Convenient one-step synthesis of pyrrolo[3,4-*c*]quinolin-1-ones *via* TMSCl-catalyzed cascade reactions of isatins and *β*-enamino ketones

Hui Xu,[a] Pan Zhou,[a] Bei Zhou,[b] Jie Zhou,[b] Yuehai Shen,[a] Ling-Ling Lu[a] and Fu-Chao Yu*[a]

[a] *Faculty of Life Science and Technology, Kunming University of Science and Technology, Kunming, 650504, P. R. China.*
[b] *Key Laboratory of Medicinal Chemistry for Natural Resource (Yunnan University), Ministry of Education, School of Chemical Science and Technology, Yunnan University, Kunming, 650091, P. R. China*

Supporting Information

Content

1. General Information

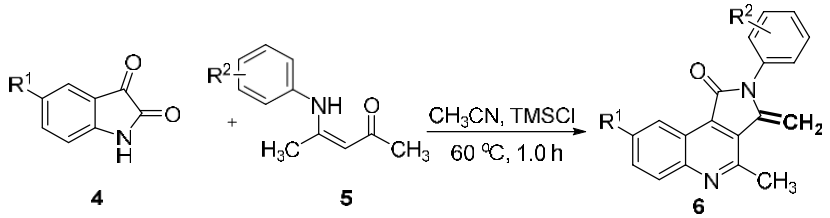
All compounds were fully characterized by spectroscopic data. The NMR spectra were recorded on a Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) and Bruker DRX500 (^{1}H: 500 MHz, ^{13}C: 125 MHz), chemical shifts (δ) are expressed in ppm, and J values are given in Hz, and deuterated $CDCl_3$ and DMSO-d_6 were used as solvent. IR spectra were recorded on a FT-IR Thermo Nicolet Avatar 360 using KBr pellet. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF_{254}. The melting points were determined on XT-4A melting point apparatus and are uncorrected. HRMs were performed on a Agilent LC/MS TOF instrument.

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 material **4** was purchased from Aldrich Corporation Limited. Compounds **5** were prepared according to the literature.[1]

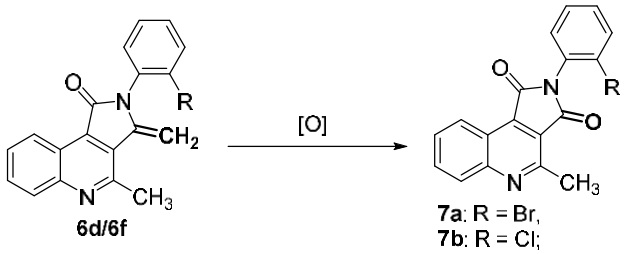
2. General Procedure

2.1 Synthesis of 3-methylene pyrrolo[3,4-*c*]quinolin-1-ones 6.



Isatins **4** (0.5 mmol) and β-enamino ketones **5** (0.5 mmol), acetonitrile (3.0 mL), TMSCl (2.0 mmol) were placed into a 10 mL round-bottom flask and the mixture was stirred at 60 ^{o}C for 1.0 h, and monitored by TLC until the β-enamino ketone substrate was used up. The mixture was cooled to room temperature, neutralized with a saturated solution of Na_2CO_3 to pH 8–9, and then EtOAc (30 mL × 2) were added. The organic phase was washed with water (20 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to afford quinoline derivative **6**.

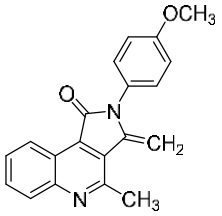
2.2 Synthesis of pyrrolo[3,4-*c*]quinolin-1,3-diones 7.[2]



The 3-methylene pyrrolo[3,4-*c*]quinolin-1-one **6d/6f** (0.2 mmol) is then dissolved in acetone, and the $KMnO_4/Al_2O_3$ powder (90 mg supported reagent, 0.3 mmol $KMnO_4$) added room temperature. After five hours of vigorous stirring, the reaction mixture is filtered and the acetone filtrate condensed. The residue is taken up into EtOAc, washed with dilute hydrochloric acid, dried over Na_2SO_4, concentrated and purified by flash column chromatography to give the product **7a**/**7b**.

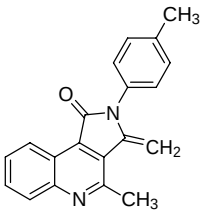
3. Characterization of products

2-(4-methoxyphenyl)-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6a).



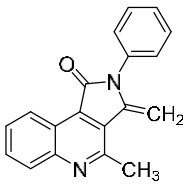
Yellow solid; mp 199–201 °C; IR (KBr): 1701, 1630, 1511, 1443, 1337, 1253, 1165, 1140, 1033, 844, 787, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.00 (s, 3H, C–CH_3), 3.87 (s, 3H, ArOCH_3), 5.06 (d, J = 2.4 Hz, 1H, C=CH_2), 5.54 (d, J = 2.0 Hz, 1H, C=CH_2), 7.06 (d, J = 8.8 Hz, 2H, ArH), 7.31 (d, J = 8.8 Hz, 2H, ArH), 7.64–7.68 (m, 1H, ArH), 7.76–7.80 (m, 1H, ArH), 8.12 (d, J = 8.4 Hz, 1H, ArH), 9.01 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.2, 55.7, 97.9, 115.0, 115.0, 122.0, 124.5, 126.6, 127.6, 128.1, 128.8, 129.9, 129.9, 130.6, 131.3, 143.3, 148.2, 153.3, 159.7, 166.4; HRMS (TOF ES^+): m/z calcd for $C_{20}H_{17}N_2O_2$ [$(M+H)^+$], 317.1285; found, 317.1282.

4-methyl-3-methylene-2-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6b).



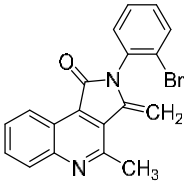
Yellow solid; mp 201–203 °C; IR (KBr): 1721, 1704, 1633, 1515, 1388, 1249, 1153, 1130, 1068, 873, 781, 704 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 2.41 (s, 3H, ArCH_3), 2.91 (s, 3H, C–CH_3), 4.97 (d, J = 2.4 Hz, 1H, C=CH_2), 5.65 (d, J = 2.4 Hz, 1H, C=CH_2), 7.32 (d, J = 8.4 Hz, 2H, ArH), 7.40 (d, J = 8.0 Hz, 2H, ArH), 7.70–7.74 (m, 1H, ArH), 7.82–7.86 (m, 1H, ArH), 8.08 (d, J = 8.8 Hz, 1H, ArH), 8.81 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.7, 25.6, 99.6, 122.0, 124.3, 128.1, 129.0, 129.5, 129.5, 129.6, 130.9, 130.9, 131.0, 131.5, 132.1, 139.1, 142.9, 148.3, 154.4, 166.1; HRMS (TOF ES^+): m/z calcd for $C_{20}H_{17}N_2O$ [$(M+H)^+$], 301.1335; found, 301.1334.

4-methyl-3-methylene-2-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6c).



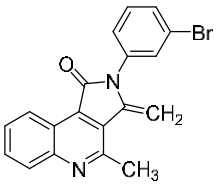
Yellow solid; mp 212–215 °C; IR (KBr): 1712, 1625, 1499, 1384, 1335, 1278, 1244, 1153, 839, 793, 770, 713 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.06 (s, 3H, C–CH_3), 5.15 (d, J = 5.0 Hz, 1H, C=CH_2), 5.62 (d, J = 5.0 Hz, 1H, C=CH_2), 7.46 (d, J= 7.75 Hz, 2H, ArH), 7.51–7.54 (m, 1H, ArH), 7.60–7.63 (m, 2H, ArH), 7.70–7.74 (m, 1H, ArH), 7.82–7.86 (m, 1H, ArH), 8.17–8.19 (m, 1H, ArH), 9.06–9.08 (m, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.6, 98.3, 122.3, 124.8, 128.0, 128.5, 129.0, 129.1, 129.1, 129.1, 130.0, 130.0, 130.9, 131.5, 134.4, 143.2, 148.5, 156.3, 166.5; HRMS (TOF ES^+): *m/z* calcd for $C_{19}H_{15}N_2O$ [$(M+H)^+$], 287.1179; found, 287.1178.

2-(2-bromophenyl)-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6d).



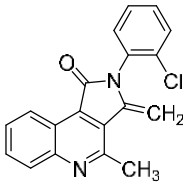
Yellow solid; mp 222–225 °C; IR (KBr): 1713, 1638, 1477, 1383, 1327, 1165, 1058, 1027, 859, 771 cm^{-1}; ^1H NMR (500 MHz, DMSO-*d6*): δ =3.10 (s, 3H, C–CH_3), 4.85 (d, J = 3.4 Hz, 1H, C=CH_2), 5.82 (d, J = 3.3 Hz, 1H, C=CH_2), 7.57–7.61 (m, 1H, ArH), 7.66–7.71 (m, 2H, ArH), 7.87–7.91 (m, 1H, ArH), 7.96–8.03 (m, 2H, ArH), 8.29 (d, J = 8.5 Hz, 1H, ArH), 8.94 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (125 MHz, DMSO-*d6*): δ = 24.2, 99.7, 121.6, 123.8, 123.9, 123.9, 127.9, 127.9, 129.2, 129.6, 131.8, 131.9, 132.3, 133.4, 133.9, 133.9, 140.9, 154.3, 164.7; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{14}BrN_2O$ [$(M+H)^+$], 365.0290; found, 365.0293.

2-(3-bromophenyl)-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6e).



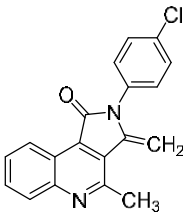
White solid; mp 211–213 °C; IR (KBr): 1706, 1634, 1477, 1334, 1278, 1148, 1126, 854, 773, 720, 680 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.02 (s, 3H, C–CH_3), 5.13 (d, J = 2.4 Hz, 1H, C=CH_2), 5.60 (d, J = 2.4 Hz, 1H, C=CH_2), 7.37 (d, J = 7.6 Hz, 1H, ArH), 7.42–7.46 (m, 1H, ArH), 7.60–7.63 (m, 2H, ArH), 7.66–7.70 (m, 1H, ArH), 7.79–7.82 (m, 1H, ArH), 8.14 (d, J = 8.4 Hz, 1H, ArH), 8.99 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.3, 98.1, 121.9, 123.0, 124.4, 127.5, 127.6, 128.3, 128.9, 130.8, 130.9, 130.9, 131.9, 132.0, 135.4, 142.5, 148.3, 153.3, 166.0; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{14}BrN_2O$ [$(M+H)^+$], 365.0284; found, 365.0281.

2-(2-chlorophenyl)-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6f).



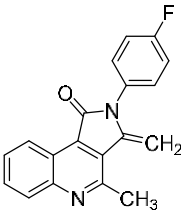
White solid; mp 217–219.5 °C; IR (KBr): 1713, 1638, 1595, 1482, 1385, 1250, 1170, 1059, 858, 771, 688 cm^{-1}; ^1H NMR (500 MHz, DMSO-*d6*): δ =3.18 (s, 3H, C–CH_3), 4.94 (d, J = 3.4 Hz, 1H, C=CH_2), 5.86 (d, J = 3.4 Hz, 1H, C=CH_2), 7.66–7.70 (m, 3H, ArH), 7.83–7.84 (m, 1H, ArH), 7.93–7.96 (m, 1H, ArH), 8.06–8.09 (m, 1H, ArH), 8.44 (d, J = 8.6 Hz, 1H, ArH), 8.96 (d, J = 8.2 Hz, 1H, ArH); ^{13}C NMR (125 MHz, DMSO-*d6*): δ = 23.1, 100.4, 121.7, 124.0, 126.2, 128.2, 129.1, 129.8, 130.8, 131.4, 131.9, 131.9, 132.2, 132.6, 133.1, 140.4, 144.3, 154.5, 164.3; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{14}ClN_2O$ [$(M+H)^+$], 321.0795; found, 321.0797.

2-(4-chlorophenyl)-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6g).



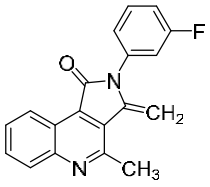
White solid; mp 236–238 °C; IR (KBr): 1708, 1634, 1494, 1390, 1253, 1087, 834, 769, 737, 684 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.00 (s, 3H, C–CH_3), 5.09 (d, J = 2.4 Hz, 1H, C=CH_2), 5.57 (d, J = 2.4 Hz, 1H, C=CH_2), 7.36 (d, J = 8.8 Hz, 2H, ArH), 7.53 (d, J = 8.4 Hz, 2H, ArH), 7.65–7.68 (m, 1H, ArH), 7.77–7.81 (m, 1H, ArH), 8.12 (d, J = 8.4 Hz, 1H, ArH), 8.98 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.2, 97.9, 121.9, 124.4, 127.6, 128.3, 128.9, 129.9, 129.9, 130.1, 130.1, 130.7, 131.0, 132.6, 134.6, 142.6, 148.2, 153.3, 166.0; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{14}ClN_2O$ [$(M+H)^+$], 321.0789; found, 321.0789.

2-(4-fluorophenyl)-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6h).



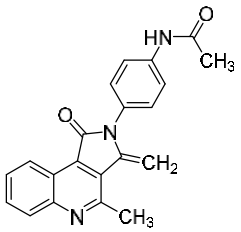
Pink solid; mp 189–191 °C; IR (KBr): 1698, 1633, 1509, 1385, 1224, 1150, 1097, 833, 773, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.01 (s, 3H, C–CH_3), 5.06 (d, J = 2.8 Hz, 1H, C=CH_2), 5.57 (d, J = 2.4 Hz, 1H, C=CH_2), 7.23–7.27 (m, 2H, ArH), 7.37–7.41 (m, 2H, ArH), 7.65–7.69 (m, 1H, ArH), 7.77–7.82 (m, 1H, ArH), 8.13 (d, J = 8.4 Hz, 1H, ArH), 8.99 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.2, 97.9, 116.7 (d, J = 22.8 Hz), 116.7 (d, J = 22.8 Hz), 121.9, 124.4, 127.6, 128.3, 128.9, 130.0 (d, J = 3.2 Hz), 130.6 (d, J = 8.6 Hz), 130.6 (d, J = 8.6 Hz), 130.7, 131.1, 143.0, 148.3, 153.3, 162.5 (d, J = 247.1 Hz), 166.3; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{14}FN_2O$ [$(M+H)^+$], 305.1085; found, 305.1082.

2-(3-fluorophenyl)-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6i).



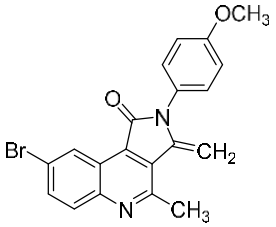
White solid; mp 233–235 °C; IR (KBr): 1706, 1626, 1590, 1497, 1450, 1224, 1145, 849, 808, 771, 748, 715, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.08 (s, 3H, C–CH_3), 5.21 (d, J = 2.8 Hz, 1H, C=CH_2), 5.67 (d, J = 2.8 Hz, 1H, C=CH_2), 7.23–7.31 (m, 3H, ArH), 7.58–7.61 (m, 1H, ArH), 7.73–7.76 (m, 1H, ArH), 7.85–7.89 (m, 1H, ArH), 8.20 (d, J = 8.4 Hz, 1H, ArH), 9.06 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.2, 98.1, 115.8 (d, J = 20.8 Hz), 116.3 (d, J = 22.9 Hz), 121.9, 124.4, 124.6 (d, J = 3.3 Hz), 127.6, 128.3, 128.9, 130.7, 130.8 (d, J = 9.3 Hz), 130.9, 135.5 (d, J = 9.8 Hz), 142.5, 148.2, 153.3, 163.1 (d, J = 246.7 Hz), 165.9; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{14}FN_2O$ [$(M+H)^+$], 305.1085; found, 305.1086.

***N*-(4-(4-methyl-3-methylene-1-oxo-1*H*-pyrrolo[3,4-*c*]quinolin-2(3*H*)-yl)phenyl)acetamide (6j).**



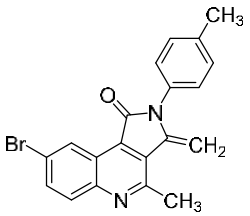
Pink solid; mp 302.5–304.5 °C; IR (KBr): 1703, 1668, 1532, 1517, 1391, 1313, 1154, 839, 772, 744, 671 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 2.10 (s, 3H, C–CH_3), 2.91 (s, 3H, C–CH_3), 4.98 (s, 1H, C=CH_2), 5.64 (s, 1H, C=CH_2), 7.36 (d, J = 8.0 Hz, 2H, ArH), 7.71–7.73 (m, 1H, ArH), 7.79 (d, J = 8.0 Hz, 2H, ArH), 7.82–7.84 (m, 1H, ArH), 8.06 (d, J = 8.0 Hz, 1H, ArH), 8.80 (d, J = 8.0 Hz, 1H, ArH), 10.20 (s, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 25.0, 25.6, 99.6, 120.6, 120.6, 122.0, 124.3, 128.1, 129.0, 129.2, 129.6, 130.1, 130.1, 131.0, 131.5, 140.4, 142.9, 148.3, 154.4, 166.2, 169.6; HRMS (TOF ES^+): m/z calcd for $C_{21}H_{18}N_3O_2$ [$(M+H)^+$], 344.1394; found, 344.1399.

8-bromo-2-(4-methoxyphenyl)-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6k.



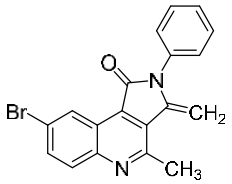
Yellow solid; mp 230–232.5 °C; IR (KBr): 1705, 1634, 1518, 1498, 1303, 1256, 1171, 1042, 987, 829, 726 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.98 (s, 3H, C–CH_3), 3.88 (s, 3H, ArOCH_3), 5.11 (d, J = 2.4 Hz, 1H, C=CH_2), 5.58 (d, J = 2.4 Hz, 1H, C=CH_2), 7.06 (d, J = 8.8 Hz, 2H, ArH), 7.29 (d, J = 8.8 Hz, 2H, ArH), 7.82–7.85 (m, 1H, ArH), 7.96 (d, J = 8.8 Hz, 1H, ArH), 9.16 (d, J = 2.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.2, 55.7, 98.7, 115.0, 115.0, 122.6, 123.0, 126.3, 126.8, 128.2, 129.9, 129.9, 130.3, 130.4, 134.1, 143.0, 146.7, 153.8, 159.8, 165.8; HRMS (TOF ES^+): m/z calcd for $C_{20}H_{16}BrN_2O_2$[$(M+H)^+$], 395.0390; found, 395.0393.

8-bromo-4-methyl-3-methylene-2-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6l).



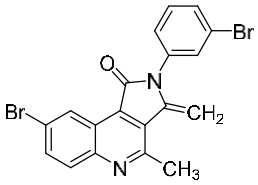
White solid; mp 231–233.5 °C; IR (KBr): 1704, 1631, 1514, 1375, 1333, 1264, 1170, 1061, 874, 814, 796, 656 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3H, ArCH_3), 2.98 (s, 3H, C–CH_3), 5.14 (d, J = 2.4 Hz, 1H, C=CH_2), 5.58 (d, J = 2.4 Hz, 1H, C=CH_2), 7.27 (d, J = 8.0 Hz,, 2H, ArH), 7.36 (d, J = 8.0 Hz, 2H, ArH), 7.82–7.85 (m, 1H, ArH), 7.97 (d, J = 8.8 Hz, 1H, ArH), 9.17 (d, J = 2.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 25.2, 98.7, 122.6, 123.0, 126.8, 128.2, 128.4, 128.4, 130.3, 130.3, 130.3, 130.4, 131.2, 134.1, 138.8, 142.8, 146.7, 153.8, 165.7; HRMS (TOF ES^+): m/z calcd for $C_{20}H_{16}BrN_2O$ [$(M+H)^+$], 379.0441; found, 379.0440.

8-bromo-4-methyl-3-methylene-2-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6m).



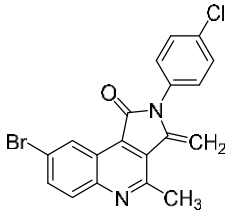
White solid; mp 235–237.5 °C; IR (KBr): 1721, 1634, 1497, 1384, 1335, 1185, 1067, 988, 785, 719 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.99 (s, 3H, C–CH_3), 5.15 (d, J = 2.8 Hz, 1H, C=CH_2), 5.60 (d, J = 2.8 Hz, 1H, C=CH_2), 7.39–7.41 (m, 2H, ArH), 7.46–7.50 (m, 1H, ArH), 7.55–7.58 (m, 2H, ArH), 7.83–7.86 (m, 1H, ArH), 7.97 (d, J = 8.8 Hz, 1H, ArH), 9.16 (d, J = 2.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.2, 98.8, 122.6, 122.9, 126.7, 128.2, 128.7, 128.7, 128.8, 129.7, 129.7, 130.2, 130.4, 133.9, 134.1, 142.6, 146.7, 153.8, 165.6; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{14}BrN_2O$ [$(M+H)^+$], 365.0284; found, 365.0283.

8-bromo-2-(3-bromophenyl)-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-on (6n).



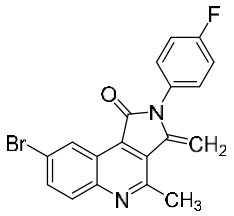
White solid; mp 223.5–225.5 °C; IR (KBr): 1707, 1631, 1586, 1476, 1441, 1371, 1333, 1171, 886, 865, 682 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.99 (s, 3H, C–CH_3), 5.17 (d, J = 2.8 Hz, 1H, C=CH_2), 5.64 (d, J = 2.8 Hz, 1H, C=CH_2), 7.37 (d, J = 8.0 Hz, 1H, ArH), 7.42–7.46 (m, 1H, ArH), 7.59–7.63 (m, 2H, ArH), 7.84–7.87 (m, 1H, ArH), 7.98 (d, J = 9.2 Hz, 1H, ArH), 9.14 (d, J = 2.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.3, 98.9, 122.8, 122.9, 123.0, 126.7, 127.4, 128.2, 129.9, 130.5, 130.9, 131.9, 132.0, 134.3, 135.2, 142.2, 146.8, 153.8, 165.4; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{13}Br_2N_2O$ [$(M+H)^+$], 442.9389; found, 442.9387.

8-bromo-2-(4-chlorophenyl)-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6o).



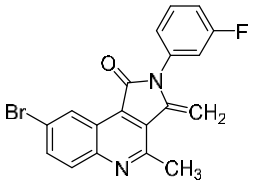
White solid; mp 244–246 °C; IR (KBr): 1704, 1634, 1496, 1378, 1333, 1174, 1089, 1016, 863, 830, 774, 736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ =2.99 (s, 3H, C–CH_3), 5.14 (d, J = 2.8 Hz, 1H, C=CH_2), 5.62 (d, J = 2.8 Hz, 1H, C=CH_2), 7.35 (d, J = 8.8 Hz, 2H, ArH), 7.55 (d, J = 8.8 Hz, 2H, ArH), 7.84–7.87 (m, 1H, ArH), 7.97 (d, J = 9.2 Hz, 1H, ArH), 9.13 (d, J = 2.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.3, 98.7, 122.8, 122.9, 126.7, 128.3, 130.0, 130.0, 130.0, 130.0, 130.0, 130.5, 132.4, 134.3, 134.7, 142.4, 146.7, 153.8, 165.5; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{13}BrClN_2O$ [$(M+H)^+$], 398.9894; found, 398.9890.

8-bromo-2-(4-fluorophenyl)-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6p).



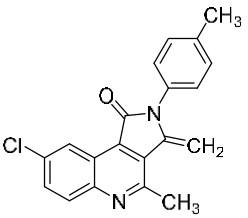
Pink solid; mp 230.5–233 °C; IR (KBr): 1702, 1633, 1512, 1393, 1222, 1182, 1160, 1061, 865, 831, 733, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.97 (s, 3H, C–CH_3), 5.10 (s, 1H, C=CH_2), 5.60 (s, 1H, C=CH_2), 7.23–7.27 (m, 2H, ArH), 7.36–7.40 (m, 2H, ArH), 7.84 (d, *J* = 9.2 Hz, 1H, ArH), 7.95 (d, *J* = 9.2 Hz, 1H, ArH), 9.11 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.2, 98.6, 116.8 (d, *J* = 22.7 Hz), 116.8 (d, *J* = 22.7 Hz), 122.7, 122.8, 126.6, 128.2, 129.7, 130.0, 130.5 (d, *J* = 12.3 Hz), 130.5 (d, *J* = 12.3 Hz), 130.5, 134.2, 142.6, 146.7, 153.8, 162.5 (d, *J* = 247.2 Hz), 165.7; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{13}BrFN_2O$ [$(M+H)^+$], 383.0190; found, 383.0194.

8-bromo-2-(3-fluorophenyl)-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6q).



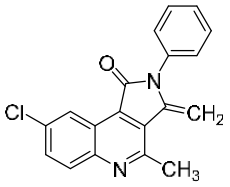
White solid; mp 226.5–230 °C; IR (KBr): 1702, 1629, 1496, 1393, 1334, 1218, 1146, 890, 857, 827, 673 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.99 (s, 3H, C–CH_3), 5.19 (d, *J* = 2.8 Hz, 1H, C=CH_2), 5.64 (d, *J* = 2.8 Hz, 1H, C=CH_2), 7.14–7.23 (m, 3H, ArH), 7.51–7.57 (m, 1H, ArH), 7.84–7.87 (m, 1H, ArH), 7.97 (d, *J* = 8.8 Hz, 1H, ArH), 9.14 (d, *J* = 2.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.3, 98.9, 115.9 (d, *J* = 20.9 Hz), 116.2 (d, *J* = 22.9 Hz), 122.8, 122.9, 124.5 (d, *J* = 3.4 Hz), 126.7, 128.2, 130.0, 130.5, 130.9 (d, *J* = 8.7 Hz), 134.3, 135.3 (d, *J* = 9.8 Hz), 142.2, 146.7, 153.8, 163.1 (d, *J* = 247.0 Hz), 165.4; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{13}BrFN_2O$ [$(M+H)^+$], 383.0190; found, 383.0192.

8-chloro-4-methyl-3-methylene-2-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6r).



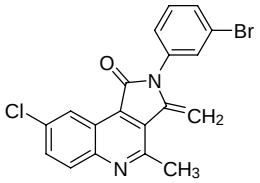
White solid; mp 223–225 °C; IR (KBr): 1702, 1626, 1499, 1402, 1340, 1169, 1071, 873, 796, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.50 (s, 3H, ArCH_3), 3.04 (s, 3H, C–CH_3), 5.19 (d, *J* = 2.4 Hz, 1H, C=CH_2), 5.63 (d, *J* = 2.4 Hz, 1H, C=CH_2), 7.32 (d, *J* = 8.0 Hz, 2H, ArH), 7.41 (d, *J* = 8.0 Hz, 2H, ArH), 7.74–7.76 (m, 1H, ArH), 8.08 (d, *J* = 9.2 Hz, 1H, ArH), 9.03 (d, *J* = 2.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 25.1, 98.6, 122.4, 123.3, 128.1, 128.3, 128.3, 130.2, 130.2, 130.2, 130.3, 131.0, 131.4, 134.1, 138.7, 142.6, 146.3, 153.5, 165.6; HRMS (TOF ES^+): m/z calcd for $C_{20}H_{16}ClN_2O$ [$(M+H)^+$], 335.0946; found, 335.0946.

8-chloro-4-methyl-3-methylene-2-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6s).



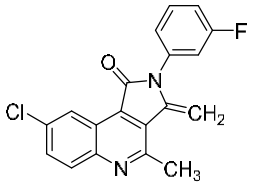
Red solid; mp 231–233 °C; IR (KBr): 1702, 1629, 1496, 1388, 1331, 1184, 1071, 897, 873, 720, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.00 (s, 3H, C–CH_3), 5.15 (d, J = 2.4 Hz, 1H, C=CH_2), 5.60 (d, J = 2.4 Hz, 1H, C=CH_2), 7.40 (d, J = 7.6 Hz, 2H, ArH), 7.46–7.50 (m, 1H, ArH), 7.55 (d, J = 7.6 Hz, 2H, ArH), 7.69–7.72 (m, 1H, ArH), 8.04 (d, J = 9.2 Hz, 1H, ArH), 8.98 (d, J = 2.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.1, 98.7, 122.4, 123.3, 128.2, 128.6, 128.6, 128.6, 128.7, 129.6, 129.6, 130.2, 131.4, 133.8, 134.2, 142.5, 146.3, 153.5, 165.5; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{14}ClN_2O$ [$(M+H)^+$], 321.0789; found, 321.0788.

2-(3-bromophenyl)-8-chloro-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6t).



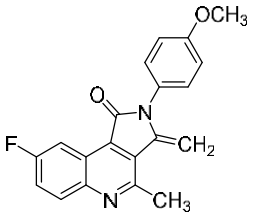
White solid; mp 193.5–195 °C; IR (KBr): 1704, 1630, 1475, 1369, 1334, 1171, 1075, 865, 782, 748, 684 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ =2.97 (s, 3H, C–CH_3), 5.16 (d, J = 2.4 Hz, 1H, C=CH_2), 5.62 (d, J = 2.4 Hz, 1H, C=CH_2), 7.36 (d, J = 8.0 Hz, 1H, ArH), 7.42 (d, J = 8.0 Hz, 1H, ArH), 7.59–7.62 (m, 2H, ArH), 7.68–7.71 (m, 1H, ArH), 8.01 (d, J = 8.8 Hz, 1H, ArH), 8.91 (d, J = 2.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.1, 98.8, 122.2, 122.9, 123.1, 127.3, 128.1, 129.9, 130.3, 130.8, 131.5, 131.7, 131.8, 134.3, 135.0, 142.1, 146.3, 153.5, 165.3; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{13}BrClN_2O$ [$(M+H)^+$], 398.9900; found, 398.9904.

8-chloro-2-(3-fluorophenyl)-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6u).



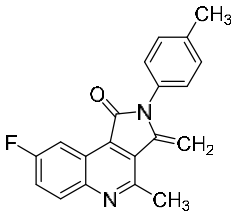
Yellow solid; mp 238–240 °C; IR (KBr): 1702, 1630, 1593, 1387, 1333, 1160, 1021, 883, 831, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.06 (s, 3H, C–CH_3), 5.25 (d, J = 2.8 Hz, 1H, C=CH_2), 5.70 (d, J = 2.8 Hz, 1H, C=CH_2), 7.21–7.32 (m, 3H, ArH), 7.57–7.62 (m, 1H, ArH), 7.77–7.79 (m, 1H, ArH), 8.11 (d, J = 8.95 Hz, 1H, ArH), 9.02 (d, J = 2.15 Hz, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.5, 99.0, 116.2 (d, J = 20.8 Hz), 116.5 (d, J = 23.0 Hz), 122.7, 123.6, 123.6, 124.8, 128.6, 130.4, 130.6, 131.1 (d, J = 8.9 Hz), 132.0, 134.8, 135.6 (d, J = 5.8 Hz), 142.5, 146.8, 153.9, 163.4 (d, J = 250.6 Hz), 165.7; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{13}ClFN_2O$ [$(M+H)^+$], 339.0695; found, 339.0695.

8-fluoro-2-(4-methoxyphenyl)-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6v).



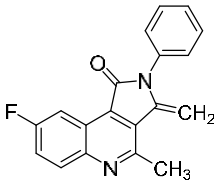
Yellow solid; mp 200–202 °C; IR (KBr): 1703, 1634, 1515, 1387, 1252, 1193, 1036, 873, 867, 810, 786, 662 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.05 (s, 3H, C–CH_3), 3.94 (s, 3H, ArOCH_3), 5.16 (d, J = 2.4 Hz, 1H, C=CH_2), 5.64 (d, J = 2.3 Hz, 1H, C=CH_2), 7.12 (d, J = 8.75 Hz, 2H, ArH), 7.36 (d, J = 8.75 Hz, 2H, ArH), 7.58–7.62 (m, 1H, ArH), 8.16–8.19 (m, 1H, ArH), 8.67–8.69 (m, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.3, 56.0, 98.8, 108.5 (d, J = 23.8 Hz), 115.3, 115.3, 121.0 (d, J = 26.3 Hz), 123.0 (d, J = 11.3 Hz), 126.7, 128.5, 130.2, 130.2, 131.2 (d, J = 6.3 Hz), 131.5 (d, J = 10 Hz), 143.4, 145.6, 152.8, 160.1, 161.5 (d, J = 250.0 Hz), 166.4; HRMS (TOF ES^+): m/z calcd for$C_{20}H_{16}FN_2O_2$ [$(M+H)^+$], 335.1190; found, 335.1194.

8-fluoro-4-methyl-3-methylene-2-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6w).



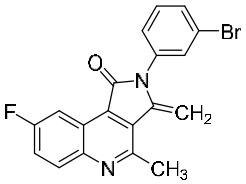
Yellow solid; mp 165.5–167 °C; IR (KBr): 1717, 1634, 1514, 1374, 1341, 1243, 1210, 1093, 873, 804, 784, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3H, ArCH_3), 3.00 (s, 3H, C–CH_3), 5.13 (d, J = 2.8 Hz, 1H, C=CH_2), 5.59 (d, J = 2.4 Hz, 1H, C=CH_2), 7.28 (d, J = 8.4 Hz, 2H, ArH), 7.36 (d, J = 8.0 Hz, 2H, ArH), 7.52–7.57 (m, 1H, ArH), 8.10–8.14 (m, 1H, ArH), 8.62–8.65 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 25.1, 98.6, 108.2 (d, J = 23.7 Hz), 120.7 (d, J = 25.9 Hz), 122.7 (d, J = 11.6 Hz), 128.2, 128.5, 128.5, 130.4, 130.4, 130.9 (d, J = 5.8 Hz), 131.2, 131.3, 133.8, 142.9, 145.3, 152.6 (d, J = 2.9 Hz), 161.6 (d, J = 248.5 Hz), 165.9; HRMS (TOF ES^+): m/z calcd for $C_{20}H_{16}FN_2O$ [$(M+H)^+$], 319.1241; found, 319.1245.

8-fluoro-4-methyl-3-methylene-2-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6x).



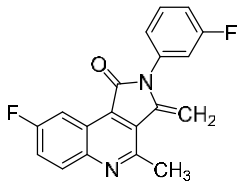
White solid; mp 204.5–206 °C; IR (KBr): 1702, 1633, 1602, 1512, 1373, 1341, 1270, 1211, 1095, 870, 840, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.00 (s, 3H, C–CH_3), 5.14 (d, J = 2.8 Hz, 1H, C=CH_2), 5.60 (d, J = 2.4 Hz, 1H, C=CH_2), 7.39–7.41 (m, 2H, ArH), 7.48–7.50 (m, 1H, ArH), 7.52–7.58 (m, 3H, ArH), 8.10–8.13 (m, 1H, ArH), 8.61–8.64 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.1, 98.6, 108.2 (d, J = 23.7 Hz), 120.8 (d, J = 25.9 Hz), 122.7 (d, J = 11.6 Hz), 128.3, 128.7, 128.7, 128.8, 129.7, 129.7, 130.9 (d, J = 6.0 Hz), 131.3 (d, J = 9.4 Hz), 133.9, 142.7, 145.3, 152.6 (d, J = 2.9 Hz), 161.7 (d, J = 248.6 Hz), 165.8; HRMS (TOF ES^+): m/z calcd for $C_{19}H_{14}FN_2O$ [$(M+H)^+$], 305.1085; found, 305.1089.

2-(3-bromophenyl)-8-fluoro-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6y).



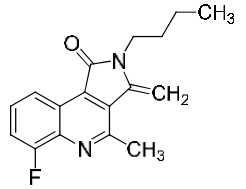
White solid; mp 197–199 °C; IR (KBr): 1705, 1635, 1514, 1478, 1375, 1340, 1241, 1194, 870, 798, 772, 679 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.99 (s, 3H, C–CH_3), 5.16 (d, J = 1.6 Hz, 1H, C=CH_2), 5.63 (s, 1H, C=CH_2), 7.26–7.36 (m, 1H, ArH), 7.42–7.46 (m, 1H, ArH), 7.53–7.63 (m, 3H, ArH), 8.10–8.13 (m, 1H, ArH), 8.56–8.60 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.1, 98.8, 108.1 (d, J = 23.8 Hz), 120.9 (d, J = 25.9 Hz), 122.6 (d, J = 11.7 Hz), 123.0, 127.5, 128.2, 130.5, 130.9, 131.4 (d, J = 9.4 Hz), 131.9, 131.9, 135.2, 142.3, 145.3, 152.5 (d, J = 2.9 Hz), 161.7 (d, J = 249 Hz), 165.6; HRMS (TOF ES^+): m/z calcd for$C_{19}H_{13}BrFN_2O$ [$(M+H)^+$], 383.0190; found, 383.0187.

8-fluoro-2-(3-fluorophenyl)-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6z).



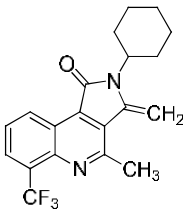
White solid; mp 221–223 °C; IR (KBr): 1700, 1633, 1596, 1514, 1494, 1376, 1344, 1223, 865, 775, 681 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.00 (s, 3H, C–CH_3), 5.18 (d, J = 2.4 Hz, 1H, C=CH_2), 5.63 (d, J = 2.4 Hz, 1H, C=CH_2), 7.15–7.26 (m, 3H, ArH), 7.53–7.57 (m, 2H, ArH), 8.10–8.13 (m, 1H, ArH), 8.57–8.60 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.1, 98.7, 108.1 (d, J = 23.7 Hz), 115.9 (d, J = 20.8 Hz), 116.3 (d, J = 23.0 Hz), 120.9 (d, J = 26.0 Hz), 122.6 (d, J = 11.7 Hz), 124.5 (d, J = 3.3 Hz), 128.2, 130.6 (d, J = 6.1 Hz), 130.9 (d, J = 9.0 Hz), 131.4 (d, J = 9.2 Hz), 135.3 (d, J = 9.9 Hz), 142.3, 145.3, 152.5 (d, J = 2.8 Hz), 161.7 (d, J = 248.7 Hz), 163.1 (d, J = 247.0 Hz), 165.3; HRMS (TOF ES^+): m/z calcd for$C_{19}H_{13}F_2N_2O$ [$(M+H)^+$], 323.0990; found, 323.0996.

2-butyl-6-fluoro-4-methyl-3-methylene-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6a′)



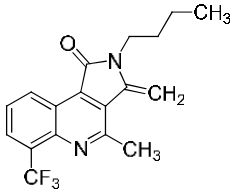
White solid; mp 90–92 °C; IR (KBr): 1699, 1510, 1469, 1227, 1089, 831, 758, 631 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.98–1.01 (m, 3H, CH_3), 1.41–1.48 (m, 2H, CH_2), 1.68–1.75 (m, 2H, CH_2), 3.03 (s, 3H, CH_3), 3.86–3.89 (m, 2H, CH_2), 5.28 (d, J = 2.8 Hz, 1H, C=CH_2), 5.62 (d, J = 2.8 Hz, 1H, C=CH_2), 7.44–7.48 (m, 1H, ArH), 7.57–7.61 (m, 1H, ArH), 8.78 (d, J = 8.5 Hz, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 20.6, 25.6, 31.0, 39.6, 97.1, 114.9 (d, J = 20.0 Hz), 120.5 (d, J = 5.0 Hz), 123.8, 128.2 (d, J = 8.8 Hz), 128.8, 131.9, 138.2 (d, J = 11.3 Hz), 141.5, 154.0, 157.8 (d, J = 253.8 Hz), 166.3; HRMS (TOF ES^+): *m/z* calcd for $C_{17}H_{18}FN_2O$ [$(M+H)^+$], 285.1398; found, 285.1399.

2-cyclohexyl-4-methyl-3-methylene-6-(trifluoromethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6b′)



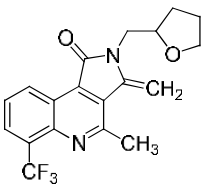
White solid; mp 164–166 °C; IR (KBr): 1691, 1511, 1375, 1303, 1133, 845, 767 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.33–1.38 (m, 1H, CH_2), 1.41–1.49 (m, 2H, CH_2), 1.77–1.80 (m, 1H, CH_2), 1.86–1.89 (m, 2H, CH_2), 1.89–1.98 (m, 2H, CH_2), 2.34–2.41 (m, 2H, CH_2), 3.05 (s, 3H, CH_3), 4.12–4.15 (m, 1H, CH), 5.46 (d, *J* = 2.9 Hz, 1H, C=CH_2), 5.69 (d, *J* = 2.9 Hz, 1H, C=CH_2), 7.68–7.71 (m, 1H, ArH), 8.11 (d, *J* = 7.3 Hz, 1H, ArH), 9.26 (d, *J* = 8.1 Hz, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.8, 26.0, 26.8, 26.8, 30.3, 30.3, 53.5, 97.7, 122.8, 124.3 (*J* = 271.3 Hz), 126.7, 127.8 (*J* = 30.0 Hz), 128.4, 128.6, 128.9, 131.7, 141.2, 144.4, 154.4, 166.7; HRMS (TOF ES^+): *m/z* calcd for $C20H_{20}F_3N_2O$ [$(M+H)^+$], 361.1522; found, 361.1526.

2-butyl-4-methyl-3-methylene-6-(trifluoromethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6c′)



White solid; mp 113–115 °C; IR (KBr): 1701, 1578, 1510, 1452, 1348, 1300, 1130, 840, 675 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 0.99–1.02 (m, 3H, CH_3), 1.42–1.49 (m, 2H, CH_2), 1.70–1.76 (m, 2H, CH_2), 3.05 (s, 3H, CH_3), 3.88–3.91 (m, 2H, CH_2), 5.30 (d, *J* = 2.9 Hz, 1H, C=CH_2), 5.65 (d, *J* = 2.9 Hz, 1H, C=CH_2), 7.69–7.72 (m, 1H, ArH), 8.12 (d, *J* = 7.3 Hz, 1H, ArH), 9.24 (d, *J* = 8.2 Hz, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 20.6, 25.8, 31.0, 39.6, 97.2, 122.8, 124.4 (*J* = 271.3 Hz), 126.8, 127.8 (*J* = 28.8 Hz), 128.5, 128.7, 128.8, 131.8, 141.4, 145.8, 154.5, 166.5; HRMS (TOF ES^+): *m/z* calcd for $C_{18}H_{18}F_3N_2O$ [$(M+H)^+$], 335.1366; found, 335.1374.

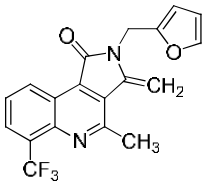
4-methyl-3-methylene-2-((tetrahydrofuran-2-yl)methyl)-6-(trifluoromethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6d′)



White solid; mp 146–148 °C; IR (KBr): 1695, 1581, 1395, 1349, 1305, 1120, 1085, 873, 786, 680, 559 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 1.76–1.81 (m, 1H, CH_2), 1.92–1.98 (m, 2H, CH_2), 2.05–2.10 (m, 1H, CH_2), 3.04 (s, 3H, CH_3), 3.76–3.80 (m, 1H, CH_2), 3.91–3.96 (m, 2H, CH_2), 4.03–4.07 (m, 1H, CH_2), 4.28–4.30 (m, 1H, CH), 5.55 (d, *J* = 2.7 Hz, 1H, C=CH_2), 5.69 (d, *J* = 2.7 Hz, 1H, C=CH_2), 7.69–7.72 (m, 1H, ArH), 8.12 (d, *J* = 7.3 Hz, 1H, ArH), 9.23 (d, *J* = 8.3 Hz, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.9, 26.0, 29.7, 44.1, 68.7, 98.6, 122.7, 124.4 (*J* = 272.5 Hz), 126.8, 127.8 (*J* = 30.0 Hz), 128.7, 128.7, 128.8, 129.0, 131.5, 141.7, 144.5, 154.6, 166.8; HRMS (TOF ES^+): *m/z* calcd for $C_{19}H_{18}F_3N_2O_2$ [$(M+H)^+$], 363.1315; found, 363.1314.

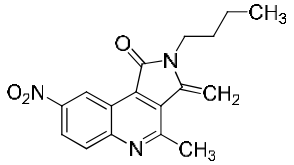
2-(furan-2-ylmethyl)-4-methyl-3-methylene-6-(trifluoromethyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-

one (6e′)



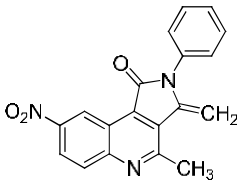
White solid; mp 141–143 °C; IR (KBr): 1705, 1630, 1509, 1346, 1135, 1083, 1011, 952, 848, 771, 676, 642 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.02 (s, 3H, CH_3), 5.08 (s, 2H, CH_2), 5.50 (d, J = 3.0 Hz, 1H, C=CH_2), 5.66 (d, J = 3.0 Hz, 1H, C=CH_2), 6.35 (d, J = 4.2 Hz, 2H, CH), 7.38 (s, 1H, CH), 7.69–7.72 (m, 1H, ArH), 8.12 (d, J = 7.3 Hz, 1H, ArH), 9.24 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.8, 36.6, 98.2, 108.8, 111.0, 122.7, 124.3 (J = 271.3 Hz), 126.9, 127.8 (J = 28.8 Hz), 128.6, 128.9, 129.0, 131.4, 140.9, 142.9, 144.5, 150.0, 154.6, 166.1; HRMS (TOF ES^+): *m/z* calcd for $C_{19}H_{14}F_3N_2O_2$ $[(M+H)^+]$, 359.1002; found, 359.1005

2-butyl-4-methyl-3-methylene-8-nitro-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6f′)



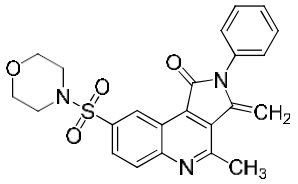
Yellow solid; mp 203–205 °C; IR (KBr): 1698, 1634, 1495, 1395, 1229, 1080, 913, 845, 760, 633, 573 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$): δ = 0.99–1.02 (m, 3H, CH_3), 1.42–1.49 (m, 2H, CH_2), 1.71–1.77 (m, 2H, CH_2), 3.04 (s, 3H, CH_3), 3.90–3.93 (m, 2H, CH_2), 5.37 (d, J = 2.9 Hz, 1H, C=CH_2), 5.69 (d, J = 2.9 Hz, 1H, C=CH_2), 8.19 (d, J = 8.3 Hz, 1H, ArH), 8.50–8.52 (m, 1H, ArH), 9.86 (d, J = 2.4 Hz, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 20.6, 25.7, 31.0, 39.8, 98.1, 121.2, 121.6, 124.1, 129.5, 130.7, 133.4, 141.1, 146.8, 149.9, 157.5, 165.6; HRMS (TOF ES^+): *m/z* calcd for $C_{17}H_{18}N_3O_3$ $[(M+H)^+]$, 312.1343; found, 312.1349.

4-methyl-3-methylene-8-nitro-2-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6g′)



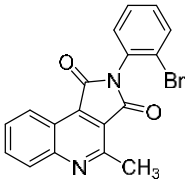
Yellow solid; mp 226–228 °C; IR (KBr): 1700, 1528, 1498, 1379, 1337, 1117, 917, 887, 723 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.10 (s, 3H, CH_3), 5.27 (d, J = 2.7 Hz, 1H, C=CH_2), 5.73 (d, J = 2.7 Hz, 1H, C=CH_2), 7.43 (d, J = 7.6 Hz, 2H, ArH), 7.51–7.54 (m, 1H, ArH), 7.59–7.62 (m, 2H, ArH), 8.25 (d, J = 9.35 Hz, 1H, ArH), 8.54–8.56 (m, 1H, ArH), 9.90 (d, J = 2.5 Hz, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.8, 100.2, 121.3, 121.6, 124.3, 128.9, 128.9, 129.3, 129.4, 130.1, 130.1, 130.8, 132.8, 133.9, 142.5, 146.9, 150.1, 157.7, 165.3; HRMS (TOF ES^+): *m/z* calcd for $C_{19}H_{14}N_3O_3$ $[(M+H)^+]$, 332.1030; found, 332.1032.

4-methyl-3-methylene-8-(morpholinosulfonyl)-2-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (6h′)



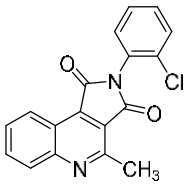
Yellow solid; mp 224–226 °C; IR (KBr): 1708, 1631, 1499, 1265, 1163, 1112, 947, 839, 741, 635, 599 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 3.10 (s, 3H, CH_3), 3.11–3.13 (m, 4H, CH_2), 3.74–3.76 (m, 4H, CH_2), 5.25 (d, J = 2.8 Hz, 1H, C=CH_2), 5.72 (d, J = 2.8 Hz, 1H, C=CH_2), 7.43 (d, J = 7.5 Hz, 2H, ArH), 7.50–7.53 (m, 1H, ArH), 7.58–7.61 (m, 2H, ArH), 8.10–8.12 (m, 1H, ArH), 8.29 (d, J = 8.9 Hz, 1H, ArH), 9.47 (d, J = 2.0 Hz, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.7, 46.5, 46.5, 66.5, 66.5, 100.0, 121.6, 125.7, 128.3, 128.9, 128.9, 129.3, 130.1, 130.1, 130.1, 130.5, 132.2, 133.9, 135.3, 142.7, 149.4, 157.0, 165.6; HRMS (TOF ES^+): *m/z* calcd for $C_{23}H_{21}N_3NaO_4S$ [$(M+Na)^+$], 458.1145; found, 458.1149.

2-(2-bromophenyl)-4-methyl-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (7a).



White solid; mp 202–204 °C; IR (KBr): 1712, 1625, 1476, 1371, 1126, 1096, 1028, 754, 737, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.10 (s, 3H, C–CH_3), 7.38–7.42 (m, 2H, ArH), 7.48–7.52 (m, 1H, ArH), 7.72–7.79 (m, 2H, ArH), 7.89–7.94 (m, 1H, ArH), 8.17 (d, J = 8.4 Hz, 1H, ArH), 8.84 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.3, 120.8, 121.8, 123.4, 125.1, 128.5, 129.2, 129.4, 131.0, 131.0, 131.2, 133.0, 133.7, 135.8, 151.8, 155.4, 166.6, 166.8; HRMS (TOF ES+): m/z calcd for $C_{18}H_{12}BrN_2O_2$ [$(M+H)^+$], 367.0082; found, 367.0085.

2-(2-chlorophenyl)-4-methyl-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (7b).



White solid; mp 184–186 °C; IR (KBr): 1714, 1624, 1483, 1373, 1115, 1065, 1029, 754, 737, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.10 (s, 3H, C–CH_3), 7.40–7.47 (m, 3H, ArH), 7.59–7.61 (m, 1H, ArH), 7.71–7.75 (m, 1H, ArH), 7.89–7.93 (m, 1H, ArH), 8.16 (d, J = 8.8 Hz, 1H, ArH), 8.83 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.3, 120.8, 121.8, 125.1, 127.8, 129.2, 129.2, 129.4, 130.5, 130.8, 130.9, 133.0, 133.3, 135.9, 151.8, 155.4, 166.6, 166.8; HRMS (TOF ES+): m/z calcd for $C_{18}H_{12}ClN_2O_2$ [$(M+H)^+$], 323.0587; found, 323.0588.

4. X-ray Structure and Data[3] of 6p (CCDC 1438897)

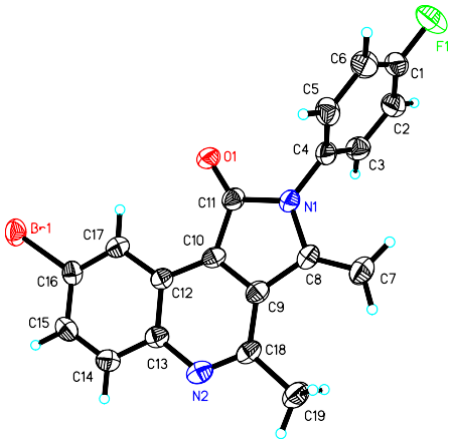


Figure S1 X-Ray crystal structure of **6p**

Table S1 Crystal data and structure refinement for **6p**

Empirical formula	$C_{19}H_{12}BrFN_2O$
Formula weight	383.22
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 17.326(3) A alpha = 90.00 deg.
	b = 17.185(3) A beta = 108.741(2) deg.
	c = 11.370(2) A gamma = 90.00 deg.
Volume	3205.9(10) A^3
Z, Calculated density	8, 1.588 Mg/m^3
Absorption coefficient	2.583 mm^-1
F(000)	1536
Crystal size	0.32 x 0.20 x 0.18 mm
Theta range for data collection	2.37 to 18.34 deg.
Limiting indices	-22<=h<=22, -22<=k<=22, -14<=l<=15
Reflection collected/unique	15065/3819[R(int) =0.0885]
Completeness to theta = 28.24	96.1%
Absorption correction	fine-focus sealed tube
Max. and min. transmission	0.9506 and 0.9811
Refinement method	phi and omega scans
Data/restraints/parameters	3819 / 0 / 218

Goodness-of-fit on F^2	0.919
Final R indices [I>2sigma(I)]	R1 = 0.1492, wR2 = 0.1347
R indices (all data)	R1 = 0.0480, wR2 = 0.1003
Semi-empirical from equivalents	0.287 and -0.354 e.A^-3

Table S2 Bond lengths [A] and angles [deg] for **6p**

F(1)-C(1)	1.351(4)
F(2)-C(12)	1.361(4)
N(1)-C(7)	1.325(4)
N(1)-C(15)	1.379(4)
N(2)-C(17)	1.378(4)
N(2)-C(18)	1.429(4)
N(2)-C(16)	1.443(4)
O(1)-C(25)	1.352(5)
O(1)-C(16)	1.442(4)
O(2)-C(17)	1.212(4)
O(3)-C(24)	1.375(5)
O(3)-C(21)	1.376(4)
O(4)-C(25)	1.179(5)
C(1)-C(2)	1.353(5)
C(1)-C(6)	1.366(5)
C(2)-C(3)	1.383(5)
C(2)-H(2)	0.9300
C(3)-C(4)	1.386(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.383(5)
C(4)-C(7)	1.483(4)
C(5)-C(6)	1.378(5)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-C(8)	1.404(4)
C(8)-C(9)	1.354(4)
C(8)-C(16)	1.500(4)
C(9)-C(10)	1.424(4)
C(9)-C(17)	1.486(5)
C(10)-C(11)	1.410(4)
C(10)-C(15)	1.411(4)
C(11)-C(12)	1.348(5)
C(11)-H(11)	0.9300
C(12)-C(13)	1.380(5)
C(13)-C(14)	1.360(4)
C(13)-H(13)	0.9300
C(14)-C(15)	1.410(4)

C(14)-H(14)	0.9300
C(16)-H(16)	0.9800
C(18)-C(23)	1.377(5)
C(18)-C(19)	1.382(4)
C(19)-C(20)	1.374(5)
C(19)-H(19)	0.9300
C(20)-C(21)	1.363(5)
C(20)-H(20)	0.9300
C(21)-C(22)	1.383(5)
C(22)-C(23)	1.377(5)
C(22)-H(22)	0.9300
C(23)-H(23)	0.9300
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
C(25)-C(26)	1.495(6)
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600

5. NMR spectra (^{1}H NMR and ^{13}C NMR)

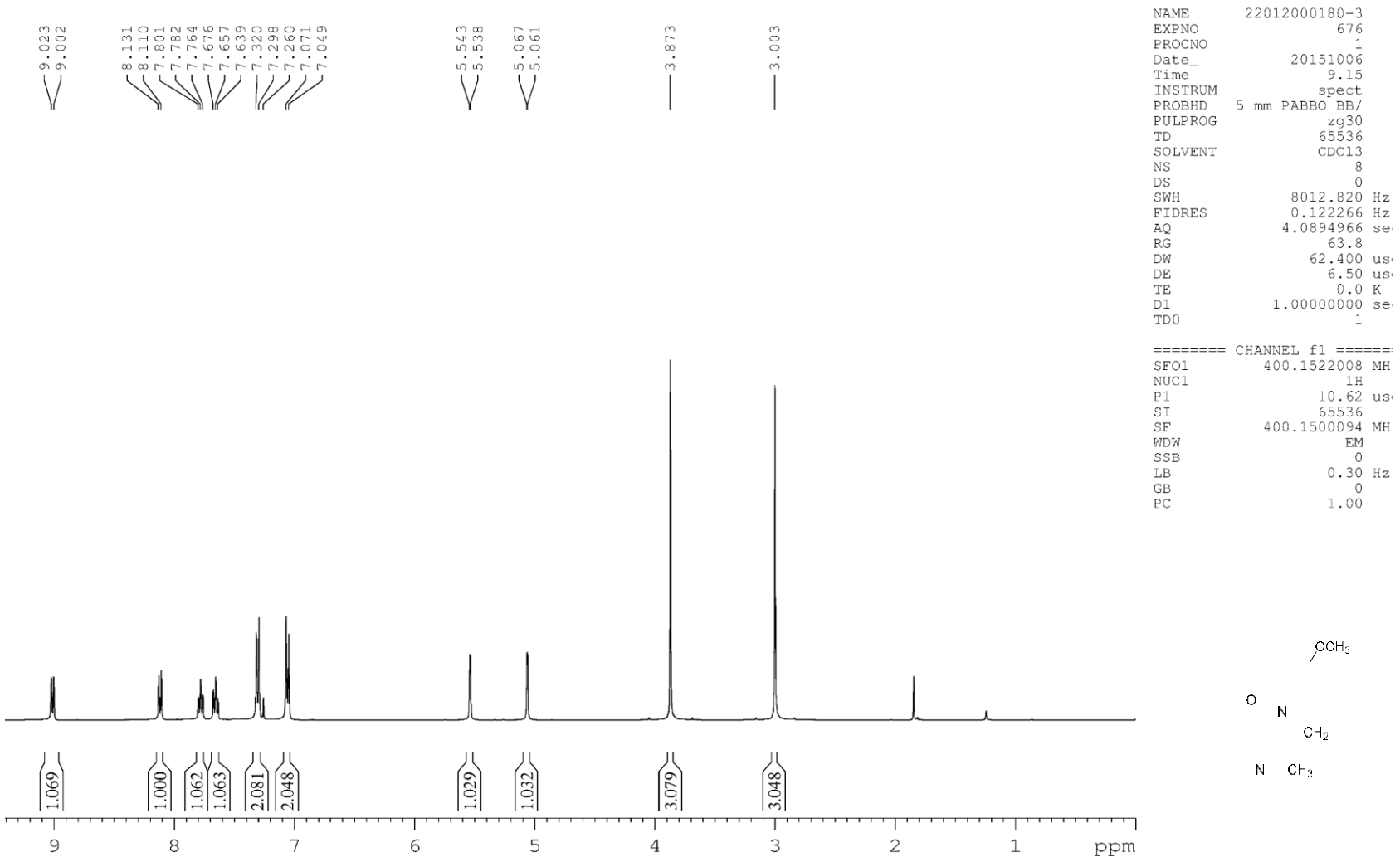


Figure 1. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6a**

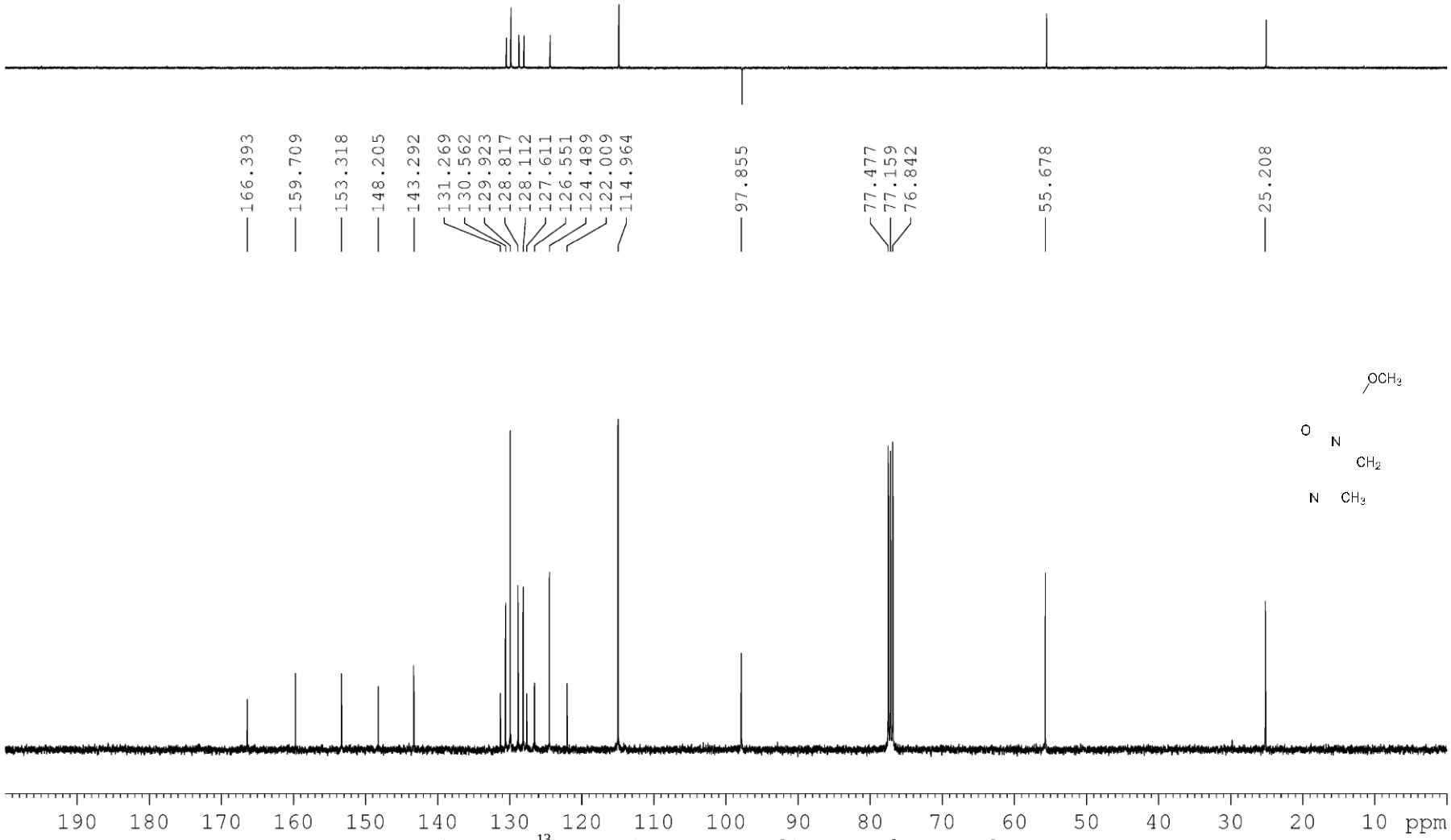


Figure 2. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6a**

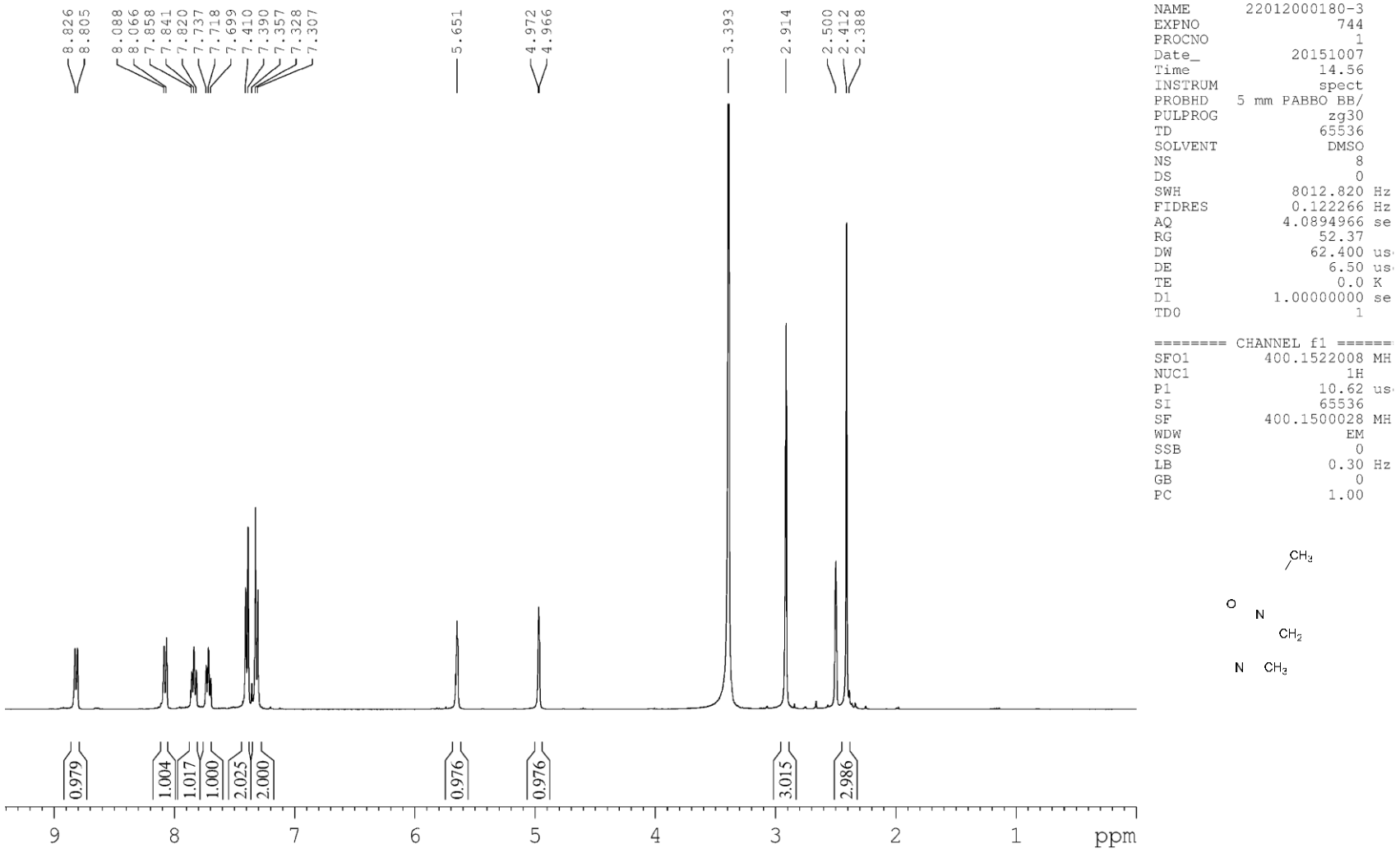


Figure 3. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **6b**

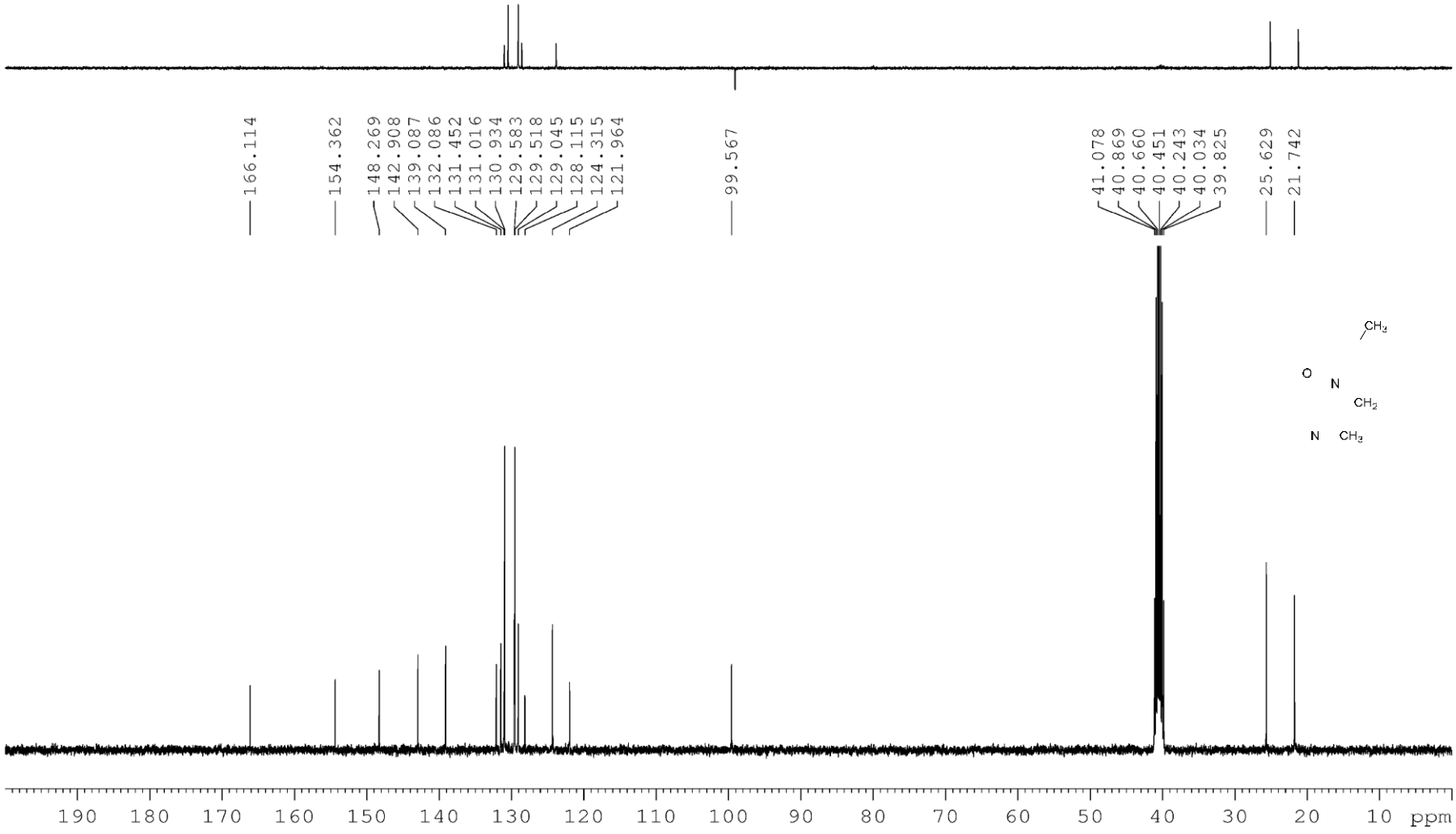


Figure 4. ^{13}C NMR (100 MHz, DMSO-d_6) spectra of compound **6b**

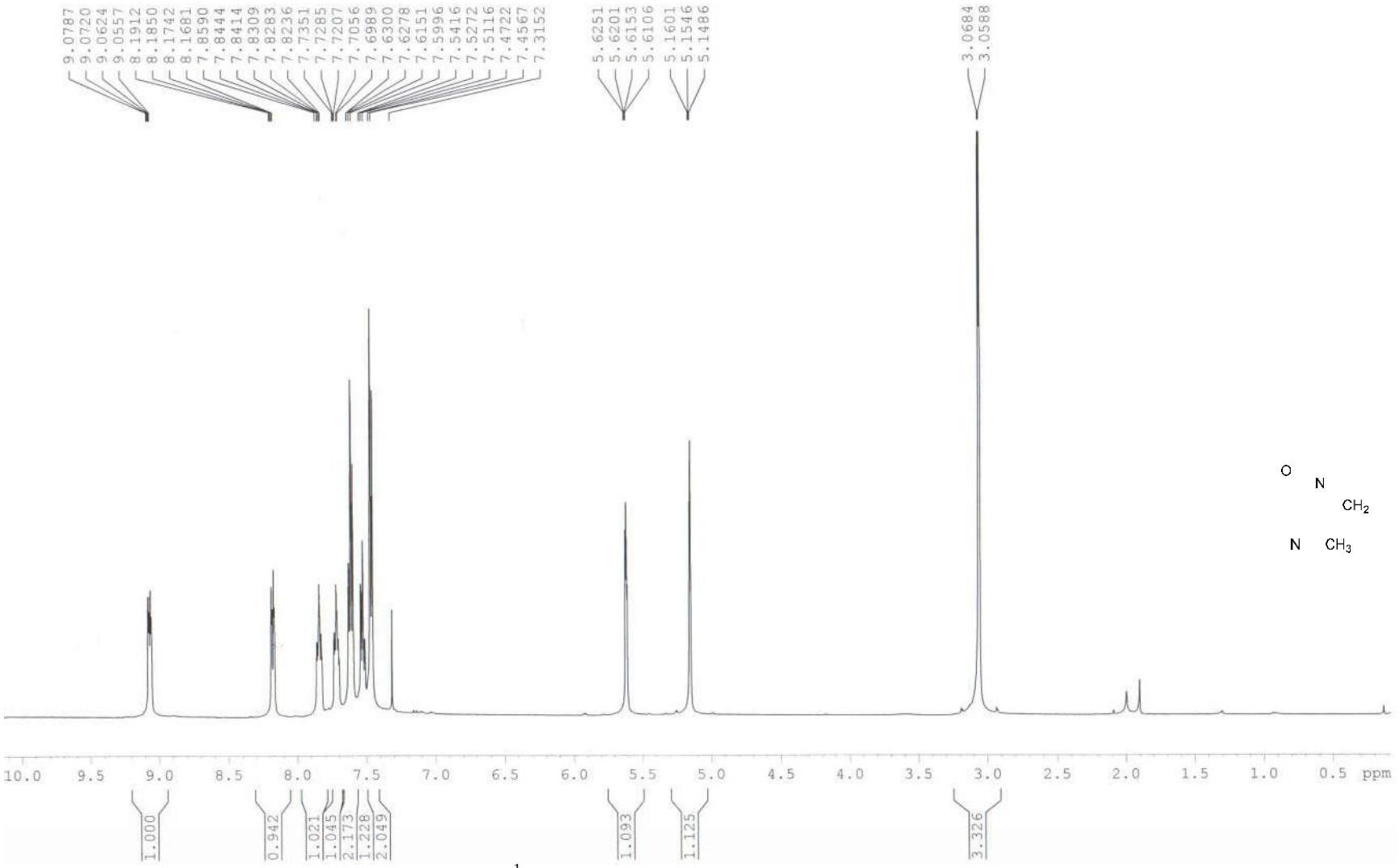


Figure 5. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **6c**

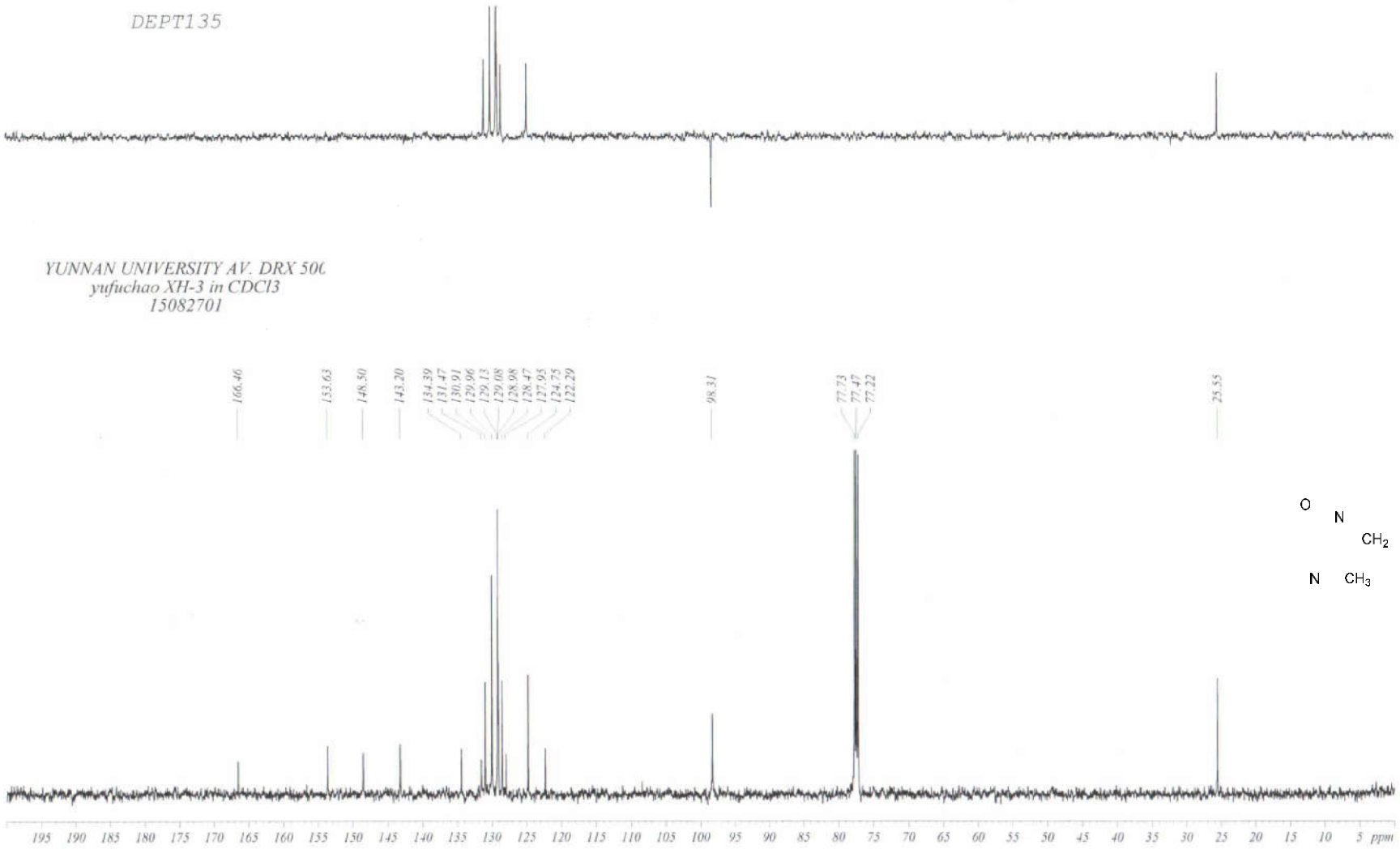


Figure 6. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **6c**

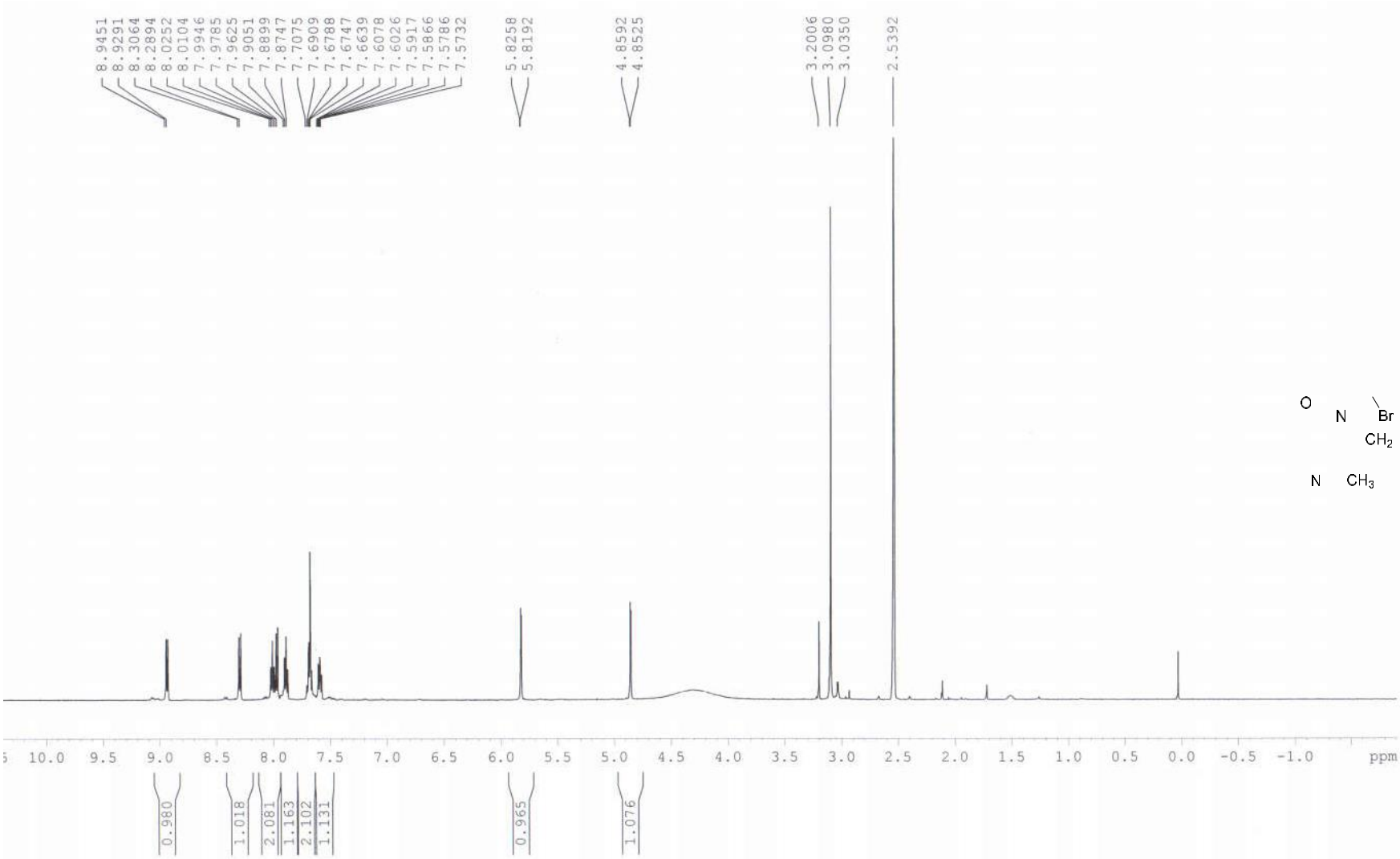


Figure 7. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **6d**

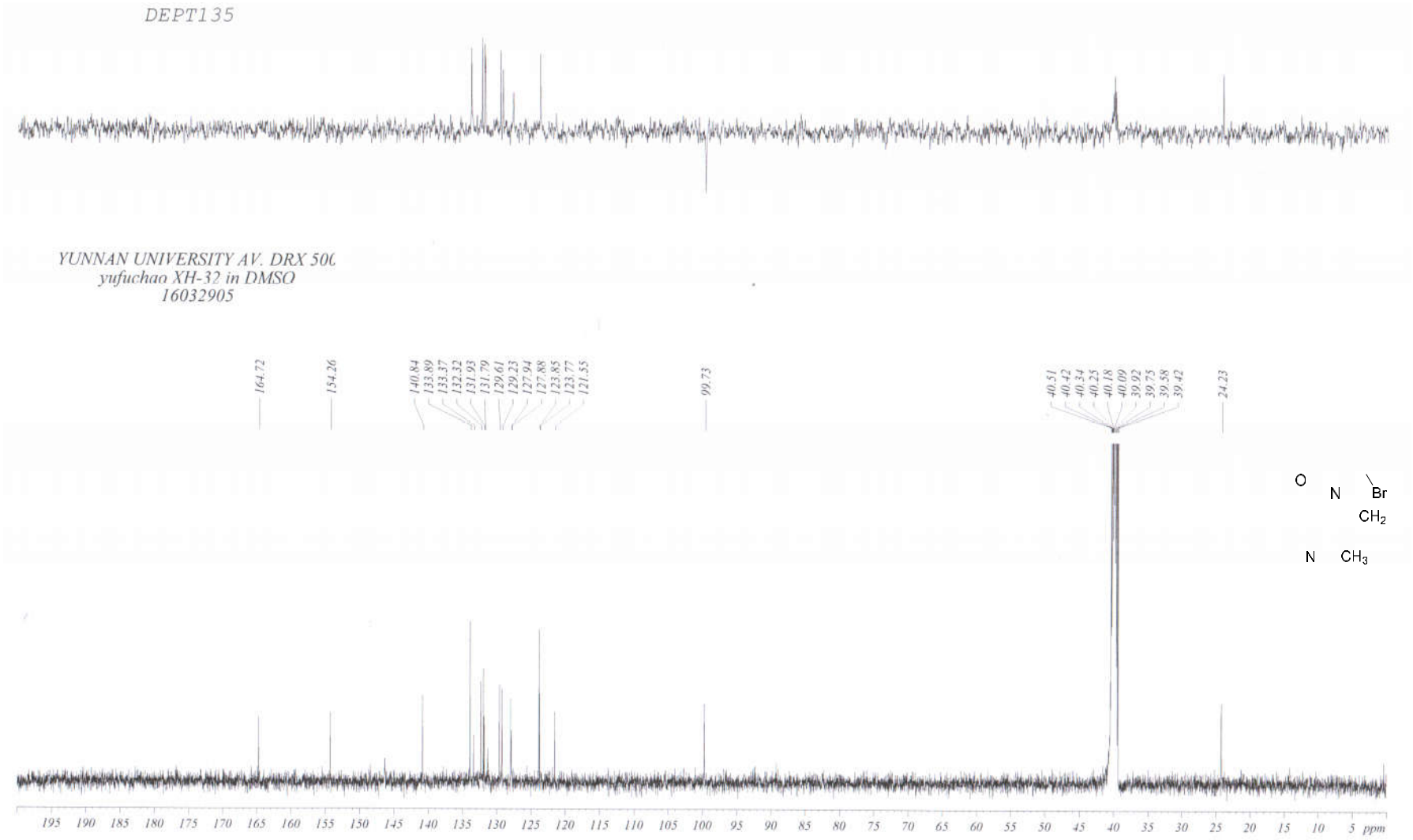


Figure 8. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **6d**

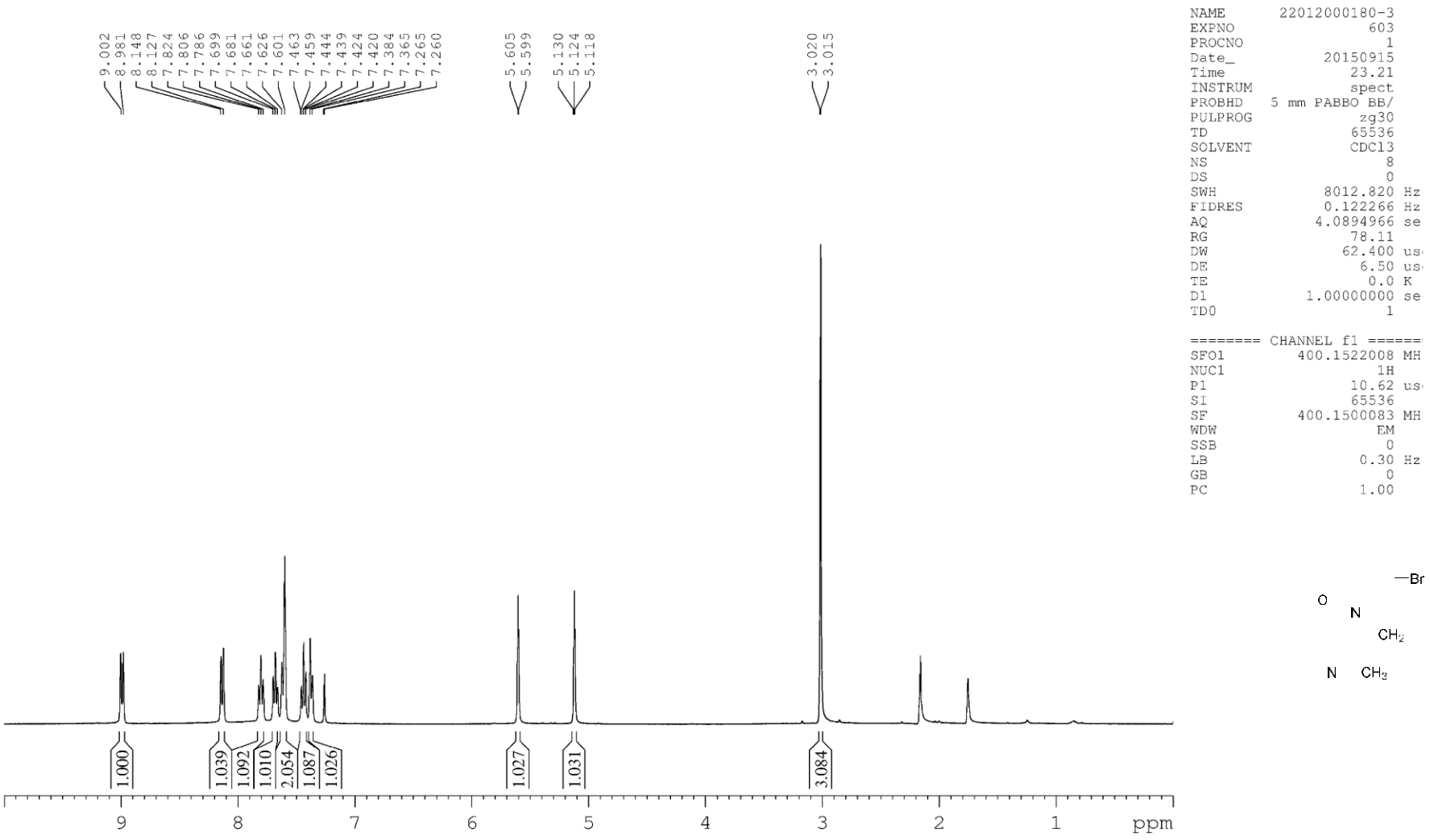


Figure 9. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6e**

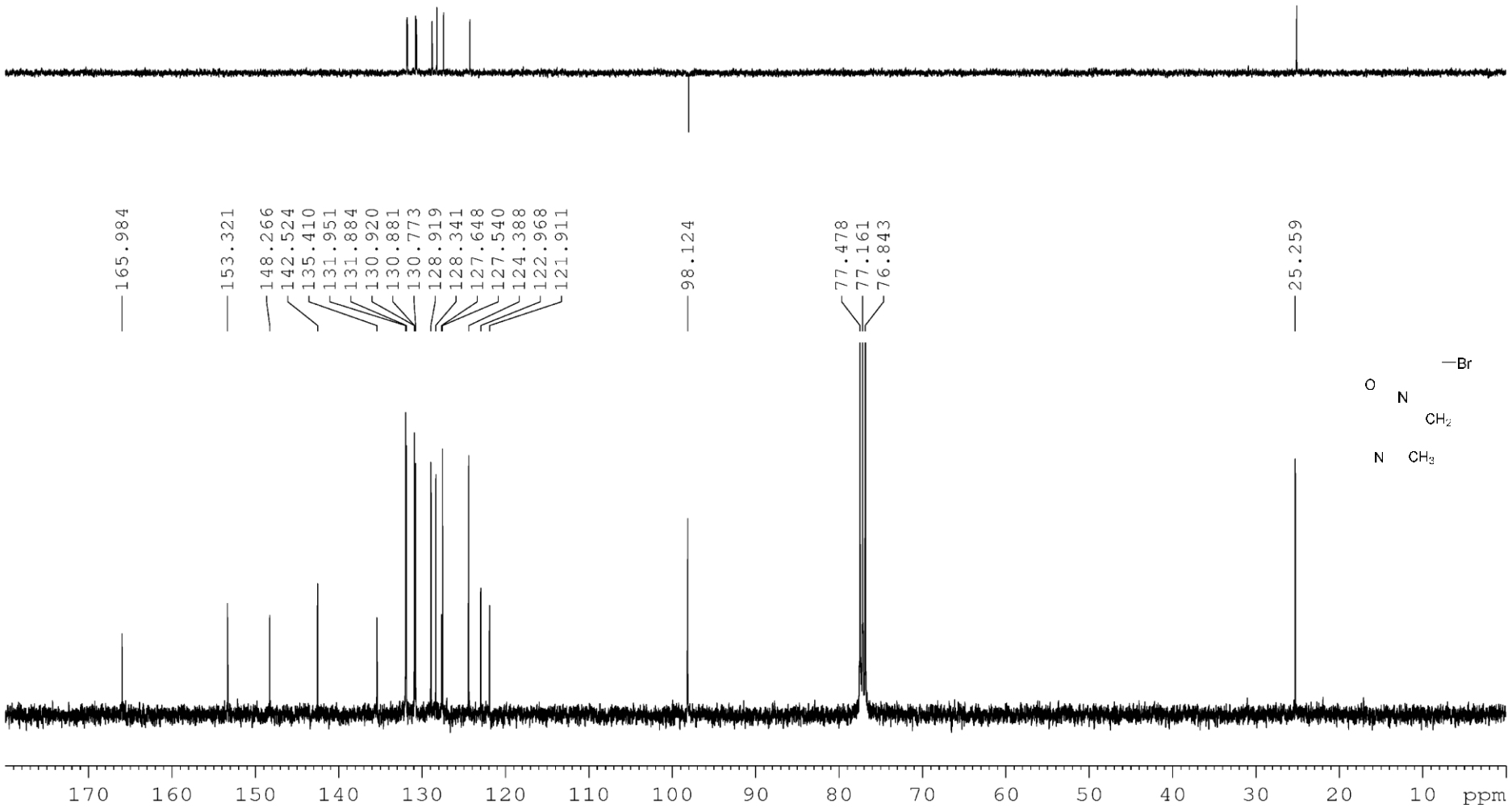


Figure 10. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6e**

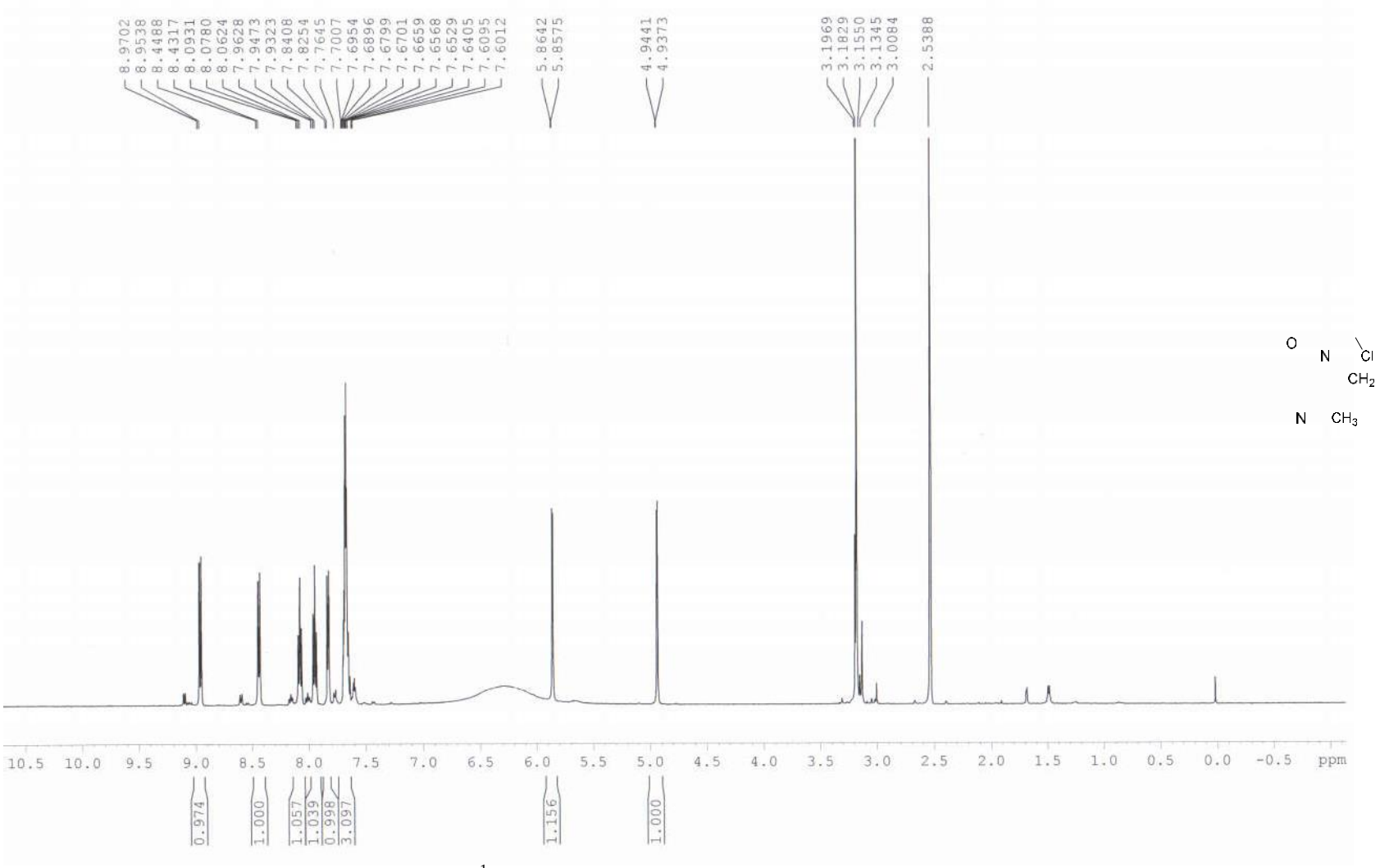


Figure 11. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **6f**

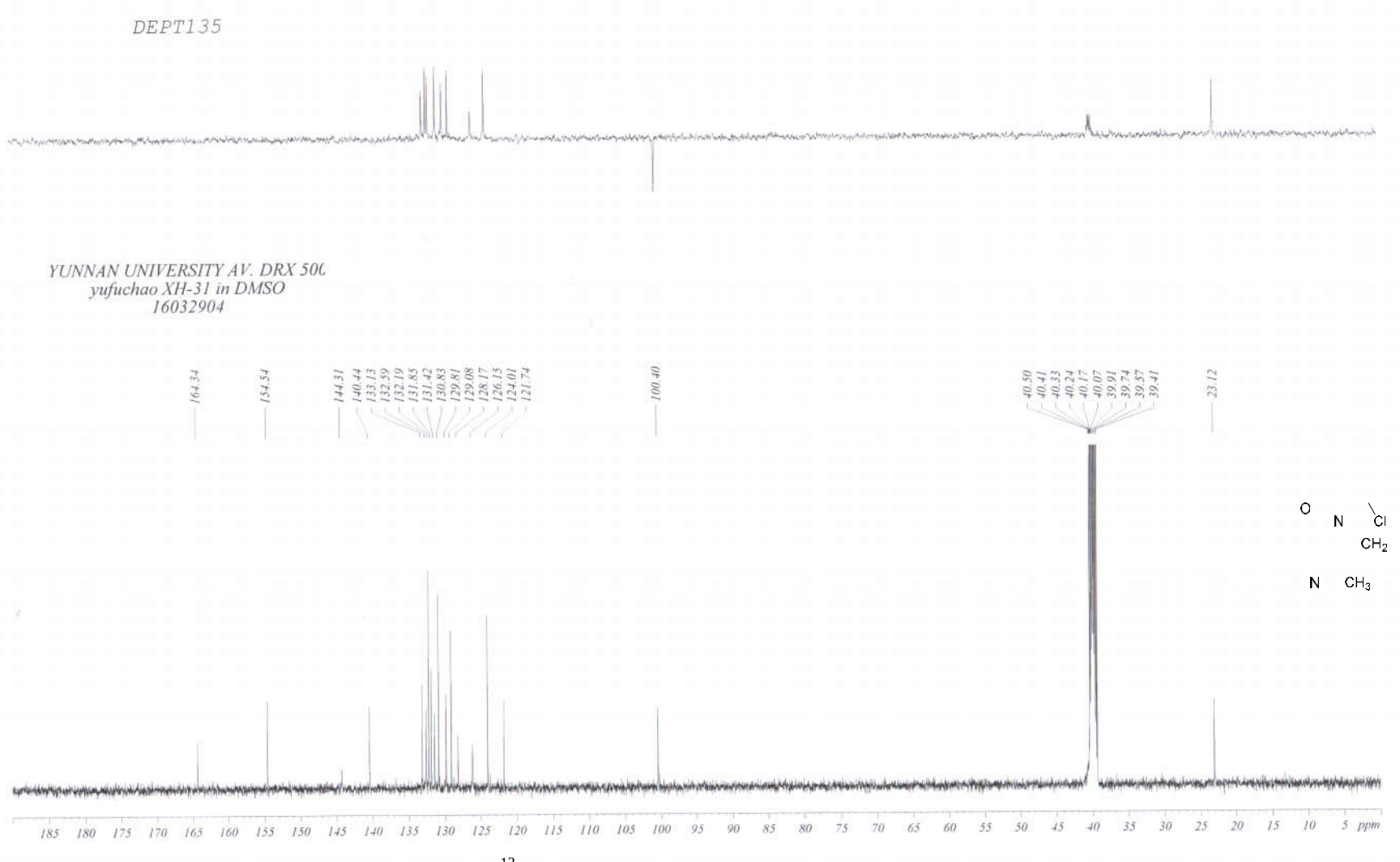


Figure 12. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **6f**

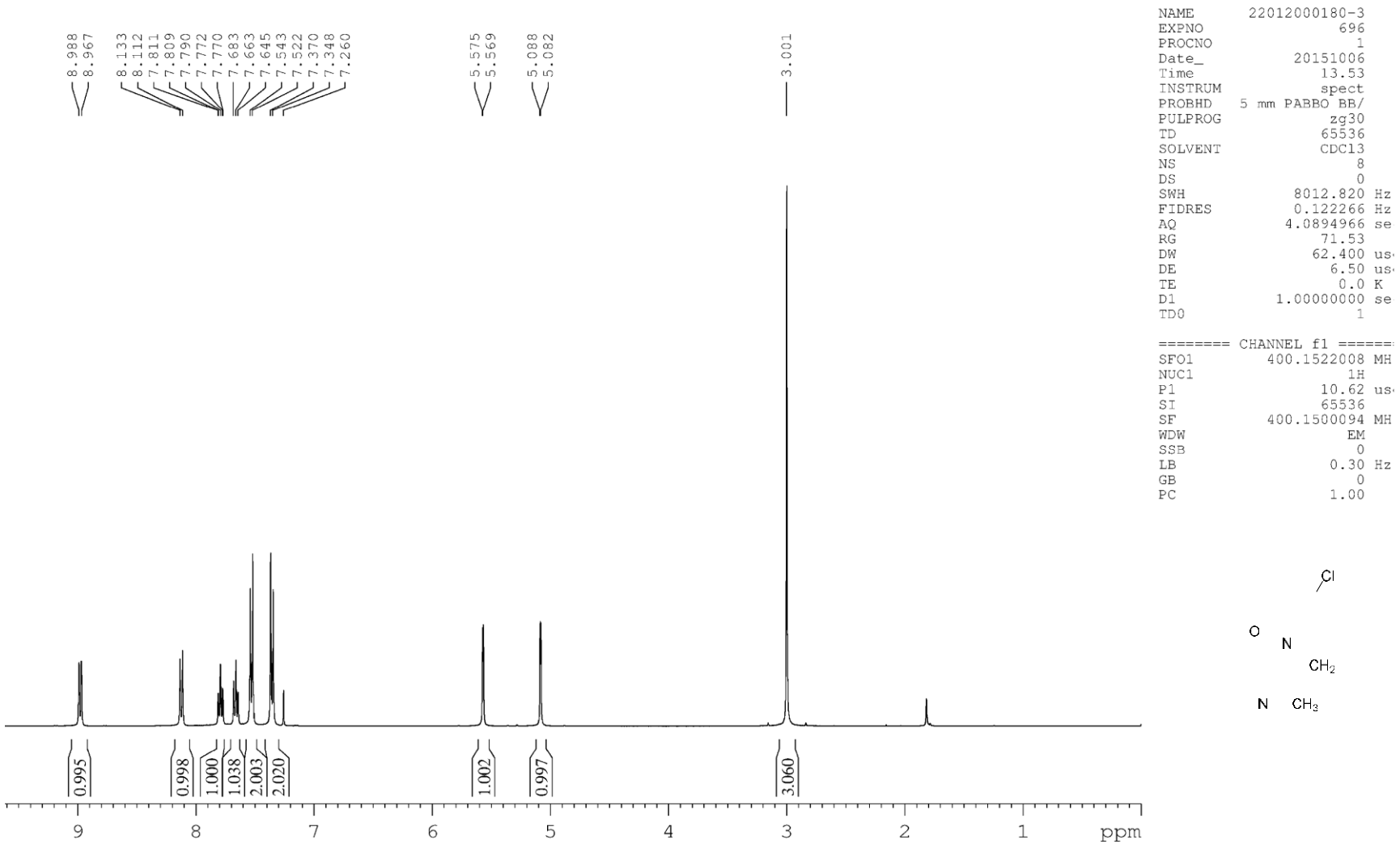


Figure 13. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6g**

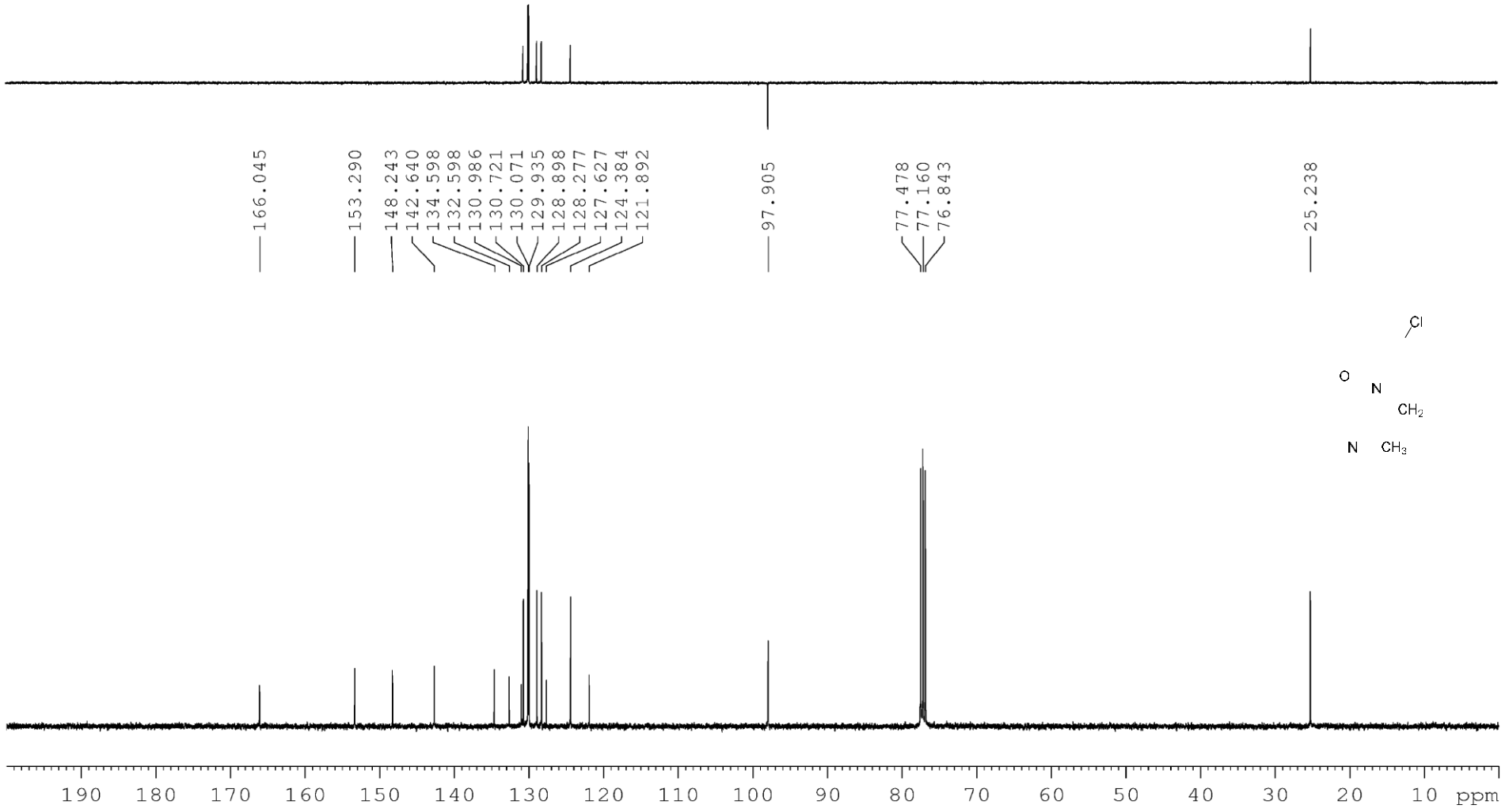


Figure 14. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6g**

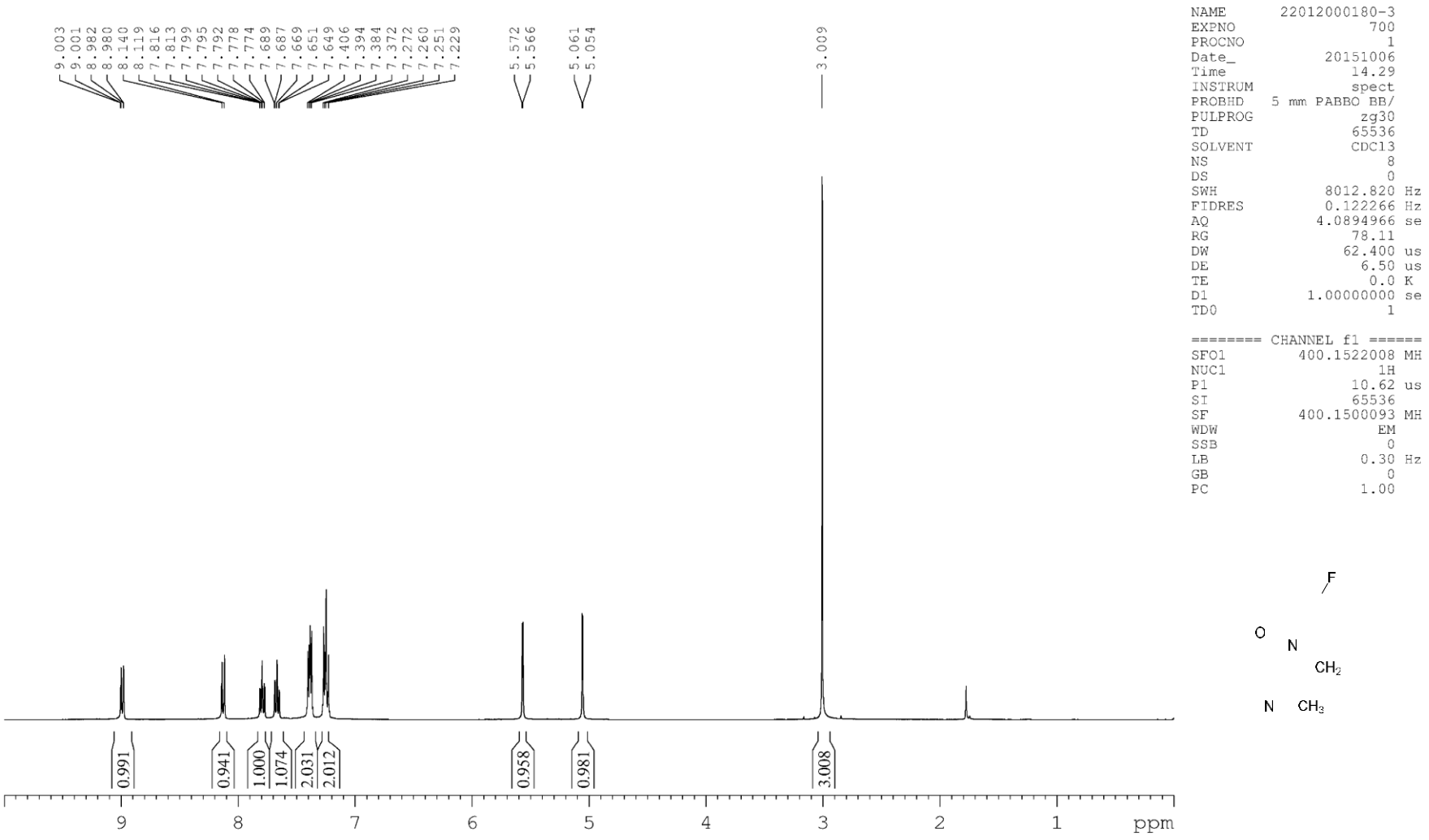


Figure 15. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6h**

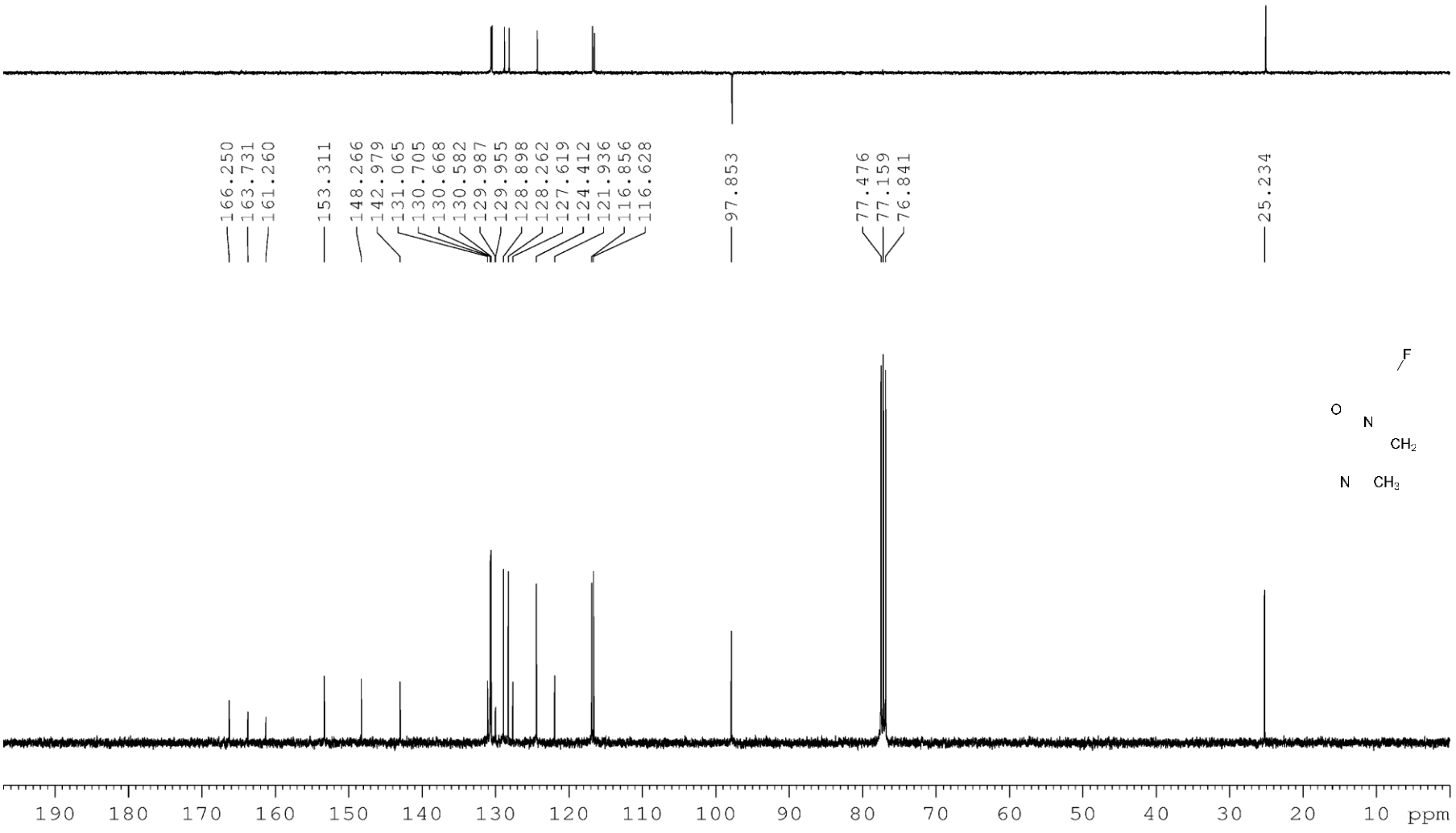


Figure 16. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6h**

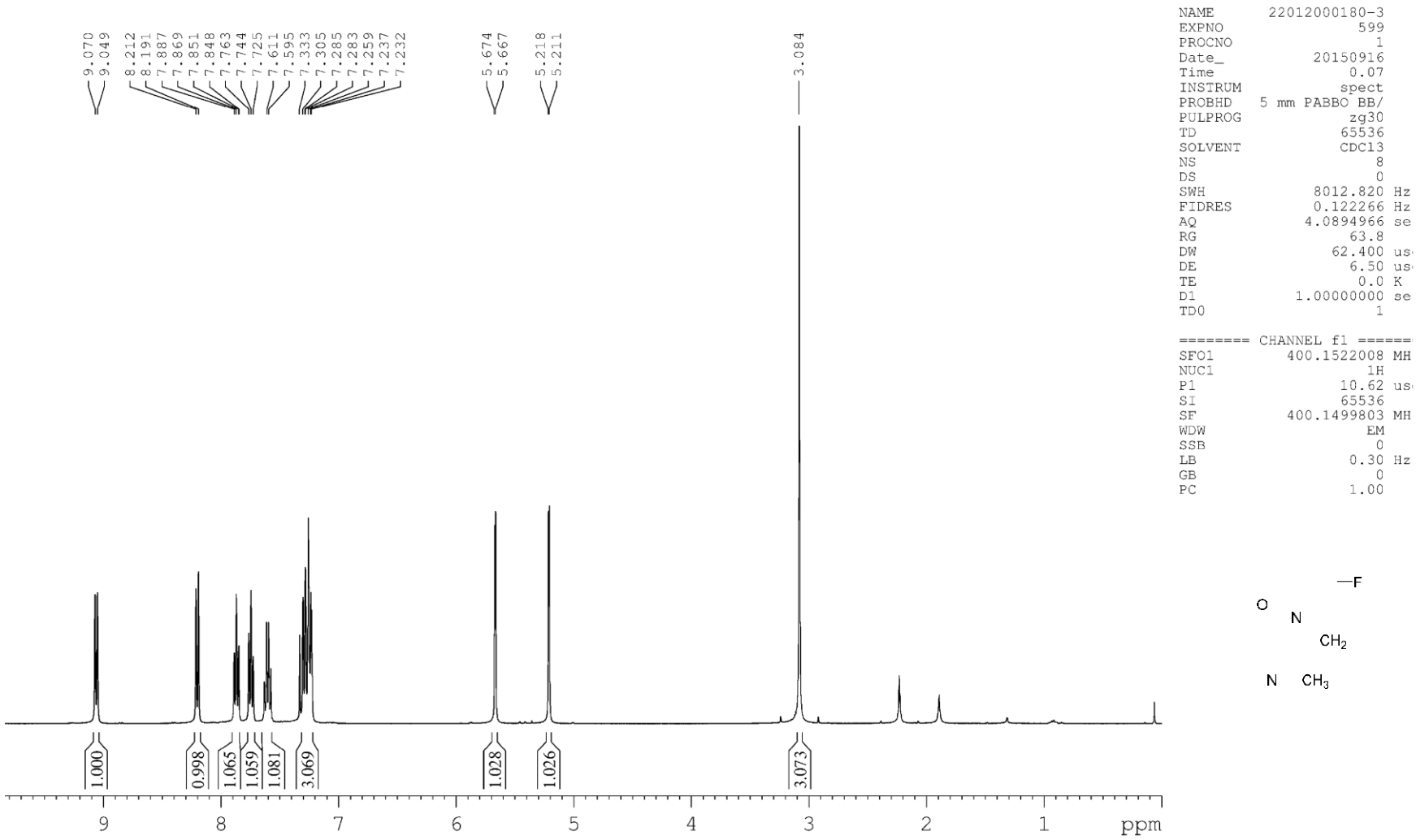


Figure 17. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6i**

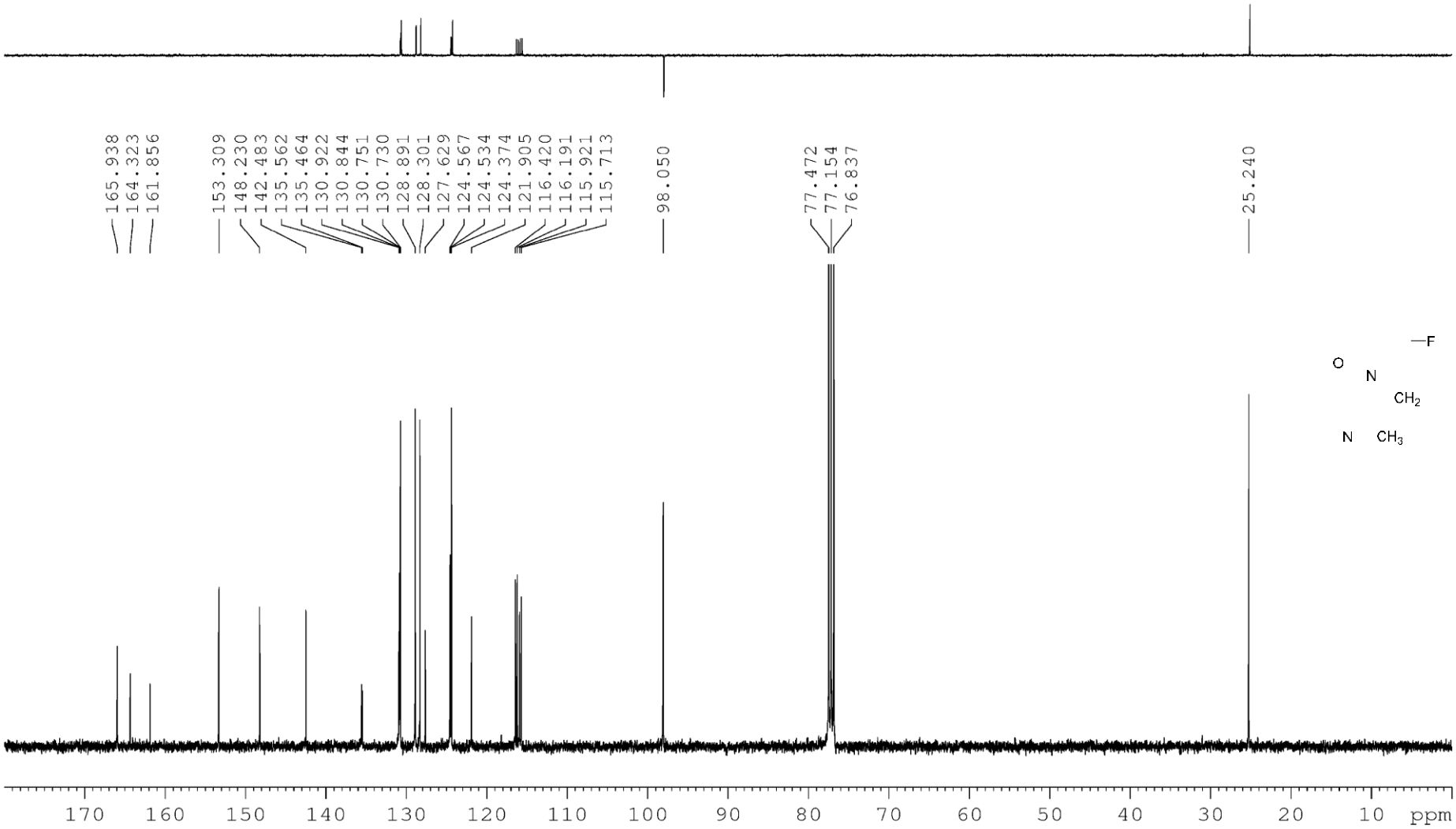


Figure 18. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6i**

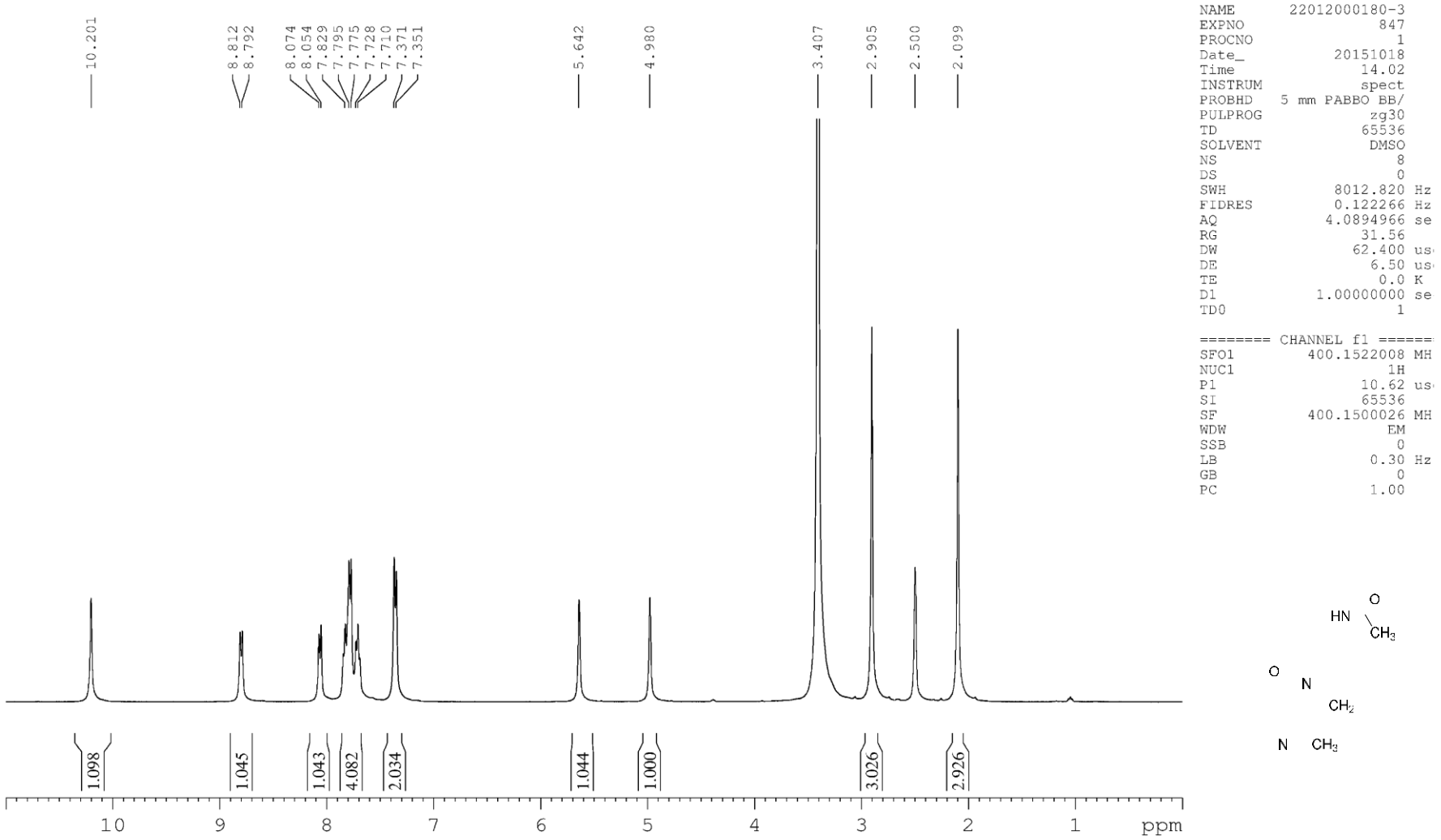


Figure 19. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **6j**

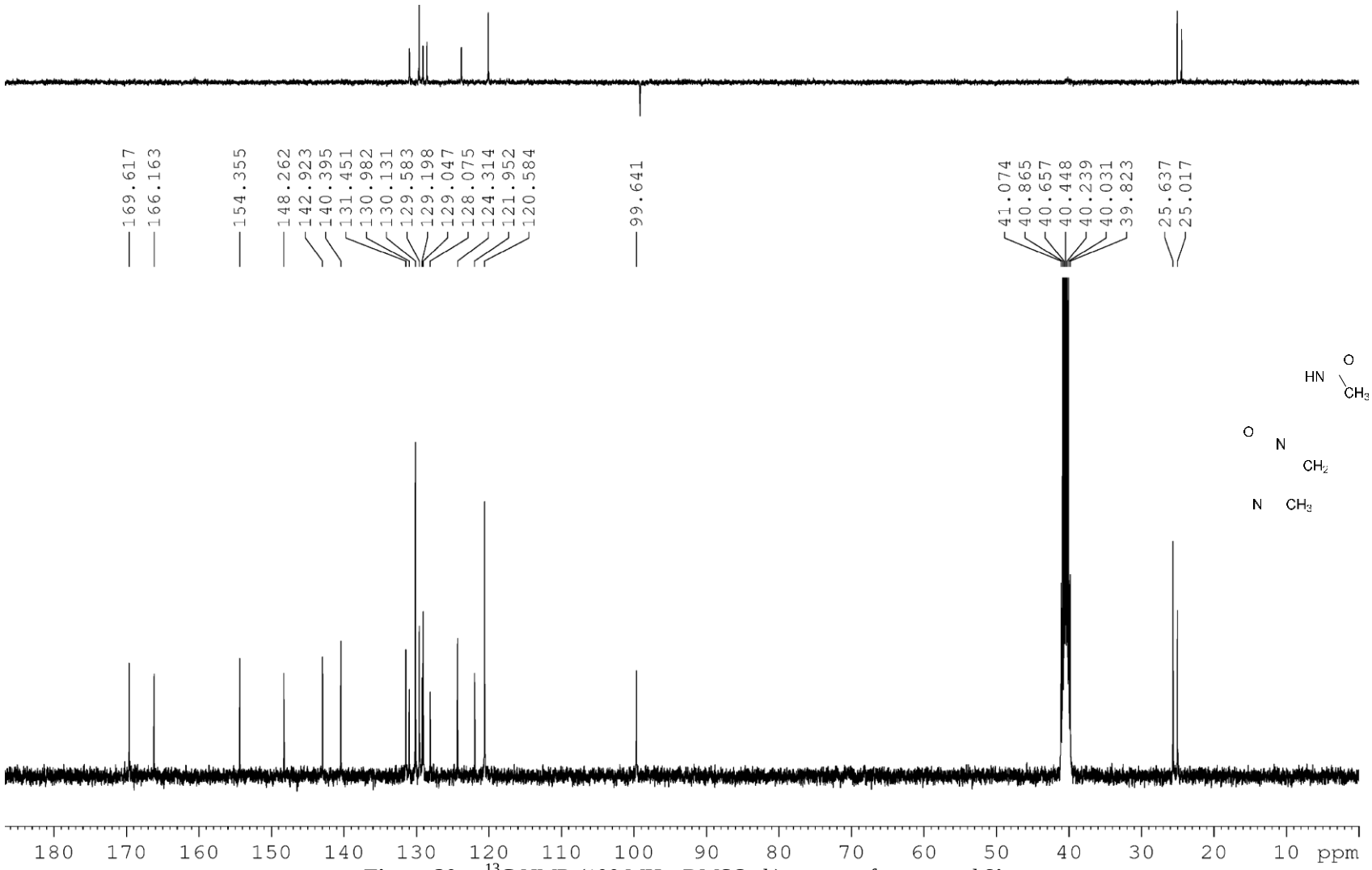


Figure 20. ^{13}C NMR (100 MHz, DMSO-d_6) spectra of compound **6j**

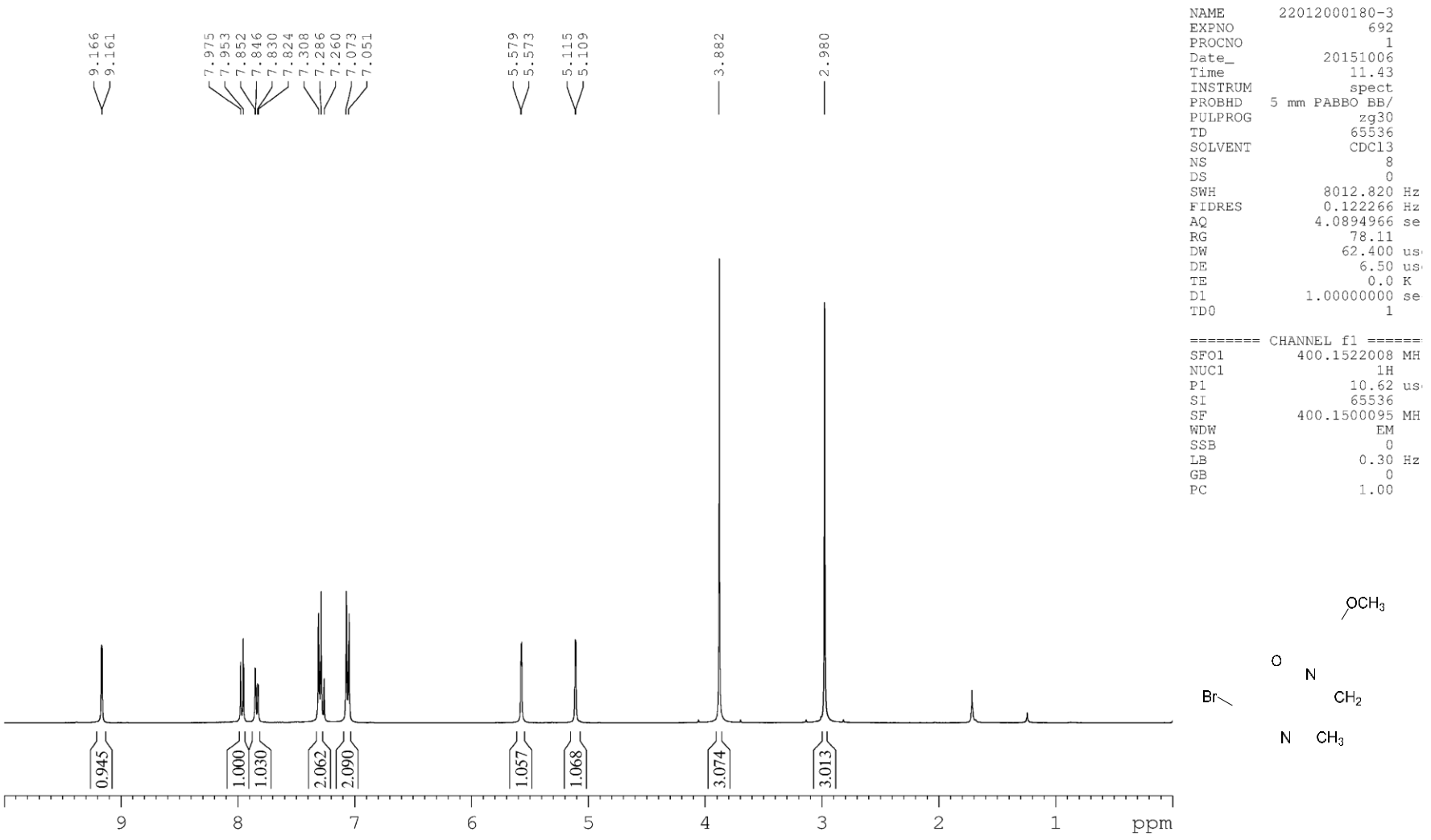


Figure 21. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6k**

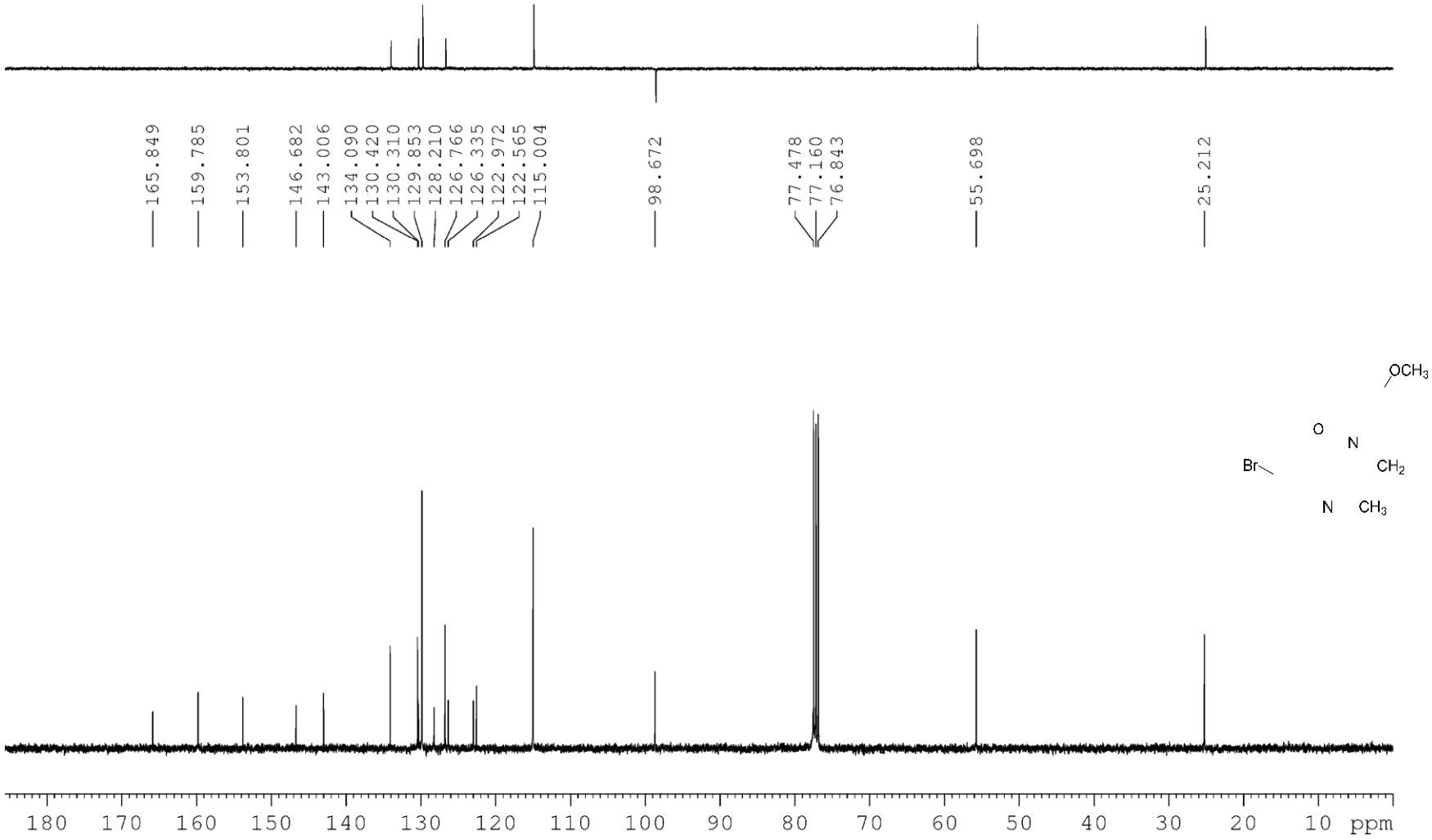


Figure 22. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6k**

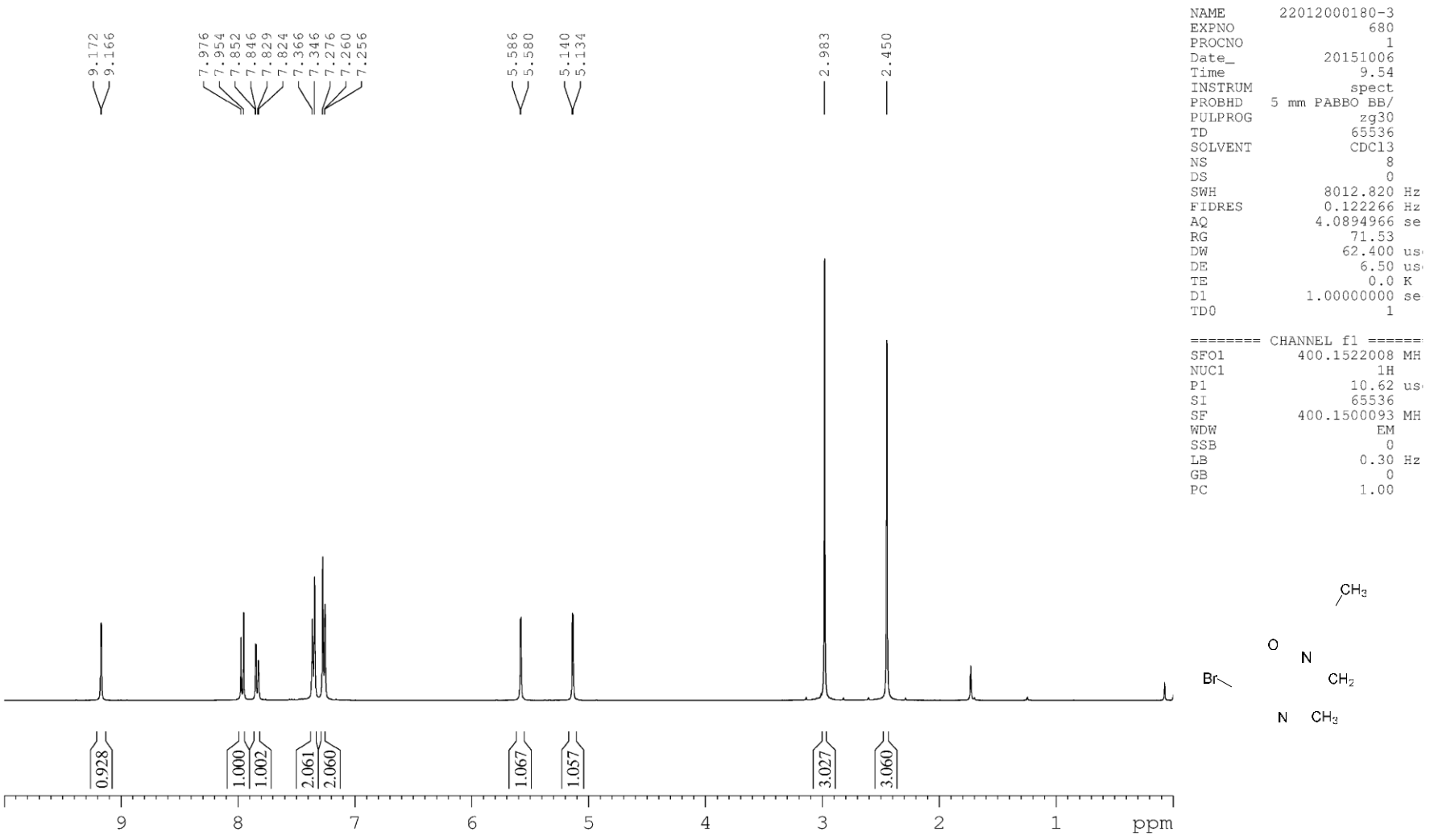


Figure 23. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6l**

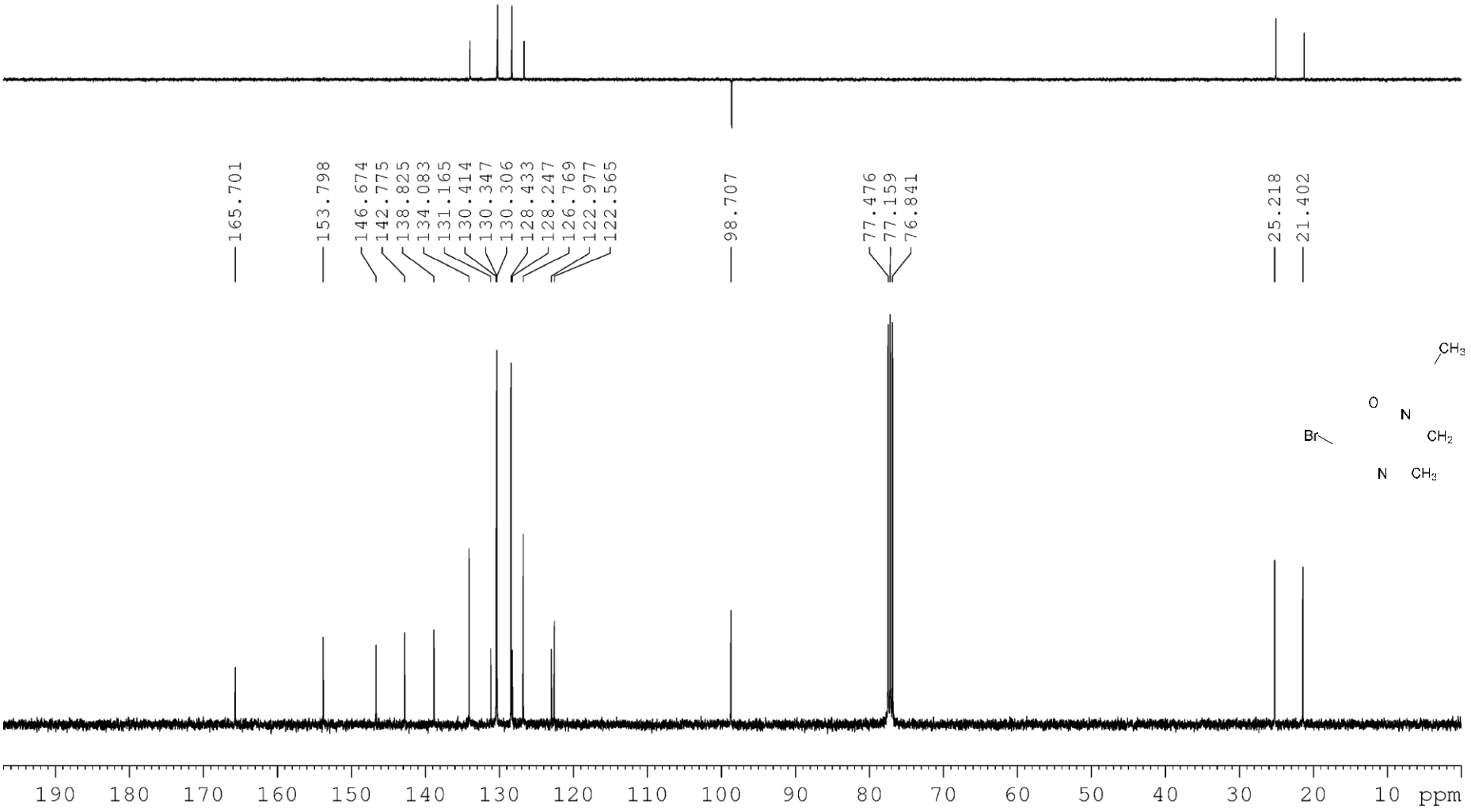


Figure 24. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6l**

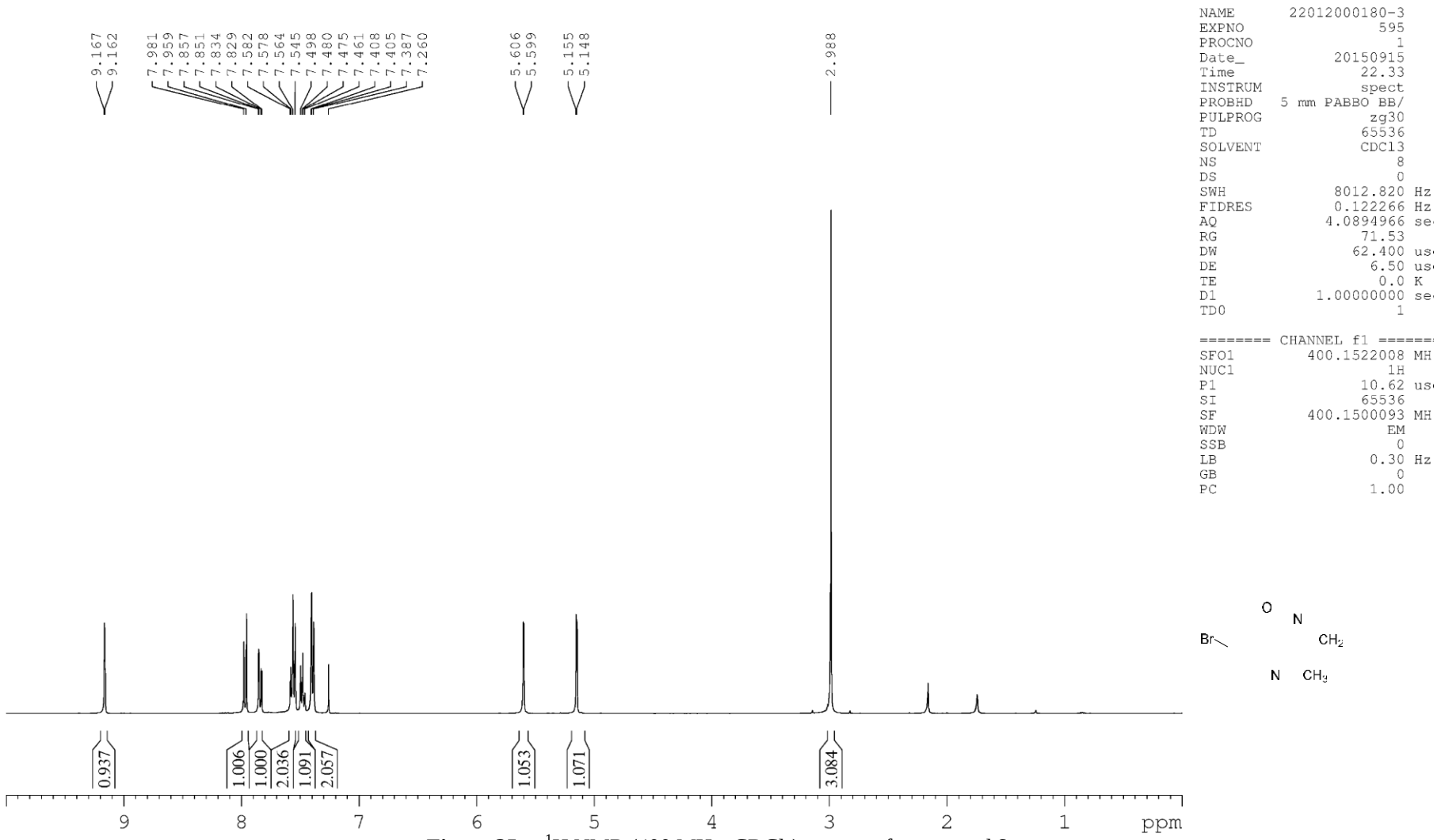


Figure 25. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6m**

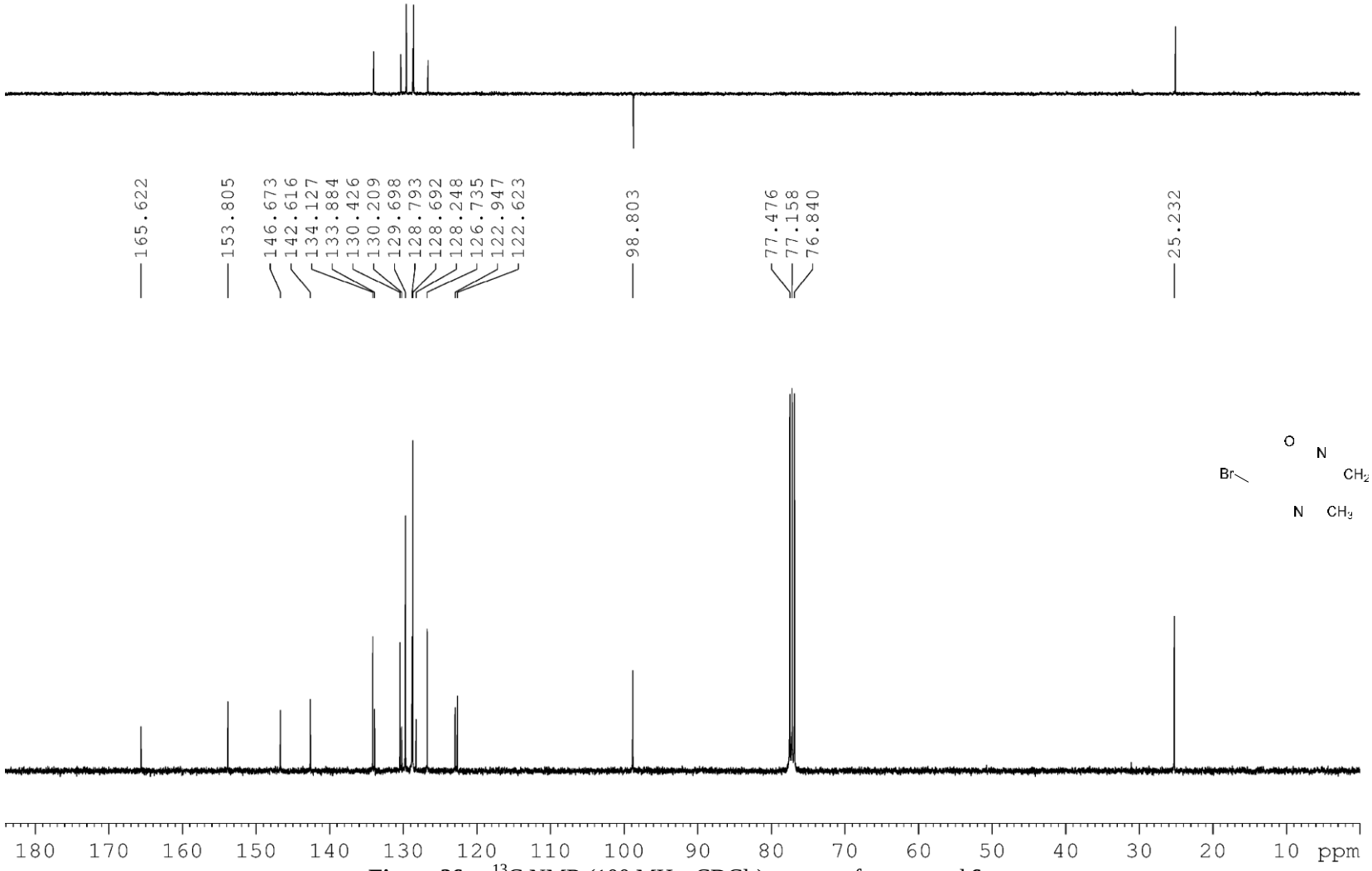


Figure 26. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6m**

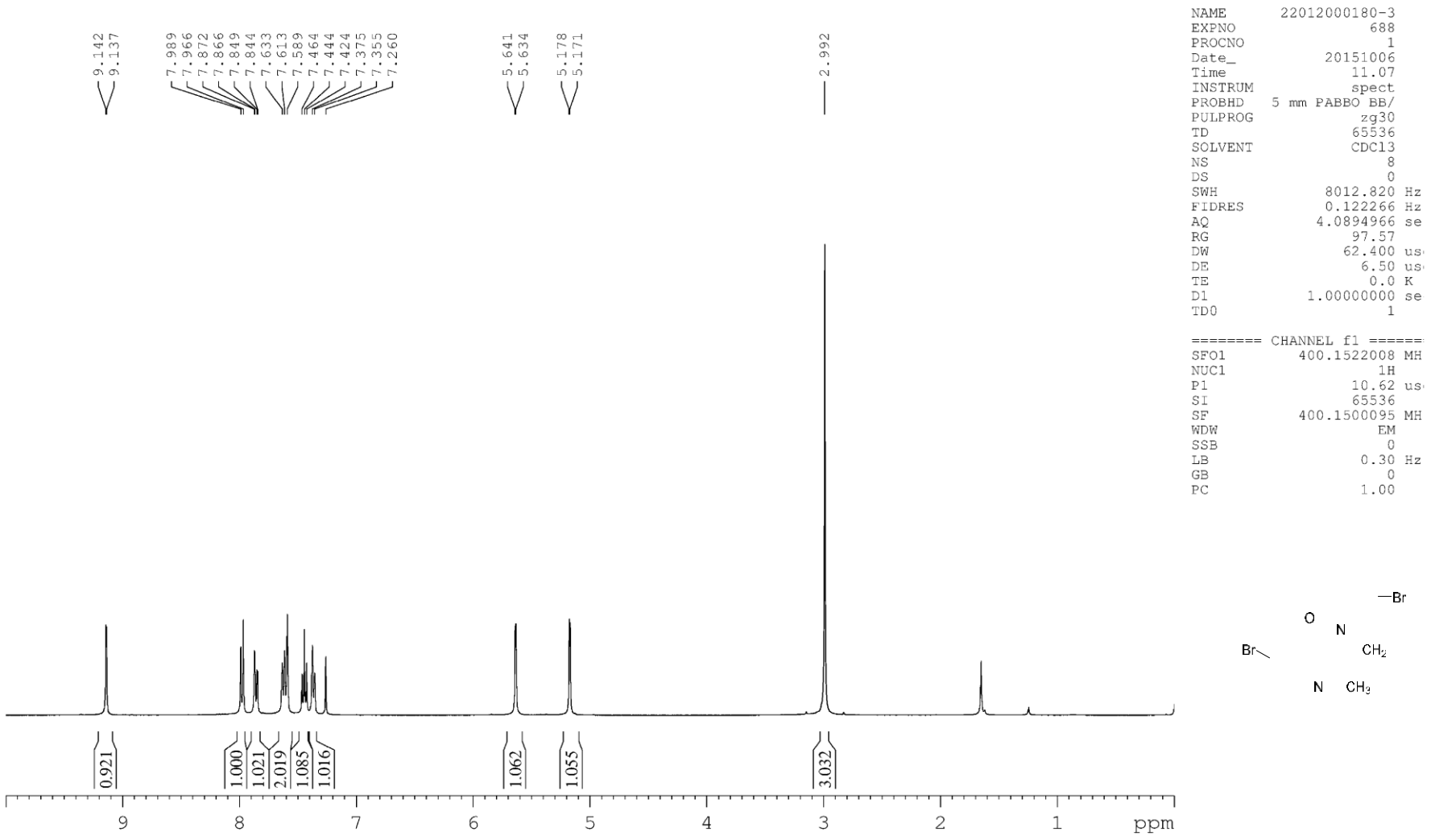


Figure 27. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6n**

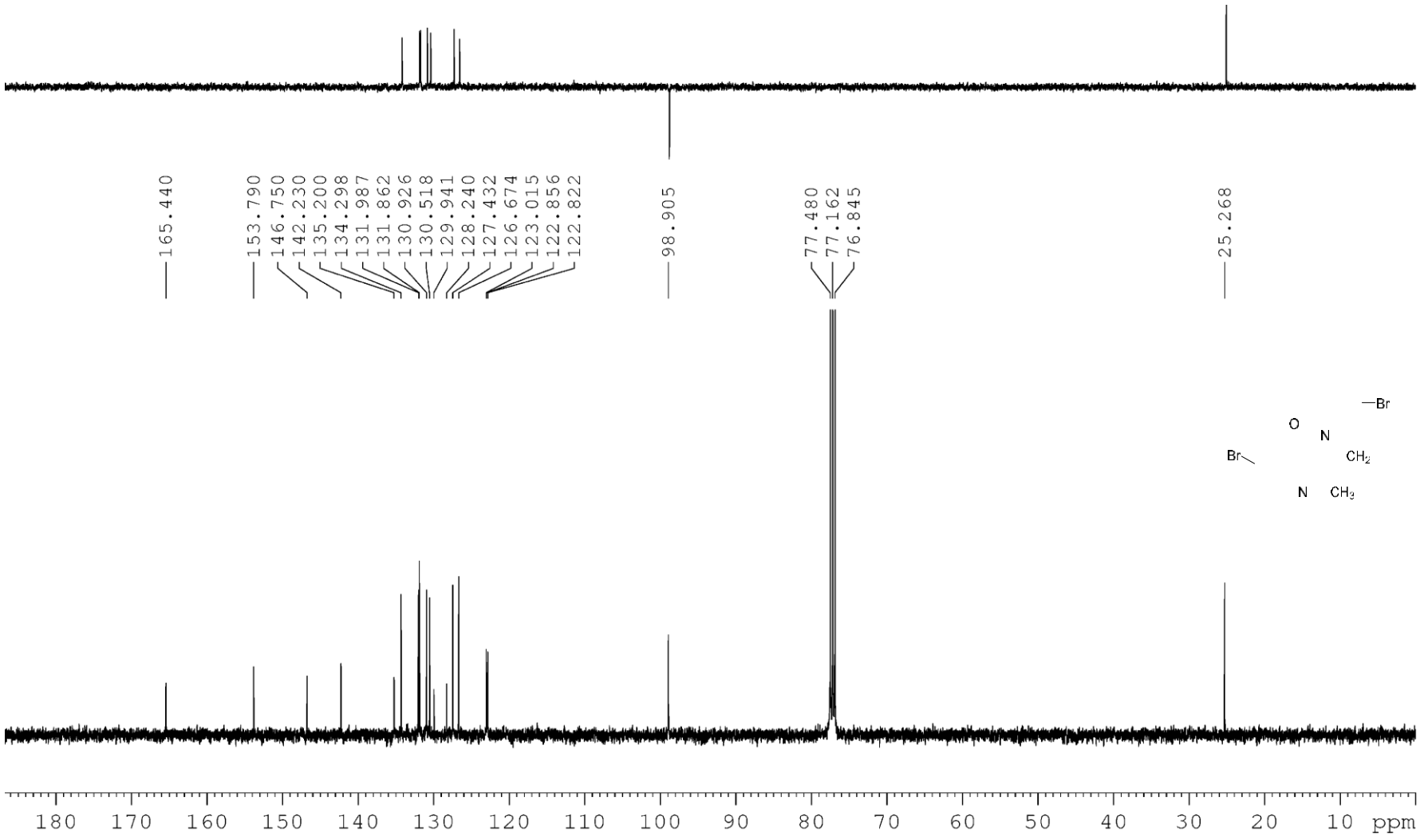


Figure 28. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6n**

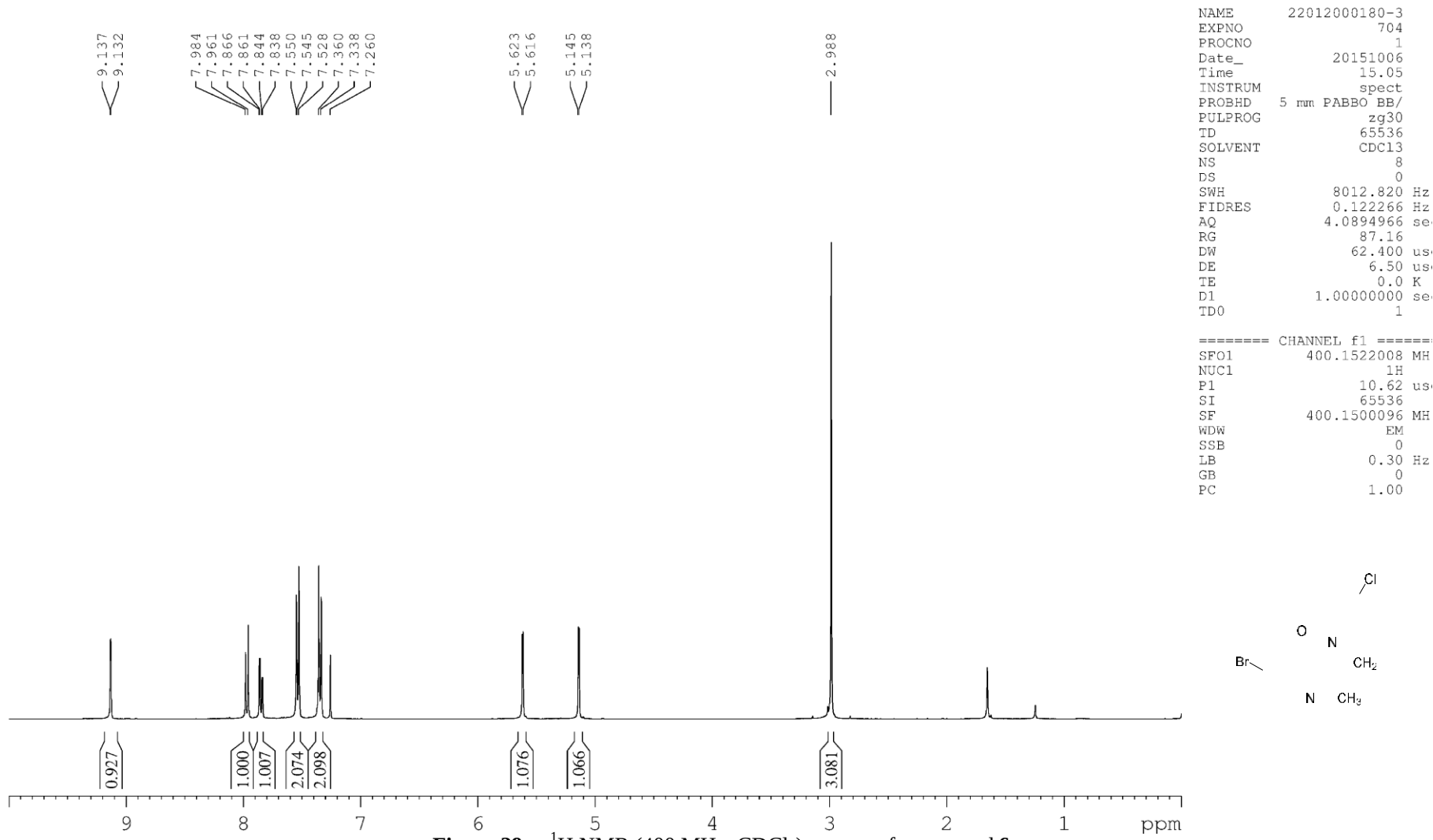


Figure 29. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6o**

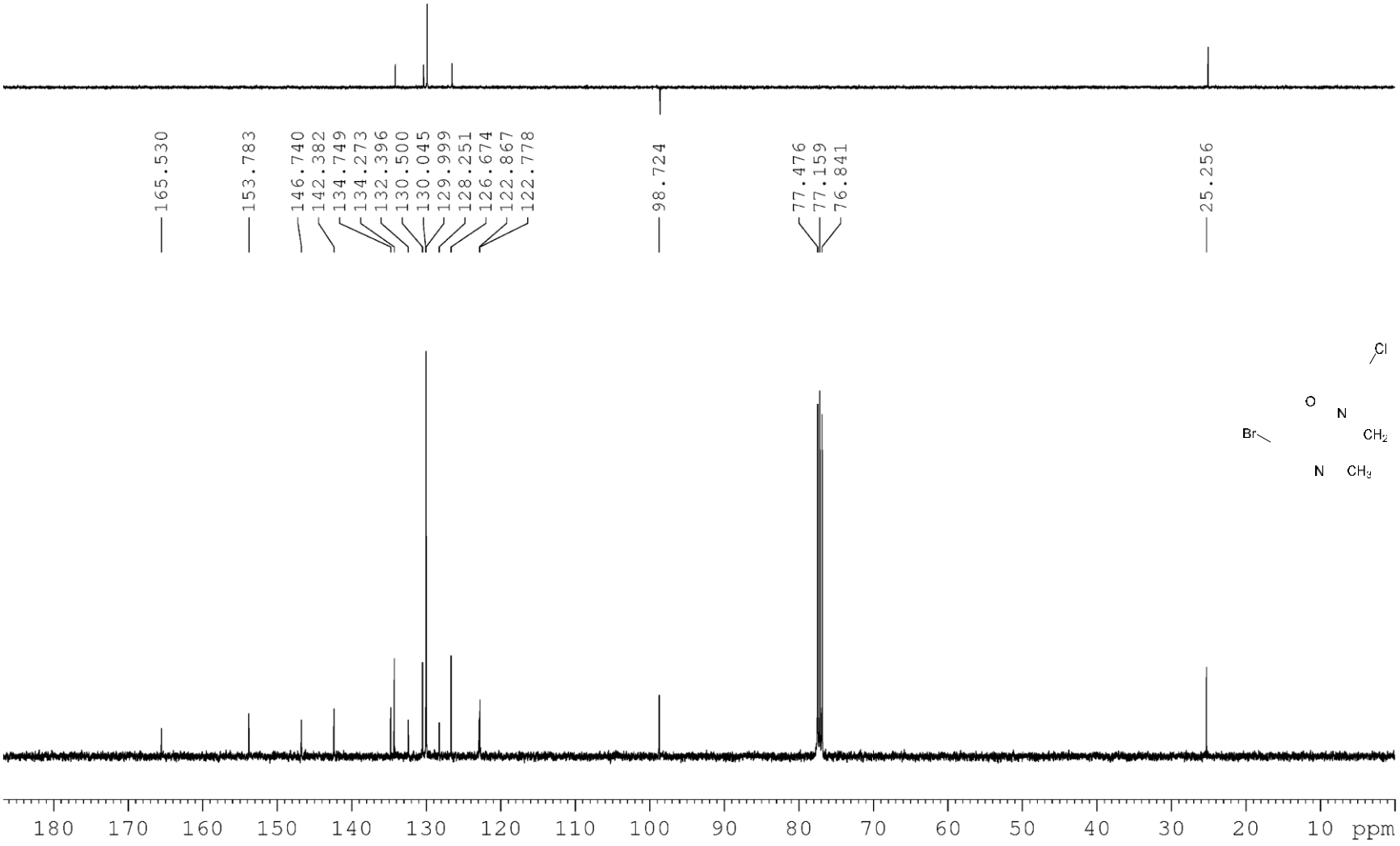


Figure 30. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6o**

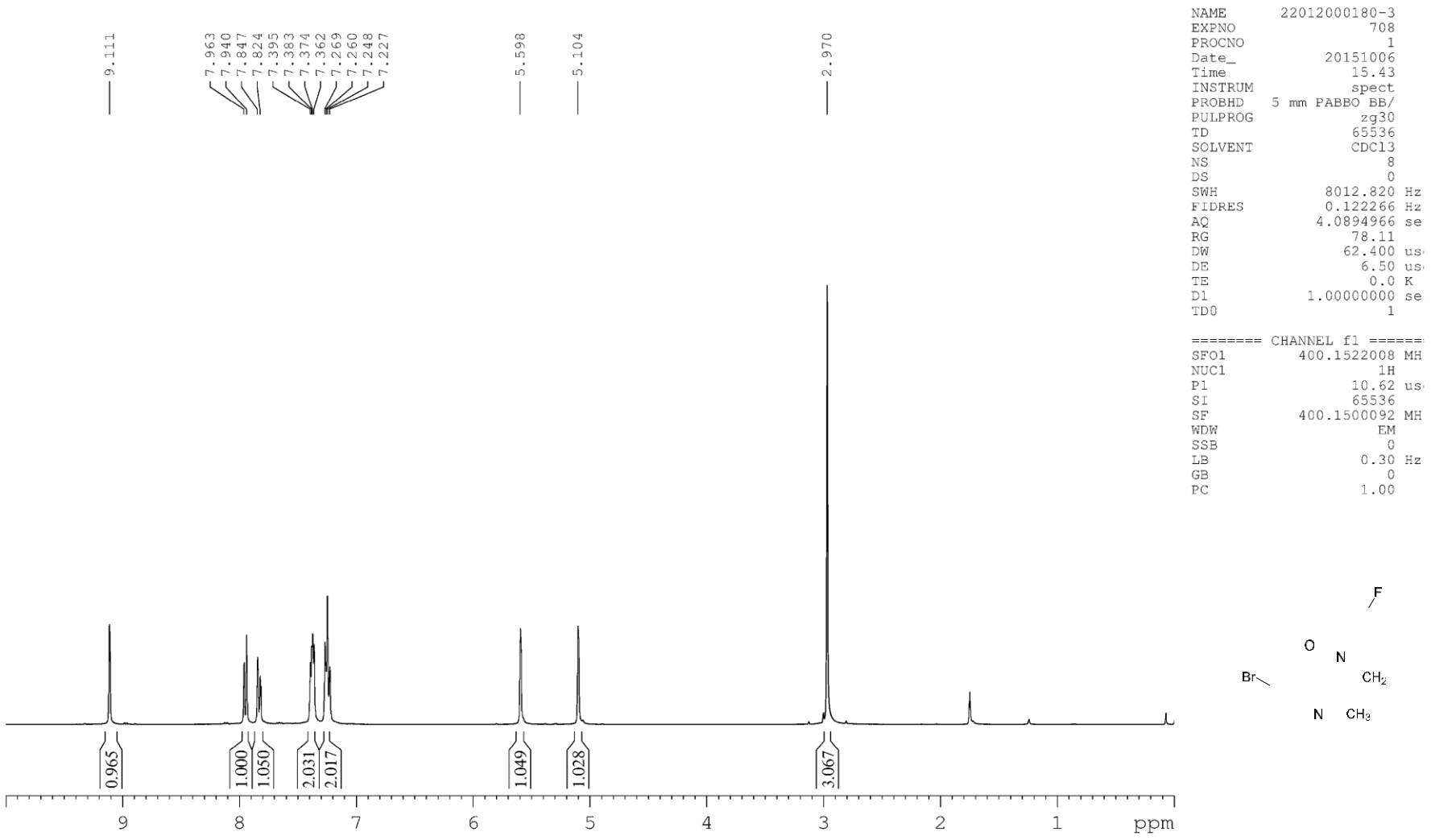


Figure 31. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6p**

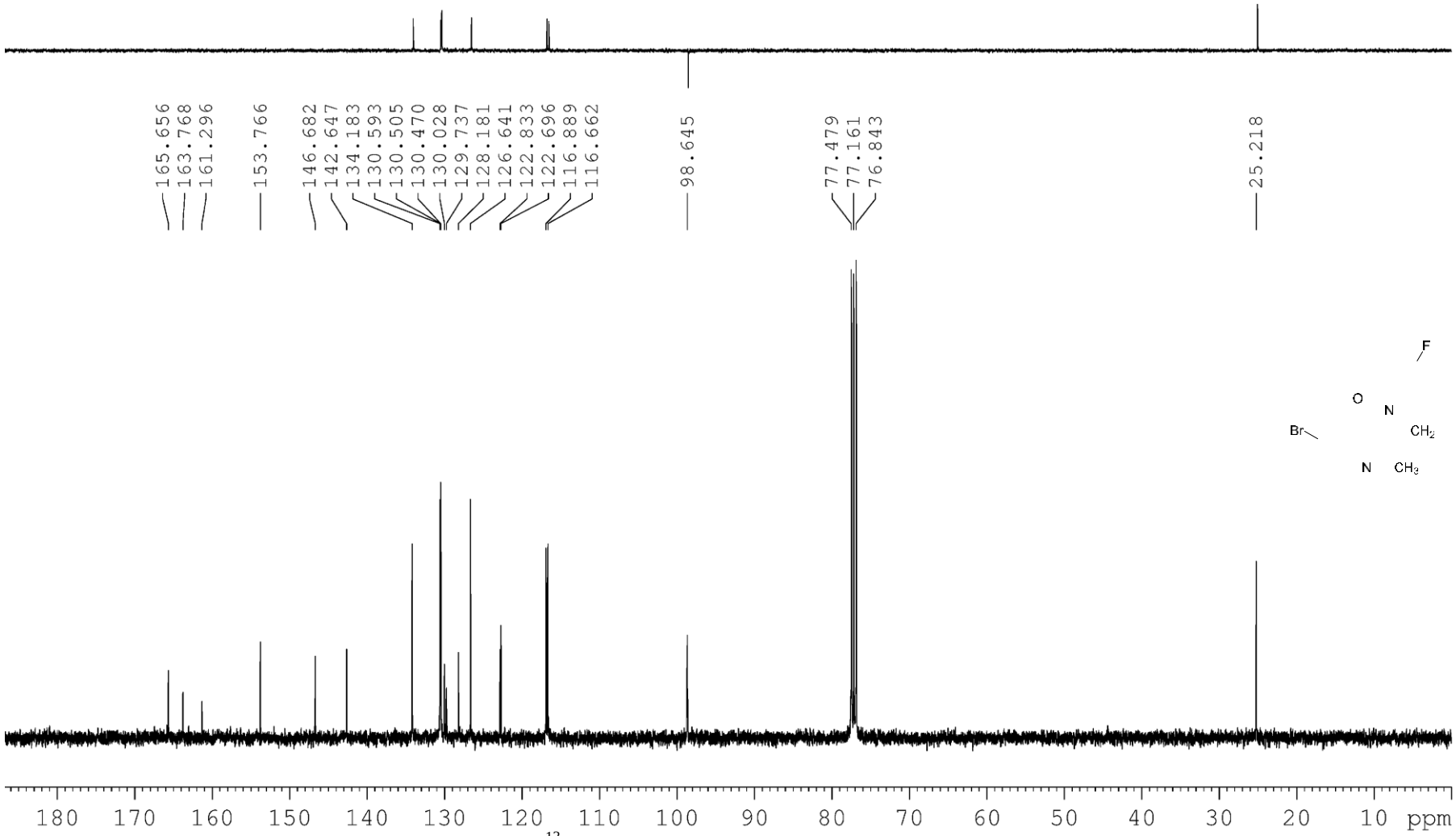
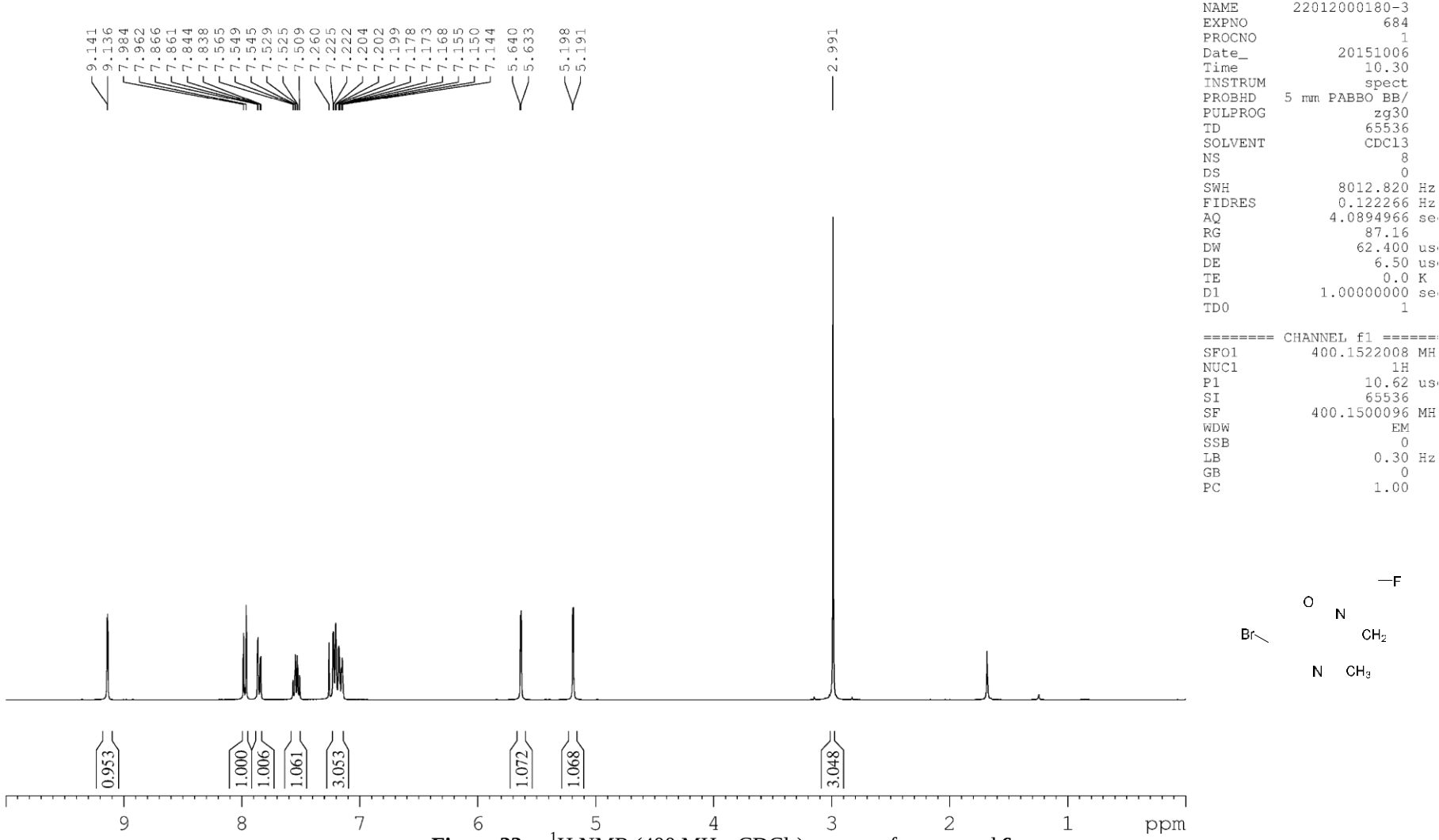


Figure 32. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6p**




```
NAME          22012000180-3
EXPNO                   684
PROCNO                    1
Date_              20151006
Time                  10.30
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                8012.820 Hz
FIDRES                0.122266 Hz
AQ                 4.0894966 se
RG                    87.16
DW                    62.400 us
DE                     6.50 us
TE                     0.0 K
D1                 1.00000000 se
TD0                       1

======== CHANNEL f1 ======
SFO1            400.1522008 MH
NUC1                      1H
P1                    10.62 us
SI                    65536
SF              400.1500096 MH
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```


Figure 33. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6q**

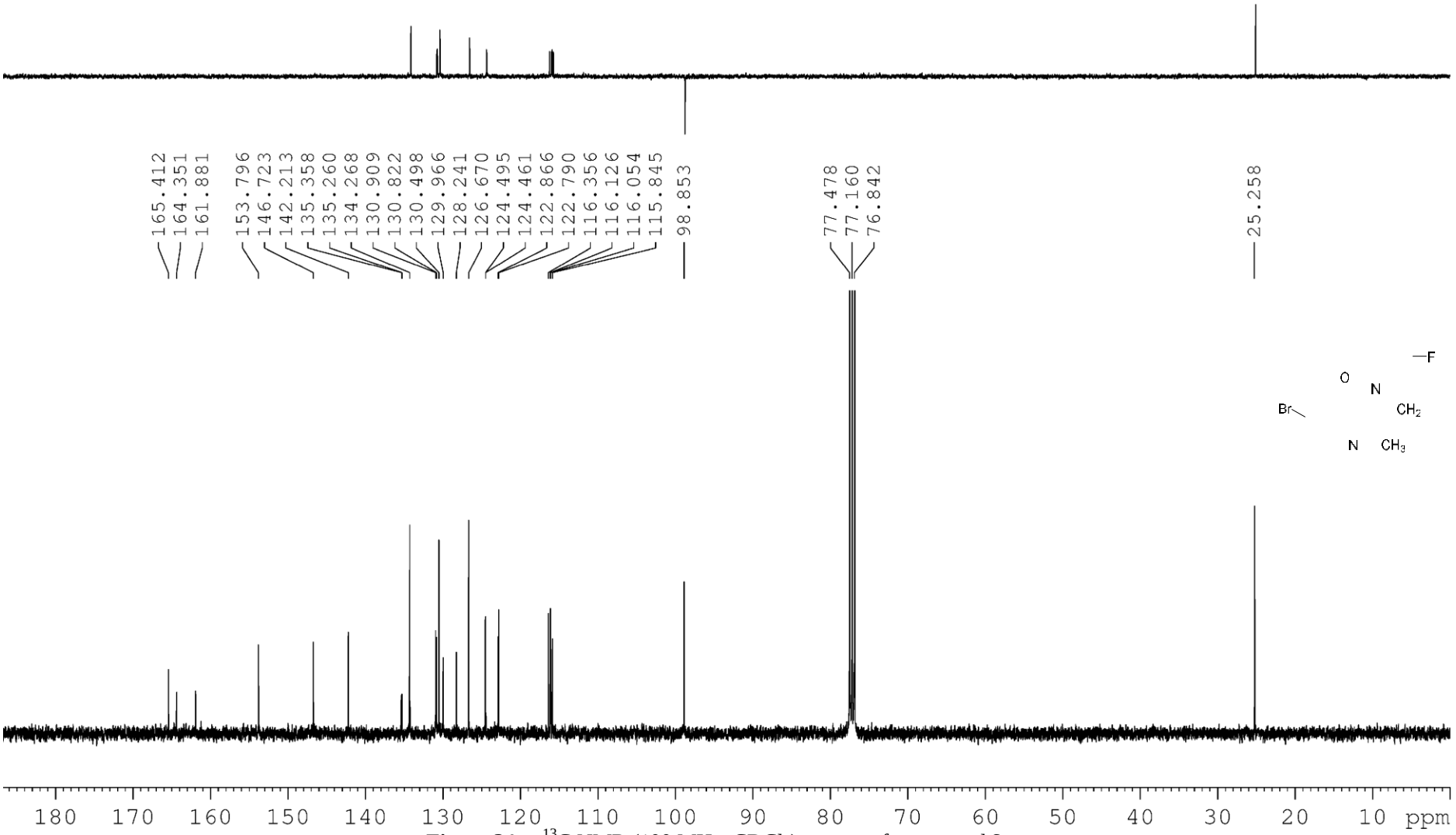


Figure 34. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6q**

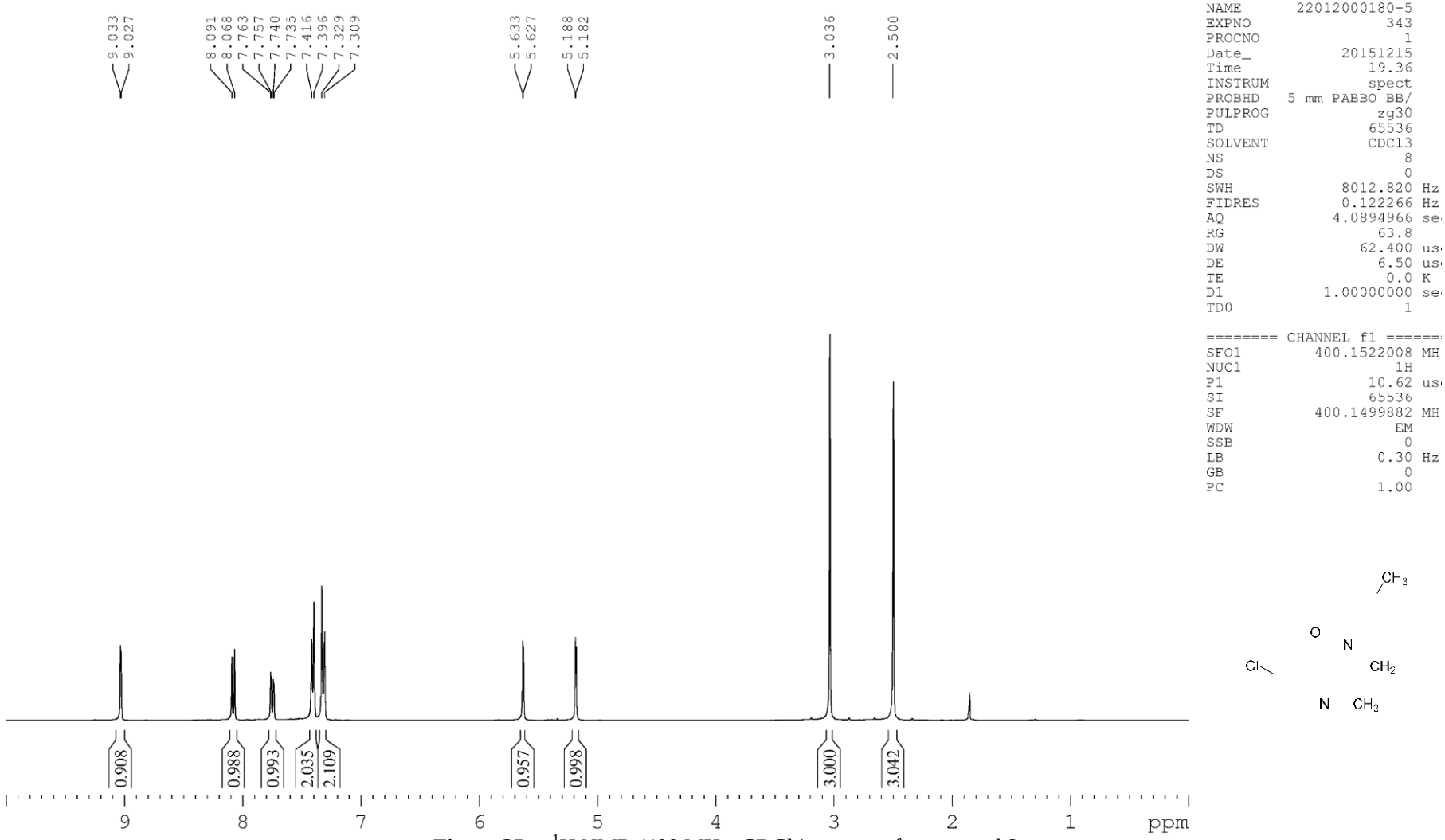


Figure 35. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6r**

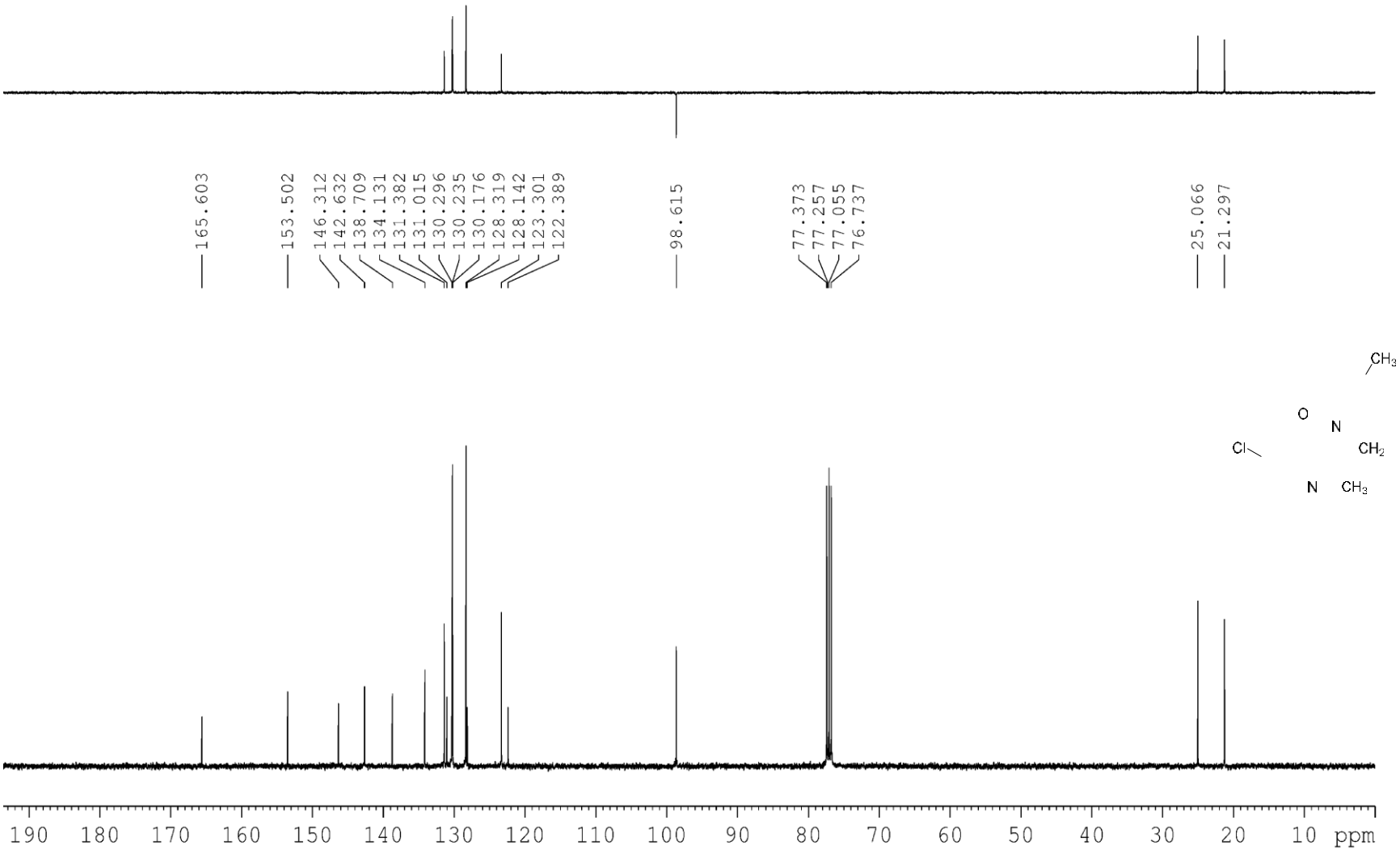
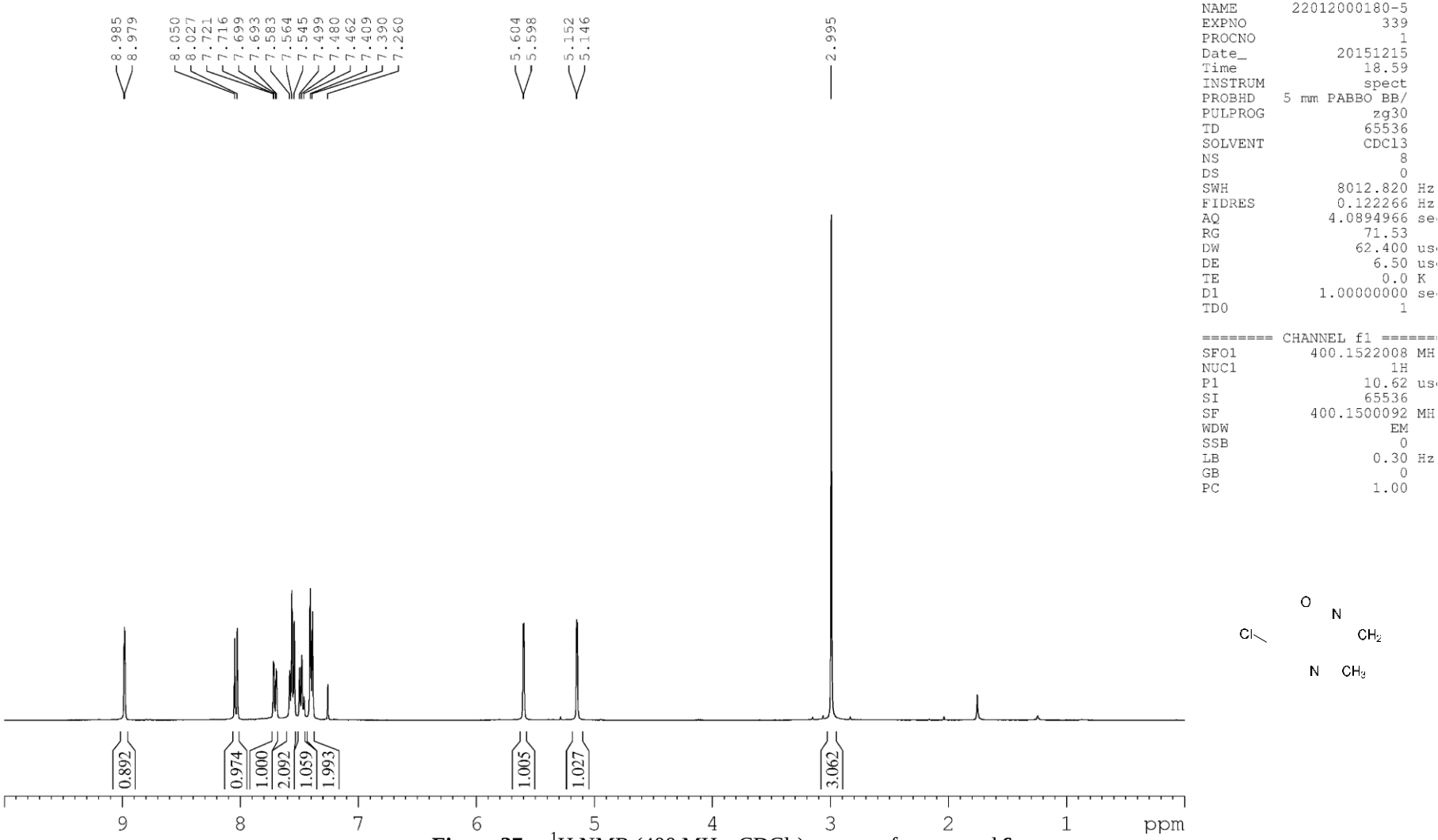


Figure 36. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6r**



NAME	22012000180-5
EXPNO	339
PROCNO	1
Date_	20151215
Time	18.59
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	0
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 se
RG	71.53
DW	62.400 us
DE	6.50 us
TE	0.0 K
D1	1.00000000 se
TD0	1
======== CHANNEL f1 =======	
SFO1	400.1522008 MH
NUC1	1H
P1	10.62 us
SI	65536
SF	400.1500092 MH
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Figure 37. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6s**

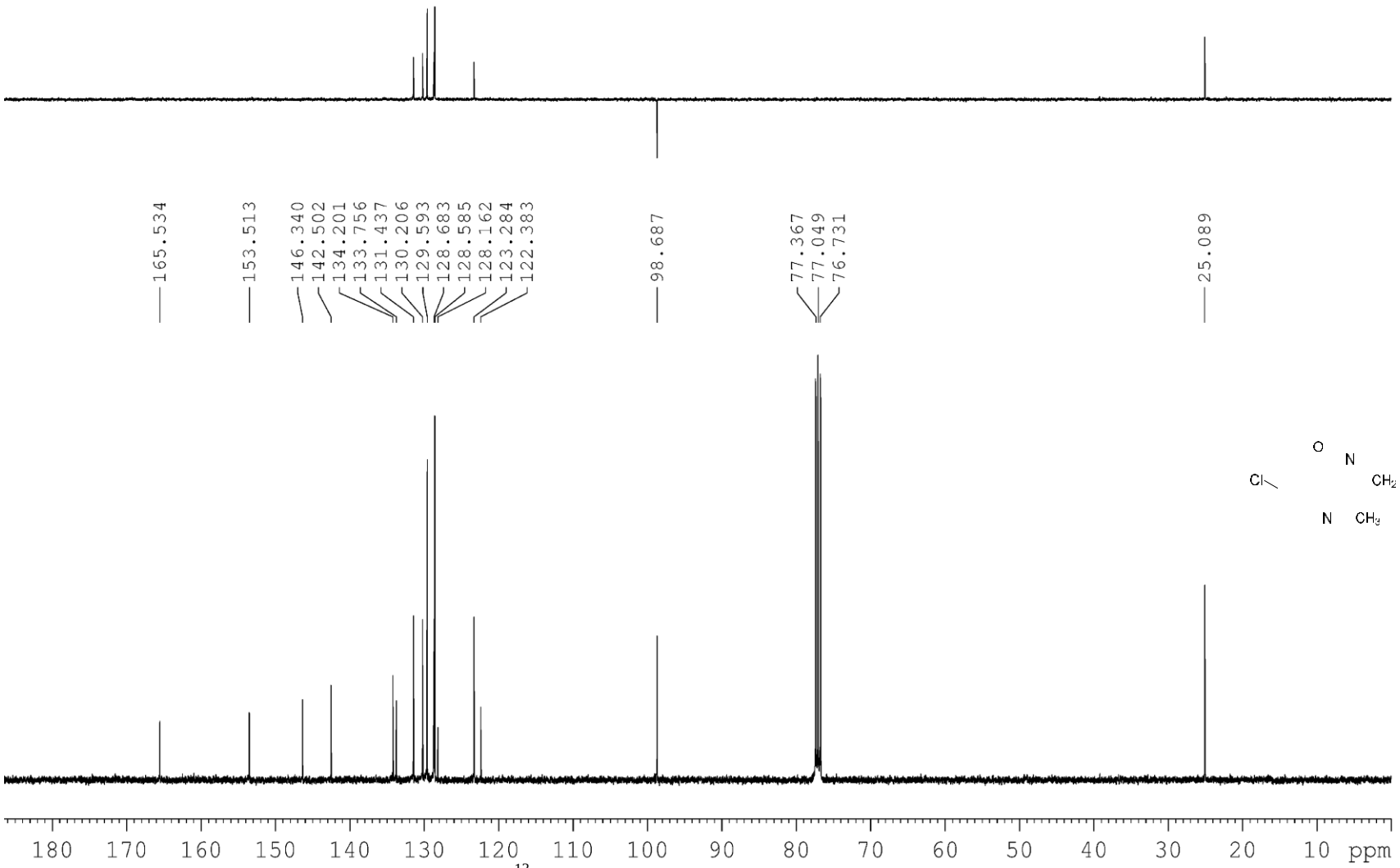


Figure 38. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6s**

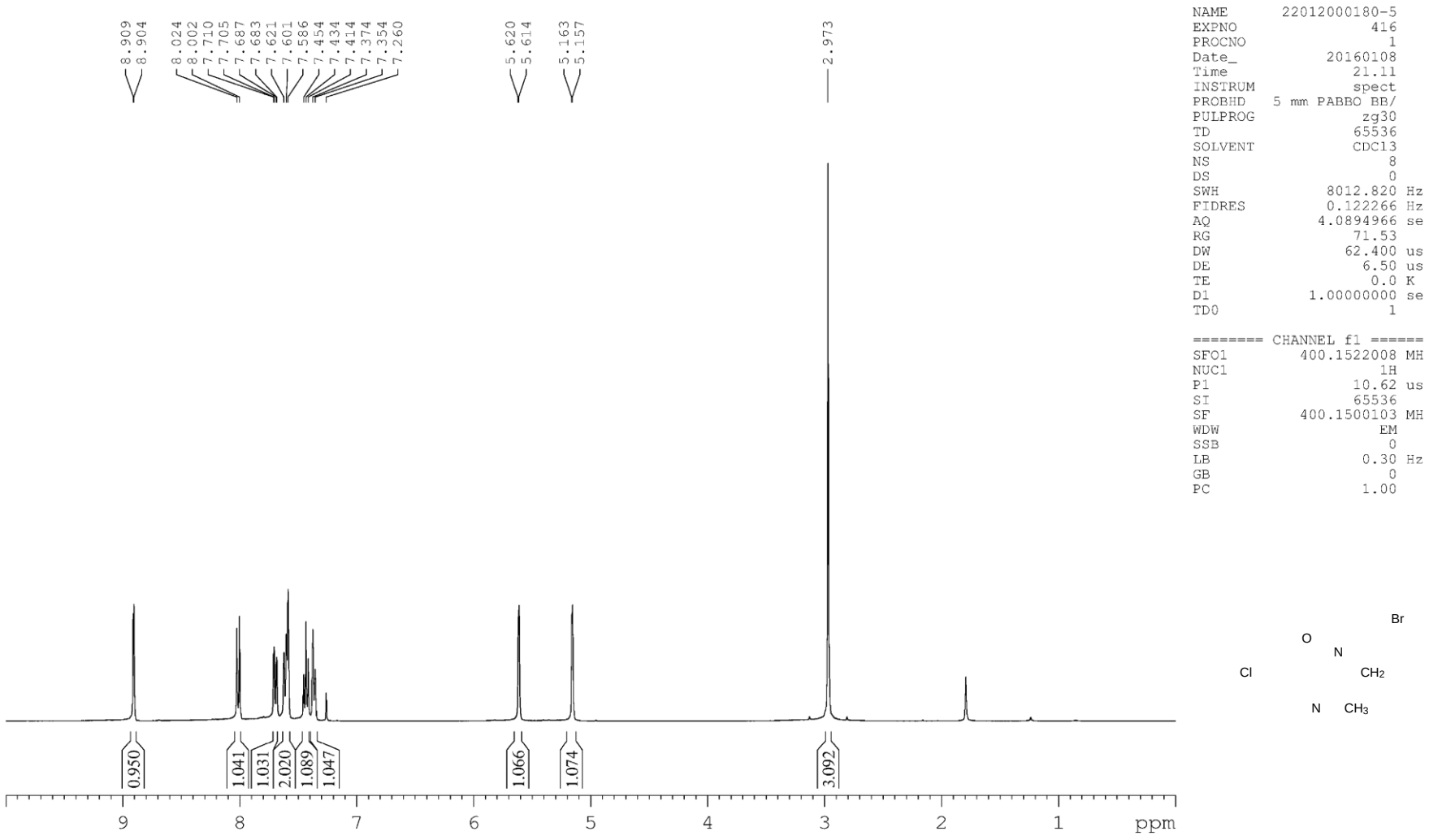


Figure 39. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6t**

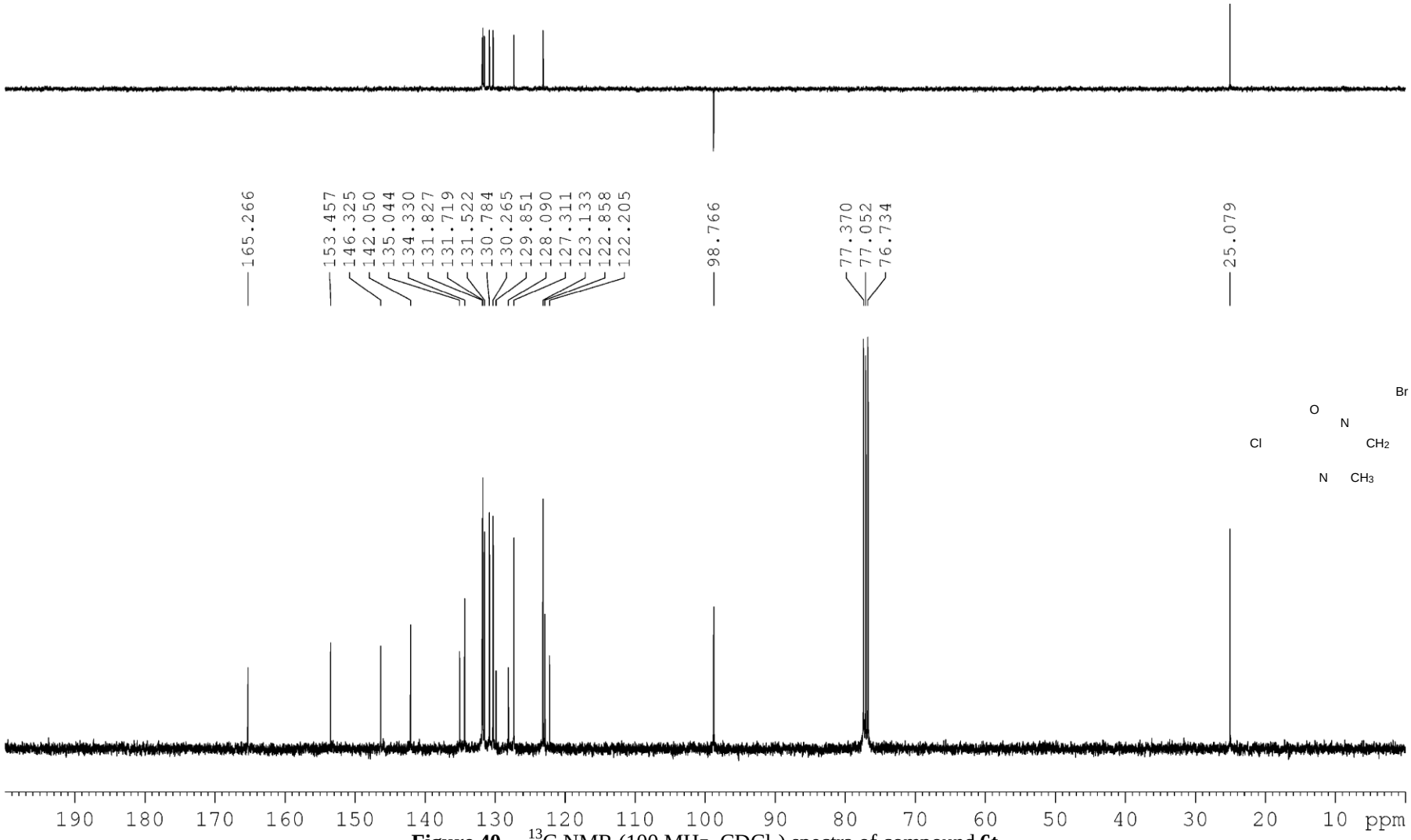


Figure 40. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6t**

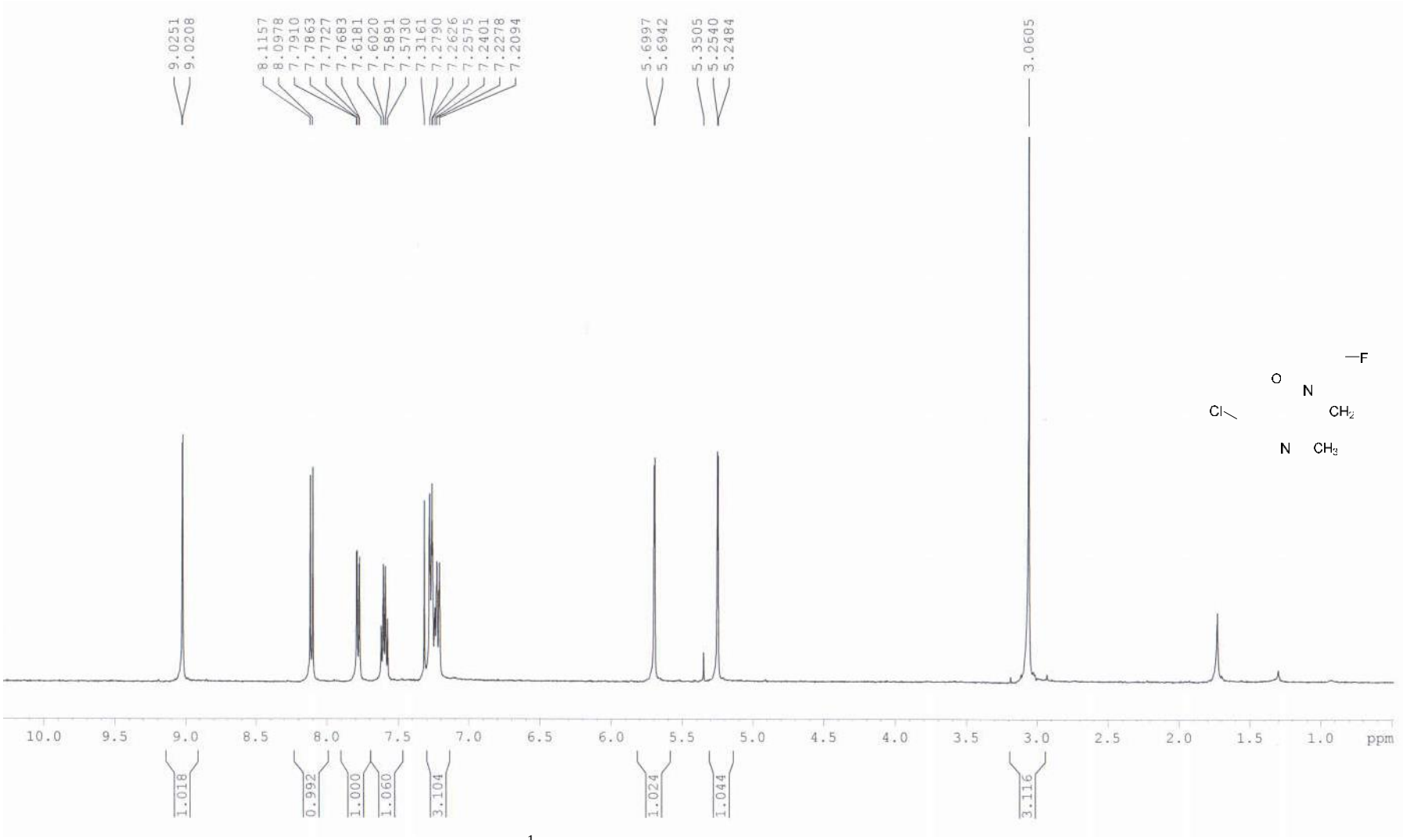


Figure 41. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **6u**

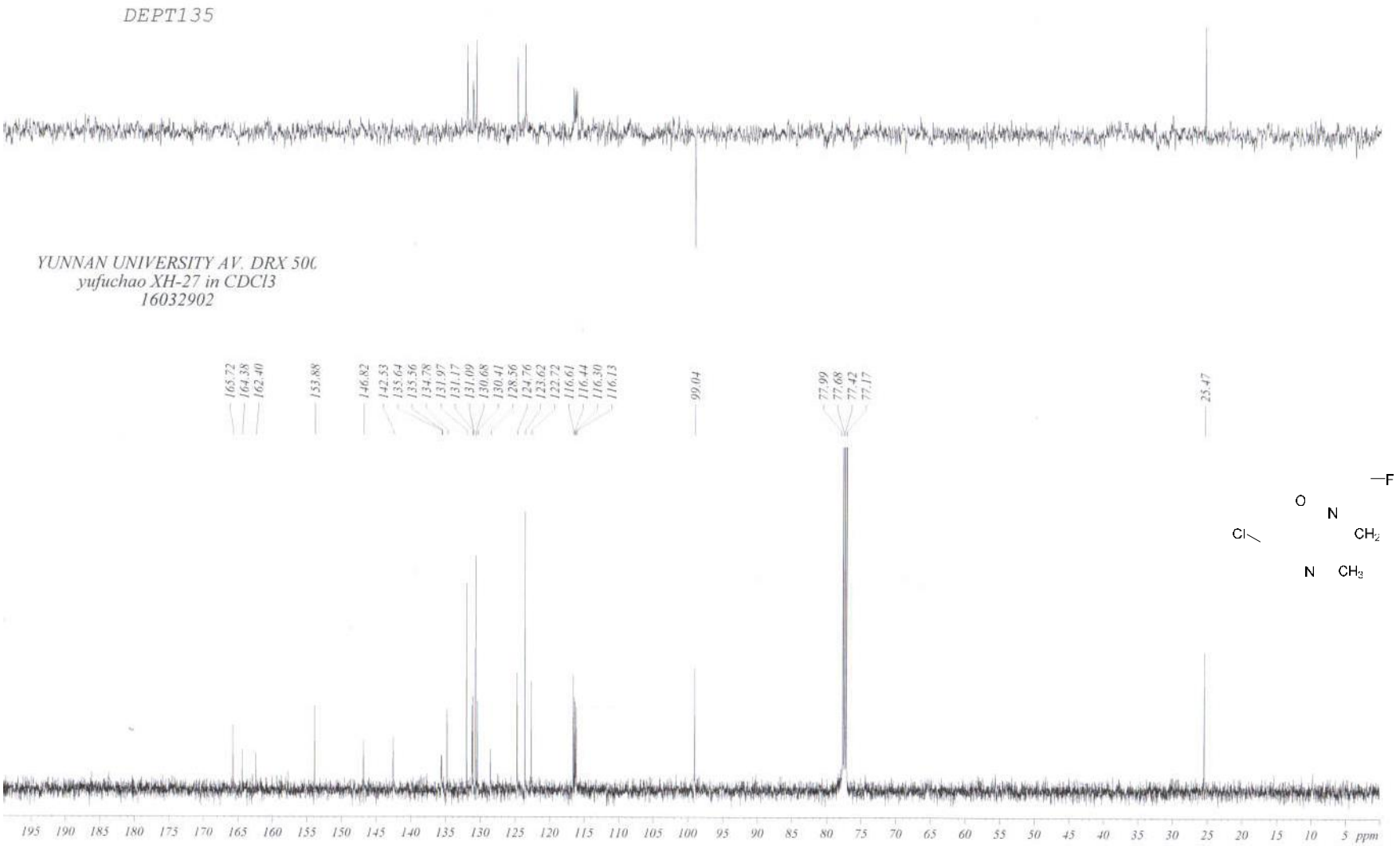


Figure 42. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **6u**

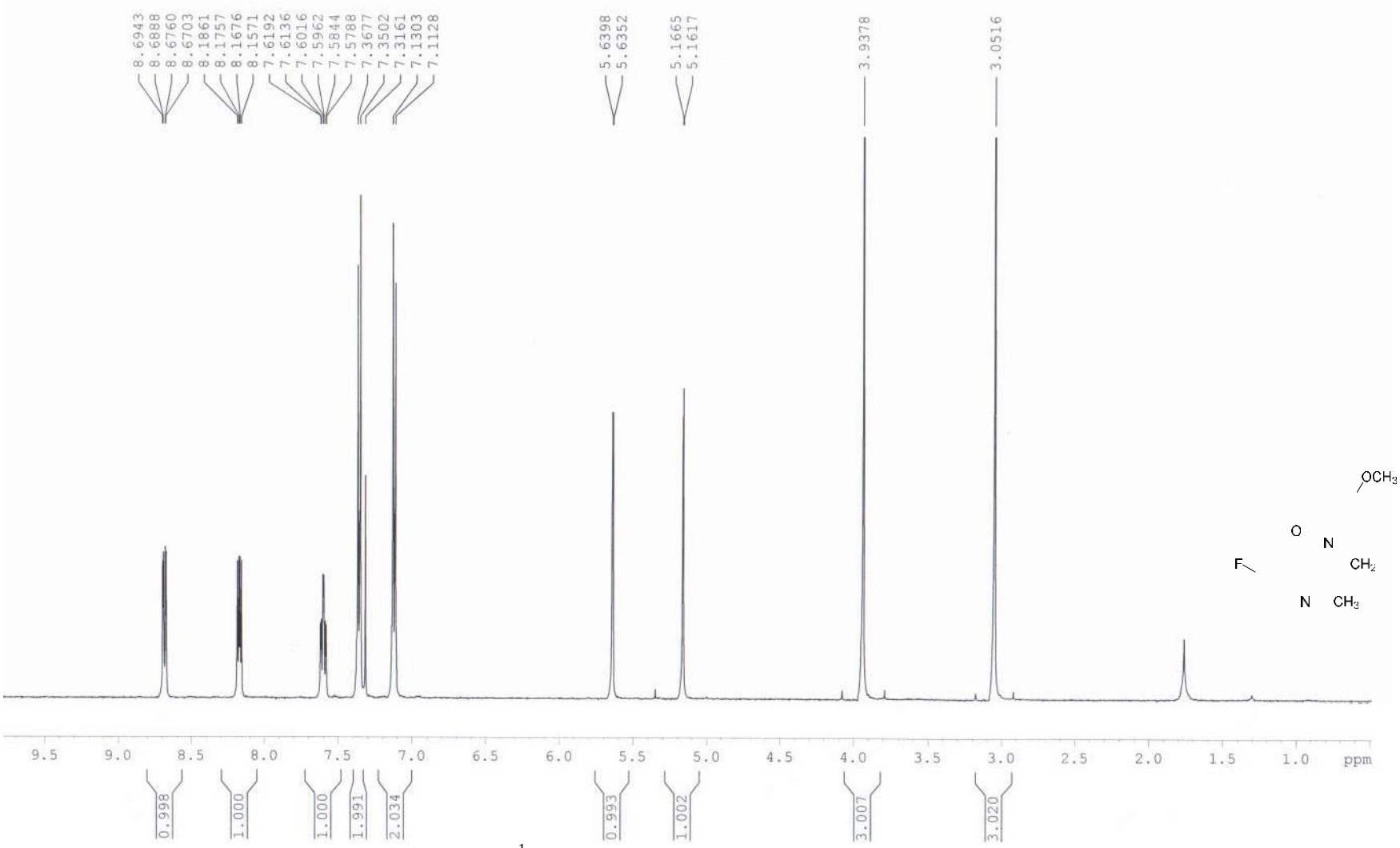


Figure 43. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **6v**

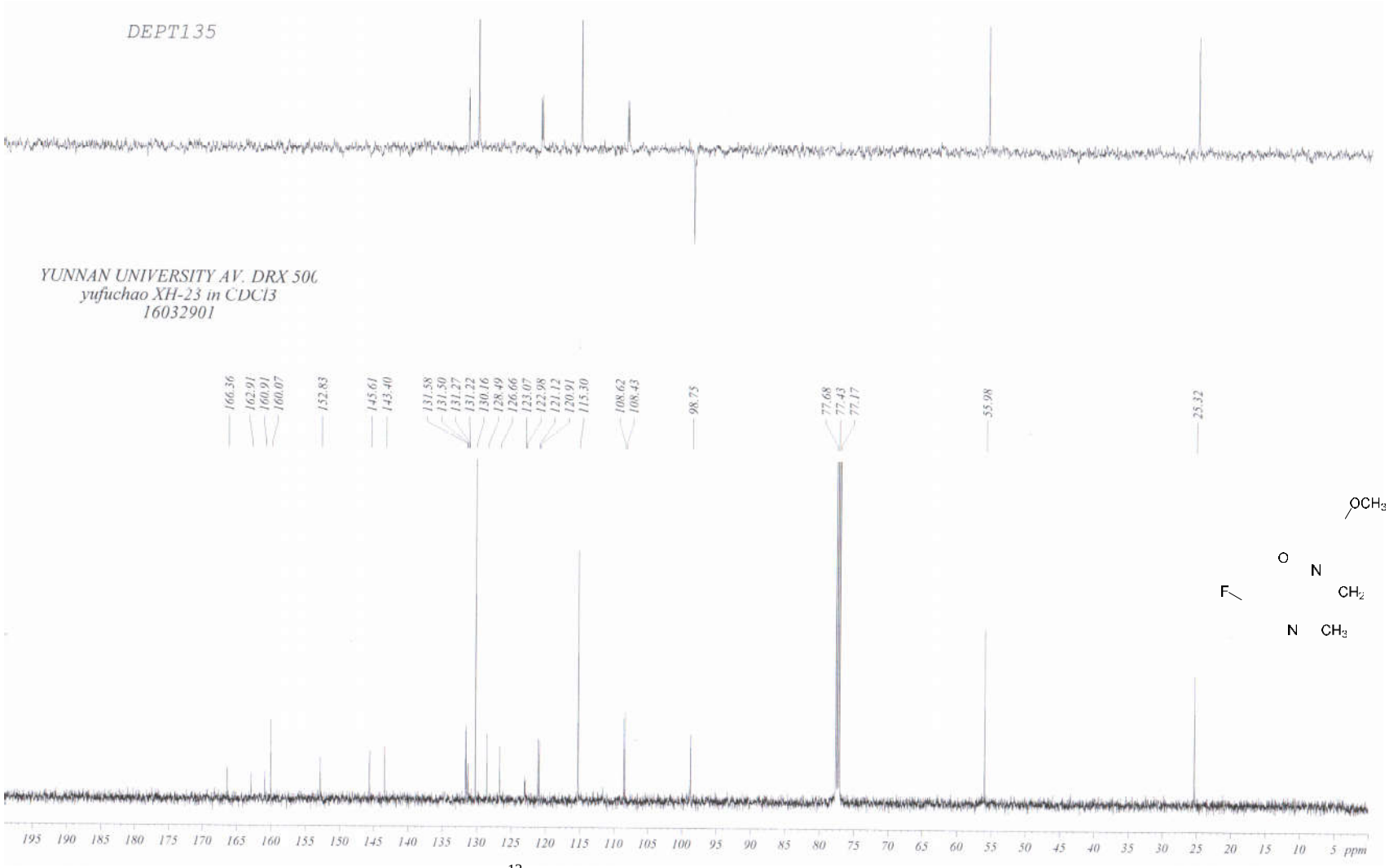


Figure 44. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **6v**

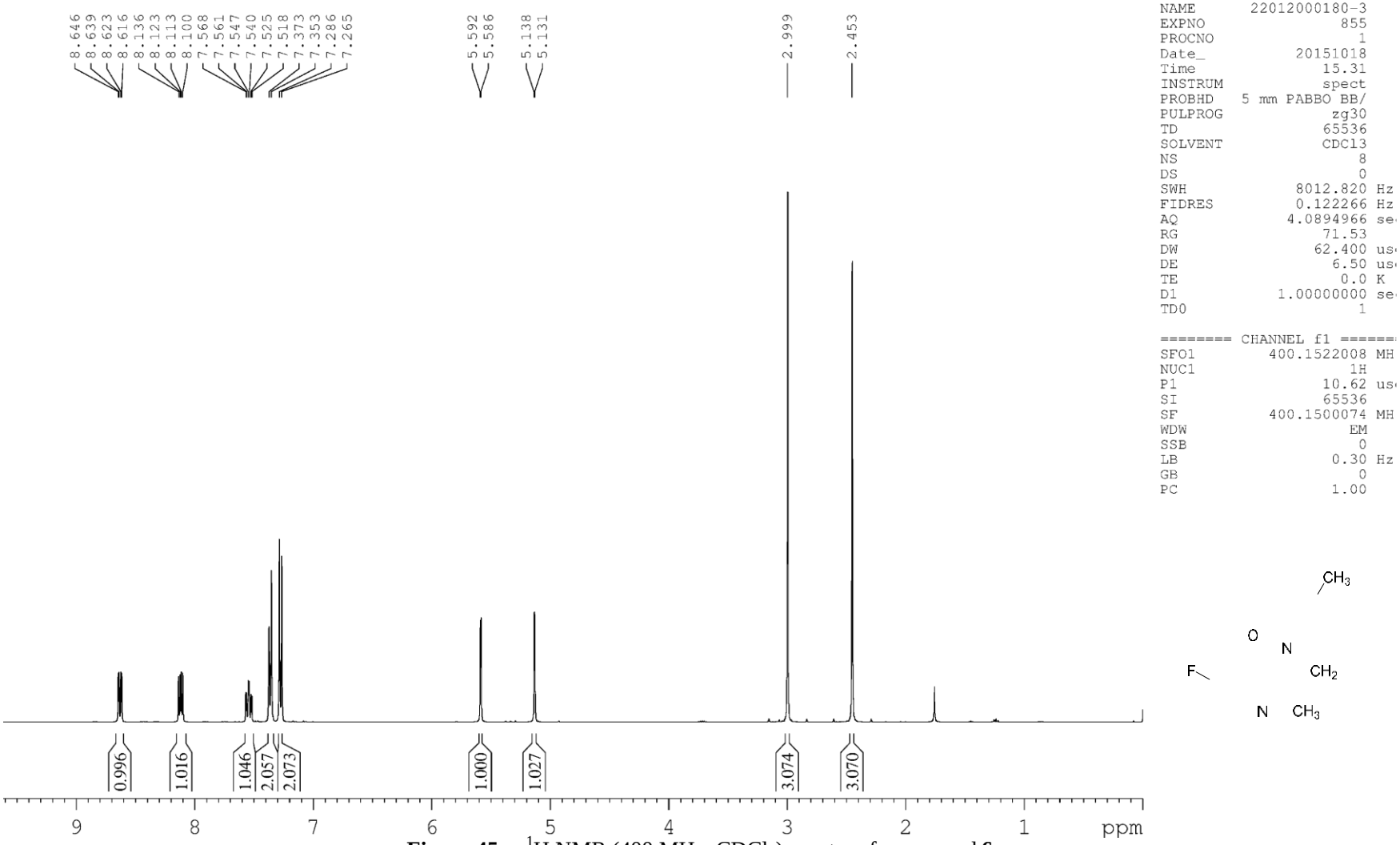


Figure 45. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6w**

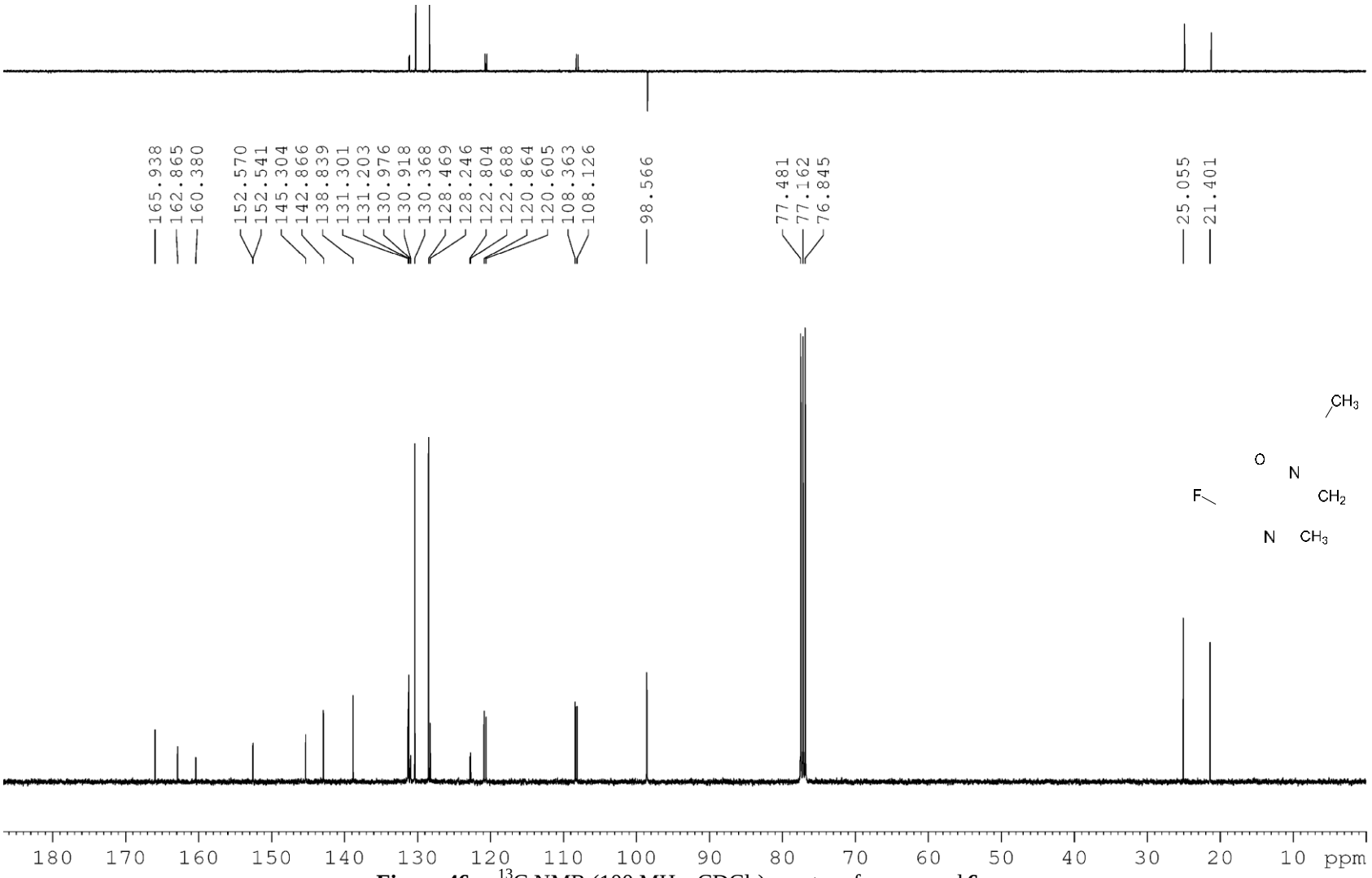


Figure 46. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6w**

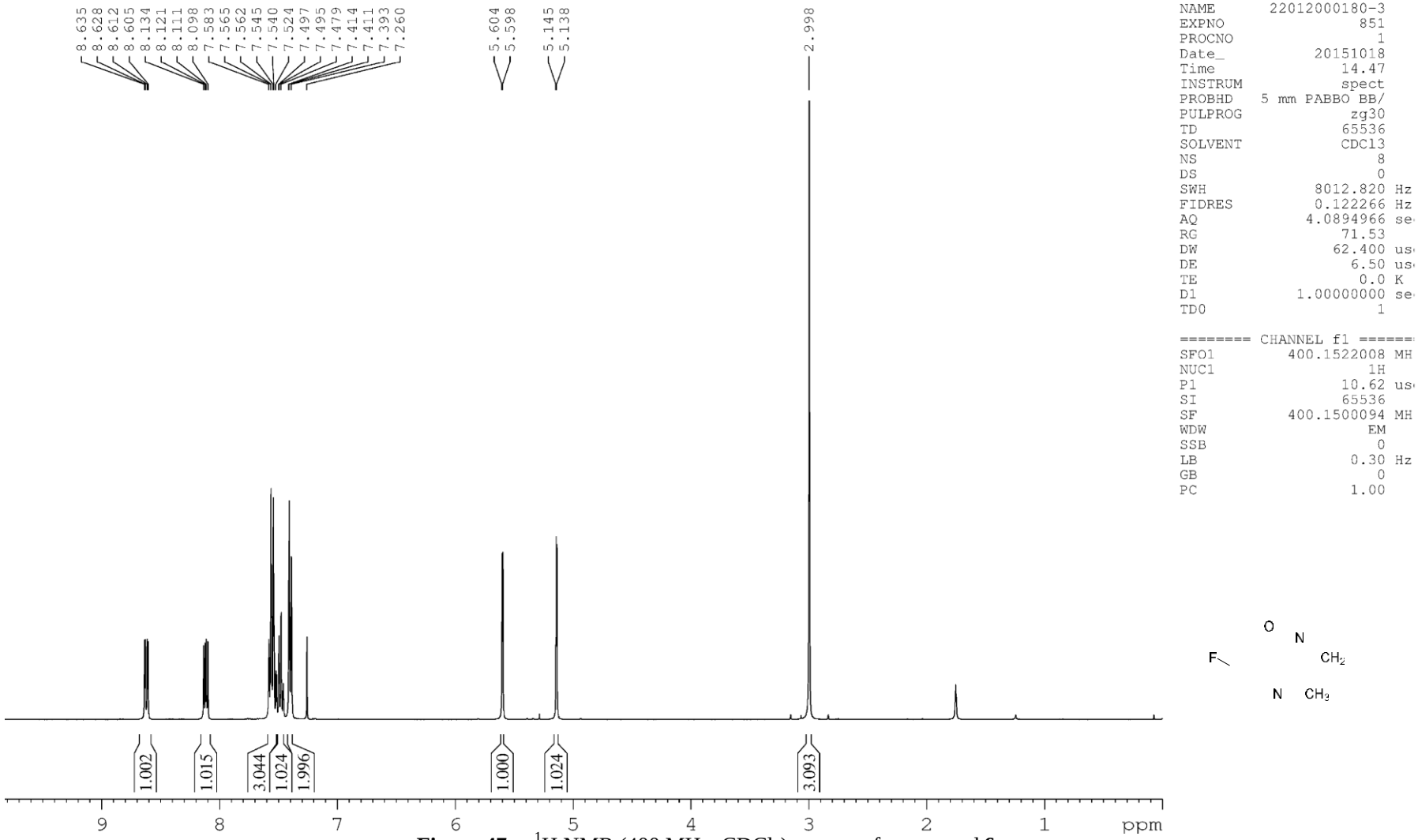


Figure 47. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6x**

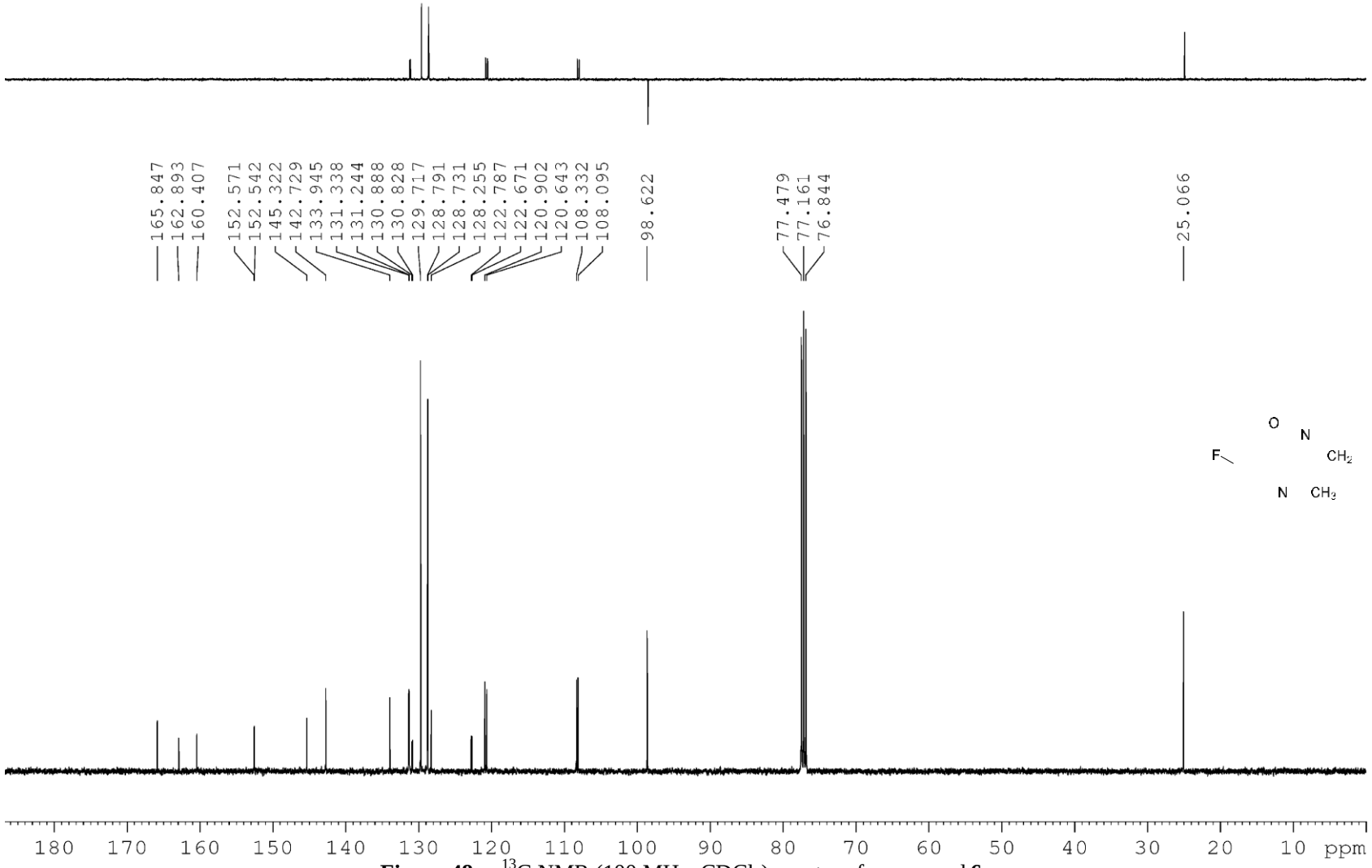


Figure 48. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6x**

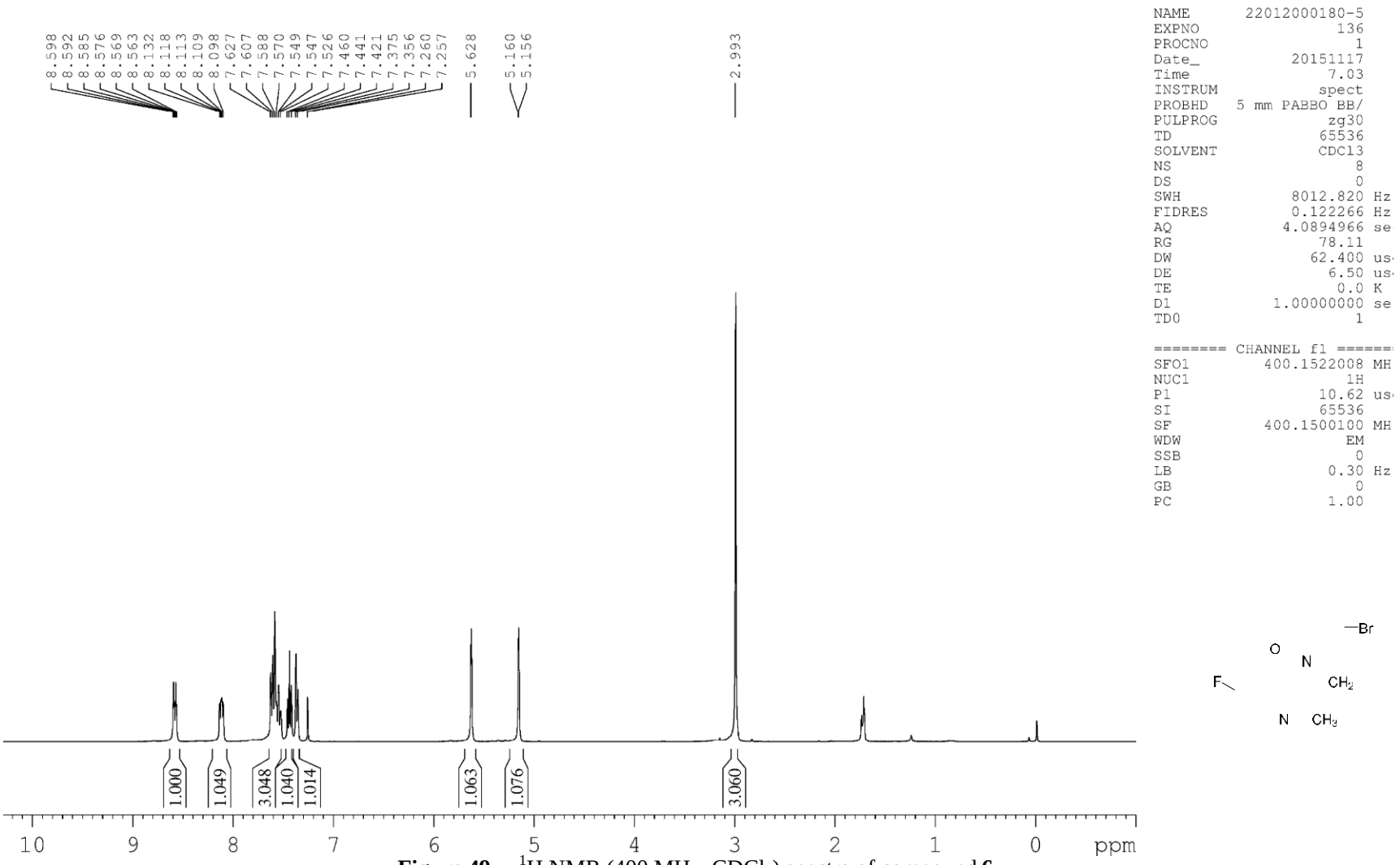


Figure 49. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6y**

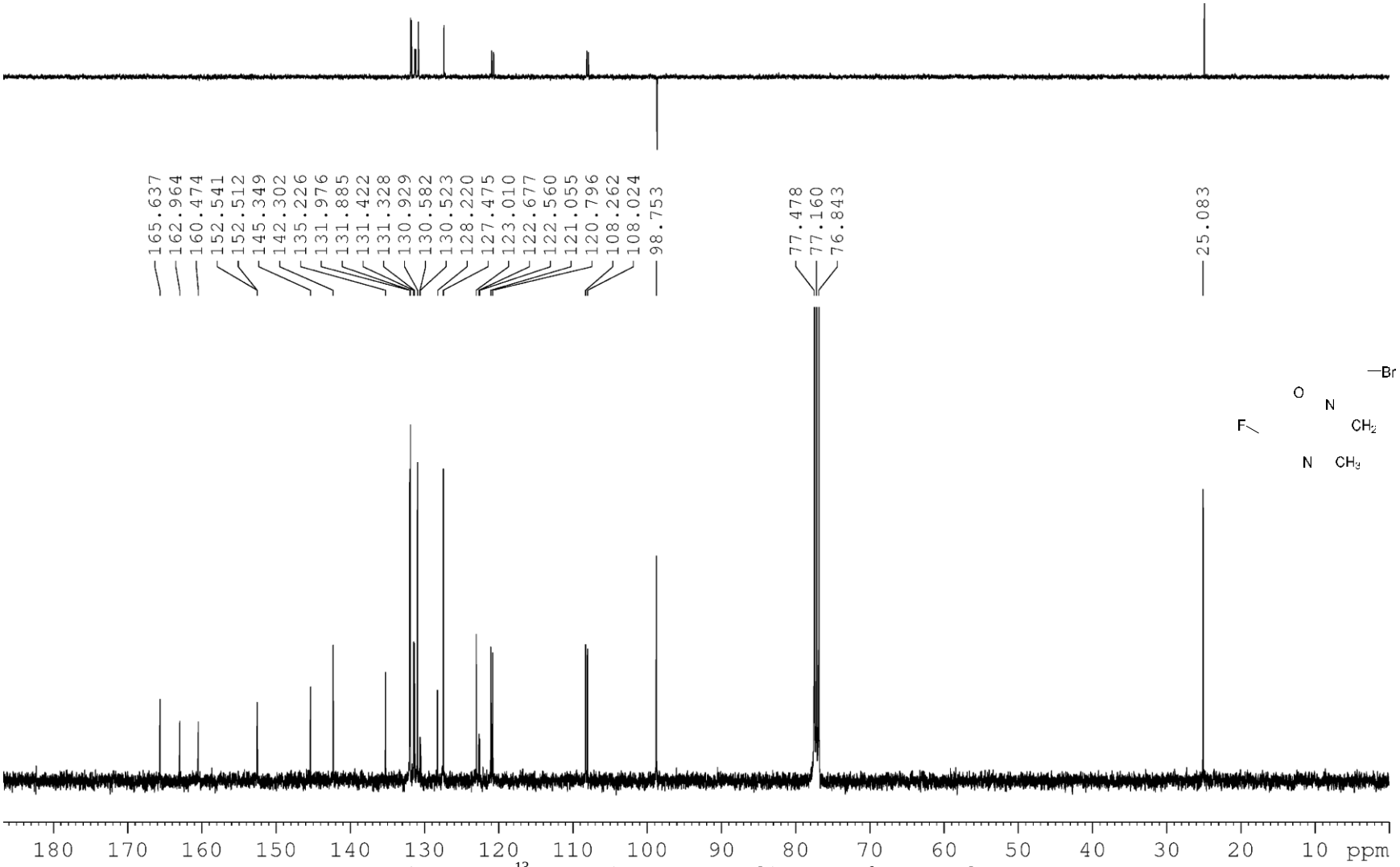


Figure 50. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **6y**

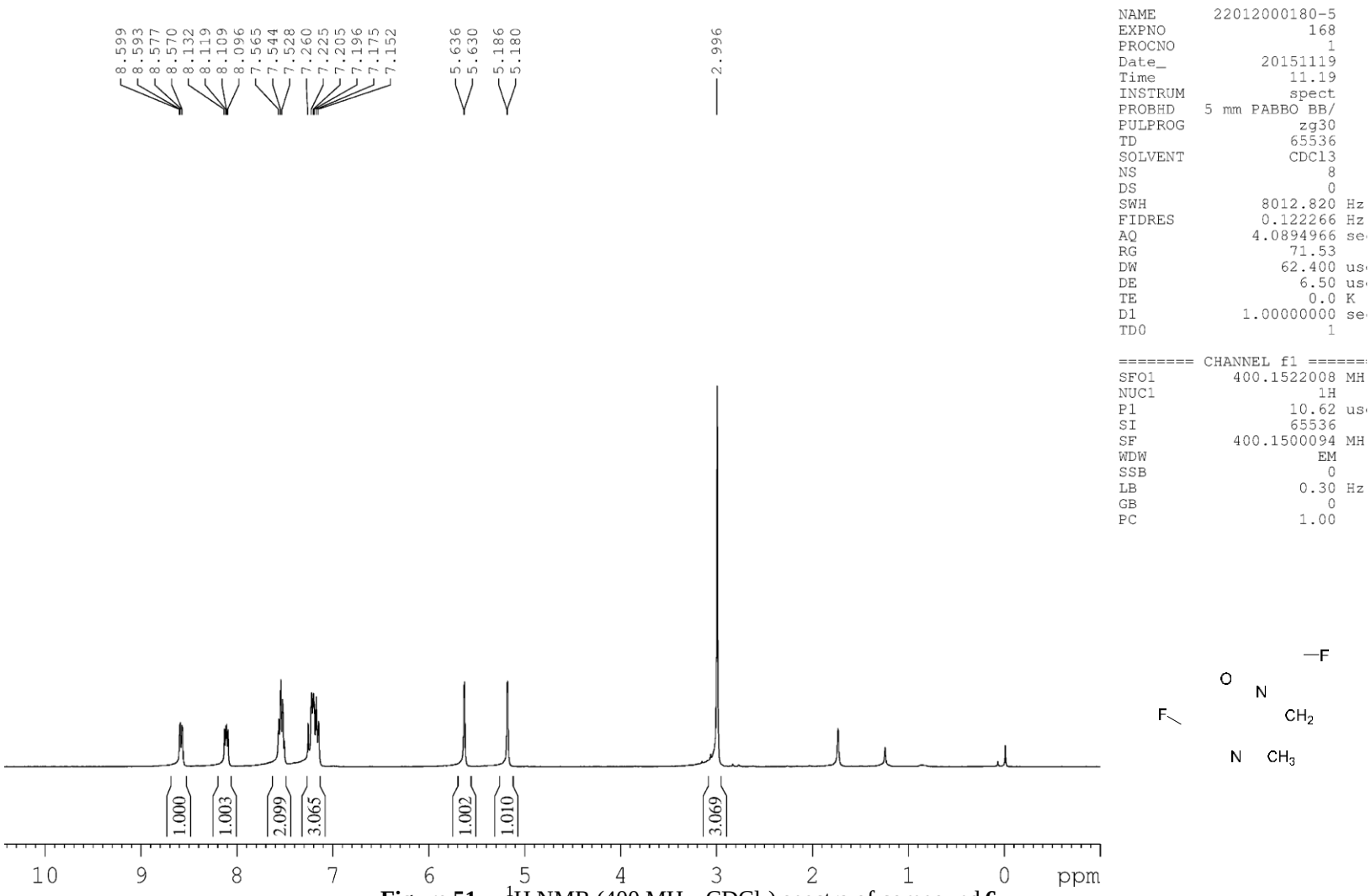


Figure 51. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6z**

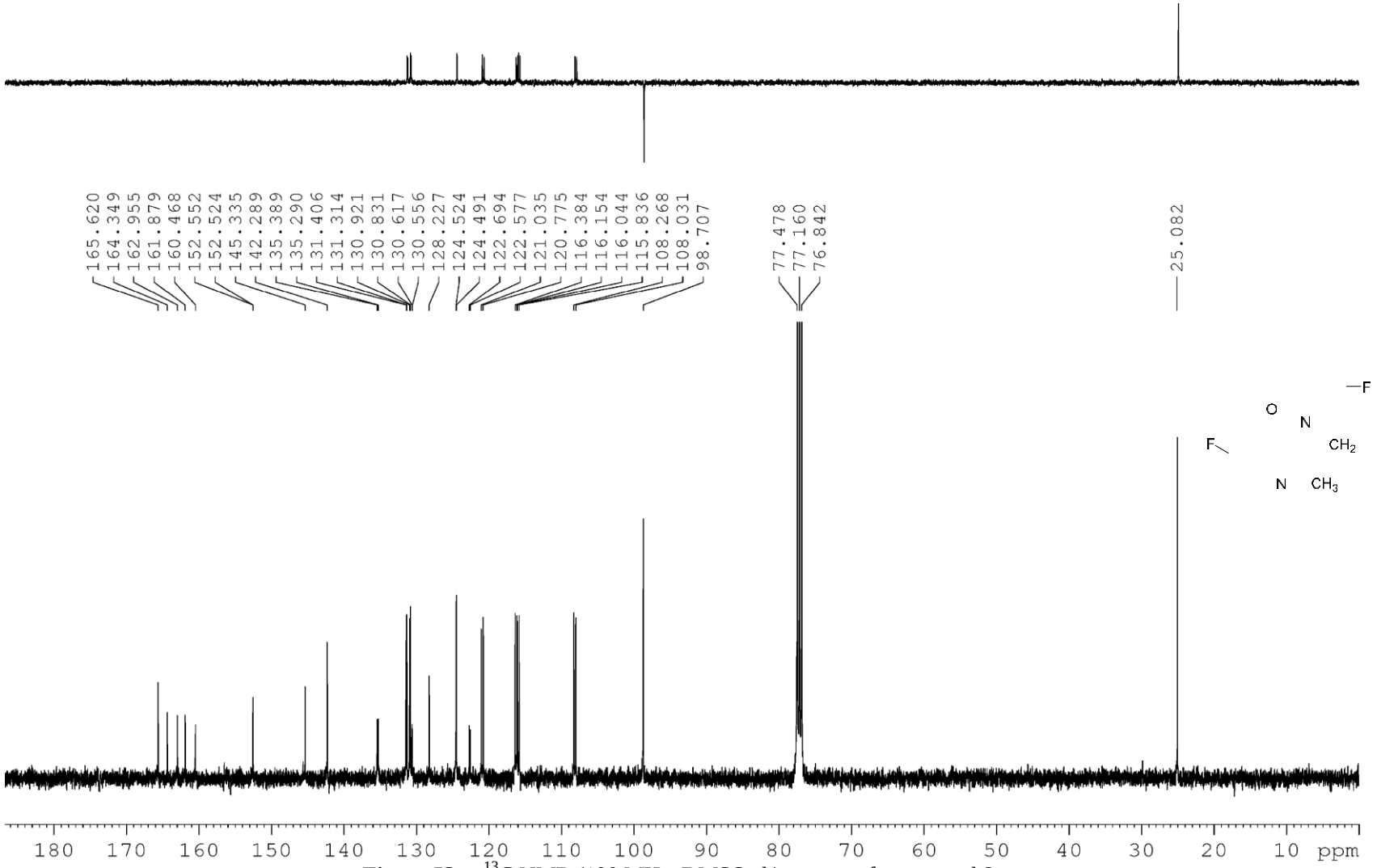


Figure 52. ^{13}C NMR (100 MHz, DMSO-d_6) spectra of compound **6z**

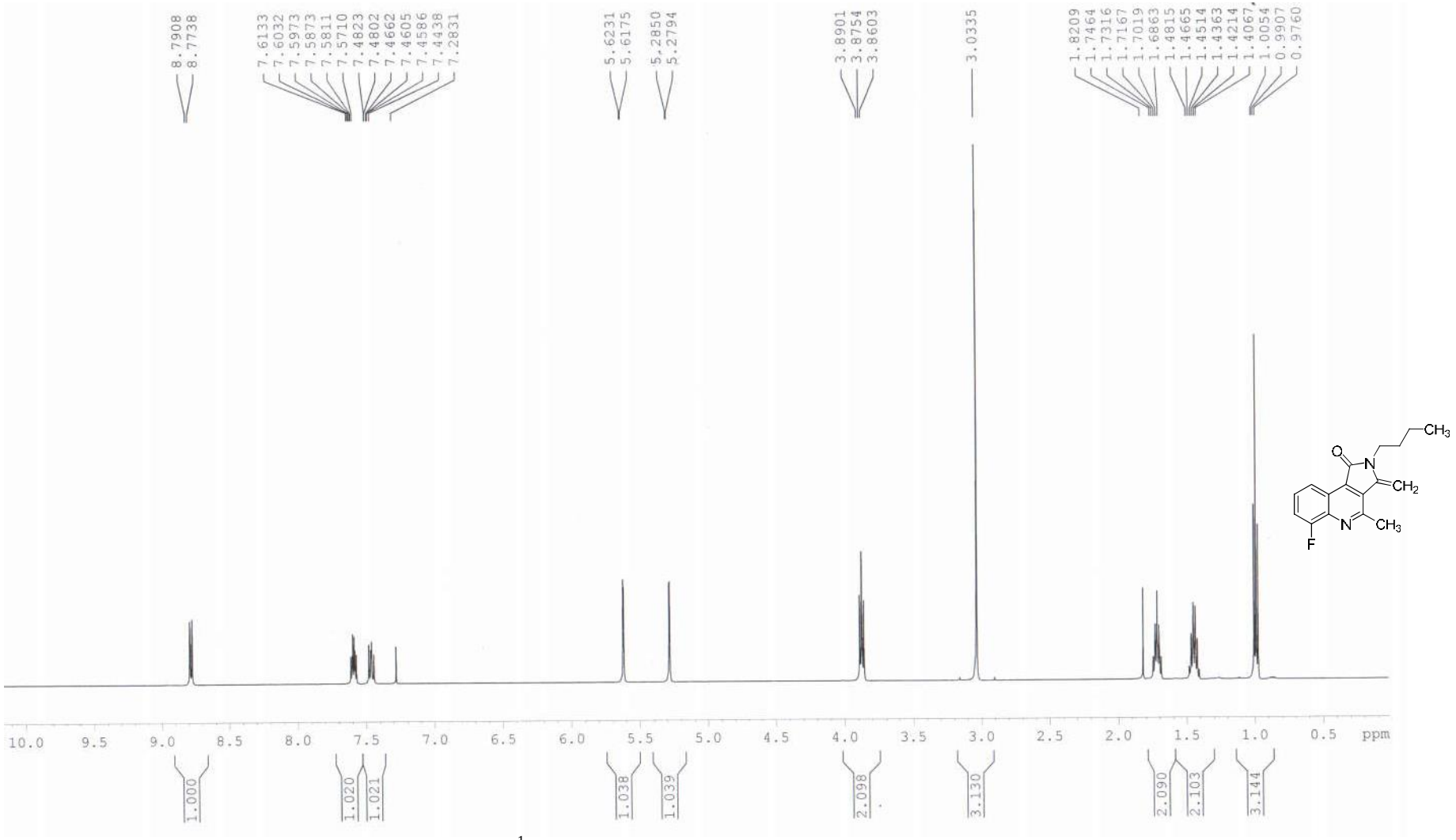


Figure 53. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **6a′**

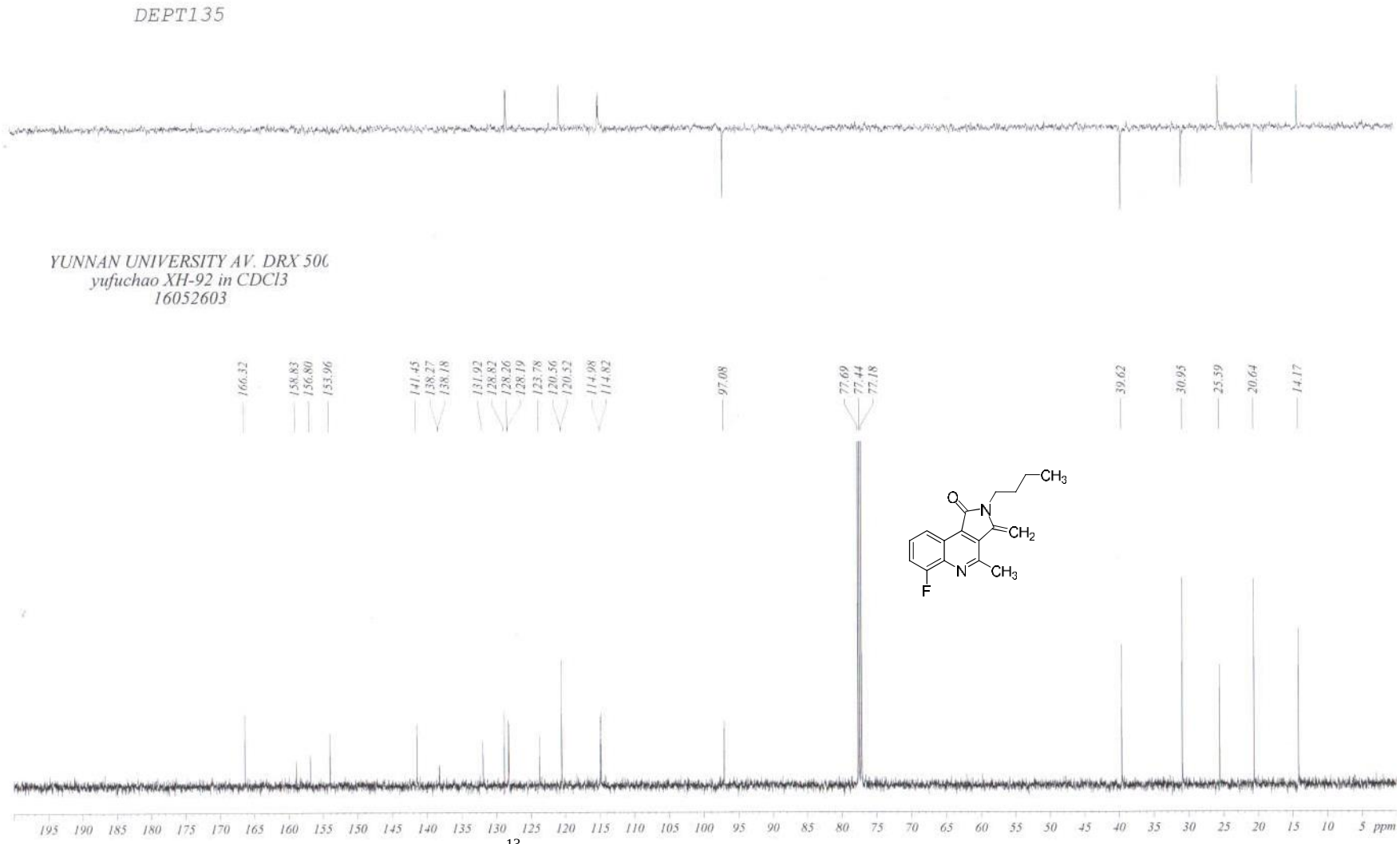


Figure 54. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **6a′**

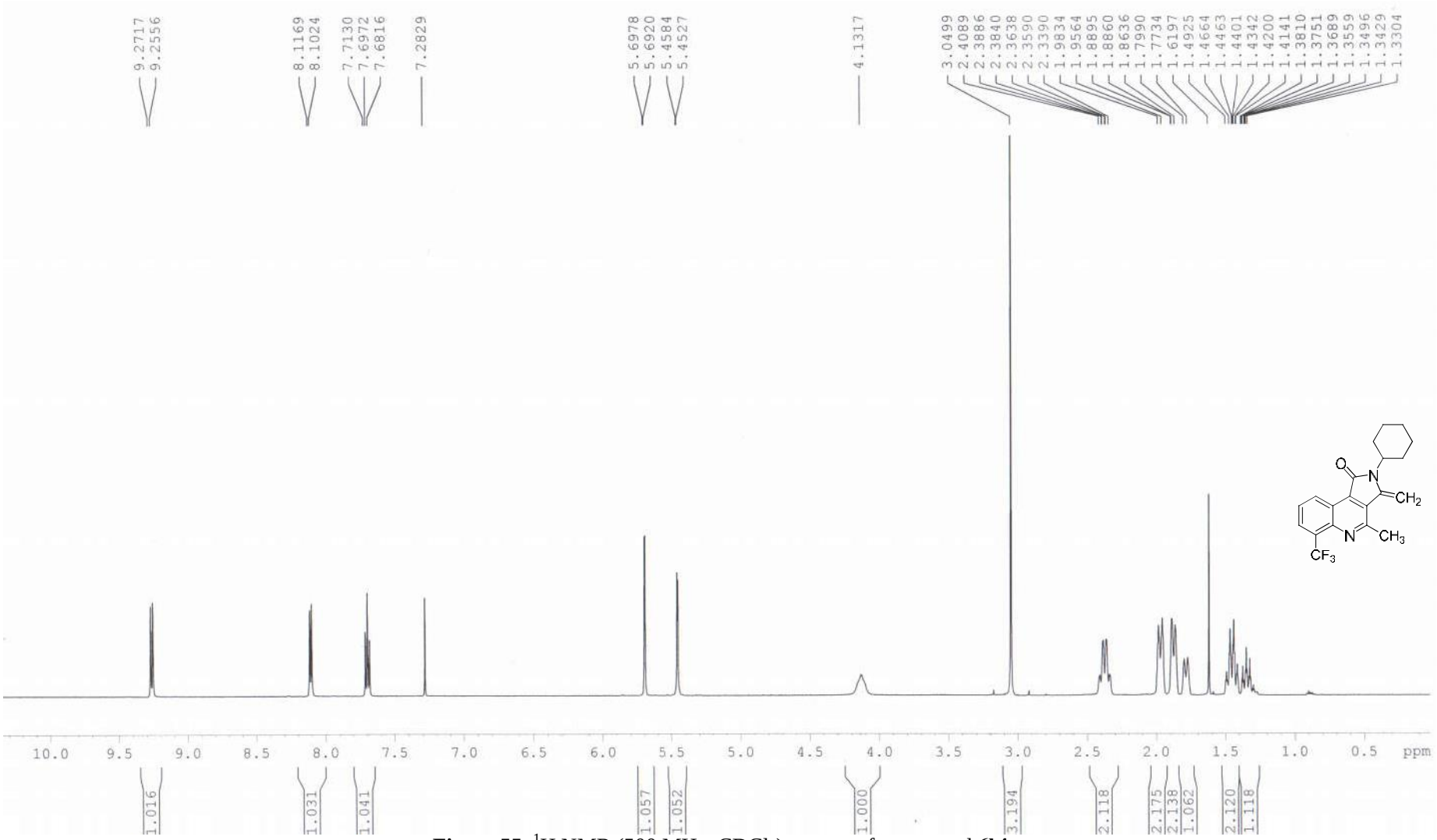


Figure 55. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **6b′**

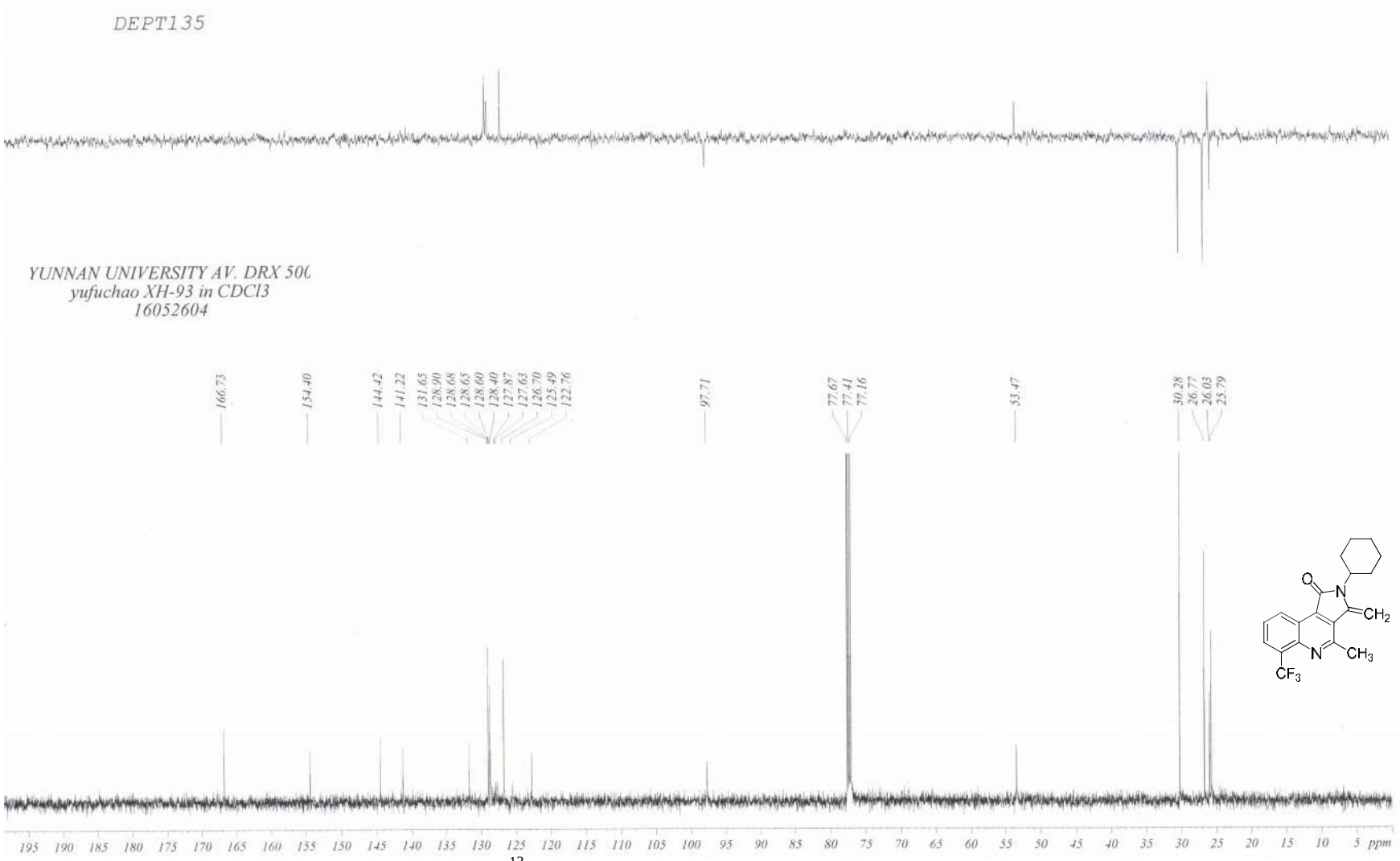


Figure 56. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **6b′**

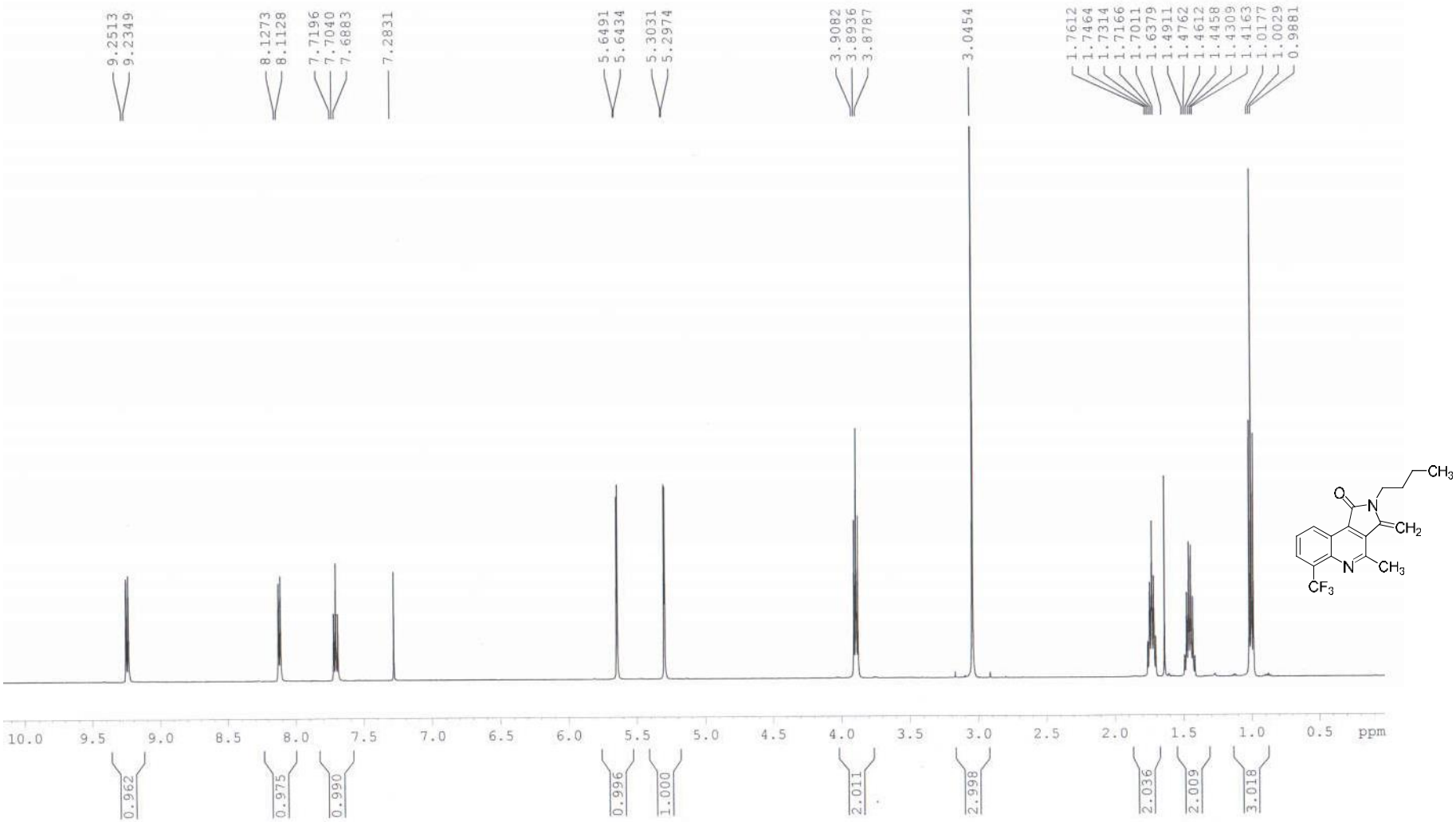


Figure 57. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **6c′**

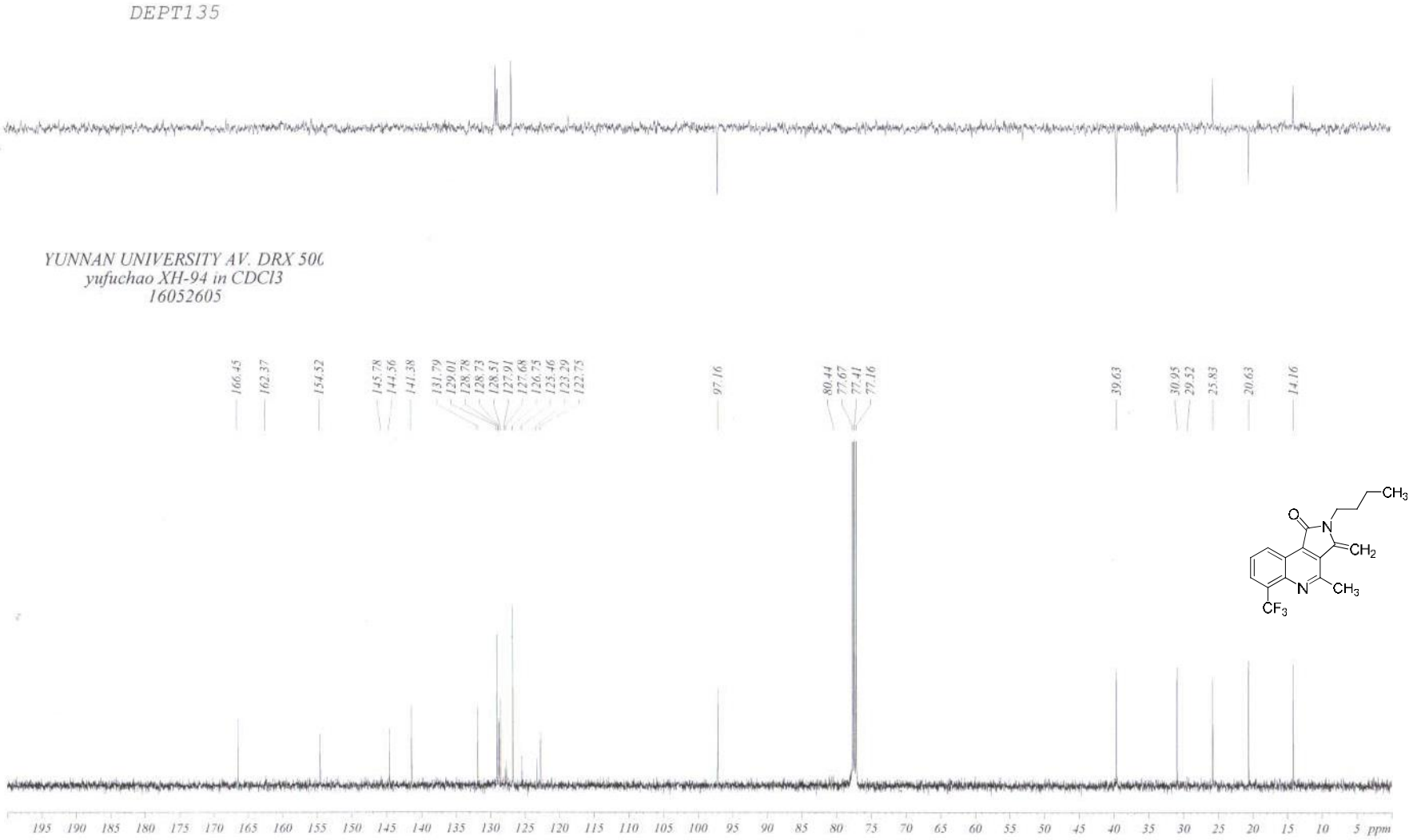


Figure 58. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **6c′**

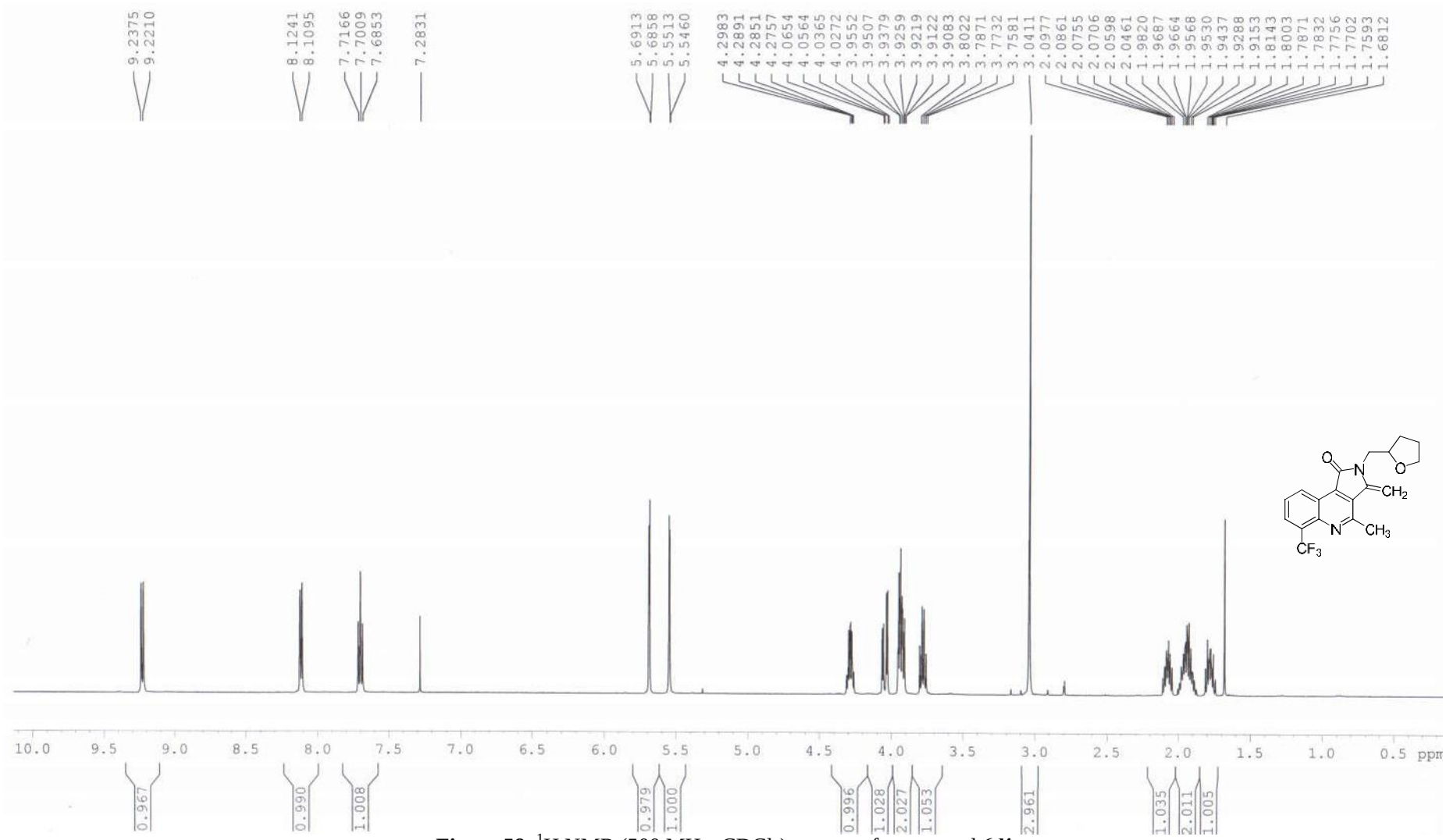


Figure 59. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **6d′**

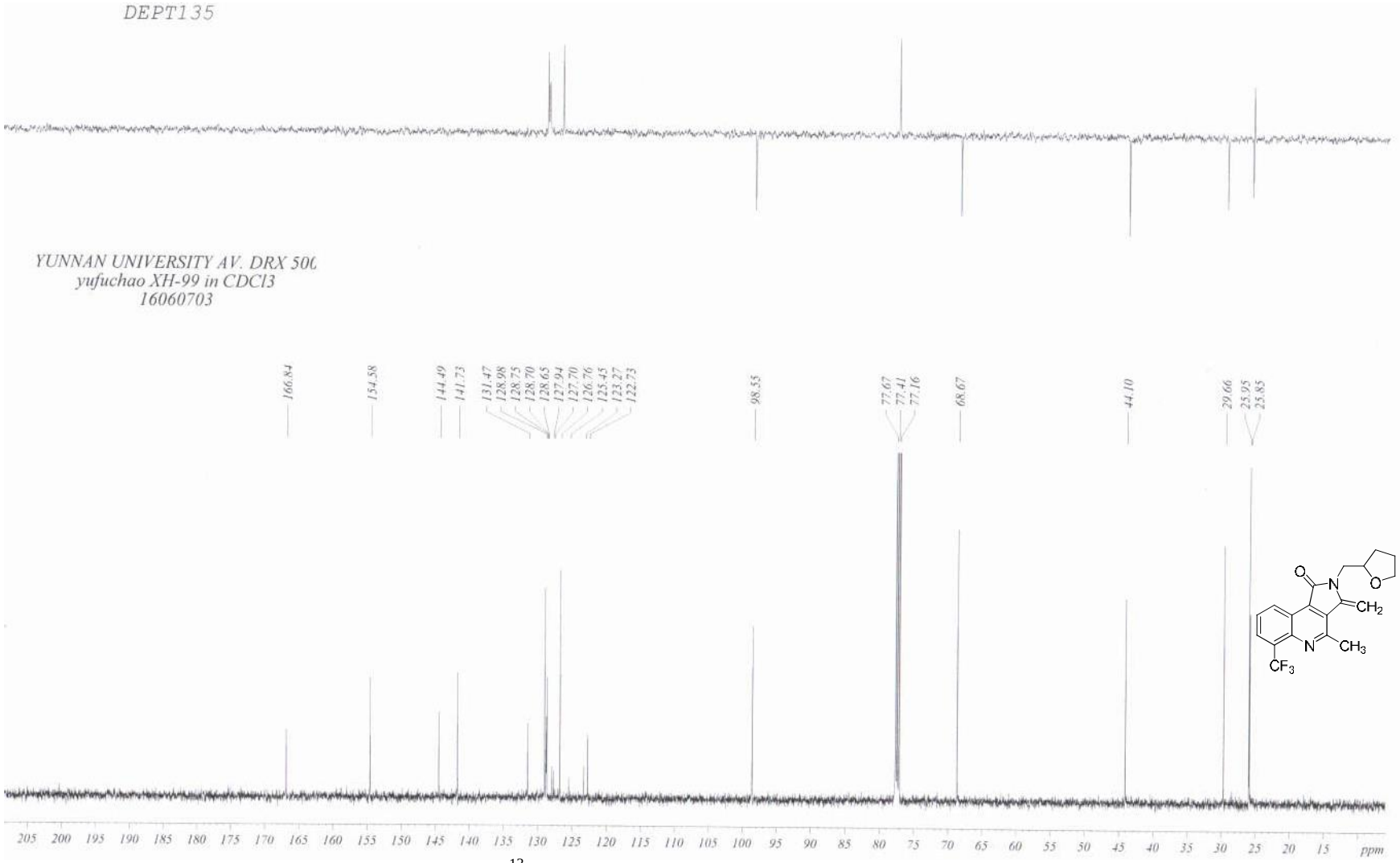


Figure 60. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **6d′**

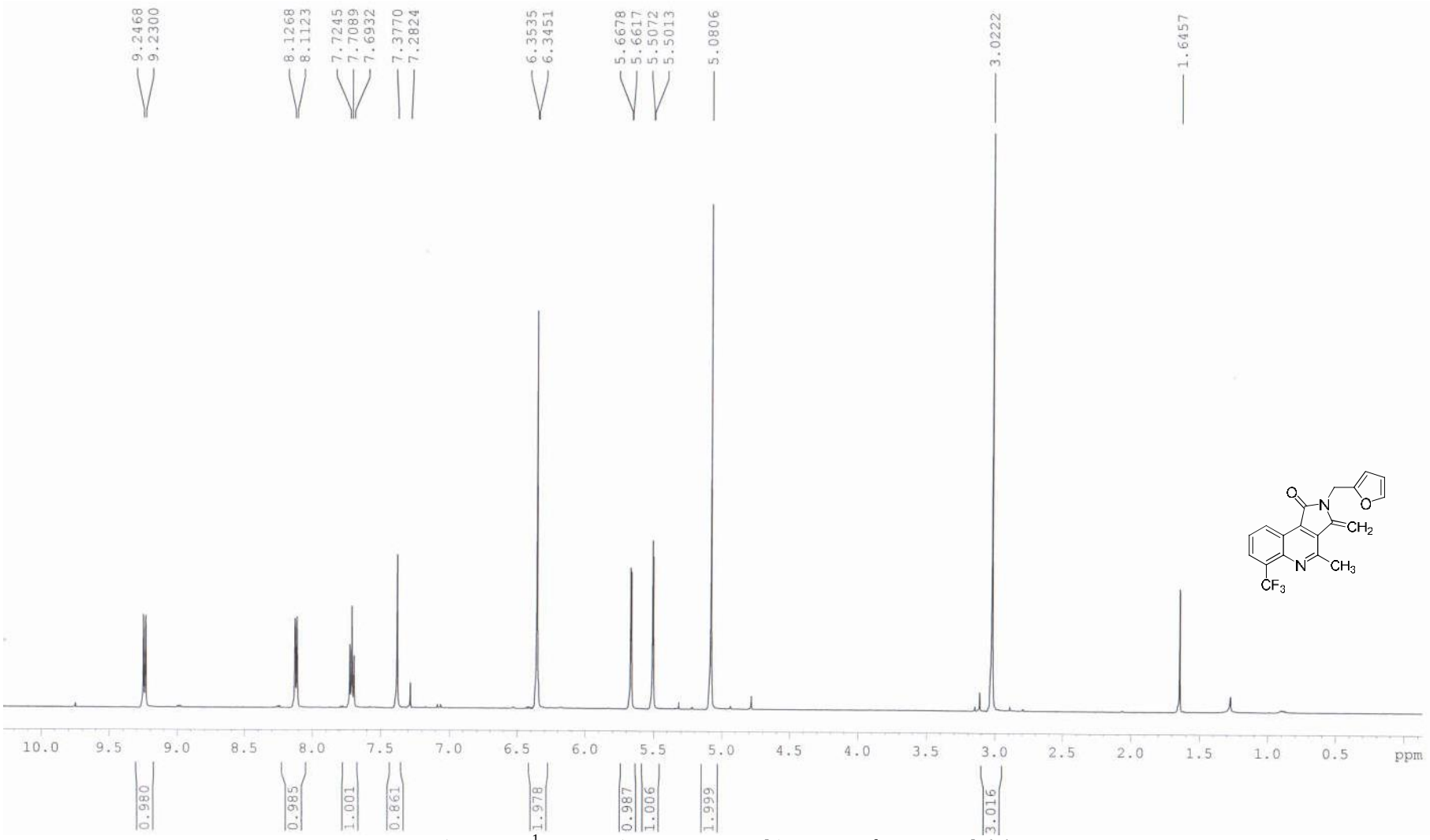


Figure 61. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **6e′**

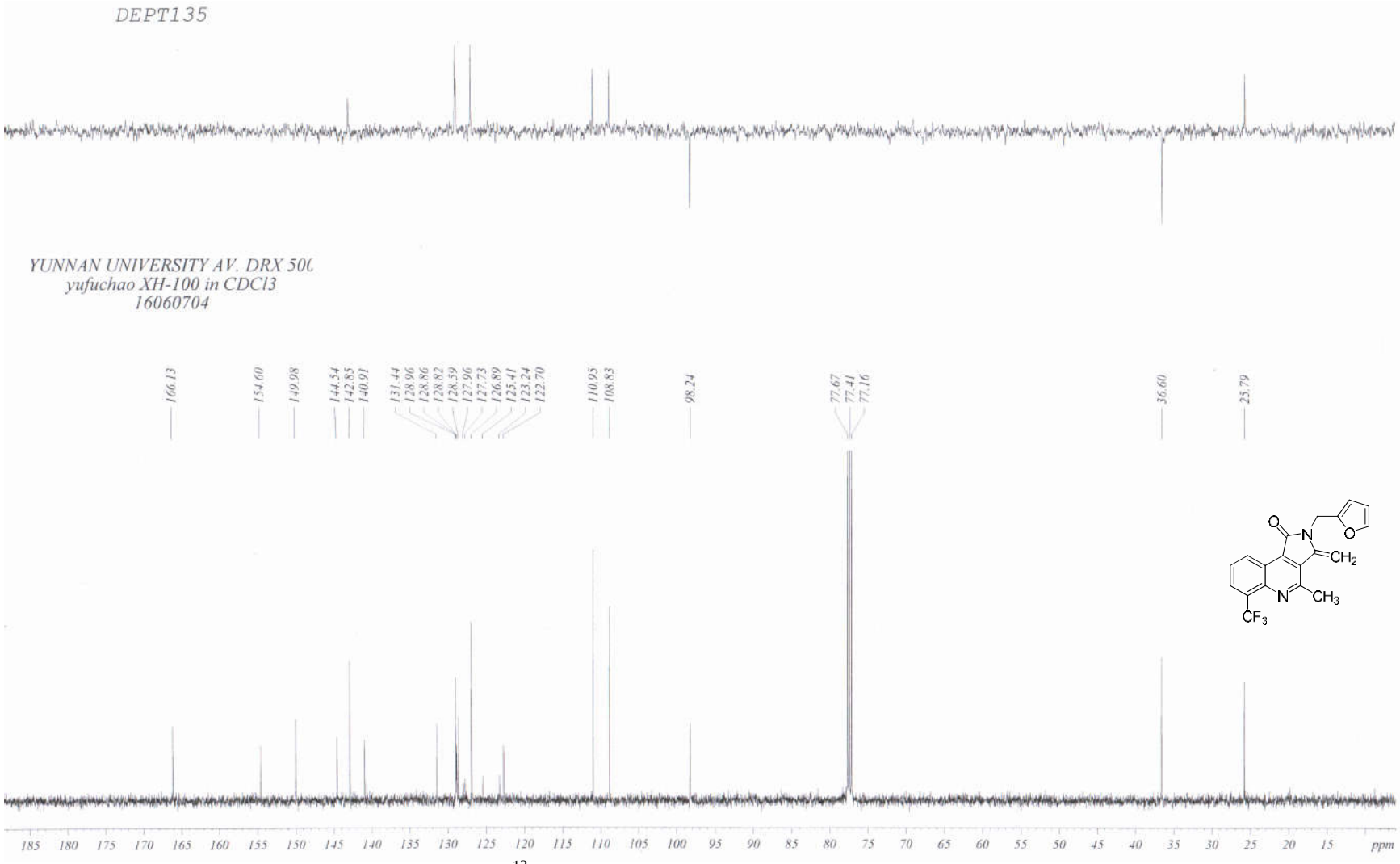


Figure 62. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **6e′**

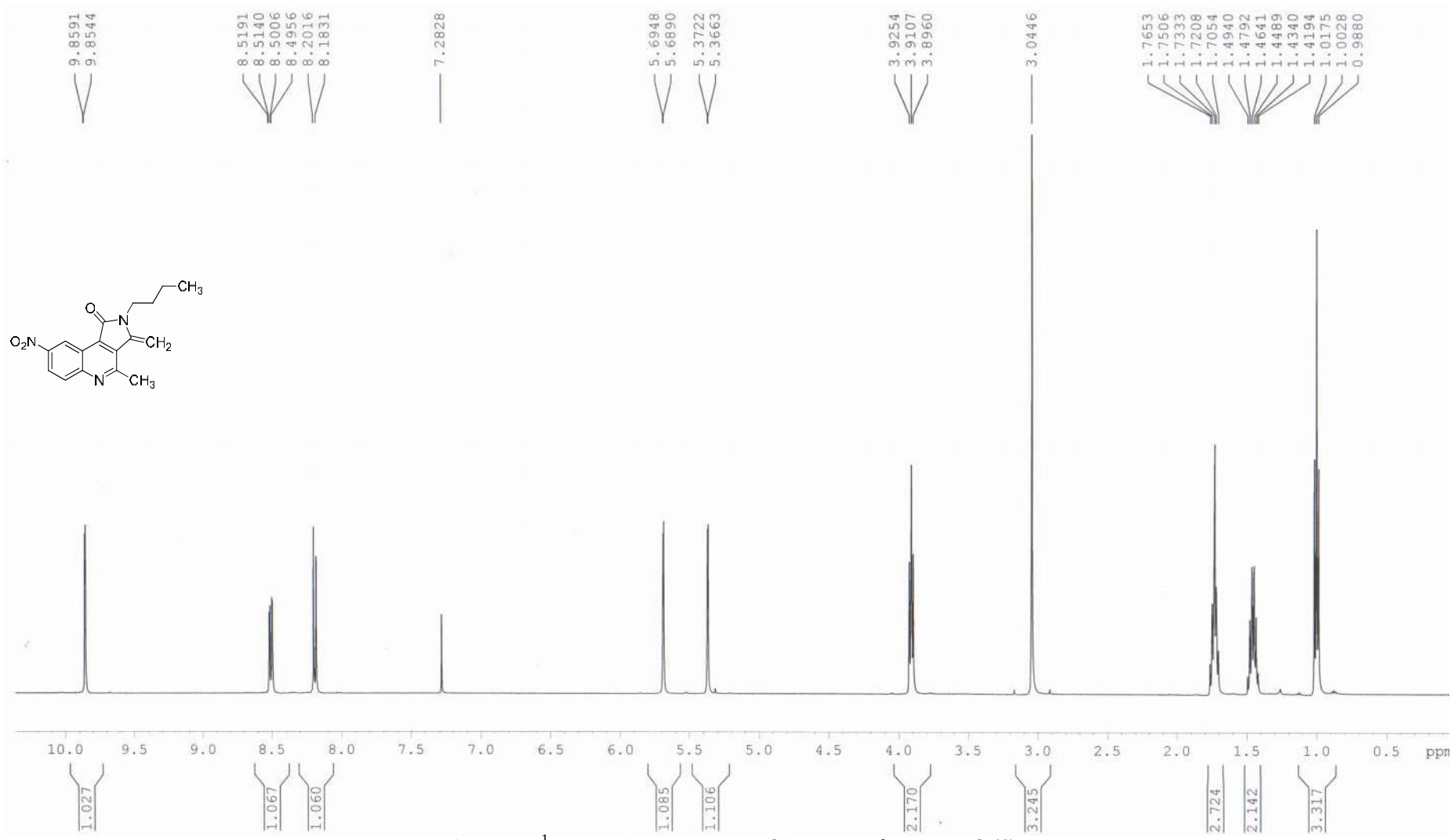


Figure 63. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **6f'**

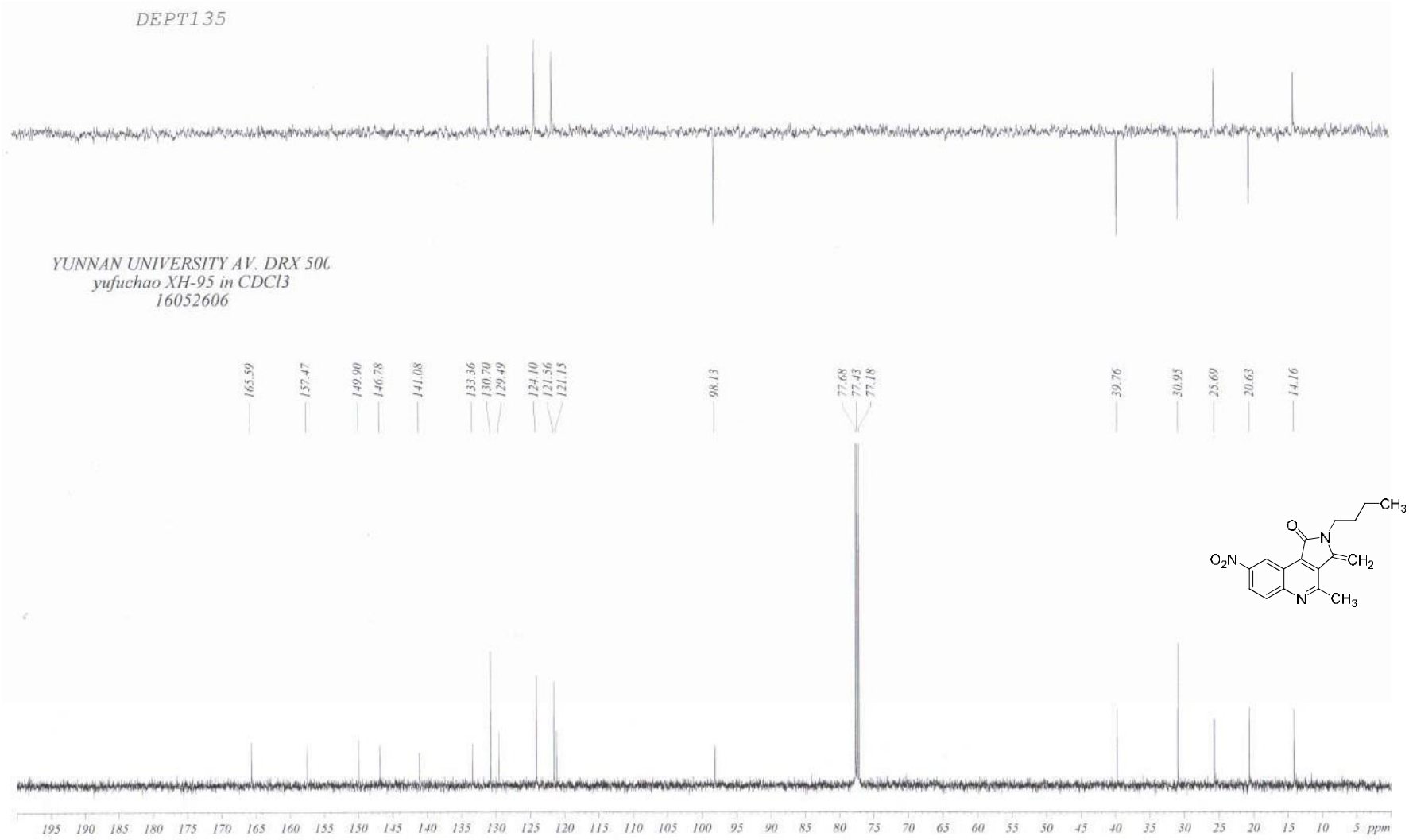


Figure 64. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **6f′**

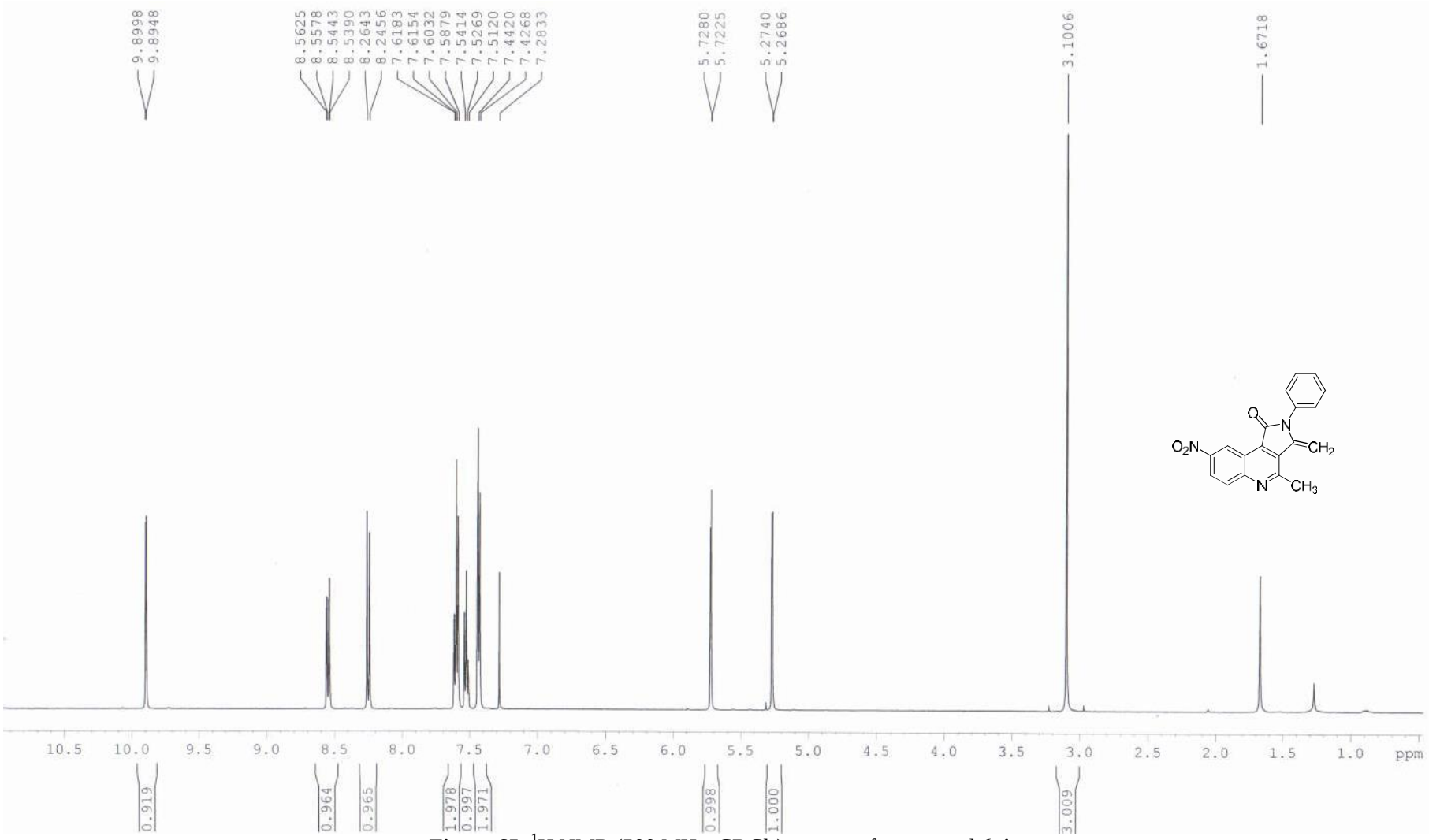


Figure 65. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **6g′**

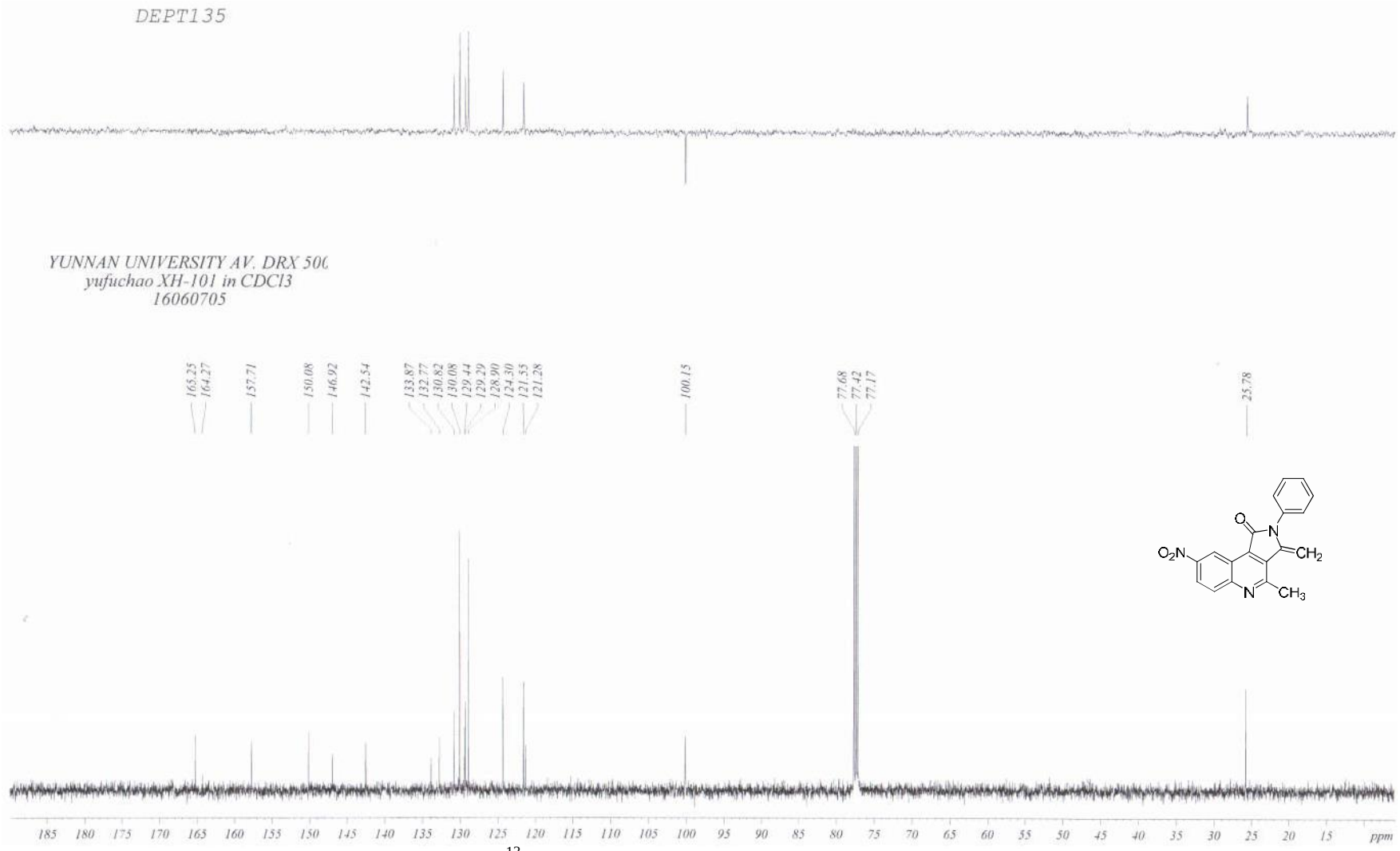


Figure 66. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **6g′**

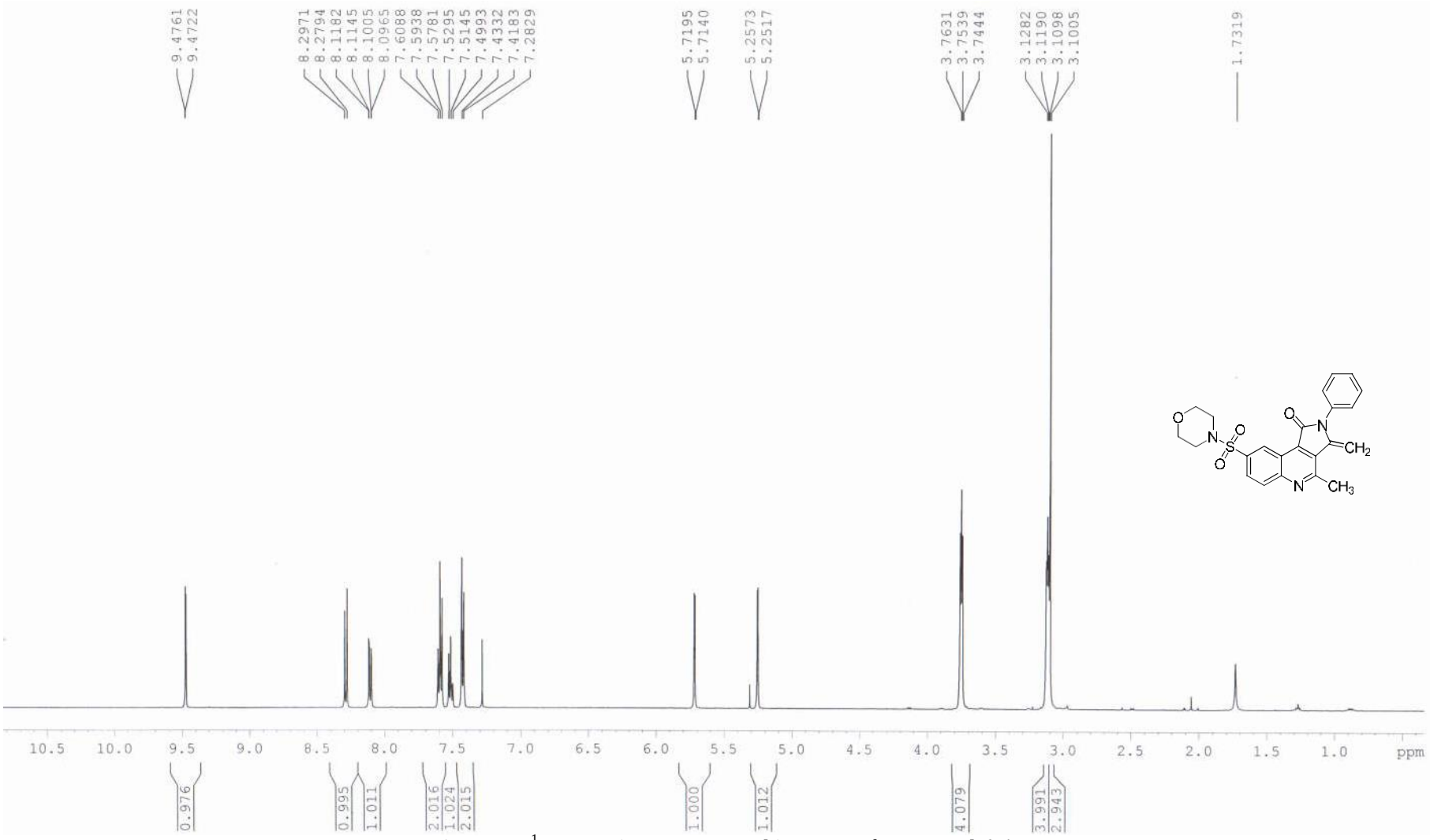


Figure 67. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **6h′**

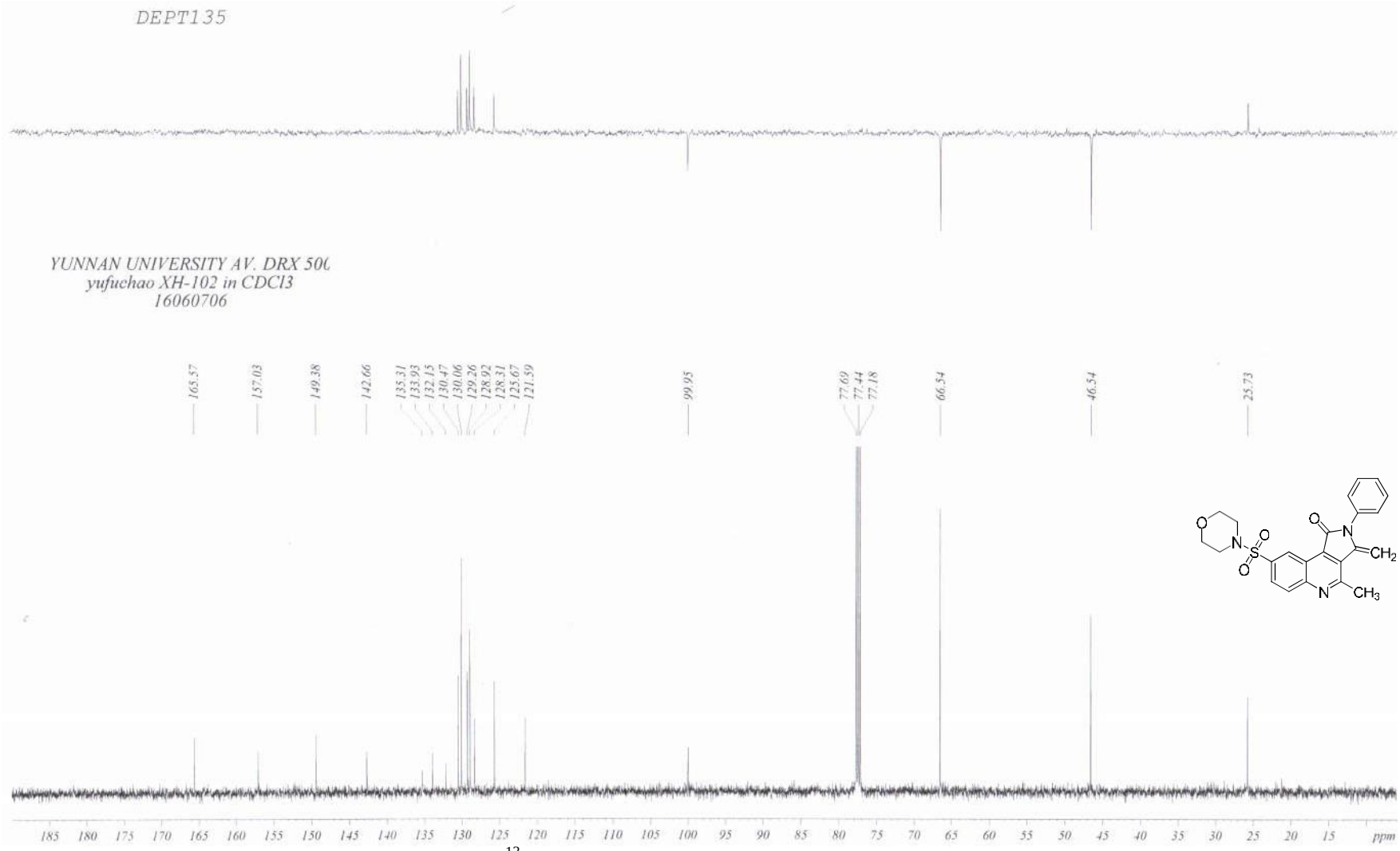


Figure 68. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **6h′**

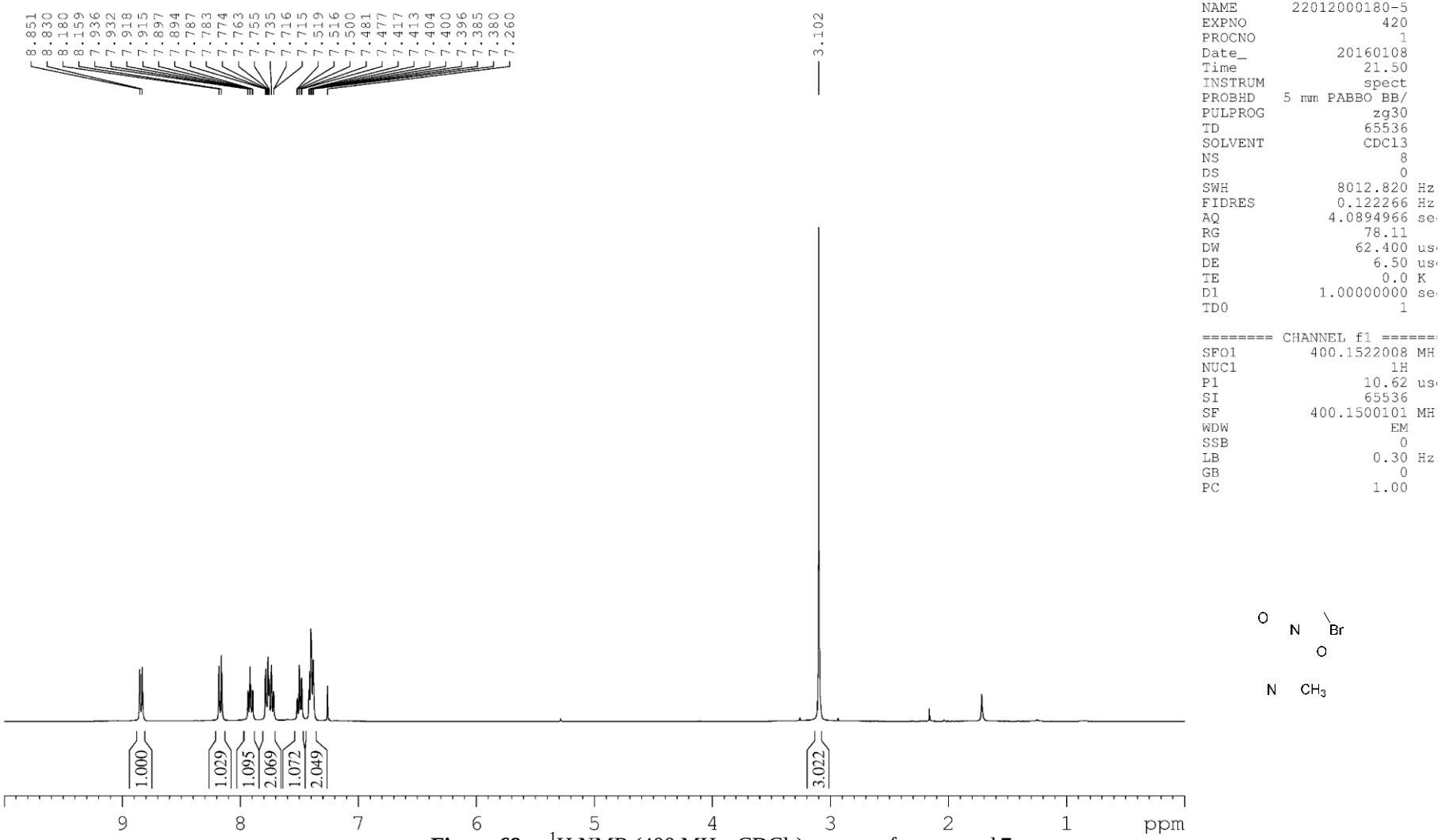


Figure 69. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **7a**

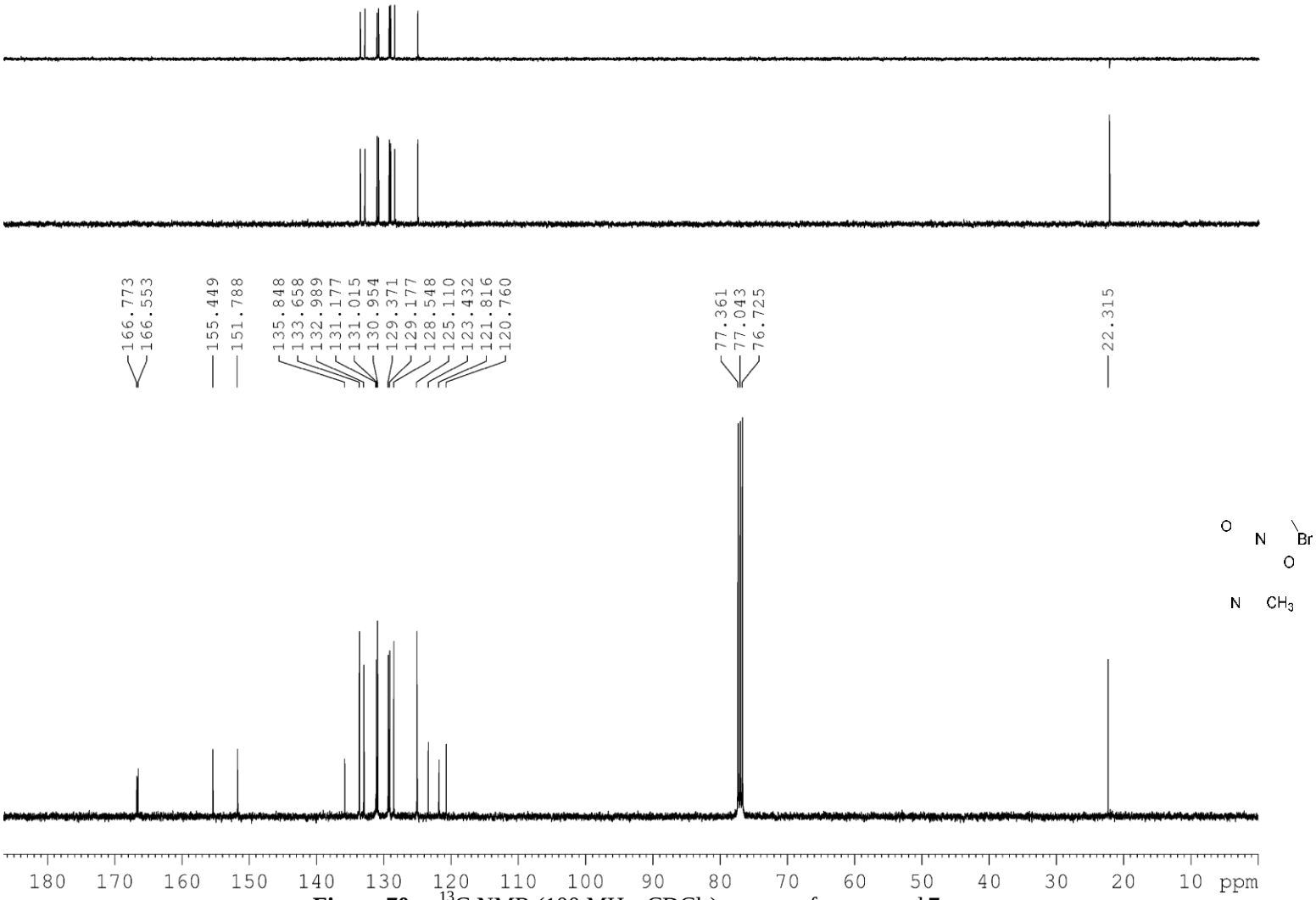


Figure 70. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **7a**

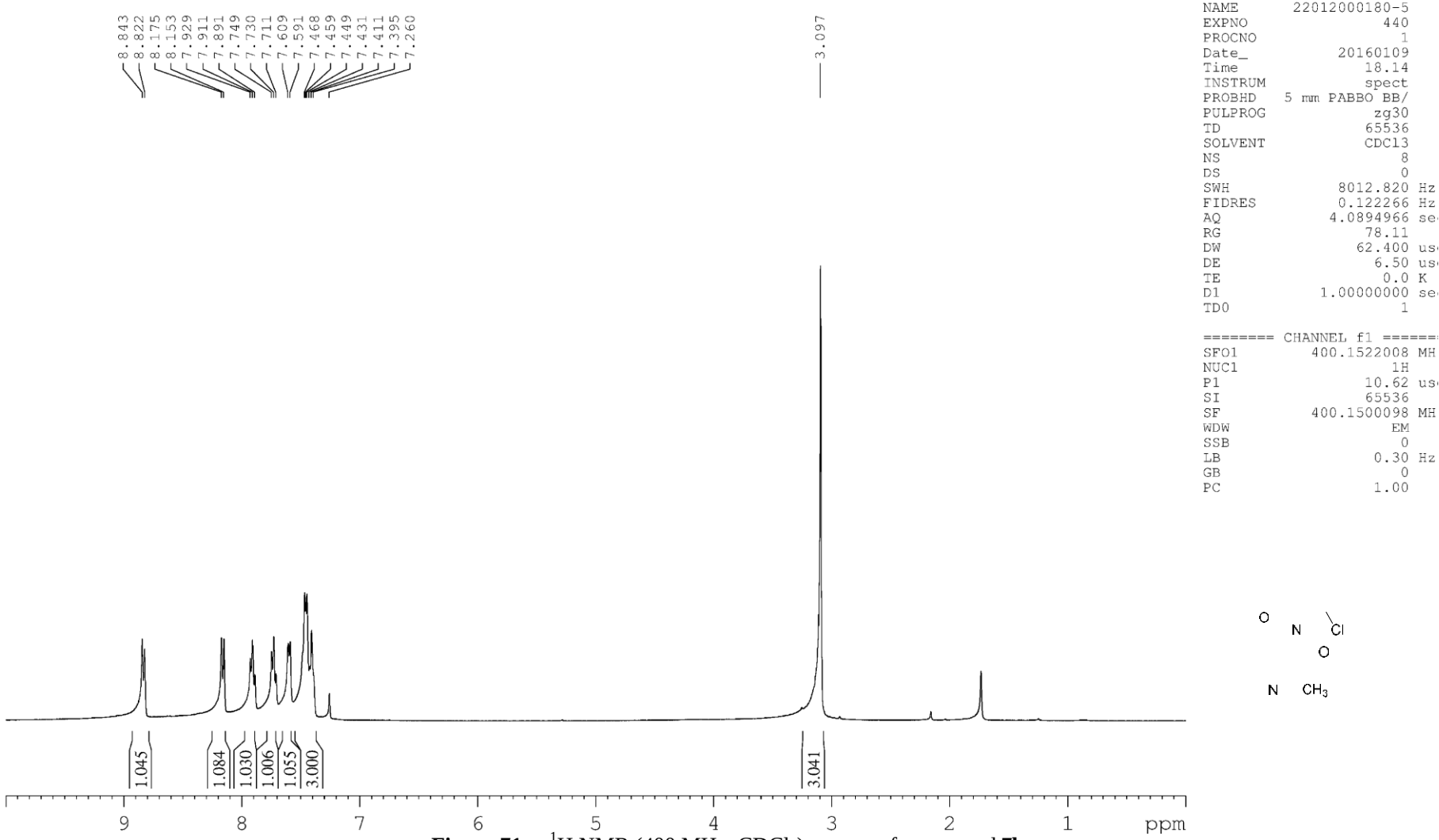


Figure 71. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **7b**

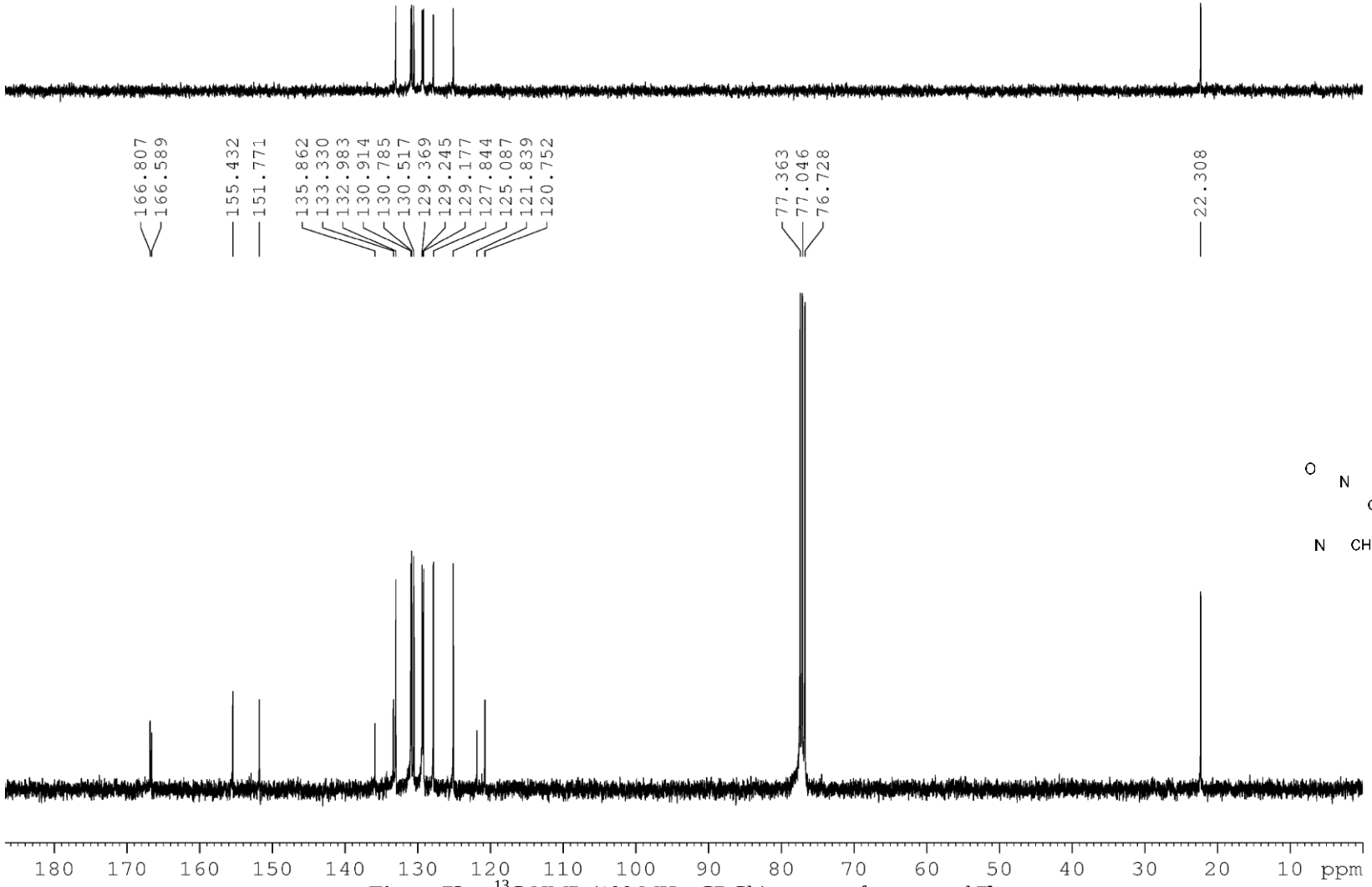


Figure 72. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **7b**

6. References and Notes

1. (*a*) Z. Duan, T. Li, X. J. Xuan, Y. J. Wu, *Chin. Chem. Lett.*, 2006, **17**, 1566; (*b*) M. M. Khodaei, A. R. Khosropour and C. Cardel, *J. Chin. Chem. Soc.*, 2008, **55**, 217.
2. C. E. Harris, W. Chrisman, S. A. Bickford, L. Y. Lee, A. E. Torreblanca and B. Singaram, *Tetrahedron Lett.*, 1997, **38**, 981.
3. CCDC **1438897** contain the supplementary crystallographic data for compound **6p**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.