# Electronic Supplementary Information

# A covalent organic framework catalyzed visible-light-induced threecomponent cascade synthesis of trifluoroalkyl and trifluoroalkenyl quinoxalin-2(1*H*)-ones

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#### I. General information

All starting materials (from energy chemical or bidepharm) and solvents were used as received and without further purification, unless otherwise specified. <sup>1</sup>H NMR spectra were recorded on Bruker 400, 500 or 600 MHz spectrometer with CDCl<sub>3</sub> as the solvent; <sup>13</sup>C NMR spectra were recorded on Bruker 101, 126 MHz or 151 MHz spectrometer with CDCl<sub>3</sub> as the solvent. <sup>19</sup>F NMR spectra were recorded on Bruker 371, 477 MHz or 565 MHz spectrometer with CDCl<sub>3</sub> as the solvent. 2D-NOSEY spectra were recorded on Bruker 500 MHz spectrometer with CDCl<sub>3</sub> as the solvent. 2D-NOSEY spectra were recorded on Bruker 500 MHz spectrometer with CDCl<sub>3</sub> as the solvent. Chemical shifts were reported in parts per million ( $\delta$ ) with TMS (0 ppm) as the internal standard. The peak patterns are indicated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). The coupling constants (*J*) are reported in Hertz (Hz). The unknown products were additionally characterized by HRMS.

Powder X-ray diffraction (PXRD) patterns of the as-prepared samples were obtained on a powder X-ray diffractometer (Cu Kα radiation source, Ultima IV, Rigaku). FT-IR spectra were collected in the range of 400-4000 cm-1 on Bruker IFS 66 v/s Fourier transform infrared spectrometer. Brunauer-EmmettTeller (BET) surface area analysis was carried out using a Micromeritics TriStar II 3020 instrument at 77 K. Scanning electron microscopy (SEM) was performed using a ZEISS Gemini 300. The solid phases <sup>13</sup>C CP/MAS NMR spectra were obtained on a Bruker 400 MHz or Agilent 600 MHz solid state NMR spectrometer.

#### II. Preparation and structure characterizations of 2D-COFs

#### (a) Preparation of 2D-COFs:

The following 2D-COFs were synthesized according to the literature and our reported methods<sup>1-6</sup>.





Scheme S1. Structures of 2D-COF-1, 2D-COF-2, 2D-COF-3, and 2D-COF-4.



Scheme S2. Synthesis of 2D-COF-5.

(b) Structure characterizations of 2D-COF-5



Figure S1. The FT-IR spectrum of fresh prepared 2D-COF-5.



Figure S2. The SEM image of fresh prepared 2D-COF-5.



Figure S3. The PXRD pattern of fresh prepared 2D-COF-5.

# **III. Optimization of light source**

 Table S1. Optimization of light source<sup>a, b</sup>



entry	variation from standard conditions	yield (%) <sup>b</sup>	
1	460 nm blue LED instead of 456 nm blue LED	20	
2	440 nm blue LED instead of 456 nm blue LED	trace	
3	427 nm blue LED instead of 456 nm blue LED	16	
<sup><i>a</i></sup> Reaction conditions: <b>1a</b> (0.1 mmol, 1 equiv.), <b>2a</b> (0.2 mmol, 2.0 equiv.), CF <sub>3</sub> SO <sub>2</sub> Na (0.2 mmol, 2 equiv.),			
2D-COF-5 (1 mg), 1.4-dioxane (2 mL), 2*40 W blue LEDs, air. r.t., 24 h. <sup>b</sup> Isolated vield.			

### IV. General procedure for the synthesis of 4 or 5



Figure S4. The photoreactor.

To a 10 mL glass tube equipped with a magnetic stir bar was charged with quinoxalin-2(1*H*)-one (1, 0.1 mmol), unsaturated hydrocarbon (2 or 3, 0.2 mmol), sodium trifluoromethanesulfinate (0.2 mmol, 31 mg) and 2D-COF-5 (1 mg) in 2 mL 1,4-dioxane. The reaction mixture was then stirred under air with the blue LED irradiation (2\*40 W blue LEDs, 456 nm, the power density is 0.003 W/ cm<sup>2</sup>, and the distance between reactor and lamp is approximately 5 cm.) for 24 h at room temperature. Upon completion, the photocatalyst was removed by centrifugation and filtration. Then 10 mL deionized water was added into the remaining mixture. The aqueous layer was extracted with ethyl acetate (5 mL × 3). The organic layers were washed with saturated brine then dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. The residue was purified on silica gel (petroleum ether and ethyl acetate) to afford the desired product **4 or 5**.







To a 10 mL glass tube equipped with a magnetic stir bar was charged with 1-methylquinoxalin-2(1*H*)-one (**1a**, 0.1 mmol, 16 mg), allylbenzene (**2a**, 0.2 mmol, 24 mg), sodium trifluoromethanesulfinate (0.2 mmol, 31 mg) and 2D-COF-5 (1 mg) in 2 mL 1,4-dioxane. The reaction mixture was then stirred under air with the blue LED irradiation (2\*40 W blue LEDs, 456 nm, the power density is 0.003 W/ cm<sup>2</sup>, and the distance between reactor and lamp is approximately 5 cm.) for 24 h at room temperature. Upon completion, the photocatalyst was removed by centrifugation, and washed with plenty of ethyl acetate, ethanol and water. Then the powder was dried at 120 °C under vacuum for 6 h to yield the recovered 2D-COF-5. Meanwhile, 10 mL deionized water was added into the remaining mixture. The aqueous layer was extracted with ethyl acetate (5 mL × 3). The organic layers were washed with saturated brine then dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. The residue was purified on silica gel (petroleum ether and ethyl acetate) to afford the desired product **4aa**. The structural characterization data of recycled 2D-COF-5 was collected after eight runs.



Figure S6. The soild <sup>13</sup>C NMR spectrum of recycled 2D-COF-5.



Figure S7. The FT-IR spectrum of recycled 2D-COF-5.



Figure S8. The PXRD pattern of recycled 2D-COF-5.



Figure S9. The SEM image of recycled 2D-COF-5.



**Figure S10.** (a) The pore size distribution of recycled 2D-COF-5 derived from  $N_2$  sorption isotherm measured at 77 K. (b)  $N_2$  adsorption and desorption isotherms of recycled 2D-COF-5 measured at 77 K.

