Supporting Information

Atom-economic synthesis of cyclobuta[*a*]naphthalen-4-ols *via* base-promoted [2 + 2] cycloaddition/1,6-nucleophilic addition cascades

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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 (δ) 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.

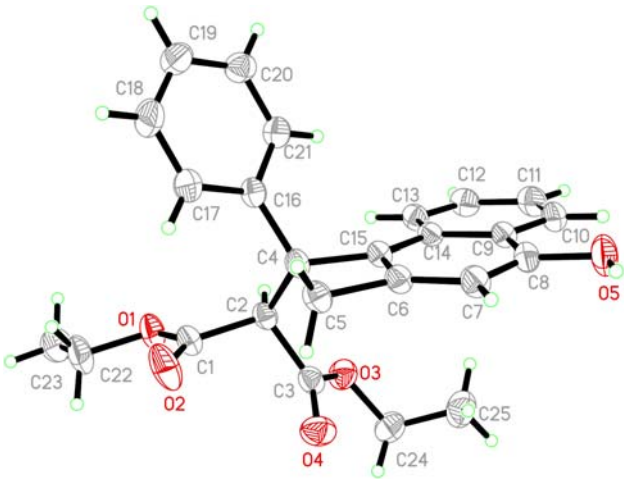


Figure S1. X-Ray Structure of Product **3a** (The ellipsoid contour 30% probability levels)

A single crystal **3a** was obtained by slowly evaporating 95% EtOH solvent at room temperature under the air conditions. Its dimensions of 0.45 mm × 0.40 mm × 0.39 mm was mounted on a Siemens P1 diffractometer equipped with a graphite mono-chromated MoKa (λ = 0.71073 Å) radiation at 298(2) K. A total of 5324 reflections were collected in the 2.24<θ<25.01° range by using an ω scan mode and 3609 were independent (R_{int} = 0.0248), of which 2305 with $I > 2\sigma(I)$ were observed. The calculations were performed with SHELXS-97 and SHELXS-97 programs and corrections for *Lp* factors and absorptions were applied. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were determined by theoretical calculations. The final cycle of refinement gave R = 0.0471 and wR = 0.1048 (w = $1/[\sigma^2(F_o^2)+(0.0474P)^2+0.0000P]$, where $P = (F_o^2+2F_c^2)/3$). S = 1.049, $(\Delta/\sigma)_{max}$ = 0.000, $(\Delta\rho)_{min}$ = 0.147 e/Å^3 and $(\Delta\rho)_{max}$ = -0.187 e/Å^3.

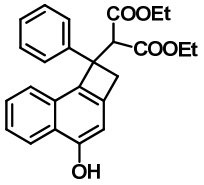
The crystal of compound **3a** belongs to Triclinic, space group *P-1* with a = 9.4624(8) Å, b = 10.6408 Å, c = 12.1773(11) Å, α = 65.5650(10)°, β = 86.673(2)°, γ = 68.9520(10)°, V = 1035.87(16) Å^3, Mr = 404.44, Z = 2, Dc = 1.297 g/cm^3, μ(Mo$K\alpha$) = 0.090 mm^{-1}, F(000) = 428, the final R = 0.0471 and wR = 0.1048.

General procedure for the synthesis of compound 3

Example for the synthesis of **3a**:

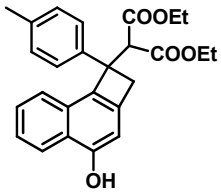
Under Ar conditions, a mixture of 1-(2-(phenylethynyl)phenyl)buta-2,3-dien-1-one (**1a**, 0.2 mmol), diethyl malonate (**2a**, 1.2 equiv.), Cs_2CO_3(1.2 equiv.) and THF(2.0 mL) were added in a Schlenk tube. Then, the reaction system was stirred at room temperature until TLC revealed that conversion of the starting material **1a** was completed. Next, the reaction mixture was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired product **3a**.

Diethyl 2-(4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3a)



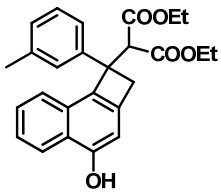
A white solid; 67.9 mg, 84% yield; mp: 136-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.18 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.47-7.43 (m, 1H), 7.41-7.38 (m, 2H), 7.35-7.30 (m, 1H), 7.20-7.15 (m, 2H), 7.12-7.08 (m, 1H), 6.47 (s, 1H), 6.10 (s, 1H), 4.45 (s, 1H), 4.19 (d, *J* = 14.0 Hz, 1H), 3.91-3.87 (m, 2H), 3.74-3.69 (m, 1H), 3.62-3.57 (m, 1H), 3.40 (d, *J* = 14.0 Hz, 1H), 0.84 (t, *J* = 7.2 Hz, 3H), 0.56 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.1, 168.1, 153.5, 144.0, 140.5, 133.9, 131.1, 128.2, 127.1, 127.0, 126.6, 124.7, 123.9, 123.9, 123.4, 104.4, 61.4, 61.2, 59.1, 55.8, 43.2, 13.6, 13.2; IR (KBr, *v*, cm^{-1}): 3431, 3054, 2978, 1748, 1701, 1628, 1520, 1441, 856, 774; HRMS (ESI) m/z calcd for $C_{25}H_{24}O_5$ $[M-H]^-$403.1545, found 403.1556.

Diethyl 2-(4-hydroxy-1-(p-tolyl)-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3b)



A white solid; 48.5 mg, 58% yield; mp: 167-169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.28 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.54-7.51 (m, 1H), 7.43-7.3 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.56 (s, 1H), 6.29 (s, 1H), 4.53 (s, 1H), 4.28 (d, *J* = 14.0 Hz, 1H), 4.03-3.98 (m, 2H), 3.83-3.78 (m, 1H), 3.70-3.66 (m, 1H), 3.47 (d, *J* = 14.0 Hz, 1H), 2.29 (s, 3H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.65 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.2(3), 168.2(0), 153.5, 141.0, 140.5, 136.1, 134.1, 131.0, 128.9, 127.0, 126.8, 124.7, 123.9, 123.8, 123.4, 104.4, 61.4, 61.2, 59.1, 55.5, 43.2, 21.0, 13.6, 13.2; IR (KBr, *v*, cm^{-1}): 3411, 3048, 2985, 1749, 1716, 1629, 1515, 1456, 860, 766; HRMS (ESI) m/z calcd for $C_{26}H_{26}O_5$ $[M-H]^-$417.1702, found 417.1716.

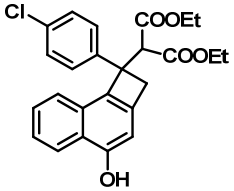
Diethyl 2-(4-hydroxy-1-(m-tolyl)-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3c)



A white solid; 59.4 mg, 71% yield; mp: 140-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.27 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.56-7.51 (m, 1H), 7.44-7.39 (m, 1H), 7.31-7.27 (m, 2H), 7.18-7.14 (m, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.57 (s, 1H), 6.13 (s, 1H), 4.53 (s, 1H), 4.28 (d, *J* = 14.0 Hz, 1H), 4.04-3.94 (m, 3.6 Hz, 2H), 3.82-3.77 (m, 1H), 3.70-3.65 (m, 1H), 3.49 (d, *J* = 14.4 Hz, 1H), 2.28 (s, 3H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.65 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.2, 168.1, 153.4, 143.9, 140.6, 137.7, 134.1, 131.1, 128.1, 127.6, 127.4, 127.1, 124.7, 124.0, 123.9, 123.3, 104.4, 61.4, 61.2, 59.1, 55.8, 43.1, 21.6, 13.6, 13.2; IR (KBr, *v*, cm^{-1}): 3404, 3051, 2983, 1747, 1712,

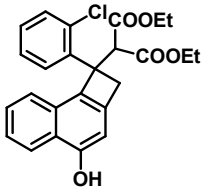
1629, 1519, 1456, 860, 765; HRMS (ESI) m/z calcd for $C_{26}H_{26}O_5$ $[M-H]^-$417.1702, found 417.07.

Diethyl 2-(1-(4-chlorophenyl)-4-hydroxy-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3d)



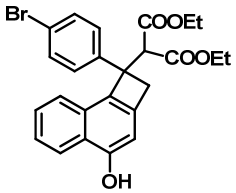
A white solid; 78.0 mg, 89% yield; mp: 162-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.28 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.57-7.52 (m, 1H), 7.45-7.39 (m, 3H), 7.25-7.20 (m, 2H), 6.57 (s, 1H), 6.17 (s, 1H), 4.48 (s, 1H), 4.26 (d, *J* = 14.0 Hz, 1H), 4.00-3.97 (m, 2H), 3.86-3.79 (m, 1H), 3.75-3.67 (m, 1H), 3.43 (d, *J* = 14.4 Hz, 1H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.70 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.0(7), 168.0(5), 153.6, 142.6, 140.4, 133.5, 132.4, 130.9, 128.4, 128.3, 127.3, 124.8, 124.1, 123.6, 123.5, 104.4, 61.6, 61.4, 58.9, 55.2, 43.4, 13.6, 13.3; IR (KBr, *v*, cm^{-1}): 3421, 3069, 2984, 1747, 1701, 1632, 1507, 1438, 843, 758; HRMS (ESI) m/z calcd for $C_{25}H_{23}ClO_5$ $[M-H]^-$437.1156, found 437.1154.

Diethyl 2-(1-(2-chlorophenyl)-4-hydroxy-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3e)



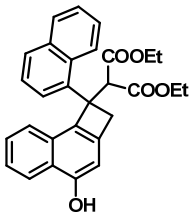
A white solid; 71.8 mg, 82% yield; mp: 183-185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.66 (d, *J* = 8.4 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.71-7.69 (m, 1H), 7.63-7.59 (m, 1H), 7.47-7.43 (m, 1H), 7.35-7.33 (m, 1H), 7.15-7.13 (m, 1H), 7.10-7.08 (m, 1H), 6.55 (s, 1H), 5.91 (s, 1H), 5.26 (s, 1H), 4.10-4.00 (m, 3H), 3.63-3.58 (m, 1H), 3.52-3.43 (m, 2H), 1.08 (t, *J* = 7.2 Hz, 3H), 0.46 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.2, 167.7, 153.7, 140.9, 132.8, 132.3, 130.2, 128.2, 127.5, 126.2, 124.9, 124.1, 123.0, 104.1, 61.2, 61.0, 56.3, 44.4, 13.8, 13.0; IR (KBr, *v*, cm^{-1}): 3446, 3069, 2981, 1750, 1701, 1626, 1520, 1465, 829, 762; HRMS (ESI) m/z calcd for $C_{25}H_{23}ClO_5$ $[M-H]^-$437.1156, found 437.1141.

Diethyl 2-(1-(4-bromophenyl)-4-hydroxy-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3f)



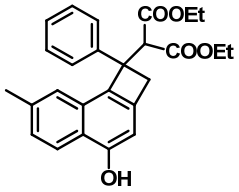
A white solid; 77.1 mg, 80% yield; mp: 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.28 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.57-7.52 (m, 1H), 7.45-7.33 (m, 5H), 6.57 (s, 1H), 6.14 (s, 1H), 4.47 (s, 1H), 4.25 (d, *J* = 14.4 Hz, 1H), 4.00-3.96 (m, 2H), 3.86-3.69 (m, 2H), 3.42 (d, *J* = 14.0 Hz, 1H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.70 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.0, 167.9, 153.7, 143.1, 140.4, 133.4, 131.3, 130.9, 128.8, 127.3, 124.8, 124.1, 123.6, 123.4, 120.5, 104.3, 61.6, 61.4, 58.8, 55.2, 43.4, 13.6, 13.3; IR (KBr, *v*, cm^{-1}): 3422, 3068, 2982, 1741, 1701, 1631, 1521, 1442, 842, 759; HRMS (ESI) m/z calcd for $C_{25}H_{23}BrO_5$ $[M-H]^-$481.0651, found 481.0653.

Diethyl 2-(4-hydroxy-1-(naphthalen-1-yl)-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3g)



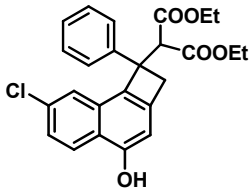
A white solid; 75.4 mg, 83% yield; mp: 178-180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.29 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 1.6 Hz, 1H), 7.78-7.71 (m, 3H), 7.60-7.53 (m, 2H), 7.46-7.40 (m, 3H), 6.62 (s, 1H), 6.08 (s, 1H), 4.67 (s, 1H), 4.36 (d, *J* = 14.4 Hz, 1H), 4.07-3.94 (m, 2H), 3.84-3.77 (m, 1H), 3.71-3.63 (m, 1H), 3.58 (d, *J* = 14.0 Hz, 1H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.64 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.1(2), 168.1(8), 153.5, 144.0, 140.5, 133.9, 131.1, 128.2, 127.1, 127.0, 126.6, 124.7, 123.9, 123.9, 123.4, 104.4, 61.4, 61.2, 59.1, 55.8, 43.2, 13.6, 13.2;IR (KBr, *v*, cm^{-1}): 3396, 3055, 2980, 1751, 1715, 1627, 1507, 1474, 858, 765; HRMS (ESI) m/z calcd for $C_{29}H_{26}O_5$ $[M-H]^-$453.1702, found 453.1702.

Diethyl 2-(4-hydroxy-7-methyl-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3h)



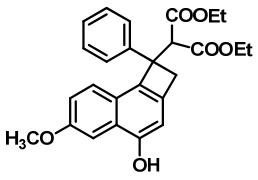
A white solid; 76.9 mg, 92% yield; mp: 133-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.17 (d, *J* = 8.4 Hz, 1H), 7.83 (s, 1H), 7.51-7.48 (m, 2H), 7.30-7.20 (m, 4H), 6.49 (s, 1H), 6.29 (s, 1H), 4.54 (s, 1H), 4.29 (d, *J* = 14.0 Hz, 1H), 4.07-3.98 (m, 2H), 3.83-3.78 (m, 1H), 3.70-3.62 (m, 1H), 3.48 (d, *J* = 14.4 Hz, 1H), 2.53 (s, 3H), 0.99 (t, *J* = 7.0 Hz, 3H), 0.66 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.2, 168.1, 153.5, 144.1, 140.7, 136.8, 133.4, 131.2, 128.3, 128.2, 127.0, 126.8, 126.6, 126.1, 123.2, 122.8, 103.6, 61.4, 61.2, 59.0, 55.7, 43.1, 22.0, 13.7, 13.1; IR (KBr, *v*, cm^{-1}): 3408, 3056, 2980, 1742, 1720, 1634, 1513, 1446, 859, 787; HRMS (ESI) m/z calcd for $C_{26}H_{26}O_5$ $[M-H]^-$417.1702, found 417.1706.

Diethyl 2-(7-chloro-4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3i)



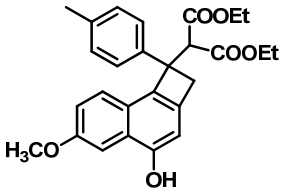
A white solid; 49.1 mg, 56% yield; mp: 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.23 (d, *J* = 9.2 Hz, 1H), 8.12 (d, *J* = 2.0 Hz, 1H), 7.44-7.40 (m, 2H), 7.36-7.34 (m, 1H), 7.30-7.27 (m, 2H), 7.23-7.19 (m, 1H), 6.53 (s, 1H), 6.47 (s, 1H), 4.53 (s, 1H), 4.24 (d, *J* = 14.4 Hz, 1H), 4.02-3.92 (m, 2H), 3.89-3.82 (m, 1H), 3.77-3.68 (m, 1H), 3.45 (d, *J* = 14.0 Hz, 1H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.0(0), 168.0(5), 153.7, 143.6, 142.2, 133.4, 133.0, 131.7, 128.4, 126.8, 125.4, 124.7, 123.0, 122.7, 104.7, 61.5, 61.4, 59.0, 55.7, 43.5, 13.6, 13.3; IR (KBr, *v*, cm^{-1}): 3365, 3023, 2974, 1735, 1712, 1627, 1509, 1426, 879, 762; HRMS (ESI) m/z calcd for $C_{25}H_{23}ClO_5$ $[M-H]^-$437.1156, found 437.1163.

Diethyl 2-(4-hydroxy-6-methoxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3j)



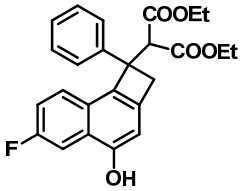
A white solid; 45.1 mg, 52% yield; mp: 166-168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.07 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 2.8 Hz, 1H), 7.46-7.44 (m, 2H), 7.27 (d, *J* = 4.4 Hz, 1H), 7.26-7.21 (m, 2H), 7.20-7.16 (m, 1H), 6.56 (s, 1H), 6.04 (s, 1H), 4.50 (s, 1H), 4.23 (d, *J* = 13.6 Hz, 1H), 4.00-3.94 (m, 2H), 3.93 (s, 3H), 3.85-3.70 (m, 2H), 3.44 (d, *J* = 13.6 Hz, 1H), 0.91 (t, *J* = 7.0 Hz, 3H), 0.72 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.0(4), 168.0(0), 156.3, 152.3, 144.0, 137.6, 134.1, 128.2, 126.9, 126.6, 126.5, 125.7, 125.5, 119.6, 104.9, 102.0, 61.4, 61.2, 59.1, 55.7, 55.3, 43.3, 13.6, 13.4; IR (KBr, *v*, cm^{-1}): 3413, 2981, 2963, 1750, 1702, 1604, 1523, 1436, 862, 757; HRMS (ESI) m/z calcd for $C_{26}H_{26}O_6$ $[M-H]^-$433.1651, found 433.1663.

Diethyl 2-(4-hydroxy-6-methoxy-1-(p-tolyl)-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3k)



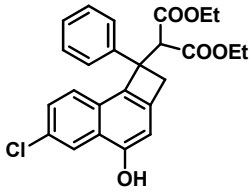
A white solid; 40.3 mg, 45% yield; mp: 107-109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.04 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 2.4 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.23-7.20 (m, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.56 (s, 1H), 5.95 (s, 1H), 4.48 (s, 1H), 4.21 (d, *J* = 14 Hz, 1H), 3.99-3.95 (m, 2H), 3.93 (s, 3H), 3.86-3.78 (m, 1H), 3.76-3.68 (m, 1H), 3.42 (d, *J* = 14.0 Hz, 1H), 2.28 (s, 3H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.72 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.1, 168.0, 156.3, 152.2, 141.0, 137.5, 136.0, 134.5, 128.9, 126.8, 126.6, 125.6, 125.6, 119.6, 104.9, 101.9, 61.3, 61.1, 59.1, 55.4, 55.3, 43.2, 21.0, 13.6, 13.3; IR (KBr, *v*, cm^{-1}): 3435, 2980, 2936, 1751, 1702, 1633, 1513, 1449, 828, 761; HRMS (ESI) m/z calcd for $C_{27}H_{28}O_6$ $[M-H]^-$447.1808, found 447.1806.

Diethyl 2-(6-fluoro-4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3l)



A white solid; 55.7 mg, 66% yield; mp: 146-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.21-8.18 (m, 1H), 7.91-7.88 (m, 1H), 7.43-7.40 (m, 2H), 7.35-7.30 (m, 1H), 7.29-7.27 (m, 1H), 7.27-7.25 (m, 1H), 7.22-7.18 (m, 1H), 6.59 (s, 1H), 6.00 (s, 1H), 4.52 (s, 1H), 4.21 (d, *J* = 14.0 Hz, 1H), 3.97-3.89 (m, 2H), 3.87-3.81 (m, 1H), 3.79-3.71 (m, 1H), 3.44 (d, *J* = 14.0 Hz, 1H), 0.87 (t, *J* = 7.2 Hz, 3H), 0.75 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.0, 167.9, 160.8, 158.4 ($^1J_{CF}$ = 240.1 Hz), 152.9, 152.8, 143.8, 139.4, 139.4, 134.0, 128.3, 128.2 ($^6J_{CF}$ = 4.8 Hz), 128.2, 127.9, 126.8, 126.7, 126.4, 126.3 ($^4J_{CF}$ = 8.4 Hz), 125.6, 125.5 ($^5J_{CF}$ = 8.4 Hz), 117.4, 117.1 ($^3J_{CF}$ = 24.9 Hz), 107.5, 107.3 ($^2J_{CF}$ = 22.2 Hz), 105.2, 61.4, 61.2, 59.0, 55.7, 43.5, 13.6, 13.4; IR (KBr, *v*, cm^{-1}): 3440, 3033, 2944, 1750, 1709, 1642, 1526, 1441, 838, 756; HRMS (ESI) m/z calcd for $C_{25}H_{23}FO_5$ $[M-H]^-$421.1451, found 421.1456.

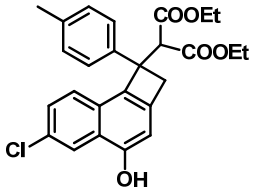
Diethyl 2-(6-chloro-4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3m)



A white solid; 63.9 mg, 73% yield; mp: 162-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.28 (d, *J* = 2.0 Hz, 1H), 8.14 (d, *J* = 9.2 Hz, 1H), 7.50-7.48 (m, 1H), 7.43-7.39 (m, 2H), 7.29-7.27 (m, 1H), 7.25 (s, 1H), 7.22-7.18 (m, 1H), 6.59 (s, 1H), 6.21 (s, 1H), 4.51 (s, 1H), 4.22 (d, *J* = 14.0 Hz, 1H), 3.97-3.75 (m, 4H), 3.44 (d, *J* = 14.0 Hz, 1H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.76 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 167.9(3), 167.9(0), 152.7, 143.7, 140.8, 133.8,

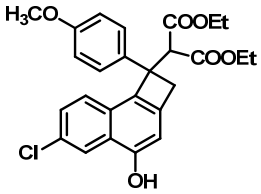
129.9, 129.4, 128.3, 128.0, 126.8, 126.7, 125.6, 125.5, 122.7, 105.3, 61.5, 61.3, 59.1, 55.7, 43.6, 13.6, 13.4; IR (KBr, *v*, cm^{-1}): 3435, 3024, 2985, 1749, 1704, 1645, 1575, 1445, 839, 769; HRMS (ESI) m/z calcd for $C_{25}H_{23}ClO_5$ $[M-H]^-$437.1156, found 437.1160.

Diethyl 2-(6-chloro-4-hydroxy-1-(p-tolyl)-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3n)



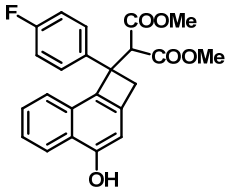
A white solid; 46.1 mg, 51% yield; mp: 138-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.27 (d, *J* = 2.0 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.50-7.47 (m, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.59 (s, 1H), 5.96 (s, 1H), 4.48 (s, 1H), 4.20 (d, *J* = 14.0 Hz, 1H), 3.99-3.92 (m, 2H), 3.87-3.72 (m, 2H), 3.42 (d, *J* = 14.4 Hz, 1H), 2.29 (s, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.75 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.0, 167.9, 152.6, 140.8, 140.7, 136.3, 134.2, 129.9, 129.3, 129.0, 127.9, 126.6, 125.6, 125.4, 122.7, 105.4, 61.4, 61.2, 59.0, 55.4, 43.5, 21.0, 13.6, 13.4; IR (KBr, *v*, cm^{-1}): 3411, 3011, 2981, 1728, 1701, 1628, 1573, 1444, 883, 757; HRMS (ESI) m/z calcd for $C_{26}H_{25}ClO_5$ $[M-H]^-$451.1312, found 451.1316.

Diethyl 2-(6-chloro-4-hydroxy-1-(4-methoxyphenyl)-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3o)



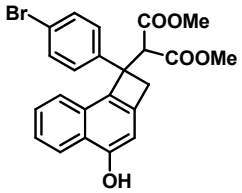
A white solid; 65.5 mg, 70% yield; mp: 129-131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.29 (d, *J* = 2.0 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 7.52-7.49 (m, 1H), 7.38-7.33 (m, 2H), 6.84-6.79 (m, 2H), 6.61 (s, 1H), 5.98 (s, 1H), 4.47 (s, 1H), 4.22 (d, *J* = 14.0 Hz, 1H), 4.01-3.95 (m, 2H), 3.88-3.80 (m, 1H), 3.77 (s, 3H), 3.76-3.74 (m, 1H), 3.43 (d, *J* = 14.0 Hz, 1H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.77 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.0, 158.2, 152.6, 140.8, 135.8, 134.2, 129.9, 129.2, 128.0(98), 128.0(95), 125.5, 125.5, 122.7, 113.6, 105.4, 61.4, 61.2, 59.2, 55.2, 55.2, 43.5, 13.6, 13.4; IR (KBr, *v*, cm^{-1}): 3457, 3072, 2980, 1751, 1703, 1631, 1526, 1442, 828, 735; HRMS (ESI) m/z calcd for $C_{26}H_{25}ClO_6$ $[M-H]^-$467.1261, found 467.1267.

Dimethyl 2-(1-(4-fluorophenyl)-4-hydroxy-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3p)



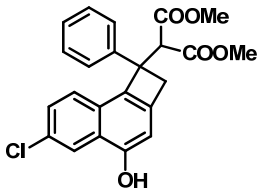
A white solid; 73.3 mg, 93% yield; mp: 193-195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.27 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.60-7.56 (m, 1H), 7.47-7.42 (m, 3H), 6.97-6.92 (m, 2H), 6.63 (s, 1H), 4.43 (s, 1H), 4.21 (d, *J* = 14.0 Hz, 1H), 3.50 (s, 3H), 3.45 (d, *J* = 14.4 Hz, 1H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.2, 168.1, 153.3, 140.4, 130.7, 128.8, 128.7 ($^2J_{CF}$ = 7.9 Hz), 127.4, 124.6, 124.1, 123.5, 123.3, 115.1, 114.9 ($^1J_{CF}$ = 21.1 Hz), 104.5, 58.9, 55.3, 52.3, 52.0, 43.5; IR (KBr, *v*, cm^{-1}): 3431, 3049, 2995, 1737, 1716, 1630, 1570, 1432, 844, 744; HRMS (ESI) m/z calcd for $C_{23}H_{19}FO_5$ $[M-H]^-$393.1138, found 393.1141.

Dimethyl 2-(1-(4-bromophenyl)-4-hydroxy-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3q)



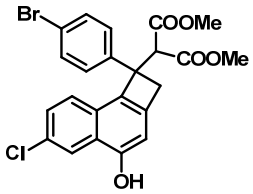
A white solid; 55.4 mg, 61% yield; mp: 167-169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.28 (d, *J* = 2.0 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 7.51-7.49 (m, 1H), 7.43-7.38 (m, 2H), 7.29-7.27 (m, 1H), 7.26 (d, *J* = 4.0 Hz, 1H), 7.23-7.19 (m, 1H), 6.59 (s, 1H), 6.01 (s, 1H), 4.51 (s, 1H), 4.20 (d, *J* = 14.0 Hz, 1H), 3.48 (s, 3H), 3.45 (d, *J* = 14.0 Hz, 1H), 3.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.3, 152.7, 143.5, 140.8, 133.7, 129.9, 129.1, 128.3, 128.1, 126.8, 125.5, 125.3, 122.8, 105.4, 58.8, 55.8, 52.4, 52.1, 43.6; IR (KBr, *v*, cm^{-1}): 3412, 3030, 2951, 1728, 1709, 1639, 1594, 1447, 829, 756; HRMS (ESI) m/z calcd for $C_{23}H_{19}BrO_5$ $[M-H]^-$453.0338, found 453.0341.

Dimethyl 2-(6-chloro-4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3r)



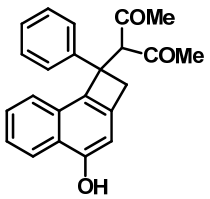
A white solid; 77.1 mg, 94% yield; mp: 177-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.27 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.58-7.54 (m, 1H), 7.45-7.43 (m, 1H), 7.40-7.32 (m, 4H), 6.60 (s, 1H), 5.75 (s, 1H), 4.45 (s, 1H), 4.20 (d, *J* = 14.0 Hz, 1H), 3.51 (s, 3H), 3.43 (d, *J* = 14.0 Hz, 1H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.2, 168.1, 153.5, 142.9, 140.4, 133.4, 133.0, 131.6, 131.5, 131.3, 130.7, 128.9, 127.5, 127.1, 124.7, 124.2, 123.4, 123.4, 120.6, 104.4, 58.6, 55.4, 52.4, 52.1, 43.5; IR (KBr, *v*, cm^{-1}): 3423, 3026, 2952, 1756, 1713, 1629, 1571, 1435, 830, 769; HRMS (ESI) m/z calcd for $C_{23}H_{19}ClO_5$ $[M-H]^-$409.0843, found 409.0840.

Dimethyl 2-(1-(4-bromophenyl)-6-chloro-4-hydroxy-1,2-dihydrocyclobuta[a]naphthalen-1-yl)malonate (3s)



A white solid; 55.6 mg, 57% yield; mp: 185-187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.28 (d, *J* = 2.0 Hz, 1H), 8.04 (d, *J* = 9.2 Hz, 1H), 7.51-7.49 (m, 1H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.28-7.26 (m, 2H), 6.60 (s, 1H), 6.05 (s, 1H), 4.44 (s, 1H), 4.16 (d, *J* = 14.4 Hz, 1H), 3.47 (s, 3H), 3.39 (d, *J* = 14.0 Hz, 1H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 168.1(9), 168.1(7), 152.8, 142.6, 140.6, 133.2, 131.4, 130.1, 129.0, 128.6, 128.3, 125.5, 125.1, 122.9, 120.7, 105.3, 58.6, 55.3, 52.4, 52.3, 43.8; IR (KBr, *v*, cm^{-1}): 3315, 3071, 2985, 1740, 1701, 1629, 1572, 1435, 831, 770; HRMS (ESI) m/z calcd for $C_{23}H_{18}BrClO_5$ $[M-H]^-$486.9948, found 486.9961.

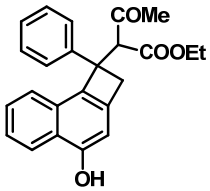
3-(4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)pentane-2,4-dione (3u)



A white solid; 53.7 mg, 78% yield; mp: 163-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.31 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.65-7.61 (m, 1H), 7.50-7.44 (m, 3H), 7.32-7.29 (m, 1H), 7.27-7.23 (m, 1H), 7.23-7.19 (m, 1H), 6.62 (s, 1H), 5.86 (s, 1H), 4.91 (s, 1H), 4.12 (d, *J* = 14.4 Hz, 1H), 3.49 (d, *J* = 14.4 Hz, 1H), 1.92 (d, *J* = 6.4 Hz, 6H); ^{13}C

NMR (100 MHz, $CDCl_3$) (δ, ppm): 204.1, 203.8, 153.4, 143.7, 140.1, 134.0, 130.9, 128.5, 127.8, 126.9, 126.7, 124.8, 124.3, 123.7, 123.2, 104.6, 74.3, 56.7, 42.6, 32.4, 30.5; IR (KBr, ν, cm-1): 3296, 3053, 2997, 1715, 1678, 1597, 1494, 868, 766; HRMS (ESI) m/z calcd for $C_{23}H_{20}O_3$ $[M-H]^-$343.1334, found 343.1335.

Ethyl 2-(4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)-3-oxobutanoate (3w)



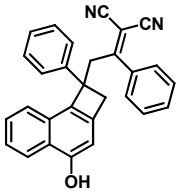
A white solid; 51.6 mg, 69% yield; mp: 126-128 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.32-8.29 (m, 2H), 8.22 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.62-7.55 (m, 2H), 7.49-7.42 (m, 6H), 7.31-7.29 (m, 2H), 7.27-7.26 (m, 2H), 7.23-7.18 (m, 2H), 6.59 (d, *J* = 6.4 Hz, 2H), 6.08 (s, 2H), 4.77 (s, 1H), 4.61 (s, 1H), 4.24-4.16 (m, 2H), 4.02-3.91 (m, 2H), 3.87-3.71 (m, 2H), 3.51-3.47 (m, 2H), 1.98 (d, *J* = 5.2 Hz, 6H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.74 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 203.0, 202.7, 168.7, 168.3, 153.5, 144.0, 143.8, 140.5, 140.5, 133.9, 133.7, 131.1, 130.8, 128.3, 127.5, 127.4, 127.1, 126.7, 126.6, 126.5, 124.8, 124.1, 124.0, 123.7, 123.7, 123.5, 123.1, 66.5, 65.4, 61.4, 61.2, 56.3, 55.5, 43.1, 42.9, 31.6, 30.2, 13.6, 13.3; IR (KBr, ν, cm-1): 3430, 3055, 2926, 1732, 1703, 1597, 1493, 843, 762; HRMS (ESI) m/z calcd for $C_{24}H_{22}O_4$ $[M-H]^-$373.1440, found 373.1407.

General procedure for the synthesis of compound 5

Example for the synthesis of **5a**:

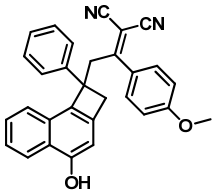
Under Ar conditions, 1-(2-(phenylethynyl)phenyl)buta-2,3-dien-1-one (**1a**, 0.2 mmol), 2-(1-phenylethylidene)malononitrile (**2a**, 1.5 equiv.), CH_3ONa (2.0 equiv.) and toluene (2.0 mL) were added in a Schlenk tube. The mixture was stirred at room temperature for about 10 hours. After the reaction was completed (indicated by TLC, petroleum ether : ethyl acetate = 3:1), the reaction mixture was concentrated by vacuum distillation and was purified by flash column chromatography to afford the desired pure product **5a** as yellow solid.

2-(2-(4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)-1-phenylethylidene)malononitrile (5a)



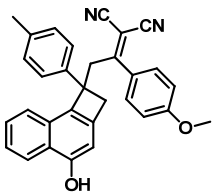
A yellow solid; 75.8 mg, 92% yield; mp: 176-178 ºC; ^{1}H NMR (400 MHz, DMSO-d_6; *δ*, ppm): 10.13 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.45-7.41 (m, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.34-7.30 (m, 3H), 7.24-7.20 (m, 1H), 7.17-7.11 (m, 3H), 7.06-7.03 (m, 2H), 6.58 (s, 1H), 4.05 (d, *J* = 13.2 Hz, 1H), 3.93 (d, *J* = 13.2 Hz, 1H), 3.40 (d, *J* = 14.0 Hz, 1H), 3.09 (d, *J* = 14.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6; *δ*, ppm): 179.0, 155.4, 145.3, 139.2, 135.0, 132.3, 131.1, 130.4, 128.8, 128.3, 127.5, 127.1, 127.0(1), 127.0(9), 125.1, 124.0, 123.7, 123.0, 113.6, 113.4, 104.1, 86.8, 56.2, 47.4, 44.0; IR (KBr, *ν*, cm^{-1}): 3497, 3024, 2952, 2225, 1630, 1519, 1442, 831, 761; HRMS (ESI) m/z calcd for $C_{29}H_{20}N_2O$ $[M-H]^-$411.1497, found 411.1503.

2-(2-(4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)-1-(4-methoxyphenyl)ethylidene)malononitrile (5b)



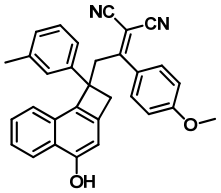
A yellow solid; 84.0 mg, 95% yield; mp: 130-132 °C; ^{1}H NMR (400 MHz, DMSO-d_6; δ, ppm): 10.06 (s, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.43-7.39 (m, 2H), 7.33-7.30 (m, 2H), 7.29-7.26 (m, 2H), 7.18 (d, J = 7.2 Hz, 1H), 7.12 (d, J = 8.8 Hz, 2H), 6.54-6.50 (m, 3H), 3.97 (d, J = 13.3 Hz, 1H), 3.81 (d, J = 13.4 Hz, 1H), 3.60 (s, 3H), 3.37 (d, J = 14.0 Hz, 1H), 3.03 (d, J = 14.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm): 178.4, 162.0, 155.3, 145.4, 139.2, 132.4, 130.4, 129.9, 128.8, 127.3, 127.1, 125.2, 124.0, 123.7, 123.2, 114.1, 114.0, 113.9, 104.1, 84.5, 56.4, 55.7, 47.2, 44.1; IR (KBr, v, cm^{-1}): 3404, 3055, 2927, 2225, 1607, 1557, 1444, 834, 761; HRMS (ESI) m/z calcd for $C_{30}H_{22}N_2O_2$ [M-H]$^-$441.1603, found 441.1605.

2-(2-(4-hydroxy-1-(p-tolyl)-1,2-dihydrocyclobuta[a]naphthalen-1-yl)-1-(4-methoxyphenyl)ethylidene)malononitrile (5c)



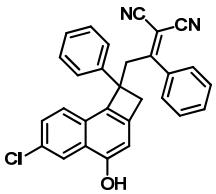
A yellow solid; 63.8 mg, 70% yield; mp: 136-138 °C; ^{1}H NMR (400 MHz, DMSO-d_6; δ, ppm): 10.04 (s, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.40-7.36 (m, 1H), 7.28-7.24 (m, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.09-7.05 (m, 4H), 6.50 (d, J = 7.6 Hz, 3H), 3.92 (d, J = 13.6 Hz, 1H), 3.90 (d, J = 13.6 Hz, 1H), 3.60 (s, 3H), 3.35 (s, 1H), 2.99 (d, J = 14.0 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm): 178.6, 162.0, 155.3, 142.4, 139.1, 136.0, 132.6, 130.3, 129.8, 129.3, 127.3, 127.0, 126.9, 125.1, 124.0, 123.6, 123.2, 114.1, 114.0, 113.8, 104.1, 100.0, 84.4, 56.1, 55.7, 47.2, 44.0, 21.0; IR (KBr, v, cm^{-1}): 3419, 3050, 2922, 2225, 1623, 1574, 1439, 814, 761; HRMS (ESI) m/z calcd for $C_{31}H_{24}N_2O_2$ [M-H]$^-$455.1760, found 455.1753.

2-(2-(4-hydroxy-1-(m-tolyl)-1,2-dihydrocyclobuta[a]naphthalen-1-yl)-1-(4-methoxyphenyl)ethylidene)malononitrile (5d)



A yellow solid; 58.3 mg, 64% yield; mp: 125-127 °C; ^{1}H NMR (400 MHz, DMSO-d_6; δ, ppm): 10.06 (s, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.42-7.38 (m, 1H), 7.29-7.25 (m, 1H), 7.15-7.08 (m, 5H), 6.97 (d, J = 6.8 Hz, 1H), 6.54-6.50 (m, 3H), 3.94 (d, J = 13.2 Hz, 1H), 3.80 (d, J = 13.2 Hz, 1H), 3.60 (s, 3H), 3.35 (d, J = 14.0 Hz, 1H), 3.03 (d, J = 14.0 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm): 178.5, 162.0, 155.3, 145.3, 139.2, 137.7, 132.6, 130.4, 129.8, 128.7, 127.8, 127.6, 127.3, 127.0, 125.1, 124.1, 124.0, 123.6, 123.2, 114.1, 114.0, 113.8, 104.1, 84.4, 56.4, 55.7, 47.2, 44.1, 21.7; IR (KBr, v, cm^{-1}): 3404, 3049, 2922, 2225, 1667, 1508, 1418, 834, 765; HRMS (ESI) m/z calcd for $C_{31}H_{24}N_2O_2$ [M-H]$^-$455.1760, found 455.1763.

