Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photoinduced double [2 + 2] cycloaddition relay of yne-allenones for highly diastereoselective synthesis of hexacyclic 1-naphthols

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Context

Experimental

General Information

PE refers to petroleum ether (b.p. 60-90 °C) and EA refers to ethyl acetate, as well as DCE refers to dichloroethane. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated. ^{1}H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, m = multiplet), coupling constant (Hz)]. HRMS (APCI) 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. The melting points were measured with digital melting point detector.

Crystallographic Data of Compound 2q

Procedure for recrystallization of compounds **2q**: A single crystal **2q** was obtained by slowly evaporating the mixed solvent of hexane and dichloromethane (v/v = 2:1) at room temperature under the air conditions

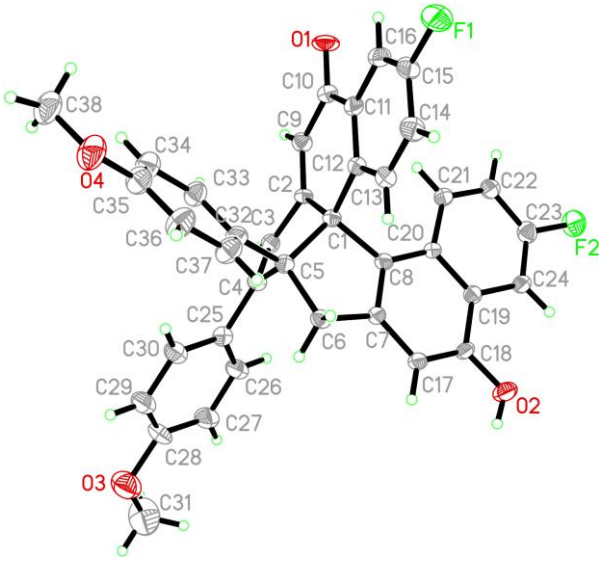
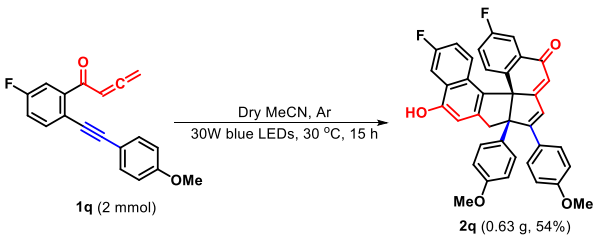


Figure S1. X-Ray Structure of **2q** (The ellipsoid contour 30% probability levels)

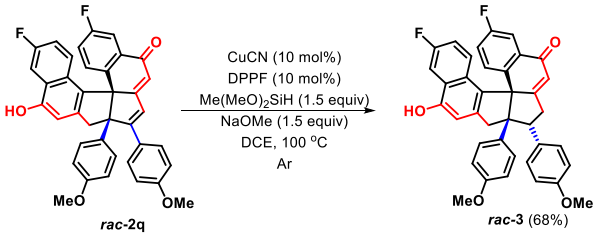
Scale-up transformation of 2q



1q (2 mmol) **2q** (0.63 g, 54%)

In a dried Schlenk flask (25 ml) under Ar conditions, 1-(2-(phenylethynyl)phenyl)buta-2,3-dien-1-one (**1q**, 2.0 mmol, 584 mg, 1 equiv), and dry acetonitrile (5 mL) were successively added. Then, the tube was stirred at 30 °C for 15 h until complete consumption of **2q**, as monitored by TLC analysis. After the reaction mixture was washed with H_2O (50 ml) and extracted with dichloromethane (3 ×25 mL). The combined organic layer was washed with brine (50 mL) and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified on a silica gel column with petroleum ether/ethyl acetate (2/1) as the eluent to afford the purified product **2q** (0.63 g, 54% yield) as a yellow solid.

CuH-catalyzed reductive coupling reaction of 2q



Under the argon conditions, **2q** (0.05 mmol, 1.0 equiv), dimethoxy(methyl)silane (1.5 equiv.), CuCN (10 mol%), DPPF (10 mol%), CH_3ONa (1.5 equiv.) and 1,2-dichloroethane (1.5 mL) were added to a 10 mL-Schlenk tube. The resulting mixture was stirring at 100 °C in oil bath for 12 h. After the reaction was completed, the solution was concentrated in vacuo and purified by flash chromatography on silica gel (PE/EA= 2/1 v/v) to afford the desired product **3** (19.9 mg, 68% yield) as yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.84 – 7.75 (m, 2H), 7.59 – 7.54 (m, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 8.8 Hz, 2H), 7.06 – 7.00 (m, 1H), 6.88 – 6.83 (m, 2H), 6.82 – 6.77 (m, 3H), 6.76 (d, J = 2.0 Hz, 1H), 6.72 – 6.60 (m, 3H), 4.39 – 4.30 (m, 3H), 3.94 – 3.86 (m, 2H), 3.77 (s, 3H), 3.70 (d, J = 6.0 Hz, 4H).^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 183.99, 170.19, 163.49, 160.43, 158.7 ($^2J_{CF}$ = 223.5 Hz), 154.05, 154.00, 140.26 ($^7J_{CF}$ = 3.0 Hz), 139.1 ($^1J_{CF}$ = 237.6 Hz), 137.90, 137.88, 134.88, 134.41, 134.34, 131.27, 129.46, 127.73, 127.48, 126.80, 125.0 ($^5J_{CF}$ = 8.4 Hz), 119.3 ($^3J_{CF}$ = 22.5 Hz), 117.26, 117.01, 114.1 ($^6J_{CF}$ = 3.8 Hz), 112.43, 107.1 ($^4J_{CF}$ = 22.1 Hz), 103.42, 70.92, 69.48, 68.28, 55.34, 55.09, 41.81, 39.01. IR (KBr, v, cm^{-1}): 3623, 1664, 1558, 1427, 1360, 589, 621; HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{38}H_{27}F_2O_4$ 585.1877; Found 585.1880.

Reference

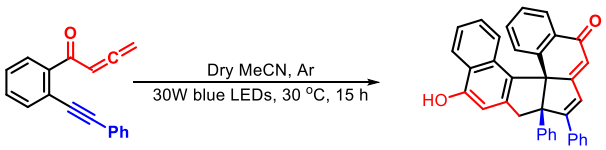
1. Li, C.-X.; Liu, R.-Y.; Buchwald, S.-L. Engaging Aldehydes in CuH-Catalyzed Reductive Coupling Reactions: Stereoselective Allylation with Unactivated 1,3-Diene Pronucleophiles. *Angew. Chem., Int. Ed.*, **2019**, *58*, 2-9.

2. O. Chuzel, J. Deschamp, C. Chausteur, O. Riant. Copper(I)-Catalyzed Enantio- and Diastereoselective Tandem Reductive Aldol Reaction. *Org. Lett*., **2006**, *8*, 5943-5946.

3. Jang, W.-J.; Yun, J. Copper‐Catalyzed Tandem Hydrocupration and Diastereo‐ and Enantioselective Borylalkyl Addition to Aldehydes. *Angew. Chem. Int. Ed.*, **2018**, *57*, 12116-12120.

General Procedure for the Synthesis of Products 2.

Example for the synthesis of **2a**:

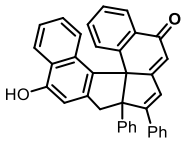


1a ***rac*-2a**

Under Ar conditions, 1-(2-(phenylethynyl)phenyl)buta-2,3-dien-1-one (**1a**, 0.2 mmol, 48.8 mg, 1 equiv.), and dry acetonitrile (2.5 mL) were successively added to a 10 mL Schlenk tube,. Then, the tube was stirred at 30 °C for 15 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 = 2:1) to afford the desired product **2a** as a yellow solid.

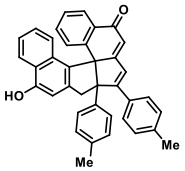
Characterization data

6-Hydroxy-4,4a-diphenyl-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2a)



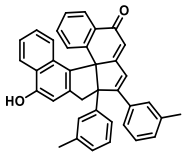
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 63.4 mg, 65% yield; mp: 270-271 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 10.30 (s, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.97 – 7.87 (m, 2H), 7.43 (s, 1H), 7.32 – 7.28 (m, 4H), 7.24 (d, J = 8.4 Hz, 3H), 7.19 (d, J = 12.4 Hz, 3H), 7.17 – 7.13 (m, 3H), 7.07 (s, 2H), 6.84 (d, J = 5.2 Hz, 2H), 4.71 (d, J = 17.2 Hz, 1H), 3.57 (d, J = 16.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 184.5, 169.8, 162.5, 154.3, 145.0, 140.5, 140.1, 134.1, 132.2, 132.0, 131.0, 130.0, 129.6, 129.2, 129.0, 128.0, 127.7, 127.2, 127.1, 126.8, 125.8, 125.0, 123.8, 123.6, 122.2, 122.1, 107.0, 71.2, 69.7, 40.5, 40.3, 40.1, 39.9, 39.7, 39.5, 39.3. IR (KBr, v, cm^{-1}): 3130, 1651, 1540, 1451, 1301, 1023, 741; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{36}H_{23}O_2$ 487.1699; Found 487.1633.

6-Hydroxy-4,4a-di-p-tolyl-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2b)



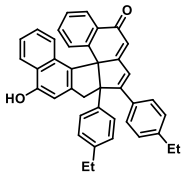
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 80.5 mg, 78% yield; mp: 242-243 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 10.27 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.93 – 7.90 (m, 1H), 7.43 (s, 1H), 7.29 (s, 1H), 7.24 (s, 1H), 7.22 (s, 1H), 7.19 (s, 1H), 7.18 – 7.13 (m, 5H), 7.09 (m, 3H), 6.97 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 1.6 Hz, 2H), 4.65 (d, J = 17.2 Hz, 1H), 3.57 (d, J = 17.2 Hz, 1H), 2.25 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 184.7, 170.3, 163.0, 154.2, 145.2, 140.6, 139.6, 137.2, 136.6, 132.4, 132.2, 131.3, 131.1, 130.0, 129.8, 129.6, 129.6, 129.3, 128.9, 128.1, 127.3, 127.1, 126.8, 126.7, 125.9, 125.0, 123.9, 123.7, 122.3, 121.7, 71.1, 69.7, 21.3, 20.9. IR (KBr, v, cm^{-1}): 3646, 1652, 1558, 1463, 1356, 862, 752; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{38}H_{27}O_2$ [M-H]$^-$ 515.2011; Found 515.2020.

6-Hydroxy-4,4a-di-m-tolyl-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2c)



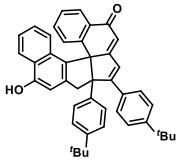
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 67.1 mg, 65% yield; mp: 245-246 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 10.27 (s, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.94 – 7.91 (m, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.27 (s, 2H), 7.21 (d, J = 10.0 Hz, 2H), 7.16 (s, 4H), 7.14 (d, J = 4.4 Hz, 2H), 7.07 – 7.03 (m, 2H), 6.96 (d, J = 7.2 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 6.83 (d, J = 4.0 Hz, 2H), 4.66 (d, J = 17.2 Hz, 1H), 3.57 (d, J = 17.2 Hz, 1H), 2.20 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 184.5, 169.9, 162.8, 154.2, 145.0, 140.5, 140.2, 138.4, 137.8, 134.2, 132.2, 132.1, 132.0, 131.1, 130.3, 129.7, 129.2, 129.0, 128.8, 128.3, 127.2, 126.7, 125.8, 125.0, 125.0, 123.7, 123.6, 122.2, 121.8, 106.0, 71.2, 69.7, 21.7, 21.4; IR (KBr, v, cm^{-1}): 3564, 1645, 1532, 1495, 1386, 890, 762;
HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{38}H_{27}O_2$ 515.2011; Found 515.2014.

4,4a-Bis(4-ethylphenyl)-6-hydroxy-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2d)



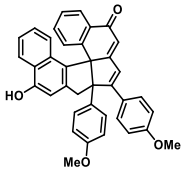
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 87.0 mg, 80% yield; mp: 205-206 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 10.27 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.93 – 7.91 (m, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.33 (d, J = 7.2 Hz, 1H), 7.25 – 7.19 (m, 4H), 7.17 (d, J = 8.0 Hz, 3H), 7.14 (d, J = 4.4 Hz, 2H), 7.11 (s, 1H), 7.08 – 7.05 (m, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 3.6 Hz, 2H), 4.66 (d, J = 17.2 Hz, 1H), 3.59 (d, J = 17.2 Hz, 1H), 2.58 – 2.53 (m, 2H), 2.43 (d, J = 7.6 Hz, 2H), 1.13 (t, J = 7.6 Hz, 3H), 1.04 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 184.6, 170.1, 162.9, 154.3, 145.6, 145.2, 142.7, 140.6, 137.6, 132.4, 132.3, 132.2, 131.6, 131.2, 129.3, 129.0, 128.7, 128.3, 128.2, 127.2, 127.1, 126.8, 125.9, 125.0, 123.8, 123.7, 122.3, 121.8, 106.1, 71.1, 69.7, 28.4, 27.8, 15.7, 15.4. IR (KBr, v, cm^{-1}): 3655, 1662, 1543, 1475, 1360, 870, 743; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{40}H_{31}O_2$ 543.2324; Found 543.2328.

4,4a-Bis(4-(tert-butyl)phenyl)-6-hydroxy-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2e)



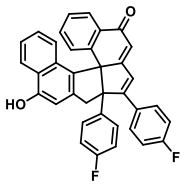
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 78.0 mg, 65% yield; mp: 260-261 °C; ^{1}H NMR (400 MHz, $CDCl_3$ (δ, ppm) 10.27 (s, 1H), 8.57 – 8.53 (m, 1H), 8.48 – 8.44 (m, 1H), 8.33 (d, J = 10.0 Hz, 1H), 7.90 (s, 3H), 7.80 – 7.75 (m, 3H), 7.70 (s, 3H), 7.62 – 7.56 (m, 3H), 7.46 – 7.43 (m, 1H), 7.32 (d, J = 4.8 Hz, 1H), 7.28 (d, J = 4.8 Hz, 1H), 7.23 (d, J = 4.0 Hz, 1H), 5.05 – 4.93 (m, 1H), 4.18 – 4.12 (m, 1H), 2.79 – 2.52 (m, 9H), 1.80 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm)
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 175.1, 168.3, 158.8, 157.0, 154.6, 149.9, 144.5, 141.6, 137.4, 137.0, 136.3, 136.3, 136.0, 133.3, 133.2, 132.4, 131.2, 130.8, 130.3, 130.1, 129.8, 128.1, 127.3, 126.3, 110.6, 75.9, 74.7, 39.5, 39.0, 36.0, 34.4. IR (KBr, v, cm^{-1}): 3658, 1638, 1545, 1429, 1354, 866, 748. HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{44}H_{39}O_2$ 599.2950; Found 599.2958.

6-Hydroxy-4,4a-bis(4-methoxyphenyl)-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2f)



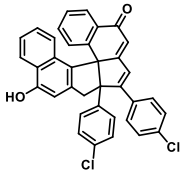
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 60.3 mg, 55% yield; mp: 279-280 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 8.05 (d, J = 8.4 Hz, 1H), 7.96 – 7.88 (m, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.28 (s, 3H), 7.23 (d, J = 8.8 Hz, 3H), 7.16 (d, J = 6.8 Hz, 2H), 6.98 – 6.78 (m, 4H), 6.72 (d, J = 8.4 Hz, 2H), 4.63 (d, J = 16.8 Hz, 1H), 3.73 (s, 3H), 3.56 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 183.2, 162.7, 160.5, 158.6, 154.6, 146.4, 142.8, 137.2, 131.9, 131.6, 131.5, 131.0, 130.6, 129.8, 128.6, 128.1, 128.0, 127.5, 126.2, 124.3, 123.3, 121.1, 114.7, 114.4, 106.7, 71.0, 70.9, 70.8, 69.0, 55.7, 55.3. IR (KBr, v, cm^{-1}): 3546, 1640, 1550, 1453, 1364, 865, 735; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{38}H_{27}O_4$ [M-H]$^-$547.1909; Found 547.1915.

4,4a-Bis(4-fluorophenyl)-6-hydroxy-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2g)



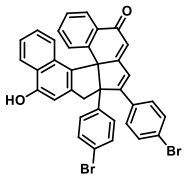
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 54.5 mg, 52% yield; mp: 250-251 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 10.56 (s, 1H), 8.17 – 8.11 (m, 1H), 8.02 – 7.96 (m, 1H), 7.43 (d, J = 17.2 Hz, 2H), 7.35 – 7.28 (m, 4H), 7.27 – 7.19 (m, 4H), 7.17 (d, J = 10.4 Hz, 1H), 7.13 – 7.10 (m, 1H), 7.04 – 6.99 (m, 2H), 6.84 (d, J = 18.4 Hz, 3H), 4.83 (d, J = 17.2 Hz, 1H), 3.55 (d, J = 17.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 184.4, 169.3, 162.8 ($^1J_{CF}$ = 246.5 Hz), 161.5 ($^2J_{CF}$ = 243.1 Hz), 160.8, 154.3, 144.7, 140.4, 136.1 ($^2J_{CF}$ = 3.4 Hz), 132.2, 132.1, 131.8, 131.0, 130.5 ($^7J_{CF}$ = 3.4 Hz), 130.2 ($^6J_{CF}$ = 8.7 Hz), 130.1, 129.3, 129.2 ($^5J_{CF}$ = 8.8 Hz), 127.3, 126.8, 125.9, 125.0, 123.8, 123.7, 122.3, 122.2, 116.3 ($^3J_{CF}$ = 216.0 Hz), 115.8 ($^4J_{CF}$ = 21.0 Hz), 105.9, 70.7, 69.7. IR (KBr, v, cm^{-1}): 3063, 1634, 1598, 1489, 1382, 859, 763; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{36}H_{21}F_2O_2$ 523.1510; Found 523.1523.

4,4a-Bis(4-chlorophenyl)-6-hydroxy-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2h)



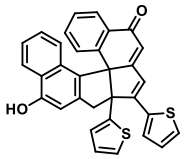
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 50.1 mg, 45% yield; mp: 279-280 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 10.34 (s, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.96 – 7.93 (m, 1H), 7.41 (d, J = 8.8 Hz, 3H), 7.38 (s, 2H), 7.32 – 7.23 (m, 5H), 7.21 – 7.17 (m, 3H), 7.10 – 7.04 (m, 1H), 6.85 (d, J = 7.6 Hz, 2H), 4.70 (d, J = 17.2 Hz, 1H), 3.54 (d, J = 17.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 179.1(1), 179.1(0), 163.6(0), 163.6(8), 155.0, 155.0, 149.1, 149.1, 139.3, 135.1, 133.6, 129.1(8), 129.1(7), 127.4, 127.0, 126.8, 126.3, 125.7, 125.6, 123.7, 122.2, 121.6, 120.7, 119.8(8), 119.8(6), 118.6, 118.4, 117.4, 116.8, 100.7, 100.0, 65.4(0), 65.4(9), 64.5, 64.4. IR (KBr, v, cm^{-1}): 3165, 1604, 1588, 1436, 1352, 825, 728; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{36}H_{21}Cl_2O_2$ 555.0919; Found 515.0920.

4,4a-Bis(4-bromophenyl)-6-hydroxy-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2i)



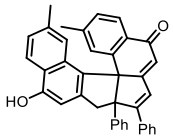
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 72.4 mg, 56% yield; mp: 210-211 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 10.34 (s, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.96 (s, 1H), 7.53 (d, J = 8.0 Hz, 3H), 7.39 (s, 6H), 7.19 (s, 6H), 7.09 (s, 1H), 6.85 (d, J = 9.2 Hz, 1H), 4.69 (d, J = 16.8 Hz, 1H), 3.54 (d, J = 16.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 179.2, 163.6, 155.1, 149.1, 139.3, 135.0, 134.0, 127.7, 127.2（2）, 127.2（5）, 127.1, 126.8, 126.6, 126.3, 125.7, 125.6, 124.7, 124.1, 124.0, 122.2, 121.6, 120.7, 119.7, 118.6, 118.4, 117.9, 117.4, 116.8, 116.2, 115.7, 100.7, 65.4, 64.4. IR (KBr, v, cm^{-1}): 3673, 1668, 1558, 1420, 1382, 741, 668; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{36}H_{21}Br_2O_2$ 644.9888; Found 644.9892.

6-Hydroxy-4,4a-di(thiophen-2-yl)-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one (2j)



Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 70.0 mg, 70% yield; mp: 245-246 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 10.30 (s, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.34 (s, 1H), 7.24 (d, J = 8.4 Hz, 3H), 7.13 – 7.07 (m, 3H), 6.97 (d, J = 8.0 Hz, 1H), 6.87 (d, J = 8.8 Hz, 3H), 6.80 (d, J = 8.4 Hz, 2H), 6.75 (d, J = 8.4 Hz, 2H), 4.69 (d, J = 16.9 Hz, 1H), 3.60 (d, J = 17.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 179.4, 164.6, 157.1, 155.0, 153.0, 148.8, 140.0, 136.7, 135.2, 130.3, 127.0, 126.6, 126.1, 125.1, 124.4, 124.1, 123.0, 122.9, 122.4, 121.3, 120.5, 120.3, 118.2, 117.8, 116.7, 116.0, 109.4, 108.8, 65.4, 64.1, 50.4, 50.0. IR (KBr, v, cm^{-1}): 3654, 1672, 1531, 1432, 1356, 721, 610; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{32}H_{19}O_2S_2$ 499.0826; Found 499.0827.

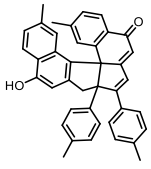
6-Hydroxy-9,13-dimethyl-4,4a-diphenyl-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one (2k)



Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 46.4 mg, 45% yield; mp: 272-273 °C; ^{1}H NMR (400 MHz, DMSO-d_6 / $CDCl_3$ = 3/10 v/v) (δ, ppm) 10.26 (s, 1H), 8.73 – 8.62 (m, 2H), 8.14 (s, 2H), 7.82 (s, 3H), 7.74 (s, 2H), 7.72 – 7.65 (m, 4H), 7.62 (d, J = 5.2 Hz, 2H), 7.52 (s, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.39 (d, J = 9.2 Hz, 2H), 4.99 (d, J = 16.8 Hz, 1H), 4.26 (d, J = 16.8 Hz, 1H), 1.84 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6 / $CDCl_3$ = 3/10 v/v) (δ, ppm) 189.8, 174.0, 167.6, 158.9, 149.8, 146.5, 144.9, 144.4, 140.4, 139.1, 136.3, 136.1, 135.0, 134.6, 134.1, 133.8, 133.7, 133.4, 133.3, 132.5, 132.0, 131.5, 130.7, 130.1, 128.1, 127.9, 126.8, 126.6, 109.8, 75.9, 74.5, 34.3, 26.7, 26.3.

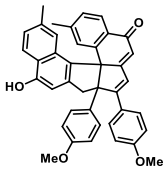
IR (KBr, v, cm^{-1}): 3129, 1656, 1533, 1465, 1321, 1032, 752; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{38}H_{27}O_2$ 515.2011; Found 515.2014.

6-Hydroxy-9,13-dimethyl-4,4a-di-p-tolyl-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one (2l)



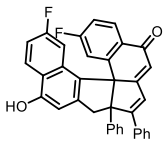
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 70.7 mg, 65% yield; mp: 264-265 °C; ^{1}H NMR (400 MHz, DMSO-d_6 / $CDCl_3$ = 3/10 v/v) (δ, ppm) 10.26 (s, 1H), 8.43 (s, 1H), 8.35 (s, 1H), 8.26 (d, *J* = 2.8 Hz, 2H), 7.51 (s, 2H), 7.47 (d, *J* = 8.0 Hz, 3H), 7.41 (s, 1H), 7.38 (s, 1H), 7.36 (s, 1H), 7.34 (s, 1H), 7.18 (d, *J* = 4.0 Hz, 2H), 7.15 (s, 1H), 4.87 (d, *J* = 16.8 Hz, 1H), 4.04 (d, *J* = 16.8 Hz, 1H), 2.73 (s, 3H), 2.65 (s, 3H), 2.61 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6 / $CDCl_3$ = 3/10 v/v)) (δ, ppm) 185.4, 169.9, 163.4, 154.3, 145.5, 142.0, 140.0, 139.3, 137.4, 136.7, 135.9, 132.1, 131.8, 131.6, 130.5, 129.6, 129.5, 129.2, 128.1, 126.9, 126.2, 125.6, 125.5, 123.5, 123.5, 123.4, 122.3(9), 122.3(7), 121.8(9), 121.8(6), 105.3, 71.2, 69.8, 22.2, 21.9, 21.6, 21.2. IR (KBr, *v*, cm^{-1}): 3624, 1621, 1523, 1434, 1345, 847, 782. HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{40}H_{31}O_2$ 543.2324; Found 543.2328.

6-Hydroxy-4,4a-bis(4-methoxyphenyl)-9,13-dimethyl-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2m)



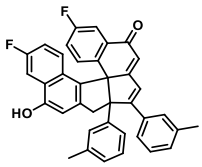
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 69.1 mg, 60% yield; mp: 230-231 °C; ^{1}H NMR (400 MHz, DMSO-d_6 / $CDCl_3$ = 3/10 v/v) (δ, ppm) 10.26 (s, 1H), 8.48 (s, 1H), 8.40 (s, 1H), 7.68 (m, 2H), 7.54 (s, 1H), 7.49 (s, 2H), 7.39 (s, 2H), 7.31 (d, *J* = 4.8 Hz, 2H), 7.22 (s, 1H), 7.19 (d, *J* = 3.6 Hz, 2H), 4.67 (d, *J* = 16.8 Hz, 1H), 4.39 (d, *J* = 16.8 Hz, 1H), 3.70 (s, 6H), 2.64 – 2.53 (m, 3H), 2.52 – 2.37 (m, 3H). ^{13}C NMR (400 MHz, DMSO-d_6 / $CDCl_3$ = 3/10 v/v) (δ, ppm) 185.0, 167.8, 156.2, 154.7, 154.6, 144.5, 144.4(3), 144.4(6), 139.5, 139.3, 137.3, 137.2, 132.4, 132.0, 131.9, 131.3, 128.6, 128.3(4), 128.3(7), 128.2, 128.1, 127.6, 127.2, 127.1, 127.0, 126.8, 126.7, 126.3, 125.7, 125.5, 125.4, 123.7, 122.6, 105.7(4), 105.7(6), 69.5, 69.4, 64.2, 24.7, 22.1. IR (KBr, *v*, cm^{-1}): 3737, 1730, 1567, 1487, 1363, 876, 709; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{40}H_{31}O_4$ 575.2222; Found 575.2228.

9,13-Difluoro-6-hydroxy-4,4a-diphenyl-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2n)



Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 73.4 mg, 70% yield; mp: 225-226 °C; ^{1}H NMR (400 MHz, DMSO-d_6 / $CDCl_3$ = 3/10 v/v) δ 10.52 (s, 1H), 8.16 (s, 1H), 8.01 (m, 3H), 7.47 (s, 3H), 7.33 (s, 2H), 7.28 – 7.26 (m, 3H), 7.21 (s, 1H), 7.13 (m, 2H), 7.02 (m, 3H), 5.75 (s, 1H), 4.83 (d, *J* = 17.2 Hz, 1H), 3.55 (d, *J* = 17.2 Hz, 1H). ^{13}C NMR (400 MHz, DMSO-d_6 / $CDCl_3$ = 3/10 v/v) (δ, ppm) 183.3, 169.5, 164.3 ($^1J_{CF}$ = 249.9 Hz), 162.4, 160.6 ($^2J_{CF}$ = 242.8 Hz), 154.8, 147.5, 147.4, 142.8, 139.8, 133.9, 131.7 ($^6J_{CF}$ = 9.3 Hz), 130.6, 129.8 ($^5J_{CF}$ = 9.5 Hz), 129.2, 129.1, 128.1, 128.0, 127.0, 122.0, 122.1, 115.5 ($^8J_{CF}$ = 5.3 Hz), 115.3 ($^7J_{CF}$ = 5.4 Hz), 113.5 ($^3J_{CF}$ = 24.8 Hz), 105.8 ($^4J_{CF}$ = 24.4 Hz), 79.8, 79.4, 79.1, 71.2, 69.5, 55.3. IR (KBr, *v*, cm^{-1}): 3677, 1626, 1588, 1044, 1390 710, 639; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{36}H_{21}F_2O_2$ 523.1510; Found 553.1514.

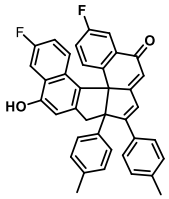
8,14-Difluoro-6-hydroxy-4,4a-di-m-tolyl-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2o)



Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 79.5 mg, 72% yield; mp: 195-196 °C; ^{1}H NMR (400 MHz, DMSO-d_6 / $CDCl_3$ = 3/10 v/v) (δ, ppm) 10.26 (s, 1H), 8.19 (t, 1H), 8.08 (d, *J* = 2.8 Hz, 1H), 7.91 – 7.85 (m, 1H), 7.53 – 7.48 (m, 1H), 7.28 – 7.17 (m, 4H), 7.17 – 7.07 (m, 3H), 6.99 – 6.91 (m, 4H), 6.88 (d, *J* = 6.8 Hz, 1H), 6.78

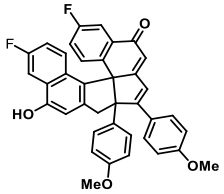
(s, 1H), 4.50 (d, *J* = 17.2 Hz, 1H), 3.80 (d, *J* = 4.8 Hz, 1H), 3.73 (d, *J* = 5.2 Hz, 3H), 3.70 (d, *J* = 4.8 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6/ $CDCl_3$ = 3/10 v/v)) (δ, ppm) 183.6, 170.2, 163.9, 160.0, 159.7, 154.0, 143.4, 141.6, 140.5, 135.6, 133.8, 133.0, 132.0(9), 132.0(6), 130.5 ($^5J_{CF}$ = 9.2 Hz), 130.0, 129.5 ($^3J_{CF}$ = 25.2 Hz), 127.3, 126.3, 126.0, 124.1, 121.7 ($^1J_{CF}$ = 232.6 Hz), 120.5 ($^2J_{CF}$ = 223.1 Hz), 120.6, 115.4, 113.1 ($^4J_{CF}$ = 19.6 Hz), 107.0, 100.0, 71.5, 69.5, 55.4, 55.3, 29.8. IR (KBr, *v*, cm^{-1}): 3646, 1691 1562, 1462, 1377, 793, 628; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{38}H_{25}F_2O_2$ 551.1823; Found 551.1825.

8,14-Difluoro-6-hydroxy-4,4a-di-p-tolyl-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2p)



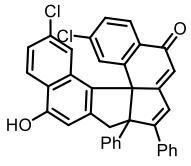
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 88.3 mg, 80% yield; mp: 199-200 °C; ^{1}H NMR (400 MHz, DMSO-d_6/ $CDCl_3$ = 3/10 v/v) (δ, ppm) 10.26 (s, 1H), 8.09 (s, 1H), 7.79 (s, 3H), 7.62 – 7.58 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.18 – 7.14 (m, 3H), 7.10 – 7.04 (m, 4H), 6.96 (s, 1H), 6.93 (s, 1H), 4.57 (d, *J* = 17.6 Hz, 1H), 3.75 (d, *J* = 16.8 Hz, 1H), 2.40 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6/ $CDCl_3$ = 3/10 v/v) (δ, ppm) 188.1, 175.2, 168.4, 165.9 ($^1J_{CF}$ = 220.6 Hz), 163.4 ($^2J_{CF}$ = 217.9 Hz), 158.6, 158.5, 144.1, 141.5, 141.4, 139.0, 138.9, 137.0(1), 136.(9), 136.0, 135.8, 134.3 ($^7J_{CF}$ = 3.0 Hz), 134.2, 133.2, 132.8, 132.7, 131.4, 131.0 ($^5J_{CF}$ = 8.1 Hz), 129.5 ($^6J_{CF}$ = 8.1 Hz), 125.9, 124.1 ($^4J_{CF}$ = 22.0 Hz), 121.1 ($^3J_{CF}$ = 22.4 Hz), 111.4, 75.9, 74.1, 34.3, 26.1, 25.7. IR (KBr, *v*, cm^{-1}): 3651, 1673 1543, 1409, 1370, 751, 662; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{38}H_{25}F_2O_2$ 551.1823; Found 551.1826. IR (KBr, *v*, cm^{-1}): 3651, 1673 1543, 1409, 1370, 751, 662; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{38}H_{25}F_2O_2$ 551.1823; Found 551.1826.

8,14-Difluoro-6-hydroxy-4,4a-bis(4-methoxyphenyl)-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2q)



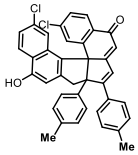
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 71.2 mg, 61% yield; mp: 270-271 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (*δ*, ppm) 10.48 (s, 1H), 7.70 – 7.66 (m, 1H), 7.59 (m, 1H), 7.48 – 7.38 (m, 2H), 7.24 (d, *J* = 8.8 Hz, 5H), 7.19 – 7.11 (m, 2H), 7.04 (d, *J* = 6.0 Hz, 1H), 6.92 – 6.80 (m, 5H), 6.74 (d, *J* = 8.4 Hz, 2H), 4.64 (d, *J* = 17.2 Hz, 1H), 3.73 (s, 3H), 3.62 (s, 3H), 3.57 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (*δ*, ppm) 183.2, 183.1, 171.1, 163.2, 160.5, 161.2 ($^2J_{CF}$ = 220.1 Hz), 158.7 ($^1J_{CF}$ = 223.5 Hz) , 158.5, 153.8, 153.8, 141.2 ($^7J_{CF}$ = 3.1 Hz), 140.2 ($^8J_{CF}$ = 2.6 Hz), 134.4, 134.3, 132.4, 132.0 ($^6J_{CF}$ = 7.9 Hz), 131.8, 129.9, 128.3, 128.2, 127.8, 126.4, 126.0 ($^5J_{CF}$ = 8.1 Hz), 121.0, 119.7($^4J_{CF}$ = 22.6 Hz), 116.9 ($^3J_{CF}$ = 24.8 Hz) 114.8, 114.3, 111.6, 111.4, 107.4, 107.2, 107.1, 100.0, 70.9, 69.3, 55.8, 55.3. IR (KBr, *v*, cm^{-1}): 3673, 1668, 1558, 1420, 1382, 741, 668; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{38}H_{25}F_2O_4$ 583.1721; Found 583.1732.

9,13-Dichloro-6-hydroxy-4,4a-diphenyl-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2r)



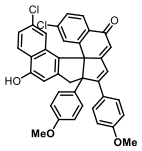
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 83.6 mg, 75% yield; mp: 300-301 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 10.65 (s, 1H), 8.18 – 8.08 (m, 1H), 7.96 – 7.91 (m, 1H), 7.49 (d, J = 6.8 Hz, 1H), 7.41 (s, 4H), 7.37 – 7.28 (m, 5H), 7.27 – 7.19 (m, 5H), 7.13 (d, J = 6.8 Hz, 1H), 7.01 (s, 1H), 6.89 (d, J = 5.6 Hz, 2H), 4.81 (d, J = 17.6 Hz, 1H), 3.56 (d, J = 17.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 183.3, 169.4, 162.4, 154.7, 146.2, 142.9, 139.7, 137.3, 133.8, 132.0, 131.5, 130.9, 130.0, 129.9, 129.8, 129.3, 129.2, 128.6, 128.1, 126.9, 126.2, 124.3, 123.4, 121.9, 121.0, 106.7, 71.2, 69.2, 38.5. IR (KBr, v, cm^{-1}): 3674, 1622, 1558, 1034, 1320 780, 669; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{36}H_{21}Cl_2O_2$ 555.0919; Found 515.0914.

9,13-Dichloro-6-hydroxy-4,4a-di-p-tolyl-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2s)



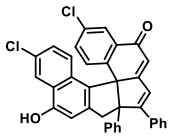
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 84.2 mg, 72% yield; mp: 251-252 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 10.63 (s, 1H), 8.08 (d, J = 8.8 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 1.2 Hz, 1H), 7.32 – 7.22 (m, 5H), 7.15 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 9.2 Hz, 3H), 6.86 (s, 2H), 4.76 (d, J = 17.6 Hz, 1H), 3.55 (d, J = 17.6 Hz, 1H), 2.25 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 183.3, 170.1, 162.8, 160.6, 158.6, 154.7, 146.5, 142.9, 137.3, 131.9, 131.9, 131.7, 131.6, 131.1, 130.7, 129.9(2), 129.9(7), 128.6, 128.2, 128.0, 126.3, 126.2, 123.4, 121.2, 114.8, 114.4, 106.8, 70.9, 69.1, 55.7, 55.4, 21.3, 20.9. IR (KBr, v, cm^{-1}): 3735, 1700, 1507, 1457, 1375, 887, 740; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{38}H_{25}Cl_2O_2$ 583.1232; Found 583.1241.

9,13-Dichloro-6-hydroxy-4,4a-bis(4-methoxyphenyl)-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2t)



Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 67.9 mg, 55% yield; mp: 255-256 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 10.63 (s, 1H), 8.08 (d, J = 9.2 Hz, 1H), 7.95 (d, J = 10.4 Hz, 1H), 7.43 (d, J = 1.2 Hz, 1H), 7.28 (d, J = 2.0 Hz, 1H), 7.25 (d, J = 8.8 Hz, 3H), 7.21 (d, J = 8.8 Hz, 3H), 7.02 (s, 1H), 6.87 (d, J = 8.0 Hz, 3H), 6.83 (s, 1H), 6.76 (d, J = 8.0 Hz, 2H), 4.74 (d, J = 17.6 Hz, 1H), 3.73 (s, 3H), 3.63 (s, 3H), 3.58 (d, J = 17.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 183.3, 170.1, 162.8(0), 162.8(7), 160.6, 158.6, 154.7, 146.5, 142.9, 137.3, 131.9, 131.7, 131.6, 131.1, 130.7, 129.9, 128.7, 128.2(2), 128.2(5), 128.0, 127.7, 126.3, 126.2, 124.3, 123.4, 121.2, 121.2, 114.8, 114.4, 106.8, 70.9, 69.1, 55.8, 55.4. IR (KBr, v, cm^{-1}): 3628, 1684, 1589, 1457, 1380, 886, 746; HRMS (ESI) m/z: [M-H]$^-$ Calcd for $C_{38}H_{25}Cl_2O_4$ 615.1130; Found 615.1132.

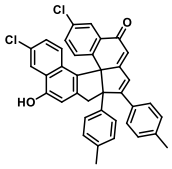
8,14-Dichloro-6-hydroxy-4,4a-diphenyl-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one (2u)



Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 79.1 mg, 71% yield; mp:301-302 °C; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 10.62 (s, 1H), 8.04 (s, 1H), 7.85 (s, 1H), 7.41 – 7.35 (m, 4H), 7.31 (d, J = 5.6 Hz, 4H), 7.26 – 7.22 (m, 3H), 7.19 (d, J = 6.4 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.90 (s, 2H), 4.71 (d, J = 17.6 Hz, 1H), 3.58 (d, J = 17.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 177.6, 164.9, 157.5, 148.5, 138.1, 136.3, 134.4, 128.6, 128.4,

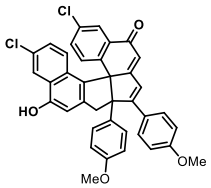
127.1, 126.8, 126.3, 126.2, 124.7, 124.6, 124.0(9), 124.0(6), 123.9, 123.7, 122.9, 122.7, 122.3, 121.7, 120.7, 120.0, 118.8, 117.4, 116.6, 102.0, 66.1, 64.0. IR (KBr, *v*, cm^{-1}): 3676, 1638, 1560, 1044, 1323, 775, 670; HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{36}H_{21}Cl_2O_2$ 555.0919; Found 555.0914.

8,14-Dichloro-6-hydroxy-4,4a-di-p-tolyl-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2v)

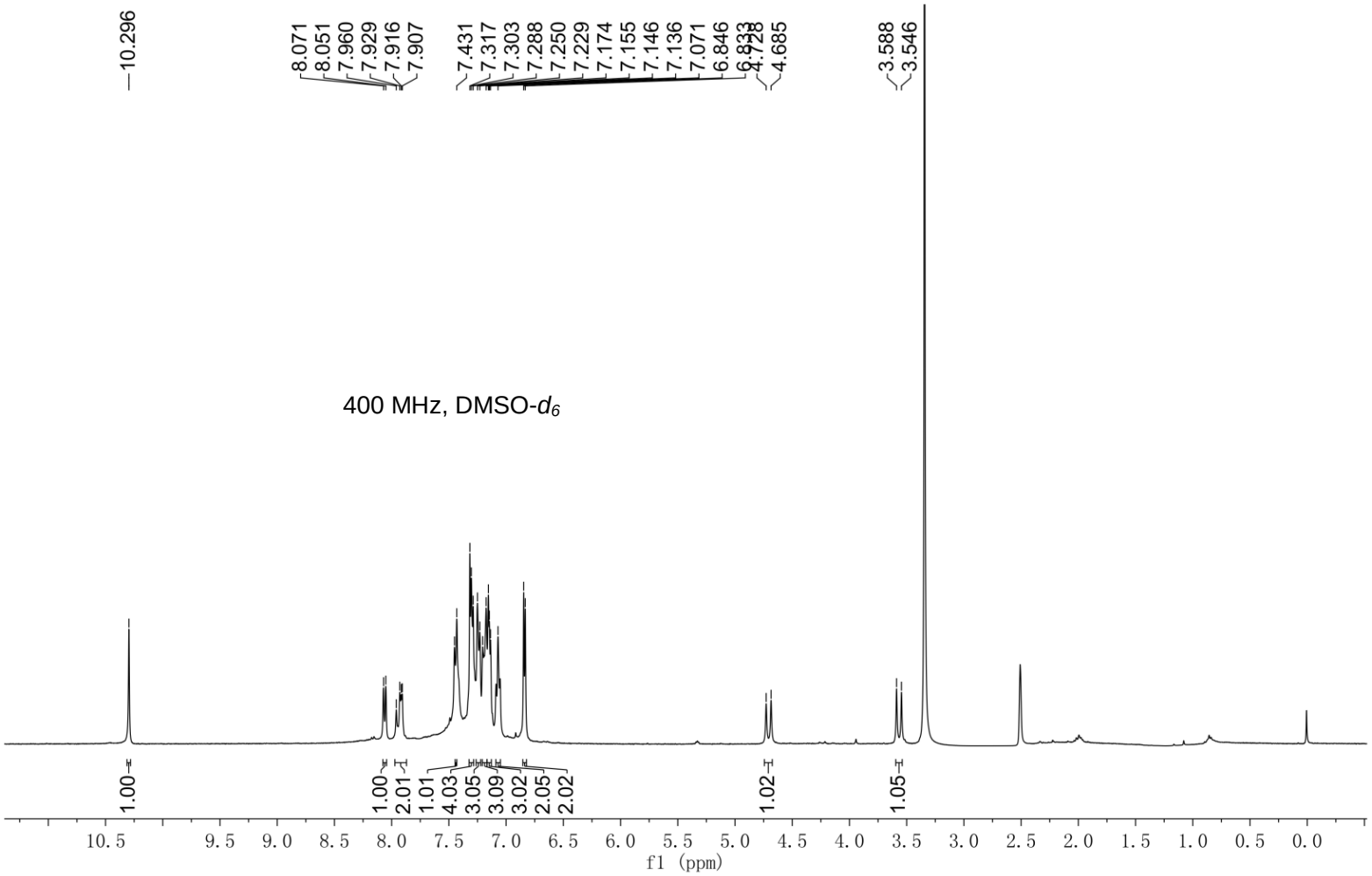


Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 95.9 mg, 82% yield; mp: 229-230 °C; ^{1}H NMR (400 MHz, DMSO-d_6 / $CDCl_3$ = 3/10 v/v) (δ, ppm) 10.25 (s, 1H), 8.20 (s, 1H), 8.07 (s, 1H), 7.96 – 7.84 (m, 2H), 7.52 (s, 1H), 7.35 (s, 1H), 7.19 (s, 3H), 7.14 (d, *J* = 9.6 Hz, 3H), 7.10 (d, *J* = 5.2 Hz, 1H), 7.05 (d, *J* = 5.2 Hz, 2H), 6.97 – 6.94 (m, 1H), 6.93 – 6.88 (m, 1H), 4.53 (d, *J* = 10.4 Hz, 1H), 3.76 (d, *J* = 10.8 Hz, 1H), 2.40 (m, 3H), 2.32 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6 / $CDCl_3$ = 3/10 v/v)) (δ, ppm) 183.6, 170.5, 164.1, 153.9(0), 153.9(6), 143.5, 140.7, 140.6, 139.7, 137.1, 136.6, 133.9, 132.9, 132.2, 131.9, 131.4, 130.6, 129.8, 129.6, 128.1(4), 128.1(0), 126.8(1), 126.8(7), 124.1, 122.9, 121.5, 107.1, 100.0, 78.9, 71.4, 71.3, 69.5(0), 69.5(6), 29.8, 21.6(1), 21.6(7), 21.2(2), 21.2(7). IR (KBr, *v*, cm^{-1}): 3638, 1641, 1548, 1421, 1350, 838, 701; HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{38}H_{25}Cl_2O_2$ 583.1232; Found 583.1235.

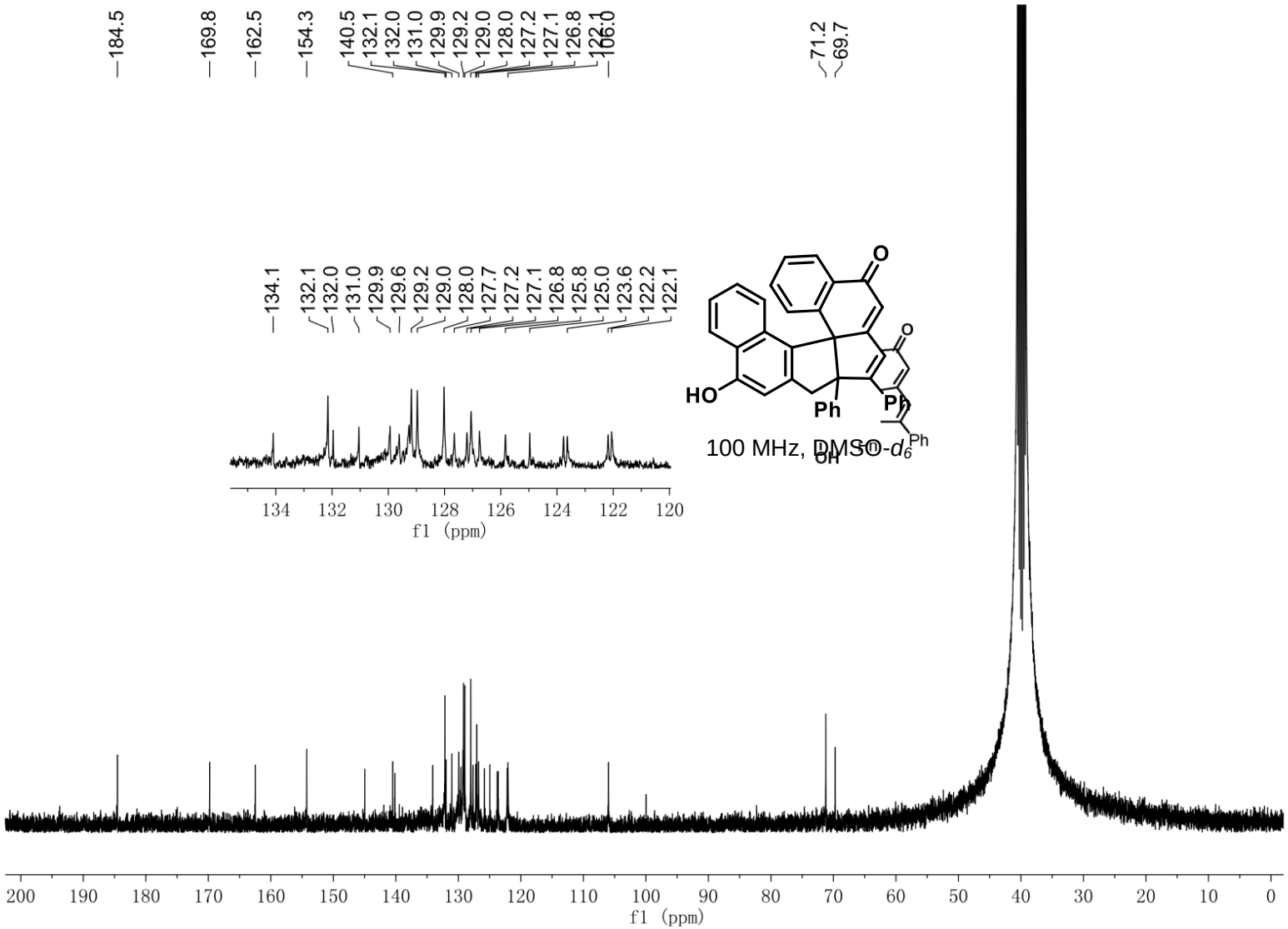
8,14-Dichloro-6-hydroxy-4,4a-bis(4-methoxyphenyl)-4a,5-dihydro-1H-pentaleno[6a,6-a:1,2-b']dinaphthalen-1-one(2w)



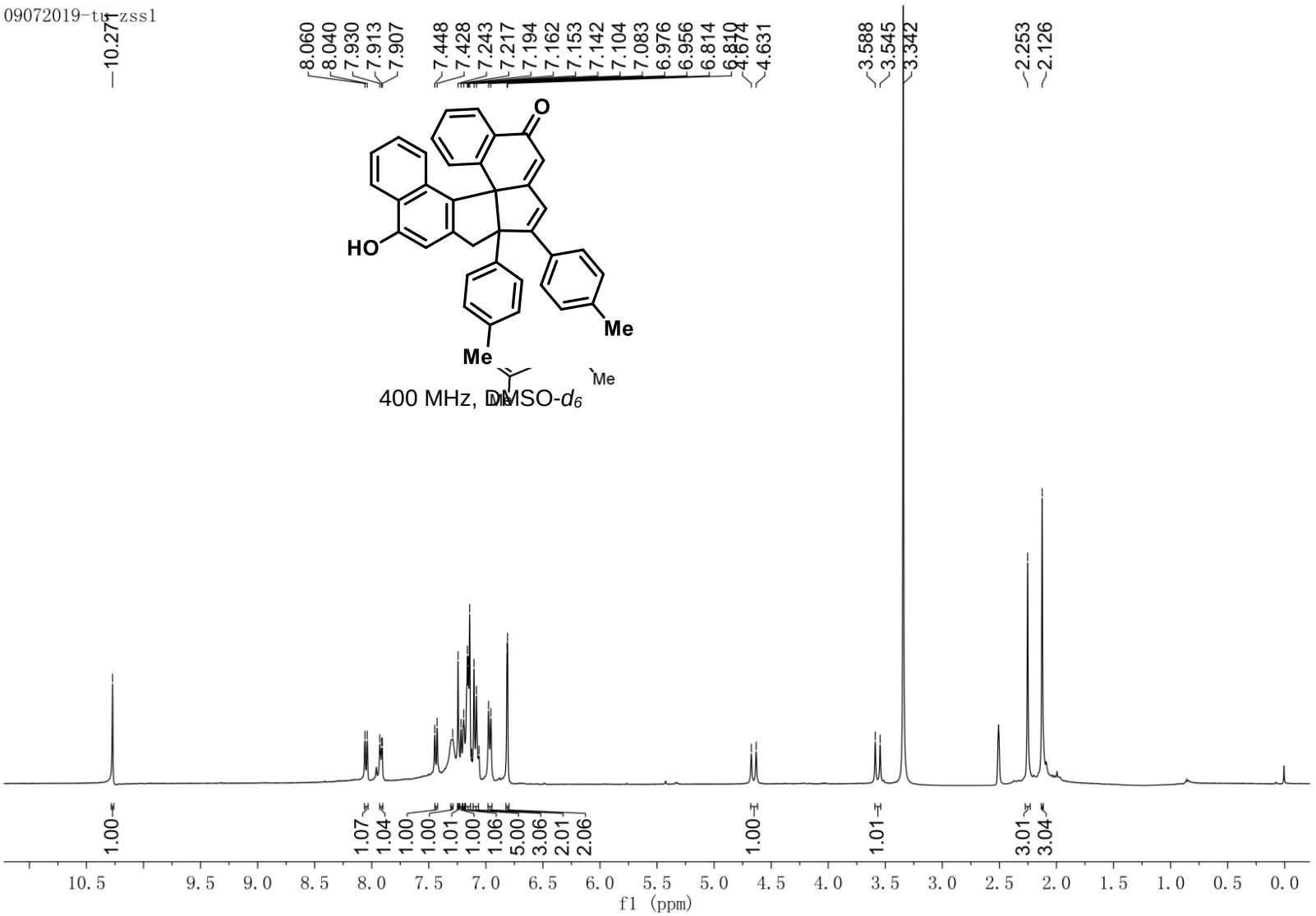
Isolation by column chromatography (PE/EA= 2/1 v/v) Yellow solid; 80.2 mg, 65% yield; mp: 230-231 °C; ^{1}H NMR (400 MHz, DMSO-*d6*; δ, ppm) 10.60 (s, 1H), 8.03 (d, *J* = 2.0 Hz, 1H), 7.86 (d, *J* = 2.0 Hz, 1H), 7.38 (s, 1H), 7.30 – 7.26 (m, 2H), 7.25 – 7.19 (m, 5H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.89 – 6.83 (m, 5H), 6.74 (d, *J* = 8.4Hz, 2H), 4.64 (d, *J* = 17.2 Hz, 1H), 3.73 (s, 3H), 3.63 (s, 3H), 3.58 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d6; δ, ppm) 182.8, 170.7, 163.1, 160.6, 158.6, 153.7, 143.6, 141.7, 133.9, 132.3, 132.1, 132.0, 131.7, 131.6, 129.9, 129.3, 128.9, 128.3, 127.8, 127.5, 126.3, 125.9, 125.3, 124.2, 122.6, 121.1, 114.8, 114.4, 107.4, 70.9, 69.1, 60.3, 55.8, 55.4, 40.3, 40.1, 39.9. IR (KBr, *v*, cm^{-1}): 3630, 1692, 1585, 1475, 1382, 862, 750; HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{38}H_{26}Cl_2O_4$ 615.1130; Found 615.1132.



