Cascade reaction for the construction of CF₃ containing tetrasubstituted furan ring
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1. General Information

Trifluoromethylketones (TFMK), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Sigma-Aldrich chemicals and used without further purification. Melting points were recorded using FP62 Mettler Toledo. FTIR spectra were recorded on a Perkin Elmer Spectrum GX spectrophotometer as KBr pellet. Mass analyses (HRMS) were performed using positive electron spray ionization (ESI+) technique on a waters Q TOF-micro mass spectrometer for all these complexes upon dissolving in CH$_3$CN solvent. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance II 500 MHz FT-NMR spectrometer. Chemical shifts for proton resonances are reported in ppm (δ) relative to tetramethyl silane (TMS) and coupling constants (J) were given in Hertz (Hz). For the product purification flash chromatography was performed using silica gel 230-400 mesh. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, m =multiplet, br = broad, q = Quintet, coupling constants are given in Hertz (Hz).

2. Synthesis and characterization of activated nitroolefin

Activated nitroolefin (2a, 2b and 2c) was prepared and characterization according to the method reported in the literature.\textsuperscript{1}

3. Typical experimental procedure

Trifluoromethylketones (1a-j) and (1a′-i′) (0.5 mmol, 1.0 eq.) and activated nitroolefin (2a, 2b and 2c) (0.6 mmol, 1.2 eq.) were taken in 0.8 mL of dry CH$_3$CN in a sample vial with a magnetic stirring bar. To the resulting solution, DBU (20 mol%) as Lewis base was added into the reaction and allowed to stir at 40 °C. After running the reaction for the specified time, the volatile components were removed under reduced pressure, and the crude product was purified by column chromatography (Hexane/AcOEt: 90/10).

4. Characterization data of trifluoromethyl ketone (TFMK) products:

4.1. Characterization data of trifluoromethyl ketone (TFMK) products with 2a:

(i). (Z)-5-(4-fluorophenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3a);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 95%; Melting point: 152-153.0 °C; FTIR (KBr): $v_{\text{max}}$ = 3402, 2363, 1681, 1239, 1193, 1033, 985, 763 cm$^{-1}$; $^1$H NMR (500MHz, CDCl$_3$, δ ppm): δ = 7.73–7.72 (m, 2H), 7.64–7.62 (m, 2H), 7.42-7.40 (m, 3H), 7.15-7.14 (m, 2H), 7.04 (s, 1H, =CH-); $^{13}$C NMR (125 MHz, CDCl$_3$, δ ppm): δ = 164.40, 162.41, 157.58, 137.41, 130.34 (d, $J_{\text{C-F}}$ = 125 Hz, -CF$_3$), 128.70, 128.56, 128.00, 123.96, 121.70, 116.00 (d, $J = 85$ Hz), 90.62-90.10 (q, $J_{\text{C-F}}$ = 260 Hz).
(ii). (Z)-5-(3-fluorophenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3b);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 92%; Melting point: 127-128 °C; FTIR (KBr): $\nu_{\text{max}}$ = 3403, 2363, 1680, 1248, 1176, 1035, 984, 763 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$), $\delta$ ppm): $\delta$ = 7.73–7.68 (m, 2H), 7.62 (m, 1H), 7.42-7.39 (m, 5H), 7.13-7.10 (m, 1H), 7.00 (s, 1H, =CH-); $^{13}$C NMR (125 MHz, CDCl$_3$), $\delta$ ppm): $\delta$ = 160.48, 155.55, 152.70, 132.79, 130.41–130.26 (d, $J_{\text{CF}}$ = 75 Hz, -CF$_3$), 125.85 (d, $J$ = 80 Hz), 125.39, 123.96, 123.31, 117.00, 115.16, 112.23 (d, $J$ = 210 Hz), 109.47 (d, $J$ = 240 Hz), 86.33, 85.66-84.39 (q, $J_{\text{CF}}$ = 650 Hz); $^{19}$F NMR (400 MHz, CDCl$_3$), $\delta$ = -77.30 (s, 3F), -111.00-111.04 (m ppm); TOF- HRMS (ESI, m/z) [M+H]$^+$ calcd for C$_{17}$H$_{12}$F$_3$NO$_2$: 338.0804, found 338.0803.

