Supporting Information

Engaging Yne-Allenones in Tunable Catalytic Silane-Mediated Conjugate Transfer Reductions

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Context

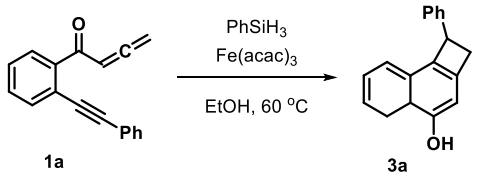
Experimental

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).

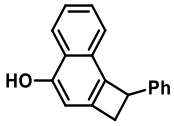
General Procedure for the Synthesis of Products 3.

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



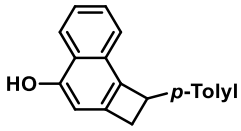
To a 10 mL Schlenk tube under Ar conditions, 1-(2-(phenylethynyl)phenyl)buta-2,3-dien-1-one (**1a**, 0.2 mmol, 1.0 equiv), $PhSiH_3$ (**2**, 0.2 mmol, 1.0 equiv), $Fe(acac)_3$ (**3**, 0.4 mmol, 2.0 equiv) and EtOH (2.5 mL) were successively added. Then, the tube was stirred at 60 °C for 1.5 h until complete consumption of **1a**, as monitored by TLC analysis. After the reaction was completed, the reaction mixture was concentrated in vacuum and the resulting residue was purified by column chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 5:1) to afford the desired product **3a** as a white solid.

1-Phenyl-1,2-dihydrocyclobuta[a]naphthalen-4-ol (3a)



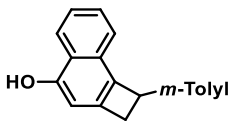
White solid; 40.0 mg, 81% yield; mp: 173-174 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.13 (s, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.43-7.28 (m, 5H), 7.24-7.19 (m, 3H), 6.80 (s, 1H), 4.80 (d, J = 4.0 Hz, 1H), 3.74-3.69 (m, 1H), 2.96 (d, J = 12.0 Hz, 1H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 154.6, 143.5, 141.6, 132.6, 130.1, 128.9, 127.2, 127.1, 126.8, 125.1, 124.2, 124.0, 121.9, 104.7, 46.2. HRMS (ESI) m/z: calcd for $C_{18}H_{15}O$ $[M+H]^+$ 247.1123, found 247.1120.

1-(p-Tolyl)-1,2-dihydrocyclobuta[a]naphthalen-4-ol (3b)



White solid; 36.9 mg, 71% yield; mp: 178-179 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.11 (s, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.41-7.30 (m, 3H), 7.12-7.08 (m, 4H), 6.80 (s, 1H), 4.75 (d, J = 4.0 Hz, 1H), 3.71-3.66 (m, 1H), 2.94-2.90 (m, 1H), 2.26 (s, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 154.5, 141.6, 140.5, 135.7, 132.9, 130.1, 129.5, 127.1, 127.0, 125.1, 124.2, 123.9, 121.9, 104.7, 45.8, 21.1. HRMS (ESI) m/z: calcd for $C_{19}H_{16}ONa$ $[M+Na]^+$ 283.1099, found 283.1100.

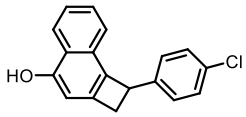
1-(m-Tolyl)-1,2-dihydrocyclobuta[a]naphthalen-4-ol (3c)



White solid; 30.7 mg, 59% yield; mp: 175-176 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.14 (s, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.42-7.32 (m, 3H), 7.19-7.16 (m, 1H), 7.04-7.00 (m, 3H), 6.80 (s, 1H), 4.75 (d, J = 3.2 Hz, 1H), 3.71-3.67

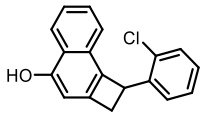
(m, 1H), 2.97-2.93 (m, 1H), 2.24 (s, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 154.6, 143.5, 141.6, 137.9, 132.7, 130.1, 128.8, 127.7, 127.5, 127.2, 125.1, 124.3, 124.2, 123.9, 121.9, 104.7, 46.1, 21.5. HRMS (ESI) m/z: calcd for $C_{19}H_{16}ONa$ $[M+Na]^+$ 283.1099, found 283.1101.

1-(4-Chlorophenyl)-1,2-dihydrocyclobuta[a]naphthalen-4-ol (3d)



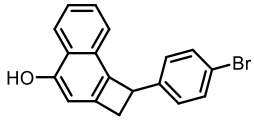
White solid; 32.5 mg, 58% yield; mp: 138-139 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.17 (s, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.43-7.31 (m, 5H), 7.24 (d, J = 12.0 Hz, 2H), 6.80 (s, 1H), 4.80 (d, J = 3.6 Hz, 1H), 3.74-3.69 (m, 1H), 2.96-2.92 (m, 1H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 154.8, 142.6, 141.6, 132.2, 131.2, 130.0, 129.0, 128.9, 127.3, 125.1, 124.3, 124.0, 121.7, 104.7, 45.4, 40.6, 40.4, 40.3, 40.2, 34.0, 39.8, 39.6, 39.4. HRMS (ESI) m/z: calcd for $C_{18}H_{13}OClNa$ $[M+Na]^+$ 303.0553, found 303.0551.

1-(2-Chlorophenyl)-1,2-dihydrocyclobuta[a]naphthalen-4-ol (3e)



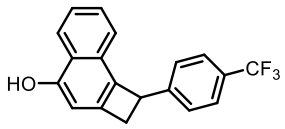
White solid; 38.1 mg, 68% yield; mp: 141-142 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.22 (s, 1H), 8.26 (d, J = 8.0 Hz, 1H), 7.52-7.39 (m, 4H), 7.29 – 7.18 (m, 2H), 7.09-7.07 (m, 1H), 6.81 (s, 1H), 5.04 (d, J = 4.0 Hz, 1H), 3.83-3.78 (m, 1H), 2.91-2.87 (m, 1H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 155.0, 141.5, 140.5, 133.2, 130.5, 130.2, 129.7, 128.6, 128.2, 127.7, 127.5, 125.2, 124.3, 124.1, 122.2, 104.8, 44.0. HRMS (ESI) m/z: calcd for $C_{18}H_{13}OClNa$ $[M+Na]^+$ 303.0553, found 303.0552.

1-(4-Bromophenyl)-1,2-dihydrocyclobuta[a]naphthalen-4-ol (3f)



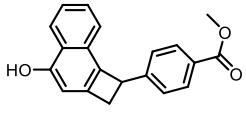
White solid; 32.4 mg, 50% yield; mp: 144-145 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.17 (s, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.42-7.31 (m, 3H), 7.18 (d, J = 8.0 Hz, 2H), 6.79 (s, 1H), 4.79 (d, J = 4.0 Hz, 1H), 3.74-3.69 (m, 1H), 2.94 (d, J = 16.0 Hz, 1H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 154.8, 142.6, 141.6, 132.2, 131.2, 130.0, 129.0, 128.9, 127.3, 125.1, 124.3, 124.0, 121.7, 104.7, 45.4. HRMS (ESI) m/z: calcd for $C_{18}H_{13}OBrNa$ $[M+Na]^+$ 347.0047, found 347.0045.

1-(4-(Trifluoromethyl)phenyl)-1,2-dihydrocyclobuta[a]naphthalen-4-ol (3g)



White solid; 34.1 mg, 55% yield; mp: 158-161 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm):10.21 (s, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 2H), 7.41 (m, 4H), 7.33 (d, J = 7.6 Hz, 1H), 6.83 (s, 1H), 4.90 (d, J = 3.2 Hz, 1H), 3.76 (m, 1H), 2.99 (d, J = 13.6 Hz, 1H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.2, 8.3, 8.2, 7.7, 7.7, 7.5, 7.4(3), 7.4(0), 7.4(8), 7.3(4), 7.3(2), 6.8, 4.9(1), 4.9(0), 3.8(8), 3.8(7), 3.8(5), 3.7, 3.0, 3.0(7). HRMS (ESI) m/z: calcd for $C_{19}H_{14}F_3O$ $[M+H]^+$ 315.0997, found 315.0999.

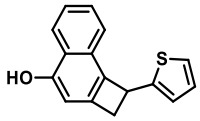
Methyl 4-(4-hydroxy-1,2-dihydrocyclobuta[a]naphthalen-1-yl)benzoate (3h)



White solid; 39.2 mg, 60% yield; mp: 178-179 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.19 (s, 1H), 8.23 (d, J =

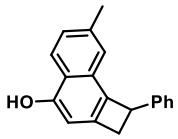
8.0 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.39 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 1H), 6.82 (s, 1H), 4.89 (d, *J* = 3.6 Hz, 1H), 3.83 (s, 3H), 3.75 (m, 1H), 2.99 (d, *J* = 14 Hz, 1H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 166.7, 154.9, 149.4, 141.7, 132.1, 130.1, 128.3, 127.6, 127.4, 125.2, 124.4, 124.2, 121.8, 104.8, 52.6, 46.1. HRMS (ESI) m/z: calcd for $C_{20}H_{16}O_3Na$ $[M+Na]^+$ 327.0997, found 327.0998.

1-(Thiophen-2-yl)-1,2-dihydrocyclobuta[a]naphthalen-4-ol (3i)



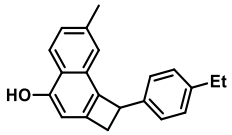
White solid; 44.4 mg, 88% yield; mp: 180-181 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.18 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.40-7.33 (m, 2H), 6.98-6.96 (m, 2H), 6.78 (s, 1H), 5.06 (d, *J* = 4.0 Hz, 1H), 3.78-3.74 (m, 1H), 3.09-3.05 (m, 1H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 154.9, 147.5, 141.4, 132.7, 129.8, 127.4, 127.3, 125.1, 124.4, 124.3, 124.2, 124.1, 121.8, 104.6, 41.2. HRMS (ESI) m/z: calcd for $C_{16}H_{12}OSNa$ $[M+Na]^+$ 275.0507, found 275.0505.

7-Methyl-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-4-ol (3j)



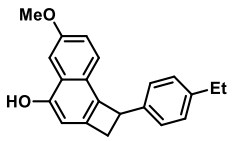
White solid; 42.1 mg, 81% yield; mp: 179-180 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.05 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.32-7.28 (m, 2H), 7.23-7.19 (m, 4H), 7.10 (s, 1H), 6.72 (s, 1H), 4.76 (d, *J* = 3.2 Hz, 1H), 3.71-3.67 (m, 1H), 2.92-2.89 (m, 1H), 2.35 (s, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 154.6, 143.7, 141.7, 136.5, 131.9, 130.4, 128.9, 127.1, 126.8, 126.1, 124.2, 123.3, 120.8, 104.0, 46.1, 21.8. HRMS (ESI) m/z: calcd for $C_{19}H_{16}ONa$ $[M+Na]^+$ 283.1099, found 283.1100.

1-(4-Ethylphenyl)-7-methyl-1,2-dihydrocyclobuta[a]naphthalen-4-ol (3k)



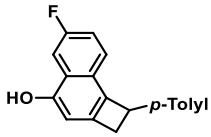
White solid; 43.2 mg, 75% yield; mp: 192-193 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.02 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 5H), 6.72 (s, 1H), 4.72 (d, *J* = 3.2 Hz, 1H), 3.69-3.64 (m, 1H), 2.90-2.87 (m, 1H), 2.57 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 1.18-1.14 (m, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 154.6, 142.1, 141.7, 140.9, 136.4, 132.0, 130.4, 128.3, 127.0, 126.0, 124.2, 123.3, 120.8, 104.0, 45.8, 28.3, 21.8, 16.0. HRMS (ESI) m/z: calcd for $C_{21}H_{20}ONa$ $[M+Na]^+$ 311.1412, found 311.1410.

1-(4-Ethylphenyl)-6-methoxy-1,2-dihydrocyclobuta[a]naphthalen-4-ol (3l)



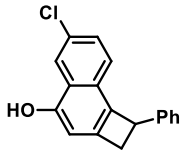
White solid; 27.4 mg, 45% yield; mp: 199-200 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.01 (s, 1H), 7.55 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.11-7.07 (m, 5H), 6.78 (s, 1H), 4.72 (d, *J* = 4.0 Hz, 1H), 3.84 (s, 3H), 3.68-3.64 (m, 1H), 2.92-2.88 (m, 1H), 2.56-2.51 (m, 2H), 1.17-1.13 (m, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 156.2, 153.5, 142.1, 140.9, 138.6, 133.0, 128.3, 127.1, 126.0, 125.6, 123.6, 119.3, 105.2, 103.0, 55.5, 45.9, 28.3, 16.1. HRMS (ESI) m/z: calcd for $C_{21}H_{20}O_2Na$ $[M+Na]^+$ 327.1361, found 327.1360.

6-Fluoro-1-(p-tolyl)-1,2-dihydrocyclobuta[a]naphthalen-4-ol (3m)



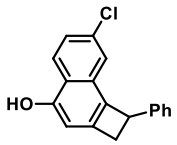
White solid; 28.8 mg, 47% yield; mp: 178-179 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.27 (s, 1H), 7.84-7.80 (m, 1H), 7.39-7.30 (m, 2H), 7.10 (s, 4H), 6.84 (s, 1H), 4.75 (d, J = 4.0 Hz, 1H), 3.71-3.66 (m, 1H), 2.95 – 2.90 (m, 1H), 2.26 (s, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 160.4, 158.0, 153.9, 140.9, 140.2, 135.9, 133.2, 129.5, 127.2, 127.0, 125.7, 125.6, 124.7, 117.3, 117.0, 107.9, 107.7, 105.7, 45.8, 21.1. HRMS (ESI) m/z: calcd for $C_{19}H_{16}OF$ $[M+H]^+$ 279.1185, found 279.1179.

6-Chloro-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-4-ol (3n)



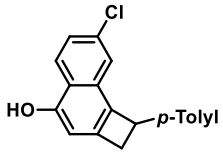
White solid; 26.3 mg, 47% yield; mp: 176-177 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.40 (s, 1H), 8.18 (d, J = 4.0 Hz, 1H), 7.45-7.42 (m, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.32-7.28 (m, 2H), 7.23-7.20 (m, 3H), 6.86 (s, 1H), 4.81 (d, J = 4.0 Hz, 1H), 3.74-3.70 (m, 1H), 2.98-2.95 (m, 1H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 153.9, 143.2, 142.5, 132.8, 129.0, 128.7, 128.3, 127.7, 127.1, 126.9, 125.8, 124.2, 123.1, 106.0, 46.1. HRMS (ESI) m/z: calcd for $C_{18}H_{13}OClNa$ $[M+Na]^+$ 303.0553, found 303.0552.

7-Chloro-1-phenyl-1,2-dihydrocyclobuta[a]naphthalen-4-ol (3o)



White solid; 46.1 mg, 82% yield; mp: 170-171 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.39 (s, 1H), 8.23 (d, J = 12.0 Hz, 1H), 7.38-7.30 (m, 4H), 7.24-7.21 (m, 3H), 6.83 (s, 1H), 4.80 (d, J = 4.0 Hz, 1H), 3.74-3.70 (m, 1H), 2.99-2.95 (m, 1H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 154.8, 143.7, 143.1, 132.1, 132.0, 130.6, 129.0, 127.1, 126.9, 126.8, 124.3, 123.4, 120.5, 105.4, 100.0, 46.1. HRMS (ESI) m/z: calcd for $C_{18}H_{14}OCl$ $[M+H]^+$ 281.0733, found 281.0732.

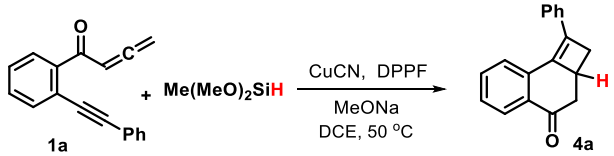
7-Chloro-1-(p-tolyl)-1,2-dihydrocyclobuta[a]naphthalen-4-ol (3p)



White solid; 28.3 mg, 48% yield; mp: 158-159 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.27 (s, 1H), 7.84-7.80 (m, 1H), 7.39-7.30 (m, 2H), 7.10 (s, 4H), 6.84 (s, 1H), 4.75 (d, J = 4.0 Hz, 1H), 3.71-3.66 (m, 1H), 2.95 – 2.90 (m, 1H), 2.26 (s, 3H). ^{13}C NMR (400 MHz, DMSO-d_6) (δ, ppm): 160.4, 158.0, 153.9, 140.9, 140.2, 135.9, 133.2, 129.5, 127.2, 127.0, 125.7, 125.6, 124.7, 117.3, 117.0, 107.9, 107.7, 105.7, 45.8, 21.1. HRMS (ESI) m/z: calcd for $C_{19}H_{16}ClO$ $[M+H]^+$ 295.0890, found 295.0885.

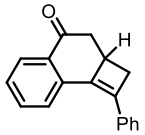
General Procedure for the Synthesis of Products 4.

Example for the synthesis of **4a**:



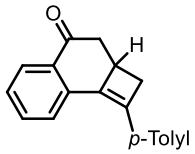
To a 10 mL Schlenk tube under Ar conditions, 1-(2-(phenylethynyl)phenyl)buta-2,3-dien-1-one (**1a**, 0.2 mmol, 1.0 equiv), $Me(MeO)_2SiH$ (**2**, 0.3 mmol, 1.5 equiv), CuCN (0.02mmol, 0.1 equiv), DPPF (0.02 mmol,0.1 equiv), NaOMe, (0.3 mmol; 1.5 equiv) and DCE (2.5 mL) were successively added. Then, the tube was stirred at 50 °C for 3 h until complete consumption of **1a**, as monitored by TLC analysis. Saturated aqueous NH_4Cl (20 mL) and ethyl acetate (20 mL) were added. The organic layer was separated and the aqueous layer was further extracted with ethyl acetate (20 mL). The combined organic layers was washed with brine, dried over Na_2SO_4, the reaction mixture was concentrated in vacuum and the resulting residue was purified by column chromatography on silica gel (eluent, petroleum ether/ethyl acetate = 5:1) to afford the desired product **4a** as a yellow oil.

1-Phenyl-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (4a)



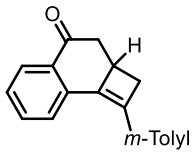
Yellow oil; 44.3 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.11-8.09 (m, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.66-7.56 (m, 3H), 7.44-7.31 (m, 4H), 3.29-3.22 (m, 2H), 3.20-3.16 (m, 1H), 2.72-7.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 198.0, 137.5, 136.7, 136.4, 135.2, 133.6, 132.5, 128.7, 128.5, 128.2, 128.1, 126.1, 126.1, 126.0, 126.0, 126.0, 125.0, 46.1, 35.9, 35.8. IR (KBr, v, cm^{-1}): 2949, 2922, 1685, 1602, 1529, 1451, 829, 728; HRMS (ESI) m/z calcd for $C_{18}H_{14}NaO$ $[M+Na]^+$ 269.0942, found 269.0944.

1-(p-Tolyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (4b)



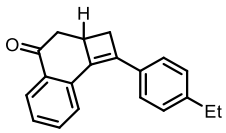
Yellow oil; 44.2 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.12-8.10 (m, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.62-7.53 (m, 3H), 7.42-7.35 (m, 1H), 7.23 (d, J = 7.6 Hz, 2H), 3.33-3.14 (m, 3H), 2.73-2.66 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 197.9, 138.5, 137.5, 136.8, 135.1, 133.5, 132.4, 132.4, 129.3, 128.1, 127.8, 125.9, 124.9, 46.1, 35.8, 35.7, 21.4. IR (KBr, v, cm^{-1}): 3005, 2909, 1683, 1592, 1510, 1461, 815, 750; HRMS (ESI) m/z calcd for $C_{19}H_{16}NaO$ $[M+Na]^+$ 283.1099, found 283.1095.

1-(m-Tolyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (4c)



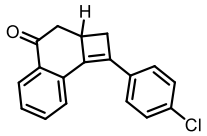
Yellow oil; 42.1 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.09 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.61-7.57 (m, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.41-7.36 (m, 2H), 7.30 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 7.6 Hz, 1H), 3.26-3.15 (m, 3H), 2.71-2.64 (m, 2H), 2.40 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 198.0, 138.2, 137.6, 136.8, 136.1, 135.1, 133.5, 132.4, 129.3, 128.5, 128.1, 128.0, 126.7, 124.9, 123.1, 46.1, 35.8(3), 35.8(0), 21.5. IR (KBr, v, cm^{-1}): 3005, 2909, 1683, 1592, 1510, 1461, 815, 750; HRMS (ESI) m/z calcd for $C_{19}H_{16}NaO$ $[M+Na]^+$ 283.1099, found 283.1098.

1-(4-Ethylphenyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (4d)



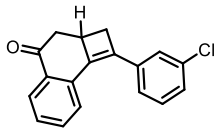
White solid; 47.9 mg, 87% yield; mp: 140-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.11-8.09 (m, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.65-7.54 (m, 3H), 7.42-7.36 (m, 1H), 7.26 (d, J = 8.4 Hz, 2H), 3.32-3.15 (m, 3H), 2.74-2.64 (m, 4H), 1.28 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 197.9, 144.9, 137.5, 136.8, 135.2, 133.4, 132.6, 132.4, 128.1, 128.0, 127.8, 126.0, 124.9, 46.1, 35.8, 35.7, 28.8, 15.5. IR (KBr, v, cm^{-1}): 3005, 2965, 1683, 1594, 1507, 1462, 3, 831, 765; HRMS (ESI) m/z calcd for $C_{20}H_{19}O$ $[M+H]^+$ 275.1436, found 275.1437.

1-(4-Chlorophenyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (4e)



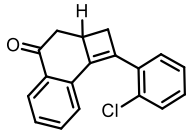
Yellow oil; 41.6 mg, 74% yield; mp: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.11-8.09 (m, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.66-7.56 (m, 3H), 7.44-7.31 (m, 4H), 3.29-3.22 (m, 2H), 3.26-3.16 (m, 1H), 2.71-2.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 197.6, 137.0, 136.3, 136.1, 134.1, 133.6, 133.5, 132.5, 128.8, 128.2, 128.2, 127.2, 124.7, 45.9, 35.9, 35.1. IR (KBr, v, cm^{-1}): 2940, 2911, 1683, 1591, 1477, 1407, 855, 763; HRMS (ESI) m/z calcd for $C_{18}H_{14}ClO$ $[M+H]^+$ 281.0733, found 281.0740.

1-(3-Chlorophenyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (4f)



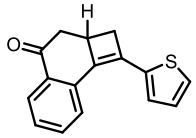
White solid; 41.0 mg, 73% yield; mp: 80-82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.11-8.09 (m, 1H), 7.75 (d, J = 7.6 Hz, 1H), 7.63-7.59 (m, 1H), 7.57-7.56 (m, 1H), 7.53-7.51 (m, 1H), 7.42-7.38 (m, 1H), 7.36-7.27 (m, 2H), 3.27-3.15 (m, 3H), 2.71-2.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 197.4, 138.0, 136.8, 136.1, 135.8, 134.7, 133.6, 132.5, 129.8, 128.4, 128.3, 128.2, 126.0, 124.8, 124.0, 45.9, 36.0, 35.7. IR (KBr, v, cm^{-1}): 2975, 2922, 1682, 1507, 1456, 1417, 762, 700; HRMS (ESI) m/z calcd for $C_{18}H_{14}ClO$ $[M+H]^+$ 281.0733, found 281.0725.

1-(2-Chlorophenyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (4g)



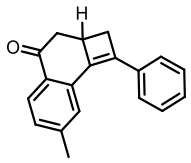
Yellow oil; 39.3 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.06 (d, J = 7.6 Hz, 1H), 7.68-7.61 (m, 1H), 7.49-7.47 (m, 2H), 7.44-7.33 (m, 2H), 7.27-7.21 (m, 2H), 3.50-3.45 (m, 1H), 3.33-3.24 (m, 1H), 3.20-3.15 (m, 1H), 2.90-2.86 (m, 1H), 2.75-2.68 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 197.7, 139.9, 135.9, 135.8, 133.9, 133.3, 132.8, 132.4, 130.4, 129.2(2), 129.2(0), 128.3, 127.9, 126.5, 124.8, 45.9, 39.7, 37.0. IR (KBr, v, cm^{-1}): 3005, 2988, 1682, 1594, 1474, 1430, 896, 750; HRMS (ESI) m/z calcd for $C_{18}H_{14}ClO$ $[M+H]^+$ 281.0733, found 281.0732.

1-(Thiophen-2-yl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (4h)



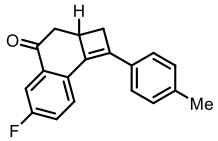
White solid; 42.0 mg,83% yield; mp: 102-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.07-8.06 (m, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.64-7.60 (m, 1H), 7.39-7.33 (m, 2H), 7.20 (d, J = 3.5 Hz, 1H), 7.08 (dd, J = 5.0, 3.6 Hz, 1H), 3.41-3.24 (m, 1H), 3.22-3.11 (m, 2H), 2.77-2.66 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 197.6, 138.0, 135.9, 133.6, 133.4, 132.2, 130.6, 128.0, 127.9, 127.5, 125.9(2), 125.9(9), 125.1, 45.8, 36.4, 36.2. IR (KBr, v, cm^{-1}): 3059, 2911, 1680, 1591, 1560, 1463, 852, 709; HRMS (ESI) m/z calcd for $C_{16}H_{13}OS$ $[M+H]^+$ 253.0687, found 253.0698.

7-Methyl-1-phenyl-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (4i)



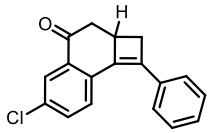
White solid; 44.2 mg, 85% yield; mp: 72-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.99 (d, J = 8.0 Hz, 1H), 7.65-7.59 (m, 3H), 7.43-7.39 (m, 2H), 7.35-7.32 (m, 1H), 7.19 (d, J = 8.0 Hz, 1H), 3.25-3.12 (m, 3H), 2.68-2.62 (m, 2H), 2.46 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 197.7, 144.4, 137.2, 136.7, 136.6, 135.2, 130.3, 129.1, 128.6, 128.4, 128.2, 126.0, 125.2, 46.0, 36.0, 35.8, 22.0. IR (KBr, v, cm^{-1}): 3005, 2989, 1684, 1605, 1493, 1474, 825, 762; HRMS (ESI) m/z calcd for $C_{17}H_{19}O$ $[M+H]^+$ 261.1279, found 261.1276.

6-Fluoro-1-(p-tolyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (4j)



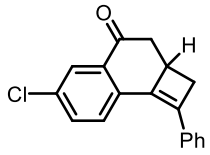
Yellow oil; 44.0 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.82-7.70 (m, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.32-7.26 (m, 1H), 7.21 (d, J = 8.0 Hz, 2H), 3.25-3.14 (m, 3H), 2.70-2.60 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 196.8, 160.0, 137.9, 135.2($^1J_{CF}$ = 269.9 Hz), 133.6, 133.5, 133.4, 132.3, 128.1, 127.8, 127.4, 126.2, 114.1, 55.4, 45.8, 35.8, 35.4. IR (KBr, v, cm^{-1}): 3025, 2914, 1686, 1603, 1511, 1417, 813, 749; HRMS (ESI) m/z calcd for $C_{19}H_{16}FO$ $[M+H]^+$ 279.1185, found 279.1192.

6-Chloro-1-phenyl-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (4k)



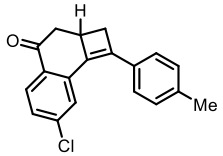
Yellow oil; 48.8 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.07 (d, J = 2.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 7.2 Hz, 2H), 7.57-7.55 (m, 1H), 7.46-7.33 (m, 3H), 3.31-3.15 (m, 3H), 2.74-2.62 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 196.6, 138.2, 134.9, 134.9, 134.8, 134.1, 133.6, 133.4, 128.7, 128.1, 126.3, 126.0, 45.7, 35.9, 35.6. IR (KBr, v, cm^{-1}): 3051, 2983, 1685, 1585, 1492, 1462, 825, 742; HRMS (ESI) m/z calcd for $C_{18}H_{14}ClO$ $[M+H]^+$ 281.0733, found 281.0729.

6-Chloro-1-phenyl-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (4l)



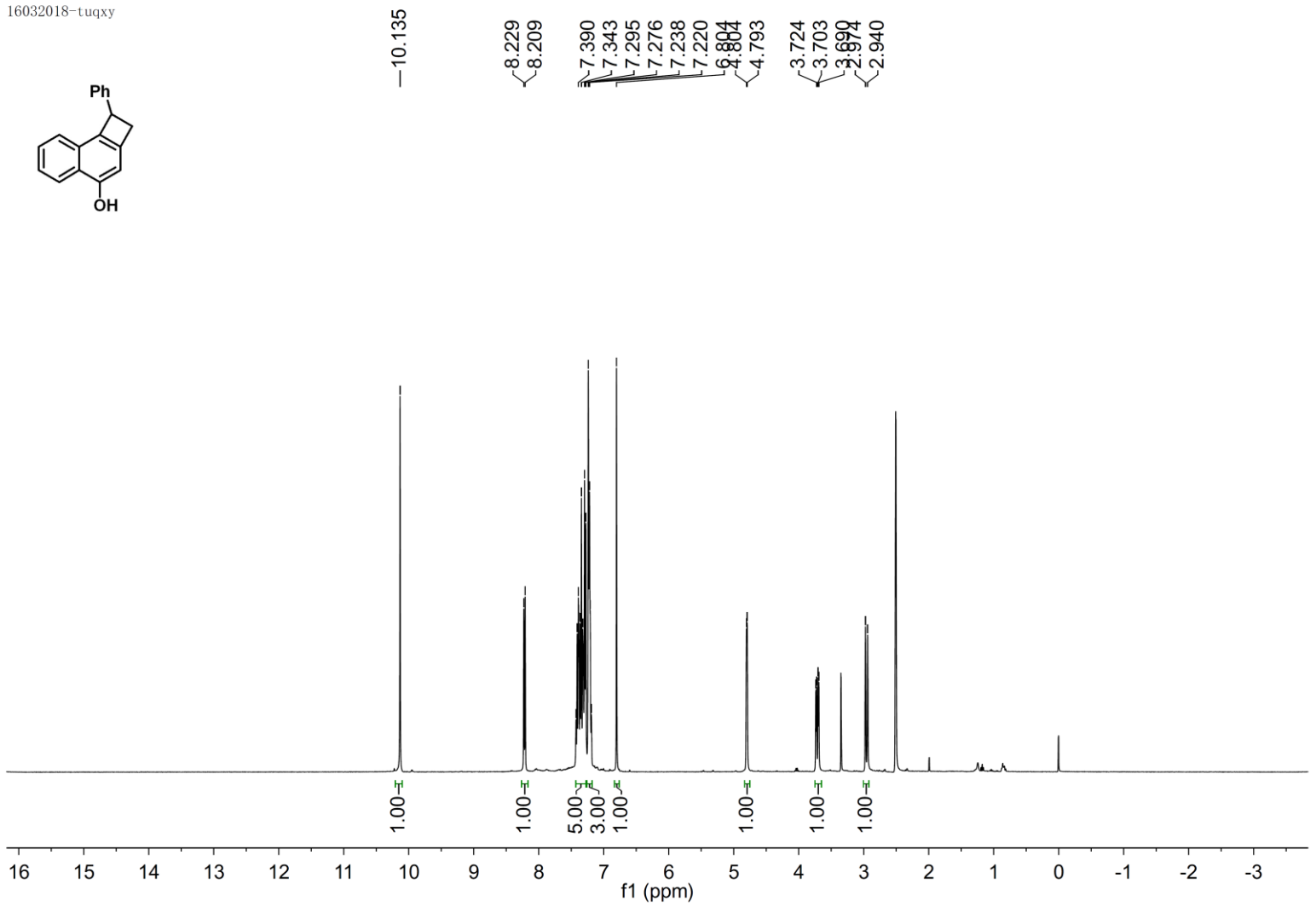
Yellow oil; 42.7 mg, 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.02 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 1.6 Hz, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.46-7.42 (m, 2H), 7.38-7.33 (m, 2H), 3.28-3.15 (m, 3H), 2.70-2.62 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 196.8, 140.0, 139.2, 137.9, 134.8, 134.7, 130.7, 129.8, 128.9, 128.8, 128.2, 126.1, 124.7, 45.8, 36.0, 35.8. IR (KBr, v, cm^{-1}): 3051, 2983, 1685, 1585, 1492, 1462, 825, 742; HRMS (ESI) m/z calcd for $C_{18}H_{14}ClO$ $[M+H]^+$ 281.0733, found 281.0732.

