Regioselective Synthesis of 9,10-Dihydro-6*H*-chromeno[4,3-*d*]imidazo -[1,2-*a*]pyridin-6-one Derivatives†

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Supporting Information

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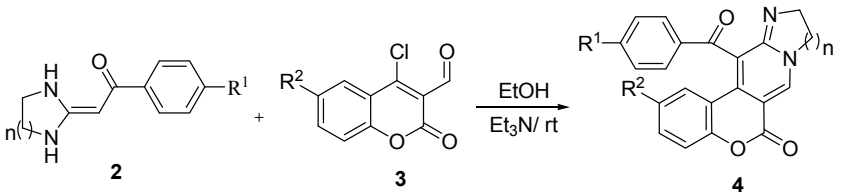
General Information

All compounds were fully characterized by spectroscopic data. The NMR spectra were recorded on a Bruker 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/Msd TOF instrument.

All chemicals and solvents were used as received without further purification unless otherwise stated.

The substrates **2** were synthesized according to the literature.[1] Compounds **3** was prepared according to the literature.[2]

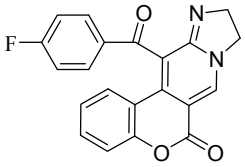
General Procedure for Regioselective Synthesis of 9,10-Dihydro-6*H*-chromeno-[4,3-*d*]imidazo[1,2-*a*]pyridin-6-ones 4



HKA derivatives **2** (0.5 mmol), 4-chloro-2-oxo-2*H*-chromene-3-carbaldehyde derivatives **3** (0.5 mmol) and ethanol (15 ml) were placed into a 25 mL round-bottom flask and the mixture was stirred at room temperature for 10 minutes. Upon completion, as monitored by TLC, trimethylamine (10 mmol%) was added and the mixture was stirred at room temperature for 5 minutes. Then the reaction mixture was cooled to room temperature and filtered to give the pure crude product, which was further washed with 95% EtOH to give pure product **4** with a yield of 80–96%. The products were further identified by FTIR, NMR and HRMS, and were found to be in good agreement with the assigned structures.

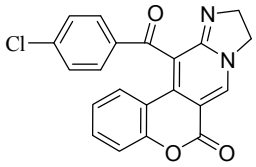
Spectroscopic Data of 9,10-Dihydro-6*H*-chromeno[4,3-*d*]imidazo[1,2-*a*]pyridin-6-ones 4

12-(4-Fluorobenzoyl)-9,10-dihydro-6*H*-chromeno[4,3-*d*]imidazo[1,2-*a*]pyridin-6-one (4a)



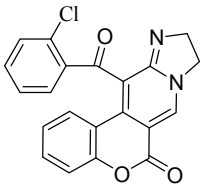
Orange solid; Mp 291–294 °C; IR (KBr): 1719, 1669, 1622, 1511, 1327, 1273, 1224, 1147, 1086, 1004, 751 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 4.10–4.12 (m, 2H, NCH_2), 4.25–4.29 (m, 2H, NCH_2), 6.97–7.00 (m, 1H, ArH), 7.20–7.24 (m, 3H, ArH), 7.41–7.46 (m, 2H, ArH), 8.15–8.18 (m, 2H, ArH), 8.50 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6+$CDCl_3$): δ = 49.1, 53.5, 98.8, 115.6, 116.6, 116.8, 118.4, 124.5, 126.9, 132.4, 132.4, 132.4, 132.6, 134.9, 145.9, 152.4, 155.0, 159.3, 165.2, 167.2, 194.1; HRMS (TOF ES^+): *m/z* calcd for $C_{21}H_{13}FN_2O_3$ [$(M+H)^+$], 361.0983; found, 361.0989.

12-(4-Chlorobenzoyl)-9,10-dihydro-6*H*-chromeno[4,3-*d*]imidazo[1,2-*a*]pyridin-6-one (4b)



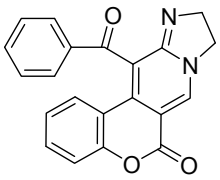
Orange solid; Mp 301–304 °C; IR (KBr): 1719, 1674, 1622, 1523, 1454, 1274, 1213, 1094, 1000, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 4.10–4.12 (m, 2H, NCH_2), 4.24–4.28 (m, 2H, NCH_2), 6.98–7.00 (m, 1H, ArH), 7.23–7.25 (m, 1H, ArH), 7.42–7.45 (m, 2H, ArH), 7.52–7.53 (m, 2H, ArH), 8.07–8.09 (m, 2H, ArH), 8.50 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6+$CDCl_3$): δ = 49.2, 53.5, 98.8, 115.4, 115.6, 118.5, 124.6, 126.9, 129.8, 131.2, 132.8, 134.5, 140.0, 146.0, 152.5, 155.0, 159.2, 194.5; HRMS (TOF ES^+): *m/z* calcd for $C_{21}H_{13}ClN_2O_3$ [$(M+H)^+$], 377.0687; found, 377.0689.

12-(2-Chlorobenzoyl)-9,10-dihydro-6*H*-chromeno[4,3-*d*]imidazo[1,2-*a*]pyridin-6-one (4c)



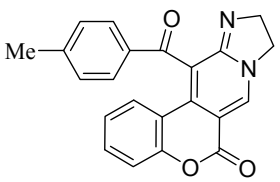
Yellow solid; Mp 256–258 °C; IR (KBr): 1695, 1592, 1504, 1422, 1375, 1282, 1196, 1046, 755 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6+$CDCl_3$): δ = 4.03–4.07 (m, 2H, CH_2), 4.84–4.88 (m, 2H, CH_2), 7.13–7.16 (m, 1H, ArH), 7.26–7.29 (m, 1H, ArH), 7.34–7.36 (d, J = 8.15 Hz, 1H, ArH), 7.47–7.49 (d, J = 8.05 Hz,, 1H, ArH), 7.54–7.62 (m, 2H, ArH), 7.78–7.79 (d, J = 7.75 Hz, 1H, ArH), 8.17 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6+$CDCl_3$): δ = 44.7, 51.5, 97.8, 112.1, 114.2, 118.7, 124.6, 127.8, 128.9, 132.1, 133.9, 134.2, 135.4, 135.6, 146.2, 153.1, 155.1, 157.6, 162.7, 194.5; HRMS (TOF ES^+): *m/z* calcd for $C_{21}H_{13}ClN_2O_3$ [$(M+H)^+$], 377.0687; found, 377.0681.

12-Benzoyl-9,10-dihydro-6*H*-chromeno[4,3-*d*]imidazo[1,2-*a*]pyridin-6-one (4d)



Orange solid; Mp 272–275 °C; IR (KBr): 1719, 1669, 1617, 1521, 1450, 1327, 1273, 1216, 1145, 1104, 743 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 3.77–3.79 (m, 2H, NCH_2), 4.17–4.21 (m, 2H, NCH_2), 7.01 (m, 1H, ArH), 7.23–7.25 (m, 1H, ArH), 7.28–7.29 (m, 1H, ArH), 7.43–7.45 (m, 1H, ArH), 7.54–7.57 (m, 2H, ArH), 7.68–7.69 (m, 1H, ArH), 8.01–8.03 (d, J = 7.80 Hz, 2H, ArH), 8.68 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 49.1, 53.4, 98.6, 115.6, 116.0, 118.6, 124.6, 126.9, 129.5, 129.5, 129.7, 129.7, 132.8, 134.7, 134.9, 135.7, 146.0, 152.4, 155.0, 159.4, 195.8; HRMS (TOF ES^+): *m/z* calcd for $C_{21}H_{14}N_2O_3$ [$(M+H)^+$], 343.1077; found, 343.1080.

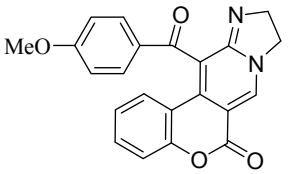
12-(4-Methylbenzoyl)-9,10-dihydro-6*H*-chromeno[4,3-*d*]imidazo[1,2-*a*]pyridin-6-one (4e)



Orange solid; Mp 271–274 °C; IR (KBr): 1724, 1664, 1618, 1519, 1450, 1323, 1271, 1222, 1139, 1094, 755 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 2.37 (s, 3H, CH_3),

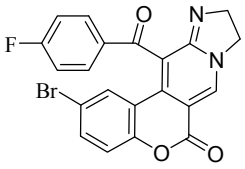
3.77 (m, 2H, CH_2), 4.17–4.21 (m, 2H, CH_2), 6.99–7.02 (m, 1H, ArH), 7.22–7.24 (d, *J* = 8.10 Hz, 1H, ArH), 7.30–7.32 (d, *J* = 8.20 Hz, 1H, ArH), 7.34–7.35 (d, *J* = 7.80 Hz, 2H, ArH), 7.42–7.45 (m, 1H, ArH), 7.89–7.91 (d, *J* = 7.85 Hz, 2H, ArH), 8.66 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 21.7, 49.1, 53.4, 98.6, 115.7, 116.2, 118.5, 124.6, 126.9, 129.6, 129.6, 130.3, 130.3, 132.8, 133.4, 134.4, 145.7, 145.9, 152.4, 155.0, 159.4, 195.2; HRMS (TOF ES$^+$): *m/z* calcd for $C_{22}H_{16}N_2O_3$ [(M+H)$^+$], 357.1234; found, 357.1233.

12-(4-Methoxybenzoyl)-9,10-dihydro-6*H*-chromeno[4,3-*d*]imidazo[1,2-*a*]pyridin-6-one (4f)



Orange solid; Mp 224–227 °C; IR (KBr): 1724, 1618, 1519, 1458, 1323, 1268, 1155, 1012, 763 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.76–3.80 (m, 2H, CH_2), 3.85 (s, 3H, OCH_3), 4.20 (m, 2H, CH_2), 7.01–7.07 (m, 3H, ArH), 7.23–7.25 (d, *J* = 8.45 Hz, 1H, ArH), 7.35–7.36 (d, *J* = 8.25 Hz, 1H, ArH), 7.43–7.46 (m, 1H, ArH), 7.97–7.98 (d, *J* = 7.00 Hz, 2H, ArH), 8.68 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 49.1, 53.4, 56.0, 98.6, 115.0, 115.0, 115.8, 116.5, 118.5, 124.6, 127.0, 128.9, 131.9, 131.9, 132.7, 134.2, 145.8, 152.4, 155.0, 159.4, 164.6, 194.0; HRMS (TOF ES$^+$): *m/z* calcd for $C_{22}H_{16}N_2O_4$ [(M+H)$^+$], 373.1183; found, 373.1189.

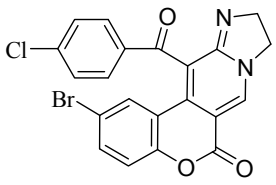
2-Bromo-12-(4-fluorobenzoyl)-9,10-dihydro-6*H*-chromeno[4,3-*d*]imidazo[1,2-*a*]-pyridin-6-one (4g)



Orange solid; Mp 296–299 °C; IR (KBr): 1721, 1669, 1623, 1513, 1327, 1224, 1145, 959, 829 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6+$CDCl_3$): δ = 3.79–3.83 (m, 2H, CH_2), 4.19–4.23 (m, 2H, CH_2), 7.18–7.20 (d, *J* = 8.70 Hz, 2H, ArH), 7.35–7.39 (m, 3H, ArH), 7.58–7.60 (d, *J* = 8.60 Hz, 1H, ArH), 8.10–8.13 (m, 2H, ArH), 8.67 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6+$CDCl_3$): δ = 49.2, 53.6, 98.2, 116.1, 116.9, 117.1, 117.6, 120.8, 129.1, 132.4, 132.5, 132.5, 133.5, 135.2, 146.3, 151.6, 154.8, 158.8,

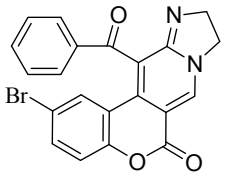
165.5, 167.7, 194.1; HRMS (TOF ES$^+$): *m/z* calcd for $C_{21}H_{12}BrFN_2O_3$ [(M+H)$^+$], 439.0088; found, 439.0090.

2-Bromo-12-(4-chlorobenzoyl)-9,10-dihydro-6*H*-chromeno[4,3-*d*]imidazo[1,2-*a*]pyridin-6-one (4h)



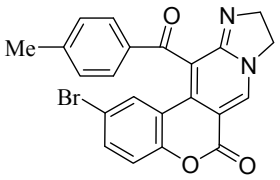
Orange solid; Mp 302–305 °C; IR (KBr): 1714, 1669, 1622, 1523, 1458, 1331, 1272, 1213, 1094, 963, 653 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.80 (m, 2H, CH_2), 4.21 (m, 2H, CH_2), 7.22–7.24 (d, J = 8.80 Hz, 1H, ArH), 7.35–7.36 (m, 1H, ArH), 7.55 (m, 1H, ArH), 7.63–7.66 (m, 3H, ArH), 8.04–8.06 (d, J = 8.40 Hz, 1H, ArH), 8.71 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 49.2, 53.5, 98.4, 115.8, 116.0, 120.9, 128.5, 129.0, 130.1, 130.1, 130.4, 131.3, 131.3, 134.3, 135.3, 140.2, 146.4, 151.7, 154.8, 158.8, 194.6; HRMS (TOF ES$^+$): *m/z* calcd for $C_{21}H_{12}BrClN_2O_3$ [(M+H)$^+$], 454.9793; found, 454.9795.

12-Benzoyl-2-bromo-9,10-dihydro-6*H*-chromeno[4,3-*d*]imidazo[1,2-*a*]pyridin-6-one (4i)



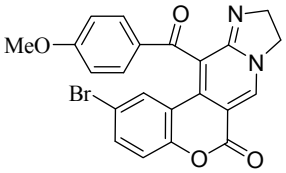
Orange solid; Mp 302.5–305 °C; IR (KBr): 1719, 1667, 1618, 1521, 1450, 1326, 1269, 1217, 1109, 963, 751 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.80 (m, 2H, CH_2), 4.19–4.21 (m, 2H, CH_2), 7.19–7.20 (m, 1H, ArH), 7.42 (s, 1H, ArH), 7.57–7.59 (m, 3H, ArH), 7.72 (m, 1H, ArH), 8.03–8.04 (m, 2H, ArH), 8.67 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 49.2, 53.6, 98.2, 116.0, 116.6, 117.7, 120.8, 129.2, 129.4, 129.4, 129.8, 129.8, 133.4, 135.2, 135.2, 135.6, 146.3, 151.7, 154.8, 158.9, 195.6; HRMS (TOF ES$^+$): *m/z* calcd for $C_{21}H_{13}BrN_2O_3$ [(M+H)$^+$], 421.0182; found, 421.0186.

2-Bromo-12-(4-methylbenzoyl)-9,10-dihydro-6*H*-chromeno[4,3-*d*]imidazo[1,2-*a*]pyridin-6-one (4j)



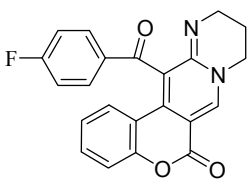
Orange solid; Mp 308–311 °C; IR (KBr): 1719, 1663, 1618, 1515, 1475, 1417, 1335, 1271, 1216, 1111, 967 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 2.40 (s, 3H, CH_3), 3.79 (m, 2H, CH_2), 4.18–4.22 (m, 2H, CH_2), 7.20–7.22 (d, J = 8.75 Hz, 1H, ArH), 7.37–7.38 (d, J = 7.60 Hz, 2H, ArH), 7.43 (s, 1H, ArH), 7.61–7.62 (d, J = 8.70 Hz, 1H, ArH), 7.91–7.93 (d, J = 7.45 Hz, 2H, ArH), 8.68 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 21.7, 49.2, 53.5, 98.1, 116.0, 116.9, 117.7, 120.8, 129.2, 129.5, 129.5, 130.4, 130.4, 133.1, 133.2, 135.1, 146.0, 146.2, 151.6, 154.8, 158.9, 195.1; HRMS (TOF ES^+): *m/z* calcd for $C_{22}H_{15}BrN_2O_3$ [$(M+H)^+$], 435.0339; found, 435.0335

2-Bromo-12-(4-methoxybenzoyl)-9,10-dihydro-6*H*-chromeno[4,3-*d*]imidazo[1,2-*a*]pyridin-6-one (4k)



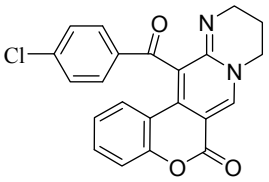
Orange solid; Mp 295–298 °C; IR (KBr): 1719, 1659, 1618, 1514, 1460, 1405, 1325, 1267, 1219, 1155, 1129, 1033, 955, 829 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 3.82 (m, 2H, CH_2), 3.85 (s, 3H, OCH_3), 4.20 (m, 2H, CH_2), 7.07–7.08 (d, J = 7.65 Hz, 2H, ArH), 7.17–7.19 (d, J = 8.40 Hz, 1H, ArH), 7.48 (s, 1H, ArH), 7.58–7.60 (d, J = 8.00 Hz, 1H, ArH), 7.99–8.01 (d, J = 7.60 Hz, 2H, ArH), 8.66 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 49.2, 53.6, 56.1, 98.1, 115.1, 115.1, 116.0, 117.1, 117.8, 120.7, 128.7, 129.3, 131.9, 131.9, 132.9, 135.0, 146.0, 151.6, 154.9, 158.9, 164.8, 193.7; HRMS (TOF ES^+): *m/z* calcd for $C_{22}H_{15}BrN_2O_4$ [$(M+H)^+$], 451.0288; found, 451.0285.

10,11-Dihydro-13-(4-fluorobenzoyl)-12-azachromeno[4,3-*b*]quinolizin-6(9*H*)-one (4l)



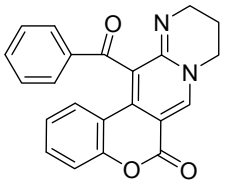
Yellow solid; Mp 284–287 °C; IR (KBr): 3422, 1720, 1677, 1617, 1550, 1485, 1301, 1232, 1149, 1099, 751 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 1.82 (m, 2H, CH_2), 3.23 (m, 2H, CH_2), 4.09 (m, 2H, CH_2), 6.96–6.97 (m, 1H, ArH), 7.16–7.18 (d, J = 7.70 Hz, 1H, ArH), 7.26–7.28 (m, 3H, ArH), 7.37–7.38 (m, 1H, ArH), 8.05 (m, 2H, ArH), 8.35 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 19.8, 44.4, 50.5, 98.4, 115.5, 116.6, 116.5, 118.4, 123.4, 124.5, 126.8, 130.7, 132.0, 132.0, 132.2, 133.2, 147.8, 148.3, 152.3, 159.5, 164.8–166.8(d, J = 251.30 Hz), 195.3; HRMS (TOF ES^+): *m/z* calcd for $C_{22}H_{15}FN_2O_3$ [$(M+H)^+$], 375.1139; found, 375.1147.

10,11-Dihydro-13-(4-chlorobenzoyl)-12-azachromeno[4,3-*b*]quinolizin-6(9*H*)-one (4m)



Yellow solid; Mp 293–296 °C; IR (KBr): 3419, 1720, 1677, 1617, 1535, 1450, 1303, 1229, 1155, 1097, 747 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 1.82 (m, 2H, CH_2), 3.26 (m, 2H, CH_2), 4.09 (m, 2H, CH_2), 7.01 (m, 1H, ArH), 7.21–7.23 (d, J = 7.20 Hz, 1H, ArH), 7.26–7.27 (d, J = 7.00 Hz, 1H, ArH), 7.43 (m, 1H, ArH), 7.57–7.58 (d, J = 6.80 Hz, 2H, ArH), 7.99–8.00 (d, J = 6.75 Hz, 2H, ArH), 8.35 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 19.8, 44.4, 50.5, 98.3, 115.5, 118.6, 123.1, 124.7, 126.7, 129.7, 129.7, 130.8, 130.8, 130.8, 132.4, 135.3, 139.2, 147.8, 148.4, 152.3, 159.5, 195.8; HRMS (TOF ES^+): *m/z* calcd for $C_{22}H_{15}ClN_2O_3$ [$(M+H)^+$], 391.0844; found, 391.0847.