(iii). (Z)-5-(3,4-difluorophenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3e);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 91%; Melting point: 133-135 °C; FTIR (KBr): $\nu_{\text{max}}$ = 3443, 2363, 1676, 1523, 1290, 1179, 1037, 983, 768, 731 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$), $\delta$ ppm): $\delta$ = 7.77–7.72 (m, 2H), 7.54-7.39 (m, 5H), 7.33-7.20 (m, 1H), 7.01 (s, 1H, =CH-); $^{13}$C NMR (125 MHz, CDCl$_3$), $\delta$ ppm): $\delta$ = 157.27, 153.78, 153.78-152.73 (dd, $J_{\text{CF}}$ = 380 Hz), 148.73-147.72 (dd, $J_{\text{CF}}$ = 360 Hz), 137.74, 130.20, 129.77 (d, $J_{\text{CF}}$ = 80 Hz, -CF$_3$), 128.72, 128.43, 128.06, 125.47, 122.96, 117.66, 116.30, 90.62-88.68 (q, $J_{\text{CF}}$ = 650 Hz); $^{19}$F NMR (400 MHz, CDCl$_3$), $\delta$ = -76.87 (s, 3F), -135.34-135.39 (m ppm); TOF- HRMS (ESI, m/z) [M+H]$^+$ calcd for C$_{17}$H$_{12}$F$_3$NO$_2$: 356.0710, found 356.0698.

(iv). (Z)-3-phenyl-5-(trifluoromethyl)-5-(3-phenylfuran-2(5H)-one oxime (3d);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 90%; Melting point: 99-101 °C; FTIR (KBr): $\nu_{\text{max}}$ = 3403, 2362, 1683, 1334, 1192, 1038, 984, 763, 684 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$), $\delta$ ppm): $\delta$ = 8.26 (brs, 1H), 7.92–7.89 (m, 2H), 7.72-7.69 (m, 3H), 7.59-7.57 (m, 1H), 7.40-7.57 (m, 3H), 7.07 (s, 1H, =CH-); $^{13}$C NMR (125 MHz, CDCl$_3$), $\delta$ ppm): $\delta$ = 157.36, 138.03, 134.02, 131.78-131.00 (q, $J_{\text{CF}}$ = 360 Hz), 130.25, 130.03-129.54 (q, $J_{\text{CF}}$ = 245 Hz, -CF$_3$), 128.78, 128.48, 128.09, 126.63, 124.79, 123.88, 123.40, 122.62, 121.61, 90.58-90.07 (q, $J_{\text{CF}}$ = 255 Hz); $^{19}$F NMR (400 MHz, CDCl$_3$), $\delta$ = -77.46 (s, 3F), -62.64 (s ppm); TOF- HRMS (ESI, m/z) [M+H]$^+$ calcd for C$_{18}$H$_{12}$F$_3$NO$_2$: 388.0772, found 388.0757.