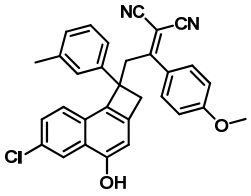
2-(2-(6-chloro-4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)-1-phenylethylidene)malononitrile (5e)



A yellow solid; 50.8 mg, 57% yield; mp: 124-126 °C; ^{1}H NMR (400 MHz, DMSO-d_6; δ, ppm): 10.32 (s, 1H), 7.94 (d, J = 2.0 Hz, 1H), 7.53 (d, J = 8.8 Hz, 1H), 7.36-7.34 (m, 1H), 7.30-7.25 (m, 4H), 7.20-7.16 (m, 1H), 7.07-7.02 (m, 3H), 6.96-6.93 (m, 2H), 6.60 (s, 1H), 4.04 (d, J = 13.2 Hz, 1H), 3.83 (d, J = 13.2 Hz, 1H), 3.45 (d, J = 14.0 Hz, 1H), 3.06 (d, J

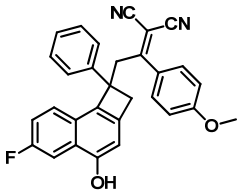
= 14.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm): 179.0, 155.4, 145.3, 139.2, 135.0, 132.3, 131.1, 130.4, 128.8, 128.3, 127.5, 127.1, 127.0(1), 127.0(9), 125.1, 124.0, 123.7, 123.0, 113.6, 113.4, 104.1, 86.8, 56.2, 47.4, 44.0; IR (KBr, v, cm^{-1}): 3335, 3058, 2925, 2224, 1635, 1558, 1444, 832. 761; HRMS (ESI) m/z calcd for $C_{29}H_{19}ClN_2O$ [M-H]$^-$445.1108, found 445.1109.

2-(2-(6-chloro-4-hydroxy-1-(m-tolyl)-1,2-dihydrocyclobuta[a]naphthalen-1-yl)-1-(4-methoxyphenyl)ethylidene)malononitrile (5f)



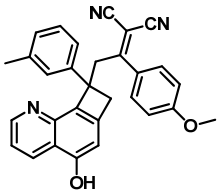
A yellow solid; 44.1 mg, 45% yield; mp: 138-140 °C; ^{1}H NMR (400 MHz, DMSO-d_6; δ, ppm): 10.29 (s, 1H), 7.94 (d, J = 2.4 Hz, 1H), 7.49 (d, J = 8.8 Hz, 1H), 7.37-7.34 (m, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 6.60 (s, 1H), 6.44 (d, J = 8.8 Hz, 2H), 3.95 (d, J = 13.2 Hz, 1H), 3.76 (d, J = 13.2 Hz, 1H), 3.60 (s, 3H), 3.44 (d, J = 14.2 Hz, 1H), 3.02 (d, J = 14.2 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm): 178.4, 161.9, 161.8, 154.5, 142.4, 139.7, 136.2, 132.4, 129.5, 129.4, 128.5, 128.4, 127.5, 127.2, 126.7, 125.8, 125.6, 122.6, 114.2, 113.9, 113.7, 105.3, 84.8, 55.9, 55.6, 47.1, 43.8, 21.0; IR (KBr, v, cm^{-1}): 3419, 3021, 2924, 2226, 1602, 1543, 1456, 833, 728; HRMS (ESI) m/z calcd for $C_{31}H_{23}ClN_2O_2$ [M-H]$^-$490.1448, found 490.1445.

2-(2-(6-fluoro-4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)-1-(4-methoxyphenyl)ethylidene)malononitrile (5g)



A yellow solid; 46.9 mg, 51% yield; mp: 157-159 °C; ^{1}H NMR (400 MHz, DMSO-d_6; δ, ppm): 10.24 (s, 1H), 7.68-7.59 (m, 2H), 7.37-7.29 (m, 5H), 7.26-7.22 (m, 1H), 7.10 (d, J = 8.8 Hz, 2H), 6.63 (s, 1H), 6.51 (d, J = 8.8 Hz, 2H), 4.06 (d, J = 13.2 Hz, 1H), 3.83 (d, J = 13.2 Hz, 1H), 3.64 (s, 3H), 3.49 (d, J = 14.0 Hz, 1H), 3.09 (d, J = 14.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm): 178.3, 161.8, 160.2, 157.8 ($^1J_{CF}$ = 239.2 Hz), 154.8, 145.3, 138.3, 138.3 ($^6J_{CF}$ = 2.4 Hz), 132.4, 129.6, 128.9, 127.5, 127.4, 127.1, 126.9 ($^3J_{CF}$ = 19.0 Hz), 126.1, 126.0 ($^4J_{CF}$ = 8.8 Hz), 125.9, 125.8 ($^5J_{CF}$ = 8.1 Hz), 116.9, 116.6 ($^2J_{CF}$ = 24.8 Hz), 114.1, 114.0, 113.7, 107.4, 107.2, 105.0, 84.8, 56.2, 55.6, 47.1, 43.8; IR (KBr, v, cm^{-1}): 3418, 3006, 2930, 2225, 1602, 1550, 1464, 834, 773; HRMS (ESI) m/z calcd for $C_{30}H_{21}FN_2O_2$ [M-H]$^-$459.1509, found 459.1503.

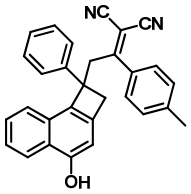
2-(2-(5-hydroxy-8-(m-tolyl)-7,8-dihydrocyclobuta[h]quinolin-8-yl)-1-(4-methoxyphenyl)ethylidene)malononitrile (5h)



A yellow solid; 42.9 mg, 47% yield; mp: 180-182 °C; ^{1}H NMR (400 MHz, DMSO-d_6; δ, ppm): 10.41 (s, 1H), 8.85-8.83 (m, 1H), 8.40-8.38 (m, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.34-7.31 (m, 1H), 7.18 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 6.64 (s, 1H), 6.57 (d, J = 8.8 Hz, 2H), 3.85 (d, J = 12.8 Hz, 1H), 3.69 (s, 1H), 3.65 (s, 3H), 3.40 (d, J = 14.4 Hz, 1H), 3.22 (d, J = 14.4 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm): 177.9, 162.0, 155.5, 150.8, 144.6, 143.6, 142.1, 135.6, 133.6, 132.3, 131.9, 130.2, 130.0, 128.8, 128.0, 127.3, 120.1, 119.3, 114.3, 113.9, 113.5, 104.9, 84.2,

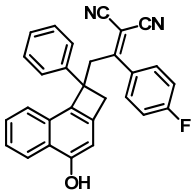
57.2, 55.8, 48.9, 43.7, 21.1; IR (KBr, *v*, cm^{-1}): 3419, 2927, 2840, 2224, 1646, 1557, 1456, 832, 786; HRMS (ESI) m/z calcd for $C_{30}H_{23}N_3O_2$ $[M-H]^-$456.1712, found 456.1711.

2-(2-(4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)-1-(p-tolyl)ethylidene)malononitrile (5i)



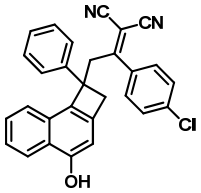
A yellow solid; 53.7 mg, 63% yield; mp: 127-129 °C; ^{1}H NMR (400 MHz, DMSO-d_6; δ, ppm): 10.12 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.45-7.41 (m, 1H), 7.38-7.31(m, 5H), 7.25-7.21 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.58 (s, 1H), 4.00 (d, *J* = 13.2 Hz, 1H), 3.90 (d, *J* = 13.2 Hz, 1H), 3.38 (d, *J* = 14.0 Hz, 1H), 3.07 (d, *J* = 14.0 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm): 179.1, 155.4, 145.4, 141.6, 139.1, 132.4, 132.4, 130.3, 128.9, 128.8, 127.6, 127.0(4), 127.0(9), 125.2, 124.0, 123.6, 123.1, 113.8, 113.6, 104.1, 85.9, 56.3, 47.4, 43.9, 21.3; IR (KBr, *v*, cm^{-1}): 3445, 3055, 2925, 2227, 1661, 1520, 1445, 823, 759; HRMS (ESI) m/z calcd for $C_{30}H_{22}N_2O$ $[M-H]^-$425.1654, found 425.1653.

2-(1-(4-fluorophenyl)-2-(4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)ethylidene)malononitrile (5j)



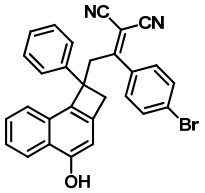
A yellow solid; 48.2 mg, 56% yield; mp: 126-128 °C; ^{1}H NMR (400 MHz, DMSO-d_6; δ, ppm): 10.14 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.40-7.37 (m, 2H), 7.34-7.31 (m, 3H), 7.25-7.21 (m, 2H), 7.18-7.14 (m, 2H), 6.79-6.75 (m, 2H), 6.60 (s, 1H), 4.07 (d, *J* = 13.6 Hz, 1H), 3.88 (d, *J* = 13.2 Hz, 1H), 3.51 (d, *J* = 14.0 Hz, 1H), 3.12 (d, *J* = 14.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm): 177.9, 164.8, 162.3 ($^1J_{CF}$ = 248.4 Hz), 155.5, 145.4, 139.0, 132.1, 131.4, 131.4($^4J_{CF}$ = 3.1 Hz), 130.3, 130.1, 130.0($^3J_{CF}$ = 8.9 Hz), 128.9, 127.0, 126.9, 125.1, 123.9, 123.7, 123.1, 115.4, 115.1($^2J_{CF}$ = 21.9 Hz), 113.6, 113.4, 104.1, 87.2, 56.0, 47.5, 43.9; IR (KBr, *v*, cm^{-1}): 3435, 3057, 2927, 2228, 1630, 1572, 1444, 840, 746; HRMS (ESI) m/z calcd for $C_{29}H_{19}FN_2O$ $[M-H]^-$429.1403, found 429.1410.

2-(1-(4-chlorophenyl)-2-(4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)ethylidene)malononitrile (5k)



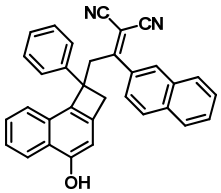
A yellow solid; 80.3 mg, 90% yield; mp: 136-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.12- 8.09 (m, 1H), 7.44-7.41 (m, 2H), 7.38-7.31 (m, 5H), 7.27 (d, *J* = 5.6 Hz, 1H), 6.83-6.80 (m, 2H), 6.68-6.65 (m, 2H), 6.54 (s, 1H), 5.41 (s, 1H), 4.08 (d, *J* = 13.2 Hz, 1H), 3.72 (d, *J* = 13.2 Hz, 1H), 3.52 (d, *J* = 14.0 Hz, 1H), 3.28 (d, *J* = 14.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 176.9, 153.7, 144.4, 138.0, 137.0, 133.4, 133.2, 130.3, 128.7, 128.4, 127.5, 127.2, 127.1, 126.5, 124.5, 124.3, 123.4, 122.7, 112.7, 112.2, 104.2, 87.9, 56.1, 47.2, 43.5; IR (KBr, *v*, cm^{-1}): 3457, 3025, 2948, 2227, 1630, 1520, 1445, 852, 746; HRMS (ESI) m/z calcd for $C_{29}H_{19}ClN_2O$ $[M-H]^-$445.1108, found 445.1114.

2-(1-(4-bromophenyl)-2-(4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)ethylidene)malononitrile (5l)

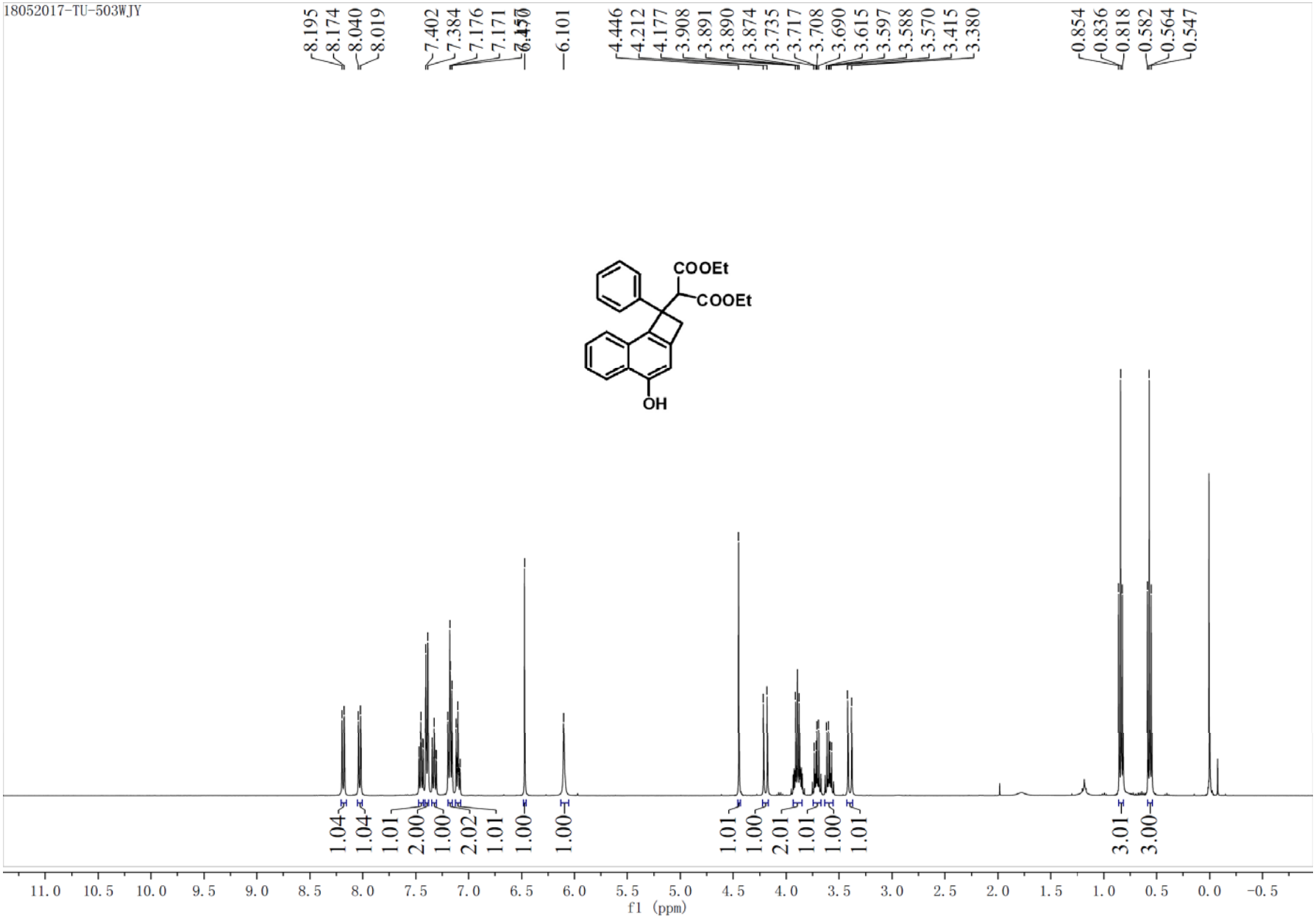


A yellow solid; 85.3 mg, 87% yield; mp: 162-164 °C; ^{1}H NMR (400 MHz, DMSO-d_6; δ, ppm): 10.07 (s, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.33-7.22 (m, 6H), 7.17-7.13 (m, 1H), 7.01 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.53 (s, 1H), 3.95 (d, J = 13.6 Hz, 1H), 3.79 (d, J = 13.6 Hz, 1H), 3.43 (d, J = 14.0 Hz, 1H), 3.04 (d, J = 14.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm): 177.7, 155.6, 145.5, 139.0, 134.1, 131.9, 131.1, 130.2, 129.6, 129.1, 128.9, 127.0, 126.8, 125.1, 124.8, 124.0, 123.7, 123.0, 113.6, 113.2, 104.1, 87.6, 56.0, 47.4, 43.7, 31.1; IR (KBr, v, cm^{-1}): 3445, 3057, 2948, 2227, 1629, 1521, 1445, 853, 743; HRMS (ESI) m/z calcd for $C_{29}H_{19}BrN_2O$ [M-H]$^-$489.0603, found 489.0602.

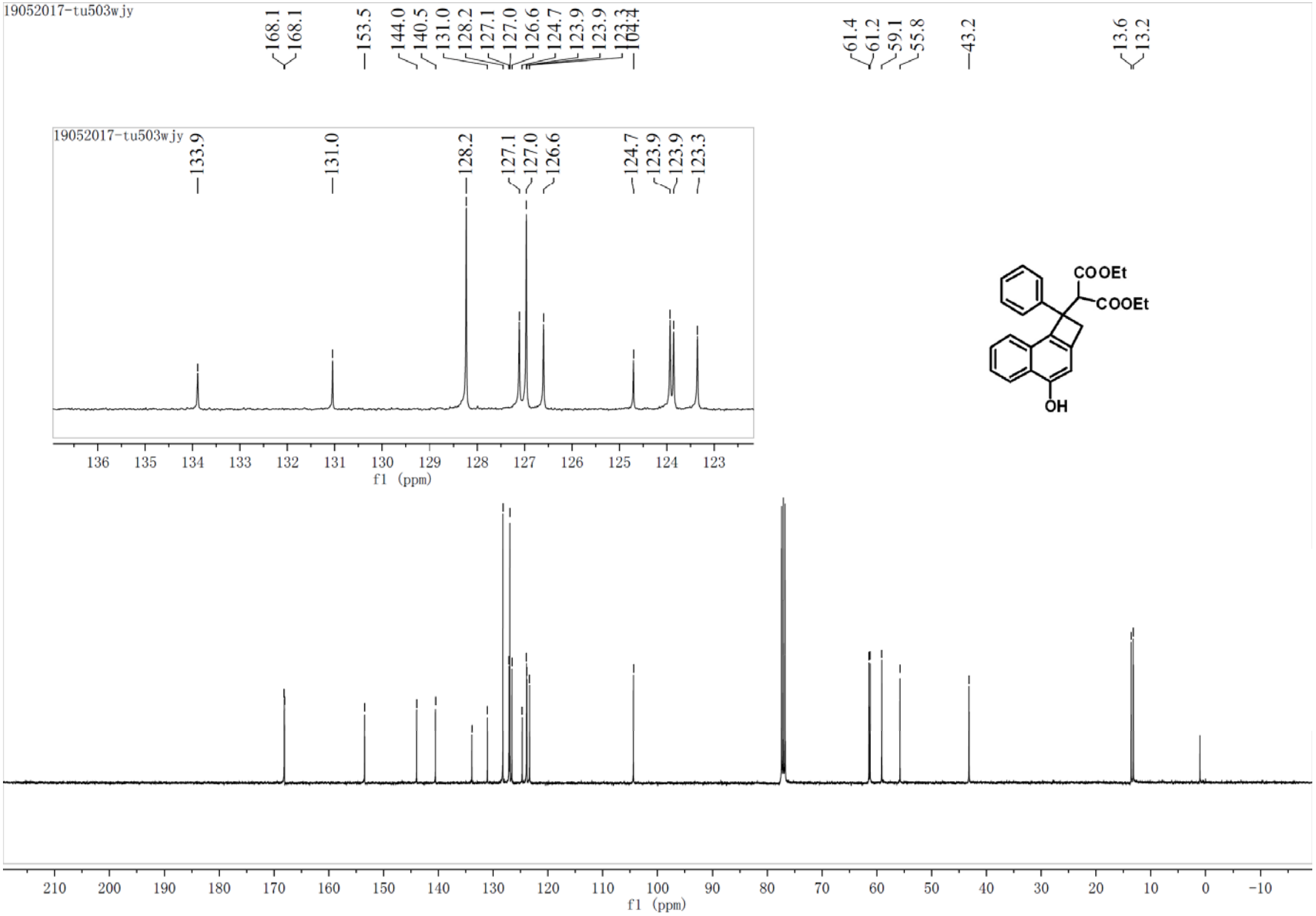
2-(2-(4-hydroxy-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-1-yl)-1-(naphthalen-2-yl)ethylidene)malononitrile (5m)



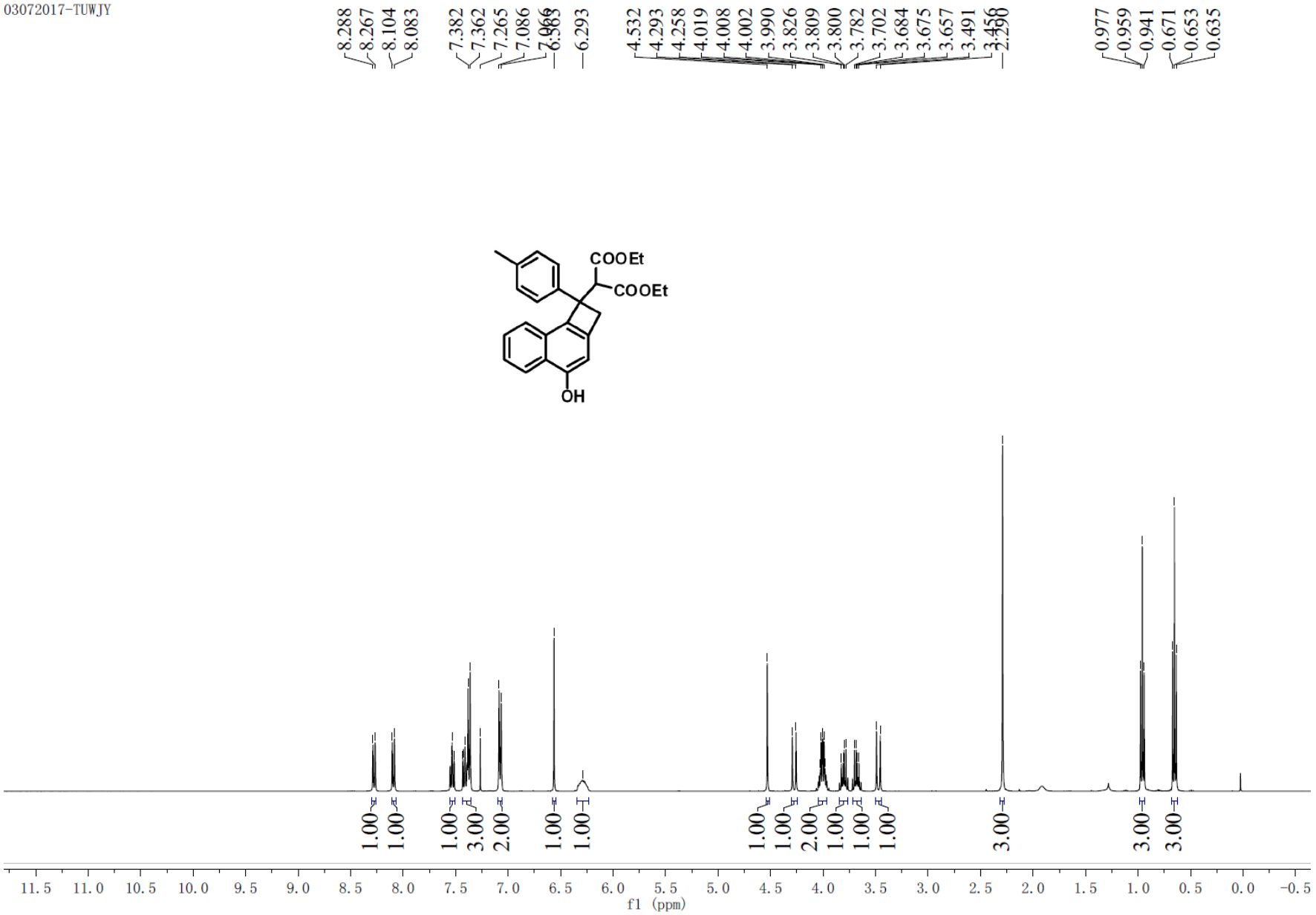
A yellow solid; 64.7 mg, 70% yield; mp: 158-160 °C; ^{1}H NMR (400 MHz, DMSO-d_6; δ, ppm): 10.02 (s, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.67-7.63 (m, 3H), 7.46-7.42 (m, 4H), 7.32 (d, J = 7.2 Hz, 2H), 7.25-7.22 (m, 2H), 7.14-7.10 (m, 1H), 7.08-7.02 (m, 2H), 6.92-6.89 (m, 1H), 6.49 (s, 1H), 4.08 (d, J = 13.2 Hz, 1H), 3.96 (d, J = 13.2 Hz, 1H), 3.38 (d, J = 14.0 Hz, 1H), 3.03 (d, J = 14.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm): 179.0, 155.5, 145.4, 139.1, 133.8, 132.7, 132.2, 131.9, 130.2, 129.2, 128.8, 128.2, 128.1, 128.0, 127.8, 127.1, 127.0, 126.9, 126.7, 124.9, 124.1, 123.6, 123.4, 122.6, 113.8, 113.6, 104.0, 86.9, 56.3, 47.5, 43.9; IR (KBr, v, cm^{-1}): 3461, 3025, 2949, 2225, 1628, 1520, 1491, 818, 774; HRMS (ESI) m/z calcd for $C_{33}H_{22}N_2O$ [M-H]$^-$461.1654, found 461.1660.