7-Chloro-1-(p-tolyl)-2a,3-dihydrocyclobuta[a]naphthalen-4(2H)-one (4m)

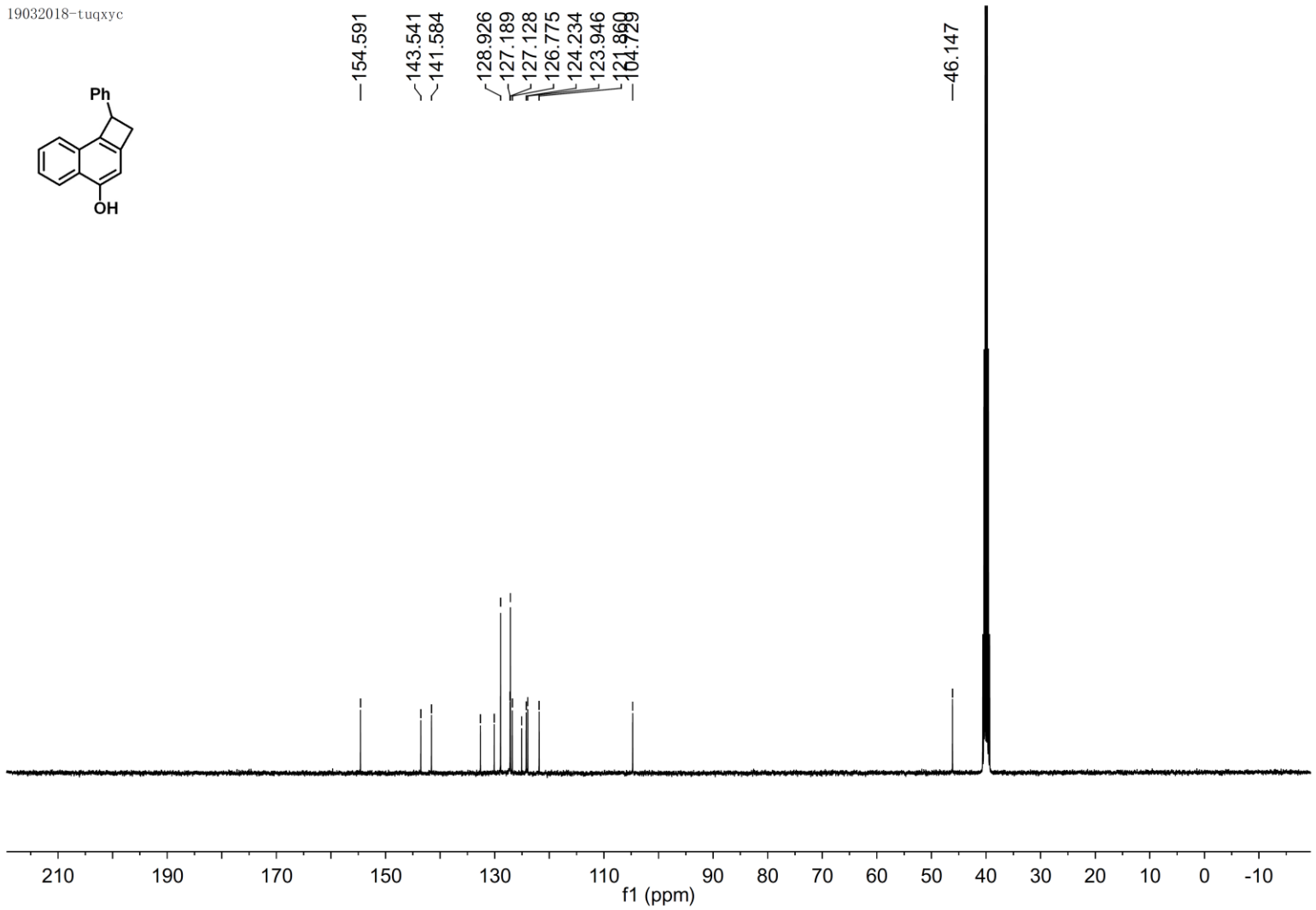


White solid; 53.4 mg, 79% yield; mp: 126-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 8.01 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 2.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.32-7.30 (m, 1H), 7.24 (d, J = 8.0 Hz, 2H), 3.25-3.12 (m, 3H), 2.68-2.60

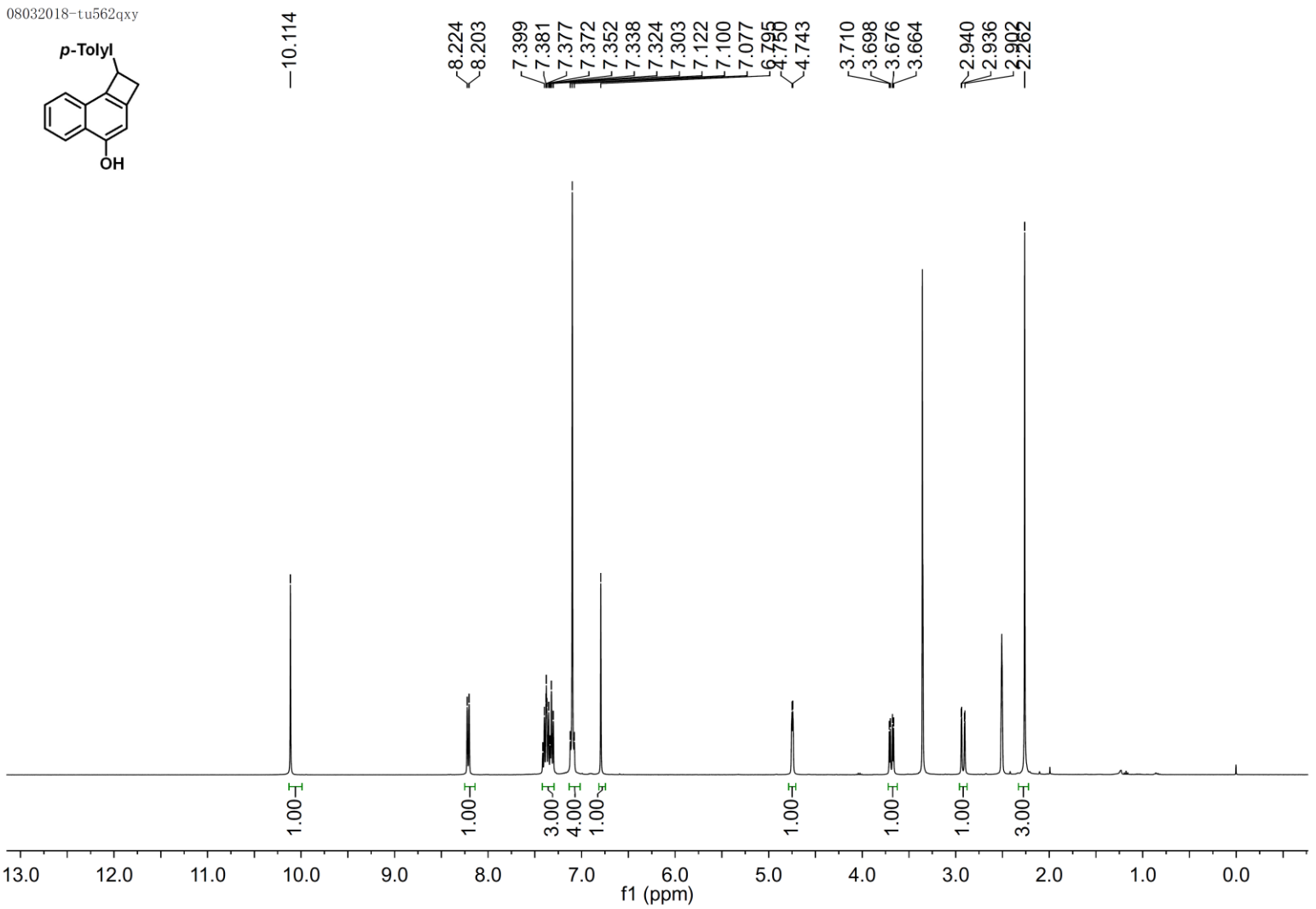
(m, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 196.9, 139.9, 139.2, 139.0, 138.0, 133.6, 132.0, 130.6, 129.7, 129.4, 128.0, 126.0, 124.6, 45.8, 35.9, 35.7, 21.5. IR (KBr, *v*, cm^{-1}): 3005, 2985, 1685, 1586, 1511, 1416, 897, 764; HRMS (ESI) m/z calcd for $C_{19}H_{16}ClO$ $[M+H]^+$ 295.0890, found 295.0894;