(v). (Z)-5-(4-chlorophenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3e);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 93%; Melting point: 145-146 °C; FTIR (KBr): $\nu_{\text{max}}$ = 3405, 2363, 1678, 1274, 1194, 1035, 985, 762, 685 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$), $\delta$ ppm): $\delta$ = 7.71–7.70 (m, 2H), 7.59–7.57 (m, 2H), 7.42-7.40 (m, 5H), 7.01 (s, 1H, =CH-); $^{13}$C NMR (125 MHz, CDCl$_3$), $\delta$ ppm): $\delta$ = 157.49, 153.70, 135.98, 131.36, 130.12, 129.09, 128.70, 128.60, 128.06, 127.92, 123.89, 121.63, 90.53-90.07 (q, $J_{\text{CF}}$ = 230 Hz); $^{19}$F NMR (400 MHz, CDCl$_3$), $\delta$ = -77.45 (s, 3F); TOF- HRMS (ESI, m/z) [M+H]$^+$ calcd for C$_{18}$H$_{12}$ClF$_3$NO$_2$: 354.0509, found 354.0521.
(vi). (Z)-3-phenyl-5-(thiophen-2-yl)-5-(trifluoromethyl)furan-2(5H)-one oxime (3f);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 90%; Melting point: 122-123 °C; FTIR (KBr): $\nu_{\max} = 3403, 2363, 1687, 1274, 1178, 1039, 982, 768, 684 \text{ cm}^{-1}$; $^1$H NMR (500MHz, CDCl$_3$ $\delta$ ppm): $\delta = 7.72$-7.69 (m, 2H), 7.42-7.34 (m, 5H), 7.09-7.04 (m, 1H), 6.94 (s, 1H, =CH-); $^{13}$C NMR (125 MHz, CDCl$_3$ $\delta$ ppm): $\delta = 157.42, 137.66, 134.48, 130.34, 130.17, 128.75, 128.58, 128.13, 127.72, 127.45, 125.43, 119.78, 89.91, 89.91-87.57 (q, $J_{CF} = 675$ Hz); $^{19}$F NMR (400 MHz, CDCl$_3$ $\delta$ = -77.42 (s, 3F) ppm; TOF- HRMS (ESI, m/z) [M+H]$^+$ calcd for C$_{15}$H$_{11}$F$_3$NO$_2$: 326.0463, found 326.0474.

(vii). (Z)-3,5-diphenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3g);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 75%; Melting point: 118-120 °C; FTIR (KBr): $\nu_{\max} = 3408, 2363, 1681, 1274, 1172, 1026, 945, 762, 683 \text{ cm}^{-1}$; $^1$H NMR (500MHz, CDCl$_3$ $\delta$ ppm): $\delta = 7.64$–7.63 (m, 2H), 7.57–7.56 (m, 2H), 7.37–7.330 (m, 6H), 6.99 (s, 1H, =CH-); $^{13}$C NMR (125 MHz, CDCl$_3$ $\delta$ ppm): $\delta = 157.82, 137.20, 132.87, 130.82, 130.06, 129.74, 128.89, 128.74 (d, $J_{CF} = 75$ Hz, -CF$_3$), 128.12, 126.53, 124.13, 121.86, 91.09-90.32 (q, $J_{CF} = 260$ Hz); $^{19}$F NMR (400 MHz, CDCl$_3$ $\delta$ = -77.32 (s, 3F) ppm; TOF- HRMS (ESI, m/z) [M+H]$^+$ calcd for C$_{15}$H$_{13}$F$_3$NO$_2$: 320.0898 found 320.0892.

(viii). (Z)-5-(4-methoxyphenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3h);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 88%; Melting point: 146-148 °C; FTIR (KBr): $\nu_{\max} = 3403, 2363, 1677, 1490, 1270, 1192, 1038, 960, 765, 683 \text{ cm}^{-1}$; $^1$H NMR (500MHz, CDCl$_3$ $\delta$ ppm): $\delta = 7.73$–7.72 (m, 2H), 7.56–7.55 (m, 2H), 7.40-7.38 (m, 3H), 7.06 (s, 1H, =CH-), 6.97-6.95 (d, $J = 10$ Hz, 2H), 3.82 (s, 3H, -OCH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$ $\delta$ ppm): $\delta = 160.54, 157.88, 136.94, 130.82, 129.91, 128.87, 128.62, 128.07, 127.94, 124.82, 114.20, 90.85-90.35 (q, $J_{CF} = 250$ Hz), 85.36; $^{19}$F NMR (400 MHz, CDCl$_3$ $\delta$ = -77.58 (s, 3F) ppm; TOF- HRMS (ESI, m/z) [M+H]$^+$ calcd for C$_{15}$H$_{13}$F$_3$NO$_2$: 350.1004, found 350.0999.

(ix). (Z)-5-(2,4-dimethoxyphenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3i);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 72%; Melting point: 156-157 °C; FTIR (KBr): $\nu_{\max} = 3402, 2361, 1688, 1489, 1278, 1173, 1030, 956, 765, 684 \text{ cm}^{-1}$; $^1$H NMR (500MHz, CDCl$_3$ $\delta$ ppm): $\delta = 7.80$–7.72 (m, 3H), 7.43–7.40 (m, 4H), 6.63-6.62 (m, 2H), 6.54 (s, 1H, =CH-), 3.90 (s, 3H, -OCH$_3$), 3.84 (s, 3H, -OCH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$ $\delta$ ppm): $\delta = 162.06, 157.81, 135.70, 132.22, 129.93, 129.55-129.40 (d, $J_{CF} = 75$ Hz, -CF$_3$), 128.52, 128.06, 125.96, 120.27, 113.61, 104.92, 99.46, 90.50-89.18 (q, $J_{CF} = 650$ Hz), 55.75, 55.45; $^{19}$F NMR (400 MHz, CDCl$_3$ $\delta$ = -77.73 (s, 3F) ppm; TOF- HRMS (ESI, m/z) [M+H]$^+$ calcd for C$_{15}$H$_{13}$F$_3$NO$_2$: 380.1110, found 380.1124.

(x). (Z)-5-(4-methylphenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3j);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 82%; Melting point: 156-158 °C; FTIR (KBr): $\nu_{\max} = 3403, 2363, 1684, 1270, 1192, 1173, 1040, 962, 768, 685
cm⁻¹; ¹H NMR (500MHz, CDCl₃, δ ppm): δ = 7.72–7.71 (m, 2 H), 7.53–7.51 (m, 2H), 7.40-7.39 (m, 3H), 7.26-7.24 (m, 2H), 7.06 (s, 1H, =CH-); ¹³C NMR (125 MHz, CDCl₃, δ ppm): δ= 157.87, 139.77, 136.94, 130.85, 129.90, 129.49, 128.86, 128.61, 128.07, 126.37, 124.12, 121.86, 90.02-90.49 (q, Jₐ-C-F = 240 Hz), 21.15; ¹⁹F NMR (400 MHz, CDCl₃) δ = -77.44 (s, 3F) ppm; TOF- HRMS (ESI, m/z) [M+H]⁺ calcld for C₁₈H₁₅F₃NO₂: 334.1055, found 334.1061.

4.2. Characterization data of trifluoromethyl ketone (TFMK) products with 2b:

(i). (Z)-3-(4-chlorophenyl)-5-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (4a);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 86%; Melting point: 149-150 °C; FTIR (KBr): νmax = 3340, 2363, 1683, 1274, 1177, 1094, 955, 823, 758 cm⁻¹; ¹H NMR (500MHz, CDCl₃, δ ppm): δ = 7.70–7.68 (d, 2H, J = 10 Hz), 7.64–7.63 (m, 2H), 7.64-7.44 (m, 3H), 7.38-7.36 (m, 2H), 7.18 (s, 1H), 7.08 (s, 1H, =CH-); ¹³C NMR (125 MHz, CDCl₃, δ ppm): δ = 157.53, 136.12, 135.97, 132.65, 130.85, 129.81, 129.44, 128.92, 127.19, 126.45, 124.02, 121.76, 116.20, 91.08-90.56 (q, Jₐ-C-F = 260 Hz); ¹⁹F NMR (400 MHz, CDCl₃) δ = -77.35 (s, 3F) ppm; TOF- HRMS (ESI, m/z) [M+Na]⁺ calcld for C₁₇H₁₁ClF₃NO₂Na: 376.0328, found 376.0337.

(ii). (Z)-3-(4-chlorophenyl)-5-(3,4-difluorophenyl)-5-(trifluoromethyl)furan-2(5H)-one oxime (4b);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 90%; Melting point: 176-178 °C; FTIR (KBr): νmax = 3403, 2363, 1683, 1334, 1192, 1038, 984, 812, 763, 684 cm⁻¹; ¹H NMR (500MHz, CDCl₃, δ ppm): δ = 7.77 (s, 1H), 7 (s, 1H), 7.52-7.48 (m, 1H), 7.40-7.36 (m, 3H), 7.28-7.23 (m, 1H), 7.09 (s, 1H), 7.00 (s, 1H, =CH-); ¹³C NMR (125 MHz, CDCl₃, δ ppm): δ = 157.01, 152.26-151.50 (dd, Jₚ-C-F = 380 Hz), 150.24-149.49 (dd, Jₚ-C-F = 375 Hz), 136.55, 136.41, 129.77, 129.59, 129.45, 128.98, 126.83, 123.73, 122.96, 122.46, 118.04, 117.89, 116.39, 116.25, 90.07-89.56 (q, Jₚ-C-F = 255 Hz); ¹⁹F NMR (400 MHz, CDCl₃) δ = -71.12, -77.50 (s, 3F), -134.25-134.31 (m), -135.17-135.22 (m) ppm; TOF- HRMS (ESI, m/z) [M+Na]⁺ calcld for C₁₇H₉ClF₅NO₂Na: 412.0140, found 412.0123.

(iii). (Z)-3-(4-chlorophenyl)-5-(trifluoromethyl)-5-(3-(trifluoromethyl)phenyl)furan-2(5H)-one oxime (4c);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 89%; Melting point: 139-140 °C; FTIR (KBr): νmax = 3403, 2362, 1683, 1334, 1274, 1177, 1094, 955, 823, 763, 684 cm⁻¹; ¹H NMR (500MHz, CDCl₃, δ ppm): δ = 7.87–7.86 (m, 2 H), 7.72–7.70 (m, 3H), 7.63-7.59 (m, 1H), 7.40-7.38 (m, 3H), 7.18 (s, 1H), 7.08 (s, 1H, =CH-).; ¹³C NMR (125 MHz, CDCl₃, δ ppm): δ = 157.04, 136.71, 136.41, 133.85, 131.37, 129.93, 129.75, 129.63, 129.48, 128.98, 128.77, 124.73, 123.78, 123.6, 122.57, 121.51, 90.52-89.73 (q, Jₚ-C-F = 260 Hz); ¹⁹F NMR (400 MHz, CDCl₃) δ = -71.12, -77.50 (s, 3F), -134.25-134.31 (m), -135.17-135.22 (m) ppm; TOF- HRMS (ESI, m/z) [M+Na]⁺ calcld for C₁₈H₁₀ClF₆NO₂Na: 444.0202 found 444.0189.

(iv). (Z)-3,5-bis(4-chlorophenyl)-5-(trifluoromethyl)furan-2(5H)-one oxime (4d);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 94%; Melting point: 142-144 °C; FTIR (KBr): νmax = 3305, 2363, 1689, 1492, 1270, 1181, 1093, 988, 820, 736
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\begin{align*}
\text{\(^1\)H NMR (500MHz, CDCl\_3, \delta ppm): } & \delta = 7.71–7.70 (m, 2H), 7.58–7.56 (m, 2H), 7.44-7.43 (m, 2H), 7.39-7.37 (m, 2H), 7.03 (s, 1H), 6.91 (s, 1H, =CH-); \\
\text{\(^{13}\)C NMR (125 MHz, CDCl\_3, \delta ppm): } & \delta = 157.24, 136.29, 136.12, 131.18, 130.24, 129.44, 129.19, 128.96, 127.90, 126.99, 123.84, 121.57; \\
\text{\(^{19}\)F NMR (400 MHz, CDCl\_3) \delta = -77.44 (s, 3F) ppm; }
\end{align*}
\]

TOF-HRMS (ESI, m/z) [M+Na\(^+\)] calcd for C\(_{17}\)H\(_{10}\)Cl\(_2\)F\(_3\)NO\(_2\)Na: 409.9938, found 409.9934.