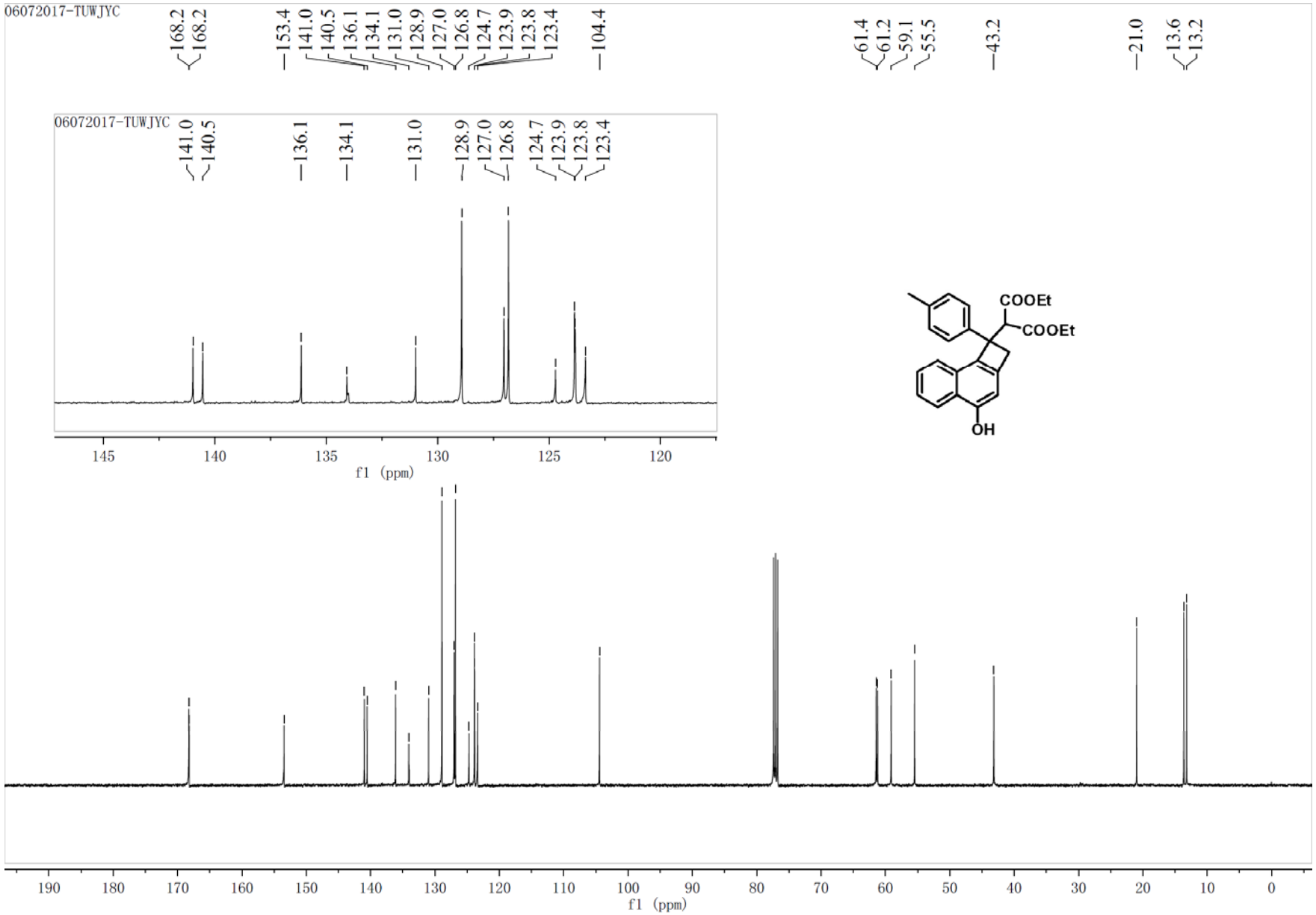
^{1}H NMR Spectrum of Compound 3a



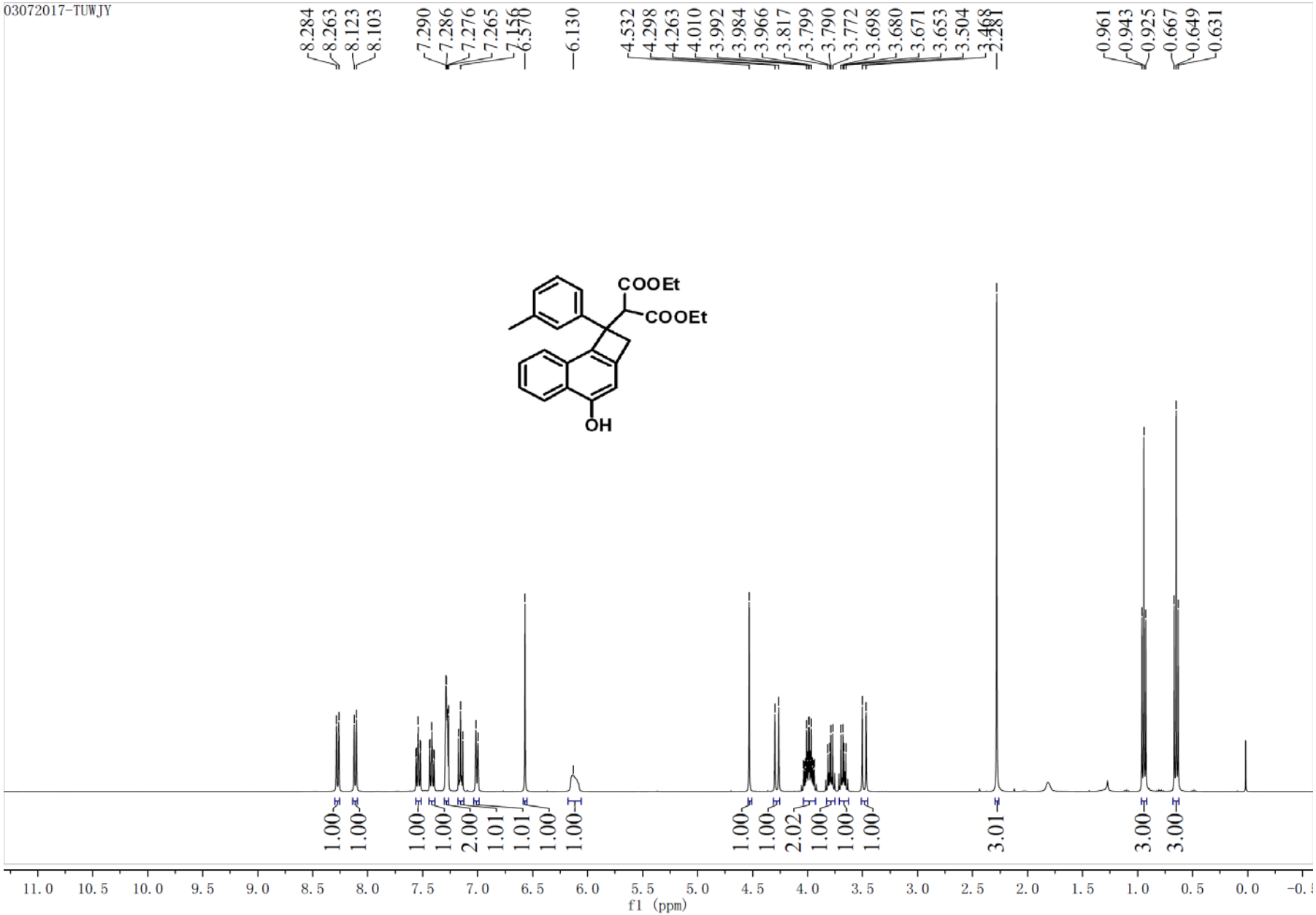
^{13}C NMR Spectrum of Compound 3a



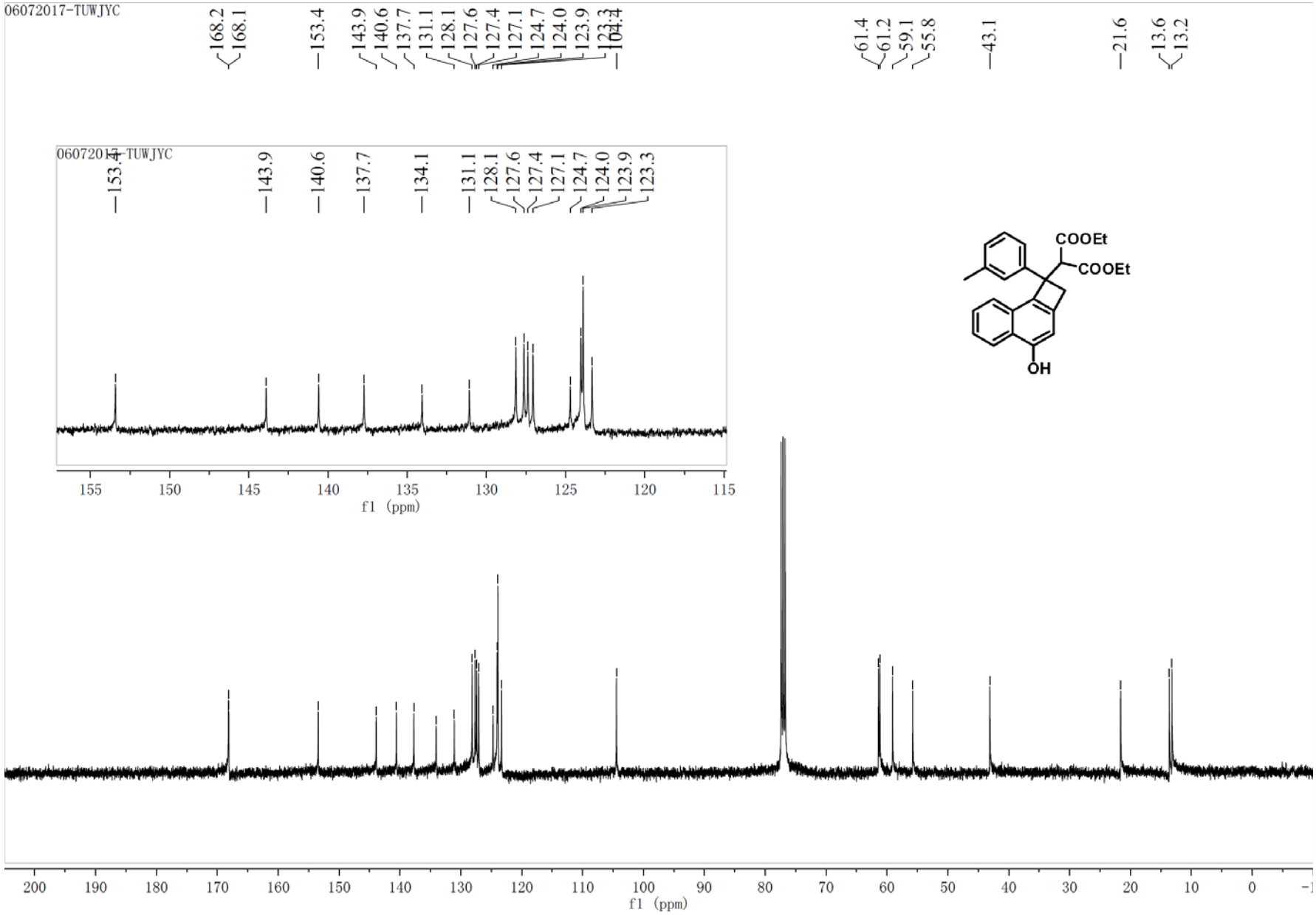
^{1}H NMR Spectrum of Compound 3b



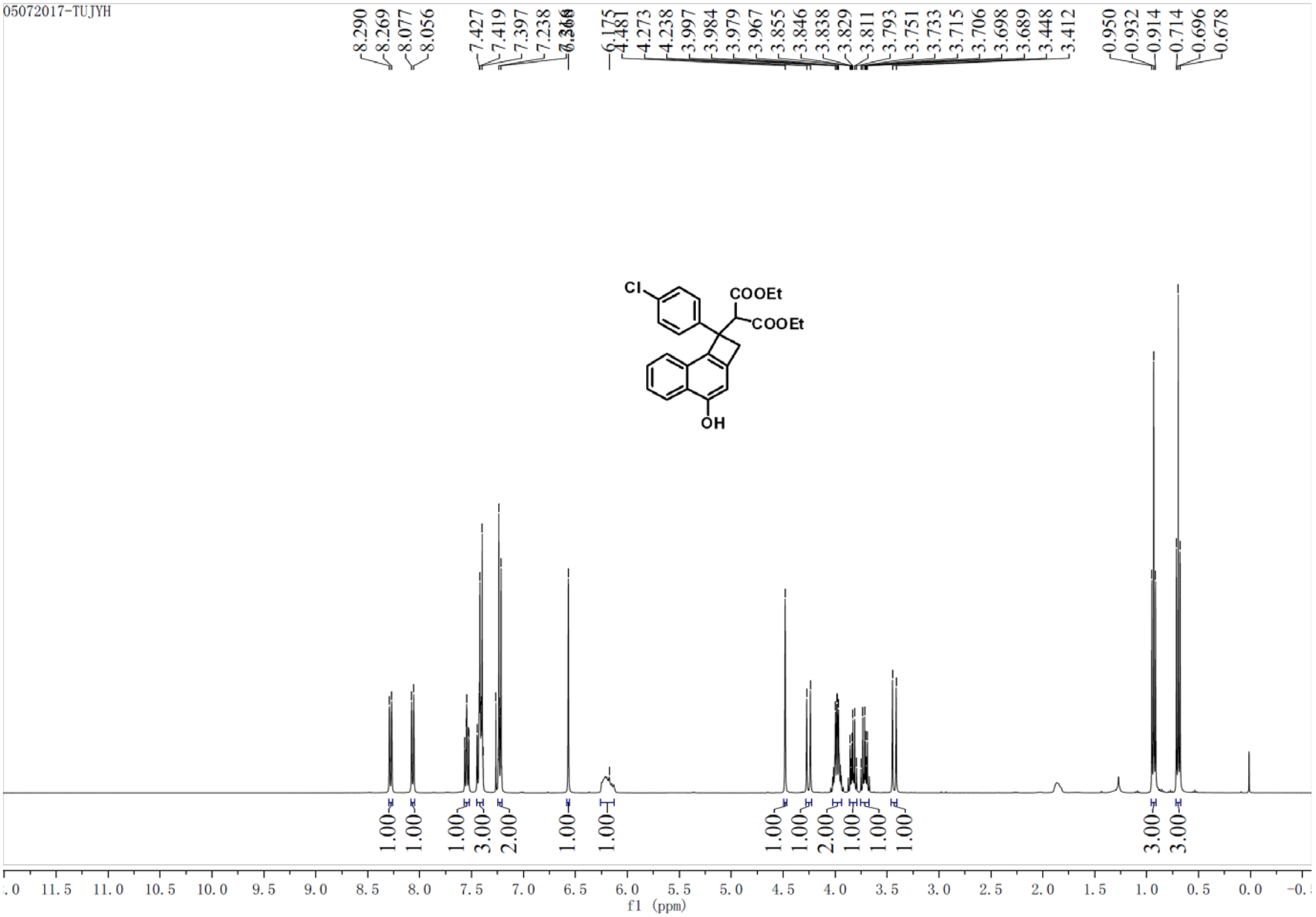
^{13}C NMR Spectrum of Compound 3b



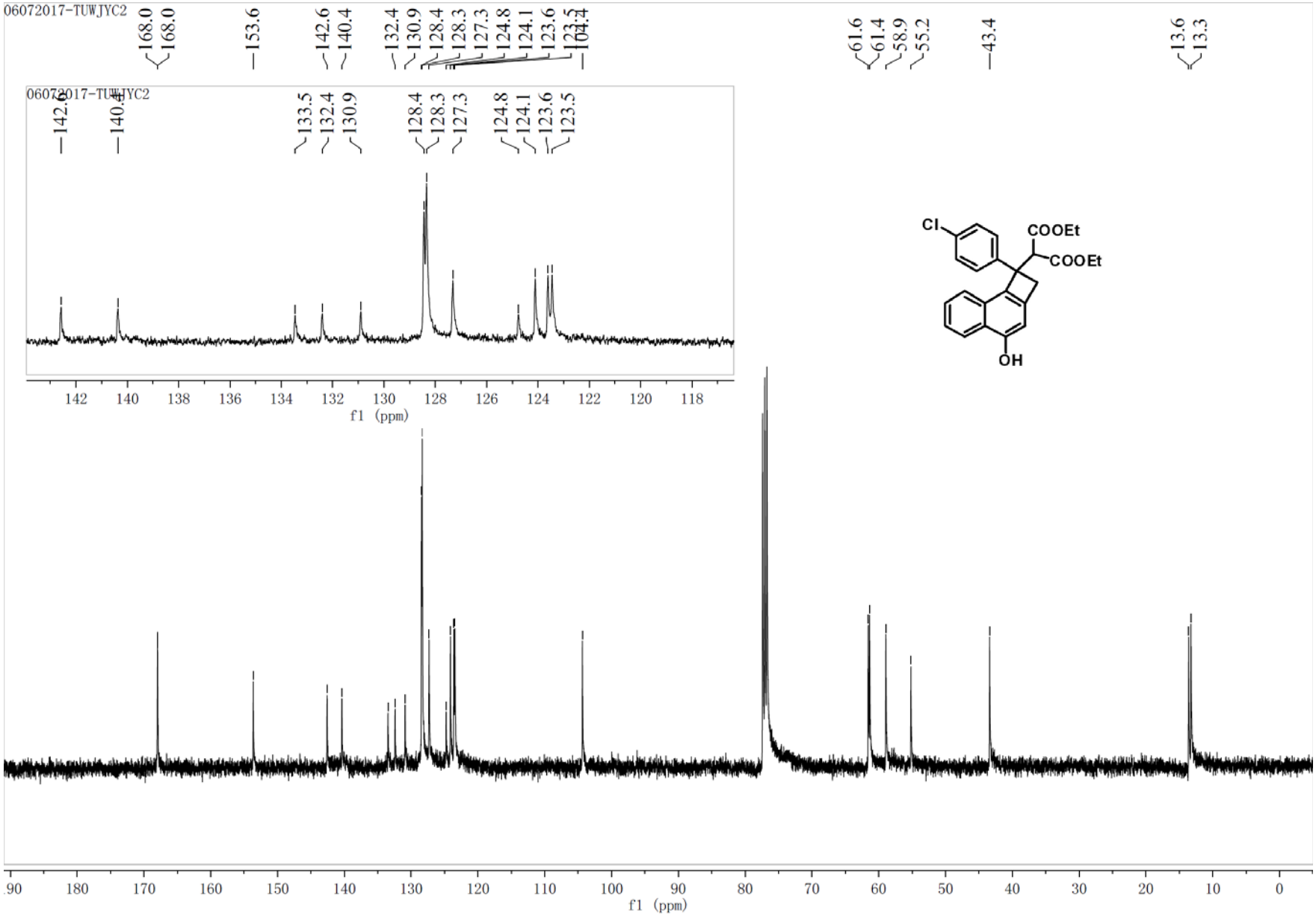
^{1}H NMR Spectrum of Compound 3c



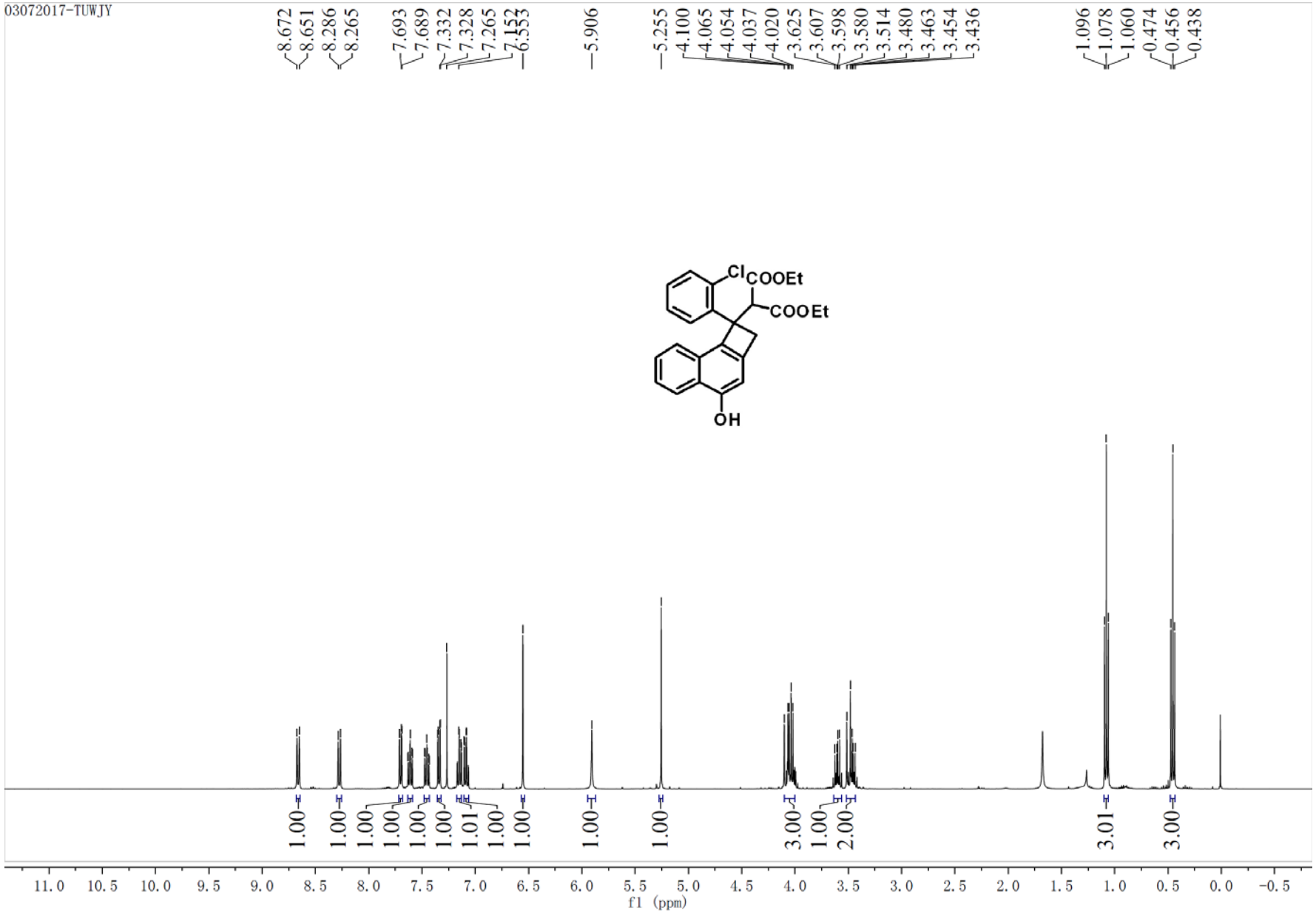
^{13}C NMR Spectrum of Compound 3c



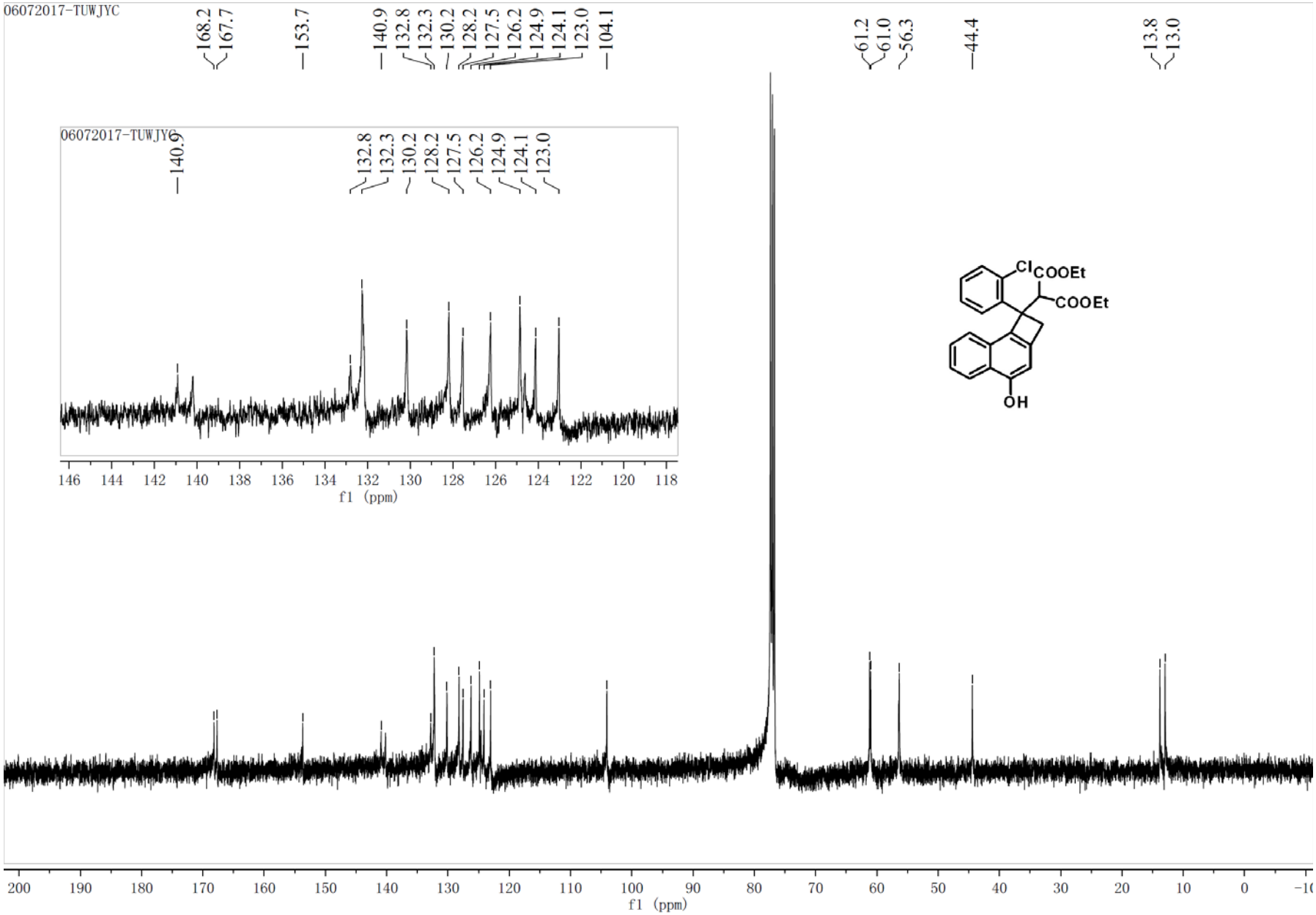
^{1}H NMR Spectrum of Compound 3d



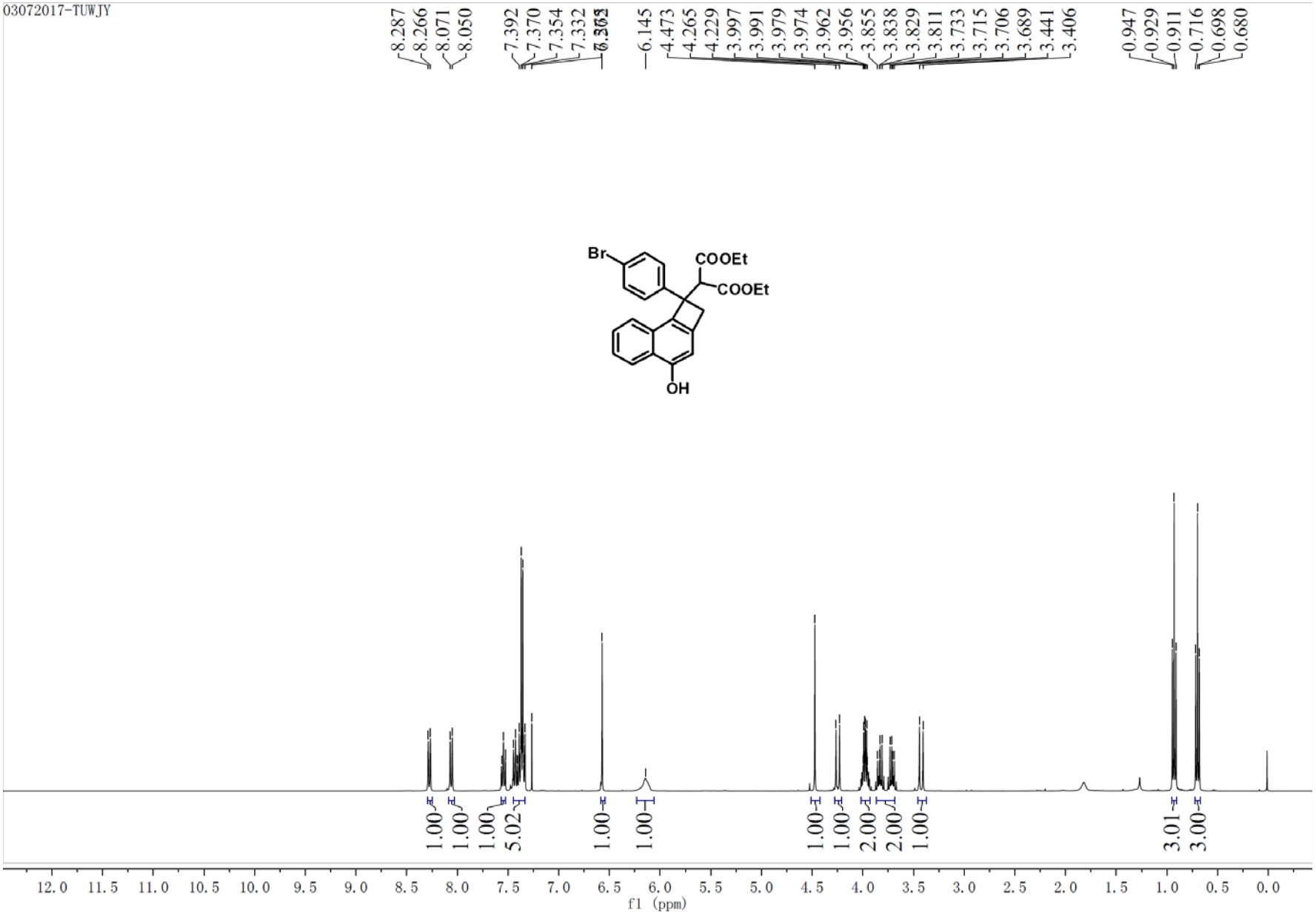
^{13}C NMR Spectrum of Compound 3d



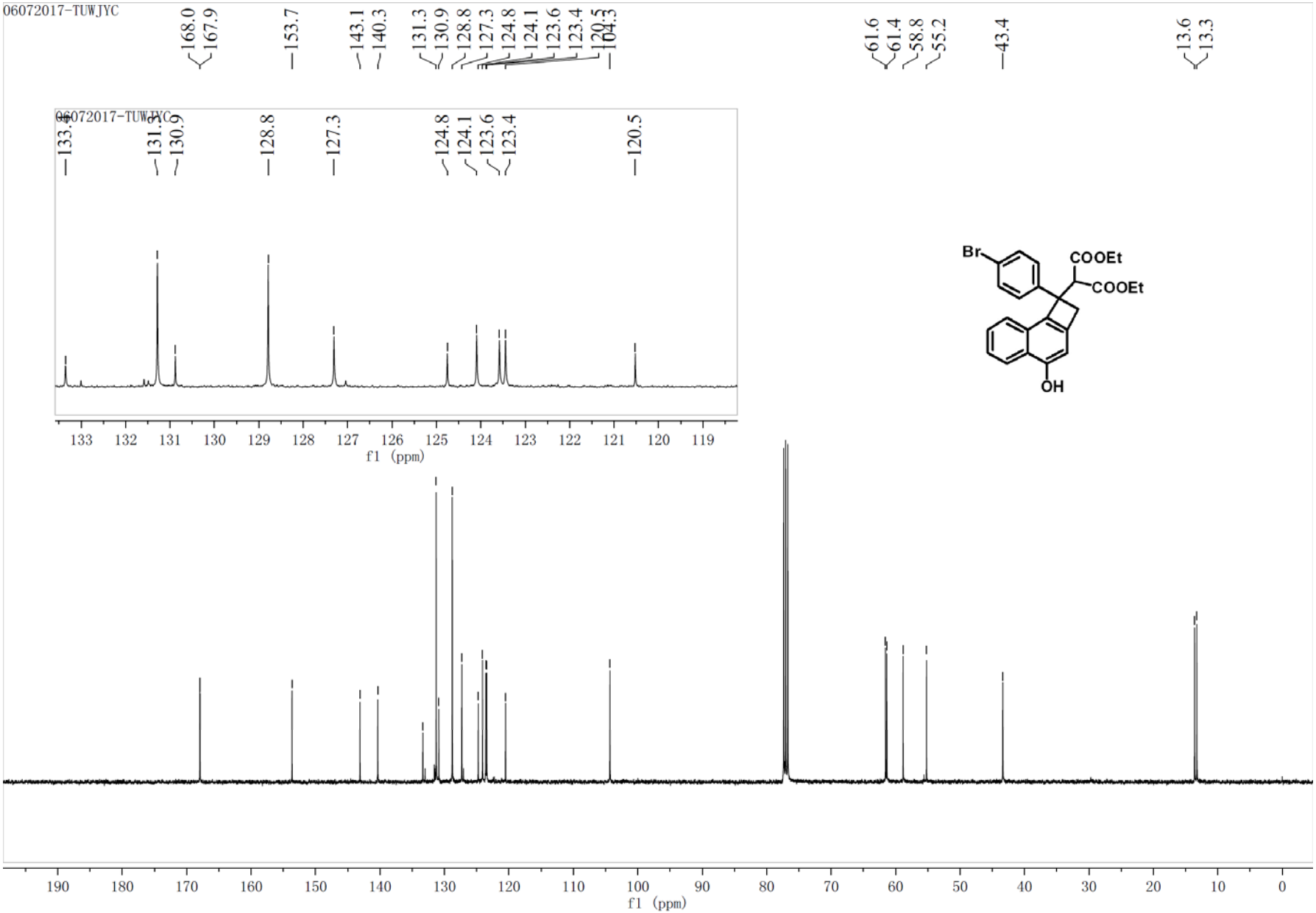
^{1}H NMR Spectrum of Compound 3e



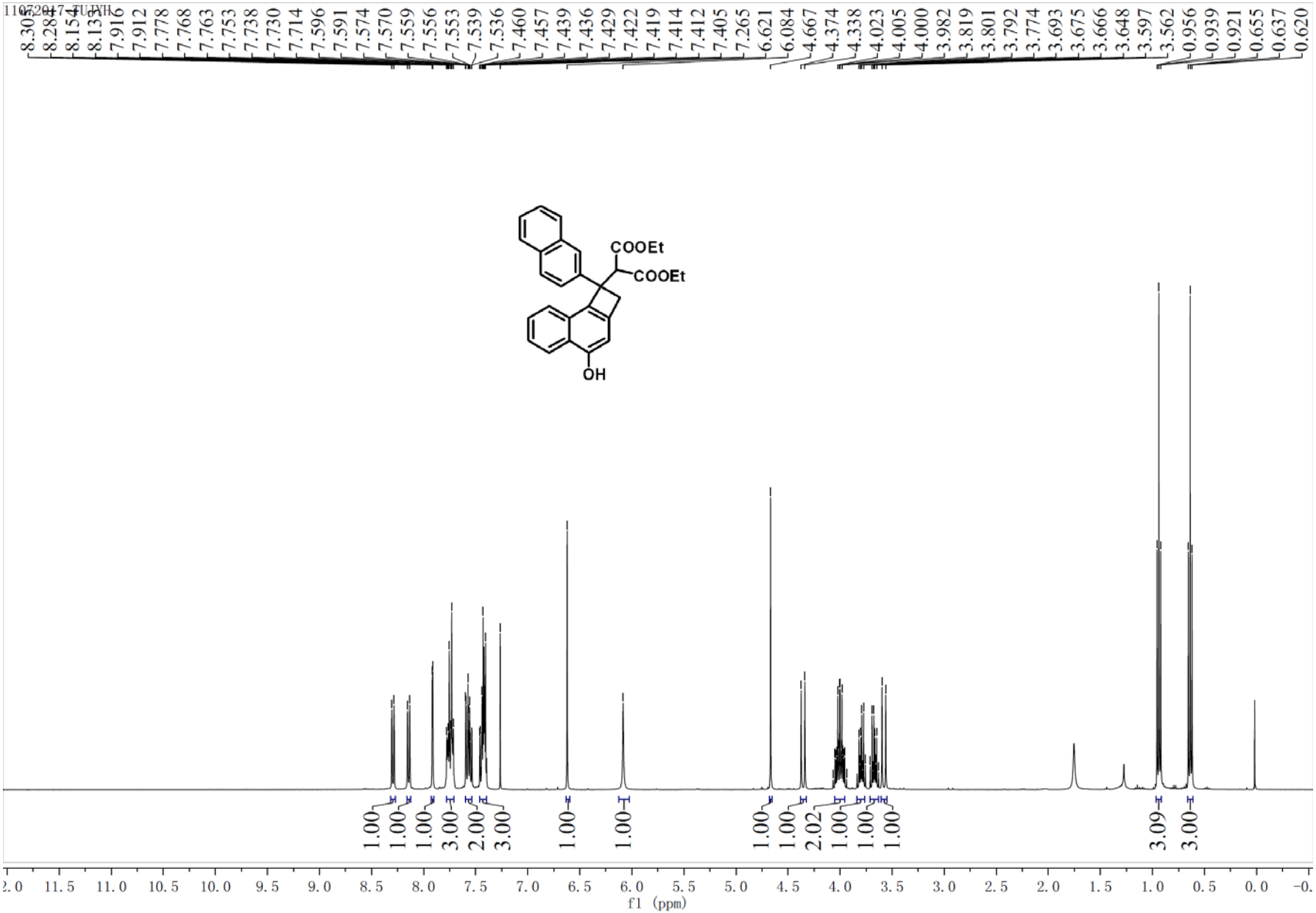
^{13}C NMR Spectrum of Compound 3e



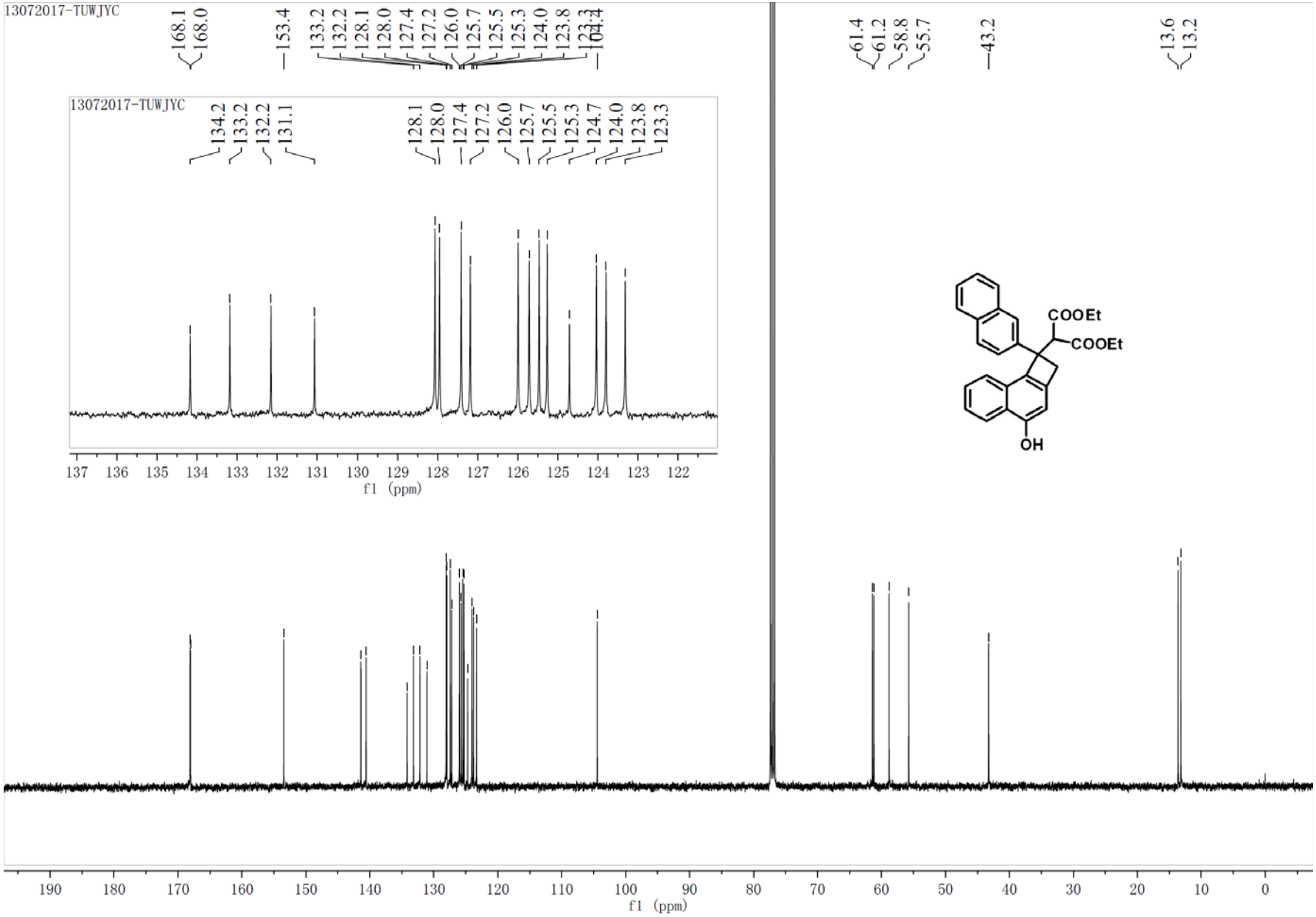
^{1}H NMR Spectrum of Compound 3f



