Cu-Catalyzed Decarboxylative Annulation of *N*-Substituted Glycines with 3-Formylchromones: Synthesis of Functionalized Chromeno[2,3-*b*]pyrrol-4(1*H*)-ones

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Supporting Information

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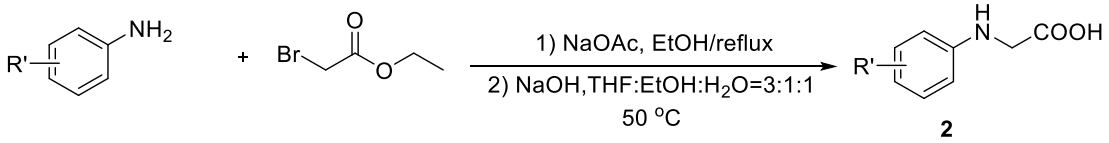
General Information

All compounds were fully characterised by spectroscopic data. The NMR spectra were recorded on a Bruker DRX600 or Bruker DRX500. Chemical shifts (δ) are expressed in ppm, J values are given in Hz, and deuterated $CDCl_3$ or Acetone-d_6/DMSO-d_6 was used as solvent. IR spectra were recorded on a FT-IR Thermo Nicolet Avatar 360 using a KBr pellet. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF_{254}. The melting points were determined on a XT-4A melting point apparatus and are uncorrected. HRMs were performed on an Agilent LC/Msd TOF instrument.

The materials were purchased from Adamas-beta Corporation Limited. All chemicals and solvents were used as received without further purification unless otherwise stated. Two kinds of reagents which were used in the experiment were commercially available reagents.

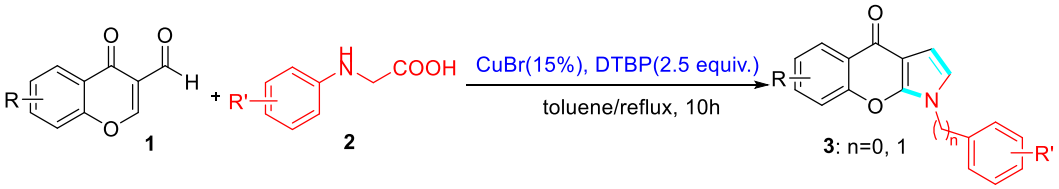
General Procedure for the Preparation of 2[1]



2

A mixture of substituted aniline (10 mmol), ethyl bromoacetate (1.2 equiv., 12 mmol) and anhydrous sodium acetate (2 equiv., 20 mmol) in 30 mL ethanol was refluxed for about 10h until the substituted aniline disappeared. After cooling to room temperature, the precipitated salts were removed by filtration. The solvent was removed b6y rotary evaporation. After obtaining the concentrate, NaOH (3.3 equiv., 33mmol) and the concentrate (1.0 equiv., 10mmol) were dissolved in H_2O (10mL), EtOH (10mL) and THF (30mL). The reaction mixture was stirred for 3h at 50℃. The organic solvent was then removed by rotary evaporation. The residue was extracted with ethyl acetate (3×10 mL). The water layer was acidified with con. HCl until pH = 2-3 and extracted with ethyl acetate (3×20 mL). The combined organic layers were concentrated by rotary evaporation to afford product substituted *N*-phenylglycine (yields: 72-98%).

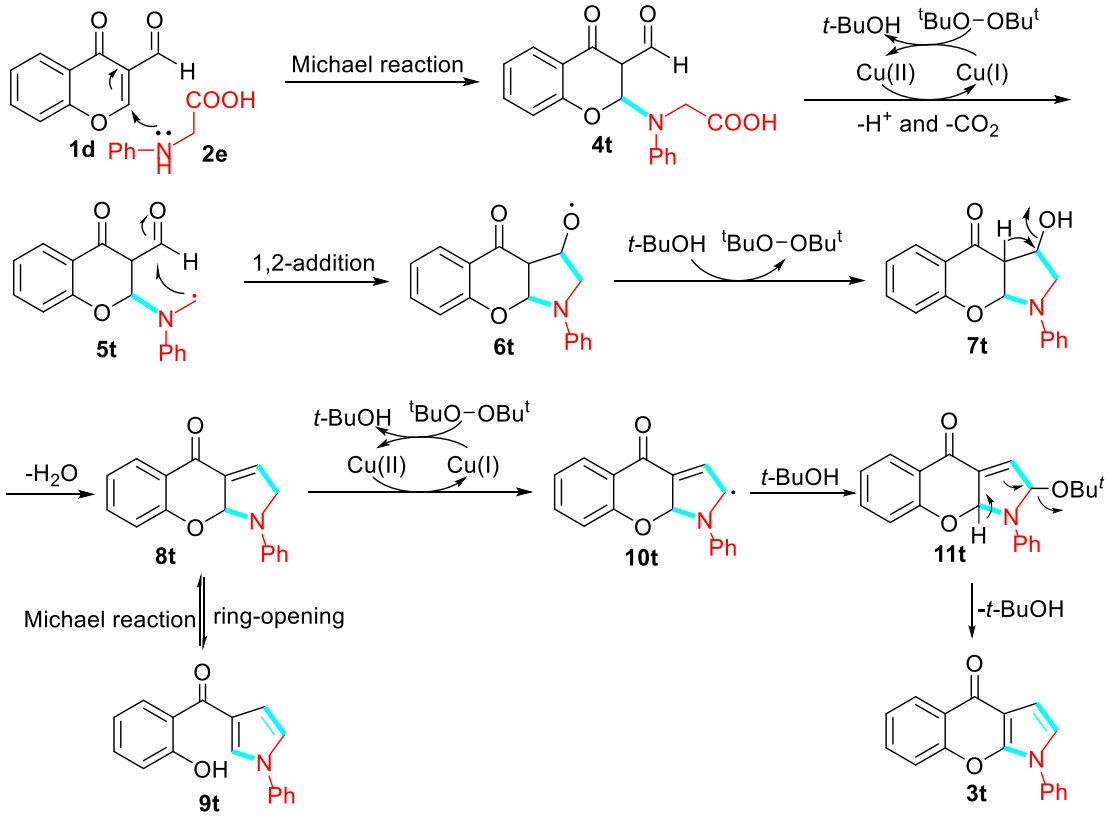
General Procedure for the Preparation of 3



Chromone-3-carboxaldehydes **1** (0.5 mmol) was charged into a round-bottom flask. Then toluene (3 mL), N-phenylglycine **2** (0.8 mmol), CuBr (15%), and DTBP (2.5 equiv.) were added to the mixture. The mixture was stirred at reflux for approximately 8-10 hours. The mixture was cooled to room temperature. Then the reaction mixture was extracted with ethyl acetate (3×15 mL), washed with water and brine, and then dried over $MgSO_4$. The combined organic phases were evaporated under reduced pressure to create the crude product. Finally, the products **3** were obtained in the pure form by column chromatography over silica gel using a mixture of petroleum ether/ethyl acetate (5:1-8:1, v/v) as the eluent.

The proposed mechanism of the cascade reaction

The proposed mechanism is shown in Scheme 2. First, the double bond of the substrate 3-formylchromone **1d** was attacked by the amino group of ***N***-phenyl glycine **2e** via the Michael reaction to produce the intermediate **4t**. Then the intermediate **4t** oxidized by Cu (II) to lose the CO_2 and proton created the intermediate **5t** by the SET mechanism. The intermediate **5t** formed the intermediate **6t** through the 1,2-addition of the radical to the acyl, which formed the intermediate **7t** oxidized by DTBP. Then the intermediate **7t** lost one molecular water to form intermediate **8t**, and it went through a ring-opening reaction to produce the intermediate **9t**. Next, the allyl carbon of intermediate **8t** was oxidized by CuBr and obtained the intermediate **10t**. Finally, the intermediate **10t** formed the intermediate **11t** and lost one molecule of tertiary butyl alcohol to produce the final products **3t**.



Scheme S1. The proposed mechanism of the cascade reaction.

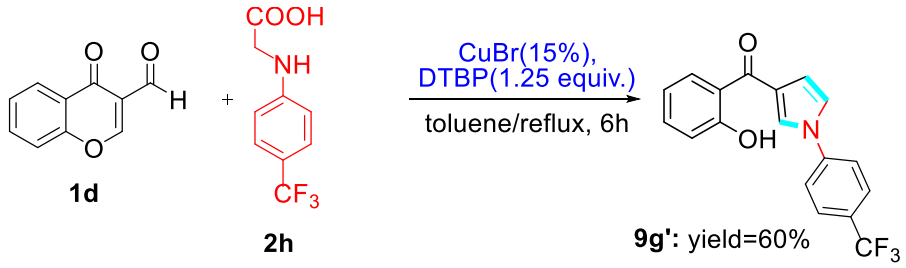
Furthermore, we tried to make the mixture of **1d** (0.1 mmol), **2e** (0.16 mmol), DTBP (0.25 mmol) and CuBr (0.015 mmol) in toluene and carried out refluxing for 1 h. Following this, we immediately injected the reaction mixture into the high-pressure liquid chromatography-high-resolution mass spectrometry (HPLC-HRMS) system. Some intermediate molecular ion peaks appeared (ESI, Figures S100–S107). The molecular ion peaks that appeared in the high-resolution mass spectrum were: HRMS (TOF ES$^+$): *m/z* calcd. for $C_{10}H_7O_3$ [M+H]$^+$, 175.0390; found, 175.0385, which is the HRMS spectrum of **1d** (SI, Figure S101); HRMS (TOF ES$^+$): *m/z* calcd. for $C_8H_{10}NO_2$ [M+H]$^+$, 152.0706; found, 152.0701, which is the HRMS spectra of **2e** (SI, Figure S102); HRMS (TOF ES$^+$): *m/z* calcd. for $C_{18}H_{16}NO_5$ [M+H]$^+$, 326.1023; found, 326.1025, which is the HRMS spectra of intermediate **4t** (SI, Figure S103); HRMS (TOF ES$^+$): *m/z* calcd. for $C_{17}H_{16}NO_3$ [M+H]$^+$, 282.1125; found, 282.1115, which is the HRMS spectra of intermediate **7t** (ESI, Figure S104); HRMS (TOF ES$^+$): *m/z* calcd. for $C_{17}H_{14}NO_2$ [M+H]$^+$, 264.1019; found, 264.1013. There is the HRMS spectra of intermediate **8t/9t** (SI, Figure S105); HRMS (TOF ES$^+$): *m/z* calcd. for $C_{21}H_{21}NNaO_3$ [M+Na]$^+$, 358.1414; found, 358.1409, which is the HRMS spectrum of target compound **11t** (SI, Figure S106). HRMS (TOF ES$^+$): *m/z* calcd. for $C_{17}H_{12}NO_2$

$[M+H]^+$, 262.0863; found, 262.0854, which is the HRMS spectrum of target compound **3t** (SI, Figure S107).

More importantly, the mixture of **1d** (0.1 mmol), **2e** (0.16 mmol), DTBP (0.25 mmol), TEMPO (0.1 mmol), and CuBr (0.015 mmol) in toluene and carried out refluxing for 1 h. Following this, we immediately injected the reaction mixture into the high-pressure liquid chromatography-high-resolution mass spectrometry (HPLC-HRMS) system. Some intermediate molecular ion peaks appeared (ESI, Figures S108–S110). The molecular ion peaks that appeared in the high-resolution mass spectrum were: HRMS (TOF ES^+): *m/z* calcd. for $C_{26}H_{33}N_2O_4$ $[M+H]^+$, 437.2435; found, 437.2429, which is the HRMS spectrum of **5t-TEMPO/6t-TEMPO** (SI, Figure S109); HRMS (TOF ES^+): *m/z* calcd. for $C_{26}H_{32}N_2NaO_4$ $[M+Na]^+$, 459.2254; found, 459.2261, which is the HRMS spectrum of **5t-TEMPO/6t-TEMPO** (SI, Figure S110).

Based on the molecular ion peaks of intermediates **4t–9t** and **11t (**ESI, Figures S100–S110) and the control experiments (ESI, Schemes S2-S3). We believe there exists ample evidence in support of the proposed mechanism.

Control Experiments



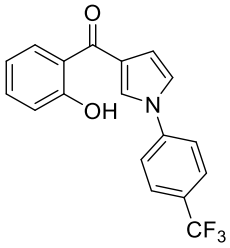
1d **2h** **9g':** yield=60%

Scheme S2. Control experiments

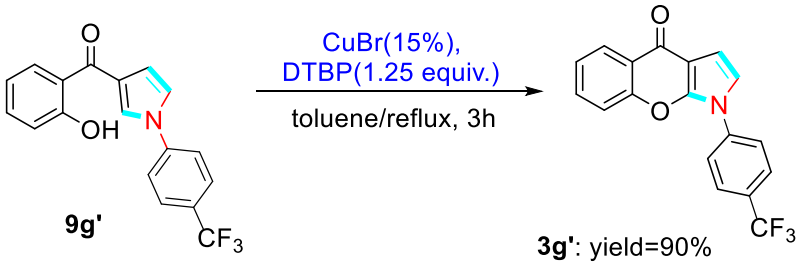
Chromone-3-carboxaldehydes **1d** (0.5 mmol) was charged into a round-bottom flask. Then toluene (3mL), *N*-phenylglycine **2h** (0.8 mmol), CuBr (15%), and DTBP (1.25 equiv.) were added to the mixture. The mixture was stirred at reflux for approximately 6 hours. The mixture was cooled to room temperature. Then the reaction mixture was extracted with ethyl acetate (3×15 mL), washed with water and brine, and then dried over $MgSO_4$. The combined organic phase was evaporated under reduced pressure to create the crude product. Finally, the product **9g'** was obtained in the pure form by

column chromatography over silica gel using a mixture of petroleum ether/ethyl acetate (20:1, v/v) as the eluent.

(2-Hydroxyphenyl)(1-(4-(trifluoromethyl)phenyl)-1*H*-pyrrol-3-yl)methanone (9g')



Yellow solid (99 mg, 60%); Mp: 129.5-130.5 ℃; IR (KBr): 3447, 1613, 1526, 1486, 1322, 1238, 1160, 1117, 1079, 839, 764, 716, 669 cm^{-1}; ^{1}H NMR (600 MHz, Acetone-d_6): δ = 6.92 (s, 1H, ArH), 6.93-7.02 (m, 2H, ArH), 7.54-7.58 (m, 2H, ArH), 7.90 (d, J = 8.5 Hz, 2H, ArH), 7.98 (d, J = 8.5 Hz, 2H, ArH), 8.14-8.16 (m, 2H, ArH), 12.20 (s, 1H, ArOH); ^{13}C NMR (150 MHz, Acetone-d_6): δ = 112.8, 117.7, 117.8, 118.9, 118.9, 120.4, 121.1, 121.3, 124.2 (q, J_1 = 270.0 Hz), 125.6, 127.0-127.1 (q, J_3 = 3.0 Hz), 127.0-127.1 (q, J_3 = 3.0 Hz), 128.0 (t, J_2 = 33.0 Hz), 132.0, 135.3, 142.5, 162.5, 193.6; ^{19}F NMR (564 MHz, Acetone-d_6): δ = -62.9. HRMS (TOF ES$^+$): *m/z* calcd for $C_{18}H_{13}F_3NO_2$ [$(M+H)^+$], 332.0893; found, 332.0889.

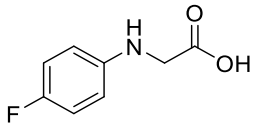


Scheme S3. Control experiments

The compound **9g'** (0.2 mmol) was charged into a round-bottom flask. Then toluene (2mL), CuBr (15%), DTBP (1.25 equiv.) were added to the mixture. The mixture was stirred at reflux for approximately 3 hours. The mixture was cooled to room temperature. Then the reaction mixture was extracted with ethyl acetate (2×10 mL), washed with water and brine, and then dried over $MgSO_4$. The combined organic phase was evaporated under reduced pressure to create the crude product. Finally, the product **3g'** was obtained in the pure form by column chromatography over silica gel using a mixture of petroleum ether/ethyl acetate (8:1, v/v) as the eluent.

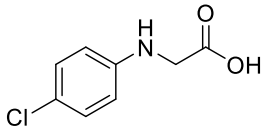
Spectroscopic Data of 2 & 3

(4-Fluorophenyl)glycine (2a)



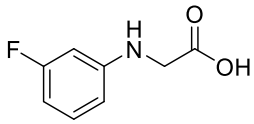
White solid (1.58g, 93%); Mp: 138.3-139.7 ℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 3.78 (s, 2H, CH_2), 6.54-6.56 (m, 2H, ArH), 6.92 (t, J = 8.8 Hz, 2H, ArH); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 45.6, 113.4 (d, J_3 = 6.0 Hz), 113.4 (d, J_3 = 6.0 Hz), 115.6 (d, J_2 = 22.5 Hz), 115.6 (d, J_2 = 22.5 Hz), 145.4, 155.0 (d, J_1 = 229.5 Hz), 173.1; ^{19}F NMR (564 MHz, DMSO-d_6): δ = -129.4. HRMS (TOF ES$^+$): *m/z* calcd for $C_8H_9FNO_2$ [(M+H)$^+$], 170.0612; found, 170.0613.

(4-Chlorophenyl)glycine (2b)



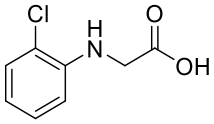
White solid (1.67g, 90%); Mp: 140.5-141.9 ℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 3.79 (s, 2H, ArH), 6.57 (d, J = 8.4 Hz, 2H, ArH), 7.10 (d, J = 8.4 Hz, 2H, ArH); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 45.1, 114.0, 114.0, 119.9, 129.0, 129.0, 147.7, 172.8. HRMS (TOF ES$^+$): *m/z* calcd for $C_8H_9ClNO_2$ [(M+H)$^+$], 186.0316; found, 186.0314.

(3-Fluorophenyl)glycine (2c)



Yellow solid (1.67g, 98%); Mp: 153.2-154.3 ℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 3.82 (s, 2H, CH_2), 6.31-6.35 (m, 2H, ArH), 6.40 (t, J = 8.3 Hz, 1H, ArH), 7.06-7.09 (m, 1H, ArH), 12.6 (s, 1H, COOH); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 45.0, 98.9 (d, J_2 = 24.0 Hz), 102.6 (d, J_2 = 21.0 Hz), 108.9, 130.6 (d, J_3 = 10.5 Hz), 150.8 (d, J_3 = 10.5 Hz), 163.9 (d, J_1 = 237.0 Hz), 172.8; ^{19}F NMR (564 MHz, DMSO-d_6): δ = -113.4. HRMS (TOF ES$^+$): *m/z* calcd for $C_8H_9FNO_2$ [(M+H)$^+$], 170.0612; found, 170.0614.

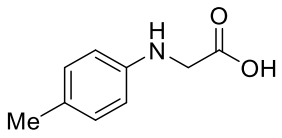
(2-Chlorophenyl)glycine (2d)



White solid (1.54g, 83%); Mp: 170.8-172.0 ℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 3.92 (s, 2H, CH_2), 5.56 (s, 1H, NH), 6.58-6.64 (m, 2H, ArH), 7.13 (t, J = 7.4 Hz,

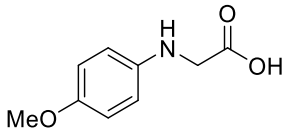
1H, ArH), 7.27 (d, *J* = 7.8 Hz, 1H, ArH); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 44.9, 111.9, 117.5, 118.3, 128.4, 129.4, 144.1, 172.6. HRMS (TOF ES$^+$): *m/z* calcd for $C_8H_9ClNO_2$ [(M+H)$^+$], 186.0316; found, 186.0313.

_p_-Tolylglycine (2f)



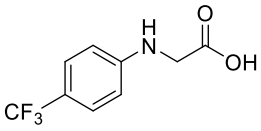
Yellow solid (1.37g, 83%); Mp: 117.5-118.3 ℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 2.15 (s, 3H, CH_3), 3.75 (s, 2H, CH_2), 6.47 (d, *J* = 8.0 Hz, 2H, ArH), 6.90 (d, *J* = 8.0 Hz, 2H, ArH); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 20.5, 45.5, 112.8, 112.8, 125.1, 129.7, 129.7, 146.3, 173.2. HRMS (TOF ES$^+$): *m/z* calcd for $C_9H_{12}NO_2$ [(M+H)$^+$], 166.0863; found, 166.0866.

(4-Methoxyphenyl)glycine (2g)



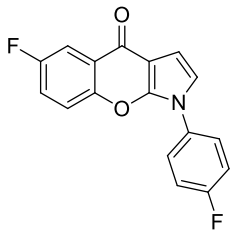
Brown solid (1.54g, 85%); Mp: 225.1-226.0 ℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 3.64 (s, 3H, OCH_3), 3.73 (s, 2H, CH_2), 6.52 (d, *J* = 8.3 Hz, 2H, ArH), 6.72 (d, *J* = 8.3 Hz, 2H, ArH); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 46.1, 55.8, 113.7, 113.7, 115.0, 115.0, 142.9, 152.5, 173.4. HRMS (TOF ES$^+$): *m/z* calcd for $C_9H_{12}NO_3$ [(M+H)$^+$], 182.0812; found, 182.0811.

(4-(Trifluoromethyl)phenyl)glycine (2h)



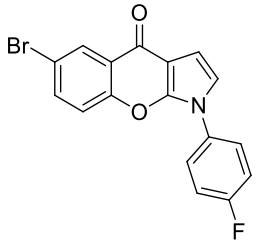
White solid (1.31g, 72%); Mp: 139.9-142.3 ℃; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 3.89 (s, 2H, CH_2), 6.64 (s, 1H, NH), 6.68 (d, *J* = 8.6 Hz, 2H, ArH), 7.39 (d, *J* = 8.6 Hz, 2H, ArH), 12.7 (s, 1H, COOH); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 44.6, 112.1, 112.1, 116.4 (q, J_2 = 31.5 Hz), 125.8 (q, J_1 = 268.5 Hz), 126.6 (q, J_3 = 4.5 Hz), 126.6 (q, J_3 = 4.5 Hz), 151.8, 172.5. HRMS (TOF ES$^+$): *m/z* calcd for $C_9H_9F_3NO_2$ [(M+H)$^+$], 220.0580; found, 220.0586.

6-Fluoro-1-(4-fluorophenyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3a)



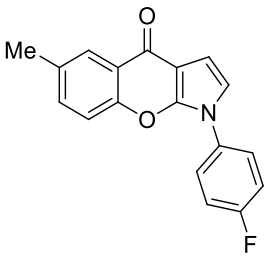
Yellow solid (117mg, 79%); Mp: 117.4-118.2 ℃; IR (KBr): 3450, 3106, 1674, 1621, 1549, 1530, 1512, 1472, 1386, 1253, 1145, 836, 784, 775, 646 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.80 (d, J = 3.1 Hz, 1H, ArH), 6.83 (d, J = 3.4 Hz, 1H, ArH), 7.27 (t, J = 8.3 Hz, 2H, ArH), 7.31-7.34 (m, 1H, ArH), 7.42-7.44 (m, 1H, ArH), 7.55-7.57 (m, 2H, ArH), 7.99-8.00 (m, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 103.5, 107.1, 111.8 (d, J_2 = 24.0 Hz), 116.7 (d, J_2 = 22.5 Hz), 116.7 (d, J_2 = 22.5 Hz), 118.9, 119.1 (d, J_3 = 7.5 Hz), 120.4 (d, J_2 = 25.5 Hz), 124.7 (d, J_3 = 7.5 Hz), 125.9 (d, J_3 = 7.5 Hz), 125.9 (d, J_3 = 7.5 Hz), 132.2, 148.6, 150.1, 159.3 (d, J_1 = 244.5 Hz), 161.9 (d, J_1 = 247.5 Hz), 172.3. HRMS (TOF ES^+): *m/z* calcd for $C_{17}H_{10}F_2NO_2$ [$(M+H)^+$], 298.0674; found, 298.0668.

6-Bromo-1-(4-fluorophenyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3b)



Yellow solid (110mg, 62%); Mp: 173.1-173.9 ℃; IR (KBr): 3503, 3114, 1658, 1607, 1527, 1460, 1397, 1334, 1298, 1230, 1127, 1021, 865, 836, 741, 684 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.85 (s, 2H, ArH), 6.29 (t, J = 8.7 Hz, 2H, ArH), 7.36 (d, J = 8.8 Hz, 1H, ArH), 7.56-7.58 (m, 2H, ArH), 7.72-7.73 (m, 1H, ArH), 8.52 (d, J = 1.4 Hz, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 103.8, 107.6, 116.8 (d, J_2 = 22.5 Hz), 116.8 (d, J_2 = 22.5 Hz), 117.9, 119.0, 119.3, 125.9 (d, J_3 = 7.5 Hz), 125.9 (d, J_3 = 7.5 Hz), 126.0, 129.5, 132.1, 135.5, 148.3, 152.8, 162.0 (d, J_1 = 247.5 Hz), 172.0, ^{19}F NMR (564 MHz, $CDCl_3$): δ = -112.7. HRMS (TOF ES^+): *m/z* calcd for $C_{17}H_{10}BrFNO_2$ [$(M+H)^+$], 357.9873; found, 357.9870.

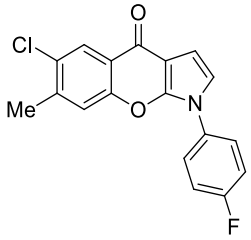
1-(4-Fluorophenyl)-6-methylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3c)



Yellow solid (92mg, 63%); Mp: 131.7-132.4 ℃; IR (KBr): 3428, 3112, 2376,

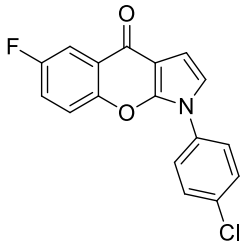
1657, 1618, 1525, 1478, 1406, 1336, 1297, 1230, 1153, 1012, 944, 830, 740, 687 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.47 (s, 3H, CH_3), 6.83 (d, J = 3.4 Hz, 1H, ArH), 6.86 (d, J = 3.5 Hz, 1H, ArH), 7.26-7.29 (m, 2H, ArH), 7.35 (d, J = 8.5 Hz, 1H, ArH), 7.44-7.46 (m, 1H, ArH), 7.56-7.59 (m, 1H, ArH), 8.20 (s, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.8, 103.8, 107.6, 116.6 (d, J_2 = 22.5 Hz), 116.6 (d, J_2 = 22.5 Hz), 117.1, 118.4, 125.8, 125.8 (d, J_3 = 9.0 Hz), 125.8 (d, J_3 = 9.0 Hz), 126.3, 132.4, 133.8, 134.4, 148.6, 152.3, 161.8 (d, J_1 = 247.5 Hz), 173.6; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -113.3. HRMS (TOF ES^+): *m/z* calcd for $C_{18}H_{13}FNO_2$ [$(M+H)^+$], 294.0925; found, 294.0925.

6-Chloro-1-(4-fluorophenyl)-7-methylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3d)



Yellow solid (96mg, 59%); Mp: 128.2-128.9 ℃; IR (KBr): 3432, 3119, 1658, 1619, 1521, 1385, 1385, 1298, 1230, 1154, 907, 840, 739, 666, 622 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.46 (s, 3H, CH_3), 6.78-6.80 (m, 2H, ArH), 7.25-7.28 (m, 2H, ArH), 7.31 (s, 1H, ArH), 7.54-7.56 (m, 2H, ArH), 8.27 (s, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.5, 103.7, 107.3, 116.7 (d, J_2 = 22.5 Hz), 116.7 (d, J_2 = 22.5 Hz), 118.7, 119.2, 122.4, 125.8 (d, J_3 = 7.5 Hz), 125.8 (d, J_3 = 7.5 Hz), 126.4, 131.0, 132.2, 141.6, 148.3, 152.2, 161.9 (d, J_1 = 247.5 Hz), 172.2. HRMS (TOF ES^+): *m/z* calcd for $C_{18}H_{12}ClFNO_2$ [$(M+H)^+$], 328.0535; found, 328.0528.

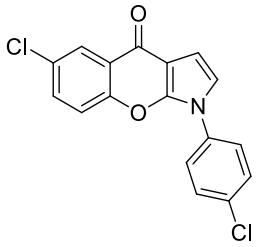
1-(4-Chlorophenyl)-6-fluorochromeno[2,3-*b*]pyrrol-4(1*H*)-one(3e)



Yellow solid (131mg, 83%); Mp: 140.5-141.7 ℃; IR (KBr): 3464, 3106, 2778, 1671, 1531, 1473, 1330, 1268, 1188, 1139, 1094, 1012, 952, 867, 774, 689 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.86 (d, J = 3.7 Hz, 1H, ArH), 6.87 (d, J = 3.6 Hz, 1H, ArH), 7.35-7.38 (m, 1H, ArH), 7.45-7.48 (m, 1H, ArH), 7.54-7.7.57 (m, 4H, ArH), 8.03-8.05 (m, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 103.9, 107.3, 111.9 (d, J = 24.0 Hz), 118.6, 119.1 (d, J = 9.0 Hz), 120.5 (d, J = 25.5 Hz), 124.7 (d, J = 6.0 Hz), 125.1, 125.1, 130.0, 130.0, 133.8, 134.6, 148.5, 150.1, 159.3 (d, J = 244.5 Hz), 172.4; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -116.4. HRMS

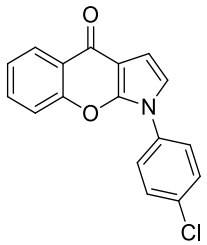
(TOF ES^+): *m/z* calcd for $C_{17}H_{10}ClFNO_2$ [$(M+H)^+$], 314.0379; found, 314.0373.

6-Chloro-1-(4-chlorophenyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3f)



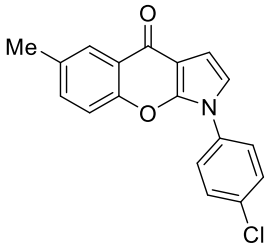
Yellow solid (127mg, 77%); Mp: 145.7-146.6 ℃; IR (KBr): 3399, 3113, 1659, 1605, 1527, 1463, 1399, 1331, 1280, 1181, 1098, 1013, 829, 723, 683 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 6.84-6.87 (m, 2H, ArH), 7,42 (d, *J* = 8.8 Hz, 1H, ArH), 7.54-7.60 (m, 5H, ArH), 8.35 (s, 1H, Ar H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 104.0, 107.7, 118.7, 119.0, 124.5, 125.1, 125.1, 126.3, 130.0, 130.0, 130.6, 132.8, 133.9, 134.6, 148.3, 152.3, 172.1. HRMS (TOF ES^+): *m/z* calcd for $C_{17}H_{10}Cl_2NO_2$ [$(M+H)^+$], 330.0083; found, 330.0084.

1-(4-Chlorophenyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3g)



Yellow solid (106mg, 72%); Mp: 158.2-159.2 ℃; IR (KBr): 3411, 3128, 1667, 1612, 1542, 1524, 1508, 1493, 1459, 1257, 1234, 1175, 1093, 1009, 964, 828, 739, 690 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 6.85 (d, *J* = 3.7 Hz, 1H, ArH), 6.87 (d, *J* = 3.6 Hz, 1H, ArH), 7.44 (d, *J* = 7.4 Hz,1H, ArH), 7.47 (d, *J* = 8.4 Hz,1H, ArH), 7.56 (s, 4H, ArH), 7.65 (s, 1H, ArH), 8.41 (d, *J* = 7.8 Hz, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 104.1, 107.8, 117.4, 118.2, 123.3, 124.7, 125.0, 125.0, 126.8, 129.9, 129.9, 132.7, 133.6, 134.8, 148.3, 154.1, 173.4. HRMS (TOF ES^+): *m/z* calcd for $C_{17}H_{11}ClNO_2$ [$(M+H)^+$], 296.0473; found, 296.0468.

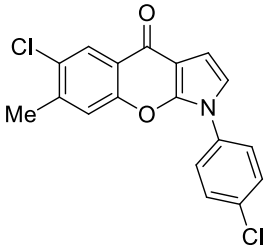
1-(4-Chlorophenyl)-6-methylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3h)



Yellow solid (108mg, 70%); Mp: 130.7-131.2 ℃; IR (KBr): 3477, 3109, 1658, 1619, 1525, 1333, 1293, 1205, 1097, 1016, 946, 830, 807, 739, 689 cm^{-1}; ^1H

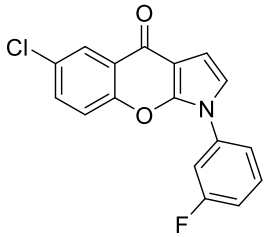
NMR (600 MHz, $CDCl_3$): δ = 2.49 (s, 3H, CH_3), 6.84 (d, J = 3.5 Hz, 1H, ArH), 6.86 (d, J = 3.4 Hz, 1H, ArH), 7.36 (d, J = 8.5 Hz, 1H, ArH), 7.46 (d, J = 8.5 Hz, 1H, ArH), 7.55 (s, 4H, ArH), 8.19 (s, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.8, 104.0, 107.8, 117.1, 118.1, 123.0, 124.9, 124.9, 126.3, 130.0, 130.0, 133.5, 133.8, 134.5, 134.8, 148.5, 152.3, 173.6. HRMS (TOF ES$^+$): *m/z* calcd for $C_{18}H_{13}ClNO_2$ [$(M+H)^+$], 310.0629; found, 310.0623.

6-Chloro-1-(4-chlorophenyl)-7-methylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3i)



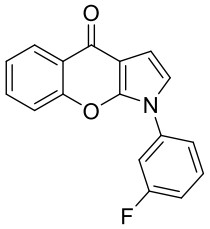
Yellow solid (127mg, 74%); Mp: 241.9-242.4 ℃; IR (KBr): 3422, 1659, 1615, 1527, 1342, 1156, 848, 621, 573 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.51 (s, 3H, CH_3), 6.86 (s, 2H, ArH), 7.37 (s, 1H, ArH), 7.54-7.57 (m, 4H, ArH), 8.35 (s, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.6, 104.1, 107.6, 118.4, 119.3, 122.5, 125.1, 125.1, 126.6, 130.0, 130.0, 131.2, 133.8, 134.7, 141.8, 148.3, 152.3, 172.3. HRMS (TOF ES$^+$): *m/z* calcd for $C_{18}H_{12}Cl_2NO_2$ [$(M+H)^+$], 344.0240; found, 344.0236.

6-Chloro-1-(3-fluorophenyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3j)



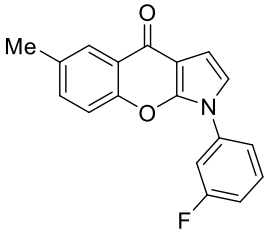
Yellow solid (96mg, 61%); Mp: 155.4-156.4 ℃; IR (KBr): 3442, 3117, 1659, 1610, 1527, 1461, 1400, 1327, 1283, 1204, 1126, 854, 814, 779, 683 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.86 (d, J = 3.6 Hz, 1H, ArH), 6.89 (d, J = 3.6 Hz, 1H, ArH), 7.16-7.19 (m, 1H, ArH), 7.35-7.40 (m, 2H, ArH), 7.46 (d, J = 8.9 Hz, 1H, ArH), 7.53-7.61 (m, 2H, ArH), 8.36 (d, J = 2.3 Hz, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 104.2, 107.8, 111.3 (d, J_2 = 25.0 Hz), 115.0 (d, J_2 = 21.3 Hz), 118.6, 119.1, 119.3 (d, J_4 = 3.8 Hz), 124.5, 126.3, 130.6, 131.1 (d, J_3 = 8.8 Hz), 132.8, 137.4 (d, J_3 = 10.0 Hz), 148.3, 152.3, 163.1 (d, J_1 = 246.3 Hz), 172.1; ^{19}F NMR (470 MHz, $CDCl_3$): δ = -109.8. HRMS (TOF ES$^+$): *m/z* calcd for $C_{17}H_{10}FClNO_2$ [$(M+H)^+$], 314.0379; found, 314.0372.

1-(3-Fluorophenyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3k)



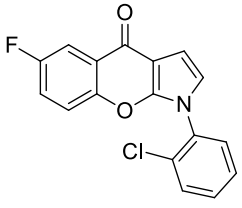
Yellow solid (84mg, 60%); Mp: 108.9-109.6 ℃; IR (KBr): 3443, 3120, 1661, 1608, 1526, 1461, 1328, 1286, 1205, 1125, 854, 814, 777, 714, 682 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.88 (t, J = 3.4 Hz, 1H, ArH), 6.90 (d, J = 3.5 Hz, 1H, ArH), 7.18 (t, J = 8.1 Hz, 1H, ArH), 7.38-7.50 (m, 3H, ArH), 7.53 (t, J = 7.9 Hz, 1H, ArH), 7.57 (d, J = 7.9 Hz, 1H, ArH), 7.67 (t, J = 7.3 Hz, 1H, ArH), 8.42 (d, J = 7.9 Hz, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 104.2, 107.9, 111.2 (d, J_2 = 25.5 Hz), 114.7 (d, J_2 = 21.0 Hz), 117.4, 118.1, 119.1 (d, J_4 = 3.0 Hz), 123.4, 124.7, 126.8, 131.1 (d, J_3 = 9.0 Hz), 132.8, 137.6 (d, J_3 = 10.5 Hz), 148.3, 154.1, 163.1 (d, J_1 = 246.0 Hz), 173.4; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -110.0. HRMS (TOF ES^+): *m/z* calcd for $C_{17}H_{11}FNO_2$ [$(M+H)^+$], 280.0768; found, 280.0766.

1-(3-Fluorophenyl)-6-methylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3l)



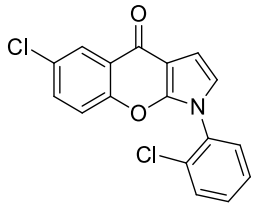
Yellow solid (92mg, 63%); Mp: 119.7-120.5 ℃; IR (KBr): 3455, 3112, 1659, 1611, 1525, 1400, 1339, 1273, 1201, 1125, 1001, 889, 854, 767, 686, 644 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.49 (s, 3H, CH_3), 6.87 (d, J = 3.5 Hz, 1H, ArH), 6.88 (d, J = 3.5 Hz, 1H, ArH), 7.15-7.18 (m, 1H, ArH), 7.38-7.42 (m, 3H, ArH), 7.47 (d, J = 8.3 Hz, 1H, ArH), 7.53-7.56 (m, 1H, ArH), 8.19 (s, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.8, 104.2, 107.9, 111.1 (d, J_2 = 25.5 Hz), 114.6 (d, J_2 = 21.0 Hz), 117.2, 117.9, 119.0 (d, J_4 = 3.0 Hz), 123.0, 126.3, 131.0 (d, J_3 = 9.0 Hz), 133.9, 134.5, 137.7 (d, J_3 = 9.0 Hz), 148.4, 152.3, 163.1 (d, J_1 = 246.0 Hz), 173.6; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -110.0. HRMS (TOF ES^+): *m/z* calcd for $C_{18}H_{13}FNO_2$ [$(M+H)^+$], 294.0925; found, 294.0920.

1-(2-Chlorophenyl)-6-fluorochromeno[2,3-*b*]pyrrol-4(1*H*)-one (3m)



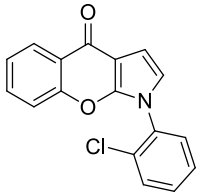
Yellow solid (100mg, 64%); Mp: 88.2-89.4 ℃; IR (KBr): 3447, 3106, 1666, 1519, 1477, 1282, 1189, 1139, 824, 772, 720, 685 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 6.73 (d, *J* = 3.7 Hz, 1H, ArH), 6.86 (d, *J* = 3.7 Hz, 1H, ArH), 7.30-7.34 (m, 1H, ArH), 7.37-7.40 (m, 1H, ArH), 7.48-7.53 (m, 3H, ArH), 7.63-7.65 (m, 1H, ArH), 8.04-8.06 (m, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 103.4, 106.6, 111.9 (d, *J* = 24.0 Hz), 119.1 (d, *J* = 7.5 Hz), 120.0, 120.3 (d, *J* = 25.5 Hz), 124.9, 127.9, 129.2, 130.6, 130.9, 132.0, 133.5, 149.5, 150.2, 159.3 (d, *J* = 243.0 Hz), 172.5; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -116.8. HRMS (TOF ES^+): *m/z* calcd for $C_{17}H_{10}FClNO_2$ [$(M+H)^+$], 314.0379; found, 314.0375.

6-Chloro-1-(2-chlorophenyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3n)



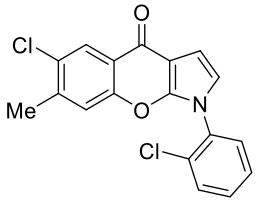
Yellow solid (103mg, 63%); Mp: 127.4-128.6 ℃; IR (KBr): 3445, 3116, 1663, 1514, 1455, 1290, 1172, 1134, 827, 775, 712, 689 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 6.75 (d, *J* = 2.9 Hz, 1H, ArH), 6.88 (d, *J* = 2.9 Hz, 1H, ArH), 7.37 (t, *J* = 8.8 Hz, 1H, ArH), 7.49-7.57 (m, 4H, ArH), 7.64 (t, *J* = 7.8 Hz, 1H, ArH), 8.55 (s, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 103.5, 106.9, 119.0, 120.0, 126.3, 127.9, 129.1, 129.1, 130.4, 130.6, 130.9, 132.0, 132.6, 133.4, 149.3, 152.5, 172.2. HRMS (TOF ES^+): *m/z* calcd for $C_{17}H_{10}Cl_2NO_2$ [$(M+H)^+$], 330.0083; found, 330.0081.

1-(2-Chlorophenyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3o)



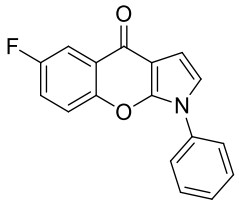
Yellow solid (88mg, 60%); Mp: 147.6-148.6 ℃; IR (KBr): 3449, 3102, 1668, 1516, 1434, 1284, 1169, 1103, 848, 766, 703, 684 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 6.74 (s, 1H, ArH), 6.89 (s, 1H, ArH), 7.30-7.49 (m, 2H, ArH), 7.50-7.61 (m, 3H, ArH), 7.62-7.66 (m, 2H, ArH), 8.43 (d, *J* = 7.8 Hz, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 103.5, 107.0, 117.4, 119.6, 123.5, 124.5, 126.8, 127.9, 129.2, 130.5, 130.8, 132.0, 132.5, 133.6, 149.4, 154.2, 173.5. HRMS (TOF ES^+): *m/z* calcd for $C_{17}H_{11}ClNO_2$ [$(M+H)^+$], 296.0473; found, 296.0472.

6-Chloro-1-(2-chlorophenyl)-7-methylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3p)



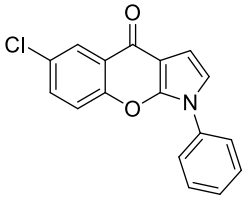
Yellow solid (122mg, 71%); Mp: 121.3-122.8 ℃; IR (KBr): 3401, 3101, 2382, 1660, 1618, 1518, 1382, 1238, 1145, 901, 747, 633 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 3.47 (s, 3H, CH_3), 6.73 (s, 1H, ArH), 6.87 (s, 1H, ArH), 7.29 (d, J = 8.5 Hz, 1H, ArH), 7.48-7.53 (m, 3H, ArH), 7.64 (d, J = 7.4 Hz, 1H, ArH), 8.35 (s, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.5, 103.5, 106.8, 119.3, 119.8, 126.5, 127.9, 129.2, 130.6, 130.8, 130.8, 131.0, 132.0, 133.5, 141.5, 149.2, 152.4, 172.4. HRMS (TOF ES^+): *m/z* calcd for $C_{18}H_{12}Cl_2NO_2$ [$(M+H)^+$], 344.0240; found, 344.0235.

6-Fluoro-1-phenylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3q)



Yellow solid (123mg, 88%); Mp: 173.7-174.8 ℃; IR (KBr): 3422, 2360, 1658, 1508, 1453, 1265, 1130, 870, 801, 763, 694 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$ + Acetone-d_6): δ = 6.73 (d, J = 3.5 Hz, 1H, ArH), 7.13 (d, J = 3.5 Hz, 1H, ArH), 7.49-7.52 (m, 2H, ArH), 7.61-7.65 (m, 3H, ArH), 7.74 (d, J = 7.9 Hz, 2H, ArH), 7.89-7.92 (m, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$ + Acetone-d_6): δ = 102.8, 107.0, 110.9 (d, J_2 = 24.0 Hz), 119.0, 119.2, 119.9 (d, J_3 = 7.5 Hz), 120.4 (d, J_2 = 25.5 Hz), 123.8, 124.7 (d, J_3 = 6.0 Hz), 127.9, 129.7, 130.0, 136.2, 148.5, 150.3, 159.2 (d, J_1 = 241,5 Hz), 171.5. HRMS (TOF ES^+): *m/z* calcd for $C_{17}H_{11}FNO_2$ [$(M+H)^+$], 280.0768; found, 280.0770.

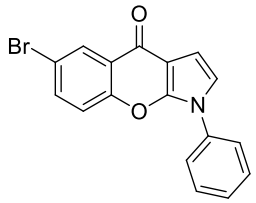
6-Chloro-1-phenylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3r)



Yellow solid (117mg, 79%); Mp: 209.3-210.4 ℃; IR (KBr): 3115, 3069, 1663, 1605, 1532, 1460, 1400, 1271, 1180, 1128, 817, 738, 688, 646 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 6.85 (d, J = 2.7 Hz, 1H, ArH), 6.90 (d, J = 2.8 Hz, 1H, ArH), 7.42 (d, J = 8.8 Hz, 1H, ArH), 7.48 (t, J = 4.1 Hz, 1H, ArH), 7.56-7.59 (m, 5H, ArH), 8.36 (s, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 103.7, 107.6,

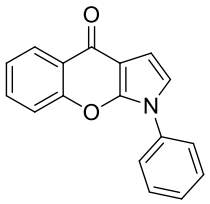
119.0, 119.1, 123.9, 123.9, 123.9, 126.3, 128.0, 129.8, 129.8, 130.4, 132.6, 136.1, 148.4, 152.4, 172.1. HRMS (TOF ES^+): *m/z* calcd for $C_{17}H_{11}ClNO_2$ $[(M+H)^+]$, 296.0473; found, 296.0471.

6-Bromo-1-phenylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3s)



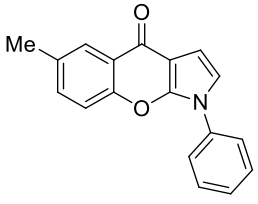
Yellow solid (137mg, 81%); Mp: 215.5-216.8 ℃; IR (KBr): 3447, 3118, 2665, 1663, 1602, 1529, 1460, 1399, 1277, 1124, 1064, 860, 743, 690 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 6.84 (s, 1H, ArH), 6.89 (s, 1H, ArH), 7.36 (d, *J* = 8.6 Hz, 1H, ArH), 7.48 (s, 1H, ArH), 7.59 (s, 4H, ArH), 7.70 (s, 1H, ArH), 8.50 (s, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 103.7, 107.6, 117.8, 119.0, 119.3, 123.9, 123.9, 124.8, 128.0, 129.4, 129.8, 129.8, 135.4, 136.1, 148.3, 152.8, 172.0. HRMS (TOF ES^+): *m/z* calcd for $C_{17}H_{11}BrNO_2$ $[(M+H)^+]$, 339.9968; found, 339.9963.

1-Phenylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3t)



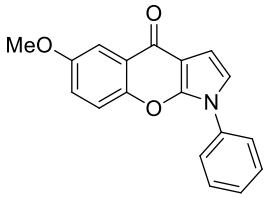
Yellow solid (106mg, 81%); Mp: 117.1-118.2 ℃; IR (KBr): 3447, 3102, 1668, 1613, 1541, 1505, 1459, 1312, 1295, 1122, 1098, 1029, 904, 749, 686, 644 cm^{-1}; ^1H NMR (600 MHz, Acetone-d_6): δ = 6.74 (d, *J* = 3.7 Hz, 1H, ArH), 7.17 (d, *J* = 3.7 Hz, 1H, ArH), 7.48-7.53 (m, 2H, ArH), 7.59 (d, *J* = 8.3 Hz, 1H, ArH), 7.65 (t, *J* = 8.0 Hz, 2H, ArH), 7.75 (t, *J* = 8.3 Hz, 1H, ArH), 7.79 (d, *J* = 7.9 Hz, 2H, ArH), 8.30 (d, *J* = 7.9 Hz, 1H, ArH); ^{13}C NMR (150 MHz, Acetone-d_6): δ = 102.9, 107.4, 117.7, 118.9, 123.4, 123.9, 123.9, 124.5, 126.1, 127.8, 129.7, 129.7, 132.8, 136.4, 148.2, 154.2, 172.2. HRMS (TOF ES^+): *m/z* calcd for $C_{17}H_{12}NO_2$ $[(M+H)^+]$, 262.0863; found, 262.0860.

6-Methyl-1-phenylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3u)



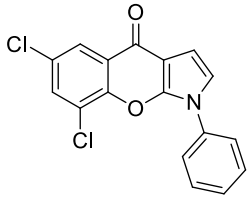
Yellow solid (89mg, 65%); Mp: 134.0-135.4 ℃; IR (KBr): 3393, 3111, 1664, 1606, 1531, 1204, 804, 747, 695, 645 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 6.88 (d, J = 4.2 Hz, 2H, ArH), 7.37 (d, J = 8.3 Hz, 1H, ArH), 7.44 (s, 1H, ArH), 7.46 (d, J = 8.3 Hz, 1H, ArH), 7.56-7.61 (m, 4H, ArH), 8.20 (s, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.8, 103.7, 107.7, 117.1, 118.4, 123.0, 123.7, 123.7, 126.3, 127.7, 129.7, 129.7, 133.7, 134.3, 136.4, 148.6, 152.4, 173.7. HRMS (TOF ES^+): *m/z* calcd for $C_{18}H_{14}NO_2$ [$(M+H)^+$], 276.1019; found, 276.1016.

6-Methoxy-1-phenylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3v)



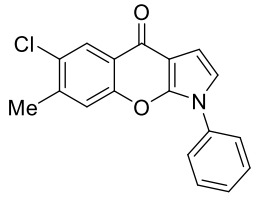
Yellow solid (80mg, 55%); Mp: 112.6-113.3 ℃; IR (KBr): 3438, 3072, 1663, 1608, 1513, 1505, 1433, 1337, 1208, 1145, 1100, 1019, 976, 826, 735 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 3.84 (s, 3H, CH_3), 6.77 (d, J = 3.4 Hz, 1H, ArH), 6.79 (d, J = 3.4 Hz, 1H, ArH), 7.12-7.14 (m, 1H, ArH), 7.30 (d, J = 9.1 Hz, 1H, ArH), 7.36 (t, J = 7.1 Hz, 1H, ArH), 7.46-7.51 (m, 4H, ArH), 7.71 (d, J = 2.8 Hz, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 54.9, 102.5, 105.7, 106.4, 117.5, 117.6, 121.0, 122.7, 122.7, 122.7, 126.7, 128.7, 128.7, 135.3, 147.6, 147.7, 155.5, 172.4. HRMS (TOF ES^+): *m/z* calcd for $C_{18}H_{14}NO_3$ [$(M+H)^+$], 292.0968; found, 292.0968.

6,8-Dichloro-1-phenylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3w)



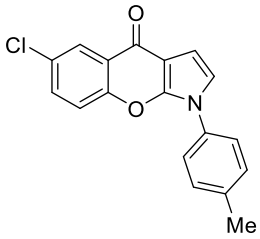
Yellow solid (127mg, 77%); Mp: 217.4-218.5 ℃; IR (KBr): 3399, 3124, 2343, 1664, 1597, 1533, 1455, 1416, 1310, 1215, 1180, 1109, 947, 871, 748, 689, 607 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$ + DMSO-d_6): δ = 6.71 (d, J = 2.8 Hz, 1H, ArH), 6.89 (d, J = 2.5 Hz, 1H, ArH), 7.35 (t, J = 7.1 Hz, 1H, ArH), 7.47 (t, J = 7.5 Hz, 2H, ArH), 7.57 (t, J = 8.0 Hz, 3H, ArH), 8.12 (s, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$ + DMSO-d_6): δ = 103.6, 107.4, 119.1, 123.0, 123.4, 123.4, 124.8, 125.4, 127.9, 129.7, 129.7, 129.9, 132.6, 135.8, 147.7, 148.3, 171.1. HRMS (TOF ES^+): *m/z* calcd for $C_{17}H_{10}Cl_2NO_2$ [$(M+H)^+$], 330.0083; found, 330.0081.

(6-Chloro-7-methyl-1-phenylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3x)



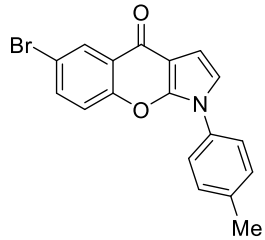
Yellow solid (124mg, 80%); Mp: 191.7-192.4 ℃; IR (KBr): 3433, 3129, 1656, 1621, 1520, 1454, 1385, 1269, 1152, 902, 744, 685 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.48 (s, 3H, CH_3), 6.84 (d, J = 3.7 Hz, 1H, ArH), 6.87 (d, J = 3.7 Hz, 1H, ArH), 7.36 (s, 1H, ArH), 7.45-7.48 (m, 1H, ArH), 7.57-7.59 (m, 4H, ArH), 8.33 (s, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.6, 103.6, 107.5, 118.7, 119.3, 122.5, 123.8, 123.8, 126.4, 127.9, 129.7, 129.7, 131.0, 136.2, 141.6, 148.3, 152.2, 172.3. HRMS (TOF ES^+): *m/z* calcd for $C_{18}H_{13}ClNO_2$ [$(M+H)^+$], 310.0629; found, 310.0625.

6-Chloro-1-(*p*-tolyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3y)



Yellow solid (126 mg, 82%); Mp: 124.1-125.4 ℃; IR (KBr): 3437, 3077, 1657, 1604, 1522, 1456, 1398, 1313, 1268, 1172, 1124, 972, 829, 720, 683, 650 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 2.46 (s, 3H, CH_3), 6.80 (d, J = 3.7 Hz, 1H, ArH), 6.84 (d, J = 3.7 Hz, 1H, ArH), 7.36 (d, J = 8.2 Hz, 2H, ArH), 7.37 (d, J = 8.9 Hz, 1H, ArH), 7.44 (d, J = 8.3 Hz, 2H, ArH), 7.53-7.55 (m, 1H, ArH), 8.33 (d, J = 2.6 Hz, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.1, 103.4, 107.5, 119.0, 119.1, 123.8, 123.8, 123.8, 124.5, 126.2, 130.3, 130.3, 132.6, 133.5, 138.1, 148.4, 152.4, 172.1. HRMS (TOF ES^+): *m/z* calcd for $C_{18}H_{13}ClNO_2$ [$(M+H)^+$], 310.0629; found, 310.0625.

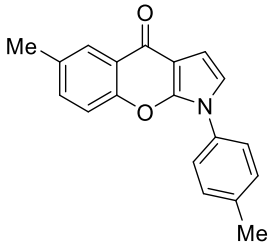
6-Bromo-1-(*p*-tolyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3z)



Yellow solid (141mg, 80%); Mp: 122.6-123.4 ℃; IR (KBr): 3473, 3081, 1659, 1601, 1522, 1454, 1393, 1268, 1169, 1124, 1065, 972, 829, 720, 681 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 2.48 (s, 3H, CH_3), 6.84 (d, J = 3.6 Hz, 1H, ArH), 6.87 (d, J = 3.6 Hz, 1H, ArH), 7.35-7.39 (m, 3H, ArH), 7.46 (d, J = 8.2 Hz, 2H,

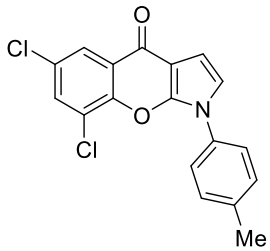
ArH), 7.70-7.72 (m, 1H, ArH), 8.53 (d, *J* = 2.2 Hz, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.1, 103.5, 107.5, 117.8, 119.1, 119.3, 123.8, 123.8, 124.9, 129.4, 130.3, 130.3, 133.5, 135.4, 138.2, 148.4, 152.9, 172.0. HRMS (TOF ES$^+$): *m/z* calcd for $C_{18}H_{13}BrNO_2$ [(M+H)$^+$], 354.0124; found, 354.0119.

6-Methyl-1-(*p*-tolyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3a')



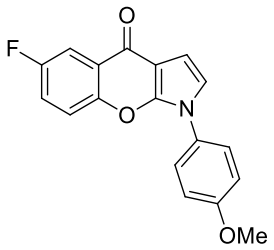
Yellow solid (88mg, 61%); Mp: 79.4-80.6 ℃; IR (KBr): 3444, 1665, 1618, 1520, 1475, 1285, 1203, 1120, 943, 809, 736, 685 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.37 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 6.75 (s, 2H, ArH), 7.25-7.38 (m, 6H, ArH), 8.10 (s, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.8, 21.1, 103.4, 107.6, 117.1, 118.5, 123.0, 123.7, 123.7, 126.3, 130.2, 130.2, 133.6, 133.8, 134.2, 137.8, 148.6, 152.4, 173.7. HRMS (TOF ES$^+$): *m/z* calcd for $C_{19}H_{16}NO_2$ [(M+H)$^+$], 290.1176; found, 290.1172.

6,8-Dichloro-1-(*p*-tolyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3b')



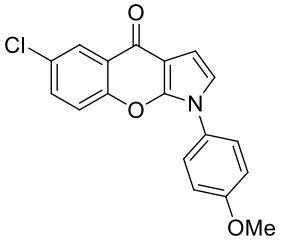
Yellow solid (127mg, 74%); Mp: 154.4-155.4 ℃; IR (KBr): 3433, 3116, 1665, 1595, 1535, 1535, 1447, 1416, 1335, 1308, 1178, 1114, 945, 871, 809, 742, 720, 653 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.47 (s, 3H, CH_3), 6.84 (d, *J* = 3.6 Hz, 1H, ArH), 6.95 (d, *J* = 3.6 Hz, 1H, ArH), 7.38 (d, *J* = 8.0 Hz, 2H, ArH), 7.55 (d, *J* = 8.1 Hz, 2H, ArH), 7.68 (d, *J* = 2.2 Hz, 1H, ArH), 8.28 (d, *J* = 2.3 Hz, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.1, 103.6, 107.4, 119.1, 123.0, 123.0, 123.4, 125.0, 125.5, 130.0, 130.3, 130.3, 132.6, 133.4, 137.9, 147.8, 148.4, 171.3. HRMS (TOF ES$^+$): *m/z* calcd for $C_{18}H_{12}Cl_2NO_2$ [(M+H)$^+$], 344.0240; found, 344.0238.

6-Fluoro-1-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3c')



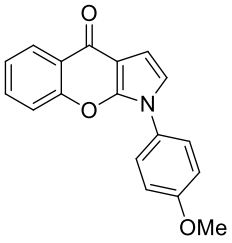
Yellow solid (122mg, 79%); Mp: 116.3-116.8 ℃; IR (KBr): 3473, 3069, 1666, 1623, 1532, 1472, 1307, 1252, 1180, 1136, 1022, 884, 831, 765, 635 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.91 (s, 3H, CH_3), 6.82 (d, J = 2.5 Hz, 2H, ArH), 7.08 (d, J = 8.7 Hz, 2H, ArH), 7.35 (d, J = 7.0 Hz, 1H, ArH), 7.43-7.49 (m, 3H, ArH), 8.04-8.05 (m, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.6, 103.0, 107.0, 111.9 (d, J = 22.5 Hz), 114.9, 114.9, 119.1 (d, J = 9.0 Hz), 119.3, 120.3 (d, J = 25.5 Hz), 124.7, 125.5, 125.5, 129.0, 148.7, 150.1, 159.2 (d, J = 243 Hz), 159.3, 172.5; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -116.9. HRMS (TOF ES^+): *m/z* calcd for $C_{18}H_{13}FNO_3$ [$(M+H)^+$], 310.0874; found, 310.0870.

6-Chloro-1-(4-methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3d')



Yellow solid (137mg, 84%); Mp: 108.4-109.7 ℃; IR (KBr): 3449, 1651, 1604, 1522, 1462, 1307, 1251, 1184, 1112, 1021, 891, 830, 720, 658 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.91 (s, 3H, OCH_3), 6.82 (s, 2H, ArH), 7.08 (d, J = 8.2 Hz, 2H, ArH), 7.40 (d, J = 8.8 Hz, 1H, ArH), 7.48 (d, J = 8.2 Hz, 2H, ArH), 7.56 (d, J = 8.8 Hz, 1H, ArH), 8.35 (s, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.6, 103.2, 107.3, 114.9, 114.9, 119.0, 119.4, 124.5, 125.5, 125.5, 126.2, 128.9, 130.3, 132.5, 148.5, 152.4, 159.3, 172.1. HRMS (TOF ES^+): *m/z* calcd for $C_{18}H_{13}ClNO_3$ [$(M+H)^+$], 326.0578; found, 326.0574.

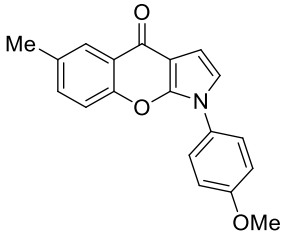
1-(4-Methoxyphenyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3e')



Yellow solid (99mg, 68%); Mp: 102.3-103.4 ℃; IR (KBr): 3418, 3118, 1661, 1610, 1527, 1508, 1459, 1355, 1251, 1176, 1106, 1020, 955, 830, 755 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.92 (s, 3H, CH_3), 6.83 (d, J = 3.4 Hz, 1H, ArH),

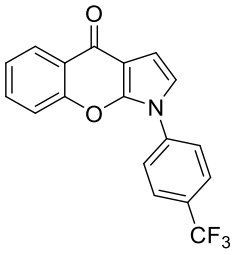
6.86 (d, J = 3.4 Hz, 1H, ArH), 7.09 (d, J = 8.7 Hz, 2H, ArH), 7.42-7.47 (m, 2H, ArH), 7.50 (d, J = 8.7 Hz, 2H, ArH), 7.64 (t, J = 7.3 Hz, 1H, ArH), 8.43 (d, J = 7.8 Hz, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 55.6, 103.2, 107.4, 114.8, 114.8, 117.4, 118.9, 123.4, 124.4, 125.5, 125.5, 126.8, 129.2, 132.5, 148.6, 154.1, 159.2, 173.5. HRMS (TOF ES$^+$): *m/z* calcd for $C_{18}H_{14}NO_3$ [(M+H)$^+$], 292.0968; found, 292.0966.