(v). (Z)-3-(4-chlorophenyl)-5-(p-tolyl)-5-(trifluoromethyl)furan-2(5H)-one oxime (4e);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 82%; Melting point: 139-141 °C; FTIR (KBr): \(\nu_{\text{max}} = 3403, 2362, 1684, 1338, 1192, 1172, 1035, 987, 820, 763, 684 \text{ cm}^{-1}; \)

\[
\begin{align*}
\text{\(^1\)H NMR (500MHz, CDCl\_3, \delta ppm): } & \delta = 7.71–7.69 (m, 2 H), 7.52–7.50 (m, 2H), 7.38-7.36 (m, 2H), 7.27-7.25 (m, 2H), 7.07 (s, 1H, =CH-), 2.38 (s, 3H, -CH\_3); \\
\text{\(^{13}\)C NMR (125 MHz, CDCl\_3, \delta ppm): } & \delta = 157.62, 139.94, 136.05, 135.76, 131.05, 129.70, 129.59, 129.44, 128.88, 127.26, 126.35, 91.29-90.82 (q, \(J_{C-F} = 235 \text{ Hz})); \\
\text{\(^{19}\)F NMR (400 MHz, CDCl\_3) \delta = -77.47 (s, 3F) ppm; }
\end{align*}
\]

TOF-HRMS (ESI, m/z) [M+Na\(^+\)] calcd for C\(_{18}\)H\(_{12}\)ClF\(_3\)NO\(_2\)Na: 389.0406, found 389.0422.

(vi). (Z)-3-(4-chlorophenyl)-5-(4-methoxyphenyl)-5-(trifluoromethyl)furan-2(5H)-one oxime (4f);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 85%; Melting point: 148-149 °C; FTIR (KBr): \(\nu_{\text{max}} = 3403, 2363, 1681, 1339, 1190, 1175, 1039, 983, 815, 763, 684 \text{ cm}^{-1}; \)

\[
\begin{align*}
\text{\(^1\)H NMR (500MHz, CDCl\_3, \delta ppm): } & \delta = 7.73–7.69 (m, 2 H), 7.56–7.52 (m, 2H), 7.39-7.35 (m, 2H), 7.07-6.94 (m, 2H), 6.8 (s, 1H, =CH-), 3.82 (s, 3H, -OCH\_3); \\
\text{\(^{13}\)C NMR (125 MHz, CDCl\_3, \delta ppm): } & \delta = 160.63, 157.63, 136.05, 135.76, 131.00, 129.44, 128.88, 127.93, 127.27, 124.61, 124.09, 114.27, 90.41, 55.42; \\
\text{\(^{19}\)F NMR (400 MHz, CDCl\_3) \delta = -77.59 (s, 3F) ppm; }
\end{align*}
\]

TOF-HRMS (ESI, m/z) [M+Na\(^+\)] calcd for C\(_{18}\)H\(_{13}\)ClF\(_3\)NO\(_3\)Na: 406.0434, found 406.0413.

(vii). (Z)-3-(4-chlorophenyl)-5-(thiophen-2-yl)-5-(trifluoromethyl)furan-2(5H)-one oxime (4g);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 82%; Melting point: 153-155 °C; FTIR (KBr): \(\nu_{\text{max}} = 3403, 2361, 1680, 1475, 1332, 1196, 1038, 983, 815, 763, 684 \text{ cm}^{-1}; \)