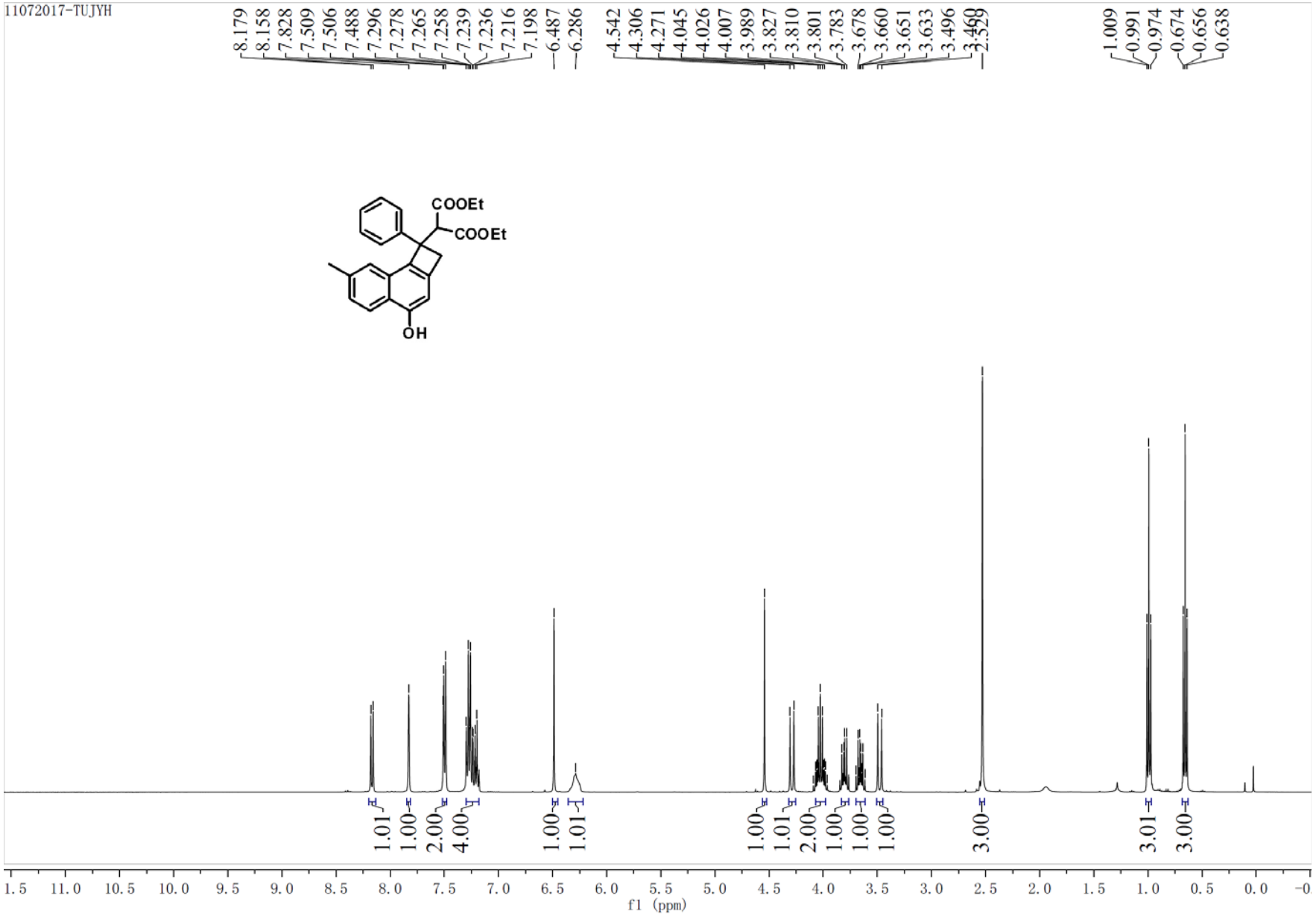
^{13}C NMR Spectrum of Compound 3f



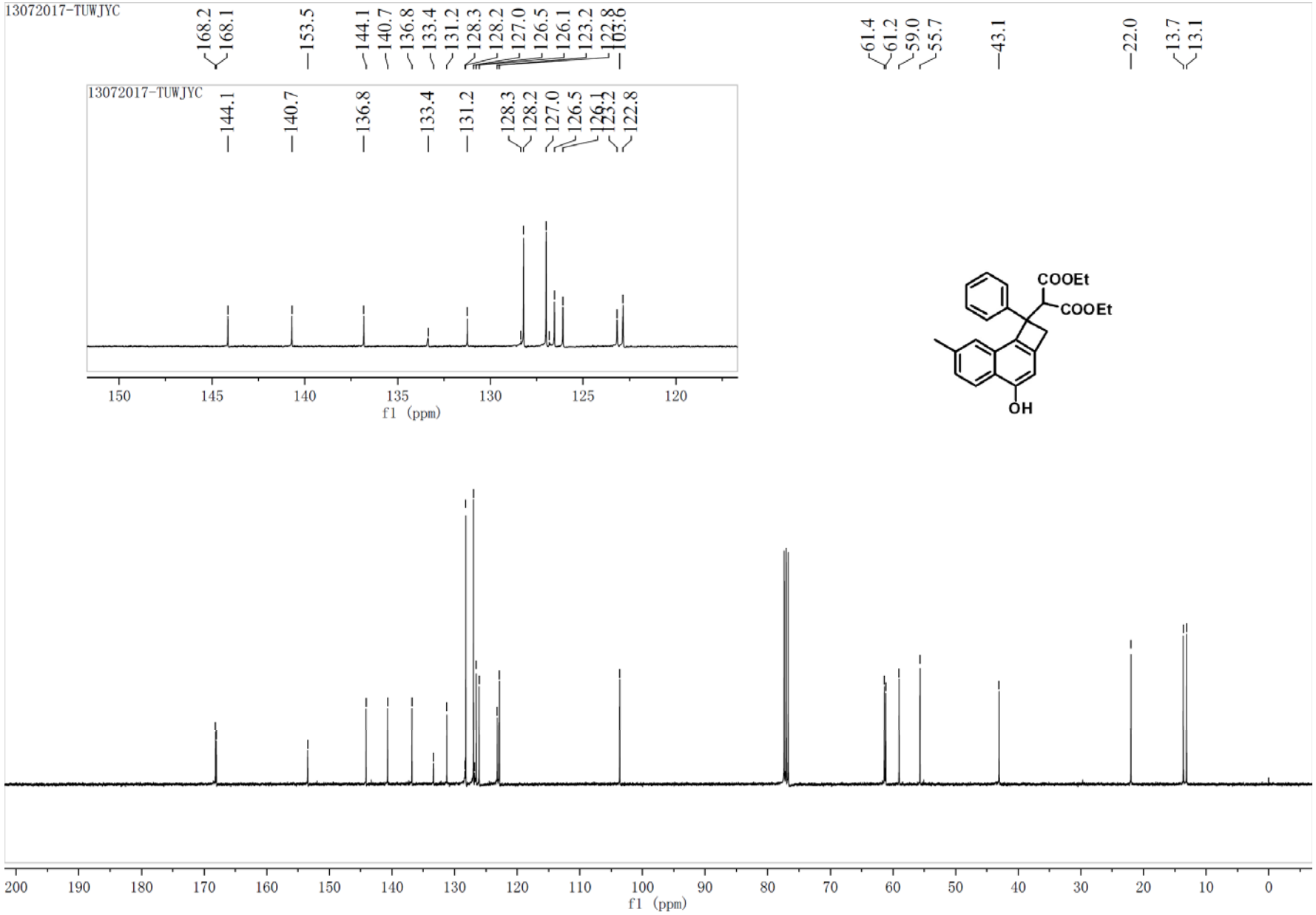
^{1}H NMR Spectrum of Compound 3g



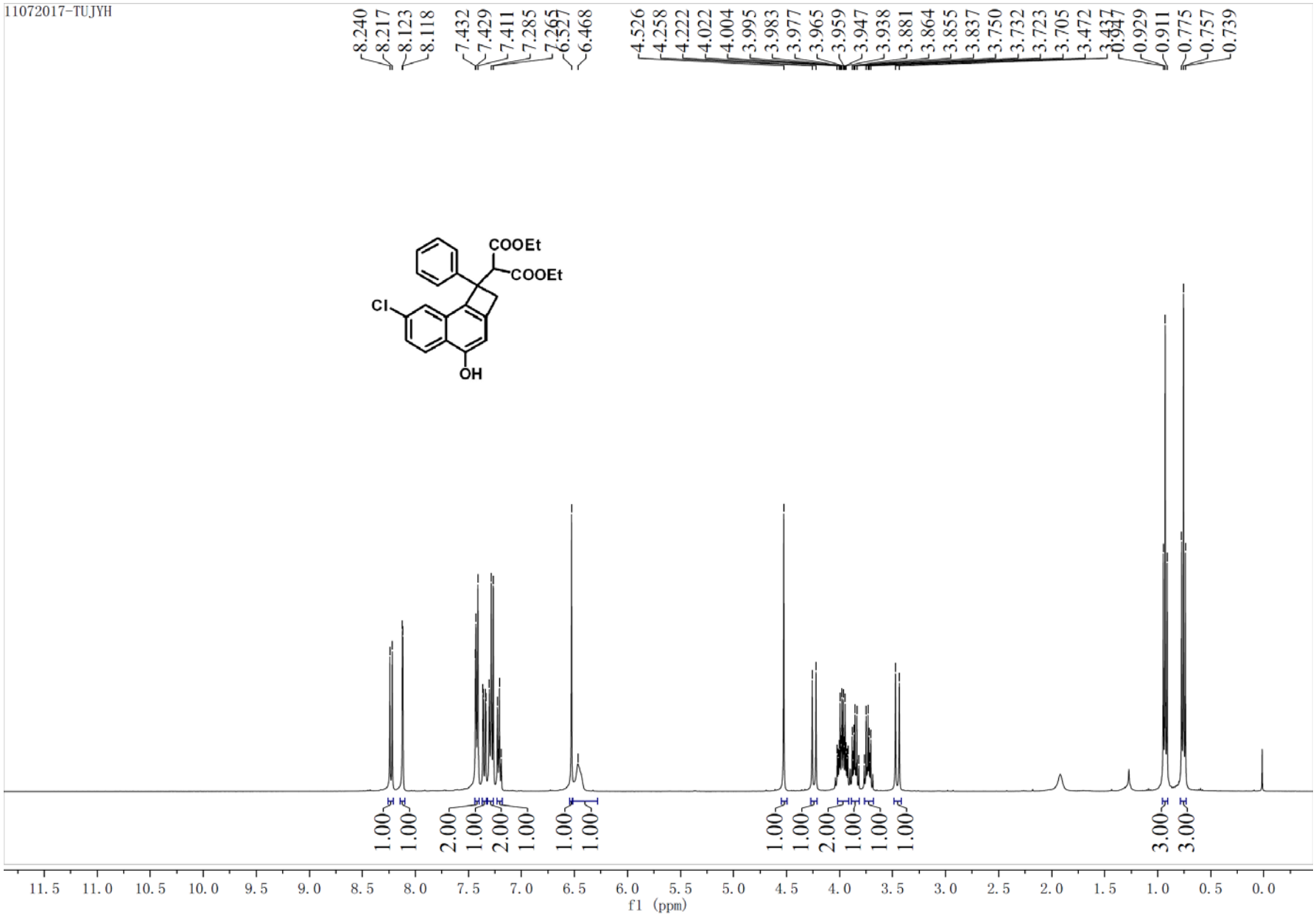
^{13}C NMR Spectrum of Compound 3g



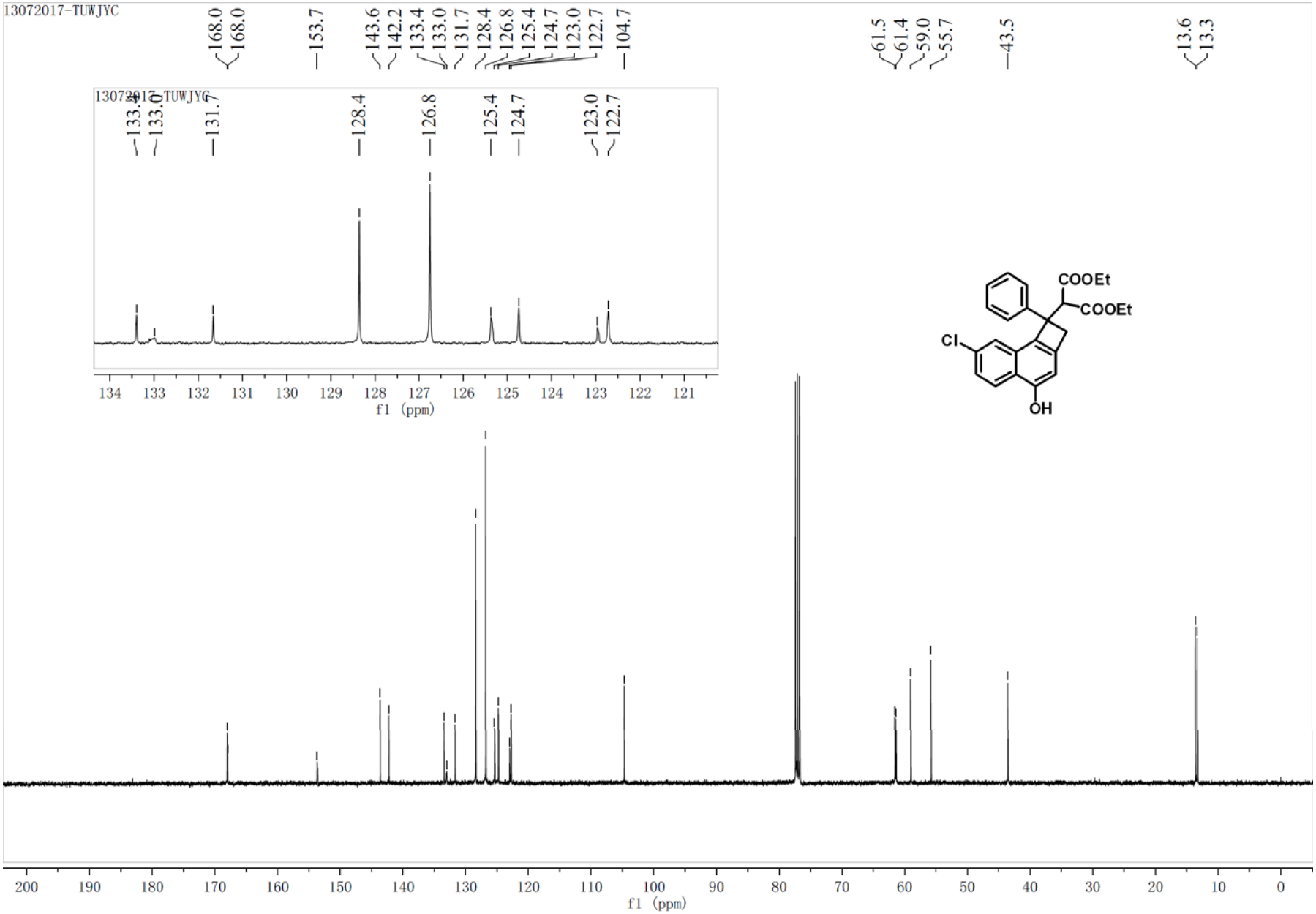
^{1}H NMR Spectrum of Compound 3h



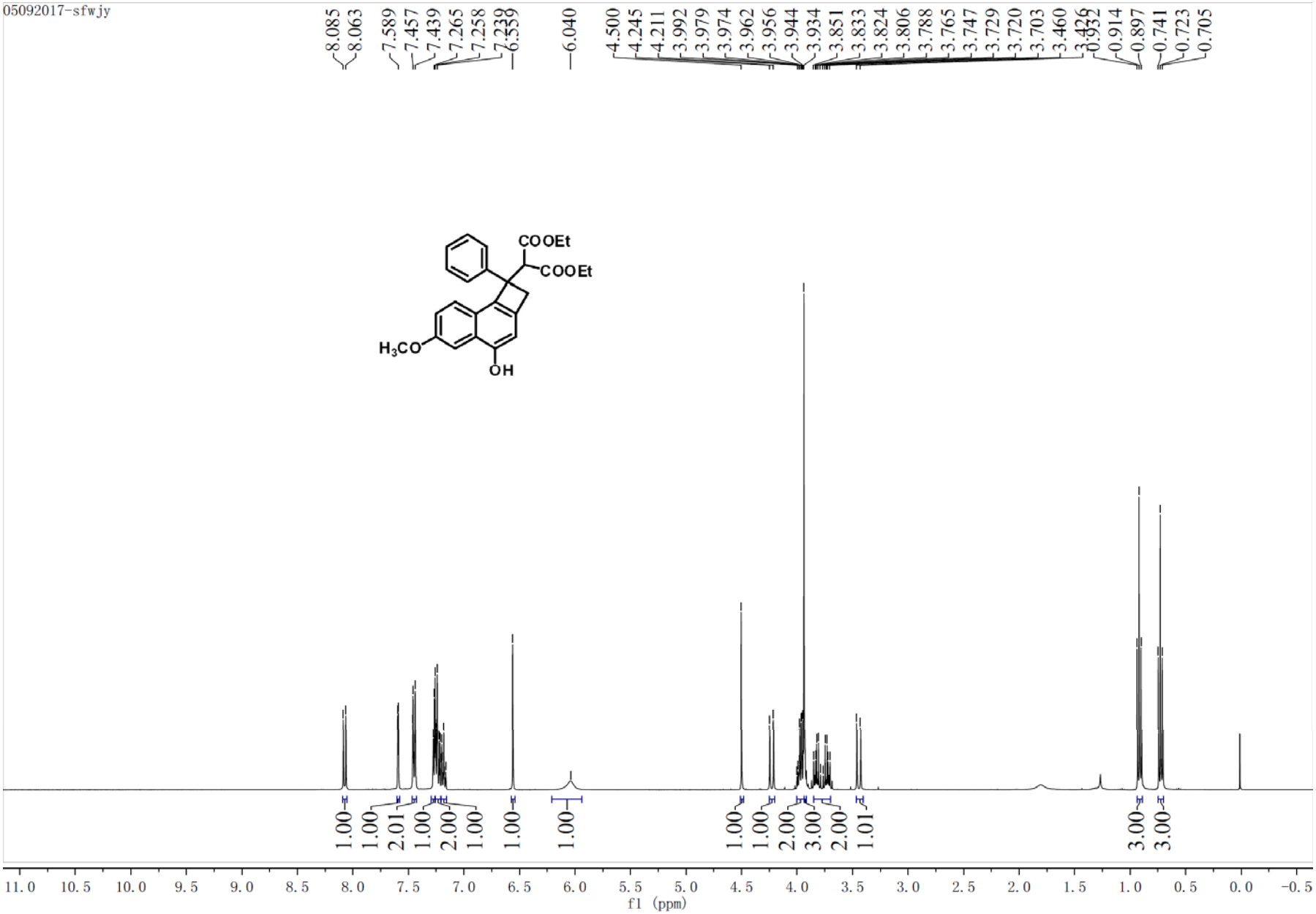
^{13}C NMR Spectrum of Compound 3h



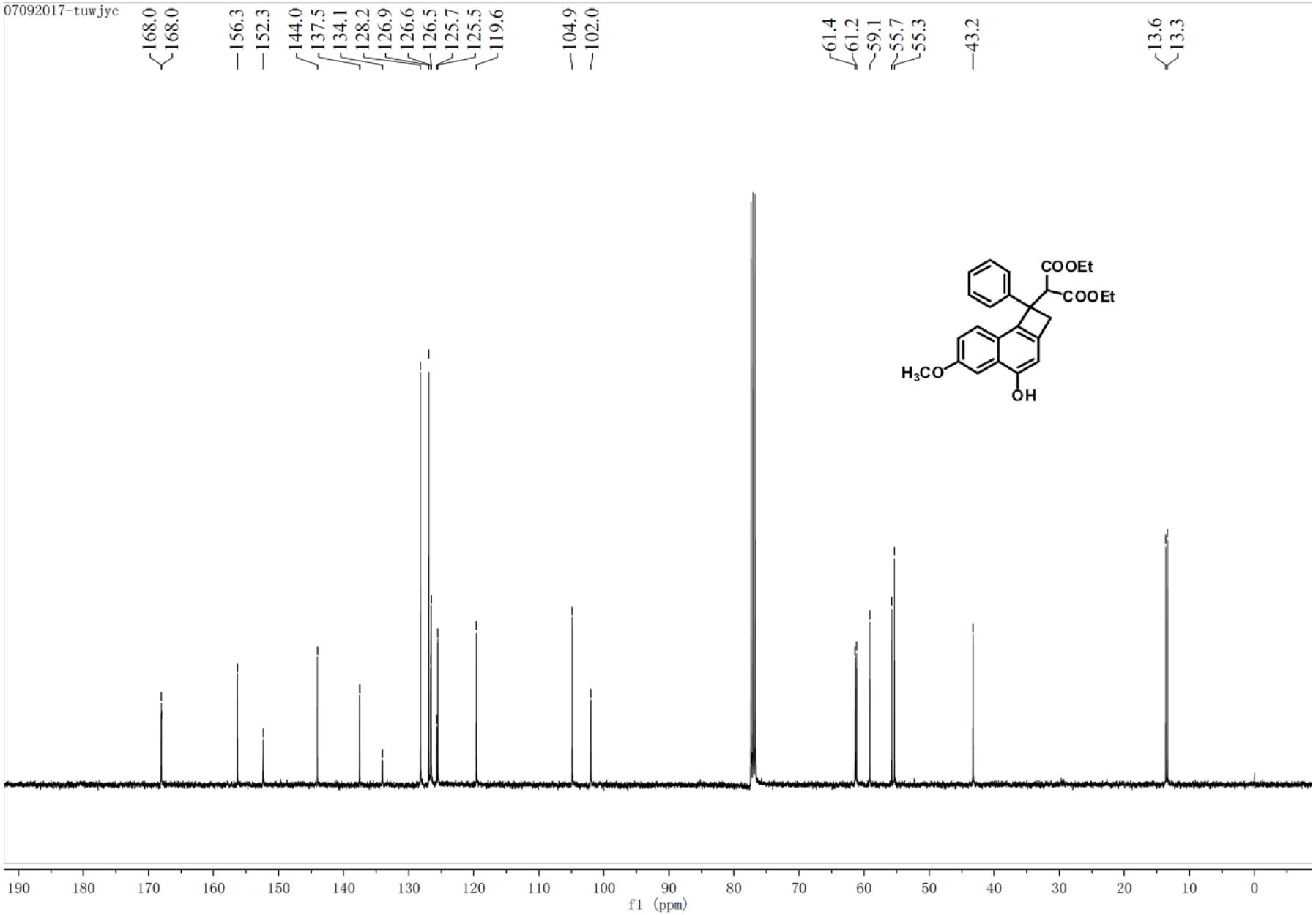
^{1}H NMR Spectrum of Compound 3i



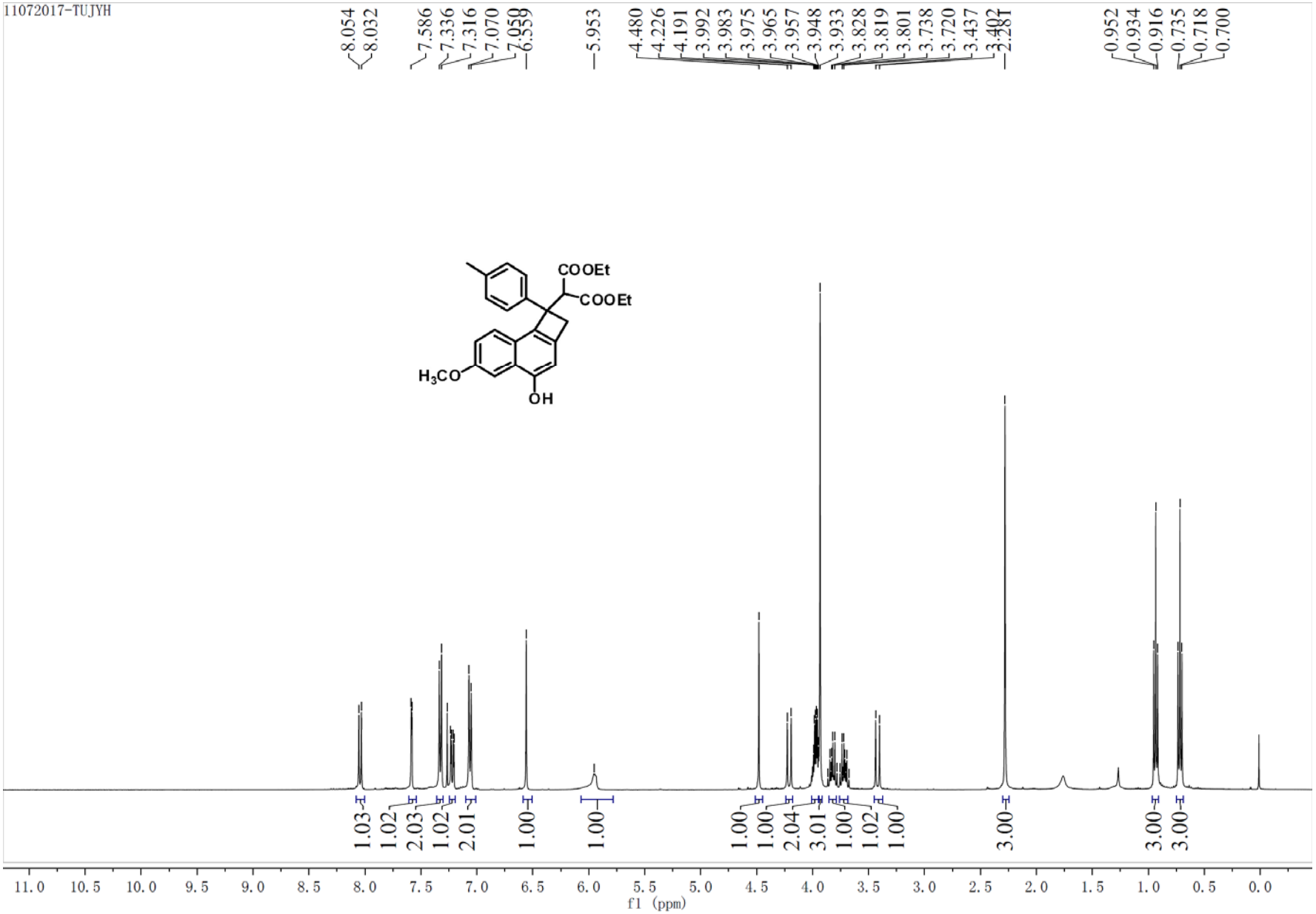
^{13}C NMR Spectrum of Compound 3i



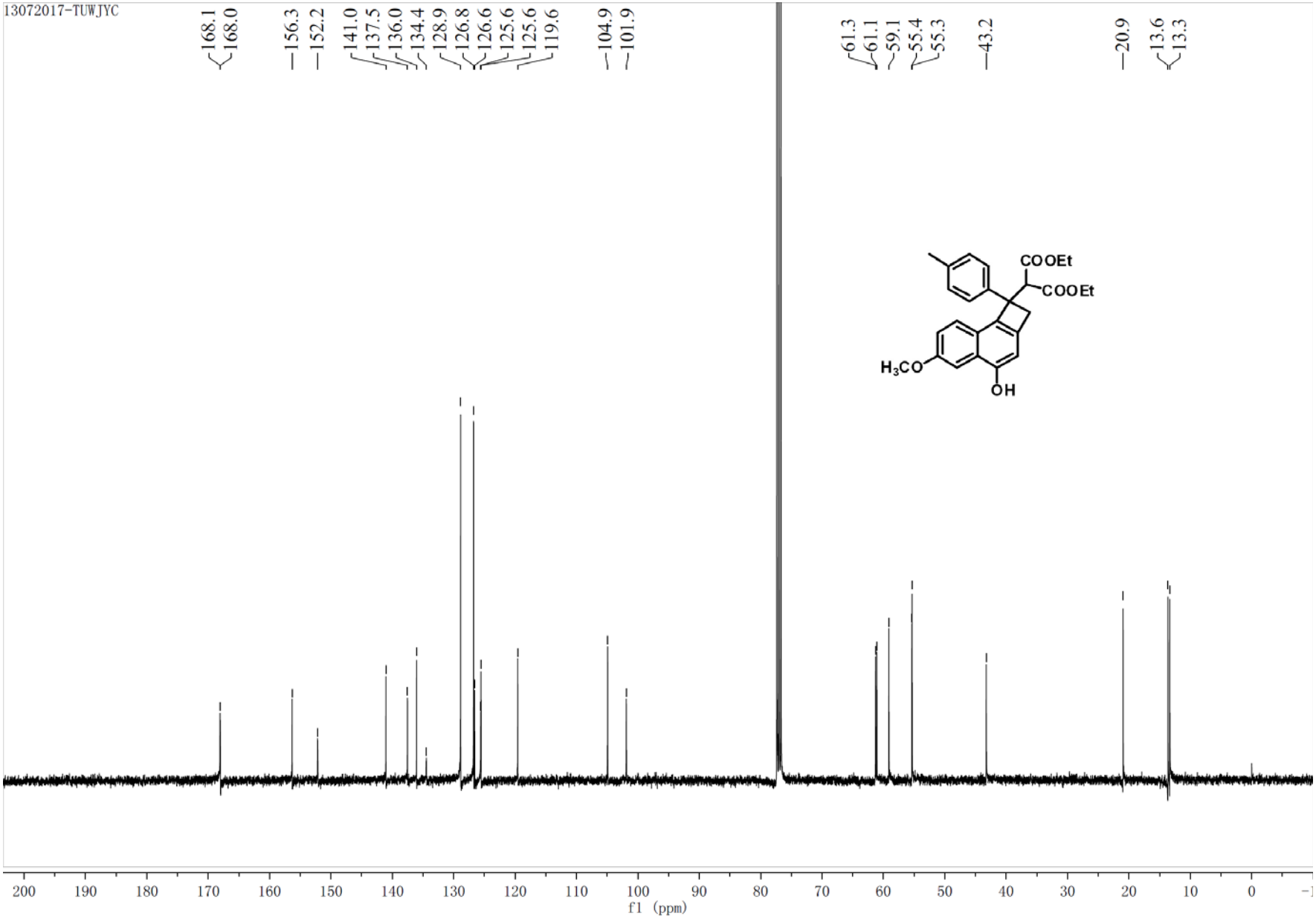
^{1}H NMR Spectrum of Compound 3j



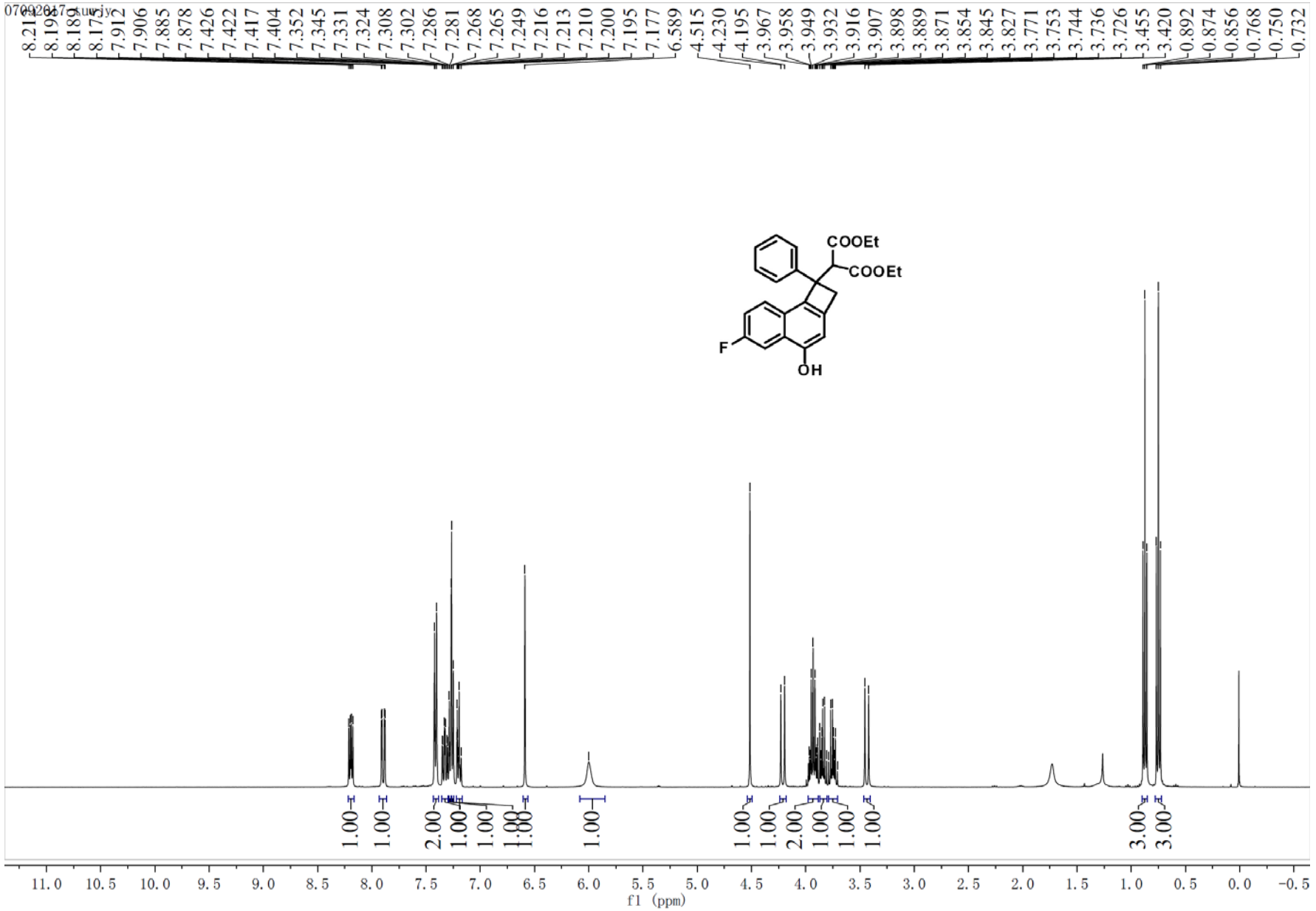
^{13}C NMR Spectrum of Compound 3j



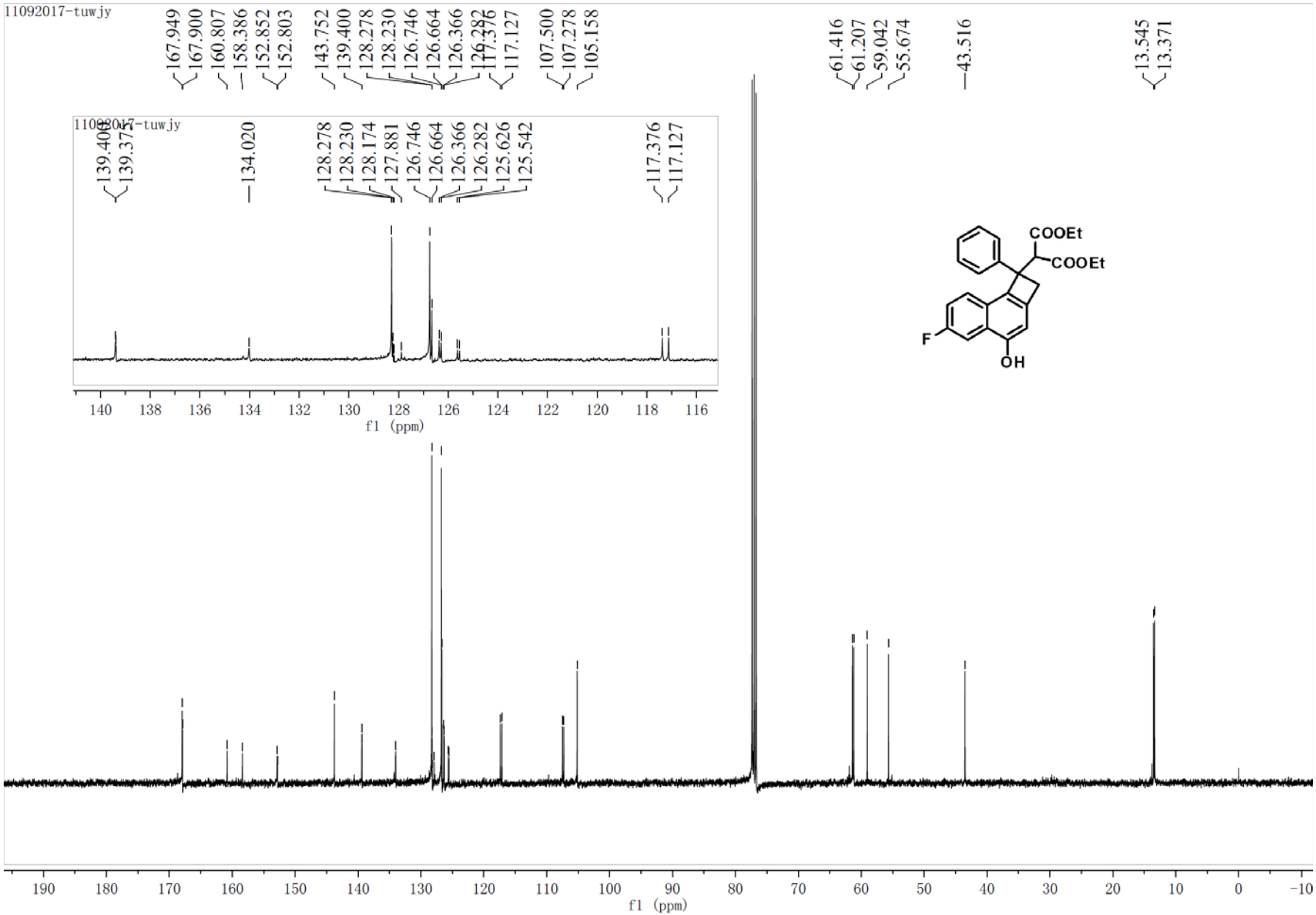
^{1}H NMR Spectrum of Compound 3k



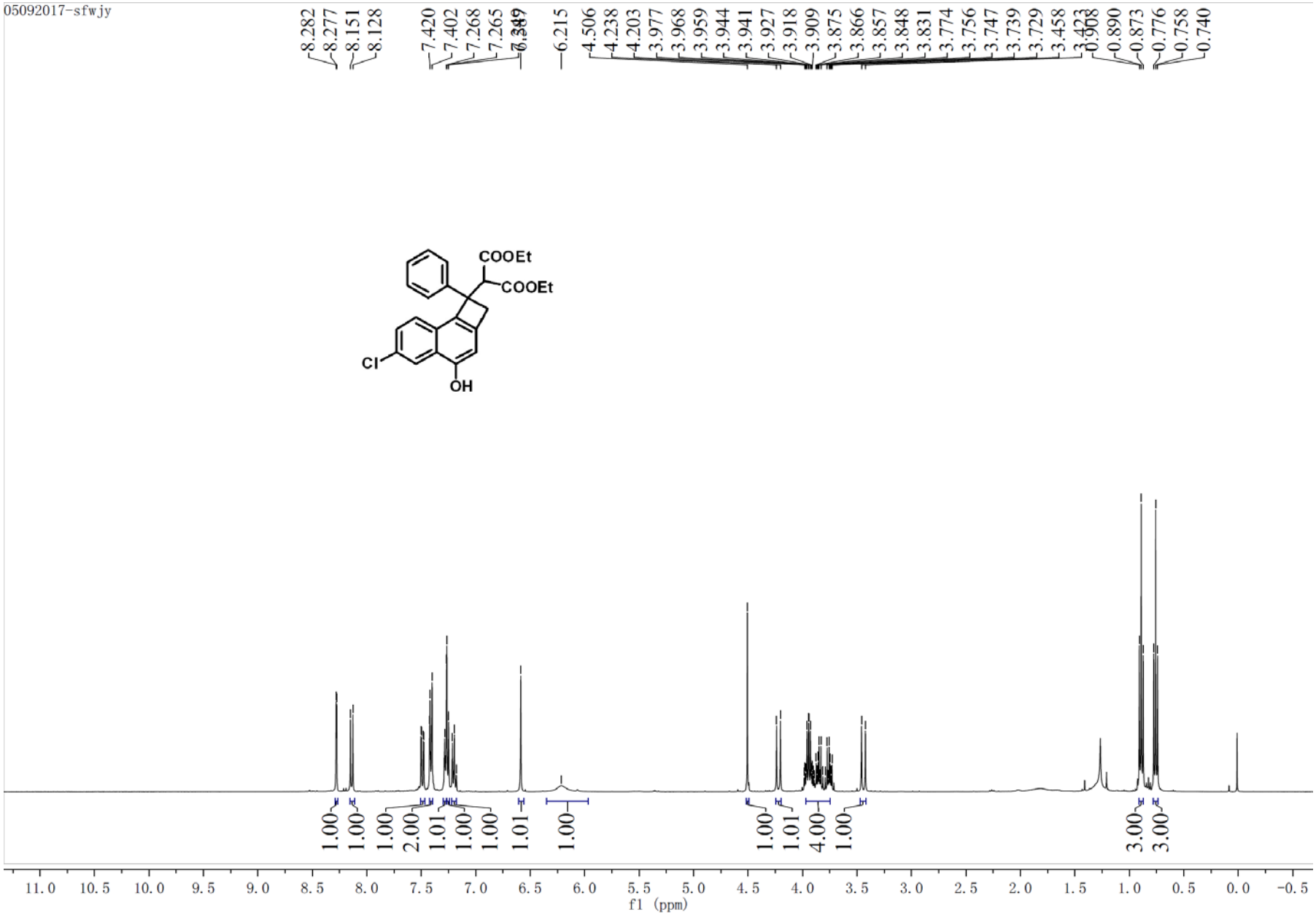
^{13}C NMR Spectrum of Compound 3k