1-(4-Methoxyphenyl)-6-methylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3f')



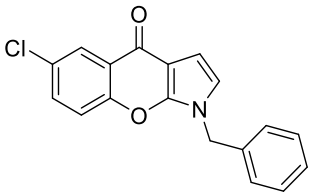
Yellow solid (111mg, 73%); Mp: 84.2-85.3 ℃; IR (KBr): 3426, 1649, 1613, 1521, 1475, 1307, 1249, 1183, 1117, 1028, 835, 720, 681, 639 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.46 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 6.79 (d, J = 3.7 Hz, 1H, ArH), 6.82 (d, J = 3.7 Hz, 1H, ArH), 7.04-7.07 (m, 2H, ArH), 7.32 (d, J = 8.5 Hz, 1H, ArH), 7.40-7.42 (m, 1H, ArH), 7.45-7.48 (m, 2H, ArH), 8.18 (d, J = 1.2 Hz, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.8, 55.6, 103.2, 107.4, 114.8, 114.8, 117.1, 118.8, 123.0, 125.4, 125.4, 126.3, 129.2, 133.6, 134.2, 148.7, 152.4, 159.1, 173.6. HRMS (TOF ES$^+$): *m/z* calcd for $C_{19}H_{16}NO_3$ [(M+H)$^+$], 306.1125; found, 306.1121.

1-(4-(Trifluoromethyl)phenyl)chromeno[2,3-*b*]pyrrol-4(1*H*)-one (3g')



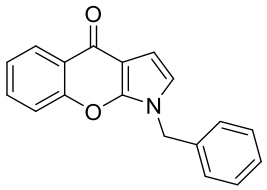
Yellow solid (118 mg, 72%); Mp: 167.8-168.9 ℃; IR (KBr): 3446, 1659, 1611, 1518, 1456, 1328, 1163, 1108, 1067, 1018, 843, 764, 686 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.90 (d, J = 3.7 Hz, 1H, ArH), 6.92 (d, J = 3.7 Hz, 1H, ArH), 7.43-7.45 (m, 1H, ArH), 7.47-7.49 (m, 1H, ArH), 7.65-7.68 (m, 1H, ArH), 7.76 (d, J = 8.4 Hz, 2H, ArH), 7.85 (d, J = 8.4 Hz, 2H, ArH), 8.40-8.41 (m, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 104.6, 108.1, 117.4, 117.9, 123.7 (q, J_1 = 271.5 Hz), 123.4, 123.6, 123.6, 124.8, 126.9-127.0 (m, J_3 = 4.5 Hz), 126.9-127.0 (q, J_3 = 4.5 Hz), 127.1, 129.4-130.1 (q, J_2 = 33.0 Hz), 132.9, 139.2, 148.4, 154.1, 173.4; ^{19}F NMR (564 MHz, $CDCl_3$): δ = -62.5. HRMS (TOF ES$^+$): *m/z* calcd for $C_{18}H_{11}F_3NO_2$ [(M+H)$^+$], 330.0736; found, 330.0740.

1-Benzyl-6-chlorochromeno[2,3-*b*]pyrrol-4(1*H*)-one (3h')



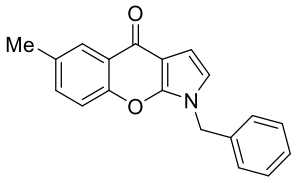
Yellow solid (117mg, 76%); Mp: 95.6-96.1 ℃; IR (KBr): 3467, 3117, 2370, 1651, 1609, 1542, 1500, 1460, 1351, 1278, 1212, 1180, 1121, 1082, 905, 822, 738, 697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.26 (s, 2H, CH_2), 6.60 (d, J = 3.4 Hz, 1H, ArH), 6.71 (d, J = 3.3 Hz, 1H, ArH), 7.24 (d, J = 7.2 Hz, 2H, ArH), 7.35-7.44 (m, 4H, ArH), 7.56 (t, J = 7.4 Hz, 1H, ArH), 8.36 (s, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 48.7, 102.8, 106.6, 118.6, 118.9, 124.6, 126.3, 127.4, 127.4, 128.4, 129.1, 129.1, 130.2, 132.4, 135.5, 149.2, 152.3, 171.9. HRMS (TOF ES^+): *m/z* calcd for $C_{18}H_{13}ClNO_2$ [$(M+H)^+$], 310.0629; found, 310.0623.

1-Benzylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3i')



Yellow solid (97mg, 71%); Mp: 64.4-65.1 ℃; IR (KBr): 3445, 3121, 1648, 1614, 1544, 1502, 1350, 1288, 1205, 1105, 917, 869, 756, 696, 611 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.27 (s, 2H, CH_2), 6.59 (s, 1H, ArH), 6.74 (s, 1H, ArH), 7.25 (d, J = 7.3 Hz, 2H, ArH), 7.34-7.43 (m, 4H, ArH), 7.49 (d, J = 8.4 Hz, 1H, ArH), 7.64 (t, J = 7.6 Hz, 1H, ArH), 8.42 (d, J = 7.9 Hz, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 48.6, 102.8, 106.7, 117.2, 118.2, 123.4, 124.4, 126.9, 127.4, 127.4, 128.3, 128.9, 129.0, 132.4, 135.7, 149.3, 154.0, 173.3. HRMS (TOF ES^+): *m/z* calcd for $C_{18}H_{14}NO_2$ [$(M+H)^+$], 276.1019; found, 276.1025.

1-Benzyl-6-methylchromeno[2,3-*b*]pyrrol-4(1*H*)-one (3j')



Yellow solid (92mg, 64%); Mp: 86.7-87.3 ℃; IR (KBr): 3436, 3028, 1653, 1614, 1538, 1499, 1285, 1206, 1115, 820, 761, 701, 601 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.48 (s, 3H, CH_3), 5.26 (s, 2H, CH_2), 6.57 (s, 1H, ArH), 6.74 (s, 1H, ArH), 7.26 (d, J = 14.1 Hz, 2H, ArH), 7.37-7.44 (m, 5H, ArH), 8.20 (s, 1H, ArH),); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.9, 48.6, 102.8, 106.6, 117.0, 118.1, 123.0, 126.4, 127.4, 127.4, 128.3, 129.0, 129.0, 133.5, 134.2, 135.8, 149.5, 152.3, 173.5.

HRMS (TOF ES$^+$): *m/z* calcd for $C_{19}H_{16}NO_2$ [$(M+H)^+$], 290.1176; found, 290.1181.

X-ray Structure and Data[2] of 3d'.

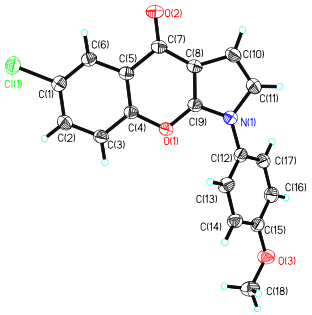


Figure S1. X-Ray crystal structure of **3d'**, ellipsoids is drawn at the 30% probability level.

Table S1. Crystal data and structure refinement for **3d'**

Identification code	1	
Empirical formula	$C_{18}H_{12}ClNO_3$	
Formula weight	325.74	
Temperature	301(2) K	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 15.6982(9) Å	α = 90 °.
	b = 12.4059(8) Å	β = 100.261(2) °.
	c = 7.6199(5) Å	γ = 90 °.
Volume	1460.24(16) Å^3	
Z	4	
Density (calculated)	1.482g/cm^3	
Absorption coefficient	0.277 mm^{-1}	
F(000)	672	
Theta range for data collection	2.105 to 25.139 °.	
Index ranges	-18<=h<=18, -14<=k<=14, -9<=l<=9	
Reflections collected	33858	
Reflections unique	2607 [R(int) = 0.0984, R(sigma) = 0.0549]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2607 / 0 / 209	
Goodness-of-fit on F^2	1.091	
Final R indexes [I>=2sigma(I)]	R_1 = 0.0437, wR_2 = 0.1133	
Final R indexes (all data)	R_1 = 0.0635, wR_2 = 0.1412	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.189 and -0.248 e.Å^{-3}	

Table S2. Bond Lengths for **3d'**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl(1)	C(1)	1.736(2)	C(7)	C(8)	1.432(3)
N(1)	C(9)	1.355(3)	C(8)	C(9)	1.372(3)
N(1)	C(11)	1.397(3)	C(8)	C(10)	1.430(3)
N(1)	C(12)	1.430(3)	C(10)	C(11)	1.343(4)
O(1)	C(9)	1.345(3)	C(10)	H(10)	0.9300
O(1)	C(4)	1.383(3)	C(11)	H(11)	0.9300
O(2)	C(7)	1.234(3)	C(12)	C(13)	1.373(3)
O(3)	C(15)	1.369(3)	C(12)	C(17)	1.382(3)
O(3)	C(18)	1.422(3)	C(13)	C(14)	1.391(3)
C(1)	C(6)	1.367(3)	C(13)	H(13)	0.9300
C(1)	C(2)	1.392(3)	C(14)	C(15)	1.375(3)
C(2)	C(3)	1.373(3)	C(14)	H(14)	0.9300
C(2)	H(2)	0.9300	C(15)	C(16)	1.384(4)
C(3)	C(4)	1.386(3)	C(16)	C(17)	1.373(4)
C(3)	H(3)	0.9300	C(16)	H(16)	0.9300
C(4)	C(5)	1.389(3)	C(17)	H(17)	0.9300
C(5)	C(6)	1.401(3)	C(18)	H(18A)	0.9600
C(5)	C(7)	1.484(3)	C(18)	H(18B)	0.9600
C(6)	H(6)	0.9300	C(18)	H(18C)	0.9600