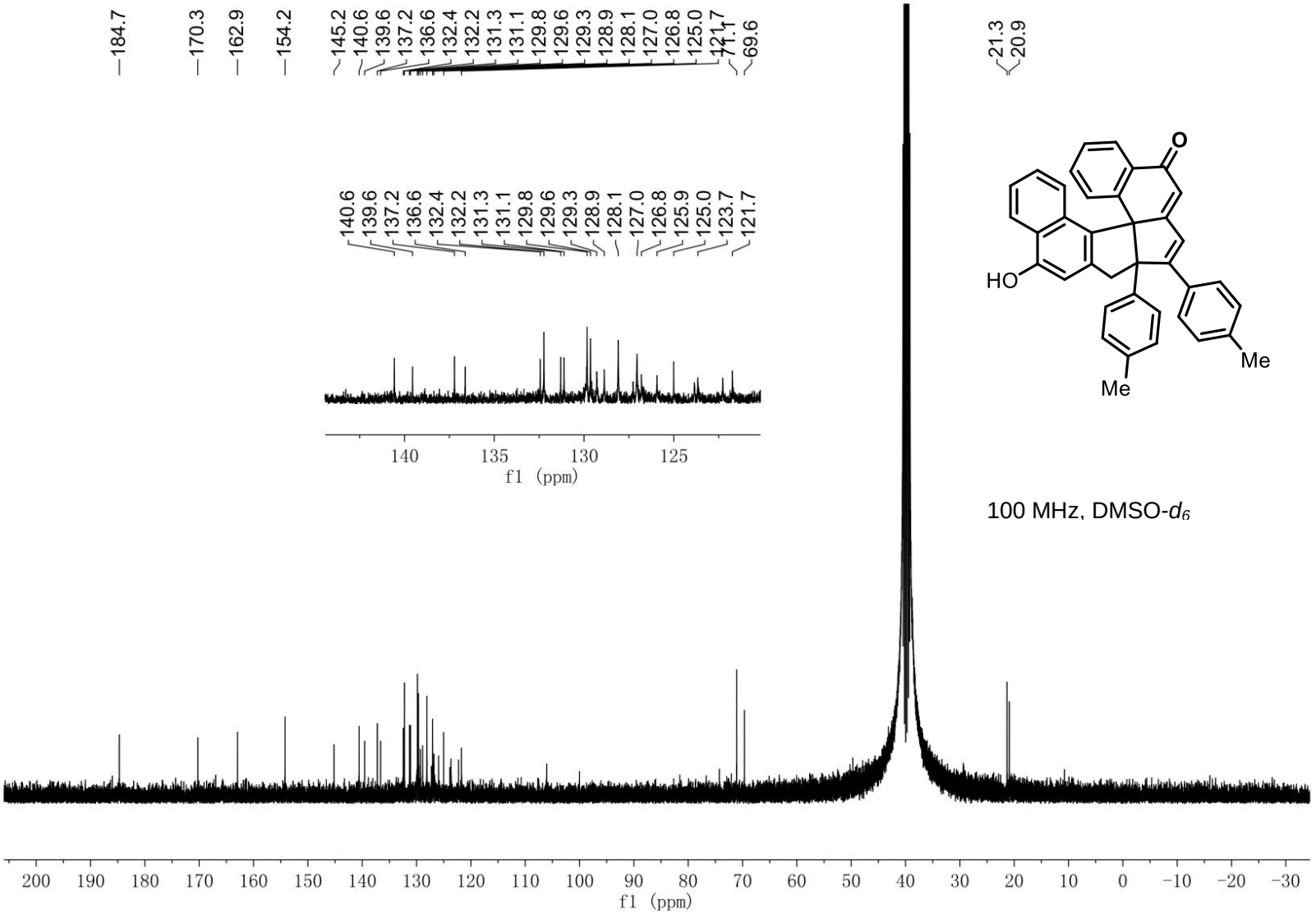
^{1}H NMR Spectrum of Compound 2a



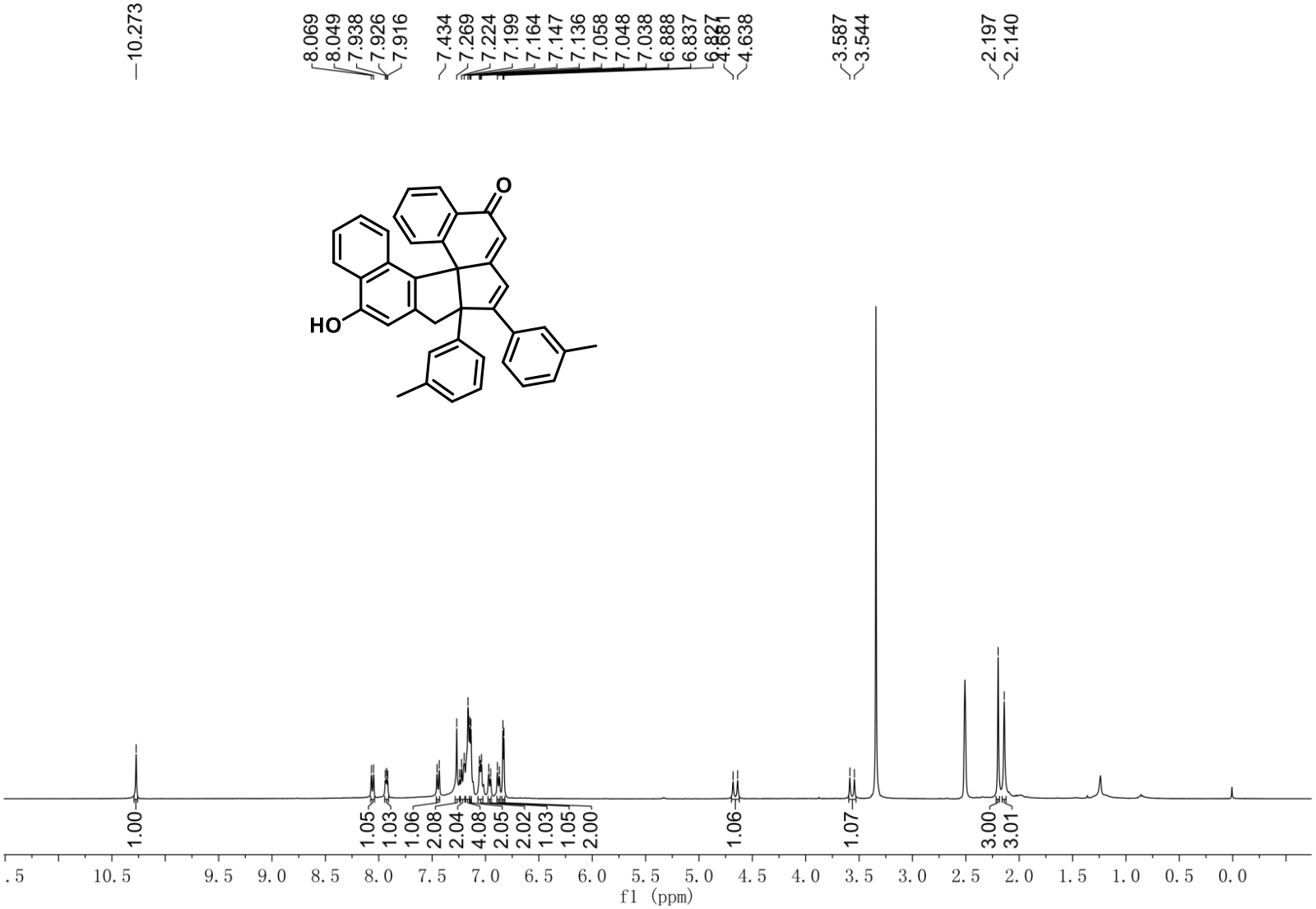
^{13}C NMR Spectrum of Compound 2a



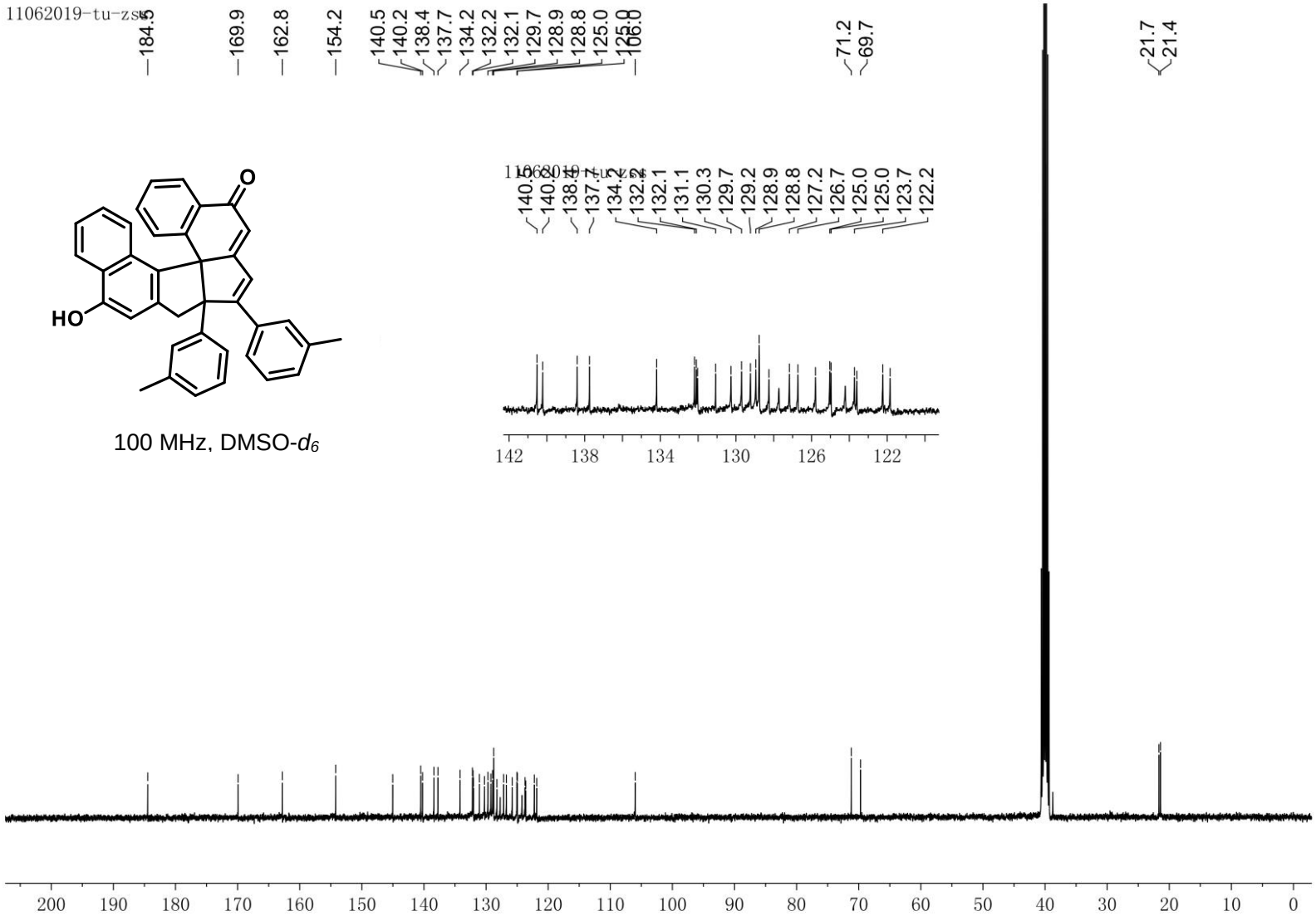
^{1}H NMR Spectrum of Compound 2b



^{13}C NMR Spectrum of Compound 2b

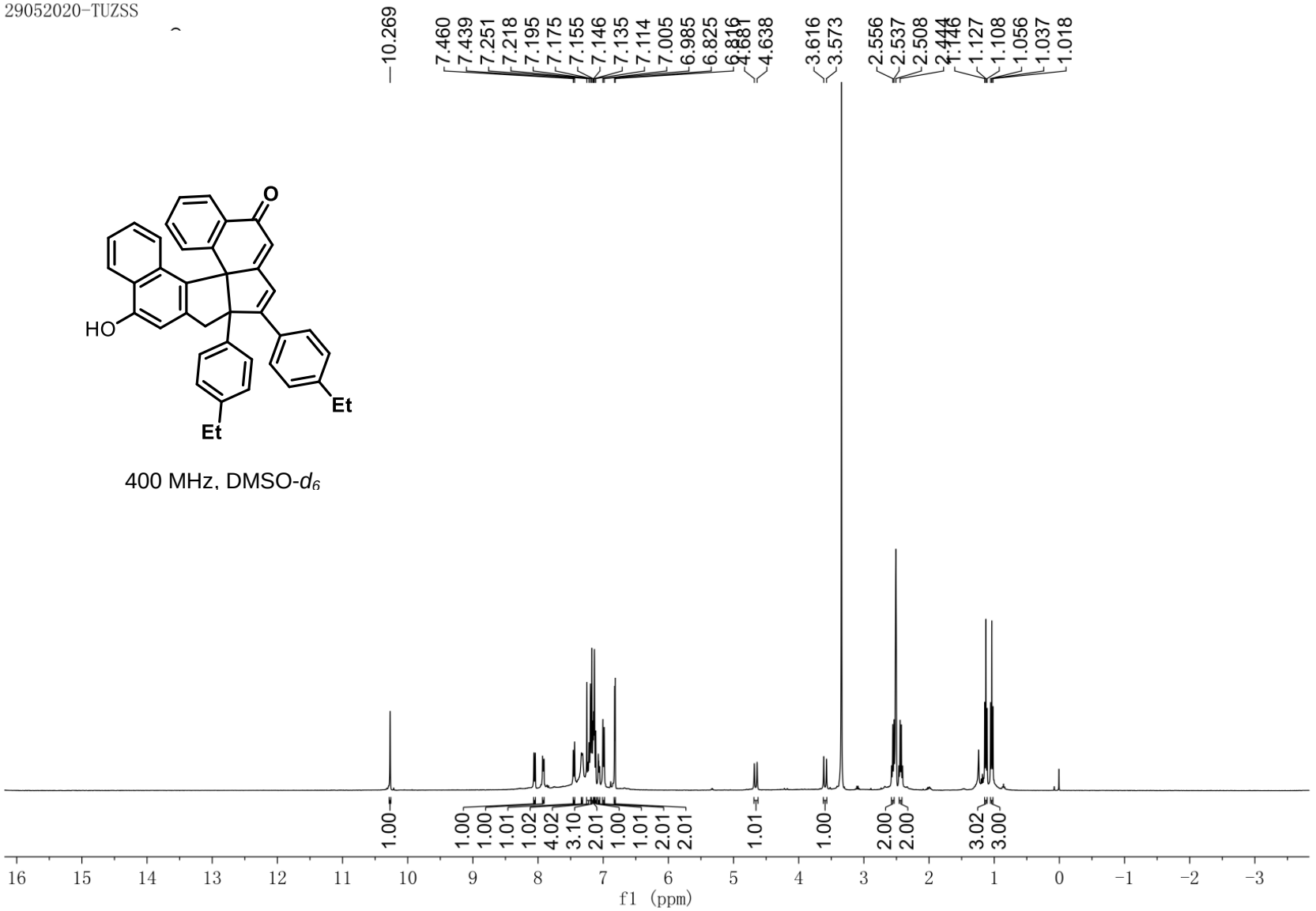


^{1}H NMR Spectrum of Compound 2c

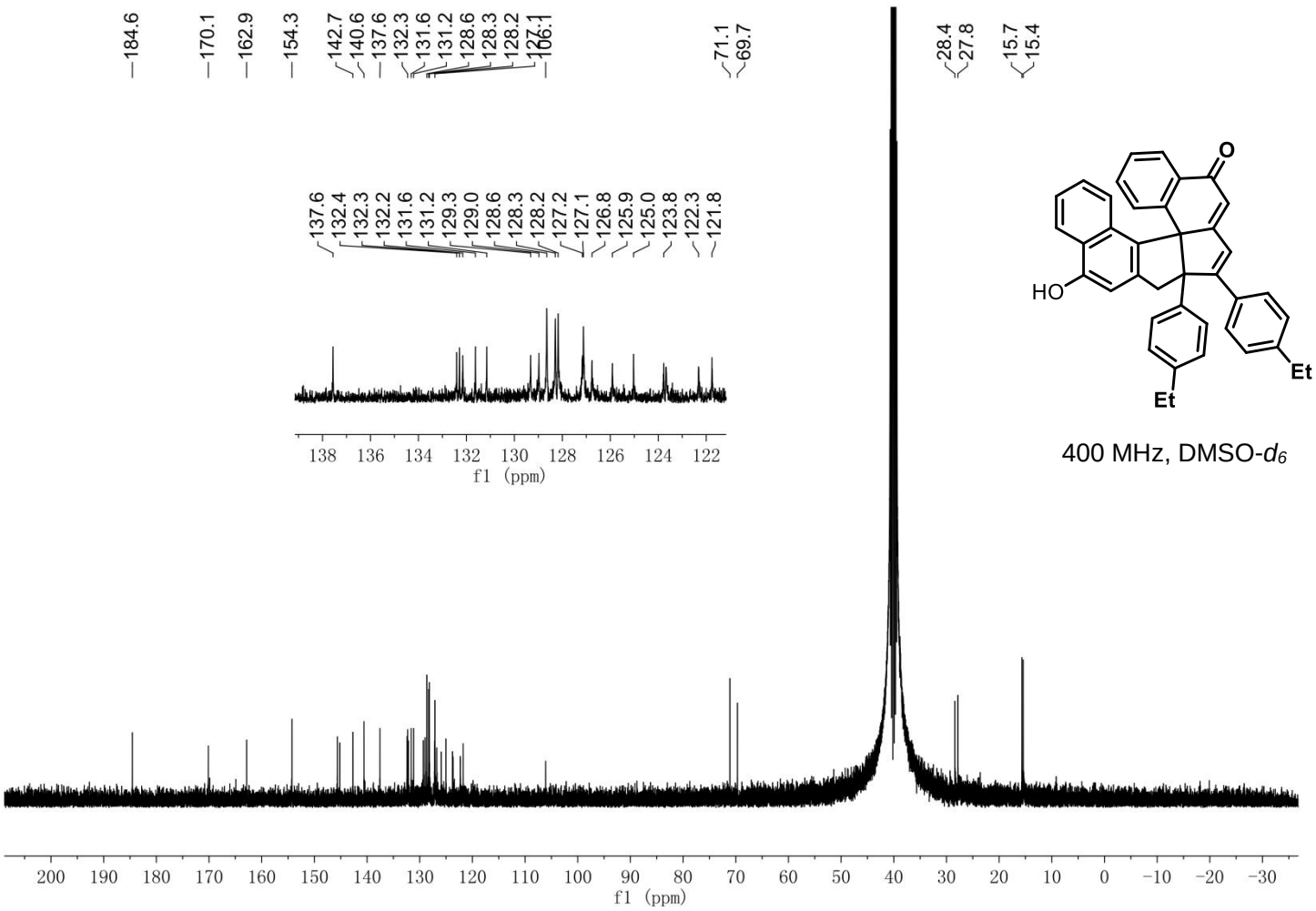


100 MHz, DMSO-d_6

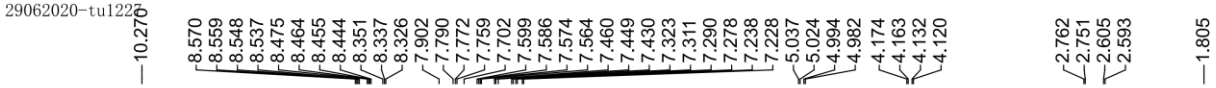
^{13}C NMR Spectrum of Compound 2c

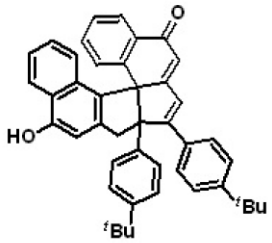


^{1}H NMR Spectrum of Compound 2d

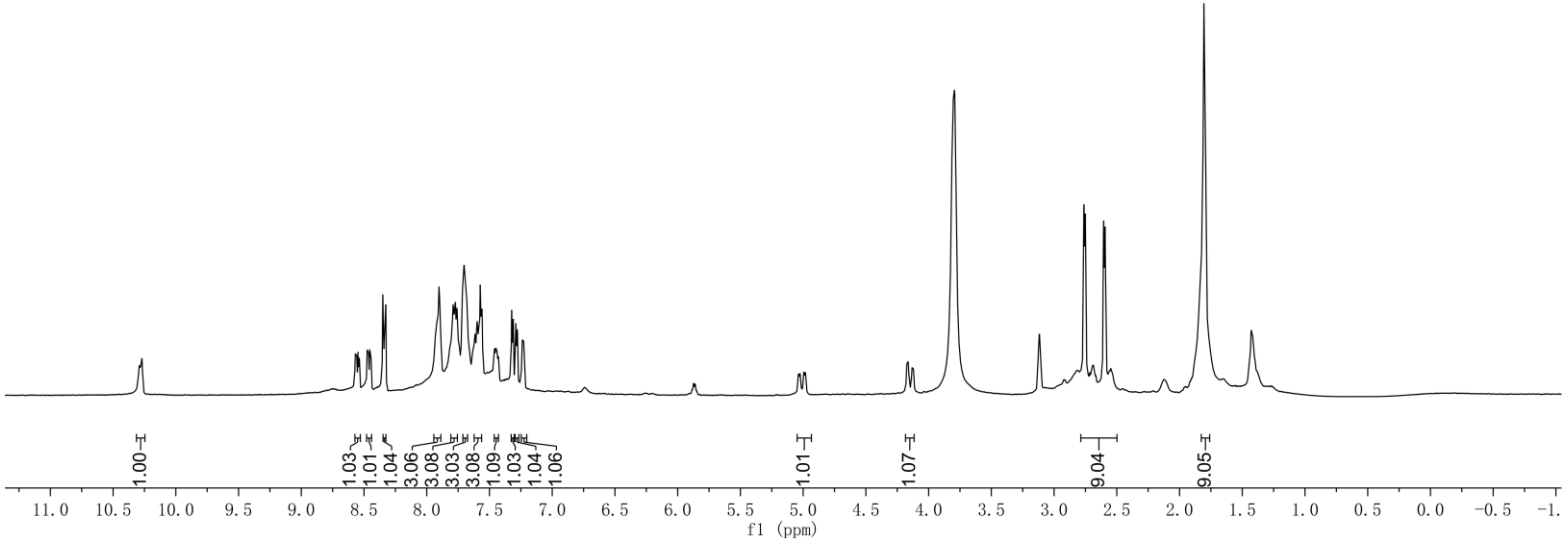


^{13}C NMR Spectrum of Compound 2d