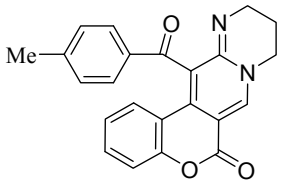
10,11-Dihydro-13-benzoyl-12-azachromeno[4,3-*b*]quinolizin-6(9*H*)-one (4n)



Yellow solid; Mp 261–264 °C; IR (KBr): 3436, 1695, 1593, 1501, 1374, 1279, 1184, 1052, 743 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 1.78–1.79 (m, 2H, CH_2), 3.28 (m, 1H, CH_2), 4.07–4.13 (m, 3H, CH_2), 6.96 (m, 1H, ArH), 7.19–7.20 (d, J = 8.25 Hz, 1H, ArH), 7.27–7.28 (d, J = 8.05 Hz, 1H, ArH), 7.39 (m, 1H, ArH), 7.49–7.52 (m, 2H, ArH), 7.63 (m, 1H, ArH), 7.97–7.99 (d, J = 7.65 Hz, 2H, ArH), 8.35 (s, 1H, CH); ^{13}C

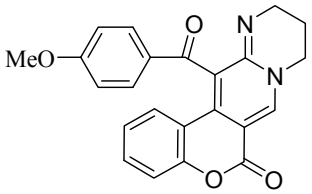
NMR (125 MHz, DMSO-d_6): δ = 19.8, 44.4, 50.4, 98.2, 115.6, 118.5, 123.7, 124.6, 126.8, 129.2, 129.2, 129.6, 129.6, 130.5, 132.3, 134.3, 136.5, 147.8, 148.3, 152.2, 159.6, 196.9; HRMS (TOF ES$^+$): *m/z* calcd for $C_{22}H_{16}N_2O_3$ [(M+H)$^+$], 357.1234; found, 357.1243.

10,11-Dihydro-13-(4-methylbenzoyl)-12-azachromeno[4,3-*b*]quinolizin-6(9*H*)-one (4o)



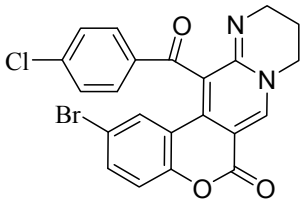
Yellow solid; Mp 279–282 °C; IR (KBr): 1720, 1677, 1535, 1450, 1303, 1229, 1155, 1097, 747 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.83 (m, 2H, CH_2), 2.37 (s, 3H, CH_3), 3.33 (m, 1H, CH_2), 4.08–4.10 (m, 3H, CH_2), 6.92–6.95 (m, 1H, ArH), 7.16–7.17 (m, *J* = 8.20 Hz, 1H, ArH), 7.28–7.33 (m, 3H, ArH), 7.36–7.39 (m, 1H, ArH), 7.86–7.87 (m, *J* = 7.95 Hz, 2H, ArH), 8.32 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 19.8, 21.6, 44.4, 50.5, 98.3, 115.6, 118.4, 124.0, 124.4, 127.0, 129.1, 129.1, 130.0, 130.0, 130.3, 132.1, 134.1, 144.7, 147.8, 148.1, 152.2, 159.6, 196.3; HRMS (TOF ES$^+$): *m/z* calcd for $C_{23}H_{18}N_2O_3$ [(M+H)$^+$], 371.1390; found, 371.1389.

10,11-Dihydro-13-(4-methoxybenzoyl)-12-azachromeno[4,3-*b*]quinolizin-6(9*H*)-one (4p)



Yellow solid; Mp 259–262 °C; IR (KBr): 1723, 1663, 1613, 1455, 1312, 1243, 1157, 1098, 1029, 747 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.79–1.80 (m, 2H, CH_2), 3.19–3.22 (m, 2H, CH_2), 3.82 (s, 3H, OCH_3), 4.08 (m, 2H, CH_2), 6.96–7.03 (m, 3H, ArH), 7.19–7.21 (d, *J* = 8.10 Hz, 1H, ArH), 7.34–7.35 (d, *J* = 8.20 Hz, 1H, ArH), 7.38–7.41 (m, 1H, ArH), 7.93–7.95 (d, *J* = 8.30 Hz, 1H, ArH), 8.34 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 19.8, 44.4, 50.5, 55.9, 98.1, 114.8, 114.8, 115.7, 118.5, 124.1, 124.6, 129.6, 129.6, 130.0, 131.4, 131.4, 132.2, 147.7, 148.2, 152.2, 159.6, 164.1, 195.2; HRMS (TOF ES$^+$): *m/z* calcd for $C_{23}H_{18}N_2O_4$ [(M+H)$^+$], 387.1339; found, 387.1340.

10,11-Dihydro-2-bromo-13-(4-chlorobenzoyl)-12-azachromeno[4,3-*b*]quinolizin-6(9*H*)-one (4q)



Yellow solid; Mp 305–308 °C; IR (KBr): 1711, 1677, 1616, 1450, 1303, 1198, 1149, 1119, 1004, 820 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 1.81 (m, 2H, CH_2), 3.22 (m, 2H, CH_2), 4.09 (m, 2H, CH_2), 7.20–7.21 (d, J = 8.20 Hz, 1H, ArH), 7.35 (s, 1H, ArH), 7.61–7.63 (m, 3H, ArH), 8.01–8.02 (d, J = 7.05 Hz, 2H, ArH), 8.37 (s, 1H, CH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 19.7, 44.4, 50.5, 97.8, 116.1, 117.5, 120.9, 123.7, 128.9, 129.6, 129.9, 129.9, 130.8, 130.8, 134.8, 135.0, 139.5, 147.7, 148.7, 151.5, 159.1, 195.7; HRMS (TOF ES^+): *m/z* calcd for $C_{22}H_{14}BrClN_2O_3$ $[(M+H)^+]$, 468.9949; found, 468.9950.

X-ray Structure and Data[3] of 4d

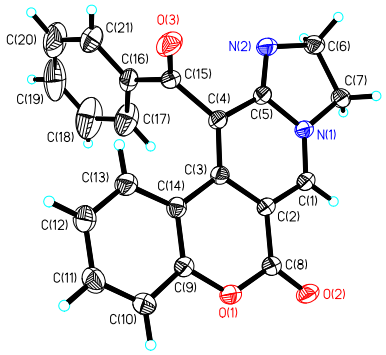


Figure S1 X-Ray crystal structure of **4d**

Table S1 Crystal data and structure refinement for **4d**

Empirical formula	$C_{21}H_{14}N_2O_3$	
Formula weight	342.34	
Temperature	298(2) K	
Wavelength	0.71073	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 5.5189(8) A	alpha = 93.688(2) deg.
	b = 9.8023(15) A	beta = 92.037(2) deg.
	c = 15.110(2) A	gamma = 90.788(2) deg.
Volume	815.1(2)	
Z, Calculated density	2, 1.395 Mg/m^3	
Absorption coefficient	0.095 mm^-1	
F(000)	356	
Crystal size	0.30 x 0.21 x 0.13 mm	
Theta range for data collection	0.9721 to 0.9878 deg.	
Limiting indices	-6<=h<=6, -11<=k<=11, -17<=l<=17	
Reflection collected/unique	13201 / 4601 [R(int) = 0.0509]	
Completeness to theta = 28.40	99.6 %	
Absorption correction	multi-scan from equivalents	
Max. and min. transmission	0.988 and 0.972	
Refinement method	SHELXL-97	
Data/restraints/parameters	2865 / 0 / 236	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0785, wR2 = 0.1234	
R indices (all data)	R1 = 0.0446, wR2 = 0.1099	
Extinction coefficient	0.009(3)	
Largest diff. peak and hole	0.157 and -0.183 e.A^-3	

Table S2 Bond lengths [A] and angles [deg] for **4d**

N(1)-C(1)	1.324(2)
N(1)-C(5)	1.409(2)
N(1)-C(7)	1.474(2)
N(2)-C(5)	1.281(2)
N(2)-C(6)	1.475(2)
O(1)-C(8)	1.375(2)
O(1)-C(9)	1.386(2)
O(2)-C(8)	1.208(2)
O(3)-C(15)	1.213(2)
C(1)-C(2)	1.378(2)
C(1)-H(1)	0.9300
C(2)-C(3)	1.444(2)
C(2)-C(8)	1.445(2)
C(3)-C(4)	1.379(2)
C(3)-C(14)	1.480(2)
C(4)-C(5)	1.448(2)
C(4)-C(15)	1.514(2)
C(6)-C(7)	1.533(3)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(9)-C(10)	1.390(3)
C(9)-C(14)	1.397(3)
C(10)-C(11)	1.372(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.385(3)
C(11)-H(11)	0.9300
C(12)-C(13)	1.376(3)
C(12)-H(12)	0.9300
C(13)-C(14)	1.401(2)
C(13)-H(13)	0.9300
C(15)-C(16)	1.490(3)
C(16)-C(17)	1.375(3)
C(16)-C(21)	1.375(3)
C(17)-C(18)	1.389(4)
C(17)-H(17)	0.9300
C(18)-C(19)	1.366(4)
C(18)-H(18)	0.9300
C(19)-C(20)	1.356(5)
C(19)-H(19)	0.9300
C(20)-C(21)	1.380(4)
C(20)-H(20)	0.9300
C(21)-H(21)	0.9300

Symmetry transformations used to generate equivalent atoms:

Table S3 Torsion angles [deg] for **4d**

C(5)-N(1)-C(1)-C(2)	-2.2(3)
C(7)-N(1)-C(1)-C(2)	179.22(17)
N(1)-C(1)-C(2)-C(3)	1.7(3)
N(1)-C(1)-C(2)-C(8)	179.68(17)
C(1)-C(2)-C(3)-C(4)	1.4(3)
C(8)-C(2)-C(3)-C(4)	-176.39(18)
C(1)-C(2)-C(3)-C(14)	-178.88(16)
C(8)-C(2)-C(3)-C(14)	3.3(3)
C(2)-C(3)-C(4)-C(5)	-4.0(3)
C(14)-C(3)-C(4)-C(5)	176.32(16)
C(2)-C(3)-C(4)-C(15)	173.04(17)
C(14)-C(3)-C(4)-C(15)	-6.6(3)
C(6)-N(2)-C(5)-N(1)	3.6(2)
C(6)-N(2)-C(5)-C(4)	-175.27(18)
C(1)-N(1)-C(5)-N(2)	-179.42(18)
C(7)-N(1)-C(5)-N(2)	-0.6(2)
C(1)-N(1)-C(5)-C(4)	-0.4(3)
C(7)-N(1)-C(5)-C(4)	178.43(15)
C(3)-C(4)-C(5)-N(2)	-177.56(19)
C(15)-C(4)-C(5)-N(2)	4.9(3)
C(3)-C(4)-C(5)-N(1)	3.6(3)
C(15)-C(4)-C(5)-N(1)	-173.94(16)
C(5)-N(2)-C(6)-C(7)	-5.1(2)
C(1)-N(1)-C(7)-C(6)	176.21(18)
C(5)-N(1)-C(7)-C(6)	-2.5(2)
N(2)-C(6)-C(7)-N(1)	4.5(2)
C(9)-O(1)-C(8)-O(2)	179.93(17)
C(9)-O(1)-C(8)-C(2)	0.4(3)
C(1)-C(2)-C(8)-O(2)	-0.1(3)
C(3)-C(2)-C(8)-O(2)	177.79(19)
C(1)-C(2)-C(8)-O(1)	179.42(15)
C(3)-C(2)-C(8)-O(1)	-2.7(3)
C(8)-O(1)-C(9)-C(10)	-177.68(16)
C(8)-O(1)-C(9)-C(14)	1.2(3)
O(1)-C(9)-C(10)-C(11)	177.84(18)
C(14)-C(9)-C(10)-C(11)	-1.0(3)
C(9)-C(10)-C(11)-C(12)	0.7(3)
C(10)-C(11)-C(12)-C(13)	-0.1(3)
C(11)-C(12)-C(13)-C(14)	-0.3(3)
O(1)-C(9)-C(14)-C(13)	-178.15(17)
C(10)-C(9)-C(14)-C(13)	0.6(3)
O(1)-C(9)-C(14)-C(3)	-0.4(3)
C(10)-C(9)-C(14)-C(3)	178.32(16)
C(12)-C(13)-C(14)-C(9)	0.1(3)
C(12)-C(13)-C(14)-C(3)	-177.48(18)?
C(4)-C(3)-C(14)-C(9)	177.97(18)
C(2)-C(3)-C(14)-C(9)	-1.7(2)

C(4)-C(3)-C(14)-C(13)	-4.5(3)
C(2)-C(3)-C(14)-C(13)	175.80(18)
C(3)-C(4)-C(15)-O(3)	99.4(2)
C(5)-C(4)-C(15)-O(3)	-83.3(2)
C(3)-C(4)-C(15)-C(16)	-84.0(2)
C(5)-C(4)-C(15)-C(16)	93.3(2)
O(3)-C(15)-C(16)-C(17)	-171.2(2)
C(4)-C(15)-C(16)-C(17)	12.2(3)
O(3)-C(15)-C(16)-C(21)	7.3(3)
C(4)-C(15)-C(16)-C(21)	-169.25(19)
C(21)-C(16)-C(17)-C(18)	-0.7(4)
C(15)-C(16)-C(17)-C(18)	177.9(2)
C(16)-C(17)-C(18)-C(19)	1.4(5)
C(17)-C(18)-C(19)-C(20)	-0.6(6)
C(18)-C(19)-C(20)-C(21)	-0.7(6)
C(17)-C(16)-C(21)-C(20)	-0.7(4)
C(15)-C(16)-C(21)-C(20)	-179.3(2)
C(19)-C(20)-C(21)-C(16)	1.4(5)

^{1}H NMR and ^{13}C NMR Spectra for 9,10-Dihydro-6*H*-chromeno[4,3-*d*]imidazo[1,2-*a*]pyridin-6-ones 4

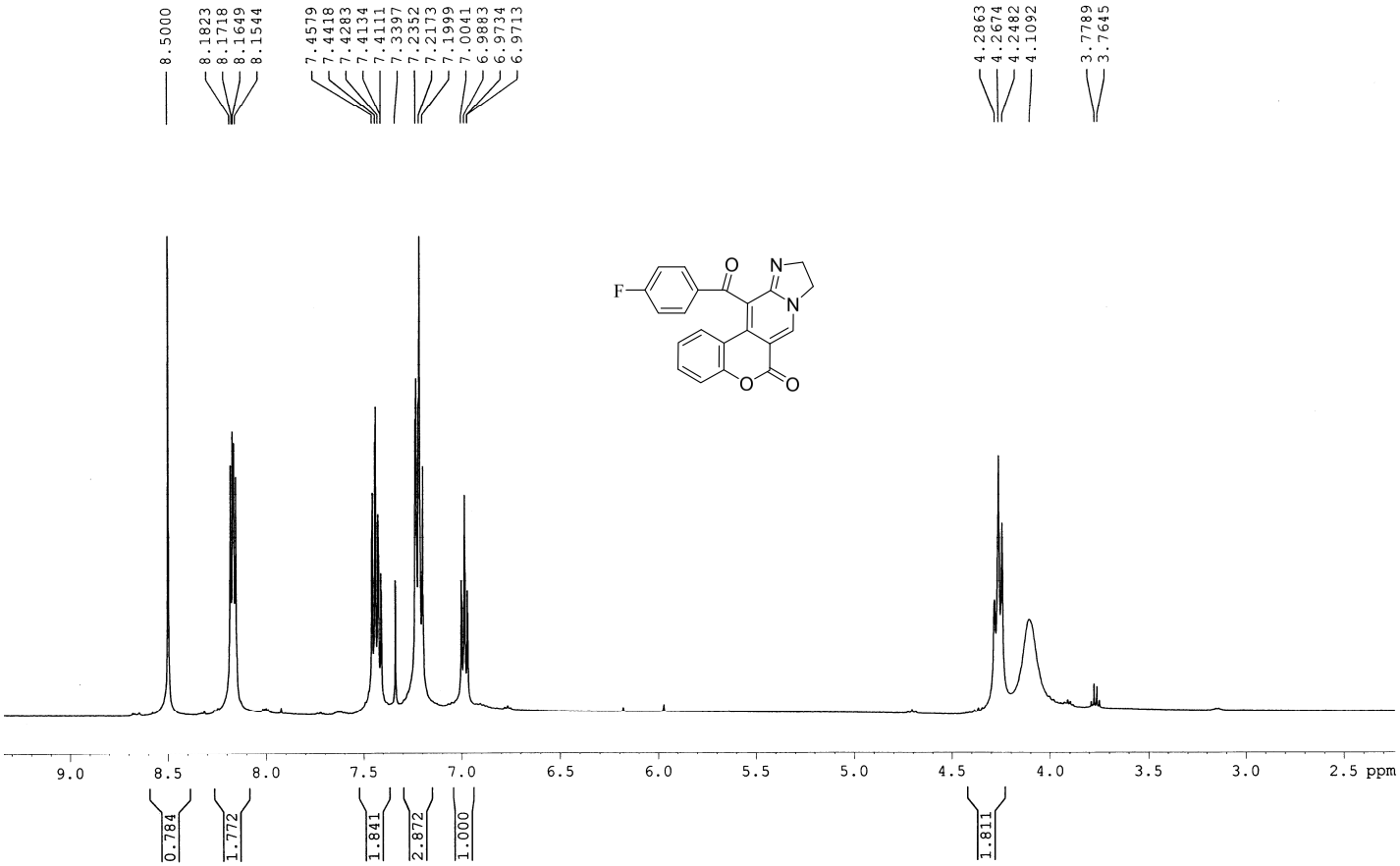


Figure 1. ^{1}H NMR (500 MHz, DMSO-d_6+$CDCl_3$) spectra of compound **4a**

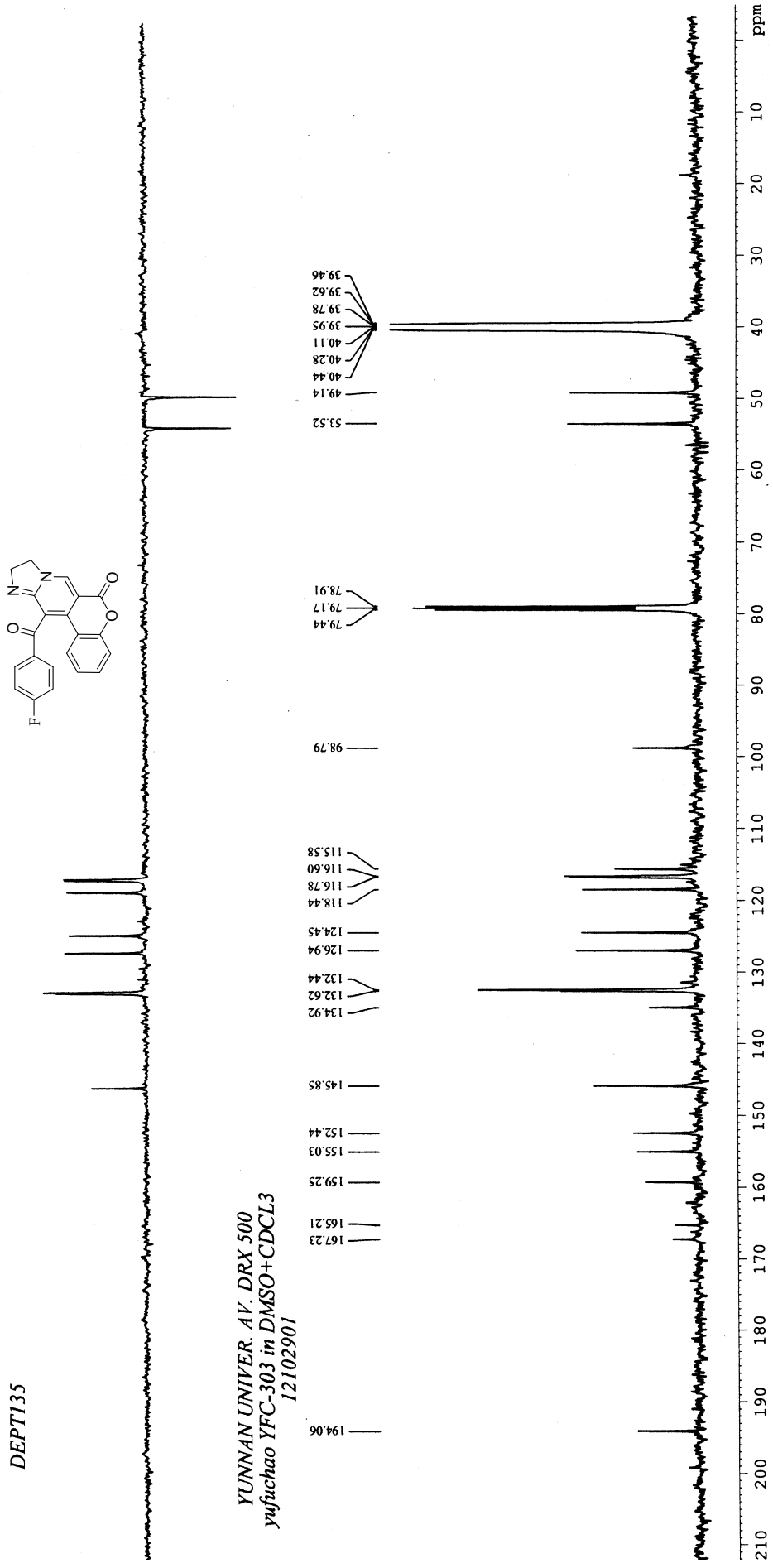


Figure 2. ^{13}C NMR (125 MHz, DMSO-d_6+$CDCl_3$) spectra of compound **4a**

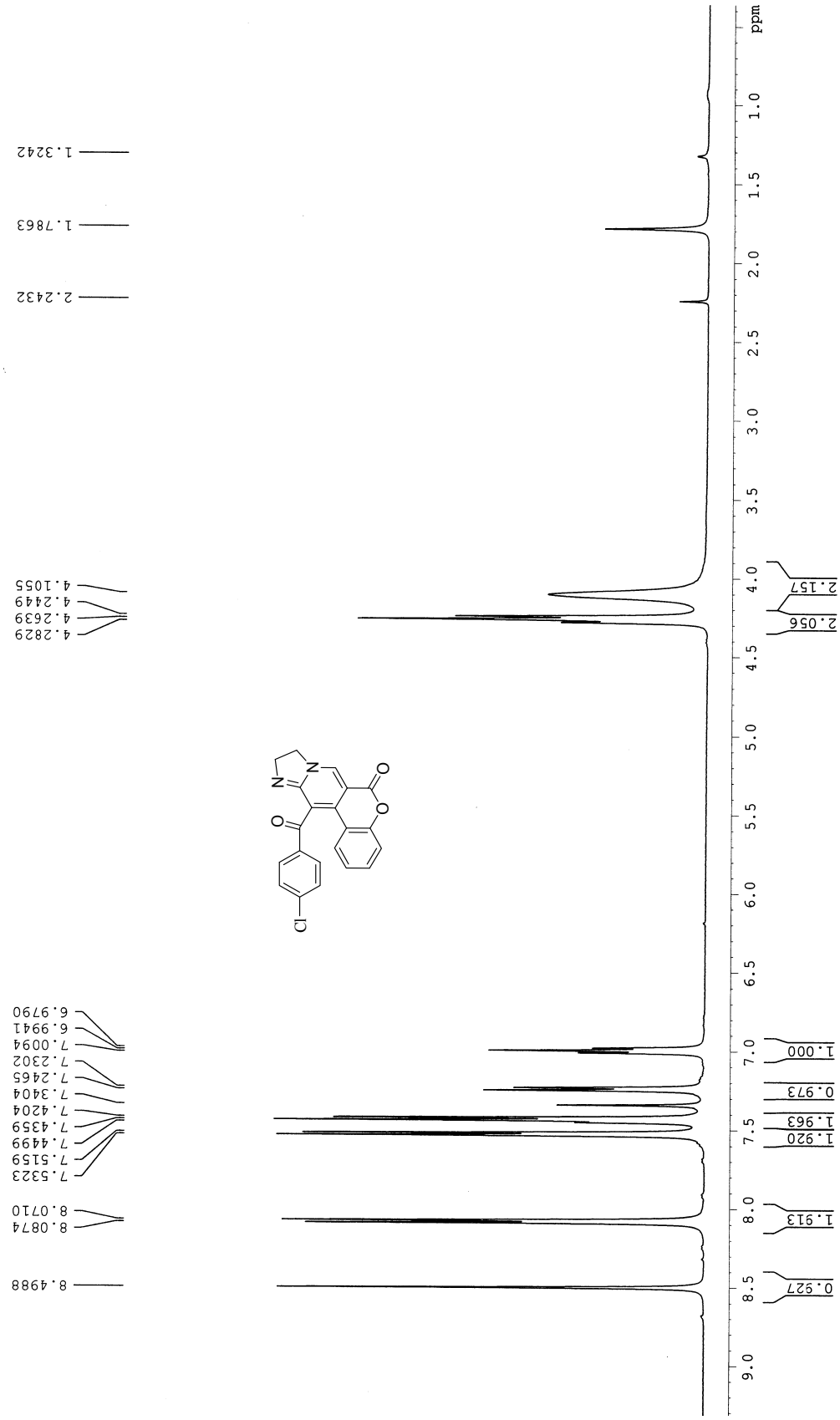


Figure 3. ^{1}H NMR (500 MHz, DMSO-d_6+$CDCl_3$) spectra of compound **4b**

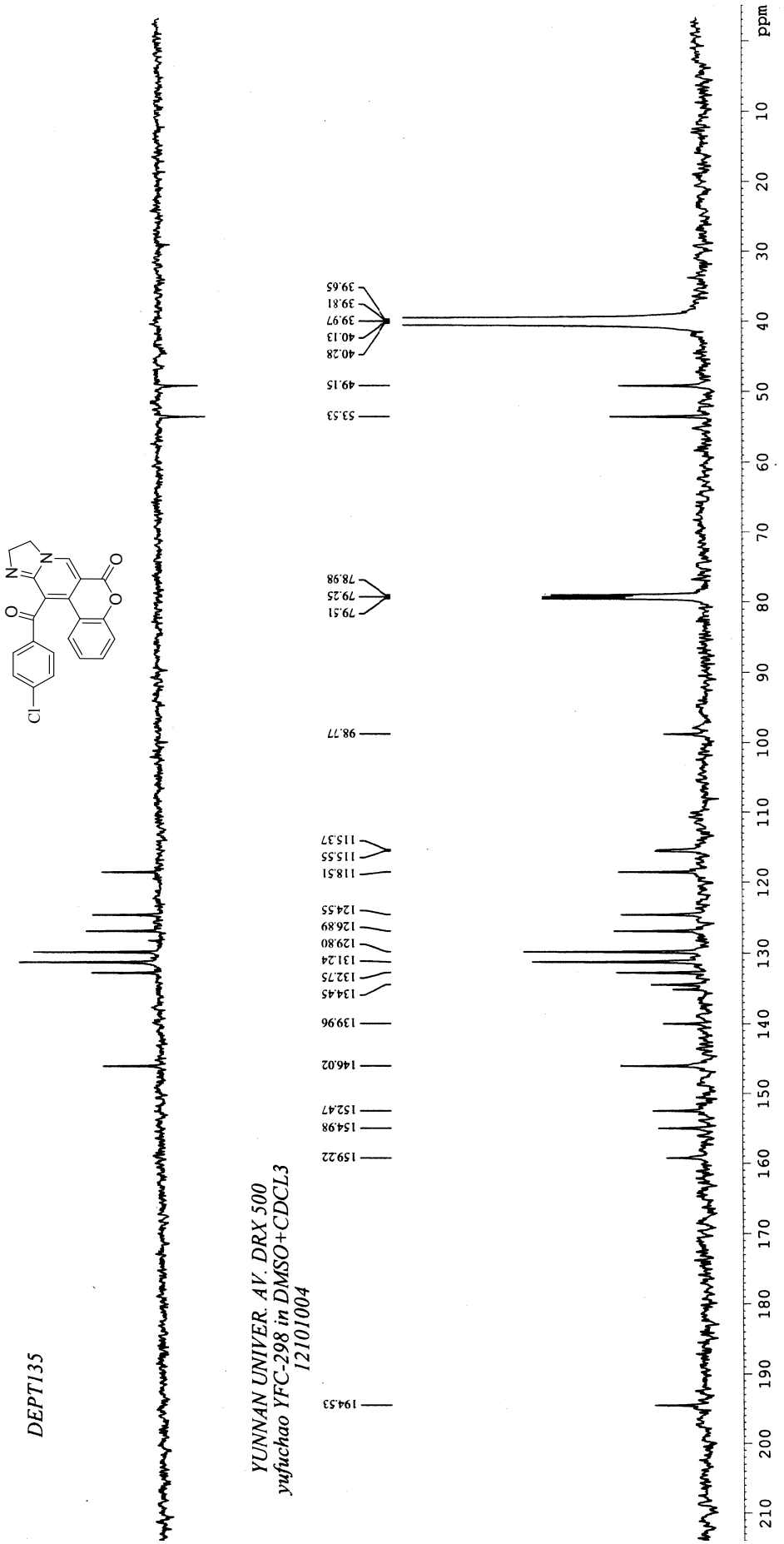


Figure 4. ^{13}C NMR (125 MHz, DMSO-d_6+$CDCl_3$) spectra of compound **4b**

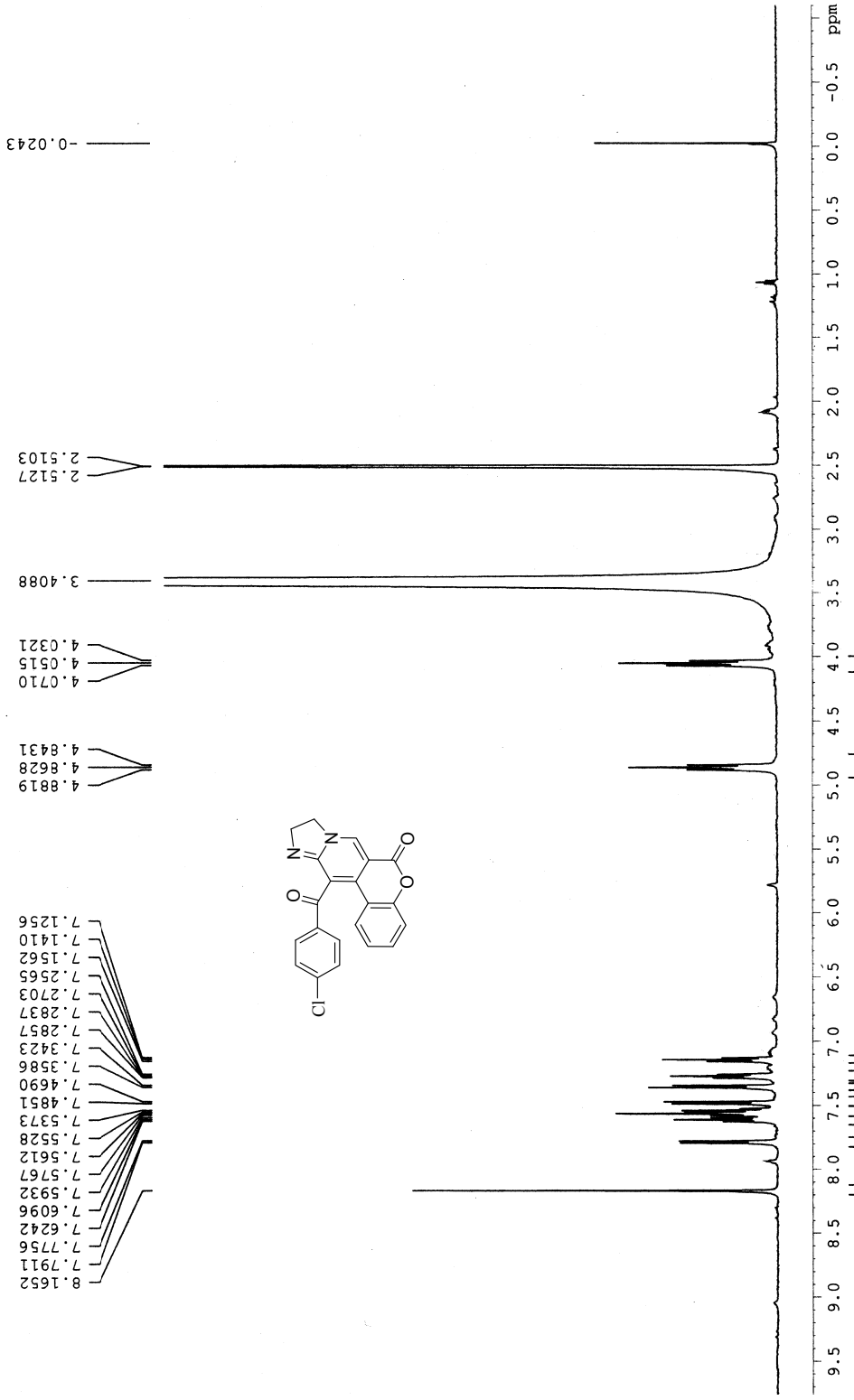


Figure 5. ^{1}H NMR (500 MHz, DMSO-d_6+$CDCl_3$) spectra of compound **4c**

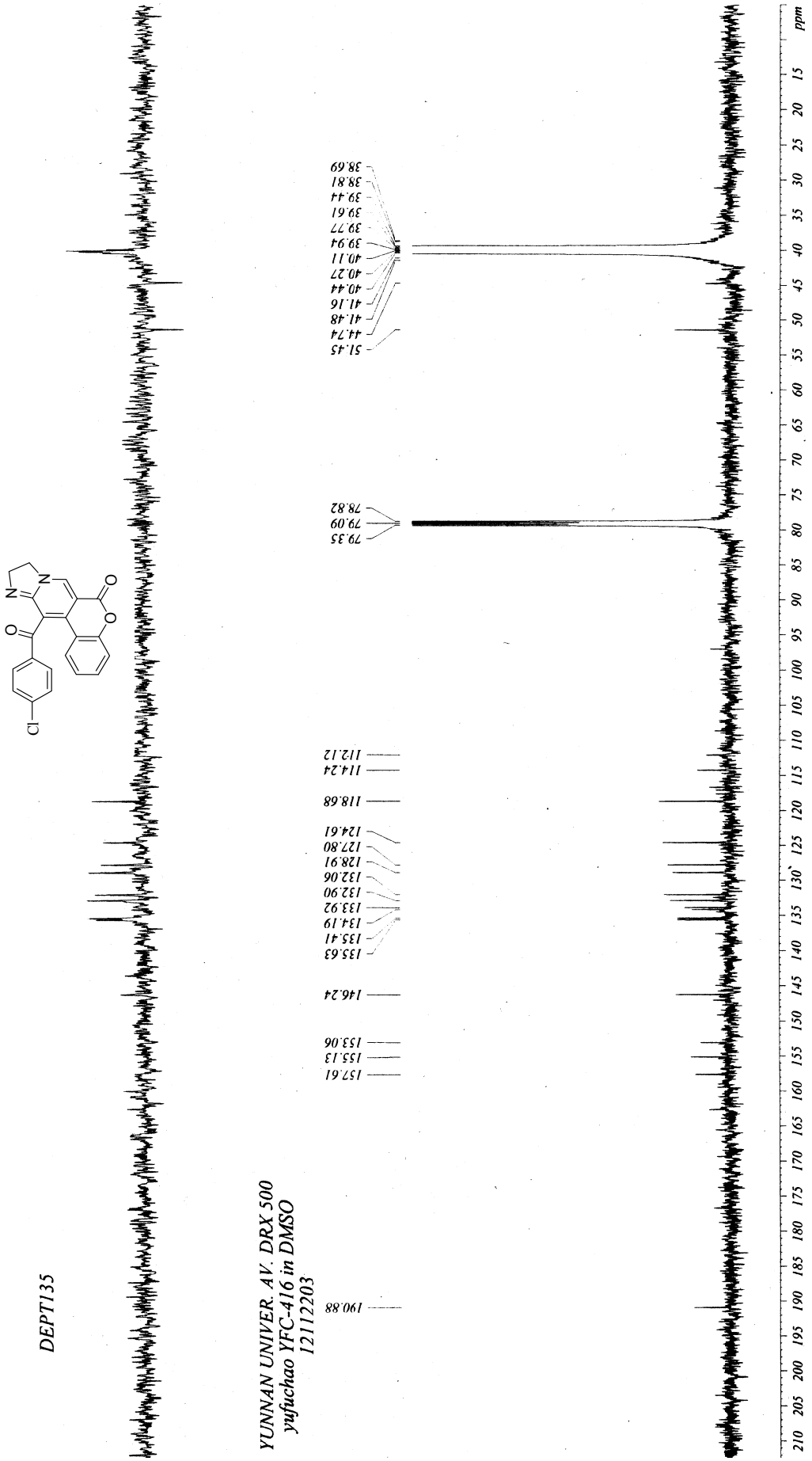


Figure 6. ^{13}C NMR (125 MHz, DMSO-d_6+$CDCl_3$) spectra of compound **4c**

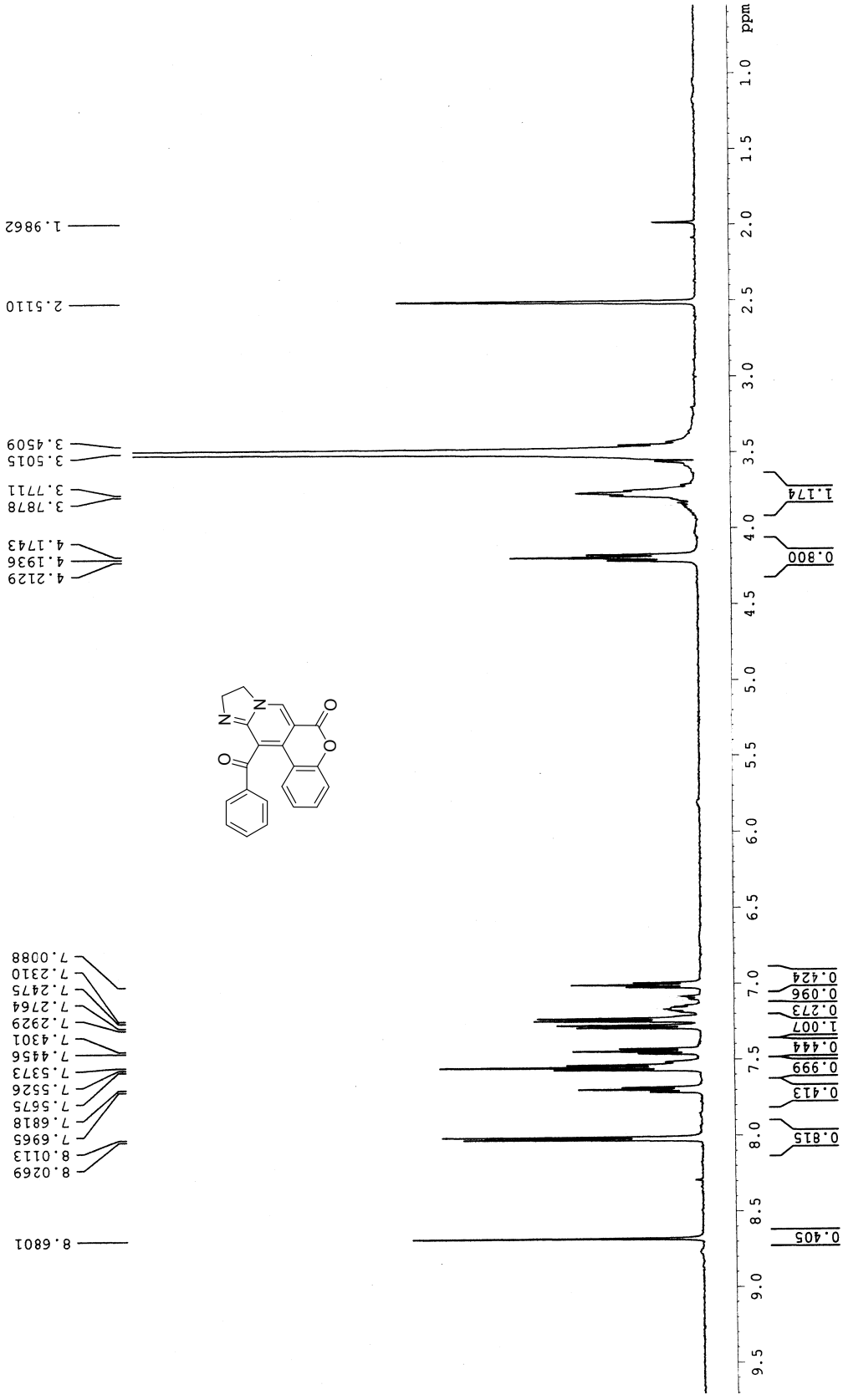


Figure 7. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4d**

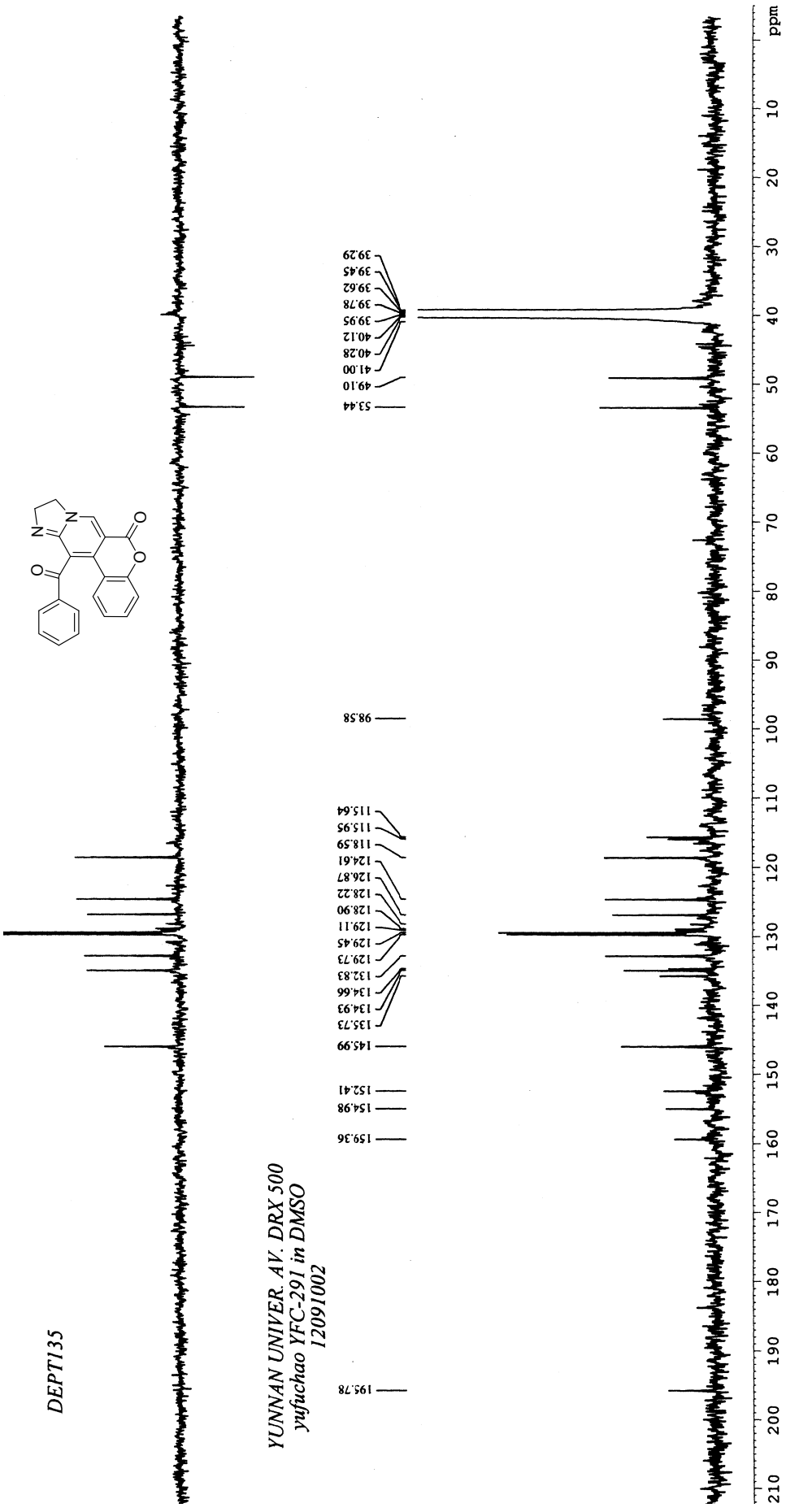


Figure 8. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4d**

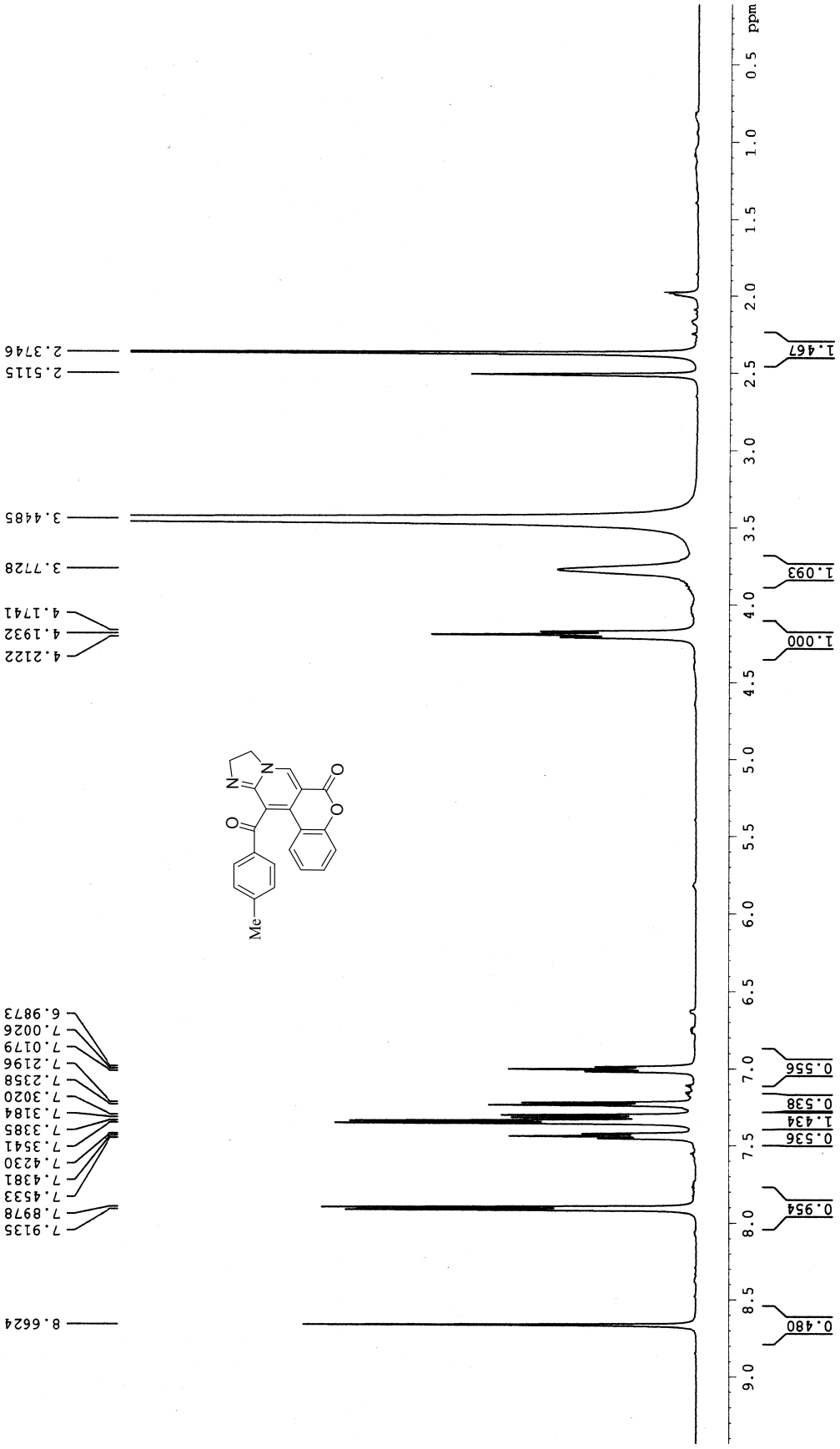


Figure 9. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4e**

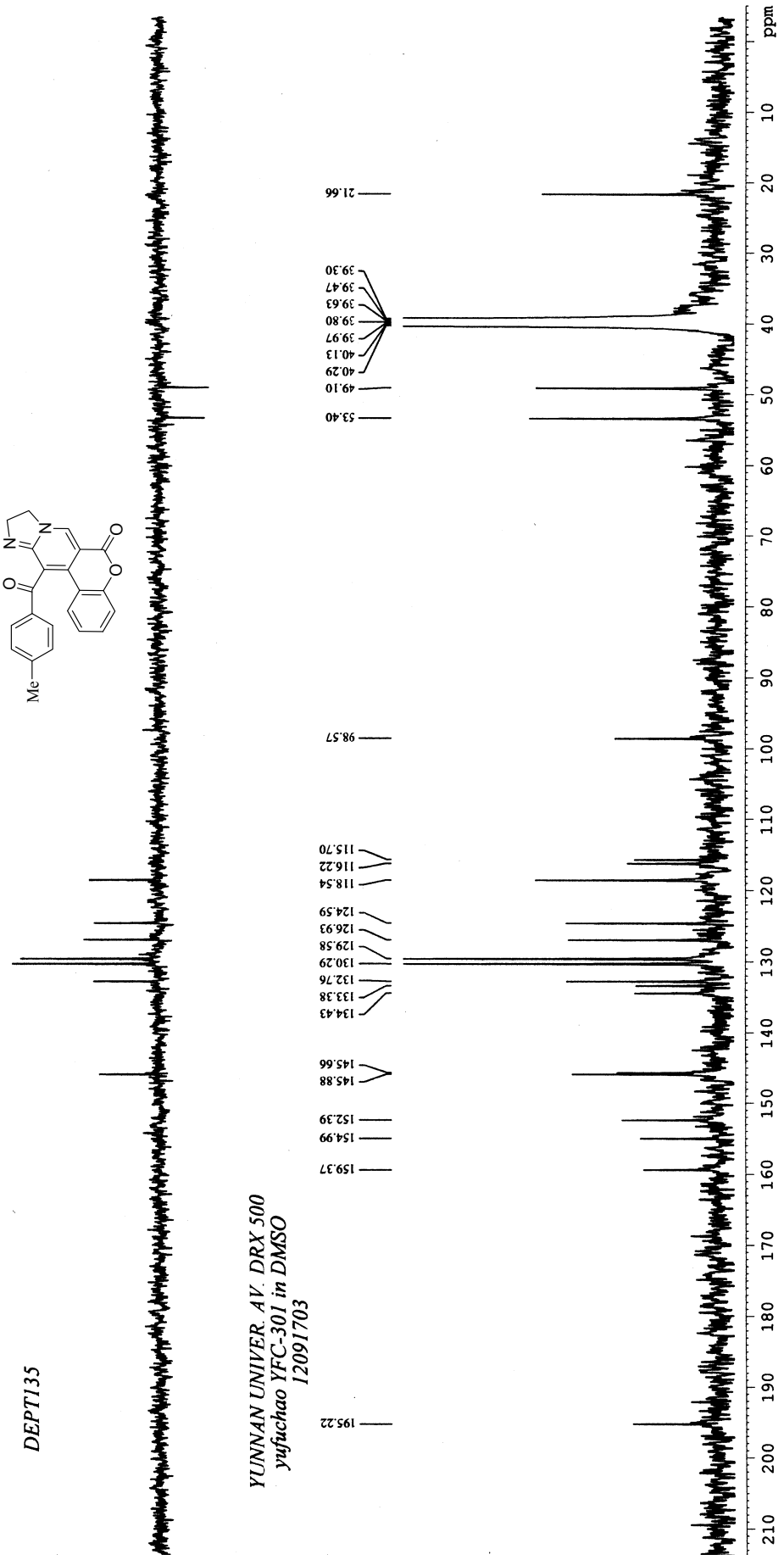


Figure 10. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4e**

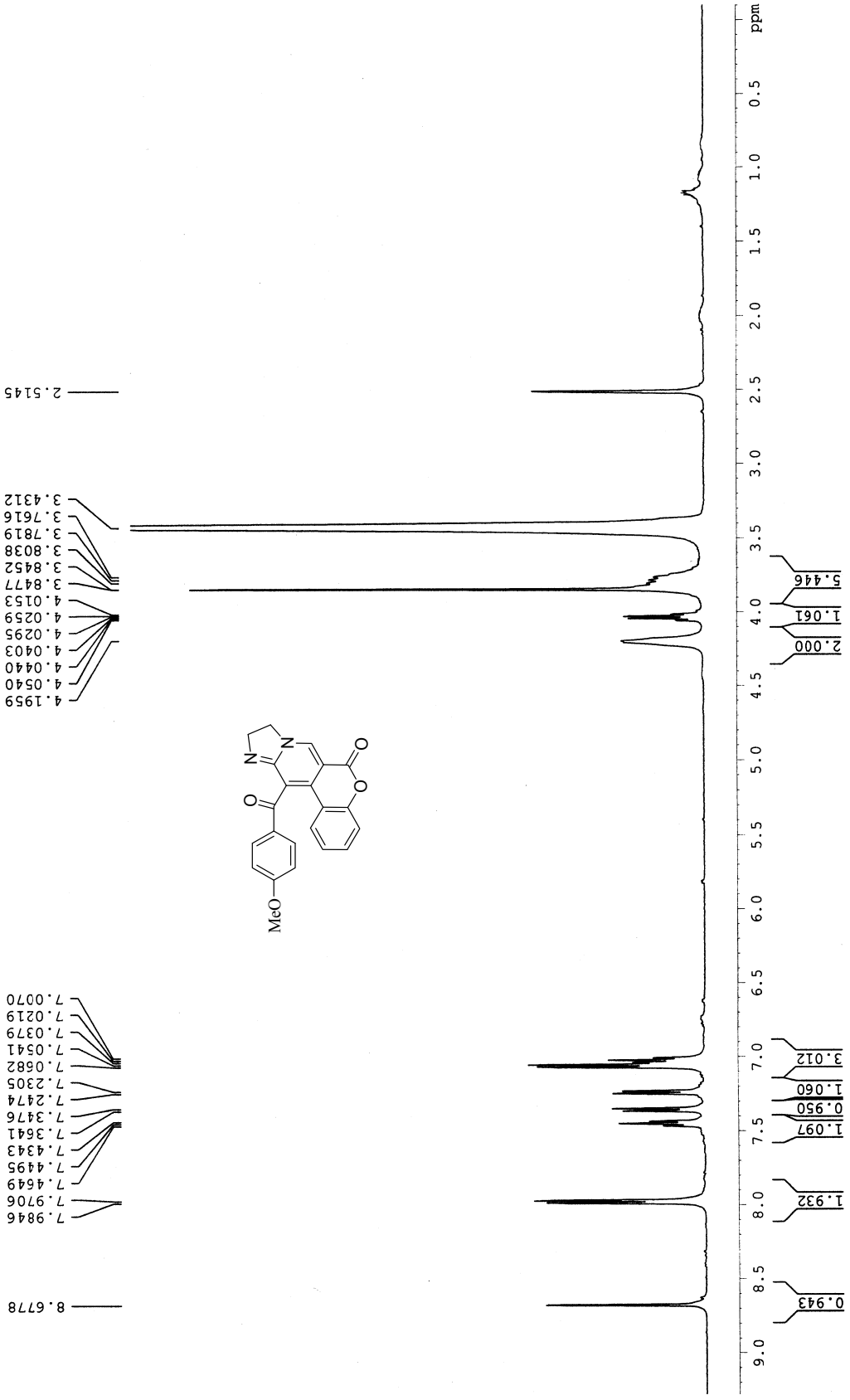


Figure 11. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4f**

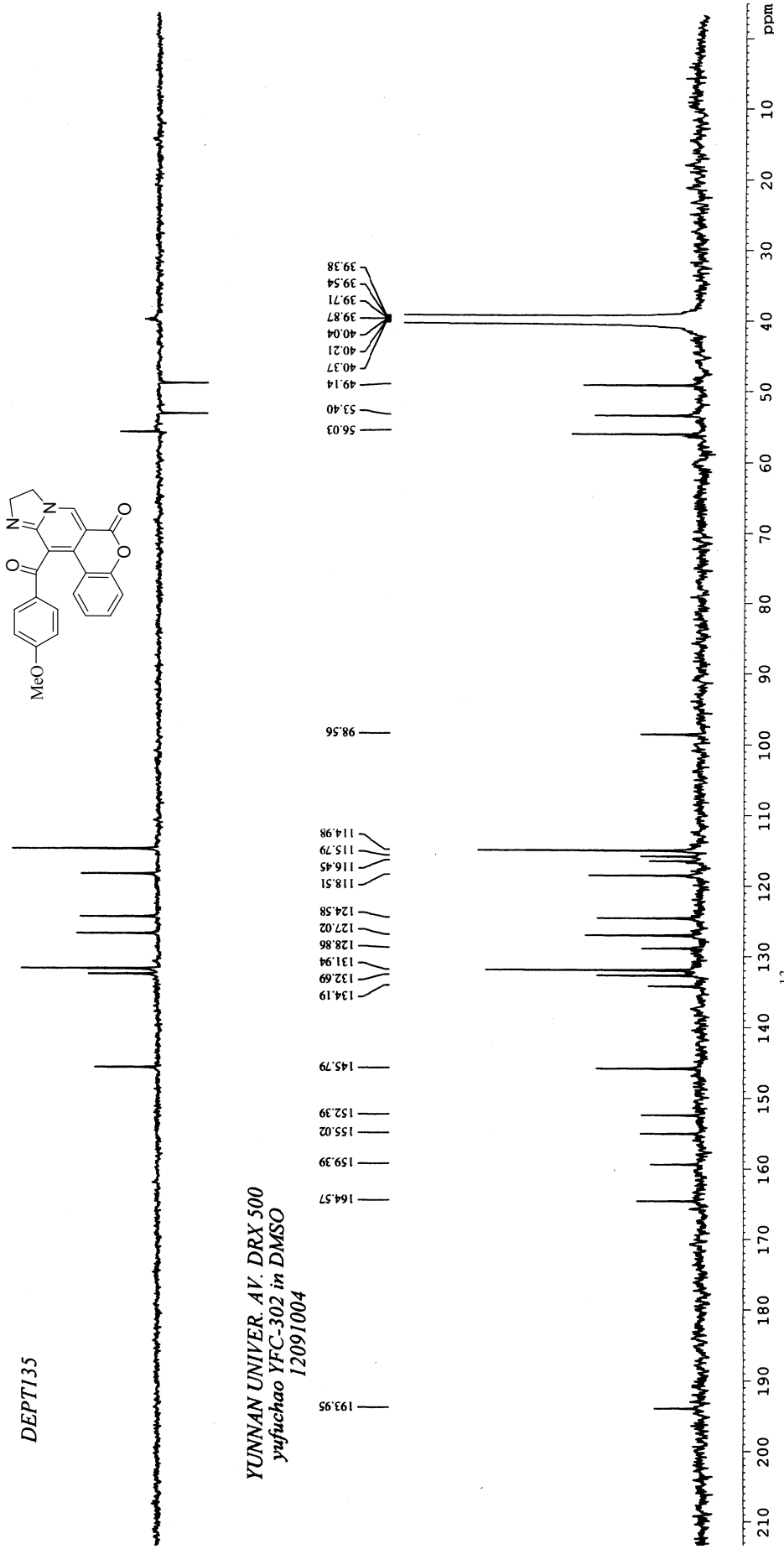


Figure 12. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4f**

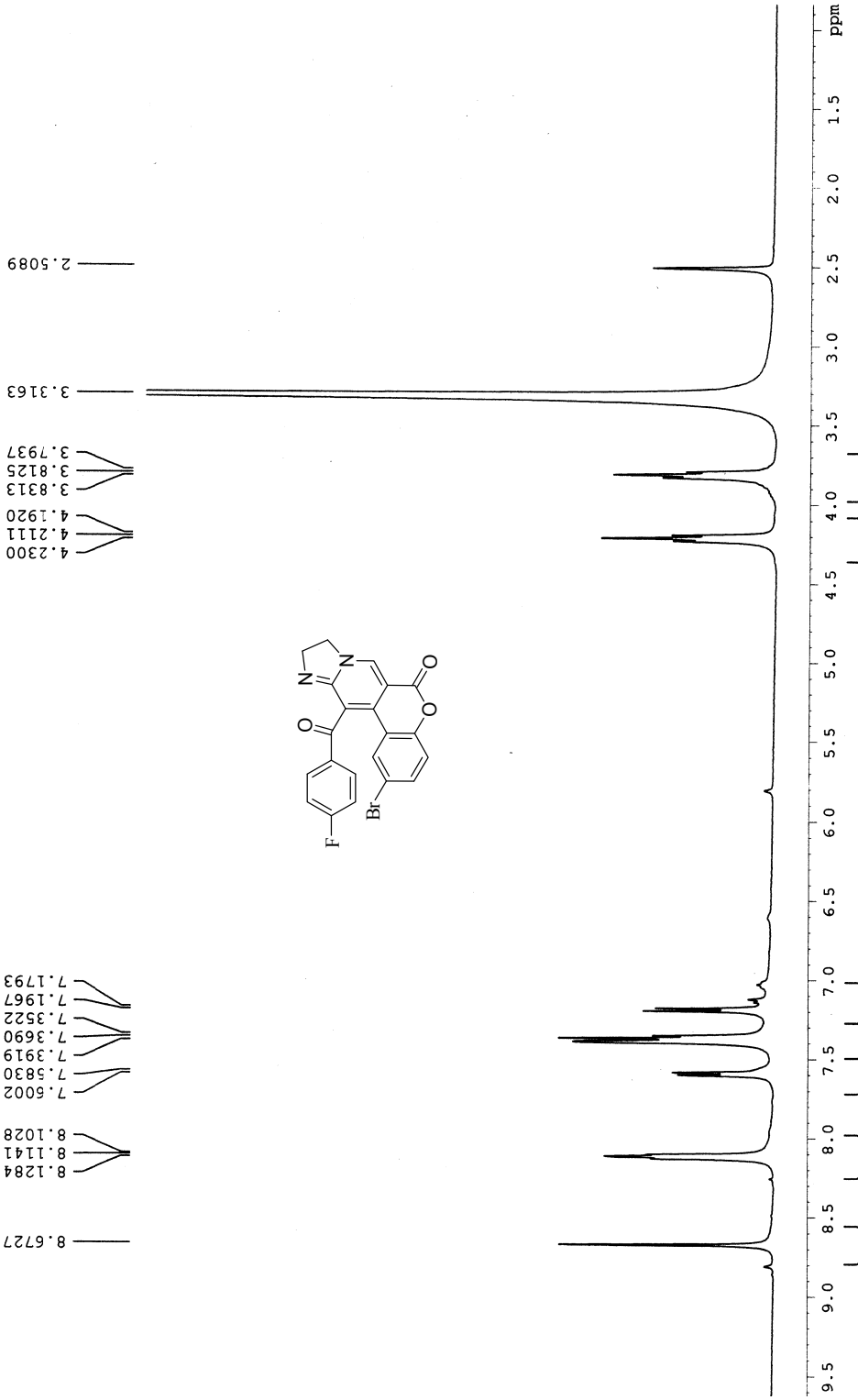


Figure 13. ^{1}H NMR (500 MHz, DMSO-d_6+$CDCl_3$) spectra of compound **4g**

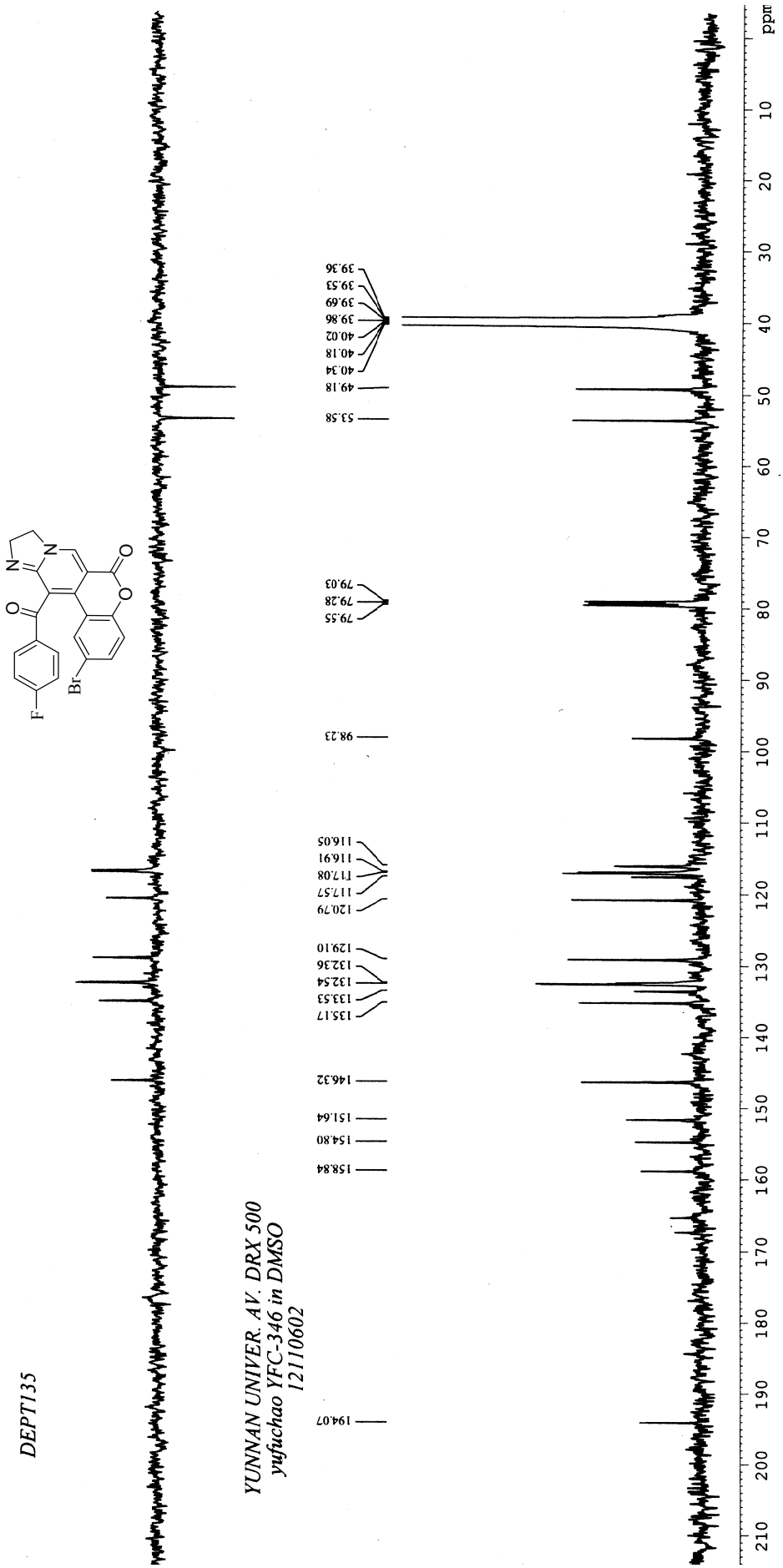


Figure 14. ^{13}C NMR (125 MHz, DMSO-d_6+$CDCl_3$) spectra of compound **4g**

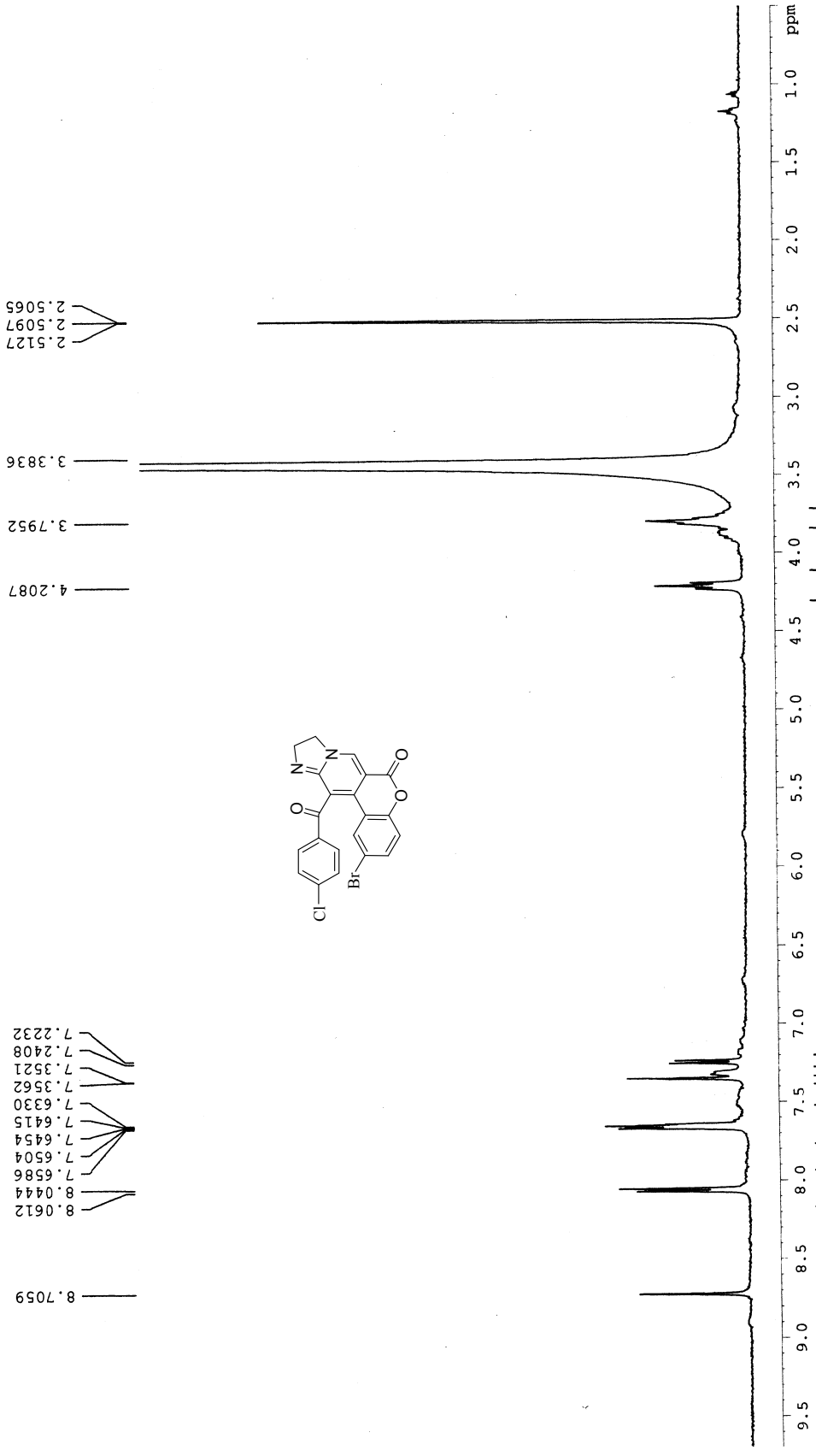


Figure 15. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4h**

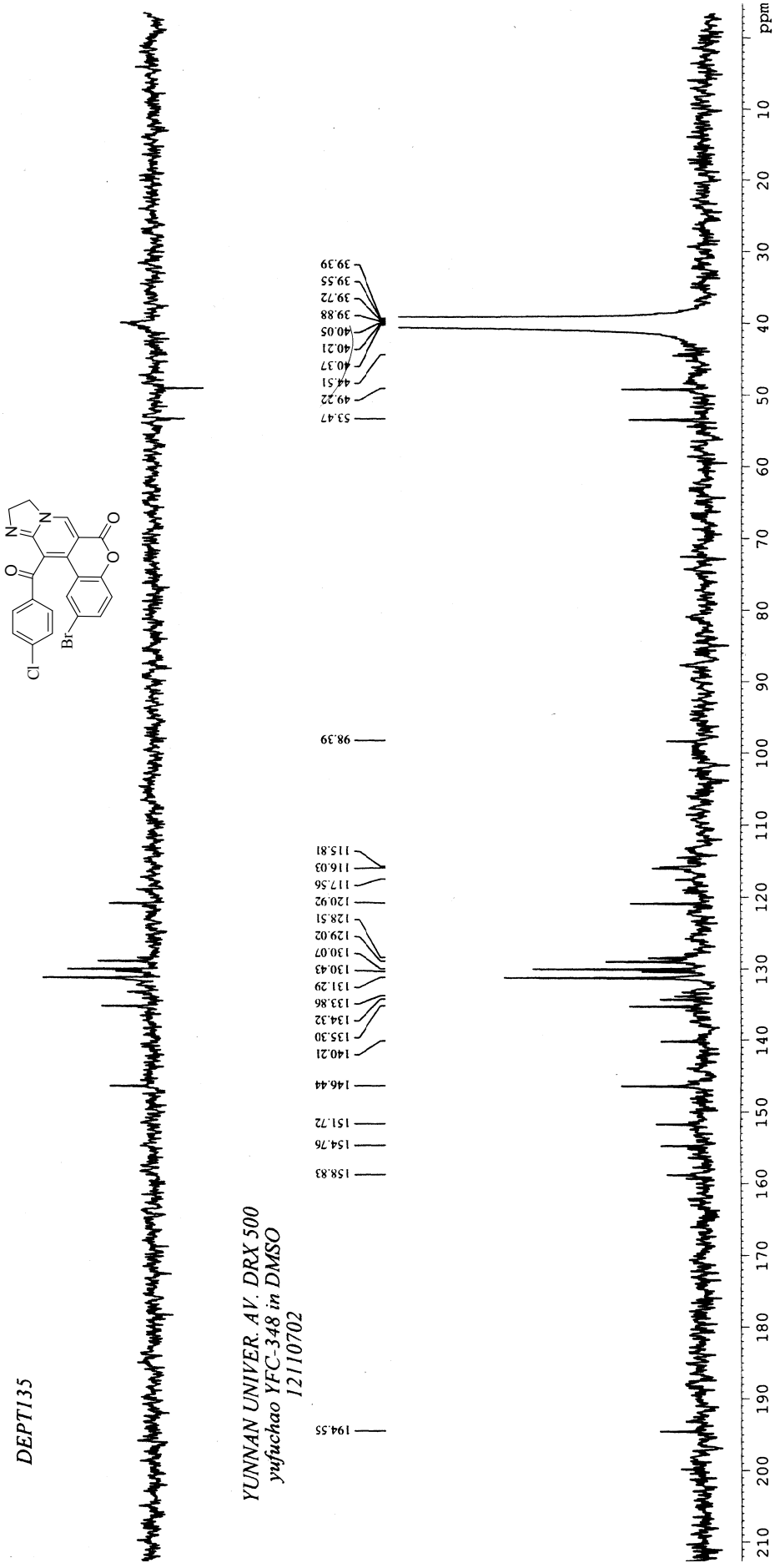


Figure 16. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4h**

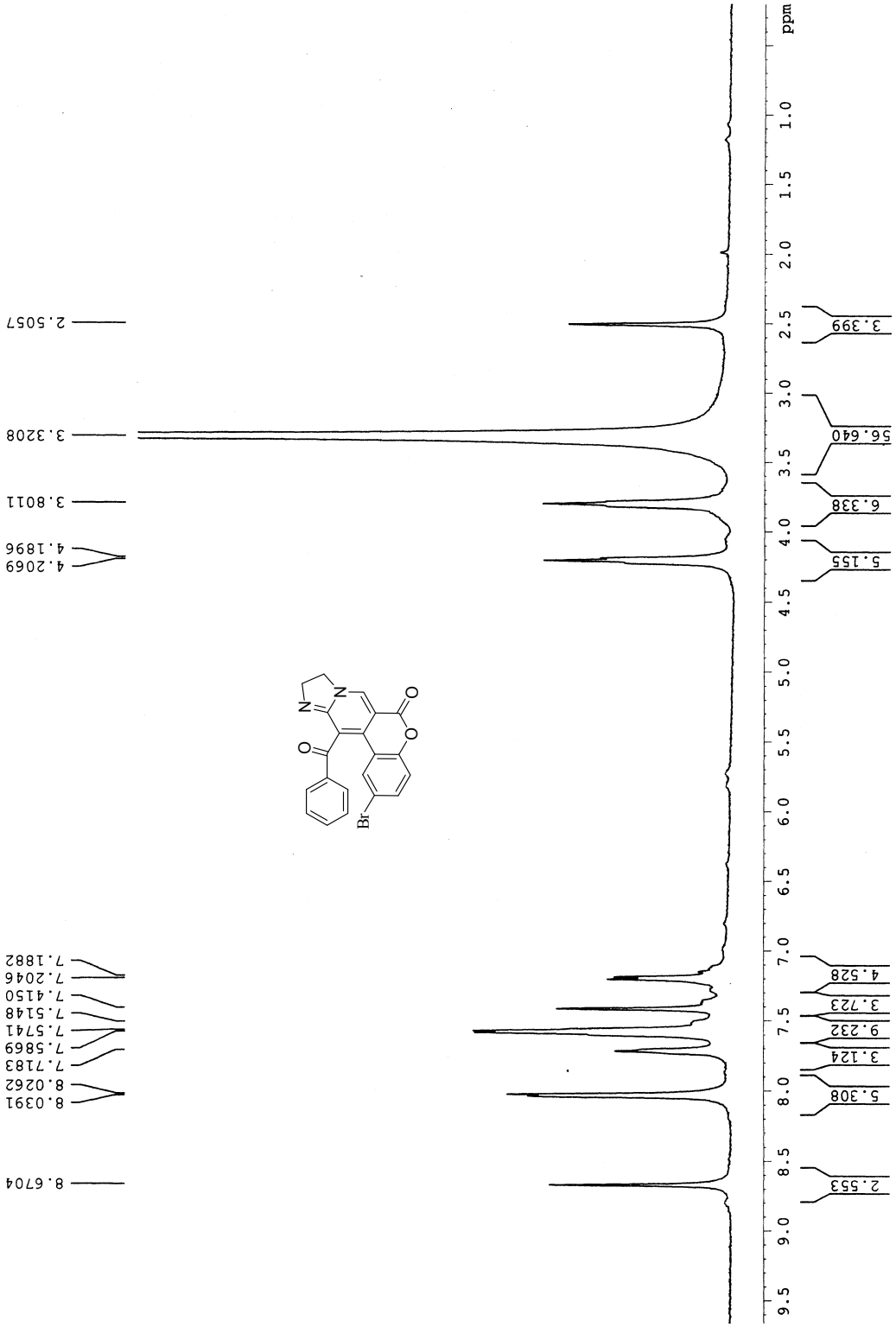


Figure 17. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4i**

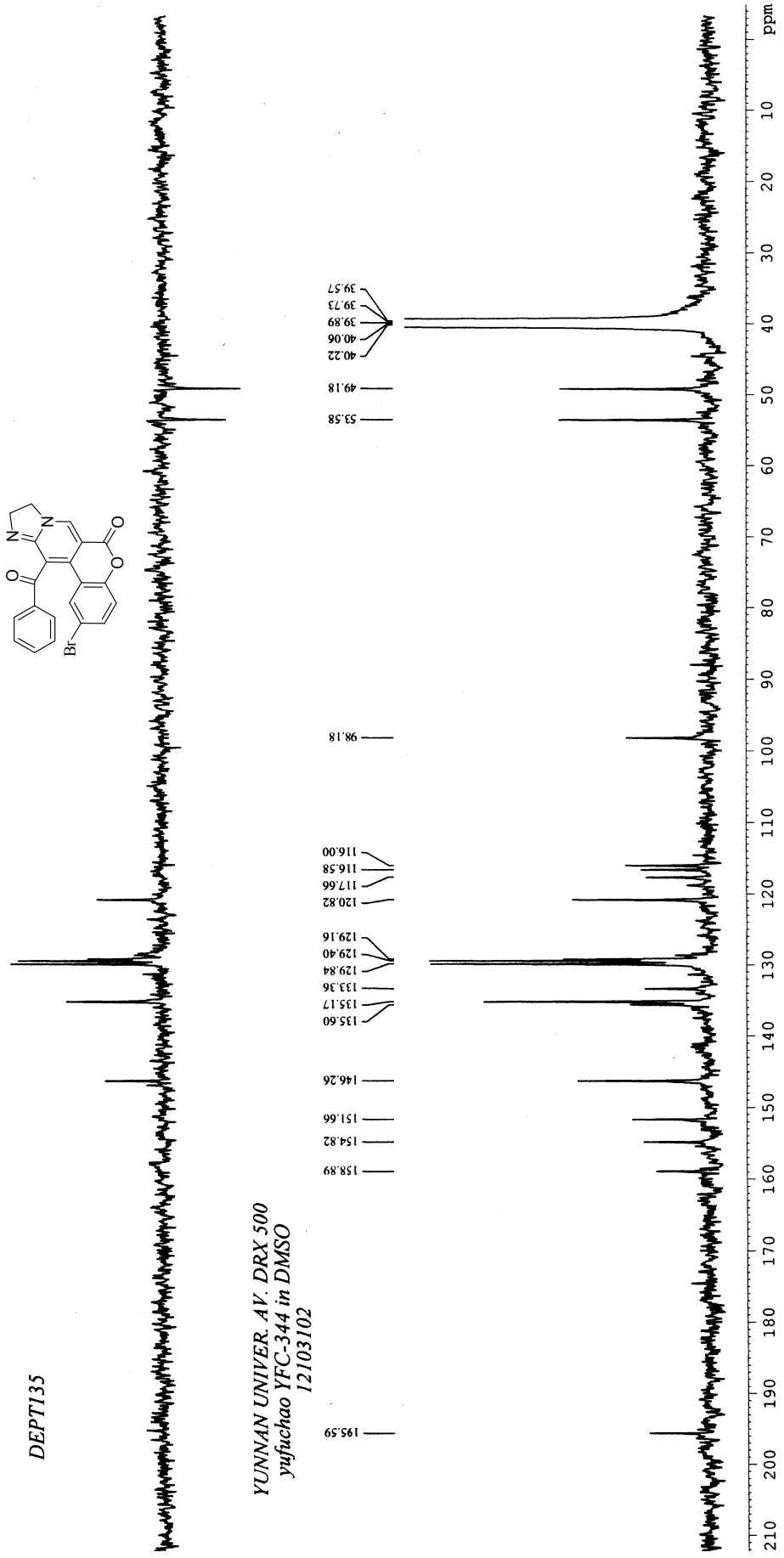


Figure 18. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4i**

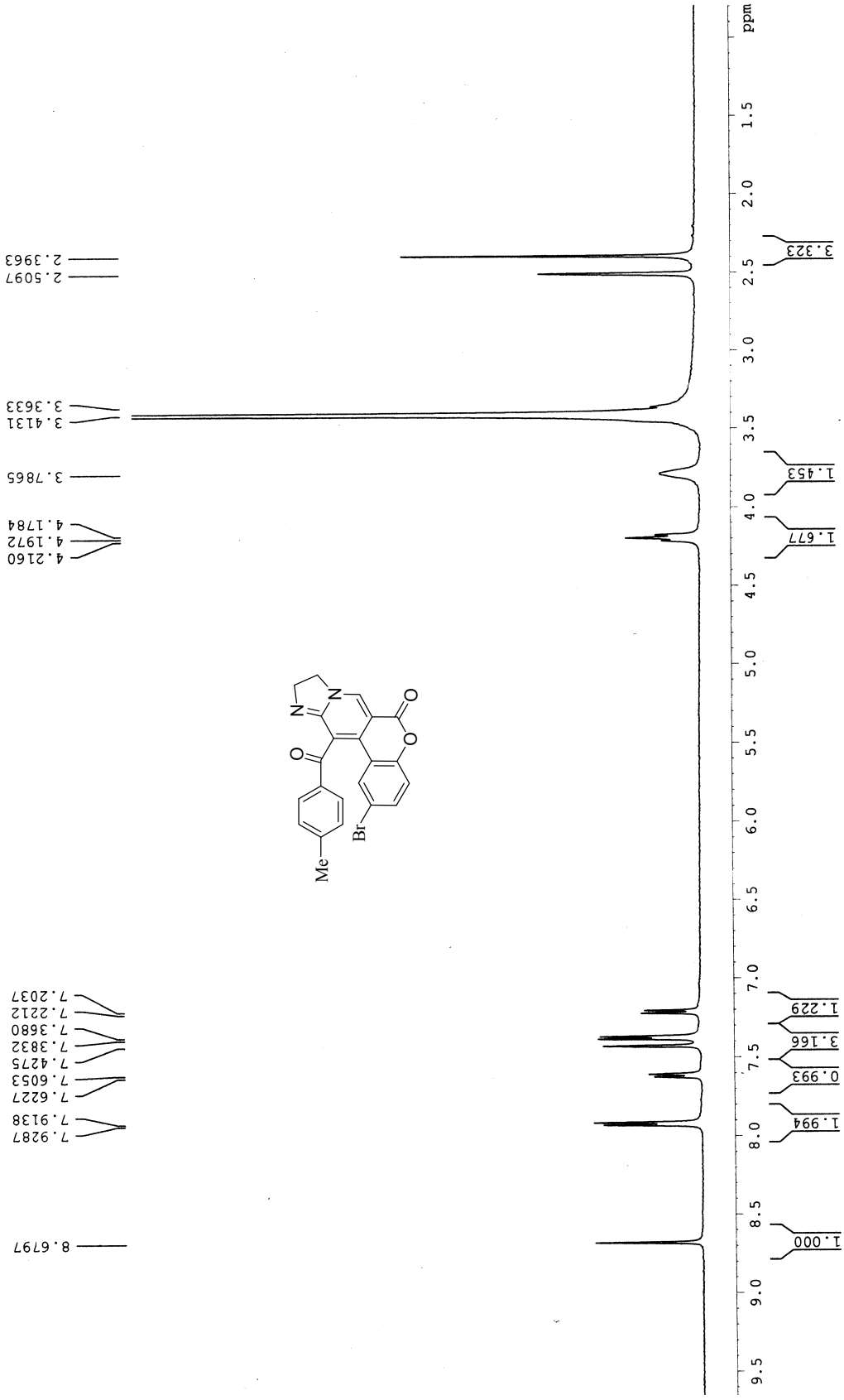


Figure 19. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4j**

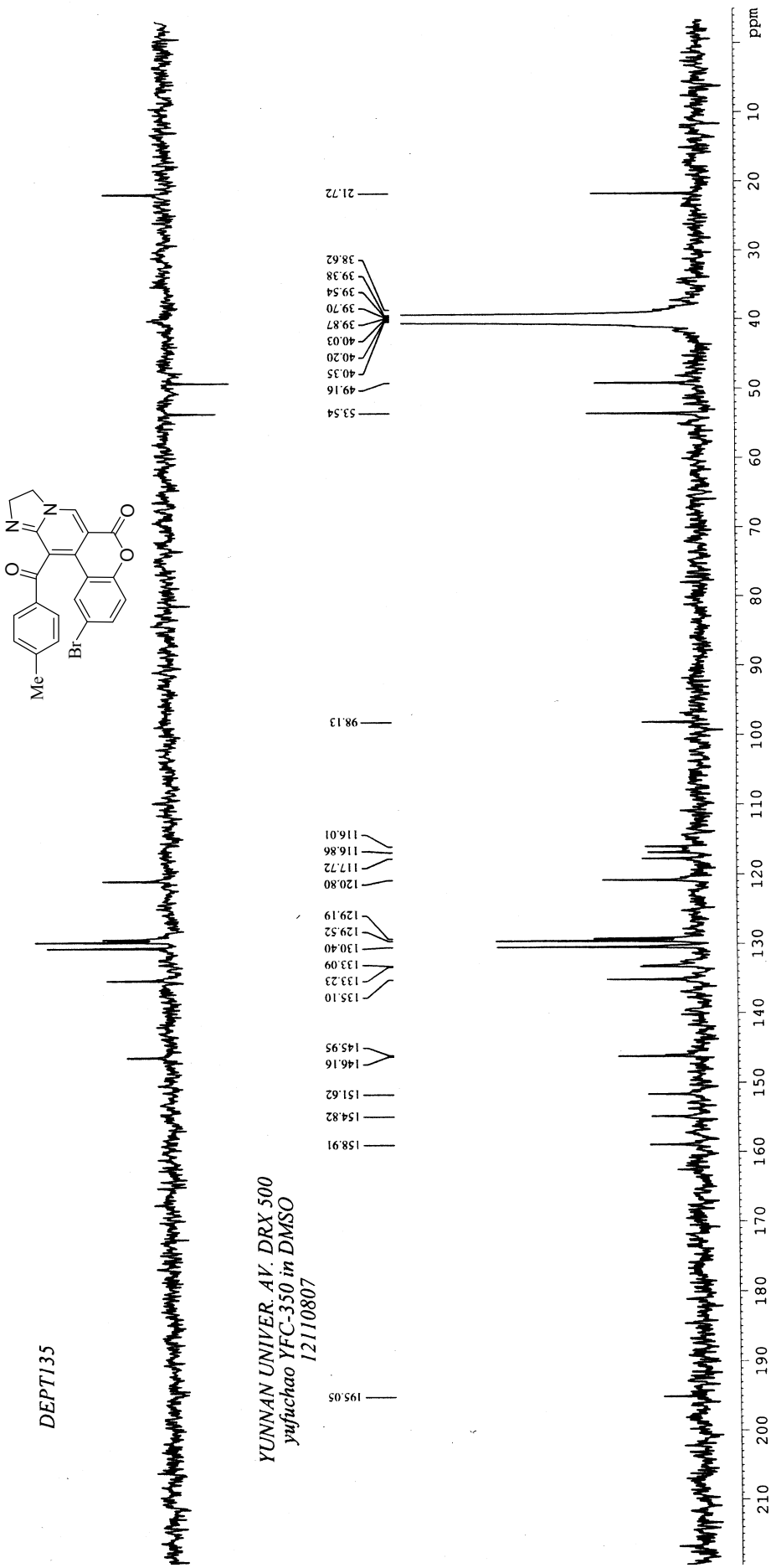


Figure 20. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4j**

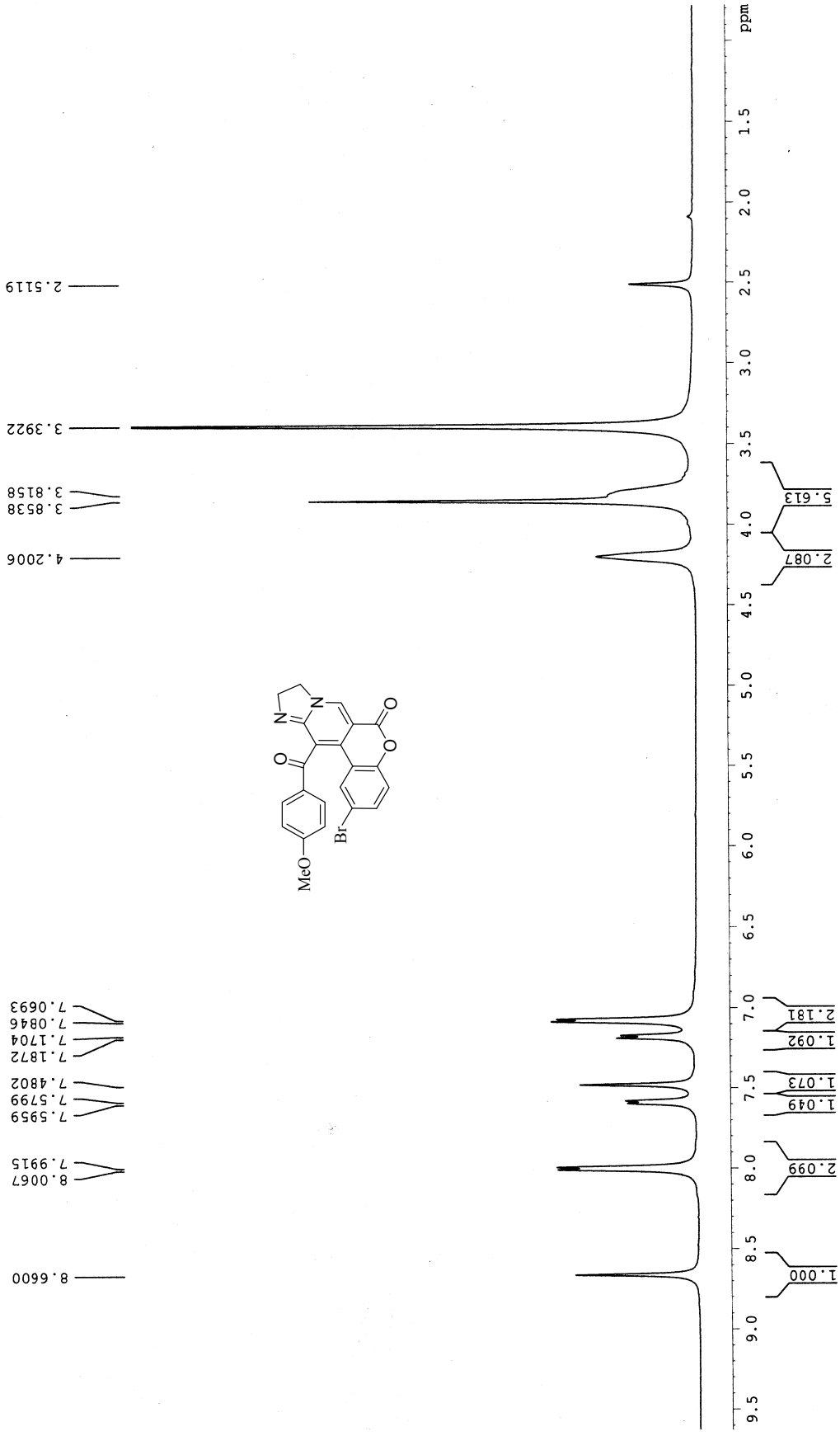


Figure 21. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4k**

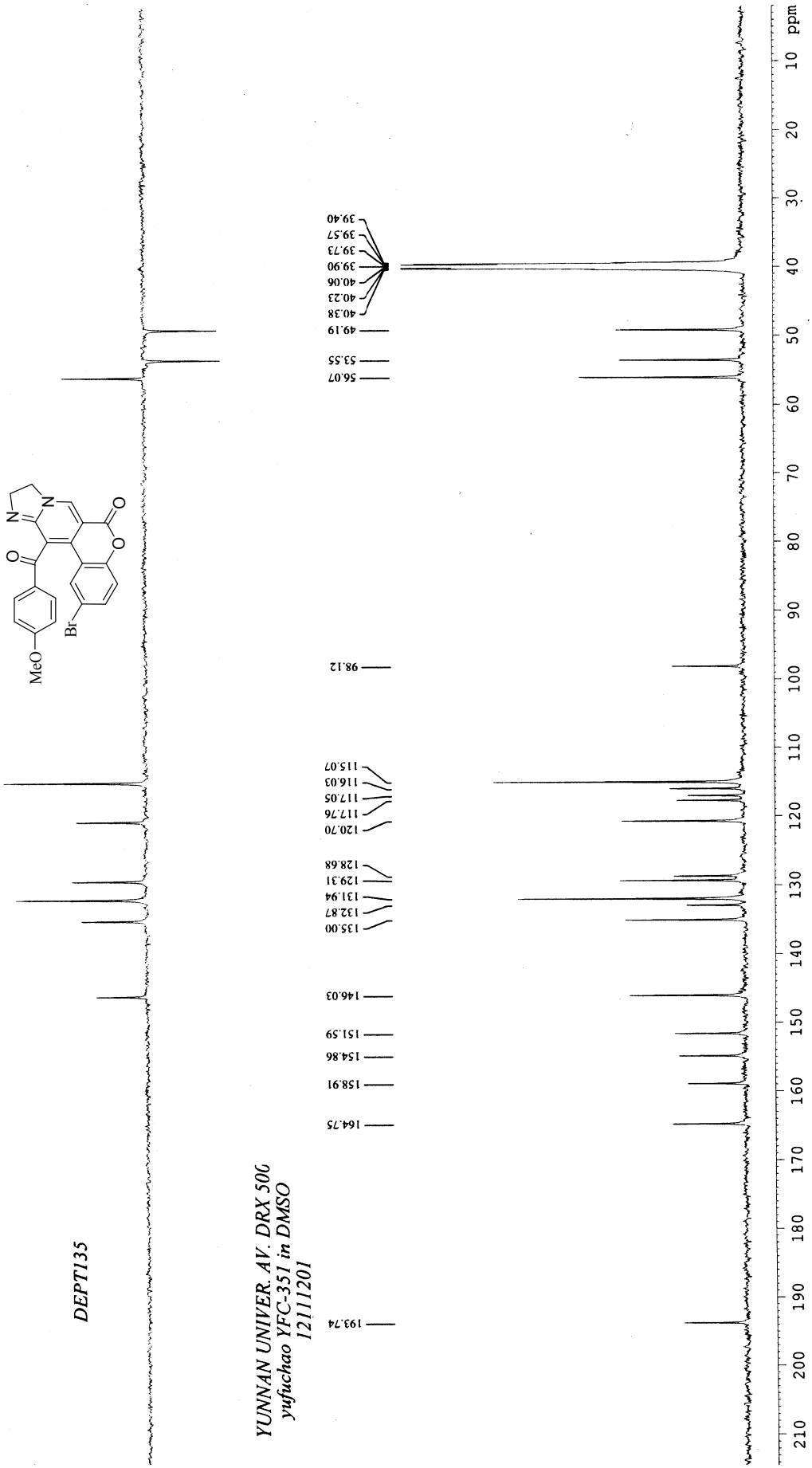


Figure 22. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4k**

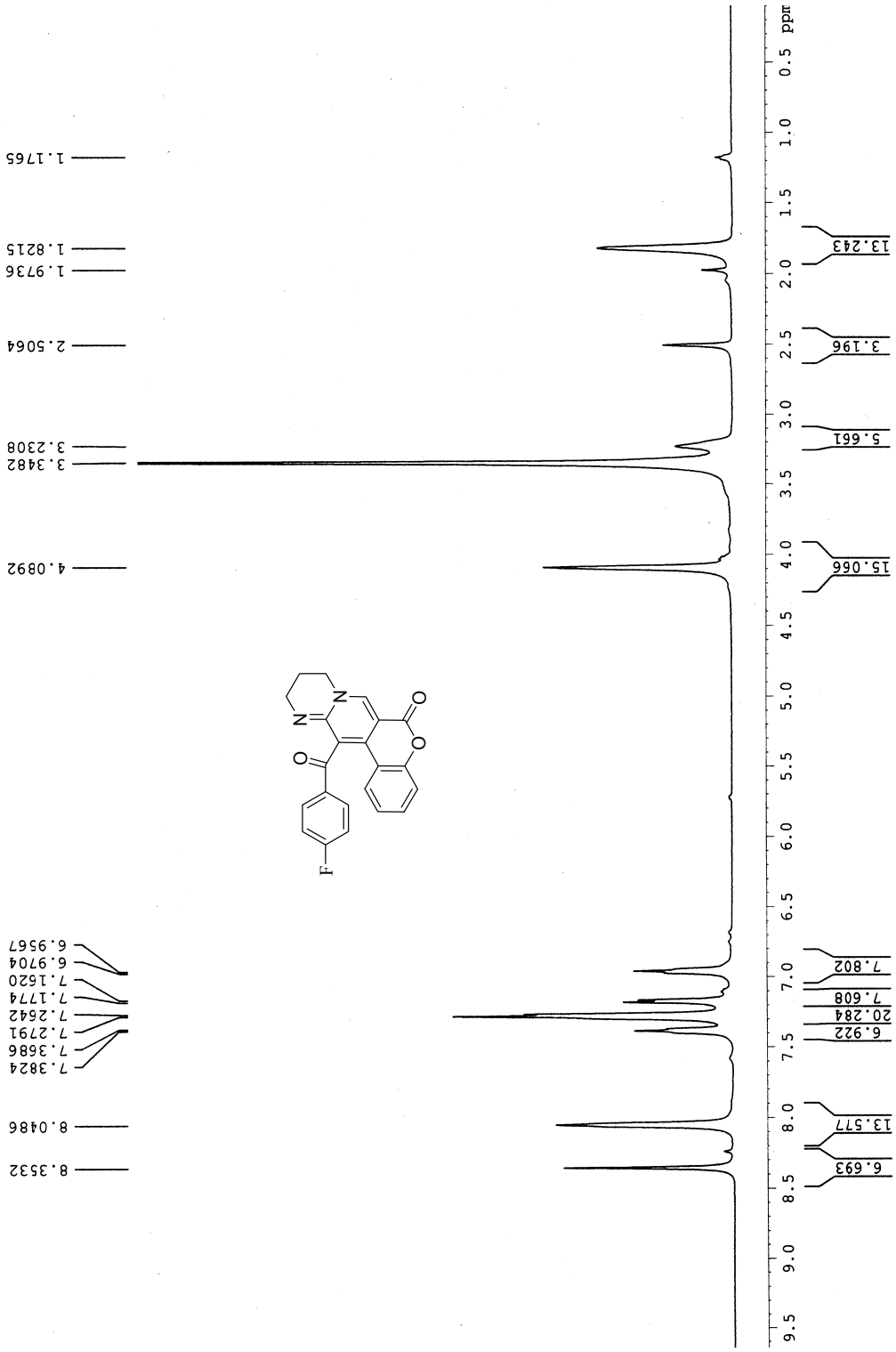


Figure 23. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4l**

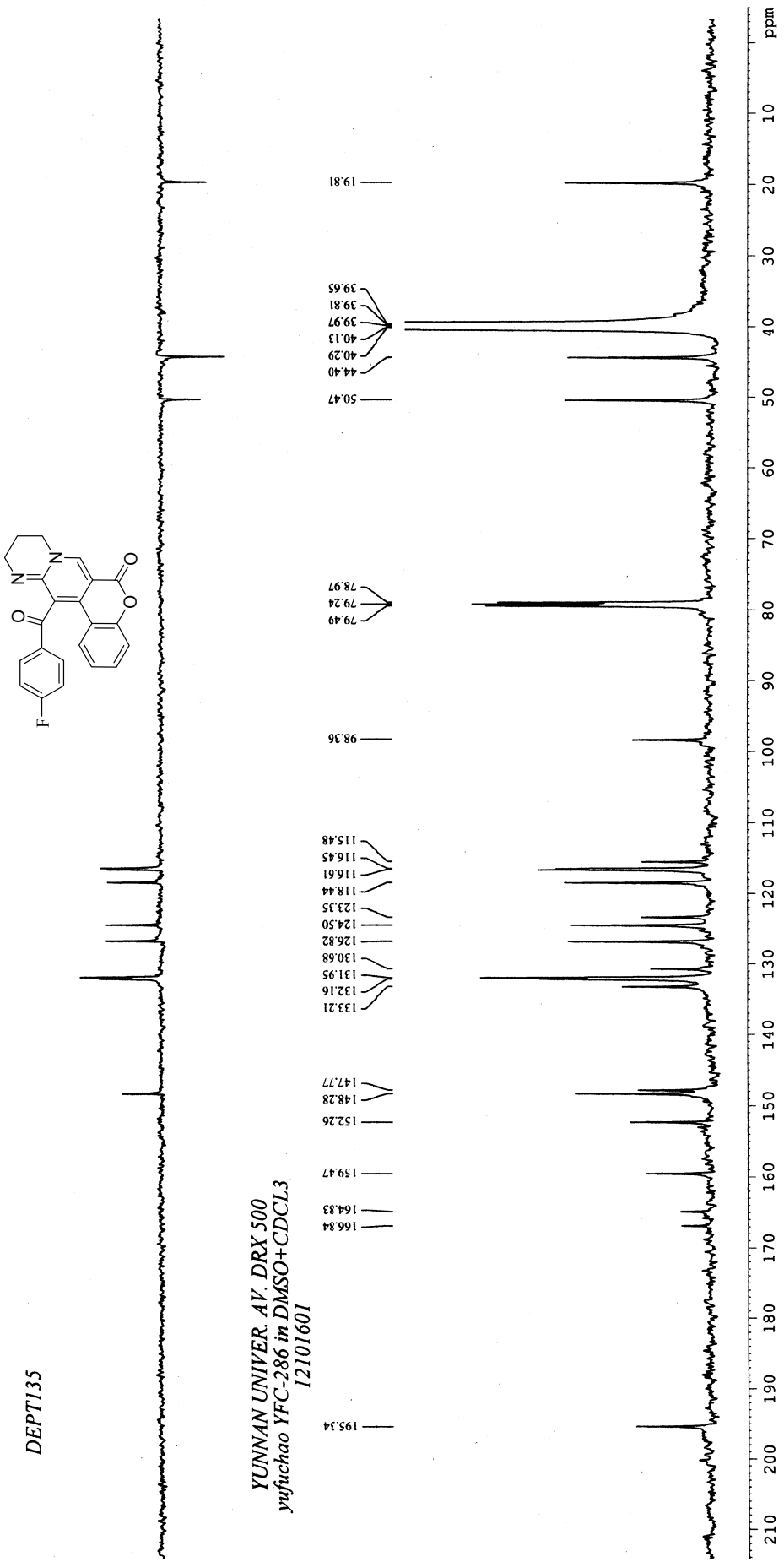


Figure 24. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4l**

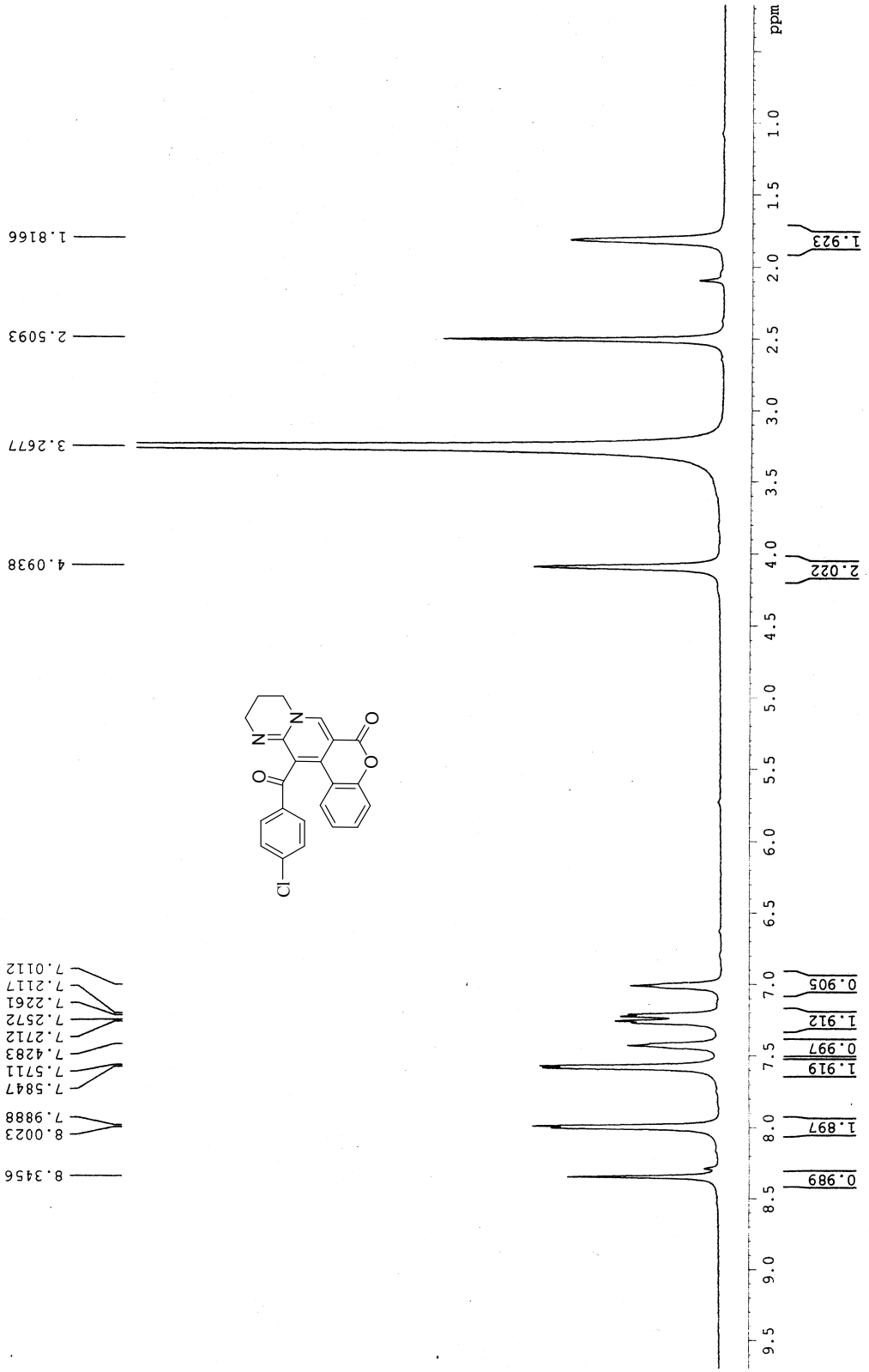


Figure 25. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4m**

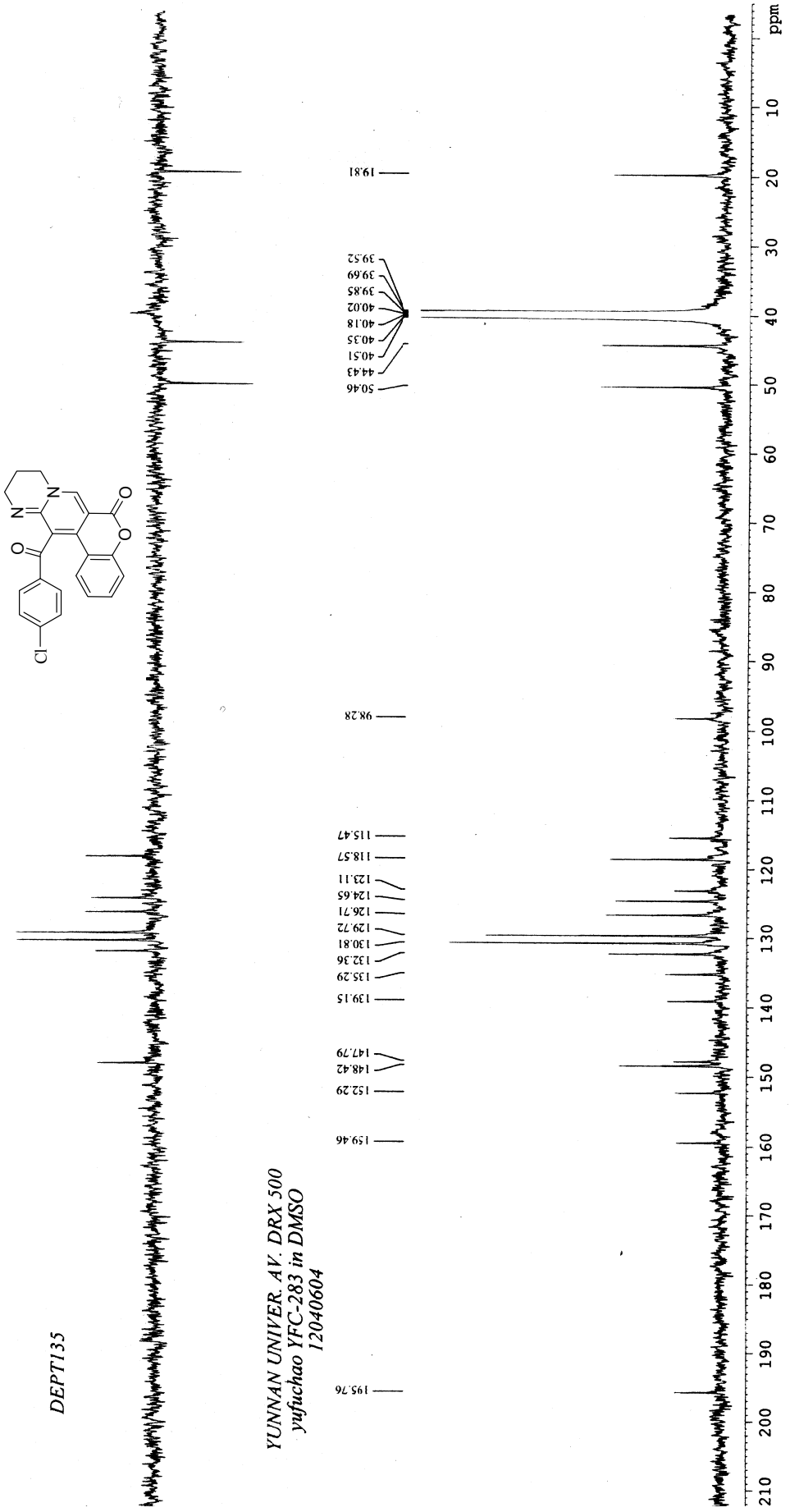


Figure 26. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4m**

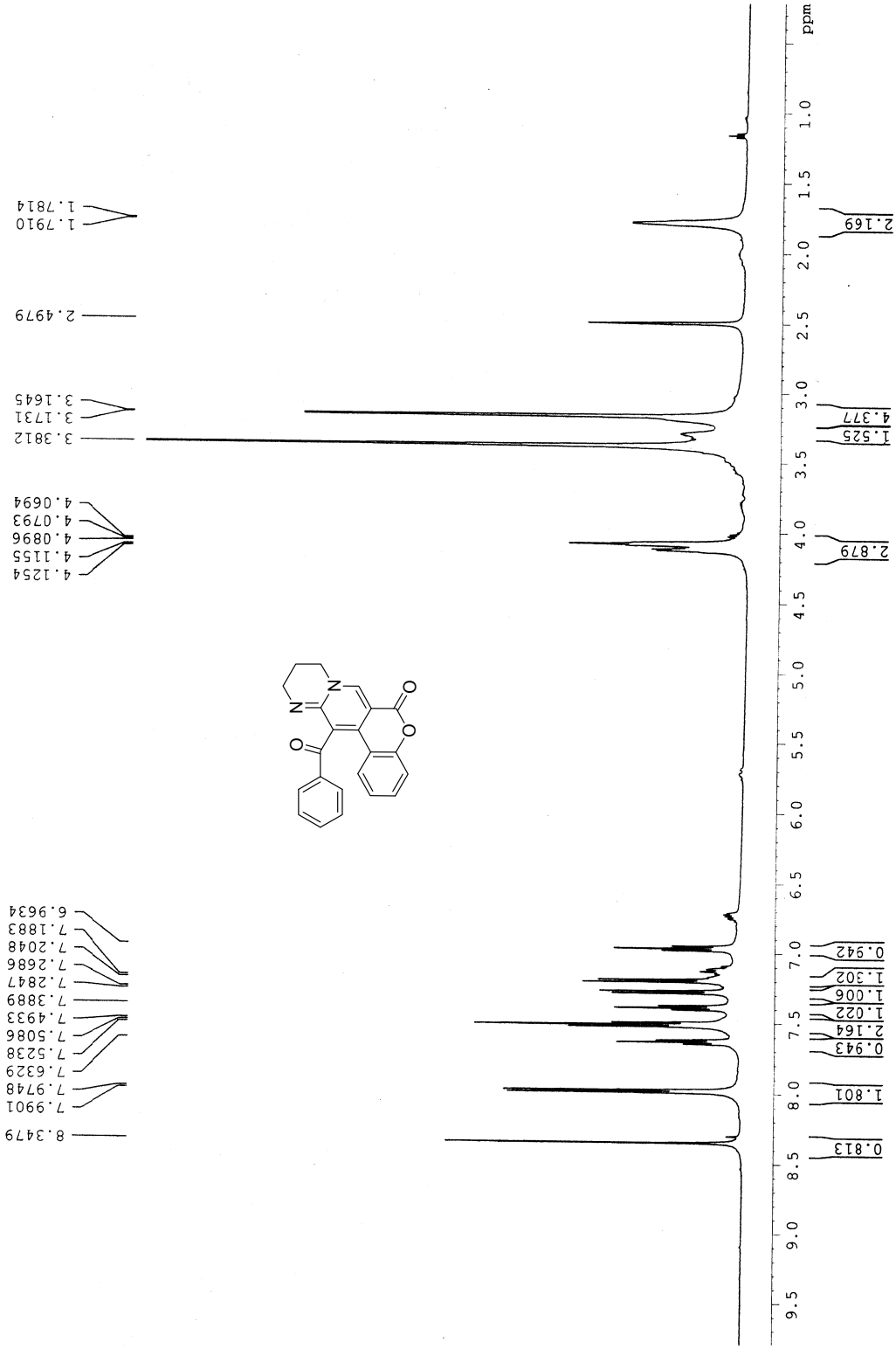


Figure 27. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4n**

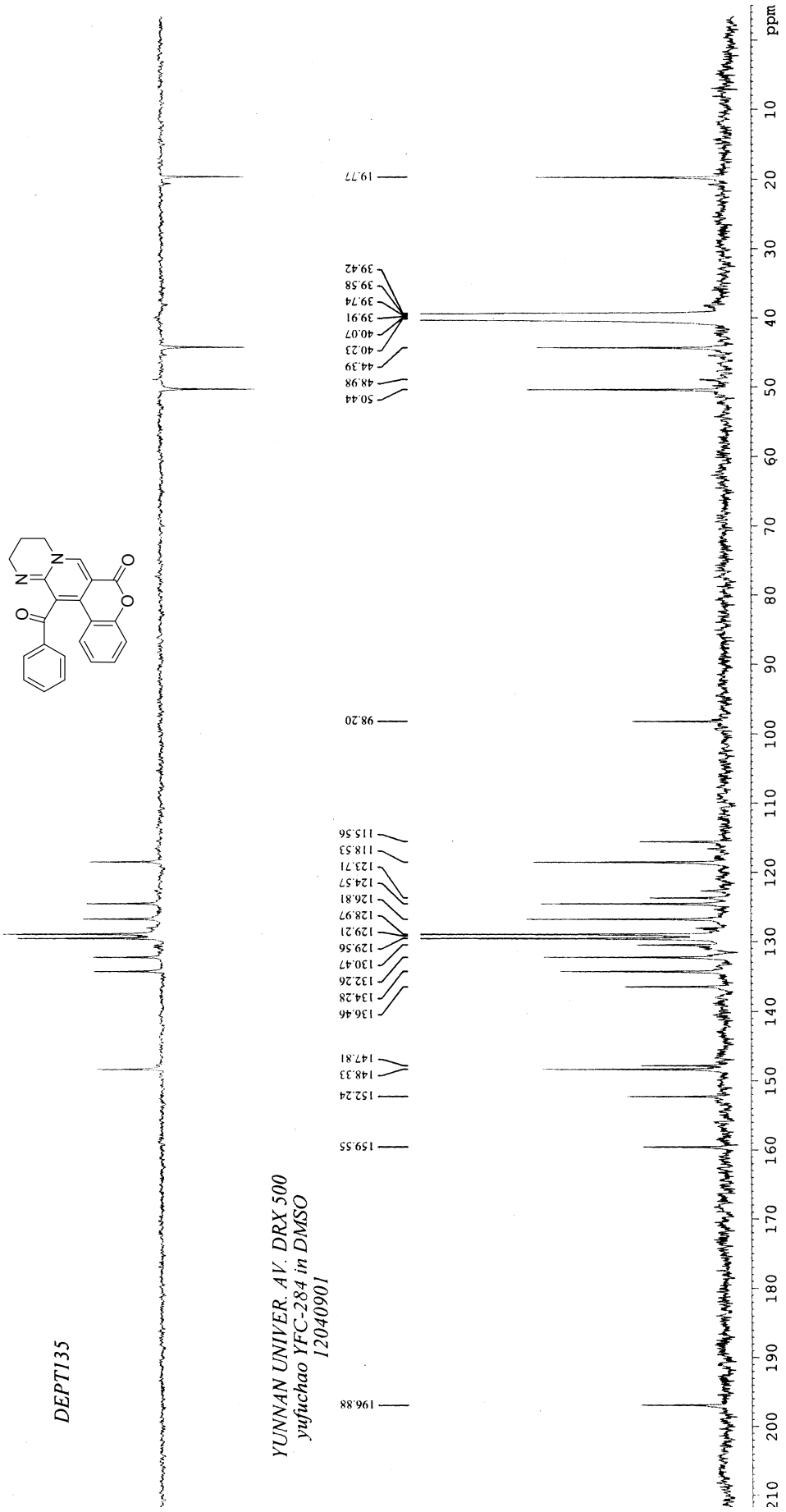


Figure 28. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4n**

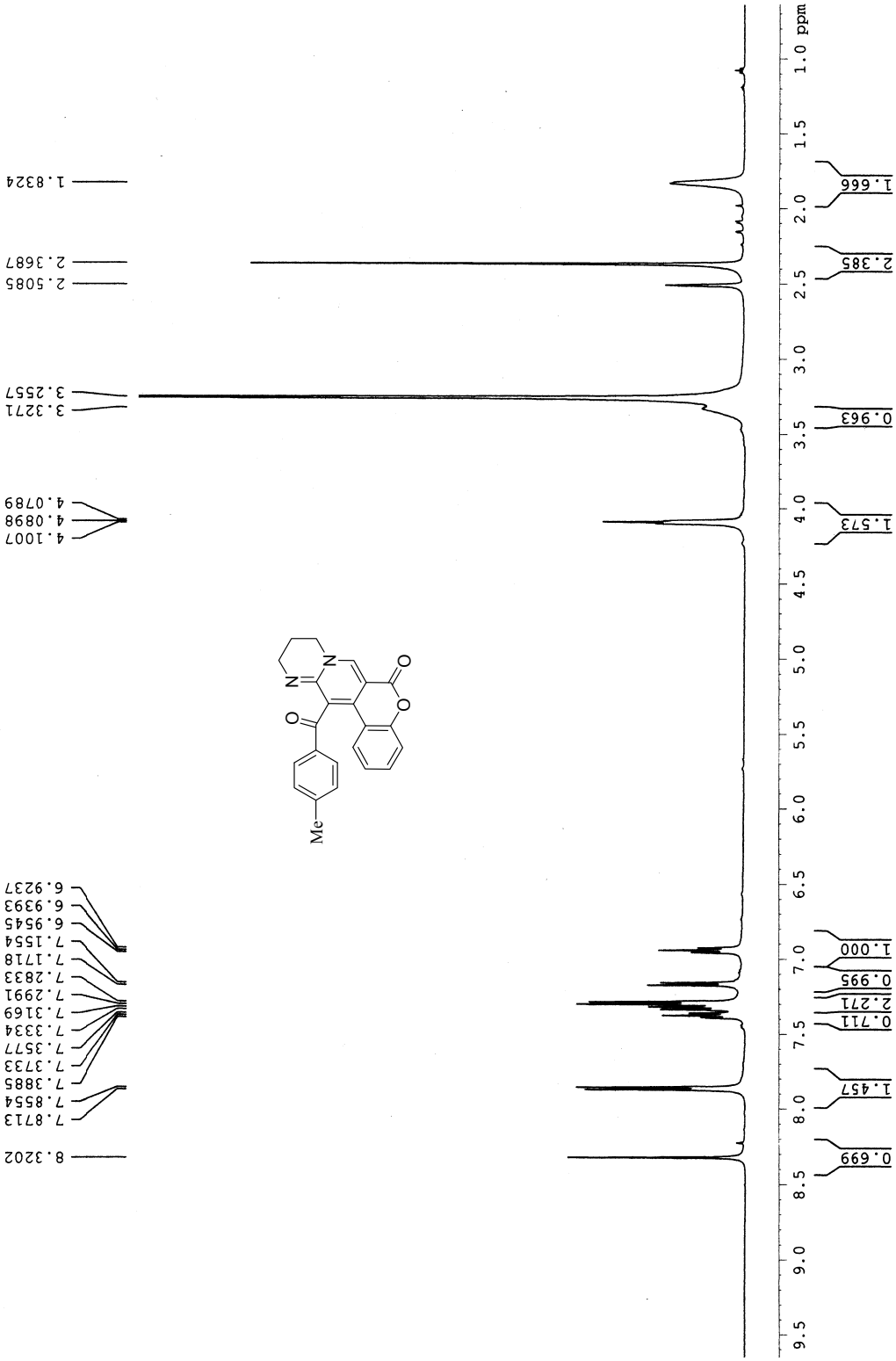


Figure 29. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4o**

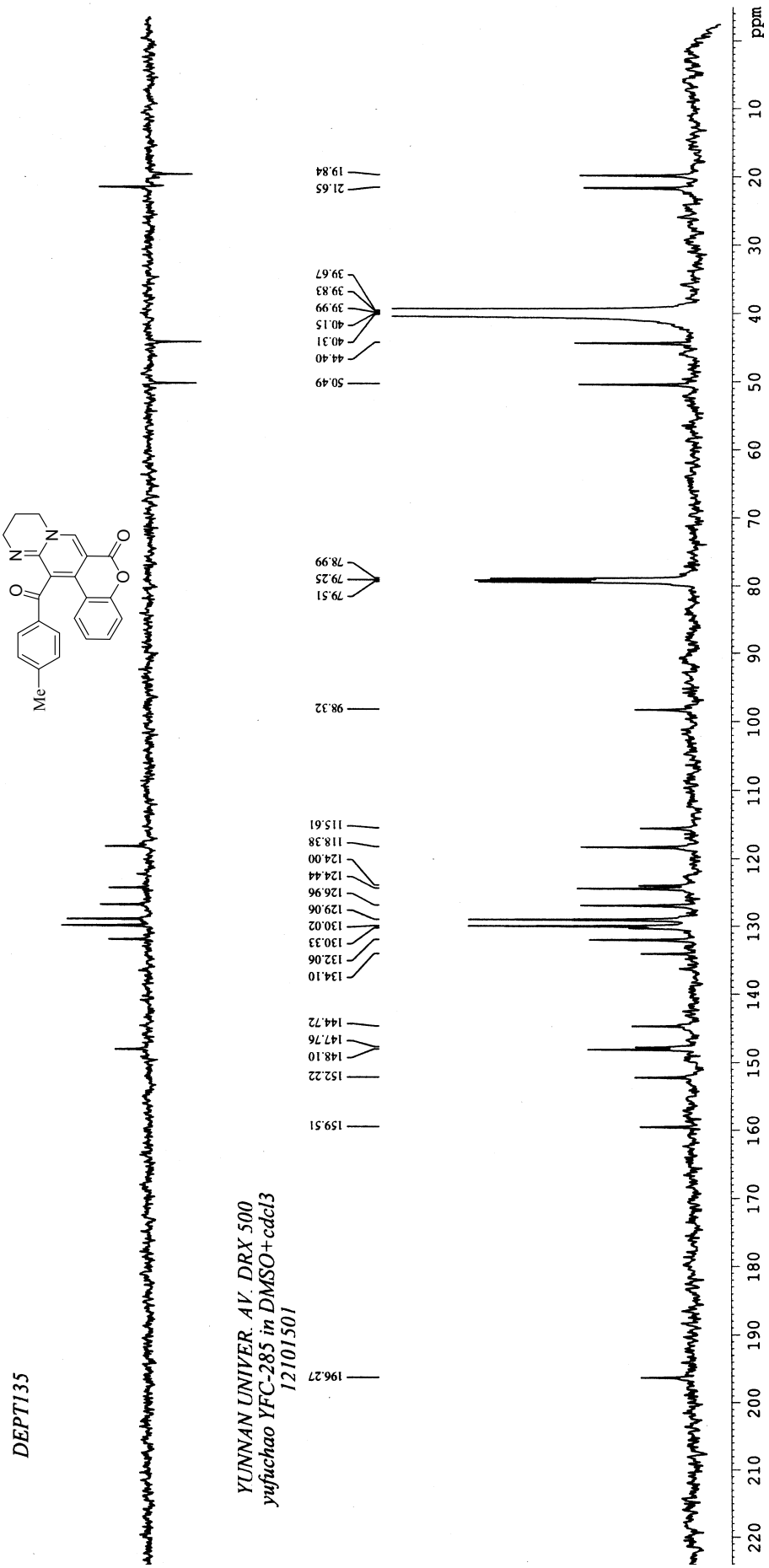


Figure 30. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4o**

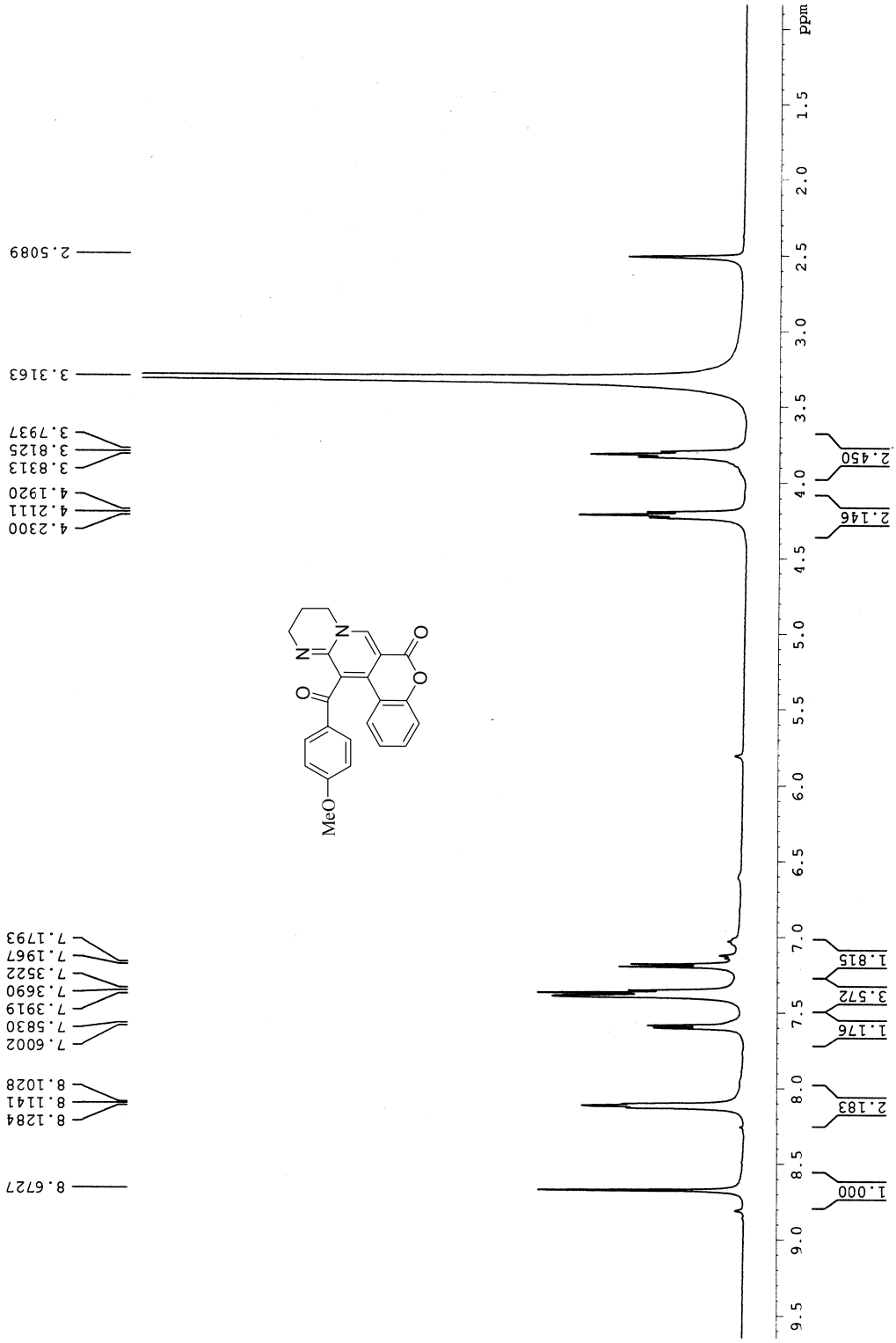


Figure 31. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4p**

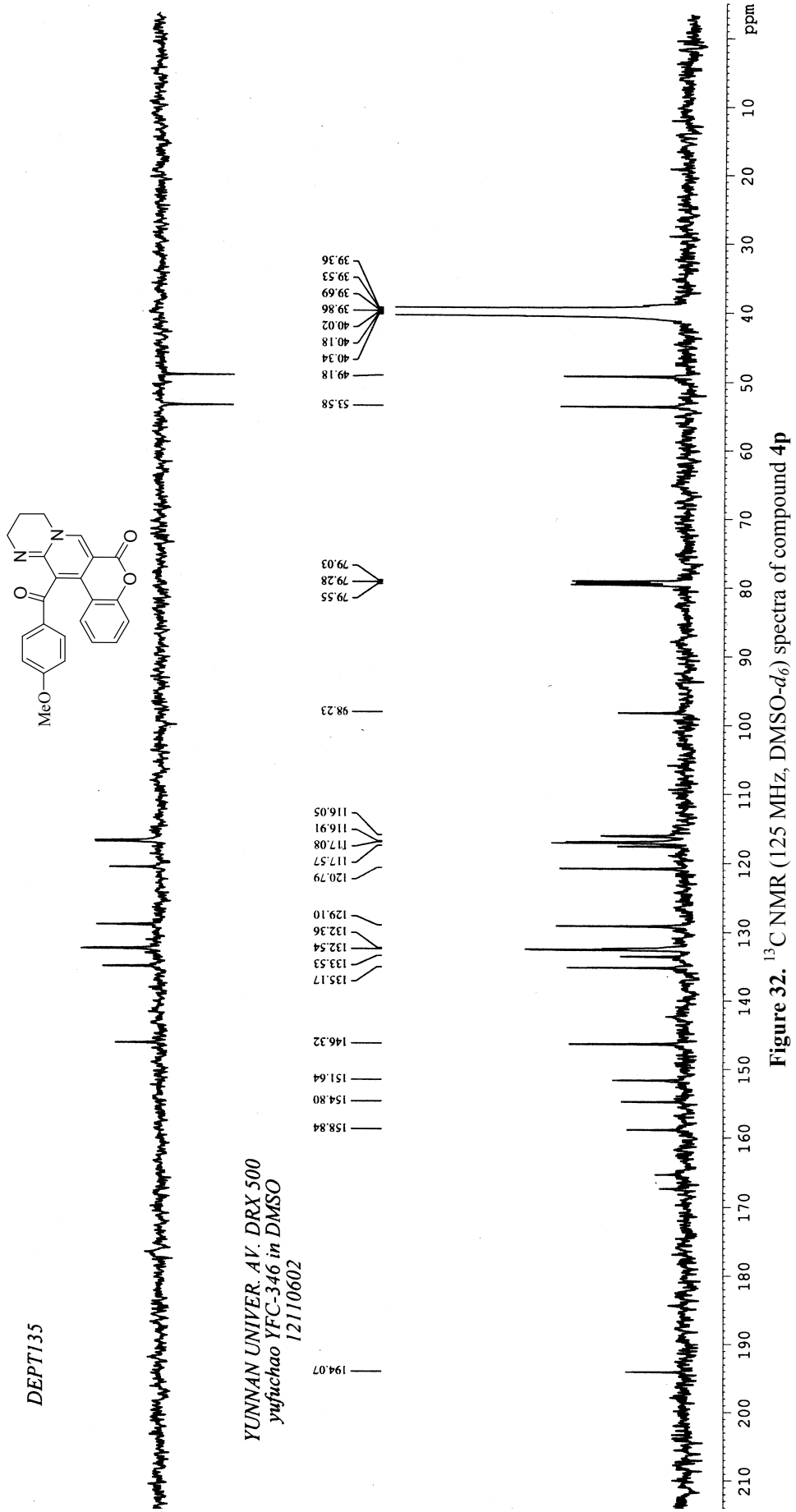


Figure 32. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4p**

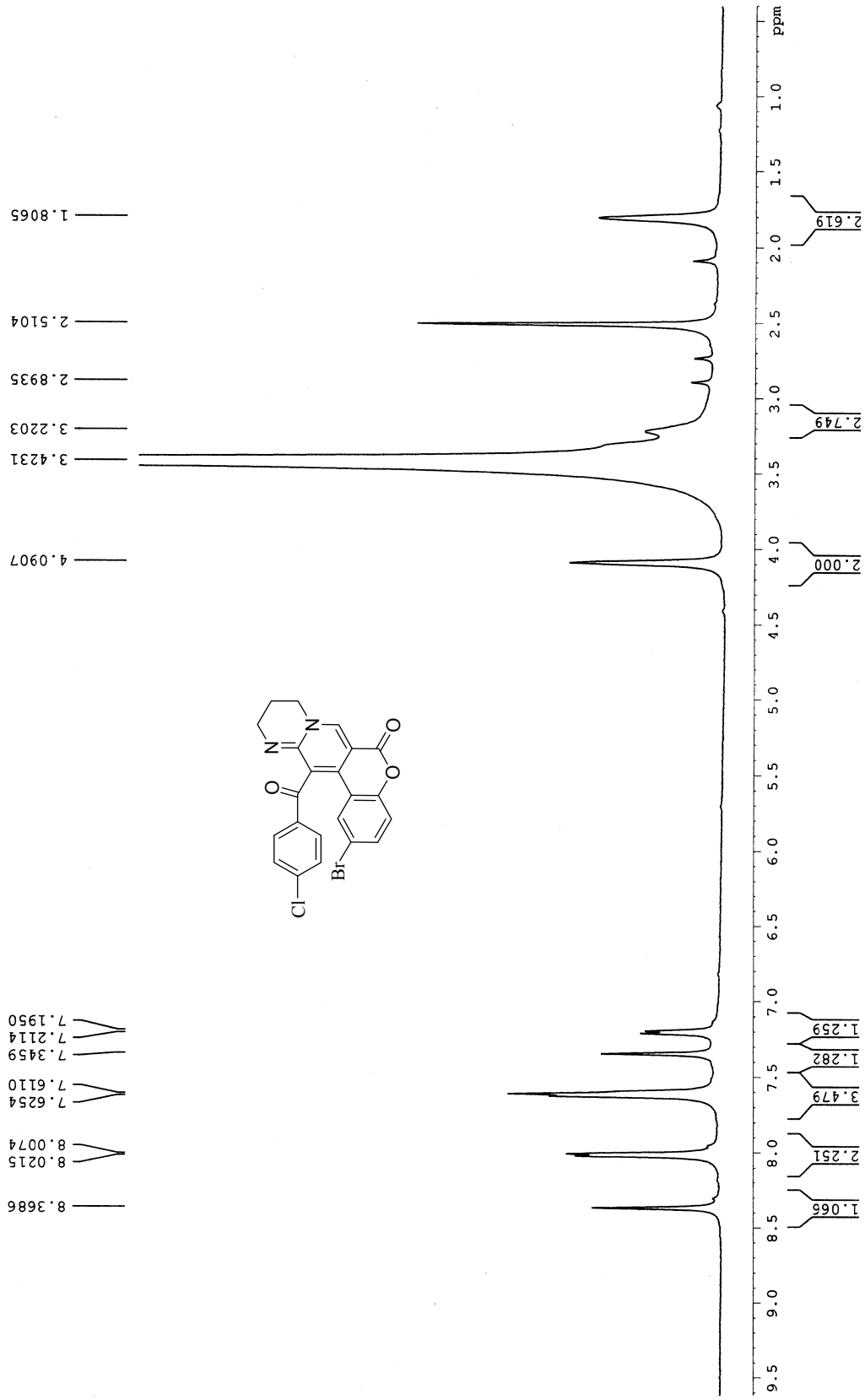


Figure 33. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4q**

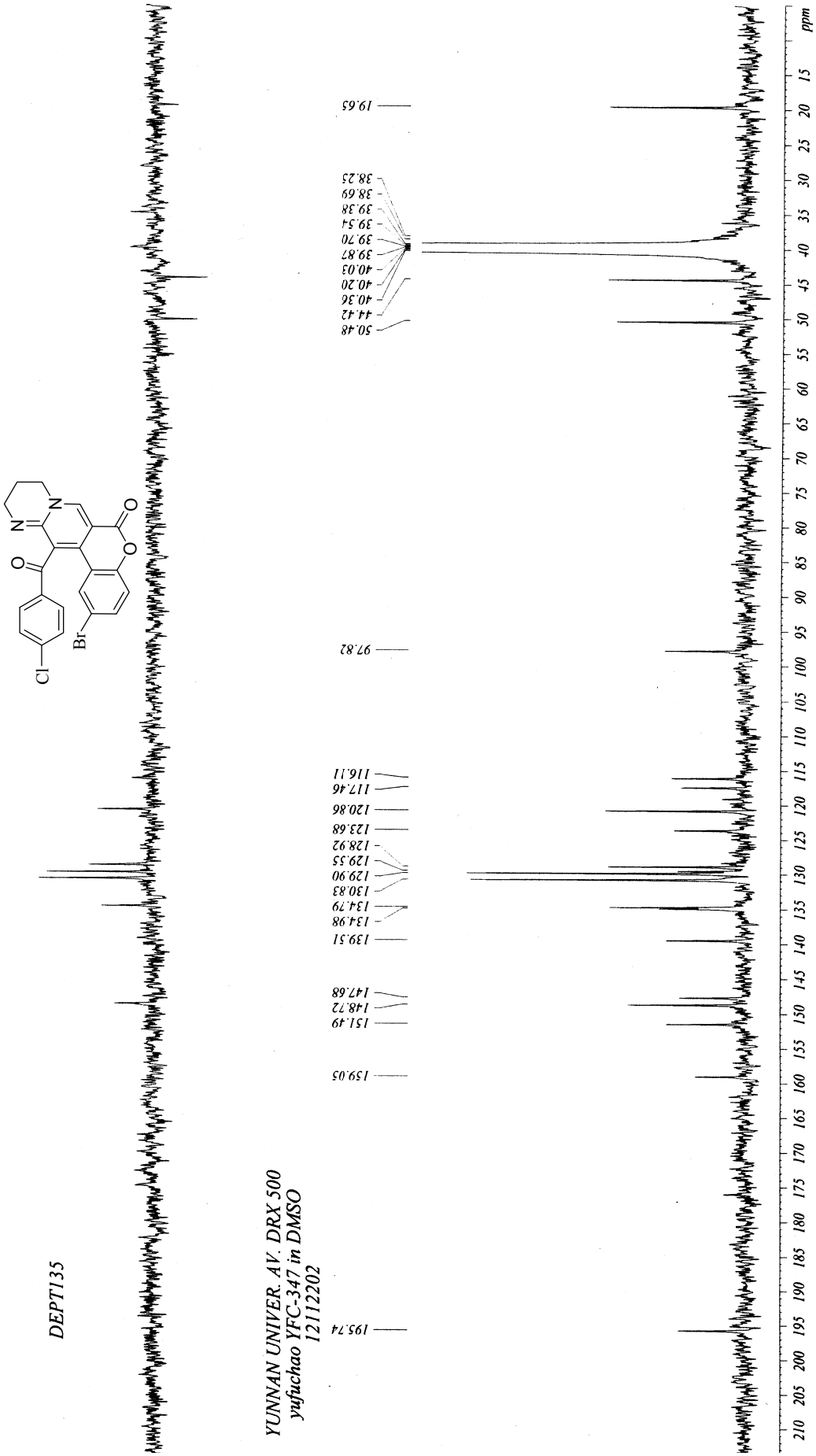


Figure 34. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4q**

References

1. Z.-T. Huang, M.-X. Wang, *Synthesis*, 1992, **12**, 1273; (*b*) Z.-J. Li, D. Charles, *Synth. Commun.,* 2001, **31**, 527.
2. A. S. Al-Ayed, *Molecules,* 2011, **16**, 10292.
3. CCDC 917318 contain the supplementary crystallographic data for compound **4d**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.