

## Supporting Information

### Visible-light induced trifluoromethylation/cyclization cascade to access CF<sub>3</sub>-containing pyrazolones by EDA complex

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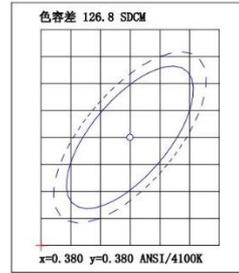
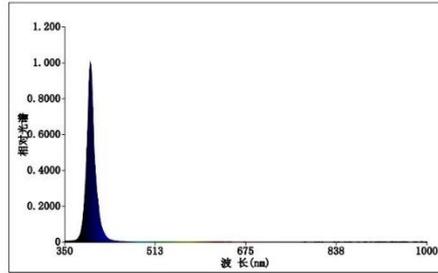
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## General information

All reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques, unless otherwise indicated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. 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) or iodine. NMR spectra were recorded on Bruker DRX-400 at 400 MHz for  $^1\text{H}$  NMR, 101 MHz for  $^{13}\text{C}$  NMR and 376 MHz for  $^{19}\text{F}$  NMR, respectively, in  $\text{CDCl}_3$  with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for  $^1\text{H}$  NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift ( $\delta$ , ppm). Mass spectrometric data were obtained using Bruker Apex IV RTMS. The N-methacryloyl hydrazones **1** were prepared according to literature procedures from commercially available substrates. <sup>[1]</sup>

The photochemical reaction was carried out under visible light irradiation by a 20W 390-400 nm purple LED. This purple LED was purchased from Xuzhou Aijia Electronic Technology Co., Ltd. The reaction vessel is a Schlenk tube. The distance between the tube and lamp is about 5.0 cm, and no filter is applied. Fans are employed to maintain the reaction temperature being around ambient temperature  $\sim 25^\circ\text{C}$ . The purple LED's energy peak wavelength is 396.2 nm and the peak width at half-height is 13.1 nm.



**颜色参数:**

色品坐标(2度):  $x=0.1846$   $y=0.0454/u'=0.2325$   $v'=0.1287$   $duv=-1.875e-001$

相关色温:  $T_c=100000K$  主波长:  $\lambda_d=436.9nm$  色纯度: Purity=88.9%

色比: R=10.3% G=69.8% B=19.9% 峰值波长:  $\lambda_p=396.2nm$  半宽度:  $\Delta\lambda_d=13.1nm$

显色指数:  $R_a=34.5$

R1 =79.33      R2 =37.93      R3 =-5.46      R4 =10.42      R5 =69.36

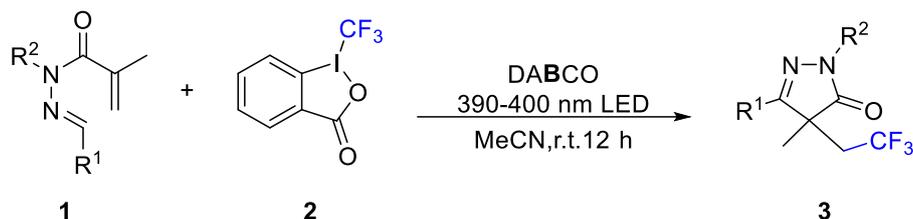
R6 =24.07      R7 =25.89      R8 =34.56      R9 =39.27      R10=-44.01

R11=26.79      R12=-86.57      R13=46.96      R14=45.93      R15=54.68

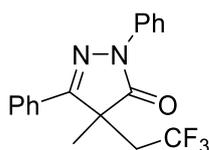
TM30 参数:  $R_f = 0.0$ ,  $R_g: -70.4$

The spectral distribution of 20 W 390-400 nm purple LED

### General procedure for the visible-light induced trifluoromethylation/cyclization cascade to access CF<sub>3</sub>-containing pyrazolones

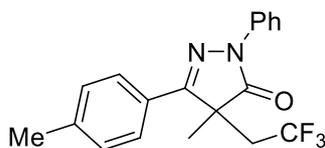


Under a nitrogen atmosphere, an oven-dried resealable Schlenk tube containing a magnetic stir bar was charged with N-methacryloyl hydrazones (0.2 mmol, 1.0 equiv.), Togni's reagent II (0.4 mmol, 2.0 equiv.), DABCO (0.4 mmol, 2.0 equiv.), and anhydrous acetonitrile (2.0 mL). The mixture was stirred at room temperature for 12 hours under irradiation with 390–400 nm LEDs. After completion of the reaction (as monitored by TLC), the mixture was diluted with water (10 mL) and extracted three times with ethyl acetate (10 mL each). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography using a gradient elution of petroleum ether and ethyl acetate (from 10:1 to 4:1 v/v) to afford the target product.



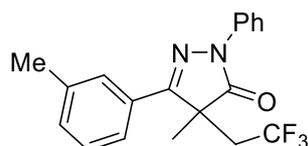
#### 4-methyl-2,5-diphenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3a)

Colorless oil (91% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 – 7.99 (m, 2H), 7.88 – 7.85 (m, 2H), 7.48 – 7.43 (m, 5H), 7.27 – 7.22 (m, 1H), 3.07 – 2.89 (m, 2H), 1.65 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.5, 159.0, 138.0, 130.69, 130.66, 129.07, 129.05, 126.4, 125.8, 124.7 (q, *J* = 279.8 Hz), 119.4, 49.6 (q, *J* = 2.2 Hz), 40.8 (q, *J* = 29.3 Hz), 23.9; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.27; HRMS (ESI) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>16</sub>F<sub>3</sub>N<sub>2</sub>O<sup>+</sup> 333.1209; found 333.1212.



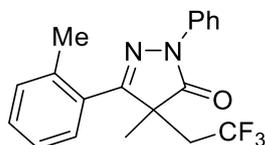
**4-methyl-2-phenyl-5-(p-tolyl)-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3b)**

White solid (81% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 – 7.99 (m, 2H), 7.77 (d,  $J = 8.3$  Hz, 2H), 7.47 – 7.43 (m, 5H), 7.29 – 7.23 (m, 3H), 3.09 – 2.87 (m, 2H), 2.42 (s, 3H), 1.64 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.4, 159.1, 141.1, 138.0, 129.8, 129.0, 127.9, 126.4, 125.7, 124.7 (q,  $J = 279.8$  Hz), 119.4, 49.6 (q,  $J = 2.4$  Hz), 40.8 (q,  $J = 29.4$  Hz), 24.0, 21.6;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.28; **HRMS** (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{N}_2\text{O}^+$  347.1366; found 347.1365.



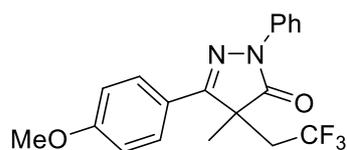
**4-methyl-2-phenyl-5-(m-tolyl)-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3c)**

Colorless oil (77% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 – 7.99 (m, 2H), 7.73 (s, 1H), 7.60 (d,  $J = 7.8$  Hz, 1H), 7.47 – 7.43 (m, 2H), 7.35 (d,  $J = 7.6$  Hz, 1H), 7.29 – 7.22 (m, 2H), 3.08 – 2.89 (m, 2H), 2.43 (s, 3H), 1.65 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.5, 159.2, 138.9, 138.0, 131.6, 130.6, 129.1, 128.9, 127.0, 125.8, 124.7 (q,  $J = 279.8$  Hz), 123.5, 119.4, 49.7 (q,  $J = 2.4$  Hz), 40.8 (q,  $J = 29.2$  Hz), 24.0, 21.7;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.24; **HRMS** (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{N}_2\text{O}^+$  347.1366; found 347.1369.



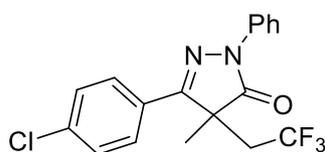
**4-methyl-2-phenyl-5-(o-tolyl)-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3d)**

Orange oil (81% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 – 7.99 (m, 2H), 7.52 (dd,  $J = 7.5, 1.4$  Hz, 1H), 7.48 – 7.44 (m, 2H), 7.40 – 7.36 (m, 2H), 7.33 – 7.30 (m, 1H), 7.27 – 7.23 (m, 1H), 3.00 – 2.78 (m, 2H), 2.67 (s, 3H), 1.67 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 159.9, 139.2, 138.1, 132.8, 129.8, 129.6, 129.1, 127.3, 125.9, 125.6, 124.7 (q,  $J = 279.8$  Hz), 119.1, 51.0 (q,  $J = 2.4$  Hz), 40.3 (q,  $J = 29.4$  Hz), 24.3, 23.3;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.88; **HRMS** (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{N}_2\text{O}^+$  347.1366; found 347.1369.



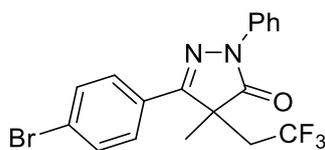
**5-(4-methoxyphenyl)-4-methyl-2-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3e)**

Colorless oil (76% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 – 8.00 (m, 2H), 7.82 (d,  $J = 8.9$  Hz, 2H), 7.47 – 7.43 (m, 2H), 7.27 – 7.22 (m, 1H), 6.99 (d,  $J = 8.9$  Hz, 2H), 3.87 (s, 3H), 3.09 – 2.85 (m, 2H), 1.64 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 161.5, 158.8, 138.1, 129.0, 128.0, 125.6, 124.7 (q,  $J = 278.8$  Hz), 123.3, 119.3, 114.4, 55.5, 49.6 (q,  $J = 2.4$  Hz), 40.9 (q,  $J = 29.3$  Hz), 24.0;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.27; **HRMS** (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_2^+$  363.1315; found 363.1320.



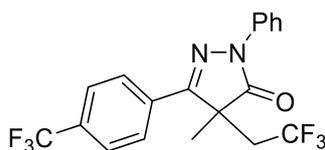
**5-(4-chlorophenyl)-4-methyl-2-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3f)**

Colorless oil (74% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 – 7.97 (m, 2H), 7.83 – 7.79 (m, 2H), 7.48 – 7.43 (m, 4H), 7.28 – 7.24 (m, 1H), 3.11 – 2.83 (m, 2H), 1.64 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 157.9, 137.8, 136.8, 129.4, 129.12, 129.10, 127.6, 125.9, 124.6 (q,  $J = 278.8$  Hz), 119.4, 49.5 (q,  $J = 2.1$  Hz), 40.8 (q,  $J = 29.4$  Hz), 23.8;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.33; **HRMS** (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{15}\text{ClF}_3\text{N}_2\text{O}^+$  367.0820; found 367.0822.



**5-(4-bromophenyl)-4-methyl-2-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3g)**

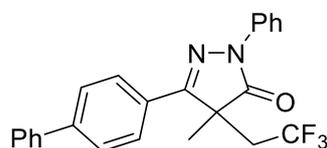
White solid (69% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 – 7.97 (m, 2H), 7.74 (d,  $J = 8.7$  Hz, 2H), 7.61 (d,  $J = 8.7$  Hz, 2H), 7.46 (dd,  $J = 8.6, 7.3$  Hz, 2H), 7.28 – 7.24 (m, 1H), 3.11 – 2.83 (m, 2H), 1.64 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 158.0, 137.8, 132.3, 129.6, 129.1, 127.8, 125.9, 125.1, 124.6 (q,  $J = 279.8$  Hz), 119.4, 49.4 (q,  $J = 2.3$  Hz), 40.8 (q,  $J = 29.4$  Hz), 23.8;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.32; **HRMS** (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{15}\text{BrF}_3\text{N}_2\text{O}^+$  411.0314; found 411.0320.



**4-methyl-2-phenyl-4-(2,2,2-trifluoroethyl)-5-(4-(trifluoromethyl)phenyl)-2,4-dihydro-3H-pyrazol-3-one (3h)**

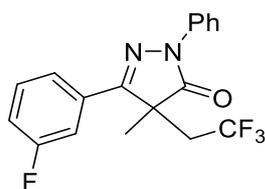
White solid (63% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.96 (m, 4H), 7.73 (d,  $J = 8.3$  Hz, 2H), 7.49 – 7.43 (m, 2H), 7.28 – 7.24 (m, 1H), 3.10 – 2.88 (m, 2H), 1.65 (s,

3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 157.5, 137.7, 133.9, 132.2 (q,  $J = 32.8$  Hz), 129.2, 126.6, 126.1, 126.0 (q,  $J = 4.0$  Hz), 124.6 (q,  $J = 279.8$  Hz), 123.8 (q,  $J = 273.7$  Hz), 119.5, 49.4 (q,  $J = 2.4$  Hz), 40.8 (q,  $J = 29.4$  Hz), 23.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.87, -63.37; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{15}\text{F}_6\text{N}_2\text{O}^+$  401.1083; found 401.1082.



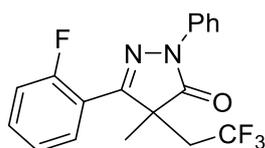
**5-([1,1'-biphenyl]-4-yl)-4-methyl-2-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3i)**

Orange oil (51% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 – 8.01 (m, 2H), 7.97 – 7.93 (m, 2H), 7.72 – 7.69 (m, 2H), 7.66 – 7.33 (m, 2H), 7.51 – 7.45 (m, 4H), 7.43 – 7.38 (m, 1H), 7.28 – 7.24 (m, 1H), 3.14 – 2.92 (m, 2H), 1.69 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.5, 158.7, 143.4, 140.0, 138.0, 129.5, 129.1, 128.1, 127.7, 127.2, 126.8, 125.8, 124.6 (q,  $J = 280.8$  Hz), 119.4, 49.6, 40.8 (q,  $J = 29.4$  Hz), 24.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.24; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{24}\text{H}_{20}\text{F}_3\text{N}_2\text{O}^+$  409.1522; found 409.1527.



**5-(3-fluorophenyl)-4-methyl-2-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3j)**

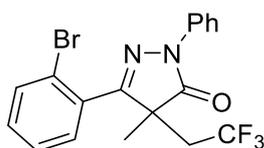
Colorless oil (58% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.96 (m, 2H), 7.63 – 7.57 (m, 2H), 7.47 – 7.41 (m, 3H), 7.27 – 7.23 (m, 1H), 7.19 – 7.14 (m, 1H), 3.10 – 2.84 (m, 2H), 1.64 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 163.1 (d,  $J = 247.1$  Hz), 157.8, 137.8, 132.7 (d,  $J = 7.9$  Hz), 130.7 (d,  $J = 8.2$  Hz), 129.1, 126.0, 124.6 (q,  $J = 278.8$  Hz), 122.0 (d,  $J = 3.3$  Hz), 119.4, 117.7 (d,  $J = 21.3$  Hz), 113.3 (d,  $J = 23.5$  Hz), 49.5 (q,  $J = 2.2$  Hz), 40.8 (q,  $J = 29.5$  Hz), 23.8;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.33, -111.18; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{15}\text{F}_4\text{N}_2\text{O}^+$  351.1115; found 351.1116.



