SUPPORTING INFORMATION

Chemoselective Reduction of α-Keto Aldehydes by Rongalite in Water: A Metal and Hydride Free Approach

Madhu Inapanuri, Hari Prasad Kokatla[a]* Rambabu Kandukuri and Neetika Singh

Department of Chemistry, National Institute of Technology Warangal, Telangana-506004, India.

E-mail: harikokatla@nitw.ac.in

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1. General Information

All chemicals and solvents were purchased from Alfa Aesar, Spectrochem, SRL, Finar, Sisco Research Laboratories Pvt. Ltd. and used as received. Thin layer chromatography was performed on 200 μm aluminium-foil backed silica gel plates and the column chromatography was performed using 100-200 mesh silica gel (Merck). NMR (^{1}H, ^{13}C and ^{19}F) spectra of all the synthesized compounds were recorded on a Bruker AVANCE HD (400 MHz, 100 MHz, and 376 MHz) spectrometer using $CDCl_3$ and DMSO-d_6 as solvents and TMS as an internal standard. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Coupling constants, *J* were reported in Hertz unit (Hz). Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.16 ppm of chloroform-*d* (a multiplet at 39.52 ppm of DMSO-d_6). Melting points were determined with a Stuart SMP30 apparatus and are uncorrected. FT-IR spectra were recorded on a Perkin Elmer spectrometer. HRMS were analyzed with Agilent Q-TOF 6230.

2. General Procedures

2.1 General procedure for synthesis of phenyl glyoxal from acetophenone (1a-1y)[1]

In an oven-dried 20 mL sealed tube equipped with a magnetic stir bar, selenium dioxide (1.85 g, 16.65 mmol) was dissolved in 1,4-dioxane/H_2O (9:1, v/v) and refluxed at 110 °C with stirring in an oil bath for 10 min. The resulting solution was cooled to room temperature, and acetophenone (1.0 g, 8.32 mmol) was added. The mixture was then refluxed at 110 °C for 16 h. After completion, the reaction mixture was cooled to room temperature and filtered through a short pad of silica gel (100–200 mesh), washing with ethyl acetate. The combined filtrate was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford 2-oxo-2-phenylacetaldehyde as a viscous yellow oil (1.10 g, 98% yield). The crude product was used directly in the subsequent transformation without further purification.

2.2 General procedure for synthesis of 2-hydroxy-1-phenylethan-1-one (3a-3y)

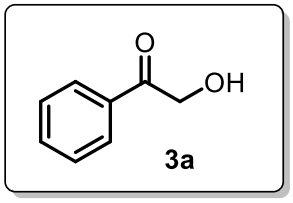
To a clean 10 mL round-bottom flask equipped with a magnetic stir bar were added phenylglyoxal **1a** (135.0 mg, 1.00 mmol) and rongalite **2** (238 mg, 2.00 mmol) in H_2O (3 mL). The suspension was stirred in an oil bath at 75 °C. Upon completion of the reaction (monitored by TLC), the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was

purified by column chromatography on silica gel (100–200 mesh) using ethyl acetate/hexane as the eluent to afford the desired product **3a**.

3. Characterization Data of Products (3a-3y)

2-hydroxy-1-phenylethan-1-one (3a)[2]

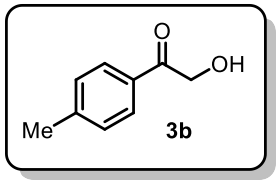
The compound was purified by using column chromatography (EtOAc:Hexanes = 20:80). Yellow White Solid; Yield (117mg, 85 %); mp: 88-90 °C.



^{1}H NMR (400 MHz, $CDCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 – 7.90 (m, 2H), 7.67 – 7.60 (m, 1H), 7.54 – 7.47 (m, 2H), 4.88 (d, J = 4.2 Hz, 2H), 3.51 (t, J = 4.6 Hz, 1H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 198.4, 134.3, 133.4, 129.0, 127.7, 65.4. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_8H_9O_2$ 137.0602; found 137.0599.

2-hydroxy-1-(p-tolyl) ethan-1-one (3b)[2]

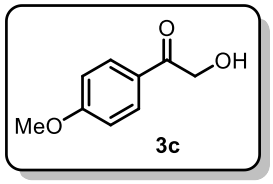
The compound was purified by using column chromatography (EtOAc:Hexanes = 20:80) Yellow White Solid; Yield (138 mg, 90%); mp: 90-92 °C.



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.84 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 4.87 (s, 2H), 3.58 (s, 1H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 198.0, 145.4, 130.9, 129.7, 127.8, 65.3, 21.8. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_9H_{11}O_2$ 151.0759; found 151.0756.

2-hydroxy-1-(4-methoxyphenyl) ethan-1-one (3c)[2]

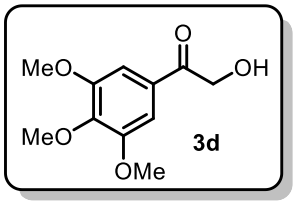
The Compound was purified by using column chromatography (EtOAc:Hexanes = 20:80). Yellow White Solid; Yield (150 mg, 89%); mp: 94-96 °C.



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.90 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 9.2 Hz, 2H), 4.82 (s, 2H), 3.89 (s, 3H), 3.59 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 196.7, 164.4, 130.0, 126.4, 114.2, 65.0, 55.6. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_9H_{11}O_3$ 167.0708; found 167.0716

2-hydroxy-1-(3,4,5-trimethoxyphenyl) ethan-1-one (3d)[2]

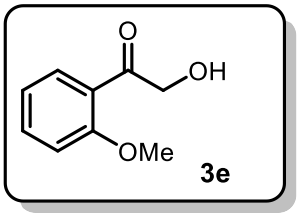
The compound was purified by using column chromatography (EtOAc: Hexanes = 20:80). Yellow White Solid; Yield (196 mg, 86%); mp: 110-112 °C.



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.17 (s, 2H), 4.85 (d, J = 4.6 Hz, 2H), 3.93 (d, J = 4.0 Hz, 9H), 3.52 (t, J = 4.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 197.2, 153.4, 143.6, 128.5, 105.2, 65.2, 61.0, 56.4. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{11}H_{15}O_5$ 227.0919; found 227.0917.

2-hydroxy-1-(2-methoxyphenyl) ethan-1-one (3e)[2]

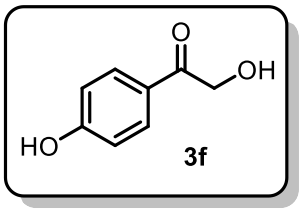
The compound was purified by using column chromatography(EtOAc:Hexanes = 15:85) **.**Yellow White



Solid ; Yield (123 mg, 81%); mp:115-117 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.71 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 8.8 Hz, 1H), 7.17 (d, J = 8.4 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 4.94 (t, J = 6.0 Hz, 1H), 4.60 (d, J = 5.8 Hz, 2H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm) 200.8, 159.4, 134.7, 130.0, 125.3, 121.1, 113.0, 69.5, 56.3; HRMS (ESI) *m/z*: [M+H]$^{+}$ calcd for $C_9H_{11}O_3$ 167.0708; found 167.0709.

2-hydroxy-1-(4-hydroxyphenyl) ethan-1-one (3f)[2]

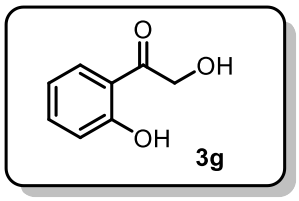
The compound was purified by using column chromatography (EtOAc:Hexanes = 30:70) .Yellow White



Solid ; Yield (147mg, 96%); mp: 170-172 °C .^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 10.42 (s, 1H), 7.81 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 4.90 (s, 1H), 4.70 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm) 197.6, 162.7, 130.5, 126.5, 115.8, 65.2. HRMS (ESI) *m/z*: [M+H] $^{+}$ calcd for $C_8H_9O_3$153.0511; found 153.0546.

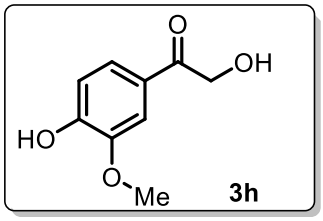
2-hydroxy-1-(2-hydroxyphenyl) ethan-1-one (3g) [2]

The compound was purified by using column chromatography (EtOAc:Hexanes = 30:70). Yellow White



Solid; Yield (142 mg, 93%); mp: 68-70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 11.42 (s, 1H), 7.52 – 7.42 (m, 2H), 6.97 (d, J = 8.4 Hz, 1H), 6.86 (t, J = 7.6 Hz, 1H), 4.84 (s, 2H), 3.34 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 202.8, 161.9, 137.3, 128.2, 119.5, 118.8, 116.6, 64.6. HRMS (ESI) *m/z*: [M+H] $^{+}$ calcd for $C_8H_9O_3$153.0511; found 153.0548.

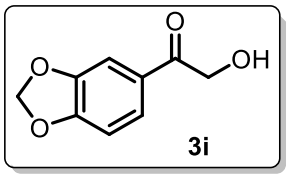
2-hydroxy-1-(4-hydroxy-3-methoxyphenyl) ethan-1-one (3h)



The compound was purified by using column chromatography (EtOAc:Hexanes = 30:70) Yellow White Solid ; Yield (150 mg, 82%); mp: 178-180 °C.^{1}H NMR (400 MHz, DMSO- d_6) δ (ppm) 10.02 (s, 1H), 7.47 (d, J = 8.2 Hz, 1H), 7.43 (d, J = 2.0 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 4.90 (s, 1H), 4.73 (s, 2H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm) 197.7, 152.4, 148.1, 126.7, 122.9, 115.5, 111.2, 65.3, 56.1. HRMS (ESI) *m/z*: [M+H] $^{+}$ calcd for $C_8H_9O_3$ 183.0657; found 183.0643.

1-(benzo[d][1,3]dioxol-5-yl)-2-hydroxyethan-1-one (3i) [2]

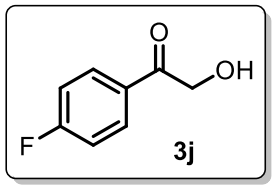
The compound was purified by using column chromatography (EtOAc:Hexanes = 35:65).Yellow



White Solid ; Yield (140 mg, 77%); mp:125-127 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.57 (dd, J = 8.2, 1.8 Hz, 1H), 7.42 (d, J = 1.8 Hz, 1H), 7.04 (d, J = 8.2 Hz, 1H), 6.14 (s, 2H), 4.99 (t, J = 5.6 Hz, 1H), 4.71 (d, J = 5.4 Hz, 2H). ^{13}C{^{1}H} NMR NMR (100 MHz, DMSO-d_6) δ (ppm) 197.6, 152.0, 148.3, 129.5, 124.3, 108.7, 107.5, 102.5, 65.6. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_9H_9O_4$181.0501; found 181.0501.

1-(4-fluorophenyl)-2-hydroxyethan-1-one (3j))[2]

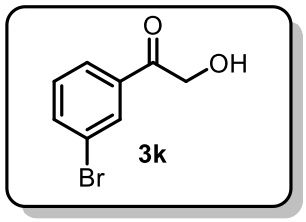
The compound was purified by using column chromatography (EtOAc:Hexanes = 20:80). White



Solid; Yield (132 mg, 85%); mp:104-107 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01 – 7.78 (m, 2H), 7.11 (d, J = 8.6 Hz, 2H), 4.78 (s, 2H), 3.42 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 196.9, 166.3 (d, $^{1}J_{C-F}$ = 255.10 Hz), 130.4 (d, $^{3}J_{C-F}$ = 9.6 Hz), 129.8 (d, $^{4}J_{C-F}$ = 3.10 Hz), 116.2 (d, $^{2}J_{C-F}$ = 21.90 Hz), 65.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -104.9. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_8H_8FO_2$ 155.0508; found 155.0480.

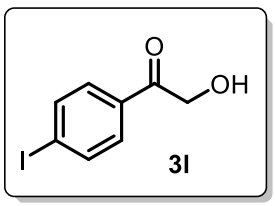
1-(3-bromophenyl)-2-hydroxyethan-1-one (3k)[2]

The compound was purified by using column chromatography (EtOAc:Hexanes = 20:80). White



Solid; Yield (170 mg, 78%); mp:130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.0 (s, 1H), 7.75 (d, J = 2.8 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.35 – 7.30 (m, 1H), 4.79 (s, 2H), 3.35 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 197.3, 137.2, 135.1, 130.8, 130.6, 126.2, 123.3, 65.6. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_8H_8BrO_2$ 214.9707 ; found 214.9679.

2-hydroxy-1-(4-iodophenyl) ethan-1-one (3l)[2]

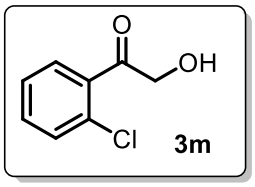


The compound was purified by using column chromatography (EtOAc:Hexanes = 20:80). Yellow oily liquid; Yield (200 mg, 76%); mp:148-150 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.92 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 5.14 (t, J = 6.0 Hz, 1H), 4.76 (d, J = 6.0

Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm) 199.3, 138.2, 137.6, 134.3, 129.8, 129.3, 102.4, 65.8. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_8H_8IO_2$ 262.9569; found 262.9539.

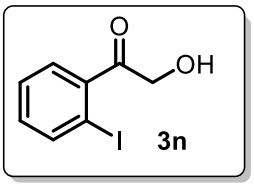
1-(2-chlorophenyl)-2-hydroxyethan-1-one (3m)[2]

The compound was purified by using column chromatography (EtOAc:Hexanes = 15:85). Yellow White Solid ; Yield (120mg,70%); mp: 103-105 °C. ^1H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.66 – 7.62 (m, 1H), 7.57 – 7.52 (m, 2H), 7.47 – 7.42 (m, 1H), 5.42 (s, 1H), 4.57 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm) 203.0, 137.2, 132.8, 130.7, 130.3, 129.6, 127.7, 68.0. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for 171.0213; found 171.0213.



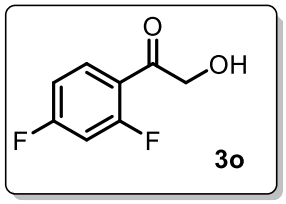
2-hydroxy-1-(2-iodophenyl) ethan-1-one (3n)[2]

The compound was purified by using column chromatography (EtOAc:Hexanes = 15:85). Yellow oily liquid; Yield (180 mg, 68%); mp:110-112 °C.^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.03 (d, J = 7.8 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.26 – 7.19 (m, 1H), 4.75 (s, 2H), 3.33 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 202.0, 141.5, 139.4, 133.0, 128.5, 128.2, 91.9, 67.1. HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $C_8H_{11}INO_2$ 279.9569; found 279.9539.



1-(2,4-difluorophenyl)-2-hydroxyethan-1-one (3o)

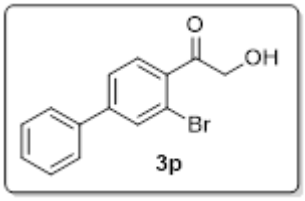
The compound was purified by sing column chromatography (EtOAc:Hexanes = 20:80). Yellow White Solid; Yield (207 mg, 78%); mp:115-117 °C. ^1H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.03 – 7.94 (m, 1H), 7.47 – 7.39 (m, 1H), 7.31 – 7.24 (m, 1H), 5.28 (t, J = 6.0 Hz, 1H), 4.66 (d, J = 3.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm) 196.8(d,J_{C-F}=5.5 Hz), 166.8 (d,J_{C-F}=13.1Hz), 164.3(d,J_{C-F}=12.4 Hz),163.7 (d, J_{C-F}=13.2 Hz) 161.2(d, J_{C-F}=13.2 Hz), 132.7-132.5(m), 120.6-120.3(m), 113.0(d, J_{C-F}=3.8 Hz), 112.8(d, J_{C-F}=3.8 Hz),105.8-105.2(m),68.5(d, J_{C-F}=10.2 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -102.49 (d, J = 11.4 Hz), -104.08 (d, J = 13.8 Hz). HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_8H_6F_2O_2$ 173.0414; found 173.0420



1-(3-bromo-[1,1'-biphenyl]-4-yl)-2-hydroxyethan-1-one (3p)

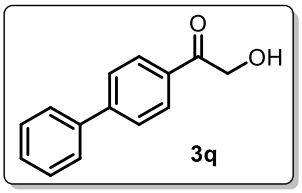
The compound was purified by using column chromatography (EtOAc:Hexanes = 20:80). Yellow White Solid ; Yield (207 mg, 70%); mp:105-107 °C. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01 (s,

1H), 7.73 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 7.2 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.45 – 7.39 (m, 1H),



4.91 (d, J = 4.6 Hz, 2H), 3.58 – 3.50 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 198.0, 147.1, 139.6, 132.0, 129.1, 128.6, 128.3, 127.6, 127.3, 65.5. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{12}BrO_2$ 291.0020; found 291.0688.

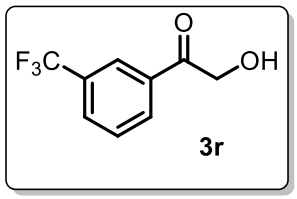
1-([1,1'-biphenyl]-4-yl)-2-hydroxyethan-1-one (3q)[2]



The compound was purified by using column chromatography (EtOAc:Hexanes = 20:80). White Solid ; Yield (160 mg, 75%); mp :122-124 °C. ^1H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.02 (d, J = 8.7 Hz, 2H), 7.82 (d, J = 8.7 Hz, 2H), 7.74 (d, J = 7.0 Hz, 2H), 7.51 (t, J = 7.4 Hz, 2H), 7.43 (t, J = 7.4 Hz, 1H), 5.13 (t, J = 5.8 Hz, 1H), 4.84 (d, J = 6.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm) 199.2, 145.2, 139.4, 133.9, 129.6, 128.9, 128.8, 127.5, 127.4, 65.9. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{13}O_2$ 213.0915; found 213.0916.

2-hydroxy-1-(3-(trifluoromethyl) phenyl) ethan-1-one (3r)[2]

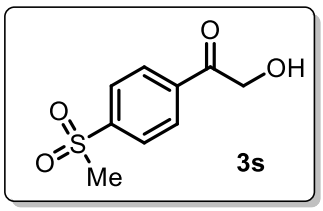
The compound was purified by using column chromatography (EtOAc:Hexanes = 30:70). Yellow



White Solid; Yield (984mg, 60%); mp:110-112 °C.^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12 (s, 1H), 8.03 (d, J = 9.6 Hz, 1H), 7.83 (d, J = 9.8 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 4.85 (s, 2H), 3.36 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 197.3, 133.9, 131.9, 131.6, 130.8, 130.7, 130.7, 129.8, 124.6(d, J_{C-F} =4.0 Hz) 65.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) 61.8. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_9H_8F_3O_2$ 205.0476 ; found 205.0643.

2-hydroxy-1-(4-(methylsulfonyl) phenyl) ethan-1-one (3s)[2]

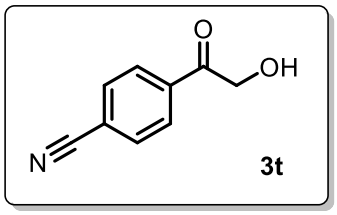
The compound was purified by using column chromatography (EtOAc:Hexanes = 30:70). White



Solid; Yield (160 mg, 74%);mp:130-132 °C.^1H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.72 (d, J = 7.8 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.06 (t, J = 7.6 Hz, 1H), 4.94 (t, J = 6.0 Hz, 1H), 4.60 (d, J = 6.0 Hz, 2H), 3.89 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm) 200.8, 159.4, 134.7, 130.0, 125.3, 121.1, 113.0, 69.5, 56.3. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_9H_{11}O_4S$ 215.0378; found 215.0376.

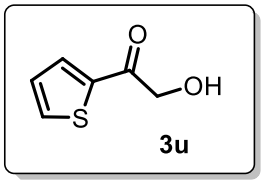
4-(2-hydroxyacetyl) benzonitrile (3t)[2]

The compound was purified by using column chromatography (EtOAc:Hexanes = 30:70).White Solid ; Yield (130 mg, 80%); mp:110-112 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.11 – 8.04 (m, 2H), 8.03 – 7.98 (m, 2H), 5.27 (t, J = 6.0 Hz, 1H), 4.83 (d, J = 6.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm) 199.3, 138.4, 133.3, 128.8, 118.6, 115.7, 66.2. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_9H_8NO_2$ 162.0555 ; found 162.0361.



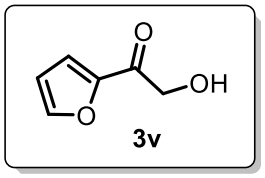
2-hydroxy-1-(thiophen-2-yl) ethan-1-one (3u)[2]

The compound was purified by using column chromatography (EtOAc:Hexanes = 20:80). Yellow Solid ; Yield (117 mg, 82%); mp: 76-78 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.01 (d, J = 5.0 Hz, 1H), 7.96 (d, J = 3.8 Hz, 1H), 7.28 – 7.22 (m, 1H), 5.35 (t, J = 6.2 Hz, 1H), 4.67 (d, J = 6.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm) 193.1, 141.2, 135.0, 133.3, 129.1, 65.9. $[M+H]^+$ calcd for $C_6H_7O_2S$ 143.0167 ; found 143.0141.



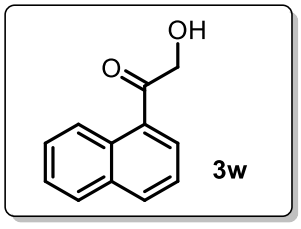
1-(furan-2-yl)-2-hydroxyethan-1-one (3v) [2]

The compound was purified by using column chromatography (EtOAc:Hexanes = 20:80). Yellow Solid; Yield (102 mg, 80%); mp: 80-82 °C ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.99 (d, J = 1.2 Hz, 1H), 7.47 (dd, J = 3.8, 0.8 Hz, 1H), 6.71 (dd, J = 3.8, 1.8 Hz, 1H), 5.26 (t, J = 6.2 Hz, 1H), 4.55 (d, J = 6.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm) 188.5, 150.5, 148.1, 118.8, 112.8, 65.1. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_6H_7O_3$ 123.0317 ; found 123.0313.



2-hydroxy-1-(naphthalen-1-yl) ethan-1-one (3w)[2]

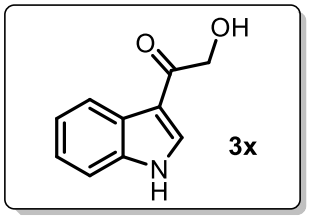
The compound was purified by using column chromatography (EtOAc:Hexanes = 20:80). Yellow White Solid ; Yield (142 mg, 76%); mp:105-107 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.80 (d, J = 8.7 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.82 (t, J = 7.2 Hz, 2H), 7.59 (t, J = 7.0 Hz, 1H), 7.54 – 7.43 (m, 2H), 4.84 (s, 2H), 3.61 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm) 204.0,



133.9, 133.5, 133.0, 130.0, 129.0, 128.3, 128.2, 126.9, 125.5, 125.3, 67.5. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{11}O_2$ 187.0759 ; found 187.0761.

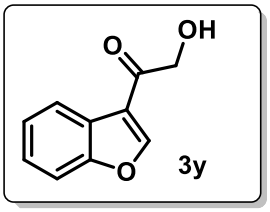
2-hydroxy-1-(1H-indol-3-yl)ethan-1-one (3x)[2]

The compound was purified by using column chromatography (EtOAc:Hexanes = 20:80). Yellow White Solid ; Yield (130 mg, 74%);mp : 95-97 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 12.02 (s, 1H), 8.40 (s, 1H), 8.23 (d, J = 4.0 Hz, 1H), 7.59 – 7.48 (m, 1H), 7.35 – 7.18 (m, 2H), 5.02 (t, J = 6.0 z, 1H), 4.64 (d, J = 5.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm) 194.9, 136.8, 133.8, 125.9, 123.3, 122.3, 121.6, 113.7, 112.6, 65.7. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{10}H_{10}NO_2$ 176.0711 ; found 176.0712.



1-(benzofuran-3-yl)-2-hydroxyethan-1-one (3y)[2]

The compound was purified by using column chromatography (EtOAc:Hexanes = 20:80). Yellow White Solid; Yield (130mg, 70%);mp: 115-117 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.76 (d, J = 8.0 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.57 – 7.51 (m, 1H), 7.39 – 7.34 (m, 1H), 4.91 (s, 2H), 2.95 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 189.9, 155.7, 150.4, 128.9, 126.6, 124.3, 123.5, 113.6, 112.5, 65.8 HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{10}H_9O_3$ 177.0551 ; found 177.0537.



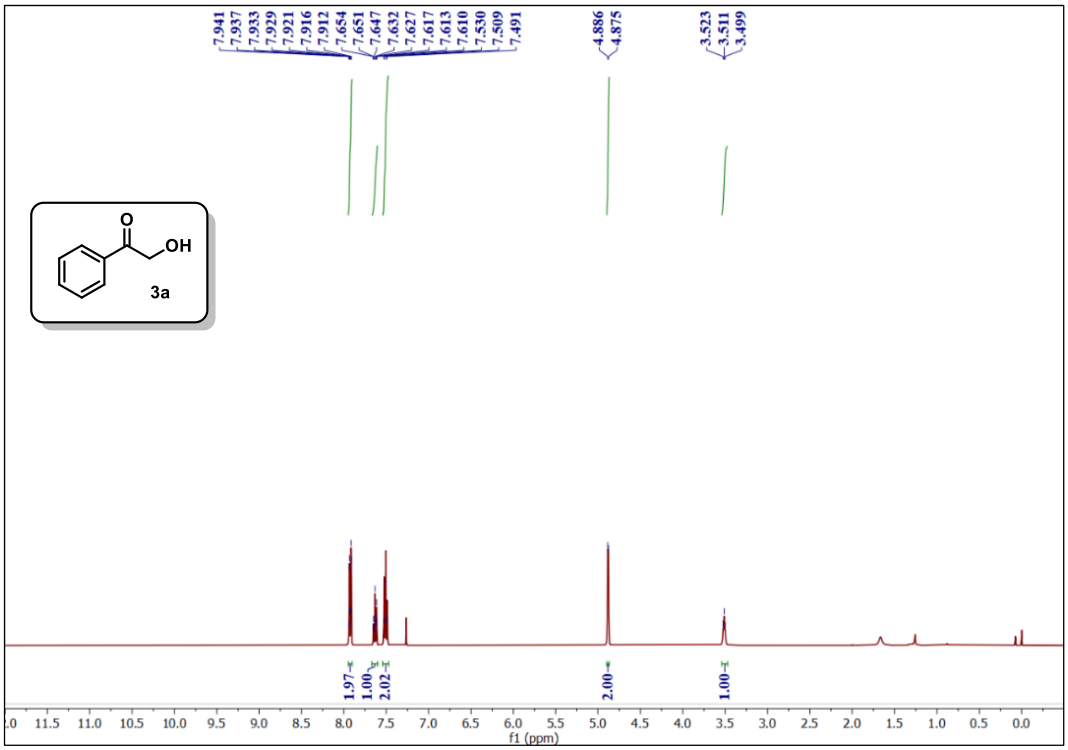
4. References

1. (a) Choudhury A. R., Manna M. S. & Mukherjee S., *Chem. Sci.*, 2017, **8**, 6686-6690; (b) Y. Subba Rao, D. Arun, N. Devunuri and S. Yaragorla, *Eur. J. Org. Chem.*, 2024, **2024**, 178–185.

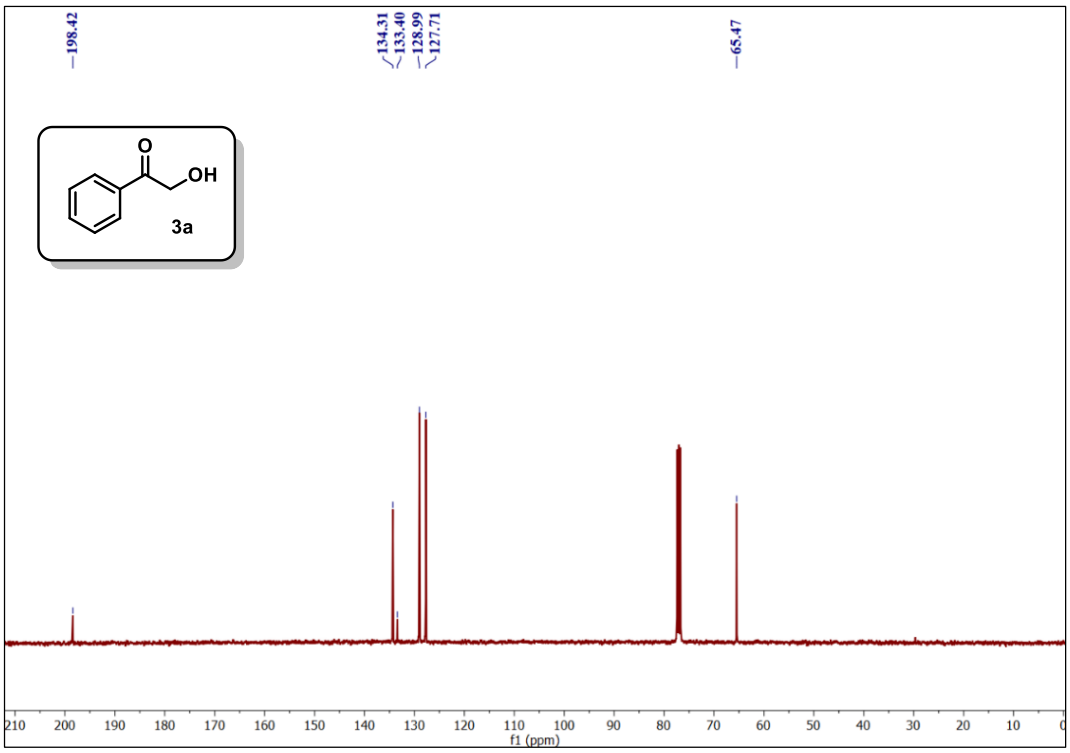
2. (a) S. Singh, S. Ray, G. Shukla and M. S. Singh, *Adv. Synth. Catal.*, 2024, **366**, 2008–2013; (b) X. Wu, Q. Gao, M. Lian, S. Liu and A. Wu, *RSC Adv.*, 2014, **4**, 51180–51183; (c) Thirunavukkarasu V. S. and Ackermann L., *Org. Lett.*, 2012, **14**, 6206-6209; (d) Jiuzhong Huang, Jianxiao Li, Jia Zheng, Wanqing Wu, Weigao Hu, Lu Ouyang and Huanfeng Jiang,*Org. Lett.*,2017,**19**,3354–3357; (e) M. Kidwai, S. Saxena, R. Venkataramanan, R. Mozumdar and A. Bhaumik,*Asian J. Org. Chem.*,2005,**35**,1059–1065;(f) A. S. Demir, P. Ayhan, A. C. Igdir and A. N. Duygu,*Tetrahedron*,2004,**60**,6509–6512; (g) Y. Li, N. Hu, Z. Xu, Y. Cui, J. Feng, P. Yao, Q. Wu, D. Zhu and Y. Ma, *Tetrahedron: Asymmetry*,2021,**32**,1234–1240.

5. Copies of ^{1}H, ^{13}C & ^{19}F NMR spectra and HRMS of compounds 3a-3y

^{1}H NMR (400 MHz, $CDCl_3$) of 2-hydroxy-1-phenylethan-1-one (3a)



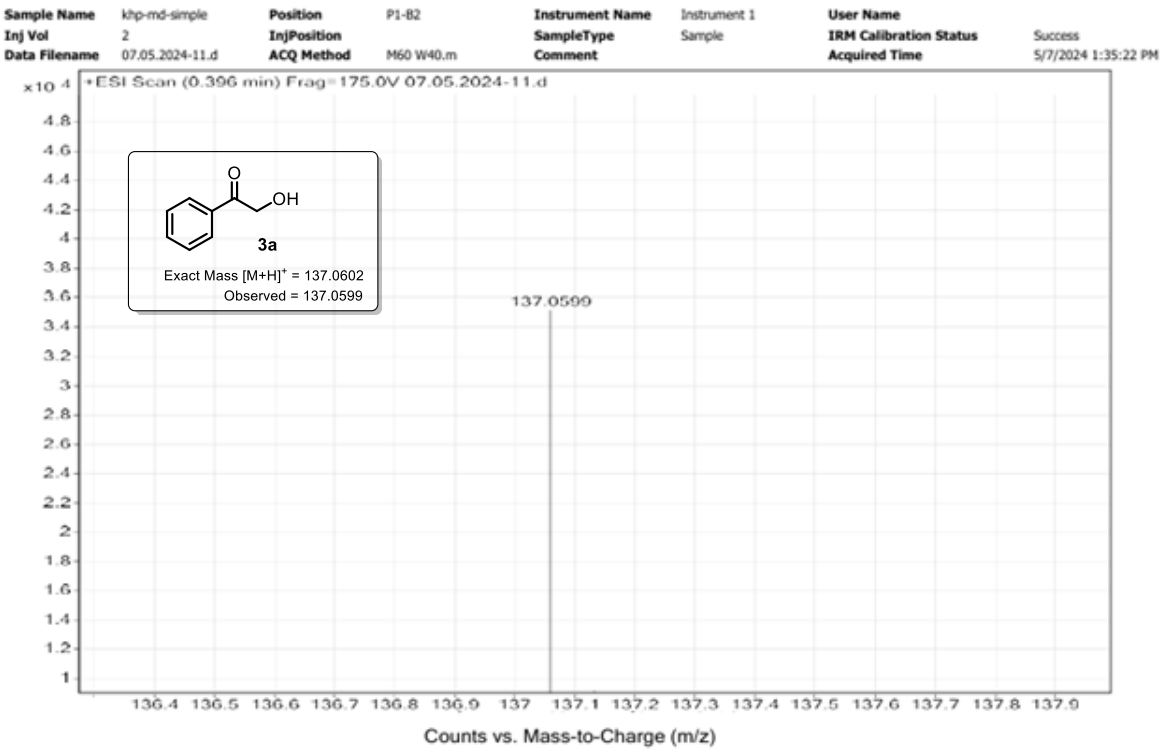
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of 2-hydroxy-1-phenylethan-1-one (3a)



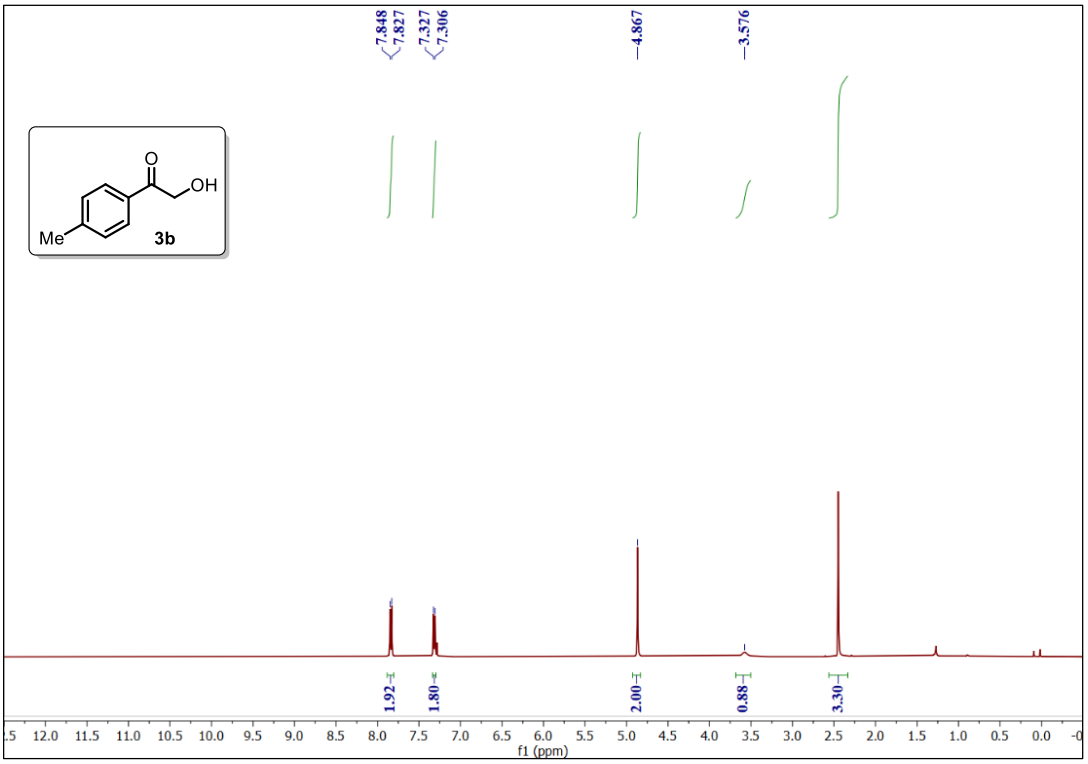
s

Mass spectrum of 2-hydroxy-1-phenylethan-1-one (3a

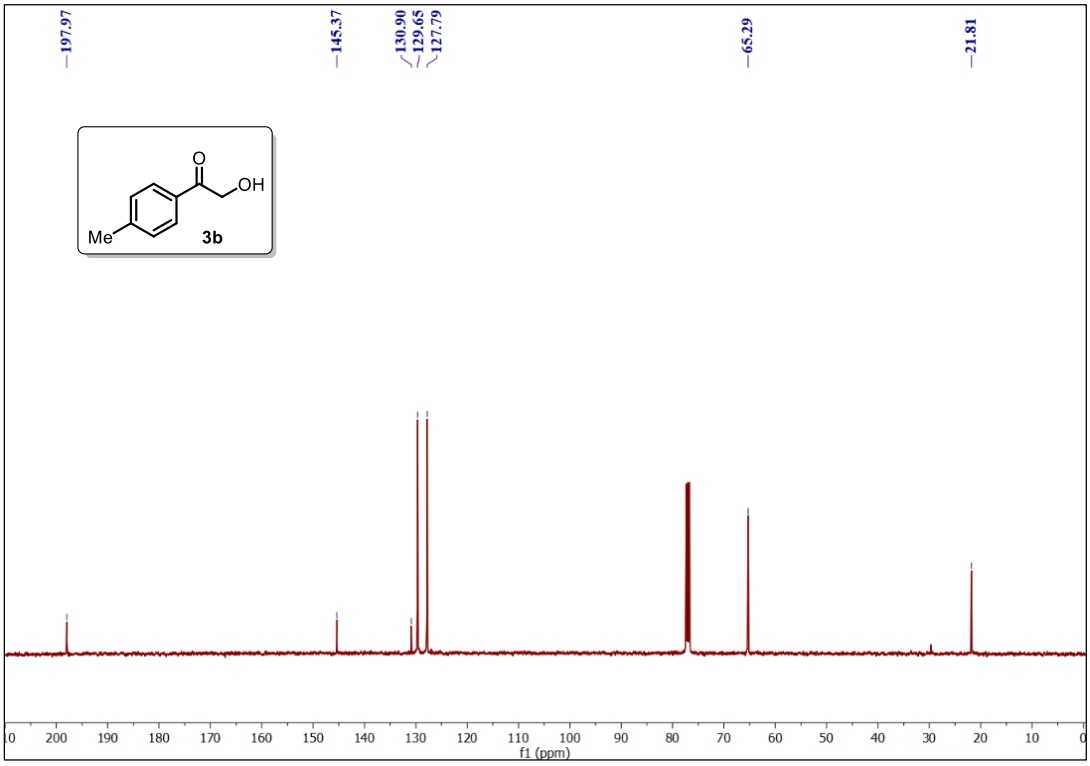
.



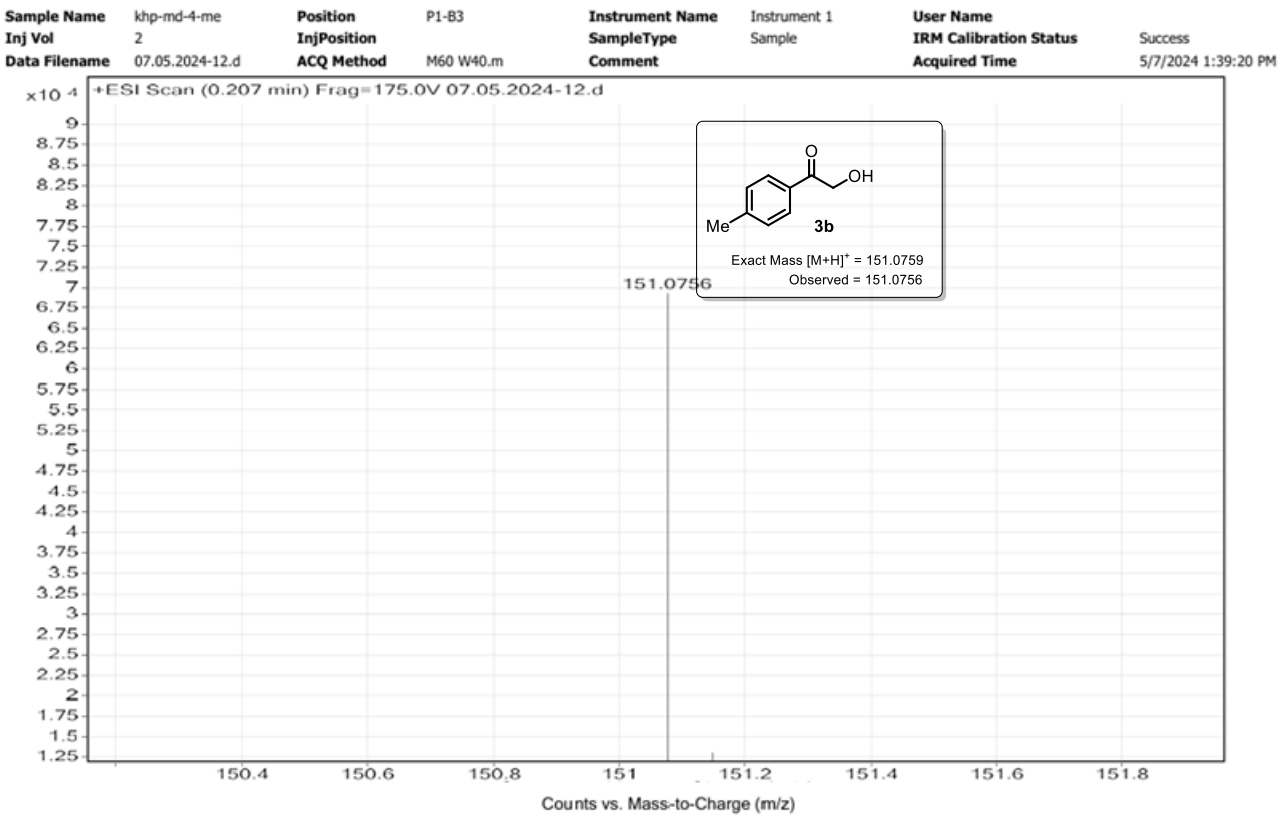
^{1}H NMR (400 MHz, $CDCl_3$) of 2-hydroxy-1-(p-tolyl)ethan-1-one (3b)



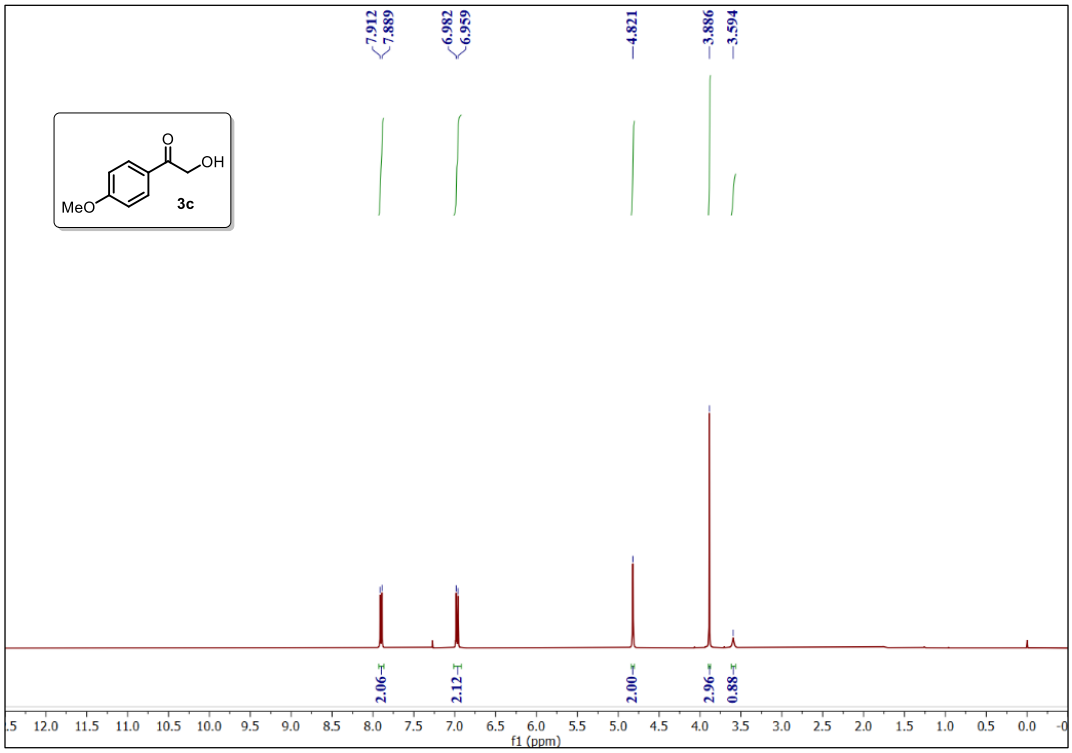
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of 2-hydroxy-1-(p-tolyl)ethan-1-one (3b)



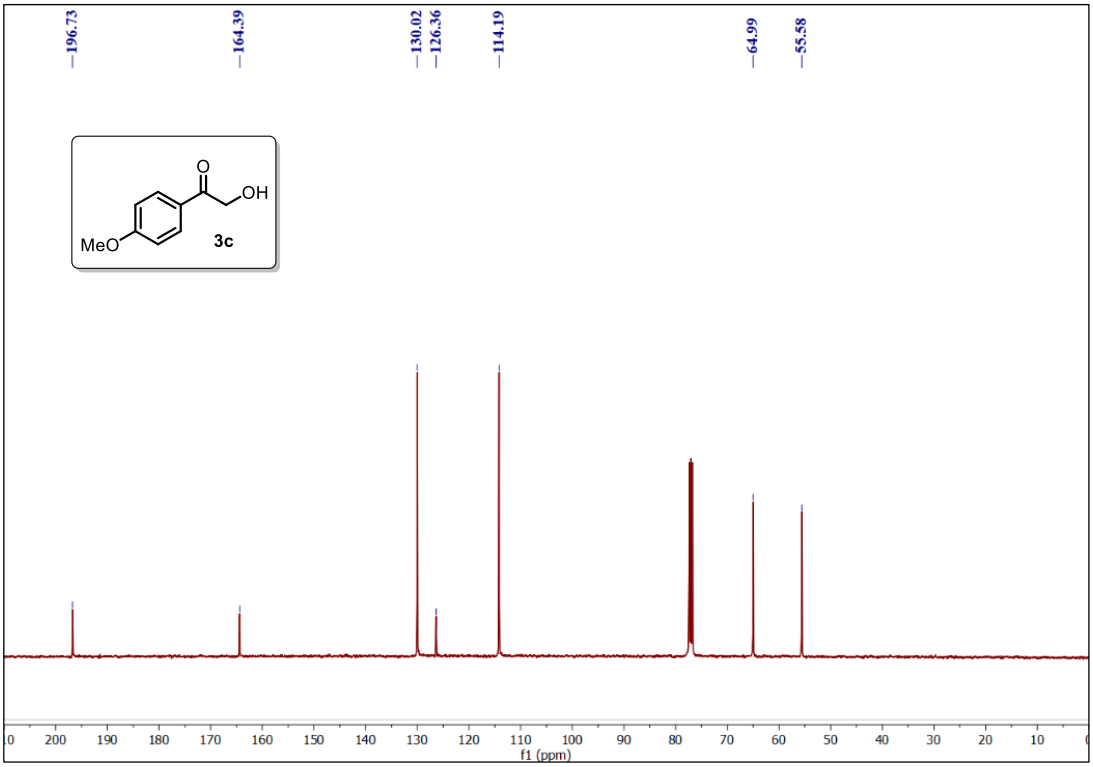
Mass spectrum of 2-hydroxy-1-(p-tolyl)ethan-1-one (3b)



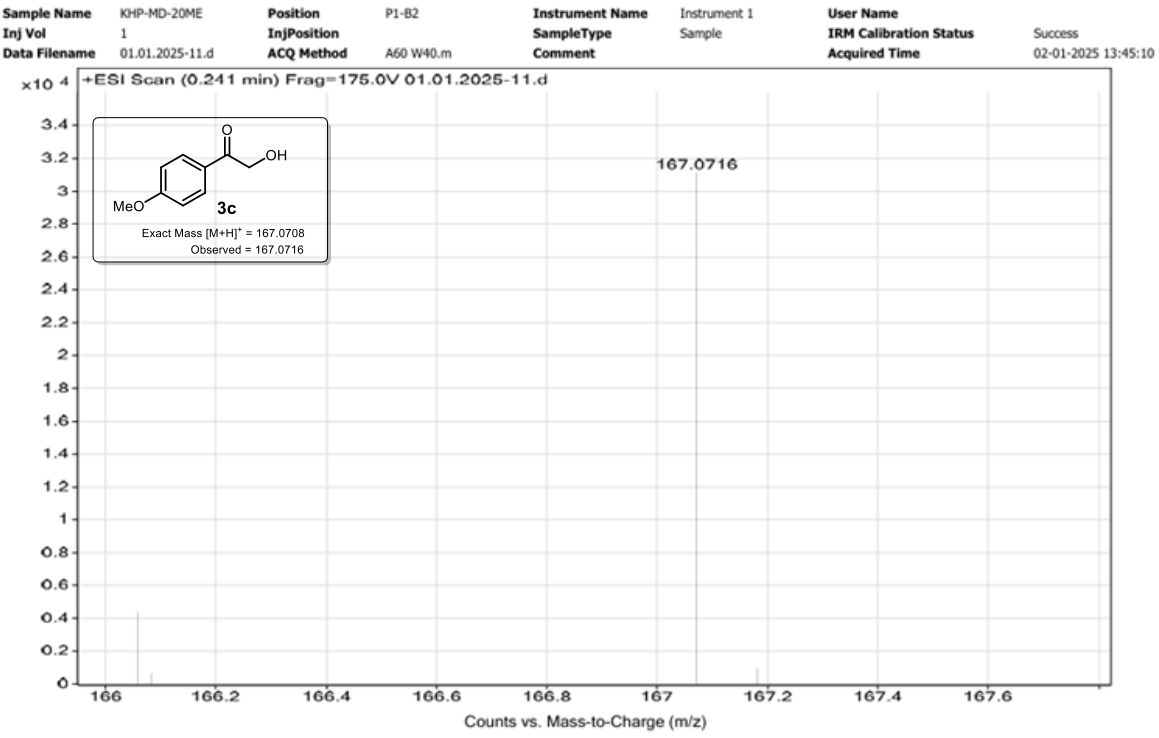
^{1}H NMR (400 MHz, $CDCl_3$) of 2-hydroxy-1-(4-methoxyphenyl) ethan-1-one (3c)



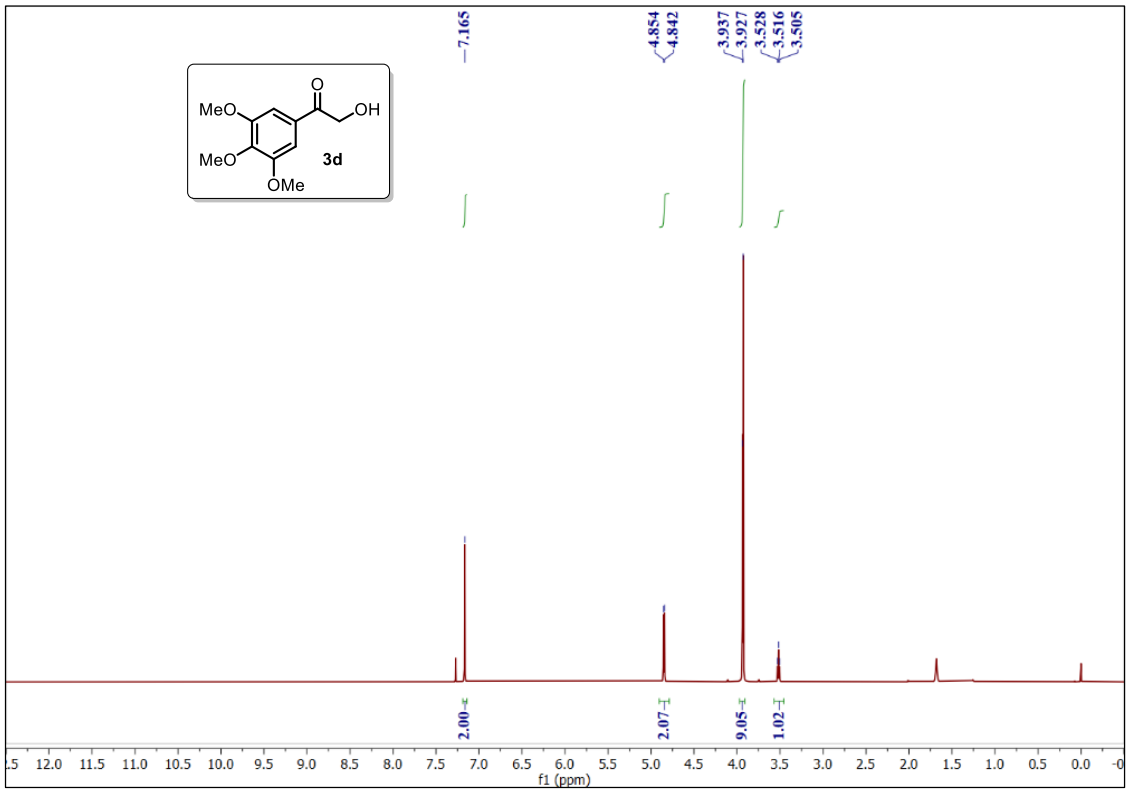
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of 2-hydroxy-1-(4-methoxyphenyl)ethan-1-one (3c)



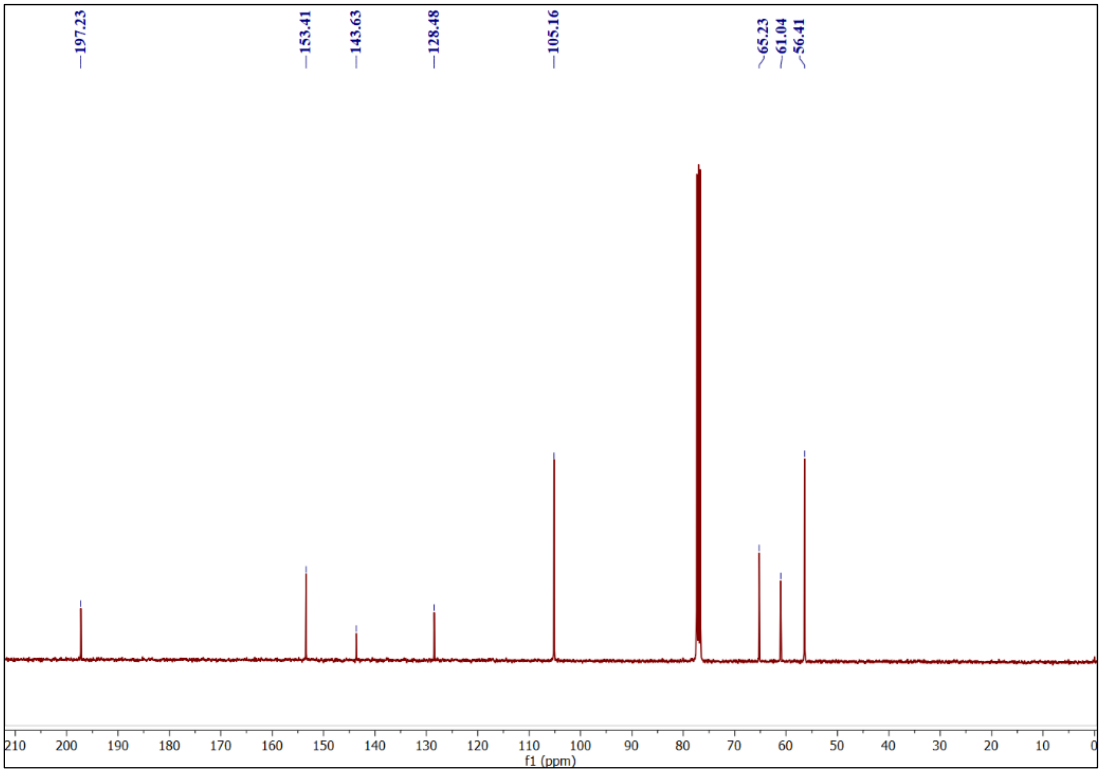
Mass spectrum of 2-hydroxy-1-(4-methoxyphenyl)ethan-1-one (3c)



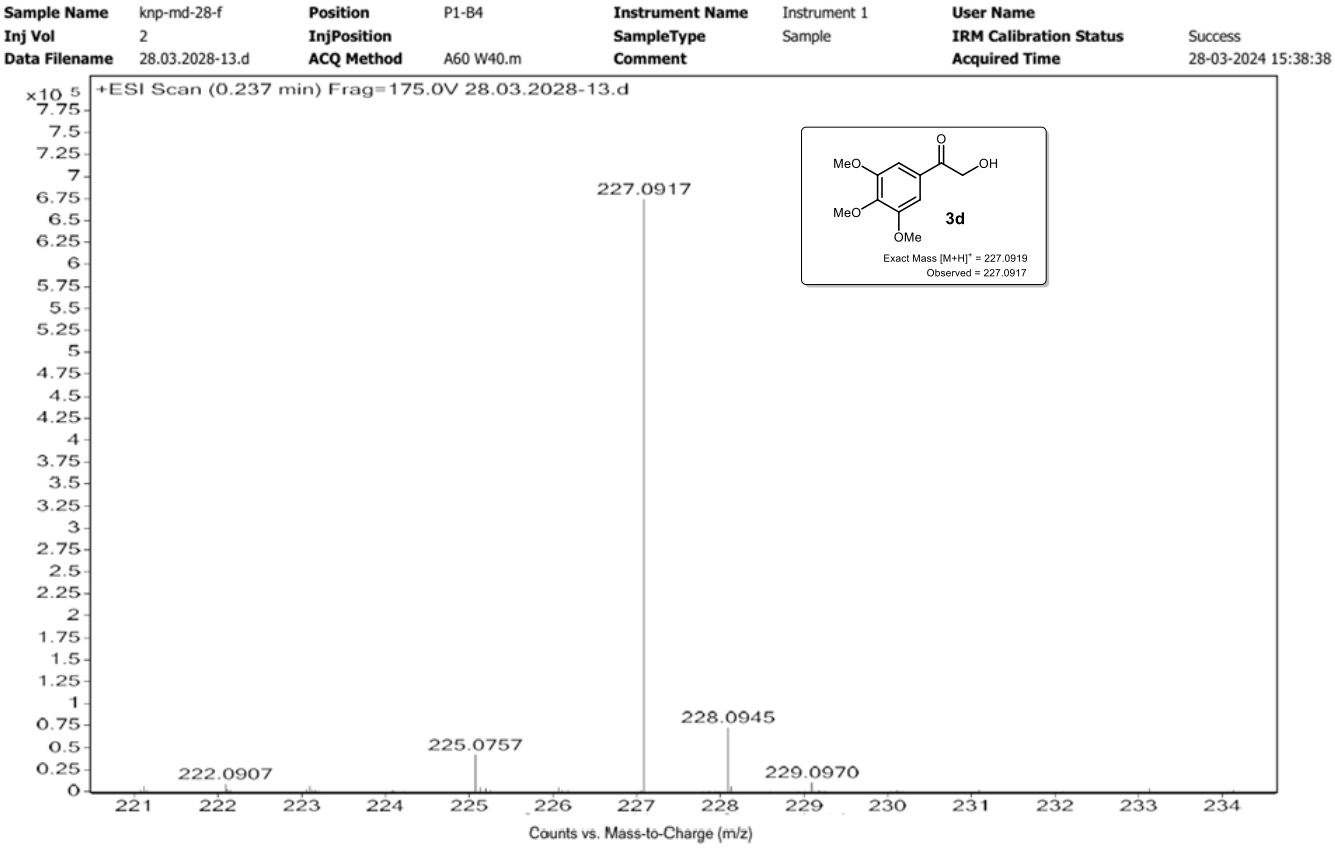
^{1}H NMR (400 MHz, $CDCl_3$) of 2-hydroxy-1-(3,4,5-trimethoxyphenyl) ethan-1-one (3d)



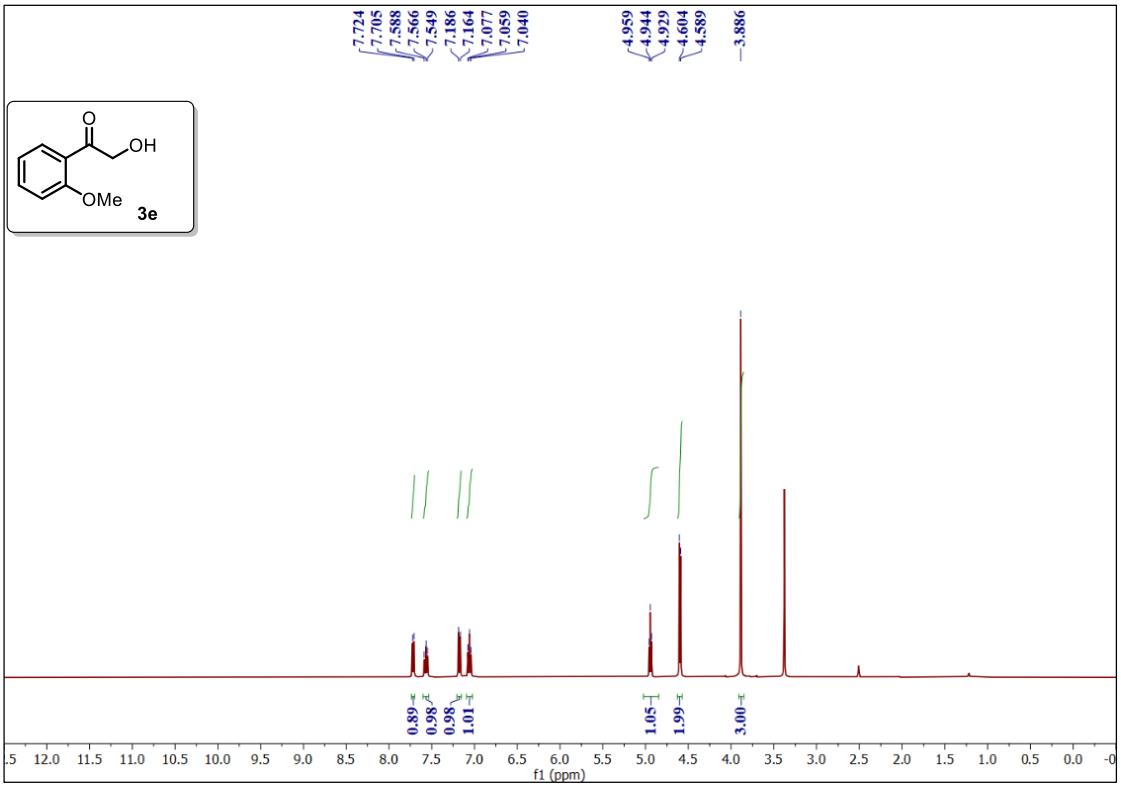
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of 2-hydroxy-1-(3,4,5-trimethoxyphenyl) ethan-1-one (3d)



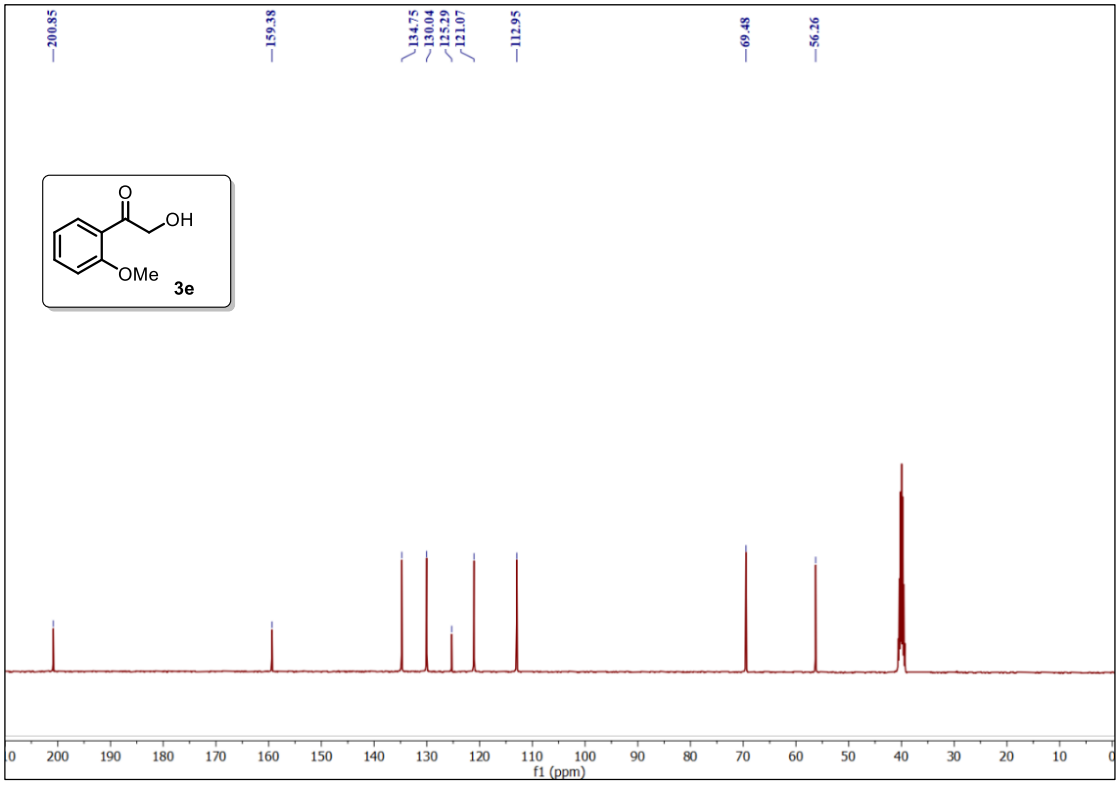
Mass spectrum of 2-hydroxy-1-(3,4,5-trimethoxyphenyl) ethan-1-one (3d)



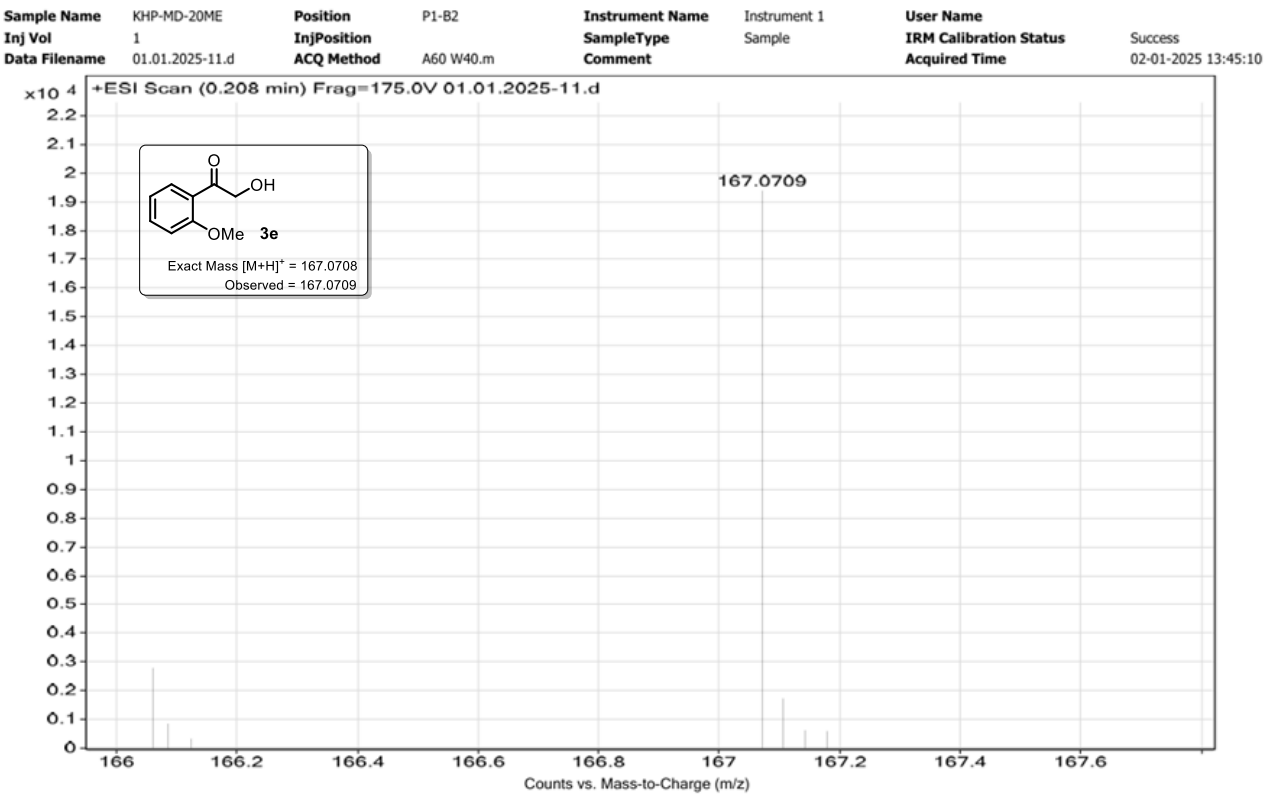
^{1}H NMR (400 MHz, DMSO-d_6) of 2-hydroxy-1-(2-methoxyphenyl) ethan-1-one(3e)



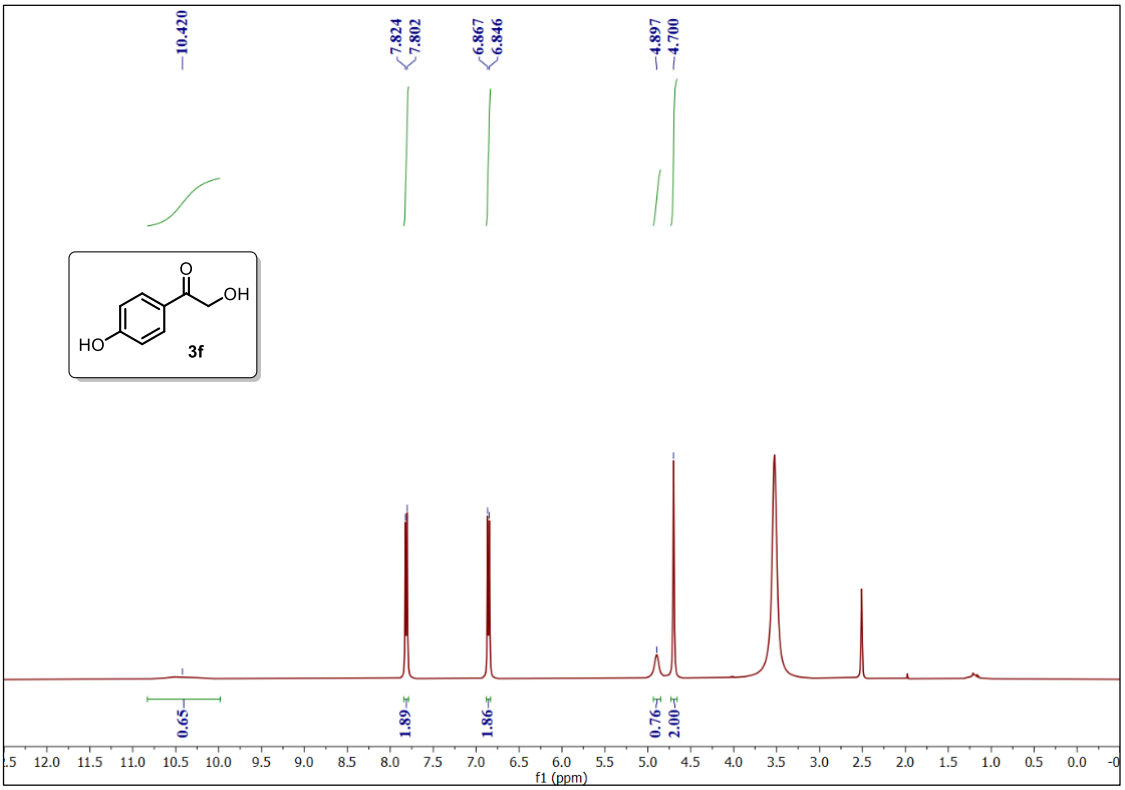
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of 2-hydroxy-1-(2-methoxyphenyl)ethan-1-one(3e)



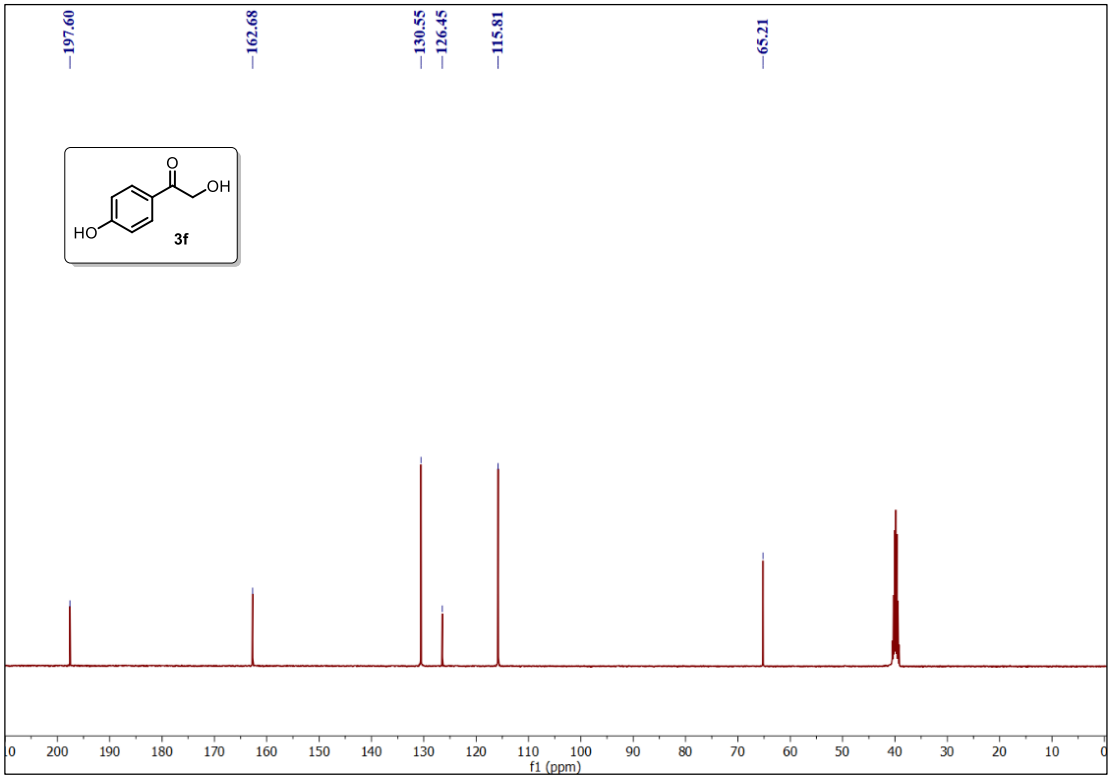
Mass spectrum of 2-hydroxy-1-(2-methoxyphenyl)ethan-1-one(3e)



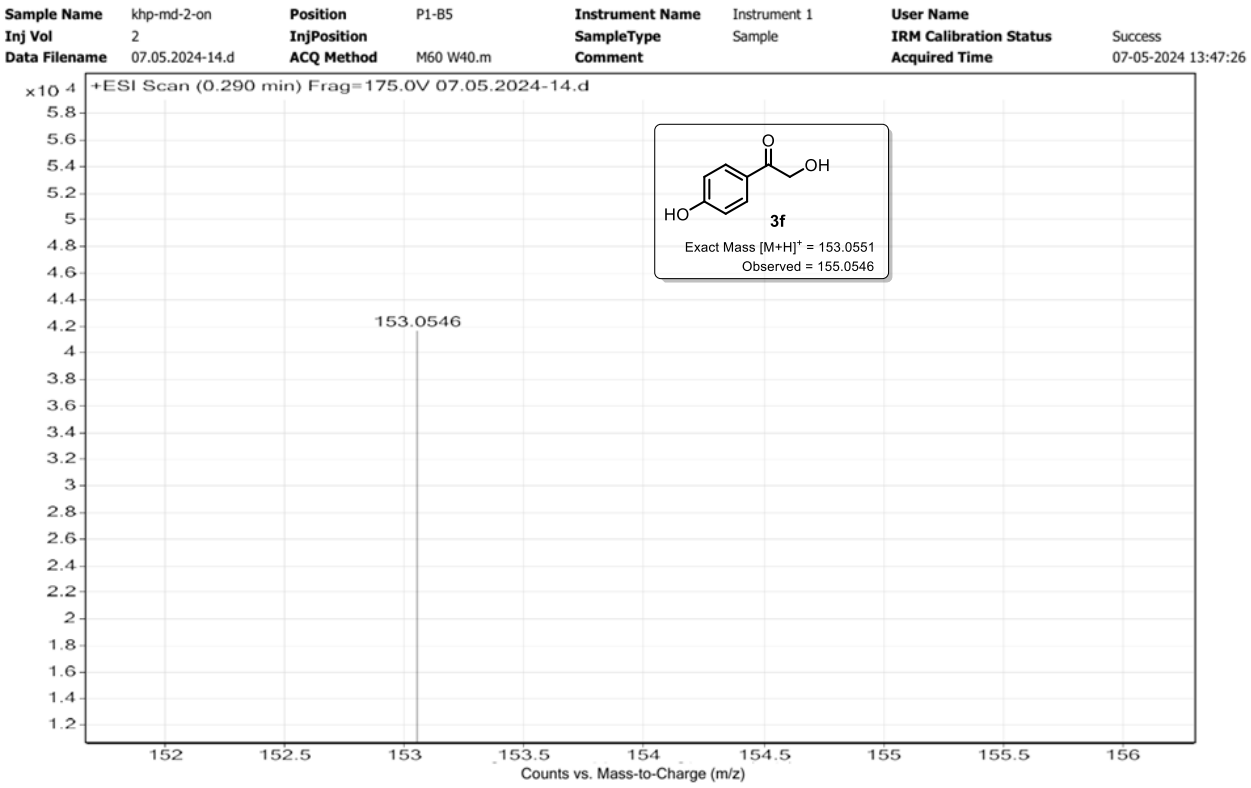
^{1}H NMR (400 MHz, DMSO-d_6) of 2-hydroxy-1-(4-hydroxyphenyl)ethan-1-one (3f)



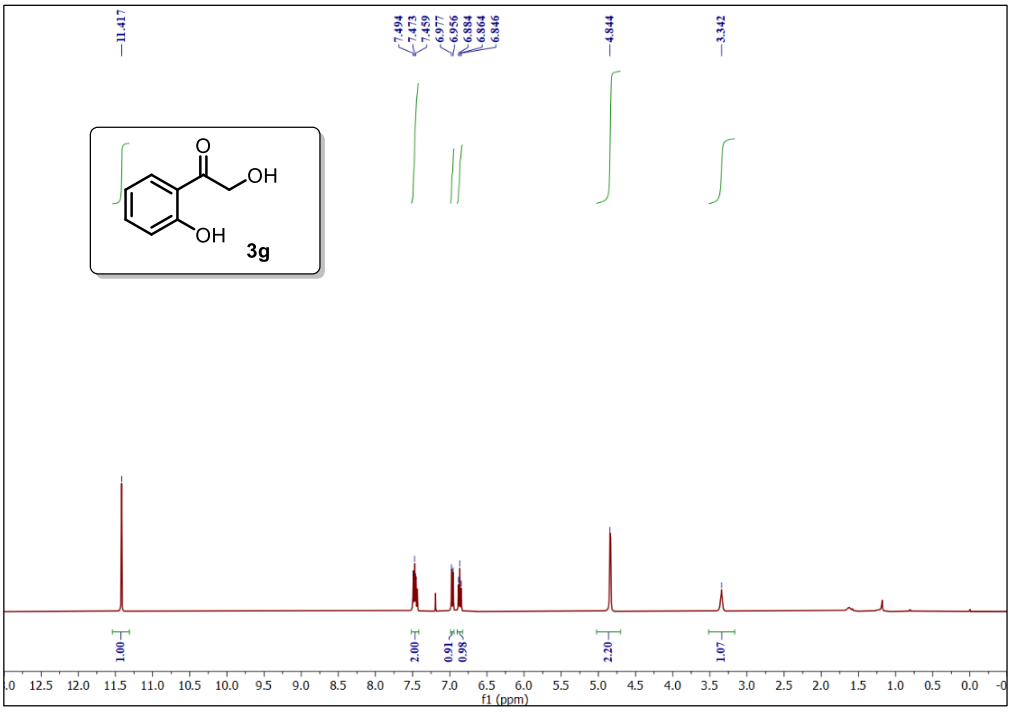
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of 2-hydroxy-1-(4-hydroxyphenyl) ethan-1-one (3f)



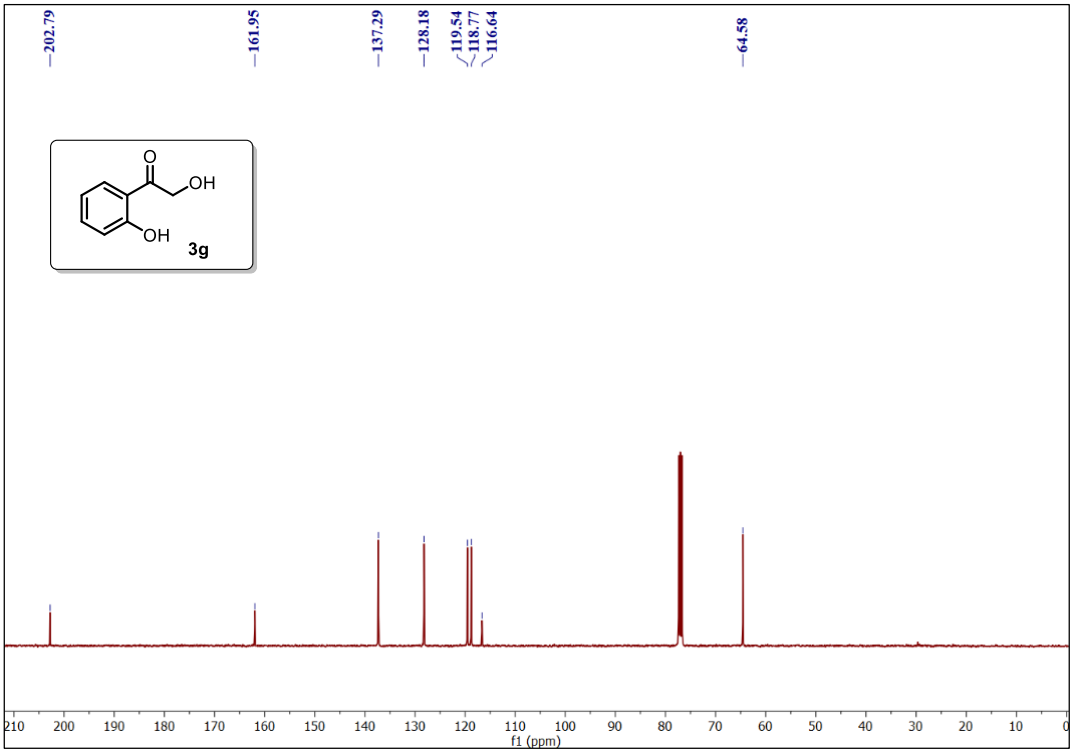
Mass spectrum of of 2-hydroxy-1-(4-hydroxyphenyl)ethan-1-one (3f)



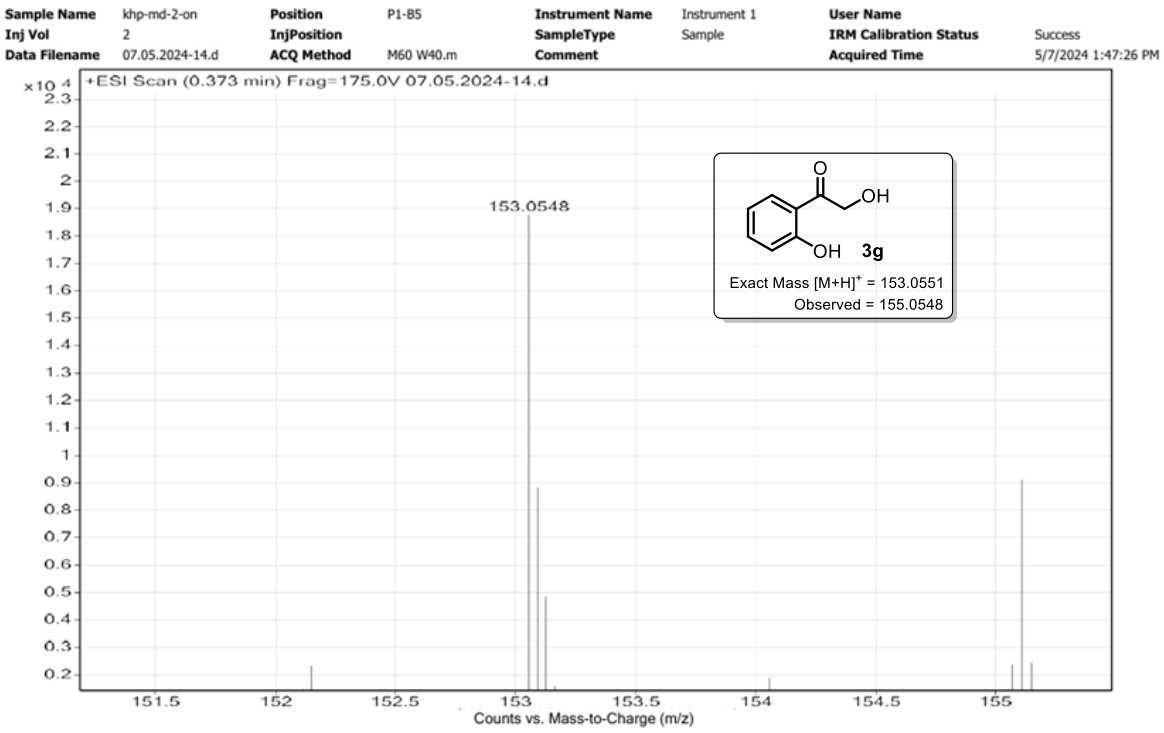
^{1}H NMR (400 MHz, $CDCl_3$) of 2-hydroxy-1-(2-hydroxyphenyl)ethan-1-one (3g)



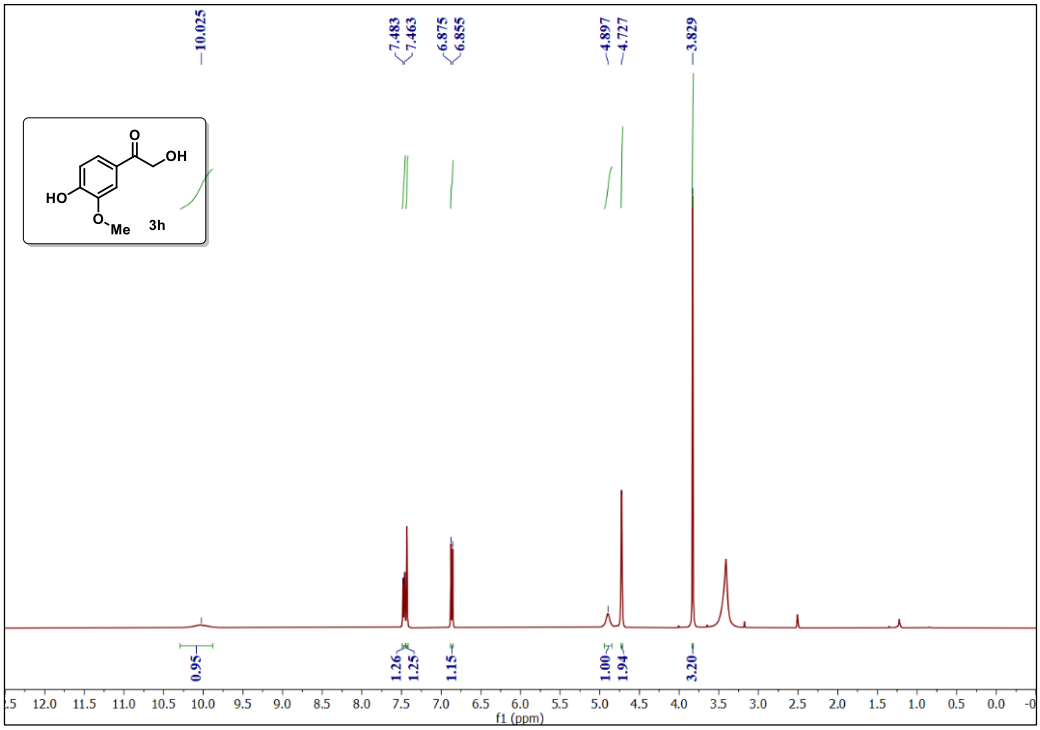
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of 2-hydroxy-1-(2-hydroxyphenyl) ethan-1-one (3g)



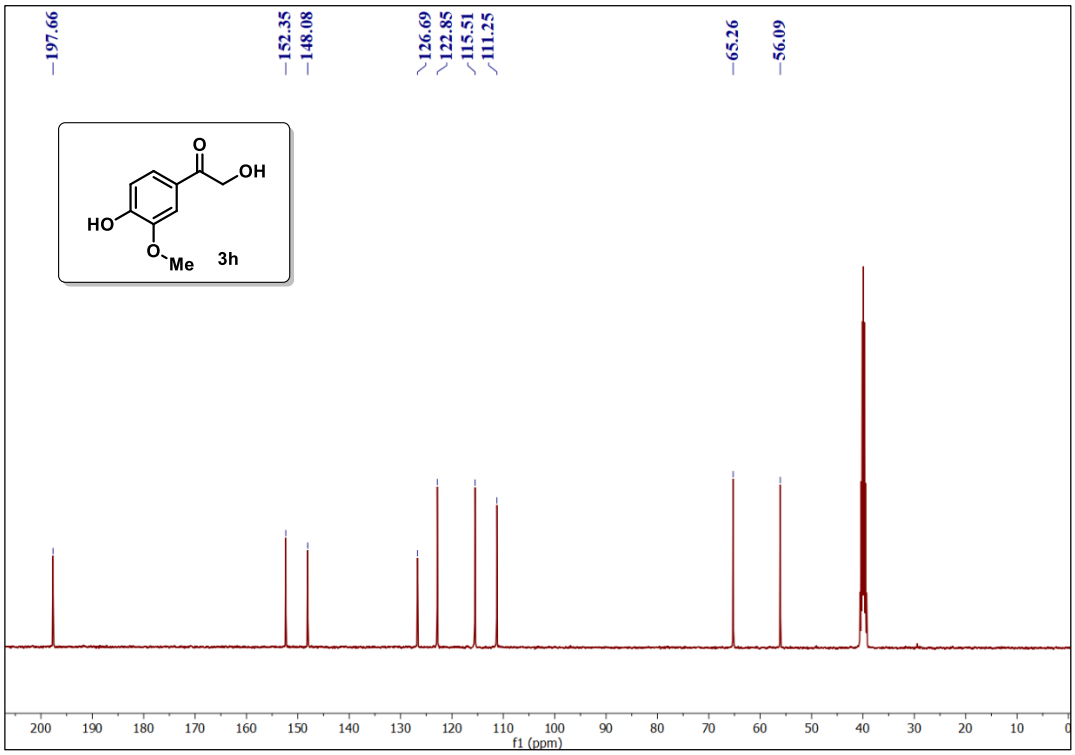
Mass spectrum of of hydroxy-1-(2-hydroxyphenyl)ethan-1-one (3g)



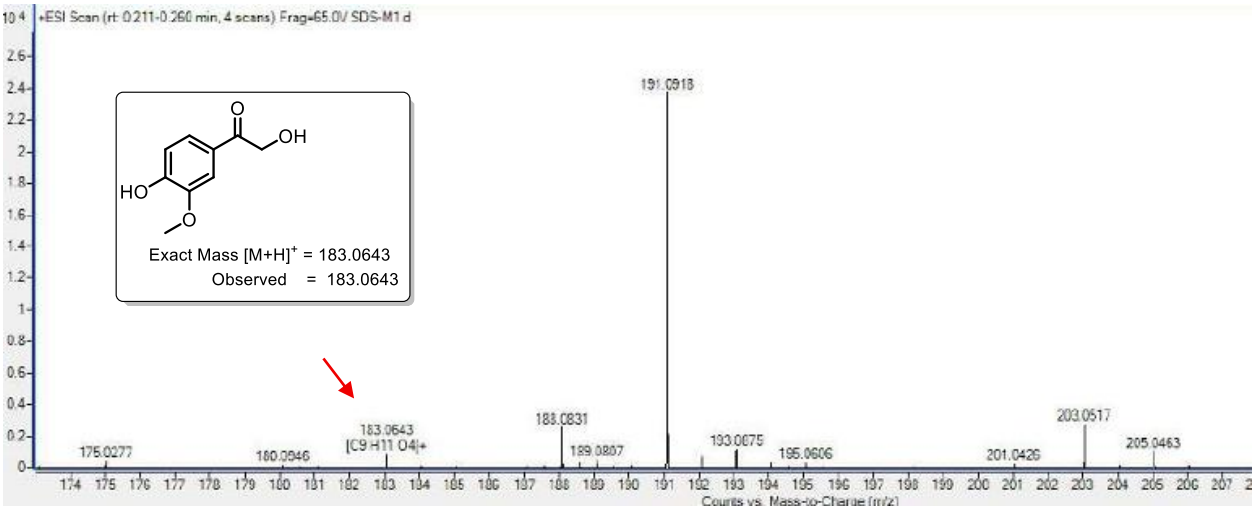
^{1}H NMR (400 MHz,DMSO-d_6) of 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)ethan-1-one (3h)



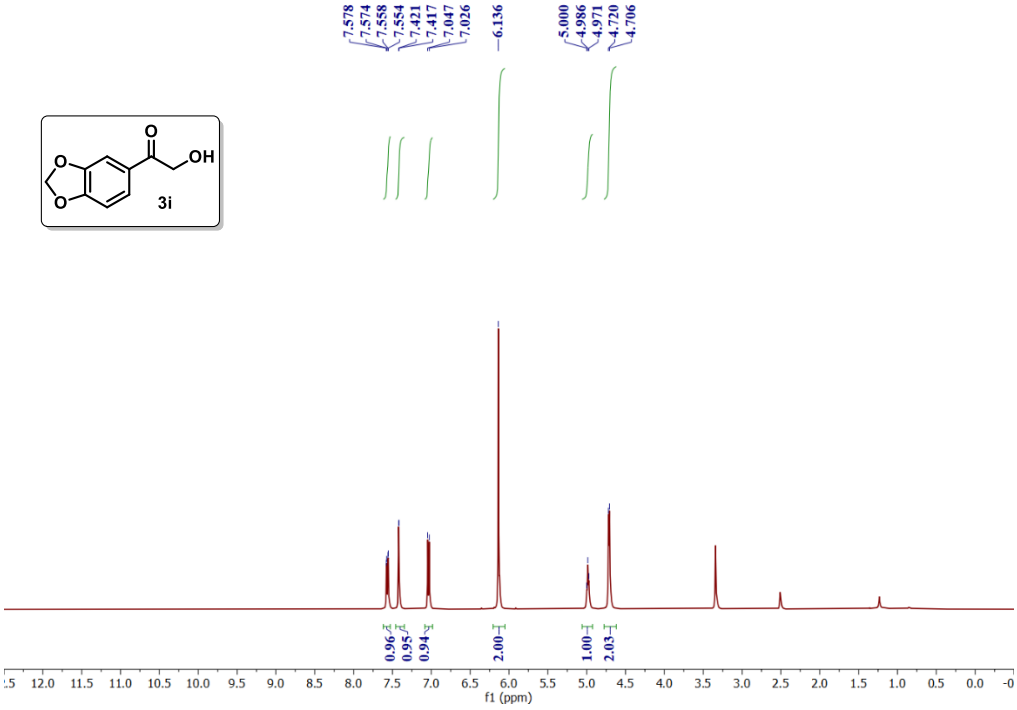
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl) ethan-1-one (3h)



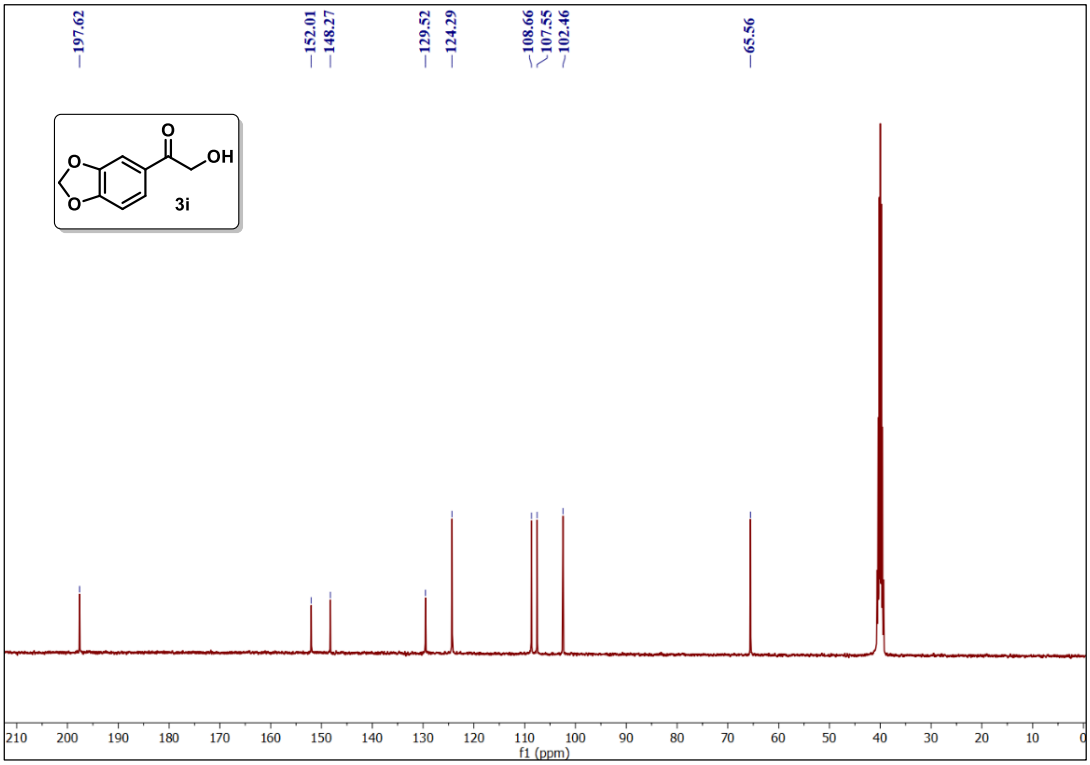
Mass spectrum of of 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)ethan-1-one (3h)



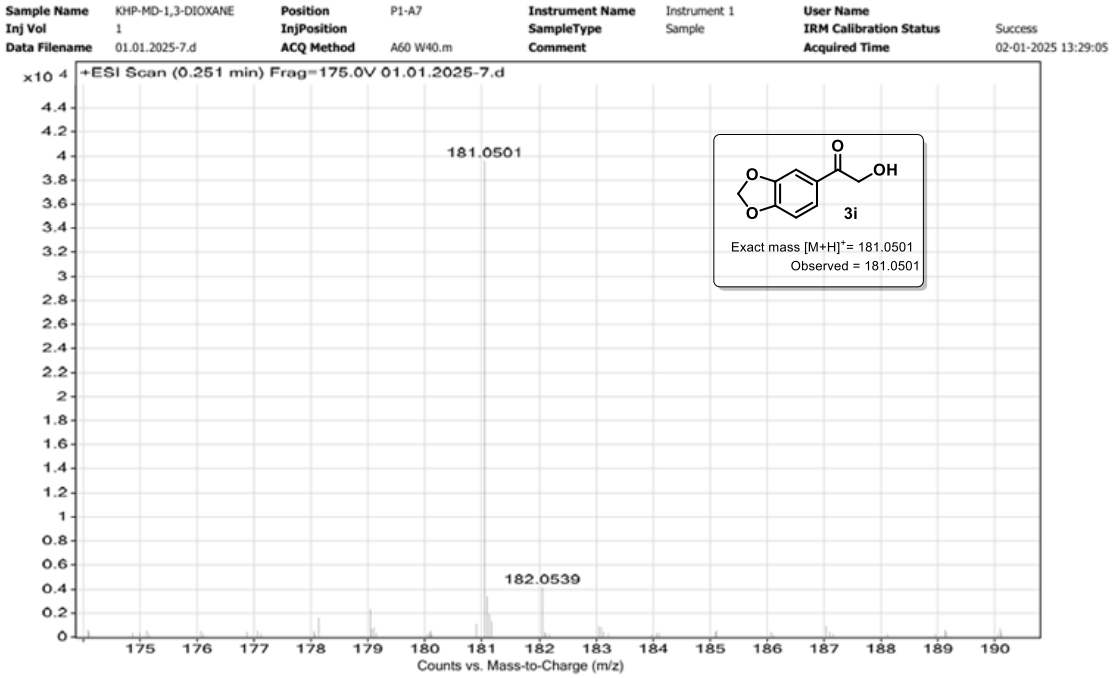
^{1}H NMR (400 MHz, DMSO-*d*$_6$) of 1-(benzo[d][1,3]dioxol-5-yl)-2-hydroxyethan-1-one (3i)



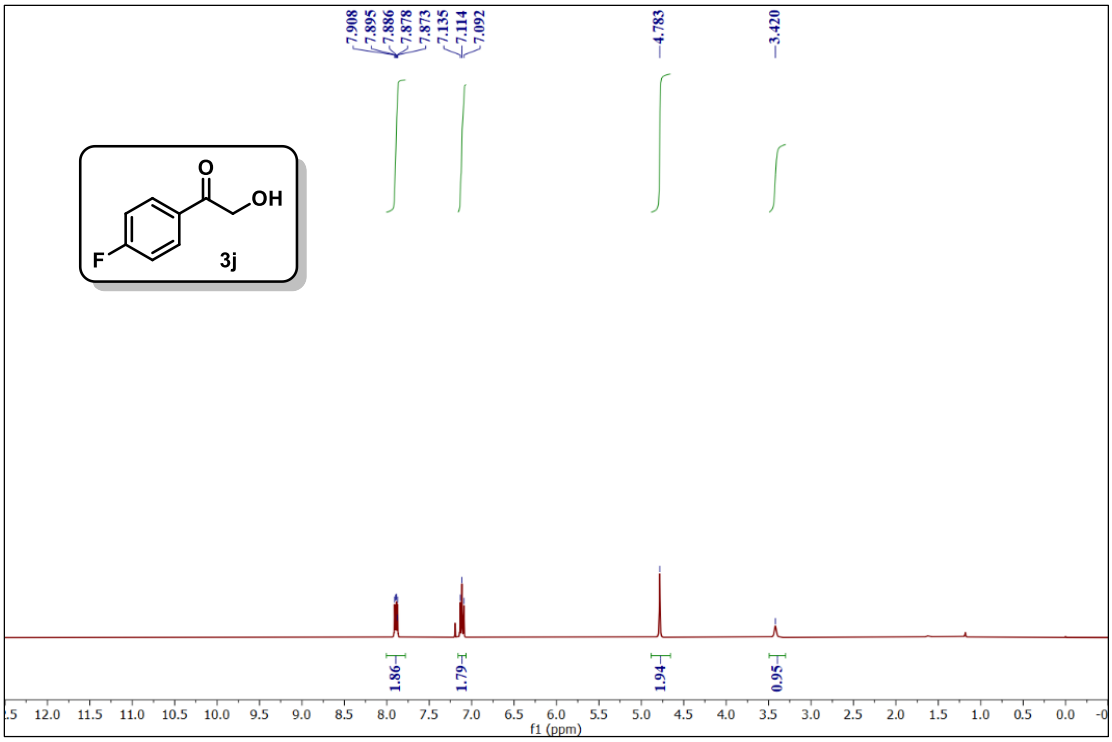
^{13}C{1H} NMR (100 MHz, DMSO-*d*$_6$) of 1-(benzo[d][1,3]dioxol-5-yl)-2-hydroxyethan-1-one (3i)



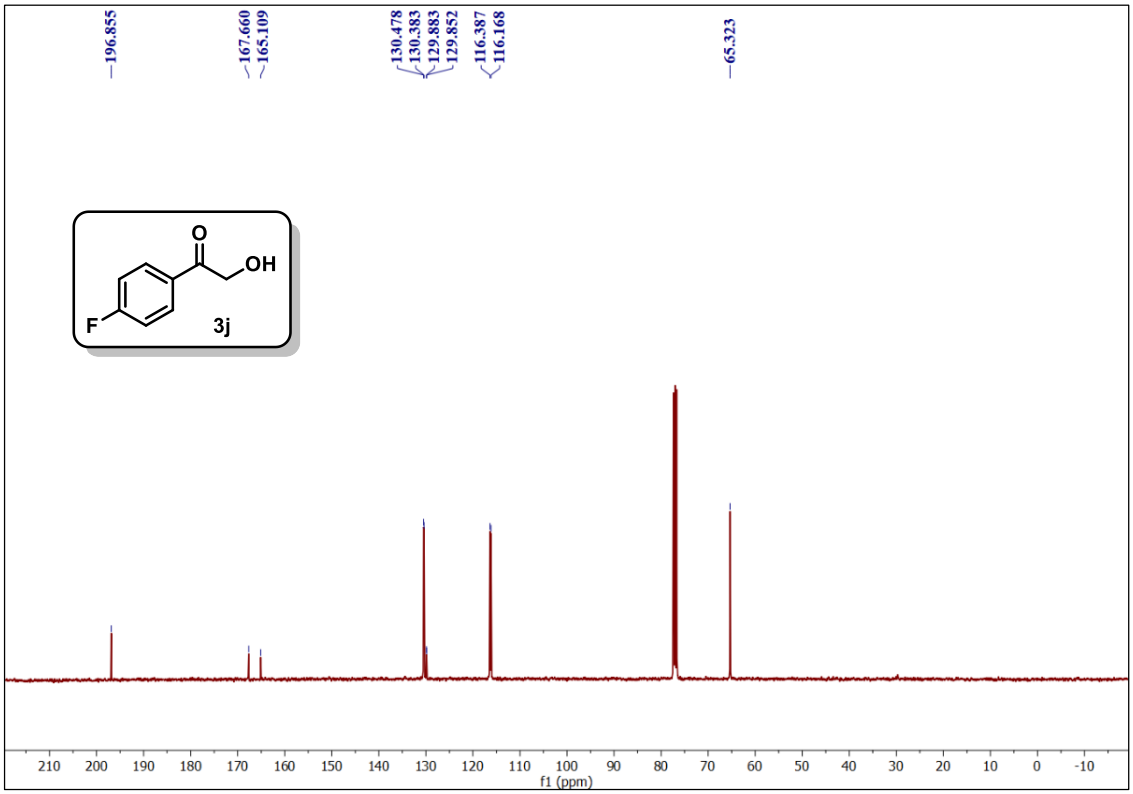
Mass spectrum of 1-(benzo[d][1,3] dioxol-5-yl)-2-hydroxyethan-1-one (3i)



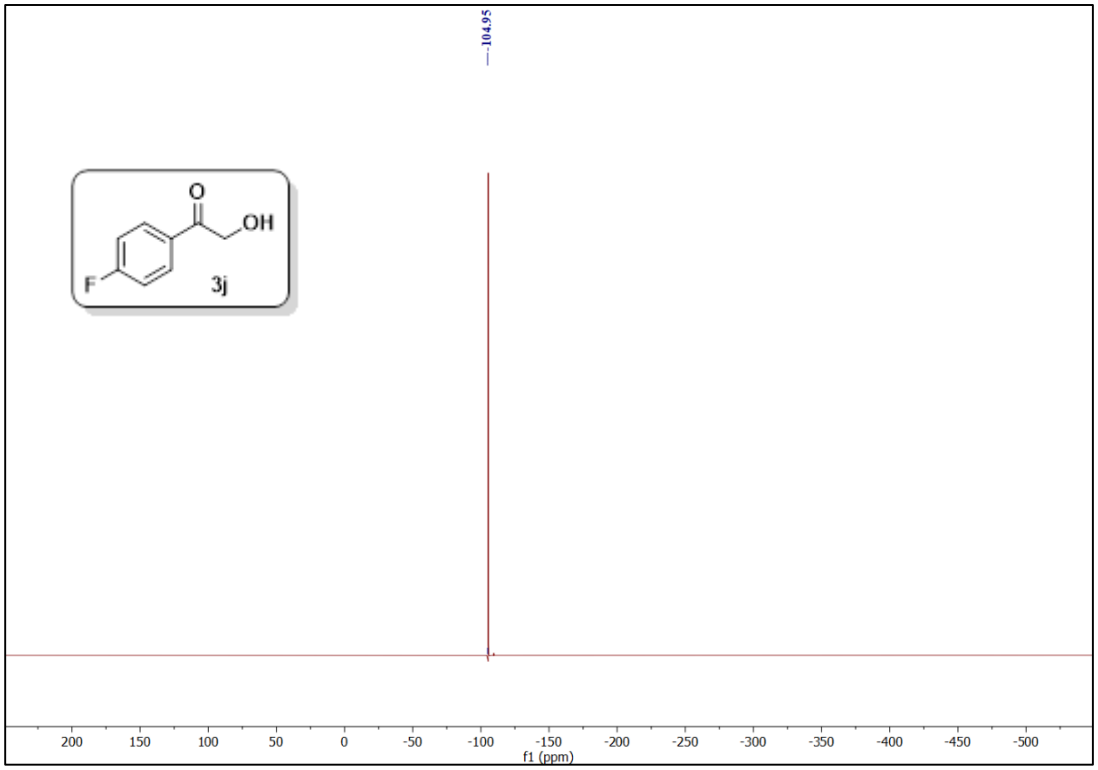
1H NMR (400 MHz, $CDCl_3$) of 1-(4-fluorophenyl)-2-hydroxyethan-1-one(3j)



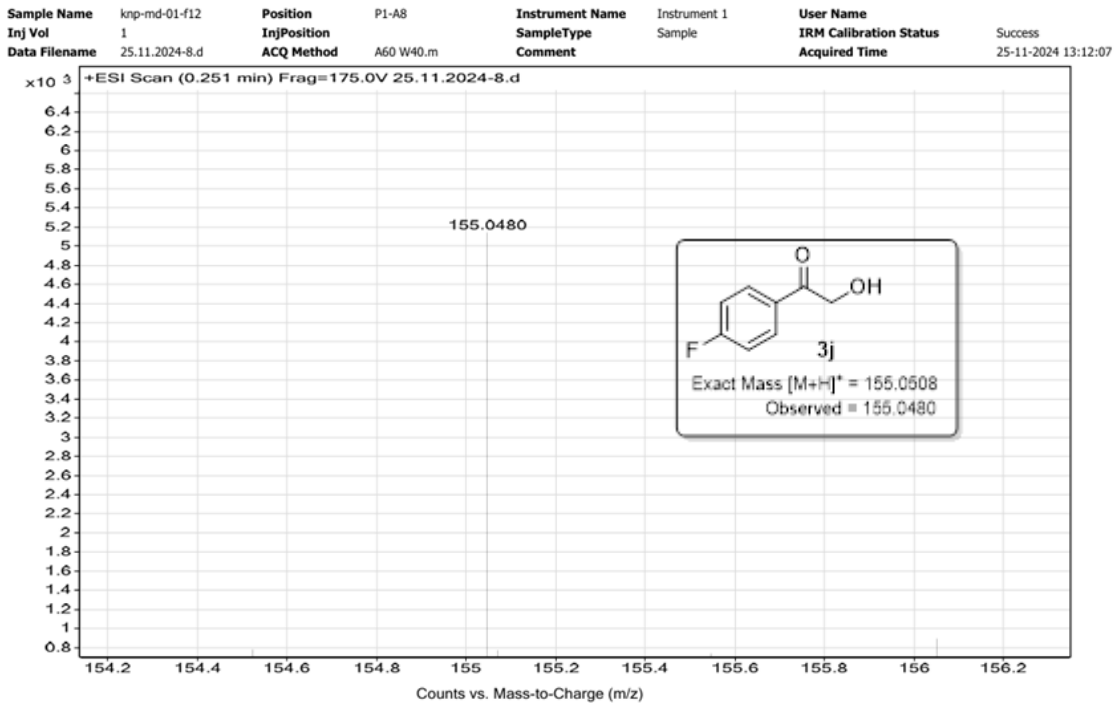
$^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) of 1-(4-fluorophenyl)-2-hydroxyethan-1-one(3l)



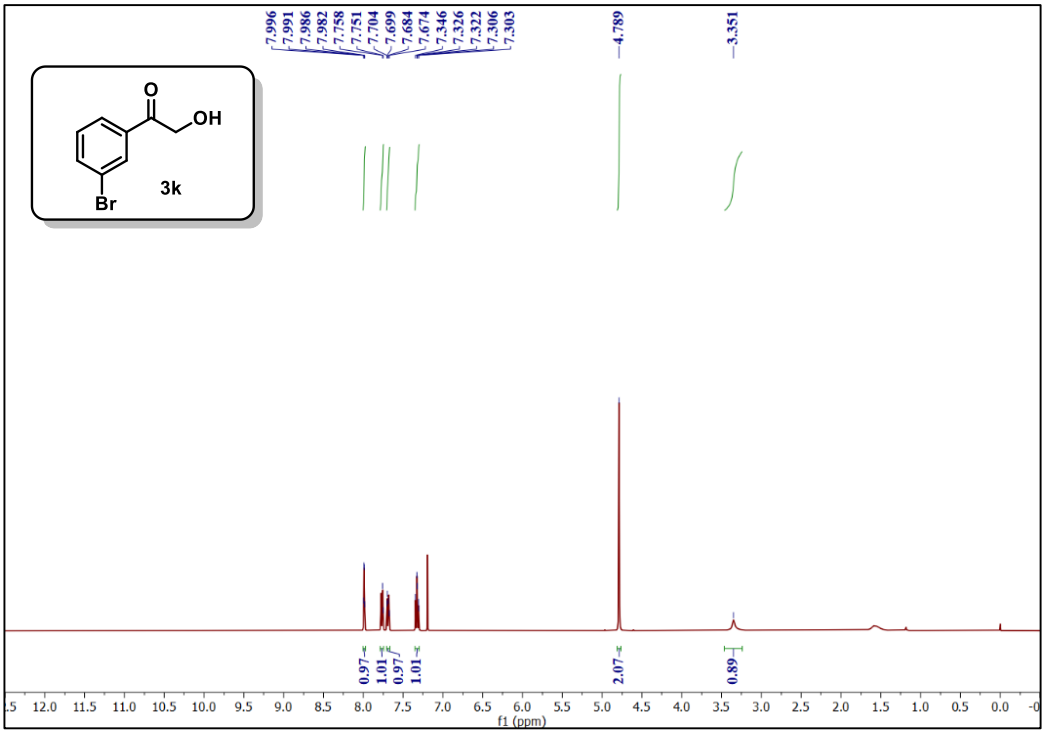
^{19}F NMR (376 MHz,$CDCl_3$) 1-(4-fluorophenyl)-2-hydroxyethan-1-one(3j)



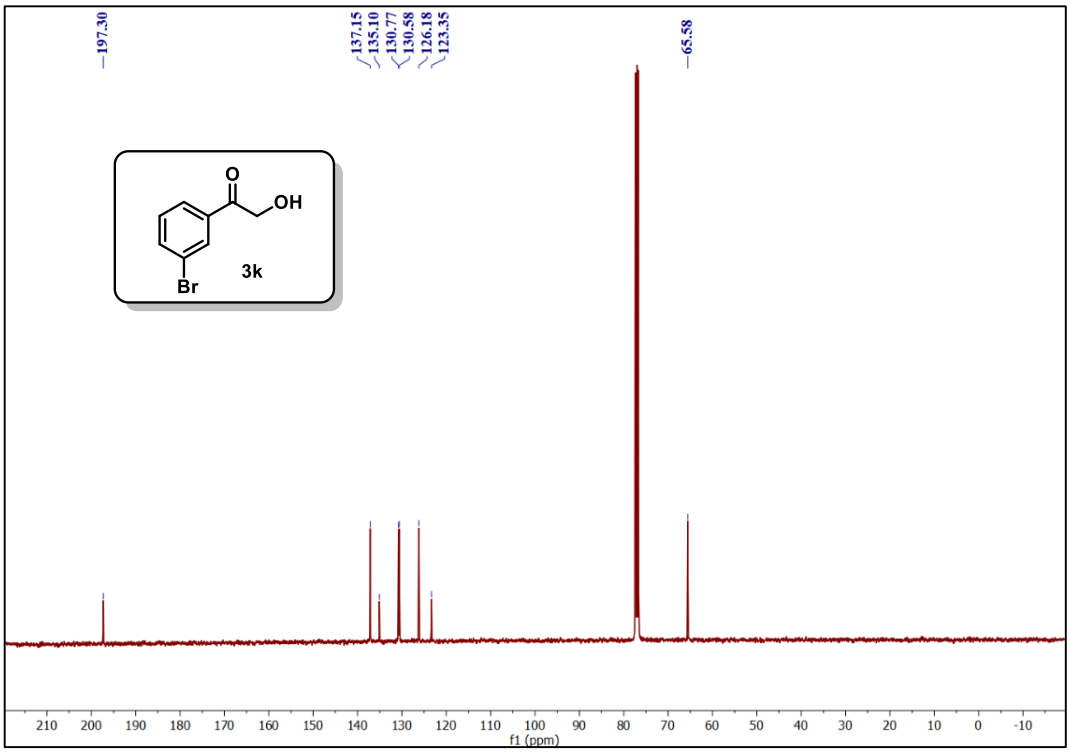
Mass spectrum of 1-(4-fluorophenyl)-2-hydroxyethan-1-one(3j)



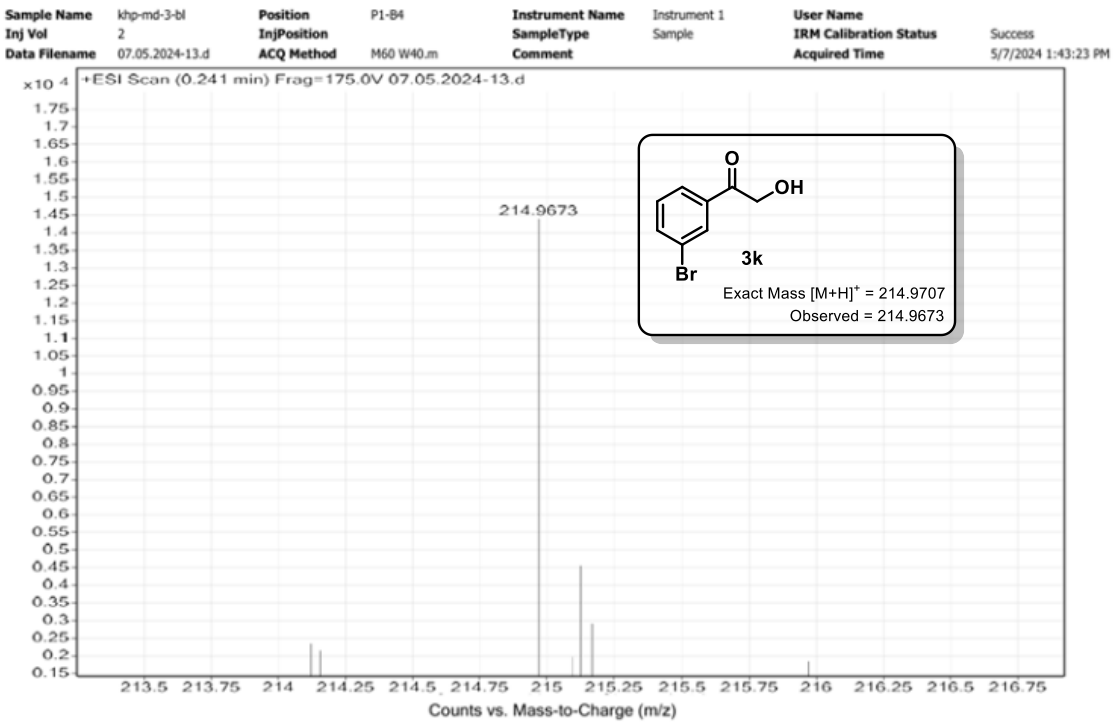
^{1}H NMR (400 MHz, $CDCl_3$) of 1-(3-bromophenyl)-2-hydroxyethan-1-one(3k)



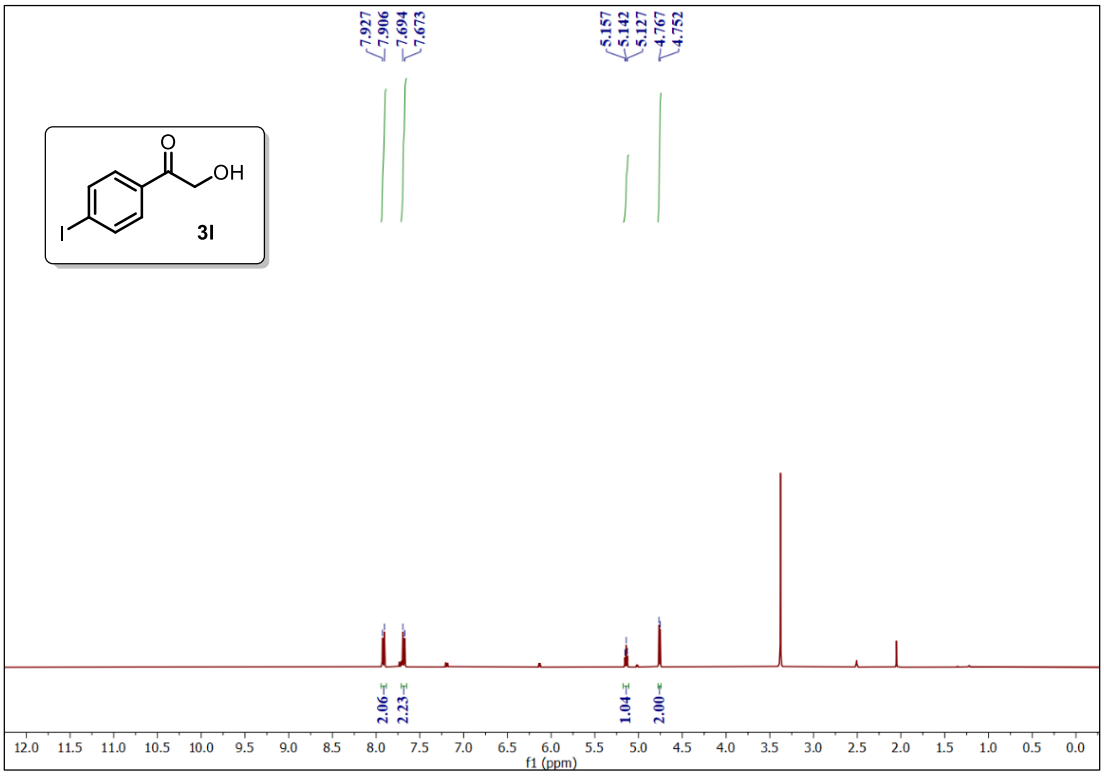
^{13}C{1H} NMR (100 MHz, $CDCl_3$) of 1-(3-bromophenyl)-2-hydroxyethan-1-one(3k)



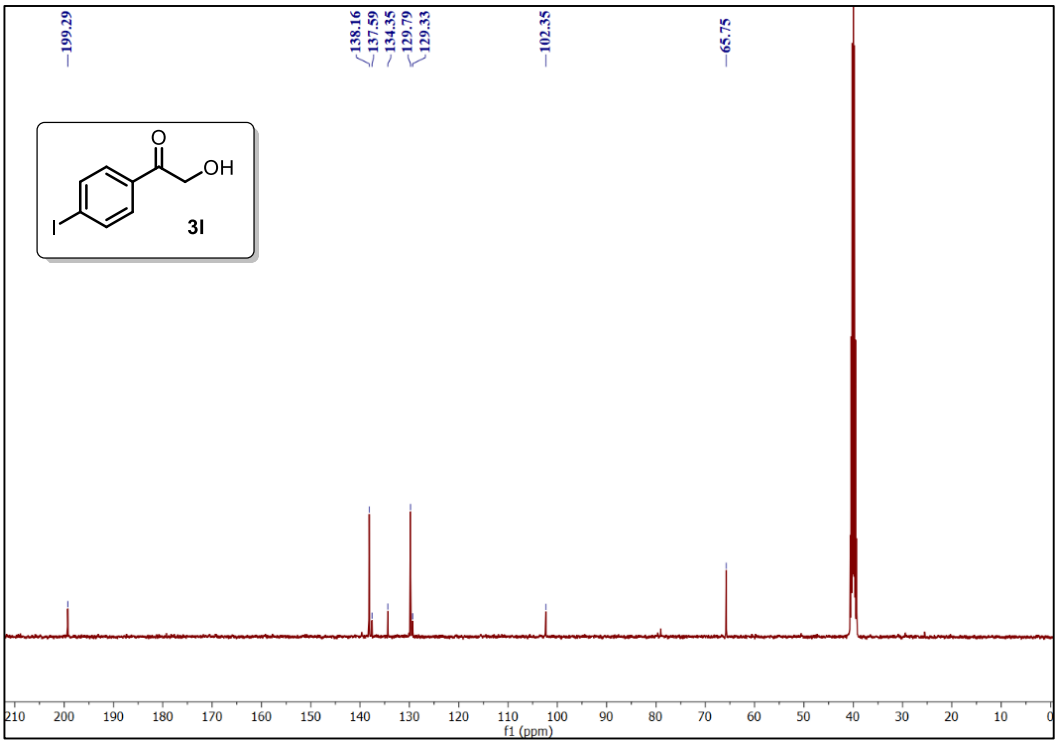
Mass spectrum of 1-(4-fluorophenyl)-2-hydroxyethan-1-one(3k)



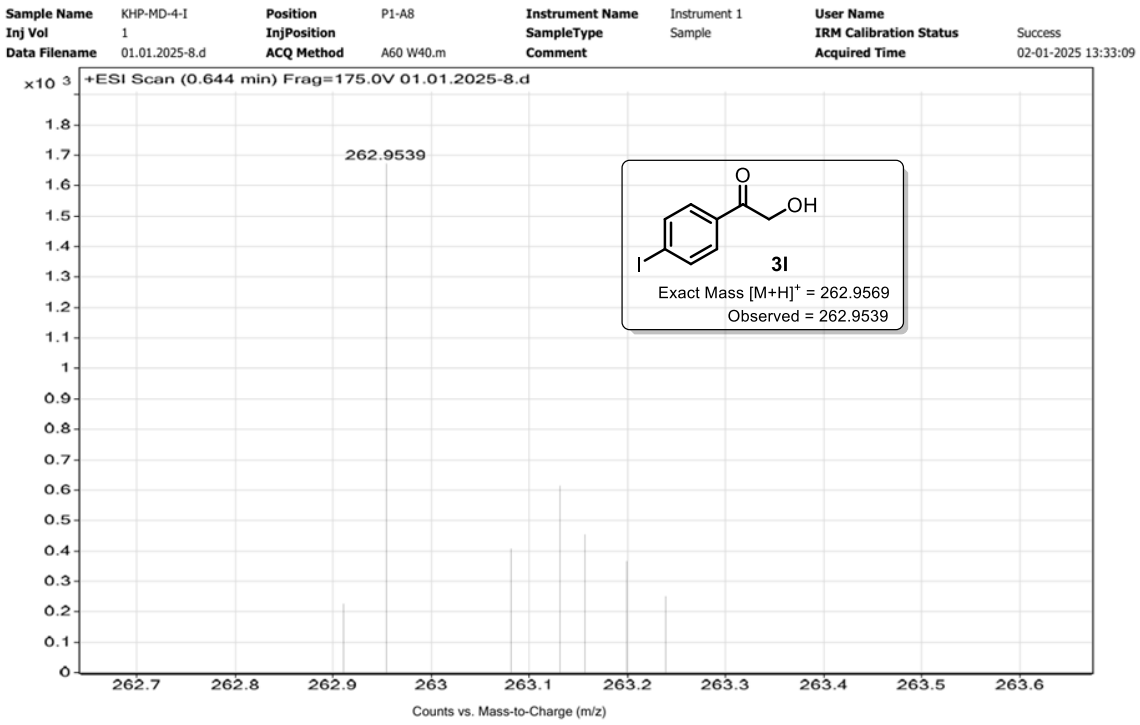
^{1}H NMR (400 MHz, DMSO-d_6) of 2-hydroxy-1-(4-iodophenyl)ethan-1-one (3l)



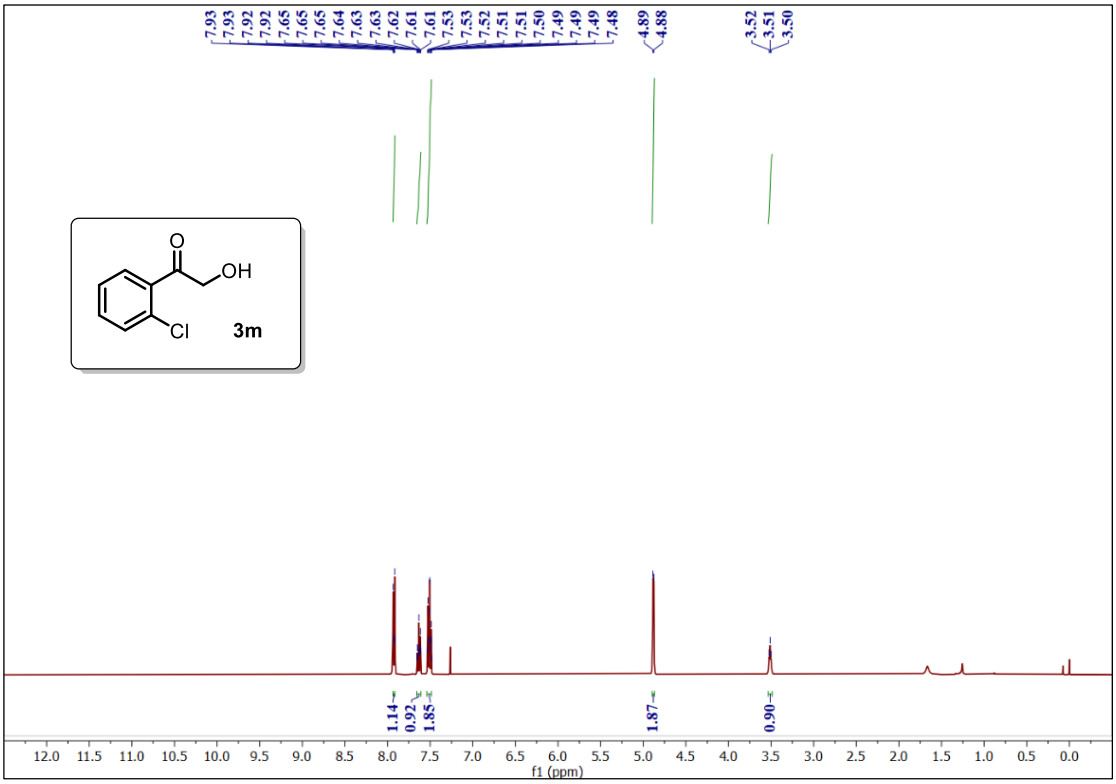
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of 2-hydroxy-1-(4-iodophenyl)ethan-1-one (3l)



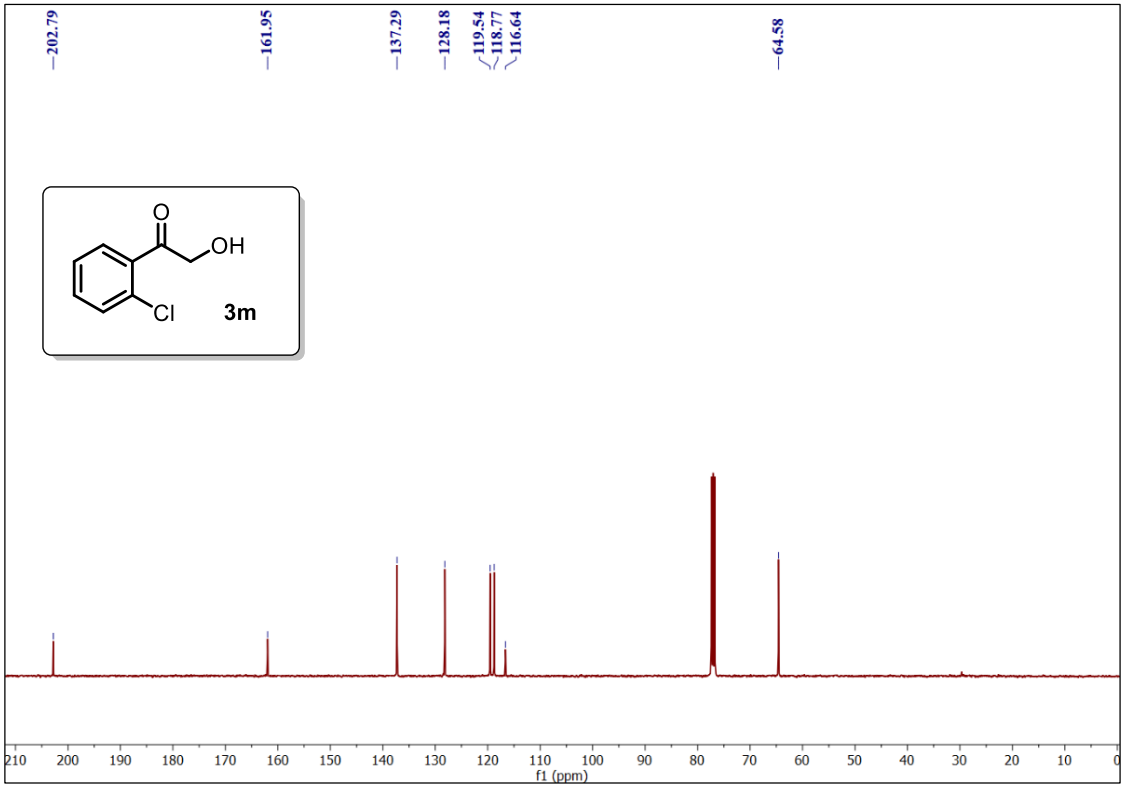
Mass spectrum of 2-hydroxy-1-(4-iodophenyl) ethan-1-one (3l)



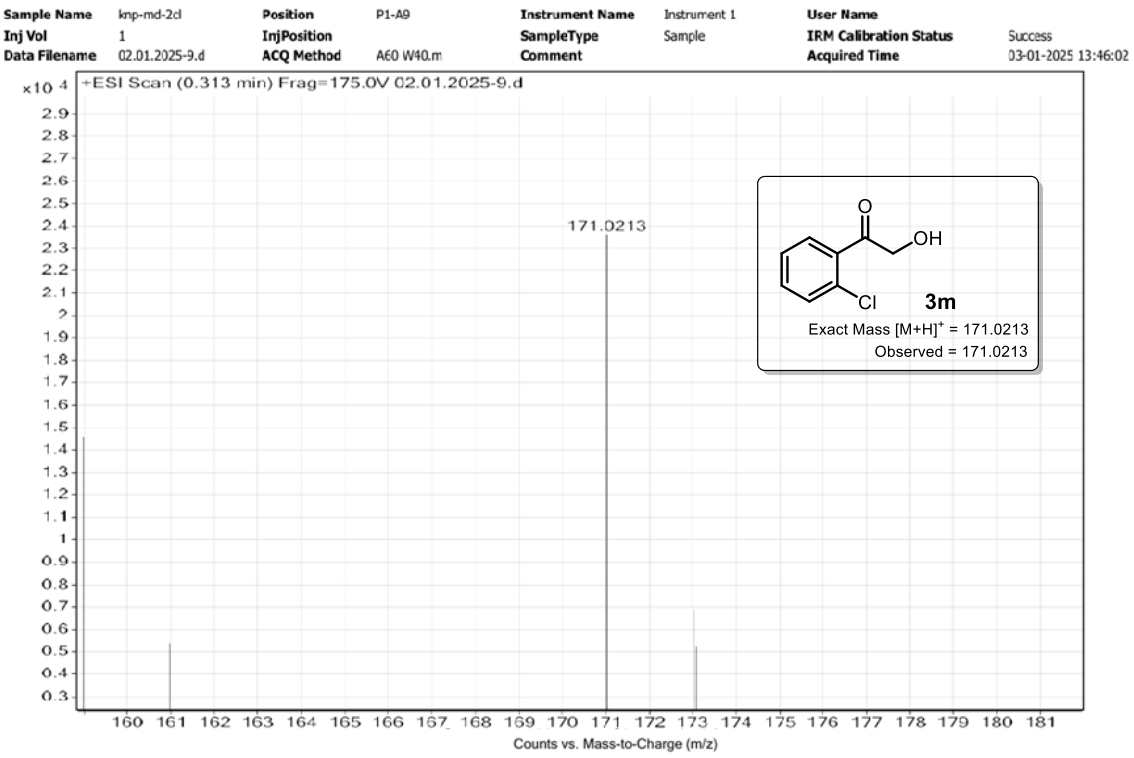
^{1}H NMR (400 MHz, $CDCl_3$) of 1-(2-chlorophenyl)-2-hydroxyethan-1-one (3m)



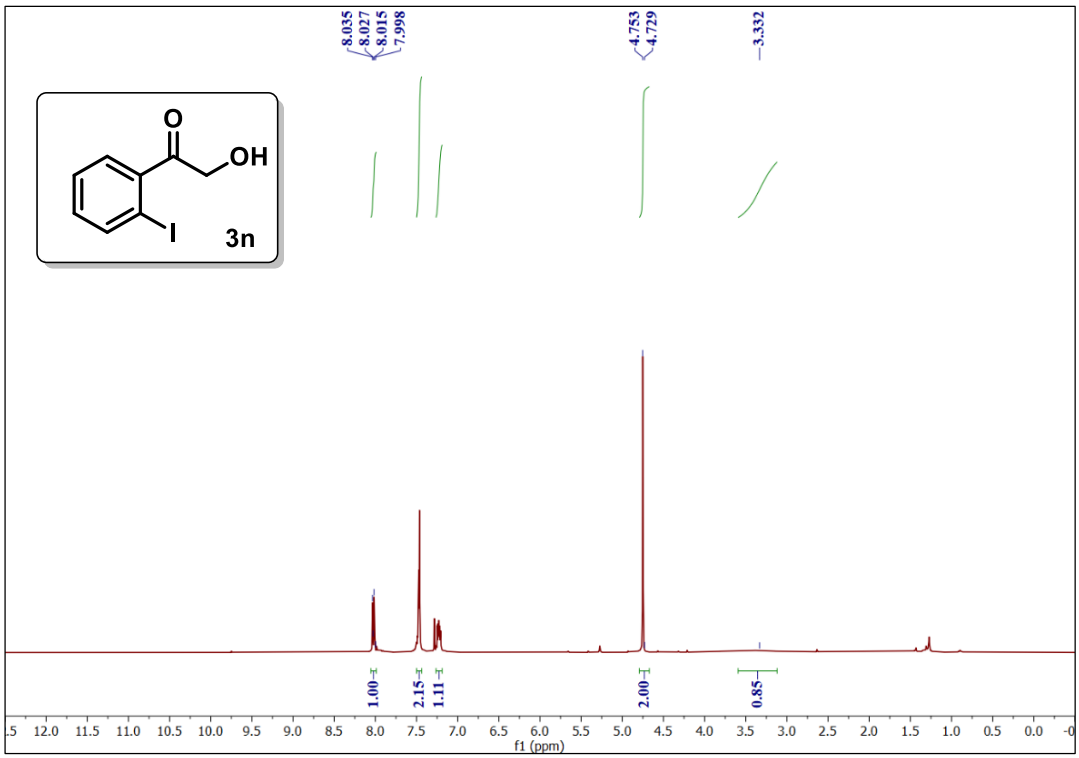
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of 1-(2-chlorophenyl)-2-hydroxyethan-1-one (3m)



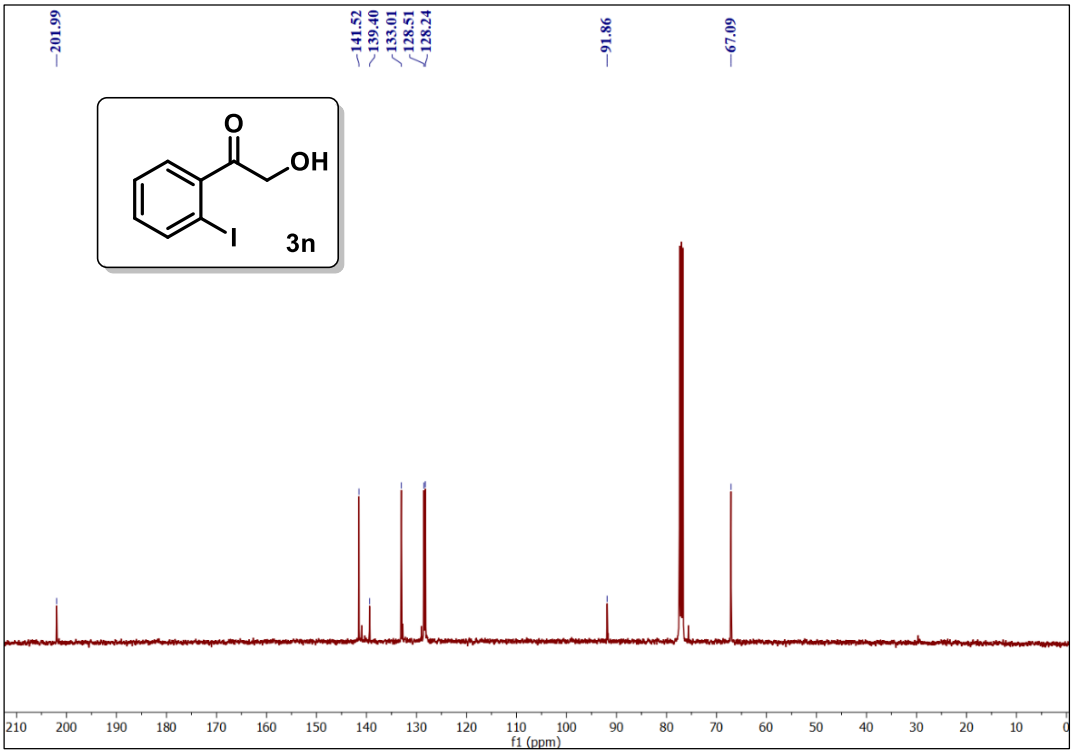
Mass spectrum of 1-(2-chlorophenyl)-2-hydroxyethan-1-one (3m)



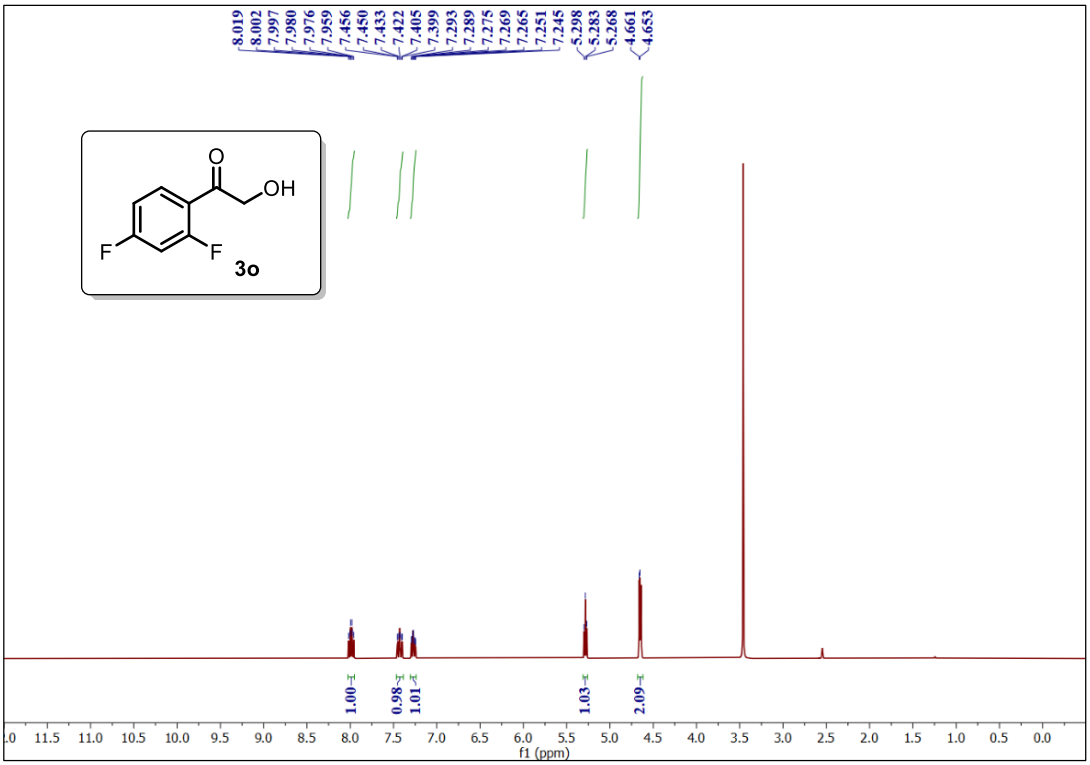
^{1}H NMR (400 MHz, $\underline{CDCl_3}$) of 2-hydroxy-1-(2-iodophenyl)ethan-1-one (3n)



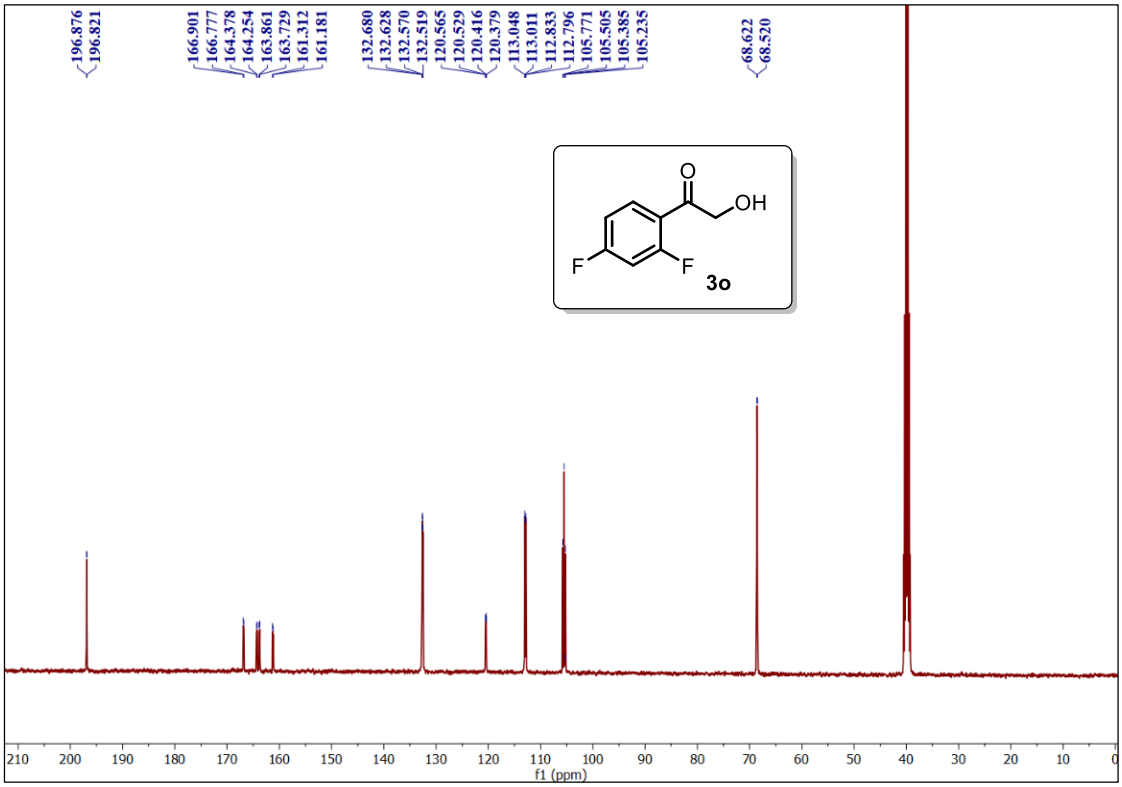
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of 2-hydroxy-1-(2-iodophenyl) ethan-1-one (3n)



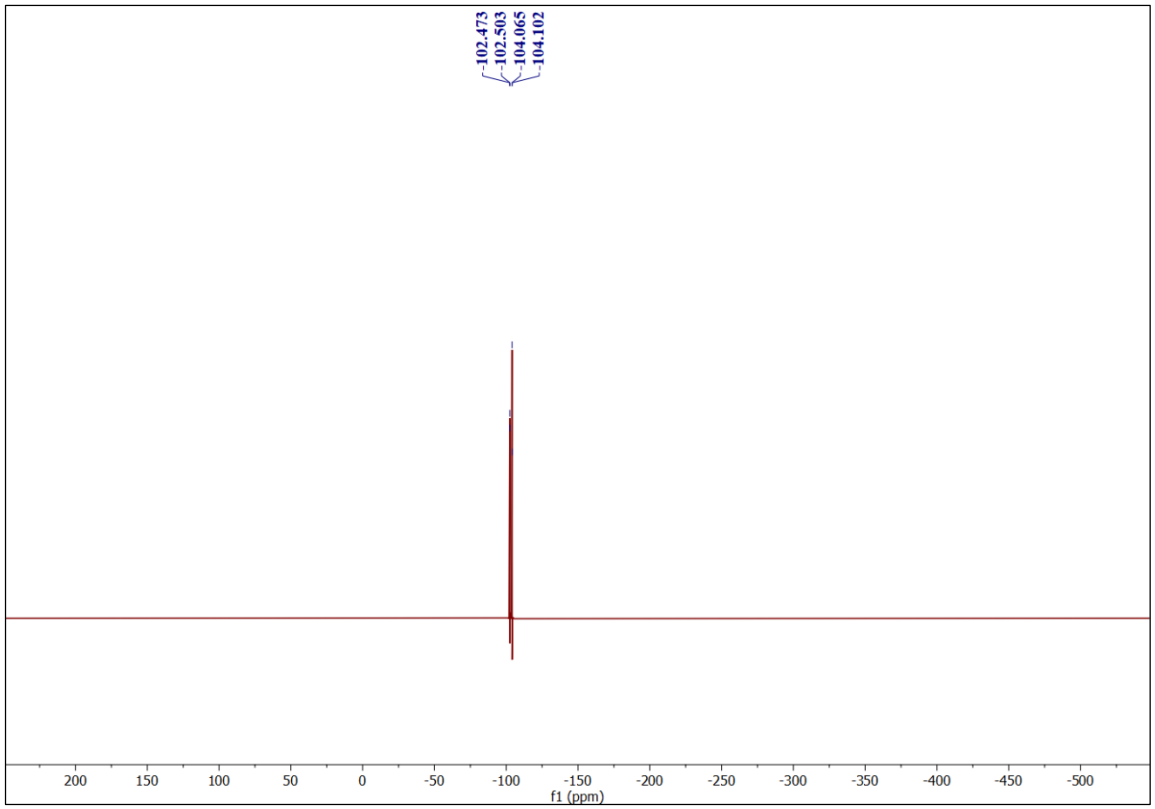
^{1}H NMR (400 MHz, DMSO-d_6) of 1-(2,4-difluorophenyl)-2-hydroxyethan-1-one(3o)



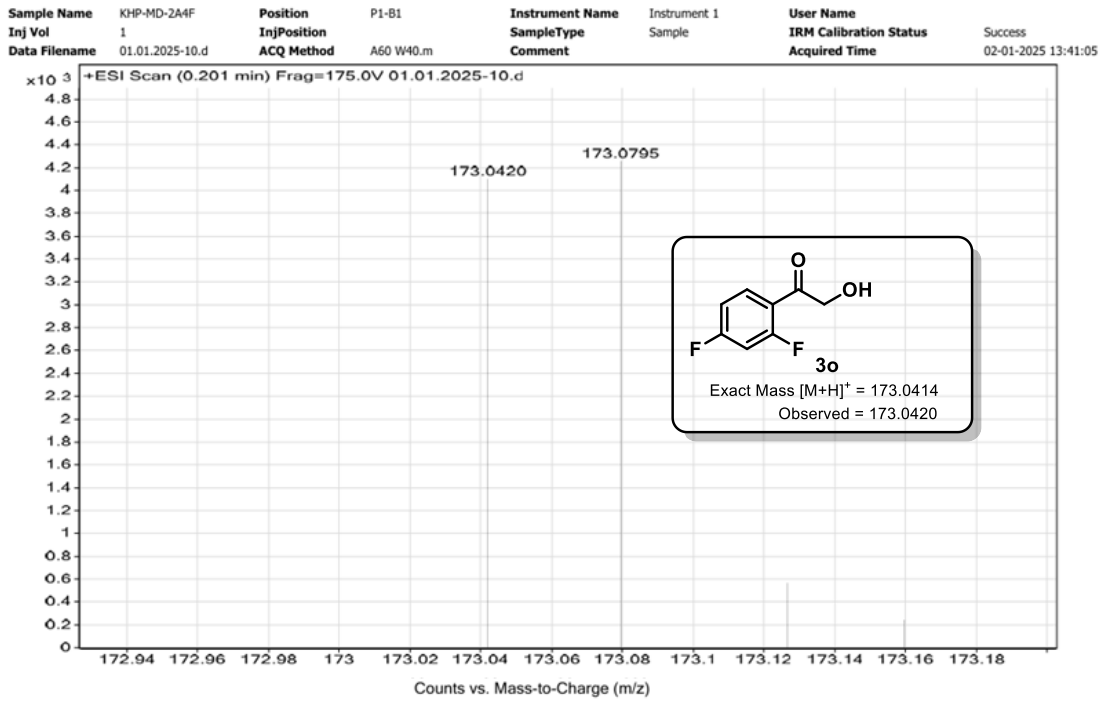
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of 1-(2,4-difluorophenyl)-2-hydroxyethan-1-one(3o)



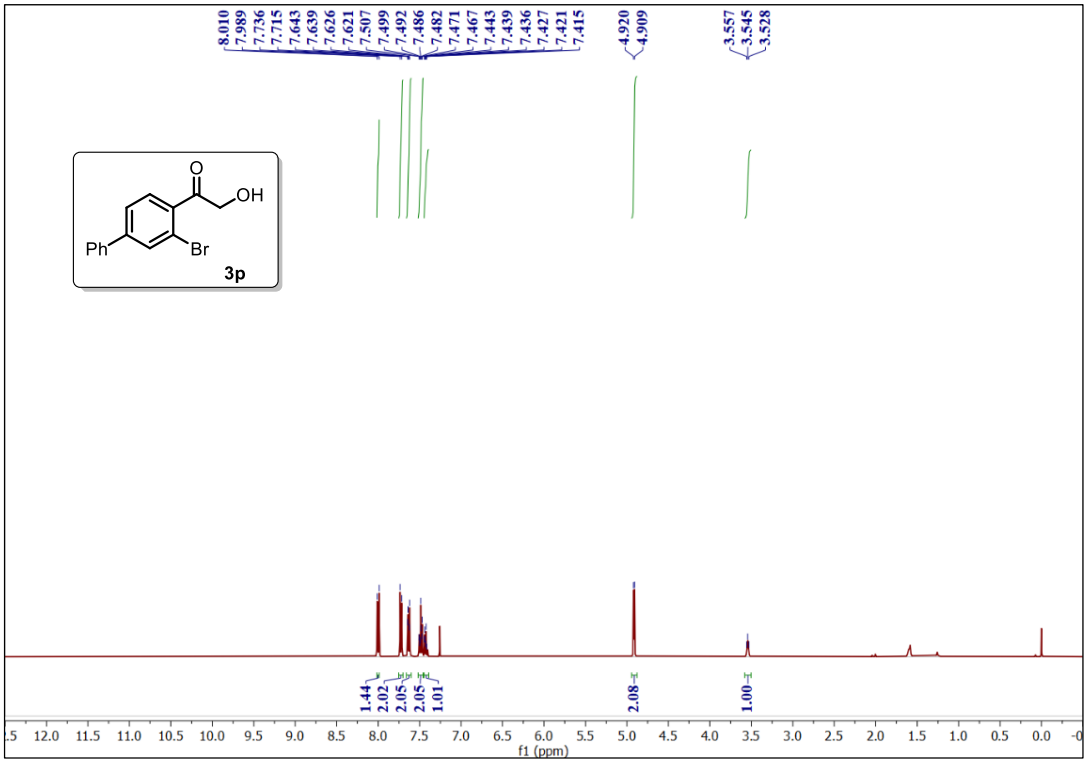
^{19}F NMR (376 MHz, $CDCl_3$) of 1-(2,4-difluorophenyl)-2-hydroxyethan-1-one(3o)



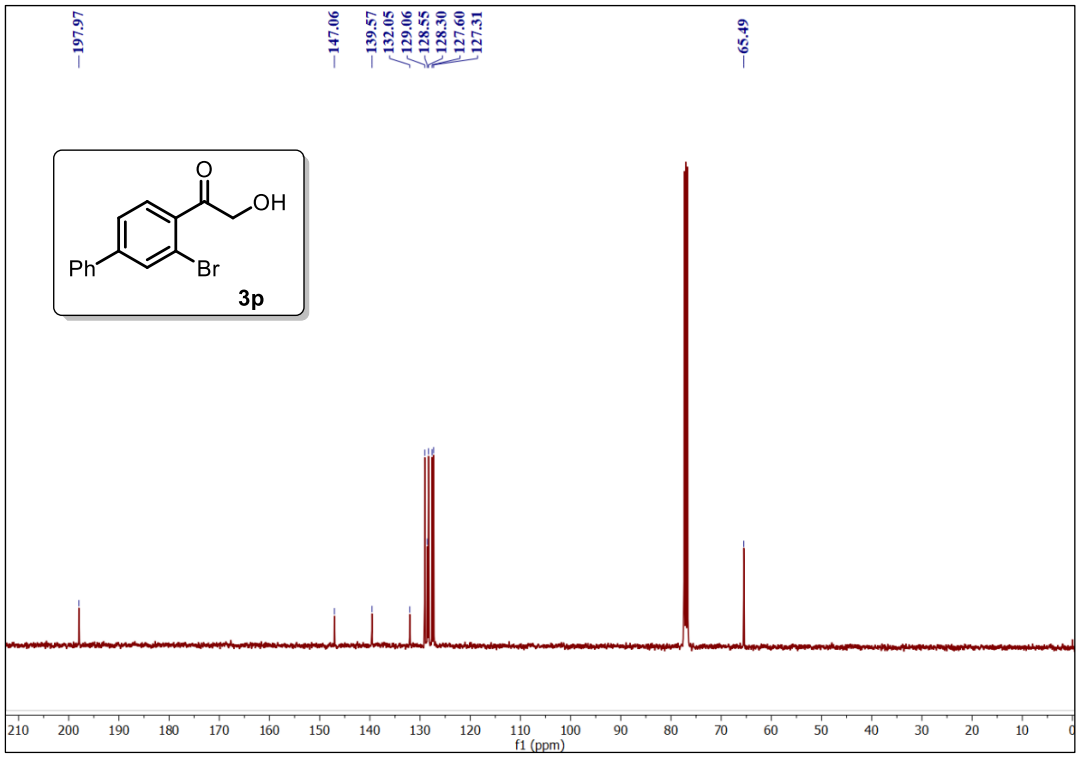
Mass spectrum of of 1-(2,4-difluorophenyl)-2-hydroxyethan-1-one(3o)



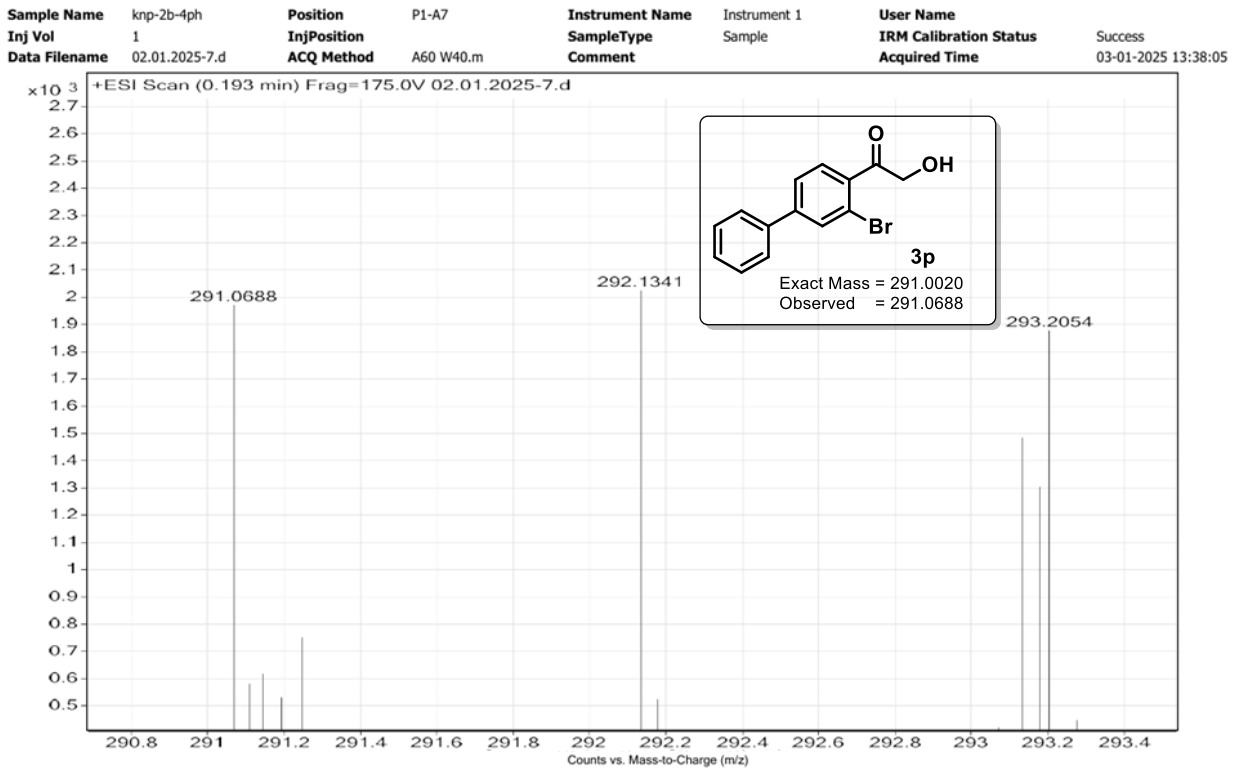
^{1}H NMR (400 MHz, $CDCl_3$) of 1-(3-bromo-[1,1'-biphenyl]-4-yl)-2-hydroxyethan-1-one (3p)



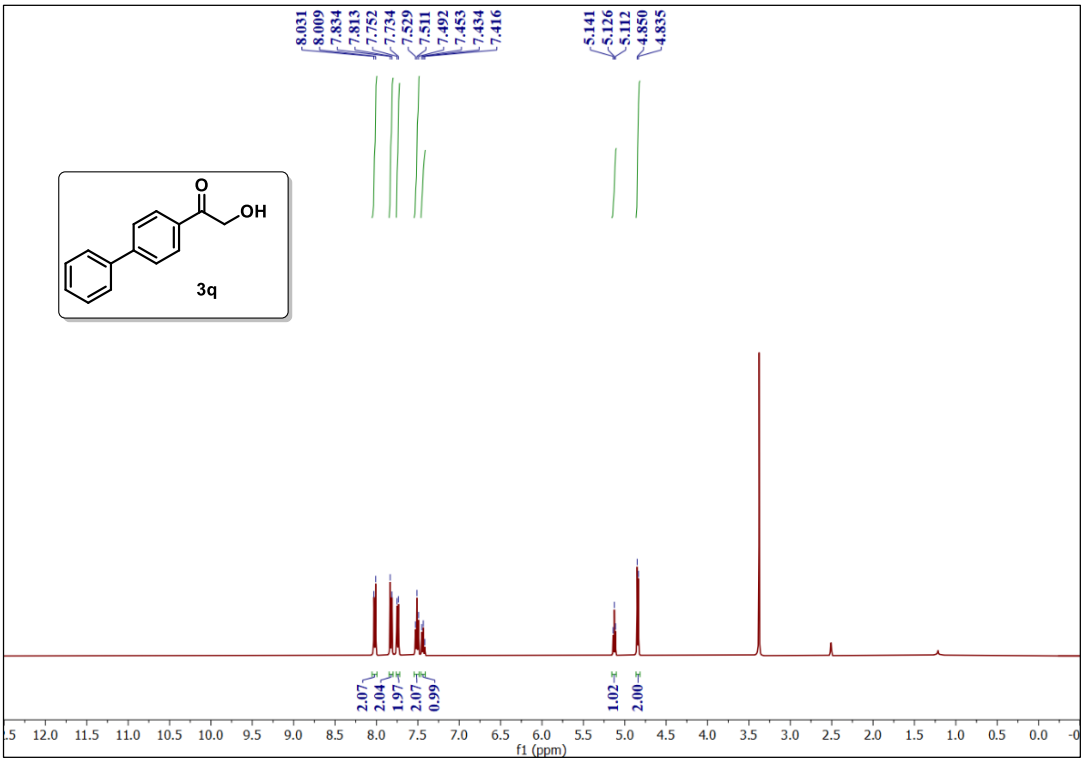
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of 1-(3-bromo-[1,1'-biphenyl]-4-yl)-2-hydroxyethan-1-one (3p)



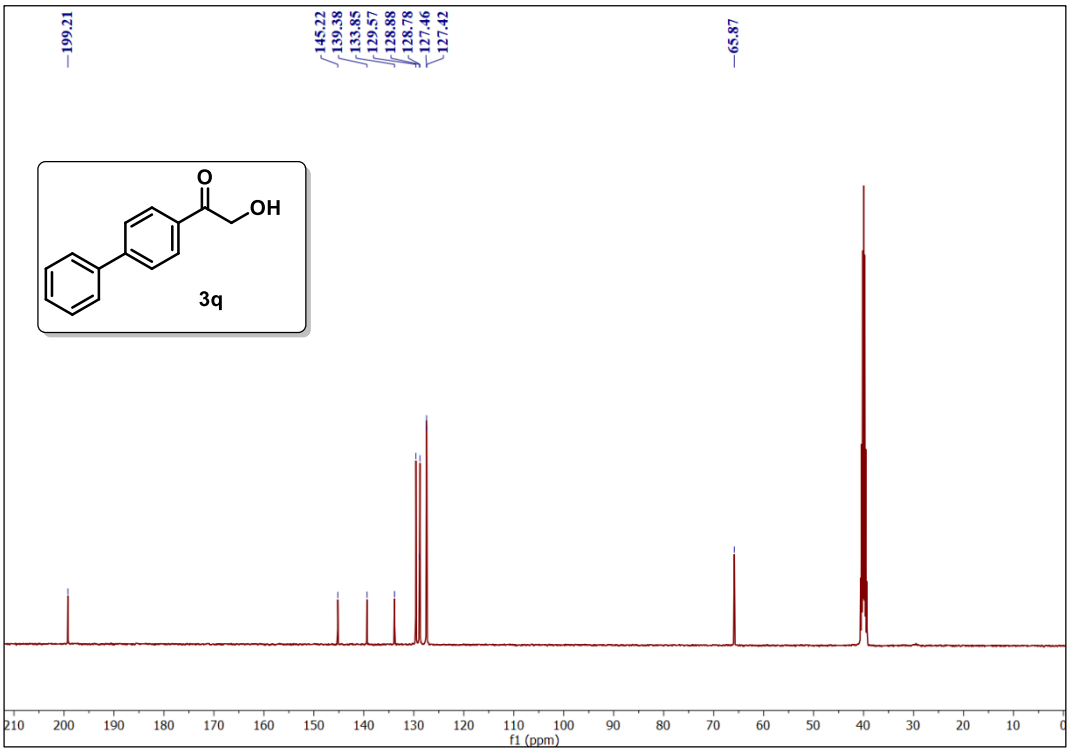
Mass spectrum of 1-([1,1'-biphenyl]-4-yl)-2-hydroxyethan-1-one(3p)



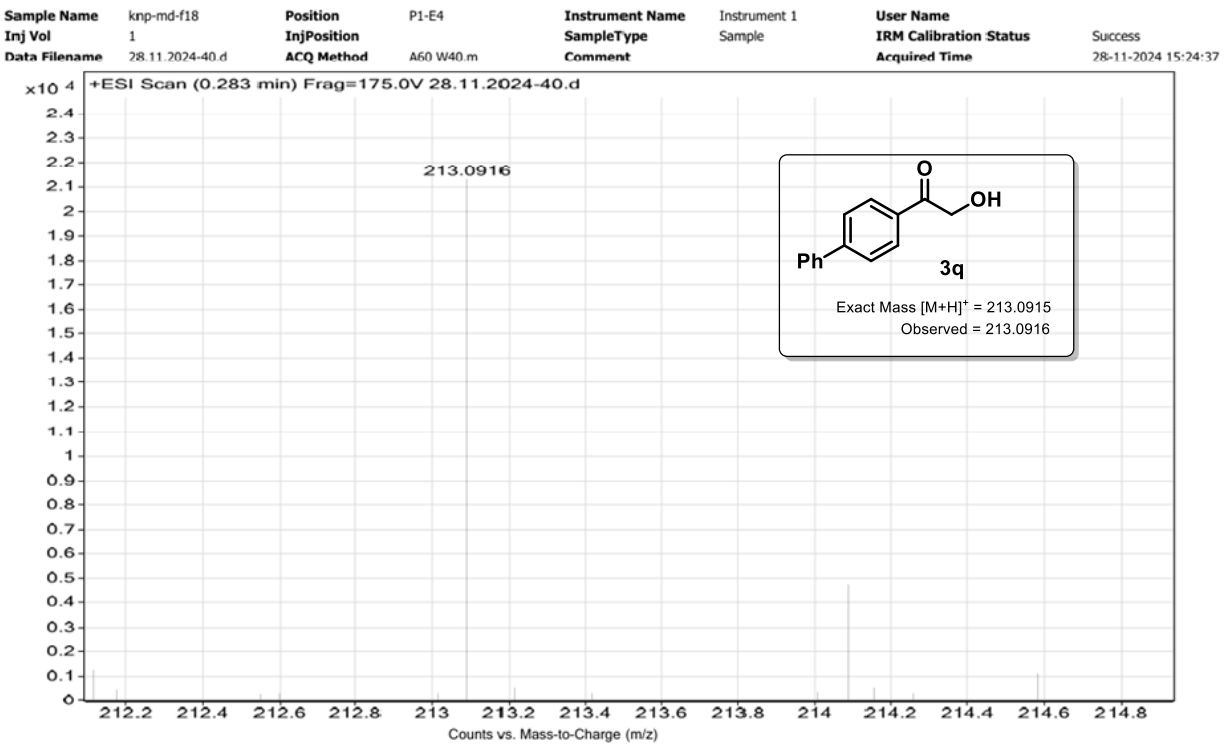
^{1}H NMR (400 MHz, DMSO-d_6) of 1-([1,1'-biphenyl]-4-yl)-2-hydroxyethan-1-one(3q)



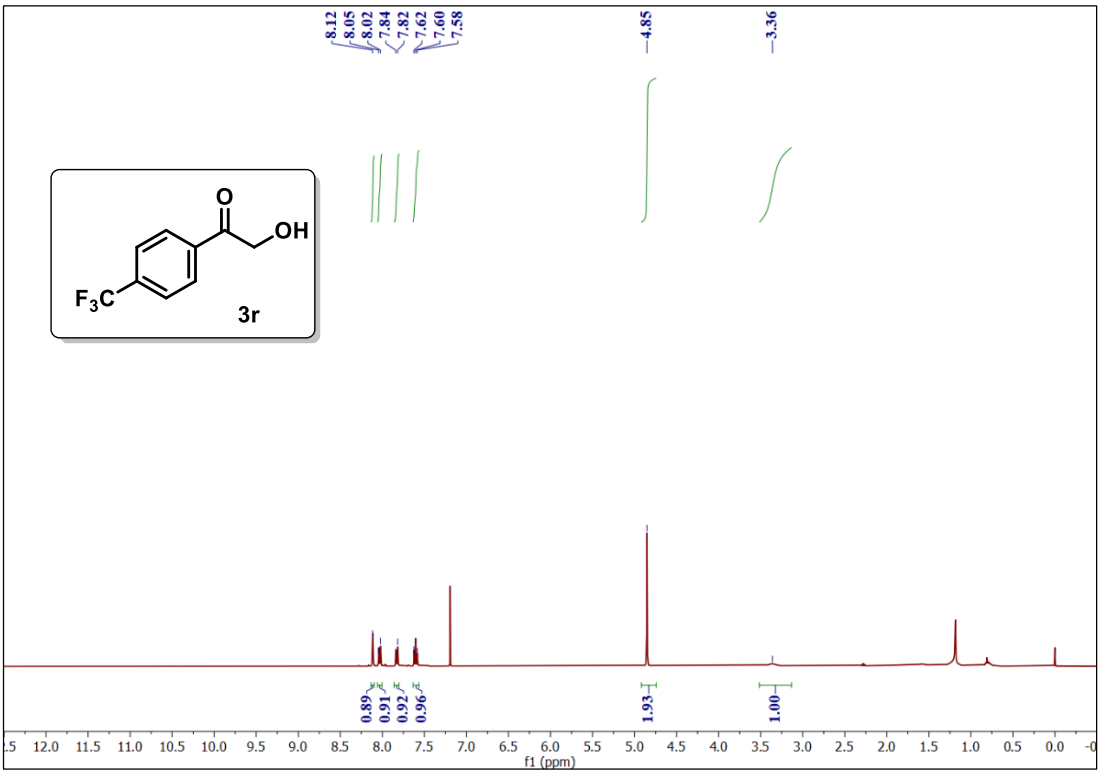
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of 1-([1,1'-biphenyl]-4-yl)-2-hydroxyethan-1-one(3q)



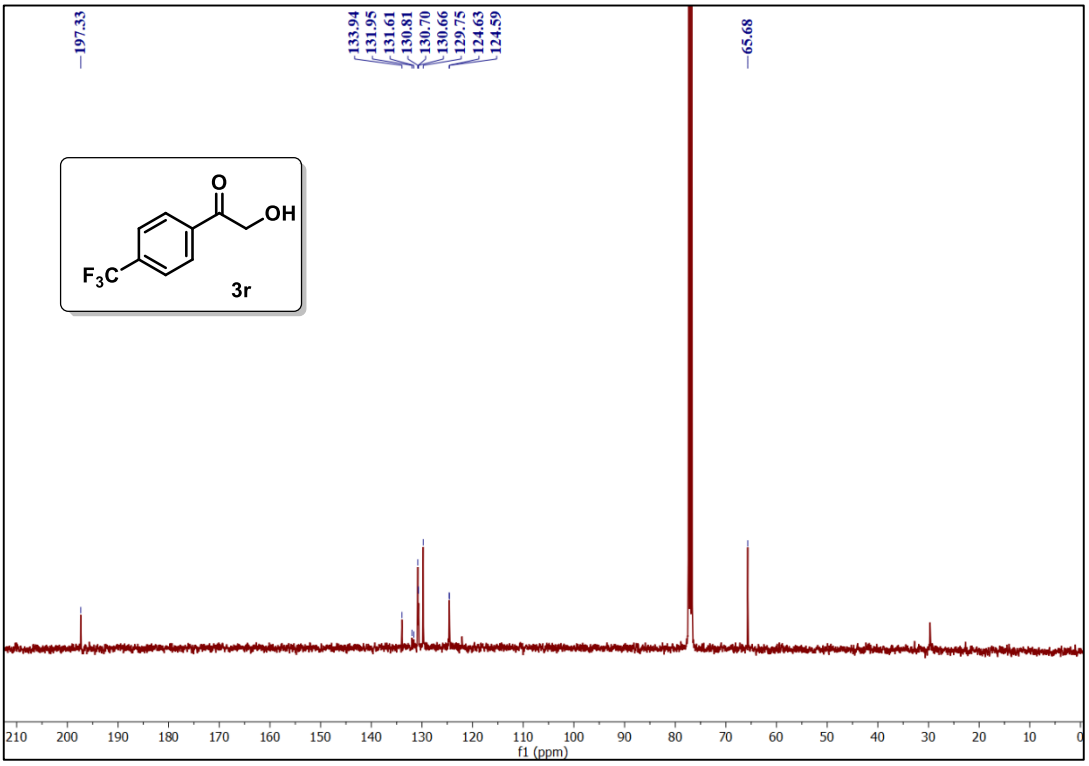
Mass spectrum of 1-([1,1'-biphenyl]-4-yl)-2-hydroxyethan-1-one(3q)



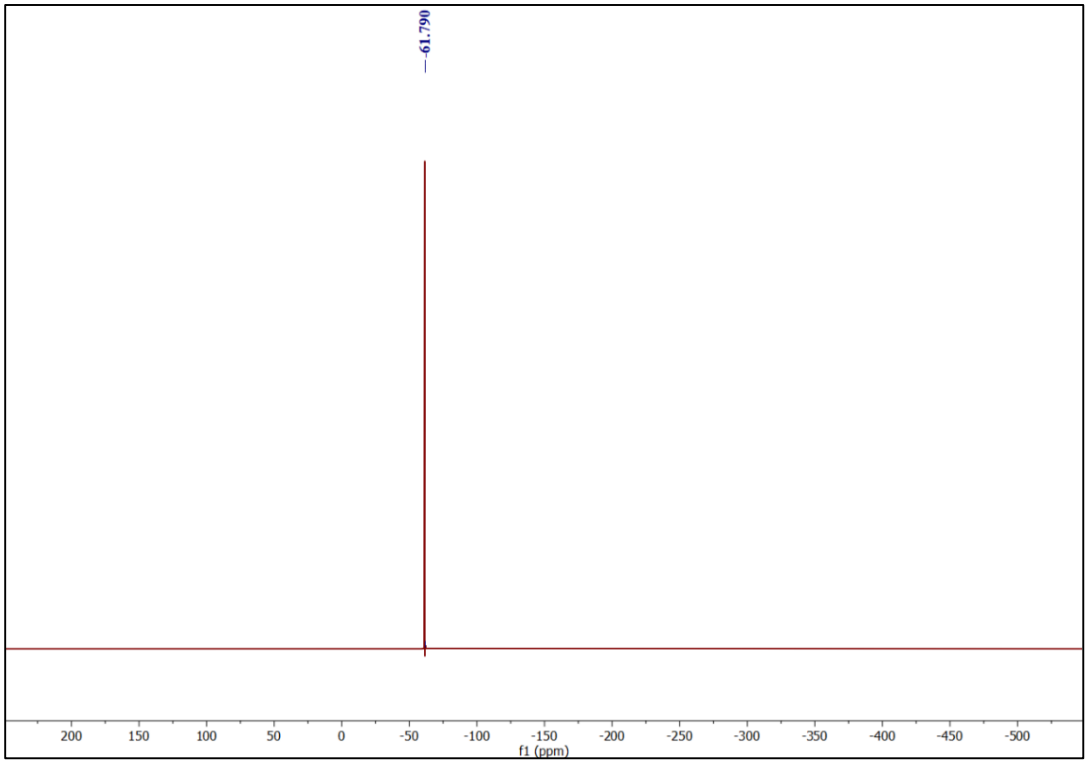
^{1}H NMR (400 MHz, $CDCl_3$) of 2-hydroxy-1-(3-(trifluoromethyl) phenyl)ethan-1-one (3r)



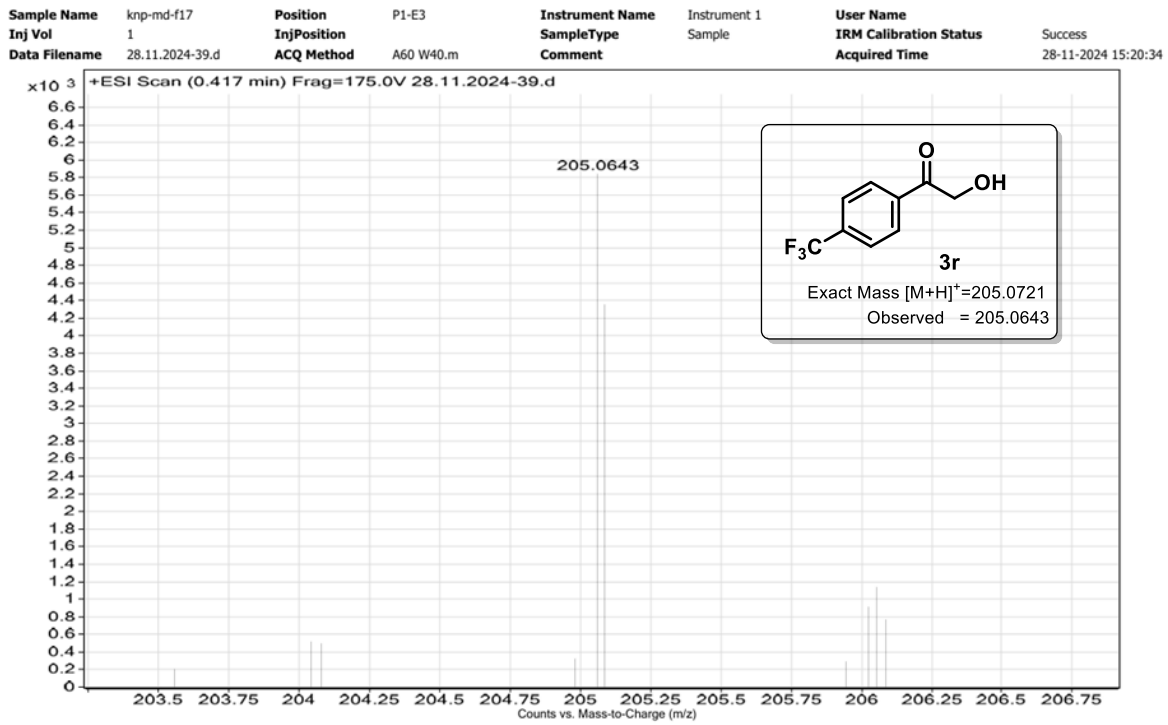
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of 2-hydroxy-1-(3-(trifluoromethyl) phenyl)ethan-1-one (3r)



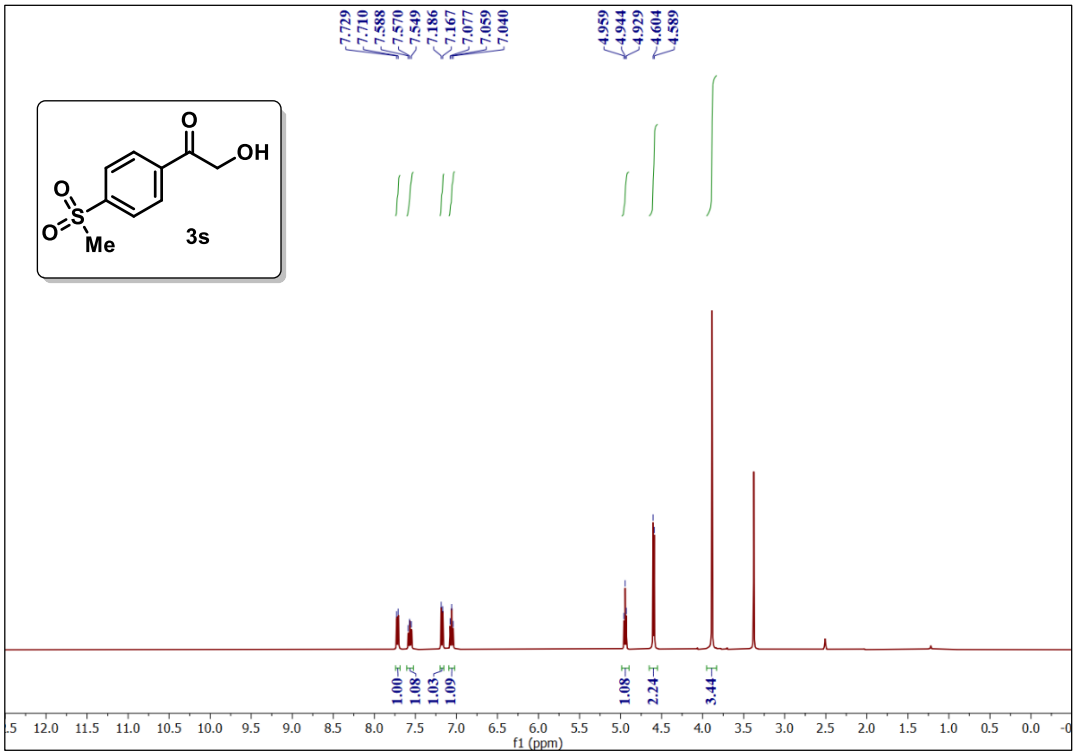
^{19}F NMR (376 MHz,$CDCl_3$) of 2-hydroxy-1-(3-(trifluoromethyl) phenyl)ethan-1-one (3r)



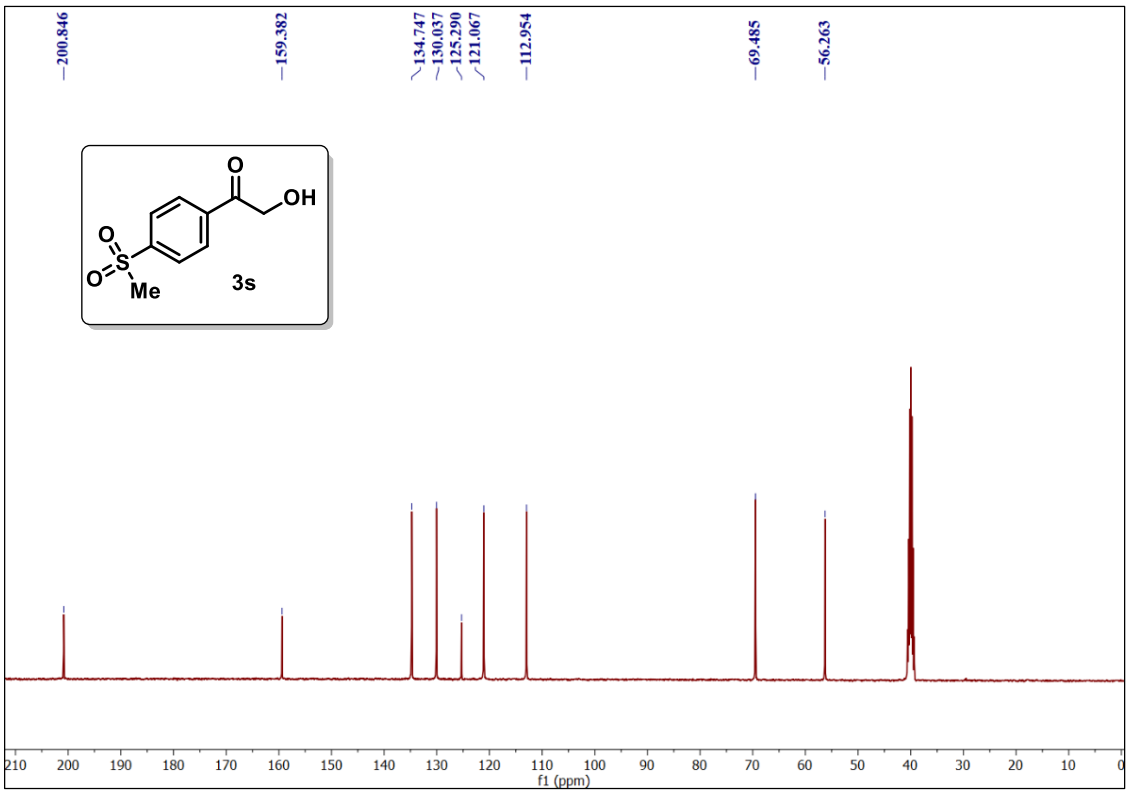
Mass spectrum of 2-hydroxy-1-(3-(trifluoromethyl) phenyl)ethan-1-one (3r)



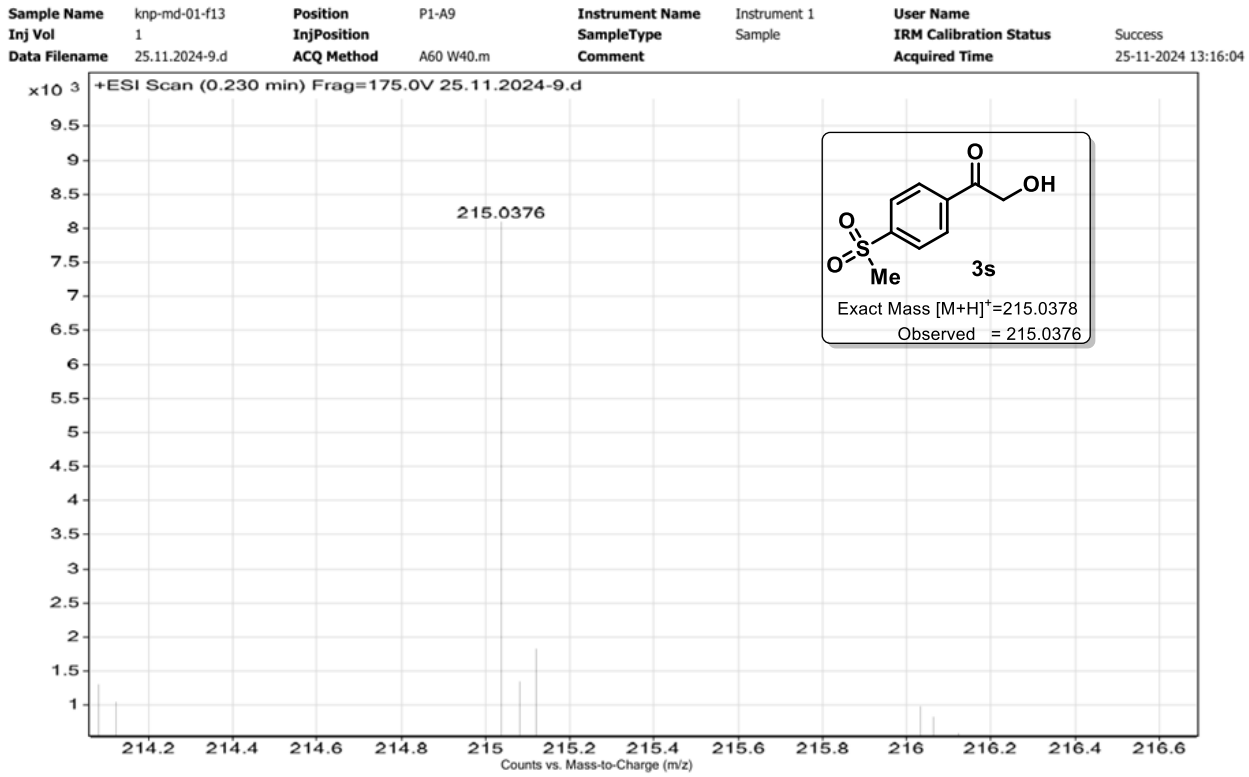
^{1}H NMR (400 MHz, DMSO-d_6)) of 2-hydroxy-1-(4-(methylsulfonyl)phenyl)ethan-1-one (3s)



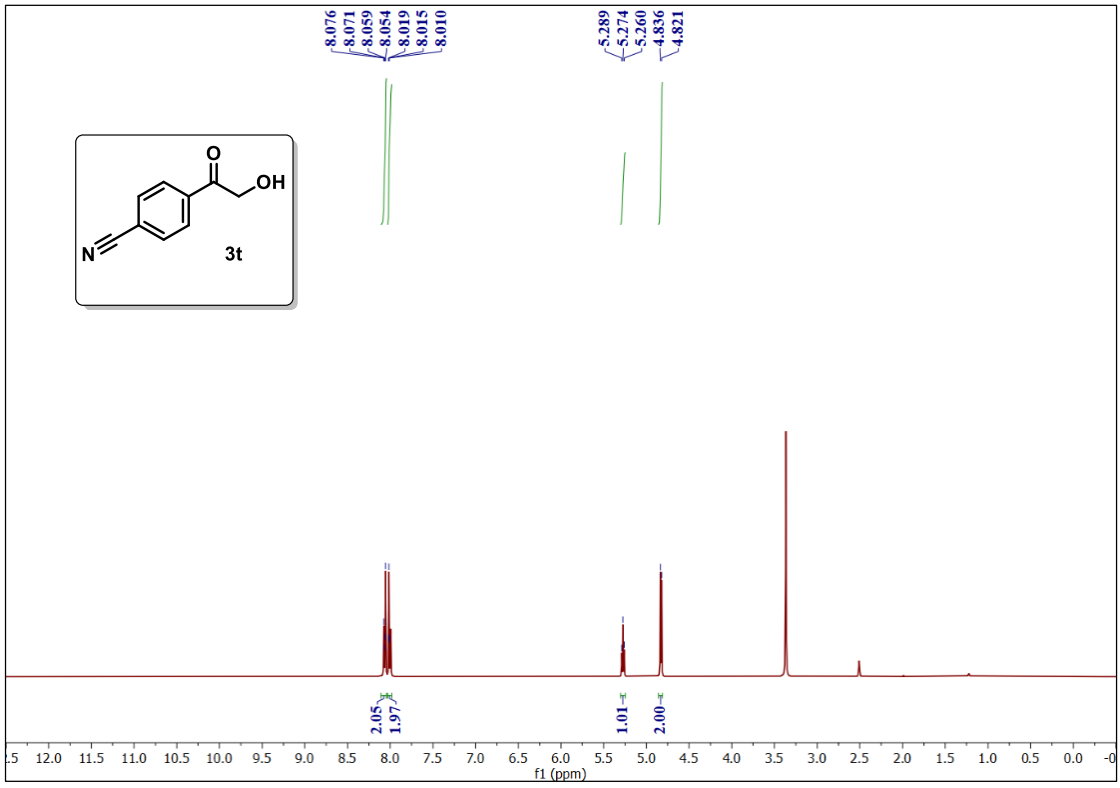
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of 2-hydroxy-1-(4-(methylsulfonyl)phenyl)ethan-1-one (3s)



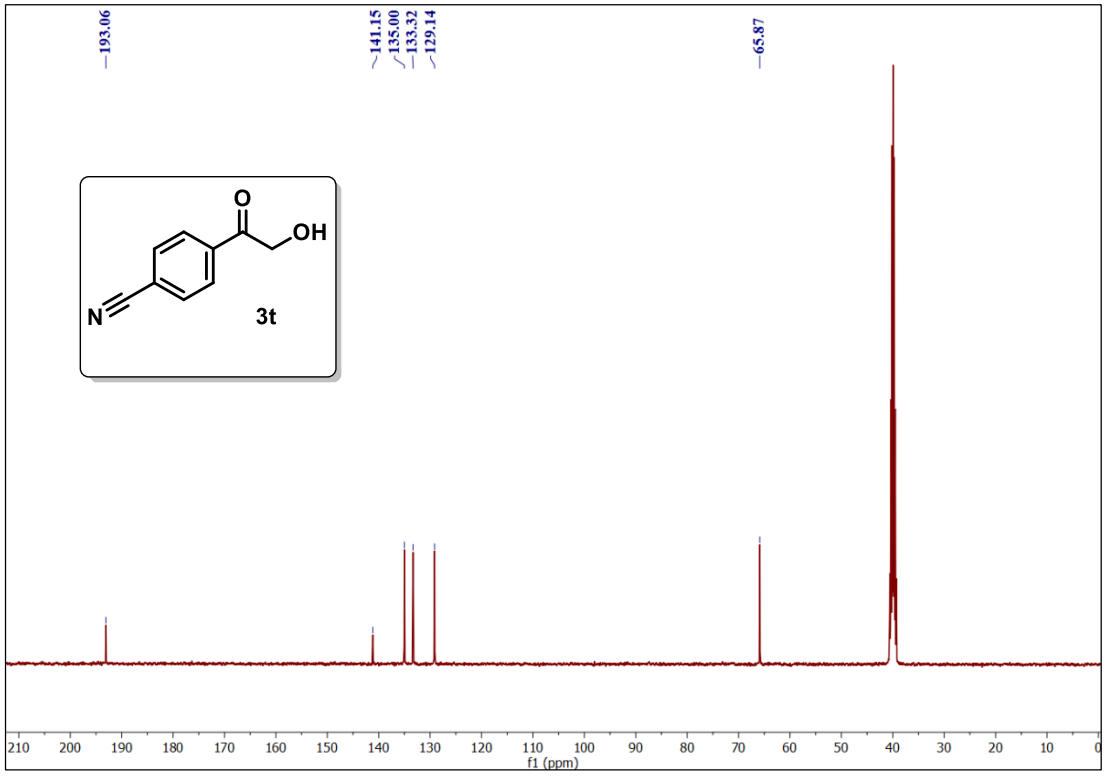
Mass spectrum of 2-hydroxy-1-(4-(methylsulfonyl) phenyl) ethan-1-one (3s)



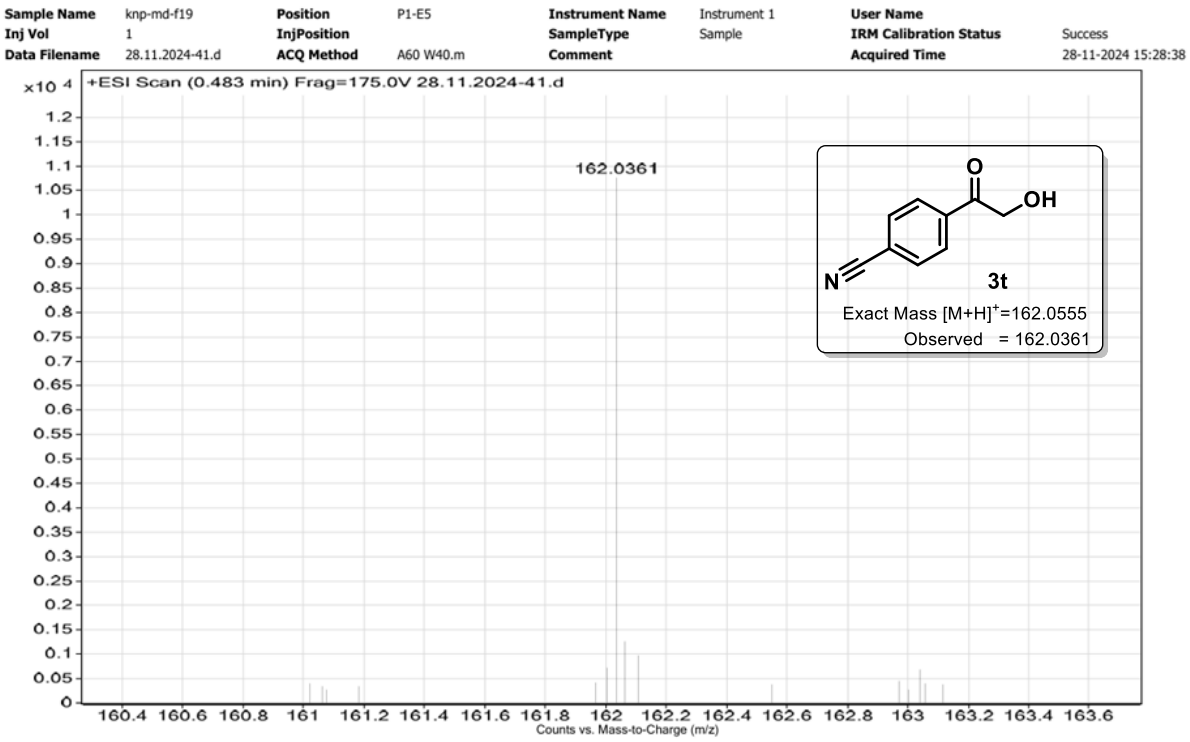
^{1}H NMR (400 MHz, DMSO-d_6)) of 4-(2-hydroxyacetyl) benzonitrile (3t)



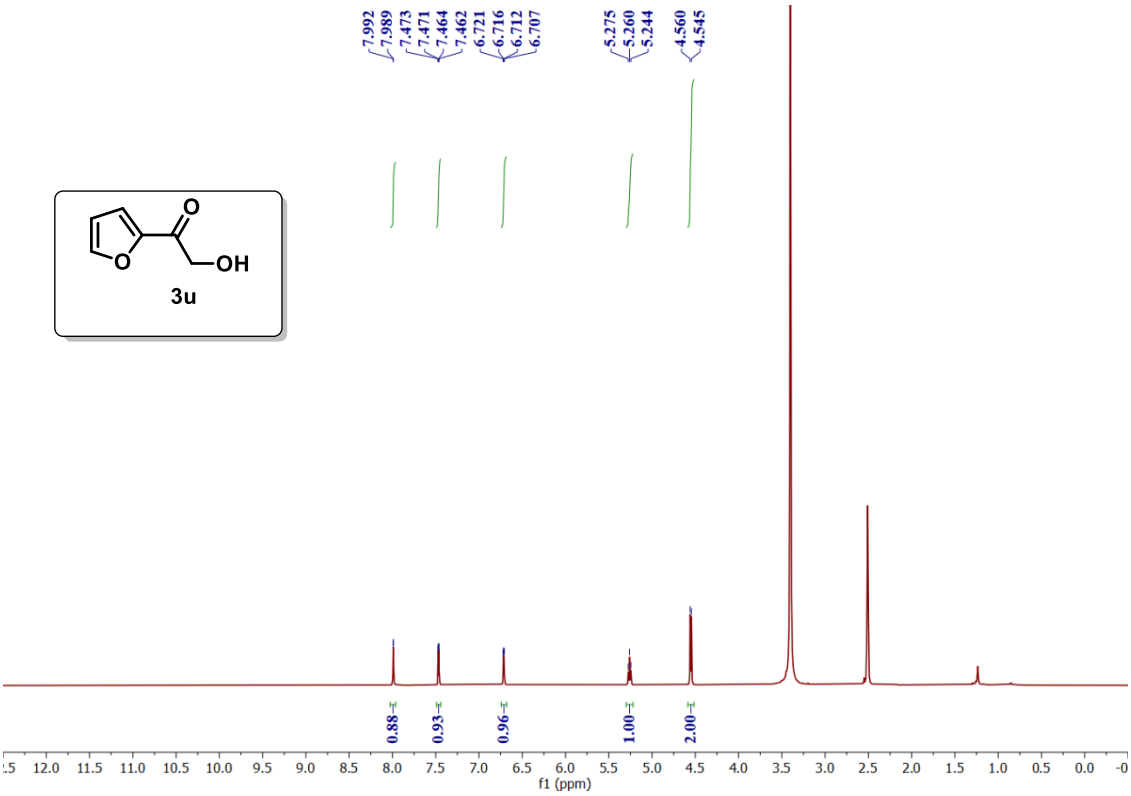
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of 4-(2-hydroxyacetyl) benzonitrile (3t)



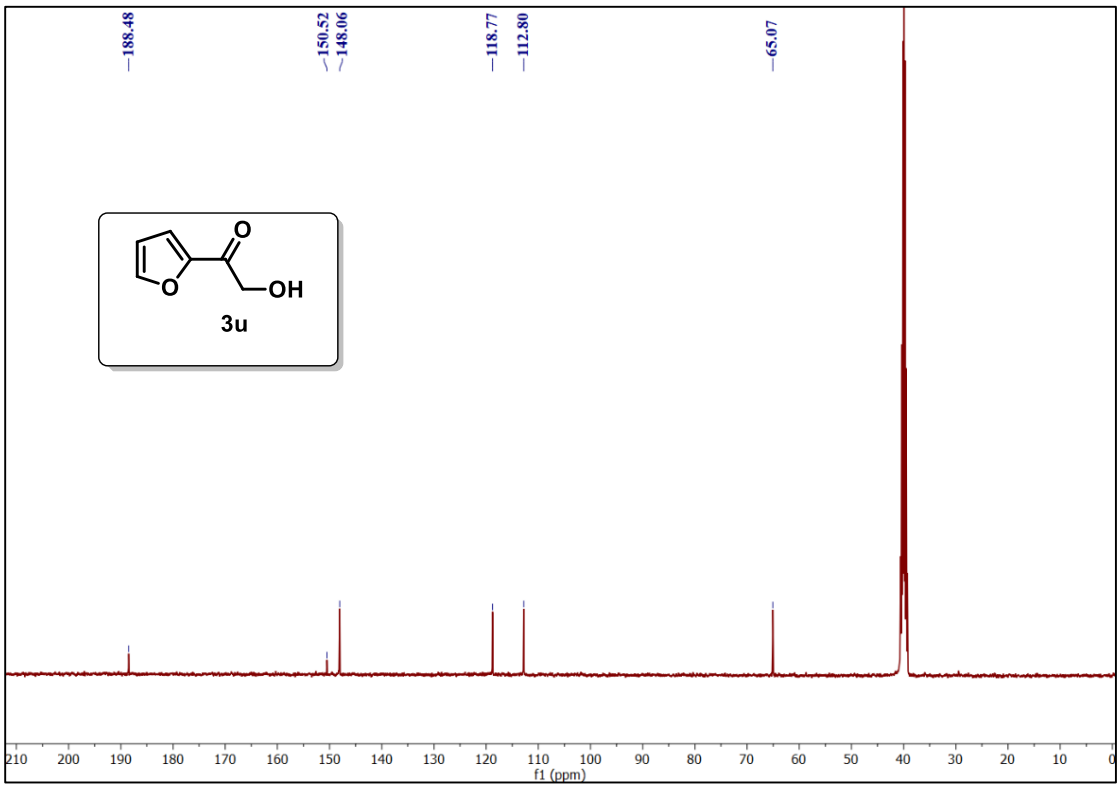
Mass spectrum of 4-(2-hydroxyacetyl) benzonitrile (3t)



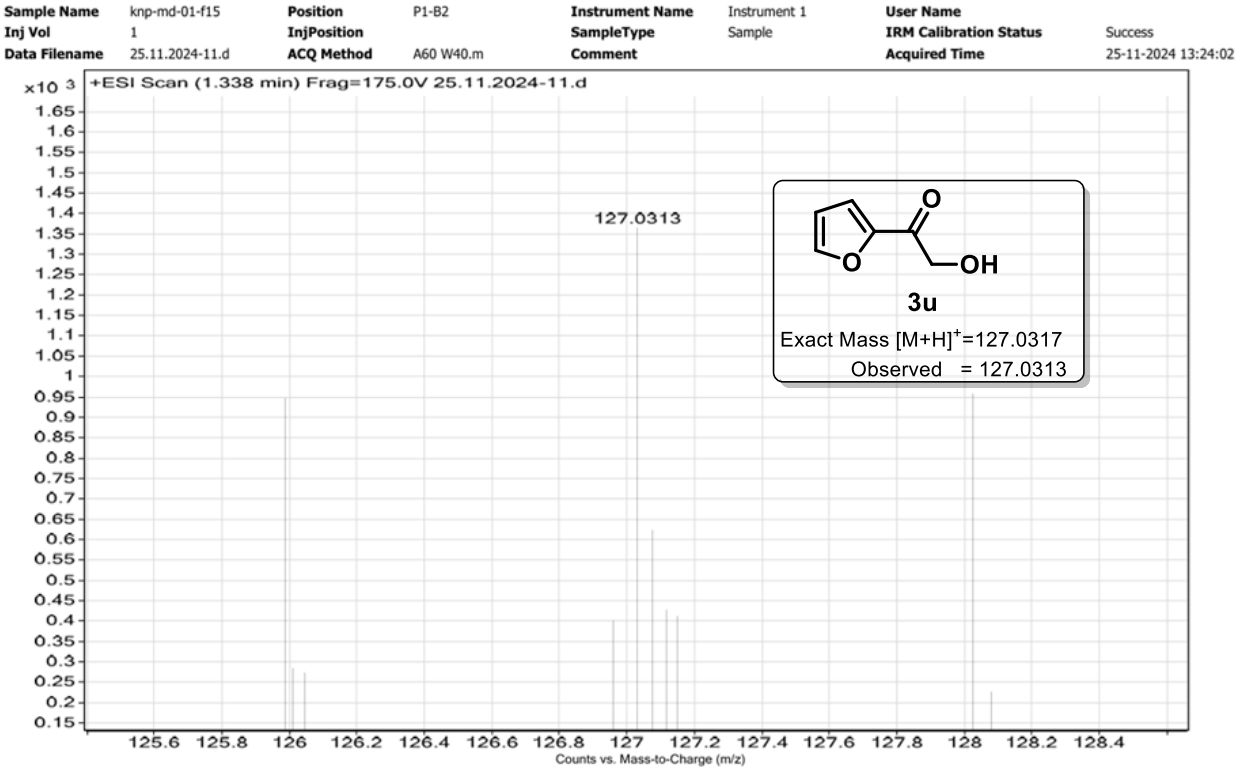
^{1}H NMR (400 MHz, DMSO-d_6)) of 1-(furan-2-yl)-2-hydroxyethan-1-one(3u)



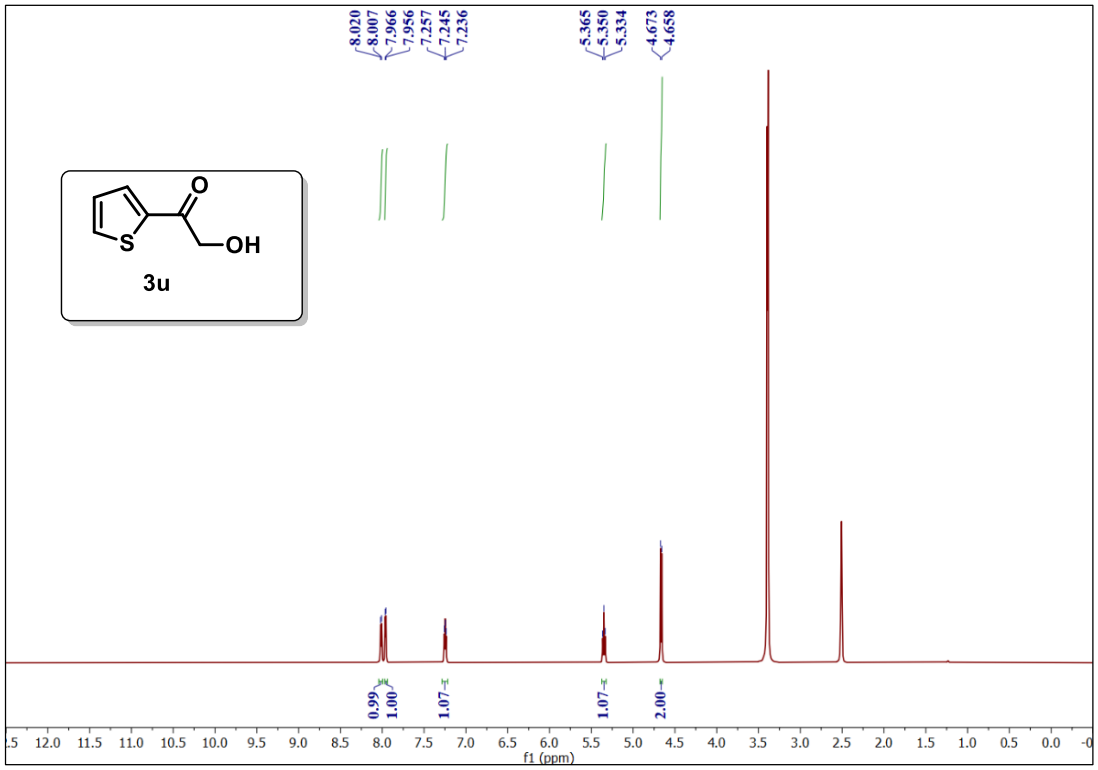
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of 1-(furan-2-yl)-2-hydroxyethan-1-one(3u)



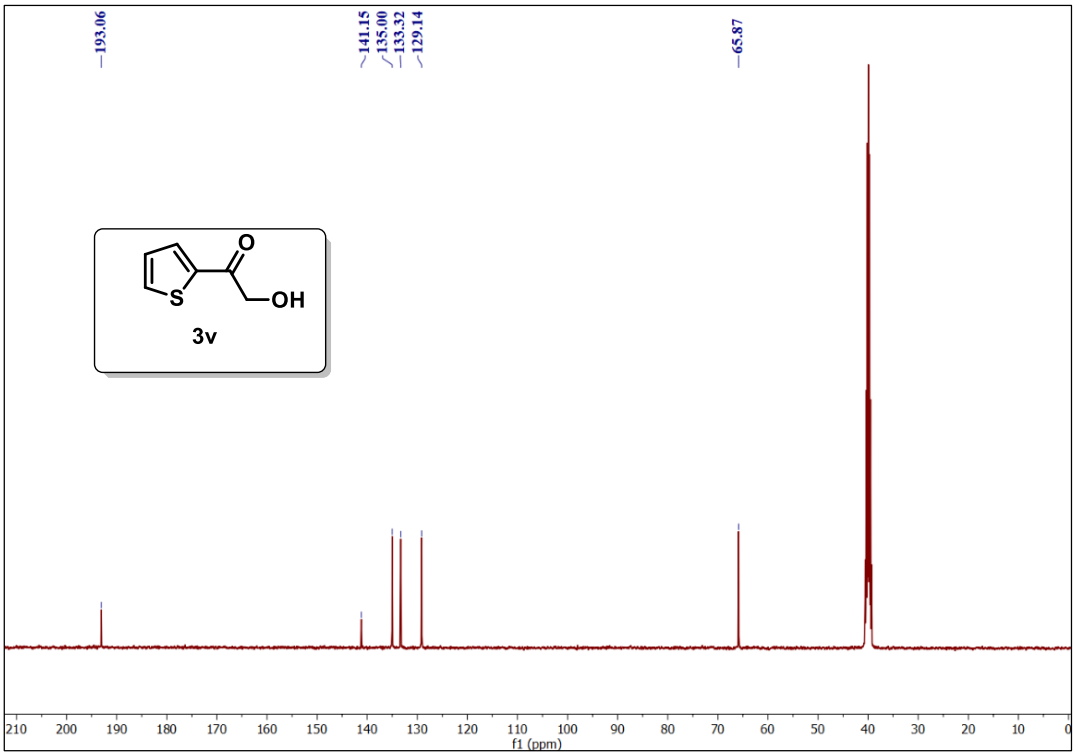
Mass spectrum of 1-(furan-2-yl)-2-hydroxyethan-1-one(3u)



^{1}H NMR (400 MHz, DMSO-d_6) of 2-hydroxy-1-(thiophen-2-yl) ethan-1-one (3v)

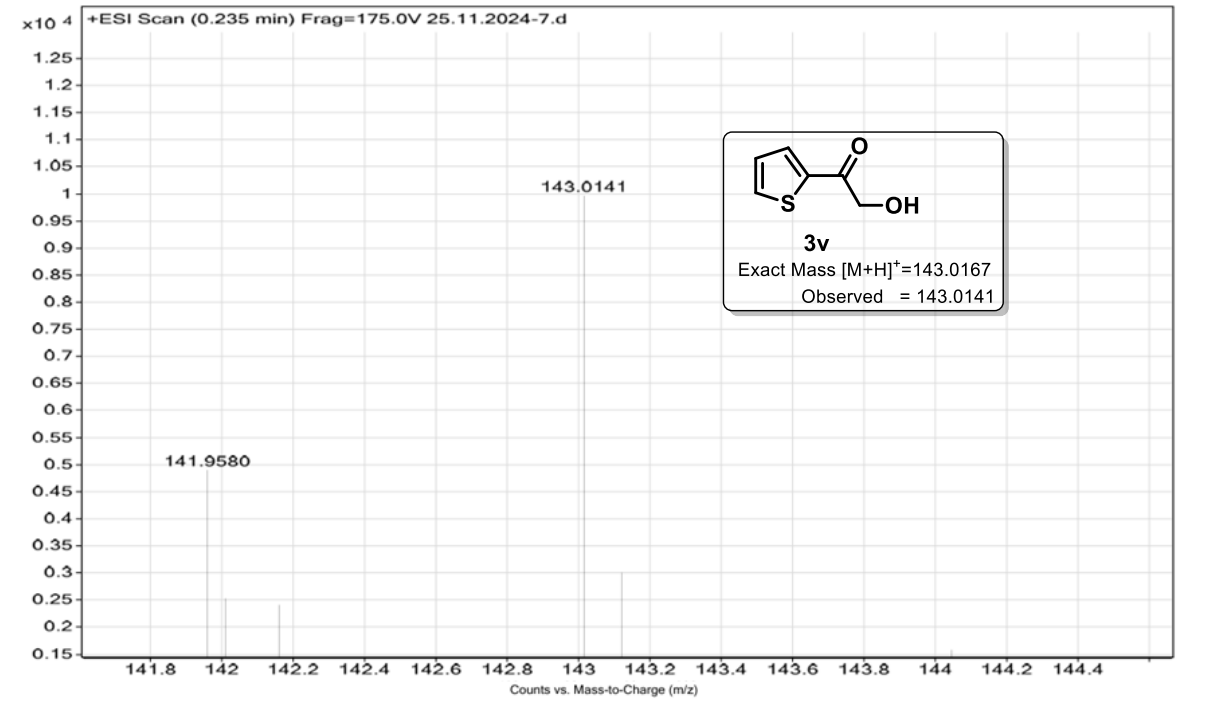


^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of 2-hydroxy-1-(thiophen-2-yl)ethan-1-one (3v)

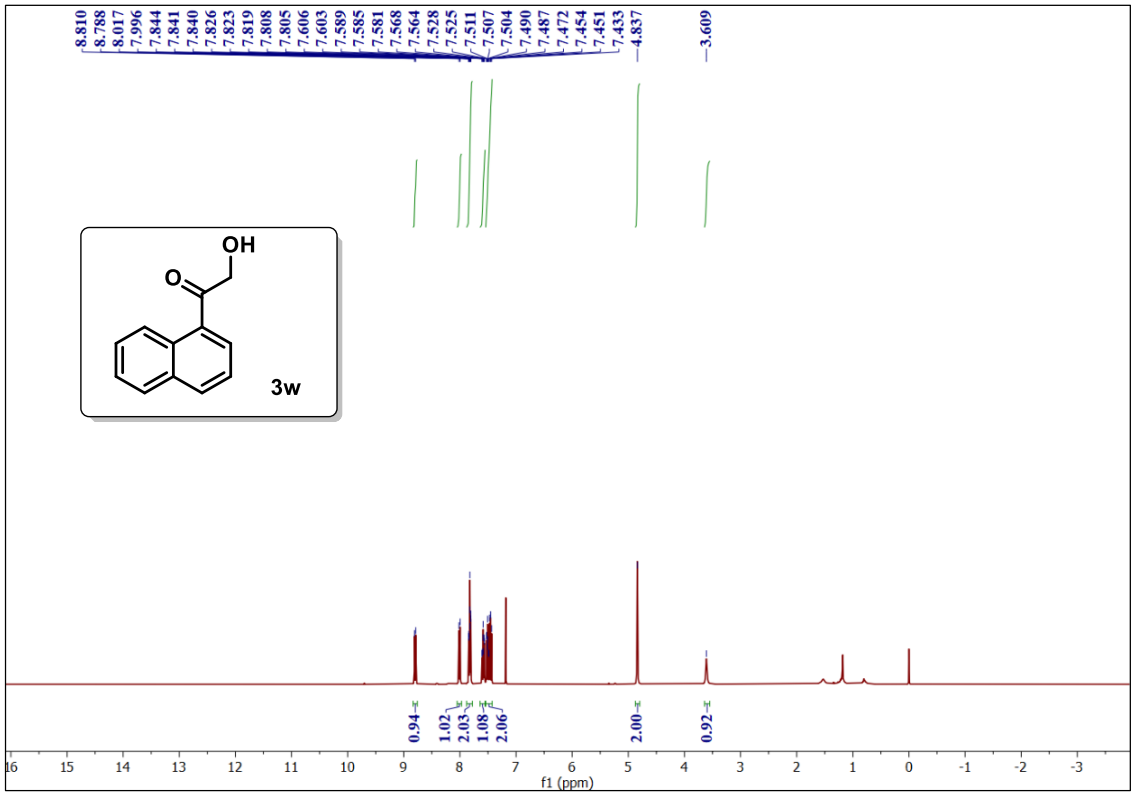


Mass spectrum of 2-hydroxy-1-(thiophen-2-yl)ethan-1-one (3v)

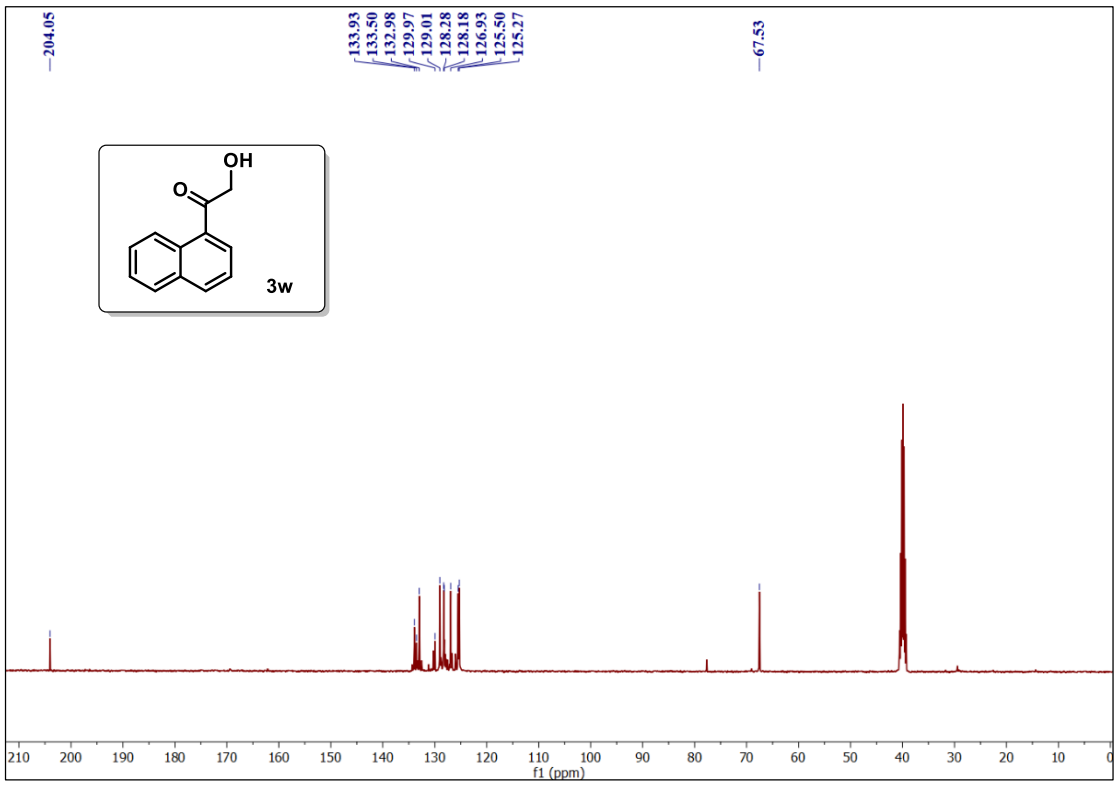
Sample Name	knp-md-01-f11	**Position**	P1-A7	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	25.11.2024-7.d	**ACQ Method**	A60 W40.m	**Comment**		**Acquired Time**	25-11-2024 13:08:09



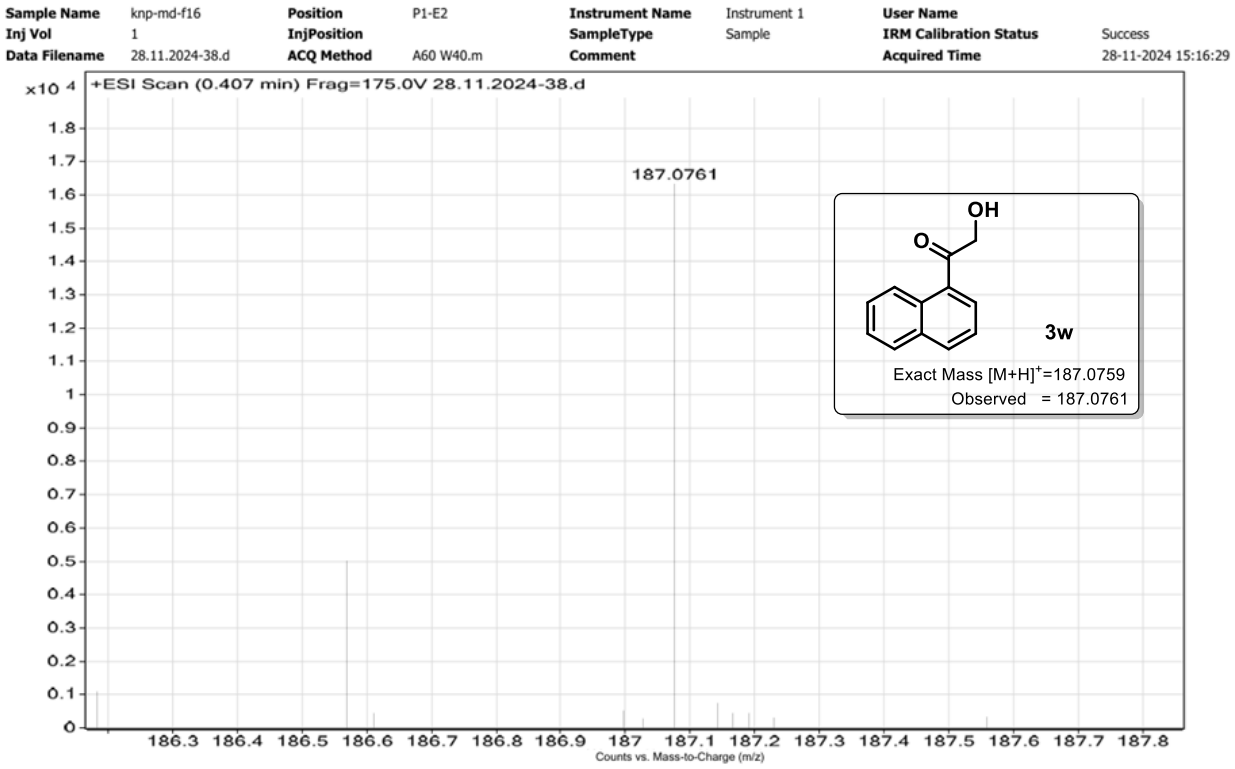
^{1}H NMR (400 MHz, $CDCl_3$)) of 2-hydroxy-1-(naphthalen-1-yl)ethan-1-one(3w)



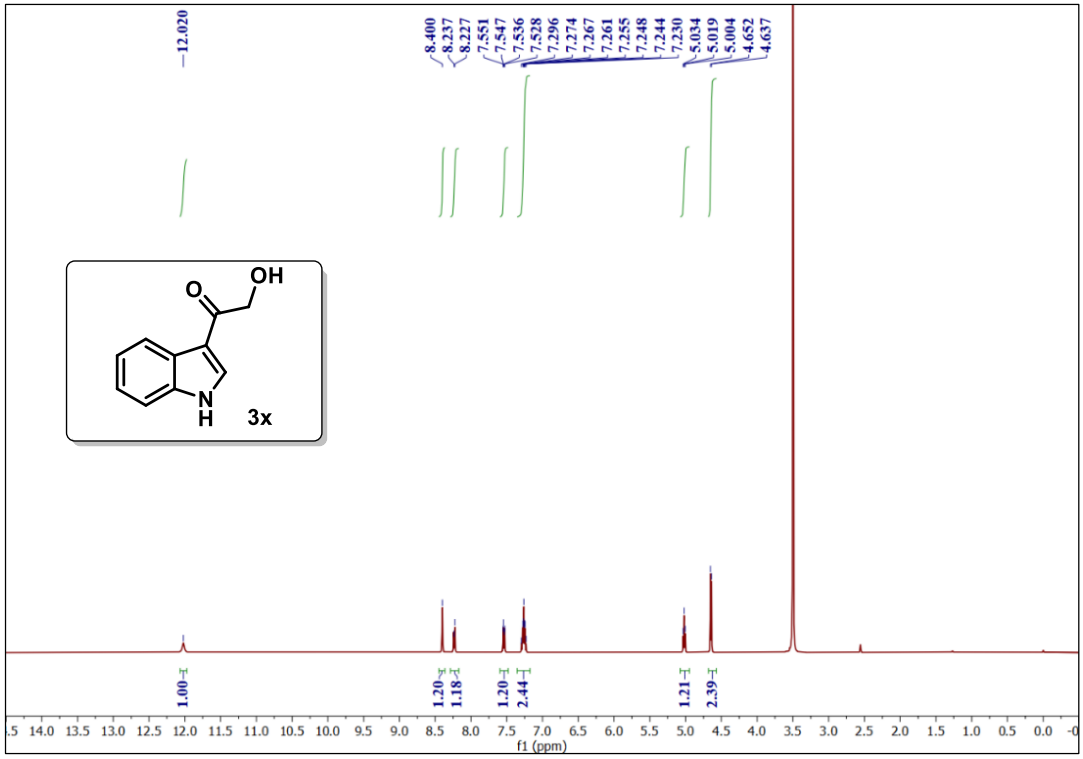
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) of 2-hydroxy-1-(naphthalen-1-yl)ethan-1-one (3w)



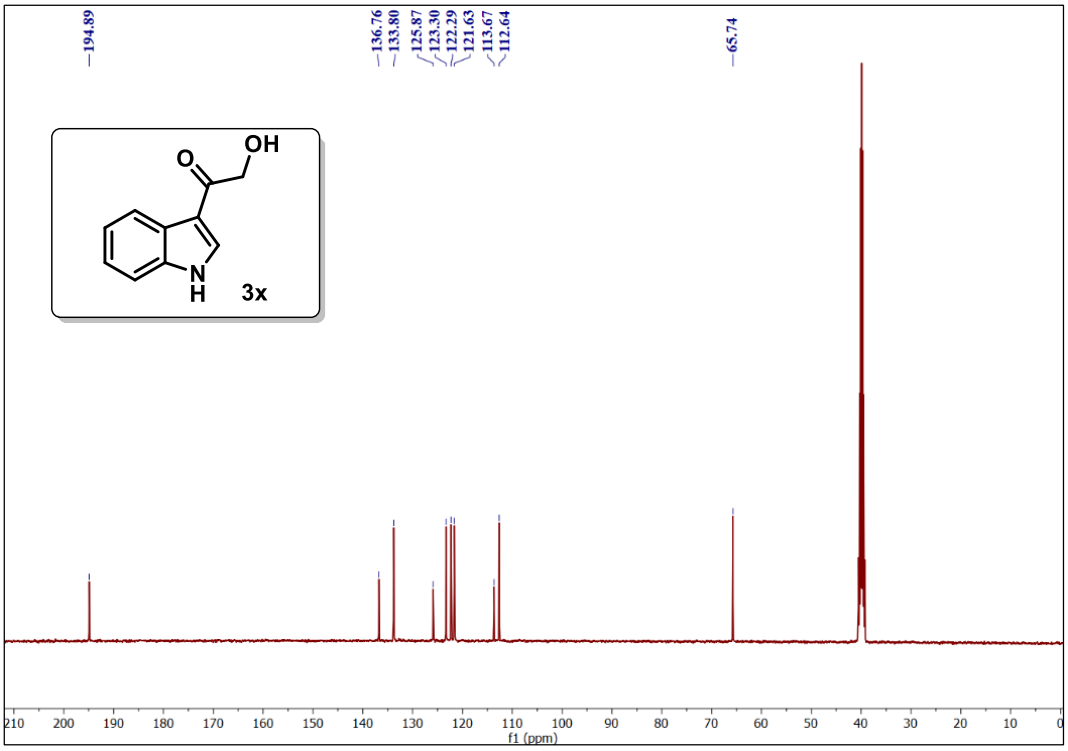
Mass Spectrum of 2-hydroxy-1-(naphthalen-1-yl) ethan-1-one (3w)



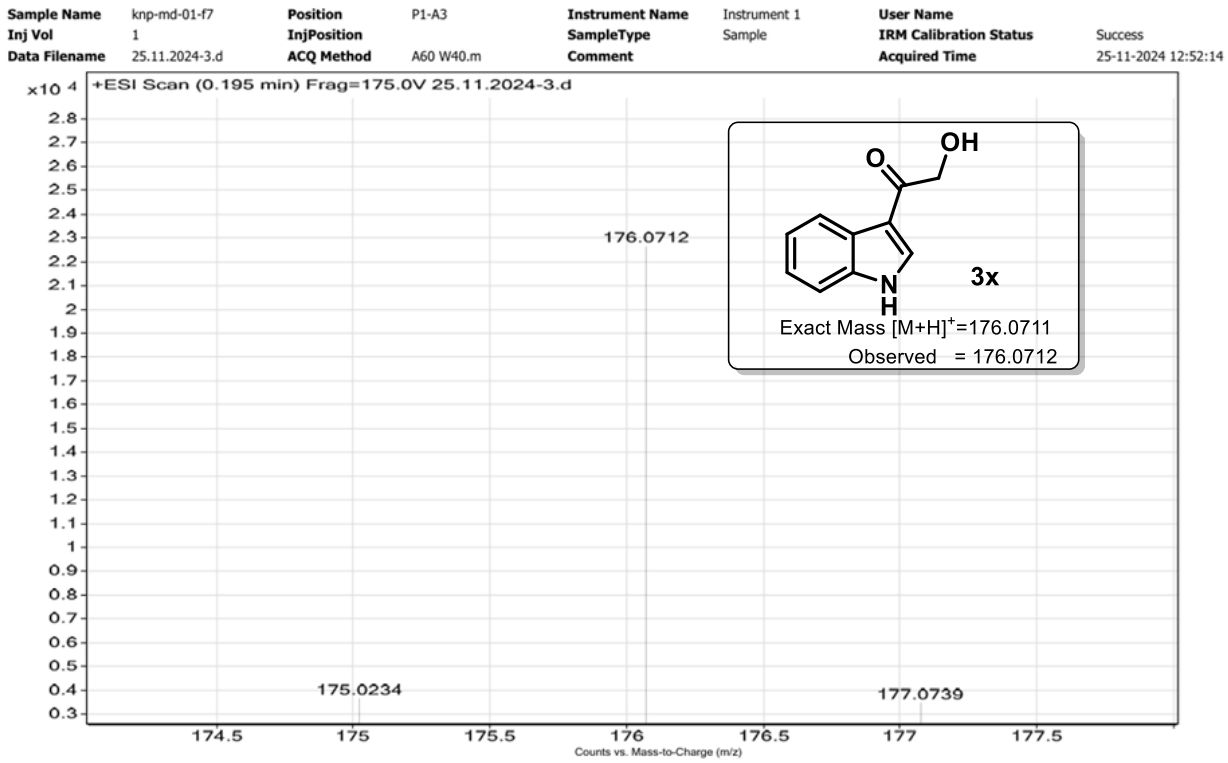
1H NMR (400 MHz,DMSO-d_6) of 2-hydroxy-1-(1H-indol-3-yl)ethan-1-one(3x)



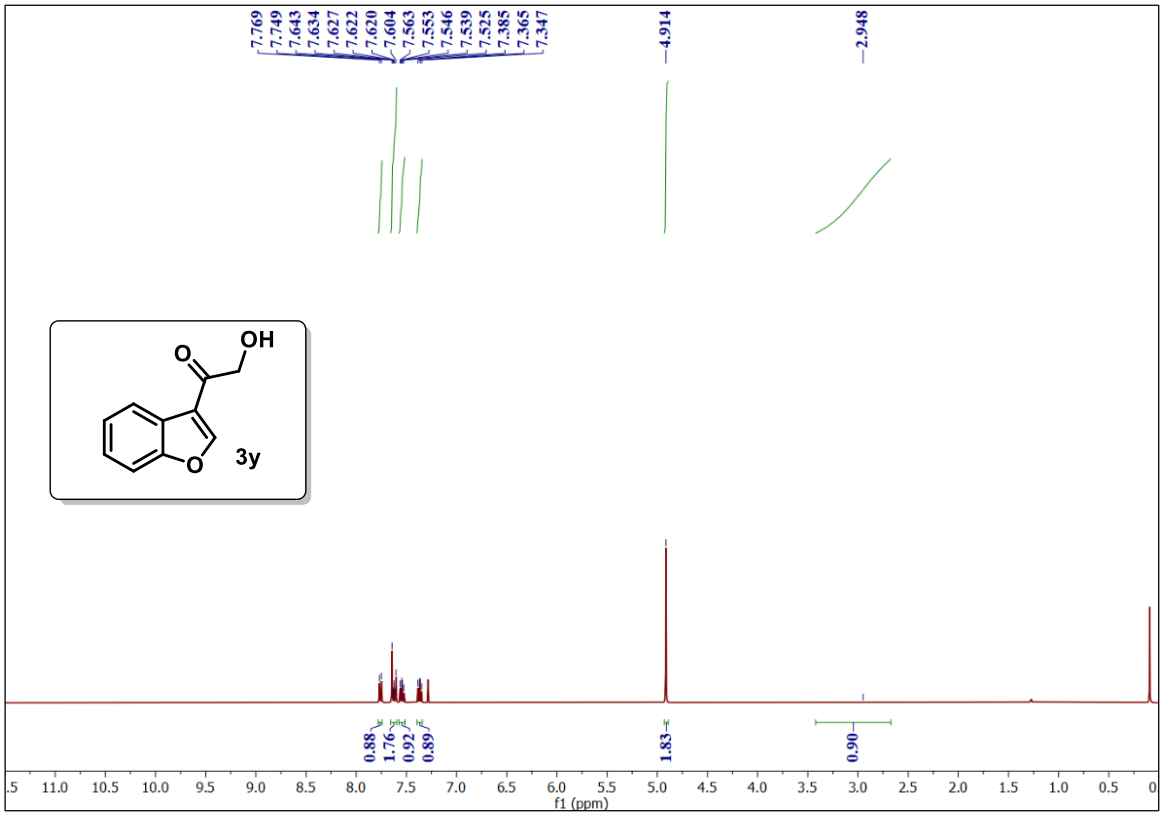
^{13}C{1H} NMR (100 MHz, DMSO-d_6) of 2-hydroxy-1-(1H-indol-3-yl)ethan-1-one(3x)



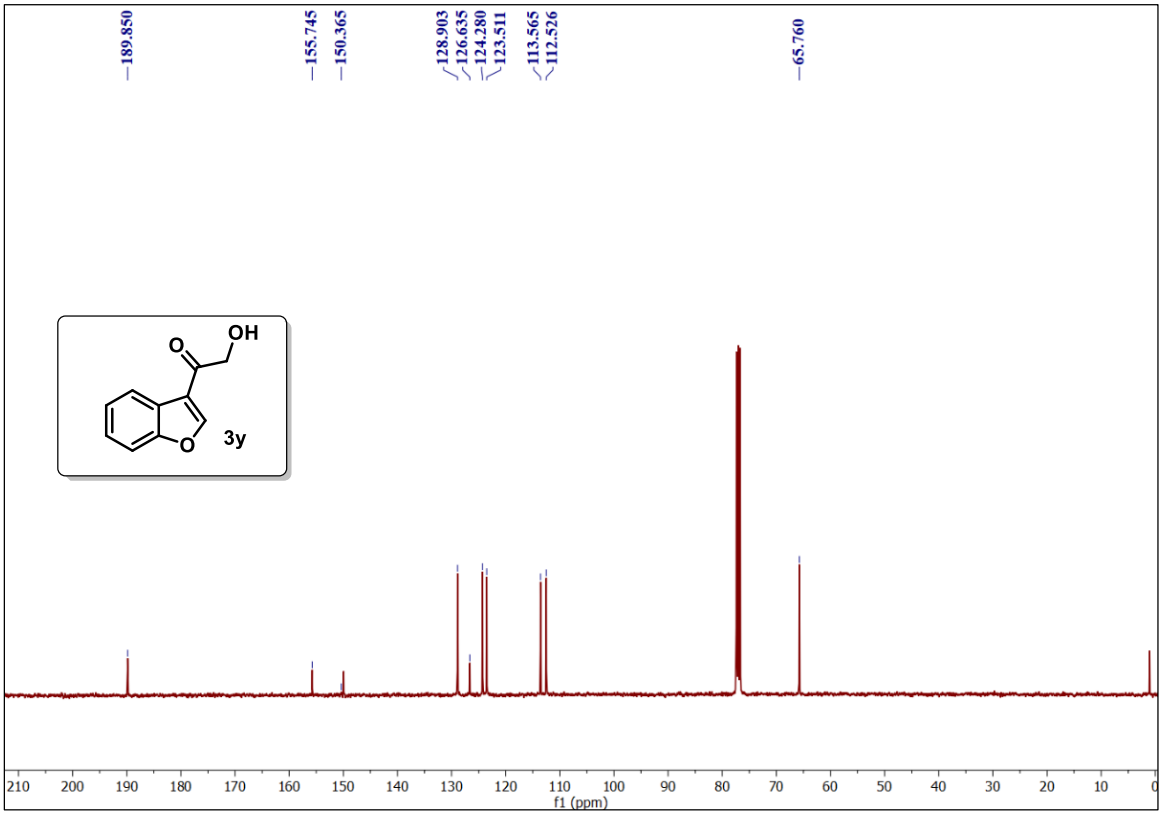
Mass Spectrum of 2-hydroxy-1-(1H-indol-3-yl)ethan-1-one(3x)



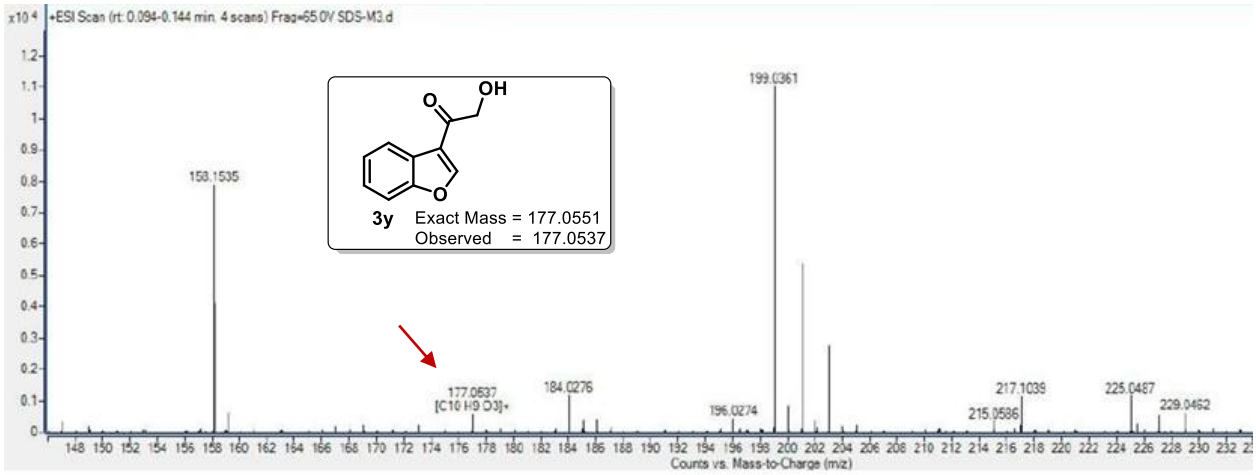
^{1}H NMR (400 MHz,DMSO-d_6) of 1-(benzofuran-3-yl)-2-hydroxyethan-1-one(3y)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of 1-(benzofuran-3-yl)-2-hydroxyethan-1-one(3y)



Mass Spectrum of 1-(benzofuran-3-yl)-2-hydroxyethan-1-one(3y)



6. Mass Spectrum of 2-hydroxy-1-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethan-1-one (4) (TEMPO adduct)