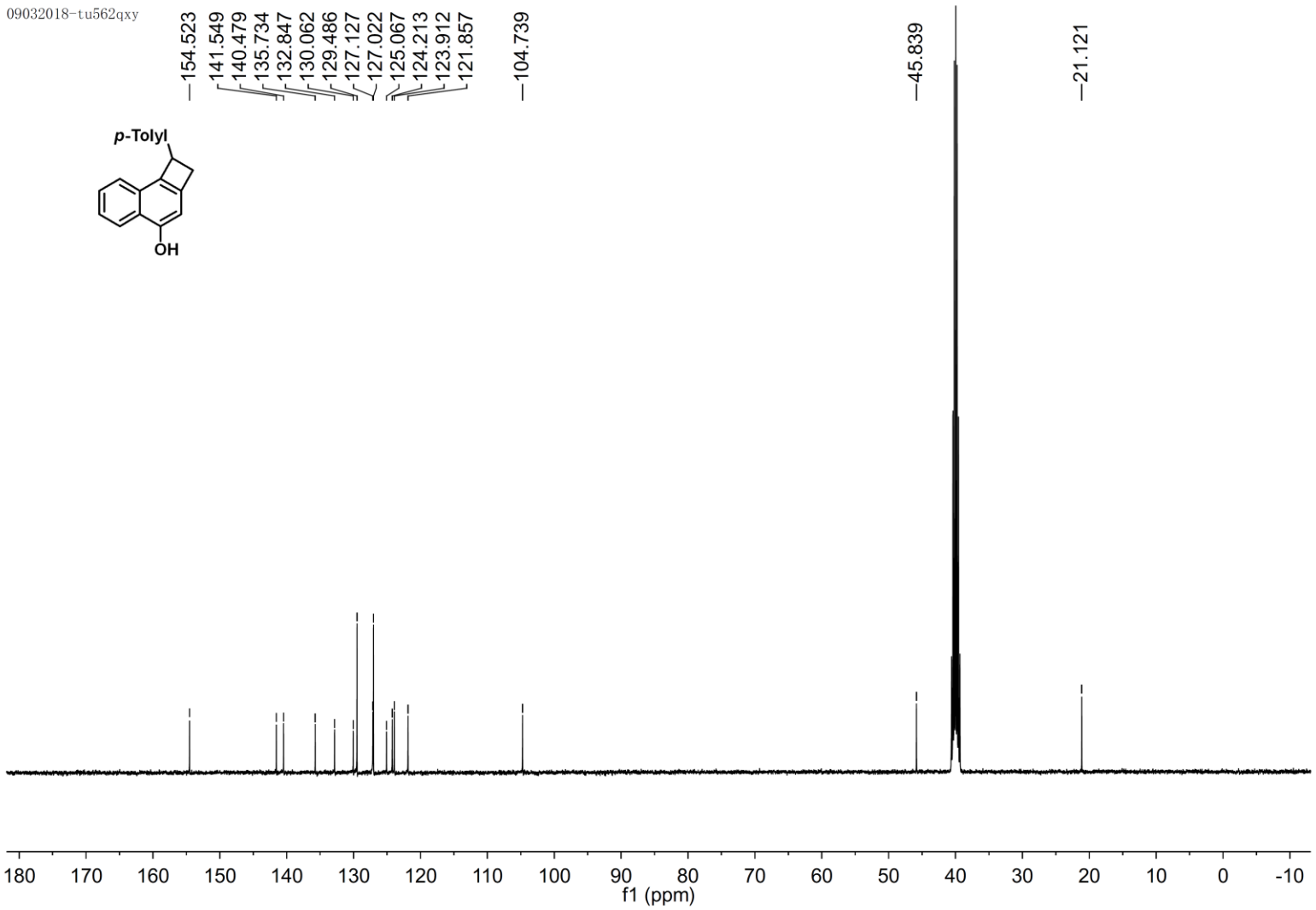
^{1}H NMR Spectrum of Compound 3a



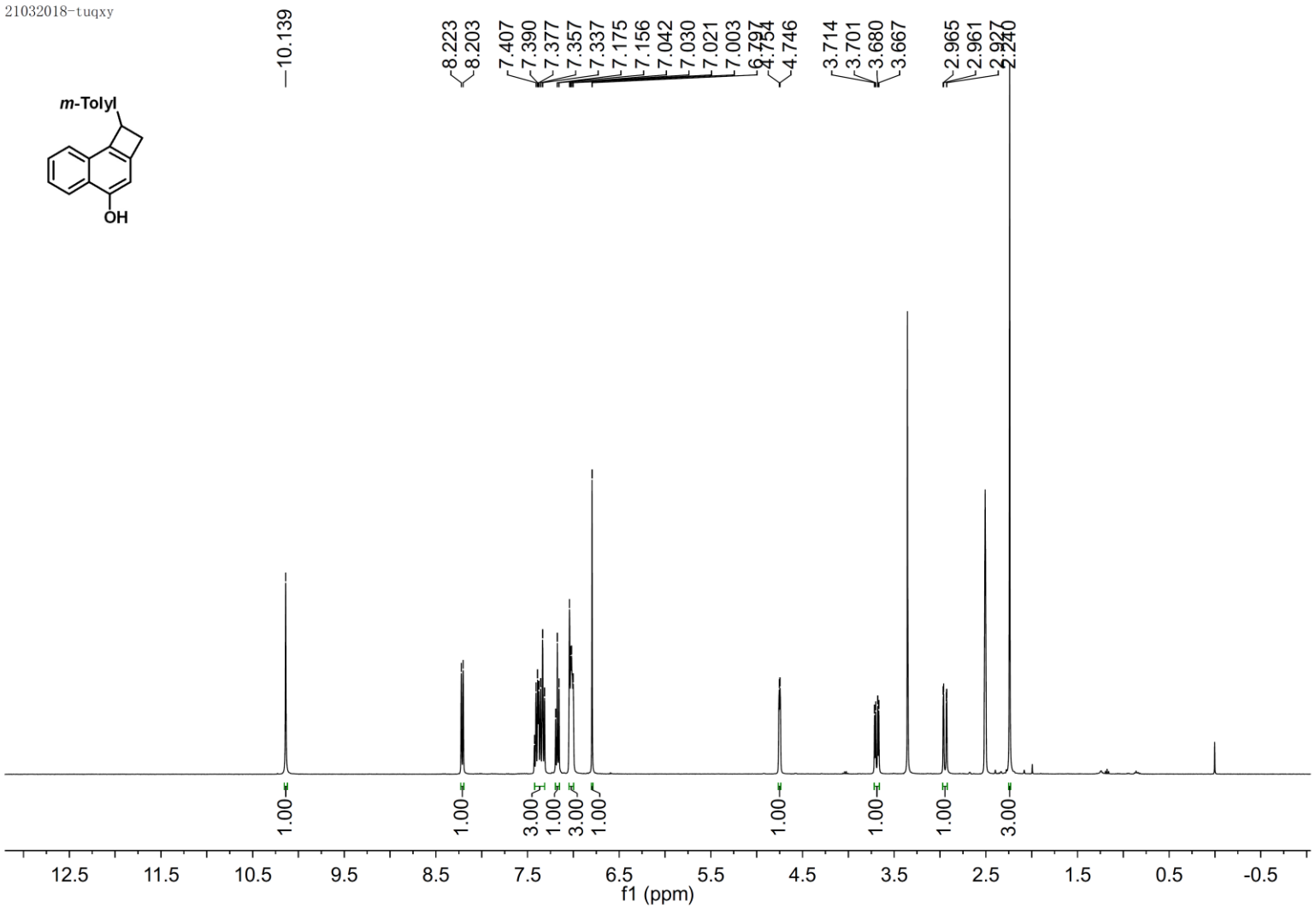
^{13}C NMR Spectrum of Compound 3a



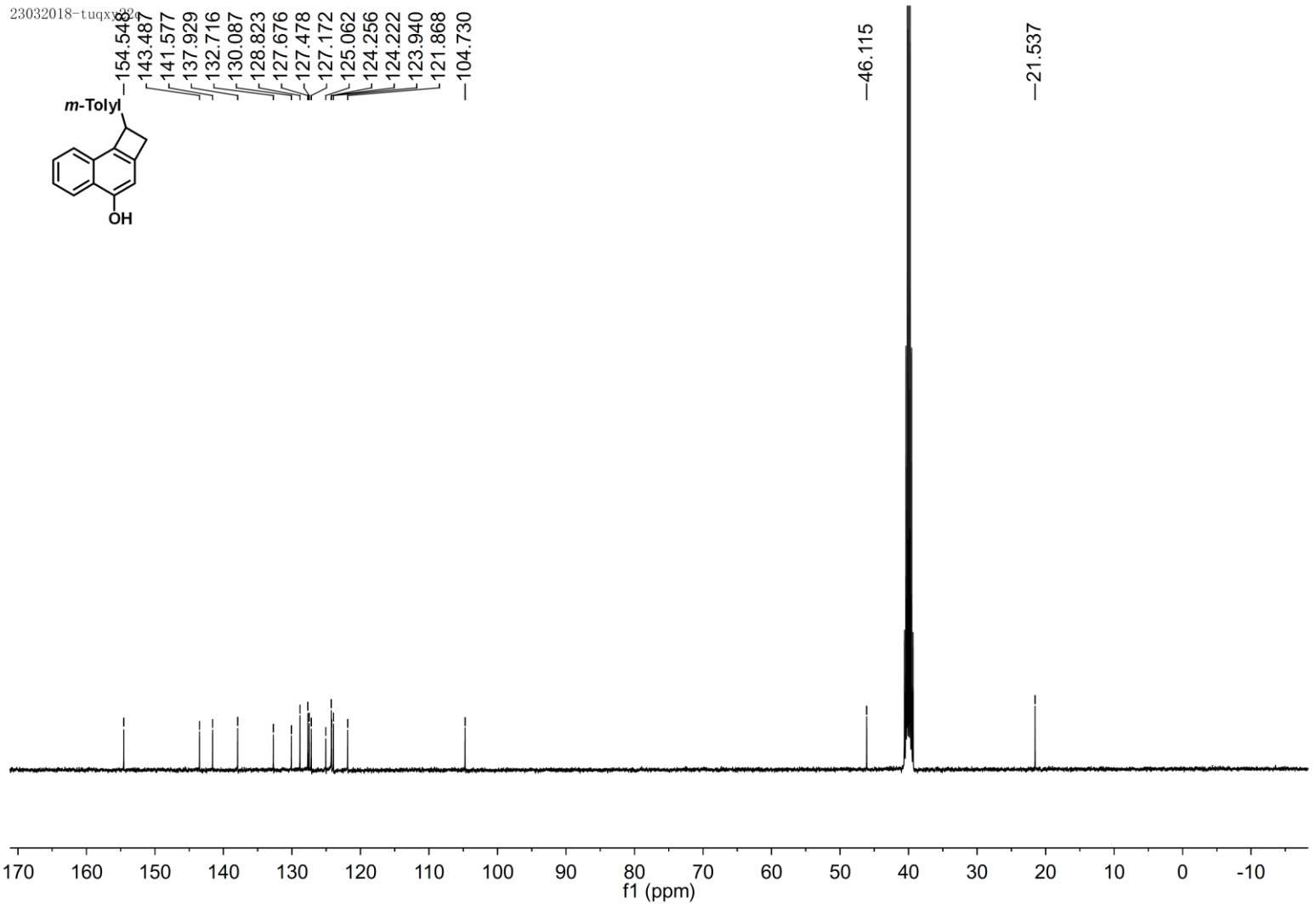
^{1}H NMR Spectrum of Compound 3b



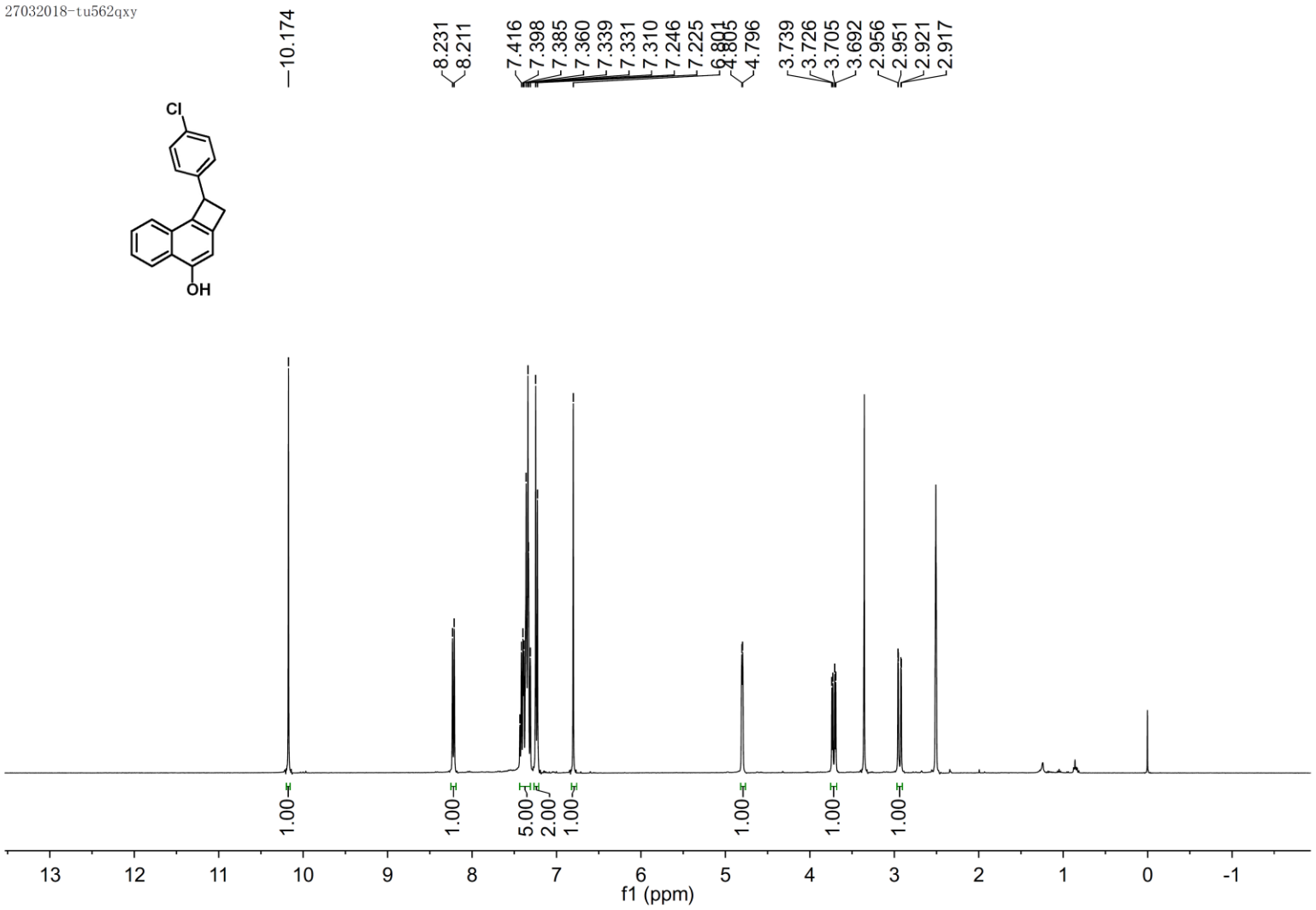
^{13}C NMR Spectrum of Compound 3b



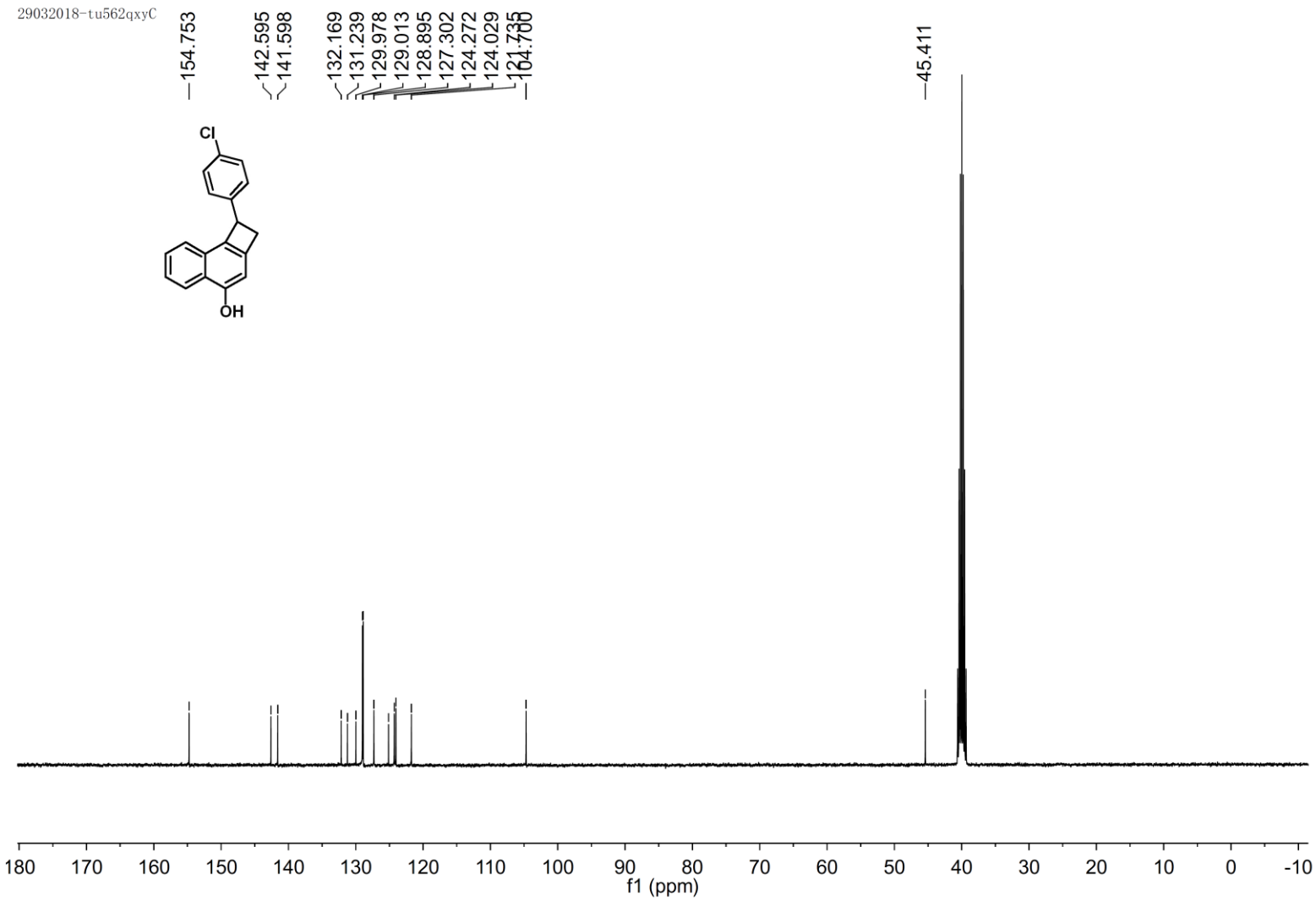
^{1}H NMR Spectrum of Compound 3c



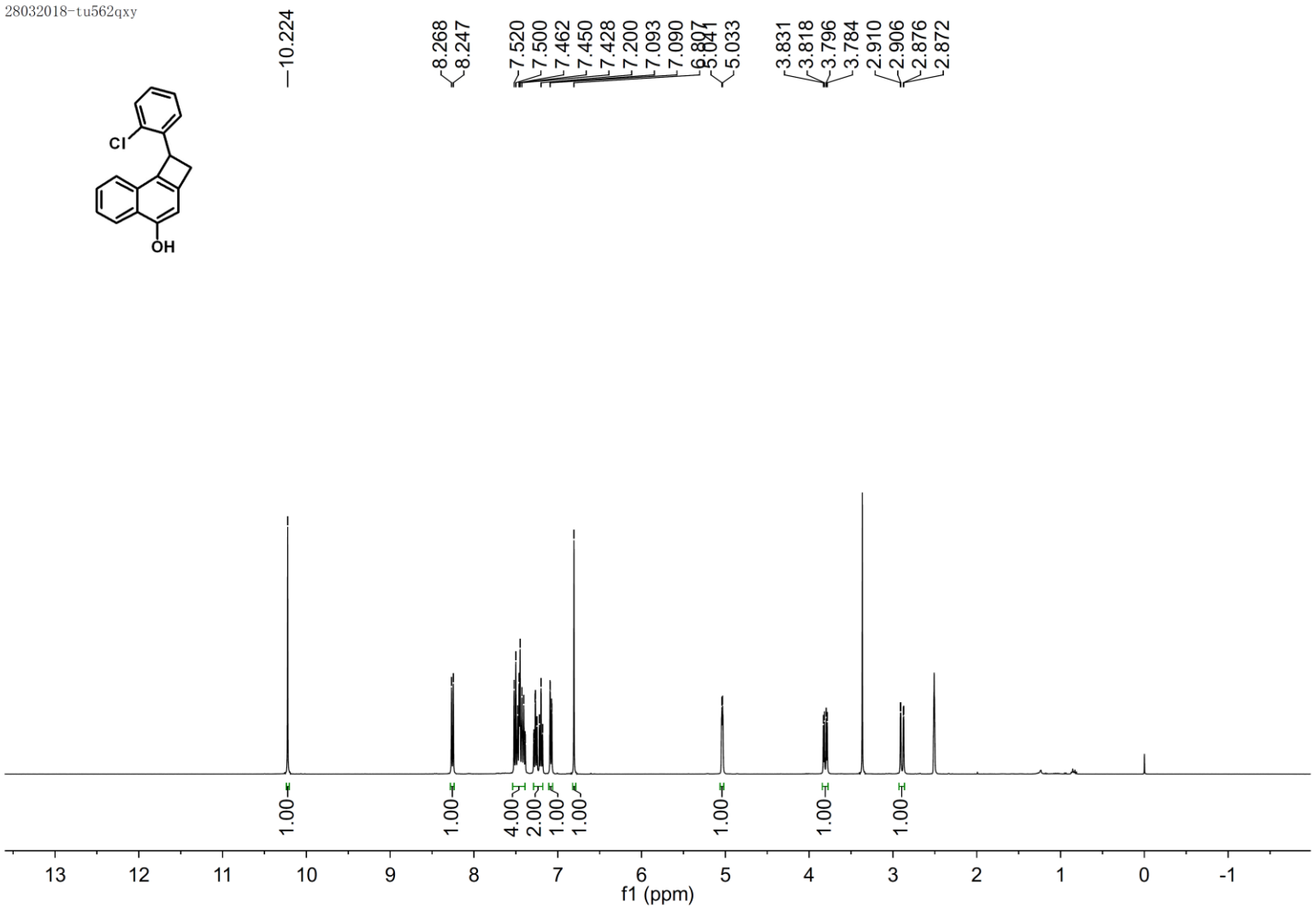
^{13}C NMR Spectrum of Compound 3c



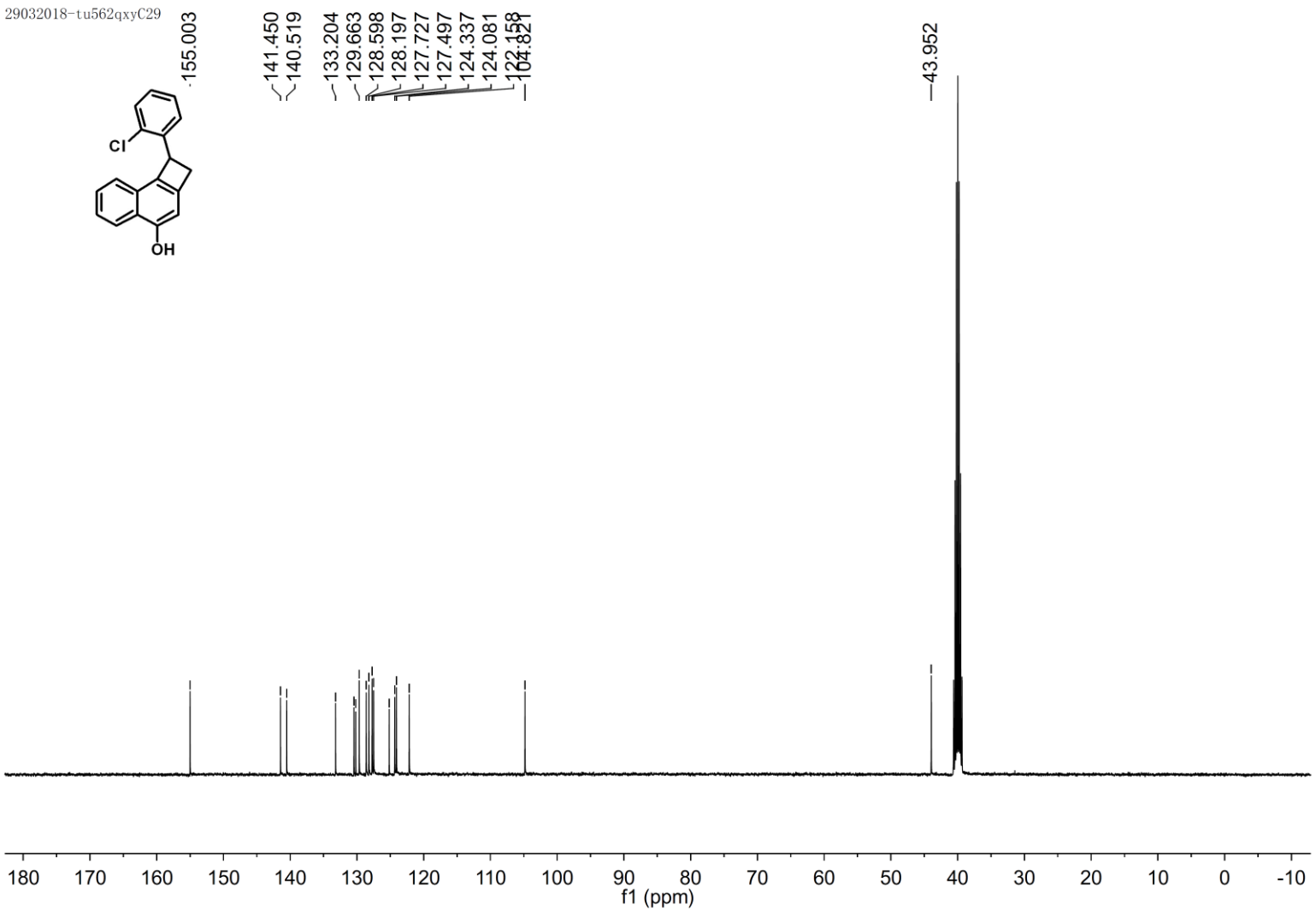
^{1}H NMR Spectrum of Compound 3d



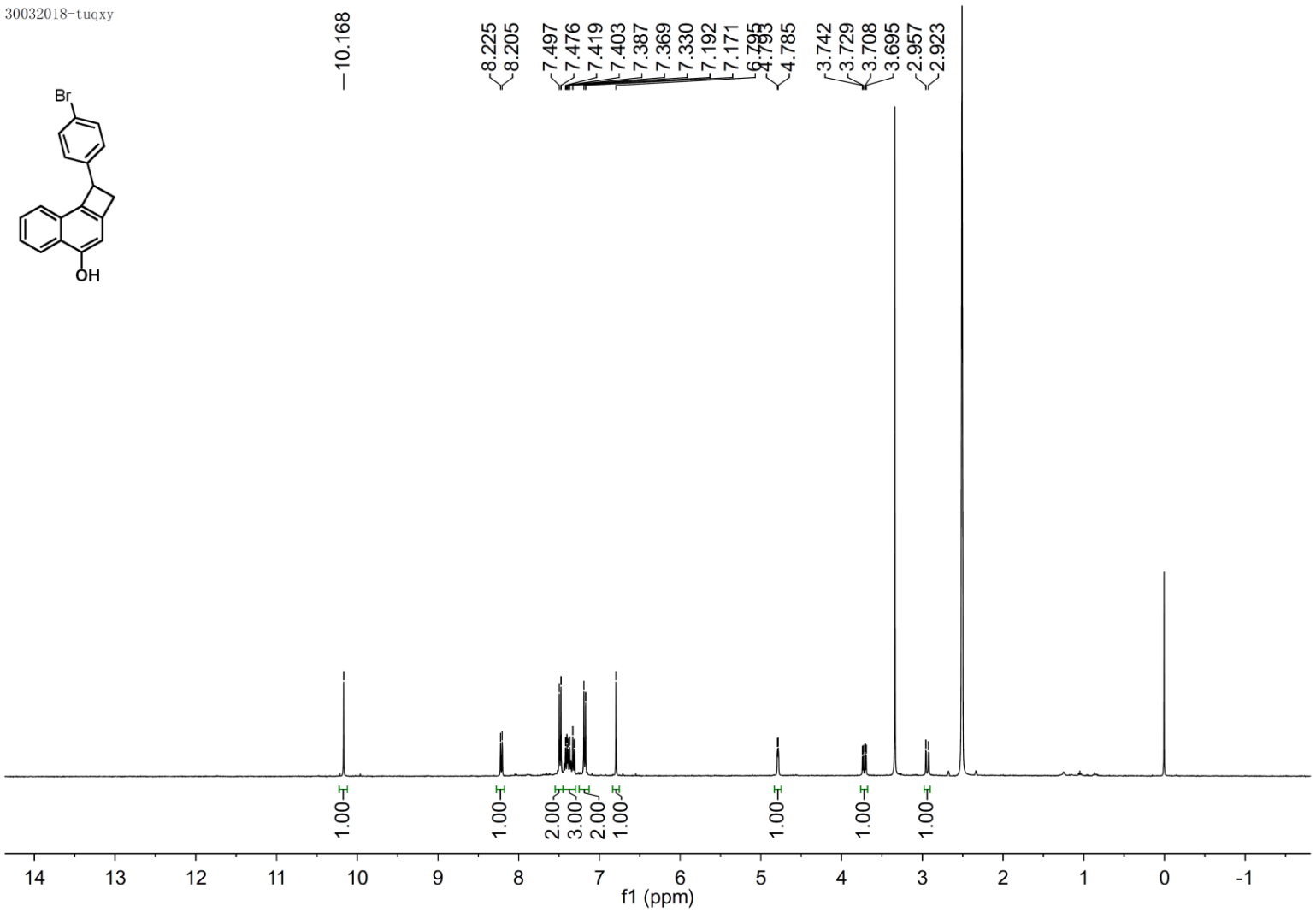
^{13}C NMR Spectrum of Compound 3d



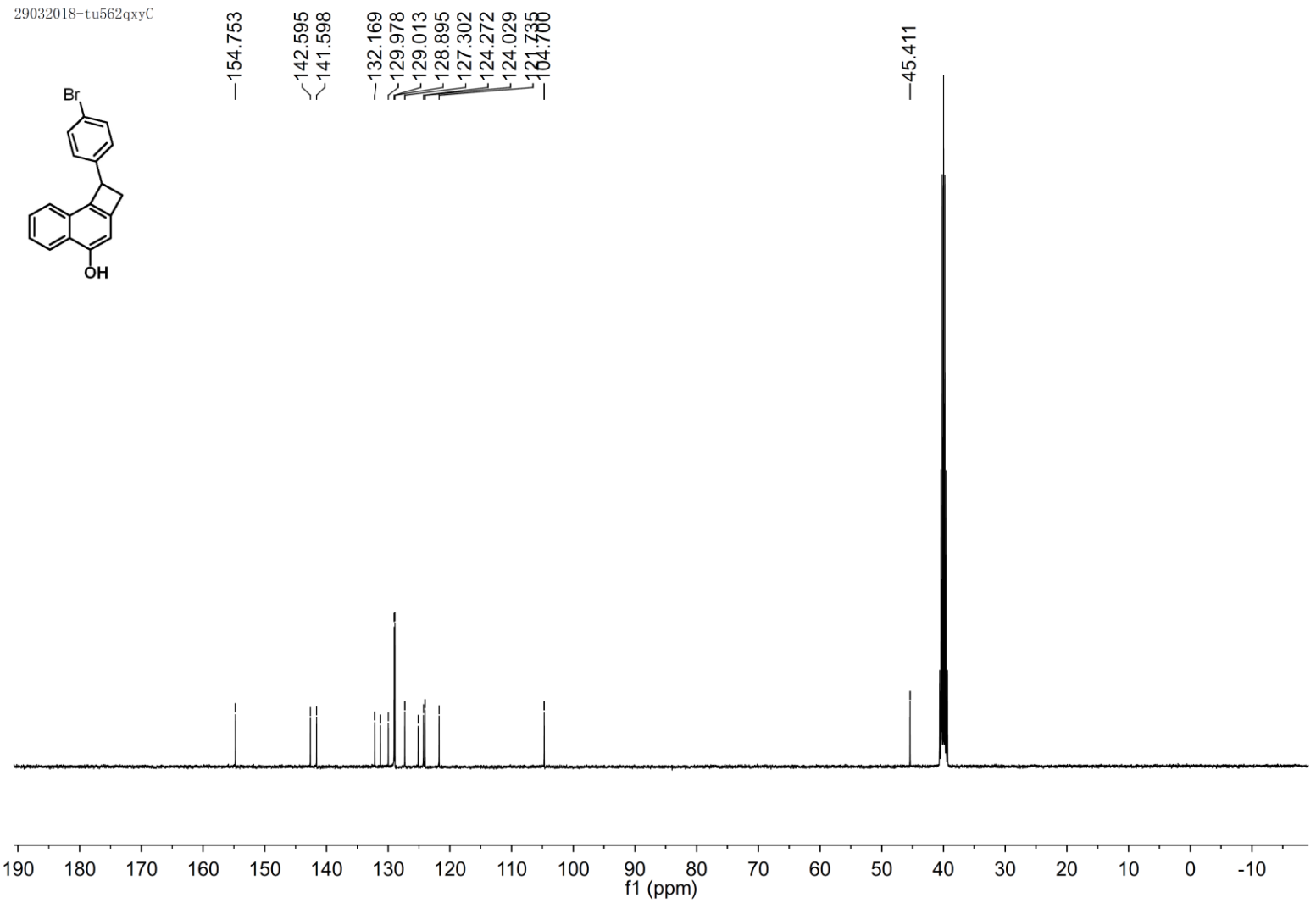
^{1}H NMR Spectrum of Compound 3e



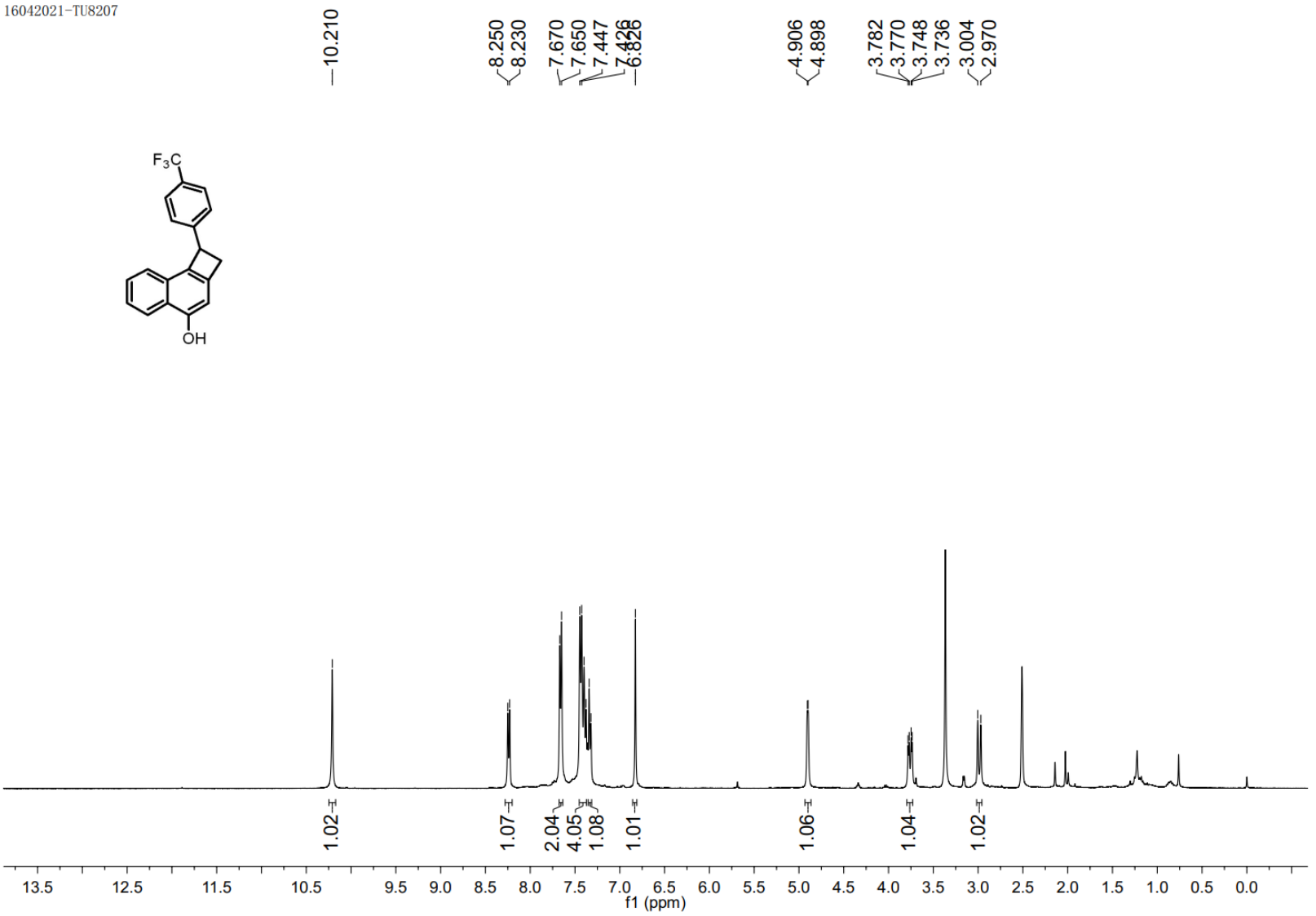
