Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Palladium-catalyzed triple coupling of 2-iodoanisoles with aryl iodides to access 6*H*-dibenzopyrans

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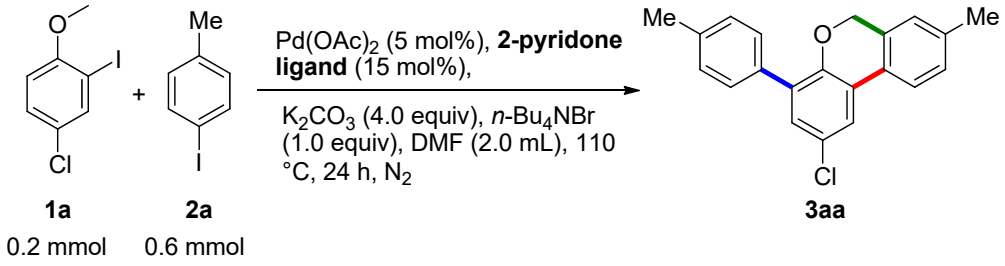
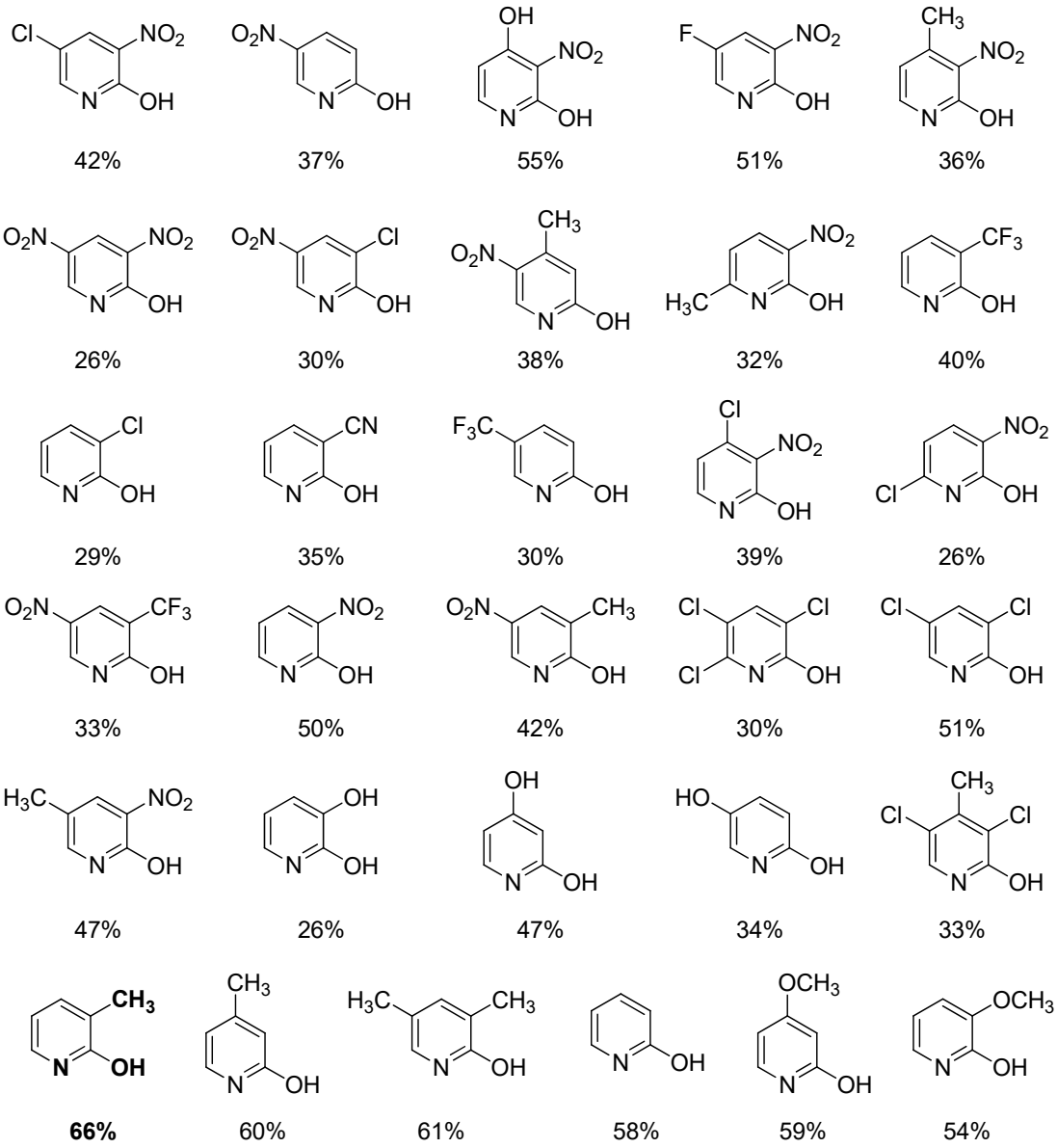
Screening of 2-pyridone ligands



1a 0.2 mmol + **2a** 0.6 mmol → **3aa**



Scheme SI-1 Screening of 2-pyridone ligands

General remarks

All of the manipulations were conducted with a Schlenk tube. ^{1}H NMR spectra were recorded on Varian 400 MHz or Bruker 600 MHz spectrometers. Chemical shifts

(in parts per million (ppm)) were referenced to tetramethylsilane (δ = 0 ppm) as an internal standard in $CDCl_3$. $^{13}C\{^1H\}$ NMR spectra were obtained by the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). High-resolution mass spectra (HRMS) were obtained using a quadrupole time-of-flight (Q-TOF) mass spectrometer with an electronspray ionization (ESI) resource, or a quadrupole fourier-transform (Q-FT) mass spectrometer with an electronspray ionization (ESI) resource or a matrix-assisted laser desorption/ionization (MALDI) resource. Melting points were determined with a melting point apparatus. Unless otherwise noted, other materials obtained from commercial suppliers were used without further purification.

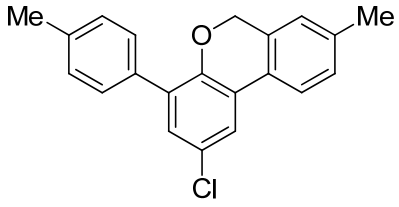
Synthesis of compounds 1 and 2

Compounds **1a**~**1m**, **2a**~**2m**, and **2k-D** were obtained from commercial suppliers. The compound **1i-D** was synthesized from 2-iodophenol and iodomethane-d_3 according to literature method.[1] Compound **1i-D** is known, and the data are consistent with the literature.[2]

General procedure for synthesis of compounds 3

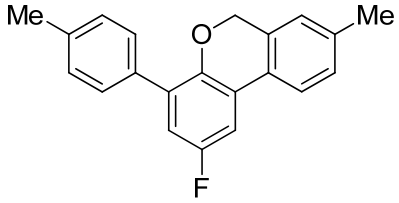
$Pd(OAc)_2$ (2.2 mg, 0.01 mmol), 3-methylpyridin-2-ol (3.3 mg, 0.03 mmol), K_2CO_3 (138.2 mg, 1.0 mmol), *n*-Bu_4NBr (64.5 mg, 0.2 mmol), 2-iodoanisole derivatives **1** (0.2 mmol) and iodobenzene derivatives **2** (0.6 mmol) were placed into a 25 mL Schlenk tube equipped with a magnetic stir bar. To this mixture was added DMF (2.0 mL) with an injection syringe under nitrogen atmosphere. The reaction mixture was stirred for 24 h at the appointed temperature in an oil bath. Then the solution was cooled to room temperature, quenched by the addition of 30 mL water, and extracted with dichloromethane (3 × 20 mL). The combined organic layer was washed with brine (3 × 30 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuum. The residue was purified by column chromatography on silica gel to afford the products **3**.

2-Chloro-8-methyl-4-(*p*-tolyl)-6*H*-benzo[*c*]chromene (3aa)



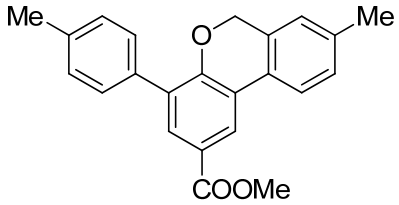
Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3aa**. White solid, 41.7 mg, 65% yield; mp 104.9−105.2 °C; IR (KBr, cm^{-1}) ν_{max} 2913, 2848, 1458, 1390, 1205, 1031, 820; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.62 (d, J = 2.4 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.43-7.41 (m, 2H), 7.25-7.22 (m, 3H), 7.19 (d, J = 7.8 Hz, 1H), 6.96 (s, 1H), 5.02 (s, 2H), 2.40 (s, 3H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 150.0, 138.4, 137.4, 133.9, 132.4, 131.4, 129.4, 129.3, 129.2, 128.9, 126.9, 126.7, 125.2, 125.1, 122.4, 121.9, 68.5, 21.3, 21.2; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{17}ClNaO$ 343.0866, Found 343.0863.

2-Fluoro-8-methyl-4-(*p*-tolyl)-6*H*-benzo[*c*]chromene (3ba)



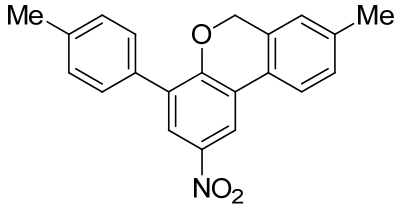
Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3ba**. White solid, 30.4 mg, 50% yield; mp 126.1−126.3 °C; IR (KBr, cm^{-1}) ν_{max} 2917, 2854, 1462, 1391, 1029, 823; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.54 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.36 (dd, J_1 = 9.0 Hz, J_2 = 3.0 Hz, 1H), 7.24 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 7.8 Hz, 1H), 7.00-6.97 (m, 2H), 5.02 (s, 2H), 2.40 (s, 3H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 157.8 (d, J = 238.05 Hz), 147.5, 138.4, 137.4, 134.1, 132.2 (d, J = 8.7 Hz), 131.7, 129.2, 129.2, 128.9, 127.1, 125.2, 124.9 (d, J = 8.55 Hz), 122.5, 116.2 (d, J = 23.7 Hz), 108.3 (d, J = 23.85 Hz), 68.5, 21.3, 21.2; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{17}FNaO$ 327.1161, Found 327.1158.

Methyl 8-methyl-4-(*p*-tolyl)-6*H*-benzo[*c*]chromene-2-carboxylate (3ca)



Purification by column chromatography (petroleum ether/ethyl acetate, 30:1 v/v) afforded **3ca**. White solid, 40.0 mg, 58% yield; mp 115.8−116.0 °C; IR (KBr, cm^{-1}) ν_{max} 3020, 2951, 2849, 1710, 1242, 1019; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 8.39 (d, J = 1.8 Hz, 1H), 7.96 (d, J = 2.4 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 8.4 Hz, 1H), 6.96 (s, 1H), 5.09 (s, 2H), 3.92 (s, 3H), 2.40 (s, 3H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 166.9, 155.2, 138.2, 137.2, 134.2, 131.5, 130.8, 130.8, 129.4, 129.2, 128.8, 126.8, 125.1, 123.8, 123.6, 123.3, 122.5, 68.6, 52.0, 21.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}O_3$ 345.1491, Found 345.1475.

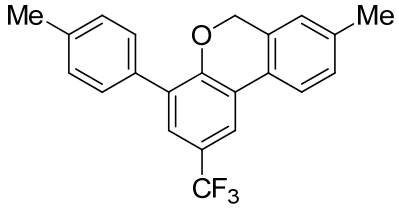
8-Methyl-2-nitro-4-(*p*-tolyl)-6*H*-benzo[*c*]chromene (3da)



Purification by column chromatography (petroleum ether/ethyl acetate, 30:1 v/v) afforded **3da**. White solid, 35.8 mg, 54% yield; mp 184.7−184.8 °C; IR (KBr, cm^{-1}) ν_{max} 2915, 2863, 1515, 1337, 1239, 1010, 812; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 8.57 (d, J = 2.4 Hz, 1H), 8.16 (d, J = 3.0 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.46 (d, J

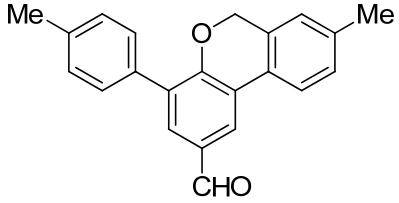
= 7.8 Hz, 2H), 7.29-7.25 (m, 3H), 7.00 (s, 1H), 5.17 (s, 2H), 2.42 (s, 3H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 156.5, 142.4, 139.4, 138.1, 132.9, 131.7, 130.5, 129.8, 129.2, 129.1, 125.7, 125.3, 125.1, 123.9, 122.7, 117.6, 68.9, 21.3, 21.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{18}NO_3$ 332.1287, Found 332.1271.

8-Methyl-4-(*p*-tolyl)-2-(trifluoromethyl)-6*H*-benzo[*c*]chromene (3ea)



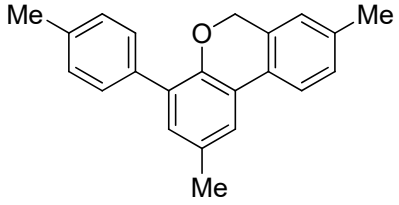
Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3ea**. White solid, 38.3 mg, 54% yield; mp 106.6−106.8 °C; IR (KBr, cm^{-1}) ν_{max} 2919, 2863, 1365, 1276, 1098, 817; ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.92 (s, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.51 (s, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 7.23 (d, J = 7.8 Hz, 1H), 6.99 (s, 1H), 5.10 (s, 2H), 2.41 (s, 3H), 2.39 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 153.8, 138.7, 137.6, 133.8, 131.4, 131.1, 129.5, 129.2, 129.0, 126.8 (q, J = 3.3 Hz), 126.4, 125.3, 124.4 (q, J = 269.7 Hz), 124.0 (q, J = 32.4 Hz), 123.9, 122.5, 119.2 (q, J = 3.3 Hz), 68.6, 21.3, 21.2; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{17}F_3NaO$ 377.1129, Found 377.1128.

8-Methyl-4-(*p*-tolyl)-6*H*-benzo[*c*]chromene-2-carbaldehyde (3fa)



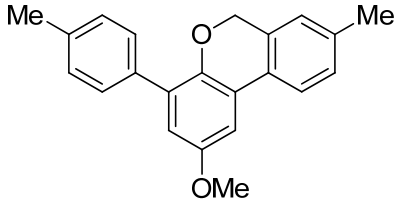
Purification by column chromatography (petroleum ether/ethyl acetate, 15:1 v/v) afforded **3fa**. Yellow solid, 44.0 mg, 70% yield; mp 109.8−110.1 °C; IR (KBr, cm^{-1}) ν_{max} 2920, 2850, 1693, 1592, 1164, 1019, 822; ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 9.95 (s, 1H), 8.19 (s, 1H), 7.76 (s, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 7.8 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 7.8 Hz, 1H), 6.95 (s, 1H), 5.11 (s, 2H), 2.40 (s, 3H), 2.37 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 191.1, 156.6, 138.6, 137.5, 133.7, 132.1, 131.5, 130.6, 130.5, 129.5, 129.2, 128.9, 126.3, 125.1, 123.9, 123.4, 122.5, 68.7, 21.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}O_2$ 315.1385, Found 315.1372.

2,8-Dimethyl-4-(*p*-tolyl)-6*H*-benzo[*c*]chromene (3ga)



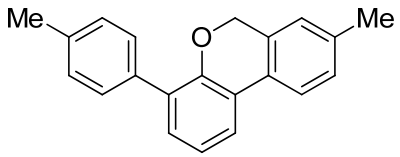
Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3ga**. White solid, 21.6 mg, 36% yield; mp 102.8−102.9 °C; IR (KBr, cm^{-1}) ν_{max} 2917, 2855, 1431, 1212, 1032, 820; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.61 (d, J = 7.8 Hz, 1H), 7.50 (s, 1H), 7.45 (d, J = 7.8 Hz, 2H), 7.23 (d, J = 6.6 Hz, 2H), 7.18 (d, J = 7.8 Hz, 1H), 7.08 (s, 1H), 6.95 (s, 1H), 5.00 (s, 2H), 2.39 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 149.4, 137.5, 136.7, 135.2, 131.7, 130.9, 130.8, 130.5, 129.3, 129.0, 128.7, 127.8, 125.2, 123.4, 122.6, 122.2, 68.5, 21.2, 20.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}O$ 301.1592, Found 301.1579.

2-Methoxy-8-methyl-4-(*p*-tolyl)-6*H*-benzo[*c*]chromene (3ha)



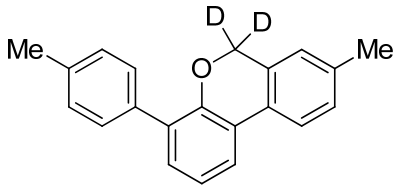
Purification by column chromatography (petroleum ether/CH_2Cl_2, 3:1 v/v) afforded **3ha**. Yellow solid, 25.3 mg, 40% yield; mp 93.5−93.8 °C; IR (KBr, cm^{-1}) ν_{max} 2918, 2847, 1606, 1510, 1430, 1201, 1058, 1016, 822; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.58 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 7.8 Hz, 2H), 7.25-7.22 (m, 3H), 7.18 (d, J = 7.8 Hz, 1H), 6.96 (s, 1H), 6.84 (d, J = 3.0 Hz, 1H), 4.98 (s, 2H), 3.85 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 154.3, 145.6, 137.8, 137.0, 135.0, 132.0, 131.6, 129.2, 129.0, 128.8, 127.7, 125.2, 124.5, 122.3, 115.5, 107.4, 68.5, 55.8, 21.2, 21.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}O_2$ 317.1542, Found 317.1526.

8-Methyl-4-(*p*-tolyl)-6*H*-benzo[*c*]chromene (3ia)



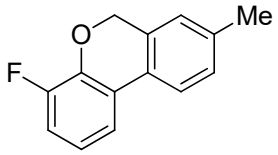
Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3ia**. White solid, 34.9 mg, 61% yield; mp 106.8−107.0 °C; IR (KBr, cm^{-1}) ν_{max} 2814, 2855, 1457, 1204, 1023, 784; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.69 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.27 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.24 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 7.8 Hz, 1H), 7.09 (t, J = 7.8 Hz, 1H), 6.97 (s, 1H), 5.04 (s, 2H), 2.40 (s, 3H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 151.5, 137.6, 136.8, 135.1, 131.6, 130.8, 130.2, 129.3, 129.1, 128.8, 127.7, 125.2, 123.7, 122.3, 122.2, 121.8, 68.5, 21.2, 21.2; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{19}O$ 287.1436, Found 287.1421.

6,6-Dideuterium-8-methyl-4-(*p*-tolyl)-6*H*-benzo[*c*]chromene (3ia-D)



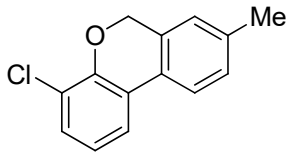
Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3ia-D**. White solid, 26.5 mg, 46% yield; mp 103.6−103.8 °C; IR (KBr, cm^{-1}) ν_{max} 2916, 2854, 1442, 1391, 1234, 1074, 782; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.70 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H), 7.27 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.24 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 7.2 Hz, 1H), 7.10 (t, J = 7.8 Hz, 1H), 6.97 (s, 1H), 2.40 (s, 3H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 151.5, 137.6, 136.8, 135.1, 131.4, 130.8, 130.2, 129.3, 129.1, 128.8, 127.7, 125.2, 123.6, 122.3, 122.2, 121.8, 21.2; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{16}D_2NaO$ 311.1381, Found 311.1380.

4-Fluoro-8-methyl-6*H*-benzo[*c*]chromene (3ja)



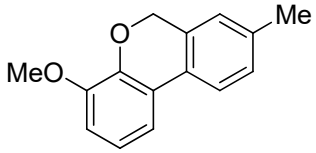
Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3ja**. White solid, 21.4 mg, 50% yield; mp 68.5−68.6 °C; IR (KBr, cm^{-1}) ν_{max} 2909, 2860, 1478, 1252, 1009, 785; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.56 (d, J = 7.8 Hz, 1H), 7.46 (d, J = 7.8 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.03-6.98 (m, 1H), 6.98 (s, 1H), 6.97-6.92 (m, 1H), 5.15 (s, 2H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 152.0 (d, J = 243.6 Hz), 142.2 (d, J = 11.85 Hz), 138.3, 131.1, 129.3, 126.5 (d, J = 3.3 Hz), 125.5 (d, J = 1.5 Hz), 125.4, 122.3, 121.5 (d, J = 7.5 Hz), 118.1 (d, J = 3.15 Hz), 115.5 (d, J = 17.55 Hz), 68.7, 21.2; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{11}FNaO$ 237.0692, Found 237.0689.

4-Chloro-8-methyl-6*H*-benzo[*c*]chromene (3ka)



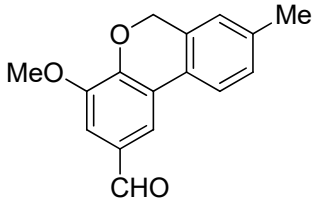
Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3ka**. White solid, 24.0 mg, 52% yield; mp 62.5−62.6 °C; IR (KBr, cm^{-1}) ν_{max} 2915, 2859, 1431, 1405, 1225, 1028, 821; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.59 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.26 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 6.98 (s, 1H), 6.96 (t, J = 7.8 Hz, 1H), 5.18 (s, 2H), 2.37 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 150.2, 138.3, 131.0, 129.3, 126.6, 125.3, 124.6, 122.4, 122.3, 122.1, 121.4, 68.9, 21.2; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{11}ClNaO$ 253.0396, Found 253.0393.

4-Methoxy-8-methyl-6*H*-benzo[*c*]chromene (3la)



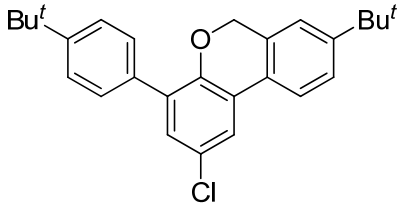
Purification by column chromatography (petroleum ether/CH_2Cl_2, 3:1 v/v) afforded **3la**. White solid, 14.9 mg, 33% yield; mp 60.9−61.2 °C; IR (KBr, cm^{-1}) ν_{max} 2919, 1564, 1474, 1250, 1023; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.56 (d, J = 7.8 Hz, 1H), 7.32 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 6.98 (t, J = 7.8 Hz, 1H), 6.97 (s, 1H), 6.84 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 5.15 (s, 2H), 3.90 (s, 3H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 148.9, 143.5, 137.7, 131.2, 129.0, 127.2, 125.2, 123.8, 122.2, 121.5, 115.1, 111.1, 68.7, 56.0, 21.2; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{14}NaO_2$ 249.0891, Found 249.0889.

4-Methoxy-8-methyl-6*H*-benzo[*c*]chromene-2-carbaldehyde (3ma)



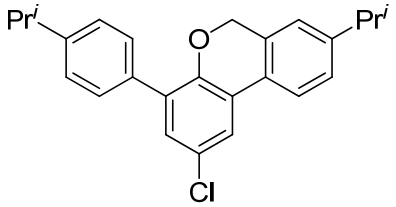
Purification by column chromatography (petroleum ether/ethyl acetate, 10:1 v/v) afforded **3ma**. White solid, 24.4 mg, 48% yield; mp 148.7−148.9 °C; IR (KBr, cm^{-1}) ν_{max} 2921, 1690, 1244, 1145; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 9.94 (s, 1H), 7.86 (d, J = 1.8 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 1.8 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.01 (s, 1H), 5.27 (s, 2H), 3.98 (s, 3H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 191.1, 149.7, 149.0, 138.8, 130.5, 130.3, 129.5, 125.9, 125.3, 123.5, 122.3, 120.0, 109.3, 69.1, 56.2, 21.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{15}O_3$ 255.1021, Found 255.1011.

8-(Tert-butyl)-4-(4-(tert-butyl)phenyl)-2-chloro-6*H*-benzo[*c*]chromene (3ab)



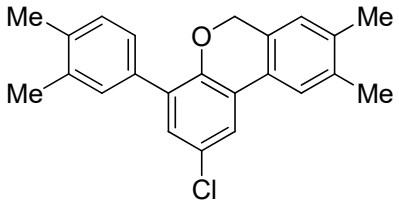
Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3ab**. White solid, 48.6 mg, 60% yield; mp 155.1−155.3 °C; IR (KBr, cm^{-1}) ν_{max} 2961, 2861, 1461, 1224, 1015, 824; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.64 (d, J = 2.4 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 9.0 Hz, 2H), 7.43 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.25 (d, J = 2.4 Hz, 1H), 7.17 (d, J = 2.4 Hz, 1H), 5.07 (s, 2H), 1.37 (s, 9H), 1.35 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 151.7, 150.5, 150.2, 133.8, 132.2, 131.1, 129.6, 128.9, 126.9, 126.7, 125.6, 125.1, 125.1, 122.3, 121.9, 121.6, 68.9, 34.7, 34.6, 31.3, 31.3; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{30}ClO$ 405.1985, Found 405.1975.

2-Chloro-8-isopropyl-4-(4-isopropylphenyl)-6*H*-benzo[*c*]chromene (3ac)



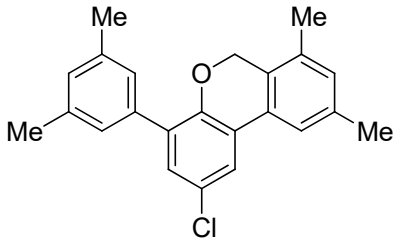
Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3ac**. White solid, 42.2 mg, 56% yield; mp 47.9−48.2 °C; IR (KBr, cm^{-1}) ν_{max} 2959, 2925, 1642, 1459, 1022, 830; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.63 (d, J = 1.2 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 7.2 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 7.27-7.23 (m, 2H), 7.01 (s, 1H), 5.05 (s, 2H), 2.99-2.88 (m, 2H), 1.29 (d, J = 7.2 Hz, 6H), 1.27 (d, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 150.1, 149.4, 148.2, 134.2, 132.4, 131.4, 129.6, 129.2, 127.1, 126.9, 126.7, 126.3, 125.2, 122.6, 122.5, 121.9, 68.7, 34.0, 33.9, 24.0, 23.9; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{25}ClNaO$ 399.1492, Found 399.1491.

2-Chloro-4-(3,4-dimethylphenyl)-8,9-dimethyl-6*H*-benzo[*c*]chromene (3ad)



Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3ad**. White solid, 36.3 mg, 52% yield; mp 181.3−181.6 °C; IR (KBr, cm^{-1}) ν_{max} 2914, 2854, 1439, 1376, 1212, 1019, 867; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.62 (d, J = 2.4 Hz, 1H), 7.44 (s, 1H), 7.29 (s, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.21 (d, J = 2.4 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 6.91 (s, 1H), 5.00 (s, 2H), 2.32 (s, 3H), 2.31 (s, 3H), 2.30 (s, 3H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 150.1, 137.0, 136.8, 136.3, 136.1, 134.4, 132.5, 130.4, 129.4, 129.3, 129.0, 126.9, 126.8, 125.8, 125.1, 123.6, 121.7, 68.3, 19.9, 19.8, 19.6, 19.5; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{21}ClO$ 348.1281, Found 348.1284.

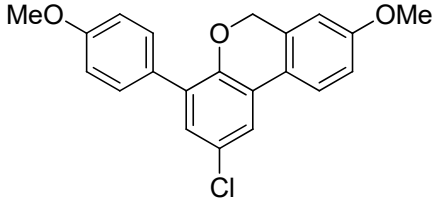
2-Chloro-4-(3,5-dimethylphenyl)-7,9-dimethyl-6*H*-benzo[*c*]chromene (3ae)



Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3ae**. White solid, 41.9 mg, 60% yield; mp 163.6−163.9 °C; IR (KBr, cm^{-1}) ν_{max} 2911, 2851, 1603, 1398, 1192, 1010, 852, 675; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.63 (d, J = 2.4 Hz, 1H), 7.34 (s, 1H), 7.22 (d, J = 2.4 Hz, 1H), 7.13 (s, 2H), 7.00 (s,

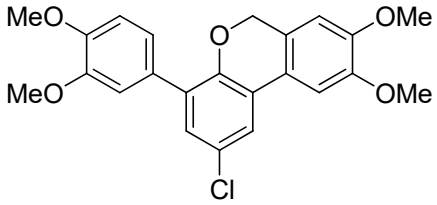
1H), 6.97 (s, 1H), 5.07 (s, 2H), 2.36 (s, 9H), 2.23 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 150.1, 137.6, 137.5, 136.7, 133.0, 132.6, 131.0, 129.7, 129.3, 129.1, 127.2, 127.1, 126.7, 125.3, 122.3, 120.8, 65.6, 21.4, 21.3, 18.2; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{21}ClNaO$ 371.1179, Found 371.1175.

2-Chloro-8-methoxy-4-(4-methoxyphenyl)-6*H*-benzo[*c*]chromene (3af)



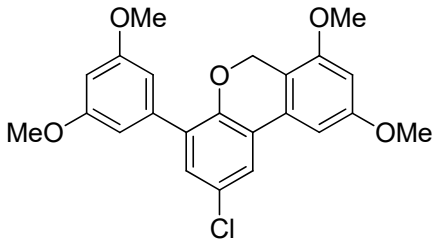
Purification by column chromatography (petroleum ether/CH_2Cl_2, 10:1 v/v) afforded **3af**. Tawny solid, 38.8 mg, 55% yield; mp 68.7−68.7 °C; IR (KBr, cm^{-1}) ν_{max} 2923, 2834, 1611, 1510, 1245, 1029, 825; ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.61 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 2.4 Hz, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 3.0 Hz, 1H), 6.97 (d, J = 9.0 Hz, 2H), 6.94 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.69 (d, J = 2.4 Hz, 1H), 5.04 (s, 2H), 3.85 (s, 3H), 3.85 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 159.9, 159.1, 149.4, 133.1, 132.0, 129.2, 128.8, 127.0, 125.1, 124.0, 122.2, 121.3, 114.1, 113.6, 110.0, 68.5, 55.4, 55.3; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{17}ClNaO_3$ 375.0764, Found 375.0760.

2-Chloro-4-(3,4-dimethoxyphenyl)-8,9-dimethoxy-6*H*-benzo[*c*]chromene (3ag)



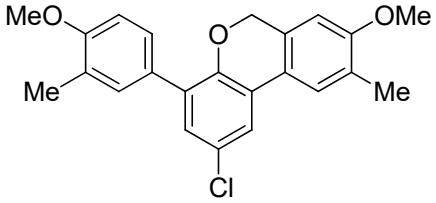
Purification by column chromatography (petroleum ether/ethyl acetate, 5:1 v/v) afforded **3ag**. White solid, 38.8 mg, 47% yield; mp 186.1−186.2 °C; IR (KBr, cm^{-1}) ν_{max} 2942, 2841, 1516, 1272, 1034, 857; ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.55 (d, J = 2.4 Hz, 1H), 7.22 (d, J = 2.4 Hz, 1H), 7.16 (s, 1H), 7.10 (dd, J_1 = 7.8 Hz, J_2 = 2.4 Hz, 1H), 7.08 (d, J = 1.8 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.67 (s, 1H), 5.03 (s, 2H), 3.99 (s, 3H), 3.93 (s, 3H), 3.92 (s, 6H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 149.5, 149.5, 149.4, 148.6, 148.5, 132.1, 129.4, 128.9, 126.9, 125.2, 124.1, 122.0, 121.7, 121.2, 112.7, 110.8, 107.7, 105.8, 68.2, 56.2, 56.1, 55.9, 55.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{22}ClO_5$ 413.1156, Found 413.1147.

2-Chloro-4-(3,5-dimethoxyphenyl)-7,9-dimethoxy-6*H*-benzo[*c*]chromene (3ah)



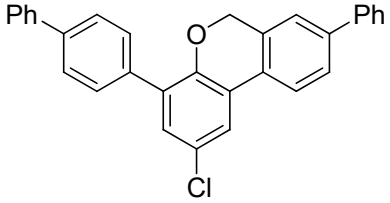
Purification by column chromatography (petroleum ether/CH_2Cl_2, 3:1 v/v) afforded **3ah**. White solid, 47.9 mg, 58% yield; mp 159.9−160.1 °C; IR (KBr, cm^{-1}) ν_{max} 2936, 2834, 1607, 1400, 1198, 1147, 1058, 826, 692; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.61 (d, J = 2.4 Hz, 1H), 7.27 (d, J = 2.4 Hz, 1H), 6.77 (d, J = 2.4 Hz, 1H), 6.68 (d, J = 2.4 Hz, 2H), 6.48 (t, J = 2.4 Hz, 1H), 6.46 (d, J = 2.4 Hz, 1H), 5.10 (s, 2H), 3.90 (s, 3H), 3.83 (s, 6H), 3.82 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 160.7, 160.4, 156.0, 150.5, 138.6, 132.3, 130.9, 129.9, 126.5, 125.0, 122.7, 112.8, 107.5, 99.9, 98.5, 63.1, 55.6, 55.5, 55.4; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{22}ClO_5$ 413.1156, Found 413.1142.

2-Chloro-8-methoxy-4-(4-methoxy-3-methylphenyl)-9-methyl-6*H*-benzo[*c*]chromene (3ai)



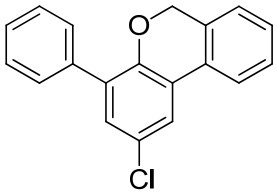
Purification by column chromatography (petroleum ether/CH_2Cl_2, 10:1 v/v) afforded **3ai**. White solid, 34.3 mg, 45% yield; mp 144.2−144.5 °C; IR (KBr, cm^{-1}) ν_{max} 2925, 2843, 1508, 1251, 1033; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.55 (d, J = 2.4 Hz, 1H), 7.45 (s, 1H), 7.34 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 7.31 (d, J = 1.2 Hz, 1H), 7.17 (d, J = 3.0 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.58 (s, 1H), 5.02 (s, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 2.27 (s, 3H), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 158.1, 157.3, 149.4, 132.1, 131.6, 130.3, 128.8, 128.6, 127.8, 126.9, 126.8, 126.3, 125.2, 125.0, 121.5, 121.1, 109.5, 106.0, 68.5, 55.5, 55.3, 16.3, 16.3; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{21}ClNaO_3$ 403.1077, Found 403.1075.

