## **Supplementary Information**

## Oximinotrifluoromethylation of Unactivated Alkenes under Ambient Conditions

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#### General information.

All reactions were carried out under argon using Schlenk techniques. Reagents were purchased at the commercial quality and used without further purification. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm), KMnO4 or iodine stain. NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400/500 MHz for <sup>1</sup>H NMR, 100/125 MHz for <sup>13</sup>C NMR and 376 MHz for <sup>19</sup>F NMR in CDCl<sub>3</sub> with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for <sup>1</sup>H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet), coupling constant (Hz), integration. Data for <sup>13</sup>C NMR are reported in terms of chemical shift (δ, ppm). <sup>19</sup>F NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer (CFCl<sub>3</sub> as an external reference (0 ppm)). Mass spectrometric data were obtained using Bruker Apex IV RTMS.

### Scheme S1 and Scheme S2



Scheme S1 Large-scale synthesis.



Scheme S2 Control experiment.

## Experimental procedure for synthesis of substrates Procedure for synthesis of linear substrates



To a solution of *N*,*O*-dimethylhydroxylamine hydrochloride (5.9 g, 60 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (60 mL) were added Et<sub>3</sub>N (16.8 mL, 120 mmol) and benzoyl chloride (7.0 mL, 30 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 1 h and quenched with saturated NaHCO<sub>3</sub> (30 mL). Dichloromethane ( $3 \times 60$  mL) was added to extract the product from the aqueous layer. The combined organic layer was washed with HCl (1M, 30 mL) and brine (30 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to afford the crude product (9.7 g). The crude product was dissolved in THF (15 mL) and added to a solution of prepared Grignard reagent (1M, 90 mL) in THF at 0 °C dropwisely. The reaction mixture was stirred at that temperature for 30 min and quenched with saturated NH<sub>4</sub>Cl (30 mL). Diethyl ether was used to extract the product from the aqueous layer ( $3 \times 60$  mL). The combined organic layer was washed with brine (30 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to afford the crude product S1 (7.9 g, 80%), which was applied to the next step without further purification.

A solution of **S1** (7.9 g, 49 mmol), TMSCN (6.8 mL, 52 mmol) and ZnI<sub>2</sub> (0.80 g, 2.5 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (60 mL) were heated to reflux for 12 h and cooled down to room temperature. The solvent was removed to afford the crude product, which was purified by flash column chromatography to afford the product **S2** as a colorless oil (9.5 g, 76%). The product **S2** was dissolved in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (50 mL). To this solution was added diisobutylaluminium hydride (DIBALH) (1M/hexane, 60 mL, 60 mmol) at –45 °C. The reaction mixture was stirred for 2 h and quenched with H<sub>2</sub>O (2 mL) and potassium

sodium tartrate (1 M, 40 mL) with vigorously stirring. Dichloromethane was used to extract the product from the aqueous layer ( $3 \times 50$  mL). The combined organic layer was washed with brine (30 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to afford the crude product (5.8 g, 78%), which was dissolved in THF (50 mL). To this solution was added HCl (3 M, 10 mL, 50 mmol) at room temperature and the reaction mixture was stirred for 1 h and quenched with H<sub>2</sub>O (10 mL). EtOAc was used to extract the product from the aqueous layer ( $3 \times 40$  mL). The combined organic layer was washed with brine (30 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product **S3** (4.0 g, 75% yield) as a colorless oil.

A solution of S3 (0.95 g, 5.0 mmol) and *O*-benzylhydroxylamine (1.2 g, 10 mmol) in pyridine (5 mL) was heated at 80 °C for 2 h and then cooled down to room temperature. The solvent was evaporated under reduced pressure. EtOAc (30 mL) was added to dissolve the crude product, which was washed with HCl (1 M, 10 mL) and brine (10 mL) sequentially. The organic layer was dried over anhydrous  $Na_2SO_4$ , filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product **1A** (1.2 g, 80% yield, 36% overall yield) as a colorless oil.

The procedure for synthesis of **1B-1O** is similar to that reported for synthesis of **1A**.

#### (E)-2-hydroxy-2-phenylhex-5-enal O-benzyl oxime (1A)



**1A**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 (s, 1H), 7.32 – 7.03 (m, 10H), 5.72 – 5.56 (m, 1H), 5.02 – 4.90 (m, 2H), 4.87 – 4.71 (m, 2H), 3.34 (s, 1H), 2.04 – 1.78 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.4, 143.3, 138.7, 137.9, 128.5, 128.4, 128.2, 128.0, 127.5,

126.2, 114.8, 78.0, 76.3, 36.7, 27.8. HRMS (ESI) m/z calcd. for C<sub>19</sub>H<sub>22</sub>O<sub>2</sub>N [M+H]<sup>+</sup> 296.1645, found 296.1641.

(E)-2-hydroxy-2-(p-tolyl)hex-5-enal O-benzyl oxime (1B)



**1B**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (s, 1H), 7.33 – 7.24 (m, 7H), 7.12 (d, *J* = 8.1 Hz, 2H), 5.83 – 5.61 (m, 1H), 5.11 – 4.99 (m, 2H), 4.98 – 4.82 (m, 2H), 3.39 (s, 1H), 2.29 (s, 3H), 2.15 – 1.83 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.8, 140.3, 138.3, 137.2, 137.0, 129.2, 128.5, 128.4, 128.1, 125.2, 114.8, 76.3, 75.5, 40.0, 27.7, 21.0. HRMS (ESI) m/z calcd. for C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>N [M+H]<sup>+</sup> 310.1802, found 310.1798.

(E)-2-hydroxy-2-(4-methoxyphenyl)hex-5-enal O-benzyl oxime (1C)



**1C**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (s, 1H), 7.38 – 7.29 (m, 7H), 6.91 – 6.83 (m, 2H), 5.87 – 5.69 (m, 1H), 5.13 – 5.04 (m, 2H), 5.02 – 4.88 (m, 2H), 4.57 (s, 1H), 3.79 (s, 3H), 2.12 – 1.94 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.9, 153.8, 138.4, 137.2, 135.3, 128.6, 128.5, 128.2, 126.6, 114.8, 113.9, 76.5, 75.3, 55.4, 40.0, 27.8. HRMS (ESI) m/z calcd. for C<sub>20</sub>H<sub>24</sub>O<sub>3</sub>N [M+H]<sup>+</sup> 326.1751, found 326.1746.

(*E*)-2-(4-fluorophenyl)-2-hydroxyhex-5-enal O-benzyl oxime (1D)



**1D**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (s, 1H), 7.41 – 7.28 (m, 7H), 7.02 (t, *J* = 8.7 Hz, 2H), 5.83 – 5.70 (m, 1H), 5.14 – 5.04 (m, 2H), 5.00 – 4.90 (m, 2H), 3.41 (s, 1H), 2.12 – 1.91 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.1 (d, *J* = 245.8 Hz), 153.4, 139.01 (d, *J* = 3.0 Hz), 138.2, 137.1, 128.6, 128.5, 128.3, 127.13 (d, *J* = 8.1 Hz), 115.5, 115.16 (d, *J* = 22.7 Hz), 76.6, 75.4, 40.2, 27.7. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -115.4. HRMS (ESI) m/z calcd. for C<sub>19</sub>H<sub>21</sub>O<sub>2</sub>NF [M+H]<sup>+</sup> 314.1551, found 314.1548.

(E)-2-(4-chlorophenyl)-2-hydroxyhex-5-enal O-benzyl oxime (1E)



**1E**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (s, 1H), 7.42 – 7.25 (m, 9H), 5.88 – 5.64 (m, 1H), 5.18 – 5.05 (m, 2H), 5.02 – 4.87 (m, 2H), 3.44 (s, 1H), 2.26 – 1.91 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.1, 141.8, 138.1, 137.0, 133.3, 128.7, 128.6, 128.5, 128.2, 126.8, 115.1, 76.6, 75.4, 40.1, 27.6. HRMS (ESI) m/z calcd. for C<sub>19</sub>H<sub>21</sub>O<sub>2</sub>NCl [M+H]<sup>+</sup> 330.1255, found 330.1251.

#### (E)-2-(4-bromophenyl)-2-hydroxyhex-5-enal O-benzyl oxime (1F)



**1F**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 (s, 1H), 7.51 – 7.24 (m, 9H), 5.83 – 5.67 (m, 1H), 5.17 – 5.04 (m, 2H), 5.00 – 4.87 (m, 2H), 3.43 (s, 1H), 2.15 – 1.91 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.1, 142.3, 138.0, 137.0, 131.6, 128.5(4), 128.5(2), 128.2, 127.2, 121.5, 115.0, 76.5, 75.4, 40.0, 27.6. HRMS (ESI) m/z calcd. for C<sub>19</sub>H<sub>21</sub>O<sub>2</sub>NBr [M+H]<sup>+</sup> 374.0750, found 374.0746.

#### (E)-2-(3-chlorophenyl)-2-hydroxyhex-5-enal O-benzyl oxime (1G)



**1G**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64 (s, 1H), 7.48 – 7.43 (m, 1H), 7.37 – 7.29 (m, 5H), 7.29 – 7.19 (m, 3H), 5.86 – 5.64 (m, 1H), 5.14 – 5.04 (m, 2H), 5.01 – 4.89 (m, 2H), 3.45 (s, 1H), 2.18 – 1.87 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.9, 145.5, 138.0, 137.0, 134.7, 129.9, 128.6, 128.5, 128.3, 127.7, 125.7, 123.5, 115.1, 76.7, 75.4, 40.1, 27.6. HRMS (ESI) m/z calcd. for C<sub>19</sub>H<sub>21</sub>O<sub>2</sub>NCl [M+H]<sup>+</sup> 330.1255, found 330.1251.

#### (E)-2-(2-chlorophenyl)-2-hydroxyhex-5-enal O-benzyl oxime (1H)



**1H**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.34 – 8.22 (m, 1H), 7.90 – 7.83 (m, 1H), 7.43 – 7.25 (m, 7H), 7.25 – 7.18 (m, 1H), 5.86 – 5.70 (m, 1H), 5.14 – 5.02 (m, 2H), 5.01 – 4.86 (m, 2H), 3.74 (s, 1H), 2.44 – 2.30 (m, 1H), 2.26 – 2.01 (m, 2H), 2.01 – 1.83 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  152.9, 140.8, 138.3, 137.3, 131.2, 130.9, 129.2, 128.6, 128.6, 128.3, 127.3, 115.0, 76.6, 75.8, 37.7, 28.0. HRMS (ESI) m/z calcd. for C<sub>19</sub>H<sub>21</sub>O<sub>2</sub>NCl [M+H]<sup>+</sup> 330.1255, found 330.1253.

(E)-2-hydroxy-2-(naphthalen-1-yl)hex-5-enal O-benzyl oxime (1I)



**II**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.42 – 8.26 (m, 1H), 7.94 – 7.89 (m, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.70 – 7.63 (m, 1H), 7.50 – 7.27 (m, 8H), 5.86 – 5.66 (m, 1H), 5.18 – 5.06 (m, 2H), 5.00 – 4.78 (m, 2H), 3.26 (brs, 1H), 2.58 – 2.45 (m, 1H), 2.40 – 2.22 (m, 1H), 2.20 – 1.94 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  154.3, 138.4, 138.2, 137.5, 134.8, 130.5, 129.3(3), 129.3(0), 128.6, 128.5, 128.1, 125.9, 125.8, 125.4, 125.0, 124.0, 114.9, 76.6, 76.5, 38.8, 28.1. HRMS (ESI) m/z calcd. for C<sub>23</sub>H<sub>24</sub>O<sub>2</sub>N [M+H]<sup>+</sup> 346.1801, found 346.1796.

(E)-2-(furan-2-yl)-2-hydroxyhex-5-enal O-benzyl oxime (1J)



**1J**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63 (s, 1H), 7.41 – 7.23 (m, 6H), 6.41 – 6.15 (m, 2H), 5.90 – 5.69 (m, 1H), 5.11 (s, 2H), 5.03 – 4.88 (m, 2H), 3.53 (s, 1H), 2.26 – 1.89 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.4, 151.0, 142.5, 138.0, 137.0, 128.5, 128.5, 128.2, 115.0, 110.4, 106.4, 76.6, 72.8, 37.5, 27.5. HRMS (ESI) m/z calcd. for C<sub>17</sub>H<sub>20</sub>O<sub>3</sub>N [M+H]<sup>+</sup> 286.1438, found 286.1437.

#### (E)-2-hydroxy-2-(thiophen-2-yl)hex-5-enal O-benzyl oxime (1K)



**1K**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.67 (s, 1H), 7.46 – 7.31 (m, 5H), 7.28 (dd, J = 5.1, 1.2 Hz, 1H), 7.01 (dd, J = 5.0, 3.6 Hz, 1H), 6.94 (dd, J = 3.6, 1.1 Hz, 1H), 5.91 – 5.74 (m, 1H), 5.21 – 5.10 (m, 2H), 5.08 – 4.94 (m, 2H), 3.80 (s, 1H), 2.27 – 1.99 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  152.4, 148.6, 138.0, 137.0, 128.6, 128.5, 128.2, 127.2, 125.0, 123.3, 115.1, 76.7, 74.7, 40.8, 27.8. HRMS (ESI) m/z calcd. for C<sub>17</sub>H<sub>19</sub>O<sub>2</sub>NNaS [M+Na]<sup>+</sup> 324.1029, found 324.1024.

(E)-2-hydroxy-2-phenethylhex-5-enal O-benzyl oxime (1L)



**1L**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 (s, 1H), 7.39 – 7.28 (m, 5H), 7.26 (d, *J* = 7.3 Hz, 2H), 7.21 – 7.17 (m, 1H), 7.16 – 7.11 (m, 2H), 5.85 – 5.72 (m, 1H), 5.12 (s, 2H), 5.02 – 4.90 (m, 2H), 3.02 (s, 1H), 2.77 – 2.66 (m, 1H), 2.56 – 2.44 (m, 1H), 2.23 – 2.11 (m, 1H), 2.05 – 1.90 (m, 2H), 1.88 – 1.72 (m, 2H), 1.72 – 1.61 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.7, 142.1, 138.4, 137.3, 128.6(3), 128.6(0), 128.5, 128.2, 126.0, 115.0, 75.7, 74.3, 41.7, 39.1, 29.8, 27.8. HRMS (ESI) m/z calcd. for C<sub>21</sub>H<sub>26</sub>O<sub>2</sub>N [M+H]<sup>+</sup> 324.1958, found 324.1951.

