Cascade reaction for the construction of CF_3 containing tetrasubstituted furan ring

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1. General Information

Trifluromethylketones (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_3CN solvent. ^1H 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.[1]

3. Typical experimental procedure

Trifluromethylketones **(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_3CN 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): ν_{max} = 3402, 2363, 1681, 1239, 1193, 1033, 985, 763 cm^{-1}; ^1H 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_{C-F} = 125 Hz, -CF_3), 128.70, 128.56, 128.06, 123.96, 121.70, 116.00 (d, *J* = 85 Hz), 90.62-90.10 (q, J_{C-F} = 260

Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ = -77.55 (s, 3F) ppm; TOF- HRMS (ESI, m/z) $[M+H]^+$ calcd for $C_{17}H_{12}F_4NO_2$: 338.0804, found 338.0807.

(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): ν_{max} = 3403, 2363, 1680, 1248, 1176, 1035, 984, 763 cm^{-1}; ^{1}H NMR (500MHz, $CDCl_3$, δ ppm): δ = 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, $CDCl_3$, δ ppm): δ = 160.48, 155.55, 152.70, 132.79, 130.41-130.26 (d, J_{C-F} = 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_{C-F} = 650 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ = -77.30 (s, 3F), -111.00-111.04 (m) ppm; TOF- HRMS (ESI, m/z) $[M+H]^+$ calcd for $C_{17}H_{12}F_4NO_2$: 338.0804, found 338.0803.

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

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): ν_{max} = 3443, 2363, 1676, 1523, 1290, 1179, 1037, 983, 768, 731 cm^{-1}; ^{1}H NMR (500MHz, $CDCl_3$, δ ppm): δ = 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, $CDCl_3$, δ ppm): δ = 157.27, 153.78, 153.78-152.73 (dd, J_{C-F} = 380 Hz), 148.73-147.72 (dd, J_{C-F} = 360 Hz), 137.74, 130.20, 129.77 (d, J_{C-F} = 80 Hz, -CF_3), 128.72, 128.43, 128.06, 125.47, 122.96, 117.66, 116.30, 90.62-88.68 (q, J_{C-F} = 645 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ = -76.87 (s, 3F), -135.34-135.39 (m) ppm; TOF- HRMS (ESI, m/z) $[M+H]^+$ calcd for $C_{17}H_{11}F_5NO_2$: 356.0710, found 356.0698.

(iv). (*Z*)-3-phenyl-5-(trifluoromethyl)-5-(3-(trifluoromethyl) phenyl)furan-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): ν_{max} = 3403, 2362, 1683, 1334, 1192, 1038, 984, 763, 684 cm^{-1}; ^{1}H NMR (500MHz, $CDCl_3$, δ ppm): δ = 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, $CDCl_3$, δ ppm): δ= 157.36, 138.03, 134.02, 131.78-131.00 (q, J_{C-F} = 360 Hz), 130.25, 130.03-129.54 (q, J_{C-F} = 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_{C-F} = 255 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ = -77.46 (s, 3F), -62.64 (s) ppm; TOF- HRMS (ESI, m/z) $[M+H]^+$ calcd for $C_{18}H_{12}F_6NO_2$: 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): ν_{max} = 3405, 2363, 1678, 1274, 1194, 1035, 985, 762, 685 cm^{-1}; ^{1}H NMR (500MHz, $CDCl_3$, δ ppm): δ = 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, $CDCl_3$, δ ppm): δ = 157.49, 137.50, 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_{C-F} = 230 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ = -77.45 (s, 3F) ppm; TOF- HRMS (ESI, m/z) $[M+H]^+$ calcd for $C_{17}H_{12}ClF_3NO_2$: 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): ν_{max} = 3403, 2363, 1687, 1274, 1178, 1039, 982, 768, 684 cm^{-1}; ^{1}H NMR (500MHz, $CDCl_3$, δ ppm): δ = 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, $CDCl_3$, δ ppm): δ = 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_{C-F} = 675 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ = -77.42 (s, 3F) ppm; TOF- HRMS (ESI, m/z) $[M+H]^+$ calcd for $C_{15}H_{11}F_3NO_2S$: 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): ν_{max} = 3408, 2363, 1681, 1274, 1172, 1026, 945, 762, 683 cm^{-1}; ^{1}H NMR (500MHz, $CDCl_3$, δ ppm): δ = 7.64–7.63 (m, 2 H), 7.57–7.56 (m, 2H), 7.37-7.330 (m, 6H), 6.99 (s, 1H, =CH-); ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): δ= 157.82, 137.20, 132.87, 130.82, 130.06, 129.74, 128.89, 128.74 (d, J_{C-F} = 75 Hz, -CF_3), 128.12, 126.53, 124.13, 121.86, 91.09-90.32 (q, J_{C-F} = 260 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ = -77.32 (s, 3F) ppm; TOF- HRMS (ESI, m/z) $[M+H]^+$ calcd for $C_{17}H_{13}F_3NO_2$: 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): ν_{max} = 3403, 2363, 1677, 1490, 1270, 1192, 1038, 960, 765, 683 cm^{-1}; ^{1}H NMR (500MHz, $CDCl_3$, δ ppm): δ = 7.73–7.72 (m, 2 H), 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, $CDCl_3$, δ ppm): δ = 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_{C-F} = 250 Hz), 85.36; ^{19}F NMR (400 MHz, $CDCl_3$) δ = -77.58 (s, 3F) ppm; TOF- HRMS (ESI, m/z) $[M+H]^+$ calcd for $C_{18}H_{15}F_3NO_3$: 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): ν_{max} = 3402, 2361, 1688, 1489, 1278, 1173, 1030, 956, 765, 684 cm^{-1}; ^{1}H NMR (500MHz, $CDCl_3$, δ ppm): δ = 7.80–7.72 (m, 3 H), 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, $CDCl_3$, δ ppm): δ = 162.06, 157.81, 135.70, 132.22, 129.93, 129.55-129.40 (d, J_{C-F} = 75 Hz, -CF_3), 128.52, 128.06, 125.96, 120.27, 113.61, 104.92, 99.46, 90.50-89.18 (q, J_{C-F} = 650 Hz), 55.75, 55.45; ^{19}F NMR (400 MHz, $CDCl_3$) δ = -77.73 (s, 3F) ppm; TOF- HRMS (ESI, m/z) $[M+H]^+$ calcd for $C_{19}H_{17}F_3NO_4$: 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): ν_{max} = 3403, 2363, 1684, 1270, 1192, 1173, 1040, 962, 768, 685

cm^{-1}; ^1H NMR (500MHz, $CDCl_3$, 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-), 2.37 (s, 3H, $-CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 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, J_{C-F} = 240 Hz), 21.15; ^{19}F NMR (400 MHz, $CDCl_3$) δ = -77.44 (s, 3F) ppm; TOF- HRMS (ESI, m/z) $[M+H]^+$ calcd for $C_{18}H_{15}F_3NO_2$: 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): ν_{max} = 3340, 2363, 1683, 1274, 1177, 1094, 955, 823, 758 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$, 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-); ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): δ = 157.53, 136.12, 135.97, 132.65, 130.95, 129.81, 129.44, 128.92, 127.19, 126.45, 124.02, 121.76, 116.20, 91.08-90.56 (q, J_{C-F} = 260 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ = -77.35 (s, 3F) ppm; TOF- HRMS (ESI, m/z) $[M+Na]^+$ calcd for $C_{17}H_{11}ClF_3NO_2Na$: 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): ν_{max} = 3403, 2363, 1683, 1334, 1192, 1038, 984, 812, 763, 684 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$, 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-); ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): δ = 157.01, 152.26-151.50 (dd, J_{C-F} = 380 Hz), 150.24-149.49 (dd, J_{C-F} = 375 Hz), 136.55, 136.41, 129.77, 129.59, 129.45, 128.98, 126.83, 123.73, 122.96, 121.46, 118.04, 117.89, 116.39, 116.25, 90.07-89.56 (q, J_{C-F} = 255 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ = -71.12, -77.50 (s, 3F), -134.25-134.31 (m), -135.17-135.22 (m) ppm; TOF- HRMS (ESI, m/z) $[M+Na]^+$ calcd for $C_{17}H_9ClF_5NO_2Na$: 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): ν_{max} = 3403, 2362, 1683, 1334, 1271, 1192, 1038, 945, 812, 763 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$, 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, 2H), 7.18 (s, 1H), 7.08 (s, 1H, =CH-).; ^{13}C NMR (125 MHz, $CDCl_3$, 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, 123.36, 122.57, 121.51, 90.52-89.73 (q, J_{C-F} = 260 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ = -62.64, -77.40 (s, 3F) ppm; TOF-HRMS (ESI, m/z) $[M+Na]^+$ calcd for $C_{18}H_{10}ClF_6NO_2Na$: 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): ν_{max} = 3305, 2363, 1689, 1492, 1270, 1181, 1093, 988, 820, 736

cm^{-1}; ^1H NMR (500MHz, $CDCl_3$, δ ppm): δ = 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-).; ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): δ = 157.24, 136.29, 136.12, 131.18, 130.24, 129.44, 129.19, 128.96, 127.90, 126.99, 123.84, 121.57; 119.31, 90.62-90.11 (q, J_{C-F} = 255 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ = -77.44 (s, 3F) ppm; TOF- HRMS (ESI, m/z) $[M+Na]^+$ calcd for $C_{17}H_{10}Cl_2F_3NO_2Na$: 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): ν_{max} = 3403, 2362, 1684, 1338, 1192, 1172, 1035, 987, 820, 763, 684 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$, δ ppm): δ = 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, $-CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): δ = 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 Hz), 21.22; ^{19}F NMR (400 MHz, $CDCl_3$) δ = -77.47 (s, 3F) ppm; TOF- HRMS (ESI, m/z) $[M+Na]^+$ calcd for $C_{18}H_{12}ClF_3NO_2Na$: 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): ν_{max} = 3403, 2363, 1681, 1339, 1190, 1175, 1039, 983, 815, 763, 684 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$, δ ppm): δ = 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, $-OCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): δ = 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; ^{19}F NMR (400 MHz, $CDCl_3$) δ = -77.59 (s, 3F) ppm; TOF- HRMS (ESI, m/z) $[M+Na]^+$ calcd for $C_{18}H_{13}ClF_3NO_3Na$: 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): ν_{max} = 3403, 2361, 1680, 1475, 1332, 1196, 1038, 983, 813, 763, 684 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$, δ ppm): δ = 7.95 (m, 2H), 7.76-7.72 (m, 2H), 7.44-7.35 (m, 3H), 7.11-7.06 (m, 1H), 6.95 (s, 1H, =CH-); ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): δ = 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_{C-F} = 675 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ = -77.43 (s, 3F) ppm; TOF- HRMS (ESI, m/z) $[M+Na]^+$ calcd for $C_{15}H_9ClF_3NO_2SNa$: 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): ν_{max} = 3400, 2361, 1688, 1470, 1338, 1190, 1030, 983, 815, 763, 686 cm^{-1}; ^1H NMR (500MHz, $CDCl_3$, δ ppm): δ = 7.77-7.74 (m, 2H), 7.58-7.57 (m, 2H), 7.44-7.42 (m, 2H),

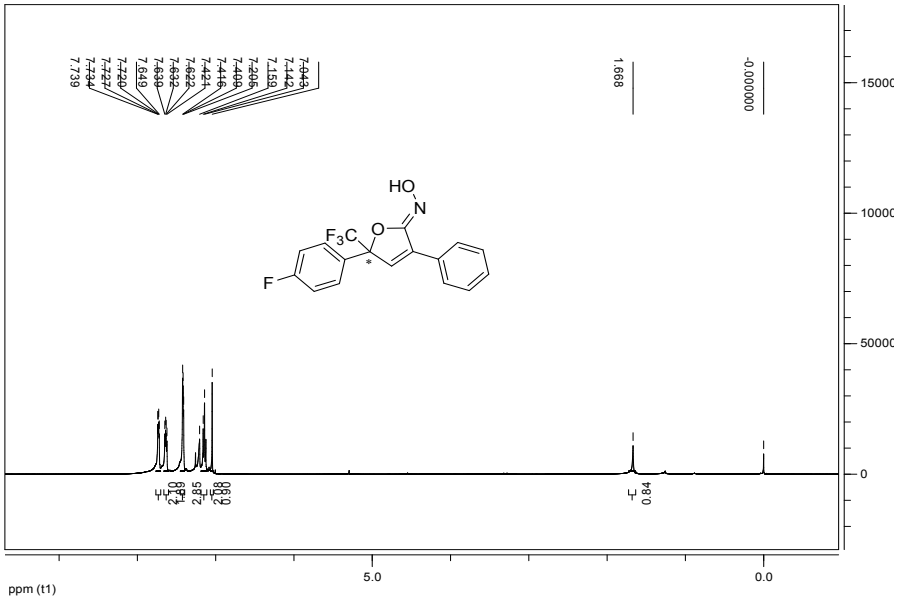
7.11-7.08 (m, 2H), 6.95 (s, 1H, =CH-); ^{13}C NMR (125 MHz, $CDCl_3$, δ ppm): δ = 164.73, 162.73, 157.38, 136.29, 136.06, 131.26, 130.18, 130.12, 129.66, 129.15, 127.87, 124.69, 123.86, 121.59, 115.86, 115.69, 90.26-89.76 (q, J_{C-F} = 250 Hz); ^{19}F NMR (400 MHz, $CDCl_3$) δ = -77.48 (s, 3F), -109.77-109.84 (m) ppm; TOF- HRMS (ESI, m/z) $[M+H]^+$ calcd for $C_{17}H_{11}ClF_4NO_2$: 372.0414, found 372.0421.

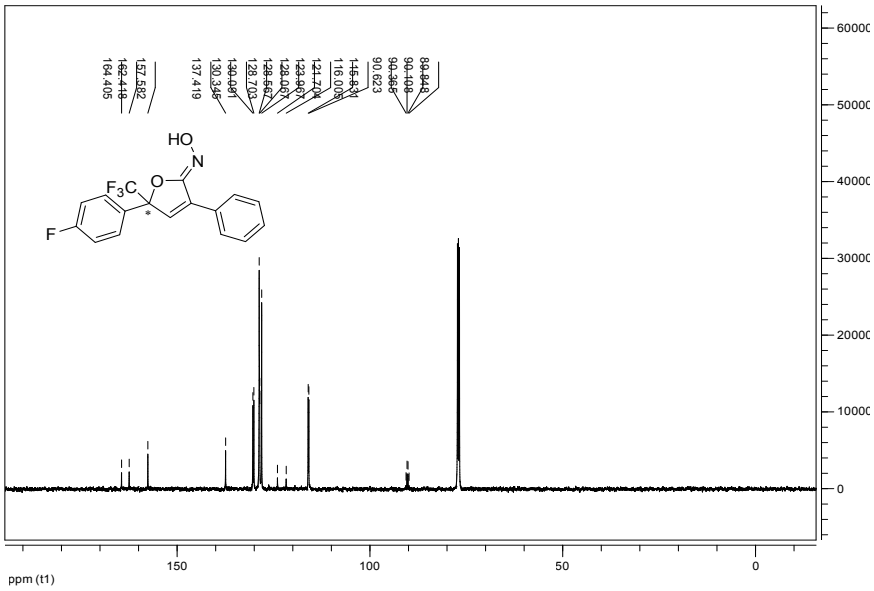
(ii). (*Z*)-5-(3-fluorophenyl)-3-(4-fluorophenyl)-5-(trifluoromethyl)furan-2(5H)-one oxime **(4i)**;

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): ν_{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) $[M+H]^+$ calcd for $C_{17}H_{11}ClF_5NO_2$: 381.0710, found 356.0707.