4-([1,1'-Biphenyl]-4-yl)-2-chloro-8-phenyl-6*H*-benzo[*c*]chromene (3aj)



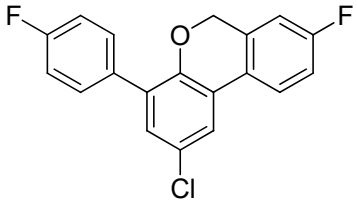
Purification by column chromatography (petroleum ether/CH_2Cl_2, 20:1 v/v) afforded **3aj**. White solid, 47.2 mg, 53% yield; mp 143.0−143.2 °C; IR (KBr, cm^{-1}) ν_{max} 3030, 2845, 1485, 1392, 1217, 1016, 837, 768, 694; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.77 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 3.0 Hz, 1H), 7.69-7.61 (m, 9H), 7.47 (t, J = 7.8 Hz, 4H), 7.41 (s, 1H), 7.40-7.35 (m, 2H), 7.34 (d, J = 2.4 Hz, 1H), 5.18 (s, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 150.3, 141.3, 140.7, 140.5, 140.2, 135.6, 132.1, 131.9, 129.9, 129.7, 128.9, 128.8, 128.4, 127.7, 127.4, 127.4, 127.2, 127.1, 126.9, 124.9, 123.3, 123.0, 122.4, 68.7; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{31}H_{21}ClNaO$ 467.1179, Found 467.1175.

2-Chloro-4-phenyl-6*H*-benzo[*c*]chromene (3ak)



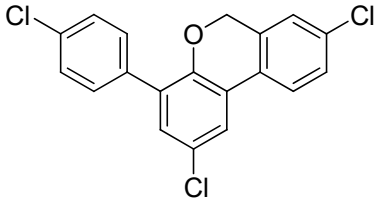
Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3ak**. Colorless liquid, 31.6 mg, 54% yield; IR (KBr, cm^{-1}) ν_{max} 3051, 2925, 2852, 1413, 1013, 702; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.66 (d, J = 2.4 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 7.8 Hz, 2H), 7.41 (t, J = 7.8 Hz, 2H), 7.38-7.33 (m, 2H), 7.29 (t, J = 7.8 Hz, 1H), 7.26 (d, J = 2.4 Hz, 1H), 7.12 (d, J = 7.2 Hz, 1H), 5.03 (s, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 150.2, 136.6, 132.5, 131.4, 130.0, 129.3, 128.6, 128.3, 128.1, 127.6, 127.0, 125.0, 124.6, 122.4, 122.3, 68.4; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{13}ClNaO$ 315.0553, Found 315.0552.

2-Chloro-8-fluoro-4-(4-fluorophenyl)-6*H*-benzo[*c*]chromene (3al)



Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3al**. White solid, 24.9 mg, 38% yield; mp 153.4−153.8 °C; IR (KBr, cm^{-1}) ν_{max} 2918, 2866, 1507, 1223, 1012, 824; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.64 (dd, J_1 = 8.4 Hz, J_2 = 4.8 Hz, 1H), 7.62 (d, J = 2.4 Hz, 1H), 7.48 (dd, J_1 = 8.4 Hz, J_2 = 5.4 Hz, 2H), 7.23 (d, J = 2.4 Hz, 1H), 7.13-7.08 (m, 3H), 6.88 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 5.03 (s, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 162.8 (d, J = 247.2 Hz), 162.4 (d, J = 245.7 Hz), 149.6, 133.5 (d, J = 7.5 Hz), 132.4 (d, J = 3.3 Hz), 131.6, 131.0 (d, J = 7.65 Hz), 129.7, 127.3, 125.5 (d, J = 3.3 Hz), 124.5 (d, J = 8.55 Hz), 124.4, 122.2, 115.7 (d, J = 21.75 Hz), 115.1 (d, J = 21.6 Hz), 111.9 (d, J = 22.8 Hz), 68.0; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{11}ClF_2NaO$ 351.0364, Found 351.0362.

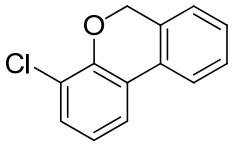
2,8-Dichloro-4-(4-chlorophenyl)-6*H*-benzo[*c*]chromene (3am)



Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3al**. White solid, 24.6 mg, 34% yield; mp 184.2−184.4 °C; IR (KBr, cm^{-1}) ν_{max} 2915, 2863, 1494, 1385, 1217, 1014, 822; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.64 (d, J = 2.4 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.37 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.25 (d, J = 2.4 Hz, 1H), 7.17 (d, J = 1.8 Hz, 1H), 5.02 (s, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 149.9,

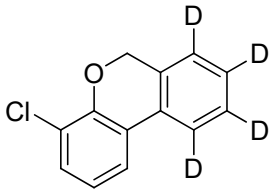
134.8, 134.3, 133.8, 132.9, 131.4, 130.6, 130.0, 128.8, 128.4, 127.8, 127.4, 124.9, 124.3, 123.9, 122.6, 67.9; HRMS (MALDI) m/z: $[M-H]^+$ calcd for $C_{19}H_{10}Cl_3O$ 358.9792, Found 358.9795.

4-Chloro-6*H*-benzo[*c*]chromene (3kk)



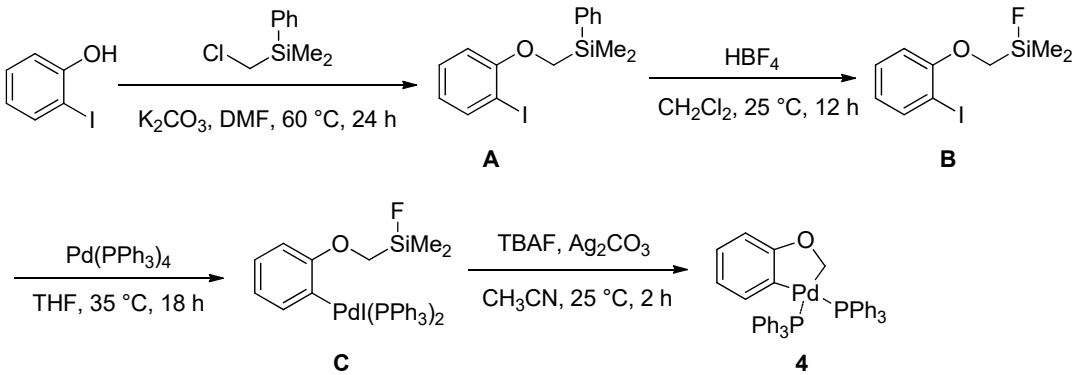
Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3kk**. White solid, 19.1 mg, 44% yield; mp 61.1−61.2 °C; IR (KBr, cm^{-1}) ν_{max} 2920, 1425, 1196, 1002, 739; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.68 (d, J = 7.8 Hz, 1H), 7.63 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.34-7.29 (m, 2H), 7.18 (d, J = 7.2 Hz, 1H), 6.99 (t, J = 7.8 Hz, 1H), 5.22 (s, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 150.5, 131.0, 129.8, 129.4, 128.6, 128.3, 124.7, 124.5, 122.5, 122.4, 122.2, 121.7, 68.9; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_9ClNaO$ 239.0240, Found 239.0239.

4-Chloro-7,8,9,10-tetradeuterium-6*H*-benzo[*c*]chromene (3kk-D)



Purification by column chromatography (petroleum ether/CH_2Cl_2, 30:1 v/v) afforded **3kk-D**. White solid, 15.0 mg, 34% yield; mp 61.0−61.1 °C; IR (KBr, cm^{-1}) ν_{max} 2919, 1455, 1227, 1005, 731; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 7.63 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.30 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 6.99 (t, J = 7.8 Hz, 1H), 5.23 (s, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 150.5, 130.9, 129.8, 129.3, 128.1 (t, J = 24.3 Hz), 127.8 (t, J = 24.6 Hz), 124.5, 124.3 (t, J = 24.15 Hz), 122.5, 122.2, 122.0 (t, J = 23.85 Hz), 121.7; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_5D_4ClNaO$ 243.0491, Found 243.0489.

Synthesis of compound 4



The compound **A** was synthesized according to literature method.[3] Compound **A** is known, and the data are consistent with the literature.[3]

The compound **B** was synthesized according to modified literature method.[3] The compound **A** (73.7 mg, 0.2 mmol) was placed into a 25 mL Schlenk tube equipped with a magnetic stir bar. To this tube was added in sequence CH_2Cl_2 (2.0 mL), HBF_4 (252 uL, 54% solution in Et_2O, 1.0 mmol) with an injection syringe. The reaction mixture was stirred for 12 h at 25 °C in an oil bath. Then the solution was cooled to 0 °C, quenched by the gradual addition of water, and extracted with dichloromethane. The combined organic layer was washed with a saturated solution of $NaHCO_3$ to neutralize the acid, dried over anhydrous $MgSO_4$, and concentrated in vacuum. The product **B** was obtained as a very pale yellow oil (55.8 mg, 90%). Compound **B** is known, and the data are consistent with the literature.[3]

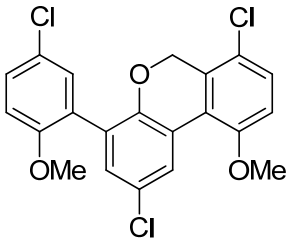
The compound **C** was synthesized according to modified literature method.[3] $Pd(PPh_3)_4$ (115.6 mg, 0.1 mmol), and compound **B** (31.0 mg, 0.1 mmol) were placed into a 25 mL Schlenk tube equipped with a magnetic stir bar. To this mixture was added THF (5.0 mL) with an injection syringe under nitrogen atmosphere. The reaction mixture was stirred for 18 h at 35 °C in an oil bath. The solvent was evaporated, and Et_2O was added into the residue. The precipitate was filtered to give as a yellow solid (59.3 mg, 63%). Compound **C** is known, and the data are consistent with the literature.[3]

The compound **4** was synthesized according to modified literature method.[3] Compound **C** (47.1 mg, 0.05 mmol), tetrabutylammonium fluoride (19.6 mg, 0.075 mmol), and Ag_2CO_3 (27.6 mg, 0.1 mmol) were placed into a 25 mL Schlenk tube equipped with a magnetic stir bar. To this mixture was added MeCN (3.0 mL) with an injection syringe under nitrogen atmosphere. The reaction mixture was stirred for 2 h at 25 °C in an oil bath. The solvent was removed under reduced pressure, and the residue was partially dissolved in CH_2Cl_2 and filtered through Celite. CH_2Cl_2 in the filtrate was removed under reduced pressure, and Et_2O was added into the residue. The mixture was filtered through Celite, and Et_2O in the filtrate was removed under reduced pressure to give as a white solid (13.2 mg, 36%). All of the manipulations were carried out in a glove box because the compound **4** is easily decomposed by water. Compound **4** is known, and the data are consistent with the literature.[4]

General procedure for synthesis of compounds 5

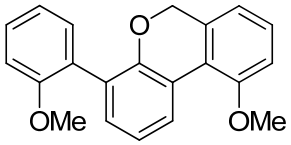
$Pd(OAc)_2$ (2.2 mg, 0.01 mmol), K_2CO_3 (138.2 mg, 1.0 mmol), *n*-Bu_4NBr (64.5 mg, 0.2 mmol) and 2-iodoanisole derivatives **1** (0.2 mmol) were placed into a 25 mL Schlenk tube equipped with a magnetic stir bar. To this mixture was added DMF (2.0 mL) with an injection syringe under nitrogen atmosphere. The reaction mixture was stirred for 24 h at 110 °C in an oil bath. Then the solution was cooled to room temperature, quenched by the addition of 30 mL water, and extracted with dichloromethane (3 × 20 mL). The combined organic layer was washed with brine (3 × 30 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuum. The residue was purified by column chromatography on silica gel to afford the products **5**.

2,7-Dichloro-4-(5-chloro-2-methoxyphenyl)-10-methoxy-6*H*-benzo[c]chromene (5a)



Purification by column chromatography (petroleum ether/CH_2Cl_2, 8:1 v/v) afforded **5a**. White solid, 14.3 mg, 51% yield; mp 80.0−80.6 °C; IR (KBr, cm^{-1}) ν_{max} 2962, 2818, 1457, 1416, 1270, 1240, 747; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 8.35 (d, J = 3.0 Hz, 1H), 7.31 (dd, J_1 = 9.0 Hz, J_2 = 2.4 Hz, 1H), 7.28 (d, J = 9.0 Hz, 1H), 7.21 (d, J = 2.4 Hz, 1H), 7.17 (d, J = 3.0 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H), 6.90 (d, J = 9.0 Hz, 1H), 5.08 (s, 2H), 3.95 (s, 3H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 155.6, 155.3, 151.1, 132.2, 130.9, 130.2, 129.3, 128.8, 128.0, 127.6, 126.3, 125.3, 122.9, 122.2, 119.9, 112.2, 112.1, 65.9, 56.0, 55.9; HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{15}Cl_3NaO_3$ 442.9984, Found 442.9985.

10-Methoxy-4-(2-methoxyphenyl)-6*H*-benzo[c]chromene (5i)[5]



Purification by column chromatography (petroleum ether/CH_2Cl_2, 5:1 v/v) afforded **5i**. White solid, 9.1 mg, 43% yield; mp 136.8−137.3 °C; IR (KBr, cm^{-1}) ν_{max} 2937, 2837, 1492, 1457, 1421, 1270, 1230, 1028, 805, 653; ^1H NMR (600 MHz, $CDCl_3$, ppm) δ 8.40 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.36-7.32 (m, 1H), 7.27 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H), 7.20 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.11 (t, J = 7.8 Hz, 1H), 7.01 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 6.95 (d, J = 7.8 Hz, 1H), 6.76 (d, J = 7.2 Hz, 1H), 4.94 (s, 2H), 3.94 (s, 3H), 3.80 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ 157.0, 156.6, 152.7, 135.0, 131.4, 130.5, 128.6, 128.3, 128.0, 127.6, 127.4, 122.3, 121.1, 120.4, 119.2, 117.1, 111.3, 110.9, 68.8, 55.6, 55.6; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{19}O_3$ 319.1334, Found 319.1330.

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1. B. Luo, J.-M. Gao and M. Lautens, Palladium-Catalyzed Norbornene-Mediated Tandem Amination/Cyanation Reaction: A Method for the Synthesis of *ortho*-Aminated Benzonitriles, *Org. Lett.,* 2016, **18**, 4166–4169.

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Intramolecular Transmetalation of Arylpalladium(II) and Arylplatinum(II) Complexes with Silanes and Stannanes, *Organometallics*, 1998, **17**, 3661–3669.
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Figure S1. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3aa

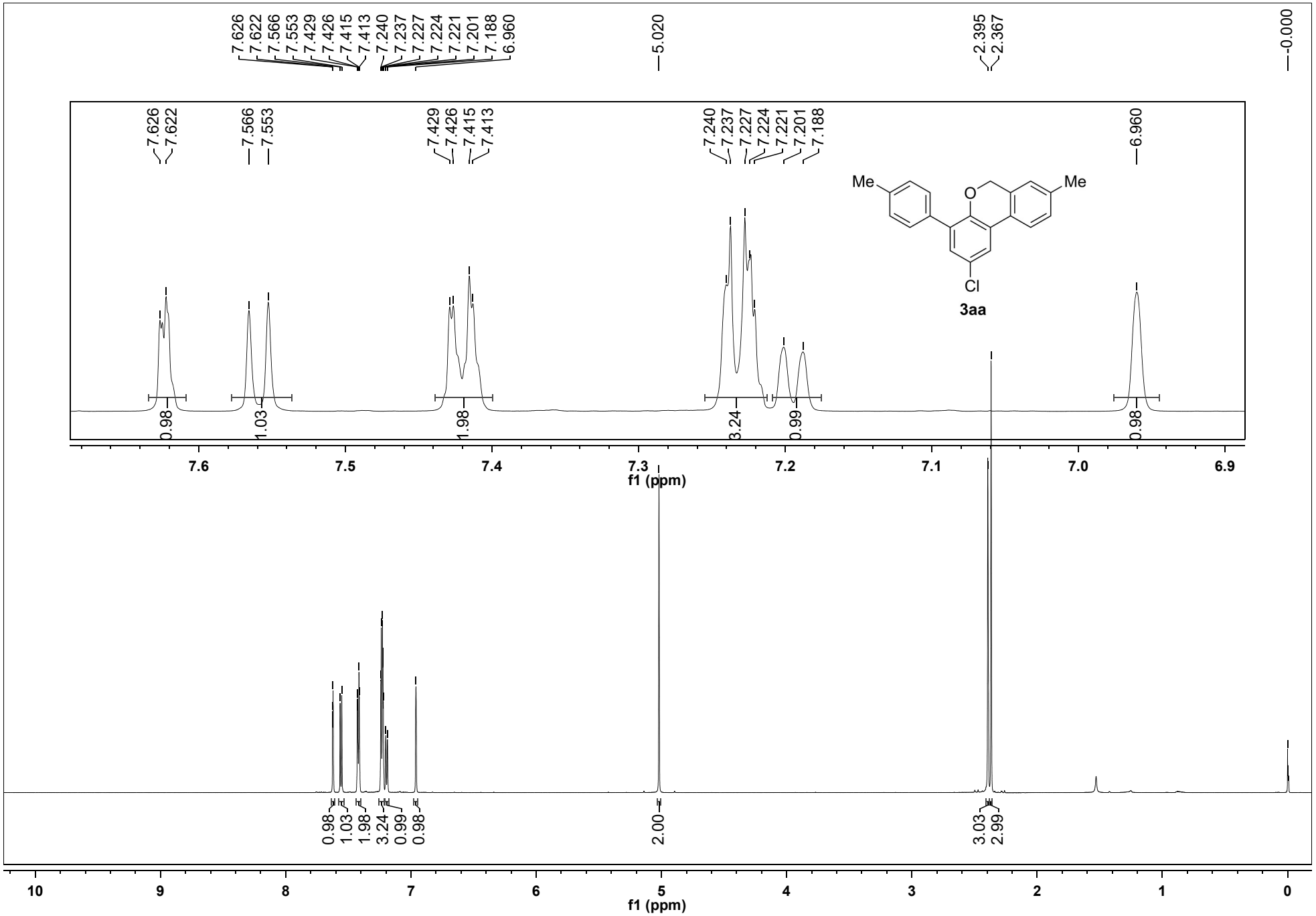

Figure S2. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3aa

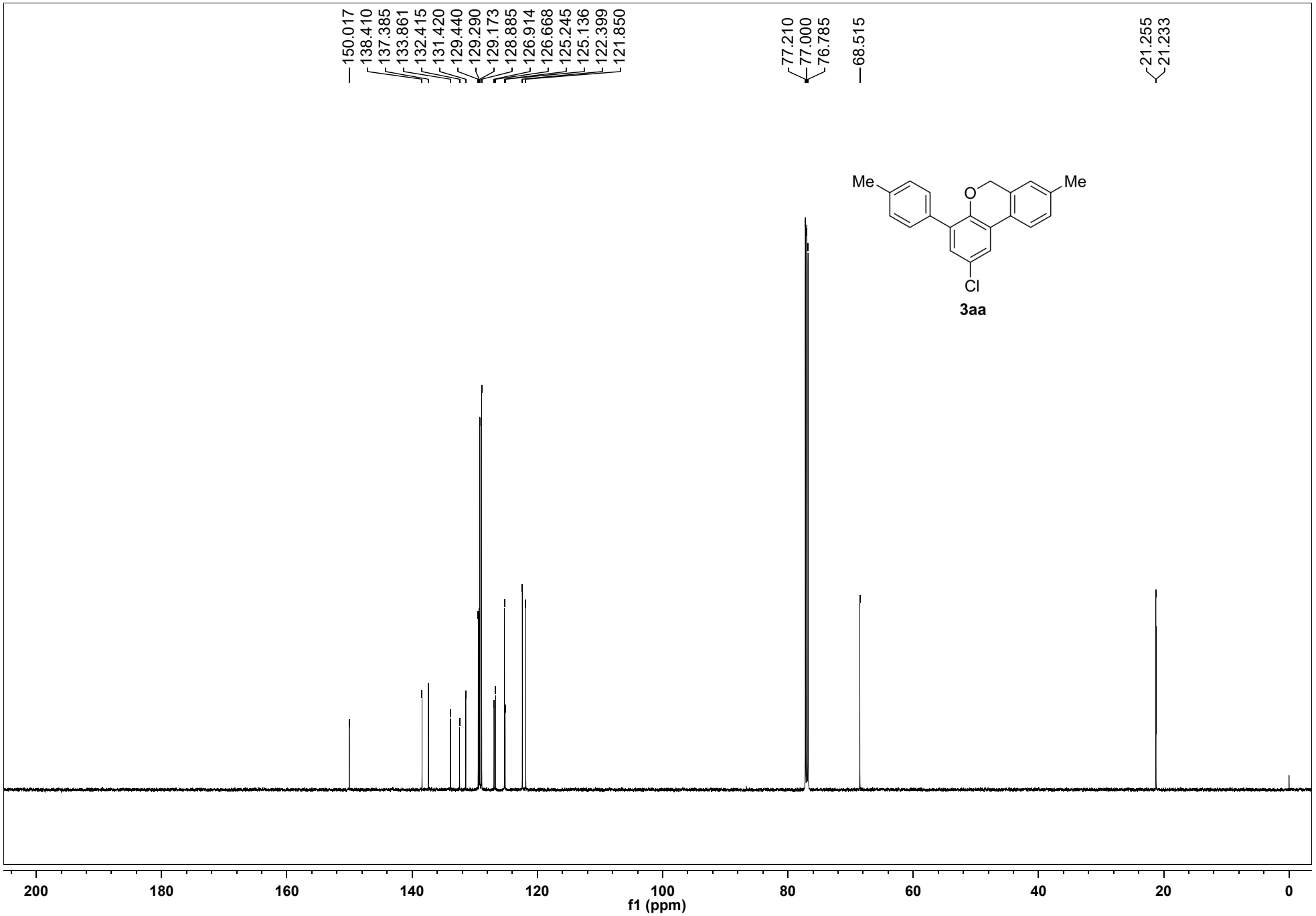

Figure S3. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ba

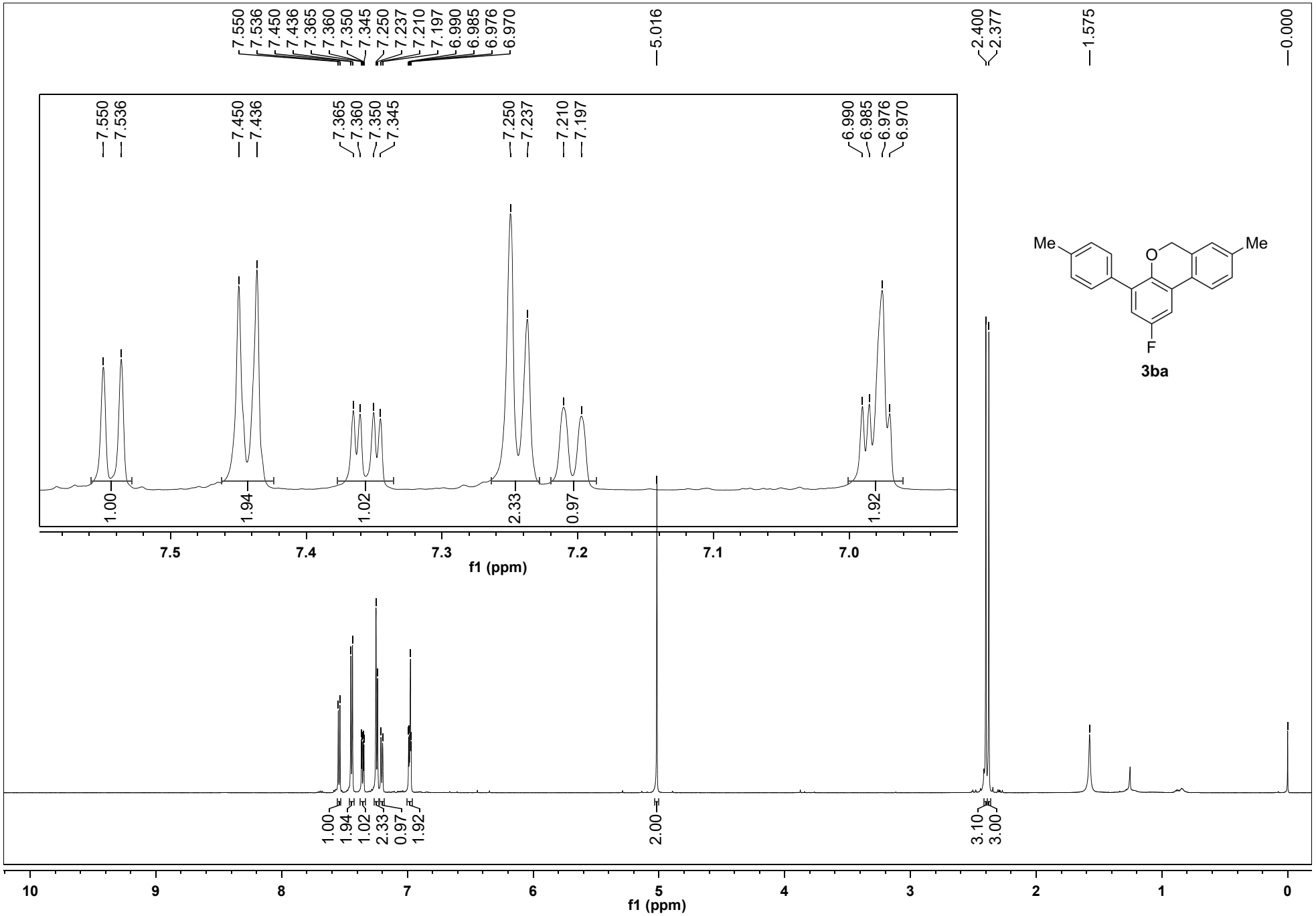

Figure S4. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ba

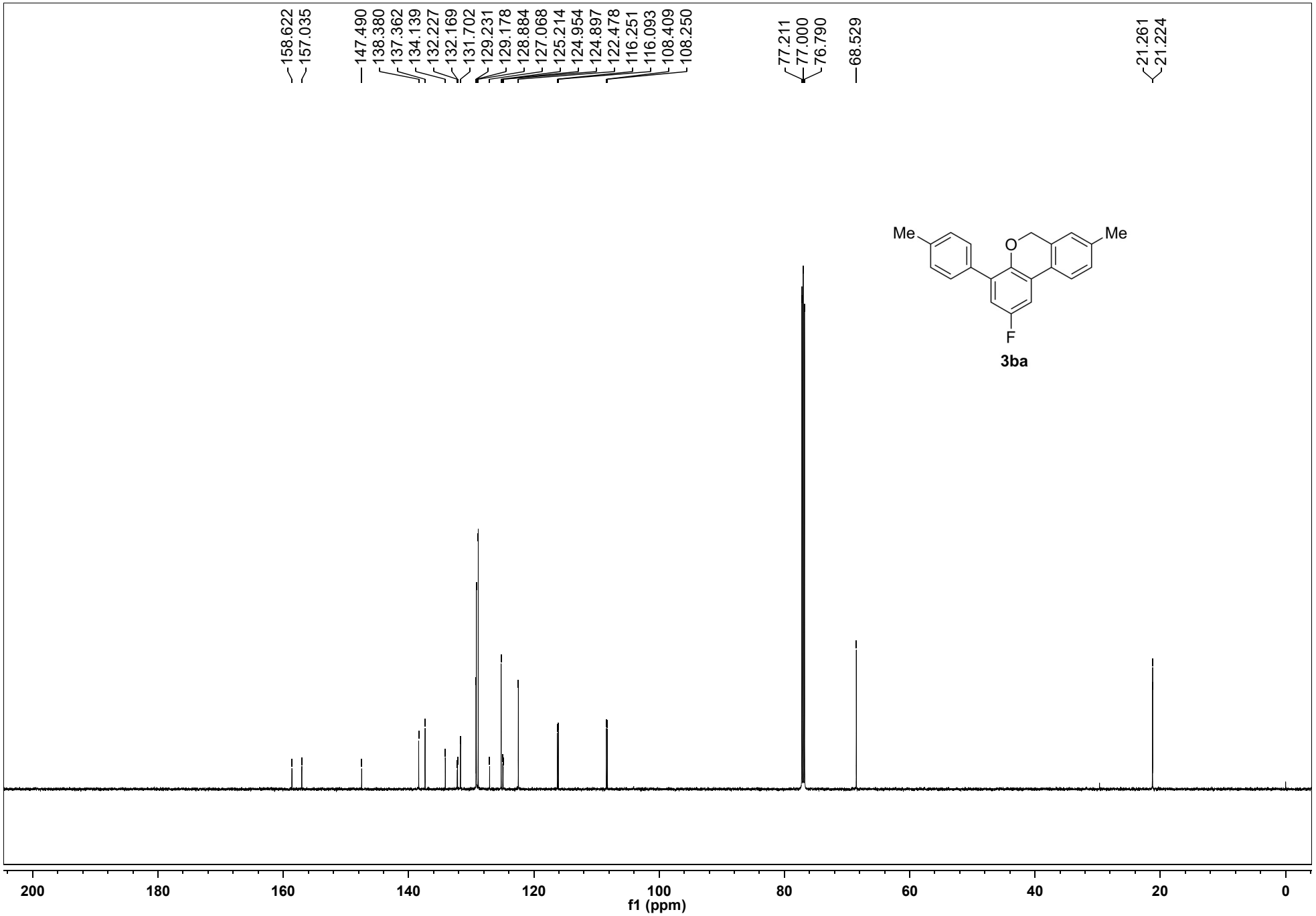

Figure S5. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ca

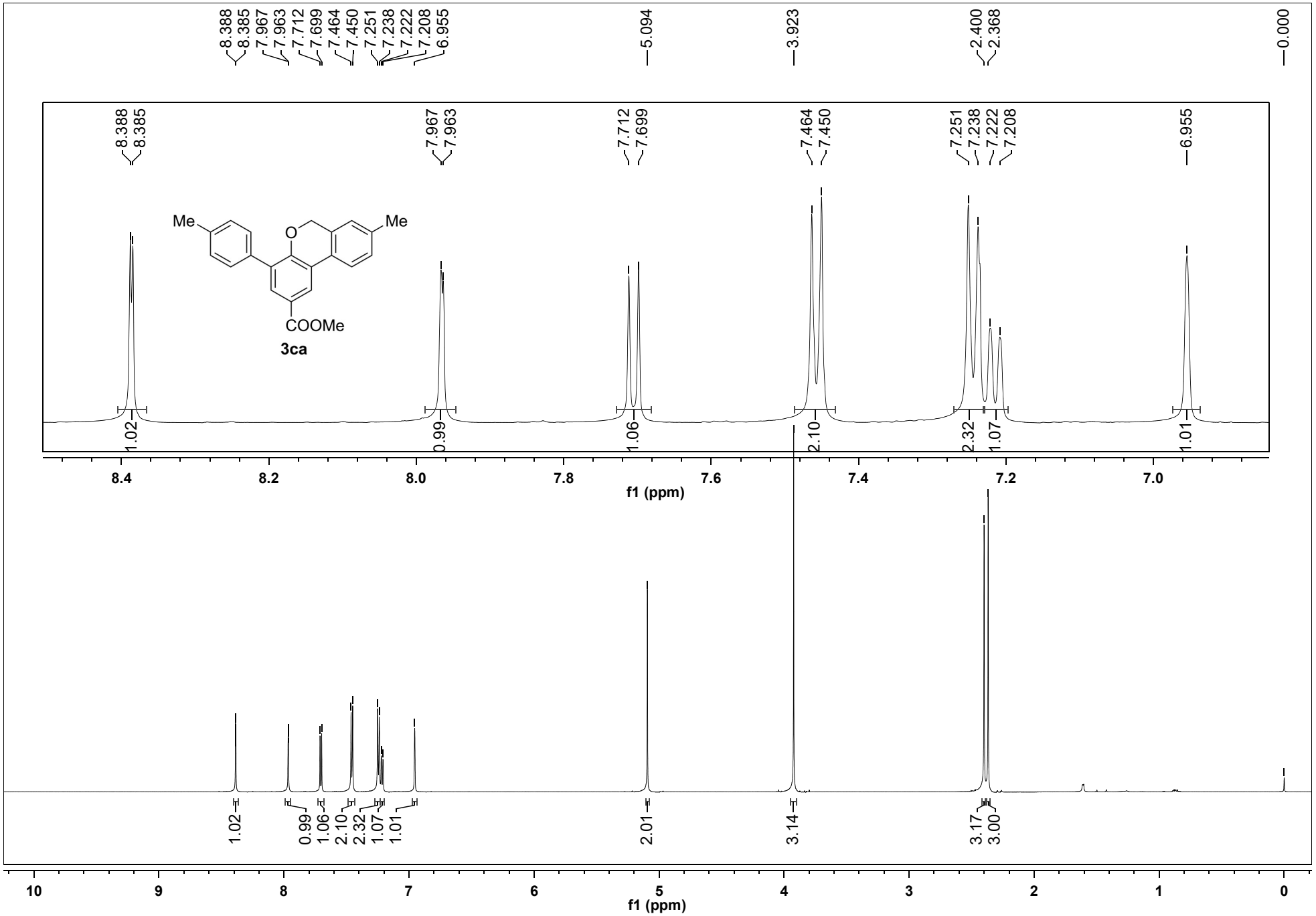

Figure S6. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ca

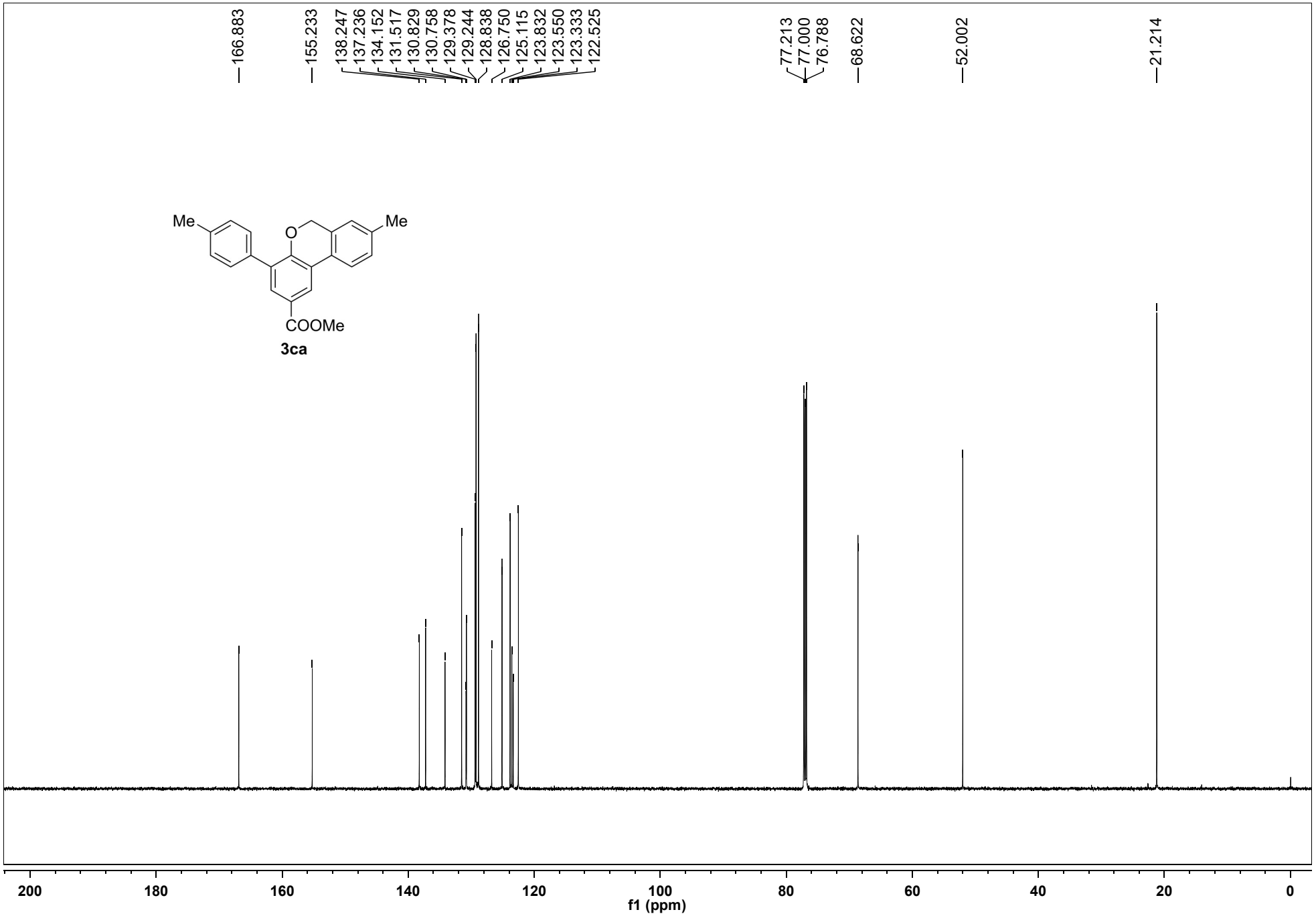

Figure S7. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3da

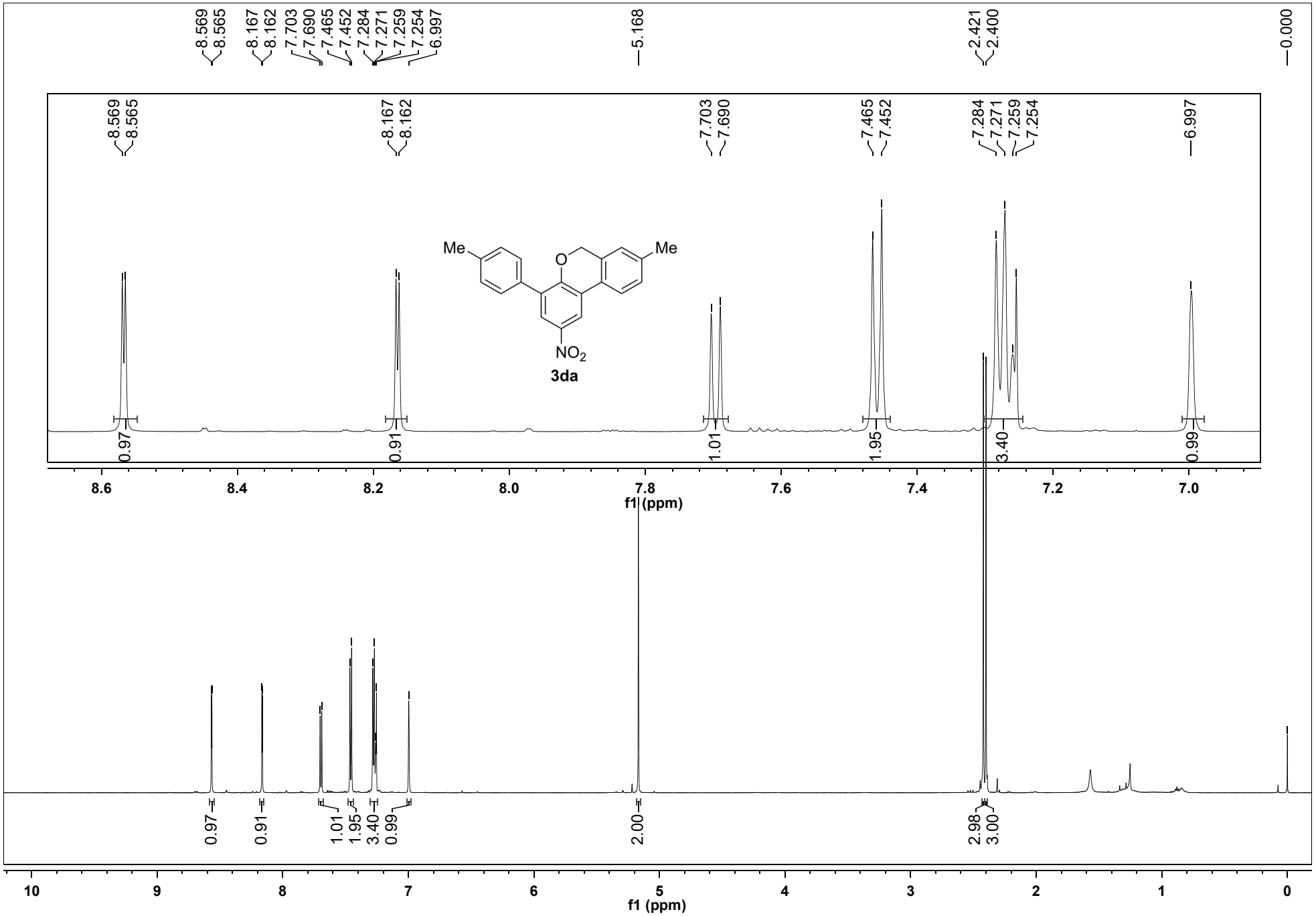

Figure S8. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3da

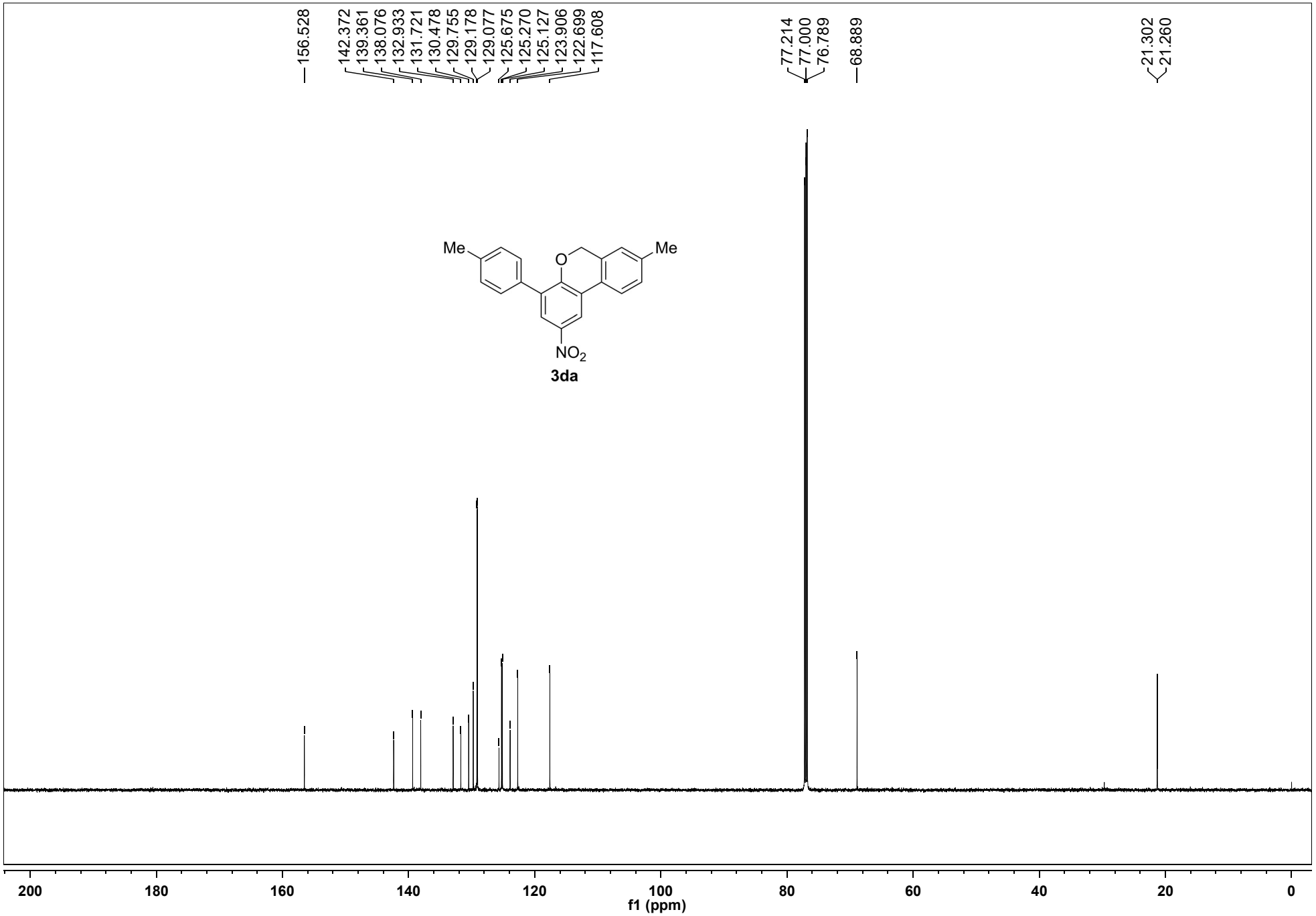

Figure S9. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ea

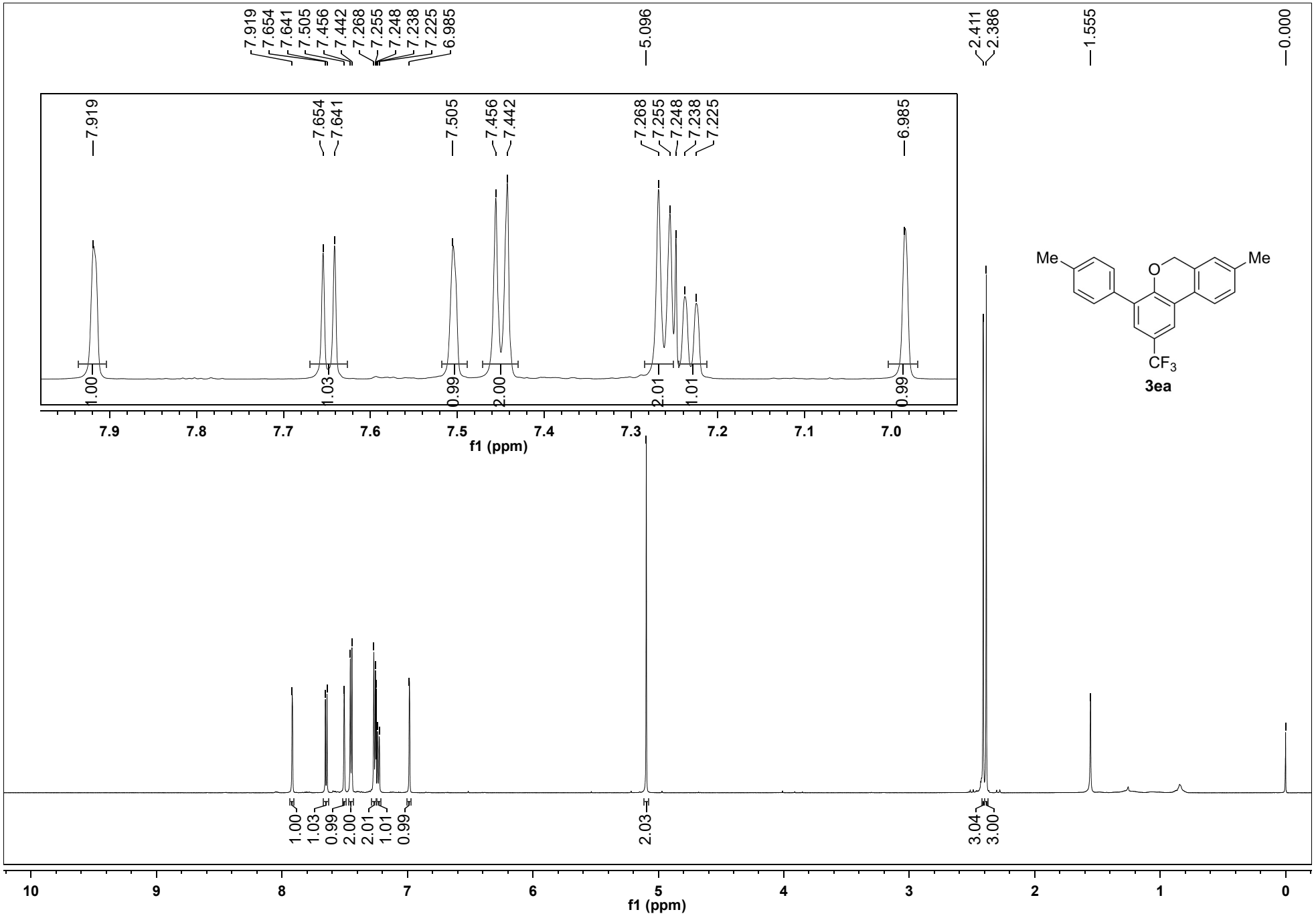

Figure S10. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ea

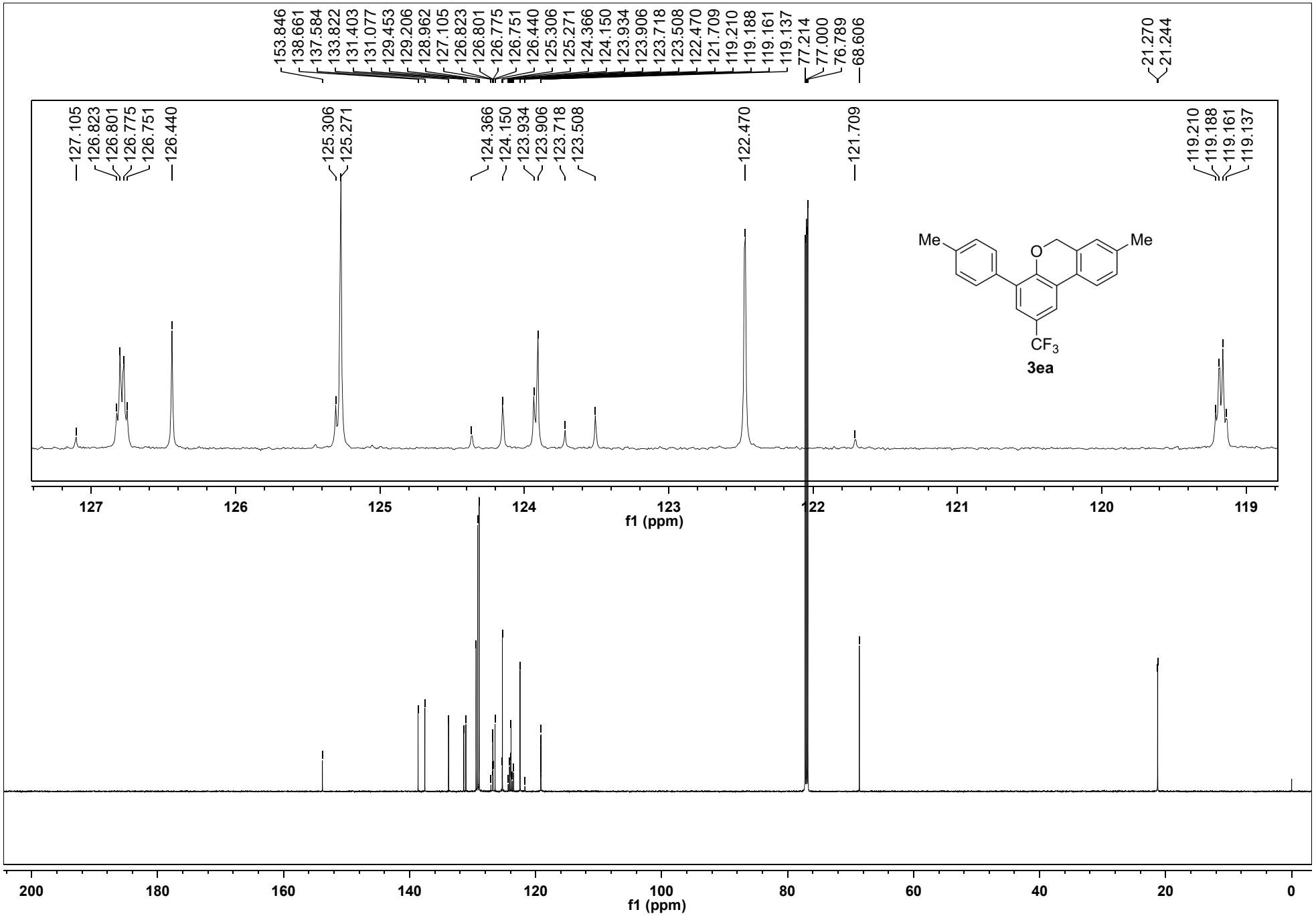

Figure S11. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3fa