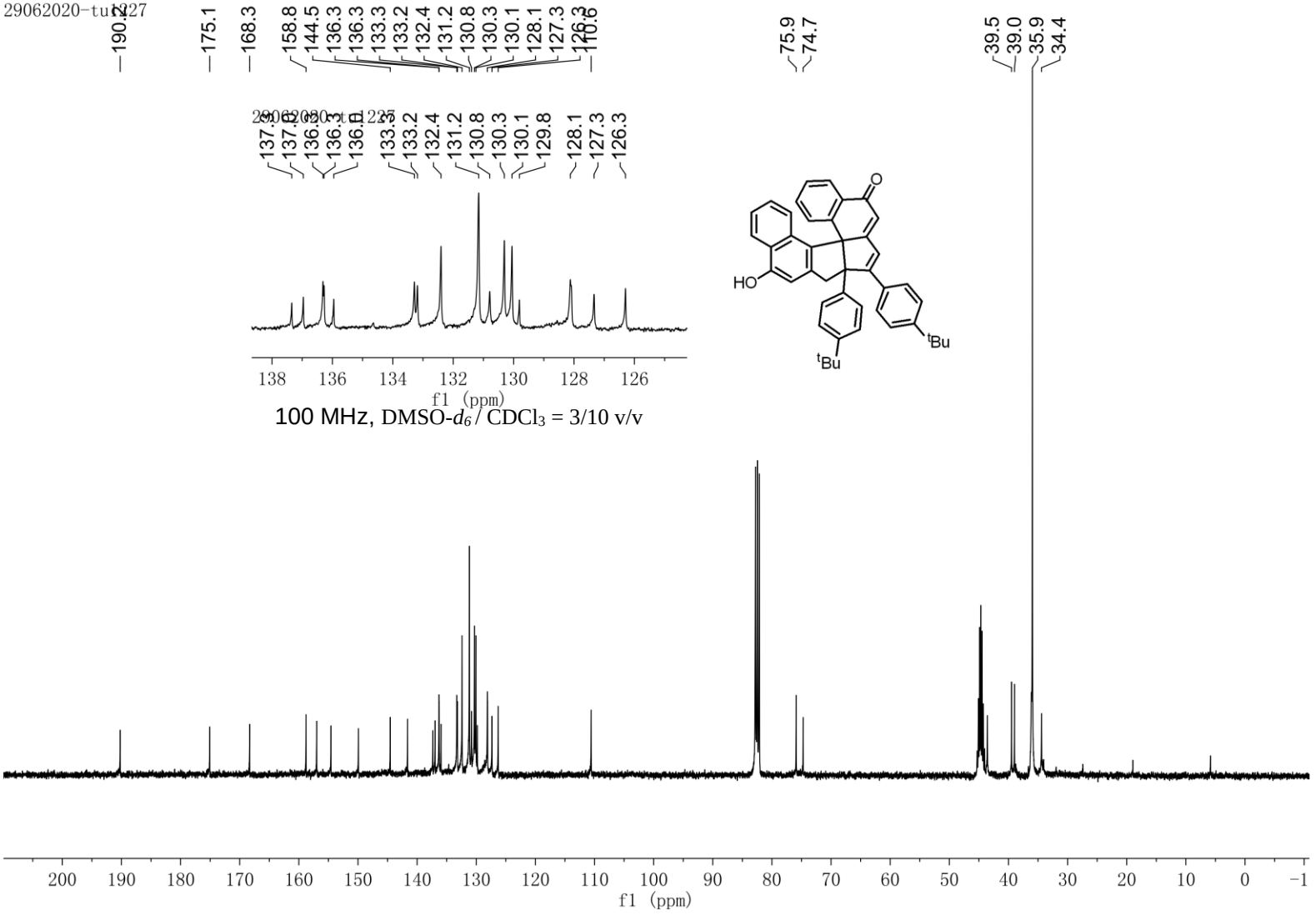




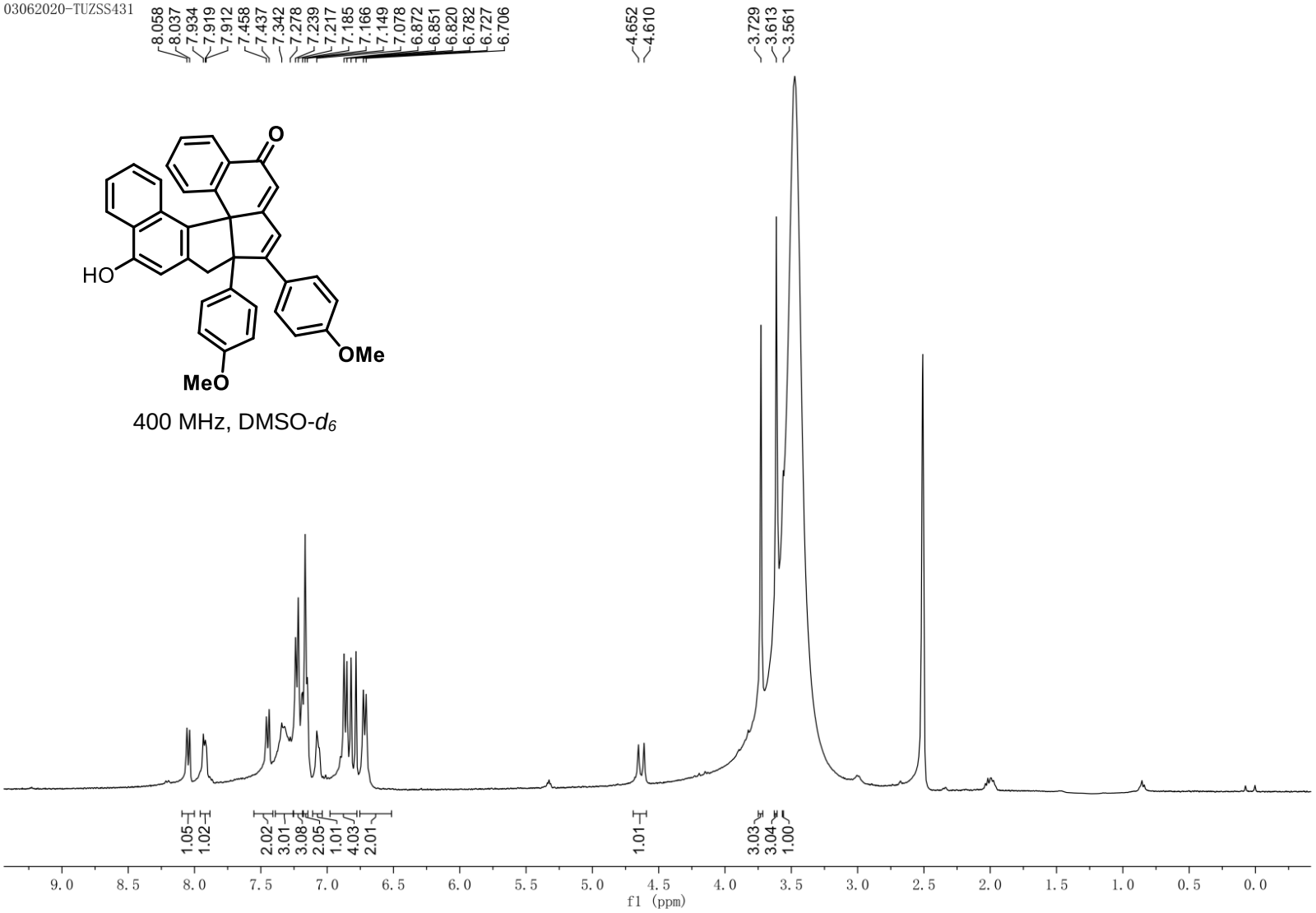
400 MHz, DMSO-d_6 / $CDCl_3$ = 3/10 v/v



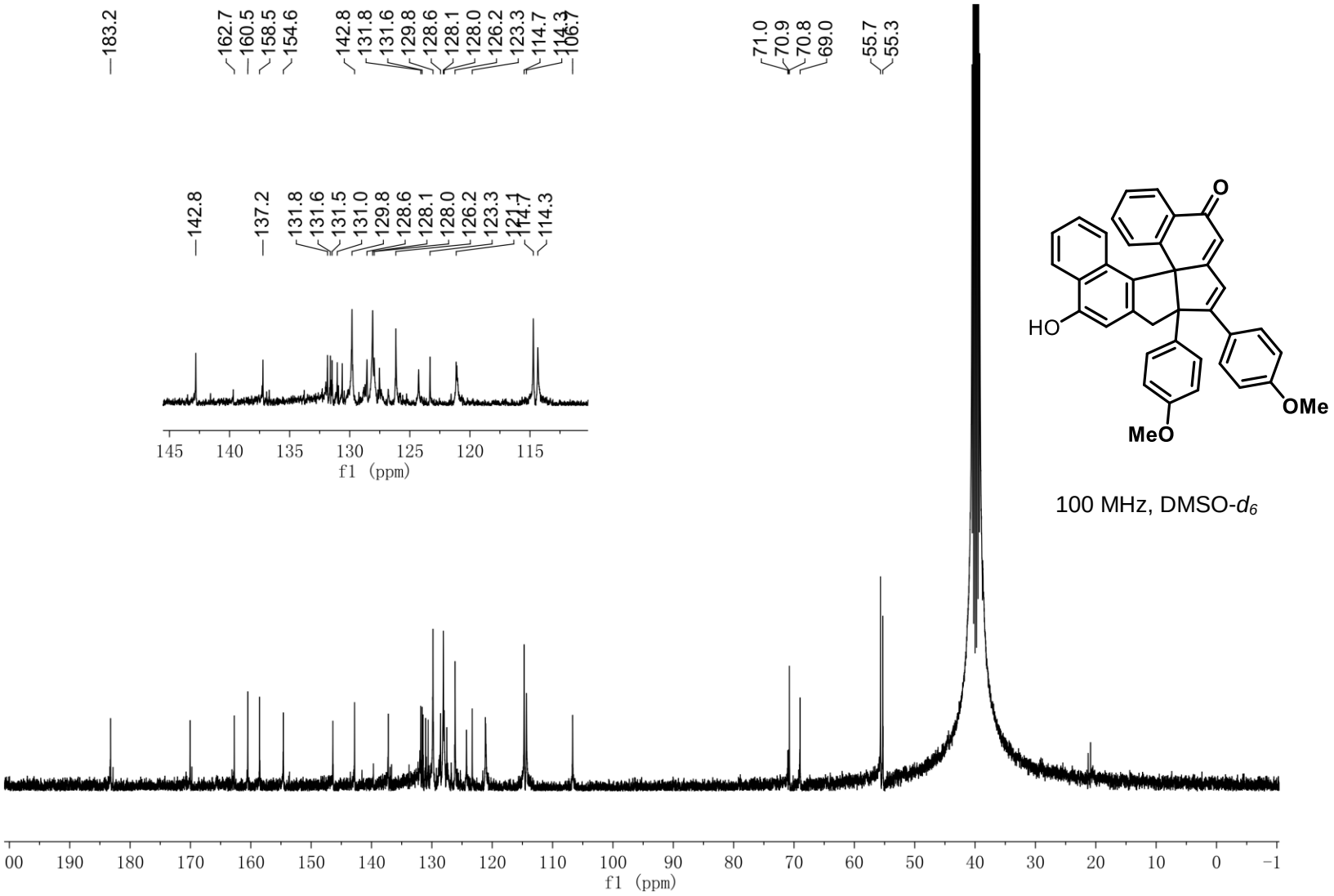
^{1}H NMR Spectrum of Compound 2e



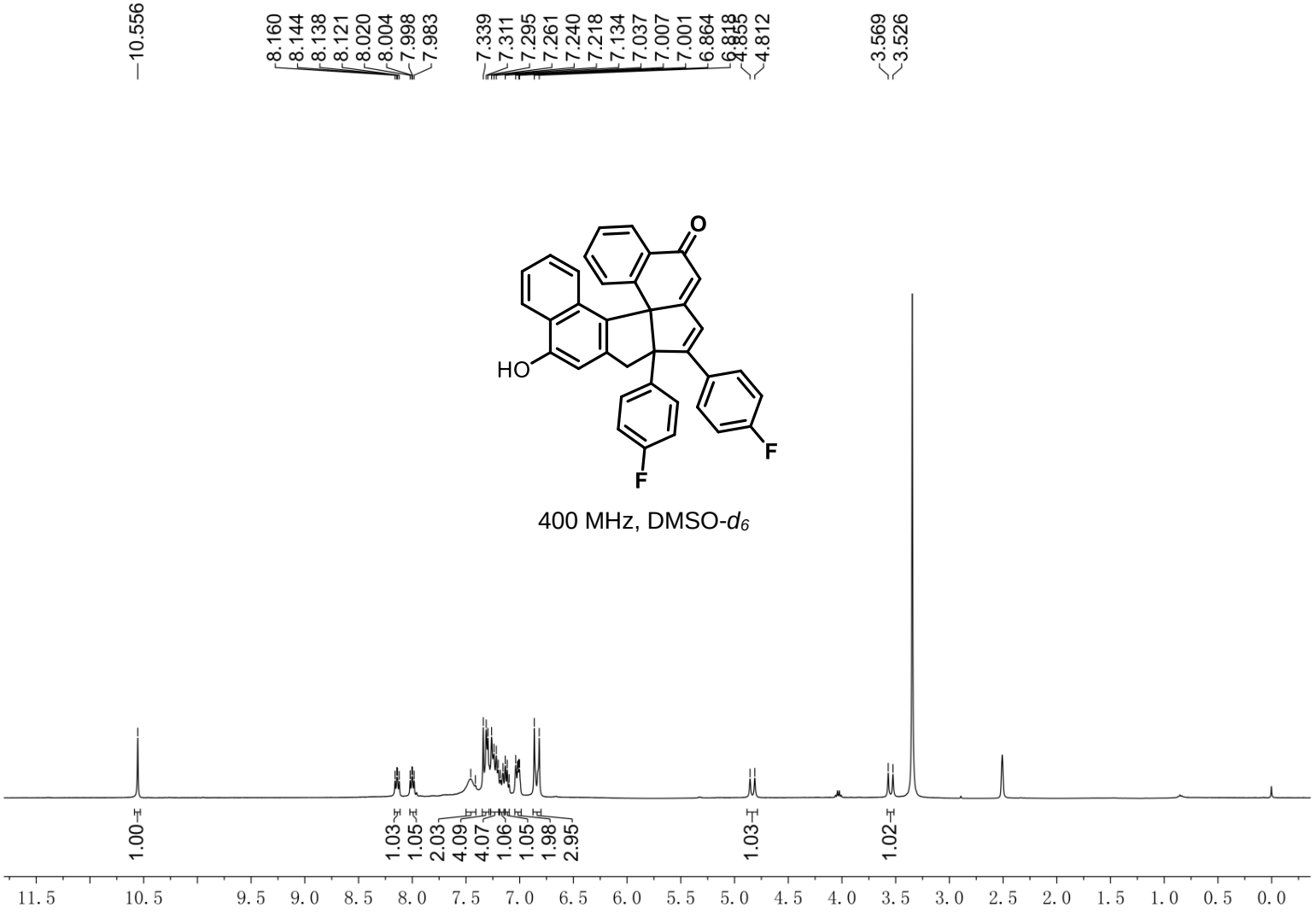
^{13}C NMR Spectrum of Compound 2e



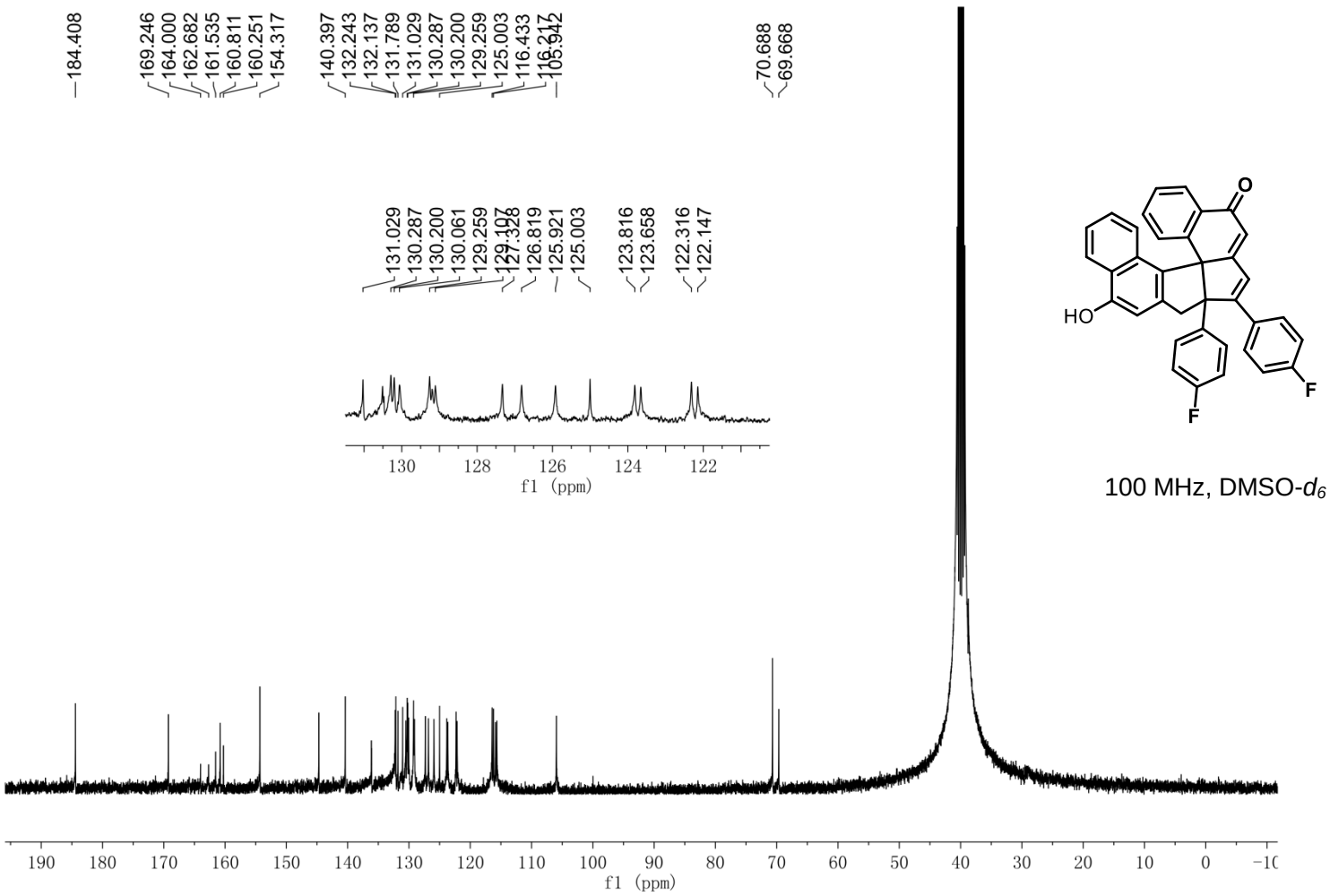
^{1}H NMR Spectrum of Compound 2f



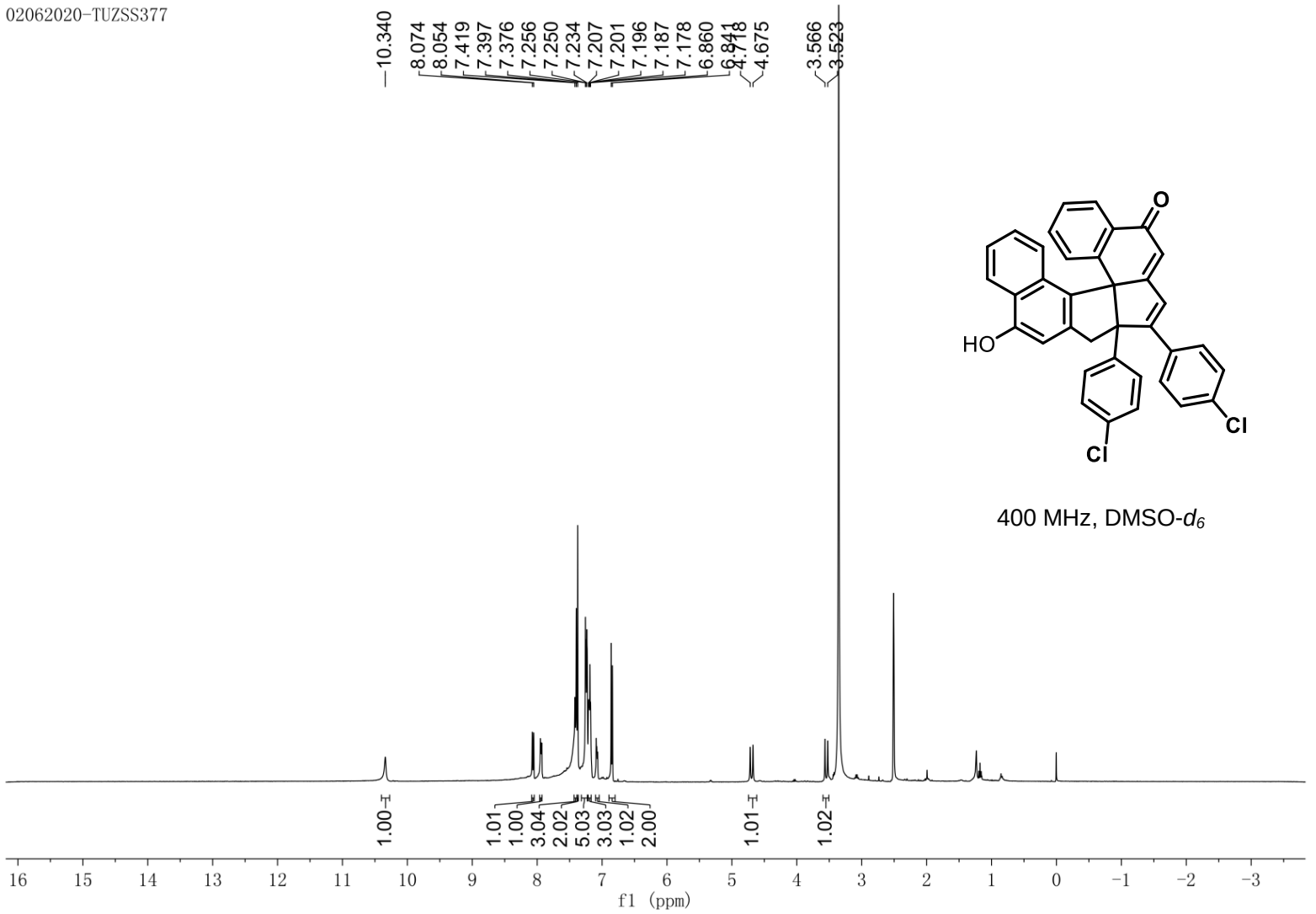
^{13}C NMR Spectrum of Compound 2f



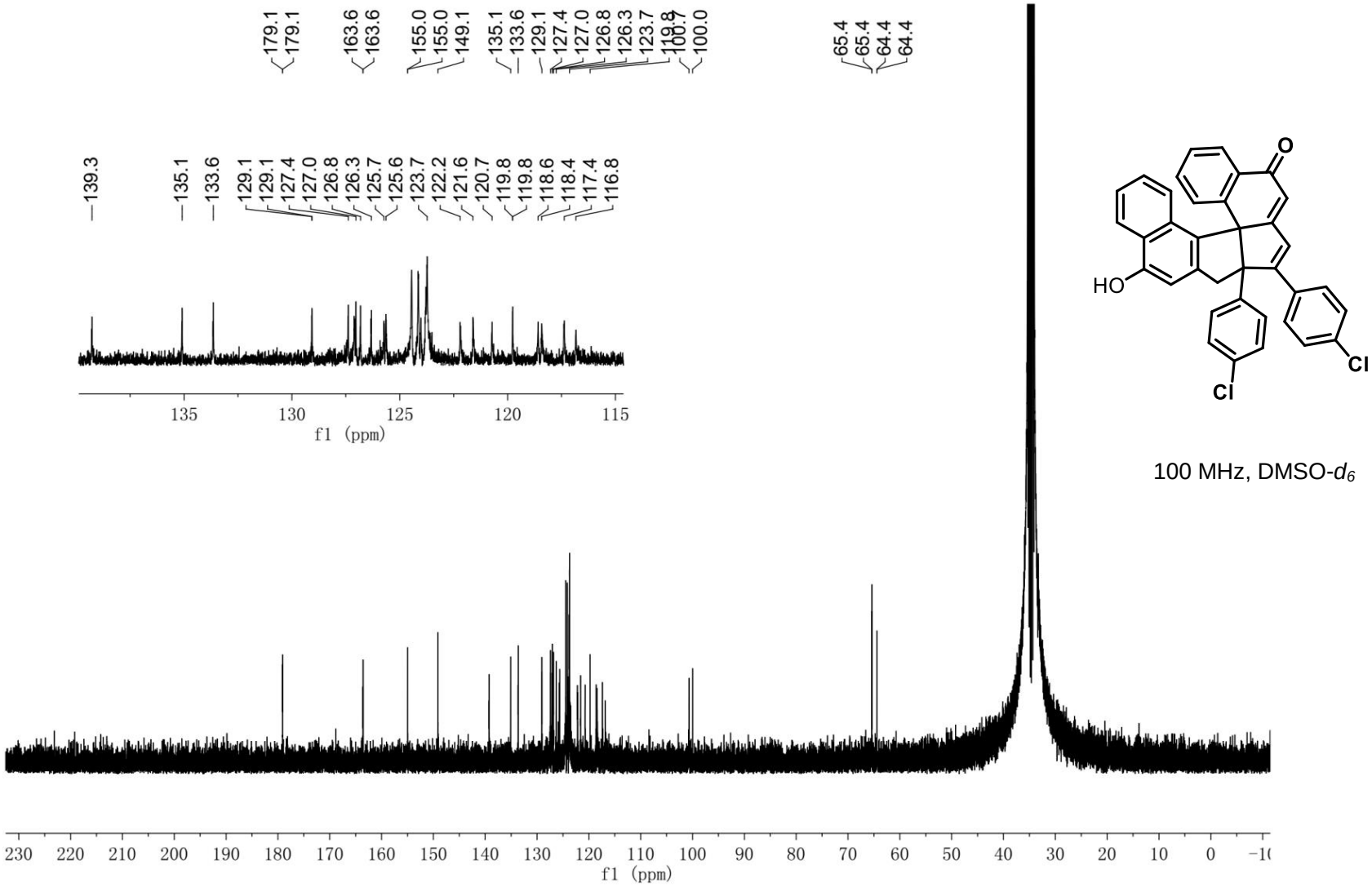
^{1}H NMR Spectrum of Compound 2g



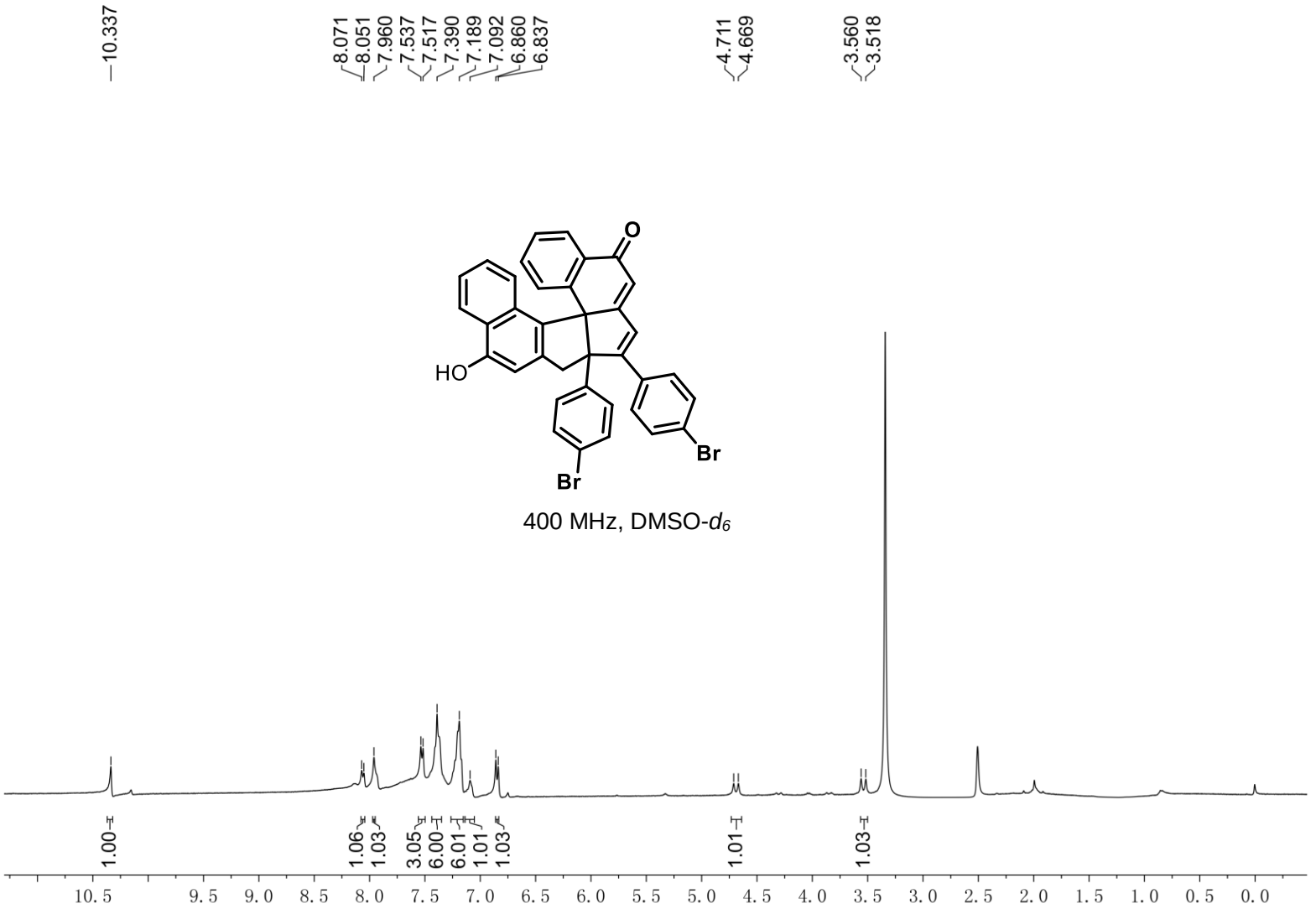
^{13}C NMR Spectrum of Compound 2g