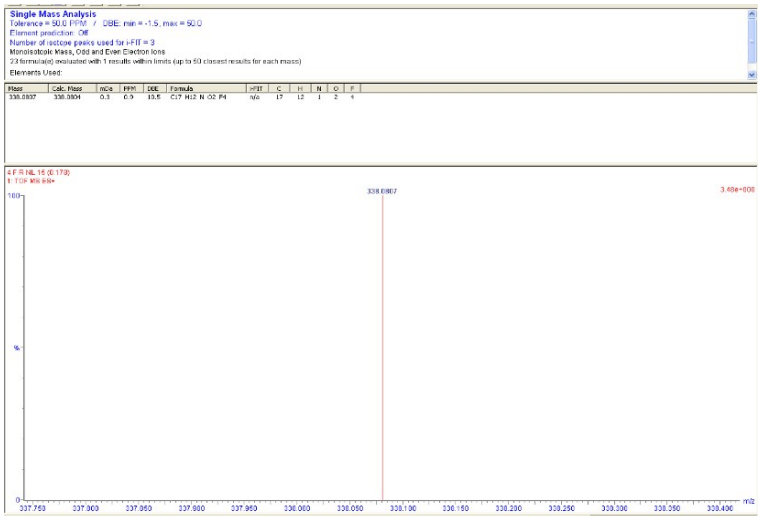
4.4. ^{1}H and ^{13}C-NMR spectra of trifluoromethylketones products with 2a:

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

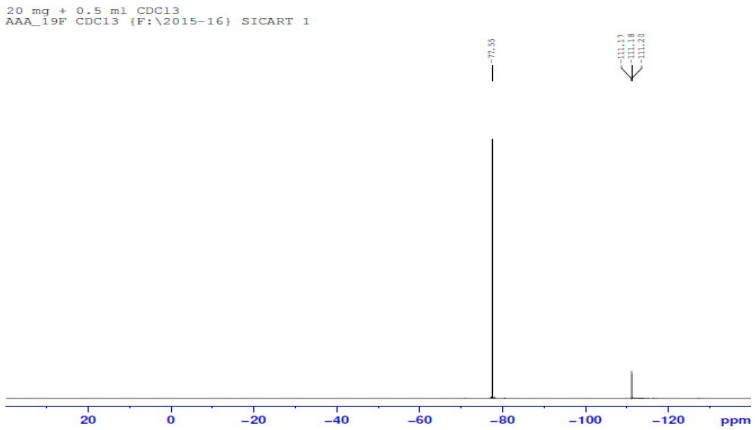




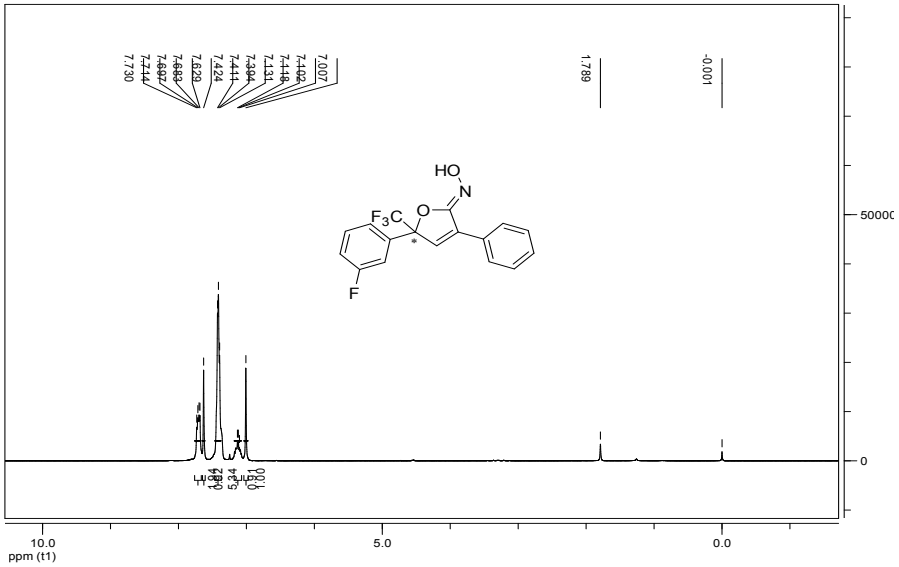
HRMS of compound **(3a)**

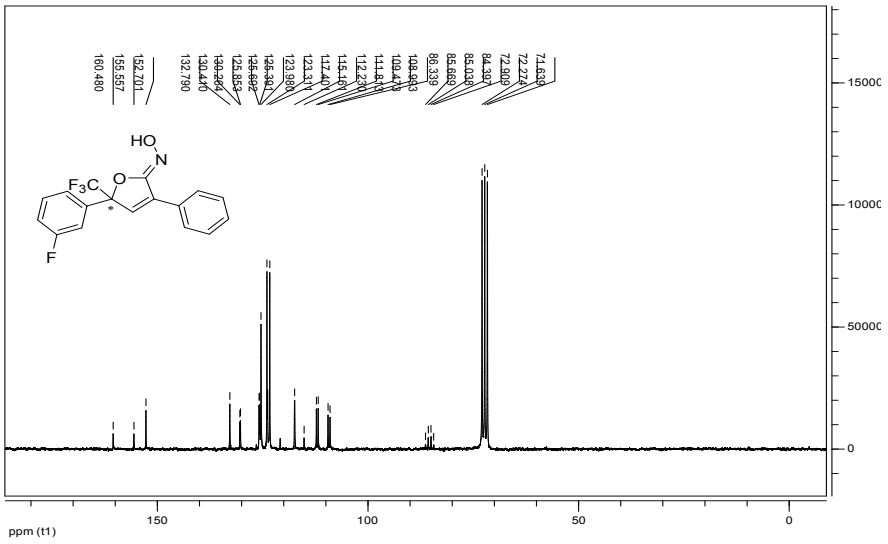


^{19}F NMR spectra of product (**3a)**

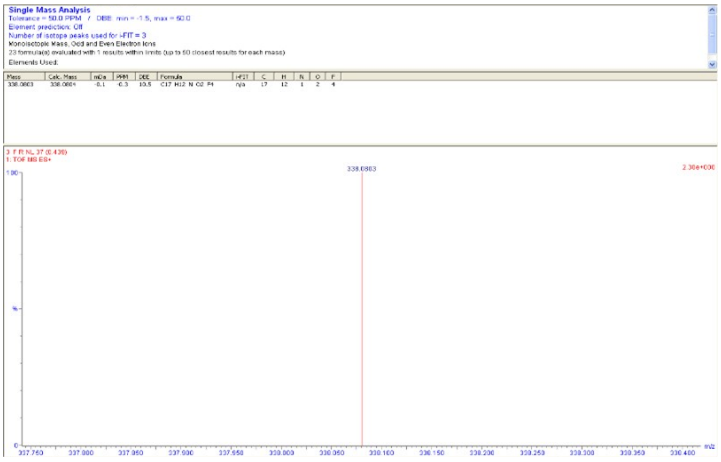


(ii). (*Z*)-5-(3-fluorophenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime **(3b)**;

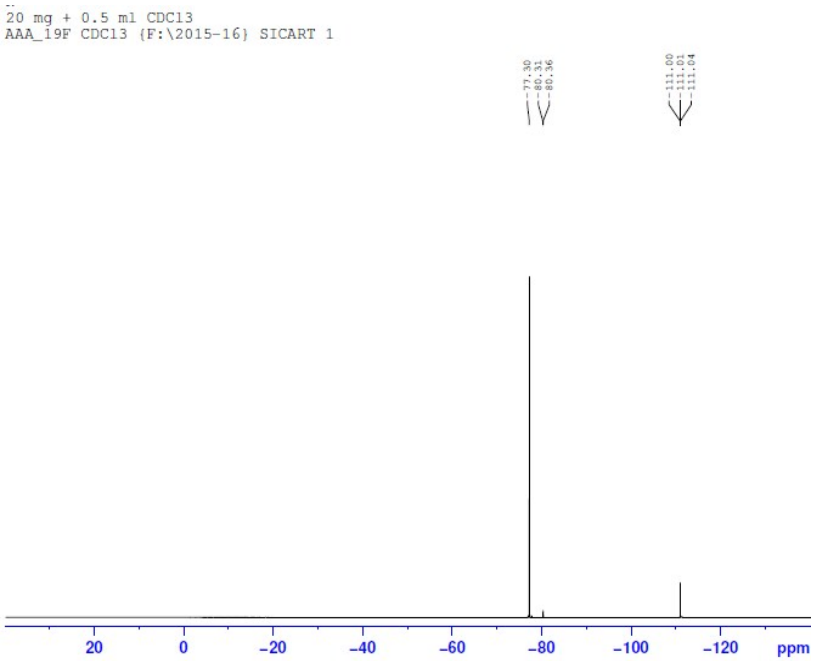


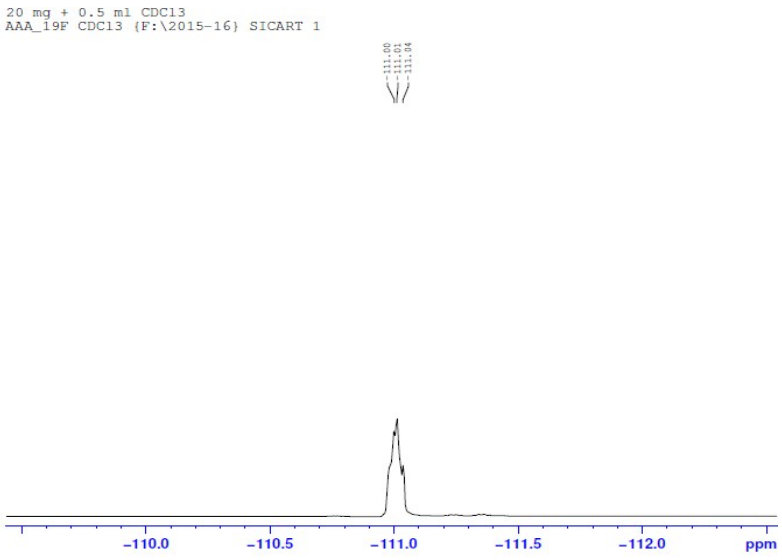


HRMS of compound **(3b)**

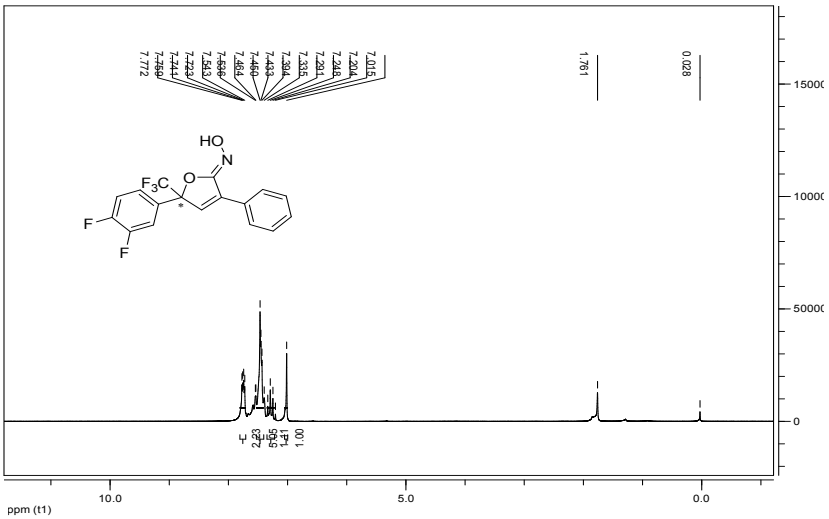


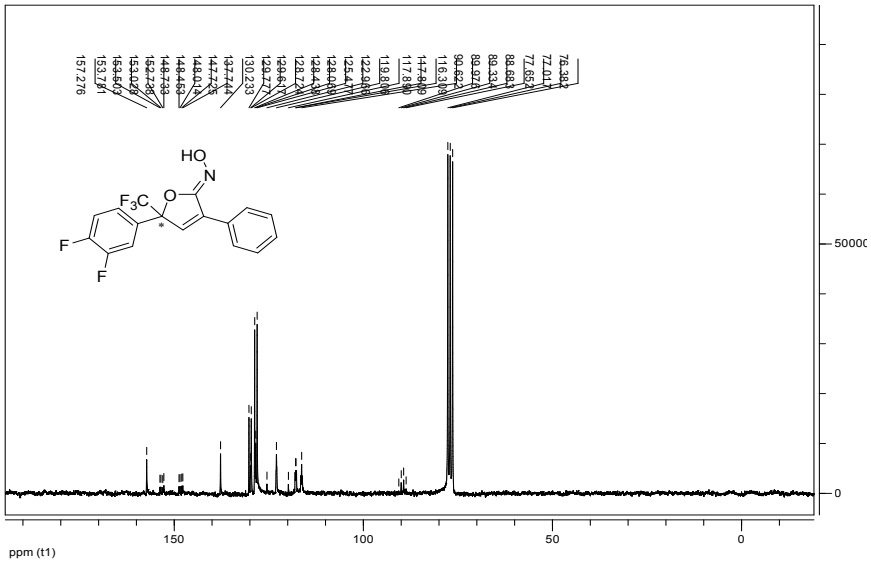
^{19}F NMR spectra of product (**3b)**



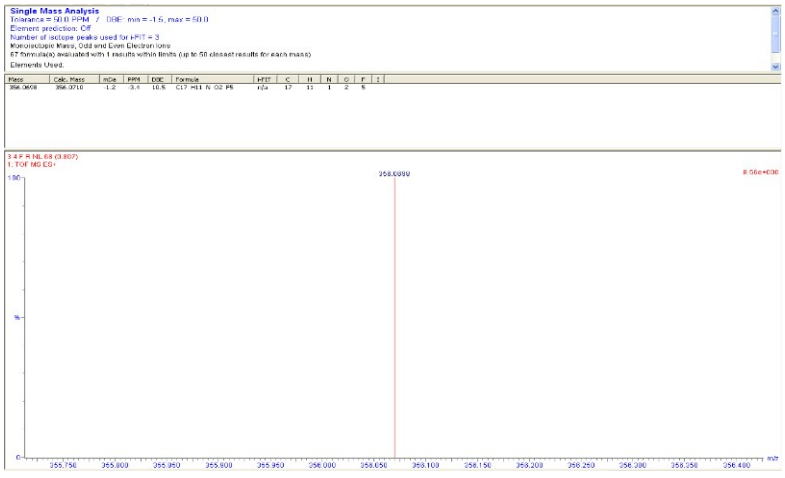


(iii). (Z)-5-(3,4-difluorophenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime **(3c)**;

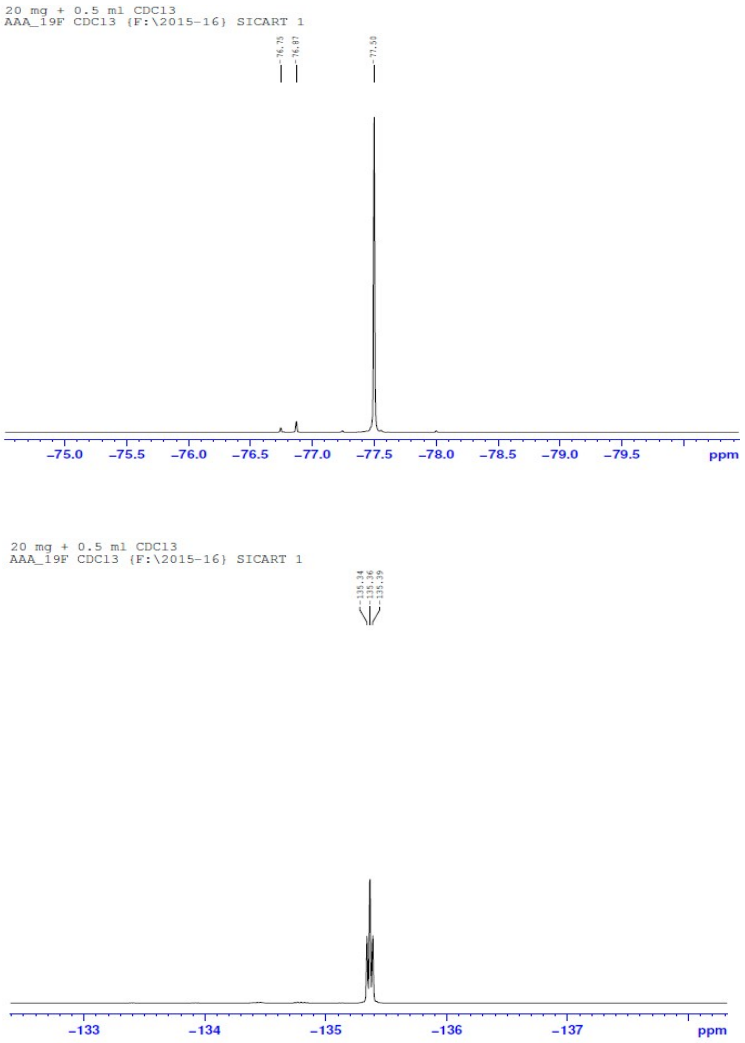




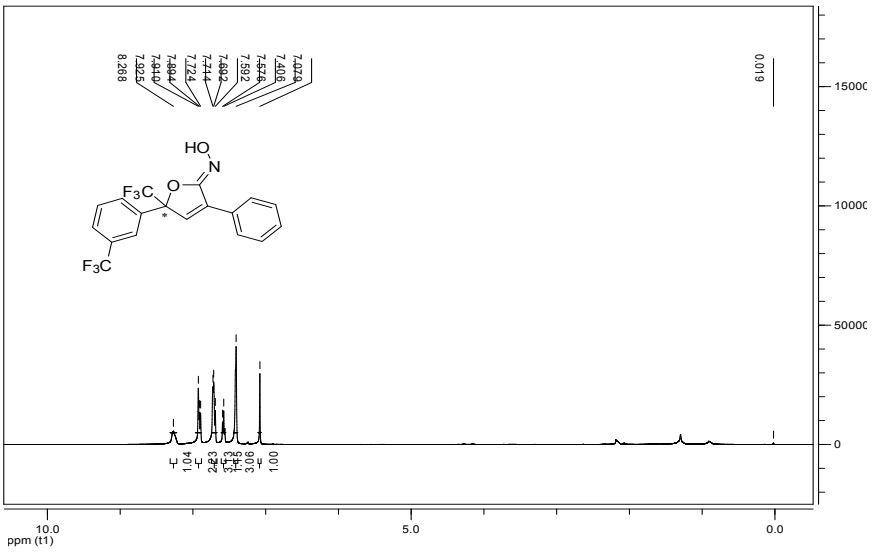
HRMS of compound **(3c)**

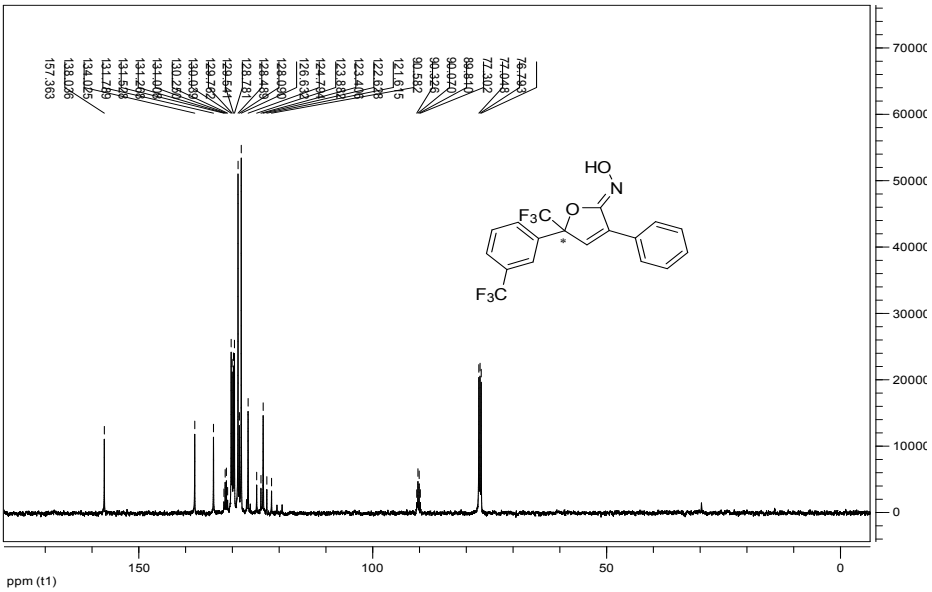


^{19}F NMR spectra of product (**3c)**

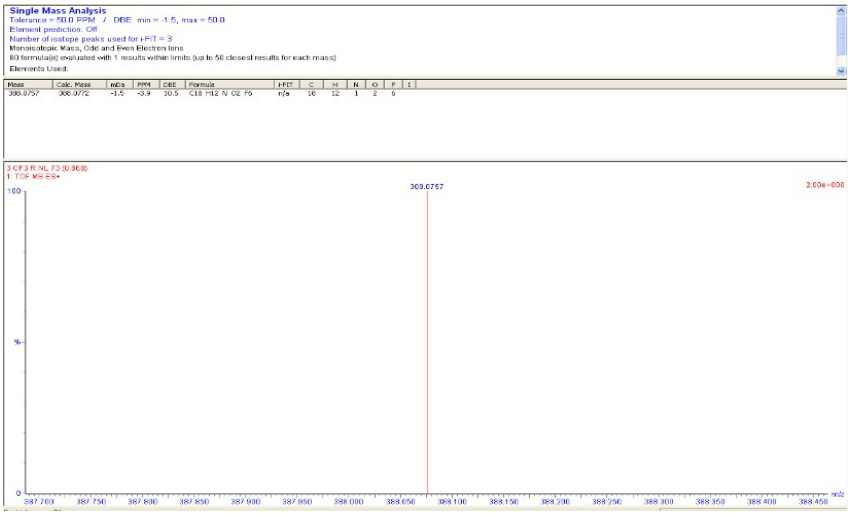


(iv). (*Z*)-3-phenyl-5-(trifluoromethyl)-5-(3-(trifluoromethyl)phenyl)furan-2(5H)-one oxime **(3d)**;

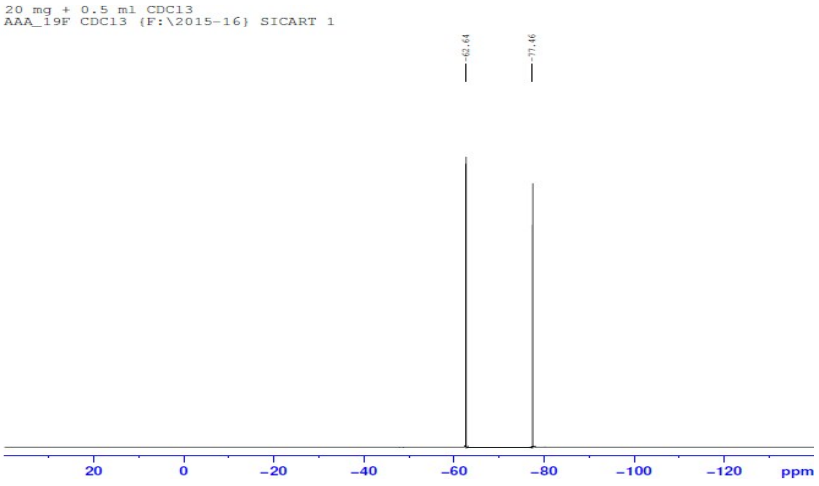




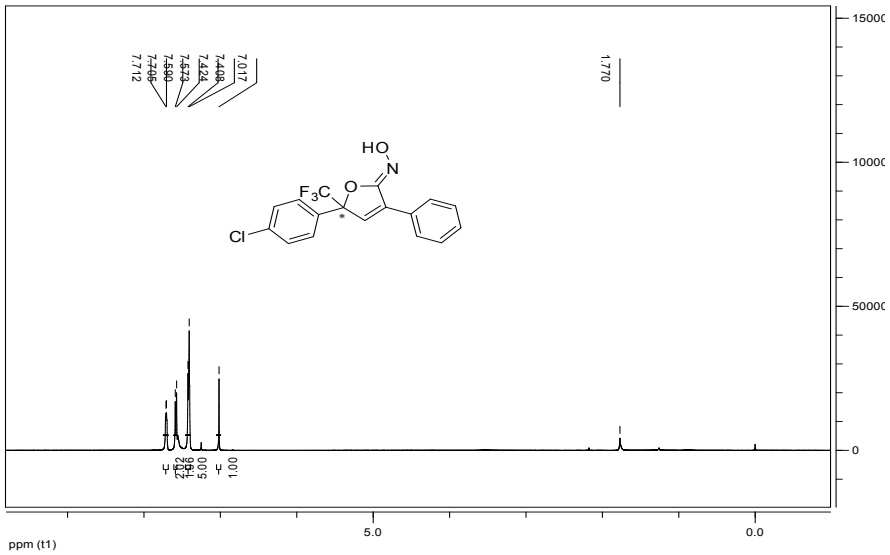
HRMS of compound **(3d)**

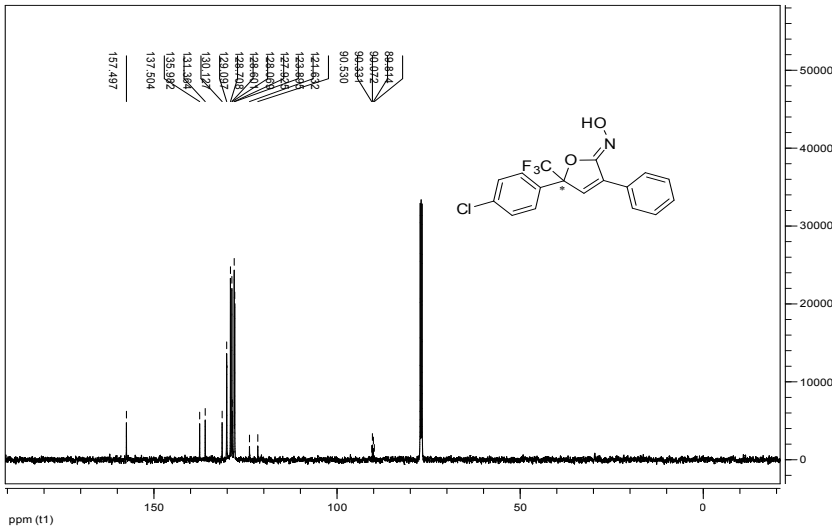


^{19}F NMR spectra of product (**3d)**

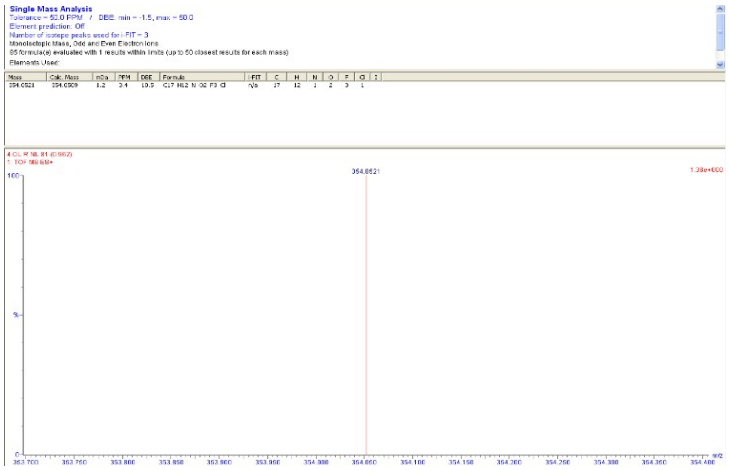


(v). (*Z*)-5-(4-chlorophenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime **(3e)**;

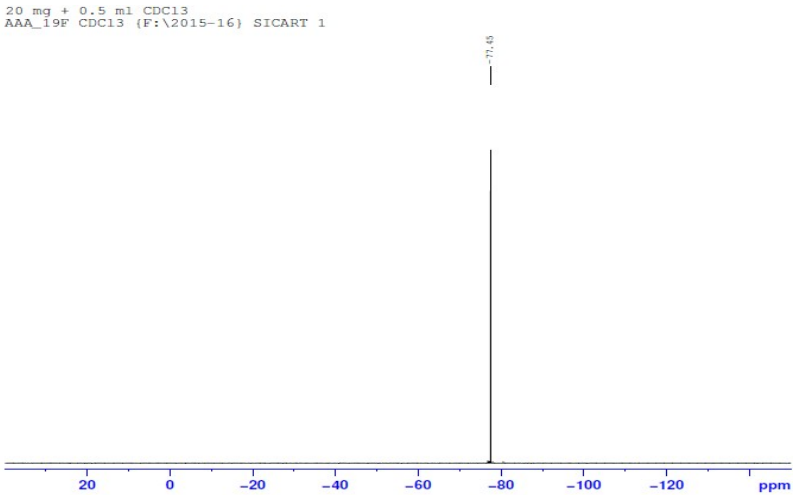




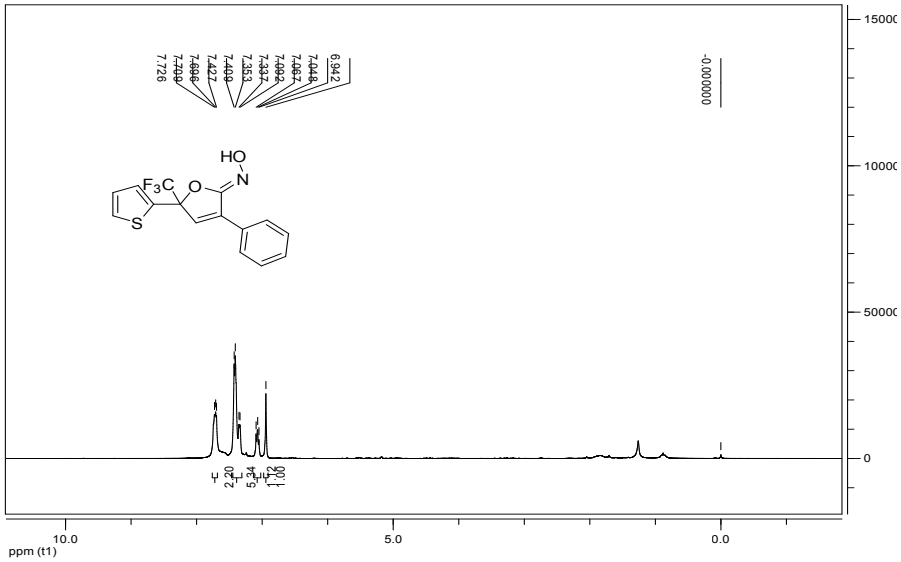
HRMS of compound **(3e)**

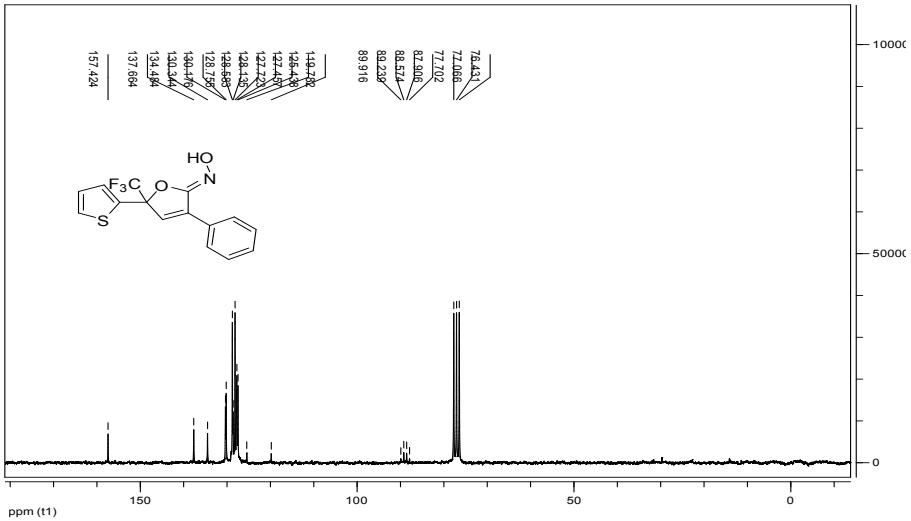


^{19}F NMR spectra of product (**3e)**

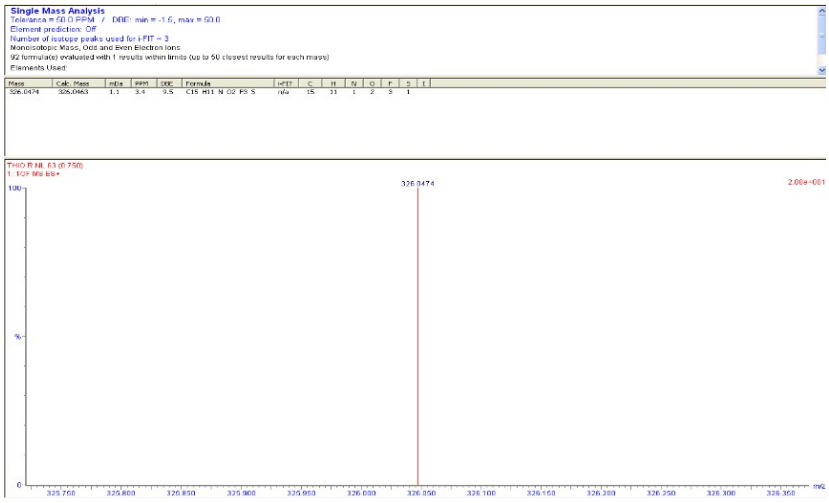


(vi). (*Z*)-3-phenyl-5-(thiophen-2-yl)-5-(trifluoromethyl)furan-2(5H)-one oxime **(3f)**;

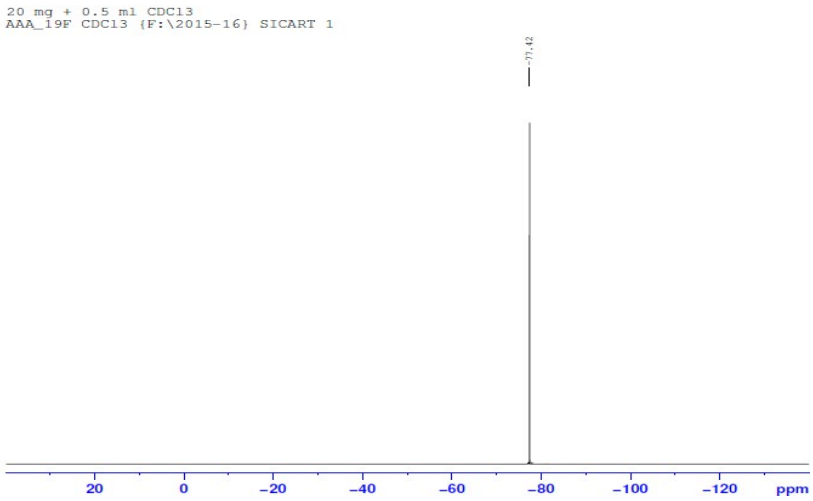




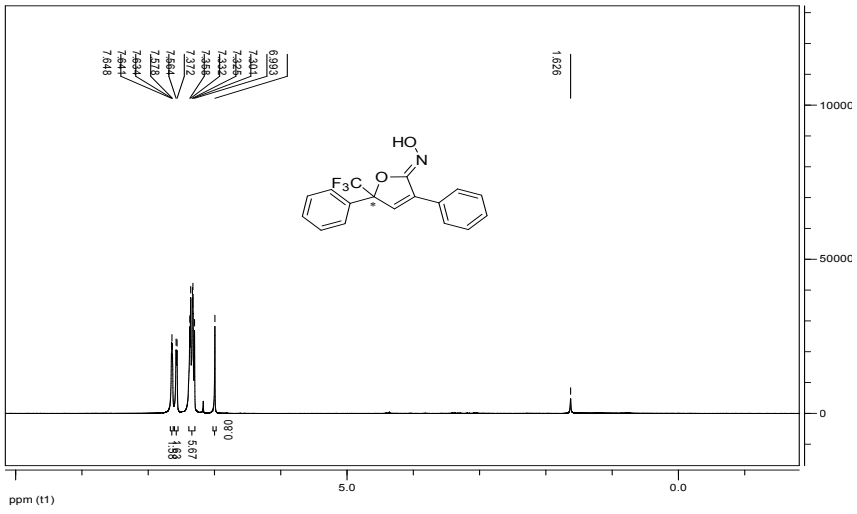
HRMS of compound **(3f)**

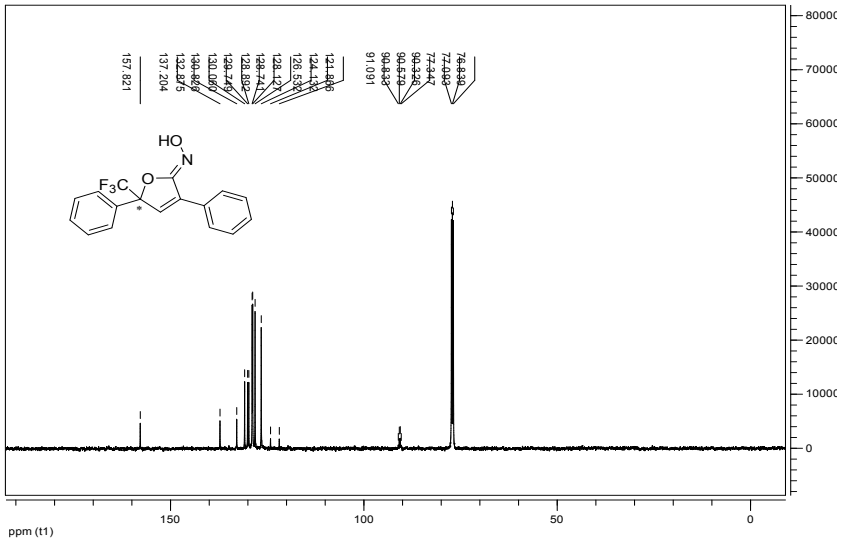


^{19}F NMR spectra of product (**3f)**

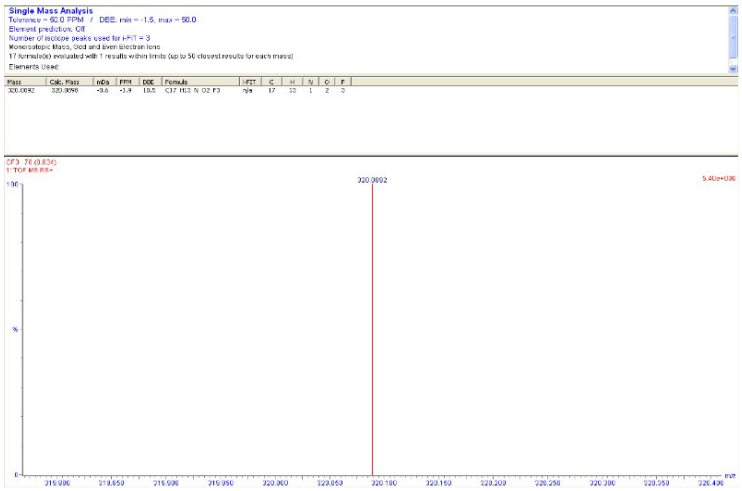


(vii). (*Z*)-3,5-diphenyl-5-(trifluoromethyl)furan-2(5H)-one oxime **(3g)**;

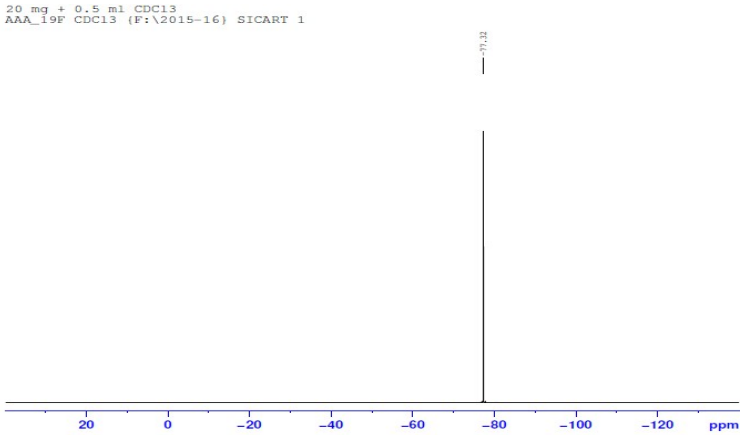




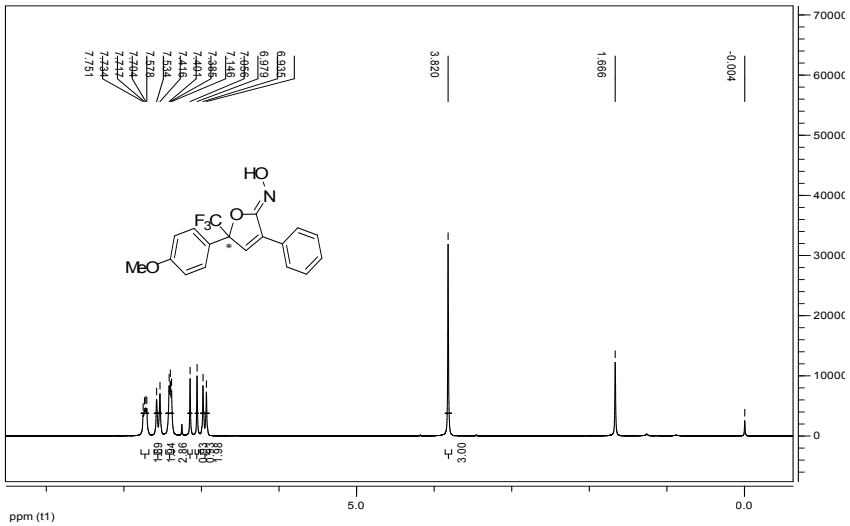
HRMS of compound **(3g)**

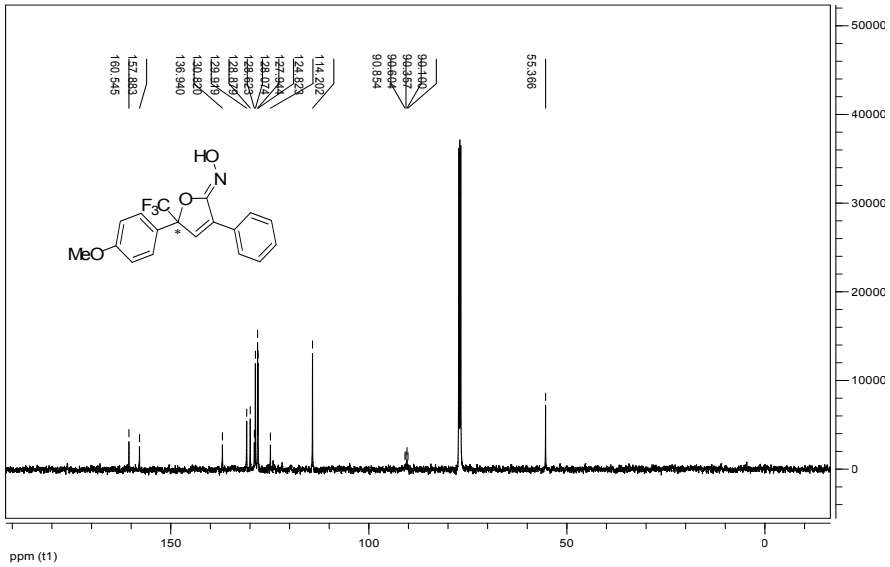


^{19}F NMR spectra of product (**3g**)

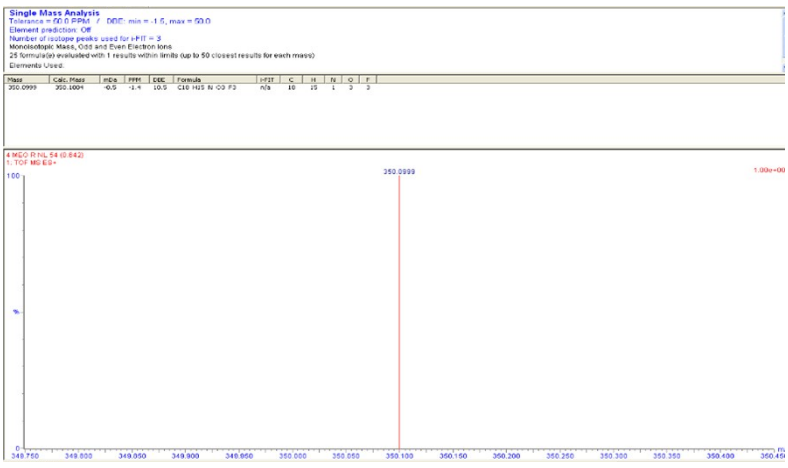


(viii). (*Z*)-5-(4-methoxyphenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime **(3h)**;

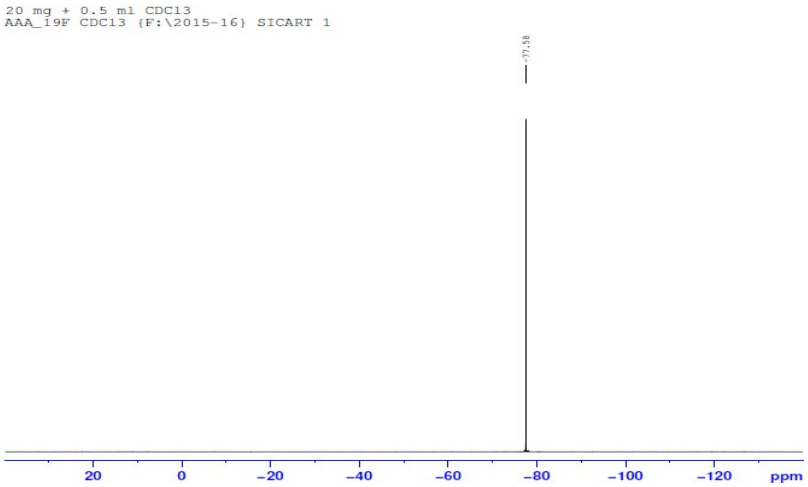




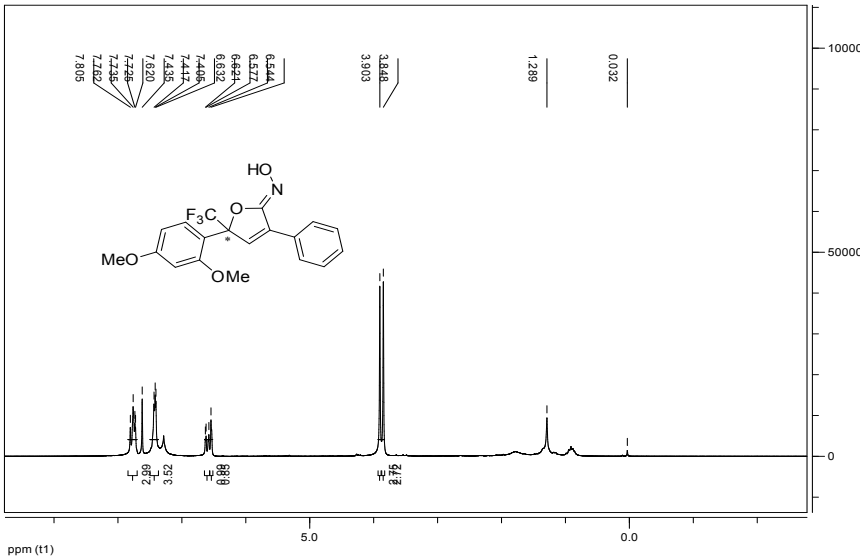
HRMS of compound **(3h)**

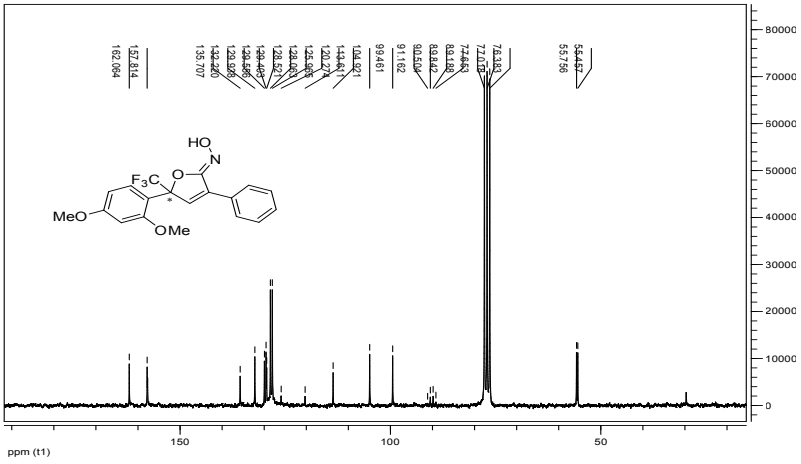


^{19}F NMR spectra of product (**3h)**

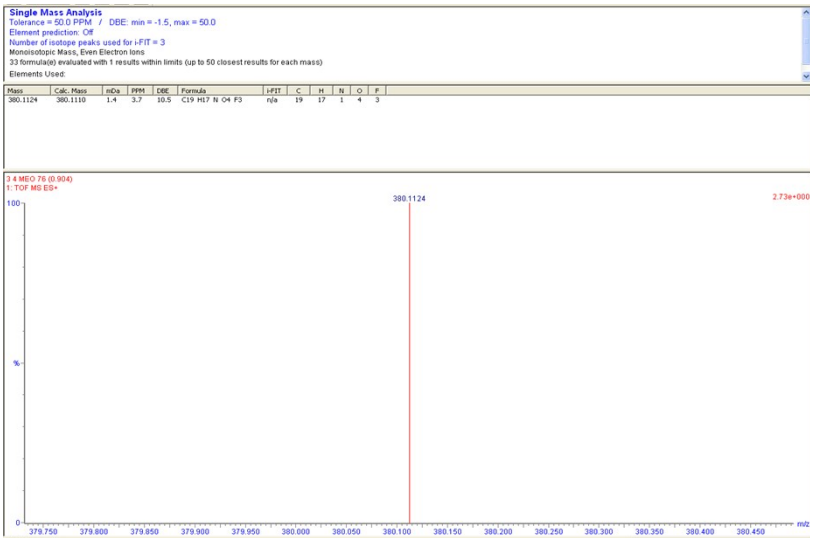


(ix). (Z)-5-(2,4-dimethoxyphenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime **(3i)**;

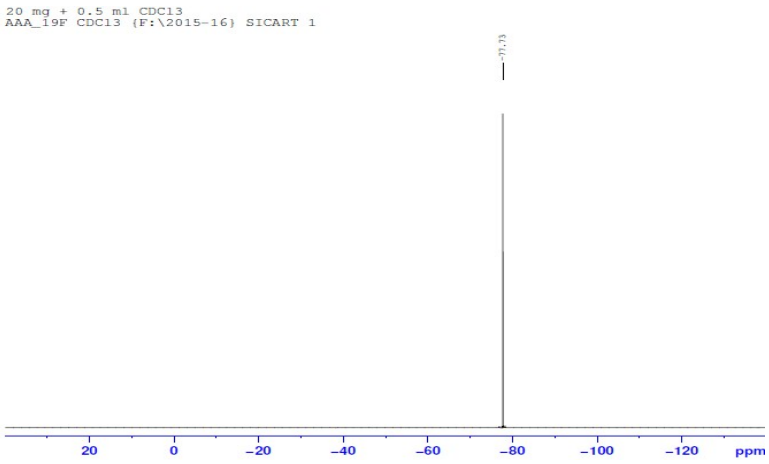




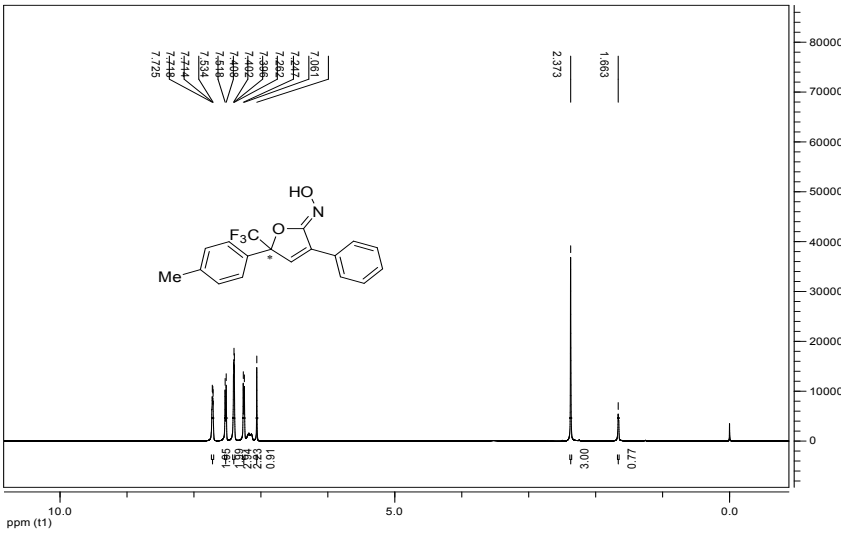
HRMS of compound **(3i)**

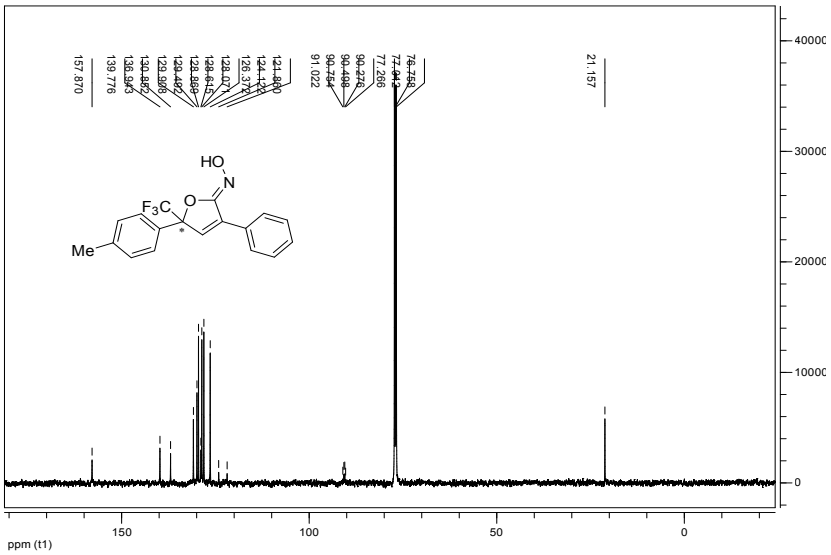


^{19}F NMR spectra of product (**3i)**

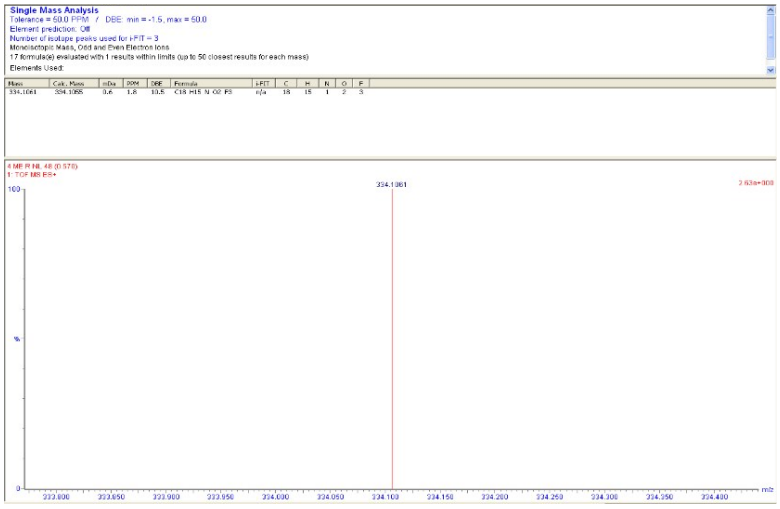


(x). (*Z*)-5-(4-methylphenyl)-3-phenyl-5-(trifluoromethyl)furan-2(5H)-one oxime **(3j)**;

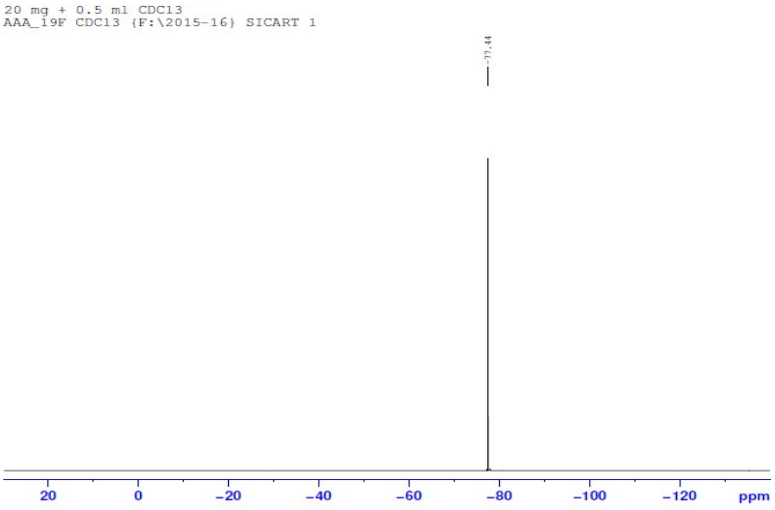




HRMS of compound **(3j)**

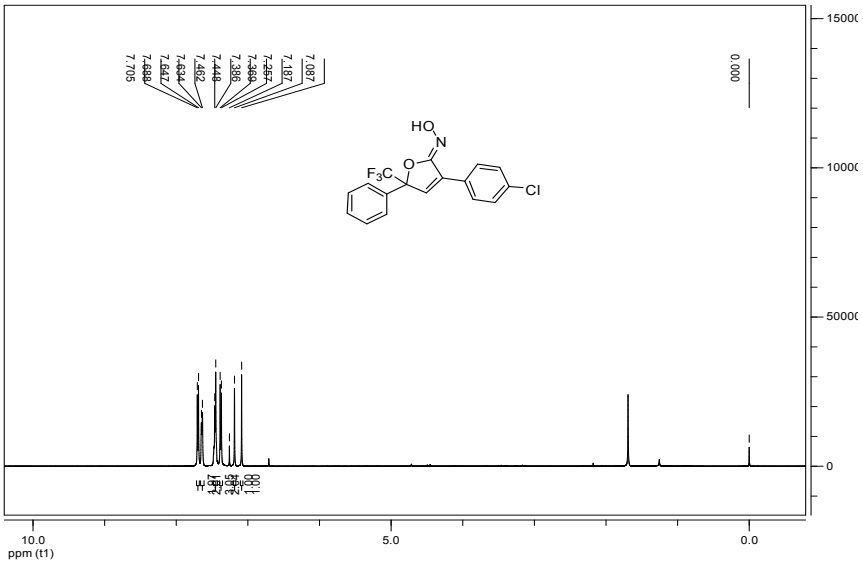


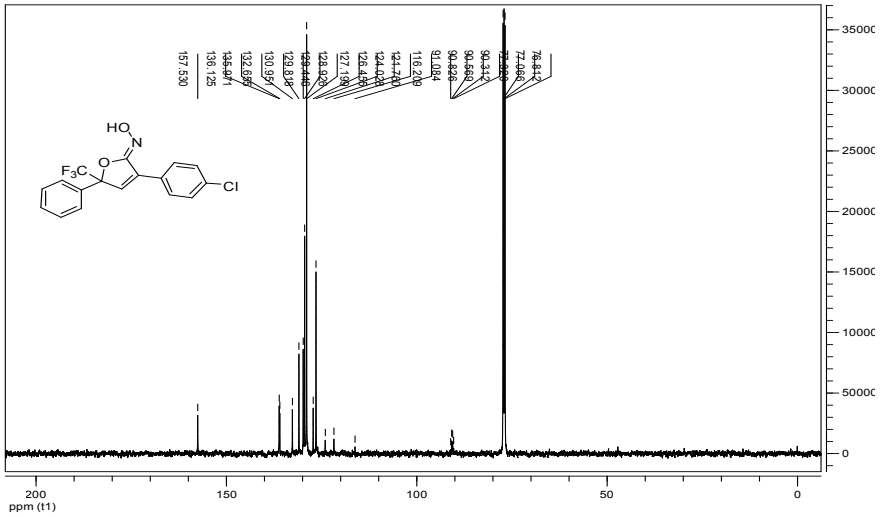
^{19}F NMR spectra of product (**3j)**



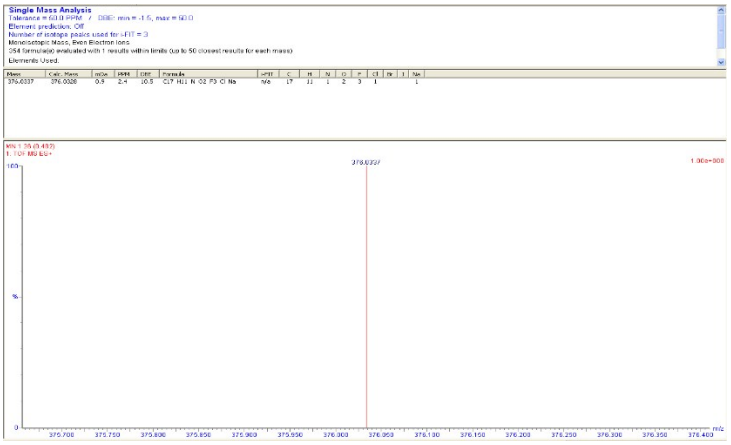
4.5. ^{1}H and ^{13}C-NMR spectra of trifluoromethylketone products with 2b:

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

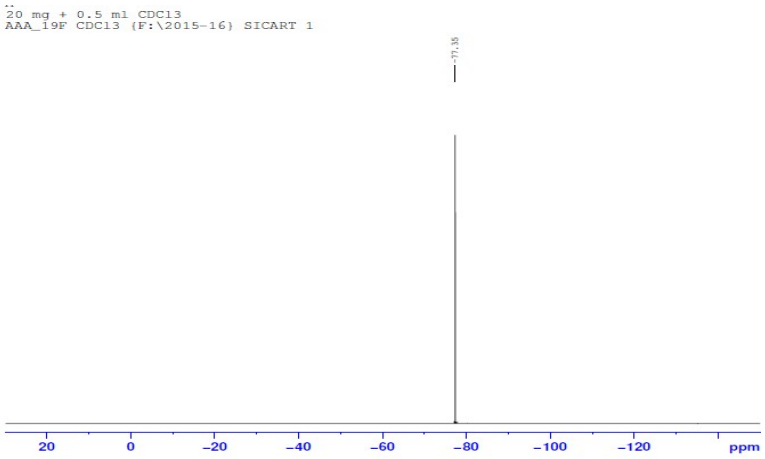




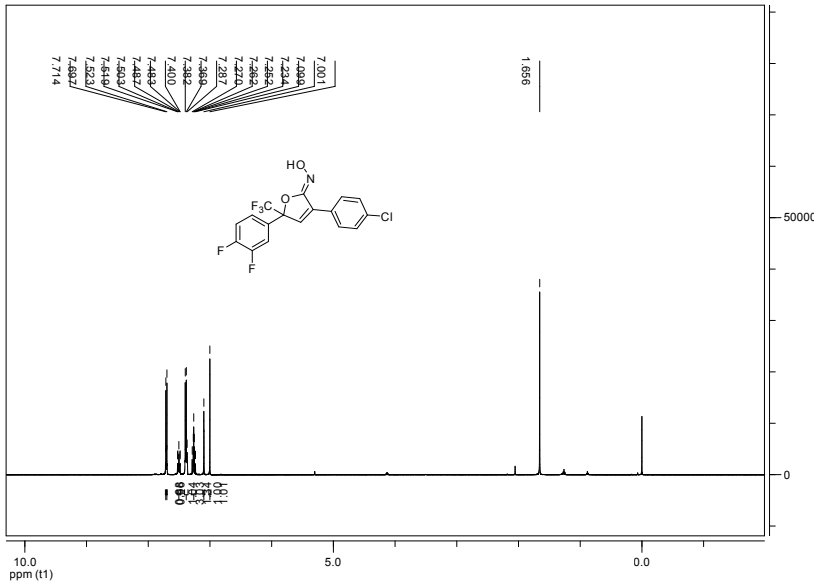
HRMS of compound **(4a)**

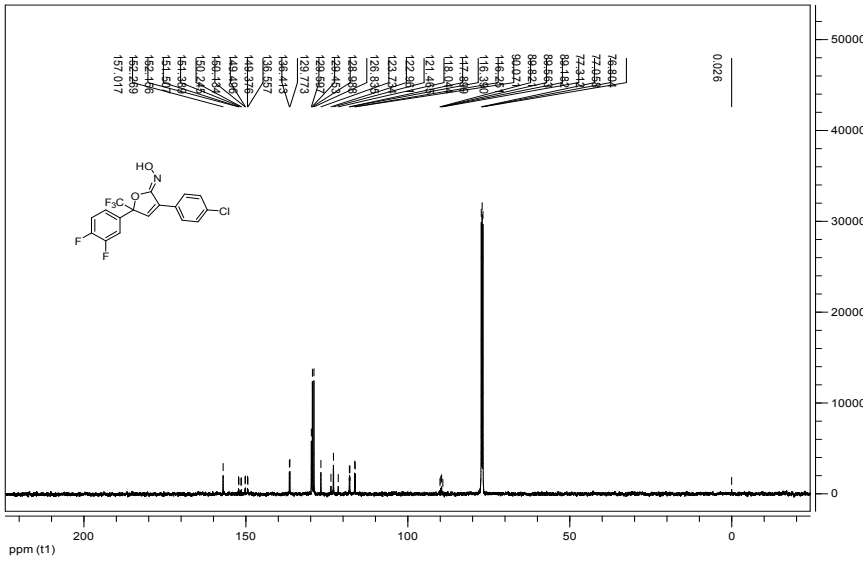


^{19}F NMR spectra of product (**4a)**

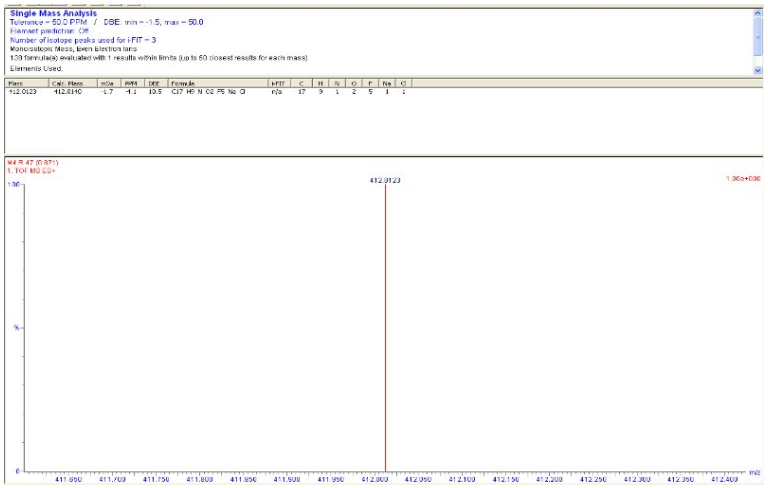


(ii). (*Z*)-3-(4-chlorophenyl)-5-(3,4-difluorophenyl)-5-(trifluoromethyl)furan-2(5H)-one oxime **(4b)**;

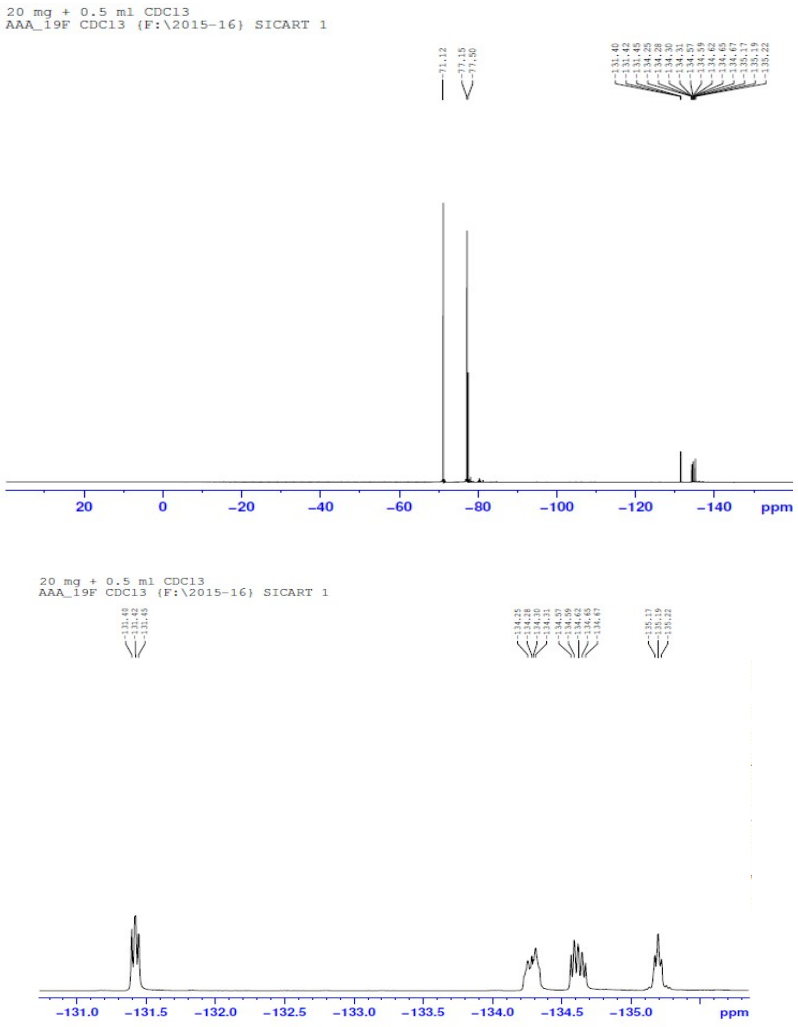




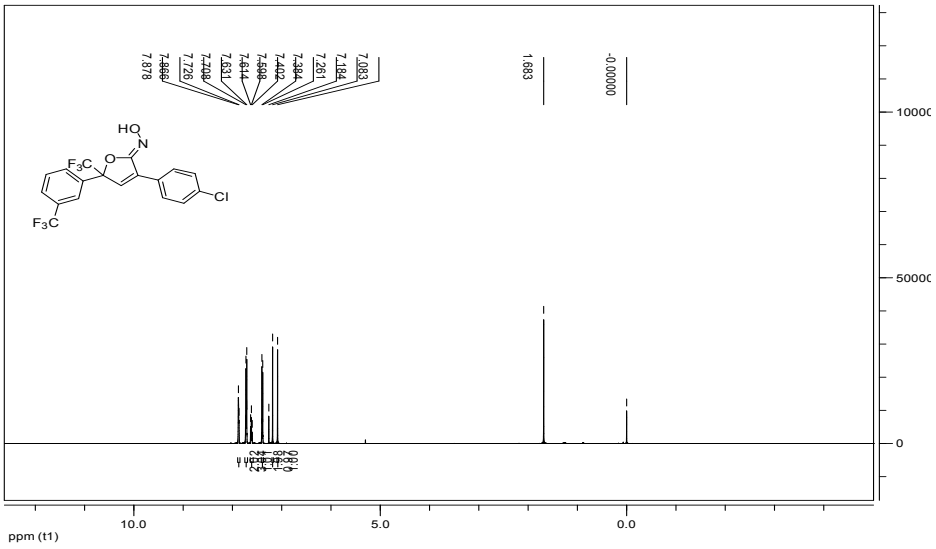
HRMS of compound **(4b)**

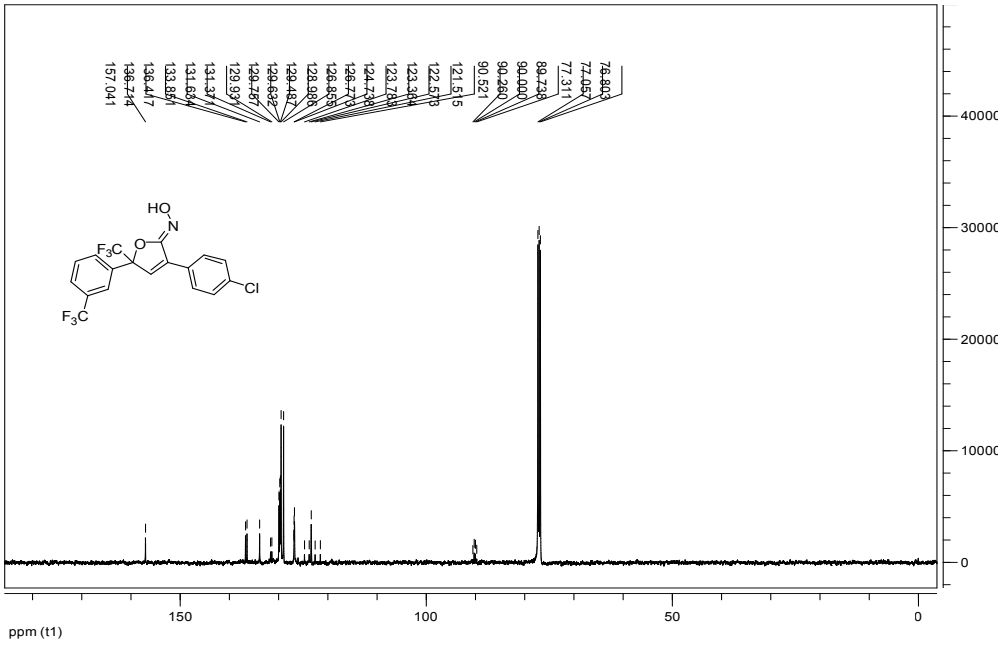


^{19}F NMR spectra of product (**4b)**

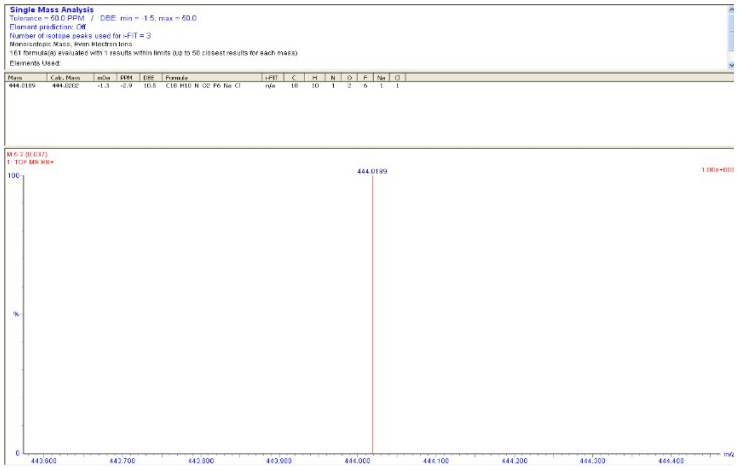


(iii). (*Z*)-3-(4-chlorophenyl)-5-(trifluoromethyl)-5-(3-(trifluoromethyl)phenyl)furan-2(5H)-one oxime **(4c)**;

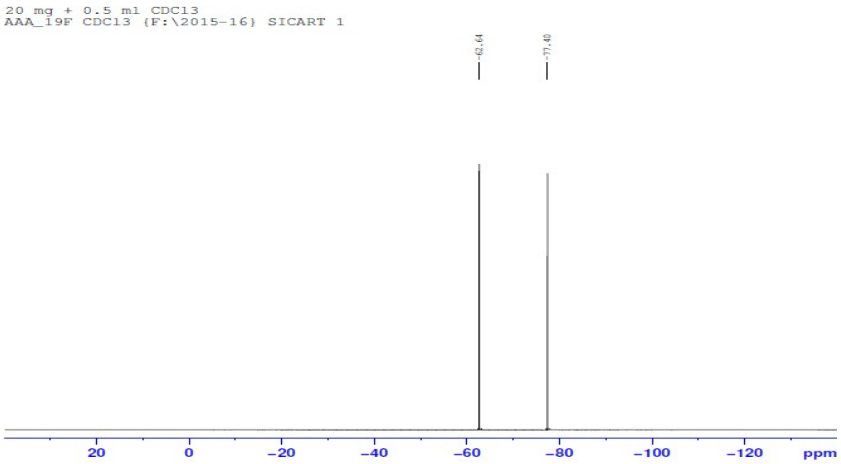




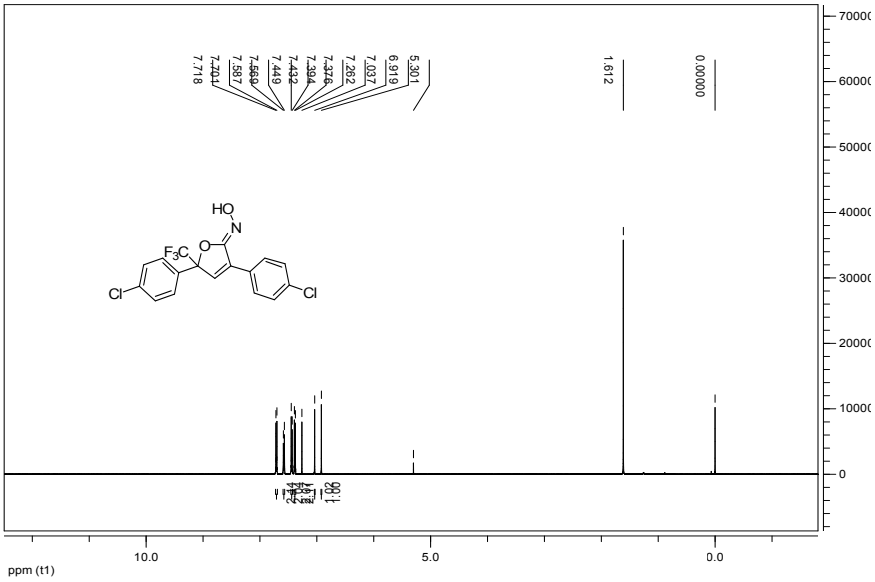
HRMS of compound **(4c)**

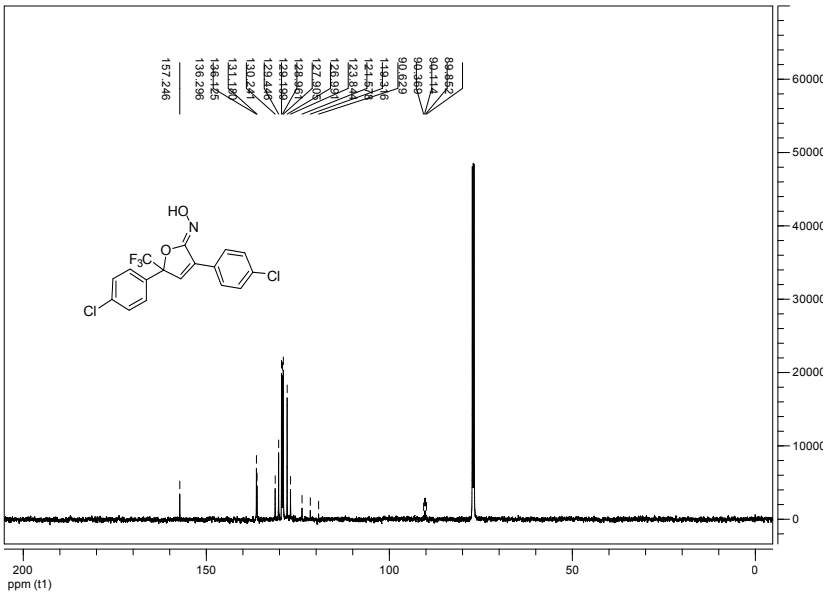


^{19}F NMR spectra of product (**4c)**

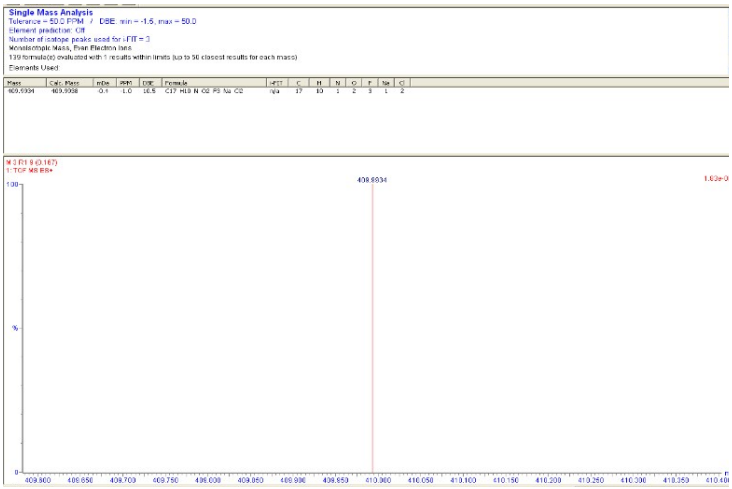


(iv). (*Z*)-3,5-bis(4-chlorophenyl)-5-(trifluoromethyl)furan-2(5H)-one oxime **(4d)**;

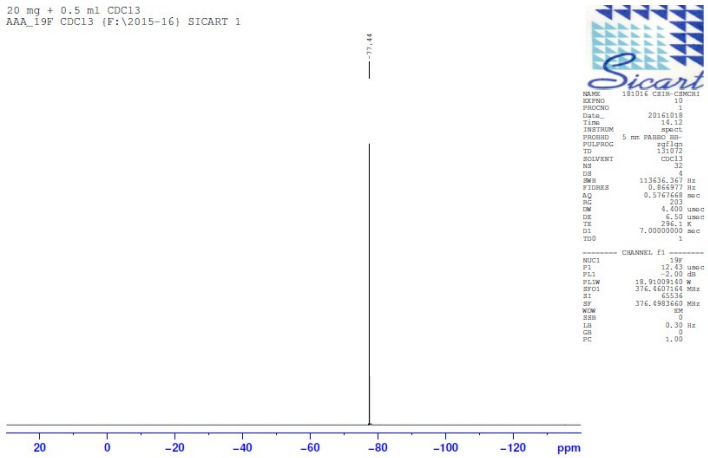




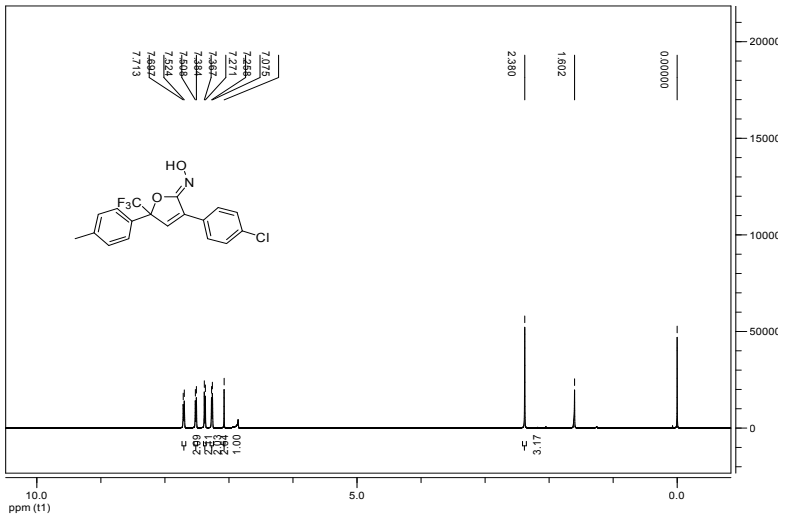
HRMS of compound **(4d)**

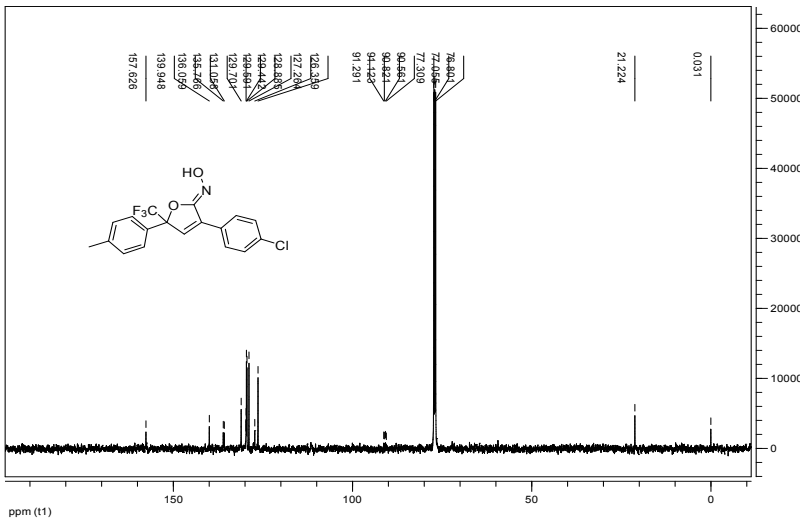


^{19}F NMR spectra of product (**4d)**

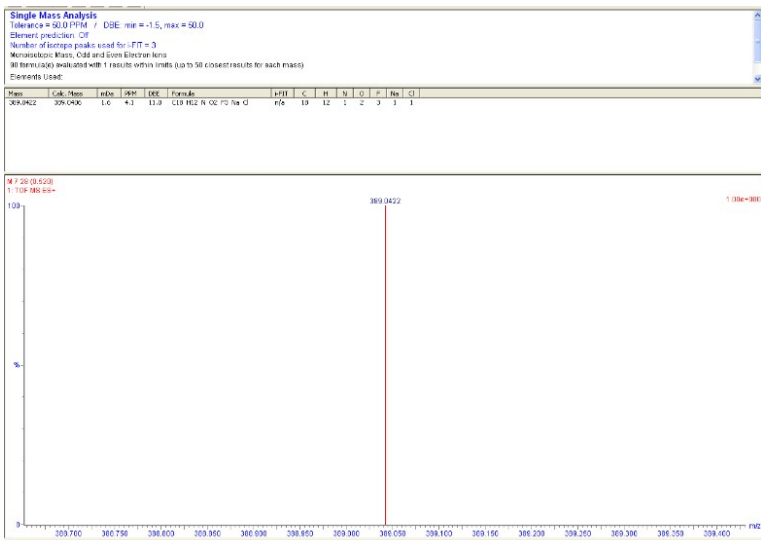


(v). (*Z*)-3-(4-chlorophenyl)-5-(*p*-tolyl)-5-(trifluoromethyl)furan-2(5H)-one oxime **(4e)**;

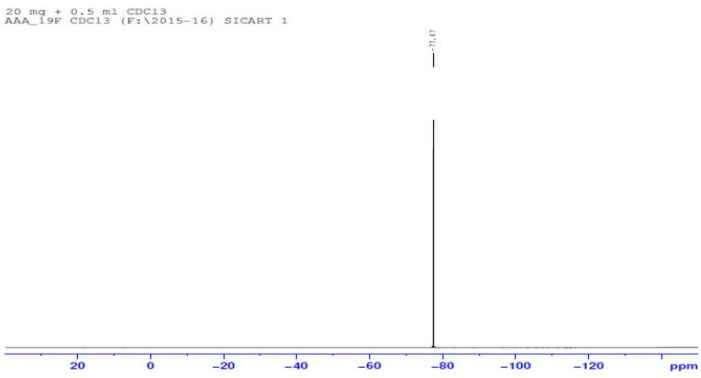




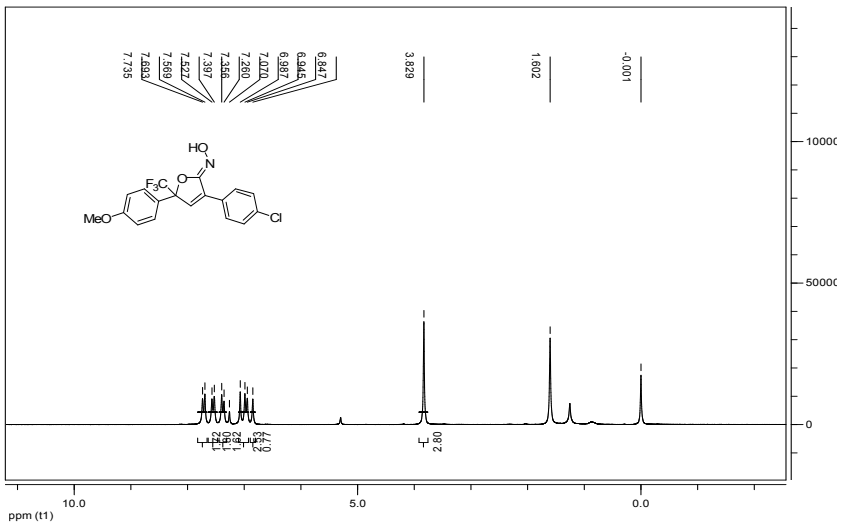
HRMS of compound **(4e)**

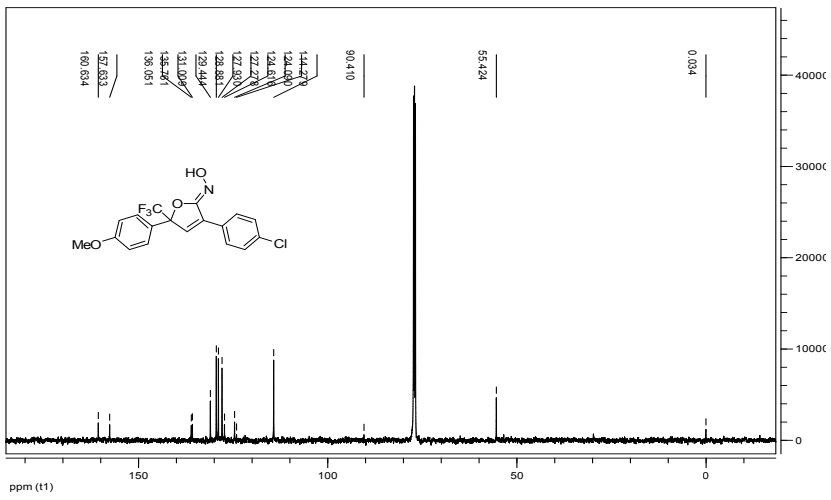


^{19}F NMR spectra of product (**4e)**

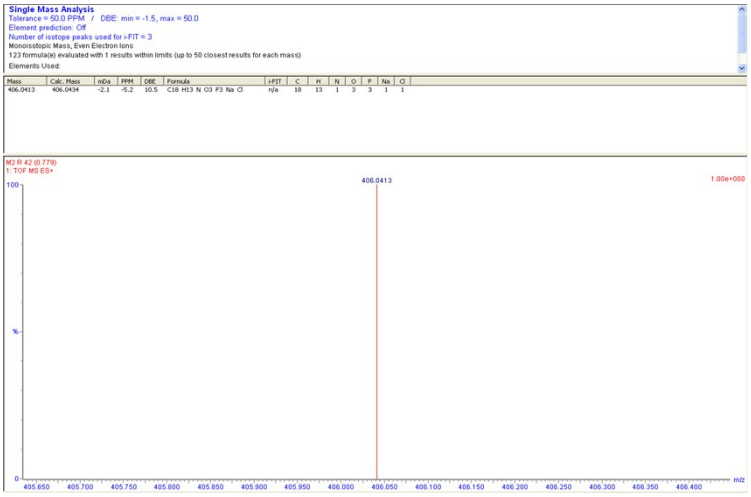


(vi). (*Z*)-3-(4-chlorophenyl)-5-(4-methoxyphenyl)-5-(trifluoromethyl)furan-2(5H)-one oxime **(4f)**;

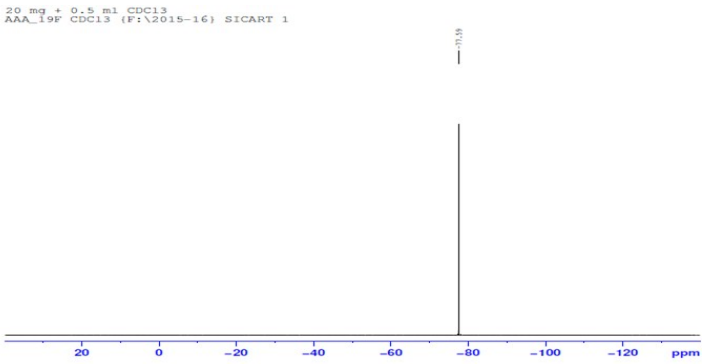




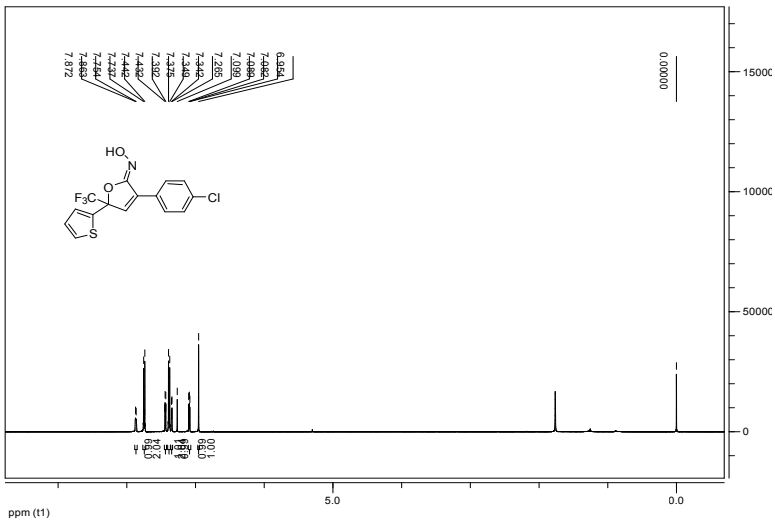
HRMS of compound **(4f)**

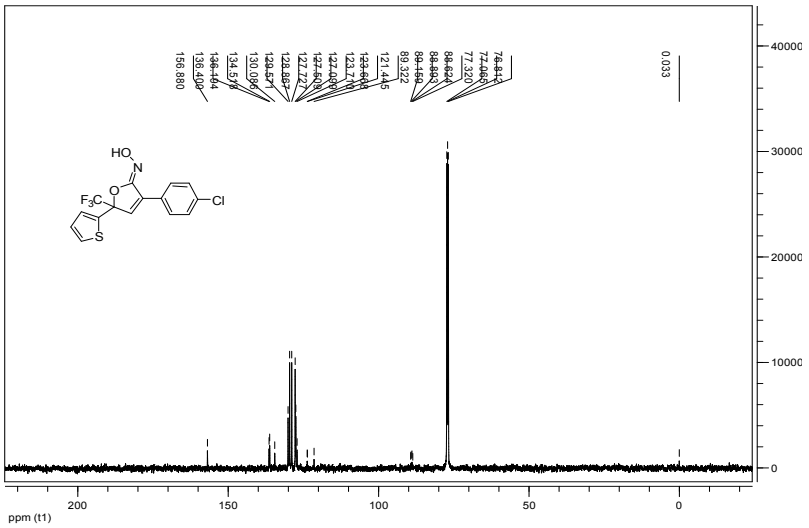


^{19}F NMR spectra of product (**4f)**

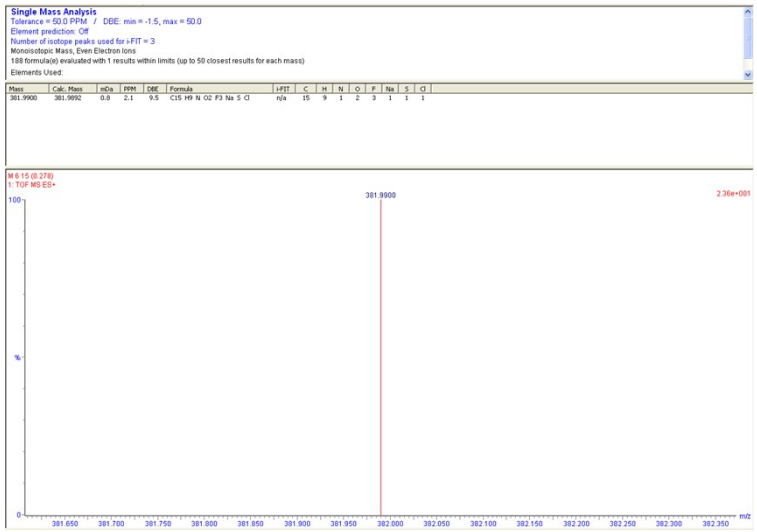


(vii). (*Z*)-3-(4-chlorophenyl)-5-(thiophen-2-yl)-5-(trifluoromethyl)furan-2(5H)-one oxime **(4g)**;

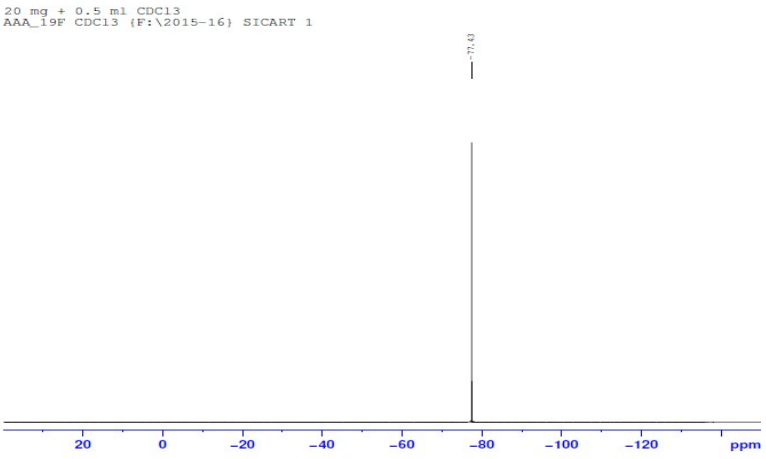




HRMS of compound **(4g)**

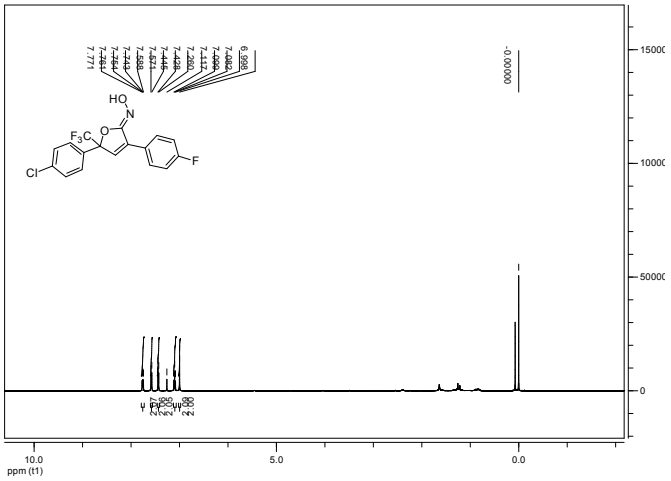


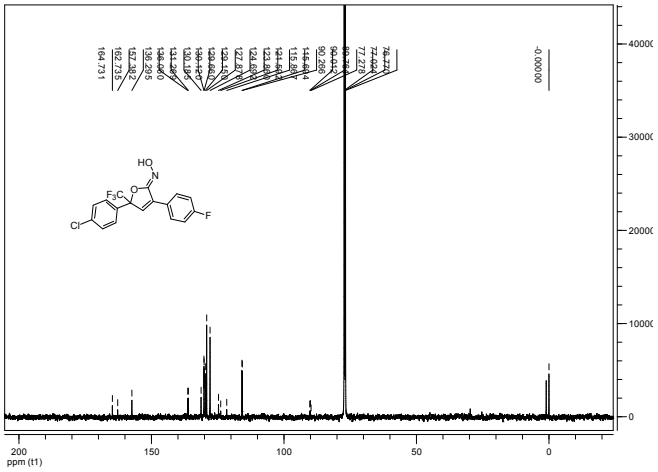
^{19}F NMR spectra of product (**4g)**



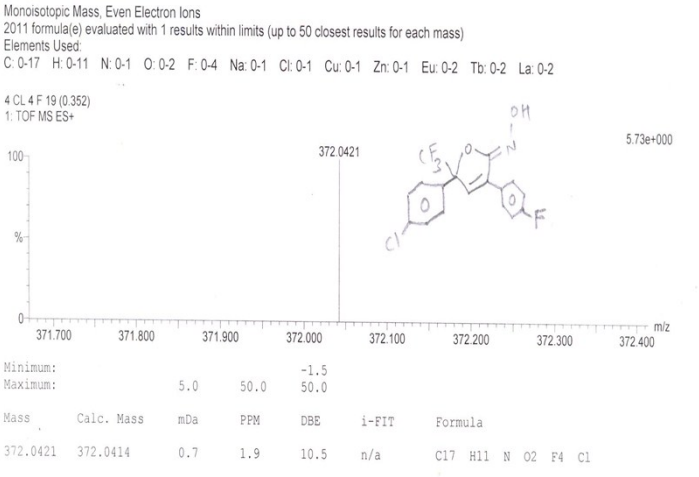
4.6. ^{1}H and ^{13}C-NMR spectra of trifluoromethylketone products with 2c:

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

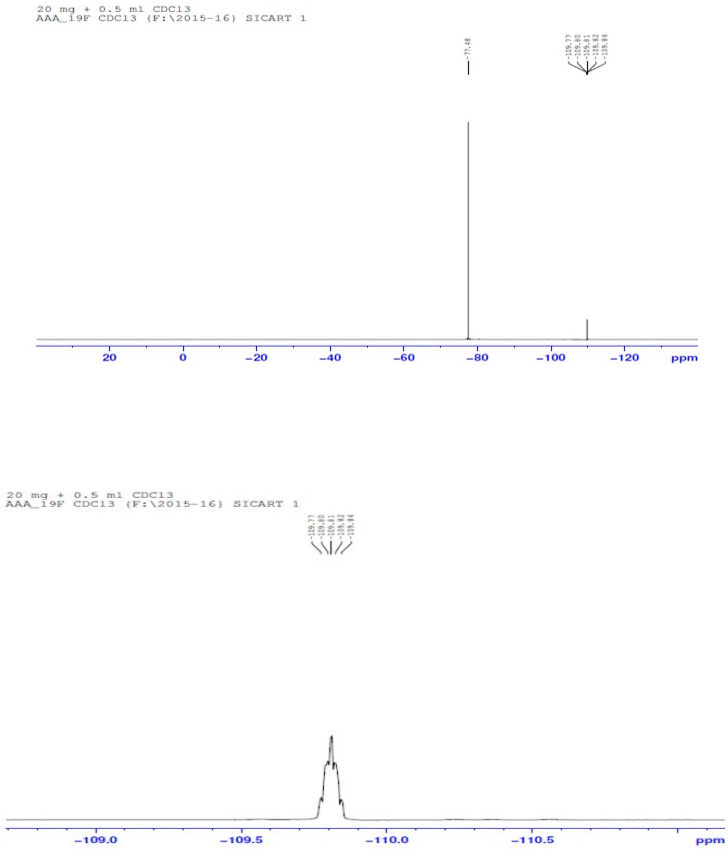




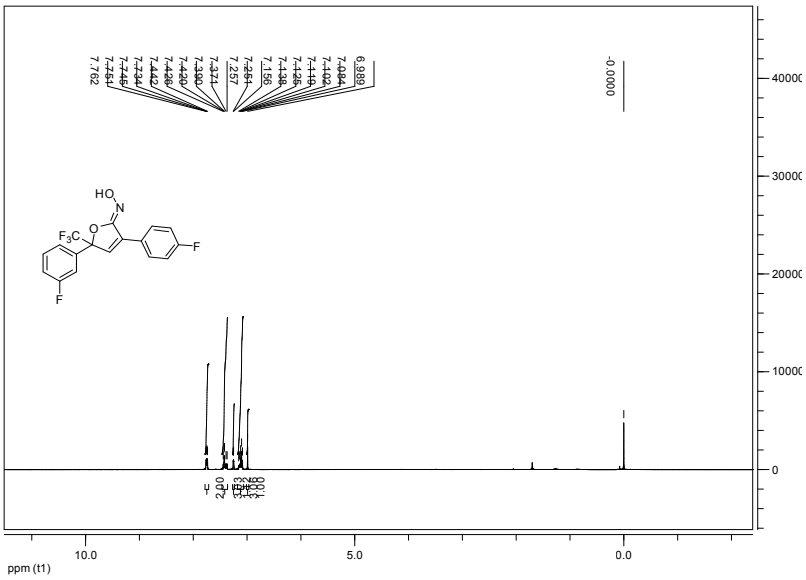
HRMS of compound **(4h)**

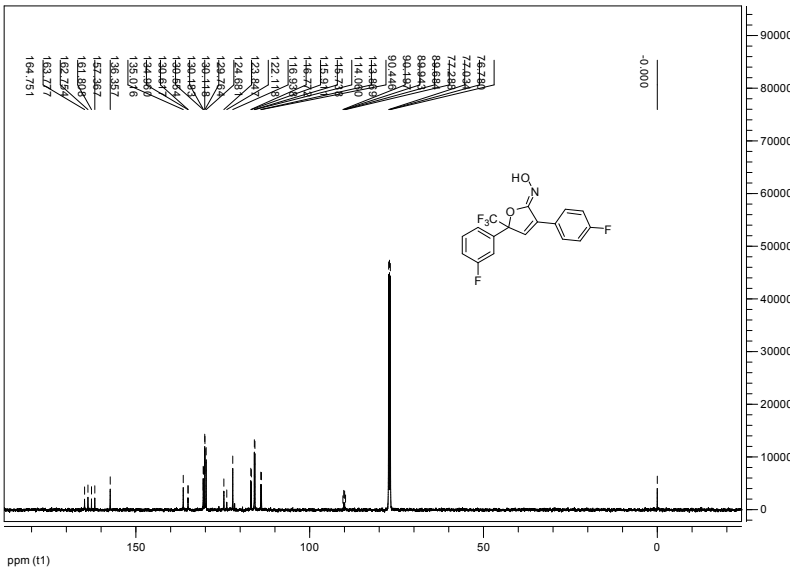


^{19}F NMR spectra of product (**4h)**

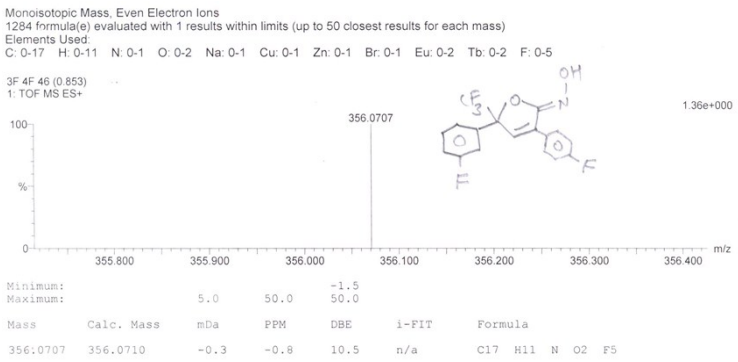


(ii). (*Z*)-5-(3-fluorophenyl)-3-(4-fluorophenyl)-5-(trifluoromethyl)furan-2(5H)-one oxime **(4i)**;

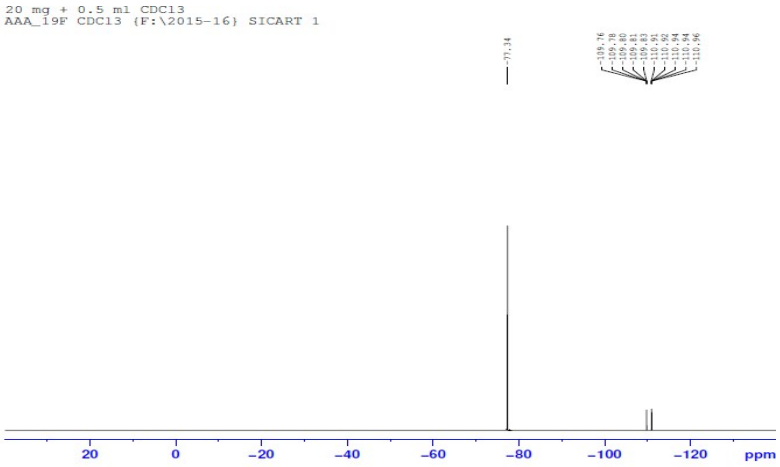


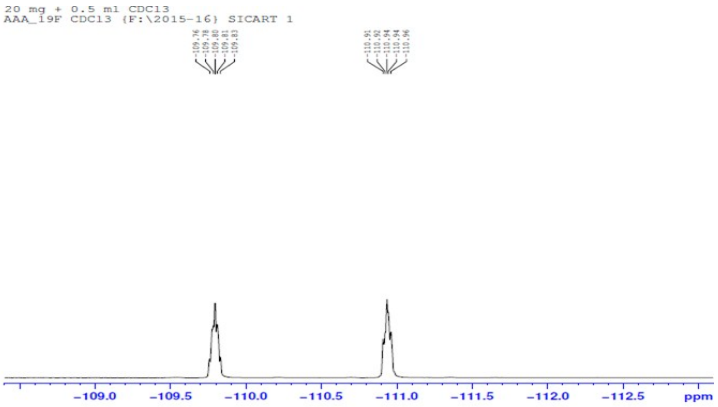


HRMS of compound **(4i)**



^{19}F NMR spectra of product (**4i**)





5. References:

1. A. J. N. Martin, L Ozores and B. List, *J. Am. Chem. Soc.*, 2007, **129**, 8976.