^{13}C NMR Spectrum of Compound 3e



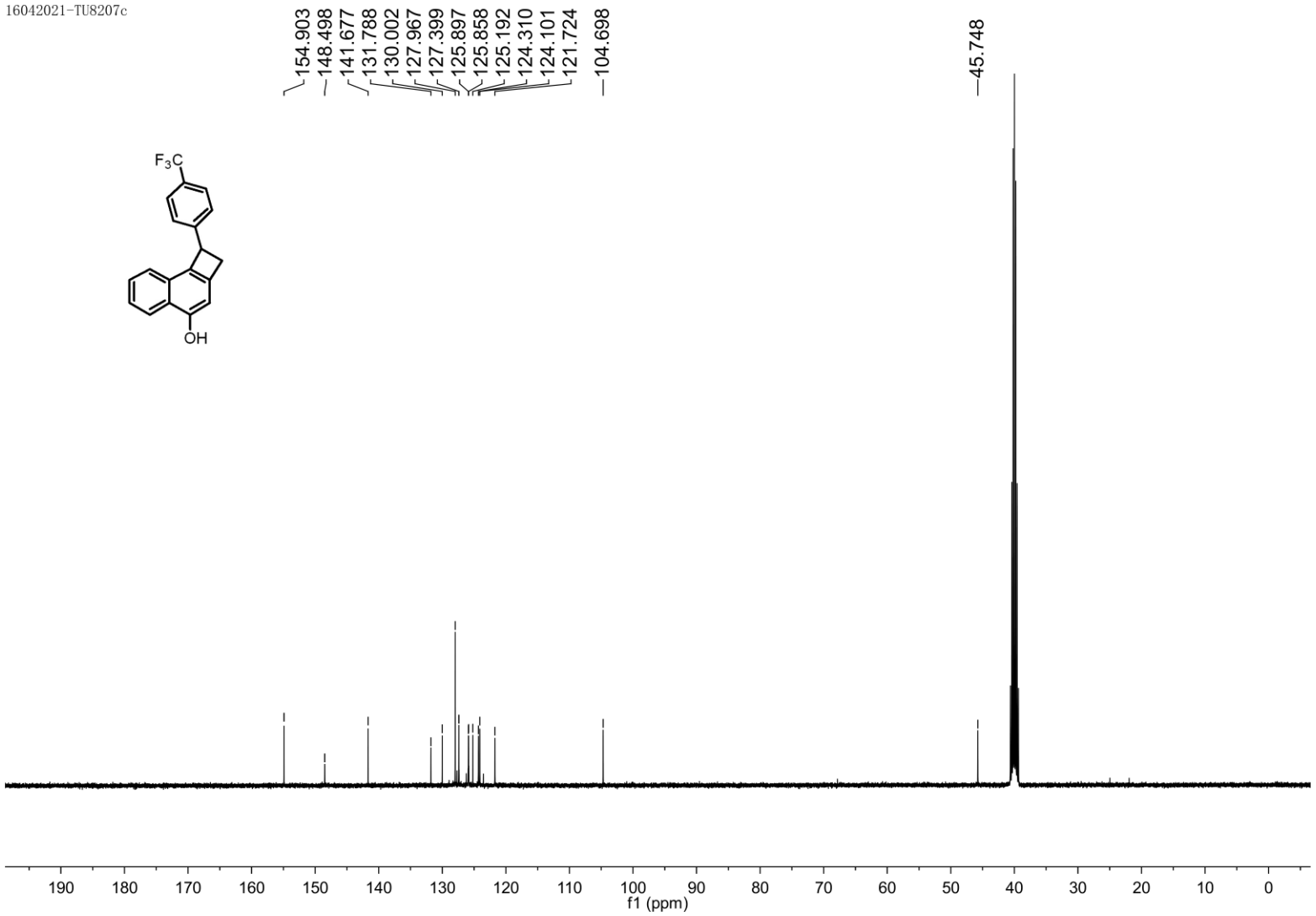
^{1}H NMR Spectrum of Compound 3f



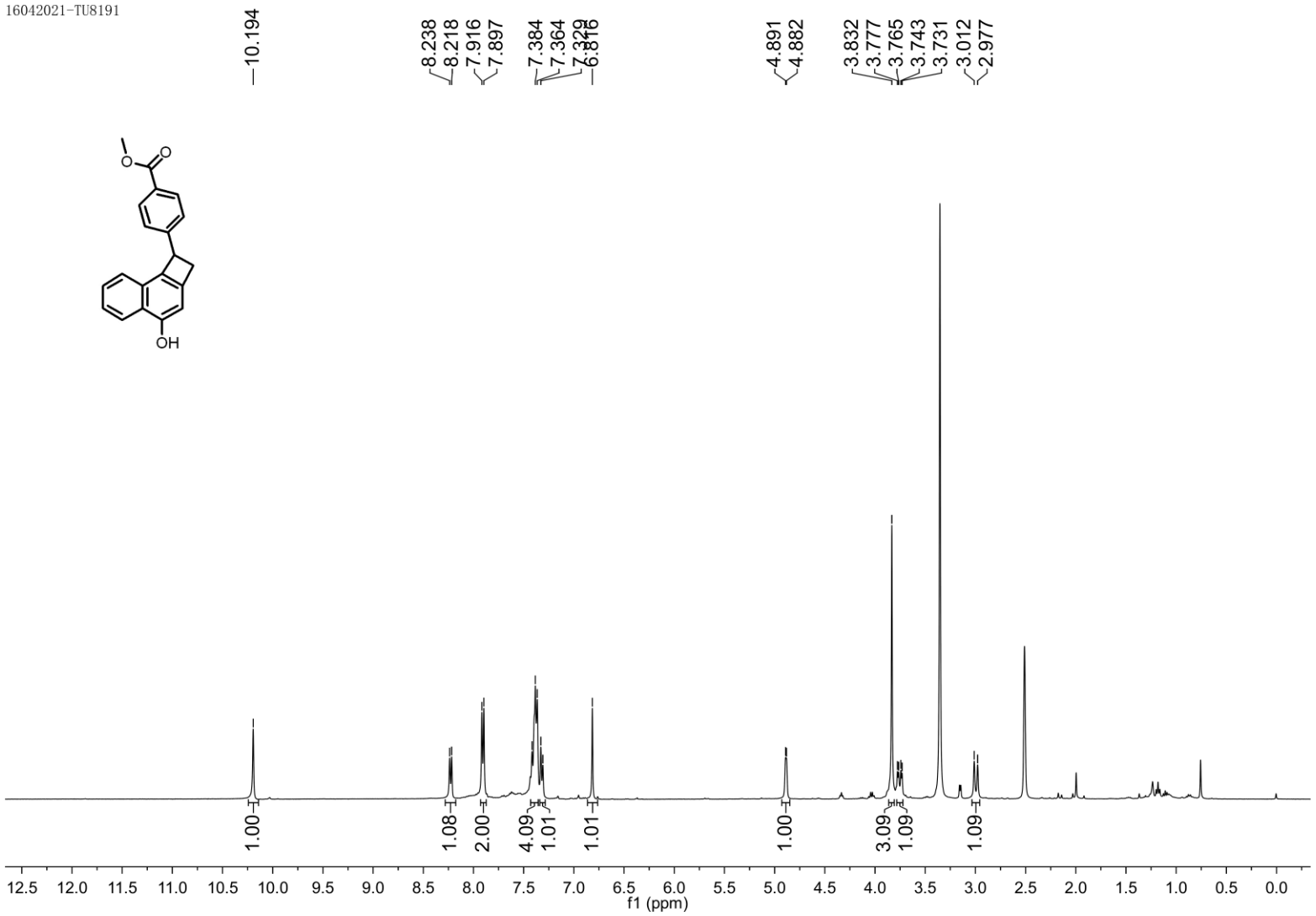
^{13}C NMR Spectrum of Compound 3f



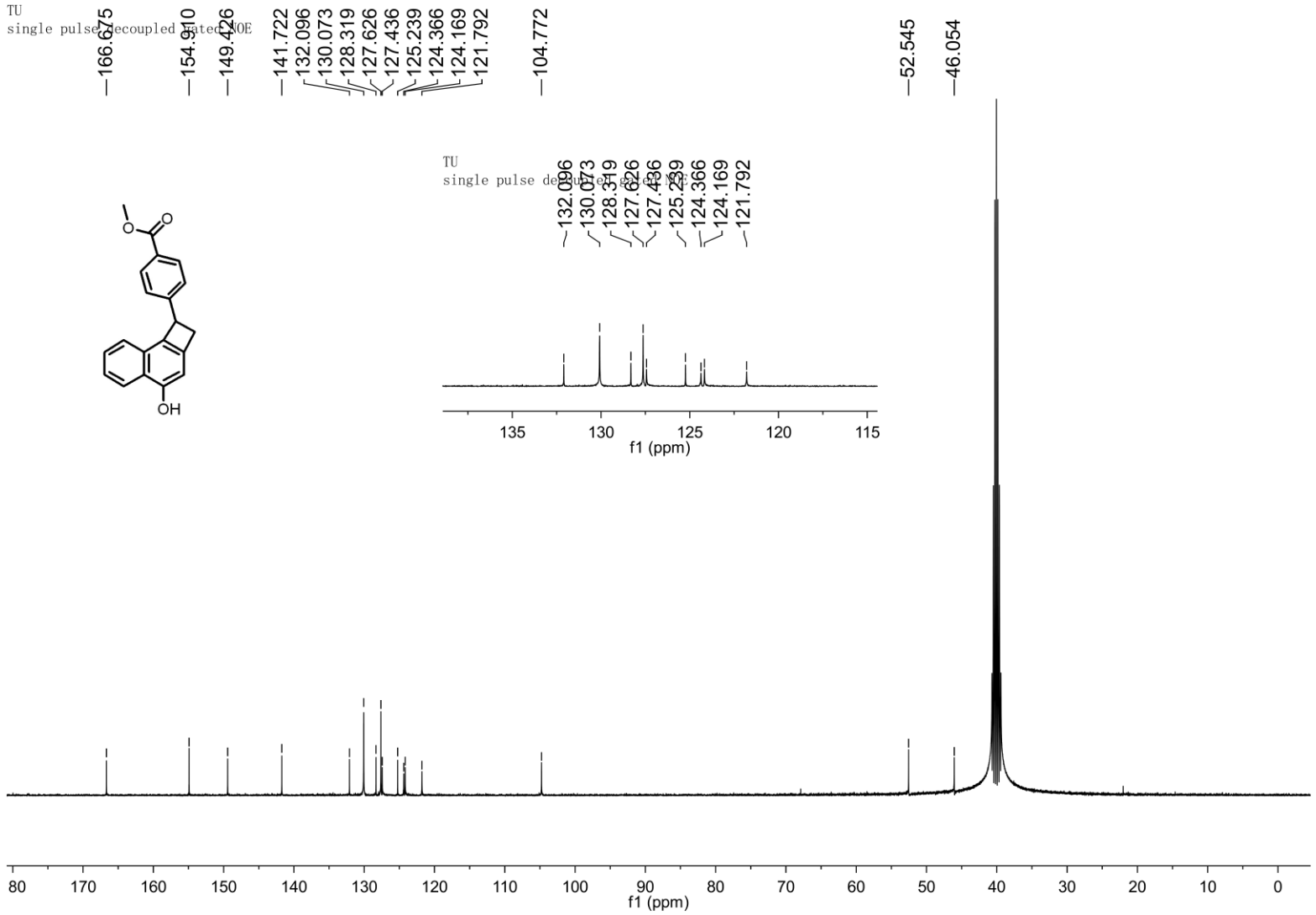
^{1}H NMR Spectrum of Compound 3g



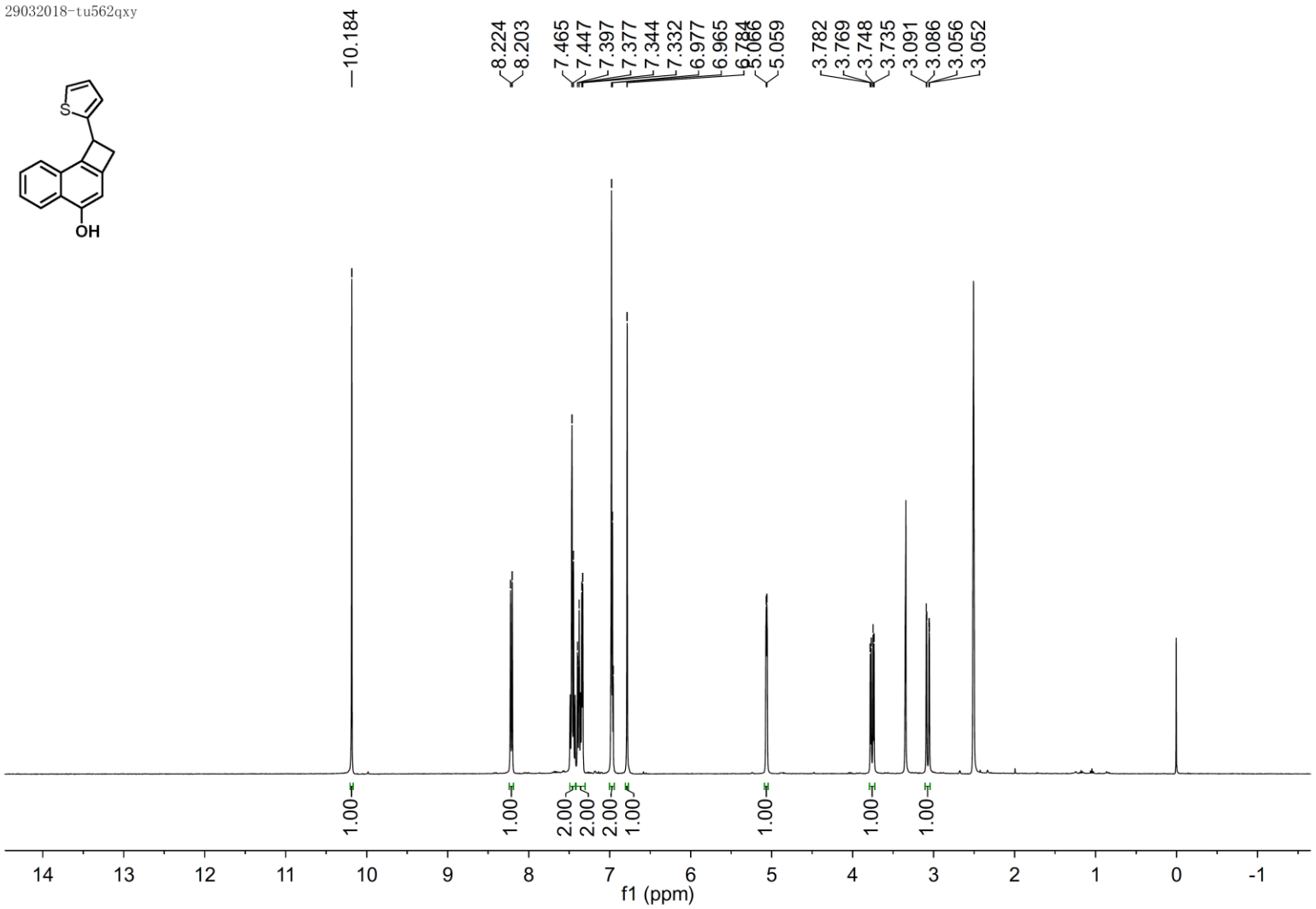
^{13}C NMR Spectrum of Compound 3g



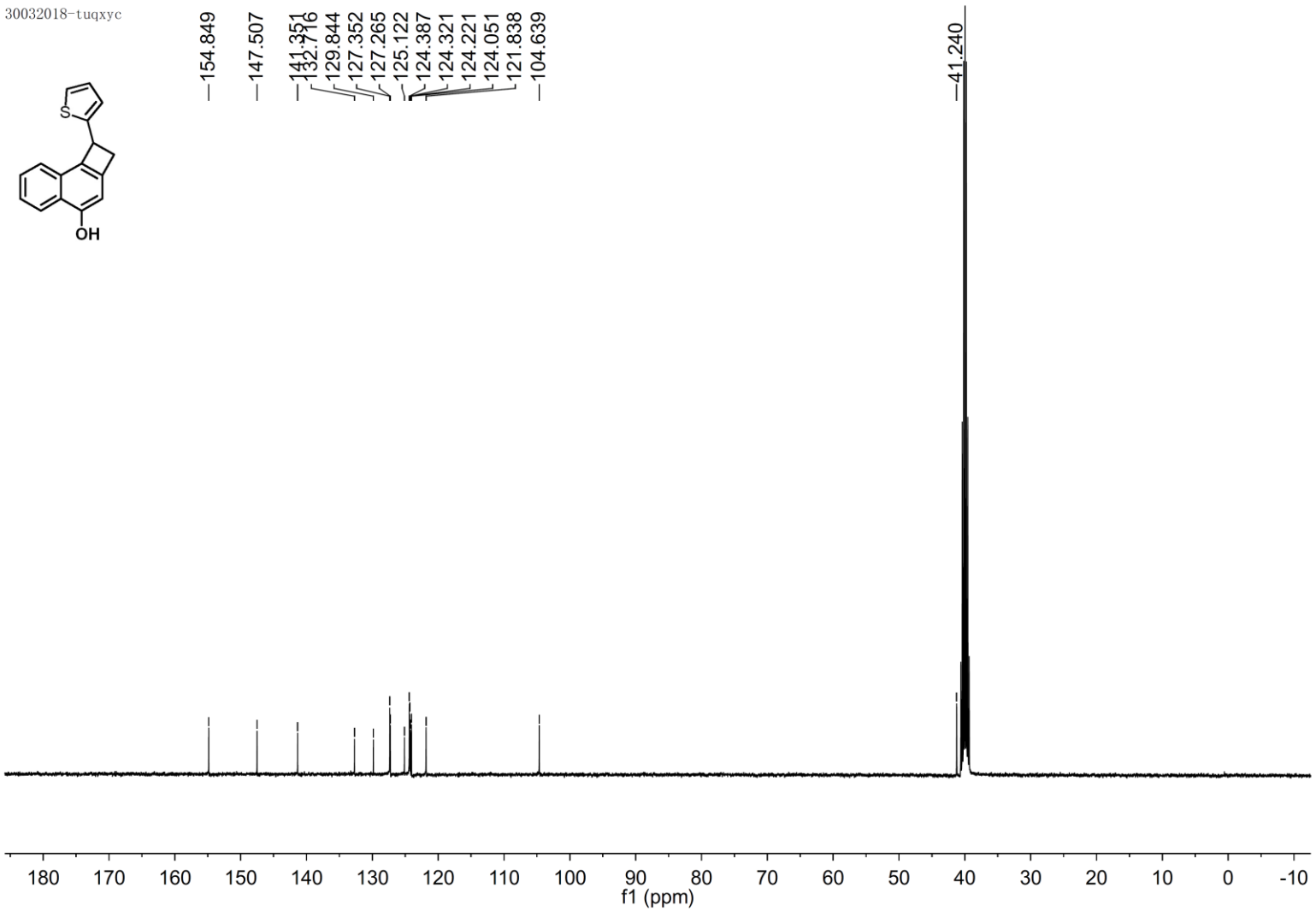
^{1}H NMR Spectrum of Compound 3h



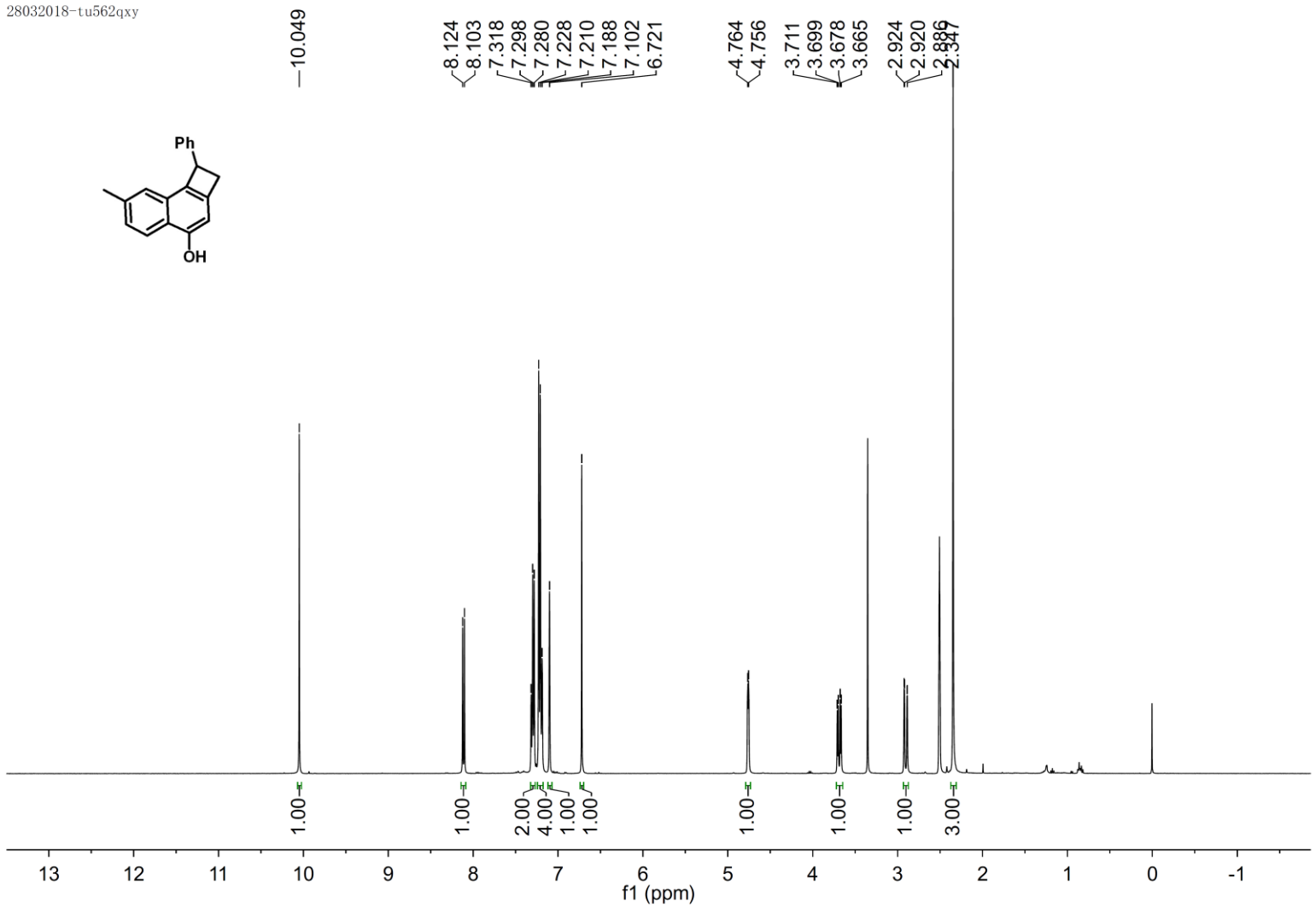
^{13}C NMR Spectrum of Compound 3h



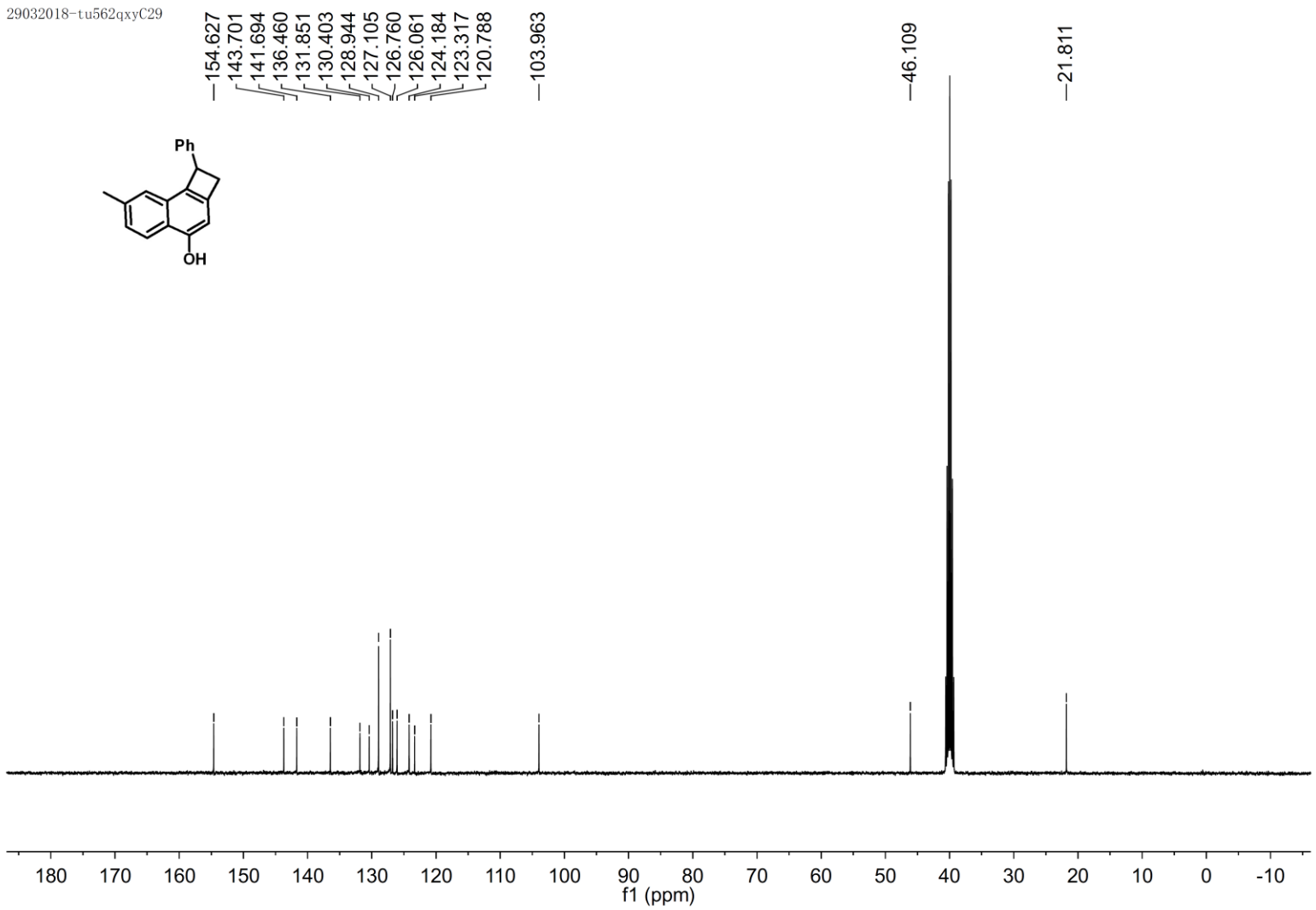
^{1}H NMR Spectrum of Compound 3i



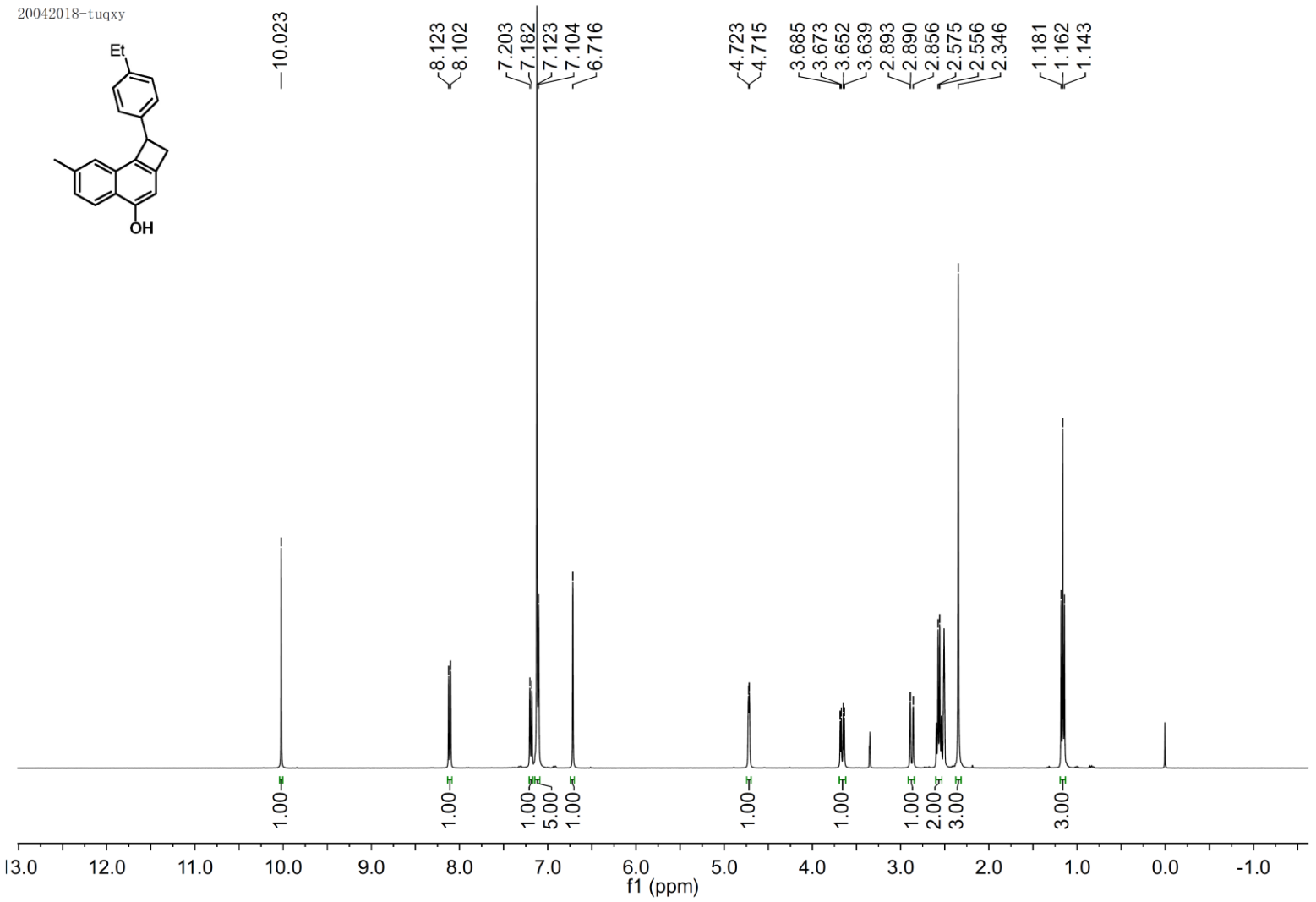
^{13}C NMR Spectrum of Compound 3i



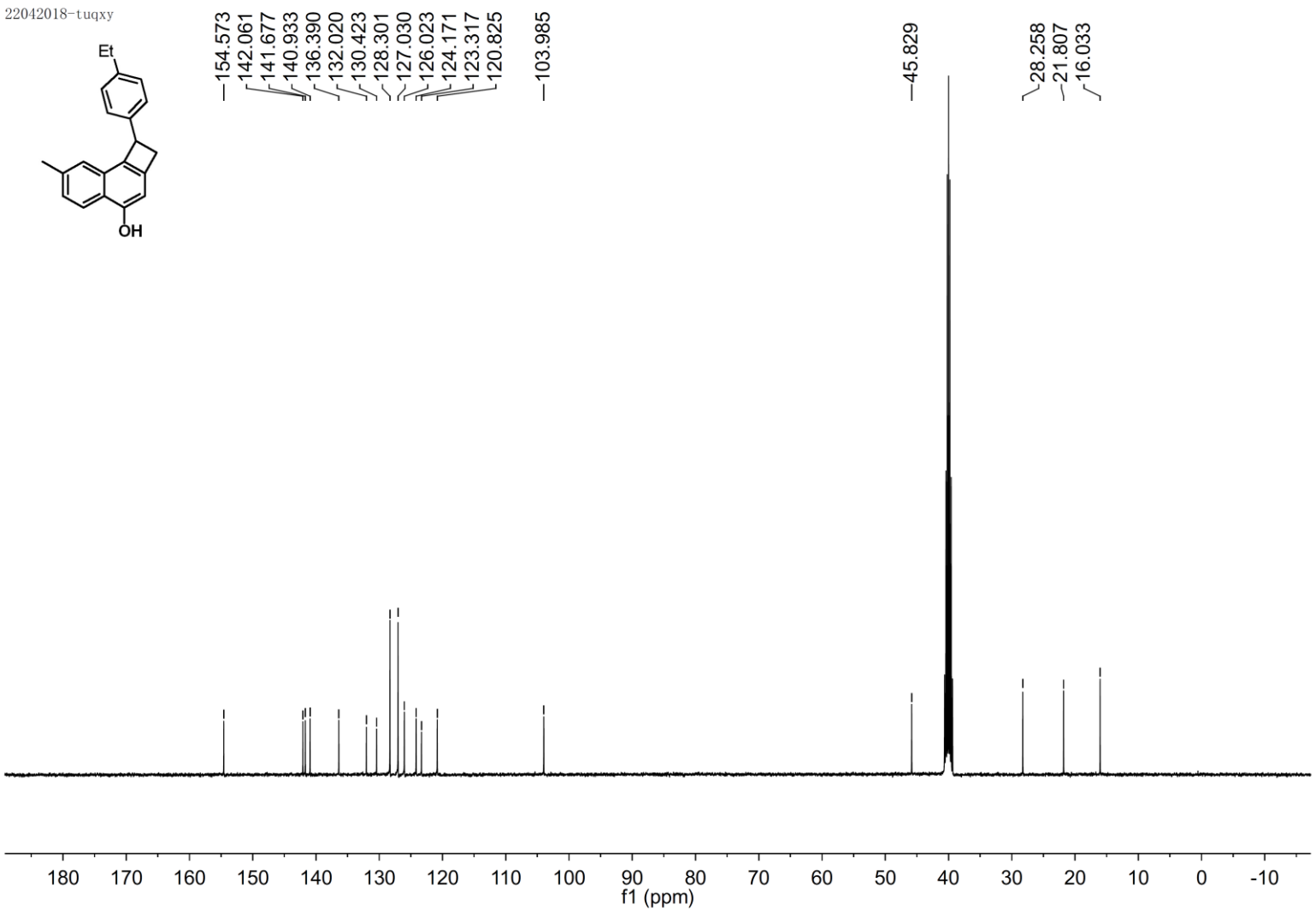
^{1}H NMR Spectrum of Compound 3j