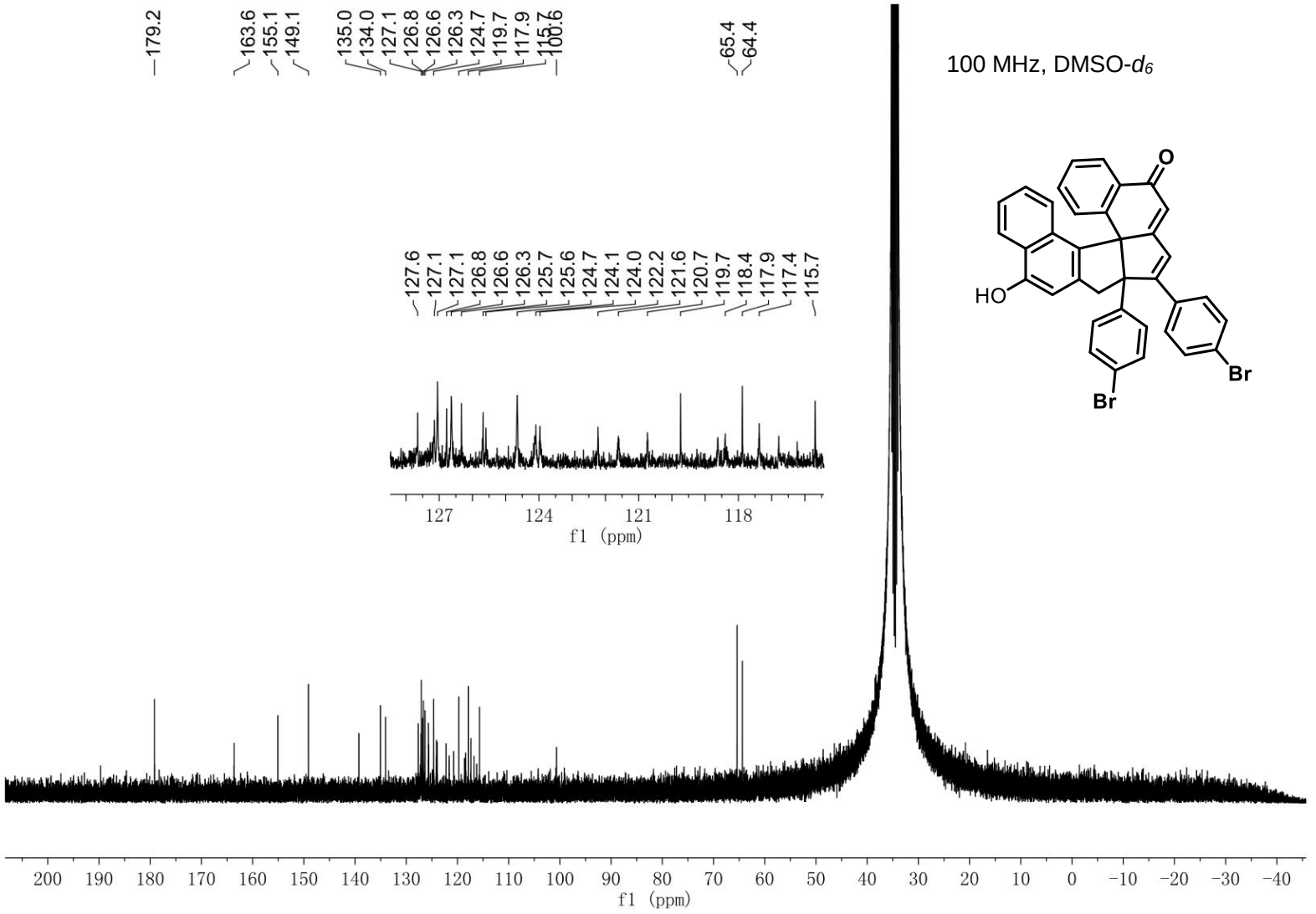
^{1}H NMR Spectrum of Compound 2h



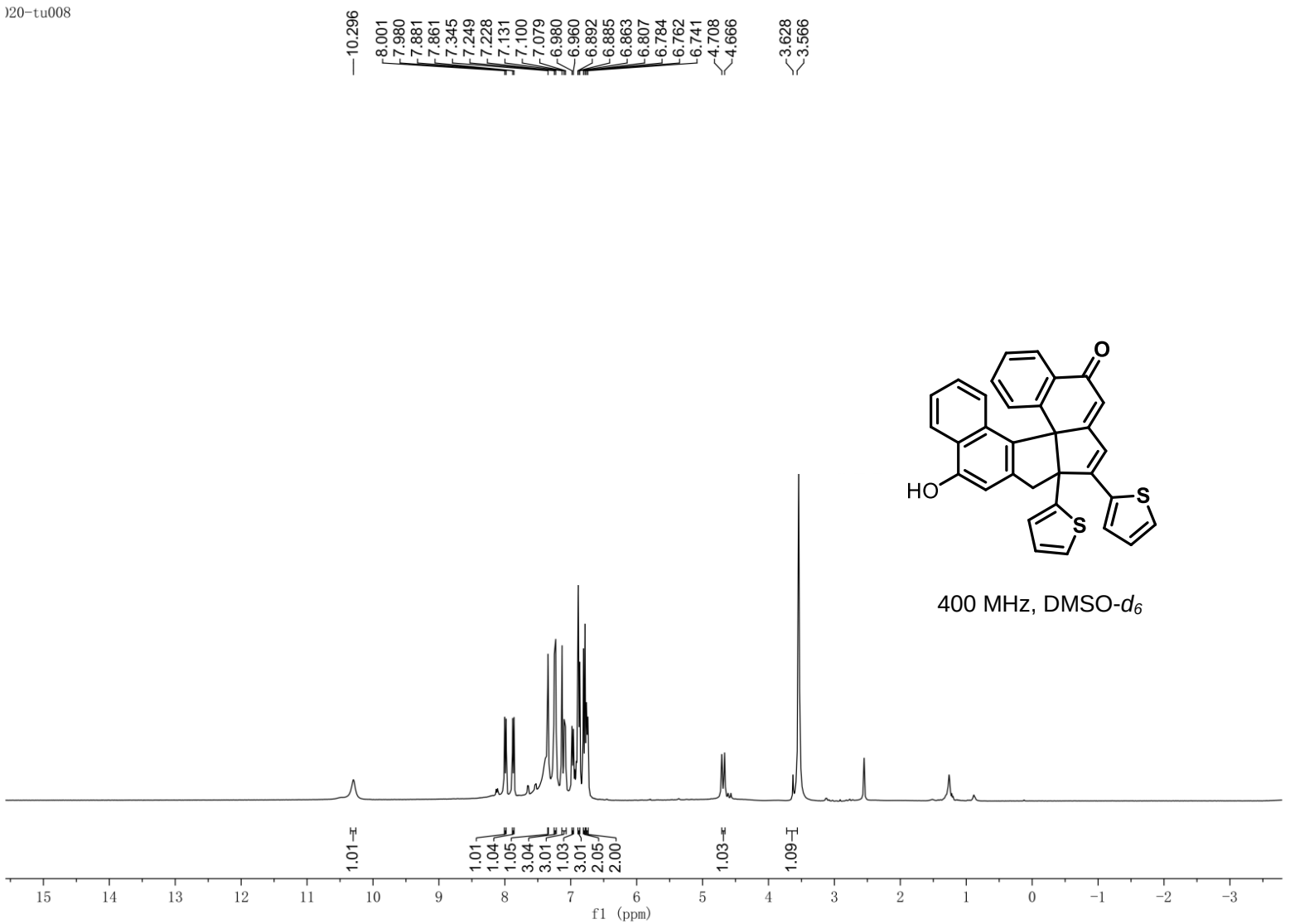
^{13}C NMR Spectrum of Compound 2h



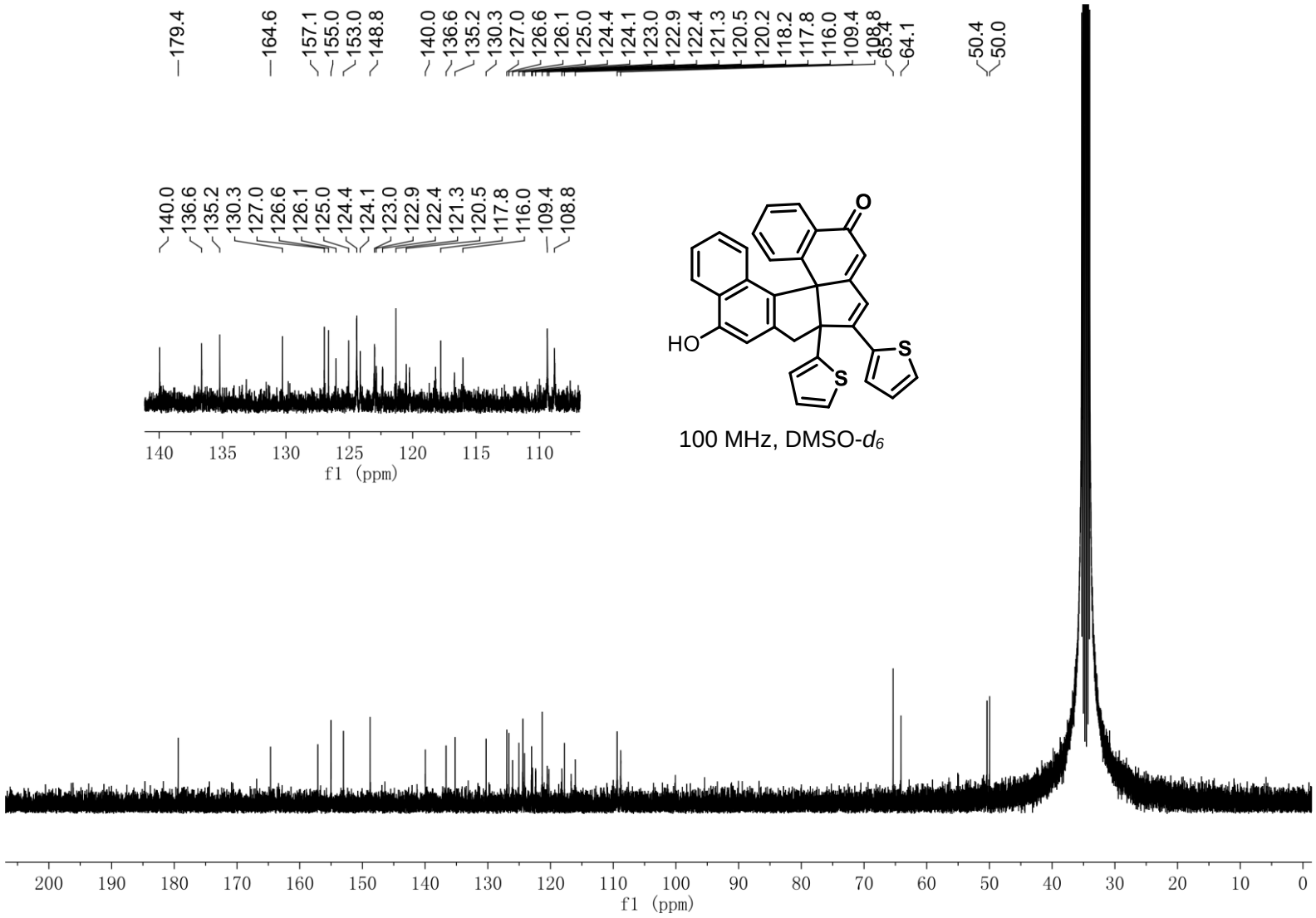
^{1}H NMR Spectrum of Compound 2i



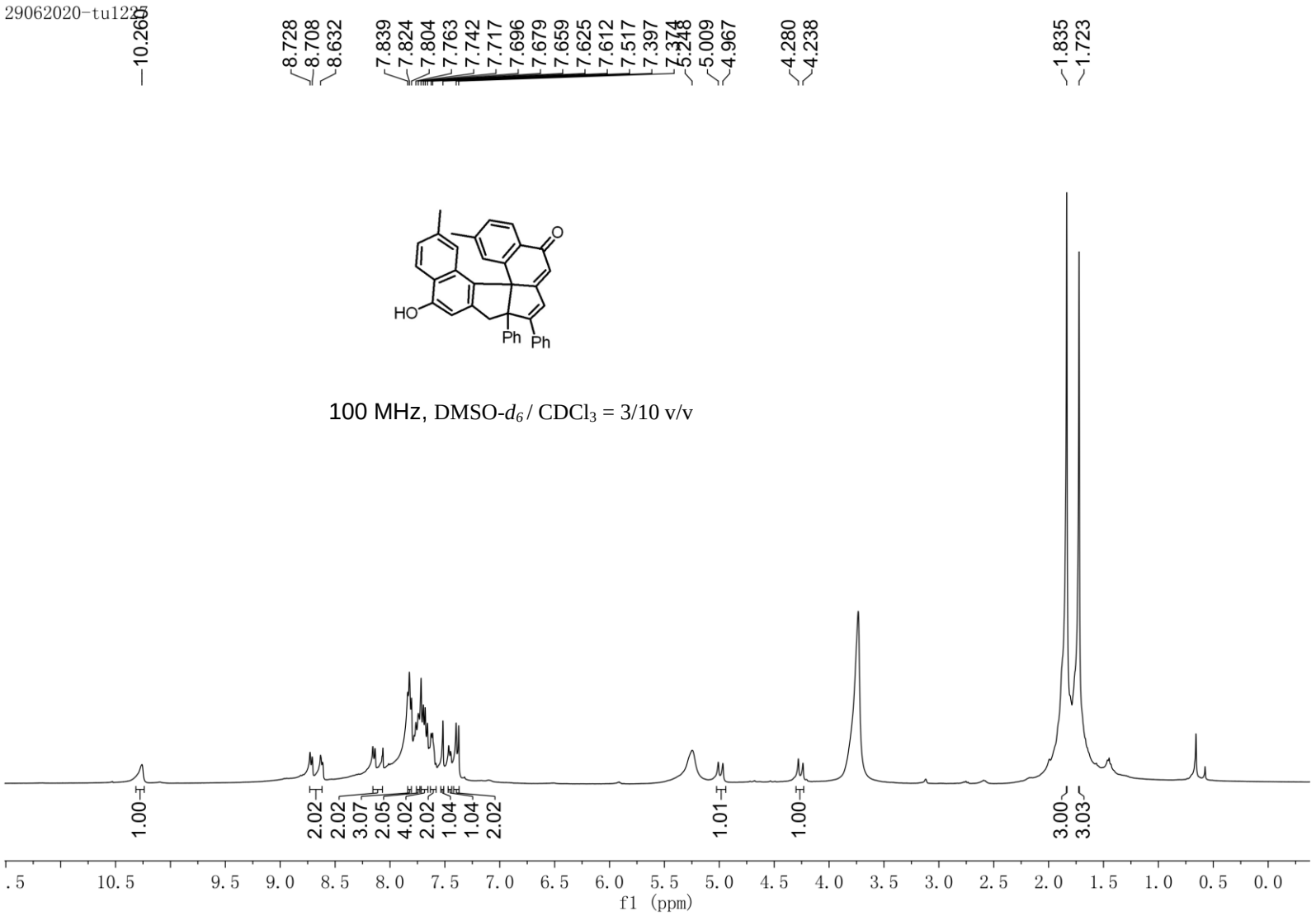
^{13}C NMR Spectrum of Compound 2i



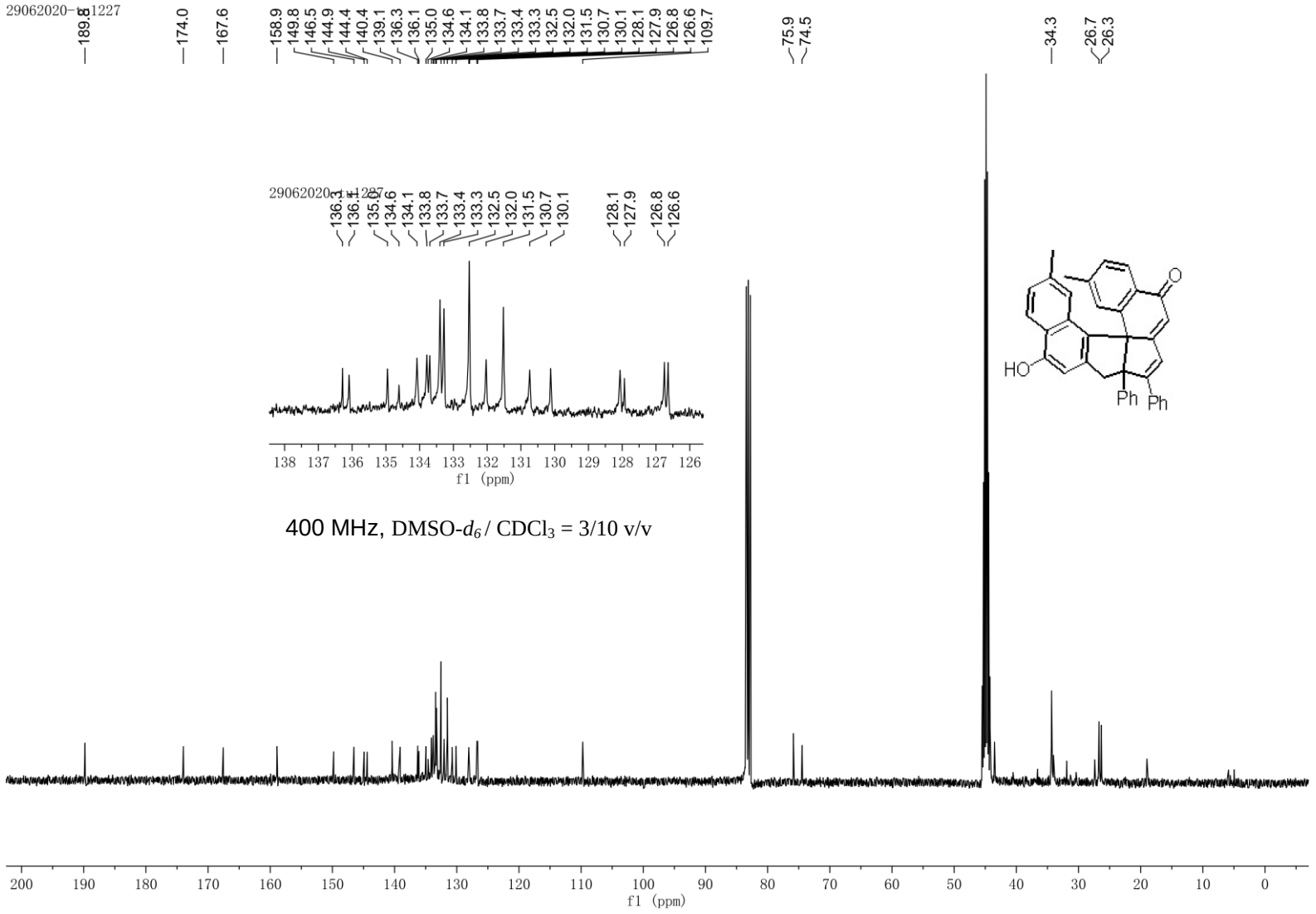
^{1}H NMR Spectrum of Compound 2j



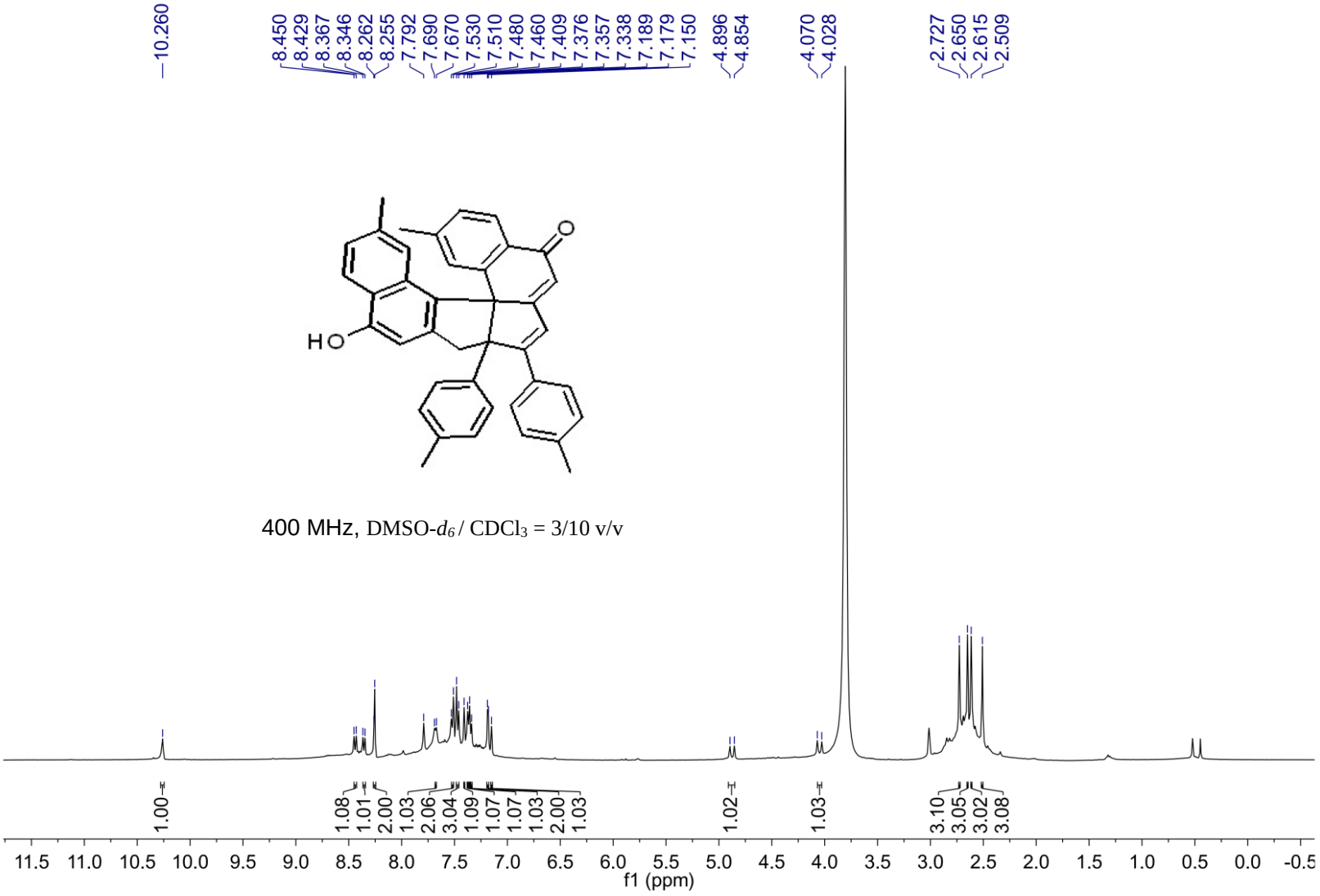
^{13}C NMR Spectrum of Compound 2j



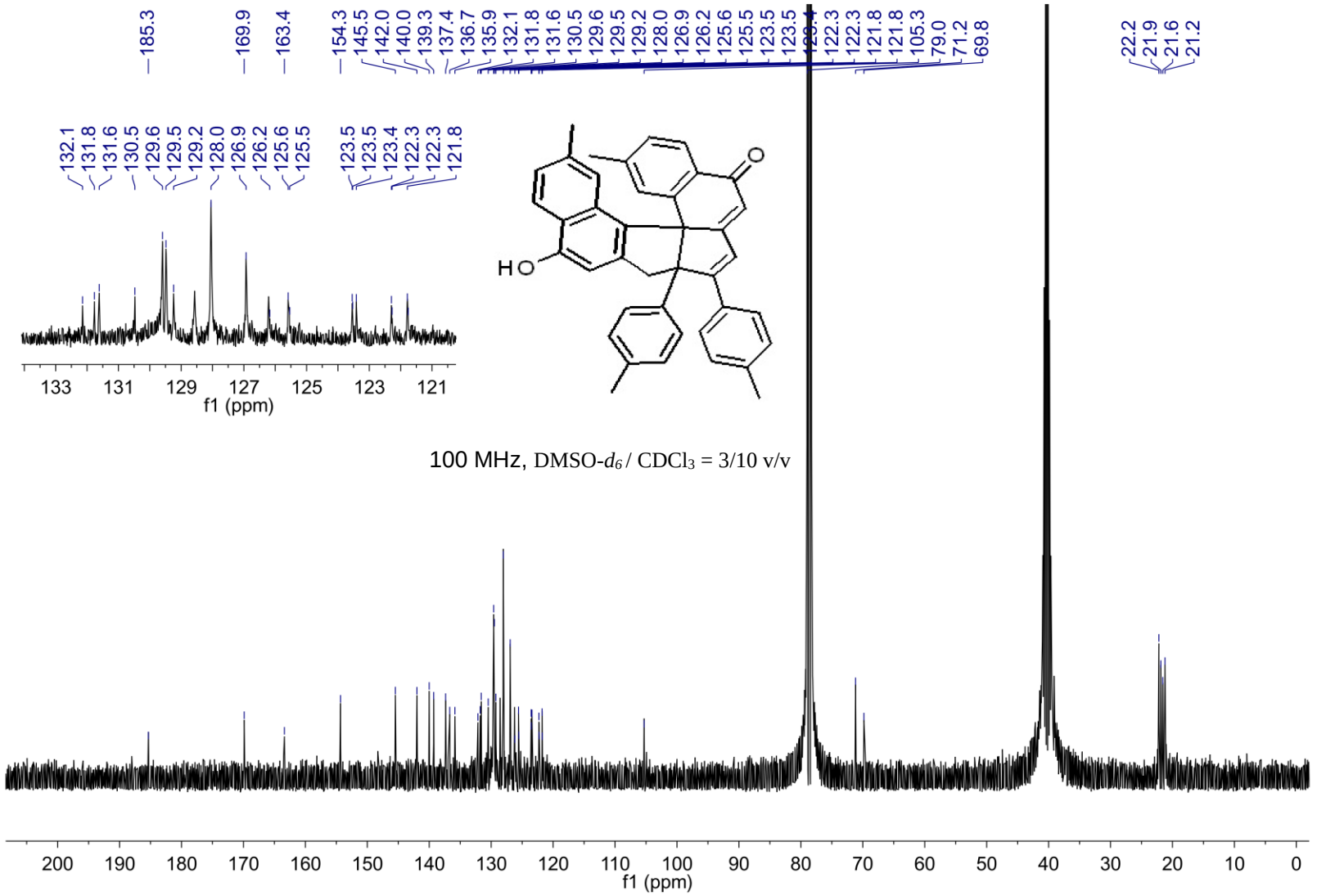
^{1}H NMR Spectrum of Compound 2k



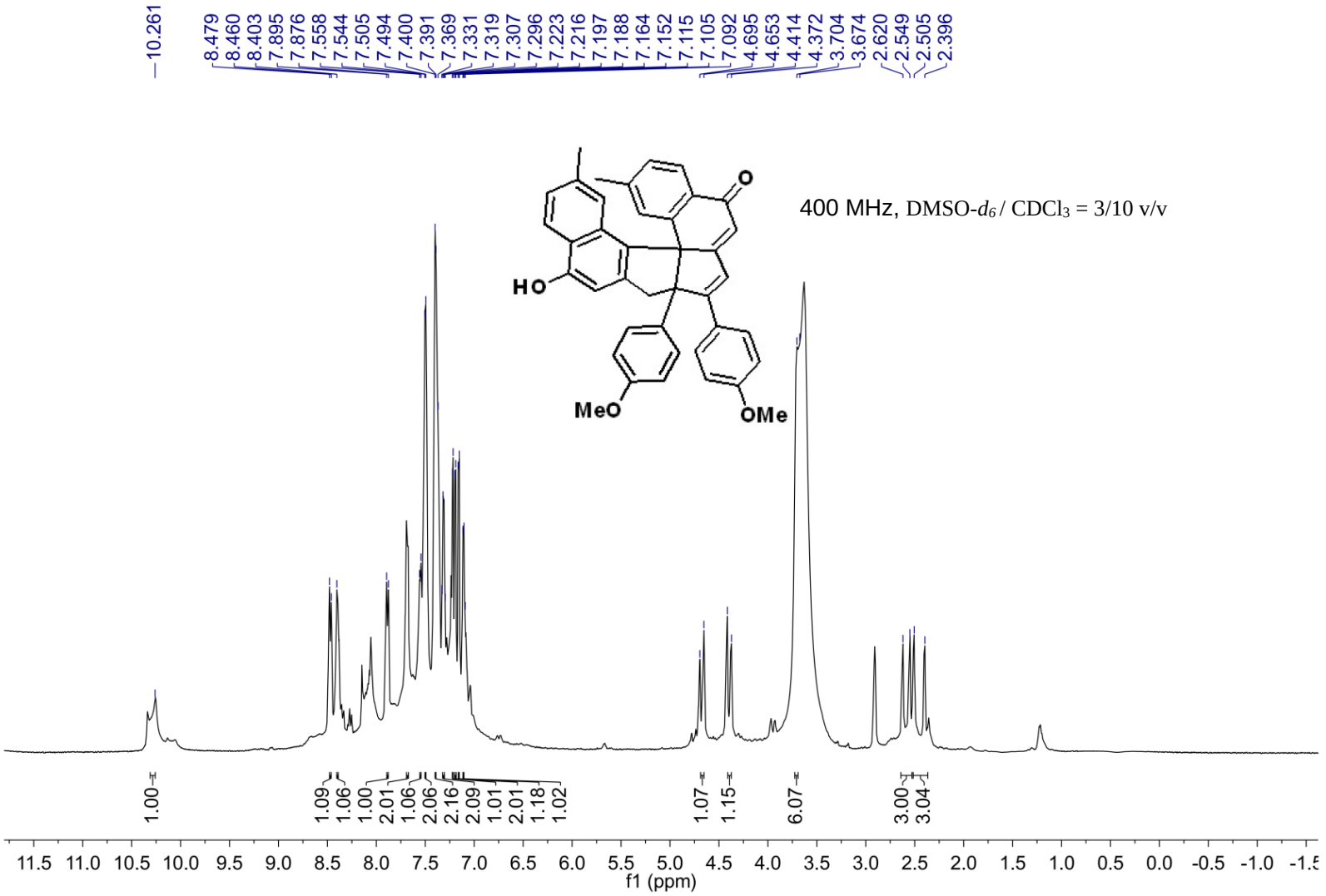
^{13}C NMR Spectrum of Compound 2k



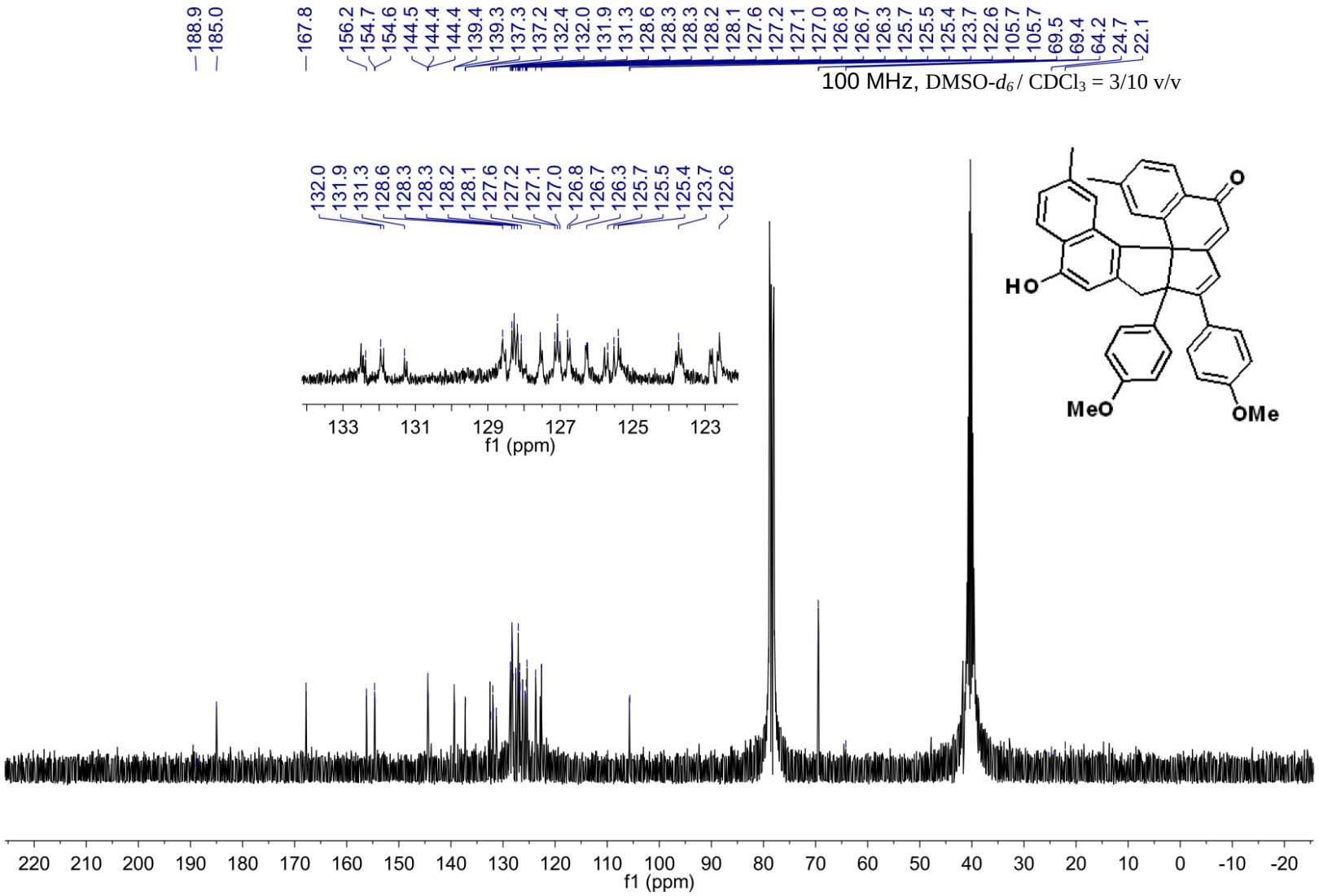
^{1}H NMR Spectrum of Compound 2l



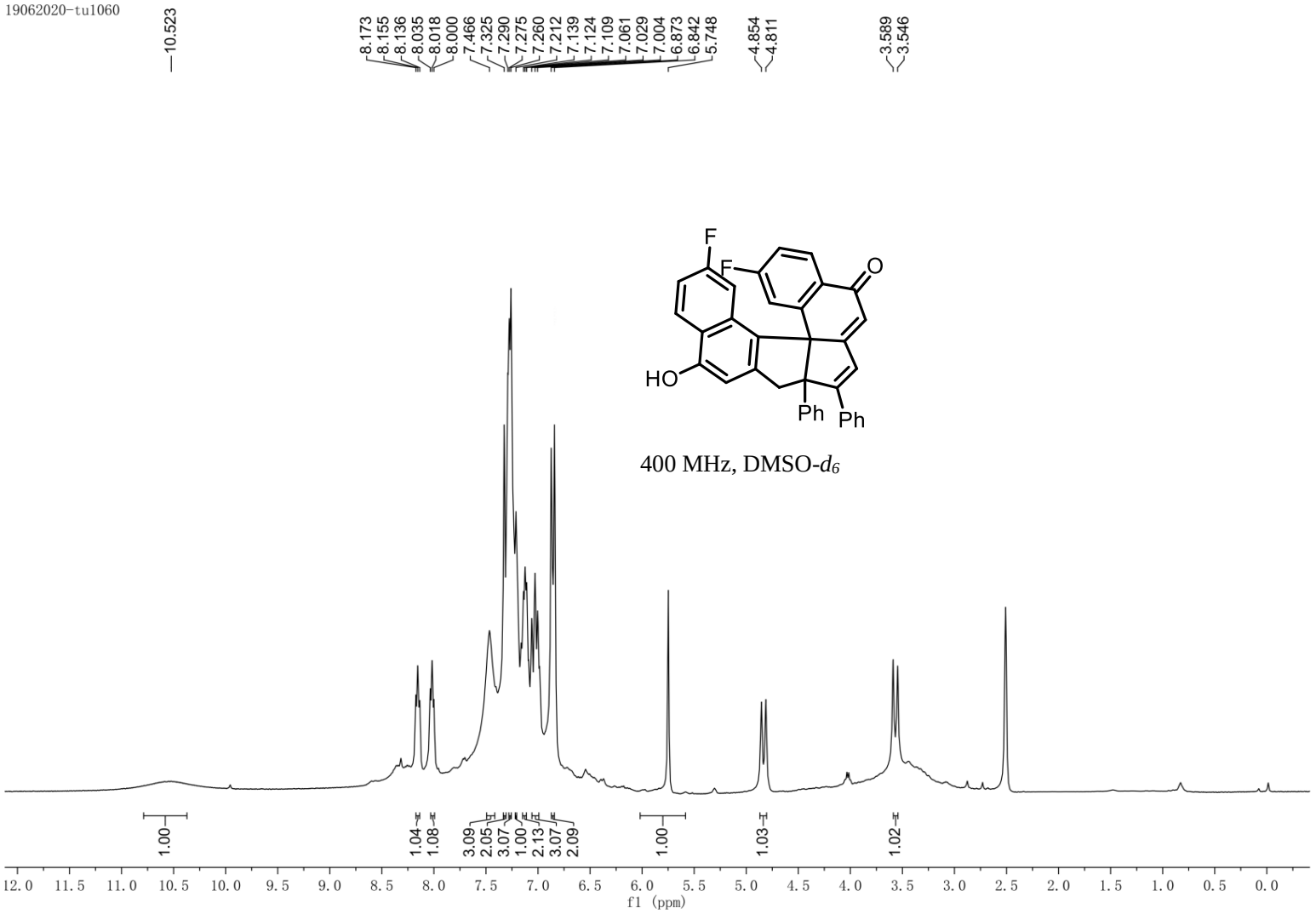
^{13}C NMR Spectrum of Compound 2l



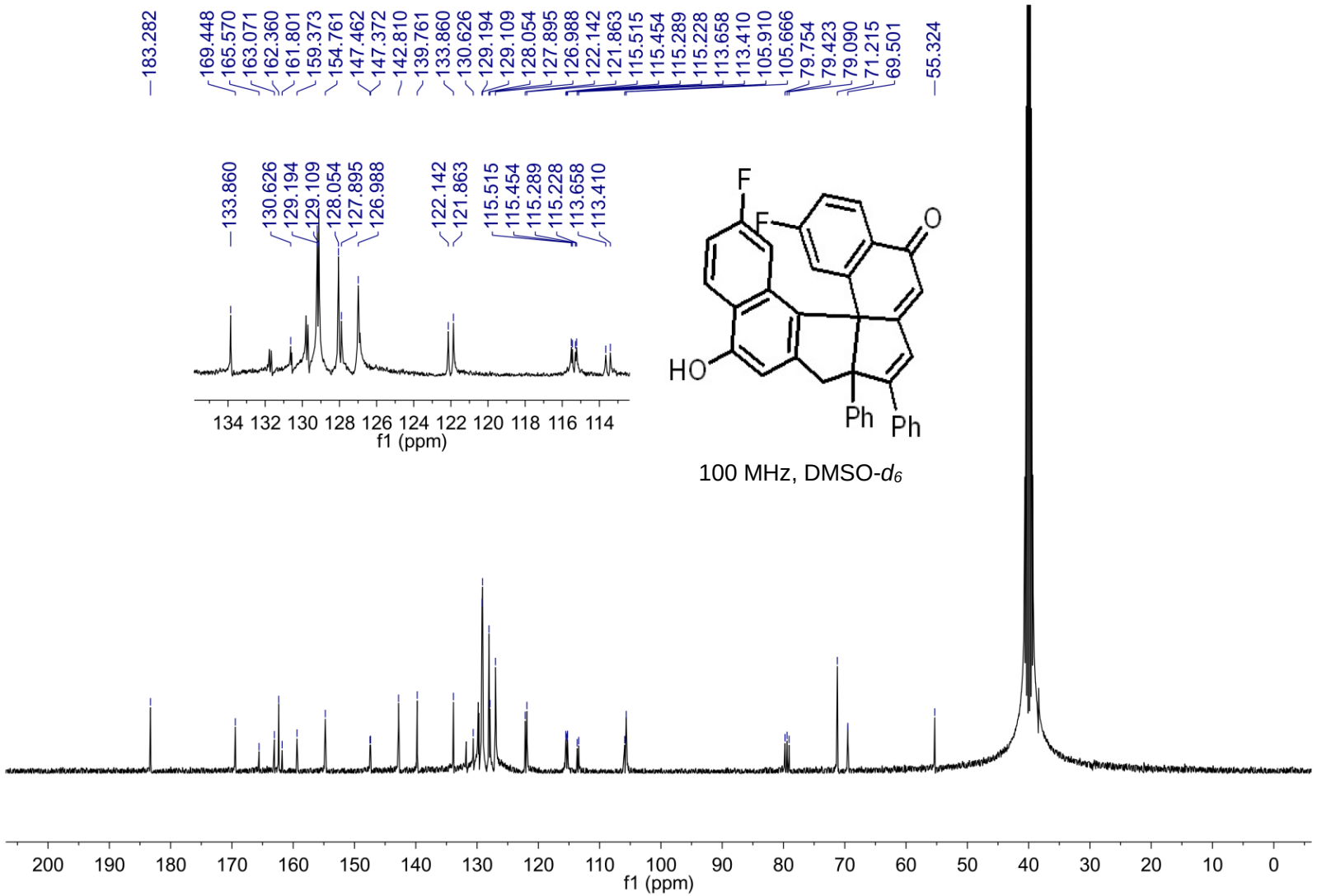
^{1}H NMR Spectrum of Compound 2m



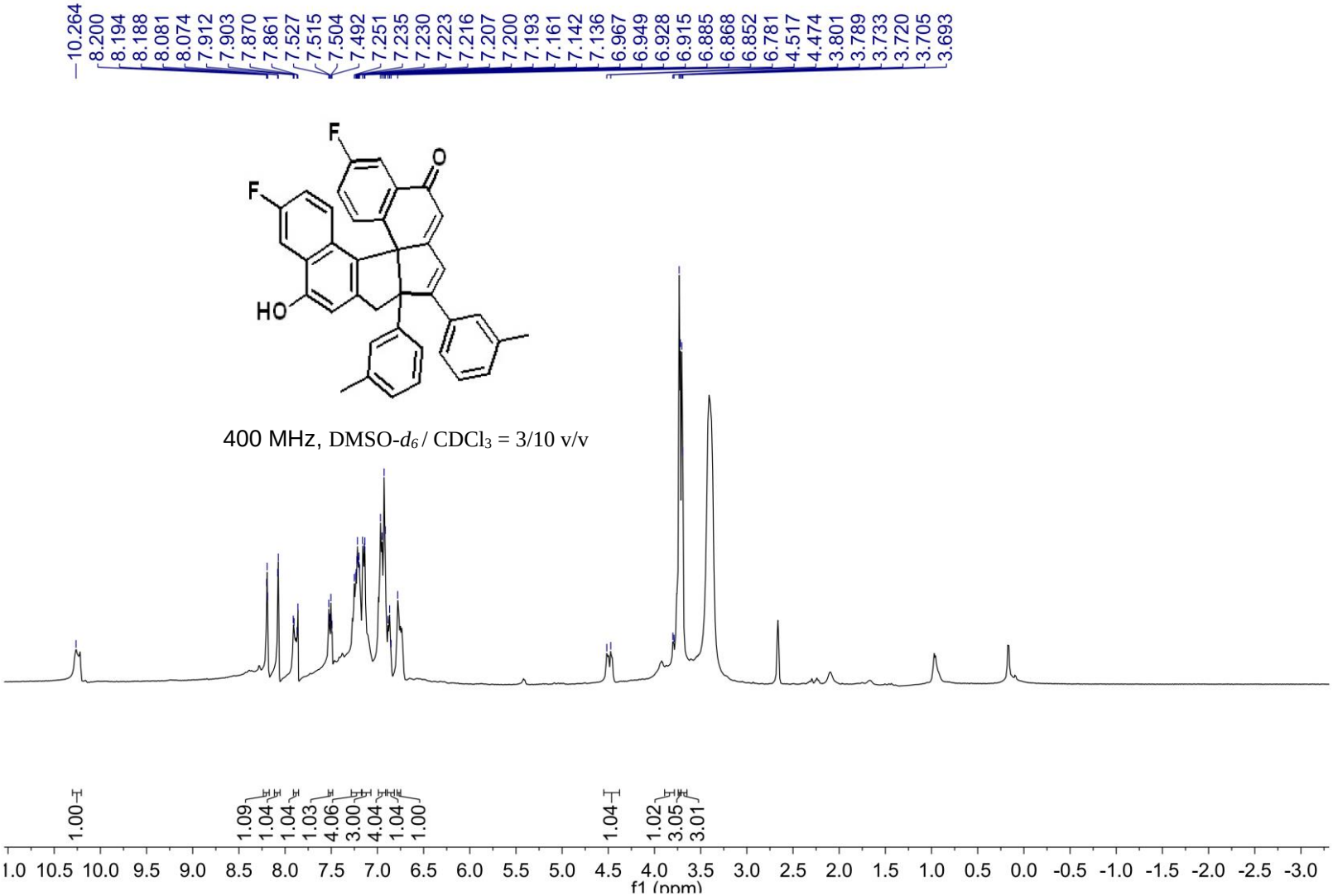
^{13}C NMR Spectrum of Compound 2m



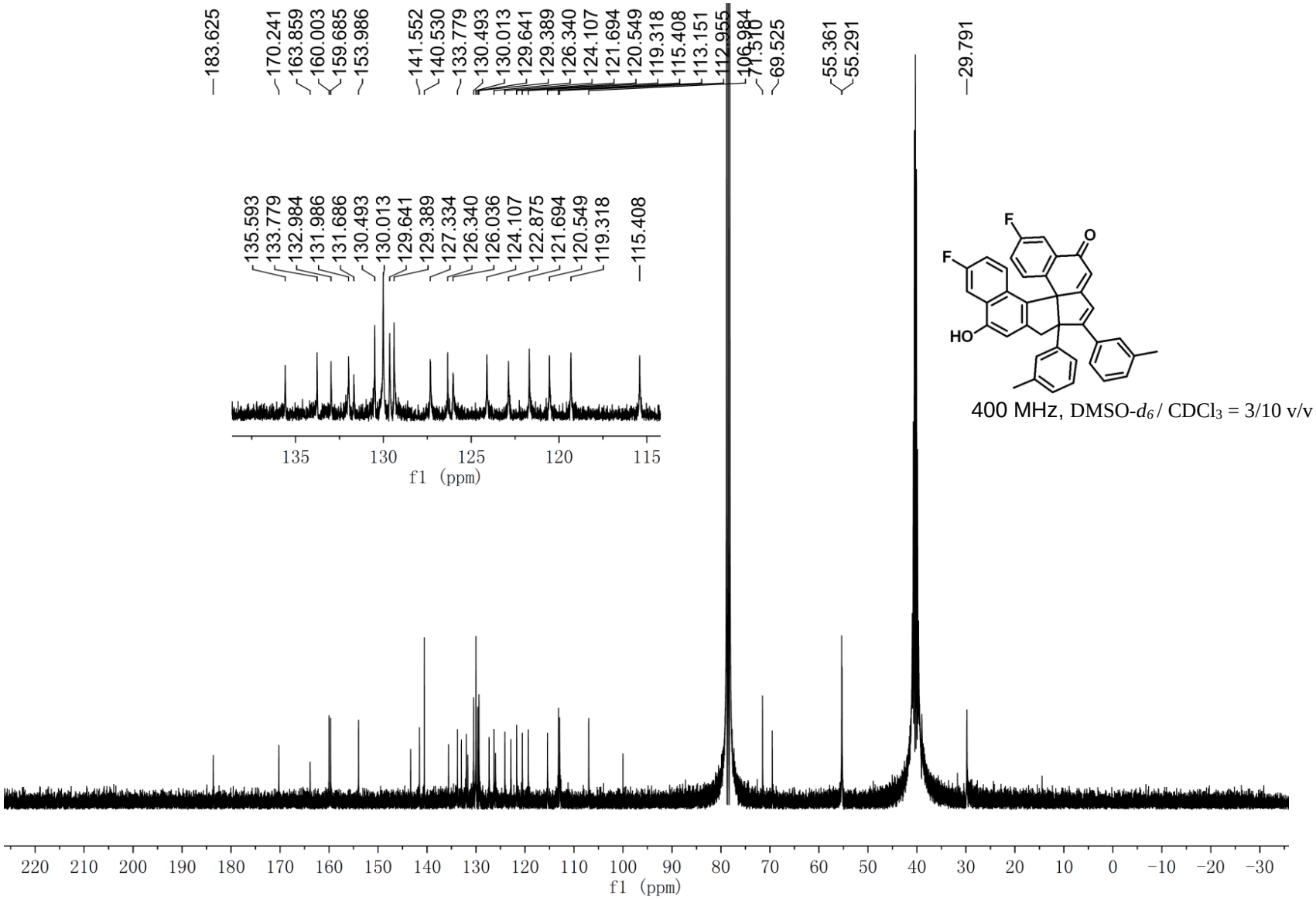
^{1}H NMR Spectrum of Compound 2n



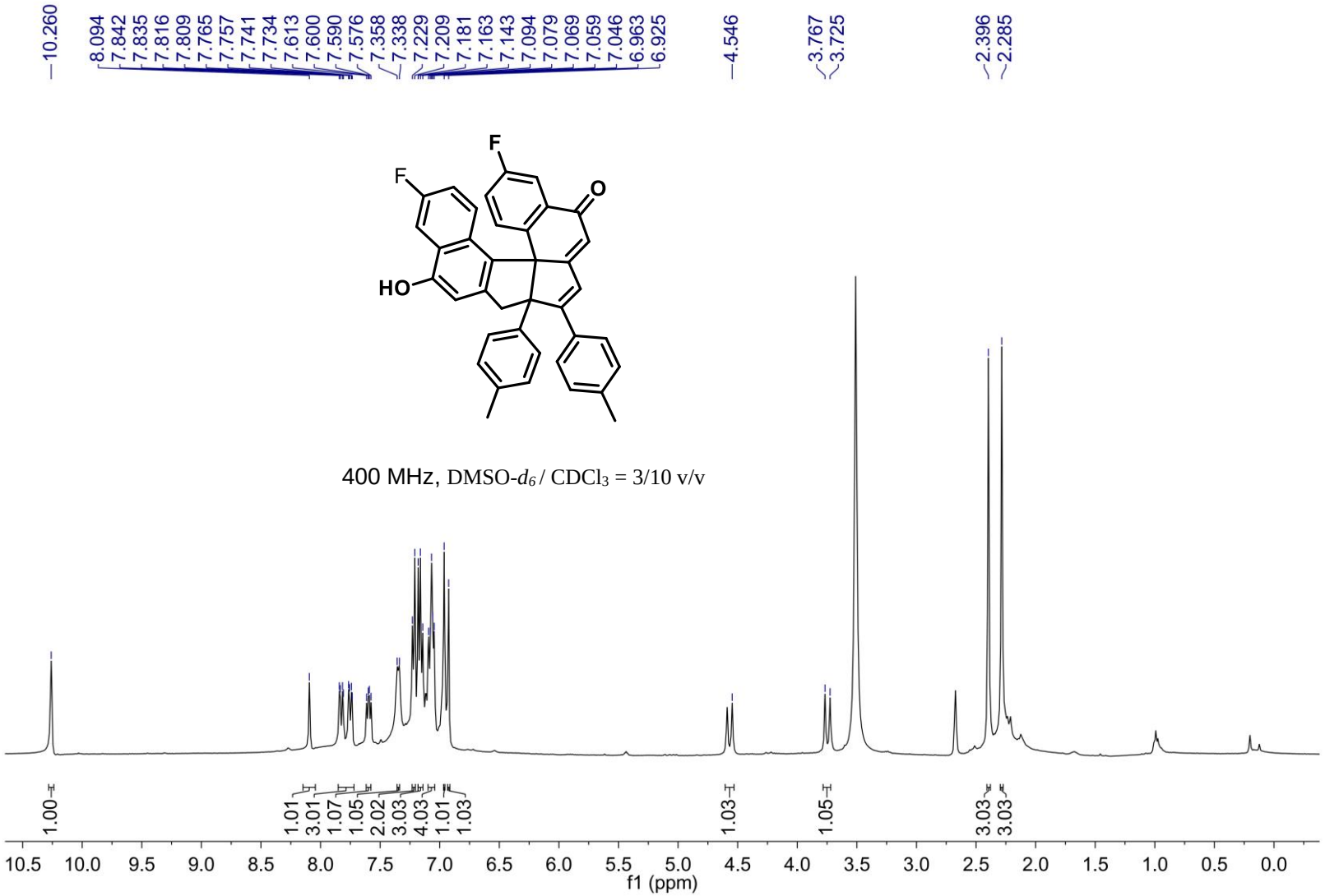
^{13}C NMR Spectrum of Compound 2n



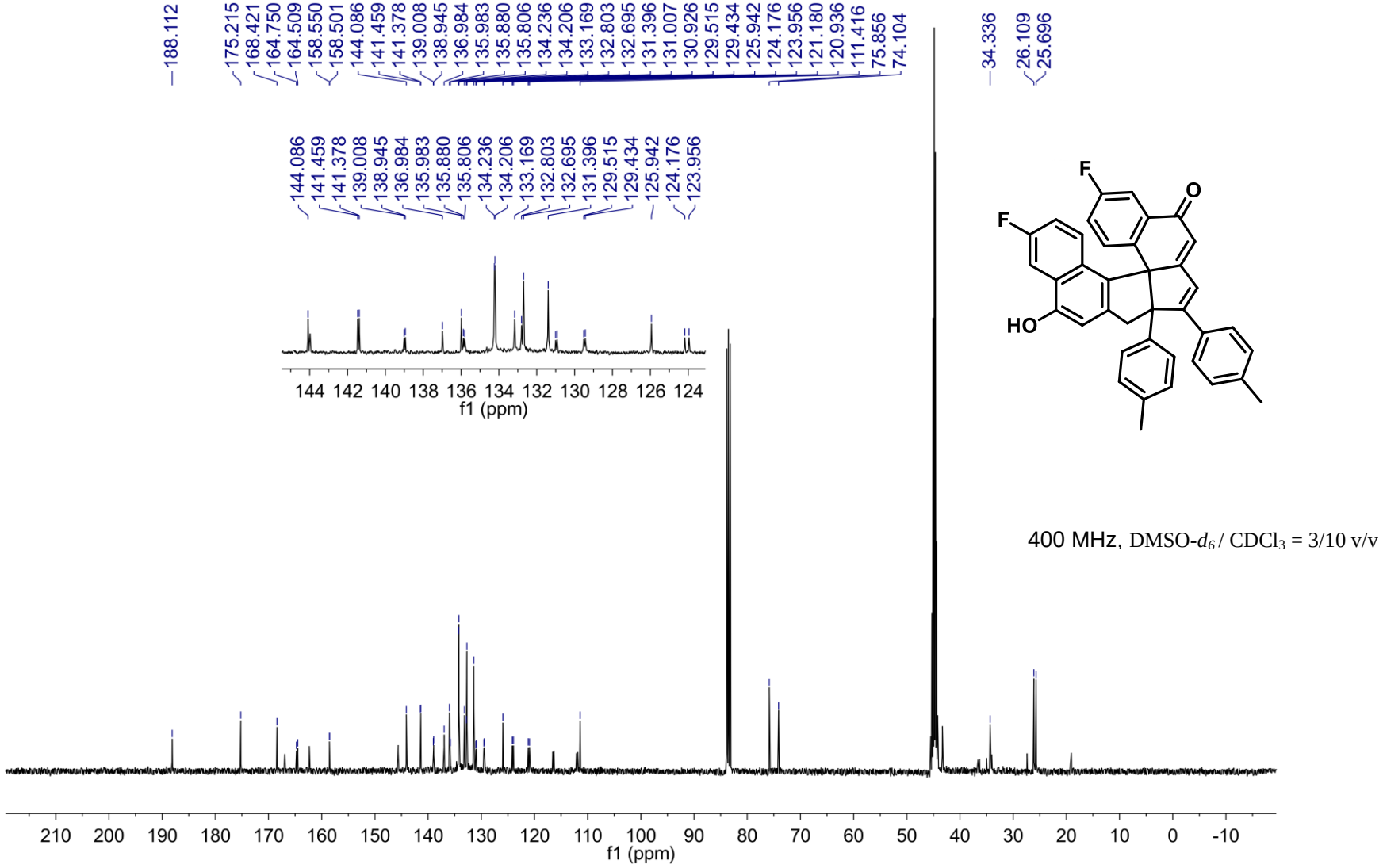
^{1}H NMR Spectrum of Compound 2o



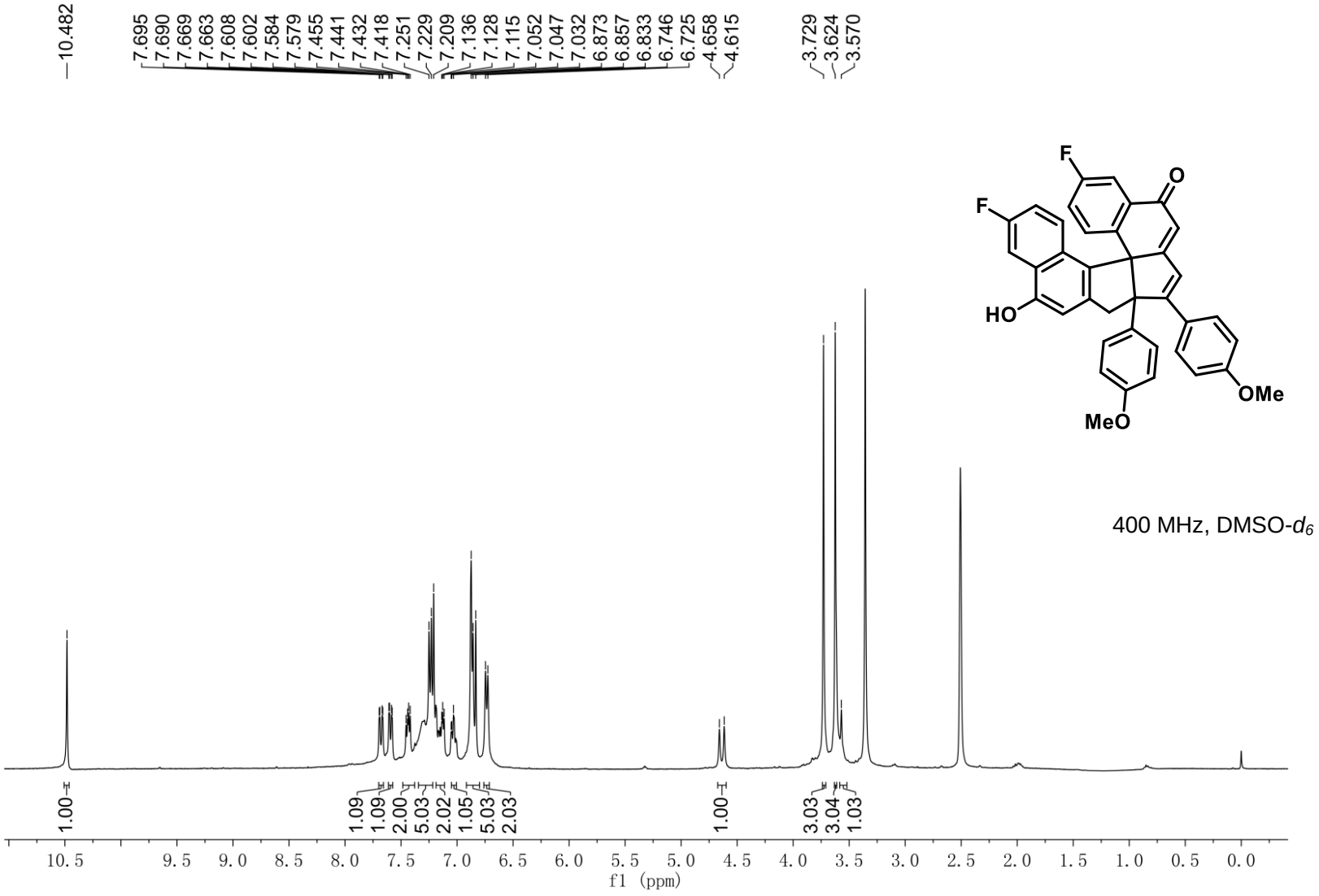
^{13}C NMR Spectrum of Compound 2o



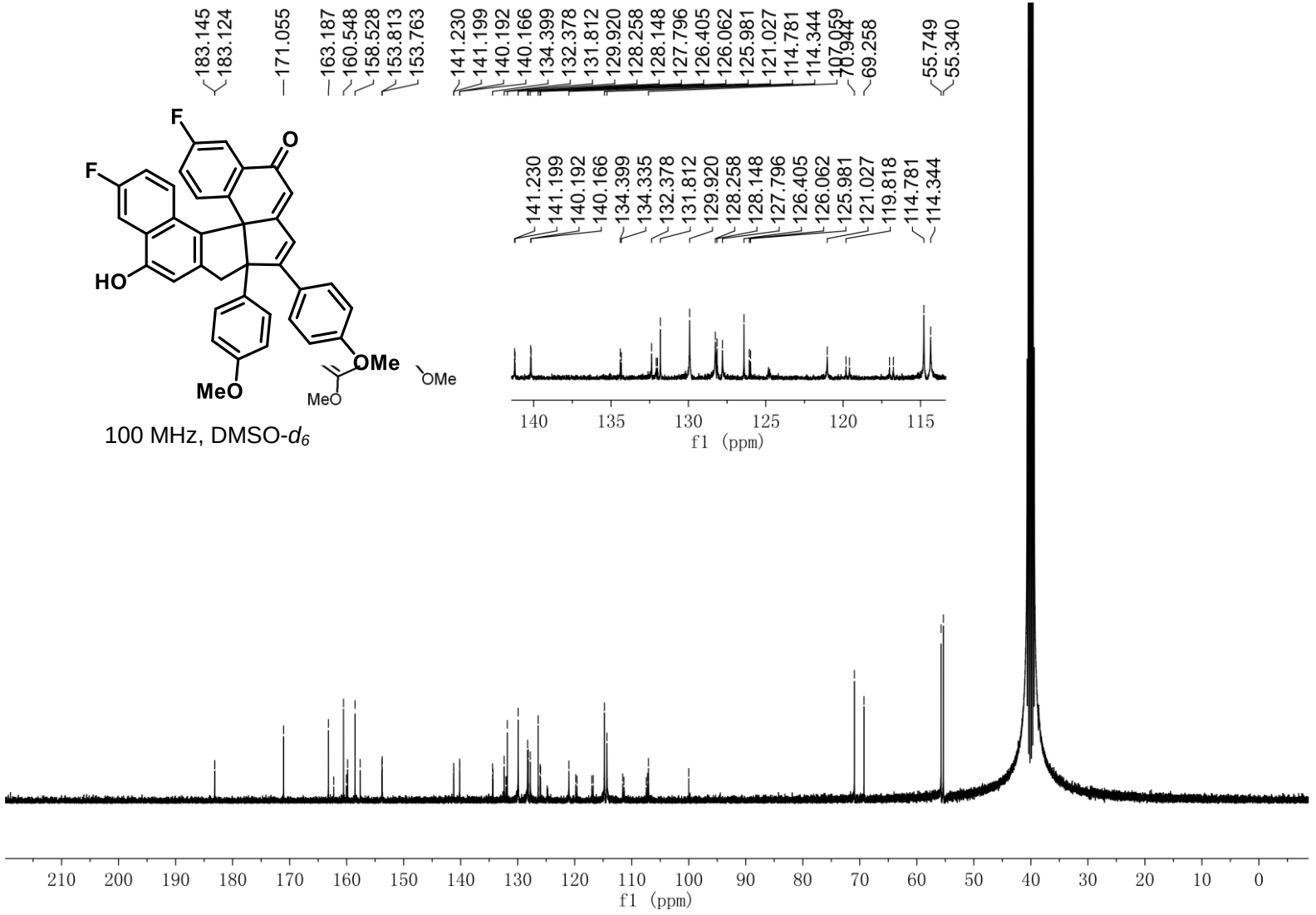