(E)-3-hydroxy-3-phenylhept-6-en-2-one O-benzyl oxime (1M)



**1M**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (s, 1H), 7.33 – 7.24 (m, 7H), 7.12 (d, *J* = 8.1 Hz, 2H), 5.83 – 5.61 (m, 1H), 5.11 – 4.99 (m, 2H), 4.98 – 4.82 (m, 2H), 3.39 (s, 1H), 2.29 (s, 3H), 2.15 – 1.83 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.4, 143.3, 138.7, 137.9, 128.5, 128.4, 128.2, 128.0, 127.5, 126.2, 114.8, 78.0, 76.3, 36.7, 27.9, 11.7. HRMS (ESI) m/z calcd. for C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>N [M+H]<sup>+</sup> 310.1802, found 310.1799.

(E)-3-hydroxy-3-methylhept-6-en-2-one O-benzyl oxime (1N)



**1N**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 – 7.24 (m, 5H), 5.83 – 5.69 (m, 1H), 5.10 (s, 2H), 5.00 – 4.86 (m, 2H), 3.82 (s, 1H), 2.15 – 2.03 (m, 1H), 1.83 (s, 3H), 1.81 – 1.57 (m, 3H), 1.31 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.2, 138.5, 137.8, 128.4, 128.1, 127.9, 114.5, 76.1, 74.4, 39.1, 27.9, 27.0, 11.0. HRMS (ESI) m/z calcd. for C<sub>15</sub>H<sub>22</sub>O<sub>2</sub>N [M+H]<sup>+</sup> 248.1645, found 248.1643.

(E)-2-hydroxy-2-phenylhex-5-enal O-(4-methoxybenzyl) oxime (1O)



**10**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 (s, 1H), 7.43 – 7.36 (m, 2H), 7.33 – 7.27 (m, 2H), 7.27 – 7.19 (m, 3H), 6.87 – 6.80 (m, 2H), 5.82 – 5.67 (m, 1H), 5.03 – 4.97 (m, 2H), 4.97 – 4.83 (m, 2H), 3.71 (s, 3H), 3.51 (s, 1H), 2.11 – 1.93 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.5, 153.4, 143.2, 130.2, 129.1, 128.4, 127.3, 125.2, 114.7, 113.8, 76.1, 75.5, 55.2, 40.0, 27.6. HRMS (ESI) m/z calcd. for C<sub>20</sub>H<sub>24</sub>O<sub>3</sub>N [M+H]<sup>+</sup> 326.1750, found 326.1750.

#### (E)-2-hydroxy-2-phenylhept-6-enal O-benzyl oxime (1P)



**1P**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65 (s, 1H), 7.41 – 7.36 (m, 2H), 7.33 – 7.15 (m, 8H), 5.80 – 5.61 (m, 1H), 5.12 – 5.01 (m, 2H), 4.99 – 4.85 (m, 2H), 3.40 (s, 1H), 2.05 – 1.82 (m, 4H), 1.37 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.7, 143.4, 138.4, 137.1, 128.4, 128.4, 128.3, 128.0, 127.2, 125.2, 114.8, 76.3, 75.6, 40.3, 33.7, 22.4. HRMS (ESI) m/z calcd. for C<sub>20</sub>H<sub>24</sub>O<sub>3</sub>N [M+H]<sup>+</sup> 310.1801, found 310.1798.

#### Procedure for synthesis of benzyl-protected cyclic oximes 9A and 9D



To a solution of **S4** (2.7 g, 15 mmol) in anhydrous THF (20 mL) was added *n*-BuLi (2.2 M/hexane, 7.0 mL, 15 mmol) at -78 °C. The reaction solution was stirred for 1 h, followed by addition of **S5** (0.75 g, 7.5 mmol). The reaction solution was warmed up to room temperature and stirred for 12 h and quenched with water (20 mL). EtOAc was used to extract the product from the aqueous layer (3 × 40 mL). The combined organic layer was washed with brine (20 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product **S6** (0.38 g, 25%) as a colorless oil.

A solution of **S6** (0.38 g, 1.9 mmol) and *O*-benzylhydroxylamine (0.46 g, 3.8 mmol) in pyridine (3 mL) was heated at 80 °C for 2 h and then cooled down to room temperature. The solvent was evaporated under reduced pressure. EtOAc (20 mL) was added to dissolve the crude product, which was washed with HCl (1 M, 10 mL) and brine (10 mL) sequentially. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product **9A** (0.29 g, 50% yield) as a colorless oil.

The procedure for synthesis of **9D** is similar to that of **9A**.

#### Procedure for synthesis of benzyl-protected cyclic oximes 9B and 9C



To a solution of S4 (1.9 g, 10 mmol) in anhydrous THF (20 mL) was added *n*-BuLi (2.2 M/hexane, 4.5 mL, 10 mmol) at -78 °C. The reaction solution was stirred for 1 h, followed by addition of S7 (1.8 g, 10 mmol). The reaction solution was warmed up to

room temperature and stirred for 2 h and quenched with water (20 mL). EtOAc was used to extract the product from the aqueous layer ( $3 \times 20$  mL). The combined organic layer was washed with brine (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to afford the crude product, which was dissolved in MeOH (10 mL). 3M HCl (4 mL) was added to the reaction mixture. The mixture was stirred for 10 min and diluted with water (15 mL). Dichloromethane was used to extract the product from the aqueous layer ( $3 \times 30$ mL). The combined organic layer was washed with brine (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product **S8** (0.95 g, 44%) as a colorless oil.

A solution of **S8** (0.95 g, 4.4 mmol) and *O*-benzylhydroxylamine (1.2 g, 10 mmol) in pyridine (5 mL) was heated at 80 °C for 2 h and then cooled down to room temperature. The solvent was evaporated under reduced pressure. EtOAc (30 mL) was added to dissolve the crude product, which was washed with HCl (1 M, 10 mL) and brine (10 mL) sequentially. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product **9B** (0.65 g, 45% yield) as a colorless oil.

The procedure for synthesis of **9C** is similar to that of **9B**.

(E)-2-hydroxy-2-(2-vinylphenyl)cyclopentan-1-one O-benzyl oxime (9A)



**9A:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 – 7.46 (m, 1H), 7.34 – 7.10 (m, 9H), 5.52 (d, J = 17.4 Hz, 1H), 5.22 (d, J = 11.0 Hz, 1H), 5.09 (s, 2H), 2.91 – 2.72 (m, 2H), 2.58 – 2.44 (m, 1H), 2.38 – 2.27 (m, 1H), 2.08 – 1.97 (m, 1H), 1.93 – 1.80 (m, 1H), 1.64 – 1.49 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.0, 140.8, 138.1, 137.1(4), 137.1(2), 128.4, 128.3, 127.9, 127.9, 127.7, 127.2, 126.8, 115.4, 82.4, 76.3, 41.1, 27.5, 20.6. HRMS (ESI) m/z calcd. for C<sub>20</sub>H<sub>22</sub>O<sub>2</sub>N [M+H]<sup>+</sup> 308.1645, found 308.1640.

(E)-2-hydroxy-2-(2-vinylphenyl)cyclohexan-1-one O-benzyl oxime (9B)



**9B:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 – 7.34 (m, 2H), 7.32 – 7.07 (m, 8H), 5.35 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.02 (s, 2H), 4.97 (dd, *J* = 10.9, 1.5 Hz, 1H), 3.93 (s, 1H), 3.01 – 2.87 (m, 1H), 2.78 – 2.65 (m, 1H), 2.07 (ddd, *J* = 14.5, 9.5, 5.1 Hz, 1H), 1.78 – 1.55 (m, 3H), 1.54 – 1.34 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.9, 139.4, 138.4, 137.9, 137.7, 128.4, 128.3, 128.2, 127.7, 127.2, 126.7, 114.9, 76.5, 75.9, 41.1, 25.5, 24.2, 22.2. HRMS (ESI) m/z calcd. for C<sub>21</sub>H<sub>24</sub>O<sub>2</sub>N [M+H]<sup>+</sup> 322.1802, found 322.1799.

#### (E)-2-hydroxy-2-(2-vinylphenyl)cycloheptan-1-one O-benzyl oxime (9C)



**9C:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 – 7.73 (m, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.50 – 7.36 (m, 5H), 7.36 – 7.27 (m, 1H), 7.22 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 7.7 Hz, 1H), 5.58 (dd, J = 17.5, 1.3 Hz, 1H), 5.29 (dd, J = 11.0, 1.4 Hz, 1H), 5.26 (s, 2H), 4.56 (s, 1H), 3.34 – 3.27 (m, 1H), 2.77 – 2.65 (m, 1H), 2.05 – 1.94 (m, 2H), 1.91 – 1.63 (m, 4H), 1.57 (dd, J = 23.7, 11.6 Hz, 1H), 1.45 – 1.30 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.3, 142.3, 138.7, 138.2, 137.8, 128.9, 128.4, 128.2, 127.9, 127.6, 127.0, 126.1, 114.9, 80.3, 76.3, 40.7, 30.2, 28.2, 26.1, 23.4. HRMS (ESI) m/z calcd. for C<sub>22</sub>H<sub>26</sub>O<sub>2</sub>N [M+H]<sup>+</sup> 336.1958, found 336.1953.

#### (E)-2-(2-allylphenyl)-2-hydroxycyclopentan-1-one O-benzyl oxime (9D)



**9D:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 – 7.15 (m, 8H), 7.12 – 7.05 (m, 1H), 6.03 – 5.86 (m, 1H), 5.09 (s, 2H), 5.06 – 4.93 (m, 2H), 3.51 – 3.45 (m, 2H), 2.88 – 2.75 (m, 1H), 2.63 – 2.47 (m, 1H), 2.27 – 2.16 (m, 1H), 2.11 – 1.99 (m, 1H), 1.98 – 1.84 (m, 1H), 1.68 – 1.50 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.3, 141.8, 138.5, 138.1, 138.1, 131.6, 128.5, 128.3, 127.9, 127.7, 127.0, 125.6, 115.8, 82.6, 76.3, 41.4, 37.9, 27.5, 20.6. HRMS (ESI) m/z calcd. for C<sub>21</sub>H<sub>24</sub>O<sub>2</sub>N [M+H]<sup>+</sup> 322.1802, found 322.1800.



In an oven-dried 10 mL Schlenk tube were added **1** (0.20 mmol), CuI (4 mg, 0.02 mmol) and Togni's reagent **2** (75 mg, 0.24 mmol). The tube was vacuumed and back-filled with argon three times and then added with 1,4-dioxane (2 mL). The reaction mixture was stirred at 25 °C for 24 h. The solvent was removed under reduced pressure to afford the crude product, which was purified by flash column chromatography to afford the product **3**.

(E)-5-oxo-5-phenyl-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (3A)



**3A**: (81% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.86 (d, J = 7.7 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.35 – 7.22 (m, 6H), 5.06 – 5.01 (m, 2H), 3.00 – 2.85 (m, 2H), 2.79 – 2.68 (m, 1H), 2.46 – 2.19 (m, 2H), 2.08 – 1.97 (m, 1H), 1.97 – 1.83 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  198.4, 151.3, 137.7, 136.7, 133.3, 128.7, 128.4, 128.2, 128.1, 127.9, 126.3 (q, J = 277.3 Hz), 75.8, 37.0 (q, J = 28.1 Hz), 35.3, 34.0 (q, J = 2.4 Hz), 26.5. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.5. HRMS (ESI) m/z calcd. For C<sub>20</sub>H<sub>21</sub>O<sub>2</sub>NF<sub>3</sub> [M+H]<sup>+</sup> 364.1519, found 364.1516.

(E)-5-oxo-5-(p-tolyl)-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (3B)



**3B**: (60% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 (d, J = 8.2 Hz, 2H), 7.36 – 7.21 (m, 7H), 5.06 – 5.04 (m, 2H), 3.01 – 2.82 (m, 2H), 2.79 – 2.68 (m, 1H), 2.41 (s, 3H), 2.40 – 2.20 (m, 2H), 2.07 – 1.97 (m, 1H), 1.95 – 1.84 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  198.7, 151.4, 144.1, 137.6, 134.3, 129.4, 128.5, 128.2(4), 128.2(3), 127.9, 126.3 (q, J = 277.3 Hz), 75.9, 37.1 (q, J = 28.1 Hz), 35.2, 34.1 (q, J = 2.4 Hz), 29.8, 26.6, 21.8. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.6. HRMS (ESI) m/z calcd. for C<sub>21</sub>H<sub>23</sub>O<sub>2</sub>NF<sub>3</sub> [M+H]+ 378.1675, found 378.1672.

(E)-5-(4-methoxyphenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (3C)



**3C**: (63% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (d, *J* = 8.9 Hz, 2H), 7.37 – 7.19 (m, 6H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.06 – 5.00 (m, 2H), 3.87 (s, 3H), 2.94 – 2.79 (m, 2H), 2.79 – 2.66 (m, 1H), 2.45 – 2.16 (m, 2H), 2.06 – 1.96 (m, 1H), 1.93 – 1.80 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  197.5, 163.6, 151.4, 137.7, 126.3 (q, *J* = 275.4 Hz), 130.4, 129.9, 128.5, 128.2, 127.9, 113.8, 75.9, 55.6, 37.1 (q, *J* = 28.1 Hz), 34.9 (q, *J* = 2.4 Hz), 26.8. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.5. HRMS (ESI) m/z calcd. for C<sub>21</sub>H<sub>23</sub>O<sub>3</sub>NF<sub>3</sub> [M+H]<sup>+</sup> 394.1624, found 394.1620.