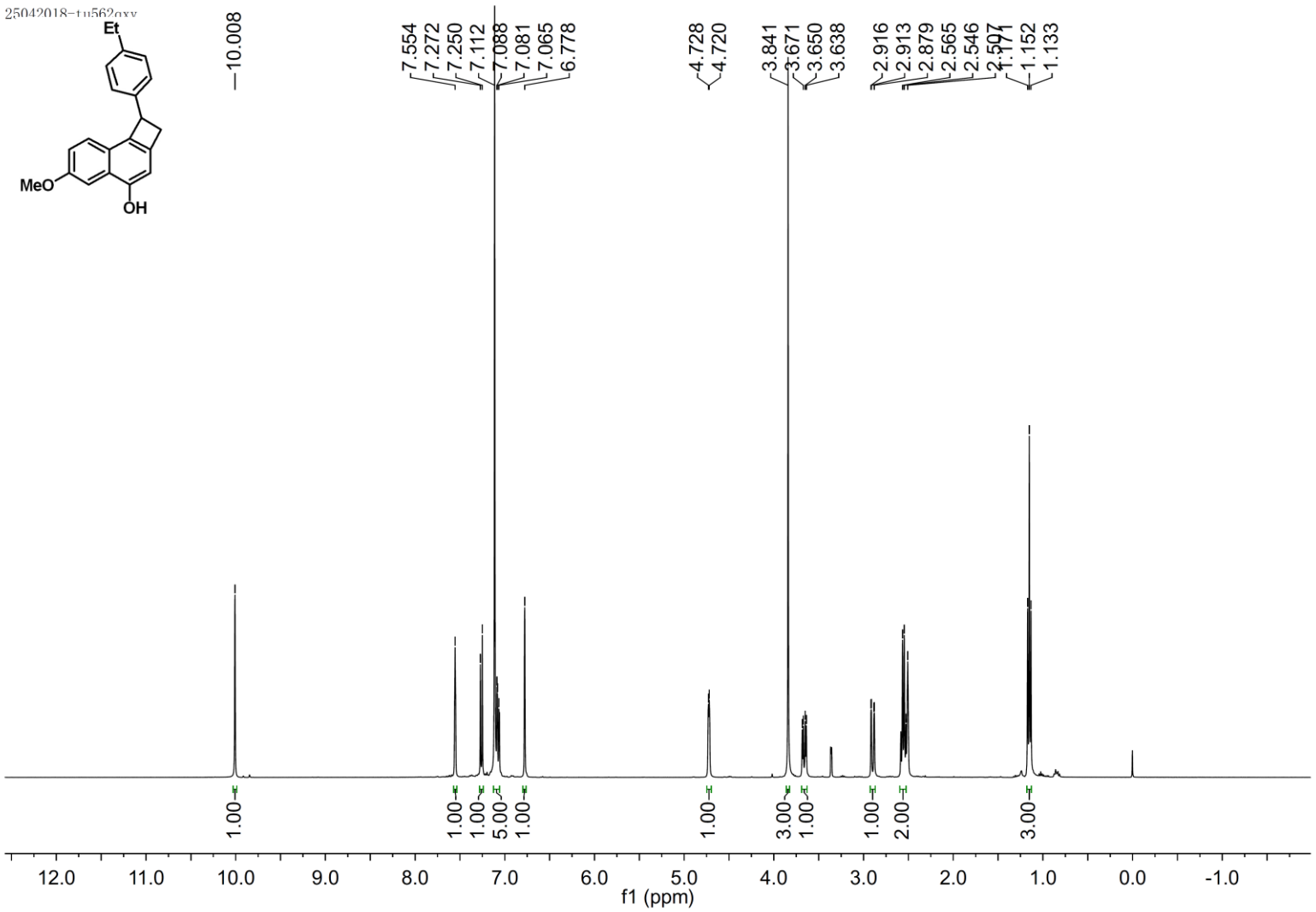
^{13}C NMR Spectrum of Compound 3j



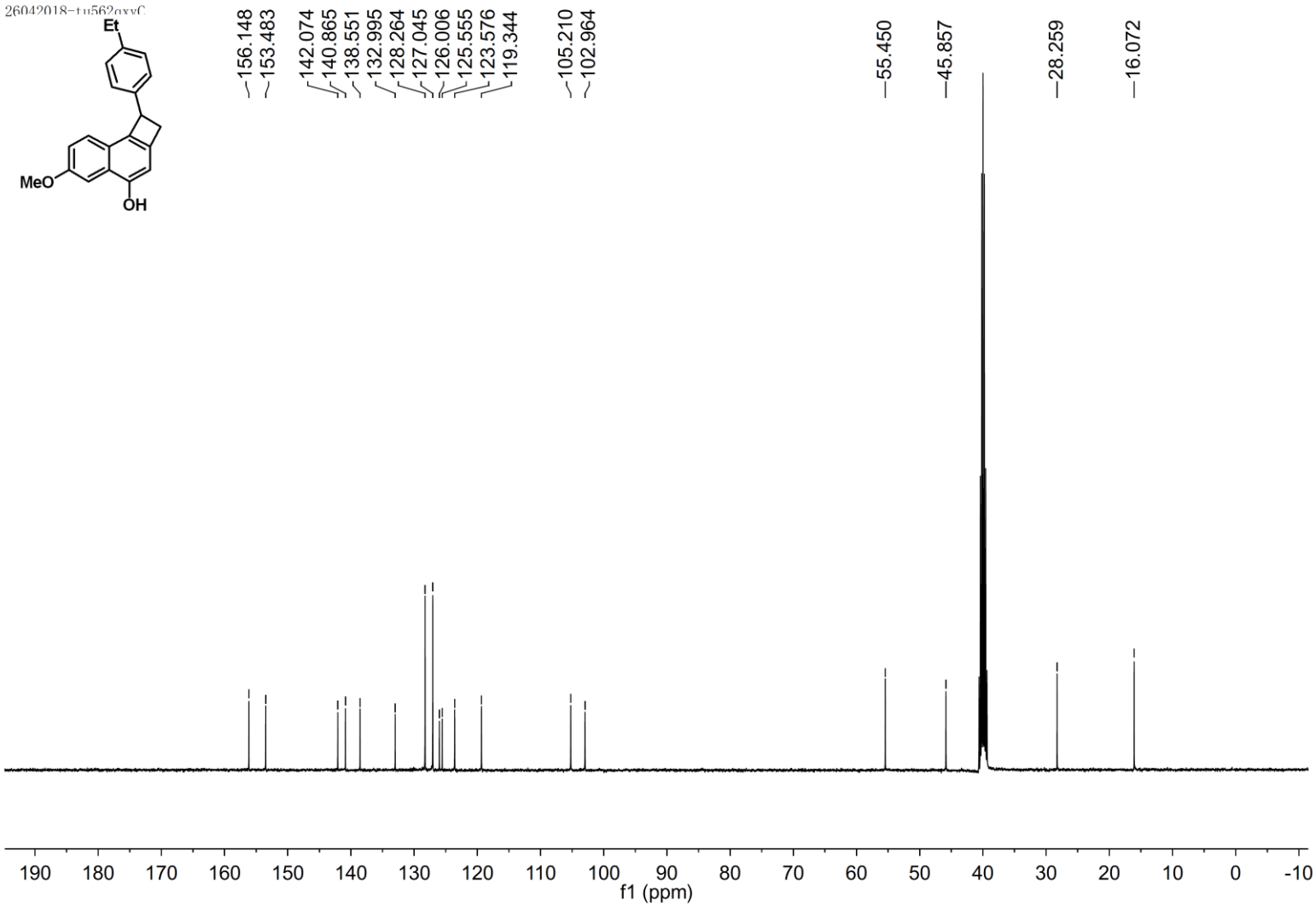
^{1}H NMR Spectrum of Compound 3k



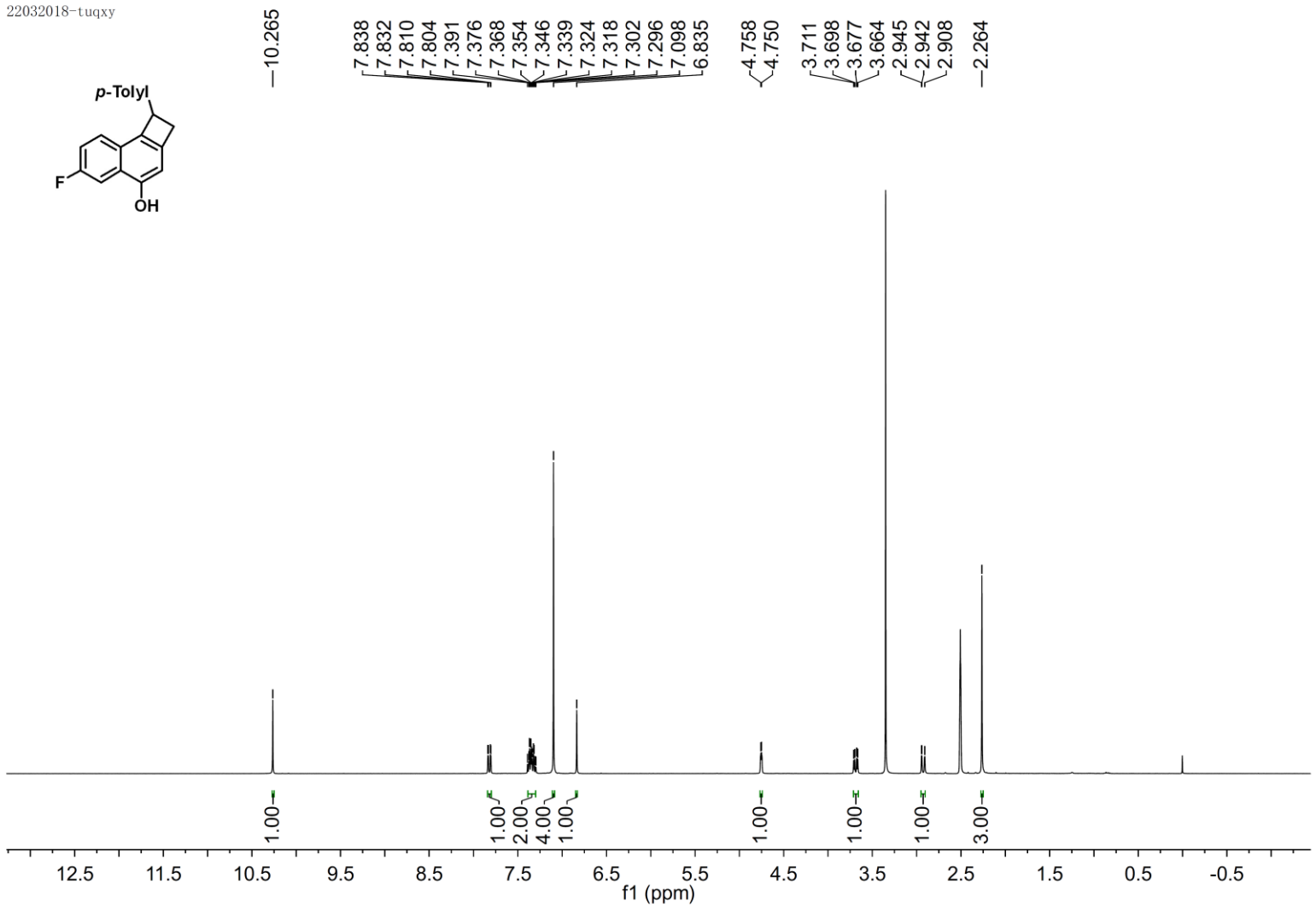
^{13}C NMR Spectrum of Compound 3k



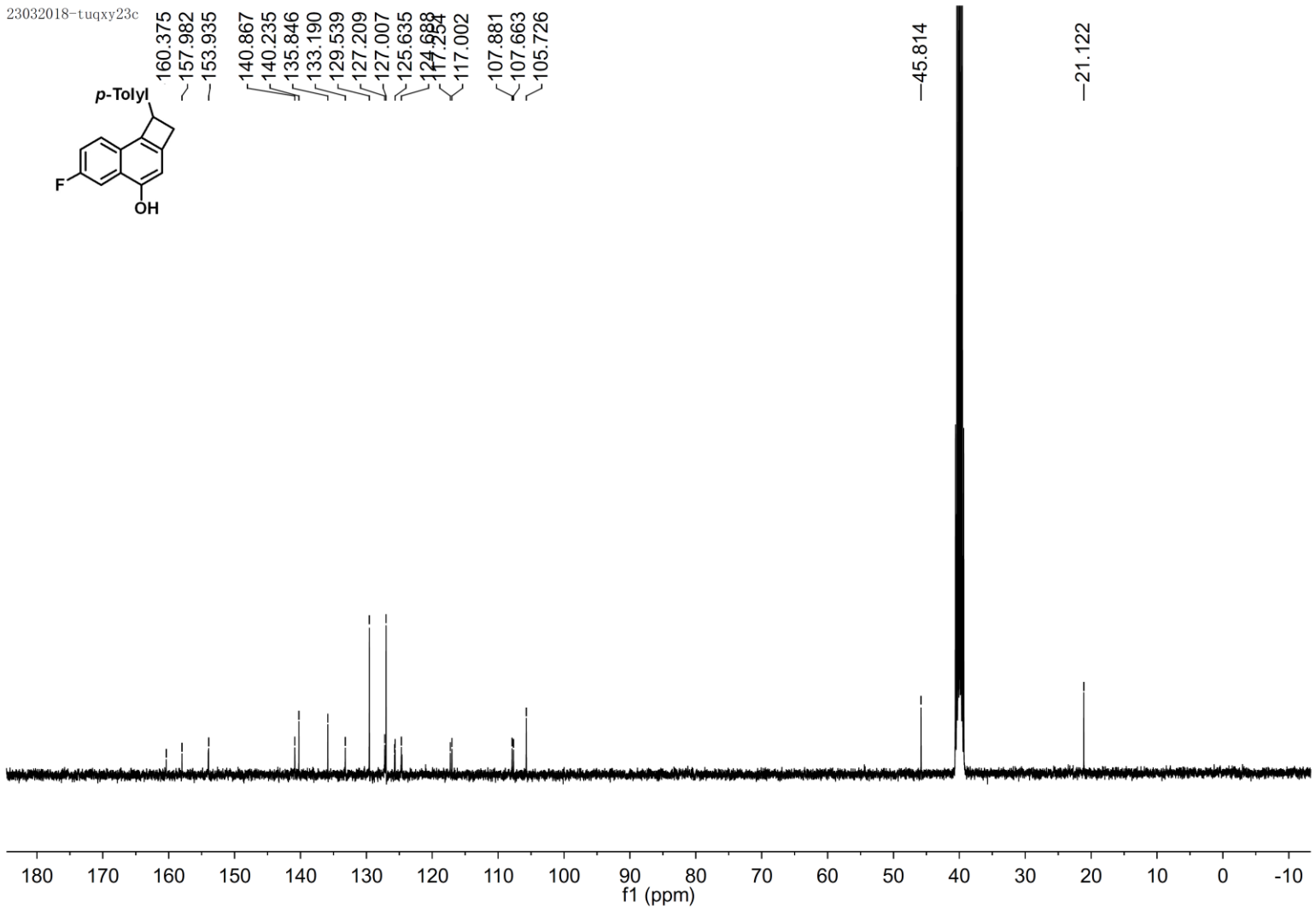
^{1}H NMR Spectrum of Compound 3l



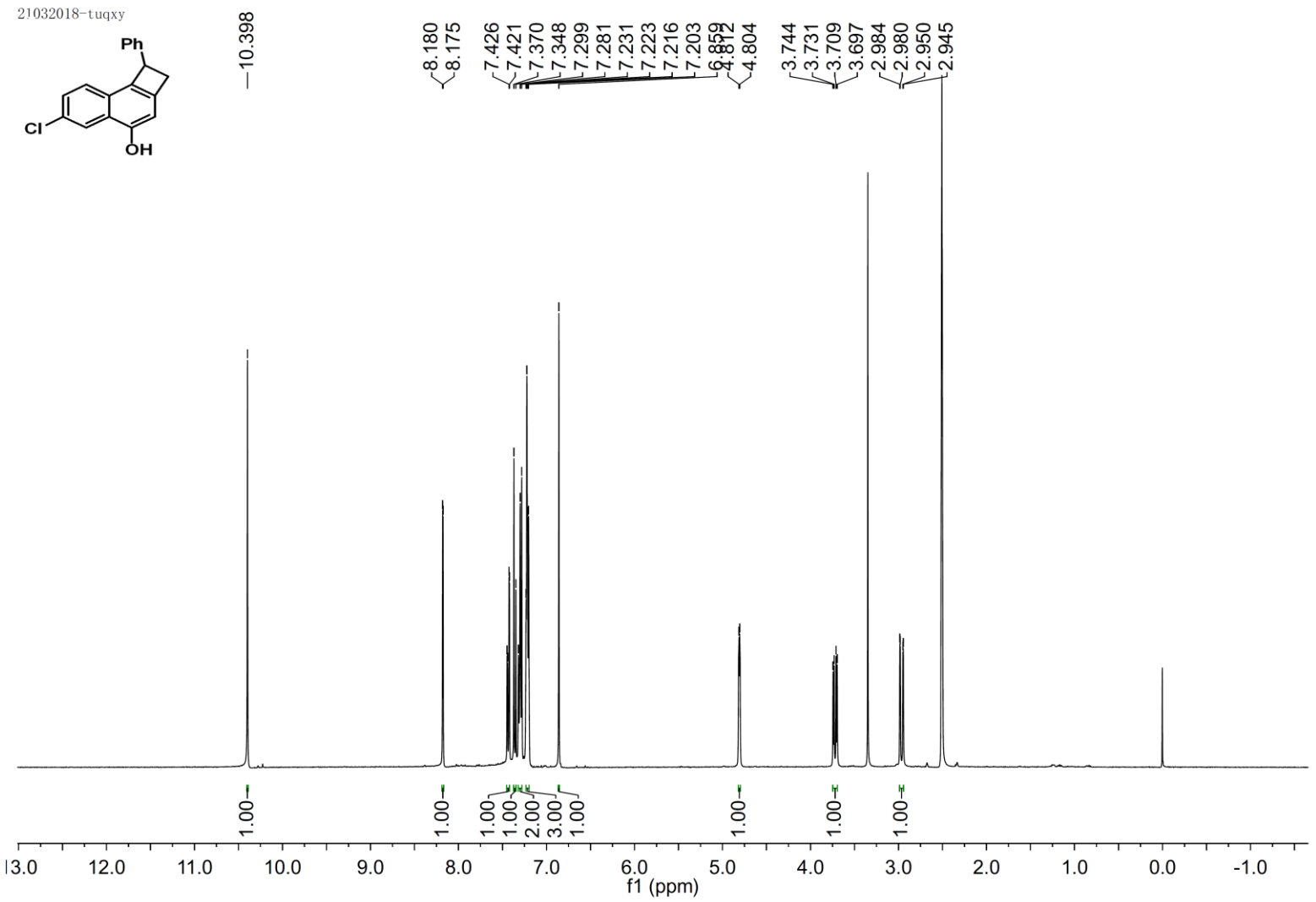
^{13}C NMR Spectrum of Compound 3l



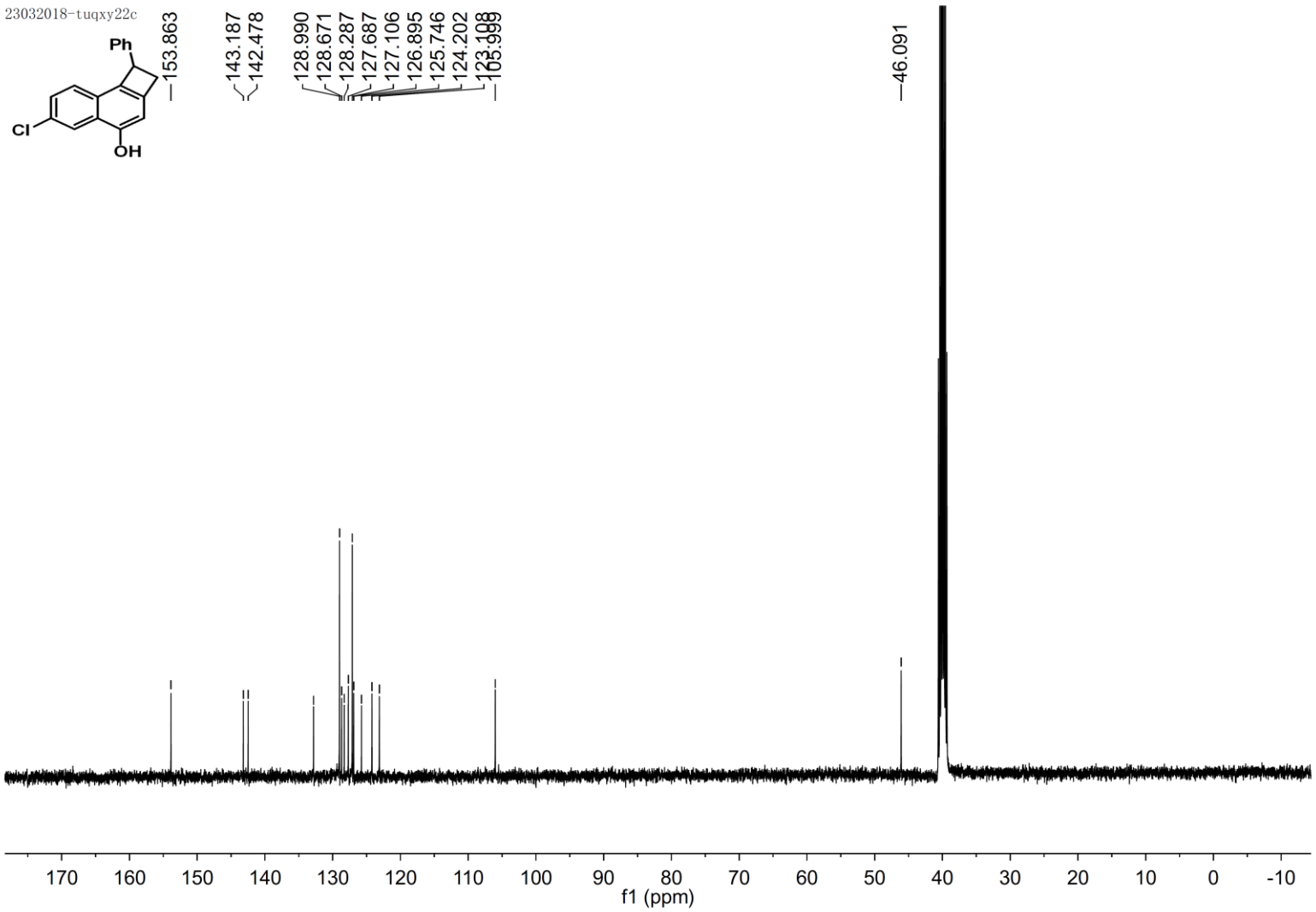
^{1}H NMR Spectrum of Compound 3m



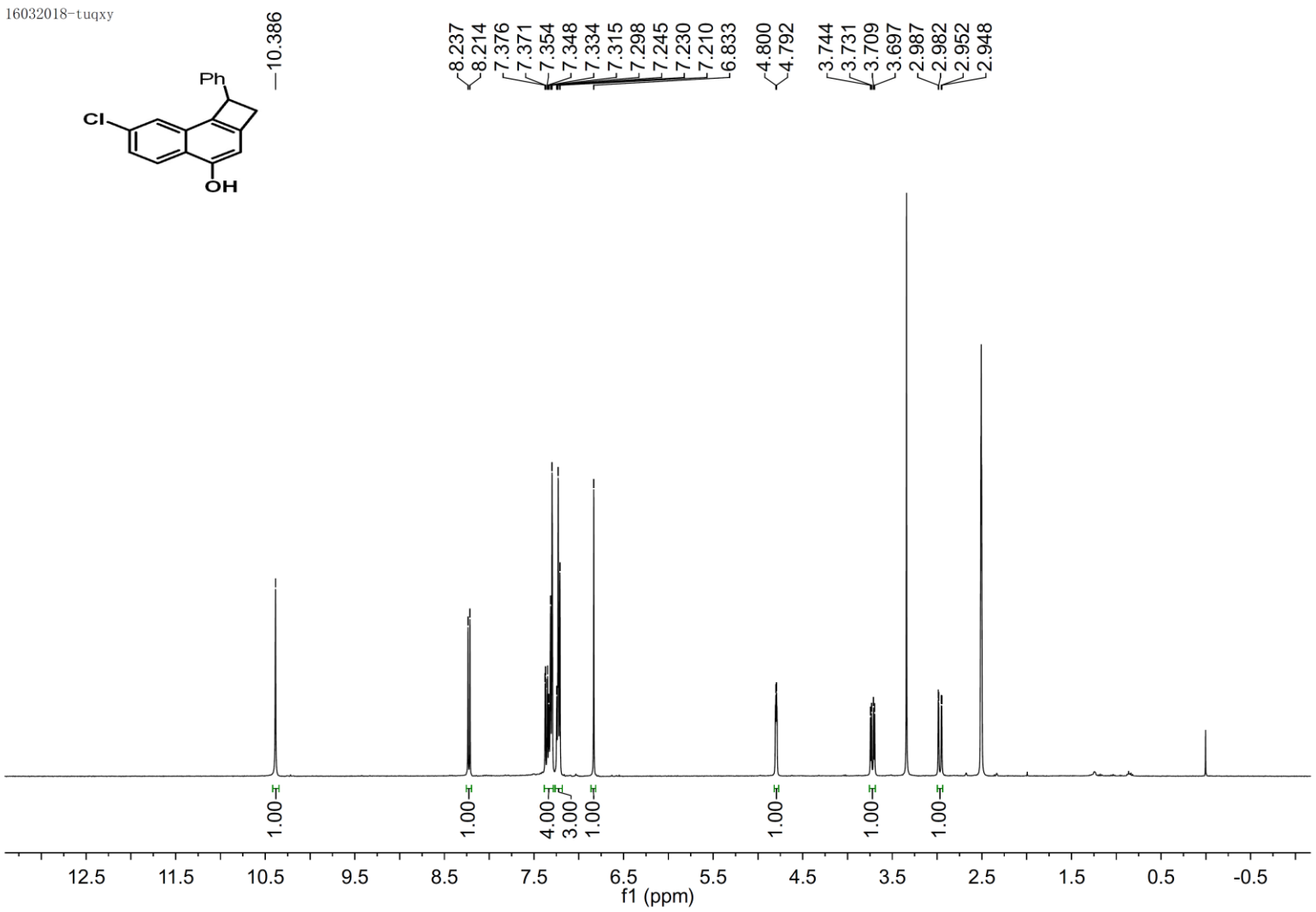
^{13}C NMR Spectrum of Compound 3m



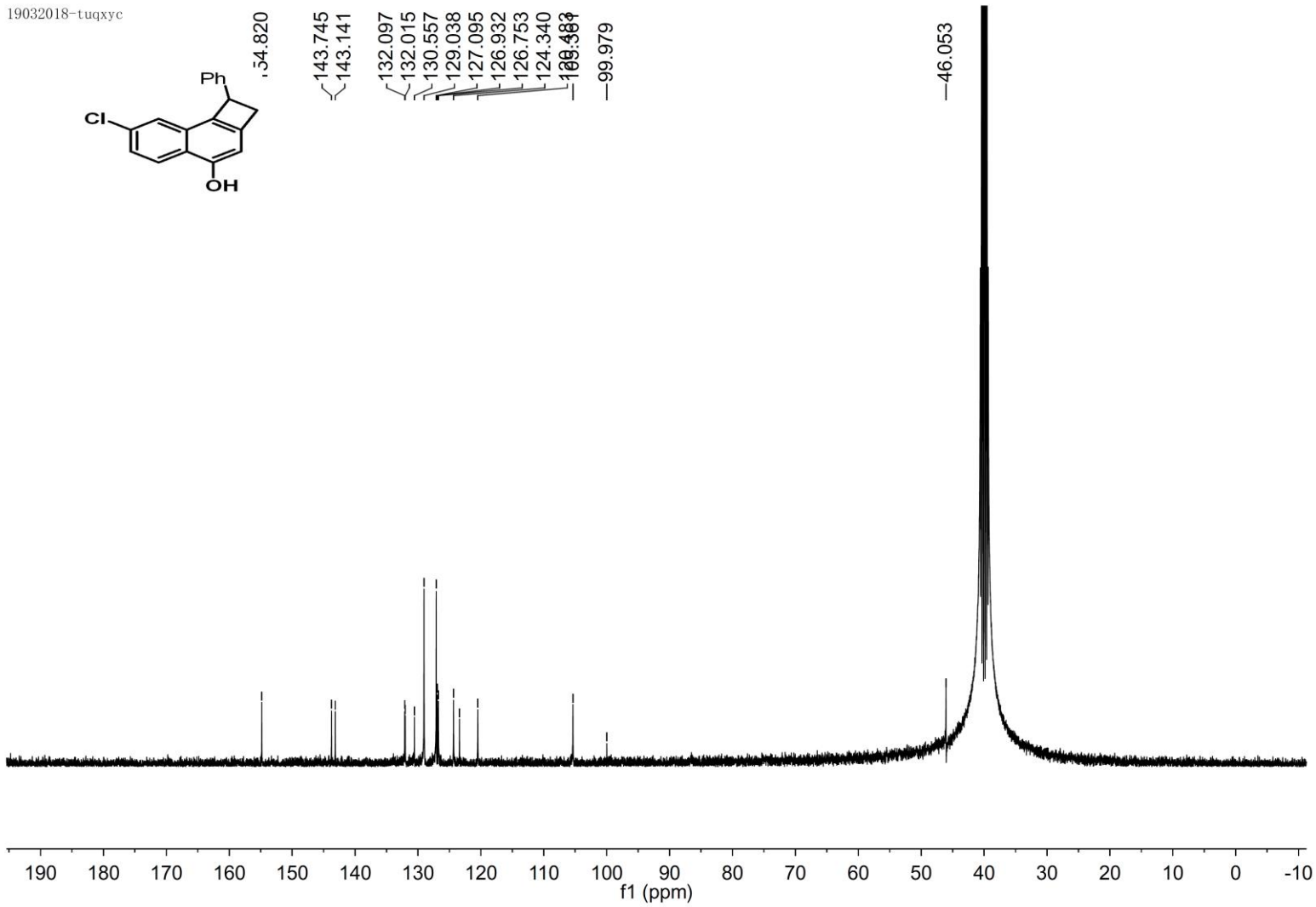
^{1}H NMR Spectrum of Compound 3n



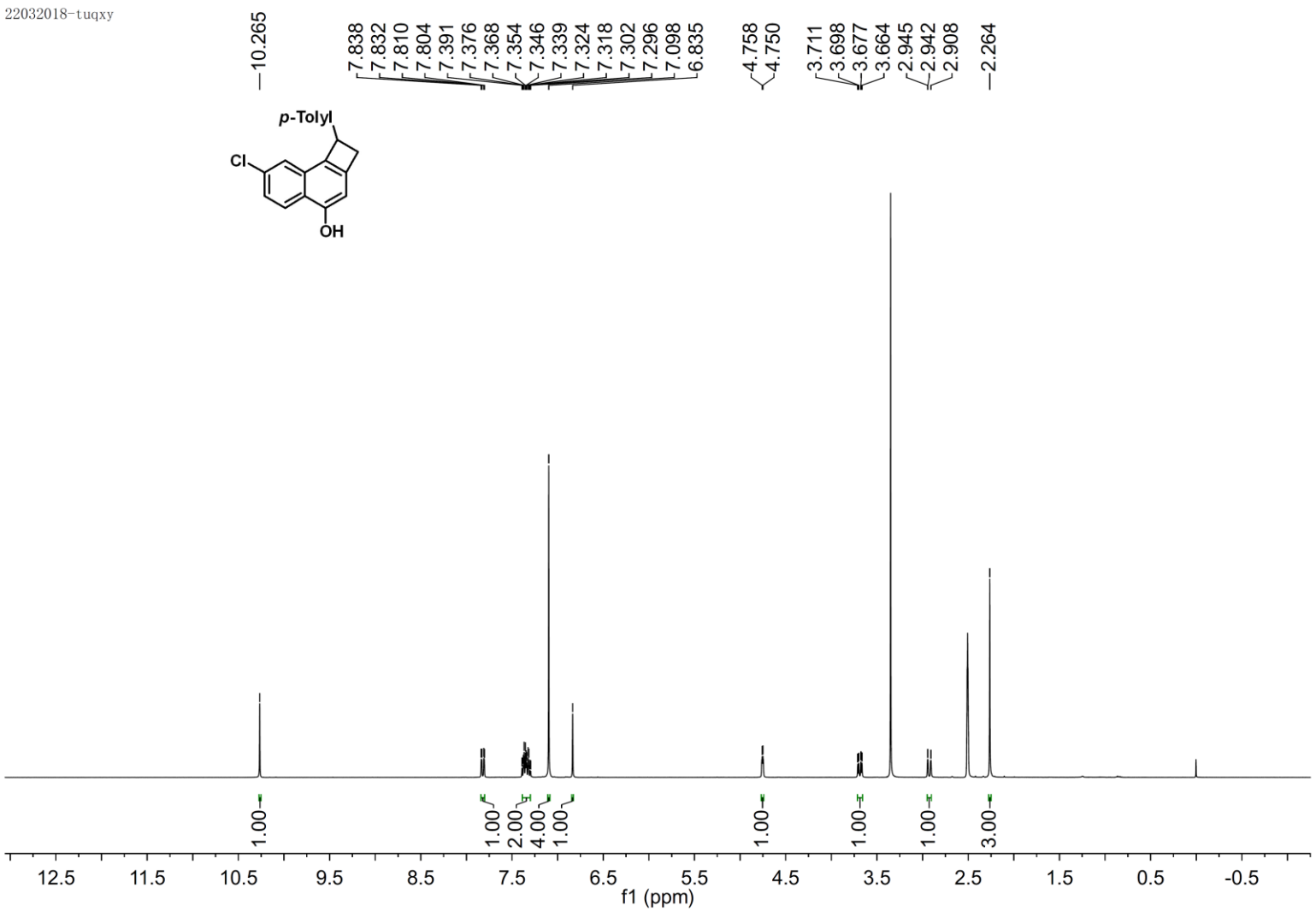
^{13}C NMR Spectrum of Compound 3n



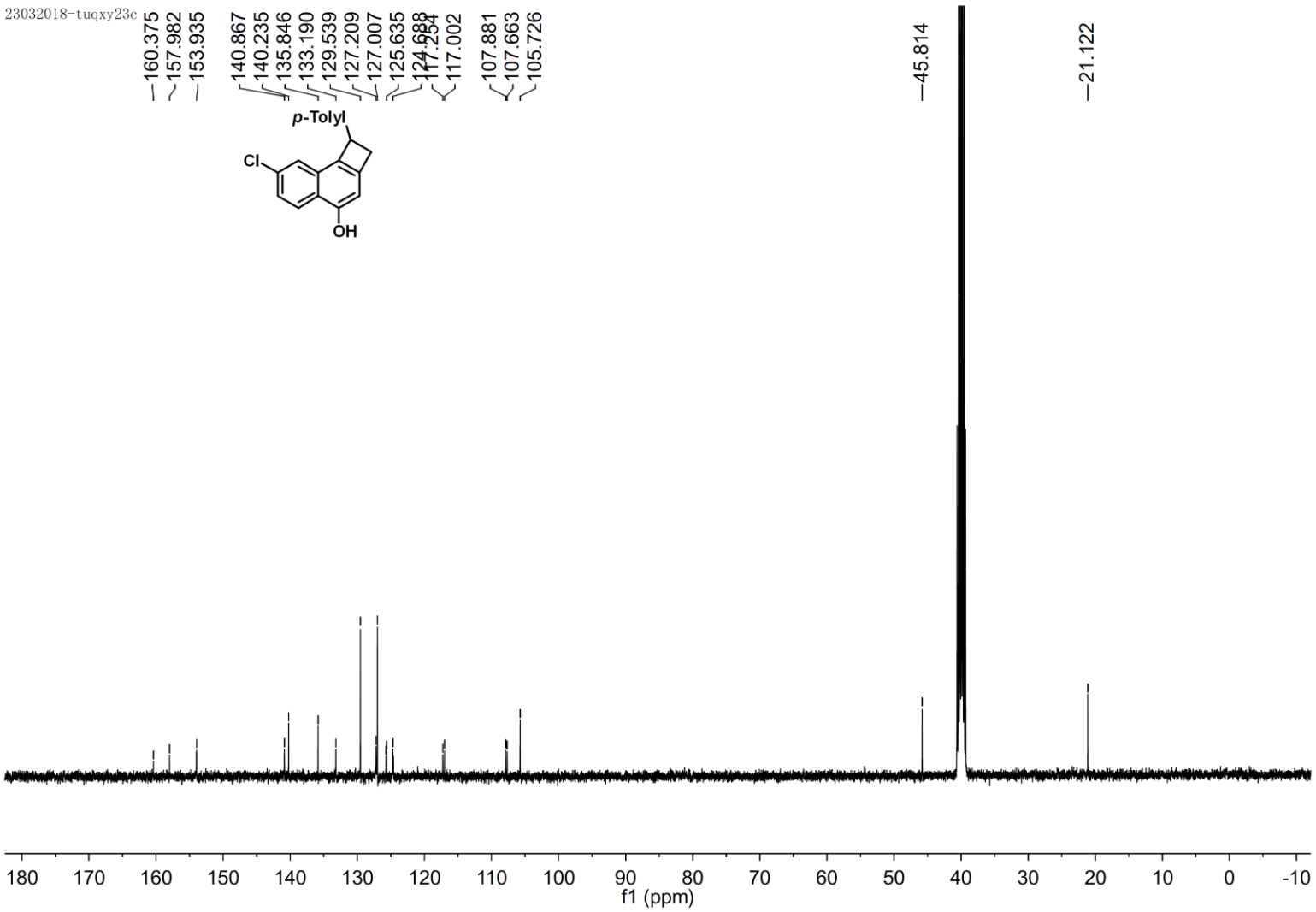
^{1}H NMR Spectrum of Compound 3o



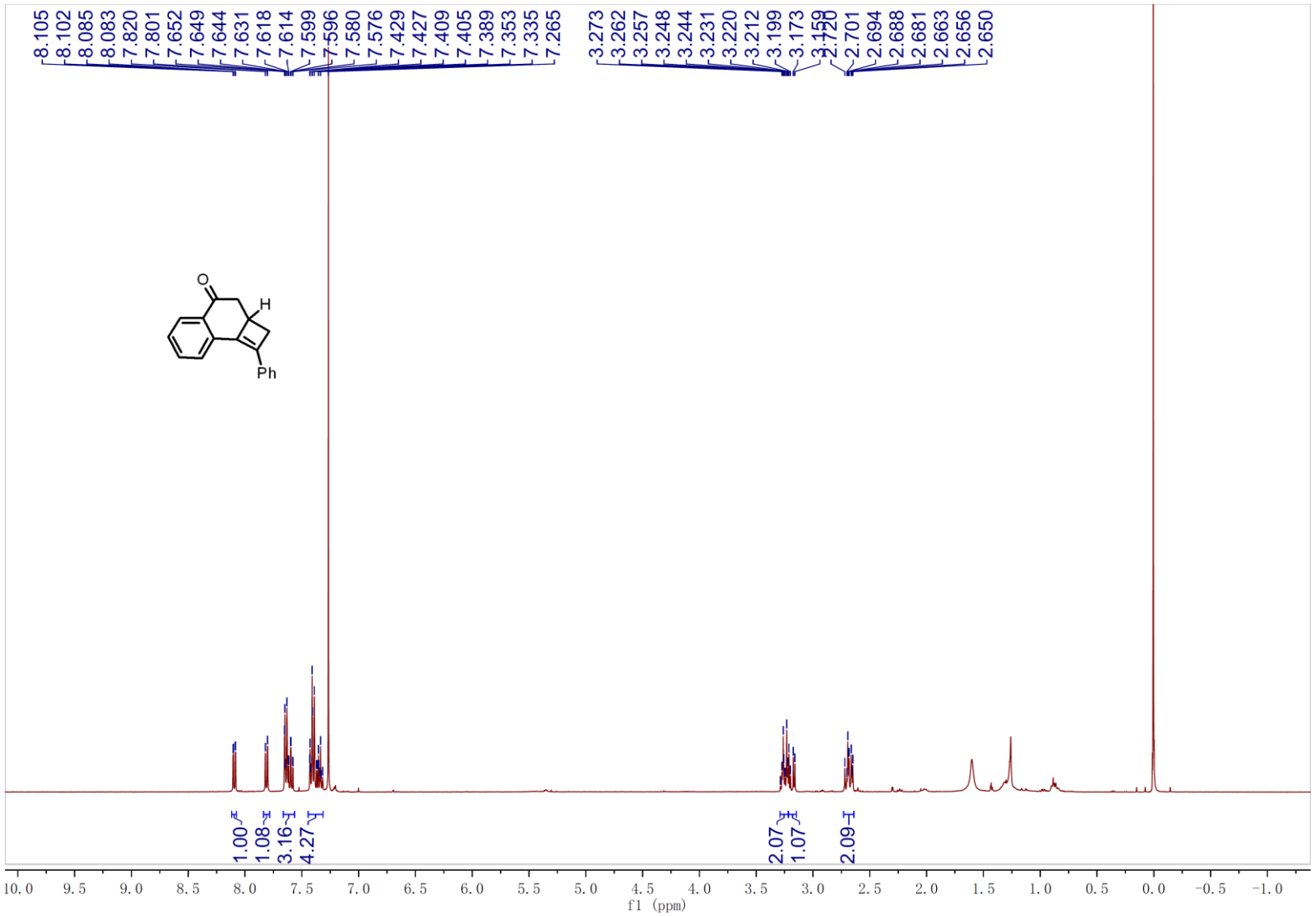
^{13}C NMR Spectrum of Compound 3o



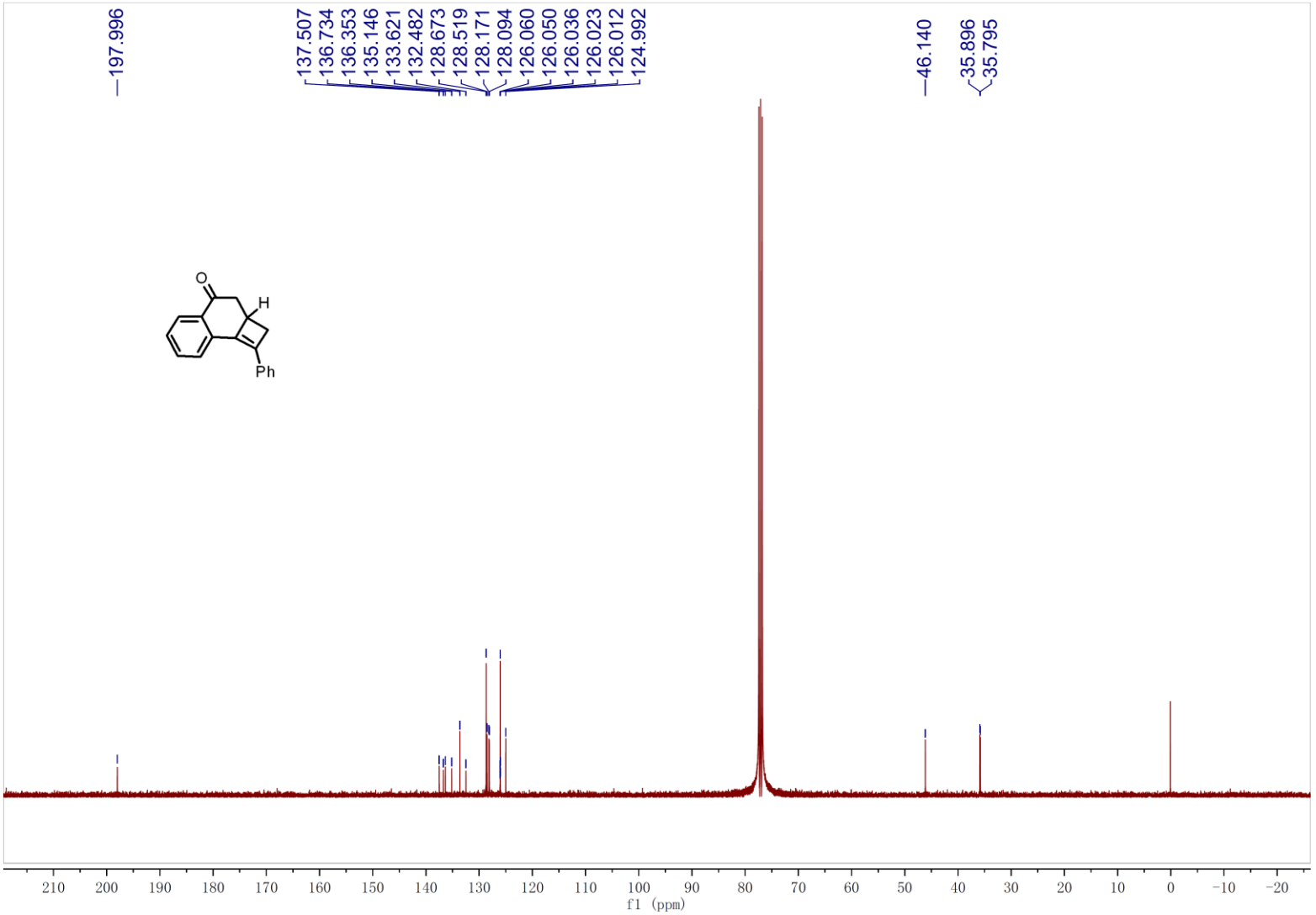
^{1}H NMR Spectrum of Compound 3p



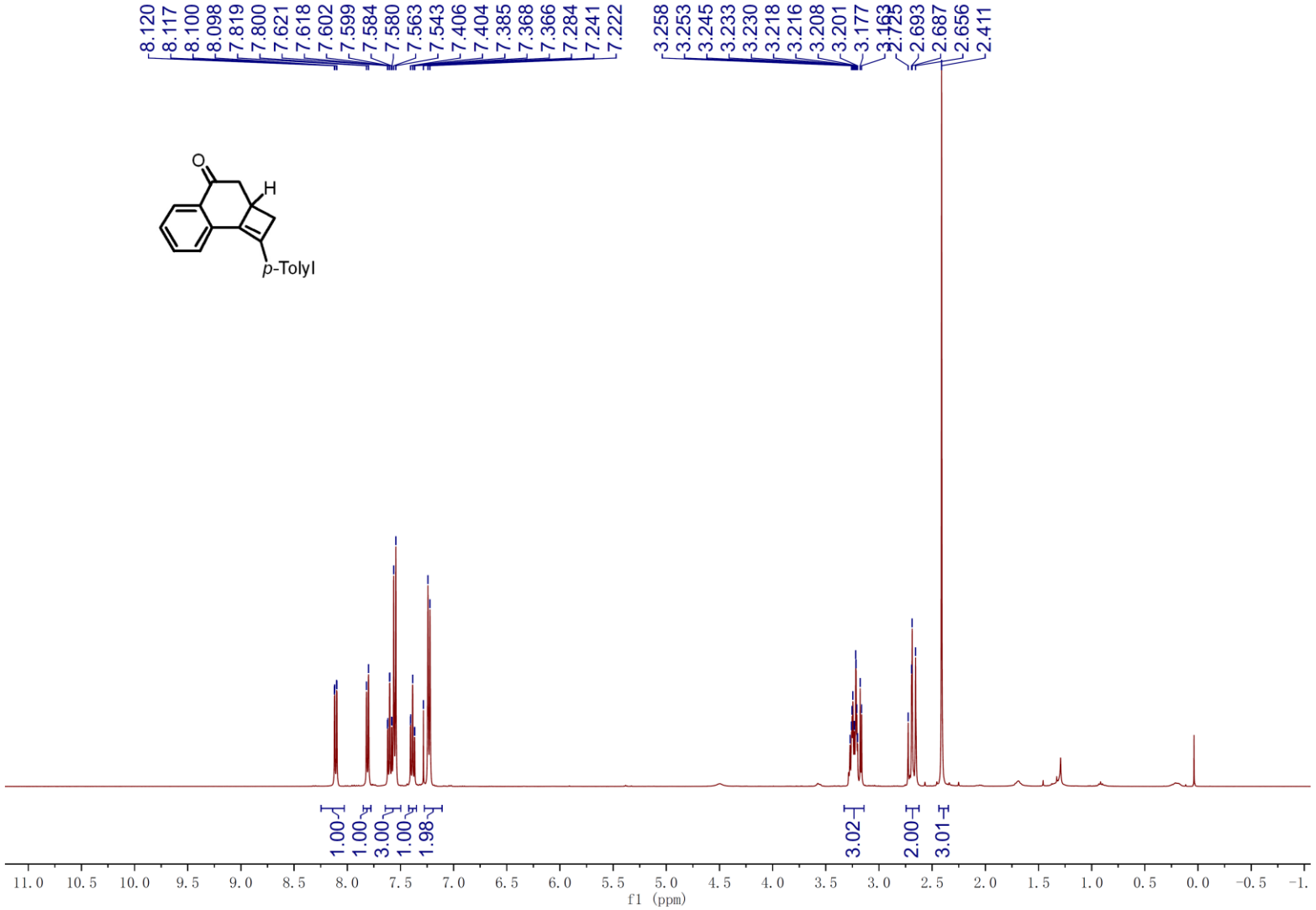
^{13}C NMR Spectrum of Compound 3p



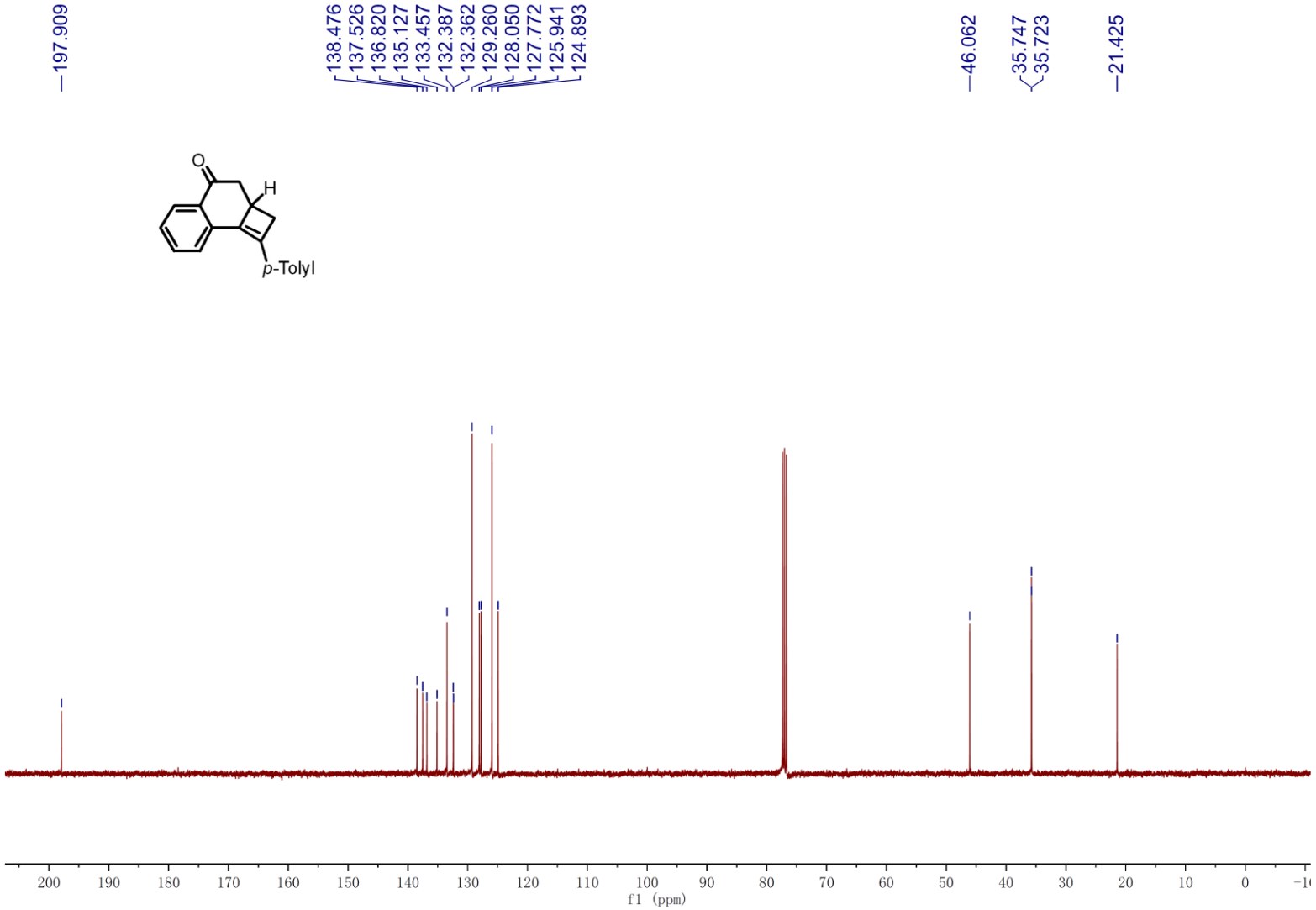
^{1}H NMR Spectrum of Compound 4a



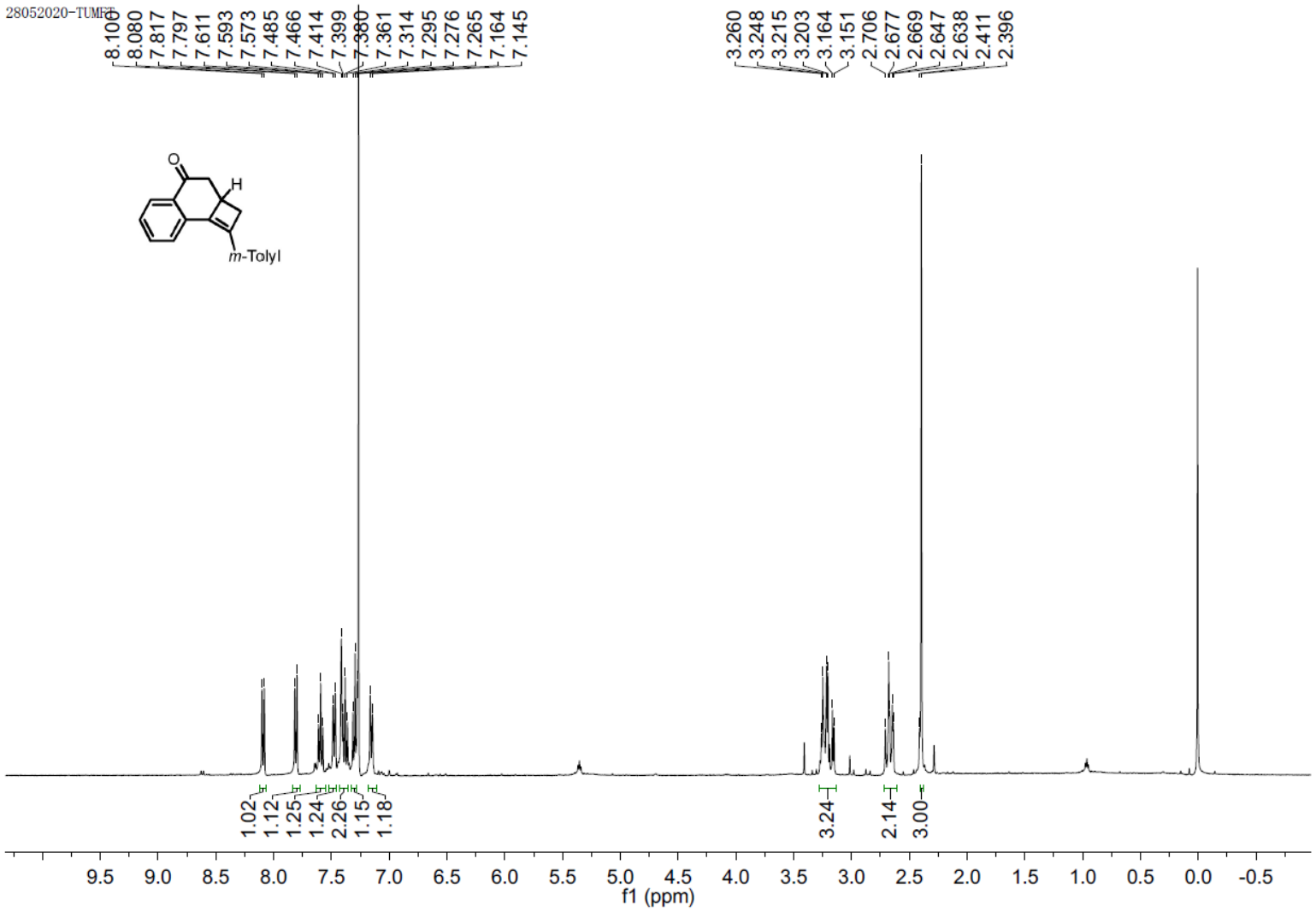
^{13}C NMR Spectrum of Compound 4a



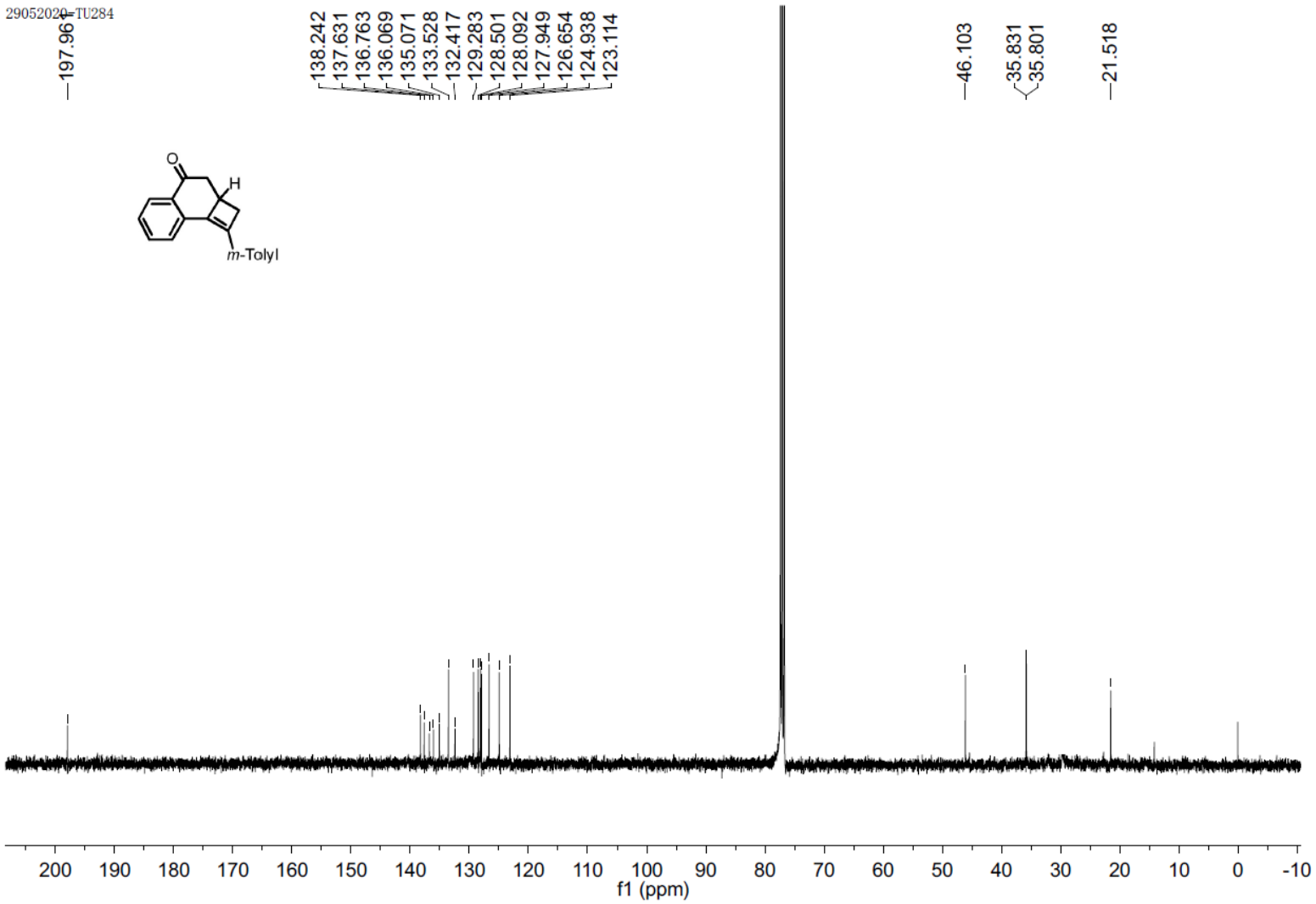
^{1}H NMR Spectrum of Compound 4b



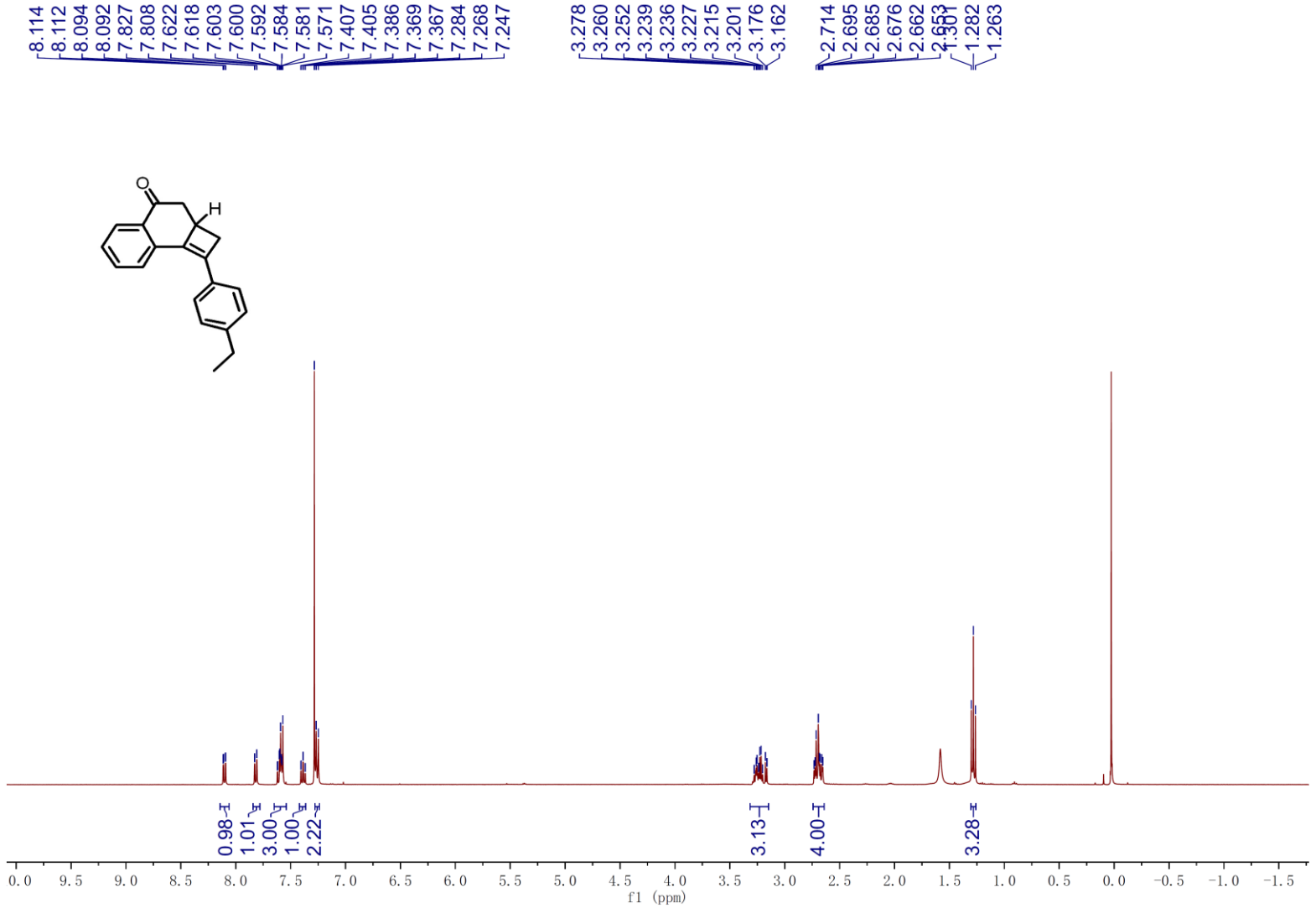
^{13}C NMR Spectrum of Compound 4b



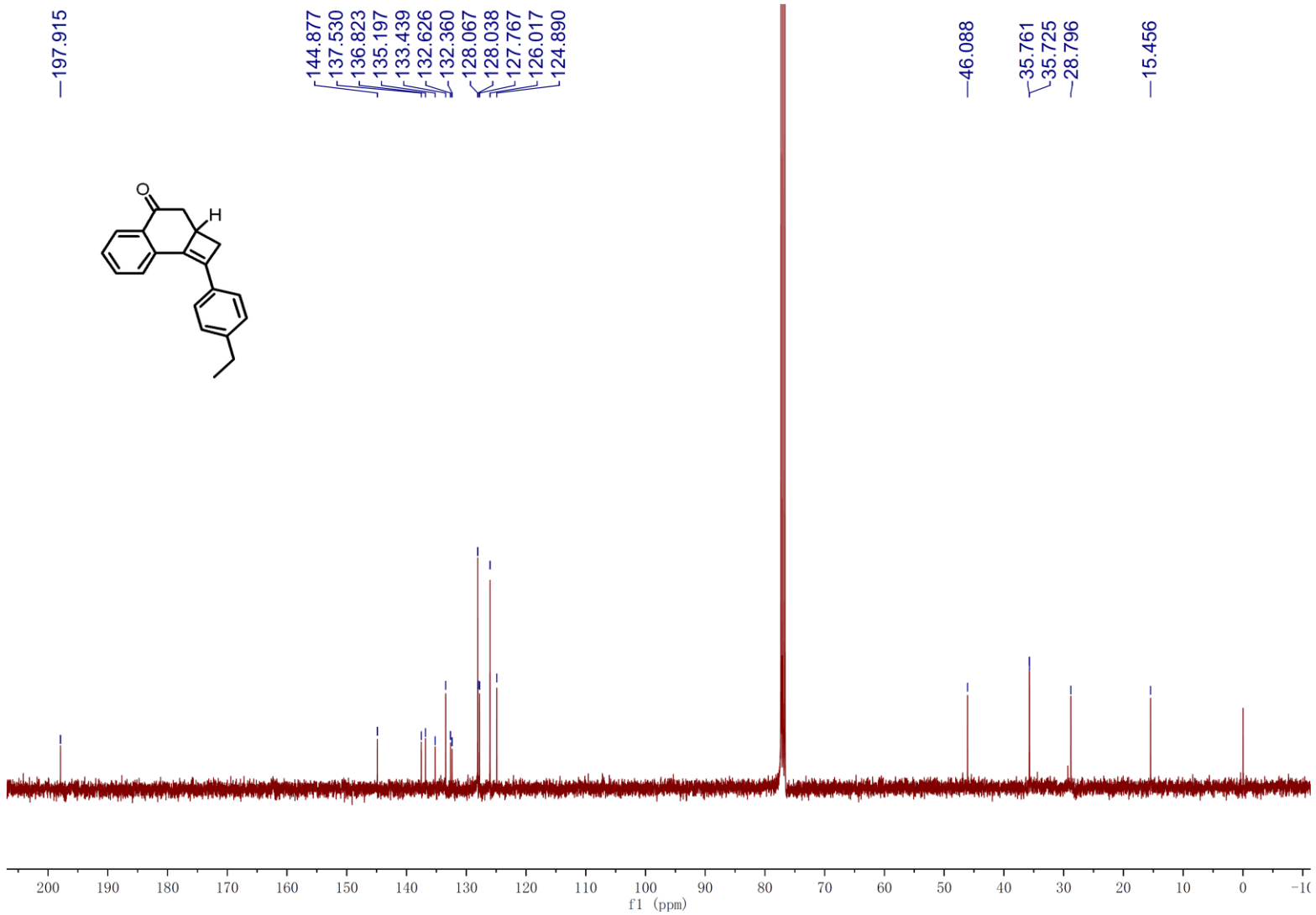
^{1}H NMR Spectrum of Compound 4c



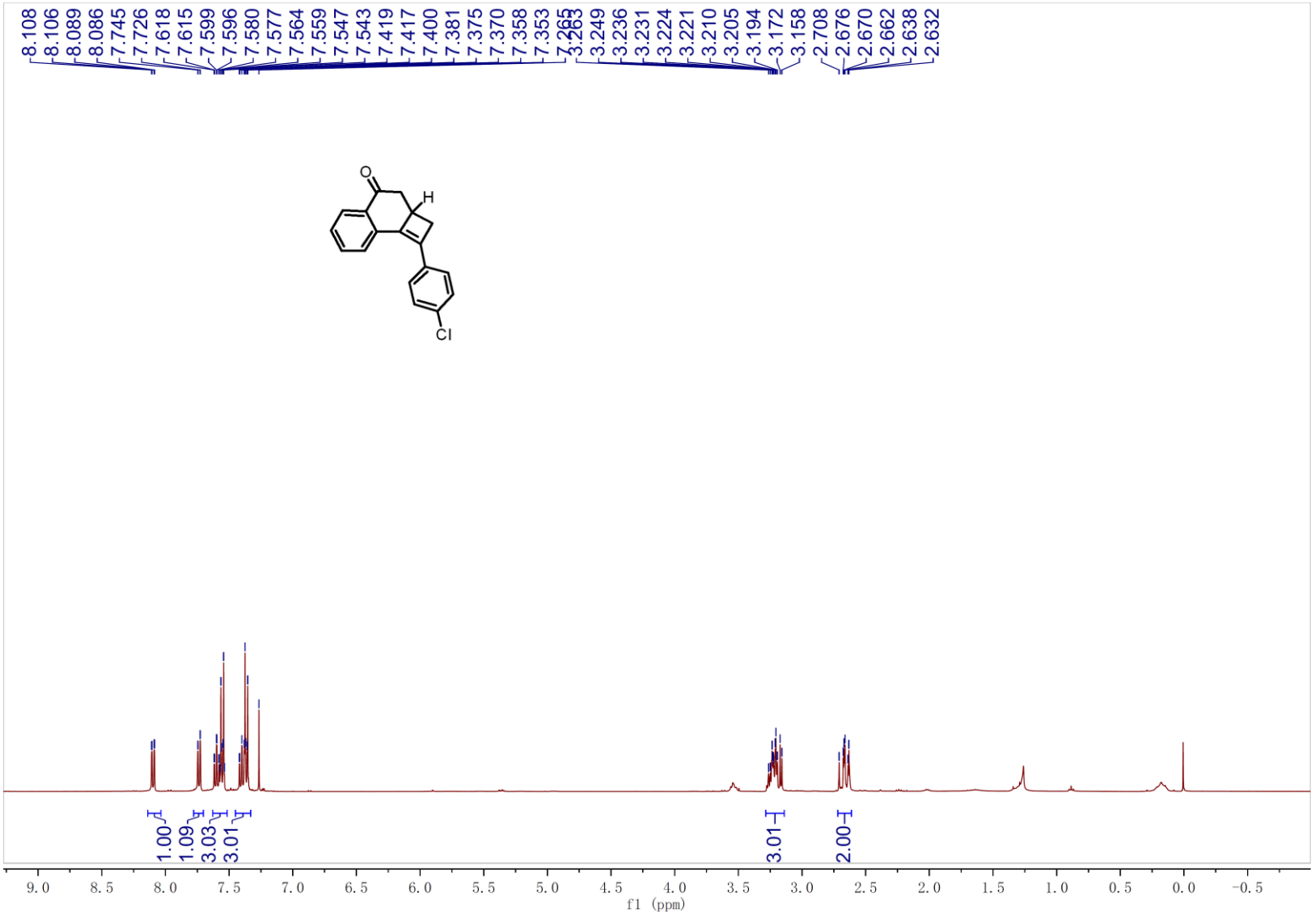