^{1}H NMR Spectrum of Compound 2p



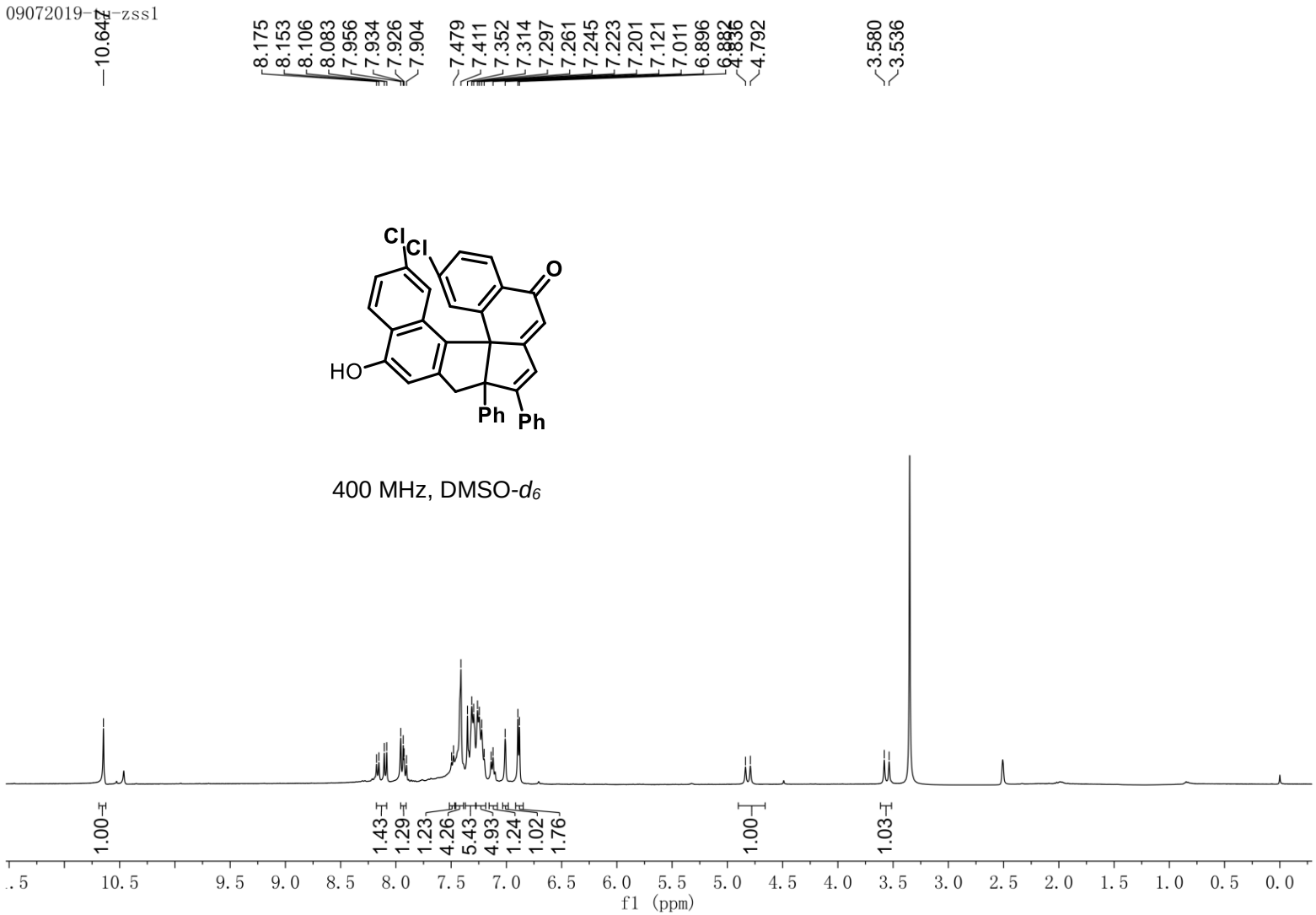
^{13}C NMR Spectrum of Compound 2p



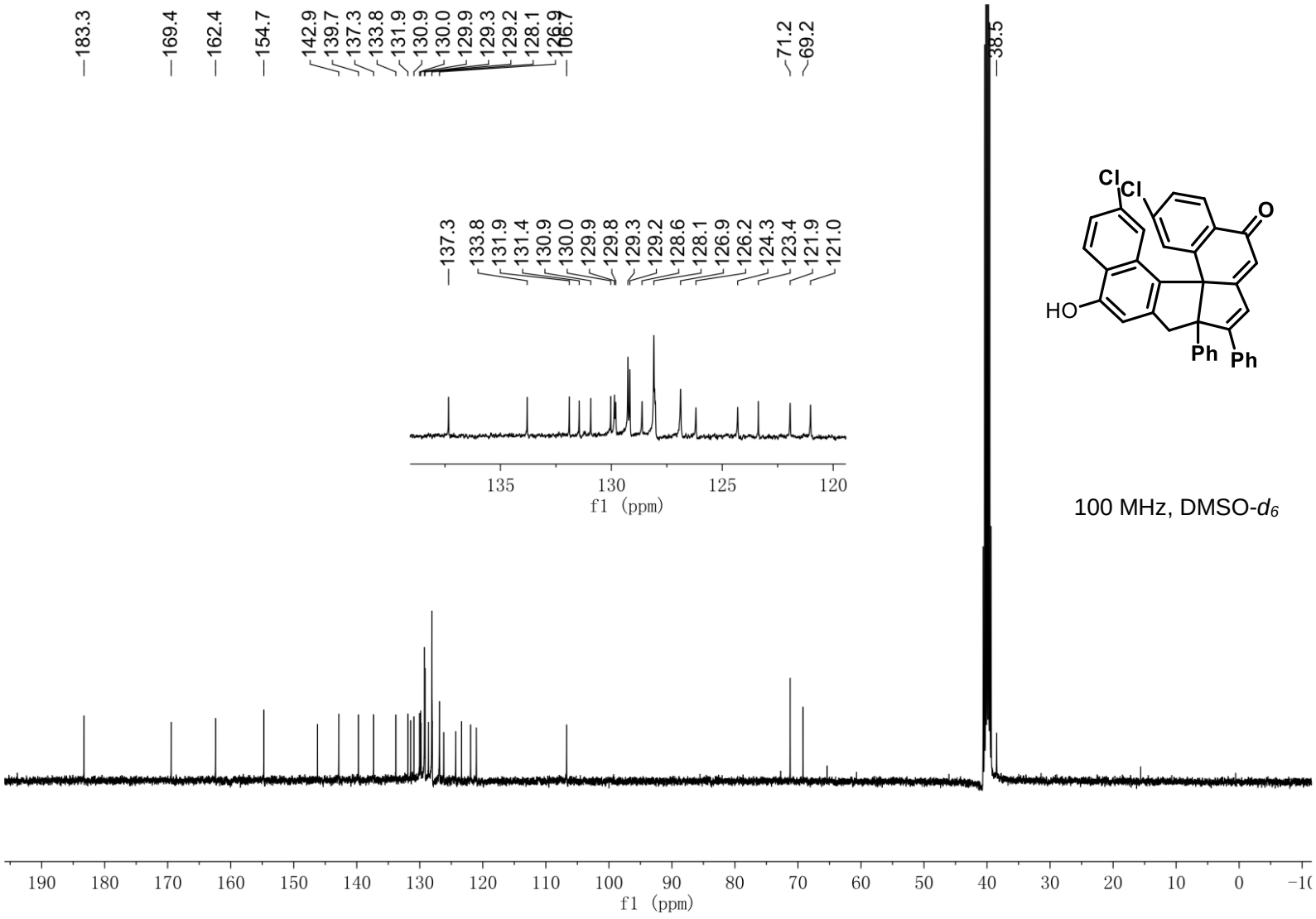
^{1}H NMR Spectrum of Compound 2q



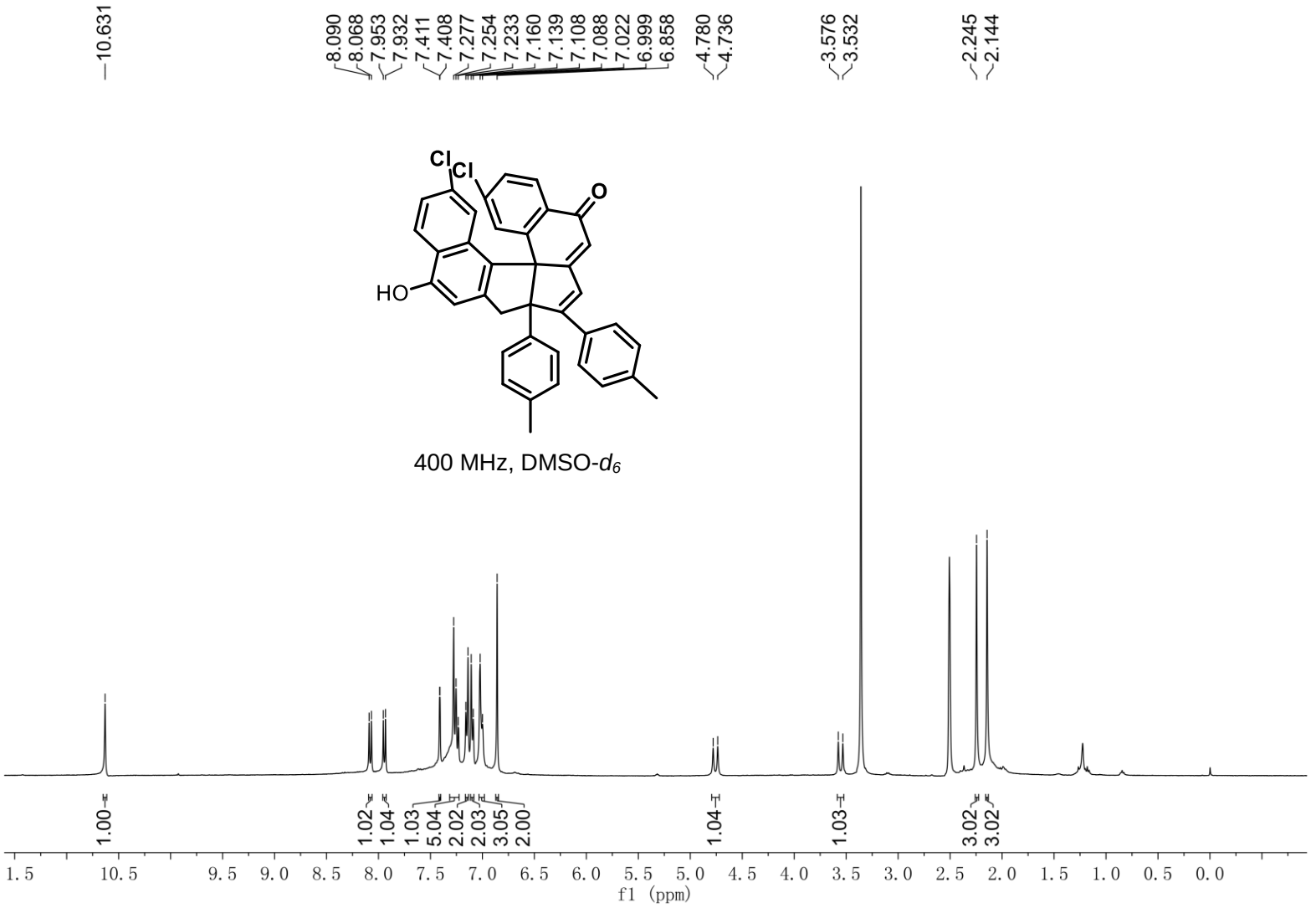
^{13}C NMR Spectrum of Compound 2q



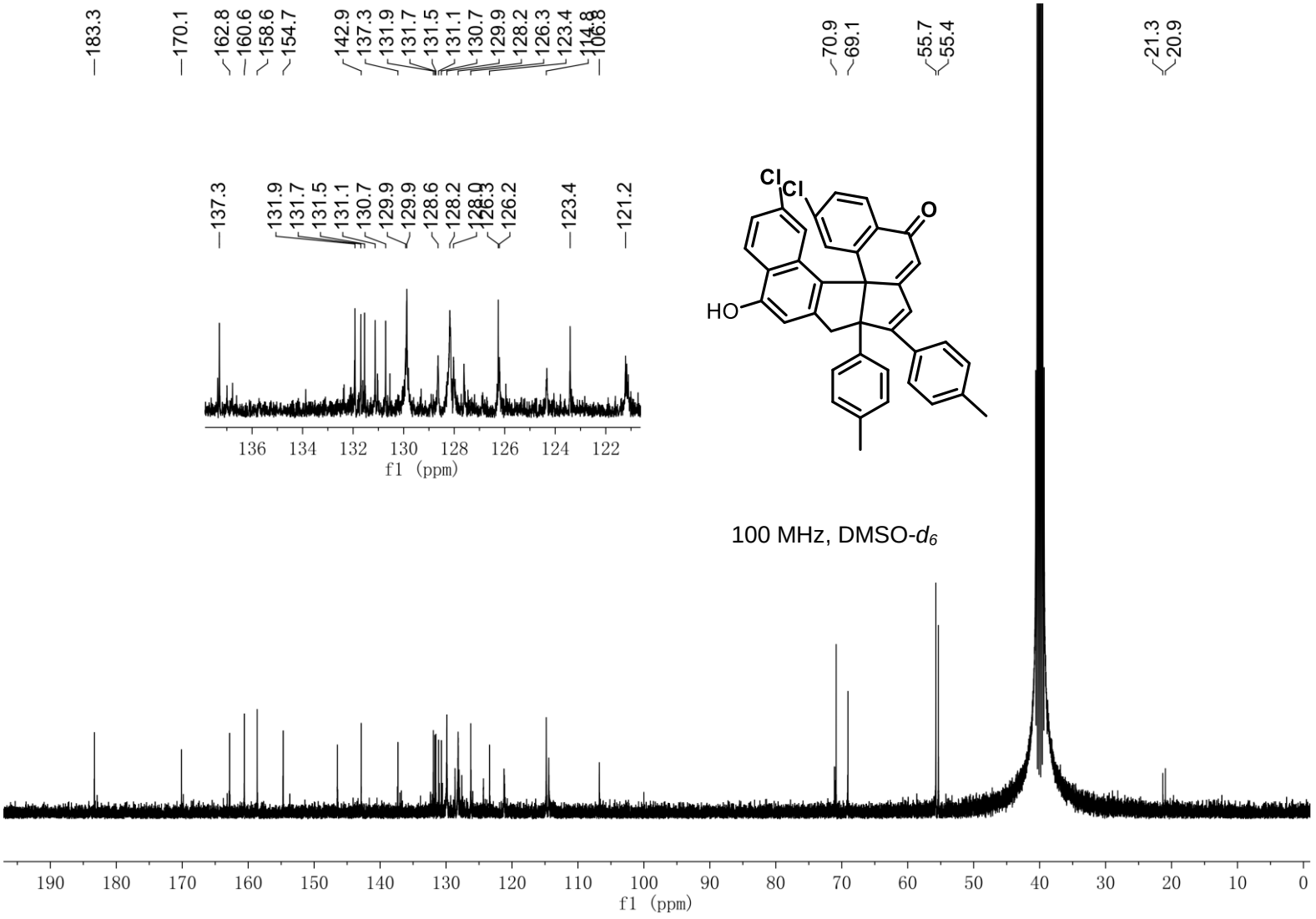
^{1}H NMR Spectrum of Compound 2r



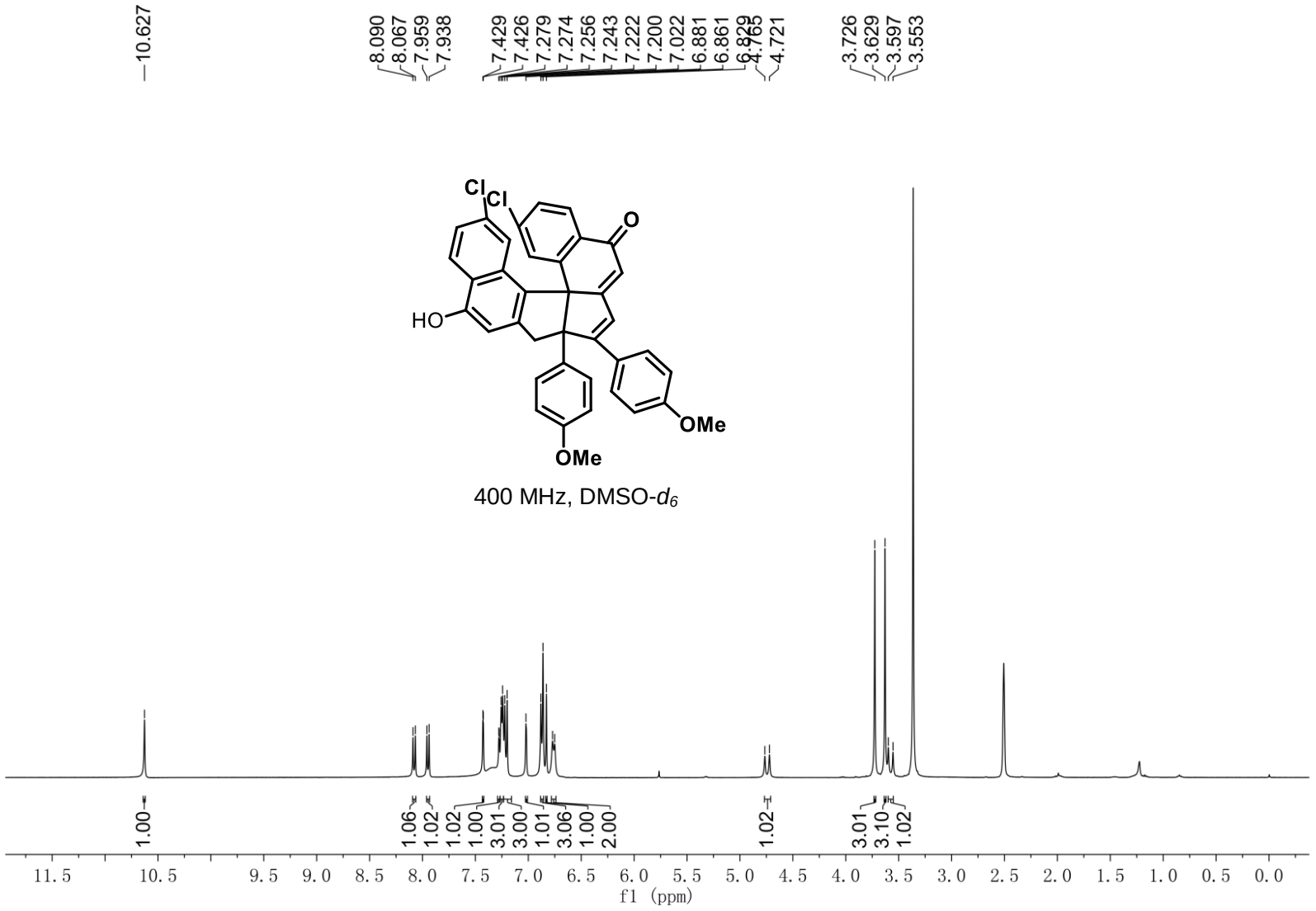
^{13}C NMR Spectrum of Compound 2r



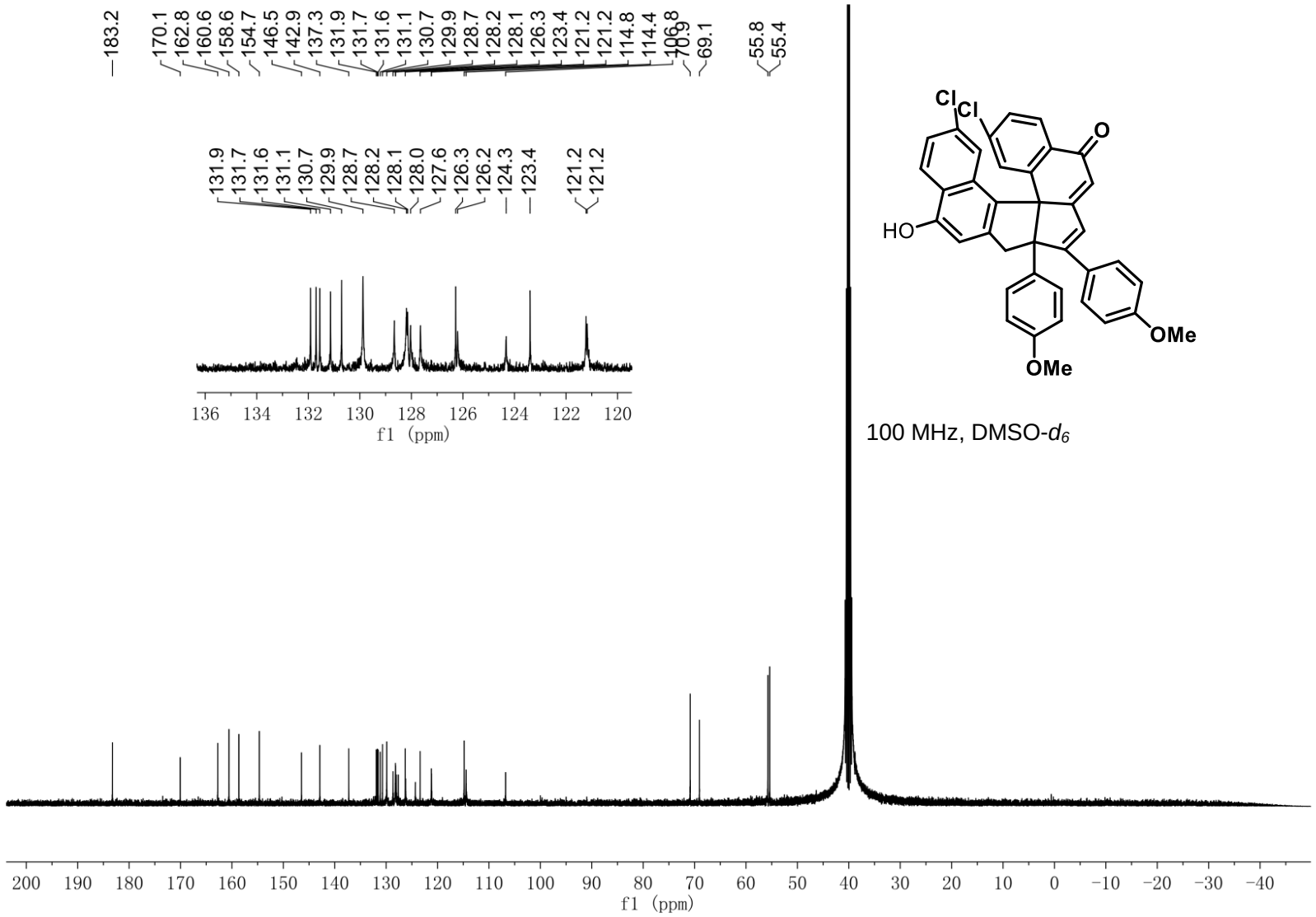
^{1}H NMR Spectrum of Compound 2s



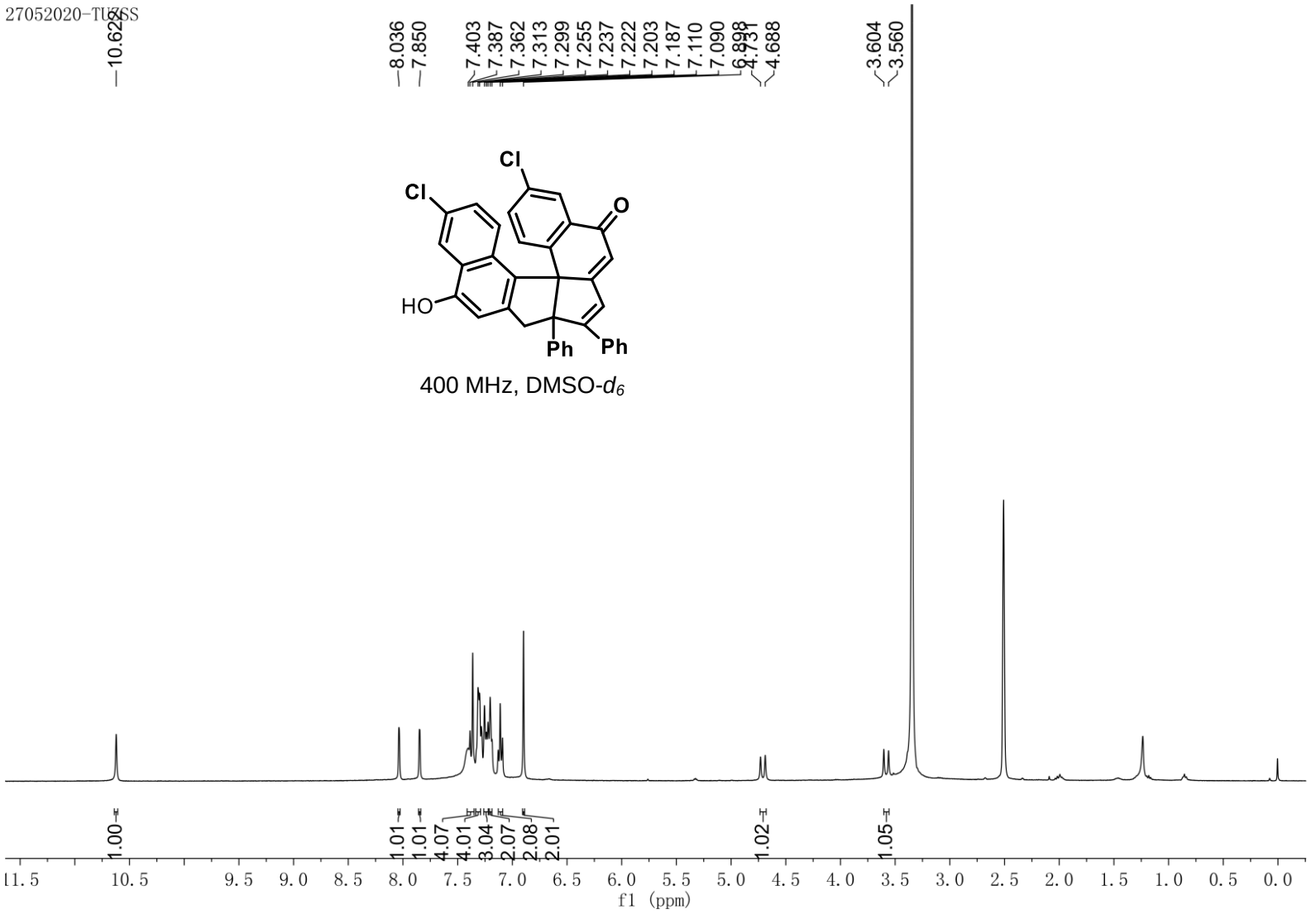
^{13}C NMR Spectrum of Compound 2s



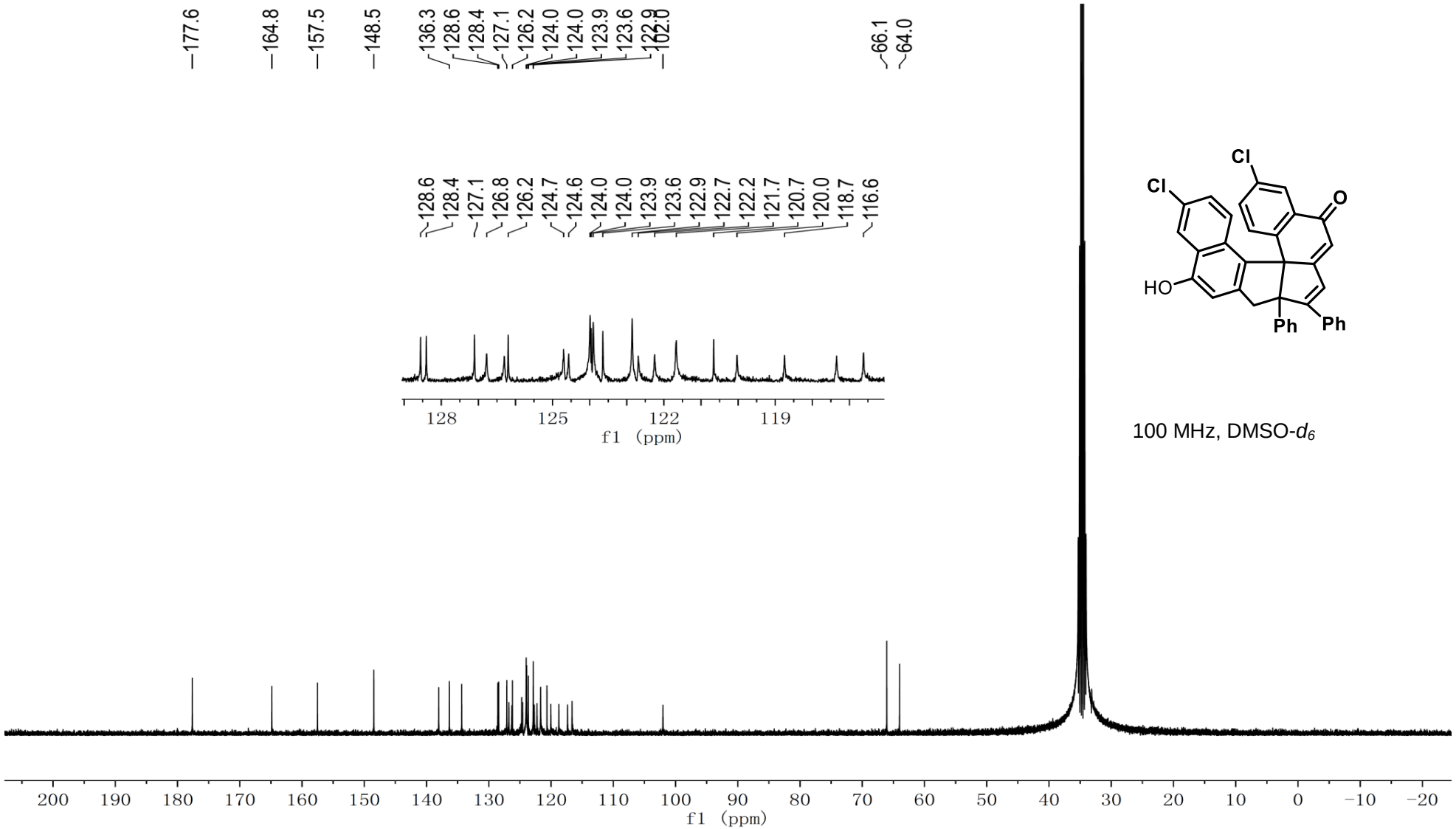
^{1}H NMR Spectrum of Compound 2t



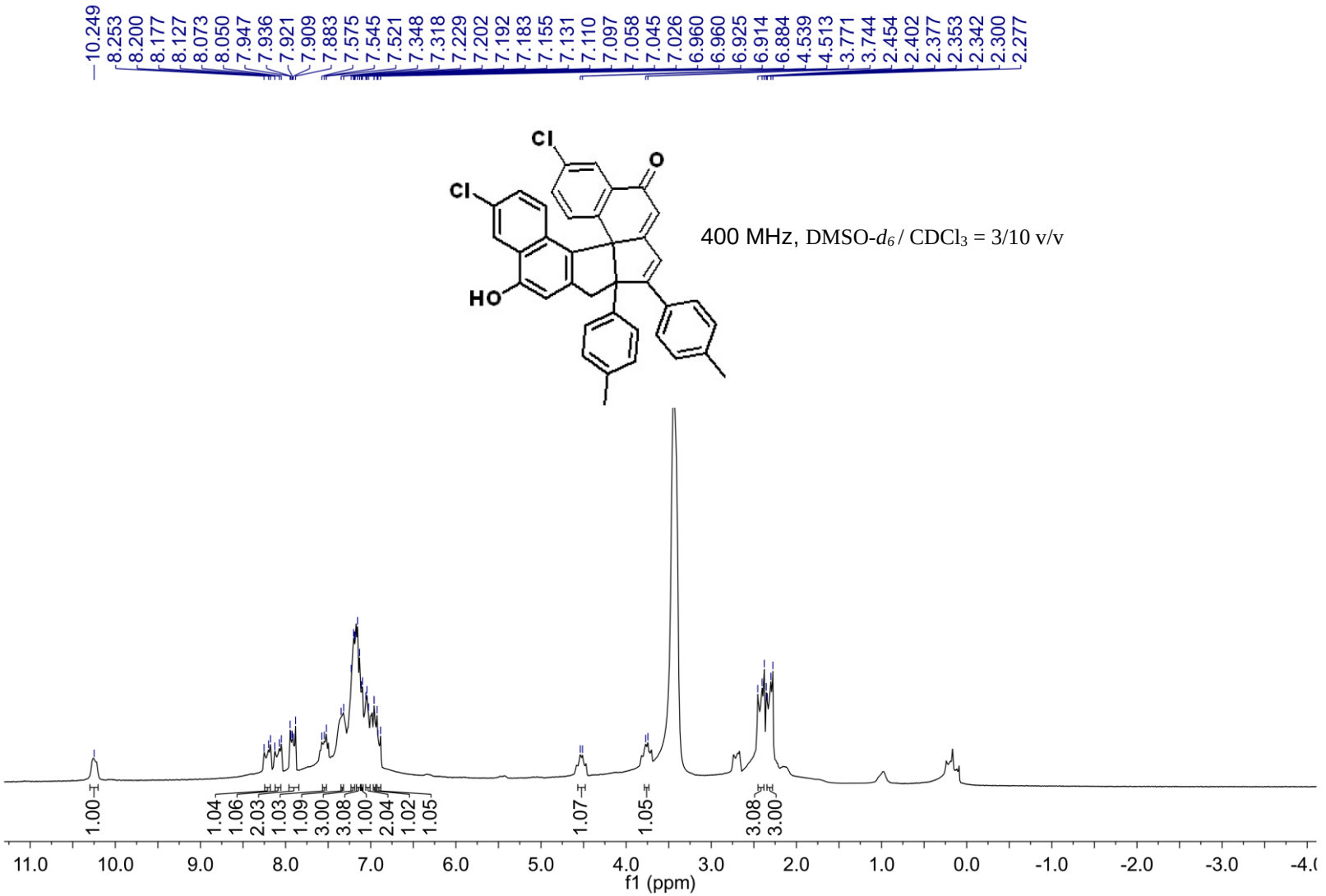
^{13}C NMR Spectrum of Compound 2t



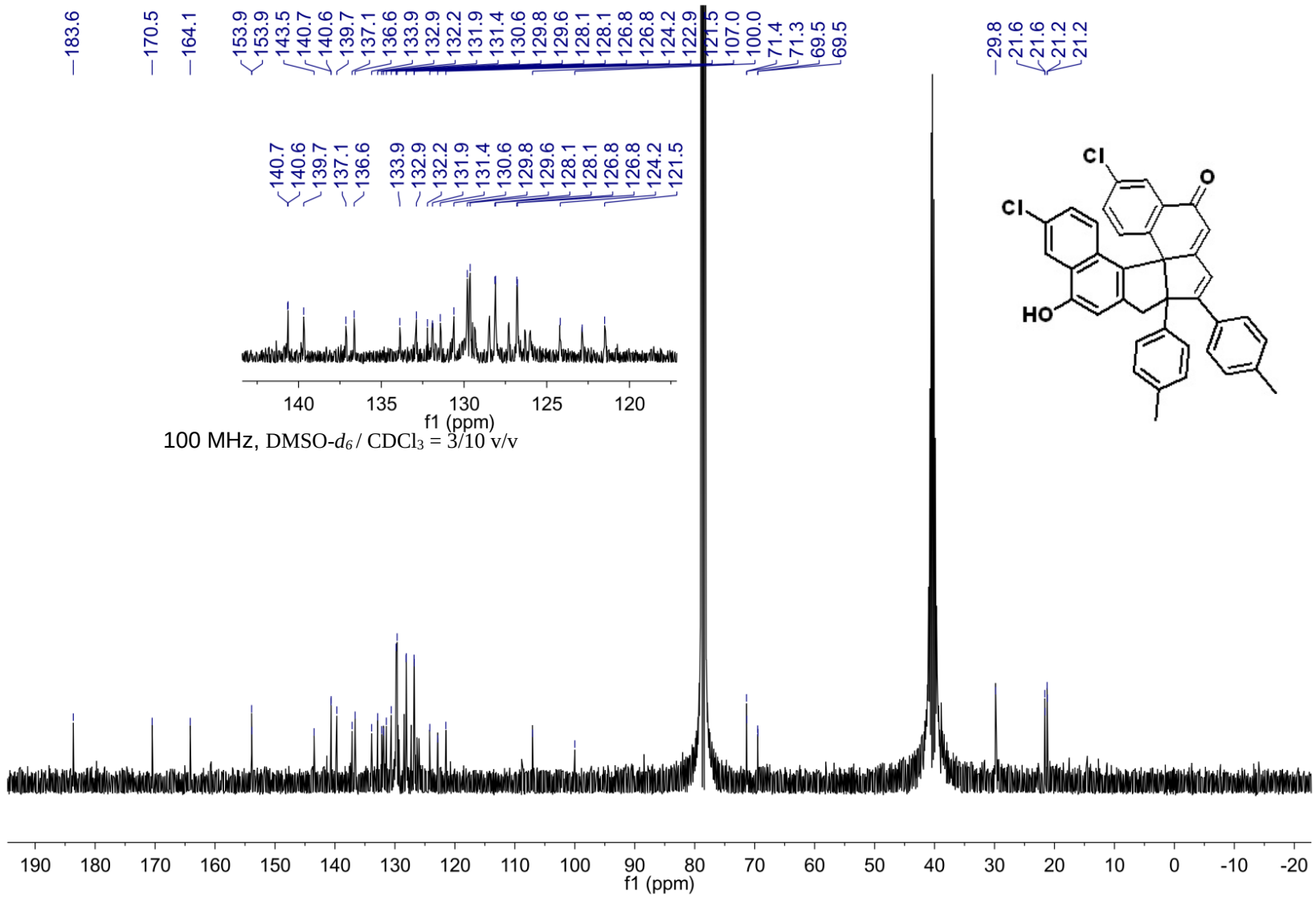
^{1}H NMR Spectrum of Compound 2u



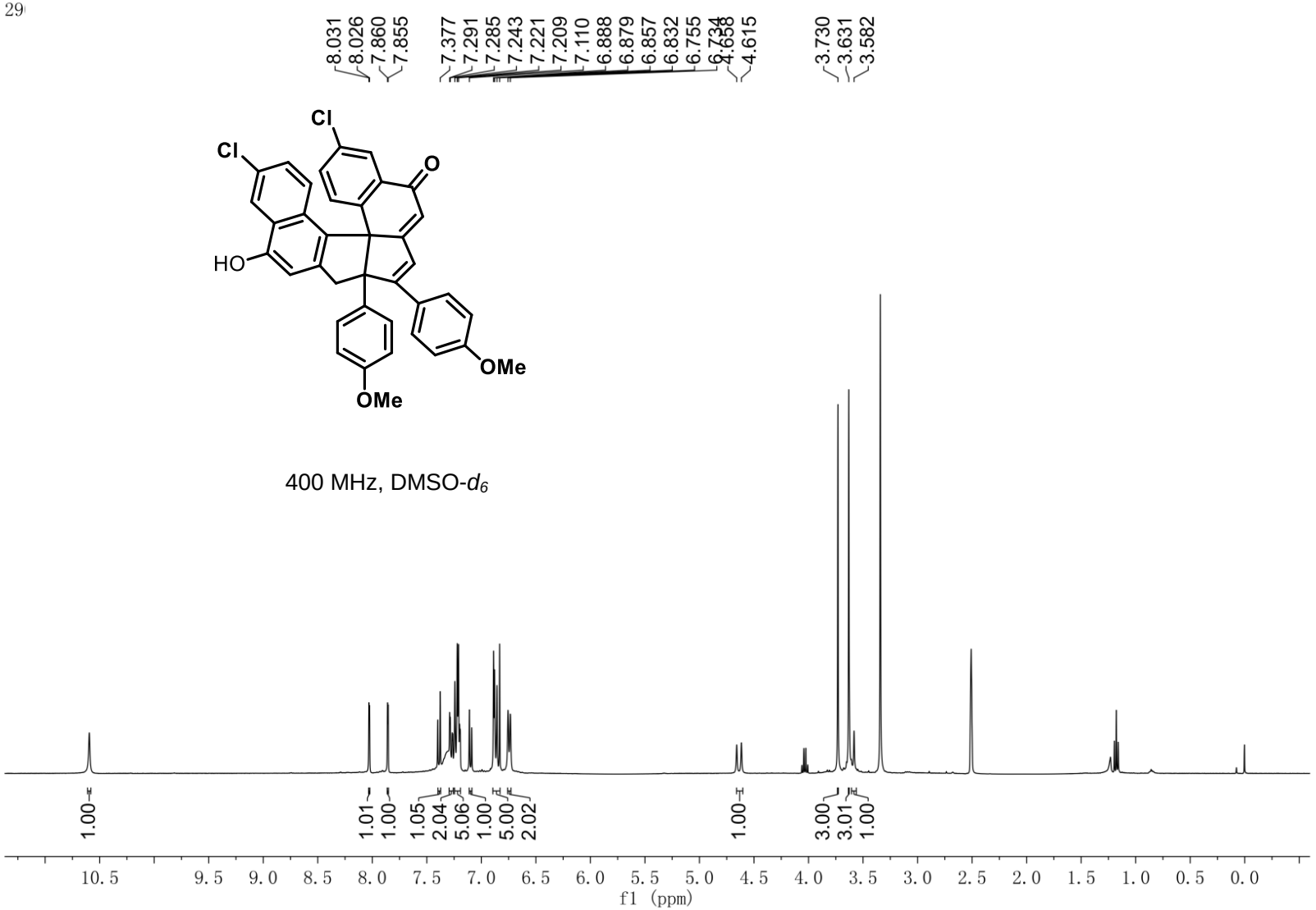
^{13}C NMR Spectrum of Compound 2u



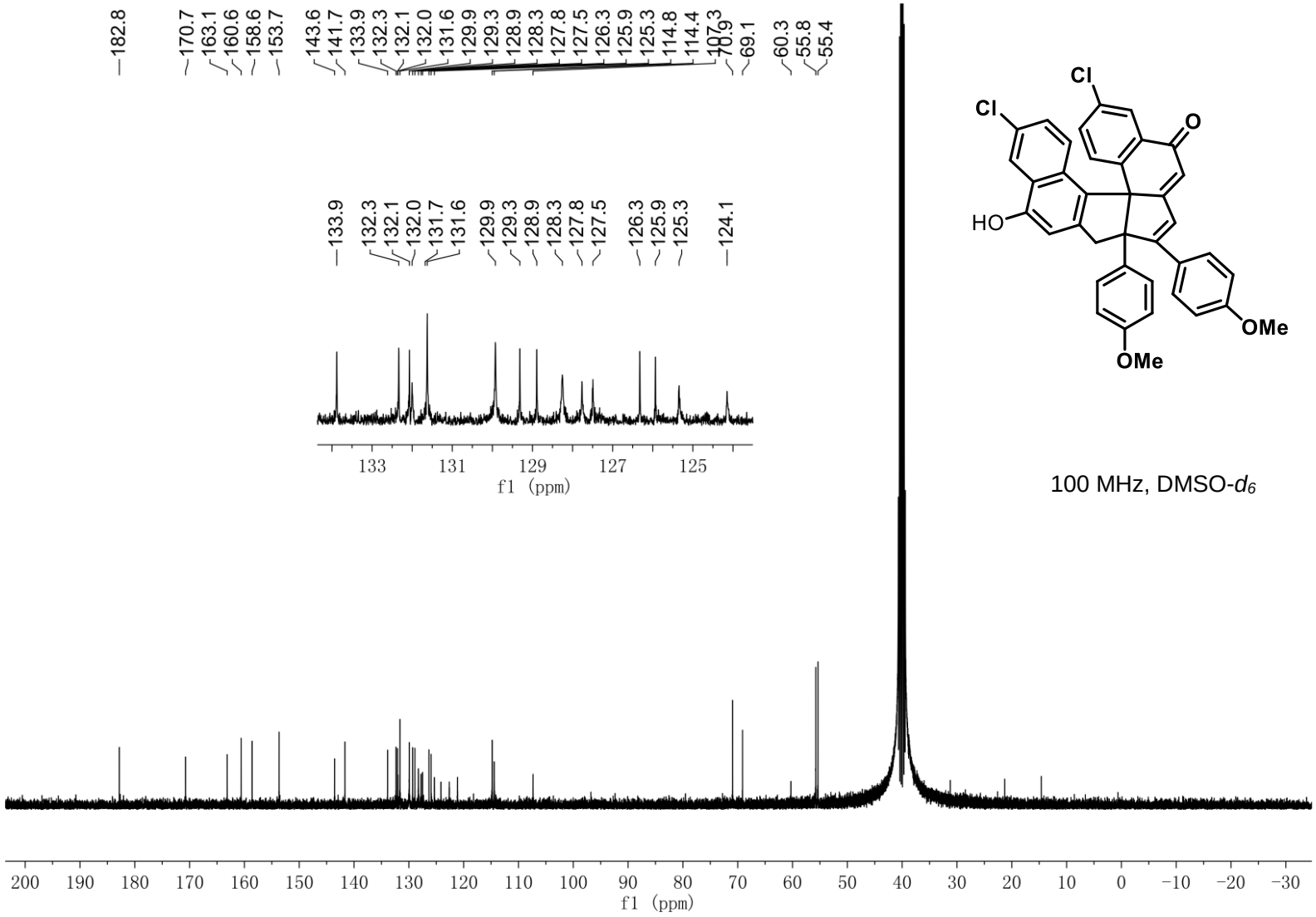
^{1}H NMR Spectrum of Compound 2v



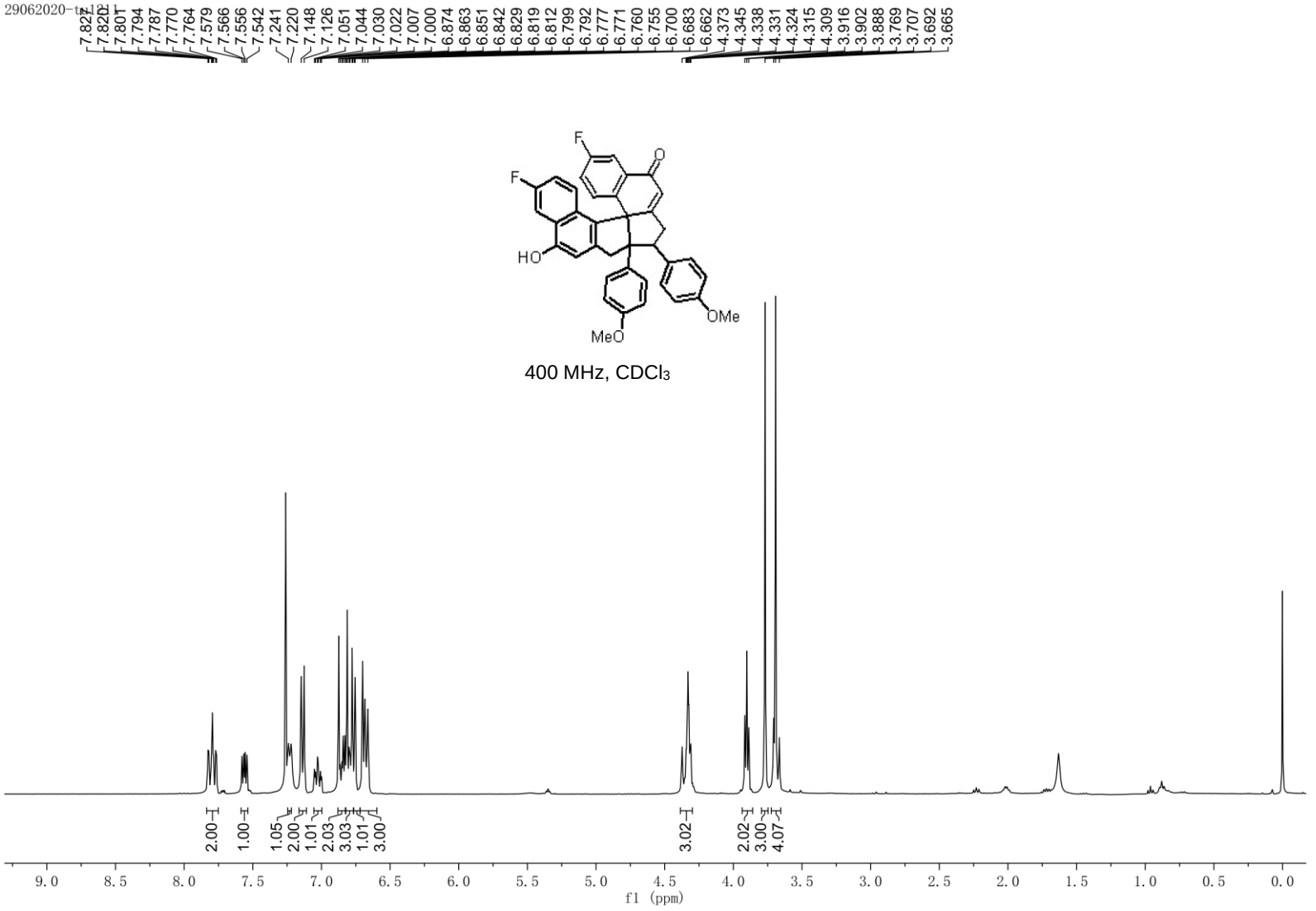
^{13}C NMR Spectrum of Compound 2v



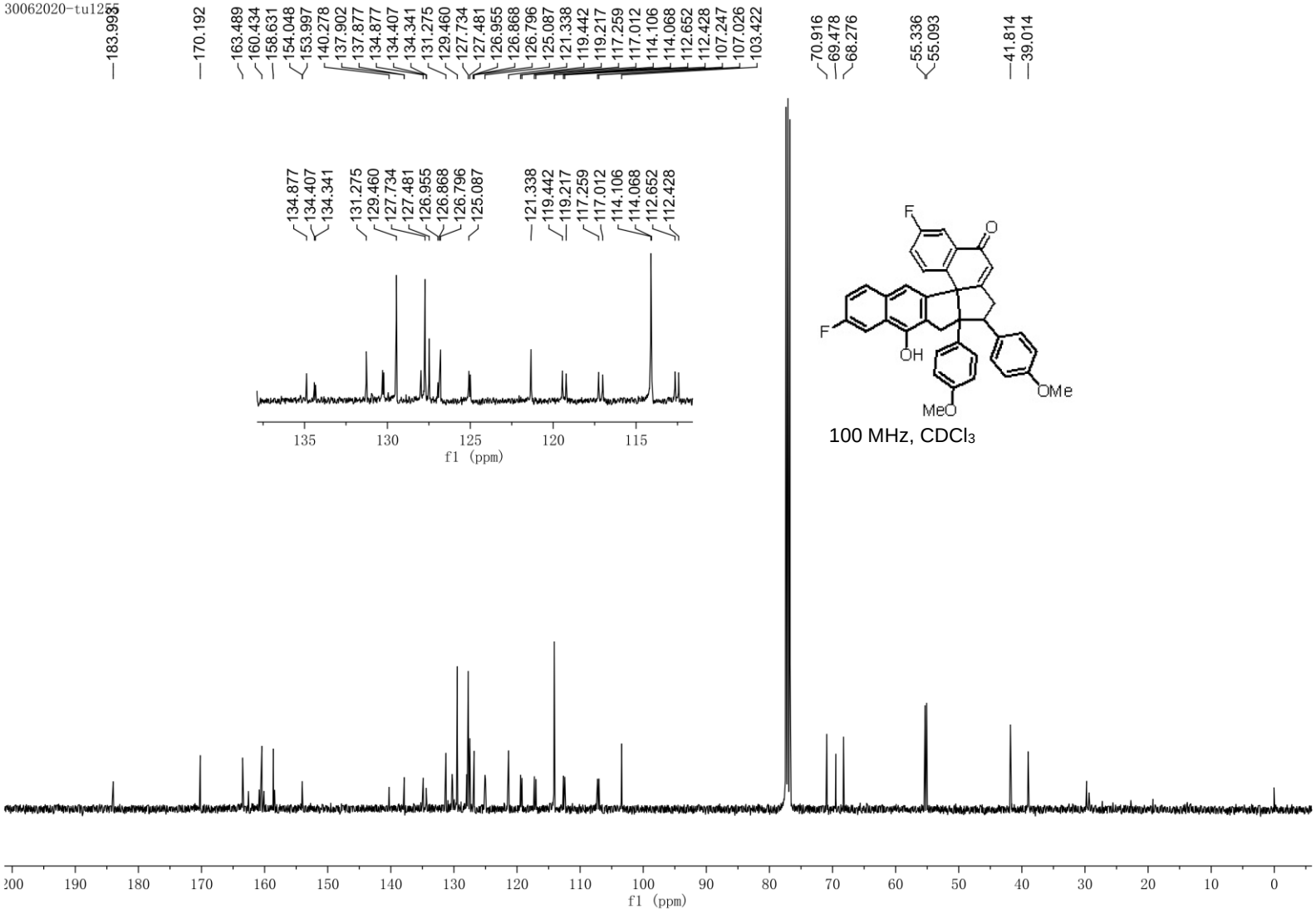
^{1}H NMR Spectrum of Compound 2w



^{13}C NMR Spectrum of Compound 2w



^{1}H NMR Spectrum of Compound 3



^{13}C NMR Spectrum of Compound 3