(E)-5-(4-fluorophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (3D)



**3D**: (70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 – 7.86 (m, 2H), 7.41 – 7.29 (m, 6H), 7.14 (t, J = 8.6 Hz, 2H), 5.10 – 5.01 (m, 2H), 2.96 – 2.88 (m, 2H), 2.81 – 2.70 (m, 1H), 2.49 – 2.23 (m, 2H), 2.12 – 2.01 (m, 1H), 1.98 – 1.86 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  197.4, 165.9 (d, J = 254.8 Hz), 151.3, 137.7, 133.2 (d, J = 3.0 Hz), 130.8 (d, J =9.2 Hz), 128.5, 128.2, 128.0, 126.3 (q, J = 277.4 Hz), 115.8 (d, J = 21.9 Hz), 75.9, 37.2 (q, J = 28.0 Hz), 35.3, 34.1 (q, J = 2.6 Hz), 26.5. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.6, -105.1. HRMS (ESI) m/z calcd. For C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>NF4 [M+H]<sup>+</sup> 382.1424, found 382.1423.

(E)-5-(4-chlorophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (3E)



**3E**: (71% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 – 7.73 (m, 2H), 7.43 – 7.39 (m, 2H), 7.34 – 7.24 (m, 6H), 5.08 – 4.99 (m, 2H), 2.91 – 2.84 (m, 2H), 2.79 – 2.68 (m, 1H), 2.44 – 2.20 (m, 2H), 2.07 – 1.96 (m, 1H), 1.93 – 1.81 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  197.7, 151.2, 139.7, 137.7, 135.1, 129.5, 129.0, 128.5, 128.2, 127.9, 126.3 (q, *J* = 274.6 Hz), 75.9, 37.1 (q, *J* = 28.3 Hz), 35.3, 34.0 (q, *J* = 2.5 Hz), 26.4. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.5. HRMS (ESI) m/z calcd. For C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>NClF<sub>3</sub> [M+H]<sup>+</sup> 398.1129, found 398.1129.

(E)-5-(4-bromophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (3F)



**3F**: (70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 – 7.82 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.36 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.33 – 7.24 (m, 5H), 5.07 – 4.99 (m, 2H), 2.98 – 2.91 (m, 2H), 2.91 – 2.82 (m, 1H), 2.48 – 2.14 (m, 2H), 2.11 – 2.00 (m, 1H), 2.00 – 1.88 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  198.0, 151.2, 137.7, 135.5, 132.0, 129.6, 128.5, 128.5, 128.3, 128.0, 126.3 (q, *J* = 275.6 Hz), 75.9, 37.2 (q, *J* = 28.2 Hz), 35.3, 34.1 (q, *J* = 2.3 Hz), 26.4. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.6. HRMS (ESI) m/z calcd. For C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>NBrF<sub>3</sub> [M+H]<sup>+</sup> 442.0624, found 442.0626.

(E)-5-(3-chlorophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (3G)



**3G**: (84% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 (s, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.36 – 7.21 (m, 6H), 5.10 – 4.98 (m, 2H), 2.96 – 2.81 (m, 2H), 2.79 – 2.66 (m, 1H), 2.46 – 2.18 (m, 2H), 2.09 – 1.97 (m, 1H), 1.96 – 1.83 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  197.7, 151.2, 138.3, 137.6, 135.1, 133.2, 130.1, 128.5, 128.3, 128.2, 128.0, 126.3 (q, J = 277.3 Hz), 126.2, 75.9, 37.2 (q, J = 28.3 Hz), 35.4, 34.0 (q, J = 2.5 Hz), 26.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.6. HRMS (ESI) m/z calcd. For C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>NClF<sub>3</sub> [M+H]<sup>+</sup> 398.1129, found 398.1130.

(E)-5-(2-chlorophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (3H)



**3H**: (71% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 – 7.35 (m, 3H), 7.35 – 7.19 (m, 7H), 5.09 – 4.99 (m, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.79 – 2.67 (m, 1H), 2.45 – 2.17 (m, 2H), 2.08 – 1.97 (m, 1H), 1.94 – 1.78 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  202.1, 151.1, 139.2, 137.5, 131.9, 131.0, 130.7, 129.0, 128.5, 128.3, 128.0, 127.1, 126.3 (q, *J* = 277.1 Hz), 76.0, 39.7, 37.0 (q, *J* = 28.3 Hz), 33.9 (q, *J* = 2.4 Hz), 26.6. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.5. HRMS (ESI) m/z calcd. For C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>NClF<sub>3</sub> [M+H]+ 398.1129, found 398.1127.

(E)-5-(naphthalen-1-yl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (3I)



**3I**: (71% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.55 (d, J = 8.5 Hz, 1H), 7.98 (d, J = 8.2 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.72 (dd, J = 7.2, 0.9 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.46 (dd, J = 8.0, 7.4 Hz, 1H), 7.35 (d, J = 6.9 Hz, 1H), 7.30 – 7.17 (m, 5H), 5.06 – 4.97 (m, 2H), 3.01 (t, J = 7.3 Hz, 2H), 2.84 – 2.71 (m, 1H), 2.47 – 2.22 (m, 2H), 2.16 – 2.04 (m, 1H), 2.01 – 1.84 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  203.1, 151.3, 137.6, 135.7, 134.0, 132.9, 130.1, 128.5(4), 128.5(1), 128.2, 128.1, 127.9, 127.7, 126.6, 126.3 (q, J = 277.3 Hz), 125.8, 124.5, 75.9, 38.7, 37.1 (q, J = 28.1 Hz), 34.1 (q, J = 2.4 Hz), 26.9. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.5. HRMS (ESI) m/z calcd. for C<sub>24</sub>H<sub>23</sub>O<sub>2</sub>NF<sub>3</sub> [M+H]<sup>+</sup> 414.1675, found 414.1673.

(E)-5-(furan-2-yl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (3J)



**3J**: (70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.56 (d, J = 1.0 Hz, 1H), 7.36 – 7.23 (m, 6H), 7.09 (d, J = 3.5 Hz, 1H), 6.52 (dd, J = 3.6, 1.7 Hz, 1H), 5.08 – 4.99 (m, 2H), 2.80 (t, J = 7.5 Hz, 2H), 2.78 – 2.66 (m, 1H), 2.45 – 2.17 (m, 2H), 2.05 – 1.95 (m, 1H), 1.88 (ddd, J = 16.6, 10.7, 4.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  188.2, 152.5, 151.2, 146.5, 137.6, 128.5, 128.3, 128.0, 126.3 (q, J = 279.9 Hz), 117.3, 112.38, 76.0, 36.9 (q, J = 28.3 Hz), 35.1, 34.0 (d, J = 2.3 Hz), 26.4. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.6. HRMS (ESI) m/z calcd. for C<sub>18</sub>H<sub>19</sub>O<sub>3</sub>NF<sub>3</sub> [M+H]<sup>+</sup> 354.1311, found 354.1309.

(E)-5-oxo-5-(thiophen-2-yl)-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (3K)



**3K**: (69% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (dd, J = 4.9, 0.9 Hz, 1H), 7.56 (dd, J = 3.8, 0.9 Hz, 1H), 7.35 – 7.22 (m, 6H), 7.10 (dd, J = 4.9, 3.9 Hz, 1H), 5.09 – 4.98 (m, 2H), 2.94 – 2.81 (m, 2H), 2.78 – 2.68 (m, 1H), 2.43 – 2.19 (m, 2H), 2.10 – 1.98 (m, 1H), 1.96 – 1.83 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  191.9, 151.2, 144.0, 137.7, 133.8, 132.1, 128.5, 128.3, 128.2, 128.0, 126.3 (q, J = 277.2 Hz), 75.9, 37.0 (q, J = 28.2 Hz), 36.0, 34.1 (q, J = 2.5 Hz), 26.7. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.5. HRMS (ESI) m/z calcd. for C<sub>18</sub>H<sub>19</sub>O<sub>2</sub>NF<sub>3</sub>S [M+H]<sup>+</sup> 370.1083, found 370.1080.

(E)-5-oxo-7-phenyl-2-(2,2,2-trifluoroethyl)heptanal O-benzyl oxime (3L)



**3L**: (40% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 – 7.24 (m, 7H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 7.3 Hz, 2H), 6.46 (d, *J* = 7.9 Hz, 1H), 5.08 (s, 2H), 3.48 – 3.33 (m, 1H), 2.83 (t, *J* = 7.6 Hz, 2H), 2.63 – 2.57 (m, 2H), 2.42 – 2.28 (m, 2H), 2.27 – 2.13 (m, 2H), 1.93 – 1.73 (m, 1H), 1.60 – 1.52 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  208.7, 152.1, 141.0, 137.7, 128.6(4), 128.6(3), 128.4, 128.2, 128.1, 126.3, 126.2 (q, *J* = 277.5 Hz), 76.3, 44.4, 40.0, 37.1 (q, *J* = 28.2 Hz), 29.8, 29.7 (q, *J* = 2.9 Hz), 26.0. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.6. HRMS (ESI) m/z calcd. for C<sub>22</sub>H<sub>25</sub>O<sub>2</sub>NF<sub>3</sub>[M+H]<sup>+</sup> 392.1832, found 392.1828.





**3M**: (79% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 – 7.77 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.20 (m, 5H), 5.08 – 4.90 (m, 2H), 2.87 – 2.77 (m, 2H), 2.76 – 2.67 (m, 1H), 2.48 – 2.35 (m, 1H), 2.30 – 2.17 (m, 1H), 2.02 – 1.88 (m, 2H), 1.84 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  199.1, 157.2, 138.4, 136.8, 133.2, 128.7, 128.4, 128.1, 127.9, 127.7, 126.4 (q, *J* = 277.1 Hz), 75.6, 38.9 (q, *J* = 2.3 Hz), 36.4 (q, *J* = 28.1 Hz), 35.3, 26.2, 11.9. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -64.2. HRMS (ESI) m/z calcd. For C<sub>21</sub>H<sub>23</sub>O<sub>2</sub>NF<sub>3</sub> [M+H]<sup>+</sup> 378.1675, found 378.1674.

(E)-5-(1-((benzyloxy)imino)ethyl)-7,7,7-trifluoroheptan-2-one (3N)



**3N**: (25% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 – 7.23 (m, 5H), 5.11 – 4.98 (m, 2H), 3.63 – 3.45 (m, 1H), 2.42 – 2.30 (m, 2H), 2.30 – 2.23 (m, 1H), 2.22 – 2.09 (m, 1H), 2.01 (s, 3H), 1.85 – 1.73 (m, 4H), 1.74 – 1.65 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  207.5, 157.2, 137.9, 128.4, 128.2, 127.9, 126.3 (q, *J* = 277.1 Hz), 75.8, 40.5, 36.1 (q, *J* = 28.3 Hz), 31.7 (q, *J* = 2.4 Hz), 29.9, 25.3, 16.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -64.7. HRMS (ESI) m/z calcd. For C<sub>19</sub>H<sub>20</sub>ONF<sub>2</sub> [M+H]<sup>+</sup> 316.1507, found 316.1517.

#### (E)-5-oxo-5-phenyl-2-(2,2,2-trifluoroethyl)pentanal O-(4-methoxybenzyl) oxime (3O)



**3O**: (80% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 (dd, J = 8.0, 1.5 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 7.3 Hz, 1H), 7.29 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.00 (s, 2H), 3.77 (s, 3H), 2.97 (td, J = 7.5, 7.0, 2.9 Hz, 2H), 2.83 – 2.73 (m, 1H), 2.49 – 2.24 (m, 2H), 2.06 (ddt, J = 14.7, 7.7, 4.5 Hz, 1H), 2.01 – 1.85 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  198.9, 159.4, 151.0, 136.7, 133.2, 129.9, 129.6, 128.6, 128.0, 126.3(q, J = 277.4 Hz), 113.8, 75.5, 55.2, 37.0 (q, J = 28.1 Hz), 35.2, 34.0 (q, J = 2.4 Hz), 26.5. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.5. HRMS (ESI) m/z calcd. For C<sub>21</sub>H<sub>23</sub>O<sub>3</sub>NF<sub>3</sub> [M+H]<sup>+</sup> 394.1625, found 394.1623.

(E)-6-oxo-6-phenyl-2-(2,2,2-trifluoroethyl)hexanal O-benzyl oxime (3P)



**3P**: (69% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 – 7.84 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.29 (m, 5H), 7.29 – 7.24 (m, 1H), 5.06 (s, 2H), 3.05 – 2.86 (m, 2H), 2.76 – 2.65 (m, 1H), 2.43 – 2.1 (m, 2H), 1.84 – 1.68 (m, 2H), 1.67 – 1.53 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  199.6, 151.6, 137.6, 136.9, 133.2, 128.8, 128.5, 128.3, 128.1, 128.0, 127.6 (q, *J* = 278.9 Hz), 76.0, 37.9, 36.5 (q, *J* = 28.1 Hz), 34.3, 32.2 (q, *J* = 2.7 Hz), 21.0. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.5. HRMS (ESI) m/z calcd. For C<sub>21</sub>H<sub>23</sub>O<sub>2</sub>NF<sub>3</sub> [M+H]<sup>+</sup> 378.1675, found 378.1673.

#### General Procedure for synthesis of fluoroalkylated oximes.



In an oven-dried 10 mL tube were added **1A** (44 mg, 0.2 mmol), sulfonyl chloride (**4**, 0.3 mmol), Na<sub>2</sub>HPO<sub>4</sub> (144 mg, 0.4 mmol) and  $[Ir(dtbbpy)(ppy)_2]PF_6$  (1.6 mg, 0.002 mmol) sequentially. The tube was vacuumed and back-filled with argon three times and then added with 1,4-dioxane (2 mL). The reaction mixture was irradiated with blue LED for 5 h at 25 °C. EtOAc (30 mL) was added and the organic layer was washed with water (5 mL) and brine (5 mL) sequentially, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product **3A** (82% yield), **5**, and **6**.

The procedure for synthesis of 8 is similar to that reported for synthesis of 3A.

(E)-2-(2,2-difluoroethyl)-5-oxo-5-phenylpentanal O-benzyl oxime (5)



5: (72% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (d, J = 7.4 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.37 – 7.23 (m, 6H), 5.84 (tdd, J = 56.5, 5.5, 4.0 Hz, 1H), 5.08 – 4.99 (m, 2H), 2.94 (t, J = 7.4 Hz, 2H), 2.67 – 2.56 (m, 1H), 2.17 – 1.83 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  199.5, 152.1, 137.7, 136.8, 133.3, 128.7, 128.5, 128.3, 128.1, 128.0, 116.1 (t, J = 239.2 Hz), 75.9, 37.2 (t, J = 21.4 Hz), 35.5, 34.4 (q, J = 4.5 Hz), 26.8. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -115.2 (q, J = 284.5 Hz). HRMS (ESI) m/z calcd. For C<sub>20</sub>H<sub>22</sub>O<sub>2</sub>NF<sub>2</sub> [M+H]<sup>+</sup> 346.1613, found 346.1610.



**6**: (58% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 – 7.82 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.36 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.33 – 7.24 (m, 5H), 5.07 – 4.99 (m, 2H), 2.98 – 2.91 (m, 2H), 2.91 – 2.82 (m, 1H), 2.48 – 2.14 (m, 2H), 2.11 – 2.00 (m, 1H), 2.00 – 1.88 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  199.0, 151.5, 137.7, 136.8, 133.3, 128.7, 128.5, 128.3, 128.1, 128.0, 120.1 – 104.0 (m), 75.9, 35.4, 33.8 (t, *J* = 21.2 Hz), 32.9, 27.2. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -81.0 – -81.1 (m), -111.4 – -113.8 (m), -122.5 – -131.0 (m). HRMS (ESI) m/z calcd. For C<sub>23</sub>H<sub>21</sub>O<sub>2</sub>NF<sub>9</sub> [M+H]<sup>+</sup> 514.1423, found 514.1422.

methyl (E)-4-(((benzyloxy)imino)methyl)-2,2-difluoro-7-oxo-7-phenylheptanoate (8)



8: (71% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 – 7.83 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.22 (m, 6H), 5.02 (s, 2H), 3.84 (s, 3H), 3.04 – 2.86 (m, 2H), 2.78 – 2.65 (m, 1H), 2.49 – 2.35 (m, 1H), 2.34 – 2.17 (m, 1H), 2.05 – 1.85 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  199.1, 164.4 (t, *J* = 32.7 Hz), 151.9, 137.7, 136.8, 133.2, 128.7, 128.5, 128.3, 128.1, 127.9, 119.7 – 112.1 (m), 75.8, 53.6, 37.7 (t, *J* = 22.9 Hz), 35.4, 33.8 (t, *J* = 3.4 Hz), 27.1. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -103.4 (dd, *J* = 631.2, 264.3 Hz). HRMS (ESI) m/z calcd. For C<sub>22</sub>H<sub>24</sub>O<sub>4</sub>NF<sub>2</sub> [M+H]<sup>+</sup> 404.1667, found 404.1664.

General procedure for ring expansion strategy for synthesis of medium-sized rings.



In an oven-dried 10 mL Schlenk tube were added **9** (0.20 mmol), CuCN (1.6 mg, 0.02 mmol) and Togni's reagent **2** (75 mg, 0.24 mmol). The tube was vacuumed and back-filled with argon three times and then added with 1,4-dioxane (2 mL). The reaction mixture was stirred at 25 °C for 24 h. The solvent was removed under reduced pressure to afford the crude product, which was purified by flash column chromatography to afford the product **10-13**.



**10** (82% overall yield). (major isomer). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 – 7.26 (m, 8H), 7.13 – 7.07 (m, 1H), 5.09 (q, *J* = 12.2 Hz, 2H), 3.90 (t, *J* = 6.7 Hz, 1H), 3.31 – 3.16 (m, 2H), 2.80 – 2.62 (m, 2H), 2.55 – 2.44 (m, 1H), 2.16 – 2.03 (m, 1H), 1.79 – 1.62 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  209.8, 156.7, 140.6, 137.6, 136.0, 130.1, 128.6, 128.4, 128.3, 127.9, 127.8, 127.0 (q, *J* = 277.2 Hz), 125.8, 76.4, 43.9, 42.9 (q, *J* = 2.7 Hz), 37.0 (q, *J* = 27.6 Hz), 27.0, 20.9. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.6. HRMS (ESI) m/z calcd. For C<sub>21</sub>H<sub>21</sub>O<sub>2</sub>NF<sub>3</sub> [M+H]<sup>+</sup> 376.1519, found 376.1518.

**10** (minor isomer). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 – 7.22 (m, 7H), 7.12 – 7.01 (m, 2H), 4.95 (q, *J* = 11.9 Hz, 2H), 4.46 (dd, *J* = 9.7, 4.2 Hz, 1H), 3.23 – 3.07 (m, 1H), 3.00 – 2.89 (m, 1H), 2.83 – 2.68 (m, 2H), 2.69 – 2.59 (m, 1H), 2.55 – 2.44 (m, 1H), 2.18 – 2.05 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  209.2, 157.9, 140.5, 137.2, 135.4, 130.8, 128.3, 128.2, 127.9, 127.8, 127.6, 127.4, 126.4 (q, *J* = 277.7 Hz), 76.2, 43.3, 38.8 (q, *J* = 2.8 Hz), 35.7 (q, *J* = 28.3 Hz), 33.67, 24.7. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -64.6. HRMS (ESI) m/z calcd. For C<sub>21</sub>H<sub>21</sub>O<sub>2</sub>NF<sub>3</sub> [M+H]<sup>+</sup> 376.1519, found 376.1517.



**11**: (76% yield, major isomer). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 – 7.26 (m, 8H), 7.13 – 7.07 (m, 1H), 5.09 (q, J = 12.2 Hz, 2H), 3.90 (t, J = 6.7 Hz, 1H), 3.31 – 3.16 (m, 1H), 2.80 – 2.62 (m, 3H), 2.55 – 2.44 (m, 1H), 2.16 – 2.03 (m, 1H), 1.79 – 1.66 (m, 1H), 1.64 – 1.49 (m, 2H), 1.46 – 1.33 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  211.6, 157.9, 140.9, 138.0, 136.1, 130.4, 129.8, 128.4, 128.3, 127.9, 127.4, 127.0 (q, J = 277.2 Hz), 124.8,

76.5, 45.1, 44.4 (q, J = 2.7 Hz), 37.4 (q, J = 27.6 Hz), 30.5, 24.8, 24.5. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -63.6. HRMS (ESI) m/z calcd. For C<sub>22</sub>H<sub>23</sub>O<sub>2</sub>NF<sub>3</sub> [M+H]<sup>+</sup> 390.1675, found 390.1672.



**12**: (77% yield, major isomer).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41 (t, J = 7.4 Hz, 1H), 7.36 – 7.22 (m, 8H), 5.07 (s, 2H), 4.56 (dd, J = 8.4, 5.0 Hz, 1H), 3.24 – 3.09 (m, 2H), 2.74 – 2.48 (m, 3H), 1.87 – 1.64 (m, 2H), 1.56 – 1.30 (m, 5H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 209.8, 160.1, 141.1, 138.1, 137.5, 130.9, 128.4, 128.2, 128.0, 127.8, 127.0, 126.7 (q, J = 278.0 Hz), 126.2, 75.9, 44.0, 36.3 (q, J = 2.5 Hz), 34.8 (q, J = 28.3 Hz), 27.7, 23.3, 22.1, 22.0. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.7. HRMS (ESI) m/z calcd. For C<sub>23</sub>H<sub>25</sub>O<sub>2</sub>NF<sub>3</sub> [M+H]<sup>+</sup> 404.1832, found 404.1830.



**13**: (67% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 – 7.22 (m, 7H), 7.17 – 7.11 (m, 2H), 5.05 – 4.83 (m, 2H), 3.53 – 3.14 (m, 1H), 2.98 – 2.47 (m, 5H), 2.44 – 2.11 (m, 3H), 2.07 – 1.72 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  210.8, 158.4, 141.0, 137.4, 136.5, 131.4, 129.6, 128.4, 128.1, 127.8, 126.6, 126.4 (q, *J* = 276.0 Hz), 124.2, 76.1, 43.3, 36.2 (q, *J* = 27.0 Hz), 35.5, 29.8 (q, *J* = 2.7 Hz, 27.2, 22.8.<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -64.7. HRMS (ESI) m/z calcd. For C<sub>22</sub>H<sub>23</sub>O<sub>2</sub>NF<sub>3</sub> [M+H]<sup>+</sup> 390.1675, found 390.1673.

## Synthetic transformations Removal of PMB group of 3O



To a solution of **3O** (158 mg, 0.4 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (16 mL) were added anisole (172 mg, 1.6 mmol) and AlCl<sub>3</sub> (210 mg, 1.6 mmol) sequentially at 0 °C. The reaction mixture was stirred at that temperature for 30 min and quenched with ice water (10 mL). Dichloromethane was used to extract the product from the aqueous layer ( $3 \times 10$ mL). The combined organic layer was washed with brine (5 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product **14** (62 mg, 57%) as a colorless oil.

14: (57% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (dd, J = 8.2, 1.4 Hz, 2H), 7.71 (brs, 1H), 7.62 – 7.56 (m, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.35 (d, J = 7.4 Hz, 1H), 3.14 – 2.97 (m, 2H), 2.85 – 2.73 (m, 1H), 2.50 – 2.26 (m, 2H), 2.14 – 2.03 (m, 1H), 2.02 – 1.90 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 199.1, 152.4, 136.8, 133.4, 128.8, 128.1, 126.3 (q, J = 277.1 Hz), 37.1 (q, J = 28.3 Hz), 35.4, 34.0 (q, J = 2.5 Hz), 26.7. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.6. HRMS (ESI) m/z calcd. For C<sub>13</sub>H<sub>15</sub>O<sub>2</sub>NF<sub>3</sub> [M+H]<sup>+</sup> 274.1049, found 274.1049.

#### Transformation of medium-sized oxime 11 to lactam 15



To a solution of **11** (39 mg, 0.10 mmol) in methanol (2 mL) was added NaOMe (23 mg, 0.40 mmol) at room temperature. The reaction mixture was heated up to 60 °C for 2 h, cooled down to room temperature and quenched with H<sub>2</sub>O (3 mL). EtOAc (10 mL) was added and the organic layer was washed with brine (5 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to afford the crude product, which was purified by flash column chromatography to afford the product **15** (12 mg, 40%).

# 10-(2,2,2-trifluoroethyl)-2,3,4,10-tetrahydrobenzo[e]cyclopenta[b]azepin-5(1H)-one (15)



**15**: (40% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (dd, J = 7.8, 1.2 Hz, 1H), 7.91 (brs, 1H), 7.49 (td, J = 7.5, 1.4 Hz, 1H), 7.39 (td, J = 7.6, 1.2 Hz, 1H), 7.14 (d, J = 7.2 Hz, 1H), 3.59 (dd, J = 8.7, 6.2 Hz, 1H), 2.72 – 2.32 (m, 6H), 2.01 – 1.88 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  168.9, 142.5, 132.9, 132.5, 131.7, 131.5, 127.8, 127.4, 124.7, 39.2 (q, J = 2.8 Hz), 36.2 (q, J = 27.1 Hz), 34.9, 33.9, 21.3. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -64.54. HRMS (ESI) m/z calcd. For C<sub>15</sub>H<sub>15</sub>ONF<sub>3</sub> [M+H]<sup>+</sup> 282.1100, found 282.1100.



The procedure for large-scale synthesis is similar to that for synthesis of **3A**.



In an oven-dried 10 mL Schlenk tube were added **1A** (0.20 mmol), CuI (4 mg, 0.02 mmol), Togni's reagent **2** (75 mg, 0.24 mmol) and TEMPO (60 mg, 0.4 mmol). The tube was vacuumed and back-filled with argon three times and then added with 1,4-dioxane (2 mL). The reaction mixture was stirred at 25 °C for 24 h. NMR showed most of **1A** existed and trace amount of **3A** was detected.

## NMR Spectra



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







N∕∕ OBn

3C

MeO

210 200 190 180 170 160 150 140 130 120 110 100 90 80 fl (ppm)

Solution
 Solution

9.0

70 60 50 20

40 30 0

10










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

7,778 7,778 7,778 7,776 7,776 7,776 7,728 7,7419 7,729 7,239



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





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

7,7555 7,7555 7,7555 7,7555 7,7555 7,7555 7,7555 7,7555 7,7555 7,7537 7,7537 7,7537 7,7537 7,7535 7,7535 7,7535 7,7255 7,2255 7,23555 7,23555 7,23555 7,23555 7,235555 7,235555557 7,23555575757575757







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



### 8,854 8,854 8,854 8,854 7,750 7,5000 7,5000 7,5000 7,5000 7,5000 7,5000 7,5000 7,5000 7,5000 7,5







## [7,634] [7,634] [7,635] [7,564] [7,564] [7,564] [7,564] [7,564] [7,554] [7,554] [7,554] [7,554] [7,554] [7,554] [7,723] [7,723] [7,723] [7,723] [7,723] [7,723] [7,723] [7,723] [7,723] [7,726] [7,







### $\begin{array}{c} 7,849\\ 7,7828\\ 7,7828\\ 7,7828\\ 7,7828\\ 7,7828\\ 7,7828\\ 7,7828\\ 7,7828\\ 7,7828\\ 7,7828\\ 7,7828\\ 7,7828\\ 7,7828\\ 7,7828\\ 7,7828\\ 7,7828\\ 7,7828\\ 7,7328\\$

















0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -18 f1 (ppm)





## 2012 002 001







7,875 7,7587 7,7587 7,7587 7,7587 7,7587 7,7587 7,7587 7,7587 7,7587 7,7587 7,7587 7,7587 7,7587 7,758 7,758 7,7288 7,229487 7,22948 7,22948 7,22948 7,22948777 7,22948 7,22948







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

### 7,7381 7,7377 7,7377 7,7377 7,7377 7,737 7,737 7,737 7,737 7,737 7,738 7,7487 7,7487 7,7487 7,7487 7,74877 7,74877





— -64.593





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





# $\begin{array}{c} 7.347\\ 7.330\\ 7.347\\ 7.330\\ 7$





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







-5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 fl (ppm) -110 -120 -130 -140



COSY of compound 15