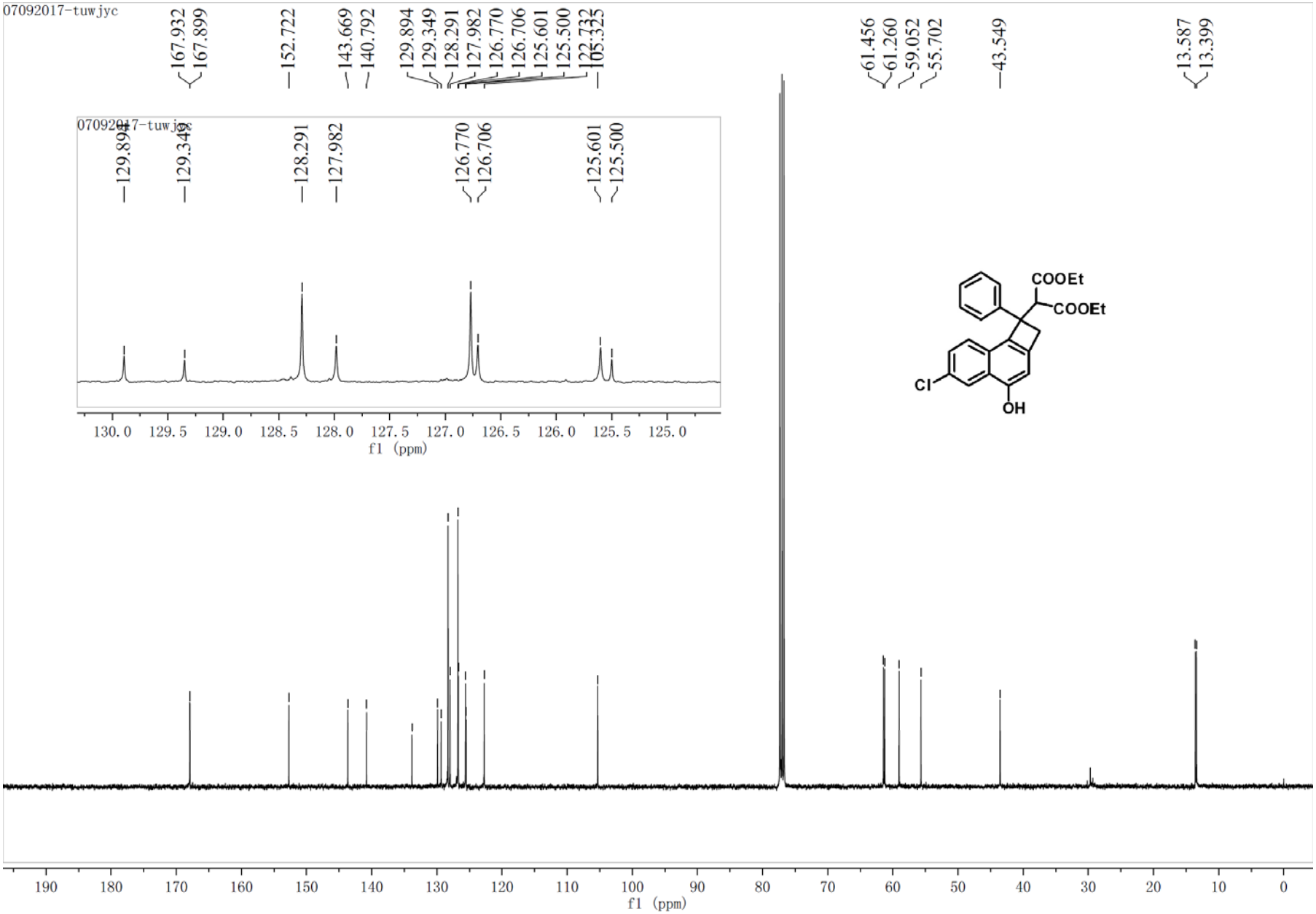
^{1}H NMR Spectrum of Compound 3l



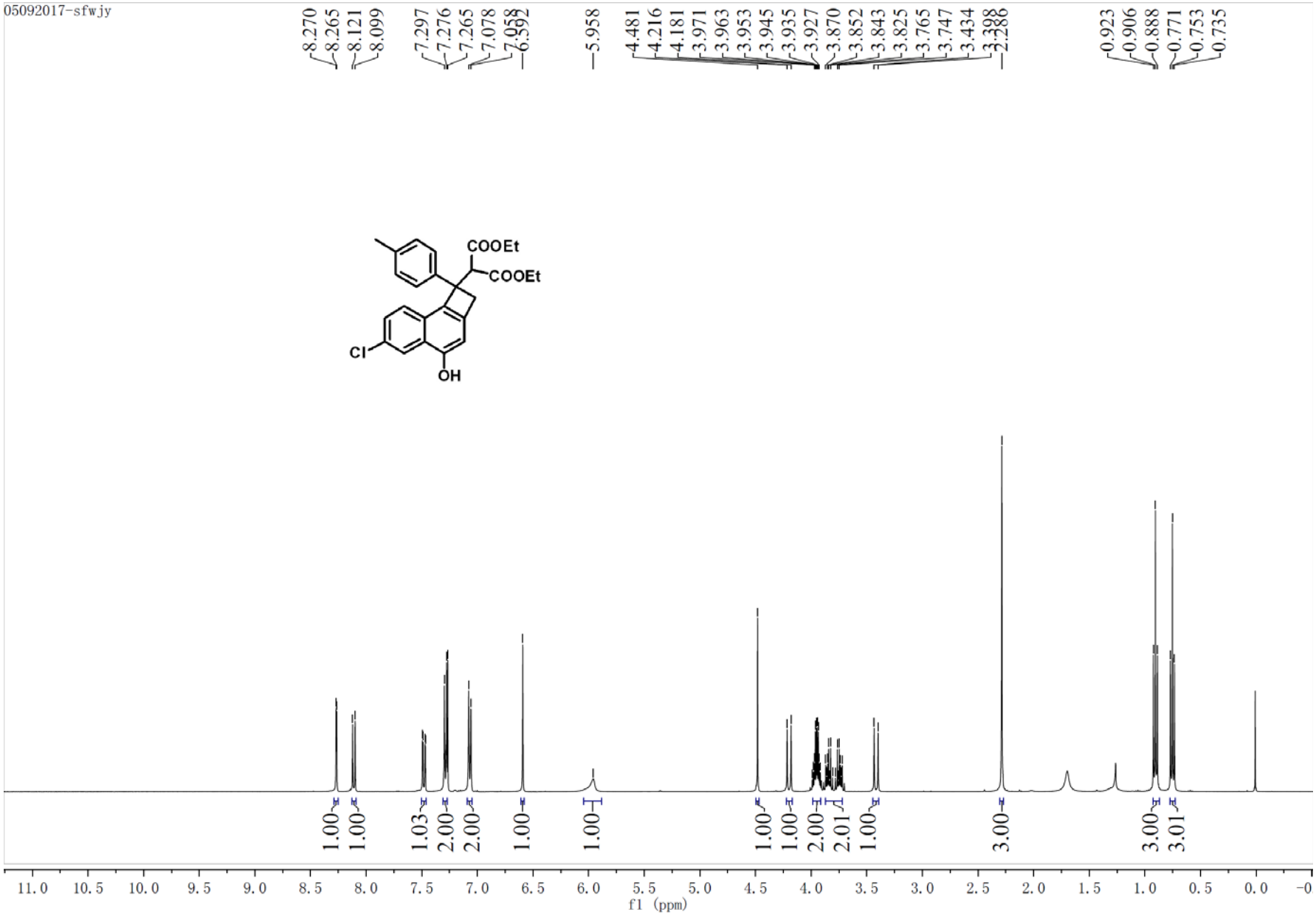
^{13}C NMR Spectrum of Compound 3l



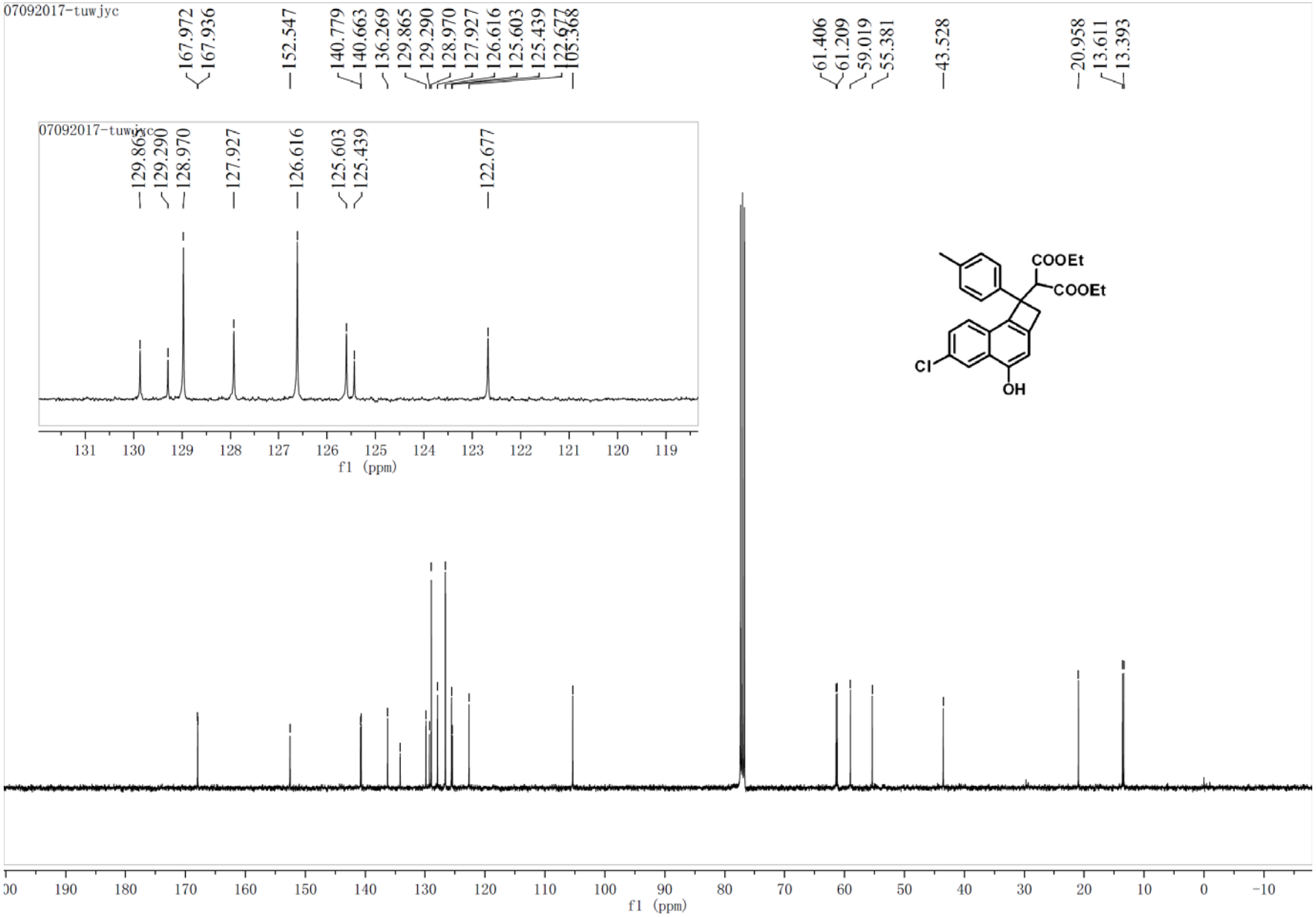
^{1}H NMR Spectrum of Compound 3m



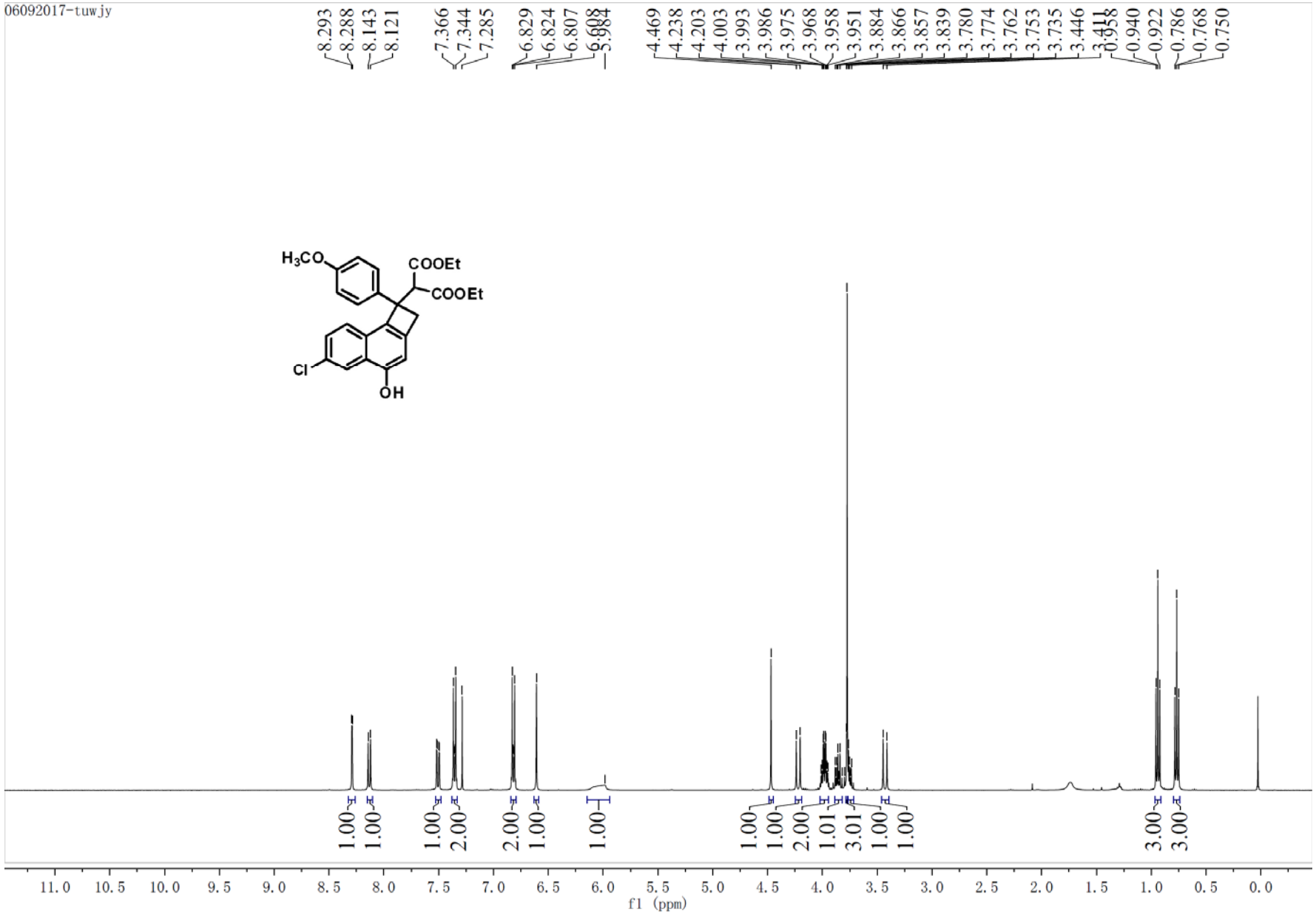
^{13}C NMR Spectrum of Compound 3m



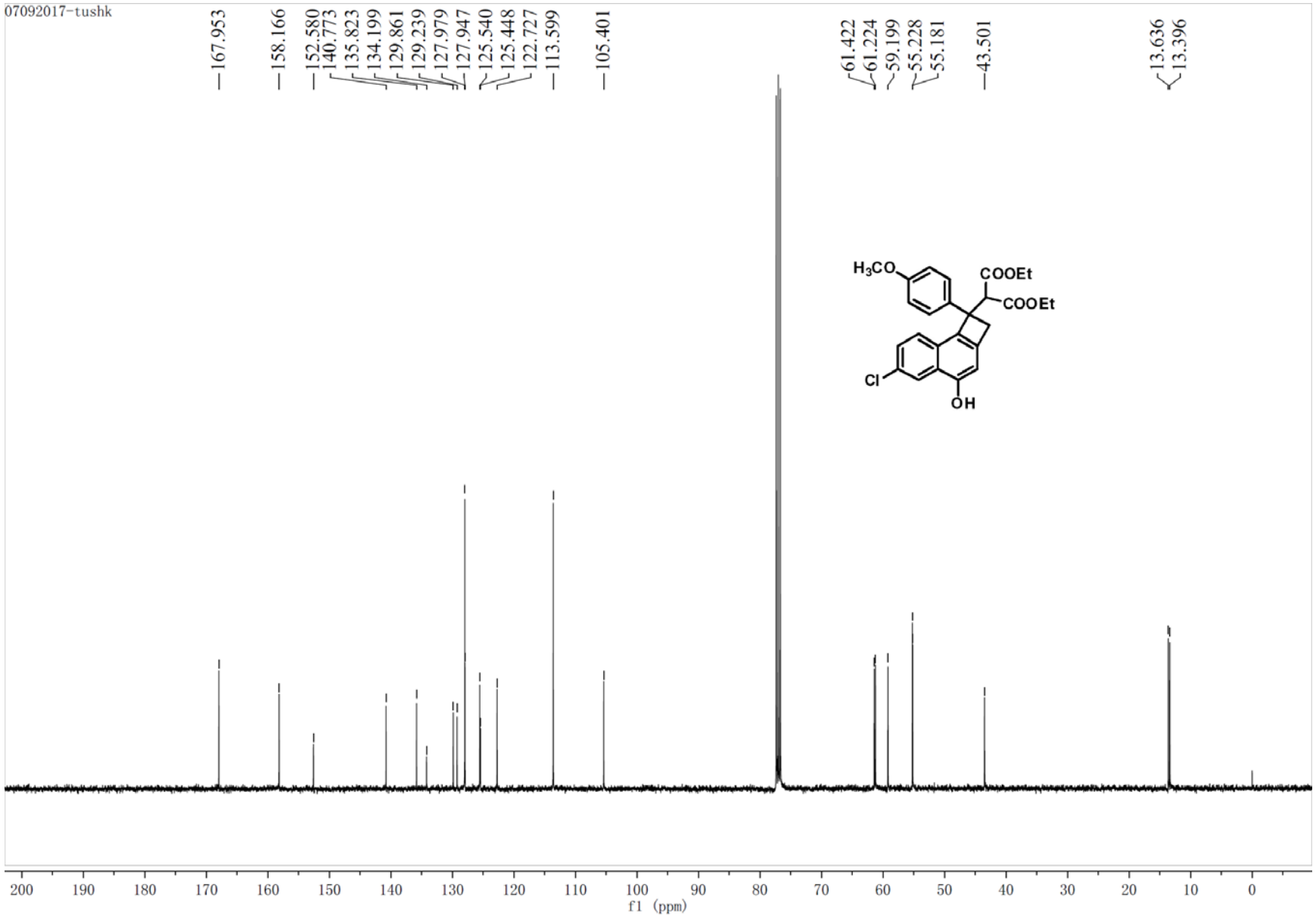
^{1}H NMR Spectrum of Compound 3n



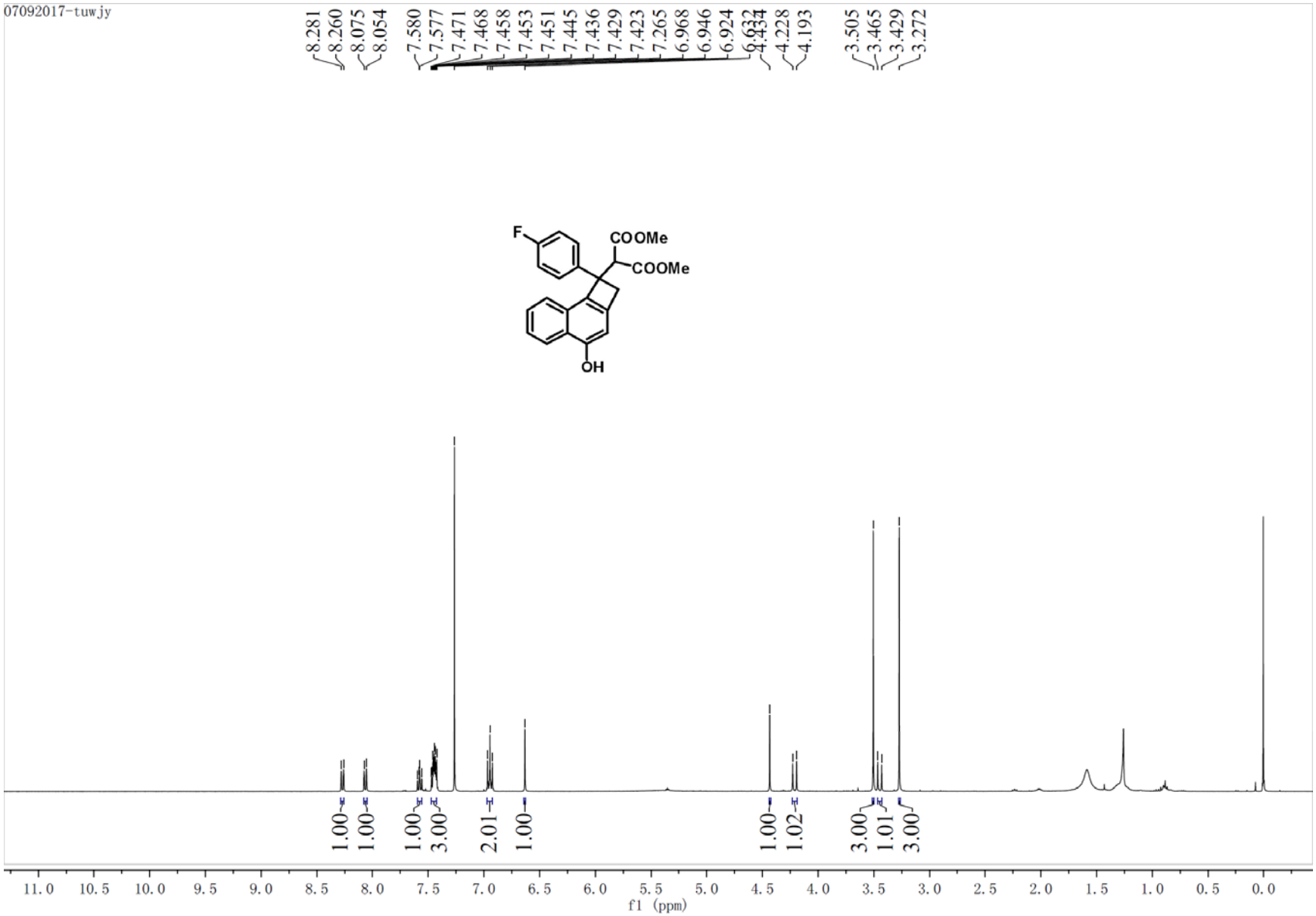
^{13}C NMR Spectrum of Compound 3n



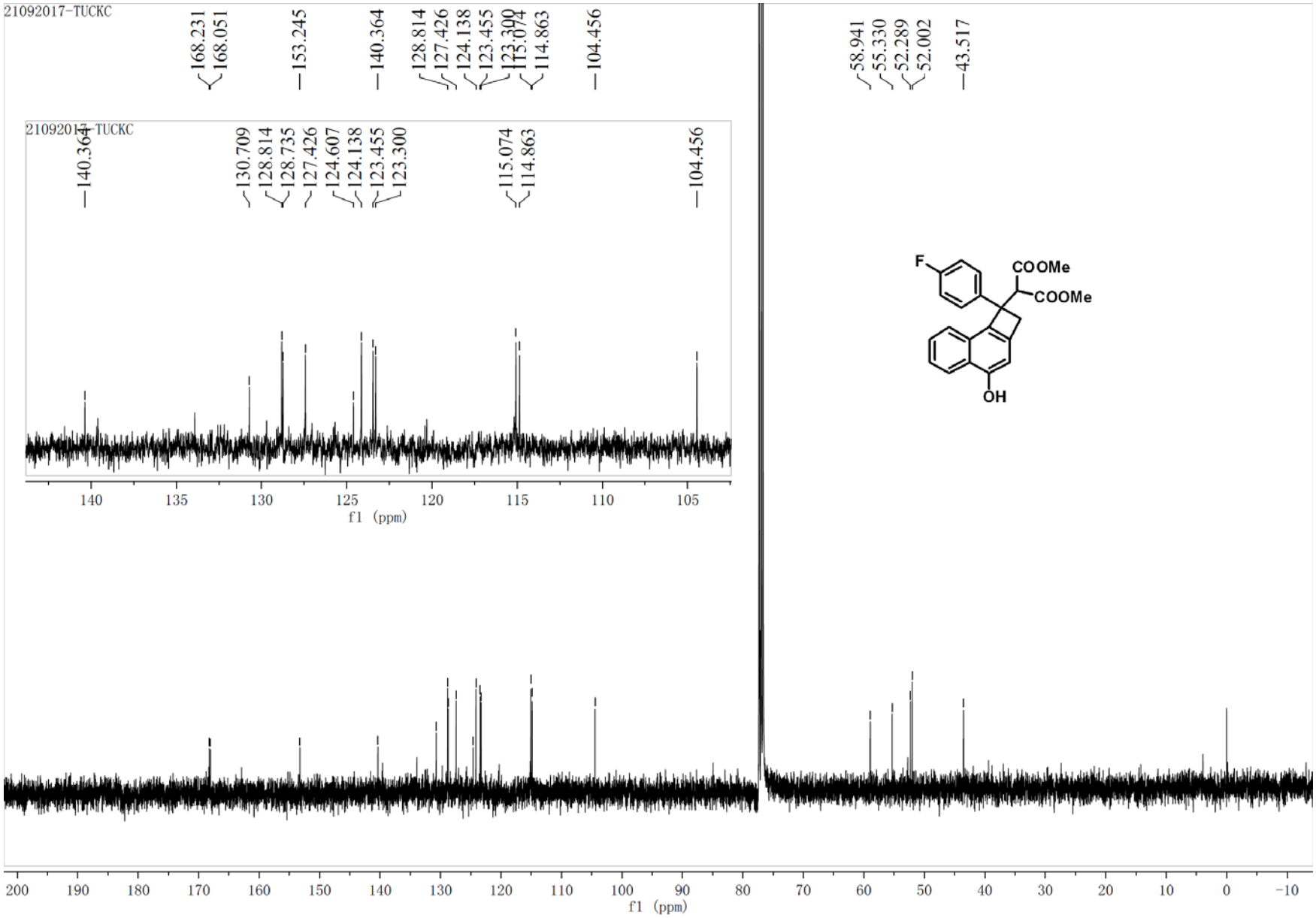
^{1}H NMR Spectrum of Compound 3o



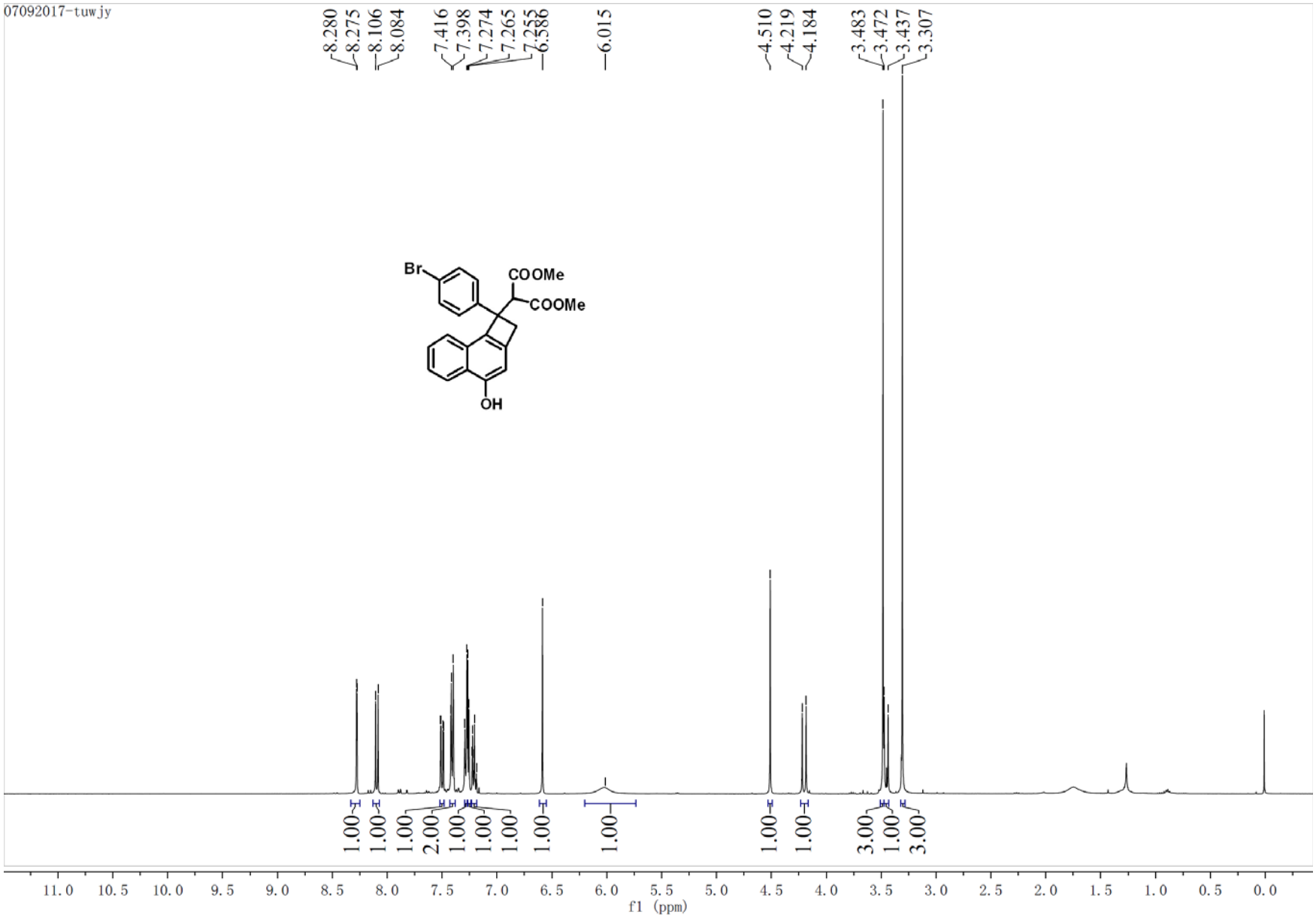
^{13}C NMR Spectrum of Compound 3o



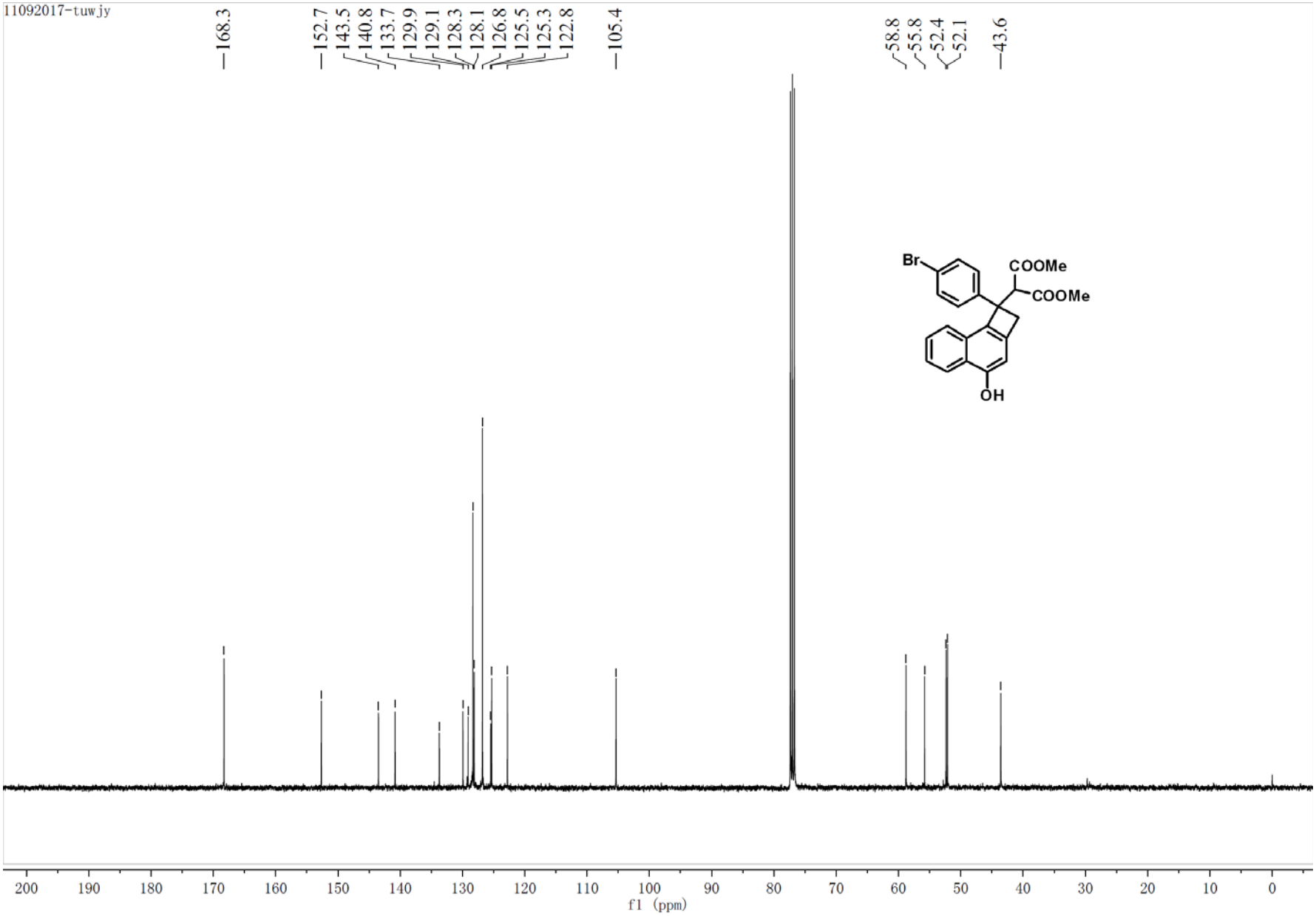
^{1}H NMR Spectrum of Compound 3p



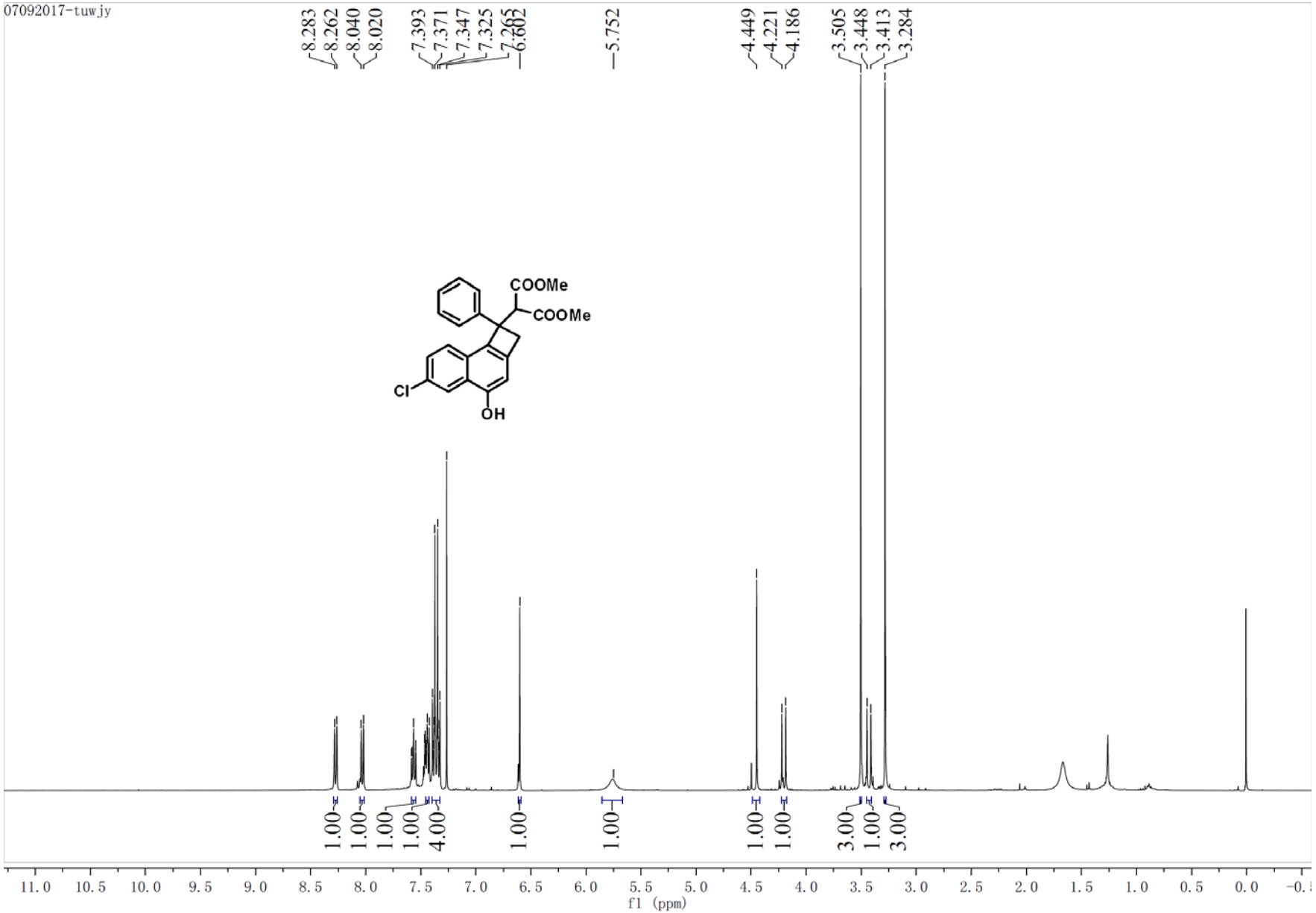
^{13}C NMR Spectrum of Compound 3p



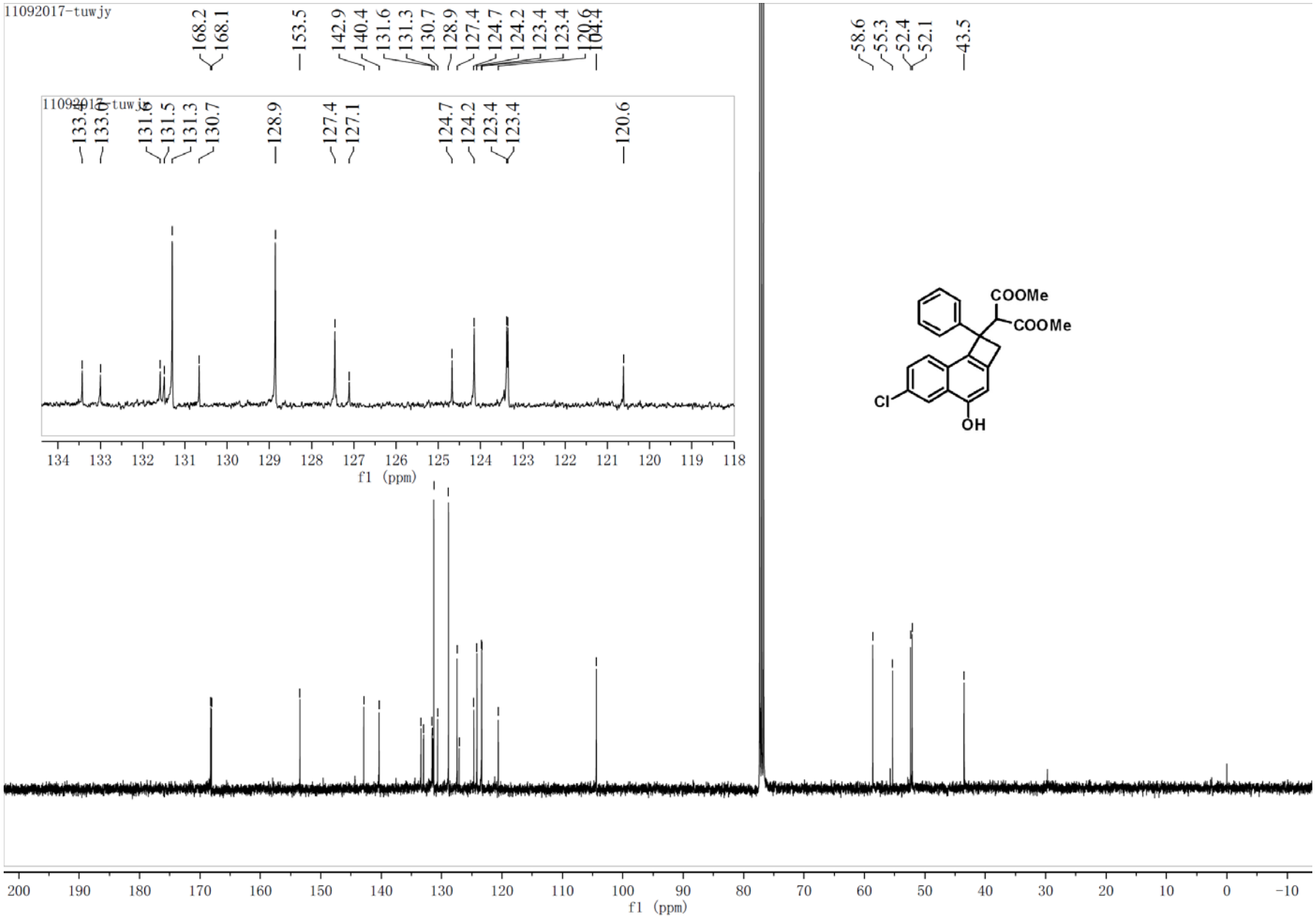
^{1}H NMR Spectrum of Compound 3q



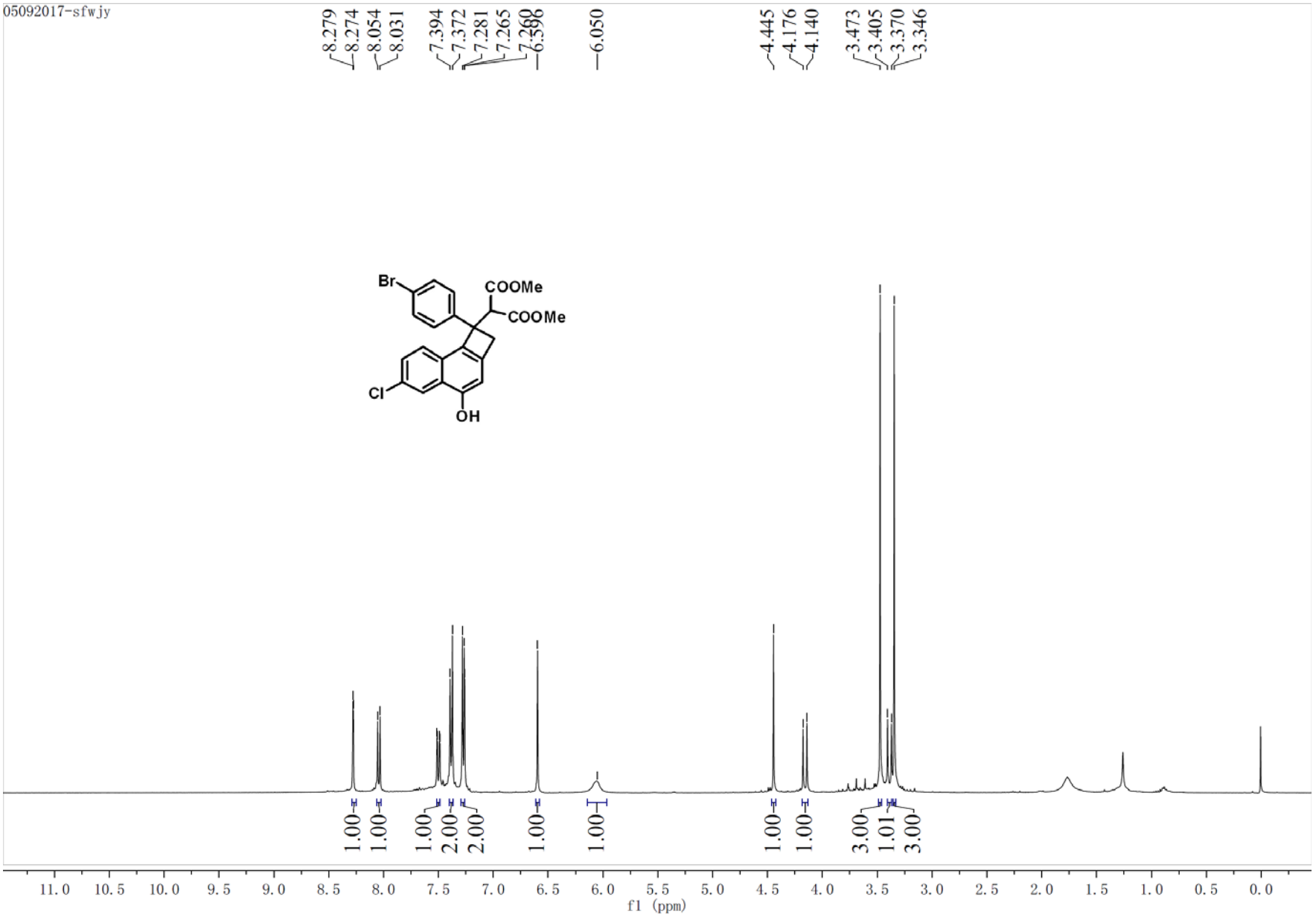
^{13}C NMR Spectrum of Compound 3q



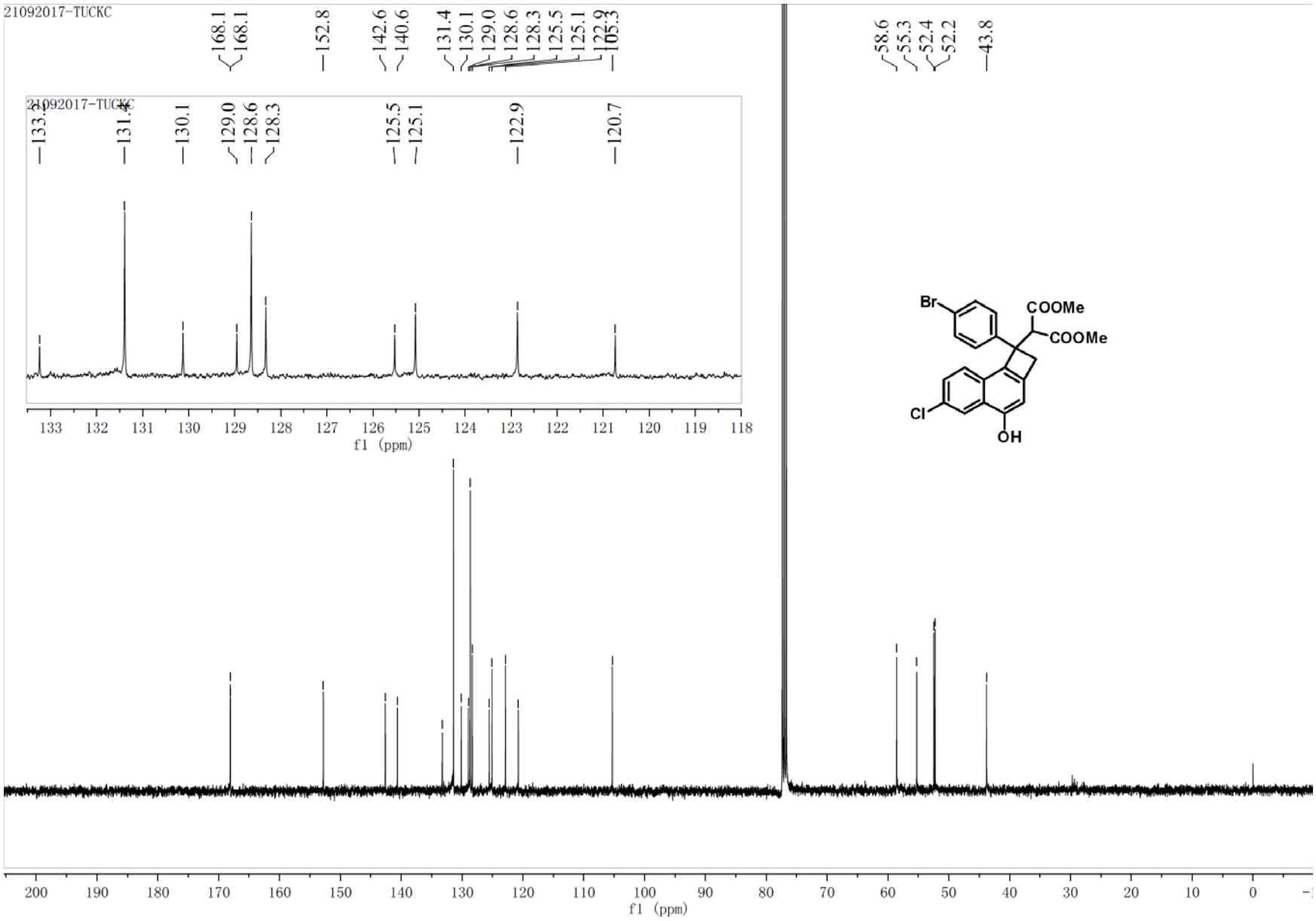
^{1}H NMR Spectrum of Compound 3r



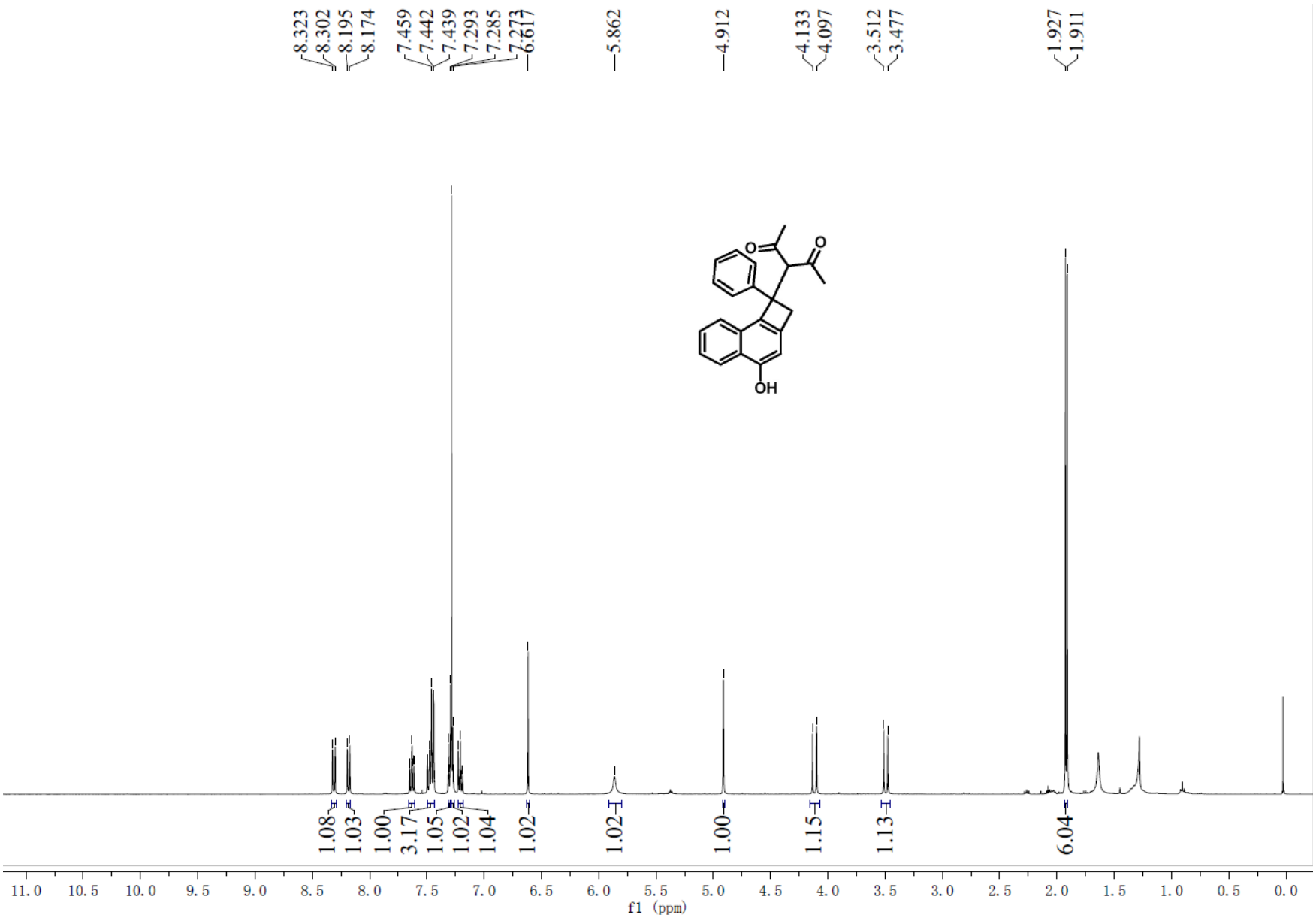
^{13}C NMR Spectrum of Compound 3r



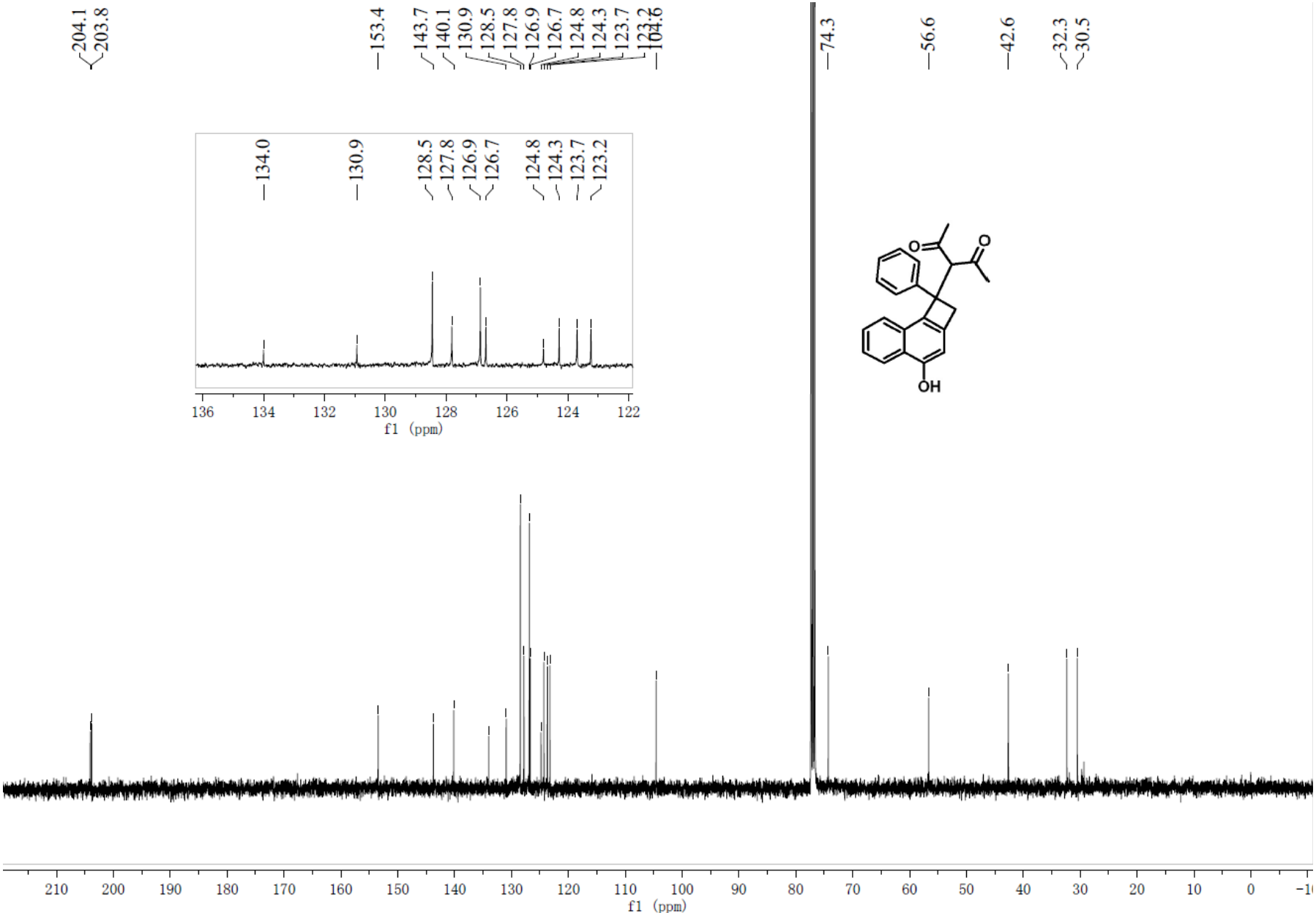
^{1}H NMR Spectrum of Compound 3s



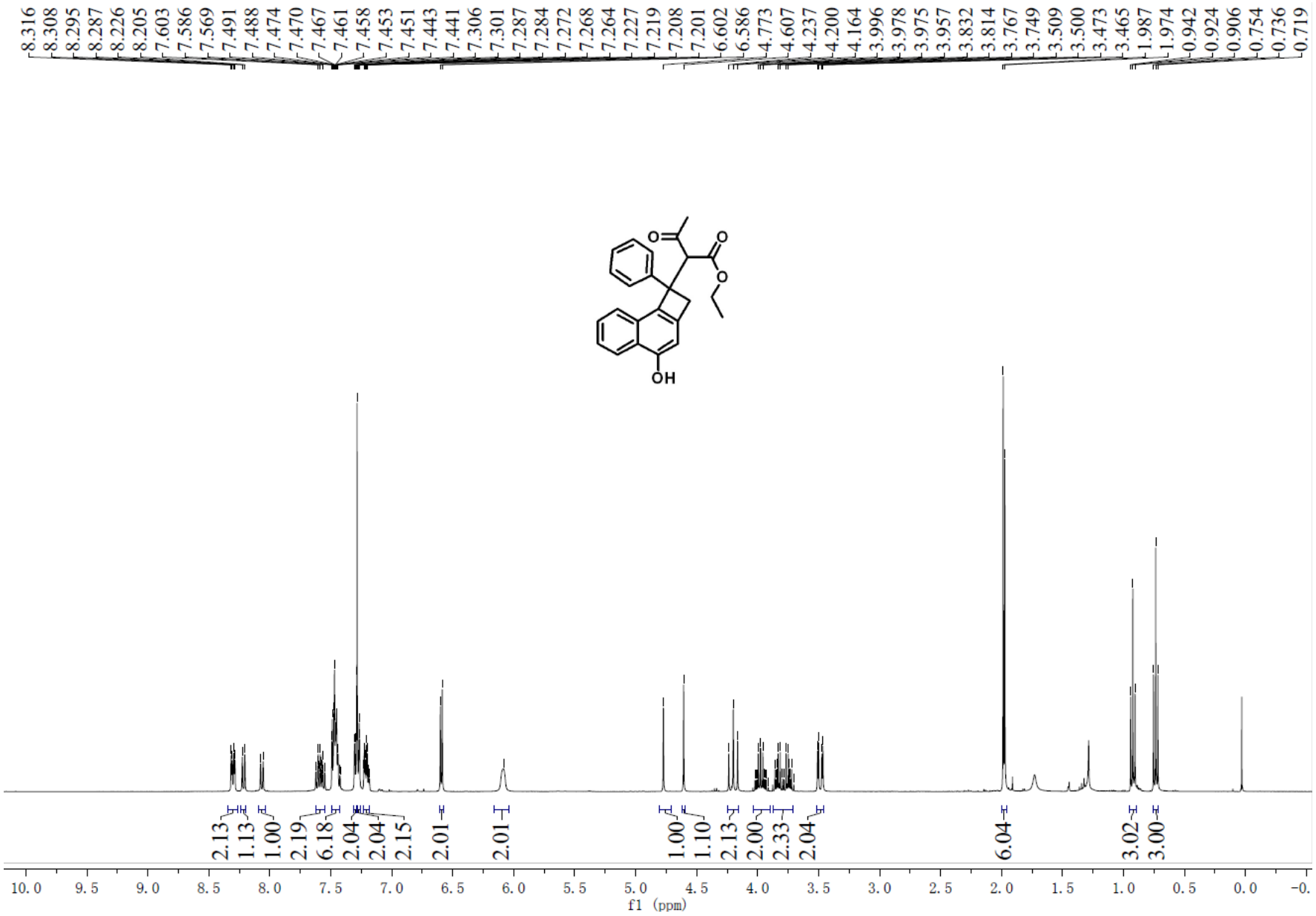
^{13}C NMR Spectrum of Compound 3s



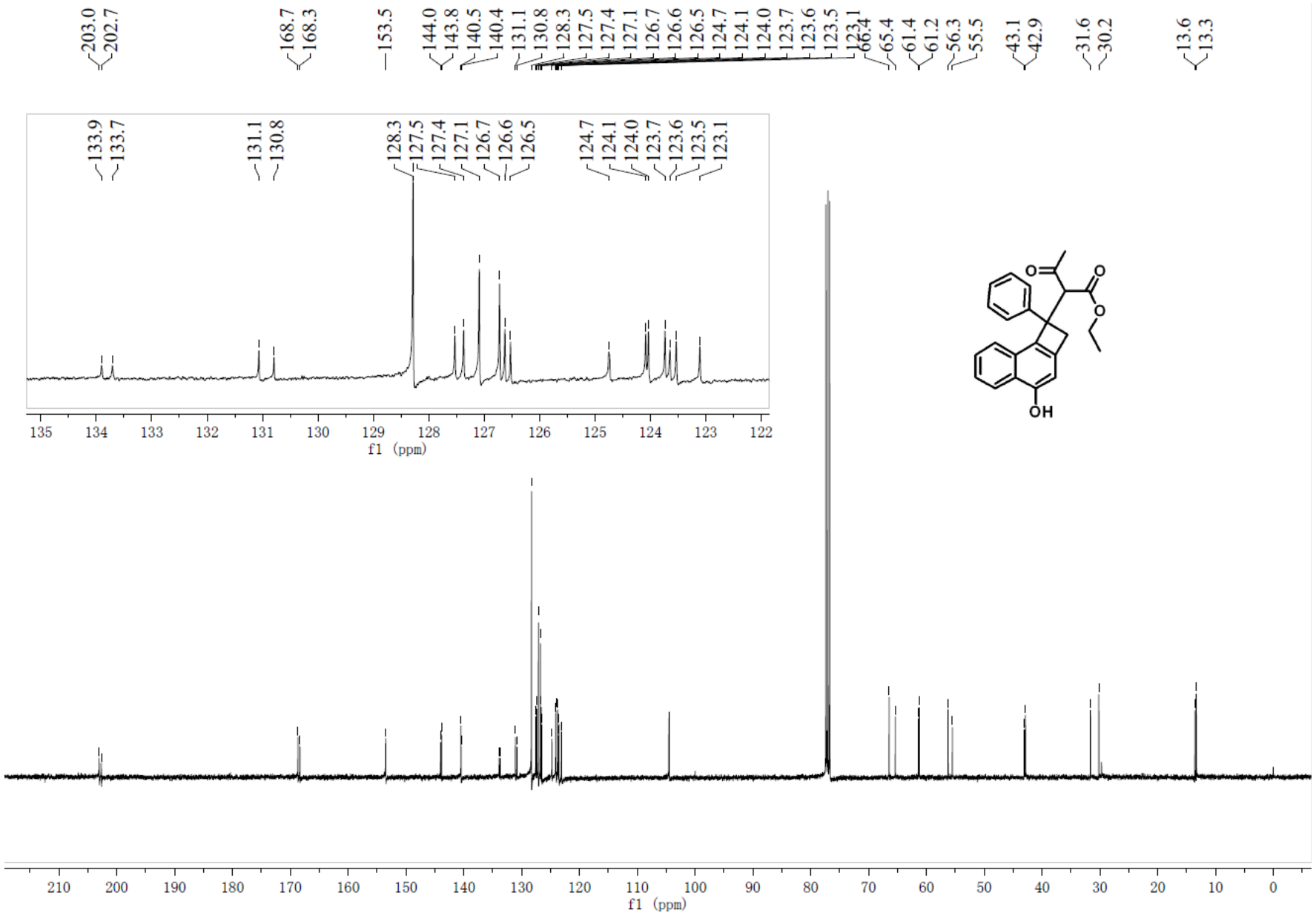
^{1}H NMR Spectrum of Compound 3u



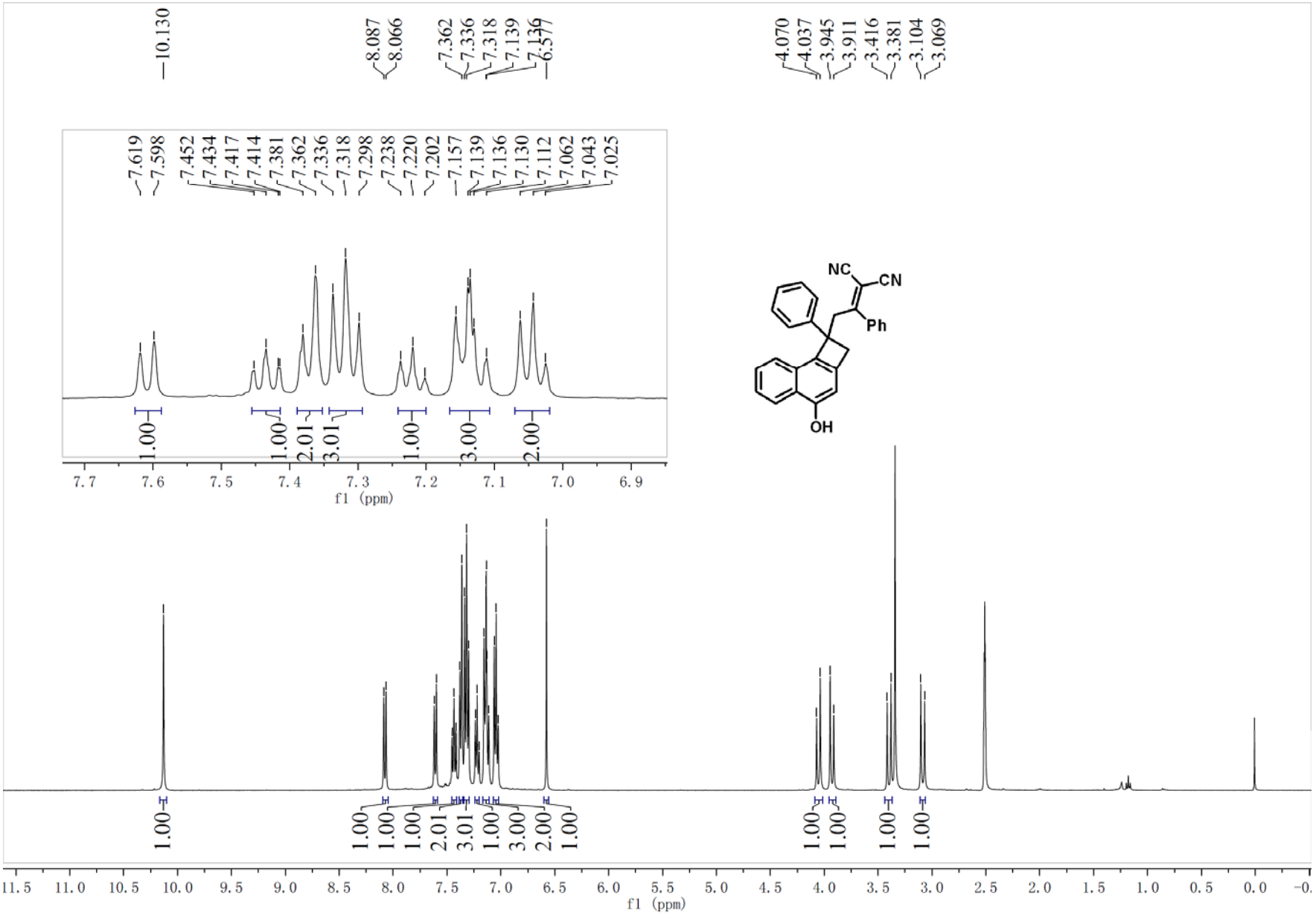
^{13}C NMR Spectrum of Compound 3u



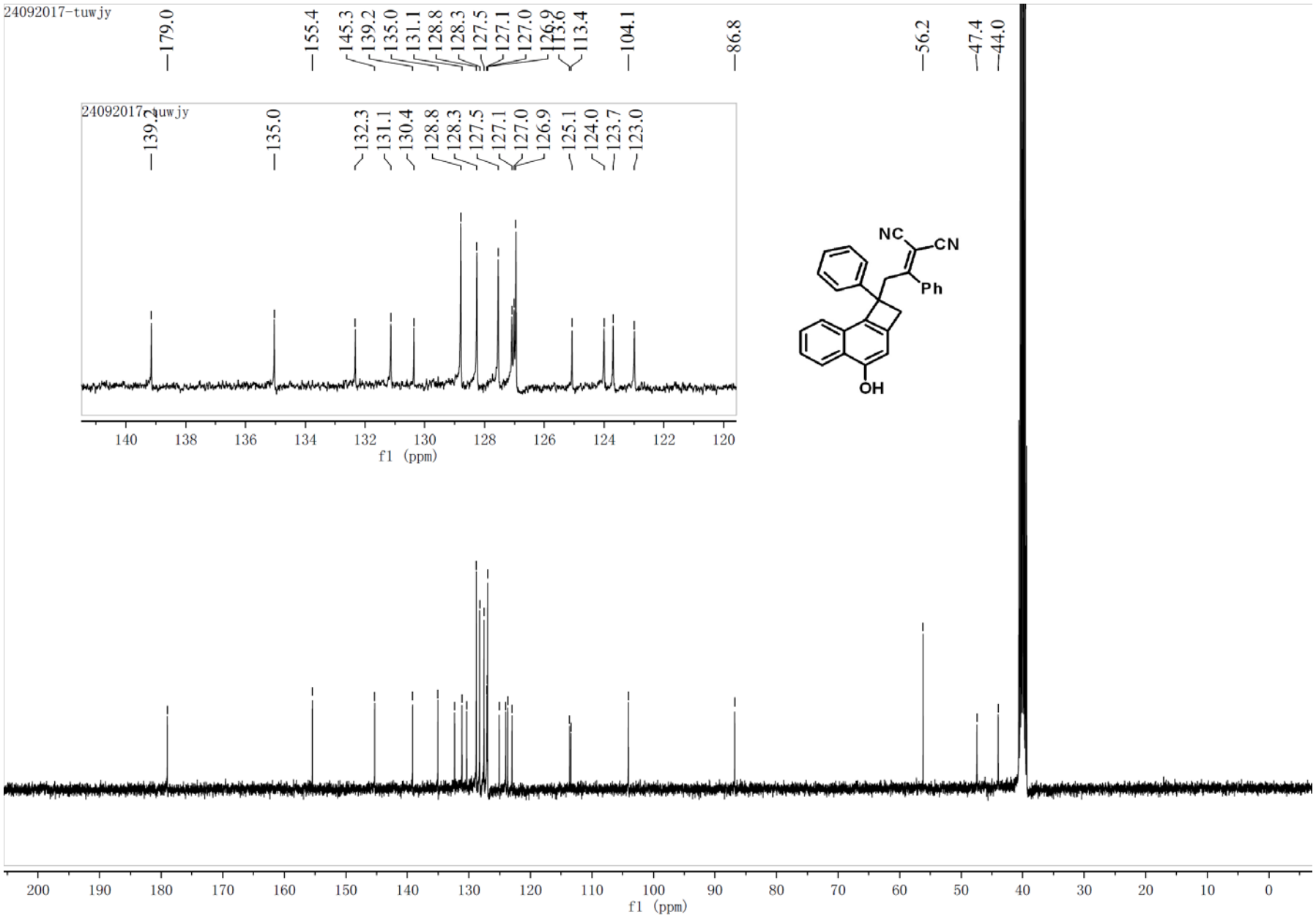
^{1}H NMR Spectrum of Compound 3v



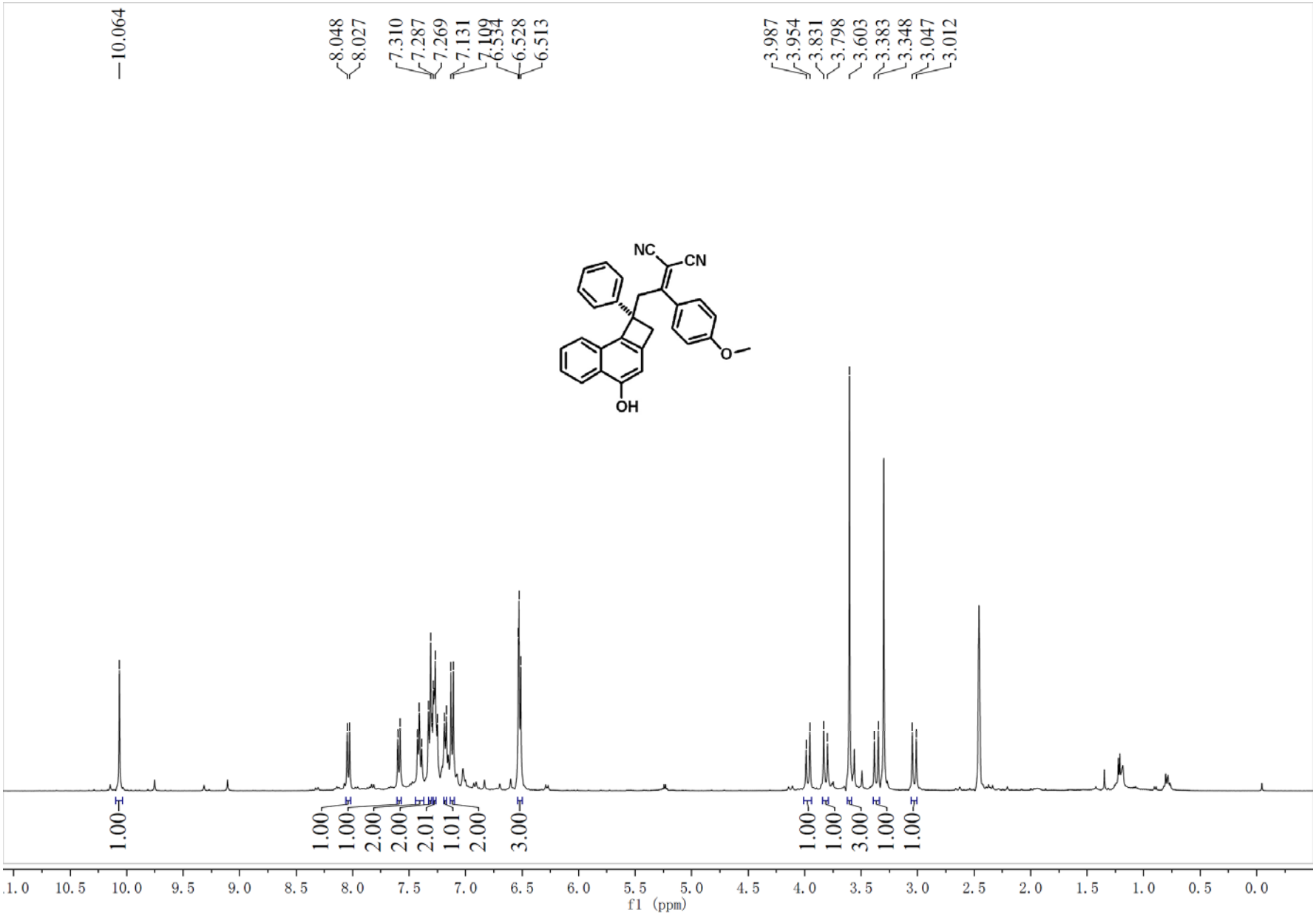
^{13}C NMR Spectrum of Compound 3v



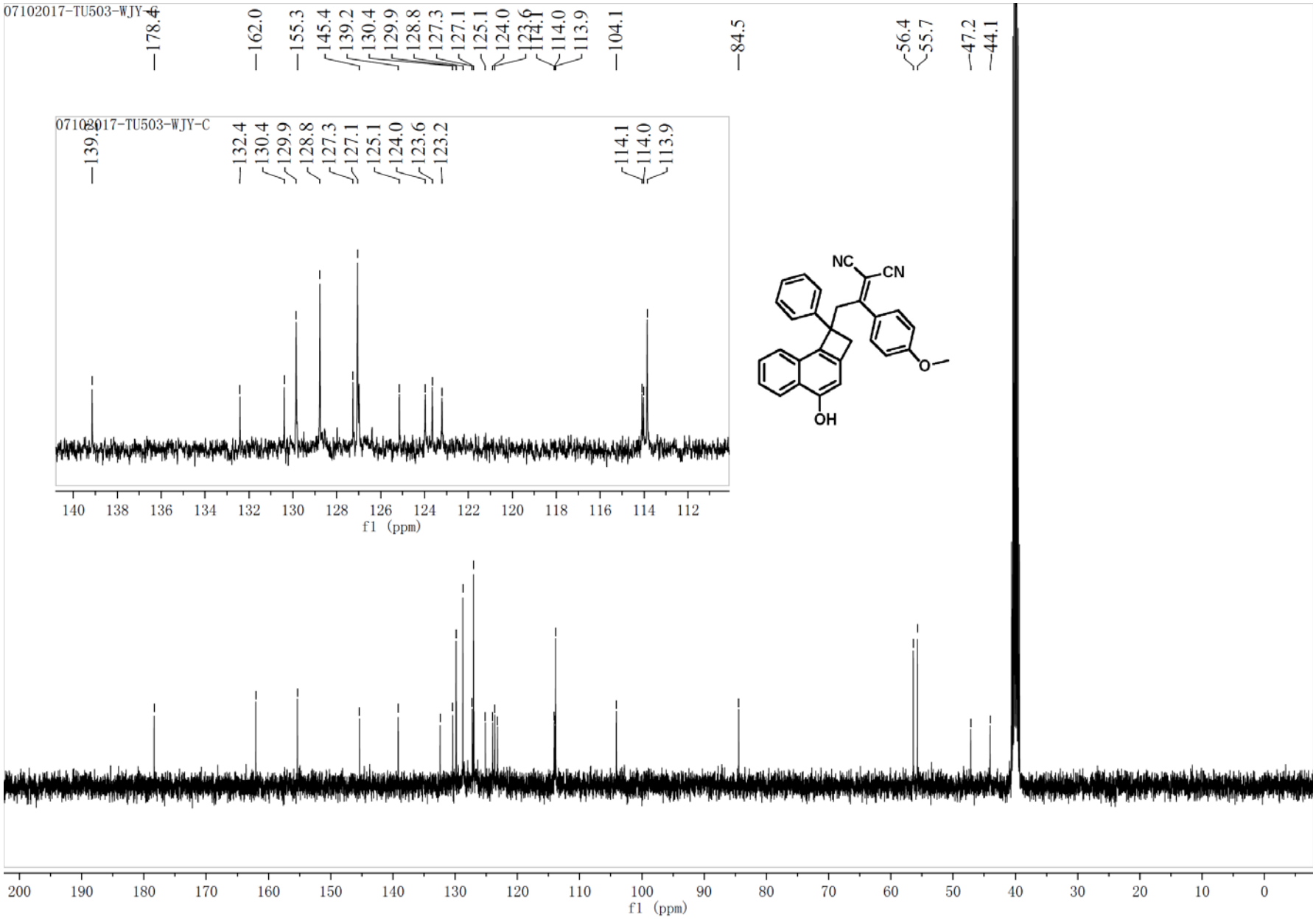
^{1}H NMR Spectrum of Compound 5a



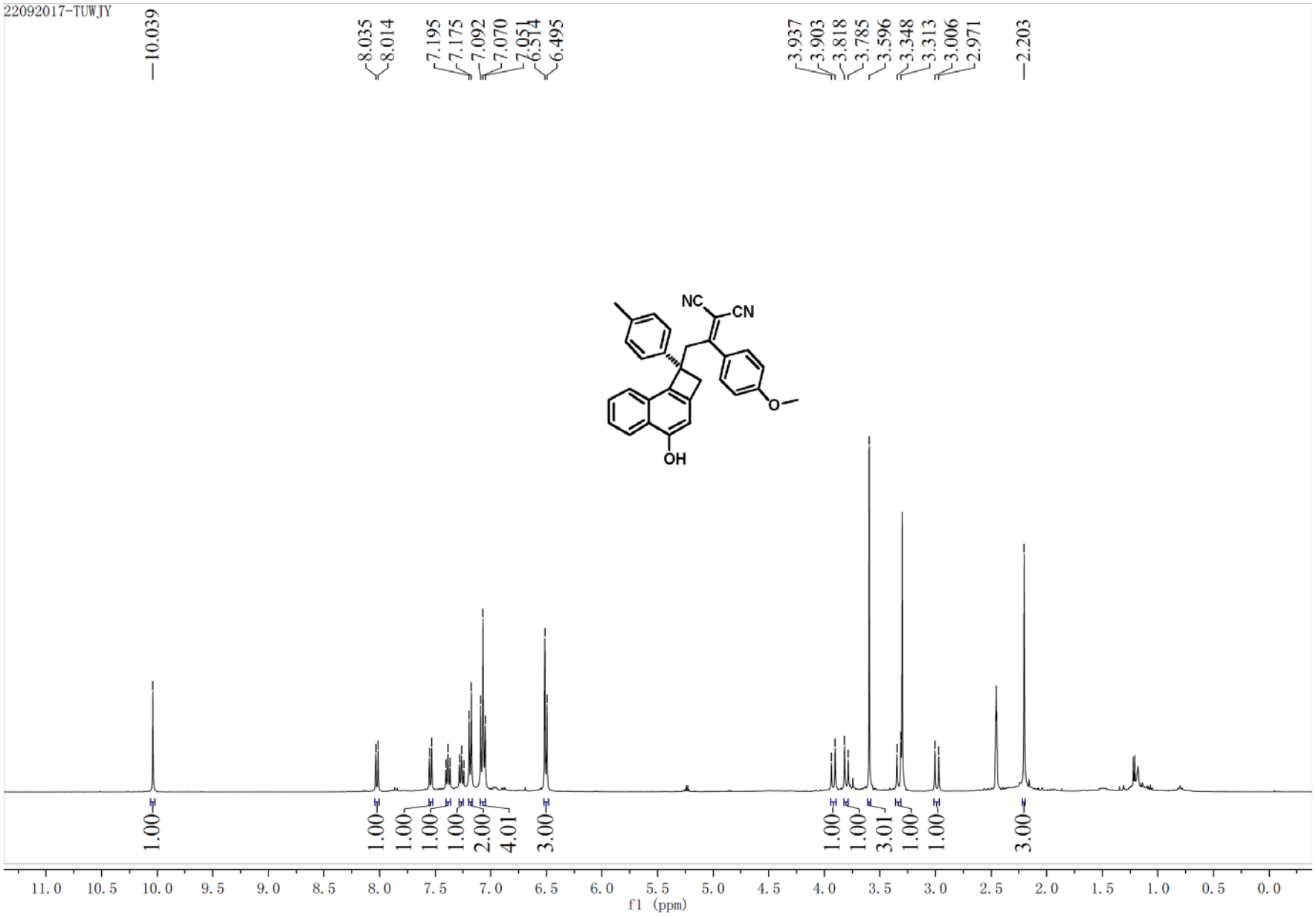
^{13}C NMR Spectrum of Compound 5a