## VI. Scale-up experiment



To a 50 mL glass tube equipped with a magnetic stir bar was charged with 1-methylquinoxalin-2(1*H*)-one (**1a**, 3.5 mmol, 0.56 g), allylbenzene (**2a**, 7 mmol, 0.82 g), sodium trifluoromethanesulfinate (7 mmol, 1.09 g) and 2D-COF-5 (35 mg) in 20 mL 1,4-dioxane. The reaction mixture was then stirred under air with the blue LED irradiation (2\*40 W blue LEDs, 456 nm, the power density is 0.003 W/ cm<sup>2</sup>, and the distance between reactor and lamp is approximately 5 cm.) for 24 h at room temperature. Upon completion, the photocatalyst was removed by centrifugation and filtration. Then 50 mL deionized water was added into the remaining mixture. The aqueous layer was extracted with ethyl acetate (50 mL × 3). The organic layers were washed with saturated brine then dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. The residue was purified on silica gel (petroleum ether and ethyl acetate) to afford the desired product **4aa** (1.67 g, 69%).

# **VII. Control experiments**

## (a) Radical intermediate capture experiment



Figure S11. The HRMS spectrum of the TEMPO-CF<sub>3</sub> adduct.

To a 10 mL glass tube equipped with a magnetic stir bar was charged with 1-methylquinoxalin-2(1*H*)-one (**1a**, 0.1 mmol, 16 mg), allylbenzene (**2a**, 0.2 mmol, 24 mg), sodium trifluoromethanesulfinate (0.2 mmol, 31 mg), 2,2,6,6-tetramethyl-1-piperinedinyloxy (TEMPO, 0.3 mmol, 47 mg) and 2D-COF-5 (1 mg) in 2 mL 1,4-dioxane. The reaction mixture was then stirred under air with the blue LED irradiation (2\*40 W blue LEDs, 456 nm, the power density is 0.003 W/ cm<sup>2</sup>, and the distance between reactor and lamp is approximately 5 cm.) for 24 h at room temperature. The reaction was found to be totally suppressed by TLC analysis. The TEMPO-CF<sub>3</sub> adduct was detected by HRMS.

(b) Addition of stoichiometric benzoquinone or sodium azide under "standard conditions"



To a 10 mL glass tube equipped with a magnetic stir bar was charged with 1-methylquinoxalin-2(1*H*)-one (**1a**, 0.1 mmol, 16 mg), allylbenzene (**2a**, 0.2 mmol, 24 mg), sodium trifluoromethanesulfinate (0.2 mmol, 31 mg), benzoquinone (0.3 mmol, 32 mg) and 2D-COF-5 (1 mg) in 2 mL 1,4-dioxane. The reaction mixture was then stirred under air with the blue LED irradiation (2\*40 W blue LEDs, 456 nm, the power density is 0.003 W/ cm<sup>2</sup>, and the distance between reactor and lamp is approximately 5 cm.) for 24 h at room temperature. The reaction was found to be totally suppressed by TLC analysis.



To a 10 mL glass tube equipped with a magnetic stir bar was charged with 1-methylquinoxalin-2(1*H*)-one (**1a**, 0.1 mmol, 16 mg), allylbenzene (**2a**, 0.2 mmol, 24 mg), sodium trifluoromethanesulfinate (0.2 mmol, 31 mg), sodium azide (0.3 mmol, 20 mg) and 2D-COF-5 (1 mg) in 2 mL 1,4-dioxane. The reaction mixture was then stirred under air with the blue LED irradiation (2\*40 W blue LEDs, 456 nm, the power density is 0.003 W/ cm<sup>2</sup>, and the distance between reactor and lamp is approximately 5 cm.) for 24 h at room temperature. The reaction was found to be totally suppressed by TLC analysis.

#### **VIII. Competition experiments**



To a 10 mL glass tube equipped with a magnetic stir bar was charged with 1-methylquinoxalin-2(1*H*)-one (**1a**, 0.1 mmol, 16 mg), allylbenzene (**2a**, 0.1 mmol, 12 mg), styrene (**2b**, 0.1 mmol, 10 mg), sodium trifluoromethanesulfinate (0.2 mmol, 31 mg) and 2D-COF-5 (1 mg) in 2 mL 1,4-dioxane. The reaction mixture was then stirred under air with the blue LED irradiation (2\*40 W blue LEDs, 456 nm, the power density is 0.003 W/ cm<sup>2</sup>, and the distance between reactor and lamp is approximately 5 cm.) for 24 h at room temperature. Upon completion, the photocatalyst was removed by centrifugation and filtration. Then 10 mL deionized water was added into the remaining mixture. The aqueous layer was extracted with ethyl acetate (5 mL × 3). The organic layers were washed with saturated brine then dried (MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. The residue was purified on silica gel (petroleum ether and ethyl acetate) to afford the desired product **4aa** (4 mg, 12 %), **4ab** (8 mg, 48 %).



To a 10 mL glass tube equipped with a magnetic stir bar was charged with 1,5-dimethylquinoxalin-2(1*H*)one (**1b**, 0.05 mmol, 8 mg), 1-methyl-7-nitroquinoxalin-2(1*H*)-one (**1h**, 0.05 mmol, 10 mg), allylbenzene (**2a**, 0.1 mmol, 12 mg), sodium trifluoromethanesulfinate (0.2 mmol, 31 mg) and 2D-COF-5 (1 mg) in 2 mL 1,4dioxane. The reaction mixture was then stirred under air with the blue LED irradiation (2\*40 W blue LEDs, 456 nm, the power density is 0.003 W/ cm<sup>2</sup>, and the distance between reactor and lamp is approximately 5 cm.) for 24 h at room temperature. Upon completion, the photocatalyst was removed by centrifugation and filtration. Then 10 mL deionized water was added into the remaining mixture. The aqueous layer was extracted with ethyl acetate (5 mL × 3). The organic layers were washed with saturated brine then dried

(MgSO<sub>4</sub>), filtered, and concentrated under reduced pressure. The residue was purified on silica gel (petroleum ether and ethyl acetate) to afford the desired product **4ba** (12 mg, 67 %), **4ha** (5 mg, 25 %).

#### IX. Characterization data of compounds

#### 3-(4,4,4-trifluoro-1-phenylbutan-2-yl)-1-methylquinoxalin-2(1H)-one (4aa)<sup>7</sup>.



It was obtained as a yellow solid; yield: 29 mg (83%). HRMS (ESI) m/z:  $[M + H]^+$  Calcd for C<sub>19</sub>H<sub>18</sub>F<sub>3</sub>N<sub>2</sub>O 347.1373; found 347.1366. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 – 7.83 (m, 1H), 7.56 – 7.53 (m, 1H), 7.36 – 7.33 (m, 1H), 7.31 – 7.29 (m, 1H), 7.26 – 7.22 (m, 4H), 7.19 (t, *J* = 7.0 Hz, 1H), 4.18 – 4.12 (m, 1H), 3.69 (s, 3H), 3.22 – 3.17 (m, 1H), 3.11 – 2.99 (m, 1H), 2.83 – 2.78 (m, 1H), 2.38 – 2.28 (m, 1H). <sup>13</sup>C NMR (151 MHz,

CDCl<sub>3</sub>) *δ*160.16, 154.46, 138.68, 133.18, 132.60, 130.31, 130.11, 129.42, 128.64, 126.93 (q, *J* = 276.3 Hz), 126.69, 123.80, 113.77, 39.47, 37.95, 34.77 (d, *J* = 28.0 Hz), 29.31.<sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) *δ* -64.15.

