An environmentally benign double Michael addition reaction of heterocyclic ketene aminals with quinone monoketals for diastereoselective synthesis of highly functionly morphan derivatives in water

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Supporting Information

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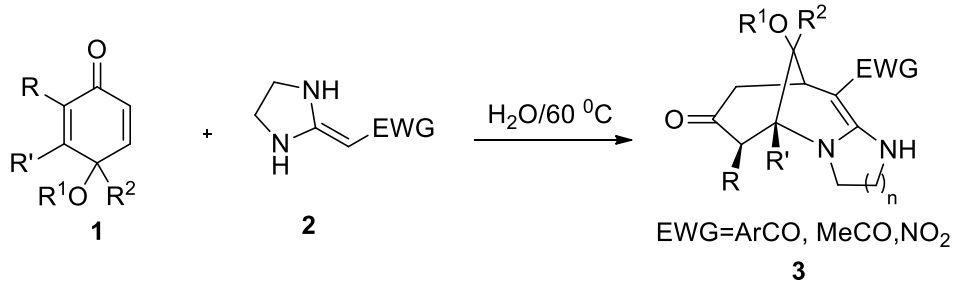
General Information

All compounds were fully characterized by spectroscopic data. The NMR spectra were recorded on a Bruker DRX300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) or Bruker DRX400 (^{1}H: 400 MHz, ^{13}C: 100 MHz), chemical shifts (δ) are expressed in ppm, and *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 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 an Agilent LC/Msd 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). X-ray diffraction was obtained by APEX DUO.

Compounds **1** were prepared according to the literature[1-5] and compounds **2** were prepared according to the literature.[6]

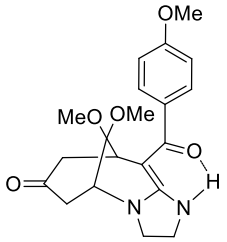
General Procedure for the Preparation of 3



Quinone monoketals **1** (1.1 mmol) was dissolved in water (15 mL) and HKAs **2** (1.0 mmol) were added to the mixture. The resulting solution was stirred at 60°C until the substrates **2** were completely consumed as indicated by TLC. The mixture was cooled to room temperature. Then the reaction mixture was then filtered to obtain the pure crude product, which was further washed with 95% EtOH to give pure product **3**. The products were further identified by FTIR, NMR and HRMS. The products were further identified by FTIR, NMR and HRMS. The products were further identified by FTIR, NMR and HRMS.

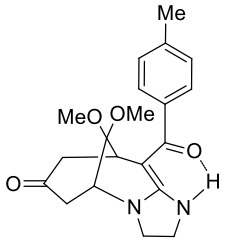
Spectroscopic Data of 3

(5*R*,9*R*)-11,11-dimethoxy-10-(4-methoxybenzoyl)-2,3,5,6,8,9-hexahydro-5,9-methanoimidazo[1,2-*a*]azocin-7(1*H*)-one (3a)



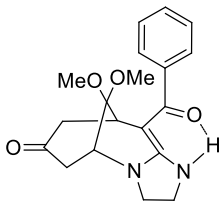
Yellow solid; mp 197–198 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.30–2.37 (m, 1H, $COCH_2$), 2.49–2.57 (m, 1H, $COCH_2$), 2.63–2.76 (m, 2H, $COCH_2$), 2.98–3.02 (m, 1H, CCH), 3.18 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3), 3.37–3.45 (m, 1H, NCH), 3.59–3.74 (m, 4H, NCH_2CH_2N), 3.81 (s, 3H, $ArOCH_3$), 6.83–6.89 (m, 2H, ArH), 7.24–7.31 (m, 2H, ArH), 9.22 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.4, 42.0, 42.7, 46.8, 47.0, 48.6, 48.7, 55.2, 86.4, 98.5, 113.4, 127.5, 135.0, 159.4, 160.2, 188.2, 209.1; IR (KBr): 3286, 2946, 2882, 2831, 1714, 1586, 1405 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{20}H_{24}N_2O_5$ [M^{+}], 372.1685; found, 372.1690.

(5*R*,9*R*)-11,11-dimethoxy-10-(4-methylbenzoyl)-2,3,5,6,8,9-hexahydro-5,9-methanoimidazo[1,2-*a*]azocin-7(1*H*)-one (3b)



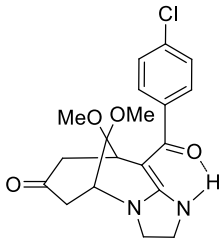
Yellow solid; mp 222–223 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.17–2.30 (m, 1H, $COCH_2$), 2.34 (s, 3H, $ArCH_3$), 2.49–2.56 (m, 1H, $COCH_2$), 2.61–2.74 (m, 2H, $COCH_2$), 2.99–3.13 (m, 1H, CCH), 3.19 (s, 3H, OCH_3), 3.29 (s, 3H, OCH_3), 3.35–3.43 (m, 1H, NCH), 3.59–3.77 (m, 4H, NCH_2CH_2N), 7.10–7.23 (AB, J = 7.8 Hz, 4H, ArH), 9.19 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 36.3, 42.0, 42.7, 46.8, 46.9, 48.6, 48.7, 55.3, 86.3, 98.5, 125.8, 128.7, 137.7, 139.5, 160.1, 188.7, 209.1; IR (KBr): 3434, 2950, 2315, 1712, 1591, 1531, 1405 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{20}H_{24}N_2O_4$ [M^{+}], 356.1736; found, 356.1753.

(5*R*,9*R*)-10-benzoyl-11,11-dimethoxy-2,3,5,6,8,9-hexahydro-5,9-methanoimidazo[1,2-*a*]azocin-7(1*H*)-one (3c)



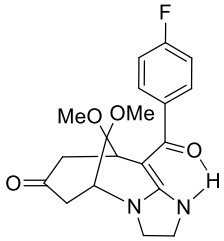
Yellow solid; mp 173–174 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28–2.35 (m, 1H, $COCH_2$), 2.49–2.56 (m, 1H, $COCH_2$), 2.60–2.73 (m, 2H, $COCH_2$), 2.98–3.12 (m, 1H, CCH), 3.20 (s, 3H, OCH_3), 3.30 (s, 3H, OCH_3), 3.38–3.47 (m, 1H, NCH), 3.58–3.79 (m, 4H, NCH_2CH_2N), 7.25–7.38 (m, 5H, ArH), 9.19 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.3, 41.9, 42.7, 46.8, 46.9, 48.6, 48.7, 55.3, 86.3, 98.5, 125.8, 128.0, 128.2, 142.3, 160.2, 188.5, 209.0; IR (KBr): 3278, 2950, 1709, 1595, 1527, 1274, 1108 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{19}H_{22}N_2O_4$ [M^{+}], 342.1580; found, 342.1586.

(5*R*,9*R*)-10-(4-chlorobenzoyl)-11,11-dimethoxy-2,3,5,6,8,9-hexahydro-5,9-methanoimidazo[1,2-*a*]azocin-7(1*H*)-one (3d)



Yellow solid; mp 189–191 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.24–2.31 (m, 1H, $COCH_2$), 2.49–2.57 (m, 1H, $COCH_2$), 2.63–2.74 (m, 2H, $COCH_2$), 2.97–3.10 (m, 1H, CCH), 3.19 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3), 3.37–3.47 (m, 1H, NCH), 3.57–3.81 (m, 4H, NCH_2CH_2N), 7.23–7.34 (AB, *J* = 8.4 Hz, 4H, ArH), 9.18 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.3, 41.9, 42.7, 46.8, 46.9, 48.6, 48.7, 55.2, 86.3, 98.3, 127.4, 128.4, 133.8, 140.8, 160.2, 186.8, 208.7; IR (KBr): 3312, 2950, 2351, 1713, 1594, 1528 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{19}H_{21}N_2O_4Cl$ [M^{+}], 376.1190; found, 376.1190.

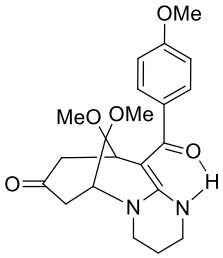
(5*R*,9*R*)-10-(4-fluorobenzoyl)-11,11-dimethoxy-2,3,5,6,8,9-hexahydro-5,9-methanoimidazo[1,2-*a*]azocin-7(1*H*)-one (3e)



Yellow solid; mp 193–194 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25–2.32 (m, 1H, $COCH_2$), 2.50–2.58 (m, 1H, $COCH_2$), 2.63–2.76 (m, 2H, $COCH_2$), 2.97–3.10 (m, 1H, CCH), 3.19 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3), 3.40–3.48 (m, 1H, NCH), 3.60–3.80

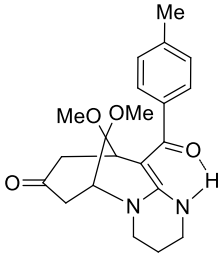
(m, 4H, NCH_2CH_2N), 6.98–7.08 (m, 2H, ArH), 7.27–7.34 (m, 2H, ArH), 9.19 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.4, 41.9, 42.7, 46.7, 46.9, 48.6, 48.7, 55.2, 86.3, 98.4, 114.9(J = 21.2 Hz), 115.2(J = 21.2 Hz), 127.8(J = 7.9 Hz), 127.9(J = 7.9 Hz), 138.5, 160.2, 160.8(J = 245.1 Hz), 164.0(J = 245.1 Hz), 187.1, 208.9; IR (KBr): 3442, 2955, 2352, 1709, 1599, 1533, 1412 cm^{-1}; HRMS (EI$^+$): *m/z* calcd. for $C_{19}H_{21}N_2O_4F$ [M$^+$], 360.1485; found, 360.1476.

(6*R*,10*R*)-12,12-dimethoxy-11-(4-methoxybenzoyl)-3,4,6,7,9,10-hexahydro-1*H*-6,10-methanopyrimido[1,2-*a*]azocin-8(2*H*)-one (3f)



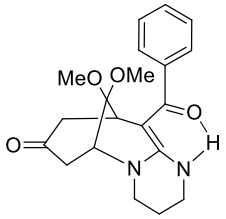
Yellow solid; mp 197–198 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.93–2.08 (m, 2H, CCH_2C), 2.24–2.31 (m, 1H, $COCH_2$), 2.46–2.53 (m, 1H, $COCH_2$), 2.56–2.68 (m, 2H, $COCH_2$), 3.06–3.11 (m, 1H, CCH), 3.16 (s, 3H, OCH_3), 3.17 (s, 3H, OCH_3), 3.17–3.67 (m, 4H, NCH_2CH_2N), 3.50–3.52 (m, 1H, NCH), 3.80 (s, 3H, $ArOCH_3$), 6.83–6.87 (m, 2H, ArH), 7.20–7.24 (m, 2H, ArH), 12.45 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 37.1, 37.8, 41.8, 46.1, 46.8, 48.5, 48.7, 55.2, 60.0, 88.2, 97.1, 113.5, 127.2, 135.9, 156.5, 158.9, 185.9, 209.0; IR (KBr): 3483, 2948, 2867, 1714, 1589, 1546, 1407, 1244 cm^{-1}; HRMS (EI$^+$): *m/z* calcd. for $C_{21}H_{26}N_2O_5$ [M$^+$], 386.1842; found, 386.1831.

(6*R*,10*R*)-12,12-dimethoxy-11-(4-methylbenzoyl)-1,2,3,4,6,7,9,10-octahydro-8*H*-6,10-methanopyrimido[1,2-*a*]azocin-8-one (3g)



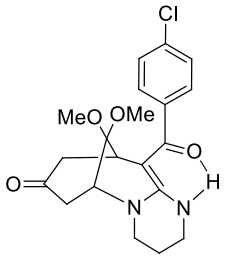
Yellow solid; mp 117–119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.92–1.98 (m, 2H, CCH_2C), 2.15–2.20 (m, 1H, $COCH_2$), 2.24 (s, 3H, $ArCH_3$), 2.39–2.44 (m, 1H, $COCH_2$), 2.48–2.57 (m, 2H, $COCH_2$), 2.94–2.99 (m, 1H, CCH), 3.14 (s, 3H, OCH_3), 3.17 (s, 3H, OCH_3), 3.16–3.29 (m, 4H, NCH_2CCH_2N), 3.42–3.47 (m, 1H, NCH), 7.01–7.09 (m, 4H, ArH), 12.31 (br., 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7, 21.2, 37.0, 37.7, 41.8, 46.0, 46.7, 48.5, 48.6, 59.9, 88.0, 97.0, 125.6, 128.7, 136.8, 140.3, 156.4, 186.0, 209,1; IR (KBr): 3432, 2952, 1715, 1585, 1415, 1244, 1112, 1064 cm^{-1}; HRMS (EI$^+$): *m/z* calcd. for $C_{21}H_{26}N_2O_4$ [M$^+$], 370.1893; found, 370.1895.

(6*R*,10*R*)-11-benzoyl-12,12-dimethoxy-1,2,3,4,6,7,9,10-octahydro-8*H*-6,10-methanopyrimido[1,2-*a*]azocin-8-one (3h)



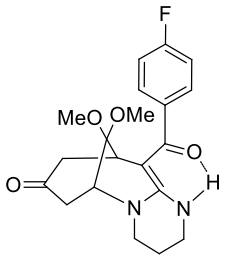
Yellow solid; mp 181–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96–2.03 (m, 2H, CCH_2C), 2.17–2.23 (m, 1H, $COCH_2$), 2.40–2.45 (m, 1H, $COCH_2$), 2.44–2.60 (m, 2H, $COCH_2$), 2.88–2.95 (m, 1H, CCH), 3.15 (s, 3H, OCH_3), 3.18 (s, 3H, OCH_3), 3.20–3.38 (m, 4H, NCH_2CH_2N), 3.42–3.49 (m, 1H, NCH), 7.16–7.27 (m, 5H, ArH), 12.30 (br., 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ =20.7, 37.0, 37.8, 41.8, 46.1, 46.7, 48.5, 48.7, 60.0, 88.0, 97.0, 125.7, 127.3, 128.2, 143.1, 156.5, 185.9, 209.0; IR (KBr): 3435, 2954, 1712, 1555, 1415, 1245, 1179, 1109 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{20}H_{24}N_2O_4$ [M^{+}], 356.1736; found, 356.1744.

(6*R*,10*R*)-11-(4-chlorobenzoyl)-12,12-dimethoxy-1,2,3,4,6,7,9,10-octahydro-8*H*-6,10-methanopyrimido[1,2-*a*]azocin-8-one (3i)



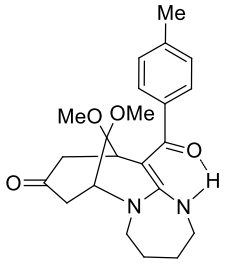
Yellow solid; mp 103–104 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.95–2.08 (m, 2H, CCH_2C), 2.17–2.25 (m, 1H, $COCH_2$), 2.45–2.55 (m, 1H, $COCH_2$), 2.55–2.69 (m, 2H, $COCH_2$), 2.95–3.10 (m, 1H, CCH), 3.22 (s, 3H, OCH_3), 3.26 (s, 3H, OCH_3), 3.29–3.39 (m, 4H, NCH_2CH_2N), 3.51–3.54 (m, 1H, NCH), 7.19–7.34 (AB, J = 8.4 Hz, 4H, ArH), 12.31 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 37.0, 37.8, 41.8, 46.1, 46.7, 48.5, 48.6, 60.0, 88.2, 96.9, 127.3, 128.4, 133.1, 141.5, 156.5, 184.4, 208.6; IR (KBr): 3423, 2951, 1716, 1584, 1415, 1245, 1110, 1068 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{20}H_{23}N_2O_4Cl$ [M^{+}], 390.1346; found, 390.1343.

(6*R*,10*R*)-11-(4-fluorobenzoyl)-12,12-dimethoxy-1,2,3,4,6,7,9,10-octahydro-8*H*-6,10-methanopyrimido[1,2-*a*]azocin-8-one (3j)



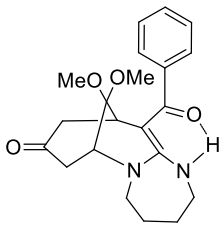
Yellow solid; mp 161–162 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.97–2.06 (m, 2H, CCH_2C), 2.20–2.26 (m, 1H, $COCH_2$), 2.48–2.54 (m, 1H, $COCH_2$), 2.56–2.69 (m, 2H, $COCH_2$), 2.99–3.02 (m, 1H, CCH), 3.19 (s, 3H, OCH_3), 3.22 (s, 3H, OCH_3), 3.26–3.38 (m, 4H, NCH_2CH_2N), 3.52–3.54 (m, 1H, NCH), 6.98–7.05 (m, 2H, ArH), 7.23–7.29 (m, 2H, ArH), 12.36 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 37.1, 37.8, 41.8, 46.1, 46.7, 48.5, 48.6, 60.0, 88.2, 97.0, 114.9(*J* = 21.2 Hz), 115.2(*J* = 21.2 Hz), 127.6(*J* = 7.9 Hz), 127.7(*J* = 7.9 Hz), 139.3, 156.5, 160.4(*J* = 244.1 Hz), 163.6(*J* = 244.1 Hz), 184.8, 208.7; IR (KBr): 3420, 2946, 1711, 1585, 1413, 1217, 1110, 1065 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{20}H_{23}N_2O_4F$ [M^{+}], 374.1642; found, 374.1637.

(7*R*,11*R*)-13,13-dimethoxy-12-(4-methylbenzoyl)-2,3,4,5,7,8,10,11-octahydro-7,11-methano[1,3]diazepino[1,2-*a*]azocin-9(1*H*)-one (3k)



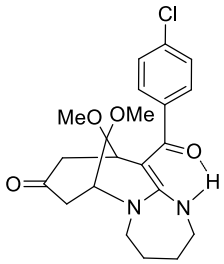
Yellow solid; mp 90–91 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.76–1.81 (m, 4H, CCH_2CH_2C), 2.20–2.26 (m, 1H, $COCH_2$), 2.33 (s, 3H, $ArCH_3$), 2.48–2.59 (m, 2H, $COCH_2$), 2.62–2.69 (m, 1H, $COCH_2$), 3.11–3.13 (m, 1H, CCH), 3.25 (s, 3H, OCH_3), 3.26 (s, 3H, OCH_3), 3.26–3.46 (m, 4H, NCH_2CH_2N), 3.62–3.64 (m, 1H, NCH), 7.10–7.30 (m, 4H, ArH), 11.68 (br., 1H, NH); ^{3}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 26.2, 26.5, 37.0, 43.1, 44.5, 46.0, 48.5, 48.7, 52.9, 61.0, 91.4, 97.3, 125.6, 128.8, 137.2, 140.4, 164.6, 188.7, 209.2; IR (KBr): 3424, 2939, 1717, 1548, 1410, 1196, 1010 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{22}H_{28}N_2O_4$ [M^{+}], 384.2049; found, 384.2049.

(7*R*,11*R*)-12-benzoyl-13,13-dimethoxy-2,3,4,5,7,8,10,11-octahydro-7,11-methano[1,3]diazepino[1,2-*a*]azocin-9(1*H*)-one (3l)



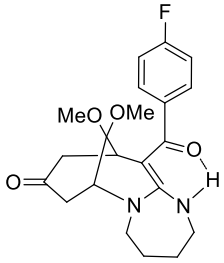
Yellow solid; mp 100–101 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70–1.76 (m, 4H, CCH_2CH_2C), 2.14–2.19 (m, 1H, $COCH_2$), 2.42–2.51 (m, 2H, $COCH_2$), 2.55–2.62 (m, 1H, $COCH_2$), 2.99–3.02 (m, 1H, CCH), 3.19 (s, 3H, OCH_3), 3.19 (s, 3H, OCH_3), 3.26–3.44 (m, 4H, NCH_2CCCH_2N), 3.55–3.57 (m, 1H, NCH), 7.18–7.28 (m, 5H, ArH), 11.69 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.1, 26.4, 37.0, 43.0, 44.4, 46.0, 48.5, 48.6, 52.8, 61.0, 91.3, 97.3, 125.6, 127.5, 128.2, 143.2, 164.5, 188.3, 209.1; IR (KBr): 3424, 2941, 1716, 1599, 1549, 1413, 1110 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{21}H_{26}N_2O_4$ [M^{+}], 370.1893; found, 370.1864.

(7*R*,11*R*)-12-(4-chlorobenzoyl)-13,13-dimethoxy-2,3,4,5,7,8,10,11-octahydro-7,11-methano[1,3]diazepino[1,2-*a*]azocin-9(1*H*)-one (3m)



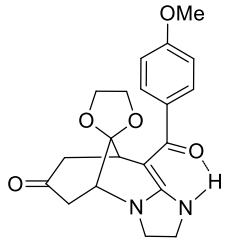
Yellow solid; mp 98–100 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.80–1.84 (m, 4H, CCH_2CH_2C), 2.13–2.20 (m, 1H, $COCH_2$), 2.48–2.60 (m, 2H, $COCH_2$), 2.64–2.71 (m, 1H, $COCH_2$), 3.02–3.04 (m, 1H, CCH), 3.25 (s, 3H, OCH_3), 3.27 (s, 3H, OCH_3), 3.28–3.49 (m, 4H, NCH_2CH_2N), 3.63–3.65 (m, 1H, NCH), 7.31 (d, *J* = 8.4 Hz, 2H, ArH), 7.22 (d, *J* = 8.4 Hz, 2H, ArH), 11.71 (br., 1H, NH); ^{3}C NMR (75 MHz, $CDCl_3$): δ = 26.0, 26.2, 37.1, 42.9, 44.4, 46.0, 48.5, 48.6, 52.6, 60.9, 91.4, 97.2, 127.3, 128.4, 133.3, 141.5, 164.5, 186.6, 208.8; IR (KBr): 3433, 2941, 2354, 1717, 1551, 1410, 1203, 1108 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{21}H_{25}N_2O_4Cl$ [M^{+}], 404.1503; found, 404.1512.

(7*R*,11*R*)-12-(4-fluorobenzoyl)-13,13-dimethoxy-2,3,4,5,7,8,10,11-octahydro-7,11-methano[1,3]diazepino[1,2-*a*]azocin-9(1*H*)-one (3n)



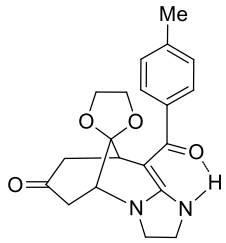
Yellow solid; mp 92–93 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.74–1.76 (m, 4H, CCH_2CH_2C), 2.07–2.14 (m, 1H, $COCH_2$), 2.39–2.52 (m, 2H, $COCH_2$), 2.57–2.64 (m, 1H, $COCH_2$), 2.99–3.00 (m, 1H, CCH), 3.19 (s, 3H, OCH_3), 3.20 (s, 3H, OCH_3), 3.26–3.41 (m, 4H, NCH_2CH_2N), 3.57–3.58 (m, 1H, NCH), 6.90–6.98 (m, 2H, ArH), 7.17–7.23 (m, 2H, ArH), 11.63 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.1, 26.3, 37.1, 43.0, 44.4, 46.0, 48.5, 48.6, 52.7, 60.9, 91.4, 97.2, 115.0(*J* = 21.2 Hz), 115.2(*J* = 21.2 Hz), 127.6(*J* = 7.9 Hz), 127.7(*J* = 7.9 Hz), 139.3, 160.5(*J* = 244.4 Hz), 163.7(*J* = 244.4 Hz),164.5, 187.0, 208.8; IR (KBr): 3424, 2944, 1717, 1551, 1412, 1214, 1108 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{17}H_{15}FN_2NaO_4$ [M^{+}], 388.1798; found, 388.1799.

(5*R*,9*R*)-10-(4-methoxybenzoyl)-2,3,5,6,8,9-hexahydrospiro[5,9-methanoimidazo[1,2-*a*]azocine-11,2'-[1,3]dioxolan]-7(1*H*)-one (3o)



Yellow solid; mp 238–239 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.15–2.21 (m, 1H, $COCH_2$), 2.48–2.54 (m, 1H, $COCH_2$), 2.69–2.84 (m, 2H, $COCH_2$), 2.93–2.97 (m, 1H, CCH), 3.32–3.43 (m, 2H, NCH_2C), 3.51–3.61 (m, 1H, NCH), 3.57–3.75 (m, 2H, NCH_2C), 3.73 (s, 3H, OCH_3), 3.95–4.10 (m, 4H, OCH_2CH_2O), 6.77–6.80 (m, 2H, ArH), 7.18–7.22 (m, 2H, ArH), 9.09 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.9, 42.6, 42.7, 46.6, 47.9, 55.2, 57.3, 65.4, 86.7, 105.9, 113.4, 127.9, 135.0, 159.3, 159.4, 188.4, 208.7; IR (KBr): 3291, 2892, 1714, 1588, 1522, 1412, 1252 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{20}H_{22}N_2O_5$ [M^{+}], 370.1529; found, 370.1535.

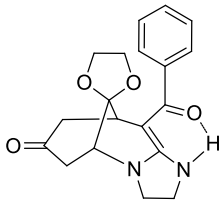
(5'*R*,9'*R*)-10'-(4-methylbenzoyl)-2',3',5',6',8',9'-hexahydrospiro[[1,3]dioxolane-2,11'-[5,9]methanoimidazo[1,2-*a*]azocin]-7'(1'*H*)-one (3p)



Yellow solid; mp 192–194 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.15–2.21 (m, 1H, $COCH_2$), 2.27 (s, 3H, $ArCH_3$), 2.48–2.54 (m, 1H, $COCH_2$), 2.67–2.83 (m, 2H, $COCH_2$), 2.89–2.91 (m, 1H, CCH), 3.33–3.42 (m, 2H, NCH_2C), 3.51–3.62 (m, 1H, NCH), 3.61–3.68 (m, 2H, NCH_2C), 3.96–4.05 (m, 4H, OCH_2CH_2O), 7.04–7.15 (m, 4H, ArH), 9.08 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3, 38.9, 42.6, 42.8,

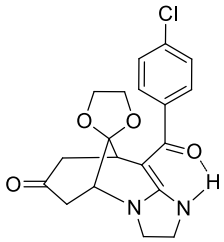
46.5, 47.8, 57.4, 65.4, 86.7, 105.9, 126.2, 128.7, 137.7, 139.6, 159.3, 189.0, 208.7; IR (KBr): 3284, 2892, 1713, 1522, 1413, 1272, 1114 cm^{-1}; HRMS (EI^+): *m/z* calcd. for $C_{20}H_{22}N_2O_4$ [M^+], 354.1580; found, 354.1588.

(5'*R*,9'*R*)-10'-benzoyl-2',3',5',6',8',9'-hexahydrospiro[[1,3]dioxolane-2,11'-[5,9]methanoimidazo[1,2-*a*]azocin]-7'(1'*H*)-one (3q)



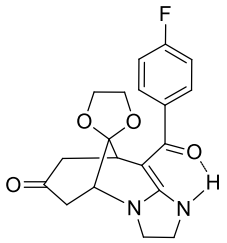
Yellow solid; mp 229–231 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.12–2.19 (m, 1H, $COCH_2$), 2.47–2.54 (m, 1H, $COCH_2$), 2.66–2.78 (m, 2H, $COCH_2$), 2.80–2.85 (m, 1H, CCH), 3.30–3.43 (m, 2H, NCH_2C), 3.52–3.58 (m, 1H, NCH), 3.61–3.65 (m, 2H, NCH_2C), 3.95–4.06 (m, 4H, OCH_2CH_2O), 7.23–7.26 (m, 5H, ArH), 9.06 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.8, 42.6, 42.7, 46.5, 47.8, 57.3, 65.3, 86.6, 105.8, 126.2, 127.9, 128.1, 142.5, 159.3, 188.8, 208.7; IR (KBr): 3282, 2890, 1711, 1590, 1522, 1413, 1274, 1116 cm^{-1}; HRMS (TOF ES^+): *m/z* calcd. for $C_{19}H_{20}N_2O_4$ [$(M+Na)^+$], 340.1423; found, 340.1426.

(5'*R*,9'*R*)-10'-(4-chlorobenzoyl)-2',3',5',6',8',9'-hexahydrospiro[[1,3]dioxolane-2,11'-[5,9]methanoimidazo[1,2-*a*]azocin]-7'(1'*H*)-one (3r)



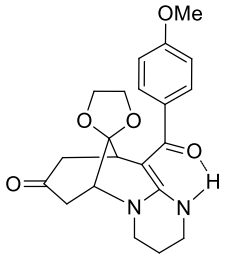
Yellow solid; mp 155–157 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.11–2.17 (m, 1H, $COCH_2$), 2.49–2.55 (m, 1H, $COCH_2$), 2.69–2.80 (m, 2H, $COCH_2$), 2.82–2.85 (m, 1H, CCH), 3.32–3.43 (m, 2H, NCH_2C), 3.50–3.64 (m, 1H, NCH), 3.63–3.71 (m, 2H, NCH_2C), 3.94–4.03 (m, 4H, OCH_2CH_2O), 7.16–7.26 (m, 4H, ArH), 9.06 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.9, 42.6, 42.7, 46.6, 47.8, 57.4, 65.4, 65.4, 86.6, 105.8, 127.8, 128.4, 133.8, 140.8, 159.4, 187.3, 208.3; IR (KBr): 3280, 2890, 1712, 1585, 1523, 1414, 1270, 1108 cm^{-1}; HRMS (EI^+): *m/z* calcd. for $C_{19}H_{19}N_2O_4Cl$ [M^+], 374.1033; found, 374.1037.

(5'*R*,9'*R*)-10'-(4-fluorobenzoyl)-2',3',5',6',8',9'-hexahydrospiro[[1,3]dioxolane-2,11'-[5,9]methanoimidazo[1,2-*a*]azocin]-7'(1'*H*)-one (3s)



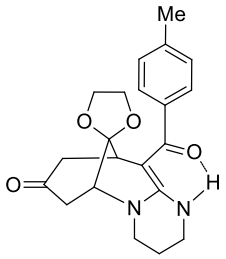
Yellow solid; mp 195–196 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.11–2.17 (m, 1H, $COCH_2$), 2.49–2.55 (m, 1H, $COCH_2$), 2.69–2.80 (m, 2H, $COCH_2$), 2.83–2.85 (m, 1H, CCH), 3.35–3.43 (m, 2H, NCH_2C), 3.53–3.59 (m, 1H, NCH), 3.58–3.71 (m, 2H, NCH_2C), 3.97–4.09 (m, 4H, OCH_2CH_2O), 6.92–6.98 (m, 2H, ArH), 7.20–7.26 (m, 2H, ArH), 9.07 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.0, 42.6, 42.7, 46.6, 47.8, 57.4, 65.4, 65.4, 86.6, 105.8, 114.9(*J* = 21.2 Hz), 115.2(*J* = 21.2 Hz), 128.2(*J* = 8.0 Hz), 128.3(*J* = 8.0 Hz), 138.5, 159.4, 160.8(*J* = 245.0 Hz), 164.0(*J* = 245.0 Hz), 187.6, 208.4; IR (KBr): 3278, 2353, 1710, 1587, 1524, 1232, 1111 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{19}H_{19}N_2O_4F$ [M^{+}], 358.1329; found, 358.1338.

(6*R*,10*R*)-11-(4-methoxybenzoyl)-3,4,6,7,9,10-hexahydro-1H-spiro[6,10-methano pyrimido[1,2-*a*]azocine-12,2'-[1,3]dioxolan]-8(2*H*)-one (3t)



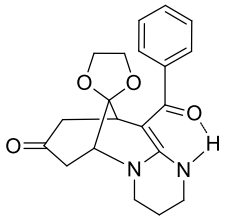
Yellow solid; mp 246–248 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.87–2.05 (m, 2H, CCH_2C), 2.10–2.16 (m, 1H, $COCH_2$), 2.46–2.52 (m, 1H, $COCH_2$), 2.57–2.66 (m, 1H, $COCH_2$), 2.76–2.83 (m, 1H, $COCH_2$), 2.89–2.91 (m, 1H, CCH), 3.13–3.17 (m, 1H, NCH), 3.18–3.31 (m, 4H, NCH_2C), 3.73 (s, 3H, OCH_3), 3.91–4.10 (m, 4H, OCH_2CH_2O), 6.78 (AB, *J* = 8.7 Hz, 2H, ArH), 7.14 (AB, *J* = 8.7 Hz, 2H, ArH), 12.24 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 37.8, 39.7, 43.0, 45.9, 47.6, 55.2, 62.3, 65.3, 88.8, 104.8, 113.5, 127.6, 135.7, 155.9, 158.8, 185.9, 208.5; IR (KBr): 3420, 2955, 1716, 1585, 1416, 1244, 1114 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{21}H_{24}N_2O_5$ [M^{+}], 384.1685; found, 384.1695.

(6'*R*,10'*R*)-11'-(4-methylbenzoyl)-1',2',3',4',6',7',9',10'-octahydro-8'*H*-spiro[[1,3]d ioxolane-2,12'-[6,10]methanopyrimido[1,2-*a*]azocin]-8'-one (3u)



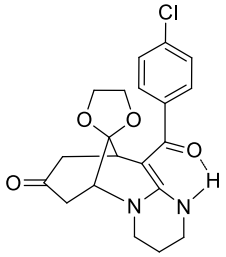
Yellow solid; mp 254–256 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85–2.01 (m, 2H, CCH_2C), 2.11–2.18 (m, 1H, $COCH_2$), 2.26 (s, 3H, $ArCH_3$), 2.44–2.52 (m, 1H, $COCH_2$), 2.56–2.66 (m, 1H, $COCH_2$), 2.74–2.80 (m, 1H, $COCH_2$), 2.79–2.90 (m, 1H, CCH), 3.10–3.18 (m, 1H, NCH), 3.16–3.31 (m, 4H, NCH_2CCH_2N), 3.91–4.10 (m, 4H, OCH_2CH_2O), 6.98–7.11 (m, 4H, ArH), 12.28 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 21.2, 37.8, 39.6, 43.0, 45.8, 47.7, 62.3, 65.3, 88.4, 104.8, 126.1, 128.8, 136.9, 140.4, 155.8, 186.7, 208.6; IR (KBr): 3433, 2958, 2352, 1716, 1585, 1415, 1114 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{21}H_{24}N_2O_4$ [M^{+}], 368.1736; found, 368.1730.

(6'*R*,10'*R*)-11'-benzoyl-1',2',3',4',6',7',9',10'-octahydro-8'*H*-spiro[[1,3]dioxolane-2,12'-[6,10]methanopyrimido[1,2-*a*]azocin]-8'-one (3v)



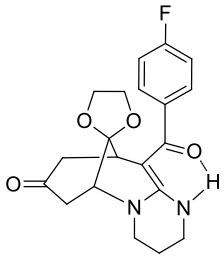
Yellow solid; mp 195–196 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.88–1.99 (m, 2H, CCH_2C), 2.10–2.16 (m, 1H, $COCH_2$), 2.45–2.51 (m, 1H, $COCH_2$), 2.56–2.64 (m, 1H, $COCH_2$), 2.74–2.77 (m, 1H, $COCH_2$), 2.76–2.82 (m, 1H, CCH), 3.12–3.17 (m, 1H, NCH), 3.20–3.30 (m, 4H, NCH_2C), 3.92–4.06 (m, 4H, OCH_2CH_2O), 7.17–7.25 (m, 5H, ArH), 12.25 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 37.8, 39.6, 43.0, 45.8, 47.6, 62.3, 65.3, 88.3, 104.8, 126.1, 127.3, 128.2, 143.2, 155.9, 186.4, 208.5; IR (KBr): 3433, 2956, 2353, 1715, 1583, 1416, 1117 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{20}H_{22}N_2O_4$ [M^{+}], 354.1580; found, 354.1578.

(6'*R*,10'*R*)-11'-(4-chlorobenzoyl)-1',2',3',4',6',7',9',10'-octahydro-8'*H*-spiro[[1,3]dioxolane-2,12'-[6,10]methanopyrimido[1,2-*a*]azocin]-8'-one (3w)



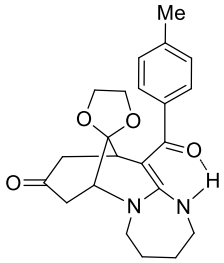
Yellow solid; mp 227–229 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.85–2.04 (m, 2H, CCH_2C), 2.04–2.13 (m, 1H, $COCH_2$), 2.45–2.52 (m, 1H, $COCH_2$), 2.60–2.67 (m, 1H, $COCH_2$), 2.76–2.78 (m, 1H, $COCH_2$) 2.78–2.84 (m, 1H, CCH), 3.13–3.22 (m, 1H, NCH), 3.22–3.31 (m, 4H, NCH_2C), 3.94–4.10 (m, 4H, OCH_2CH_2O), 7.13 (AB, *J* = 8.4 Hz, 2H, ArH), 7.23 (AB, *J* = 8.4 Hz, 2H, ArH) , 12.19 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 37.8, 39.7, 42.9, 45.8, 47.7, 62.3, 65.3, 88.5, 104.7, 127.7, 128.4, 133.1, 141.6, 155.9, 184.9, 208.2; IR (KBr): 3435, 2951, 1720, 1532, 1416, 1206, 1109 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{20}H_{21}N_2O_4Cl$ [M^{+}],388.1190; found,388.1198.

(6'*R*,10'*R*)-11'-(4-fluorobenzoyl)-1',2',3',4',6',7',9',10'-octahydro-8'*H*-spiro[[1,3]dioxolane-2,12'-[6,10]methanopyrimido[1,2-*a*]azocin]-8'-one (3x)



Yellow solid; mp 202–203 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.86–2.00 (m, 2H, CCH_2C), 2.07–2.13 (m, 1H, $COCH_2$), 2.46–2.52 (m, 1H, $COCH_2$), 2.59–2.66 (m, 1H, $COCH_2$), 2.77–2.80 (m, 1H, $COCH_2$), 2.81–2.84 (m, 1H, CCH), 3.11–3.18 (m, 1H, NCH), 3.16–3.31 (m, 4H, NCH_2C), 3.91–4.10 (m, 4H, OCH_2CH_2O), 6.91–6.97 (m, 2H, ArH), 7.15–7.22 (m, 2H, ArH), 12.23 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 37.8, 39.7, 42.9, 45.8, 47.6, 62.3, 65.3, 88.5, 104.7, 114.9(*J* = 21.2 Hz), 115.2(*J* = 21.2 Hz), 127.9(*J* = 7.9 Hz), 128.0(*J* = 7.9 Hz), 139.3, 155.9, 160.4(*J* = 244.2 Hz), 163.6(*J* = 244.2 Hz), 185.2, 208.3; IR (KBr): 3446, 2899, 1713, 1585, 1555, 1412, 1231 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{20}H_{21}N_2O_4F$ [M^{+}], 372.1485; found,372.1483.

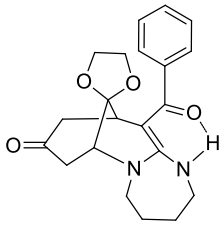
(7'*R*,11'*R*)-12'-(4-methylbenzoyl)-2',3',4',5',7',8',10',11'-octahydrospiro[[1,3]dioxolane-2,13'-[7,11]methano[1,3]diazepino[1,2-*a*]azocin]-9'(1'*H*)-one (3y)



Yellow solid; mp 173–175 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.51–1.78 (m, 4H, CCH_2CH_2C), 2.05–2.14 (m, 1H, $COCH_2$), 2.26 (s, 3H, $ArCH_3$), 2.44–2.55 (m, 1H, $COCH_2$), 2.54–2.63 (m, 1H, $COCH_2$), 2.73–2.82 (m, 1H, $COCH_2$), 2.83–2.97 (m, 1H,

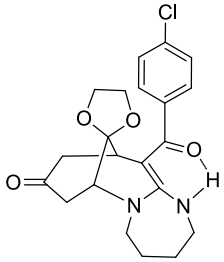
CCH), 3.15–3.25 (m, 1H, NCH), 3.20–3.38 (m, 4H, NCH_2C), 3.91–4.10 (m, 4H, OCH_2CH_2O), 6.97–7.15 (m, 4H, ArH), 11.35 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 26.5, 26.8, 39.4, 44.6, 44.7, 46.7, 53.8, 63.7, 65.2, 65.4, 92.0, 105.2, 126.1, 128.7, 137.2, 140.4, 164.2, 189.5, 208.7; IR (KBr): 3421, 2934, 1717, 1596, 1547, 1274, 1111 cm^{-1}; HRMS (EI^+): *m/z* calcd. for $C_{22}H_{26}N_2O_4$ [M^+], 382.1893; found, 382.1895.

(7'*R*,11'*R*)-12'-benzoyl-2',3',4',5',7',8',10',11'-octahydrospiro[[1,3]dioxolane-2,13'-[7,11]methano[1,3]diazepino[1,2-*a*]azocin]-9'(1'*H*)-one (3z)



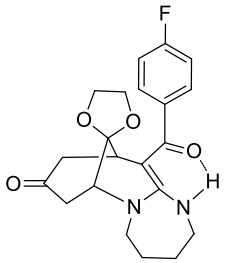
Yellow solid; mp 219–221 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.60–1.75 (m, 4H, CCH_2CH_2C), 2.08–2.14 (m, 1H, $COCH_2$), 2.45–2.51 (m, 1H, $COCH_2$), 2.55–2.62 (m, 1H, $COCH_2$), 2.75–2.82 (m, 1H, $COCH_2$), 2.81–2.88 (m, 1H, CCH), 3.17–3.25 (m, 1H, NCH), 3.15–3.40 (m, 4H, NCH_2CCCH_2N), 3.92–4.10 (m, 4H, OCH_2CH_2O), 7.18–7.26 (m, 5H, ArH), 11.42 (br., 1H, NH); ^3C NMR (75 MHz, $CDCl_3$): δ = 26.4, 26.8, 39.4, 44.5, 44.7, 46.7, 53.8, 63.8, 65.2, 65.4, 91.9, 105.2, 126.1, 127.5, 128.2, 143.2, 164.2, 189.2, 208.6; IR (KBr): 3416, 2935, 1718, 1549, 1367, 1269, 1102 cm^{-1}; HRMS (EI^+): *m/z* calcd. for $C_{21}H_{24}N_2O_4$ [M^+], 368.1736; found, 368.1732.

(7'*R*,11'*R*)-12'-(4-chlorobenzoyl)-2',3',4',5',7',8',10',11'-octahydrospiro[[1,3]dioxolane-2,13'-[7,11]methano[1,3]diazepino[1,2-*a*]azocin]-9'(1'*H*)-one (3a')



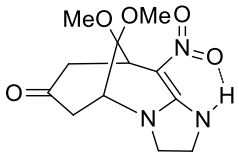
Yellow solid; mp 84–86 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.60–1.80 (m, 4H, CCH_2CH_2C), 2.03–2.09 (m, 1H, $COCH_2$), 2.45–2.52 (m, 1H, $COCH_2$), 2.57–2.65 (m, 1H, $COCH_2$), 2.75–2.80 (m, 1H, $COCH_2$), 2.78–2.88 (m, 1H, CCH), 3.20–3.28 (m, 1H, NCH), 3.25–3.40 (m, 4H, NCH_2CCCH_2N), 3.90–4.10 (m, 4H, OCH_2CH_2O), 7.10–7.31 (m, 5H, ArH), 11.45 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.2, 26.5, 39.6, 44.4, 44.6, 46.8, 53.4, 63.7, 65.2, 65.4, 91.9, 105.1, 127.6, 128.4, 133.3, 141.6, 164.1, 187.4, 208.3; IR (KBr): 3434, 2934, 1717, 1549, 1411, 1271, 1105 cm^{-1}; HRMS (EI^+): *m/z* calcd. for $C_{21}H_{23}N_2O_4Cl$ [M^+], 402.1346; found, 402.1355.

(7'*R*,11'*R*)-12'-(4-fluorobenzoyl)-2',3',4',5',7',8',10',11'-octahydrospiro[[1,3]dioxolane-2,13'-[7,11]methano[1,3]diazepino[1,2-*a*]azocin]-9'(1'*H*)-one (3b')



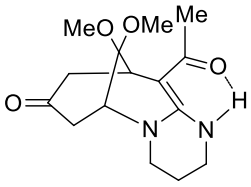
Yellow solid; mp 80–82 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.60–1.78 (m, 4H, CCH_2CH_2C), 2.01–2.15 (m, 1H, $COCH_2$), 2.45–2.55 (m, 1H, $COCH_2$), 2.55–2.64 (m, 1H, $COCH_2$), 2.74–2.80 (m, 1H, $COCH_2$), 2.79–2.91 (m, 1H, CCH), 3.19–3.31 (m, 1H, NCH), 3.25–3.41 (m, 4H, NCH_2CCCH_2N), 3.91–4.11 (m, 4H, OCH_2CH_2O), 6.91–6.98 (m, 2H, ArH), 7.17–7.22 (m, 2H, ArH), 11.41 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.3, 26.6, 39.6, 44.4, 44.6, 46.8, 53.6, 63.7, 65.2, 65.4, 92.0, 105.1, 114.9(*J* = 21.2 Hz), 115.2(*J* = 21.2 Hz), 128.0(*J* = 8.0 Hz), 128.1(*J* = 8.0 Hz), 139.3, 160.5(*J* = 244.7 Hz), 163.8(*J* = 244.7 Hz), 164.2, 187.8, 208.4; IR (KBr): 3428, 2945, 1717, 1597, 1549, 1412, 1215 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{21}H_{23}N_2O_4F$ [M^{+}], 386.1642; found, 386.1643.

(5*R*,9*R*)-11,11-dimethoxy-10-nitro-2,3,5,6,8,9-hexahydro-5,9-methanoimidazo[1,2-*a*]azocin-7(1*H*)-one (3c')



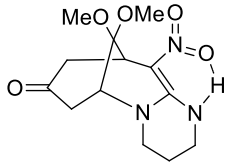
Yellow solid; mp 164–166 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.57–2.69 (m, 2H, $COCH_2$), 2.74–2.81 (m, 2H, $COCH_2$), 3.27 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3), 3.63–3.66 (m, 1H, CCH), 3.81–3.85 (m, 4H, NCH_2CH_2N), 3.91–3.93 (m, 1H, NCH), 8.33 (br., 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.1, 41.9, 42.3, 42.8, 47.6, 48.9, 49.1, 54.7, 97.4, 104.8, 156.0, 207.6; IR (KBr): 3373, 2964, 1712, 1600, 1548, 1380, 1294, 1096 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{12}H_{17}N_3O_5$ [M^{+}], 284.1241; found, 284.1242.

(6*R*,10*R*)-11-acetyl-12,12-dimethoxy-3,4,6,7,9,10-hexahydro-1*H*-6,10-methanopyrimido[1,2-*a*]azocin-8(2*H*)-one (3d')



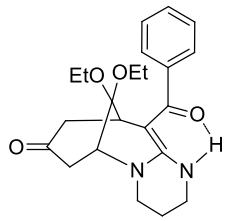
Yellow solid; mp 175–177 °C; δ = 1.90–2.05 (m, 2H, CCH_2C), 1.98 (s, 3H, $COCH_3$), 2.37–2.39 (m, 1H, $COCH_2$), 2.41–2.43 (m, 1H, $COCH_2$), 2.65–2.70 (m, 1H, $COCH_2$), 2.82–2.87 (m, 1H, $COCH_2$), 3.17–3.21 (m, 1H, CCH), 3.21–3.42 (m, 4H, 2 × NCH_2), 3.26 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 3.49–3.51 (m, 1H, NCH), 12.24 (br., 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 25.1, 37.0, 37.6, 42.1, 45.9, 46.1, 48.6, 59.6, 87.2, 96.9, 155.6, 185.4, 208.8; IR (KBr): 3419, 2943, 1716, 1584, 1316, 1269, 1066 cm^{-1}; HRMS (EI$^+$): *m/z* calcd. for $C_{15}H_{22}N_2O_4$ [M^+], 295.1652; found, 295.1649.

(6*R*,10*R*)-12,12-dimethoxy-11-nitro-3,4,6,7,9,10-hexahydro-1*H*-6,10-methanopyrimido[1,2-*a*]azocin-8(2*H*)-one (3e')



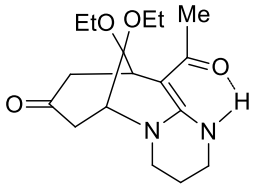
Yellow solid; mp 132–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.02–2.10 (m, 2H, CCH_2C), 2.54–2.75 (m, 2H, $COCH_2$), 2.60–2.81 (m, 2H, $COCH_2$), 3.26 (s, 3H, OCH_3), 3.37 (s, 3H, OCH_3), 3.36–3.79 (m, 4H, 2 × NCH_2), 2.68–3.71 (m, 1H, CCH), 3.02–3.41 (m, 1H, NCH), 11.47 (br., 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ =20.1, 37.1, 38.2, 41.1, 42.5, 46.5, 48.8, 49.0, 60.2, 95.7, 107.5, 152.0, 207.1; IR (KBr): 3431, 2964, 1708, 1593, 1369, 1296, 1155 cm^{-1}; HRMS (EI$^+$): *m/z* calcd. for $C_{13}H_{19}N_3O_5$ [M^+], 298.1397; found, 298.1399.

(6*R*,10*R*)-11-benzoyl-12,12-diethoxy-1,2,3,4,6,7,9,10-octahydro-8*H*-6,10-methanopyrimido[1,2-*a*]azocin-8-one (3f')



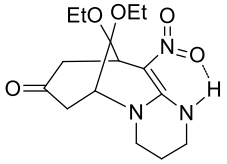
Yellow solid; mp 89–91 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11–1.28 (m, 6H, 2 × CCH_3), 1.91–2.10 (m, 2H, CCH_2C), 2.20–2.31 (m, 1H, $COCH_2$), 2.44–2.45 (m, 1H, $COCH_2$), 2.45–2.47 (m, 2H, $COCH_2$), 2.96–3.05 (m, 1H, CCH), 3.15–3.25 (m, 1H, NCH), 3.24–3.65 (m, 4H, NCH_2CCCH_2N), 3.24–3.65 (m, 4H, OCH_2), 7.23–7.35 (m, 5H, ArH), 12.38 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.2, 15.3, 20.8, 37.8, 37.8, 42.0, 46.1, 46.9, 56.3, 60.9, 88.3, 96.8, 125.7, 127.3, 128.2, 143.3, 156.6, 185.8, 209.4; IR (KBr): 3426, 2971, 1715, 1584, 1415, 1242, 1111 cm^{-1}; HRMS (EI$^+$): *m/z* calcd. for $C_{22}H_{28}N_2O_4$ [M^+], 384.2049; found, 384.2052.

(6*R*,10*R*)-11-acetyl-12,12-diethoxy-3,4,6,7,9,10-hexahydro-1*H*-6,10-methanopyrimido[1,2-*a*]azocin-8(2*H*)-one (3g')



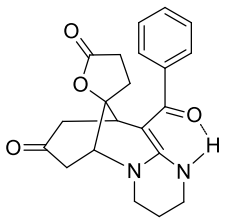
White solid; mp 186–188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (t, 3H, CCH_3), 1.20 (t, 3H, CCH_3), 1.79–1.97 (m, 2H, CCH_2C), 1.90 (s, 3H, $COCH_3$), 2.29–2.45 (m, 2H, $COCH_2$), 2.59–2.84 (m, 2H, $COCH_2$), 3.01–3.10 (m, 1H, CCH), 3.23–3.29 (m, 4H, 2 × NCH_2), 3.44–3.49 (m, 4H, OCH_2), 3.62–3.66 (m, 1H, NCH), 12.15 (br., 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.2, 15.3, 21.0, 25.1, 37.6, 37.8, 42.3, 46.0, 46.1, 56.2, 56.3, 60.5, 87.5, 96.6, 155.7, 185.2, 209.2; IR (KBr): 3447, 2973, 1709, 1588, 1421, 1243, 1070 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{17}H_{26}N_2O_4$ [M^{+}], 323.1965; found, 323.1964.

(6*R*,10*R*)-12,12-diethoxy-11-nitro-3,4,6,7,9,10-hexahydro-1*H*-6,10-methanopyrimido[1,2-*a*]azocin-8(2*H*)-one (3h')



White solid; mp 191–193 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (t, 3H, CCH_3), 1.26 (t, 3H, CCH_3), 2.02–2.11 (m, 2H, CCH_2C), 2.52–2.56 (m, 1H, $COCH_2$), 2.73–2.79 (m, 2H, $COCH_2$), 2.81–2.83 (m, 1H, $COCH_2$), 3.31–3.33 (m, 1H, CCH), 3.41–3.52 (m, 4H, NCH_2CCCH_2N), 3.48–3.71 (m, 4H, OCH_2), 4.00–4.06 (m, 1H, NCH), 11.52 (br., 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.1, 15.2, 20.1, 37.8, 38.2, 41.3, 42.7, 46.6, 56.7, 56.9, 61.0, 95.5, 107.9, 152.1, 207.3; IR (KBr): 3450, 2979, 1709, 1593, 1377, 1300, 1095 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{15}H_{23}N_3O_5$ [M^{+}], 326.1710; found, 326.1707.

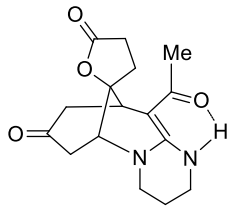
(2'R,6R,10R)-11-benzoyl-3,4,6,7,9,10-hexahydro-1H,3'H-spiro[6,10-methanopyrimido[1,2-a]azocine-12,2'-furan]-5',8(2H,4'H)-dione (3i')



Yellow solid; mp 272–275 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.91–2.10 (m, 2H, CCH_2C), 2.23–2.48 (m, 4H, $COCH_2CH_2$), 2.53–2.75 (m, 4H, CH_2COCH_2), 2.91–4.02 (m, 1H, CCH), 3.17–3.38 (m, 4H, NCH_2CH_2N), 3.40–3.51 (m, 1H, NCH), 7.13–7.18 (m, 2H, ArH), 7.24–7.31 (m, 3H, ArH), 12.13 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 28.4, 29.0, 37.8, 40.0, 41.9, 45.7, 46.9, 63.3, 81.7, 87.1, 125.9,

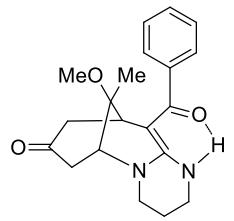
127.5, 128.4, 142.9, 155.7, 175.0, 186.1, 206.0; IR (KBr): 3419, 2949, 2866, 1775, 1716, 1579, 1417, 1186 cm^{-1}; HRMS (EI^+): *m/z* calcd. for $C_{21}H_{22}N_2O_4$ [M^+], 366.1580; found, 366.1577.

(2'*R*,6*R*,10*R*)-11-acetyl-3,4,6,7,9,10-hexahydro-1*H*,3'*H*-spiro[6,10-methanopyrimido[1,2-*a*]azocine-12,2'-furan]-5',8(2*H*,4'*H*)-dione (3j')



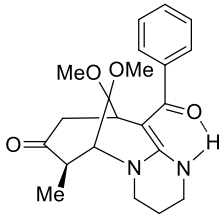
White solid; mp 127–129 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.85–2.16 (m, 2H, CCH_2C), 1.94 (s, 3H, $COCH_3$), 2.50–2.78 (m, 4H, $COCH_2CH_2$), 2.60–2.87 (m, 4H, CH_2COCH_2), 3.14–3.19 (m, 1H, CCH), 3.17–3.30 (m, 4H, NCH_2CH_2N), 3.41–3.43 (m, 1H, NCH), 12.15 (br., 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 25.3, 28.5, 29.4, 37.6, 40.5, 42.3, 46.0, 46.2, 63.1, 81.8. 86.4, 154.8, 174.8, 186.0, 205.5; IR (KBr): 3421, 2964, 1772, 1587, 1418, 1193, 1040 cm^{-1}; HRMS (EI^+): *m/z* calcd. for $C_{16}H_{20}N_2O_4$ [M^+], 305.1496; found, 305.1495.

(6*R*,10*R*,12*R*)-11-benzoyl-12-methoxy-12-methyl-1,2,3,4,6,7,9,10-octahydro-8*H*-6,10-methanopyrimido[1,2-*a*]azocin-8-one (3k')



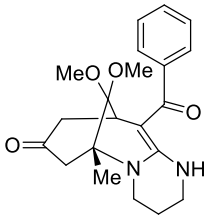
Yellow solid; mp 93–95 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.47 (s, 3H, CCH_3), 1.91–2.10 (m, 2H, CCH_2C), 2.35–2.44 (m, 2H, $COCH_2$), 2.46–2.53 (m, 2H, $COCH_2$), 2.83–2.87 (m, 1H, CCH), 3.11–3.23 (m, 1H, NCH), 3.22 (s, 3H, OCH_3), 3.21–3.46 (m, 4H, NCH_2CH_2N), 7.25–7.34 (m, 5H, ArH), 12.40 (br., 1H, NH),; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9, 20.8, 37.8, 37.9, 42.5, 46.0, 47.4, 49.4, 64.7, 71.8, 87.9, 125.7, 127.2, 128.2, 143.4, 156.6, 185.6, 208.3; IR (KBr): 3411, 2940, 1714, 1580, 1415, 1244, 1201 cm^{-1}; HRMS (EI^+): *m/z* calcd. for $C_{20}H_{24}N_2O_3$ [M^+], 340.1787; found, 340.1798.

(6*R*,7*S*,10*R*)-11-benzoyl-12,12-dimethoxy-7-methyl-1,2,3,4,6,7,9,10-octahydro-8*H*-6,10-methanopyrimido[1,2-*a*]azocin-8-one (3l')



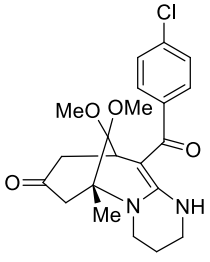
Yellow solid; mp 190–192 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14 (s, 3H, CCH_3), 1.91–2.10 (m, 2H, CCH_2C), 2.04–2.10 (m, 1H, $COCH_2$), 2.18–2.27 (m, 1H, $COCH_2$), 2.48–2.55 (m, 1H, $COCH_2$), 2.73–2.82 (m, 1H, $COCH_2$), 2.98–3.07 (m, 1H, CCH), 3.25 (s, 3H, OCH_3), 3.27 (s, 3H, OCH_3), 3.30–3.43 (m, 4H, NCH_2CCH_2N), 3.43–3.50 (m, 1H, NCH), 7.23–7.34 (m, 5H, ArH), 12.45 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.9, 20.9, 37.9, 38.1, 45.9, 45.9, 48.5, 48.7, 50.0, 66.4, 88.0, 97.7, 125.7, 127.2, 128.2, 143.2, 157.3, 186.2, 210.3; IR (KBr): 3417, 2953, 1716, 1556, 1411, 1189, 1115 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{21}H_{26}N_2O_4$ [M^{+}], 370.1893; found, 370.1891.

(6*R*,10*R*)-11-benzoyl-12,12-dimethoxy-6-methyl-1,2,3,4,6,7,9,10-octahydro-8*H*-6,10-methanopyrimido[1,2-*a*]azocin-8-one (3m')



Yellow solid; mp 106–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.38 (s, 3H, CCH_3), 1.76–1.88 (m, 1H, CCH_2C), 1.96–2.07 (m, 1H, CCH_2C), 2.27–2.44 (m, 2H, $COCH_2$), 2.56–2.73 (m, 2H, $COCH_2$), 3.08–3.12 (m, 1H, CCH), 3.15–3.31 (m, 3H, NCH_2CCH_2N), 3.30–3.48 (m, 1H, NCH_2CCH_2N), 3.38 (s, 6H, 2 × OCH_3), 3.30–3.48 (m, 1H, NCH), 7.26–7.34 (m, 5H, ArH), 12.62 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9, 21.3, 36.6, 37.8, 40.4, 47.4, 48.0, 50.8, 51.5, 66.2, 88.2, 98.4, 125.6, 127.4, 128.2, 143.2, 157.0, 185.0, 208.8; IR (KBr): 3393, 2957, 1710, 1151, 1418, 1325, 1060 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{21}H_{26}N_2O_4$ [M^{+}], 370.1893; found, 370.1900.

(6*R*,10*R*)-11-(4-chlorobenzoyl)-12,12-dimethoxy-6-methyl-1,2,3,4,6,7,9,10-octahydro-8*H*-6,10-methanopyrimido[1,2-*a*]azocin-8-one (3n')



Yellow solid; mp 225–227 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 3H, CCH_3), 1.71–1.78 (m, 1H, CCH_2C), 1.91–1.96 (m, 1H, CCH_2C), 2.16–2.38 (m, 2H, $COCH_2$), 2.53–2.68 (m, 2H, $COCH_2$), 2.96–3.01 (m, 1H, CCH), 3.11–3.23 (m, 4H, NCH_2CCH_2N), 3.29 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 3.23–3.38 (m, 1H, NCH), 7.13–7.28 (m, 4H, ArH), 12.48 (br., 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9, 21.3, 36.7, 37.8, 40.4, 47.4, 48.0, 50.8, 51.4, 66.3, 88.4, 98.3, 127.3, 128.5, 133.2, 141.5, 156.9, 183.4, 208.6; IR (KBr): 3439, 2952, 1711, 1584, 1411, 1325, 1062 cm^{-1}; HRMS (EI^{+}): *m/z* calcd. for $C_{21}H_{25}N_2O_4Cl$ [M^{+}], 404.1503; found, 404.1505.

X-ray Structure and Data[7] of 3j, 3l' & 3n'

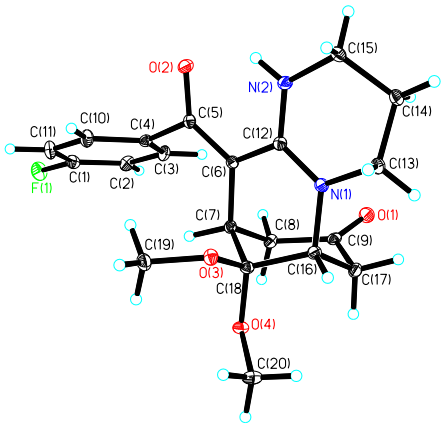


Figure S1 X-Ray crystal structure of **3j**

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

Empirical formula	C_{40} H_{48} F_2 N_4 O_9
Formula weight	766.82
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P c
Unit cell dimensions	a = 12.3686(8) A alpha = 90 deg. b = 15.9846(11) A beta = 113.5910(10) deg. c = 9.9812(7) A gamma = 90 deg.
Volume	1808.4(2) A^3
Z, Calculated density	2, 1.408 Mg/m^3
Absorption coefficient	0.107 mm^-1
F(000)	812
Crystal size	0.40 x 0.20 x 0.18 mm
Theta range for data collection	1.27 to 30.07 deg.
Limiting indices	-17<=h<=16, -21<=k<=22, -13<=l<=13
Reflection collected/unique	19064 / 9463 [R(int) = 0.0222]
Completeness to theta = 30.07	96.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9811 and 0.9586
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9463 / 2 / 500
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0345, wR2 = 0.0888
R indices (all data)	R1 = 0.0385, wR2 = 0.0938
Extinction coefficient	-0.2(4)
Largest diff. peak and hole	0.363 and -0.192 e.A^-3

Table S2 Bond lengths [A] and angles [deg] for **3j**

F(1)-C(1)	1.3688(17)
F(2)-C(29)	1.3637(17)
O(1)-C(9)	1.2133(18)
O(1S)-H(1SA)	0.8433
O(1S)-H(1SB)	0.8705
O(2)-C(5)	1.2726(18)
O(3)-C(18)	1.4093(17)
O(3)-C(19)	1.4331(17)
O(4)-C(18)	1.4215(17)
O(4)-C(20)	1.4357(19)
O(5)-C(21)	1.2182(19)
O(6)-C(25)	1.2771(18)
O(7)-C(38)	1.4126(18)
O(7)-C(39)	1.426(2)
O(8)-C(38)	1.4090(18)
O(8)-C(40)	1.4322(19)
N(1)-C(12)	1.3477(19)
N(1)-C(13)	1.4697(17)
N(1)-C(16)	1.4699(18)
N(2)-C(12)	1.3368(18)
N(2)-C(15)	1.4605(18)
N(2)-H(2)	0.8800
N(3)-C(34)	1.3535(19)
N(3)-C(33)	1.4645(19)
N(3)-C(37)	1.4710(19)
N(4)-C(34)	1.3392(19)
N(4)-C(35)	1.4602(19)
N(4)-H(4)	0.8800
C(1)-C(2)	1.374(2)
C(1)-C(11)	1.379(2)
C(2)-C(3)	1.393(2)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.395(2)
C(3)-H(3)	0.9500
C(4)-C(10)	1.389(2)
C(4)-C(5)	1.5117(19)
C(5)-C(6)	1.407(2)
C(6)-C(12)	1.4403(18)
C(6)-C(7)	1.5147(19)
C(7)-C(18)	1.534(2)
C(7)-C(8)	1.556(2)
C(7)-H(7)	1.0000
C(8)-C(9)	1.513(2)

C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(17)	1.513(2)
C(10)-C(11)	1.391(2)
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(13)-C(14)	1.510(2)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.515(2)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(18)	1.5329(19)
C(16)-C(17)	1.537(2)
C(16)-H(16)	1.0000
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(22)	1.506(2)
C(21)-C(32)	1.519(2)
C(22)-C(23)	1.546(2)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-C(24)	1.520(2)
C(23)-C(38)	1.532(2)
C(23)-H(23)	1.0000
C(24)-C(25)	1.401(2)
C(24)-C(34)	1.4406(19)
C(25)-C(26)	1.5118(19)
C(26)-C(27)	1.393(2)
C(26)-C(30)	1.396(2)
C(27)-C(28)	1.389(2)
C(27)-H(27)	0.9500
C(28)-C(29)	1.382(2)
C(28)-H(28)	0.9500
C(29)-C(31)	1.380(2)
C(30)-C(31)	1.395(2)
C(30)-H(30)	0.9500

C(31)-H(31)	0.9500
C(32)-C(33)	1.538(2)
C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900
C(33)-C(38)	1.5359(19)
C(33)-H(33)	1.0000
C(35)-C(36)	1.518(2)
C(35)-H(35A)	0.9900
C(35)-H(35B)	0.9900
C(36)-C(37)	1.518(2)
C(36)-H(36A)	0.9900
C(36)-H(36B)	0.9900
C(37)-H(37A)	0.9900
C(37)-H(37B)	0.9900
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
H(1SA)-O(1S)-H(1SB)	105.0
C(18)-O(3)-C(19)	114.89(11)
C(18)-O(4)-C(20)	114.99(11)
C(38)-O(7)-C(39)	115.46(12)
C(38)-O(8)-C(40)	115.60(11)
C(12)-N(1)-C(13)	121.69(12)
C(12)-N(1)-C(16)	122.90(11)
C(13)-N(1)-C(16)	115.25(11)
C(12)-N(2)-C(15)	124.20(12)
C(12)-N(2)-H(2)	117.9
C(15)-N(2)-H(2)	117.9
C(34)-N(3)-C(33)	121.24(12)
C(34)-N(3)-C(37)	121.10(13)
C(33)-N(3)-C(37)	116.99(12)
C(34)-N(4)-C(35)	124.83(13)
C(34)-N(4)-H(4)	117.6
C(35)-N(4)-H(4)	117.6
F(1)-C(1)-C(2)	118.96(14)
F(1)-C(1)-C(11)	118.27(14)
C(2)-C(1)-C(11)	122.77(14)
C(1)-C(2)-C(3)	117.95(14)
C(1)-C(2)-H(2A)	121.0
C(3)-C(2)-H(2A)	121.0
C(2)-C(3)-C(4)	120.93(13)
C(2)-C(3)-H(3)	119.5

C(4)-C(3)-H(3)	119.5
C(10)-C(4)-C(3)	119.38(13)
C(10)-C(4)-C(5)	120.09(12)
C(3)-C(4)-C(5)	120.09(12)
O(2)-C(5)-C(6)	125.43(13)
O(2)-C(5)-C(4)	114.70(12)
C(6)-C(5)-C(4)	119.86(12)
C(5)-C(6)-C(12)	120.22(12)
C(5)-C(6)-C(7)	122.32(12)
C(12)-C(6)-C(7)	117.29(12)
C(6)-C(7)-C(18)	107.60(11)
C(6)-C(7)-C(8)	114.84(12)
C(18)-C(7)-C(8)	109.02(12)
C(6)-C(7)-H(7)	108.4
C(18)-C(7)-H(7)	108.4
C(8)-C(7)-H(7)	108.4
C(9)-C(8)-C(7)	113.08(12)
C(9)-C(8)-H(8A)	109.0
C(7)-C(8)-H(8A)	109.0
C(9)-C(8)-H(8B)	109.0
C(7)-C(8)-H(8B)	109.0
H(8A)-C(8)-H(8B)	107.8
O(1)-C(9)-C(17)	122.62(13)
O(1)-C(9)-C(8)	121.86(13)
C(17)-C(9)-C(8)	115.52(12)
C(4)-C(10)-C(11)	120.21(14)
C(4)-C(10)-H(10)	119.9
C(11)-C(10)-H(10)	119.9
C(1)-C(11)-C(10)	118.75(14)
C(1)-C(11)-H(11)	120.6
C(10)-C(11)-H(11)	120.6
N(2)-C(12)-N(1)	119.45(12)
N(2)-C(12)-C(6)	119.40(12)
N(1)-C(12)-C(6)	121.14(13)
N(1)-C(13)-C(14)	110.53(12)
N(1)-C(13)-H(13A)	109.5
C(14)-C(13)-H(13A)	109.5
N(1)-C(13)-H(13B)	109.5
C(14)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	108.1
C(13)-C(14)-C(15)	108.74(12)
C(13)-C(14)-H(14A)	109.9
C(15)-C(14)-H(14A)	109.9
C(13)-C(14)-H(14B)	109.9
C(15)-C(14)-H(14B)	109.9

H(14A)-C(14)-H(14B)	108.3
N(2)-C(15)-C(14)	109.62(12)
N(2)-C(15)-H(15A)	109.7
C(14)-C(15)-H(15A)	109.7
N(2)-C(15)-H(15B)	109.7
C(14)-C(15)-H(15B)	109.7
H(15A)-C(15)-H(15B)	108.2
N(1)-C(16)-C(18)	110.19(11)
N(1)-C(16)-C(17)	109.56(11)
C(18)-C(16)-C(17)	110.53(11)
N(1)-C(16)-H(16)	108.8
C(18)-C(16)-H(16)	108.8
C(17)-C(16)-H(16)	108.8
C(9)-C(17)-C(16)	110.07(12)
C(9)-C(17)-H(17A)	109.6
C(16)-C(17)-H(17A)	109.6
C(9)-C(17)-H(17B)	109.6
C(16)-C(17)-H(17B)	109.6
H(17A)-C(17)-H(17B)	108.2
O(3)-C(18)-O(4)	111.35(11)
O(3)-C(18)-C(16)	105.36(11)
O(4)-C(18)-C(16)	111.83(12)
O(3)-C(18)-C(7)	114.24(12)
O(4)-C(18)-C(7)	106.36(11)
C(16)-C(18)-C(7)	107.76(11)
O(3)-C(19)-H(19A)	109.5
O(3)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
O(3)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(4)-C(20)-H(20A)	109.5
O(4)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(4)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(5)-C(21)-C(22)	122.60(15)
O(5)-C(21)-C(32)	121.17(14)
C(22)-C(21)-C(32)	116.20(13)
C(21)-C(22)-C(23)	110.11(12)
C(21)-C(22)-H(22A)	109.6
C(23)-C(22)-H(22A)	109.6
C(21)-C(22)-H(22B)	109.6
C(23)-C(22)-H(22B)	109.6

H(22A)-C(22)-H(22B)	108.2
C(24)-C(23)-C(38)	109.32(12)
C(24)-C(23)-C(22)	112.50(12)
C(38)-C(23)-C(22)	108.89(11)
C(24)-C(23)-H(23)	108.7
C(38)-C(23)-H(23)	108.7
C(22)-C(23)-H(23)	108.7
C(25)-C(24)-C(34)	119.51(13)
C(25)-C(24)-C(23)	120.81(12)
C(34)-C(24)-C(23)	119.66(13)
O(6)-C(25)-C(24)	125.85(13)
O(6)-C(25)-C(26)	114.97(12)
C(24)-C(25)-C(26)	119.18(13)
C(27)-C(26)-C(30)	119.79(13)
C(27)-C(26)-C(25)	120.16(13)
C(30)-C(26)-C(25)	119.92(13)
C(28)-C(27)-C(26)	120.26(14)
C(28)-C(27)-H(27)	119.9
C(26)-C(27)-H(27)	119.9
C(29)-C(28)-C(27)	118.48(13)
C(29)-C(28)-H(28)	120.8
C(27)-C(28)-H(28)	120.8
F(2)-C(29)-C(31)	118.67(13)
F(2)-C(29)-C(28)	118.28(13)
C(31)-C(29)-C(28)	123.02(14)
C(31)-C(30)-C(26)	120.51(13)
C(31)-C(30)-H(30)	119.7
C(26)-C(30)-H(30)	119.7
C(29)-C(31)-C(30)	117.94(13)
C(29)-C(31)-H(31)	121.0
C(30)-C(31)-H(31)	121.0
C(21)-C(32)-C(33)	113.29(12)
C(21)-C(32)-H(32A)	108.9
C(33)-C(32)-H(32A)	108.9
C(21)-C(32)-H(32B)	108.9
C(33)-C(32)-H(32B)	108.9
H(32A)-C(32)-H(32B)	107.7
N(3)-C(33)-C(38)	109.19(11)
N(3)-C(33)-C(32)	111.82(12)
C(38)-C(33)-C(32)	110.73(12)
N(3)-C(33)-H(33)	108.3
C(38)-C(33)-H(33)	108.3
C(32)-C(33)-H(33)	108.3
N(4)-C(34)-N(3)	119.68(13)
N(4)-C(34)-C(24)	119.76(13)

N(3)-C(34)-C(24)	120.55(13)
N(4)-C(35)-C(36)	109.45(13)
N(4)-C(35)-H(35A)	109.8
C(36)-C(35)-H(35A)	109.8
N(4)-C(35)-H(35B)	109.8
C(36)-C(35)-H(35B)	109.8
H(35A)-C(35)-H(35B)	108.2
C(37)-C(36)-C(35)	109.20(13)
C(37)-C(36)-H(36A)	109.8
C(35)-C(36)-H(36A)	109.8
C(37)-C(36)-H(36B)	109.8
C(35)-C(36)-H(36B)	109.8
H(36A)-C(36)-H(36B)	108.3
N(3)-C(37)-C(36)	110.13(12)
N(3)-C(37)-H(37A)	109.6
C(36)-C(37)-H(37A)	109.6
N(3)-C(37)-H(37B)	109.6
C(36)-C(37)-H(37B)	109.6
H(37A)-C(37)-H(37B)	108.1
O(8)-C(38)-O(7)	112.25(12)
O(8)-C(38)-C(23)	114.07(12)
O(7)-C(38)-C(23)	106.05(11)
O(8)-C(38)-C(33)	104.15(11)
O(7)-C(38)-C(33)	112.87(12)
C(23)-C(38)-C(33)	107.52(12)
O(7)-C(39)-H(39A)	109.5
O(7)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
O(7)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
O(8)-C(40)-H(40A)	109.5
O(8)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
O(8)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5

Symmetry transformations used to generate equivalent atoms:

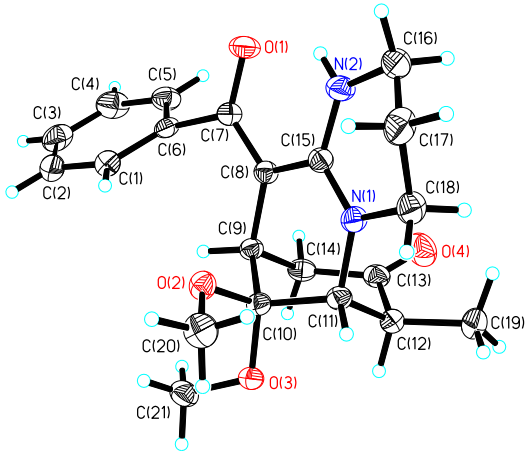


Figure S2 X-Ray crystal structure of **3l'**

Table S3 Crystal data and structure refinement for **3l'**

Empirical formula	$C_{42}\,H_{52}\,N_4\,O_8$
Formula weight	740.88
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 14.6978(15) A alpha = 90 deg. b = 12.2595(12) A beta = 108.6090(10) deg. c = 21.830(2) A gamma = 90 deg.
Volume	3727.9(6) A^3
Z, Calculated density	4, 1.320 Mg/m^3
Absorption coefficient	0.092 mm^-1
F(000)	1584
Crystal size	0.38 x 0.24 x 0.22 mm
Theta range for data collection	1.97 to 25.15 deg.
Limiting indices	-15<=h<=17, -12<=k<=14, -26<=l<=24
Reflection collected/unique	10383 / 3342 [R(int) = 0.0310]
Completeness to theta = 28.2	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9801 and 0.9660
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3342 / 0 / 248
Goodness-of-fit on F^2	0.981
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 =0.1296
R indices (all data)	R1 = 0.0629, wR2 = 0.1494
Extinction coefficient	0.0057(8)
Largest diff. peak and hole	0.194 and -0.160 e.A^-3

Table S4 Bond lengths [A] and angles [deg] for **3l'**

N(1)-C(15)	1.355(2)
N(1)-C(11)	1.471(2)
N(1)-C(18)	1.474(2)
N(2)-C(15)	1.340(2)
N(2)-C(16)	1.449(2)
N(2)-H(2A)	0.8600
O(1)-C(7)	1.273(2)
O(2)-C(10)	1.406(2)
O(2)-C(20)	1.431(2)
O(3)-C(10)	1.424(2)
O(3)-C(21)	1.426(2)
O(4)-C(13)	1.207(2)
C(1)-C(6)	1.383(3)
C(1)-C(2)	1.389(3)
C(1)-H(1)	0.9300
C(2)-C(3)	1.378(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.360(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.373(3)
C(4)-H(4)	0.9300
C(5)-C(6)	1.387(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.509(2)
C(7)-C(8)	1.404(3)
C(8)-C(15)	1.425(2)
C(8)-C(9)	1.519(2)
C(9)-C(10)	1.533(2)
C(9)-C(14)	1.549(2)
C(9)-H(9)	0.9800
C(10)-C(11)	1.531(2)
C(11)-C(12)	1.549(3)
C(11)-H(11)	0.9800
C(12)-C(13)	1.518(3)
C(12)-C(19)	1.523(3)
C(12)-H(12)	0.9800
C(13)-C(14)	1.504(3)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(16)-C(17)	1.502(3)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(17)-C(18)	1.505(3)

C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(15)-N(1)-C(11)	121.60(14)
C(15)-N(1)-C(18)	121.62(15)
C(11)-N(1)-C(18)	116.78(15)
C(15)-N(2)-C(16)	125.08(17)
C(15)-N(2)-H(2A)	117.5
C(16)-N(2)-H(2A)	117.5
C(10)-O(2)-C(20)	116.33(15)
C(10)-O(3)-C(21)	115.08(14)
C(6)-C(1)-C(2)	120.61(19)
C(6)-C(1)-H(1)	119.7
C(2)-C(1)-H(1)	119.7
C(3)-C(2)-C(1)	119.8(2)
C(3)-C(2)-H(2)	120.1
C(1)-C(2)-H(2)	120.1
C(4)-C(3)-C(2)	120.0(2)
C(4)-C(3)-H(3)	120.0
C(2)-C(3)-H(3)	120.0
C(3)-C(4)-C(5)	120.4(2)
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-H(4)	119.8
C(4)-C(5)-C(6)	121.1(2)
C(4)-C(5)-H(5)	119.5
C(6)-C(5)-H(5)	119.5
C(1)-C(6)-C(5)	118.12(18)
C(1)-C(6)-C(7)	122.49(17)
C(5)-C(6)-C(7)	119.09(17)
O(1)-C(7)-C(8)	125.42(16)
O(1)-C(7)-C(6)	114.15(15)
C(8)-C(7)-C(6)	120.38(15)
C(7)-C(8)-C(15)	120.21(16)
C(7)-C(8)-C(9)	121.75(15)
C(15)-C(8)-C(9)	118.04(15)

C(8)-C(9)-C(10)	109.29(13)
C(8)-C(9)-C(14)	111.62(14)
C(10)-C(9)-C(14)	109.21(14)
C(8)-C(9)-H(9)	108.9
C(10)-C(9)-H(9)	108.9
C(14)-C(9)-H(9)	108.9
O(2)-C(10)-O(3)	110.76(13)
O(2)-C(10)-C(11)	113.67(14)
O(3)-C(10)-C(11)	105.48(14)
O(2)-C(10)-C(9)	106.41(14)
O(3)-C(10)-C(9)	113.34(13)
C(11)-C(10)-C(9)	107.29(14)
N(1)-C(11)-C(10)	109.56(14)
N(1)-C(11)-C(12)	112.34(14)
C(10)-C(11)-C(12)	110.77(14)
N(1)-C(11)-H(11)	108.0
C(10)-C(11)-H(11)	108.0
C(12)-C(11)-H(11)	108.0
C(13)-C(12)-C(19)	113.33(16)
C(13)-C(12)-C(11)	109.87(15)
C(19)-C(12)-C(11)	114.48(15)
C(13)-C(12)-H(12)	106.2
C(19)-C(12)-H(12)	106.2
C(11)-C(12)-H(12)	106.2
O(4)-C(13)-C(14)	121.90(18)
O(4)-C(13)-C(12)	122.59(19)
C(14)-C(13)-C(12)	115.51(15)
C(13)-C(14)-C(9)	112.37(14)
C(13)-C(14)-H(14A)	109.1
C(9)-C(14)-H(14A)	109.1
C(13)-C(14)-H(14B)	109.1
C(9)-C(14)-H(14B)	109.1
H(14A)-C(14)-H(14B)	107.9
N(2)-C(15)-N(1)	118.88(16)
N(2)-C(15)-C(8)	119.55(16)
N(1)-C(15)-C(8)	121.52(15)
N(2)-C(16)-C(17)	109.29(17)
N(2)-C(16)-H(16A)	109.8
C(17)-C(16)-H(16A)	109.8
N(2)-C(16)-H(16B)	109.8
C(17)-C(16)-H(16B)	109.8
H(16A)-C(16)-H(16B)	108.3
C(16)-C(17)-C(18)	110.09(18)
C(16)-C(17)-H(17A)	109.6
C(18)-C(17)-H(17A)	109.6

C(16)-C(17)-H(17B)	109.6
C(18)-C(17)-H(17B)	109.6
H(17A)-C(17)-H(17B)	108.2
N(1)-C(18)-C(17)	111.29(16)
N(1)-C(18)-H(18A)	109.4
C(17)-C(18)-H(18A)	109.4
N(1)-C(18)-H(18B)	109.4
C(17)-C(18)-H(18B)	109.4
H(18A)-C(18)-H(18B)	108.0
C(12)-C(19)-H(19A)	109.5
C(12)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(12)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(2)-C(20)-H(20A)	109.5
O(2)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(2)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(3)-C(21)-H(21A)	109.5
O(3)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
O(3)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

Symmetry transformations used to generate equivalent atoms:

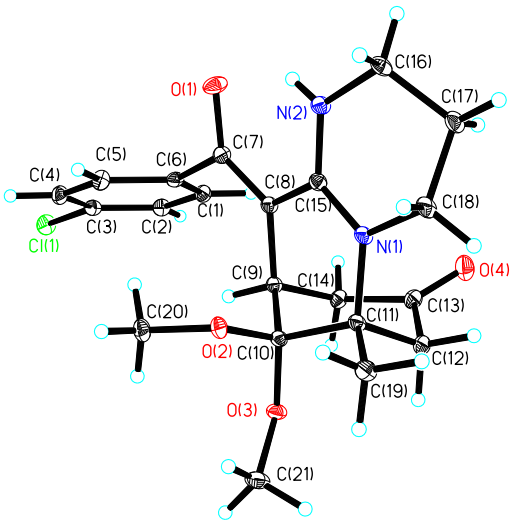


Figure S3 X-Ray crystal structure of **3n'**

Table S5 Crystal data and structure refinement for **3n'**

Empirical formula	$C_{42}\ H_{56}\ Cl_2\ N_4\ O_{11}$
Formula weight	863.81
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C 2/c
Unit cell dimensions	a = 23.064(2) A alpha = 90 deg. b = 9.1067(9) A beta = 102.558(2) deg. c = 19.757(2) A gamma = 90 deg.
Volume	4050.5(7) A^3
Z, Calculated density	4, 1.416 Mg/m^3
Absorption coefficient	0.228 mm^-1
F(000)	1832
Crystal size	0.75 × 0.50 × 0.40 mm
Theta range for data collection	1.81 to 28.00 deg.
Limiting indices	-27 < = h < = 30, -12 < = k < = 11, -26 < = l < = 26
Reflection collected/unique	18766 / 4882 [R(int) = 0.0241]
Completeness to theta = 28.2	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9143 and 0.8475
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4882 / 3 / 280
Goodness-of-fit on F^2	1.080
Final R indices [I>2sigma(I)]	R1 = 0.0528, wR2 = 0.1552
R indices (all data)	R1 = 0.0573, wR2 = 0.1596
Largest diff. peak and hole	0.707 and -1.290 e.A^-3

Table S6 Bond lengths [A] and angles [deg] for **3n'**

Cl(1)-C(3)	1.7483(18)
O(1S)-H(1SB)	0.827(10)
O(1S)-H(1SA)	0.824(10)
O(4)-C(13)	1.221(2)
O(2S)-H(2SA)	0.8205
O(2)-C(10)	1.401(2)
O(2)-C(20)	1.432(2)
O(3)-C(10)	1.423(2)
O(3)-C(21)	1.437(2)
O(1)-C(7)	1.283(2)
N(1)-C(15)	1.356(2)
N(1)-C(18)	1.480(2)
N(1)-C(11)	1.503(2)
N(2)-C(15)	1.341(2)
N(2)-C(16)	1.458(2)
N(2)-H(1A)	0.80(3)
C(3)-C(4)	1.384(3)
C(3)-C(2)	1.390(3)
C(2)-C(1)	1.393(3)
C(2)-H(2)	0.9500
C(1)-C(6)	1.392(2)
C(1)-H(1)	0.9500
C(6)-C(5)	1.399(3)
C(6)-C(7)	1.510(2)
C(7)-C(8)	1.394(2)
C(8)-C(15)	1.435(2)
C(8)-C(9)	1.506(2)
C(9)-C(10)	1.537(2)
C(9)-C(14)	1.551(2)
C(9)-H(9)	1.0000
C(14)-C(13)	1.508(2)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(13)-C(12)	1.514(2)
C(5)-C(4)	1.390(3)
C(5)-H(5)	0.9500
C(4)-H(4)	0.9500
C(11)-C(19)	1.531(2)
C(11)-C(12)	1.541(3)
C(11)-C(10)	1.552(2)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(12)-H(12A)	0.9900

C(12)-H(12B)	0.9900
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(18)-C(17)	1.521(3)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(17)-C(16)	1.517(3)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
H(1SB)-O(1S)-H(1SA)	102(2)
C(10)-O(2)-C(20)	116.25(14)
C(10)-O(3)-C(21)	119.84(15)
C(15)-N(1)-C(18)	119.24(15)
C(15)-N(1)-C(11)	124.27(14)
C(18)-N(1)-C(11)	116.48(14)
C(15)-N(2)-C(16)	125.10(16)
C(15)-N(2)-H(1A)	114(2)
C(16)-N(2)-H(1A)	120(2)
C(4)-C(3)-C(2)	121.91(17)
C(4)-C(3)-Cl(1)	119.20(14)
C(2)-C(3)-Cl(1)	118.88(14)
C(3)-C(2)-C(1)	118.81(17)
C(3)-C(2)-H(2)	120.6
C(1)-C(2)-H(2)	120.6
C(6)-C(1)-C(2)	120.78(17)
C(6)-C(1)-H(1)	119.6
C(2)-C(1)-H(1)	119.6
C(1)-C(6)-C(5)	118.78(16)
C(1)-C(6)-C(7)	122.06(16)
C(5)-C(6)-C(7)	118.85(16)
O(1)-C(7)-C(8)	125.17(17)
O(1)-C(7)-C(6)	114.23(15)
C(8)-C(7)-C(6)	120.61(16)
C(7)-C(8)-C(15)	120.71(16)
C(7)-C(8)-C(9)	122.75(16)
C(15)-C(8)-C(9)	116.52(15)
C(8)-C(9)-C(10)	108.64(14)
C(8)-C(9)-C(14)	113.71(14)
C(10)-C(9)-C(14)	109.80(14)

C(8)-C(9)-H(9)	108.2
C(10)-C(9)-H(9)	108.2
C(14)-C(9)-H(9)	108.2
C(13)-C(14)-C(9)	113.50(14)
C(13)-C(14)-H(14A)	108.9
C(9)-C(14)-H(14A)	108.9
C(13)-C(14)-H(14B)	108.9
C(9)-C(14)-H(14B)	108.9
H(14A)-C(14)-H(14B)	107.7
O(4)-C(13)-C(14)	122.92(17)
O(4)-C(13)-C(12)	121.63(17)
C(14)-C(13)-C(12)	115.44(16)
C(4)-C(5)-C(6)	121.38(17)
C(4)-C(5)-H(5)	119.3
C(6)-C(5)-H(5)	119.3
C(3)-C(4)-C(5)	118.33(17)
C(3)-C(4)-H(4)	120.8
C(5)-C(4)-H(4)	120.8
N(2)-C(15)-N(1)	119.88(16)
N(2)-C(15)-C(8)	119.09(16)
N(1)-C(15)-C(8)	121.03(16)
N(1)-C(11)-C(19)	108.89(14)
N(1)-C(11)-C(12)	108.00(14)
C(19)-C(11)-C(12)	110.45(14)
N(1)-C(11)-C(10)	108.85(13)
C(19)-C(11)-C(10)	112.08(14)
C(12)-C(11)-C(10)	108.48(14)
O(2)-C(10)-O(3)	112.45(14)
O(2)-C(10)-C(9)	113.68(14)
O(3)-C(10)-C(9)	104.35(14)
O(2)-C(10)-C(11)	105.49(14)
O(3)-C(10)-C(11)	112.67(14)
C(9)-C(10)-C(11)	108.32(14)
O(2)-C(20)-H(20A)	109.5
O(2)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(2)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(13)-C(12)-C(11)	110.13(14)
C(13)-C(12)-H(12A)	109.6
C(11)-C(12)-H(12A)	109.6
C(13)-C(12)-H(12B)	109.6
C(11)-C(12)-H(12B)	109.6
H(12A)-C(12)-H(12B)	108.1

O(3)-C(21)-H(21A)	109.5
O(3)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
O(3)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(11)-C(19)-H(19A)	109.5
C(11)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(11)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
N(1)-C(18)-C(17)	110.46(14)
N(1)-C(18)-H(18A)	109.6
C(17)-C(18)-H(18A)	109.6
N(1)-C(18)-H(18B)	109.6
C(17)-C(18)-H(18B)	109.6
H(18A)-C(18)-H(18B)	108.1
C(16)-C(17)-C(18)	108.16(15)
C(16)-C(17)-H(17A)	110.1
C(18)-C(17)-H(17A)	110.1
C(16)-C(17)-H(17B)	110.1
C(18)-C(17)-H(17B)	110.1
H(17A)-C(17)-H(17B)	108.4
N(2)-C(16)-C(17)	108.25(15)
N(2)-C(16)-H(16A)	110.0
C(17)-C(16)-H(16A)	110.0
N(2)-C(16)-H(16B)	110.0
C(17)-C(16)-H(16B)	110.0
H(16A)-C(16)-H(16B)	108.4

Symmetry transformations used to generate equivalent atoms:

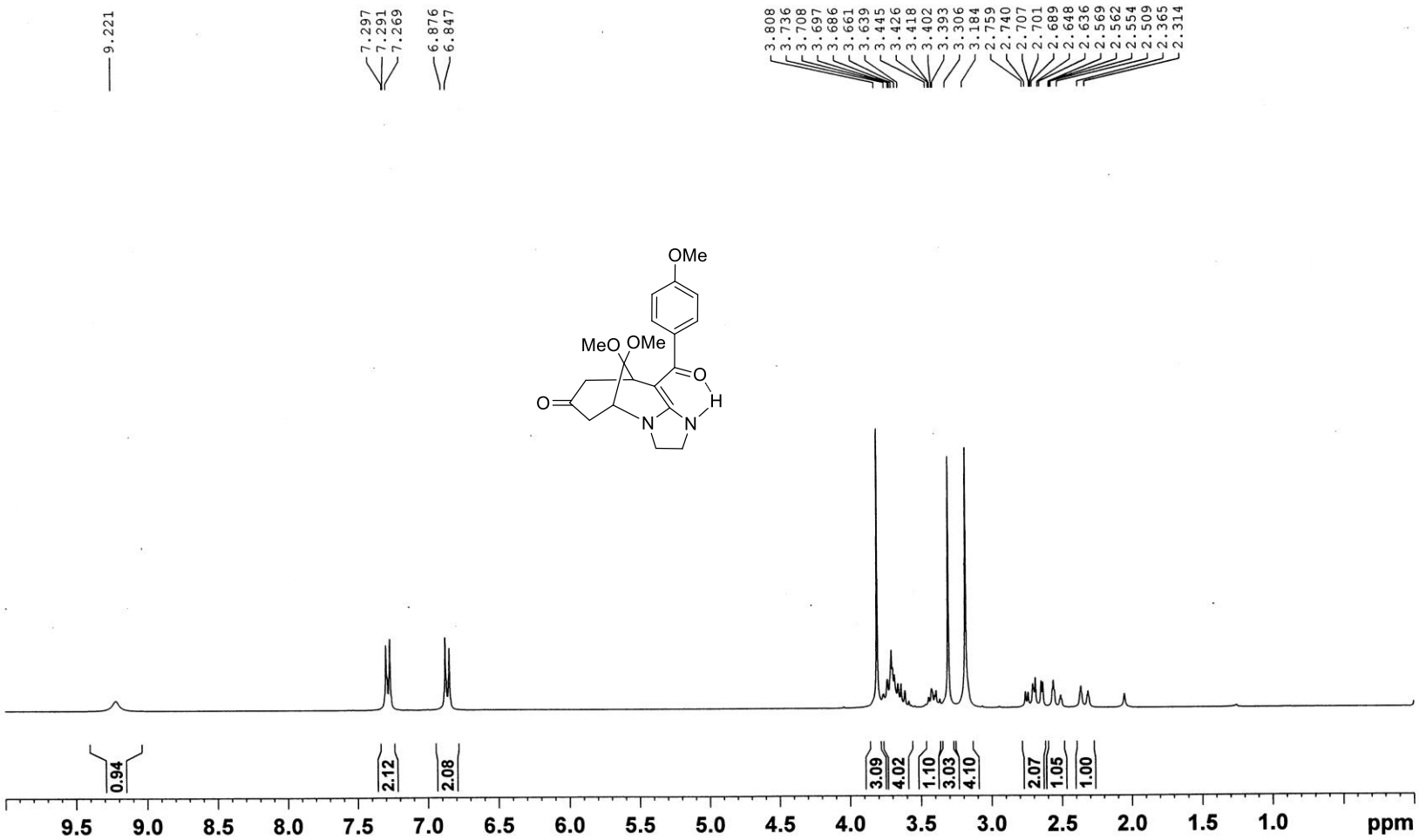


Figure 1. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3a**

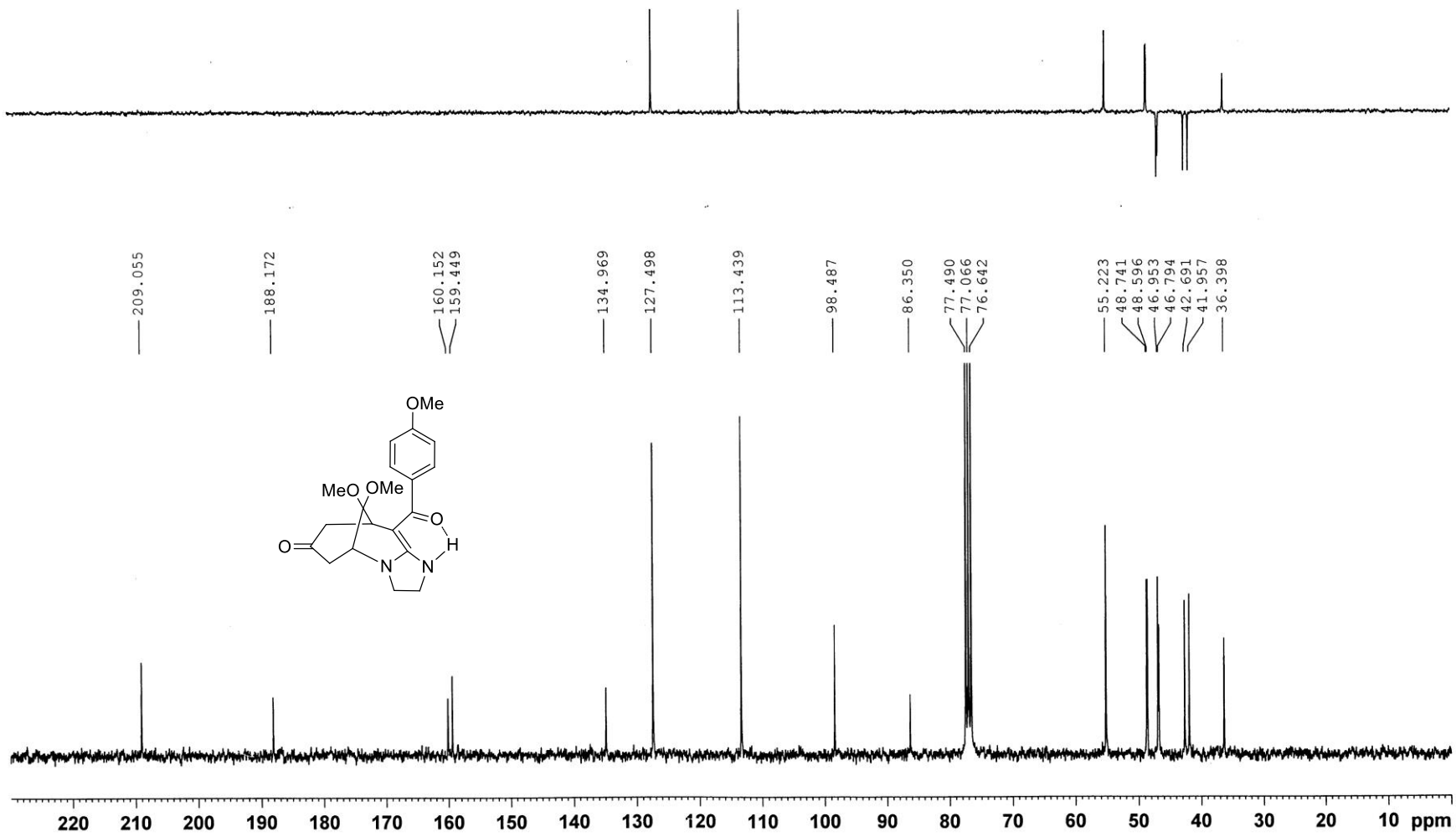


Figure 2. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3a**

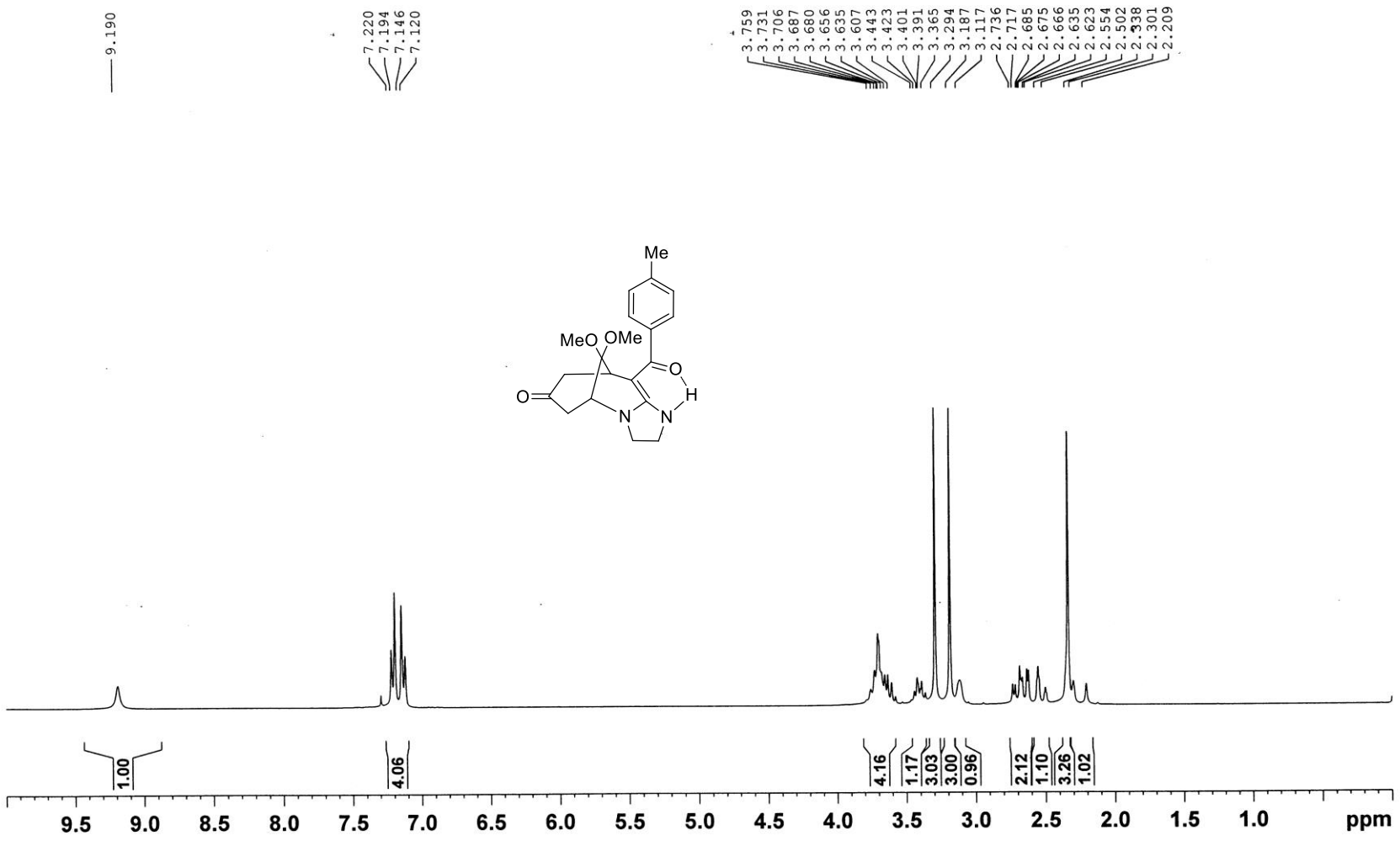


Figure 3. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3b**

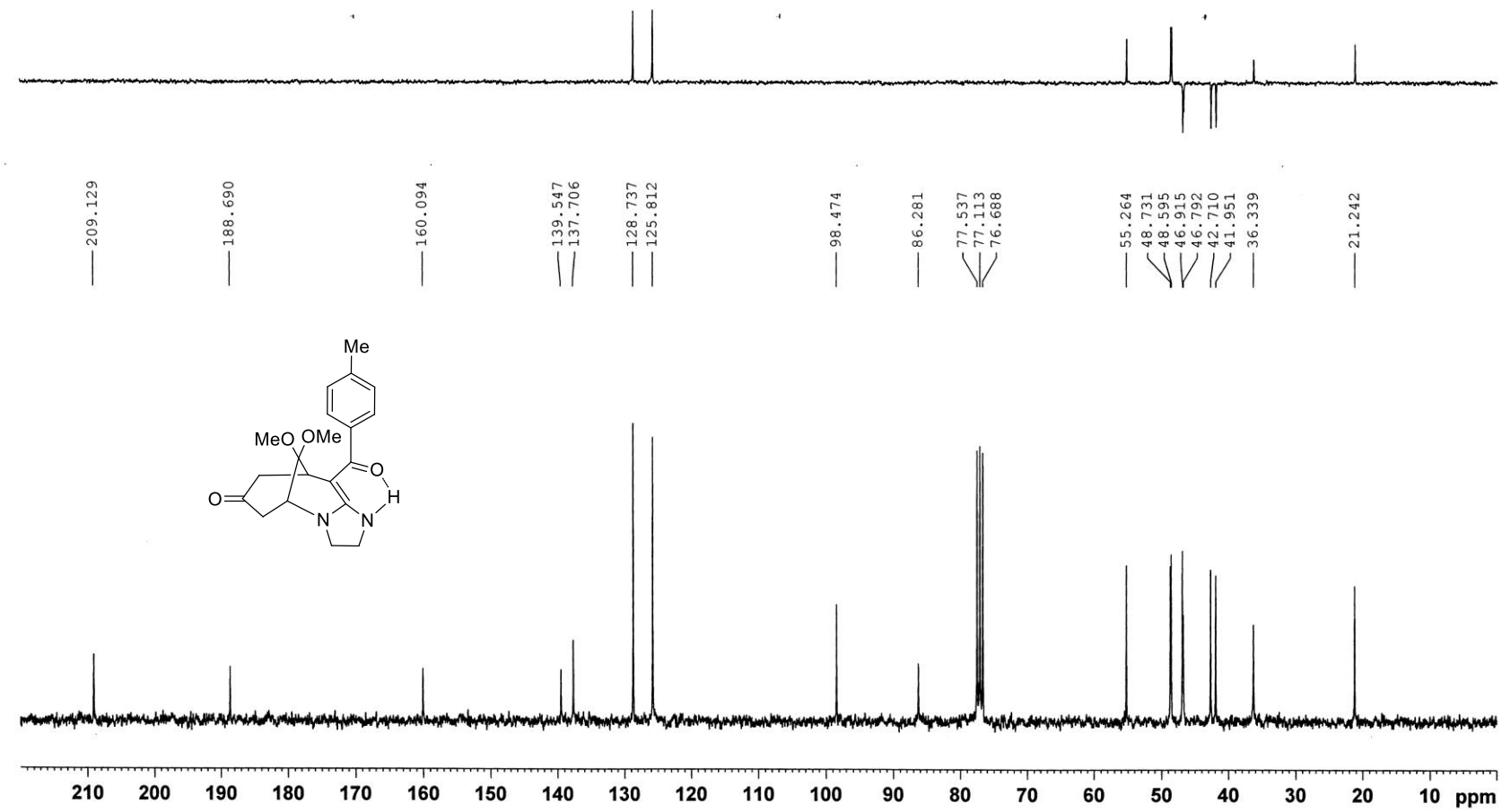


Figure 4. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3b**

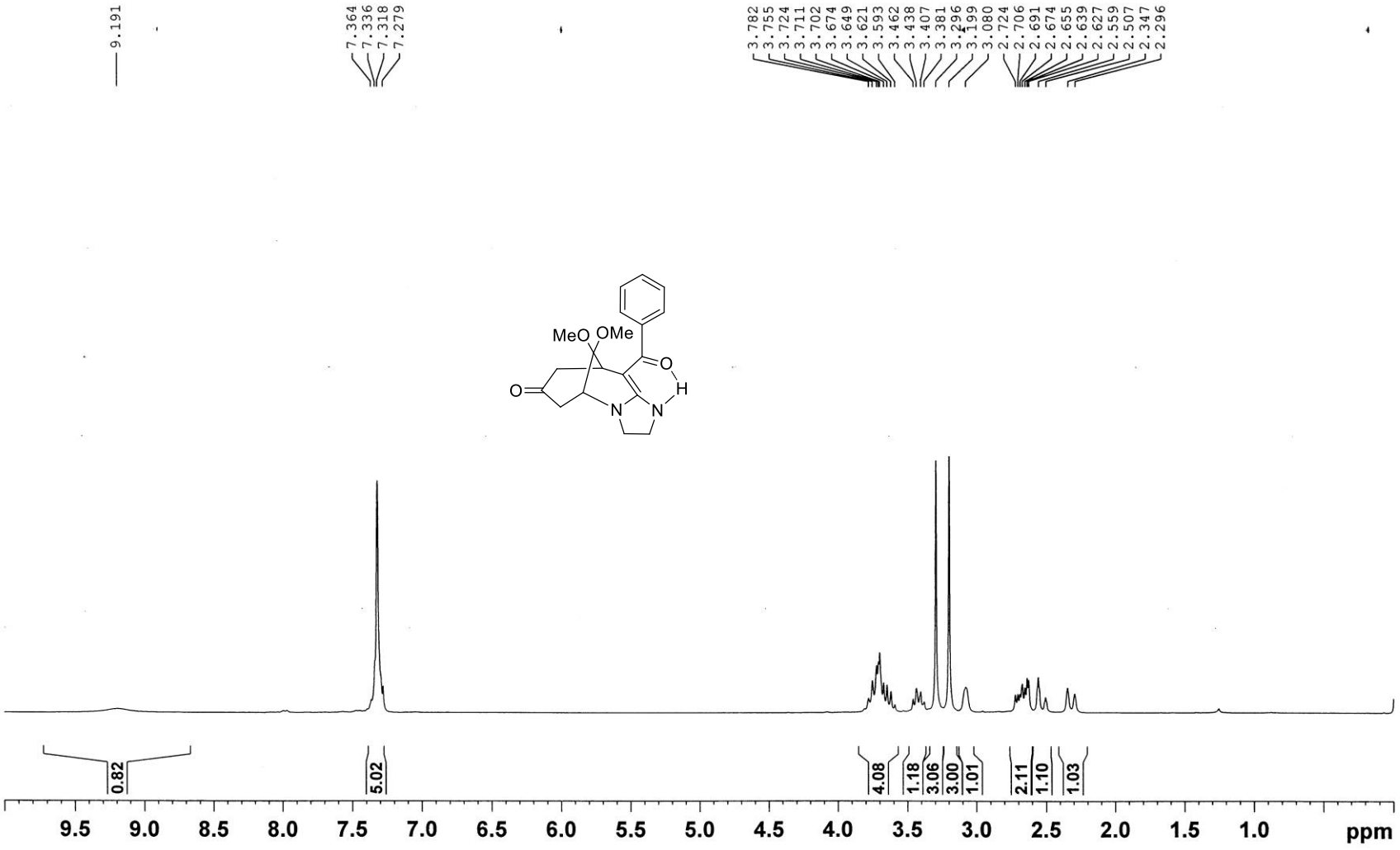


Figure 5. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3c**

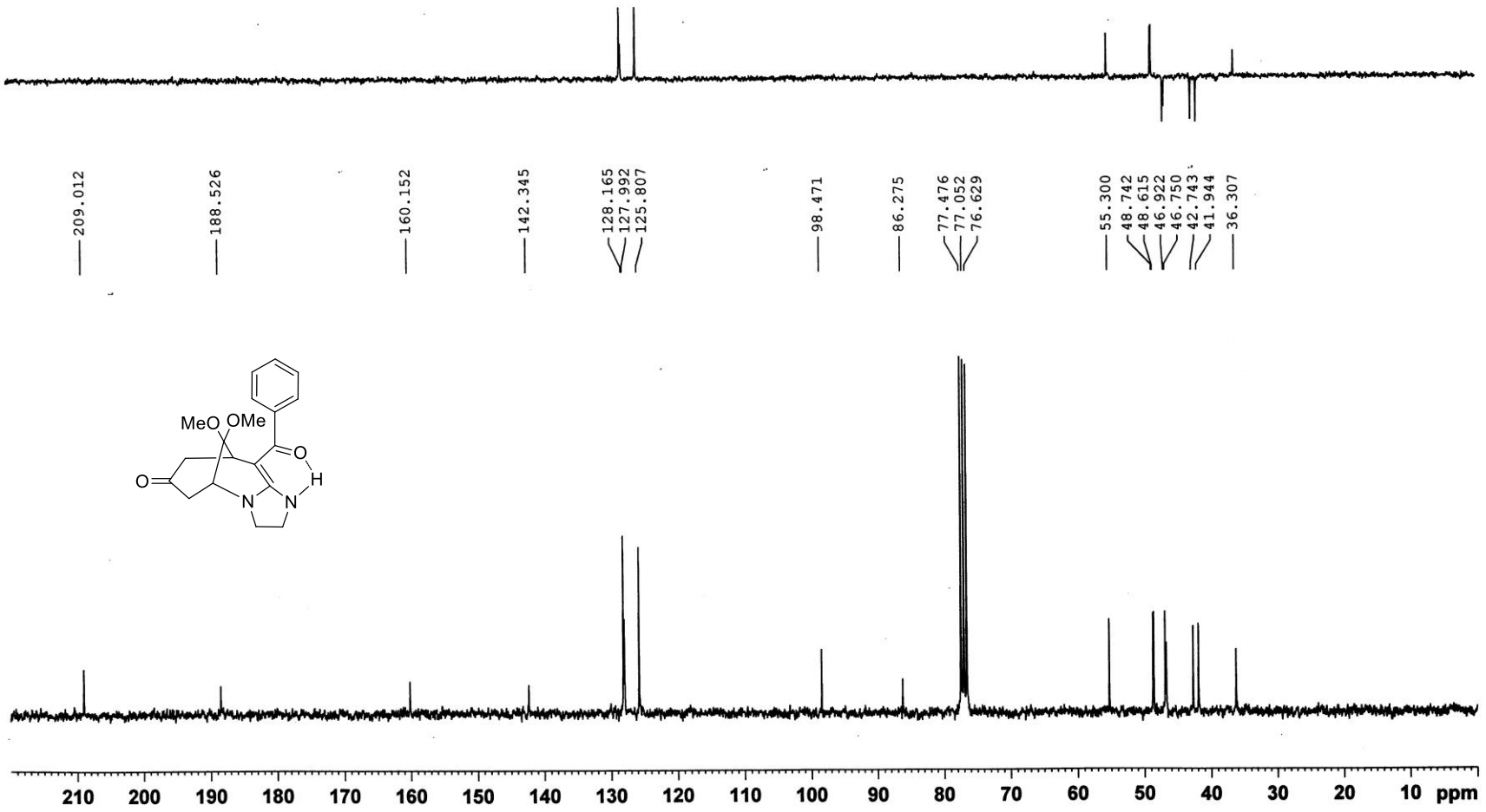


Figure 6. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3c**

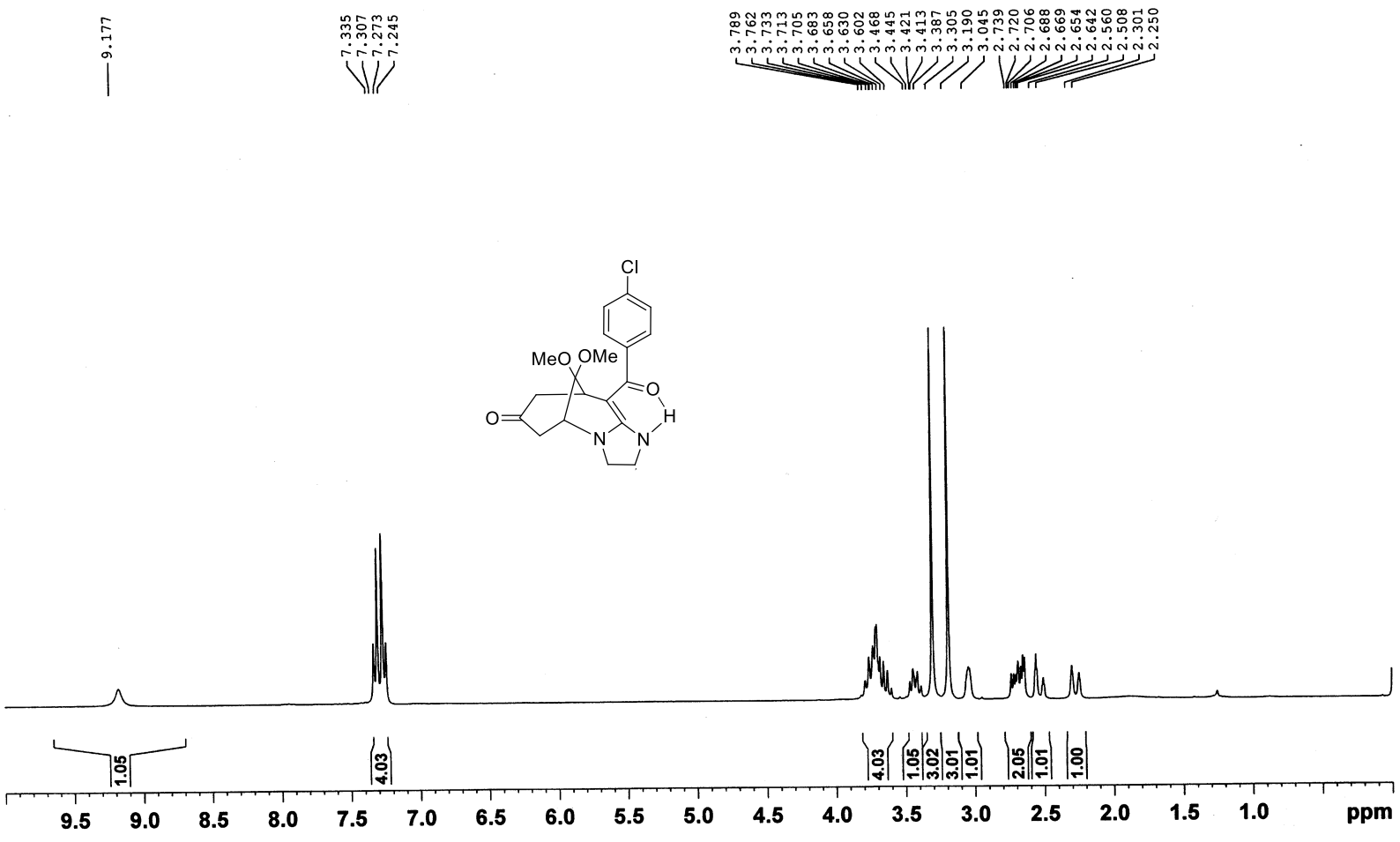


Figure 7. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3d**

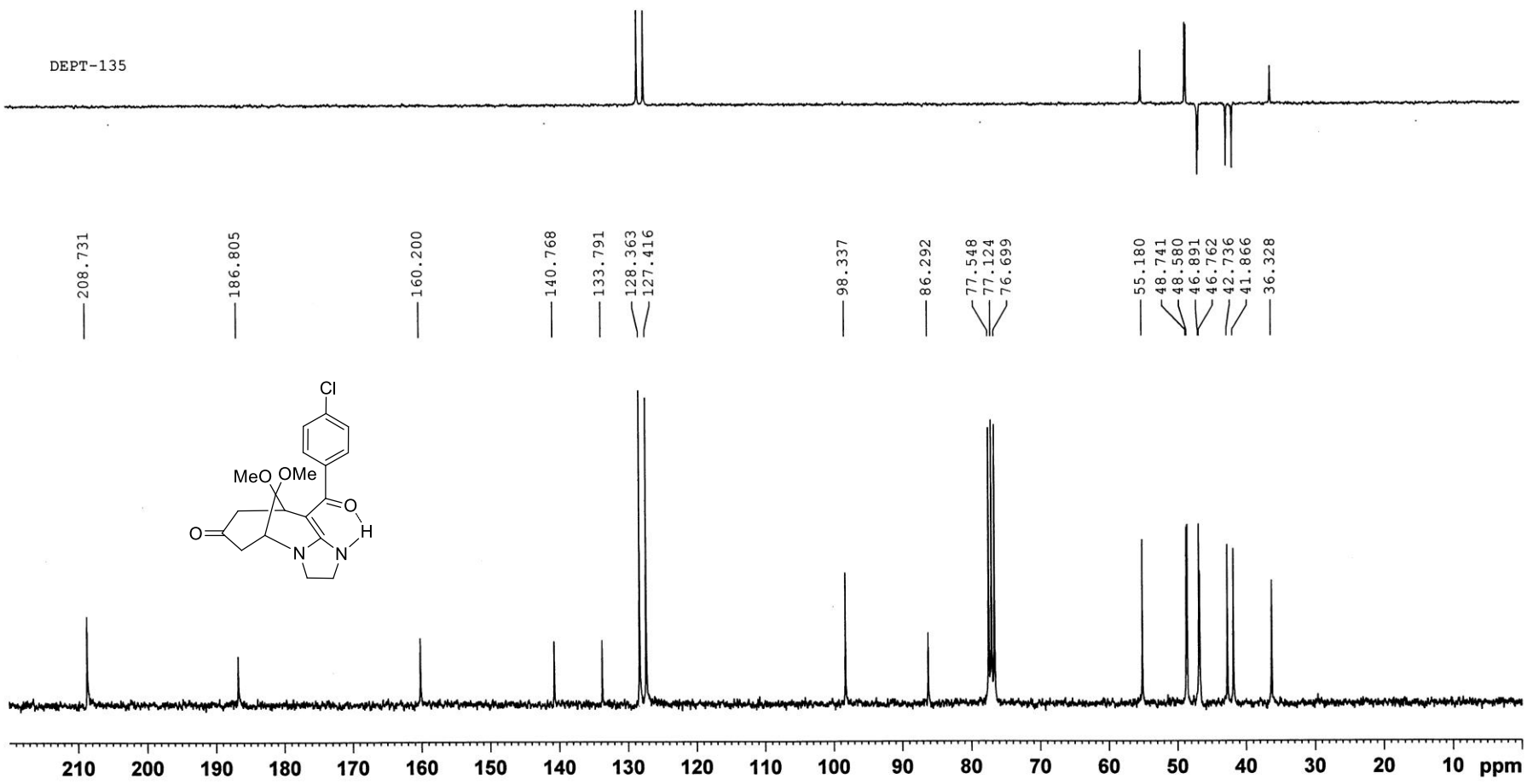


Figure 8. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3d**

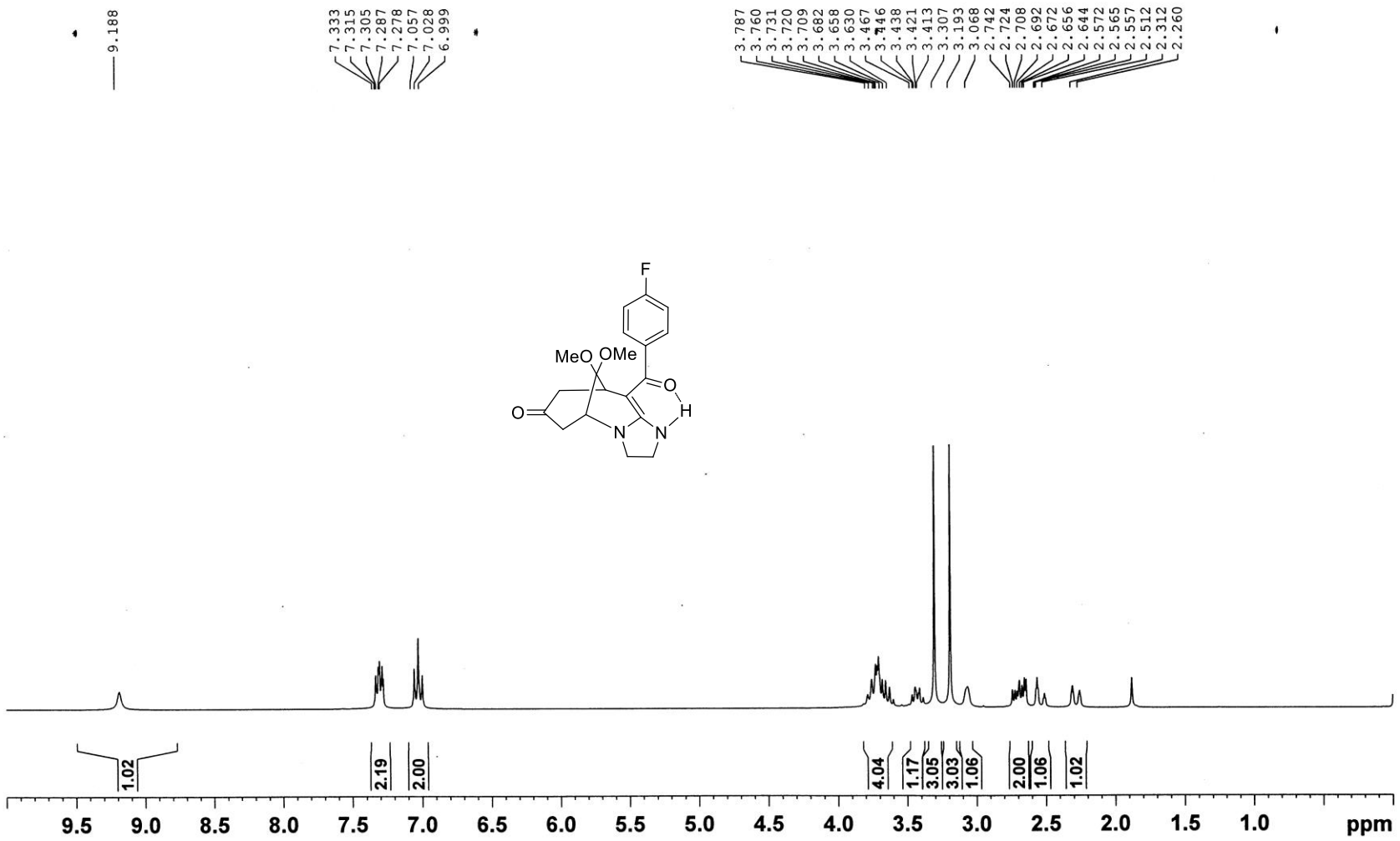


Figure 9. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3e**

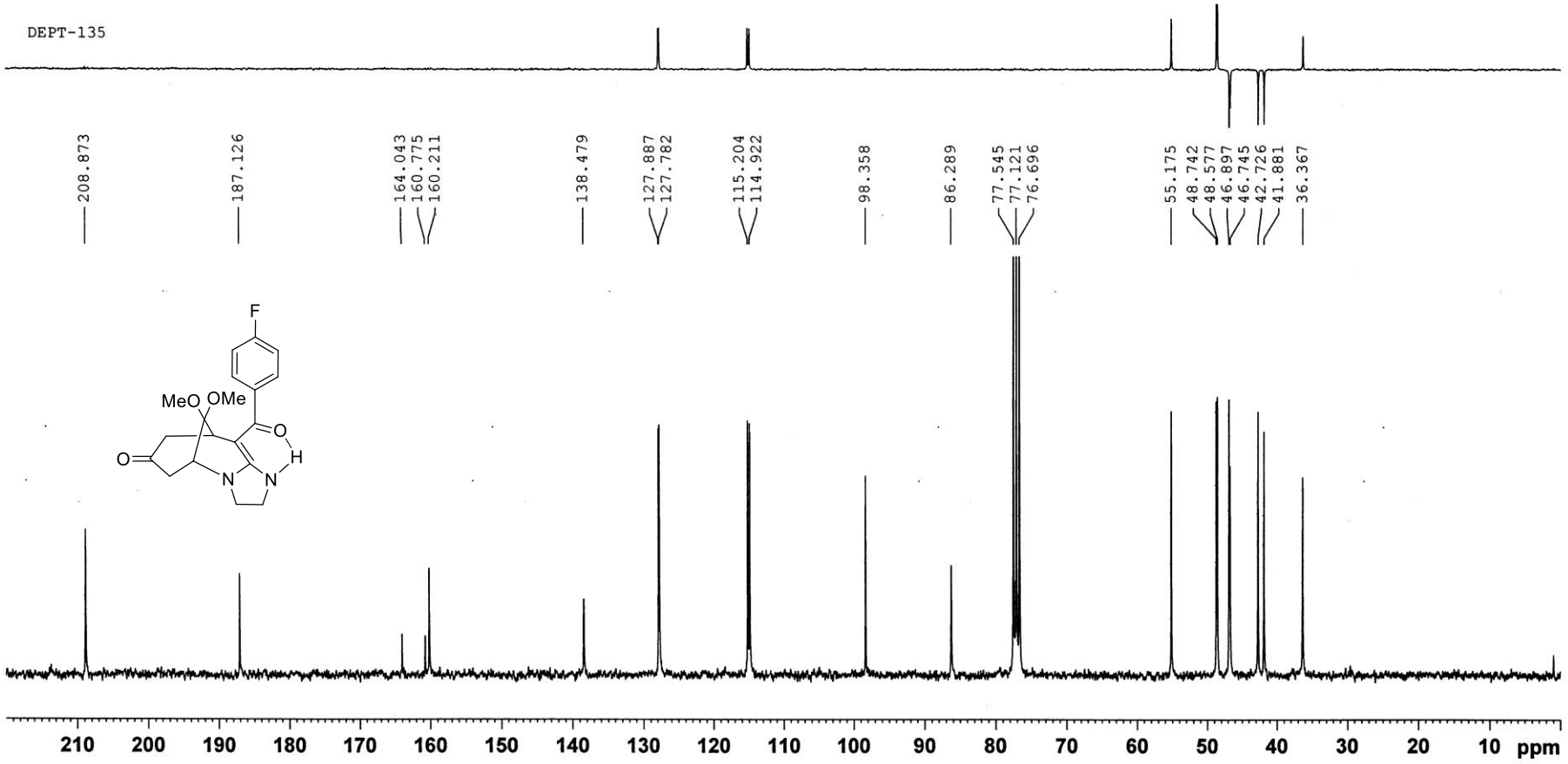


Figure 10. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3e**

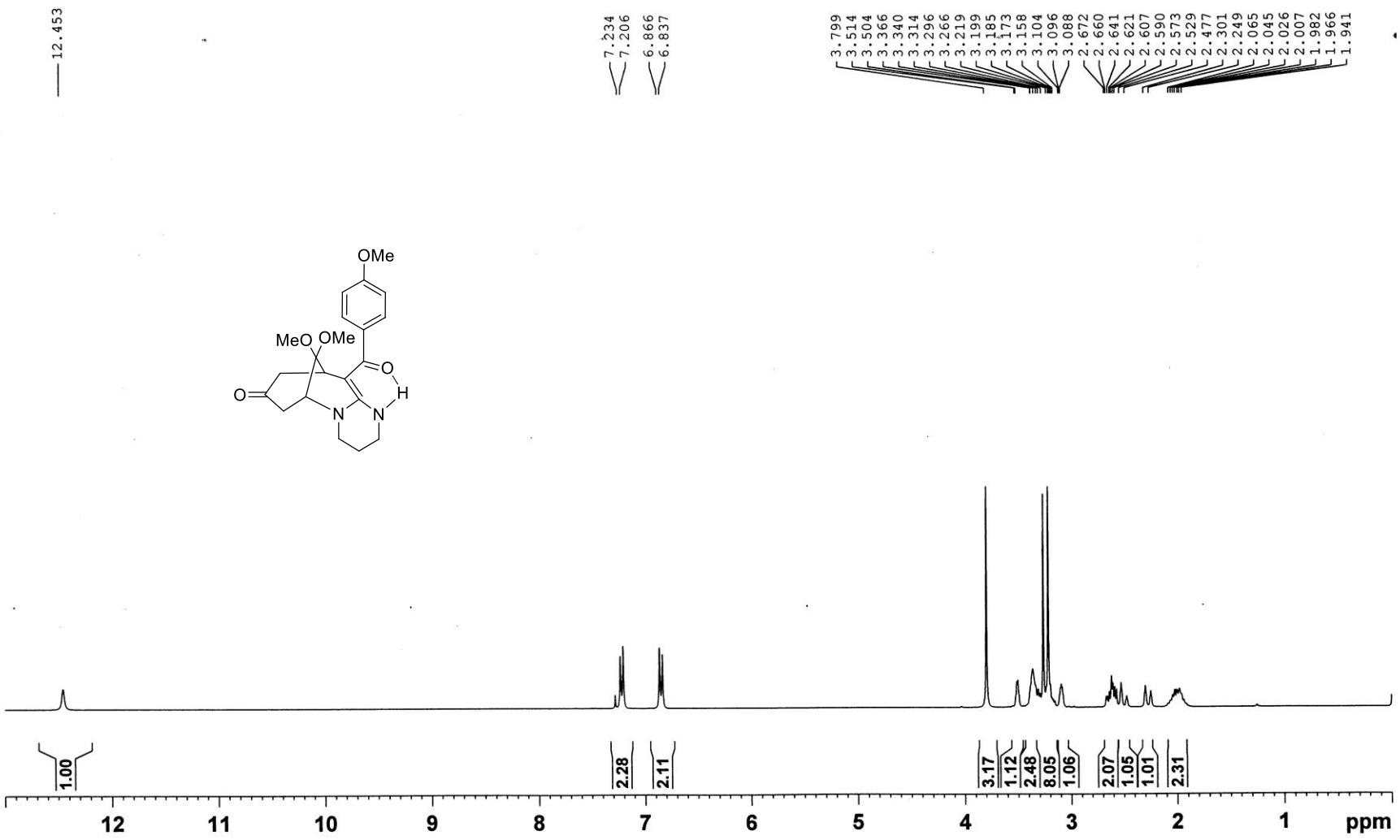


Figure 11. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3f**

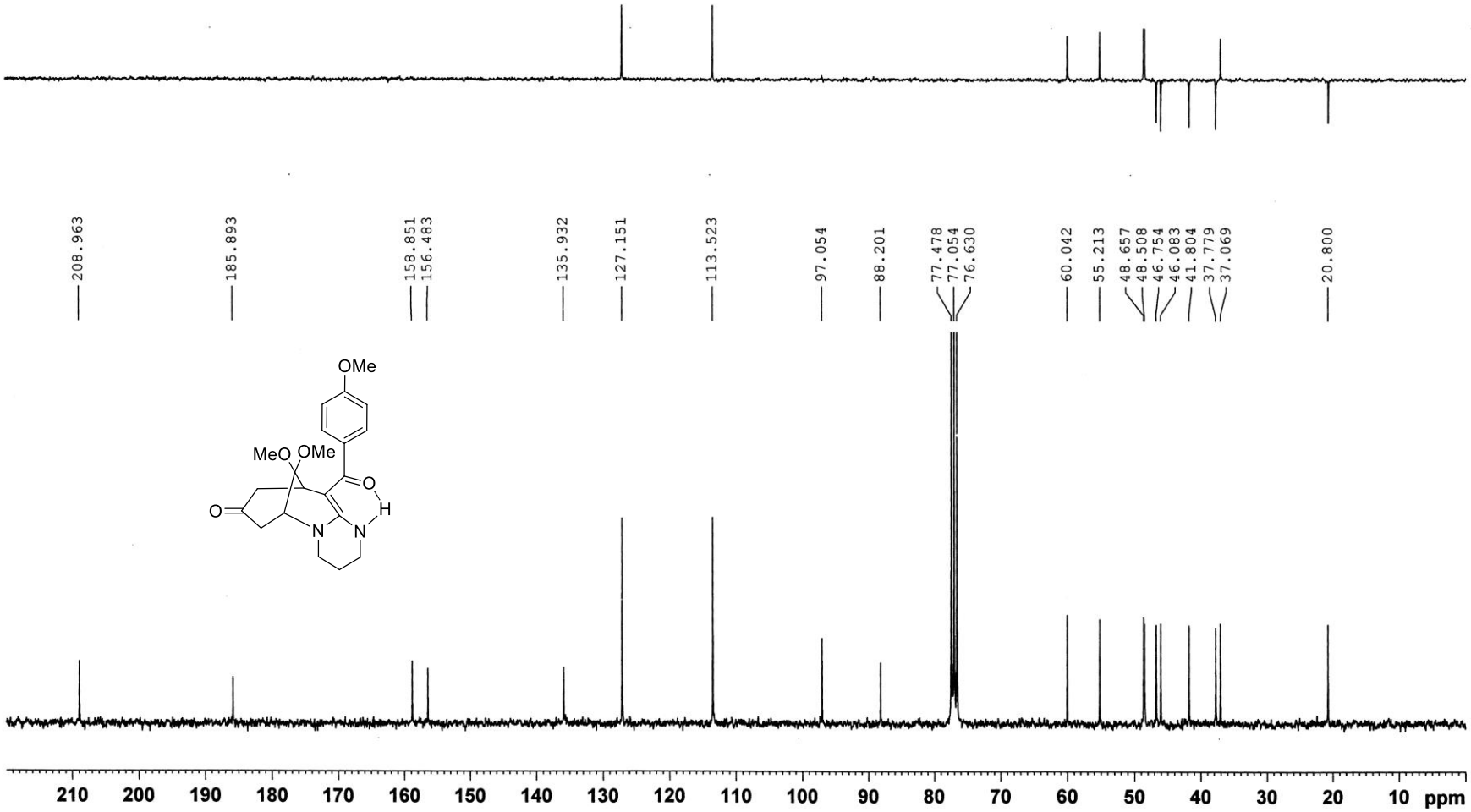


Figure 12. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3f**

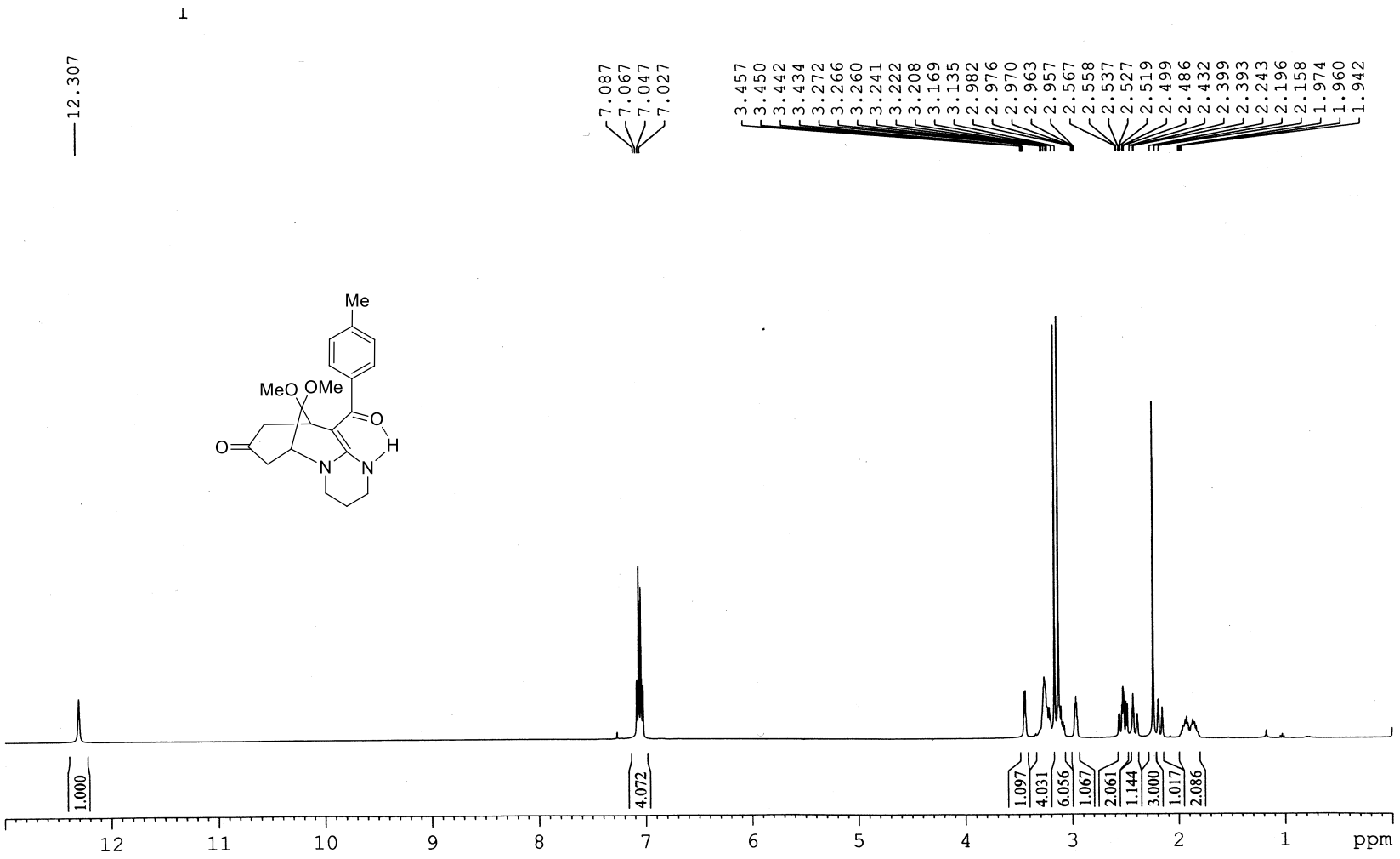


Figure 13. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3g**

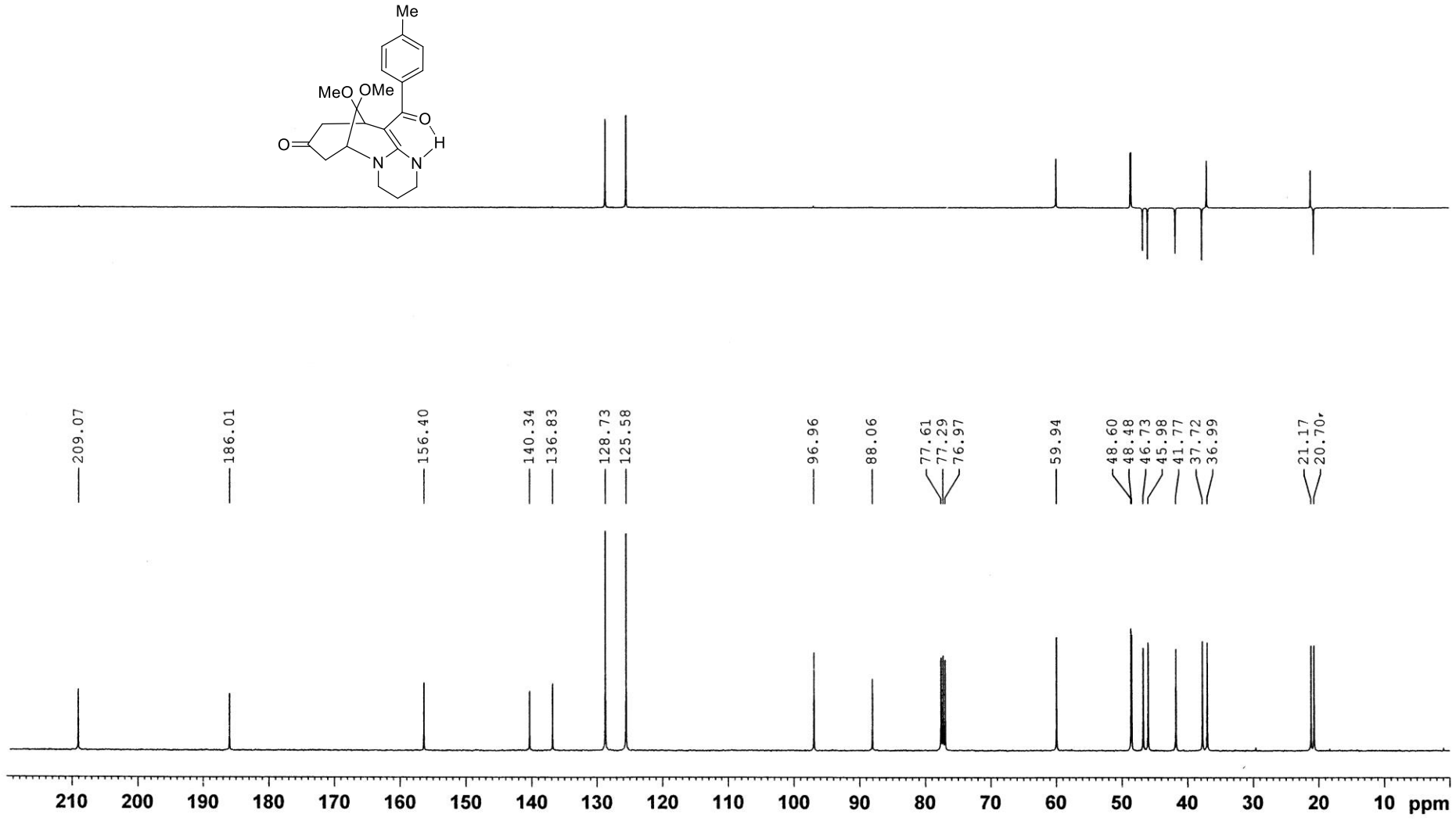


Figure 14. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3g**

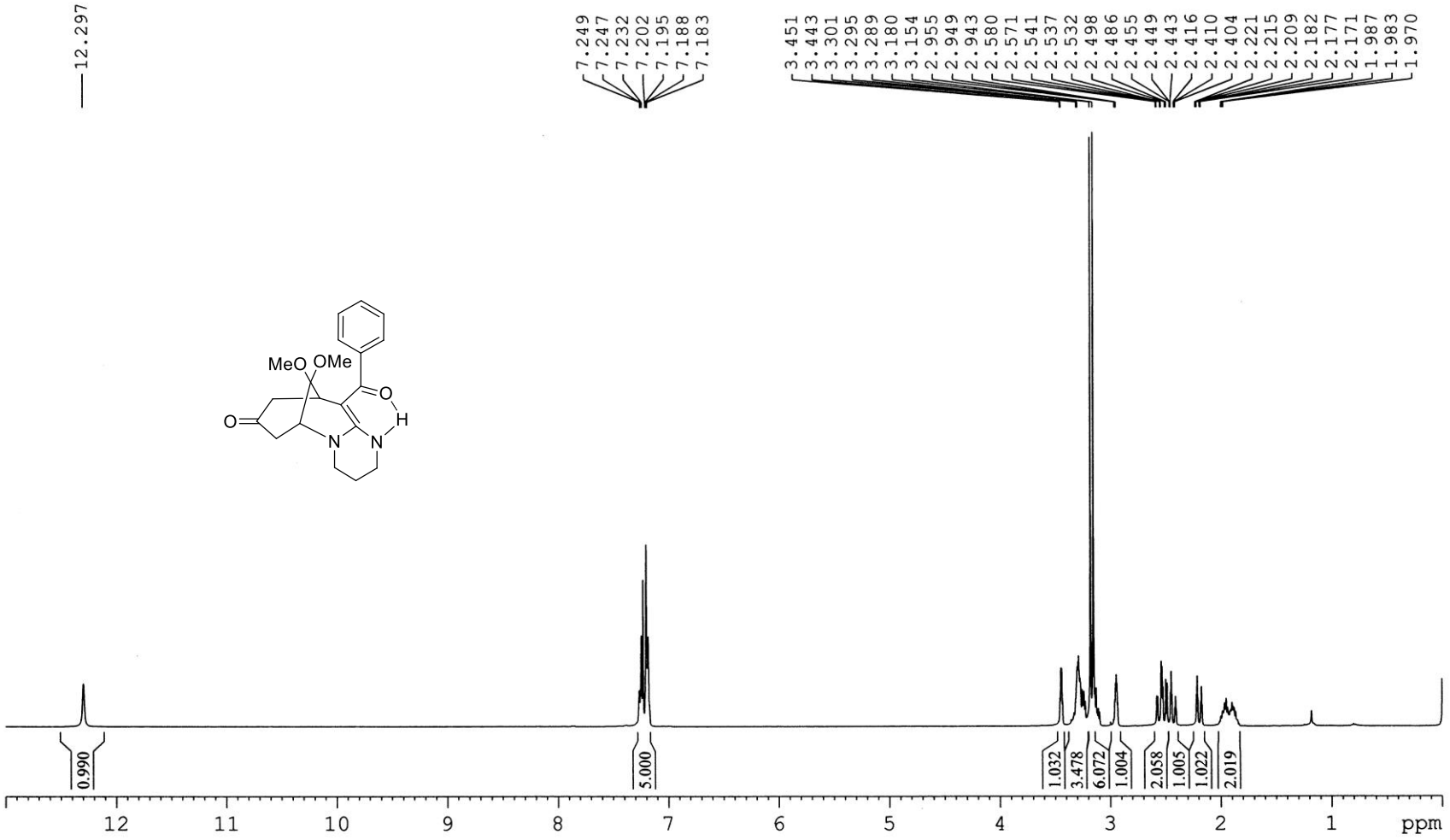


Figure 15. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3h**

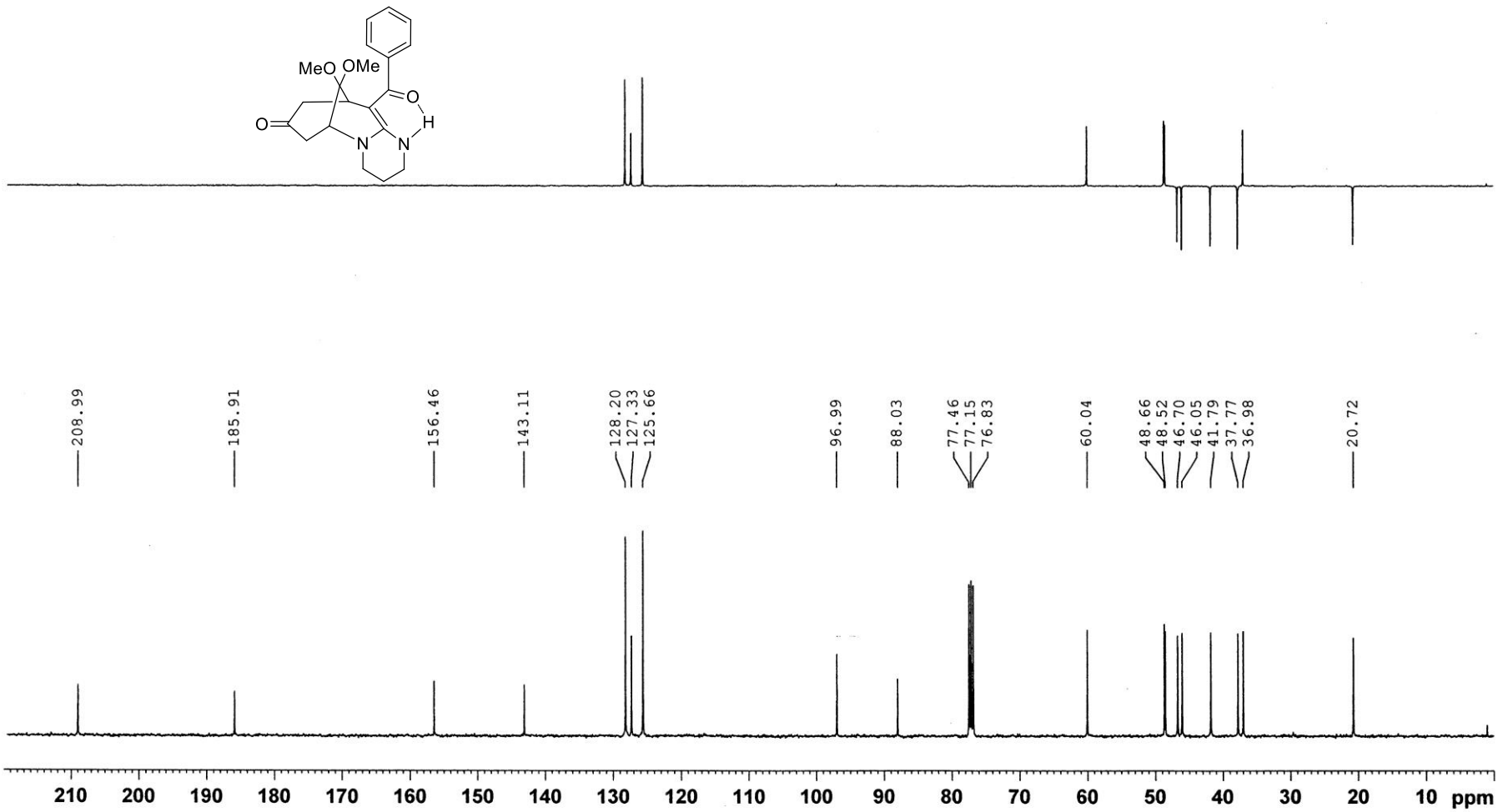


Figure 16. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3h**

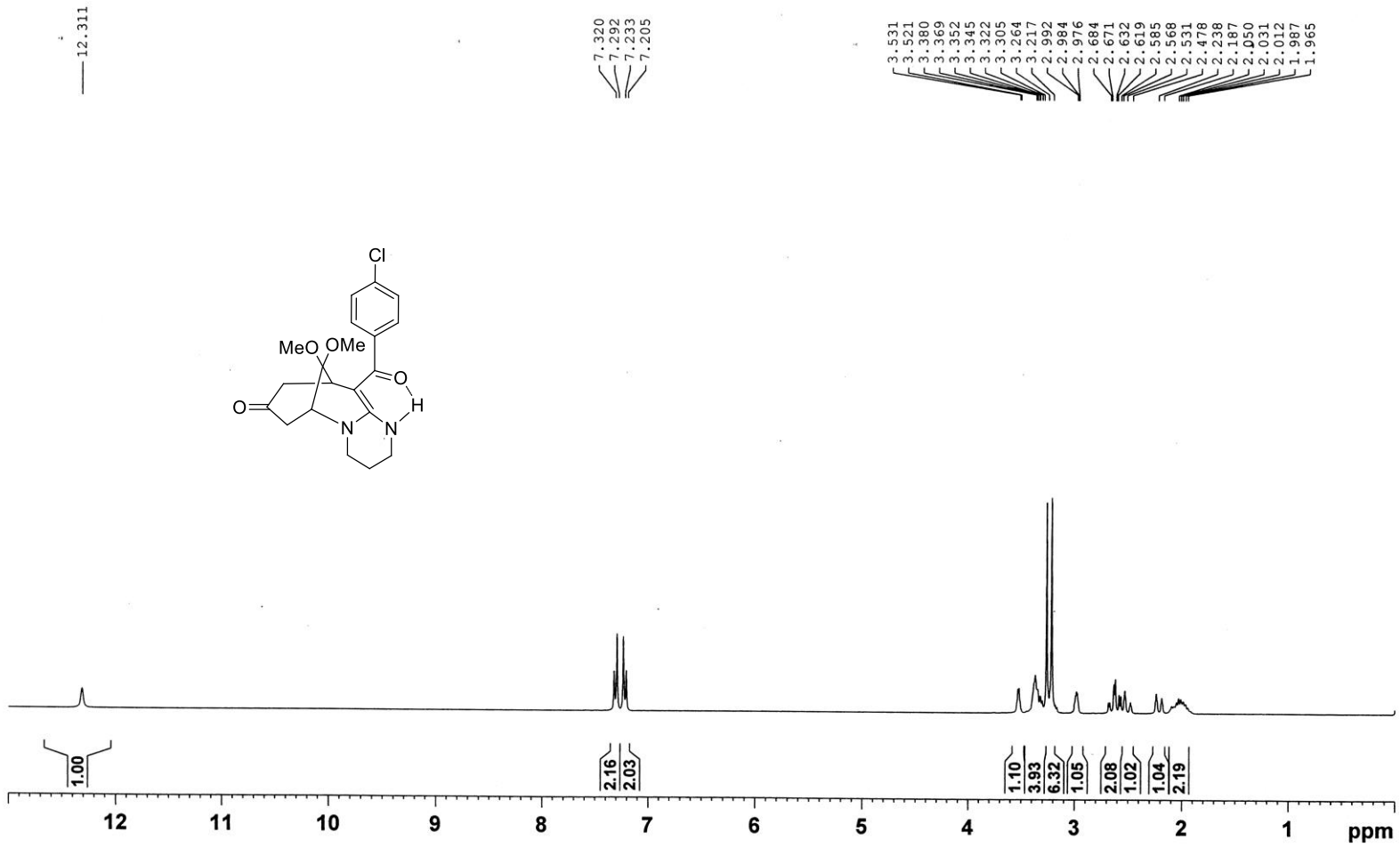


Figure 17. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3i**

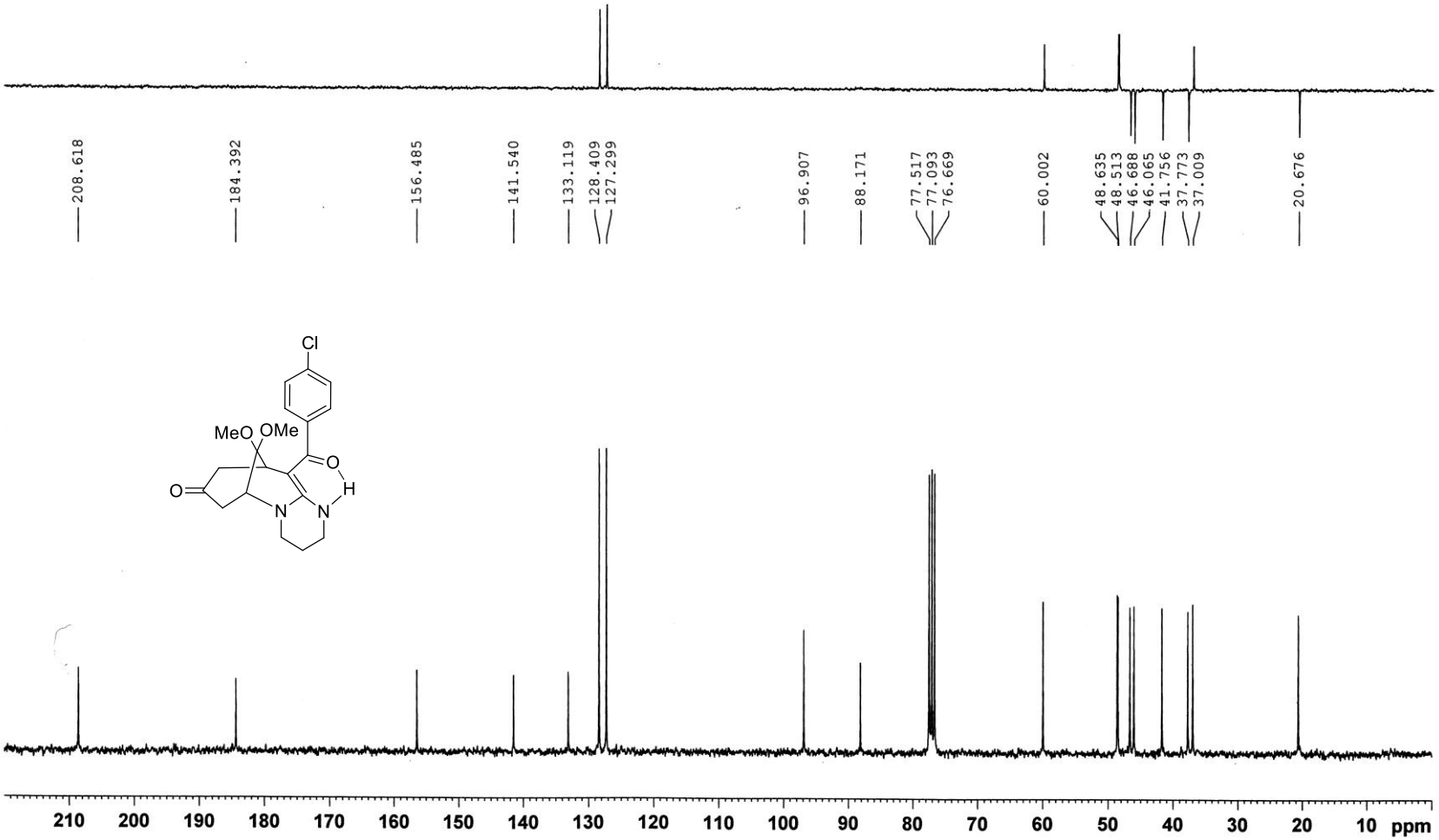


Figure 18. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3i**

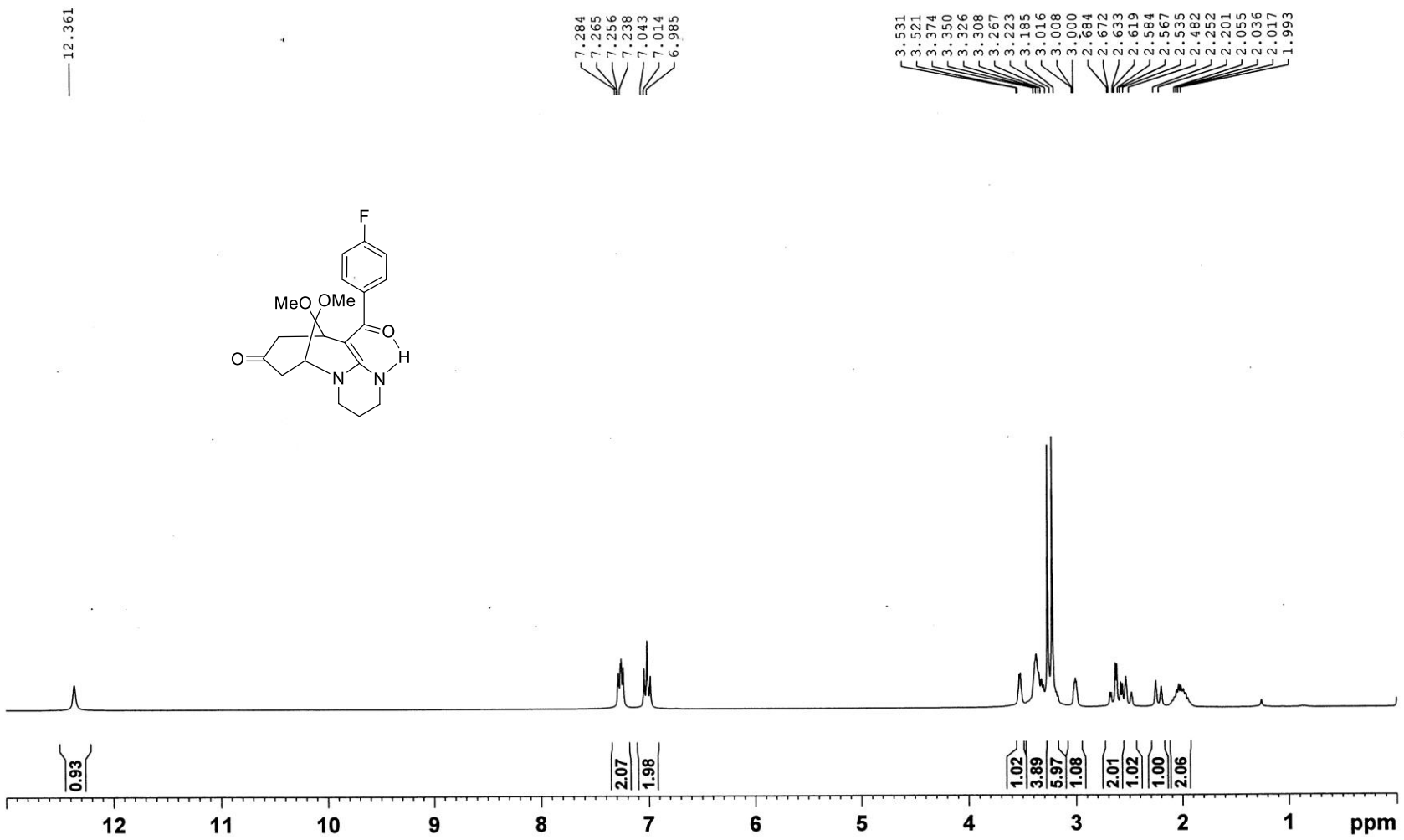


Figure 19. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3j**

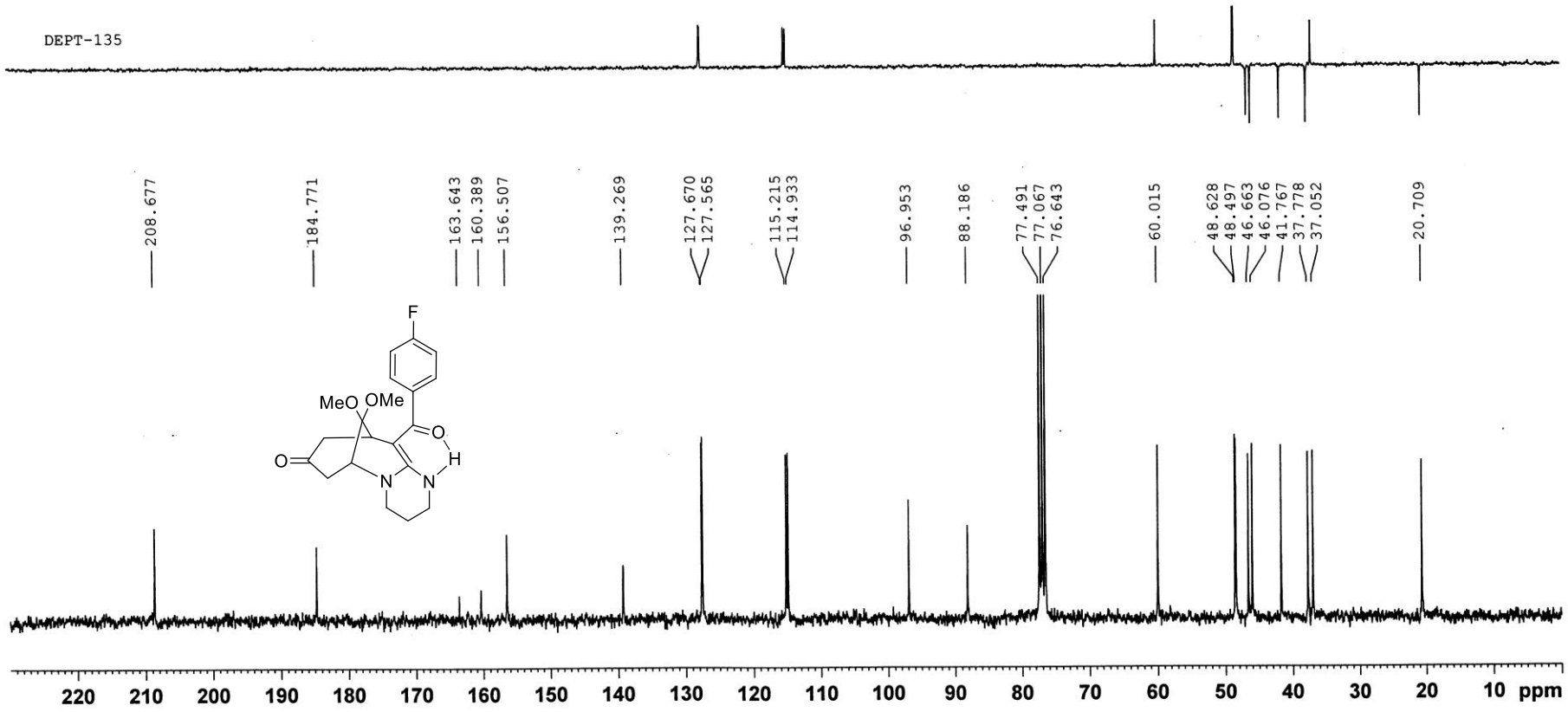


Figure 20. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3j**

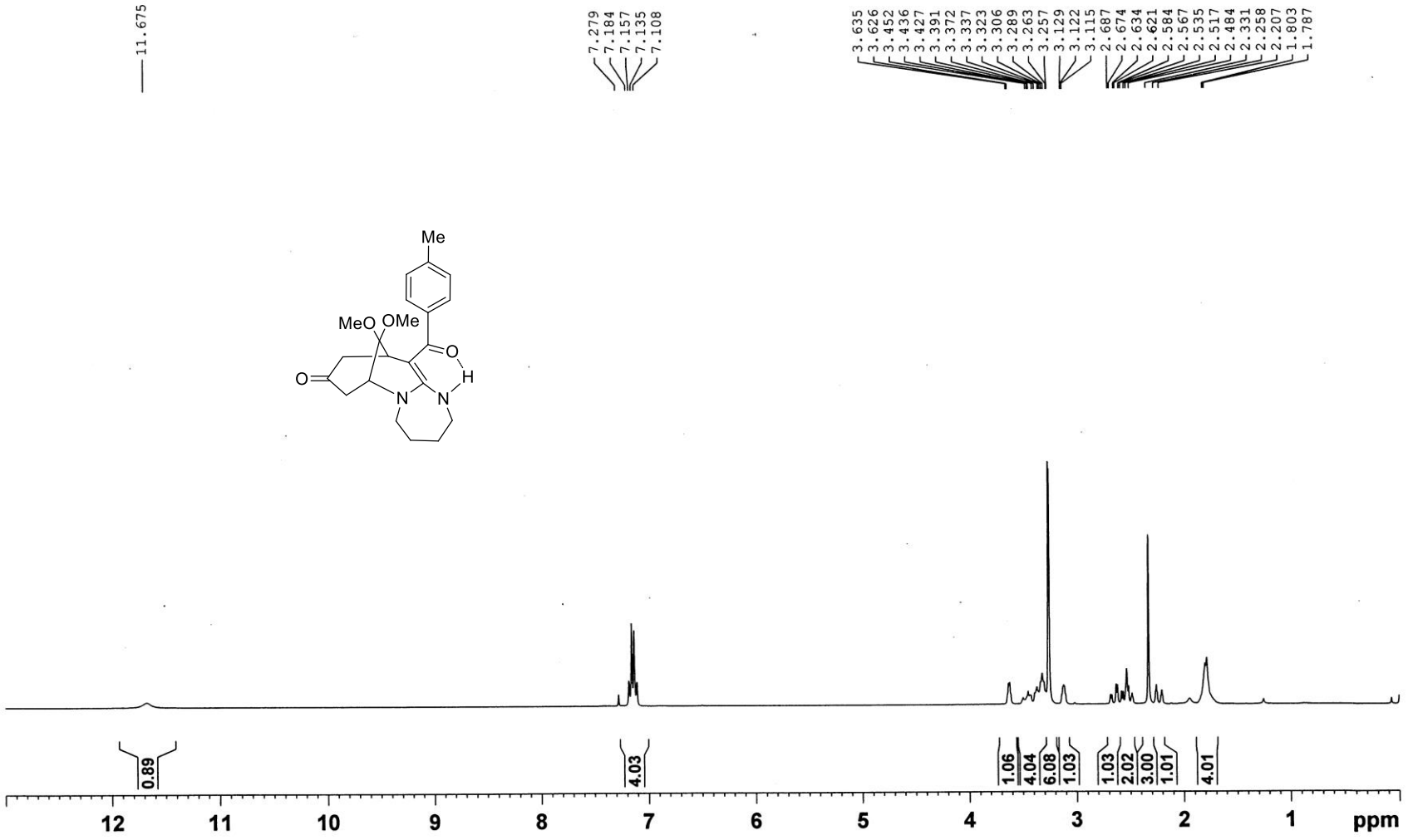


Figure 21. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3k**

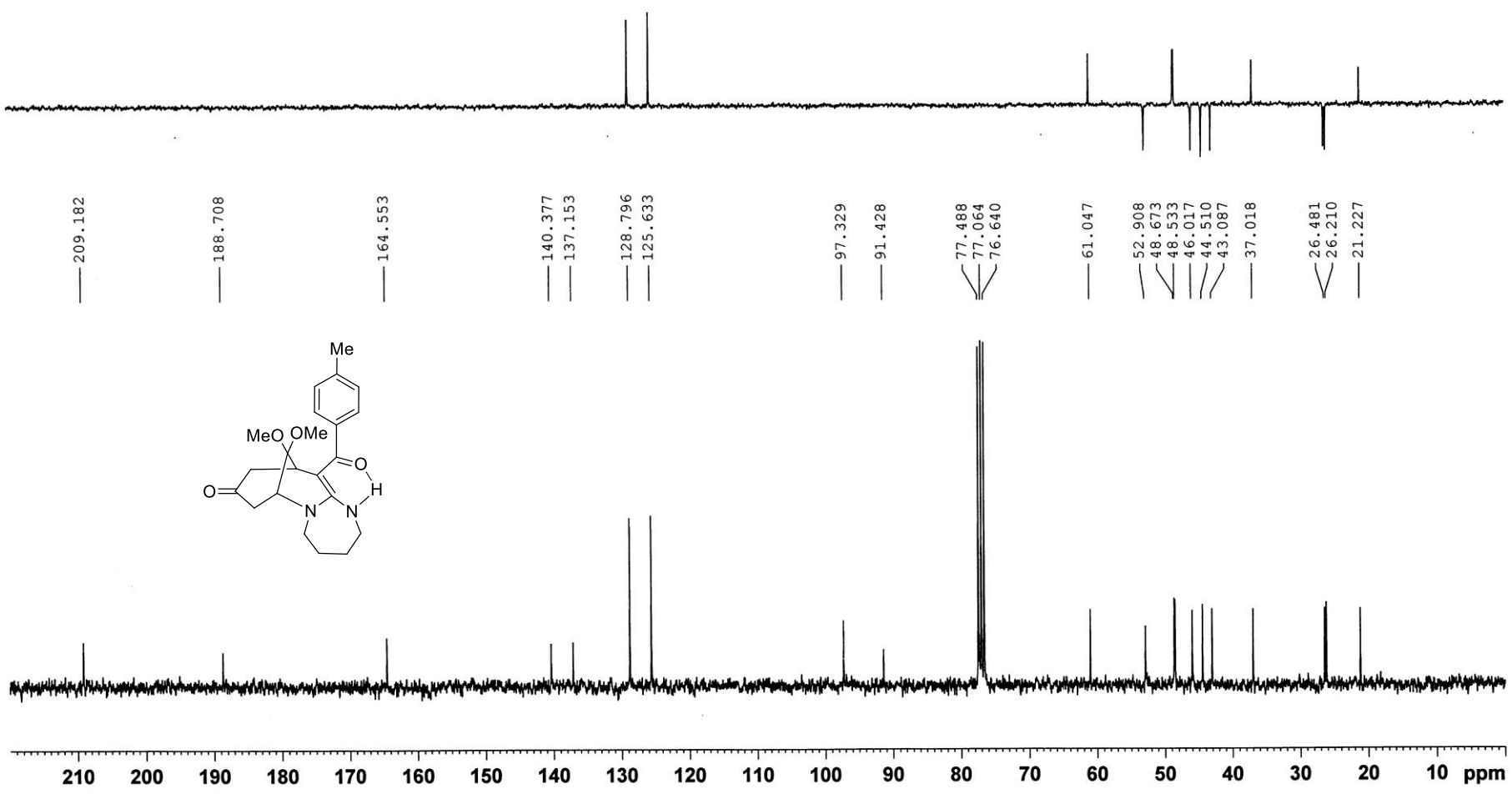


Figure 22. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3k**

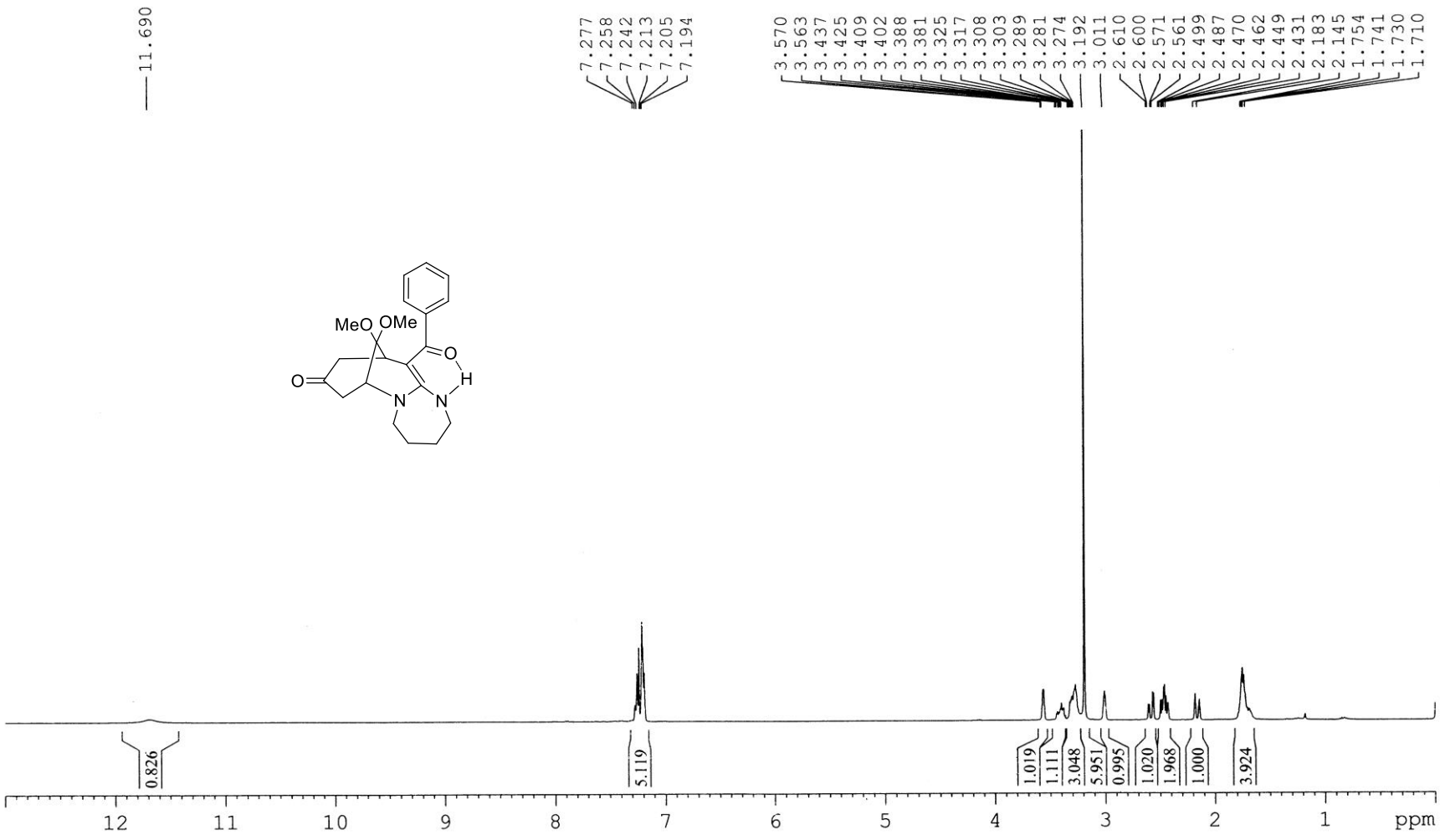


Figure 23. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3l**

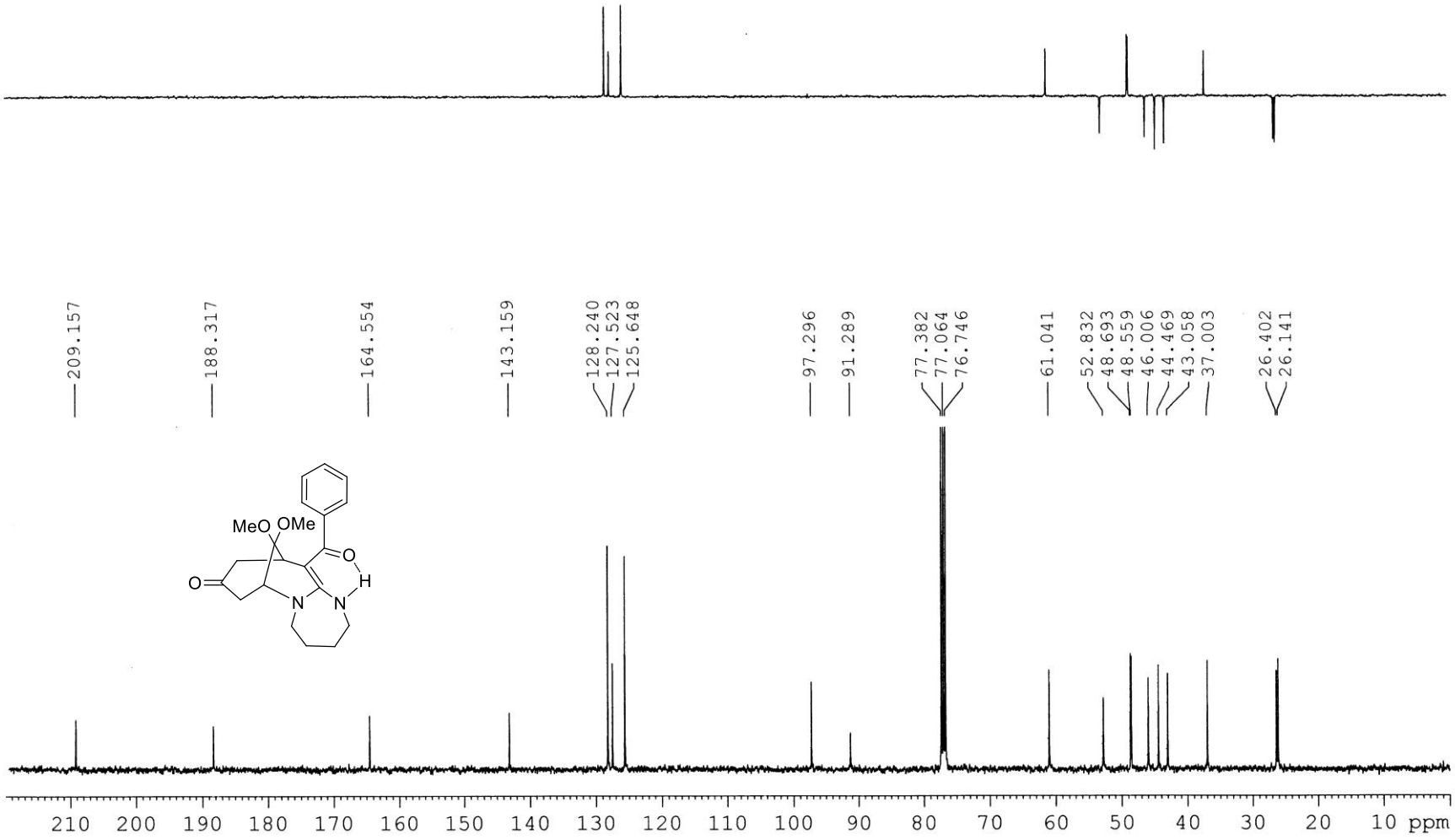


Figure 24. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3l**

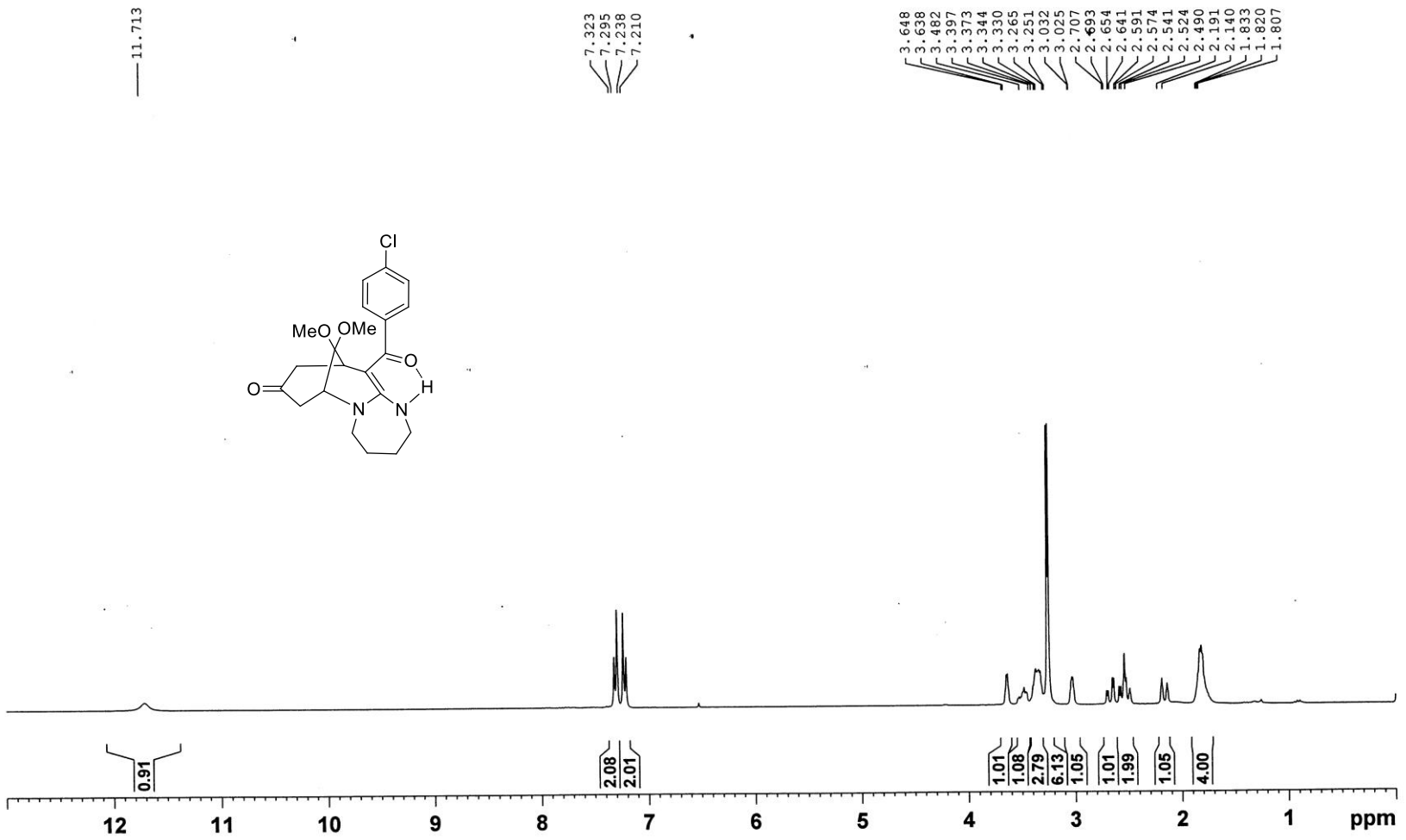


Figure 25. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3m**

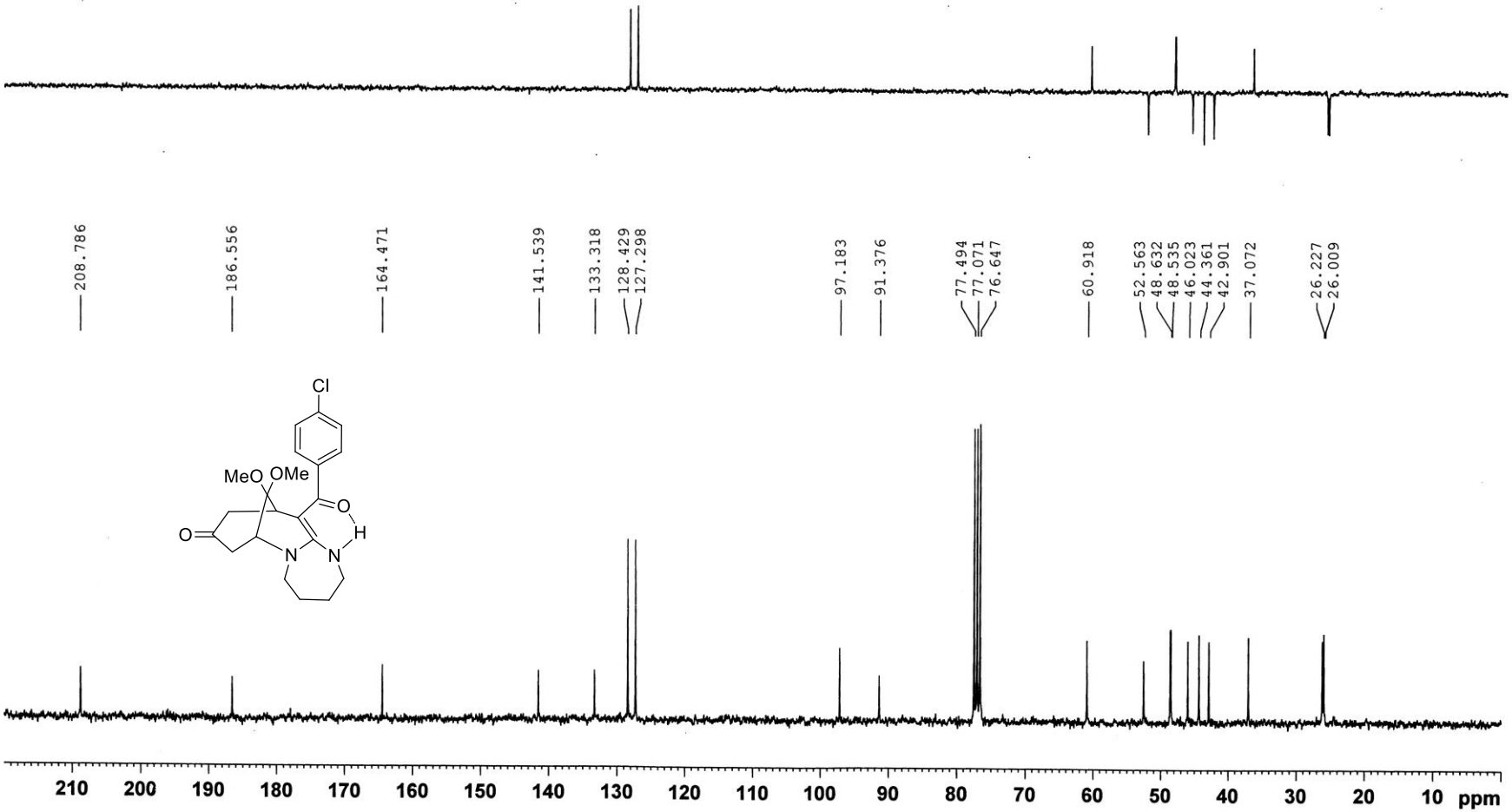


Figure 26. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3m**

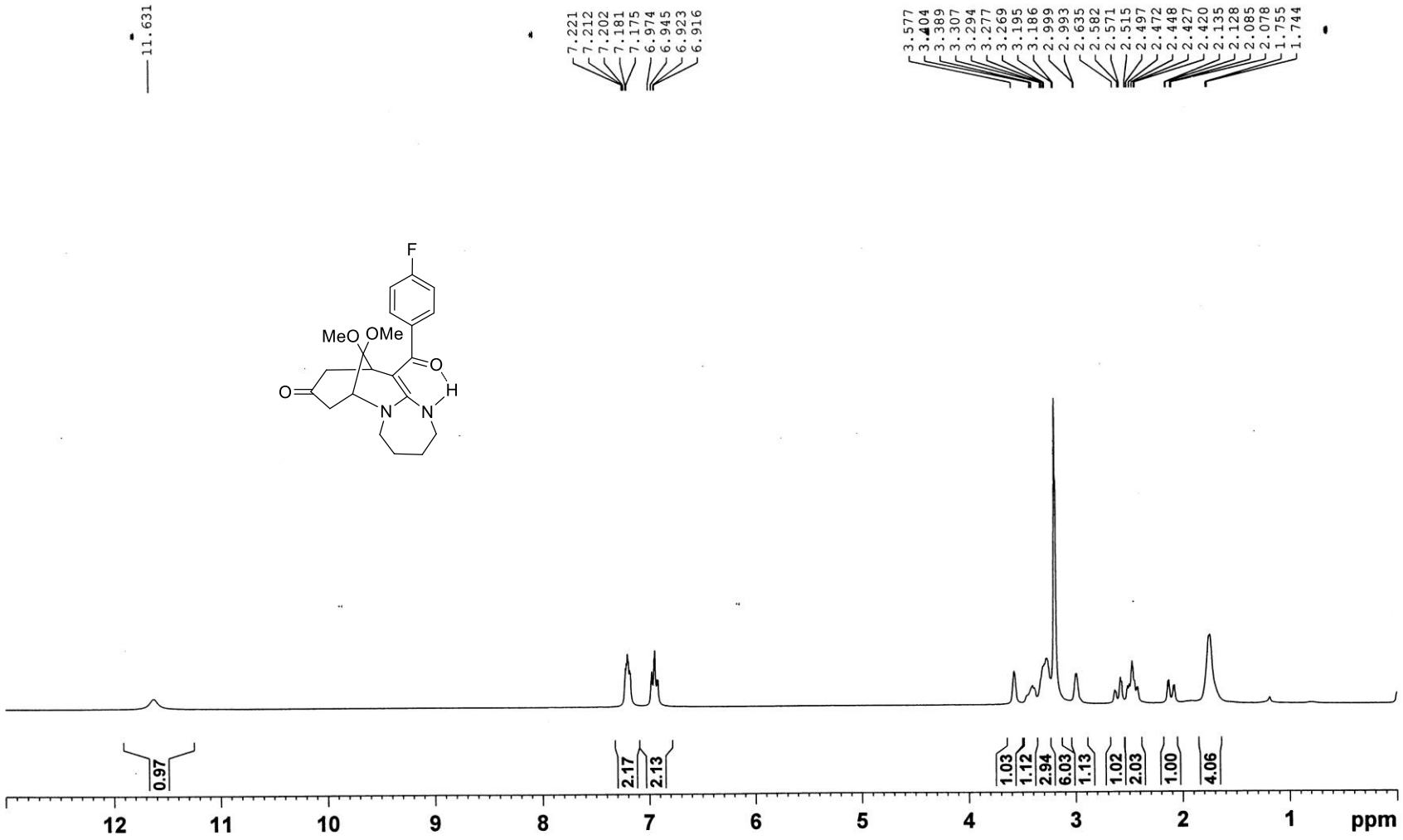


Figure 27. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3n**

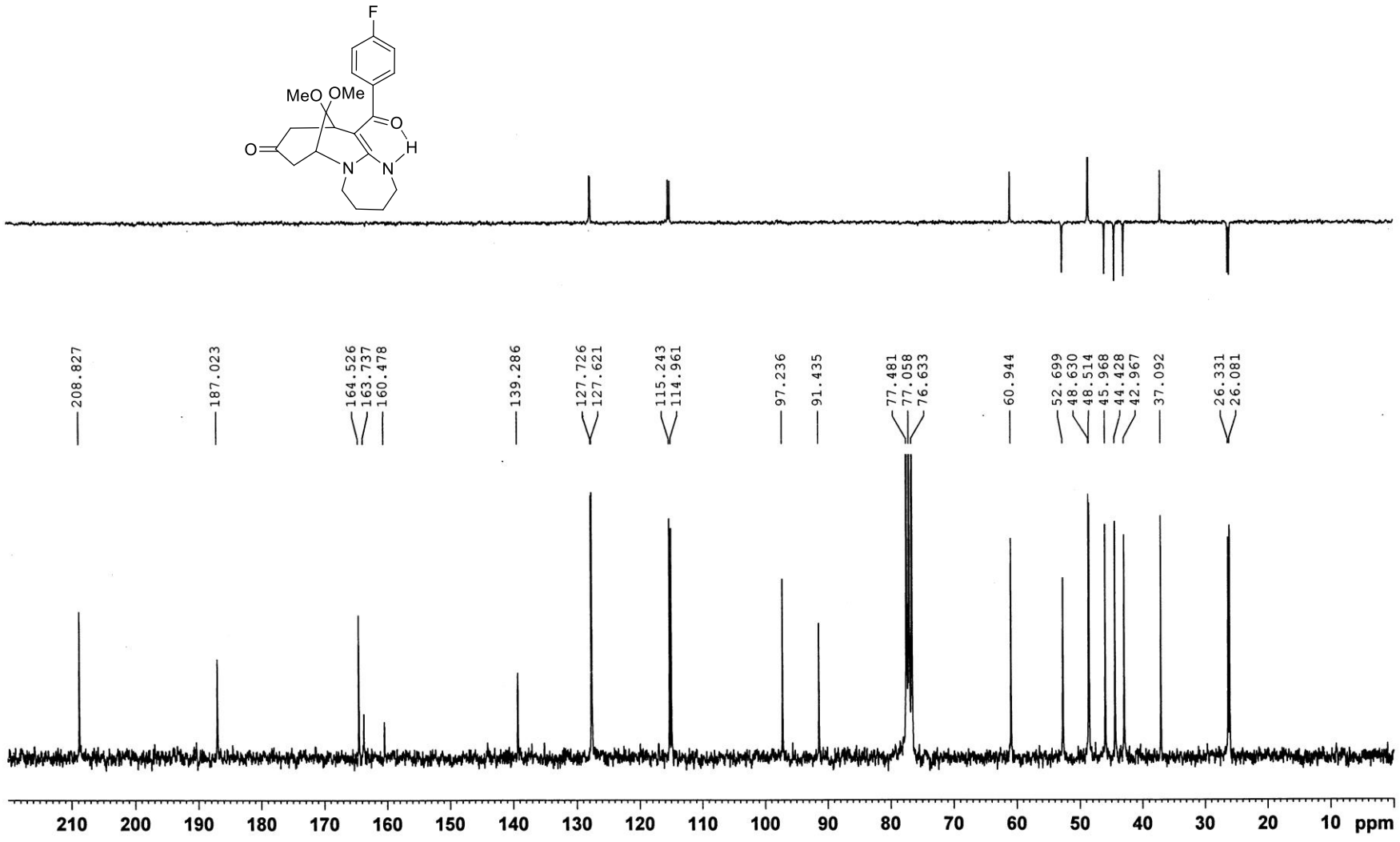


Figure 28. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3n**

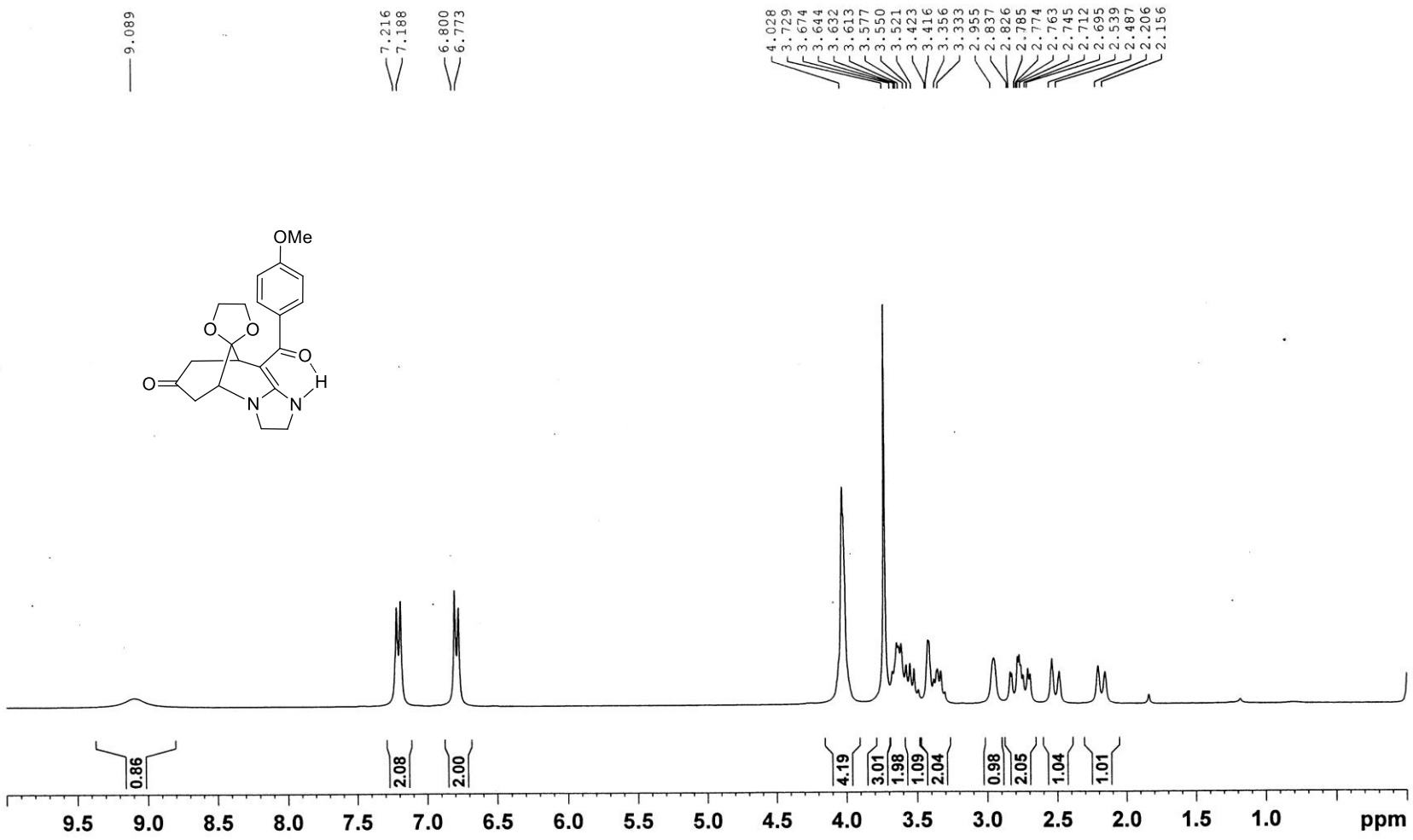


Figure 29. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3o**

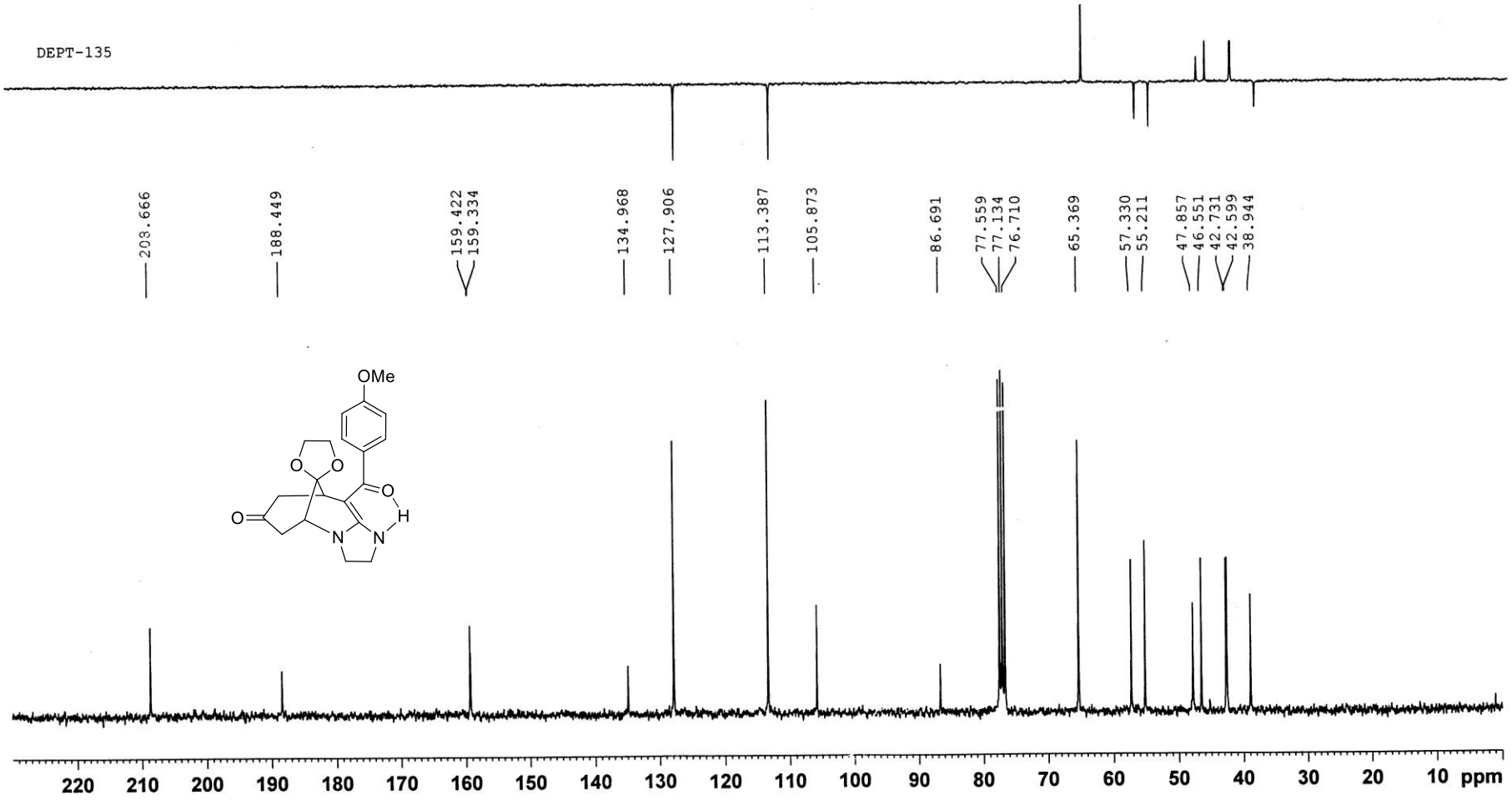


Figure 30. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3o**

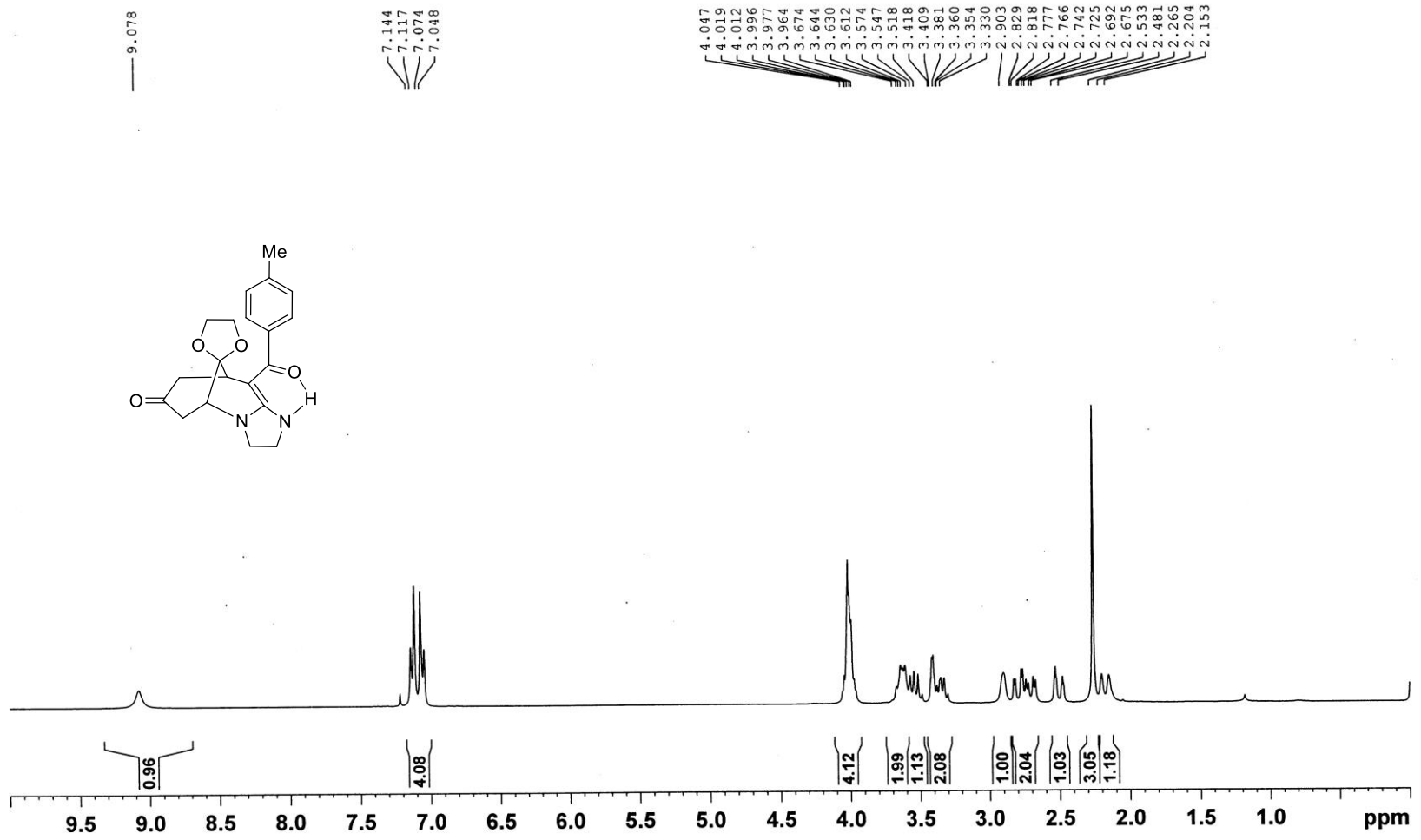


Figure 31. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3p**

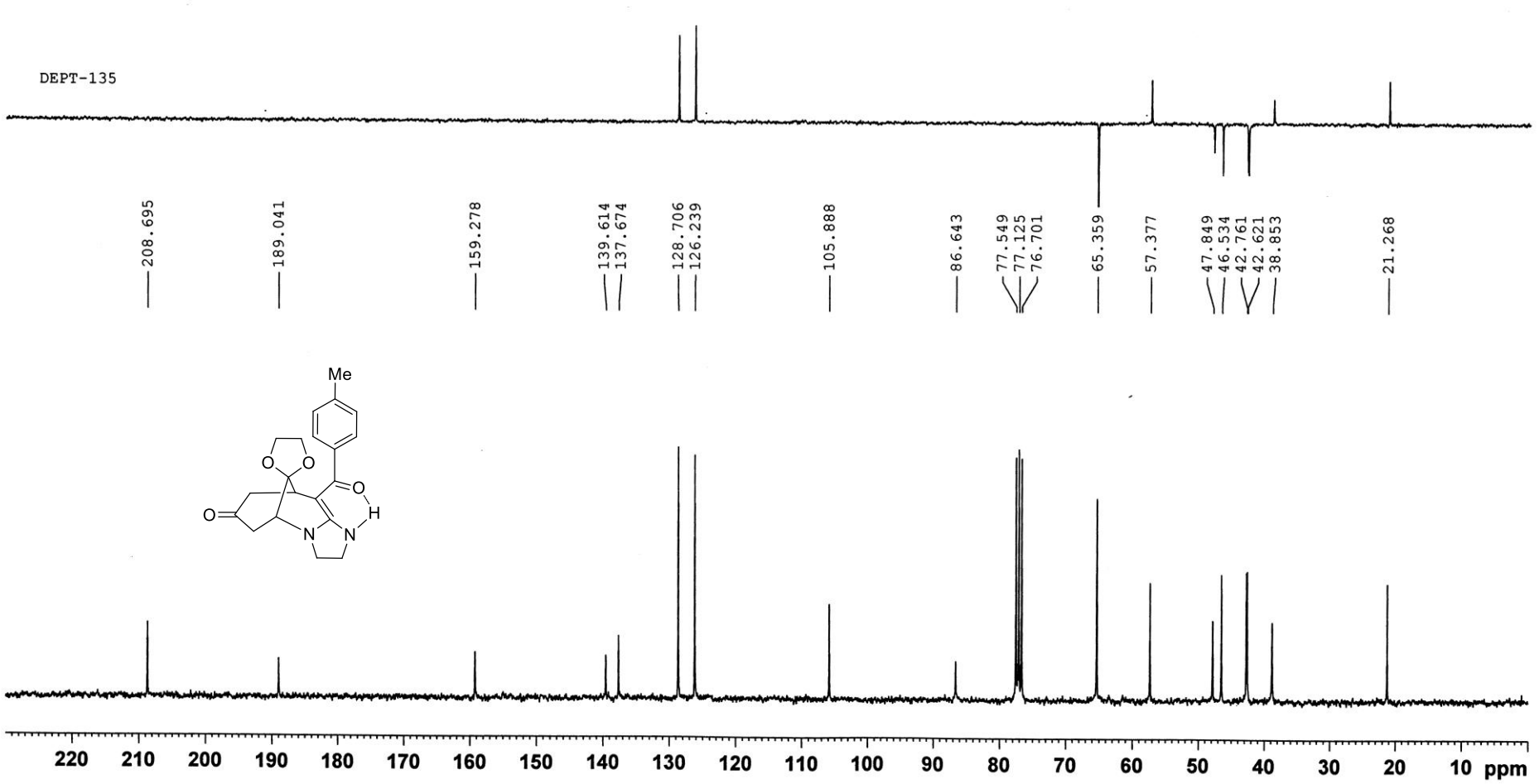


Figure 32. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3p**

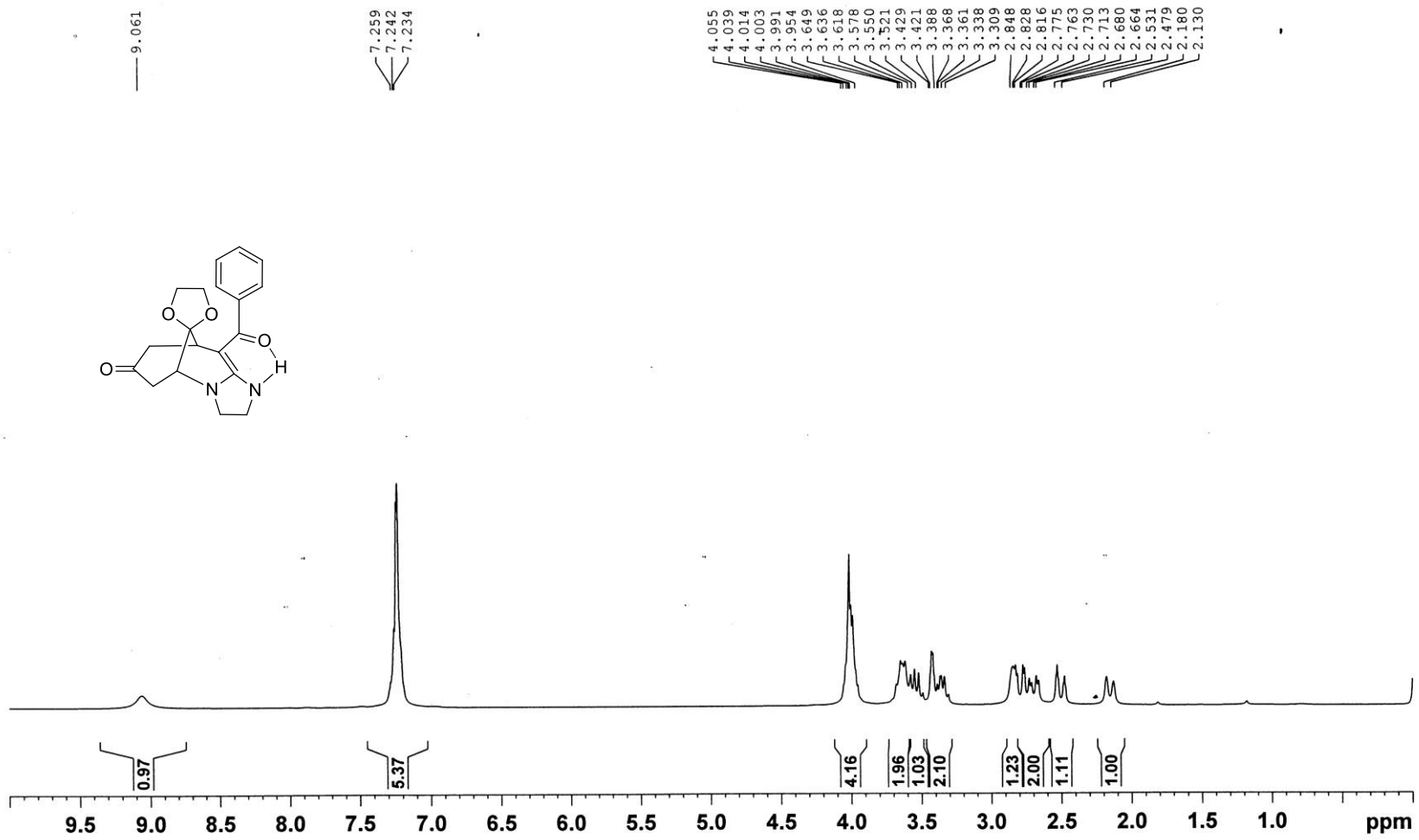


Figure 33. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3q**

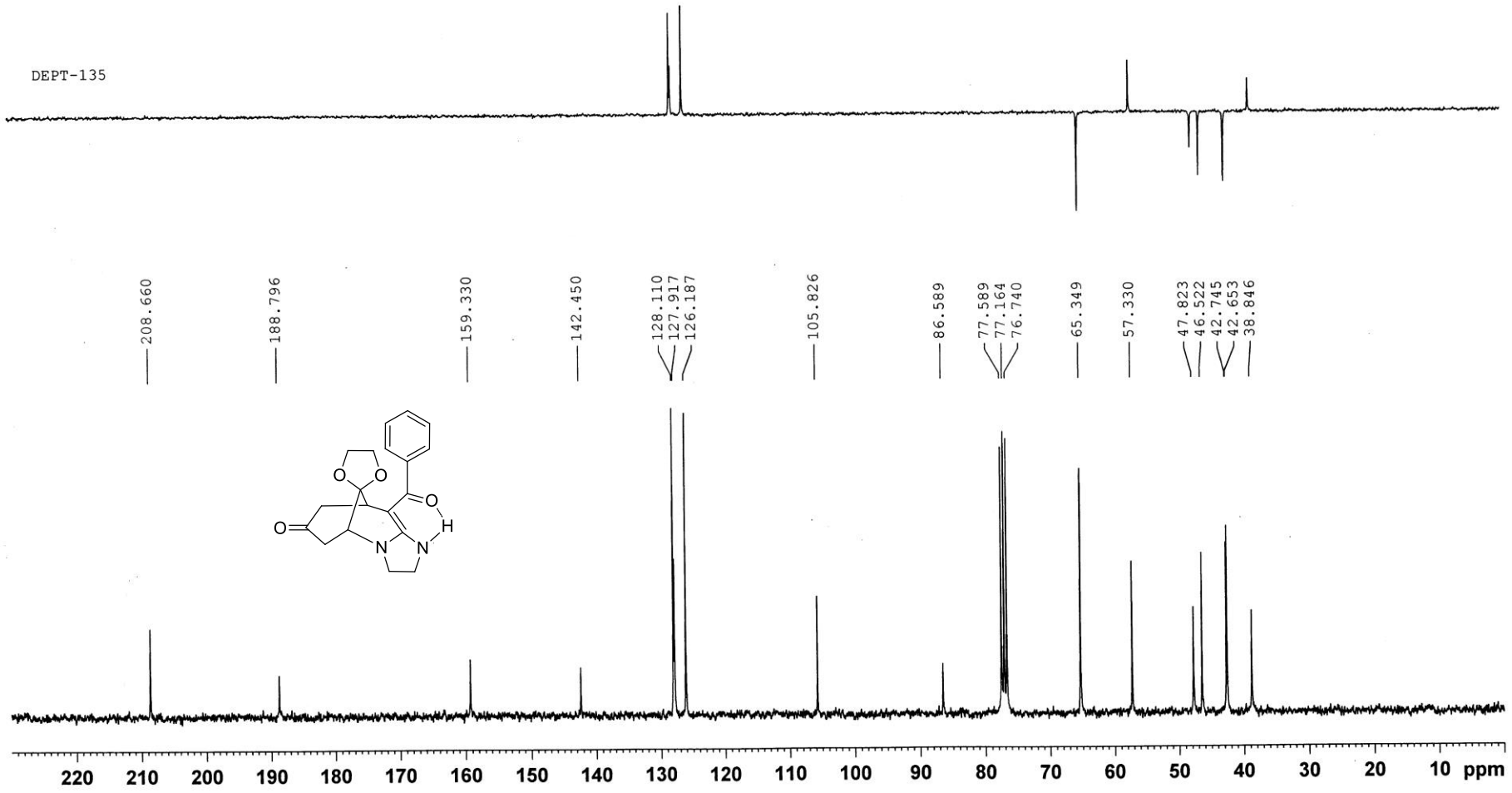


Figure 34. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3q**

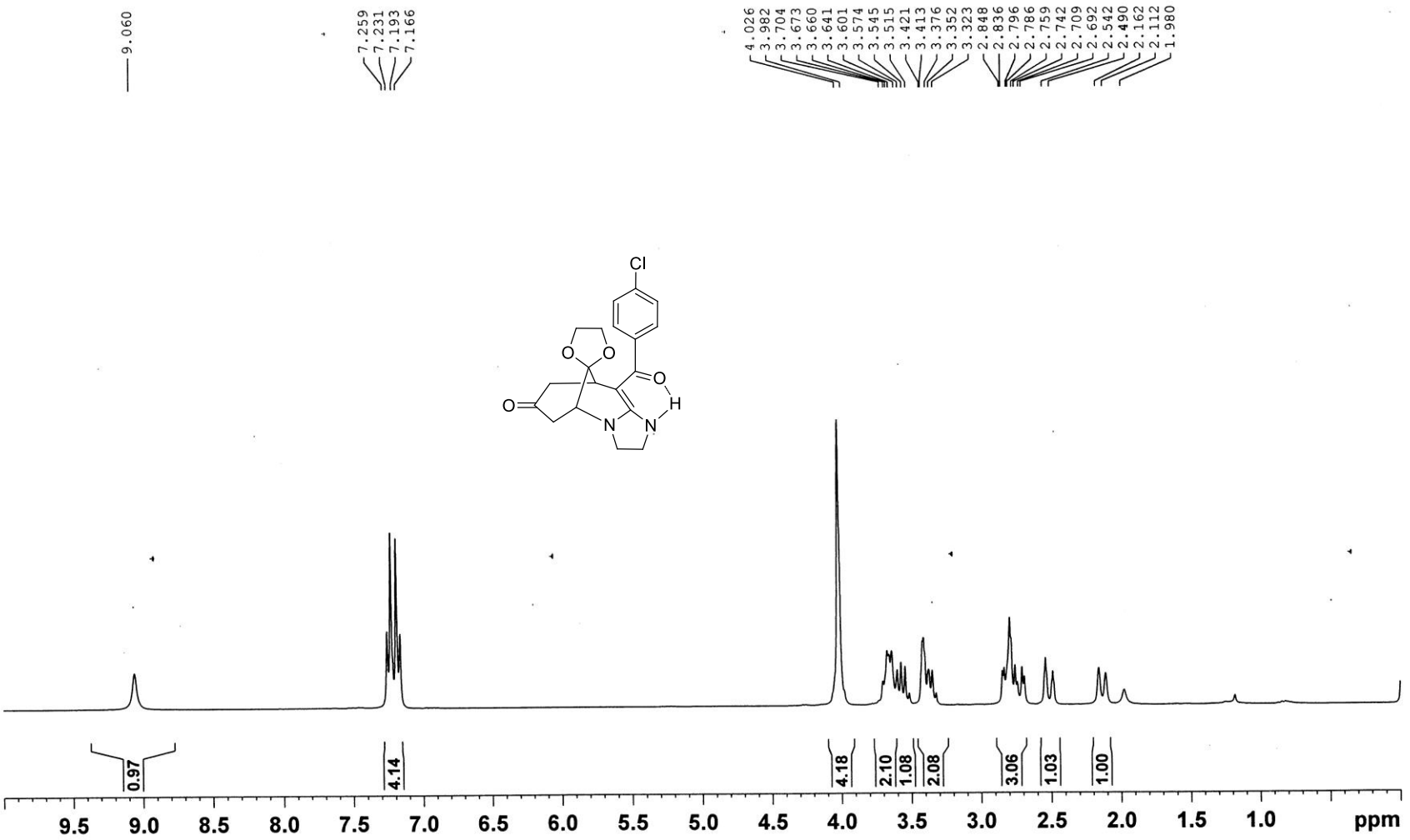


Figure 35. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3r**

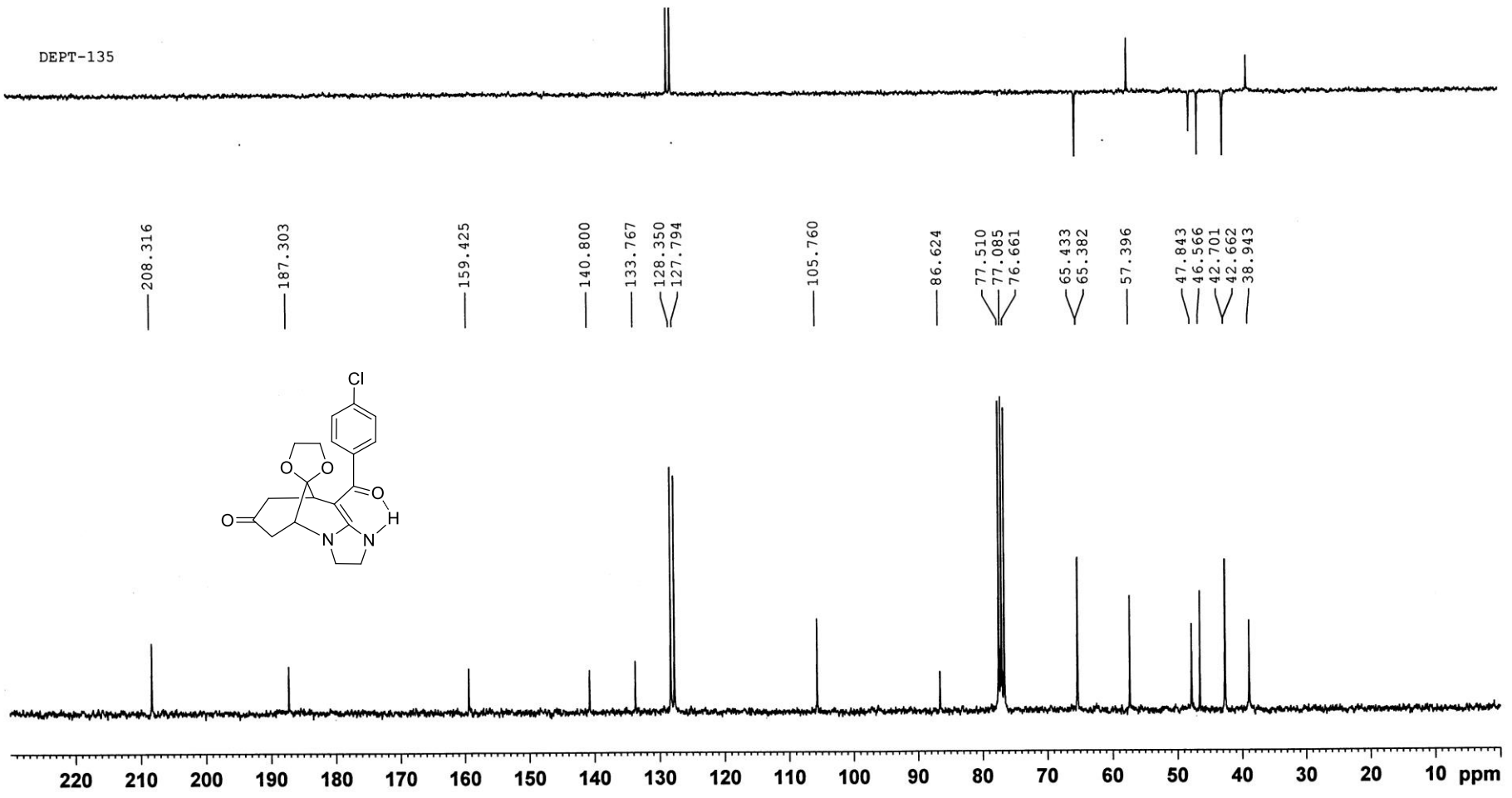


Figure 36. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3r**

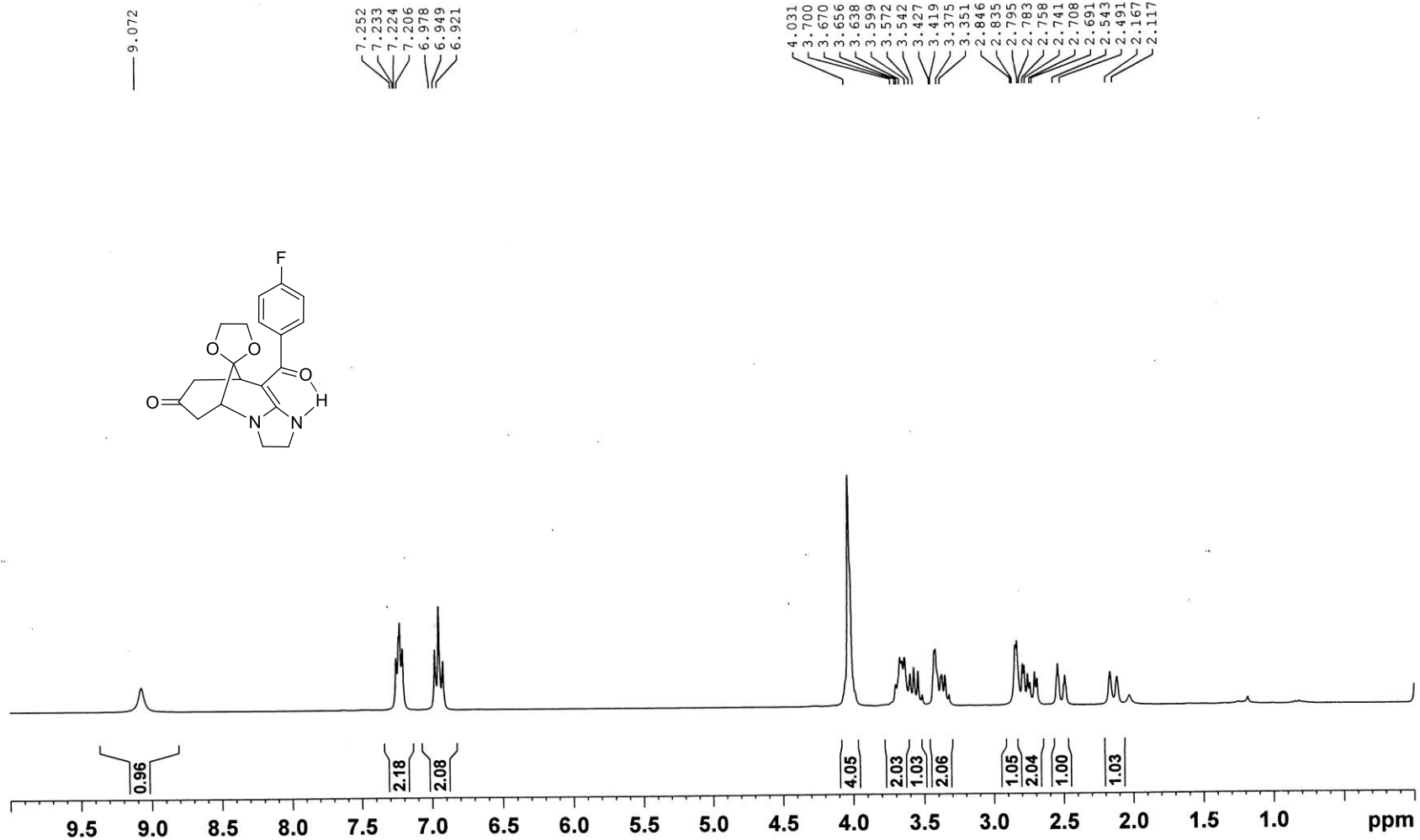


Figure 37. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3s**

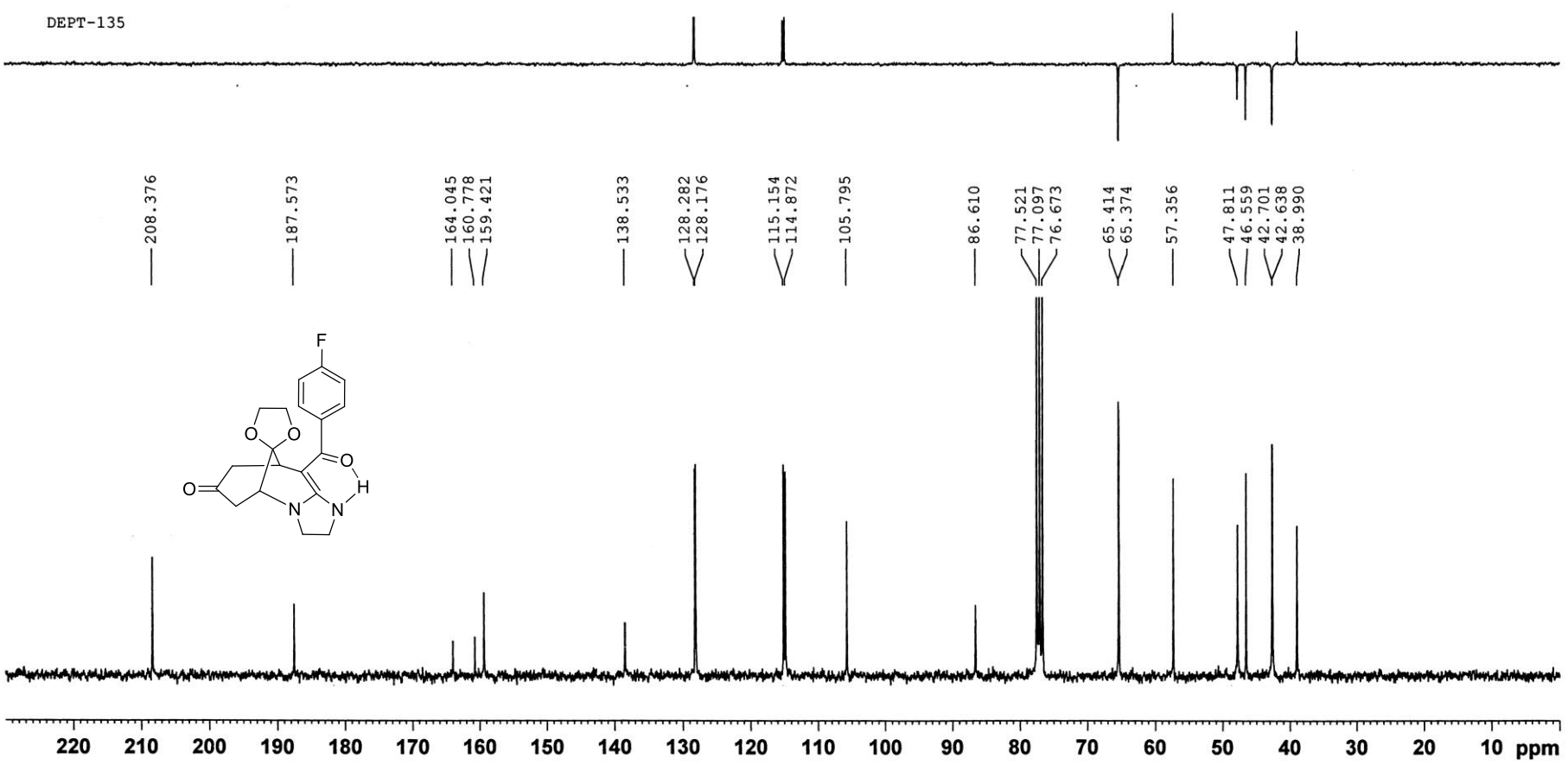


Figure 38. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3s**

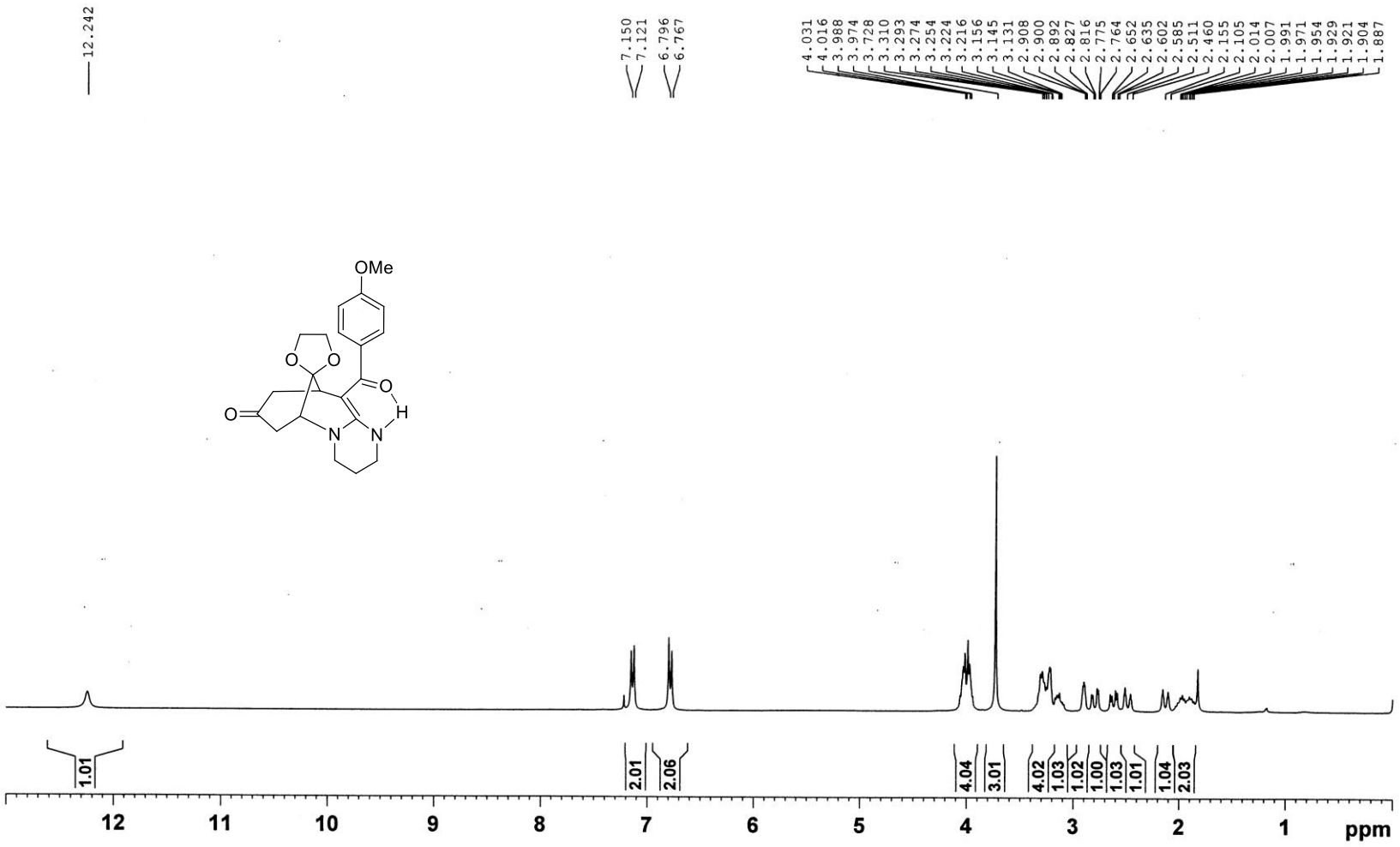


Figure 39. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3t**

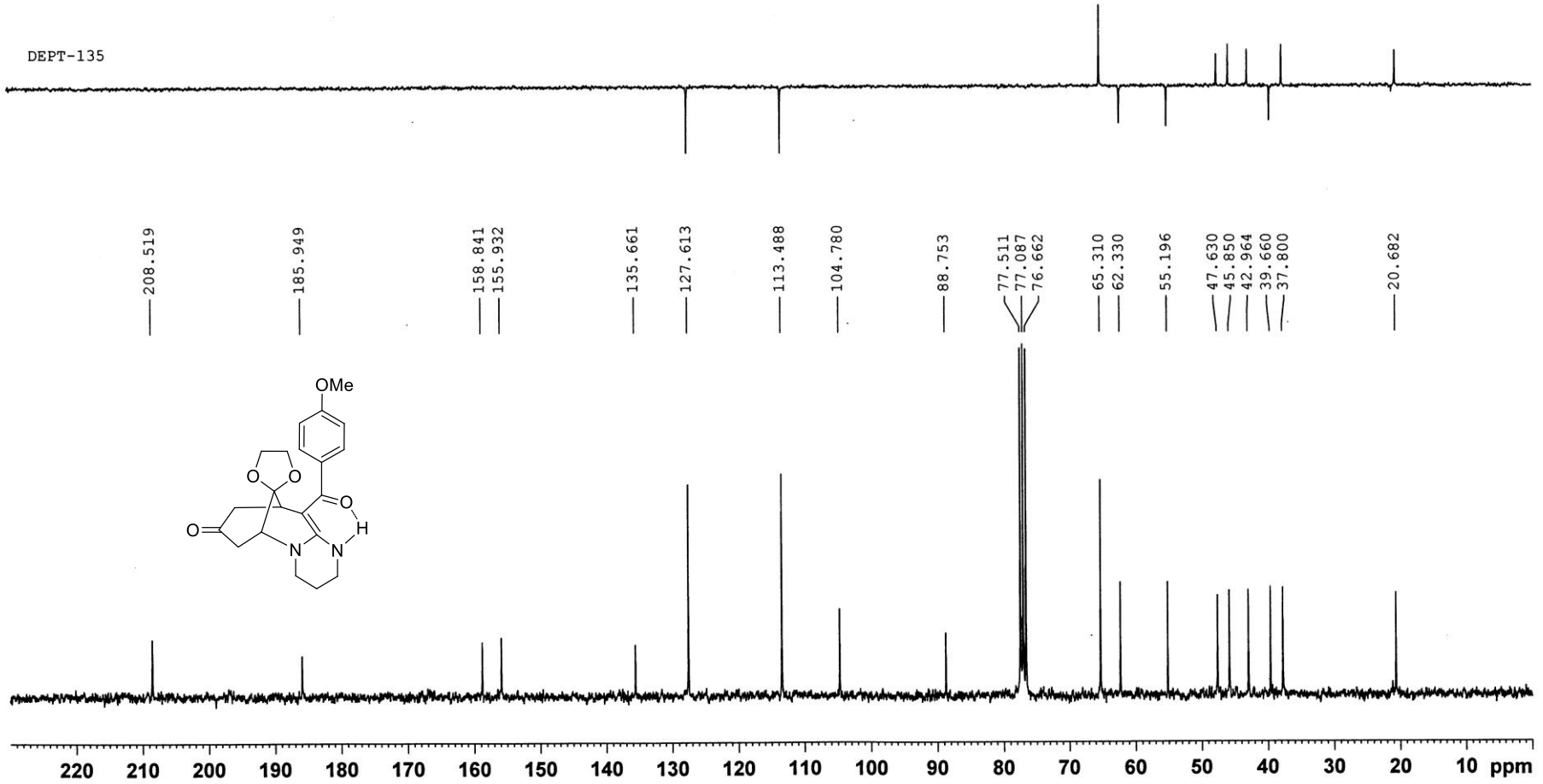


Figure 40. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3t**

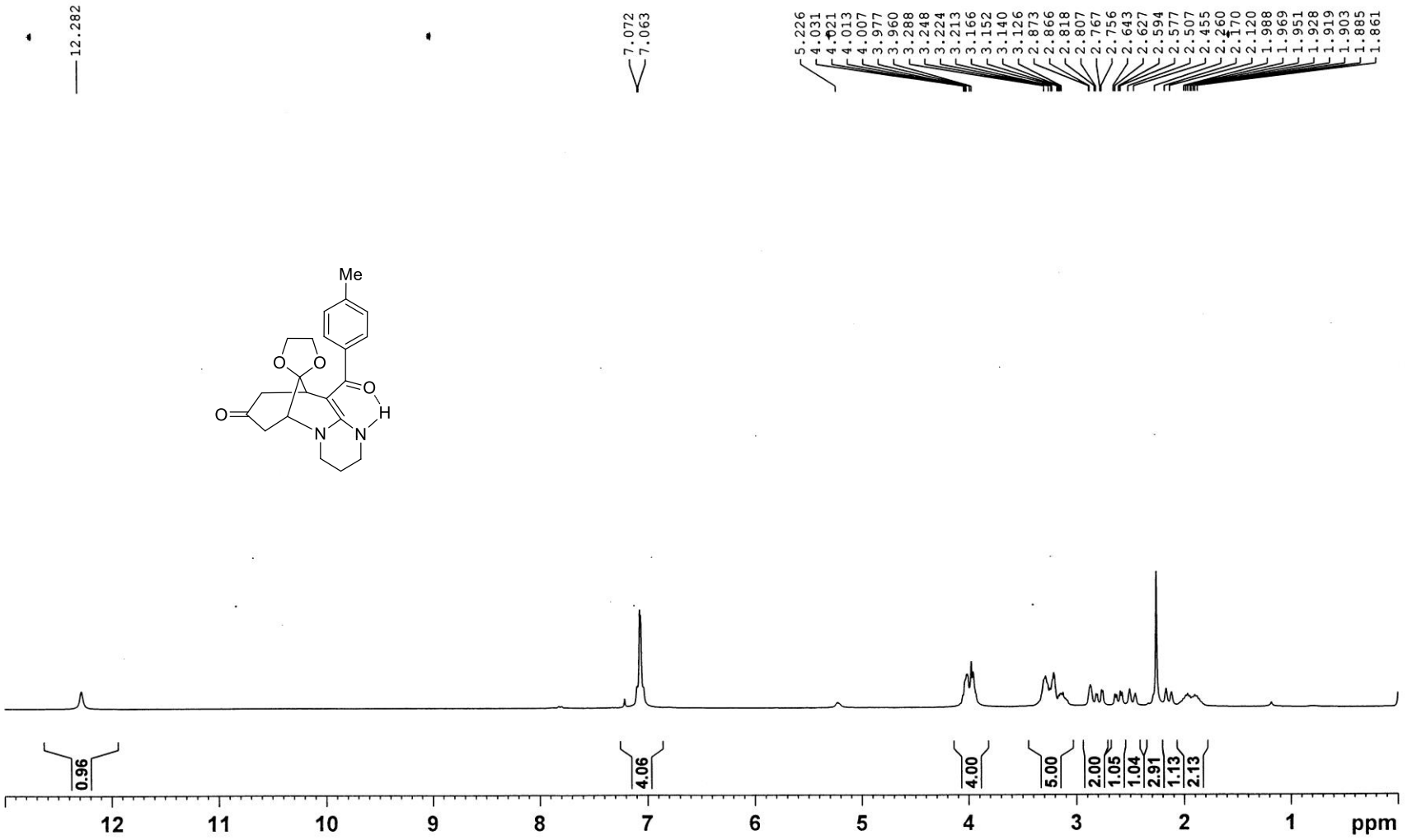


Figure 41. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3u**

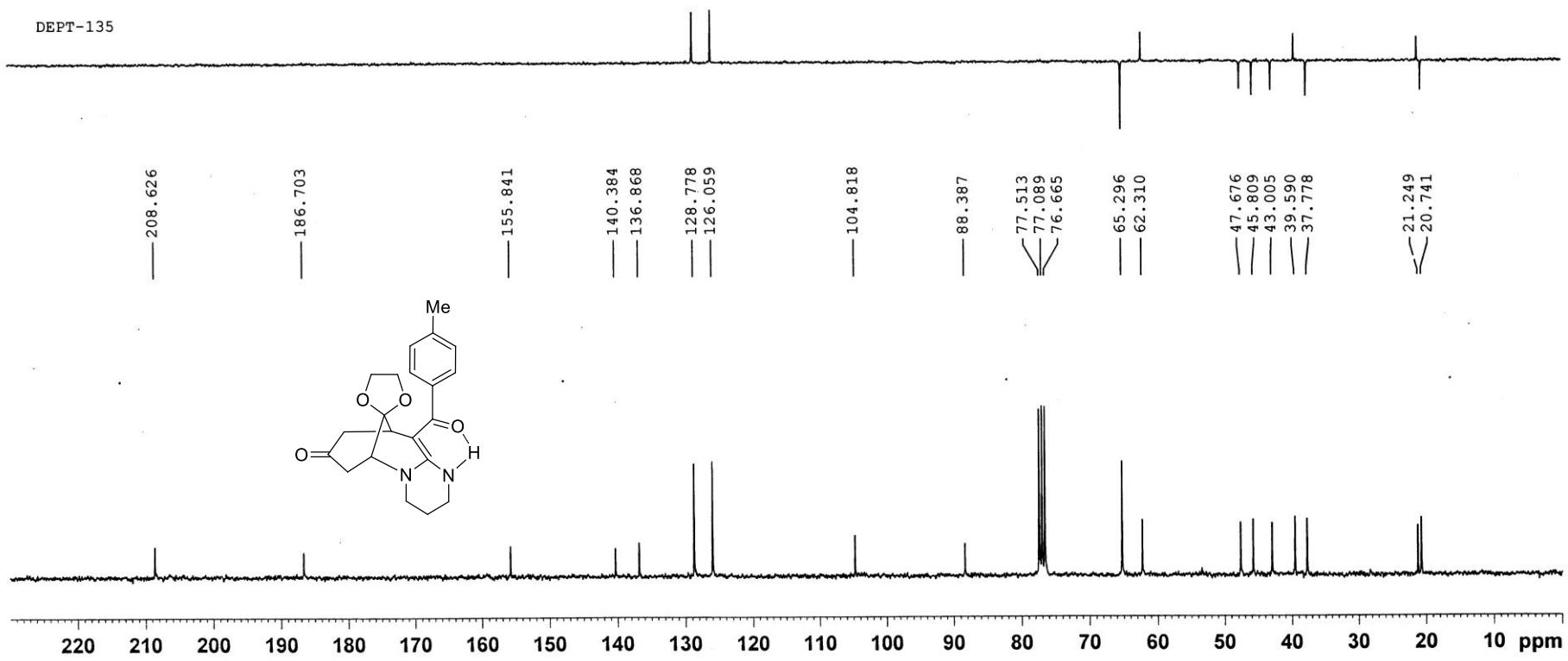


Figure 42. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3u**

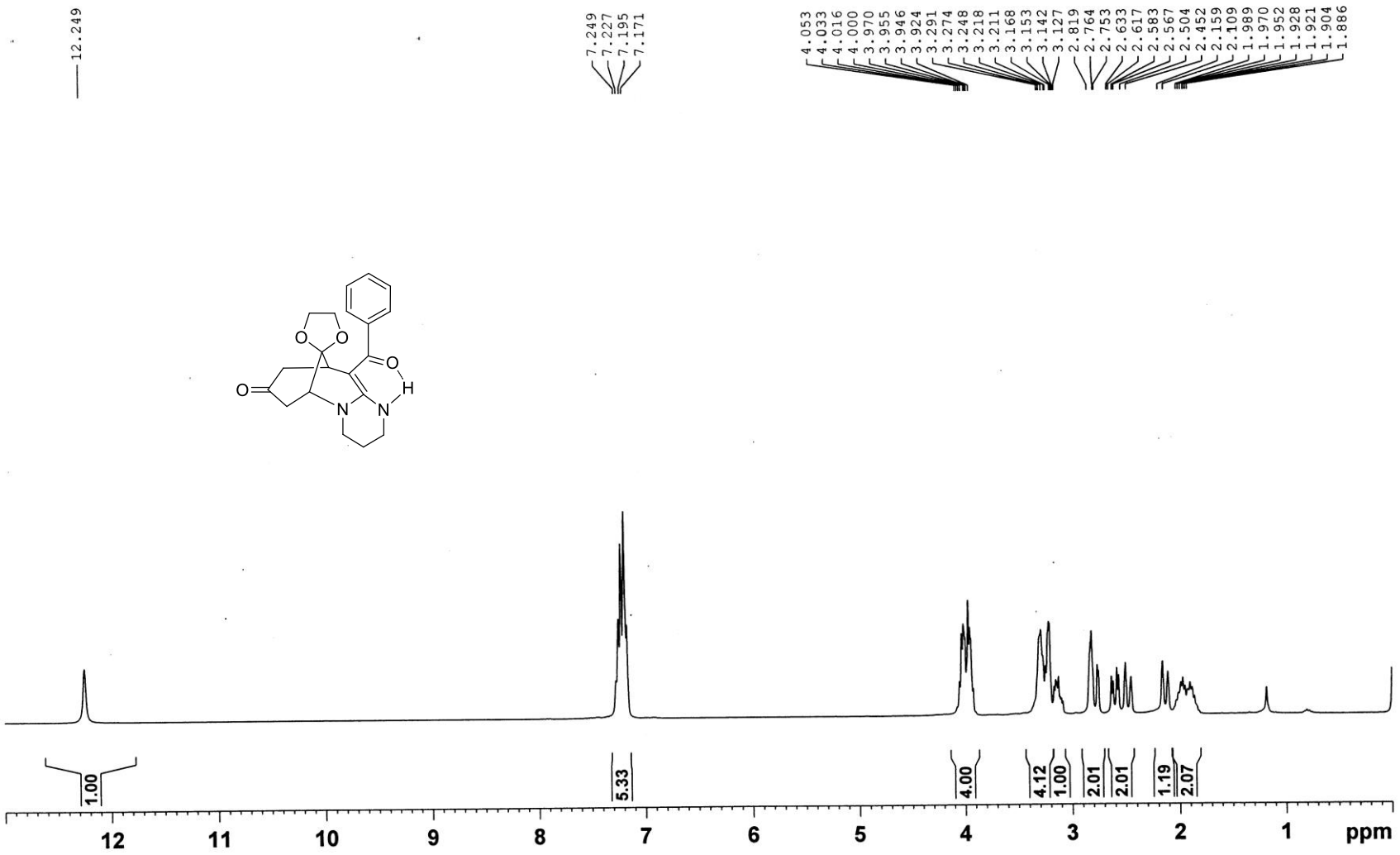


Figure 43. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3v**

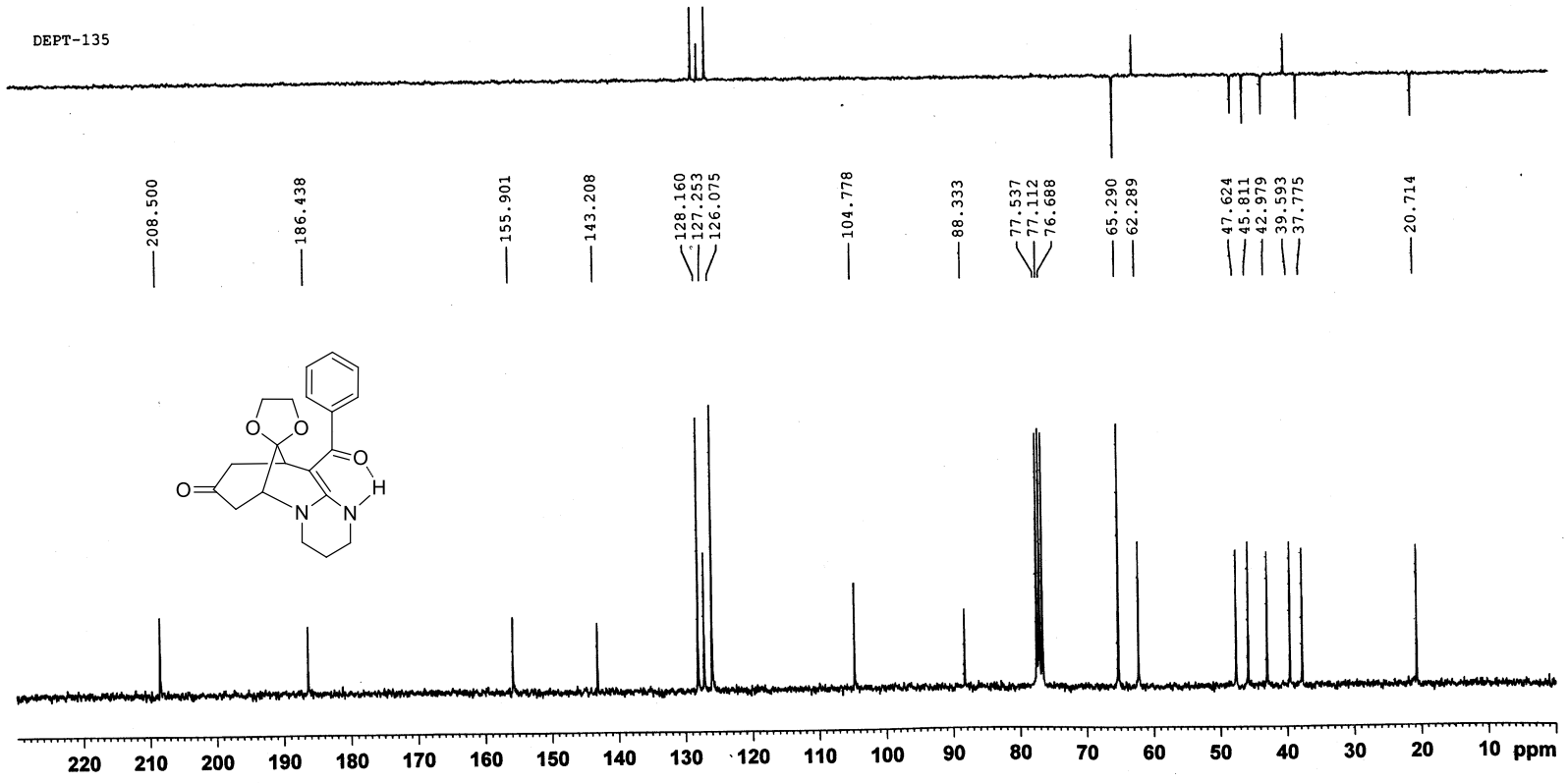


Figure 44. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3v**

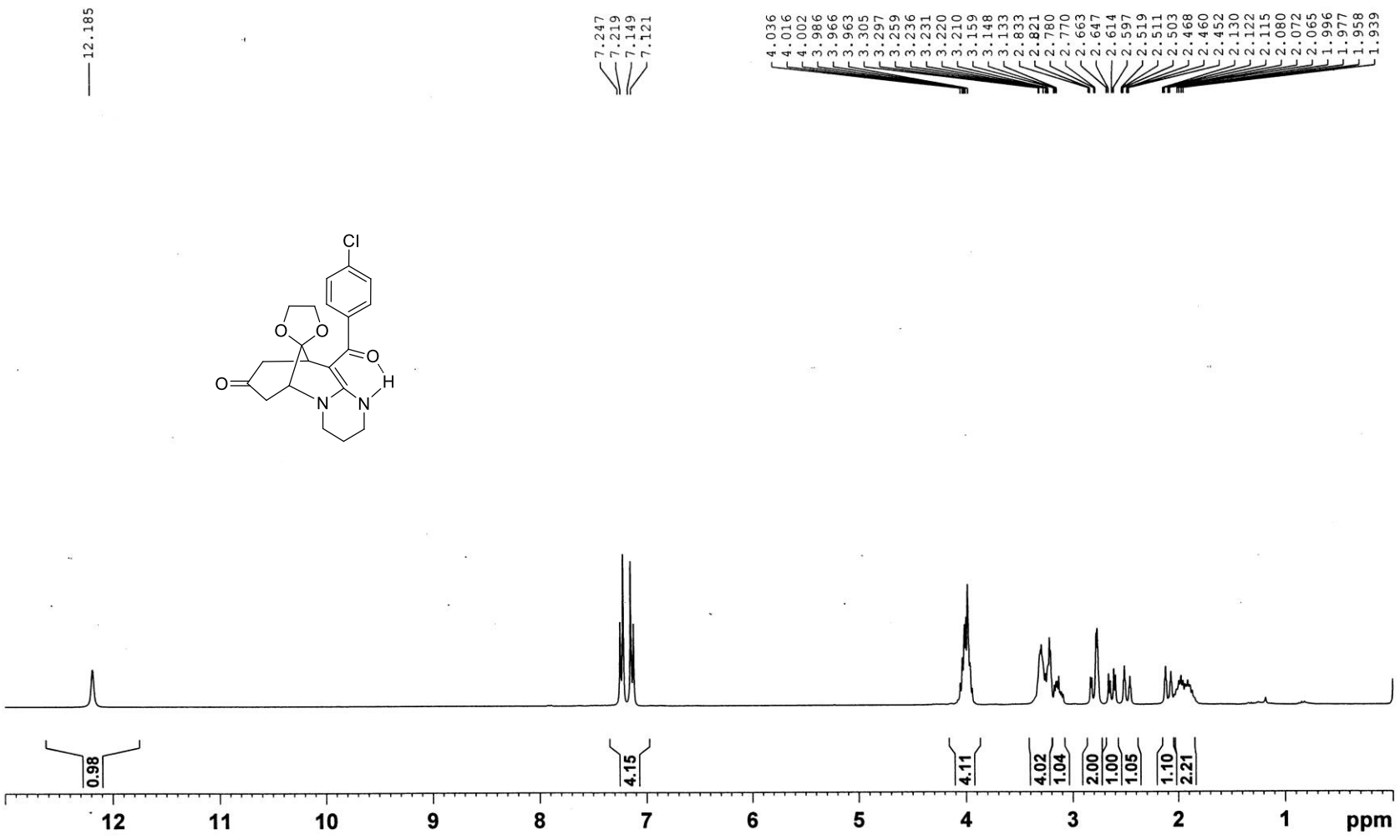


Figure 45. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3w**

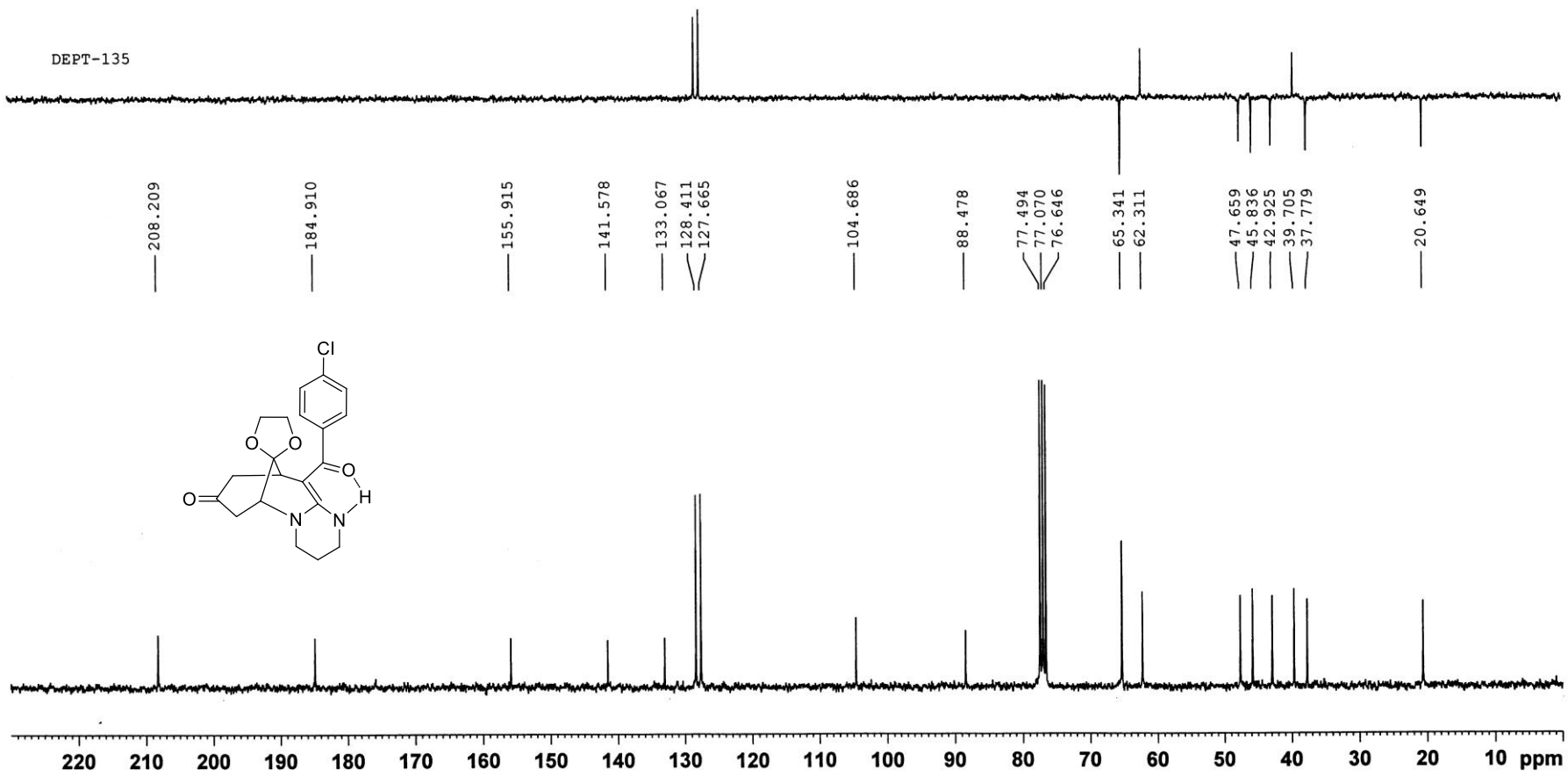


Figure 46. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3w**

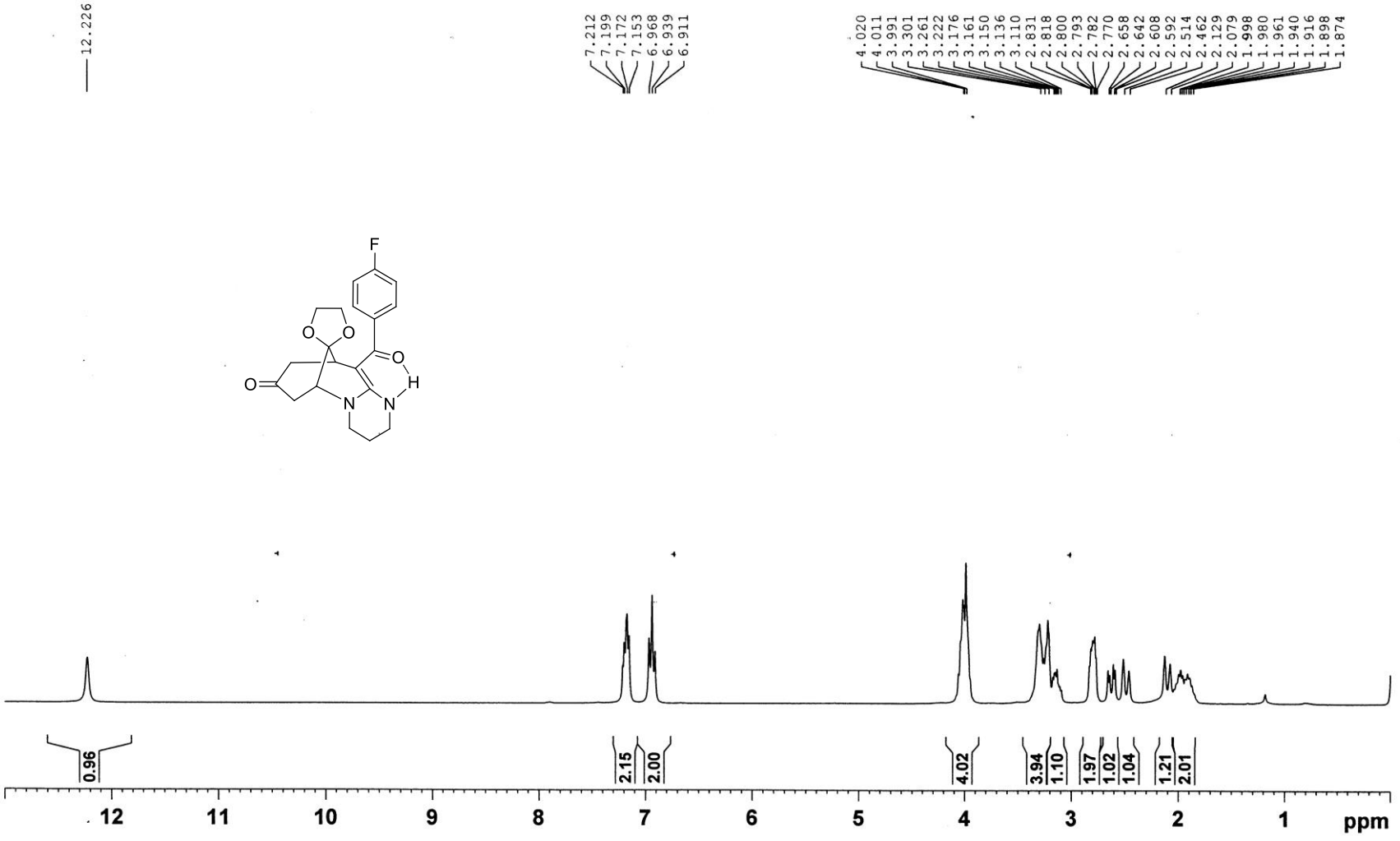


Figure 47. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3x**

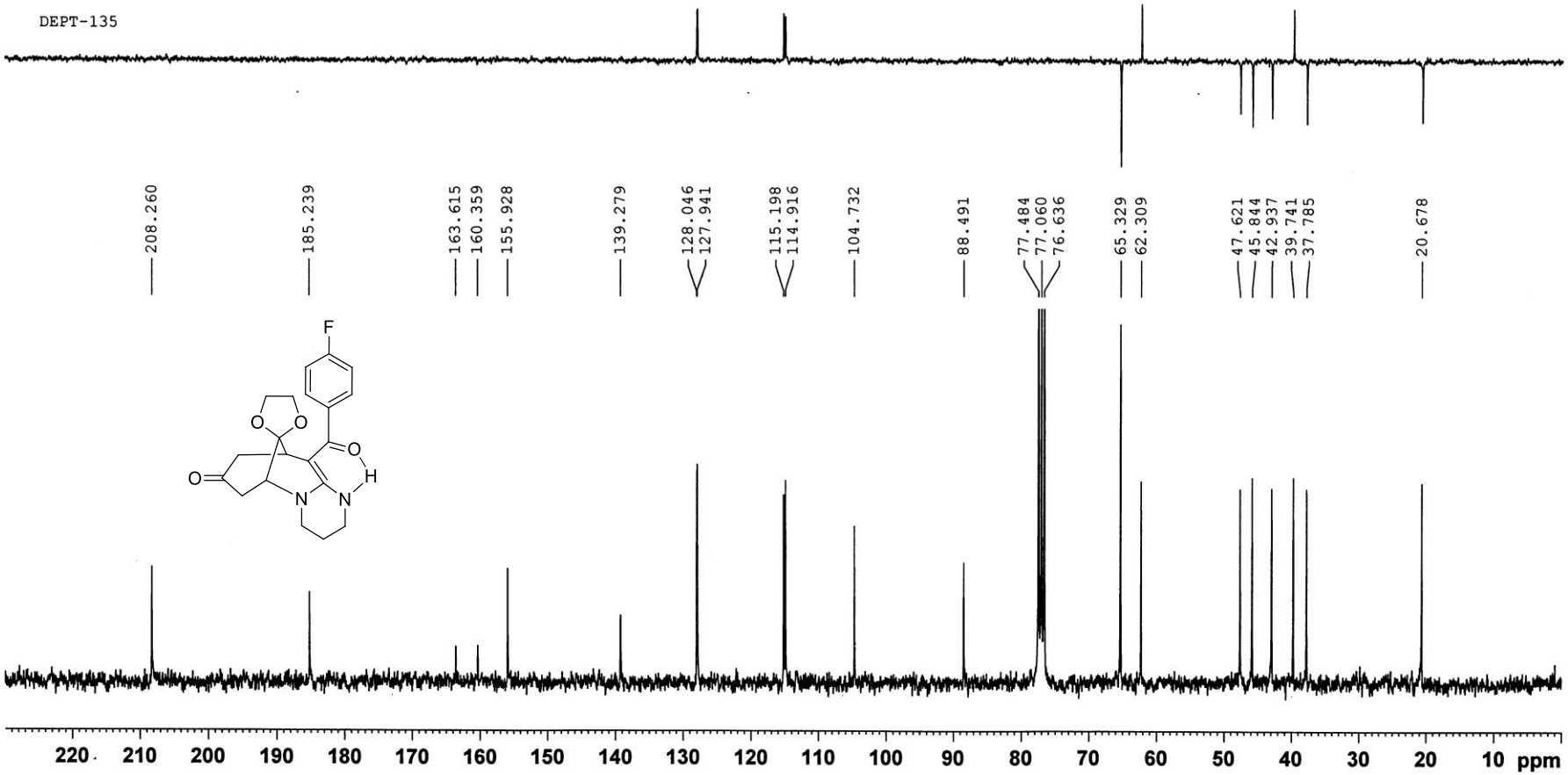


Figure 48. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3x**

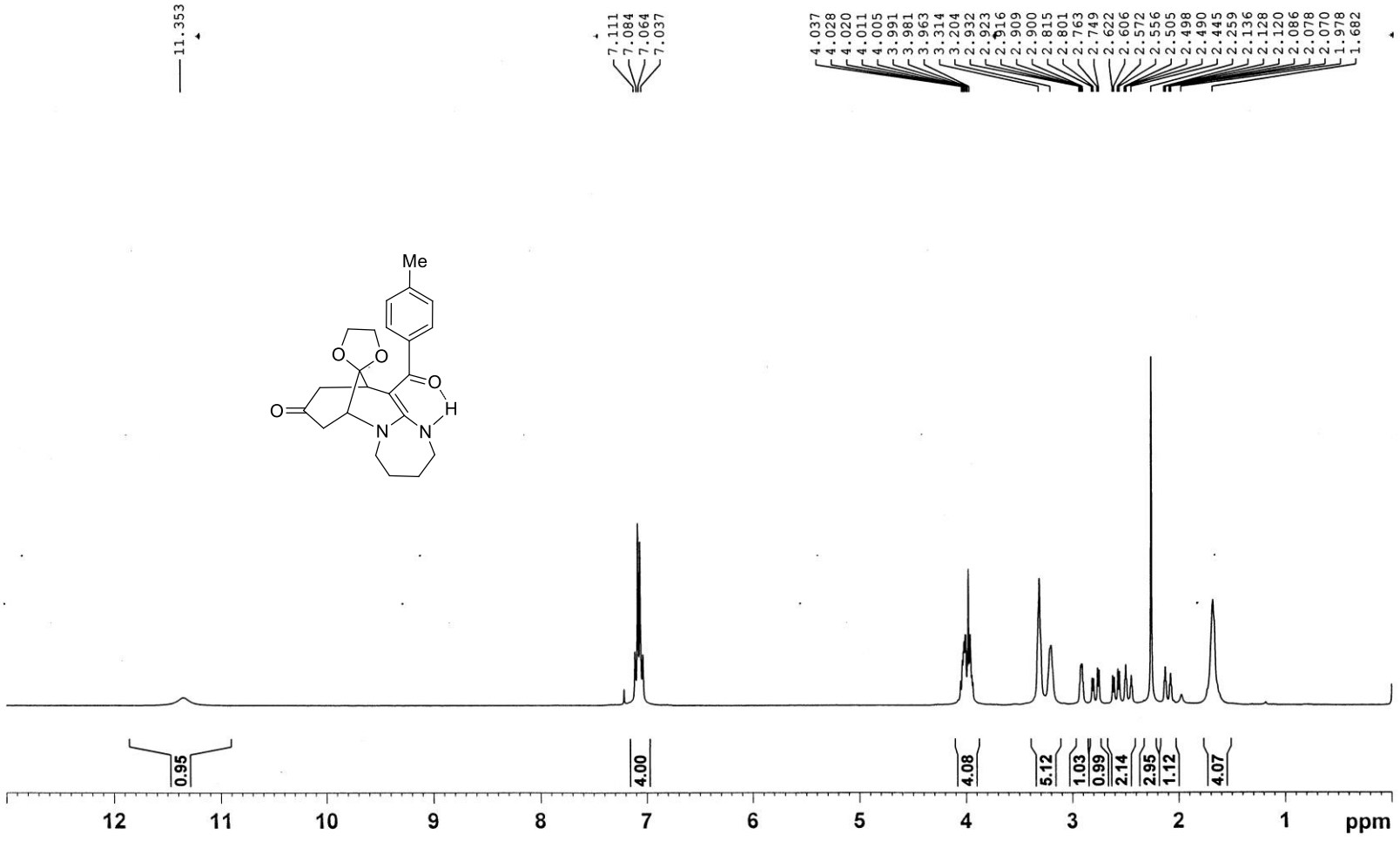


Figure 49. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3y**

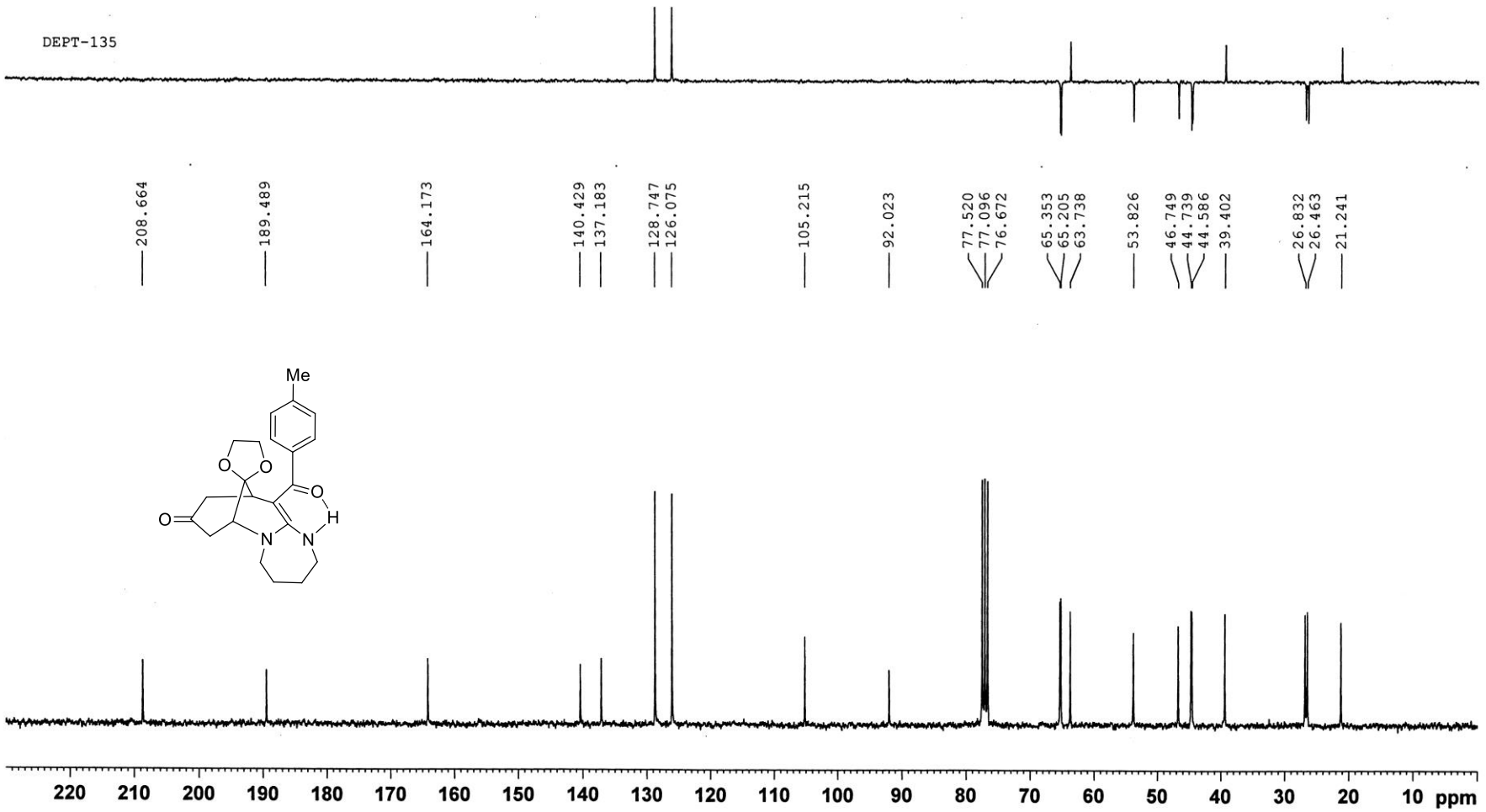


Figure 50. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3y**

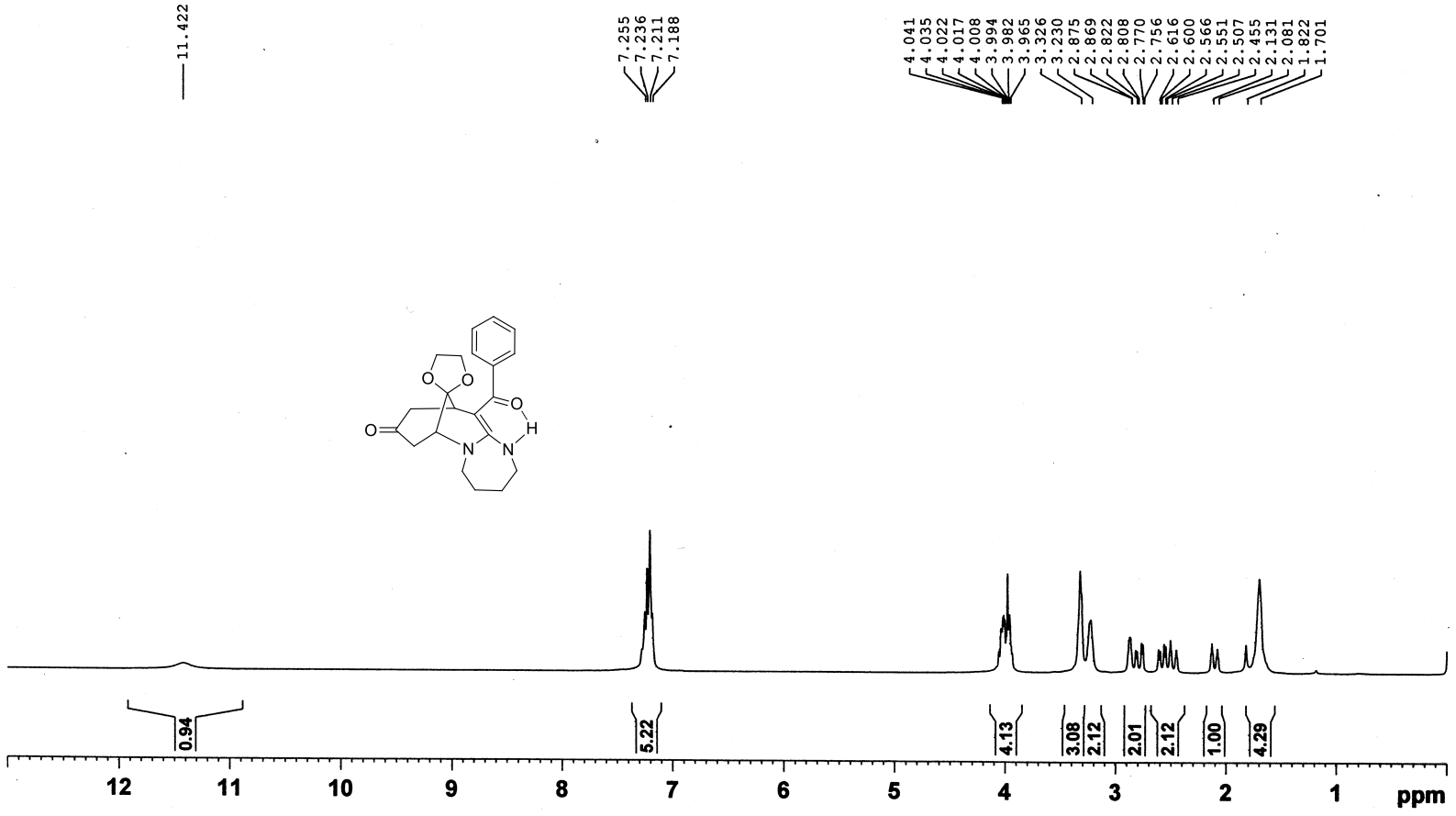


Figure 51. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3z**

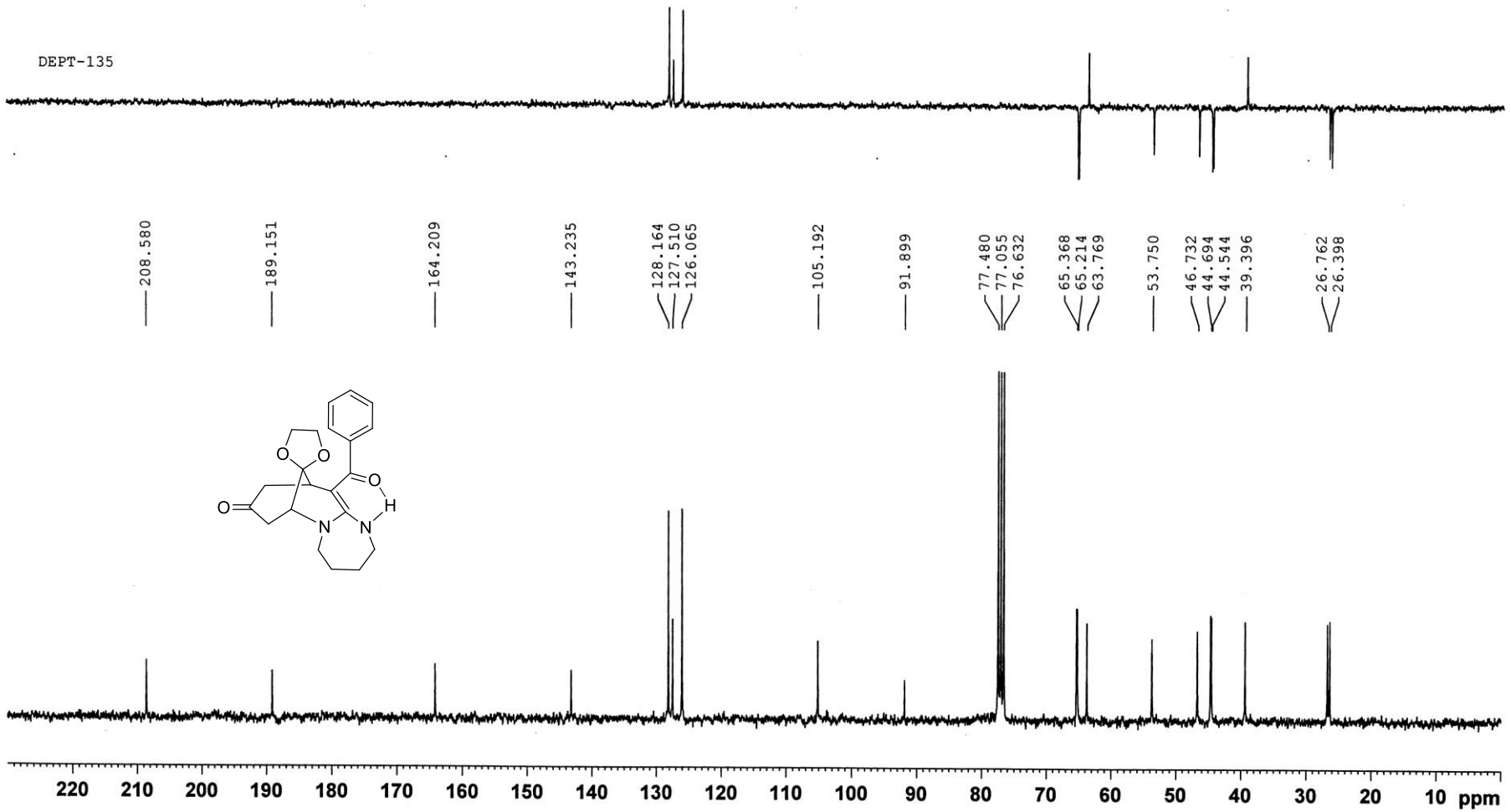


Figure 52. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3z**

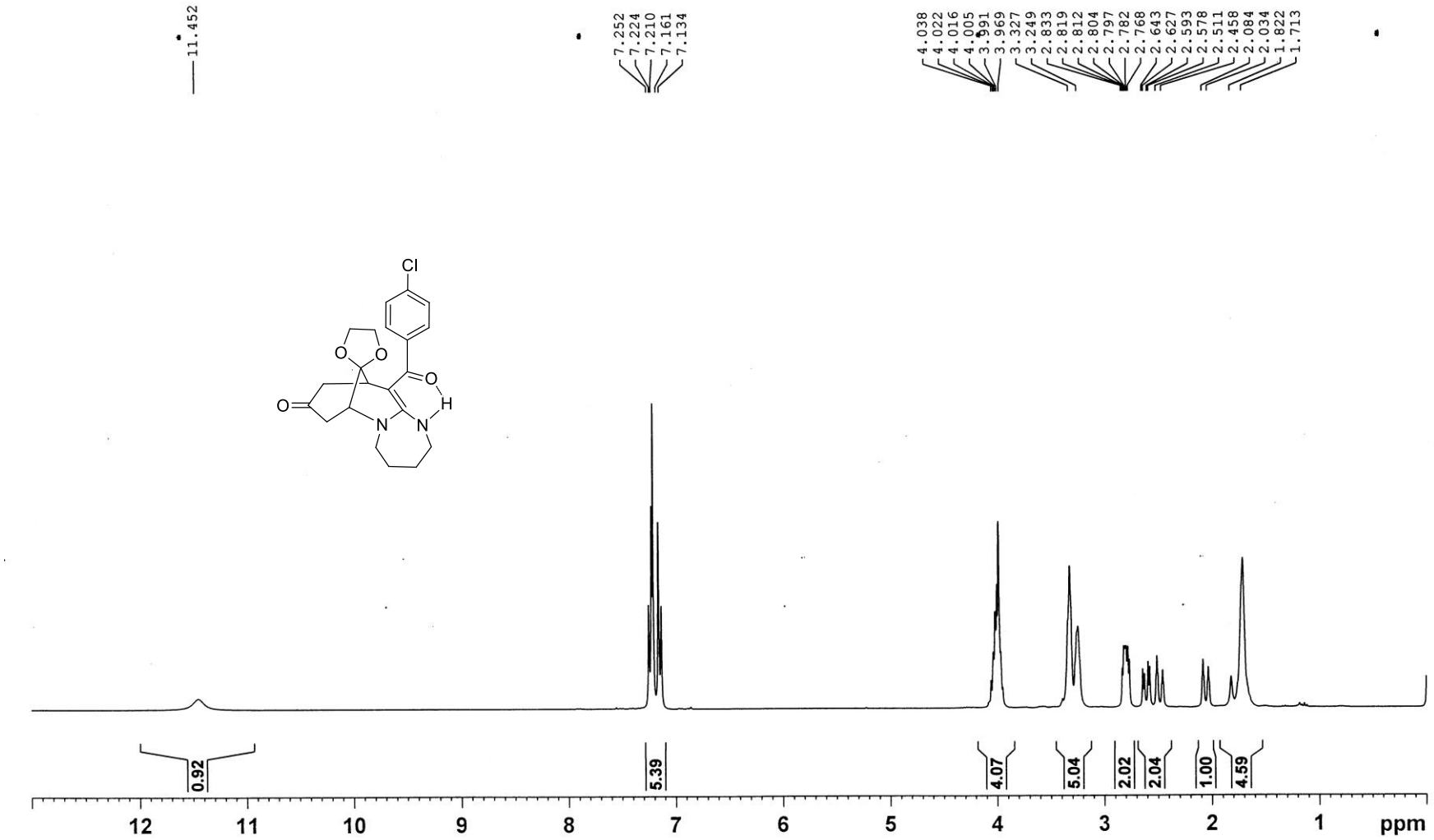


Figure 53. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3a'**

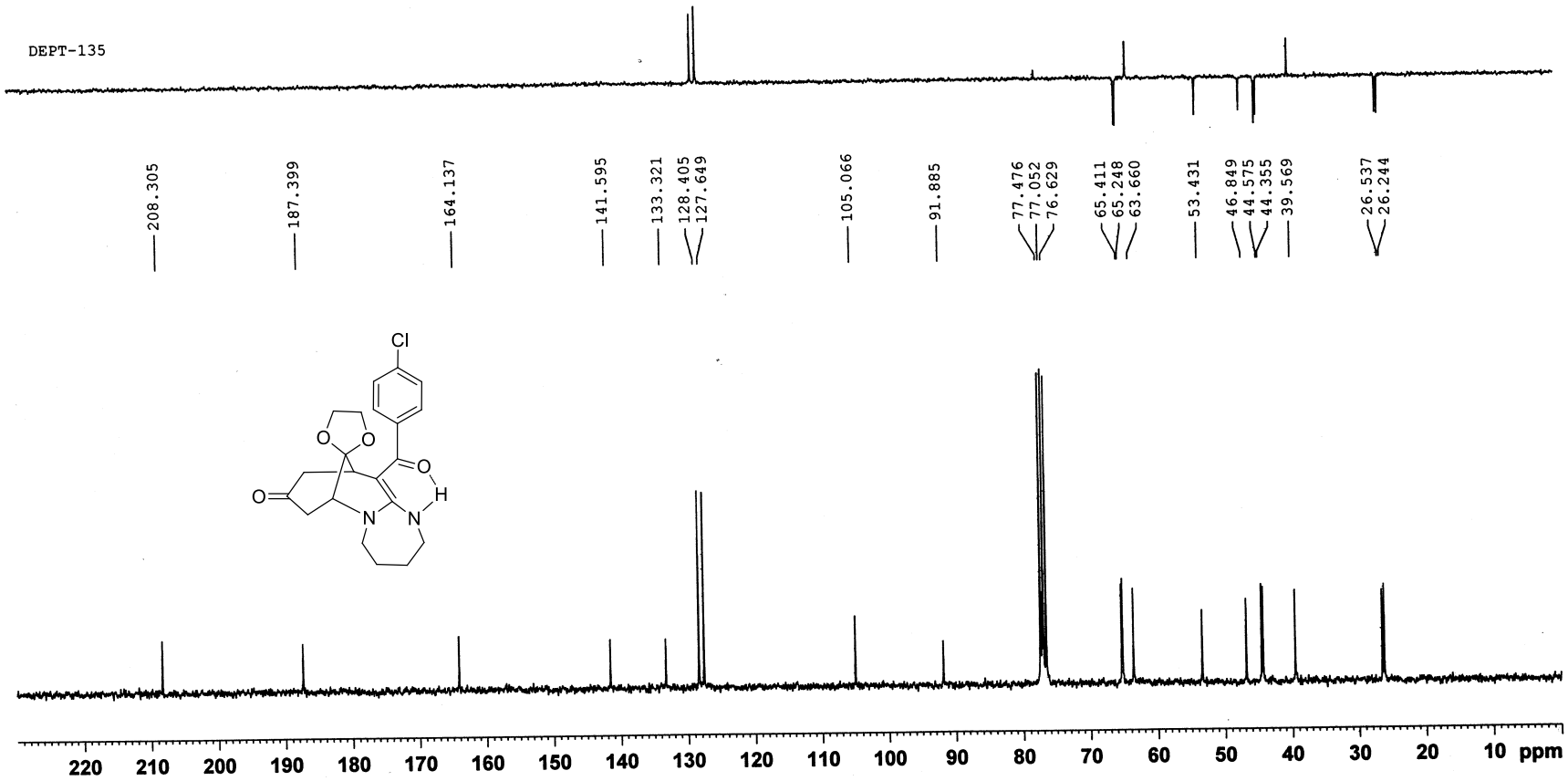


Figure 54. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3a'**

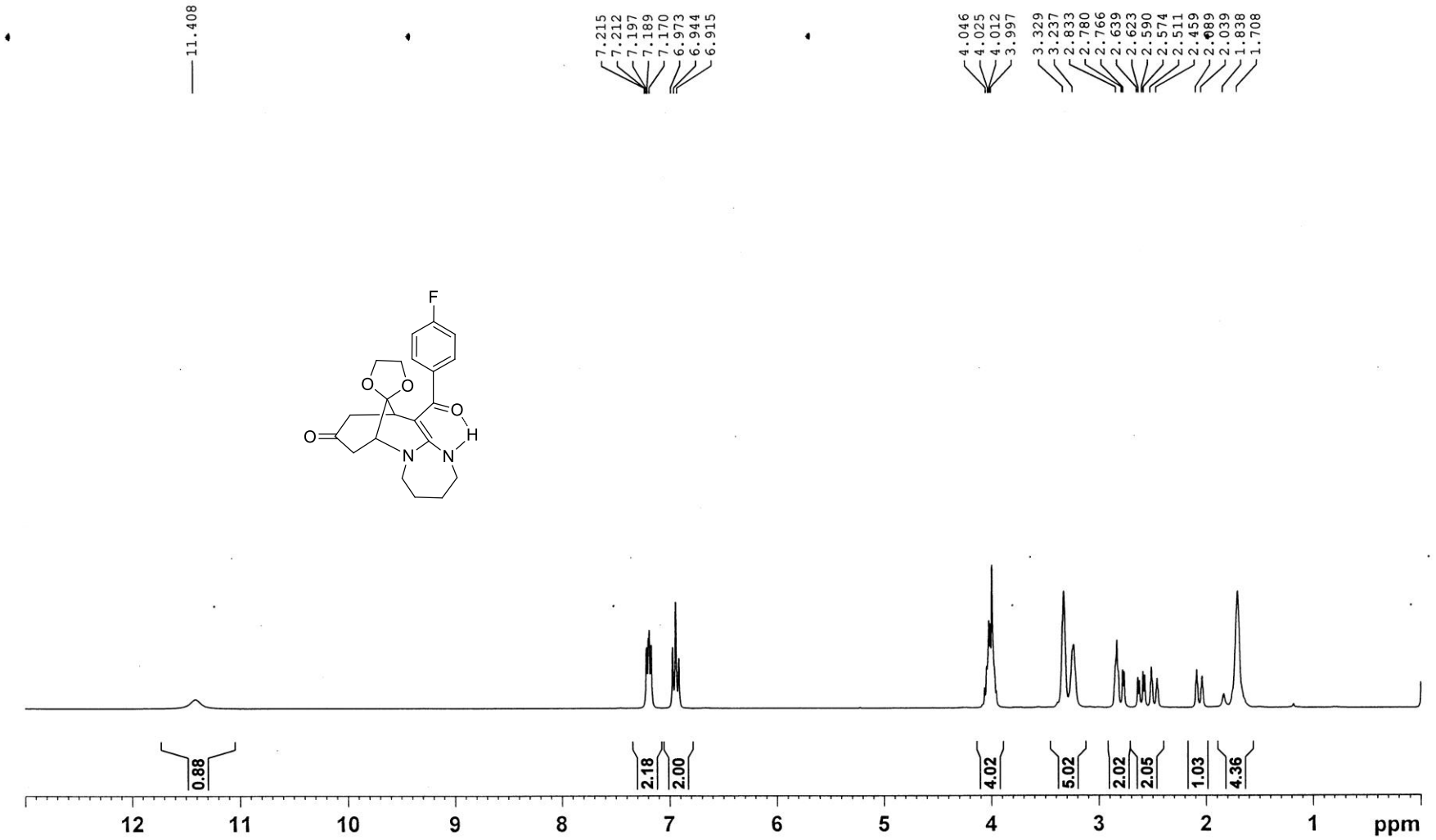


Figure 55. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3b'**

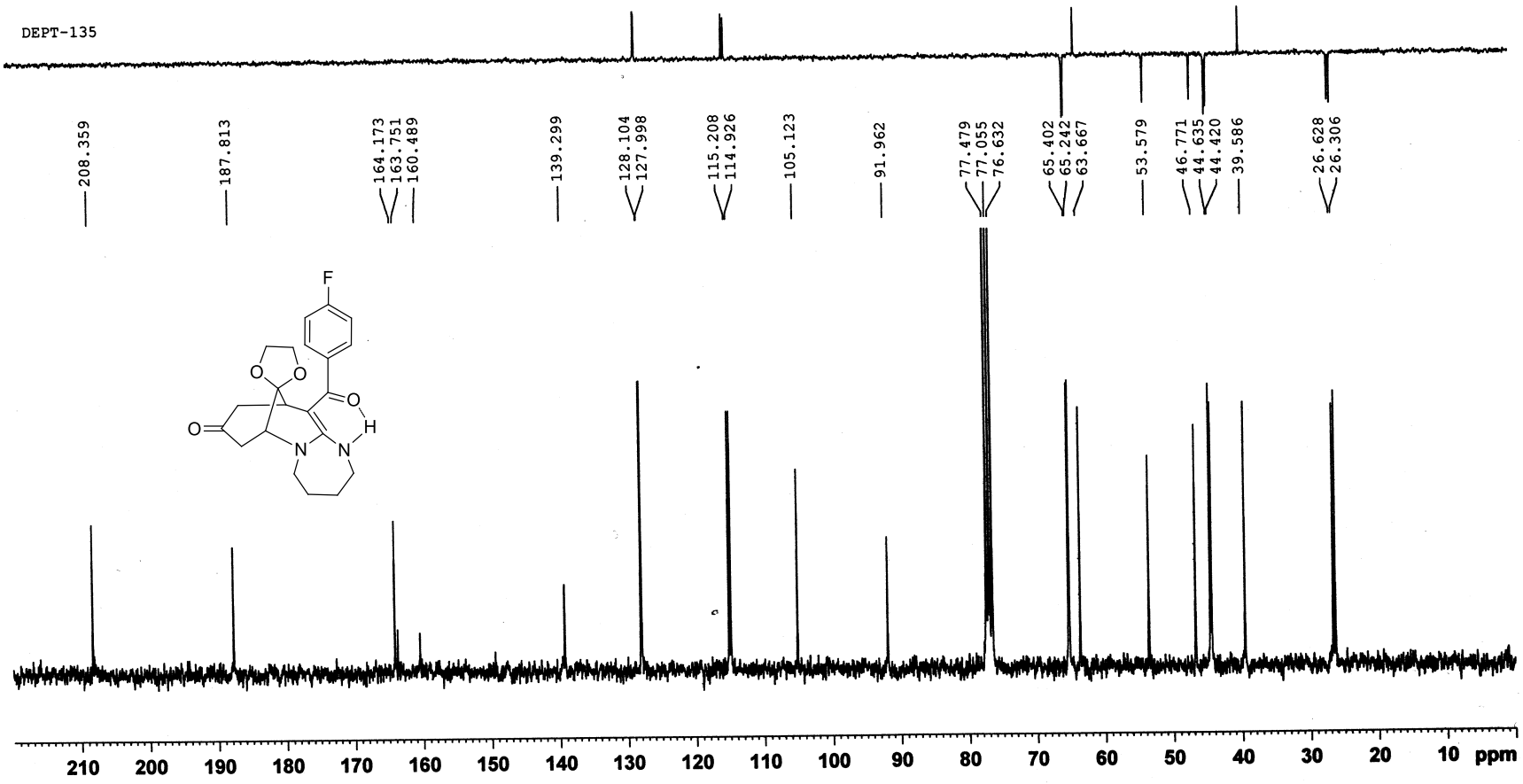


Figure 56. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3b'**

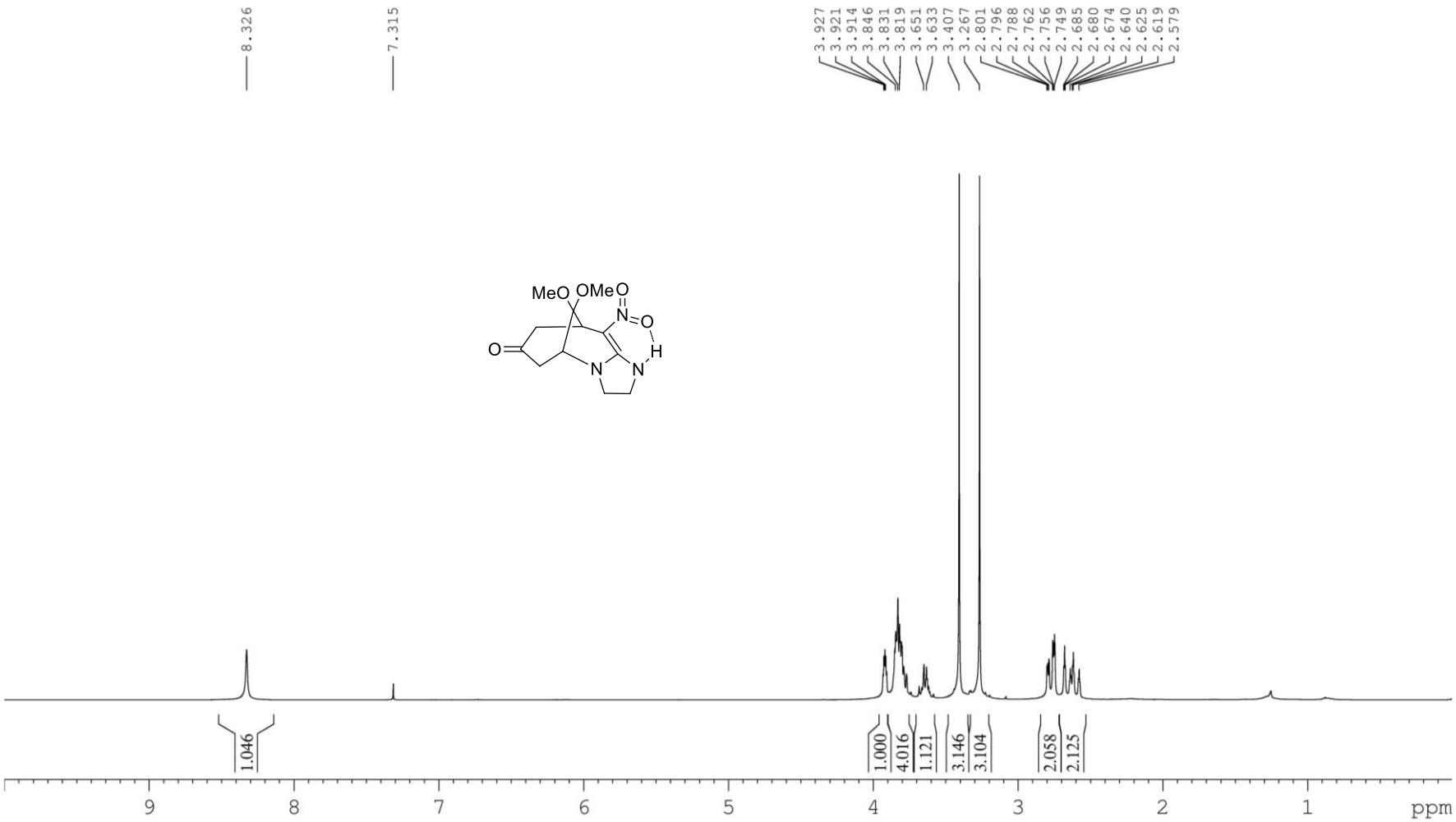


Figure 57. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3c'**

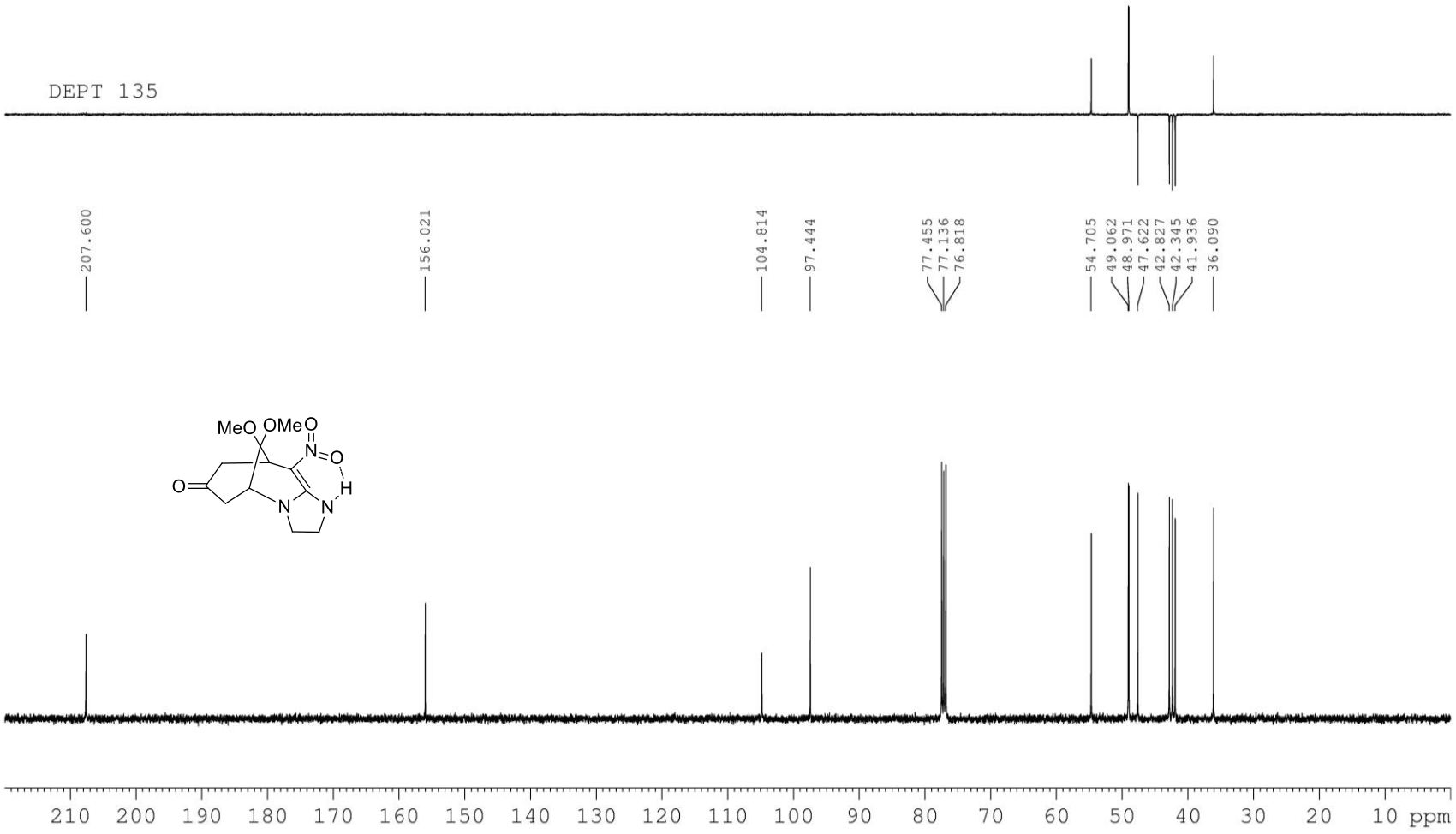


Figure 58. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3c'**

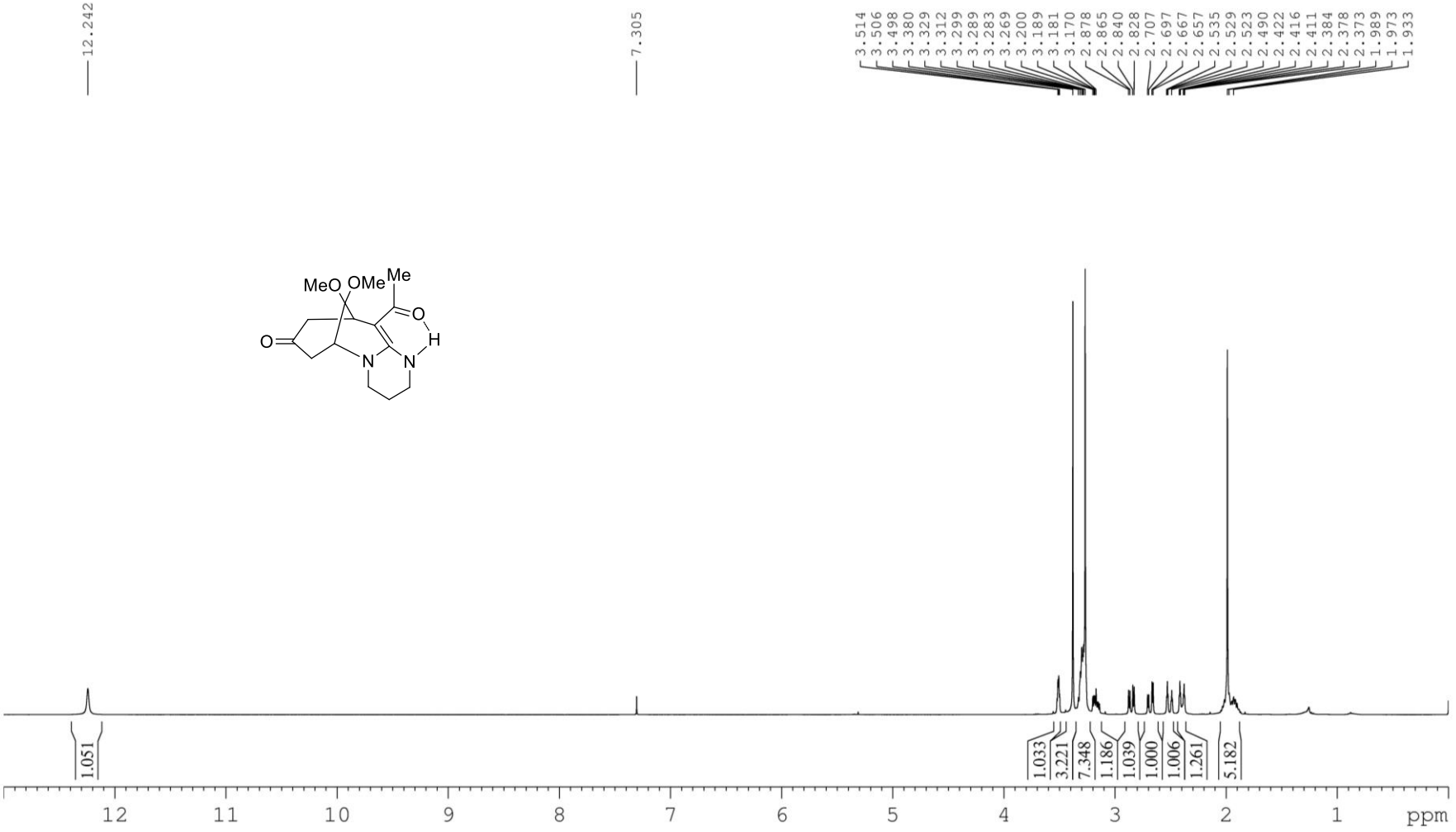


Figure 59. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3d'**

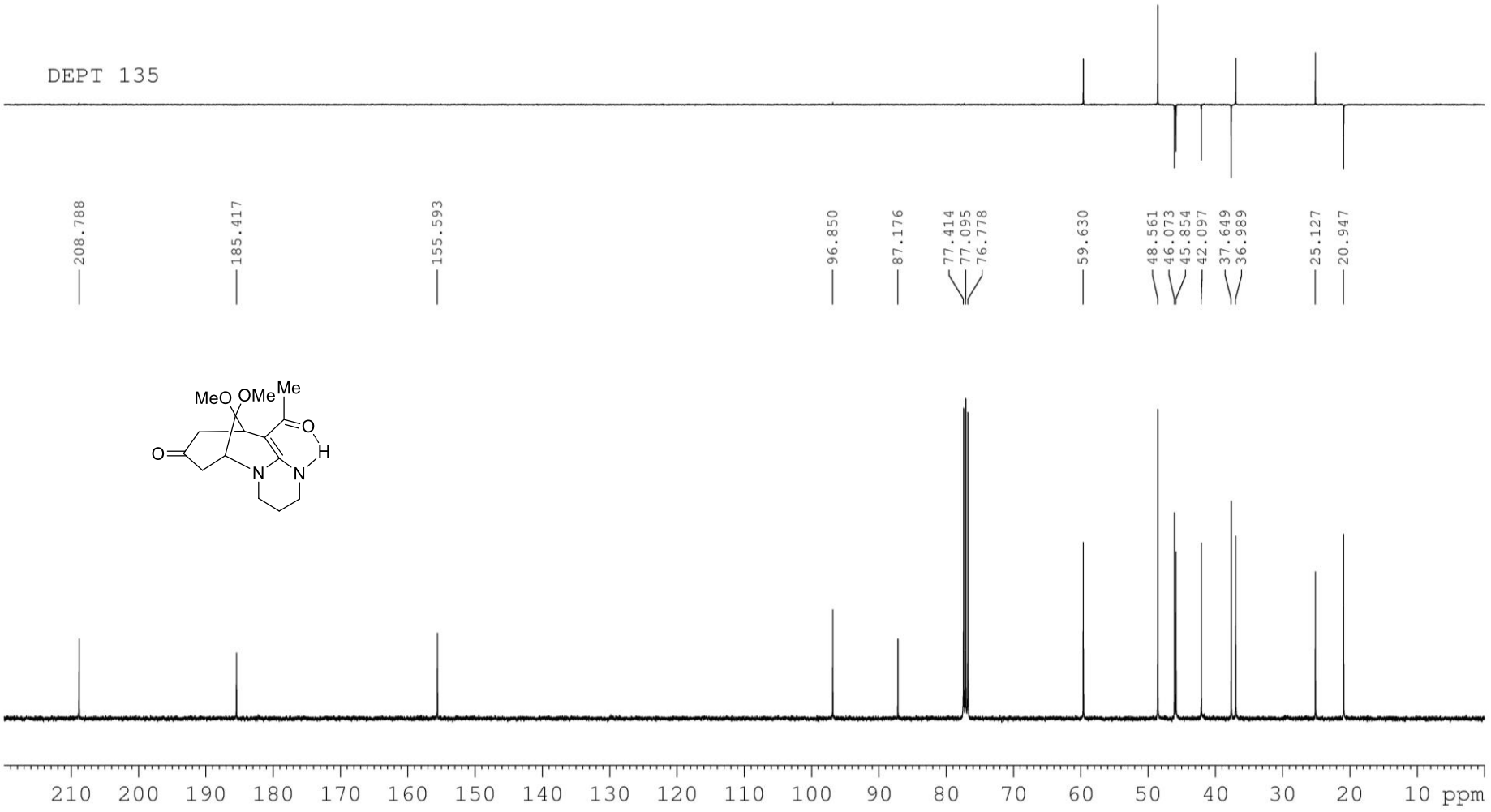


Figure 60. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3d'**

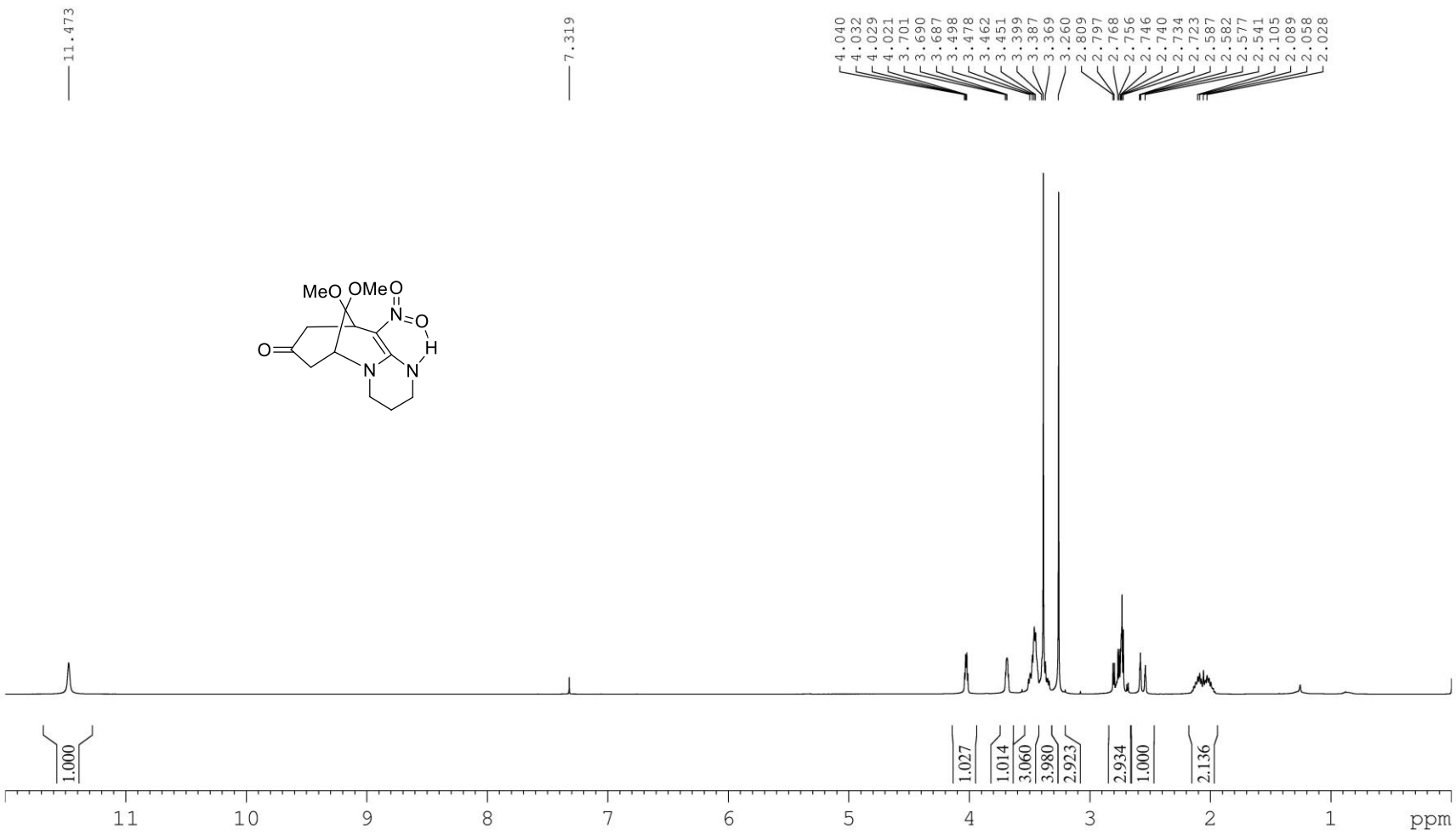


Figure 61. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3e'**

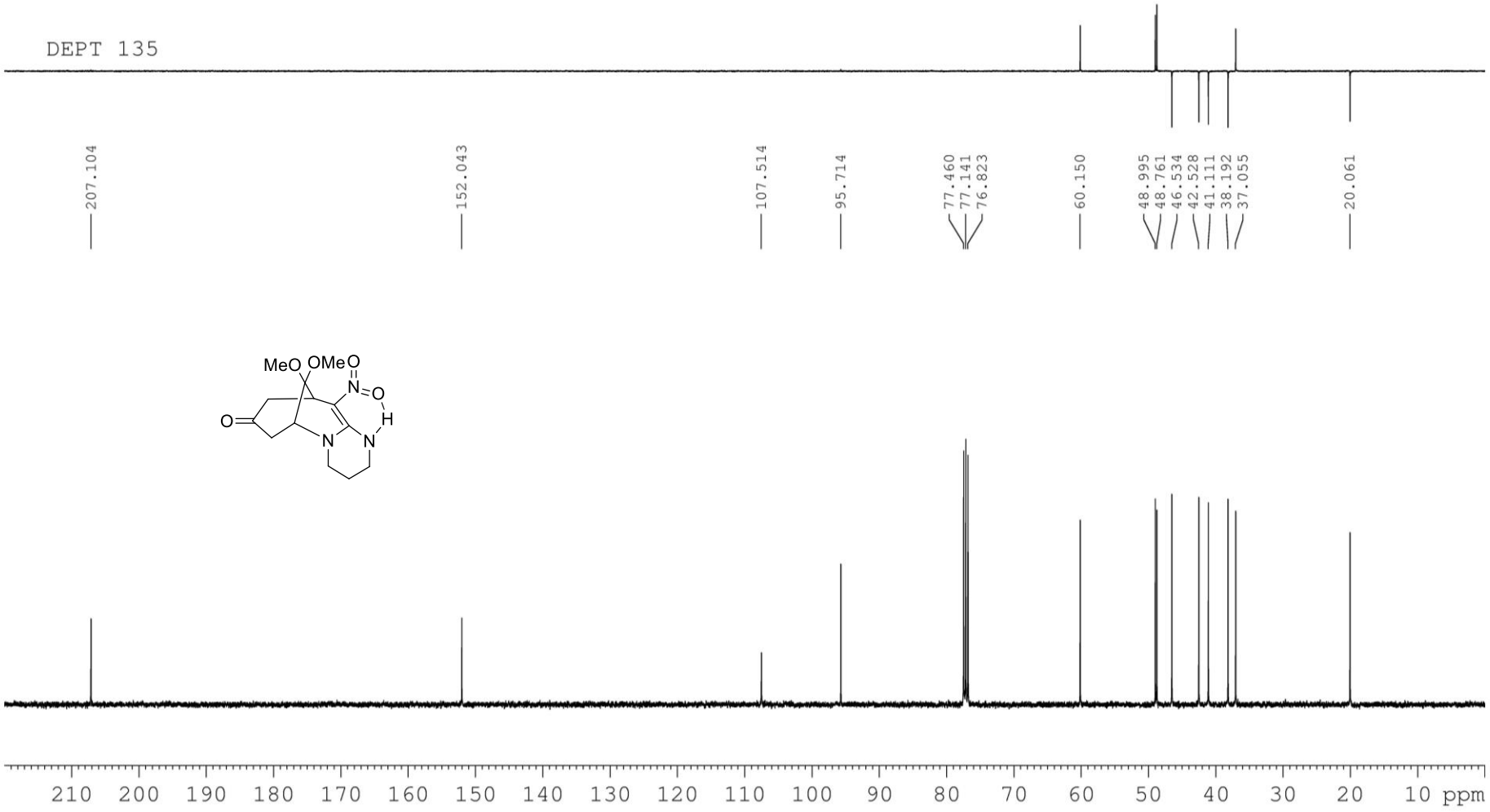


Figure 62. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3e'**

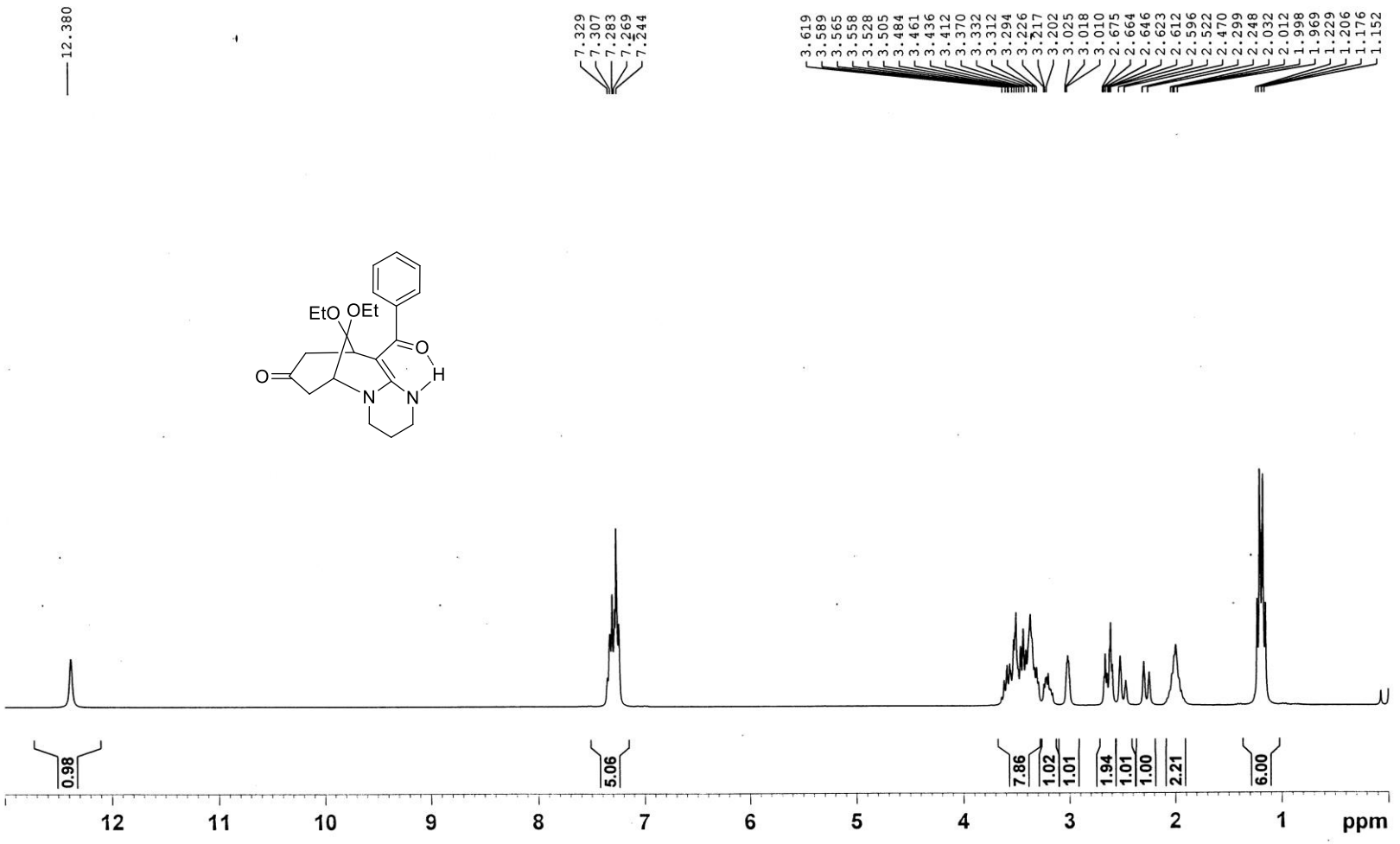


Figure 63. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3f'**

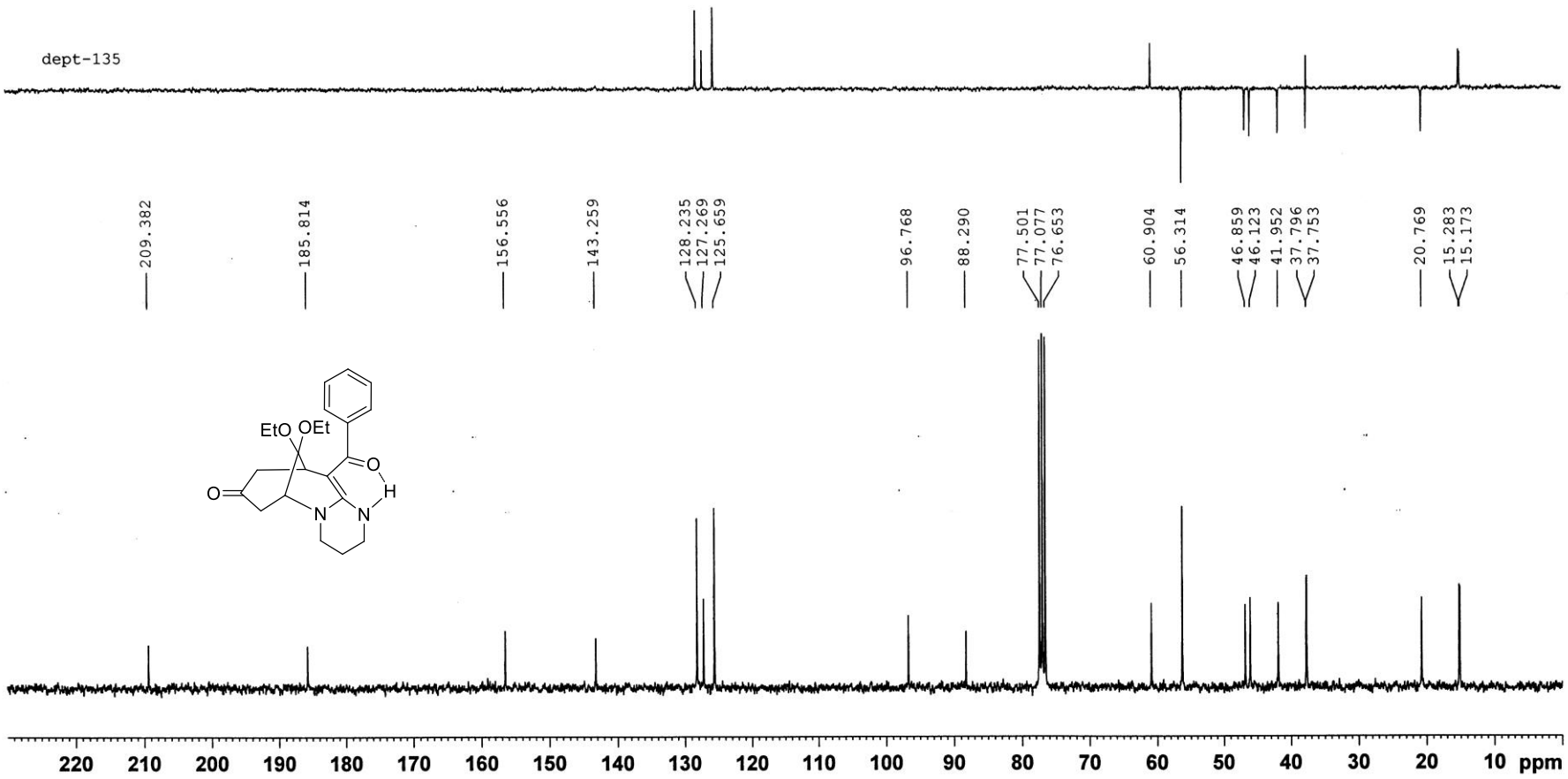


Figure 64. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3f'**

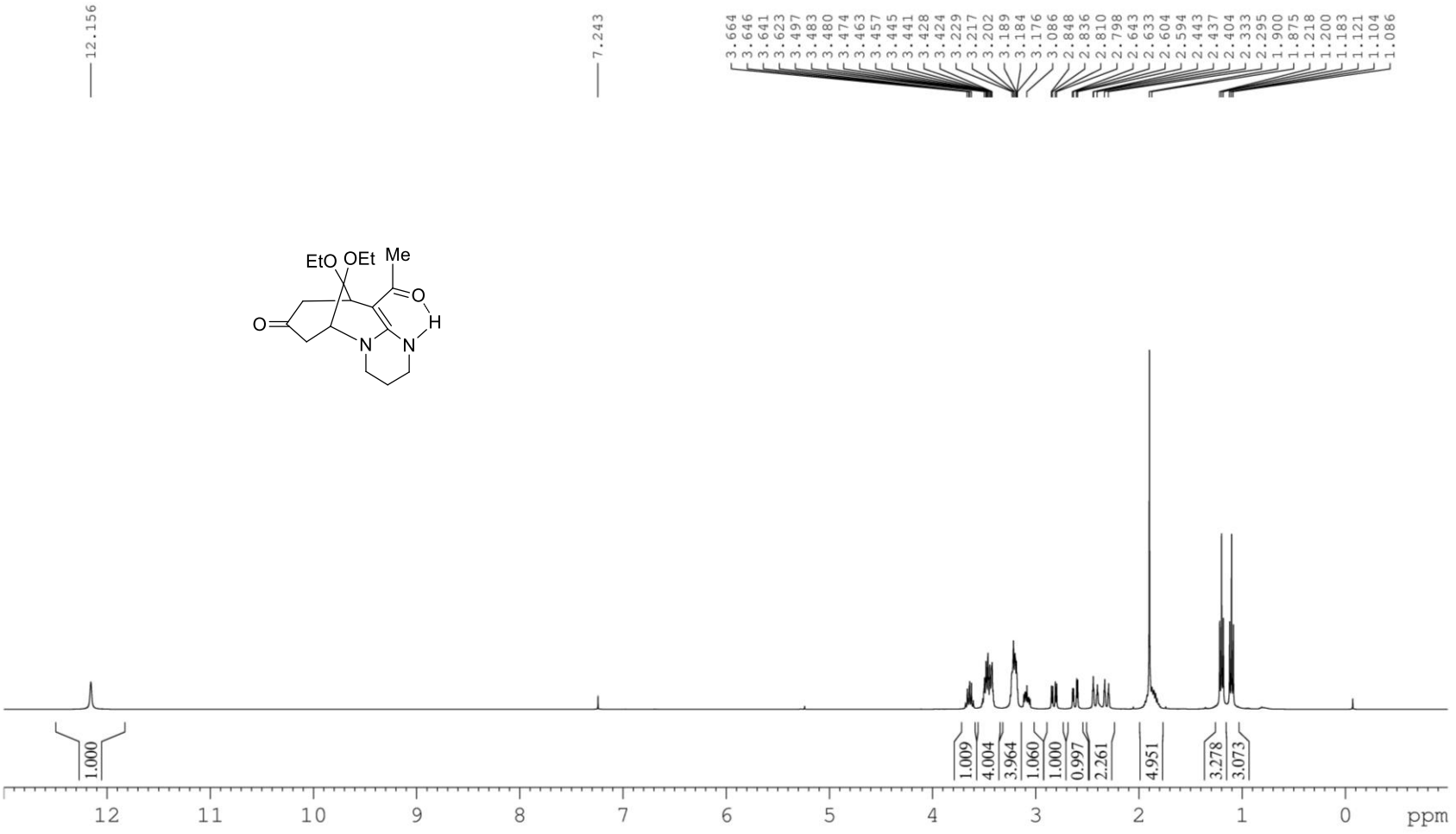


Figure 65. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3g'**

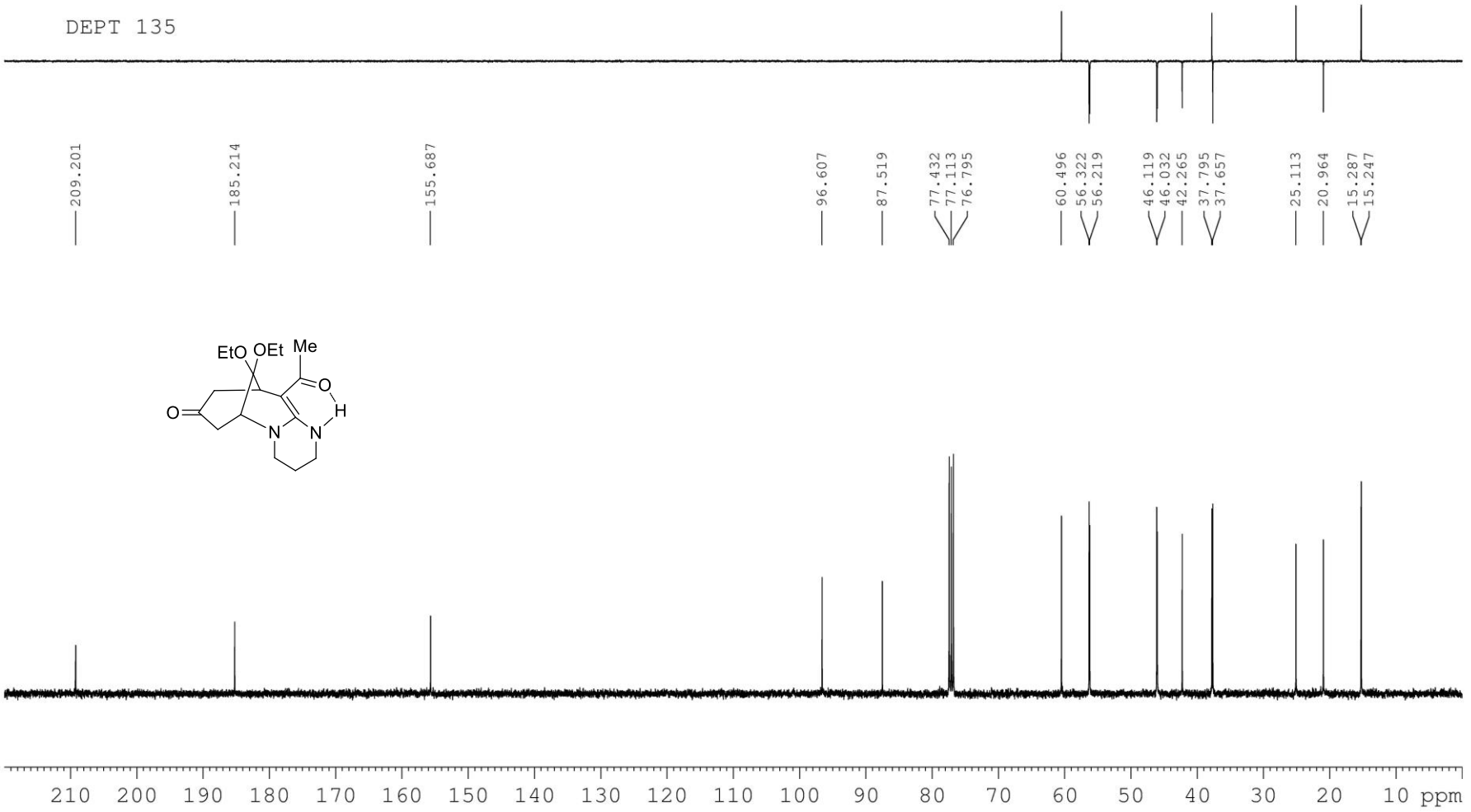


Figure 66. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3g'**

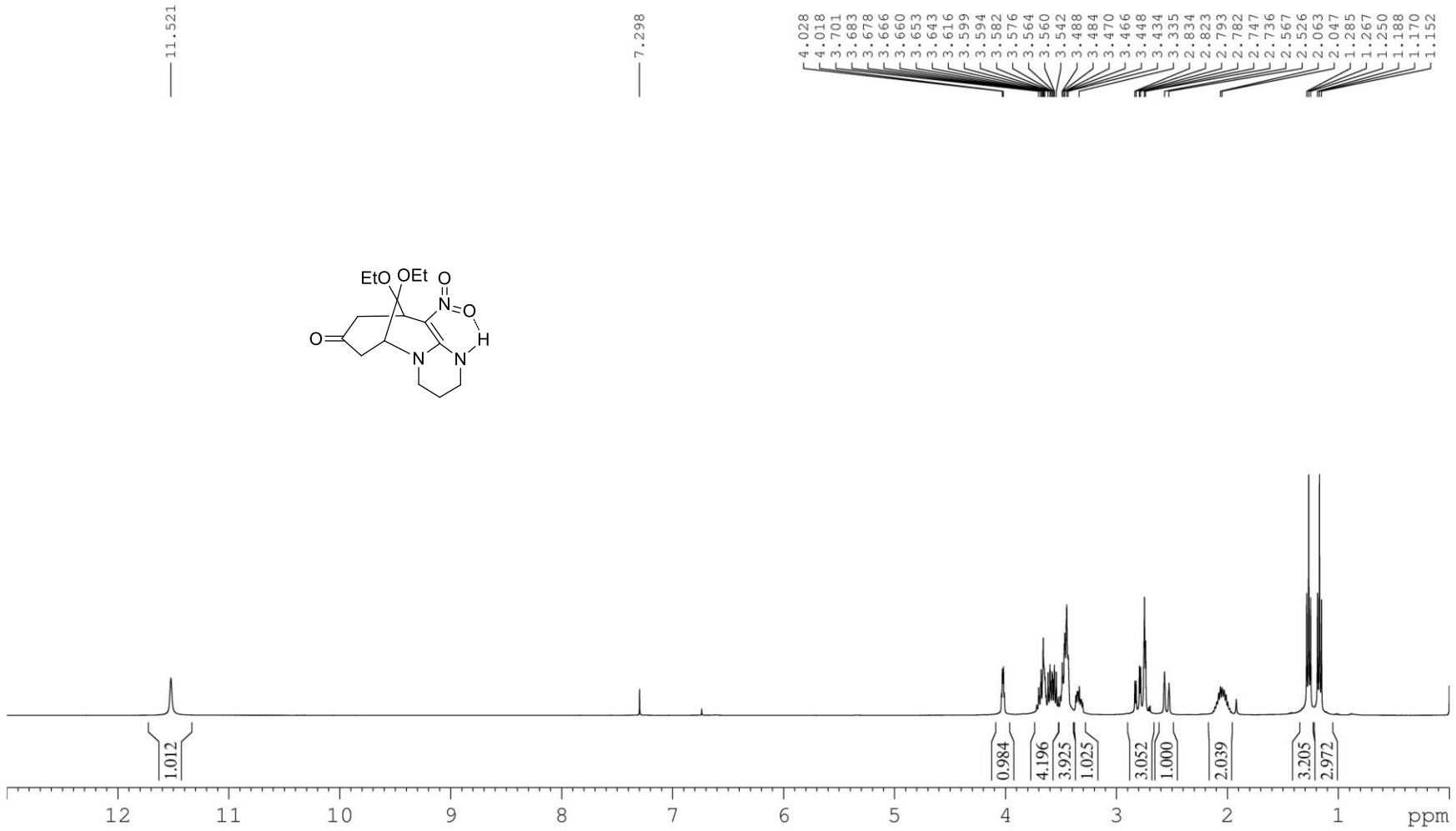


Figure 67. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3h'**

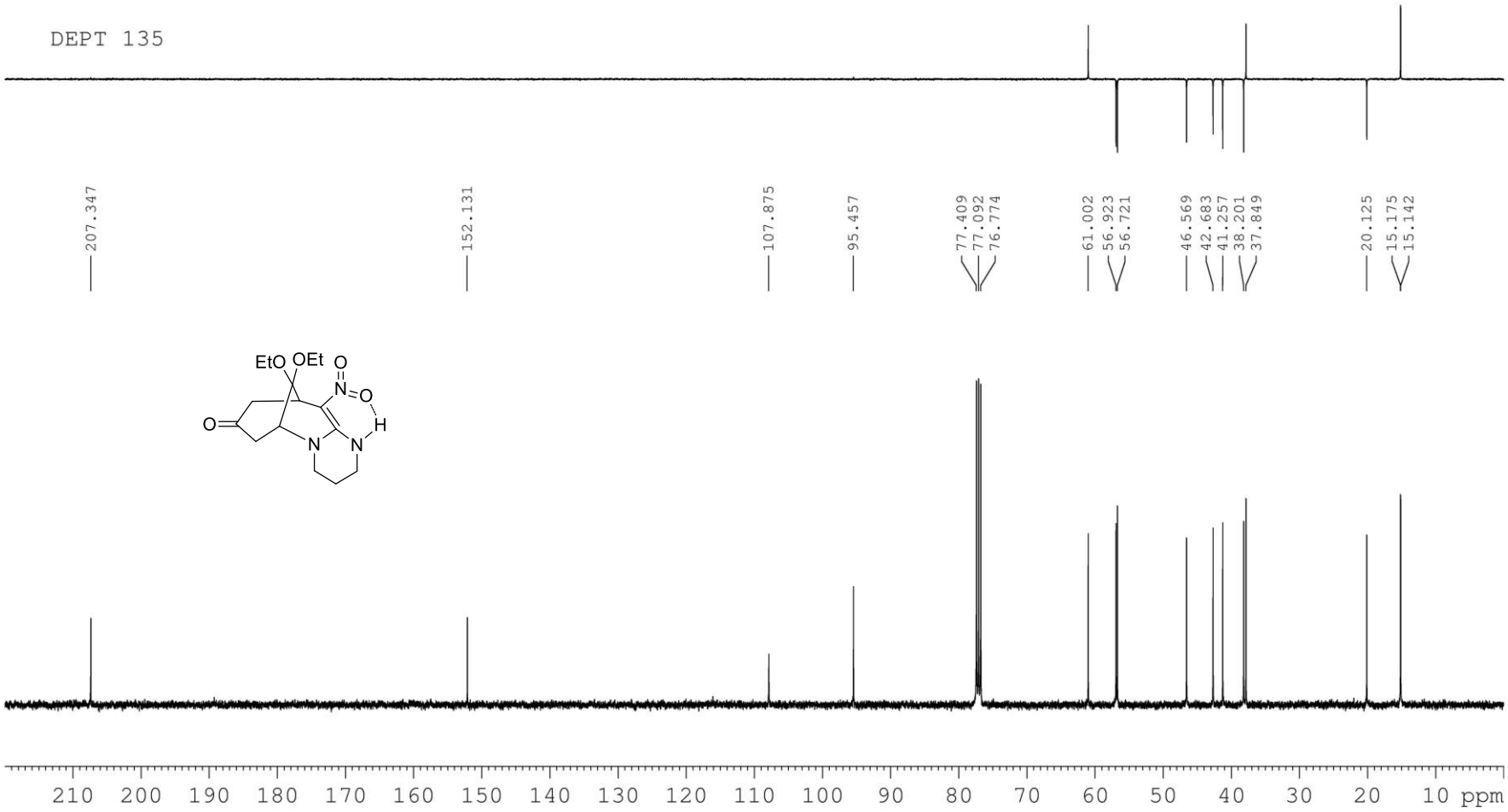


Figure 68. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3h'**

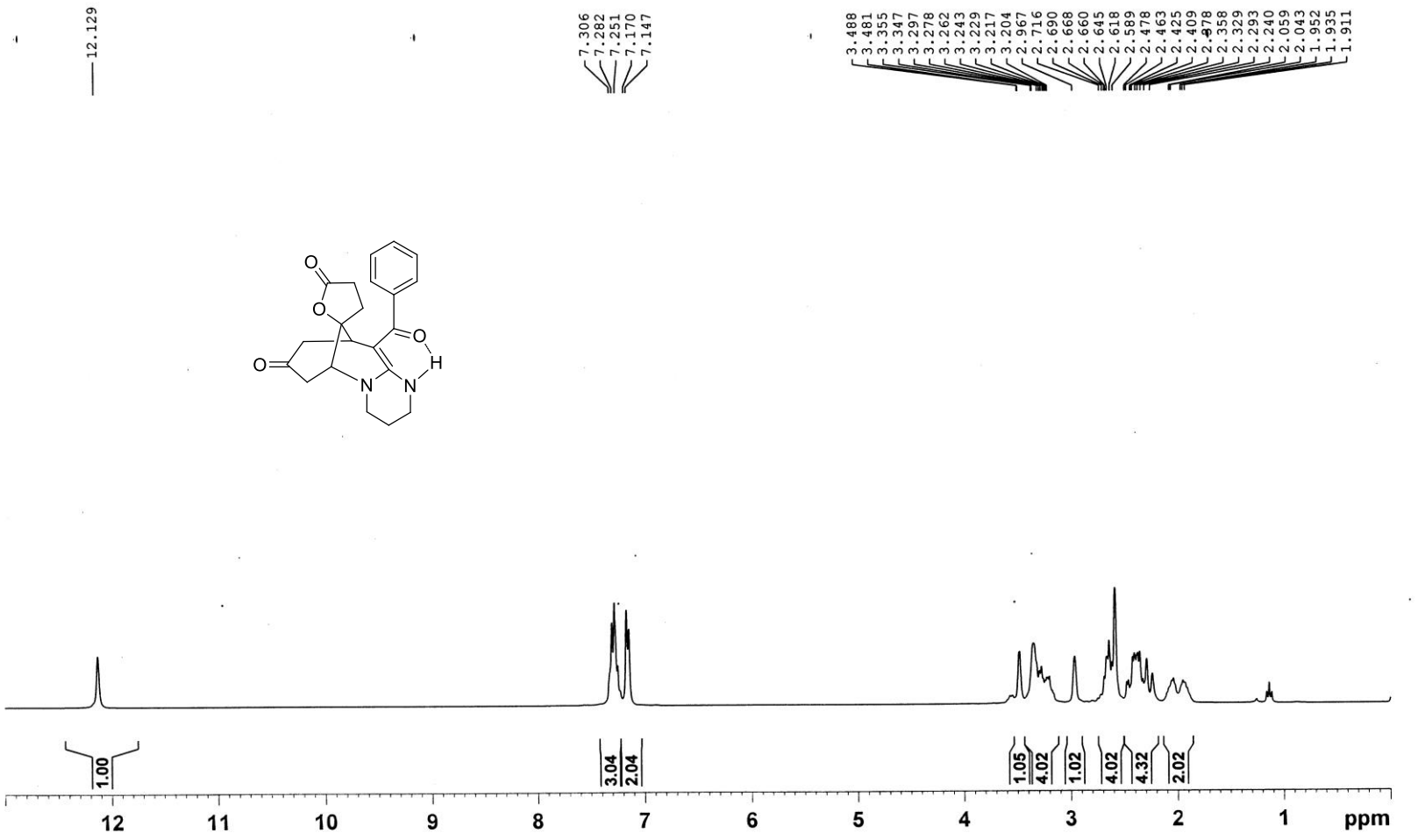


Figure 69. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3i'**

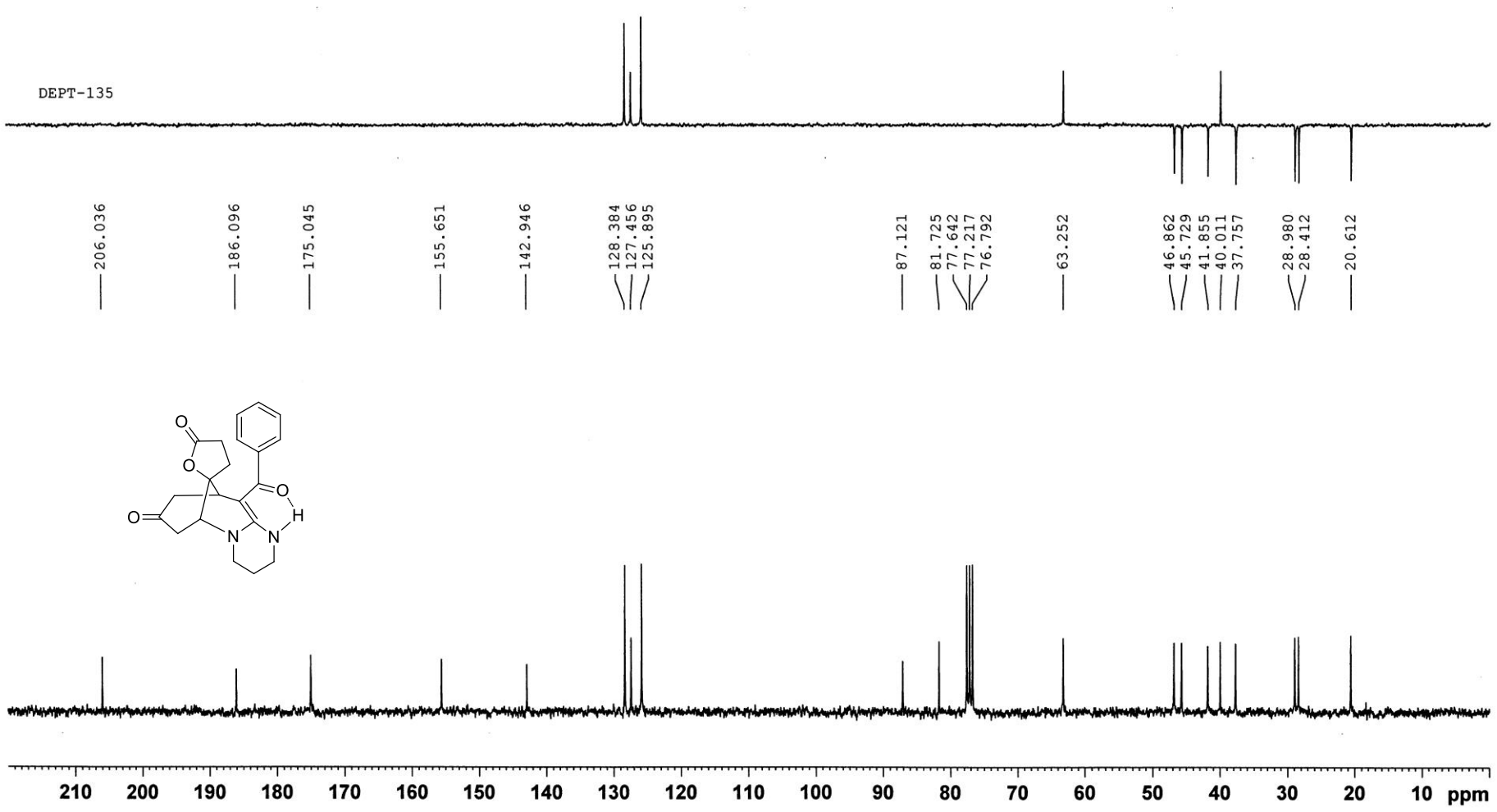


Figure 70. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3i'**

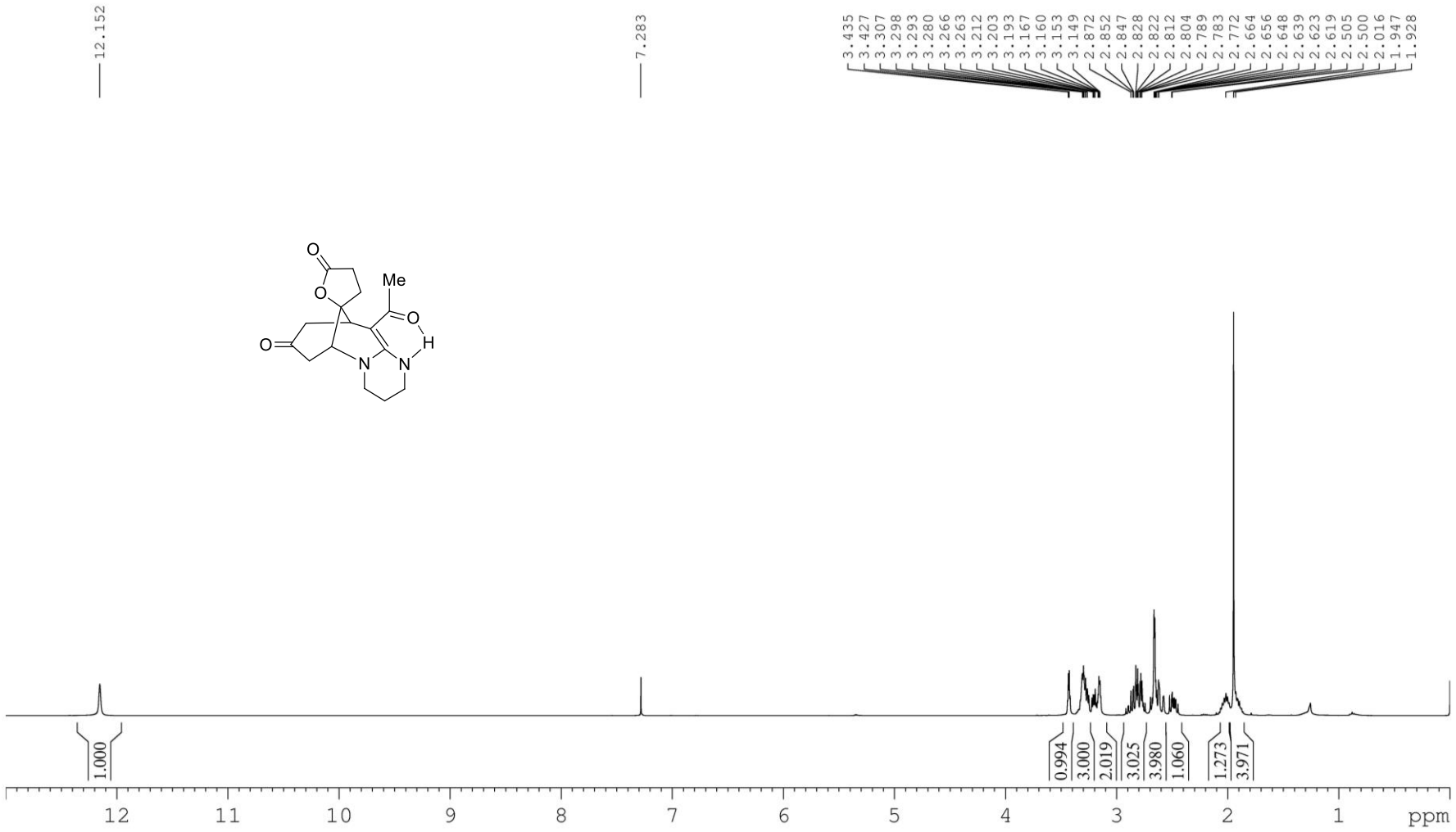


Figure 71. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3j'**

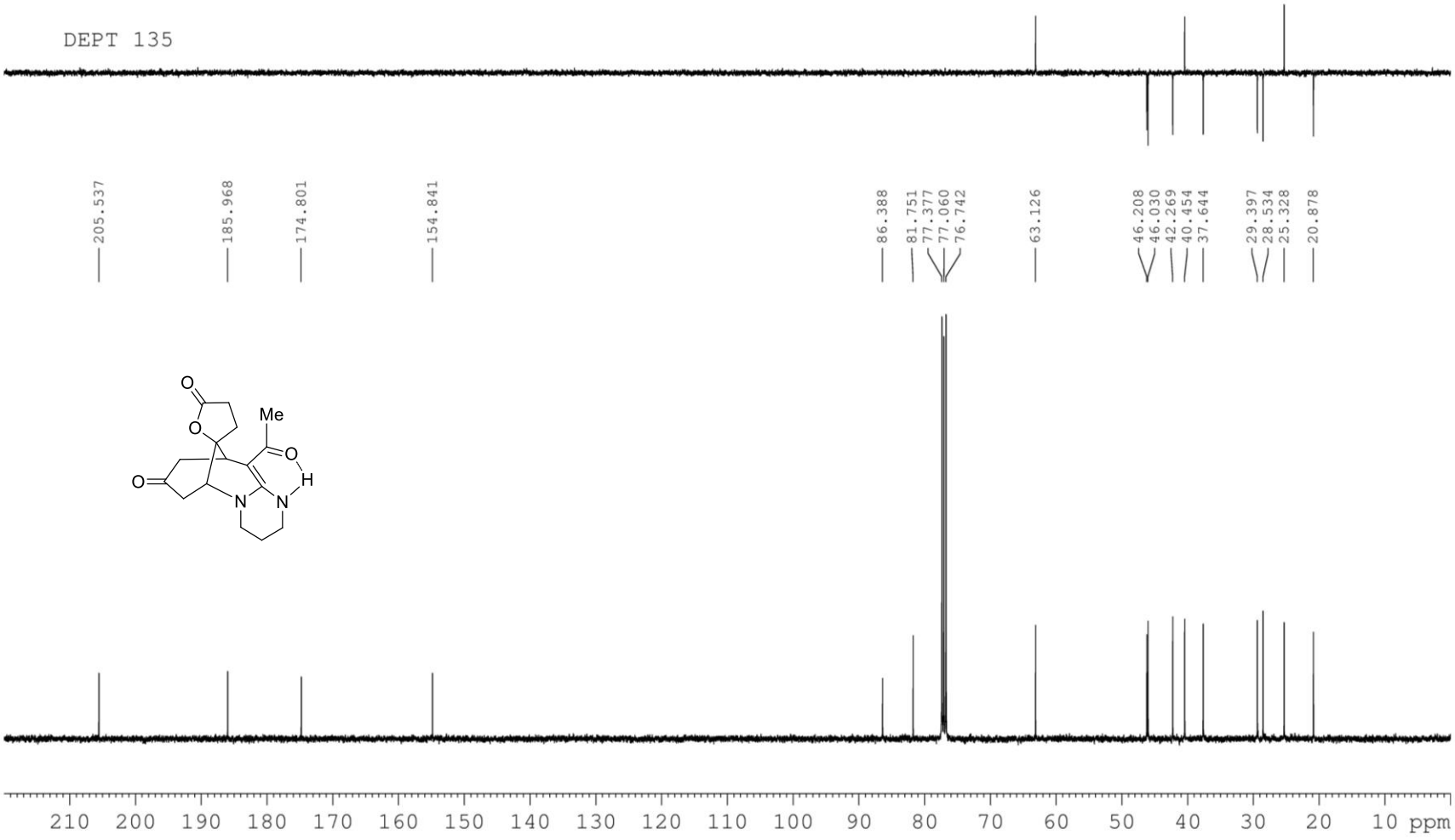


Figure 72. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3j'**

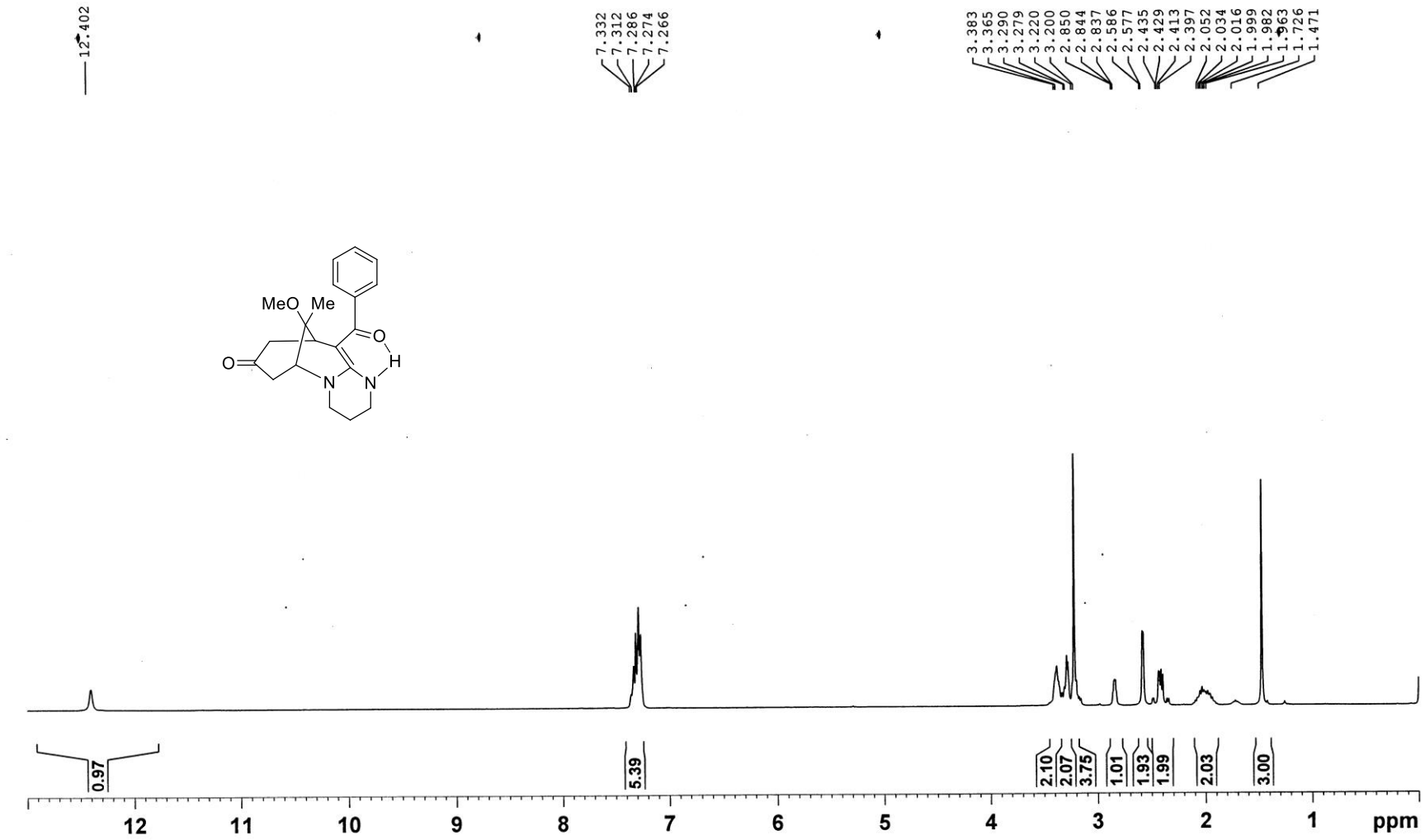


Figure 73. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3k'**

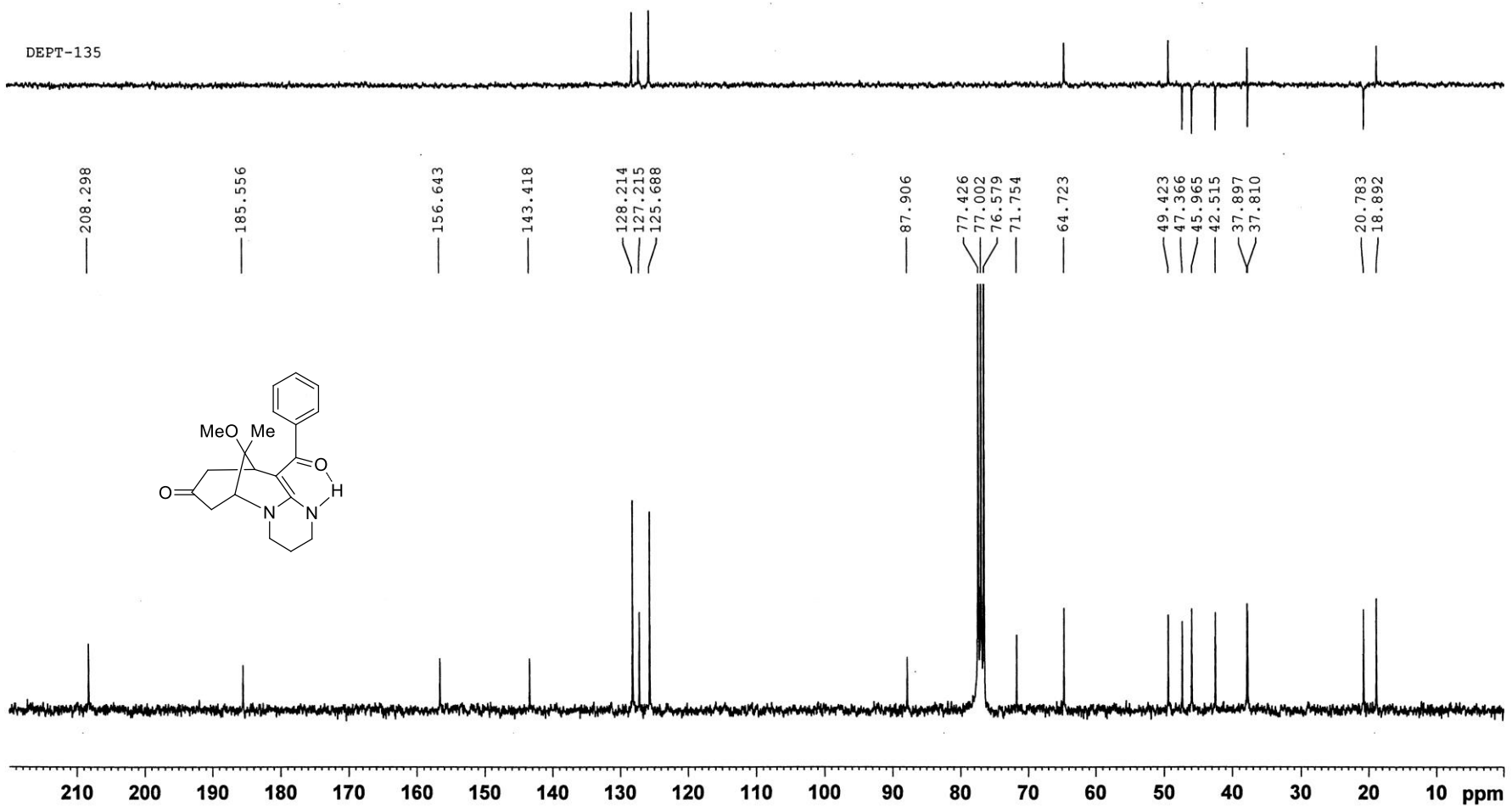


Figure 74. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3k'**

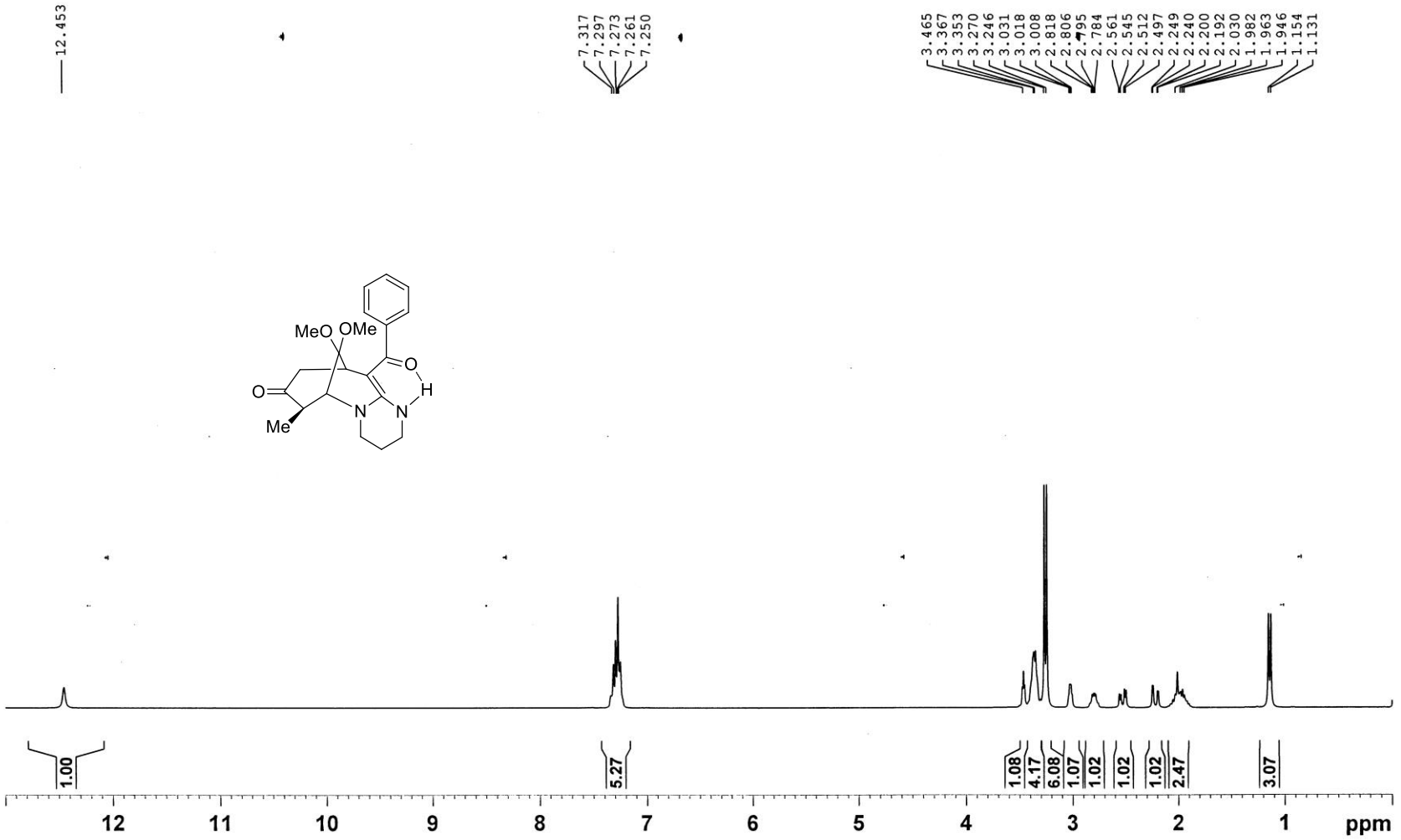


Figure 75. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3l'**

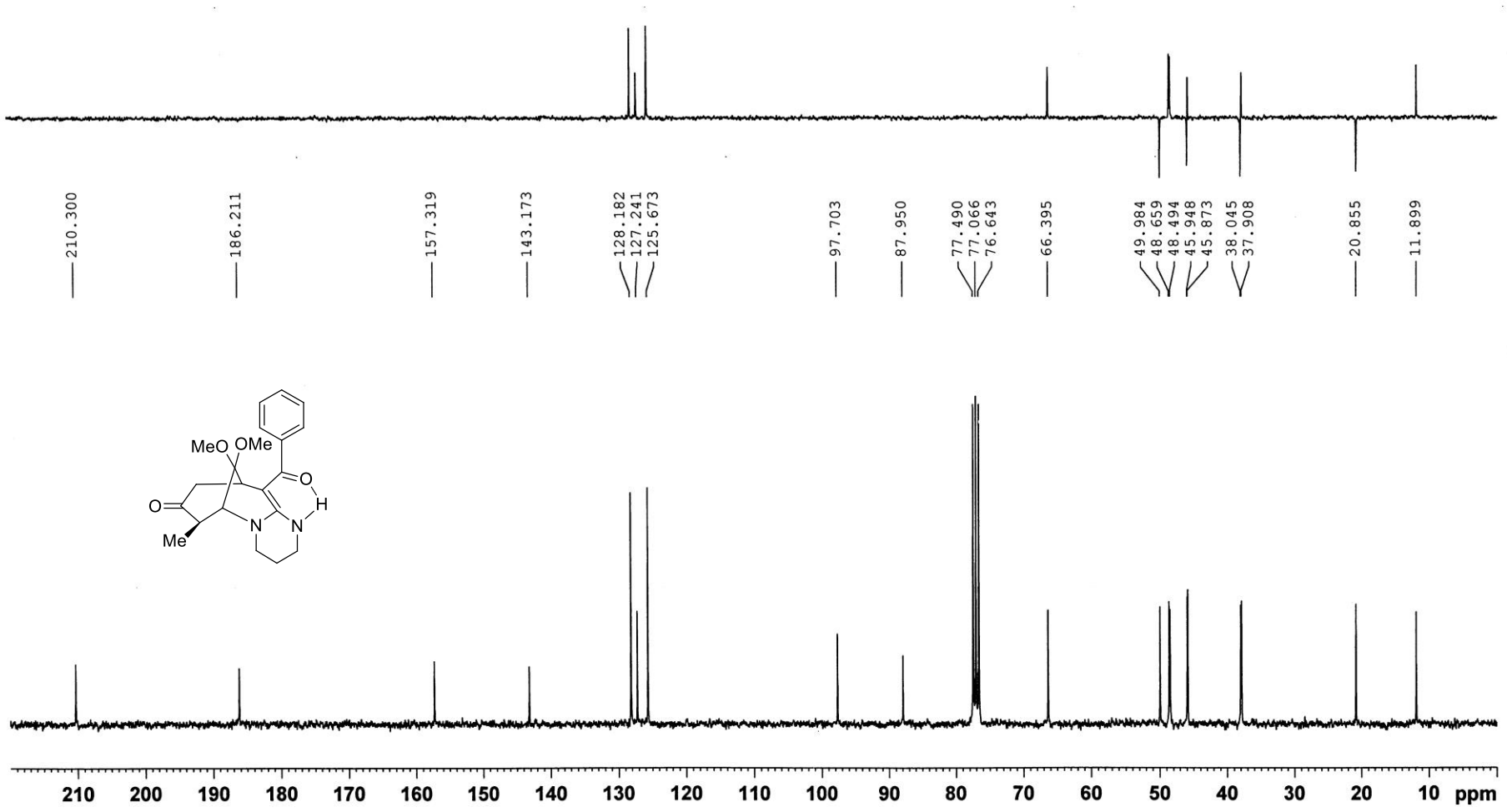


Figure 76. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3l'**

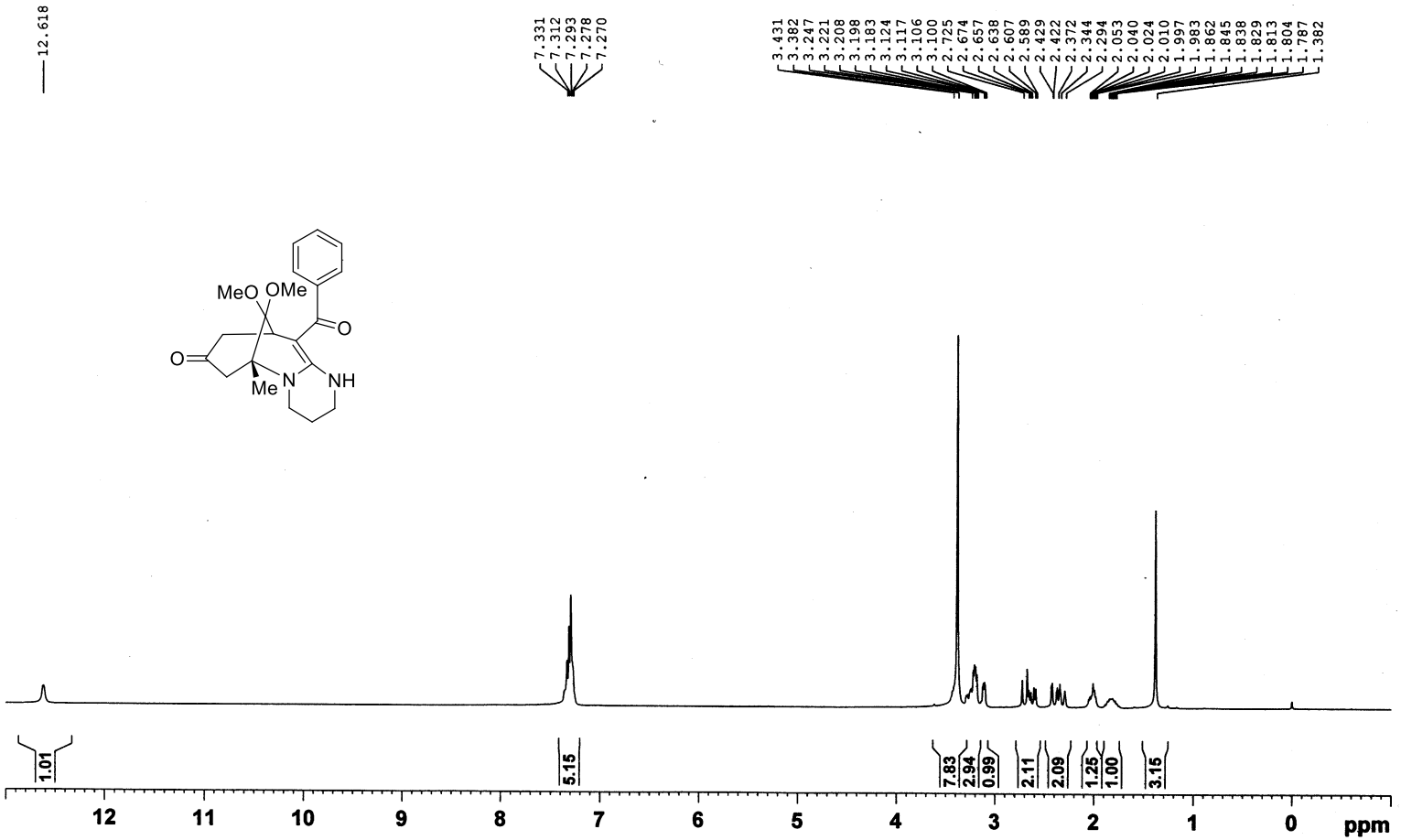


Figure 77. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3m'**

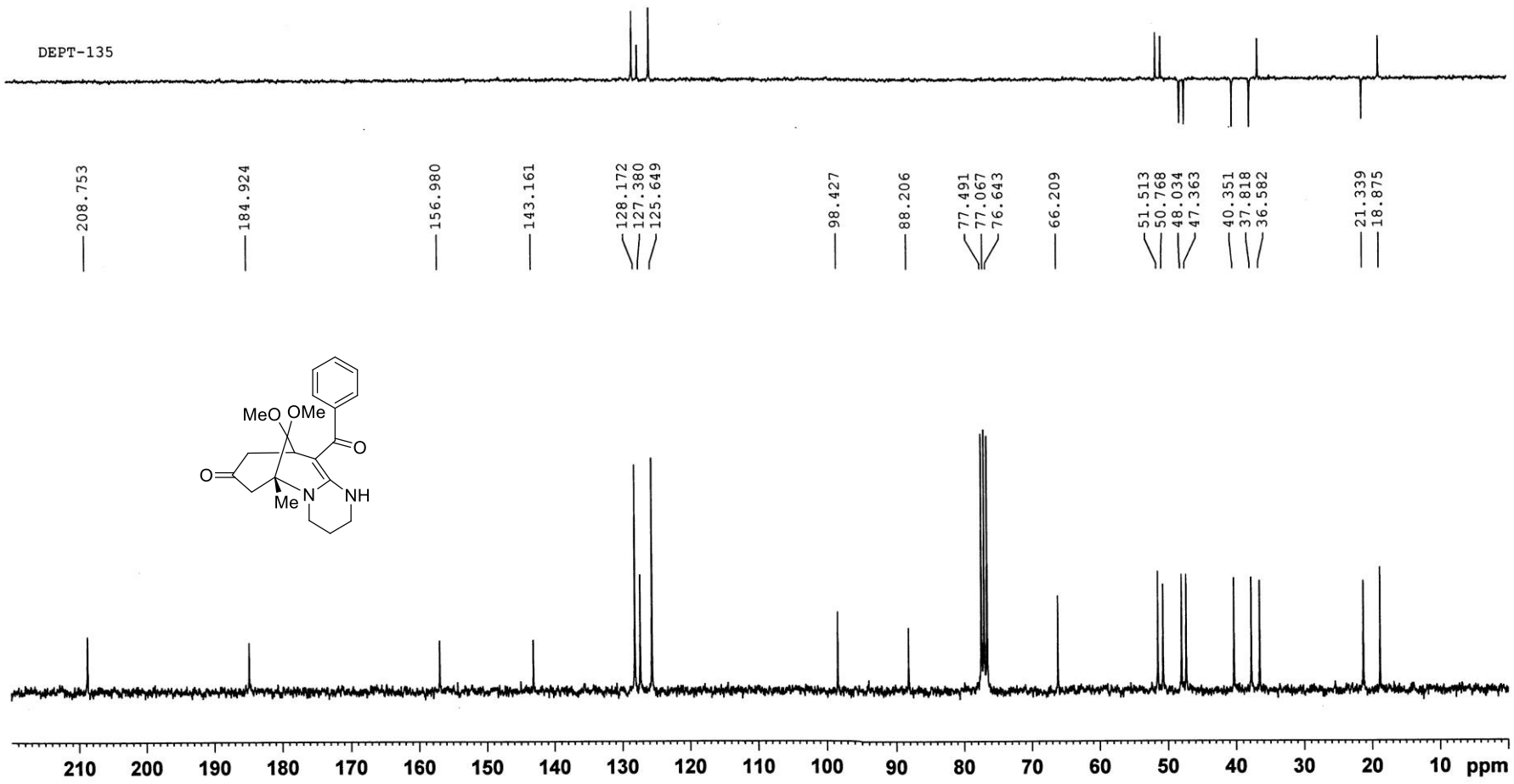


Figure 78. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3m'**

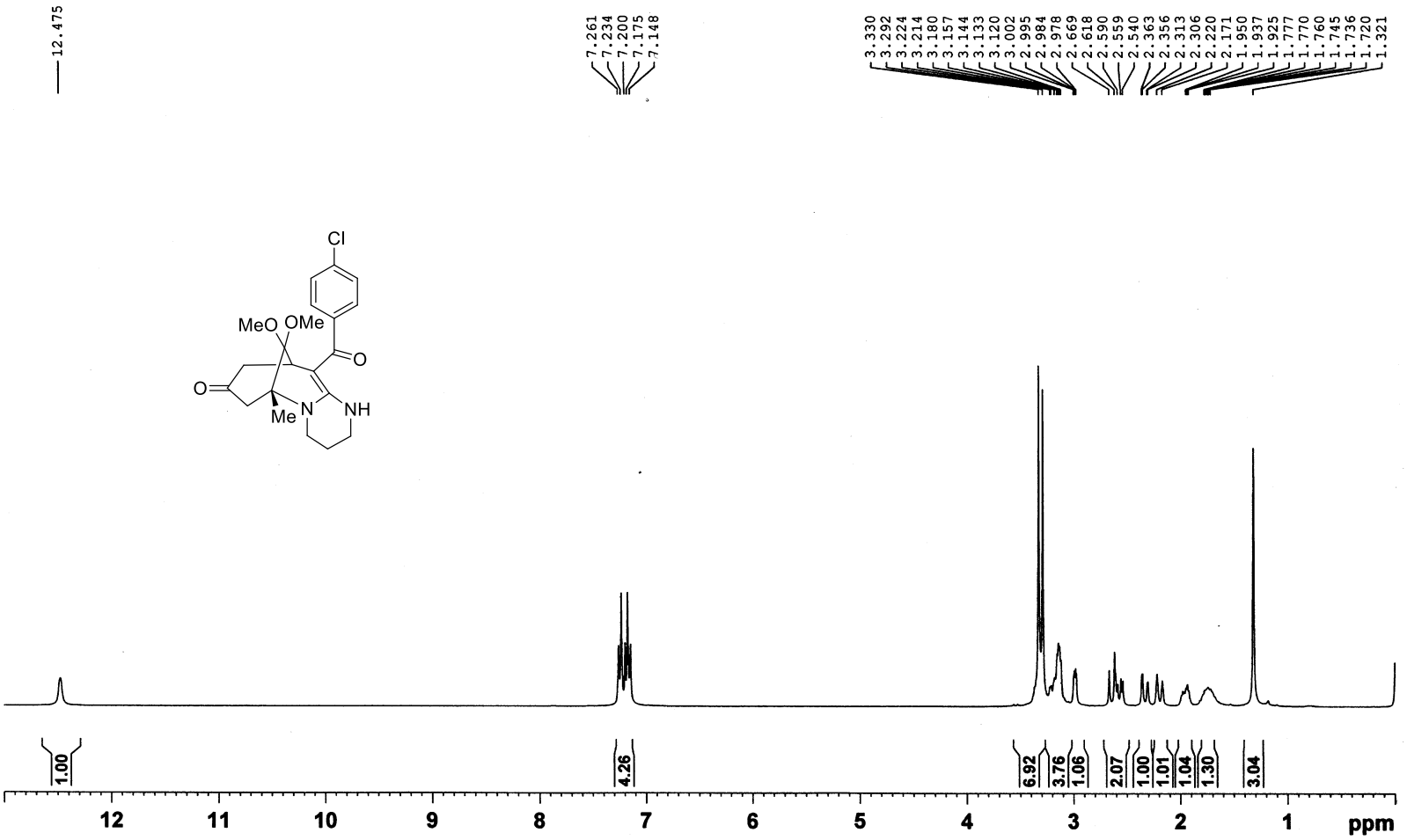


Figure 79. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **3n'**

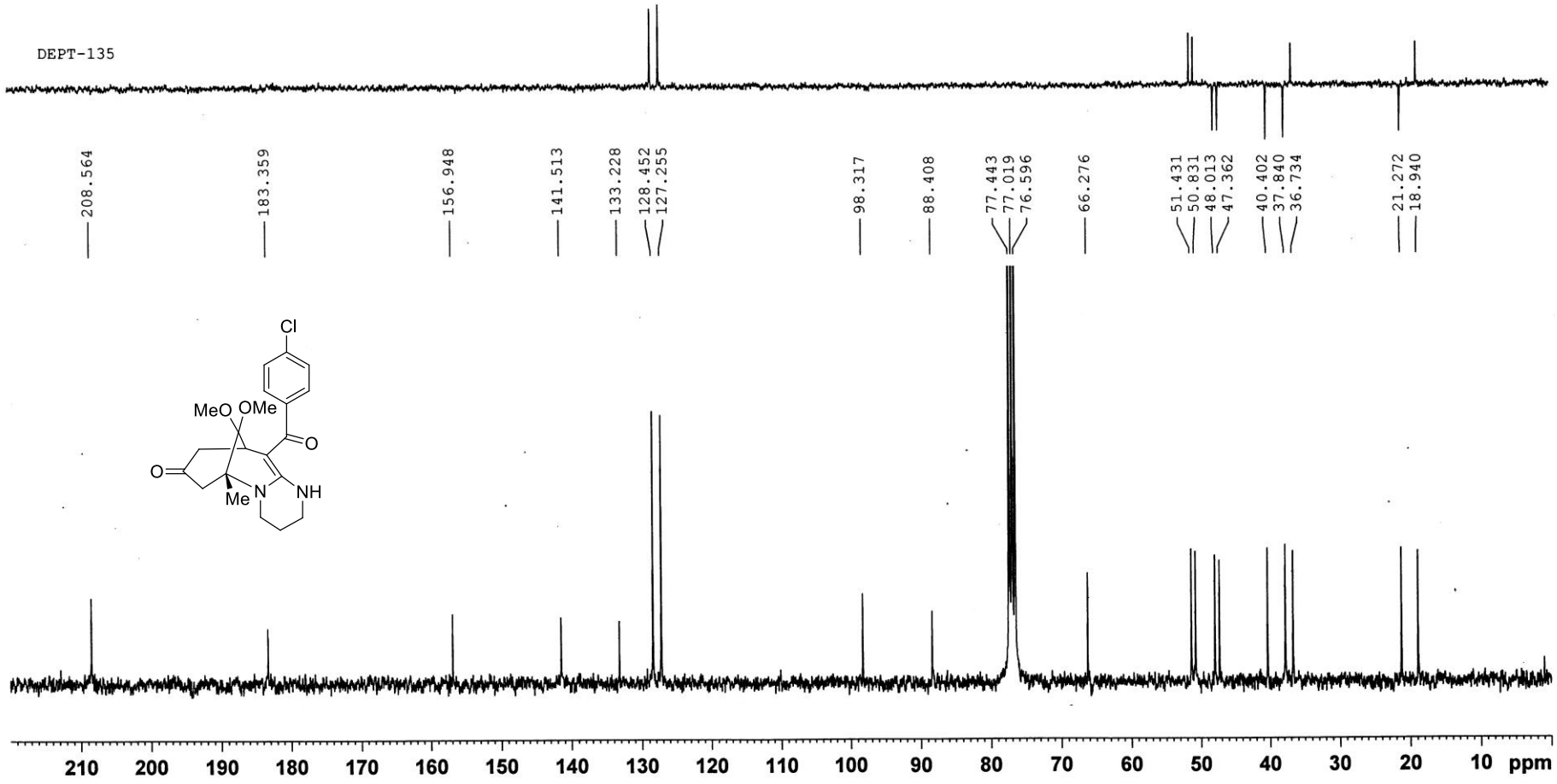


Figure 80. ^{13}C NMR (75 MHz, $CDCl_3$) spectra of compound **3n'**

References and Notes

1. *a*) A. Pelter, S. Elgendy, *Tetrahedron Lett*. **1988**, *29*, 677–680. *b*) A. S. Mitchell, R. A. Russell, *Tetrahedron* **1997**, *53*, 4387–4410. *c*) L. C. Konkol, F. Guo, A. A. Sarjeant, R. J. Thomson, *Angew. Chem. Int. Ed.* **2011**, *50*, 9931–9934.
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7. CCDC 1547075, CCDC 1547077 ＆ CCDC 1547076 contain the supplementary crystallographic data for compound **3j**, **3l'** ＆ **3n'**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.