**5-(2-fluorophenyl)-4-methyl-2-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3k)**

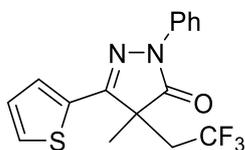
Orange oil (83% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.25 (d,  $J = 7.9, 1.8$  Hz, 1H),

8.00 – 7.97 (m, 2H), 7.48 – 7.43 (m, 3H), 7.28 – 7.25 (m, 2H), 7.19 – 7.14 (m, 1H), 3.10 – 2.84 (m, 2H), 1.58 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.7, 159.8 (d,  $J = 250.4$  Hz), 156.2 (d,  $J = 2.8$  Hz), 137.8, 132.4 (d,  $J = 79.1$  Hz), 129.4 (d,  $J = 3.8$  Hz), 129.1, 125.9, 125.1 (q,  $J = 279.8$  Hz), 124.9 (d,  $J = 2.9$  Hz), 119.4, 118.6 (d,  $J = 12.3$  Hz), 116.9 (d,  $J = 24.1$  Hz), 50.4 (q,  $J = 2.2$  Hz), 39.8 (dq,  $J = 29.2, 10.9$  Hz), 22.3 (d,  $J = 7.6$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.71, -109.93; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{15}\text{F}_4\text{N}_2\text{O}^+$  351.1115; found 351.1118.



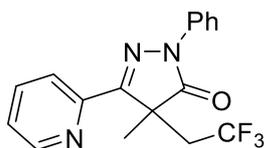
**5-(2-bromophenyl)-4-methyl-2-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3l)**

White solid (54% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 – 7.95 (m, 2H), 7.78 (dd,  $J = 8.1, 1.2$  Hz, 1H), 7.48 – 7.41 (m, 4H), 7.36 – 7.32 (m, 1H), 7.27 – 7.23 (m, 1H), 2.90 – 2.67 (m, 2H), 1.54 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 159.0, 137.8, 134.8, 131.4, 131.3, 129.5, 129.1, 127.6, 126.2, 124.8 (q,  $J = 279.8$  Hz), 123.8, 119.5, 51.4 (q,  $J = 2.4$  Hz), 39.2 (q,  $J = 29.5$  Hz), 21.8;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.38; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{15}\text{BrF}_3\text{N}_2\text{O}^+$  411.0314; found 411.0312.



**4-methyl-2-phenyl-5-(thiophen-2-yl)-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3m)**

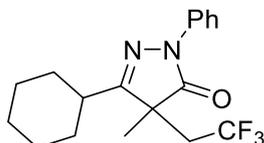
Orange oil (67% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 – 7.96 (m, 2H), 7.49 – 7.42 (m, 4H), 7.27 – 7.23 (m, 1H), 7.14 (dd,  $J = 5.1, 3.7$  Hz, 1H), 3.07 – 2.85 (m, 2H), 1.64 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 155.3, 137.8, 134.0, 129.1, 128.6, 127.9, 127.1, 126.0, 124.6 (q,  $J = 279.8$  Hz), 119.4, 49.7 (q,  $J = 2.3$  Hz), 40.7 (q,  $J = 29.5$  Hz), 24.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.21; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{14}\text{F}_3\text{N}_2\text{OS}^+$  339.0773; found 339.0773.



**4-methyl-2-phenyl-5-(pyridin-2-yl)-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3n)**

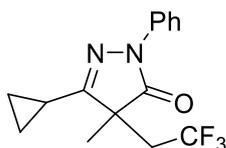
White solid (64% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.61 (dd,  $J = 4.8, 1.3$  Hz, 1H),

8.20 (d,  $J = 8.0$  Hz, 1H), 8.01 – 7.99 (m, 2H), 7.79 (td,  $J = 7.8, 1.8$  Hz, 1H), 7.46 (dd,  $J = 8.6, 7.4$  Hz, 2H), 7.34 – 7.30 (m, 1H), 7.27 – 7.24 (m, 1H), 3.67 – 3.56 (m, 1H), 2.94 – 2.83 (m, 1H), 1.73 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.3, 159.5, 150.3, 149.1, 138.0, 136.6, 129.1, 125.8, 125.3 (q,  $J = 279.8$  Hz), 124.6, 121.0, 119.4, 49.8 (q,  $J = 2.5$  Hz), 39.9 (q,  $J = 28.8$  Hz), 23.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.94; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{F}_3\text{N}_3\text{O}^+$  334.1162; found 334.1159.



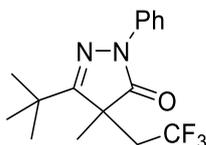
**5-cyclohexyl-4-methyl-2-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3o)**

Colorless oil (48% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 – 7.89 (m, 2H), 7.42 – 7.38 (m, 2H), 7.21 – 7.17 (m, 1H), 2.83 – 2.72 (m, 1H), 2.63 – 2.52 (m, 1H), 2.40 – 2.33 (m, 1H), 2.01 – 1.74 (m, 7H), 1.41 (s, 3H), 1.38 – 1.31 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.6, 168.0, 138.2, 128.9, 125.3, 124.7 (q,  $J = 278.8$  Hz), 119.1, 50.7 (q,  $J = 2.5$  Hz), 39.5 (q,  $J = 28.8$  Hz), 38.4, 33.7, 29.9, 26.5, 26.2, 25.9, 22.8;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.12; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{22}\text{F}_3\text{N}_2\text{O}^+$  339.1679; found 339.1677.



**5-cyclopropyl-4-methyl-2-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3p)**

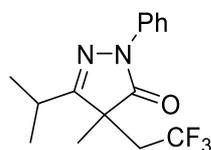
Colorless oil (54% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 – 7.85 (m, 2H), 7.40 – 7.36 (m, 2H), 7.21 – 7.17 (m, 1H), 2.91 – 2.79 (m, 1H), 2.68 – 2.57 (m, 1H), 1.59 – 1.52 (m, 1H), 1.44 (s, 3H), 1.33 – 1.26 (m, 1H), 1.06 – 1.00 (m, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.9, 166.2, 138.1, 128.9, 125.2, 124.8 (q,  $J = 279.8$  Hz), 119.0, 50.7 (q,  $J = 2.4$  Hz), 39.3 (q,  $J = 29.6$  Hz), 22.6, 10.6, 8.7, 7.8;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.12; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{16}\text{F}_3\text{N}_2\text{O}^+$  297.1209; found 297.1214.



**5-(tert-butyl)-4-methyl-2-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3q)**

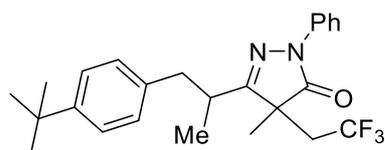
Colorless oil (71% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 – 7.88 (m, 2H), 7.41 – 7.37 (m, 2H), 7.21 – 7.16 (m, 1H), 2.82 – 2.74 (m, 2H), 1.49 (s, 3H), 1.38 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 169.6, 138.1, 128.9, 125.3, 124.7 (q,  $J = 278.8$  Hz),

119.1, 50.1 (q,  $J = 2.3$  Hz), 40.8 (q,  $J = 28.8$  Hz), 36.8, 29.8, 22.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.05; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{20}\text{F}_3\text{N}_2\text{O}^+$  313.1522; found 313.1526.



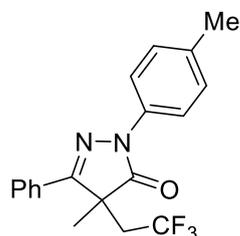
**5-isopropyl-4-methyl-2-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3r)**

Colorless oil (66% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 – 7.90 (m, 2H), 7.43 – 7.39 (m, 2H), 7.22 – 7.17 (m, 1H), 2.82 – 2.71 (m, 2H), 2.60 – 2.54 (m, 1H), 1.43 (s, 3H), 1.37 (d,  $J = 6.8$  Hz, 3H), 1.31 (d,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 168.7, 138.1, 128.9, 125.3, 124.7 (q,  $J = 278.8$  Hz), 119.1, 50.7 (q,  $J = 2.2$  Hz), 39.6 (q,  $J = 29.4$  Hz), 36.8, 29.8, 22.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.14; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{18}\text{F}_3\text{N}_2\text{O}^+$  299.1366; found 299.1371.



**5-(1-(4-(tert-butyl)phenyl)propan-2-yl)-4-methyl-2-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3s)**

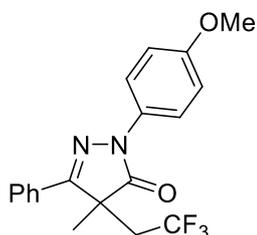
Colorless oil (86% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (dd,  $J = 8.6, 1.2$  Hz, 2H), 7.43 (dd,  $J = 8.6, 7.3$  Hz, 2H), 7.34 (d,  $J = 8.2$  Hz, 2H), 7.25 – 7.19 (m, 1H), 7.15 (d,  $J = 8.3$  Hz, 2H), 3.16 (dd,  $J = 13.5, 3.7$  Hz, 1H), 2.89 (d,  $J = 13.4, 10.6$  Hz, 1H), 2.82 – 2.74 (m, 1H), 2.72 – 2.48 (m, 2H), 1.44 (s, 3H), 1.32 (s, 9H), 1.22 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 168.4, 149.4, 138.1, 137.0, 129.1, 129.0, 125.44, 125.43, 124.8 (q,  $J = 278.8$  Hz), 119.2, 50.9 (q,  $J = 2.4$  Hz), 39.8, 39.2 (q,  $J = 29.4$  Hz), 35.9, 34.5, 31.5, 22.6, 20.1;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.71; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{25}\text{H}_{30}\text{F}_3\text{N}_2\text{O}^+$  431.2305; found 431.2313.



**4-methyl-5-phenyl-2-(p-tolyl)-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3t)**

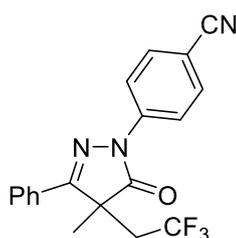
Colorless oil (75% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 – 7.85 (m, 4H), 7.47 – 7.45 (m, 3H), 7.25 (d,  $J = 8.3$  Hz, 2H), 3.06 – 2.88 (m, 2H), 2.37 (s, 3H), 1.64 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 158.9, 135.6, 130.7, 130.6, 129.6, 129.1, 126.4,

124.7 (q,  $J = 279.8$  Hz), 119.5, 49.5 (q,  $J = 2.3$  Hz), 40.8 (q,  $J = 29.3$  Hz), 23.9, 21.1;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.27; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{N}_2\text{O}^+$  347.1366; found 347.1368.



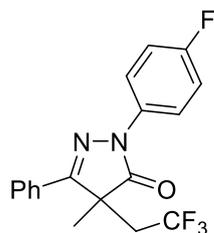
**2-(4-methoxyphenyl)-4-methyl-5-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3u)**

Orange oil (59% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 – 7.84 (m, 4H), 7.48 – 7.46 (m, 3H), 6.99 – 6.97 (m, 2H), 3.84 (s, 3H), 3.06 – 2.81 (m, 2H), 1.65 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 158.9, 157.6, 131.3, 130.7, 130.6, 128.9, 126.4, 124.7 (q,  $J = 279.8$  Hz), 121.3, 114.2, 55.6, 49.4 (q,  $J = 2.4$  Hz), 40.8 (q,  $J = 29.4$  Hz), 23.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.21; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_2^+$  363.1315; found 363.1310.