#### 1,5-dimethyl-3-(4,4,4-trifluoro-1-phenylbutan-2-yl)quinoxalin-2(1*H*)-one (4ba).



It was obtained as a yellow solid; yield: 25 mg (70%). HRMS (ESI) m/z:  $[M + H]^+$  Calcd for C<sub>20</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub>O 361.1527; found 361.1523. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 (t, *J* = 7.9 Hz, 1H), 7.29 (dd, *J* = 13.4, 6.4 Hz, 4H), 7.25 – 7.22 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 1H), 4.26 – 4.19 (m, 1H), 3.72 (s, 3H), 3.27 (dd, *J* = 13.7, 5.9 Hz, 1H), 3.14 – 3.00 (m, 1H), 2.83 (dd, *J* = 13.7, 8.6 Hz, 1H), 2.70 (s,

3H), 2.45 – 2.32 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.02, 154.39, 138.91, 138.78, 133.27, 130.98, 130.05, 129.45, 128.57, 126.98(q, *J* = 278.8 Hz), 126.63, 125.07, 111.68, 39.55, 37.75, 34.89(q, *J* = 28.2 Hz), 29.43, 17.58. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -63.87.

#### 6-fluoro-1-methyl-3-(4,4,4-trifluoro-1-phenylbutan-2-yl)quinoxalin-2(1H)-one (4ca)<sup>7</sup>.



It was obtained as a yellow solid; yield: 25 mg (69%). HRMS (ESI) m/z:  $[M + H]^+$ Calcd for C<sub>19</sub>H<sub>17</sub>F<sub>3</sub>N<sub>2</sub>O 365.1277; found 365.1279. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 7.56 – 7.53 (m, 1H), 7.30 – 7.25 (m, 4H), 7.25 – 7.21 (m, 2H), 7.21 – 7.18 (m, 1H), 4.19 – 4.14 (m, 1H), 3.68 (s, 3H), 3.20 (dd, *J* = 13.6, 6.0 Hz, 1H), 3.09 – 2.98 (m, 1H), 2.83 – 2.79 (m, 1H), 2.40 – 2.30 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  161.78,

158.83(d, J = 244.4 Hz), 154.07, 138.45, 133.08(d, J = 11.3 Hz), 129.82(d, J = 2.0 Hz), 129.37, 128.65, 126.85(q, J = 278.5 Hz), 126.76, 117.53(d, J = 23.9 Hz), 115.48(d, J = 22.7 Hz), 114.86(d, J = 8.8 Hz), 39.41, 38.03, 34.76(q, J = 27.7 Hz), 29.54. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -64.16, -107.29.

#### 6-Chloro-3-(4,4,4-trifluoro-1-phenylbutan-2-yl)-1-methylquinoxalin-2(1H)-one (4da)<sup>7</sup>.



It was obtained as a yellow solid; yield: 25 mg (65%). HRMS (ESI) m/z:  $[M + H]^+$ Calcd for C<sub>19</sub>H<sub>17</sub>ClF<sub>3</sub>N<sub>2</sub>O 381.0981; found 381.0990. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.79 (d, J = 8.5 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.30 – 7.27 (m, 2H), 7.24 (d, J = 7.3 Hz, 3H), 4.20 – 4.13 (m, 1H), 3.68 (s, 3H), 3.24 – 3.19 (m, 1H), 3.12 – 2.98 (m, 1H), 2.85 (dd, J = 13.6, 8.8 Hz, 1H), 2.44 – 2.31 (m, 1H). <sup>13</sup>C NMR (101 MHz,

CDCl<sub>3</sub>) *δ* 160.31, 154.17, 138.45, 136.29, 134.02, 131.13, 131.07, 129.37, 128.66, 126.86(q, *J* = 277.6 Hz), 126.76, 124.19, 113.86, 39.44, 37.93, 34.81(q, *J* = 27.3 Hz), 29.42. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) *δ* -64.14.

#### 7-Chloro-3-(4,4,4-trifluoro-1-phenylbutan-2-yl)-1-methylquinoxalin-2(1H)-one (4ea).



It was obtained as a yellow solid; yield: 26 mg (69%). HRMS (ESI) m/z:  $[M + H]^+$ Calcd for C<sub>19</sub>H<sub>17</sub>ClF<sub>3</sub>N<sub>2</sub>O 381.0976; found 381.0990. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.76 (d, J = 2.1 Hz, 1H), 7.41 (dd, J = 8.9, 2.1 Hz, 1H), 7.16 (t, J = 7.0 Hz, 3H), 7.13 – 7.09 (m, 3H), 4.06 (q, J = 9.3 Hz, 1H), 3.58 (s, 3H), 3.09 (dd, J = 13.6, 6.0 Hz, 1H), 2.95 – 2.88 (m, 1H), 2.71 (dd, J = 13.6, 8.8 Hz, 1H), 2.30 – 2.19 (m, 1H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 161.69, 154.11, 138.41, 133.05, 131.86, 130.32, 129.43, 129.38, 129.16, 128.68, 126.83(q, *J* = 276.3 Hz), 126.79, 114.94, 39.45, 37.96, 34.81(q, *J* = 28.7 Hz), 29.51. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -64.15.

#### 7-bromo-1-methyl-3-(4,4,4-trifluoro-1-phenylbutan-2-yl)quinoxalin-2(1H)-one (4fa).



It was obtained as a yellow solid; yield: 23 mg (53%). HRMS (ESI) m/z:  $[M + H]^+$ Calcd for C<sub>19</sub>H<sub>17</sub>BrF<sub>3</sub>N<sub>2</sub>O 425.0476; found 425.0455. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 (d, J = 2.2 Hz, 1H), 7.54 (dd, J = 8.9, 2.2 Hz, 1H), 7.17 (d, J = 7.6 Hz, 2H), 7.12 (dd, J = 7.7, 3.6 Hz, 3H), 7.08 (d, J = 8.9 Hz, 1H), 4.09 – 4.03 (m, 1H), 3.57 (s, 3H), 3.11 – 3.07 (m, 1H), 2.96 – 2.88 (m, 1H), 2.71 (dd, J = 13.6, 8.8 Hz, 1H),

2.30 – 2.20 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  161.64, 154.09, 138.39, 133.34, 133.04, 132.46, 132.29, 129.37, 126.82(q, *J* = 277.8 Hz), 128.68, 126.79, 116.38, 115.24, 39.45, 37.93, 34.80(q, *J* = 27.2 Hz), 29.46. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -64.13.

4-methyl-3-oxo-2-(4,4,4-trifluoro-1-phenylbutan-2-yl)-3,4-dihydroquinoxaline-6-carbonitrile (4ga).



It was obtained as a yellow solid; yield: 20 mg (54%). HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>17</sub>F<sub>3</sub>N<sub>3</sub>O 372.1318; found 372.1326. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (d, *J* = 8.6 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.29 – 7.25 (m, 2H), 7.23 – 7.18 (m, 3H), 4.22 – 4.15 (m, 1H), 3.69 (s, 3H), 3.19 (dd, *J* = 13.6, 6.1 Hz, 1H), 3.07 – 2.97 (m, 1H), 2.82 (dd, *J* = 13.6, 8.8 Hz, 1H), 2.43 – 2.33 (m, 1H). <sup>13</sup>C

NMR (126 MHz, CDCl<sub>3</sub>) δ 163.95, 153.85, 138.06, 134.58, 133.53, 130.97, 129.31, 128.72, 126.91, 126.71(q, *J* = 277.2 Hz), 126.70, 118.19, 117.99, 113.44, 39.45, 38.17, 34.83(q, *J* = 27.7 Hz), 29.51. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -64.16.

#### 1-methyl-7-nitro-3-(4,4,4-trifluoro-1-phenylbutan-2-yl)quinoxalin-2(1H)-one (4ha).



It was obtained as a yellow solid; yield: 19 mg (48%). HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>17</sub>F<sub>3</sub>N<sub>3</sub>O<sub>3</sub> 392.1226; found 392.1217. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.26 – 8.15 (m, 2H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.21 (t, *J* = 6.2 Hz, 3H), 4.24 – 4.17 (m, 1H), 3.76 (s, 3H), 3.20 (dd, *J* = 13.6, 6.1 Hz, 1H), 3.08 – 2.99 (m, 1H), 2.84 (dd, *J* = 13.6, 8.8 Hz, 1H), 2.44 – 2.35 (m, 1H).

<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 164.60, 153.93, 147.99, 138.01, 135.80, 133.52, 131.10, 129.34, 128.77, 126.97, 126.71(q, *J* = 277.2 Hz), 118.39, 109.78, 39.50, 38.27, 34.88(q, *J* = 27.7 Hz), 29.82. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -64.17.

#### 1,6,7-trimethyl-3-(4,4,4-trifluoro-1-phenylbutan-2-yl)quinoxalin-2(1H)-one (4ia)<sup>7</sup>.



It was obtained as a yellow solid; yield: 26 mg (69%). MS (ESI) m/z:  $[M + H]^+$ Calcd for C<sub>21</sub>H<sub>22</sub>F<sub>3</sub>N<sub>2</sub>O 375.2; found 375.2. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.60 (s, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 6.2 Hz, 3H), 7.18 (t, *J* = 6.9 Hz, 1H), 7.06 (s, 1H), 4.17 – 4.11 (m, 1H), 3.66 (s, 3H), 3.22 – 3.18 (m, 1H), 3.07 – 3.00 (m, 1H), 2.84 – 2.80 (m, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 2.34 – 2.28 (m, 1H). <sup>13</sup>C NMR

(126 MHz, CDCl<sub>3</sub>)  $\delta$  158.75, 154.52, 140.12, 138.83, 132.68, 131.18, 131.04, 130.15, 129.40, 128.57, 126.98(q, *J* = 278.5 Hz), 126.59, 114.32, 39.45, 37.90, 34.82(q, *J* = 27.7 Hz), 29.16, 20.61, 19.21. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -64.08.

#### 1-propyl-3-(4,4,4-trifluoro-1-phenylbutan-2-yl)quinoxalin-2(1H)-one (4ja)<sup>7</sup>.



It was obtained as a yellow oil; yield: 27 mg (72%). MS (ESI) m/z:  $[M + H]^+$  Calcd for C<sub>21</sub>H<sub>22</sub>F<sub>3</sub>N<sub>2</sub>O 375.2; found 375.2. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.35 (dd, *J* = 17.9, 8.2 Hz, 2H), 7.31 – 7.25 (m, 4H), 7.24 – 7.21 (m, 1H), 4.27 – 4.18 (m, 3H), 3.23 (dd, *J* = 13.5, 6.2 Hz, 1H), 3.13 – 3.04 (m, 1H), 2.88 (dd, *J* = 13.5, 8.8 Hz, 1H), 2.45 – 2.32 (m, 1H), 1.84 – 1.74 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  160.21, 154.21, 138.68, 132.86, 132.34,

130.32, 130.18, 129.40, 128.61, 126.95(q, J = 278.8 Hz), 126.65, 123.55, 113.79, 43.95, 39.58, 37.90, 34.95(q, J = 27.3 Hz), 20.75, 11.40. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  -64.14.

#### 1-butyl-3-(4,4,4-trifluoro-1-phenylbutan-2-yl)quinoxalin-2(1*H*)-one (4ka).



It was obtained as a yellow oil; yield: 26 mg (67%). HRMS (ESI) m/z:  $[M + H]^+$  Calcd for C<sub>22</sub>H<sub>24</sub>F<sub>3</sub>N<sub>2</sub>O 389.1840; found 389.1844. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, J = 7.9 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.29 – 7.26 (m, 3H), 7.22 (dd, J = 13.1, 5.7 Hz, 2H), 4.26 (q, J = 7.2 Hz, 2H), 4.22 – 4.16 (m, 1H), 3.23 (dd, J = 13.5, 6.3 Hz, 1H), 3.14 – 3.04 (m, 1H), 2.88 (dd, J = 13.5, 8.8 Hz, 1H), 2.45 – 2.34 (m, 1H), 1.72 (q, J = 7.9, 7.1 Hz, 2H), 1.47 (q, J = 7.5 Hz, 2H), 1.02 (t, J = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  160.19, 154.16, 138.68, 132.88, 132.33, 130.32,

130.18, 129.40, 128.60, 126.95(q, J = 278.8 Hz), 126.42, 123.54, 113.77, 42.32, 39.60, 37.86, 34.95(q, J = 28.3 Hz), 29.43, 20.33, 13.91. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)  $\delta$  -64.14.

#### 1-pentyl-3-(4,4,4-trifluoro-1-phenylbutan-2-yl)quinoxalin-2(1H)-one (4la).



It was obtained as a yellow oil; yield: 28 mg (70%). HRMS (ESI) m/z:  $[M + H]^+$  Calcd for C<sub>23</sub>H<sub>26</sub>F<sub>3</sub>N<sub>2</sub>O 403.1997; found 403.1995. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.30 – 7.24 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 1H), 4.31 – 4.22 (m, 2H), 4.22 – 4.15 (m, 1H), 3.23 (dd, *J* = 13.5, 6.2 Hz, 1H), 3.15 – 3.01 (m, 1H), 2.88 (dd, *J* = 13.5, 8.8 Hz, 1H), 2.46 – 2.32 (m, 1H), 1.79 – 1.70 (m, 2H), 1.48 – 1.39 (m, 4H), 0.95 (t, *J* = 6.6 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  160.19, 154.15, 138.69, 132.88, 132.34, 130.33, 130.19, 129.41, 128.60, 126.95(q,

J = 278.8 Hz), 126.65, 123.53, 113.76, 42.53, 39.58, 37.89, 34.94(q, J = 28.3 Hz), 29.16, 27.09, 22.52, 14.09. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -64.13.

#### 6,7-dichloro-1-methyl-3-(4,4,4-trifluoro-1-phenylbutan-2-yl)quinoxalin-2(1H)-one (4ma).



It was obtained as a yellow solid; yield: 21 mg (53%). HRMS (ESI) m/z:  $[M + H]^+$ Calcd for C<sub>18</sub>H<sub>14</sub>ClF<sub>3</sub>N<sub>2</sub>O 401.0430; found 401.0426. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  12.33 (s, 1H), 7.97 (s, 1H), 7.42 (s, 1H), 7.26 – 7.23 (m, 2H), 7.19 – 7.13 (m, 3H), 4.23 – 4.17 (m, 1H), 3.17 (dd, *J* = 13.6, 7.0 Hz, 1H), 3.04 – 2.97 (m, 1H), 2.92 (dd, *J* = 13.6, 7.9 Hz, 1H), 2.49 – 2.39 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)

δ 162.43, 155.85, 138.12, 134.79, 131.71, 130.19, 130.02, 129.29, 128.73, 128.43, 126.94, 126.75(q, *J* = 277.2 Hz)117.02, 40.04, 36.90, 35.61(q, *J* = 27.7 Hz) <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -64.15.

#### 3-(4,4,4-trifluoro-1-phenylbutan-2-yl)quinoxalin-2(1H)-one (4na)<sup>7</sup>.



It was obtained as a yellow soild; yield: 24 mg (80%).MS (ESI) m/z:  $[M + H]^+$  Calcd for C<sub>18</sub>H<sub>16</sub>F<sub>3</sub>N<sub>2</sub>O 333.1; found 333.2. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  12.70 (s, 1H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.40 – 7.35 (m, 2H), 7.25 (d, *J* = 6.3 Hz, 4H), 7.18 – 7.14 (m, 1H), 4.27 – 4.21 (m, 1H), 3.25 (dd, *J* = 13.7, 6.5 Hz, 1H), 3.13 – 3.04 (m, 1H), 2.92 (dd, *J* = 13.7, 8.4 Hz, 1H), 2.48 – 2.38 (m, 1H). <sup>13</sup>C NMR (126 MHz,

CDCl<sub>3</sub>)  $\delta$  160.69, 156.40, 138.58, 132.81, 130.98, 129.37, 129.12, 128.66, 126.95(q, *J* = 277.2 Hz), 126.76, 124.43, 115.98, 39.77, 36.96, 35.3(q, *J* = 27.7 Hz). <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -64.12.

#### 1-allyl-3-(4,4,4-trifluoro-1-phenylbutan-2-yl)quinoxalin-2(1H)-one (40a).



It was obtained as a yellow oil; yield: 28 mg (76%). HRMS (ESI) m/z:  $[M + H]^+$  Calcd for C<sub>21</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub>O 373.1518; found 373.1522. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.28 (m, 2H), 7.26 (d, *J* = 4.2 Hz, 2H), 7.25 – 7.18 (m, 2H), 5.98 – 5.89 (m, 1H), 5.26 (d, *J* = 10.5 Hz, 1H), 5.07 (d, *J* = 17.3 Hz, 1H), 4.97 – 4.85 (m, 2H), 4.25 – 4.17 (m, 1H), 3.24 (dd, *J* = 13.5, 6.4 Hz, 1H), 3.16 – 3.02 (m, 1H), 2.91 (dd, *J* = 13.5, 8.7 Hz, 1H), 2.48 – 2.34 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.25, 154.01, 138.61, 132.76, 132.35, 130.54, 130.21, 130.17, 129.41, 128.61, 126.93(q, *J* = 277.8 Hz), 126.67, 123.75, 117.93, 114.32, 44.59, 39.58, 37.97, 35.04(q, *J* = 28.3 Hz). <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -64.10.

#### 1-(prop-2-yn-1-yl)-3-(4,4,4-trifluoro-1-phenylbutan-2-yl)quinoxalin-2(1H)-one (4pa).



It was obtained as a yellow soild; yield: 22 mg (58%). HRMS (ESI) m/z:  $[M + H]^+$  Calcd for C<sub>21</sub>H<sub>18</sub>F<sub>3</sub>N<sub>2</sub>O 371.1371; found 371.1360. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 (d, *J* = 7.9 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.24 – 7.18 (m, 3H), 5.11 – 4.97 (m, 2H), 4.17 – 4.12 (m, 1H), 3.21 (dd, *J* = 13.6, 5.9 Hz, 1H), 3.12 – 3.00 (m, 1H), 2.83 (dd, *J* = 13.6, 9.0 Hz, 1H), 2.41 – 2.33 (m, 1H), 2.30 (t, *J* = 2.3 Hz, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  160.05,

153.41, 138.51, 132.74, 131.62, 130.42, 130.23, 129.37, 128.66, 126.88(q, *J* = 277.8 Hz), 126.73, 124.18, 114.26, 77.37, 73.40, 39.44, 38.07, 34.671(q, *J* = 27.2 Hz), 31.72. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ -64.10.

#### 1-(3-hydroxypropyl)-3-(4,4,4-trifluoro-1-phenylbutan-2-yl)quinoxalin-2(1H)-one (4qa)<sup>8</sup>.



It was obtained as a yellow soild; yield: 27 mg (68%). HRMS (ESI) m/z:  $[M + H]^+$ Calcd for C<sub>21</sub>H<sub>22</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub> 391.1636; found 391.1628. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 7.92 (dd, J = 8.3, 1.2 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.41 (t, J = 7.4 Hz, 3H), 7.28 (d, J = 4.8 Hz, 2H), 7.23 (d, J = 6.9 Hz, 2H), 4.51 – 4.38 (m, 3H), 4.27 – 4.22 (m, 1H), 3.51 – 3.47 (m, 1H), 3.39 – 3.36 (m, 1H), 3.22 – 3.18 (m, 1H), 3.10 – 3.03 (m, 1H),

2.95 – 2.91 (m, 1H), 2.46 – 2.40 (m, 1H), 2.02 – 1.98 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  159.96, 155.20, 138.43, 133.21, 131.87, 130.54, 130.48, 129.34, 128.62, 126.87(q, *J* = 277.2 Hz), 126.73, 124.14, 113.86, 58.08, 39.90, 39.06, 37.54, 35.51(q, *J* = 27.7 Hz), 30.15. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -64.09.

#### 1-methyl-3-(3,3,3-trifluoro-1-phenylpropyl)quinoxalin-2(1H)-one (4ab)<sup>7</sup>.



It was obtained as a yellow soild; yield: 16 mg (47%). MS (ESI) m/z:  $[M + H]^+$ Calcd for C<sub>18</sub>H<sub>16</sub>F<sub>3</sub>N<sub>2</sub>O 333.1; found 333.2. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (d,  $^{2}CF_{3}$  J = 7.9 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.45 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.29 – 7.24 (m, 3H), 7.20 (t, J = 7.3 Hz, 1H), 5.08 (t, J = 6.9 Hz, 1H), 3.62 (s, 3H), 3.51 – 3.44 (m, 1H), 2.83 – 2.75 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ 

158.67, 154.19, 139.57, 133.30, 132.51, 130.35, 130.31, 128.78, 128.55, 127.45, 126.59(q, J = 277.2 Hz), 123.79, 113.74, 41.35(q, J = 1.3 Hz), 37.63(q, J = 27.7 Hz), 29.32. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -64.33.

#### 3-(3,3,3-trifluoro-1-(4-fluorophenyl)propyl)-1-methylquinoxalin-2(1H)-one (4ac)<sup>7</sup>.



It was obtained as a yellow soild; yield: 22 mg (64%). HRMS (ESI) m/z:  $[M + H]^+$ Calcd for C<sub>18</sub>H<sub>15</sub>F<sub>4</sub>N<sub>2</sub>O 351.1115 ; found 351.1122. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (dd, J = 8.0, 1.2 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.44 – 7.40 (m, 2H), 7.39 – 7.36 (m, 1H), 7.28 (d, J = 8.4 Hz, 1H), 6.96 (t, J = 8.7 Hz, 2H), 5.06 (t, J = 7.0 Hz, 1H), 3.64 (s, 3H), 3.45 – 3.35 (m, 1H), 2.84 – 2.75 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  162.22 (d, J = 245.9 Hz), 158.51, 154.16, 135.20 (d, J = 3.2 Hz), 133.32, 132.49, 130.51,

130.34, 130.16 (d, *J* = 8.1 Hz), 126.76 (q, *J* = 277.4 Hz), 123.90, 115.67 (d, *J* = 21.5 Hz), 113.82, 40.68(q, *J* = 2.8 Hz), 37.70 (q, *J* = 27.9 Hz), 29.36. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ -64.24, -115.24.

#### 3-(1-(4-bromophenyl)-3,3,3-trifluoropropyl)-1-methylquinoxalin-2(1H)-one (4ad)<sup>7</sup>.



It was obtained as a yellow soild; yield: 26 mg (64%). HRMS (ESI) m/z:  $[M + H]^+$  Calcd for C<sub>18</sub>H<sub>15</sub>BrF<sub>3</sub>N<sub>2</sub>O 411.0319 ; found 411.0314. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (dd, J = 8.0, 1.1 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.38 (t, J = 7.5 Hz, 3H), 7.31 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.4 Hz, 1H), 5.01 (t, J = 7.0 Hz, 1H), 3.63 (s, 3H), 3.42 – 3.33 (m, 1H), 2.81 – 2.74 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  158.16, 154.10, 138.48, 133.29, 132.45, 131.92, 130.60, 130.36, 130.30, 126.69(q, J = 277.8 Hz), 123.94, 121.58,

113.84, 40.91, 37.45(q, J = 28.7 Hz), 29.38. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -64.22.

#### 3-(3,3,3-trifluoro-1-(4-(trifluoromethyl)phenyl)propyl)-1-methylquinoxalin-2(1H)-one (4ae)<sup>7</sup>.



It was obtained as a yellow soild; yield: 20 mg (50%). HRMS (ESI) m/z:  $[M + H]^+$ Calcd for C<sub>19</sub>H<sub>15</sub>F<sub>6</sub>N<sub>2</sub>O 399.0927; found 399.0923. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 3H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 5.13 (t, *J* = 7.0 Hz, 1H), 3.64 (s, 3H), 3.46 – 3.39 (m, 1H), 2.87 – 2.79 (m, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  157.88, 154.10, 143.47, 133.29, 132.43, 130.75, 130.40, 129.74(q, *J* = 26.5 Hz), 128.96, 128.59(q, *J* = 262.1

Hz), 125.75(q, *J* = 3.0 Hz), 124.18(q, *J* = 252.0 Hz), 124.02, 113.88, 41.28(q, *J* = 2.6 Hz), 37.46(q, *J* = 28.2 Hz), 29.41. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ -62.59, -64.23.

#### 3-(4,4,4-trifluoro-1-(2-methoxyphenyl)butan-2-yl)-1-methylquinoxalin-2(1H)-one (4af)<sup>7</sup>.



It was obtained as a yellow soild; yield: 25 mg (66%). MS (ESI) m/z: [M + H]<sup>+</sup> Calcd for  $C_{20}H_{20}F_3N_2O_2$  377.2; found 377.2. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 (dd, J = 8.0, 1.3 Hz, 1H), 7.57 – 7.53 (m, 1H), 7.37 – 7.34 (m, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 4.15 - 4.09 (m, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.15 (dd, J = 13.8, 6.0 Hz, 1H), 3.08 – 3.00 (m, 1H), 2.77 (dd, J = 13.7, 8.9 Hz,

1H), 2.39 – 2.30 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  160.32, 158.42, 154.48, 133.18, 132.63, 130.68, 130.38, 130.26, 130.10, 126.99(q, J = 278.5 Hz), 123.77, 114.06, 113.76, 55.35, 38.65, 38.14(q, J = 27.7 Hz), 34.79, 29.30. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -64.13.

#### 1-methyl-3-(1,1,1-trifluoroheptan-3-yl)quinoxalin-2(1H)-one (4ag).



It was obtained as a yellow soild; yield: 19 mg (62%). HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub>O 313.1527; found 313.1533. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (d, J = 7.8 Hz, 1H), 7.54 (t, J = 7.7 Hz, 1H), 7.36 – 7.30 (m, 2H), 3.86 – 3.81 (m, 1H), 3.71 (s, 3H), 3.09 - 3.00 (m, 1H), 2.45 - 2.37 (m, 1H), 1.89 - 1.83 (m, 1H), 1.69 - 1.63 (m, 1H), 1.33 – 1.30 (m, 2H), 1.30 – 1.20 (m, 2H), 0.86 (t, J = 6.9 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  161.09, 154.60, 133.15, 132.64, 130.07, 130.13, 127.11(q, J = 277.2 Hz), 123.71, 113.72, 36.02(q, J = 25.2 Hz), 35.68, 33.66, 29.18, 29.30, 22.72, 14.00. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -64.40.

#### 1-methyl-3-(1,1,1-trifluorotridecan-3-yl)quinoxalin-2(1*H*)-one (4ah).



It was obtained as a yellow soild; yield: 15 mg (37%). HRMS (ESI) m/z:  $[M + H]^+$  Calcd for  $C_{22}H_{32}F_3N_2O$  397.2461; found 397.2473. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 (d, J = 7.9 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 3.86 – 3.80

(m, 1H), 3.71 (s, 3H), 3.10 – 2.98 (m, 1H), 2.46 – 2.35 (m, 1H), 1.37 – 1.20 (m, 18H), 0.86 (t, J = 7.0 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 161.12, 154.61, 133.16, 132.65, 130.09, 130.13, 127.12(q, J = 277.2 Hz), 123.71, 113.72, 36.02(q, J = 27.7 Hz), 36.26, 33.94, 32.02, 29.69, 29.65, 29.55, 29.43, 29.31, 27.06, 22.80, 14.22. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -64.39.

#### 1-methyl-3-(2-(trifluoromethyl)cyclohexyl)quinoxalin-2(1H)-one (4ai)<sup>7</sup>.



It was obtained as a yellow soild; yield: 16 mg (53%). MS (ESI) m/z:  $[M + H]^+$  Calcd for C<sub>16</sub>H<sub>18</sub>F<sub>3</sub>N<sub>2</sub>O 311.2; found 311.2. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.85 – 7.79 (m, 1H), 7.55 – 7.50 (m, 1H), 7.35 – 7.28 (m, 2H), 3.70 (s, 3H), 3.55 (t, *J* = 9.7 Hz, 1H), 3.11 – 3.00 (m, 1H), 2.16 – 2.10 (m, 1H), 1.94 – 1.88 (m, 2H), 1.86 – 1.81 (m, 1H), 1.76 –

1.70 (m, 1H), 1.52 – 1.40 (m, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  161.92, 154.51, 133.09, 132.79, 127.92(q, J = 280.9 Hz), 123.66, 113.70, 43.48(q, J = 23.9 Hz), 30.98, 29.26, 25.40, 25.18(q, J = 2.5 Hz), 24.52. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -69.95.

#### 1-methyl-3-(3-(trifluoromethyl)bicyclo[2.2.1]heptan-2-yl)quinoxalin-2(1H)-one (4aj)<sup>9</sup>.



It was obtained as a yellow soild; yield: 16 mg (50%). HRMS (ESI) m/z:  $[M + H]^+$ Calcd for C<sub>17</sub>H<sub>18</sub>F<sub>3</sub>N<sub>2</sub>O 323.1366; found 323.1358. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.87 - 7.84 (m, 1H), 7.55 - 7.51 (m, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 3.85 - 3.83 (m, 1H), 3.70 (s, 3H), 3.37 - 3.29 (m, 1H), 2.90 (s, 1H), 2.56 (d, *J* = 3.8

Hz, 1H), 1.98 (d, J = 9.7 Hz, 1H), 1.59 (t, J = 8.5 Hz, 1H), 1.44 (d, J = 9.6 Hz, 1H), 1.31 – 1.27 (m, 1H), 1.25 (dd, J = 9.1, 4.9 Hz, 1H), 1.13 – 1.07 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  158.09, 155.04, 133.24, 132.33, 130.31, 130.05, 128.04(q, J = 278.5 Hz), 123.67, 113.68, 46.03(q, J = 26.5 Hz), 45.71, 40.70, 39.70, 38.34, 29.75, 29.23, 22.86. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -69.90.

#### (Z/E)-1-methyl-3-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)quinoxalin-2(1H)-one (5aa)<sup>10</sup>.



It was obtained as a yellow solid; yield: 18 mg (55%). Z/E = 1.6:1. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>14</sub>F<sub>3</sub>N<sub>2</sub>O 331.1053; found 331.1059. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d, J = 7.7 Hz, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.34 (d, J = 7.7 Hz, 2H), 7.29 – 7.28 (m, 3H), 7.27 (d, 2H), 6.18 (d, J = 8.2 Hz, 1H), 3.61 (s, 3H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.19, 153.77, 147.31(q, J = 5.0 Hz), 136.35, 133.76, 132.68, 131.37, 130.98,

129.89, 128.97, 127.04, 124.10, 122.84(q, *J* = 272.2 Hz), 118.52(q, *J* = 34.2Hz), 113.99, 29.32. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) *δ* -58.35.

(Z/E)-3-(1-(4-(tert-butyl)phenyl)-3,3,3-trifluoroprop-1-en-1-yl)-1-methylquinoxalin-2(1H)-one (5ab).



It was obtained as a yellow solid; yield: 17 mg (44%). Z/E > 20:1. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>22</sub>F<sub>3</sub>N<sub>2</sub>O 387.1684; found 387.1676. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 (d, J = 8.0 Hz, 1H), 7.63 (t, J = 7.7 Hz, 1H), 7.40 (dd, J = 15.3, 7.7 Hz, 2H), 7.36 (s, 4H), 6.29 – 6.24 (m, 1H), 3.71 (s, 3H), 1.29 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$ 155.42, 153.82, 153.17, 146.93, 133.75, 133.27, 132.71, 131.29, 130.97, 126.72, 125.98, 124.08, 123.43(q, J = 272.6 Hz), 117.55(q, J = 34.0 Hz), 113.97, 34.85, 31.31,

29.35. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -58.17.

#### (Z/E)-3-(1-(4-bromophenyl)-3,3,3-trifluoroprop-1-en-1-yl)-1-methylquinoxalin-2(1H)-one (5ac).



It was obtained as a yellow solid; yield: 19 mg (46%). Z/E = 12:1. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>13</sub>BrF<sub>3</sub>N<sub>2</sub>O 409.0158; found 409.0156. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 7.2 Hz, 1H), 7.49 (d, J = 8.5 Hz, 2H), 7.43 (t, J = 7.7 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 8.5 Hz, 2H), 6.27 (q, J = 8.0 Hz, 1H), 3.71 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  154.46, 154.70, 153.56, 146.18, 135.23, 133.62, 132.52, 132.08, 131.47, 130.91, 128.51, 124.11, 122.49(q, J = 270.9

Hz), 118.99(q, J = 35.3 Hz), 113.92, 29.24. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -58.44.

# (*Z/E*)-1-methyl-3-(3,3,3-trifluoro-1-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)quinoxalin-2(1*H*)-one (5ad).



It was obtained as a yellow solid; yield: 21 mg (53%). Z/E > 20:1. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>13</sub>F<sub>6</sub>N<sub>2</sub>O 399.0932; found 399.0923. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 (dd, J = 8.0, 1.1 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.62 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H), 7.44 (t, J = 7.7 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 6.32 (q, J = 7.9 Hz, 1H), 3.71 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  154.34, 153.69, 146.27(q, J = 5.2 Hz), 140.02, 133.75, 132.67, 131.74, 131.71(q, J = 32.8 Hz), 131.07, 127.53, 125.98(q, J

= 3.78 Hz), 124.31, 123.93(q, *J* = 272.8 Hz), 122.46(q, *J* = 272.2 Hz), 120.56(q, *J* = 34.7 Hz), 114.09, 29.38. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -58.70, -62.84.





It was obtained as a yellow solid; yield: 22 mg (54%). Z/E = 12:1. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>18</sub>F<sub>3</sub>N<sub>2</sub>O 407.1366; found 407.1362. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 – 7.99 (m, 1H), 7.67 – 7.64 (m, 1H), 7.59 – 7.55 (m, 4H), 7.51 (d, J = 8.3 Hz, 2H), 7.43 (t, J = 7.7 Hz, 3H), 7.39 (d, J = 8.4 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 6.34 (q, J = 8.1 Hz, 1H), 3.72 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.16, 153.84, 146.85(q, J = 5.0 Hz), 142.79, 140.33, 131.41, 131.03, 128.97, 127.87, 127.71, 127.48, 127.23, 126.6(q, J = 272.2 Hz), 124.14, 118.29(q, J = 34.0 Hz), 114.01, 77.41, 77.16, 76.91,

29.36. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -58.19.

#### (Z/E)-3-(1-(4-(tert-butyl)phenyl)-3,3,3-trifluoroprop-1-en-1-yl)quinoxalin-2(1H)-one (5nb).



It was obtained as a yellow solid; yield: 18 mg (48%). Z/E = 12:1. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub>O 373.1527; found 373.1517. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  12.82 (s, 1H), 7.92 (dd, J = 8.1, 1.0 Hz, 1H), 7.51 (d, J = 7.2 Hz, 1H), 7.39 (d, J = 2.4Hz, 4H), 7.36 – 7.34 (m, 1H), 7.27 (d, J = 8.2 Hz, 1H), 6.36 (d, J = 8.2 Hz, 1H), 1.28 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.88, 155.83, 153.32, 145.90(q, J = 2.5 Hz), 133.41, 132.78, 131.53, 131.31, 129.80, 126.86, 125.99, 124.84, 124.66, 123.02(q,

J = 270.9 Hz), 117.78(q, J = 34.0 Hz), 116.34, 34.86, 31.29. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -58.29.

#### (Z/E)-3-(3,3,3-trifluoro-1-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)quinoxalin-2(1H)-one (5nd).



It was obtained as a yellow solid; yield: 17 mg (44%). Z/E > 20:1. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>11</sub>F<sub>6</sub>N<sub>2</sub>O 385.0775; found 385.0761. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  12.72 (s, 1H), 7.96 – 7.92 (m, 1H), 7.66 – 7.59 (m, 4H), 7.56 (dd, J = 15.5, 1.2 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.21 (d, J = 8.1 Hz, 1H), 6.40 (q, J = 7.9 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.69, 154.64, 145.22(q, J = 5.4 Hz), 140.17, 132.77, 131.84, 131.81(q, J = 32.8 Hz), 131.47, 130.00, 127.67, 125.99(q, J = 3.8 Hz), 125.02,

123.90(q, *J* = 273.4 Hz), 122.47(q, *J* =271.7 Hz), 121.98(q, *J* = 34.7 Hz), 116.21. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -58.86, -62.82.

#### (Z/E)-3-(1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl)quinoxalin-2(1H)-one(5nf).



It was obtained as a yellow solid; yield: 13 mg (37%). Z/E > 20:1. HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>11</sub>ClF<sub>3</sub>N<sub>2</sub>O 351.0512; found 351.0506. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  12.45 (s, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.41 (dd, J = 7.8, 4.4 Hz, 3H), 7.35 (d, J = 8.6 Hz, 2H), 7.19 (d, J = 8.1 Hz, 1H), 6.34 (d, J = 8.0 Hz, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  155.54, 155.06, 145.23, 136.18, 134.98, 132.72, 131.71, 131.46, 129.98, 129.29, 128.52, 125.89(q, J = 277.6 Hz), 124.91, 119.42(q, J

= 34.7 Hz), 116.15. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>)  $\delta$  -58.57.

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# X. Copies of NMR spectra





<sup>13</sup>C NMR Spectrum of Compound **4ba** (101 MHz, CDCl<sub>3</sub>)



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: f1 (ppm)









 $^{19}\mathsf{F}$  NMR Spectrum of Compound **4ea** (565 MHz, CDCl\_3)



<sup>1</sup>H NMR Spectrum of Compound **4fa** (500 MHz, CDCl<sub>3</sub>)





20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22( f1 (ppm)













ÇF₃






20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2 f1 (ppm)





O ÇF3 





20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2 f1 (ppm)







13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 f1 (ppm)



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2 f1 (ppm)



S44





20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2 f1 (ppm)







<sup>19</sup>F NMR Spectrum of Compound **4qa** (471 MHz, CDCl<sub>3</sub>)



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: f1 (ppm)











20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)



<sup>19</sup>F NMR Spectrum of Compound **4ae** (565 MHz, CDCl<sub>3</sub>)











20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: f1 (ppm)













ÇF₃

-64.



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: f1 (ppm)

2D-NOESY Spectrum of Compound **5aa** (500 MHz,  $CDCl_3$ )





S64





20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: 11 (ppm)

2D-NOESY Spectrum of Compound **5ab** (500 MHz, CDCl<sub>3</sub>)

-3 ÇF₃ -2 -1 0 1 - 2 - 3 f1 (ppm) 4 - 5 - 6 7 - 8 9 - 10 - 11 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 f2 (ppm)



 $^{19}\mathrm{F}$  NMR Spectrum of Compound **5ac** (565 MHz, CDCl\_3)



## 2D-NOESY Spectrum of Compound **5ac** (500 MHz, CDCl<sub>3</sub>)









2D-NOESY Spectrum of Compound 5ad (500 MHz, CDCl<sub>3</sub>)





 $^{19}\mathsf{F}$  NMR Spectrum of Compound **5ae** (471 MHz, CDCl\_3)



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2' f1 (ppm)

2D-NOESY Spectrum of Compound 5ae (500 MHz,  $\text{CDCl}_3\text{)}$ 





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




20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: f1 (ppm)

2D-NOESY Spectrum of Compound  ${\bf 5nb}$  (500 MHz, CDCl\_3)













20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: f1 (ppm)

2D-NOESY Spectrum of Compound **5nd** (500 MHz, CDCl<sub>3</sub>)





 $^{19}\mathsf{F}$  NMR Spectrum of Compound **5nf** (565 MHz, CDCl\_3)



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22( f1 (ppm)

2D-NOESY Spectrum of Compound **5nf** (500 MHz, CDCl<sub>3</sub>)

