Supporting Information

# Thiazolium salt-catalyzed C–C triple bond cleavage for accessing substituted 1-naphthols via benzannulation

Peng Zhou,[a,b,1] Jia-Yin Wang,[a,1] Tian-Shu Zhang,[a] Guigen Li,*[,b,c] Wen-Juan Hao,[a] Shu-Jiang Tu,*[,a] and Bo Jiang*[,]

[a] School of Chemistry and Chemical Engineering, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou 221116, P. R. China; email jiangchem@jsnu.edu.cn (B.J.); laotu@jsnu.edu.cn (S.J.T.)

[b] Institute of Chemistry & BioMedical Sciences, Collaborative Innovation Center of Chemistry for Life Sciences, Nanjing University, Nanjing 210093, P. R. China

[c] Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, United States; emailguigen.li@ttu.edu (G.L.).

[1]Those authors contributed equally

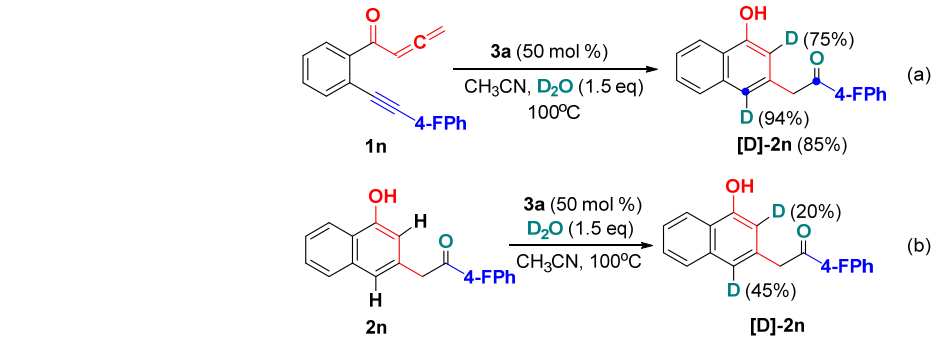
## Context

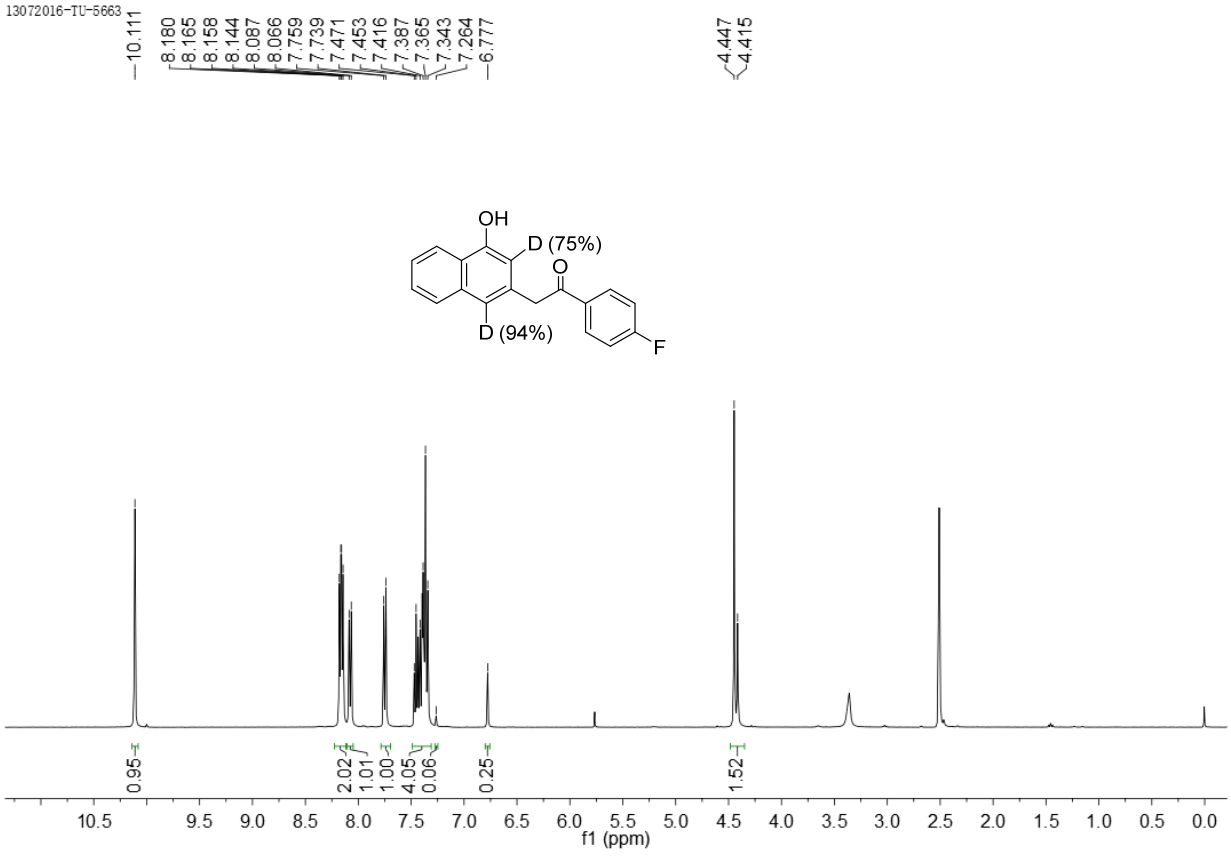
Experimental

## General Information

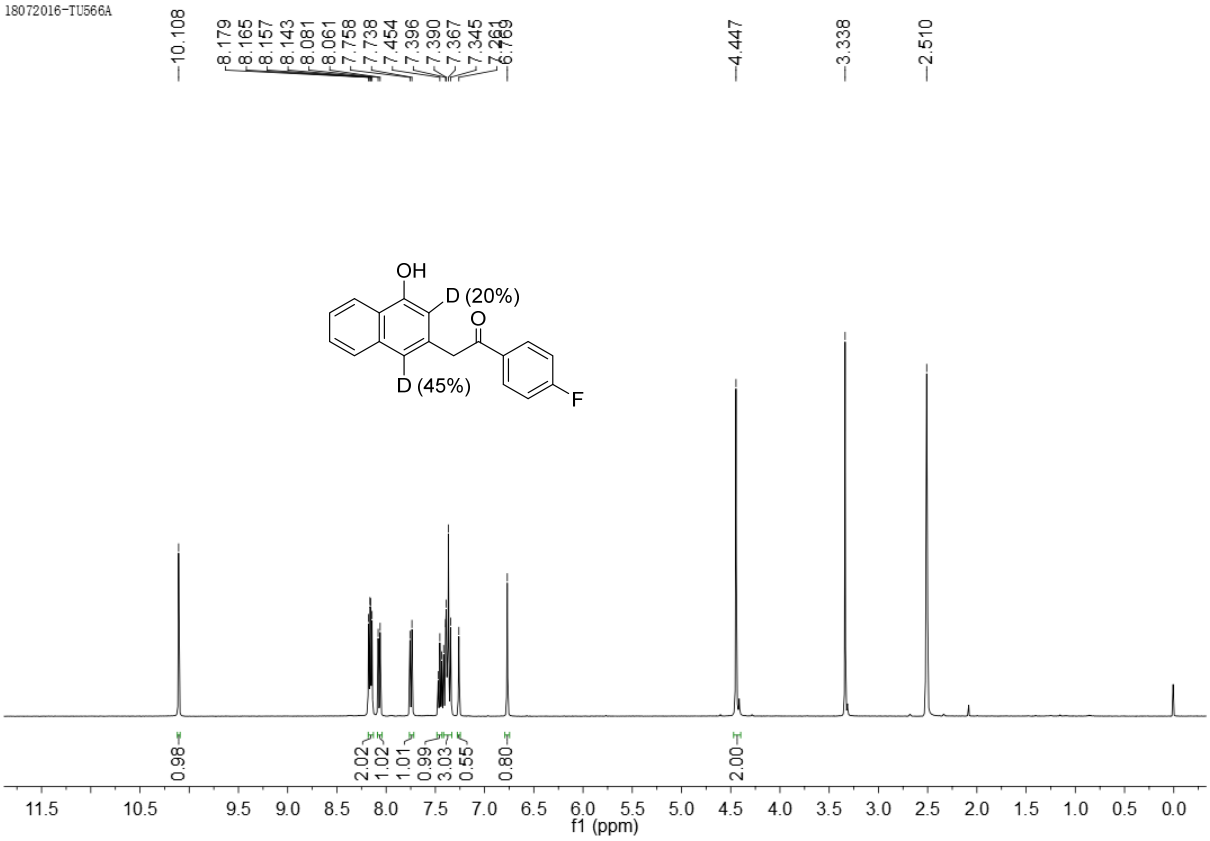
$^{1}$H NMR ($^{13}$C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ (DMSO-$d_6$) with chemical shift ($\delta$) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (ESI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

**Scheme 1.** Hydrogen–Deuterium Exchange Experiments



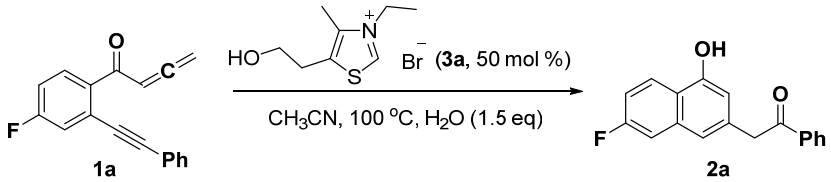

**Hydrogen–Deuterium Exchange of** [D]-**2n** (Scheme S1a)



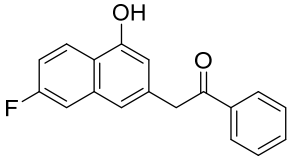

**Hydrogen–Deuterium Exchange of** [D]-**2n** (Scheme S1b)

## General Procedure for the Synthesis of Products 2

Example for the synthesis of **2a** ***2-(7-Fluoro-4-hydroxynaphthalen-2-yl)-1-phenylethanone***




A mixture of allene-yne **1a** (0.2 mmol), $H_2O$ (0.3 mmol), thiazolium salt **3a** (0.1 mmol) and $CH_3CN$ (3.0 mL) were added in a 10-mL reaction vial, which was sealed and heated at 100 °C until TLC (petroleum ether ethyl acetate 5:1) revealed that conversion of the starting material **1a** was completed. Then the reaction mixture was cooled to room temperature, and water was added (20 mL). Next, the suspension was extracted with ethyl acetate and brine. The organic layers were dried by anhydrous $MgSO_4$, filtered and concentrated under vacuum, and was purified by flash column chromatography (silica gel, mixtures of petroleum ether / acetic ester, 20:1, v/v) to afford the desired pure product **2a** as white solid.




mp 156-157 °C;

$^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) 8.11-8.02 (m, 3H), 7.60–7.56 (m, 1H), 7.49 –7.45 (m, 2H), 7.36-7.33 (m, 1H), 7.25 (s, 1H), 7.19–7.14 (m, 1H), 6.72 (s, 1H), 6.06 (d, $J$ = 20.0 Hz), 4.38 (s, 2H).

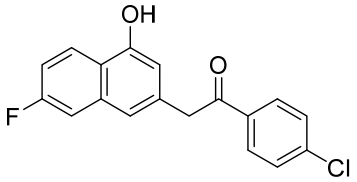
$^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 198.4, 161.4 ($^1J_{CF}$ = 244.9 Hz), 152.2, 136.3, 135.9 ($^4J_{CF}$ = 9.4 Hz), 133.8, 133.6, 128.8 ($^6J_{CF}$ = 2.2 Hz), 124.7 ($^5J_{CF}$ = 9.3 Hz), 120.7, 120.1, 120.0, 115.1 ($^2J_{CF}$ = 24.9 Hz), 110.4 ($^3J_{CF}$ = 20.4 Hz), 109.3, 45.8.

IR (KBr, $v$, cm$^{-1}$) 3312, 3012, 2973, 1670, 1584, 1398, 1219, 1075, 880, 617.

HRMS (APCI-TOF) m/z calcd for $C_{18}H_{13}FO_2Na$, 303.0797 $[M+Na]^+$; found 303.0786.

***1-(4-Chlorophenyl)-2-(7-fluoro-4-hydroxynaphthalen-2-yl)ethanone (2b)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v)




mp 150-151 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.29 (s, 1H), 8.14-8.10 (m, 1H), 8.08 (d, $J$ = 8.8 Hz, 2H), 7.62 (d, $J$ = 8.8 Hz, 2H), 7.55-7.52 (m, 1H), 7.31-7.26 (m, 1H), 7.23 (s, 1H), 6.73 (s, 1H), 4.46 (s, 2H).

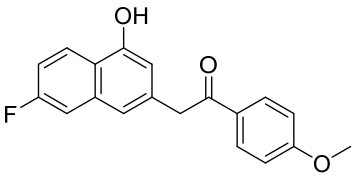
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.21, 161.3 ($^1J_{CF}$ = 242.1 Hz), 153.8, 138.7, 135.8 ($^4J_{CF}$ = 9.5 Hz), 135.5 ($^6J_{CF}$ = 3.9 Hz), 130.8, 129.4, 125.5 ($^5J_{CF}$ = 9.4 Hz), 121.1, 118.8, 118.7, 114.6 ($^2J_{CF}$ = 25.1 Hz), 110.5 ($^3J_{CF}$ = 20.2 Hz), 109.9, 45.7.

IR (KBr, $v$, cm$^{-1}$) 3502, 3004, 2893, 1669, 1521, 1385, 1198, 1075, 880, 687.

HRMS (APCI-TOF) m/z calcd for $C_{18}H_{12}ClFO_2Na$, 337.0408 $[M+Na]^+$; found 337.0397.

***2-(7-Fluoro-4-hydroxynaphthalen-2-yl)-1-(4-methoxyphenyl)ethanone (2c)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v)




mp 176-177 °C;

$^1$H NMR (400 MHz, $CDCl_3$; $\delta$, ppm) 8.11 (m, 1H), 8.03 (d, $J$ = 9.2 Hz, 2H), 7.36 –7.32 (m, 1H), 7.20-7.15 (m, 1H), 6.93 (d, $J$ = 8.8 Hz, 2H), 6.72 (s, 1H), 5.82 (s, 1H), 4.32 (s, 2H), 3.86 (s, 3H).

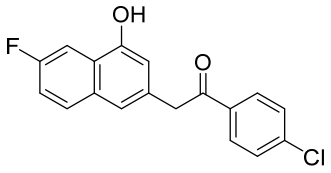
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 196.6, 162.4 ($^1J_{CF}$ = 277.2 Hz), 152.1, 134.4, 131.2 ($^4J_{CF}$ = 9.6 Hz), 129.4 ($^6J_{CF}$ = 2.5 Hz), 124.6 ($^5J_{CF}$ = 9.1 Hz), 120.0(1), 120.0(0), 115.1 ($^2J_{CF}$ = 24.9 Hz), 113.9, 110.4 ($^3J_{CF}$ = 20.5 Hz), 109.2(8), 109.2(5), 55.5, 45.6.

IR (KBr, $\nu$, cm$^{-1}$) 3368, 3092, 2984, 1653, 1540, 1394, 1267, 1026, 831, 668.

HRMS (APCI-TOF) m/z calcd for $C_{19}H_{15}FO_3Na$, 333.0903 $[M+Na]^+$; found 333.0881.

***1-(4-Chlorophenyl)-2-(6-fluoro-4-hydroxynaphthalen-2-yl)ethanone (2d)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v)




mp 161-162 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.26 (s, 1H), 8.08 (d, $J$ = 8.8 Hz, 2H), 7.87-7.83(m, 1H), 7.71-7.68 (m, 1H), 7.61 (d, $J$ = 8.4 Hz, 2H), 7.39-7.34 (m, 1H), 7.30 (s, 1H), 6.82 (s, 1H), 4.46 (s, 2H).

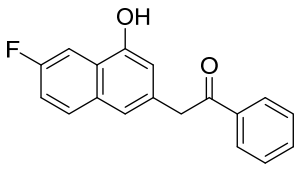
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.3, 159.8 ($^1J_{CF}$ = 240.5 Hz), 153.1, 153.0, 138.7, 135.5, 133.1 ($^6J_{CF}$ = 2.5 Hz), 131.9, 130.8, 130.5 ($^4J_{CF}$ = 8.7 Hz), 129.4, 124.5 ($^5J_{CF}$ = 8.5 Hz), 124.4, 119.3, 116.8 ($^2J_{CF}$ = 25.0 Hz), 111.2, 105.7 ($^3J_{CF}$ = 21.5 Hz), 45.5.

IR (KBr, $\nu$, cm$^{-1}$) 3270, 3057, 2900, 1668, 1538, 1385, 1271, 1093, 817, 667.

HRMS (APCI-TOF) m/z calcd for $C_{18}H_{12}ClFO_2Na$, 337.0408 $[M+Na]^+$; found 337.0393.

***2-(6-Fluoro-4-hydroxynaphthalen-2-yl)-1-phenylethanone (2e)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 156-157 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.28 (s, 1H), 8.07 (d, $J$ = 7.6 Hz, 2H), 7.87 –7.83 (m, 1H), 7.70-7.62 (m, 2H), 7.56-7.52 (m, 2H), 7.39-7.30 (m, 2H), 6.82 (s, 1H), 4.45 (s, 2H).

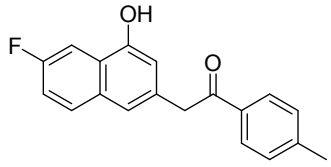
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 198.3, 159.7 ($^1J_{CF}$ = 240.4 Hz), 153.0(2), 153.0(0), 136.8, 133.8, 133.3 ($^6J_{CF}$ = 2.5 Hz), 131.9, 130.5 ($^4J_{CF}$ = 8.6 Hz), 129.3, 128.9, 124.4($^5J_{CF}$ = 8.5 Hz), 119.3, 116.8 ($^2J_{CF}$ = 25.1 Hz), 111.3, 105.7 ($^3J_{CF}$ = 21.6 Hz), 45.5.

IR (KBr, $v$, cm$^{-1}$) 3265, 3017, 2869, 1662, 1520, 1339, 1217, 955, 818, 679.

HRMS (APCI-TOF) m/z calcd for $C_{18}H_{13}FO_2Na$, 303.0797 $[M+Na]^+$; found 303.0780.

***2-(6-Fluoro-4-hydroxynaphthalen-2-yl)-1-(p-tolyl)ethanone (2f)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 150-151 ºC;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.23 (s, 1H), 7.97 (d, $J$ = 8.4 Hz, 2H), 7.87-7.83 (m, 1H), 7.69 –7.66 (m, 1H), 7.39-7.33 (m, 3H), 7.31 (s, 1H), 6.82 (s, 1H), 4.41 (s, 2H), 2.37 (s, 3H).

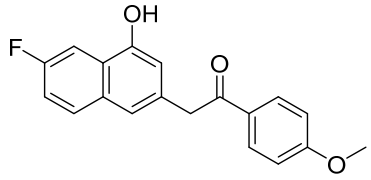
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.8, 153.0(2), 153.0(0), 144.2, 134.3, 134.1, 133.50 ($^5J_{CF}$ = 2.4 Hz), 131.9, 130.5 ($^3J_{CF}$ = 8.8 Hz), 129.8, 129.1, 124.4($^4J_{CF}$ = 8.5 Hz), 119.3, 116.8 ($^1J_{CF}$ = 25.0 Hz), 111.2, 105.7 ($^2J_{CF}$ = 21.5 Hz), 45.4, 21.6.

IR (KBr, $v$, cm$^{-1}$) 3447, 3029, 2901, 1653, 1569, 1328, 1212, 1029, 839, 668.

HRMS (APCI-TOF) m/z calcd for $C_{19}H_{14}FO_2$, 293.0978 $[M-H]^-$; found 293.0969.

***2-(6-Fluoro-4-hydroxynaphthalen-2-yl)-1-(4-methoxyphenyl)ethanone (2g)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 162-163 ºC;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.24 (s, 1H), 8.05 (d, $J$ = 8.8 Hz, 2H), 7.87-7.83 (m, 1H), 7.69-7.66 (m, 1H),7.38-7.36 (m, 1H), 7.31 (s, 1H), 7.05 (d, $J$ = 8.8 Hz, 2H), 6.82 (s, 1H), 4.38 (s, 2H), 3.84 (s, 3H).

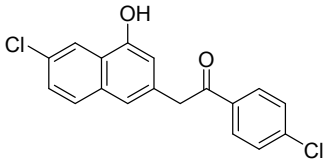
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 196.6, 162.3 ($^1J_{CF}$ = 274.6 Hz), 153.0(2), 153.0(0), 133.8 ($^6J_{CF}$ = 3.2 Hz), 131.9, 131.3, 130.5 ($^4J_{CF}$ = 8.6 Hz), 129.7, 119.1($^5J_{CF}$ = 8.6 Hz), 116.8 ($^2J_{CF}$ = 25.5 Hz), 114.4, 111.1, 105.7 ($^3J_{CF}$ = 21.7 Hz), 56.0, 45.2.

IR (KBr, $v$, cm$^{-1}$) 3363, 3047, 2962, 1670, 1569, 1328, 1212, 1029, 839, 608.

HRMS (APCI-TOF) m/z calcd for $C_{19}H_{15}FO_3Na$, 333.0903 $[M+Na]^+$; found 333.0885.

***2-(6-Chloro-4-hydroxynaphthalen-2-yl)-1-(4-chlorophenyl)ethanone (2h)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).



mp 164-165 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.35 (s, 1H), 8.08 (d, $J$ = 8.4 Hz, 2H), 8.04 (d, $J$ = 2.0 Hz, 1H), 7.81 (d, $J$ = 8.8 Hz, 1H), 7.62 (d, $J$ = 8.4 Hz, 2H), 7.48-7.45 (m, 1H), 7.29 (s, 1H), 6.82 (s, 1H), 4.47 (s, 2H).

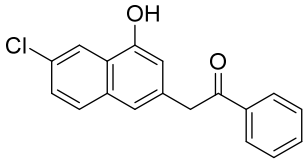
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.2, 152.8, 138.8, 138.7, 135.5, 134.5, 133.1, 130.8, 129.9, 129.5, 129.4, 127.3, 124.5, 121.2, 119.3, 111.6, 45.5.

IR (KBr, $v$, cm$^{-1}$) 3446, 3051, 2966, 1669, 1571, 1384, 1297, 1081, 749, 557.

HRMS (APCI-TOF) m/z calcd for $C_{18}H_{11}Cl_2O_2$, 329.0136 $[M-H]^-$; found 329.0130.

***2-(6-Chloro-4-hydroxynaphthalen-2-yl)-1-phenylethanone (2i)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).



mp 178-179 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.36 (s, 1H), 8.09-8.06 (m, 2H), 8.03 (d, $J$ = 2.0 Hz, 1H), 7.82 (d, $J$ = 8.8 Hz, 1H), 7.67– 7.64 (m, 1H), 7.57-7.53 (m, 2H), 7.48-7.45 (m, 1H), 7.31 (s, 1H), 6.84 (d, $J$ = 0.8 Hz, 1H), 4.47 (s, 2H).

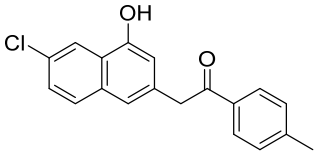
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 198.1, 152.7, 136.8, 134.8, 133.8, 133.1, 129.9, 129.5, 129.3, 128.9, 127.2, 124.5, 121.2, 119.3, 111.6, 45.6.

IR (KBr, $v$, cm$^{-1}$) 3397, 3010, 2908, 1662, 1569, 1395, 1302, 1002, 804, 608.

HRMS (APCI-TOF) m/z calcd for $C_{18}H_{13}ClO_2Na$, 319.0502 $[M+Na]^+$; found 319.0486.

***2-(6-Chloro-4-hydroxynaphthalen-2-yl)-1-(p-tolyl)ethanone (2j)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).



mp 177-178 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.34 (s, 1H), 8.03 (d, $J$ = 2.0 Hz, 1H), 7.97 (d, $J$ = 8.4 Hz, 2H), 7.81 (d, $J$ = 8.8 Hz, 1H), 7.47-7.44 (m, 1H), 7.34 (d, $J$ = 8.0 Hz, 2H), 7.30 (s, 1H), 6.83 (d, $J$ = 1.2 Hz, 1H), 4.42 (s, 2H), 2.37 (s, 3H).

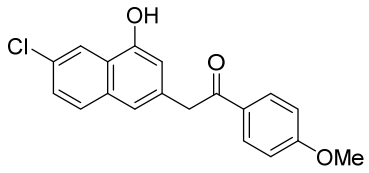
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.7, 152.7, 144.2, 134.9, 134.3, 133.1, 129.9, 129.8, 129.4, 129.1, 127.2, 124.5, 121.1, 119.2, 111.5, 45.5, 21.6.

IR (KBr, $v$, cm$^{-1}$) 3447, 3049, 2923, 1653, 1540, 1384, 1231, 1100, 807, 608.

HRMS (APCI-TOF) m/z calcd for $C_{19}H_{14}ClO_2$, 309.0682 $[M-H]^-$; found 309.0677.

***2-(6-Chloro-4-hydroxynaphthalen-2-yl)-1-(4-methoxyphenyl)ethanone (2k)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 194-195 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.34 (s, 1H), 8.06 –8.02 (m, 3H), 7.81 (d, $J$ = 8.8 Hz, 1H), 7.47-7.44 (m, 1H), 7.30 (s, 1H), 7.05 (d, $J$ = 9.2 Hz, 2H), 6.83 (s, 1H), 4.38 (s, 2H), 3.83 (s, 3H, $OCH_3$).

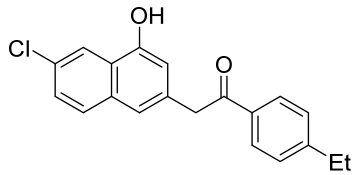
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 196.5, 163.7, 152.7, 135.1, 133.1, 131.3, 129.9, 129.7, 129.4, 127.2, 124.5, 121.1, 119.1, 114.4, 111.5, 56.0, 45.3.

IR (KBr, $v$, cm$^{-1}$) 3447, 3011, 2892, 1684, 1571, 1384, 1261, 1100, 816, 608.

HRMS (APCI-TOF) m/z calcd for $C_{19}H_{15}ClO_3Na$, 349.0607 $[M+Na]^+$; found 349.0599.

***2-(6-Chloro-4-hydroxynaphthalen-2-yl)-1-(4-ethylphenyl)ethanone (2l)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 188-189 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm)10.34 (s, 1H), 8.03-7.99 (m, 3H), 7.81 (d, $J$ = 8.8 Hz, 1H), 7.47-7.44 (m, 1H), 7.37 (d, $J$ = 8.4 Hz, 2H), 7.30 (s, 1H), 6.83 (s, 1H), 4.43 (s, 2H), 2.70-2.65(m, 2H), 1.19 (t, $J$ = 7.6 Hz, 3H).

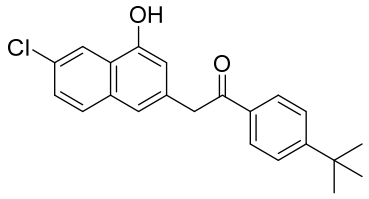
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.7, 152.7, 150.3, 134.9, 134.5, 133.1, 129.9, 129.4, 129.2, 128.6, 127.2, 124.5, 121.1, 119.2, 111.5, 45.5, 28.6, 15.6.

IR (KBr, $v$, cm$^{-1}$) 3429, 3023, 2965, 1647, 1560, 1384, 1207, 980, 874, 617.

HRMS (APCI-TOF) m/z calcd for $C_{20}H_{16}ClO_2$, 323.0839 $[M-H]^-$; found 323.0827.

***1-(4-(tert-Butyl)phenyl)-2-(6-chloro-4-hydroxynaphthalen-2-yl)ethanone (2m)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 207-208 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.35 (s, 1H), 8.03-8.00 (m, 3H), 7.82 (d, $J$ = 8.8 Hz, 1H), 7.55 (d, $J$ = 8.4 Hz, 2H), 7.48-7.45 (m, 1H), 7.31 (s, 1H), 6.83 (s, 1H), 4.43 (s, 2H), 1.30 (s, 9H, $C_4H_9$).

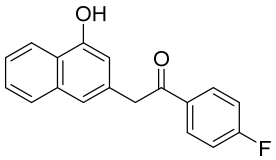
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.6, 156.9, 152.8, 134.9, 134.2, 133.1, 129.9, 129.4, 129.0, 127.2, 126.1, 124.5, 121.1, 119.2, 111.5, 45.5, 35.3, 31.3.

IR (KBr, $v$, cm$^{-1}$) 3447, 3049, 2969, 1653, 1540, 1364, 1268, 1099, 822, 668.

HRMS (APCI-TOF) m/z calcd for $C_{22}H_{20}ClO_2$, 351.1152 $[M-H]^-$; found 351.1160.

***1-(4-Fluorophenyl)-2-(4-hydroxynaphthalen-2-yl)ethanone (2n)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 159-160 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.12 (s, 1H), 8.18-8.14 (m, 2H), 8.07 (d, $J$ = 8.2 Hz, 1H), 7.75 (d, $J$ = 8.0 Hz, 1H), 7.47-7.34 (m, 4H), 7.26 (s, 1H), 6.77 (s, 1H), 4.45 (s, 2H).

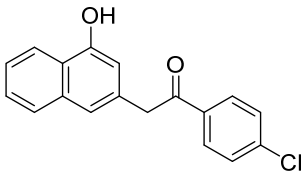
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 196.9, 165.5 ($^1J_{CF}$ = 252.6 Hz), 153.5, 134.8, 133.8, 133.5 ($^4J_{CF}$ = 2.8 Hz), 132.0 ($^3J_{CF}$ = 9.4 Hz), 127.5, 126.8, 124.8, 124.0, 122.3, 119.3, 116.3 ($^2J_{CF}$ = 21.8 Hz), 110.2, 45.7.

IR (KBr, $v$, cm$^{-1}$)3272, 3068, 2893, 1670, 1594, 1408, 1219, 1001, 777, 582.

HRMS (APCI-TOF) m/z calcd for $C_{18}H_{13}FO_2Na$, 303.0797 $[M+Na]^+$; found 3.0784.

***1-(4-Chlorophenyl)-2-(4-hydroxynaphthalen-2-yl)ethanone (2o)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 156-157 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.12 (s, 1H), 8.10-8.06(m, 3H), 7.74 (d, $J$ = 8.0 Hz, 1H), 7.64-7.59 (m, 2H), 7.47-7.38(m, 2H), 7.25 (s, 1H), 6.76 (d, $J$ = 1.6 Hz, 1H), 4.45 (s, 2H).

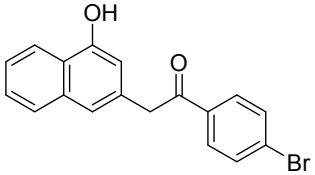
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.3, 153.5, 138.7, 135.5, 134.8, 133.6, 130.9, 129.4, 127.5, 126.8, 124.8, 124.0, 122.3, 119.3, 110.2, 45.7.

IR (KBr, $v$, cm$^{-1}$) 3428, 3059, 2903, 1663, 1588, 1399, 1211, 1092, 761, 598.

HRMS (APCI-TOF) m/z calcd for $C_{18}H_{13}ClO_2Na$, 319.0502 $[M+Na]^+$; found 319.0481.

***1-(4-Bromophenyl)-2-(4-hydroxynaphthalen-2-yl)ethanone (2p)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 127-128 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm)10.12 (d, $J$ = 1.6 Hz, 1H), 8.09 (d, $J$ = 10.8 Hz, 1H), 8.00 (d, $J$ = 8.8 Hz, 1H), 7.76-7.73 (m, 3H), 7.61 (d, $J$ = 46.8 Hz, 1H), 7.47-7.38 (m, 2H), 7.26 (d, $J$ = 6.4 Hz, 1H), 6.77 (d, $J$ = 8.4 Hz, 1H), 4.46 (d, $J$ = 13.6 Hz, 2H).

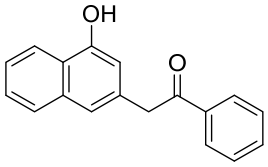
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.6, 197.6, 153.6, 136.5, 135.8, 134.8, 133.9, 133.7, 133.6, 132.4, 132.3, 132.2, 131.0, 129.3, 127.9, 127.5, 127.1, 126.8, 124.8, 124.0, 123.3, 122.3, 121.4, 119.3, 119.3, 110.3, 110.2, 91.8, 90.2, 45.7, 45.7.

IR (KBr, $v$, cm$^{-1}$) 3345, 3056, 2901, 1663, 1579, 1399, 1275, 1002, 823, 600.

HRMS (APCI-TOF) m/z calcd for $C_{18}H_{13}BrO_2Na$, 362.9997 $[M+Na]^+$; found 362.9976.

***2-(4-Hydroxynaphthalen-2-yl)-1-phenylethanone (2q)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 128-129 $^o$C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.15 (s, 1H), 8.09-8.05 (m, 3H), 7.75 (d, $J$ = 8.0 Hz, 1H), 7.66-7.62 (m, 1H), 7.56-7.52(m, 2H), 7.47-7.38 (m, 7.6 Hz, 2H), 7.26 (s, 1H), 6.78 (s, 1H), 4.45 (s, 2H).

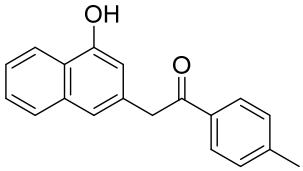
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 198.3, 153.5, 136.8, 134.8, 133.9, 133.8, 129.2, 129.0, 127.5, 126.8, 124.8, 123.9, 122.3, 119.3, 110.3, 45.7.

IR (KBr, $v$, cm$^{-1}$) 3421, 3054, 2907, 1662, 1578, 1384, 1273, 1079, 748, 596.

HRMS (APCI-TOF) m/z calcd for $C_{18}H_{14}O_2Na$, 285.0891 $[M+Na]^+$; found 285.0878.

***2-(4-Hydroxynaphthalen-2-yl)-1-(p-tolyl)ethanone (2r)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 125-126 $^o$C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.14 (s, 1H), 8.06 (d, $J$ = 8.20 Hz, 1H), 7.97 (d, $J$ = 8.0 Hz, 2H), 7.74 (d, $J$ = 8.0 Hz, 1H), 7.46-7.37 (m, 2H), 7.33 (d, $J$ = 8.0 Hz, 2H), 7.25 (s, 1H), 6.77 (s, 1H), 4.40 (s, 2H), 2.36 (s, 3H).

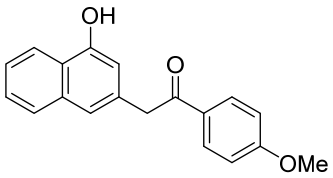
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.8, 153.5, 144.2, 134.8, 134.3, 134.1, 129.8, 129.1, 127.5, 126.8, 124.8, 123.9, 122.3, 119.2, 110.2, 45.6, 21.6.

IR (KBr, $v$, cm$^{-1}$) 3401, 3046, 2917, 1667, 1579, 1404, 1275, 1080, 787, 616.

HRMS (APCI-TOF) m/z calcd for $C_{19}H_{16}O_2Na$, 299.1048 $[M+Na]^+$; found 299.1031.

***2-(4-Hydroxynaphthalen-2-yl)-1-(4-methoxyphenyl)ethanone (2s)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




A white solid; Mp 174-175 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.10 (s, 1H), 8.08-8.04 (m, 3H), 7.74 (d, $J$ = 8.0 Hz, 1H), 7.47-7.37 (m, 2H), 7.26 (s, 1H), 7.05 (d, $J$ = 8.8 Hz, 2H), 6.77 (s, 1H), 4.37 (s, 2H), 3.83 (s, 3H, $OCH_3$).

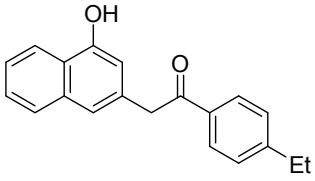
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 196.7, 163.6, 153.5, 134.8, 134.3, 131.4, 129.7, 127.5, 126.8, 124.7, 123.9, 122.3, 119.1, 114.4, 110.2, 56.0, 45.5.

IR (KBr, $v$, cm$^{-1}$) 3310, 3074, 2901, 1670, 1574, 1398, 1267, 1007, 832, 617.

HRMS (APCI-TOF) m/z calcd for $C_{19}H_{16}O_3Na$, 315.0997 $[M+Na]^+$; found 315.0982.

***1-(4-Ethylphenyl)-2-(4-hydroxynaphthalen-2-yl)ethanone (2t)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 134-135 °C;

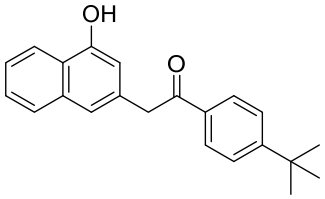
$^1$H NMR(400 MHz, DMSO-$d_6$; $\delta$, ppm) 8.12 (d, $J$ = 8.0 Hz, 1H), 7.99 (d, $J$ = 8.4 Hz, 2H), 7.74 (d, $J$ = 7.6 Hz, 1H), 7.48-7.39 (m, 2H), 7.32 (s, 1H), 7.27 (s, 1H), 7.25 (s, 1H), 6.84 (d, $J$ = 1.2 Hz, 1H), 6.59 (d, $J$ = 10.8 Hz, 1H), 4.36 (s, 2H), 2.71-2.65 (m, 2H), 1.23 (t, $J$ = 7.6 Hz, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 198.7, 152.2, 150.6, 134.8, 134.0, 132.5, 129.2, 128.2, 127.3, 126.6, 124.9, 123.7, 121.9, 120.5, 109.8, 46.0, 29.0, 15.1.

IR (KBr, $v$, cm$^{-1}$) 3304, 3060, 2963, 1654, 1579, 1405, 1271, 1082, 748, 603.

HRMS (APCI-TOF) m/z calcd for $C_{20}H_{18}O_2Na$, 313.1204 $[M+Na]^+$; found 313.1187.

***1-(4-(tert-Butyl)phenyl)-2-(4-hydroxynaphthalen-2-yl)ethanone (2u)***




mp 196-197 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 8.12 (d, $J$ = 8.0 Hz, 1H), 7.99 (d, $J$ = 8.4 Hz, 2H), 7.75 (d, $J$ = 7.6 Hz, 1H), 7.48-7.45 (m, 4H), 7.34 (s, 1H), 6.81-6.79 (m, 1H), 5.82 (s, 1H), 4.36 (s, 2H), 1.32 (s, 9H, $C_4H_9$).

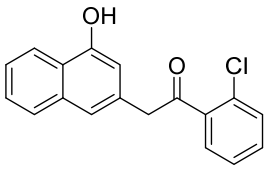
$^{13}$C NMR (100 MHz, $CDCl_3$; $\delta$, ppm) 197.9, 157.2, 151.9, 134.8, 133.8, 132.6, 128.8, 127.3, 126.7, 125.7, 125.0, 123.5, 121.7, 120.7, 109.9, 45.9, 35.2, 31.1.

IR (KBr, $v$, cm$^{-1}$) 3390, 3047, 2963, 1657, 1577, 1397, 1300, 1081, 749, 591.

HRMS (APCI-TOF) m/z calcd for $C_{22}H_{21}O_2$, 317.1542 $[M-H]^-$; found 317.1532.

***1-(2-Chlorophenyl)-2-(4-hydroxynaphthalen-2-yl)ethanone (2v)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




A yellow oil;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.20 (s, 1H), 8.14 (d, $J$ = 7.8 Hz, 1H), 7.74 (d, $J$ = 7.8 Hz, 2H), 7.53-7.48 (m, 2H), 7.46-7.42 (m, 3H), 7.23 (s, 1H), 6.84 (s, 1H), 4.38 (s, 2H).

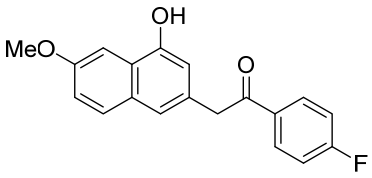
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 200.7, 153.6, 139.1, 134.8, 132.7, 132.6, 130.8, 130.2, 129.6, 127.7, 127.6, 126.8, 124.9, 124.1, 122.4, 119.6, 110.5, 49.6.

IR (KBr, $v$, cm$^{-1}$) 3390, 3032, 2960, 1662, 1578, 1397, 1300, 1071, 827, 668.

HRMS (APCI-TOF) m/z calcd for $C_{18}H_{13}ClO_2Na$, 319.0502 $[M+Na]^+$; found 319.0487.

***1-(4-Fluorophenyl)-2-(4-hydroxy-6-methoxynaphthalen-2-yl)ethanone (2x)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 159-160 $^o$C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.03 (s, 1H), 8.18-8.12 (m, 2H), 7.67 (d, $J$ = 8.8 Hz, 1H), 7.39-7.34 (m, 3H), 7.20 (s, 1H), 7.12-7.10 (m, 1H), 6.77 (s, 1H), 4.40 (s, 2H), 3.85 (s, 3H, $OCH_3$).

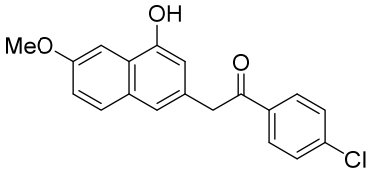
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.0, 165.5 ($^1J_{CF}$ = 250.3 Hz), 156.8, 152.6, 133.5 ($^4J_{CF}$ = 2.8 Hz), 131.9 ($^3J_{CF}$ = 9.4 Hz), 131.0, 130.2, 129.2, 124.8, 119.2, 119.2, 116.2 ($^2J_{CF}$ = 21.7 Hz), 110.7, 100.7, 55.5, 45.5.

IR (KBr, $v$, cm$^{-1}$) 3274, 3042, 2967, 1683, 1521, 1385, 1263, 1164, 827, 668.

HRMS (APCI-TOF) m/z calcd for $C_{19}H_{15}FO_3Na$, 333.0903 $[M+Na]^+$; found 333.0890.

***1-(4-Chlorophenyl)-2-(4-hydroxy-6-methoxynaphthalen-2-yl)ethanone (2y)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 165-166 $^o$C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.05 (s, 1H), 8.09-8.05 (m, 2H), 7.67 (d, $J$ = 9.2 Hz, 1H), 7.60 (d, $J$ = 8.4 Hz, 2H), 7.38 (d, $J$ = 2.4 Hz, 1H), 7.19 (s, 1H), 7.12-7.09 (m, 1H), 6.74 (s, 1H), 4.40 (s, 2H), 3.84 (s, 3H, $OCH_3$).

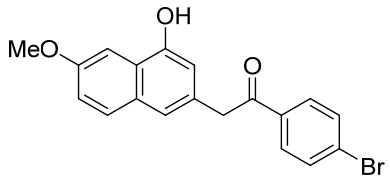
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.5, 156.8, 152.6, 138.6, 135.5, 130.9, 130.2, 129.3, 129.3, 124.8, 119.2, 110.7, 100.7, 55.5, 45.5.

IR (KBr, $v$, cm$^{-1}$) 3447, 3039, 2924, 1654, 1507, 1384, 1210, 1029, 812, 668.

HRMS (APCI-TOF) m/z calcd for $C_{19}H_{15}ClO_3Na$, 349.0607 $[M+Na]^+$; found 349.0593.

***1-(4-Bromophenyl)-2-(4-hydroxy-6-methoxynaphthalen-2-yl)ethanone (2z)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 159-160 $^o$C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.01 (s, 1H), 7.99 (d, $J$ = 8.4 Hz, 2H), 7.75 (d, $J$ = 8.4 Hz, 2H), 7.67 (d, $J$ = 9.2 Hz, 1H), 7.38 (d, $J$ = 2.8 Hz, 1H), 7.19 (s, 1H), 7.12-7.09 (m, 1H), 6.74 (s, 1H), 4.39 (s, 2H), 3.85 (s, 3H, $OCH_3$).

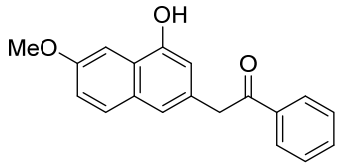
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.7, 156.8, 152.6, 135.8, 132.3, 131.0, 130.8, 130.2, 129.2, 127.8, 124.8, 119.2, 110.7, 100.7, 55.5, 45.5.

IR (KBr, $v$, cm$^{-1}$) 3409, 3060, 2894, 1674, 1544, 1395, 1260, 1075, 890, 669.

HRMS (APCI-TOF) m/z calcd for $C_{19}H_{14}BrO_3$, 369.0126 $[M-H]^-$; found 369.0133.

***2-(4-Hydroxy-6-methoxynaphthalen-2-yl)-1-phenylethanone (2aa)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 162-163 $^o$C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.01 (s, 1H), 8.09-8.06 (m, 2H), 7.69-7.62 (m, 2H), 7.55-7.52 (m, 2H), 7.38 (d, $J$ = 2.4 Hz, 1H), 7.20 (s, 1H), 7.12-7.09 (m, 1H), 6.76 (d, $J$ = 1.2 Hz, 1H), 4.40 (s, 2H), 3.85 (s, 3H, $OCH_3$).

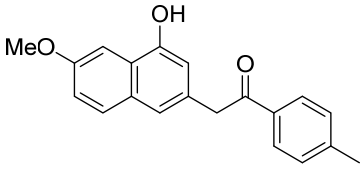
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 198.4, 156.8, 152.6, 136.8, 133.7, 131.1, 130.2, 129.2, 129.0, 124.7, 119.2, 110.7, 100.7, 55.5, 45.5.

IR (KBr, $v$, cm$^{-1}$) 3422, 3021, 2933, 1683, 1540, 1382, 1209, 1017, 820, 682.

HRMS (APCI-TOF) m/z calcd for $C_{19}H_{16}O_3Na$, 315.0997 $[M+Na]^+$; found 315.0988.

***2-(4-Hydroxy-6-methoxynaphthalen-2-yl)-1-(p-tolyl)ethanone (2bb)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 160-161 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.01 (s, 1H), 7.97 (d, $J$ = 8.0 Hz, 2H), 7.67 (d, $J$ = 9.2 Hz, 1H), 7.38 (s, 1H), 7.33 (d, $J$ = 8.0 Hz, 2H), 7.20 (s, 1H), 7.12 –7.09 (m, 1H), 6.76 (s, 1H), 4.36 (s, 2H), 3.84 (s, 3H), 2.36 (s, 3H).

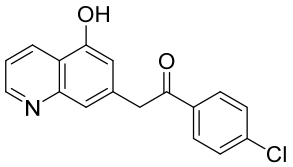
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.9, 156.8, 152.6, 144.1, 134.3, 131.3, 130.2, 129.8, 129.2, 129.1, 124.7, 119.2, 119.1, 110.7, 100.7, 55.5, 45.4, 21.6.

IR (KBr, $v$, cm$^{-1}$) 3325, 3014, 2967, 1643, 1507, 1384, 1179, 976, 804, 667.

HRMS (APCI-TOF) m/z calcd for $C_{20}H_{18}O_3Na$, 329.1154 $[M+Na]^+$; found 329.1138.

***1-(4-Chlorophenyl)-2-(5-hydroxyquinolin-7-yl)ethanone (2cc)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 222-223 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.49 (s, 1H), 8.83-8.81 (m, 1H), 8.46-8.43 (m, 1H), 8.12-8.09 (m, 2H), 7.63 (d, $J$ = 8.4 Hz, 2H), 7.43-7.40 (m, 2H), 6.83 (d, $J$ = 0.8 Hz, 1H), 4.54 (s, 2H).

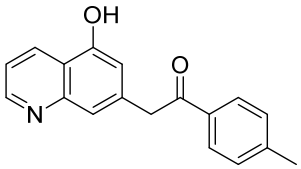
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.1, 153.5, 151.1 149.3, 138.8, 137.5, 135.5, 130.9, 129.4, 120.5, 120.3, 119.0, 110.7, 45.7.

IR (KBr, $v$, cm$^{-1}$) 3446, 3072, 2934, 1683, 1559, 1384, 1204, 1004, 813, 617.

HRMS (APCI-TOF) m/z calcd for $C_{17}H_{12}ClNO_2Na$, 320.0454 $[M+Na]^+$; found 320.0441.

***2-(5-Hydroxyquinolin-7-yl)-1-(p-tolyl)ethanone (2dd)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).




mp 215-216 °C;

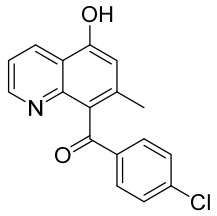
$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.47 (s, 1H), 8.82-8.81 (m, 1H), 8.44 (d, $J$ = 8.4 Hz, 1H), 8.00-7.91 (m, 2H), 7.42-7.34 (m, 4H), 6.83 (s, 1H), 4.50 (d, $J$ = 11.6 Hz, 2H), 2.38 (d, $J$ = 6.4 Hz, 3H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 197.6, 153.4, 151.1, 149.3, 144.2, 137.9, 134.3, 130.8, 129.8, 129.1, 120.4, 120.2, 118.9, 110.6, 45.6, 21.6.

IR (KBr, $v$, cm$^{-1}$) 3446, 3049, 2920, 1670, 1576, 1384, 1223, 1079, 812, 668.

HRMS (APCI-TOF) m/z calcd for $C_{18}H_{15}NO_2Na$, 300.1000 $[M+Na]^+$; found 300.0987.

***(4-Chlorophenyl)(5-hydroxy-7-methylquinolin-8-yl)methanone (4a)***




mp 227-228 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.86 (s, 1H), 8.65-8.64 (m, 1H), 8.51-8.49 (m, 1H), 7.63 (d, $J$ = 8.4 Hz, 2H), 7.53 (d, $J$ = 8.8 Hz, 2H), 7.42-7.39 (m, 1H), 6.88 (s, 1H), 2.22 (s, 3H).

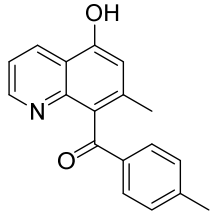
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 198.1, 154.2, 151.1, 147.6, 138.7, 137.5, 137.3, 131.2, 131.1, 129.4, 128.0, 120.3, 118.0, 111.2, 19.8.

IR (KBr, $v$, cm$^{-1}$) 3446, 3021, 2917, 1683, 1507, 1385, 1238, 1096, 814, 668.

HRMS (APCI-TOF) m/z calcd for $C_{17}H_{12}ClNO_2Na$, 320.0454 $[M+Na]^+$; found 320.0446.

***(5-Hydroxy-7-methylquinolin-8-yl)(p-tolyl)methanone (4b)***

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v).



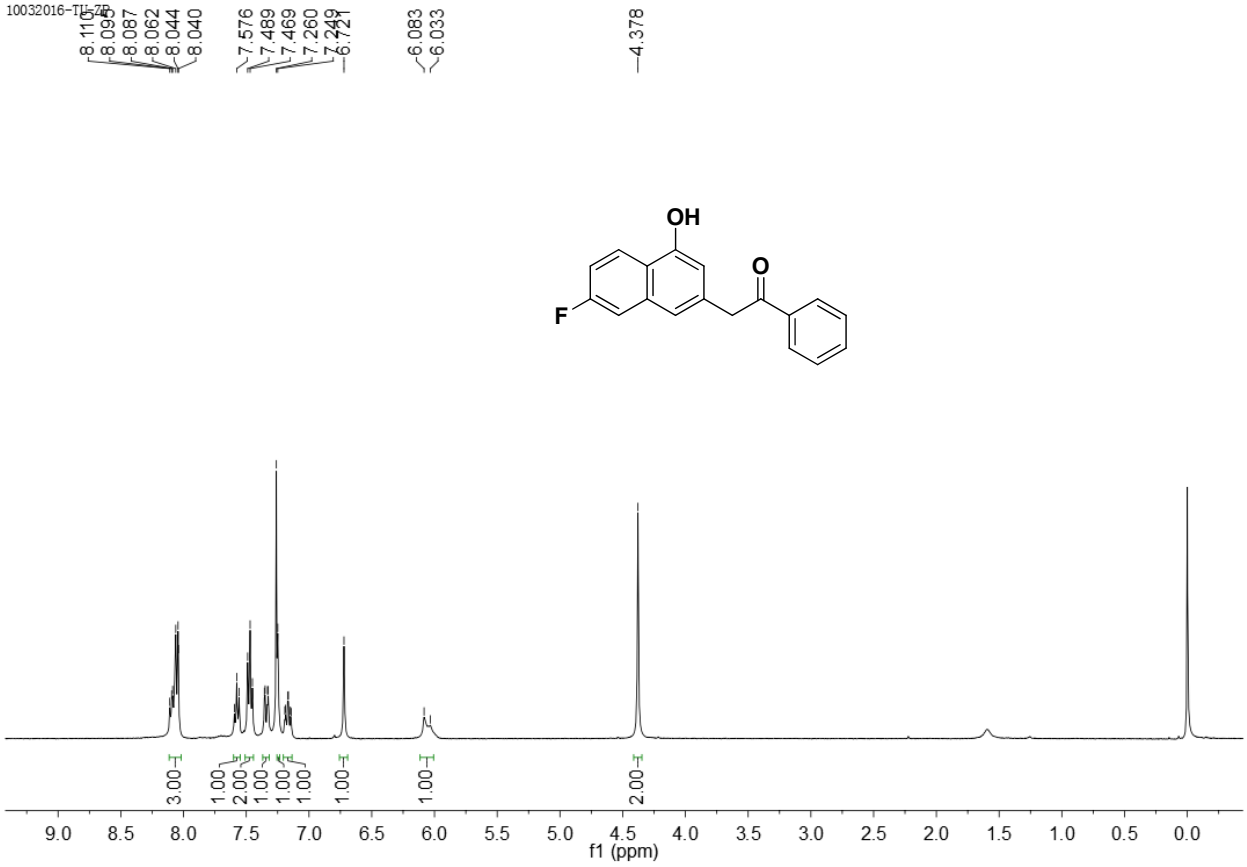

mp 206-207 °C;

$^1$H NMR (400 MHz, DMSO-$d_6$; $\delta$, ppm) 10.77 (s, 1H), 8.66-8.63 (m, 1H), 8.50 (d, $J$ = 8.4 Hz, 1H), 7.54 (d, $J$ = 8.4 Hz, 2H), 7.41-7.38 (m, 1H), 7.26 (d, $J$ = 8.0 Hz, 2H), 6.87 (s, 1H), 2.35 (s, 3H), 2.20 (s, 3H).

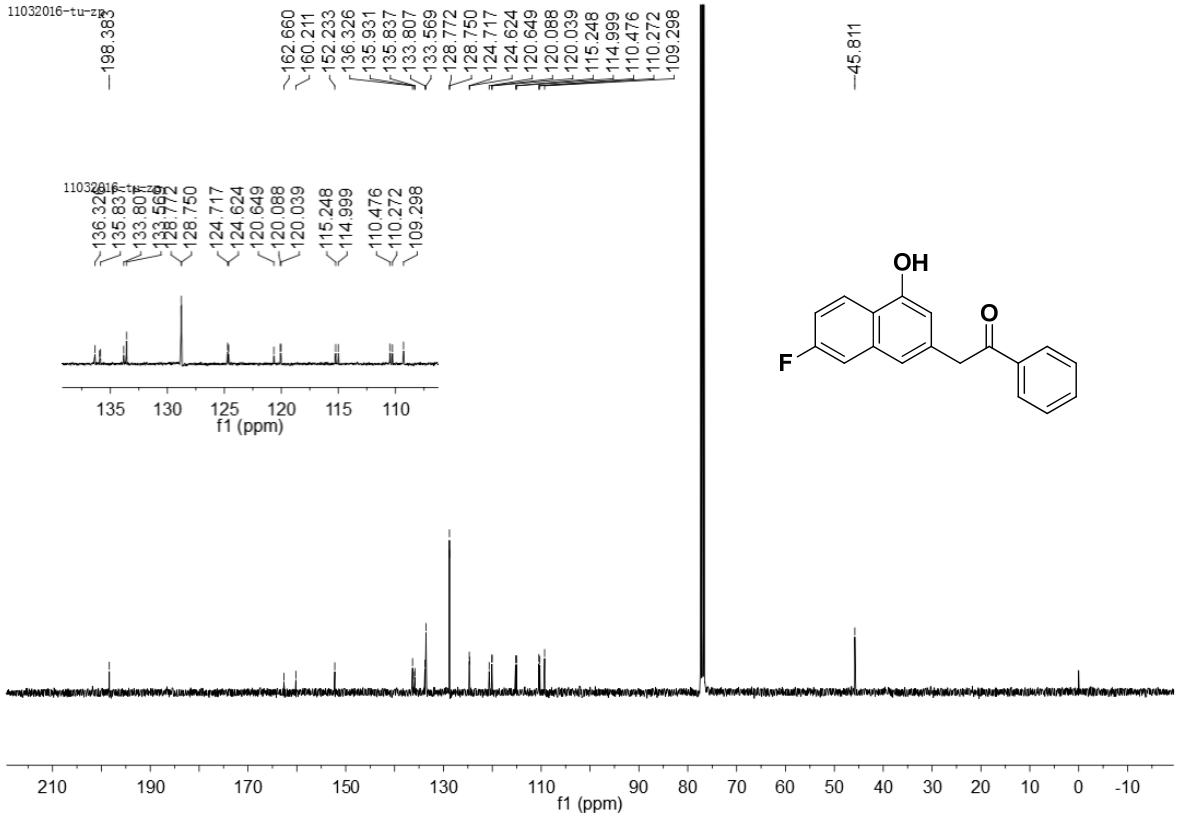
$^{13}$C NMR (100 MHz, DMSO-$d_6$; $\delta$, ppm) 198.7, 153.9, 150.9, 147.5, 144.1, 136.9, 136.2, 131.0, 129.8, 129.6, 128.9, 120.1, 117.9, 111.1, 21.7, 19.8.

IR (KBr, $v$, cm$^{-1}$) 3446, 3074, 2908, 1668, 1489, 1397, 1271, 1095, 794, 668.

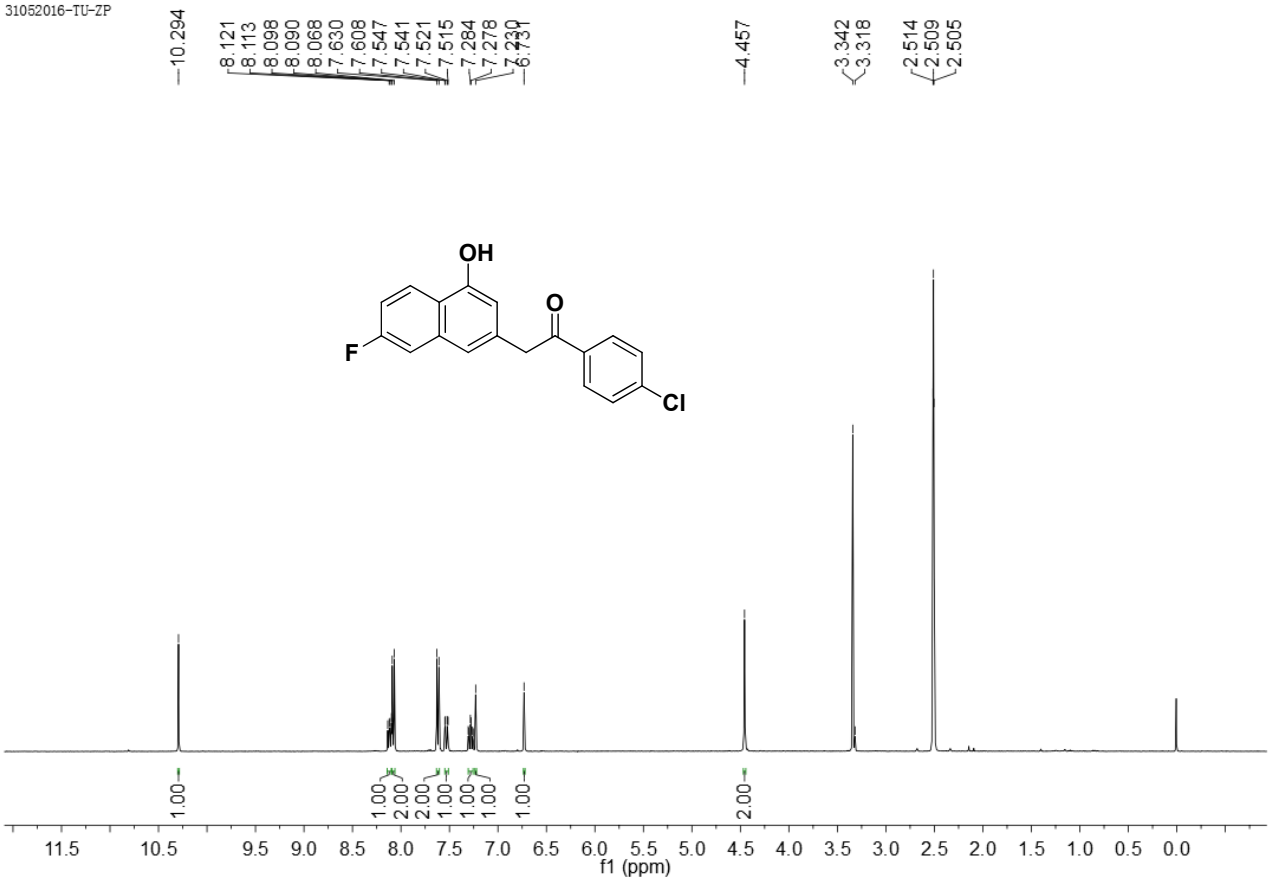
HRMS (APCI-TOF) m/z calcd for $C_{18}H_{15}NO_2Na$, 300.1000 $[M+Na]^+$; found 300.1001.



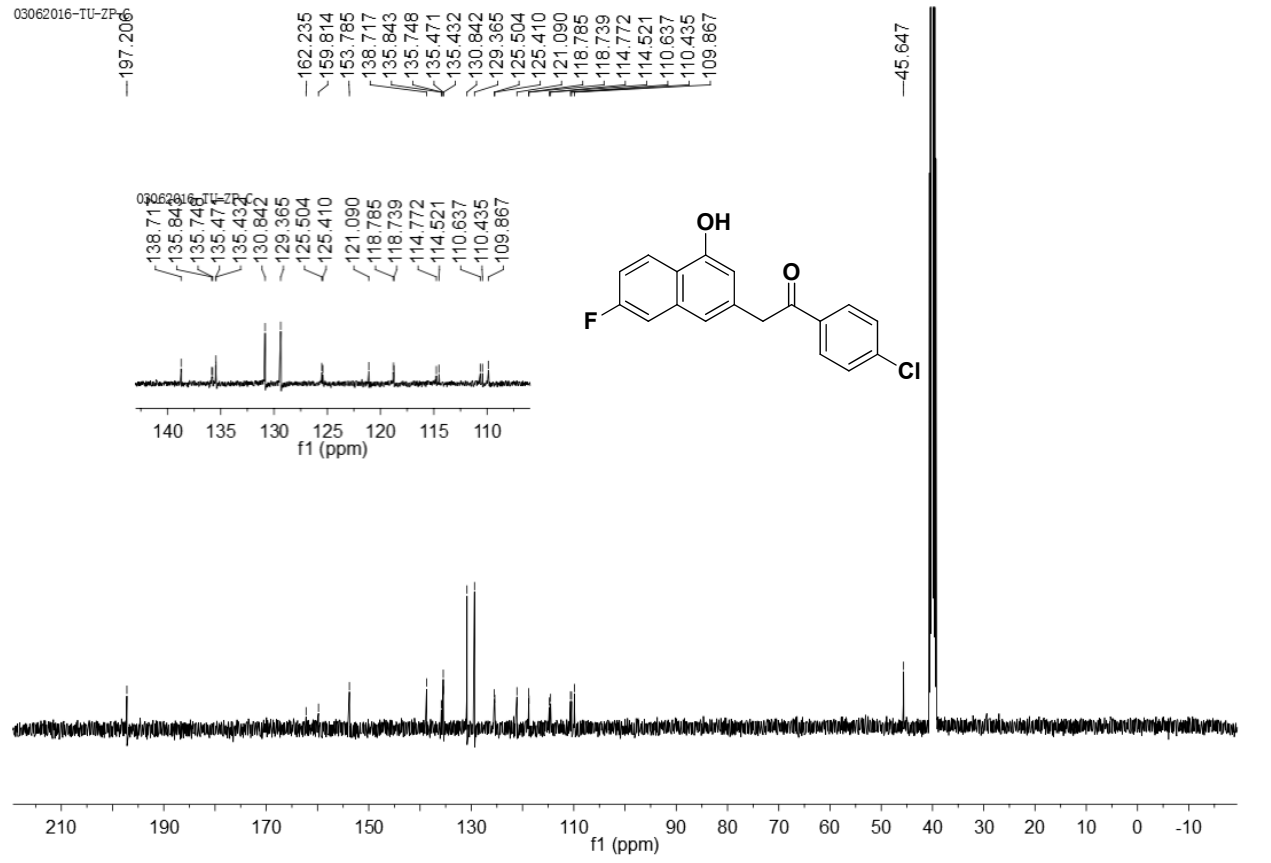

**$^{1}$H NMR Spectrum of Compound 2a**



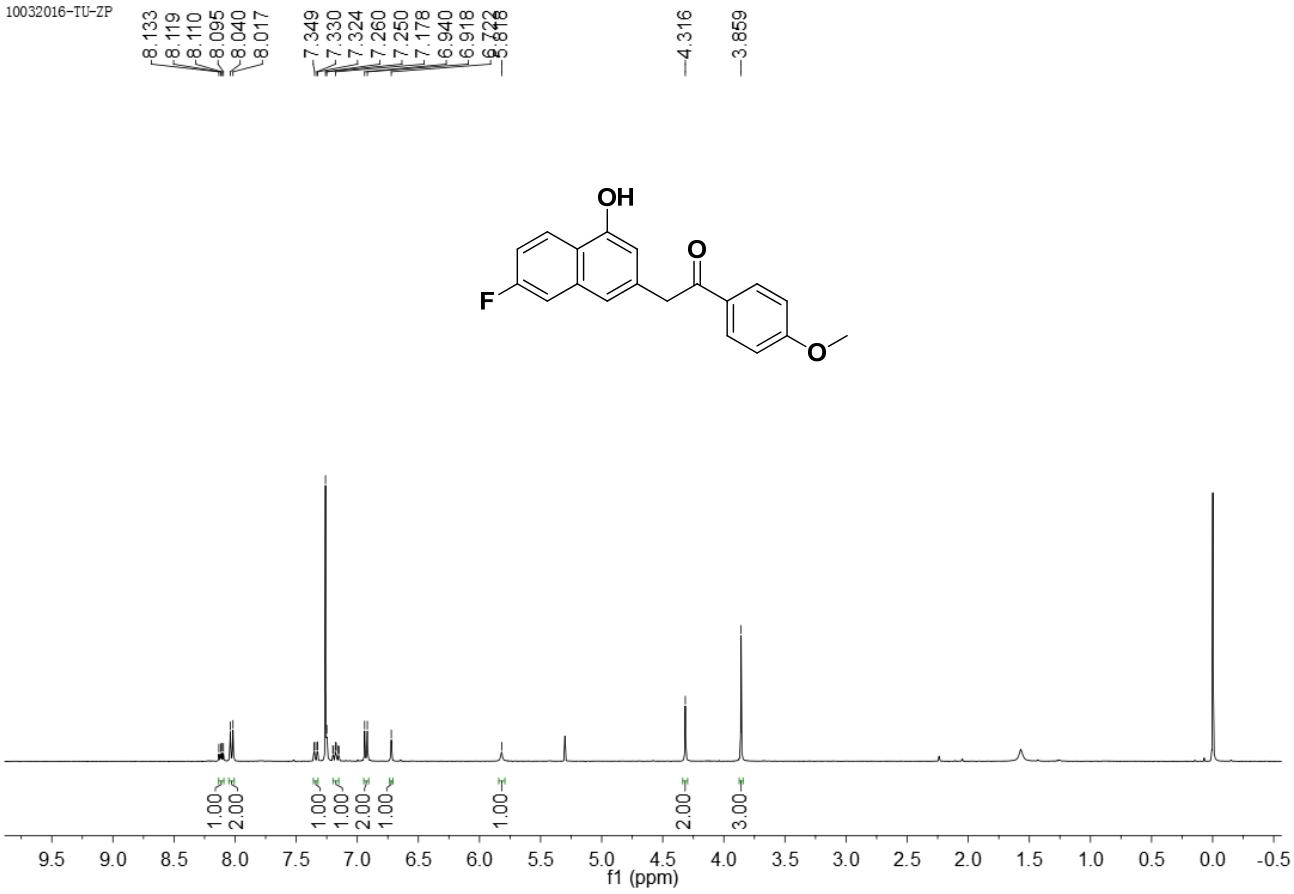

**$^{13}$C NMR Spectrum of Compound 2a**



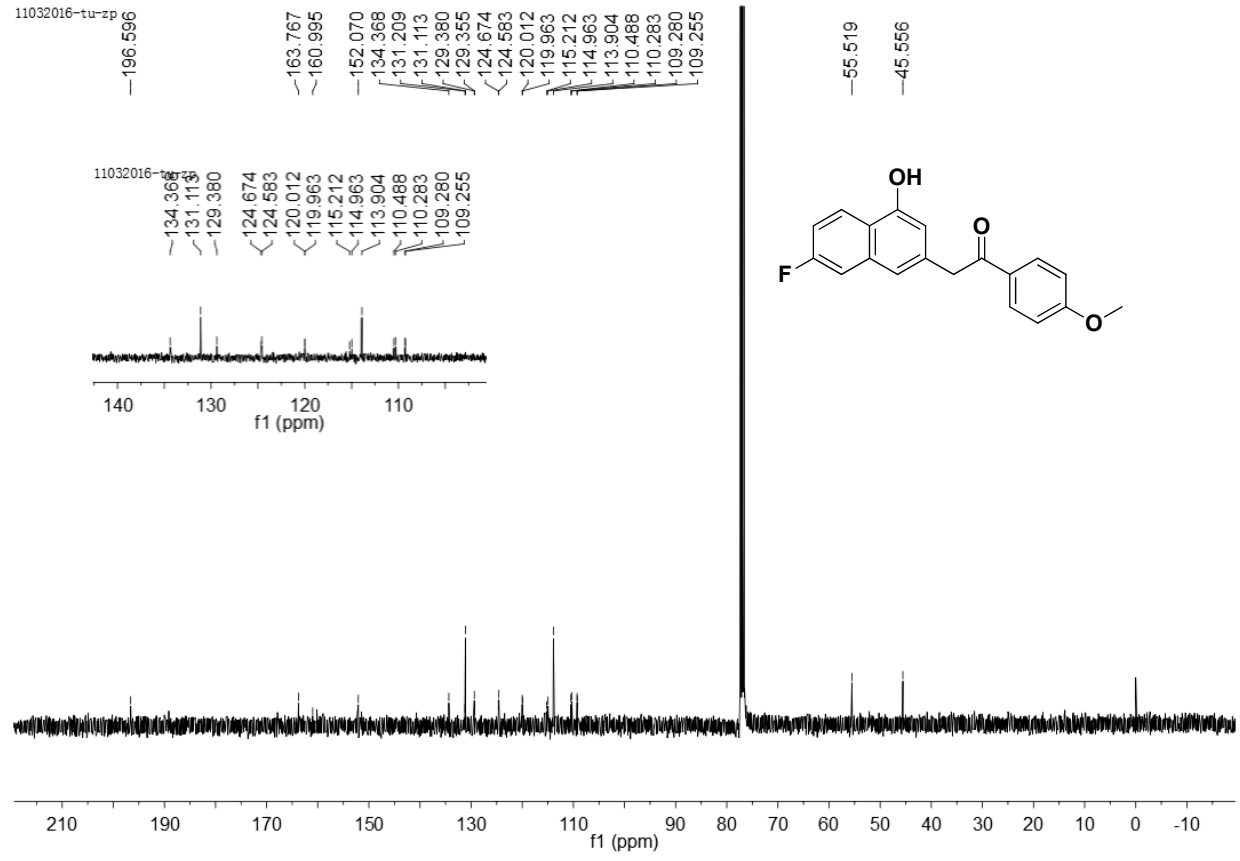

**$^{1}$H NMR Spectrum of Compound 2b**



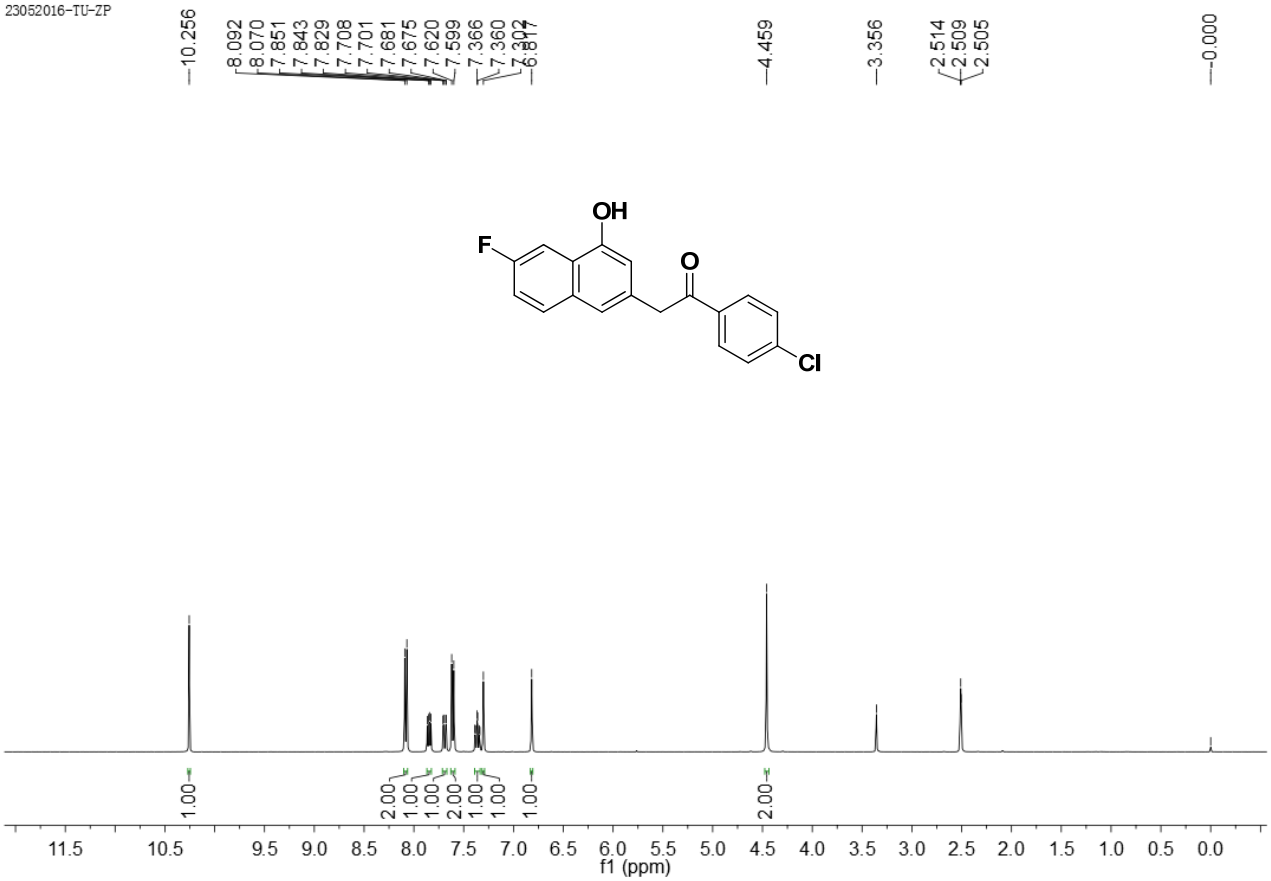

**$^{13}$C NMR Spectrum of Compound 2b**



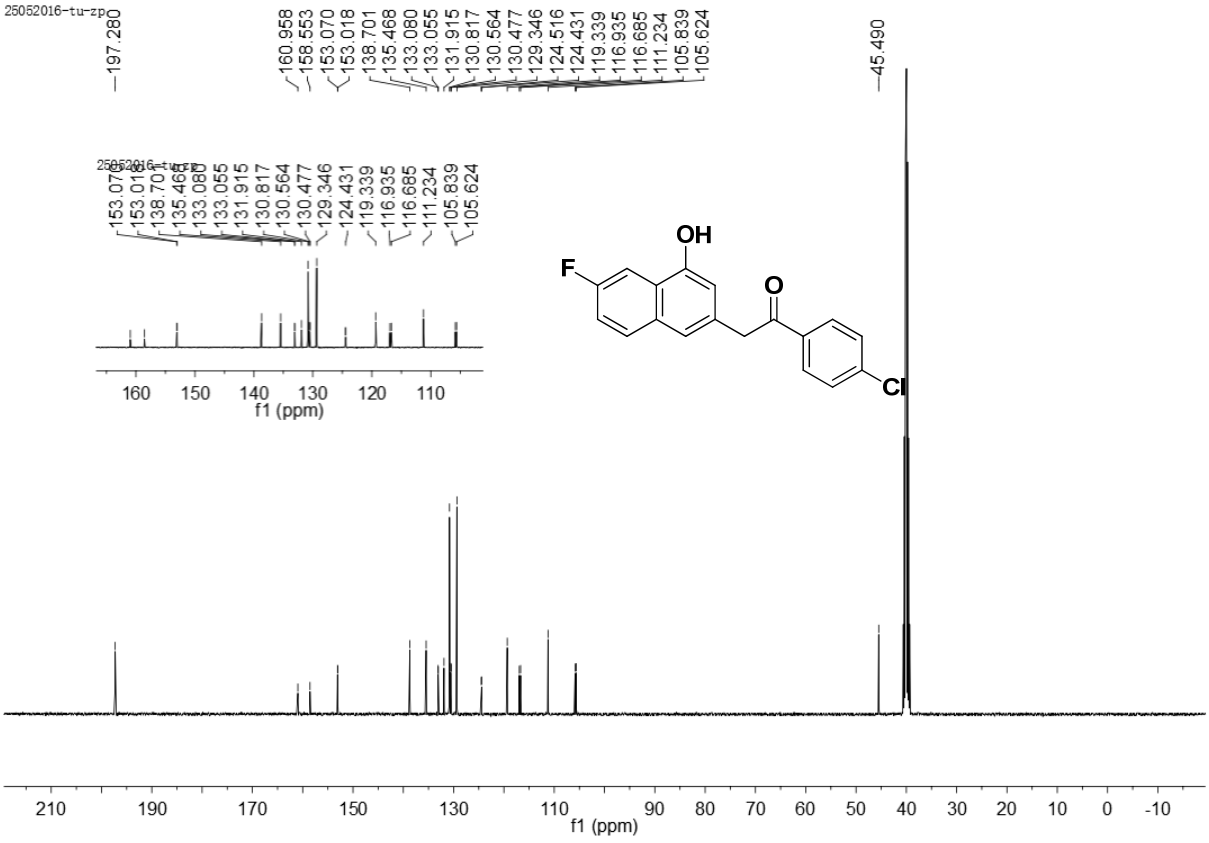

**$^{1}$H NMR Spectrum of Compound 2c**



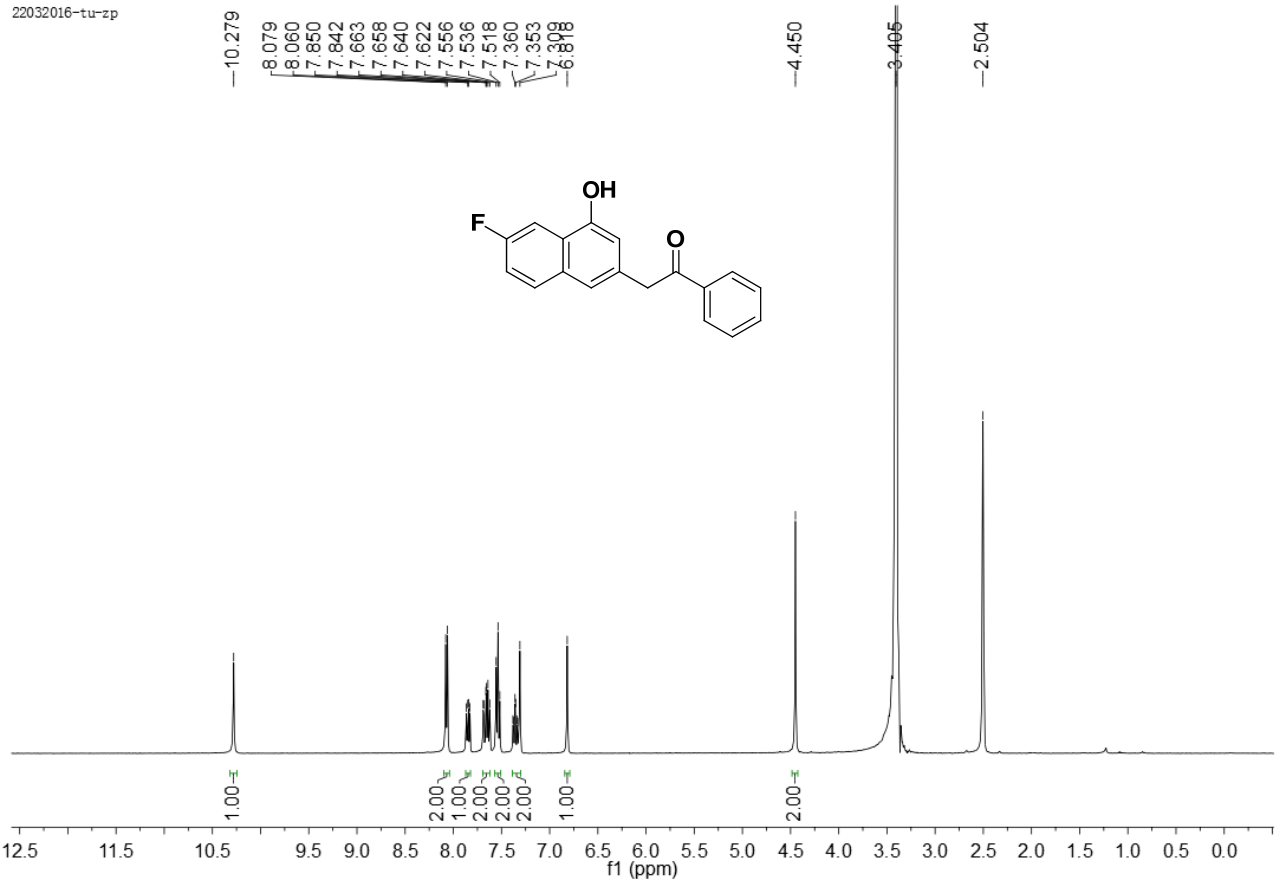

**$^{13}$C NMR Spectrum of Compound 2c**



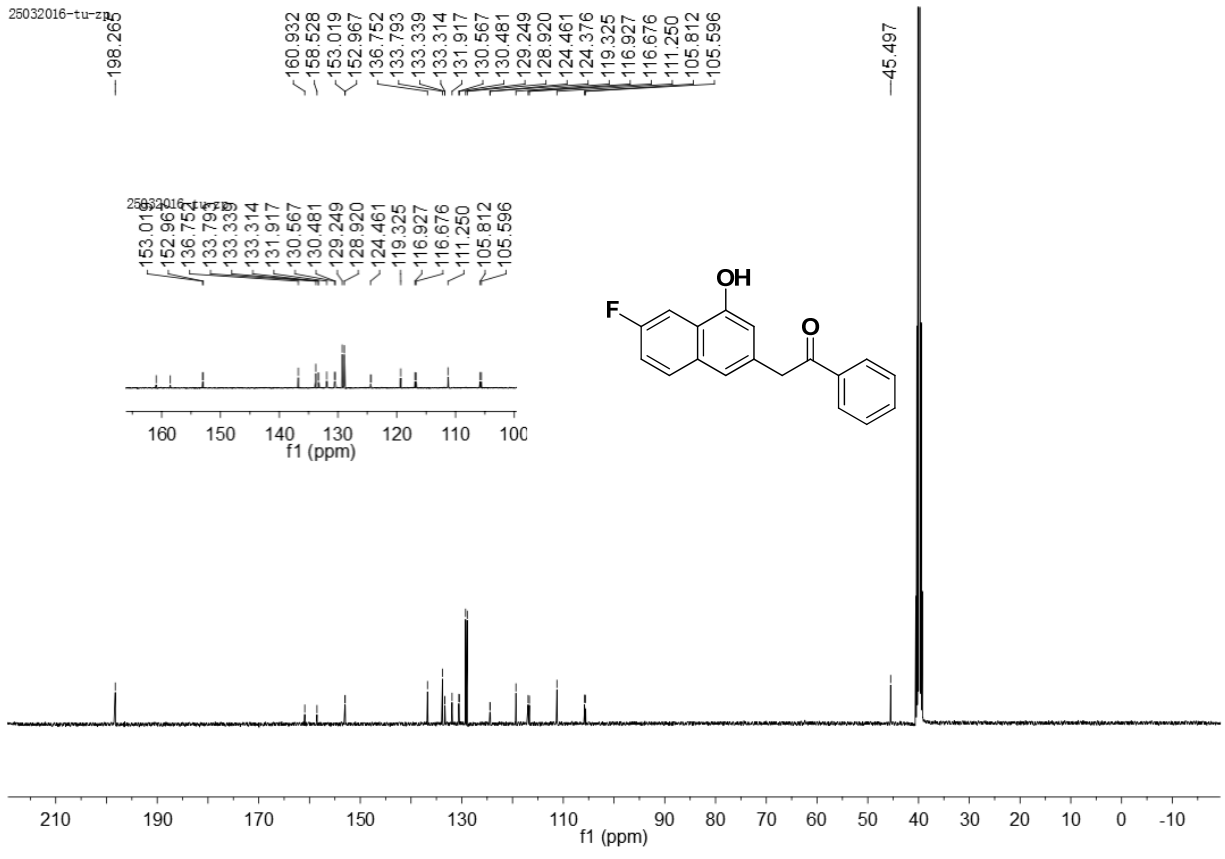

**$^{1}$H NMR Spectrum of Compound 2d**



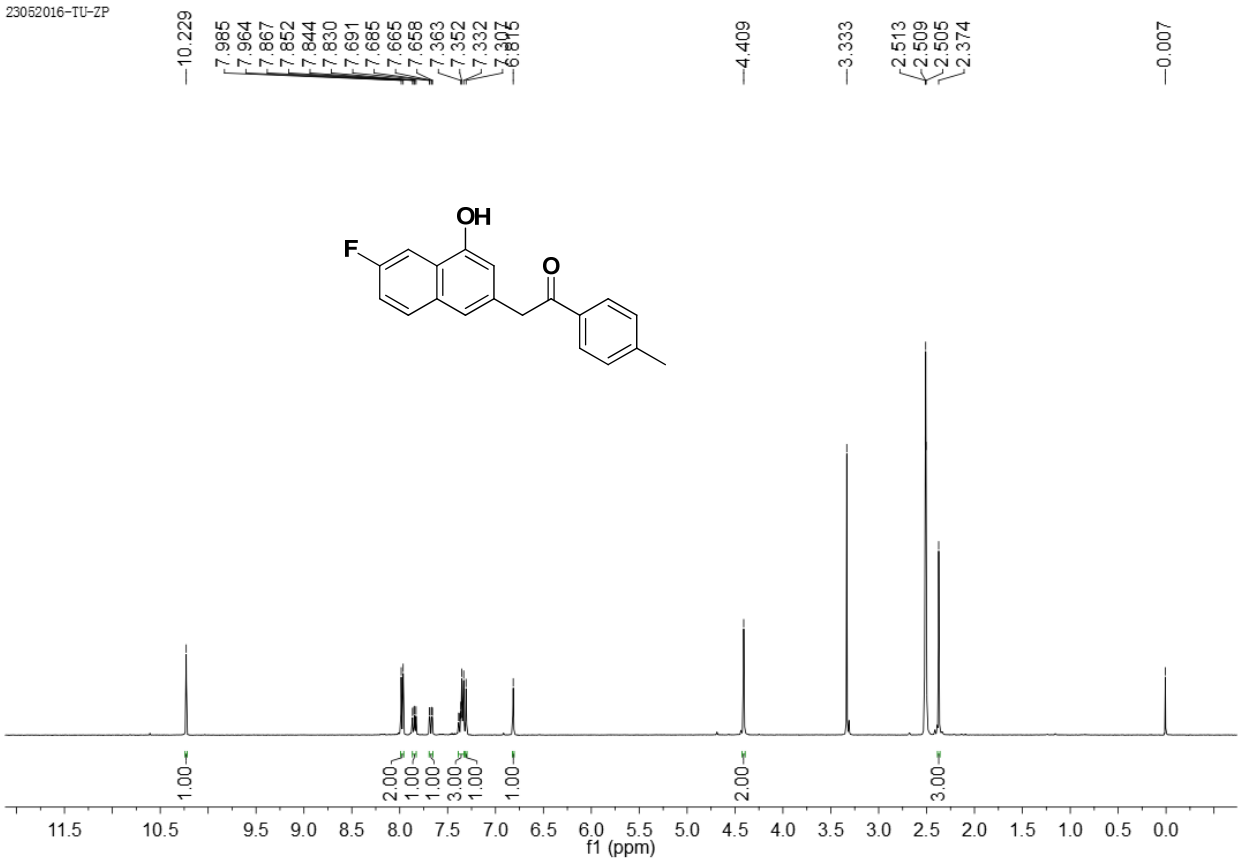

**$^{13}$C NMR Spectrum of Compound 2d**



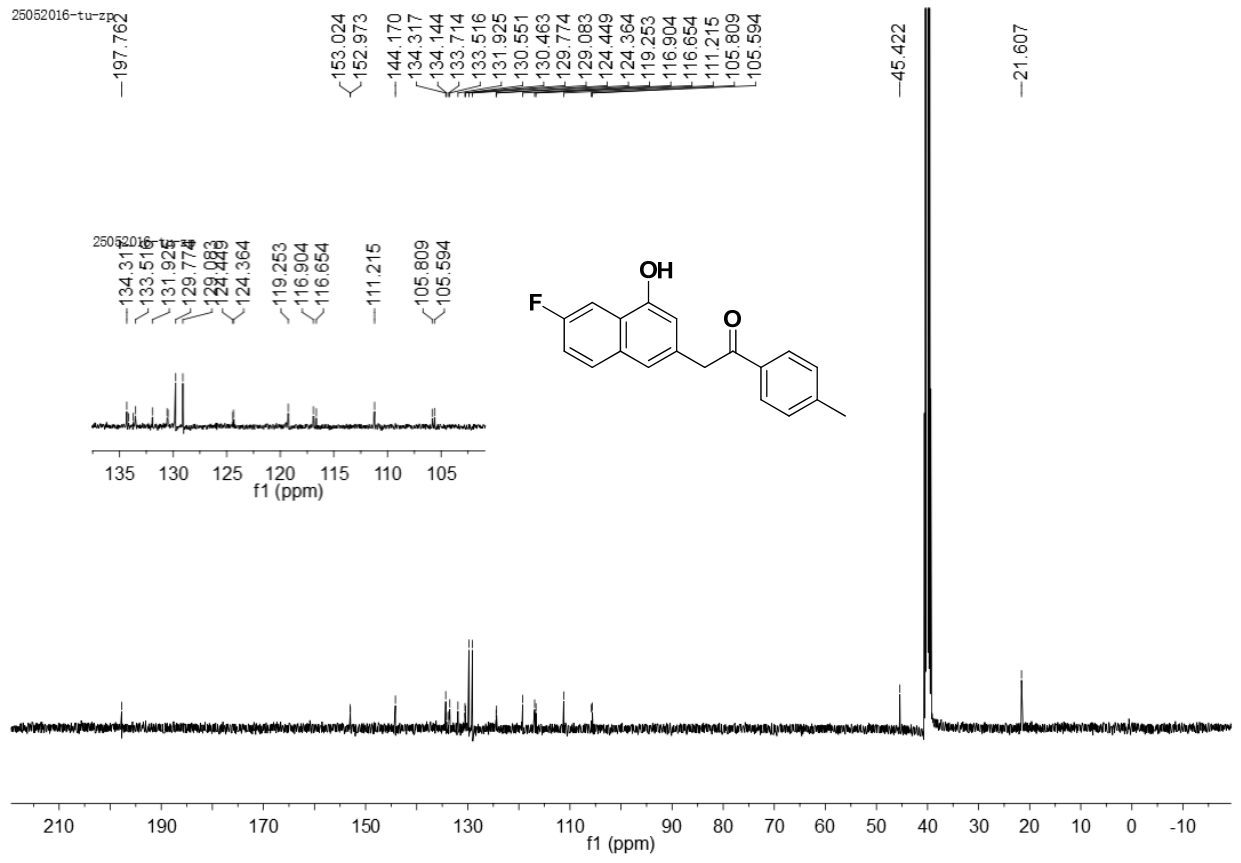

**$^{1}$H NMR Spectrum of Compound 2e**



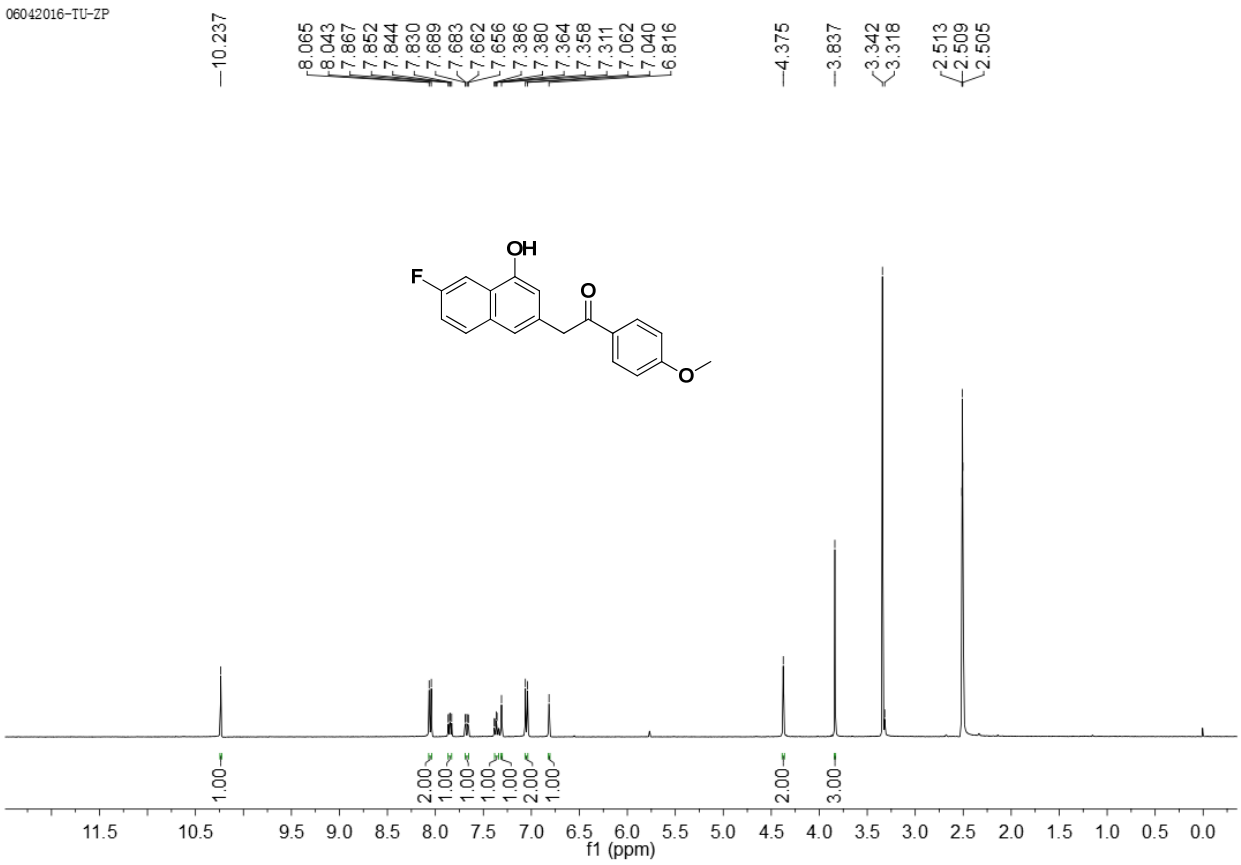

**$^{13}$C NMR Spectrum of Compound 2e**



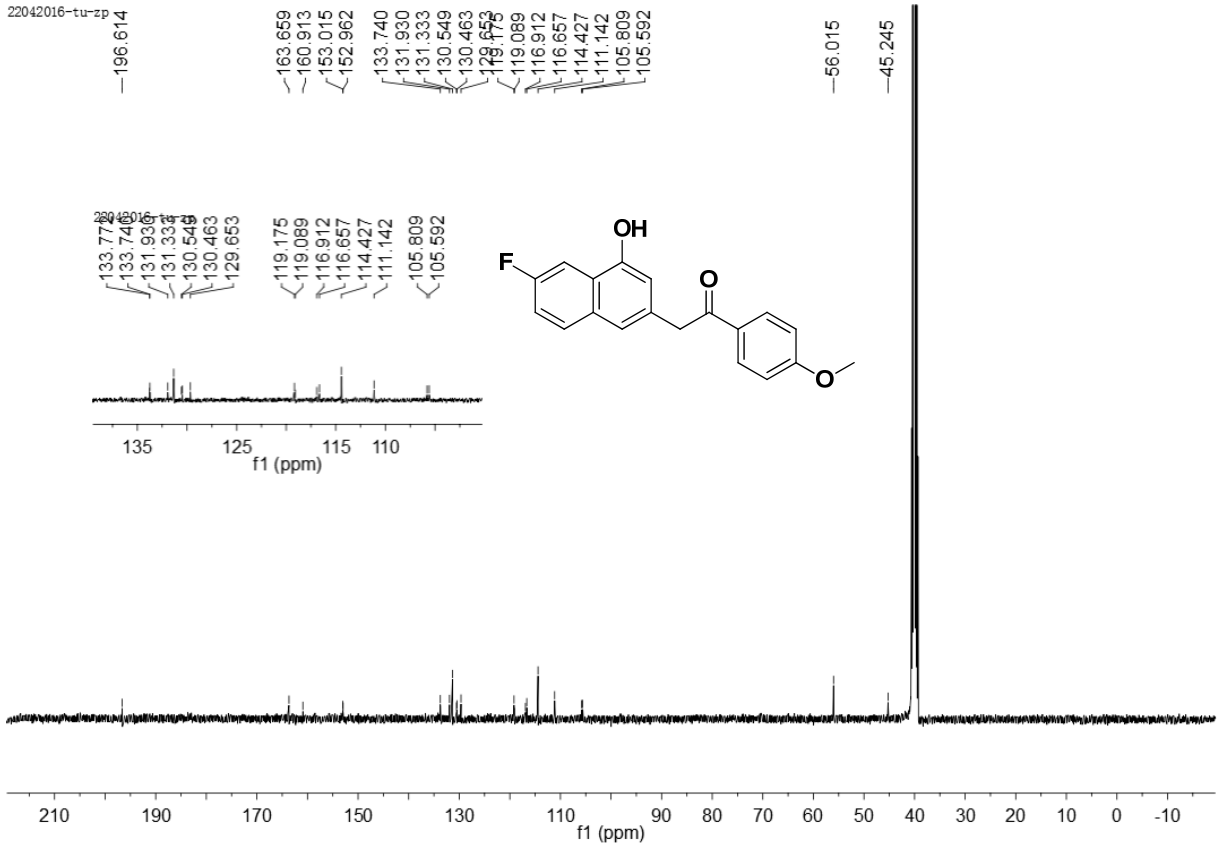

**$^{1}$H NMR Spectrum of Compound 2f**



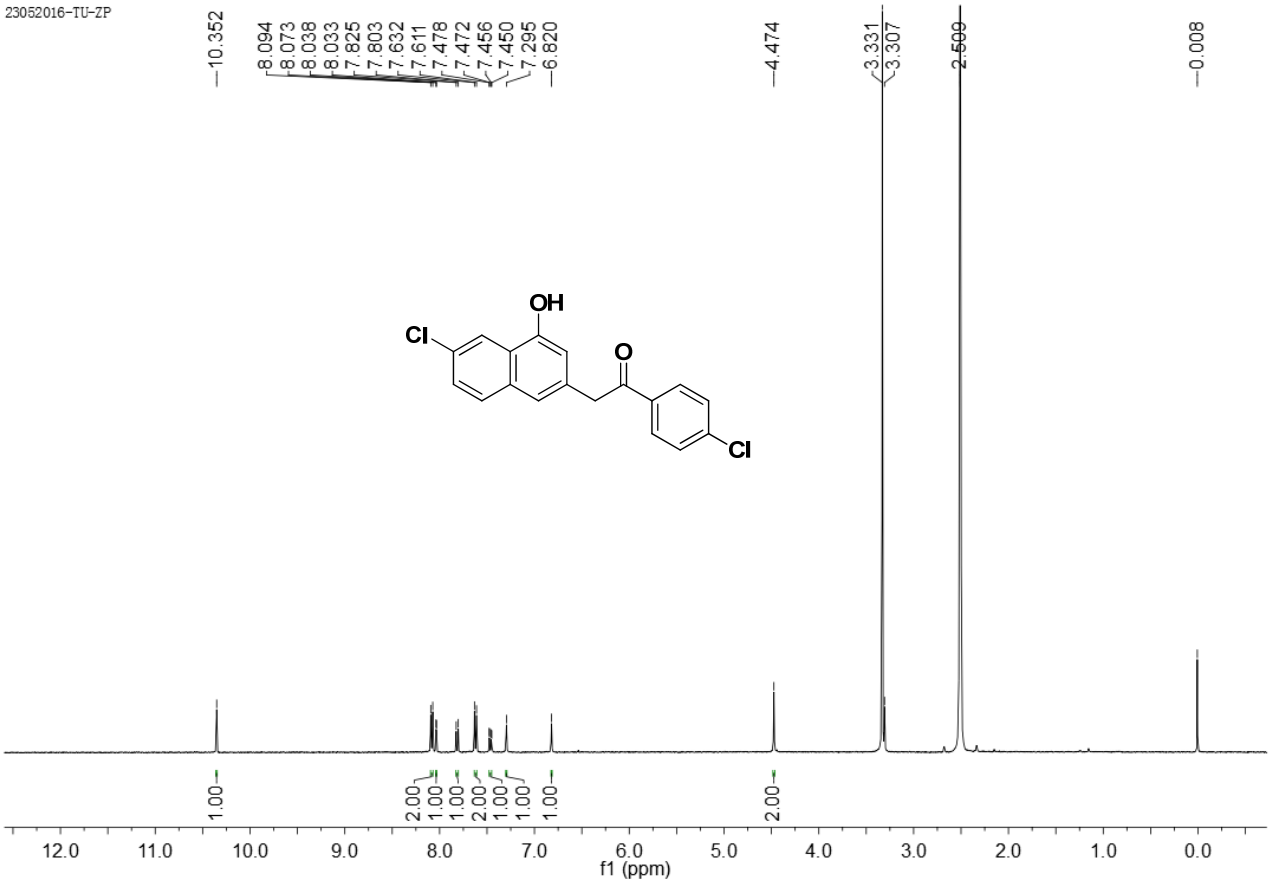

**$^{13}$C NMR Spectrum of Compound 2f**



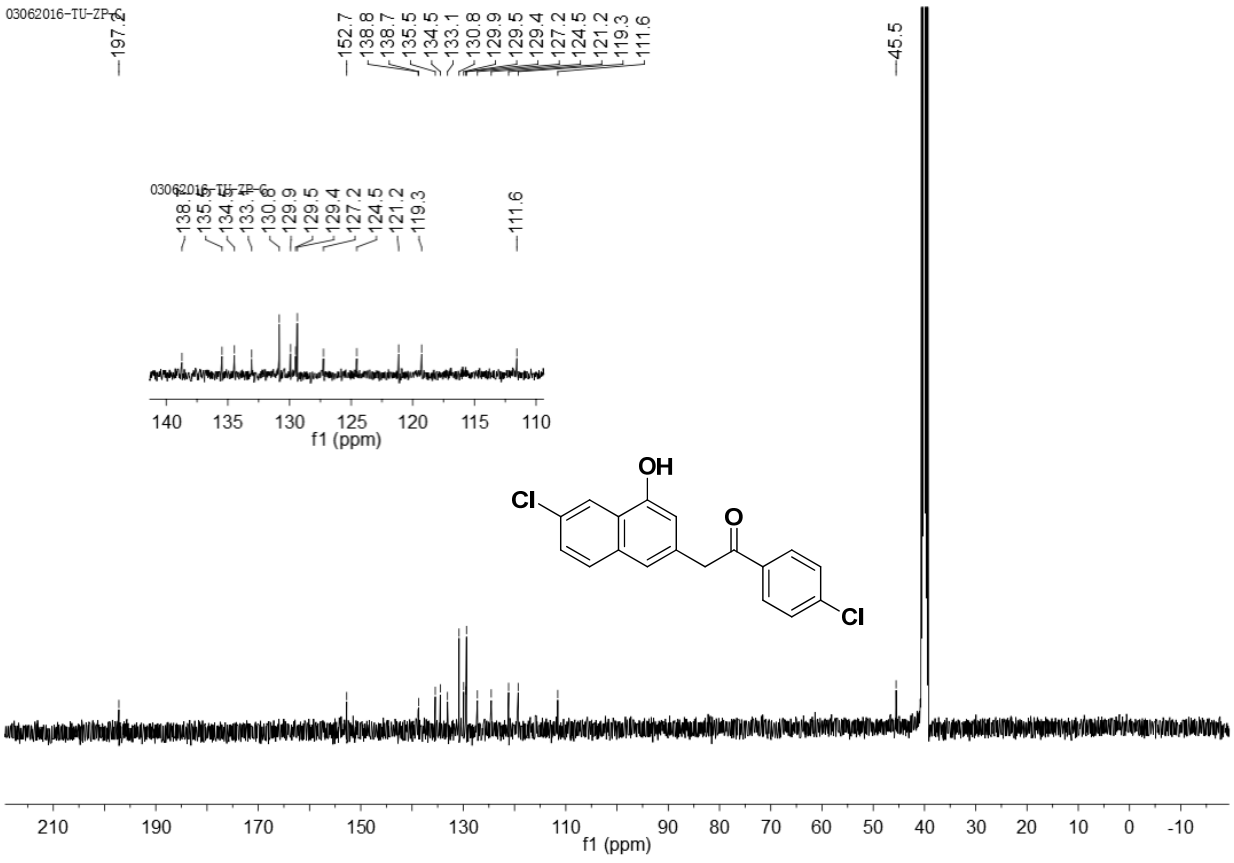

**$^{1}$H NMR Spectrum of Compound 2g**



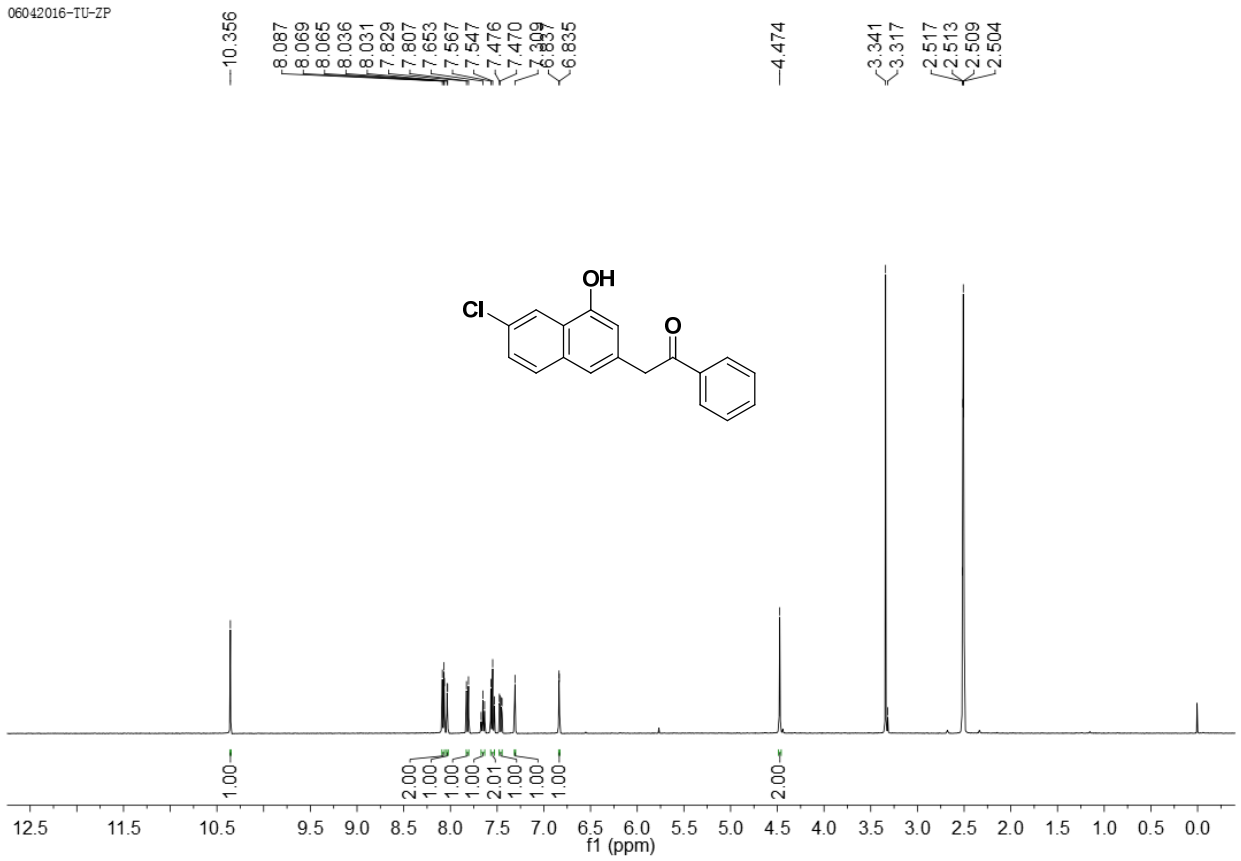

**$^{13}$C NMR Spectrum of Compound 2g**



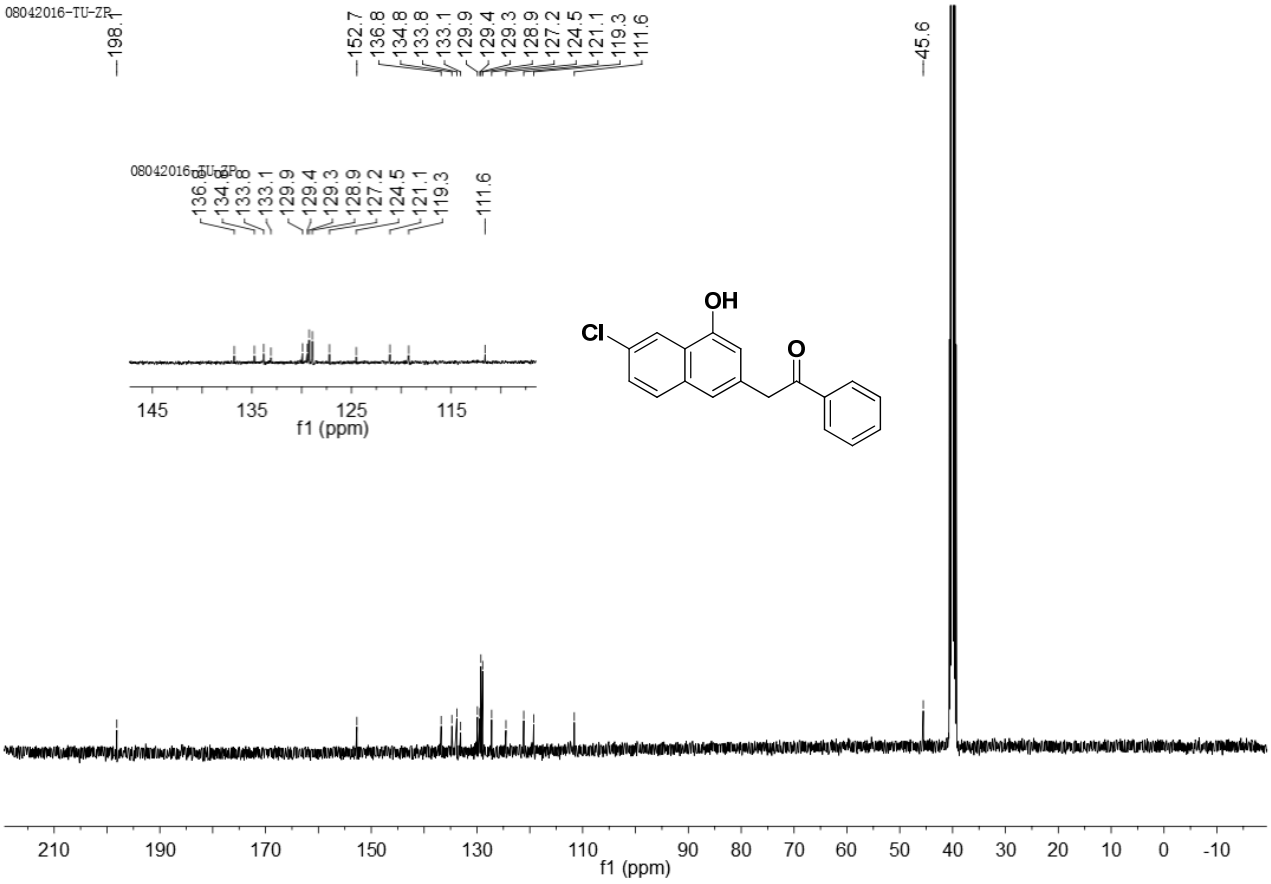

**$^{1}$H NMR Spectrum of Compound 2h**



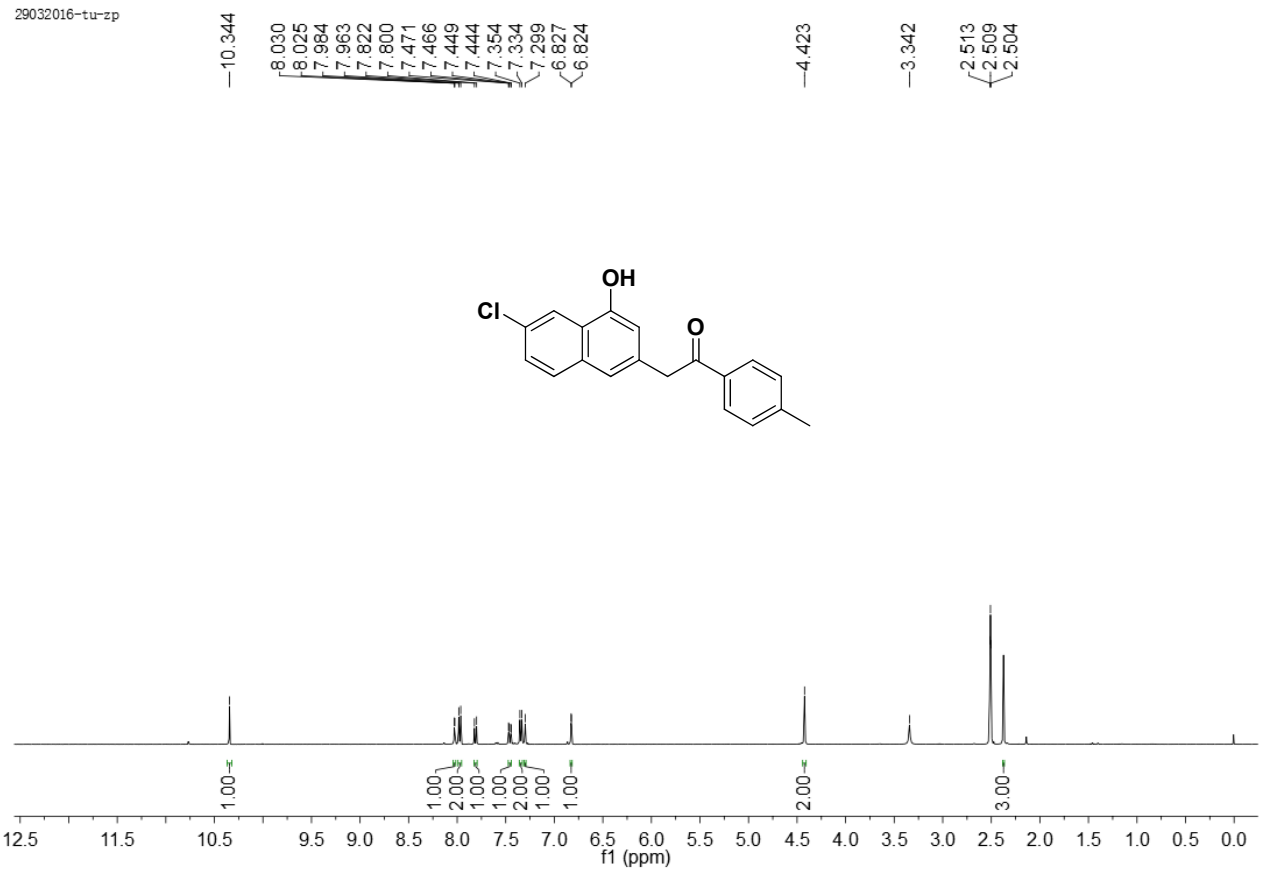

**$^{13}$C NMR Spectrum of Compound 2h**



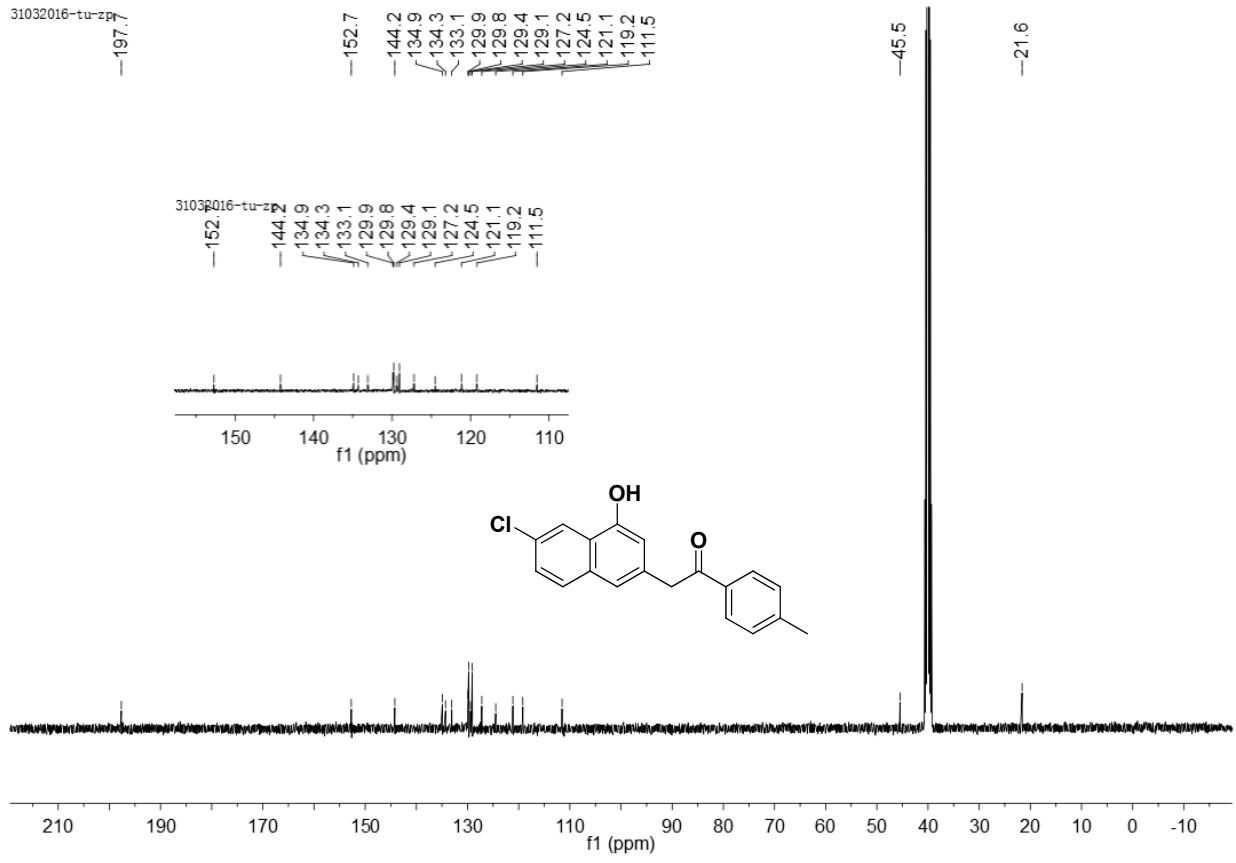

**$^{1}$H NMR Spectrum of Compound 2i**



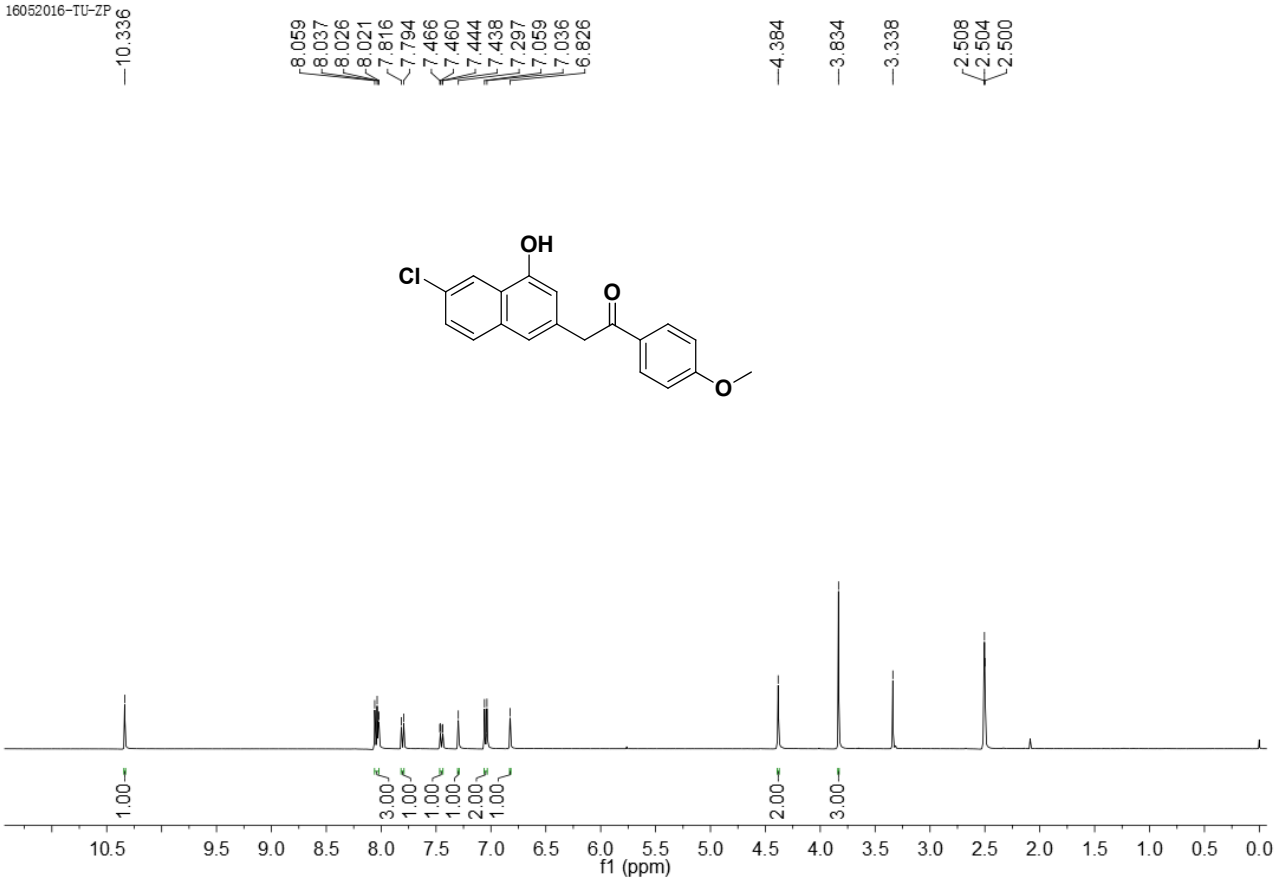

**$^{13}$C NMR Spectrum of Compound 2i**



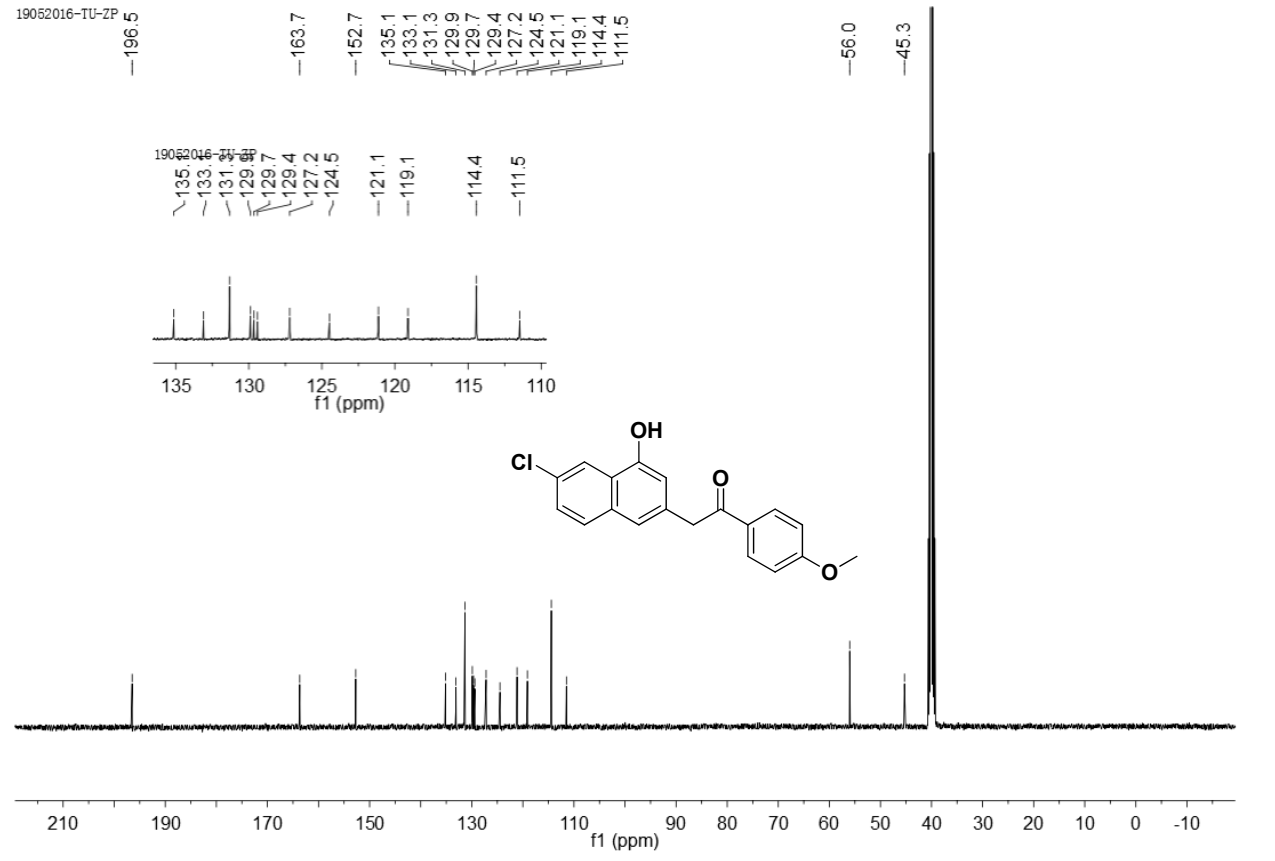

**$^{1}$H NMR Spectrum of Compound 2j**



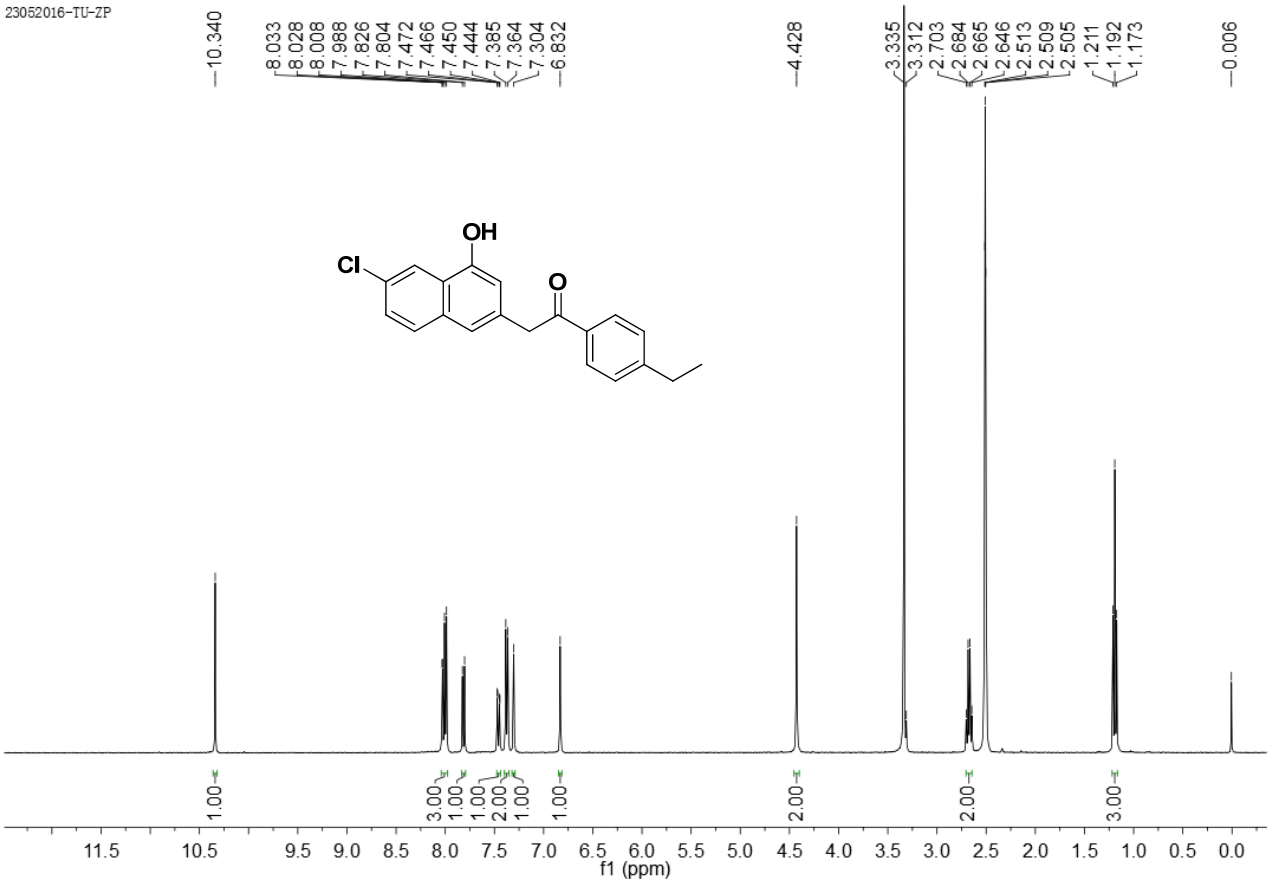

**$^{13}$C NMR Spectrum of Compound 2j**



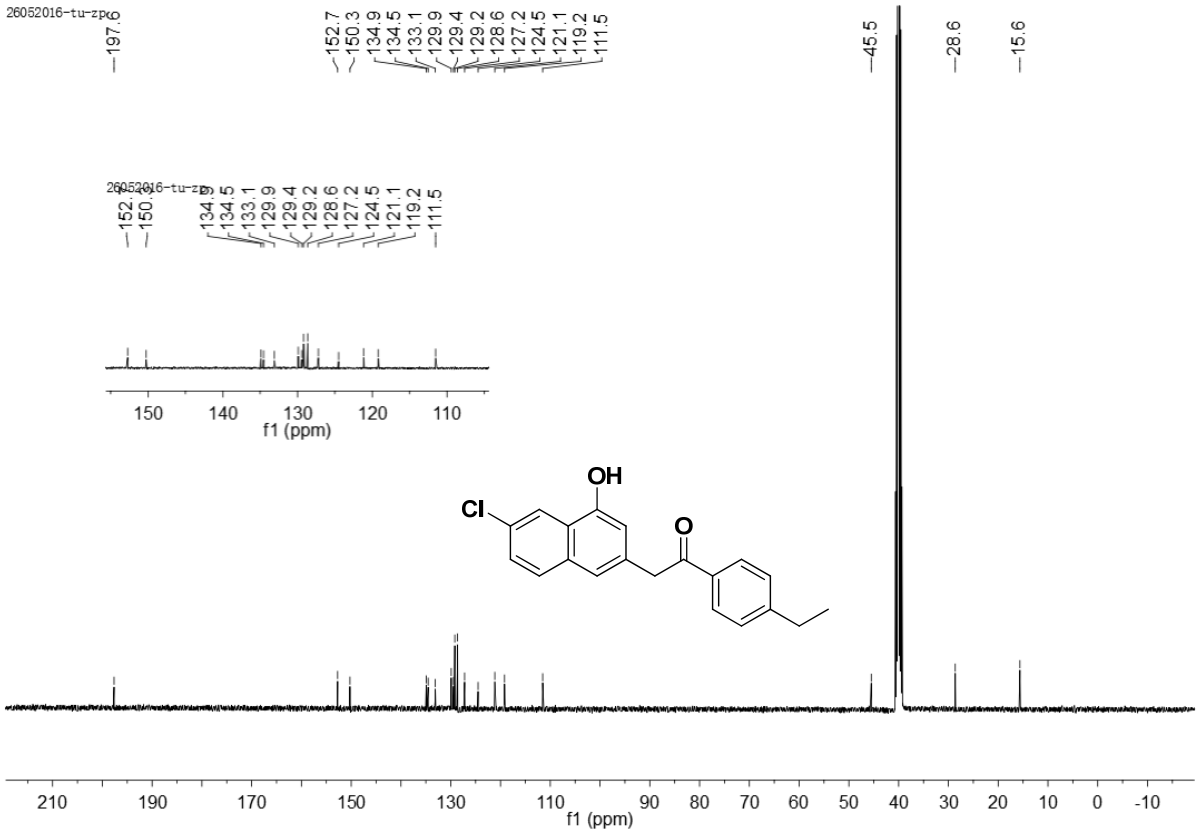

**$^{1}$H NMR Spectrum of Compound 2k**



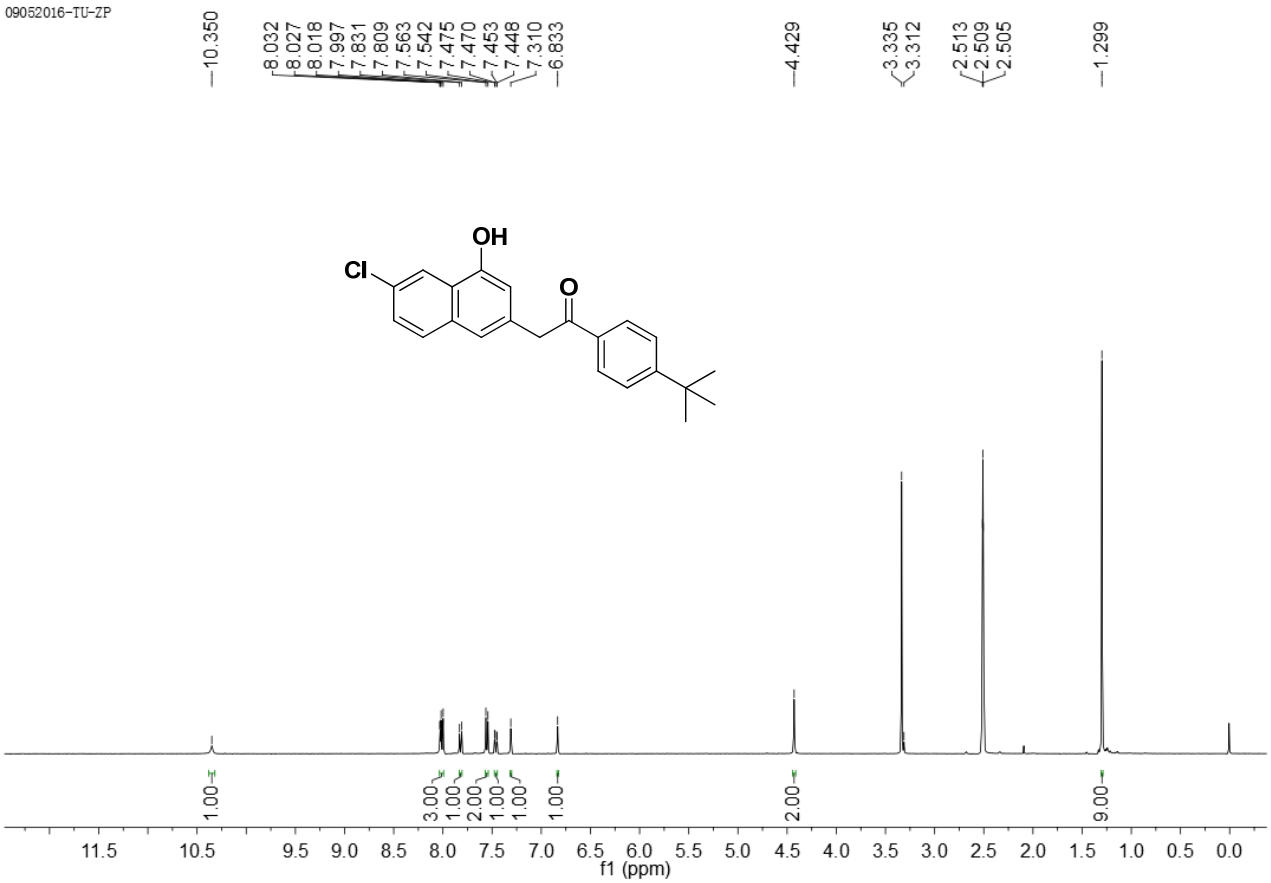

**$^{13}$C NMR Spectrum of Compound 2k**



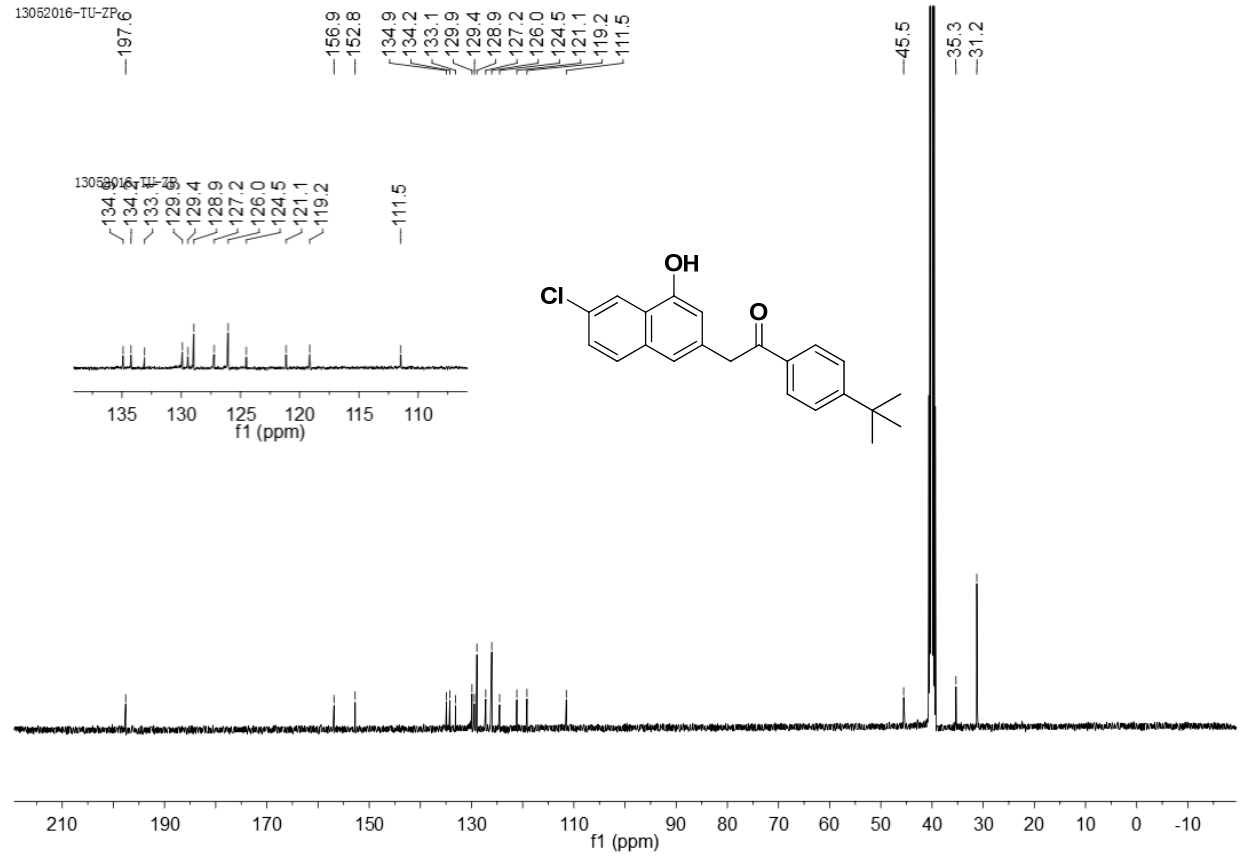

**$^{1}$H NMR Spectrum of Compound 2l**



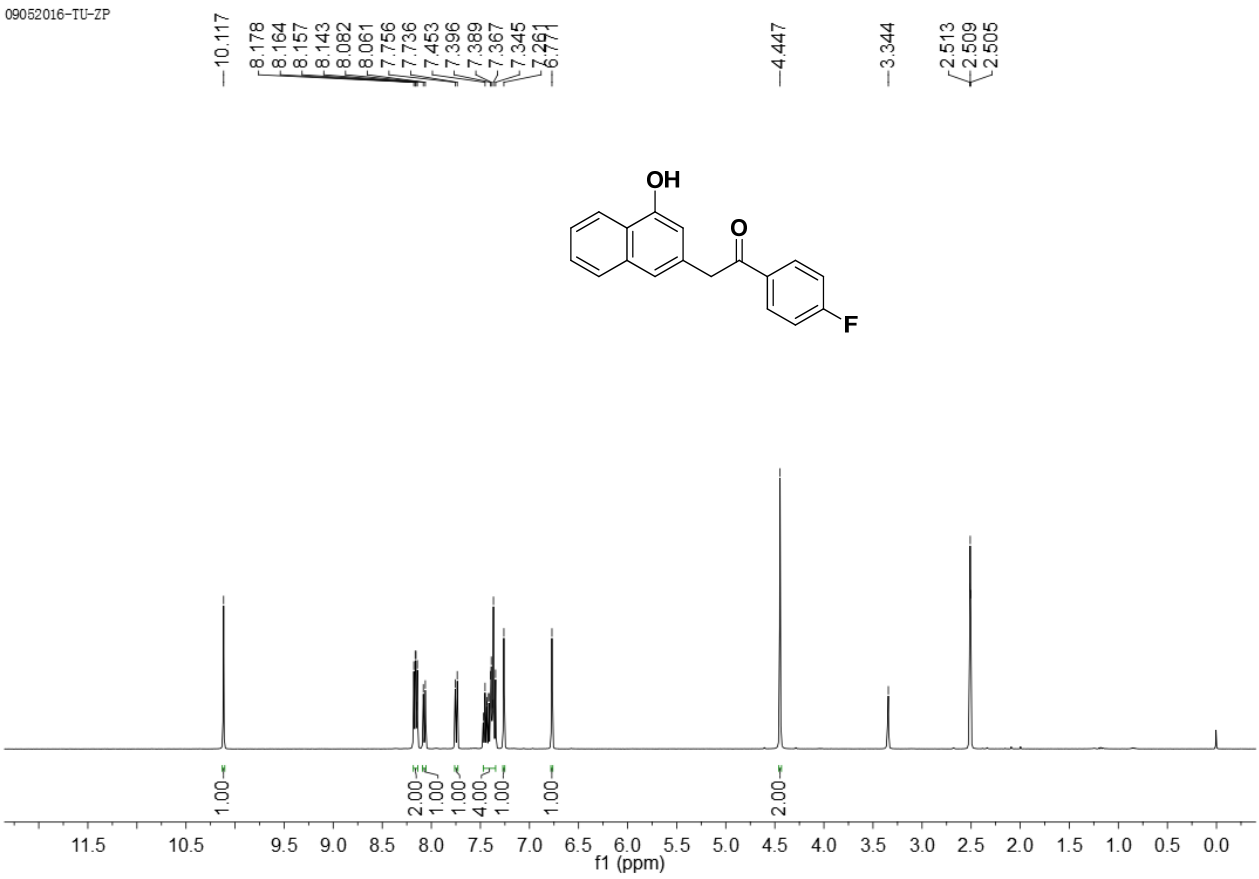

**$^{13}$C NMR Spectrum of Compound 2l**



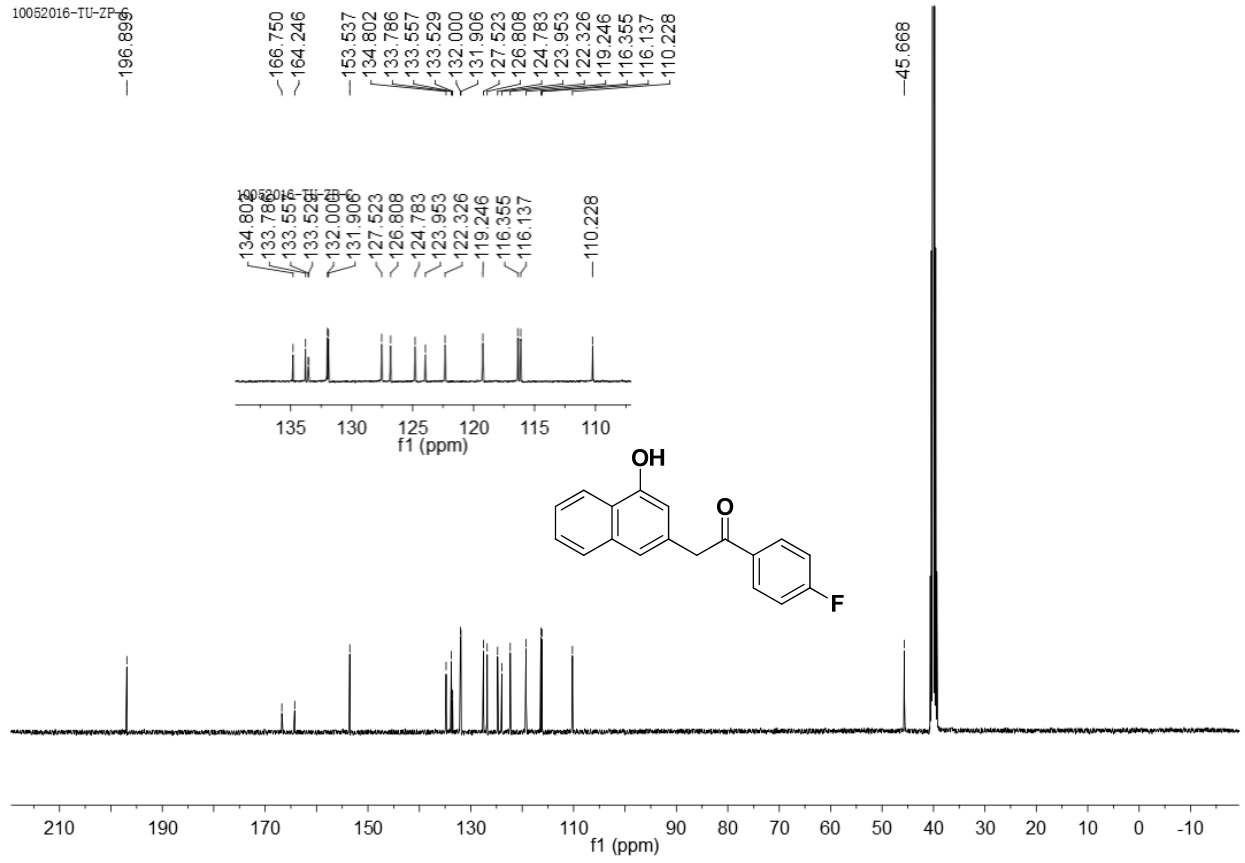

**$^{1}$H NMR Spectrum of Compound 2m**



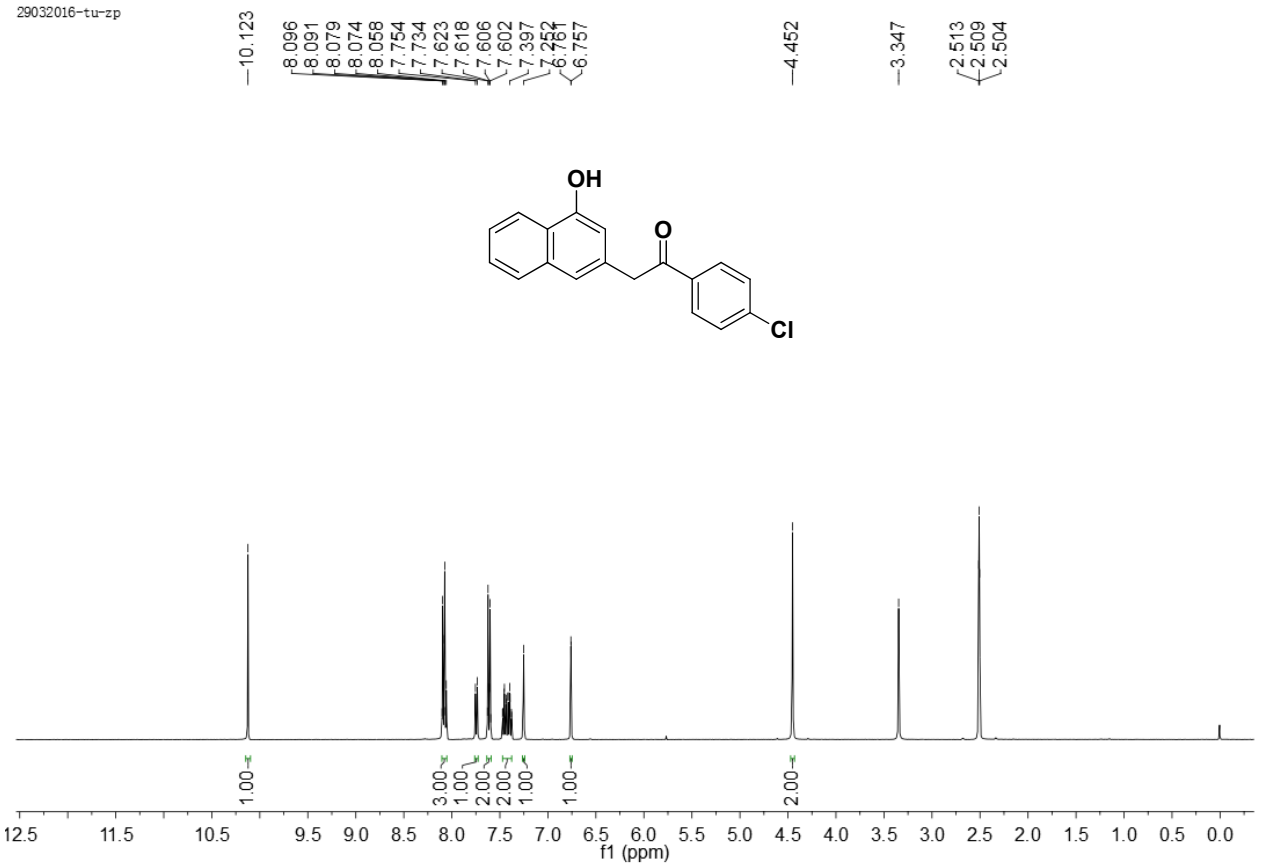

**$^{13}$C NMR Spectrum of Compound 2m**



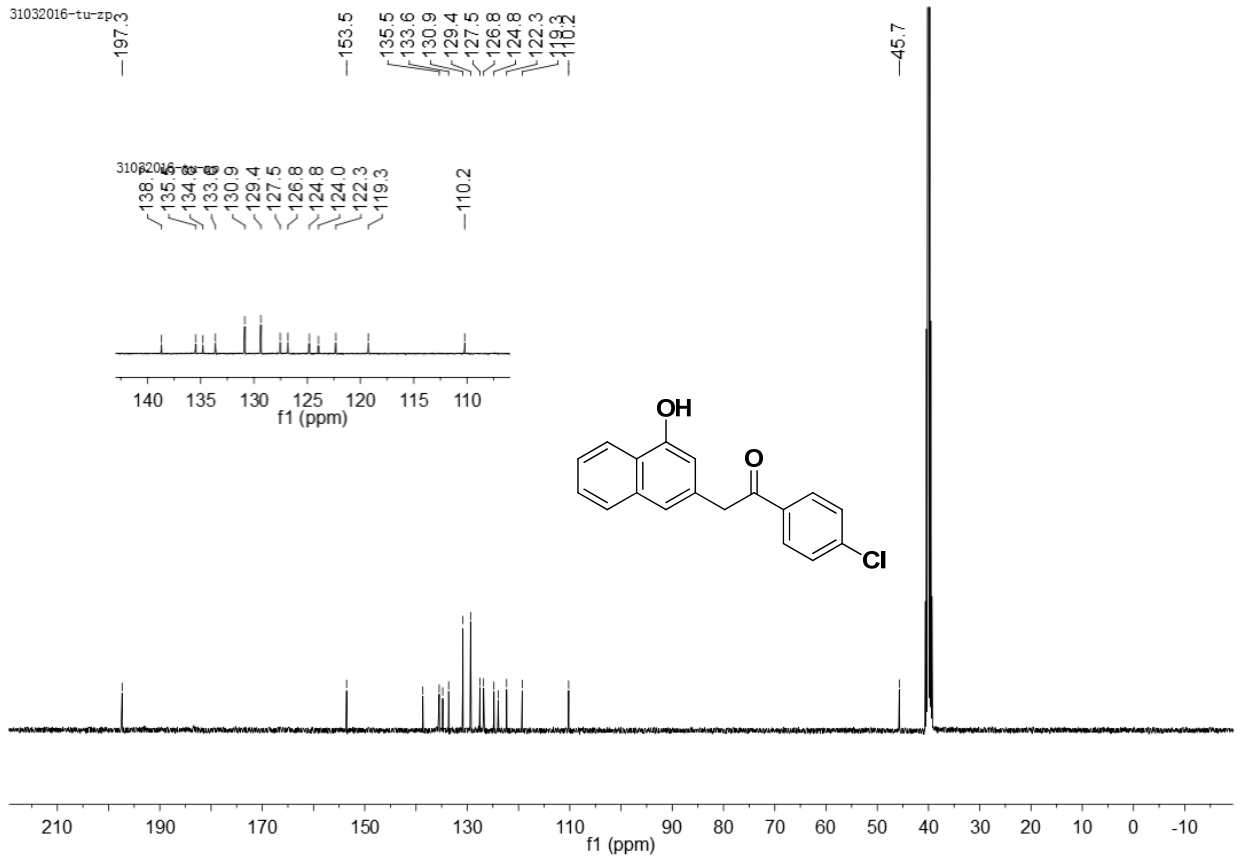

**$^{1}$H NMR Spectrum of Compound 2n**




**$^{13}$C NMR Spectrum of Compound 2n**

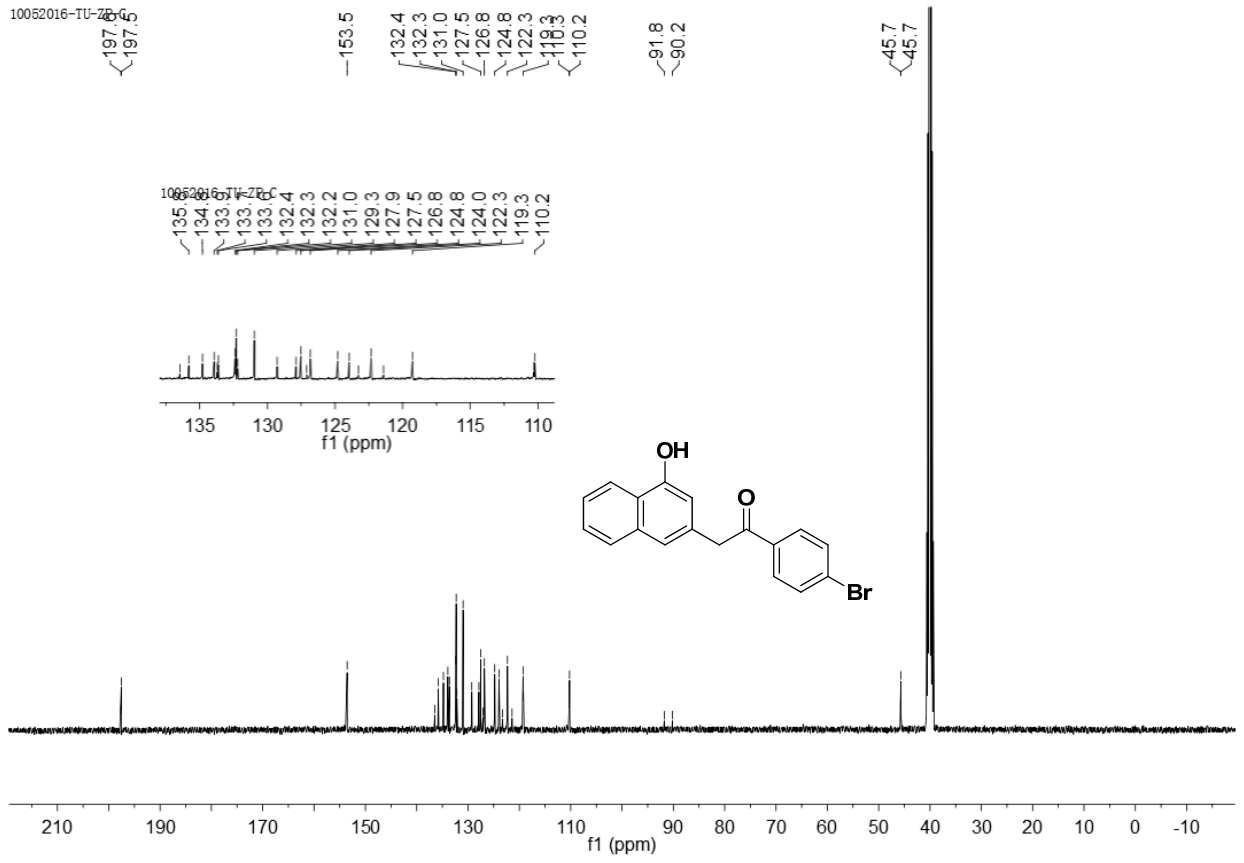



**$^{1}$H NMR Spectrum of Compound 2o**

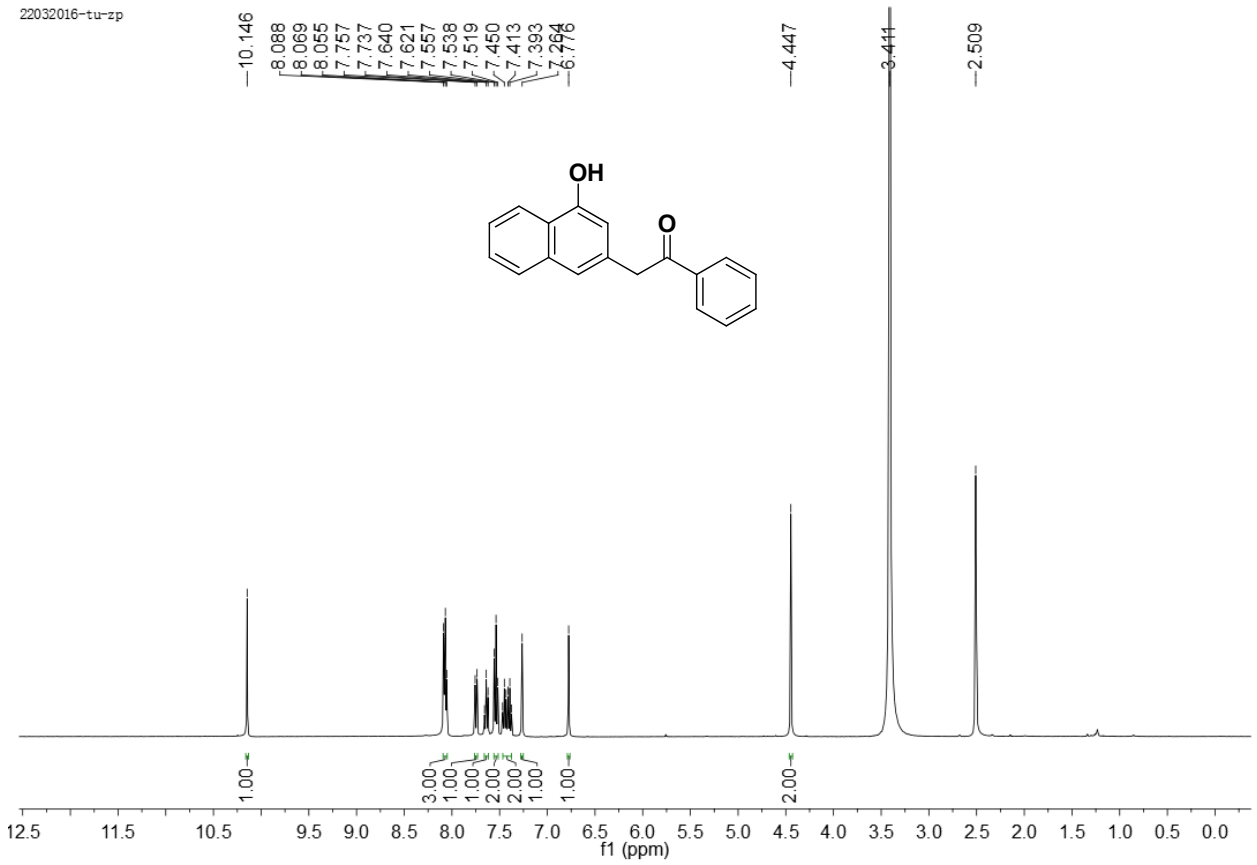



**$^{13}$C NMR Spectrum of Compound 2o**

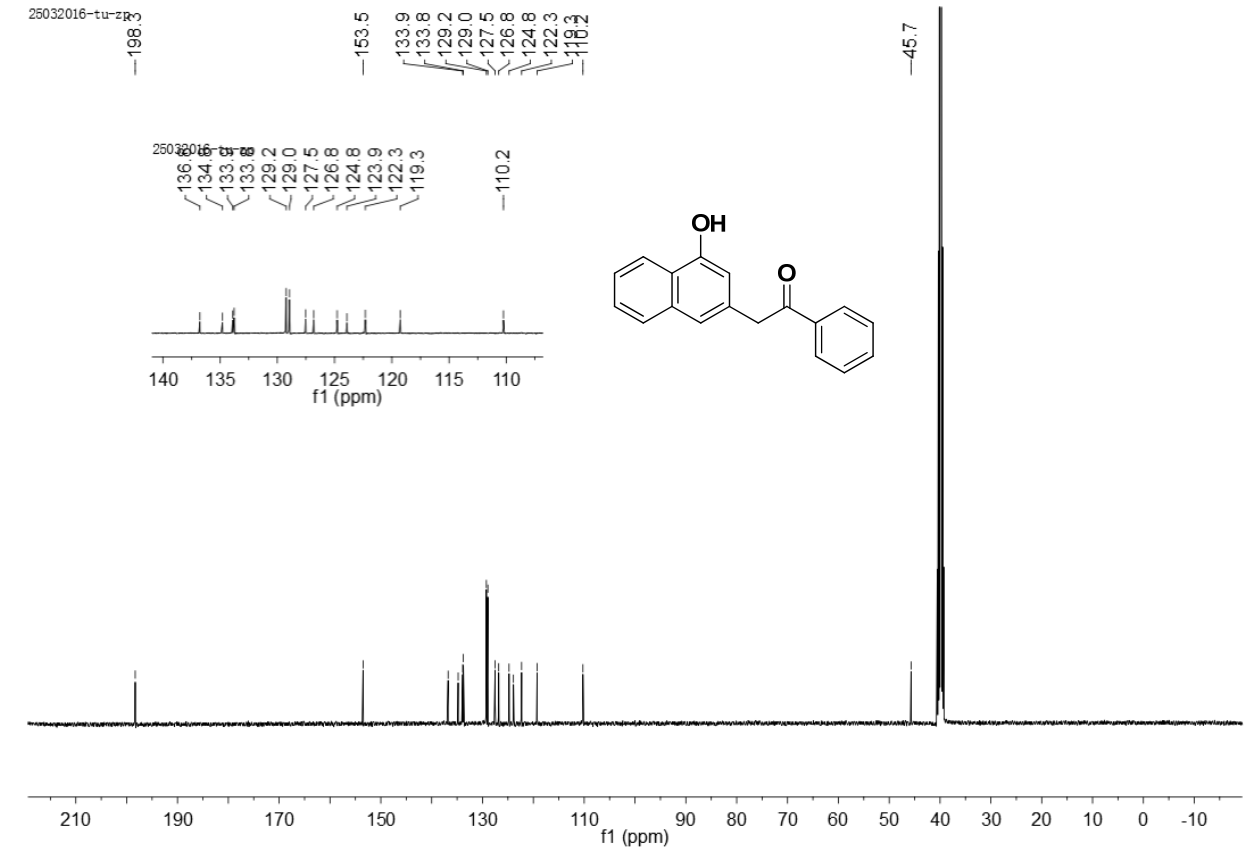

**$^{1}$H NMR Spectrum of Compound 2p**



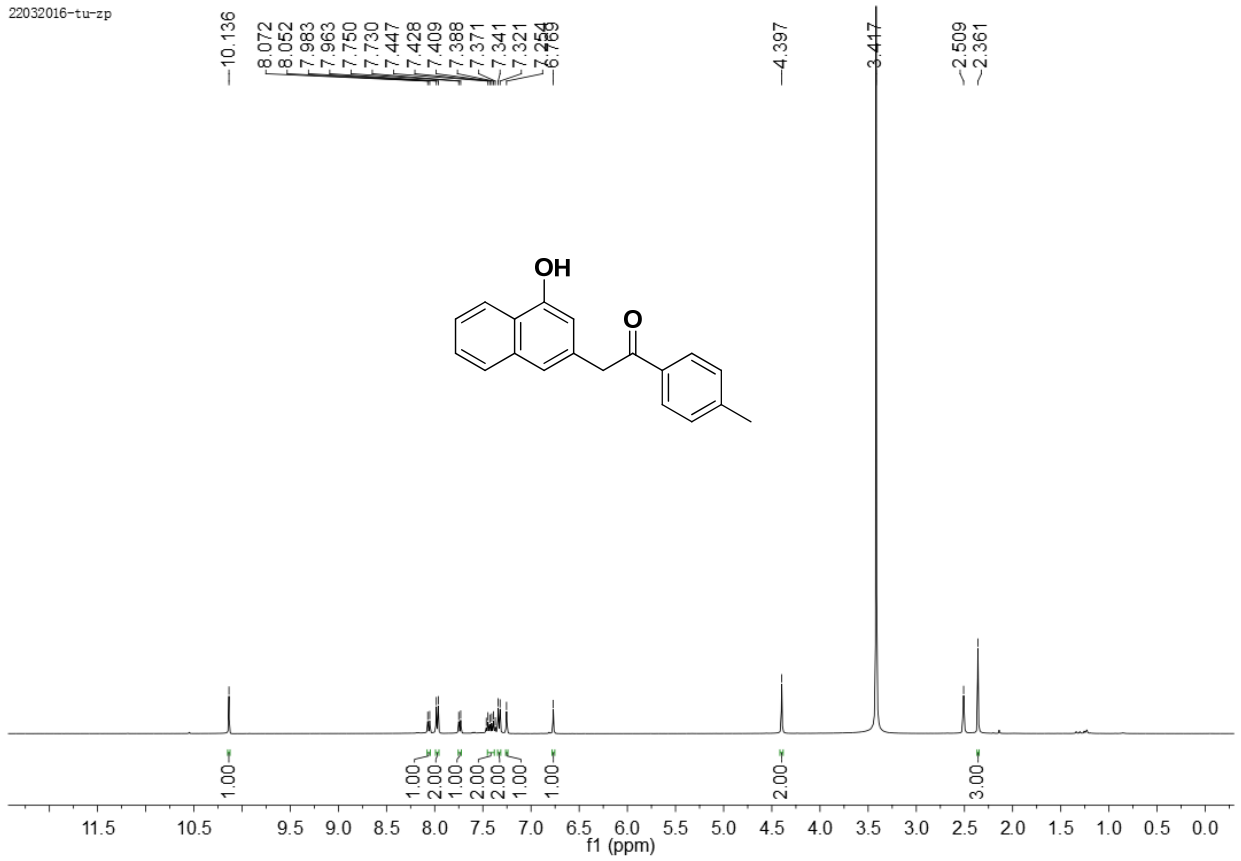

**$^{13}$C NMR Spectrum of Compound 2p**



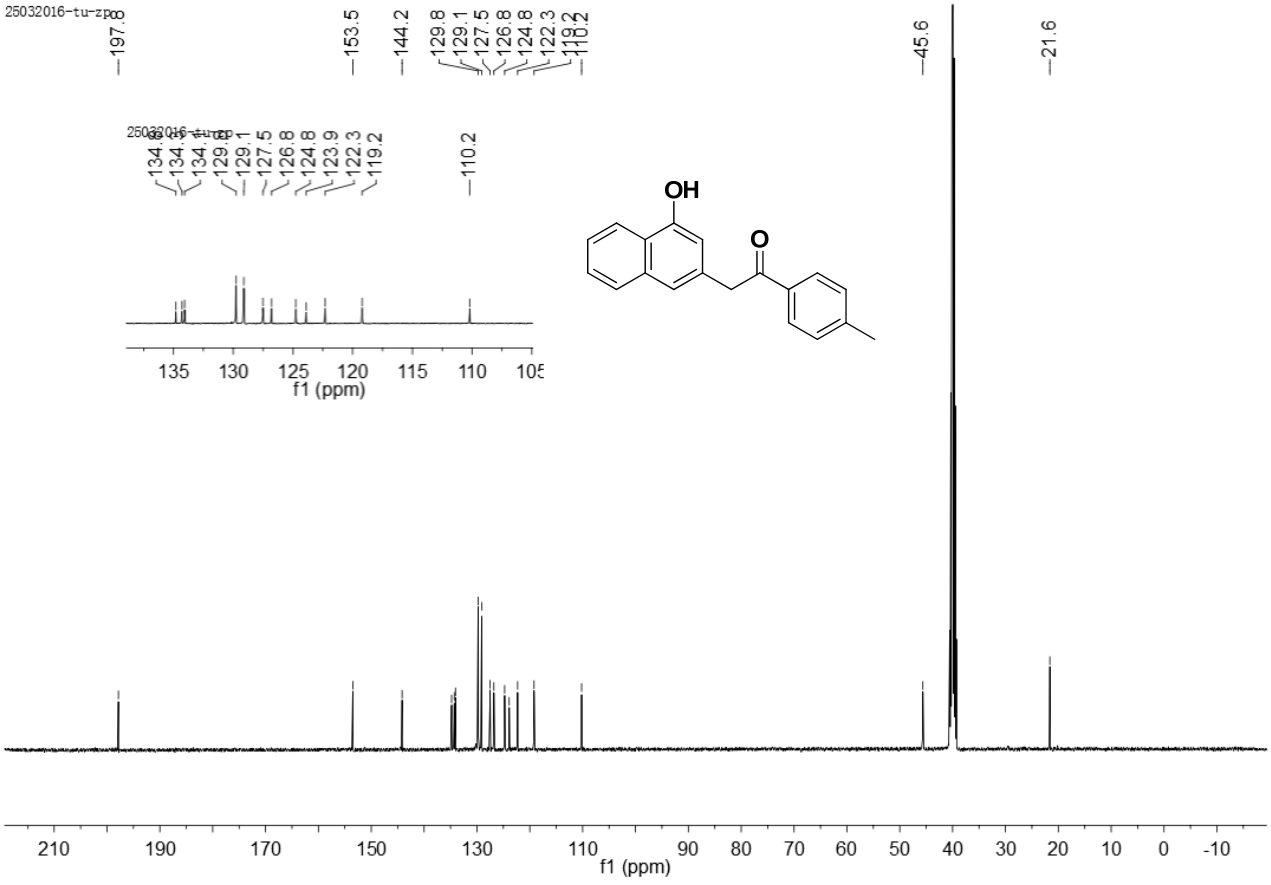

**$^{1}$H NMR Spectrum of Compound 2q**



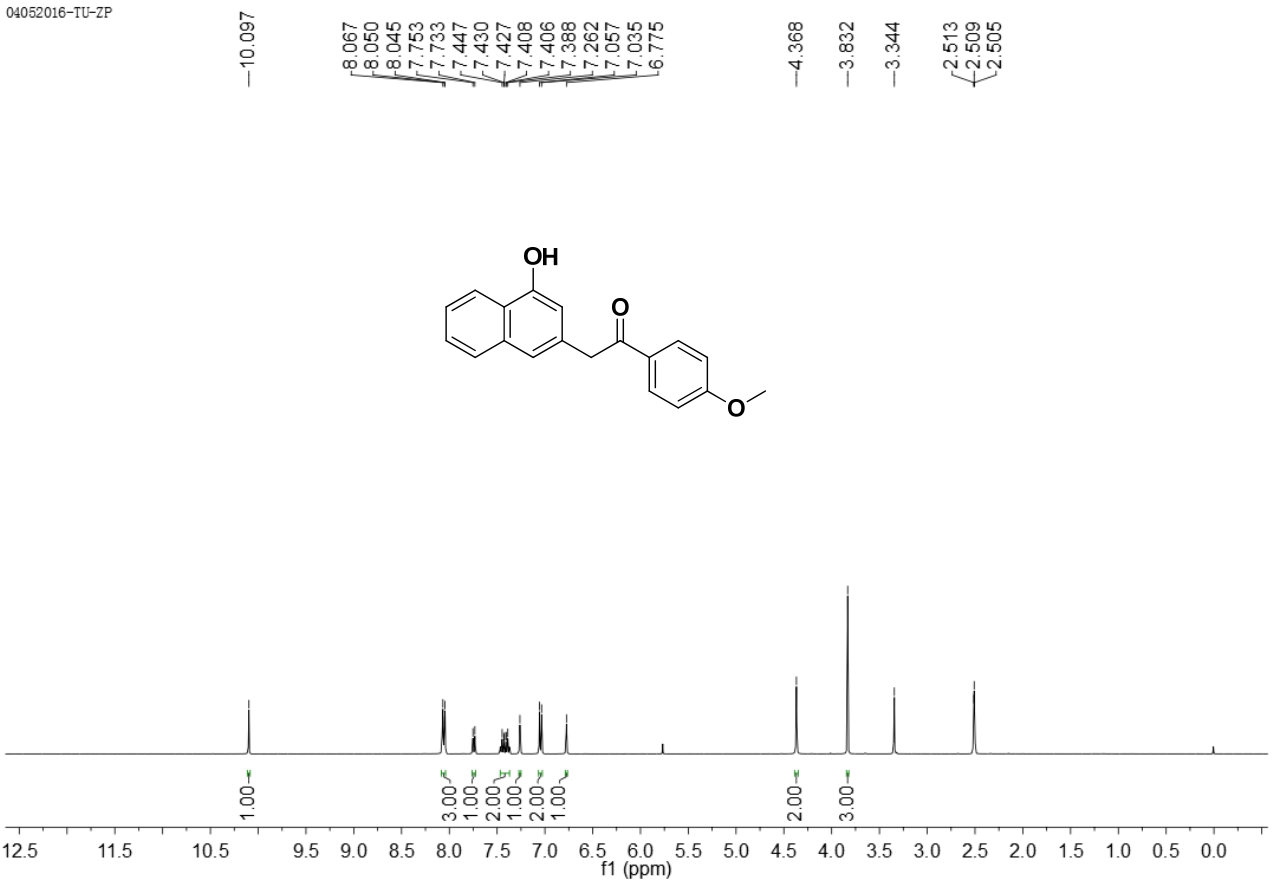

**$^{13}$C NMR Spectrum of Compound 2q**



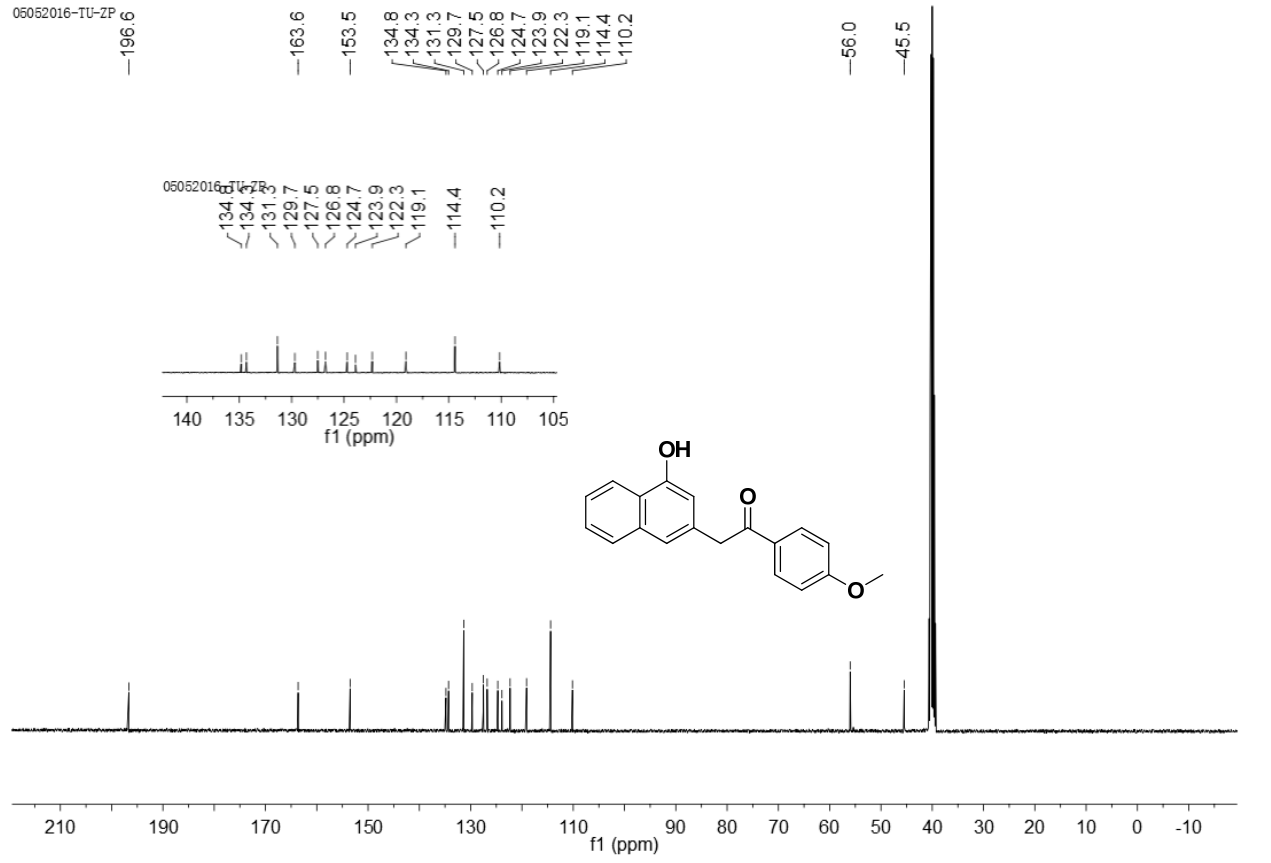

**$^{1}$H NMR Spectrum of Compound 2r**



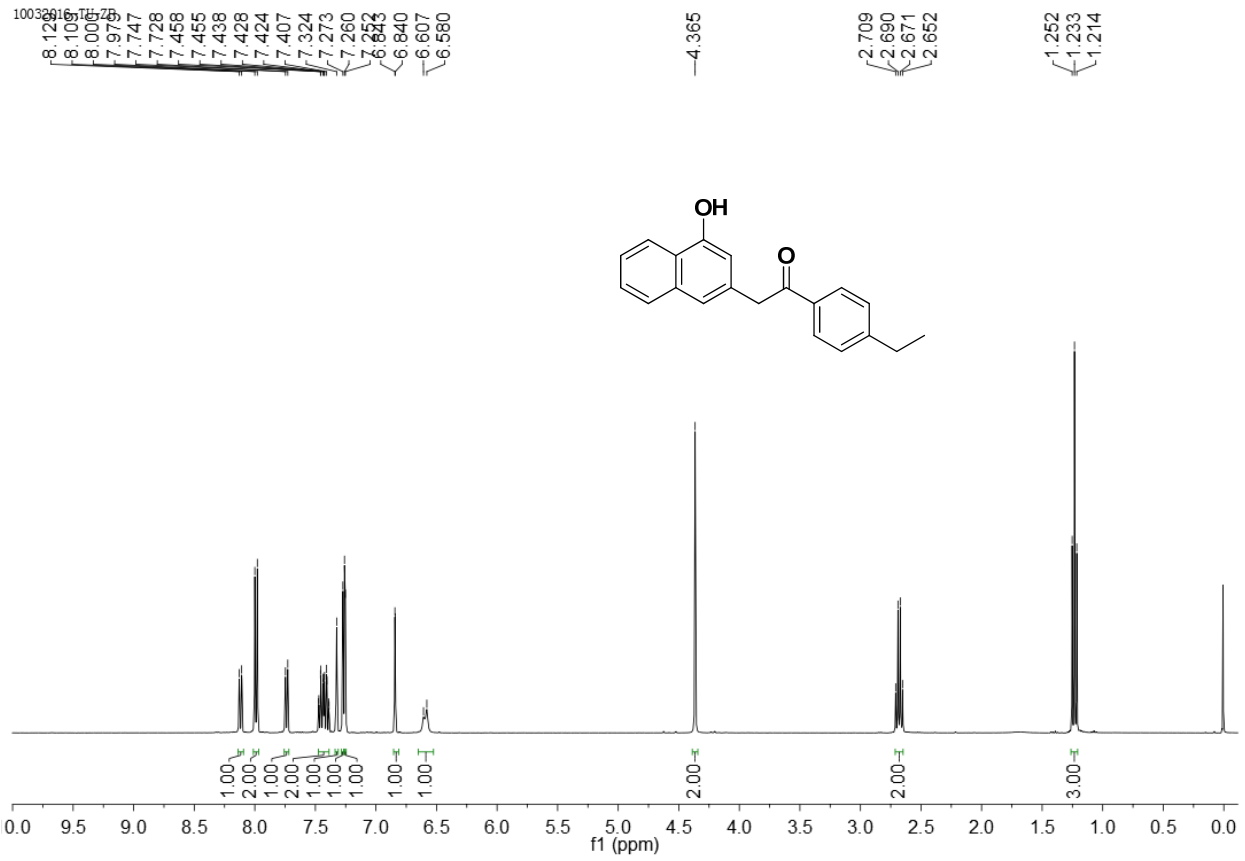

**$^{13}$C NMR Spectrum of Compound 2r**



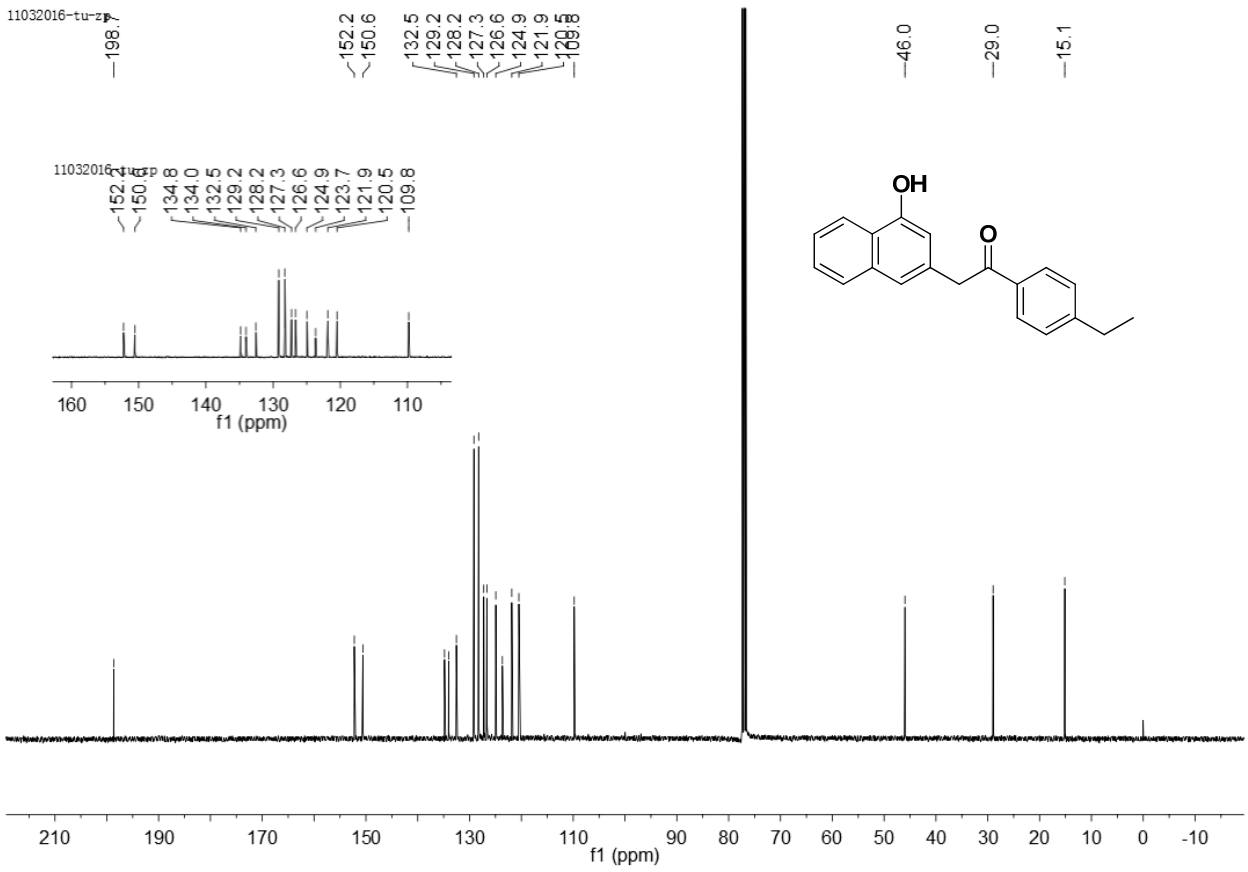

**$^{1}$H NMR Spectrum of Compound 2s**



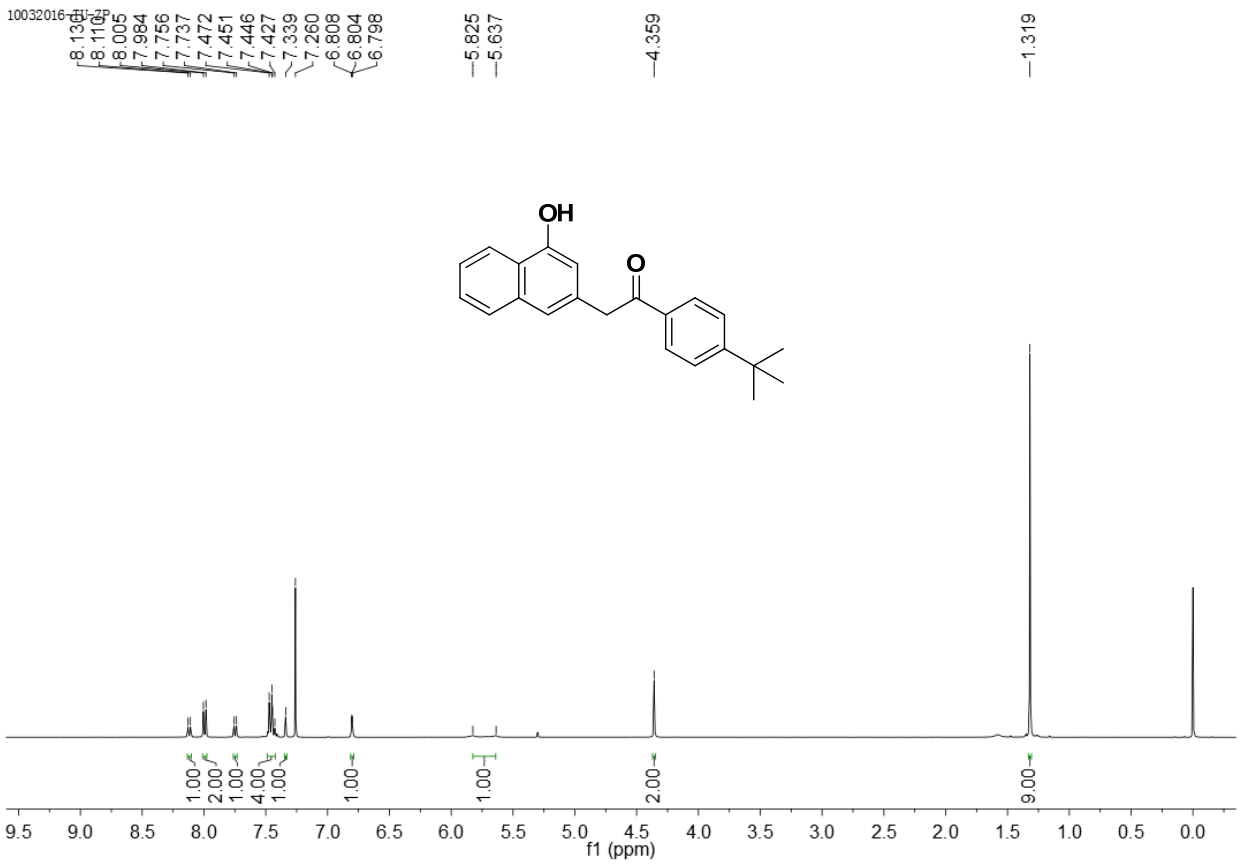

**$^{13}$C NMR Spectrum of Compound 2s**



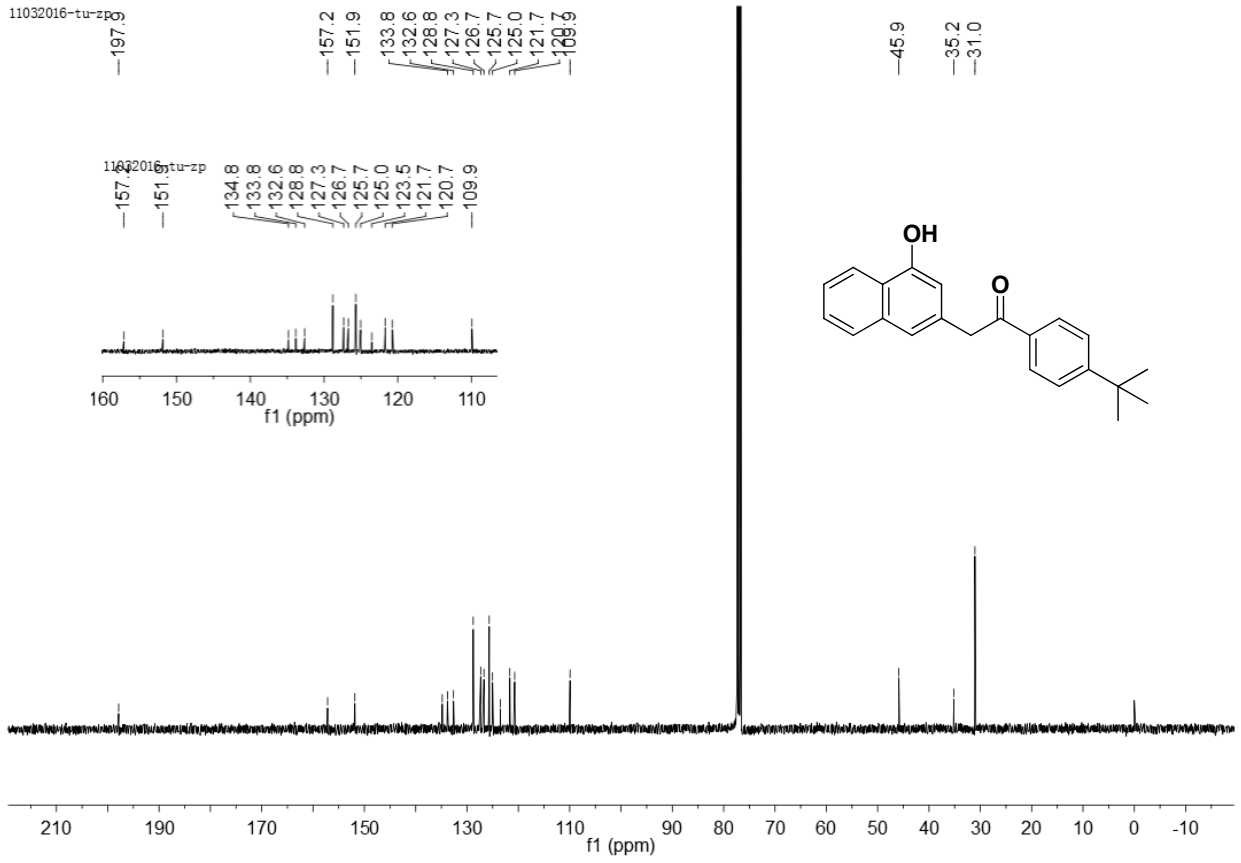

**$^{1}$H NMR Spectrum of Compound 2t**



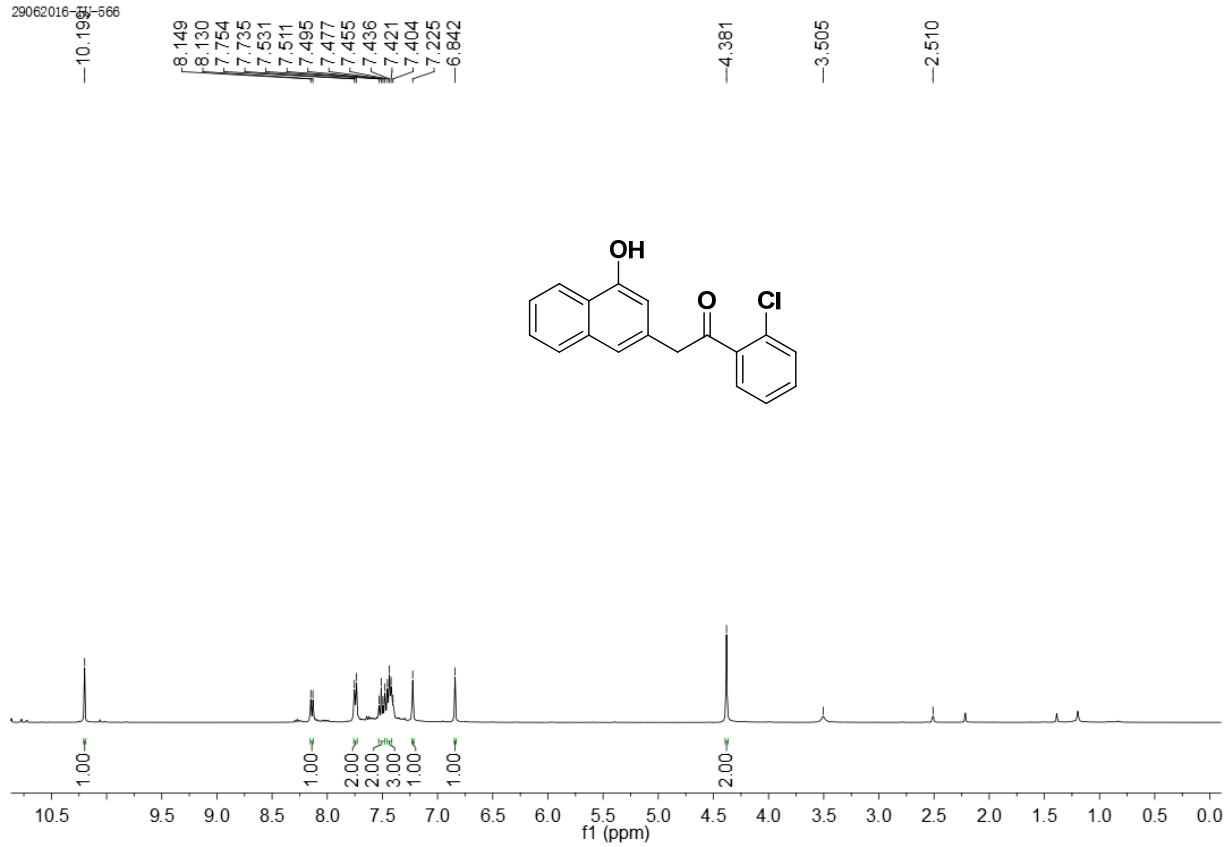

**$^{13}$C NMR Spectrum of Compound 2t**



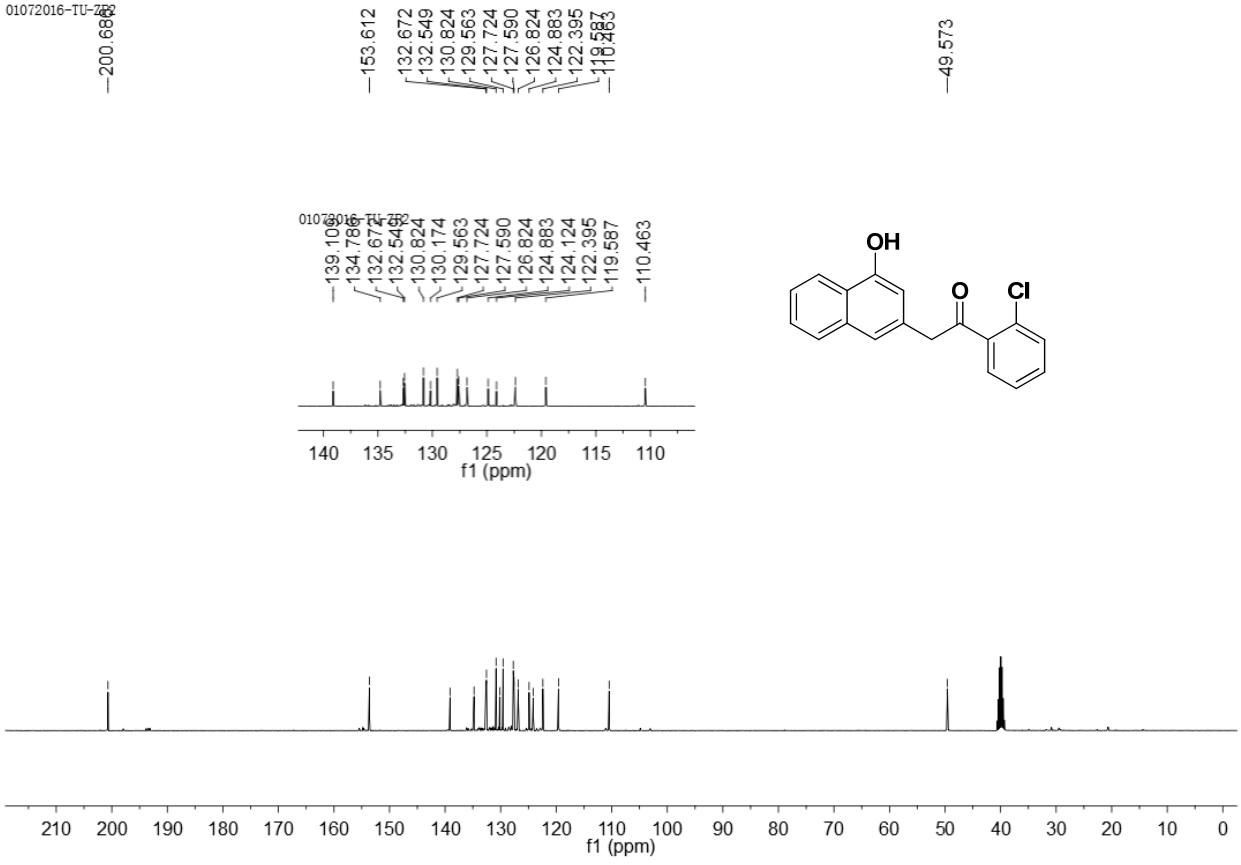

**$^{1}$H NMR Spectrum of Compound 2u**



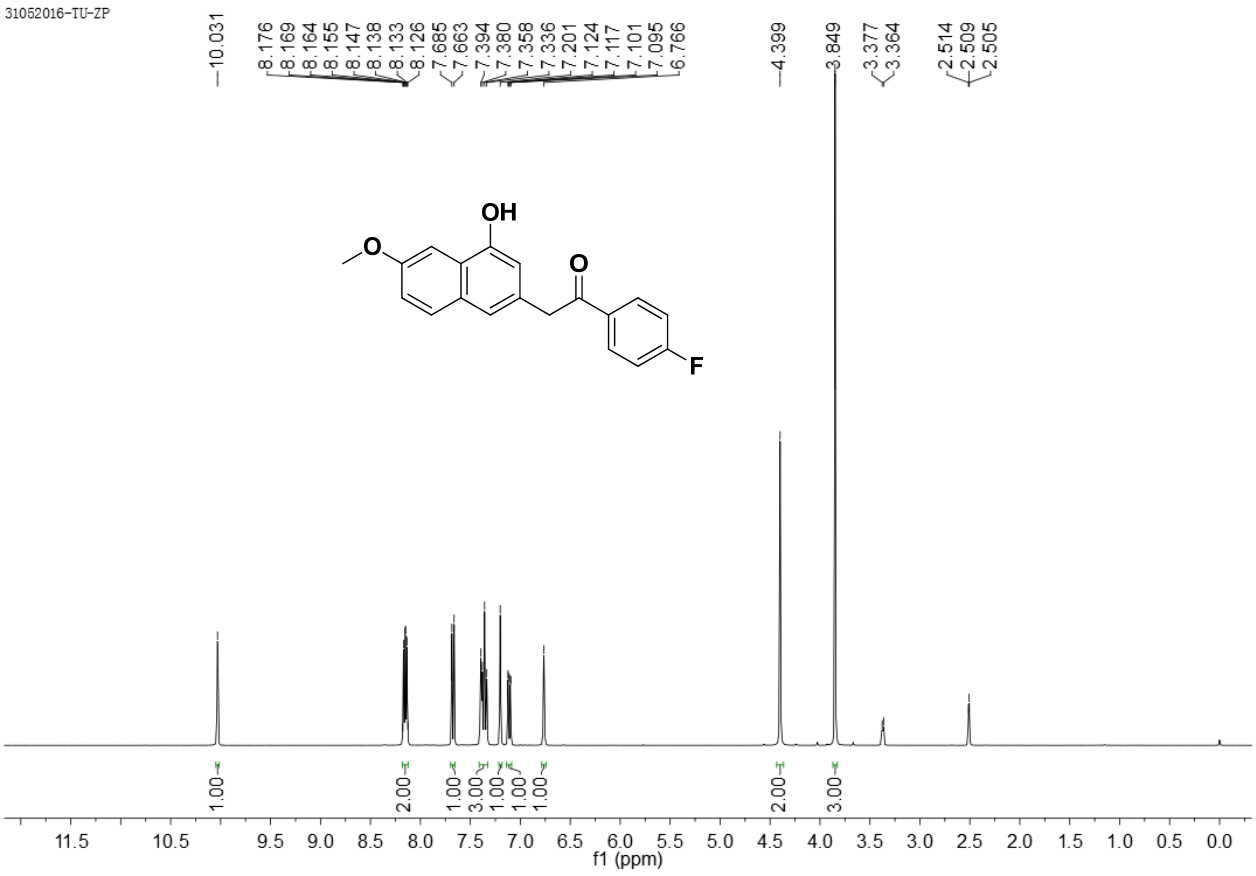

**$^{13}$C NMR Spectrum of Compound 2u**



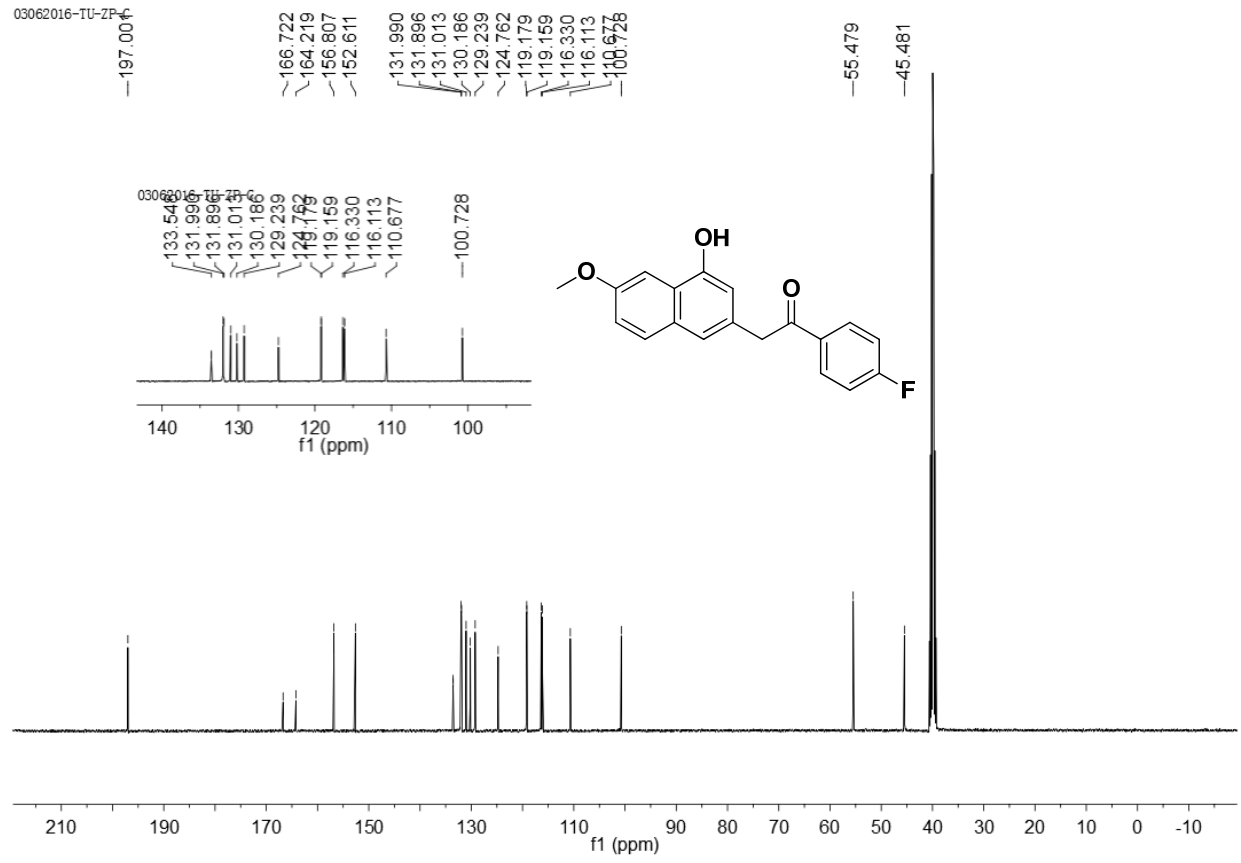

**$^{1}$H NMR Spectrum of Compound 2v**



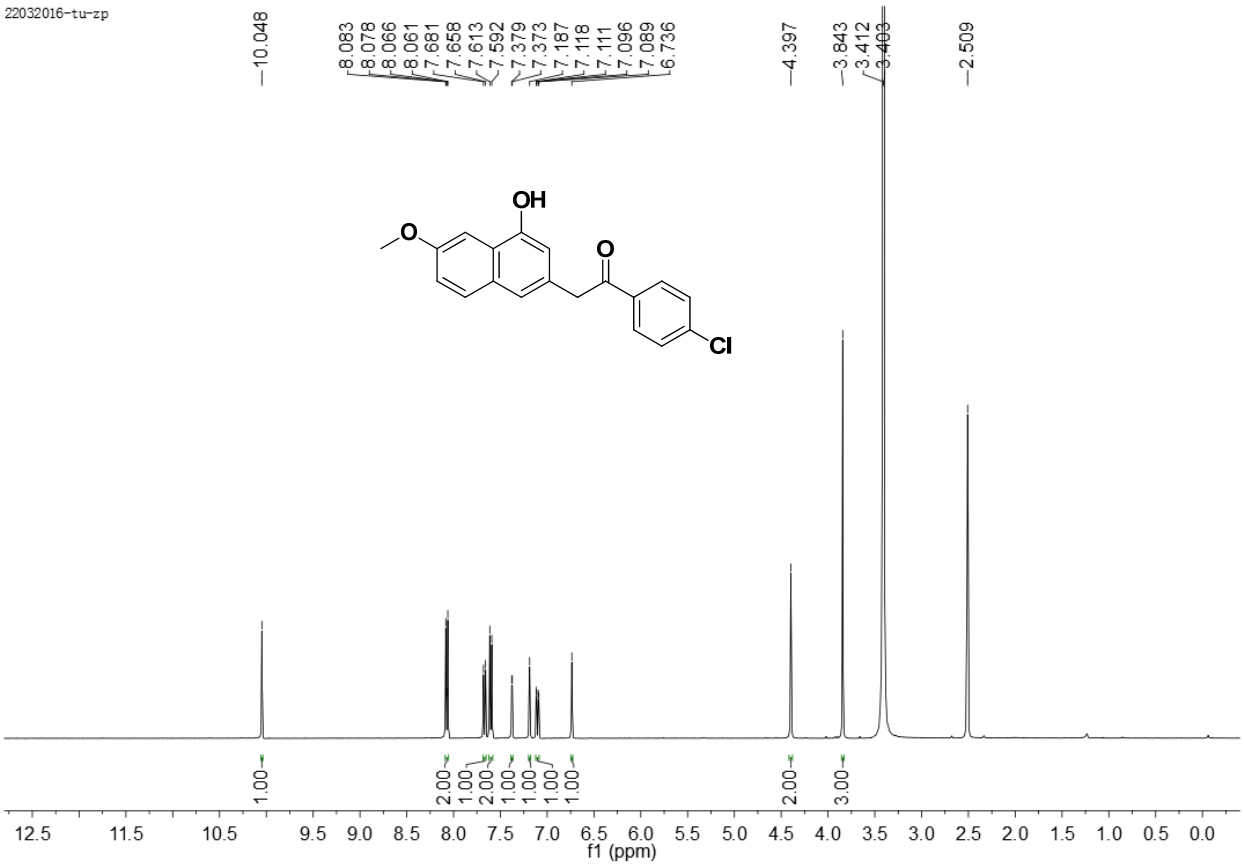

**$^{13}$C NMR Spectrum of Compound 2v**



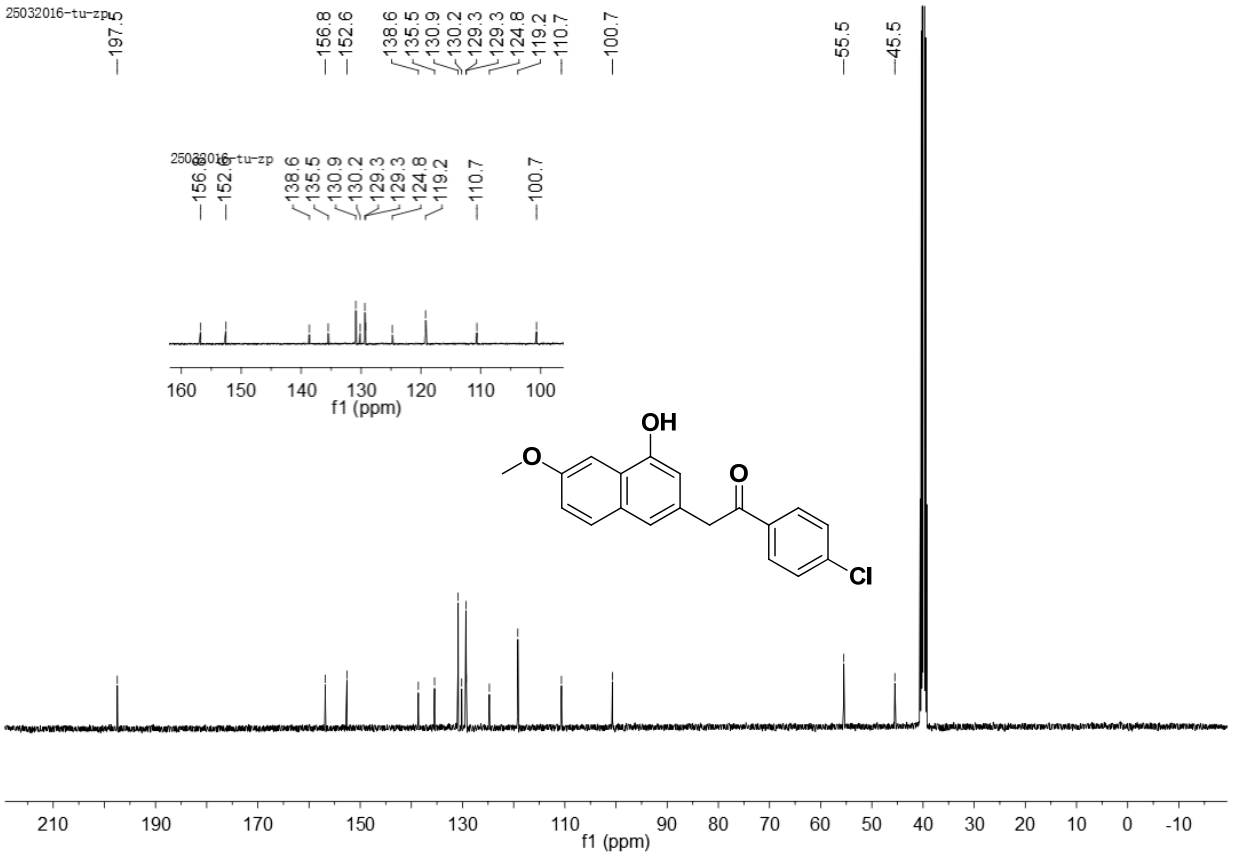

**$^{1}$H NMR Spectrum of Compound 2x**



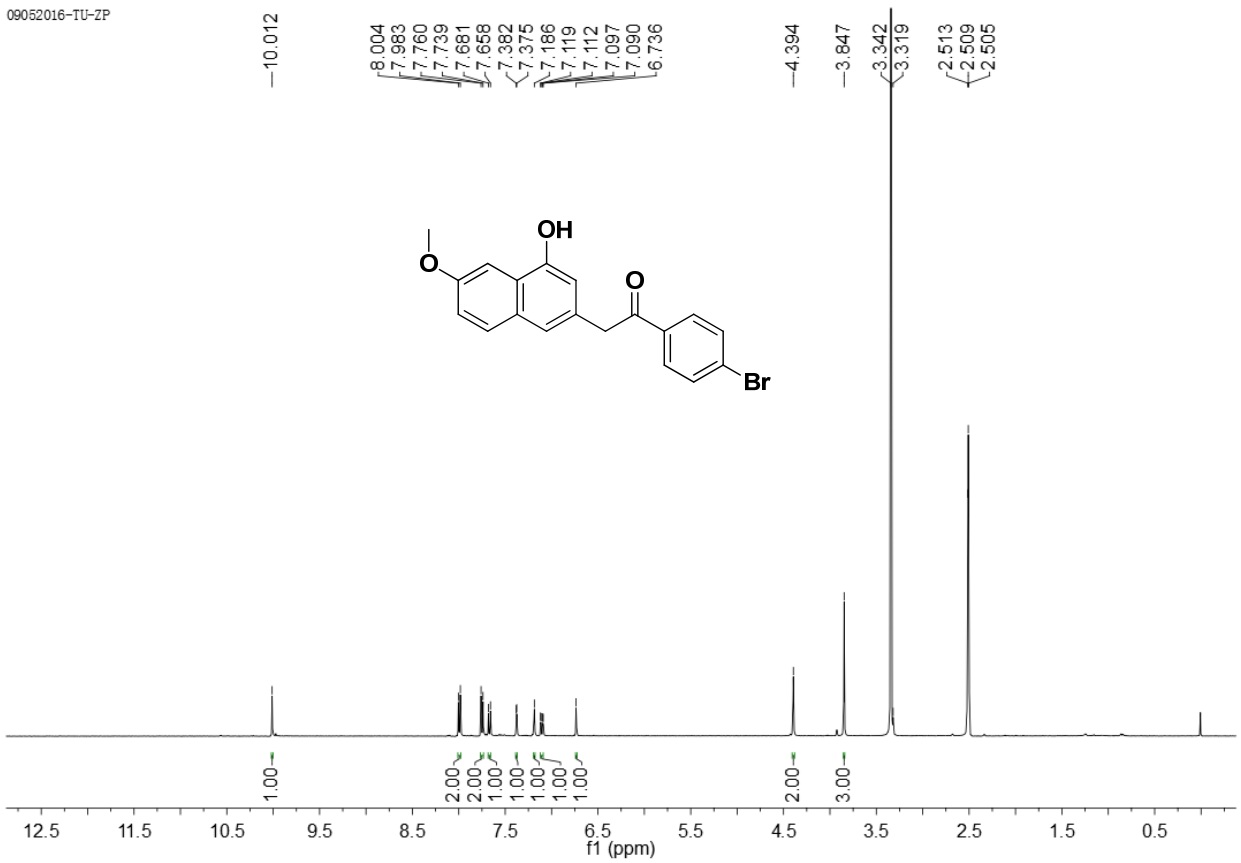

**$^{13}$C NMR Spectrum of Compound 2x**



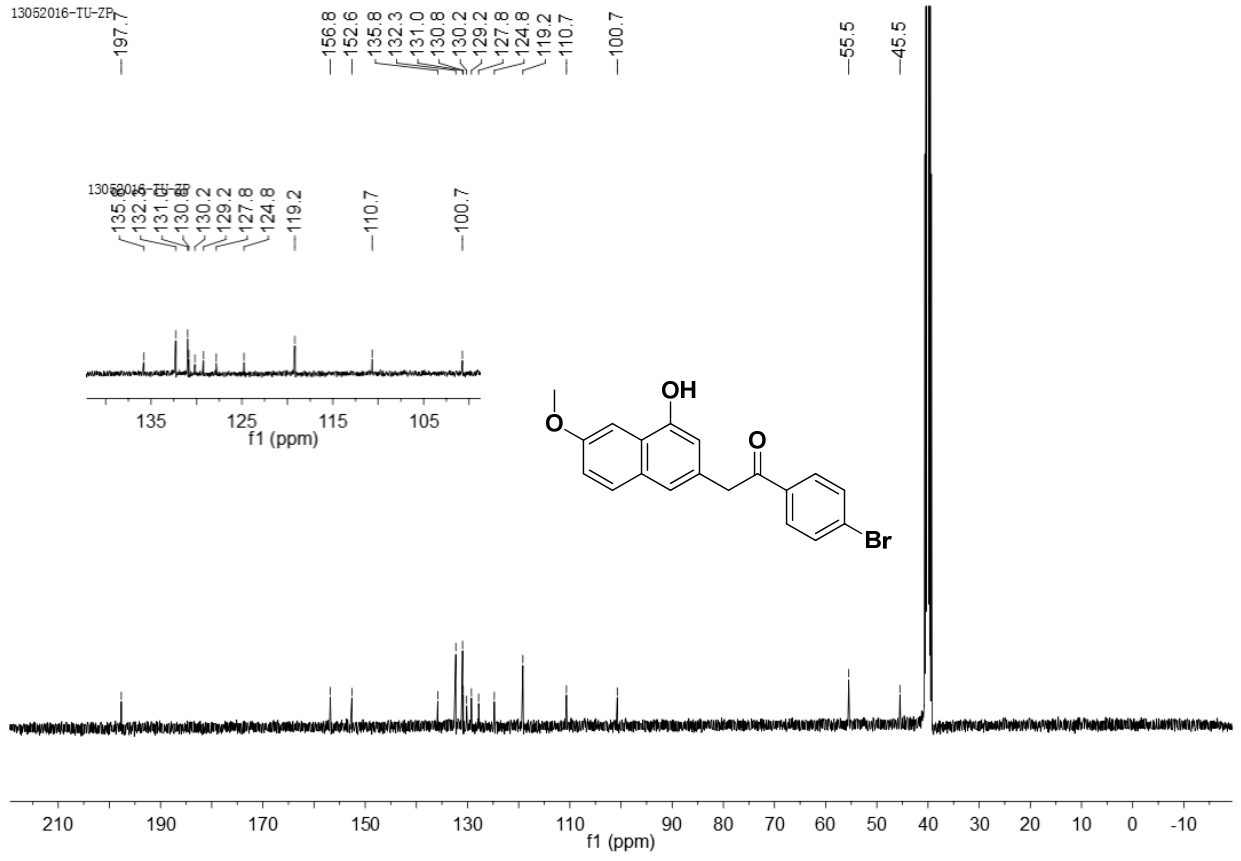

**$^{1}$H NMR Spectrum of Compound 2y**



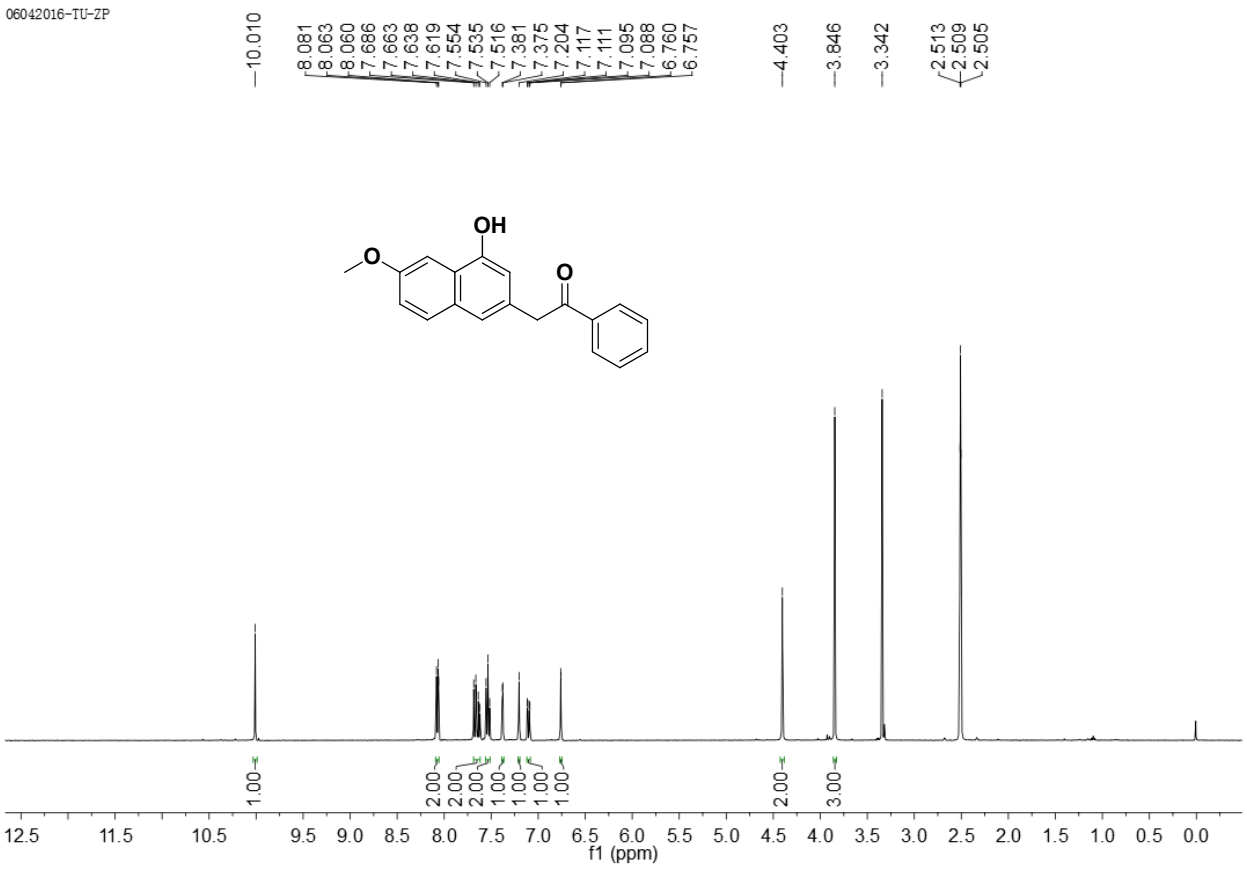

**$^{13}$C NMR Spectrum of Compound 2y**



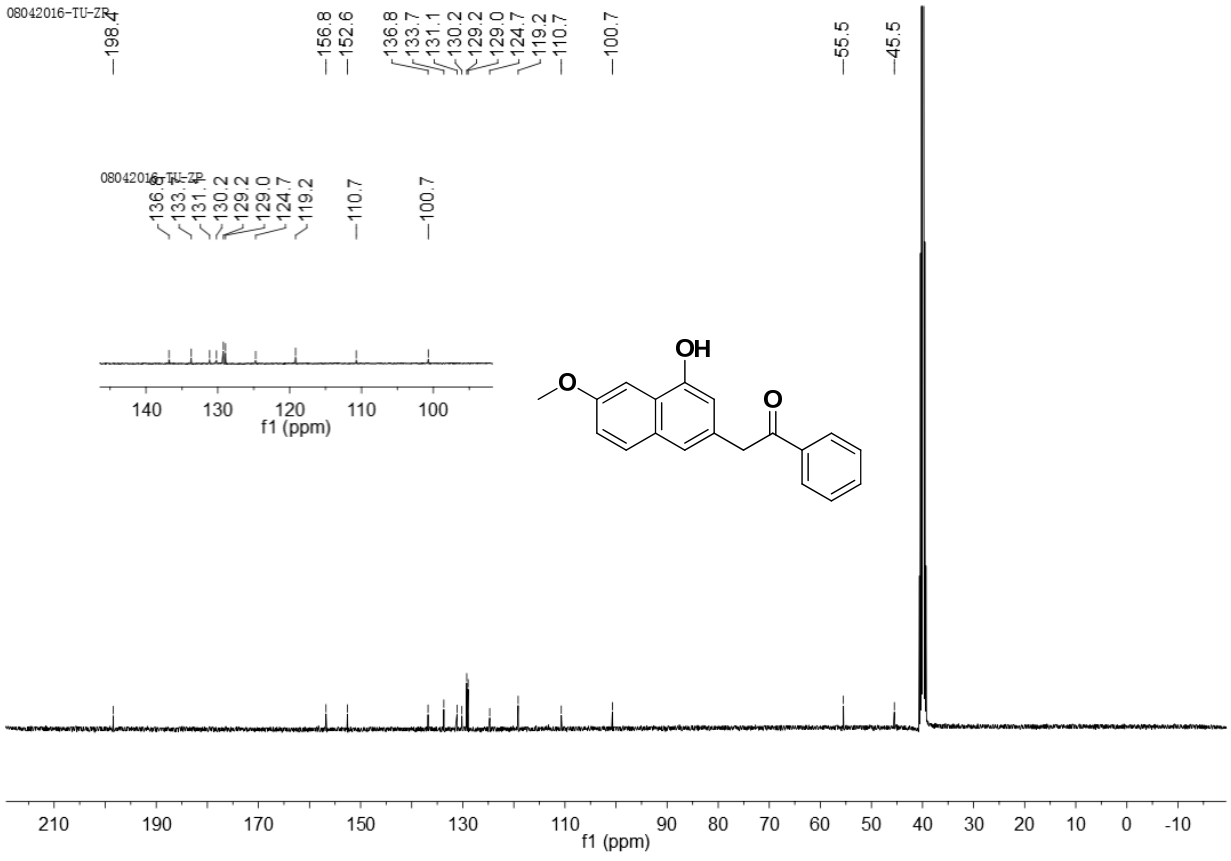

**$^{1}$H NMR Spectrum of Compound 2z**



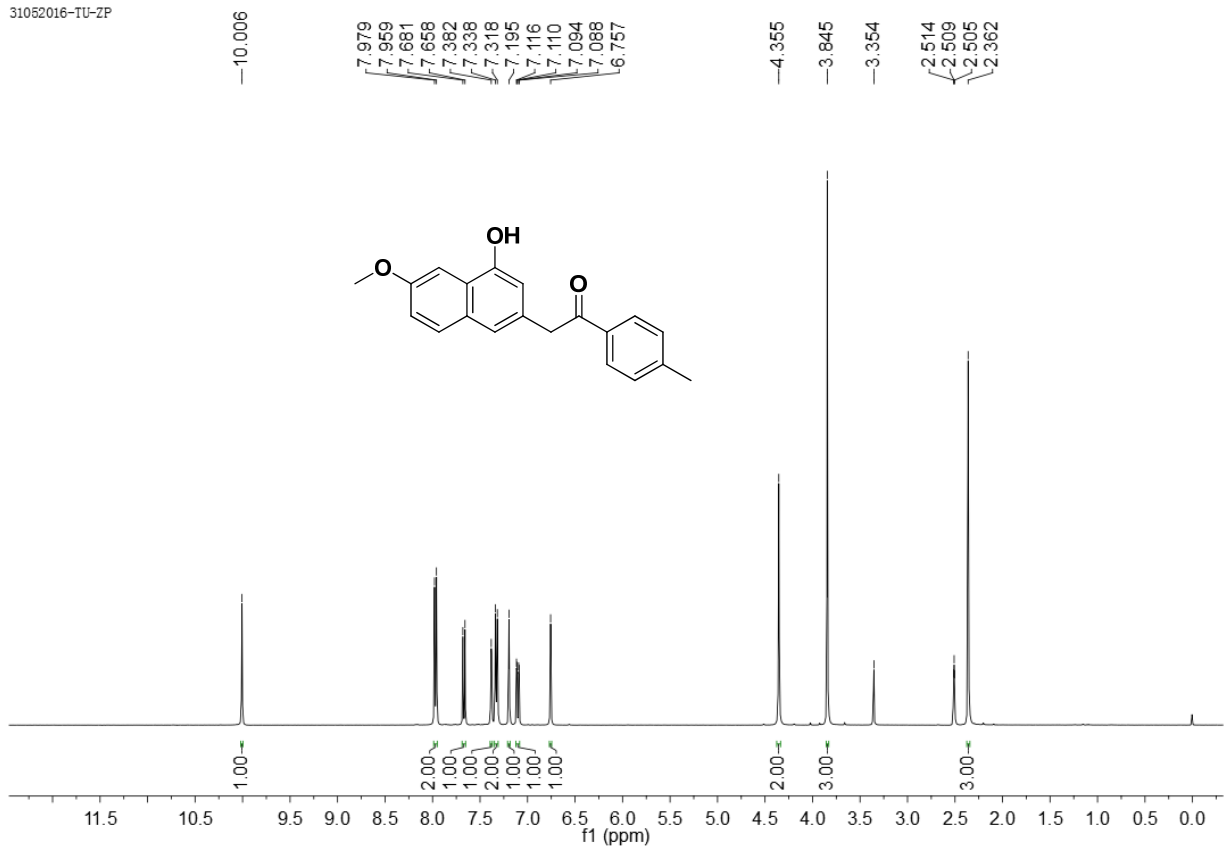

**$^{13}$C NMR Spectrum of Compound 2z**



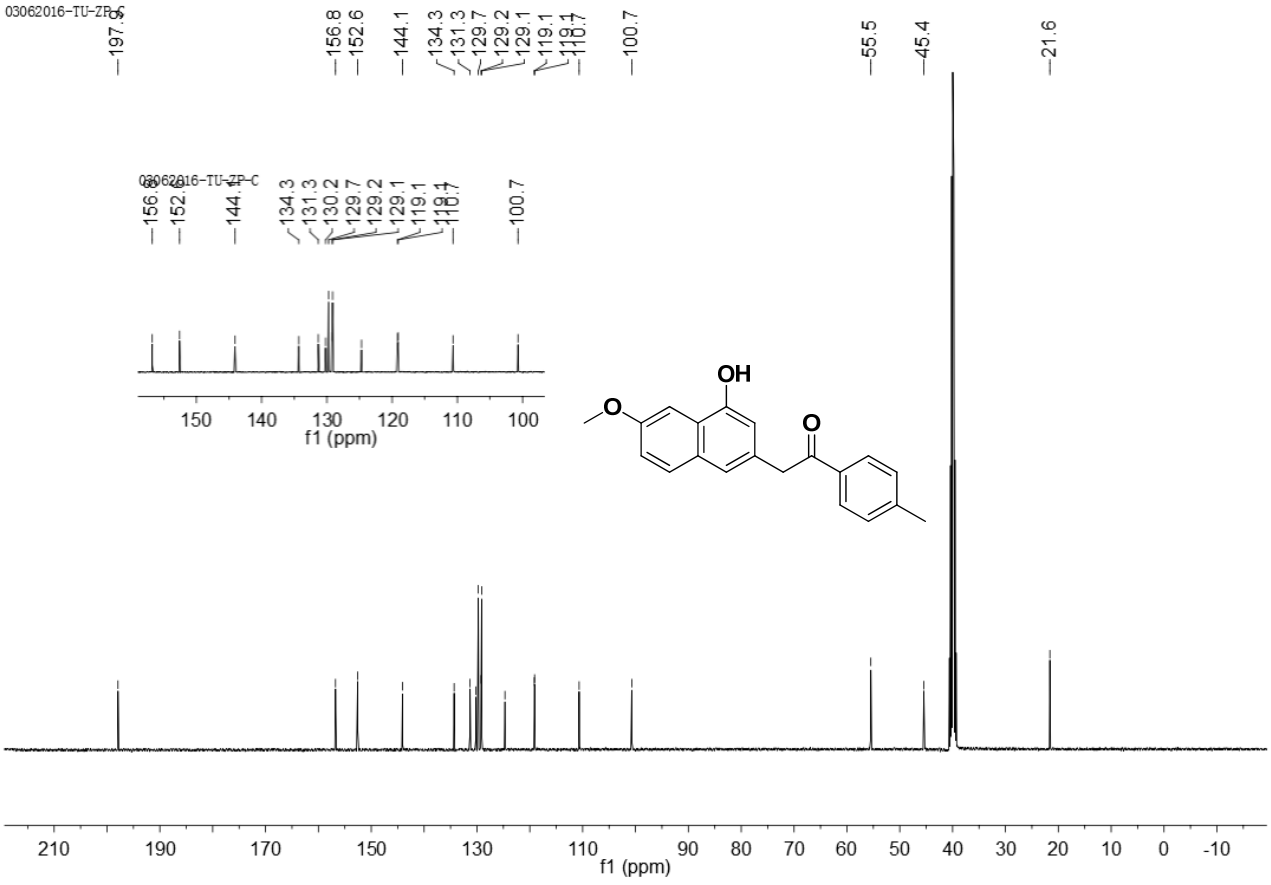

**$^{1}$H NMR Spectrum of Compound 2aa**



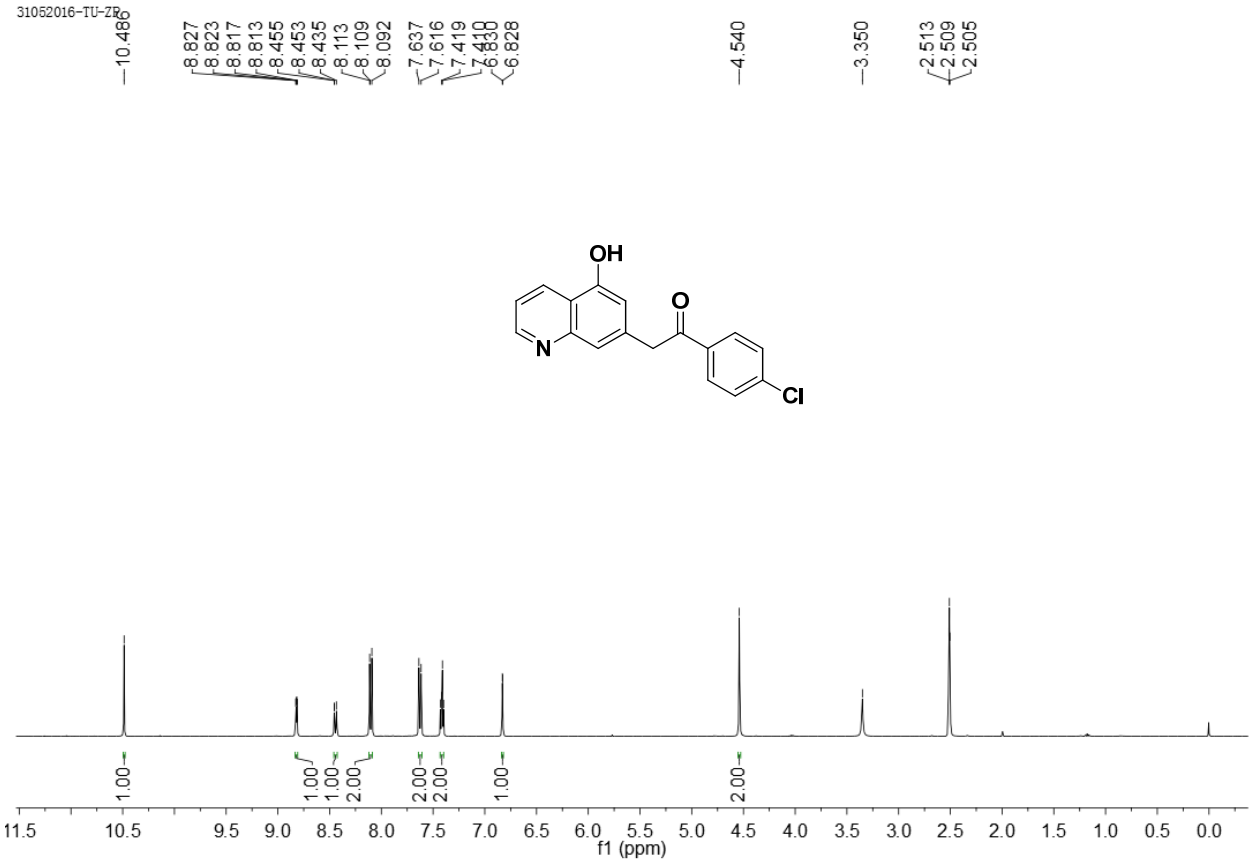

**$^{13}$C NMR Spectrum of Compound 2aa**



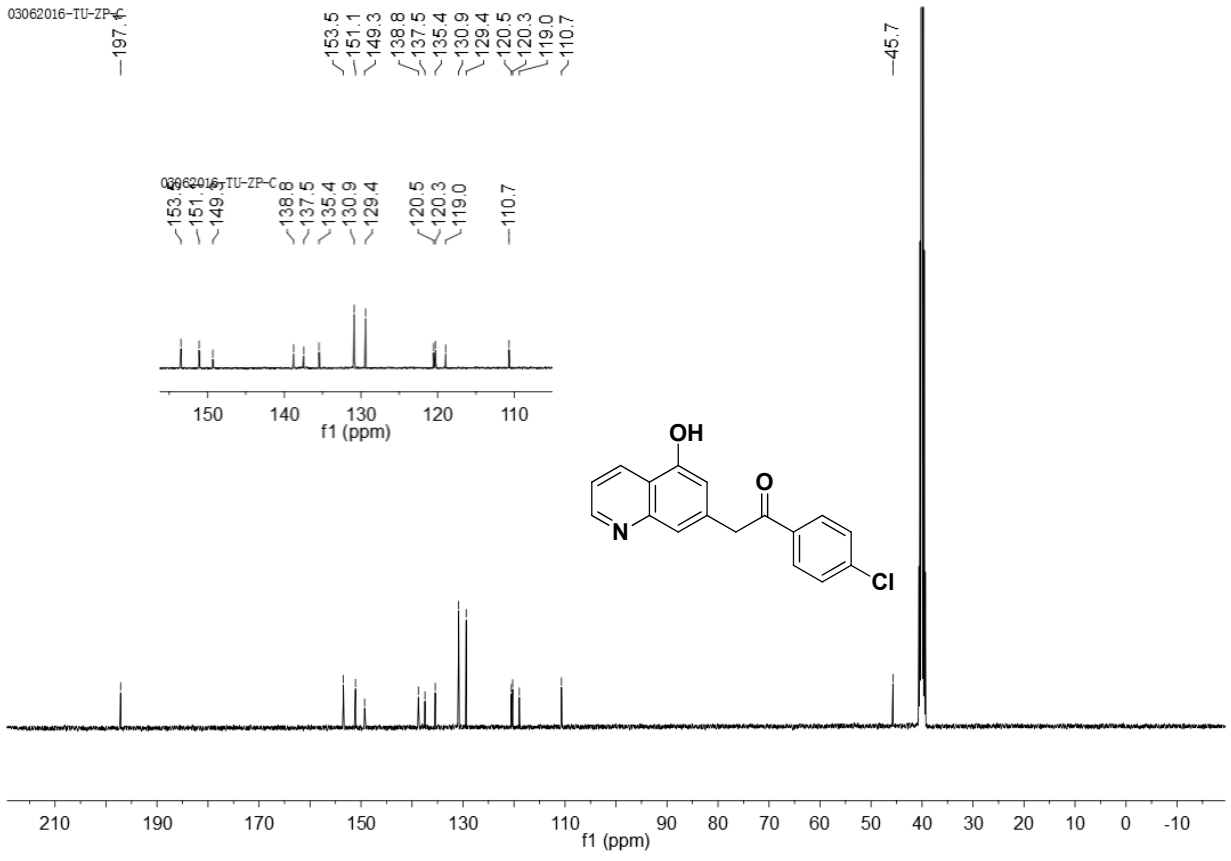

**$^{1}$H NMR Spectrum of Compound 2bb**



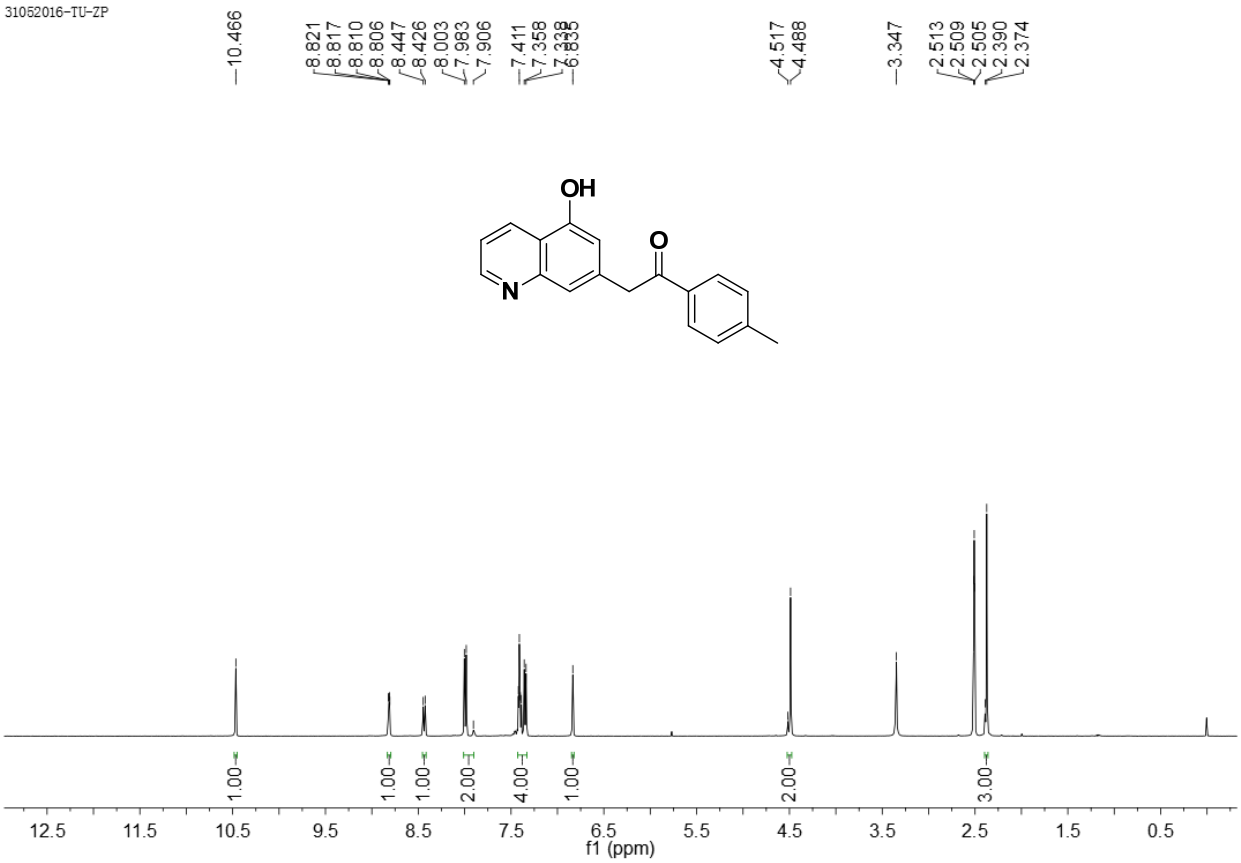

**$^{13}$C NMR Spectrum of Compound 2bb**



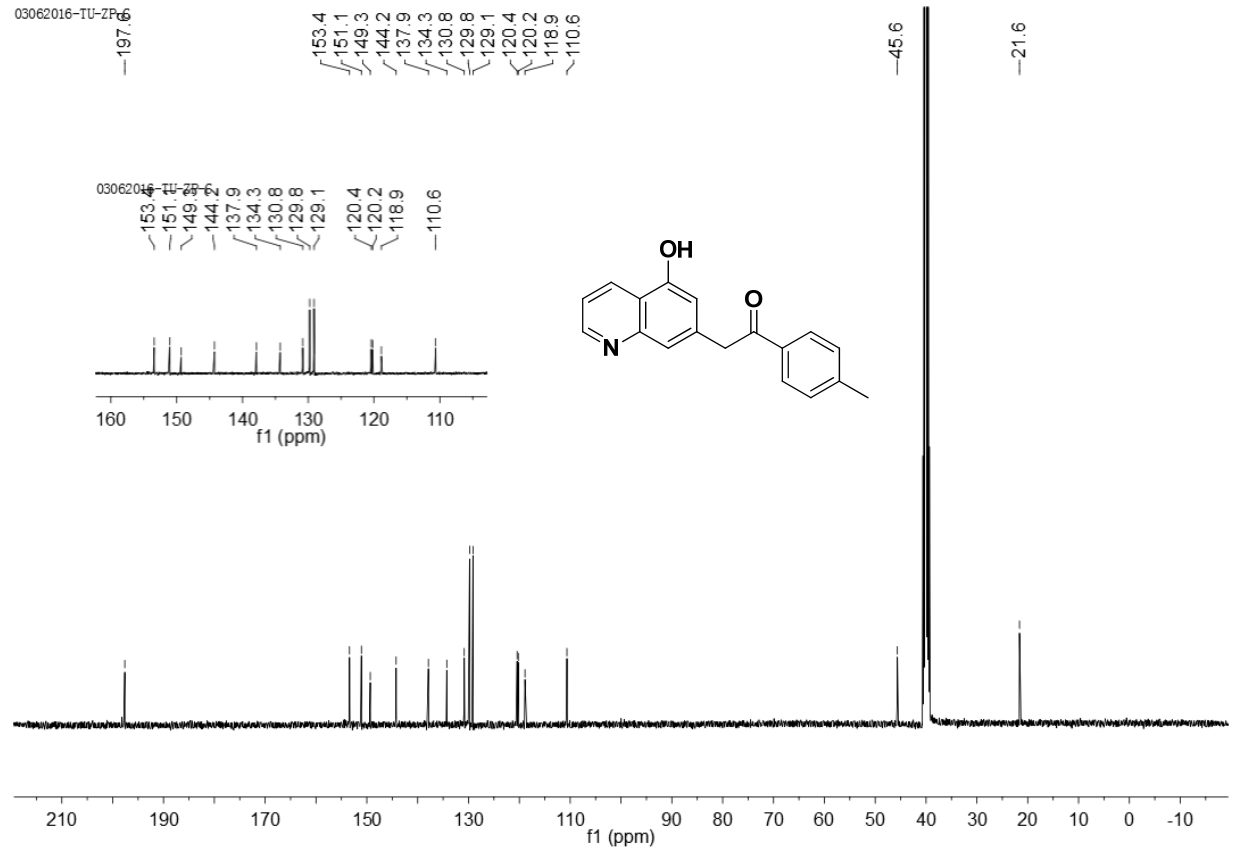

**$^{1}$H NMR Spectrum of Compound 2cc**



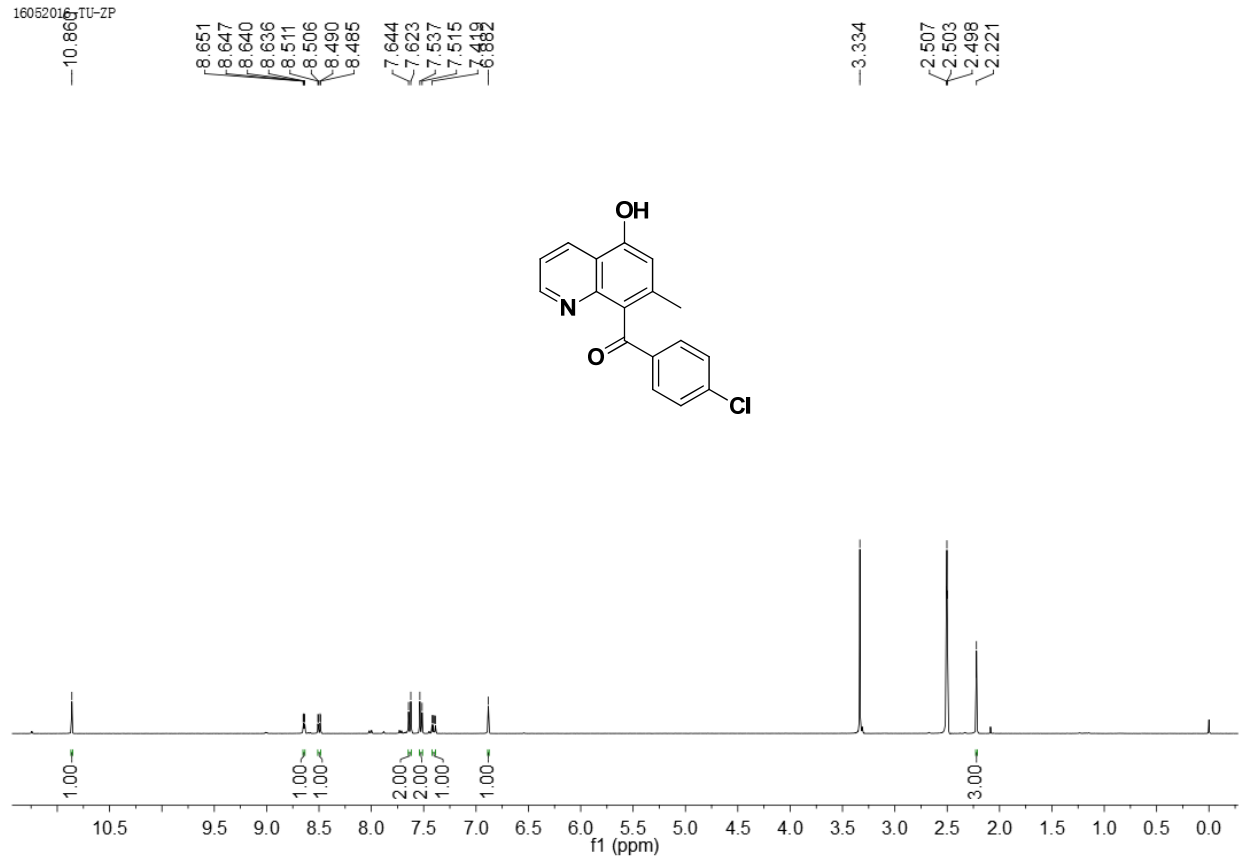

**$^{13}$C NMR Spectrum of Compound 2cc**



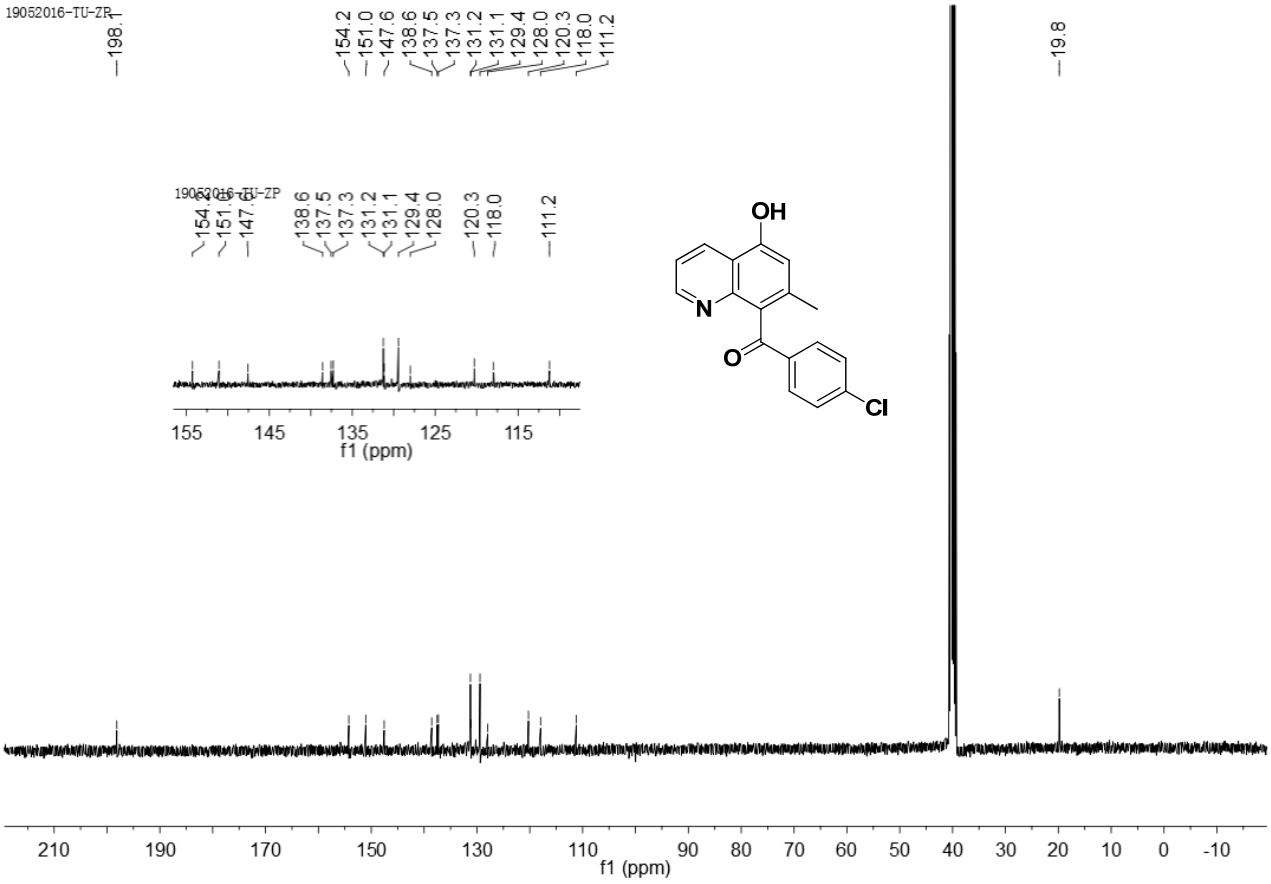

**$^{1}$H NMR Spectrum of Compound 2dd**



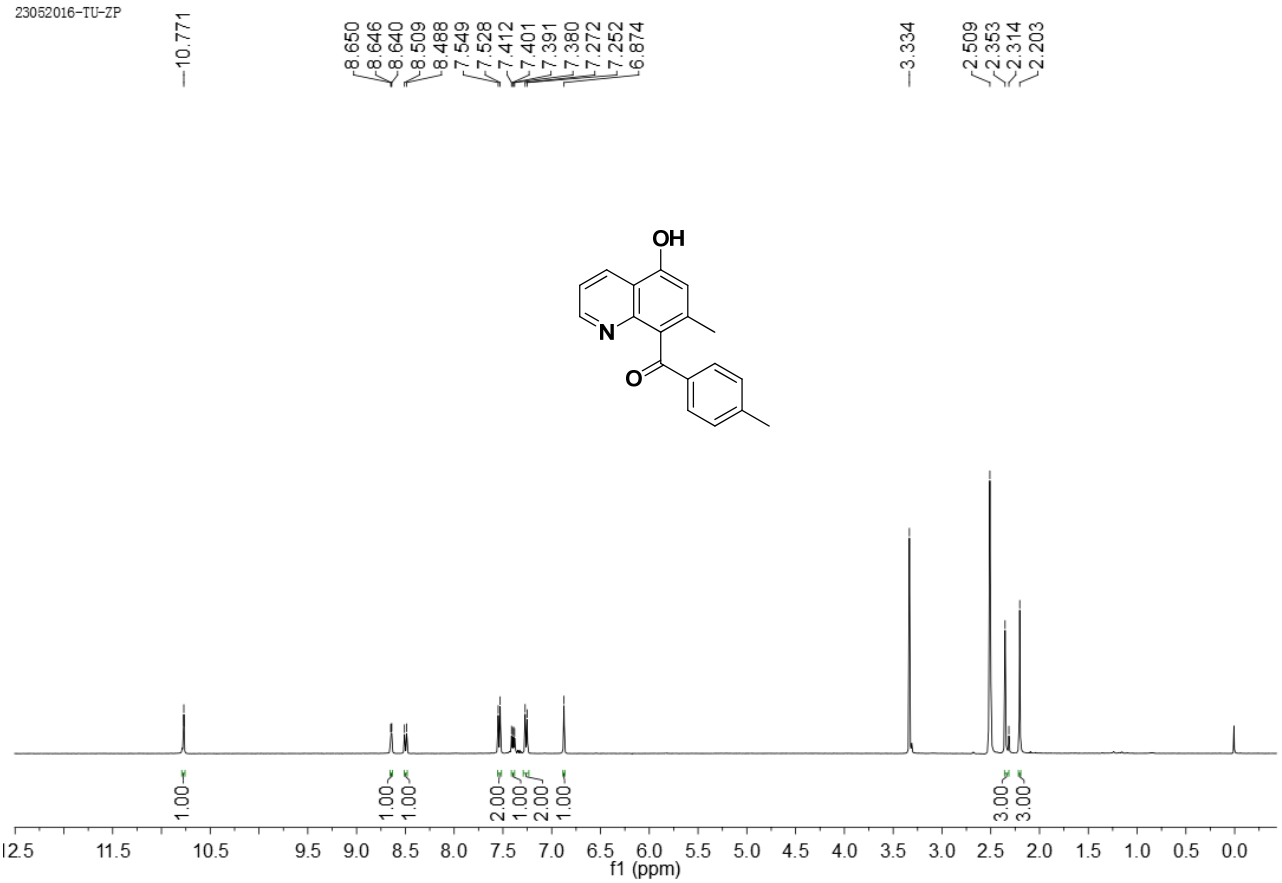

**$^{13}$C NMR Spectrum of Compound 2dd**



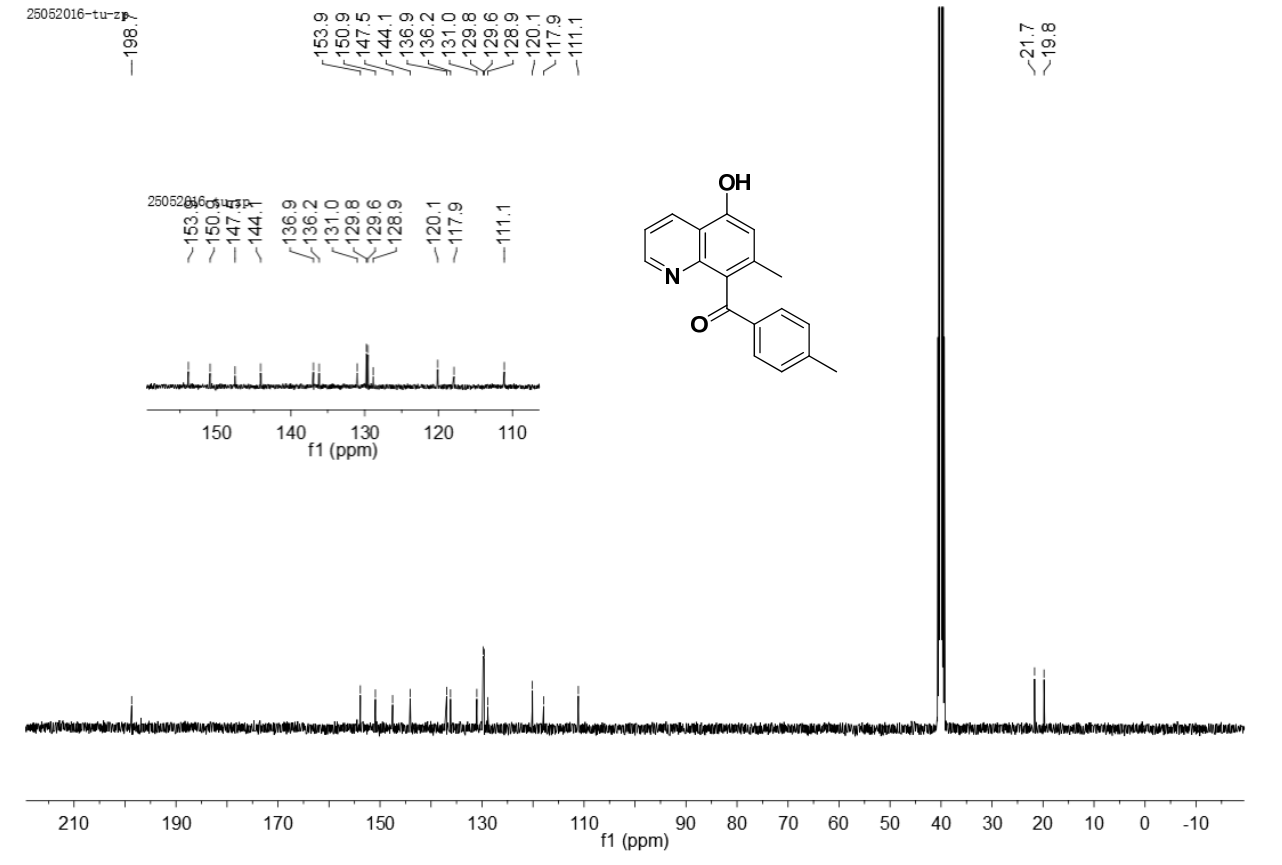

**$^{1}$H NMR Spectrum of Compound 4a**




**$^{13}$C NMR Spectrum of Compound 4a**




**$^{1}$H NMR Spectrum of Compound 4b**




**$^{13}$C NMR Spectrum of Compound 4b**