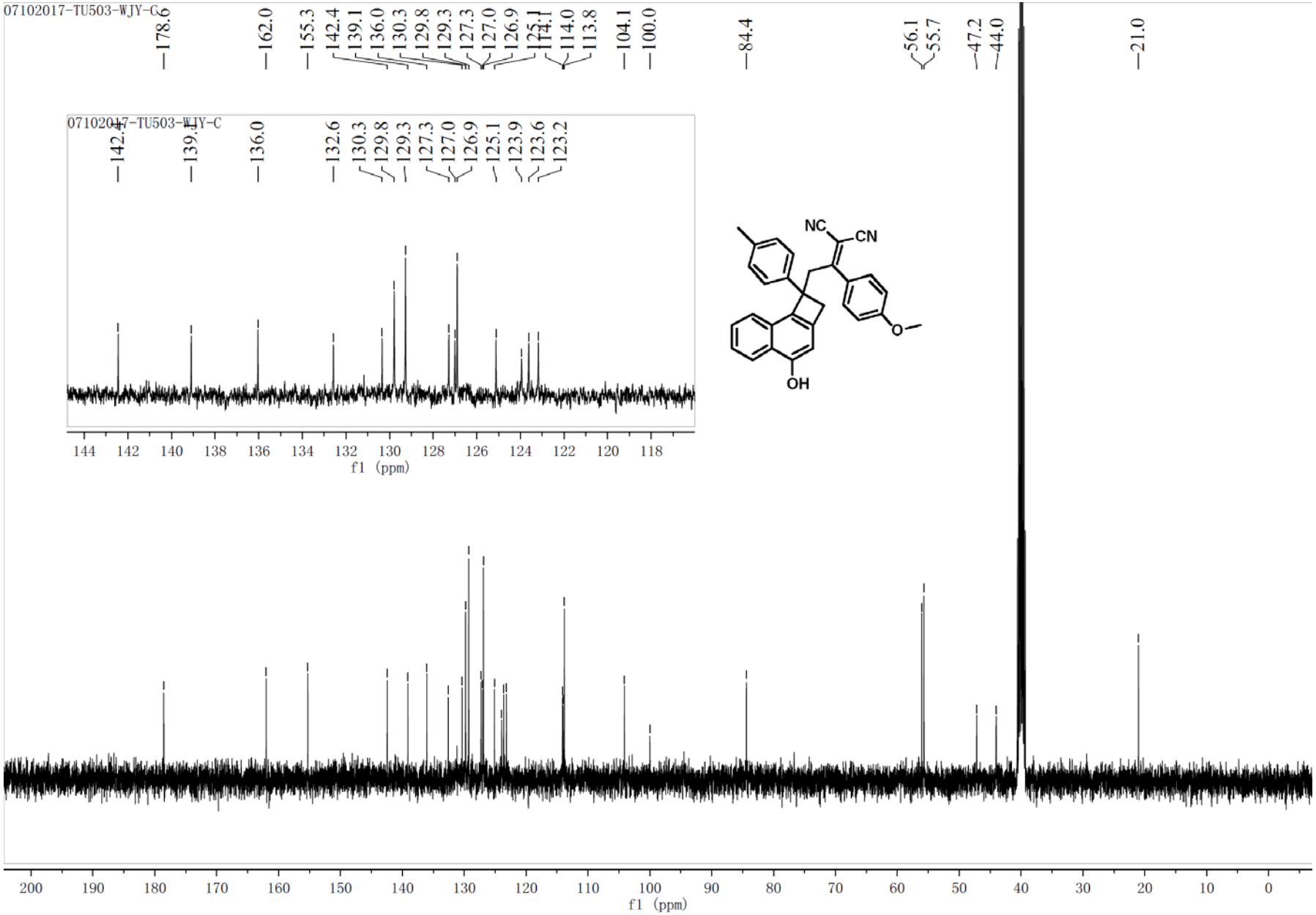
^{1}H NMR Spectrum of Compound 5b



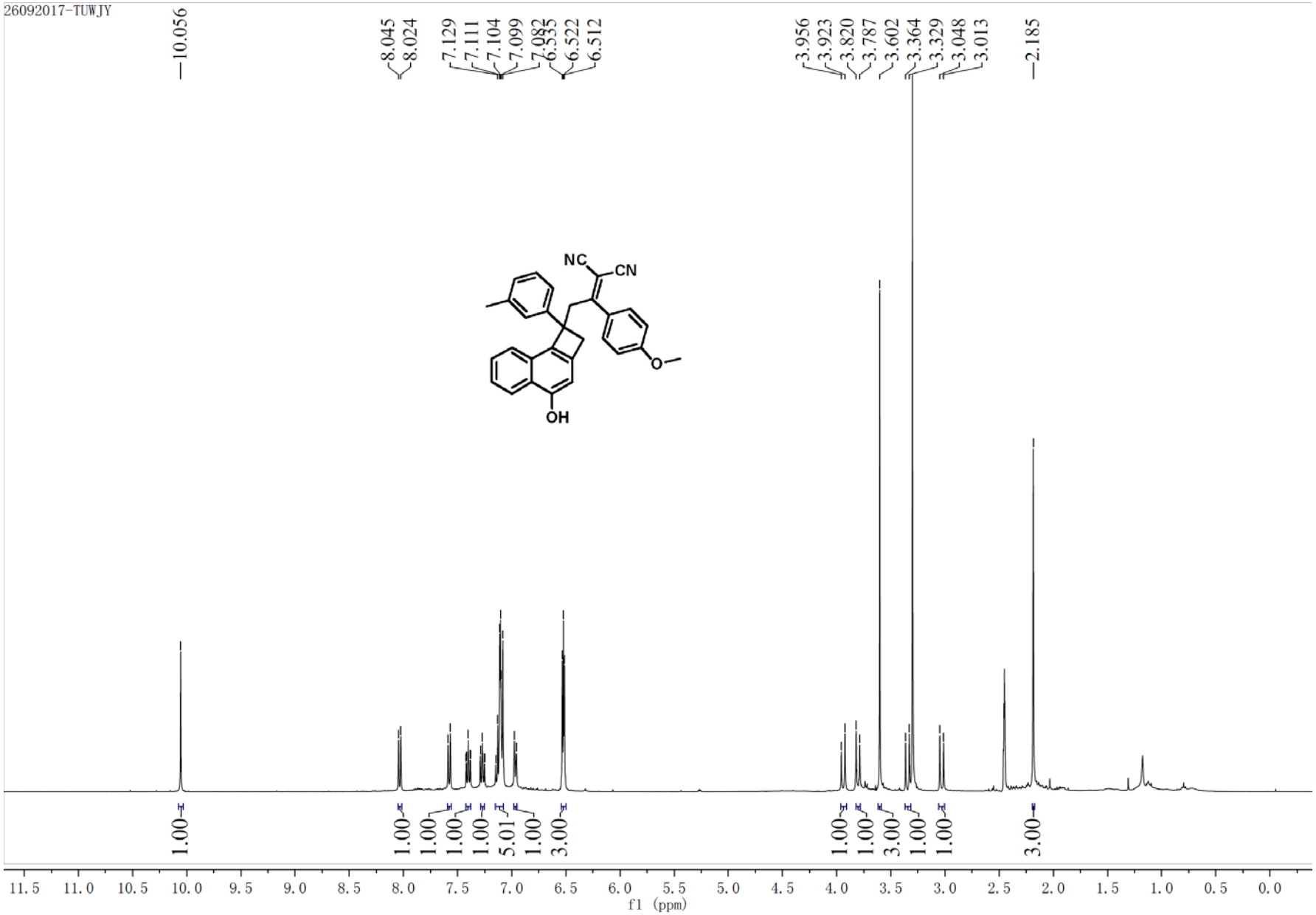
^{13}C NMR Spectrum of Compound 5b



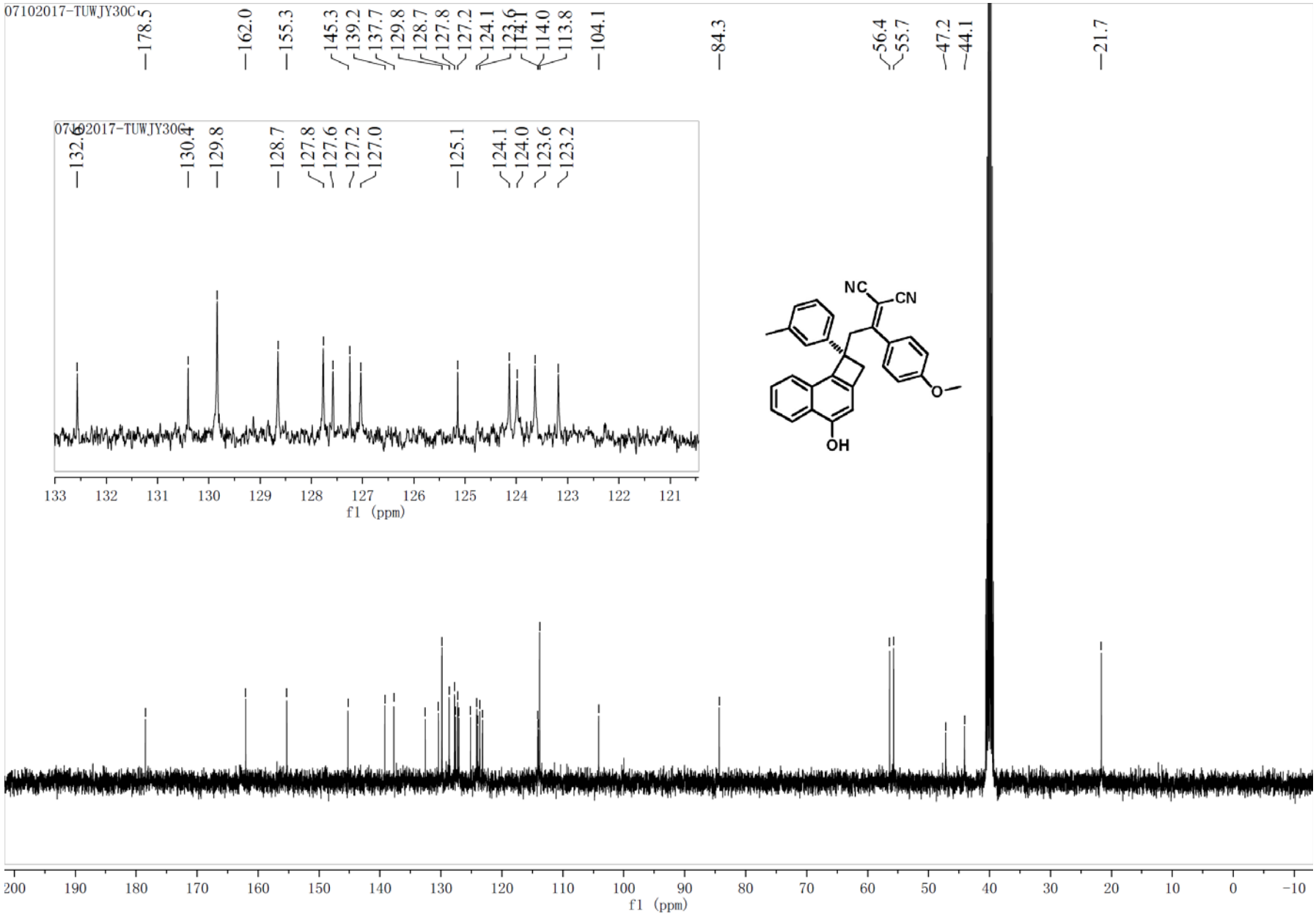
^{1}H NMR Spectrum of Compound 5c



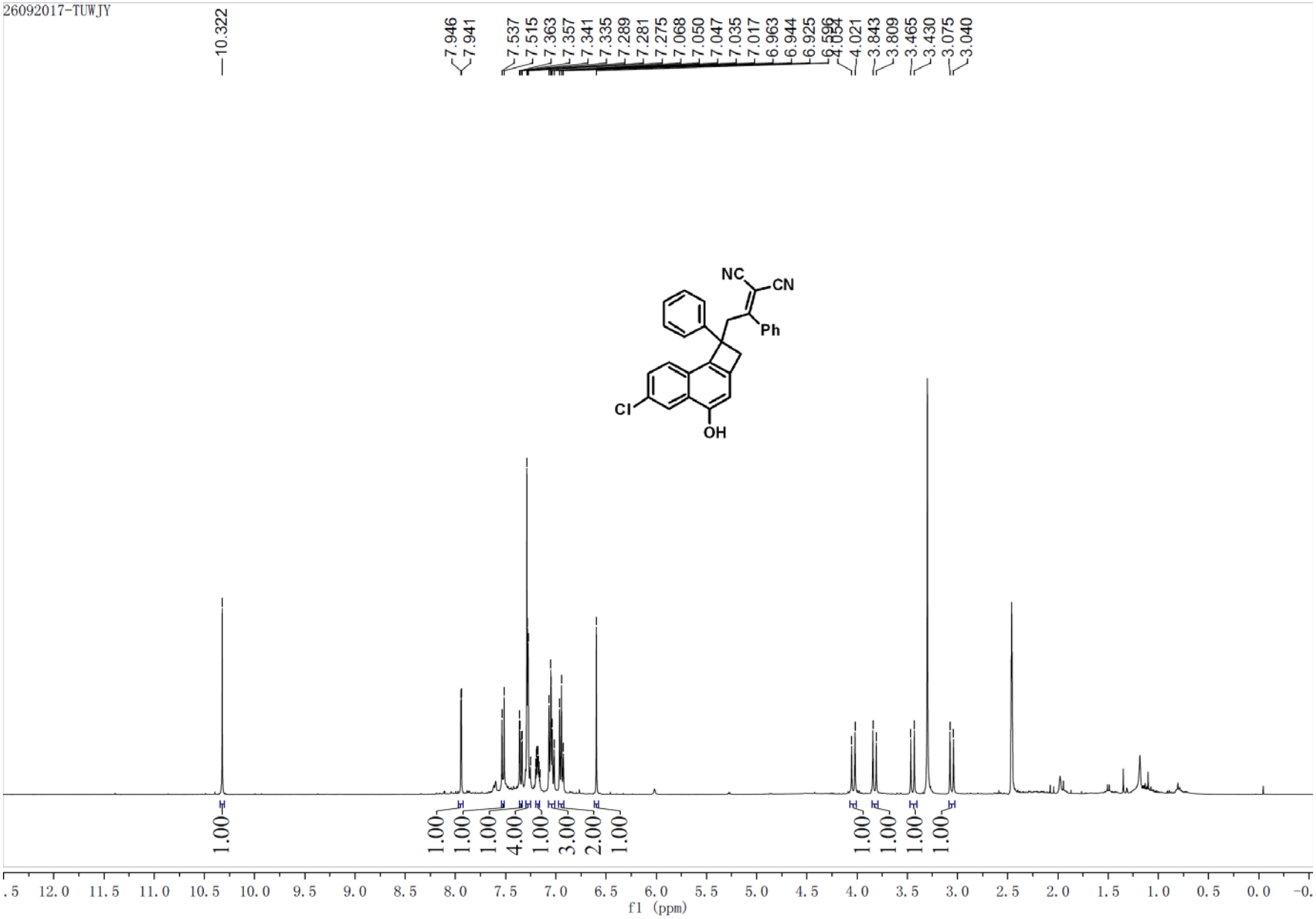
^{13}C NMR Spectrum of Compound 5c



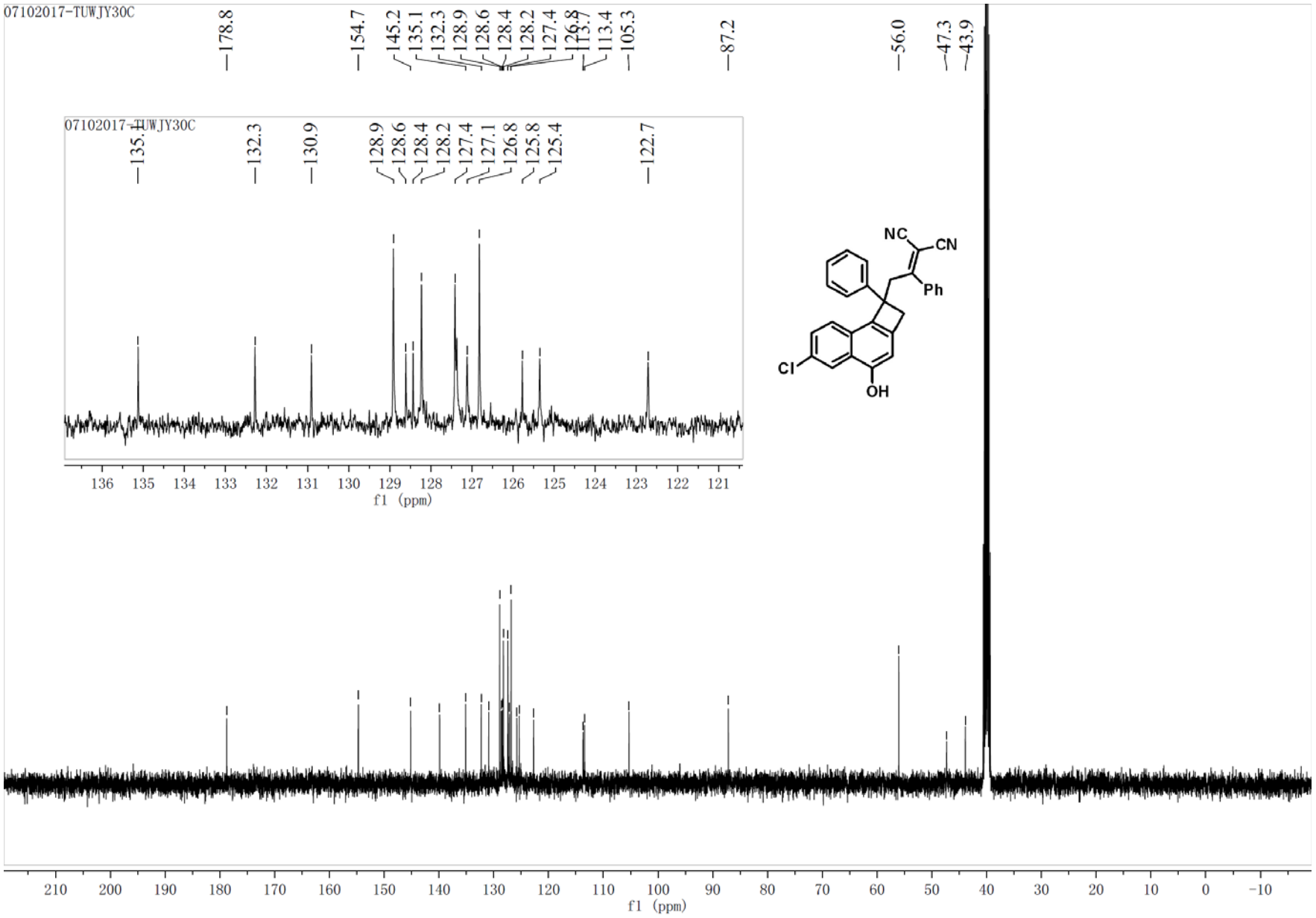
^{1}H NMR Spectrum of Compound 5d



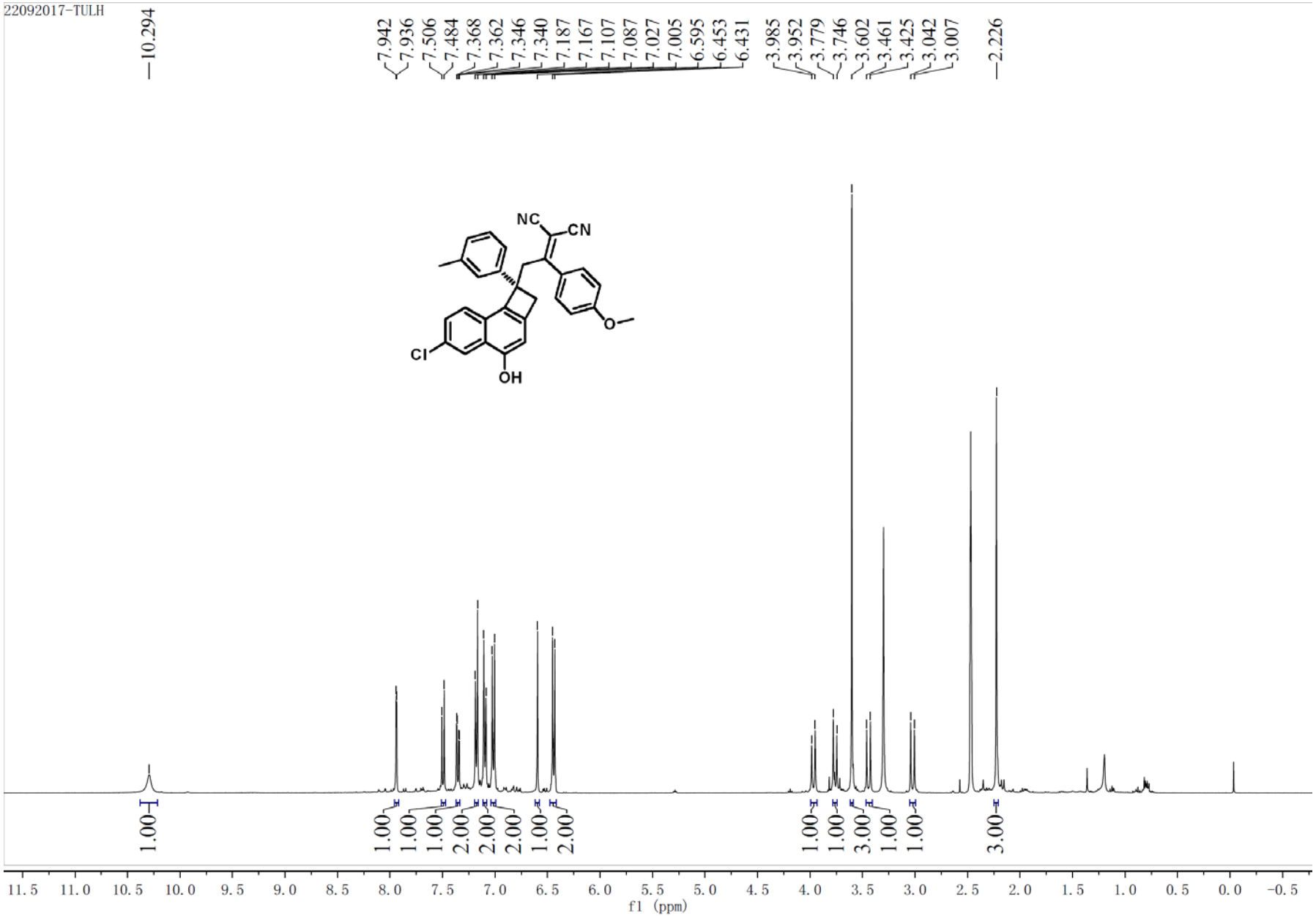
^{13}C NMR Spectrum of Compound 5d



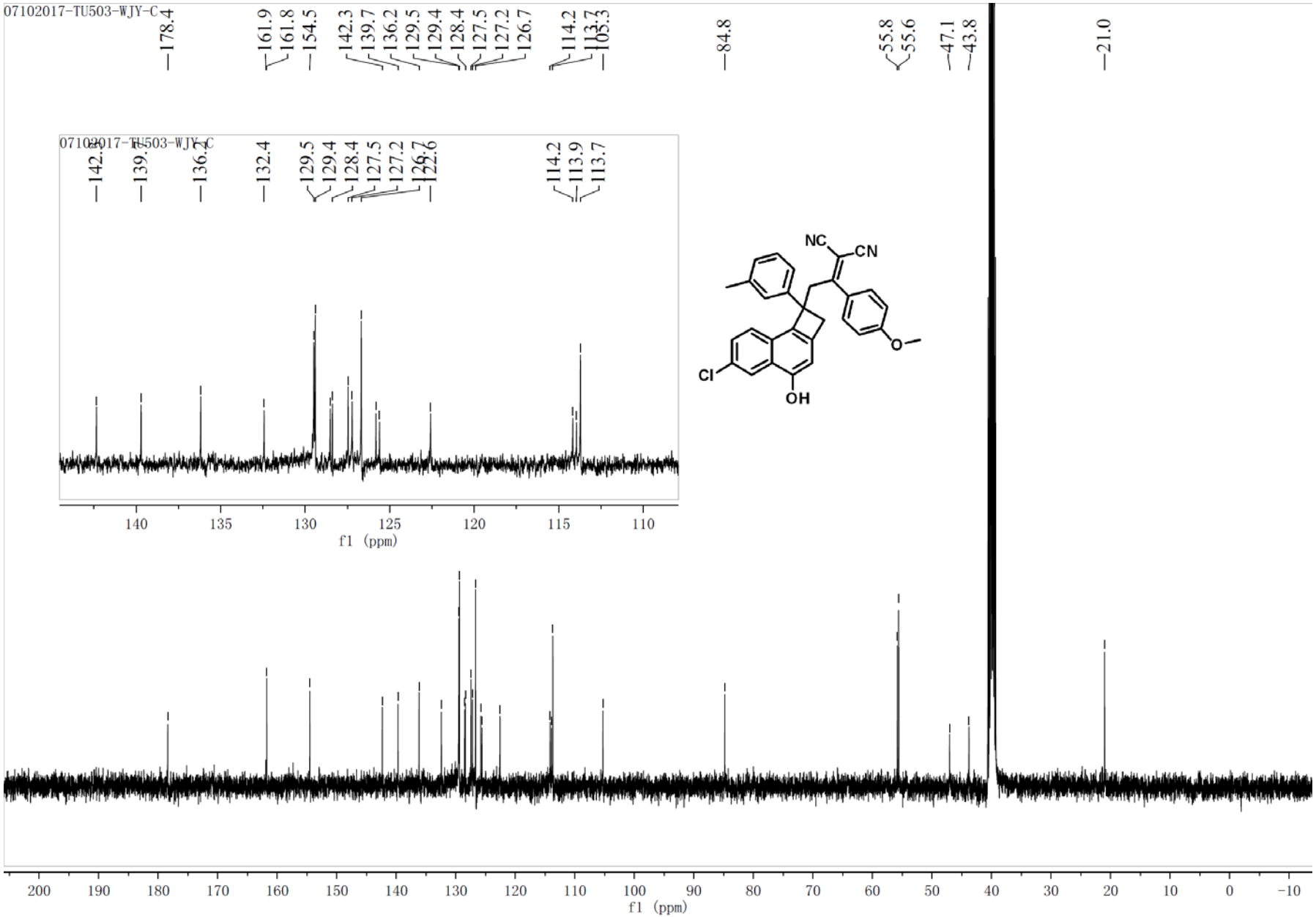
^{1}H NMR Spectrum of Compound 5e



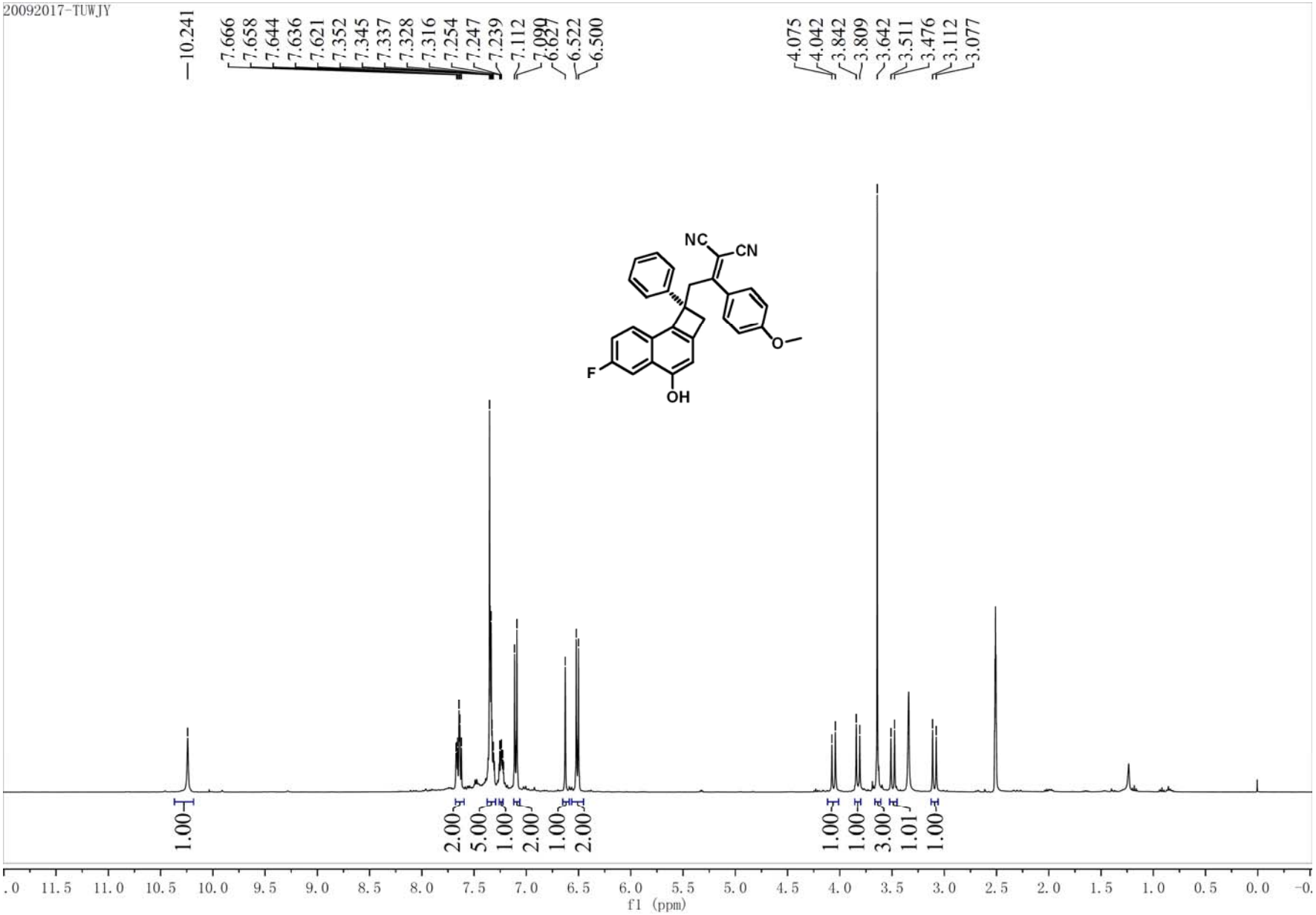
^{13}C NMR Spectrum of Compound 5e



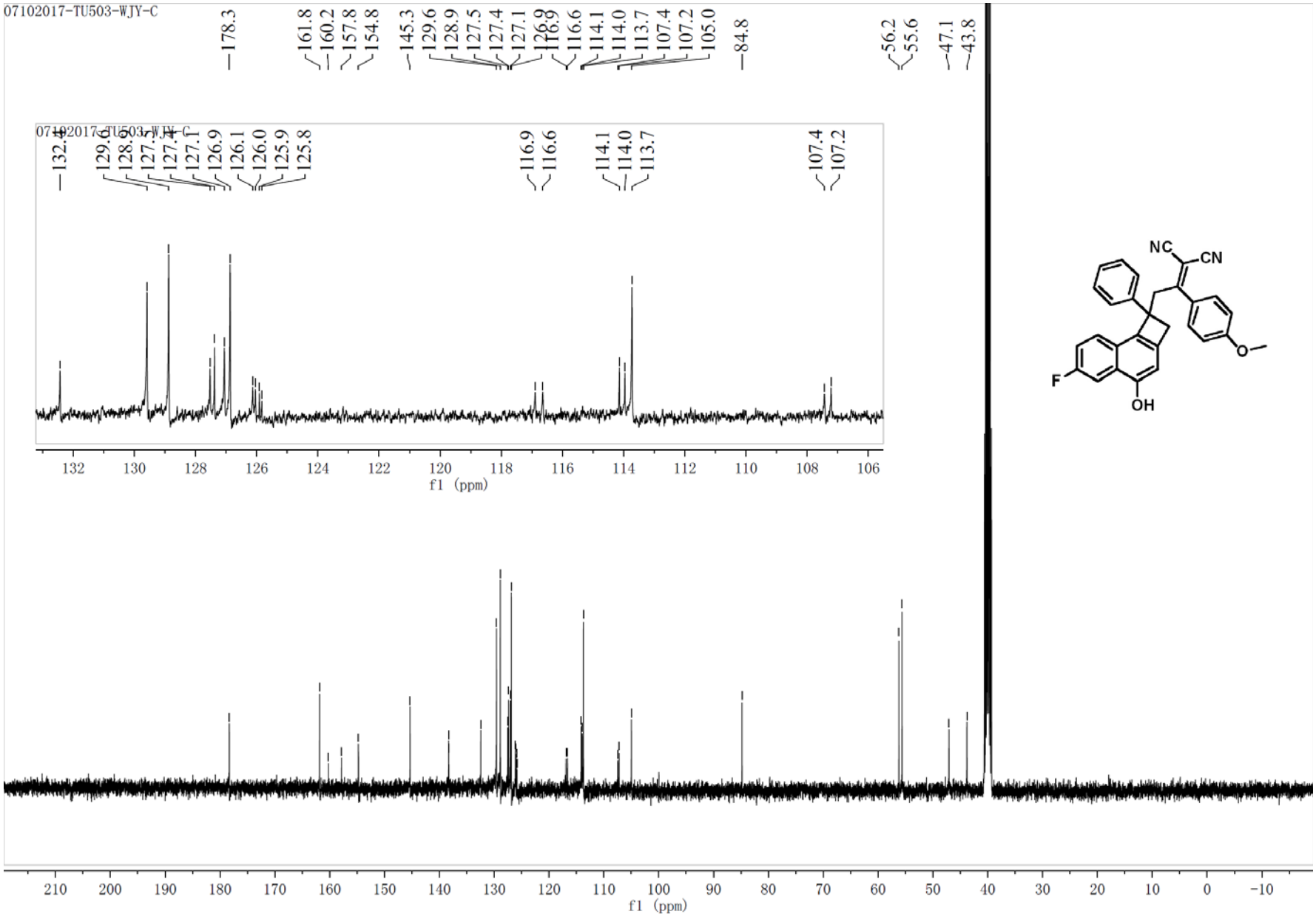
^{1}H NMR Spectrum of Compound 5f



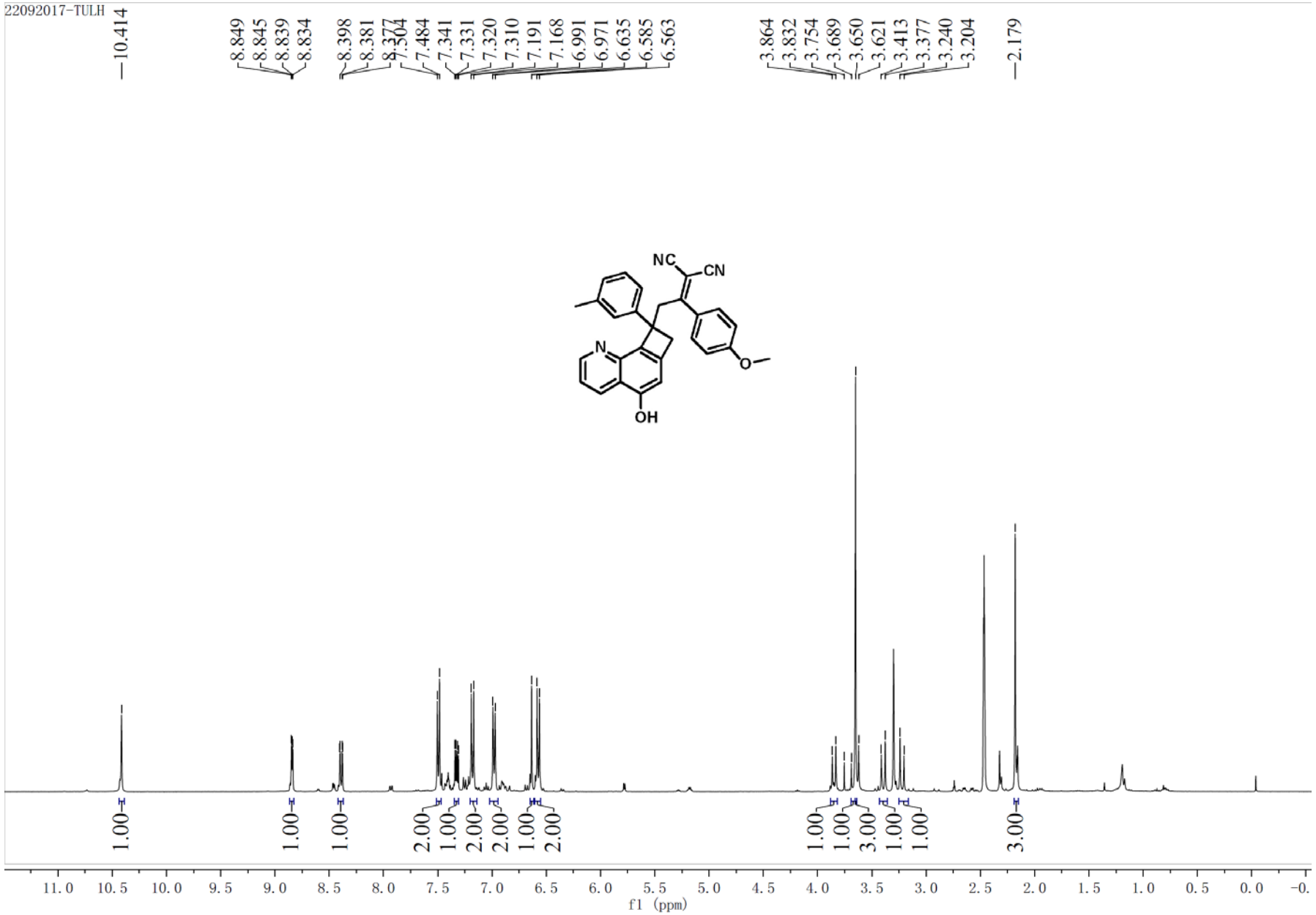
^{13}C NMR Spectrum of Compound 5f



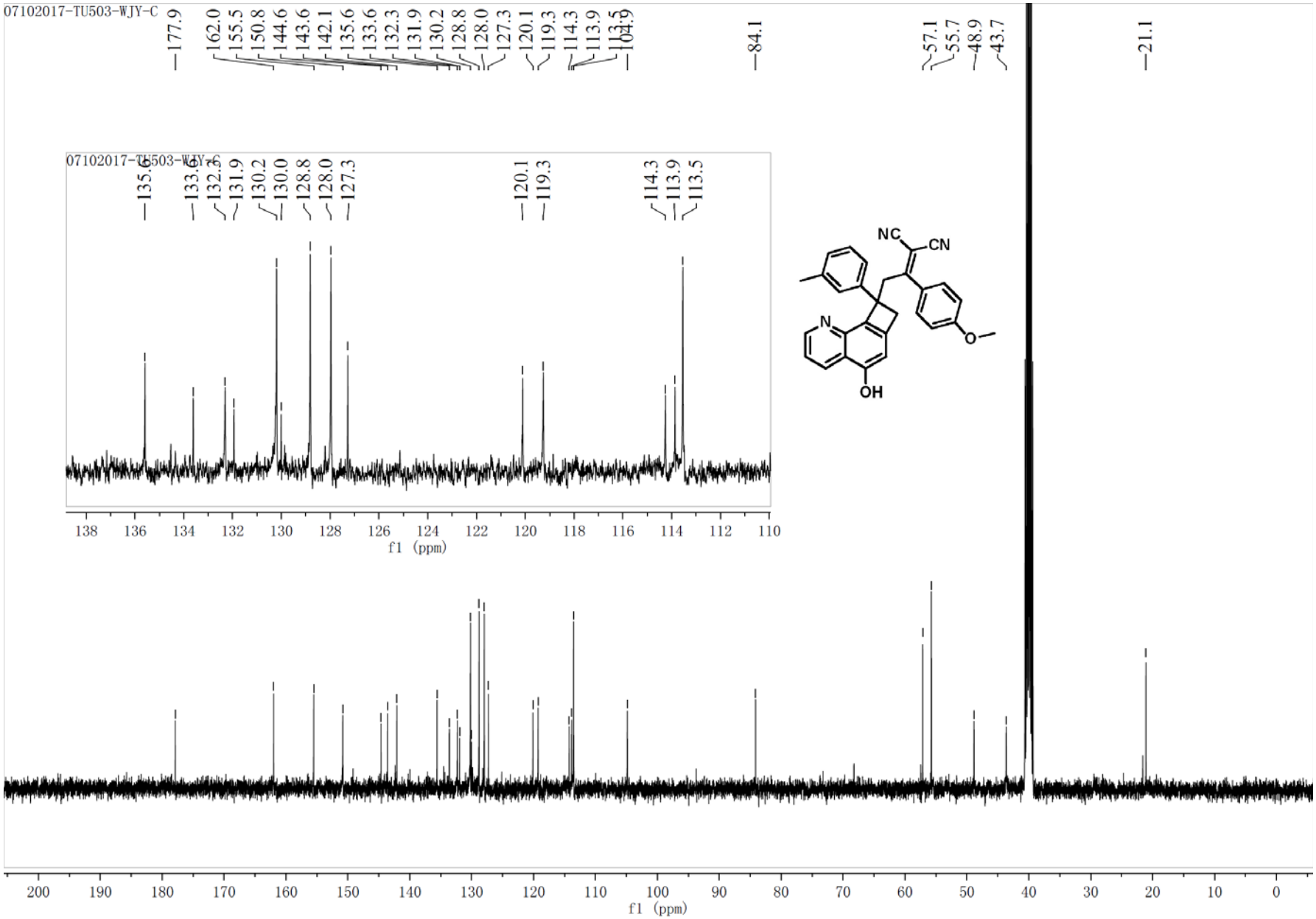
^{1}H NMR Spectrum of Compound 5g



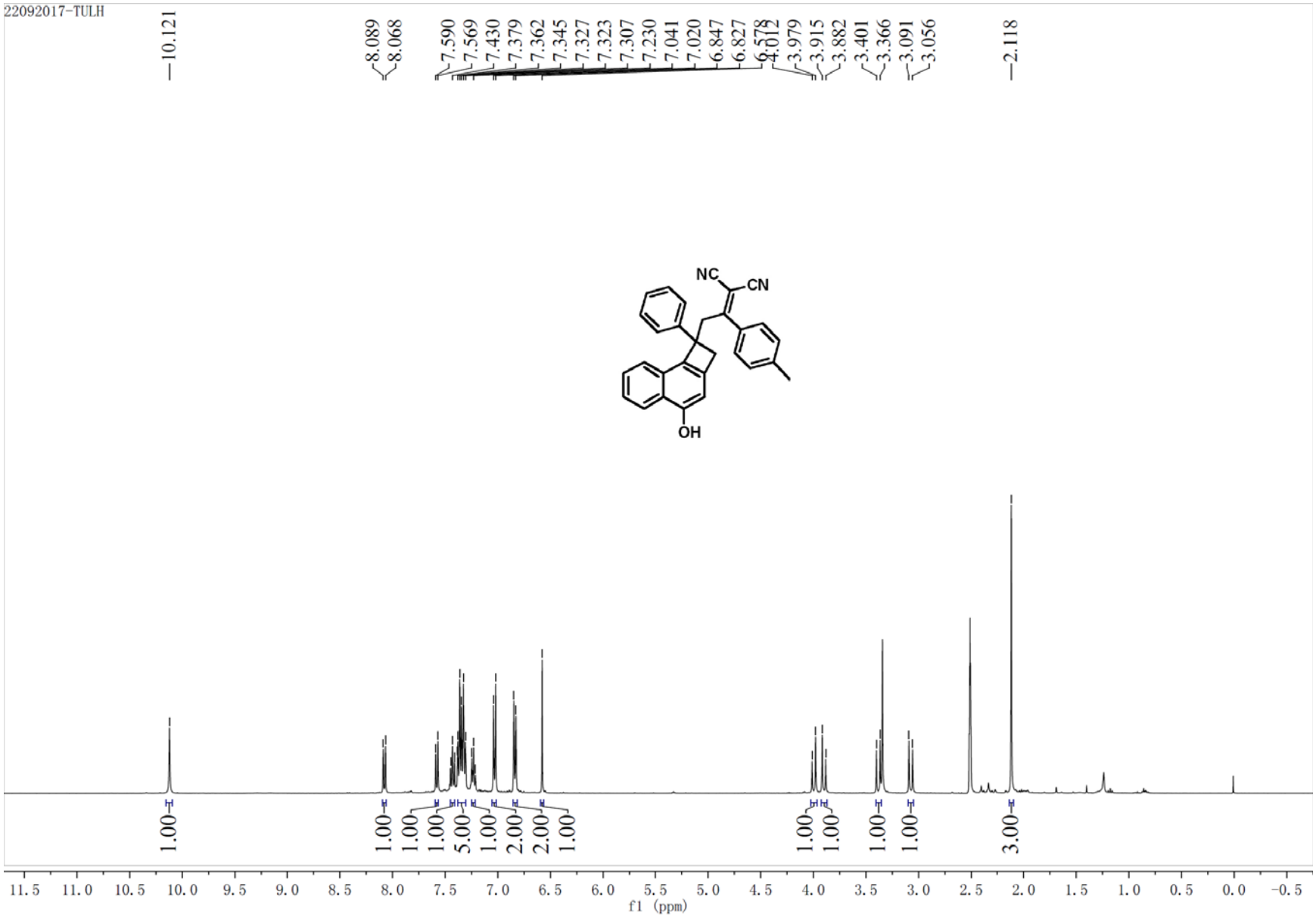
^{13}C NMR Spectrum of Compound 5g



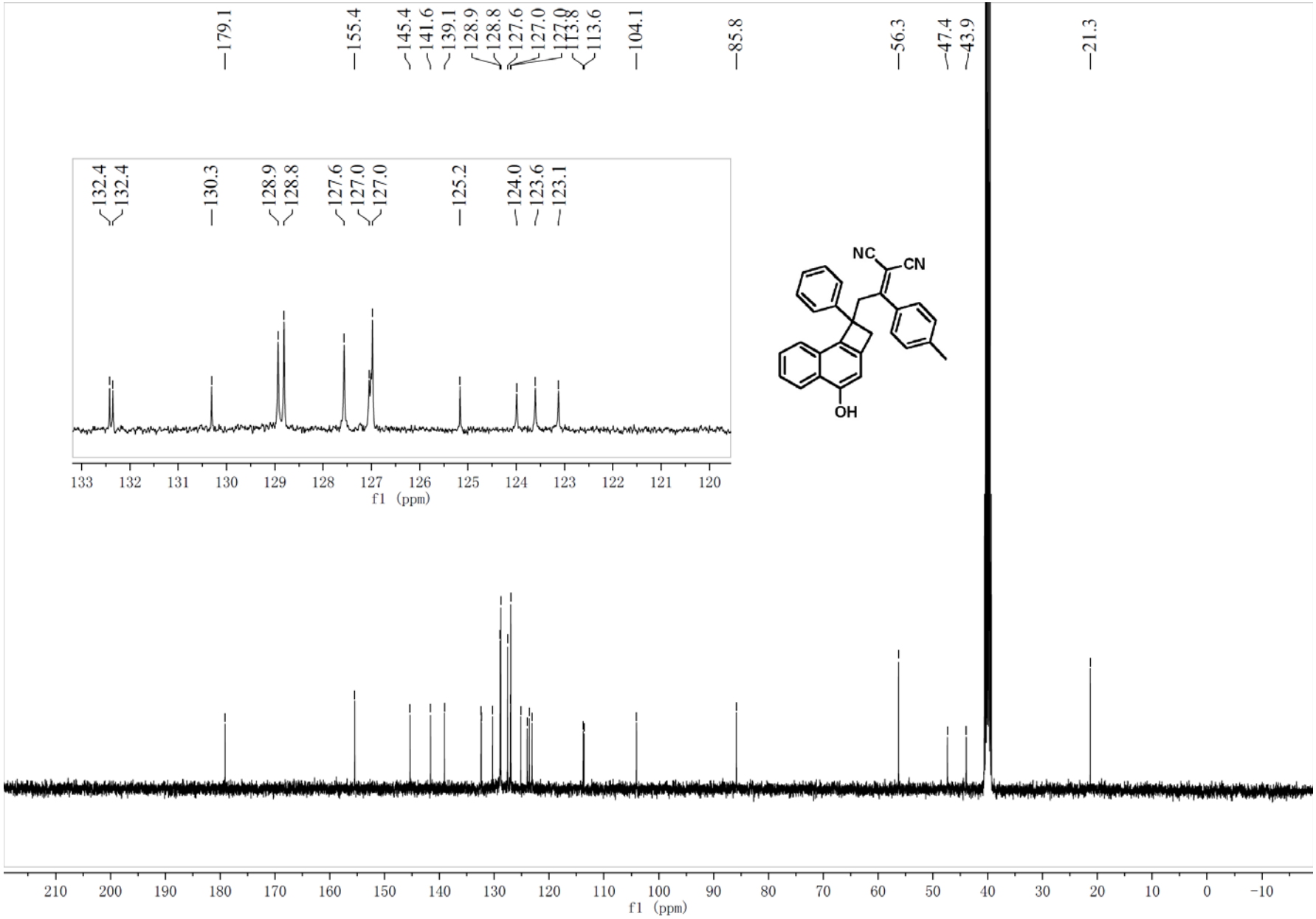
^{1}H NMR Spectrum of Compound 5h



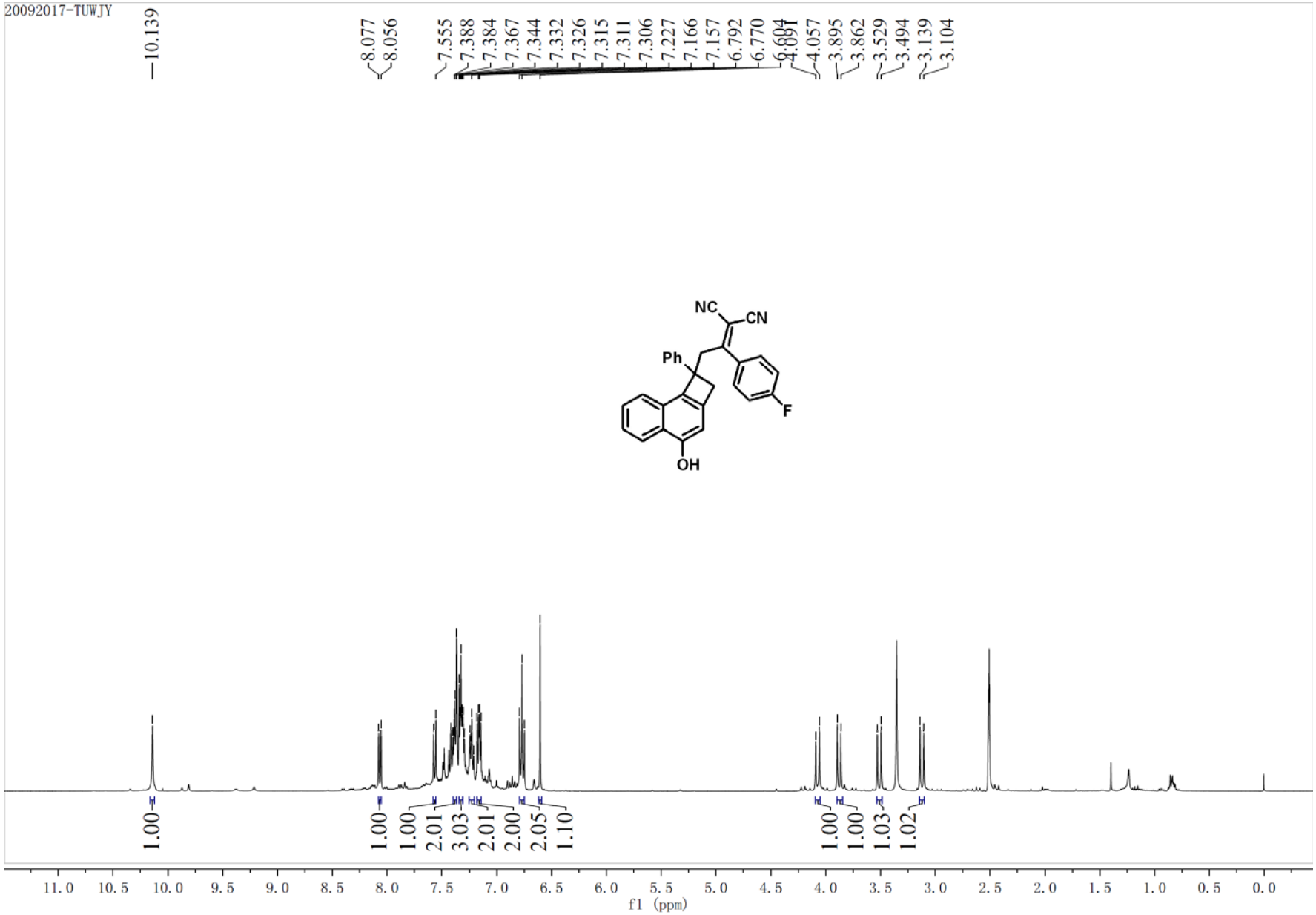
^{13}C NMR Spectrum of Compound 5h



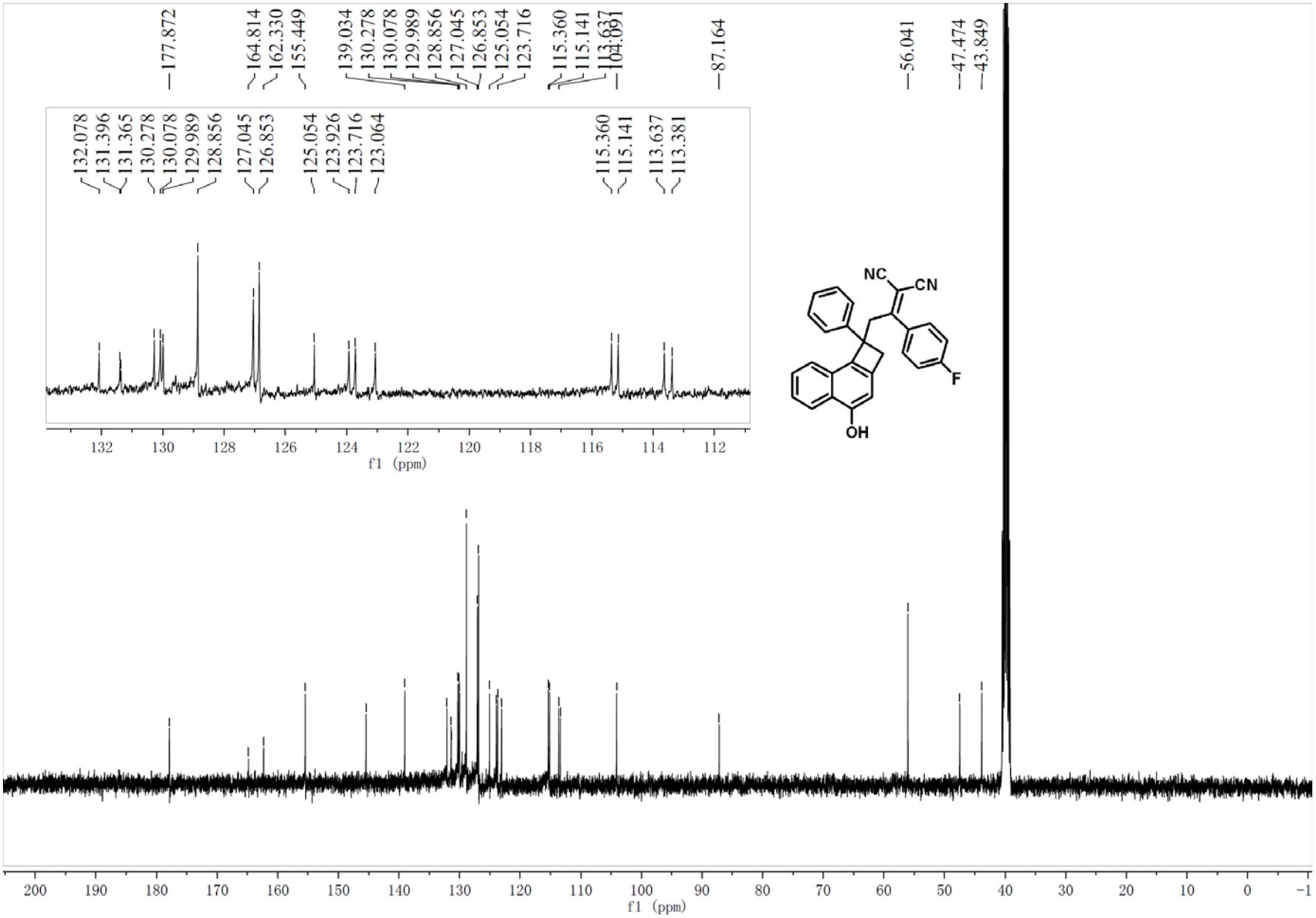
^{1}H NMR Spectrum of Compound 5i



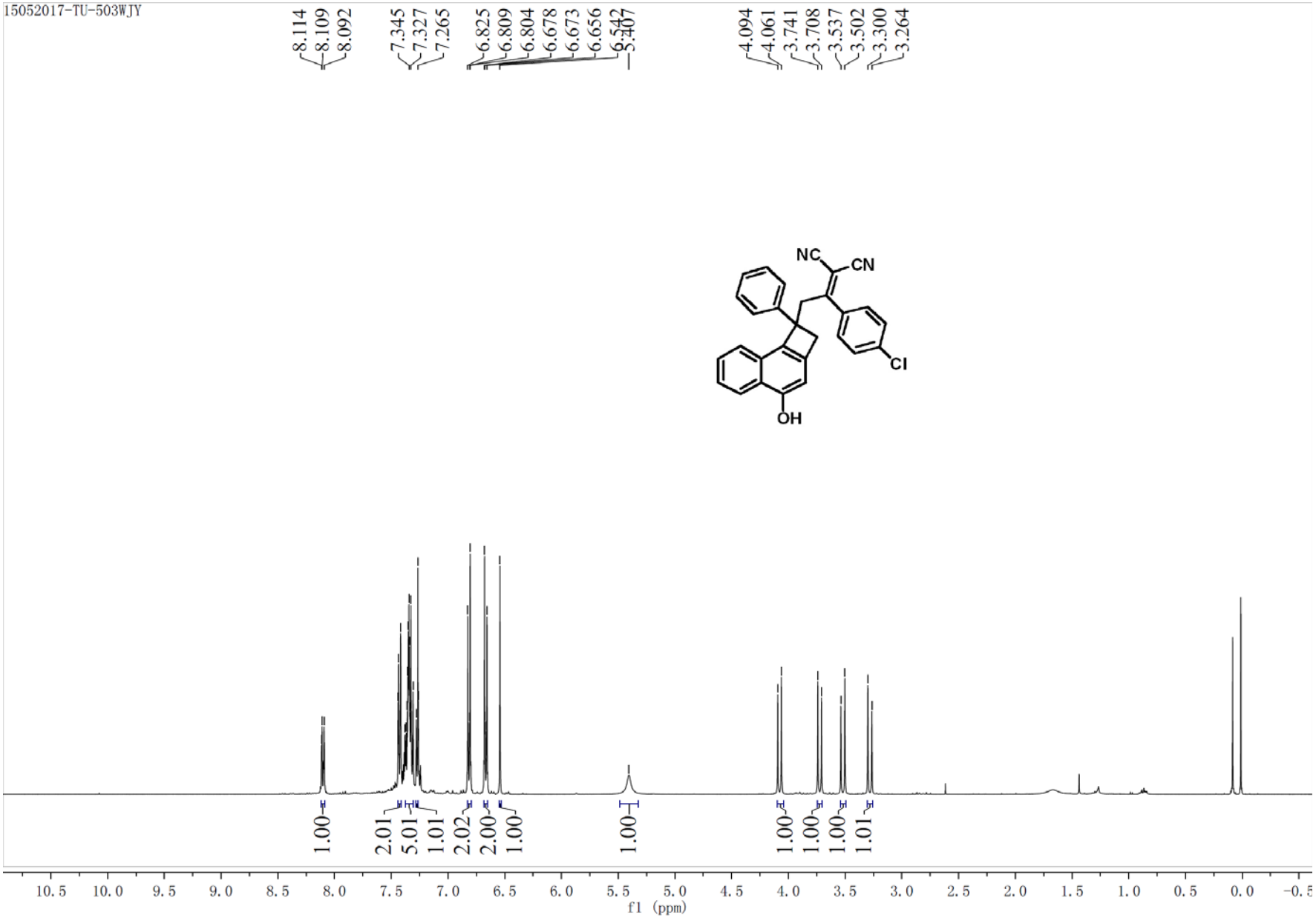
^{13}C NMR Spectrum of Compound 5i



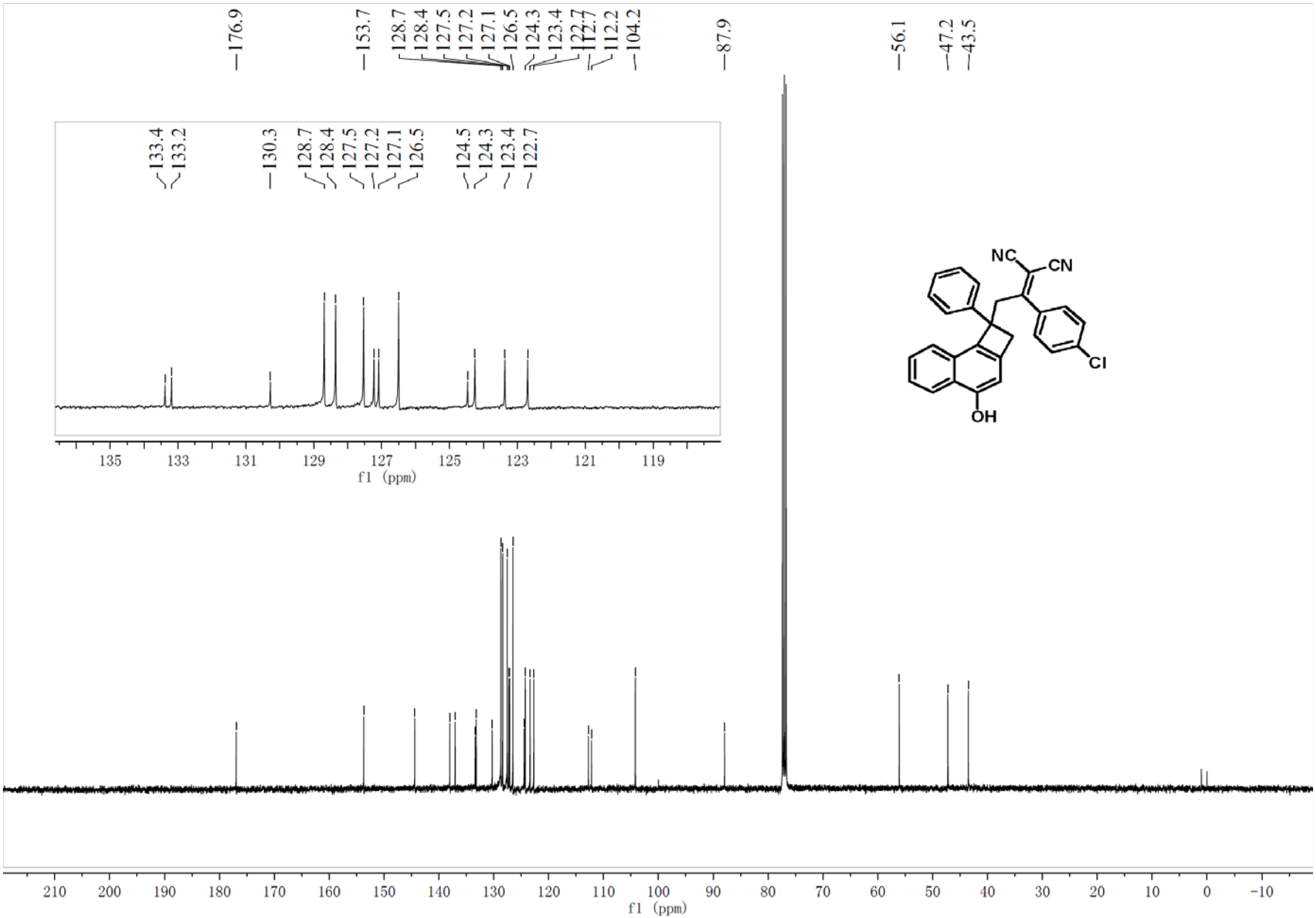
^{1}H NMR Spectrum of Compound 5j



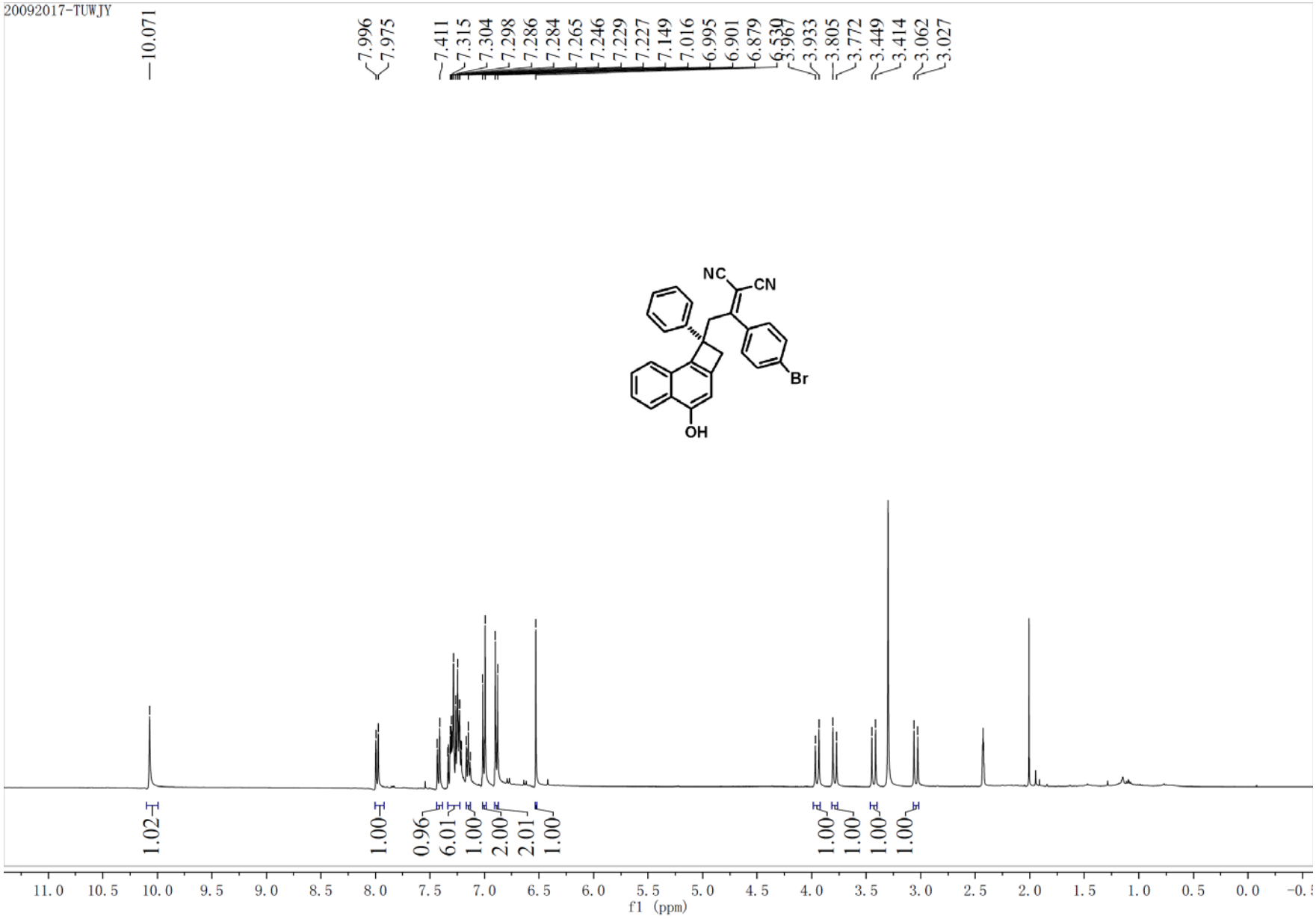
^{13}C NMR Spectrum of Compound 5j



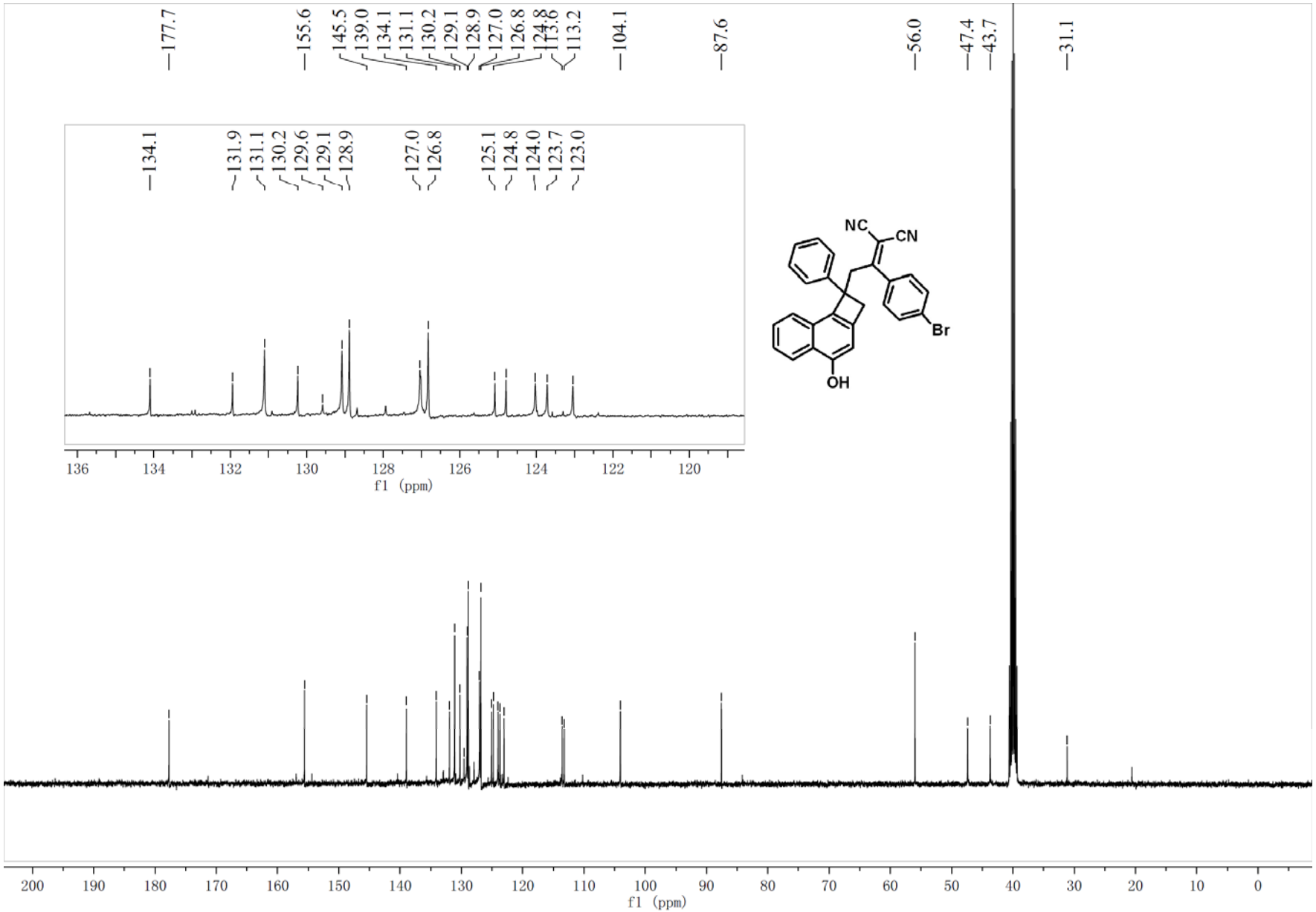
^{1}H NMR Spectrum of Compound 5k



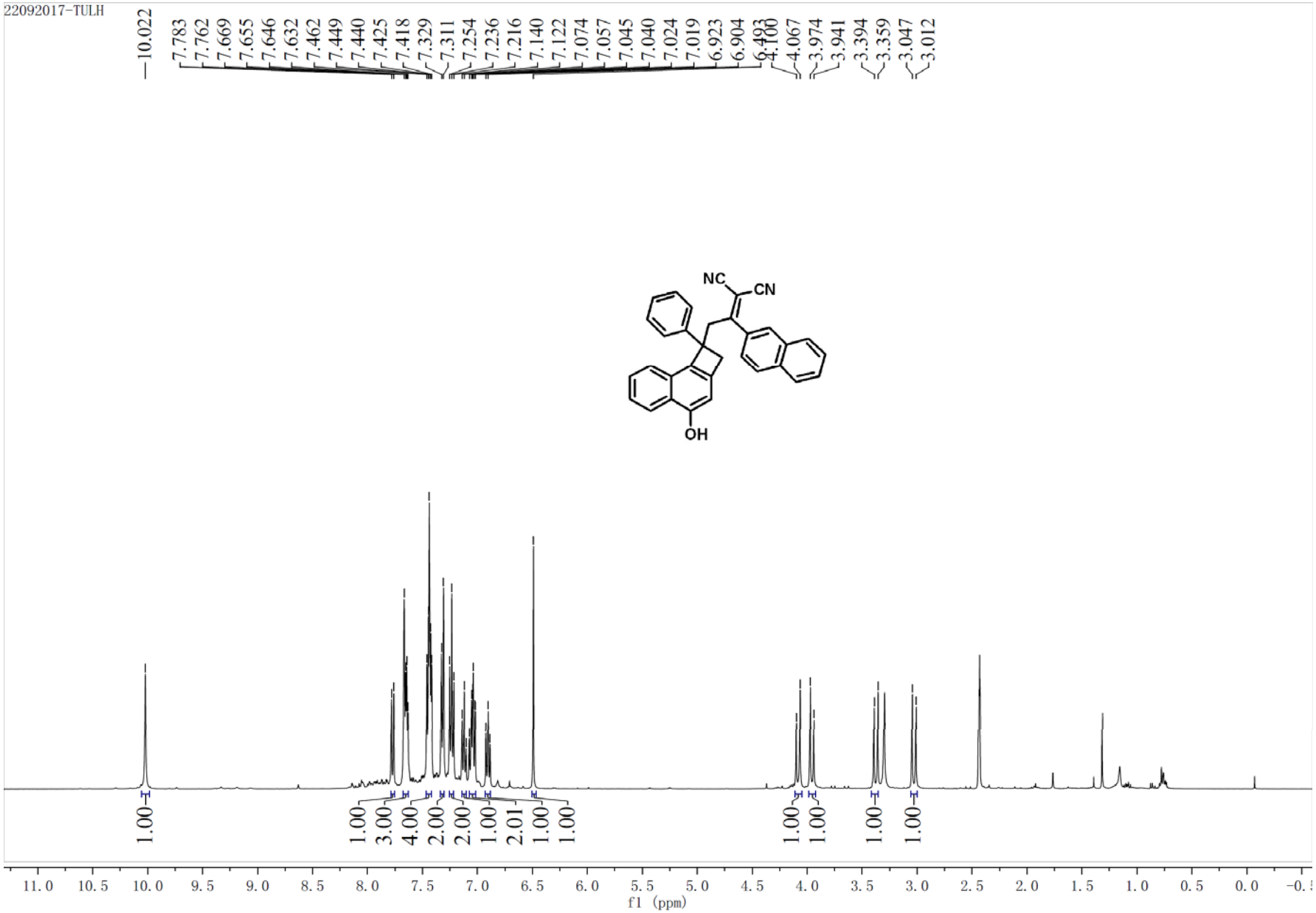
^{13}C NMR Spectrum of Compound 5k



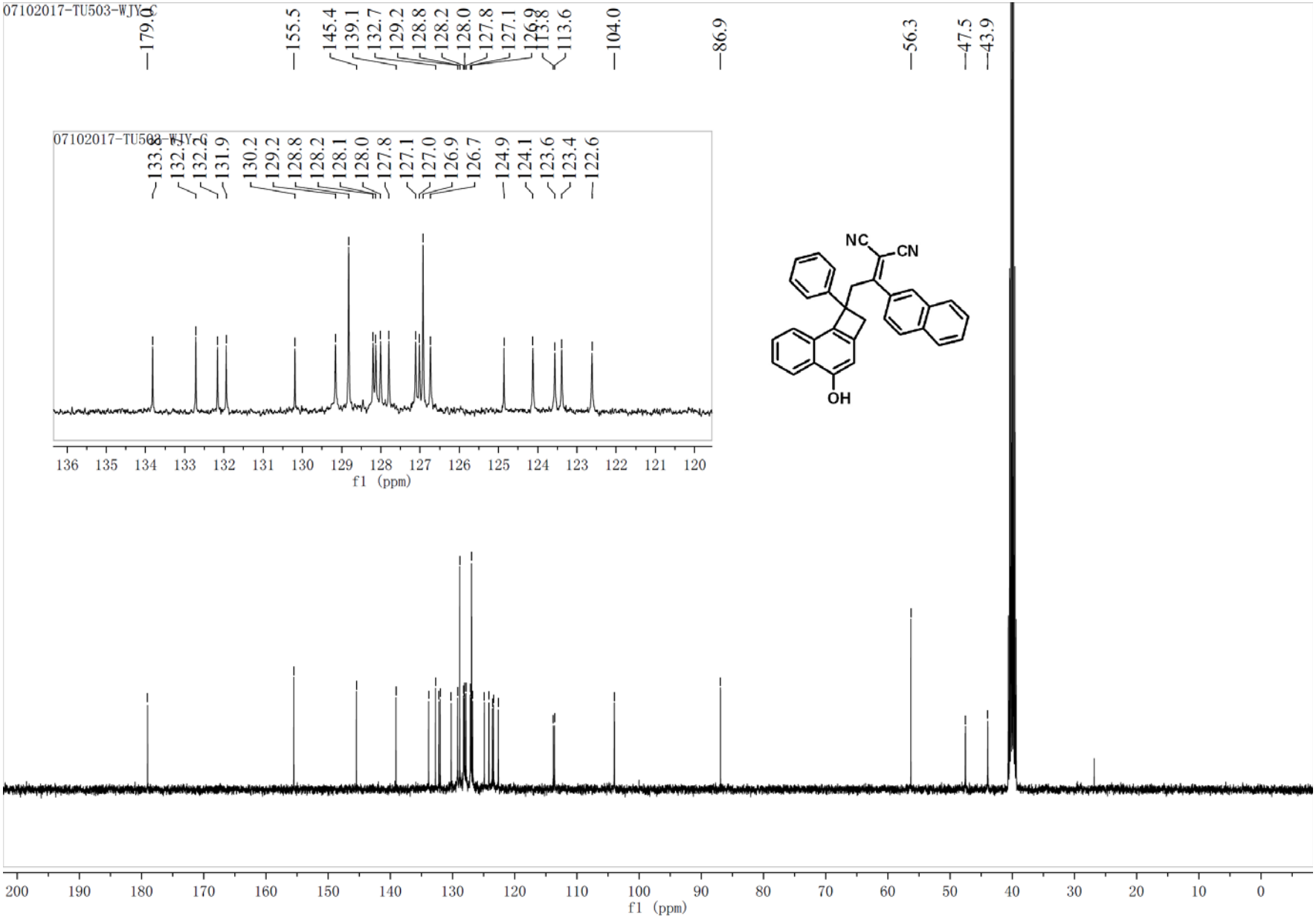
^{1}H NMR Spectrum of Compound 5l



^{13}C NMR Spectrum of Compound 5l



^{1}H NMR Spectrum of Compound 5m



^{13}C NMR Spectrum of Compound 5m