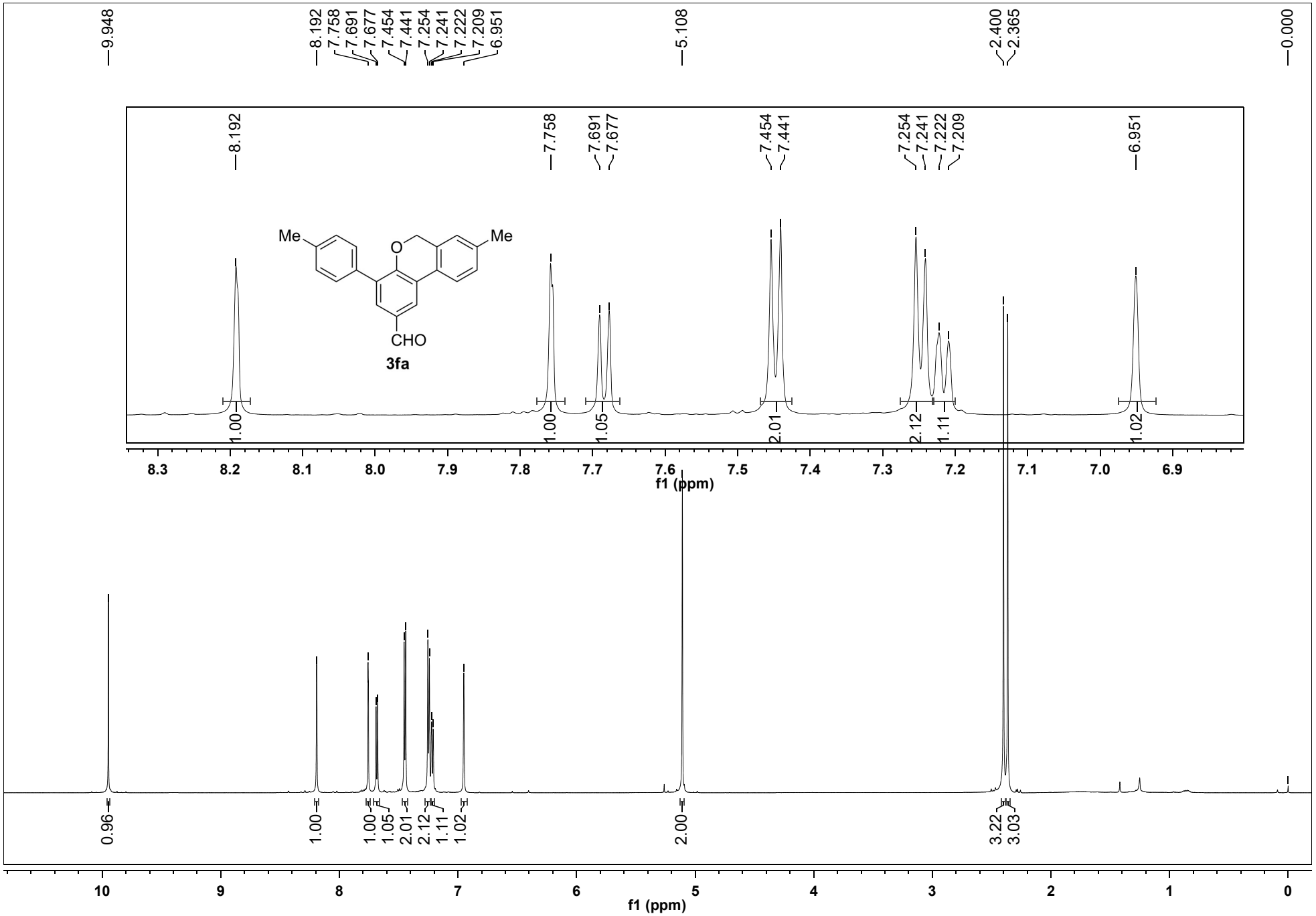

Figure S12. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3fa

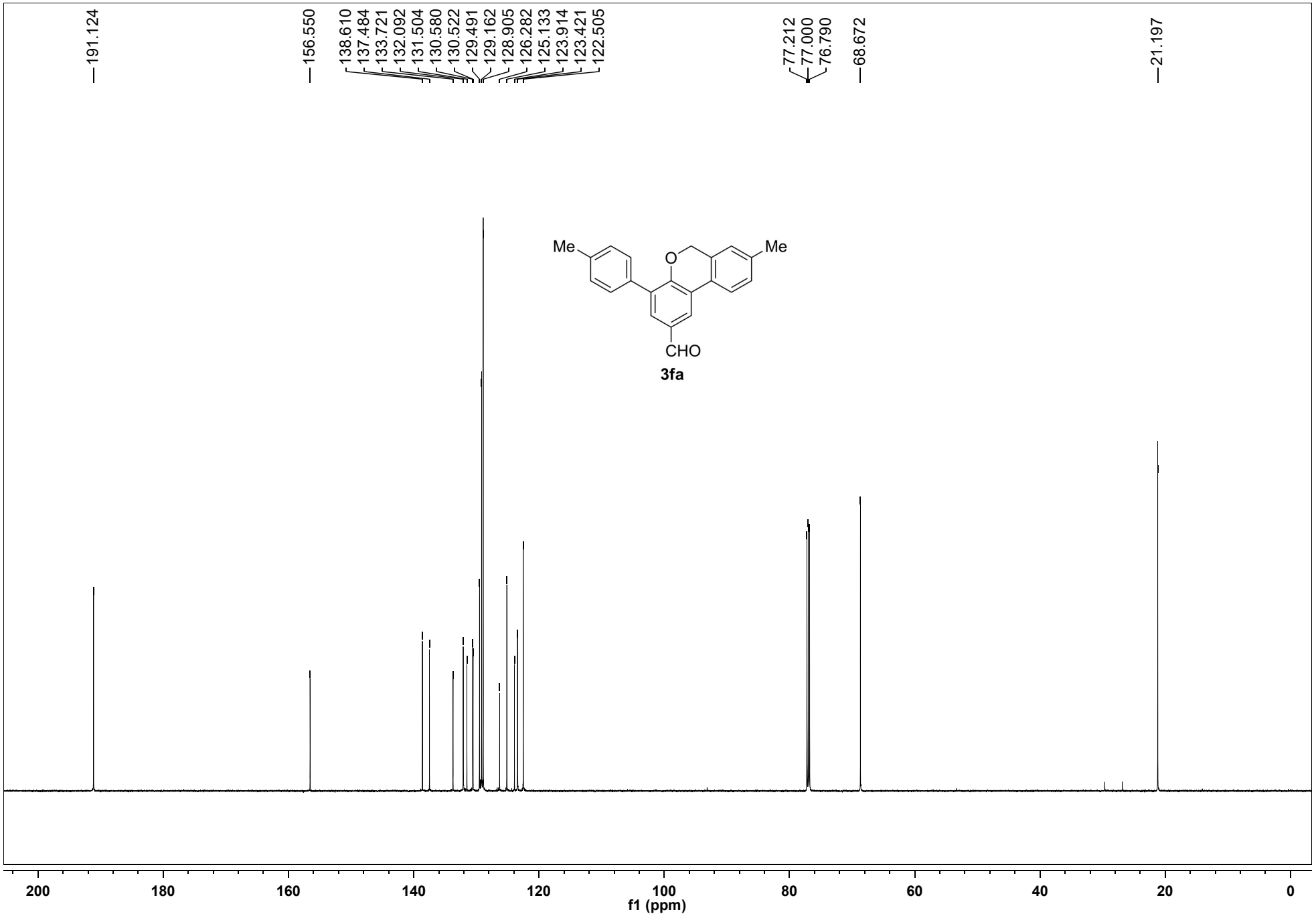

Figure S13. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ga

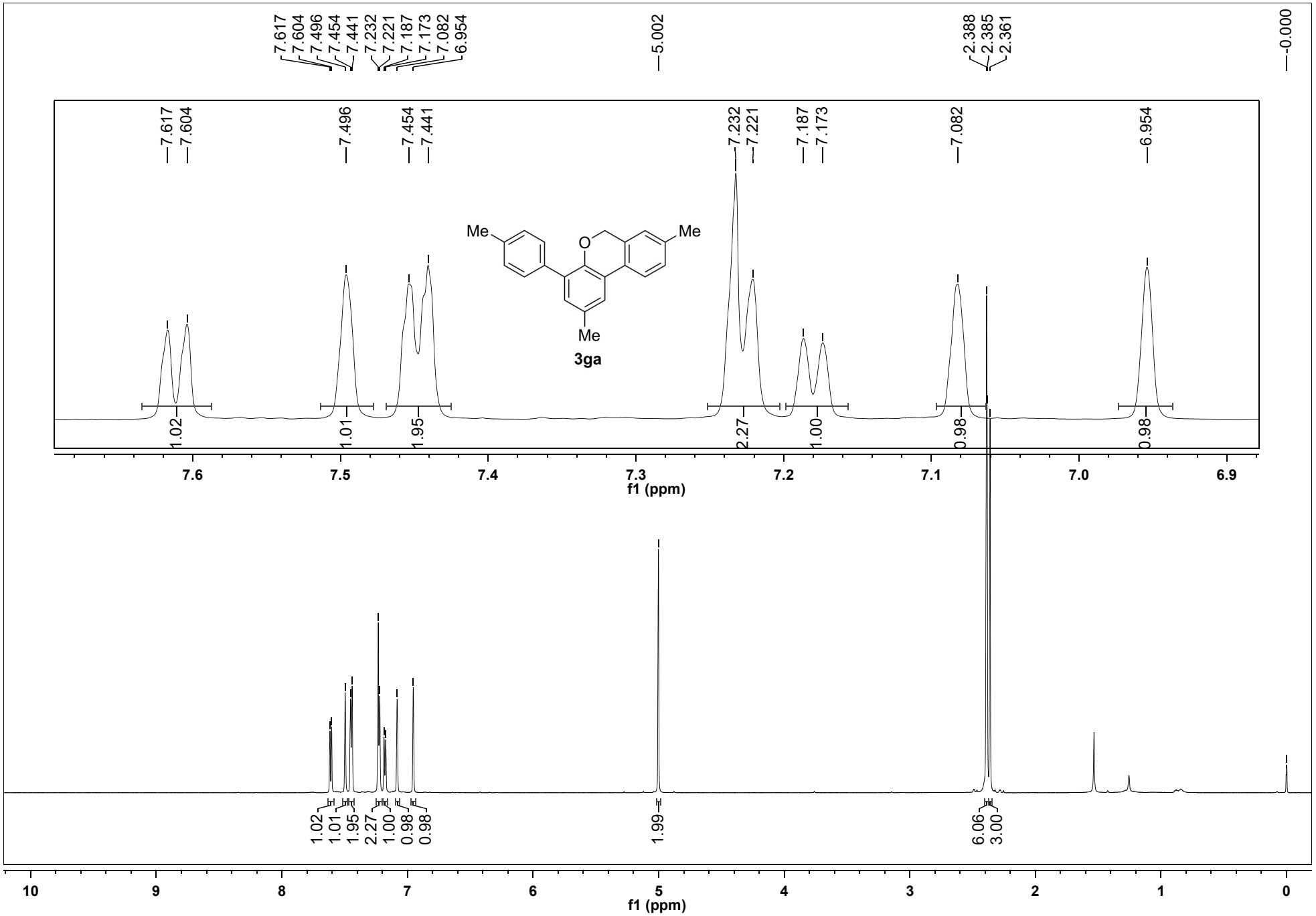

Figure S14. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ga

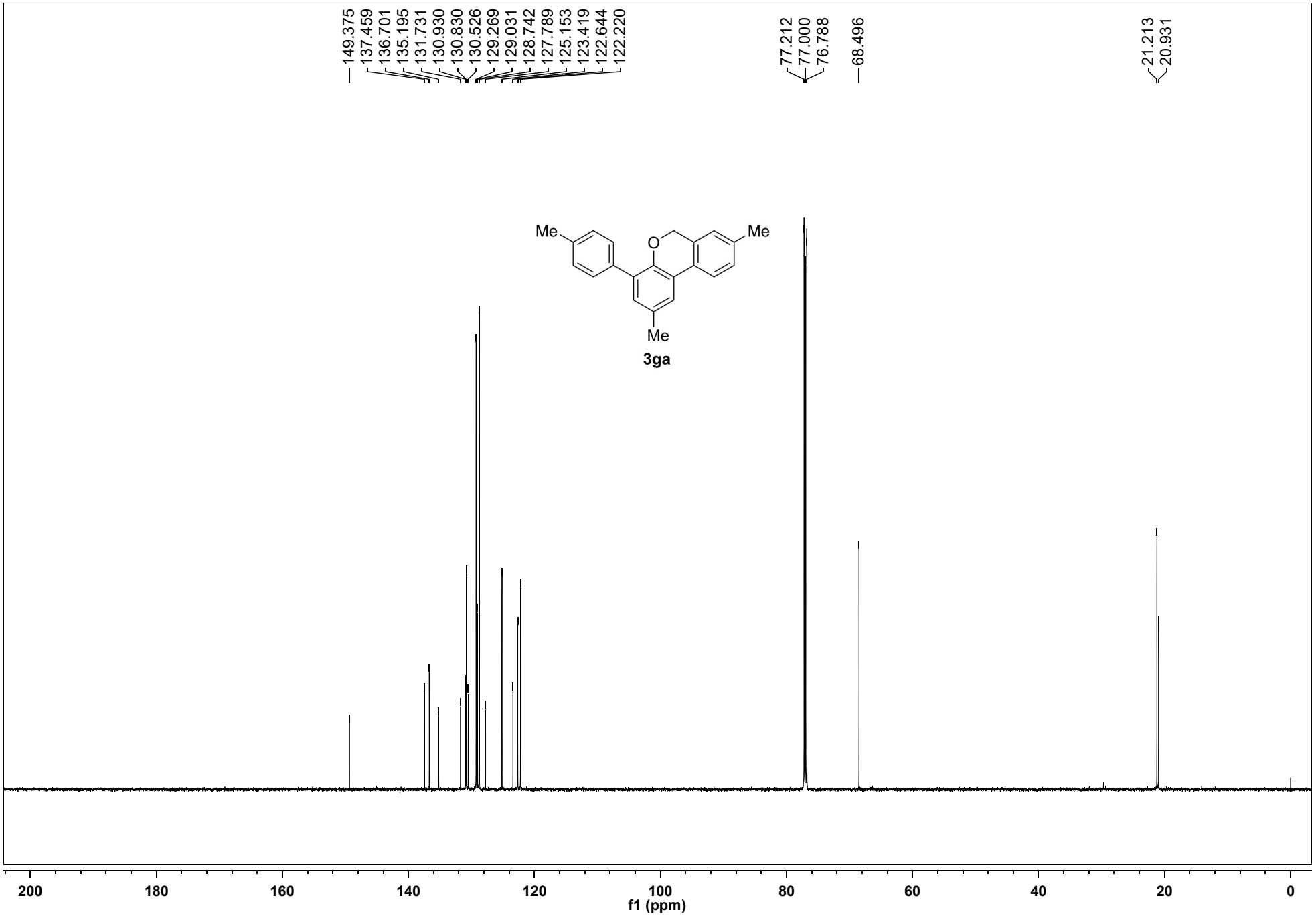

Figure S15. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ha

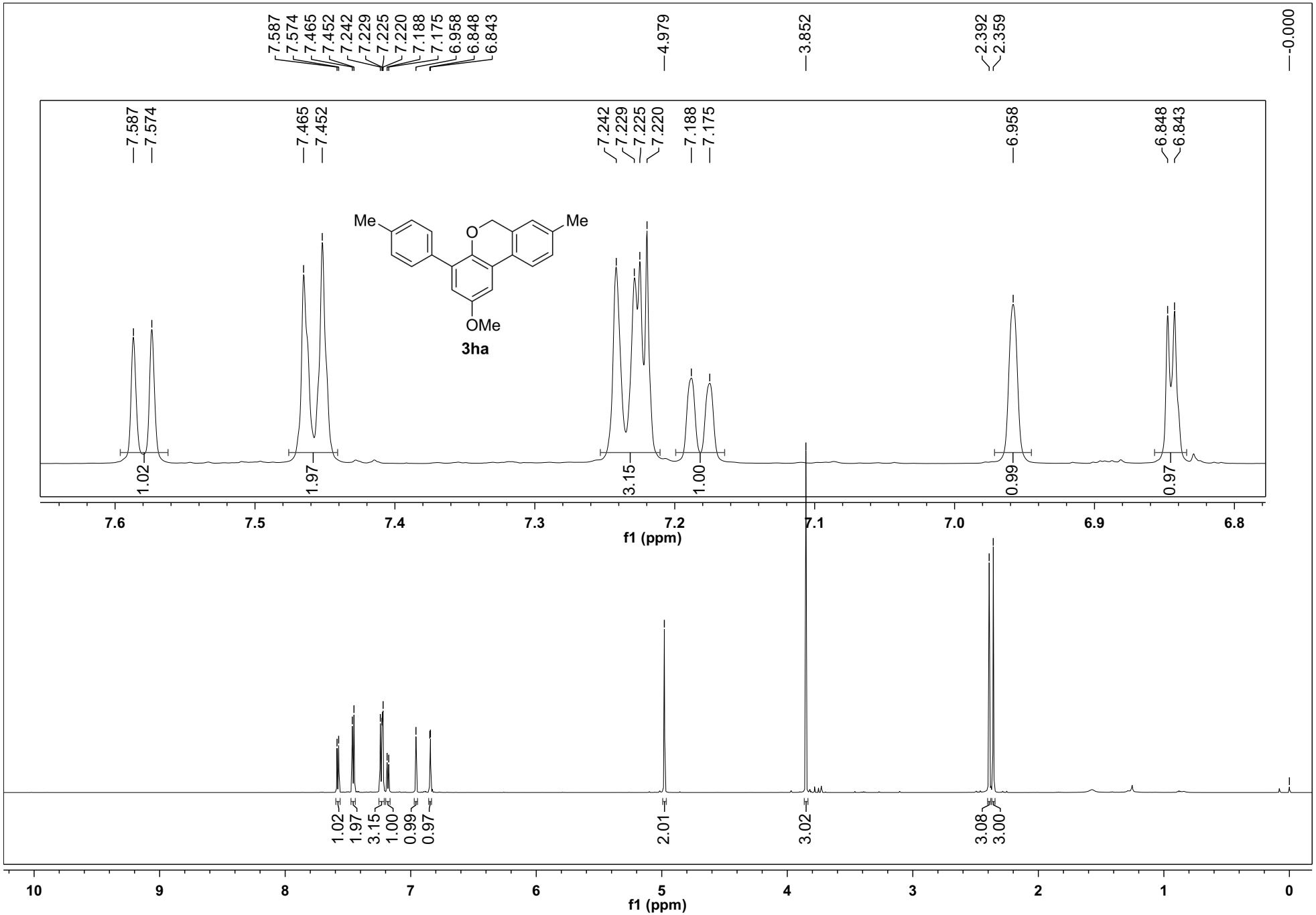

Figure S16. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ha

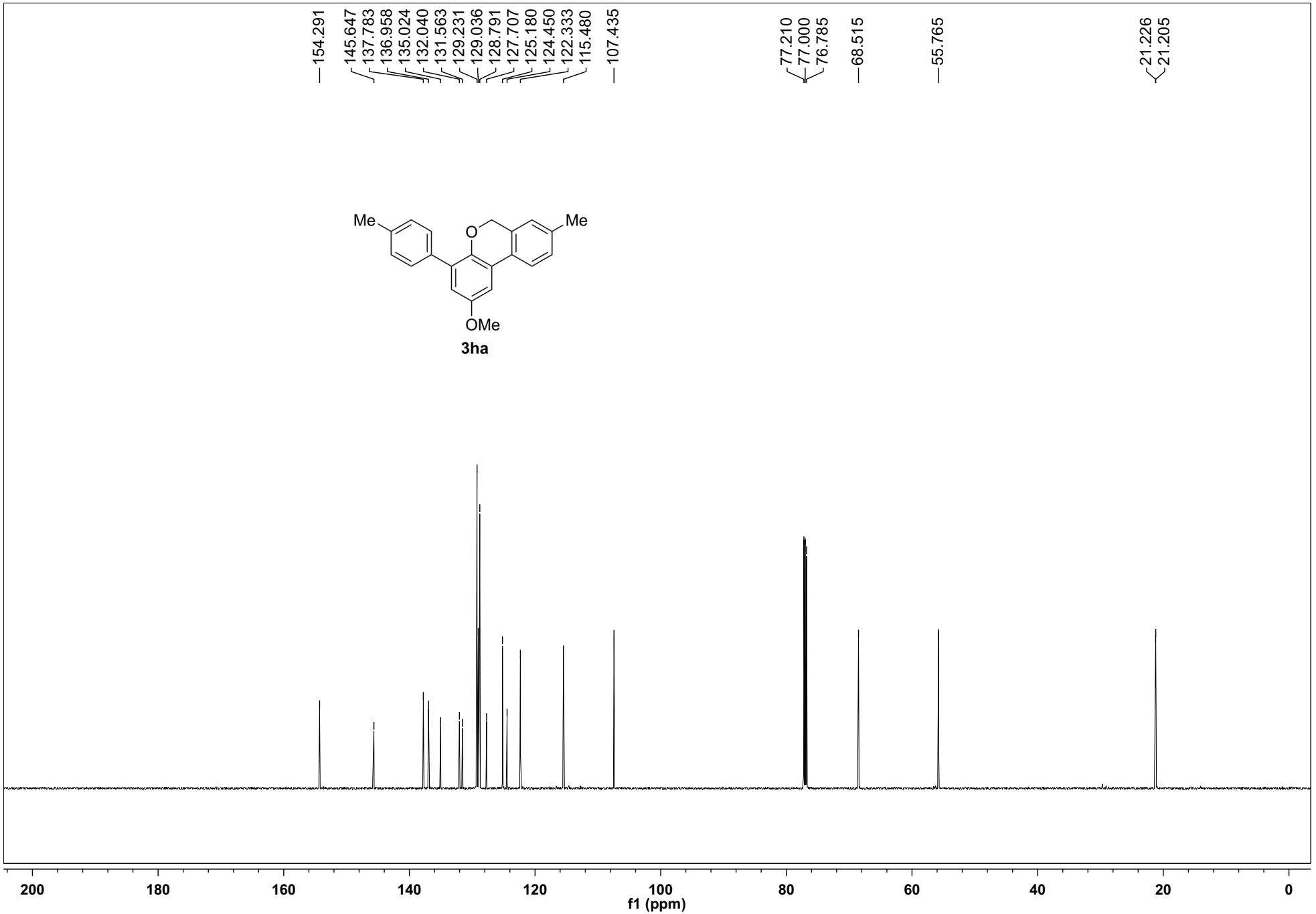

Figure S17. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ia

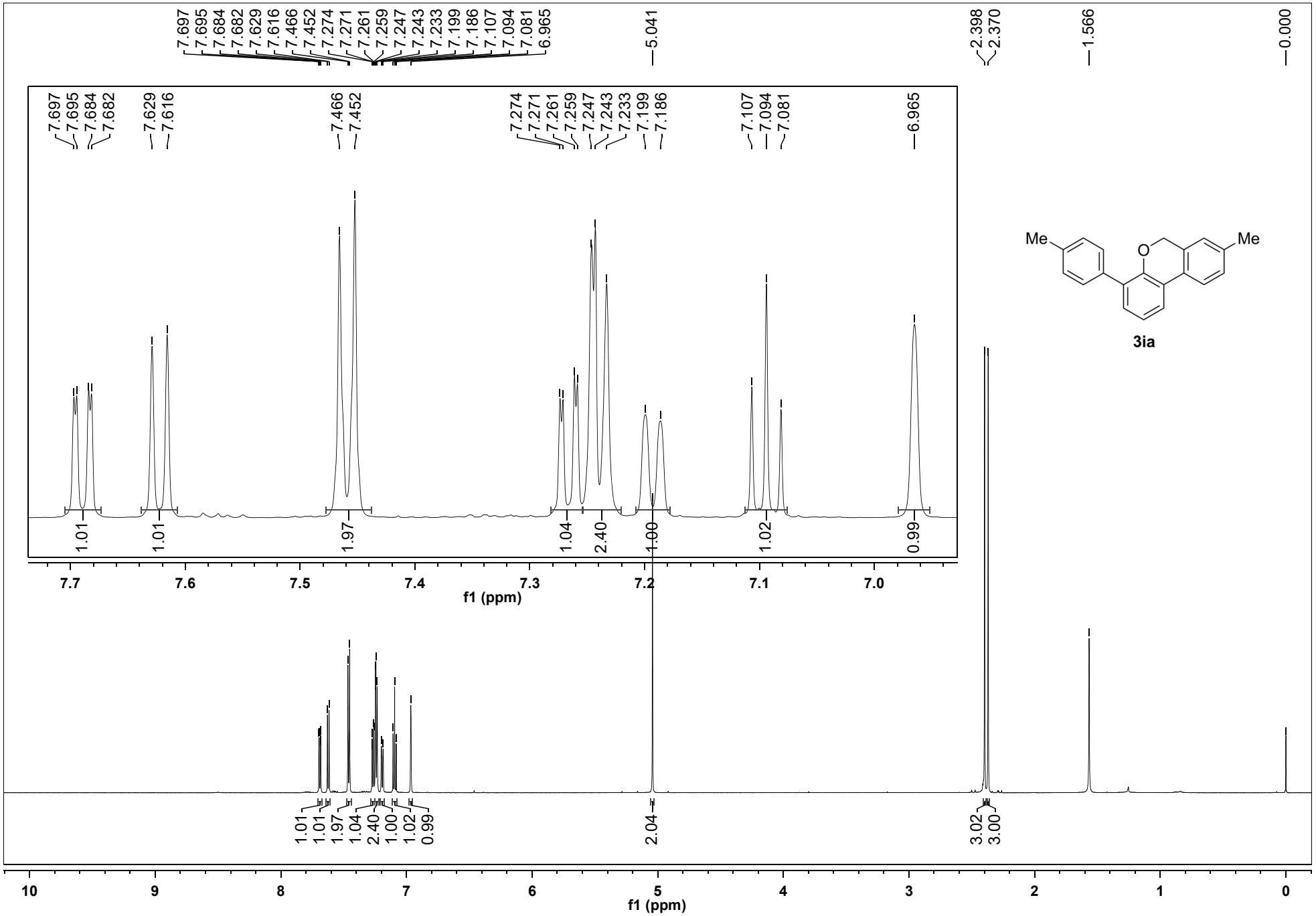

Figure S18. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ia

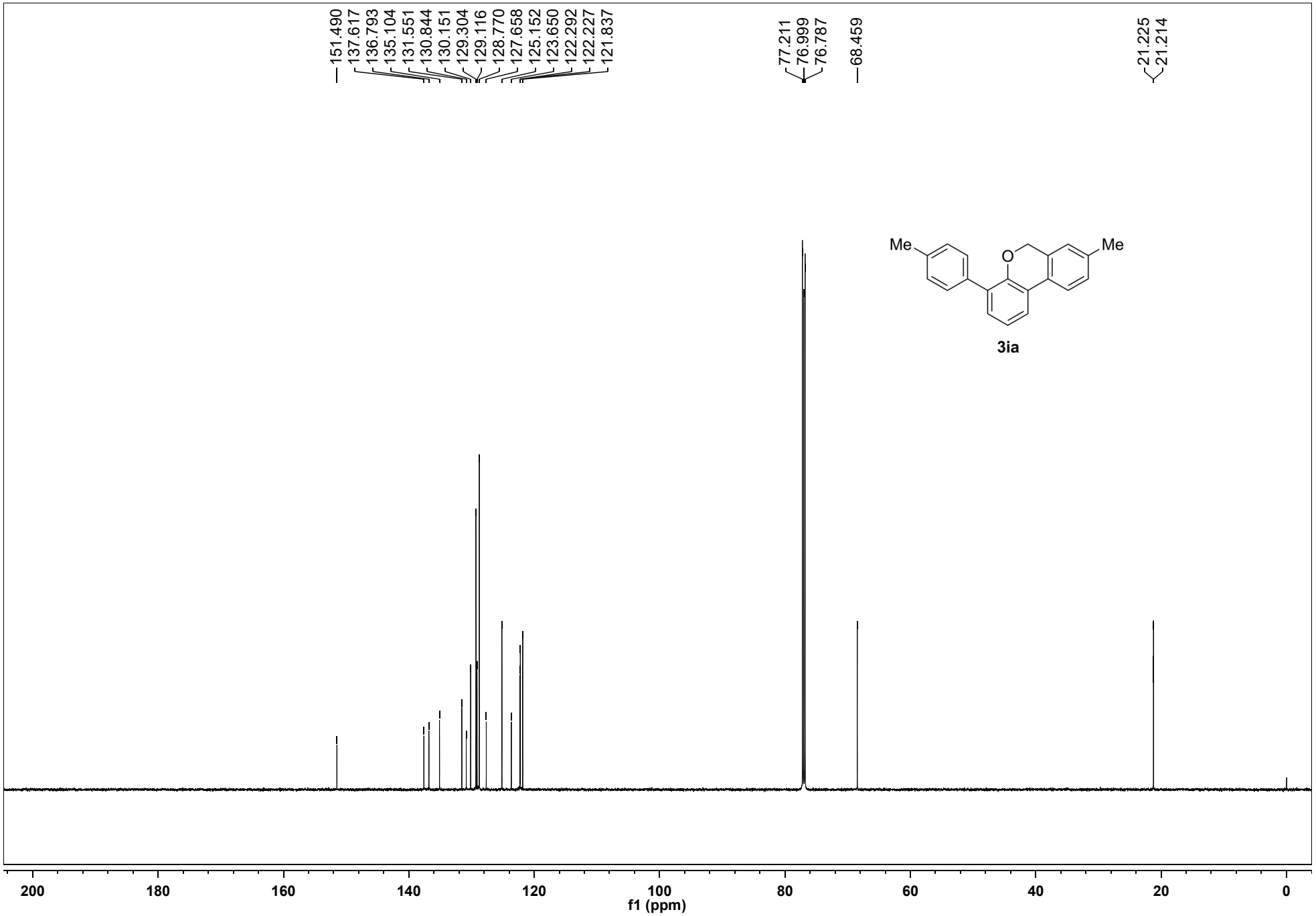

Figure S19. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ia-D

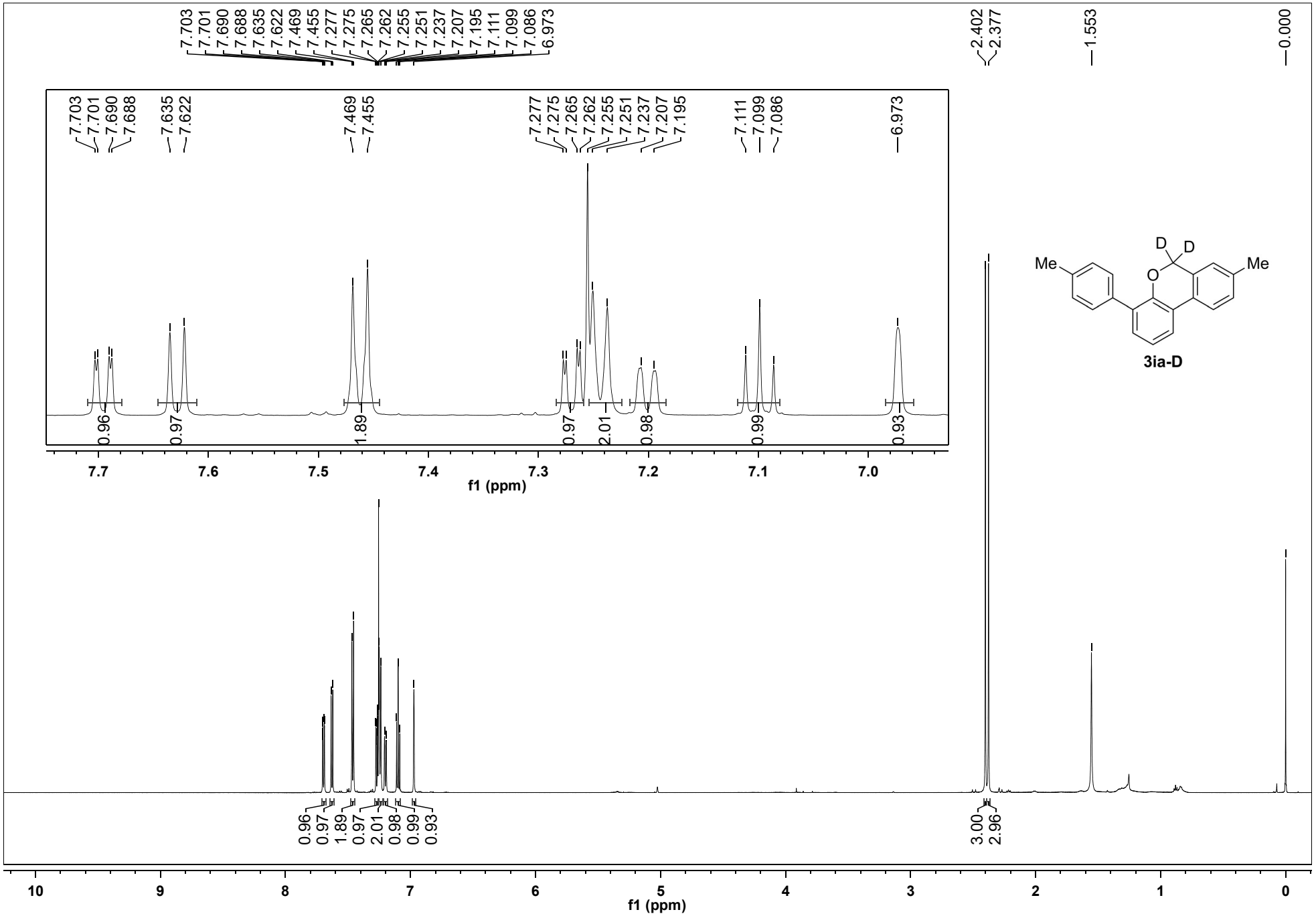

Figure S20. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ia-D

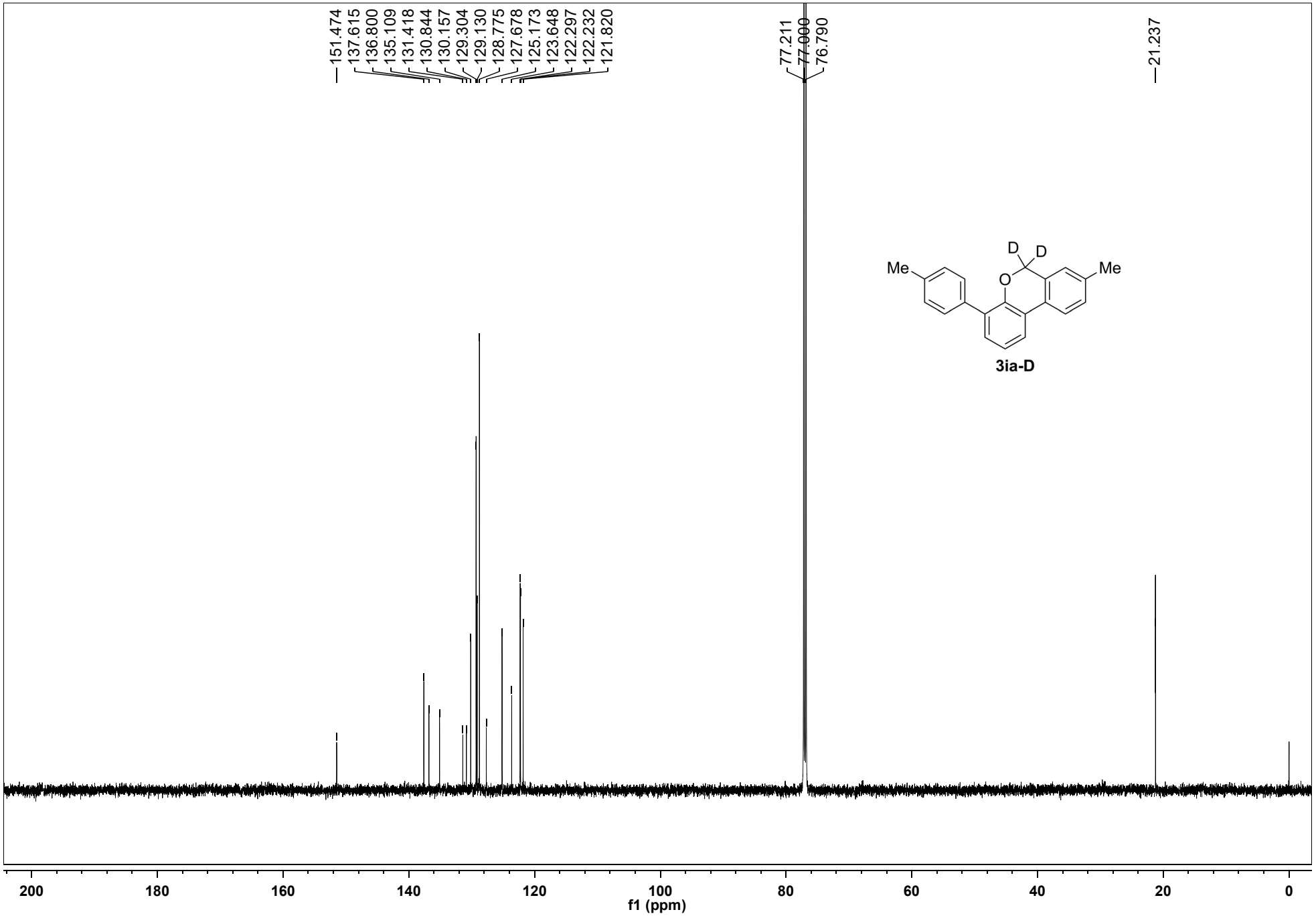

Figure S21. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ja