^{13}C NMR Spectrum of Compound 4c



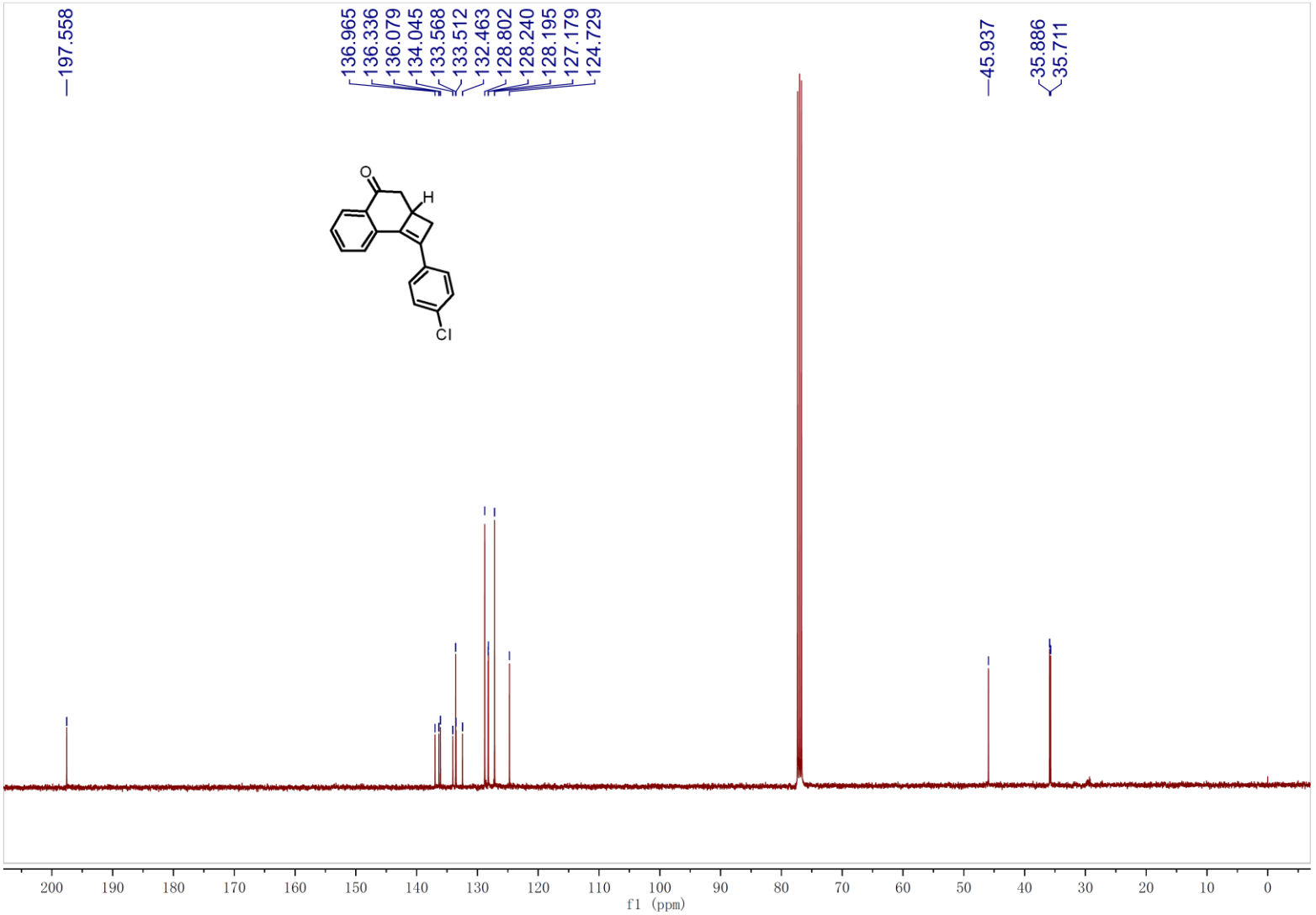
^{1}H NMR Spectrum of Compound 4d



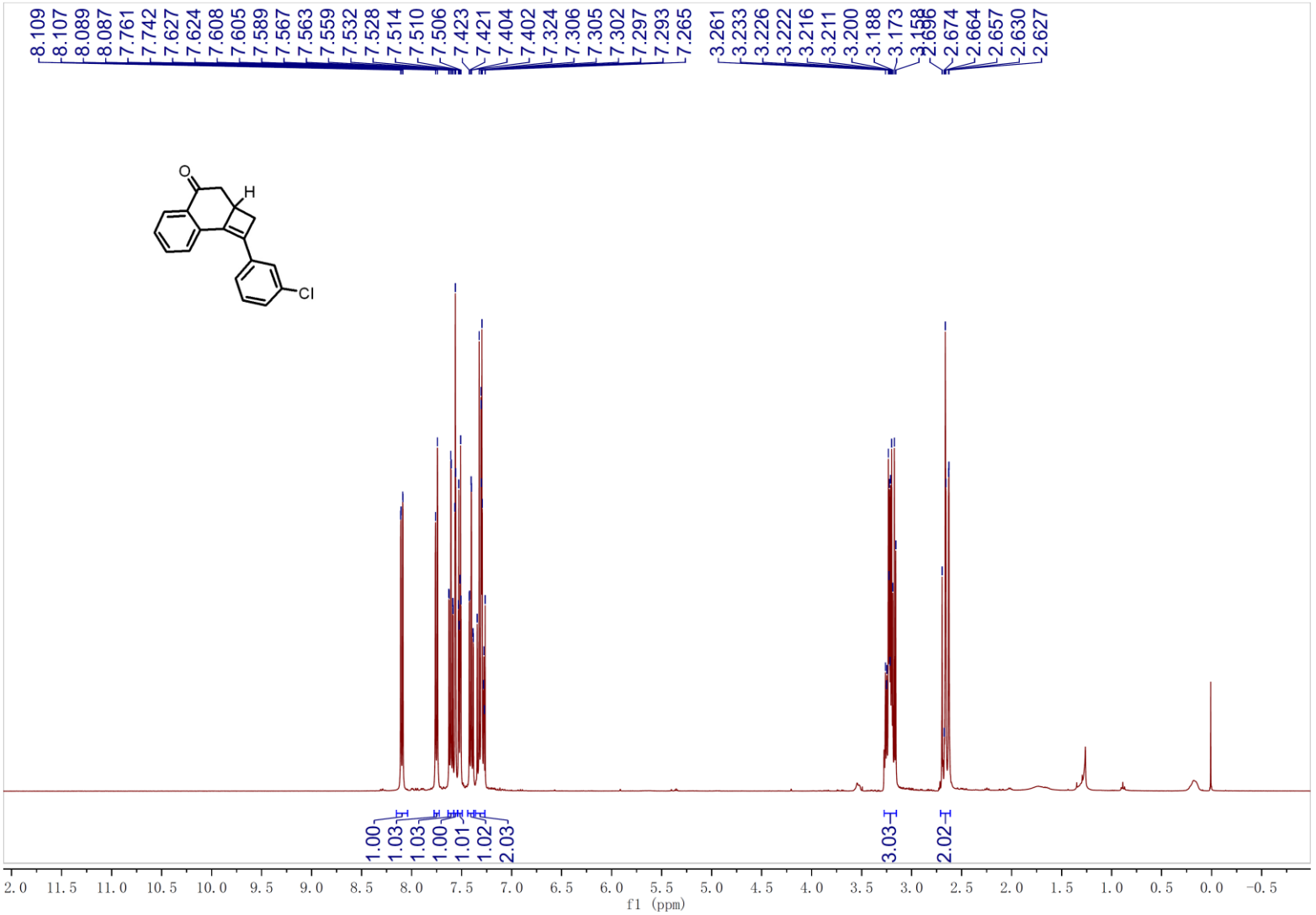
^{13}C NMR Spectrum of Compound 4d



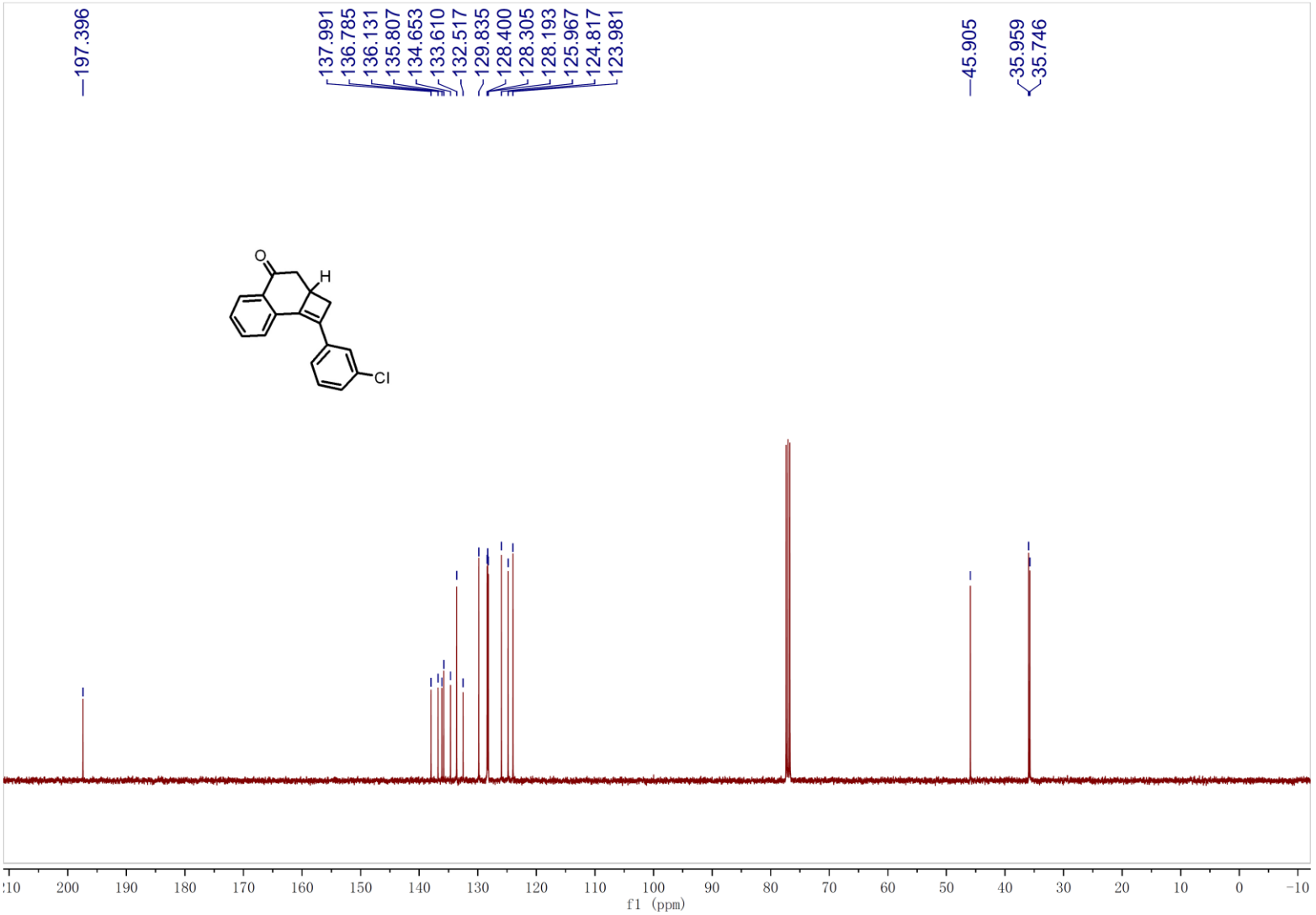
^{1}H NMR Spectrum of Compound 4e



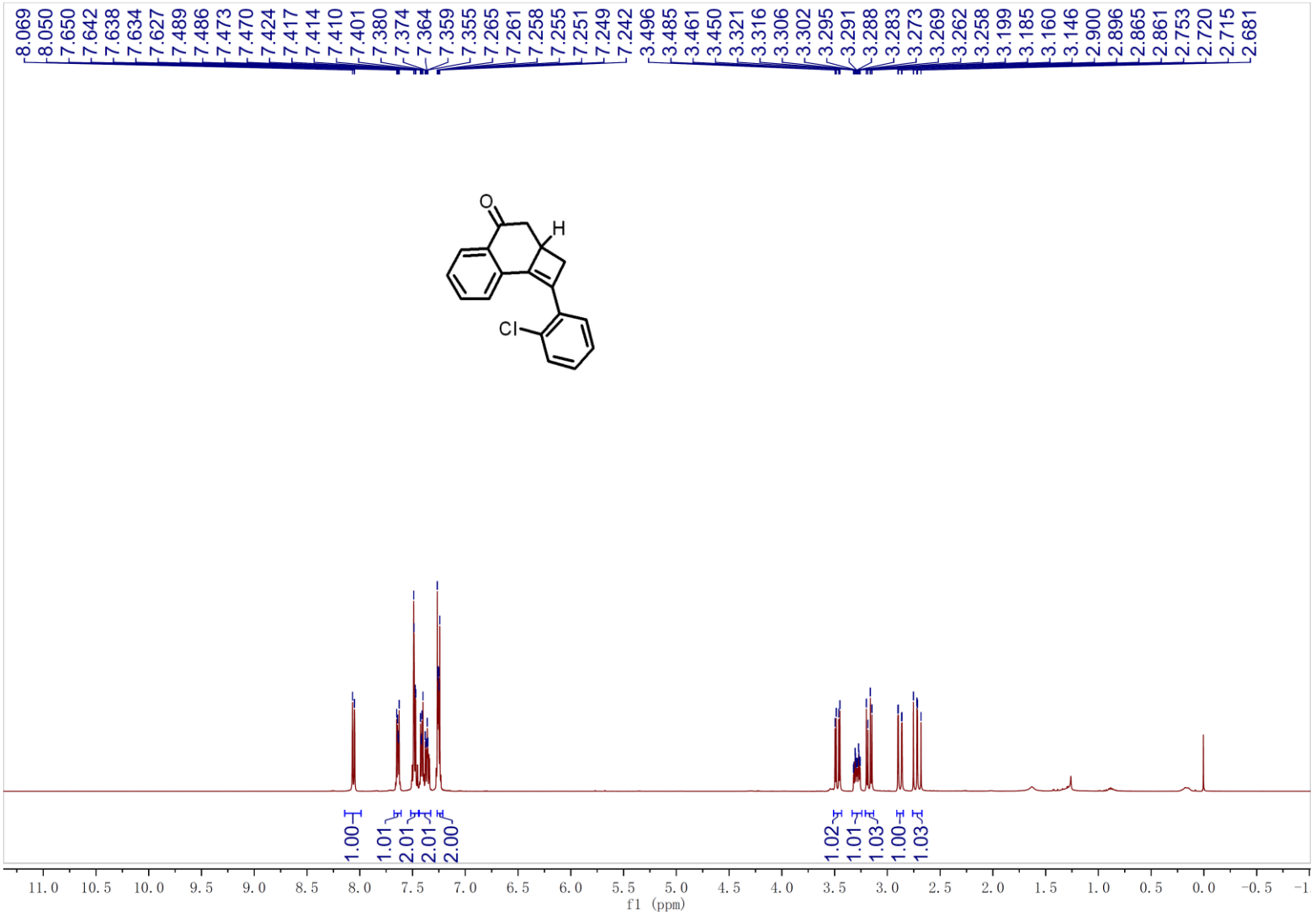
^{13}C NMR Spectrum of Compound 4e



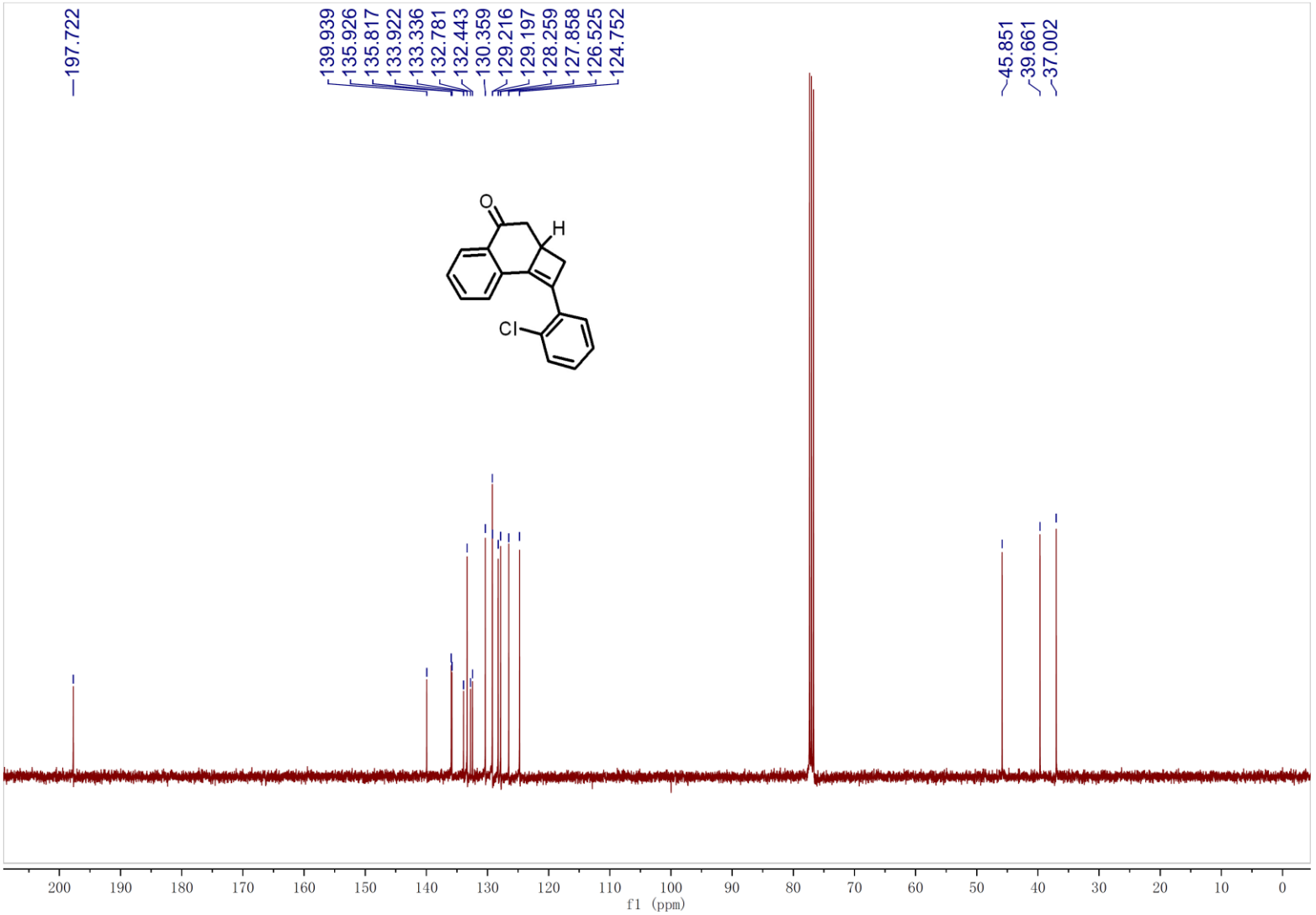
^{1}H NMR Spectrum of Compound 4f



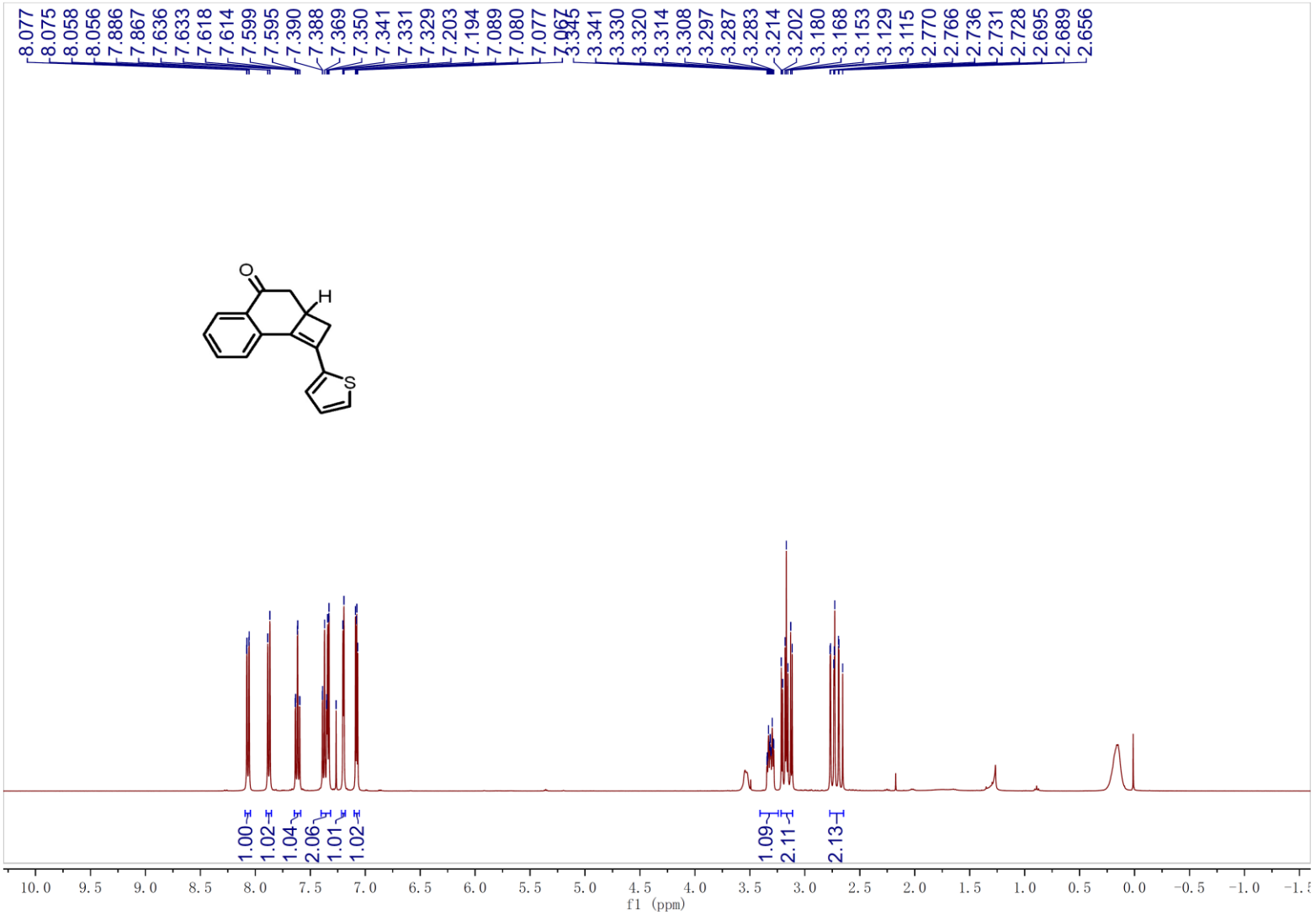
^{13}C NMR Spectrum of Compound 4f



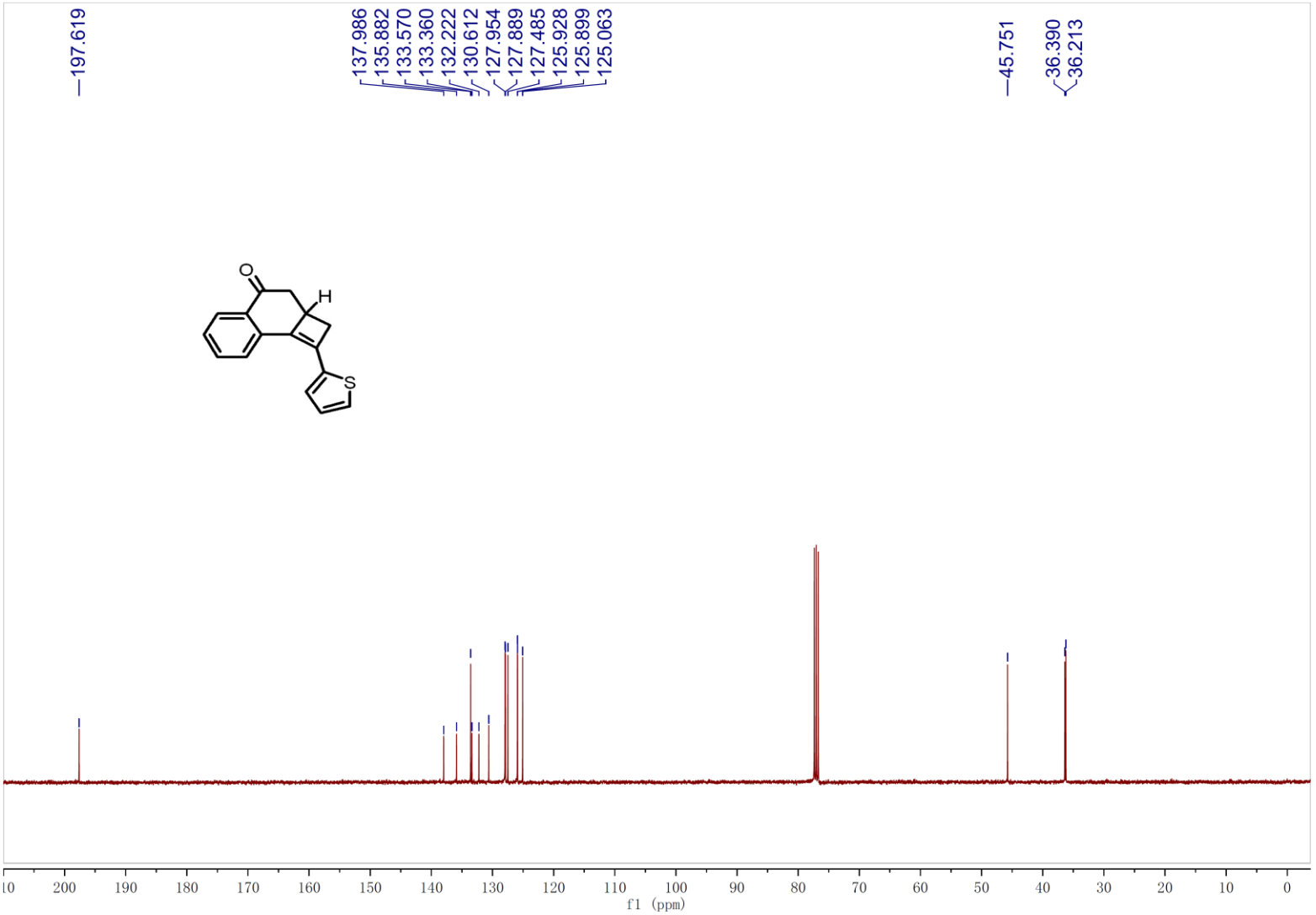
^{1}H NMR Spectrum of Compound 4g



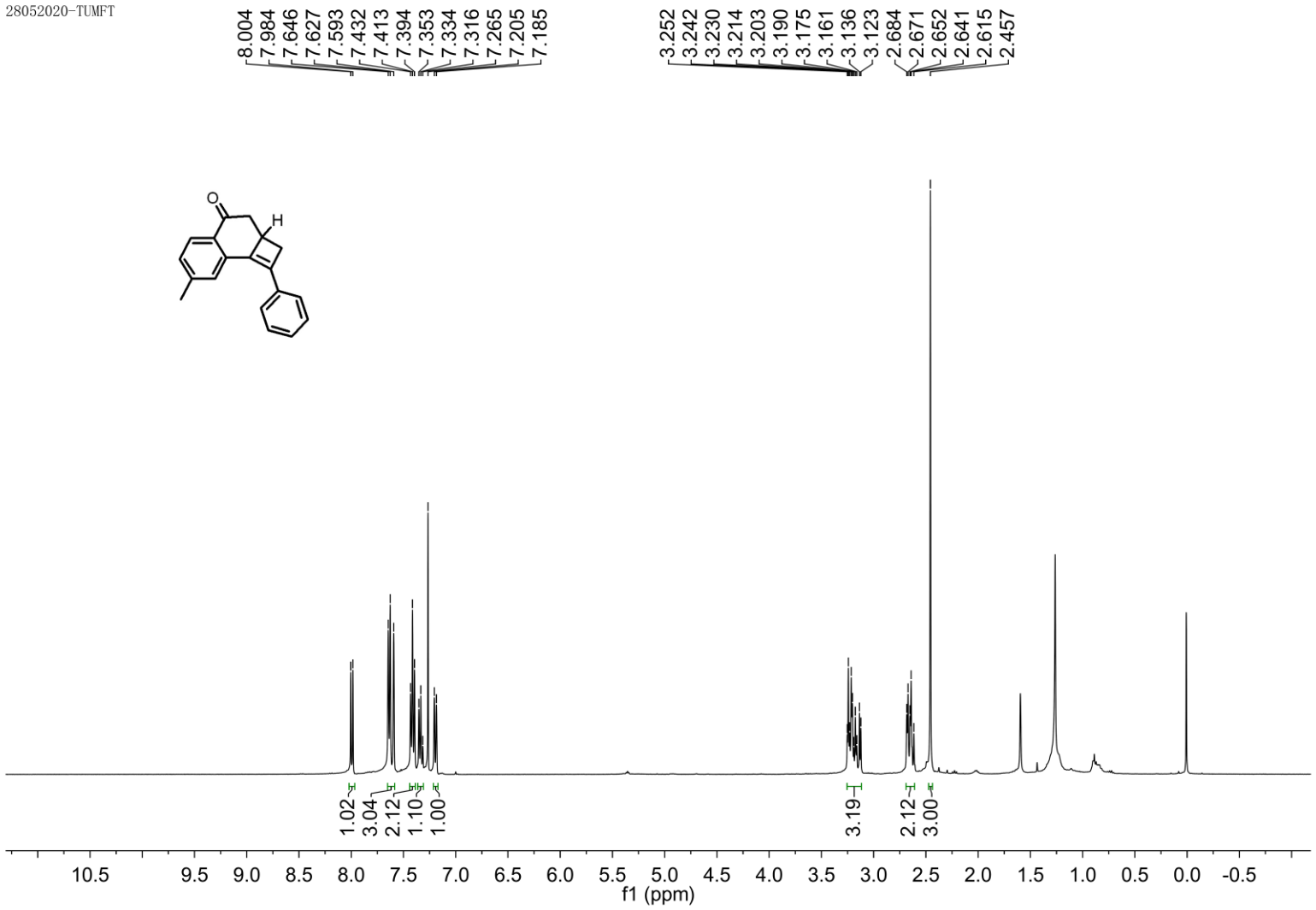
^{13}C NMR Spectrum of Compound 4g



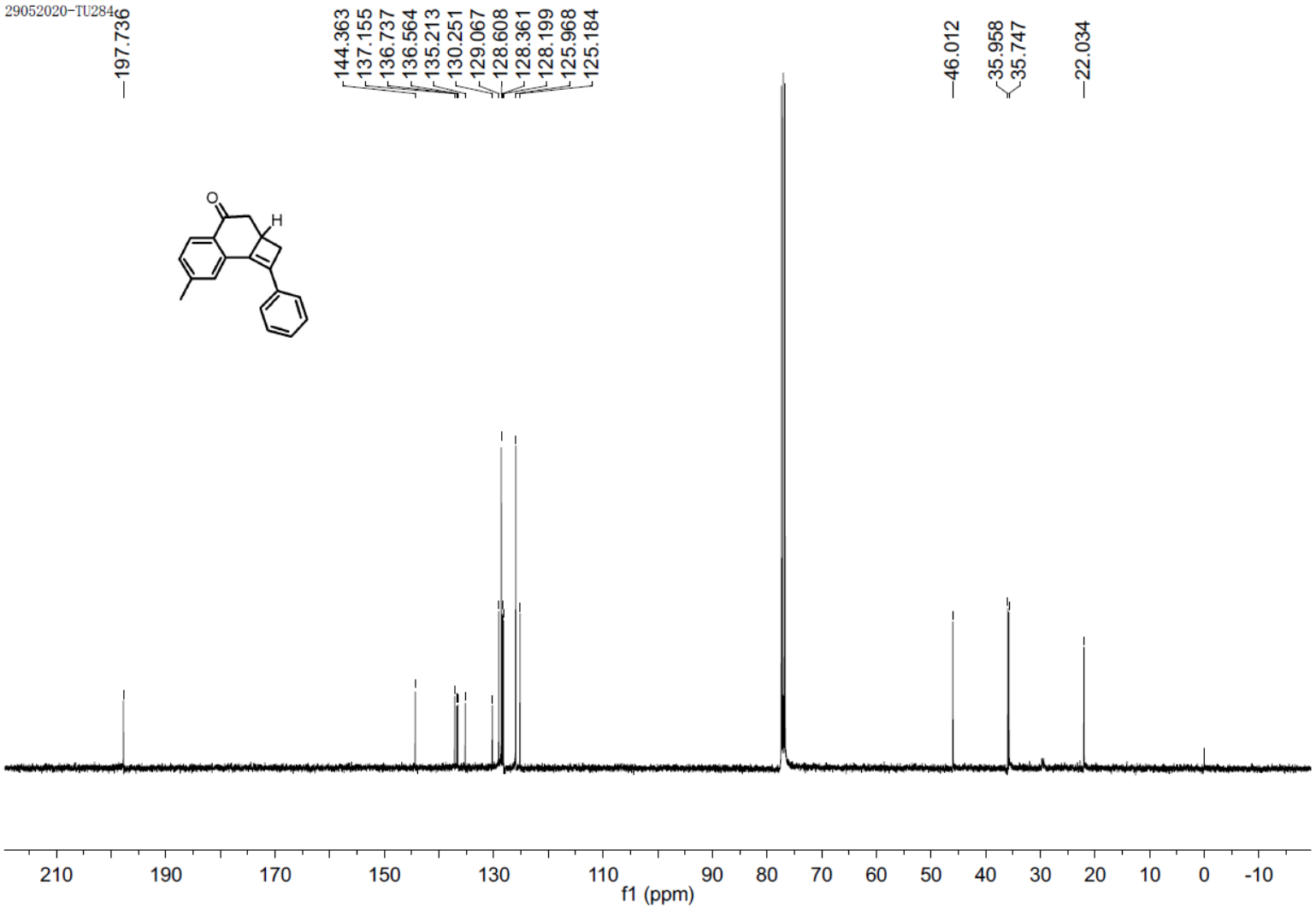
^{1}H NMR Spectrum of Compound 4h