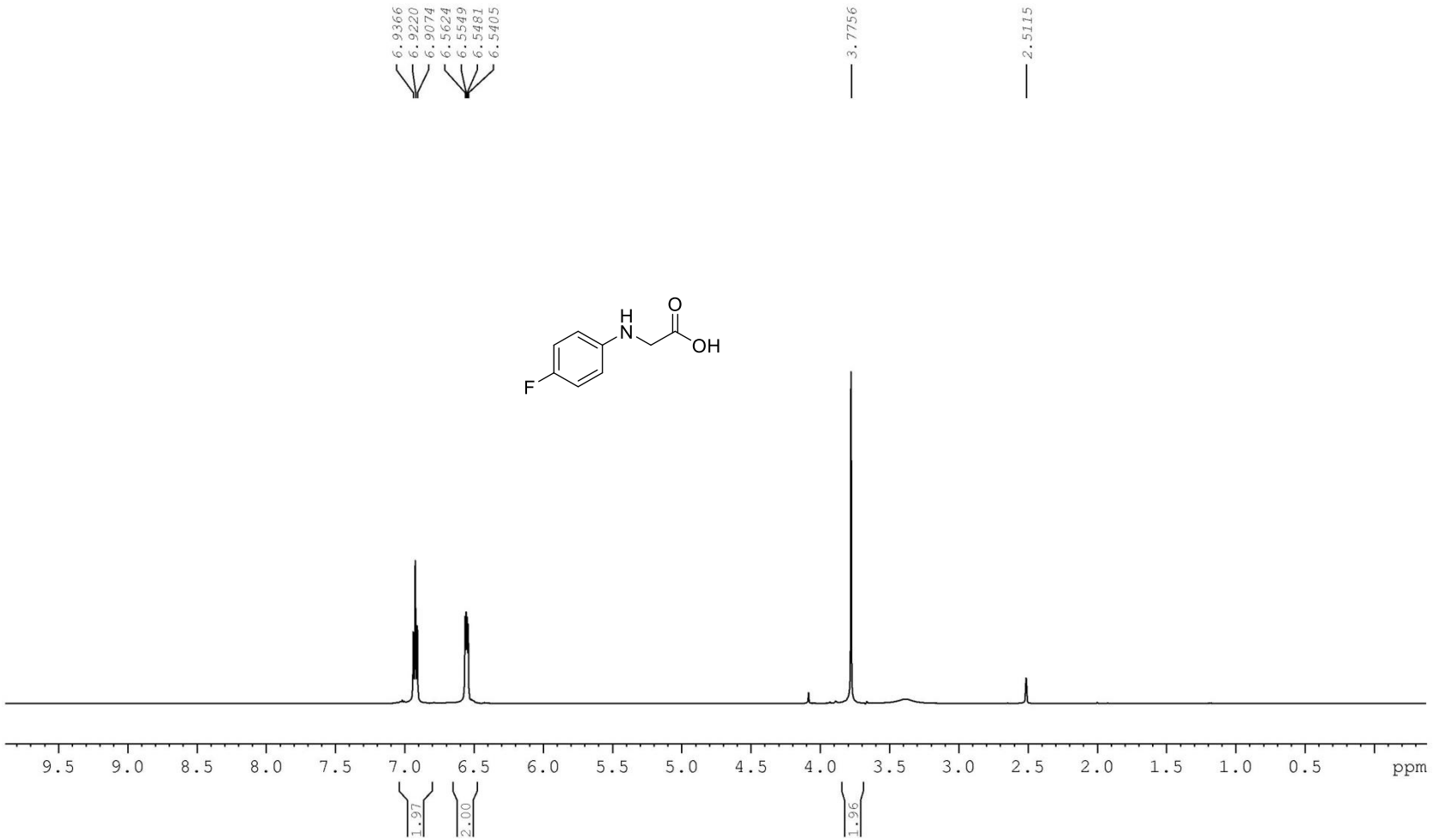


Figure S2. ^{1}H NMR (**600** MHz, DMSO-d_6) spectra of compound **2a**

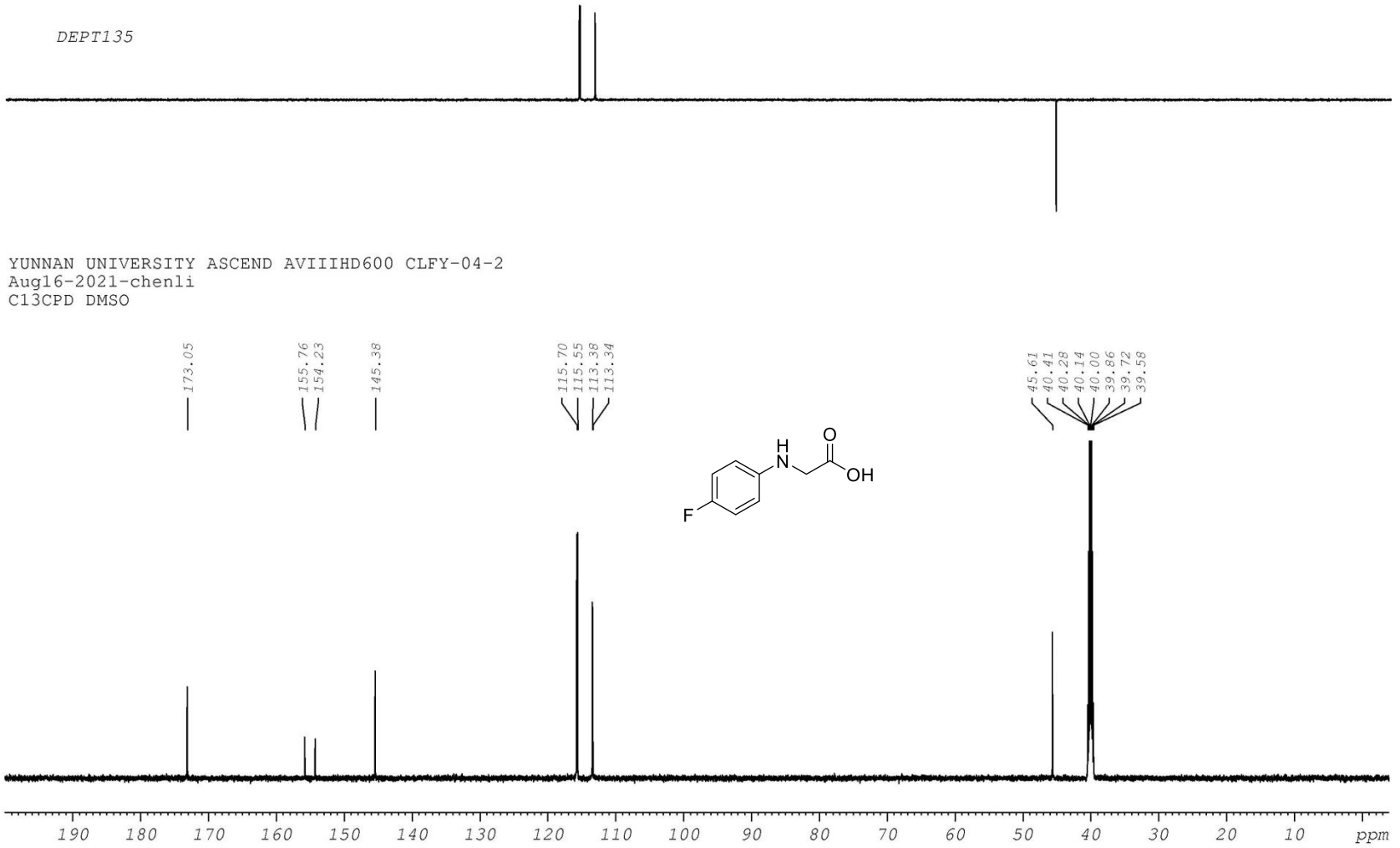


Figure S3. ^{13}C NMR (**150** MHz, DMSO-d_6) spectra of compound **2a**

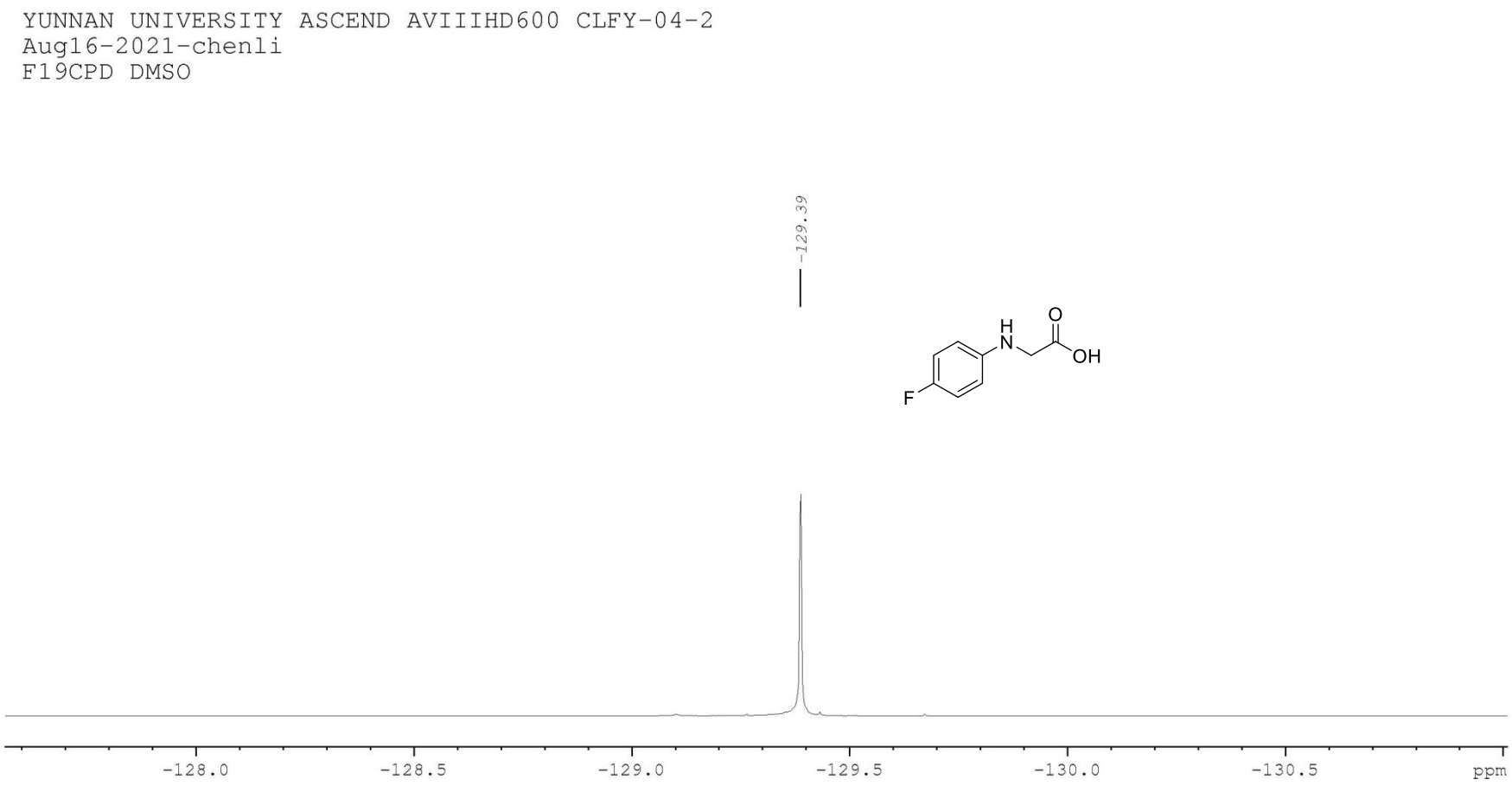


Figure S4. ^{19}F NMR (**564** MHz, DMSO-d_6) spectra of compound **2a**

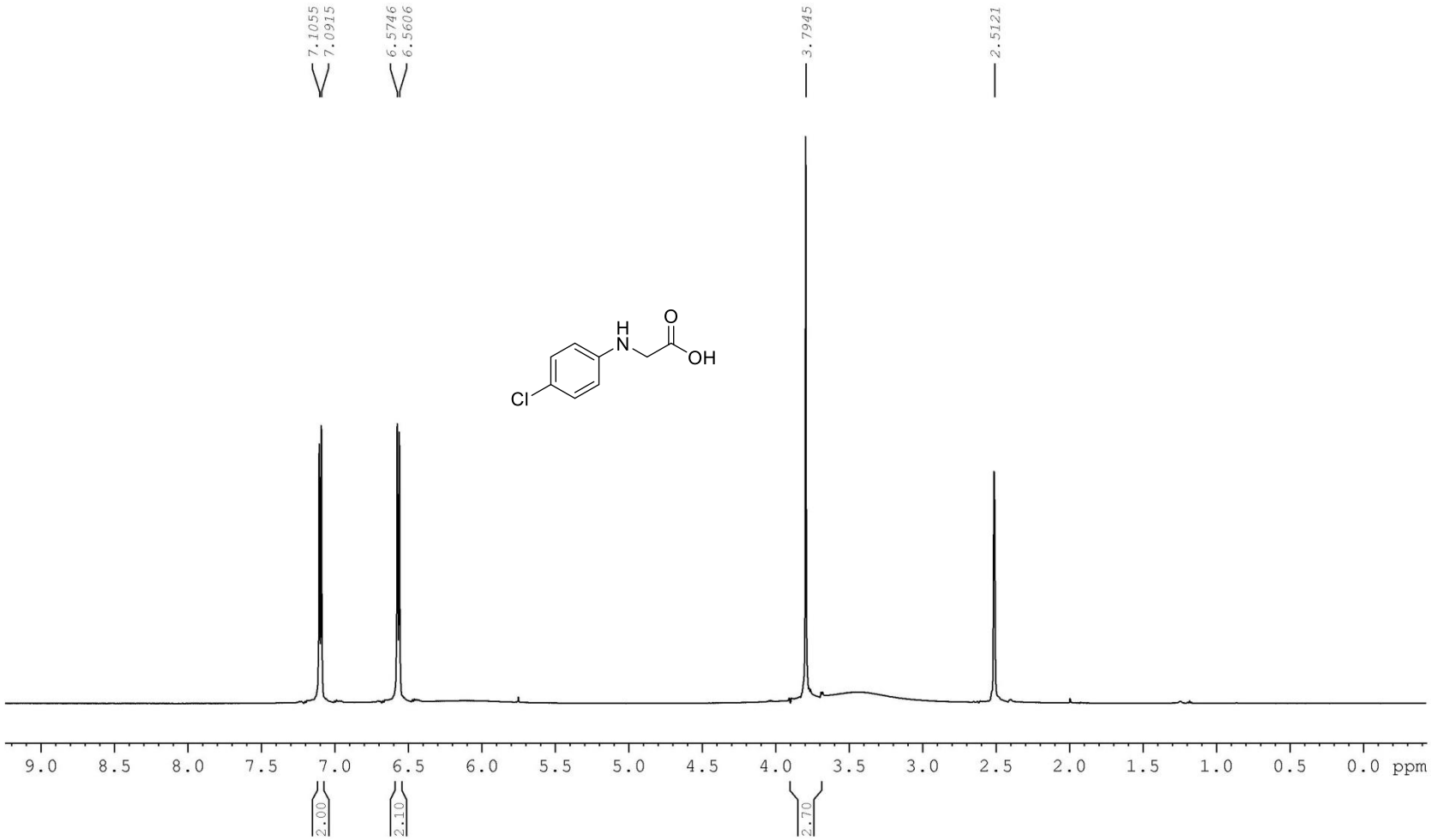


Figure S5. ^{1}H NMR (**600** MHz, DMSO-d_6) spectra of compound **2b**

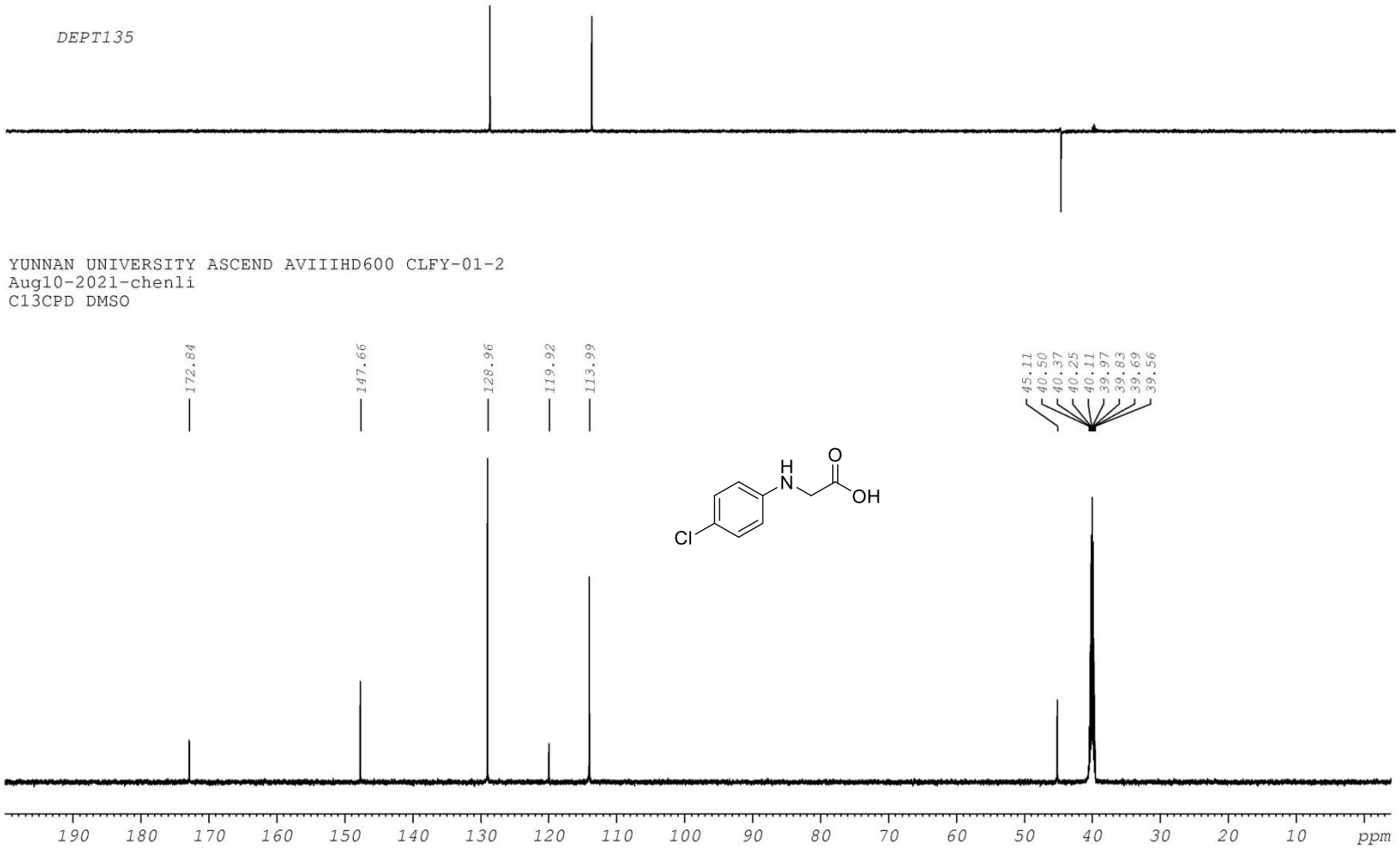


Figure S6. ^{13}C NMR (**150** MHz, DMSO-d_6) spectra of compound **2b**

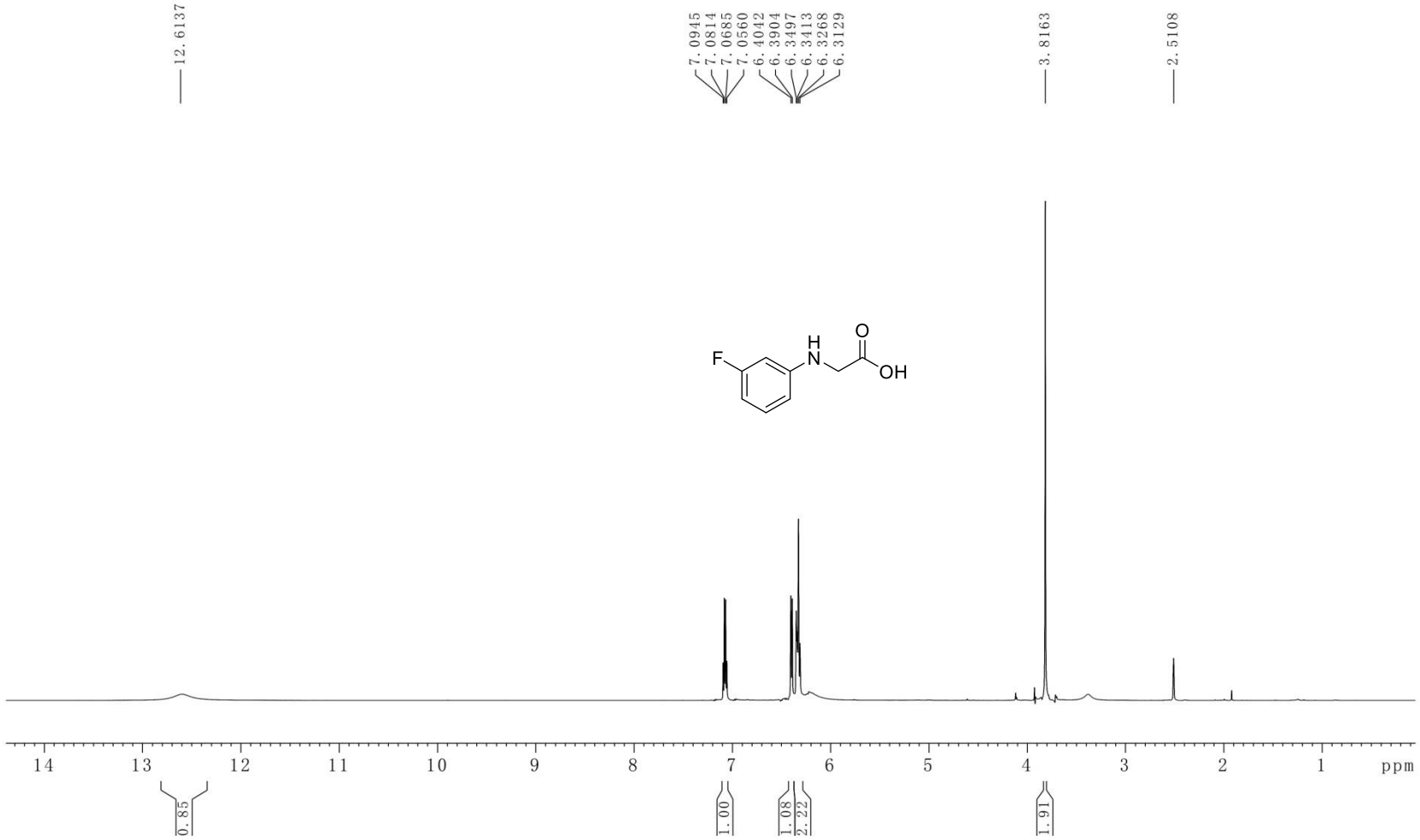


Figure S7. ^{1}H NMR (**600** MHz, DMSO-d_6) spectra of compound **2c**

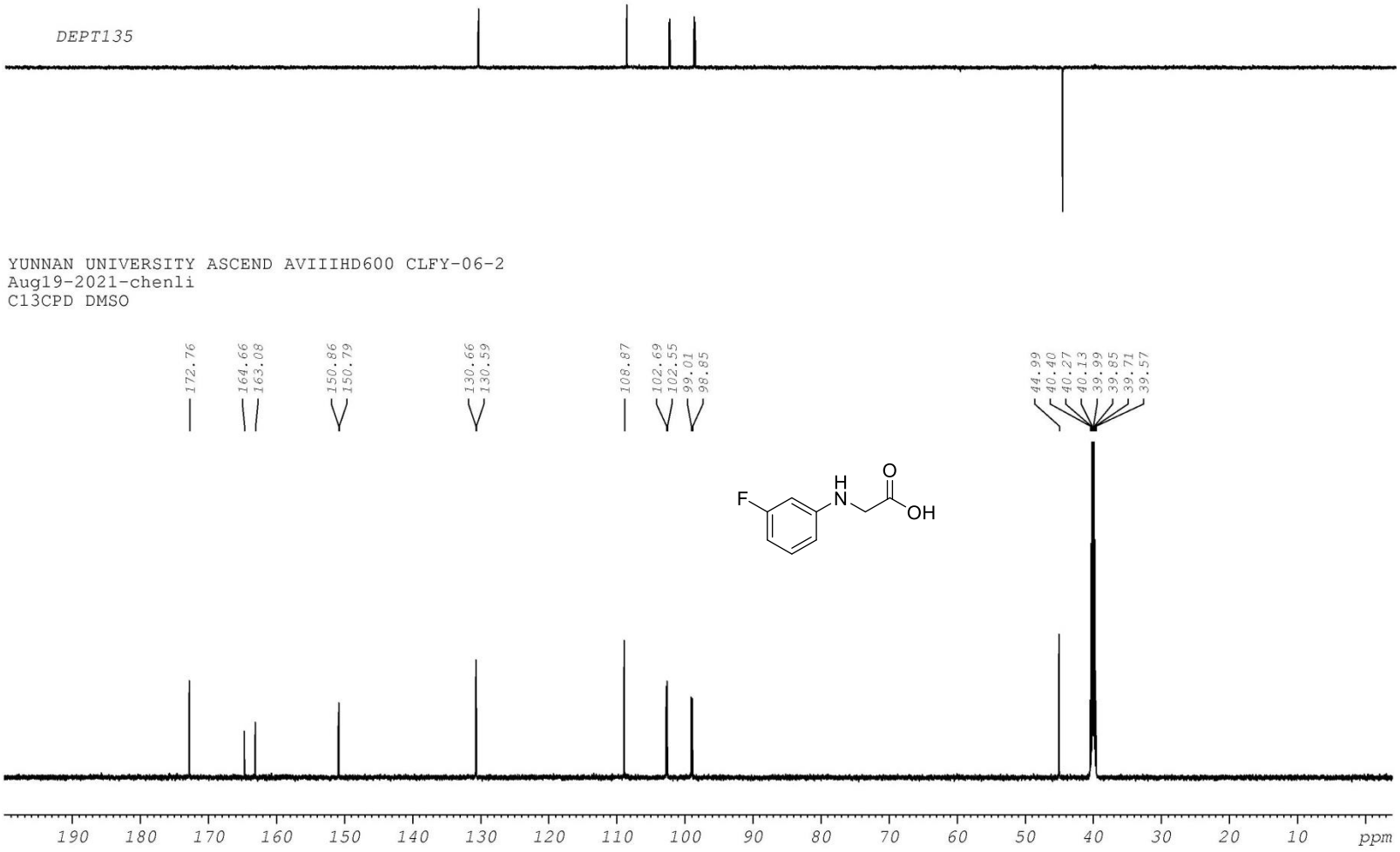


Figure S8. ^{13}C NMR (**150** MHz, DMSO-d_6) spectra of compound **2c**

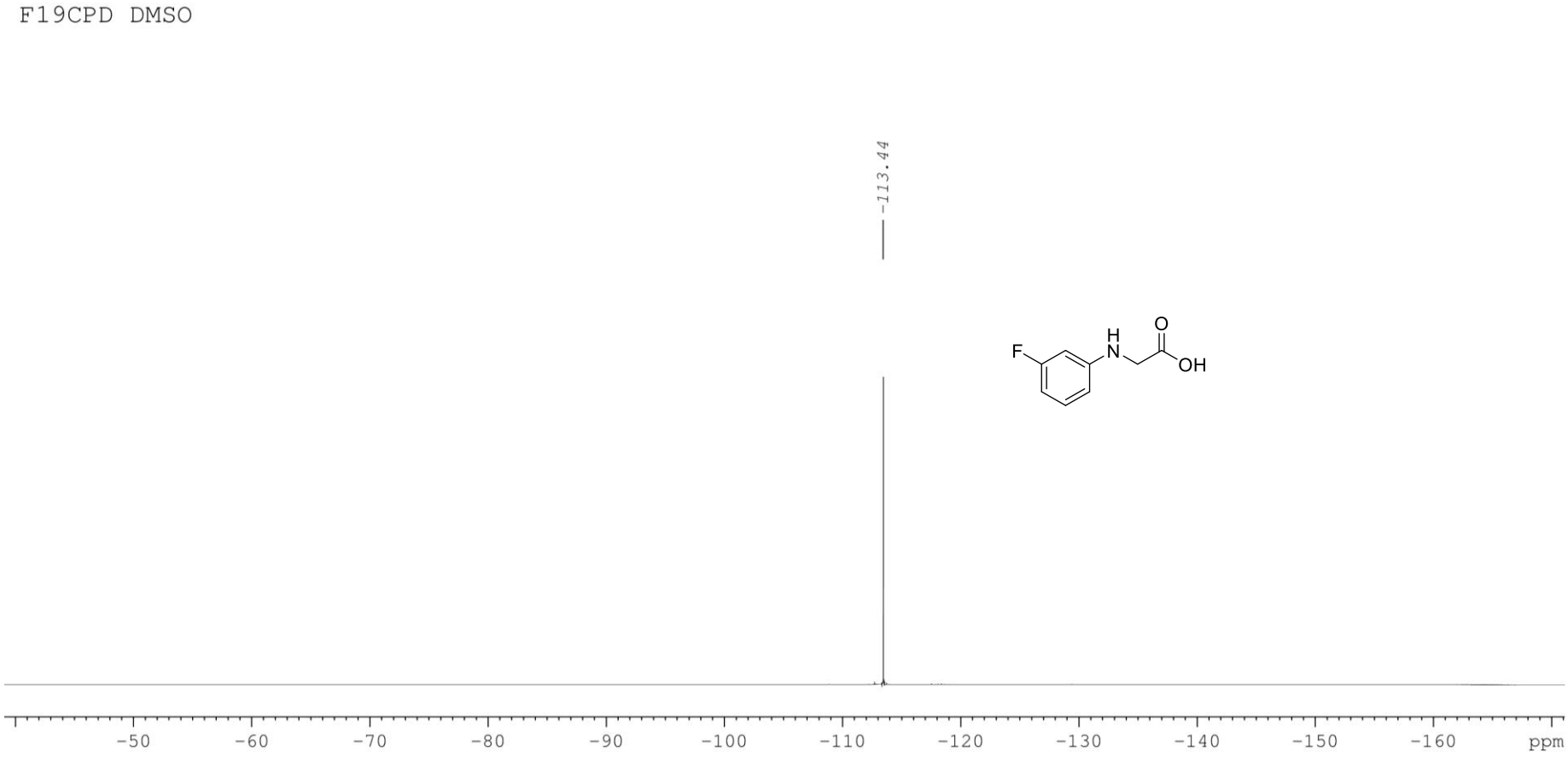


Figure S9. ^{19}F NMR (**564** MHz, DMSO-d_6) spectra of compound **2c**

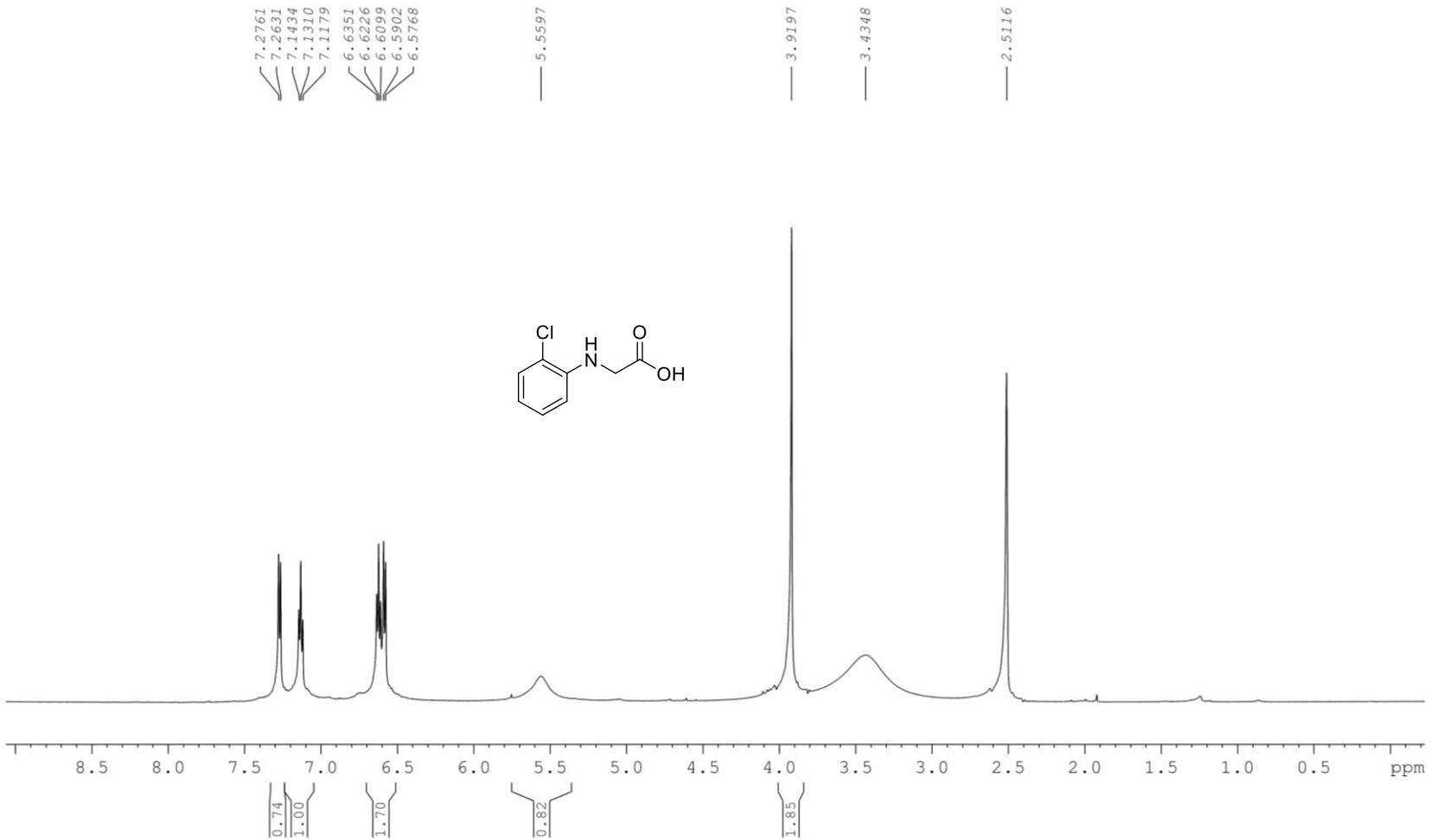


Figure S10. ^{1}H NMR (**600** MHz, DMSO-d_6) spectra of compound **2d**

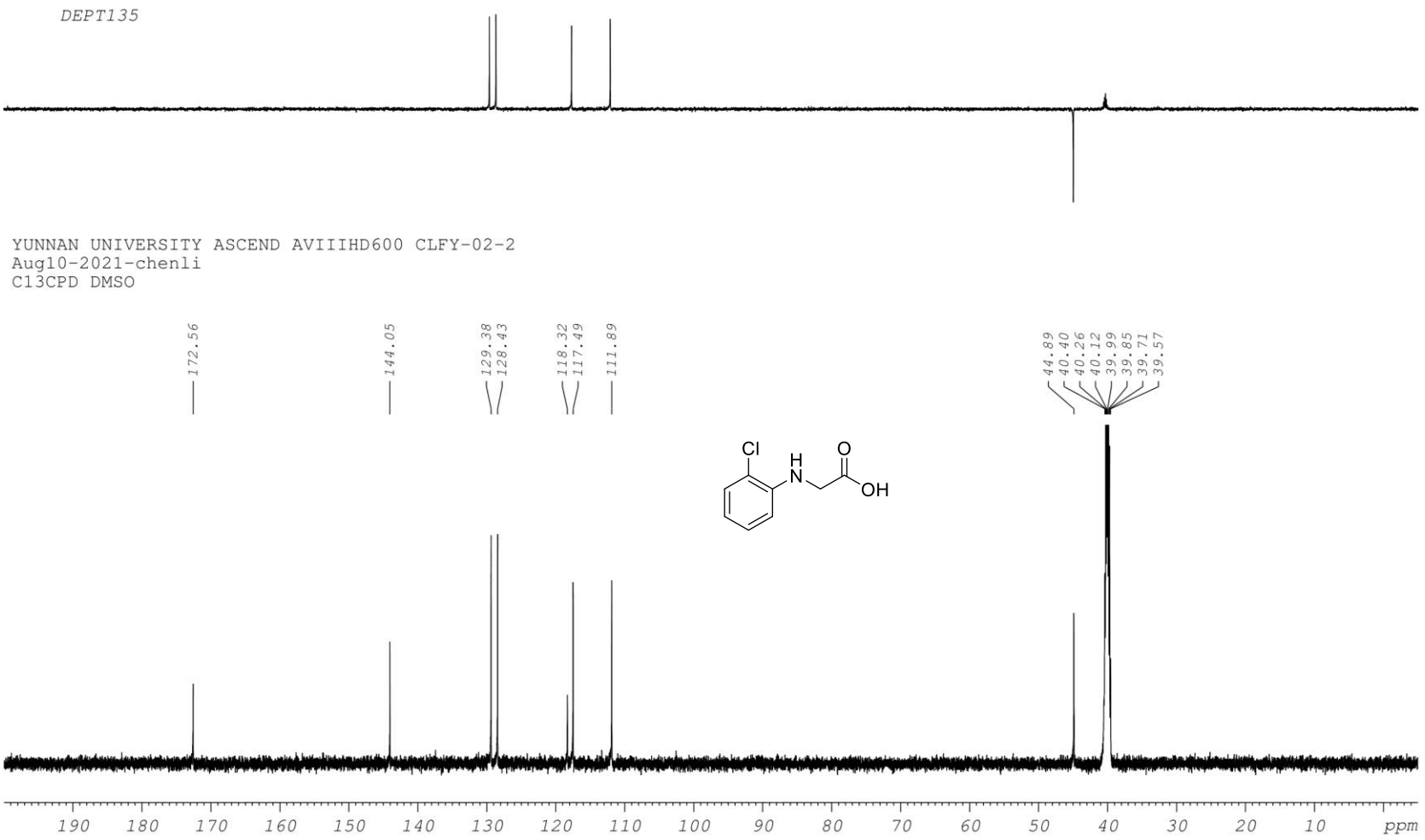


Figure S11. ^{13}C NMR (**150** MHz, DMSO-d_6) spectra of compound **2d**

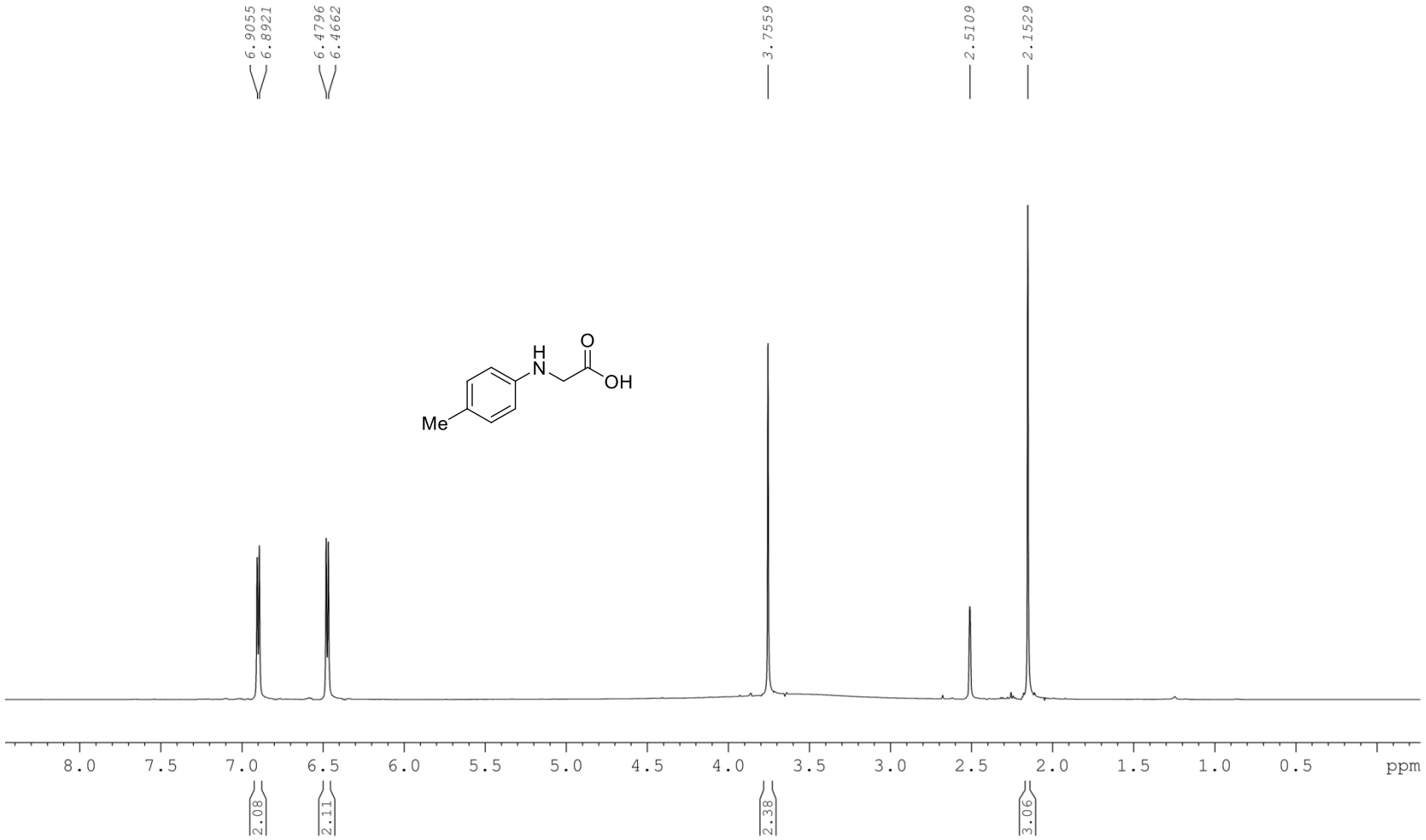


Figure S12. ^{1}H NMR (**600** MHz, DMSO-d_6) spectra of compound **2f**

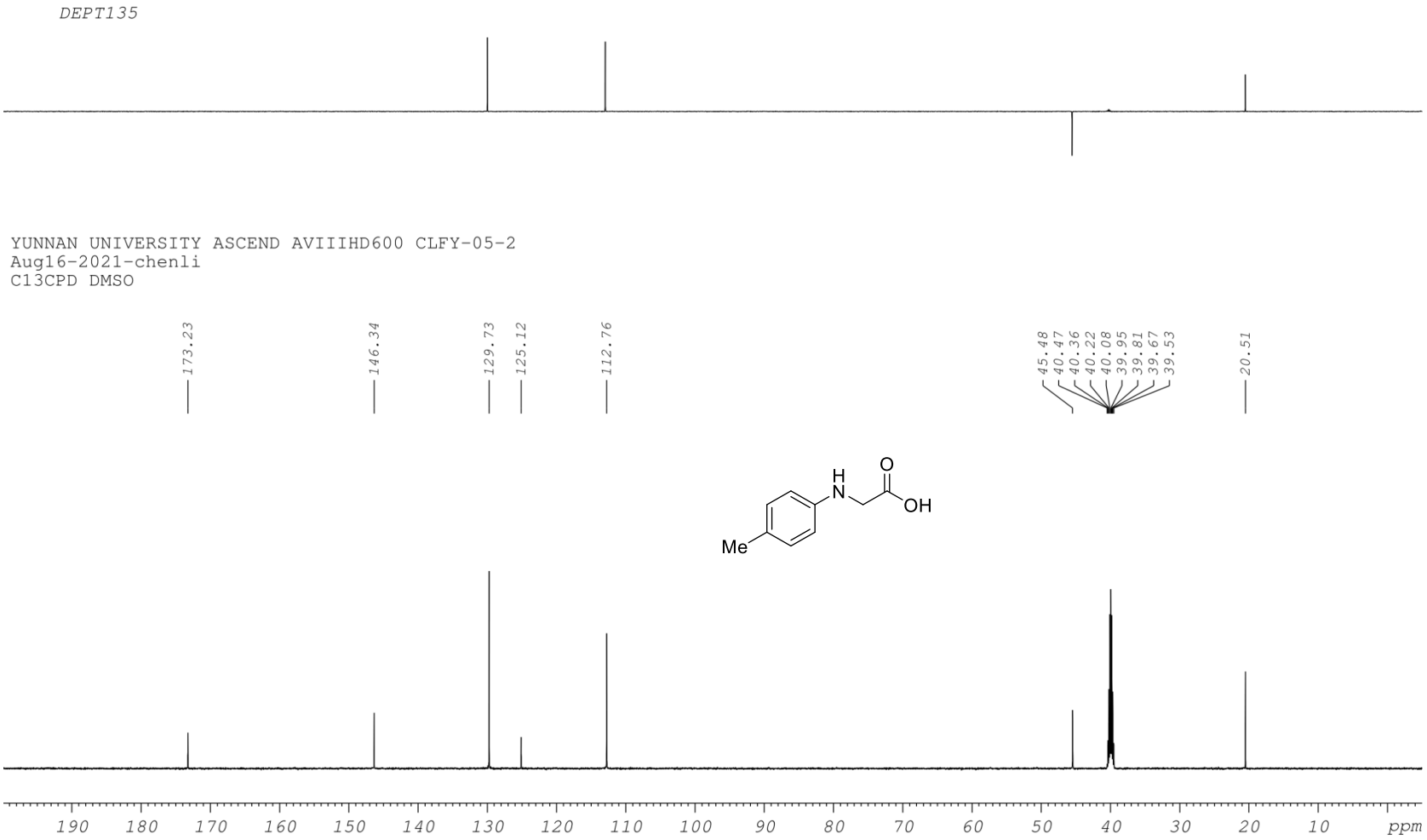


Figure S13. ^{13}C NMR (**150** MHz, DMSO-d_6) spectra of compound **2f**

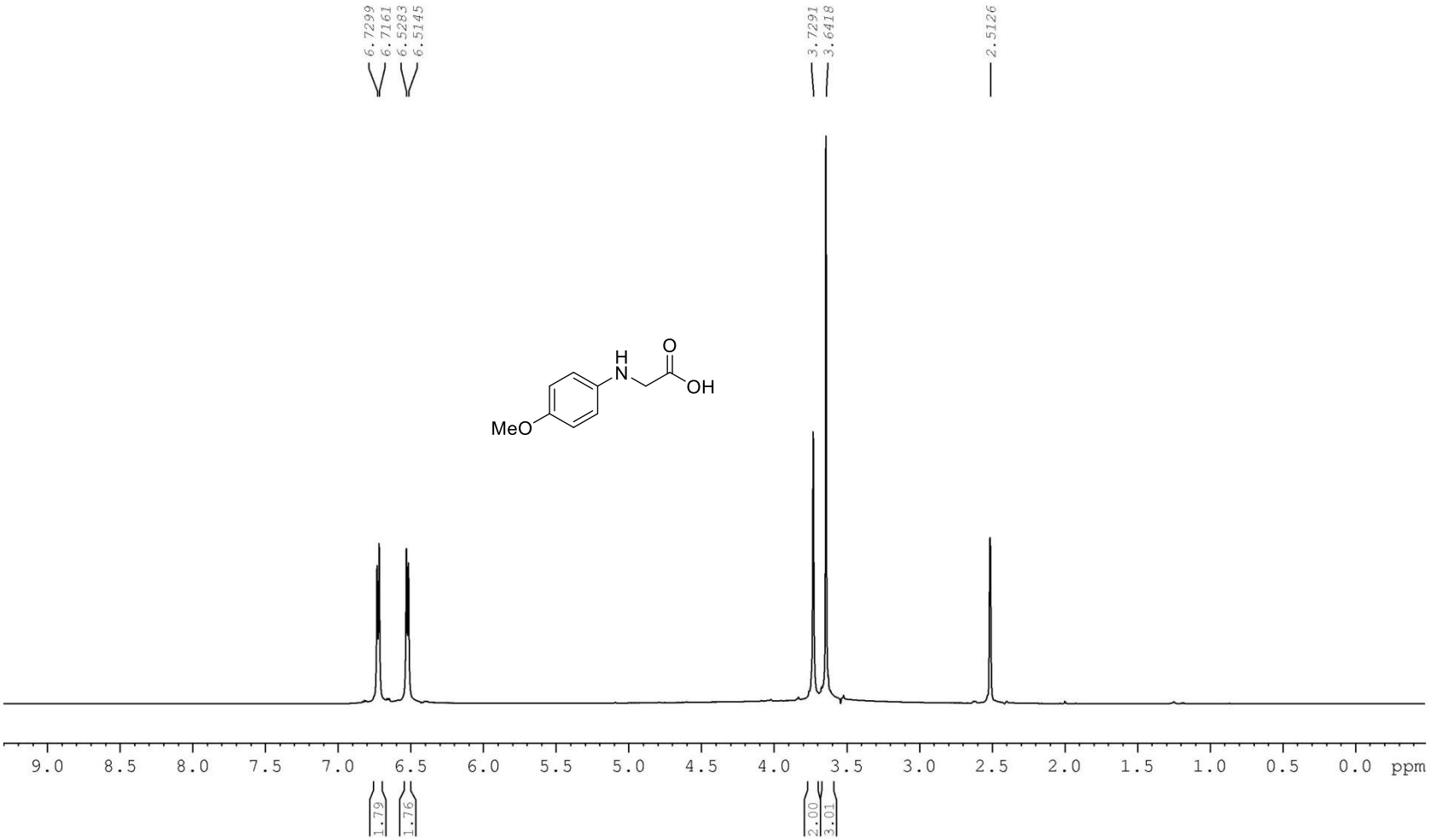


Figure S14. ^{1}H NMR (**600** MHz, DMSO-d_6) spectra of compound **2g**

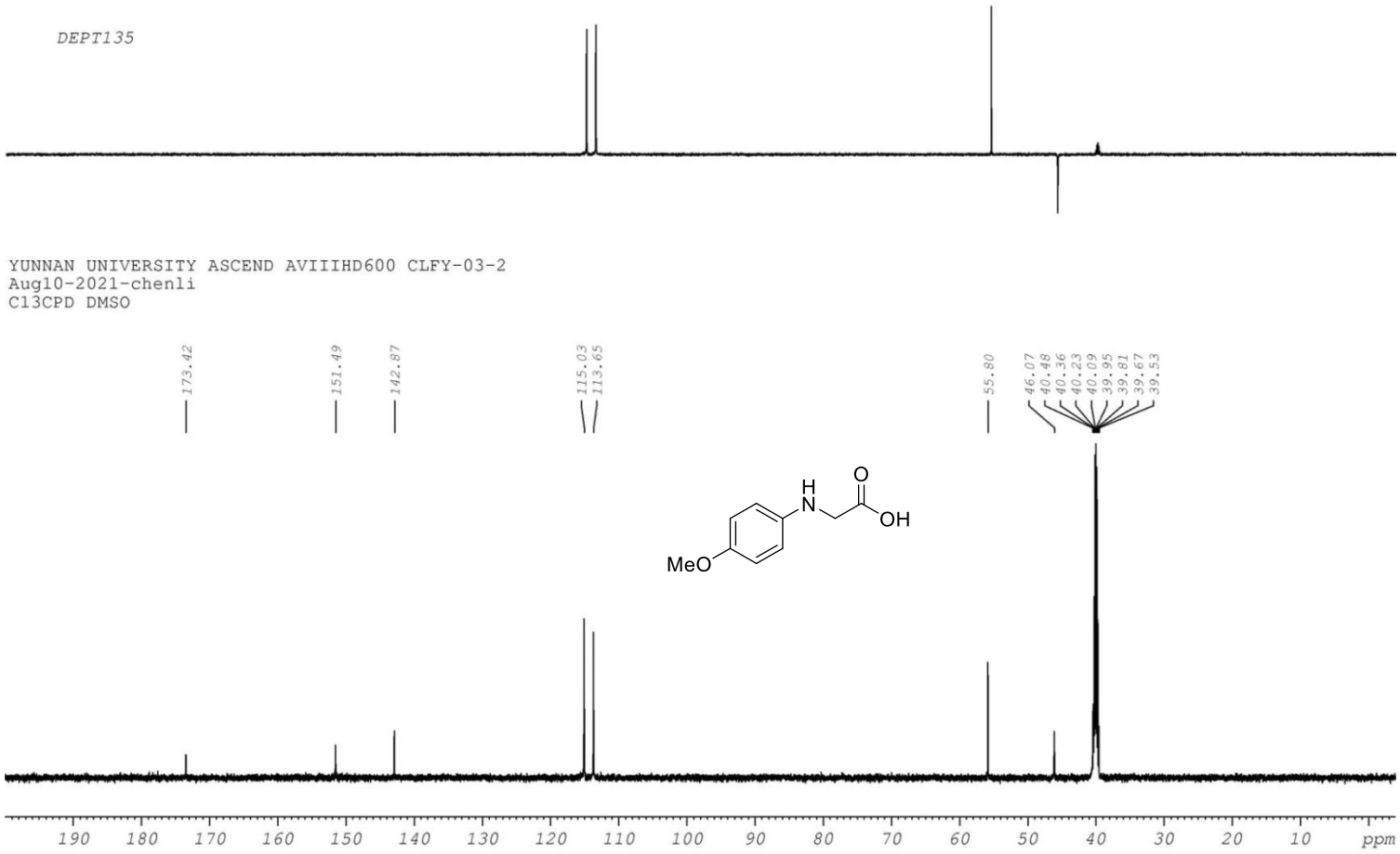


Figure S15. ^{13}C NMR (**150** MHz, DMSO-d_6) spectra of compound **2g**

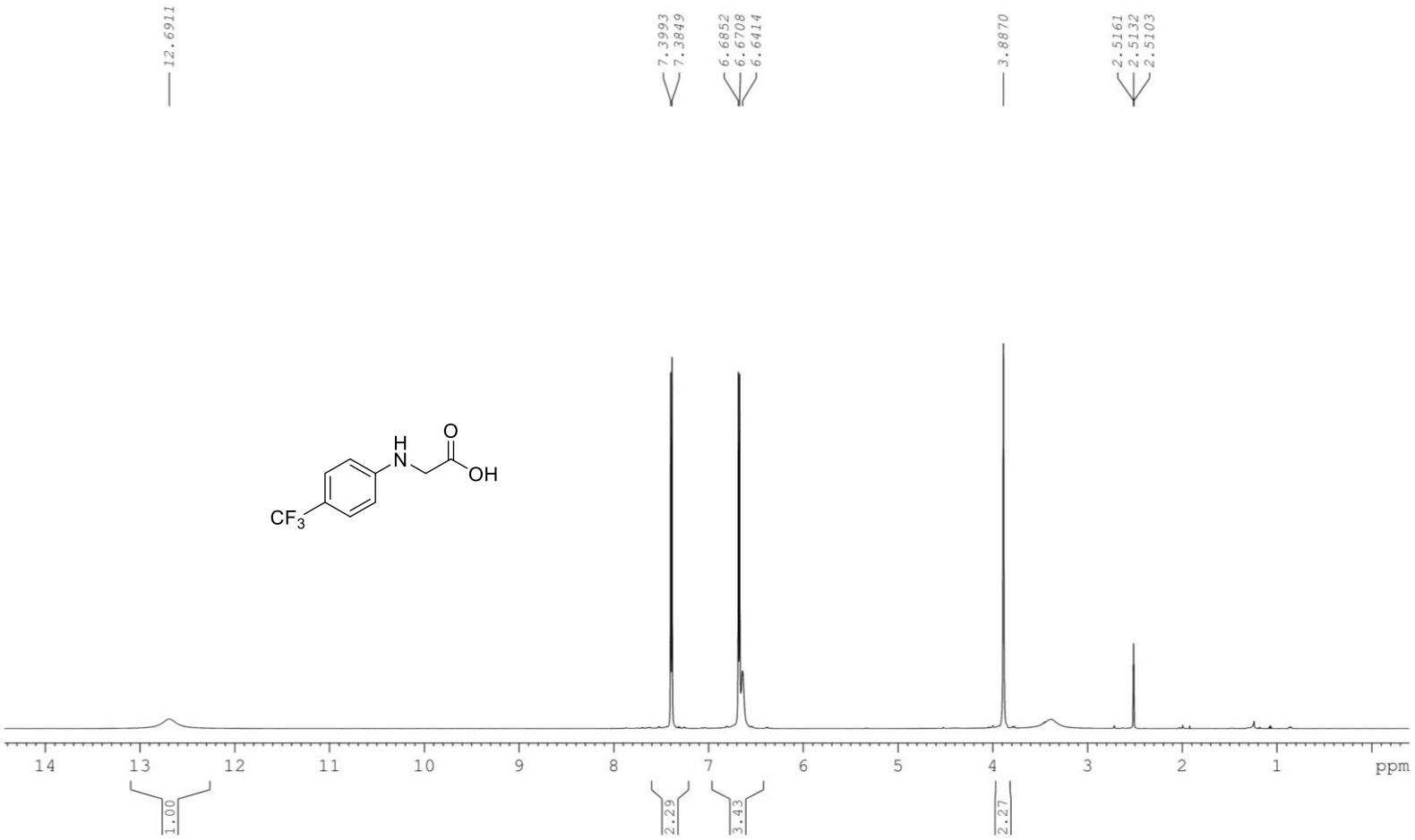


Figure S16. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **2h**

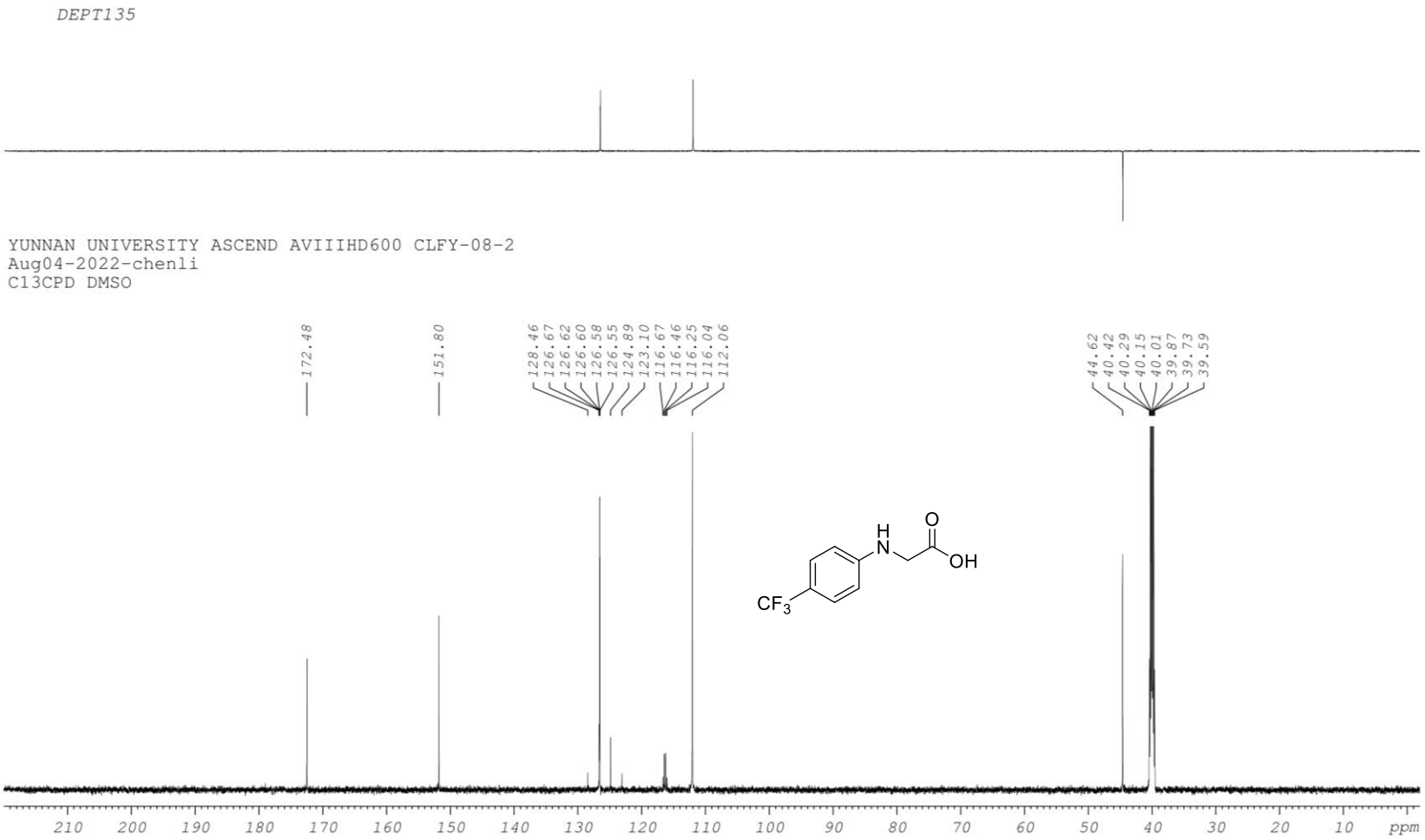


Figure S17. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **2h**

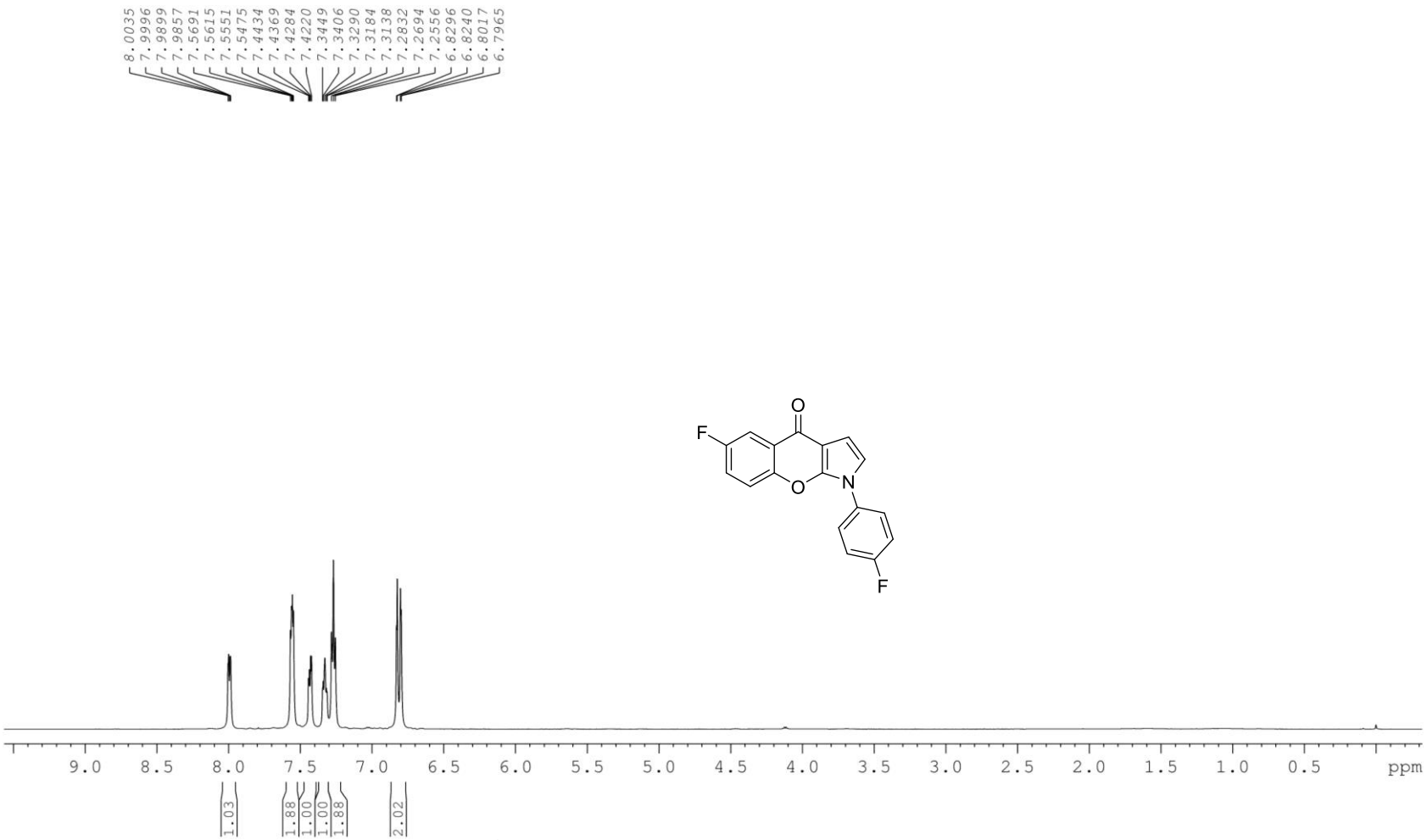


Figure S18. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3a**

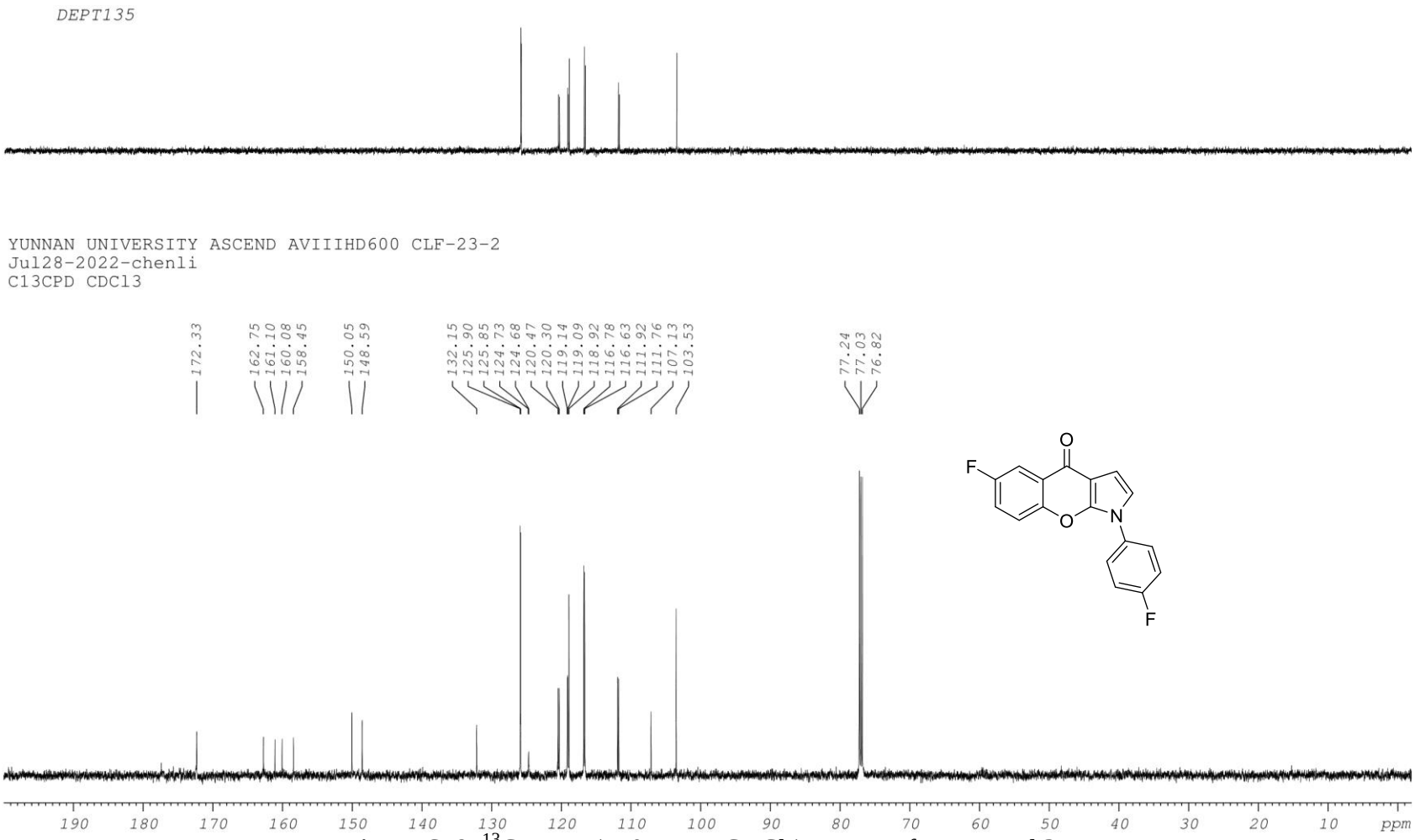


Figure S19. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3a**

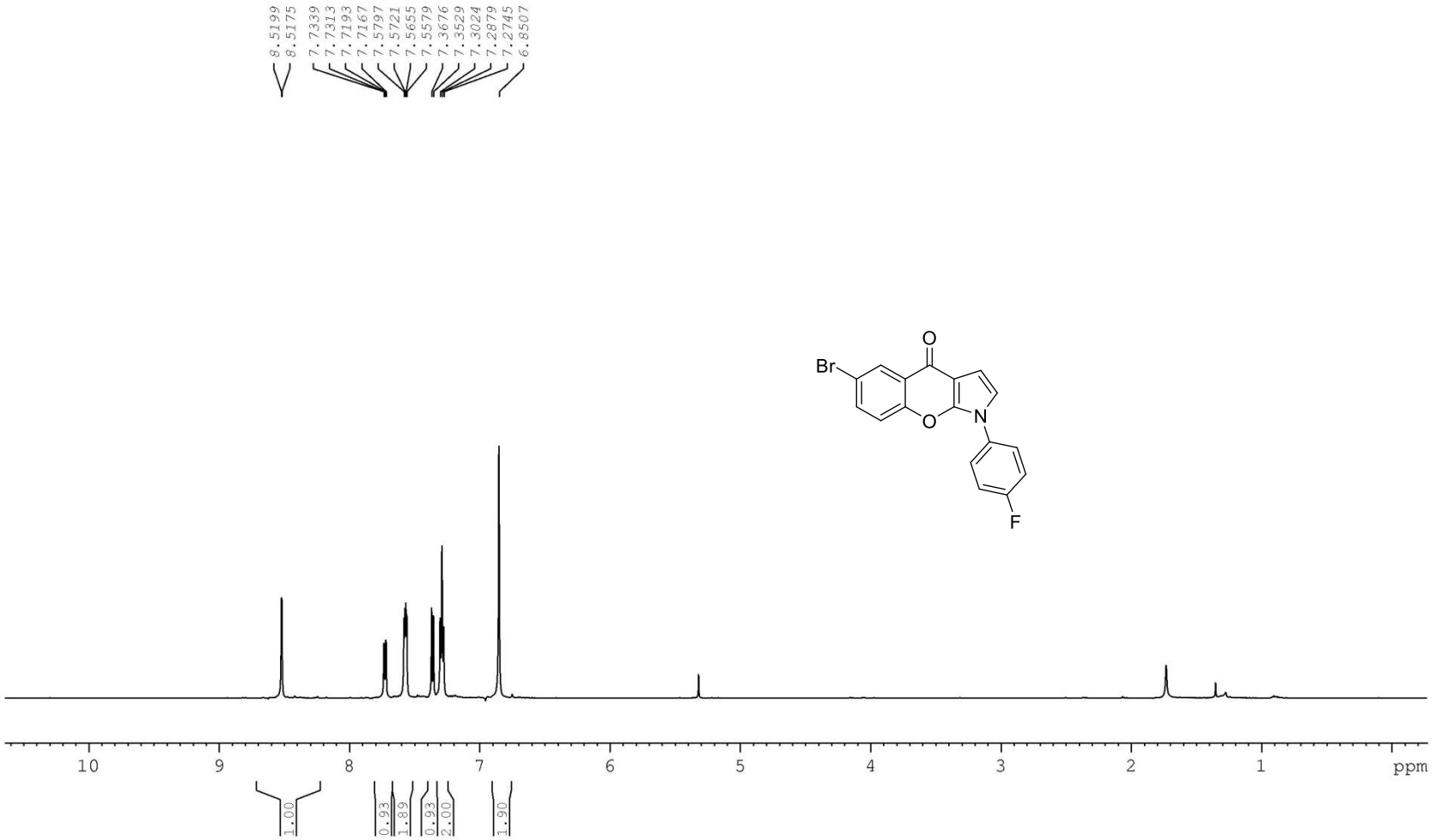


Figure S20. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3b**

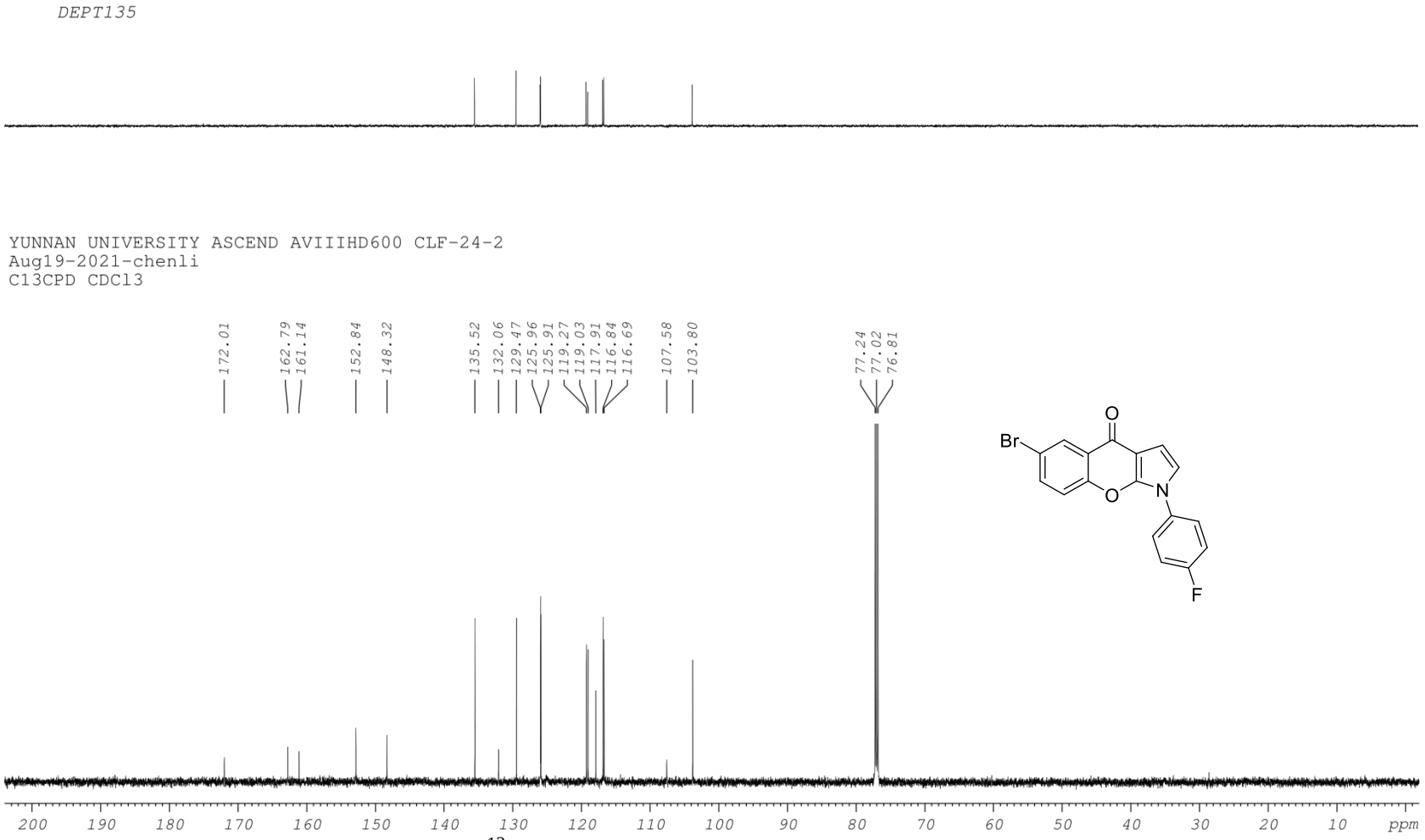


Figure S21. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3b**

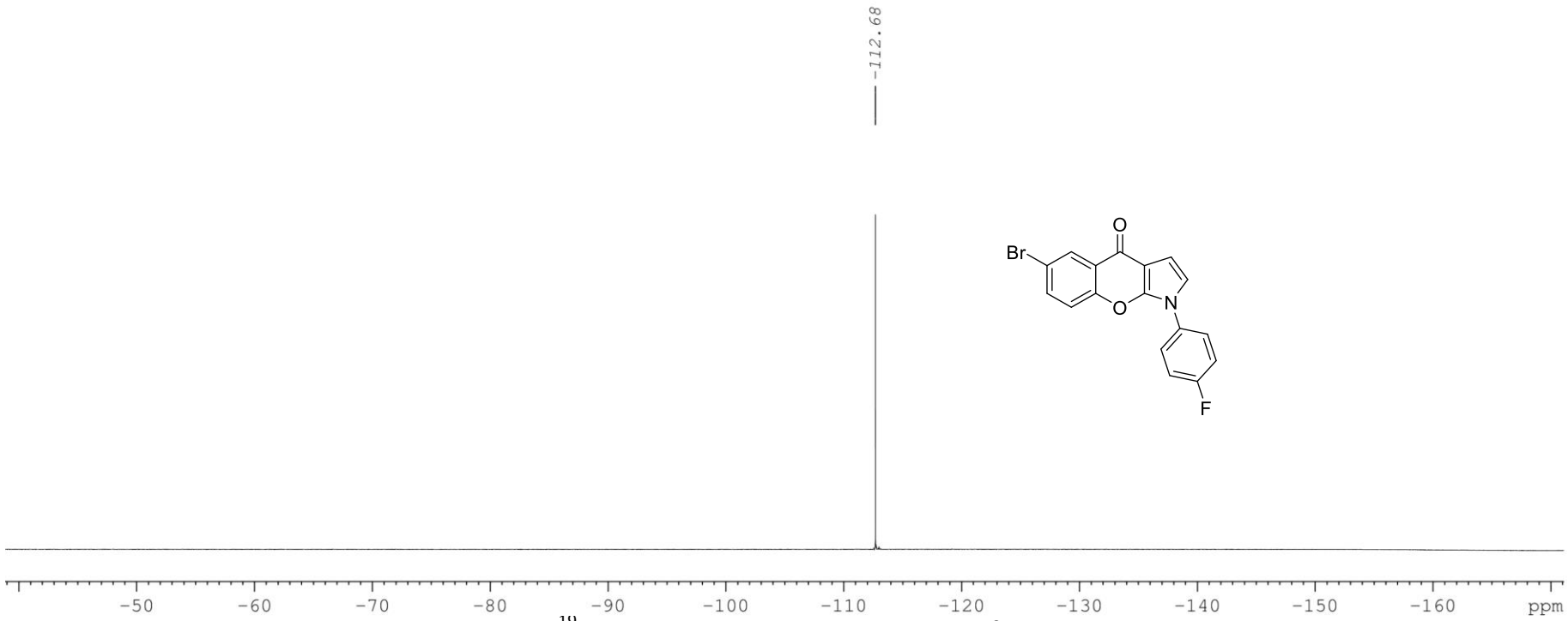


Figure S22. ^{19}F NMR (**564** MHz, $CDCl_3$) spectra of compound **3b**

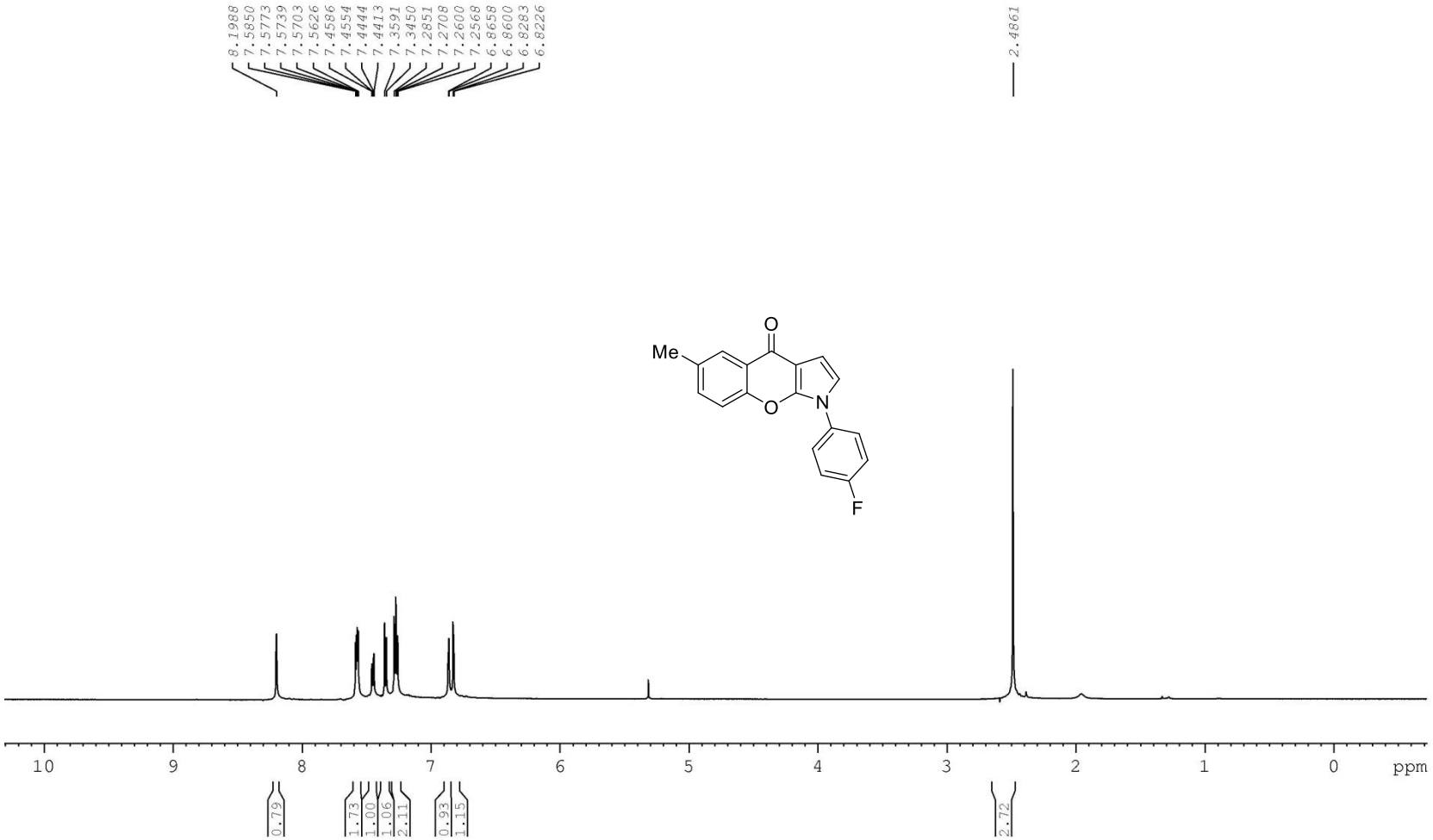


Figure S23. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3c**

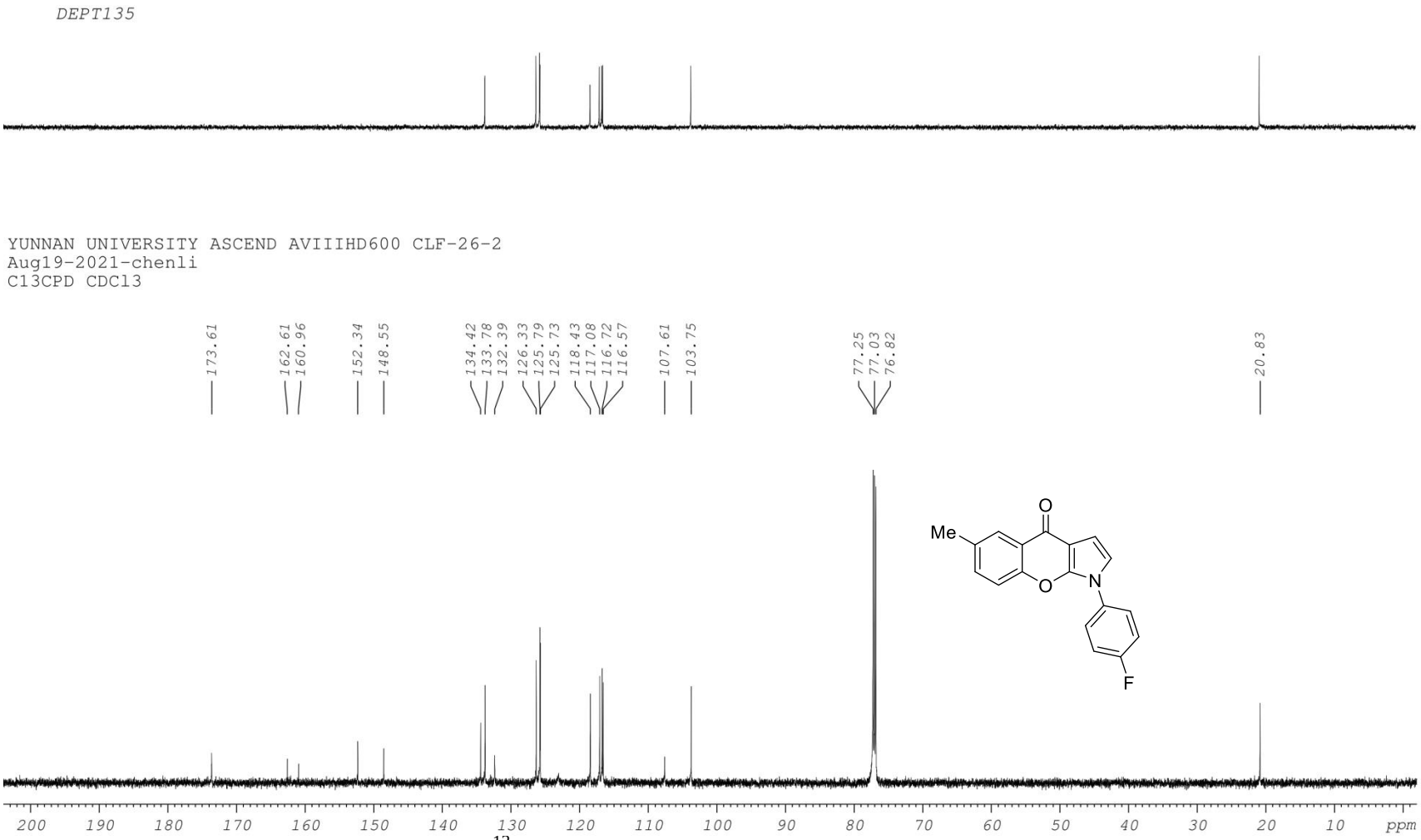


Figure S24. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3c**

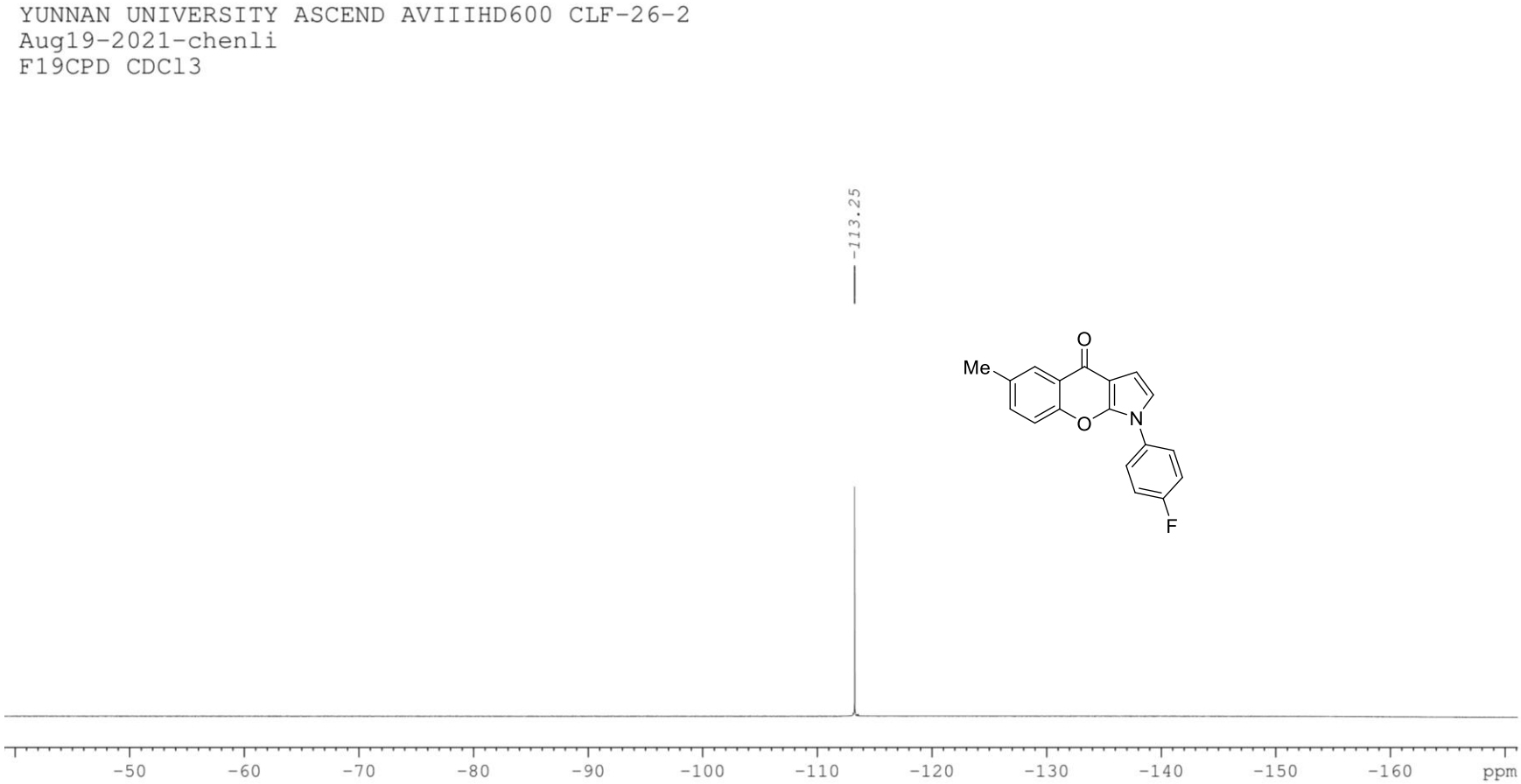


Figure S25. ^{19}F NMR (**564** MHz, $CDCl_3$) spectra of compound **3c**

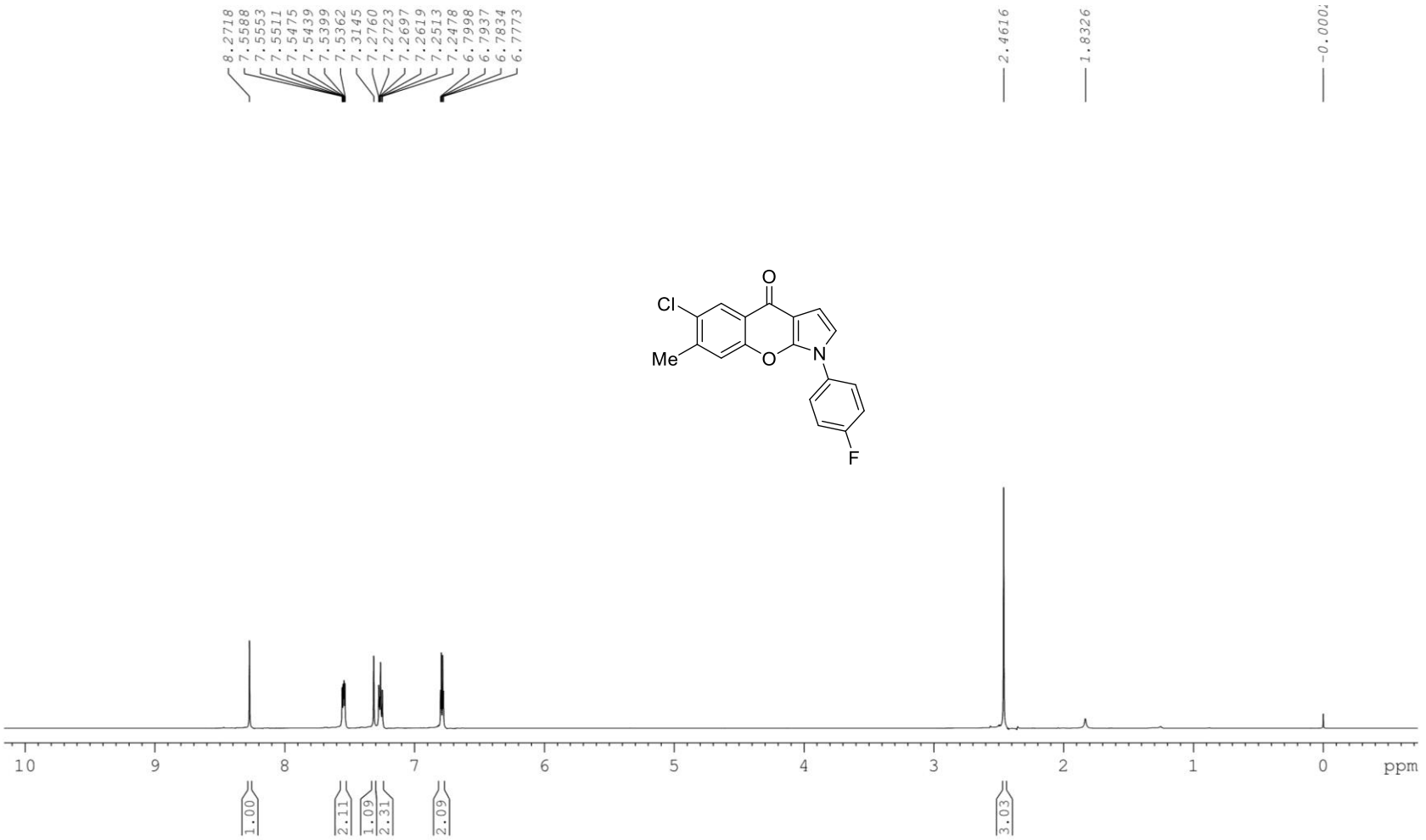


Figure S26. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3d**

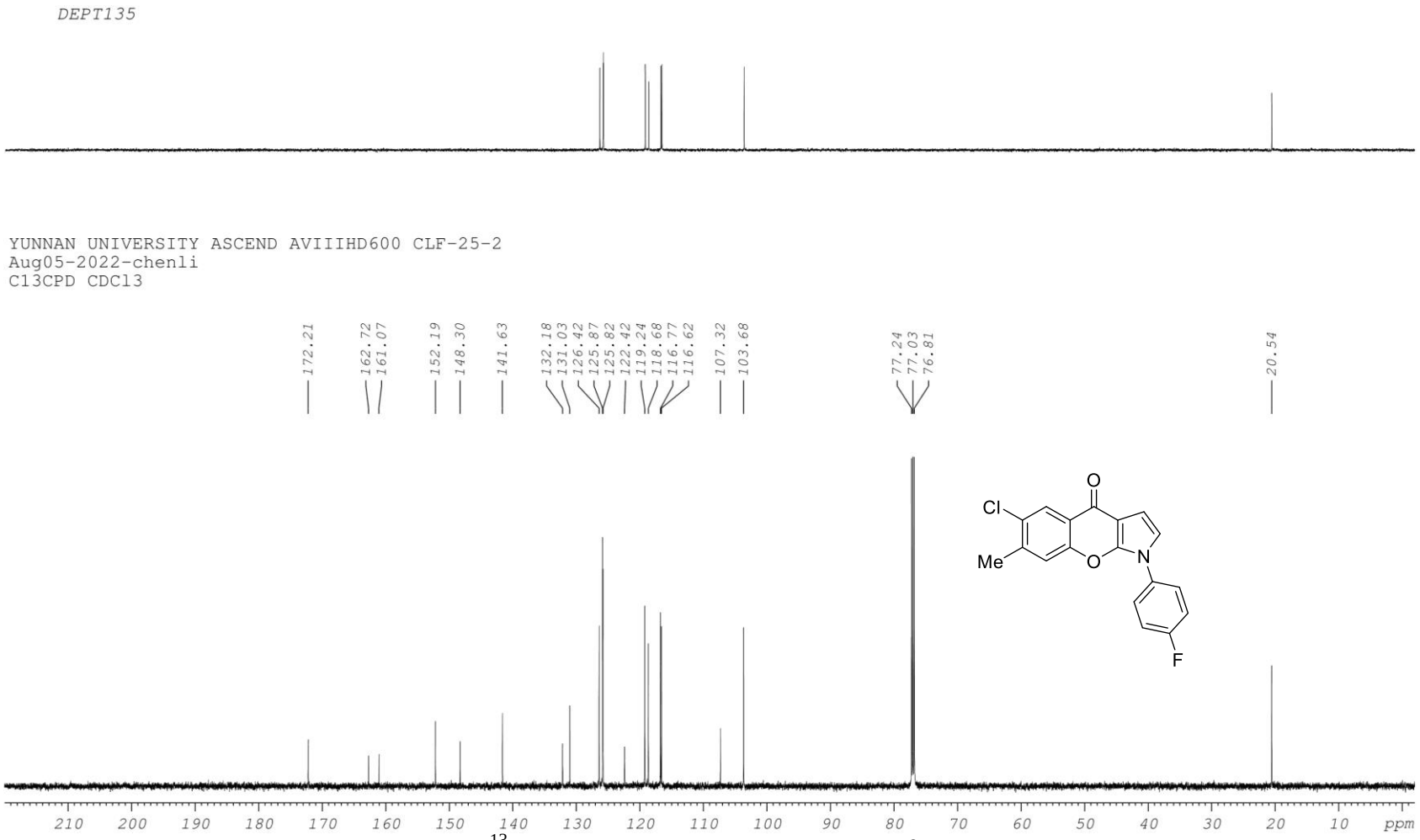


Figure S27. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3d**

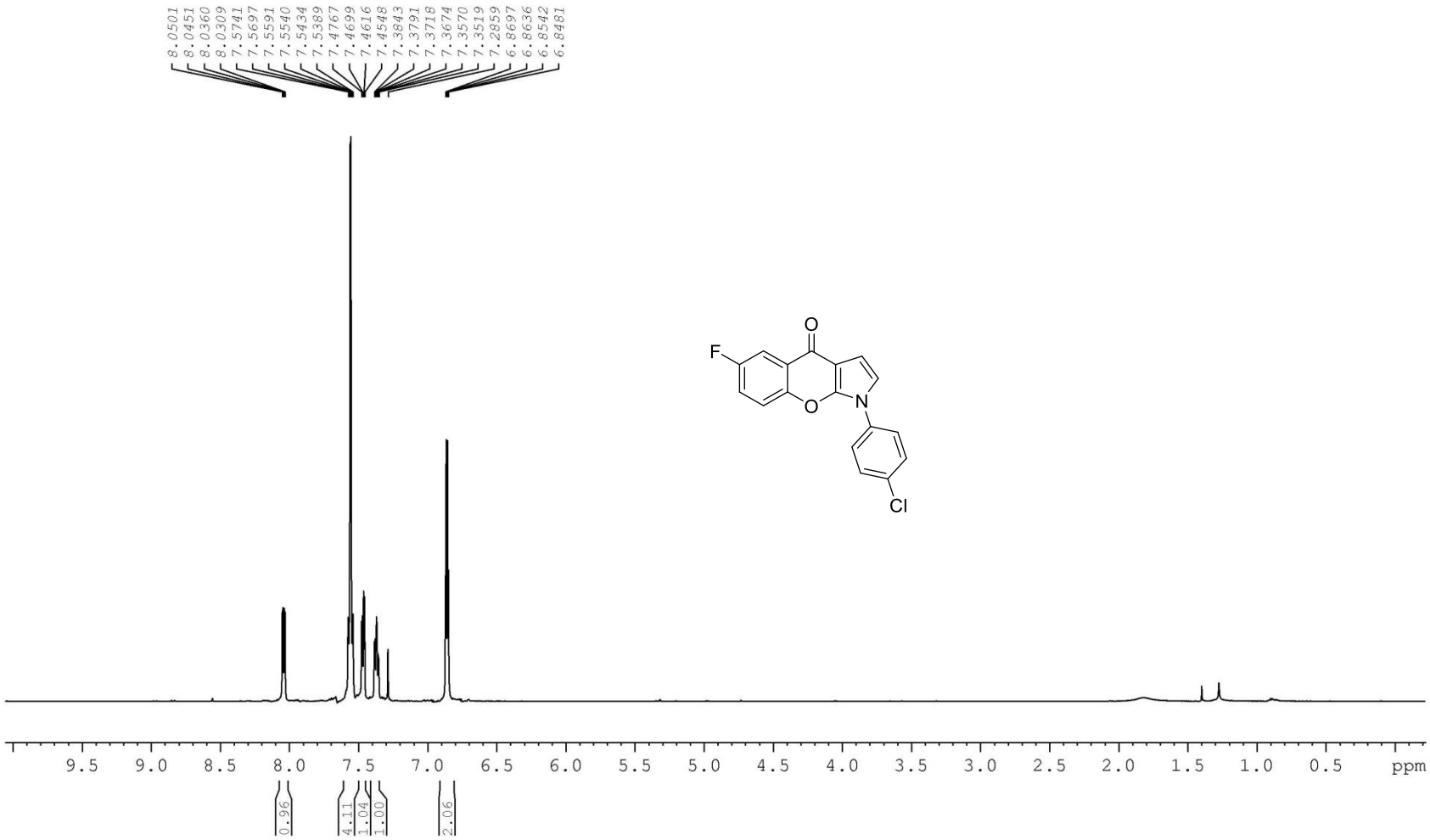


Figure S28. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3e**

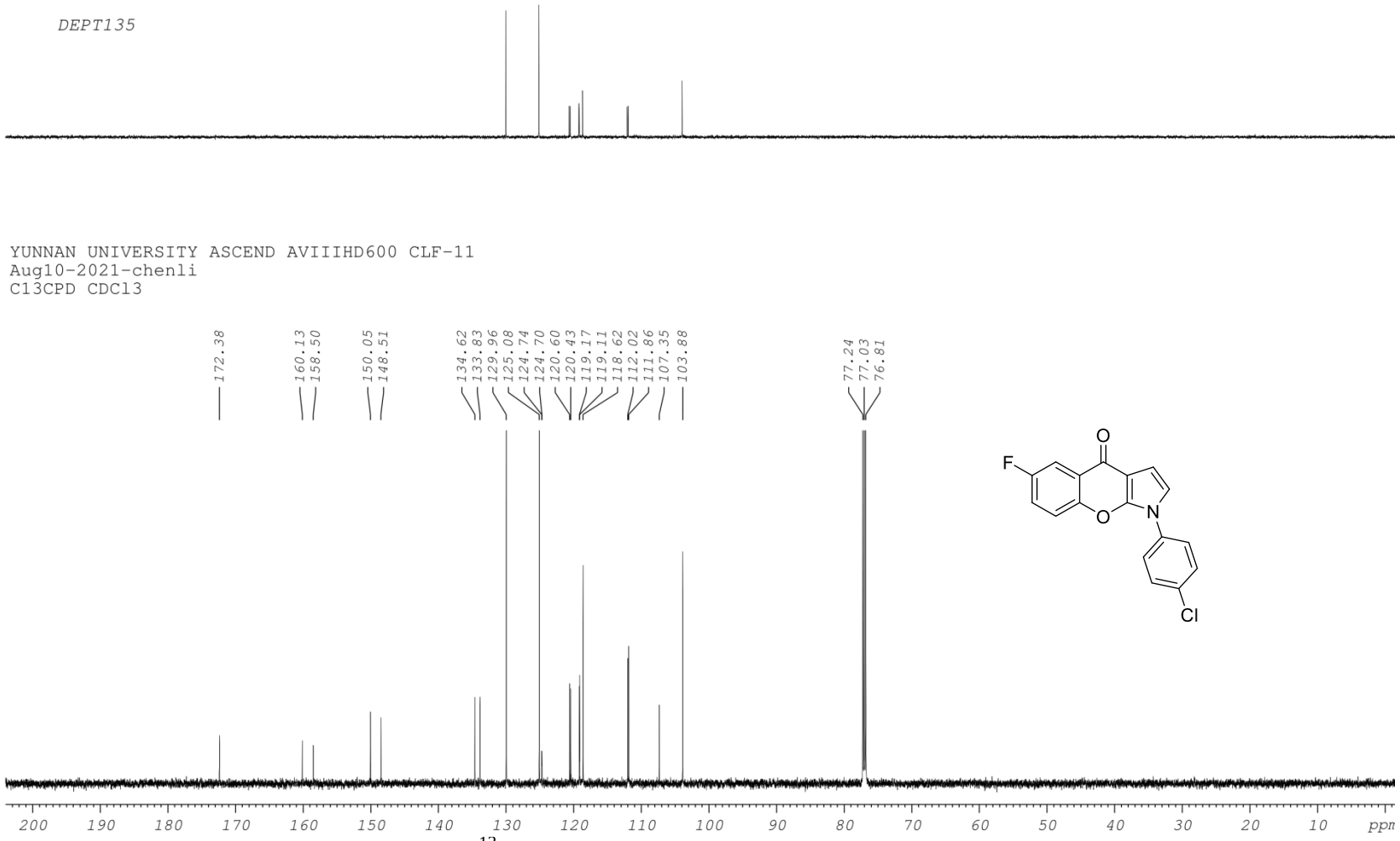


Figure S29. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3e**

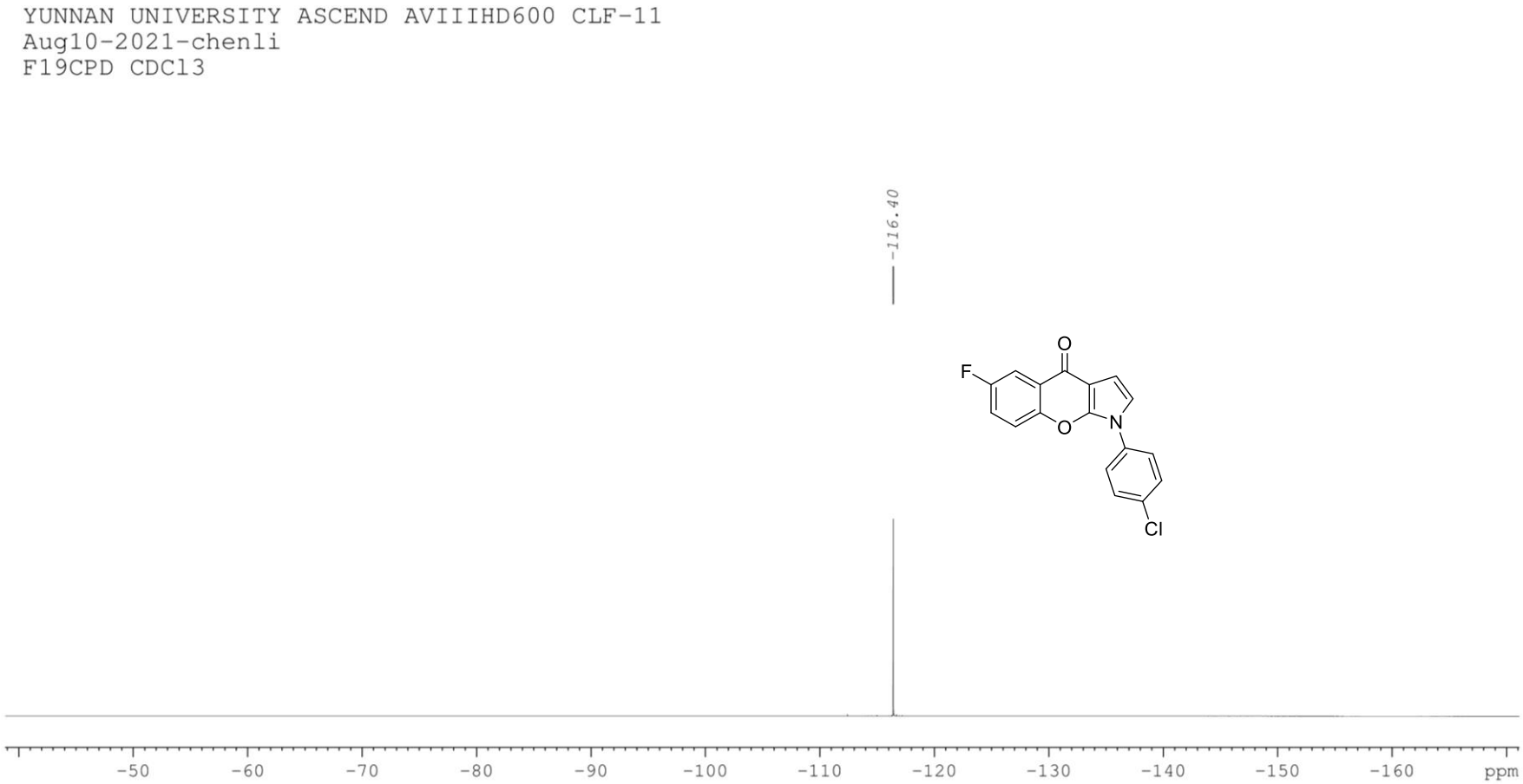


Figure S30. ^{19}F NMR (**564** MHz, $CDCl_3$) spectra of compound **3e**

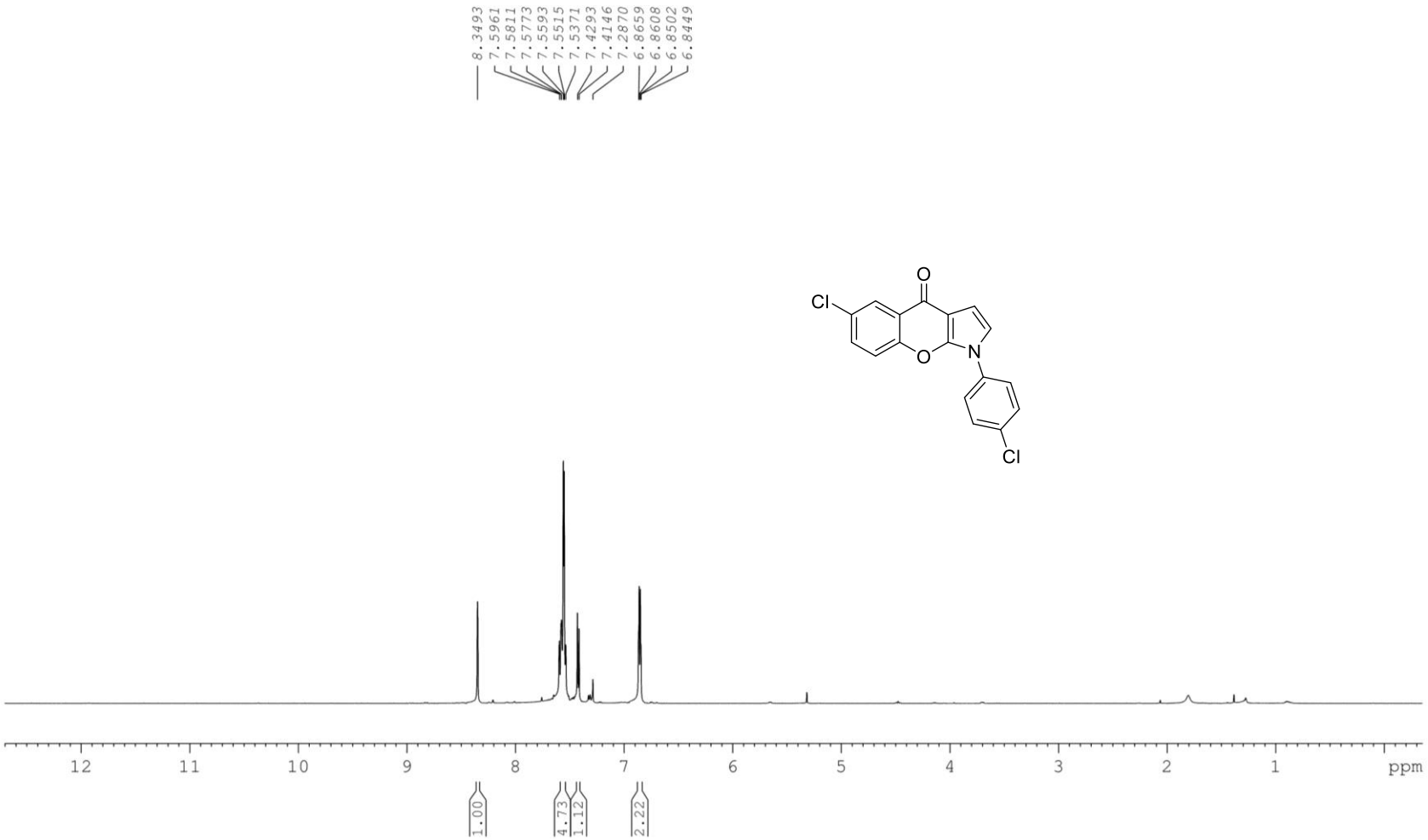


Figure S31. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3f**

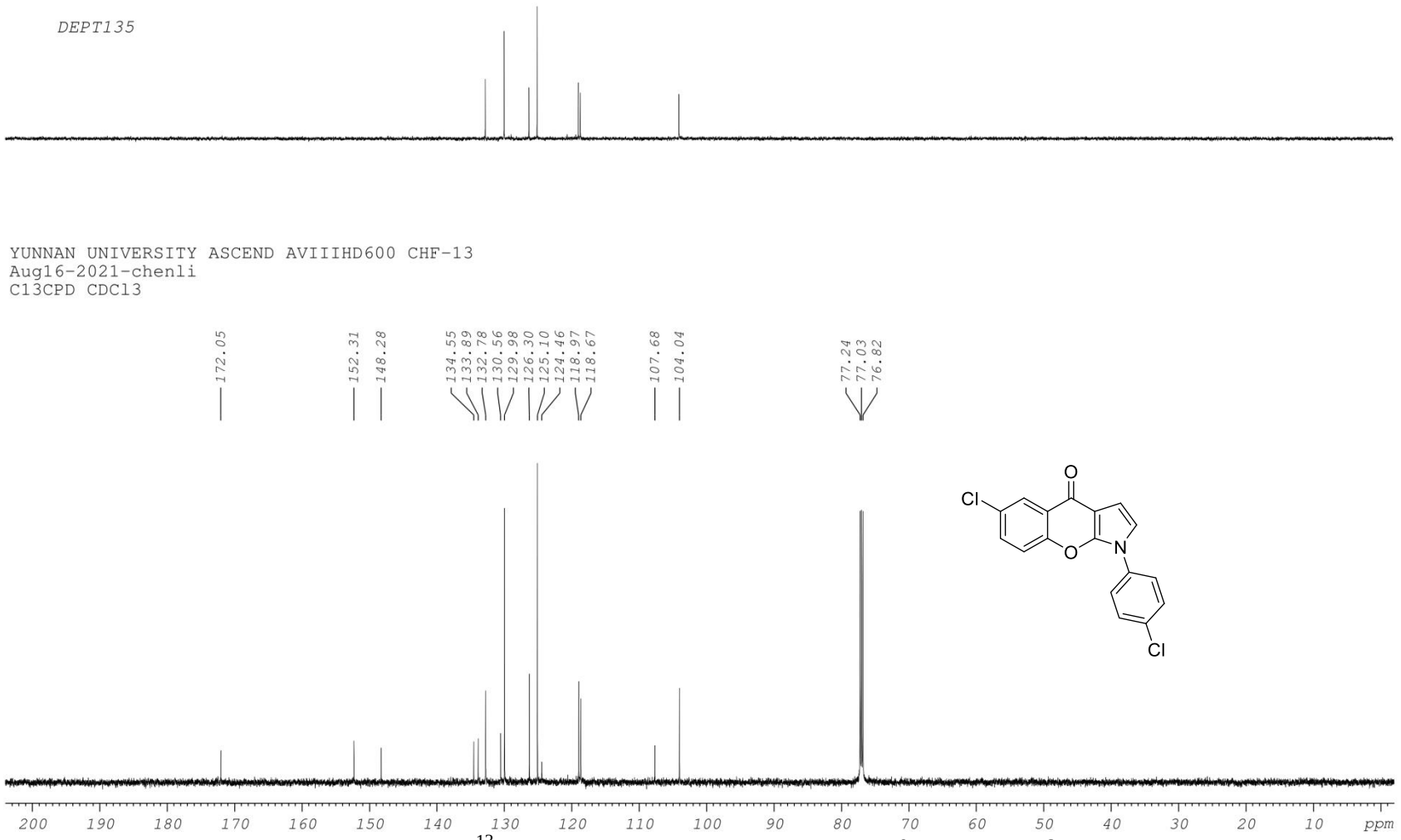


Figure S32. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3f**

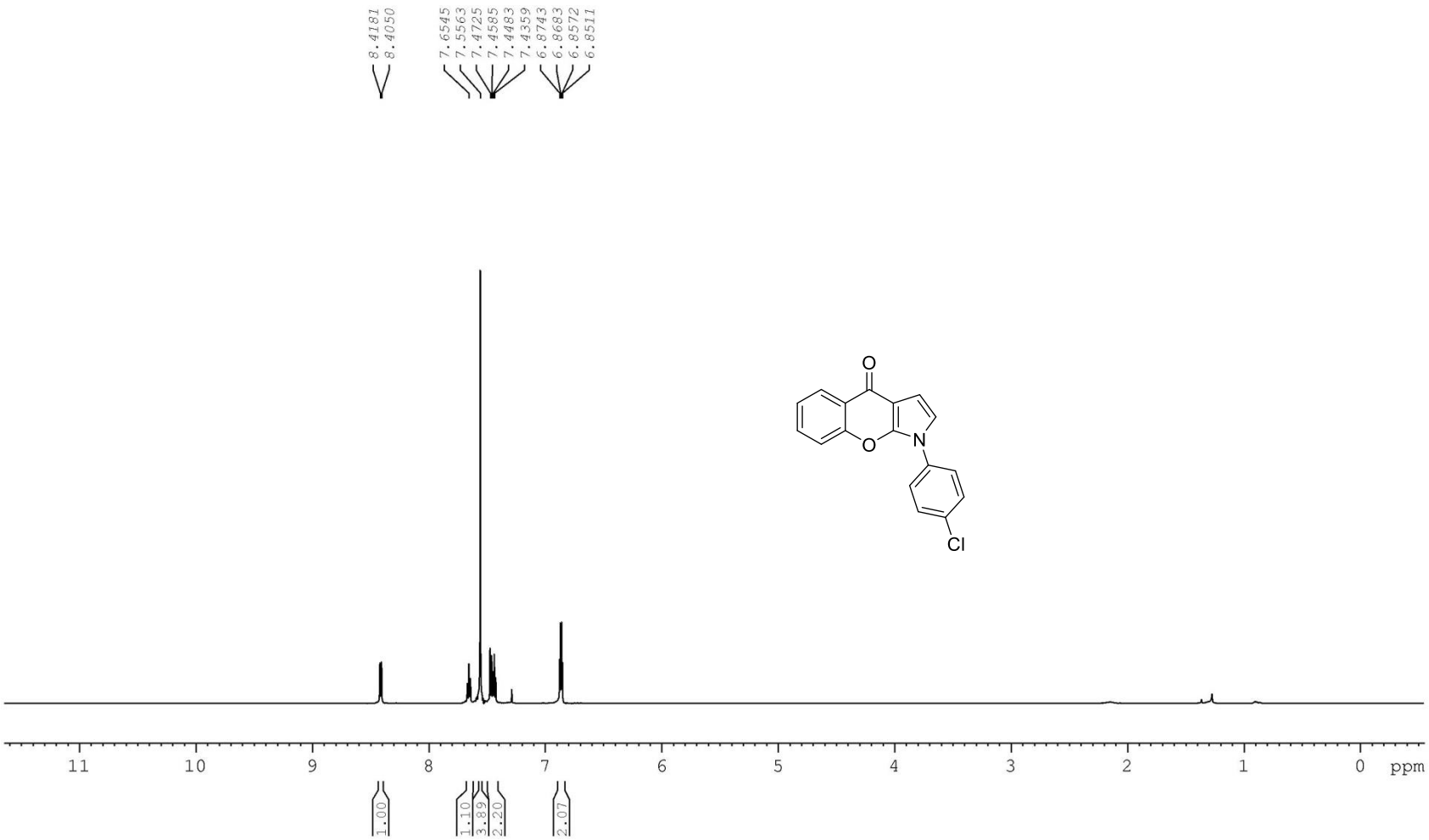


Figure S33. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3g**

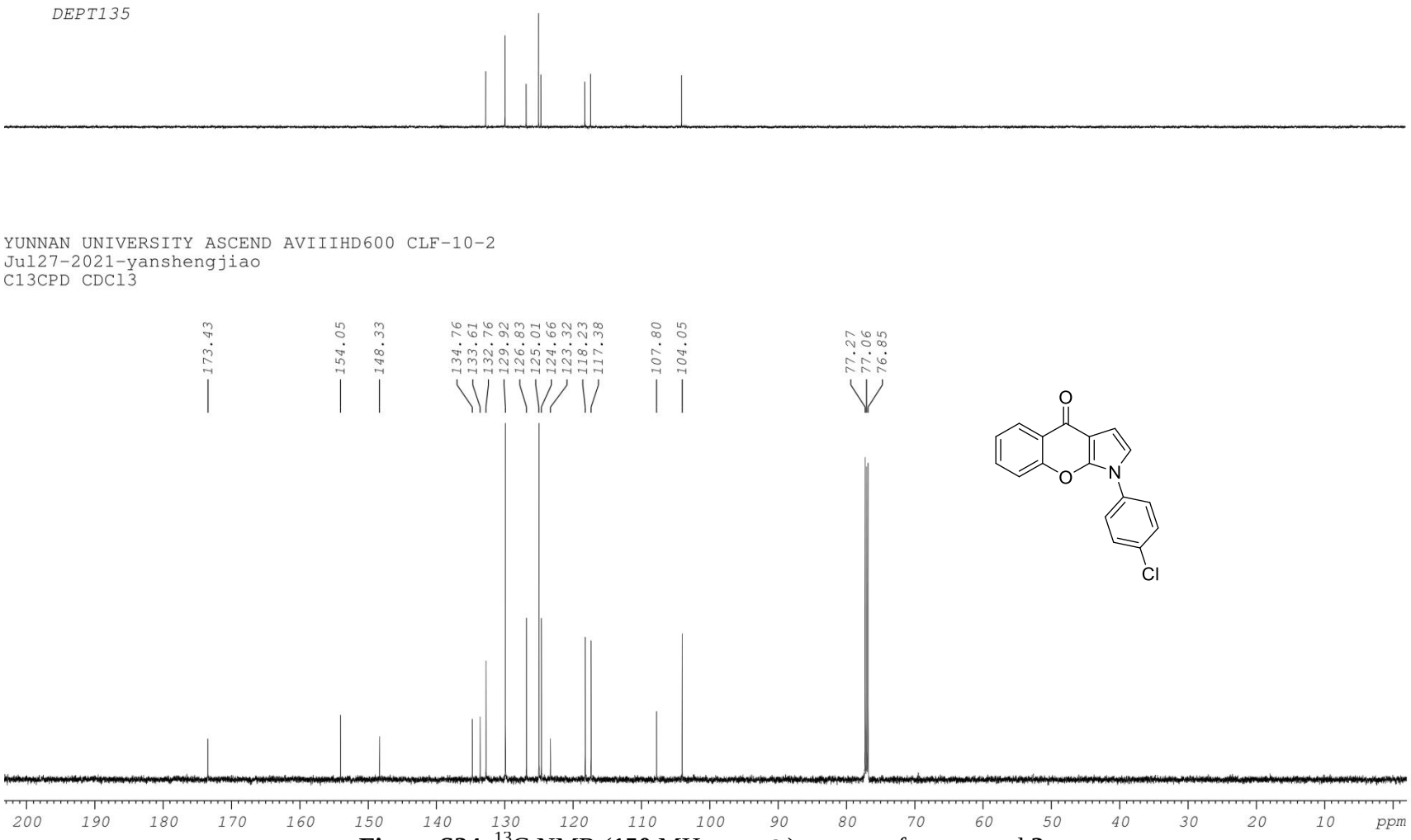


Figure S34. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3g**

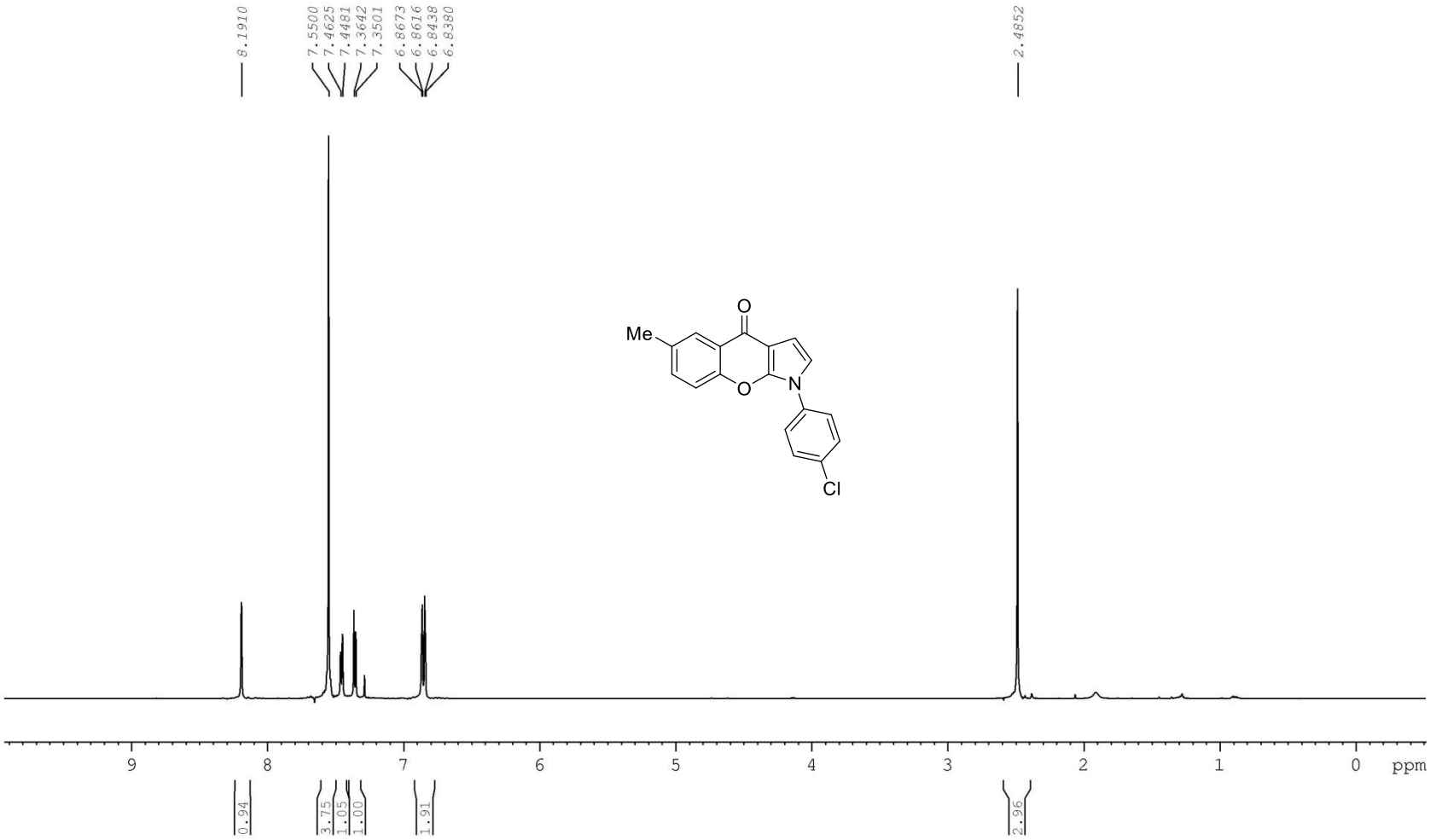


Figure S35. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3h**

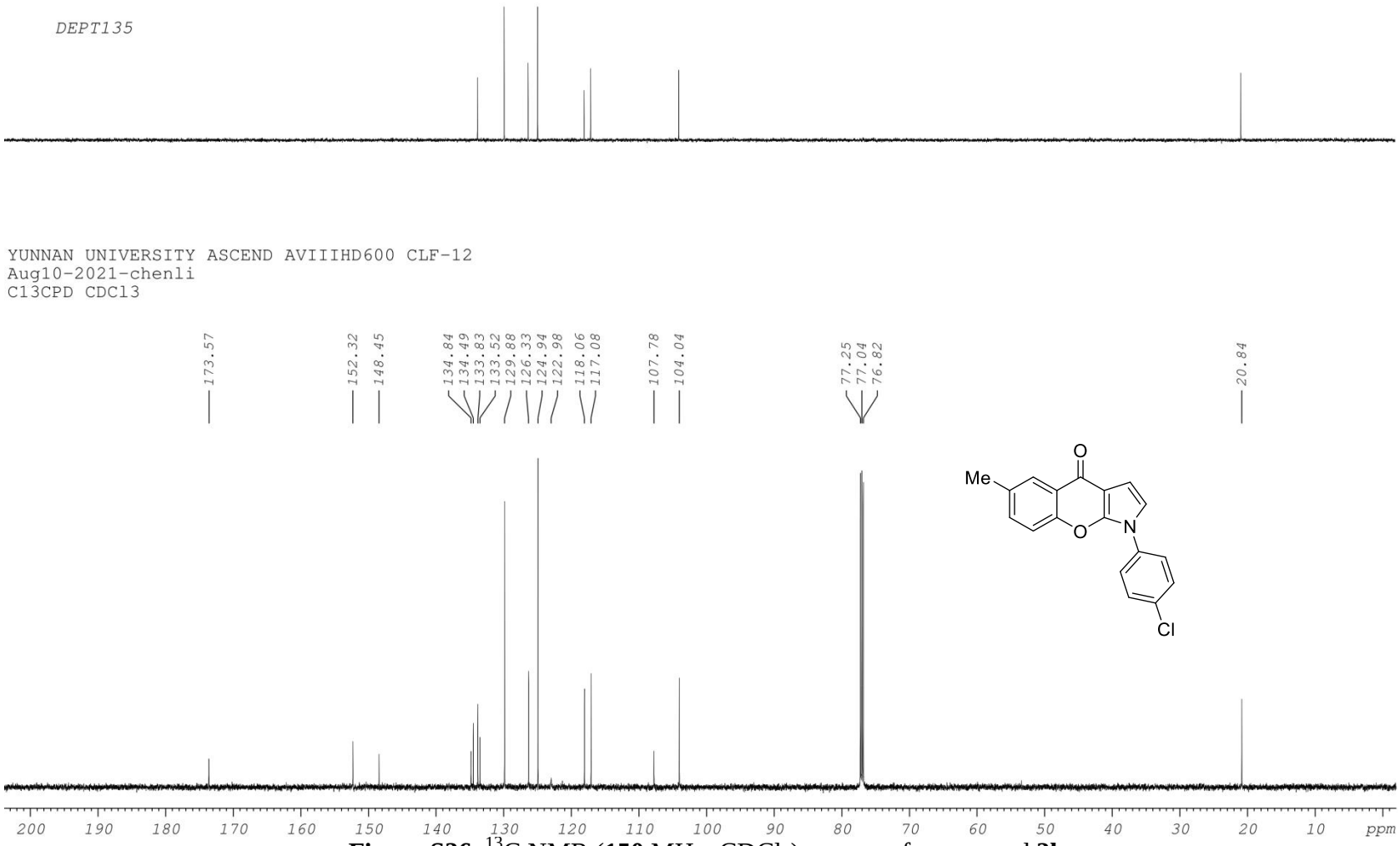


Figure S36. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3h**

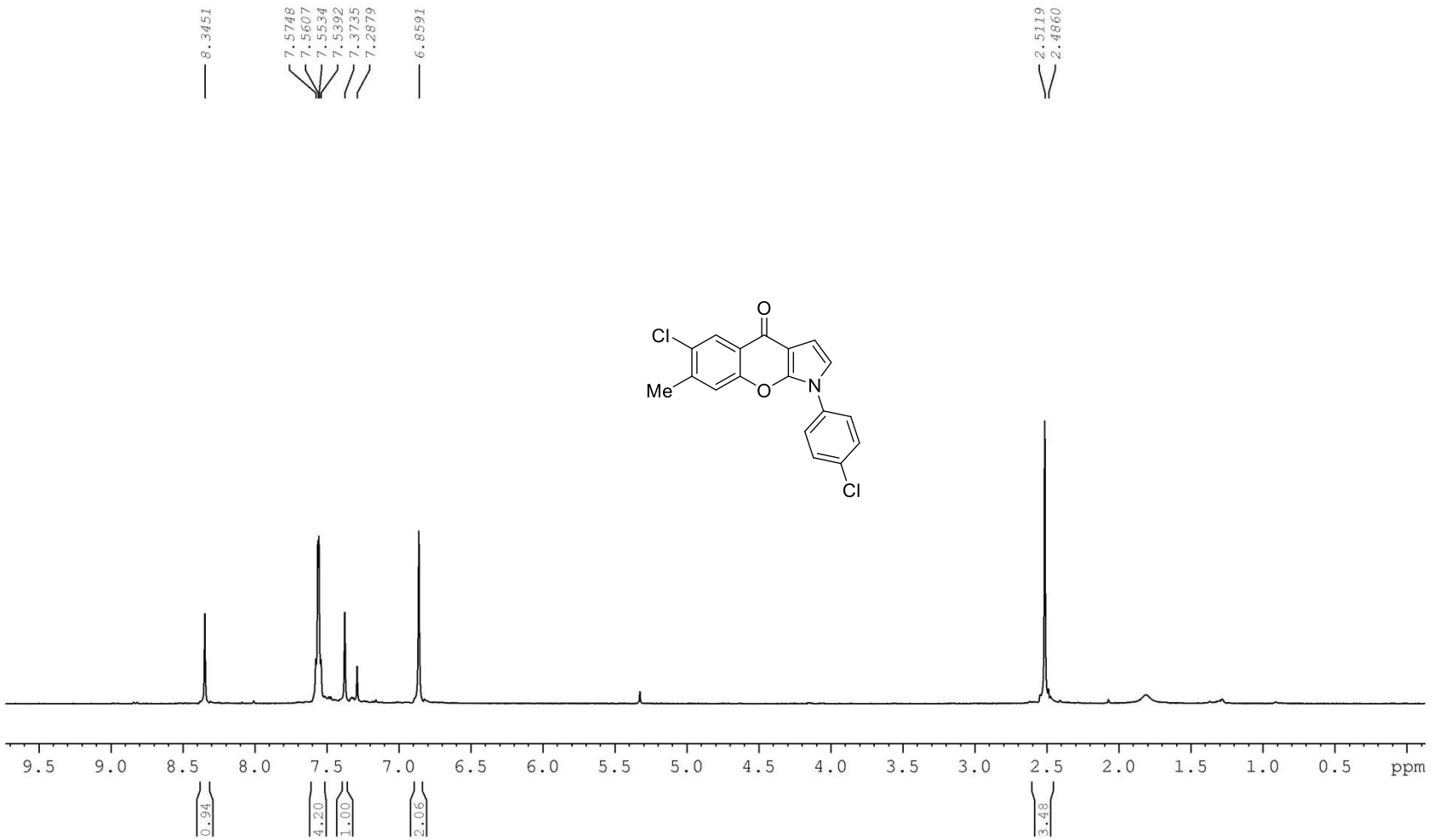


Figure S37. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3i**

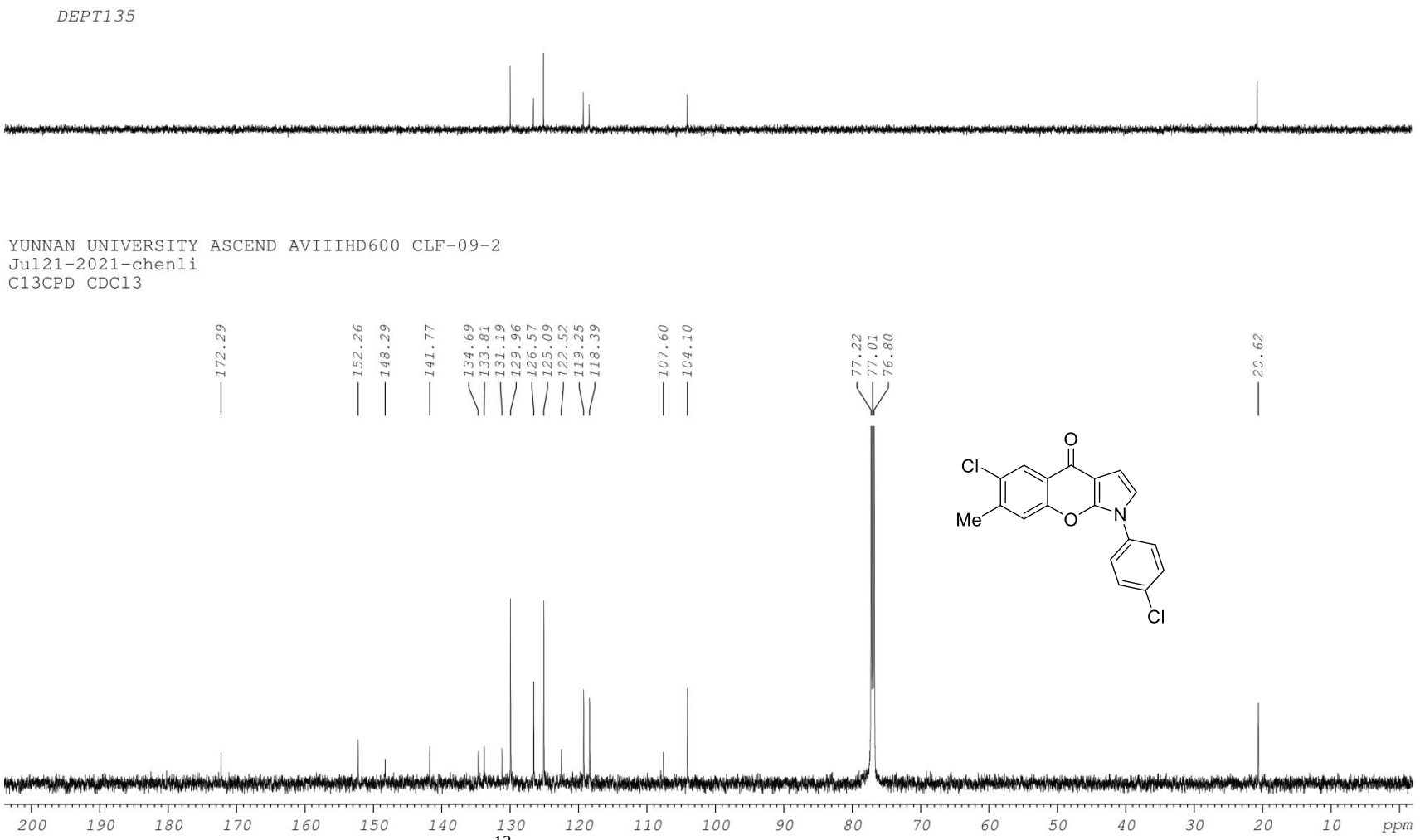


Figure S38. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3i**

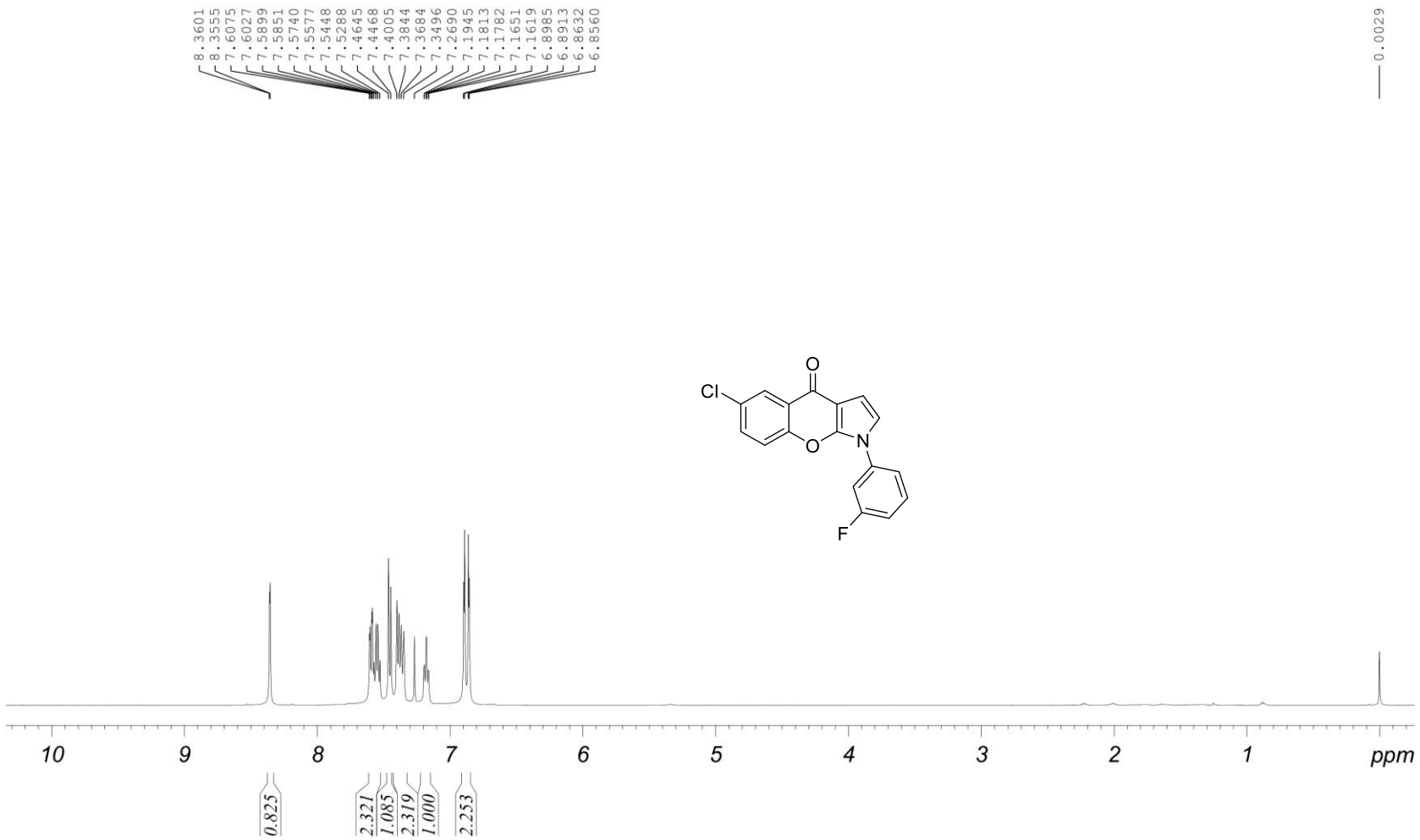


Figure S39. ^{1}H NMR (**500** MHz, $CDCl_3$) spectra of compound **3j**

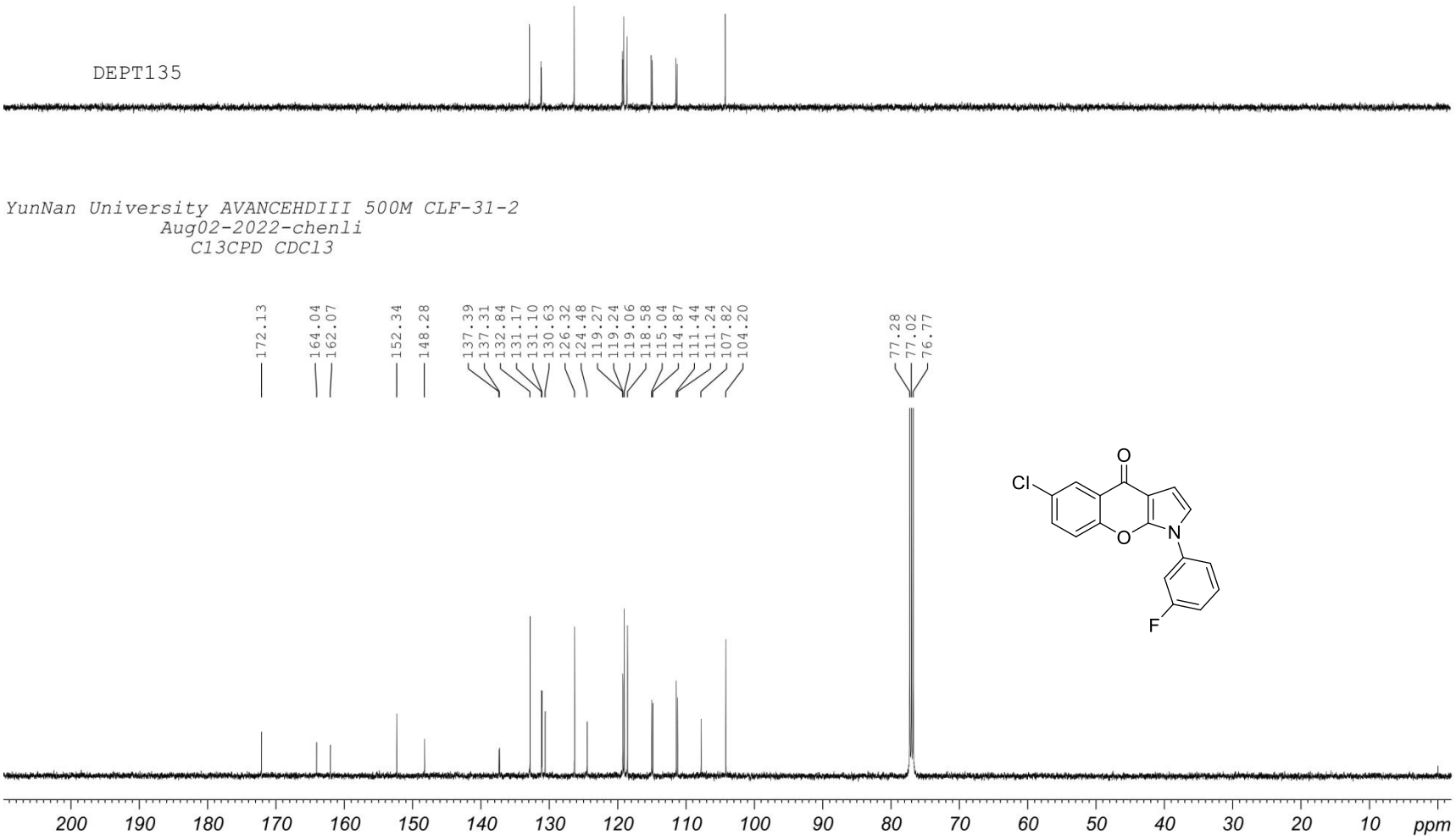


Figure S40. ^{13}C NMR (**125** MHz, $CDCl_3$) spectra of compound **3j**

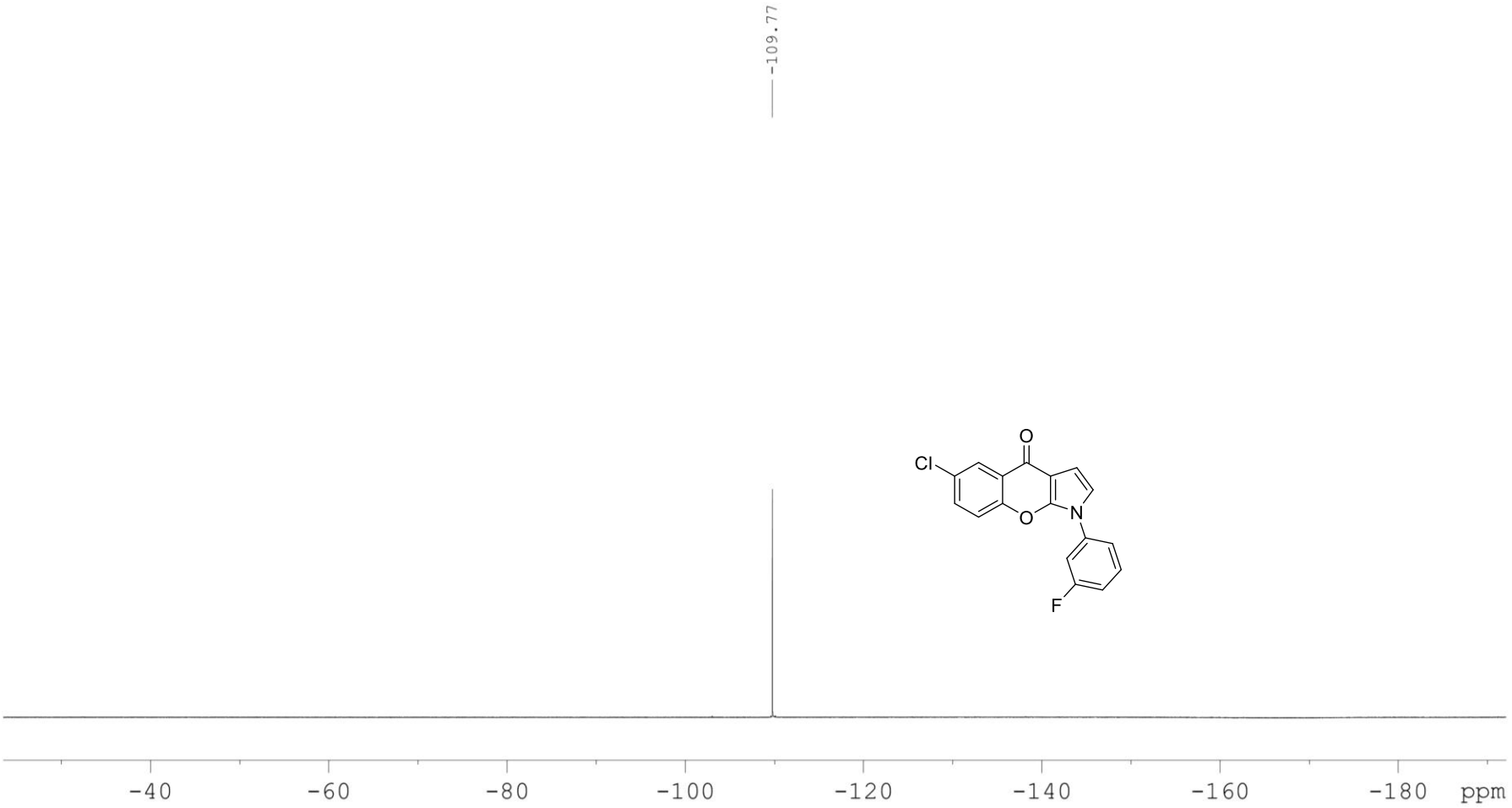


Figure S41. ^{19}F NMR (**470** MHz, $CDCl_3$) spectra of compound **3j**

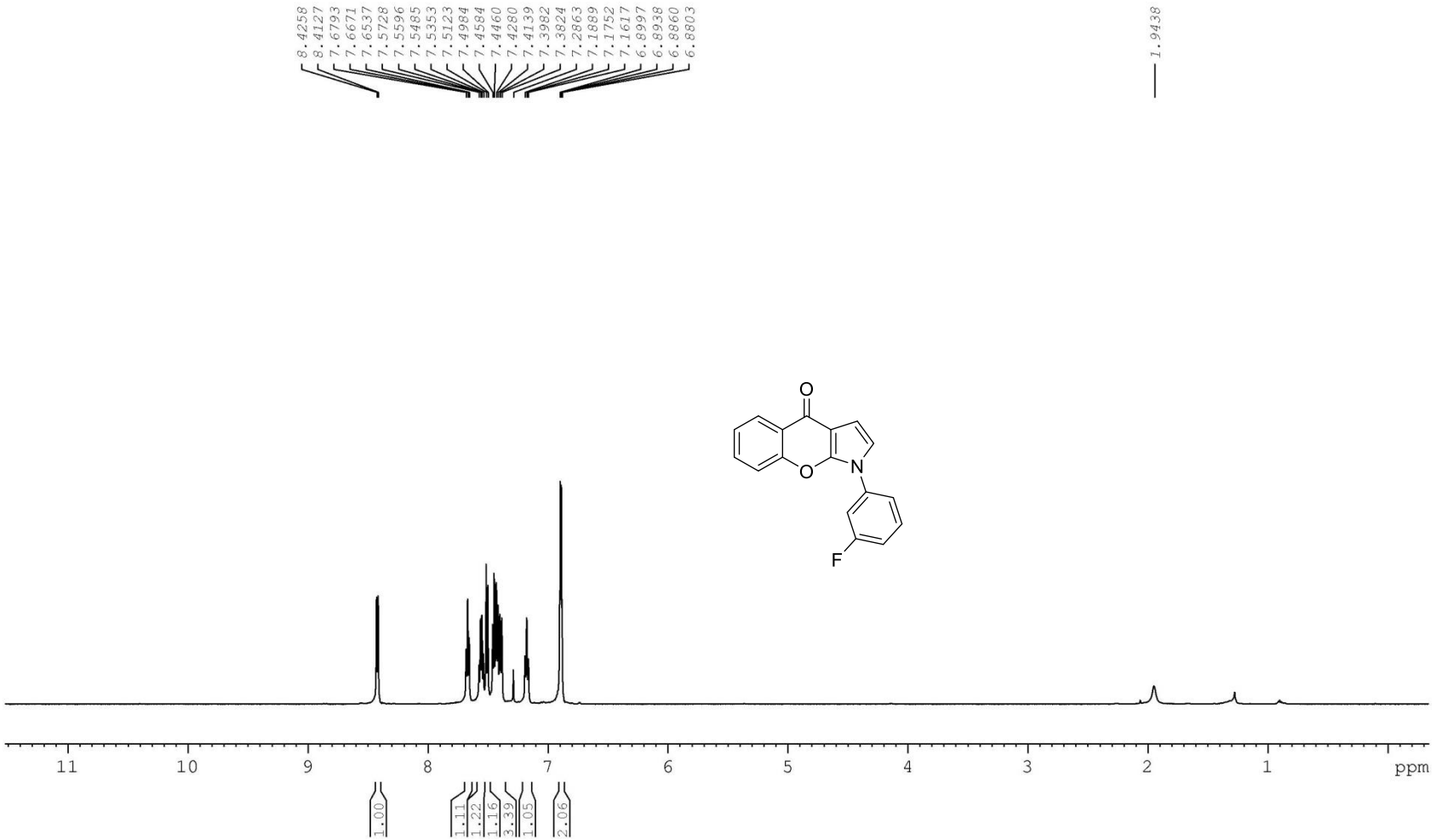


Figure S42. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3k**

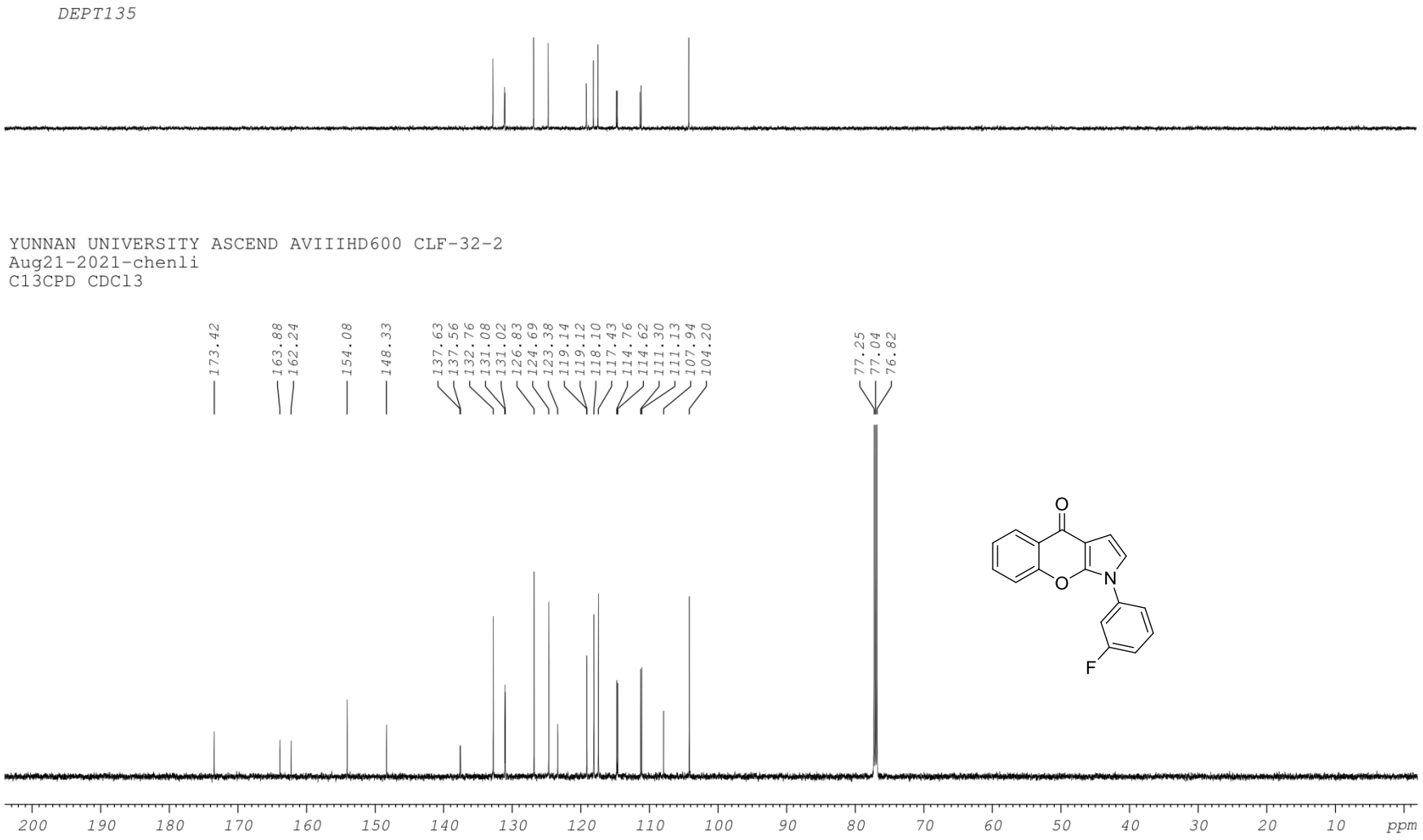


Figure S43. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3k**

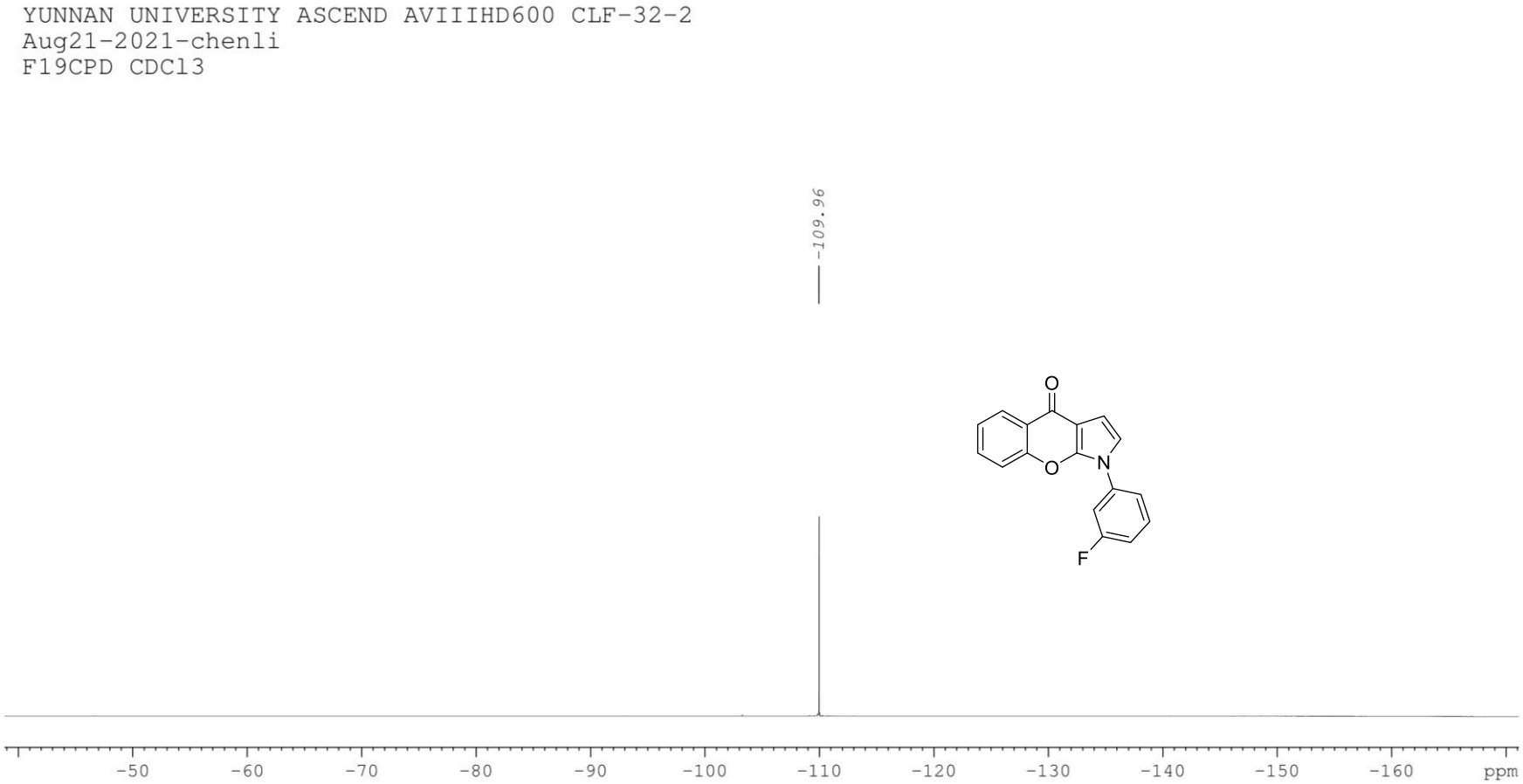


Figure S44. ^{19}F NMR (**564** MHz, $CDCl_3$) spectra of compound **3k**

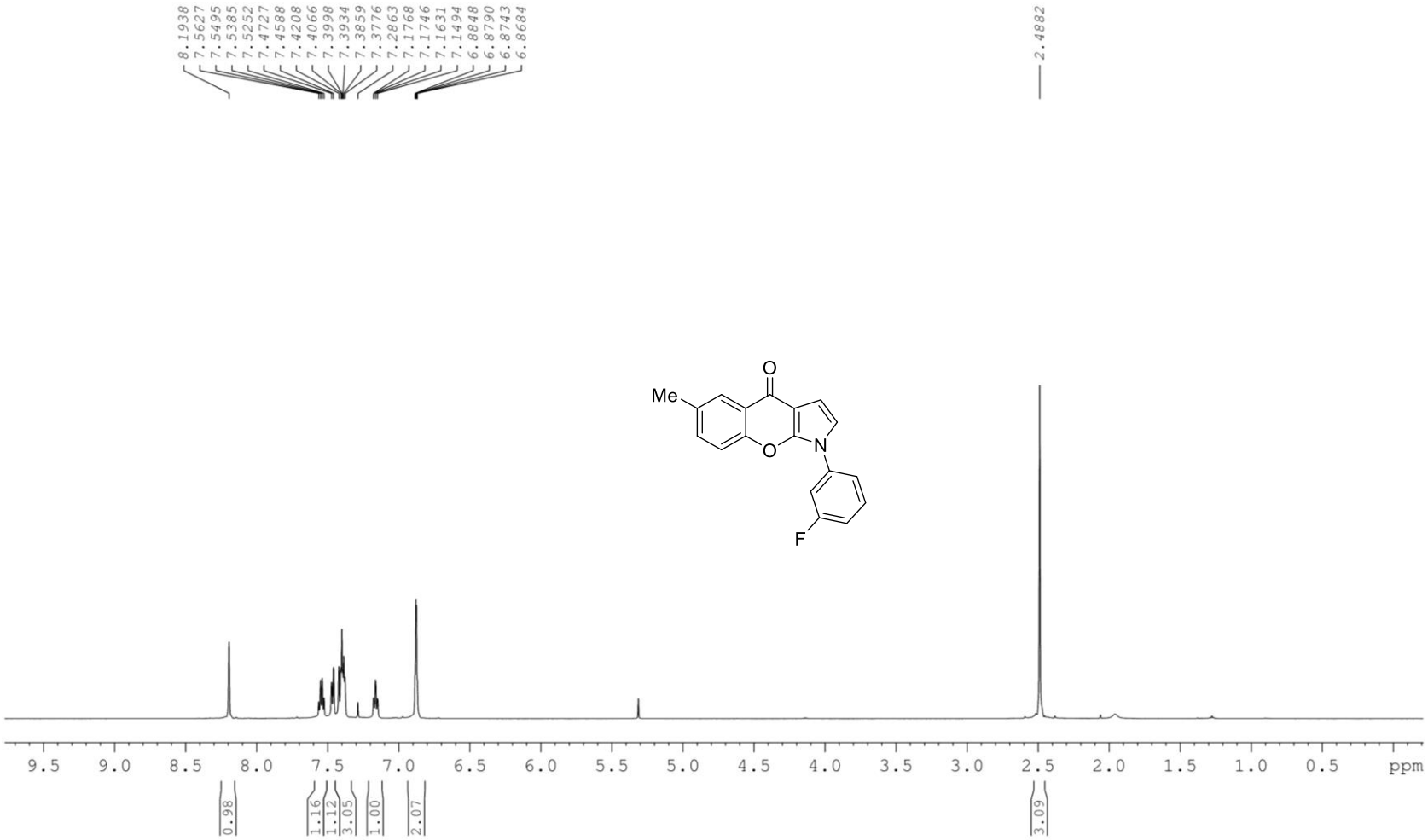


Figure S45. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3l**

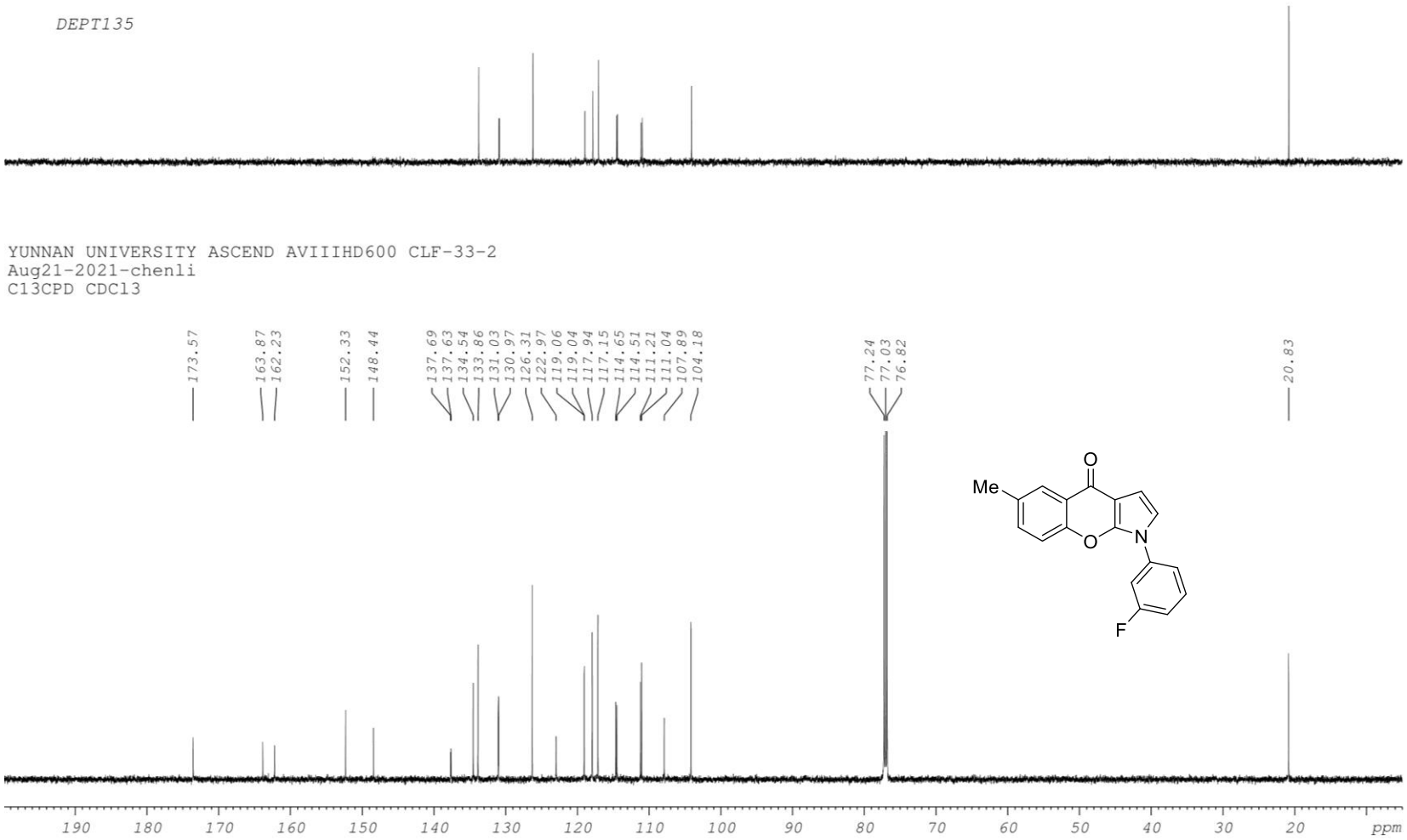


Figure S46. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3l**

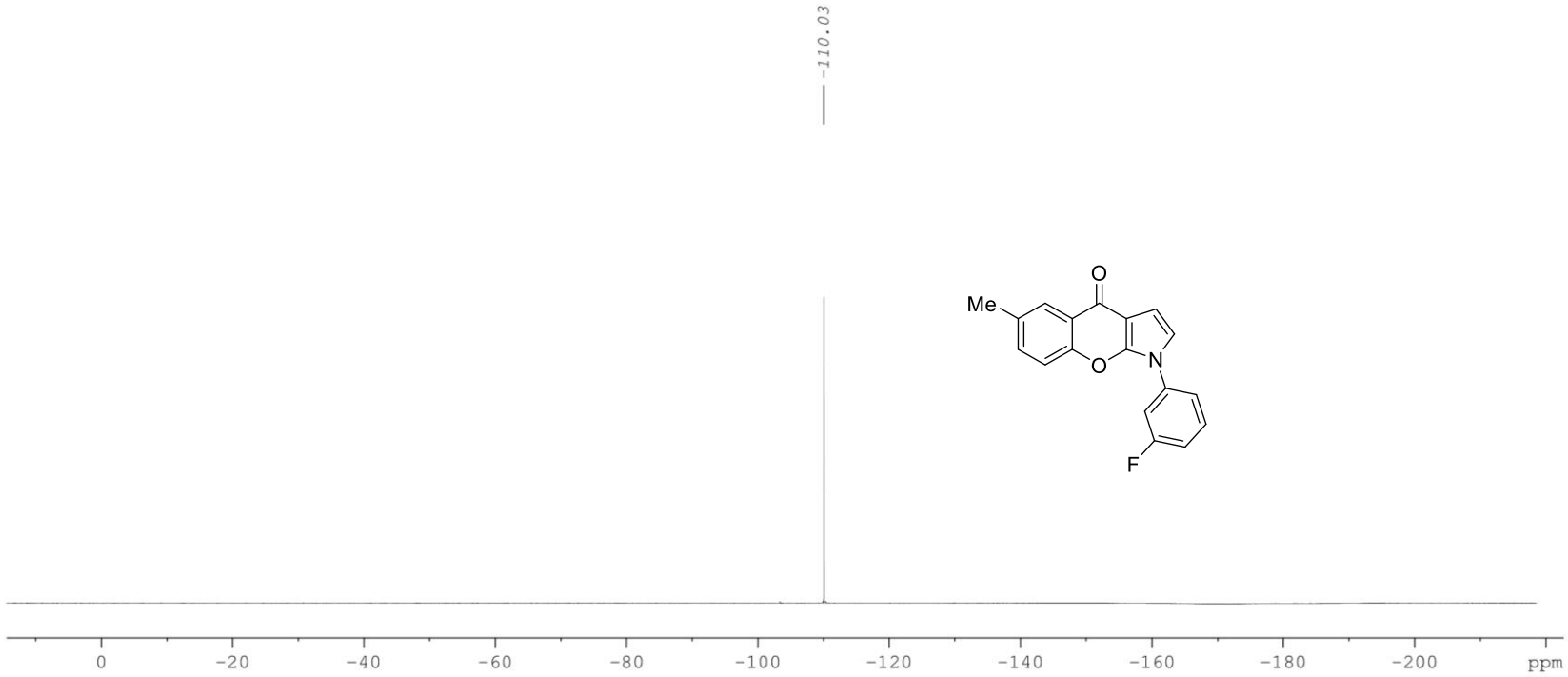


Figure S47. ^{19}F NMR (**564** MHz, $CDCl_3$) spectra of compound **3l**

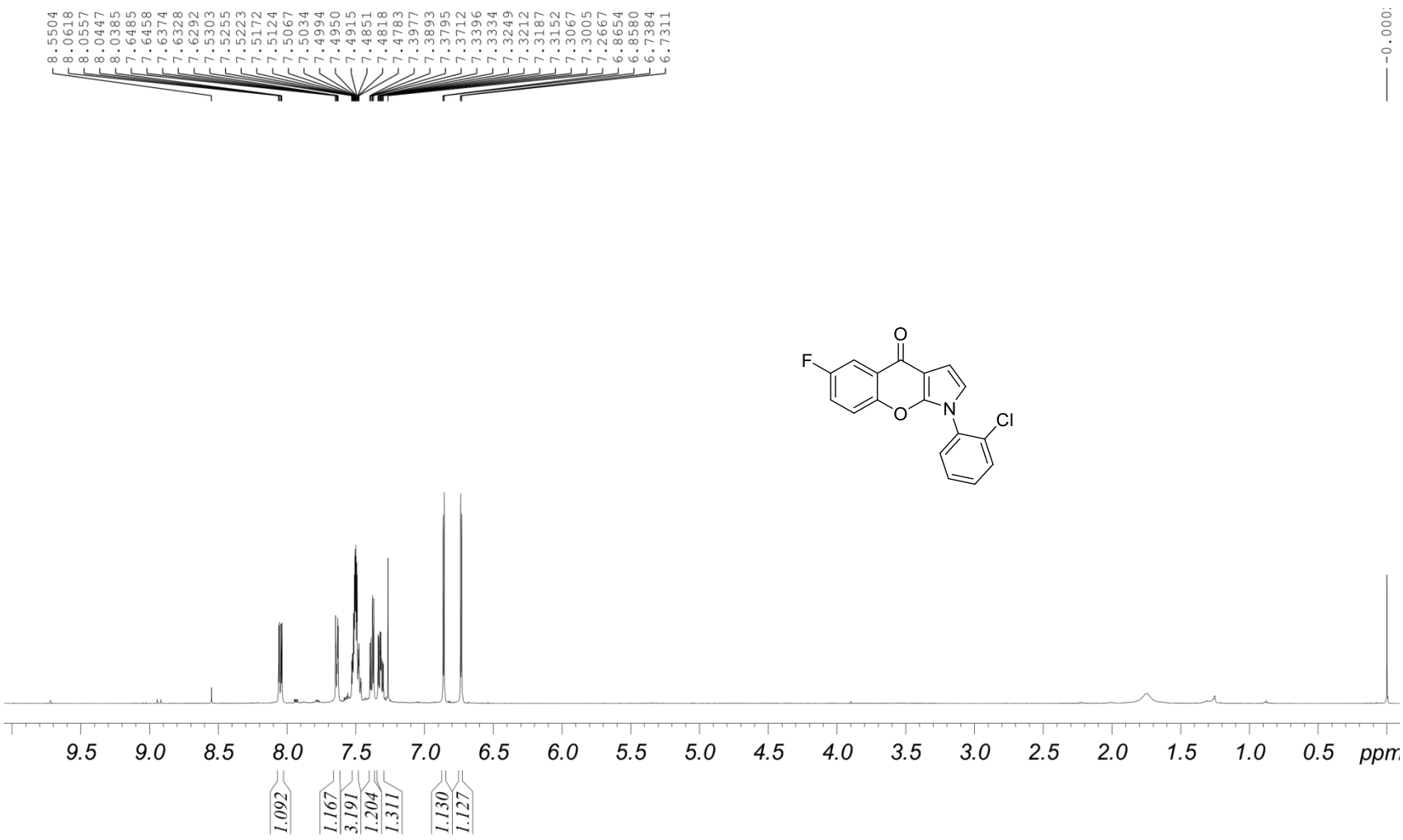


Figure S48. ^{1}H NMR (**500** MHz, $CDCl_3$) spectra of compound **3m**

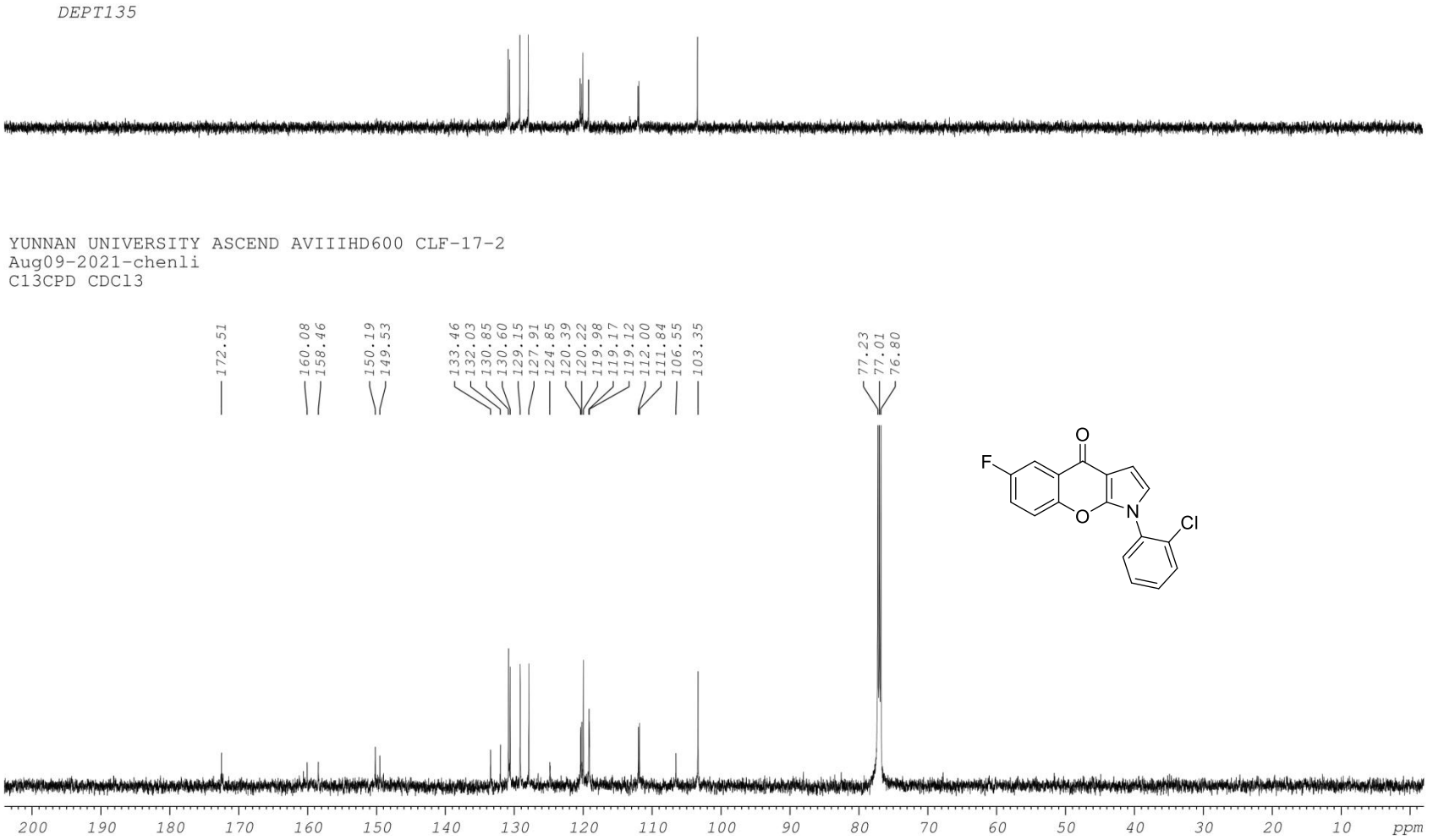


Figure S49. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3m**

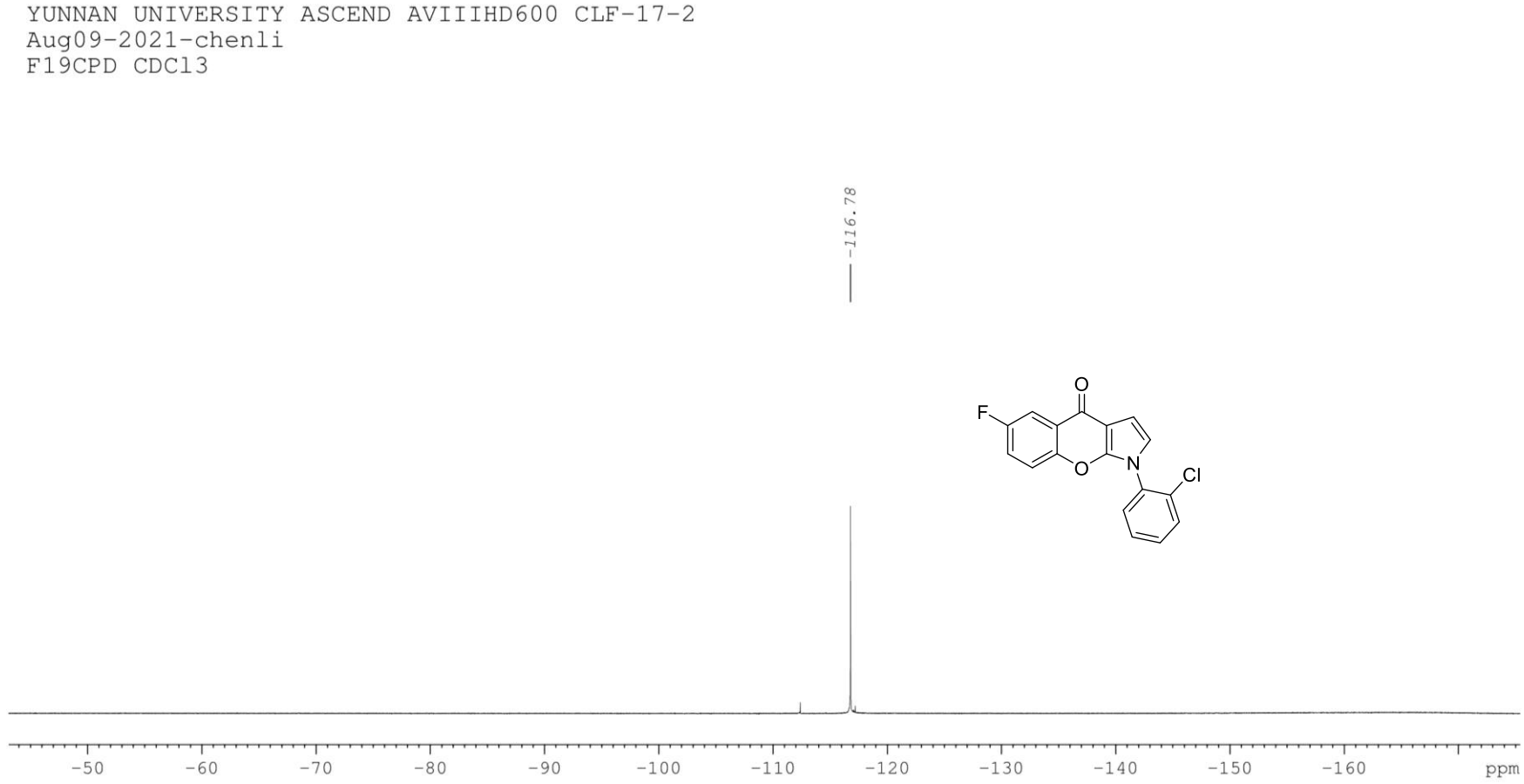


Figure S50. ^{19}F NMR (**564** MHz, $CDCl_3$) spectra of compound **3m**

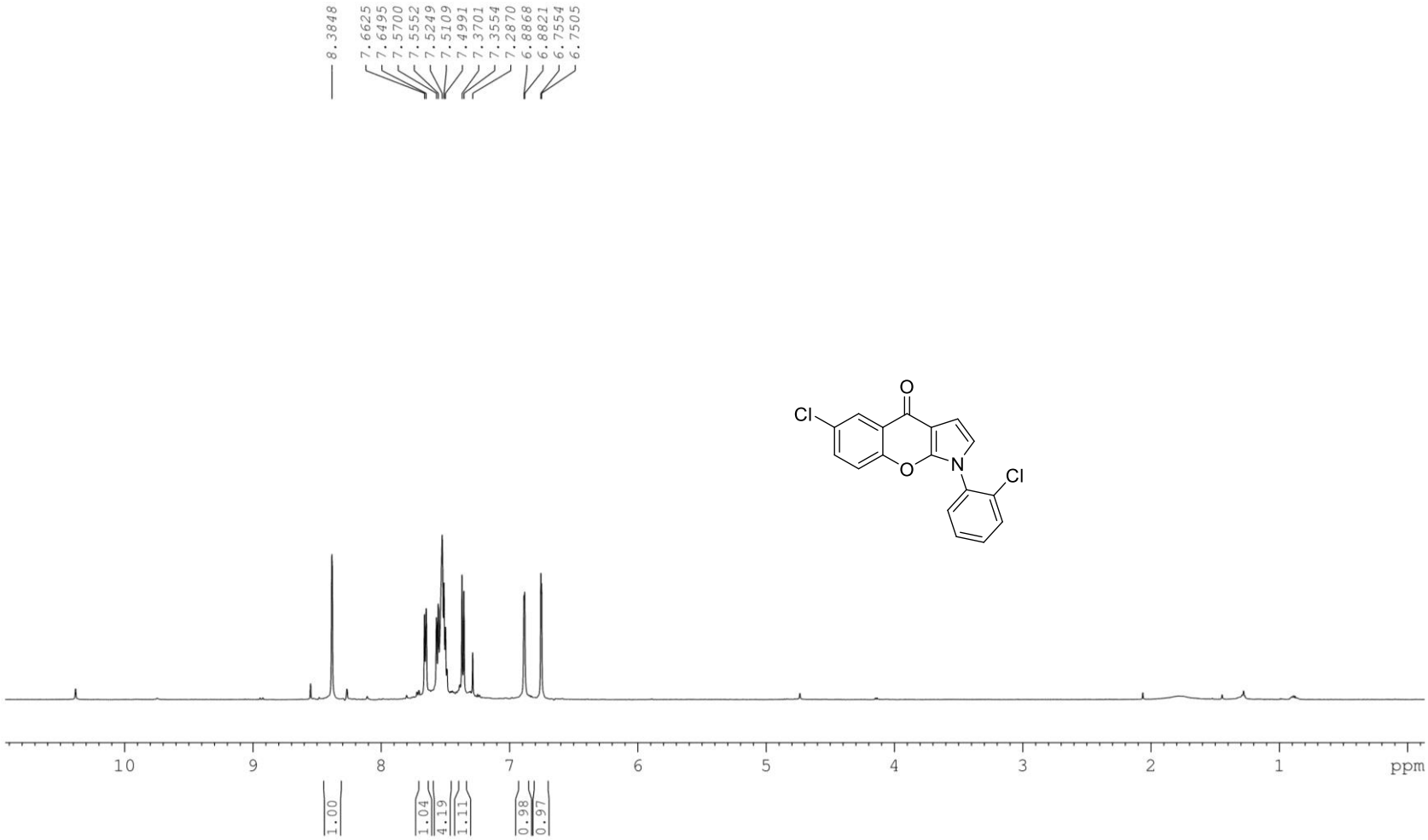


Figure S51. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3n**

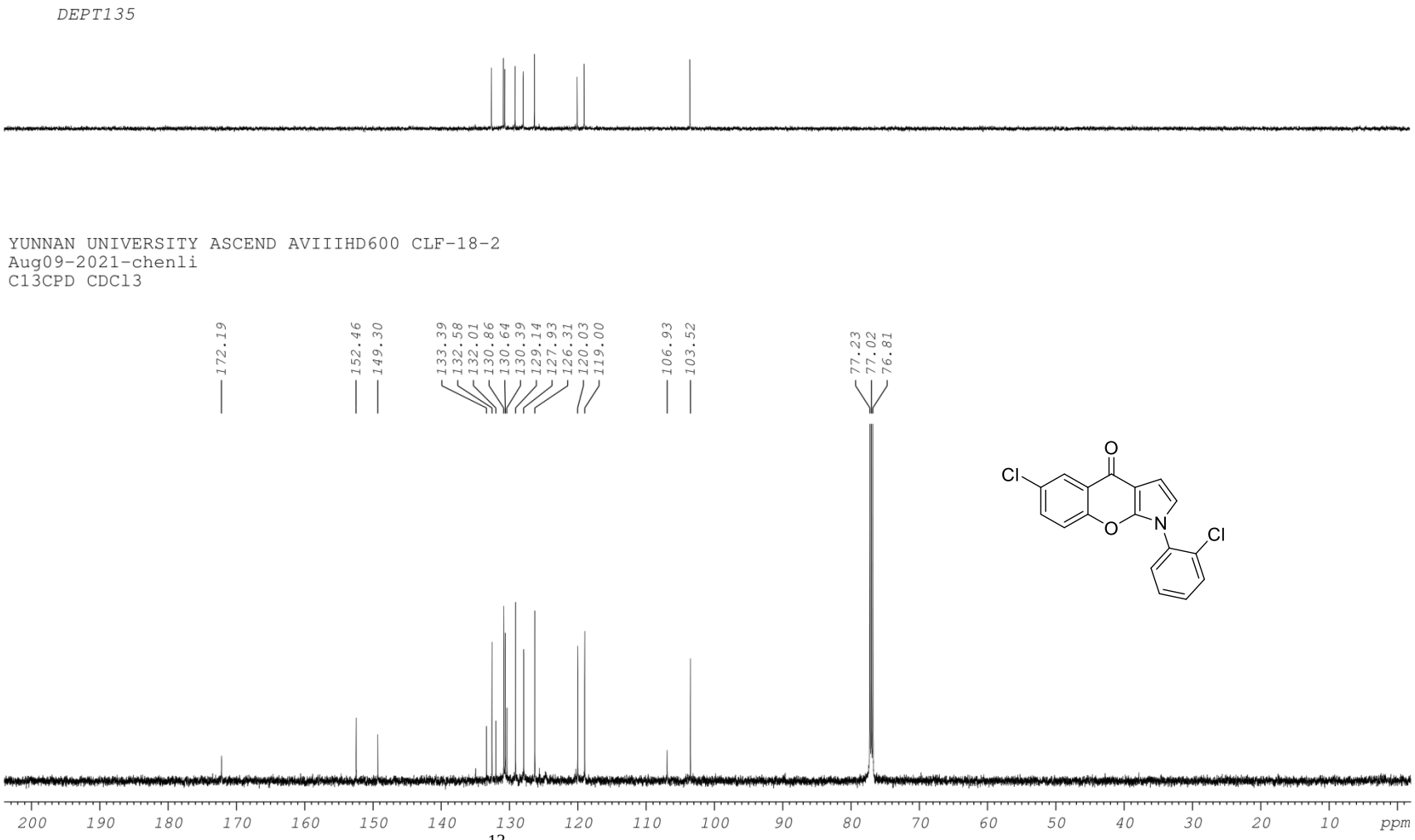


Figure S52. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3n**

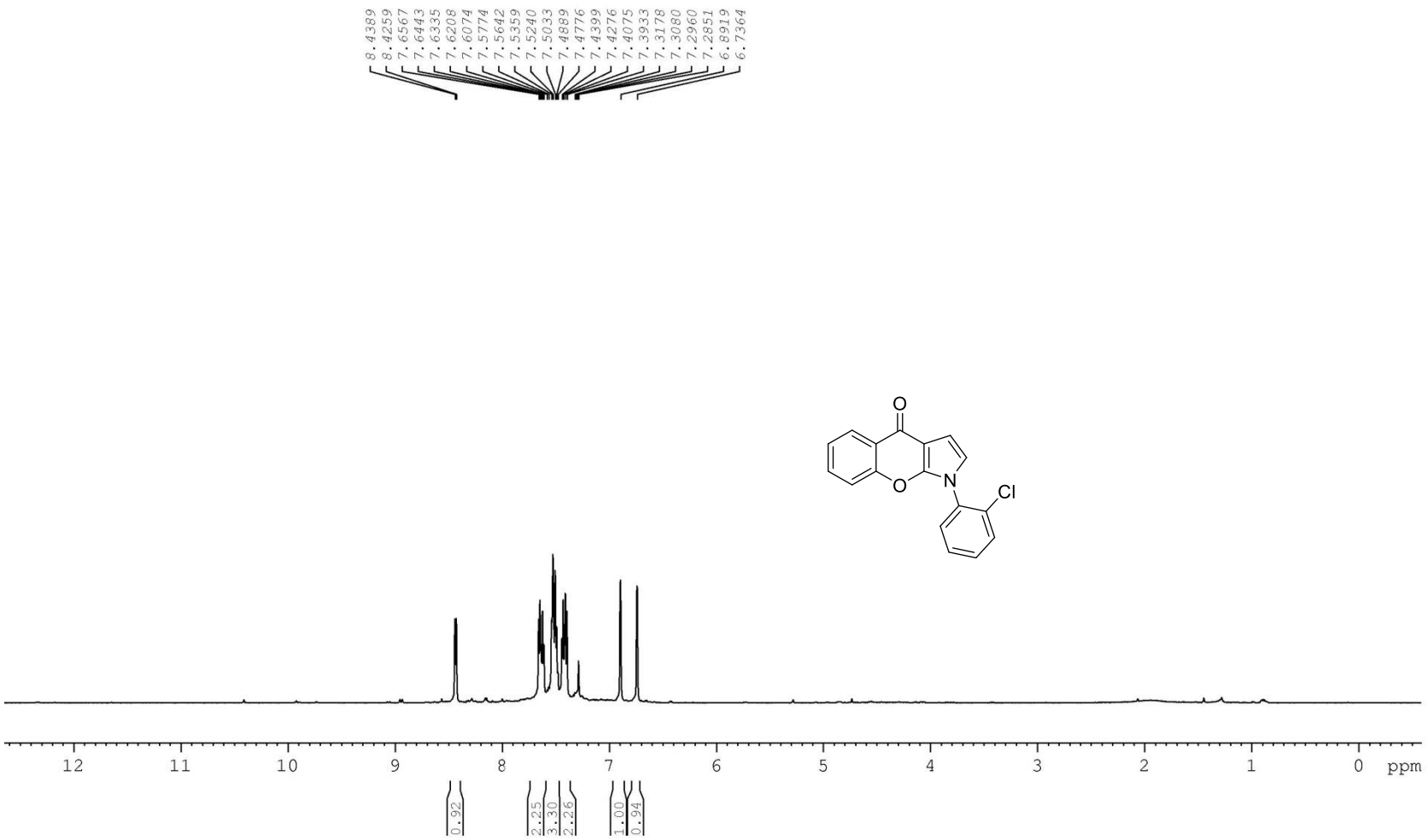


Figure S53. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3o**

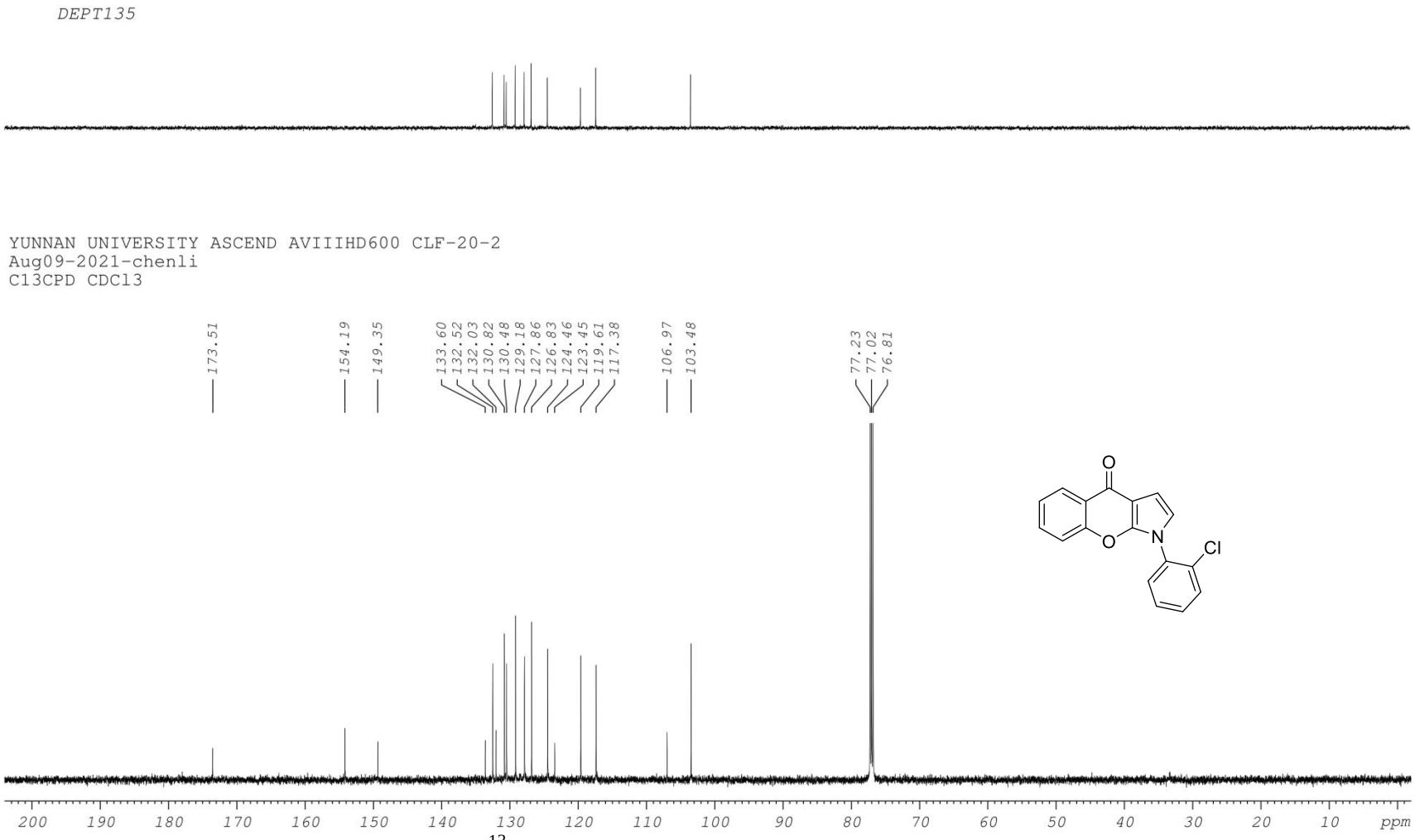


Figure S54. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3o**

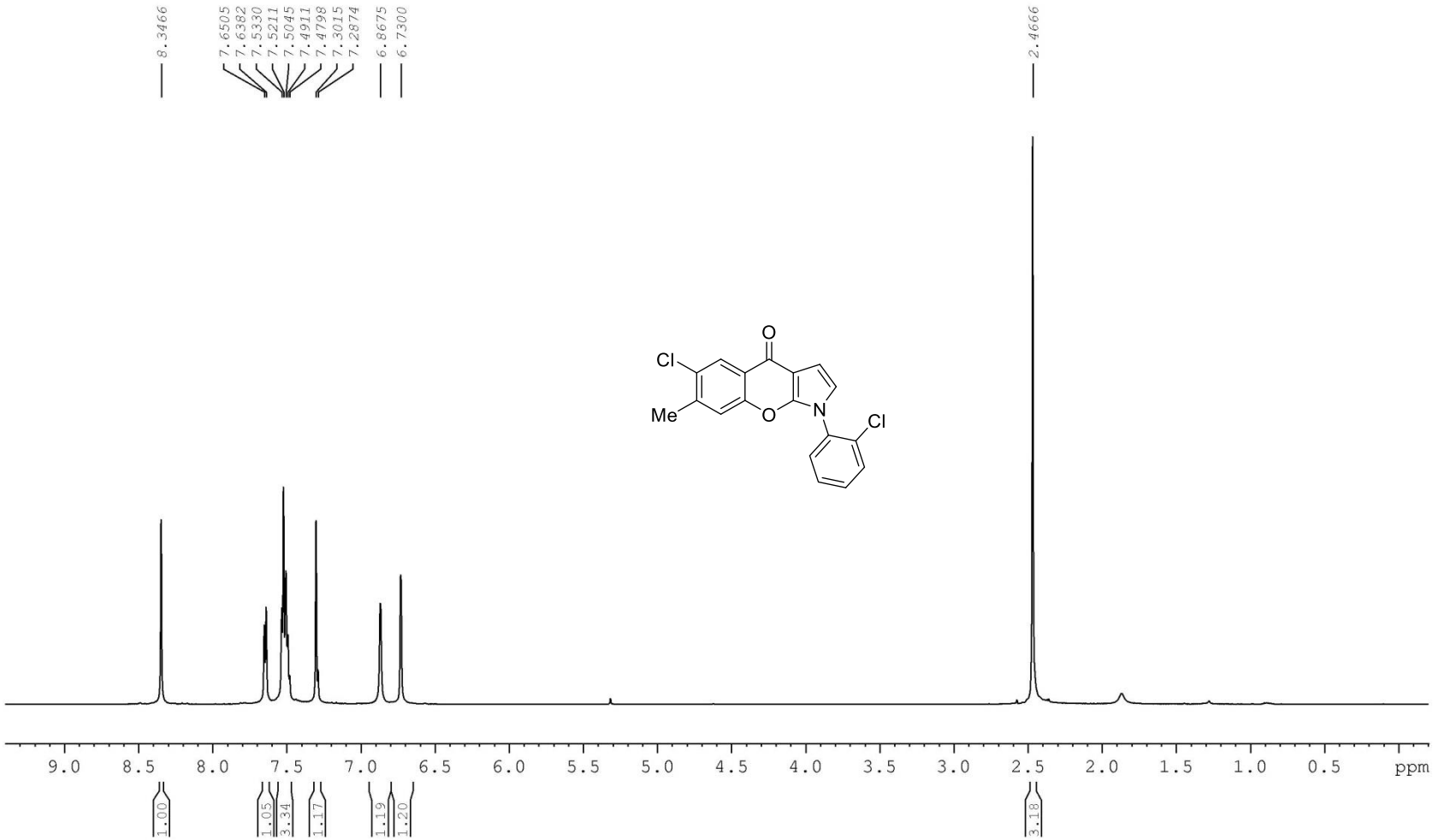


Figure S55. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3p**

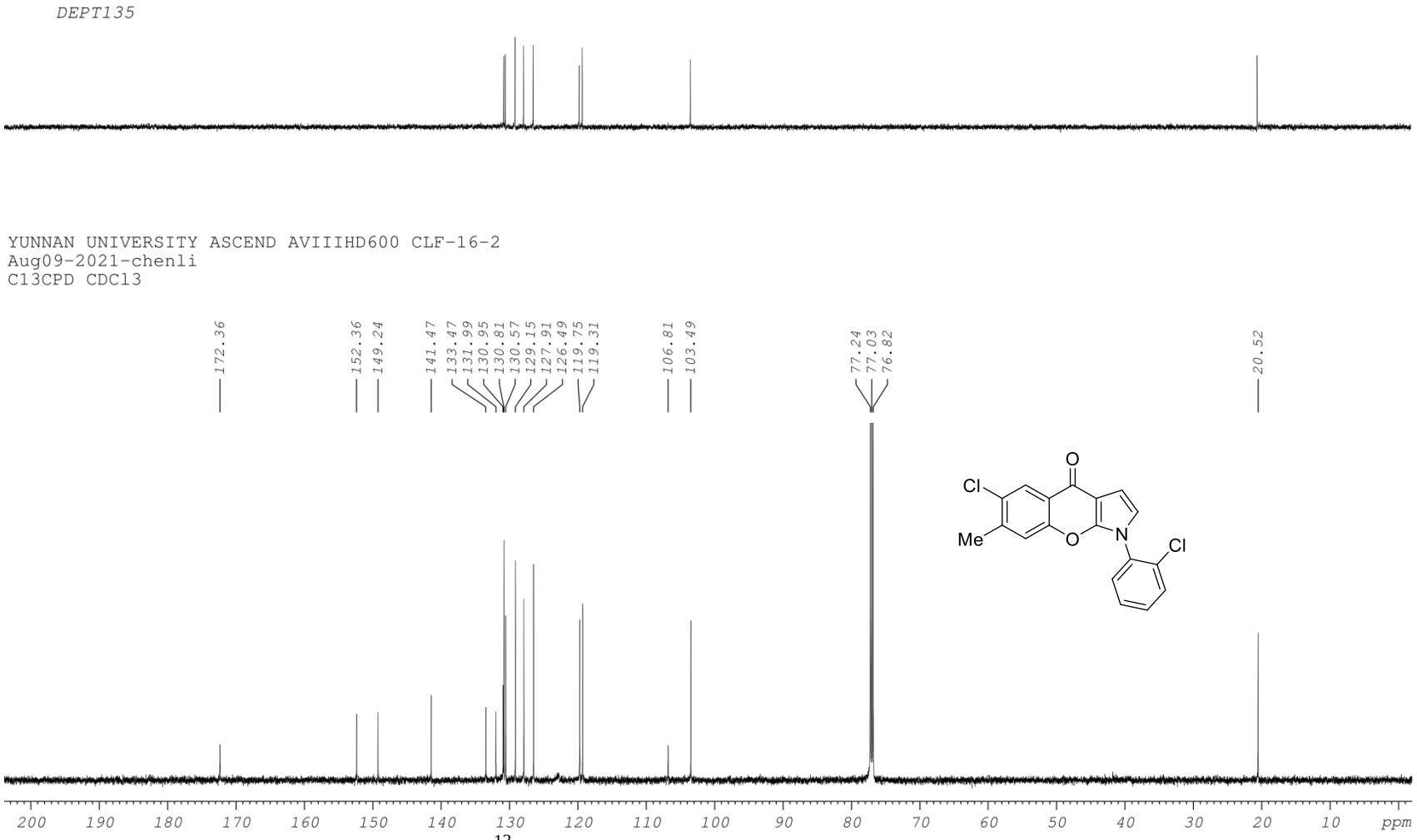


Figure S56. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3p**

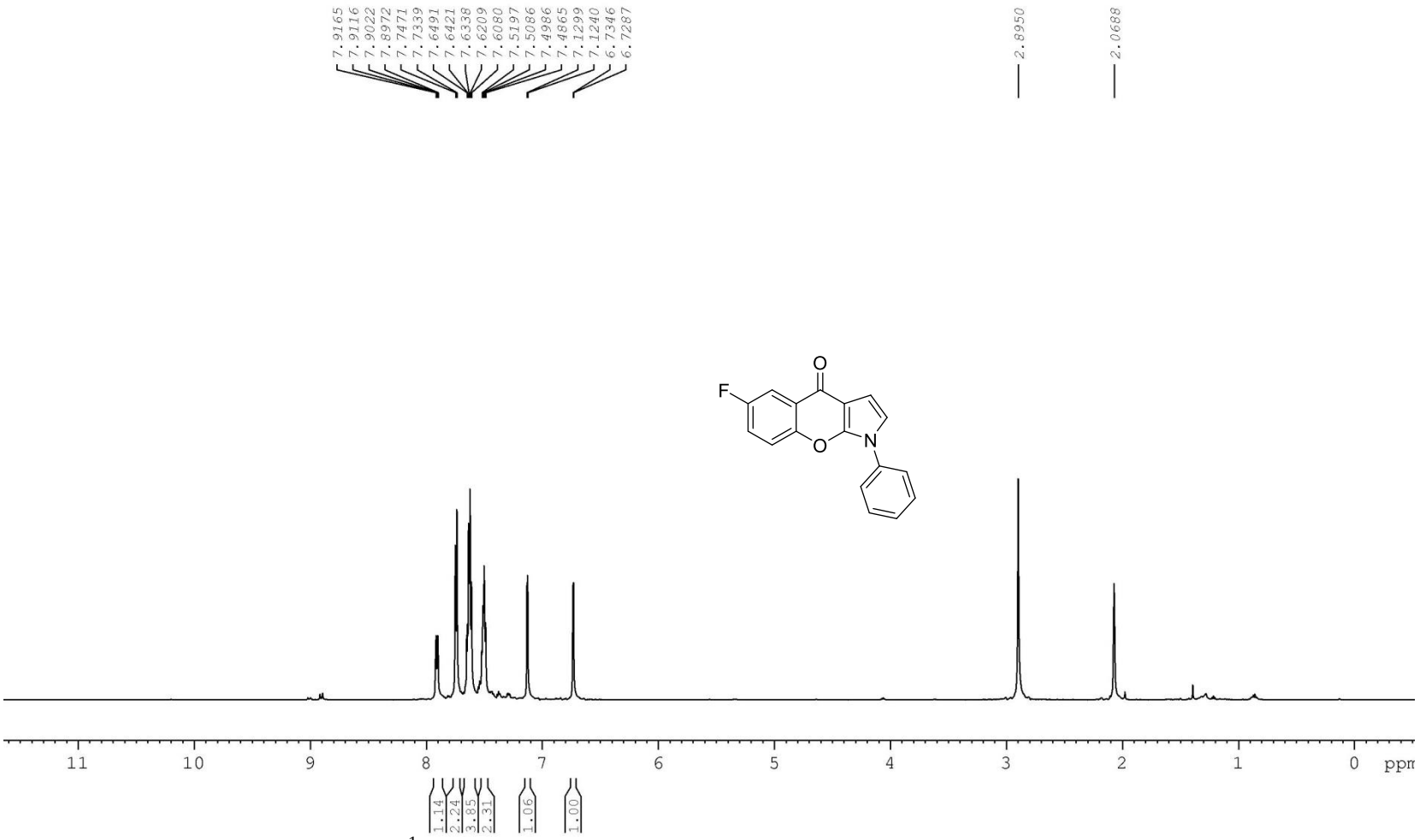


Figure S57. ^{1}H NMR (**600** MHz, $CDCl_3$ + Acetone-d_6) spectra of compound **3q**

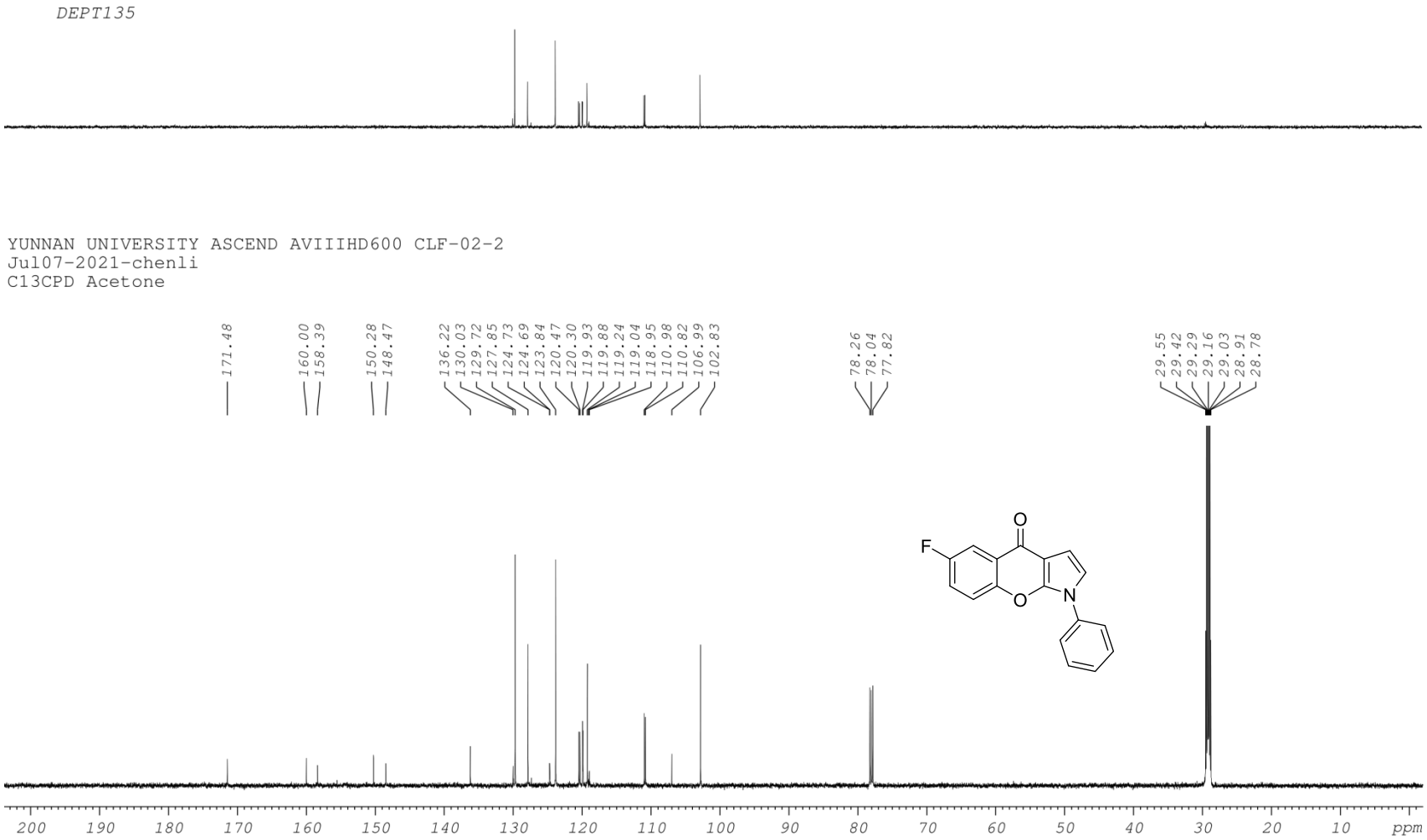


Figure S58. ^{13}C NMR (**150** MHz, $CDCl_3$ + Acetone-d_6) spectra of compound **3q**

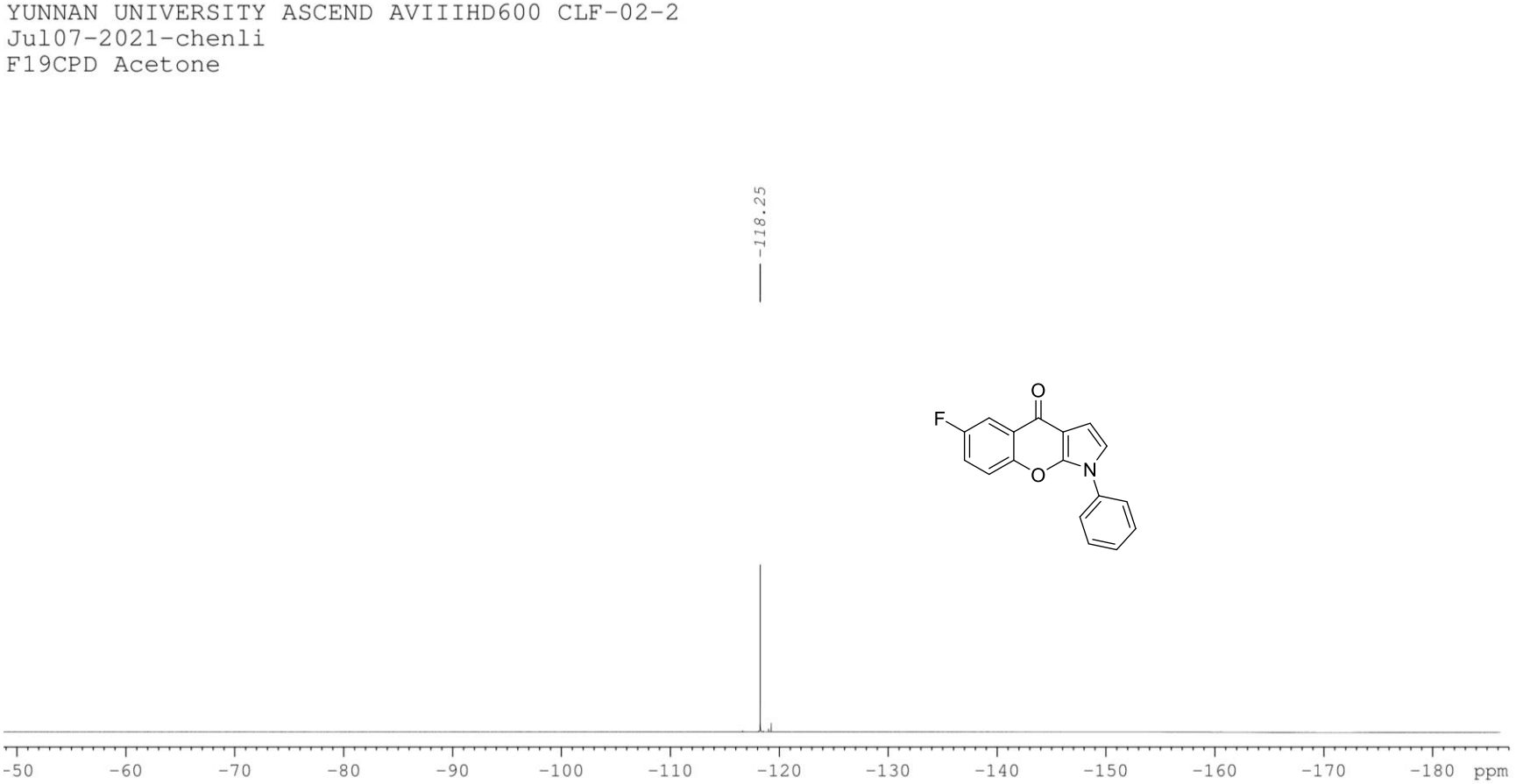


Figure S59. ^{19}F NMR (**564** MHz, $CDCl_3$ + Acetone-d_6) spectra of compound **3q**

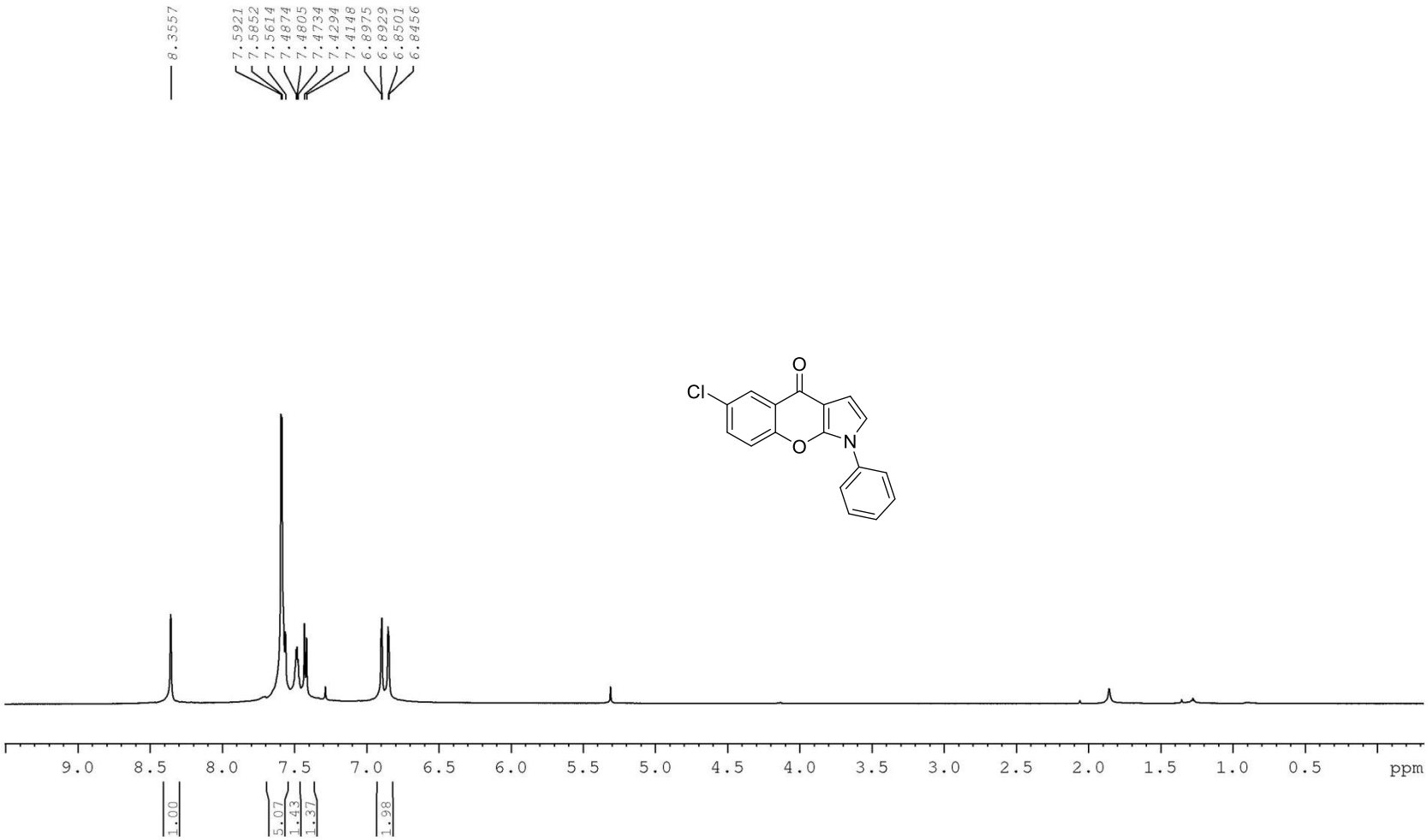


Figure S60. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3r**

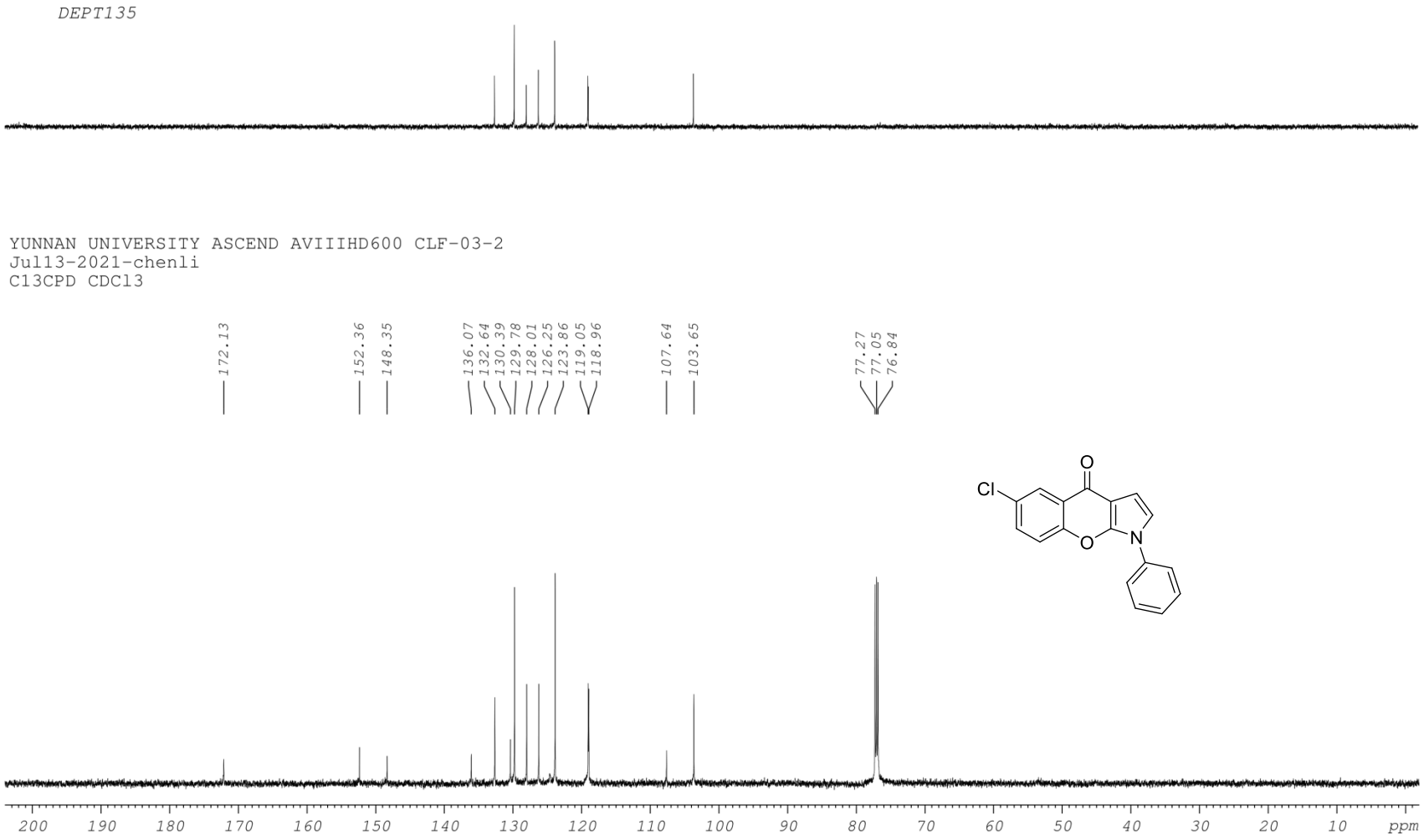


Figure S61. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3r**

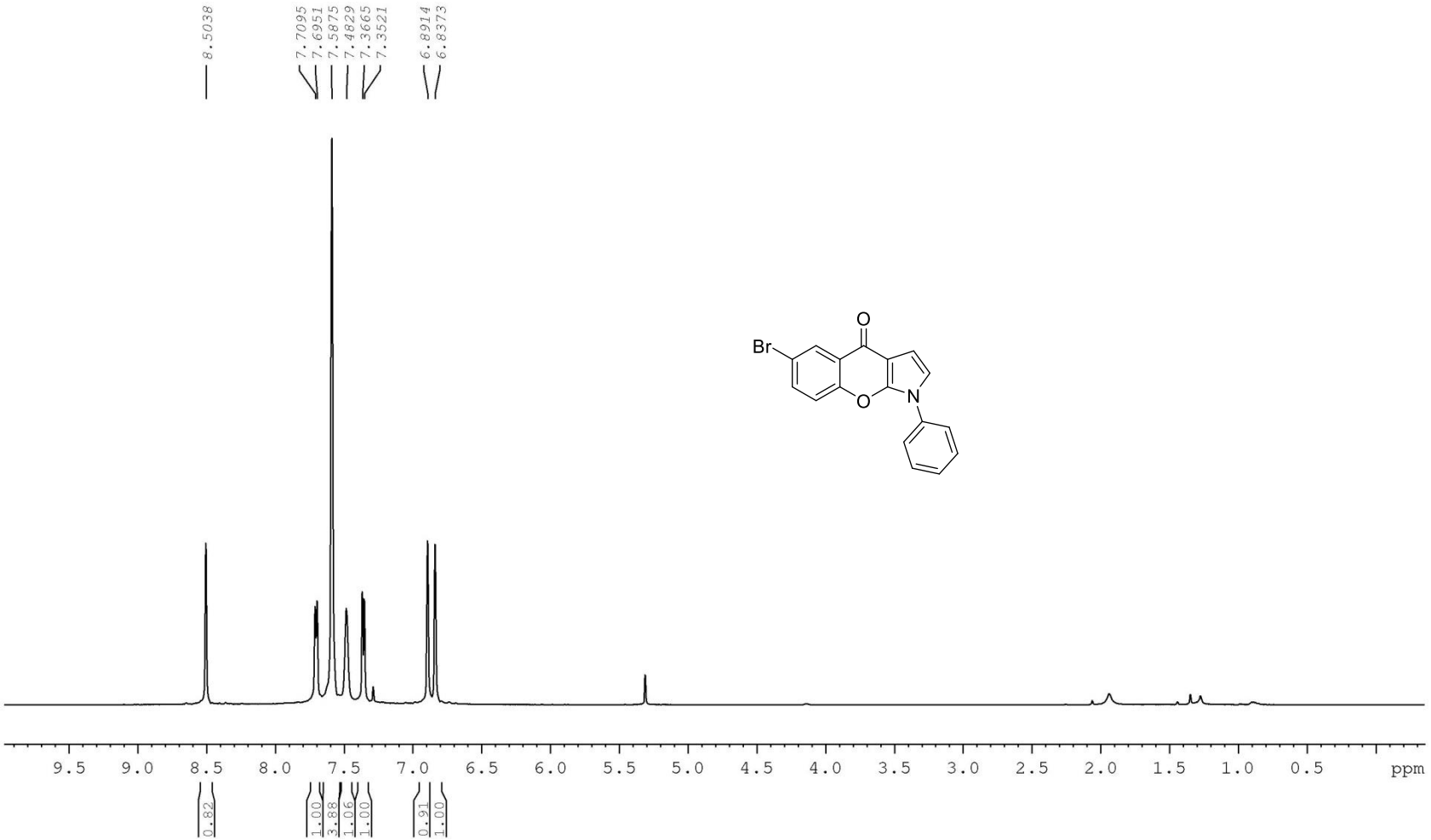


Figure S62. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3s**

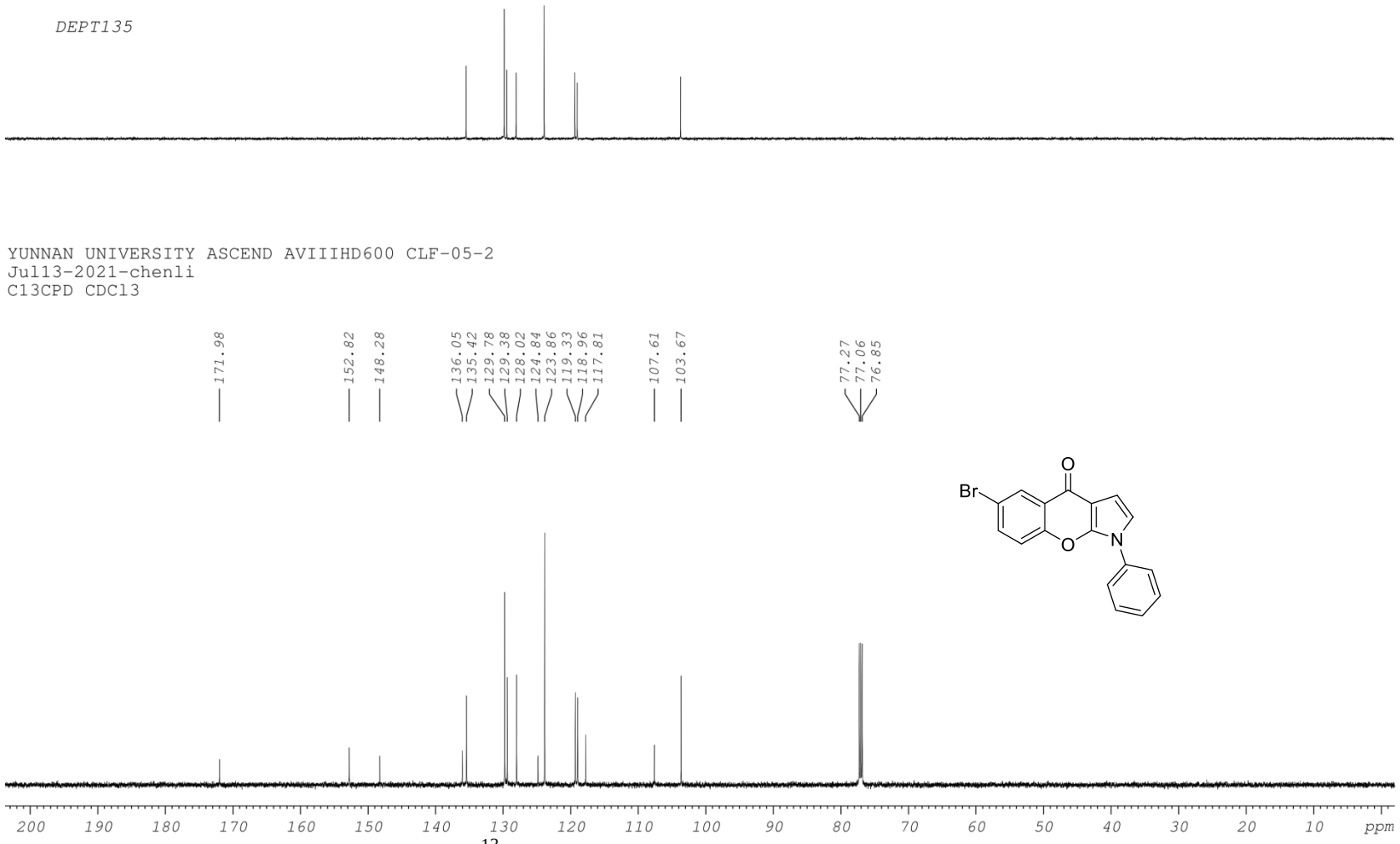


Figure S63. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3s**

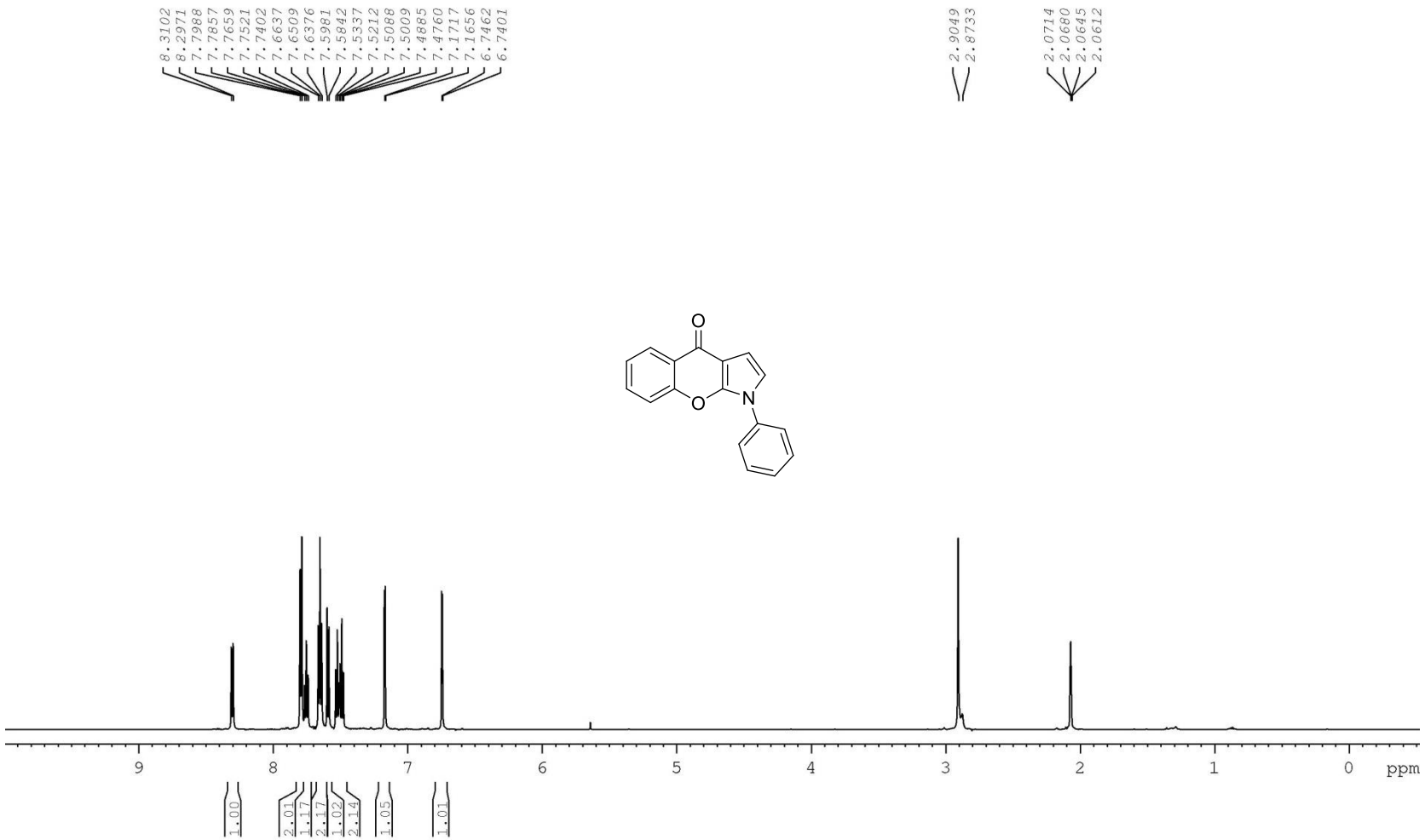


Figure S64. ^{1}H NMR (**600** MHz, Acetone-d_6) spectra of compound **3t**

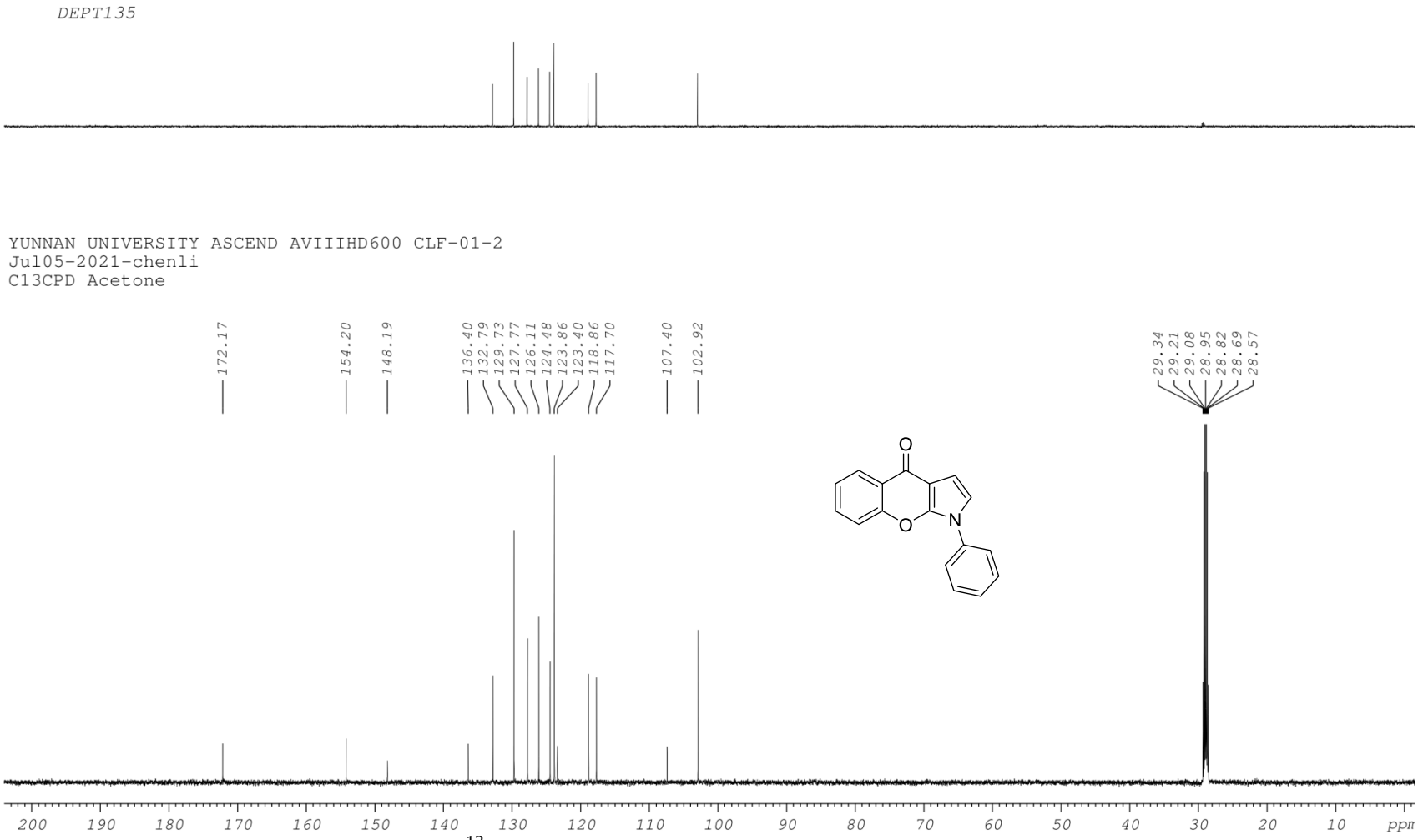


Figure S65. ^{13}C NMR (**150** MHz, Acetone-d_6) spectra of compound **3t**

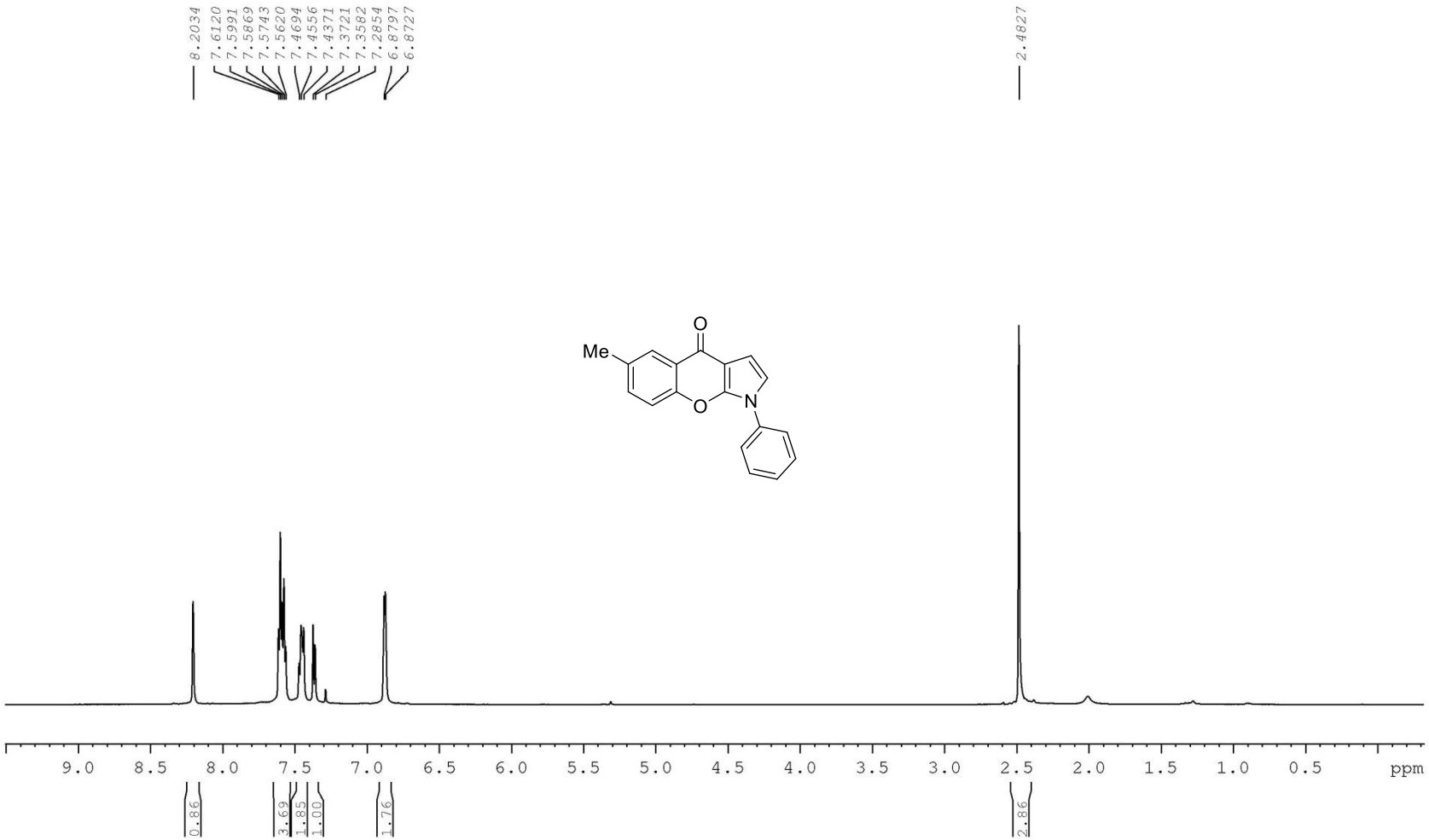


Figure S66. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3u**

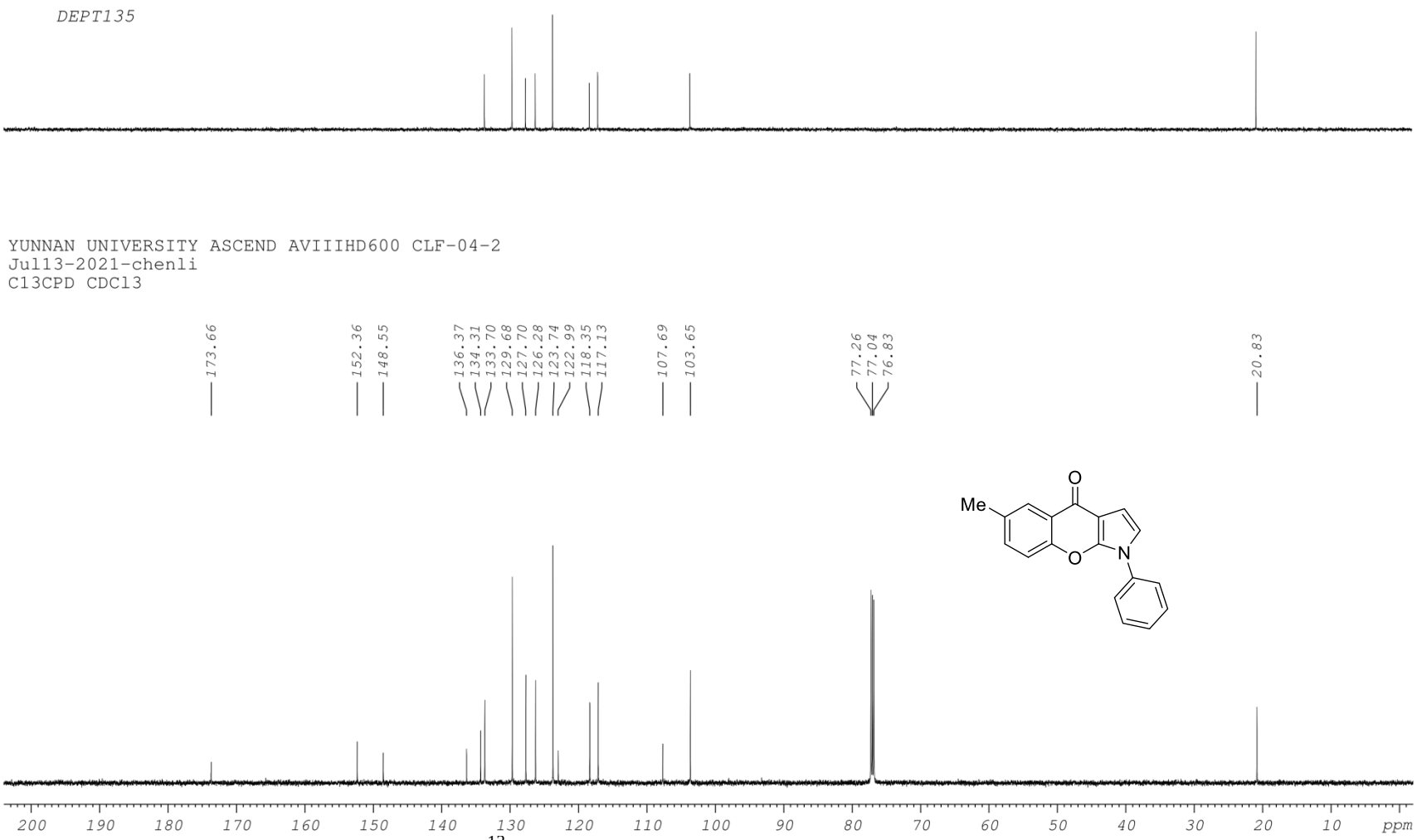


Figure S67. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3u**

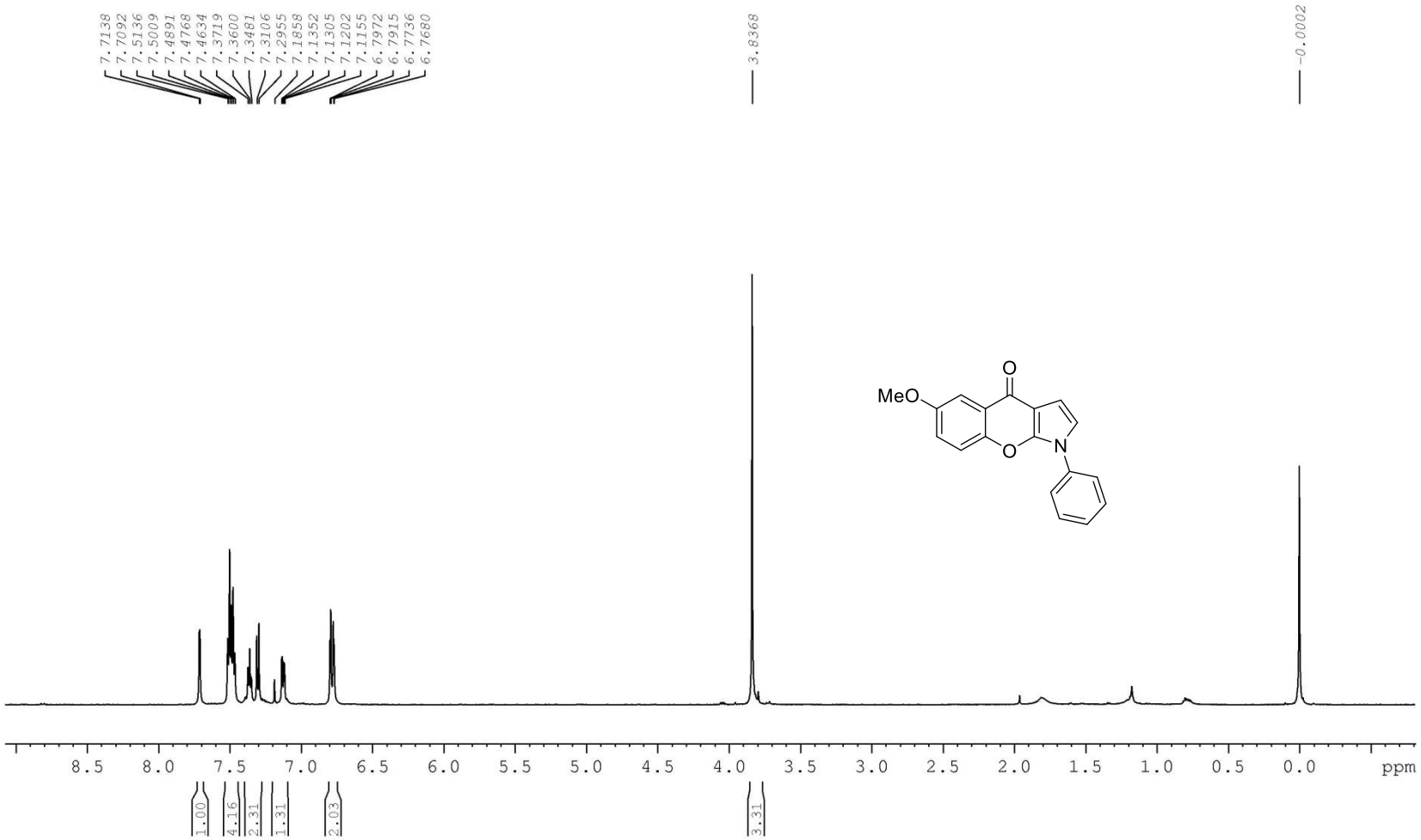


Figure S68. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3v**

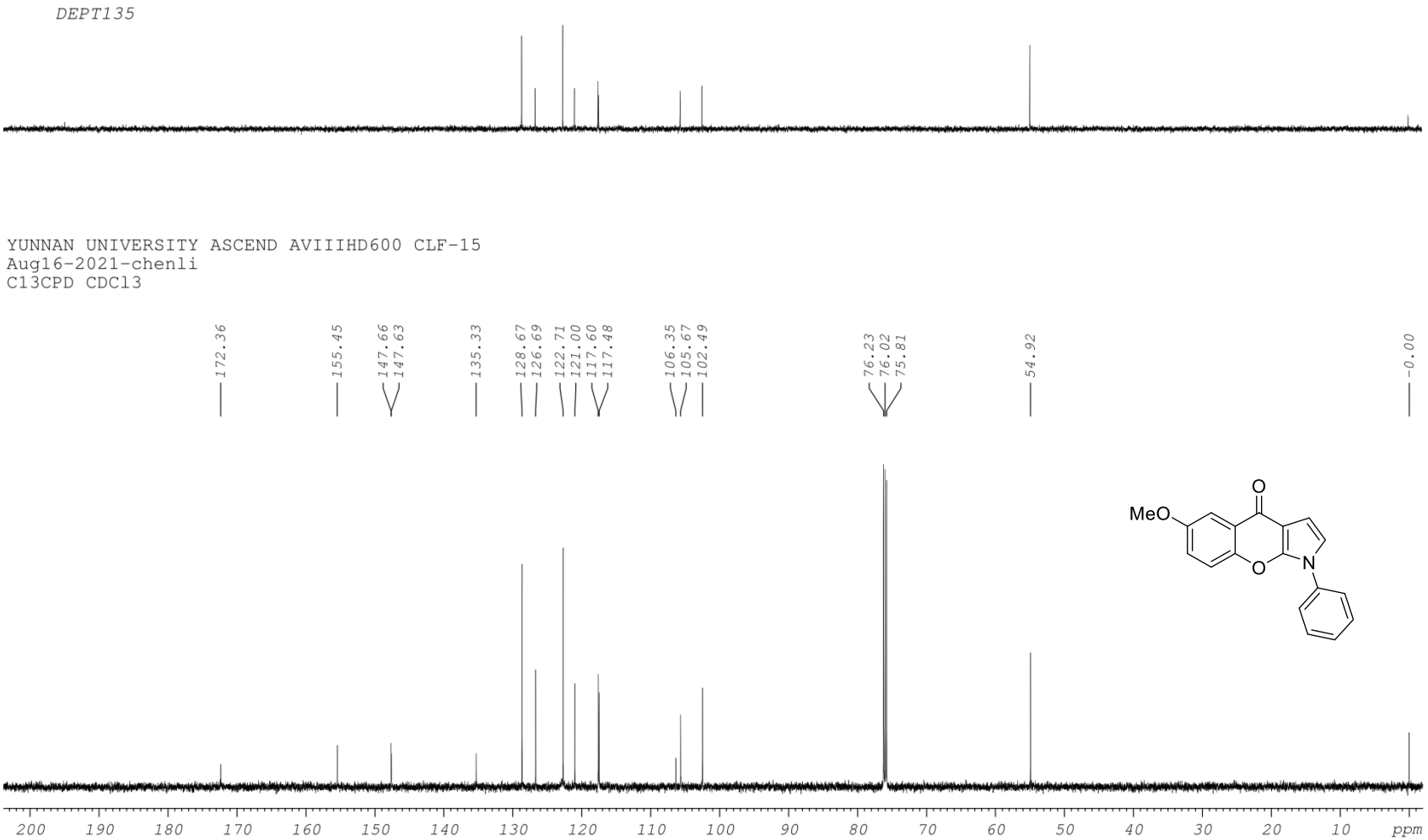


Figure S69. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3v**

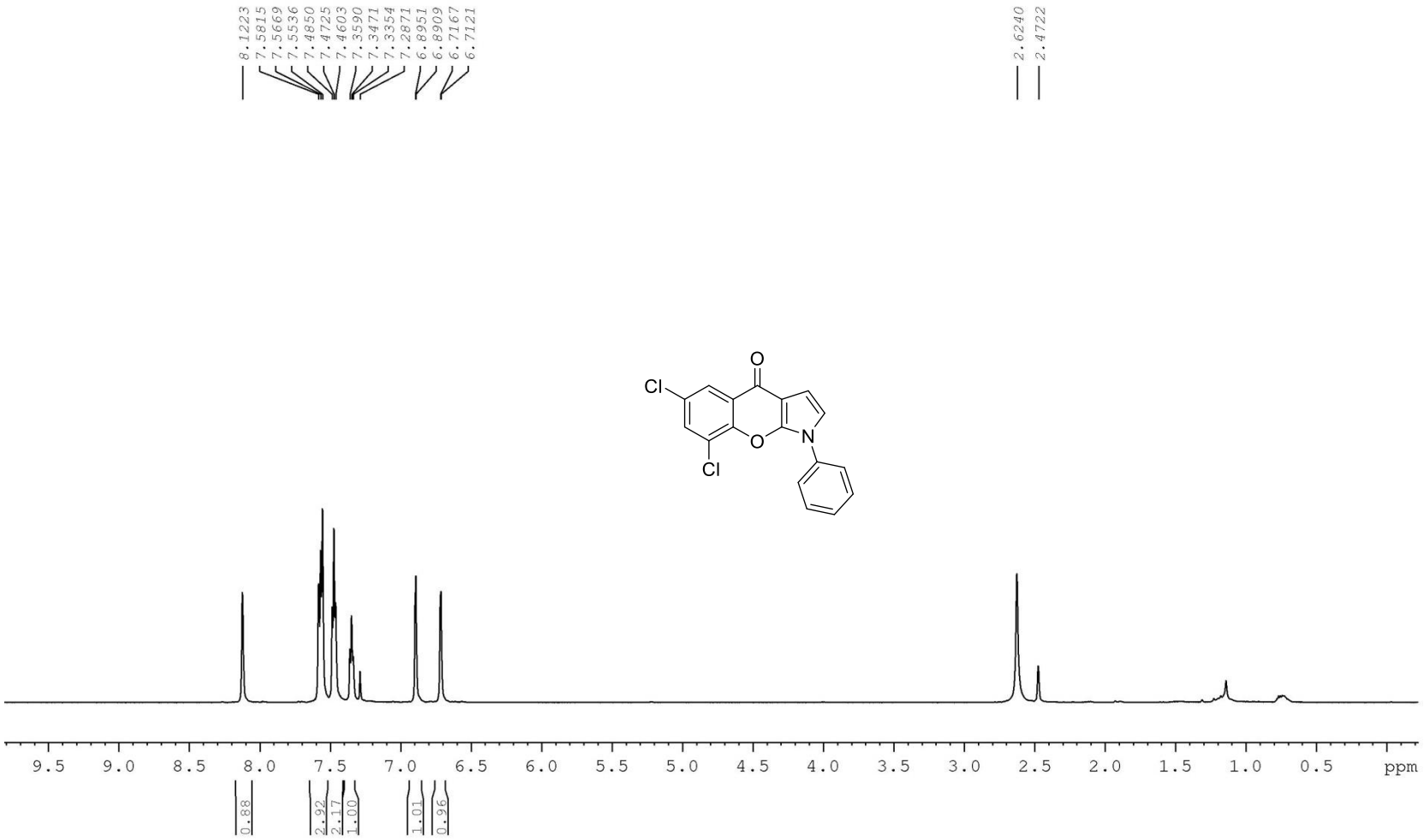


Figure S70. ^{1}H NMR (**600** MHz, $CDCl_3$+DMSO-d_6) spectra of compound **3w**

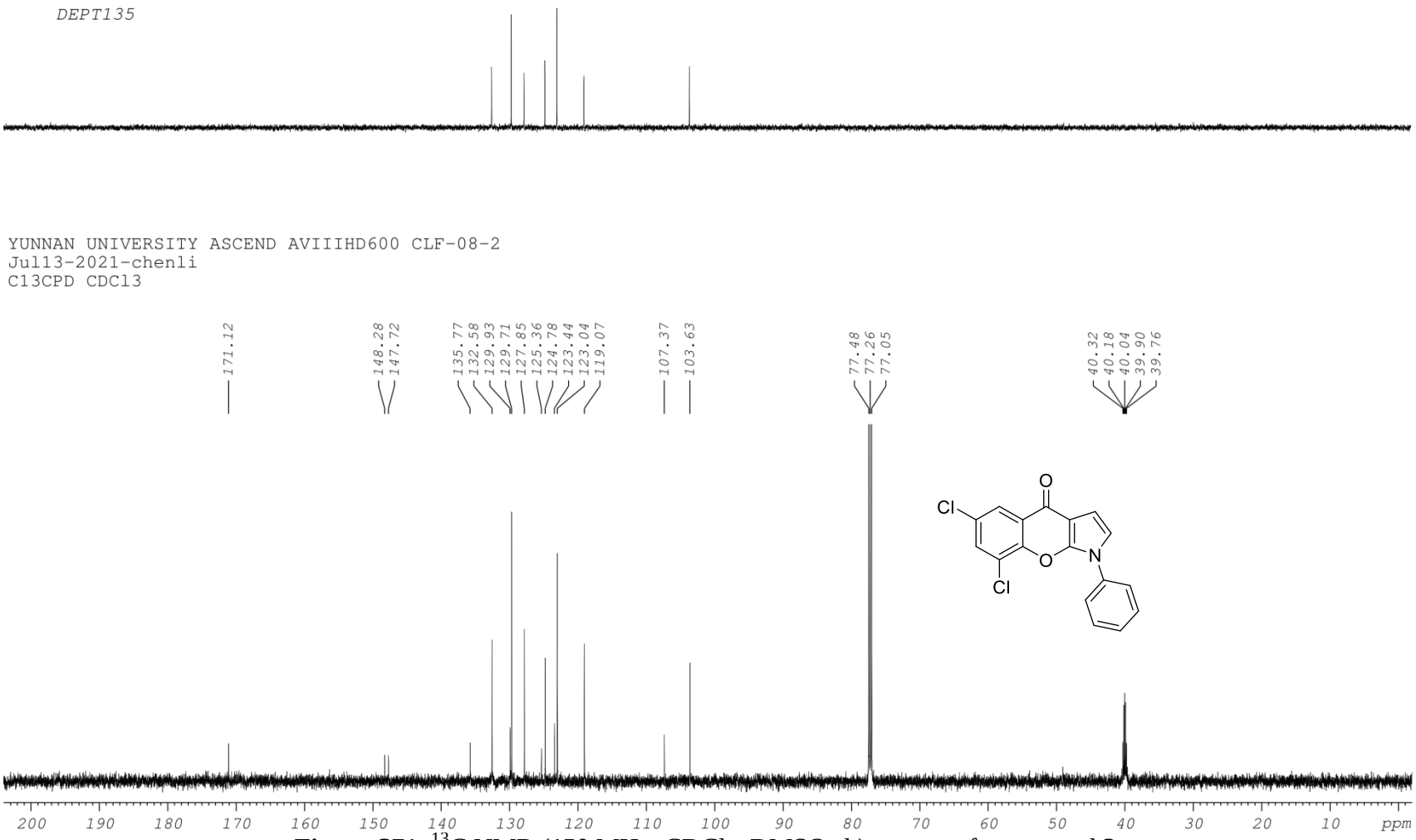


Figure S71. ^{13}C NMR (**150** MHz, $CDCl_3$+DMSO-d_6) spectra of compound **3w**

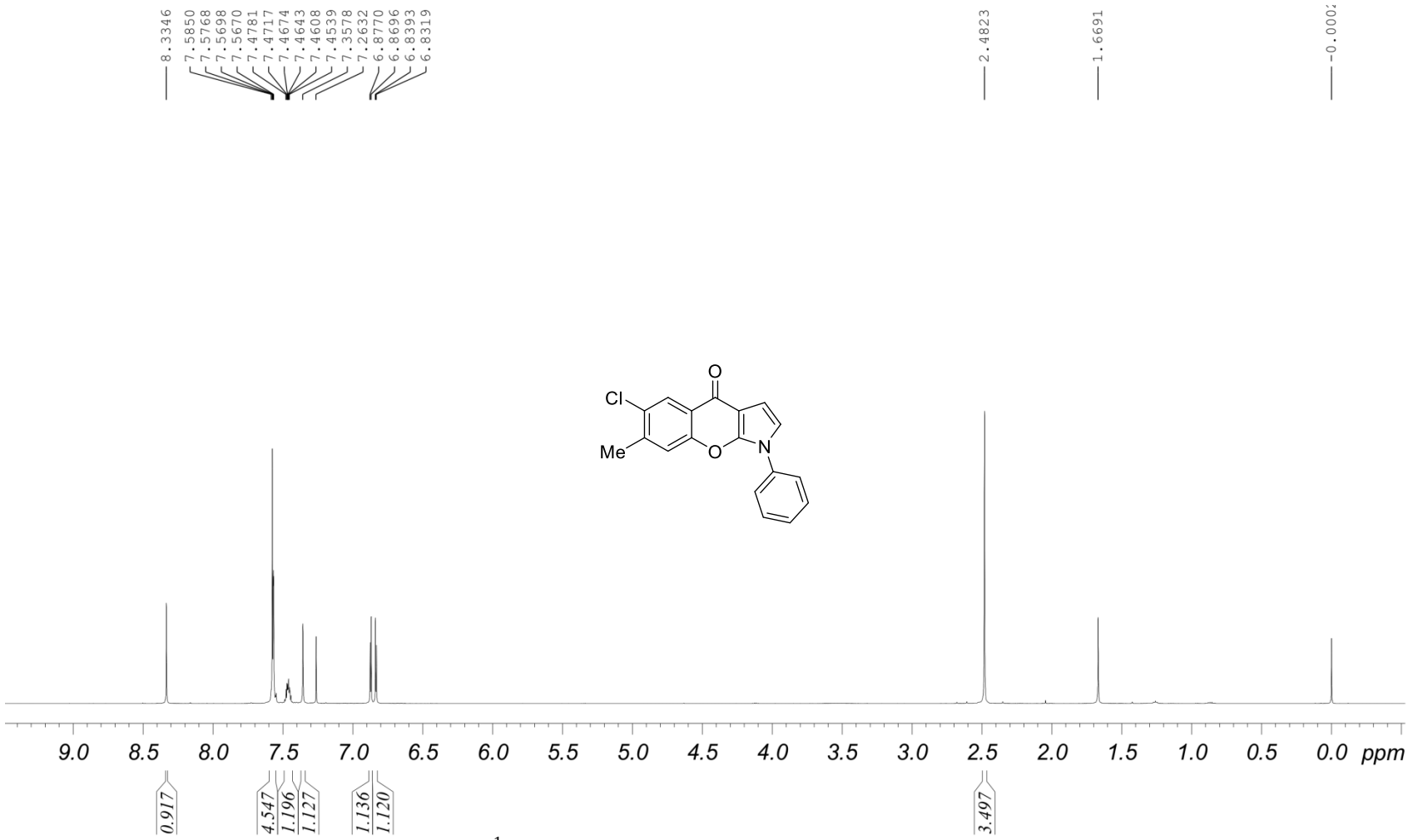


Figure S72. ^{1}H NMR (**500** MHz, $CDCl_3$) spectra of compound **3x**

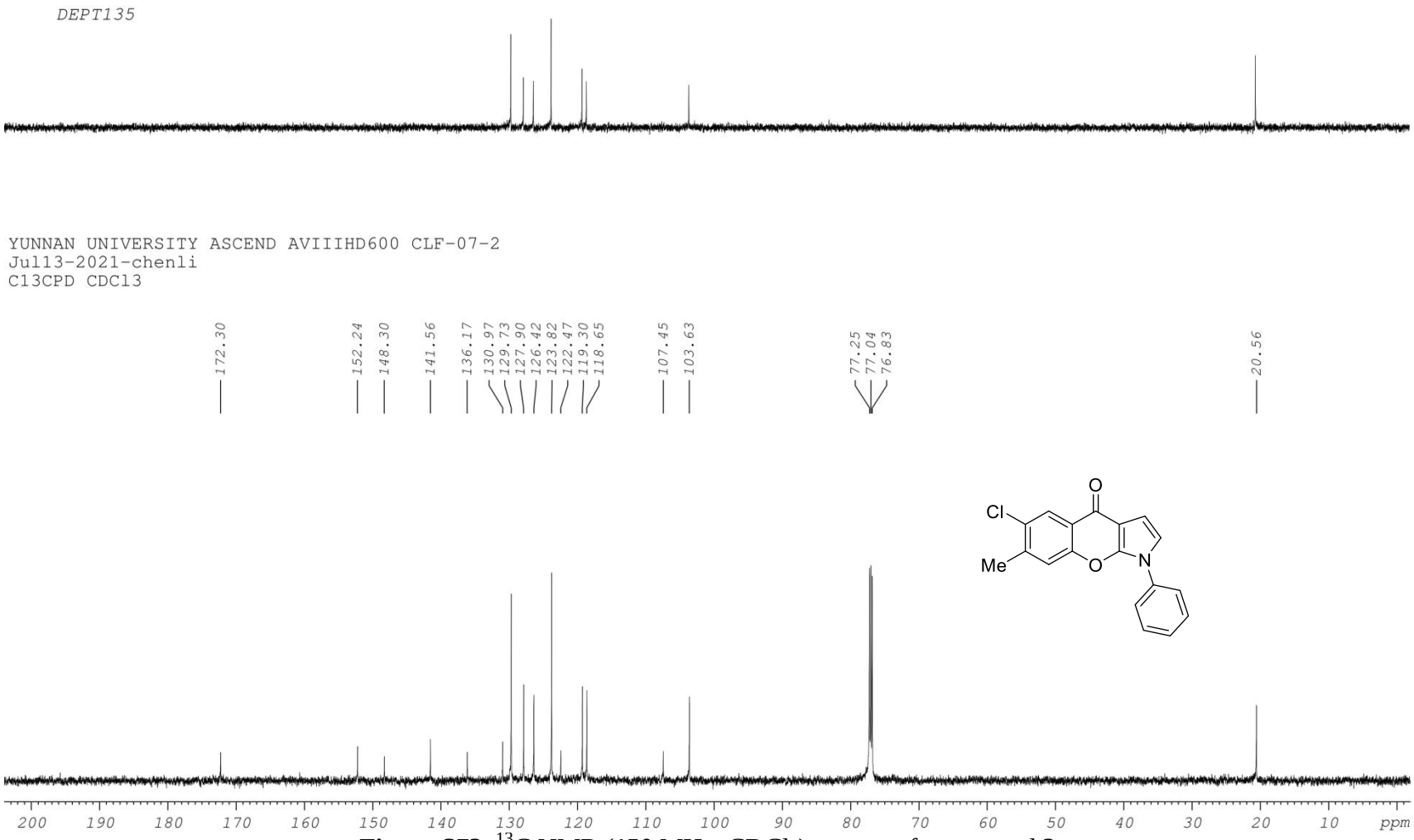


Figure S73. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3x**

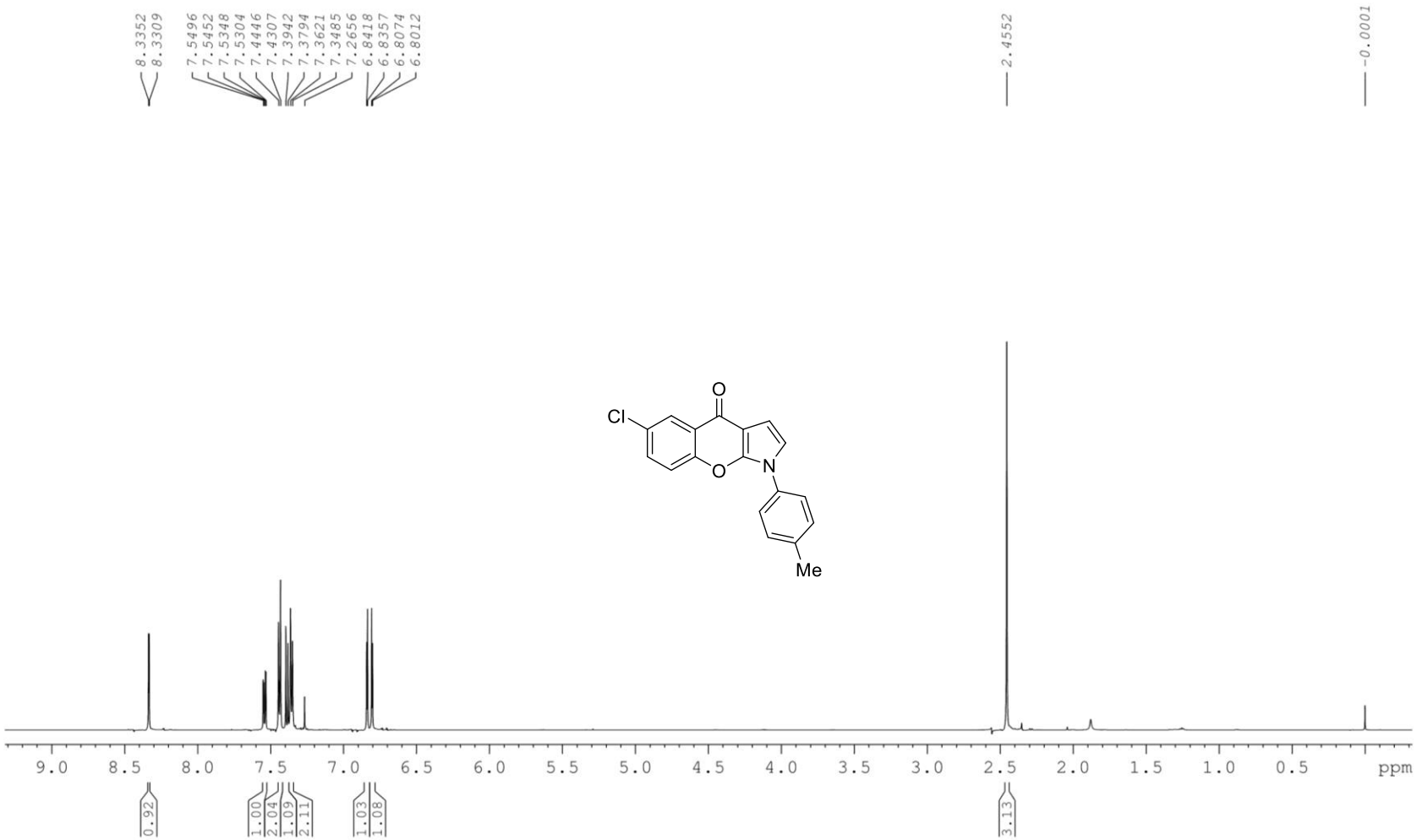


Figure S74. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3y**

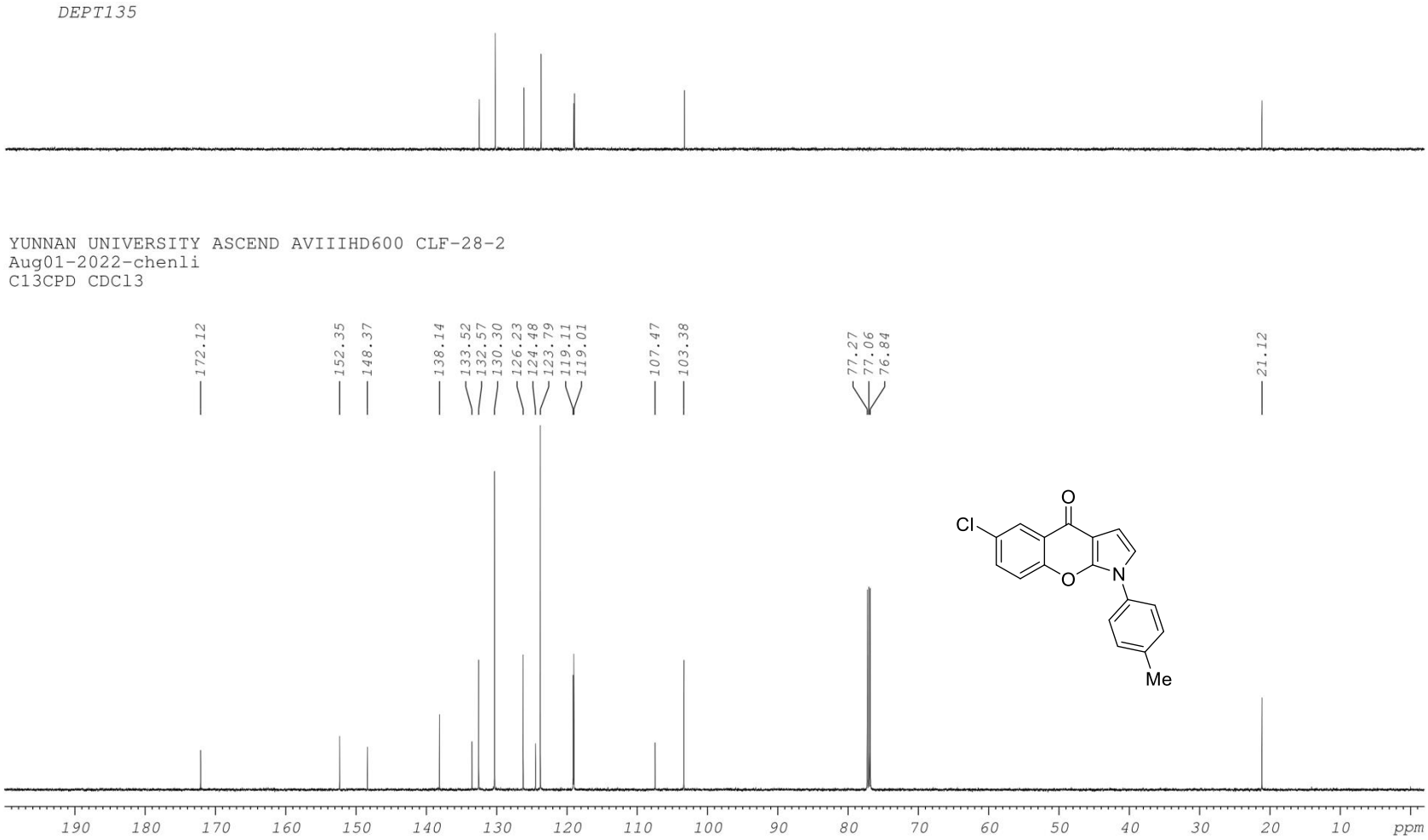


Figure S75. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3y**

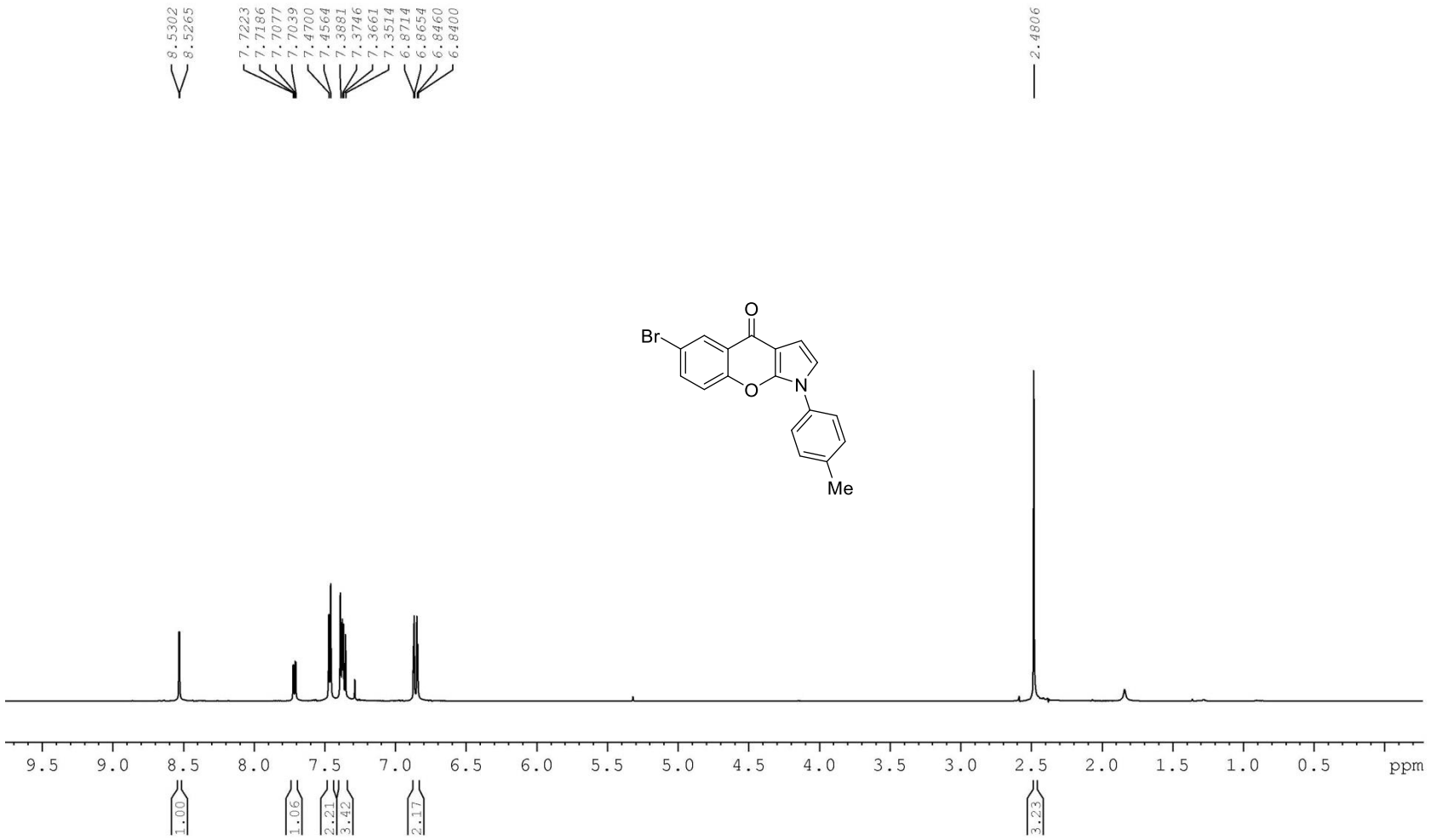


Figure S76. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3z**

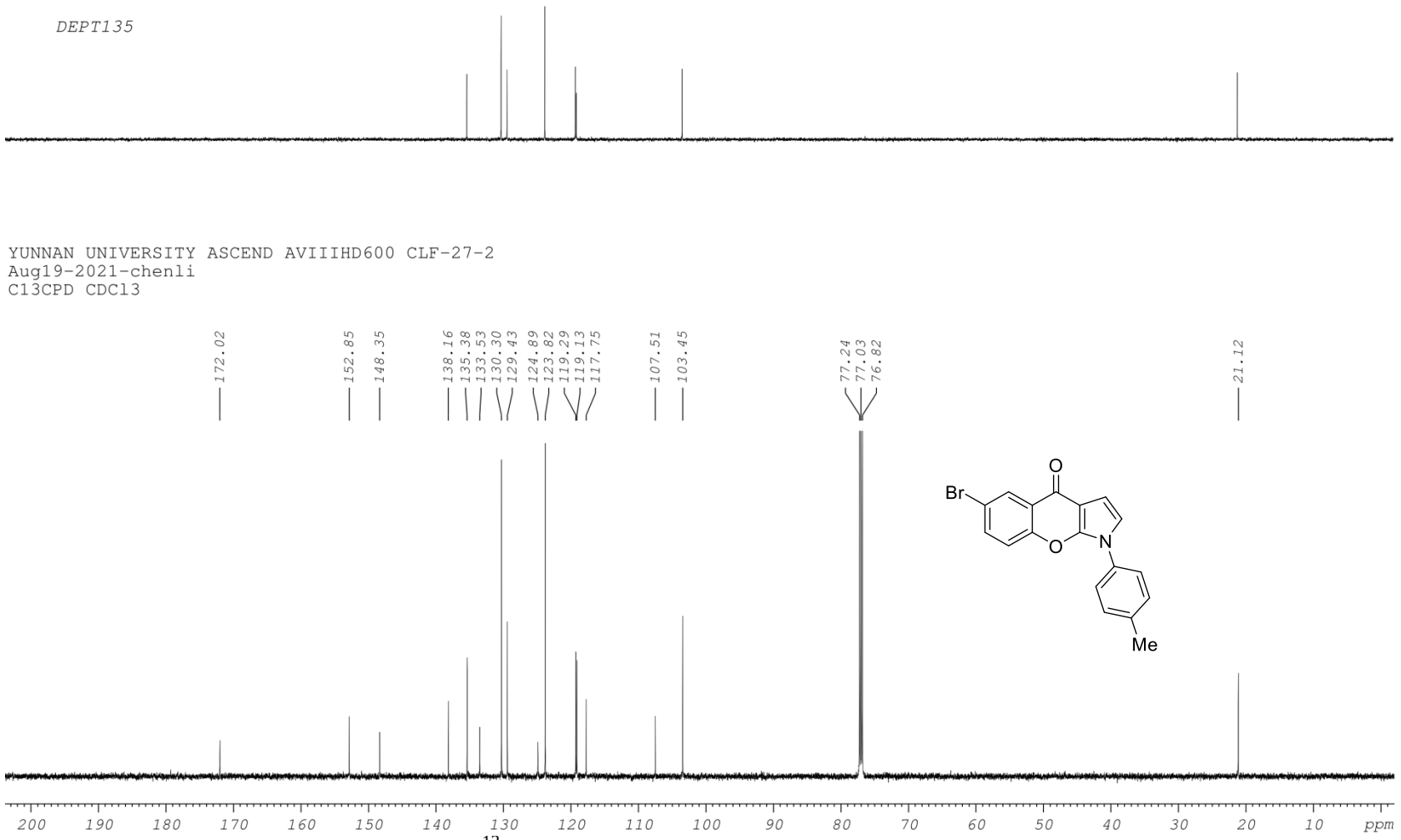


Figure S77. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3z**

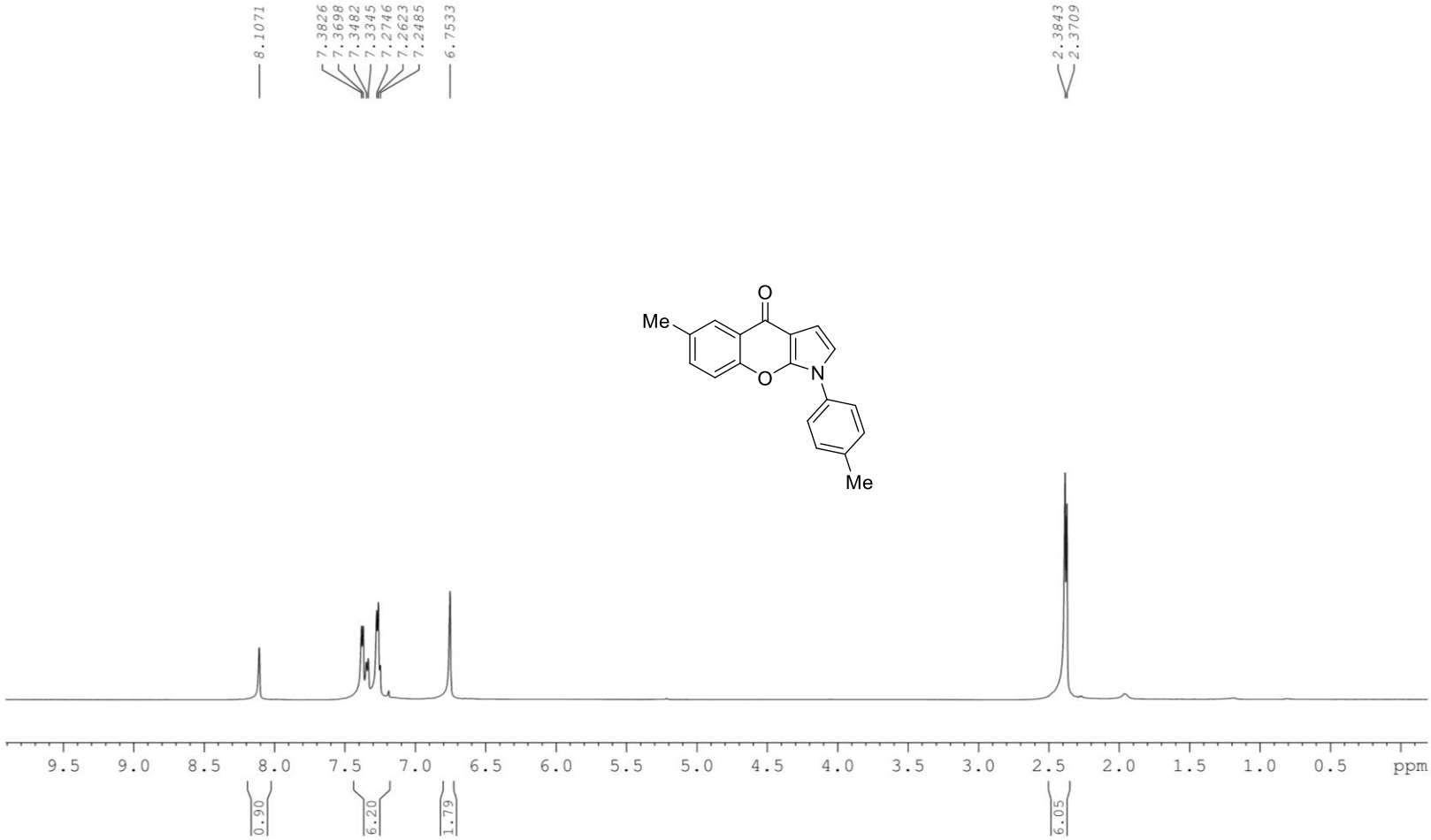


Figure S78. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3a'**

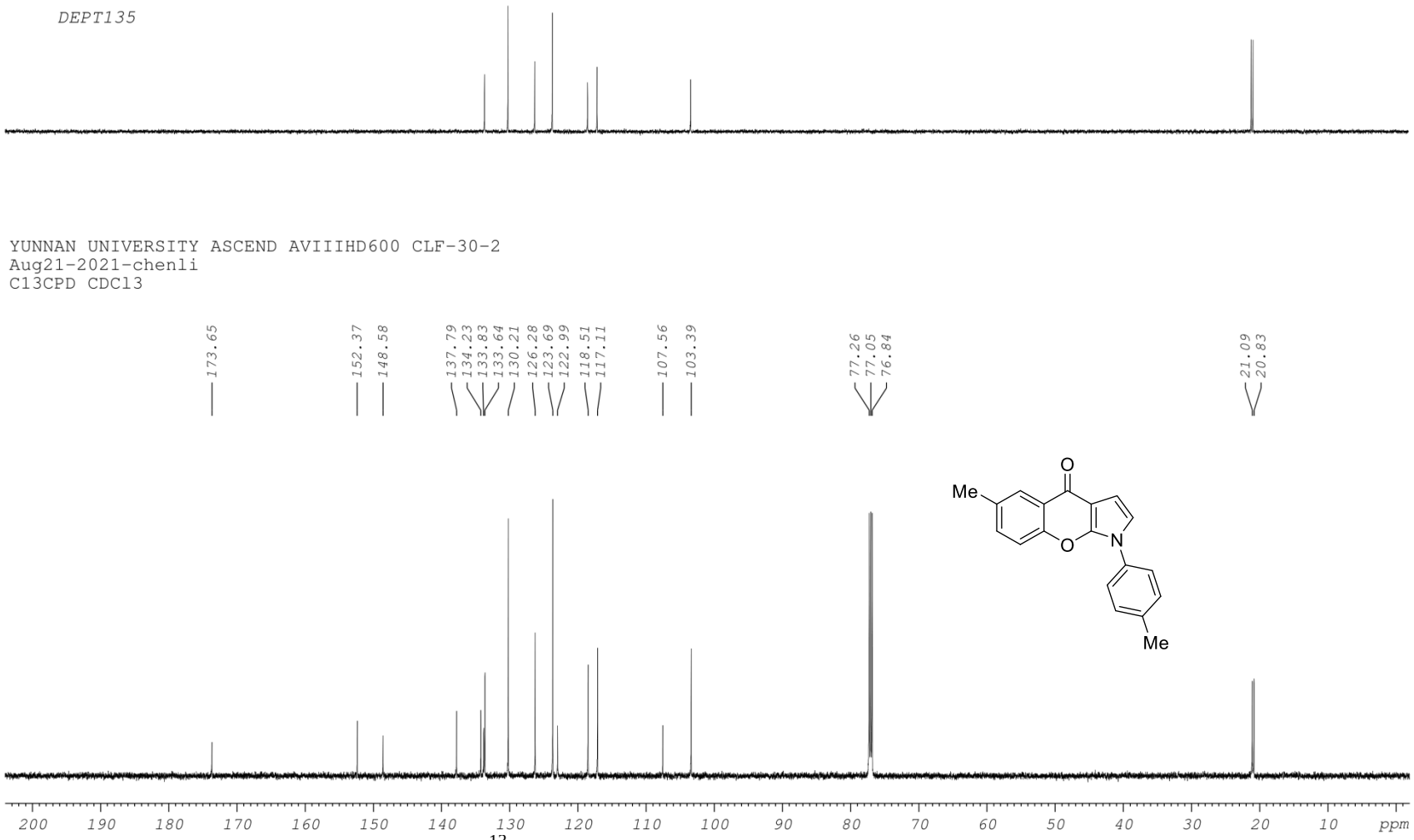


Figure S79. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3a'**

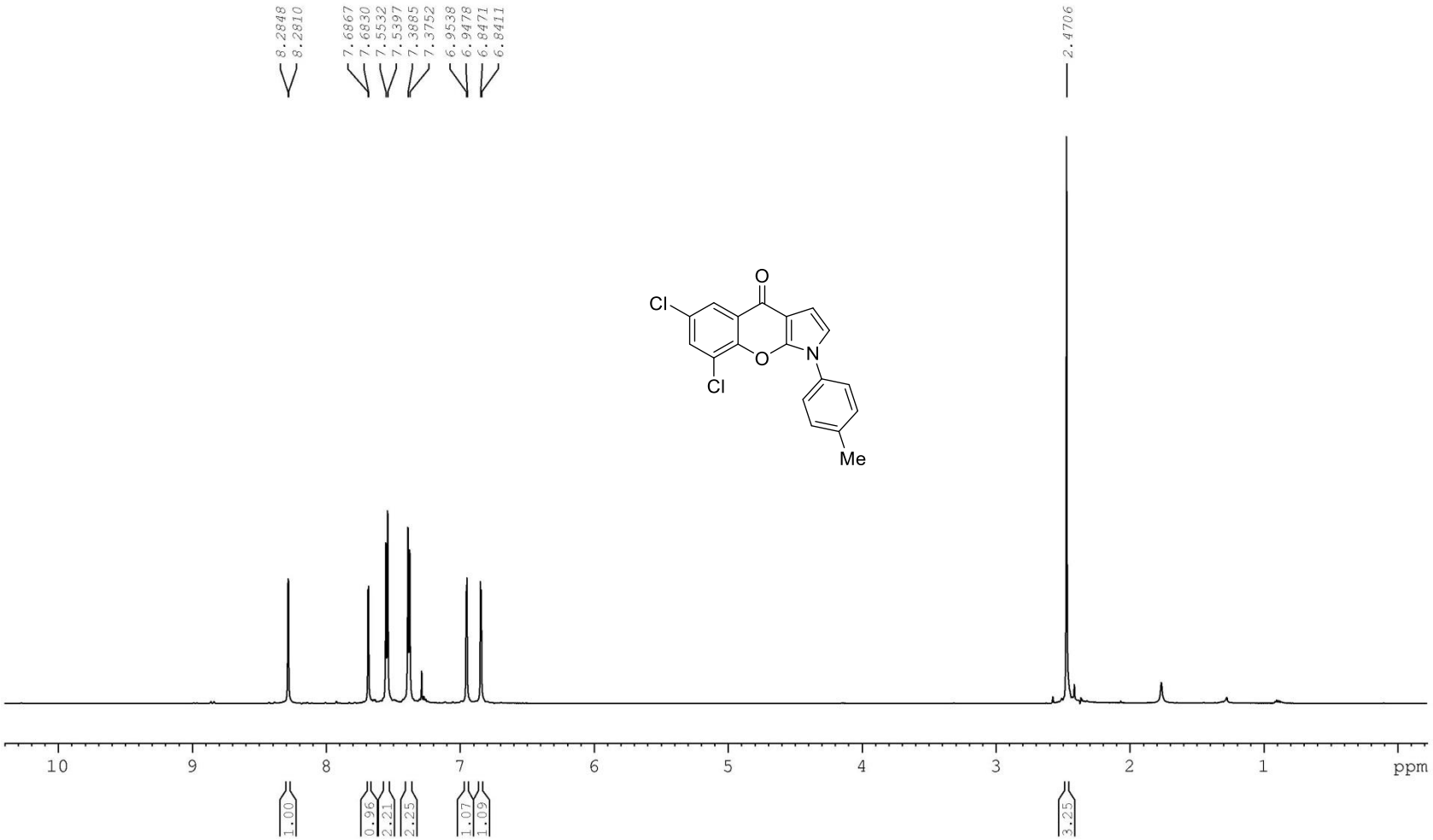


Figure S80. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3b'**

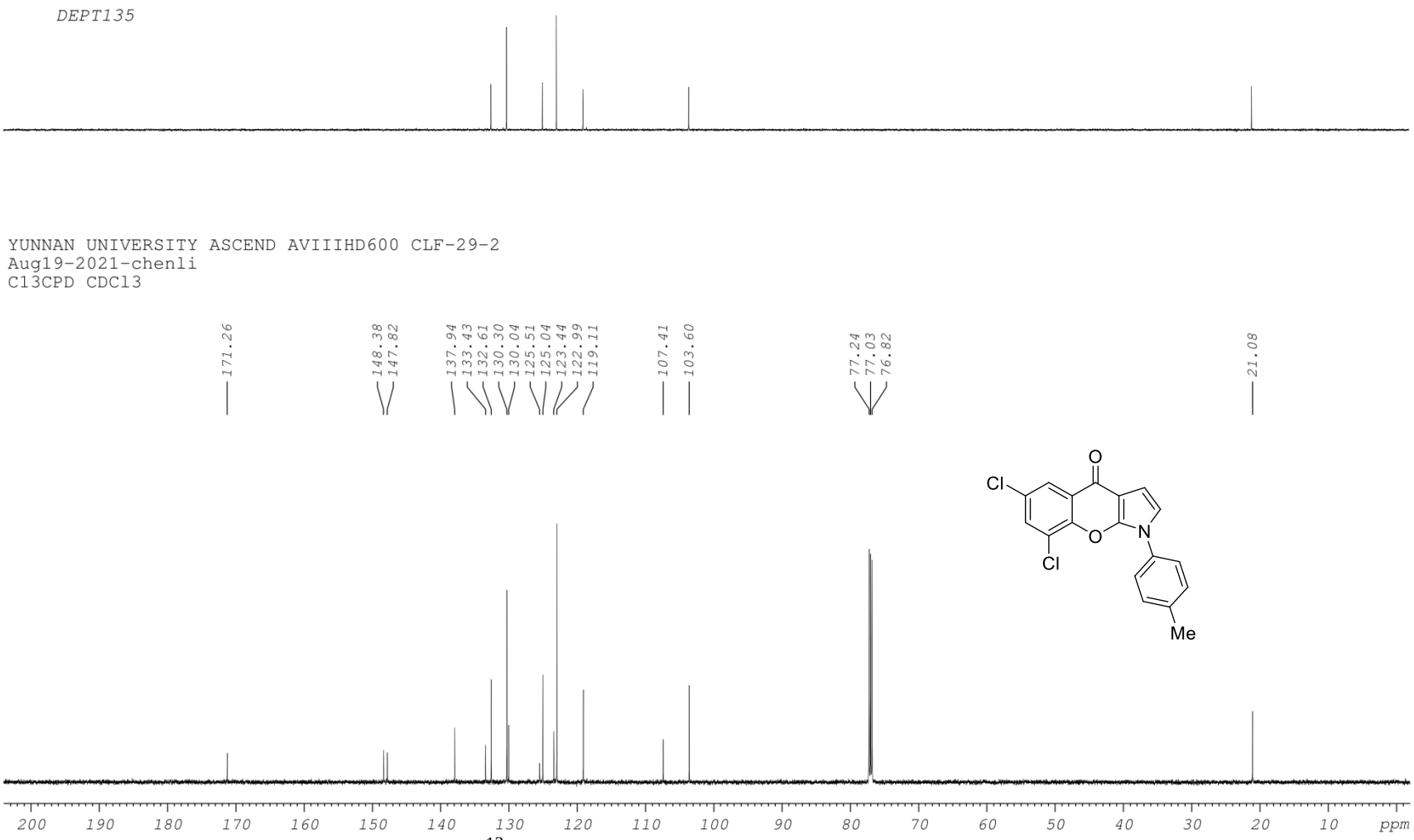


Figure S81. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3b'**

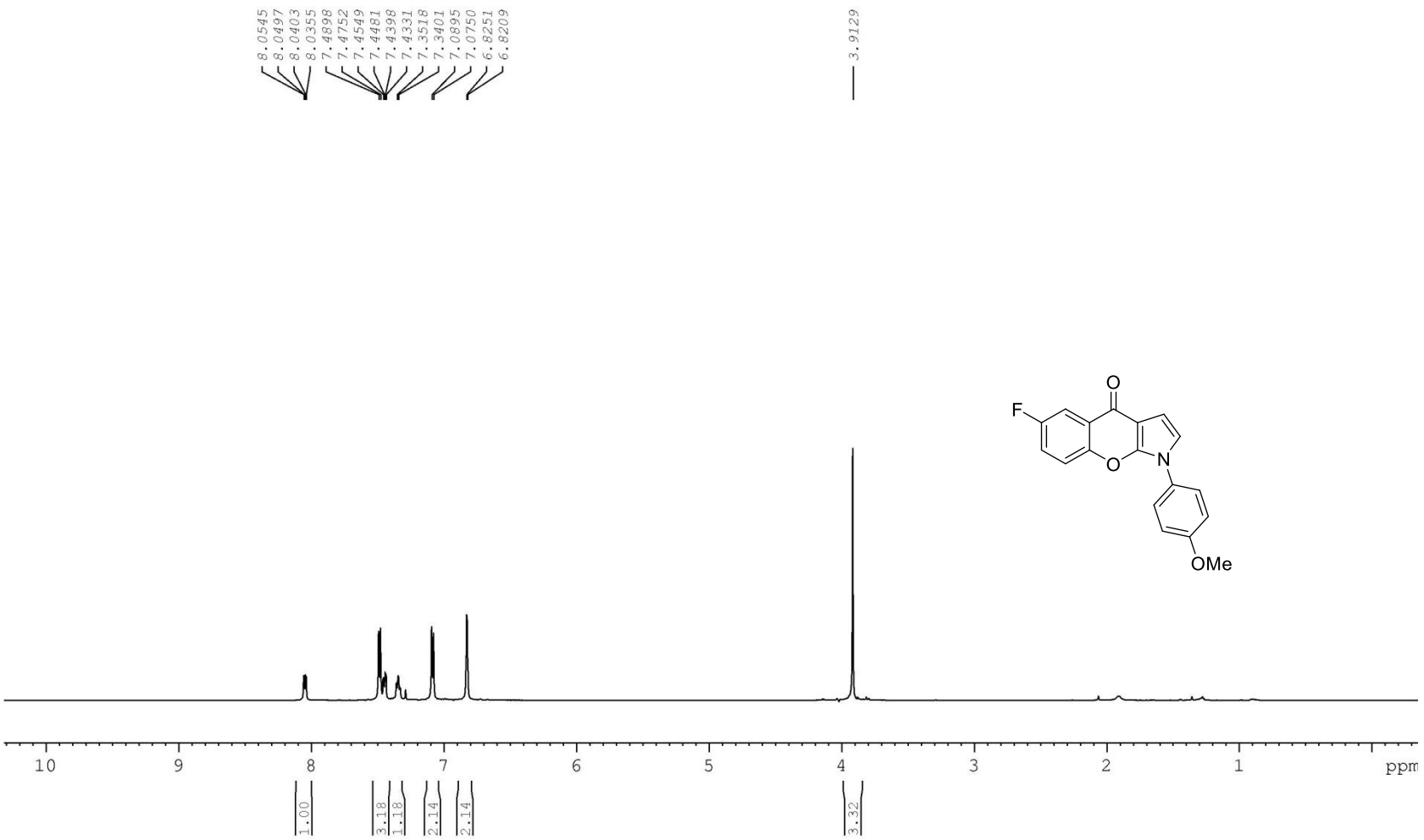


Figure S82. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3c'**

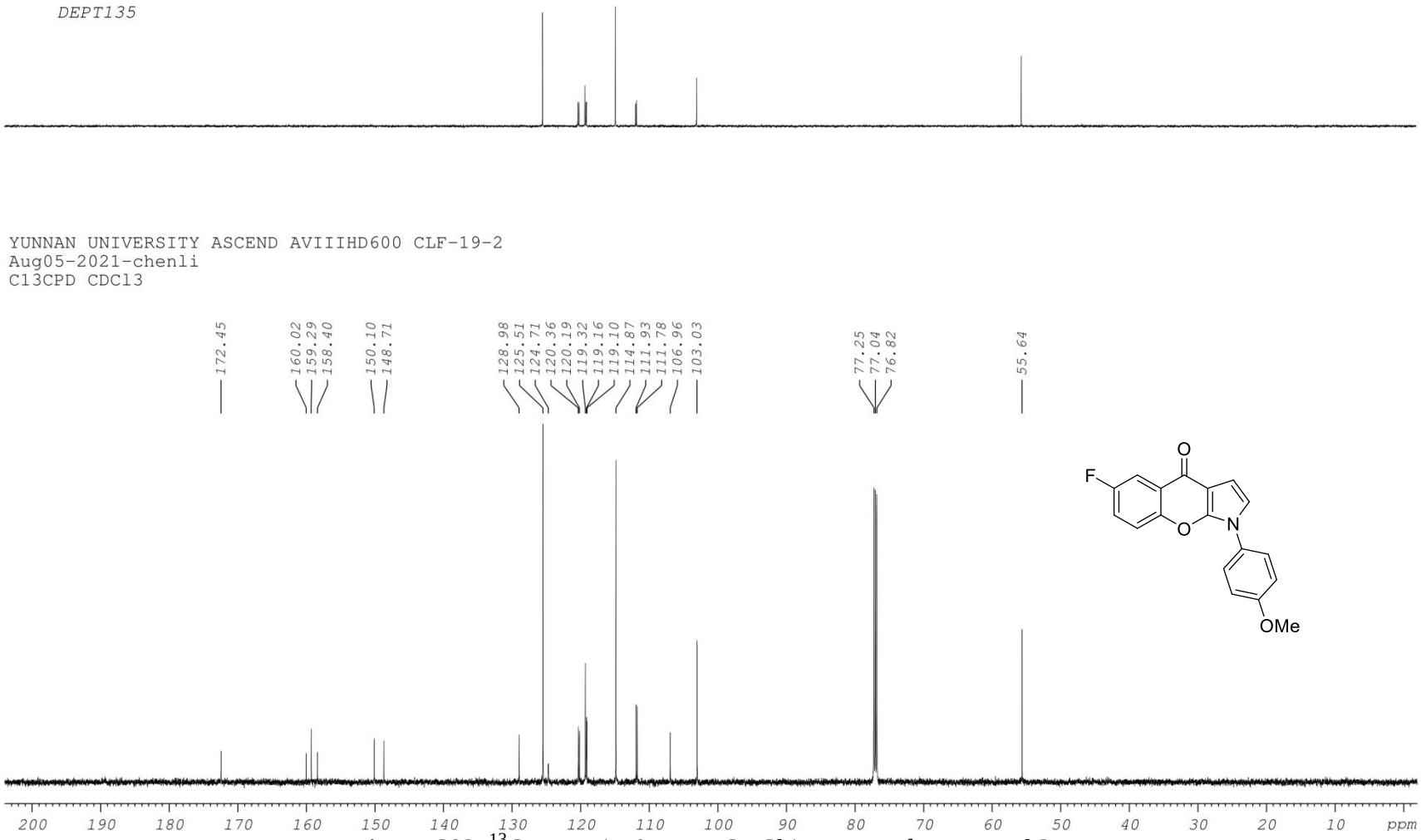


Figure S83. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3c'**

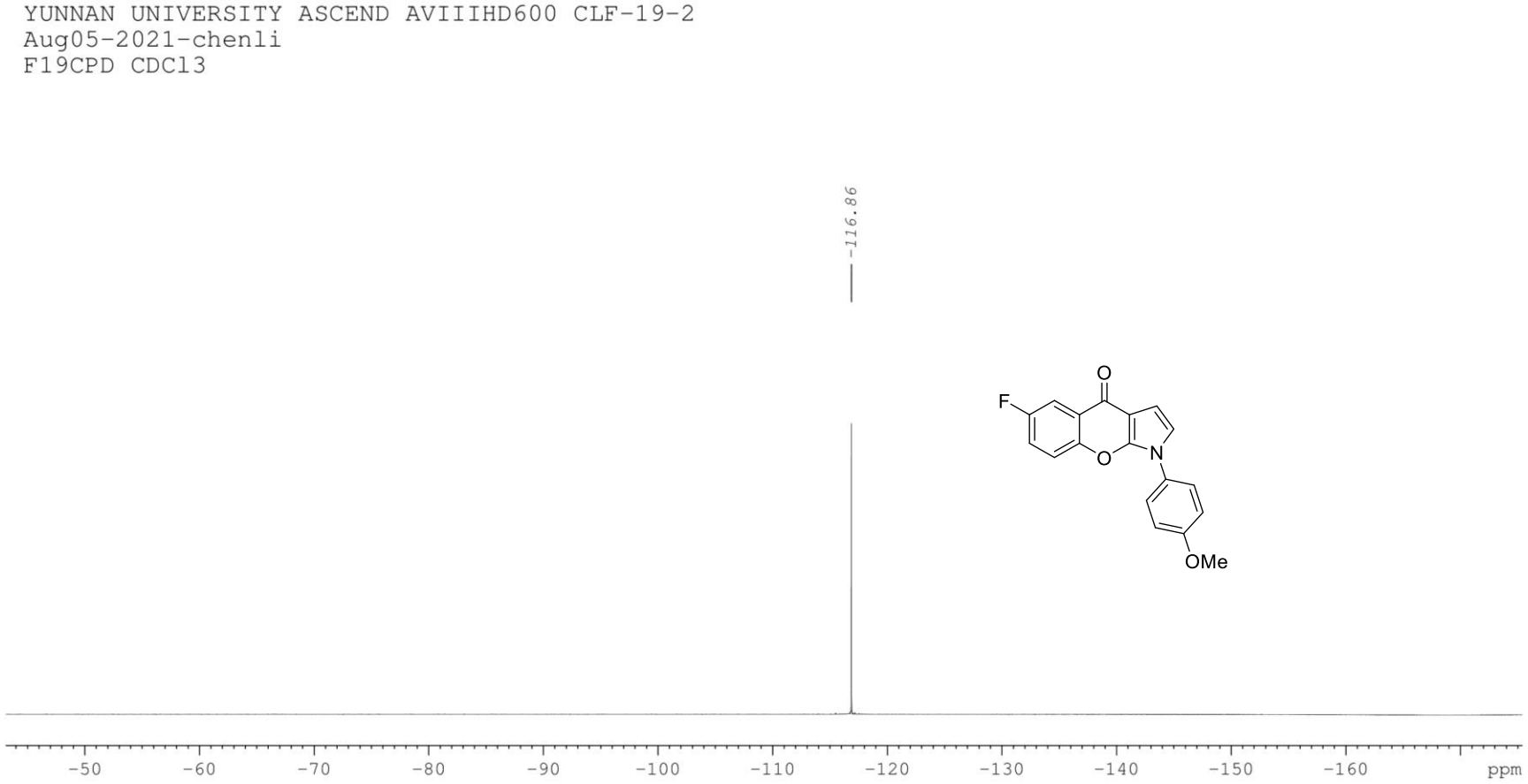


Figure S84. ^{19}F NMR (**564** MHz, $CDCl_3$) spectra of compound **3c'**

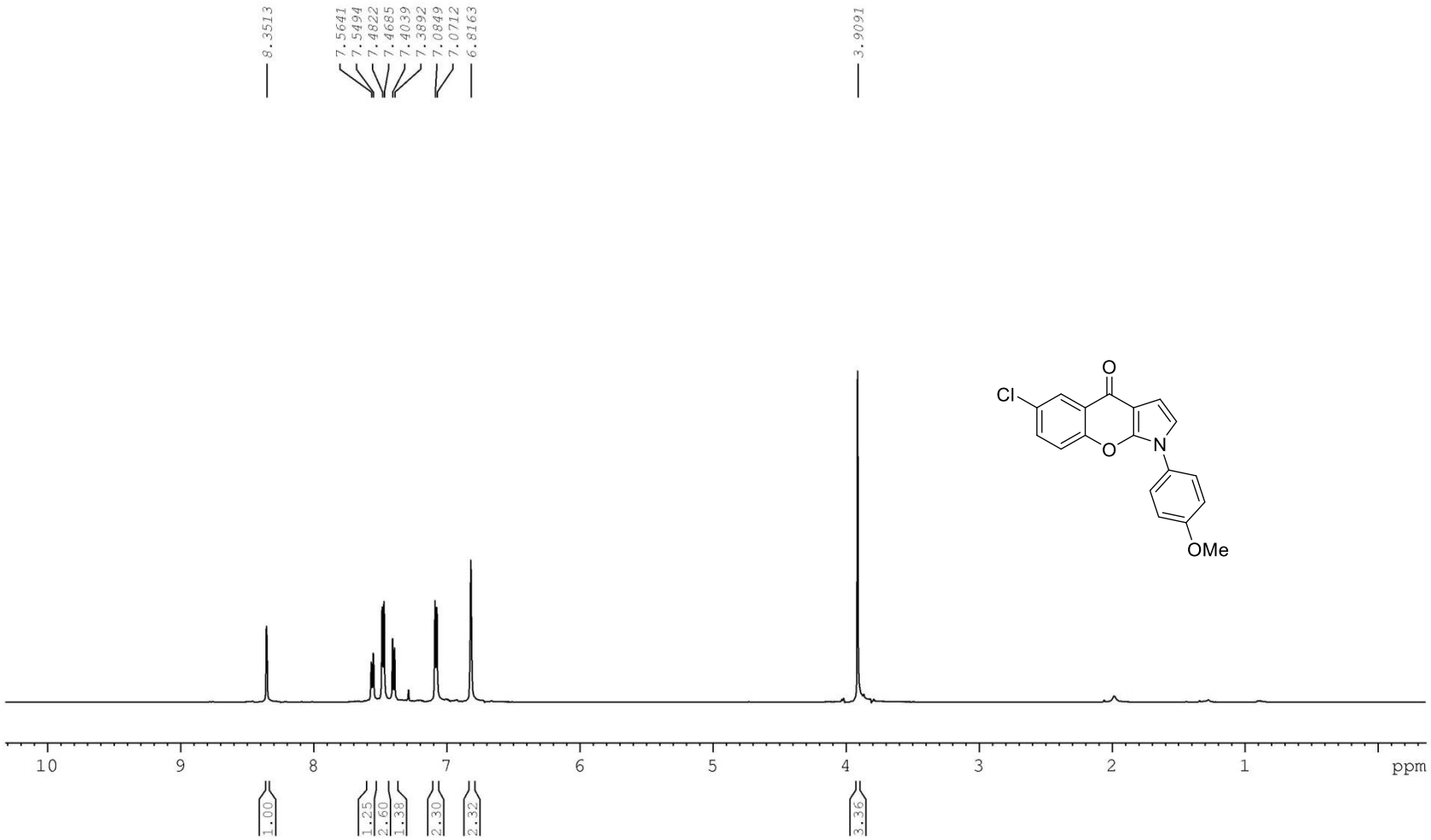


Figure S85. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3d'**

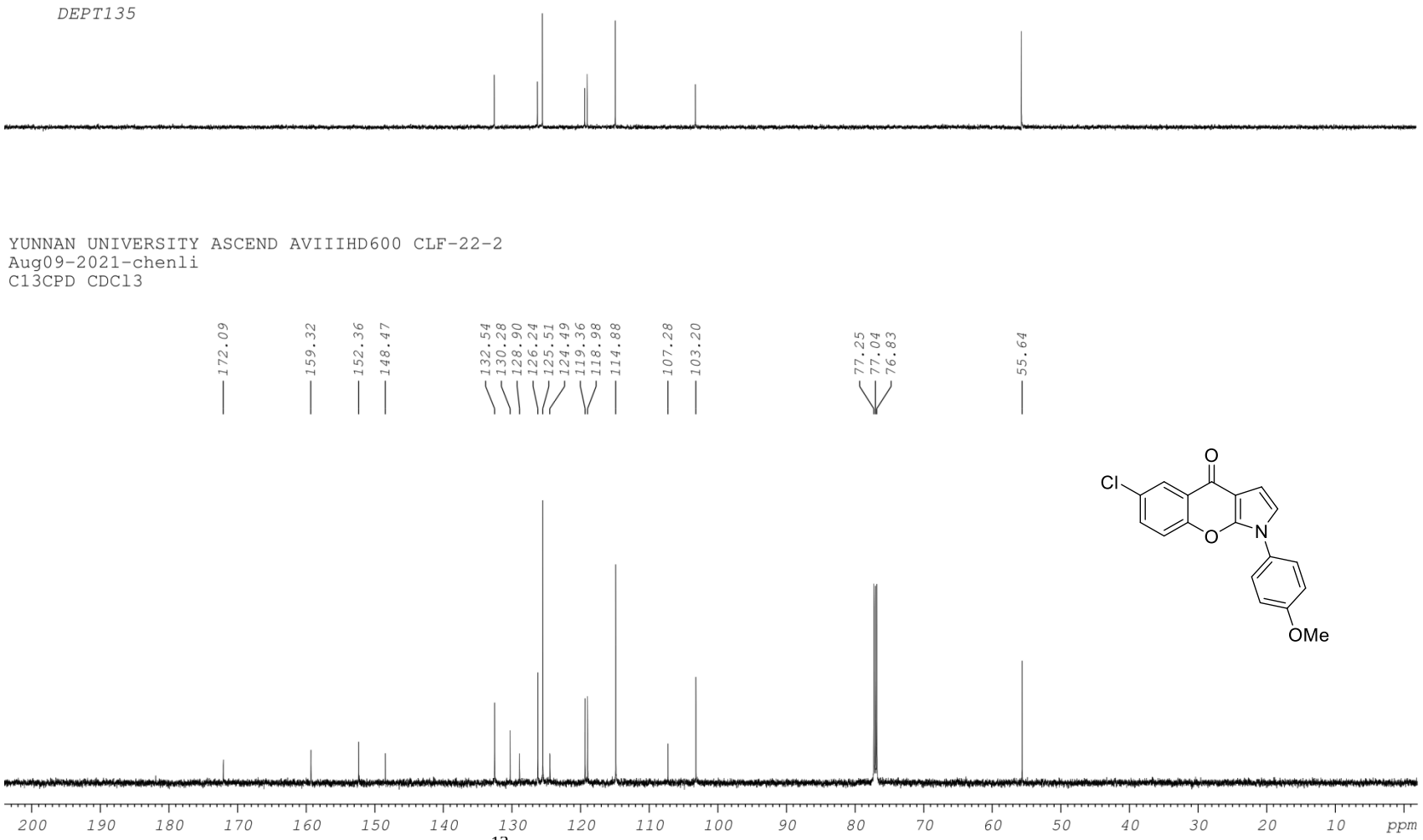


Figure S86. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3d'**

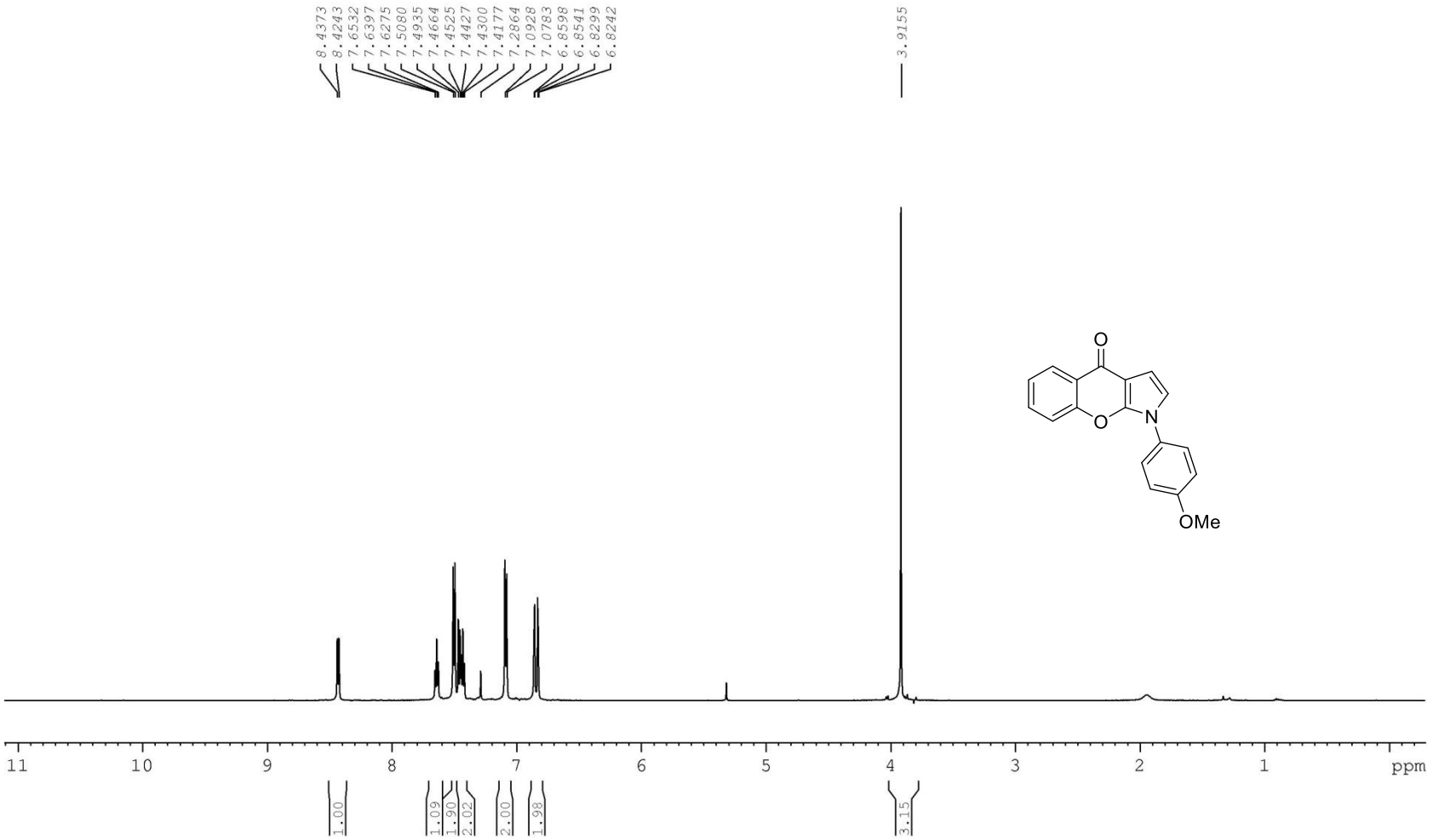


Figure S87. ^{1}H NMR (**600** MHz, $CDCl_3$) spectra of compound **3e'**

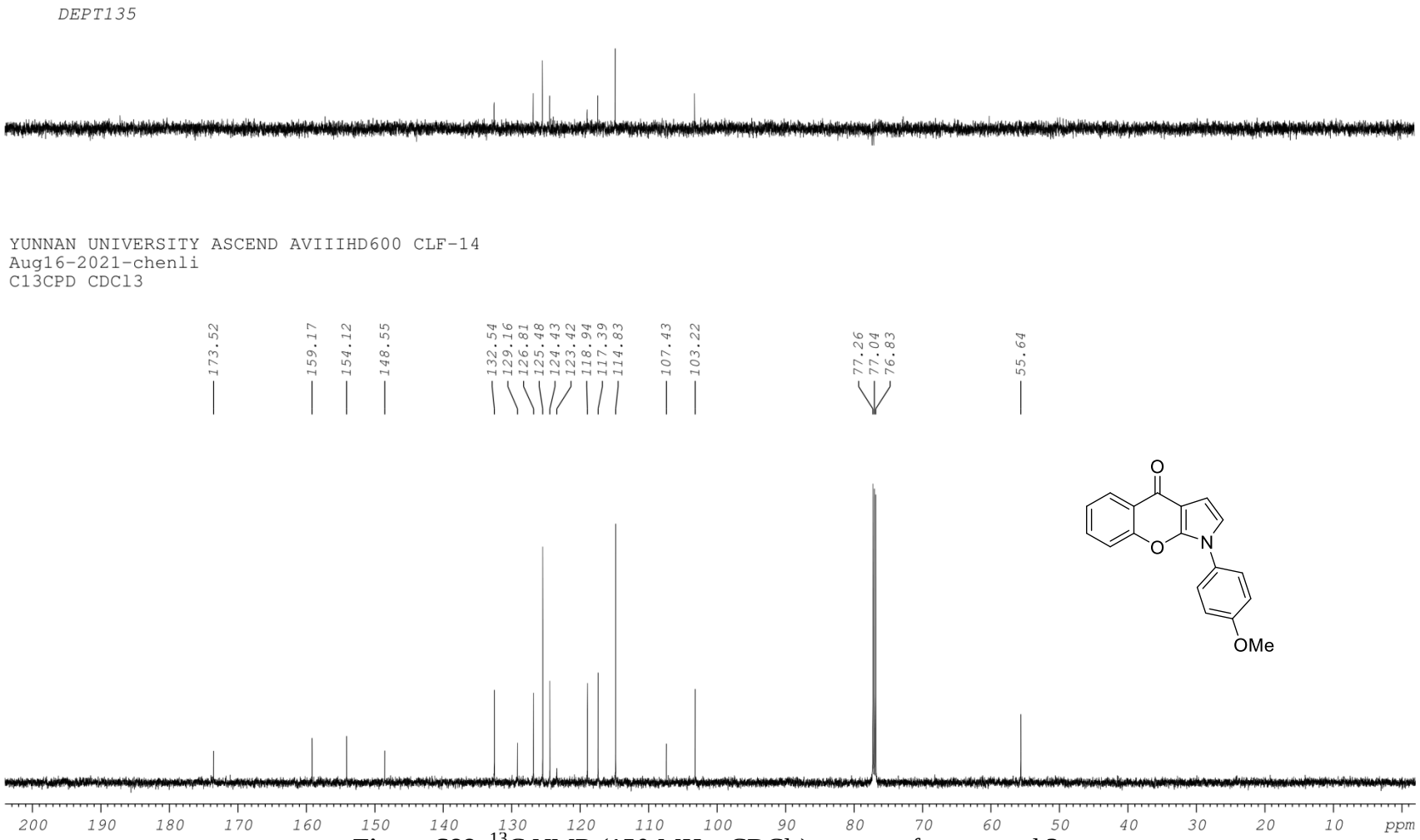


Figure S88. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3e'**

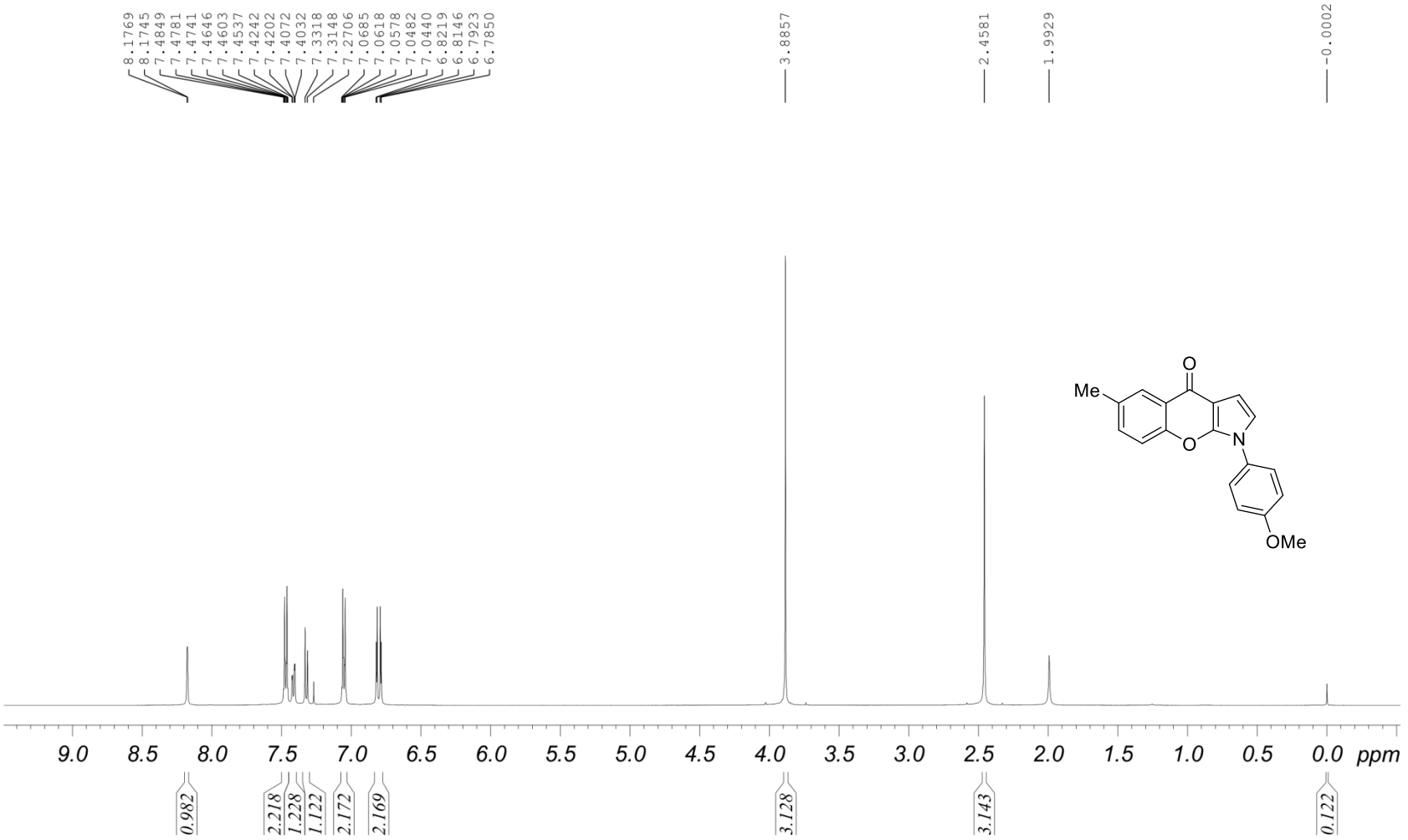


Figure S89. ^{1}H NMR (**500** MHz, $CDCl_3$) spectra of compound **3f'**

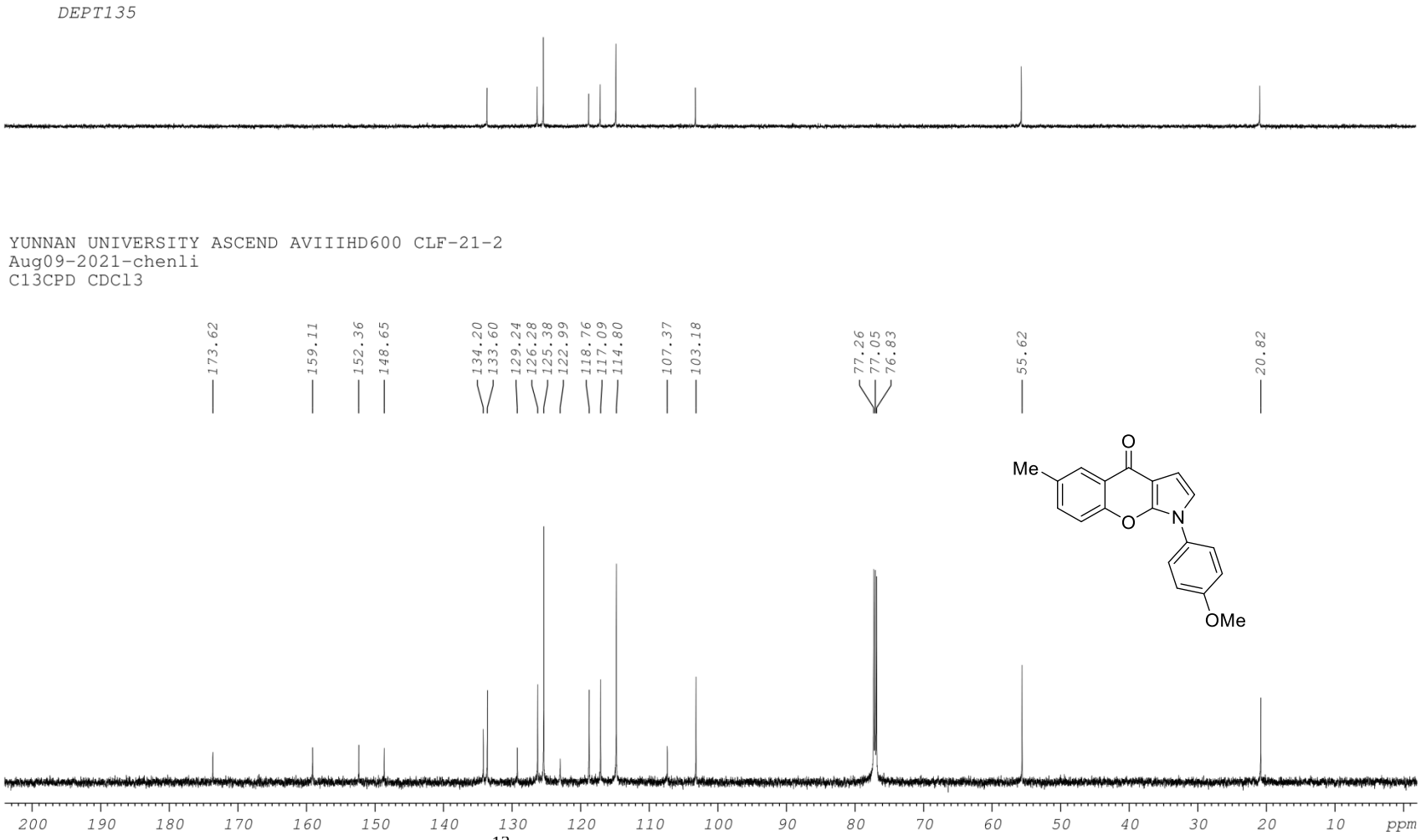


Figure S90. ^{13}C NMR (**150** MHz, $CDCl_3$) spectra of compound **3f'**

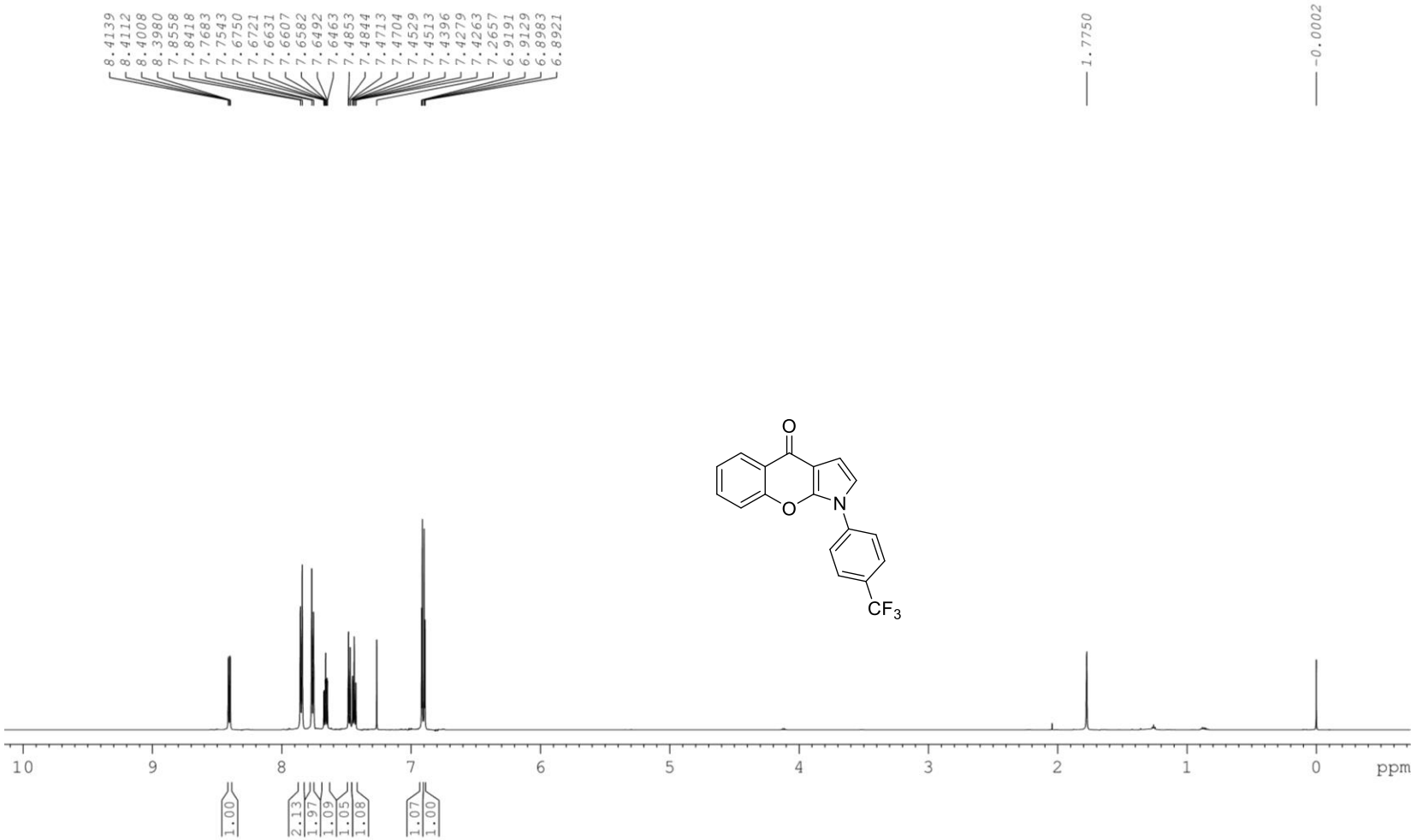


Figure S91. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3g'**

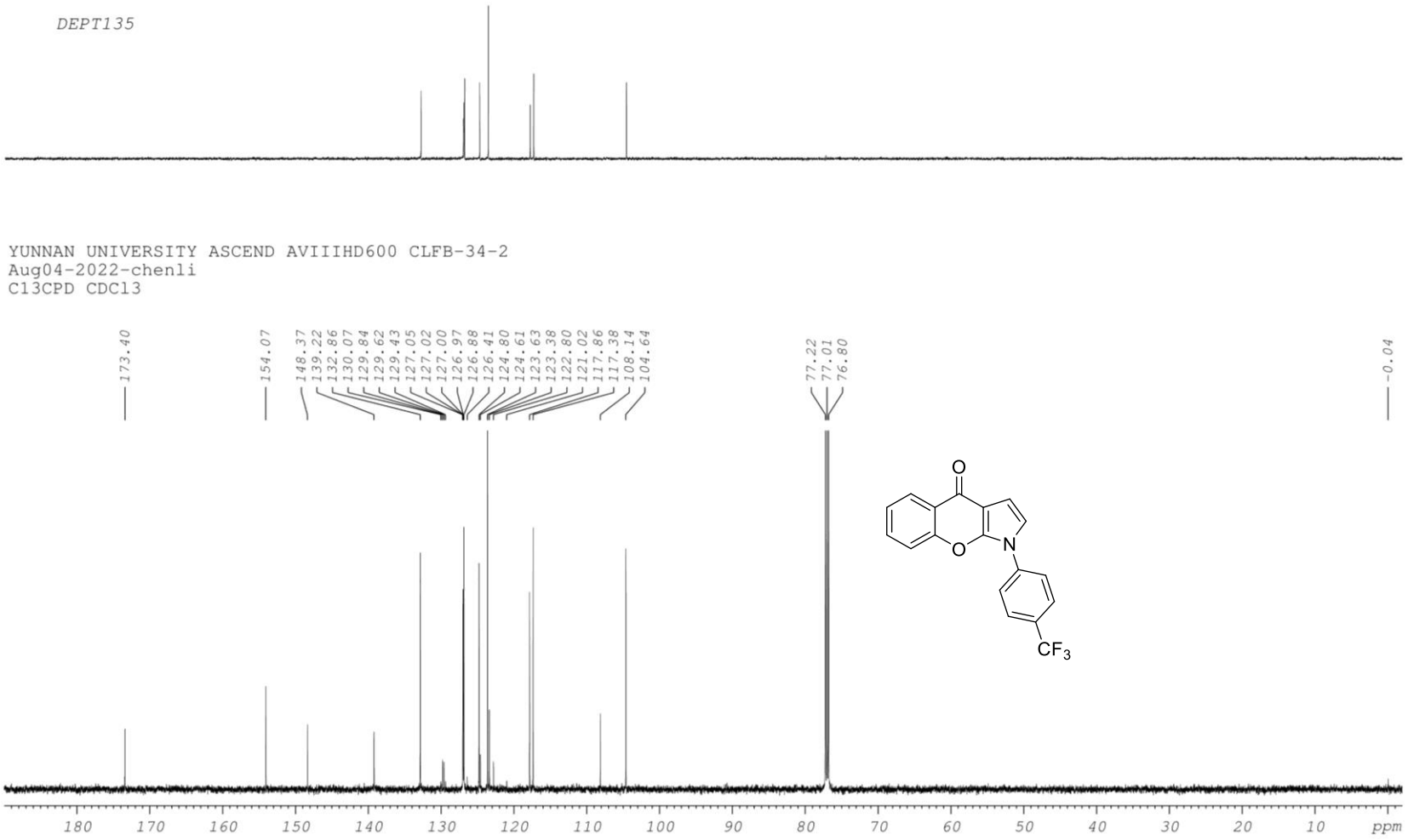


Figure S92. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3g'**

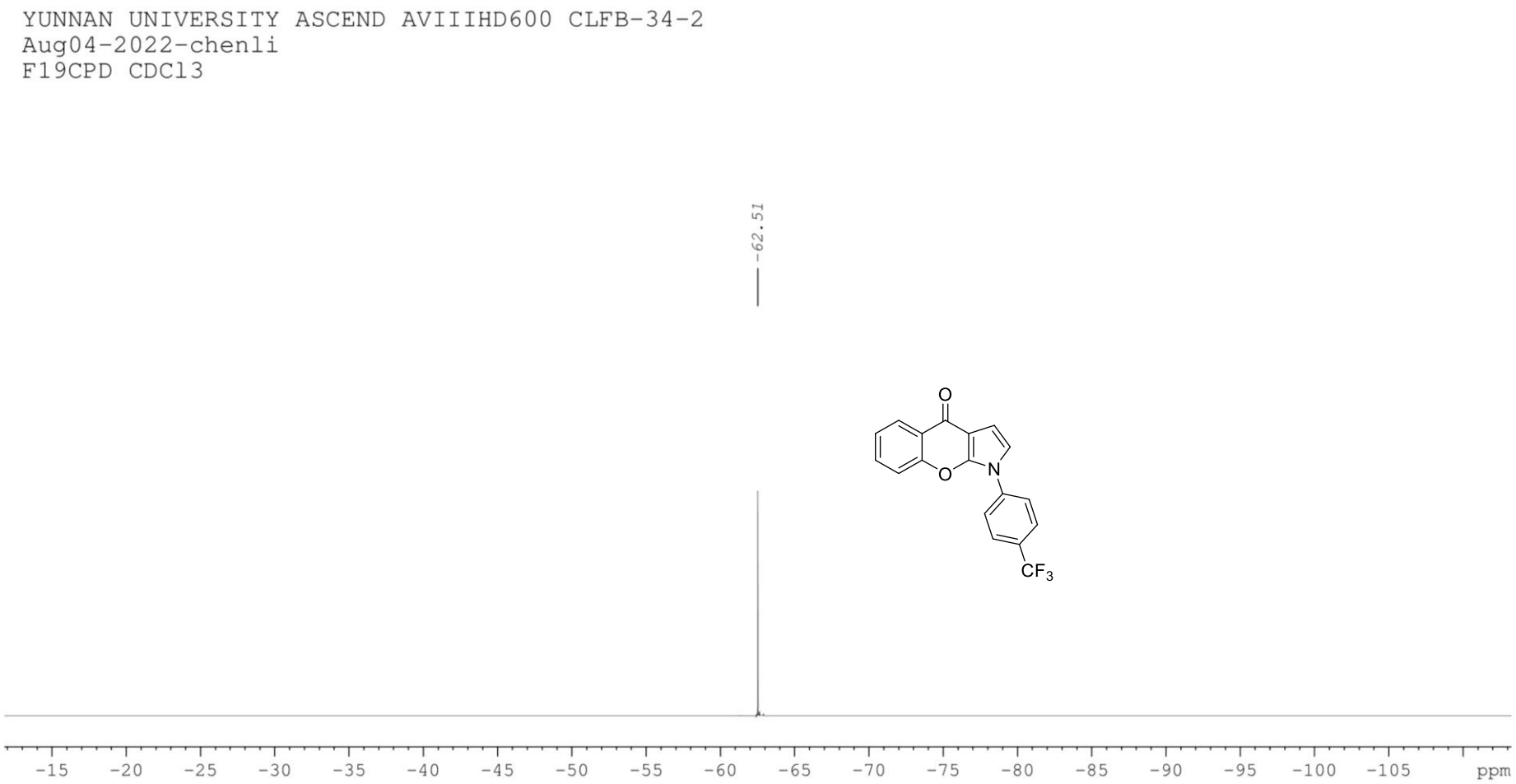


Figure S93. ^{19}F NMR (564 MHz, $CDCl_3$) spectra of compound **3g'**

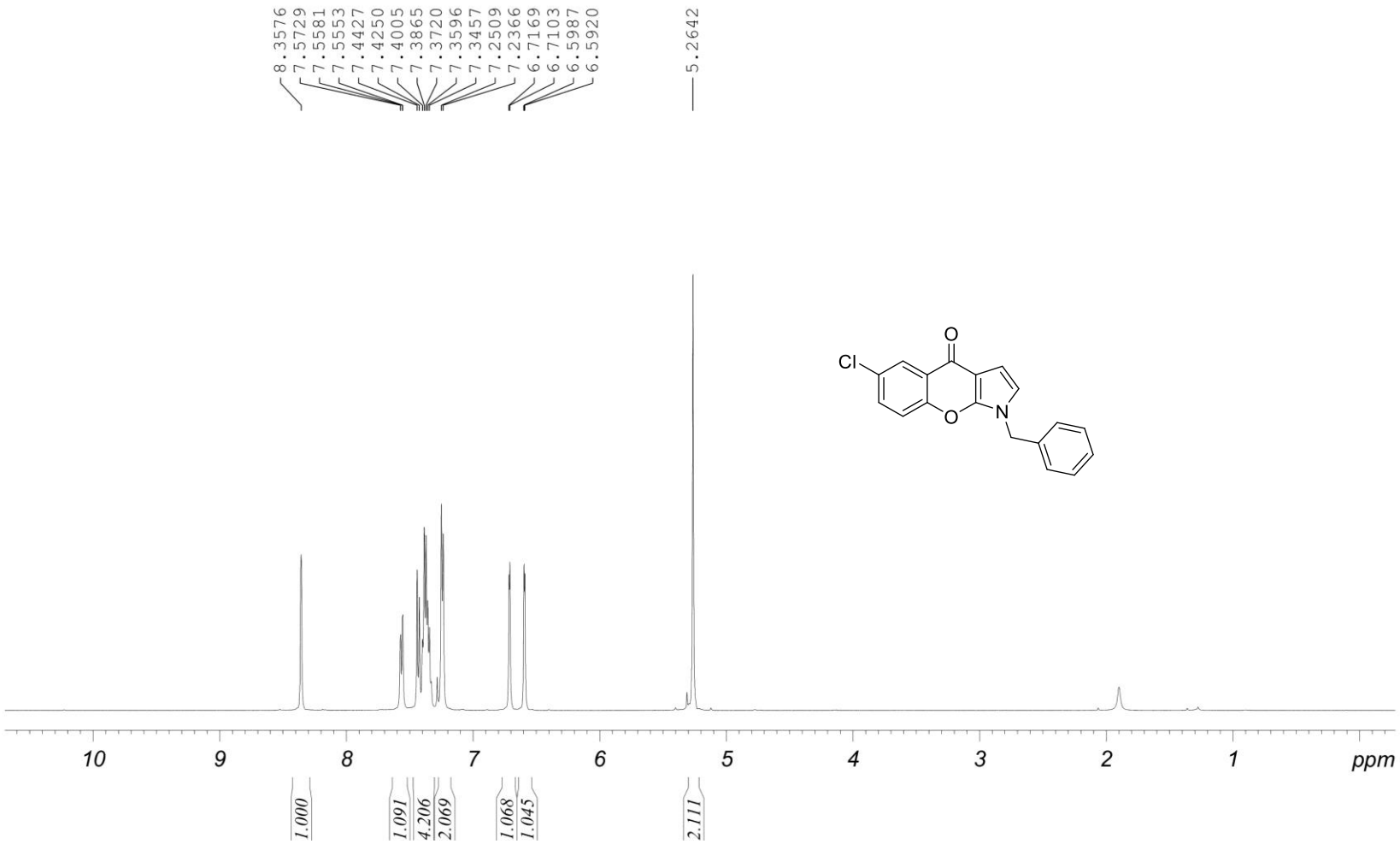


Figure S94. ^{1}H NMR (**500** MHz, $CDCl_3$) spectra of compound **3h'**

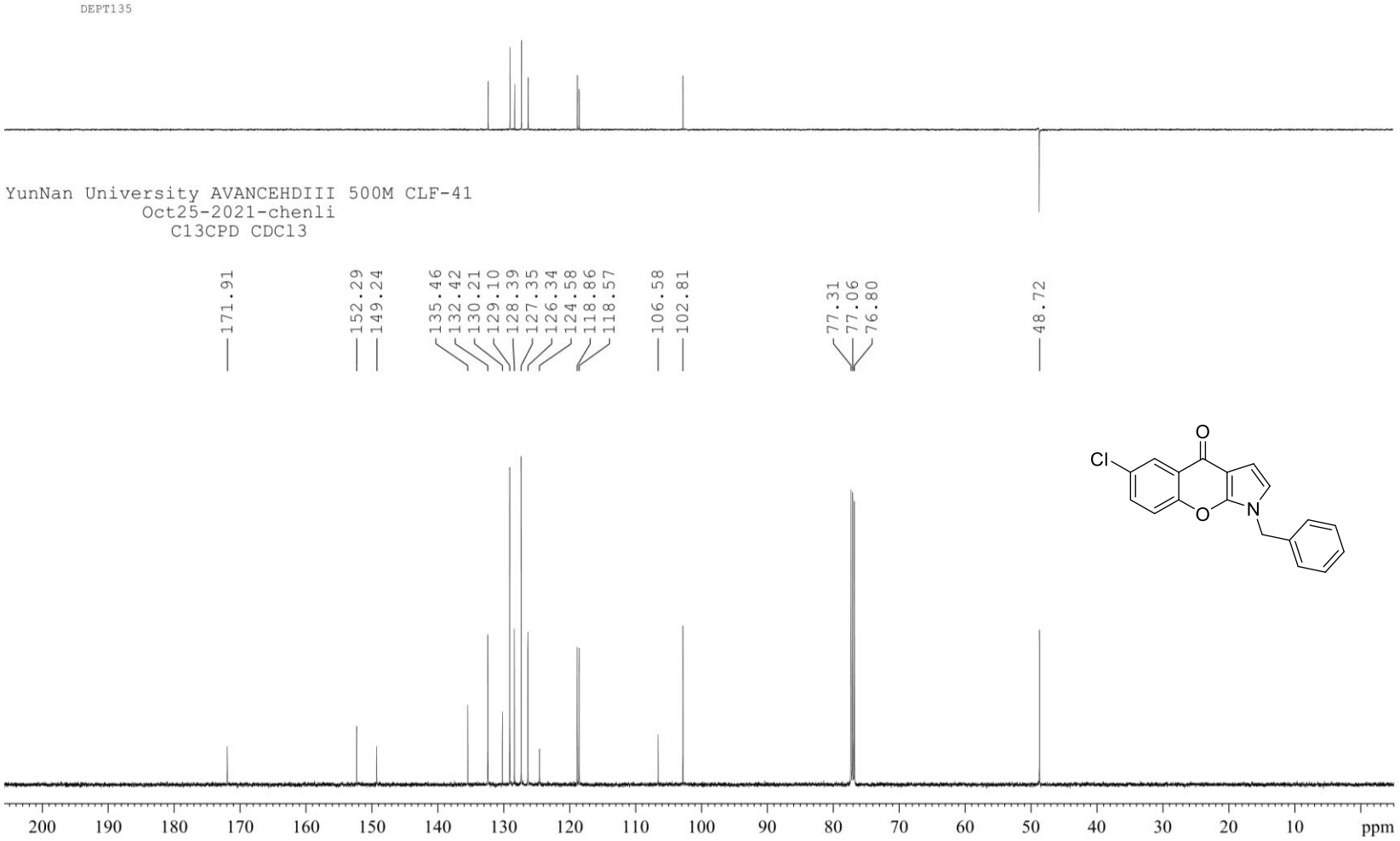


Figure S95. ^{13}C NMR (**125** MHz, $CDCl_3$) spectra of compound **3h'**

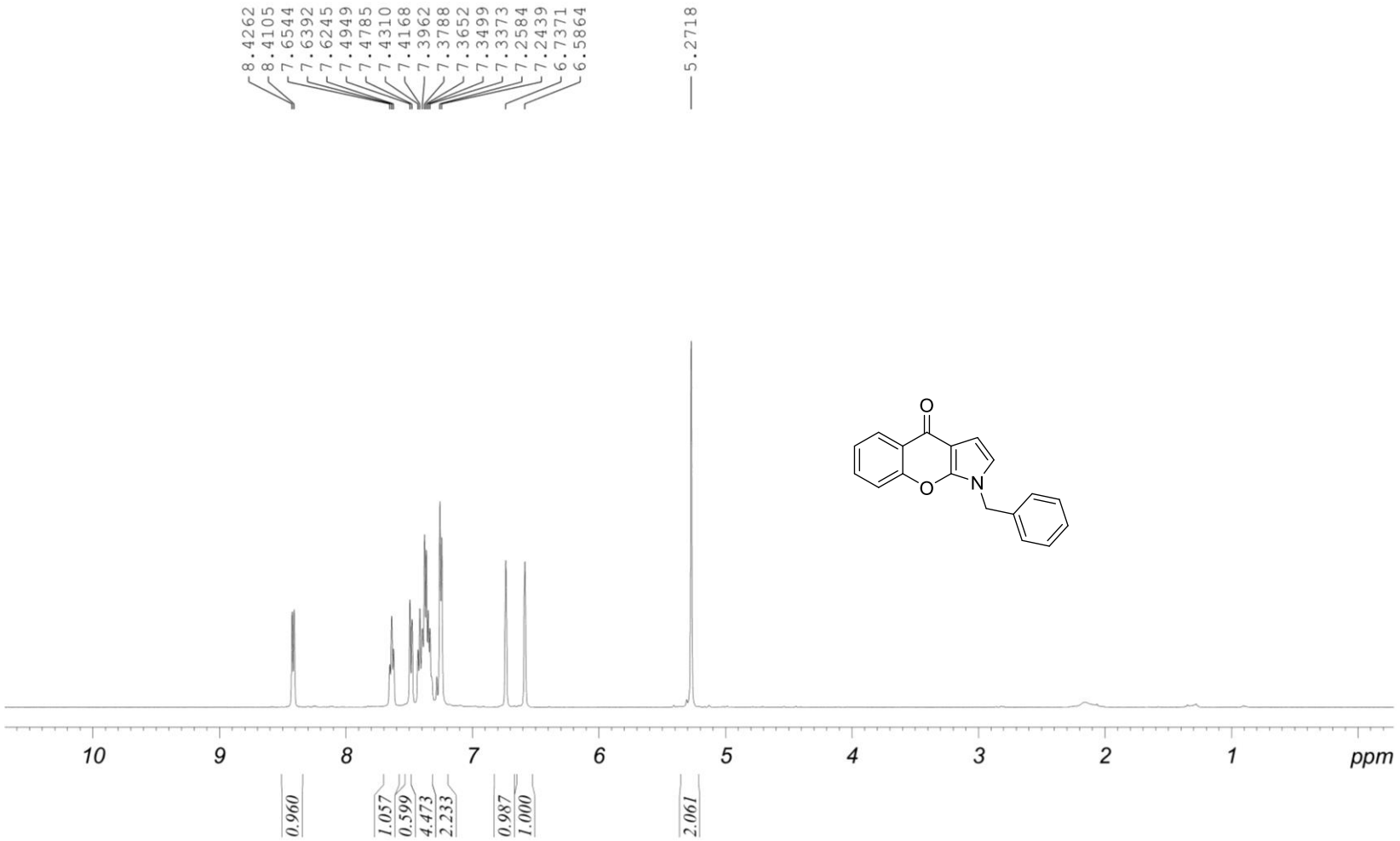


Figure S96. ^{1}H NMR (**500** MHz, $CDCl_3$) spectra of compound **3i'**

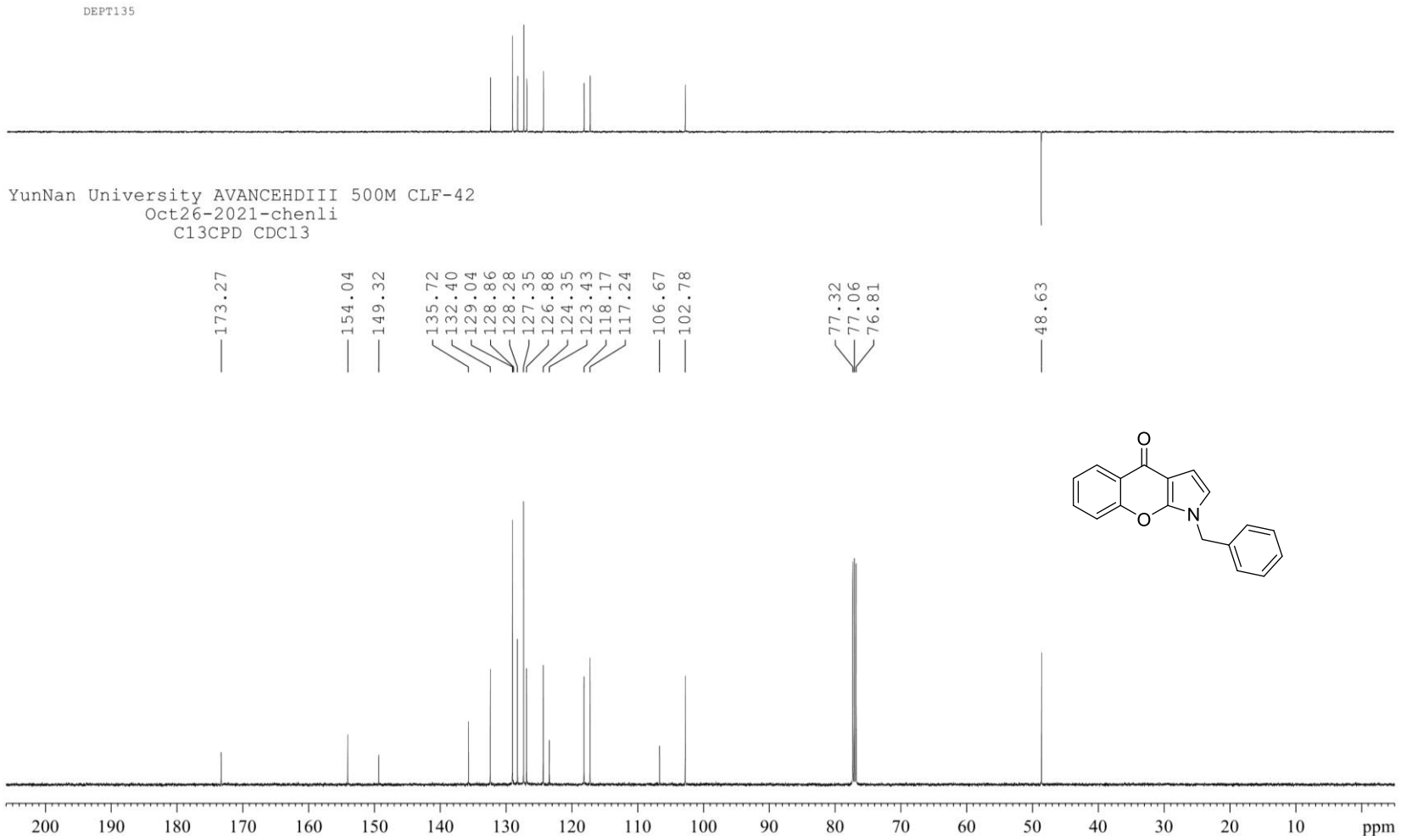


Figure S97. ^{13}C NMR (**125** MHz, $CDCl_3$) spectra of compound **3i'**

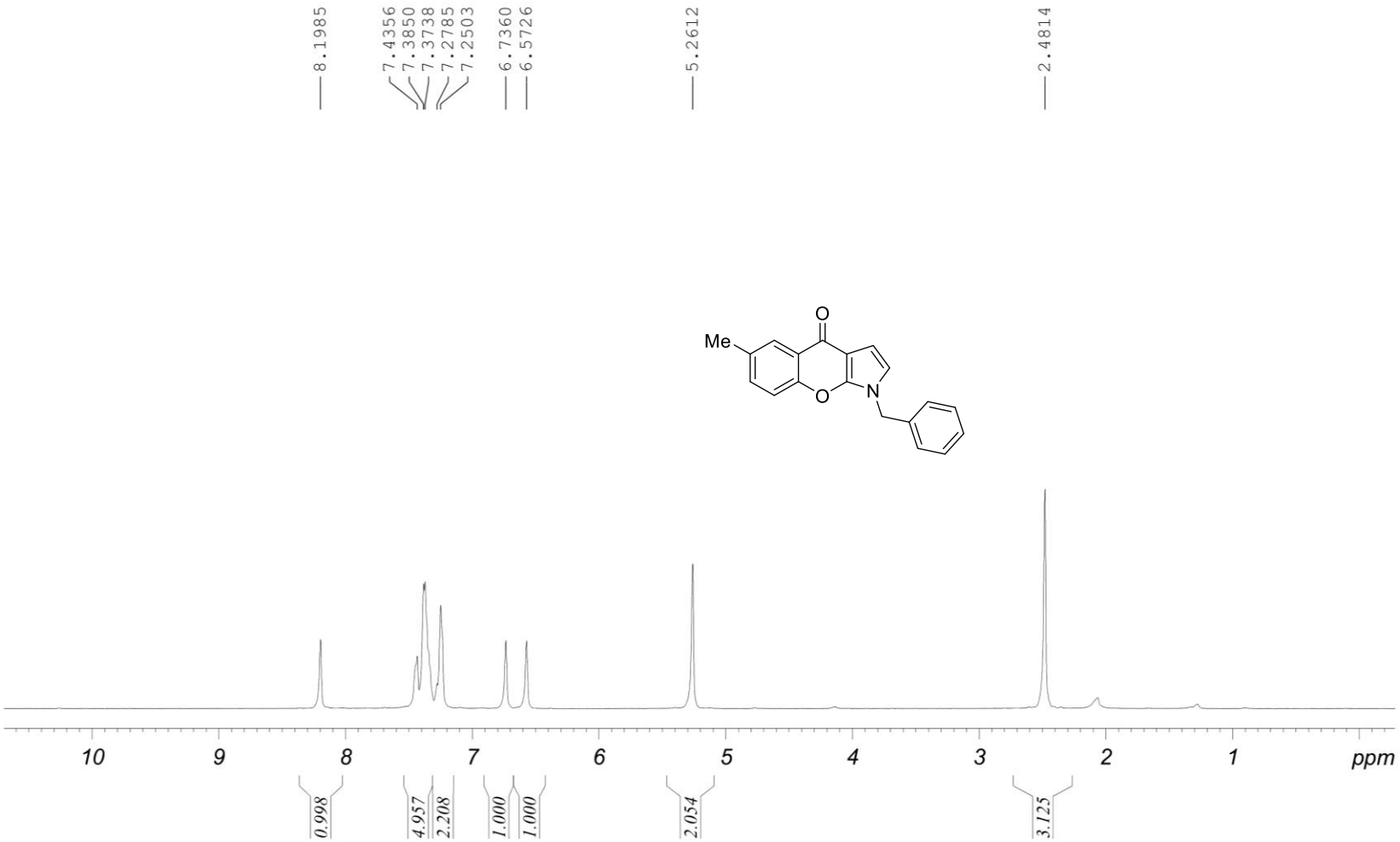


Figure S98. ^{1}H NMR (**500** MHz, $CDCl_3$) spectra of compound **3j'**

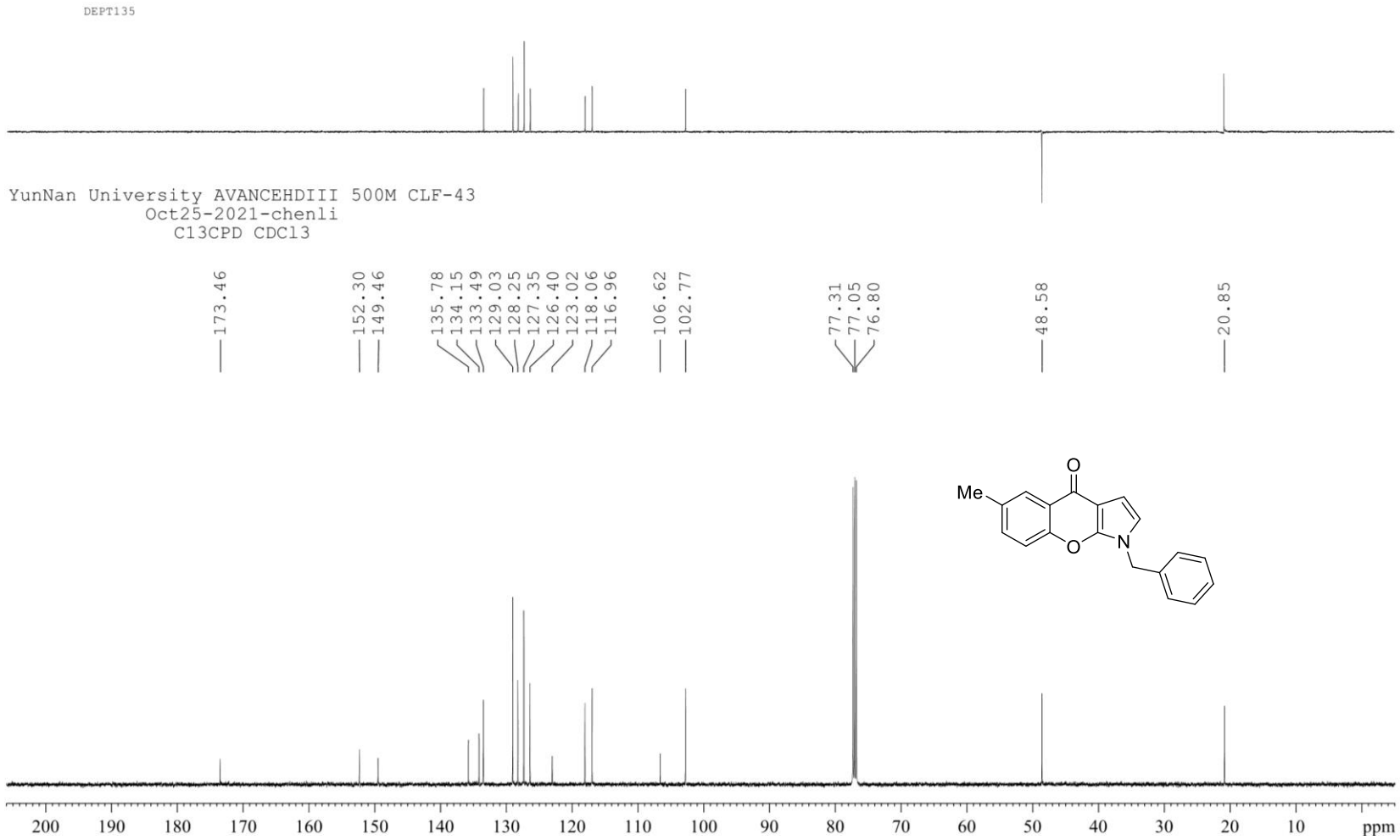


Figure S99. ^{13}C NMR (**125** MHz, $CDCl_3$) spectra of compound **3j'**

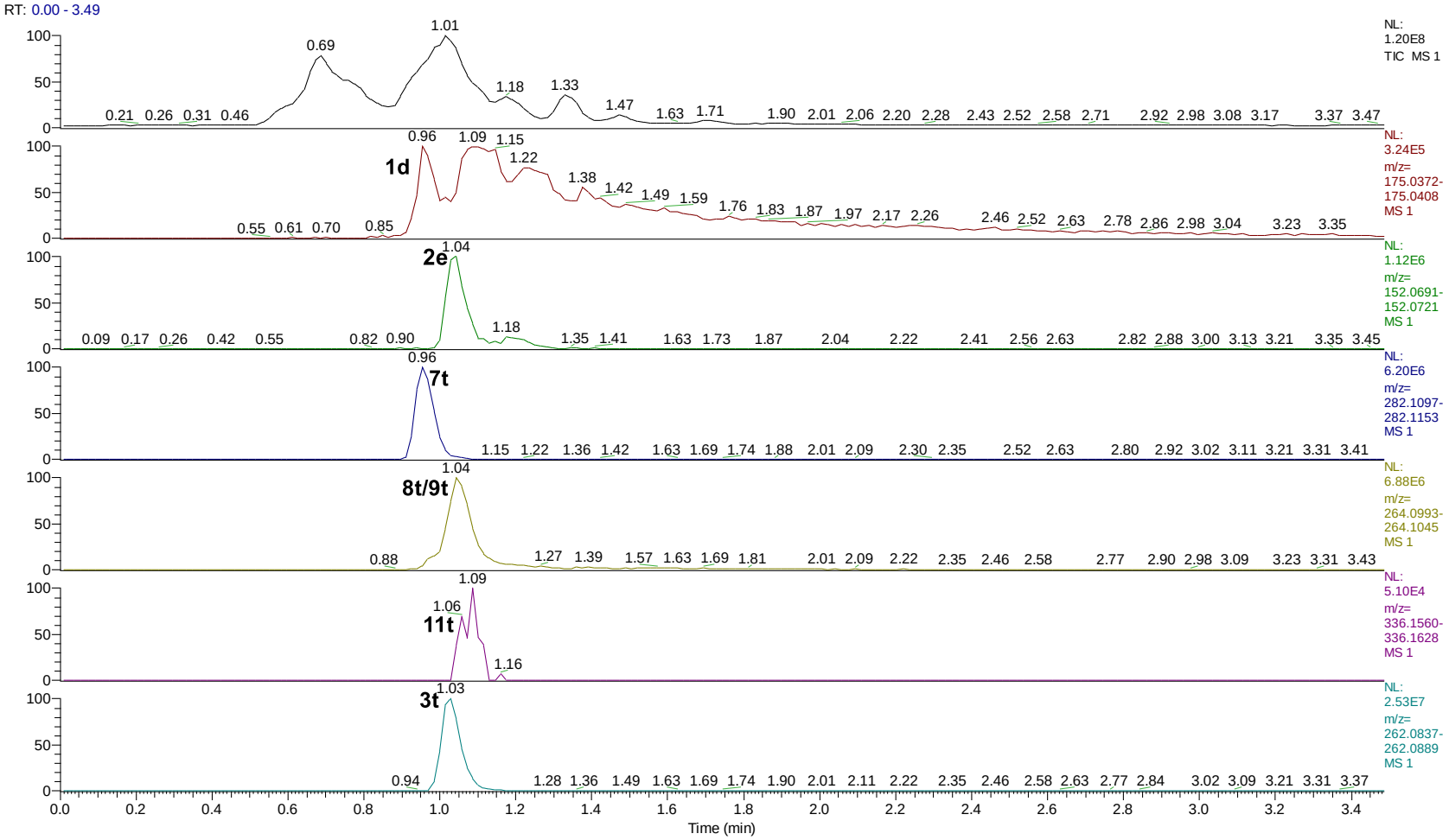


Figure S100. HPLC of the reaction mixture

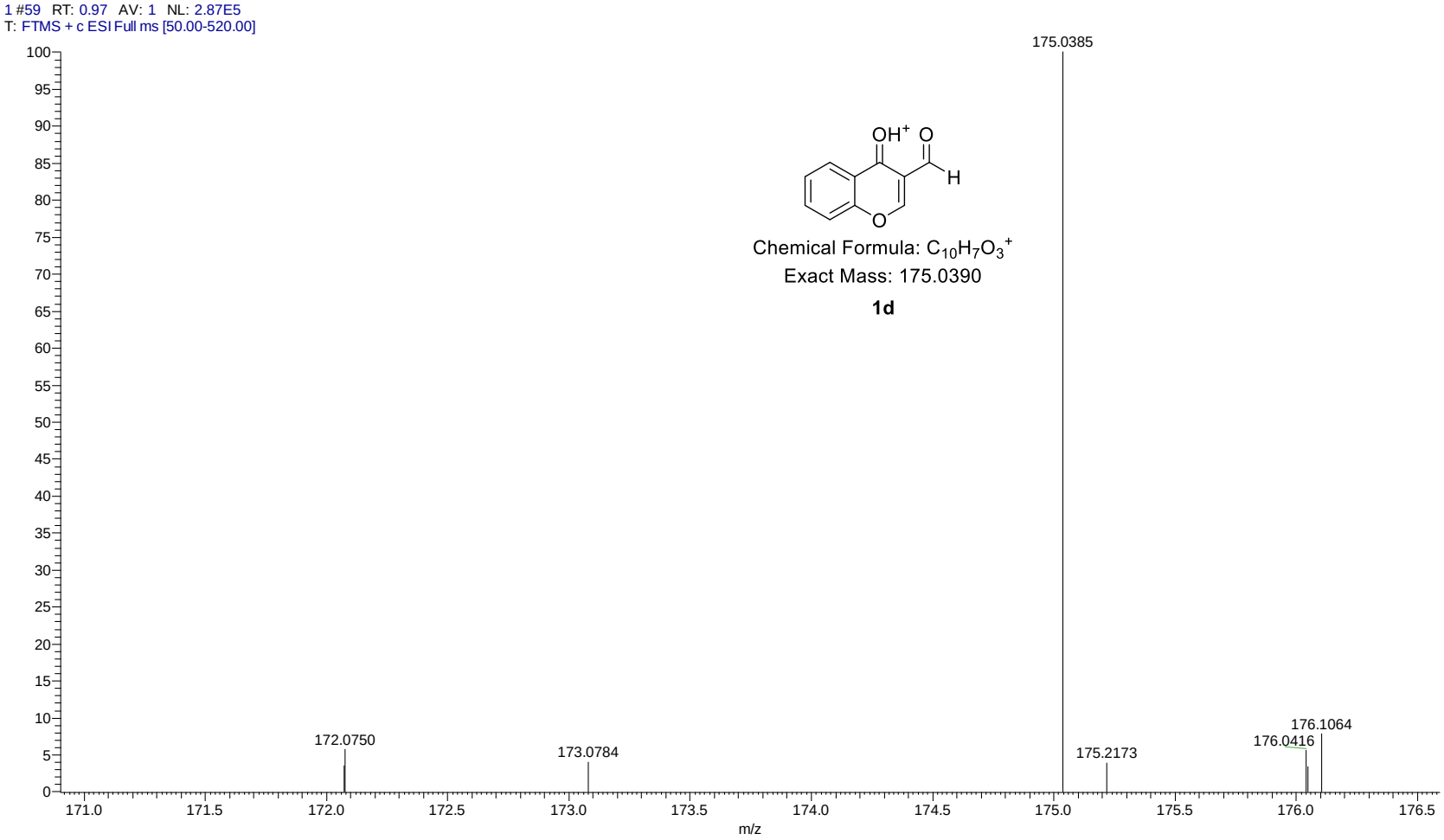


Figure S101. HRMS of intermediate **1d**

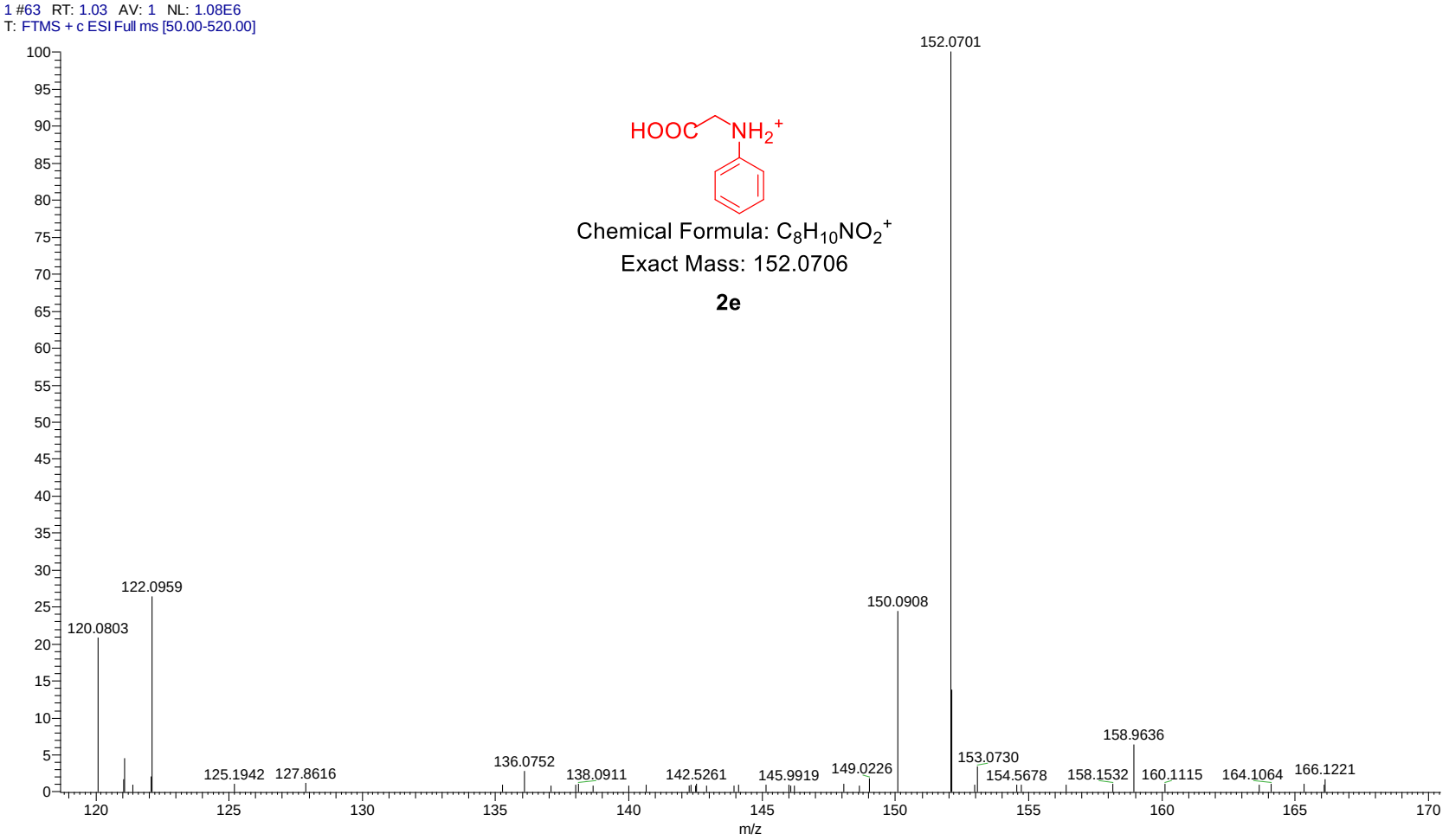


Figure S102. HRMS of intermediate **2e**

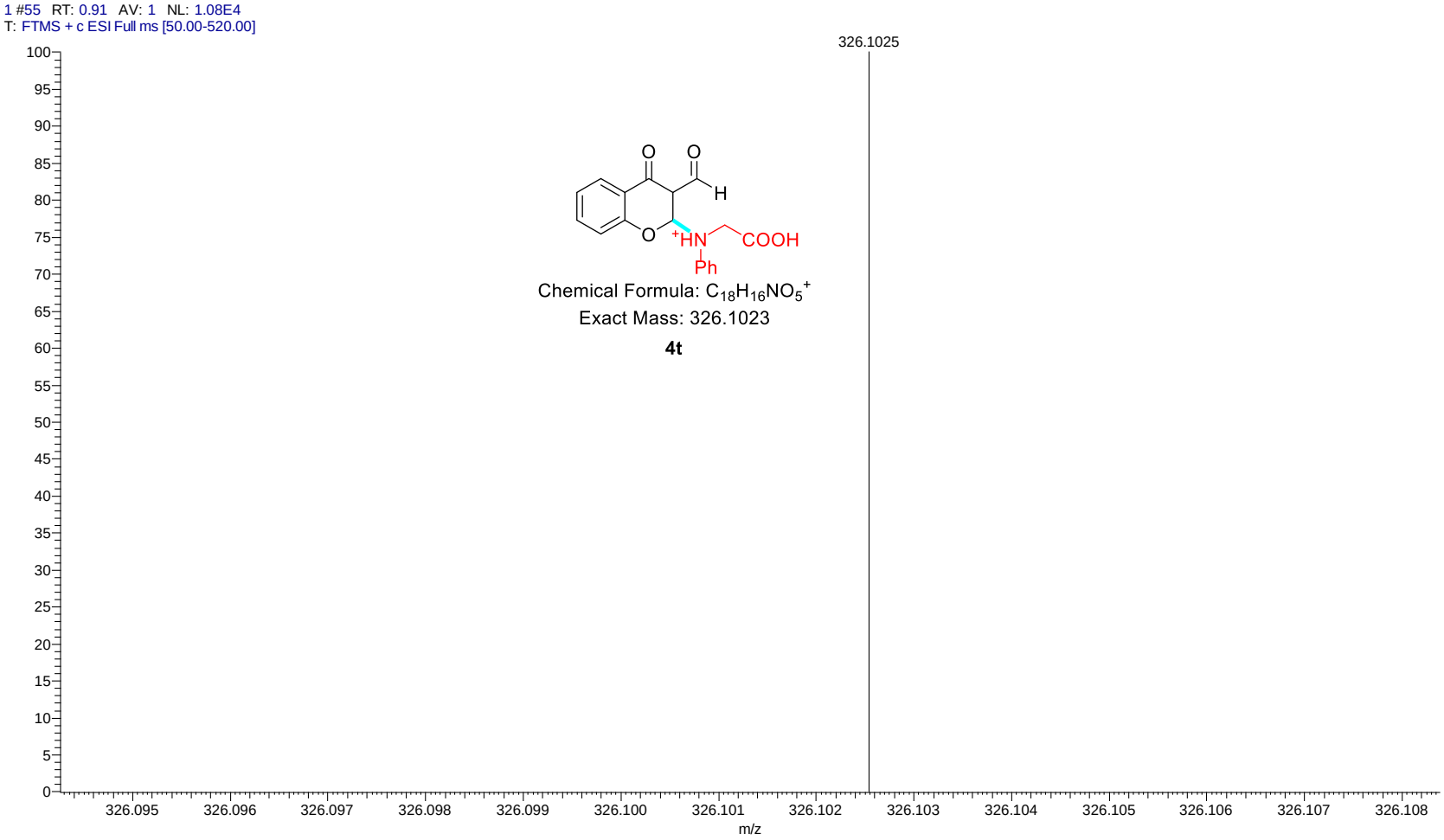


Figure S103. HRMS of intermediate **4t**

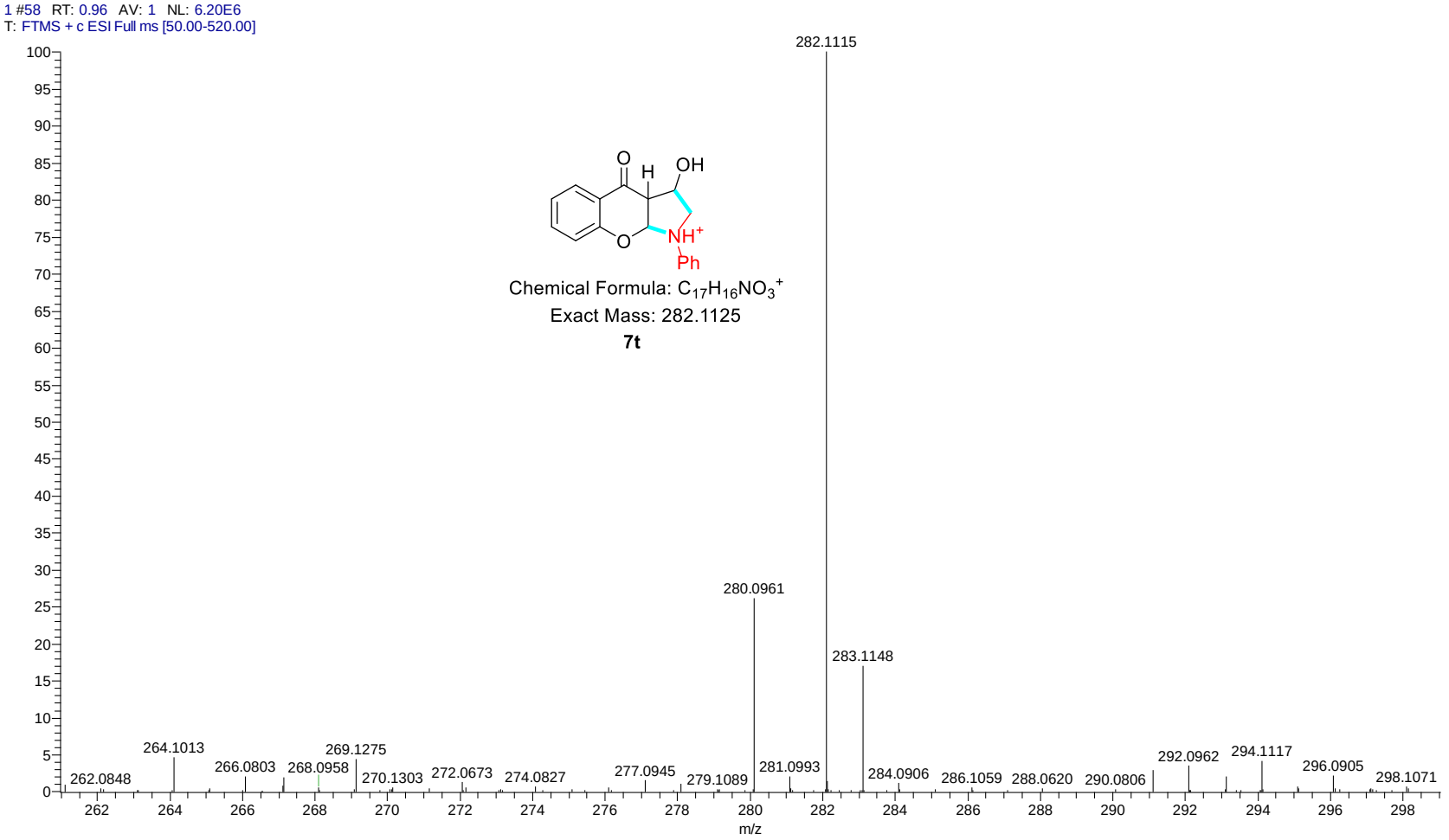


Figure S104. HRMS of intermediate **7t**

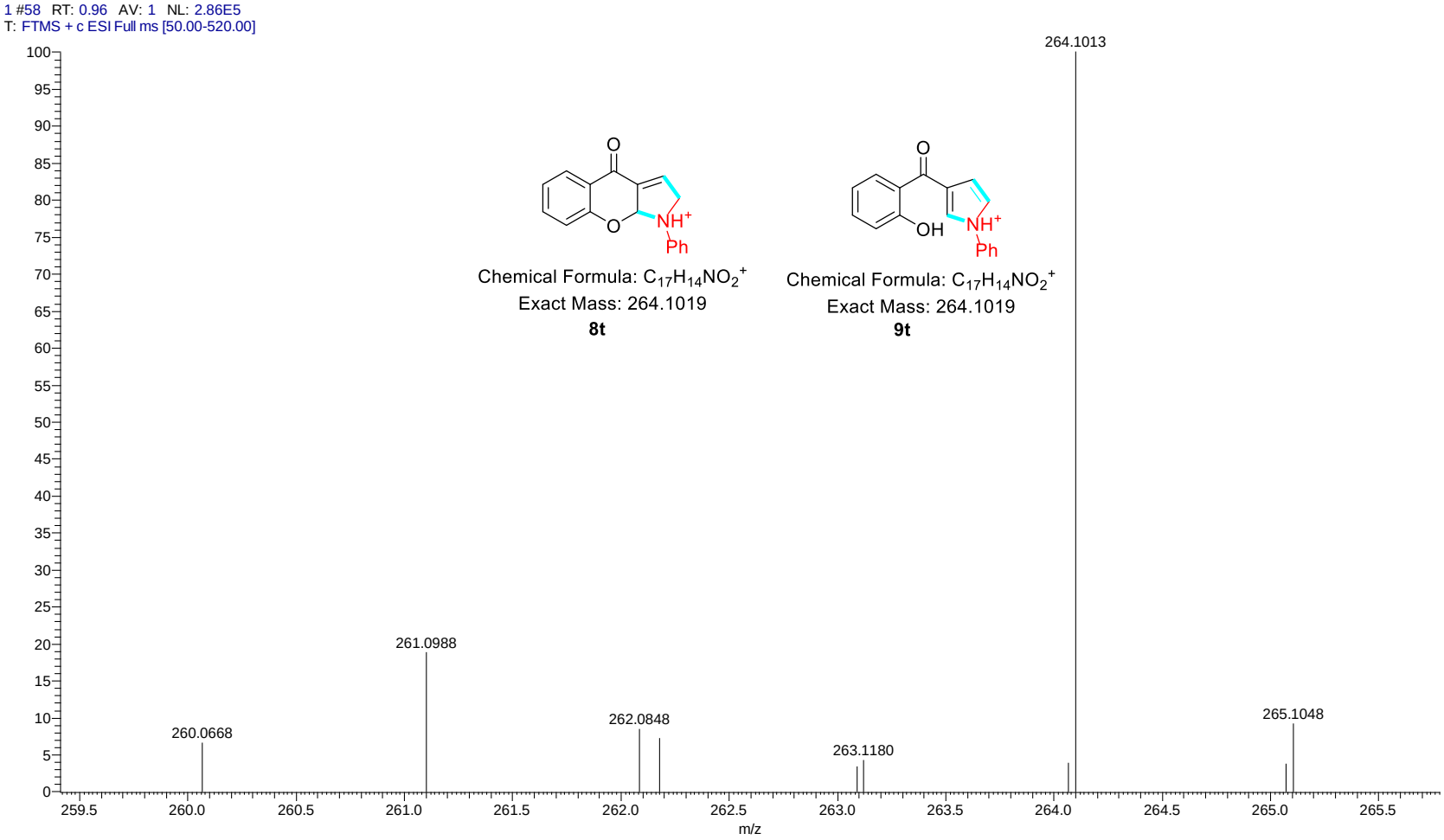


Figure S105. HRMS of intermediate **8t/9t**

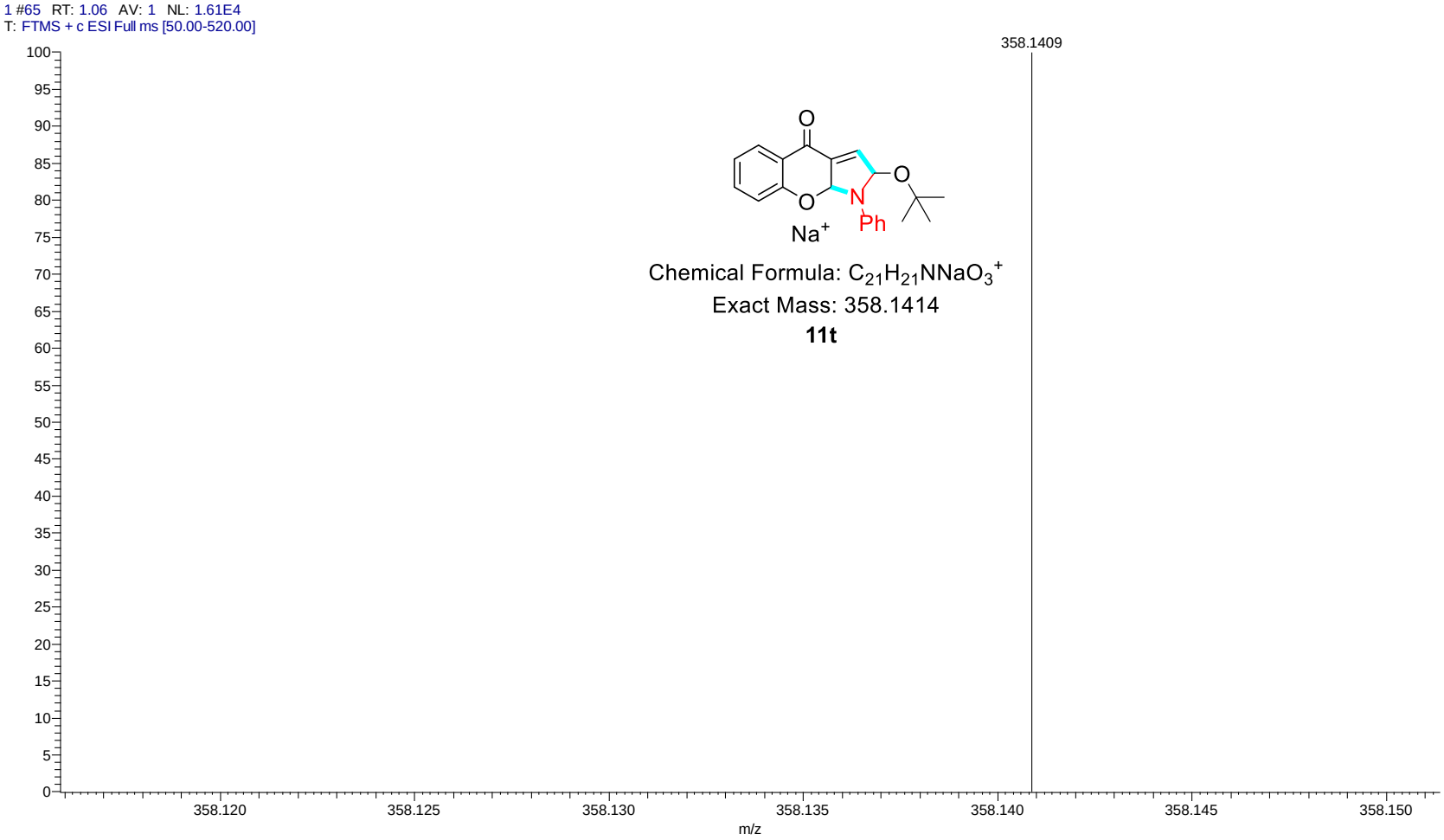


Figure S106. HRMS of intermediate **11t**

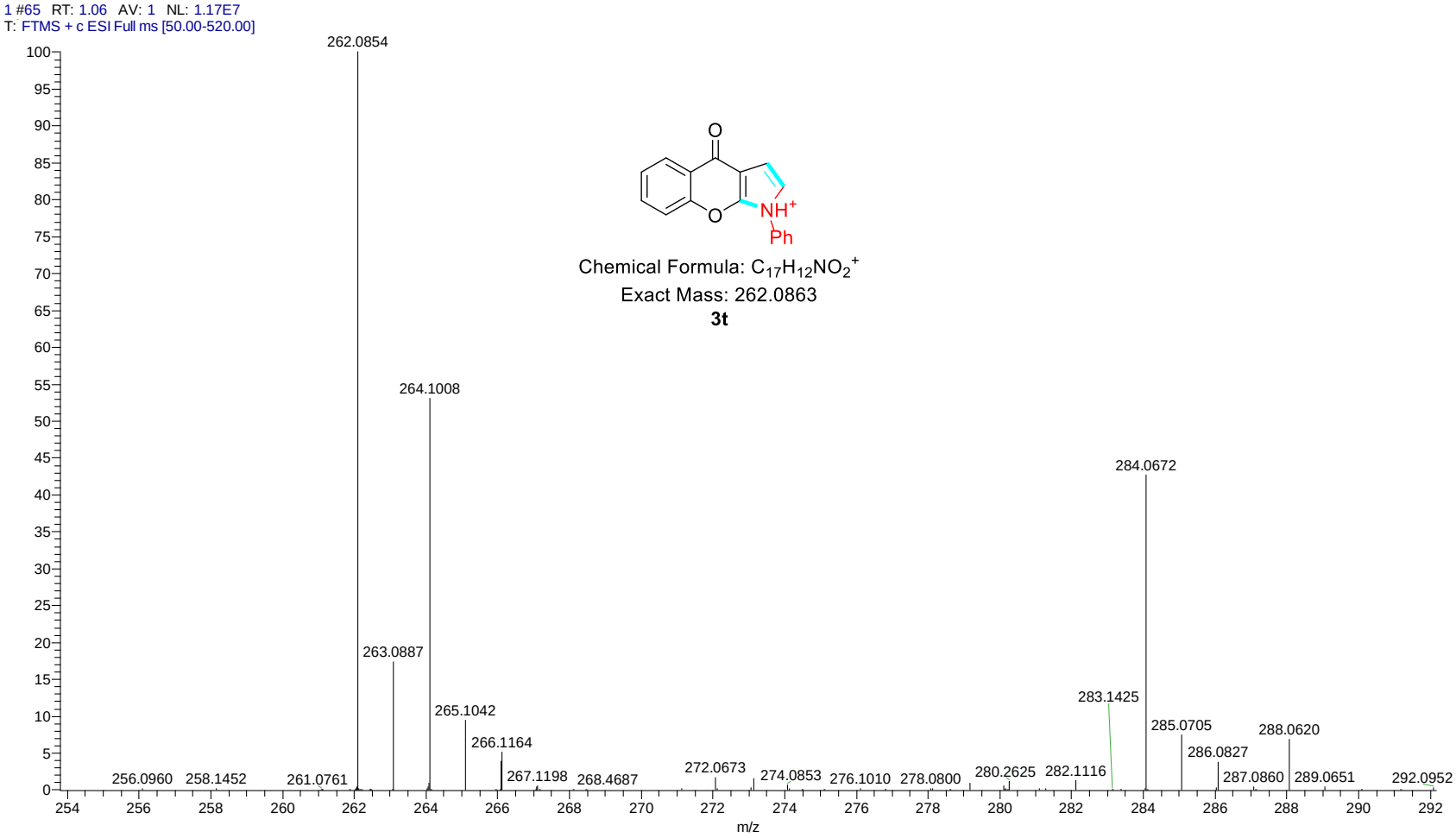


Figure S107. HRMS of compound **3t**

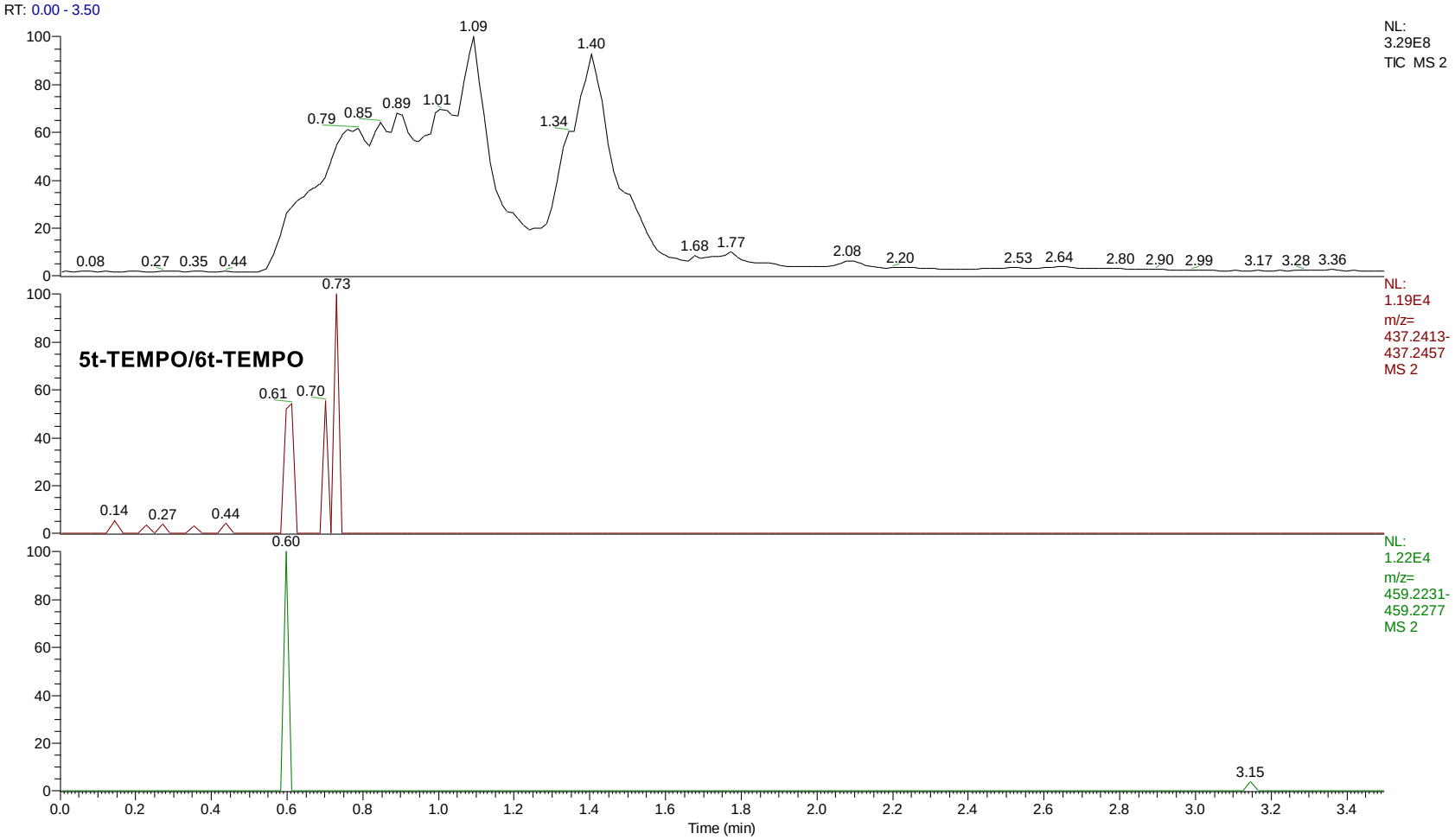


Figure S108. HPLC of the reaction mixture

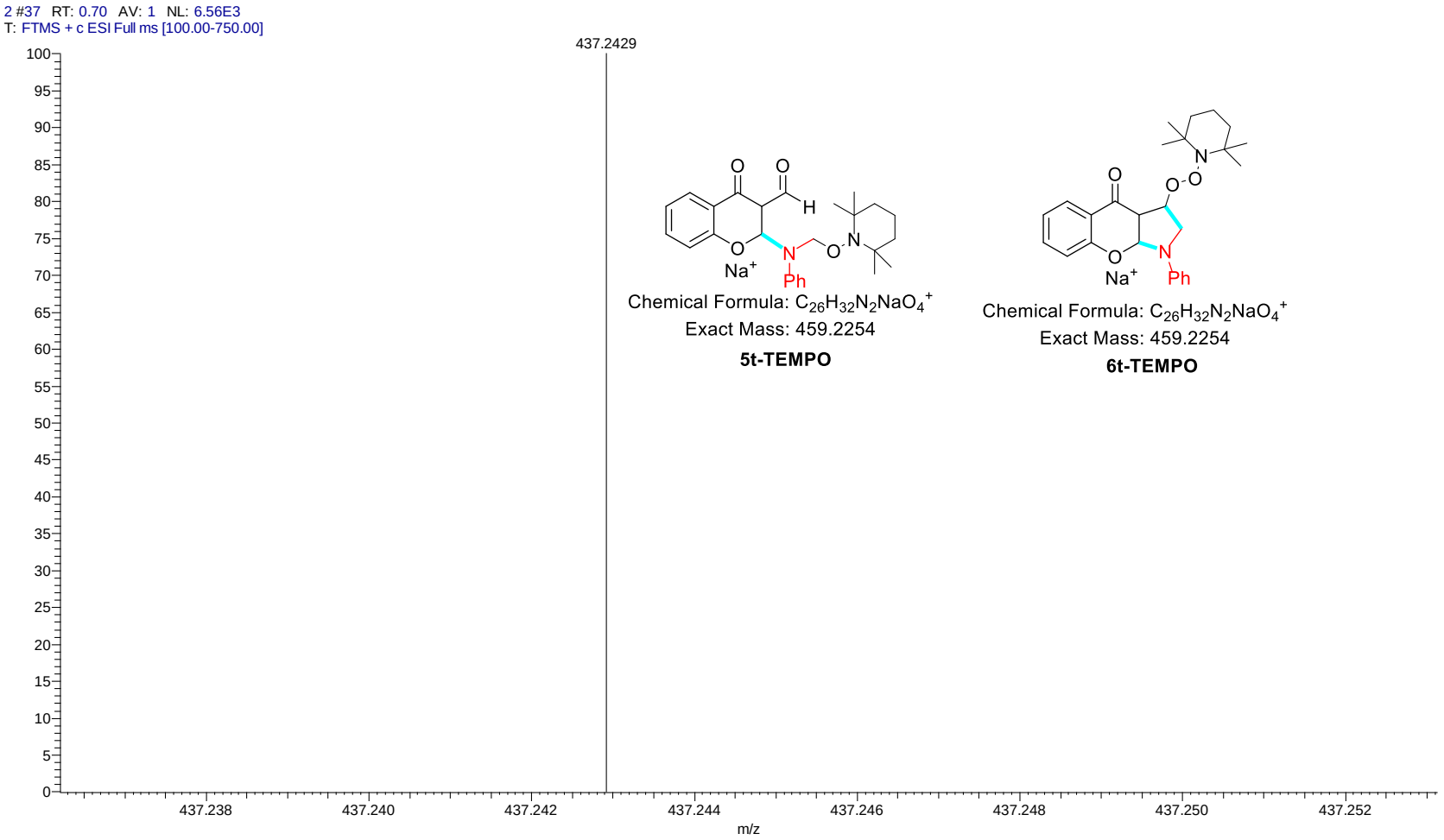


Figure S109. HRMS of intermediate **5t-TEMPO/6t-TEMPO**

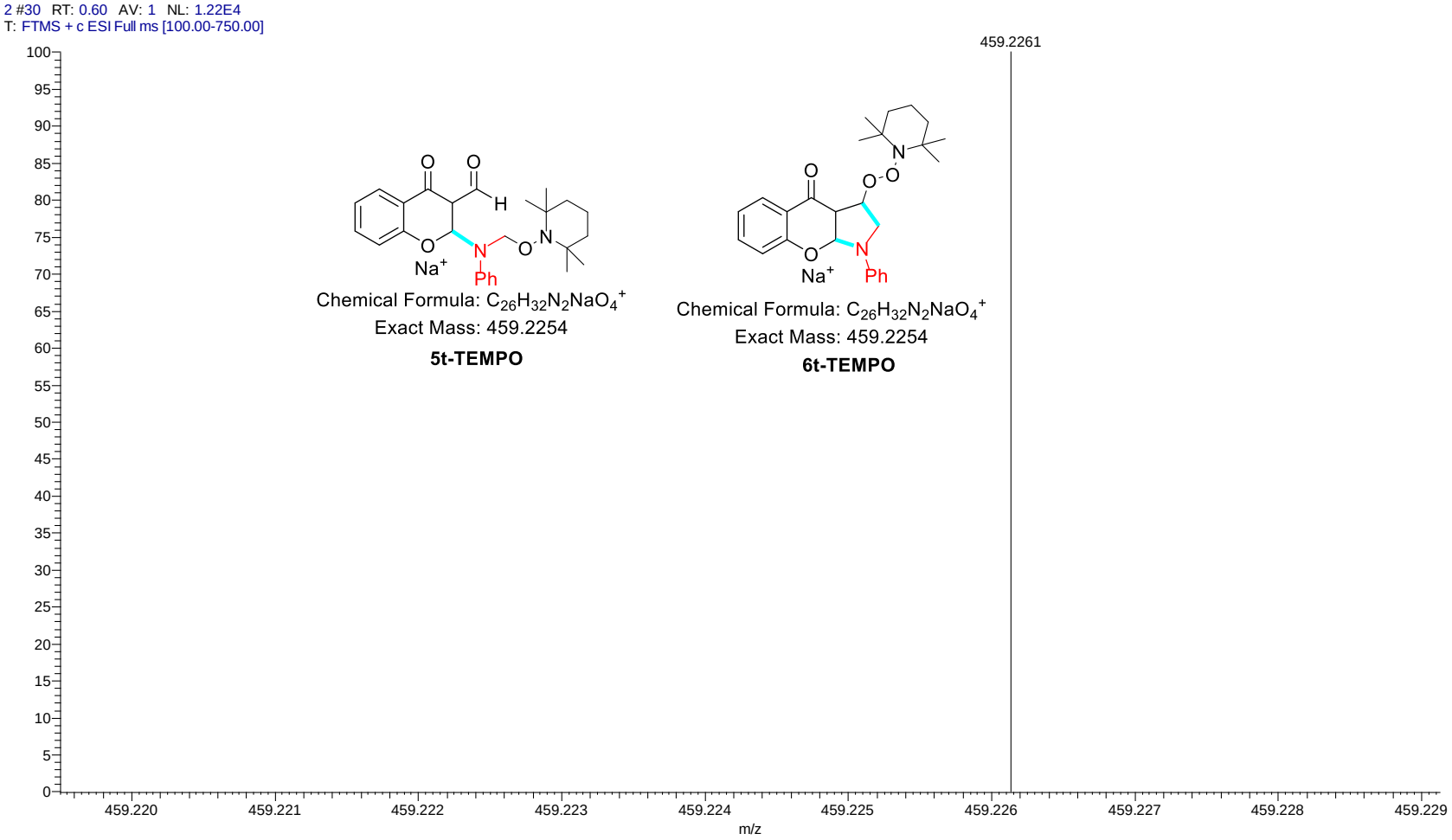


Figure S110. HRMS of intermediate **5t-TEMPO/6t-TEMPO**

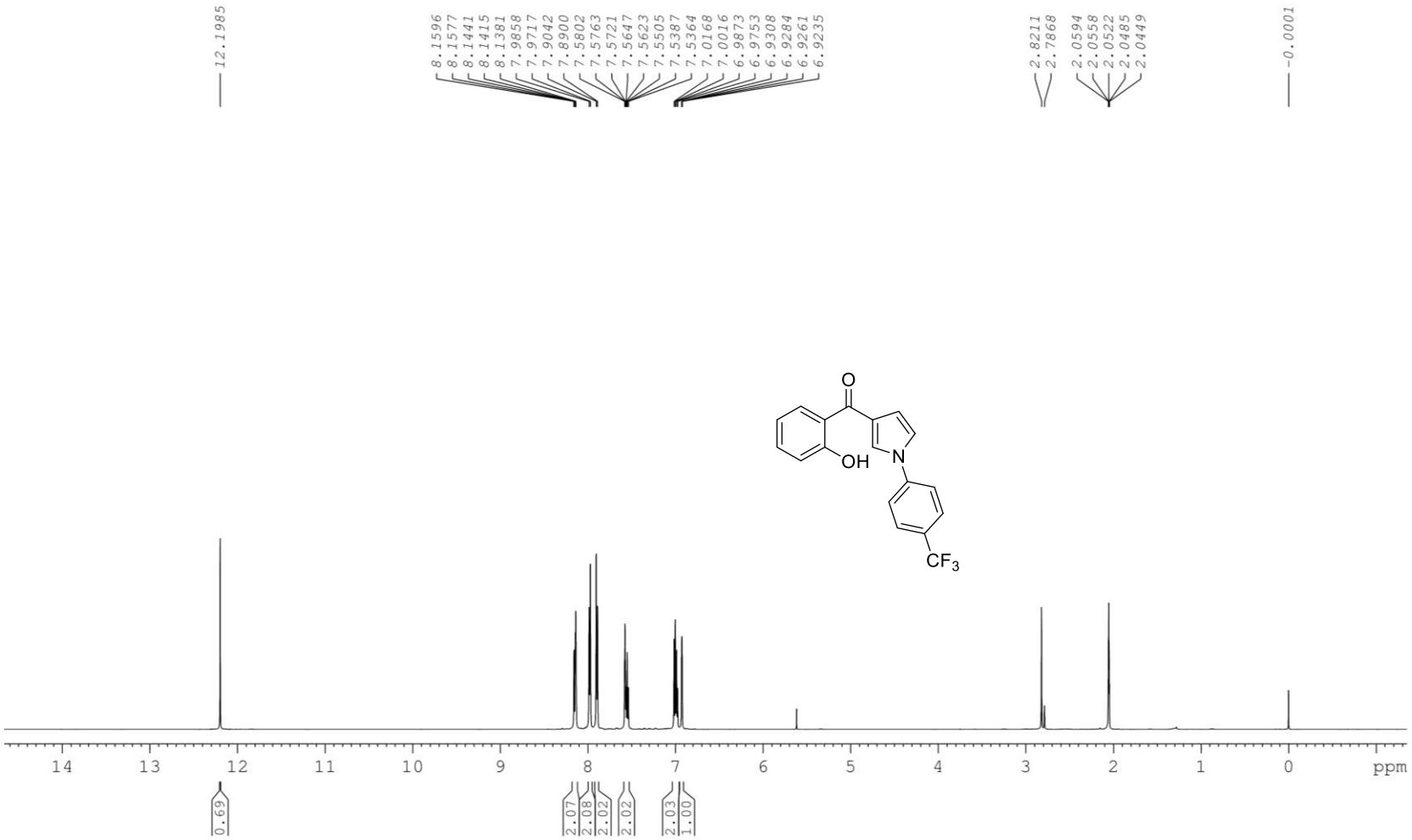


Figure S111. ^{1}H NMR (600 MHz, Acetone-d_6) spectra of intermediate **9g'**

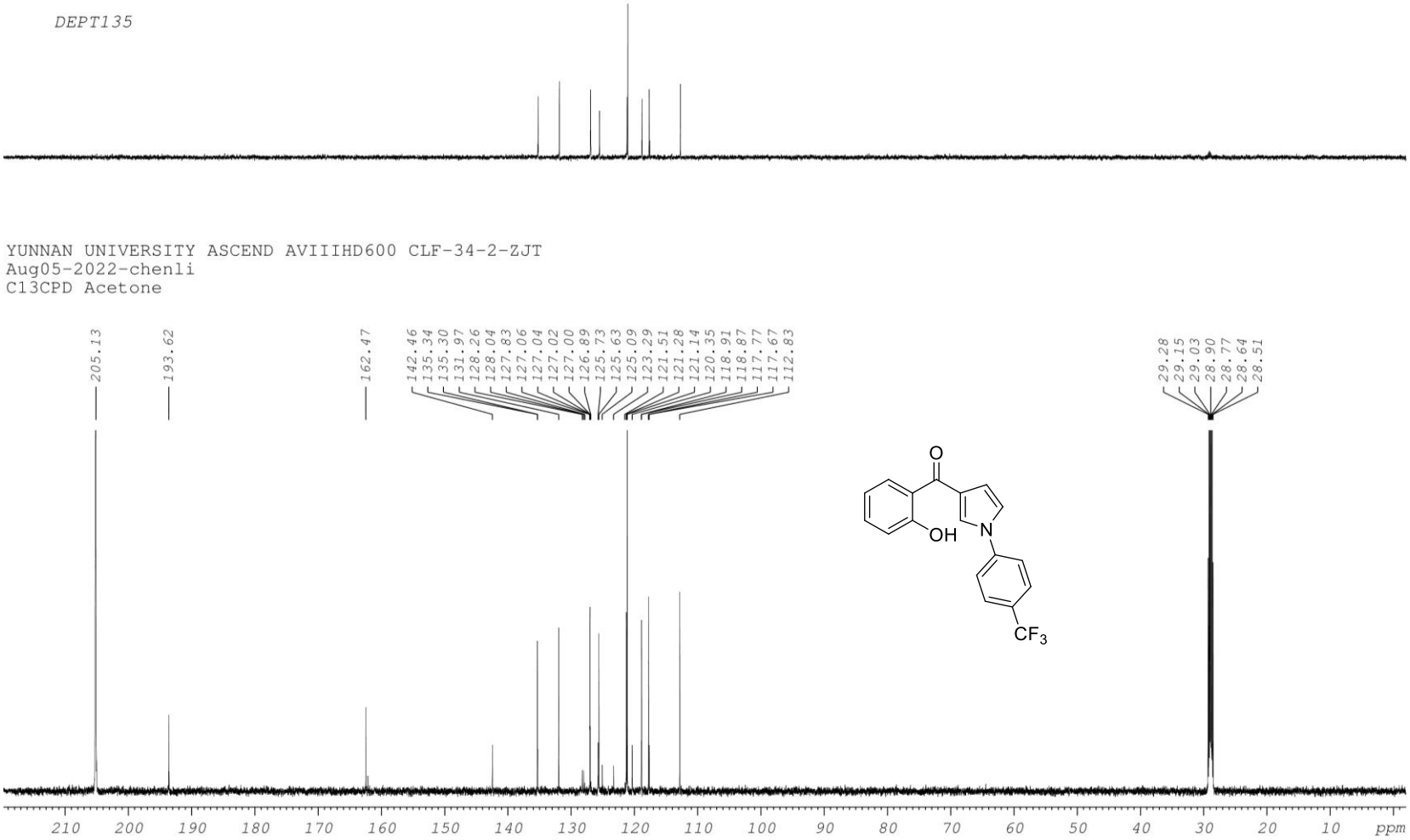


Figure S112. ^{13}C NMR (150 MHz, Acetone-d_6) spectra of intermediate **9g'**

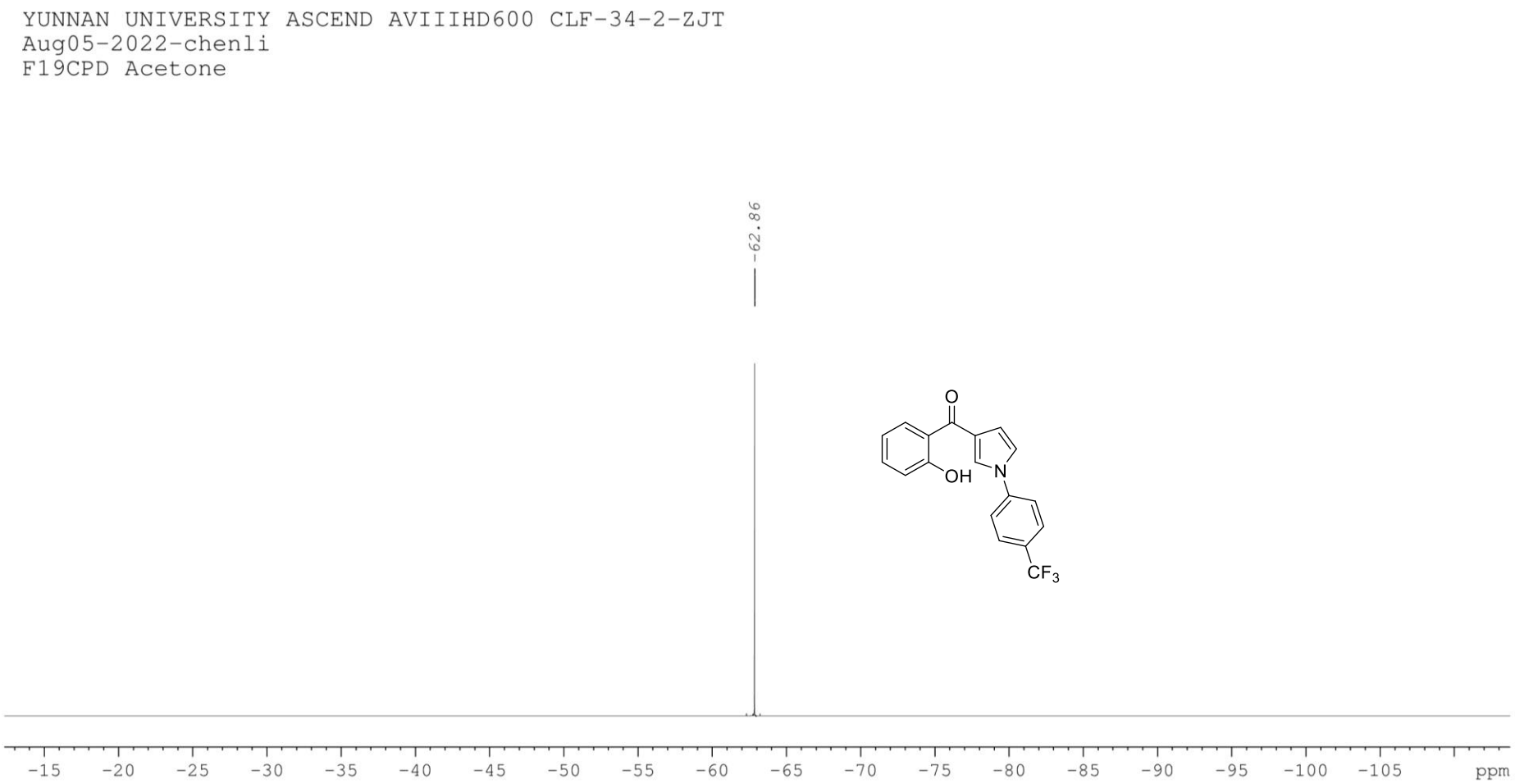


Figure S113. ^{19}F NMR (564 MHz, Acetone-d_6) spectra of intermediate **9g'**

References and Notes

1. C. Zhou, M. Li, J.-W. Sun, J. Cheng and S. Sun, Photoredox-Catalyzed *α*-Aminomethyl Carboxylation of Styrenes with Sodium Glycinates: Synthesis of *γ*-Amino Acids and *γ*-Lactams. *Org. Lett.* 2021, **23**, 2895.

2. CCDC 2181906 contains the supplementary crystallographic data for compounds **3d'**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif