sub>16</sub><sup>79</sup>BrNNa [M + Na]<sup>+</sup>: 300.0358, found: 300.0356.



**4-Benzyl-6-(4-chlorophenyl)hept-6-enenitrile** (**7r**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 15:1) to give a colorless oil; 65% yield (40 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 – 7.24 (m, 4H), 7.24 – 7.20 (m, 1H), 7.14 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 7.4 Hz, 2H), 5.31 (s, 1H), 5.11 (s, 1H), 2.59 – 2.50 (m, 3H), 2.40 – 2.33 (m, 1H), 2.30 – 2.19 (m, 2H), 1.83 – 1.77 (m, 1H), 1.72 – 1.64 (m, 1H), 1.63 – 1.55 (m, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  145.6, 139.7, 138.9, 133.6, 129.2, 128.7, 128.6, 127.6, 126.5, 119.7, 115.5, 40.1, 39.7, 37.5, 29.2, 14.9; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2917, 2239, 1495, 1007, 704; HRMS (ESI) calcd C<sub>20</sub>H<sub>21</sub><sup>35</sup>CIN [M + H]<sup>+</sup>: 310.1357, found: 310.1358.



**4-Methyl-6-(naphthalen-2-yl)hept-6-enenitrile** (7s): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 10:1) to give a colorless oil; 77% yield (38 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 – 7.78 (m, 4H), 7.55 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.51 – 7.43 (m, 2H), 5.46 (d, *J* = 1.4 Hz, 1H), 5.17 (d, *J* = 1.2 Hz, 1H), 2.72 – 2.61 (m, 1H), 2.52 – 2.43 (m, 1H), 2.39 – 2.21 (m, 2H), 1.86 – 1.68 (m, 2H), 1.55 – 1.42 (m, 1H), 0.93 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  146.6, 138.2, 133.5, 133.0, 128.2, 128.1, 127.7, 126.3, 126.0, 125.0, 124.7, 120.0, 115.2, 42.8, 32.1, 30.8, 18.9, 15.0; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2921, 2243, 1618, 1131, 814; HRMS (ESI) calcd C<sub>18</sub>H<sub>20</sub>N [M + H]<sup>+</sup>: 250.1590, found: 250.1587.



**Ethyl 6-cyano-2-methylenehexanoate (7t):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 10:1) to give a colorless oil; 40% yield (15 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.18 (s, 1H), 5.55 (d, J = 1.2 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 2.40 – 2.29 (m, 4H), 1.74 – 1.59 (m, 4H), 1.31 (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 167.1, 140.0, 125.3, 119.7, 60.9, 31.2, 27.7, 25.1, 17.1, 14.4; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2935, 2247, 1625, 1021, 817; HRMS (ESI) calcd C<sub>10</sub>H<sub>15</sub>NO<sub>2</sub>Na [M + Na]<sup>+</sup>: 204.0995, found: 204.0991.

*tert*-Butyl 6-cyano-4-methyl-2-methylenehexanoate (7u): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 10:1) to give a colorless oil; 56% yield (25 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  6.11 (d, J = 1.5 Hz, 1H), 5.44 (s, 1H), 2.44 – 2.32 (m, 2H), 2.30 (dd, J = 13.4, 5.8 Hz, 1H), 2.09 (dd, J = 13.6, 7.8 Hz, 1H), 1.84 – 1.76 (m, 1H), 1.75 – 1.67 (m, 1H), 1.48 (s, 9H), 1.48 – 1.44 (m, 1H), 0.90 (d, J = 6.7 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  166.5, 140.3, 125.8, 119.9, 80.9, 39.1, 32.1, 31.6, 28.2, 18.8, 15.1; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2931, 2240, 1709, 938, 848; HRMS (ESI) calcd C<sub>13</sub>H<sub>21</sub>NO<sub>2</sub>Na [M + Na]<sup>+</sup>: 246.1465, found: 246.1470.

**Benzyl 6-cyano-4-methyl-2-methylenehexanoate** (**7v**): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 10:1) to give a colorless oil; 58% yield (30 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 – 7.30 (m, 5H), 6.28 (d, *J* = 1.3 Hz, 1H), 5.57 (d, *J* = 1.0 Hz, 1H), 5.20 (s, 2H), 2.41 – 2.25 (m, 3H), 2.14 (dd, *J* = 13.7, 7.8 Hz, 1H), 1.86 – 1.66 (m, 2H), 1.54 – 1.40 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  166.9, 138.6, 136.0, 128.7, 128.4, 128.3, 127.3, 119.9, 66.7, 39.0, 32.1, 31.6, 18.8, 15.1; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2921, 2240, 1709, 1145, 694; HRMS (ESI) calcd C<sub>16</sub>H<sub>19</sub>NO<sub>2</sub>Na [M + Na]<sup>+</sup>: 280.1308, found: 280.1309.

NC

(*E*)-4-Methyl-6-phenylhex-5-enenitrile (8a): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 10:1) to give a colorless oil; 57% yield (21 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 – 7.35 (m, 2H), 7.35 – 7.30 (m, 2H), 7.25 – 7.21 (m, 1H), 6.45 (d, *J* = 15.8 Hz, 1H), 5.97 (dd, *J* = 15.8, 8.5 Hz, 1H), 2.52 – 2.43 (m, 1H), 2.42 – 2.29 (m, 2H), 1.85 – 1.78 (m, 1H), 1.72 – 1.64 (m, 1H), 1.16 (d, *J* =

6.7 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  137.1, 133.5, 130.6, 128.7, 127.5, 126.2, 119.9, 36.8, 32.3, 20.6, 15.4; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2918, 2237, 1488, 1148, 737; HRMS (ESI) calcd C<sub>13</sub>H<sub>16</sub>N [M + H]<sup>+</sup>: 186.1277, found: 186.1274.

Ph. CN/ Мe

**Methyl-6-phenylhex-5-ynenitrile (8b):** Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 10:1) to give a colorless oil; 45% yield (19 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 – 7.37 (m, 2H), 7.31 – 7.27 (m, 3H), 2.87 – 2.80 (m, 1H), 2.63 – 2.53 (m, 2H), 1.95 – 1.88 (m, 1H), 1.85 – 1.78 (m, 1H), 1.32 (d, *J* = 6.9 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  131.7, 128.4, 128.1, 123.3, 119.6, 91.5, 82.7, 32.6, 26.2, 20.9, 15.6; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2928, 2239, 1495, 1067, 754; HRMS (ESI) calcd C<sub>13</sub>H<sub>13</sub>NNa [M + Na]<sup>+</sup>: 206.0940, found: 206.0939.



**4-Methyl-6-(phenylsulfonyl)hexanenitrile** (8c): Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 100:1 to 10:1) to give a colorless oil; 83% yield (42 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.1 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 2H), 3.19 – 2.98 (m, 2H), 2.41 – 2.23 (m, 2H), 1.82 – 1.72 (m, 1H), 1.71 – 1.53 (m, 3H), 1.52 – 1.39 (m, 1H), 0.90 (d, *J* = 5.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.1, 133.9, 129.5, 128.1, 119.4, 54.1, 31.8, 31.2, 28.7, 18.3, 14.9; FT-IR (thin film, KBr): v (cm<sup>-1</sup>): 2918, 2247, 1449, 1138, 691; HRMS (ESI) calcd C<sub>13H17</sub>NO<sub>2</sub>SNa [M + Na]<sup>+</sup>: 274.0872, found: 274.0873.

## 7. NMR Spectra for the substrates and products

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



<sup>1</sup>H NMR of **1aa** 



<sup>13</sup>C NMR of **1aa** 





<sup>13</sup>C NMR of **1ab** 



<sup>1</sup>H NMR of **1ac** 



<sup>13</sup>C NMR of **1ac** 





<sup>&</sup>lt;sup>13</sup>C NMR of **1b** 





<sup>13</sup>C NMR of **1c** 













<sup>13</sup>C NMR of **1e** 





<sup>13</sup>C NMR of **1f** 





<sup>13</sup>C NMR of **1g** 







<sup>13</sup>C NMR of **1h** 



## <sup>1</sup>H NMR of **1i**



# <sup>13</sup>C NMR of **1i**







 $^{1}$ H NMR of **1**k



<sup>13</sup>C NMR of **1**k



#### $^{1}$ H NMR of **1**l



<sup>13</sup>C NMR of **11** 





<sup>&</sup>lt;sup>13</sup>C NMR of **1m** 









<sup>1</sup>H NMR of **10** 



110 100 f1 (ppm) 130 120 







130 120

110 100 f1 (ppm)

80 70





 $^{1}$ H NMR of 1r



<sup>&</sup>lt;sup>13</sup>C NMR of **1r** 



### <sup>1</sup>H NMR of 1s



### <sup>13</sup>C NMR of **1s**











<sup>1</sup>H NMR of **3b** 











<sup>13</sup>C NMR of **3c** 











<sup>1</sup>H NMR of **3e** 




















<sup>13</sup>C NMR of **3i** 







-- (Phu





 $^{1}$ H NMR of **3**l



### <sup>1</sup>H NMR of 3m









#### <sup>1</sup>H NMR of **3n**



```
<sup>13</sup>C NMR of 3n
```



<sup>1</sup>H NMR of **30** 



<sup>13</sup>C NMR of **30** 





<sup>1</sup>H NMR of **3p** 



<sup>13</sup>C NMR of **3p** 





### <sup>1</sup>H NMR of 3q













<sup>1</sup>H NMR of **3s** 



<sup>13</sup>C NMR of **3s** 



<sup>1</sup>H NMR of 3t



## <sup>1</sup>H NMR of **3u**



<sup>13</sup>C NMR of **3u** 



#### <sup>1</sup>H NMR of 3v









 $^{1}$ H NMR of **4b** 



<sup>1</sup>H NMR of 4c



```
<sup>13</sup>C NMR of 4c
```





 $^{1}$ H NMR of **4d** 





### <sup>1</sup>H NMR of **4e**



<sup>13</sup>C NMR of **4e** 







<sup>13</sup>C NMR of **4f** 



<sup>1</sup>H NMR of 4g







### $^{1}$ H NMR of **5**















00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 fl (ppm)































### <sup>1</sup>H NMR of 7c



# <sup>13</sup>C NMR of **7c**





### $^{1}$ H NMR of **7d**



# <sup>13</sup>C NMR of **7d**














## $^{1}$ H NMR of **7**g







```
<sup>13</sup>C NMR of 7i
```









<sup>13</sup>C NMR of **7k** 





<sup>13</sup>C NMR of **7** 





<sup>13</sup>C NMR of **7m** 

















<sup>1</sup>H NMR of 7r



<sup>13</sup>C NMR of **7r** 



## <sup>1</sup>H NMR of **7s**













<sup>1</sup>H NMR of 8a









S126

<sup>1</sup>H NMR of **8c** 



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