**4-(4-methyl-5-oxo-3-phenyl-4-(2,2,2-trifluoroethyl)-4,5-dihydro-1H-pyrazol-1-yl)benzonitrile (3v)**

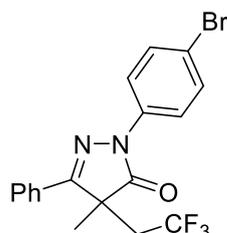
Colorless oil (71% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 – 8.21 (m, 2H), 7.89 – 7.86 (m, 2H), 7.75 – 7.73 (m, 2H), 7.52 – 7.49 (m, 3H), 3.08 – 2.93 (m, 2H), 1.68 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.8, 160.0, 141.4, 133.3, 131.2, 130.1, 129.2, 126.6, 124.5 (q,  $J = 279.8$  Hz), 118.9, 108.5, 49.9, (q,  $J = 2.4$  Hz), 40.9 (q,  $J = 29.4$  Hz), 23.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.26; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{15}\text{F}_3\text{N}_2\text{O}^+$  358.1162; found 358.1168.



**2-(4-fluorophenyl)-4-methyl-5-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3w)**

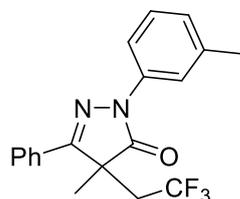
Orange oil (81% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 – 7.94 (m, 2H), 7.86 – 7.83

(m, 2H), 7.48 – 7.46 (m, 3H), 7.15 – 7.10 (m, 3H), 3.08 – 2.87 (m, 2H), 1.65 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.3, 160.4 (d,  $J = 246.4$  Hz), 159.2, 134.1 (d,  $J = 2.9$  Hz), 130.8, 130.5, 129.1, 126.4, 124.7 (q,  $J = 278.8$  Hz), 121.2 (d,  $J = 8.1$  Hz), 115.8 (d,  $J = 22.6$  Hz), 49.6 (q,  $J = 2.2$  Hz), 40.8 (q,  $J = 29.3$  Hz), 23.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.31, -116.21; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{15}\text{F}_4\text{N}_2\text{O}^+$  351.1115; found 351.1118.



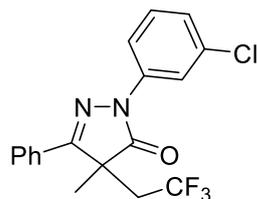
**2-(4-bromophenyl)-4-methyl-5-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3x)**

Colorless oil (59% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 – 7.92(m, 2H), 7.88 – 7.85 (m, 2H), 7.58 – 7.55 (m, 3H), 7.50 – 7.47 (m, 3H), 3.09 – 2.88 (m, 2H), 1.66 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.4, 159.3, 137.0, 132.1, 130.9, 130.4, 129.1, 126.5, 124.6 (q,  $J = 279.8$  Hz), 120.7, 118.6, 49.7 (q,  $J = 2.4$  Hz), 40.8 (q,  $J = 29.4$  Hz), 23.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.30; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{15}\text{BrF}_3\text{N}_2\text{O}^+$  411.0314; found 411.0317.



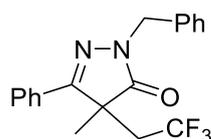
**4-methyl-5-phenyl-2-(m-tolyl)-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3y)**

Orange oil (66% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 – 7.85 (m, 2H), 7.83 – 7.77 (m, 2H), 7.48 – 7.45 (m, 3H), 7.33 (t,  $J = 7.8$  Hz, 1H), 7.07 – 7.05 (m, 1H), 3.06 – 2.89 (m, 2H), 2.42 (s, 3H), 1.64 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.4, 159.0, 139.0, 137.9, 130.7, 130.6, 129.0, 128.8, 126.6, 126.4, 124.7 (q,  $J = 278.8$  Hz), 120.0, 116.6, 49.6 (q,  $J = 2.2$  Hz), 40.8 (q,  $J = 29.2$  Hz), 23.9, 21.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.35; HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{N}_2\text{O}^+$  347.1366; found 347.1370.



**2-(3-chlorophenyl)-4-methyl-5-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (3z)**

Colorless oil (67% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (t,  $J = 2.0$  Hz, 1H), 7.98 – 7.96 (m, 1H), 7.87 – 7.85 (m, 2H), 7.50 – 7.46 (m, 3H), 7.36 (t,  $J = 8.1$  Hz, 1H), 7.22 – 7.19 (m, 1H), 3.07 – 2.87 (m, 2H), 1.65 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.5, 159.4, 139.0, 134.8, 130.9, 130.4, 130.1, 129.1, 126.5, 125.6, 124.6 (q,  $J = 278.8$  Hz), 119.2, 117.0, 49.8 (q,  $J = 2.2$  Hz), 40.8 (q,  $J = 29.2$  Hz), 23.9;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.27; **HRMS** (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{15}\text{ClF}_3\text{N}_2\text{O}^+$  367.0820; found 367.0824.

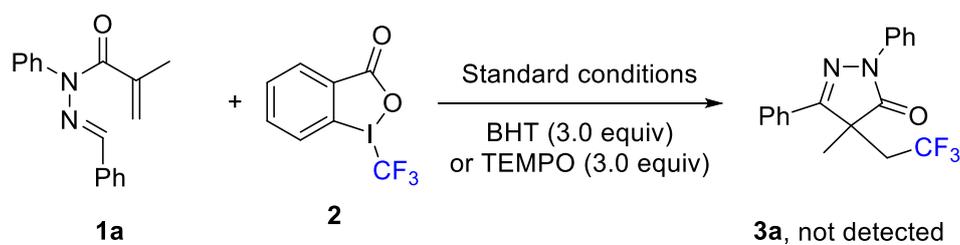


### 2-benzyl-4-methyl-5-phenyl-4-(2,2,2-trifluoroethyl)-2,4-dihydro-3H-pyrazol-3-one (**3aa**)

Orange oil (63% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 – 7.72 (m, 2H), 7.42 – 7.39 (m, 3H), 7.38 – 7.29 (m, 5H), 4.98 (d,  $J = 1.3$  Hz 2H), 2.99 – 2.82 (m, 2H), 1.55 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.7, 158.7, 136.3, 130.9, 130.3, 128.9, 128.7, 128.2, 127.8, 126.1, 124.7 (q,  $J = 278.8$  Hz), , 48.5, 48.2 (q,  $J = 2.3$  Hz), 40.3 (q,  $J = 29.2$  Hz), 23.8;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.27; **HRMS** (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{N}_2\text{O}^+$  347.1366; found 347.1367.

## Mechanism Study

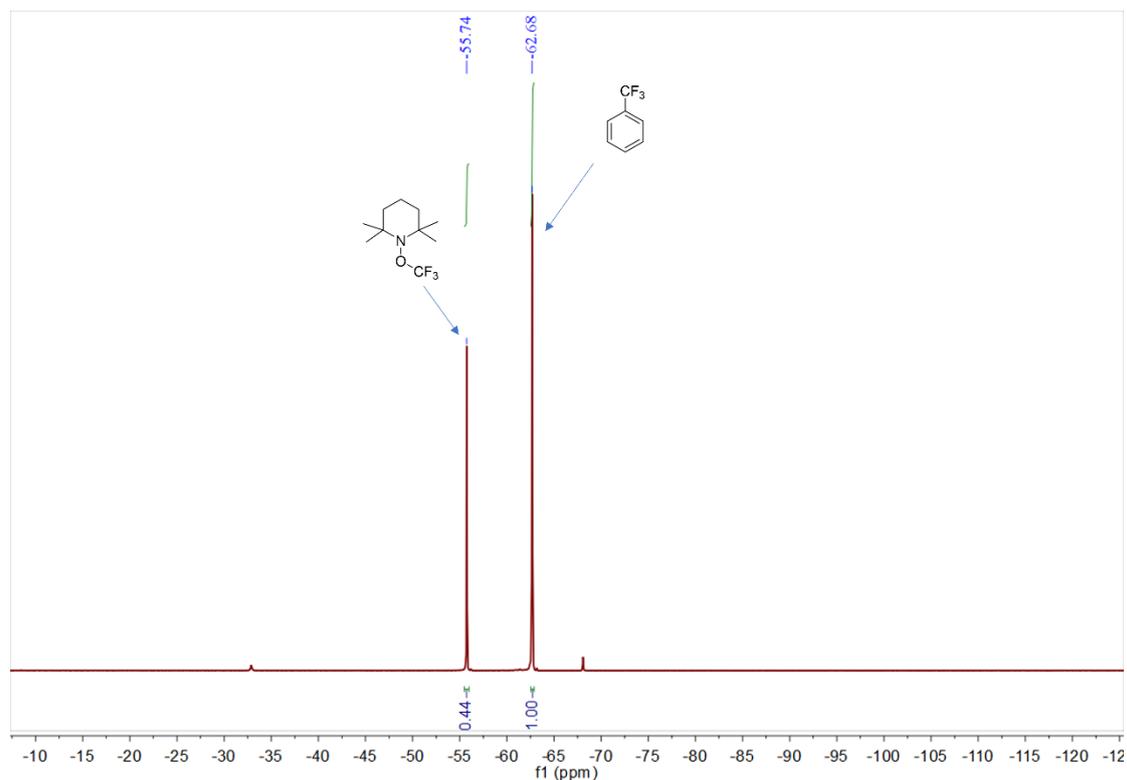
### Radical inhibition experiment



entry	additive	yield
1	no	91%
2	BHT	0
3	TEMPO	0

Under nitrogen atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with N-methacryloyl hydrazone **1a** (0.2 mmol, 1.0 equiv.), Togni's reagent **2** (0.4 mmol, 2.0 equiv.), DABCO (0.4 mmol, 2.0 equiv.), additive (0.6 mmol), and anhydrous MeCN (2.0 mL). Then, the reaction mixture was

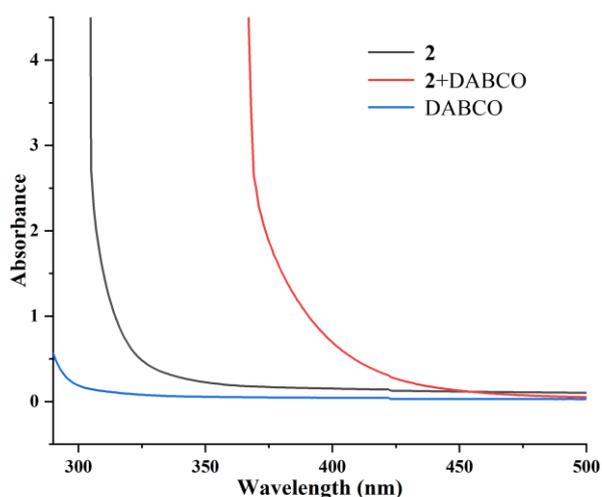
stirred at room temperature for 12 h upon a 390-400 nm LEDs. The reaction mixture was monitored by TLC and the target product **3a** was strongly suppressed when BHT and TEMPO were added in standard condition. The corresponding free radical adducts **4a** was also identified by  $^{19}\text{F}$  NMR,<sup>[2]</sup> and these findings strongly suggested the crucial role of radical intermediates in this transformation.



Crude  $^{19}\text{F}$  NMR of TEMPO- $\text{CF}_3$  adduct

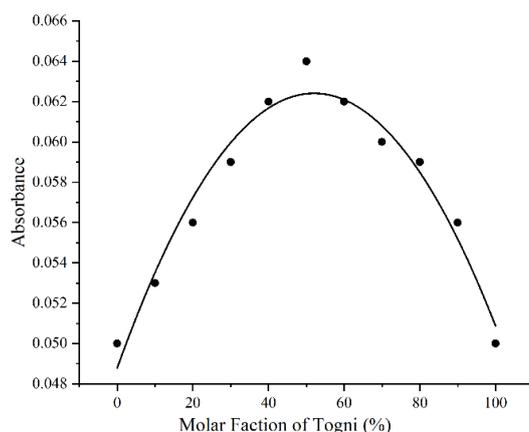
### UV/Vis absorption spectra

The UV/Vis absorption spectra of Togni's reagent **2** and DABCO were recorded at room temperature in acetonitrile to investigate a potential bathochromic shift resulting from the formation of an EDA complex. The spectrum of Togni's reagent **2** is represented by the black curve, that of DABCO by the blue curve, and the mixture of the **2** and DABCO by the red curve. When **2** and DABCO were combined in MeCN (0.1 M), a distinct red shift in UV absorption was noted, with the tail extending into the visible range. These results provide strong evidence for the emergence of an EDA complex between **2** and DABCO in the mixed solution.



### Stoichiometry of the EDA complex Togni's reagent II **2** and DABCO

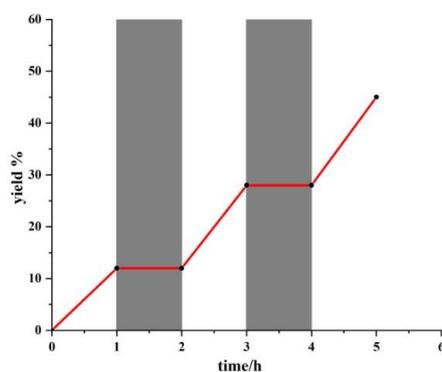
The stoichiometry of the EDA complex formed between Togni's reagent II **2** and DABCO was determined using the Job's plot. To construct the Job's plot, the absorption of acetonitrile solutions at 385 nm was measured while varying the donor/acceptor ratio, keeping the total concentration constant at 0.02 M. The absorbance values were then plotted as a function of the molar fraction (%) of Togni's reagent II **2**. The maximum absorbance occurred at a molar fraction of 50%, indicating a 1:1 stoichiometry for the EDA complex in solution.



### Light on/off experiments

Under nitrogen atmosphere, an oven-dried resealable Schlenk tube equipped with a

magnetic stir bar was charged with N-methacryloyl hydrazone **1a** (0.2 mmol, 1.0 equiv.), Togni's reagent 2 (0.4 mmol, 2.0 equiv.), DABCO (0.4 mmol, 2.0 equiv.), fluorobenzene (0.2 mmol, 1.0 equiv.), and anhydrous MeCN (2.0 mL). Then, the reaction mixture was stirred at room temperature upon a 390-400 nm LEDs. During light-off procedures, completely encase the Schlenk tube in aluminum foil. Following the specified reaction time, a 100  $\mu$ L the reaction mixture was withdrawn and diluted in CDCl<sub>3</sub> to prepare a crude NMR sample. Product yields were quantified by <sup>19</sup>F NMR spectroscopy with fluorobenzene as an internal standard.



#### Supplementary references:

- (a) S. P. Panda, R. Dash, S. K. Hota and S. Murarka, *Org. Lett.*, 2024, **26**, 3667-3672.  
(b) S. Yu, Y. Cheng, C. Pan and J.-T. Yu, *Chem. Commun.*, 2025, **61**, 1196-1199.
- P. Gao, Y.-W. Shen, R. Fang, X.-H. Hao, Z.-H. Qiu, F. Y., X.-B. Yan, Q. Wang, X.-J. Gong, X.-Y. Liu and Y.-M. Liang, *Angew. Chem. Int. Ed.*, 2014, **53**, 7629-7633.

# NMR spectra