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\begin{align*}
\text{\(^1\)H NMR (500MHz, CDCl\_3, \delta ppm): } & \delta = 7.95 (m, 2H), 7.76-7.72 (m, 2H), 7.44-7.42 (m, 3H), 7.11-7.06 (m, 1H), 6.95 (s, 1H, =CH-); \\
\text{\(^{13}\)C NMR (125 MHz, CDCl\_3, \delta ppm): } & \delta = 157.42, 137.66, 134.48, 130.17, 128.75, 128.58, 128.13, 127.72, 127.45, 125.43, 119.78, 89.91, 89.91-87.57 (q, \(J_{C-F} = 675 \text{ Hz}); \)
\end{align*}
\]

\[
\begin{align*}
\text{\(^{19}\)F NMR (400 MHz, CDCl\_3) \delta = -77.43 (s, 3F) ppm; }
\end{align*}
\]

TOF-HRMS (ESI, m/z) [M+Na\(^+\)] calcd for C\(_{15}\)H\(_9\)ClF\(_3\)NO\(_2\)SNa: 381.9892, found 381.9900.

4.3. Characterization data of trifluoromethyl ketone (TFMK) products with 2c:

(i). (Z)-5-(4-chlorophenyl)-3-(4-fluorophenyl)-5-(trifluoromethyl)furan-2(5H)-one oxime (4h);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 86%; Melting point: 145-148 °C; FTIR (KBr): \(\nu_{\text{max}} = 3403, 2361, 1680, 1475, 1332, 1196, 1038, 983, 815, 763, 684 \text{ cm}^{-1}; \)

\[
\begin{align*}
\text{\(^1\)H NMR (500MHz, CDCl\_3, \delta ppm): } & \delta = 7.77-7.74 (m, 2H), 7.58-7.57 (m, 2H), 7.44-7.42 (m, 2H),
\end{align*}
\]
7.11-7.08 (m, 2H), 6.95 (s, 1H, =CH-); $^{13}$C NMR (125 MHz, CDCl$_3$, δ ppm): δ = 164.73, 162.73, 157.38, 136.29, 136.06, 131.26, 130.18, 130.12, 129.66, 129.15, 127.87, 124.69, 123.86, 121.59, 115.86, 115.69, 90.26-89.76 (q, $J_{C-F}$ = 250 Hz); $^{19}$F NMR (400 MHz, CDCl$_3$) δ = -77.48 (s, 3F), -109.77-109.84 (m) ppm; TOF-HRMS (ESI, m/z) [M+H]$^+$ calec for C$_{17}$H$_{11}$ClF$_4$NO$_2$: 372.0414, found 372.0421.

(ii). (Z)-5-(3-fluorophenyl)-3-(4-fluorophenyl)-5-(trifluoromethyl)furan-2(5H)-one oxime (4i);

The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a White solid; Yield: 90%; Melting point: 130-132 °C; FTIR (KBr): $\nu_{max}$ = 3408, 2365, 1677, 1478, 1330, 1198, 1040, 983, 813, 768, 680 cm$^{-1}$; $^1$H NMR (500MHz, CDCl$_3$, δ ppm): δ = 7.76-7.73 (m, 2H), 7.44-7.37 (m, 3H), 7.28-7.25 (m, 1H), 7.15-7.08 (m, 3H), 6.98 (s, 1H, =CH-); $^{13}$C NMR (125 MHz, CDCl$_3$, δ ppm): δ = 164.75, 163.77, 162.75, 157.36, 136.35, 135.01, 134.96, 130.61, 130.55, 130.18, 129.76, 124.68, 123.84, 122.11, 116.93, 116.77, 115.91, 114.06, 90.44-89.68 (q, $J_{C-F}$ = 255 Hz); $^{19}$F NMR (400 MHz, CDCl$_3$) δ = -77.34 (s, 3F), -109.76-109.63 (m), -110.91-110.96 (m) ppm; TOF-HRMS (ESI, m/z) [M+H]$^+$ calec for C$_{17}$H$_{11}$ClF$_5$NO$_2$: 381.0710, found 356.0707.

4.4. $^1$H and $^{13}$C-NMR spectra of trifluoromethylketones products with 2a:

(i). (Z)-5-(4-fluorophenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3a);
HRMS of compound (3a)

19F NMR spectra of product (3a)
(ii). (Z)-5-(3-fluorophenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3b);

HRMS of compound (3b)
$^{19}$F NMR spectra of product (3b)
(iii) (Z)-5-(3,4-difluorophenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3c);
$^{19}$F NMR spectra of product (3e)

(iv). (Z)-3-phenyl-5-(trifluoromethyl)-5-(3-(trifluoromethyl)phenyl)furan-2(5H)-one oxime (3d);

![FMR spectra image]

![Diagram of molecular structure]
HRMS of compound (3d)

$^{19}$F NMR spectra of product (3d)
(v). (Z)-5-(4-chlorophenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3e);

HRMS of compound (3e)
19F NMR spectra of product (3e)

(vi). (Z)-3-phenyl-5-(thiophen-2-yl)-5-(trifluoromethyl)furan-2(5H)-one oxime (3f);
HRMS of compound (3f)

$^{19}$F NMR spectra of product (3f)

(vii). (Z)-3,5-diphenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3g);
HRMS of compound (3g)

$^{19}$F NMR spectra of product (3g)
(viii). (Z)-5-(4-methoxyphenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3h);
$^{19}$F NMR spectra of product (3h)

(ix) (Z)-5-(2,4-dimethoxyphenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3i);
HRMS of compound (3i)

\( ^{19}\text{F} \) NMR spectra of product (3i)

(x). (Z)-5-(4-methylphenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (3j);
HRMS of compound (3j)

$^{19}$F NMR spectra of product (3j)
4.5. $^1$H and $^{13}$C-NMR spectra of trifluoromethylketone products with 2b:

(i). (Z)-3-(4-chlorophenyl)-5-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime (4a);

HRMS of compound (4a)
$^{19}$F NMR spectra of product (4a)

(ii). (Z)-3-(4-chlorophenyl)-5-(3,4-difluorophenyl)-5-(trifluoromethyl)furan-2(5H)-one oxime (4b);
HRMS of compound (4b)

$^{19}$F NMR spectra of product (4b)
(iii). (Z)-3-(4-chlorophenyl)-5-(trifluoromethyl)-5-(3-(trifluoromethyl)phenyl)furan-2(5H)-one oxime (4c);
HRMS of compound (4c)

19F NMR spectra of product (4c)

(iv). (Z)-3,5-bis(4-chlorophenyl)-5-(trifluoromethyl)furan-2(5H)-one oxime (4d);
HRMS of compound (4d)

$^{19}$F NMR spectra of product (4d)
(v) (Z)-3-(4-chlorophenyl)-5-(p-tolyl)-5-(trifluoromethyl)furan-2(5H)-one oxime (4e);
\[ ^{19}\text{F} \text{NMR spectra of product (4e)} \]

(vi). (Z)-3-(4-chlorophenyl)-5-(4-methoxyphenyl)-5-(trifluoromethyl)furan-2(5H)-one oxime (4f);
HRMS of compound (4f)

\[ \text{(vii). } (Z)-3-(4\text{-chlorophenyl})-5-(\text{thiophen-2-yl})-5\text{-}(\text{trifluoromethyl})\text{furan-2(5H)-one oxime (4g);} \]
HRMS of compound (4g)

19F NMR spectra of product (4g)
4.6. $^1$H and $^{13}$C-NMR spectra of trifluoromethylketone products with 2c:

(i). (Z)-5-(4-chlorophenyl)-3-(4-fluorophenyl)-5-(trifluoromethyl)furan-2(5H)-one oxime (4h):

HRMS of compound (4h)
$^{19}\text{F} \text{NMR spectra of product (4h)}$

(ii). (Z)-5-(3-fluorophenyl)-3-(4-fluorophenyl)-5-(trifluoromethyl)furan-2(5H)-one oxime (4i);
HRMS of compound (4i)

$^{19}$F NMR spectra of product (4i)
5. References: