# Cu-Catalyzed Decarboxylative Annulation of Proline Derivatives: Multi-component Synthesis of Functionalized Chromeno[2,3-*c*]pyrrol-9(1*H*)-one Derivatives

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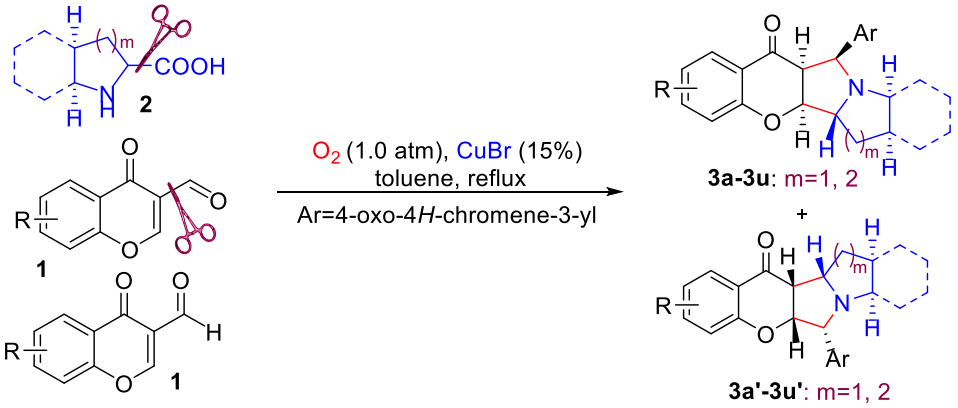
# General Information

All compounds were fully characterised by spectroscopic data. The NMR spectra were recorded on a Bruker DRX600， Bruker DRX500 or Bruker DRX400. Chemical shifts ($\delta$) are expressed in ppm, $J$ values are given in Hz, and deuterated $CDCl_3$ 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. Column chromatography was performed on silica gel (200–300 mesh). The 3-formylchromones **1** and proline derivatives **2** were commercially available reagents.

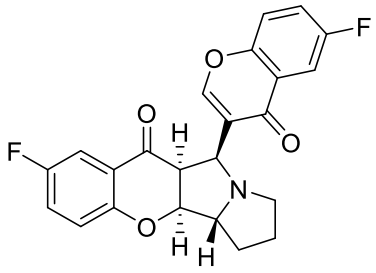
# General Procedure for the Preparation of 3 & 3'




Chromone-3-carboxaldehydes **1** (1.0 mmol) was charged into a round-bottom flask. Then, toluene (3mL), proline **2** (0.8 mmol) and CuBr (15%) were added to the mixture. The mixture was stirred at reflux under oxygen atmosphere for approximately 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 afford the crude product. Finally, the product **3** or **3'** was obtained in the pure form by column chromatography over silica gel using a mixture of petroleum ether/ethyl acetate (8:1-12:1, v/v) as the eluent.

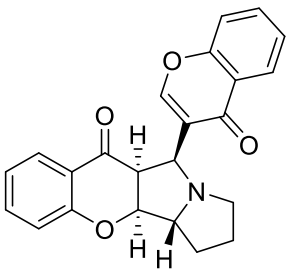
## Spectroscopic Data of 3a-3u'

**(3a*R*,3b*S*,9a*S*,10*S*)-7-Fluoro-10-(6-fluoro-4-oxo-4*H*-chromen-3-yl)-2,3,3a,3b,9a,10-hexahydro-1*H*,9*H*-chromeno[2,3-*a*]pyrrolizin-9-one (3a)**



White solid (127 mg, 62%); Mp: 157.0-157.7 ℃; IR (KBr): 3441, 3079, 2968, 1688, 1649, 1587, 1483, 1395, 1303, 1275, 1185, 1120, 899, 831, 722, 630, 601 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 1.32 (t, $J$ = 6.5 Hz, 1H, $CH_2$), 1.70-1.74 (m, 2H, $CH_2$), 1.87 (t, $J$ = 2.6 Hz, 1H, $CH_2$), 2.97-3.02 (m, 2H, $CH_2$), 3.23 (s, 1H, CH), 4.01 (t, $J$ = 7.0 Hz, 1H, CH), 4.62 (s, 1H, CH), 4.95 (d, $J$ = 4.4 Hz, 1H, CH), 6.97-6.99 (m, 1H, ArH), 7.14-7.19 (m, 1H, ArH), 7.31-7.35 (m, 1H, ArH), 7.41-7.46 (m, 2H, ArH), 7.75-7.77 (m, 1H, ArH), 8.14 (s, 1H, ArH); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ = 27.0, 28.9, 49.5, 56.3, 67.3, 70.0, 86.6, 110.4 (d, $J_2$ = 22.5 Hz), 111.5 (d, $J_2$ = 23.8 Hz), 120.3 (d, $J_3$ = 7.5 Hz), 120.4 (d, $J_3$ = 7.5 Hz), 122.1(d, $J_2$ = 20.0 Hz), 122.1, 122.2, 124.0 (d, $J_2$ = 23.8 Hz), 124.9 (d, $J_3$ = 7.5 Hz), 155.2, 152.9, 156.7, 157.5 (d, $J_1$ = 241.3 Hz), 159.6 (d, $J_1$ = 246.3 Hz), 176.5, 191.1. HRMS (TOF $ES^+$): *m/z* calcd for $C_{23}H_{18}F_2NO_4$ [$(M+H)^+$], 410.1198; found, 410.1194.

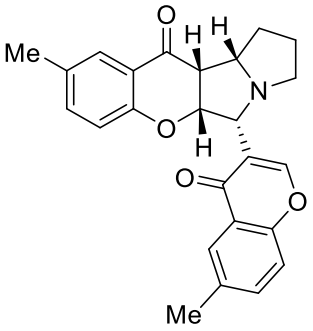
**(3a*R*,3b*S*,9a*S*,10*S*)-10-(4-Oxo-4*H*-chromen-3-yl)-2,3,3a,3b,9a,10-hexahydro-1*H*,9*H*-chromeno[2,3-*a*]pyrrolizin-9-one (3b)**



Yellow solid (110 mg, 59%); Mp: 133.8-134.5 ℃; IR (KBr): 3443, 2926, 2324, 1685, 1638, 1610, 1470, 1400, 1313, 1220, 1149, 1034, 910, 855, 760, 631 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.43 (t, $J$ = 7.8 Hz, 1H, $CH_2$), 1.77-1.82 (m, 3H, $CH_2$), 3.09-3.13 (m, 2H, $CH_2$), 3.32 (s, 1H, CH), 4.12 (t, $J$ = 7.1 Hz, 1H, CH), 4.74 (s, 1H, CH), 5.06 (d, $J$ = 3.9 Hz, 1H, CH), 7.03-7.08 (m, 2H, ArH), 7.43 (t, $J$

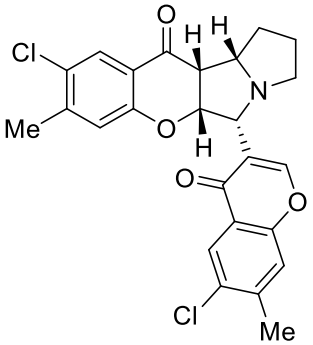
= 7.3 Hz, 1H, ArH), 7.49-7.54 (m, 2H, ArH), 7.69 (t, *J* = 7.6 Hz, 1H, ArH), 7.89 (d, *J* = 7.7 Hz, 1H, ArH), 8.23 (t, *J* = 7.9 Hz, 2H, ArH); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 27.0, 28.9, 49.9, 56.3, 67.4, 70.1, 86.4, 118.2, 118.7, 121.7, 123.5, 123.8, 123.8, 125.2, 125.7, 126.5, 133.7, 136.4, 154.9, 156.6, 160.6, 177.3, 191.9. HRMS (TOF ES$^+$): *m/z* calcd for $C_{23}H_{20}NO_4$ [(M+H)$^+$], 374.1387; found, 374.1385.

**(5*R*,5a*R*,11a*R*,11b*S*)-9-Methyl-5-(6-methyl-4-oxo-4*H*-chromen-3-yl)-2,3,5,5a,11a, 11b-hexahydrochromeno[3,2-*a*]pyrrolizin-11(1*H*)-one (3c')**



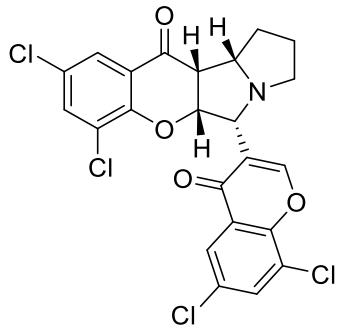

Yellow solid (128 mg, 64%); Mp: 81.2-81.9 ℃; IR (KBr): 3433, 2932, 1670, 1643, 1611, 1489, 1410, 1379, 1300, 1241, 1142, 847, 739, 711, 606 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 1.83-2.00 (m, 2H, $CH_2$), 2.01-2.05 (m, 2H, $CH_2$), 2.26 (s, 3H, $CH_3$), 2.48 (s, 3H, $CH_3$), 2.62-2.66 (m, 1H, $CH_2$), 2.80-2.83 (m, 1H, $CH_2$), 2.96-3.01 (m, 1H, CH), 3.79-3.84 (m, 1H, CH), 4.32 (d, *J* = 2.0 Hz, 1H, CH), 5.36 (t, *J* = 3.4 Hz, 1H, CH), 6.68 (d, *J* = 8.5 Hz, 1H, ArH), 7.18-7.20 (m, 1H, ArH), 7.43 (d, *J* = 8.6 Hz, 1H, ArH), 7.50-7.52 (m, 1H, ArH), 7.65 (d, *J* = 1.7 Hz, 1H, ArH), 8.03 (s, 1H, ArH), 8.30 (d, *J* = 1.0 Hz, 1H, ArH); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 20.4, 21.0, 25.0, 31.1, 54.6, 56.3, 66.2, 67.7, 82.7, 118.0, 118.1, 118.8, 120.8, 123.4, 125.0, 126.3, 130.9, 134.8, 135.0, 137.2, 154.9, 155.7, 158.7, 177.7, 192.6. HRMS (TOF ES$^+$): *m/z* calcd for $C_{25}H_{24}NO_4$ [(M+H)$^+$], 402.1700; found, 402.1701.

**(5*R*,5a*R*,11a*R*,11b*S*)-9-Chloro-5-(6-chloro-7-methyl-4-oxo-4*H*-chromen-3-yl)-8-m ethyl-2,3,5,5a,11a,11b-hexahydrochromeno[3,2-*a*]pyrrolizin-11(1*H*)-one (3d')**



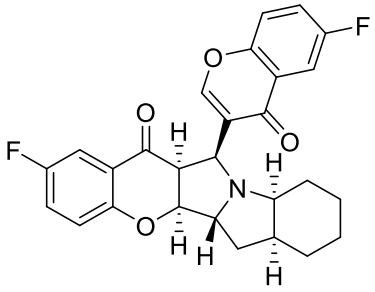
White solid (124 mg, 53%); Mp: 127.2-128.7 ℃; IR (KBr): 3454, 2948, 2788, 1690, 1636, 1600, 1456, 1411, 1347, 1300, 1222, 1119, 884, 762, 700, 616 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.85-1.93 (m, 2H, $CH_2$), 1.99-2.03 (m, 2H, $CH_2$), 2.26 (s, 3H, $CH_3$), 2.52 (s, 3H, $CH_3$), 2.61-2.65 (5m, 1H, $CH_2$), 2.79-2.81 (m, 1H, $CH_2$), 2.97-3.00 (m, 1H, CH), 3.76-3.79 (m, 1H, CH), 4.29 (d, *J* = 1.7 Hz, 1H, CH), 5.37 (t, *J* = 3.0 Hz, 1H, CH), 6.68 (s, 1H, ArH), 7.41 (s, 1H, ArH), 7.79 (s, 1H, ArH), 8.18 (s, 1H, ArH), 8.26 (s, 1H, ArH); $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ = 20.6, 20.7, 25.1, 31.0, 54.7, 55.9, 66.2, 67.7, 83.0, 118.2, 120.0, 120.3, 121.0, 122.8, 125.4, 126.5, 127.7, 131.8, 142.8, 145.1, 154.9, 155.6, 158.7, 176.4, 190.8. HRMS (TOF $ES^+$): *m/z* calcd for $C_{25}H_{22}Cl_2NO_4$ [$(M+H)^+$], 470.0920; found, 470.0918.

**(5*R*,5a*R*,11a*R*,11b*S*)-7,9-Dichloro-5-(6,8-dichloro-4-oxo-4*H*-chromen-3-yl)-2,3,5,5a,11a,11b-hexahydrochromeno[3,2-*a*]pyrrolizin-11(1*H*)-one (3e')**



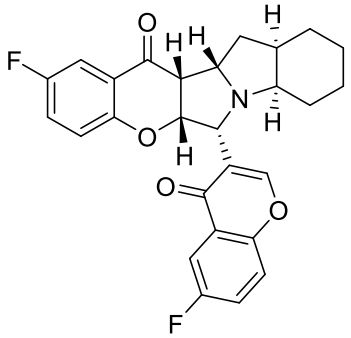

White solid (127 mg, 50%); Mp: 227.8-228.6 ℃; IR (KBr): 3454, 2942, 2789, 1668, 1599, 1489, 1405, 1390, 1300, 1236, 1116, 894, 765, 623 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.87-2.05 (m, 4H, $CH_2$), 2.63-2.68 (m, 1H, $CH_2$), 2.86-2.89 (m, 1H, $CH_2$), 2.98-3.04 (m, 1H, CH), 3.77-3.83 (m, 1H, CH), 4.37-4.38 (m, 1H, CH), 5.43 (t, *J* = 3.5 Hz, 1H, CH), 7.47 (d, *J* = 2.6 Hz, 1H, ArH), 7.74-7.76 (m, 2H, ArH), 8.12 (d, *J* = 2.5 Hz, 1H, ArH), 8.43 (d, *J* = 1.2 Hz, 1H, ArH); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 25.1, 30.9, 54.7, 55.6, 66.2, 67.5, 83.5, 120.5, 121.4, 123.8, 124.3, 124.6, 124.9, 125.3, 126.7, 130.8, 133.9, 135.8, 151.0, 154.5, 156.2, 175.9, 190.3. HRMS (TOF $ES^+$): *m/z* calcd for $C_{23}H_{16}Cl_4NO_4$ [$(M+H)^+$], 509.9828; found, 509.9832.

**(5a*S*,5b*R*,6a*S*,10a*S*,12*S*,12a*S*)-2-Fluoro-12-(6-fluoro-4-oxo-4*H*-chromen-3-yl)-5a,5b,6a,7,8,9,10,10a,12,12a-decahydro-6*H*,13*H*-chromeno[2',3':3,4]pyrrolo[1,2-*a*]indol-13-one (3f)**



White solid (123 mg, 53%); Mp: 227.1-227.9 ℃; IR (KBr): 3445, 2923, 1661, 1605, 1457, 1244, 1200, 1136, 1054, 957, 877, 803, 633 $cm^{-1}$; $[\alpha]_D^{25.4}$ = -190.2 (c = 0.1, $CH_2Cl_2$); $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 1.24-1.31 (m, 2H, $CH_2$), 1.47-1.71 (m, 7H, $CH_2$), 1.98-2.04 (m, 1H, $CH_2$), 2.18-2.23 (m, 1H, CH), 2.88 (t, $J$ = 4.8 Hz, 1H, CH), 3.48 (t, $J$ = 6.6 Hz, 1H, CH), 4.05-4.08 (m, 1H, CH), 4.56 (d, $J$ = 6.9 Hz, 1H, CH), 4.78-4.80 (m, 1H, CH), 6.66-6.68 (m, 1H, ArH), 6.89-6.93 (m, 1H, ArH), 7.27-7.36 (m, 3H, ArH), 7.68-7.70 (m, 1H, ArH), 8.07 (s, 1H, ArH); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ = 21.5, 23.6, 26.9, 29.0, 35.3, 37.6, 49.5, 63.0, 65.3, 68.1, 86.0, 110.4 (d, $J_2$ = 23.8 Hz), 111.7 (d, $J_2$ = 23.8 Hz), 119.0 (d, $J_3$ = 7.5 Hz), 119.8 (d, $J_3$ = 7.5 Hz), 121.3, 121.5 (d, $J_2$ = 25.0 Hz), 123.1 (d, $J_2$ = 25.0 Hz), 123.5, 124.2 (d, $J_3$ = 6.3 Hz), 152.3, 154.7, 155.3, 157.0 (d, $J_1$ = 241.3 Hz), 159.3 (d, $J_1$ = 243.8 Hz), 176.2, 189.7; $^{19}F$ NMR (470 MHz, $CDCl_3$): $\delta$ = -115.6, -121.8. HRMS (TOF $ES^+$): *m/z* calcd for $C_{27}H_{24}F_2NO_4$ [$(M+H)^+$], 464.1668; found, 496.1664.

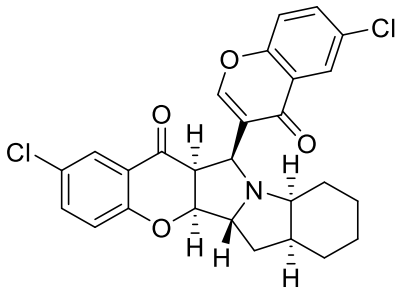
**(5a*R*,6*R*,7a*R*,11a*R*,12a*S*,12b*R*)-2-Fluoro-6-(6-fluoro-4-oxo-4*H*-chromen-3-yl)-5a,7a,8,9,10,11,11a,12,12a,12b-decahydrochromeno[3',2':3,4]pyrrolo[1,2-*a*]indol-13(6*H*)-one (3f')**



Yellow solid (67 mg, 29%); Mp: 109.8-111.3 ℃; IR (KBr): 3447, 2947, 1696, 1646, 1574, 1467, 1412, 1362, 1300, 1221, 1156, 876, 757, 710, 627 $cm^{-1}$; $[\alpha]_D^{27.1}$ = -398.5 (c = 0.1, $CH_2Cl_2$); $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 1.26-1.31 (m, 2H, $CH_2$), 1.43-1.47 (m, 1H, $CH_2$), 1.52-1.60 (m, 5H, $CH_2$), 1.94-2.00 (m, 2H, $CH_2$), 2.30-2.34 (m, 1H, CH), 2.85-2.91 (m, 2H, CH), 3.96-4.00 (m, 1H, CH), 4.42 (t, $J$ = 2.5 Hz, 1H, CH), 5.33 (t, $J$ = 3.4 Hz, 1H, CH), 6.74-6.77 (m, 1H, ArH), 7.09-7.13 (m, 1H, ArH), 7.42-7.46 (m, 1H, ArH), 7.49-7.51 (m, 1H, ArH),

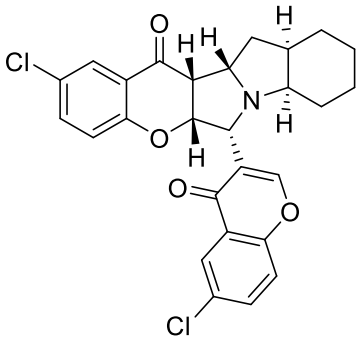
7.53-7.56 (m, 1H, ArH), 7.87-7.90 (m, 1H, ArH), 8.41 (d, $J$ = 0.8 Hz, 1H, ArH) ; $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 22.2, 23.2, 27.5, 28.7, 34.7, 38.5, 56.9, 65.3, 65.9, 66.8, 83.4, 110.5 (d, $J_2$ = 23.8 Hz), 111.2 (d, $J_2$ = 23.8 Hz), 119.7 (d, $J_3$ = 6.3 Hz), 120.0 (d, $J_3$ = 7.5 Hz), 120.4 (d, $J_3$ = 7.5 Hz), 121.3, 121.8 (d, $J_2$ = 25.0 Hz), 123.6 (d, $J_2$ = 23.8 Hz), 124.8 (d, $J_3$ = 7.5 Hz), 152.8, 156.0, 156.6, 157.3 (d, $J_1$ = 241.3 Hz), 159.6 (d, $J_1$ = 245.0 Hz), 176.6, 191.5; $^{19}$F NMR (470 MHz, $CDCl_3$): $\delta$ = -115.3, -121.1. HRMS (TOF ES$^+$): *m/z* calcd for $C_{27}H_{24}F_2NO_4$ [(M+H)$^+$], 464.1668; found, 464.1668.

**(5a*S*,5b*R*,6a*S*,10a*S*,12*S*,12a*S*)-2-Chloro-12-(6-chloro-4-oxo-4*H*-chromen-3-yl)-5a, 5b,6a,7,8,9,10,10a,12,12a-decahydro-6*H*,13*H*-chromeno[2',3':3,4]pyrrolo[1,2-*a*]in dol-13-one (3g)**



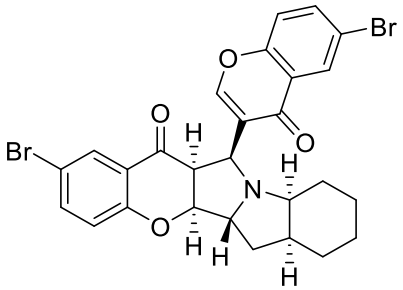

Yellow solid (116 mg, 47%); Mp: 135.8-136.2 ℃; IR (KBr): 3455, 2930, 2343, 1691, 1639, 1609, 1468, 1277, 1209, 1157, 1107, 1044, 937, 867, 818, 634 cm$^{-1}$; $[\alpha]_D^{25.5}$ = -177.84 (c = 0.125, $CH_2Cl_2$); $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 1.31 (s, 2H, $CH_2$), 1.51-1.69 (m, 7H, $CH_2$), 2.00-2.04 (m, 1H, $CH_2$), 2.22 (s, 1H, CH), 2.89 (d, $J$ = 3.6 Hz, 1H, CH), 3.49 (t, $J$ = 6.0 Hz, 1H, CH), 4.09 (s, 1H, CH), 4.53 (d, $J$ = 6.7 Hz, 1H, CH), 4.81 (s, 1H, CH), 6.63 (d, $J$ = 8.8 Hz, 1H, ArH), 7.09 (d, $J$ = 8.6 Hz, 1H, ArH), 7.31 (d, $J$ = 8.9 Hz, 1H, ArH), 7.54 (d, $J$ = 8.8 Hz, 1H, ArH), 8.03 (s, 1H, ArH), 8.07 (s, 1H, ArH); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 21.5, 23.6, 27.0, 29.0, 35.3, 37.6, 49.6, 63.1, 65.3, 68.3, 86.0, 119.0, 119.5, 121.7, 124.0, 124.2, 125.1, 126.2, 126.8, 130.8, 133.5, 135.3, 154.4, 154.6, 157.6, 172.9, 189.4. HRMS (TOF ES$^+$): *m/z* calcd for $C_{27}H_{24}Cl_2NO_4$ [(M+H)$^+$], 496.1077; found, 496.1068.

**(5a*R*,6*R*,7a*R*,11a*R*,12a*S*,12b*R*)-2-Chloro-6-(6-chloro-4-oxo-4*H*-chromen-3-yl)-5a, 7a,8,9,10,11,11a,12,12a,12b-decahydrochromeno[3',2':3,4]pyrrolo[1,2-*a*]indol-13(6*H*)-one (3g')**



Yellow solid (84 mg, 34%); Mp: 225.0-225.9 ℃; IR (KBr): 3443, 2938, 2301, 1697, 1626, 1600, 1476, 1408, 1336, 1208, 1188, 1065, 919, 854, 744, 604 $cm^{-1}$; $[\alpha]_D^{25.5}$ = -385.8 (c = 0.04, $CH_2Cl_2$); $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.27-1.32 (m, 2H, $CH_2$), 1.45-1.47 (m, 1H, $CH_2$), 1.55-1.67 (m, 5H, $CH_2$), 1.95-2.02 (m, 2H, $CH_2$), 2.34 (d, *J* = 5.6 Hz, 1H, CH), 2.88-2.92 (m, 2H, CH), 3.98 (s, 1H, CH), 4.44 (s, 1H, CH), 5.36 (s, 1H, CH), 6.75 (d, *J* = 8.8 Hz, 1H, ArH), 7.34 (d, *J* = 8.7 Hz, 1H, ArH), 7.51 (d, *J* = 8.9 Hz, 1H, ArH), 7.67 (d, *J* = 8.6 Hz, 1H, ArH), 7.83 (s, 1H, ArH), 8.23 (s, 1H, ArH), 8.42 (s, 1H, ArH); $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ = 22.2, 23.2, 27.5, 28.7, 34.7, 38.5, 56.8, 65.4, 65.9, 66.8, 83.4, 119.98, 120.0, 120.0, 122.0, 124.6, 125.2, 126.1, 127.1, 131.1, 133.8, 135.9, 154.9, 155.9, 158.8, 176.2, 191.1. HRMS (TOF $ES^+$): *m/z* calcd for $C_{27}H_{24}Cl_2NO_4$ $[(M+H)^+]$, 496.1077; found, 496.1078.

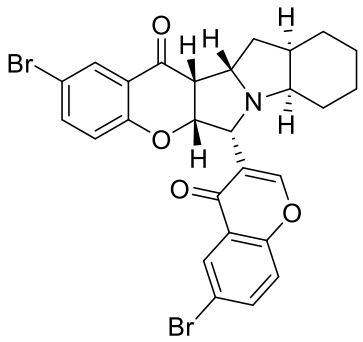
**(5a*S*,5b*R*,6a*S*,10a*S*,12*S*,12a*S*)-2-Bromo-12-(6-bromo-4-oxo-4*H*-chromen-3-yl)-5a, 5b,6a,7,8,9,10,10a,12,12a-decahydro-6*H*,13*H*-chromeno[2',3':3,4]pyrrolo[1,2-*a*]indol-13-one (3h)**



Yellow solid (164 mg, 56%); Mp: 268.9-269.7 ℃; IR (KBr): 3475, 2932, 2301, 1697, 1646, 1568, 1406, 1298, 1202, 1155, 1111, 1043, 931, 862, 808, 629 $cm^{-1}$; $[\alpha]_D^{25.4}$ = -77.7 (c = 0.1, $CH_2Cl_2$); $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 1.26-1.30 (m, 2H, $CH_2$), 1.49-1.67 (m, 7H, $CH_2$), 1.97-2.02 (m, 1H, $CH_2$), 2.19 (t, *J* = 4.7 Hz, 1H, CH), 2.71 (t, *J* = 4.6 Hz, 1H, CH), 3.45-3.48 (m, 1H, CH), 4.05-4.09 (m, 1H, CH), 4.56 (d, *J* = 6.8 Hz, 1H, CH), 4.77-4.79 (m, 1H, CH), 6.54 (d, *J* = 8.8 Hz, 1H, ArH), 7.18-7.23 (m, 2H, ArH), 7.64-7.67 (m, 1H, ArH), 7.75 (d, *J* = 2.5 Hz, 1H, ArH), 8.04 (d, *J* = 1.0 Hz, 1H, ArH), 8.17 (d, *J* = 2.4 Hz, 1H, ArH); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ = 21.4, 23.7, 27.0, 29.0, 35.4, 37.7, 49.6, 63.1, 65.3, 68.5,

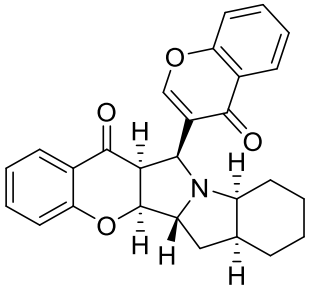
86.0, 113.9, 118.3, 119.2, 119.7, 122.2, 124.3, 124.3, 128.4, 129.3, 136.2, 138.1, 154.5, 154.8, 158.0, 175.7, 189.3. HRMS (TOF $ES^+$): *m/z* calcd for $C_{27}H_{24}Br_2NO_4$ [$(M+H)^+$], 584.0067; found, 584.0069.

**(5a*R*,6*R*,7a*R*,11a*R*,12a*S*,12b*R*)-2-Bromo-6-(6-bromo-4-oxo-4*H*-chromen-3-yl)-5a,7a,8,9,10,11,11a,12,12a,12b-decahydrochromeno[3',2':3,4]pyrrolo[1,2-*a*]indol-13(6*H*)-one (3h')**



Yellow solid (122 mg, 42%); Mp: 208.6-209.7 ℃; IR (KBr): 3456, 2938, 1699, 1635, 1600, 1493, 1411, 1339, 1210, 1180, 1063, 912, 845, 748, 624 $cm^{-1}$; $[\alpha]_D^{25.8}$ = -287.0 (c = 0.1, $CH_2Cl_2$); $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 1.25-1.30 (m, 2H, $CH_2$), 1.39-1.59 (m, 6H, $CH_2$), 1.92-2.02 (m, 2H, $CH_2$), 2.28-2.33 (m, 1H, CH), 2.84-2.91 (m, 2H, CH), 3.93-3.98 (m, 1H, CH), 4.41 (d, *J* = 2.9 Hz, 1H, CH), 5.34 (d, *J* = 3.3 Hz, 1H, CH), 6.67 (d, *J* = 8.9 Hz, 1H, ArH), 7.42-7.46 (m, 2H, ArH), 7.77-7.79 (m, 1H, ArH), 7.96 (d, *J* = 2.4 Hz, 1H, ArH), 8.37 (d, *J* = 2.3 Hz, 1H, ArH), 8.39 (s, 1H, ArH); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ = 22.2, 23.2, 27.4, 28.7, 34.7, 38.5, 56.8, 65.3, 65.9, 66.8, 83.3, 114.2, 118.5, 120.26, 120.33, 120.5, 122.1, 125.0, 128.4, 129.2, 136.5, 138.7, 155.3, 155.9, 159.2, 176.1, 191.0. HRMS (TOF $ES^+$): *m/z* calcd for $C_{27}H_{24}Br_2NO_4$ [$(M+H)^+$], 584.0067; found, 584.0065.

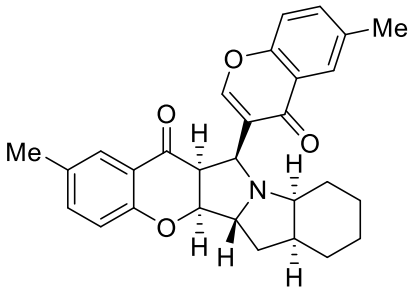
**(5a*S*,5b*R*,6a*S*,10a*S*,12*S*,12a*S*)-12-(4-Oxo-4*H*-chromen-3-yl)-5a,5b,6a,7,8,9,10,10a,12,12a-decahydro-6*H*,13*H*-chromeno[2',3':3,4]pyrrolo[1,2-*a*]indol-13-one (3i)**



Yellow solid (124 mg, 58%); Mp: 123.8-124.5 ℃; IR (KBr): 3444, 2936, 2305, 1695, 1630, 1601, 1495, 1410, 1334, 1209, 1178, 1064, 913, 855, 740, 634 $cm^{-1}$;

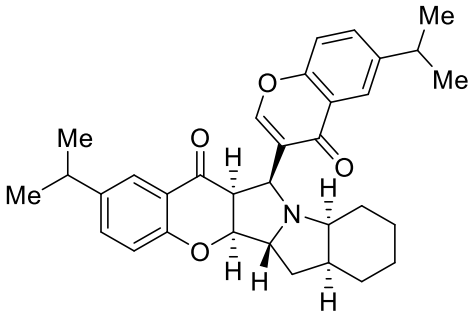
$[\alpha]_D^{25.4}$ = -125.6 (c = 0.1, $CH_2Cl_2$); $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 1.18-1.22 (m, 2H, $CH_2$), 1.42-1.61 (m, 7H, $CH_2$), 1.91-1.95 (m, 1H, $CH_2$), 2.13 (t, *J* = 4.6 Hz, 1H, CH), 2.83 (t, *J* = 4.6 Hz, 1H, CH), 3.42 (t, *J* = 5.6 Hz, 1H, CH), 4.02-4.05 (m, 1H, CH), 4.52 (d, *J* = 6.9 Hz, 1H, CH), 4.72-4.73 (m, 1H, CH), 6.59-6.62 (m, 2H, ArH), 7.07 (t, *J* = 7.2 Hz, 1H, ArH), 7.18-7.20 (m, 1H, ArH), 7.24 (d, *J* = 8.4 Hz, 1H, ArH), 7.47 (t, *J* = 7.1 Hz, 1H, ArH), 7.58 (d, *J* = 7.8 Hz, 1H, ArH), 7.96 (d, *J* = 8.0 Hz, 1H, ArH), 8.00 (s, 1H, ArH); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 21.4, 23.7, 27.0, 29.1, 35.4, 37.7, 49.8, 63.1, 65.3, 68.4, 85.9, 117.2, 117.7, 121.0, 121.0, 123.1, 124.2, 124.6, 125.7, 126.8, 133.0, 135.5, 154.5, 156.1, 159.2, 176.9, 191.5. HRMS (TOF ES$^+$): *m/z* calcd for $C_{27}H_{26}NO_4$ [(M+H)$^+$], 428.1856; found, 428.1850.

**(5a*S*,5b*R*,6a*S*,10a*S*,12*S*,12a*S*)-2-Methyl-12-(6-methyl-4-oxo-4*H*-chromen-3-yl)-5a,5b,6a,7,8,9,10,10a,12,12a-decahydro-6*H*,13*H*-chromeno[2',3':3,4]pyrrolo[1,2-*a*]indol-13-one (3j)**



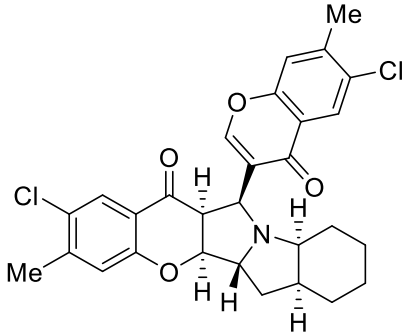

Yellow solid (145 mg, 63%); Mp: 110.2-110.8 ℃; IR (KBr): 3422, 2928, 2860, 1686, 1625, 1491, 1441, 1305, 1224, 1160, 1045, 942, 868, 815, 530 cm$^{-1}$; $[\alpha]_D^{26.2}$ = -99.3 (c = 0.1, $CH_2Cl_2$); $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 1.19 (d, *J* = 10.1 Hz, 2H, $CH_2$), 1.43-1.57 (m, 7H, $CH_2$), 1.90-1.93 (m, 1H, $CH_2$), 1.96 (s, 3H, $CH_3$), 2.11 (d, *J* = 3.8 Hz, 1H, CH), 2.31 (s, 3H, $CH_3$), 2.82 (d, *J* = 3.8 Hz, 1H, CH), 3.37 (t, *J* = 5.6 Hz, 1H, CH), 4.02 (s, 1H, CH), 4.52 (d, *J* = 6.7 Hz, 1H, CH), 4.68 (d, *J* = 2.6 Hz, 1H, CH), 6.45 (d, *J* = 8.3 Hz, 1H, ArH), 6.84 (d, *J* = 8.2 Hz, 1H, ArH), 7.13 (d, *J* = 8.4 Hz, 1H, ArH), 7.28 (d, *J* = 8.3 Hz, 1H, ArH), 7.36 (s, 1H, ArH), 7.73 (s, 1H, ArH), 7.96 (s, 1H, ArH); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 20.0, 20.8, 21.4, 23.8, 27.1, 29.1, 35.5, 37.8, 49.9, 63.2, 65.3, 68.6, 85.8, 116.9, 117.4, 120.7, 122.8, 124.0, 125.0, 126.4, 130.3, 134.1, 134.2, 136.4, 154.3, 154.4, 157.2, 177.0, 190.9. HRMS (TOF ES$^+$): *m/z* calcd for $C_{29}H_{30}NO_4$ [(M+H)$^+$], 456,2169; found, 456.2159.

**(5a*S*,5b*R*,6a*S*,10a*S*,12*S*,12a*S*)-2-Isopropyl-12-(6-isopropyl-4-oxo-4*H*-chromen-3-yl)-5a,5b,6a,7,8,9,10,10a,12,12a-decahydro-6*H*,13*H*-chromeno[2',3':3,4]pyrrolo[1,2-*a*]indol-13-one (3k)**



Yellow solid (156 mg, 61%); Mp: 91.0-92.3 ℃; IR (KBr): 3421, 2922, 2858, 1690, 1627, 1500, 1431, 1309, 1221, 1158, 1042, 941, 860, 805, 523 $cm^{-1}$; $[\alpha]_D^{25.1}$ = -87.6 (c = 0.1, $CH_2Cl_2$); $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 0.96 (t, $J$ = 6.0 Hz, 6H, $CH_3$), 1.23 (t, $J$ = 7.0 Hz, 6H, $CH_3$), 1.26-1.30 (m, 2H, $CH_2$), 1.47-1.67 (m, 7H, $CH_2$), 1,95-1.99 (m, 1H, $CH_2$), 2.18 (d, $J$ = 3.8 Hz, 1H, CH), 2.58-2.63 (m, 1H, CH), 2.90-2.97 (m, 2H, CH), 3.47 (t, $J$ = 5.7 Hz, 1H, CH), 4.11-4.14 (m, 1H, CH), 4.60 (d, $J$ = 7.0 Hz, 1H, CH), 4.77-4.78 (m, 1H, CH), 6.60 (d, $J$ = 8.5 Hz, 1H, ArH), 7.02-7.04 (m, 1H, ArH), 7.23 (d, $J$ = 8.6 Hz, 1H, ArH), 7.39-7.41 (m, 1H, ArH), 7.49 (d, $J$ = 2.2 Hz, 1H, ArH), 7.89 (d, $J$ = 2.0 Hz, 1H, ArH), 8.04 (s, 1H, ArH); $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ = 21.3, 23.6, 23.7, 23.8, 23.85, 23.94, 27.0, 29.1, 33.0, 33.7, 35.4, 37.8, 49.9, 63.3, 65.5, 68.8, 85.9, 117.0, 117.6, 120.6, 122.4, 122.8, 123.6, 124.1, 131.9, 134.2, 141.4, 145.3, 154.4, 154.5, 157.5, 177.0, 190.9. HRMS (TOF $ES^+$): *m/z* calcd for $C_{33}H_{38}NO_4$ $[(M+H)^+]$, 512.2795; found, 512.2797.

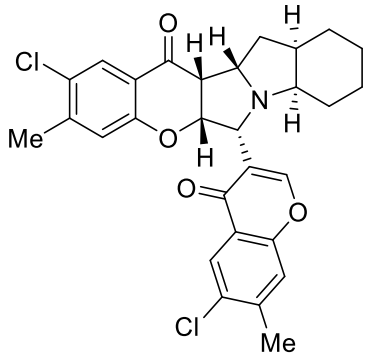
**(5a*S*,5b*R*,6a*S*,10a*S*,12*S*,12a*S*)-2-Chloro-12-(6-chloro-7-methyl-4-oxo-4*H*-chromen-3-yl)-3-methyl-5a,5b,6a,7,8,9,10,10a,12,12a-decahydro-6*H*,13*H*-chromeno[2',3':3,4]pyrrolo[1,2-*a*]indol-13-one (3l)**



Yellow solid (126 mg, 48%); Mp: 269.1-269.7 ℃; IR (KBr): 3434, 2926, 2855, 1696, 1648, 1605, 1459, 1416, 1344, 1288, 1183, 1156, 1110, 1064, 912, 833, 704, 657, 626 $cm^{-1}$; $[\alpha]_D^{26.9}$ = -182.6 (c = 0.1, $CH_2Cl_2$); $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.25-1.28 (m, 2H, $CH_2$), 1.48-1.67 (m, 7H, $CH_2$), 1.97-2.01 (m, 1H, $CH_2$), 2.11 (s, 1H, $CH_3$), 2.19 (t, $J$ = 4.6 Hz, 1H, CH), 2.45 (s, 3H, $CH_3$), 2.86 (d, $J$ = 4.3 Hz, 1H, CH), 3.44 (t, $J$ = 6.0 Hz, 1H, CH), 4.02-4.05 (m, 1H, CH), 4.55 (d, $J$ = 6.8 Hz, 1H, CH), 4.75 (t, $J$ = 4.9 Hz, 1H, CH), 6.53 (s, 1H, ArH), 7.20 (s, 1H, ArH),

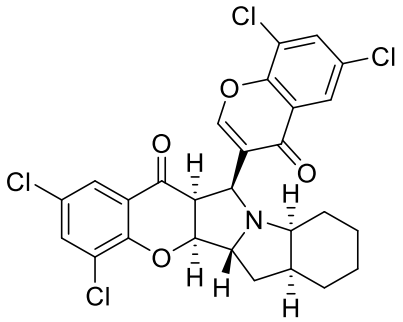
7.59 (s, 1H, ArH), 7.99 (s, 1H, ArH), 7.99 (s, 1H, ArH); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 20.4, 20.6, 21.5, 23.6, 27.0, 29.0, 35.3, 37.6, 49.5, 63.1, 65.2, 68.2, 85.9, 119.2, 119.4, 120.1, 122.2, 124.0, 125.5, 126.6, 127.5, 131.5, 142.2, 144.5, 154.2, 154.4, 157.4, 175.8, 189.1. HRMS (TOF ES$^+$): *m/z* calcd for $C_{29}H_{28}Cl_2NO_4$ [(M+H)$^+$], 524.1390; found, 524.1384.

**(5a*R*,6*R*,7a*R*,11a*R*,12a*S*,12b*R*)-2-Chloro-6-(6-chloro-7-methyl-4-oxo-4*H*-chromen-3-yl)-3-methyl-5a,7a,8,9,10,11,11a,12,12a,12b-decahydrochromeno[3',2':3,4]pyrrolo[1,2-*a*]indol-13(6*H*)-one (3l')**



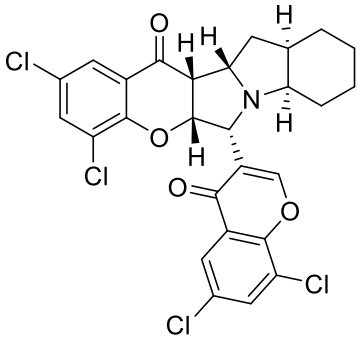

Yellow solid (81 mg, 31%); Mp: 179.8-180.4 ℃; IR (KBr): 3438, 2922, 2856, 1699, 1644, 1606, 1449, 1412, 1349, 1280, 1181, 1110, 1038, 911, 832, 708, 654 cm$^{-1}$; $[\alpha]_D^{26.9}$ = -385.7 (c = 0.1, $CH_2Cl_2$); $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 1.28-1.31 (m, 2H, $CH_2$), 1.44-1.46 (m, 1H, $CH_2$), 1.54-1.60 (m, 5H, $CH_2$), 1.93-2.02 (m, 2H, $CH_2$), 2.28 (s, 3H, $CH_3$), 2.31-2.33 (m, 1H, CH), 2.54 (s, 3H, $CH_3$), 2.87 (t, *J* = 2.9 Hz, 2H, CH), 3.95 (t, *J* = 10.5 Hz, 2H, CH), 4.41 (s, 1H, CH), 5.33 (s, 1H, CH), 6.68 (s, 1H, ArH), 7.42 (s, 1H, ArH), 7.80 (s, 1H, ArH), 8.20 (s, 1H, ArH), 8.36 (s, 1H, ArH); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta$ = 20.6, 20.8, 22.2, 23.2, 27.5, 28.7, 34.7, 38.5, 56.8, 65.4, 65.9, 66.8, 83.3, 118.2, 120.0, 120.3, 121.8, 122.7, 125.4, 126.4, 127.7, 131.8, 142.8, 145.1, 154.9, 155.7, 158.6, 176.2, 191.0. HRMS (TOF ES$^+$): *m/z* calcd for $C_{29}H_{28}Cl_2NO_4$ [(M+H)$^+$], 524.1390; found, 524.1394.

**(5a*S*,5b*R*,6a*S*,10a*S*,12*S*,12a*S*)-2,4-Dichloro-12-(6,8-dichloro-4-oxo-4*H*-chromen-3-yl)-5a,5b,6a,7,8,9,10,10a,12,12a-decahydro-6*H*,13*H*-chromeno[2',3':3,4]pyrrolo[1,2-*a*]indol-13-one (3m)**



White solid (124 mg, 44%); Mp: 215.5-216.3 ℃; IR (KBr): 3443, 2933, 2301, 1676, 1628, 1594, 1488, 1404, 1327, 1211, 1175, 1062, 903, 854, 733, 636 $cm^{-1}$; $[\alpha]_D^{25.4}$ = -233.0 (c = 0.1, $CH_2Cl_2$); $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 1.24-1.33 (m, 2H, $CH_2$), 1.55-1.71 (m, 7H, $CH_2$), 2.03-2.07 (m, 1H, $CH_2$), 2.19-2.22 (m, 1H, CH), 2.90 (d, *J* = 5.4 Hz, 1H, CH), 3.48 (t, *J* = 6.4 Hz, 1H, CH), 4.17-4.21 (m, 1H, CH), 4.58 (d, *J* = 6.8 Hz, 1H, CH), 4.88-4.89 (m, 1H, CH), 7.17 (d, *J* = 2.5 Hz, 1H, ArH), 7.51 (d, *J* = 2.5 Hz, 1H, ArH), 7.65 (d, *J* = 2.4 Hz, 1H, ArH), 7.87 (d, *J* = 2.4 Hz, 1H, ArH), 8.18 (s, 1H, ArH); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ = 21.2, 23.8, 27.0, 29.0, 35.3, 37.8, 49.4, 63.2, 65.3, 68.9, 86.5, 122.4, 123.2, 123.7, 124.1, 124.4, 124.6, 124.9, 126.5, 130.6, 133.5, 134.7, 150.4, 153.3, 154.6, 175.2, 188.6. HRMS (TOF $ES^+$): *m/z* calcd for $C_{27}H_{22}Cl_4NO_4$ [$(M+H)^+$], 564.0297; found, 564.0294.

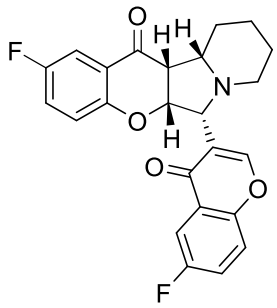
**(5a*R*,6*R*,7a*R*,11a*R*,12a*S*,12b*R*)-2,4-Dichloro-6-(6,8-dichloro-4-oxo-4*H*-chromen-3-yl)-5a,7a,8,9,10,11,11a,12,12a,12b-decahydrochromeno[3',2':3,4]pyrrolo[1,2-*a*]indol-13(6*H*)-one (3m')**



Yellow solid (70 mg, 25%); Mp: 167.3-168.4 ℃; IR (KBr): 3453, 2936, 2300, 1686, 1621, 1595, 1489, 1413, 1326, 1210, 1178, 1052, 908, 853, 734, 635 $cm^{-1}$; $[\alpha]_D^{28.1}$ = -389.6 (c = 0.1, $CH_2Cl_2$); $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.32-1.37 (m, 3H, $CH_2$), 1.51-1.58 (m, 1H, $CH_2$), 1.60-1.69 (m, 4H, $CH_2$), 1.98-2.01 (m, 1H, $CH_2$), 2.02-2.09 (m, 1H, $CH_2$), 3.37 (t, *J* = 5.5 Hz, 1H, CH), 2.96-3.01 (m, 2H, CH), 4.01-4.05 (m, 1H, CH), 4.55 (d, *J* = 2.8 Hz, 1H, CH), 5.46 (t, *J* = 3.5 Hz, 1H, CH), 7.52 (d, *J* = 2.6 Hz, 1H, ArH), 7.79 (d, *J* = 2.6 Hz, 1H, ArH), 7.81 (d, *J* = 2.5 Hz, 1H, ArH), 8.19 (d, *J* = 2.5 Hz, 1H, ArH), 8.56 (s, 1H, ArH); $^{13}C$ NMR (150

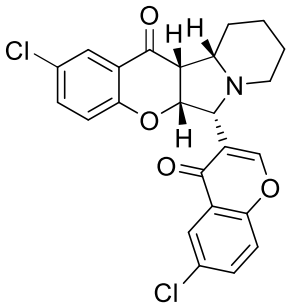
MHz, $CDCl_3$): $\delta$ = 22.0, 23.4, 27.6, 28.5, 34.9, 39.0, 56.5, 65.6, 65.9, 66.5, 84.0, 120.6, 122.3, 123.9, 124.2, 124.5, 124.8, 125.3, 126.7, 130.8, 133.8, 135.7, 151.0, 154.3, 156.1, 175.7, 190.2. HRMS (TOF $ES^+$): *m/z* calcd for $C_{27}H_{22}Cl_4NO_4$ [$(M+H)^+$], 564.0297; found, 564.0305.

**(5a*R*,6*R*,11a*S*,11b*R*)-2-Fluoro-6-(6-fluoro-4-oxo-4*H*-chromen-3-yl)-5a,6,8,9,10,11,11a,11b-octahydro-12*H*-chromeno[3,2-*a*]indolizin-12-one (3n')**




White solid (142 mg, 67%); Mp: 154.2-155.4 ℃; IR (KBr): 3460, 2944, 2775, 1688, 1661, 1624, 1459, 1409, 1372, 1301, 1211, 1158, 873, 756, 711, 600 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.25-1.43 (m, 3H, $CH_2$), 1.59 (d, *J* = 13.1 Hz, 1H, $CH_2$), 1.86-1.90 (m, 2H, $CH_2$), 1.99 (d, *J* = 12.8 Hz, 1H, $CH_2$), 2.58-2.61 (m, 1H, $CH_2$), 2.97 (t, *J* = 11.3 Hz, 1H, CH), 3.34 (t, *J* = 8.0 Hz, 1H, CH), 4.09 (d, *J* = 6.9 Hz, 1H, CH), 5.33-5.35(m, 1H, CH), 6.32-6.35 (m, 1H, ArH), 6.93-6.96 (m, 1H, ArH), 7.41-7.47 (m, 3H, ArH), 7.50 (d, *J* = 0.6 Hz, 1H, ArH), 7.91-7.93 (m, 1H, ArH); $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ = 24.7, 25.0, 27.8, 50.0, 52.8, 66.1, 66.8, 77.6, 110.6 (d, $J_2$ = 24.0 Hz), 111.4 (d, $J_2$ = 22.5 Hz), 118.4, 119.0 (d, $J_3$ = 6.0 Hz), 120.2 (d, $J_3$ = 9.0 Hz), 122.0 (d, $J_2$ = 25.5 Hz), 122.4 (d, $J_3$ = 6.0 Hz), 123.1 (d, $J_2$ = 24.0 Hz), 124.8 (d, $J_3$ = 7.5 Hz), 152.4, 155.4, 156.9 (d, $J_1$ = 240.0 Hz), 156.8, 159.6 (d, $J_1$ = 246.0 Hz), 176.7, 190.5; $^{19}F$ NMR (564 MHz, $CDCl_3$): $\delta$ = -114.9, -121.4. HRMS (TOF $ES^+$): *m/z* calcd for $C_{24}H_{20}F_2NO_4$ [$(M+H)^+$], 424.1355; found, 424.1358.

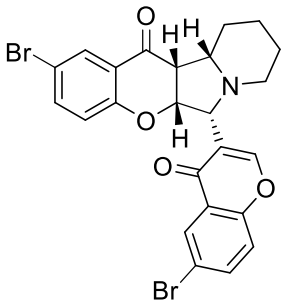
**(5a*R*,6*R*,11a*S*,11b*R*)-2-Chloro-6-(6-chloro-4-oxo-4*H*-chromen-3-yl)-5a,6,8,9,10,11,11a,11b-octahydro-12*H*-chromeno[3,2-*a*]indolizin-12-one (3o')**




Yellow solid (144 mg, 63%); Mp: 303.1-303.9 ℃; IR (KBr): 3452, 2940, 2788,

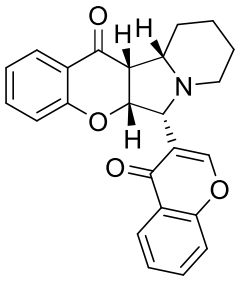
1689, 1643, 1621, 1488, 1406, 1387, 1301, 1223, 1146, 874, 766, 712, 605 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 1.26-1.42 (m, 3H, $CH_2$), 1.59 (d, *J* = 12.8 Hz, 1H, $CH_2$), 1.87 (t, *J* = 11.1 Hz, 2H, $CH_2$), 1.98 (d, *J* = 10.0 Hz, 1H, $CH_2$), 2.59 (t, *J* = 8.5 Hz, 1H, $CH_2$), 2.97 (d, *J* = 11.1 Hz, 1H, CH), 3.35 (t, *J* = 8.1 Hz, 1H, CH), 4.08 (d, *J* = 6.7 Hz, 1H, CH), 5.34 (t, *J* = 7.6 Hz, 1H, CH), 6.34 (d, *J* = 8.8 Hz, 1H, ArH), 7.16 (t, *J* = 1.8 Hz, 1H, ArH), 7.42 (d, *J* = 8.9 Hz, 1H, ArH), 7.51 (s, 1H, ArH), 7.64 (d, *J* = 9.0 Hz, 1H, ArH), 7.71 (s, 1H, ArH), 8.24 (s, 1H, ArH); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ = 24.7, 25.0, 27.8, 50.0, 52.7, 66.2, 66.8, 77.8, 119.0, 119.1, 119.9, 122.7, 124.5, 125.2, 125.7, 126.6, 131.2, 134.0, 135.5, 154.5, 155.4, 159.0, 176.3, 190.2. HRMS (TOF $ES^+$): *m/z* calcd for $C_{24}H_{20}Cl_2NO_4$ $[(M+H)^+]$, 456.0764; found, 456.0766.

**(5a*R*,6*R*,11a*S*,11b*R*)-2-Bromo-6-(6-bromo-4-oxo-4*H*-chromen-3-yl)-5a,6,8,9,10,11,11a,11b-octahydro-12*H*-chromeno[3,2-*a*]indolizin-12-one (3p')**



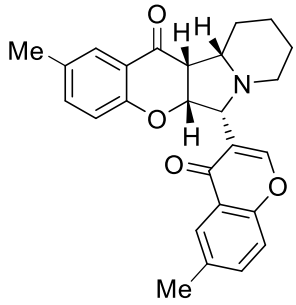

Yellow solid (171 mg, 63%); Mp: 165.1-166.7 ℃; IR (KBr): 3455, 2944, 2765, 1688, 1642, 1617, 1463, 1414, 1389, 1320, 1212, 1138, 867, 765, 703, 609 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.27-1.36 (m, 2H, $CH_2$), 1.38-1.42 (m, 1H, $CH_2$), 1.59 (d, *J* = 13.1 Hz, 1H, $CH_2$), 1.85-1.89 (m, 2H, $CH_2$), 1.97 (d, *J* = 8.6 Hz, 1H, $CH_2$), 2.58 (t, *J* = 10.1 Hz, 1H, $CH_2$), 2.97 (d, *J* = 11.2 Hz, 1H, CH), 3.35 (t, *J* = 8.1 Hz, 1H, CH), 4.07 (d, *J* = 6.7 Hz, 1H, CH), 5.34 (t, *J* = 7.3 Hz, 1H, CH), 6.29 (d, *J* = 8.8 Hz, 1H, ArH), 7.29-7.31 (m, 1H, ArH), 7.36 (d, *J* = 8.9 Hz, 1H, ArH), 7.52 (s, 1H, ArH), 7.77-7.78 (m, 1H, ArH), 7.86 (d, *J* = 2.3 Hz, 1H, ArH), 8.40 (d, *J* = 2.2 Hz, 1H, ArH); $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ = 24.7, 25.0, 27.8, 50.0, 52.7, 66.2, 66.9, 77.8, 113.7, 118.7, 119.1, 119.4, 120.1, 123.1, 124.9, 128.5, 128.8, 136.7, 138.3, 155.0, 155.4, 159.4, 176.2, 189.9. HRMS (TOF $ES^+$): *m/z* calcd for $C_{24}H_{20}Br_2NO_4$ $[(M+H)^+]$, 543.9754; found, 543.9753.

**(5a*R*,6*R*,11a*S*,11b*R*)-6-(4-Oxo-4*H*-chromen-3-yl)-5a,6,8,9,10,11,11a,11b-octahydro-12*H*-chromeno[3,2-*a*]indolizin-12-one (3q')**



Yellow solid (114 mg, 59%); Mp: 156.3-157.4 ℃; IR (KBr): 3457, 2938, 2795, 1681, 1649, 1611, 1468, 1416, 1382, 1307, 1221, 1148, 877, 760, 713, 606 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 1.25-1.40 (m, 3H, $CH_2$), 1.57 (d, $J$ = 12.8 Hz, 1H, $CH_2$), 1.84-1.91 (m, 2H, $CH_2$), 1.97-2.01 (m, 1H, $CH_2$), 2.59 (t, $J$ = 8.2 Hz, 1H, $CH_2$), 2.98 (d, $J$ = 11.4 Hz, 1H, CH), 3.36 (t, $J$ = 8.1 Hz, 1H, CH), 4.11 (d, $J$ = 6.6 Hz, 1H, CH), 5.32-5.36 (m, 1H, CH), 6.38 (d, $J$ = 8.4 Hz, 1H, ArH), 6.92 (t, $J$ = 7.2 Hz, 1H, ArH), 7.20-7.24 (m, 1H, ArH), 7.42-7.47 (m, 2H, ArH), 7.51 (s, 1H, ArH), 7.67-7.71 (m, 1H, ArH), 7.75-7.77 (m, 1H, ArH), 8.29-8.31 (m, 1H, ArH); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 24.8, 25.0, 27.8, 50.3, 52.6, 66.1, 66.8, 77.5, 117.5, 118.1, 118.8, 121.1, 122.1, 123.7, 125.2, 125.8, 126.2, 133.6, 135.7, 155.5, 156.2, 160.7, 177.6, 191.4. HRMS (TOF $ES^+$): *m/z* calcd for $C_{24}H_{22}NO_4$ $[(M+H)^+]$, 388.1543; found, 388.1537.

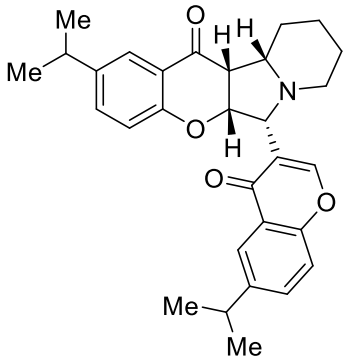
**(5a*R*,6*R*,11a*S*,11b*R*)-2-Methyl-6-(6-methyl-4-oxo-4*H*-chromen-3-yl)-5a,6,8,9,10,11,11a,11b-octahydro-12*H*-chromeno[3,2-*a*]indolizin-12-one (3r')**



Yellow solid (120 mg, 57%); Mp: 99.1-99.2 ℃; IR (KBr): 3444, 2988, 1660, 1605, 1543, 1469, 1356, 1259, 1168, 1036, 931, 834, 786, 644 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.18-1.31 (m, 3H, $CH_2$), 1.48 (d, $J$ = 12.5 Hz, 1H, $CH_2$), 1.78 (t, $J$ = 10.2 Hz, 2H, $CH_2$), 1.90 (d, $J$ = 10.6 Hz, 1H, $CH_2$), 2.18 (s, 3H, $CH_3$), 2.41 (s, 3H, $CH_3$), 2.49 (t, $J$ = 9.1 Hz, 1H, $CH_2$), 2.89 (d, $J$ = 10.8 Hz, 1H, CH), 3.26 (t, $J$ = 8.1 Hz, 1H, $CH_2$), 4.00 (d, $J$ = 6.5 Hz, 1H, CH), 5.21 (t, $J$ = 7.4 Hz, 1H, CH), 6.19 (d, $J$ = 8.3 Hz, 1H, ArH), 6.95 (d, $J$ = 8.3 Hz, 1H, ArH), 7.25 (d, $J$ = 8.5 Hz, 1H, ArH), 7.41 (s, 1H, ArH), 7.46 (s, 1H, ArH), 7.99 (s, 1H, ArH); $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ = 20.4, 21.0, 24.8, 25.0, 27.9, 50.4, 52.6, 66.3, 66.9, 77.3, 117.3, 117.8, 118.6, 121.7, 123.4, 125.1, 125.8, 130.4, 134.8, 135.1, 136.7, 154.5, 155.4, 158.7, 177.7, 191.6. HRMS (TOF $ES^+$): *m/z* calcd for $C_{26}H_{26}NO_4$

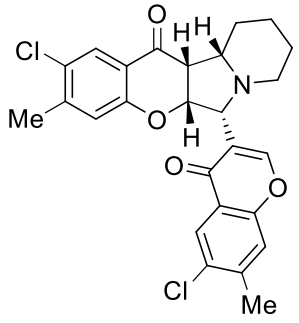
[(M+H)$^+$], 416,1856; found, 416.1847.

**(5a*R*,6*R*,11a*S*,11b*R*)-2-Isopropyl-6-(6-isopropyl-4-oxo-4*H*-chromen-3-yl)-5a,6,8,9,10,11,11a,11b-octahydro-12*H*-chromeno[3,2-*a*]indolizin-12-one (3s')**



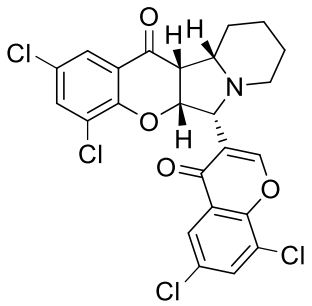
Yellow solid (141 mg, 60%); Mp: 95.1-96.2 ℃; IR (KBr): 3448, 2967, 1679, 1602, 1545, 1465, 1359, 1277, 1162, 1033, 931, 835, 796, 643 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 1.20 (s, 3H, $CH_3$), 1.21 (s, 3H, $CH_3$), 1.26-1.32 (m, 2H, $CH_2$), 1.33 (s, 3H, $CH_3$), 1.34 (s, 3H, $CH_3$), 1.40 (d, *J* = 12.3 Hz, 1H, $CH_2$), 1.56 (d, *J* = 13.1 Hz, 1H, $CH_2$), 1.83-1.90 (m, 1H, $CH_2$), 1.99 (d, *J* = 11.2 Hz, 1H, $CH_2$), 2.60 (d, *J* = 8.6 Hz, 1H, $CH_2$), 2.82-2.85 (m, 1H, CH), 2.97 (d, *J* = 11.1 Hz, 1H, CH), 3.05-3.08 (m, 1H, CH), 3.34 (t, *J* = 8.3 Hz, 1H, CH), 4.10 (d, *J* = 6.4 Hz, 1H, CH), 5.25-5.28 (m, 1H, CH), 6.35 (d, *J* = 8.5 Hz, 1H, ArH), 7.10-7.13 (m, 1H, ArH), 7.36 (d, *J* = 8.6 Hz, 1H, ArH), 7.53-7.60 (m, 3H, ArH), 8.13 (d, *J* = 2.1 Hz, 1H, ArH); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 23.8, 23.9, 23.95, 23.98, 24.9, 25.0, 27.9, 33.2, 33.8, 50.3, 52.5, 65.9, 66.9, 77.3, 117.4, 117.9, 118.4, 121.4, 122.5, 123.1, 123.5, 132.5, 134.4, 141.5, 146.0, 154.7, 155.6, 159.0, 177.8, 191.6. HRMS (TOF ES$^+$): *m/z* calcd for $C_{30}H_{34}NO_4$ [(M+H)$^+$], 472.2482; found, 472.2487.

**(5a*R*,6*R*,11a*S*,11b*R*)-2-Chloro-6-(6-chloro-7-methyl-4-oxo-4*H*-chromen-3-yl)-3-methyl-5a,6,8,9,10,11,11a,11b-octahydro-12*H*-chromeno[3,2-*a*]indolizin-12-one (3t')**



White solid (126 mg, 52%); Mp: 189.2-190.1 ℃; IR (KBr): 3455, 2999, 1677, 1607, 1566, 1465, 1346, 1239, 1167, 1034, 933, 831, 726, 639 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.25-1.39 (m, 3H, $CH_2$), 1.58 (d, $J$ = 12.8 Hz, 1H, $CH_2$), 1.84-1.90 (m, 2H, $CH_2$), 1.97 (d, $J$ = 9.7 Hz, 1H, $CH_2$), 2.13 (s, 3H, $CH_3$), 2.52 (s, 3H, $CH_3$), 2.58 (t, $J$ = 8.6 Hz, 1H, $CH_2$), 2.96 (d, $J$ = 11.0 Hz, 1H, CH), 3.30 (t, $J$ = 8.1 Hz, 1H, CH), 4.07 (d, $J$ = 6.5 Hz, 1H, CH), 5.29 (t, $J$ = 7.4 Hz, 1H, CH), 6.25 (s, 1H, ArH), 7.33 (s, 1H, ArH), 7.48 (s, 1H, ArH), 7.70 (s, 1H, ArH), 8.23 (s, 1H, ArH); $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ = 20.4, 20.8, 24.8, 25.0, 27.8, 49.9, 52.6, 65.9, 66.8, 77.8, 118.7, 119.4, 119.7, 120.9, 122.8, 125.5, 126.0, 127.2, 132.0, 143.0, 144.7, 154.5, 155.3, 158.9, 176.3, 189.8. HRMS (TOF $ES^+$): *m/z* calcd for $C_{26}H_{24}Cl_2NO_4$ $[(M+H)^+]$, 484.1077; found, 484.1077.

**(5a*R*,6*R*,11a*S*,11b*R*)-2,4-Dichloro-6-(6,8-dichloro-4-oxo-4*H*-chromen-3-yl)-5a,6,8,9,10,11,11a,11b-octahydro-12*H*-chromeno[3,2-*a*]indolizin-12-one (3u')**




White solid (155 mg, 59%); Mp: 211.0-212.3 ℃; IR (KBr): 3442, 2982, 1678, 1621, 1546, 1458, 1354, 1255, 1170, 1032, 933, 837, 790, 634 $cm^{-1}$; $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.21-1.47 (m, 3H, $CH_2$), 1.67 (d, $J$ = 12.8 Hz, 1H, $CH_2$), 1.93 (t, $J$ = 9.5 Hz, 2H, $CH_2$), 2.03 (d, $J$ = 12.6 Hz, 1H, $CH_2$), 2.66 (t, $J$ = 9.1 Hz, 1H, $CH_2$), 3.07 (d, $J$ = 11.3 Hz, 1H, CH), 3.50 (t, $J$ = 8.3 Hz, 1H, CH), 4.13 (d, $J$ = 6.5 Hz, 1H, CH), 5.55 (t, $J$ = 7.9 Hz, 1H, CH), 7.44 (d, $J$ = 2.2 Hz, 1H, ArH), 7.66 (s, 1H, ArH), 7.71 (d, $J$ = 2.2 Hz, 1H, ArH), 7.81 (d, $J$ = 2.1 Hz, 1H, ArH), 8.21 (d, $J$ = 2.1 Hz, 1H, ArH); $^{13}C$ NMR (150 MHz, $CDCl_3$): $\delta$ = 24.6, 24.8, 27.9, 50.1, 52.8, 66.6, 67.1, 78.7, 119.0, 123.6, 123.6, 123.9, 124.4, 124.4, 125.6, 126.4, 130.9, 133.8, 135.1, 150.7, 154.5, 155.2, 175.8, 189.5. HRMS (TOF $ES^+$): *m/z* calcd for $C_{24}H_{18}Cl_4NO_4$ $[(M+H)^+]$, 523.9984; found, 523.9989.

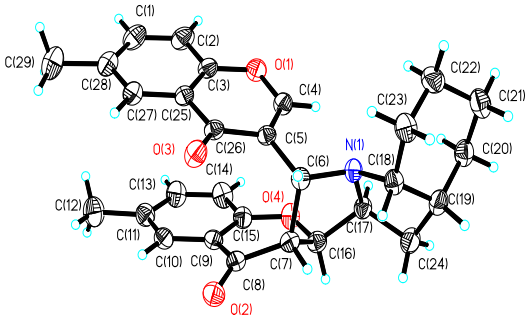



**Figure S1.** X-Ray crystal structure of **3j**

**Table S1.** Crystal data and structure refinement for **3j**

| | | |
|---|---|---|
| Identification code | 1 | |
| Empirical formula | $C_{39}H_{29}NO_4$ | |
| Formula weight | 455.53 | |
| Temperature | 298(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system, space group | Monoclinic, P2(1) | |
| Unit cell dimensions | a = 6.8138(6) Å | α = 90.0 °. |
| | b = 10.4409(11) Å | β = 93.287(4) °. |
| | c = 16.4586(19) Å | γ = 90.0 °. |
| Volume | 1169.0(2) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.294 $Mg/m^3$ | |
| Absorption coefficient | 0.086 $mm^{-1}$ | |
| F(000) | 484 | |
| Theta range for data collection | 2.311 to 28.297 °. | |
| Crystal size | 0.420 x 0.210 x 0.180 mm | |
| Limiting indices | -9<=h<=8, -13<=k<=13, -19<=l<=21 | |
| Reflections collected / unique | 15794 / 6022 [R(int) = 0.0618] | |
| Independent reflections | 6522 [R(int) = 0.0207, R(sigma) = 0.0549] | |
| Completeness to theta = 25.242 | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5940 / 1 / 310 | |
| Goodness-of-fit on $F^2$ | 1.055 | |
| Final R indexes [I>=2sigma(I)] | $R_1$ = 0.0569, $wR_2$ = 0.1112 | |
| Final R indexes (all data) | $R_1$ = 0.1172, $wR_2$ = 0.1449 | |
| Extinction coefficient | 0.055(5) | |
| Largest diff. peak and hole | 0.162 and -0.229 e.$Å^{-3}$ | |

**Table S2.** Bond Lengths [**Å**] for **3j**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| O(1) | C(4) | 1.349(5) | C(13) | H(3) | 0.9300 |
| O(1) | C(3) | 1.372(5) | C(14) | C(15) | 1.394(6) |
| O(2) | C(8) | 1.221(5) | C(14) | H(29) | 0.9300 |
| O(3) | C(26) | 1.233(4) | C(16) | C(17) | 1.526(5) |
| O(4) | C(15) | 1.360(5) | C(16) | H(28) | 0.9800 |
| O(4) | C(16) | 1.445(5) | C(17) | C(24) | 1.533(6) |
| N(1) | C(6) | 1.459(5) | C(17) | H(27) | 0.9800 |
| N(1) | C(18) | 1.475(5) | C(18) | C(23) | 1.512(6) |
| N(1) | C(17) | 1.497(5) | C(18) | C(19) | 1.516(6) |
| C(1) | C(2) | 1.371(7) | C(18) | H(19) | 0.9800 |
| C(1) | C(28) | 1.380(7) | C(19) | C(20) | 1.526(6) |
| C(1) | H(1) | 0.9300 | C(19) | C(24) | 1.535(6) |
| C(2) | C(3) | 1.388(6) | C(19) | H(18) | 0.9800 |
| C(2) | H(22) | 0.9300 | C(20) | C(21) | 1.521(7) |
| C(3) | C(25) | 1.381(5) | C(20) | H(14) | 0.9700 |
| C(4) | C(5) | 1.337(5) | C(20) | H(15) | 0.9700 |
| C(4) | H(21) | 0.9300 | C(21) | C(22) | 1.509(7) |
| C(5) | C(26) | 1.453(5) | C(21) | H(12) | 0.9700 |
| C(5) | C(6) | 1.506(6) | C(21) | H(13) | 0.9700 |
| C(6) | C(7) | 1.576(6) | C(22) | C(23) | 1.510(6) |
| C(6) | H(20) | 0.9800 | C(22) | H(8) | 0.9700 |
| C(7) | C(8) | 1.509(6) | C(22) | H(11) | 0.9700 |
| C(7) | C(16) | 1.512(5) | C(23) | H(10) | 0.9700 |
| C(7) | H(7) | 0.9800 | C(23) | H(9) | 0.9700 |
| C(8) | C(9) | 1.463(6) | C(24) | H(16) | 0.9700 |
| C(9) | C(10) | 1.394(6) | C(24) | H(17) | 0.9700 |
| C(9) | C(15) | 1.398(5) | C(25) | C(27) | 1.385(5) |
| C(10) | C(11) | 1.384(6) | C(25) | C(26) | 1.467(6) |
| C(10) | H(4) | 0.9300 | C(27) | C(28) | 1.383(7) |
| C(11) | C(13) | 1.391(6) | C(27) | H(26) | 0.9300 |
| C(11) | C(12) | 1.496(7) | C(28) | C(29) | 1.509(7) |
| C(12) | H(5) | 0.9600 | C(29) | H(25) | 0.9600 |
| C(12) | H(2) | 0.9600 | C(29) | H(24) | 0.9600 |
| C(12) | H(6) | 0.9600 | C(29) | H(23) | 0.9600 |
| C(13) | C(14) | 1.372(6) | | | |

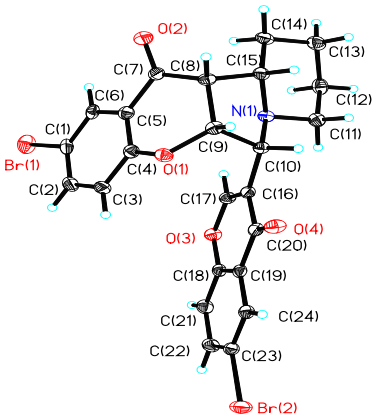



**Figure S2.** X-Ray crystal structure of **3p'**

**Table S3.** Crystal data and structure refinement for **3p'**

| | | |
|---|---|---|
| Identification code | 1 | |
| Empirical formula | $C_{24}H_{19}Br_2NO_4$ | |
| Formula weight | 545.22 | |
| Temperature | 150.00 K | |
| Crystal system | Monoclinic | |
| Space group | P 1 21/n 1 | |
| Unit cell dimensions | a = 11.9588(12) Å | α = 90 °. |
| | b = 14.9466(14) Å | β = 110.475(5) °. |
| | c = 12.5105(14) Å | γ = 90 °. |
| Volume | 2094.9(4) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.729g/$cm^3$ | |
| Absorption coefficient | 3.902 $mm^{-1}$ | |
| F(000) | 1088 | |
| Theta range for data collection | 2.028 to 28.331 °. | |
| Index ranges | -15<=h<=14, -19<=k<=19, -16<=l<=16 | |
| Reflections collected | 28620 | |
| Reflections unique | 5157 [R(int) = 0.0955] | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5157 / 0 / 280 | |
| Goodness-of-fit on $F^2$ | 1.040 | |
| Final R indexes [I>=2sigma(I)] | $R_1$ = 0.0440, $wR_2$ = 0.0909 | |
| Final R indexes (all data) | $R_1$ = 0.1054, $wR_2$ = 0.1188 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.770 and -0.848 e.$Å^{-3}$ | |

**Table S4.** Bond Lengths [Å] for **3p'**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Br(1) | C(1) | 1.896(4) | C(10) | C(16) | 1.495(5) |
| Br(2) | C(23) | 1.899(4) | C(11) | H(11A) | 0.9900 |
| O(1) | C(4) | 1.368(5) | C(11) | H(11B) | 0.9900 |
| O(1) | C(9) | 1.435(5) | C(11) | C(12) | 1.516(5) |
| O(2) | C(7) | 1.217(4) | C(12) | H(12A) | 0.9900 |
| O(3) | C(17) | 1.357(4) | C(12) | H(12B) | 0.9900 |
| O(3) | C(18) | 1.370(4) | C(12) | C(13) | 1.523(6) |
| O(4) | C(20) | 1.227(4) | C(13) | H(13A) | 0.9900 |
| N(1) | C(10) | 1.459(4) | C(13) | H(13B) | 0.9900 |
| N(1) | C(11) | 1.466(5) | C(13) | C(14) | 1.526(6) |
| N(1) | C(15) | 1.474(5) | C(14) | H(14A) | 0.9900 |
| C(1) | C(2) | 1.380(6) | C(14) | H(14B) | 0.9900 |
| C(1) | C(6) | 1.373(6) | C(14) | C(15) | 1.518(5) |
| C(2) | H(2) | 0.9500 | C(15) | H(15) | 1.0000 |
| C(2) | C(3) | 1.378(6) | C(16) | C(17) | 1.335(5) |
| C(3) | H(3) | 0.9500 | C(16) | C(20) | 1.456(5) |
| C(3) | C(4) | 1.391(5) | C(17) | H(17) | 0.9500 |
| C(4) | C(5) | 1.386(5) | C(18) | C(19) | 1.387(5) |
| C(5) | C(6) | 1.404(6) | C(18) | C(21) | 1.392(5) |
| C(5) | C(7) | 1.474(5) | C(19) | C(20) | 1.468(5) |
| C(6) | H(6) | 0.9500 | C(19) | C(24) | 1.401(5) |
| C(7) | C(8) | 1.512(5) | C(21) | H(21) | 0.9500 |
| C(8) | H(8) | 1.0000 | C(21) | C(22) | 1.370(6) |
| C(8) | C(9) | 1.549(5) | C(22) | H(22) | 0.9500 |
| C(8) | C(15) | 1.543(6) | C(22) | C(23) | 1.390(6) |
| C(9) | H(9) | 1.0000 | C(23) | C(24) | 1.373(5) |
| C(9) | C(10) | 1.559(5) | C(24) | H(24) | 0.9500 |
| C(10) | H(10) | 1.0000 | | | |

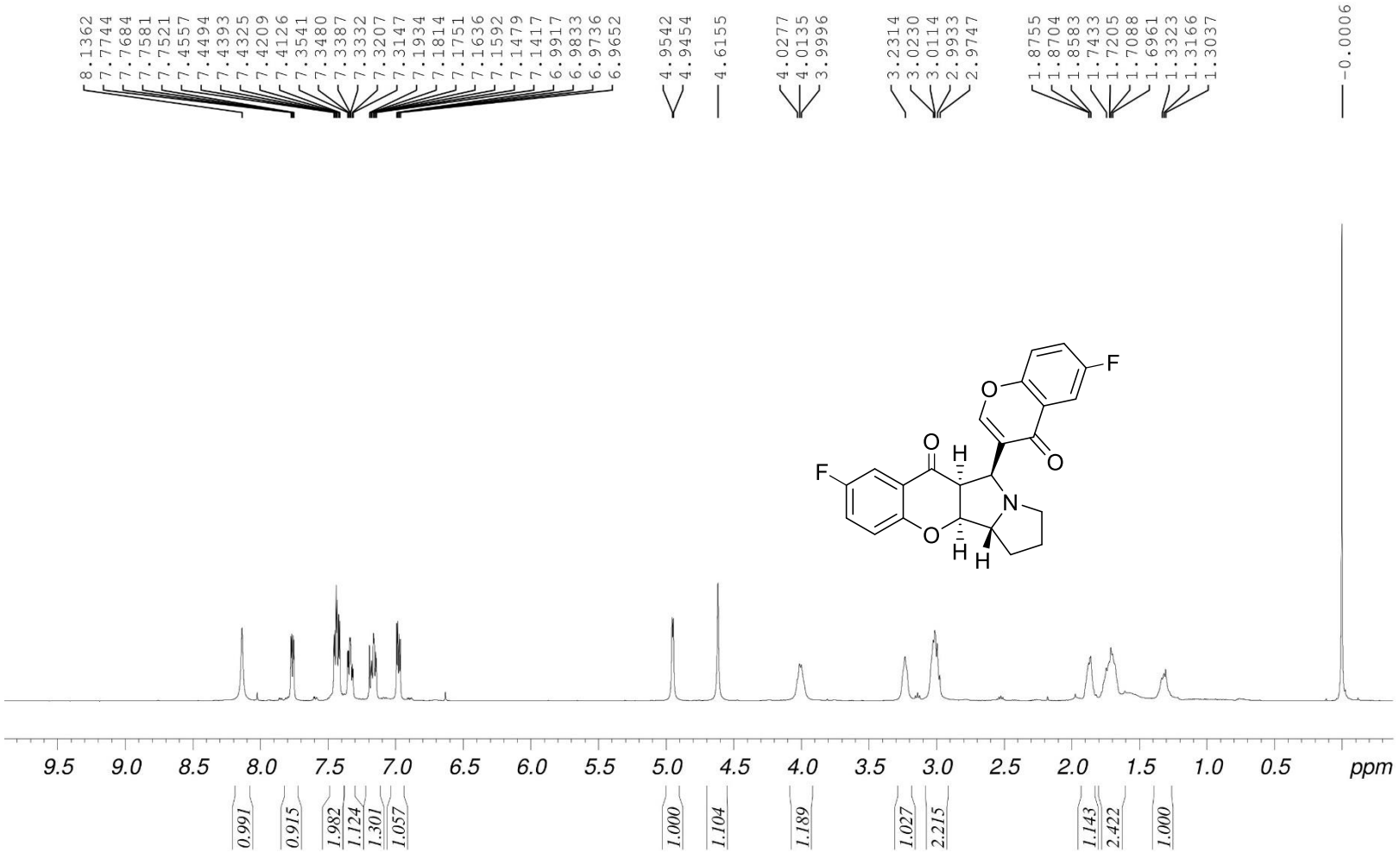



**Figure S3.** $^{1}$H NMR (500 MHz, $CDCl_3$) spectra of compound **3a**

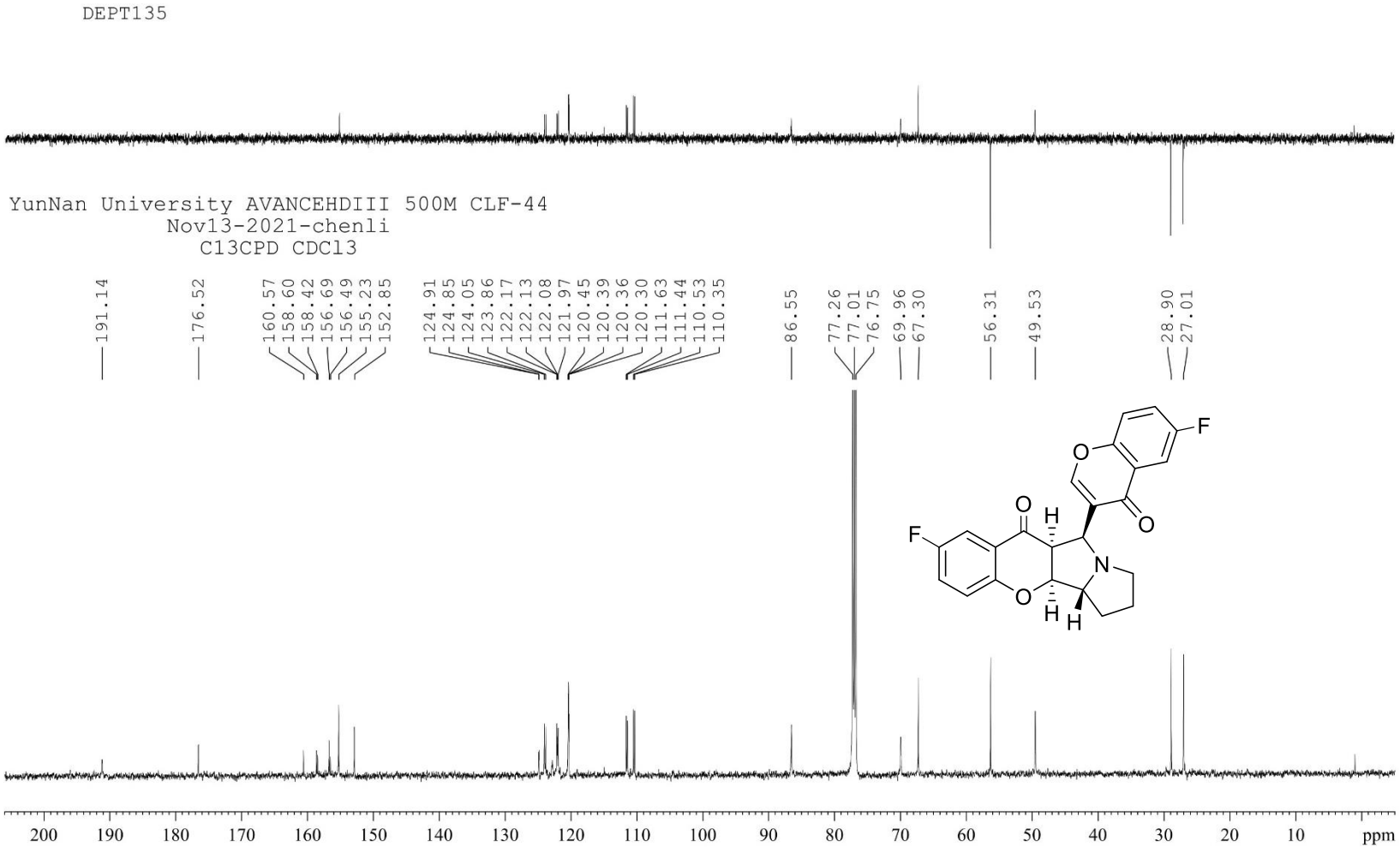



**Figure S4.** $^{13}C$ NMR (125 MHz, $CDCl_3$) spectra of compound **3a**

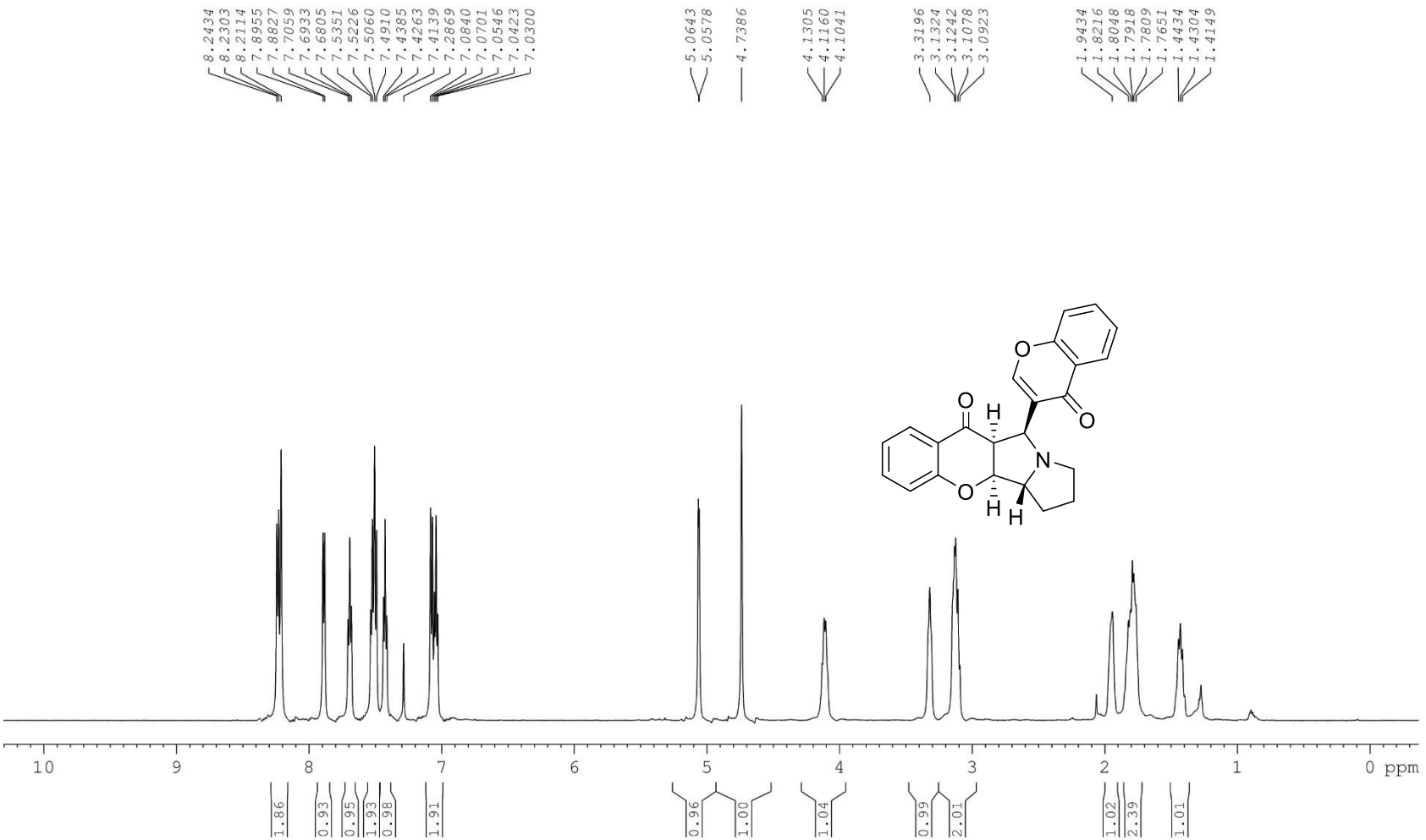



**Figure S5.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectra of compound **3b**

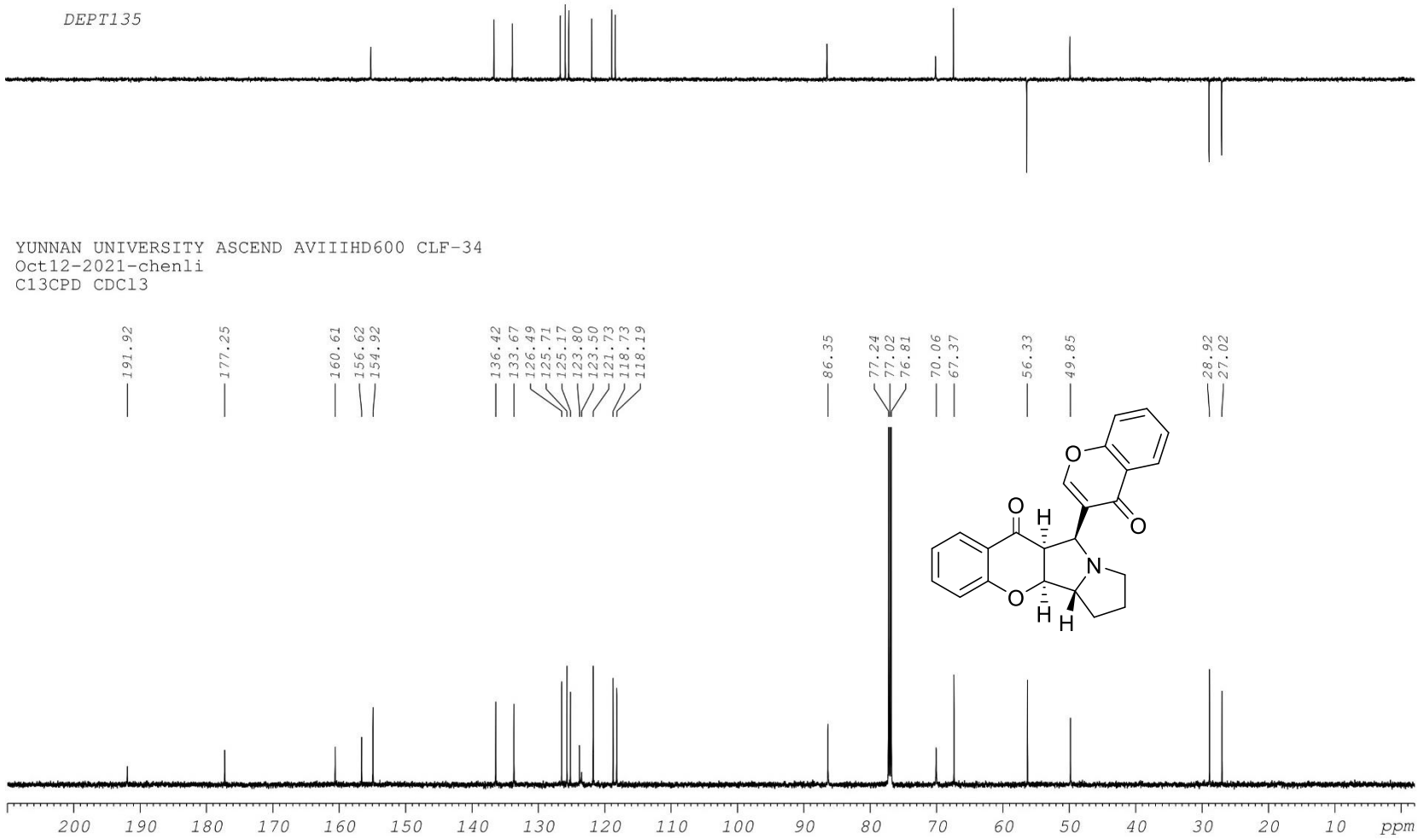



**Figure S6.** $^{13}C$ NMR (150 MHz, $CDCl_3$) spectra of compound **3b**

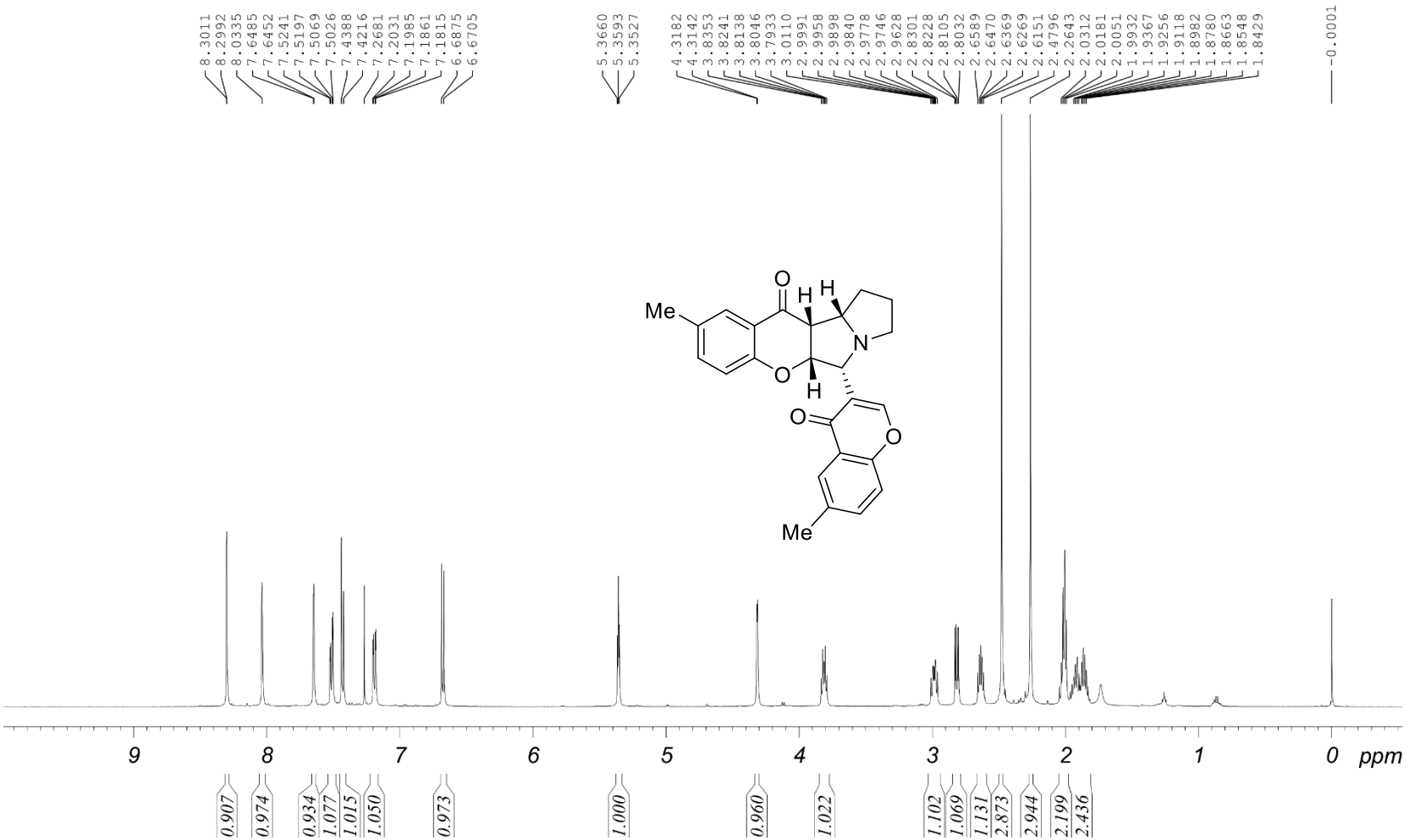



**Figure S7.** $^{1}$H NMR (500 MHz, $CDCl_3$) spectra of compound **3c'**

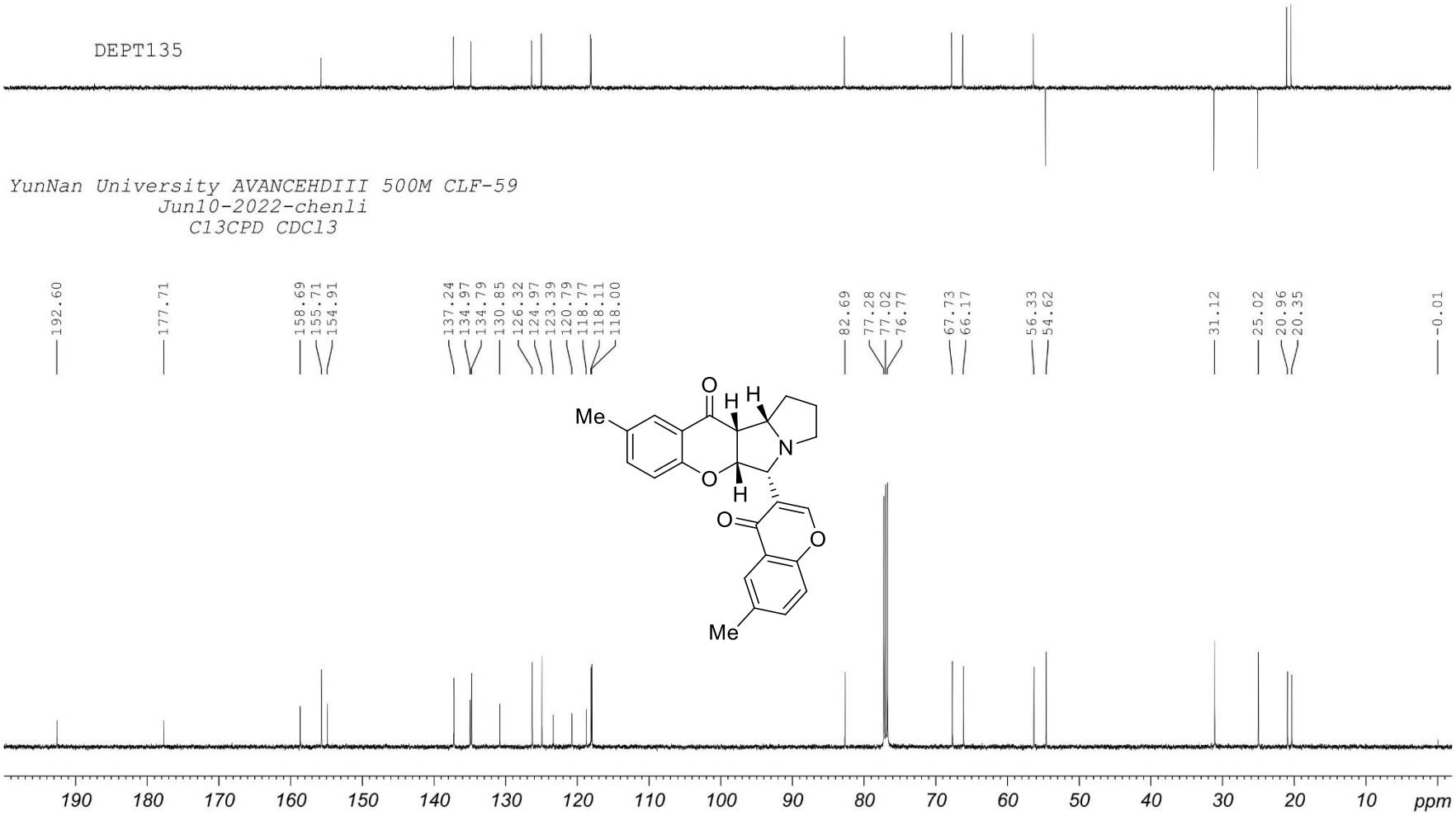



**Figure S8.** $^{13}C$ NMR (125 MHz, $CDCl_3$) spectra of compound **3c'**

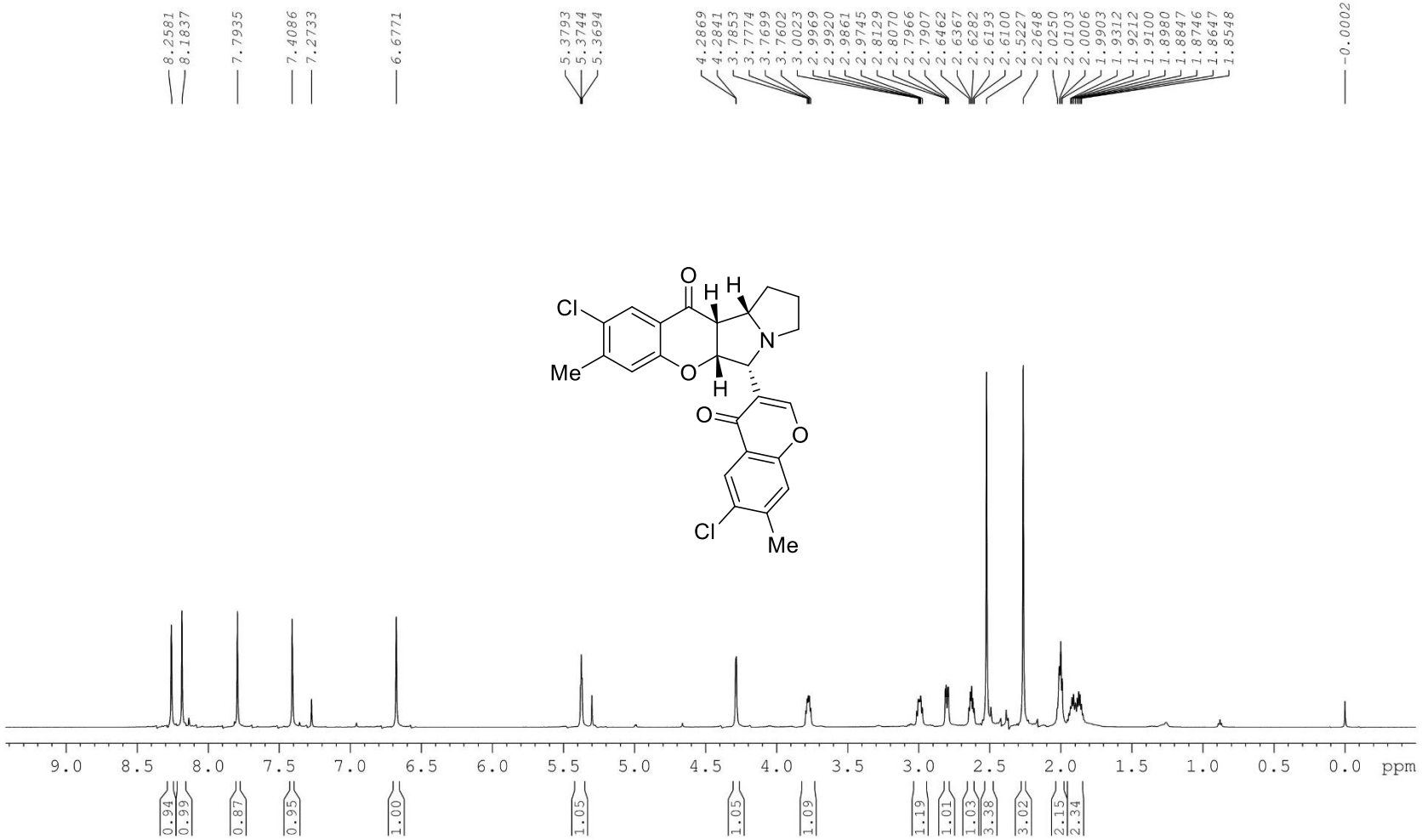



**Figure S9.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectra of compound **3d'**

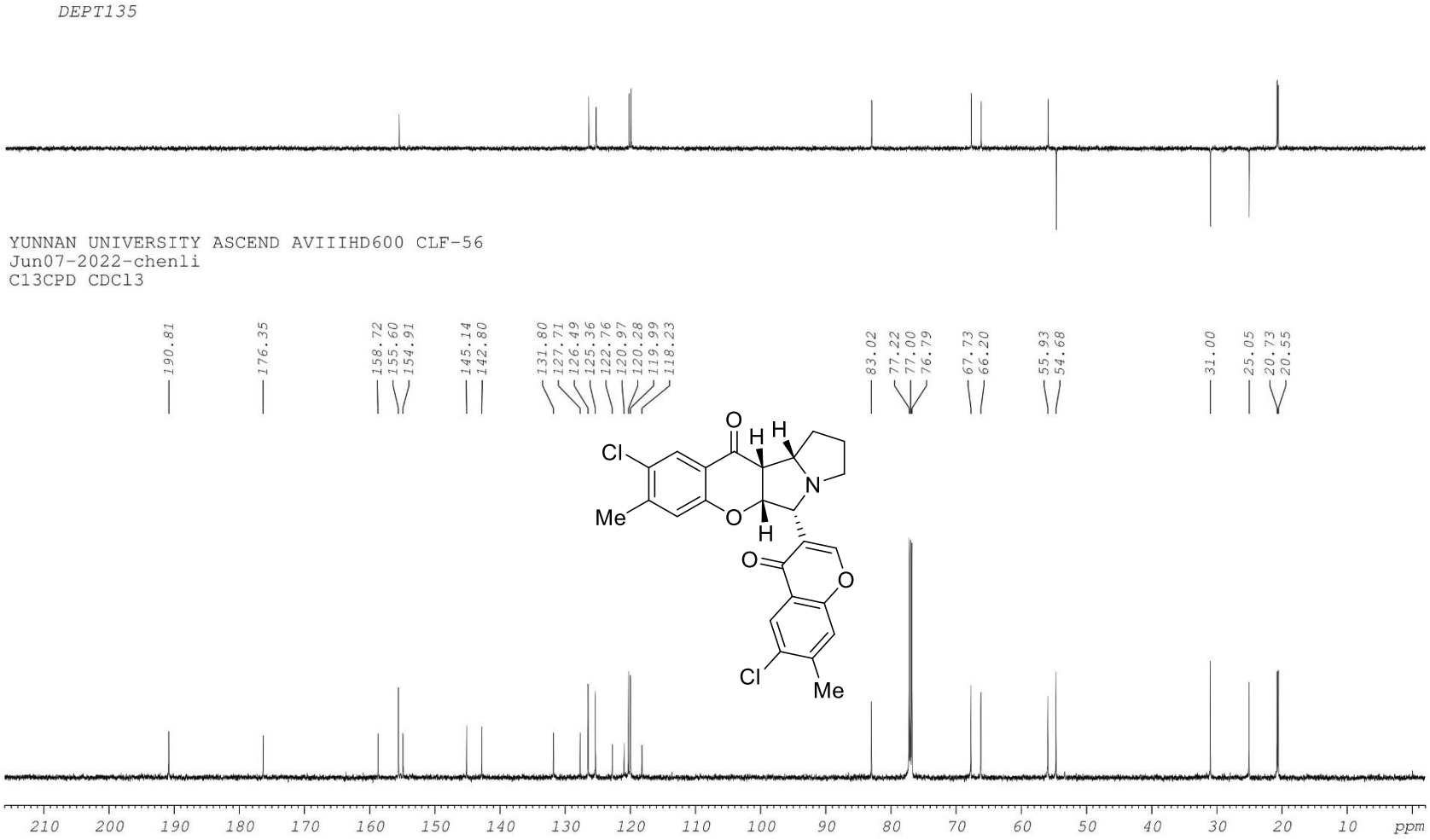



**Figure S10.** $^{13}C$ NMR (**150** MHz, $CDCl_3$) spectra of compound **3d'**

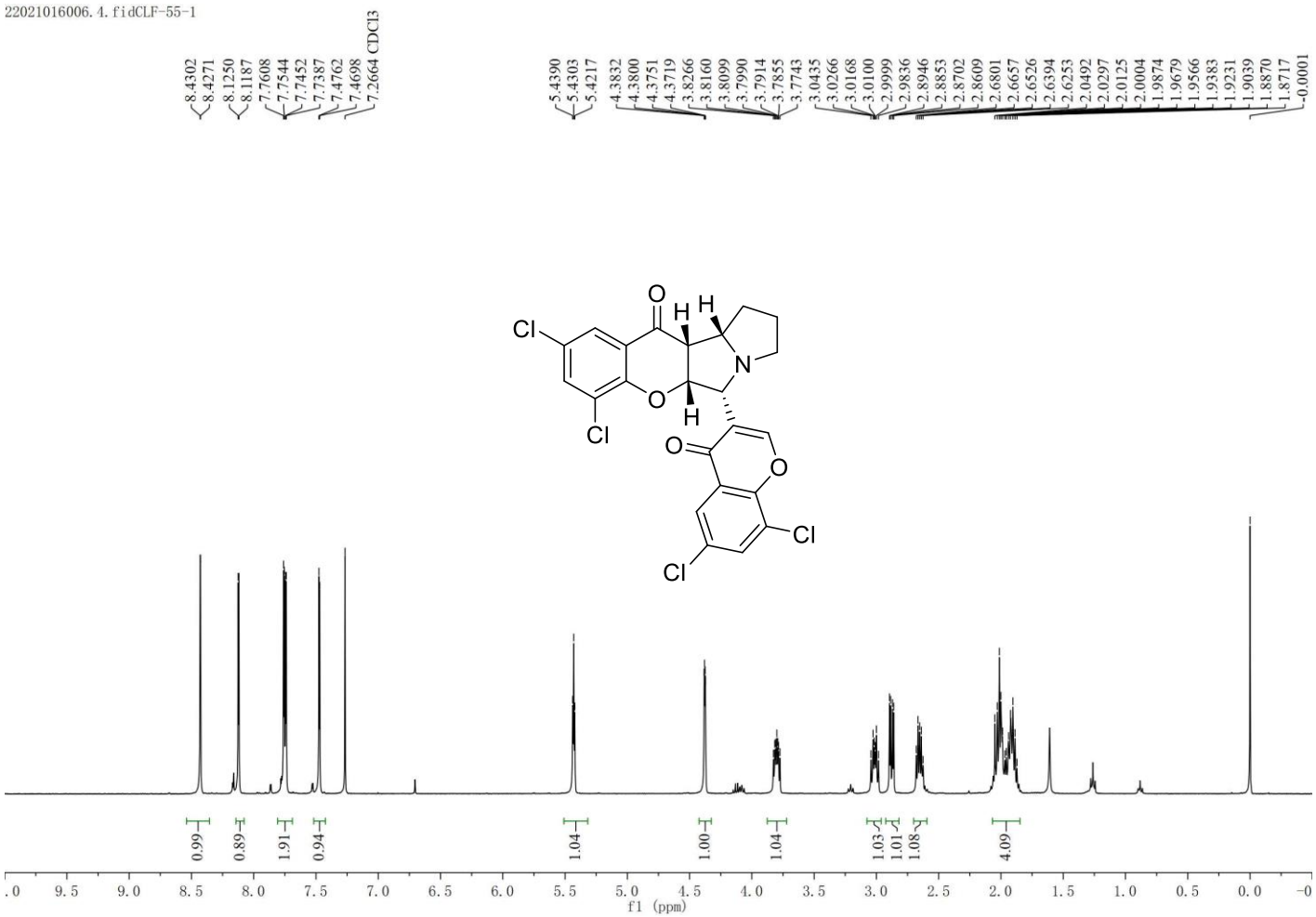



**Figure S11.** $^{1}H$ NMR (400 MHz, $CDCl_3$) spectra of compound **3e'**

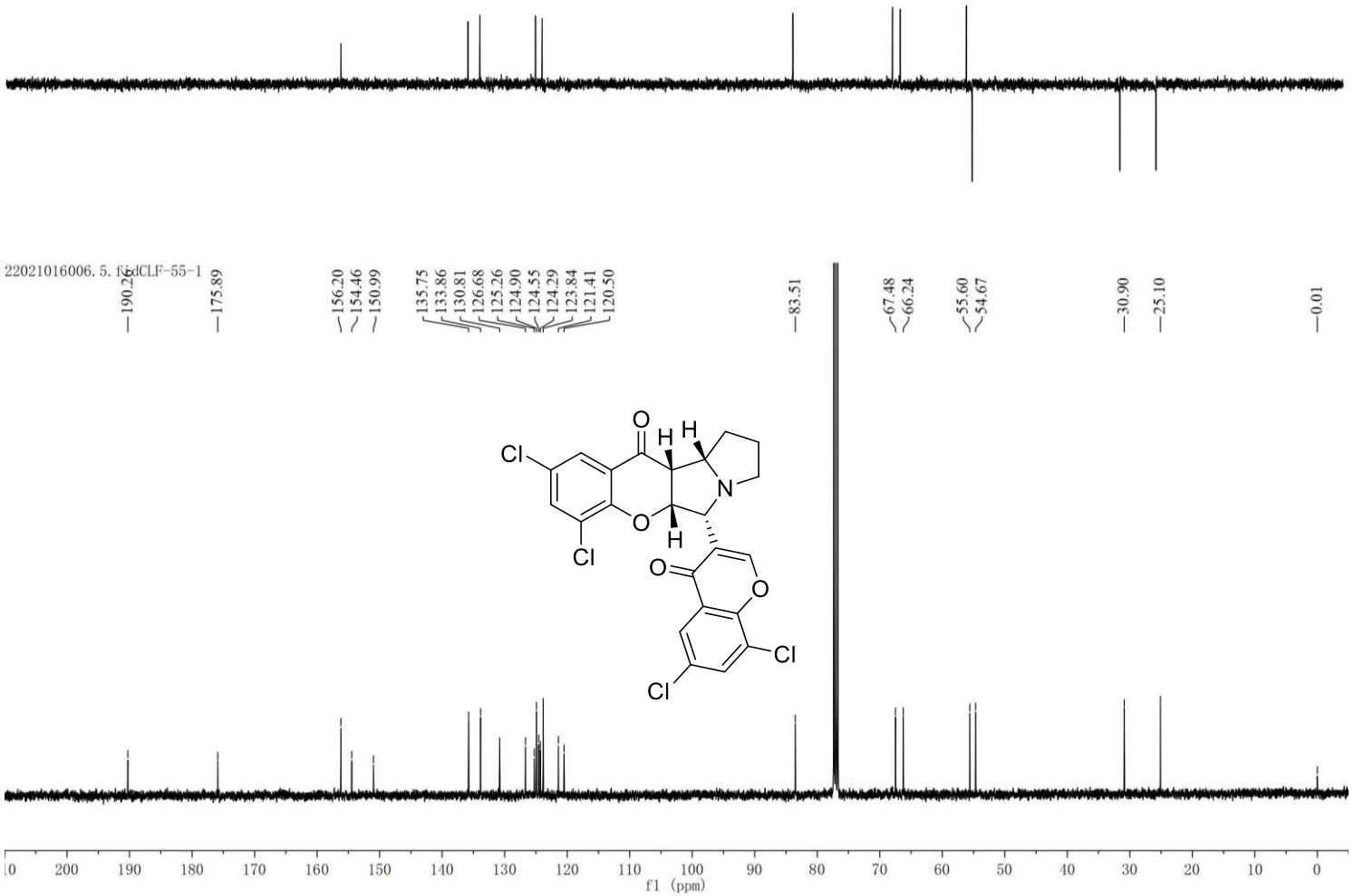



**Figure S12.** $^{13}C$ NMR (100 MHz, $CDCl_3$) spectra of compound **3e'**

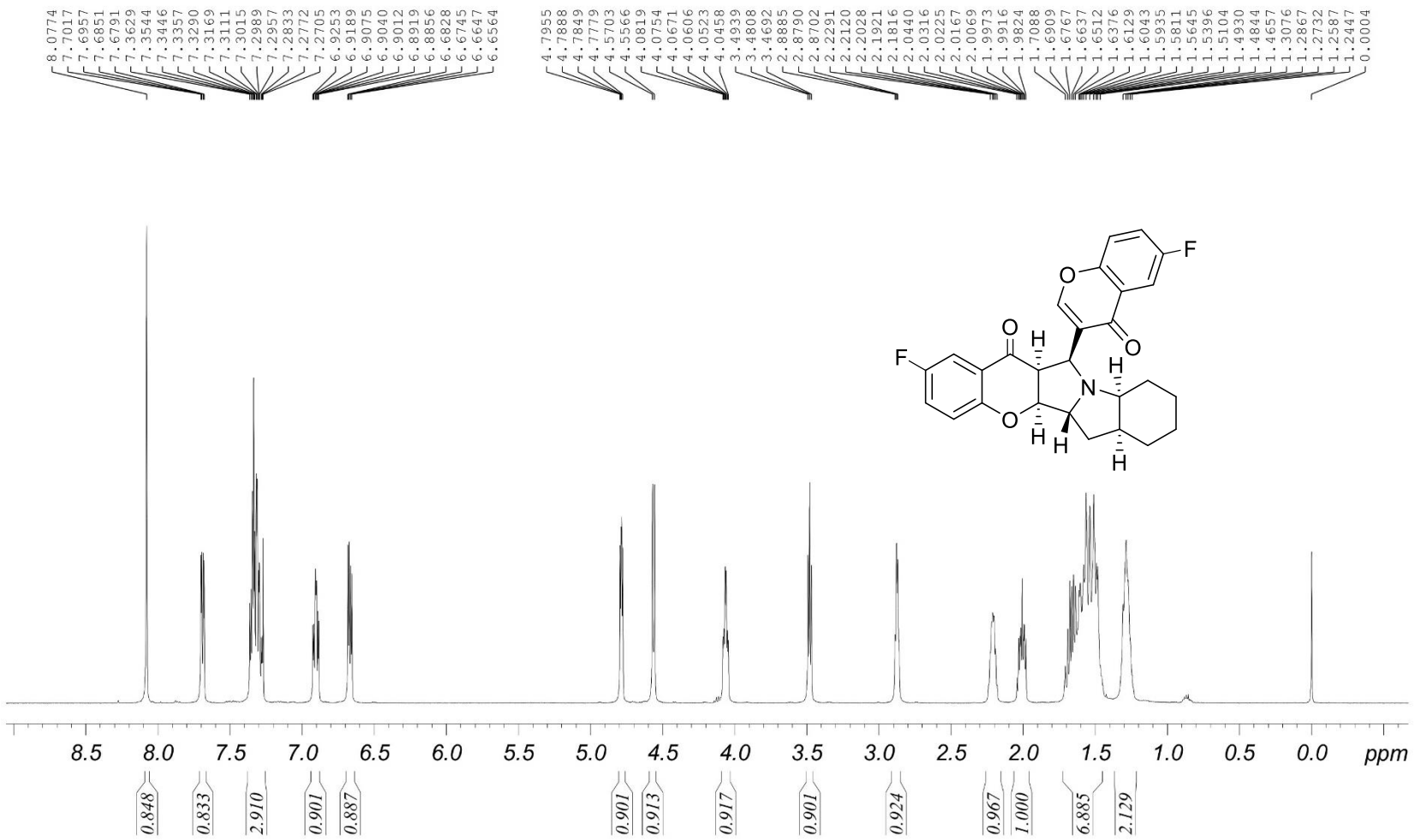



**Figure S13.** $^{1}$H NMR (500 MHz, $CDCl_3$) spectra of compound **3f**

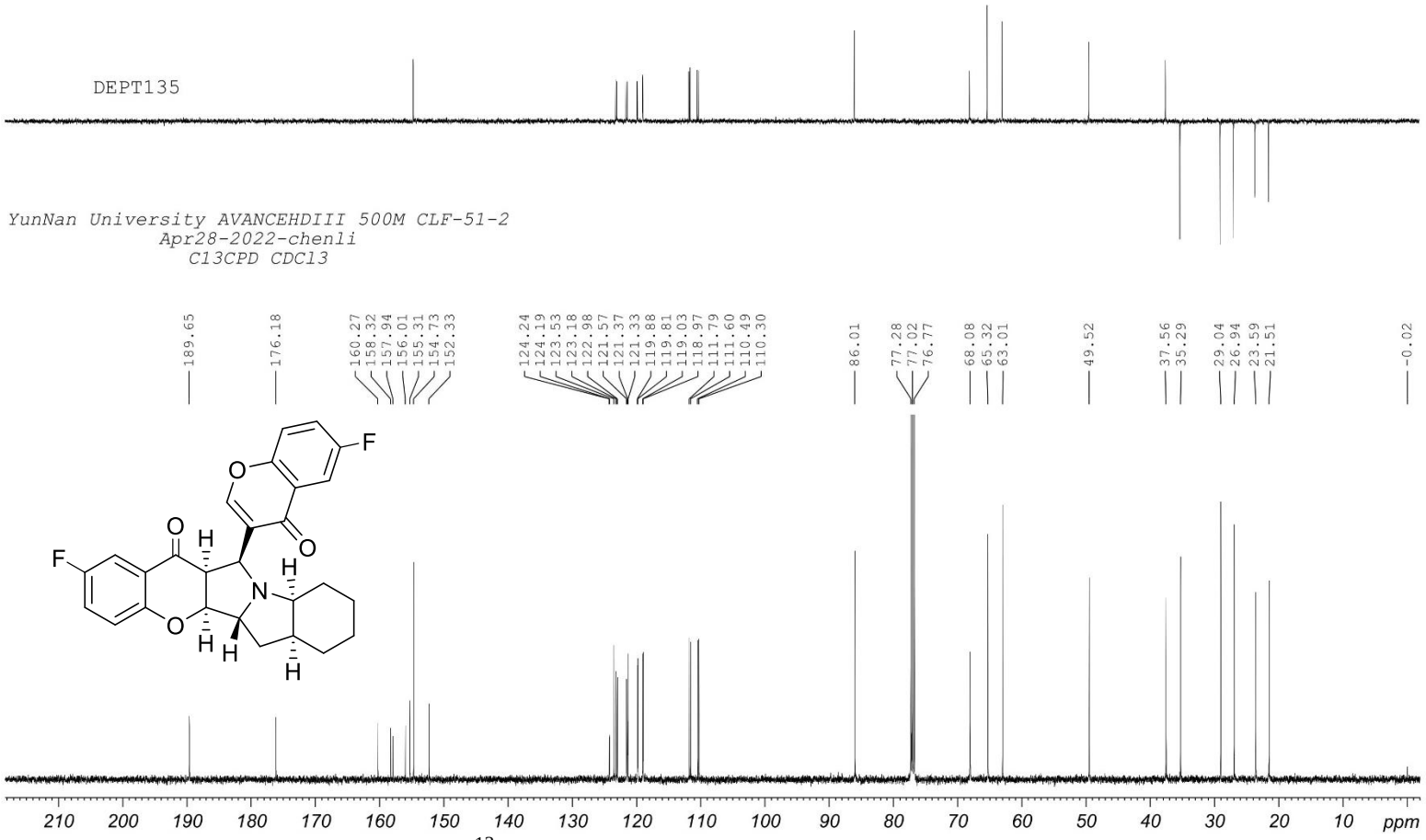



**Figure S14.** $^{13}C$ NMR (125 MHz, $CDCl_3$) spectra of compound **3f**

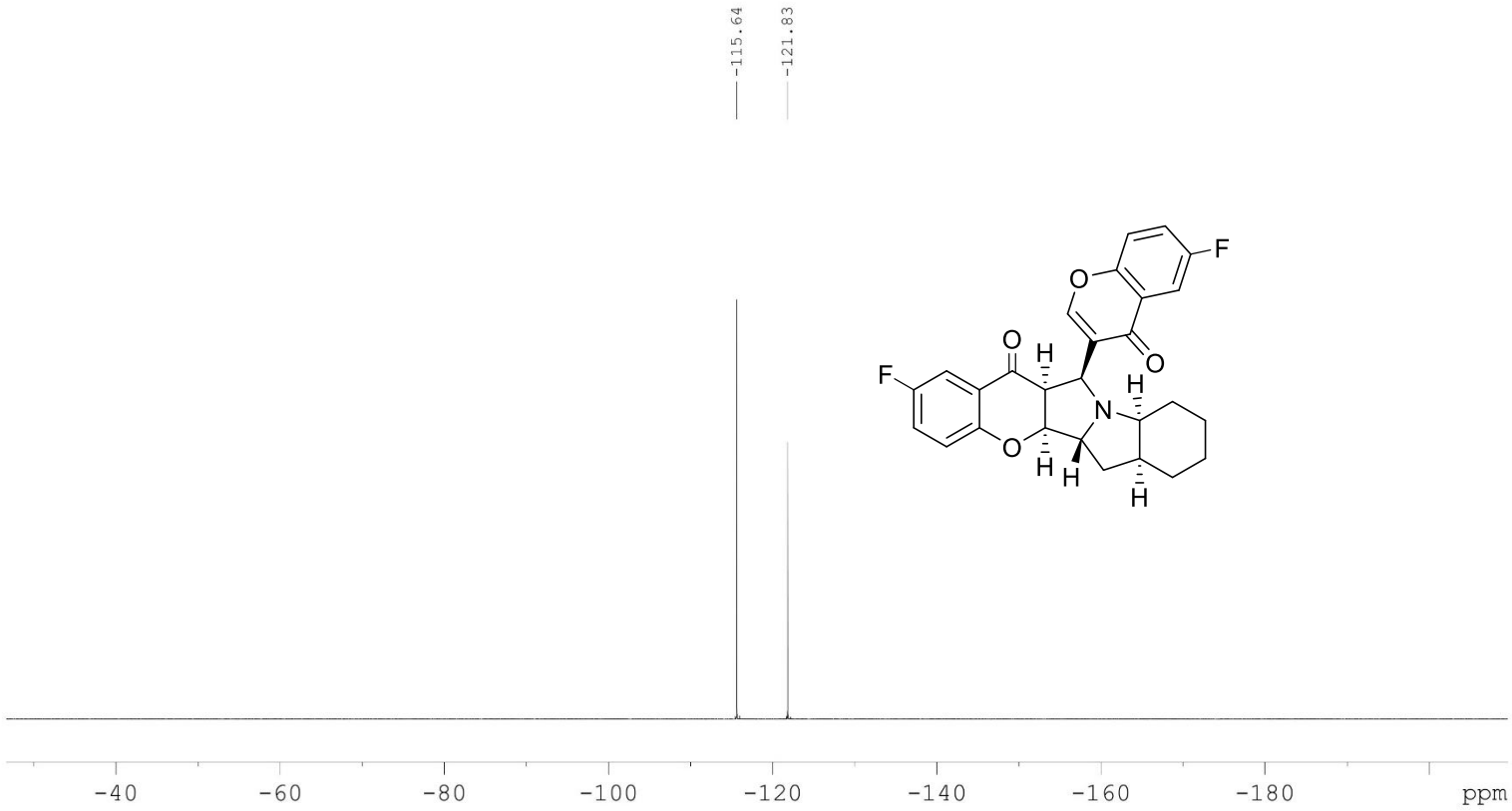



**Figure S15.** $^{19}F$ NMR (470 MHz, $CDCl_3$) spectra of compound **3f**

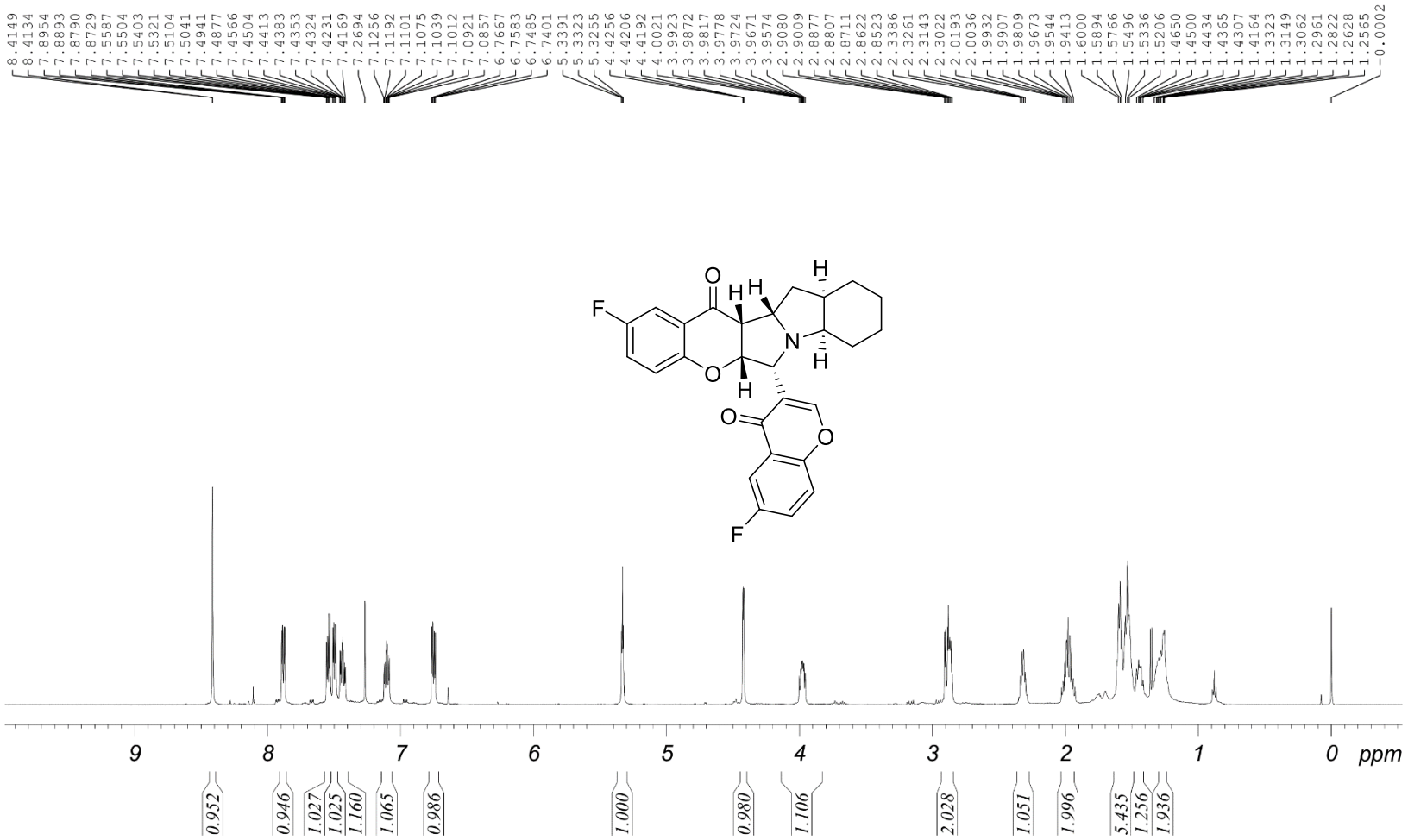



**Figure S16.** $^{1}$H NMR (500 MHz, $CDCl_3$) spectra of compound **3f'**

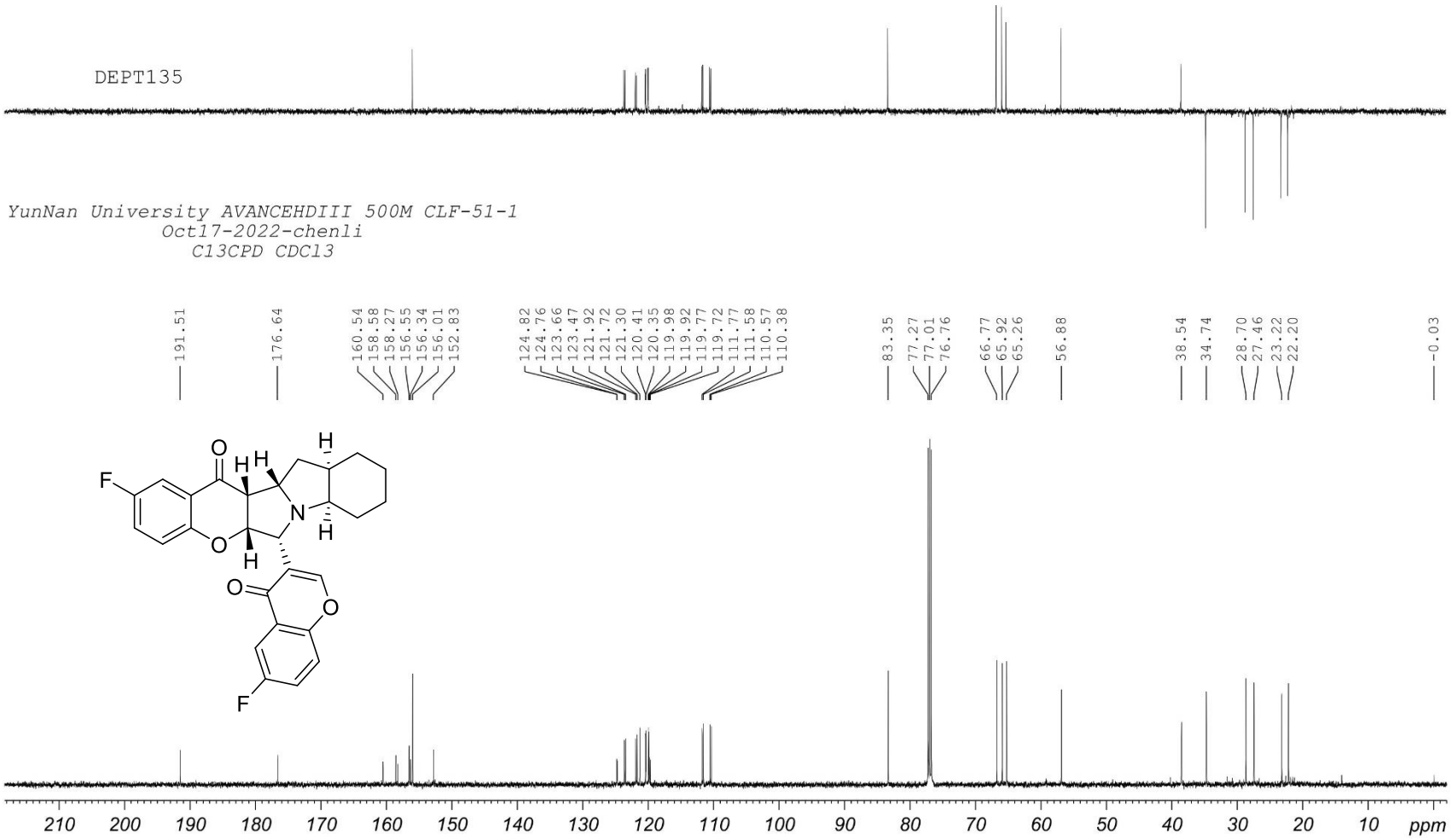



**Figure S17.** $^{13}C$ NMR (125 MHz, $CDCl_3$) spectra of compound **3f'**

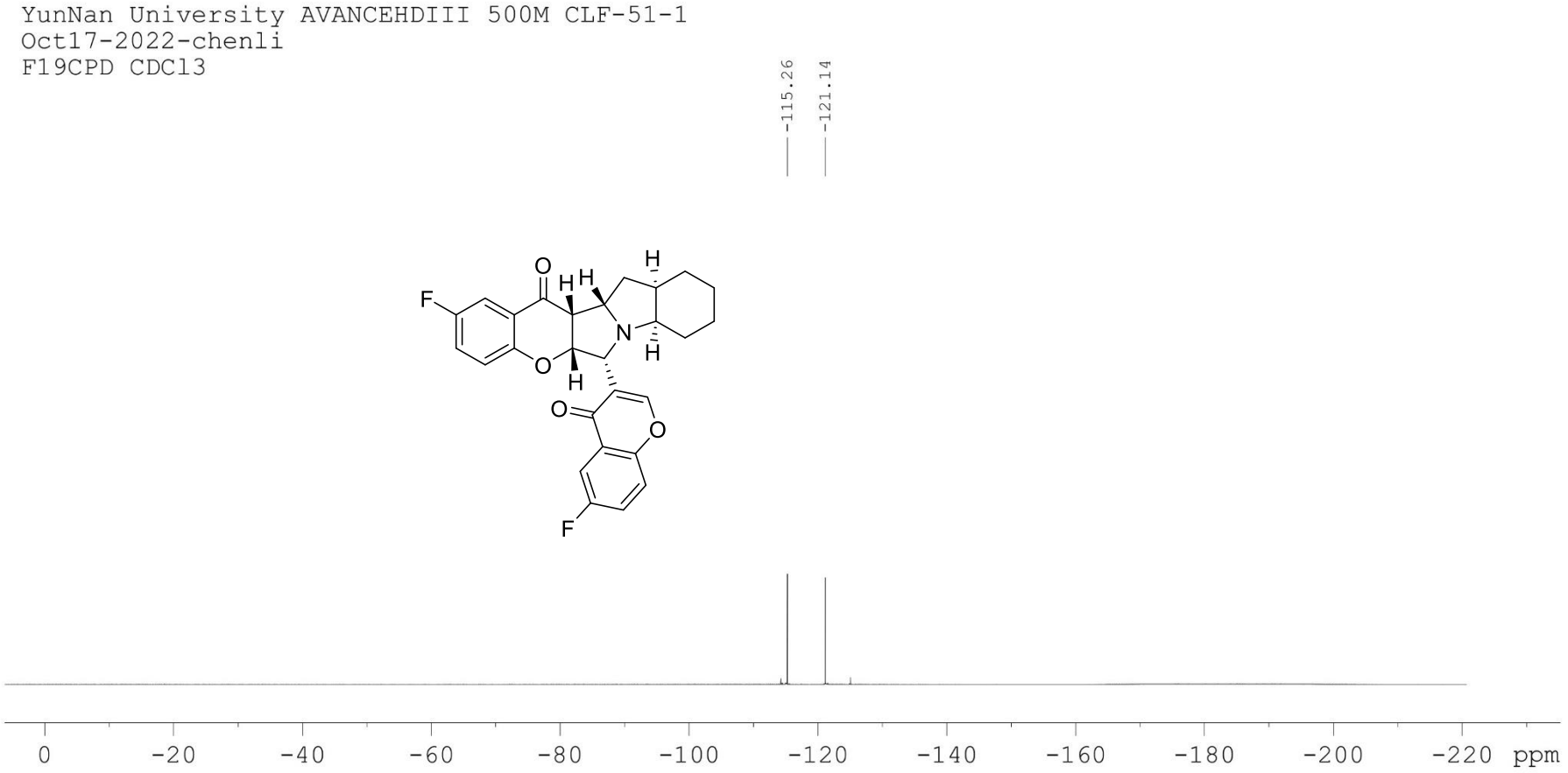



**Figure S18.** $^{19}F$ NMR (470 MHz, $CDCl_3$) spectra of compound **3f'**

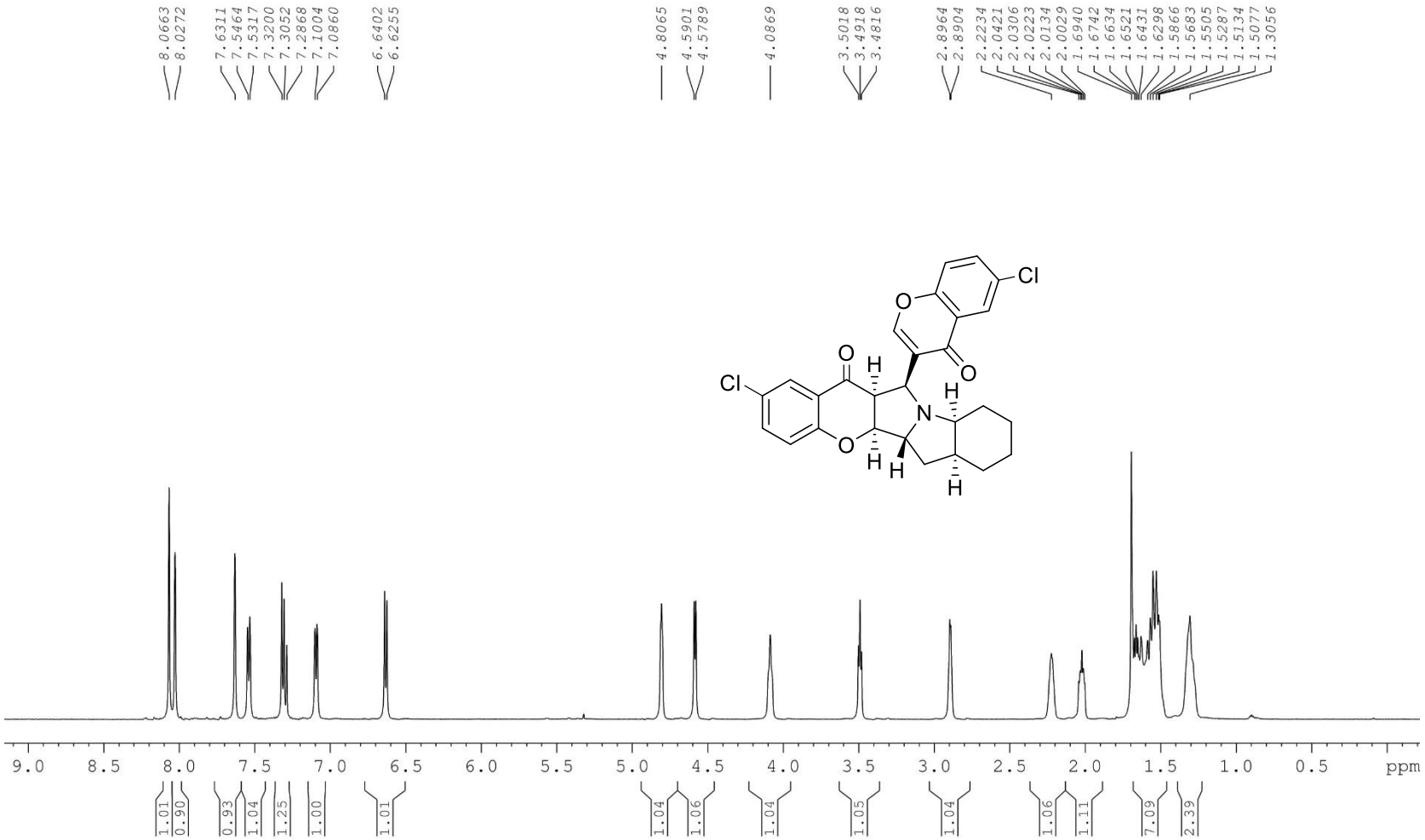



**Figure S19.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectra of compound **3g**

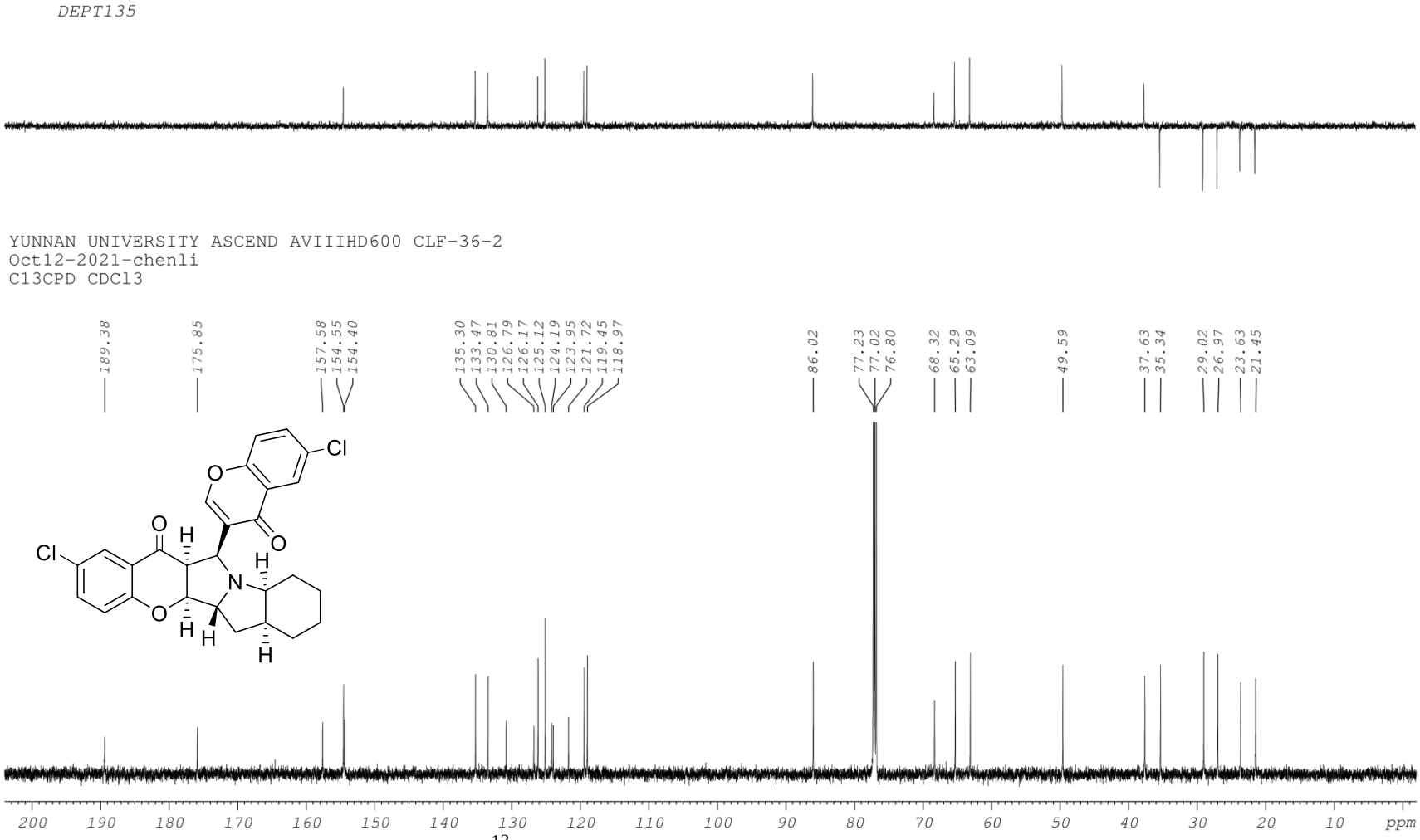



**Figure S20.** $^{13}C$ NMR (150 MHz, $CDCl_3$) spectra of compound **3g**

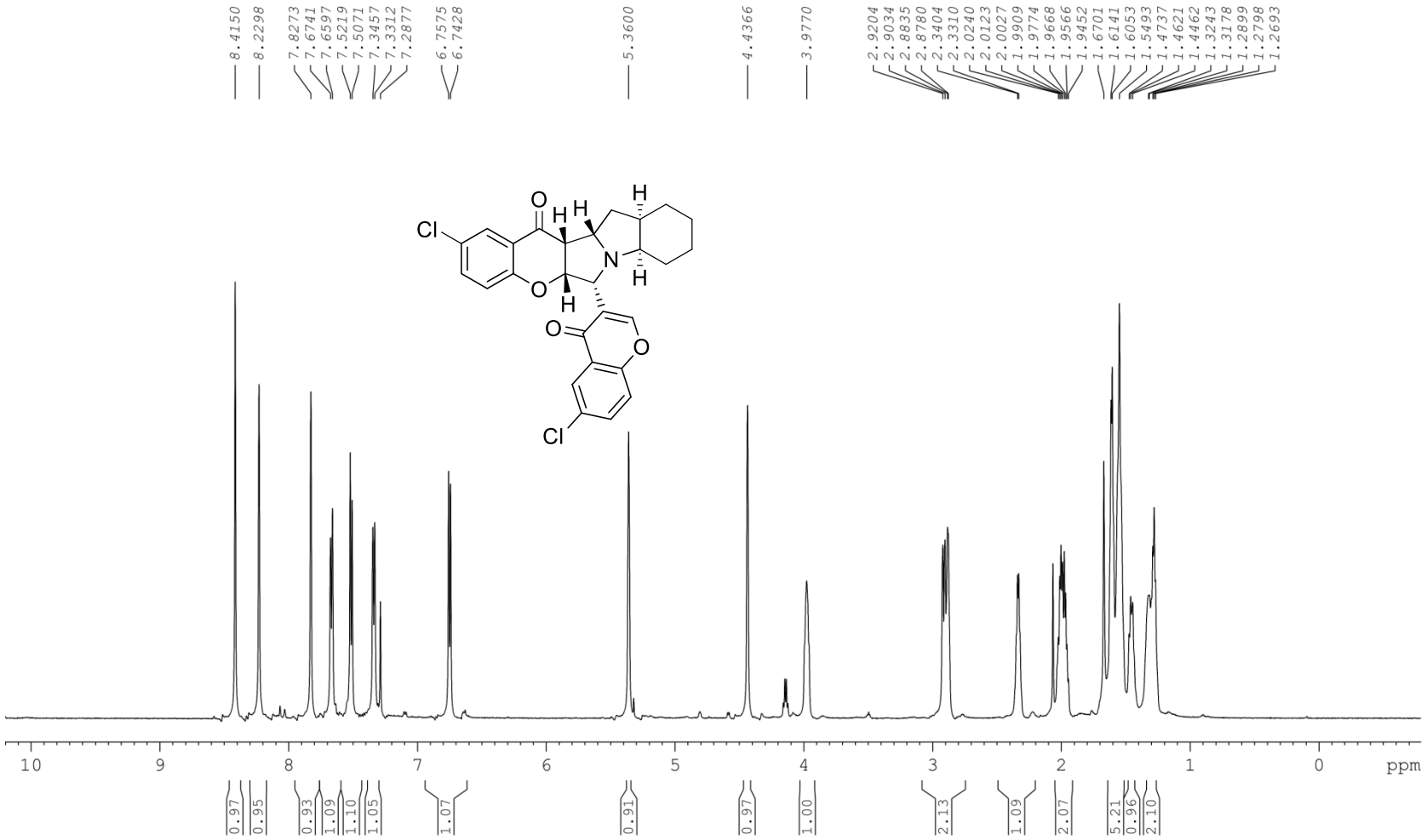



**Figure S21.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectra of compound **3g'**

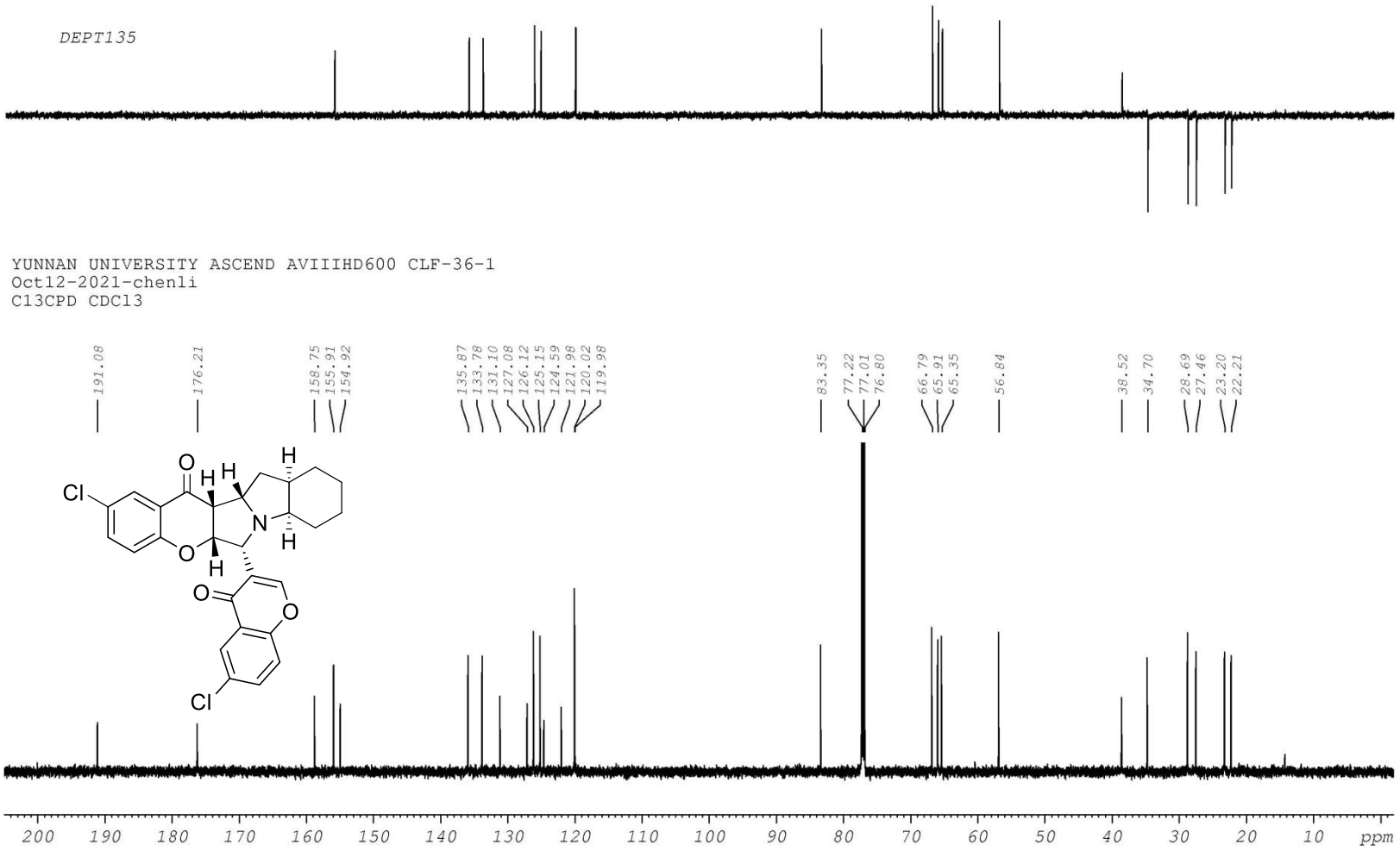



**Figure S22.** $^{13}C$ NMR (150 MHz, $CDCl_3$) spectra of compound **3g'**

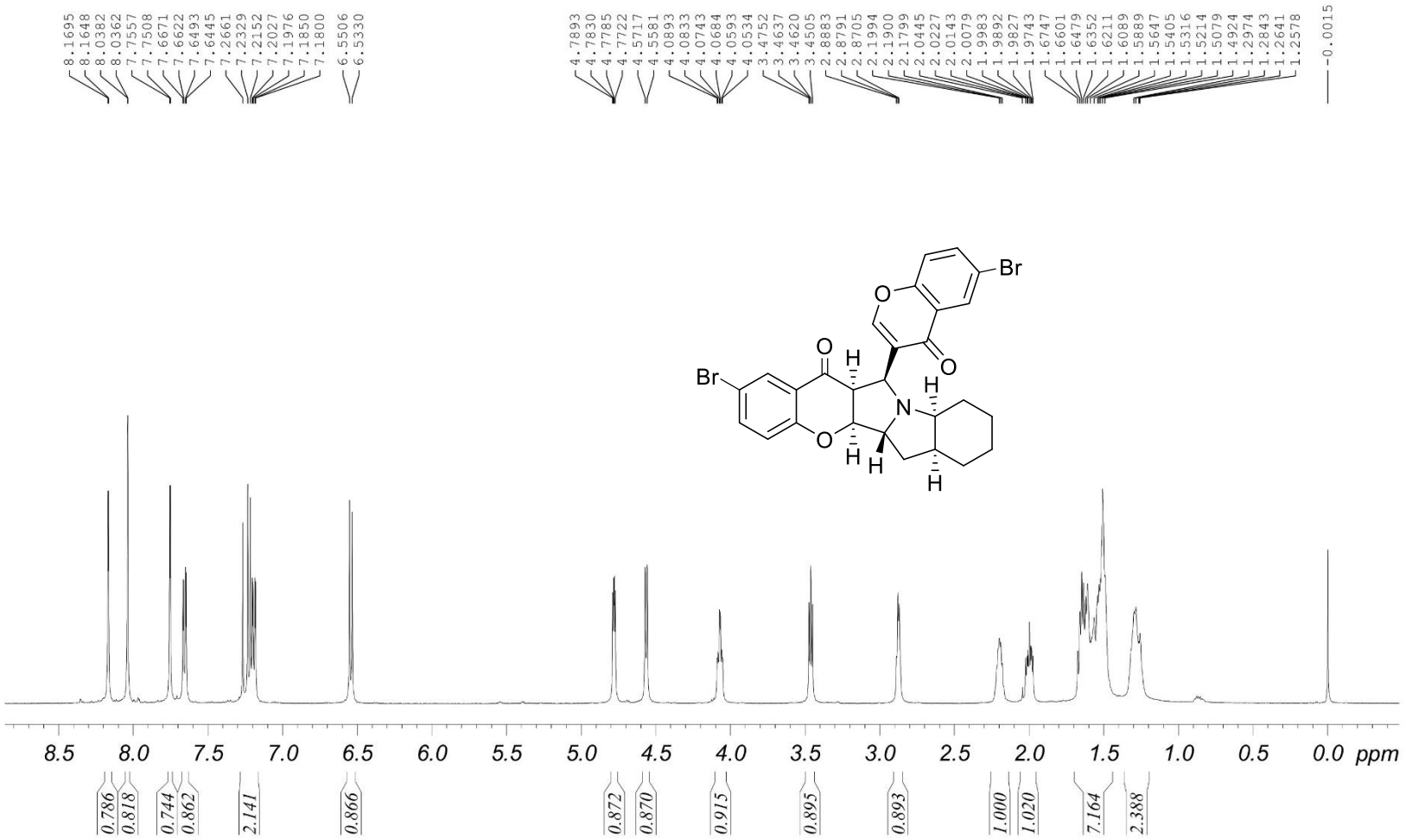



**Figure S23.** $^{1}$H NMR (500 MHz, $CDCl_3$) spectra of compound **3h**

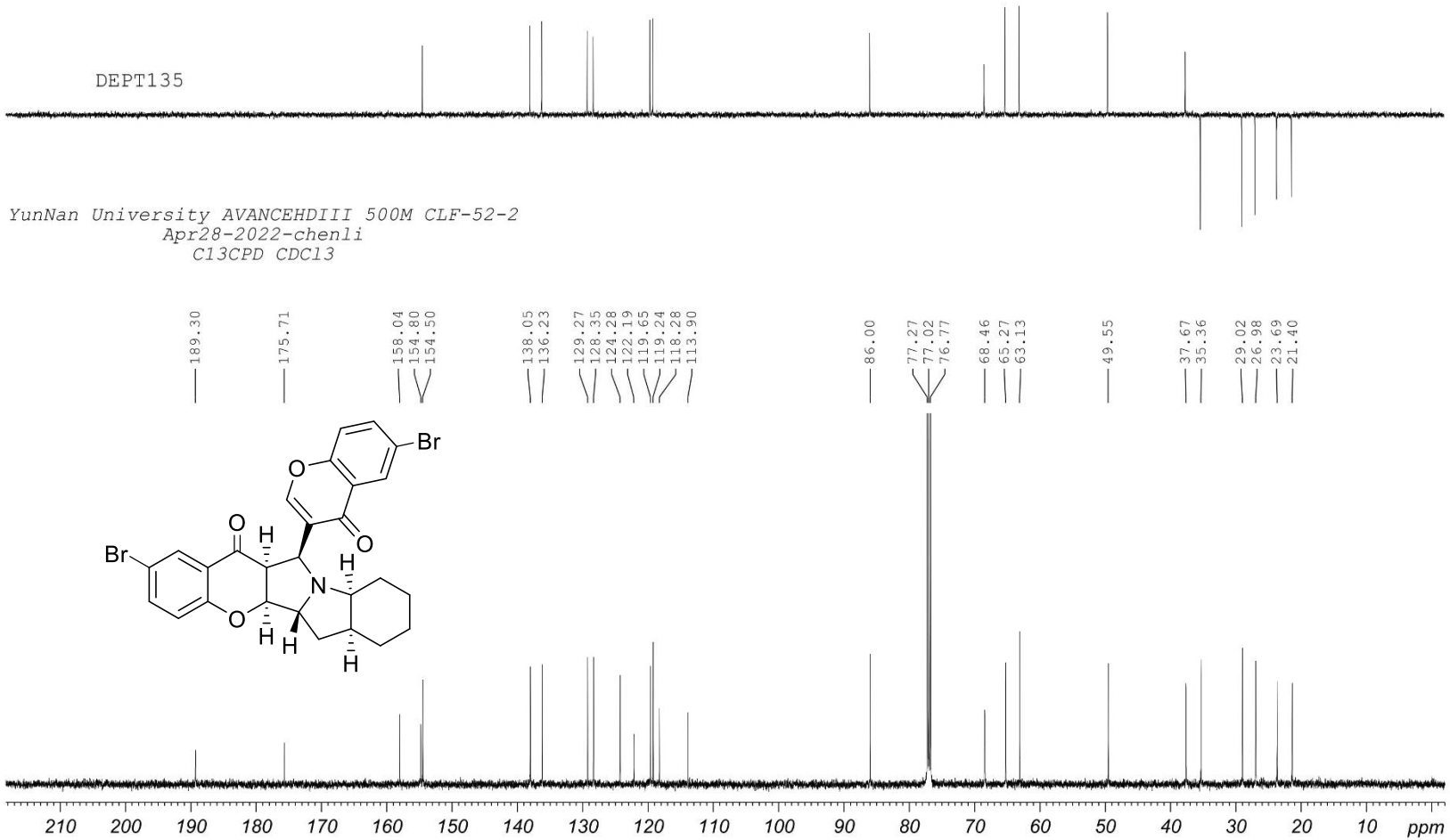



**Figure S24.** $^{13}C$ NMR (125 MHz, $CDCl_3$) spectra of compound **3h**

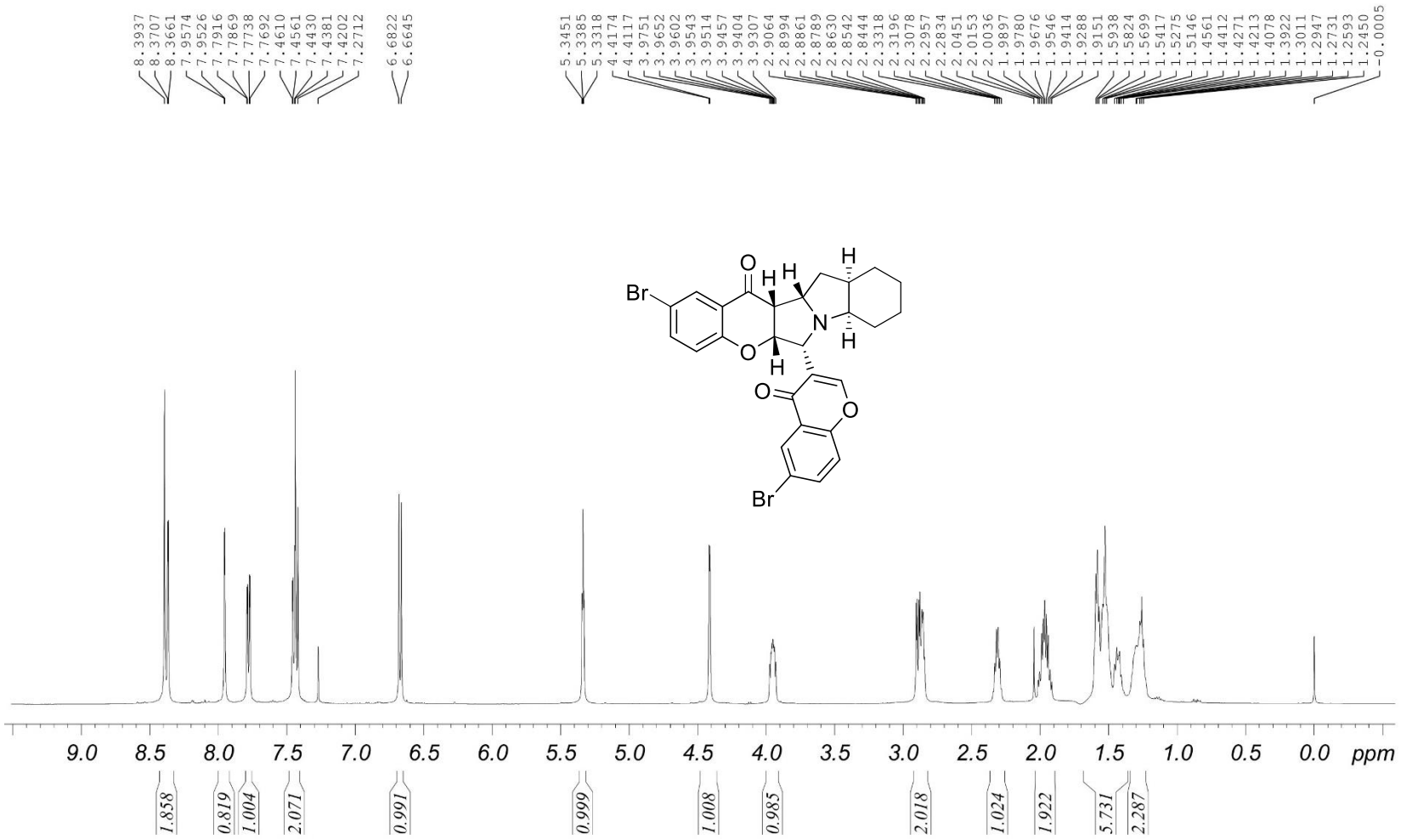



**Figure S25.** $^{1}$H NMR (500 MHz, $CDCl_3$) spectra of compound **3h'**

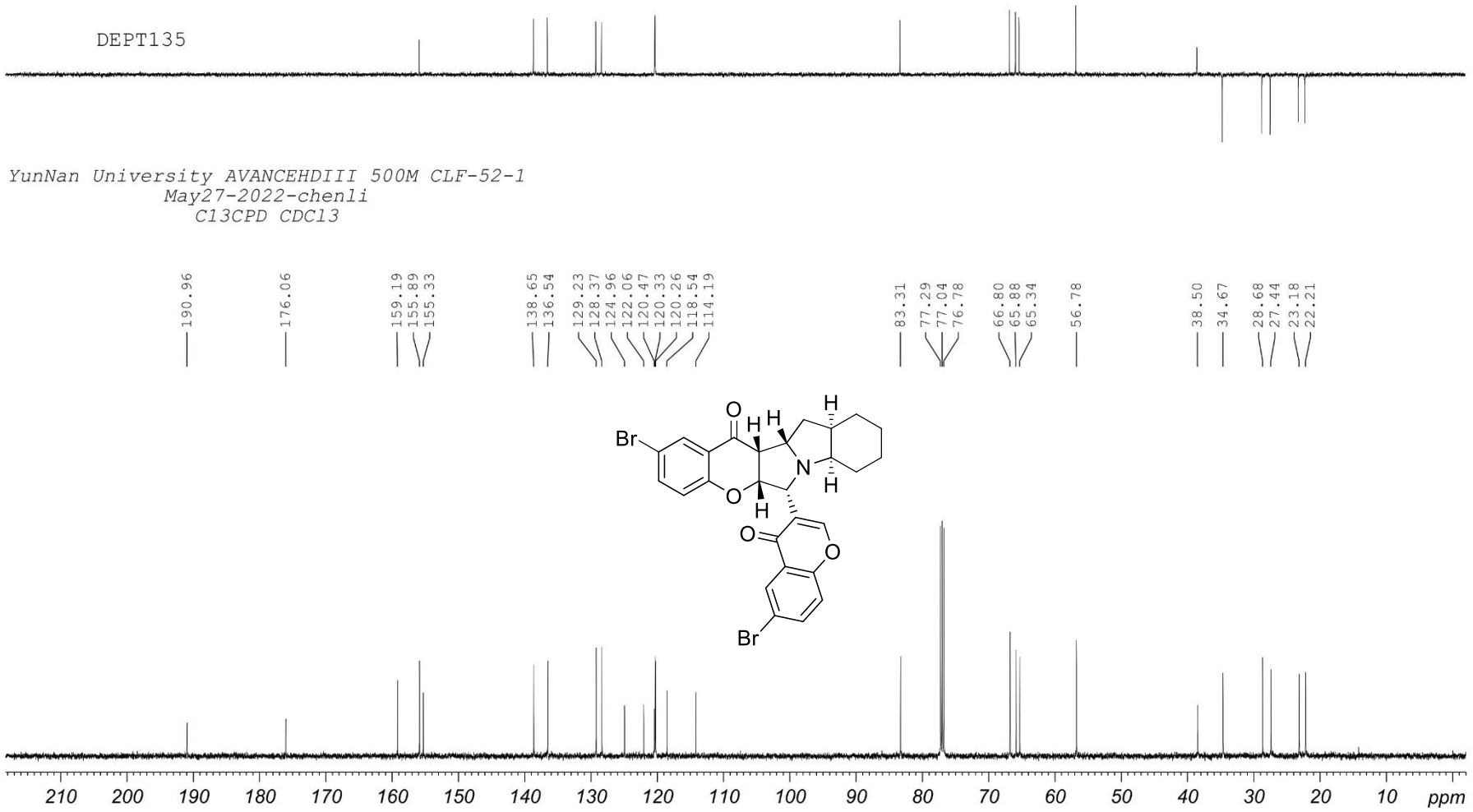



**Figure S26.** $^{13}C$ NMR (125 MHz, $CDCl_3$) spectra of compound **3h'**

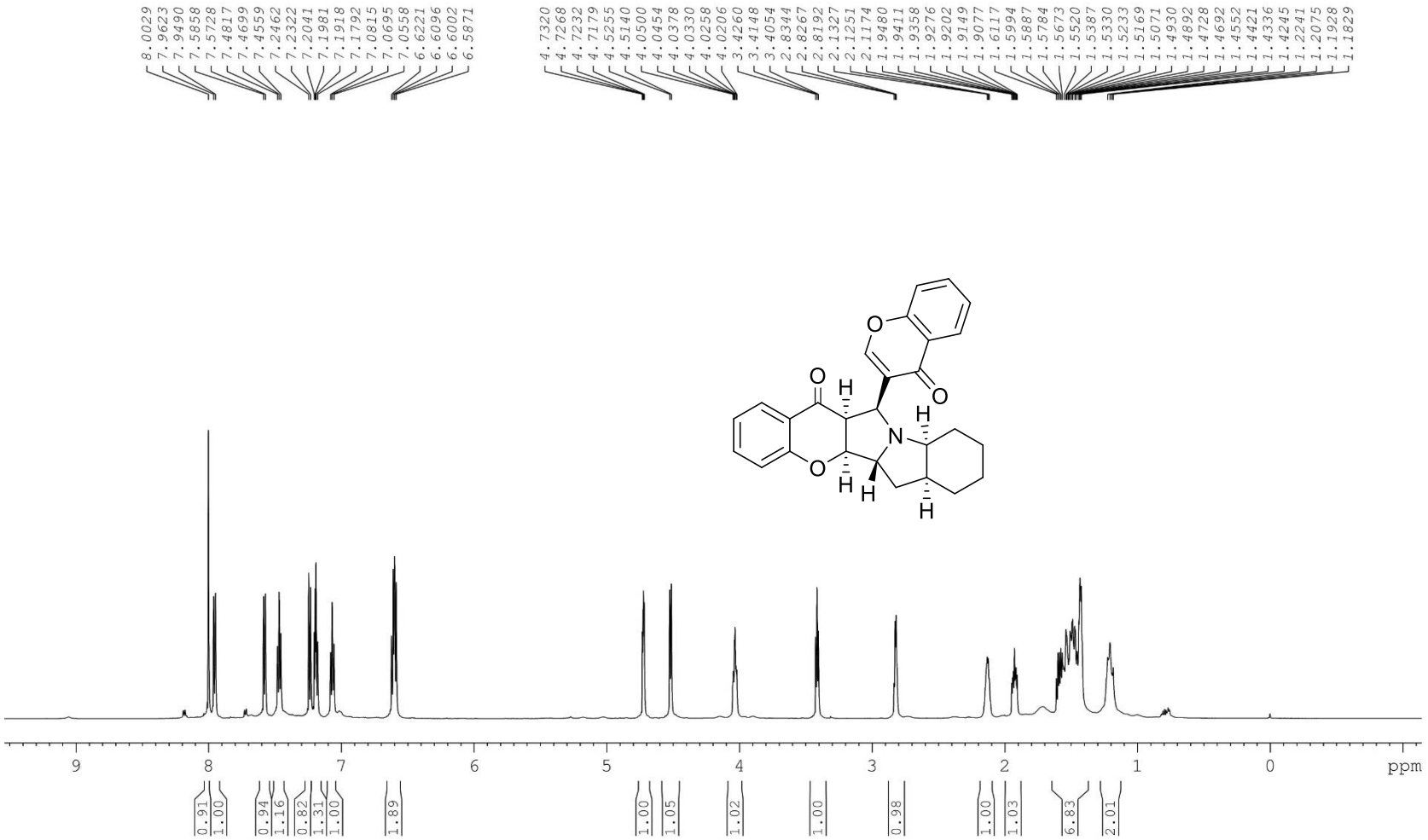



**Figure S27.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectra of compound **3i**

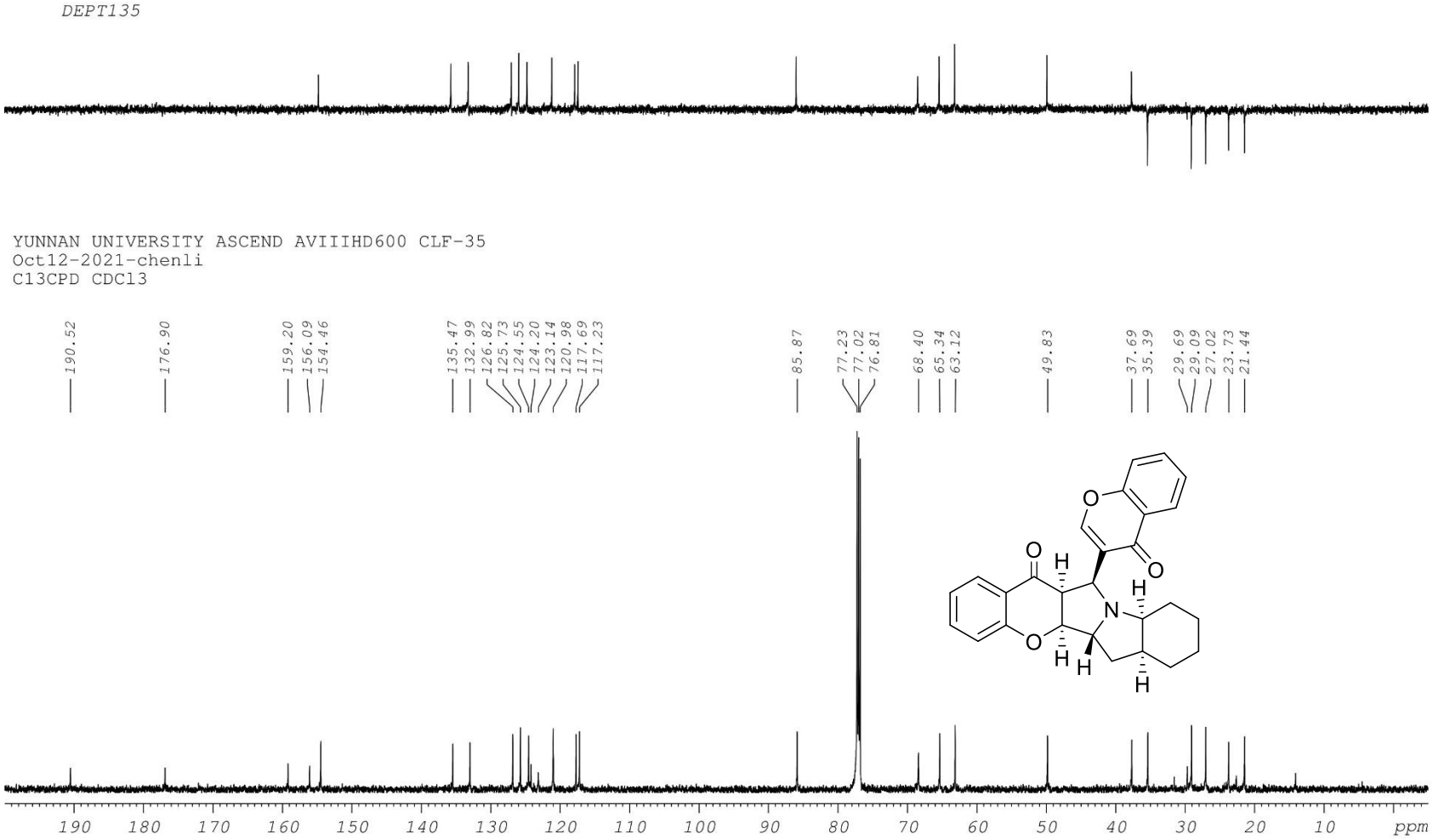



**Figure S28.** $^{13}C$ NMR (150 MHz, $CDCl_3$) spectra of compound **3i**

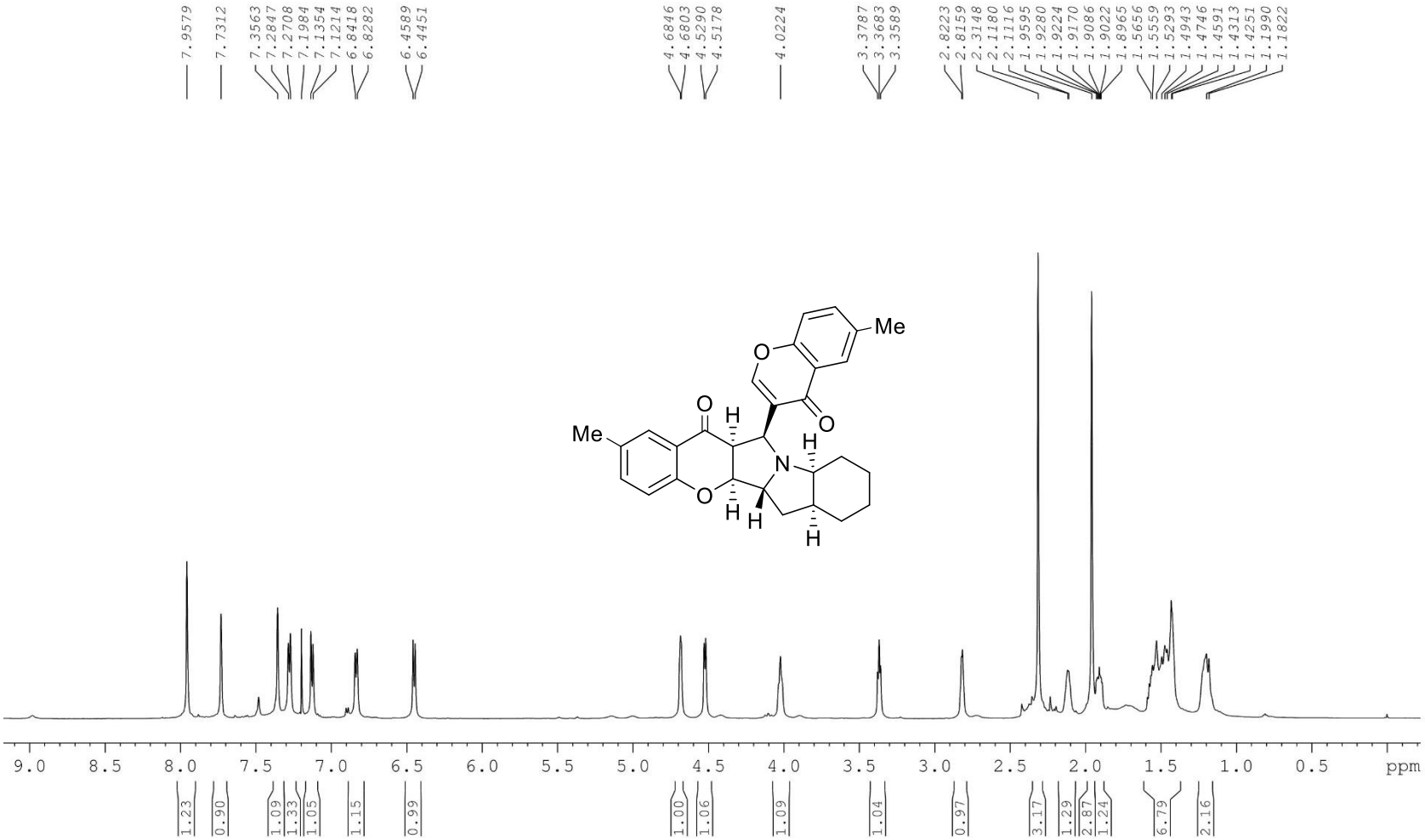



**Figure S29.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectra of compound **3j**

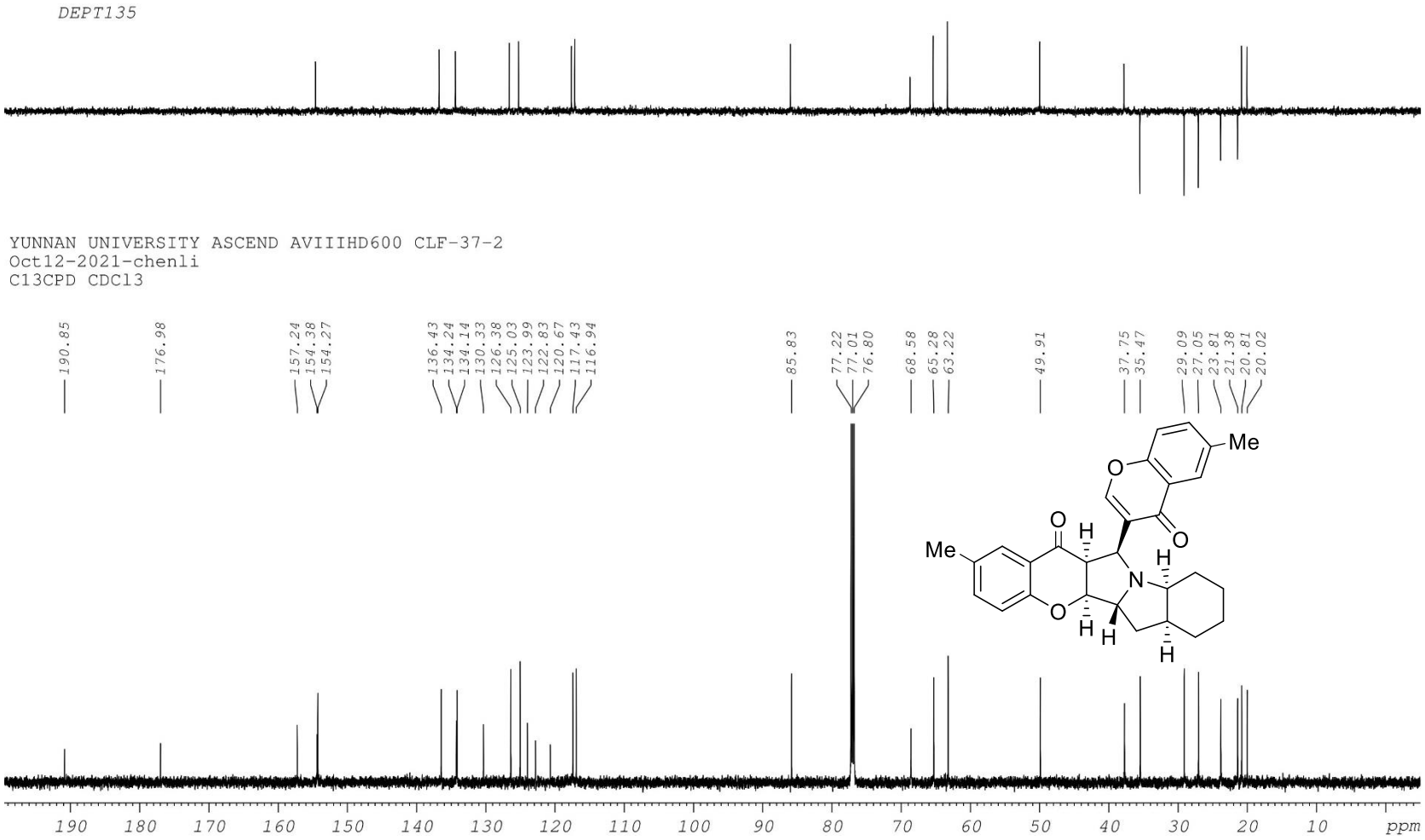



**Figure S30.** $^{13}C$ NMR (150 MHz, $CDCl_3$) spectra of compound **3j**

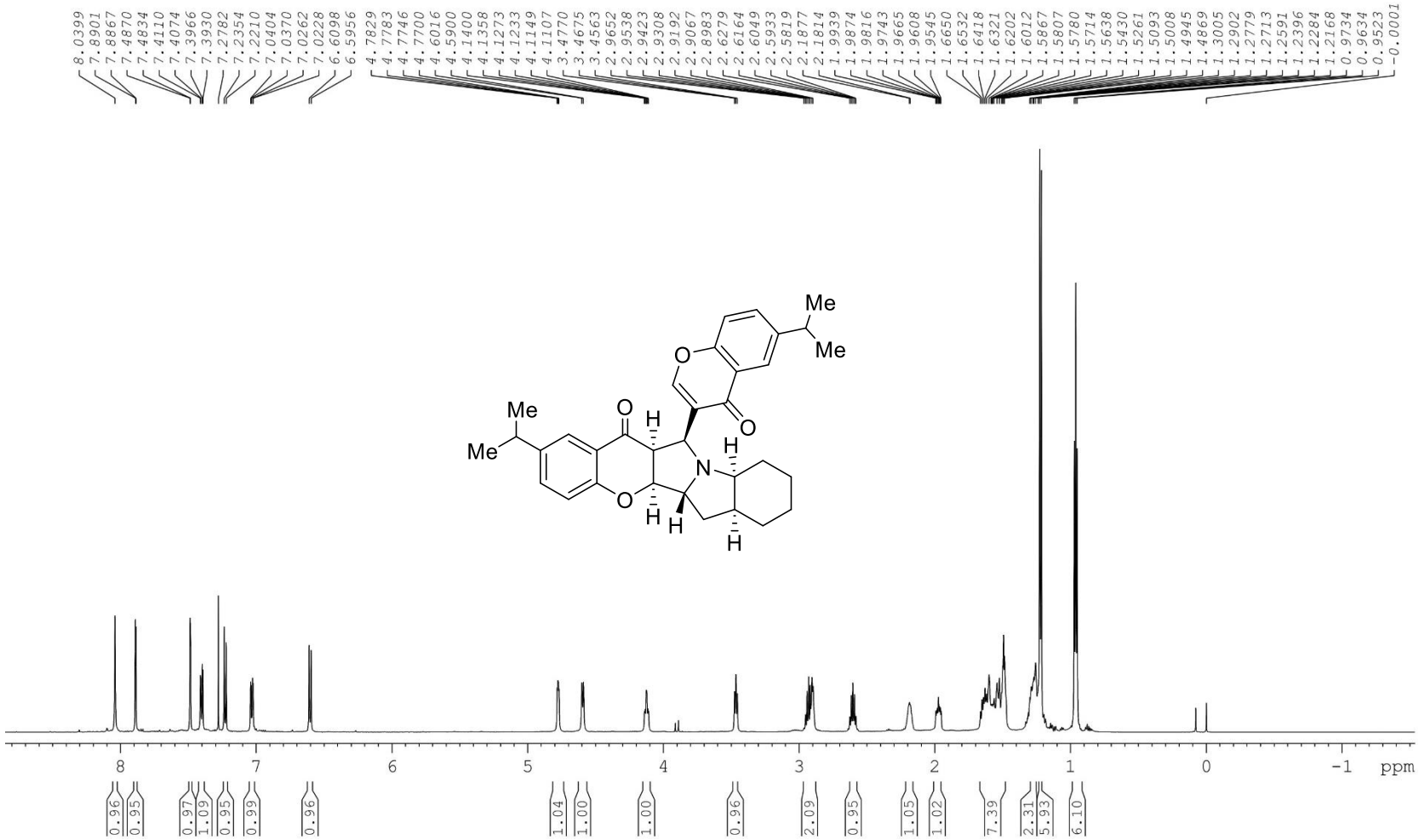



**Figure S31.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectra of compound **3k**

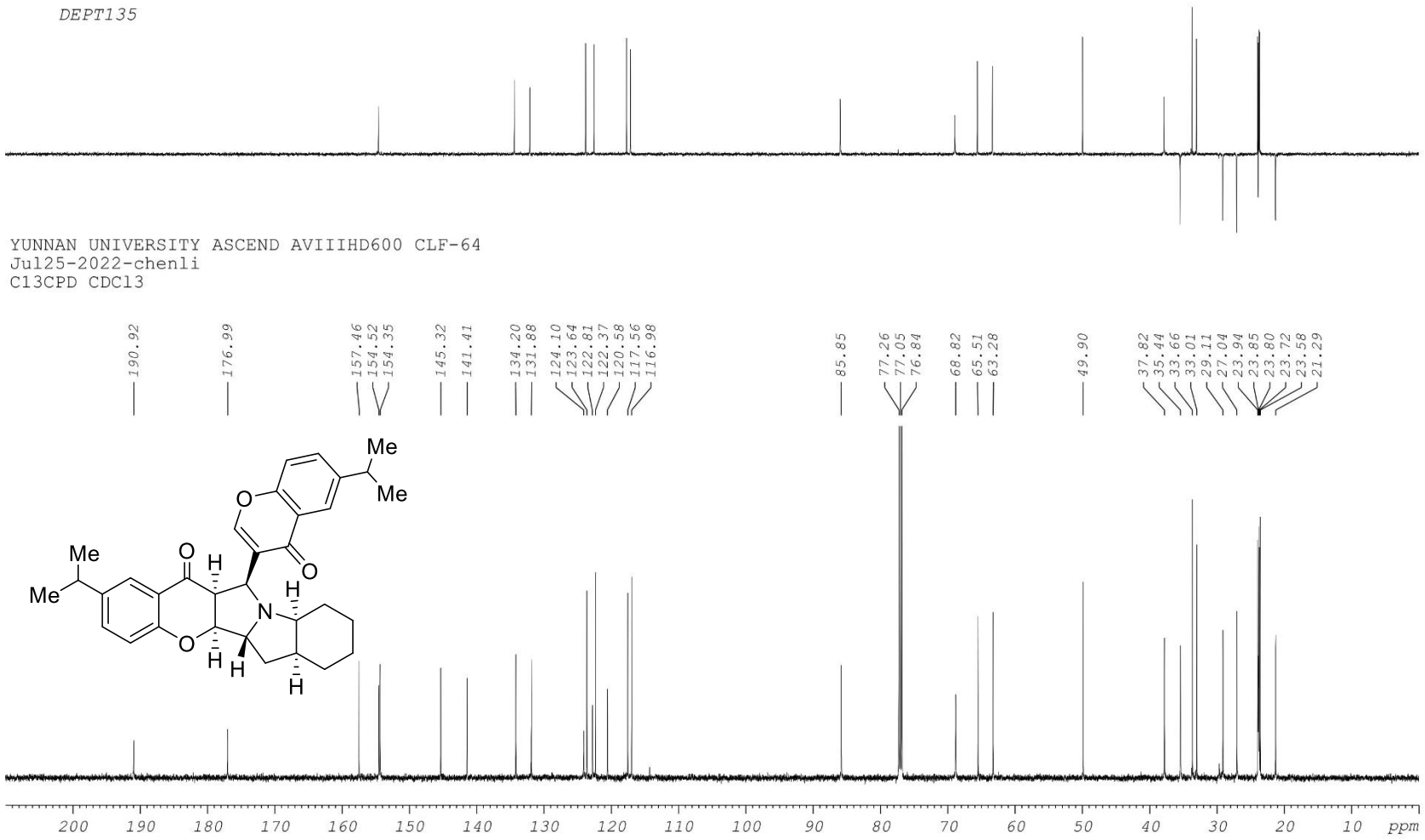



**Figure S32.** $^{13}C$ NMR (150 MHz, $CDCl_3$) spectra of compound **3k**

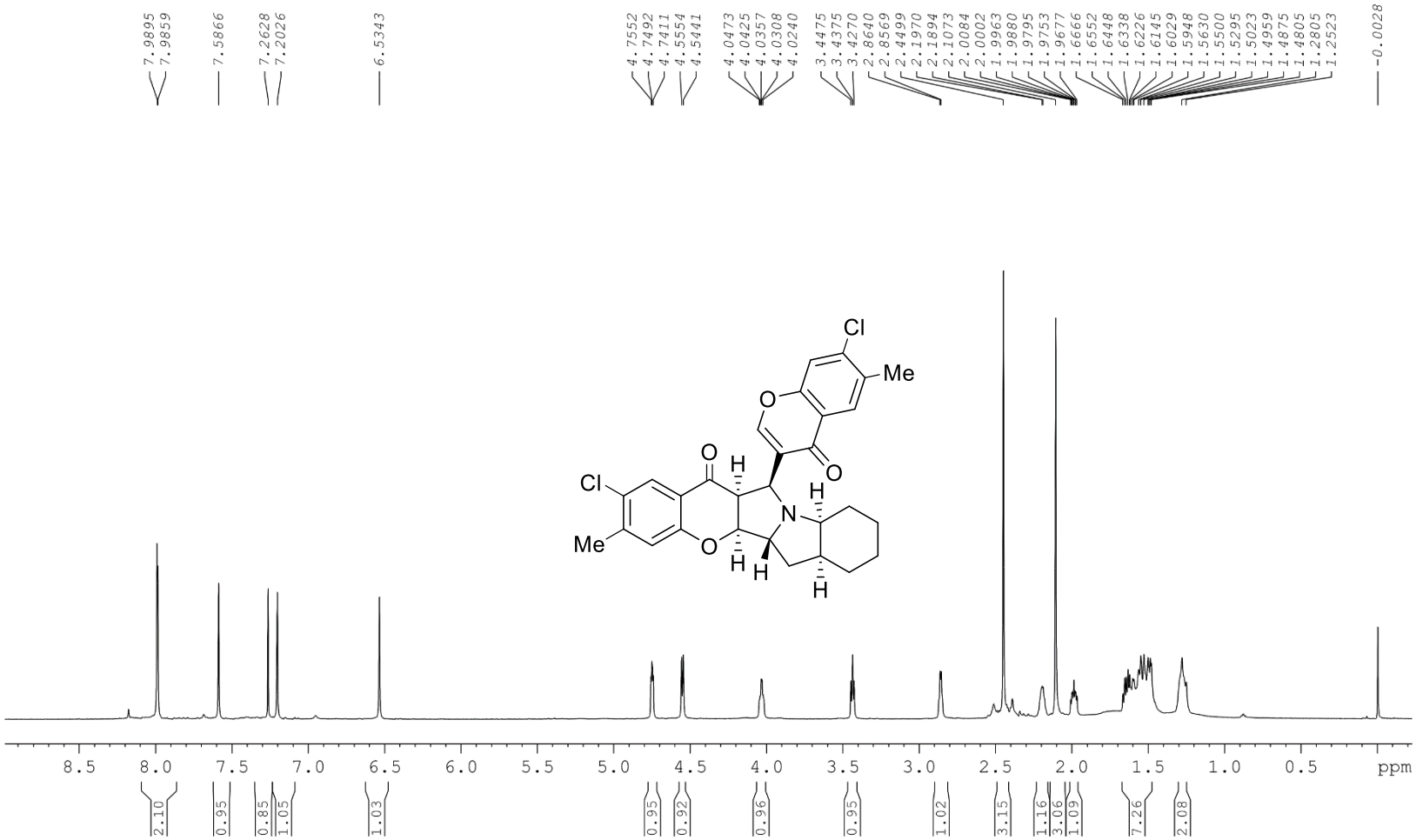



**Figure S33.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectra of compound **3l**

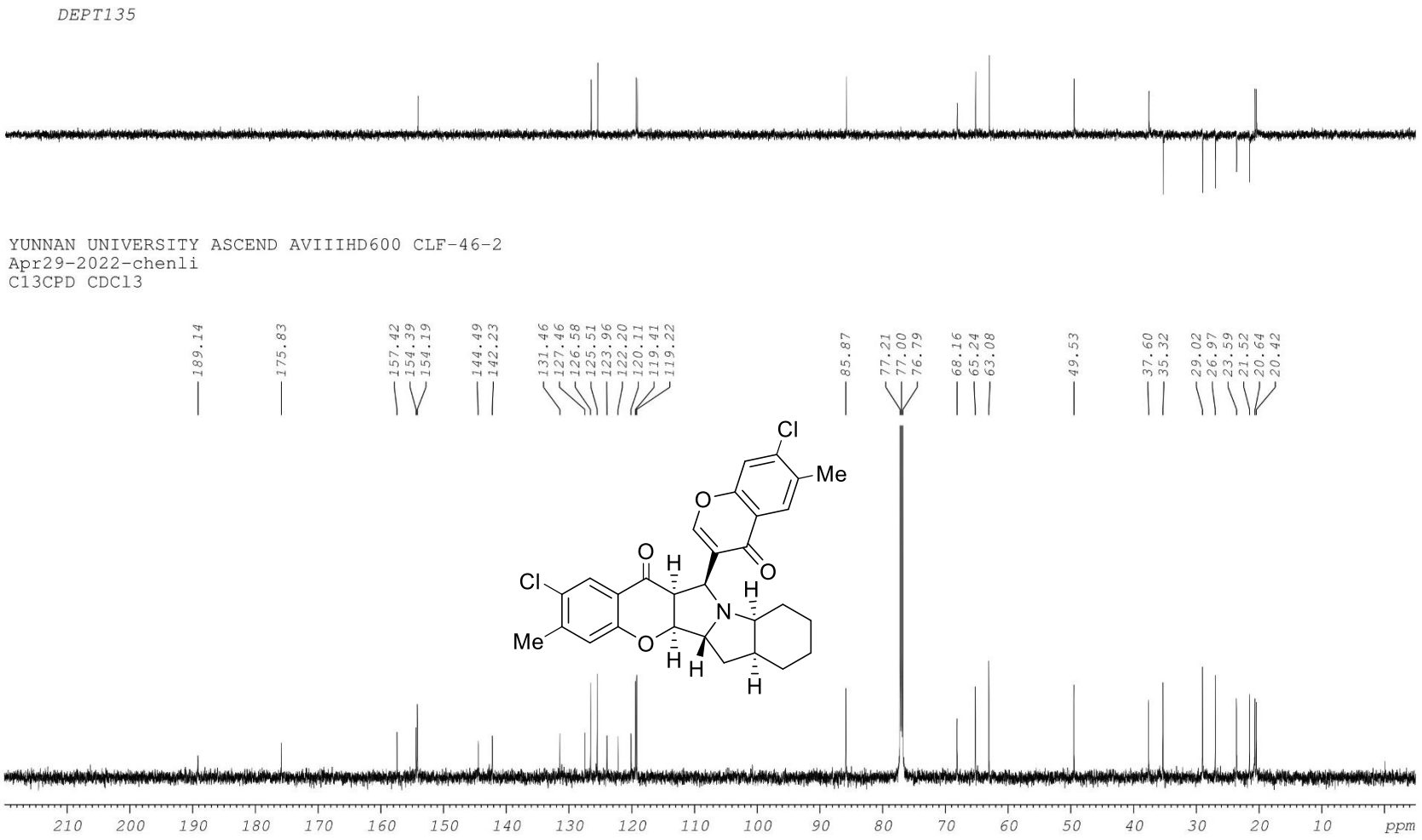



**Figure S34.** $^{13}C$ NMR (150 MHz, $CDCl_3$) spectra of compound **3l**

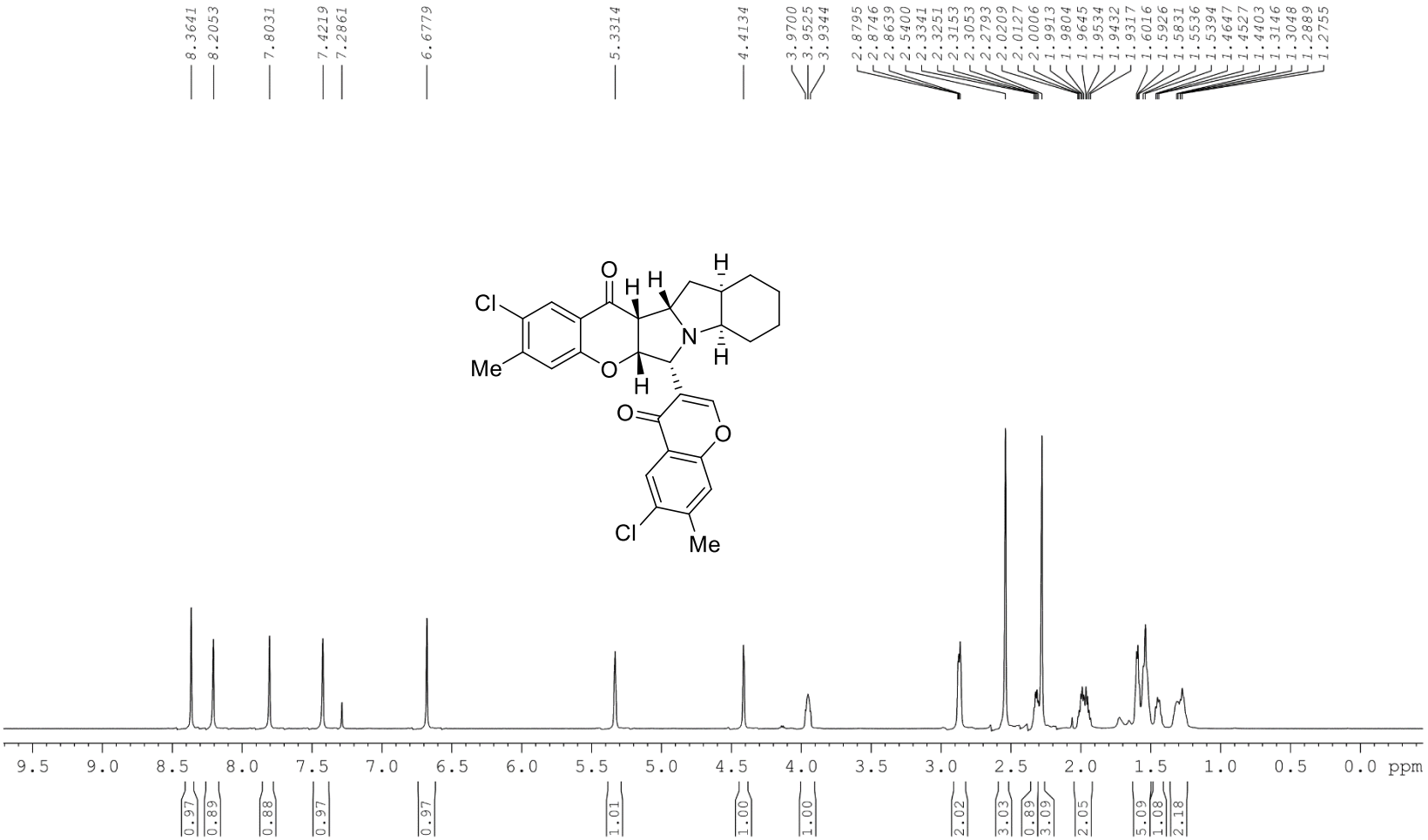



**Figure S35.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectra of compound **3l'**

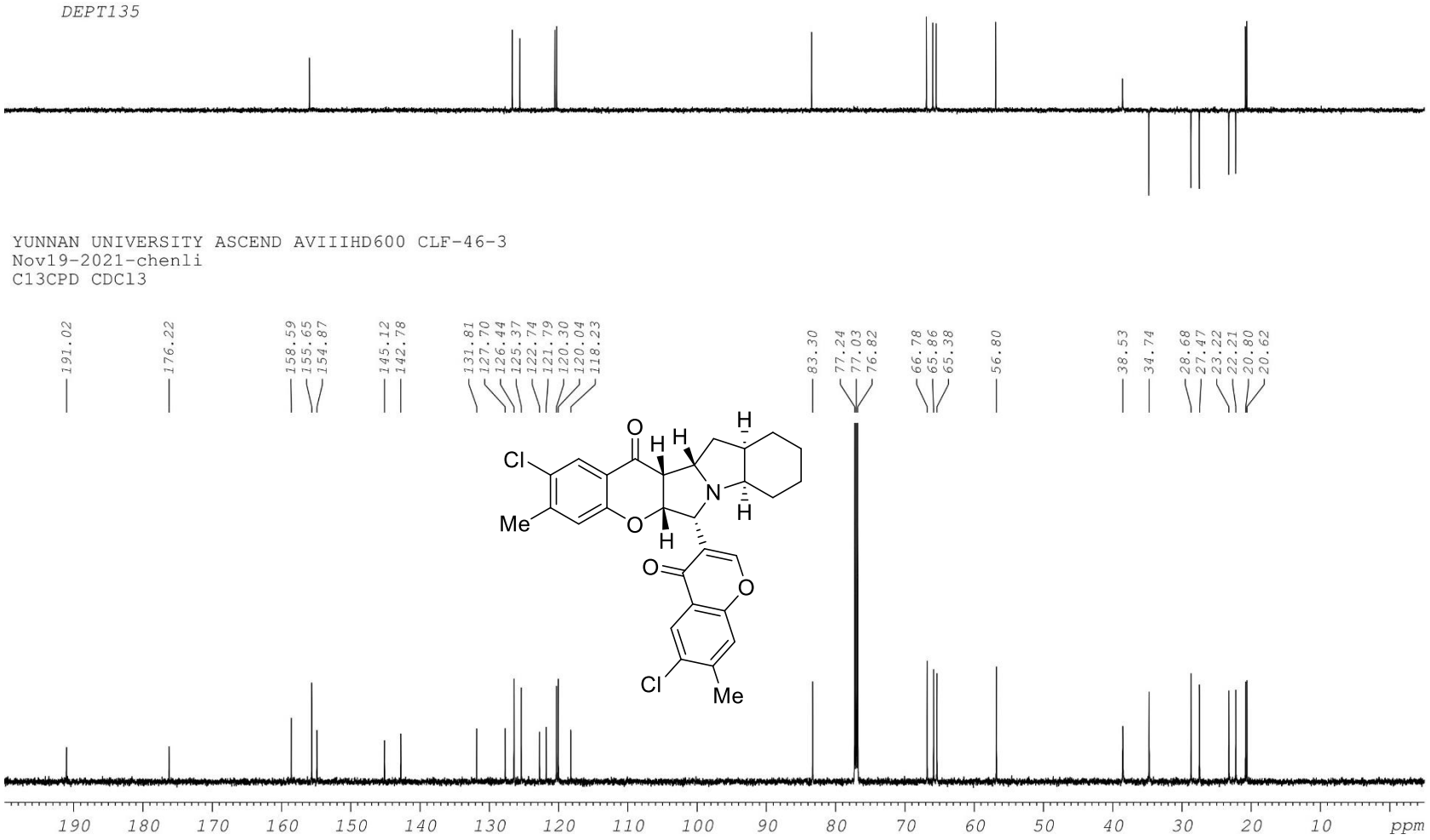



**Figure S36.** $^{13}C$ NMR (150 MHz, $CDCl_3$) spectra of compound **3l'**

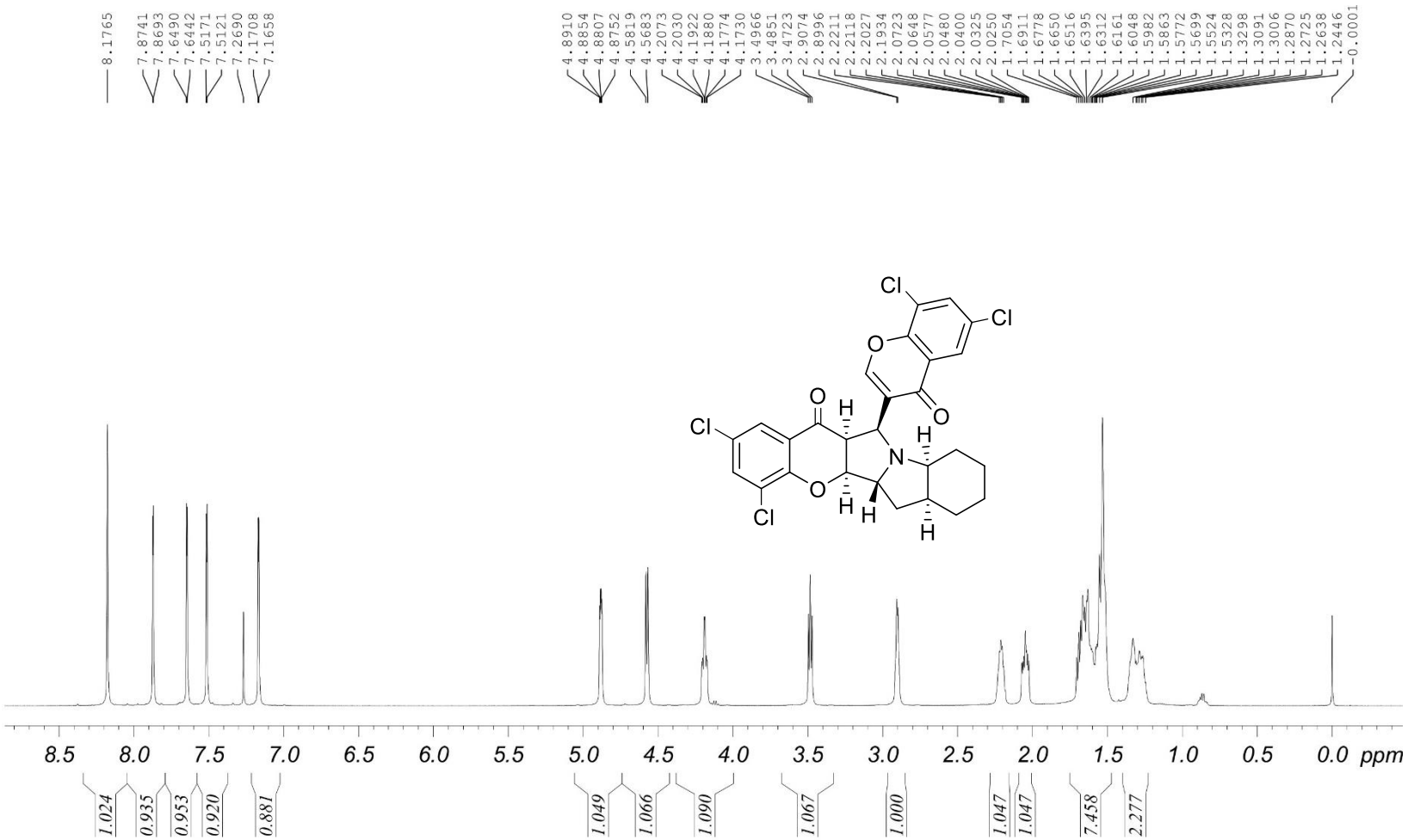



**Figure S37.** $^{1}$H NMR (500 MHz, $CDCl_3$) spectra of compound **3m**

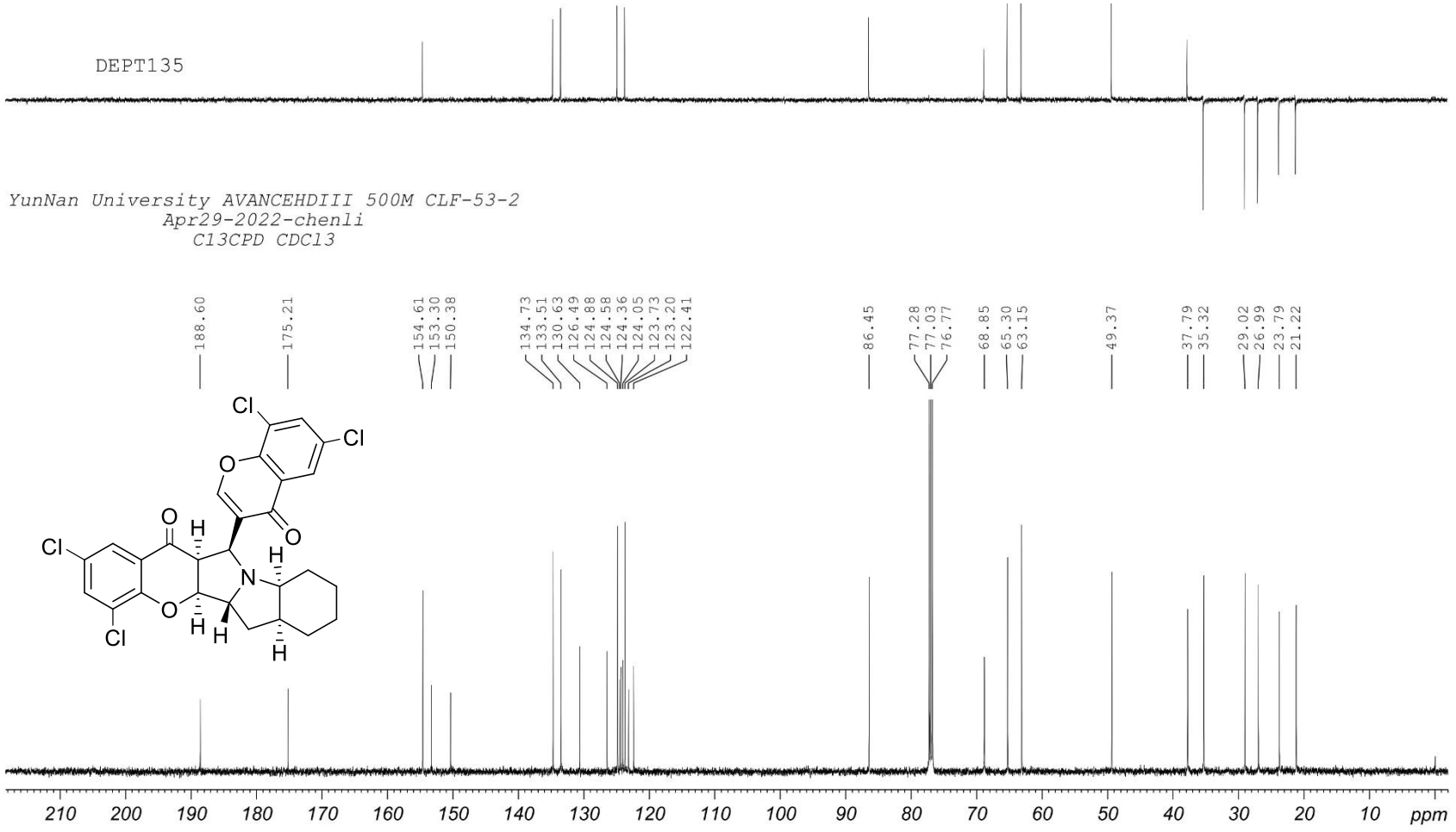



**Figure S38.** $^{13}C$ NMR (125 MHz, $CDCl_3$) spectra of compound **3m**

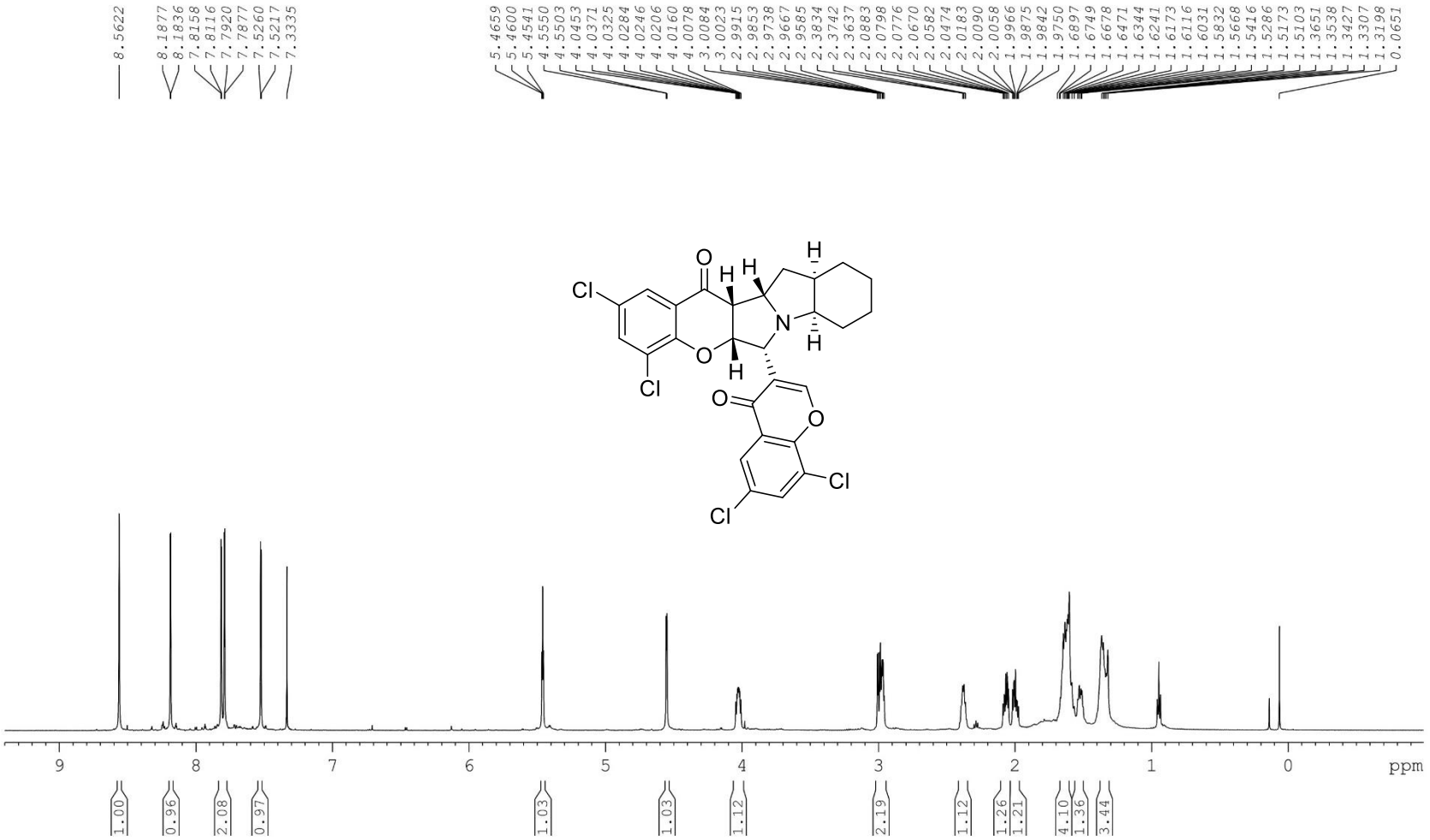



**Figure S39.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectra of compound **3m'**

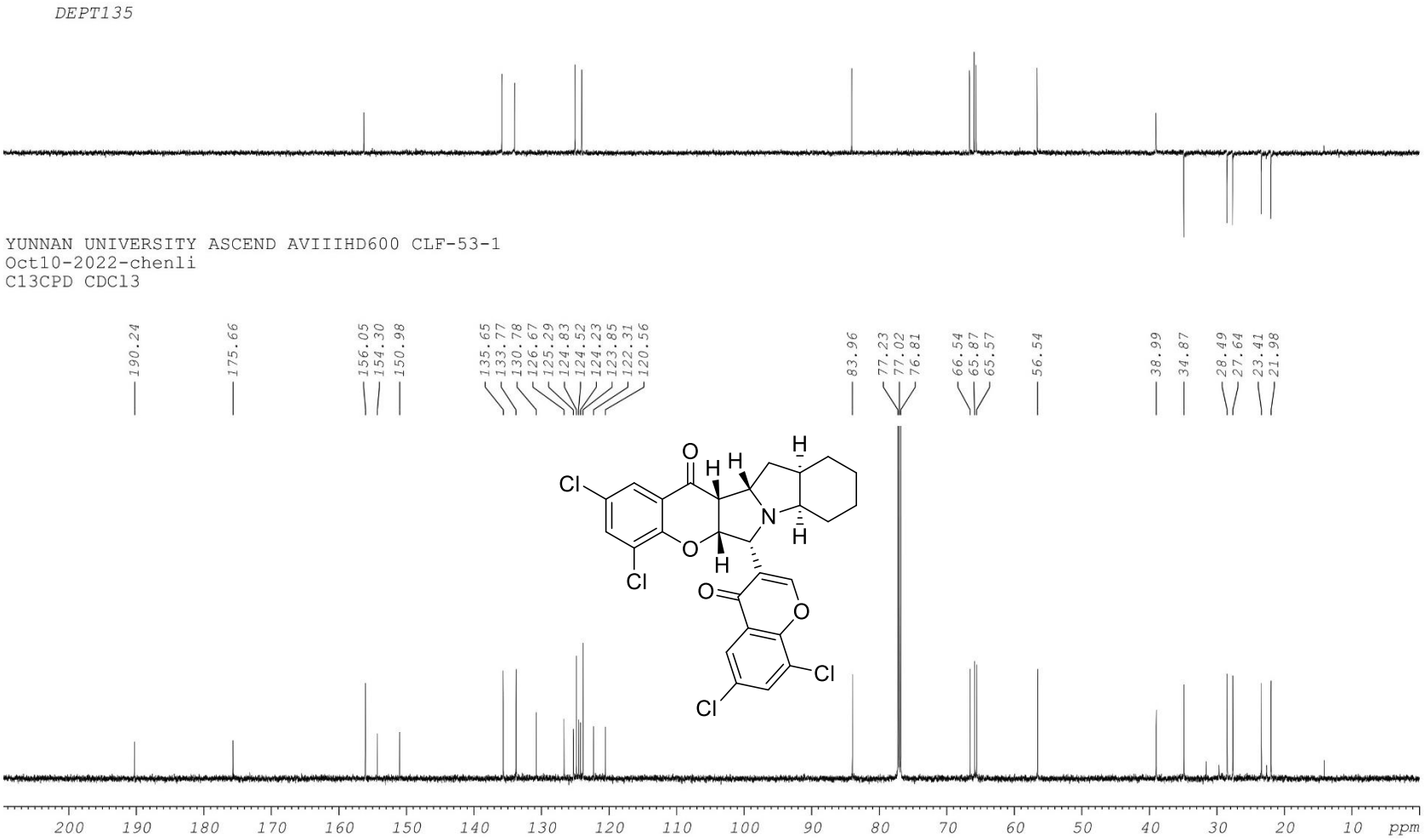



**Figure S40.** $^{13}C$ NMR (150 MHz, $CDCl_3$) spectra of compound **3m'**

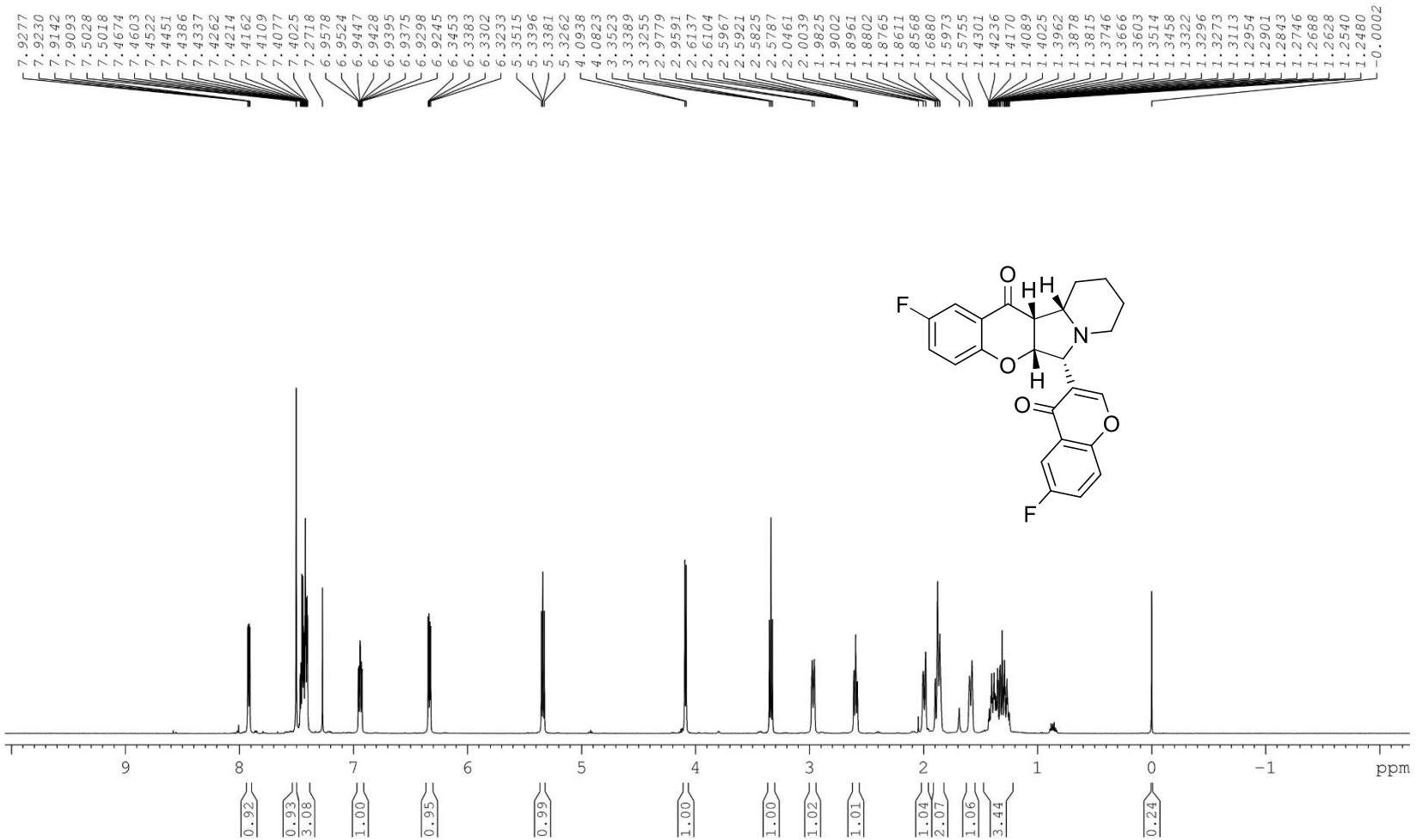



**Figure S41.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectra of compound **3n'**

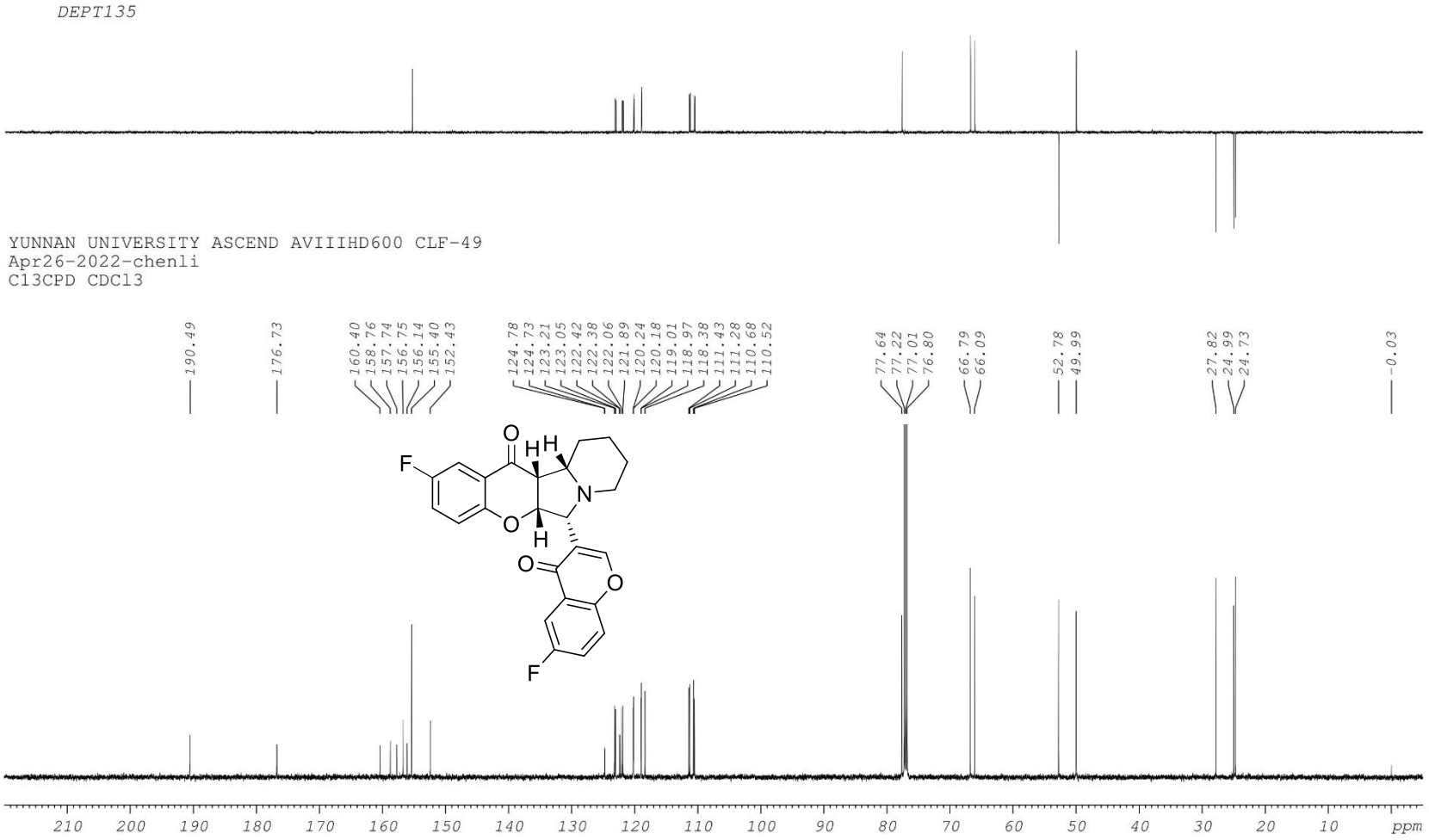



**Figure S42.** $^{13}C$ NMR (150 MHz, $CDCl_3$) spectra of compound **3n'**

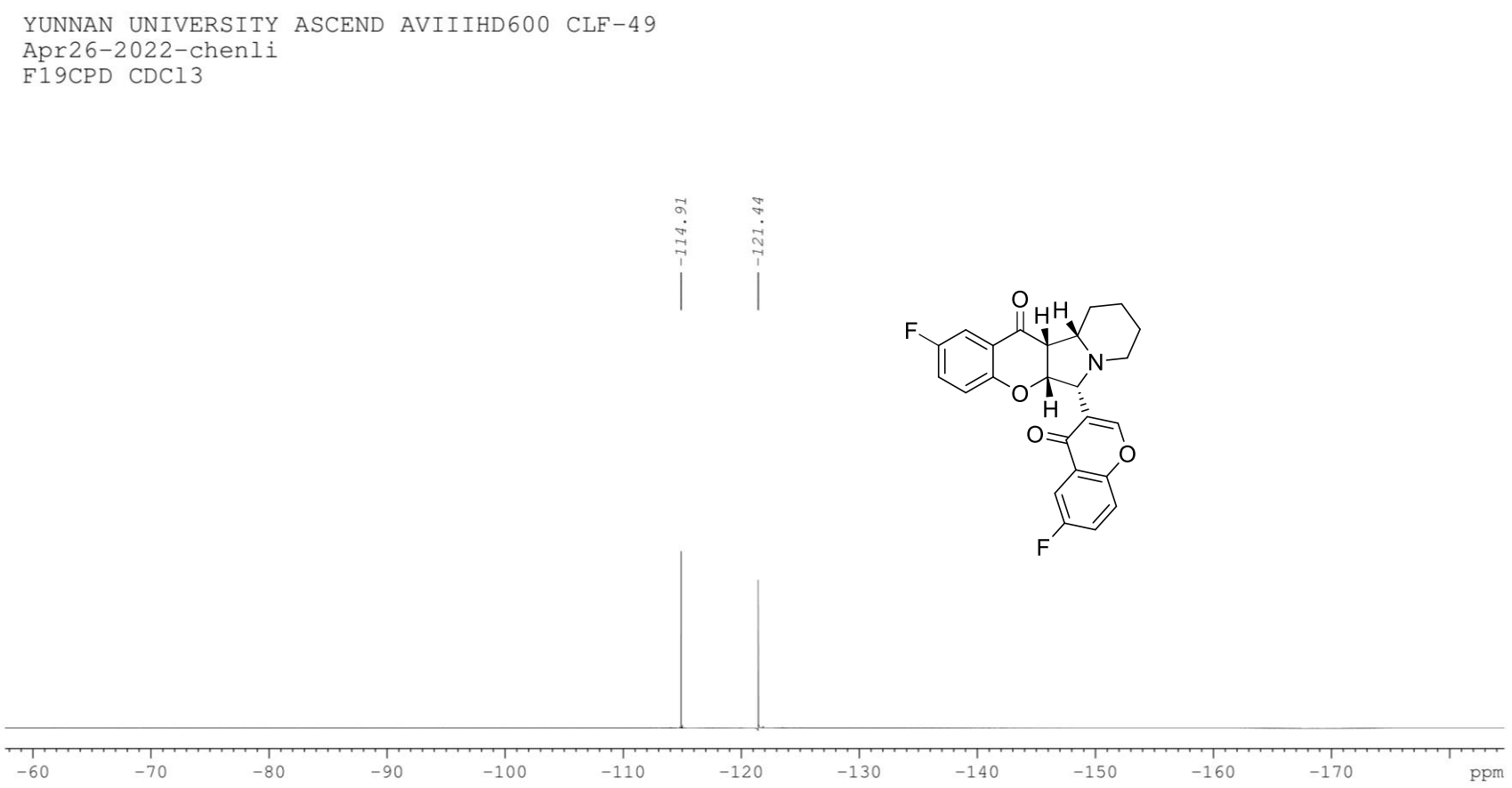



**Figure S43.** $^{19}$F NMR (564 MHz, $CDCl_3$) spectra of compound **3n'**

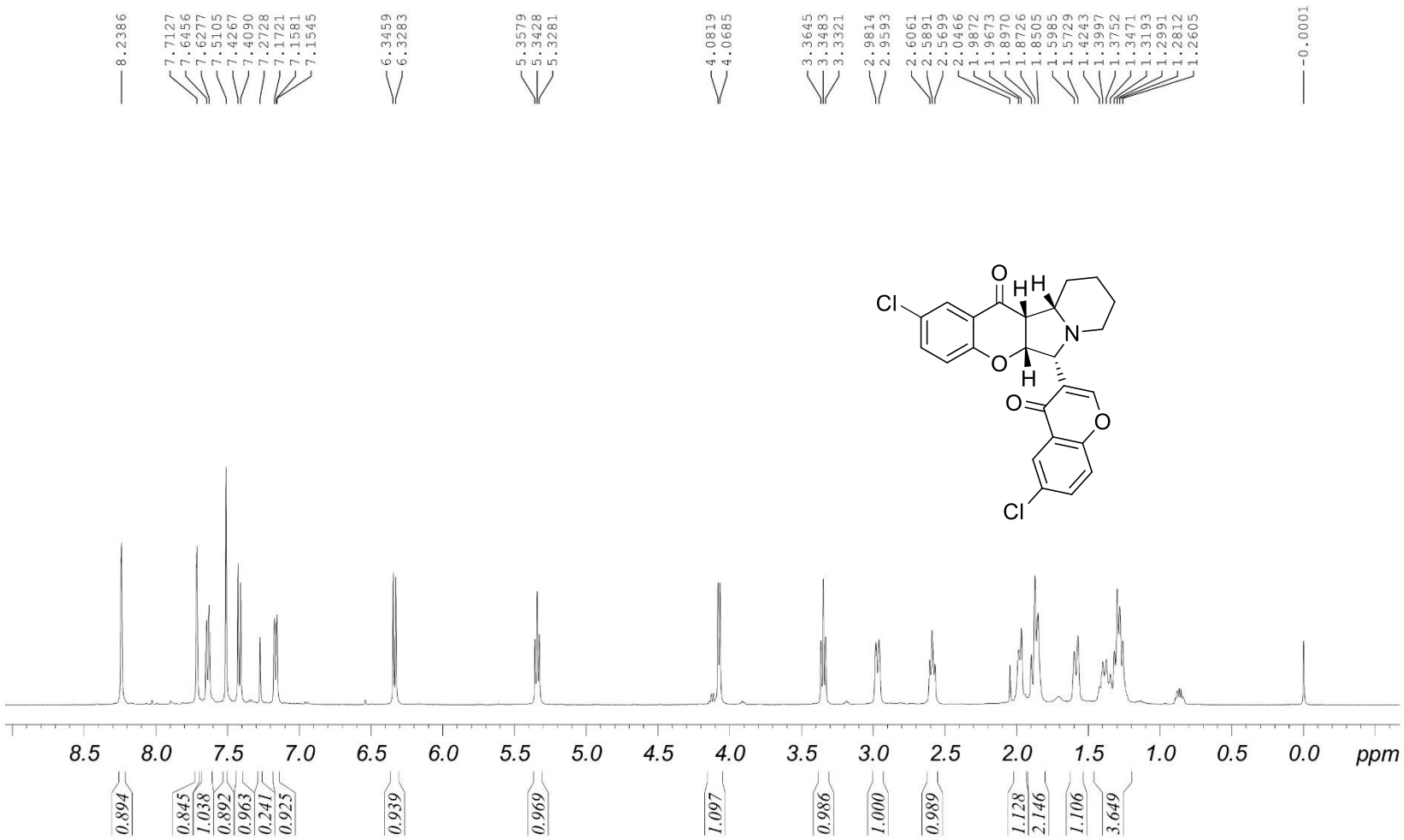



**Figure S44.** $^{1}$H NMR (500 MHz, $CDCl_3$) spectra of compound **3o'**

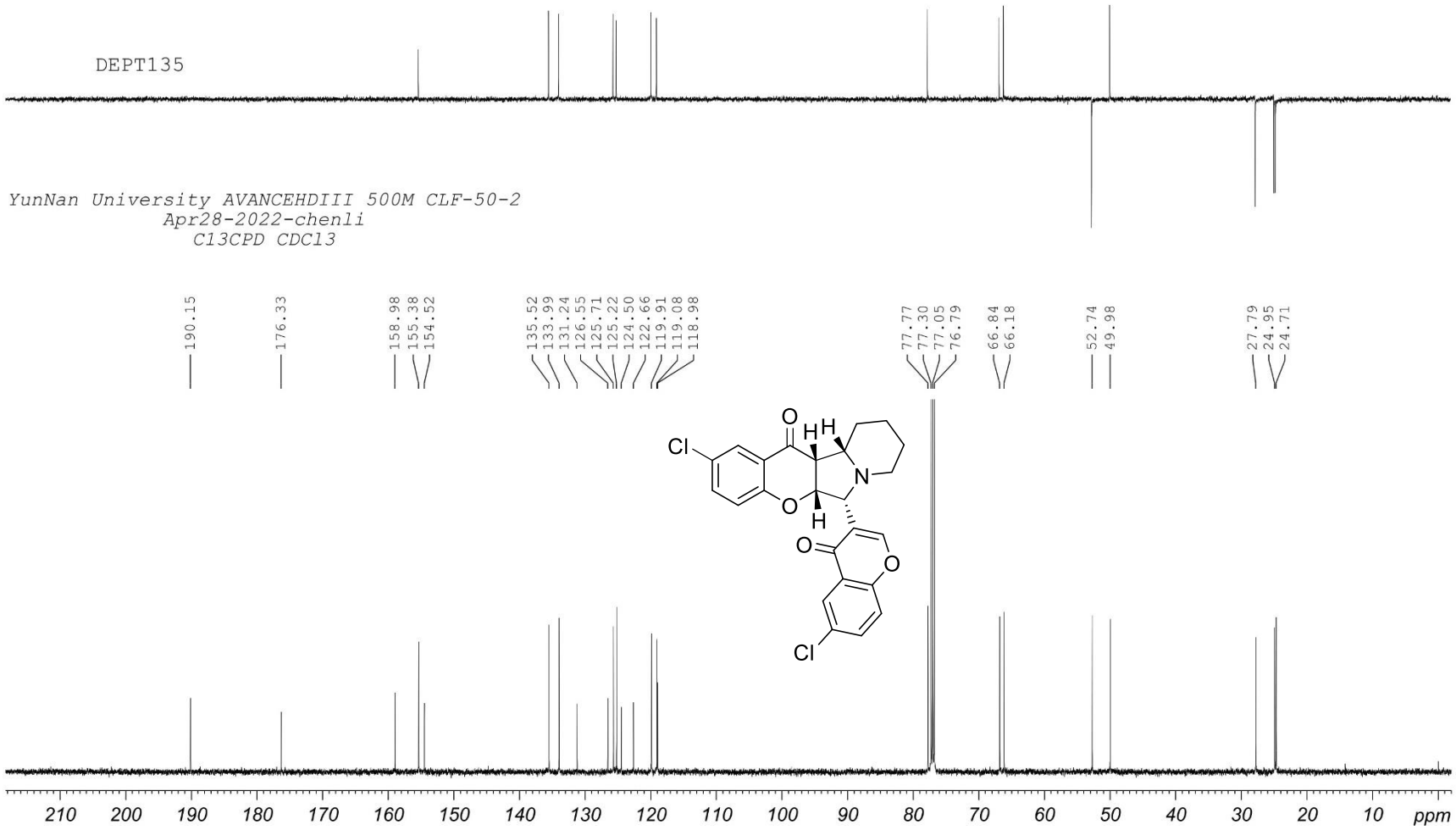



**Figure S45.** $^{13}C$ NMR (125 MHz, $CDCl_3$) spectra of compound **3o'**

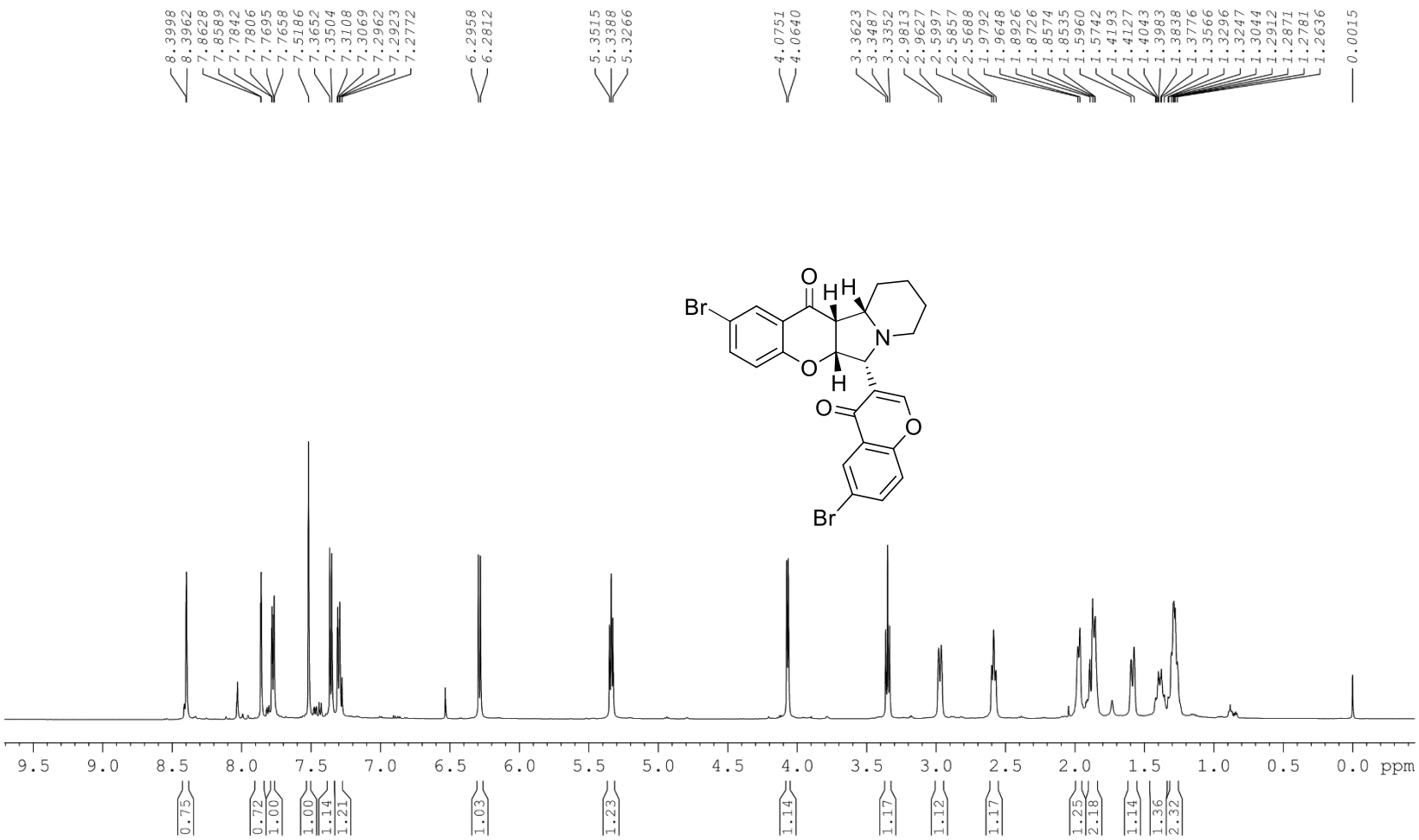



**Figure S46.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectra of compound **3p'**

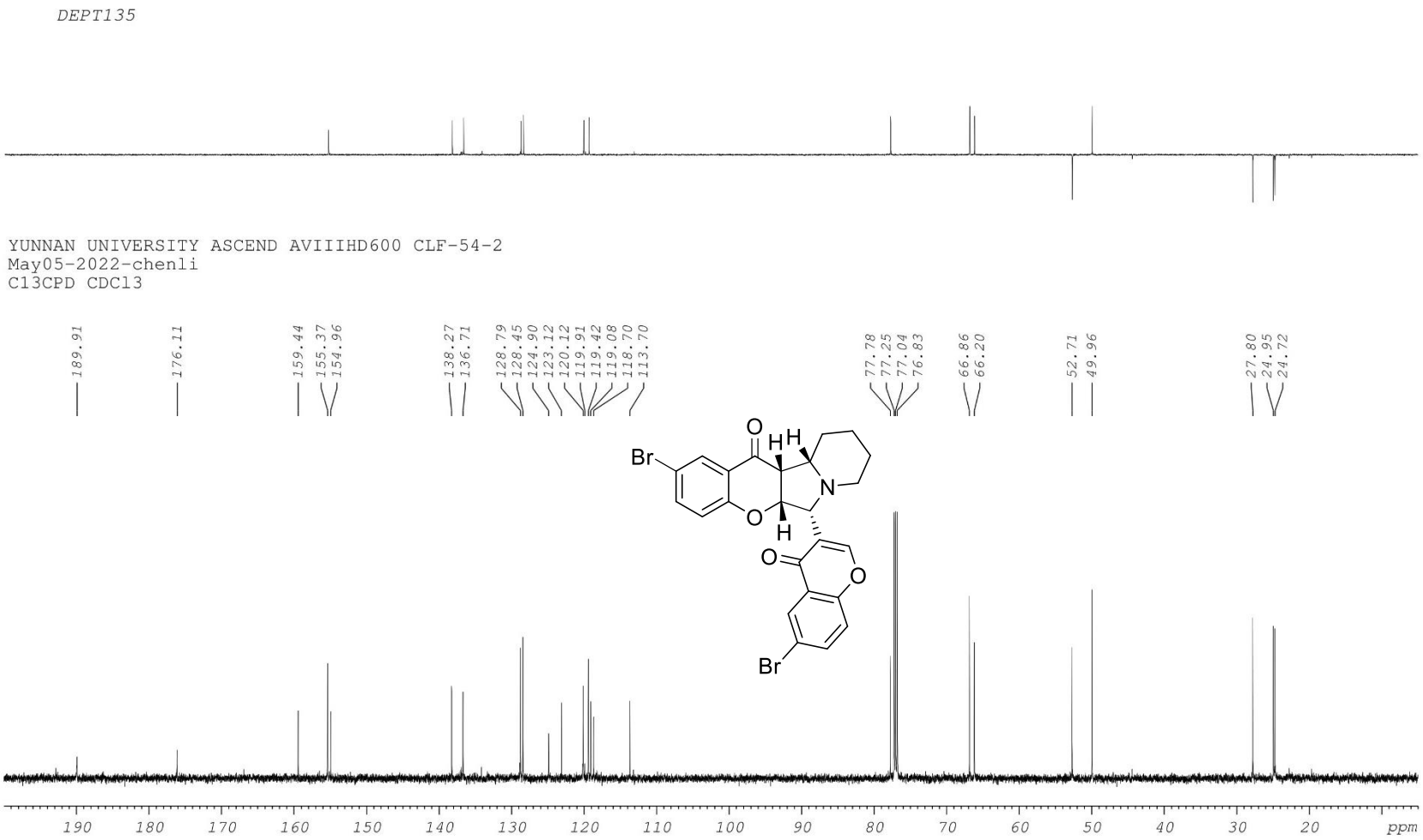



**Figure S47.** $^{13}C$ NMR (150 MHz, $CDCl_3$) spectra of compound **3p'**

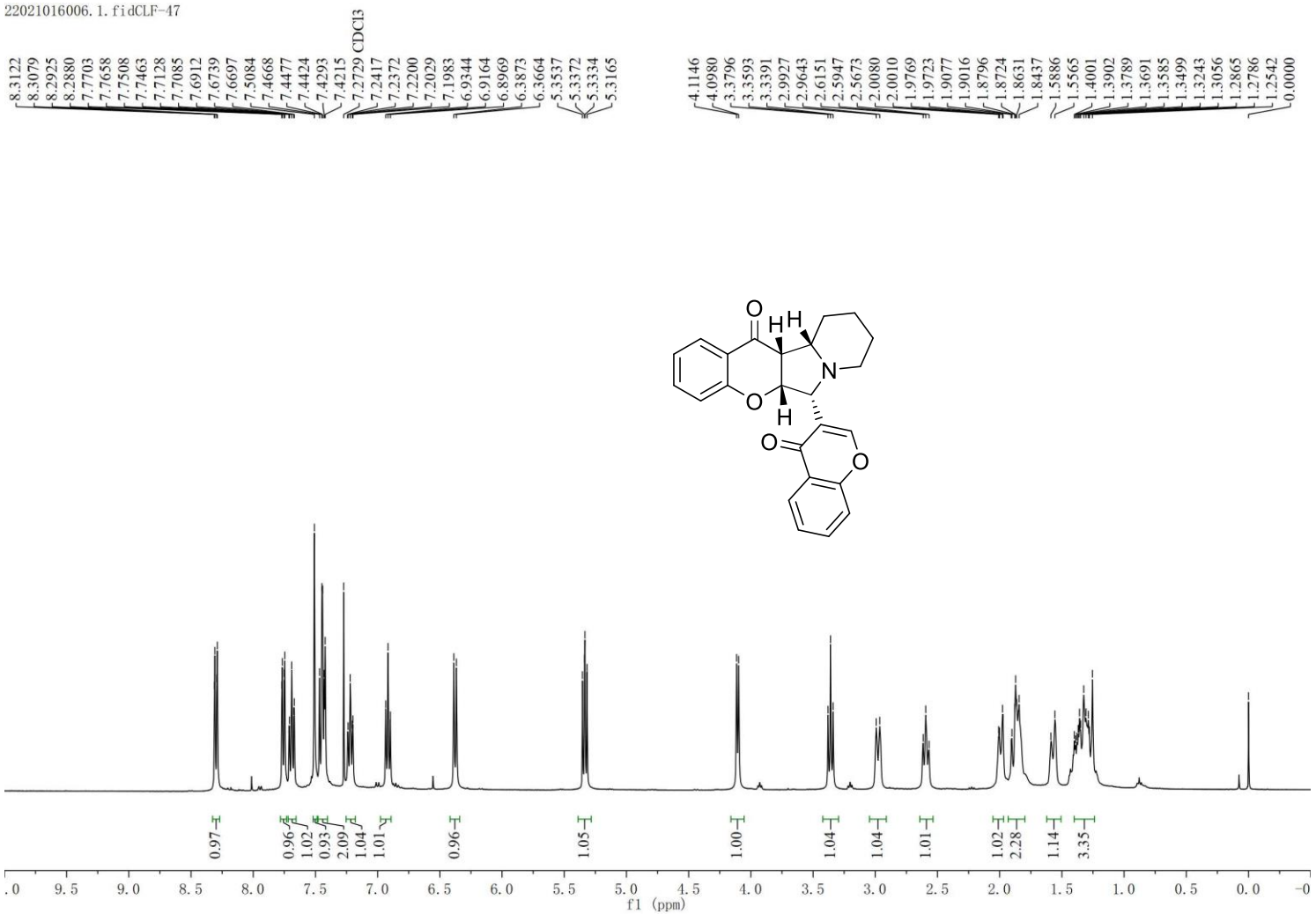



**Figure S48.** $^{1}$H NMR (400 MHz, $CDCl_3$) spectra of compound **3q'**

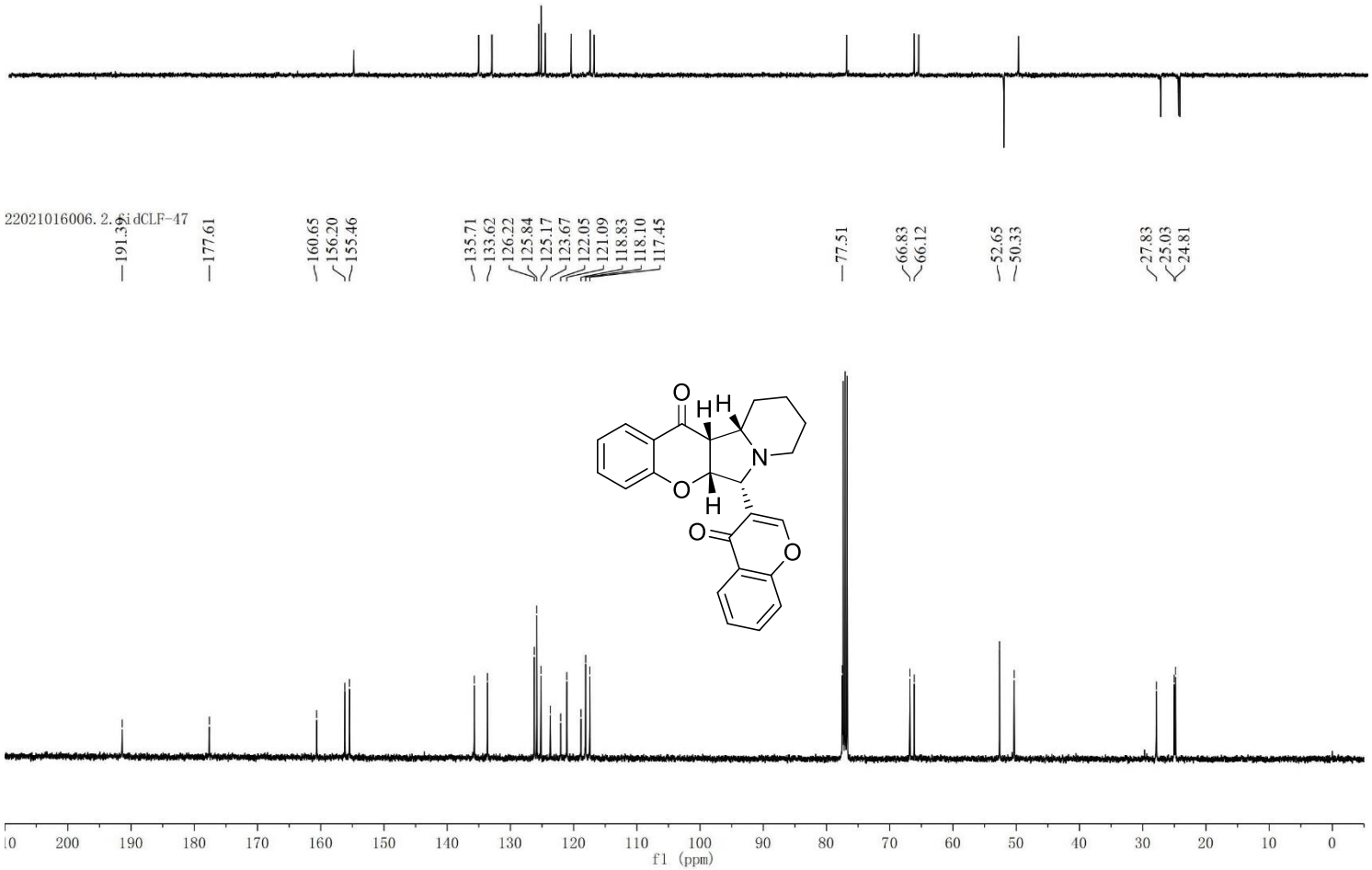



**Figure S49.** $^{13}C$ NMR (100 MHz, $CDCl_3$) spectra of compound **3q'**

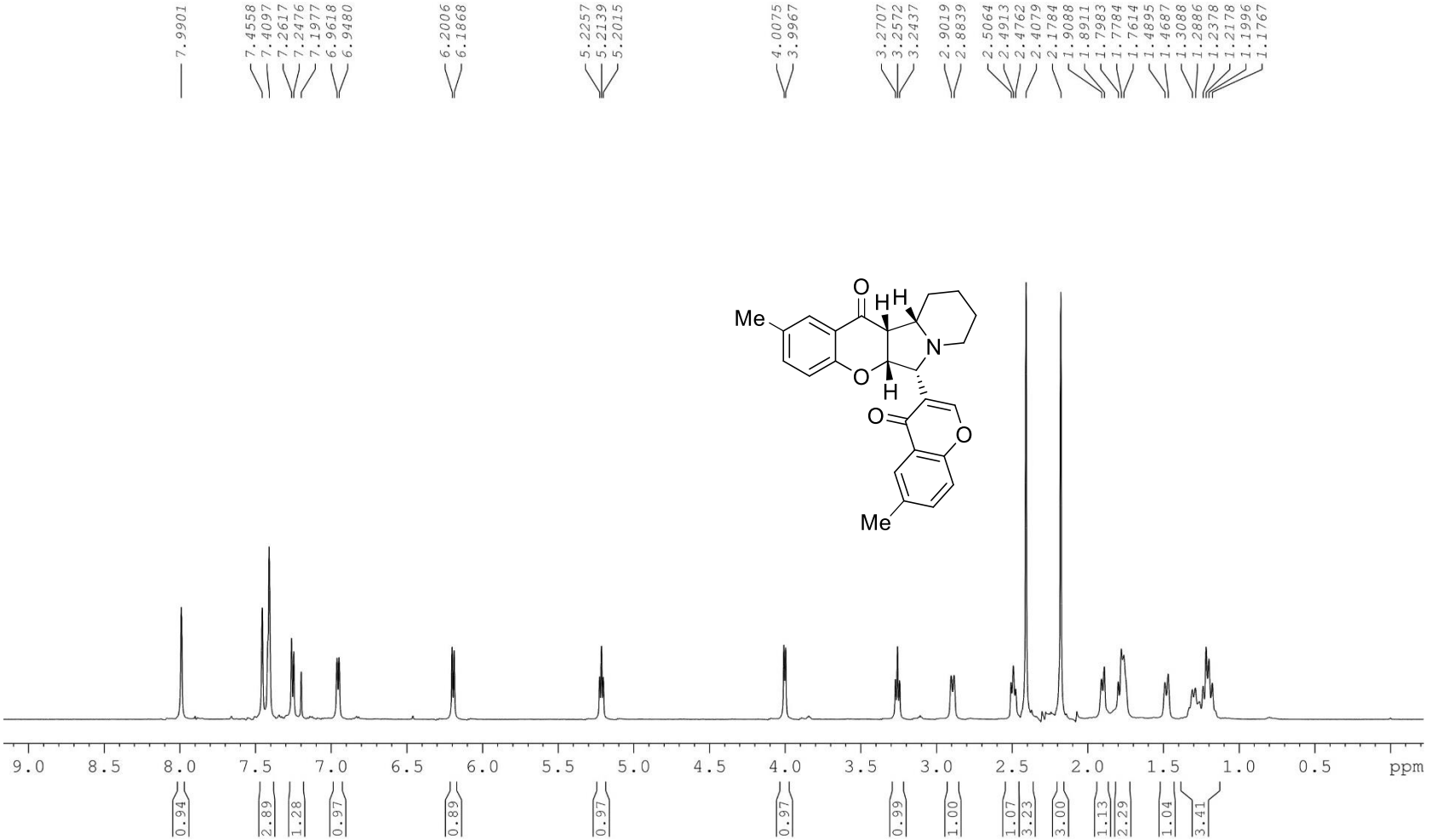



**Figure S50.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectra of compound **3r'**

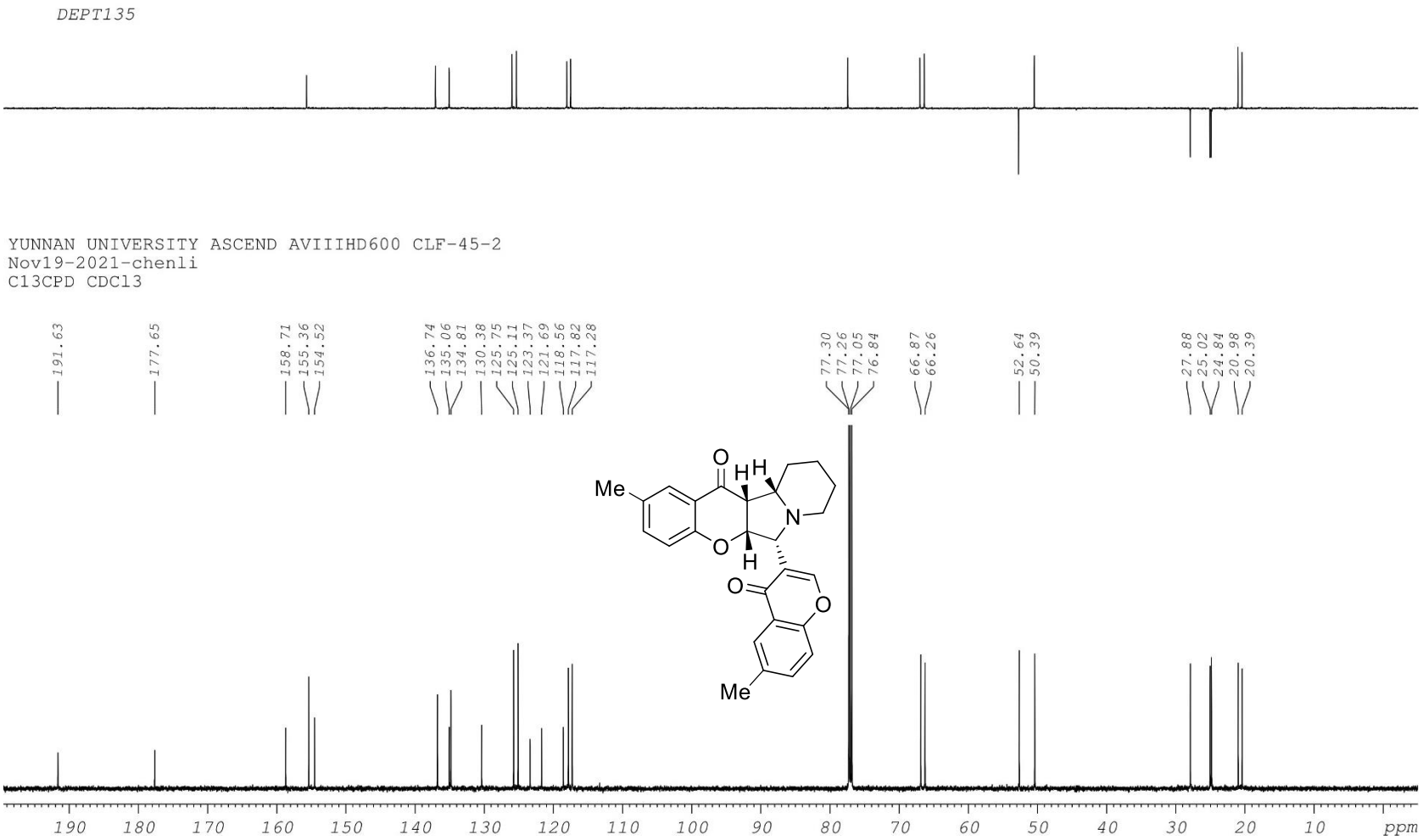



**Figure S51.** $^{13}C$ NMR (150 MHz, $CDCl_3$) spectra of compound **3r'**

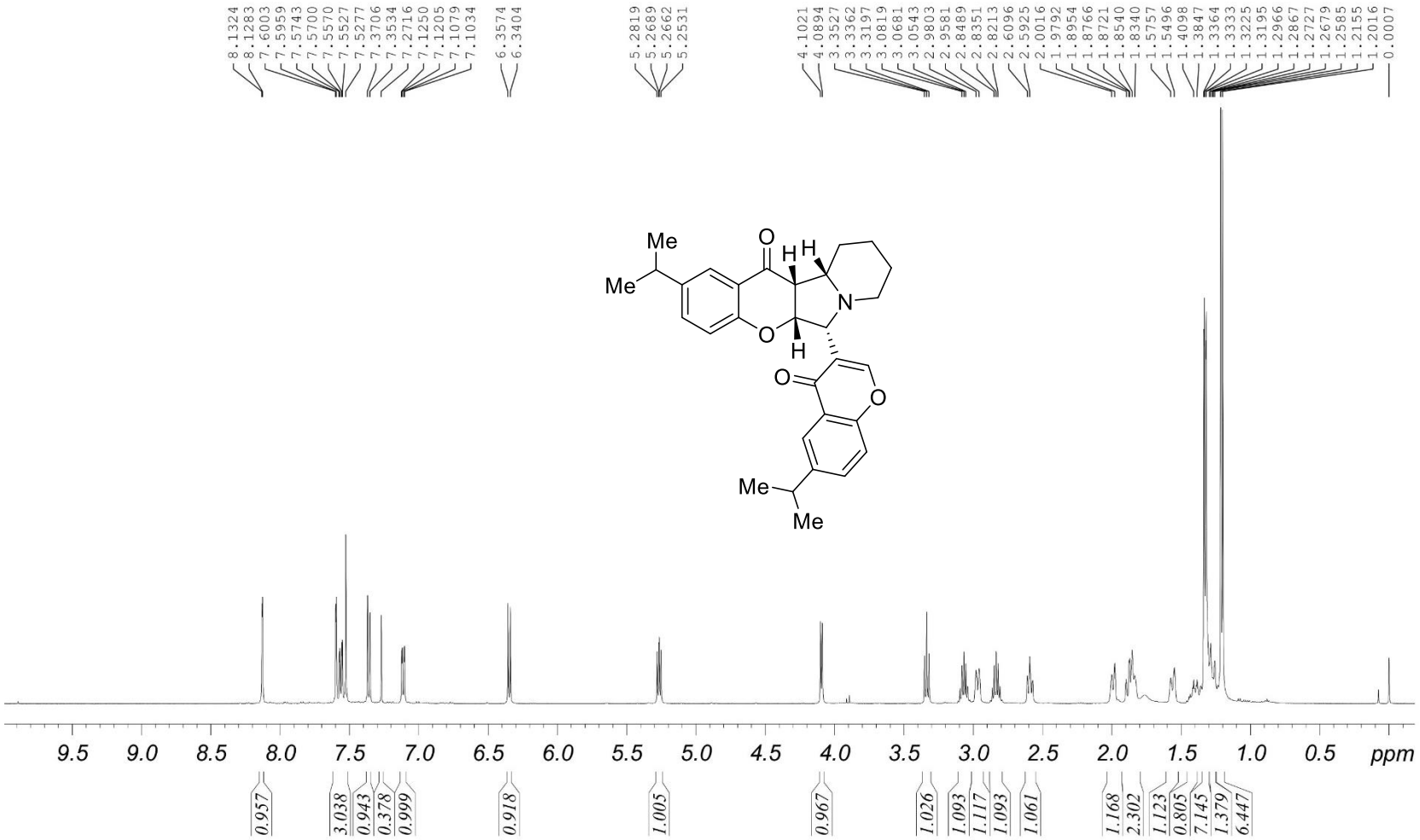



**Figure S52.** $^{1}$H NMR (500 MHz, $CDCl_3$) spectra of compound **3s'**

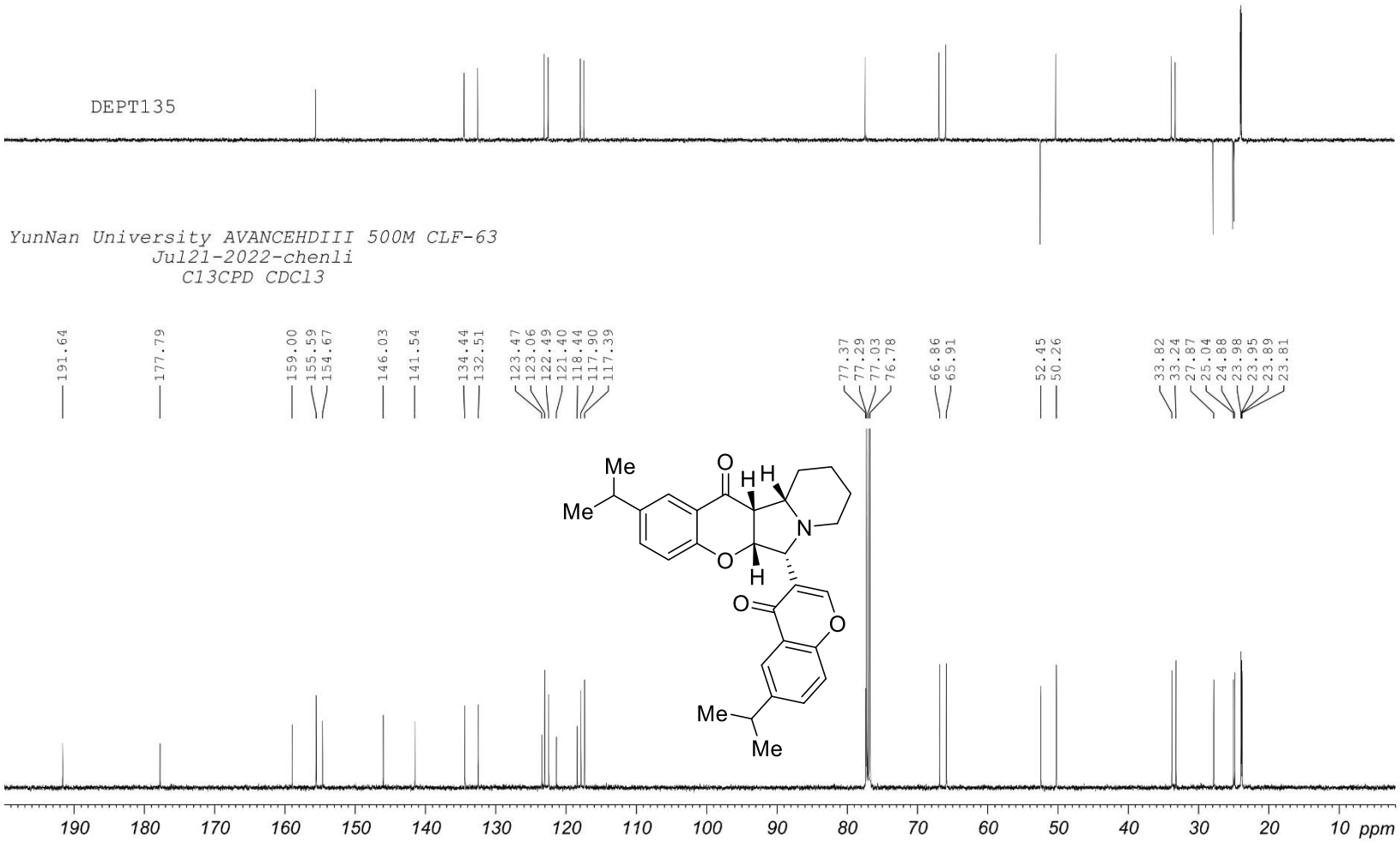



**Figure S53.** $^{13}C$ NMR (125 MHz, $CDCl_3$) spectra of compound **3s'**

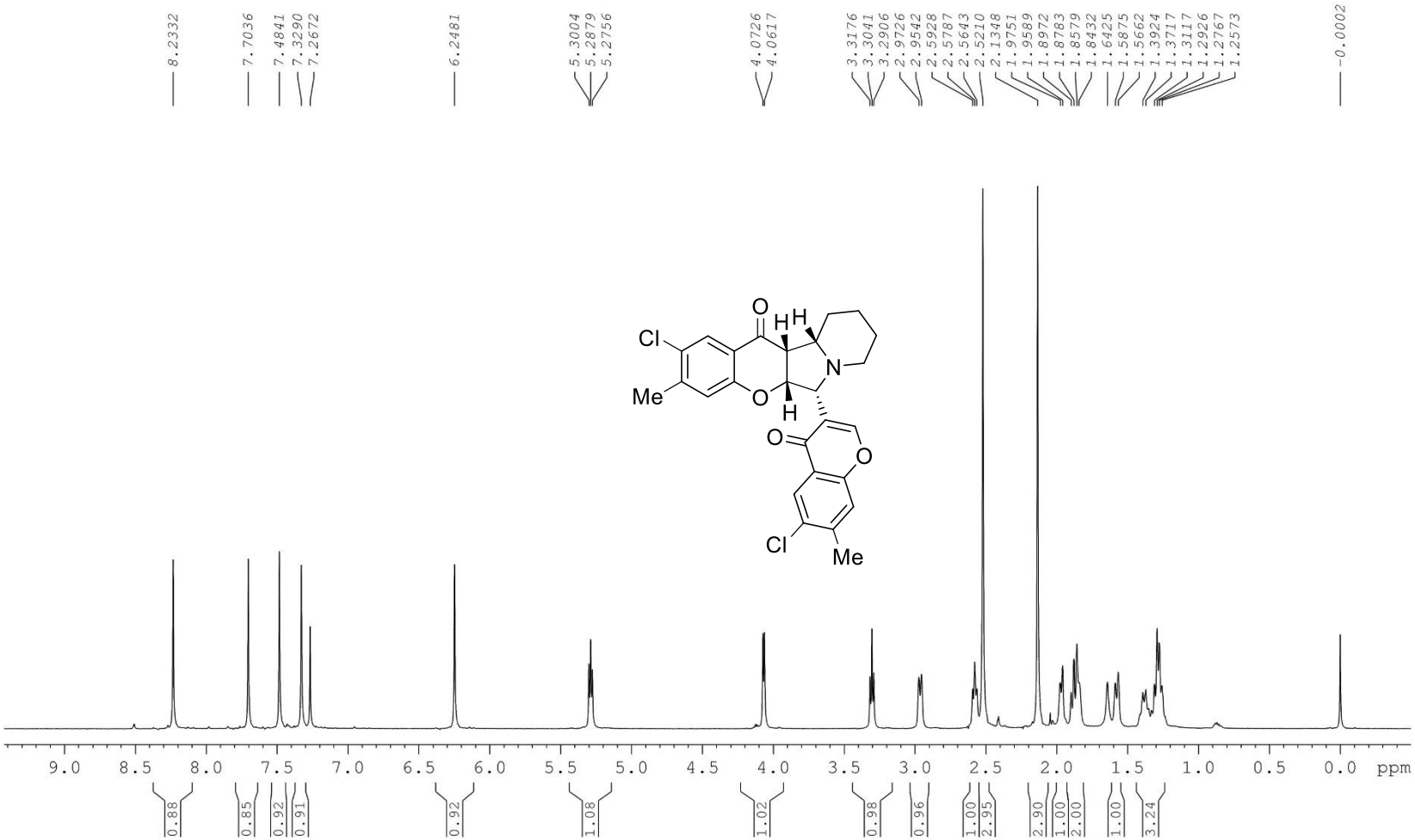



**Figure S54.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectra of compound **3t'**

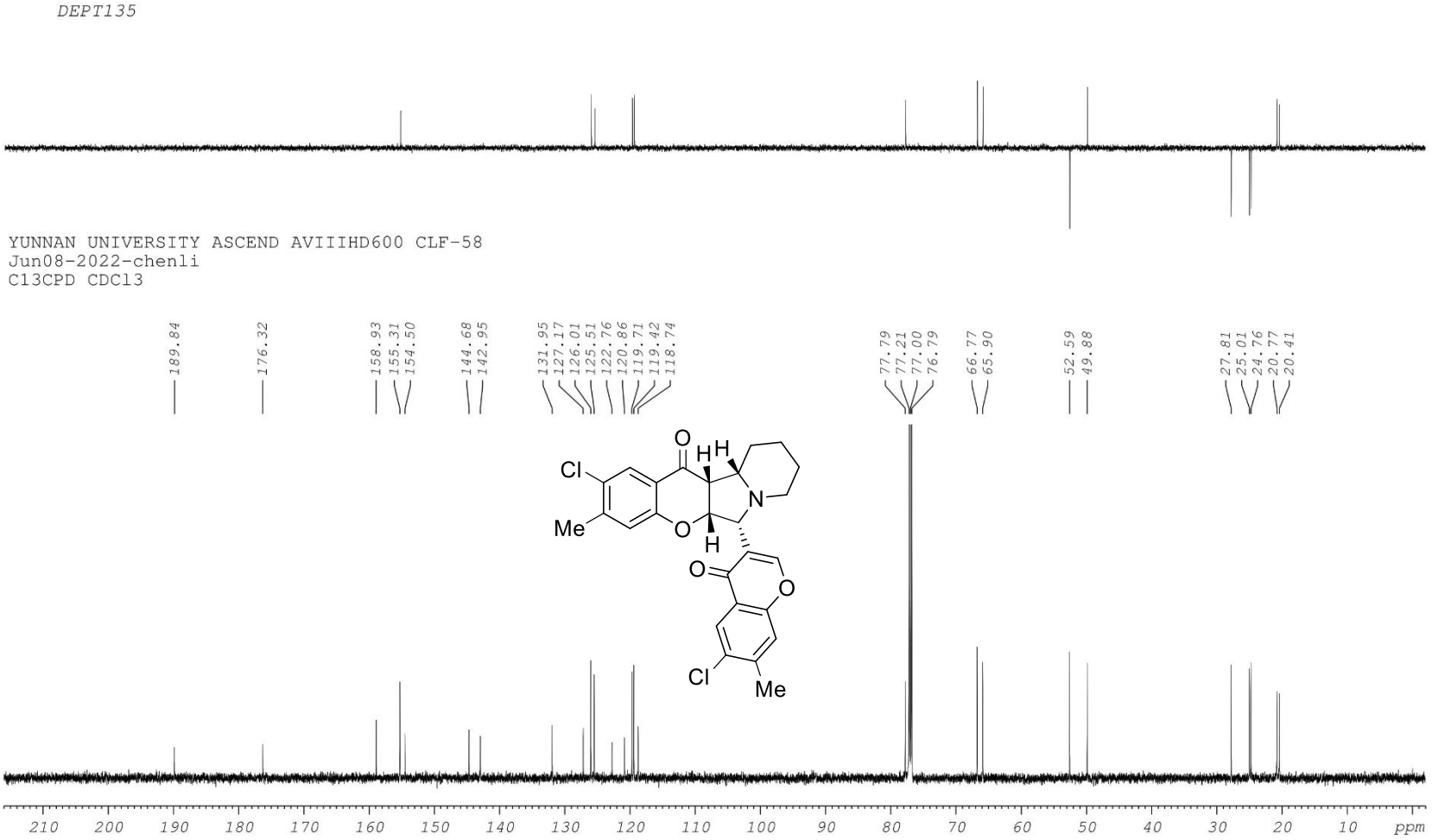



**Figure S55.** $^{13}C$ NMR (150 MHz, $CDCl_3$) spectra of compound **3t'**

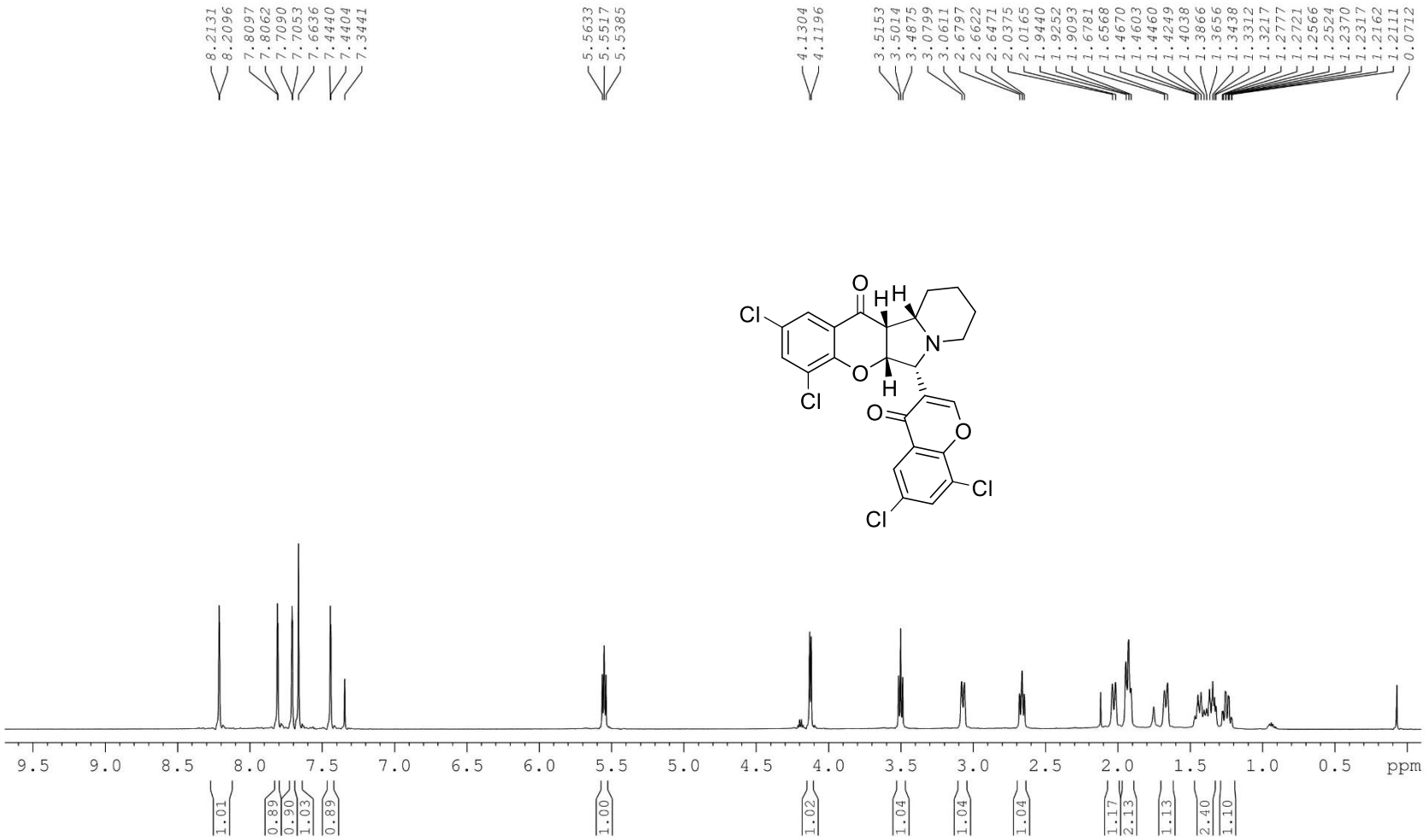



**Figure S56.** $^{1}$H NMR (600 MHz, $CDCl_3$) spectra of compound **3u'**

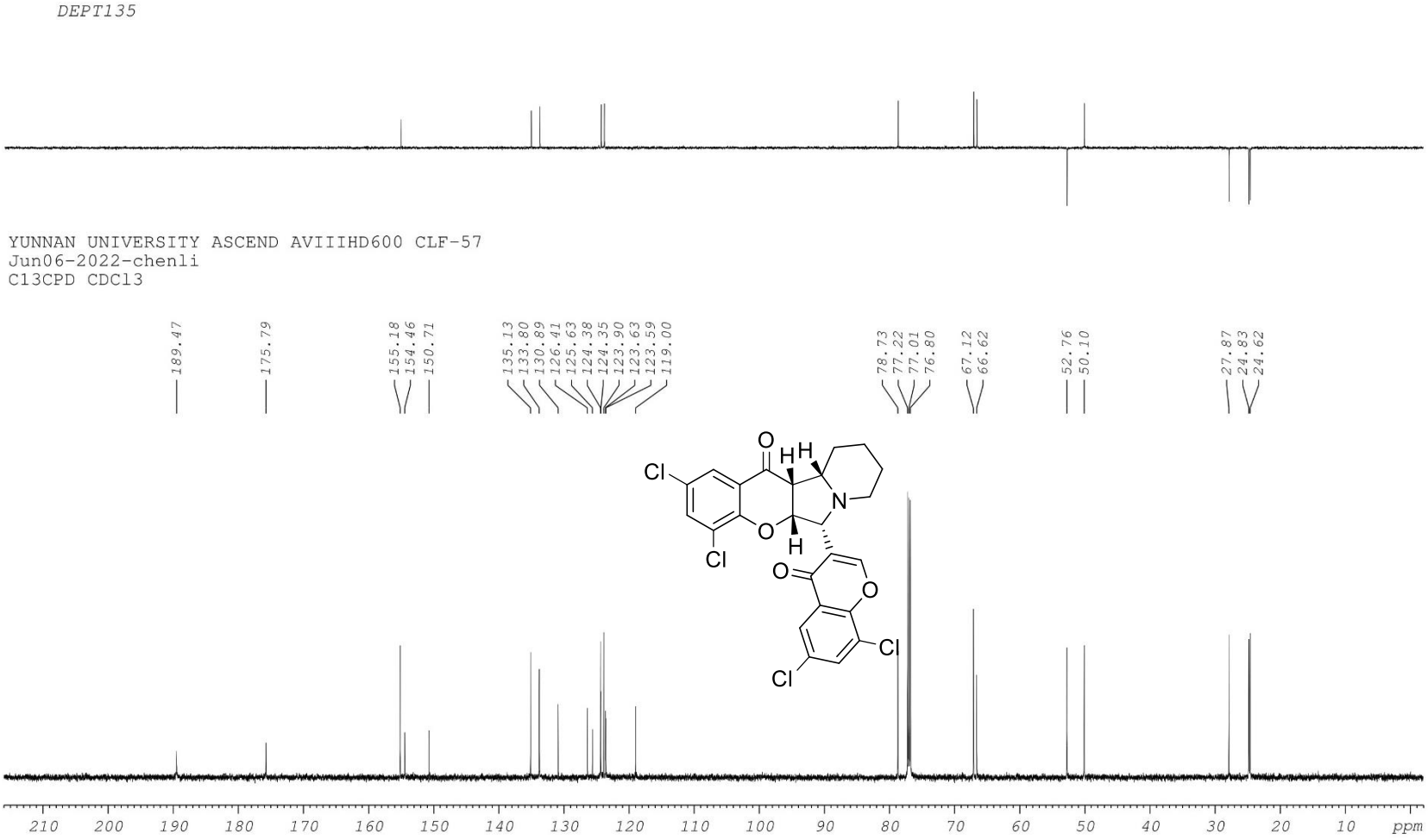



**Figure S57.** $^{13}C$ NMR (150 MHz, $CDCl_3$) spectra of compound **3u'**

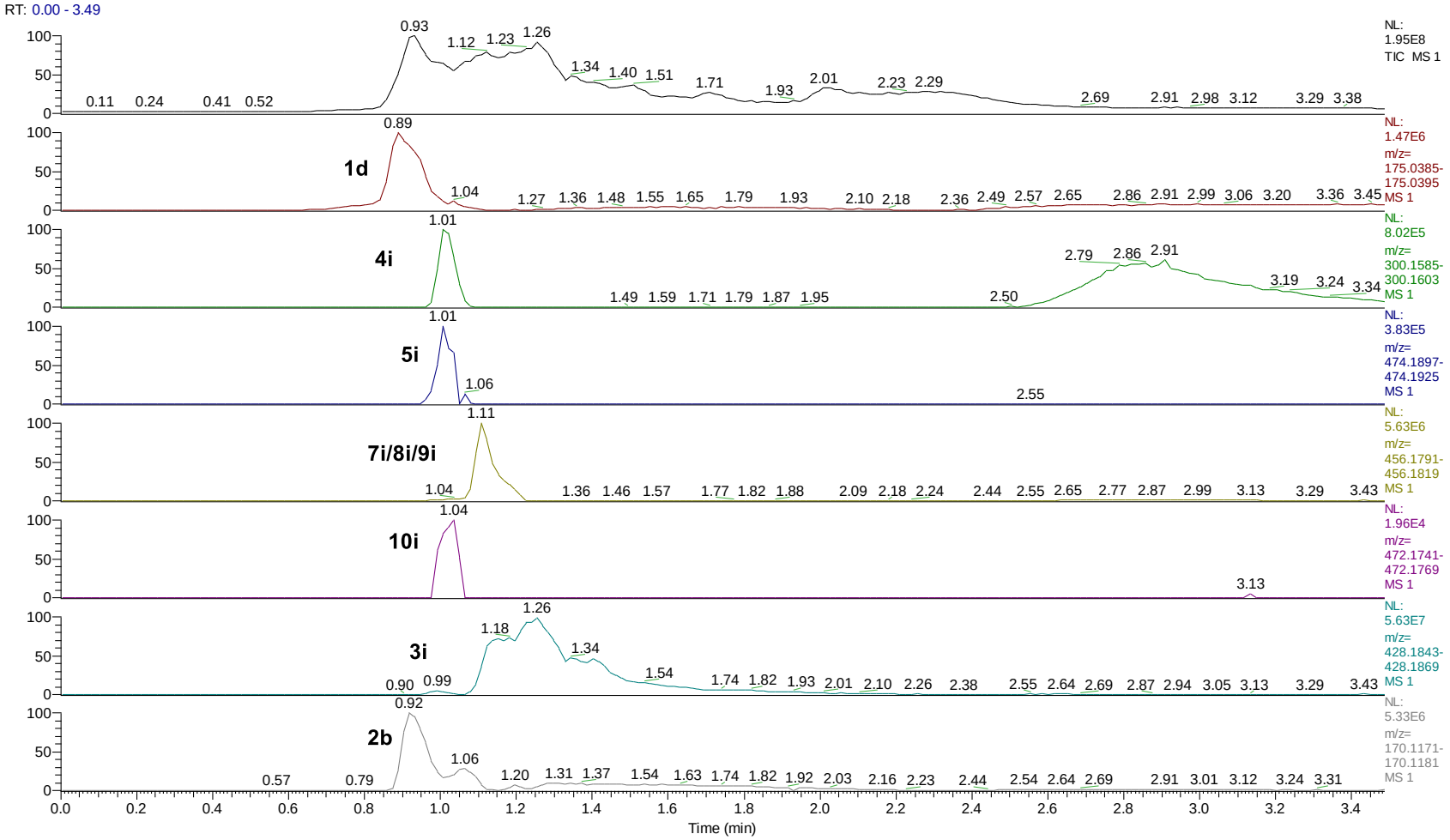



**Figure S58.** HPLC of the reaction mixture

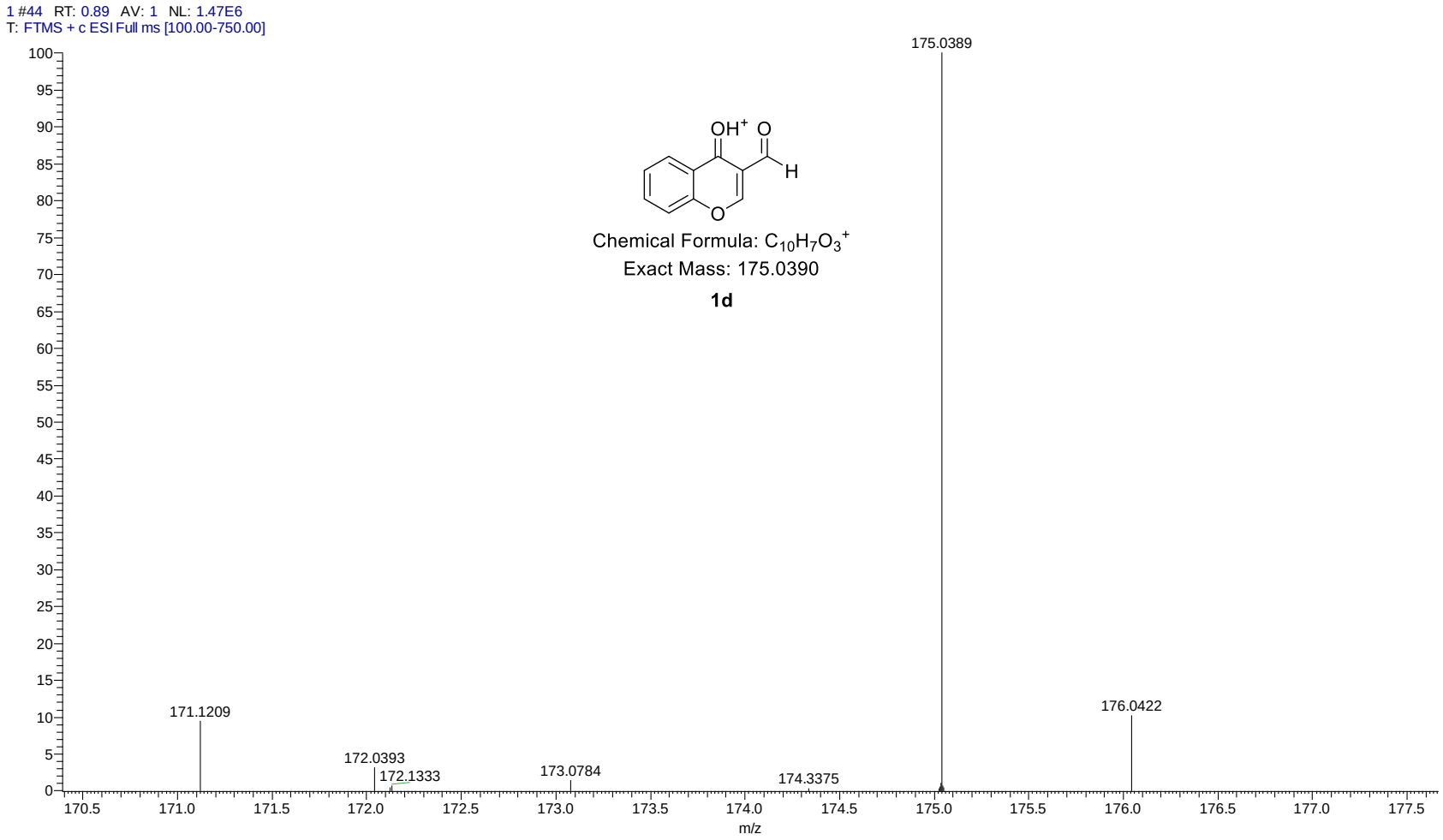



**Figure S59.** HRMS of intermediate **1d**

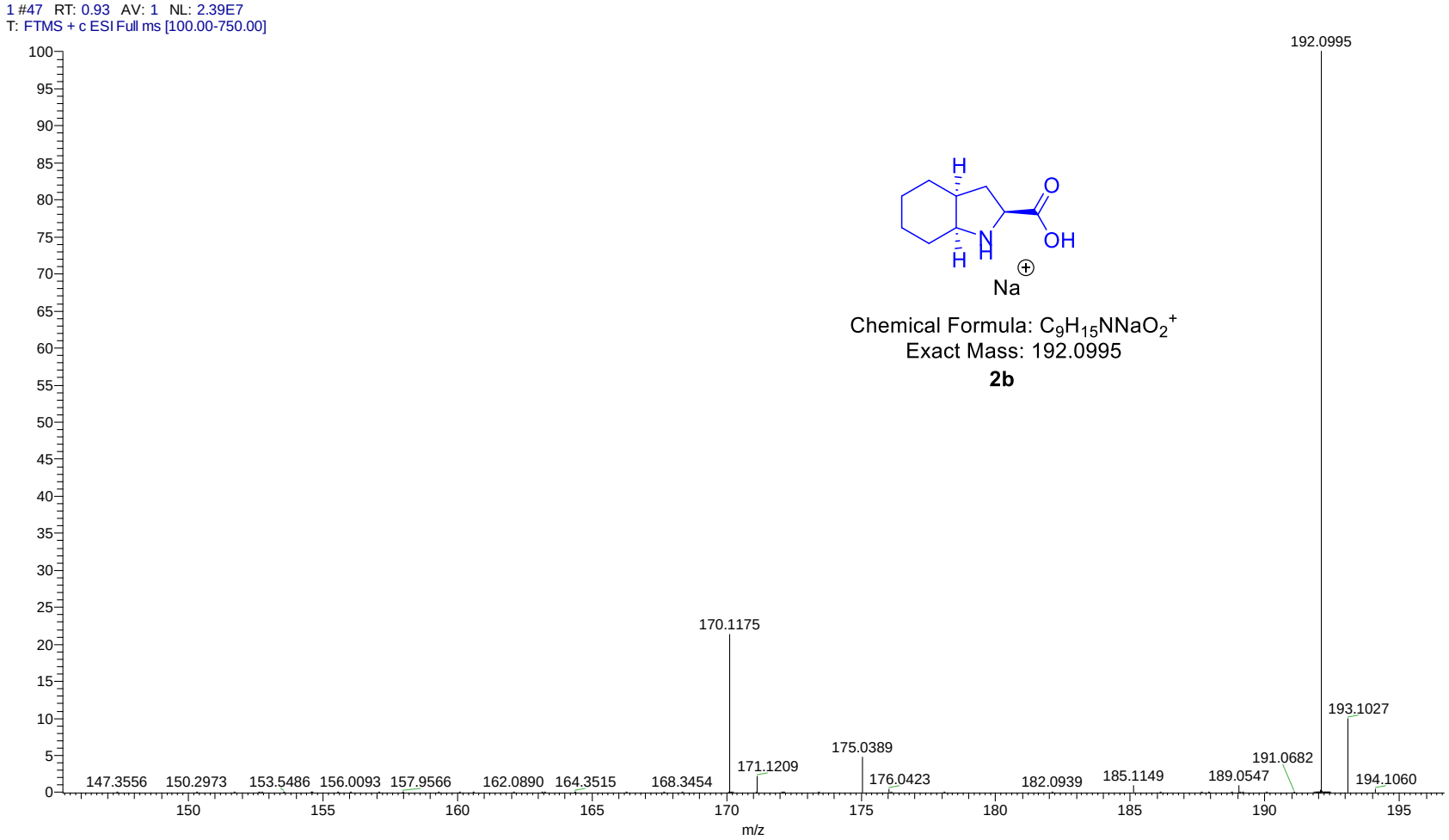



**Figure S60.** HRMS of intermediate **2b**

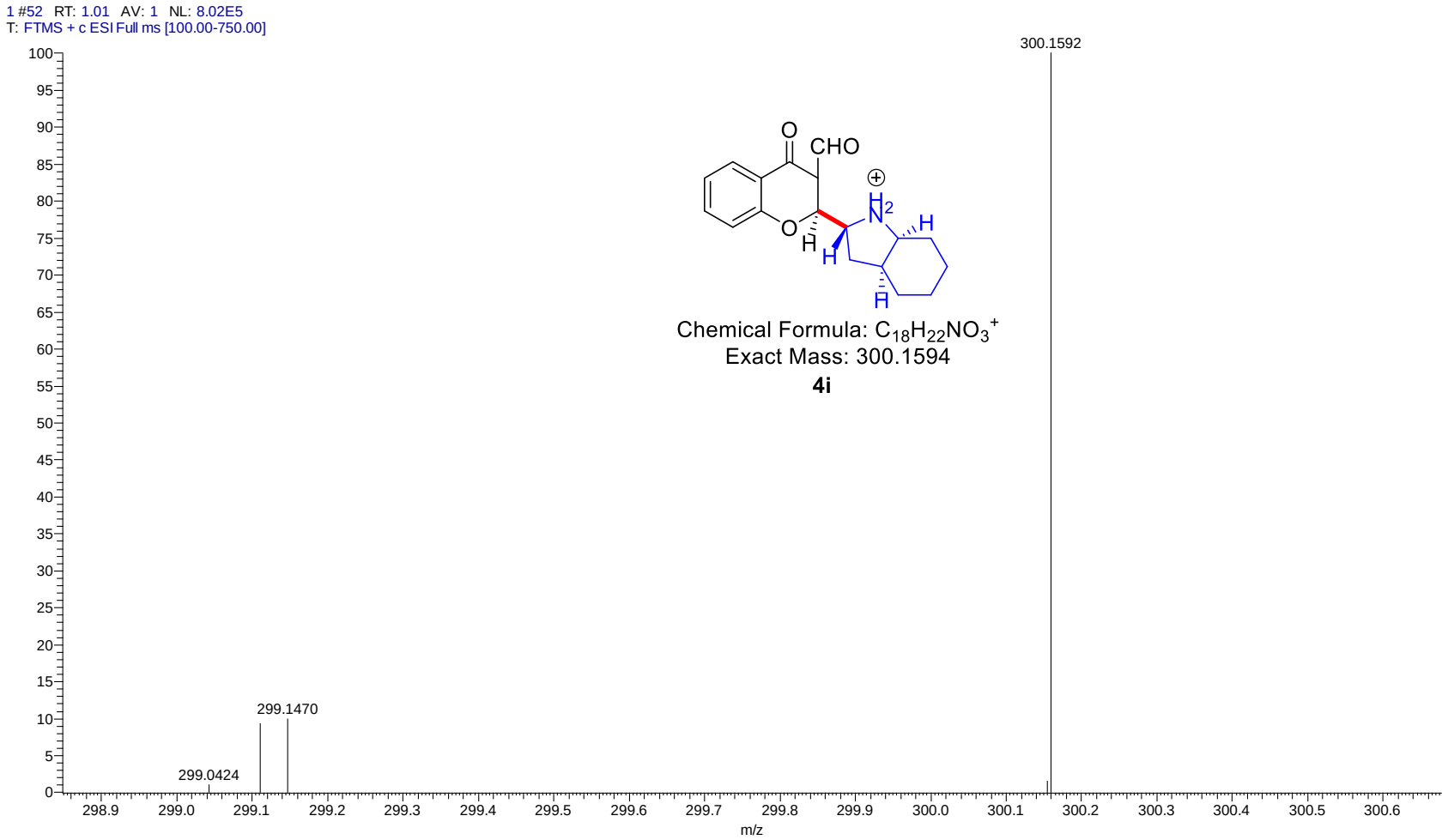



**Figure S61.** HRMS of intermediate **4i**

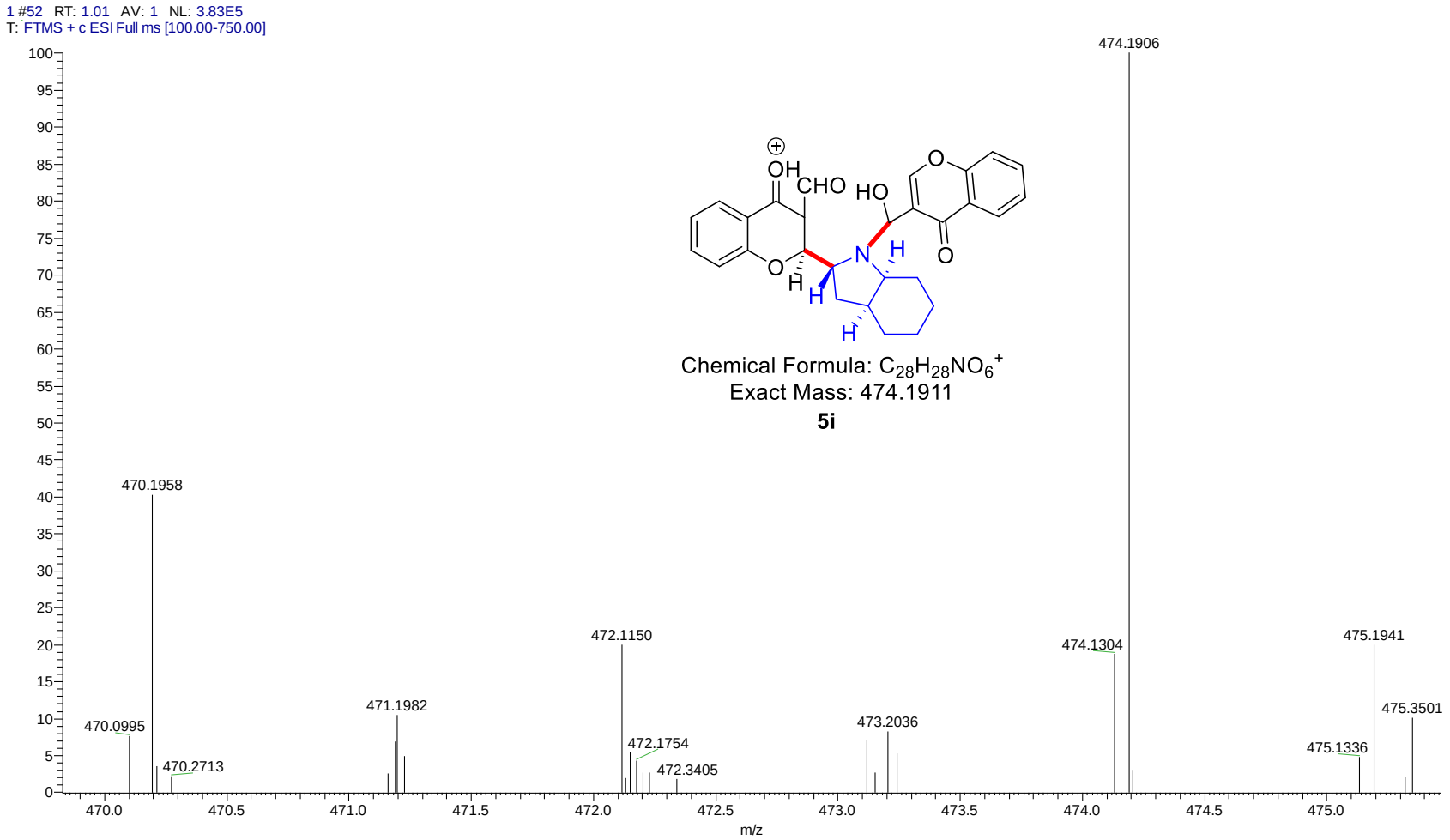



**Figure S62.** HRMS of intermediate **5i**

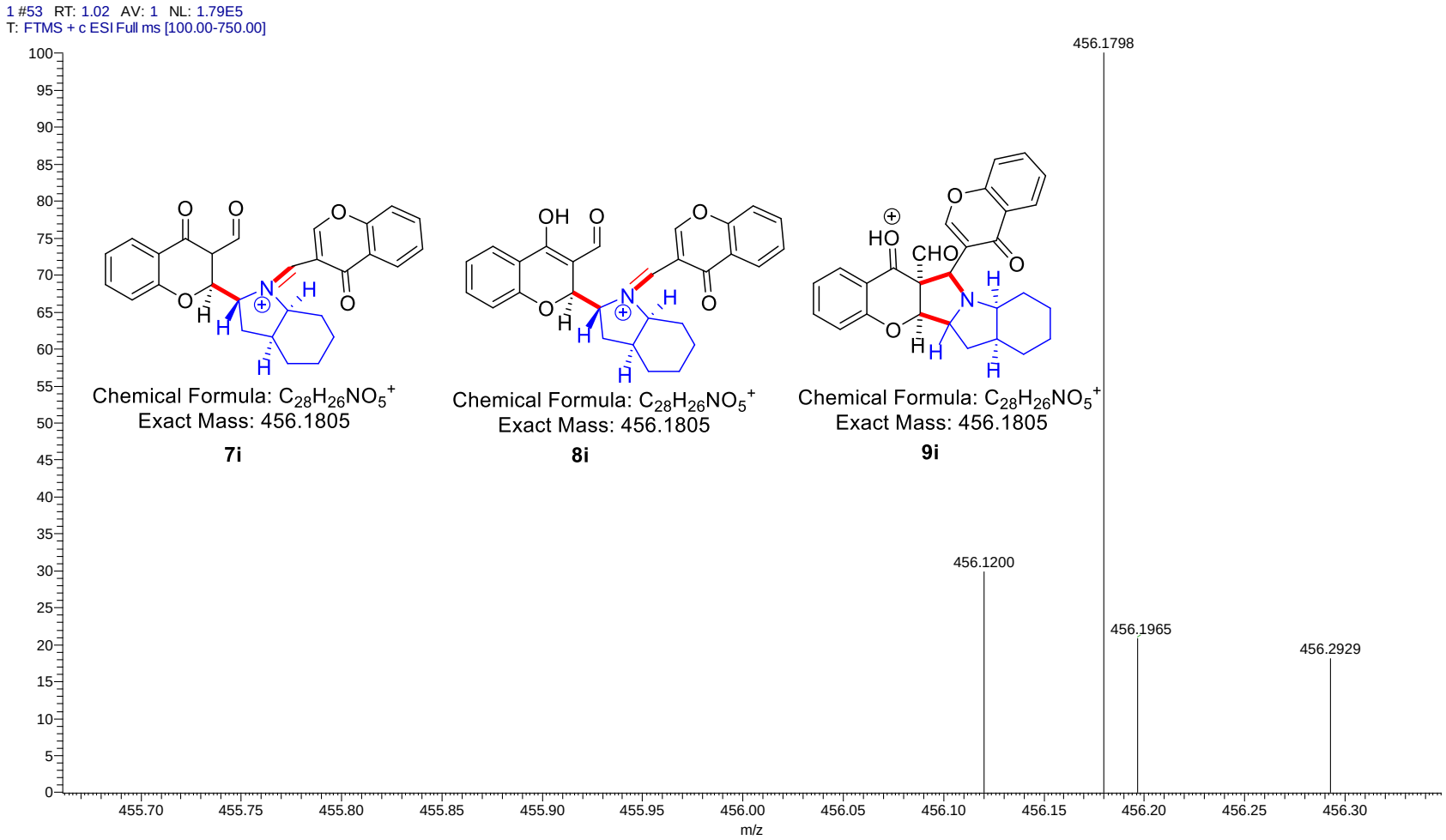



**Figure S63.** HRMS of intermediate **7i/8i/9i**

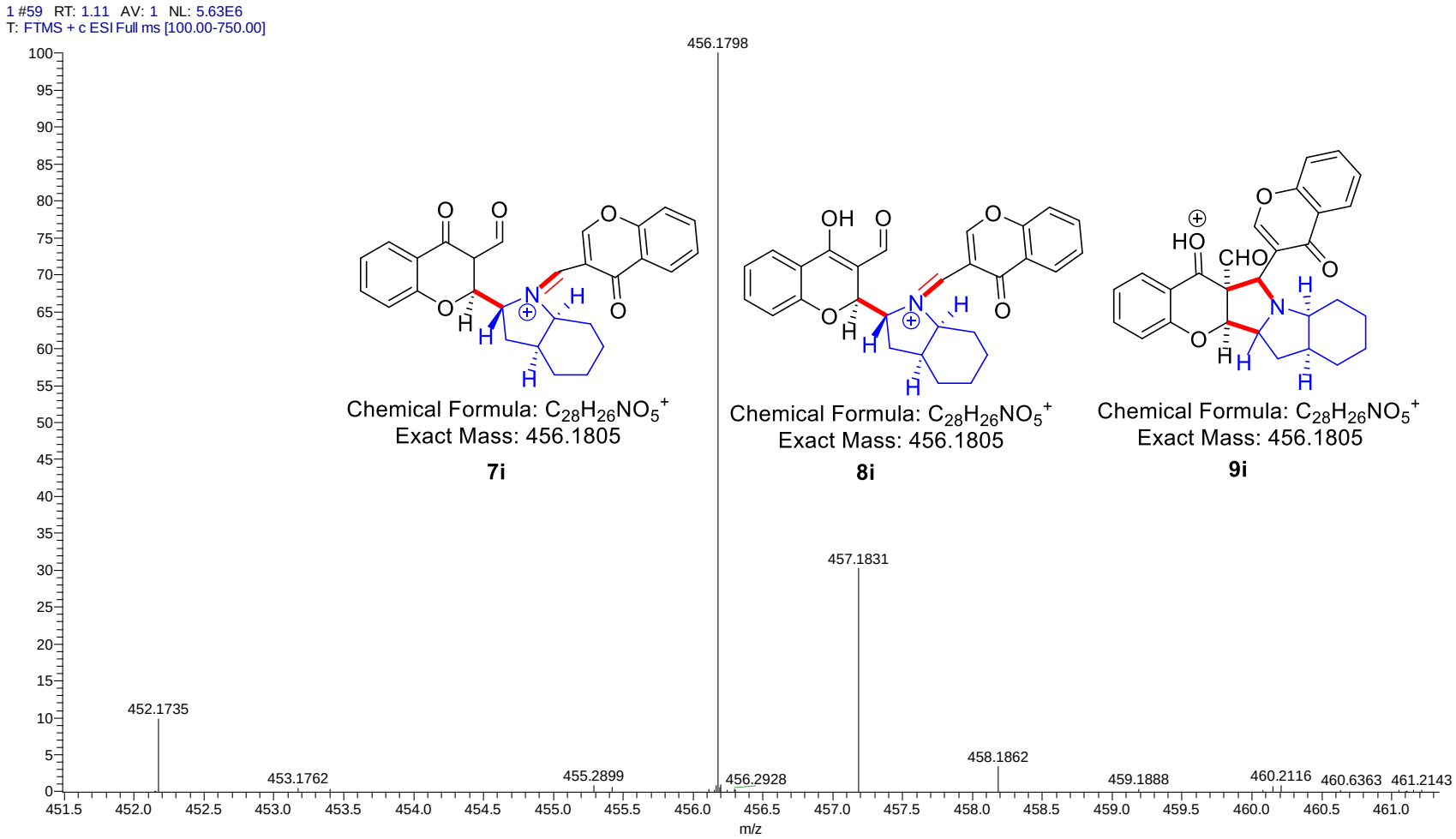



**Figure S64.** HRMS of intermediate **7i/8i/9i**

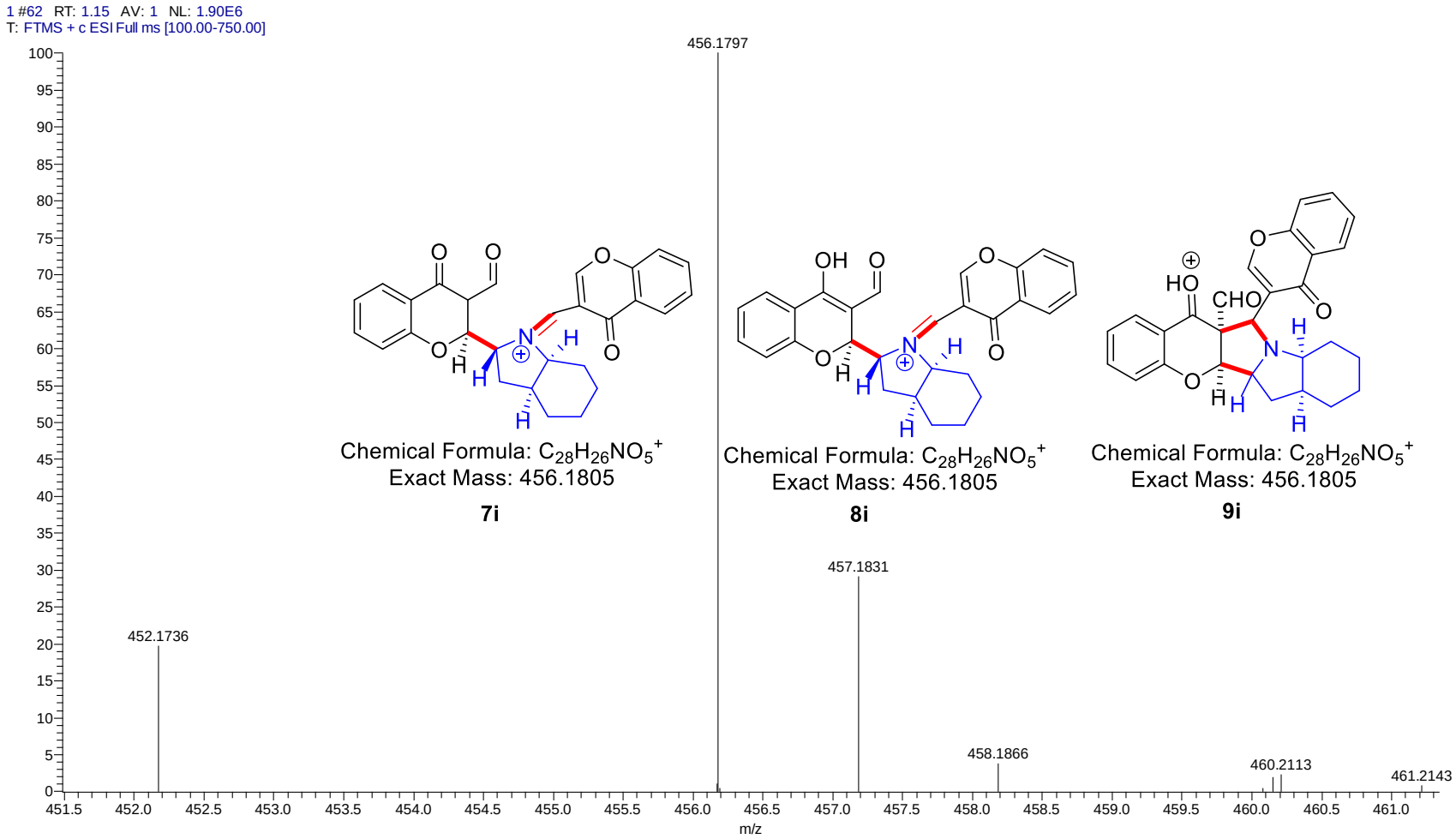



**Figure S65.** HRMS of intermediate **7i/8i/9i**

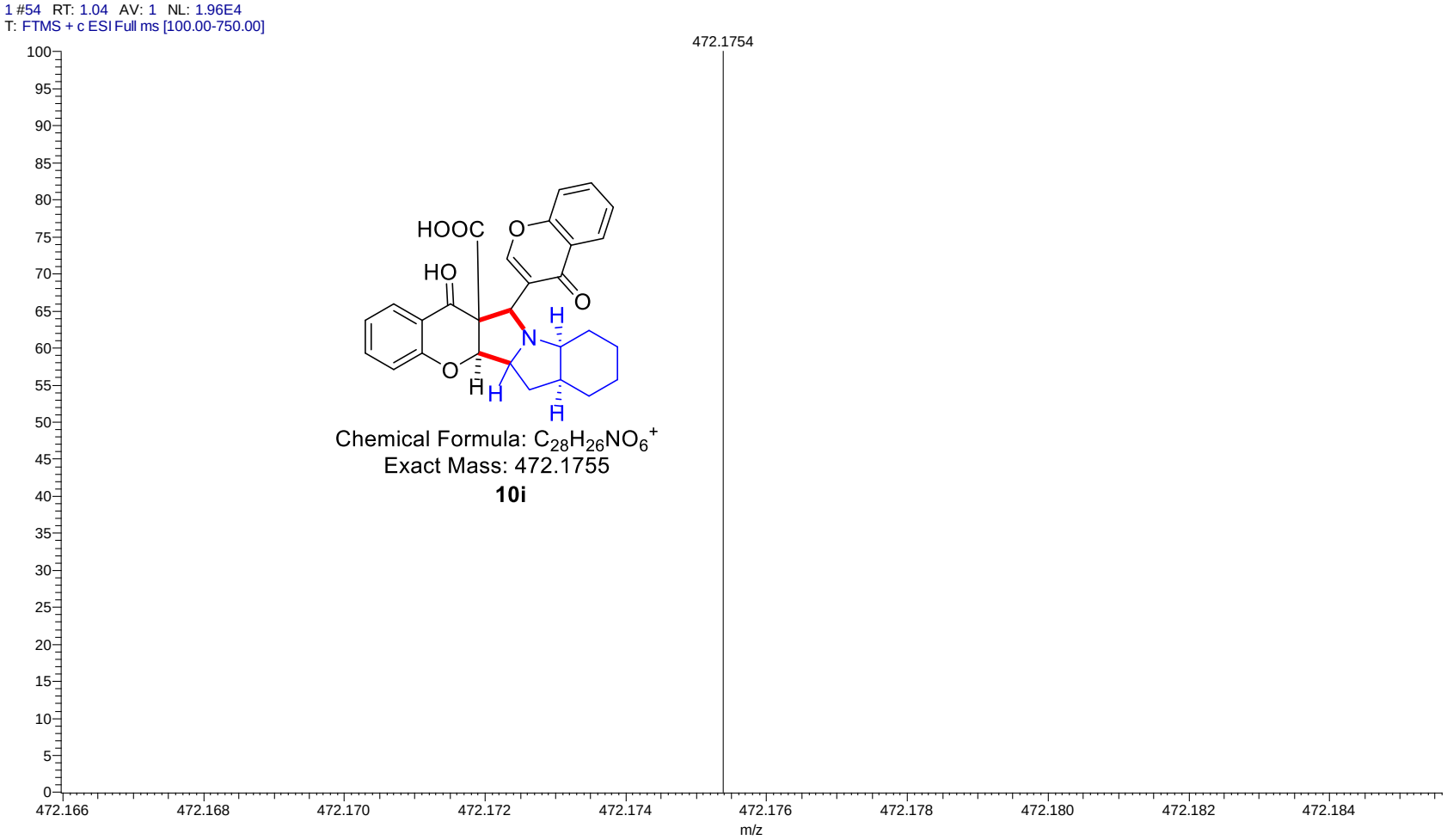



**Figure S66.** HRMS of intermediate **10i**

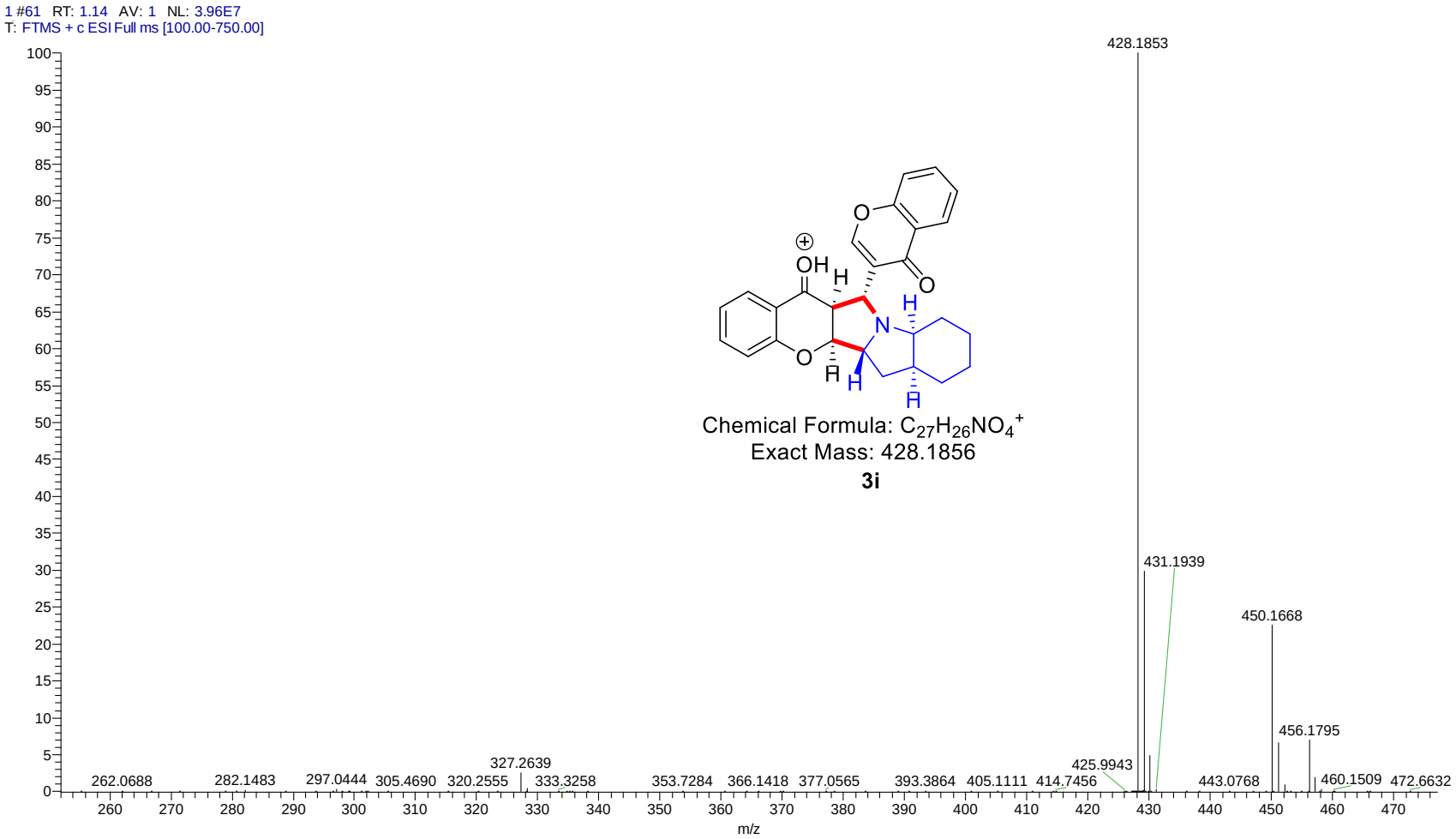



**Figure S67.** HRMS of intermediate **3i**

## References and Notes

1. CCDC 2182166 and 2181908 contains the supplementary crystallographic data for compounds **3j** and **3p'**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif