# Supporting Information for

# Synthesis of α-Trifluoromethyl Ethanone Oximes via the Three-component Reaction of Aryl-substituted Ethylenes, tert-Butyl Nitrite, and the Langlois Reagent

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## 1) General information

All solvents were distilled prior to use. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded at 400 MHz, 100 MHz and 376 MHz with Brucker ARX 400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. HRMS was performed on an FTMS mass instrument.

## 2) Effect of water on the reaction

A 10 mL sealing tube with a magnetic stirring bar was charged with Langlois reagent (156 mg, 1.0 mmol), DMSO containing 5% water (1 mL) was added via syringe with gentle stirring. Then 1-chloro-4-vinylbenzene (1a) (69 mg, 0.5 mmol) and tert-butyl nitrite (90% purity) (114 mg, 1.0 mmol) were added to the reaction mixture and the mixture was heated to 40 °C by a preheated oil bath for 48h. The reaction mixture diluted with ethyl acetate (10 mL) and washed with water (10 mL) three times. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated to give a residue which was purified by silica gel chromatography (PE : EA = 10 : 1), to give product compound 4a (90 mg, 76%) as a white solid.

A 10 mL sealing tube with a magnetic stirring bar was charged with Langlois reagent (156 mg, 1.0 mmol), DMSO containing 10% water (1 mL) was added via syringe with gentle stirring. Then 1-chloro-4-vinylbenzene (1a) (69 mg, 0.5 mmol) and tert-butyl nitrite (90% purity) (114 mg, 1.0 mmol) were added to the reaction mixture and the mixture was heated to 40 °C by a preheated oil bath for 48h. The reaction mixture diluted with ethyl acetate (10 mL) and washed with water (10 mL) three times. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated to give a residue which was purified by silica gel chromatography (PE : EA = 10 : 1), to give product compound 4a (89

mg, 75%) as a white solid.

#### 3) <sup>18</sup>O-labeling experiment

A 10 mL sealing tube with a magnetic stirring bar was charged with Langlois reagent (156 mg, 1.0 mmol), dry DMSO (1 mL) and H<sub>2</sub><sup>18</sup>O (100 mg, 5 mmol) were added via syringe with gentle stirring. Then 1-chloro-4-vinylbenzene (**1a**) (69 mg, 0.5 mmol) and tert-butyl nitrite (90% purity) (114 mg, 1.0 mmol) were added to the reaction mixture and the mixture was heated to 40 °C by a preheated oil bath for 48h. The reaction mixture diluted with ethyl acetate (10 mL) and washed with water (10 mL) three times. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated to give a residue which was purified by silica gel chromatography (PE : EA = 10 : 1), to give the mixture **4a** and **4a'** (89 mg, 75%) as a colorless oil. Analysis of this mixture by HRMS (ESI) was performed. **4a** calcd for C<sub>9</sub>H<sub>8</sub>ClF<sub>3</sub>NO<sup>+</sup> (M+H)<sup>+</sup> 238.0241, found 238.0230. **4a'** calcd for C<sub>9</sub>H<sub>8</sub>ClF<sub>3</sub>N<sup>18</sup>O<sup>+</sup> (M+H)<sup>+</sup> 240.0283, found 240.0271.

#### 4) The spectral data of the products



(E)-1-(4-chlorophenyl)-3,3,3-trifluoropropan-1-one oxime (4a): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 4a was isolated as a white solid (92 mg, 77 %); R<sub>f</sub>(PE : EA = 5 : 1) = 0.60; mp (melting point) = 94-96 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.23 (s, 1H), 7.57 (d, *J* = 8.64 Hz, 2H), 7.40 (d, *J* = 8.60 Hz, 2H), 3.74 (q, *J* = 10.36 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  149.0 (d, *J* = 2.05 Hz), 136.4, 132.9, 129.2, 127.8, 124.5 (q, *J* = 276.63 Hz), 30.5 (q, *J* = 31.61 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = -61.3 (s, 3F). HRMS (ESI) m/z calcd for C<sub>9</sub>H<sub>8</sub>ClF<sub>3</sub>NO<sup>+</sup> (M+H)<sup>+</sup> 238.0241, found 238.0240.



(E)-3,3,3-trifluoro-1-phenylpropan-1-one oxime (4b): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 4b was isolated as a white solid (61 mg, 60 %); R<sub>f</sub> (PE : EA = 5 : 1) = 0.47; mp (melting point) = 88-90 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.42 (s, 1H), 7.65-7.63 (m, 2H), 7.45-7.42 (m, 3H), 3.78 (q, *J* = 10.40 Hz, 2H ). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  149.8 (d, *J* = 1.95 Hz), 134.4, 130.1, 128.9, 126.6, 124.6 (q, *J* = 276.69 Hz), 30.6 (q, *J* = 31.37 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = – 61.3 (s, 3F). HRMS (ESI) m/z calcd for C<sub>9</sub>H<sub>9</sub>F<sub>3</sub>NO<sup>+</sup> (M+H)<sup>+</sup> 204.0631, found 204.0630.



(E)-1-(4-bromophenyl)-3,3,3-trifluoropropan-1-one oxime (4c)<sup>1</sup>: after purification by silica gel

column chromatography (PE : EA = 10 : 1), compound **4c** was isolated as a white solid (89 mg, 63 %);  $R_f(PE : EA = 5 : 1) = 0.60$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.02 (s, 1H), 7.56-7.50 (m, 4H), 3.72 (q, *J* = 10.40 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  148.9 (d, *J* = 1.96 Hz), 133.3, 132.1, 128.0, 124.6, 124.5 (q, *J* = 276.82 Hz), 30.3 (q, *J* = 31.59 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = -61.3 (s, 3F).



(E)-3,3,3-trifluoro-1-(4-fluorophenyl)propan-1-one oxime (4d): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 4b was isolated as a white solid (72 mg, 65 %);  $R_f(PE : EA = 5 : 1) = 0.59$ ; mp (melting point) = 64-66 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.19 (s, 1H), 7.65-7.62 (m, 2H), 7.12-7.08 (m, 2H), 3.73 (q, J = 10.40 Hz, 2H ). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  164.0 (d, J = 249.02 Hz), 148.9 (d, J = 1.95 Hz), 130.6 (d, J = 3.30 Hz), 128.5 (d, J = 8.35 Hz), 124.5 (q, J = 276.80 Hz), 115.9 (d, J = 21.78 Hz), 30.5 (q, J = 31.47 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta = -61.3$  (s, 3F), -110.8 (s, 1F). HRMS (ESI) m/z calcd for C<sub>9</sub>H<sub>8</sub>F<sub>4</sub>NO<sup>+</sup> (M+H)<sup>+</sup> 222.0537, found 222.0535.



(E)-3,3,3-trifluoro-1-(4-nitrophenyl)propan-1-one oxime (4e): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 4e was isolated as a white solid (84 mg, 68 %);  $R_f(PE : EA = 5 : 1) = 0.43$ ; mp (melting point) = 138-140 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.46 (s, 1H), 8.26 (d, J = 9.04 Hz, 2H), 7.84 (d, J = 9.00 Hz, 2H), 3.78 (q, J = 10.28 Hz, 2H). <sup>13</sup>C NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  147.6, 145.8 (d, J = 1.78 Hz), 141.0, 127.1, 125.0 (q, J = 275.70 Hz), 123.6, 28.6 (q, J = 29.96 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta = -61.3$  (s, 3F). HRMS (ESI) m/z calcd for C<sub>9</sub>H<sub>8</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> (M+H)<sup>+</sup> 249.0482, found 249.0480.



(E)-4-(3,3,3-trifluoro-1-(hydroxyimino)propyl)benzonitrile (4f): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 4f was isolated as a white solid (66 mg, 58 %);  $R_f(PE : EA = 5 : 1) = 0.30$ ; mp (melting point) = 99-101 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.84 (s, 1H), 7.77 (d, J = 8.56 Hz, 2H), 7.70 (d, J = 8.60 Hz, 2H), 3.76 (q, J = 10.32 Hz, 2H). <sup>13</sup>C NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  146.0 (d, J = 1.99 Hz), 139.2, 132.4, 126.8, 125.0 (q, J = 276.69 Hz), 118.5, 111.6, 28.5 (q, J = 29.87 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta = -61.3$  (s, 3F). HRMS (ESI) m/z calcd for C<sub>10</sub>H<sub>8</sub>F<sub>3</sub>N<sub>2</sub>O<sup>+</sup> (M+H)<sup>+</sup> 229.0583, found 229.0579.



(E)-3,3,3-trifluoro-1-(4-(trifluoromethyl)phenyl)propan-1-one oxime (4g): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 4g was isolated as a white solid (93 mg, 69 %);  $R_f$  (PE : EA = 5 : 1) = 0.63; mp (melting point) = 87-89 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.52 (s, 1H), 7.76 (d, *J* = 8.32 Hz, 2H), 7.68 (d, *J* = 8.32 Hz, 2H), 3.78 (q, *J* = 10.32 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  148.8, 137.8, 132.0 (q, *J* = 32.72 Hz), 126.9, 125.8, 124.4 (q, *J* = 274.40 Hz), 124.0 (q, *J* = 274.40 Hz), 30.4 (q, *J* = 31.74 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = -61.3 (s, 3F), -62.9 (s, 3F). HRMS (ESI) m/z calcd for C<sub>10</sub>H<sub>8</sub>F<sub>6</sub>NO<sup>+</sup> (M+H)<sup>+</sup> 272.0505, found 272.0506.



(E)-3,3,3-trifluoro-1-(p-tolyl)propan-1-one oxime (4h): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 4h was isolated as a white solid (72 mg, 67 %); R<sub>f</sub> (PE : EA = 5 : 1) = 0.53; mp (melting point) = 98-100 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.91 (s, 1H), 7.53 (d, *J* = 8.24 Hz, 2H), 7.23 (d, *J* = 8.04 Hz, 2H), 3.75 (q, *J* = 10.44 Hz, 2H ), 2.39 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  149.6 (d, *J* = 2.07 Hz), 140.3, 131.6, 129.6, 126.4, 124.6 (q, *J* = 277.34 Hz), 30.4 (q, *J* = 31.35 Hz), 21.4. <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = – 61.3 (s, 3F). HRMS (ESI) m/z calcd for C<sub>10</sub>H<sub>11</sub>F<sub>3</sub>NO<sup>+</sup> (M+H)<sup>+</sup> 218.0787, found 218.0788.



(E)-1-(4-(tert-butyl)phenyl)-3,3,3-trifluoropropan-1-one oxime (4i): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 4i was isolated as a white solid (87 mg, 67 %); R<sub>f</sub>(PE : EA = 5 : 1) = 0.59; mp (melting point) = 90-92 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.39 (s, 1H), 7.58 (d, *J* = 8.80 Hz, 2H), 7.43 (d, *J* = 8.52 Hz, 2H), 3.74 (q, *J* = 10.48 Hz, 2H ), 1.34 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.5, 149.5 (d, *J* = 1.99 Hz), 131.5, 126.2, 125.9, 124.7 (q, *J* = 276.67 Hz), 34.9, 31.3, 30.5 (q, *J* = 31.40 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = -61.2 (s, 3F). HRMS (ESI) m/z calcd for C<sub>13</sub>H<sub>17</sub>F<sub>3</sub>NO<sup>+</sup> (M+H)<sup>+</sup> 260.1257, found 260.1258.



(E)-methyl 4-(3,3,3-trifluoro-1-(hydroxyimino)propyl)benzoate (4j): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 4j was isolated as a white solid (95 mg,

73 %); R<sub>f</sub>(PE : EA = 5 : 1) = 0.40; mp (melting point) = 130-132 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.62 (s, 1H), 8.08 (d, *J* = 8.44 Hz, 2H), 7.72 (d, *J* = 8.44 Hz, 2H), 3.94 (s, 3H), 3.77 (q, *J* = 10.36 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  166.8, 148.9 (d, *J* = 2.04 Hz), 138.6, 131.4, 130.0, 126.5, 124.5 (q, *J* = 276.62 Hz), 52.5 (d, *J* = 3.92 Hz), 30.3 (q, *J* = 31.53 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = - 61.3 (s, 3F). HRMS (ESI) m/z calcd for C<sub>11</sub>H<sub>11</sub>F<sub>3</sub>NO<sub>3</sub><sup>+</sup> (M+H)<sup>+</sup> 262.0686, found 262.0689.



(E)-4-(3,3,3-trifluoro-1-(hydroxyimino)propyl)phenyl acetate (4k): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 4k was isolated as a white solid (74 mg, 56 %); R<sub>f</sub>(PE : EA = 3 : 1) = 0.49; mp (melting point) = 120-122 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.15 (s, 1H), 7.69-7.65 (m, 2H), 7.16-7.13 (m, 2H), 3.72 (q, *J* = 10.44 Hz, 2H), 2.31 (s, 3H). <sup>13</sup>C NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  169.0, 151.2, 146.3, 132.5, 127.2, 125.1 (q, *J* = 276.56 Hz), 121.9, 28.7 (q, *J* = 29.82 Hz), 20.8. <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = - 61.2 (s, 3F). HRMS (ESI) m/z calcd for C<sub>11</sub>H<sub>11</sub>F<sub>3</sub>NO<sub>3</sub><sup>+</sup> (M+H)<sup>+</sup> 262.0686, found 262.0686.



(E)-1-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoropropan-1-one oxime (4l): after purification by silica gel column chromatography (PE : EA = 5 : 1), compound 4l was isolated as a white solid (92 mg, 66 %); R<sub>f</sub> (PE : EA = 3 : 1) = 0.64; mp (melting point) = 173-175 °C; <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  11.18 (s, 1H), 6.97 (d, *J* = 8.40 Hz, 2H), 6.87-6.84 (m, 4H), 6.61 (t, *J* = 7.48 Hz, 2H), 6.52 (t, *J* = 7.24 Hz, 1H), 3.12 (q, *J* = 11.32 Hz, 2H). <sup>13</sup>C NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  146.6, 140.8, 139.3, 134.0, 129.0, 127.8, 126.7, 126.64, 126.60, 125.2 (q, *J* = 282.91 Hz), 28.7 (q, *J* = 29.86 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = - 61.2 (s, 3F). HRMS (ESI) m/z calcd for C<sub>15</sub>H<sub>13</sub>F<sub>3</sub>NO<sup>+</sup> (M+H)<sup>+</sup> 280.0944, found 280.0947.



(E)-3,3,3-trifluoro-1-(4-(pyridin-2-yl)phenyl)propan-1-one oxime (4m): after purification by silica gel column chromatography (PE : EA = 5 : 1), compound 4m was isolated as a white solid (90 mg, 64 %);  $R_f(PE : EA = 2 : 1) = 0.37$ ; mp (melting point) = 172-174 °C; <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  12.09 (s, 1H), 8.69 (d, *J* = 4.64 Hz, 1H), 8.14 (d, *J* = 8.48 Hz, 2H), 8.02 (d, *J* = 7.92 Hz, 1H), 7.92-7.85 (m, 3H), 7.39-7.36 (m, 1H) 3.99 (q, *J* = 11.32 Hz, 2H). <sup>13</sup>C NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  155.2, 149.6, 146.6, 139.2, 137.2, 135.4, 126.4 (d, *J* = 14 Hz), 124.9 (q, *J* = 227.34

Hz), 122.8, 120.3, 28.7 (q, J = 29.76 Hz). <sup>19</sup>F NMR (375 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta = -60.3$  (s, 3F). HRMS (ESI) m/z calcd for C<sub>14</sub>H<sub>12</sub>F<sub>3</sub>N<sub>2</sub>O<sup>+</sup> (M+H)<sup>+</sup> 281.0896, found 281.0899.



(E)-1-(2-chlorophenyl)-3,3,3-trifluoropropan-1-one oxime (4n): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 4n was isolated as a white solid (71 mg, 60 %, 1:1 *E/Z* ratio); R<sub>f</sub>(PE : EA = 5 : 1) = 0.60; *E*-isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.20 (s, 1H), 7.47-7.44 (m, 1H), 7.38-7.34 (m, 2H), 7.31-7.30 (m, 1H), 3.80 (q, *J* = 10.64 Hz, 2H ). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  150.0 (d, *J* = 2.08 Hz), 133.9, 131.8, 131.0, 130.7, 129.9, 127.1, 124.7 (q, *J* = 276.25 Hz), 39.4 (q, *J* = 30.01 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = – 61.5 (s, 3F). *Z*-isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.63 (s, 1H), 7.43-7.41 (m, 1H), 7.34-7.31 (m, 2H), 7.24-7.22 (m, 1H), 3.42 (q, *J* = 10.24 Hz, 2H ). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  148.7 (d, *J* = 3.07 Hz), 132.7, 131.1, 130.5, 129.7, 129.5, 126.8, 124.4 (q, *J* = 276.40 Hz), 32.5 (q, *J* = 30.64 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = – 63.1 (s, 3F). HRMS (ESI) m/z calcd for C<sub>9</sub>H<sub>8</sub>ClF<sub>3</sub>NO<sup>+</sup> (M+H)<sup>+</sup> 238.0241, found 238.0243.



(E)-1-(3-chlorophenyl)-3,3,3-trifluoropropan-1-one oxime (40): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 40 was isolated as a white solid (80 mg, 67 %);  $R_f$  (PE : EA = 5 : 1) = 0.60; mp (melting point) = 63-65 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.97 (s, 1H), 7.67 (s, 1H), 7.51 (d, J = 7.64 Hz, 1H), 7.41-7.32 (m, 2H), 3.72 (q, J = 10.36 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  148.8 (d, J = 2.01 Hz), 136.2, 135.0, 130.14, 130.08, 126.7, 124.7, 124.4 (q, J = 276.87 Hz), 30.5 (q, J = 31.72 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = -61.3 (s, 3F). HRMS (ESI) m/z calcd for C<sub>9</sub>H<sub>8</sub>ClF<sub>3</sub>NO<sup>+</sup> (M+H)<sup>+</sup> 238.0241, found 238.0240.



(E)-1-(3-bromophenyl)-3,3,3-trifluoropropan-1-one oxime (4p): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 4p was isolated as a white solid (94 mg, 66 %); R<sub>f</sub>(PE : EA = 5 : 1) = 0.63; mp (melting point) = 61-63 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.93 (s, 1H), 7.82 (s, 1H) 7.55 (d, *J* = 7.92 Hz, 2H), 7.29 (d, *J* = 7.92 Hz, 1H), 3.71 (q, *J* = 10.32 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  148.7 (d, *J* = 12.74 Hz), 136.4 (d, *J* = 4.21 Hz), 133.1 (d, *J* = 5.57 Hz), 130.3 (d, *J* = 3.86 Hz), 129.6, 125.2, 124.4 (q, *J* = 277.34 Hz), 123.1, 30.4 (q, *J* = 31.52 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = - 61.3 (s, 3F). HRMS (ESI) m/z calcd for C<sub>9</sub>H<sub>8</sub>BrF<sub>3</sub>NO<sup>+</sup> (M+H)<sup>+</sup> 281.9736, found 281.9740.



(E)-1-(3,4-dichlorophenyl)-3,3,3-trifluoropropan-1-one oxime (4q): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 4q was isolated as a white solid (73 mg, 63 %); R<sub>f</sub>(PE : EA = 5 : 1) = 0.57; mp (melting point) = 111-113 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.49 (s, 1H), 7.75 (d, *J* = 1.72 Hz, 1H), 7.50-7.45 (m, 2H), 3.71 (q, *J* = 10.32 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  147.9 (d, *J* = 1.97 Hz), 134.4, 134.3, 133.3, 130.8, 128.4, 125.6, 124.3 (q, *J* = 276.73 Hz), 30.2 (q, *J* = 31.67 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = - 61.3 (s, 3F). HRMS (ESI) m/z calcd for C<sub>9</sub>H<sub>7</sub>Cl<sub>2</sub>F<sub>3</sub>NO<sup>+</sup> (M+H)<sup>+</sup> 271.9851, found 271.9855.



(E)-3,3,3-trifluoro-1-(pyridin-2-yl)propan-1-one oxime (4r): after purification by silica gel column chromatography (PE : EA = 5 : 1), compound 4r was isolated as a white solid (66 mg, 65 %); R<sub>f</sub> (PE : EA = 2 : 1) = 0.49; mp (melting point) = 134-136 °C; <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  11.45 (s, 1H), 7.76 (d, *J* = 4.76 Hz, 1H), 7.05 (d, *J* = 8.00 Hz, 1H), 7.00-6.95 (m, 1H), 6.57-6.54 (m, 1H),3.14 (q, *J* = 11.24 Hz, 2H ). <sup>13</sup>C NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  152.5, 148.7 (d, *J* = 10.06 Hz), 147.8, 136.9, 125.2 (q, *J* = 276.67 Hz), 124.1, 119.9, 27.6 (q, *J* = 30.36 Hz). <sup>19</sup>F NMR (375 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  = – 60.2 (s, 3F). HRMS (ESI) m/z calcd for C<sub>8</sub>H<sub>8</sub>F<sub>3</sub>N<sub>2</sub>O<sup>+</sup> (M+H)<sup>+</sup> 205.0583, found 205.0584.



(E)-3,3,3-trifluoro-1-(quinolin-2-yl)propan-1-one oxime (4s): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 4s was isolated as a yellow solid (63 mg, 50 %); R<sub>f</sub>(PE : EA = 5 : 1) = 0.49; mp (melting point) = 138-140 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.16-8.09 (m, 3H), 8.01 (d, *J* = 8.64 Hz, 1H), 7.83 (d, *J* = 8.24 Hz, 1H),7.75-7.71 (m, 1H), 7.59-7.55 (m, 1H), 4.23 (q, *J* = 10.60 Hz, 2H ). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  152.3, 151.4, 147.5, 136.6, 130.0, 129.9, 128.4, 127.6, 127.5, 125.0 (q, *J* = 276.56 Hz), 118.3, 28.5 (q, *J* = 31.52 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = – 61.4 (s, 3F). HRMS (ESI) m/z calcd for C<sub>12</sub>H<sub>10</sub>F<sub>3</sub>N<sub>2</sub>O<sup>+</sup> (M+H)<sup>+</sup> 255.0740, found 255.0741.



(E)-3,3,3-trifluoro-1-(naphthalen-2-yl)propan-1-one oxime (4t): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound 4t was isolated as a white solid (64 mg, 50 %);  $R_f(PE : EA = 5 : 1) = 0.55$ ; mp (melting point) = 124-126 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.90 (s, 1H), 8.04 (s, 1H), 7.91-7.85 (m, 4H), 7.56-7.51 (m, 2H), 3.89 (q, *J* = 10.40 Hz, 2H). <sup>13</sup>C

NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  149.6, 134.1, 133.1, 131.8, 128.8, 128.6, 127.8, 127.3, 126.8, 126.7, 124.7 (q, J = 276.71 Hz), 123.4, 30.3 (q, J = 31.30 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta = -61.1$  (s, 3F). HRMS (ESI) m/z calcd for C<sub>13</sub>H<sub>11</sub>F<sub>3</sub>NO<sup>+</sup> (M+H)<sup>+</sup> 254.0787, found 254.0790.



(E)-2-(trifluoromethyl)-2,3-dihydro-1H-inden-1-one oxime (4u): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound (4u) was isolated as a yellow solid (38 mg, 36 %); R<sub>f</sub>(PE : EA = 5 : 1) = 0.46; *E*-isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.68 (s, 1H), 8.48 (d, *J* = 7.24 Hz, 1H), 7.38-7.29 (m, 3H), 3.82-3.71 (m, 1H), 3.33-3.22 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  154.1 (d, *J* = 1.96 Hz), 145.4, 131.8, 129.7, 127.6, 126.1 (q, *J* = 276.86 Hz), 125.18, 121.7, 45.0 (q, *J* = 28.32 Hz), 30.3 (d, *J* = 2.03 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = - 70.4 (s, 3F). *Z*-isomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.08 (s, 1H), 7.68 (d, *J* = 7.64 Hz, 1H), 7.46-7.40 (m, 3H), 4.33-4.24 (m, 1H), 3.43-3.32 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  155.8, 144.6, 135.2, 132.7, 131.0, 127.7, 125.8 (q, *J* = 278.90 Hz), 125.22, 42.9 (q, *J* = 29.51 Hz), 31.0 (d, *J* = 2.78 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = - 68.2(s, 3F). HRMS (ESI) m/z calcd for C<sub>10</sub>H<sub>9</sub>F<sub>3</sub>NO<sup>+</sup> (M+H)<sup>+</sup> 216.0631, found 216.0633.



(E)-1-(benzo[b]thiophen-2-yl)-3,3,3-trifluoropropan-1-one oxime (4v): after purification by silica gel column chromatography (PE : EA = 10 : 1), compound (4v) was isolated as a yellow solid (46 mg, 36 %); R<sub>f</sub>(PE : EA = 5 : 1) = 0.62; mp (melting point) = 167-169 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.95 (s, 1H), 7.81-7.77 (m, 2H), 7.51 (s, 1H), 7.40-7.34 (m, 2H), 3.78 (q, *J* = 10.36 Hz, 2H). <sup>13</sup>C NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  143.7, 139.3, 139.2, 138.7, 125.8, 124.9 (q, *J* = 276.56 Hz), 124.7, 124.5, 124.1, 122.2, 29.4 (q, *J* = 30.29 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = -61.6 (s, 3F). HRMS (ESI) m/z calcd for C<sub>11</sub>H<sub>9</sub>F<sub>3</sub>NOS<sup>+</sup> (M+H)<sup>+</sup> 260.0352, found 260.0356.



**3-(p-tolyl)-2-(trifluoromethyl)-2H-azirine** (14h)<sup>1</sup>: after purification by silica gel column chromatography (PE : EA = 60 : 1), compound 14h was isolated as a colorless oil (64 mg, 64 %);  $R_f(PE : EA = 30 : 1) = 0.64$ ; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.81 (d, J = 8.08 Hz, 2H), 7.41 (d, J = 7.92 Hz, 2H), 2.68 (q, J = 4.64 Hz, 1H), 2.48 (s, 3H). <sup>13</sup>C NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):  $\delta$  160.3, 145.7, 130.6, 130.3, 124.5 (q, J = 271.94 Hz), 119.5, 29.4 (q, J = 42.30 Hz), 22.1. <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta = -66.7$  (s, 3F).



**3-(naphthalen-2-yl)-2-(trifluoromethyl)-2H-azirine**  $(14t)^1$ : after purification by silica gel column chromatography (PE : EA = 60 : 1), compound 14twas isolated as a white solid (89 mg,

76 %); R<sub>f</sub>(PE : EA = 30 : 1) = 0.58; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.36 (s, 1H), 8.05-7.98 (m, 3H), 7.94 (d, J = 8.04 Hz, 1H), 7.70-7.61 (m, 2H), 2.82 (q, J = 4.60 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  160.9 (d, J = 1.11 Hz), 136.2, 133.3, 132.8, 129.7, 129.5, 129.4, 128.3, 127.7, 124.6, 124.5 (q, J = 271.95 Hz), 119.6, 29.9 (q, J = 42.28 Hz). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):  $\delta$  = - 67.5 (s, 3F).

#### 5) Reference

1 Y.-J. Huang, B. Qiao, F.-G. Zhang and J.-A. Ma, *Tetrahedron* 2018, 74, 3791.

<sup>1</sup>H,<sup>13</sup>C and <sup>19</sup>F NMR spectra of (E)-1-(4-chlorophenyl)-3,3,3-trifluoropropan-1-one oxime (4a) in CDCl<sub>3.</sub>





<sup>1</sup>H,<sup>13</sup>C and <sup>19</sup>F NMR spectra of (E)-3,3,3-trifluoro-1-phenylpropan-1-one oxime (4b) in CDCl<sub>3</sub>.













 $^{1}$ H, $^{13}$ C and  $^{19}$ F NMR spectra of (E)-3,3,3-trifluoro-1-(4-fluorophenyl)propan-1-one oxime (4d) in CDCl<sub>3.</sub>





<sup>1</sup>H,<sup>13</sup>C and <sup>19</sup>F NMR spectra of (E)-3,3,3-trifluoro-1-(4-nitrophenyl)propan-1-one oxime (4e).





 $^{1}$ H, $^{13}$ C and  $^{19}$ F NMR spectra of (E)-4-(3,3,3-trifluoro-1-(hydroxyimino)propyl)benzonitrile (4f).













 ${}^{1}$ H,  ${}^{13}$ C and  ${}^{19}$ F NMR spectra of (E)-3,3,3-trifluoro-1-(p-tolyl)propan-1-one oxime (4h) in CDCl<sub>3.</sub>





<sup>1</sup>H,<sup>13</sup>C and <sup>19</sup>F NMR spectra of **(E)-1-(4-(tert-butyl)phenyl)-3,3,3-trifluoropropan-1-one oxime (4i)** in CDCl<sub>3.</sub>





<sup>1</sup>H,<sup>13</sup>C and <sup>19</sup>F NMR spectra of (E)-methyl 4-(3,3,3-trifluoro-1-(hydroxyimino)propyl)benzoate (4j) in CDCl<sub>3</sub>.





<sup>1</sup>H,<sup>13</sup>C and <sup>19</sup>F NMR spectra of (E)-4-(3,3,3-trifluoro-1-(hydroxyimino)propyl)phenyl acetate (4k).





<sup>1</sup>H,<sup>13</sup>C and <sup>19</sup>F NMR spectra of (E)-1-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoropropan-1-one oxime (4l).







 $^{1}$ H, $^{13}$ C and  $^{19}$ F NMR spectra of (E)-3,3,3-trifluoro-1-(4-(pyridin-2-yl)phenyl)propan-1-one oxime (4m) in (CD<sub>3</sub>)<sub>2</sub>SO.





<sup>1</sup>H,<sup>13</sup>C and <sup>19</sup>F NMR spectra of **(E)-1-(2-chlorophenyl)-3,3,3-trifluoropropan-1-one oxime (4n)** in CDCl<sub>3</sub>.





<sup>1</sup>H,<sup>13</sup>C and <sup>19</sup>F NMR spectra of **(E)-1-(3-chlorophenyl)-3,3,3-trifluoropropan-1-one oxime (40)** in CDCl<sub>3</sub>.







<sup>1</sup>H,<sup>13</sup>C and <sup>19</sup>F NMR spectra of **(E)-1-(3-bromophenyl)-3,3,3-trifluoropropan-1-one oxime (4p)** in CDCl<sub>3</sub>.











<sup>1</sup>H,<sup>13</sup>C and <sup>19</sup>F NMR spectra of (E)-3,3,3-trifluoro-1-(pyridin-2-yl)propan-1-one oxime (4r) in (CD<sub>3</sub>)<sub>2</sub>SO.





<sup>1</sup>H,<sup>13</sup>C and <sup>19</sup>F NMR spectra of **(E)-3,3,3-trifluoro-1-(quinolin-2-yl)propan-1-one oxime (4s)** in CDCl<sub>3</sub>.







<sup>1</sup>H,<sup>13</sup>C and <sup>19</sup>F NMR spectra of (E)-3,3,3-trifluoro-1-(naphthalen-2-yl)propan-1-one oxime (4t) in CDCl<sub>3</sub>.











 $^{1}$ H, $^{13}$ C and  $^{19}$ F NMR spectra of (E)-1-(benzo[b]thiophen-2-yl)-3,3,3-trifluoropropan-1-one oxime (4v) in CDCl<sub>3</sub>.











<sup>1</sup>H,<sup>13</sup>C and <sup>19</sup>F NMR spectra of **3-(naphthalen-2-yl)-2-(trifluoromethyl)-2H-azirine (14t)** in CDCl<sub>3</sub>.







 $^{19}\mathrm{F}$  NMR spectra of  $4p,\,5$  and 6 in (CD<sub>3</sub>)<sub>2</sub>SO.