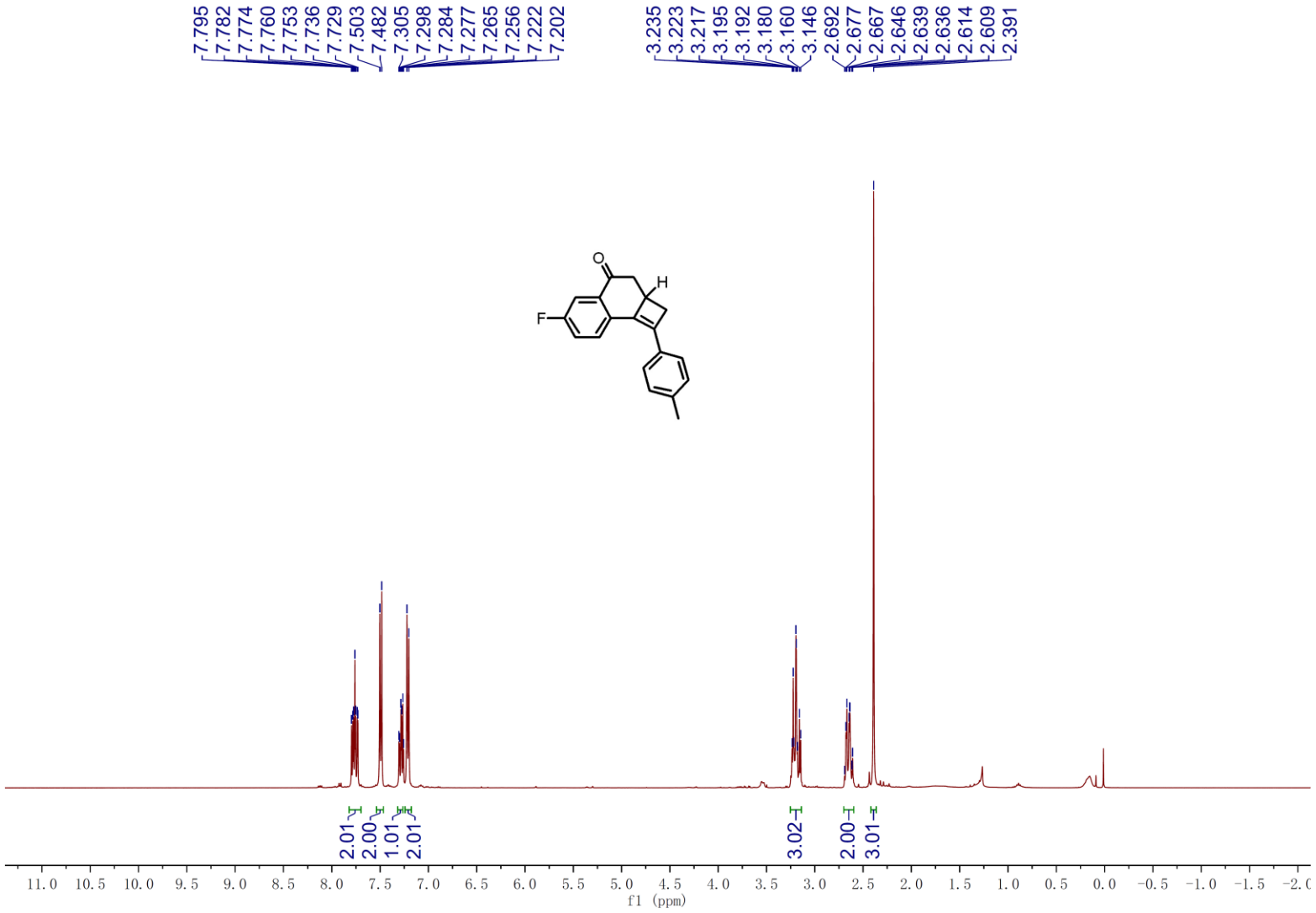
^{13}C NMR Spectrum of Compound 4h



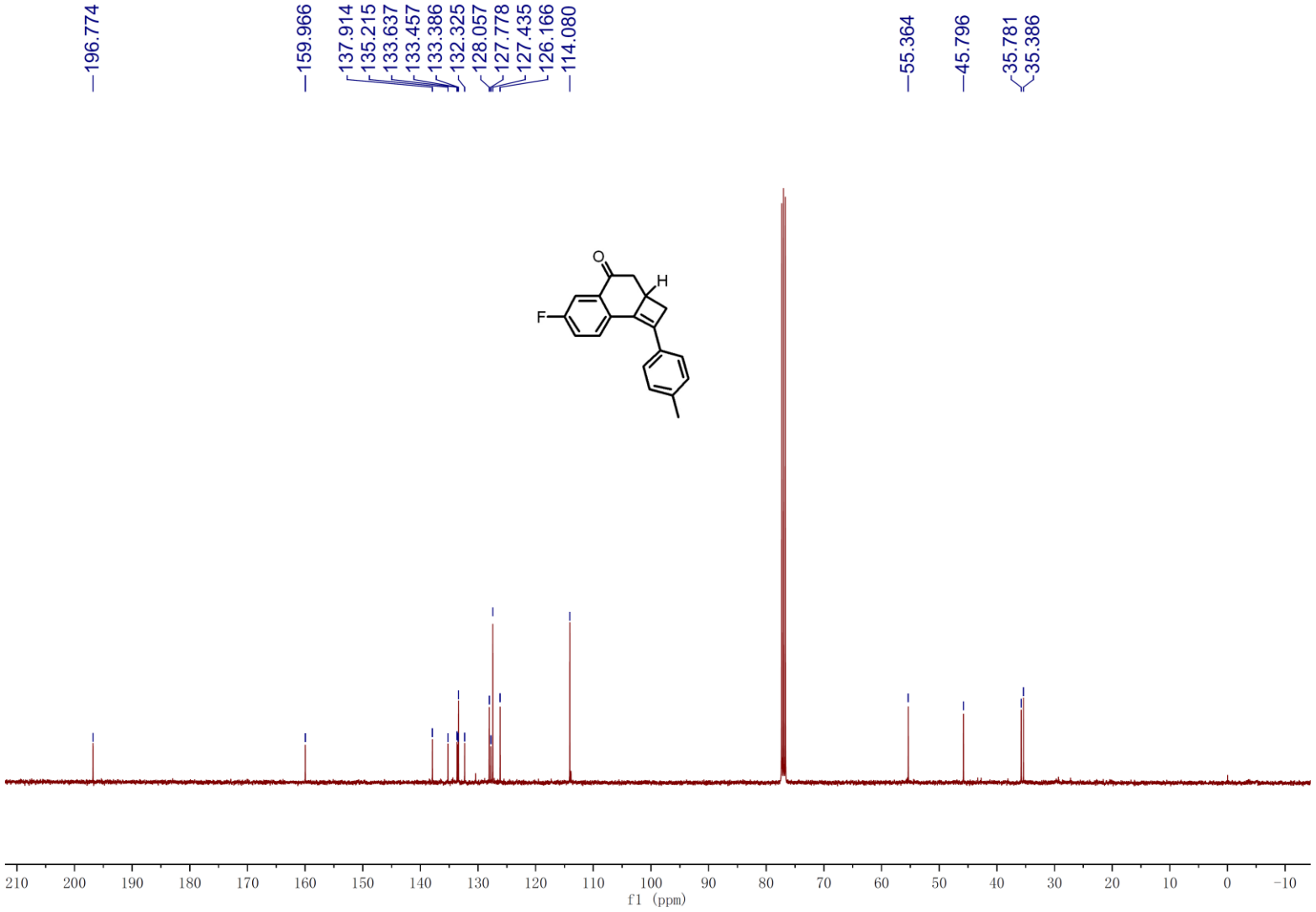
^{1}H NMR Spectrum of Compound 4i



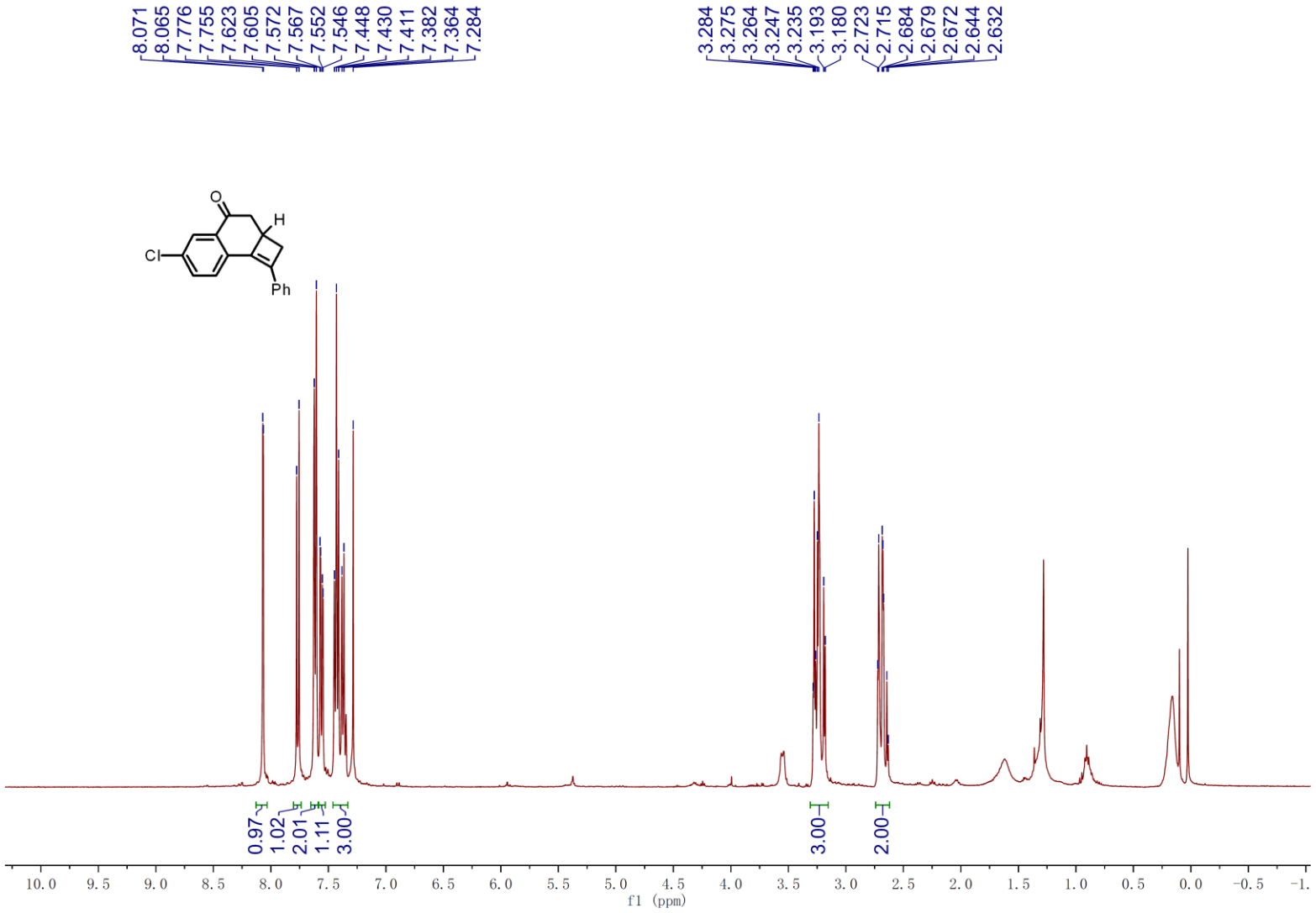
^{13}C NMR Spectrum of Compound 4i



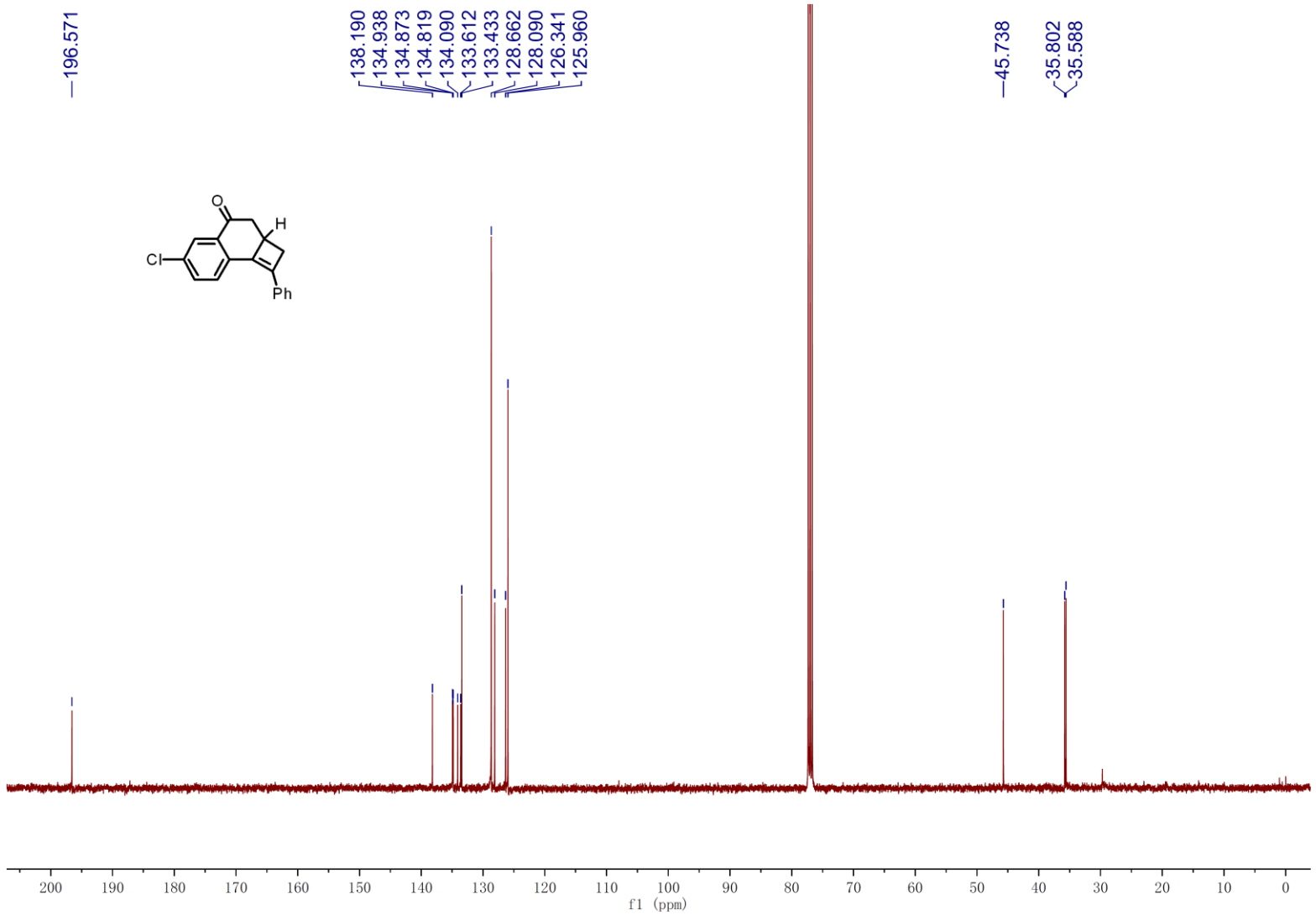
^{1}H NMR Spectrum of Compound 4j



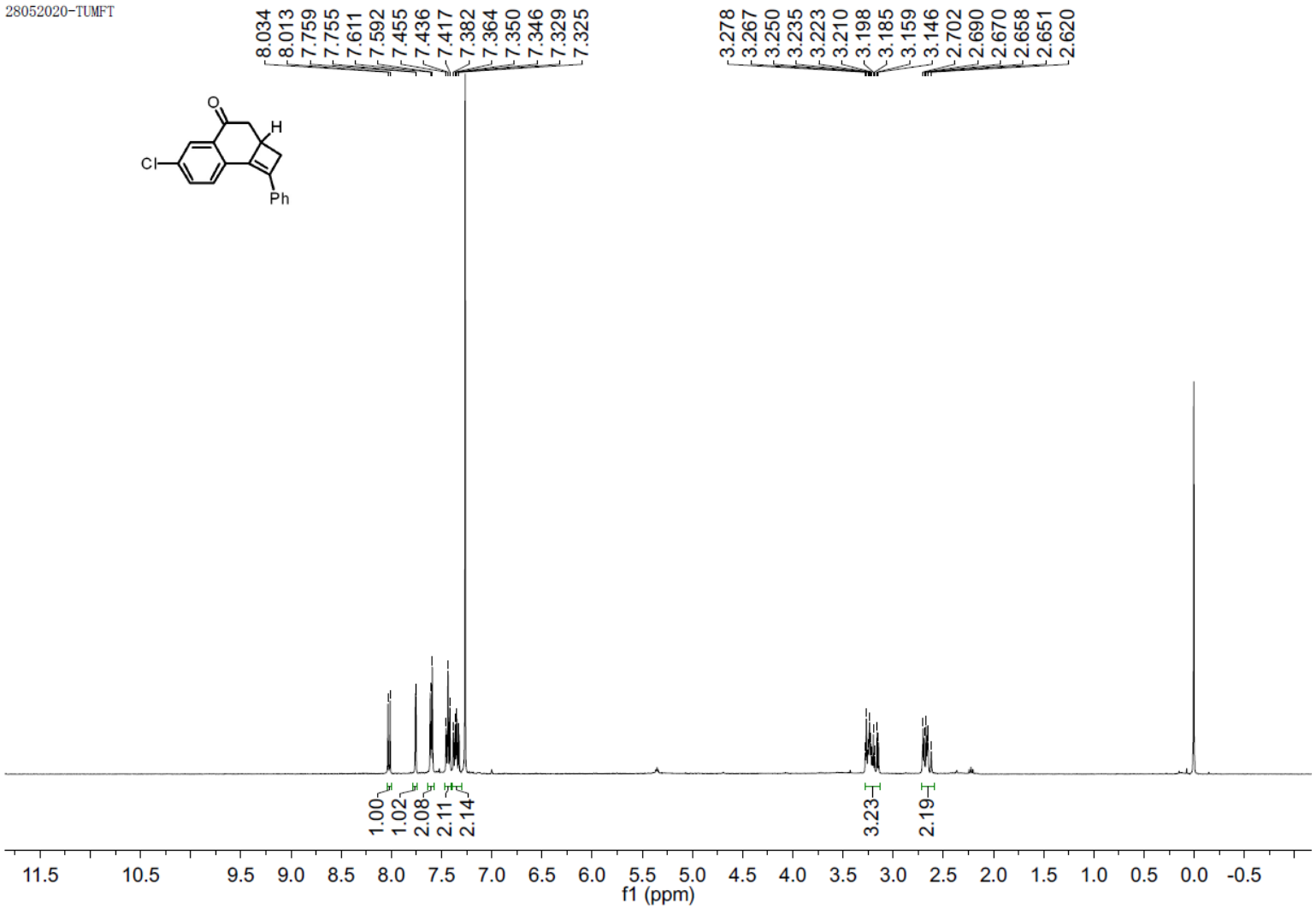
^{13}C NMR Spectrum of Compound 4j



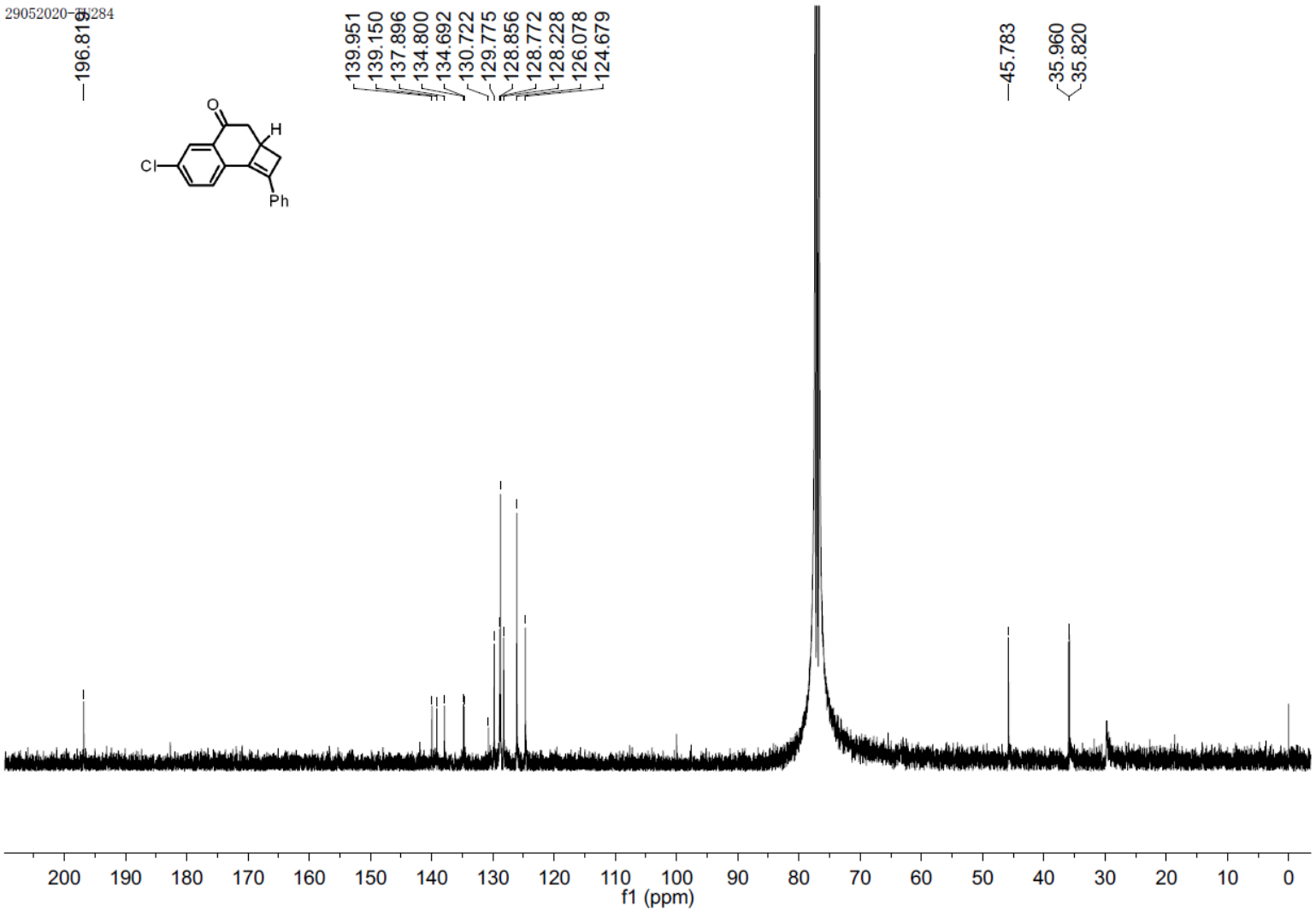
^{1}H NMR Spectrum of Compound 4k



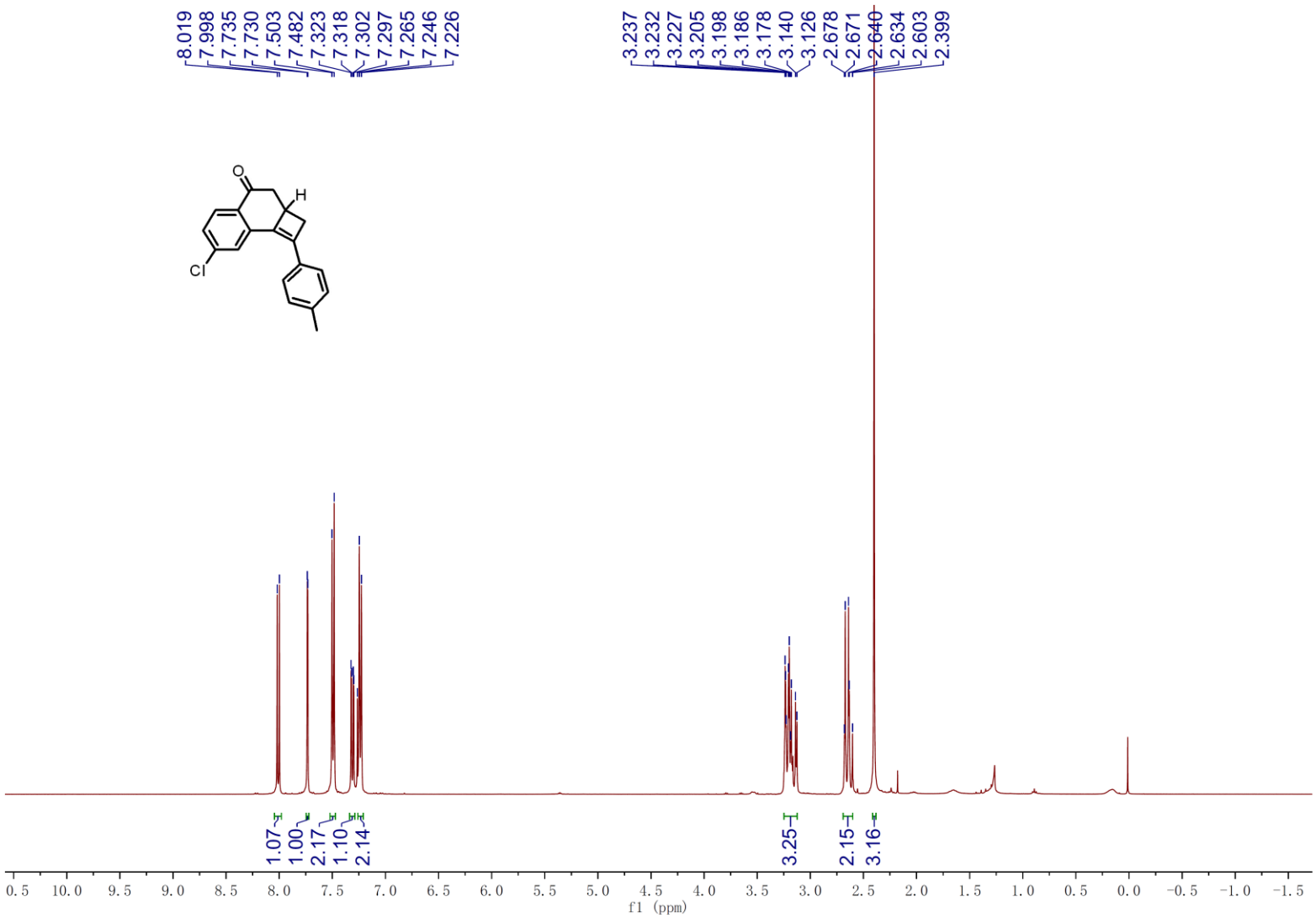
^{13}C NMR Spectrum of Compound 4k



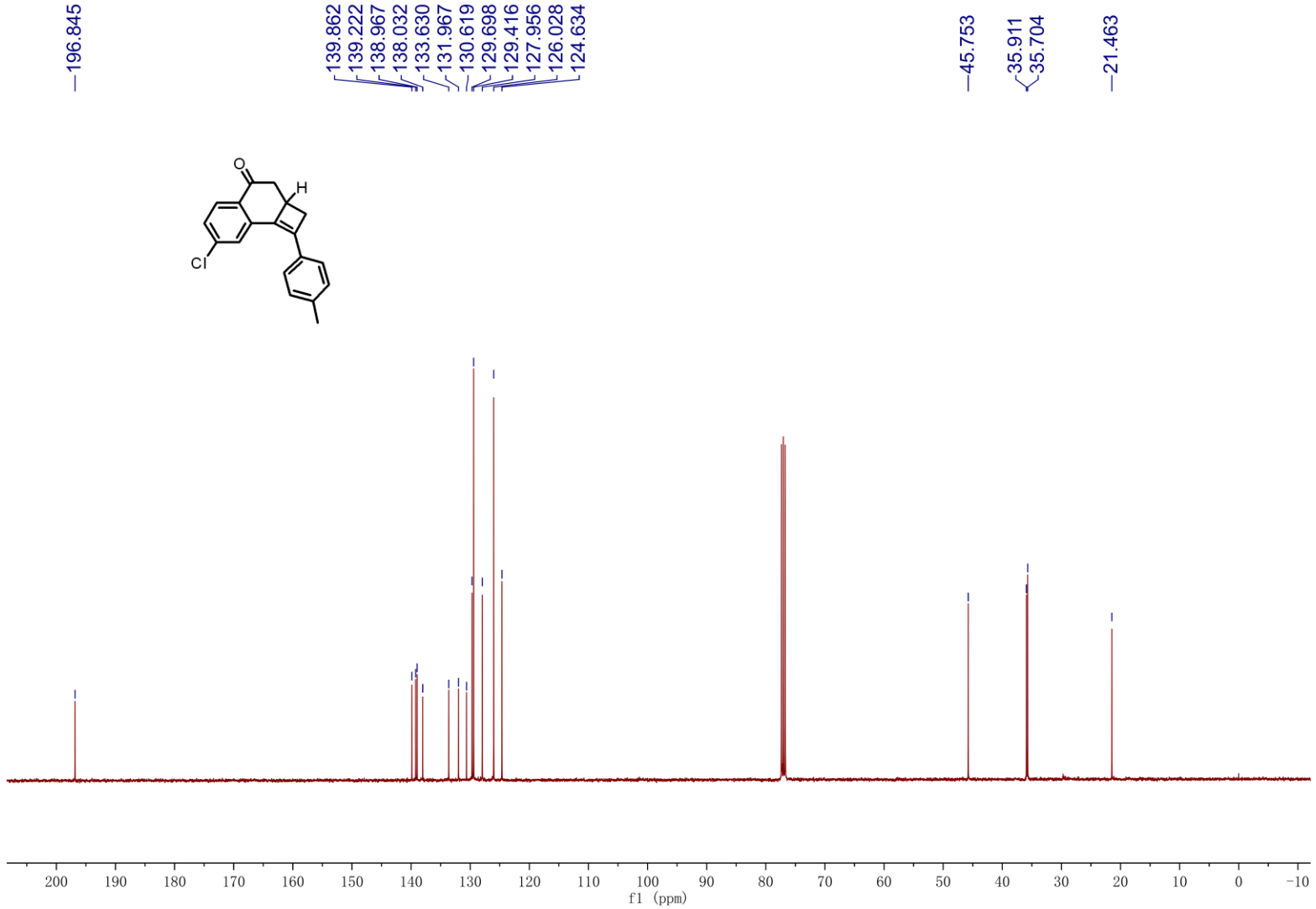
^{1}H NMR Spectrum of Compound 4l



^{13}C NMR Spectrum of Compound 4l



[1]H NMR Spectrum of Compound 4m



^{13}C NMR Spectrum of Compound 4m