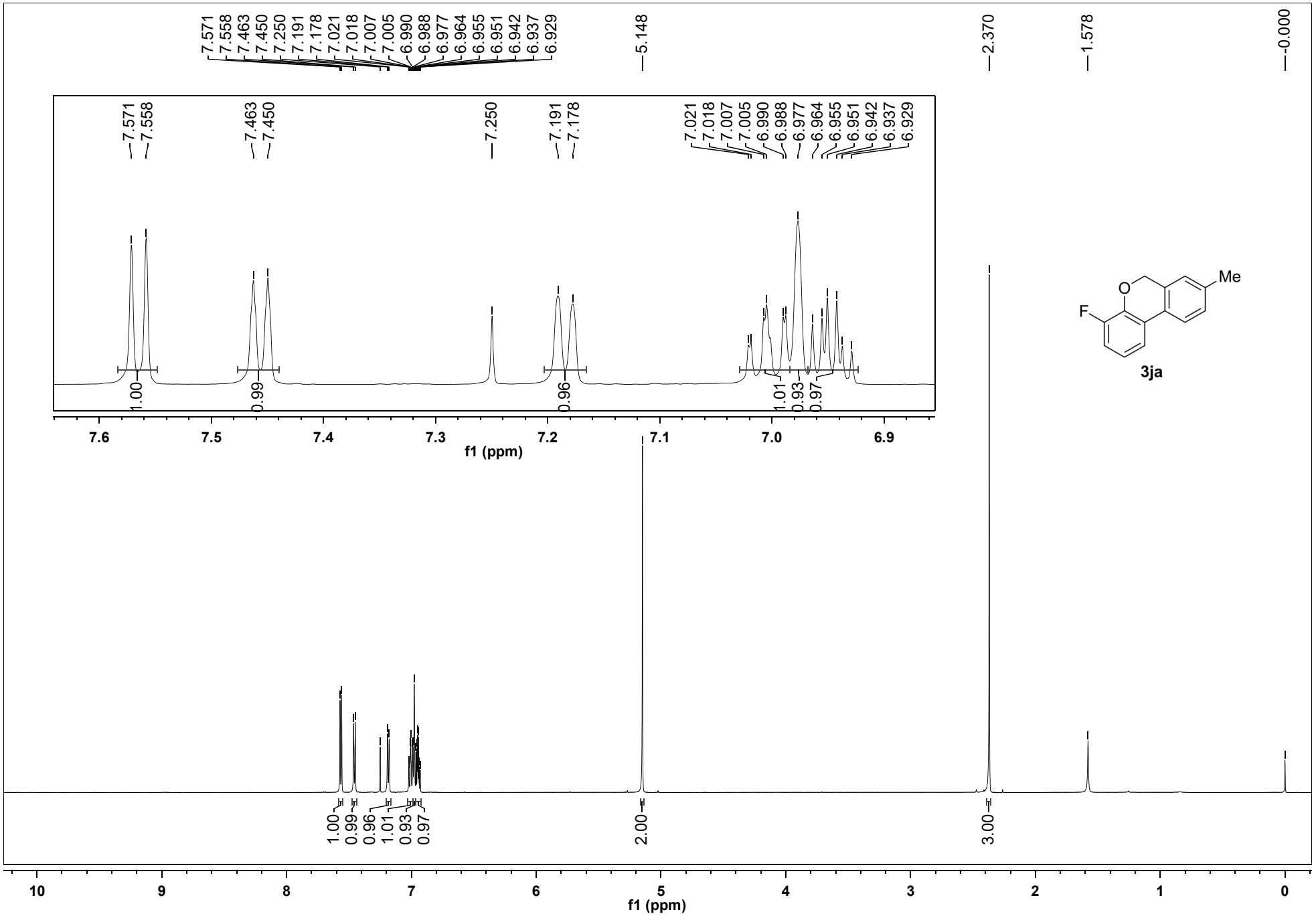

Figure S22. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ja

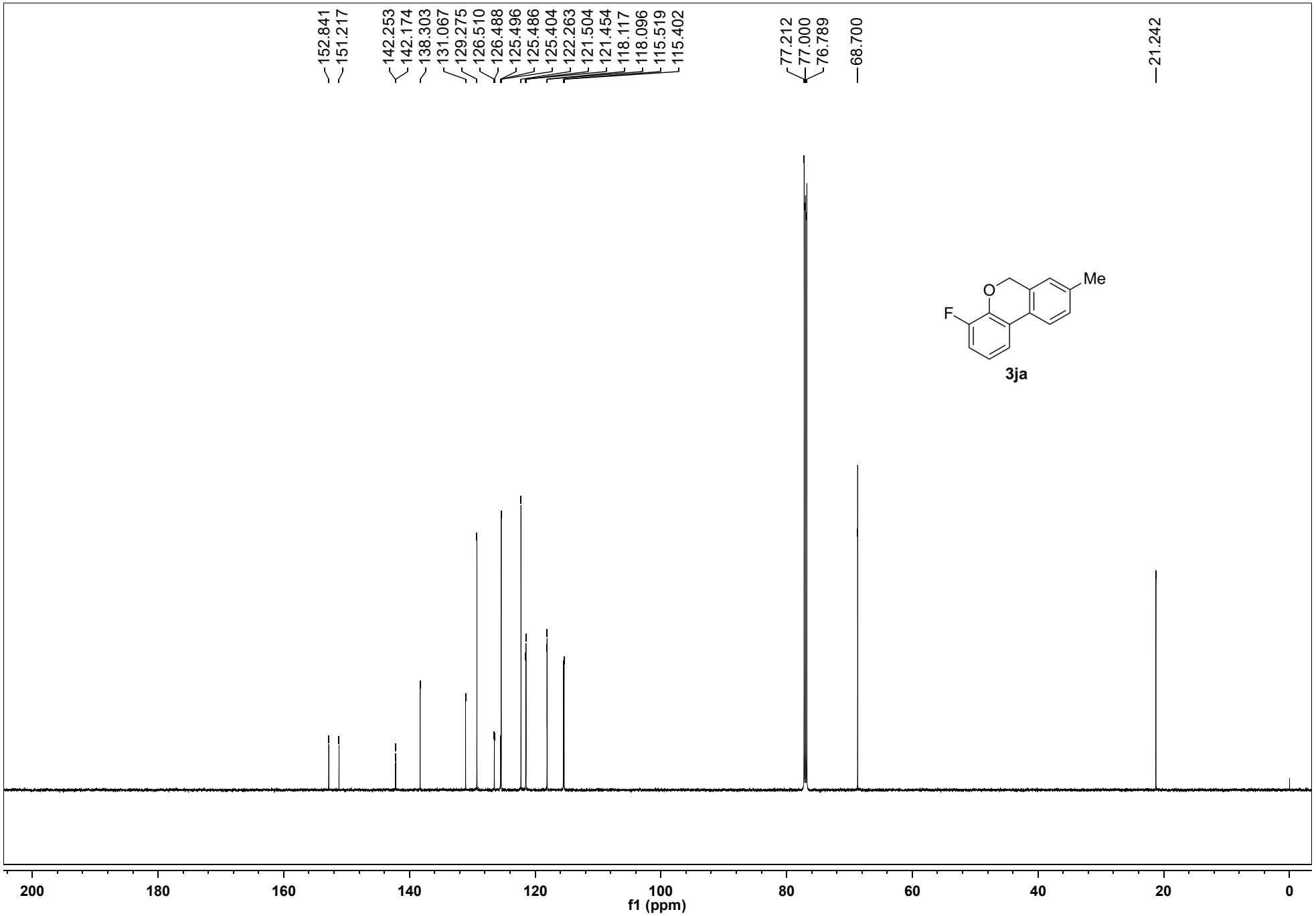

Figure S23. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ka

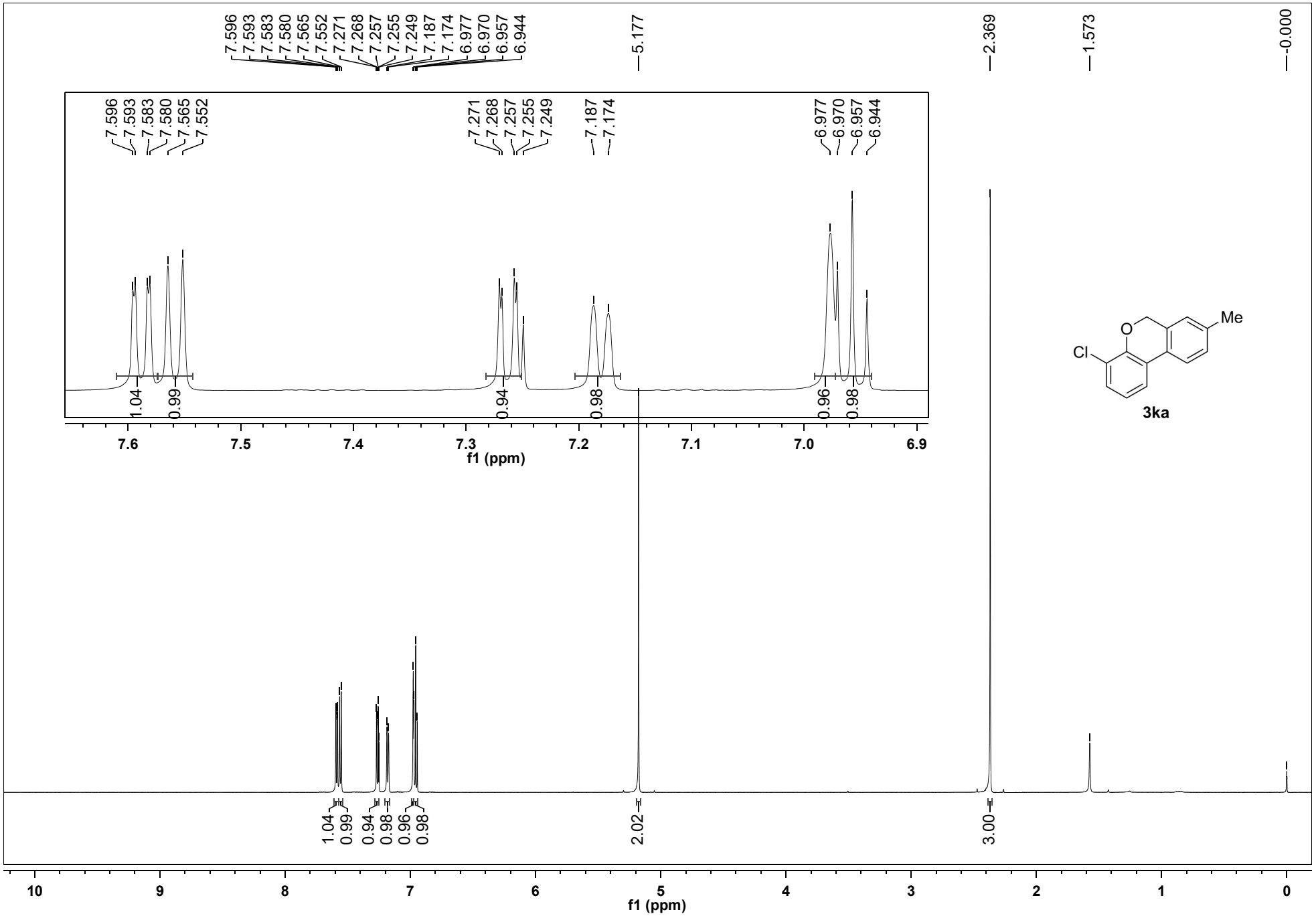

Figure S24. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ka

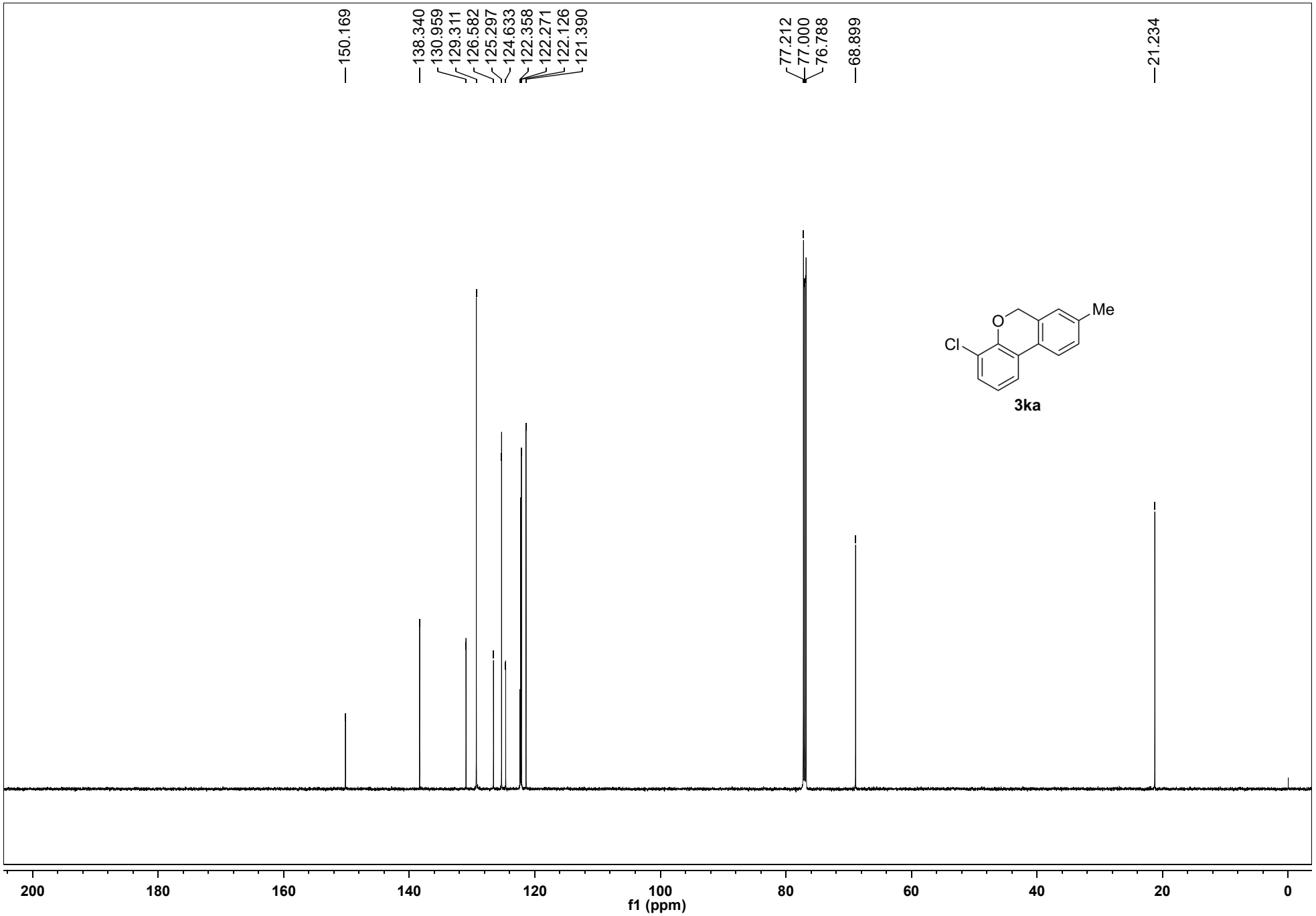

Figure S25. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3la

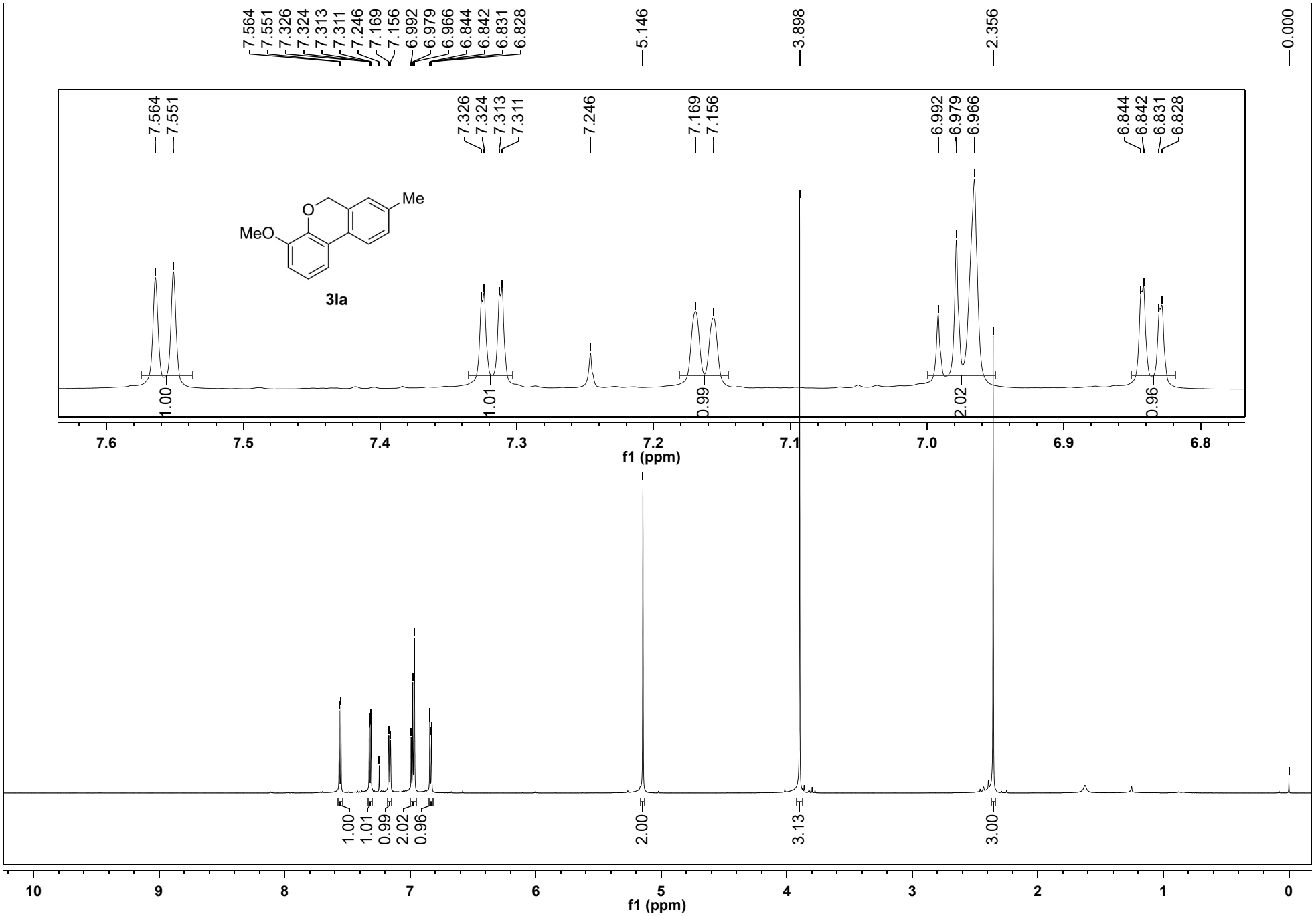

Figure S26. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3la

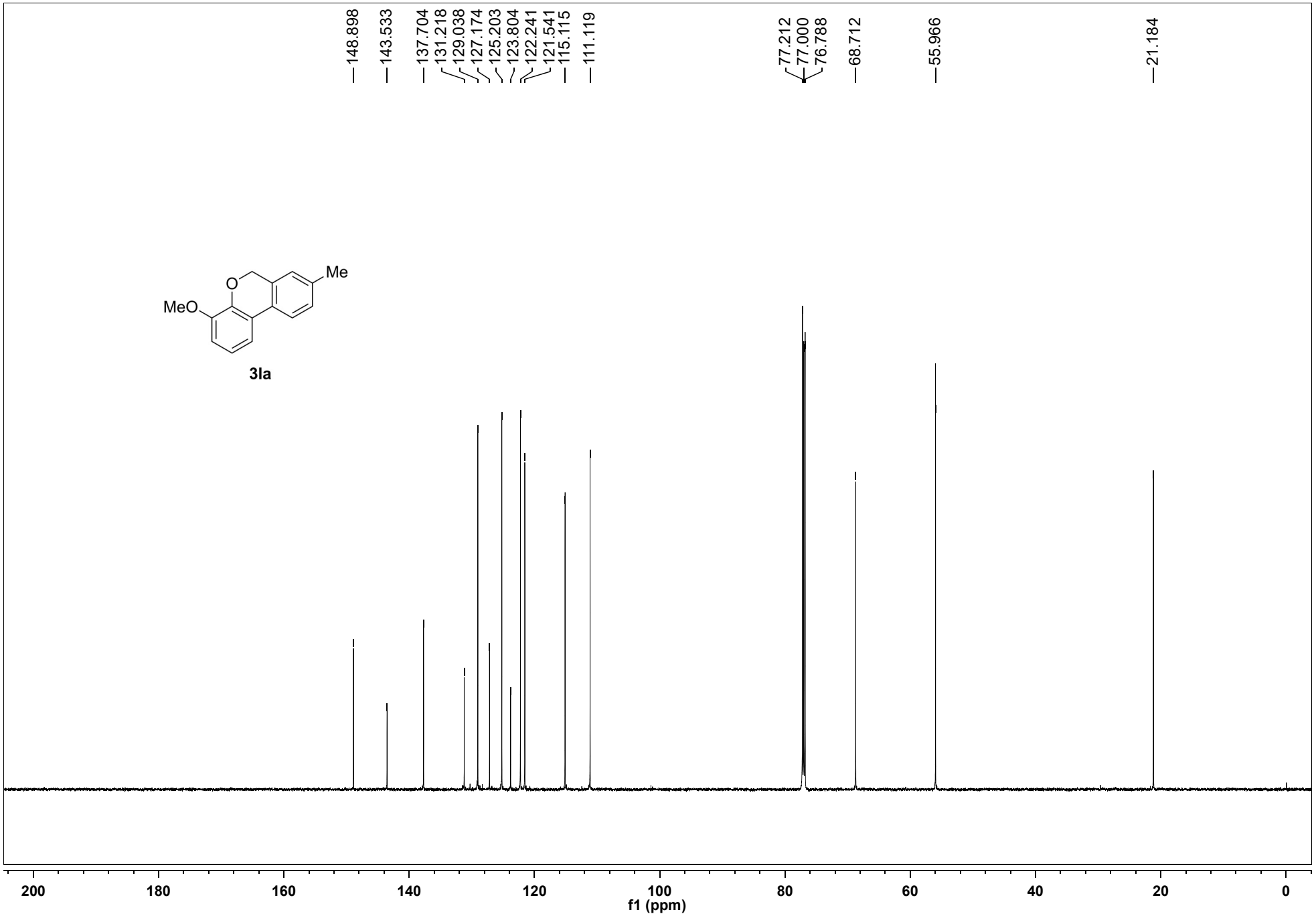

Figure S27. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ma

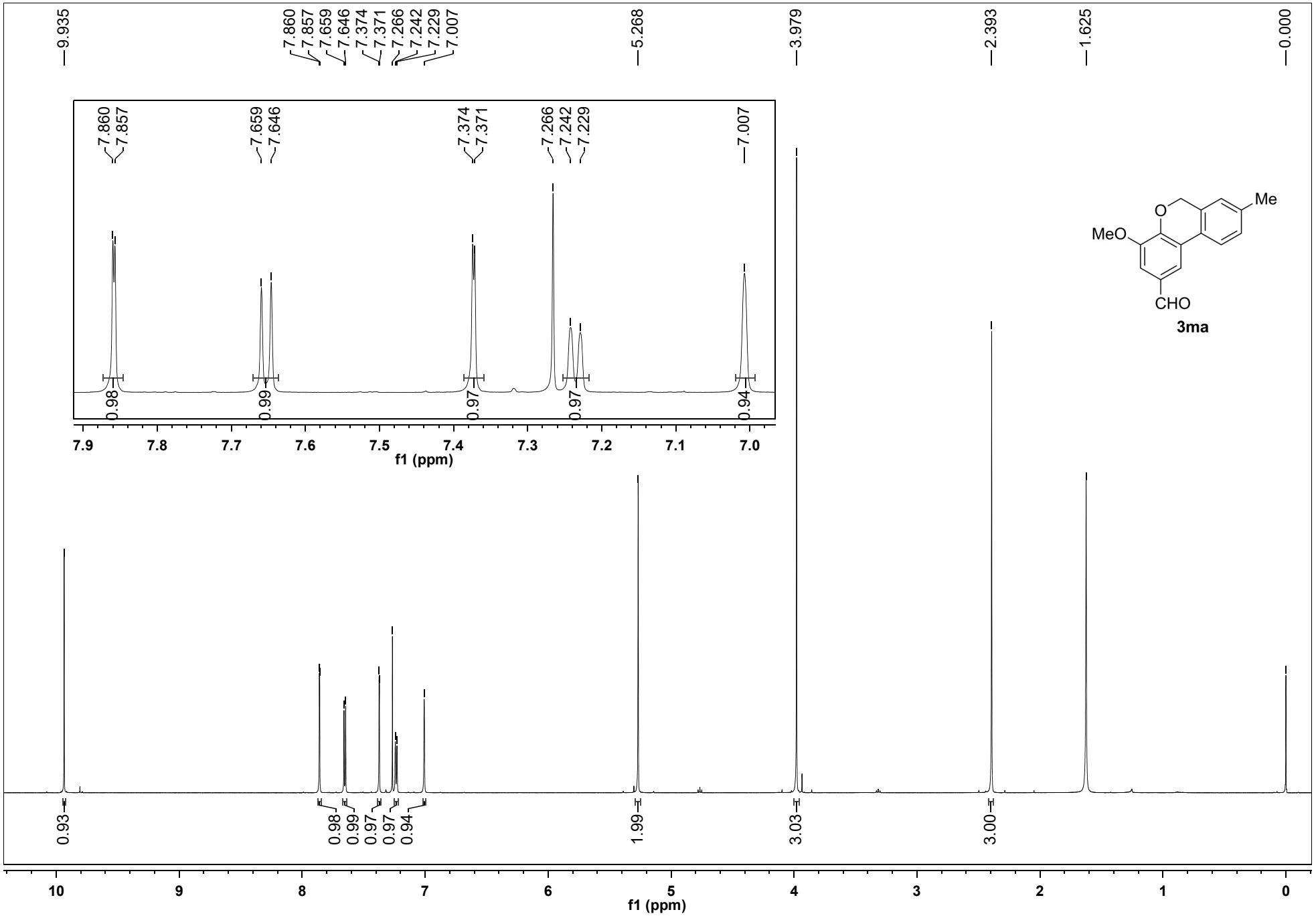

Figure S28. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ma

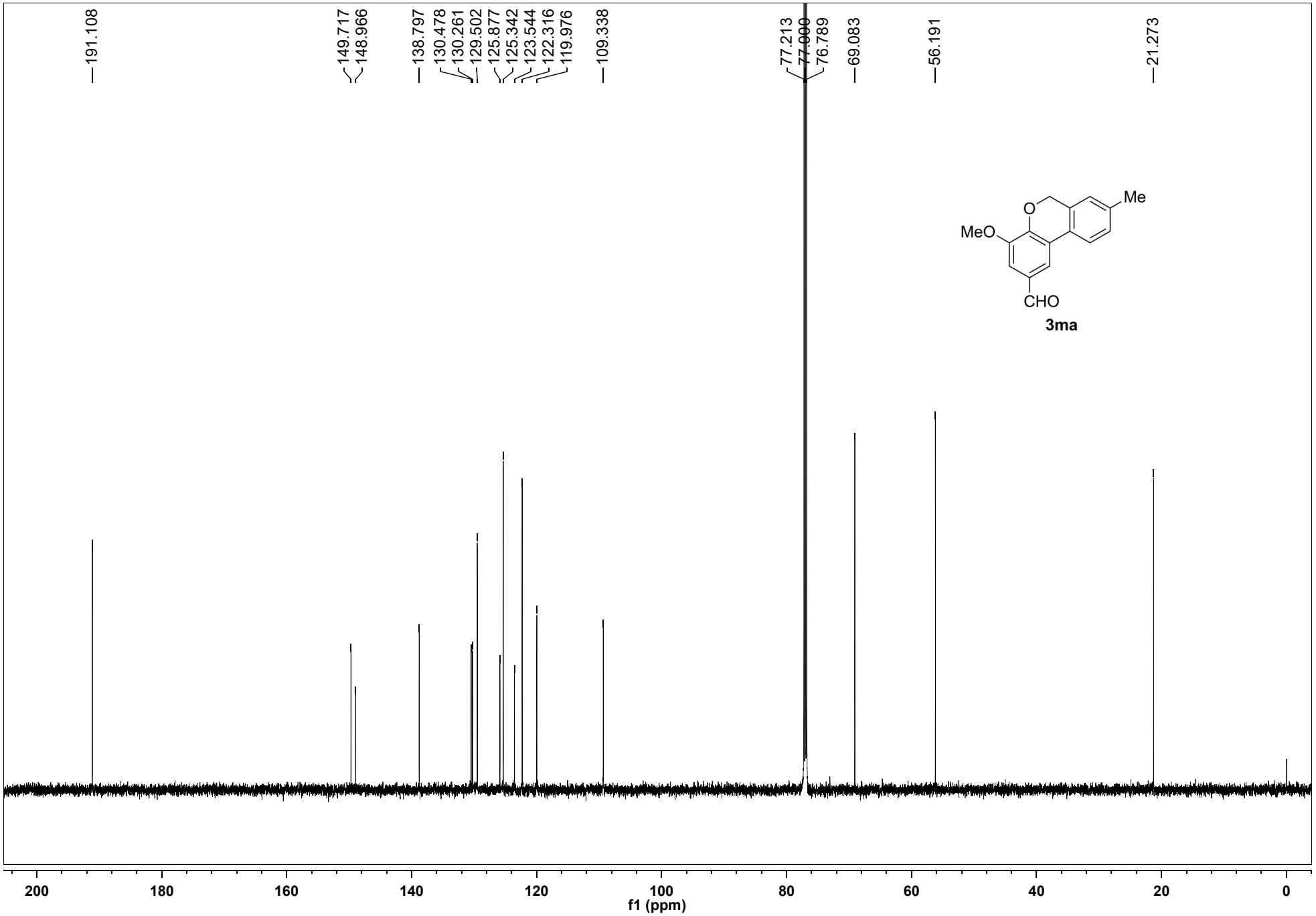

Figure S29. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ab

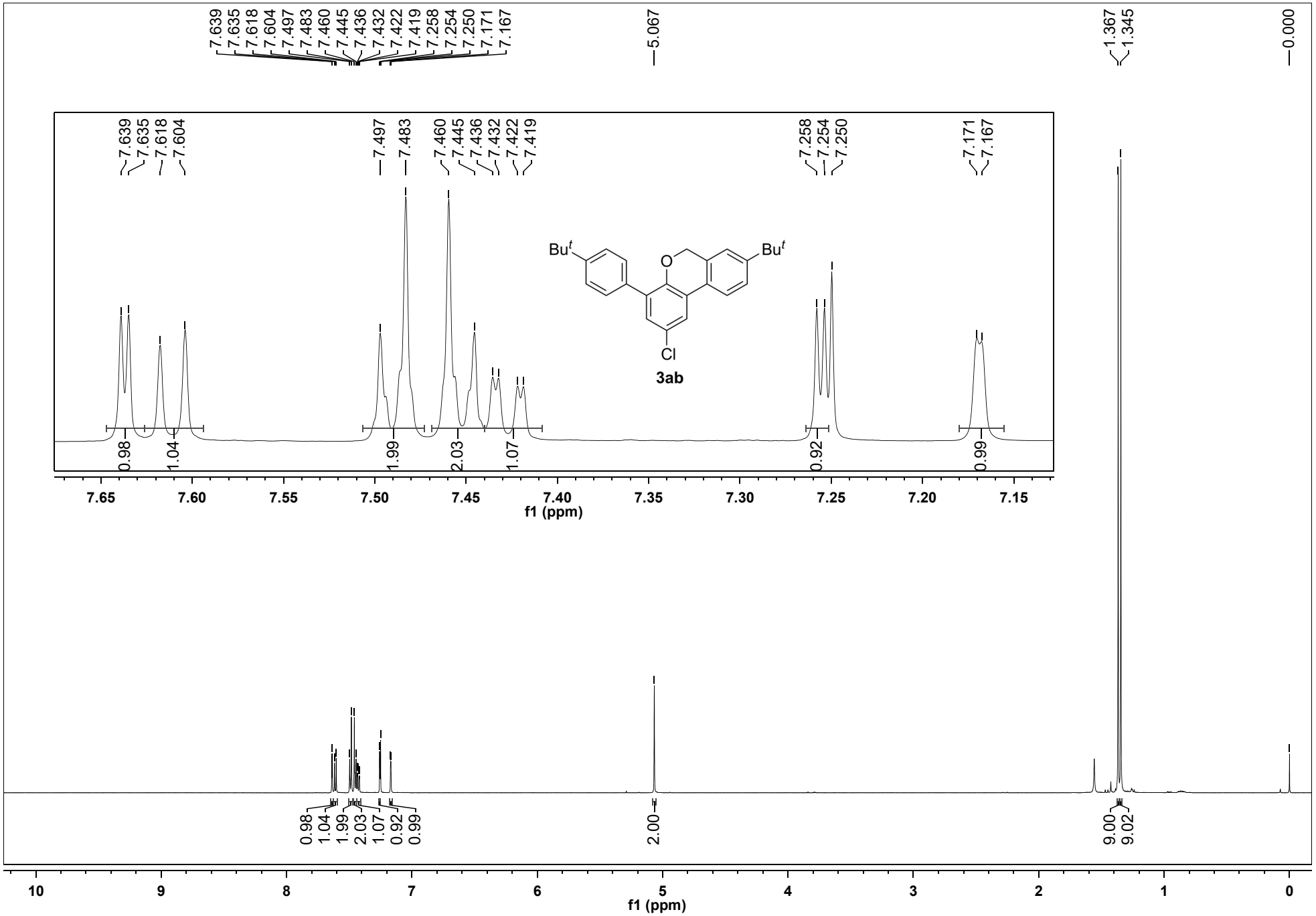

Figure S30. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ab

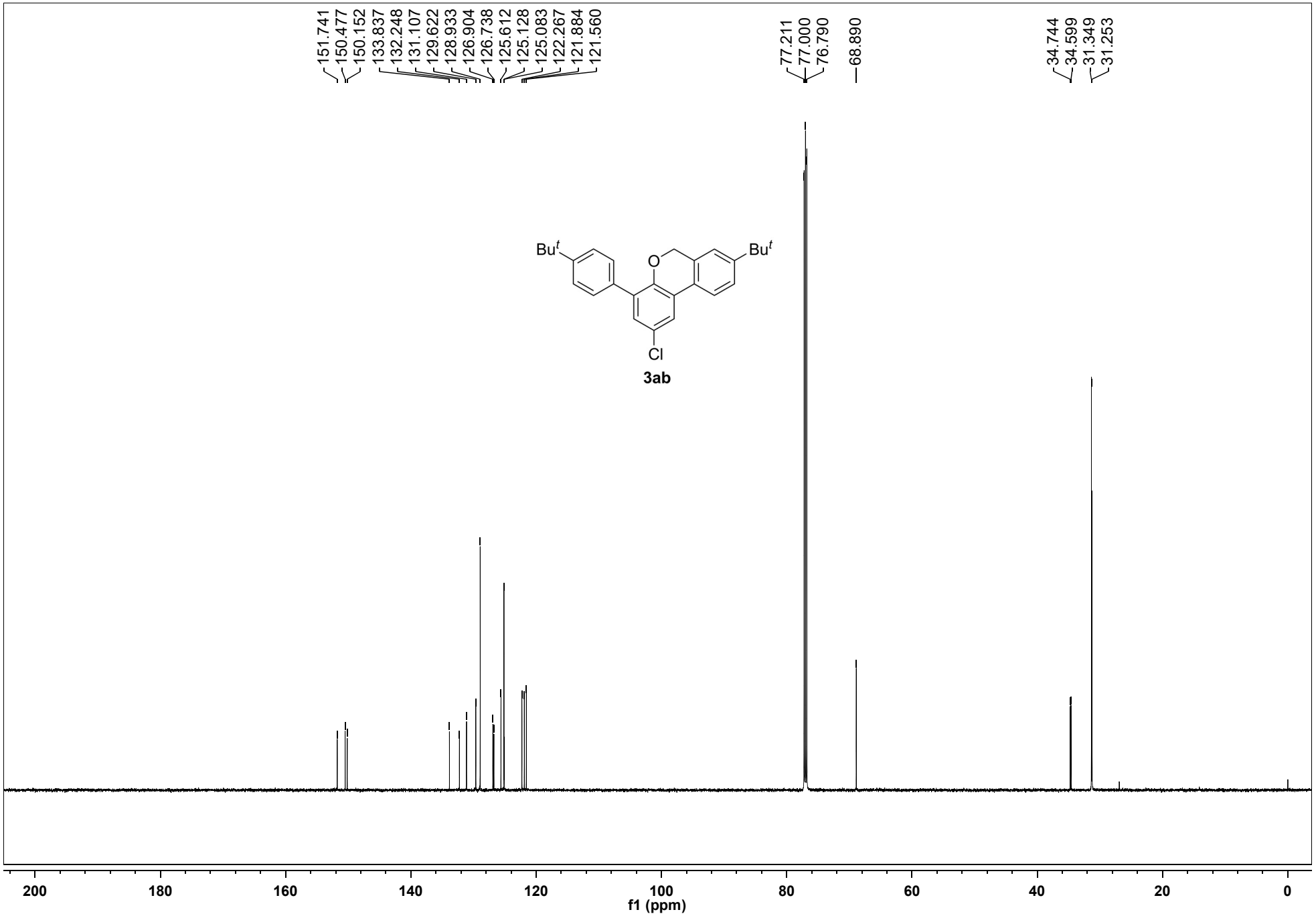

Figure S31. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ac

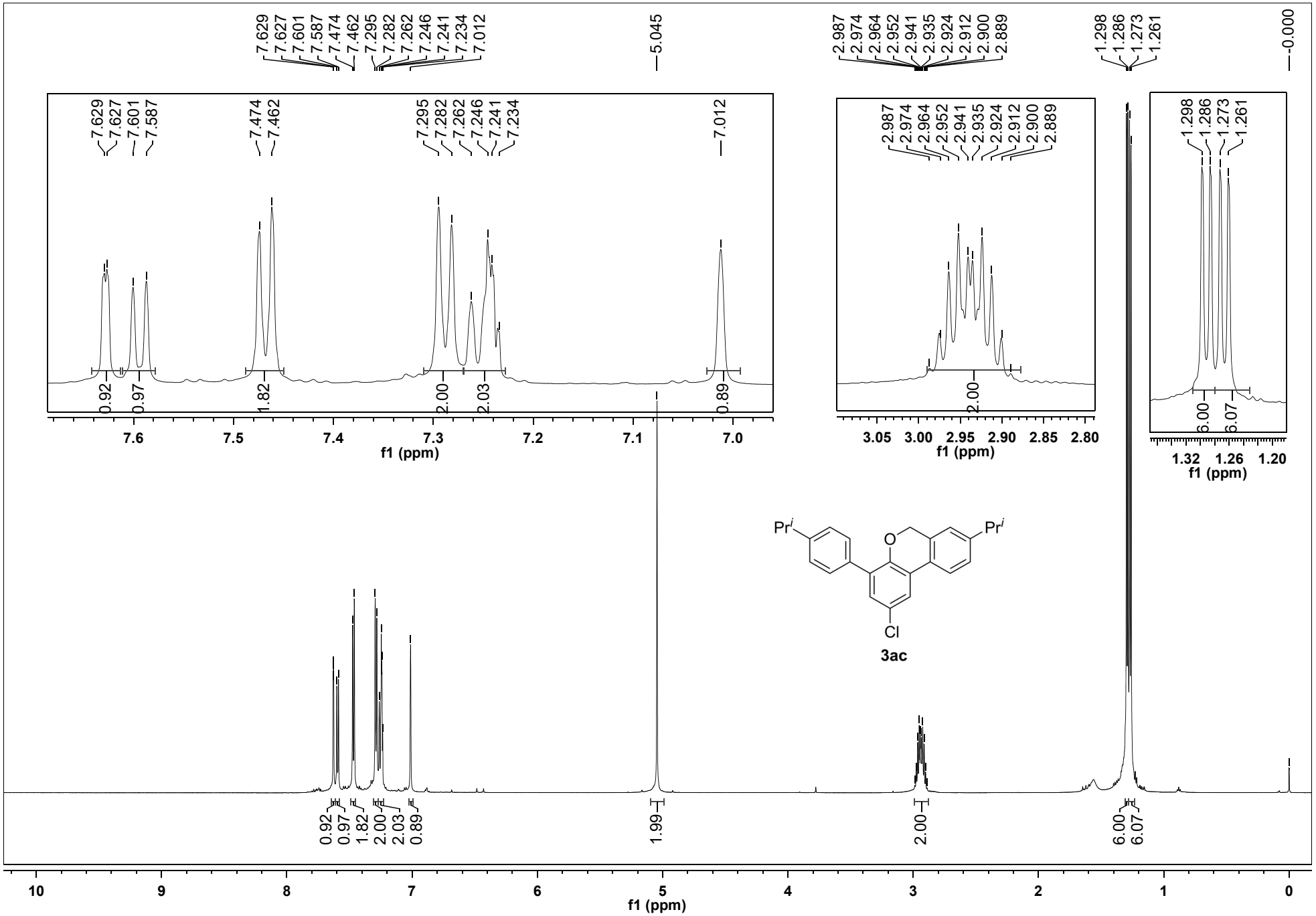

Figure S32. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ac

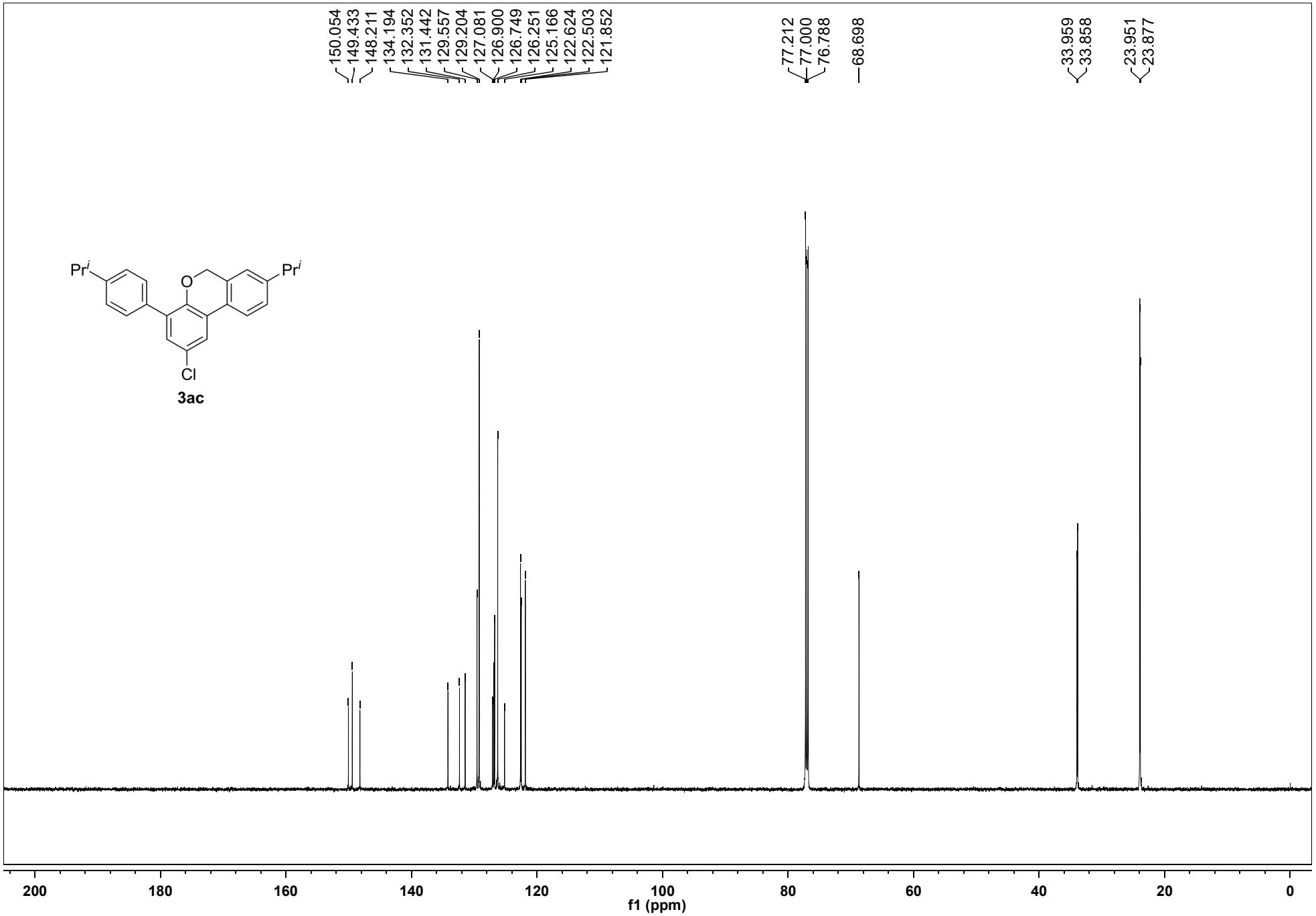

Figure S33. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ad

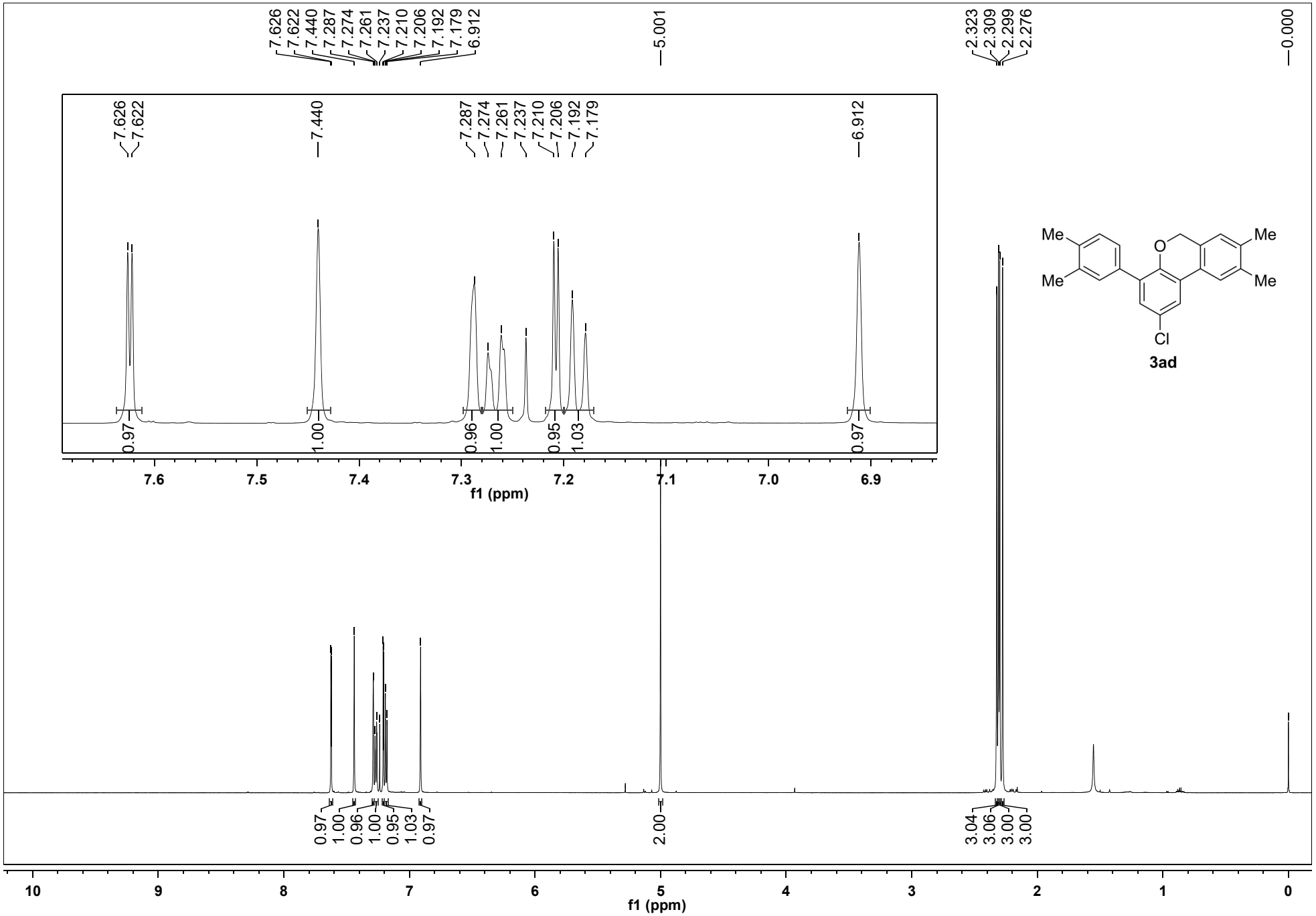

Figure S34. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ad

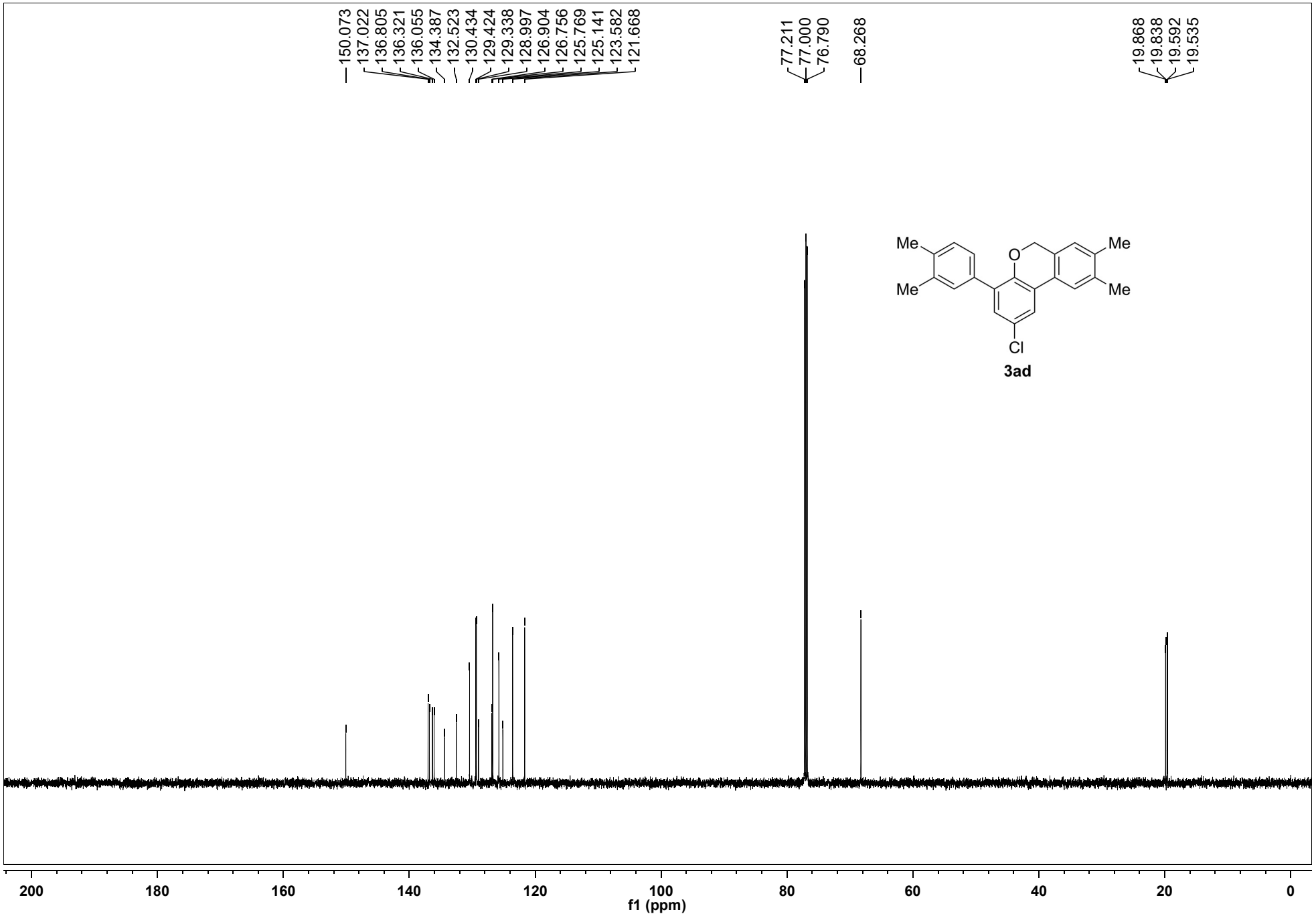

Figure S35. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ae

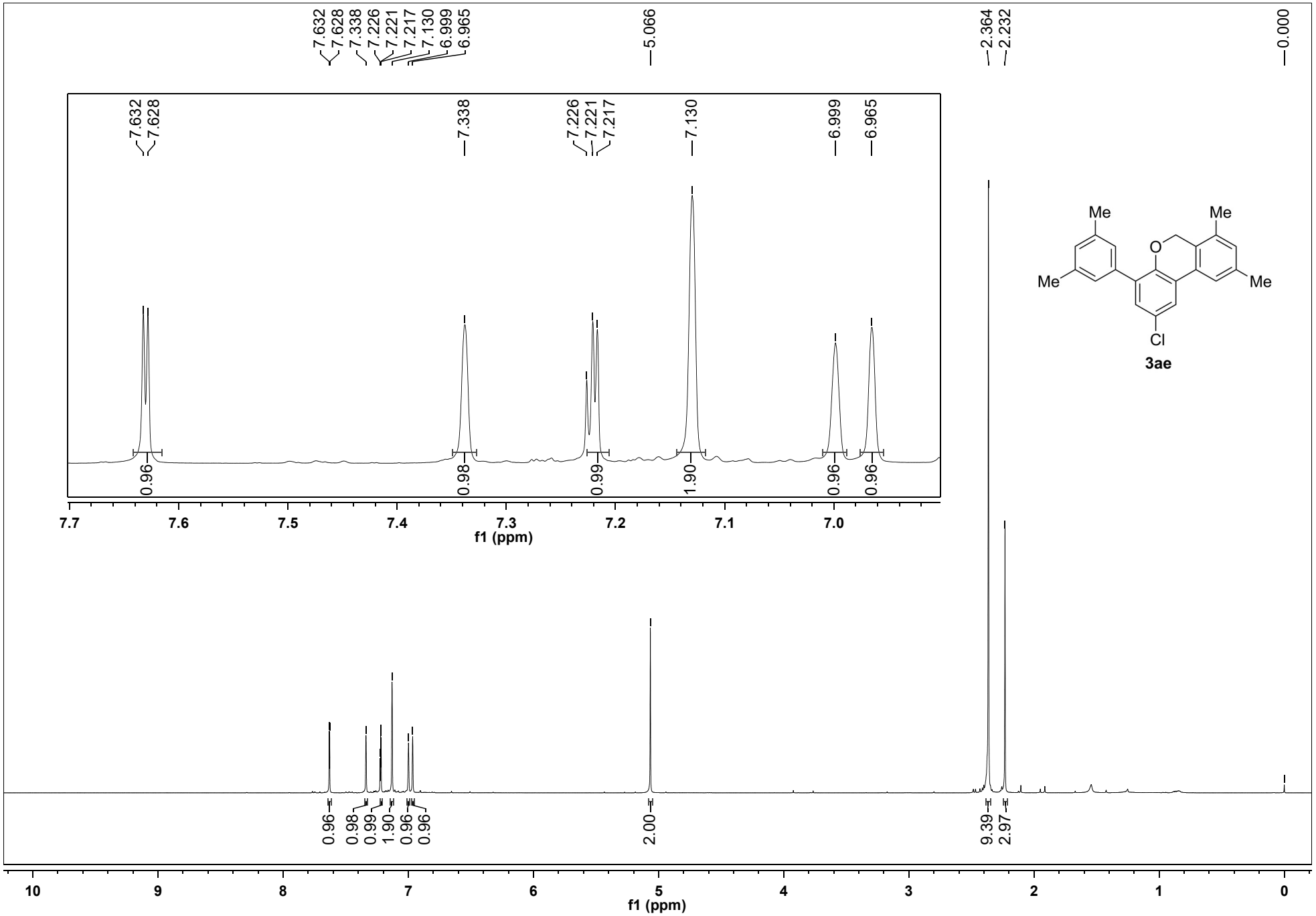

Figure S36. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ae

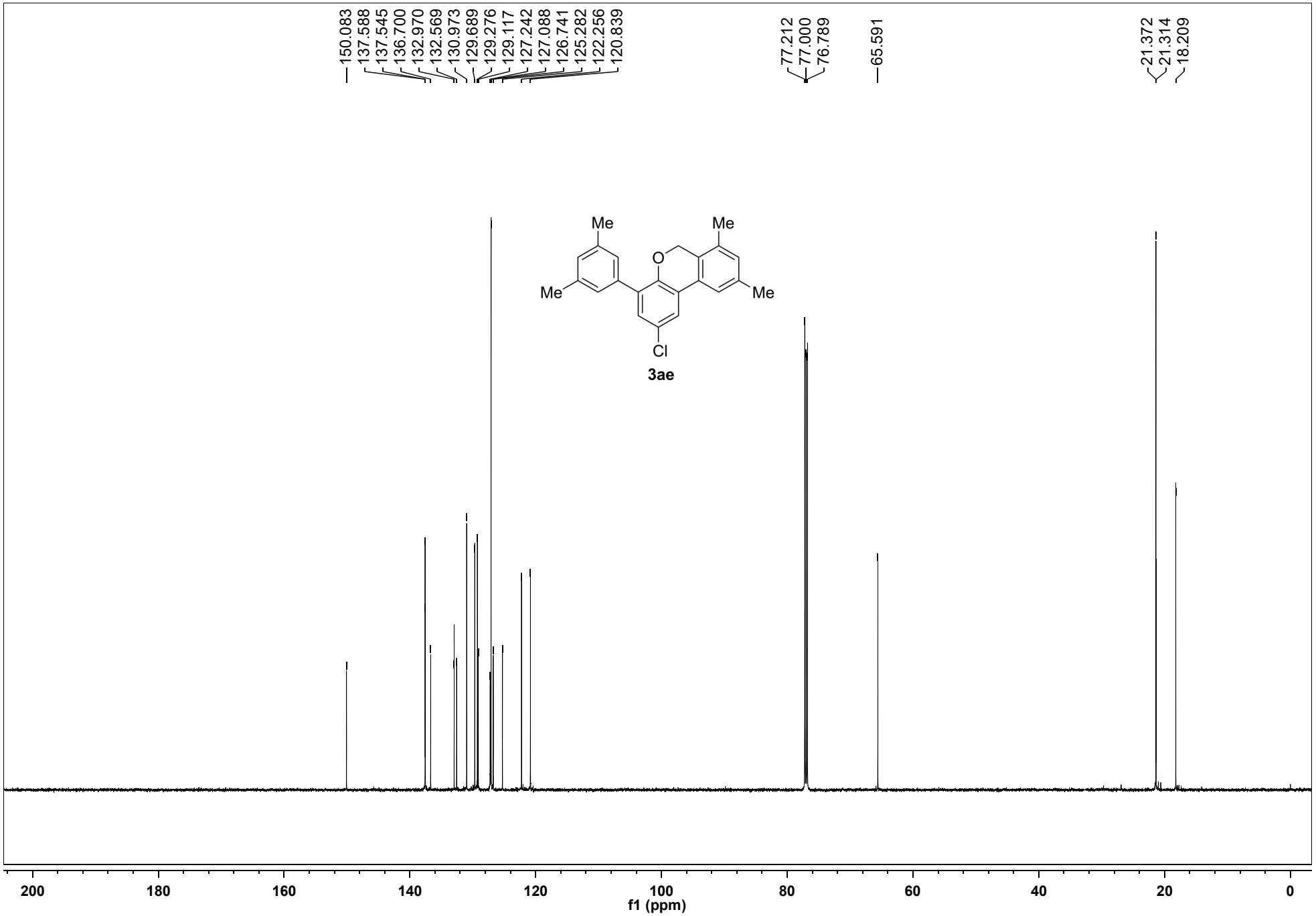

Figure S37. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3af

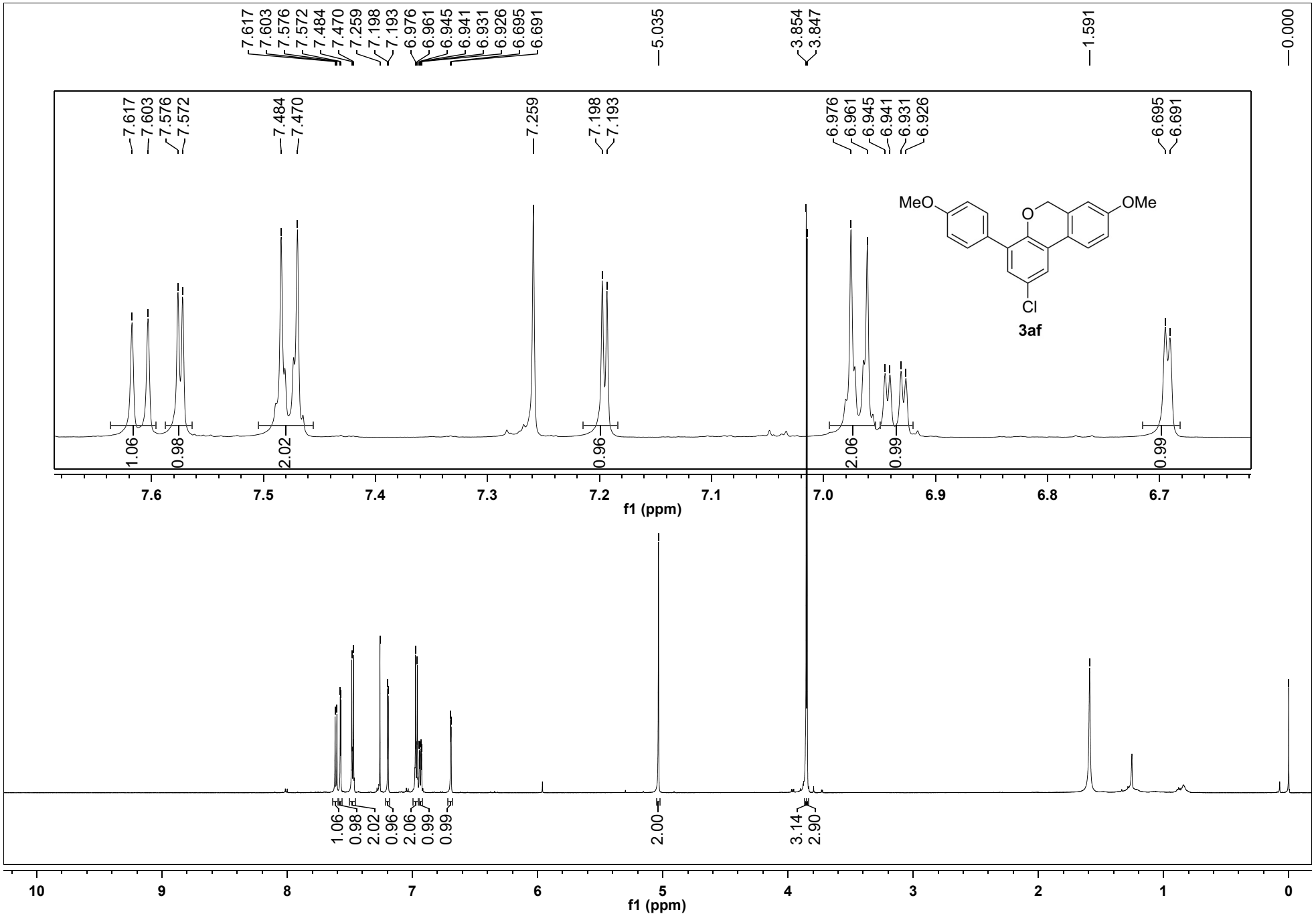

Figure S38. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3af

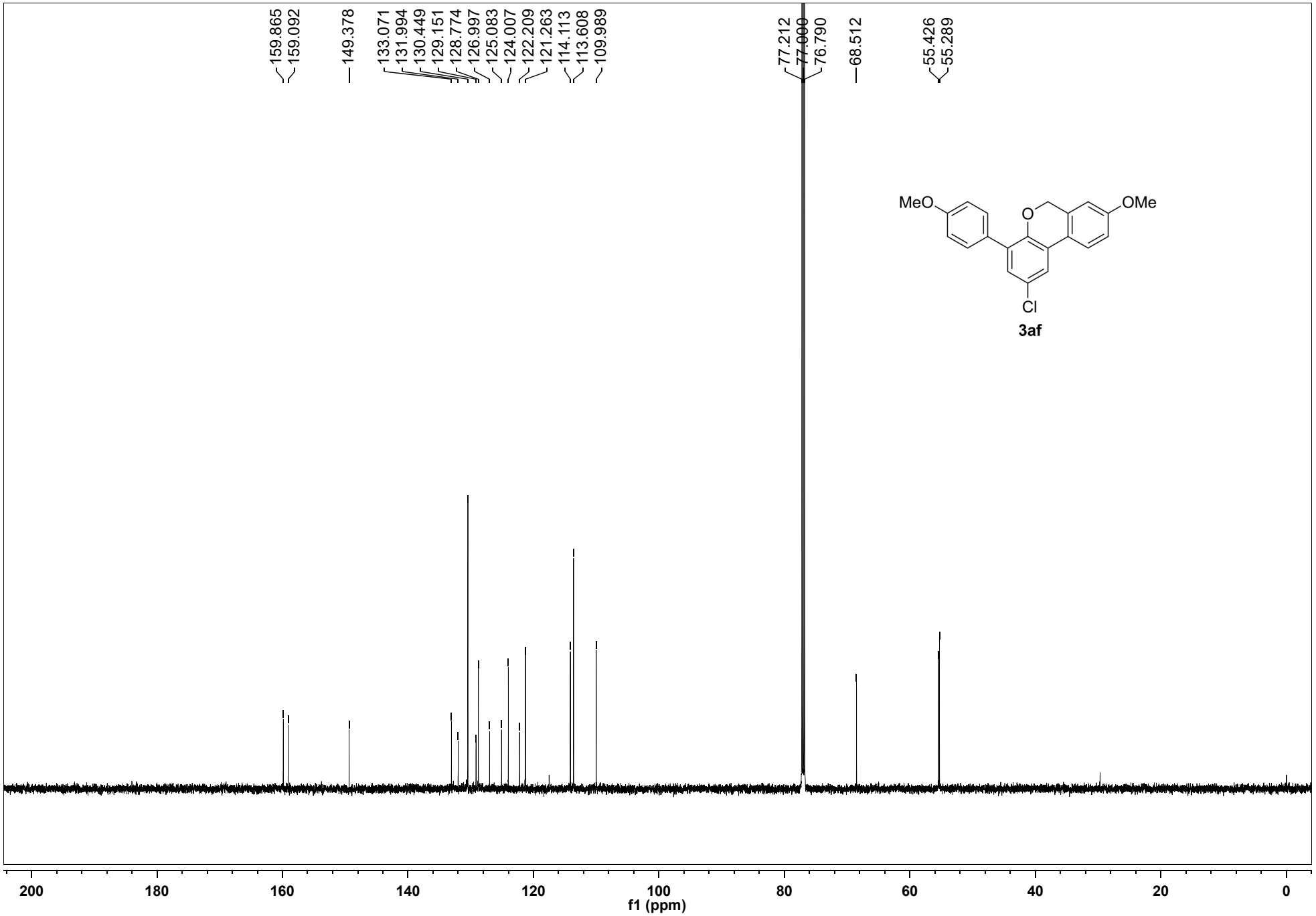

Figure S39. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ag

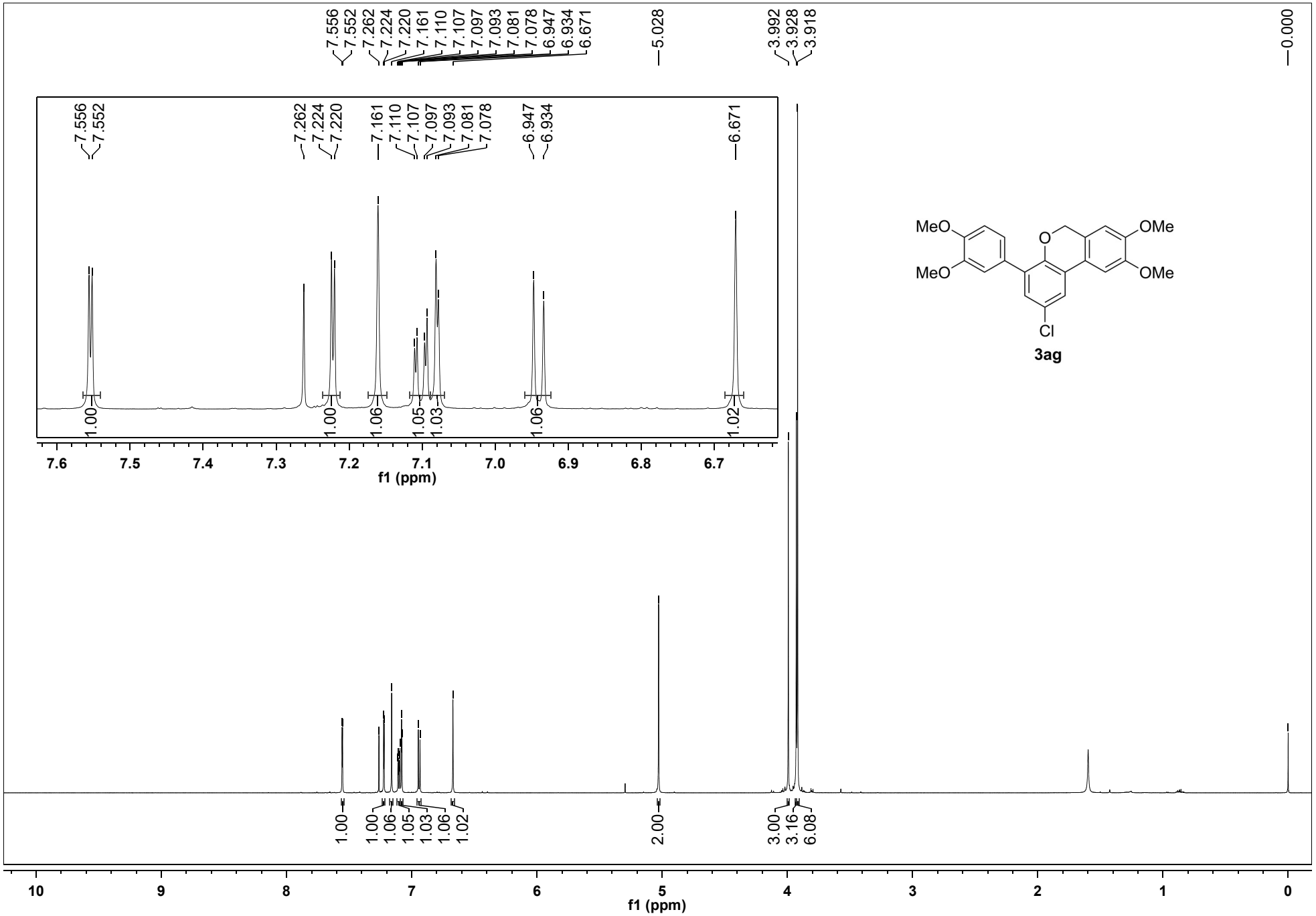

Figure S40. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ag

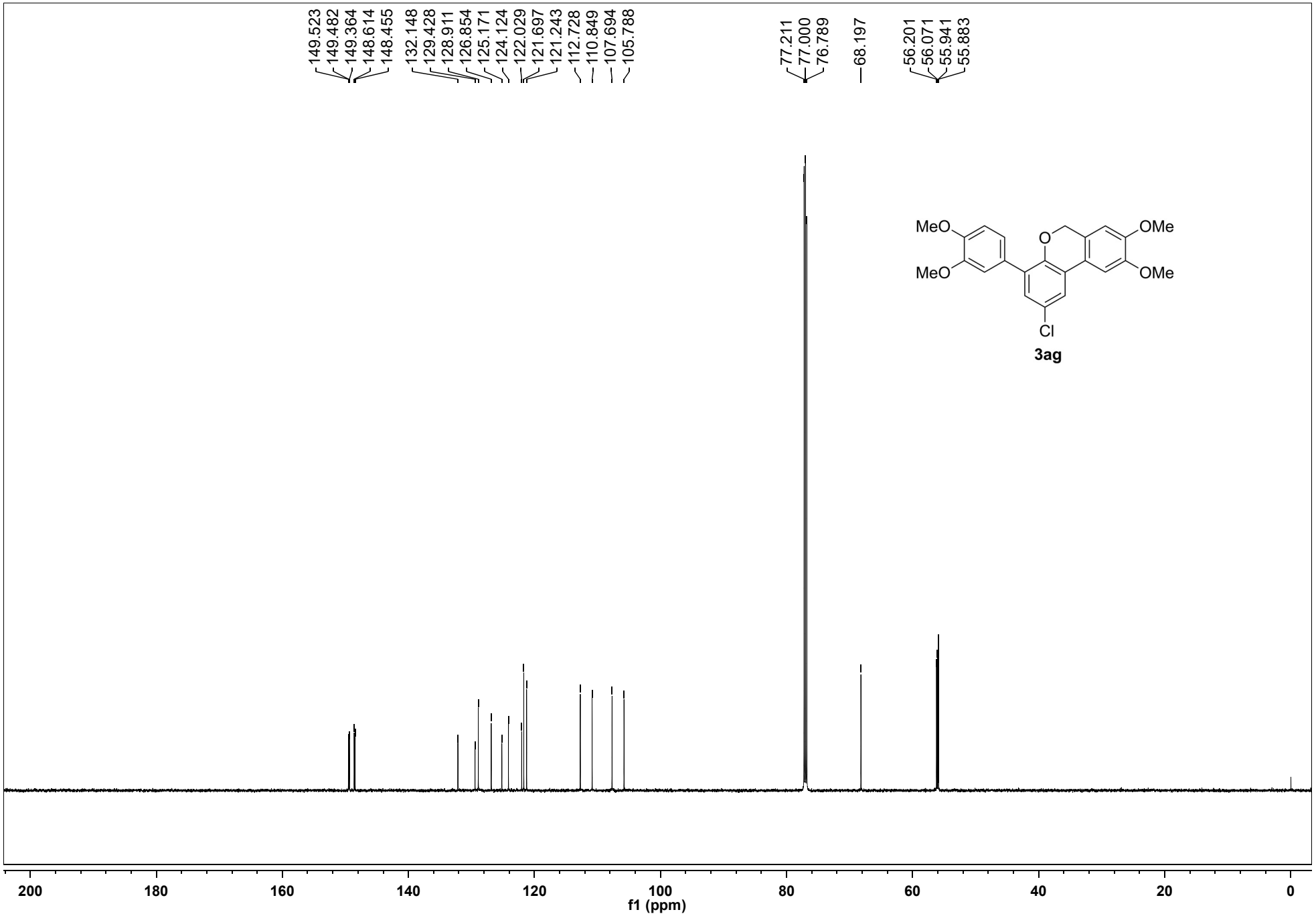

Figure S41. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ah

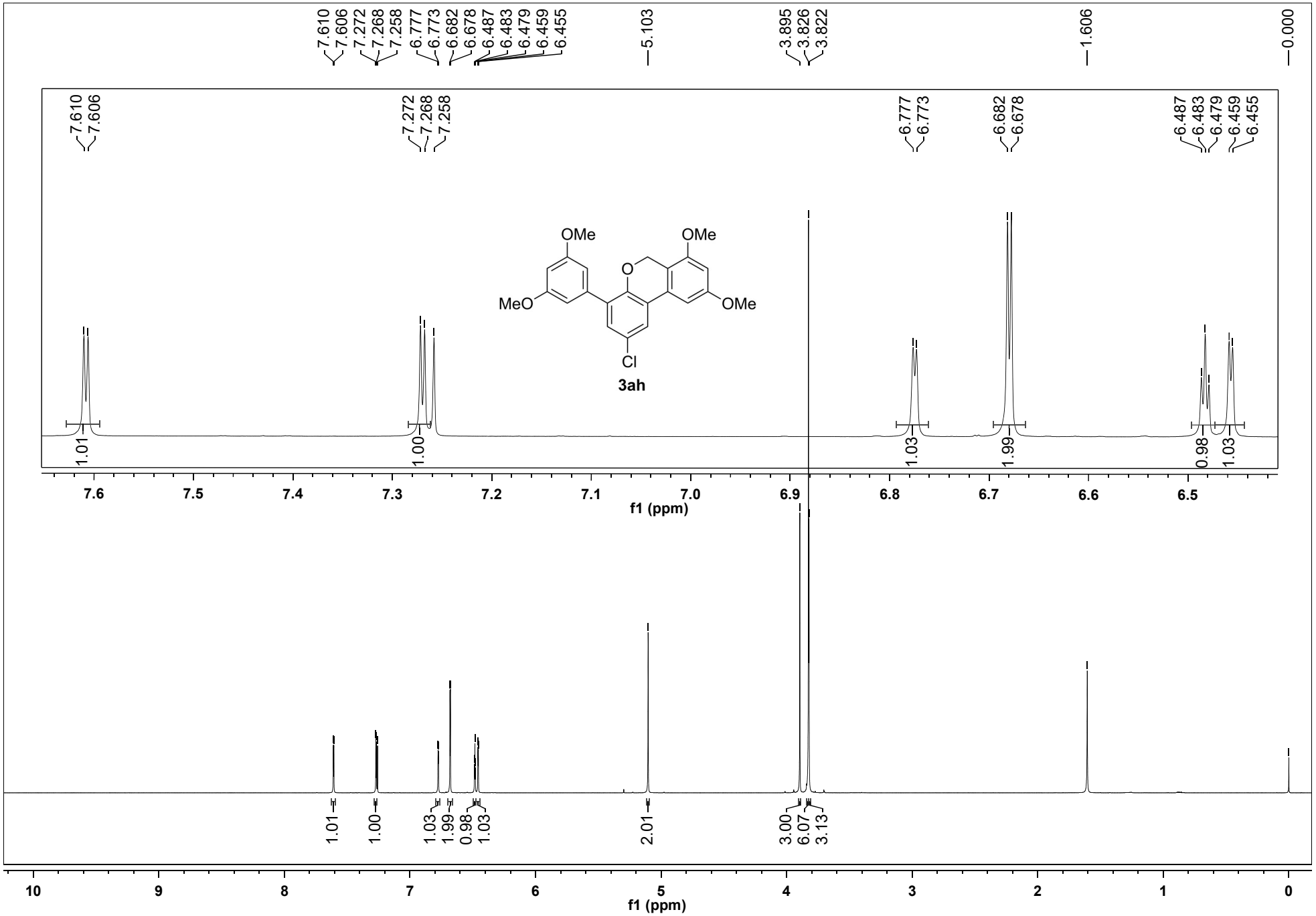

Figure S42. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ah

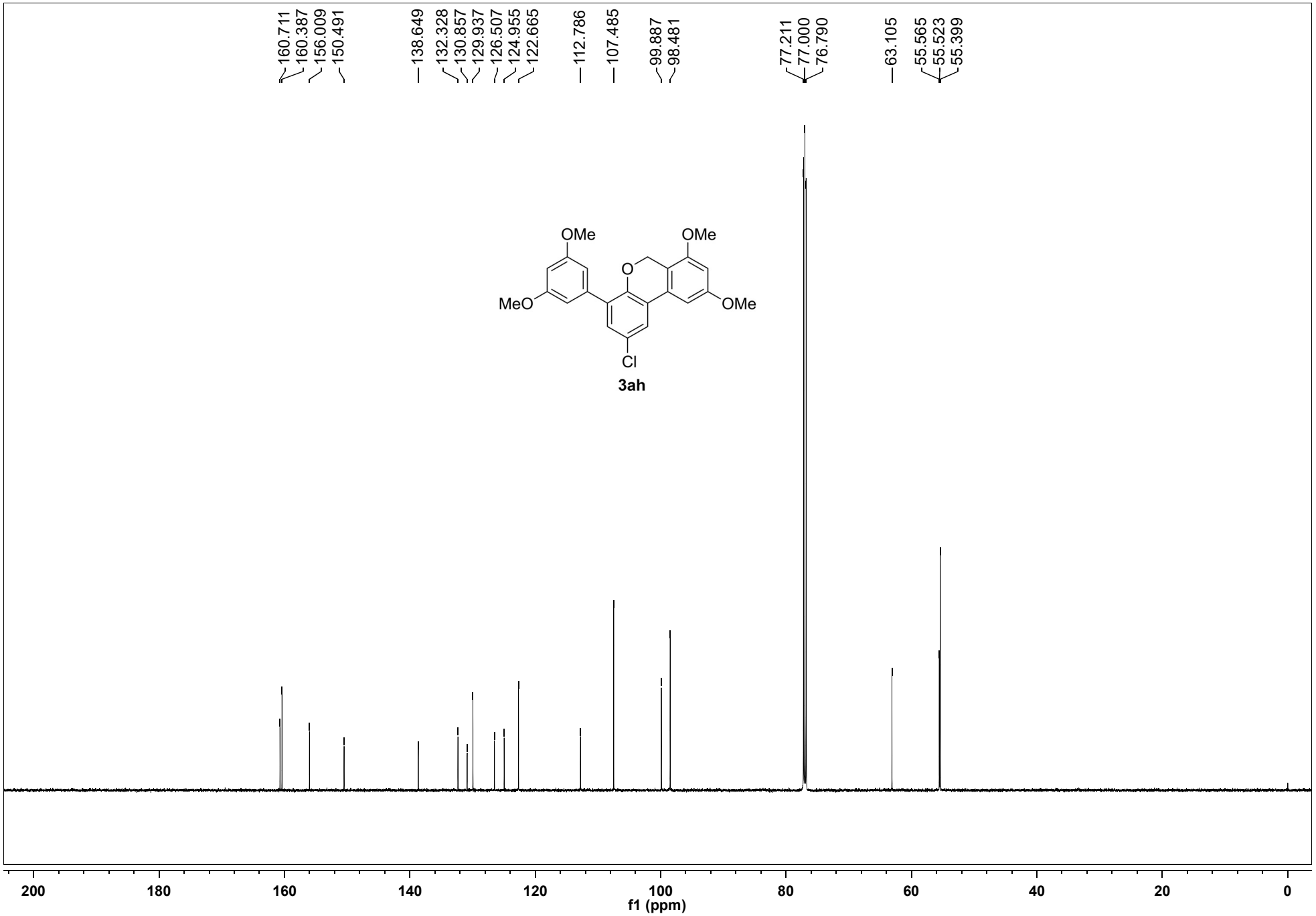

Figure S43. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ai

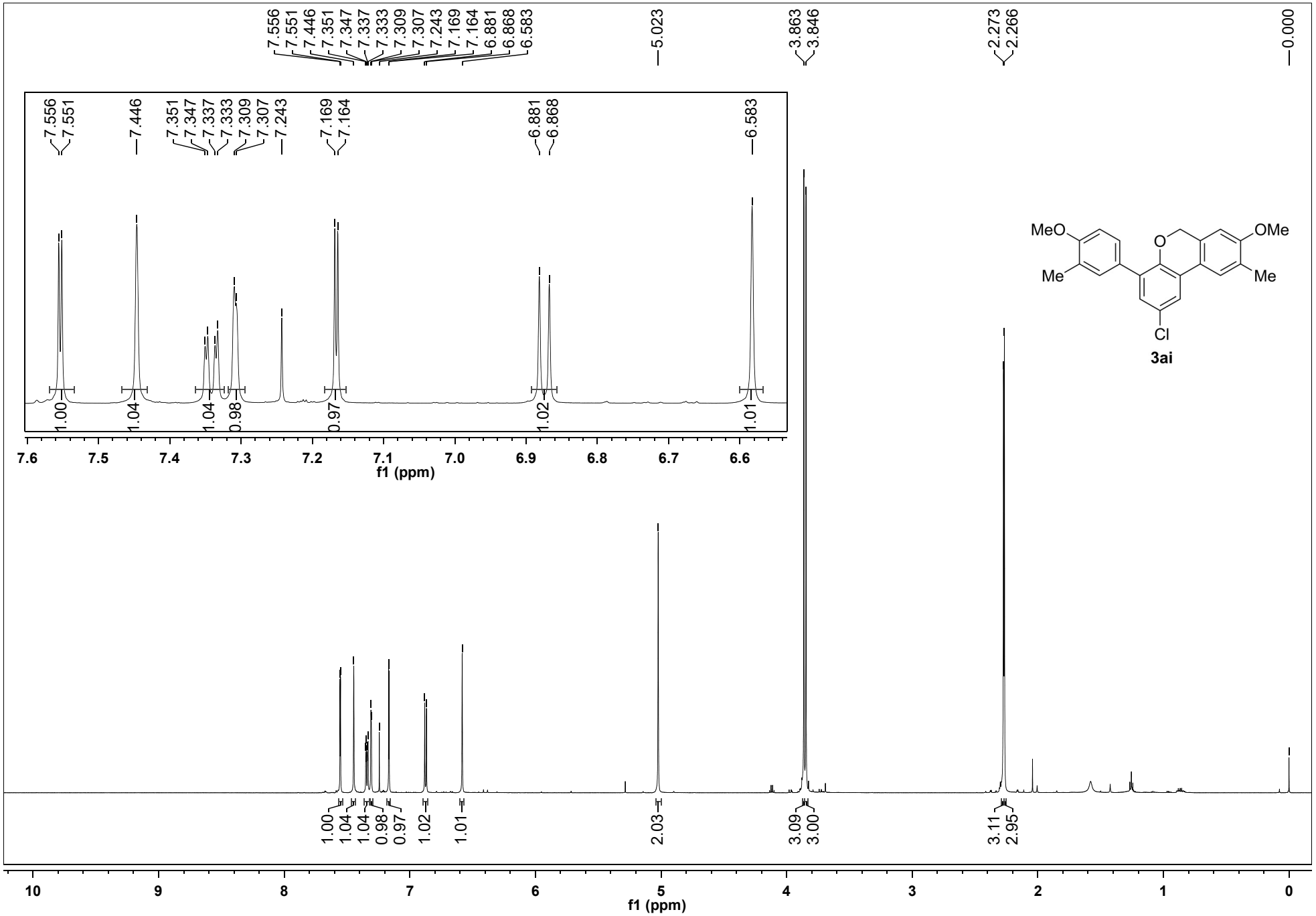

Figure S44. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ai

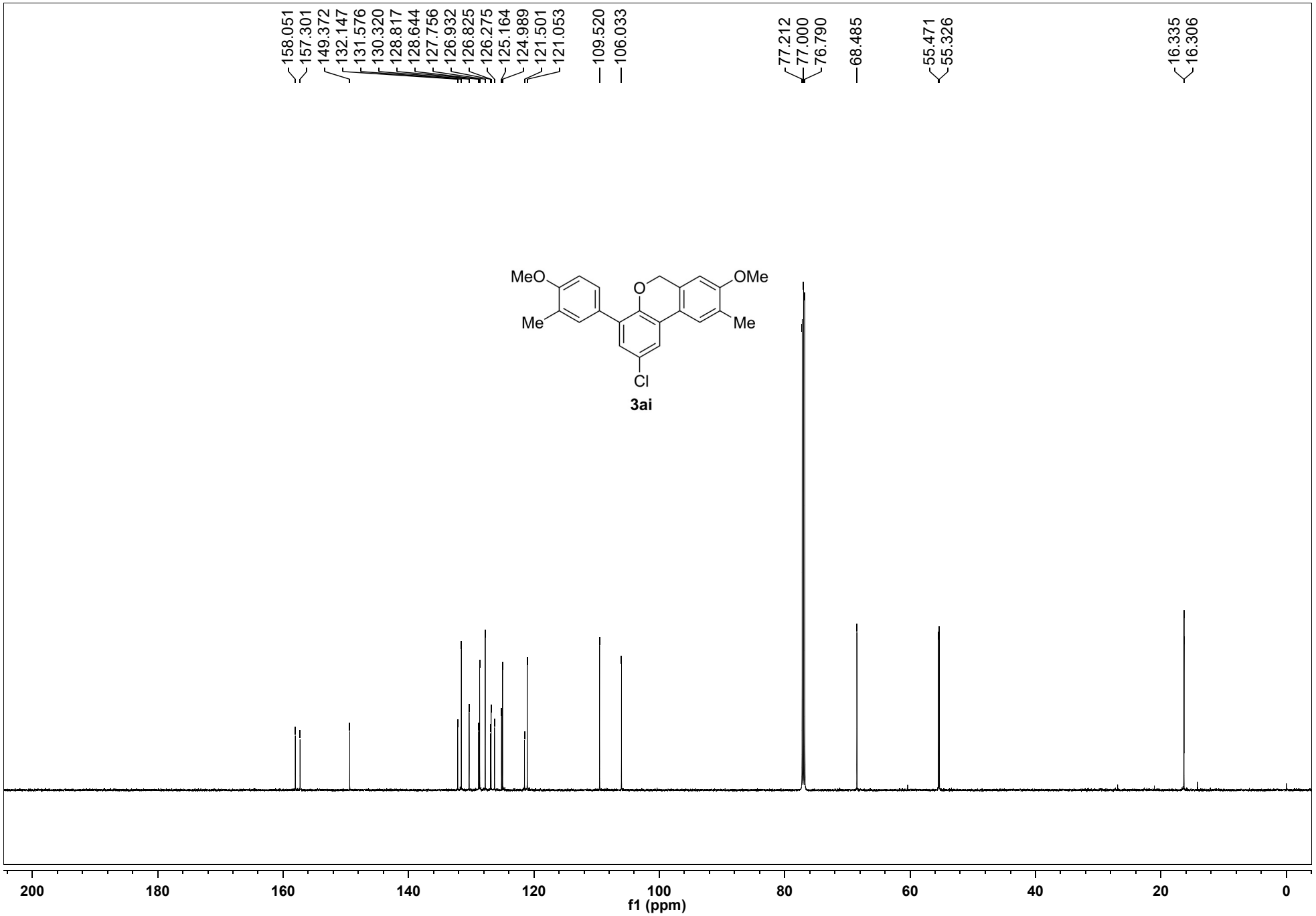

Figure S45. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3aj

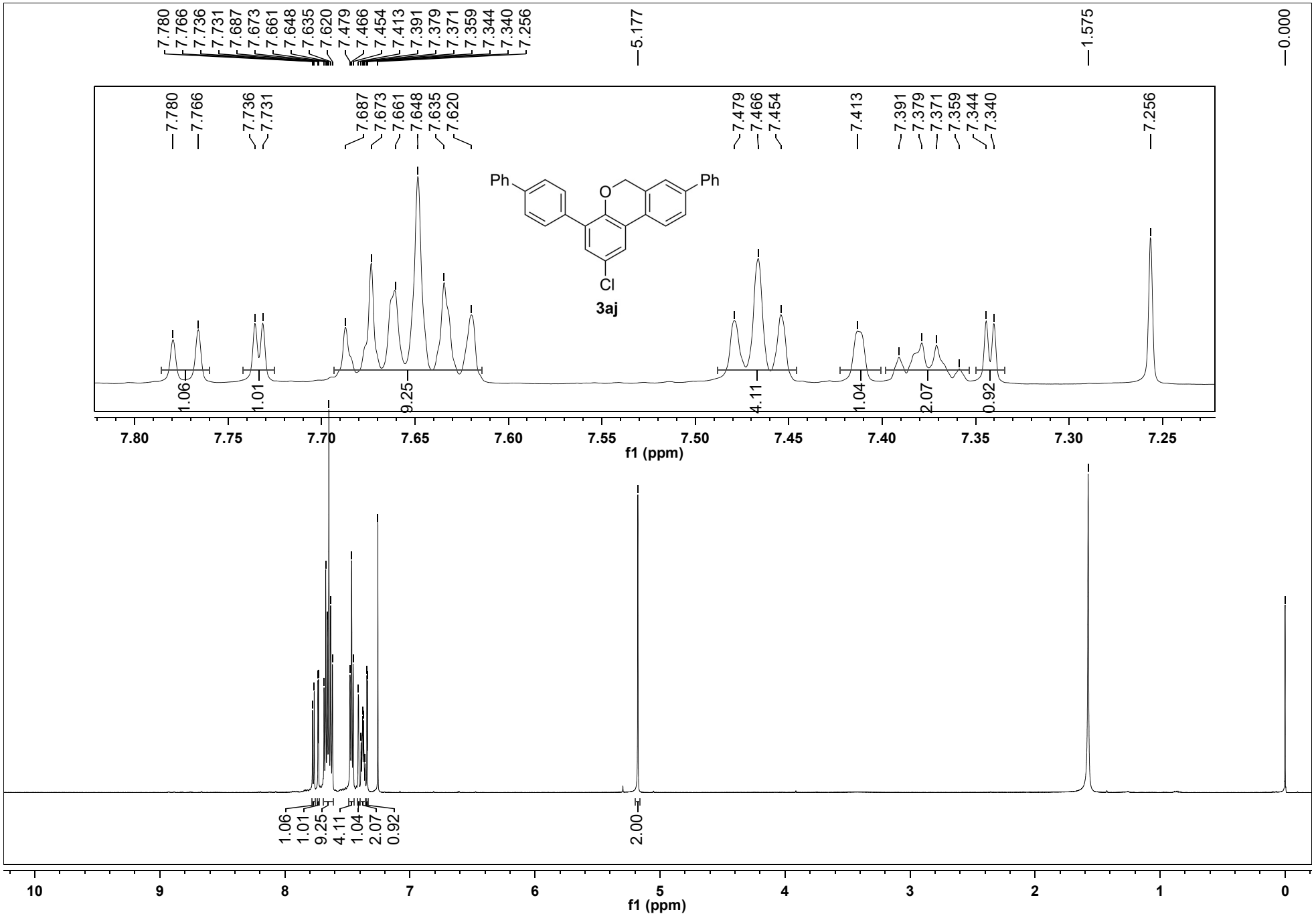

Figure S46. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3aj

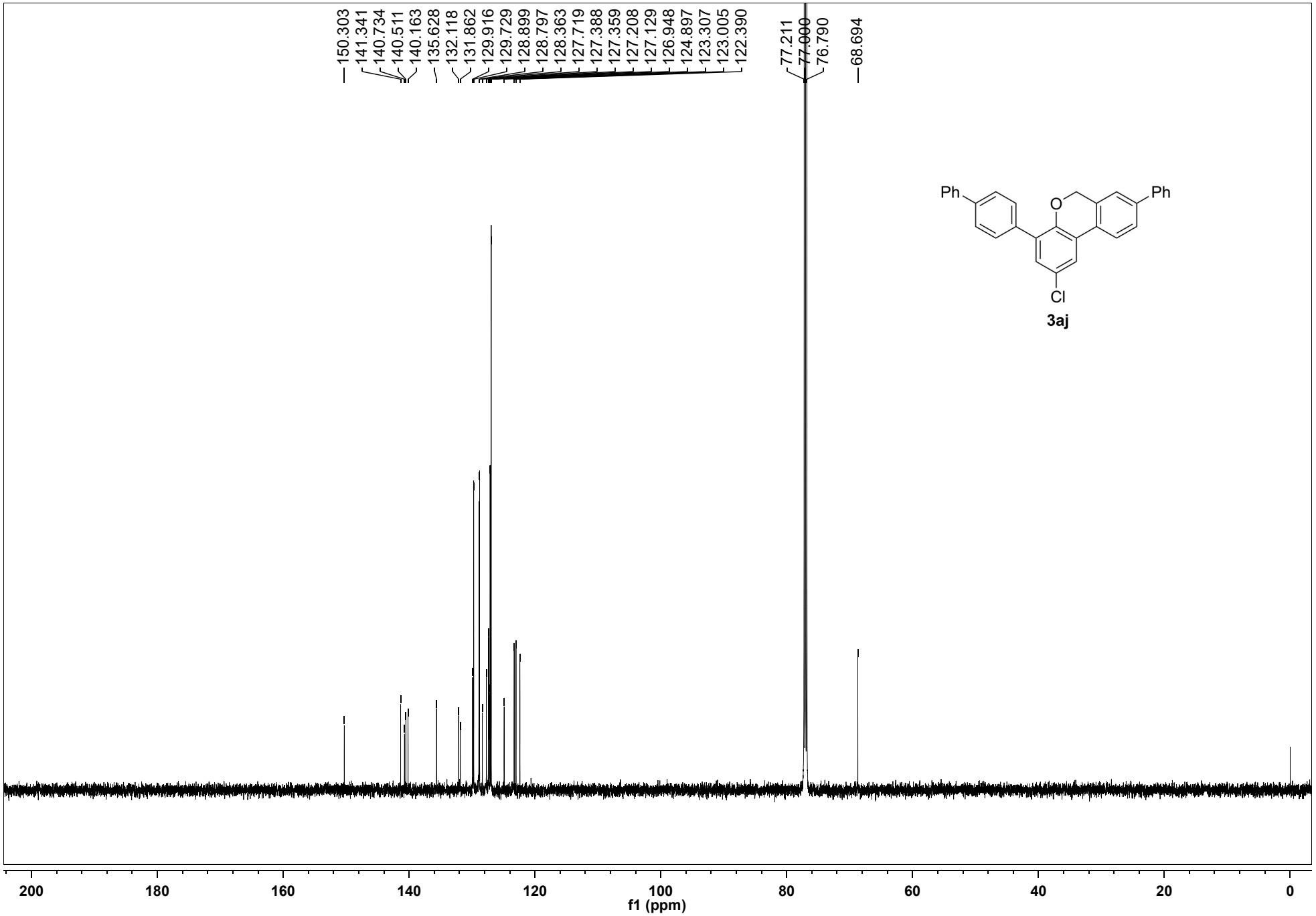

Figure S47. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ak

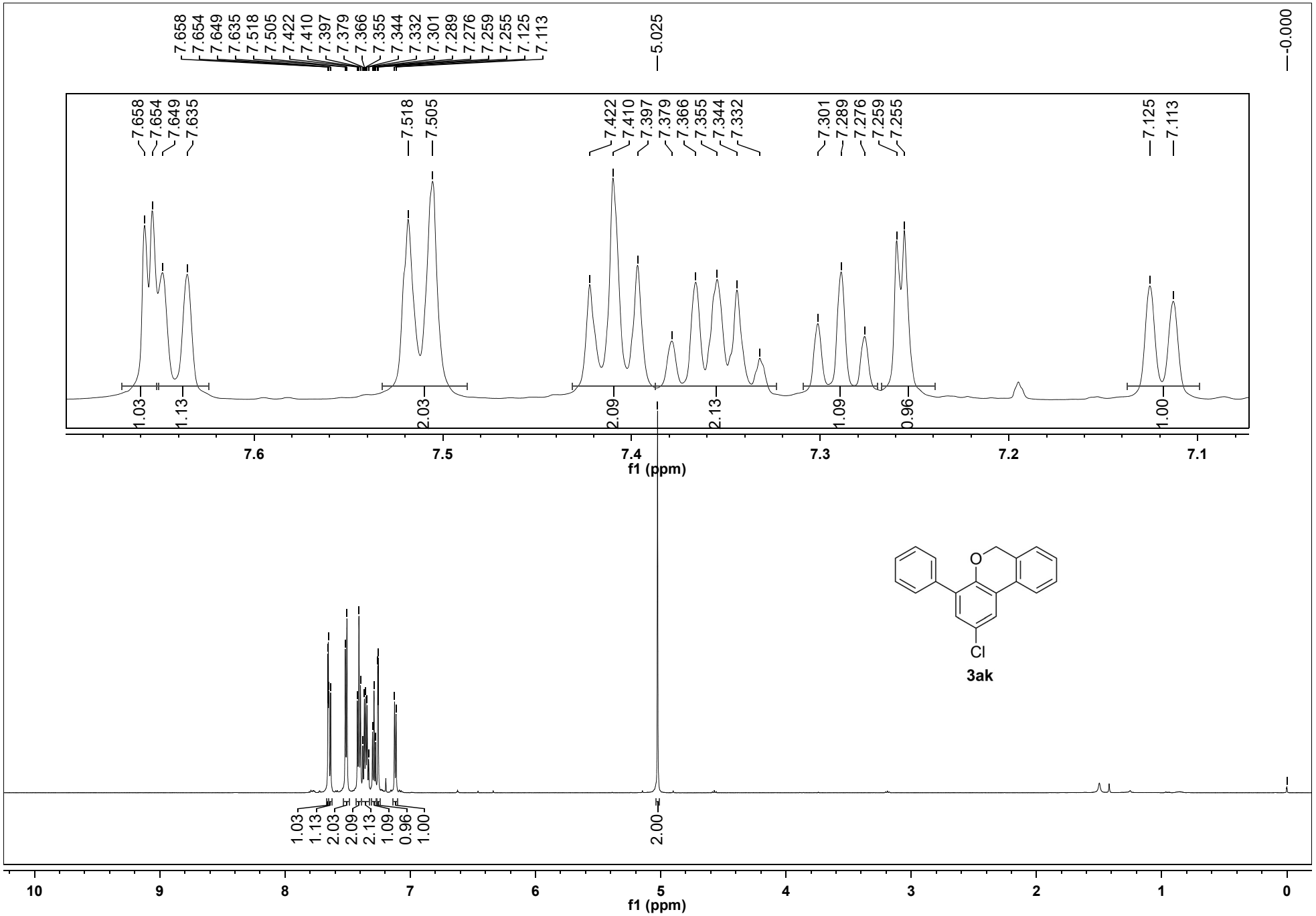

Figure S48. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3ak

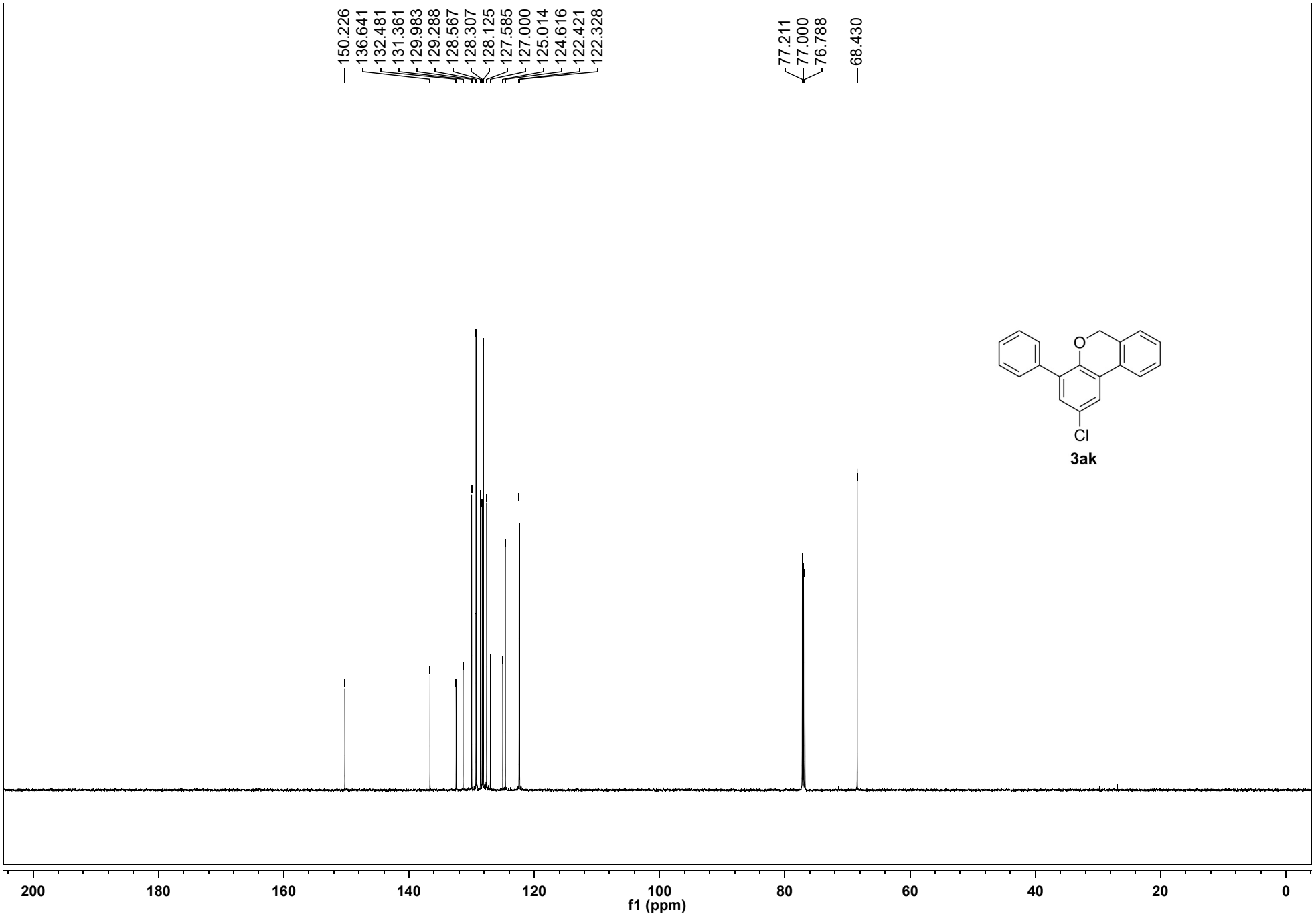

Figure S49. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3al

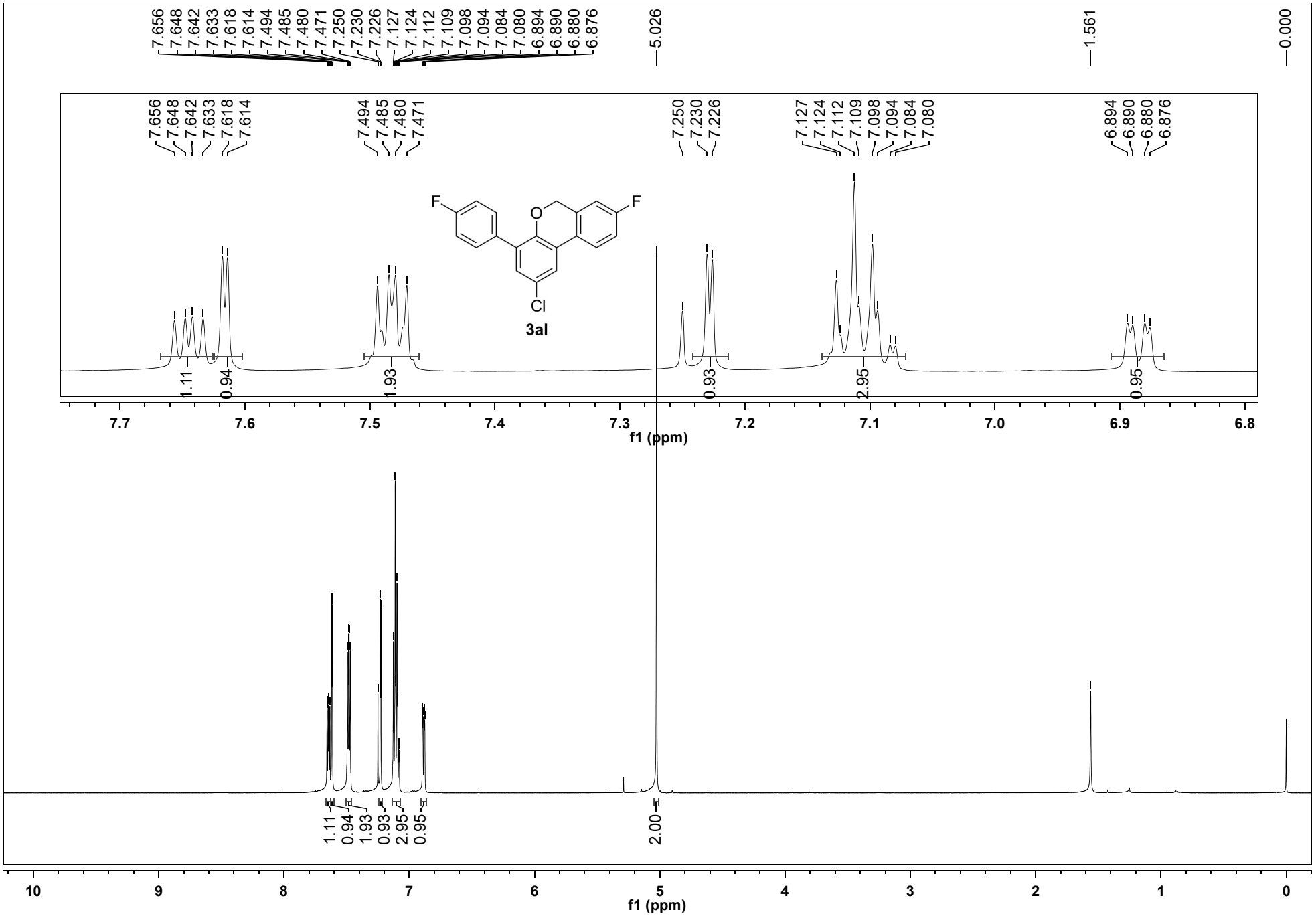

Figure S50. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3al

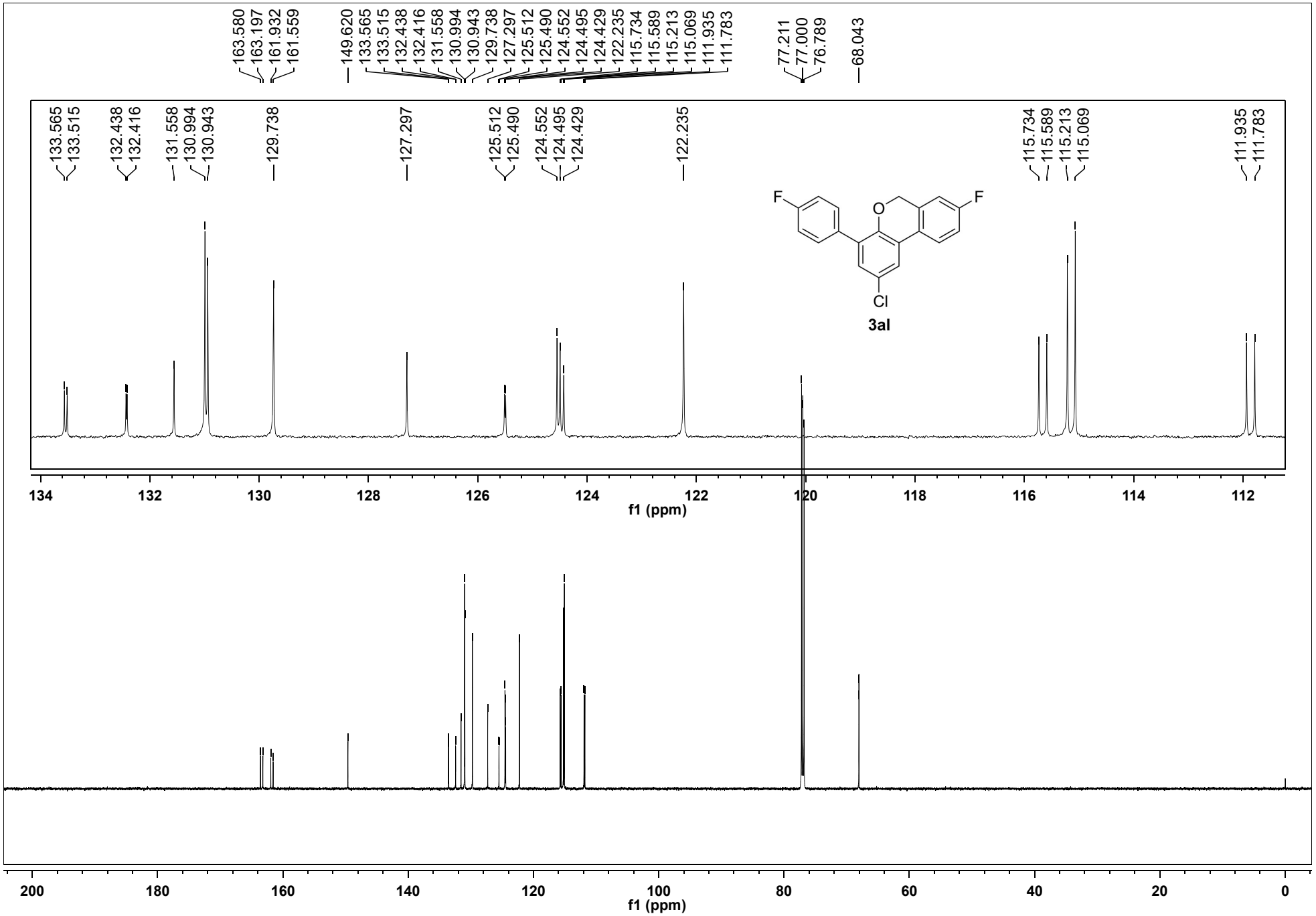

Figure S51. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3am

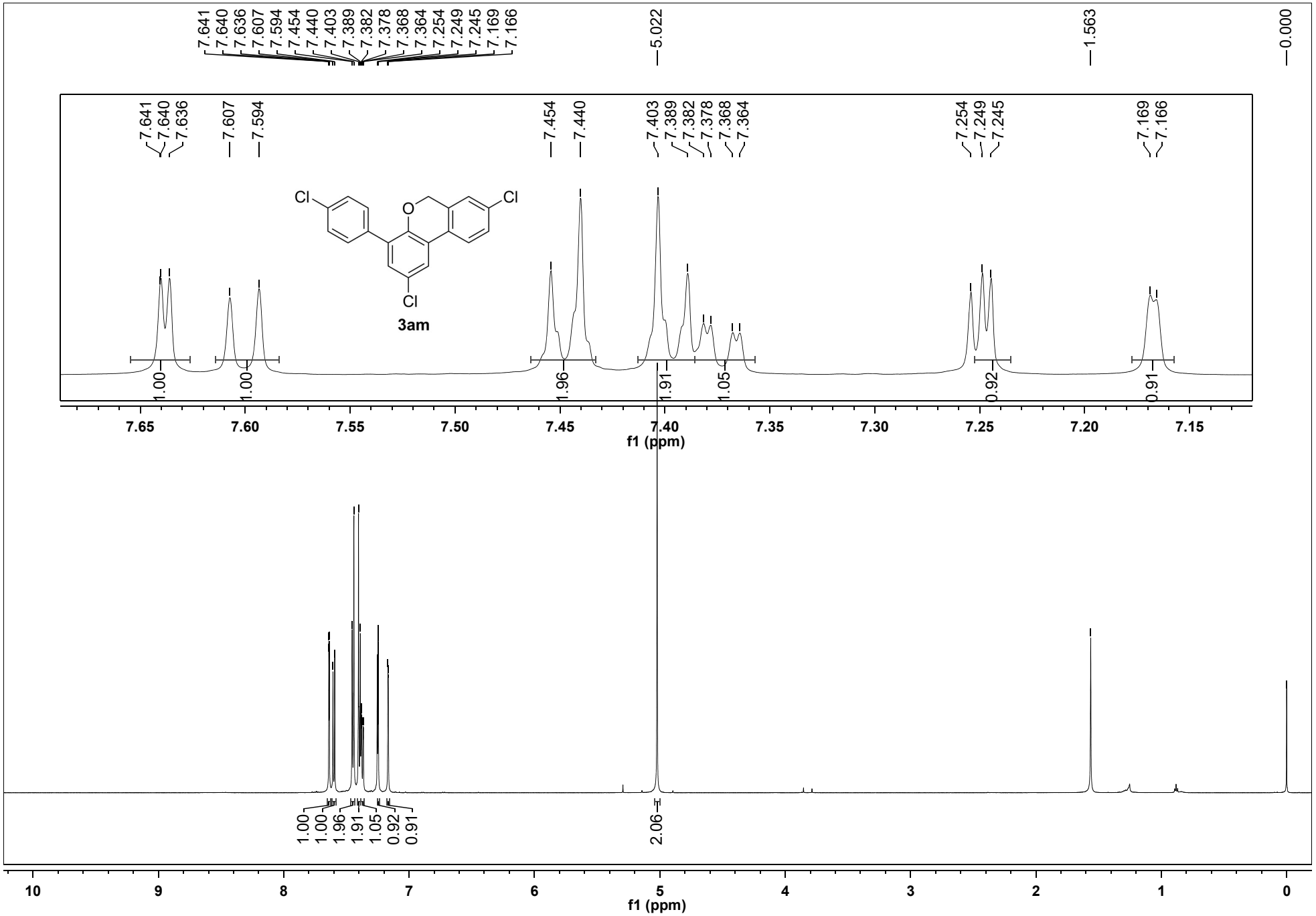

Figure S52. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3am

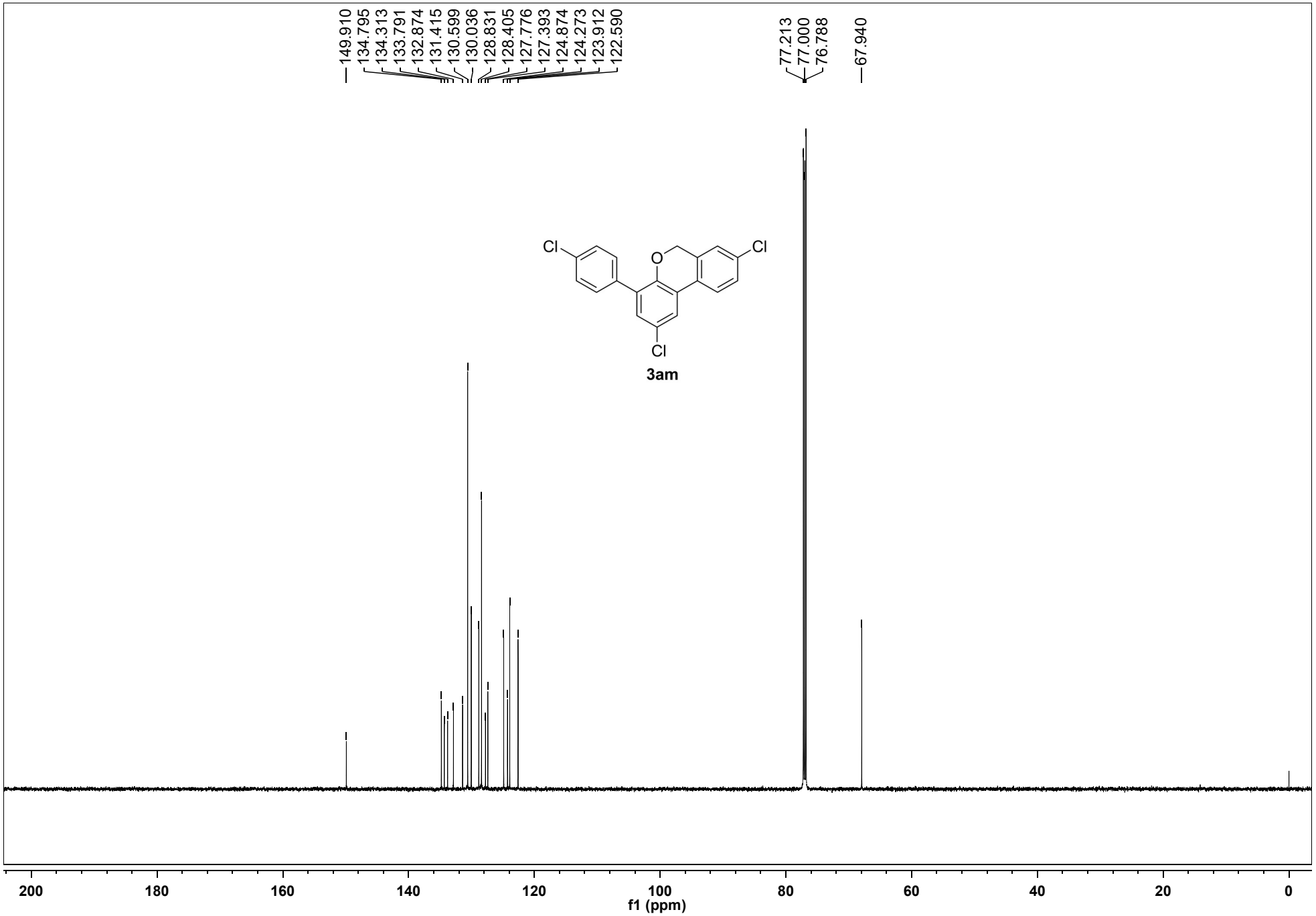

Figure S53. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3kk

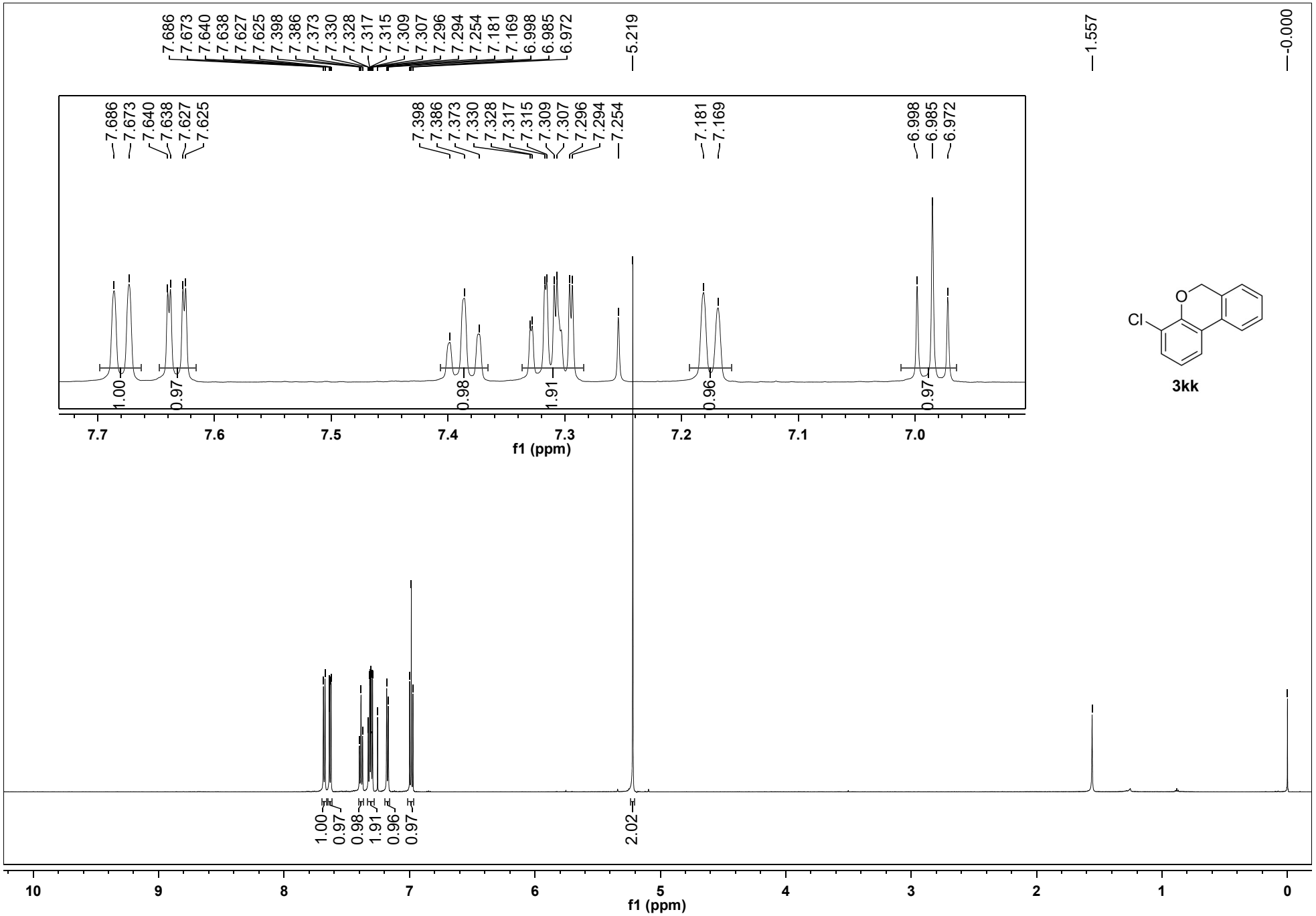

Figure S54. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3kk

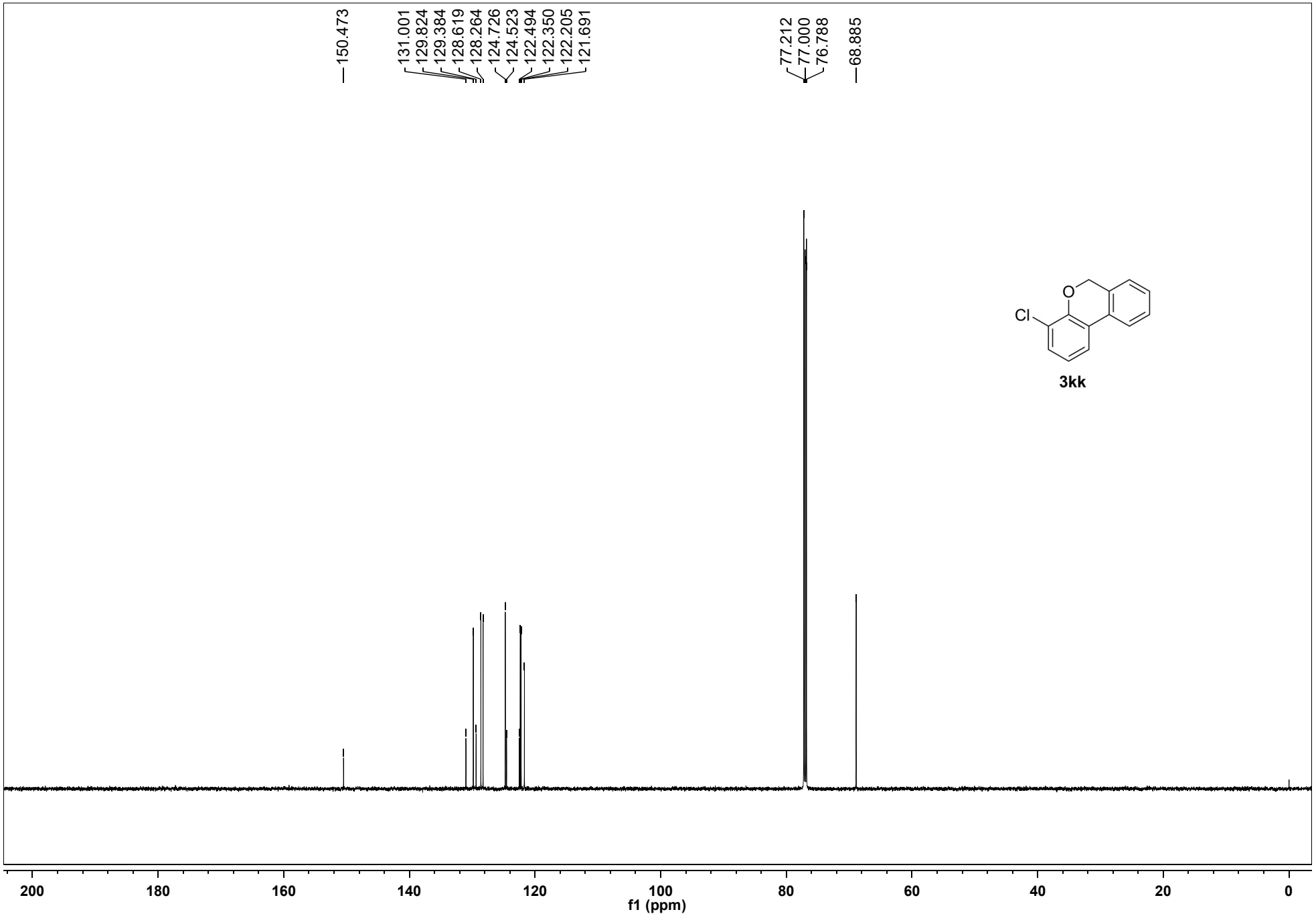

Figure S55. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3kk-D

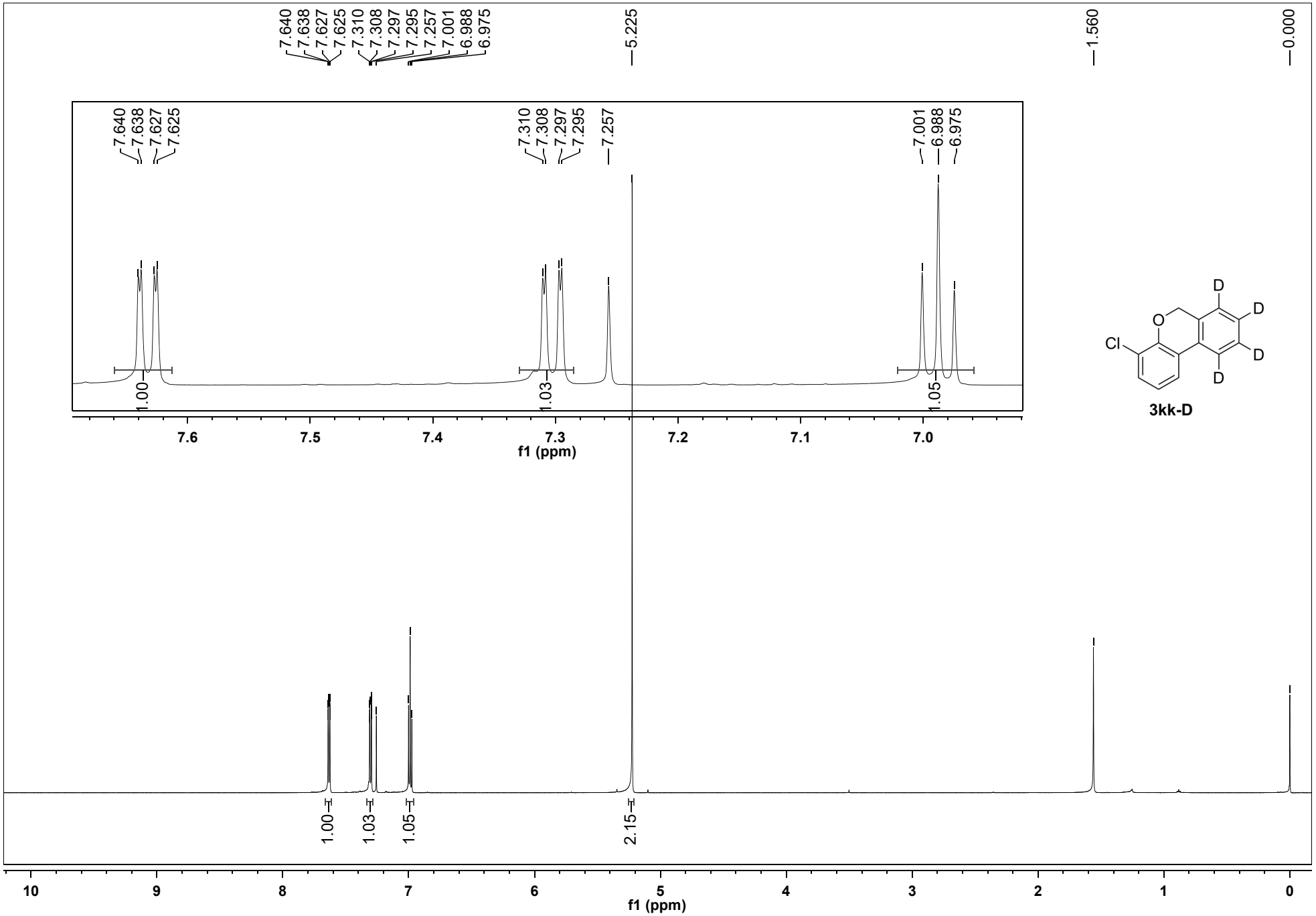

Figure S56. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 3kk-D

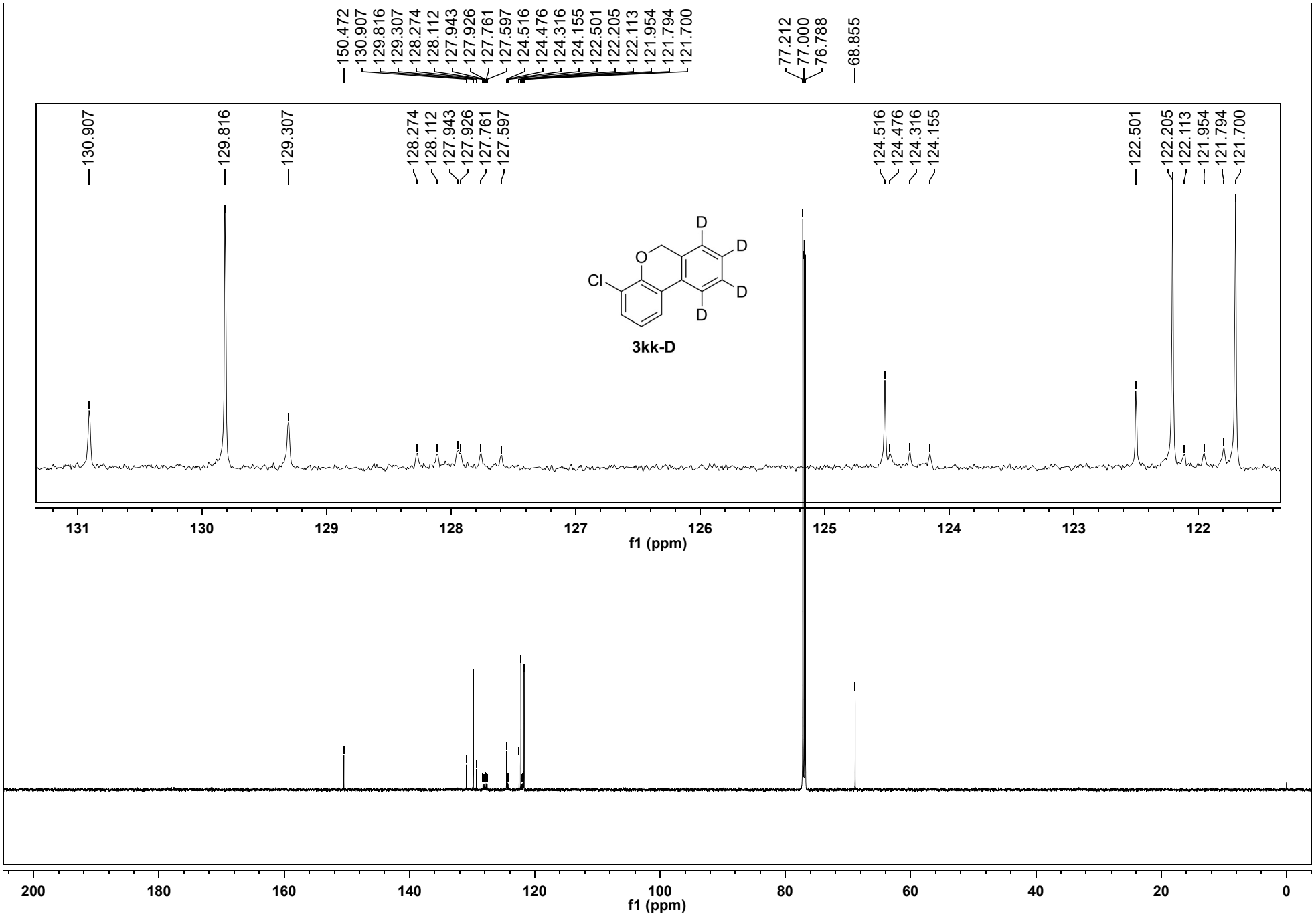

Figure S57. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 5a

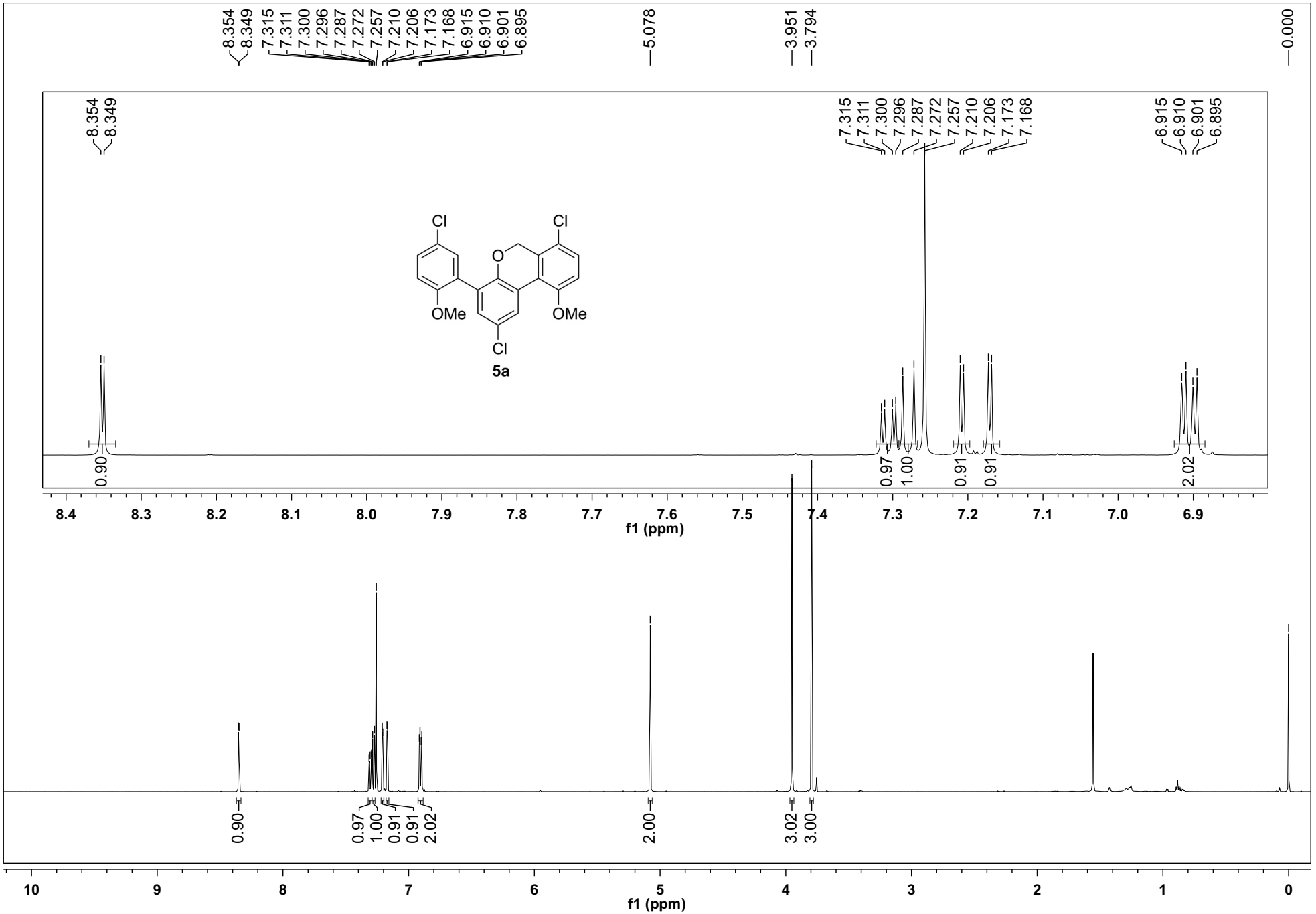

Figure S58. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 5a

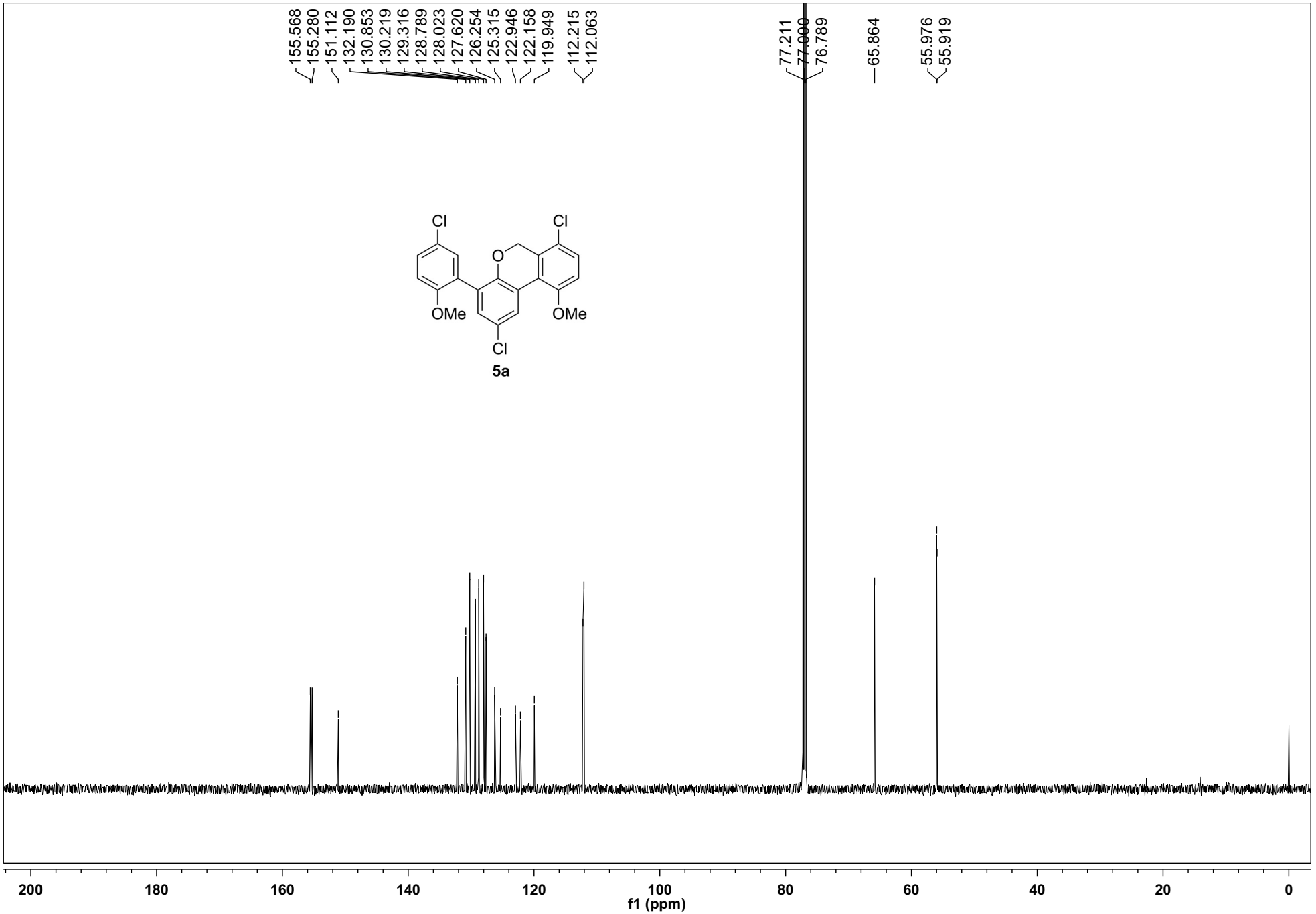

Figure S59. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 5i

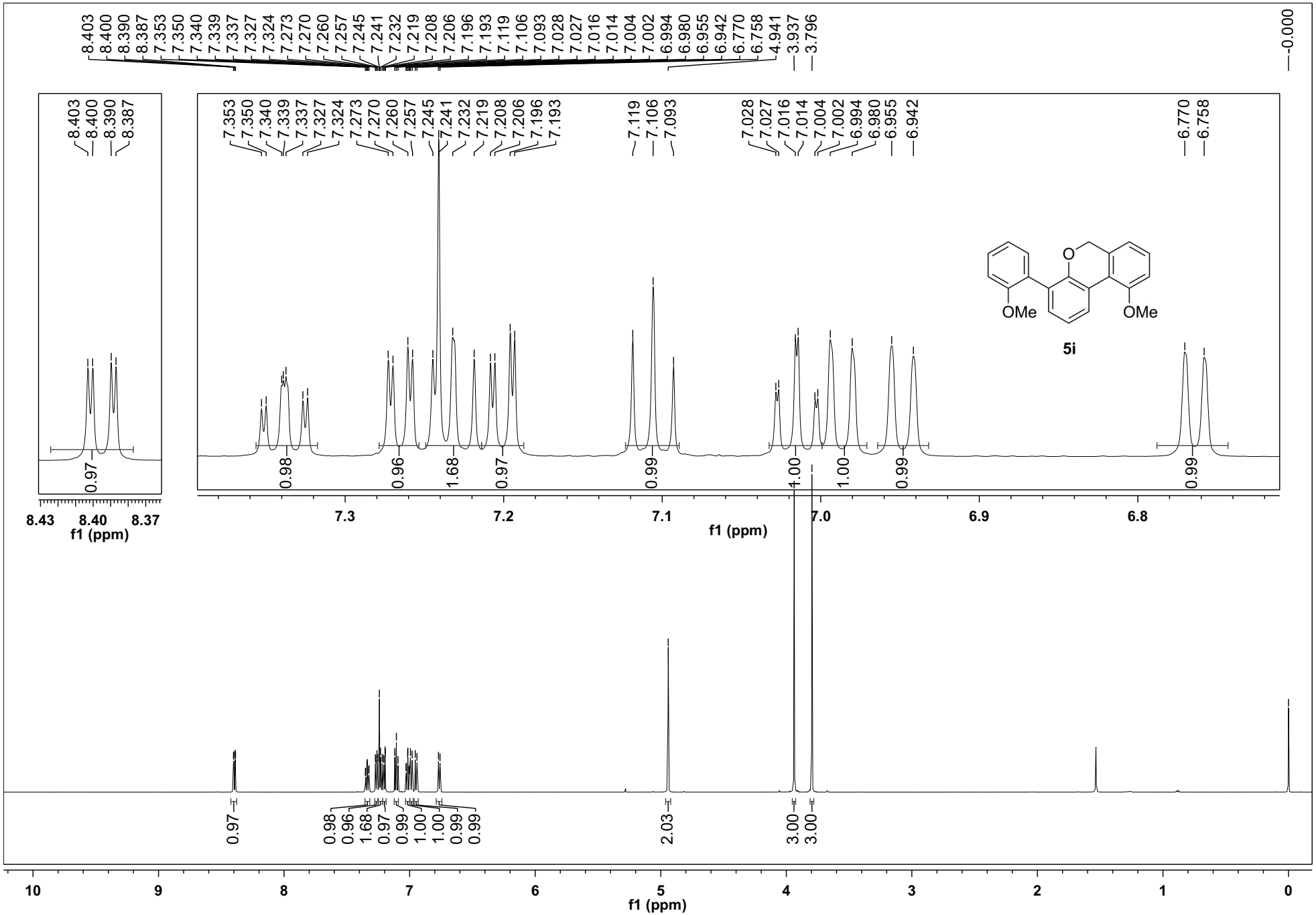

Figure S60. $^{13}C\{1H\}$ NMR spectrum (150 MHz, $CDCl_3$) of 5i