

Supporting Information

Base-Promoted Synthesis of Dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridines from 4-Chloro-3-Substituted Coumarins and α -Aminomaleimides

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Experimental Section

General remarks:

All reactions were monitored by thin-layer chromatography (TLC) on Merck silica gel 60 F254 plates. The temperatures were monitored using a mercury laboratory thermometer. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded as KBr pellets on a Nicolet FT-IR 100 spectrophotometer. ¹H NMR (300 MHz) and ¹³C{¹H} NMR (75 MHz) spectra were obtained using Bruker DRX-500 Avance and Bruker DRX-300 Avance spectrometers. All NMR spectra were recorded at r.t in DMSO-*d*₆. Chemical shifts are reported in parts per million (δ) downfield from an internal TMS reference. Coupling constants (*J* values) are reported in hertz (Hz), and standard abbreviations were used to indicate spin multiplicities. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a

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Finnigan-MATT 8430 mass spectrometer operating at an ionization potential of 70 eV. Single crystals of compound **3b** was formed in the mixture of CH₂Cl₂ and absolute EtOH (1:1 v/v).

General procedure for the preparation of dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine derivatives 3a-3h.

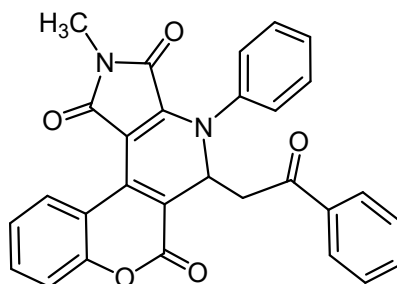
A mixture of α -aminomaleimides (1.0 mmol), 4-chloro-3-vinyl coumarins (1.0 mmol), and triethylamine (50 mol%) in 5 mL ethanol was stirred at reflux temperature until all starting materials had been consumed (the reaction was monitored with TLC). And a red solid was isolated by simple filtration. Derivatives **3a-3g** were purified by washing with hot EtOH twice and derivative **3h** was purified by column chromatography (hexane/AcOEt, 4/1, v/v).

General procedure for the preparation of dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine derivatives 3'a-3'd.

A mixture of α -aminomaleimides (2.0 mmol), 4-chloro-3-formyl coumarin (1.0 mmol), and triethylamine (50 mol%) in 5 mL ethanol was stirred at reflux until all starting materials had been consumed (the reaction was monitored with TLC). And a red solid was isolated by simple filtration. Derivatives **3'a-3'c** were purified by washing with hot EtOH twice and derivative **3d'** was purified by column chromatography (hexane/AcOEt, 4/1, v/v).

Characteristic data for compounds 3a-3h and 3'a-3'd.

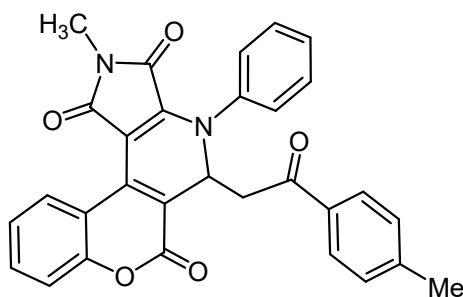
2-Methyl-5-(2-oxo-2-phenylethyl)-4-phenyl-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3a).



Light red solid, m.p = 120-122 °C (dec.), 0.42 g, yield: 88%. IR (KBr) (ν_{\max} , cm⁻¹): 1697 (OCNCO and COO), 1672 (C=O), 1606, 1570 and 1437 (Ar), 1251 and 1101 (C-O), 1202 (C-N), 741 (C-H) cm⁻¹. ¹H NMR (300.13 MHz, DMSO-*d*₆): 2.90 (3H, s, Me), 3.57 (1H, ABqd, ³J_{HH} = 16.1 Hz, ²J_{HH} =

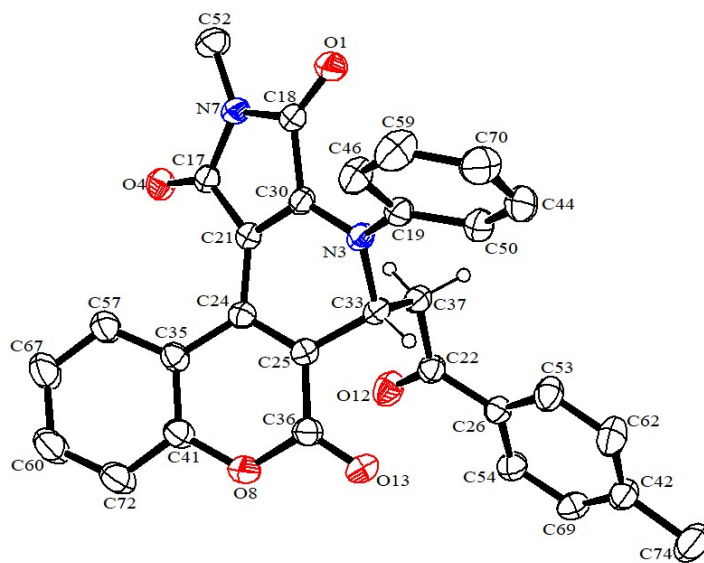
5.1 Hz, CH of CH₂), 3.84 (1H, ABqd, ³J_{HH} = 16.1 Hz, ²J_{HH} = 6.2 Hz, CH of CH₂), 5.81 (1H, t, ³J_{HH} = 5.6 Hz, CHN), 7.32-7.47 (7H, m, 5CH of Ph and 2CH of coumarin), 7.59 (1H, t, ³J_{HH} = 7.1 Hz, CH of Ph), 7.63 (1H, d, ³J_{HH} = 8.7 Hz, CH⁹ of coumarin), 7.72 (2H, d, ³J_{HH} = 7.9 Hz, 2CH of Ph), 7.90 (2H, d, ³J_{HH} = 7.9 Hz, 2CH of Ph), 9.1 (1H, dd, ³J_{HH} = 8.8 Hz, ²J_{HH} = 1.8 Hz, CH¹¹ of coumarin). ¹³C NMR (75.46 MHz, DMSO-*d*₆): 23.90 (Me), 41.89 (CH₂), 58.54 (CHN), 107.92 (C^{5a}), 108.27 (CH^{11a}), 115.32 (CH^{11a}), 116.75 (CH⁸ of coumarin), 124.14 (CH of Ph), 124.87 (2CH of Ph), 127.64 (CH¹⁰ of coumarin), 128.19 (2CH of Ph), 128.69 (2CH of Ph), 128.90 (CH¹¹ of coumarin), 129.08 (2CH of Ph), 131.93 (CH⁹ of coumarin), 133.43 (CH of Ph), 136.53 (C_{ipso}-CO), 136.84 (C_{ipso}-N), 141.54 (C^{3a}), 148.76 (C^{11b}), 152.35 (C^{7a}), 158.55 (COO), 161.92 (CON), 166.78 (CON), 196.9 (CO). MS (EI, 70 eV) *m/z* (%): 476 (M⁺, 7), 371 (12), 358 (53), 357 (100), 281 (12), 104 (41), 90 (23), 77 (78), 50 (13). Anal. calcd. for C₂₉H₂₀N₂O₅ (476.14): C, 73.10; H, 4.23; N, 5.88. Found: C, 73.15; H, 4.25; N, 5.81%.

2-Methyl-5-[2-(4-methylphenyl)-2-oxoethyl]-4-phenyl-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3b).



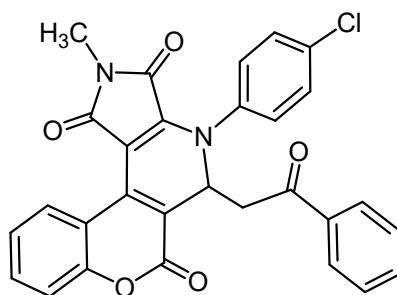
Light red solid, m.p = 157-159 °C (dec.), 0.41 g, yield: 85%. IR (KBr) (ν_{\max} , cm⁻¹): 1701 (OCNCO and COO), 1664 (C=O), 1598, 1566 and 1430 (Ar), 1261 and 1091 (C-O), 1197 (C-N), 764 (C-H) cm⁻¹. ¹H NMR (300.13 MHz, DMSO-*d*₆): 2.31 (3H, s, Me), 2.89 (3H, s, Me), 3.47 (H, ABq, ³J_{HH} = 15.8 Hz, CH of CH₂), 3.82 (H, ABq, ³J_{HH} = 15.8 Hz, CH of CH₂), 5.75 (1H, bs, CHN), 7.23 (2H, d, ³J_{HH} = 7.7 Hz, 2CH of Ar), 7.39 (1H, d, ³J_{HH} = 8.4 Hz, CH of CH⁸ of coumarin), 7.40- 7.46 (4H, m, CH¹⁰ of coumarin and 4CH of Ar), 7.58 (2H, d, ³J_{HH} = 8.2 Hz, 2CH of Ar), 7.63 (1H, t, ³J_{HH} = 7.5 Hz, CH⁹ of coumarin), 7.78 (2H, d, ³J_{HH} = 7.7 Hz, 2CH of Ar), 9.05 (1H, d, ³J_{HH} = 8.1 Hz, CH¹¹ of coumarin). ¹³C NMR (75.46 MHz, DMSO-*d*₆): 21.13 (Me), 23.89 (Me), 41.74 (CH₂), 58.31 (CHN),

108.31 (C^{5a}), 108.91 (CH^{11a}), 115.26 (CH^{11c}), 116.76 (CH⁸ of coumarin), 124.15 (CH¹⁰ of coumarin), 126.69 (2CH of Ar), 128.31 (2CH of Ar), 128.86 (CH of Ar), 128.98 (2CH of Ar), 129.22 (2CH of Ar), 131.95 (CH⁹ and CH¹¹ of coumarin), 134.06 (C_{ipso}-N), 136.76 (C_{ipso}-CO), 140.38 (C^{3a}), 143.97 (C_{ipso}-Me), 148.57 (C^{11b}), 152.35 (C^{7a}), 158.47 (COO), 161.99 (CON), 166.77 (CON), 196.39 (CO). MS (EI, 70 eV) *m/z* (%): 490 (M⁺, 3), 371 (4), 358 (26), 357 (100), 294 (11), 281 (7), 272 (6), 244 (5), 216 (4), 197 (6), 119 (46), 105 (25), 106 (6), 93 (5), 91 (43), 89 (6), 79 (9), 77 (75), 65 (25), 51 (16). Anal. calcd. for C₃₀H₂₂N₂O₅ (490.15): C, 73.46; H, 4.52; N, 5.71. Found: C, 73.40; H, 4.55; N, 5.74%. Crystal data for **3b** C₃₀H₂₂N₂O₅ (CCDC 2254629): M_w = 490.49, monoclinic, P 1 21/c 1, a = 11.679(2) Å, b = 15.814(3) Å, c = 13.357(3) Å, α = 90, β = 101.12(3), γ = 90, V = 2420.6(9) Å³, Z = 4, D_c = 1.346 mg/m³, F(000) = 1024, crystal dimension 0.45 × 0.32 × 0.28 mm, radiation, Mo Kα (λ = 0.71073 Å), 1.777 ≤ 2θ ≤ 25.000, intensity data were collected at 293.15 K with a Bruker APEX area-detector diffractometer, and employing ω/2θ scanning technique, in the range of -13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -15 ≤ l ≤ 15, the structure was solved by a direct method, all non-hydrogen atoms were positioned and anisotropic thermal parameters refined from 3675 observed reflections with R (into) = 0.0378 by a full-matrix least-squares technique converged to R1 = 0.0536, and wR2 = 0.1211 [I > 2σ(I)].



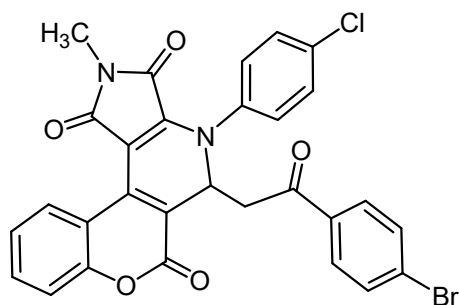
Ortep diagram of compound **3b**

4-(4-Chlorophenyl)-2-methyl-5-(2-oxo-2-phenylethyl)-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3c).



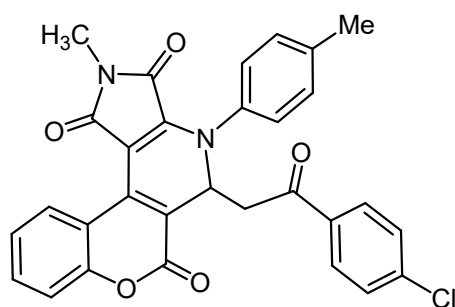
Light red solid, m.p = 227-228 °C (dec.), 0.39 g, yield: 77%. IR (KBr) (ν_{\max} , cm^{-1}): 1702 (OCNCO and COO), 1670 (C=O), 1612, 1572 and 1458 (Ar), 1250 and 1105 (C-O), 1197 (C-N), 1012 (C-Cl), 759 (C-H) cm^{-1} . ^1H NMR (300.13 MHz, $\text{DMSO-}d_6$): 2.89 (3H, s, Me), 3.53 (1H, ABqd, $^3J_{\text{HH}} = 16.6$ Hz, $^2J_{\text{HH}} = 4.8$ Hz, CH of CH_2), 3.88 (1H, ABqd, $^3J_{\text{HH}} = 16.6$ Hz, $^2J_{\text{HH}} = 6.0$ Hz, CH of CH_2), 5.78 (1H, t, $^3J_{\text{HH}} = 5.6$ Hz, CHN), 7.39 (2H, d, $^3J_{\text{HH}} = 8.3$ Hz, 2CH of Ar), 7.40 (2H, d, $^3J_{\text{HH}} = 8.3$ Hz, CH^8 of coumarin), 7.42 (1H, t, $^3J_{\text{HH}} = 8.4$ Hz, CH^{10} of coumarin), 4.44-7.48 (3H, m, 3H of Ar), 7.59 (1H, t, $^3J_{\text{HH}} = 8.3$ Hz, 2CH of Ar), 7.63 (1H, t, $^3J_{\text{HH}} = 7.5$ Hz, CH^9 of coumarin), 7.89 (2H, d, $^3J_{\text{HH}} = 7.7$ Hz, 2CH of Ar), 9.07 (1H, d, $^3J_{\text{HH}} = 8.1$ Hz, CH^{11} of coumarin). ^{13}C NMR (75.46 MHz, $\text{DMSO-}d_6$): 23.90 (Me), 41.85 (CH_2), 58.19 (CHN), 108.25 (C^{5a}), 108.89 (CH^{11a}), 115.26 (CH^{11c}), 116.75 (CH^8 of coumarin), 124.16 (CH^{10} of coumarin), 126.73 (2CH of Ar), 128.18 (2CH of Ar), 128.68 (2CH of Ar), 128.85 (C-Cl), 128.98 (2CH of Ar), 131.96 (CH^9 and CH^{11} of coumarin), 133.47 (CH of Ar), 136.42 ($\text{C}_{\text{ipso-N}}$), 136.77 ($\text{C}_{\text{ipso-CO}}$), 140.36 (C^{3a}), 148.58 (C^{11b}), 152.34 (C^{7a}), 158.48 (COO), 162.02 (CON), 166.77 (CON), 196.87 (CO). MS (EI, 70 eV) m/z (%): 510 (M^+ , 2), 405 (4), 394 (8), 393 (35), 392 (25), 391 (100), 294 (17), 111 (5), 105 (7), 77 (9). Anal. calcd. for $\text{C}_{29}\text{H}_{19}\text{ClN}_2\text{O}_5$ (510.10): C, 68.17; H, 3.75; N, 5.48. Found: C, 68.20; H, 3.77; N, 5.53%.

5-[2-(4-Bromophenyl)-2-oxoethyl]-4-(4-chlorophenyl)-2-methyl-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3d).



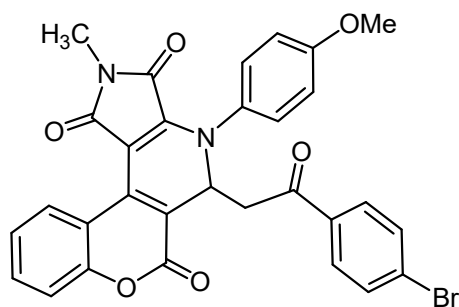
Light red solid, m.p = 238-239 °C (dec.), 0.44 g, yield: 75%. IR (KBr) (ν_{\max} , cm^{-1}): 1701 (OCNCO and COO), 1678 (C=O), 1612, 1572 and 1445 (Ar), 1250 and 1212 (C-O), 1198 (C-N), 1086 (C-Cl), 1009 (C-Br), 761 (C-H) cm^{-1} . ^1H NMR (300.13 MHz, $\text{DMSO}-d_6$): 2.91 (3H, s, Me), 3.52 (1H, ABqd, $^3J_{\text{HH}} = 16.9$ Hz, $^2J_{\text{HH}} = 4.7$ Hz, CH of CH_2), 3.87 (1H, ABqd, $^3J_{\text{HH}} = 16.5$ Hz, $^2J_{\text{HH}} = 6.1$ Hz, CH of CH_2), 5.76 (1H, t, $^3J_{\text{HH}} = 6.6$ Hz, CHN), 7.39 (2H, d, $^3J_{\text{HH}} = 8.4$ Hz, 2CH of Ar), 7.45 (1H, t, $^3J_{\text{HH}} = 7.0$ Hz, CH^{10} of coumarin), 7.46 (2H, d, $^3J_{\text{HH}} = 7.6$ Hz, 2CH of Ar), 7.47 (1H, d, $^3J_{\text{HH}} = 7.3$ Hz, CH^8 of coumarin), 7.63 (1H, t, $^3J_{\text{HH}} = 8.2$ Hz, CH^9 of coumarin), 7.65 (2H, d, $^3J_{\text{HH}} = 8.4$ Hz, CH of Ar), 7.81 (2H, d, $^3J_{\text{HH}} = 7.7$ Hz, 2CH of Ar), 9.07 (1H, d, $^3J_{\text{HH}} = 8.2$ Hz, CH^{11} of coumarin). ^{13}C NMR (75.46 MHz, $\text{DMSO}-d_6$): 23.92 (Me), 41.93 (CH_2), 58.12 (CHN), 108.14 (C^{5a}), 108.76 (CH^{11a}), 115.24 (CH^{11c}), 116.77 (CH^8 of coumarin), 124.19 (CH^{10} of coumarin), 126.74 (C-Br and 2CH of Ar), 127.69 (2CH of Ar), 128.87 (C-Br), 128.99 (2CH of Ar), 130.17 (2CH of Ar), 131.75 (CH^{11} of coumarin), 132.00 (CH^9 of coumarin), 135.44 ($\text{C}_{\text{ipso}}\text{-CO}$), 136.78 ($\text{C}_{\text{ipso}}\text{-N}$), 140.30 (C^{3a}), 148.56 (C^{11b}), 152.34 (C^{7a}), 158.47 (COO), 162.00 (CON), 166.76 (CON), 196.14 (CO). MS (EI, 70 eV) m/z (%): 590 (M^{+2} , 1), 588 (M^+ , 1), 394 (8), 393 (36), 392 (25), 391 (100), 75 (5). Anal. calcd. for $\text{C}_{29}\text{H}_{18}\text{BrClN}_2\text{O}_5$ (588.01): C, 59.05; H, 3.08; N, 4.75. Found: C, 59.10; H, 3.10; N, 4.68%.

5-[2-(4-Chlorophenyl)-2-oxoethyl]-2-methyl-4-(4-methylphenyl)-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3e).



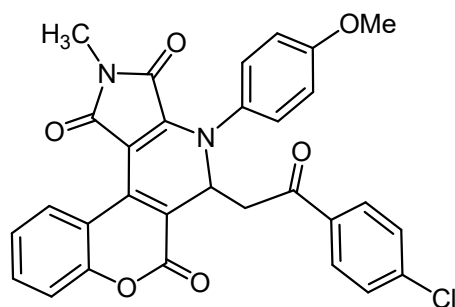
Light red solid, m.p = 225-226 °C (dec.), 0.46 g, yield: 89%. IR (KBr) (ν_{\max} , cm^{-1}): 1702 (OCNCO and COO), 1684 (C=O), 1612, 1572 and 1458 (Ar), 1250 and 1180 (C-O), 1197 (C-N), 1012 (C-Cl), 761 (C-H) cm^{-1} . ^1H NMR (300.13 MHz, $\text{DMSO-}d_6$): 2.32 (3H, s, Me), 2.89 (3H, s, Me), 3.55 (1H, ABqd, $^3J_{\text{HH}} = 16.1$ Hz, $^2J_{\text{HH}} = 5.2$ Hz, CH of CH_2), 3.81 (1H, ABqd, $^3J_{\text{HH}} = 16.1$ Hz, $^2J_{\text{HH}} = 6.1$ Hz, CH of CH_2), 5.74 (1H, t, $^3J_{\text{HH}} = 5.6$ Hz, CHN), 7.20 (2H, d, $^3J_{\text{HH}} = 8.0$ Hz, 2CH of Ar), 7.37 (2H, d, $^3J_{\text{HH}} = 8.0$ Hz, 2CH of Ar), 7.39 (1H, d, $^3J_{\text{HH}} = 8.0$ Hz, CH^8 of coumarin), 7.40 (1H, t, $^3J_{\text{HH}} = 8.6$ Hz, CH^{10} of coumarin), 7.50 (2H, d, $^3J_{\text{HH}} = 8.5$ Hz, 2CH of Ar), 7.63 (1H, t, $^3J_{\text{HH}} = 8.7$ Hz, CH^9 of coumarin), 7.89 (2H, d, $^3J_{\text{HH}} = 8.5$ Hz, 2CH of Ar), 9.10 (1H, dd, $^3J_{\text{HH}} = 8.6$ Hz, $^2J_{\text{HH}} = 1.7$ Hz, CH^{11} of coumarin). ^{13}C NMR (75.46 MHz, $\text{DMSO-}d$): 20.64 (Me), 23.88 (Me), 42.06 (CH_2), 58.61 (CHN), 107.17 (C^{5a}), 107.55 (CH^{11a}), 115.32 (CH^{11c}), 116.75 (CH^8 of coumarin), 124.14 (CH^{10} of coumarin), 124.78 (2CH of Ar), 128.78 (CH^{11} of coumarin), 128.98 (2CH of Ar), 129.56 (2CH of Ar), 130.07 (2CH of Ar), 131.94 (CH^9 of coumarin), 135.22 ($\text{C}_{\text{ipso}}\text{-Me}$), 136.87 ($\text{C}_{\text{ipso}}\text{-CO}$), 137.45 ($\text{C}_{\text{ipso}}\text{-N}$), 138.41 (C-Cl), 139.07 (C^{3a}), 148.70 (C^{11b}), 152.31 (C^{7a}), 158.56 (COO), 161.86 (CON), 166.75 (CON), 195.86 (CO). MS (EI, 70 eV) m/z (%): 524 (M^+ , 1), 455 (1), 372 (25), 371 (100), 294 (7), 139 (6), 91 (15), 65 (6). Anal. calcd. for $\text{C}_{30}\text{H}_{21}\text{ClN}_2\text{O}_5$ (524.11): C, 68.64; H, 4.03; N, 5.34. Found: C, 68.70; H, 4.05; N, 5.38%.

5-[2-(4-Bromophenyl)-2-oxoethyl]-4-(4-methoxyphenyl)-2-methyl-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3f).



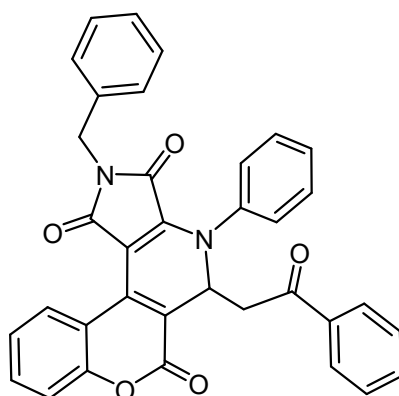
Light red solid, m.p = 190-191 °C (dec.), 0.54 g, yield: 92%. IR (KBr) (ν_{\max} , cm^{-1}): 1710 (OCNCO and COO), 1681 (C=O), 1613, 1574 and 1459 (Ar), 1240, 1200 and 1099 (C-O), 1177 (C-N), 1007 (C-Br), 760 (C-H) cm^{-1} . ^1H NMR (300.13 MHz, $\text{DMSO-}d_6$): 2.87 (3H, s, Me), 3.76 (3H, s, OMe), 3.49 (1H, ABq, $^3J_{\text{HH}} = 17.7$ Hz, CH of CH_2), 3.81 (1H, ABq, $^3J_{\text{HH}} = 17.7$ Hz, CH of CH_2), 5.70 (1H, bs, CHN), 6.92 (2H, d, $^3J_{\text{HH}} = 8.4$ Hz, 2CH of Ar), 7.36 (1H, d, $^3J_{\text{HH}} = 8.3$ Hz, CH^8 of coumarin), 7.38 (1H, d, $^3J_{\text{HH}} = 8.3$ Hz, CH^{10} of coumarin), 7.45 (2H, d, $^3J_{\text{HH}} = 8.0$ Hz, 2CH of Ar), 7.61 (1H, t, $^3J_{\text{HH}} = 7.5$ Hz, CH^9 of coumarin), 7.63 (2H, d, $^3J_{\text{HH}} = 8.0$ Hz, 2CH of Ar), 7.79 (2H, d, $^3J_{\text{HH}} = 8.3$ Hz, 2CH of Ar), 9.12 (1H, d, $^3J_{\text{HH}} = 8.0$ Hz, CH^{11} of coumarin). ^{13}C NMR (75.46 MHz, $\text{DMSO-}d$): 23.86 (Me), 42.09 (CH_2), 55.50 (OMe), 58.90 (CHN), 105.85 (C^{5a}), 106.99 (CH^{11a}), 114.24 (2CH of Ar), 115.41 (CH^{11a}), 116.73 (CH^8 of coumarin), 124.11 (CH^{10} of coumarin), 126.67 (2CH of Ar), 127.60 (C-Br), 128.93 ($\text{C}_{\text{ipso-N}}$), 130.14 (2CH of Ar), 131.72 (2CH of Ar), 131.89 (CH^{11} of coumarin), 134.42 (CH^9 of coumarin), 135.55 ($\text{C}_{\text{ipso-CO}}$), 137.02 (C^{3a}), 148.77 (C^{11b}), 152.30 (C^{7a}), 158.60 (COO), 158.84 ($\text{C}_{\text{ipso-OMe}}$), 161.82 (CON), 166.75 (CON), 196.04 (CO). MS (EI, 70 eV) m/z (%): 586 (M^{+1} , 1), 584 (M^+ , 1), 455 (7), 388 (14), 387 (59), 328 (8), 309 (6), 294 (10), 293 (18), 92 (11), 91 (100), 77 (5), 65 (7). Anal. calcd. for $\text{C}_{30}\text{H}_{21}\text{BrN}_2\text{O}_6$ (584.06): C, 61.55; H, 3.62; N, 4.79. Found: C, 61.50; H, 3.60; N, 4.86%.

5-[2-(4-Chlorophenyl)-2-oxoethyl]-4-(4-methoxyphenyl)-2-methyl-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3g)



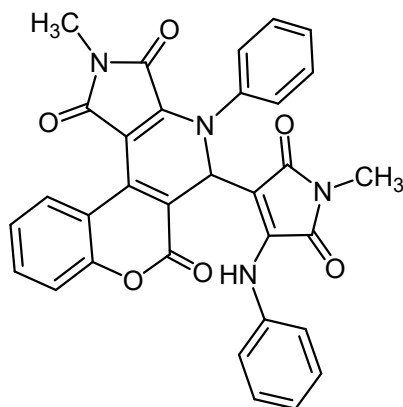
Light red solid, m.p = 199-200 °C (dec.), 0.48 g, yield: 90%. IR (KBr) (ν_{\max} , cm^{-1}): 1702 (OCNCO and COO), 1684 (C=O), 1612, 1572 and 1458 (Ar), 1251, 1210 and 1104 (C-O), 1197 (C-N), 1013 (C-Cl), 761 (C-H) cm^{-1} . ^1H NMR (300.13 MHz, $\text{DMSO-}d_6$): 2.89 (3H, s, Me), 3.78 (3H, s, OMe), 3.50 (1H, ABqd, $^3J_{\text{HH}} = 16.1$ Hz, $^2J_{\text{HH}} = 5.1$ Hz, CH of CH_2), 3.82 (1H, ABqd, $^3J_{\text{HH}} = 16.1$ Hz, $^2J_{\text{HH}} = 6.0$ Hz, CH of CH_2), 5.72 (1H, t, $^3J_{\text{HH}} = 6.0$ Hz, CHN), 6.92 (2H, d, $^3J_{\text{HH}} = 8.4$ Hz, 2CH of Ar), 7.37 (1H, d, $^3J_{\text{HH}} = 8.0$ Hz, CH^8 of coumarin), 7.39 (1H, t, $^3J_{\text{HH}} = 8.0$ Hz, CH^{10} of coumarin), 7.45 (2H, d, $^3J_{\text{HH}} = 8.2$ Hz, 2CH of Ar), 7.50 (2H, d, $^3J_{\text{HH}} = 8.2$ Hz, 2CH of Ar), 7.62 (1H, t, $^3J_{\text{HH}} = 7.6$ Hz, CH^9 of coumarin), 7.88 (2H, d, $^3J_{\text{HH}} = 8.3$ Hz, 2CH of Ar), 9.14 (1H, d, $^3J_{\text{HH}} = 8.1$ Hz, CH^{11} of coumarin). ^{13}C NMR (75.46 MHz, $\text{DMSO-}d_6$): 23.85 (Me), 42.11 (CH_2), 55.49 (OMe), 58.88 (CHN), 105.86 (C^{5a}), 107.01 (CH^{11a}), 114.24 (2CH of Ar), 115.42 (CH^{11c}), 116.73 (CH^8 of coumarin), 124.11 (CH^{10} of coumarin), 126.67 (2CH of Ar), 128.76 (2CH of Ar), 128.93 ($\text{C}_{\text{ipso}}\text{-CO}$), 130.06 (2CH of Ar), 131.88 (CH^{11} of coumarin), 134.42 (CH^9 of coumarin), 135.22 ($\text{C}_{\text{ipso}}\text{-CO}$), 137.01 (C-Cl), 138.39 (C^{3a}), 148.77 (C^{11b}), 152.31 (C^{7a}), 158.60 (COO), 158.83 ($\text{C}_{\text{ipso}}\text{-OMe}$), 161.84 (CON), 166.76 (CON), 195.83 (CO). MS (EI, 70 eV) m/z (%): 540 (M^+ , 1), 388 (28), 387 (100), 344 (5), 294 (13), 247 (4), 139 (8), 111 (6), 77 (4). Anal. calcd. for $\text{C}_{30}\text{H}_{21}\text{ClN}_2\text{O}_6$ (540.11): C, 66.61; H, 3.91; N, 5.18. Found: C, 66.68; H, 3.89; N, 5.13%.

2-Benzyl-5-(2-oxo-2-phenylethyl)-4-phenyl-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3h).



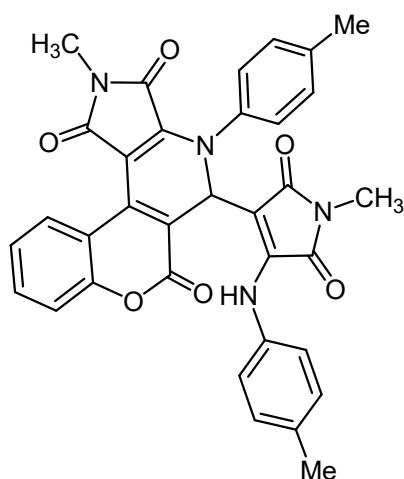
Light red solid, m.p = 210-212 °C (dec.), 0.30 g, yield: 55%. IR (KBr) (ν_{\max} , cm^{-1}): 1700 (OCNCO and COO), 1637 (C=O), 1607, 1568 and 1492 (Ar), 1248, 1200 and 1092 (C-O), 1197 (C-N), 754 (C-H) cm^{-1} . ^1H NMR (300.13 MHz, CDCl_3): 3.28 (1H, ABqd, $^3J_{\text{HH}} = 14.7$ Hz, $^2J_{\text{HH}} = 4.9$ Hz, CH of CH_2), 3.60 (1H, ABqd, $^3J_{\text{HH}} = 14.7$ Hz, $^2J_{\text{HH}} = 6.2$ Hz, CH of CH_2), 4.67 (1H, t, $^3J_{\text{HH}} = 4.2$ Hz, CHN), 5.91 (2H, ABq, $^2J_{\text{HH}} = 7.7$ Hz, 2CH of CH_2). 7.24-7.43 (13H, m, 10H of Ph and 3H of coumarin), 7.56 (2H, d, $^3J_{\text{HH}} = 7.6$ Hz, CH of Ph), 7.51 (1H, t, $^3J_{\text{HH}} = 7.6$ Hz, CH of Ph), 7.77 (2H, d, $^3J_{\text{HH}} = 7.5$ Hz, CH of Ph), 9.09 (1H, d, $^3J_{\text{HH}} = 7.8$ Hz, CH^{11} of coumarin). ^{13}C NMR (75.46 MHz, CDCl_3): 41.24 (CH_2), 41.83 (CH_2), 60.24 (CHN), 105.06 ($\text{C}^{5\text{a}}$), 108.45 ($\text{CH}^{11\text{a}}$), 115.29 ($\text{CH}^{11\text{c}}$), 116.84 (CH^8 of coumarin), 124.35 (CH^{10} of coumarin), 125.72 (2CH of Ph), 127.88 (CH of Ph), 128.17 (CH of Ar), 128.68 (2CH of Ph), 128.69 (2CH of Ph), 129.42 (CH^{11} of coumarin), 131.88 (CH^9 of coumarin), 133.41 (CH of Ph), 136.08 ($\text{C}_{\text{ipso}}\text{-CO}$), 136.72 ($\text{C}_{\text{ipso}}\text{-Ph}$), 139.11 ($\text{C}^{3\text{a}}$), 140.56 ($\text{C}_{\text{ipso}}\text{-Bn}$), 149.34 ($\text{C}^{11\text{b}}$), 152.77 ($\text{C}^{7\text{a}}$), 159.54 (COO), 166.11 (CON), 170.16 (CON), 196.80 (CO). MS (EI, 70 eV) m/z (%): 552 (M^+ , 5), 459 (5), 433 (100), 417 (5), 370 (9), 326 (12), 107 (60), 91 (97), 77 (83), 65 (19). Anal. calcd. for $\text{C}_{35}\text{H}_{24}\text{N}_2\text{O}_5$ (552.17): C, 76.08; H, 4.38; N, 5.07. Found: C, 76.04; H, 4.40; N, 5.09%

5-(4-Anilino-1-methyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)-2-methyl-4-phenyl-4,5-dihydrochromeno[4,3-d]pyrrolo[3,4-b]pyridine-1,3,6(2H)-trione (3'a).



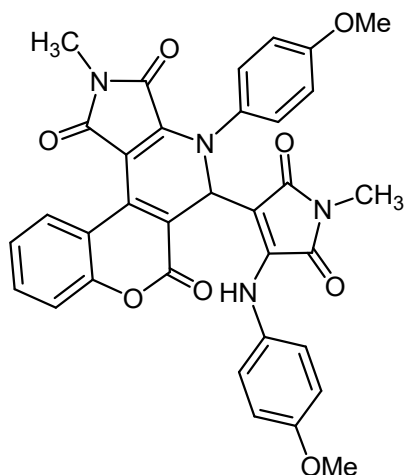
Light red solid, m.p = 284-285°C (dec.), 0.44 g, yield: 80%. IR (KBr) (ν_{\max} , cm^{-1}): 3237 (NH), 1703 (OCNCO and COO), 1610, 1571 and 1449 (Ar), 1242 and 1098 (C-O), 1197 (C-N), 763 (C-H) cm^{-1} . ^1H NMR (300.13 MHz, $\text{DMSO-}d_6$): 2.81 (3H, s, Me), 2.86 (3H, s, Me), 6.64 (2H, d, $^3J_{\text{HH}} = 6.6$ Hz, 2CH of Ph), 7.04 (1H, t, $^3J_{\text{HH}} = 7.0$ Hz, CH of Ph), 7.06 (2H, t, $^3J_{\text{HH}} = 7.0$ Hz, 2CH of Ph), 7.27 (1H, d, $^3J_{\text{HH}} = 8.5$ Hz, CH^8 of coumarin), 7.32 (2H, t, $^3J_{\text{HH}} = 7.0$ Hz, 2CH of Ph), 7.33 (1H, t, $^3J_{\text{HH}} = 7.3$ Hz, CH^{10} of coumarin), 7.50 (1H, t, $^3J_{\text{HH}} = 7.0$ Hz, CH of Ph), 7.52 (2H, d, $^3J_{\text{HH}} = 7.0$ Hz, 2CH of Ph), 7.55 (1H, t, $^3J_{\text{HH}} = 7.3$ Hz, CH^9 of coumarin), 9.29 (1H, d, $^3J_{\text{HH}} = 8.2$ Hz, CH^{11} of coumarin), 9.56 (1H, bs, NH). ^{13}C NMR (75.45 MHz, $\text{DMSO-}d_6$): 23.60 (Me), 23.70 (Me), 55.84 (CHN), 97.81 (C^3), 98.94 (C^{5a}), 107.80 (C^{11a}), 115.55 (C^{11c}), 116.43 (CH^8 of coumarin), 123.83 (CH^{10} of coumarin), 124.26 (2CH of Ph), 125.34 (CH of Ph), 127.61 (2CH of Ph), 128.38 (2CH of Ph), 129.06 (CH of Ph), 129.35 (2CH of Ph), 129.66 (CH^{11} of coumarin), 131.77 (CH^9 of coumarin), 138.31 ($\text{C}_{\text{ipso-Ph}}$), 138.86 (C^4), 140.22 ($\text{C}_{\text{ipso-Ph}}$), 141.54 (C^{3a}), 150.16 (C^{11b}), 152.12 (C^{7a}), 158.56 (COO), 161.45 (CON), 166.44 (CON), 166.88 (CON), 171.46 (CON). MS (EI, 70 eV) m/z (%): 559 (M^+ , 15), 558 (M^+ , 44), 481 (9), 472 (6), 467 (29), 466 (100), 381 (13), 369 (6), 358 (23), 357 (88), 300 (7), 281 (11), 279 (8), 270 (7), 180 (27), 144 (11), 105 (7), 104 (6), 93 (60), 78 (6), 77 (70). Anal. calcd. for $\text{C}_{32}\text{H}_{22}\text{N}_4\text{O}_6$ (558.15): C, 68.81; H, 3.97; N, 10.03. Found: C, 68.85; H, 4.00; N, 10.10%.

2-Methyl-5-{1-methyl-4-[(4-methylphenyl)amino]-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl}-4-(4-methylphenyl)-4,5-dihydrochromeno[4,3-d]pyrrolo[3,4-b]pyridine-1,3,6(2H)-trione (3'b).



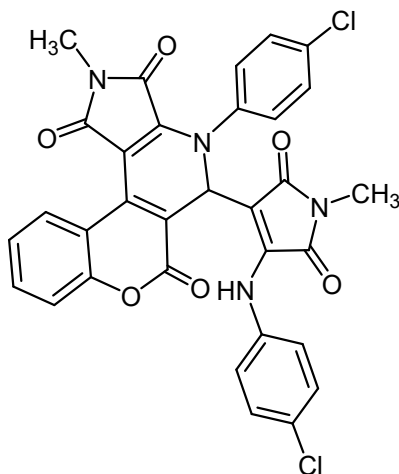
Light red solid, m.p = 246-247 °C (dec.), 0.45 g, yield: 78%. IR (KBr) (ν_{\max} , cm^{-1}): 3310 (NH), 1695 (OCNCO and COO), 1610, 1573 and 1439 (Ar), 1249 and 1100 (C-O), 1199 (C-N), 749 (C-H) cm^{-1} . ^1H NMR (300.13 MHz, $\text{DMSO}-d_6$): 2.20 (3H, s, Me), 2.038 (3H, s, Me), 2.80 (3H, s, Me), 2.84 (3H, s, Me), 5.76 (1H, s, CHN), 6.67 (2H, d, $^3J_{\text{HH}} = 7.8$ Hz, 2CH of Ar), 6.83 (2H, d, $^3J_{\text{HH}} = 7.8$ Hz, 2CH of Ar), 7.15 (2H, d, $^3J_{\text{HH}} = 8.0$ Hz, 2CH of Ar), 7.26 (2H, d, $^3J_{\text{HH}} = 8.0$ Hz, 2CH of Ar), 7.27 (1H, d, $^3J_{\text{HH}} = 8.2$ Hz, CH⁸ of coumarin), 7.34 (1H, t, $^3J_{\text{HH}} = 7.8$ Hz, CH¹⁰ of coumarin), 7.55 (1H, t, $^3J_{\text{HH}} = 7.8$ Hz, CH⁹ of coumarin), 9.30 (1H, d, $^3J_{\text{HH}} = 8.2$ Hz, CH¹¹ of coumarin), 9.53 (1H, bs, NH). ^{13}C NMR (75.45 MHz, $\text{DMSO}-d_6$): 20.59 (Me), 20.82 (Me), 23.57 (Me), 23.67 (Me), 55.98 (CHN), 97.33 (C³), 98.16 (C^{5a}), 107.80 (C^{11a}), 115.60 (C^{11c}), 116.43 (CH⁸ of coumarin), 123.81 (CH¹⁰ of coumarin), 124.40 (2CH of Ph), 127.38 (2CH of Ar), 128.79 (2CH of Ar), 129.70 (2CH of Ar and CH¹¹ of coumarin), 131.72 (CH⁹ of coumarin), 134.74 (C_{ipso}-Me), 135.53 (C_{ipso}-Me), 137.68 (C_{ipso}-Ar), 138.62 (C_{ipso}-Ar), 139 (C⁴), 141.69 (C^{3a}), 150.16 (C^{11b}), 152.14 (C^{7a}), 158.57 (COO), 161.41 (CON), 166.49 (CON), 166.85 (CON), 171.49 (CON). MS (EI, 70 eV) m/z (%): 586 (M⁺, 17), 481 (12), 480 (39), 395 (8), 386 (6), 385 (5), 293 (4), 217 (13), 216 (75), 208 (6), 159 (14), 158 (83), 132 (6), 131 (40), 130 (43), 129 (8), 119 (7), 118 (6), 116 (8), 107 (74), 106 (18), 104 (9), 103 (15), 102 (6), 92 (12), 91 (100), 90 (20), 89 (21), 88 (6), 79 (9), 78 (12), 77 (25), 76 (7), 68 (7), 66 (7), 65 (74), 64 (12), 63 (20), 62 (7), 58 (18), 57 (12), 56 (10), 52 (12), 51 (19), 50 (10). Anal. calcd. for C₃₄H₂₆N₄O₆ (586.19): C, 69.62; H, 4.47; N, 9.55. Found: C, 69.68; H, 4.45; N, 9.51%.

4-(4-Methoxyphenyl)-5-{4-[(4-methoxyphenyl)amino]-1-methyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl}-2-methyl-4,5-dihydrochromeno[4,3-*d*]pyrrolo[3,4-*b*]pyridine-1,3,6(2*H*)-trione (3'c).

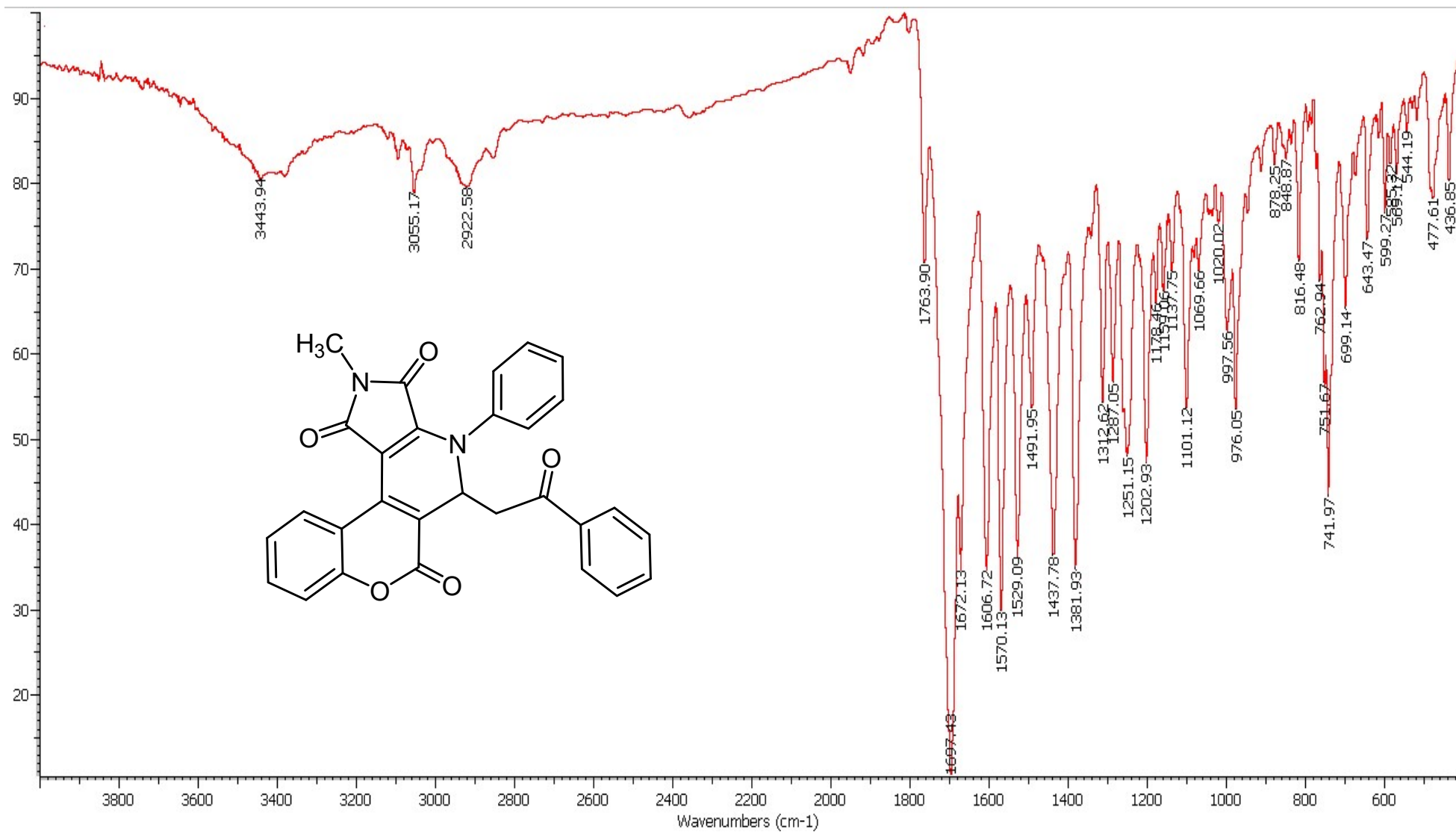


Light red solid, m.p = 244-245 °C (dec.), 0.51 g, yield: 82%. IR (KBr) (ν_{\max} , cm^{-1}): 3097 (NH), 1698 (OCNCO and COO), 1610, 1574 and 1441 (Ar), 1248, 1172 and 1028 (C-O), 1196 (C-N), 736 (C-H) cm^{-1} . ^1H NMR (300.13 MHz, $\text{DMSO-}d_6$): 2.81 (3H, s, Me), 20.85 (3H, s, Me), 3.69 (3H, s, OMe), 3.83 (3H, s, OMe), 5.64 (1H, s, CHN), 6.58 (4H, m, 4CH of Ar), 7.01 (2H, dd, $^3J_{\text{HH}} = 8.8$ Hz, $^2J_{\text{HH}} = 1.0$ Hz, 2CH of Ar), 7.20 (2H, dd, $^3J_{\text{HH}} = 8.8$ Hz, $^2J_{\text{HH}} = 1.0$ Hz, 2CH of Ar), 7.28 (1H, d, $^3J_{\text{HH}} = 8.2$ Hz, CH⁸ of coumarin), 7.33 (1H, t, $^3J_{\text{HH}} = 7.8$ Hz, CH¹⁰ of coumarin), 7.56 (1H, t, $^3J_{\text{HH}} = 7.8$ Hz, CH⁹ of coumarin), 9.32 (1H, d, $^3J_{\text{HH}} = 8.2$ Hz, CH¹¹ of coumarin), 9.49 (1H, bs, NH). ^{13}C NMR (75.45 MHz, $\text{DMSO-}d_6$): 20.54 (Me), 20.64 (Me), 55.17 (OMe), 55.53 (OMe), 56.11 (CHN), 96.75 (C³), 96.93 (C^{5a}), 107.61 (C^{11a}), 113.41 (2CH of Ar), 114.43 (2CH of Ar), 115.57 (C^{11c}), 116.38 (CH⁸ of coumarin), 123.75 (CH¹⁰ of coumarin), 126.30 (2CH of Ar), 129.05 (2CH of Ar), 129.68 (CH¹¹ of coumarin), 130.58 (C_{ipso}-Ar), 131.68 (CH⁹ of coumarin), 132.87 (C_{ipso}-Ar), 139 (C⁴), 142.17 (C^{3a}), 150.40 (C^{11b}), 152.11 (C^{7a}), 157.03 (C_{ipso}-OMe), 158.57 (COO), 159.53 (C_{ipso}-OMe), 161.37 (CON), 166.56 (CON), 166.81 (CON), 171.62 (CON). MS (EI, 70 eV) m/z (%): 496 (4), 388 (17), 387 (59), 368 (5), 294 (5), 233 (13), 232 (100), 217 (29), 160 (8), 147 (15), 146 (21), 132 (18), 123 (11), 108 (15), 97 (9), 95 (6), 92 (8), 85 (7), 83 (9), 82 (8), 77 (14), 71 (9), 69 (13), 57 (16), 55 (12). Anal. calcd. for $\text{C}_{34}\text{H}_{26}\text{N}_4\text{O}_8$ (618.18): C, 66.02; H, 4.24; N, 9.06. Found: C, 65.95; H, 4.27; N, 9.10%.

4-(4-Chlorophenyl)-5-(4-((4-chlorophenyl)amino)-1-methyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)-2-methyl-4,5-dihydrochromeno[4,3-d]pyrrolo[3,4-b]pyridine-1,3,6(2H)-trione (3'd).

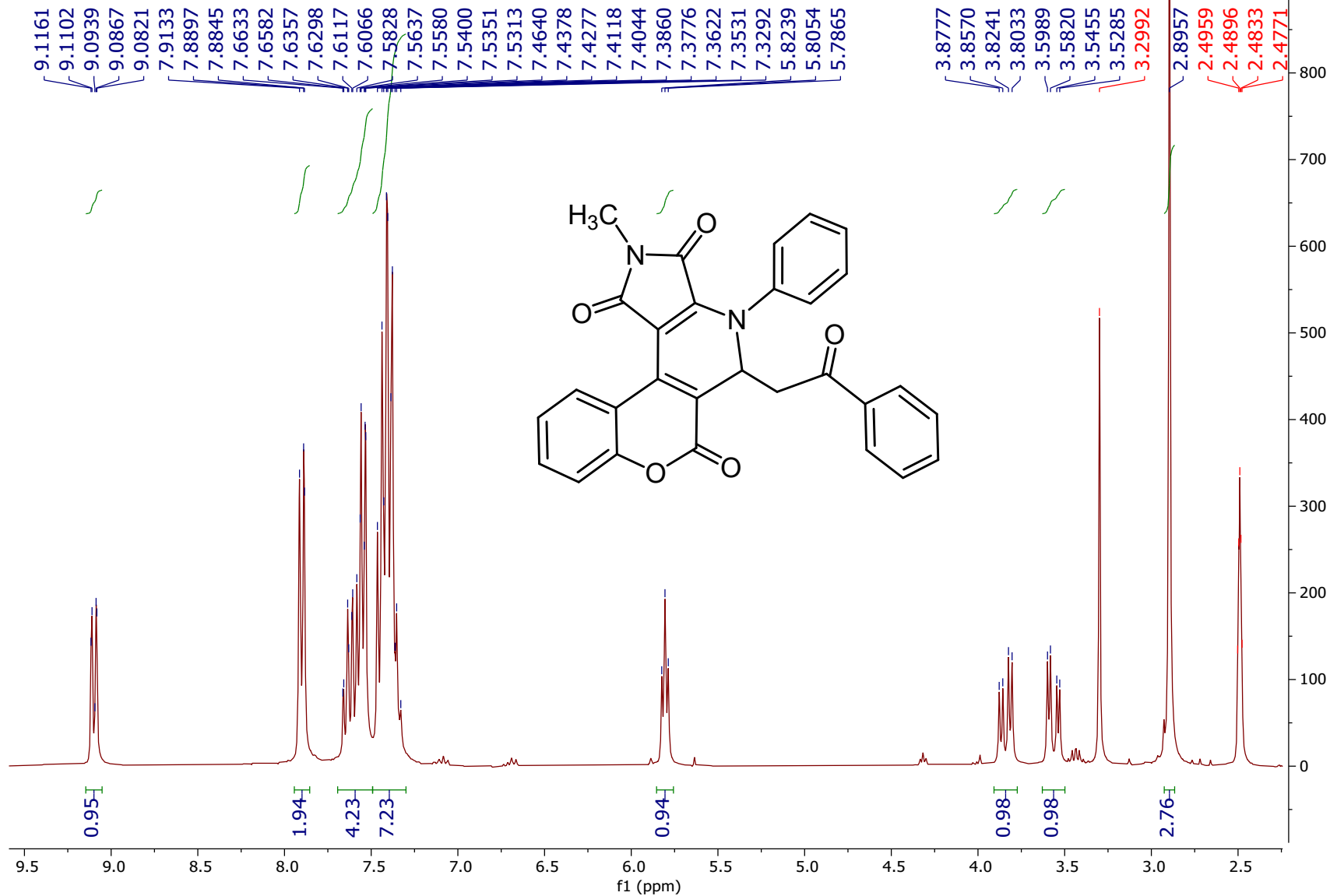


Light red solid, m.p = 245-246 °C (dec.), 0.25 g, yield: 41%. IR (KBr) (ν_{\max} , cm^{-1}): 3126 (NH), 1700 (OCNCO and COO, 1610, 1573 and 1508 (Ar), 1246, 1173 (C-O), 1092 (C-N), 762 (C-H), 1028 (C-Cl) cm^{-1} . ^1H NMR (300.13 MHz, CDCl_3): 2.97 (3H, s, Me), 3.05 (3H, s, Me), 5.88 (1H, s, CHN), 6.88 (2H, d, $^3J_{\text{HH}} = 8.6$ Hz, 2CH of Ar), 7.10 (2H, d, $^3J_{\text{HH}} = 8.6$ Hz, 2CH of Ar), 7.18 (2H, dd, $^3J_{\text{HH}} = 8.0$ Hz), 7.29 (1H, t, $^3J_{\text{HH}} = 8.0$ Hz, CH⁹ of coumarin), 7.30 (1H, d, $^3J_{\text{HH}} = 8.0$ Hz, CH⁸ of coumarin), 7.55 (1H, dt, $^3J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{HH}} = 1.5$ Hz, CH¹⁰ of coumarin), 7.78 (1H, bs, NH), 9.40 (1H, dd, $^3J_{\text{HH}} = 8.2$ Hz, $^4J_{\text{HH}} = 1.5$ Hz, CH¹¹ of coumarin). MS (EI, 70 eV) m/z (%): 627 (10), 433 (52), 392 (5), 325 (5), 280 (5), 236 (52), 178 (94), 151 (52), 127 (57), 91 (73), 57 (100). Anal. calcd. $\text{C}_{32}\text{H}_{20}\text{Cl}_2\text{N}_4\text{O}_6$ (626.08): C, 61.26; H, 3.21; N, 8.93. Found: C, 61.24; H, 3.20; N, 8.96%.

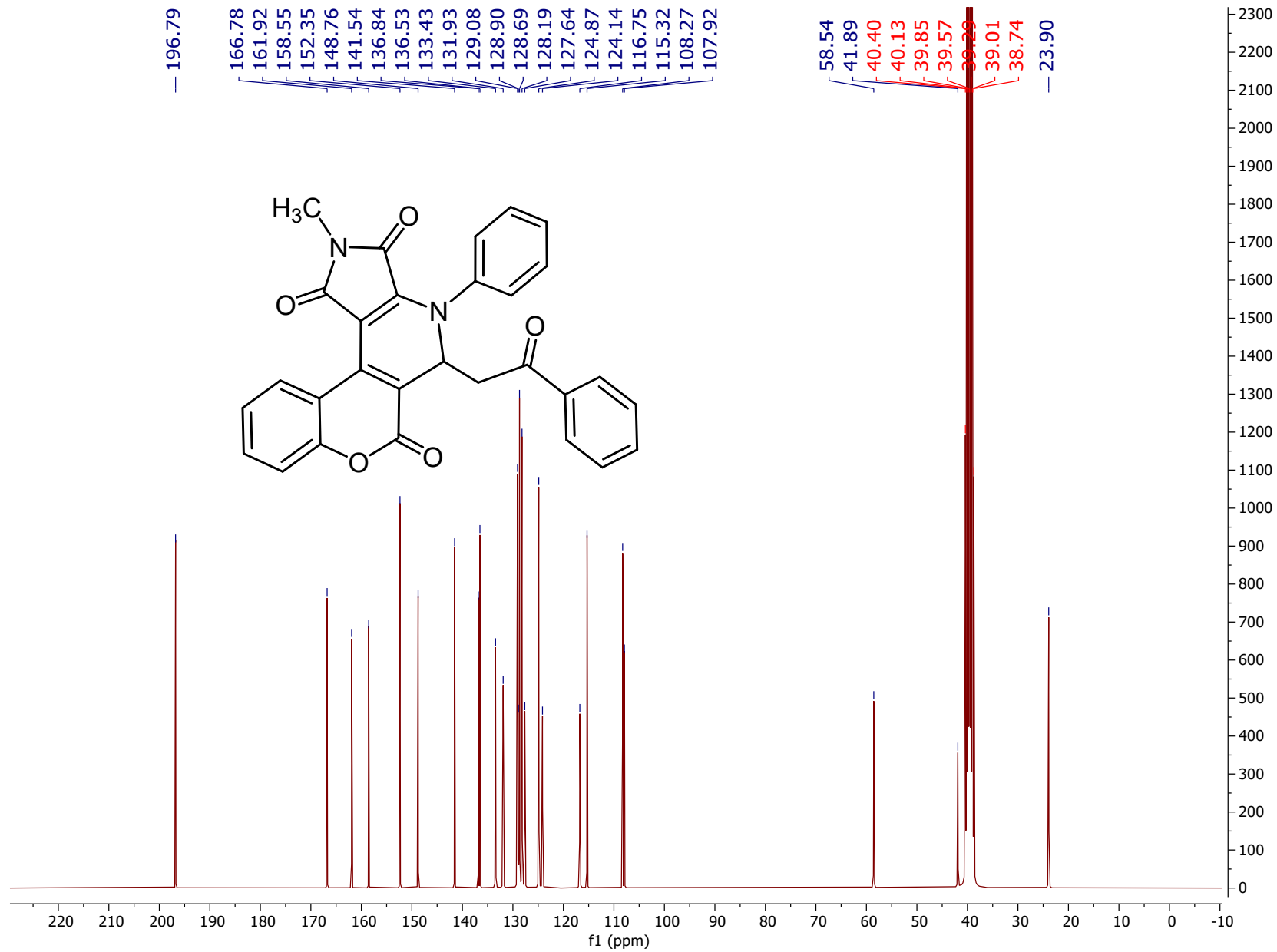


IR spectrum of 3a

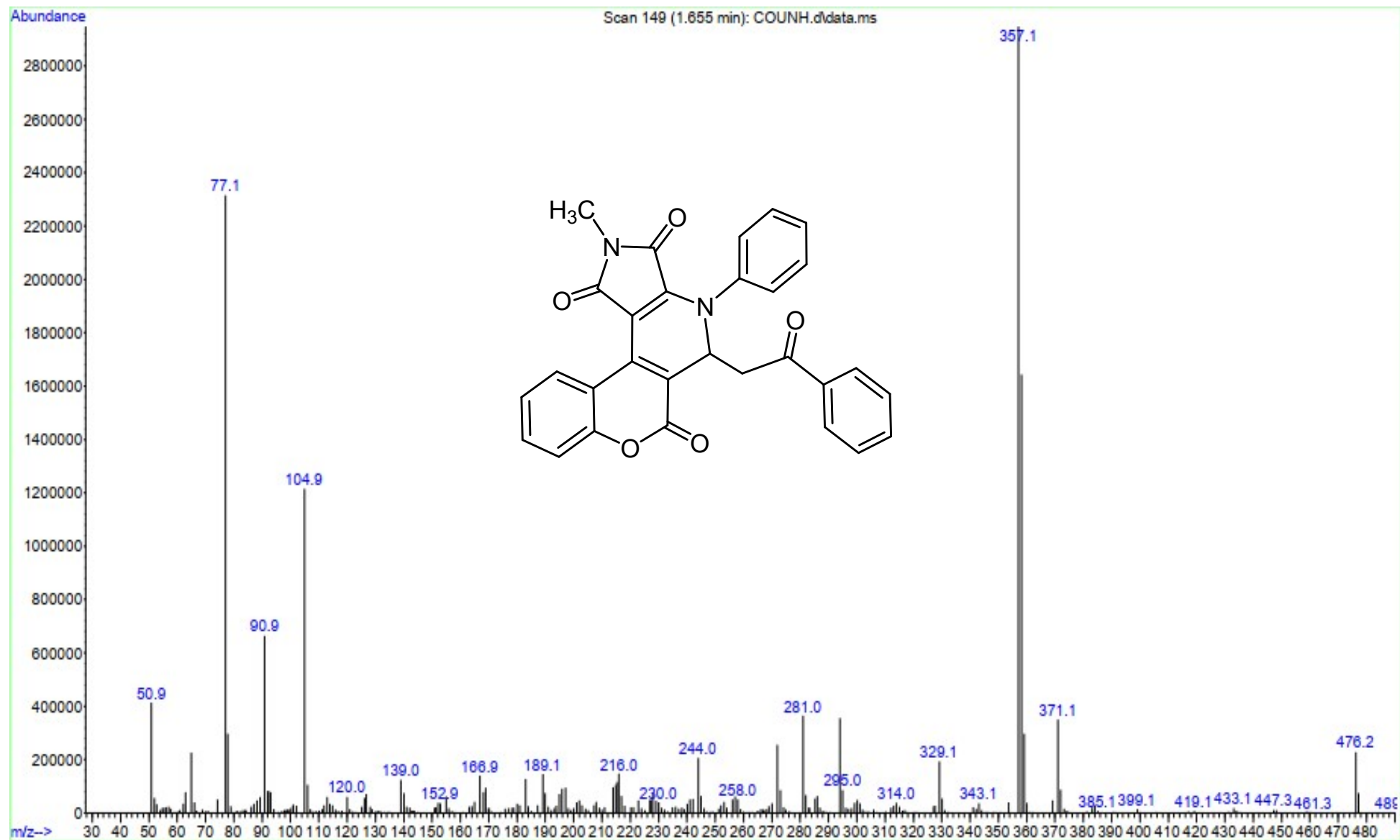
Rostampoor.3.fid
D296
1H NMR



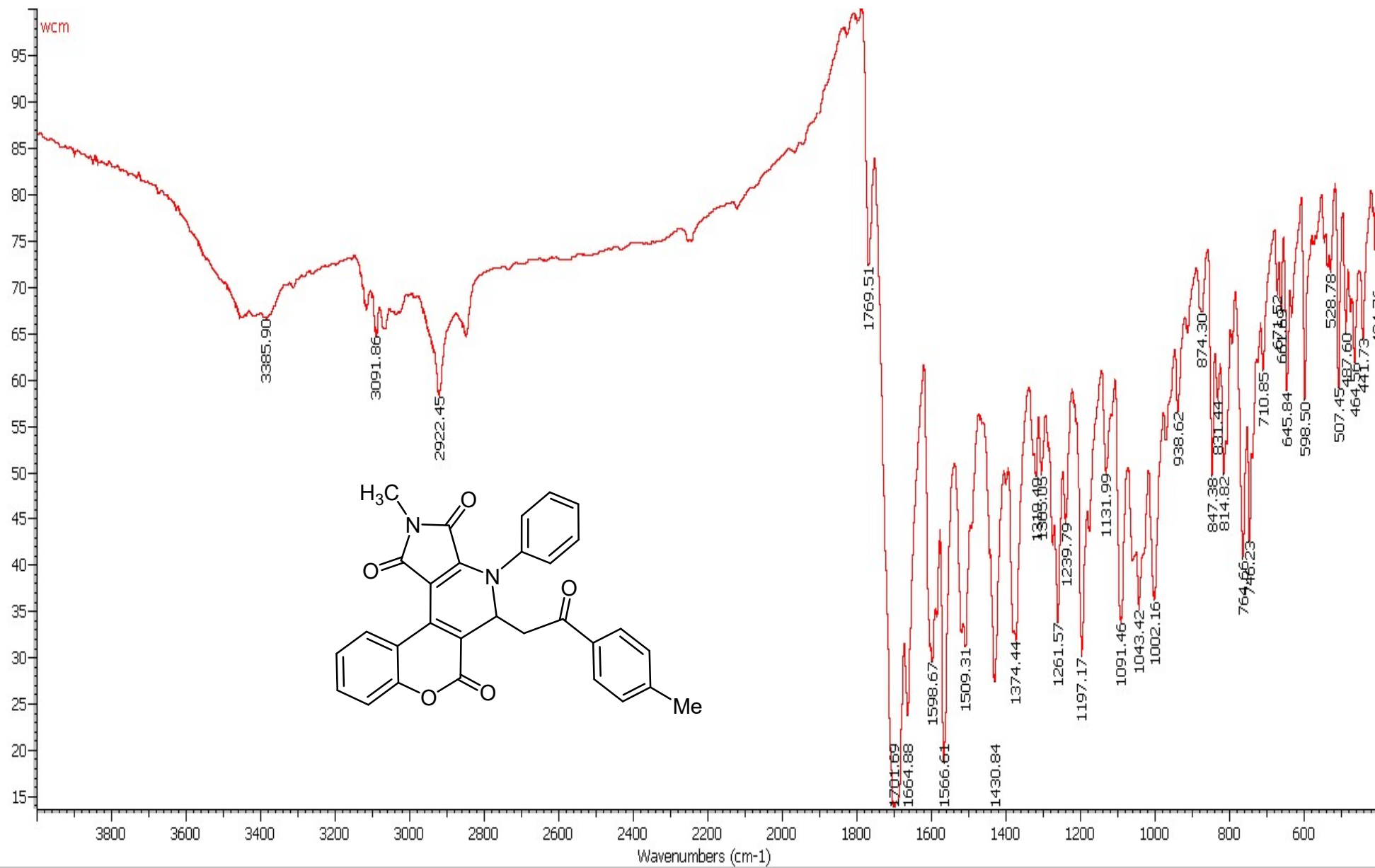
¹H NMR Spectrum of 3a



¹³C NMR Spectrum of 3a
S17

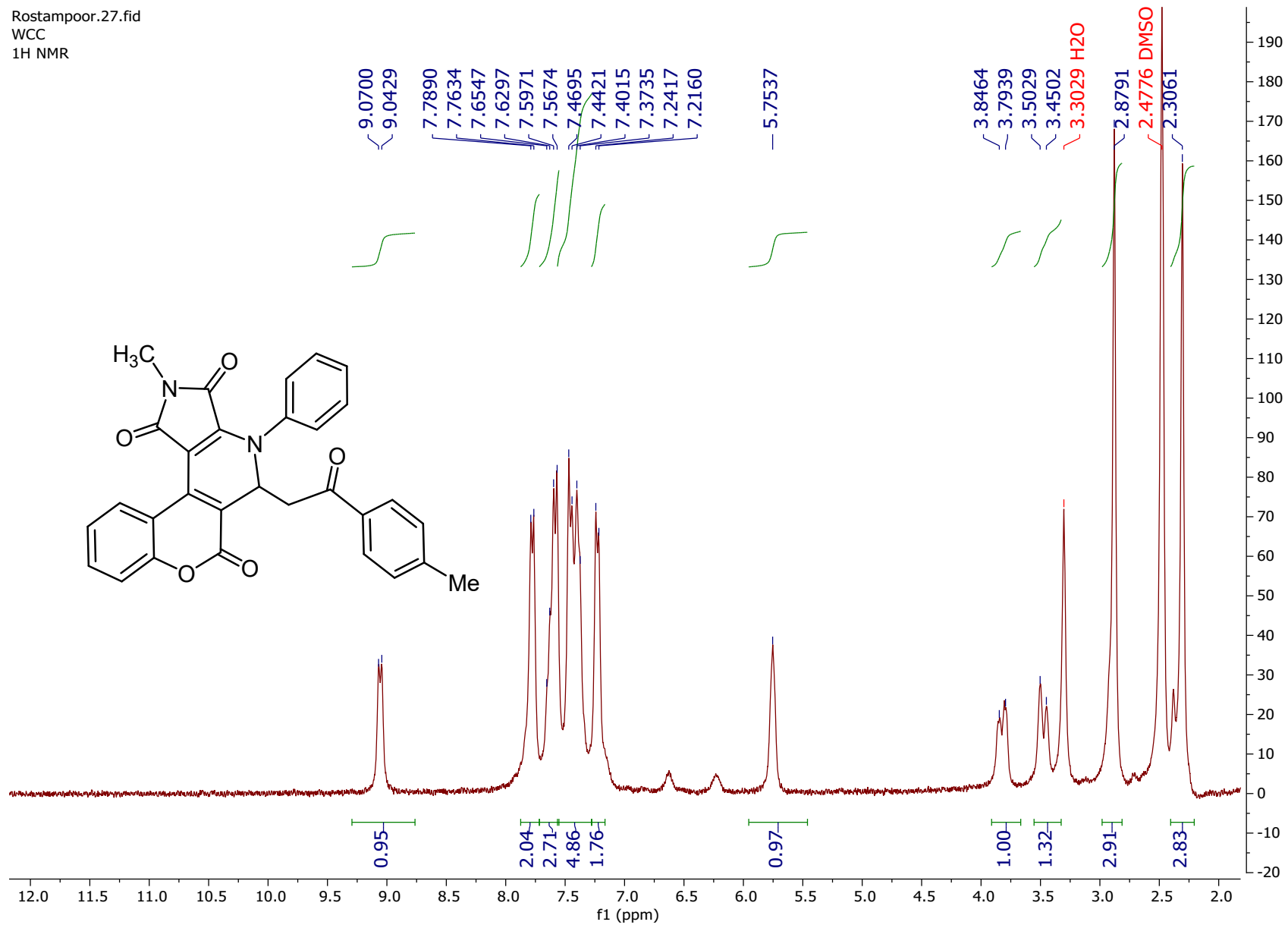


Mass spectrum of 3a



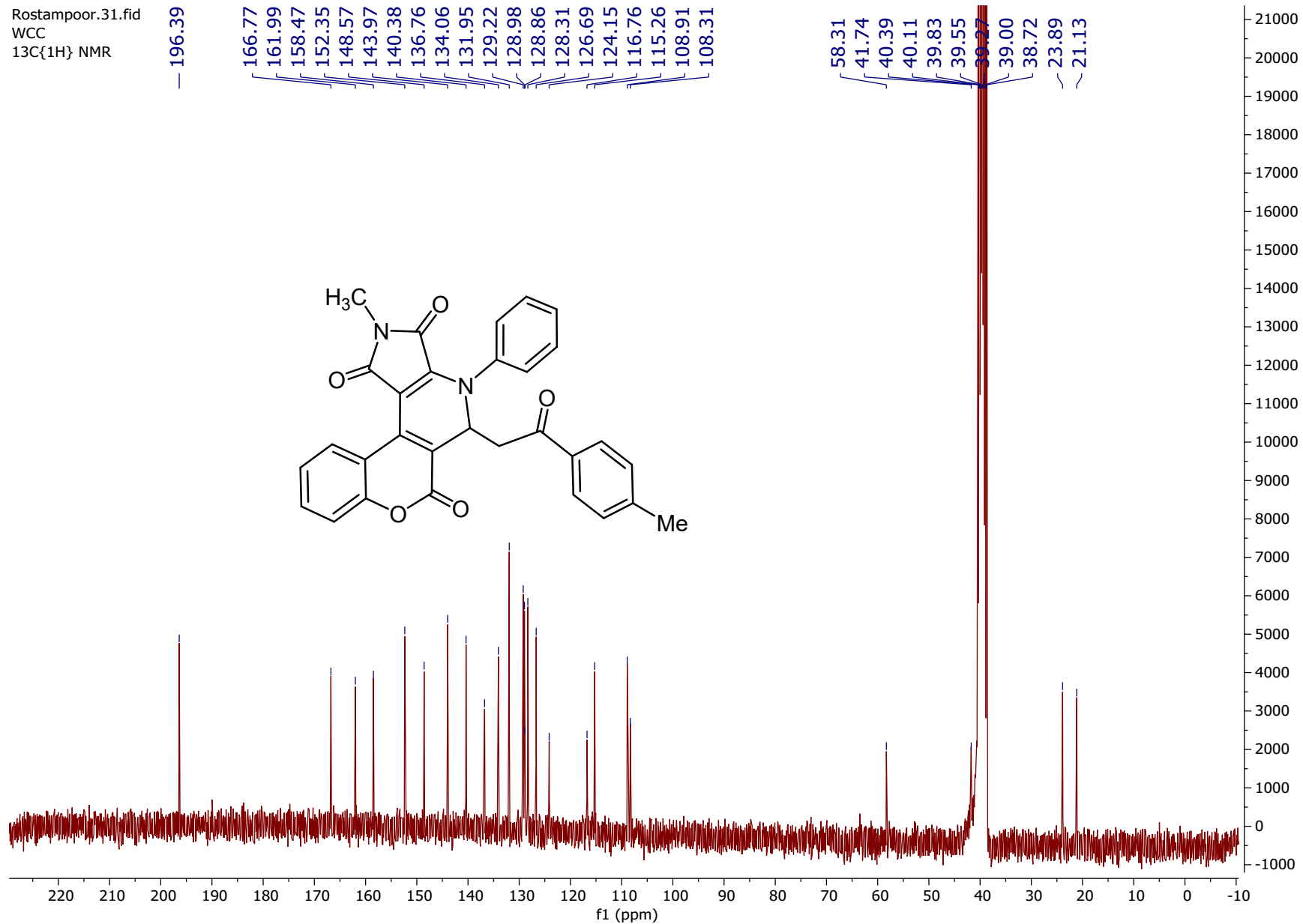
IR spectrum of **3b**

Rostampoor.27.fid
WCC
1H NMR



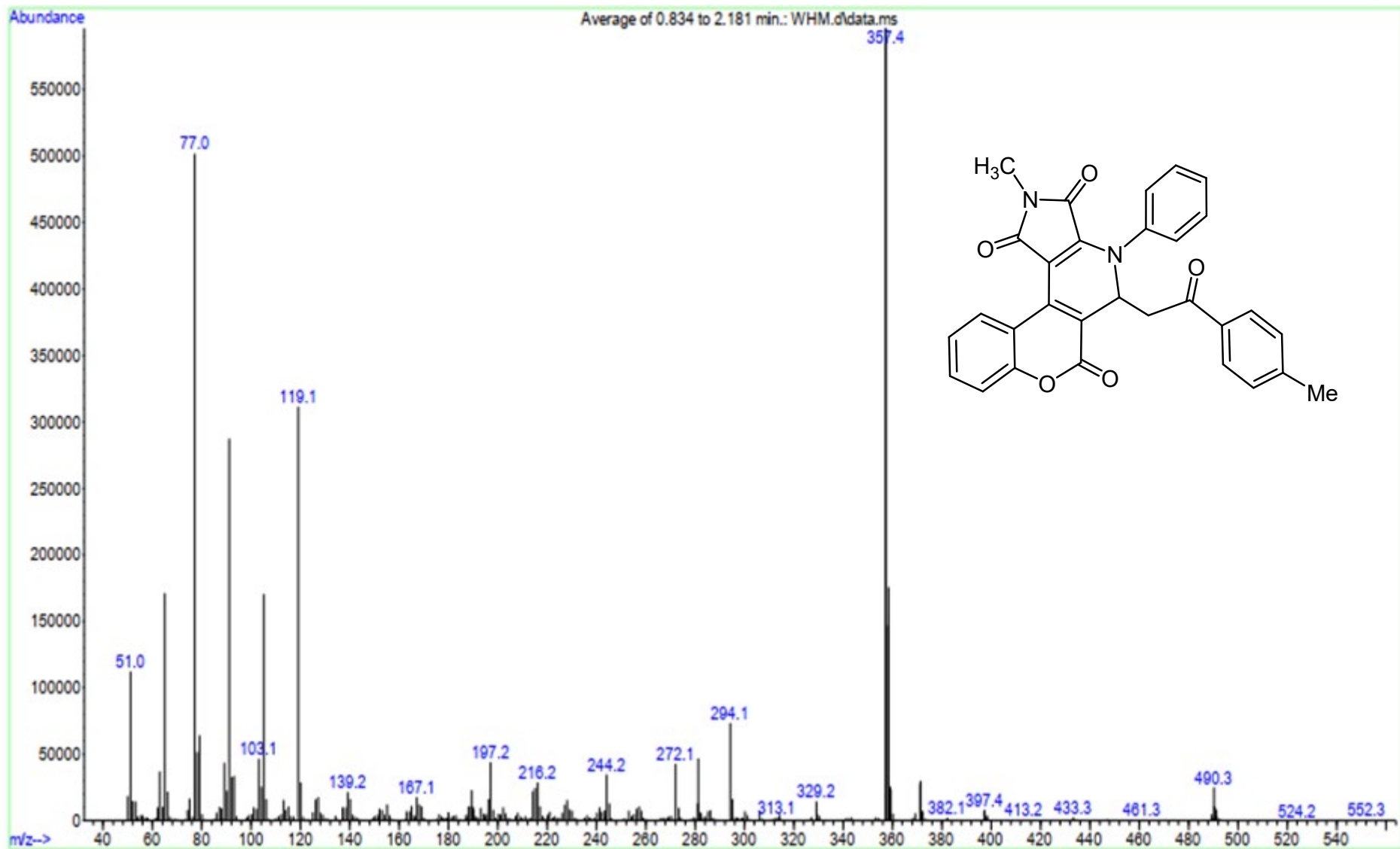
¹H NMR Spectrum of **3b**

Rostampoor.31.fid
WCC
13C{1H} NMR

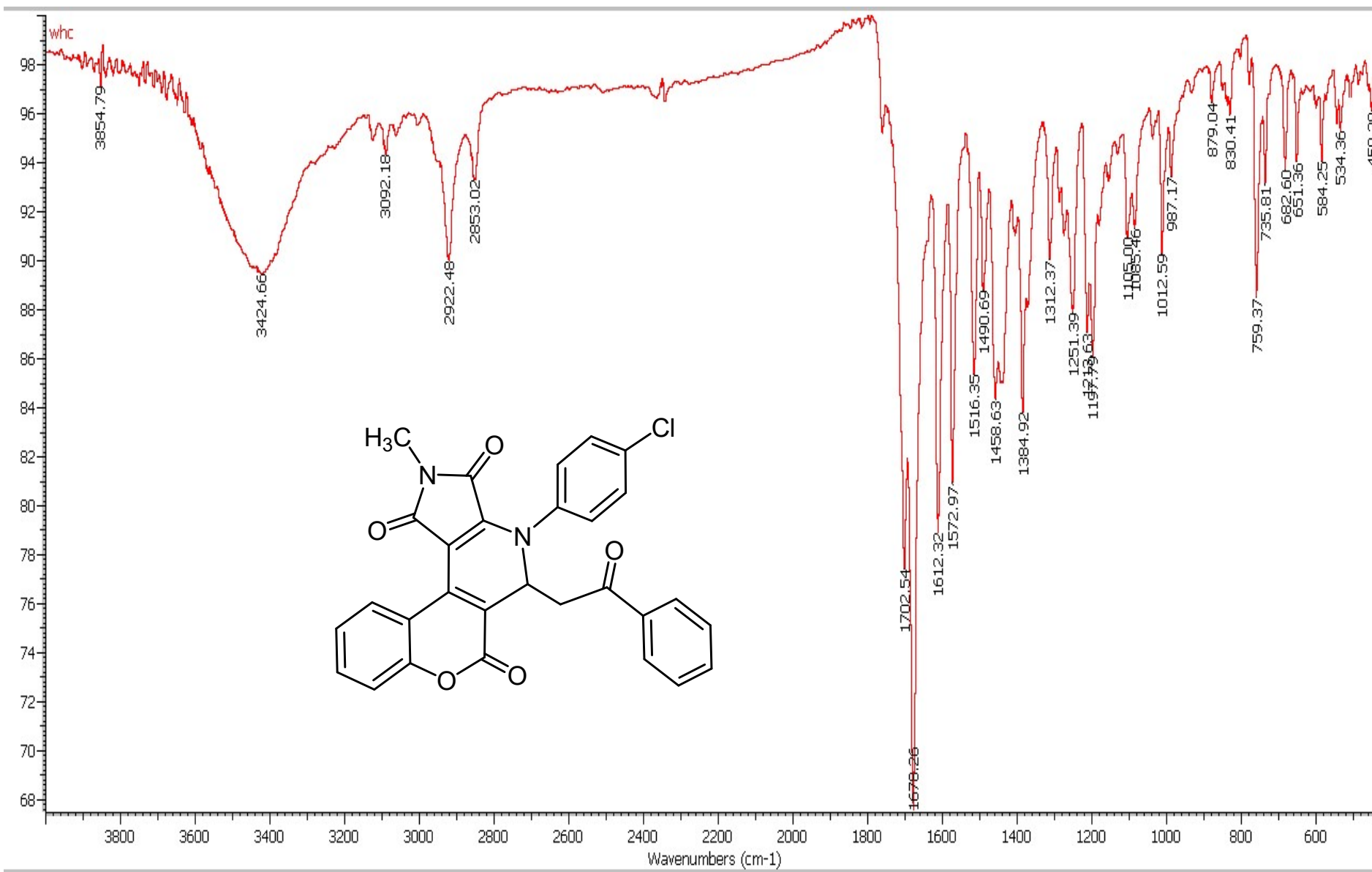


¹³C NMR Spectrum of **3b**

S21



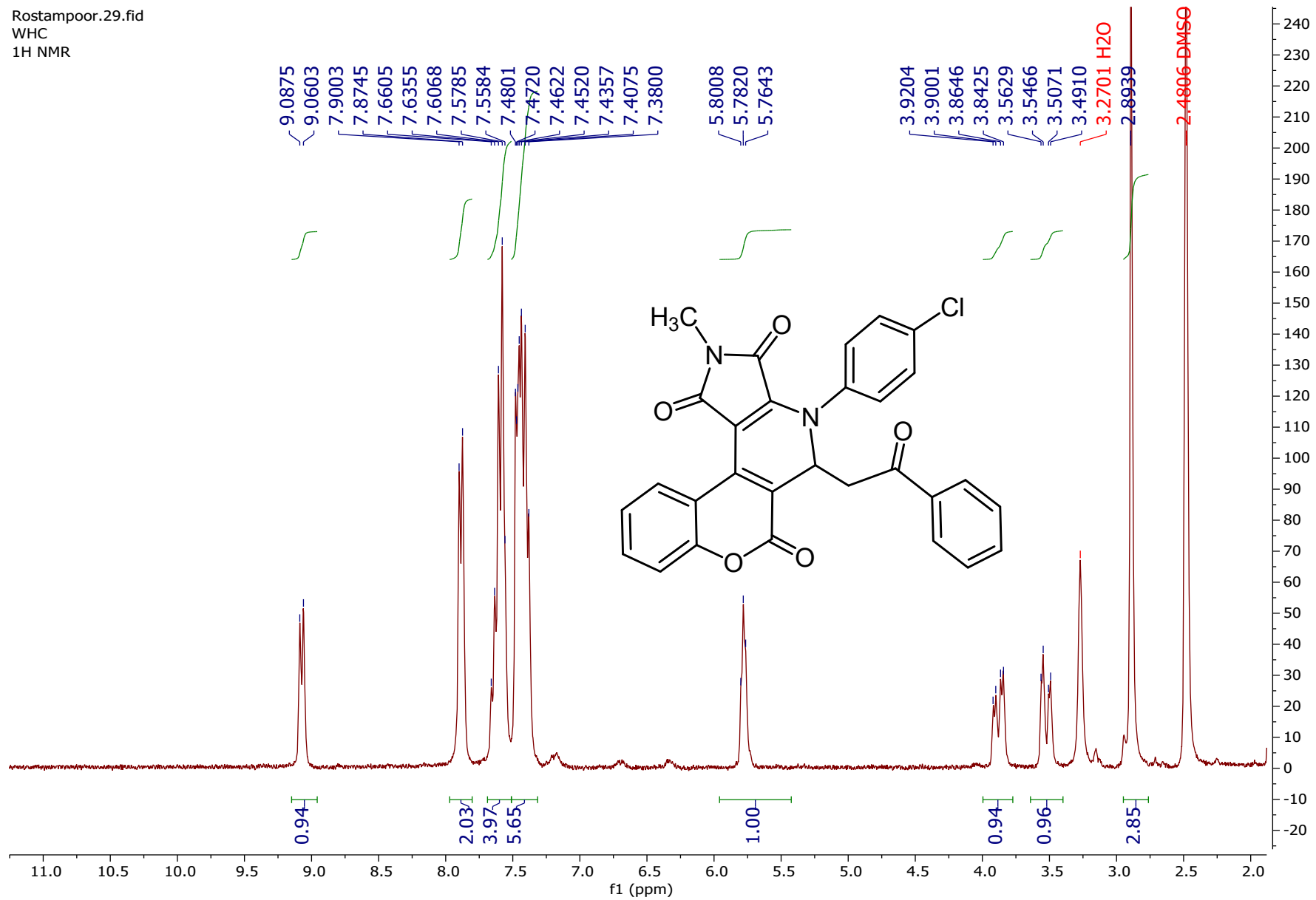
Mass spectrum of **3b**



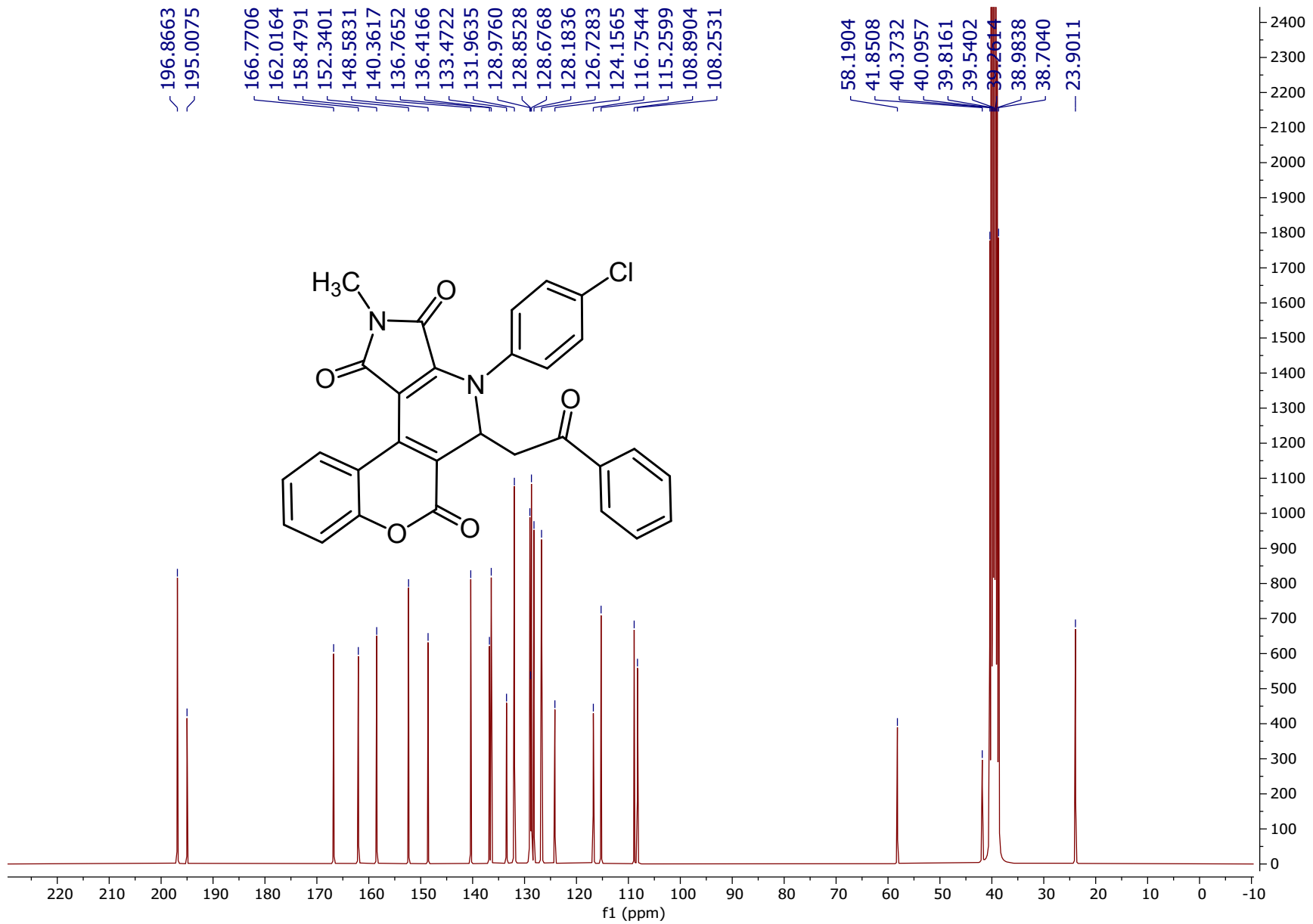
IR spectrum of 3c

S23

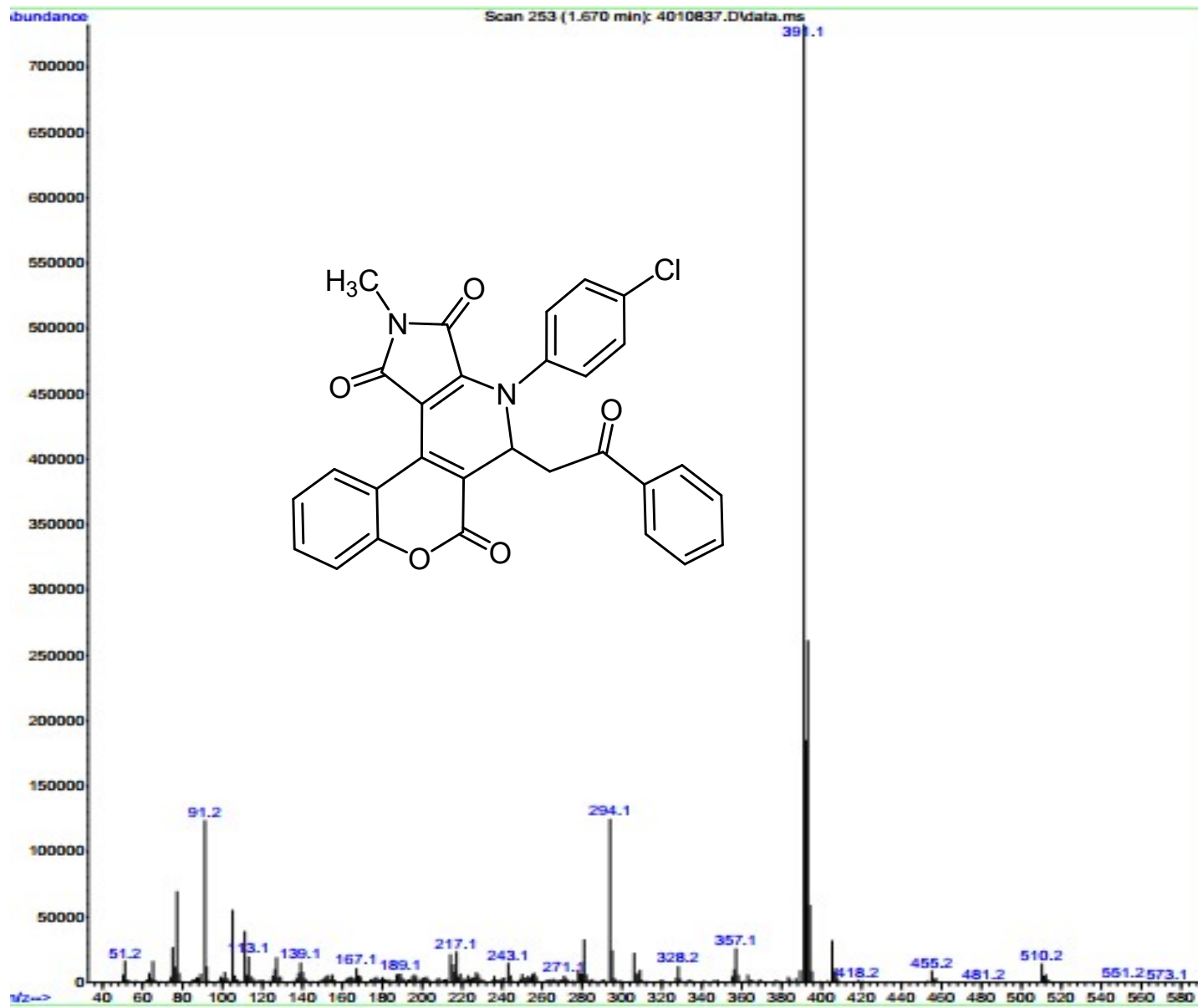
Rostampoor.29.fid
WHC
1H NMR



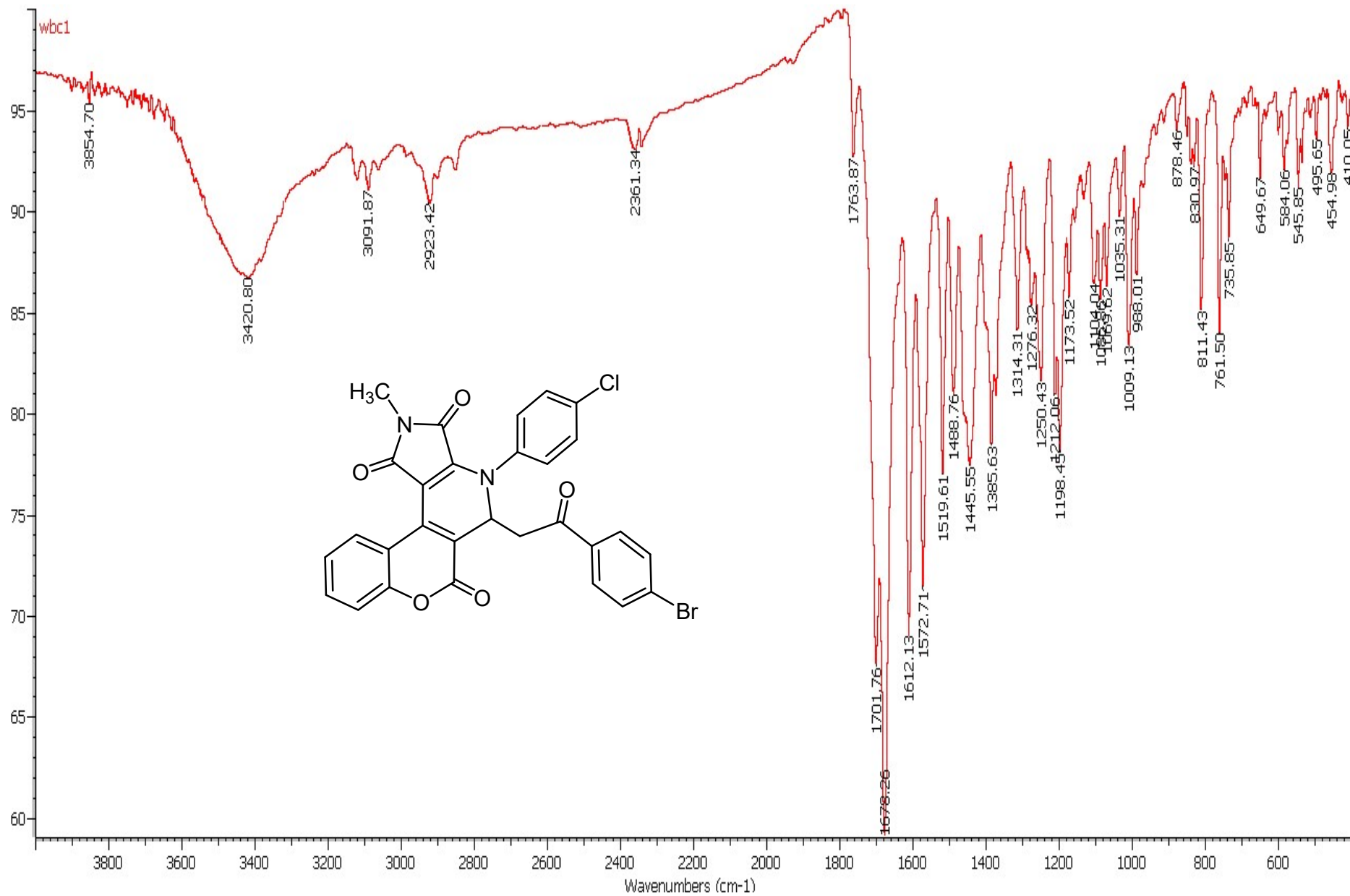
¹H NMR Spectrum of 3c



¹³C NMR Spectrum of 3c

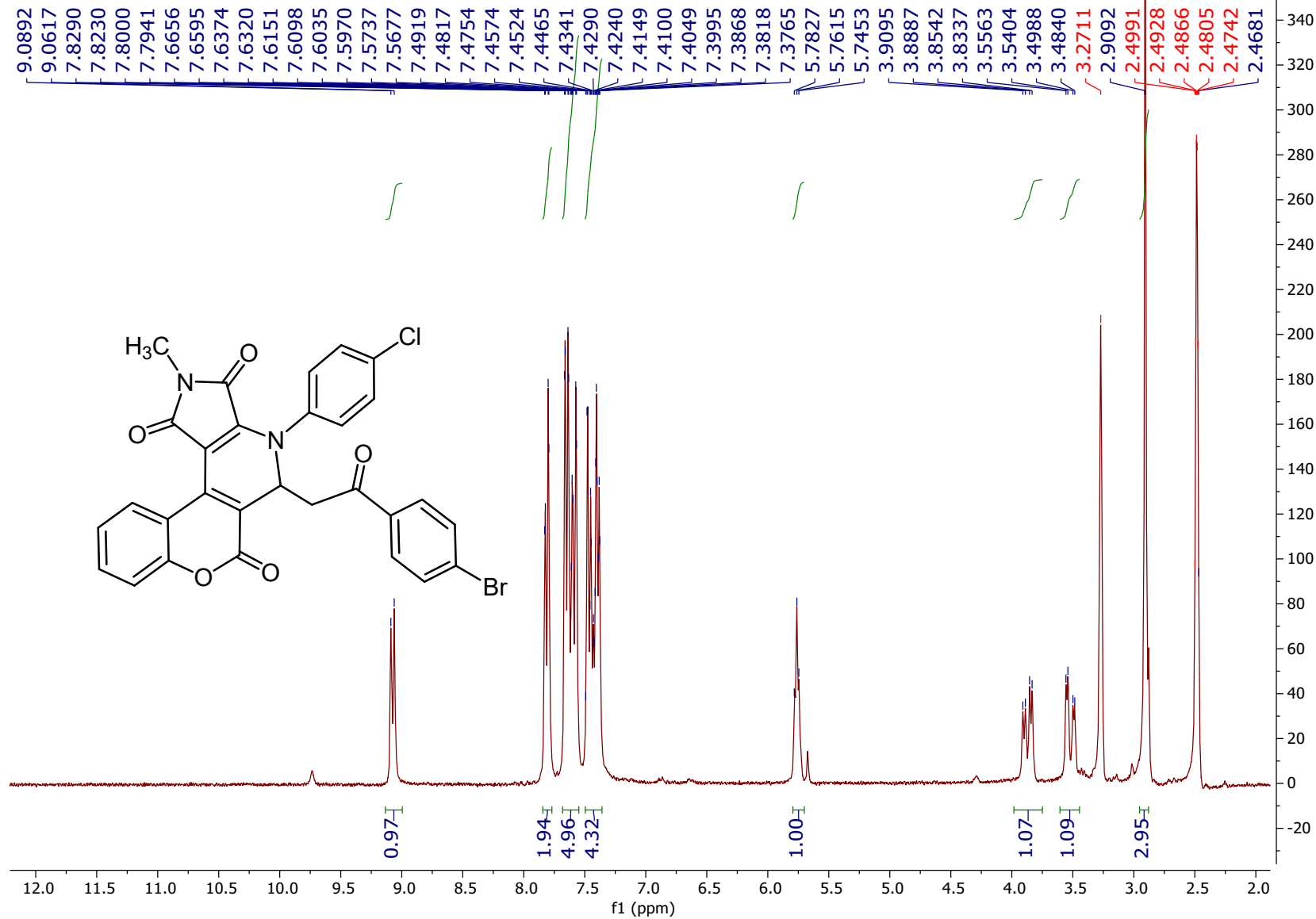


Mass spectrum of **3c**



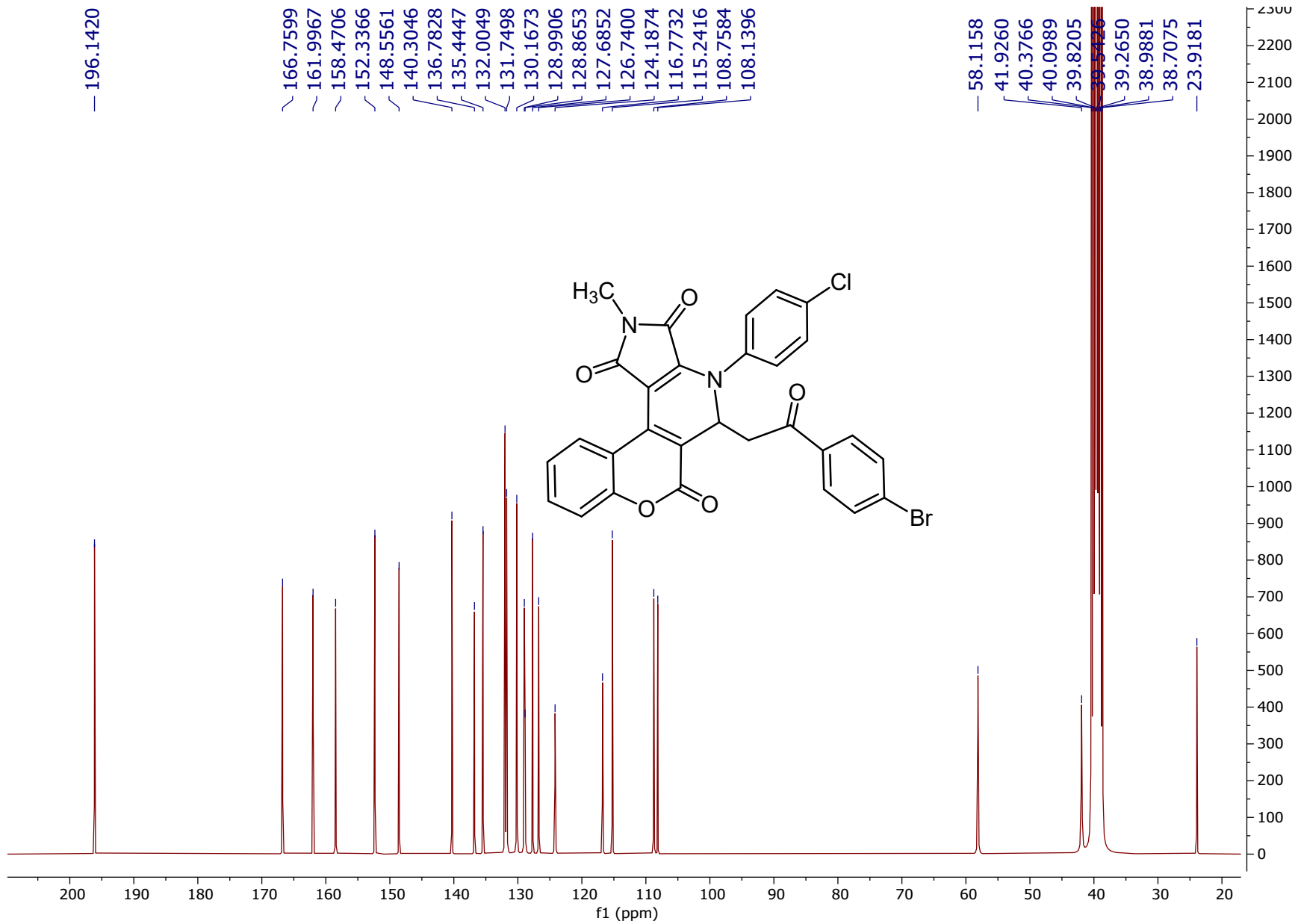
IR spectrum of 3d

Rostampoor.25.fid
WBC
1H NMR



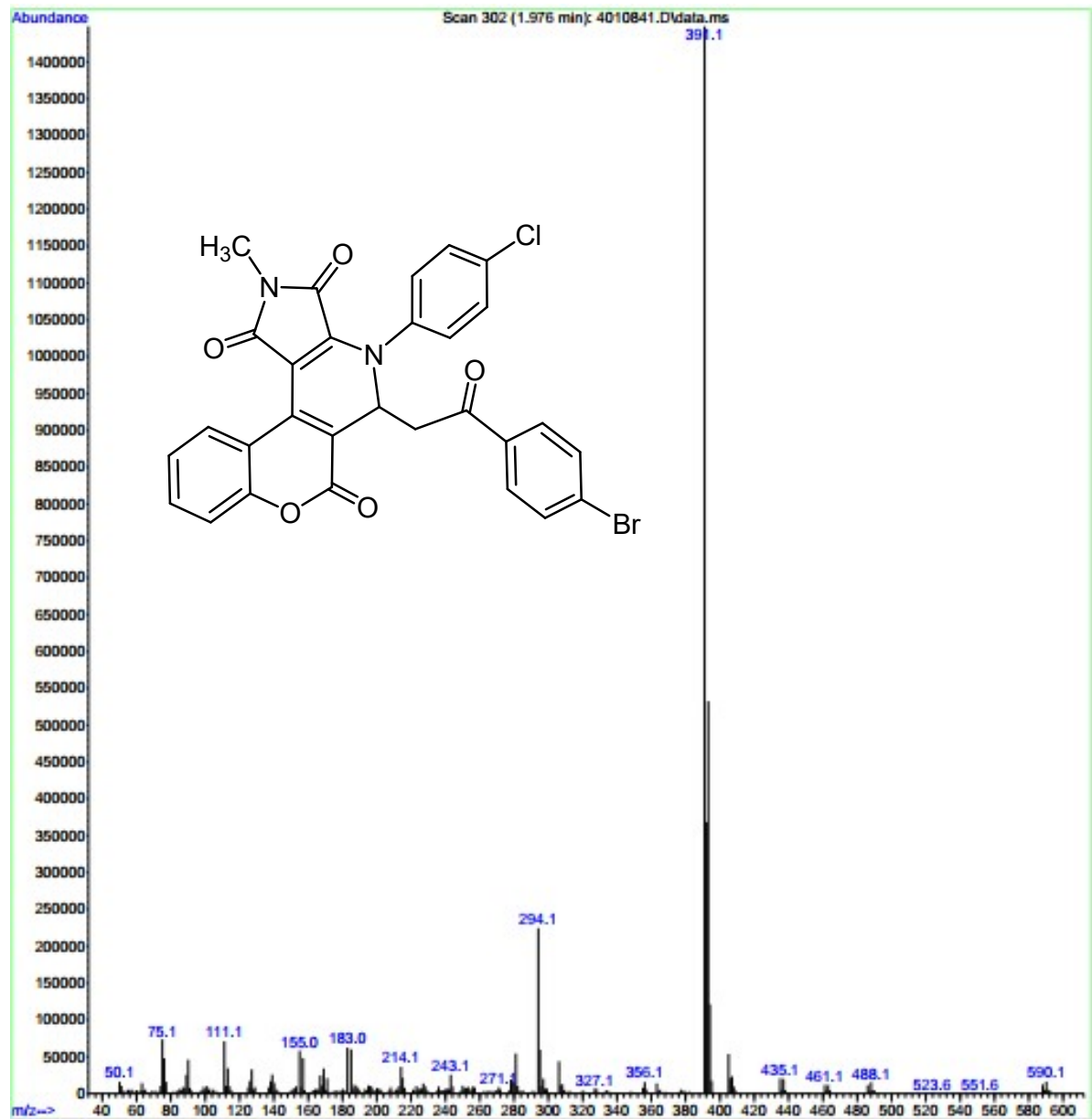
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7.8000
7.7941
7.6656
7.6595
7.6374
7.6320
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7.6098
7.6035
7.5970
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5.7453
3.9095
3.8887
3.8542
3.8337
3.5563
3.5404
3.4988
3.4840
3.2711 H2O
2.9092
2.4991 DMSO
2.4928 DMSO
2.4866 DMSO
2.4805 DMSO
2.4742 DMSO
2.4681

¹H NMR Spectrum of 3d
S28

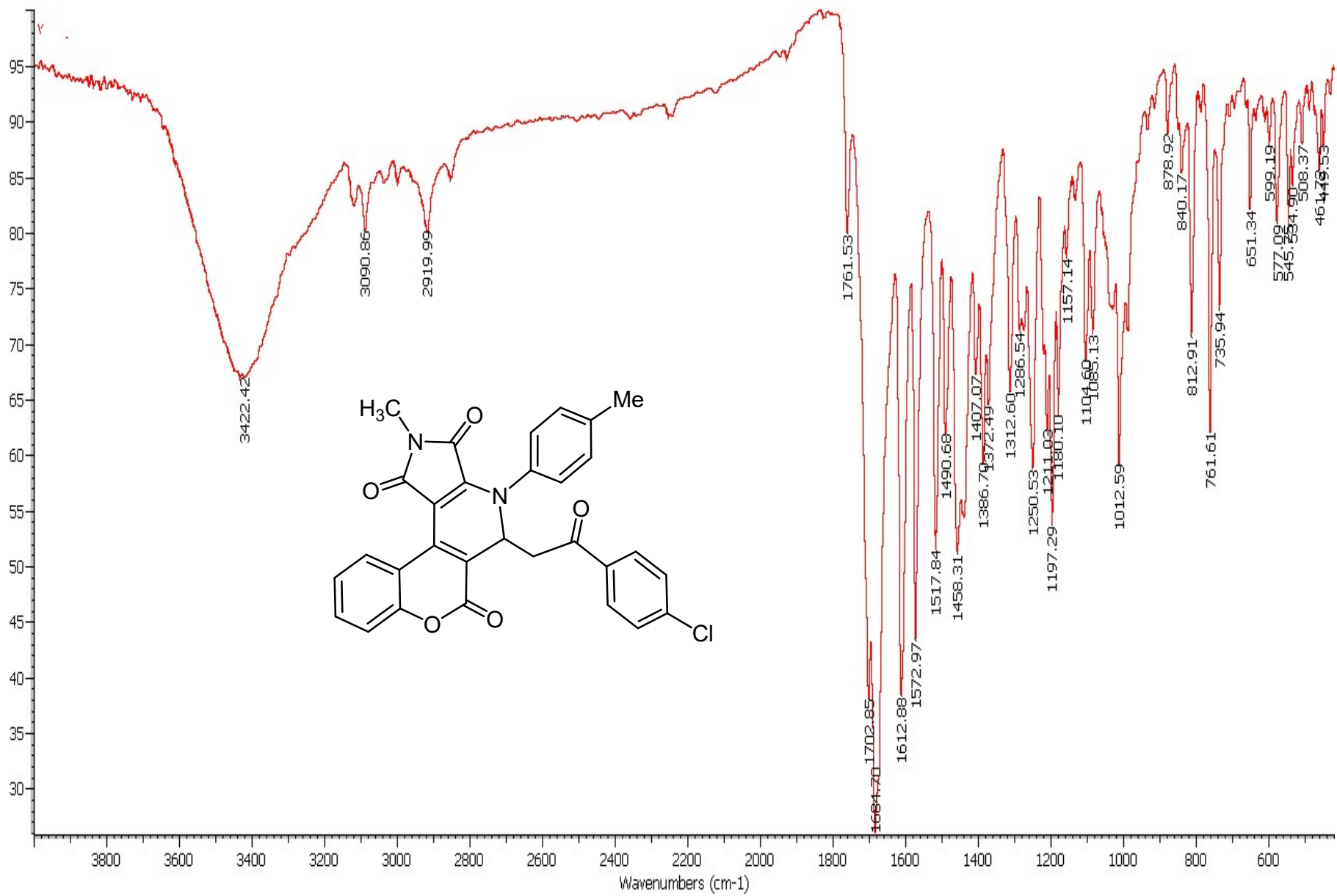


¹³C NMR Spectrum of 3d

S29

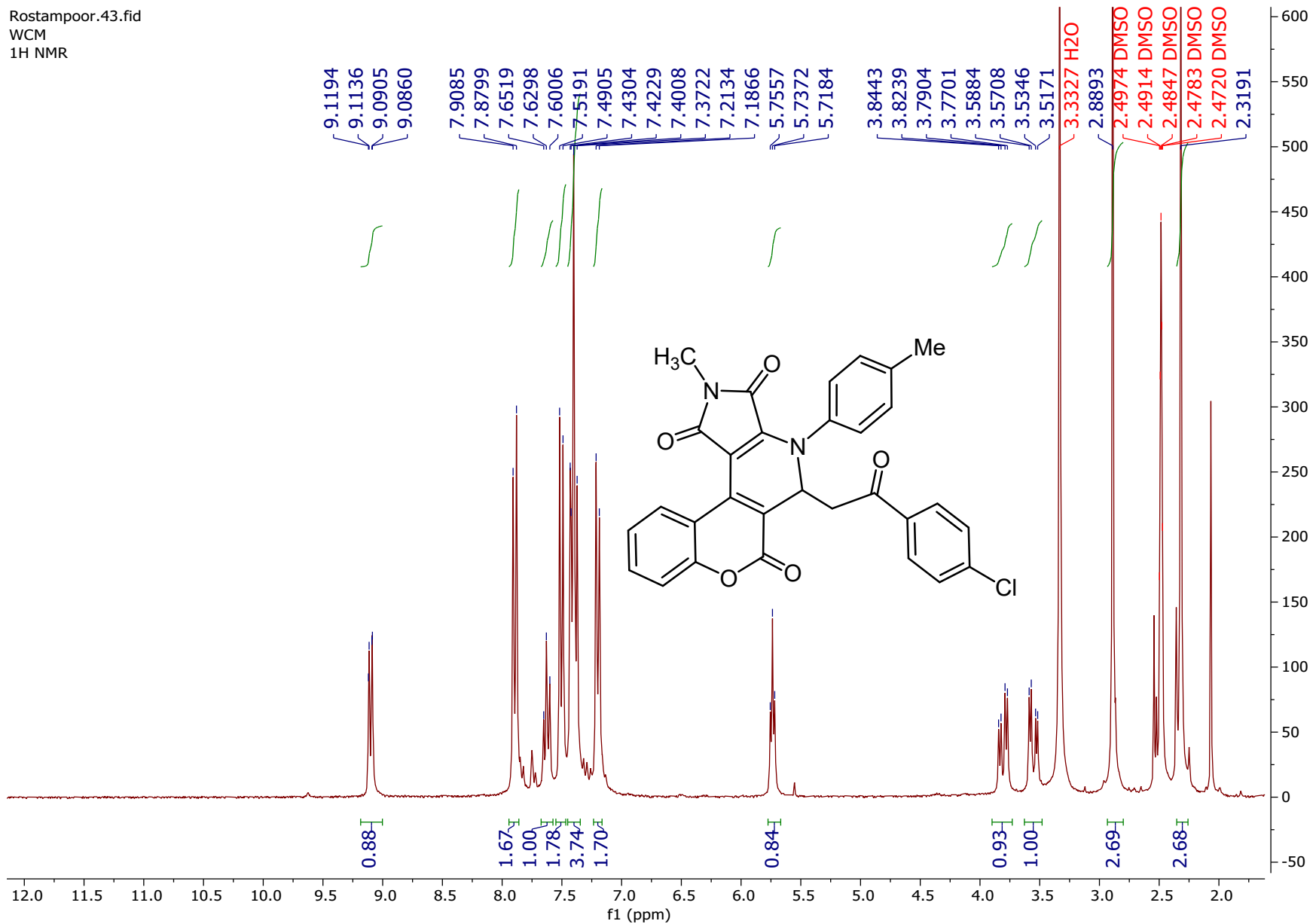


Mass spectrum of 3d
S30

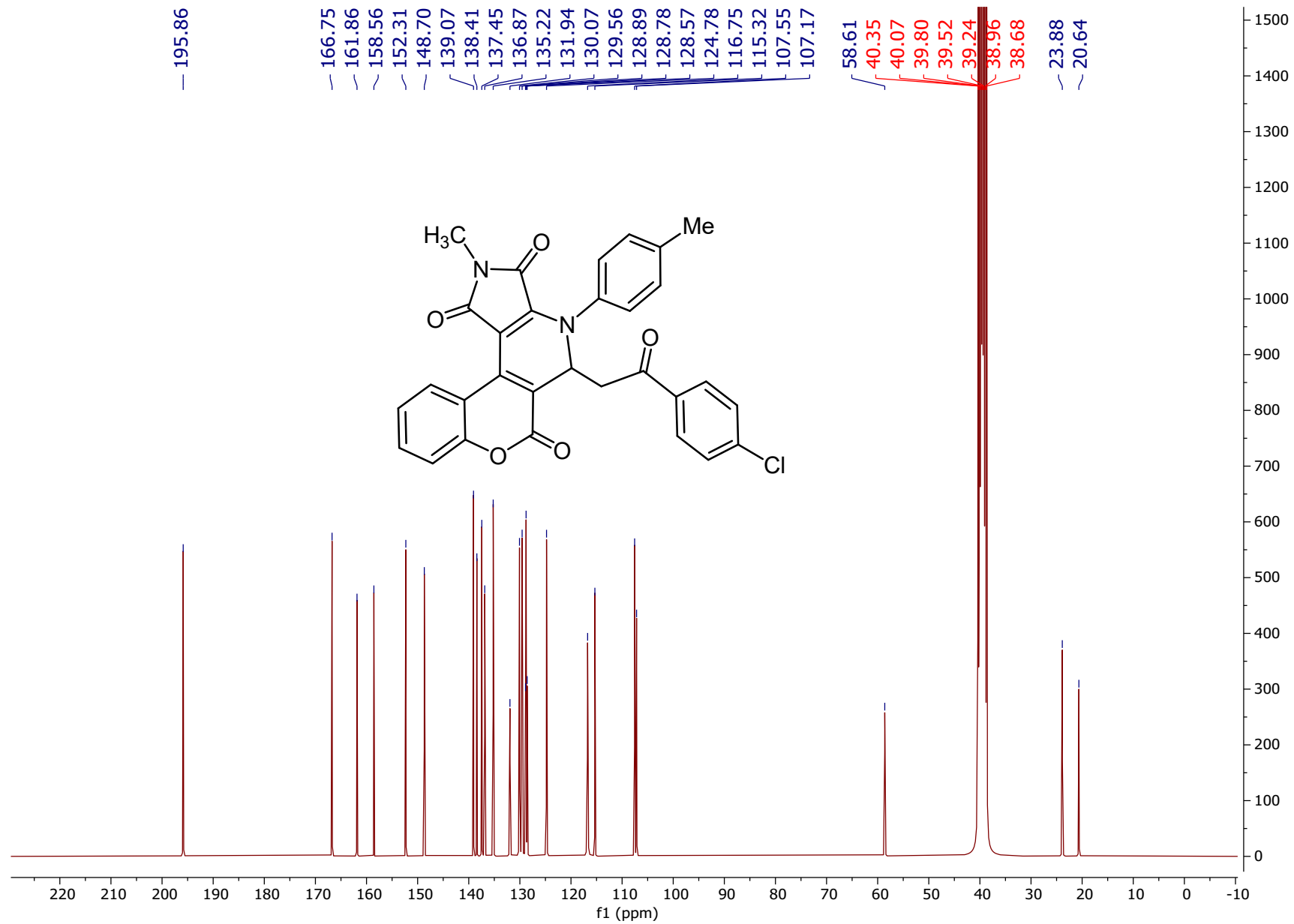


IR spectrum of 3e

Rostampoor.43.fid
WCM
1H NMR

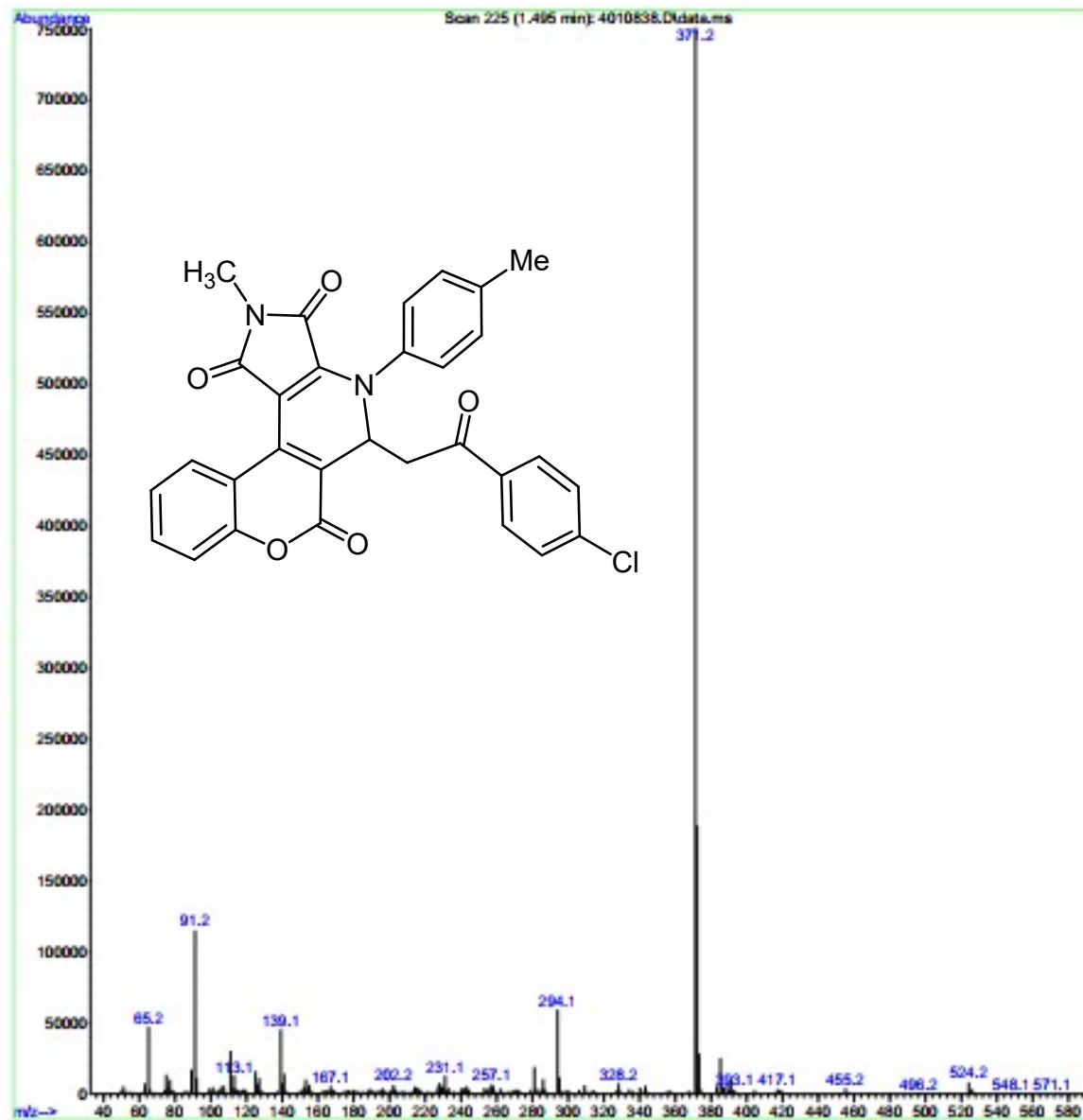


¹H NMR Spectrum of **3e**



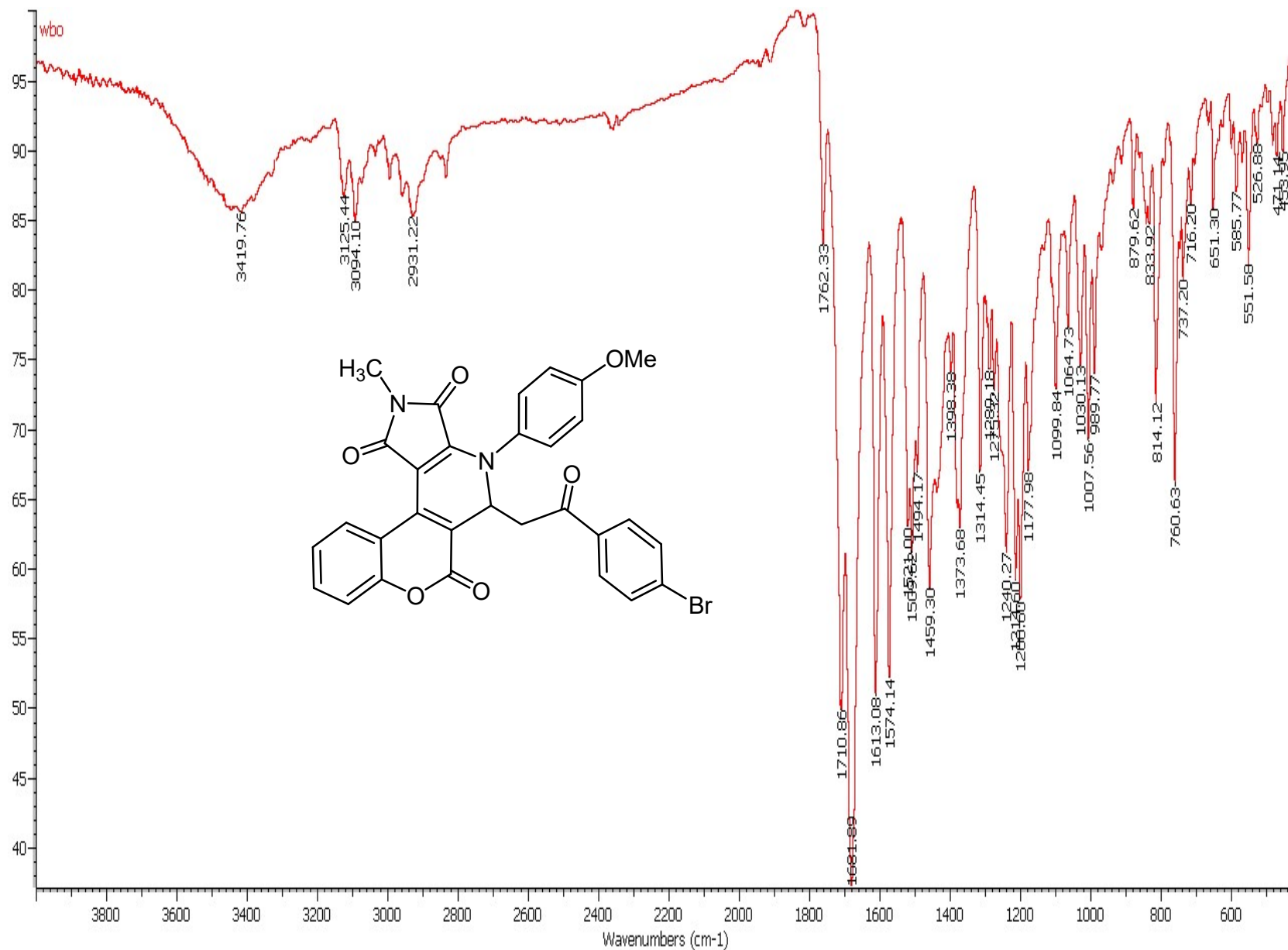
¹³C NMR Spectrum of 3e

S33



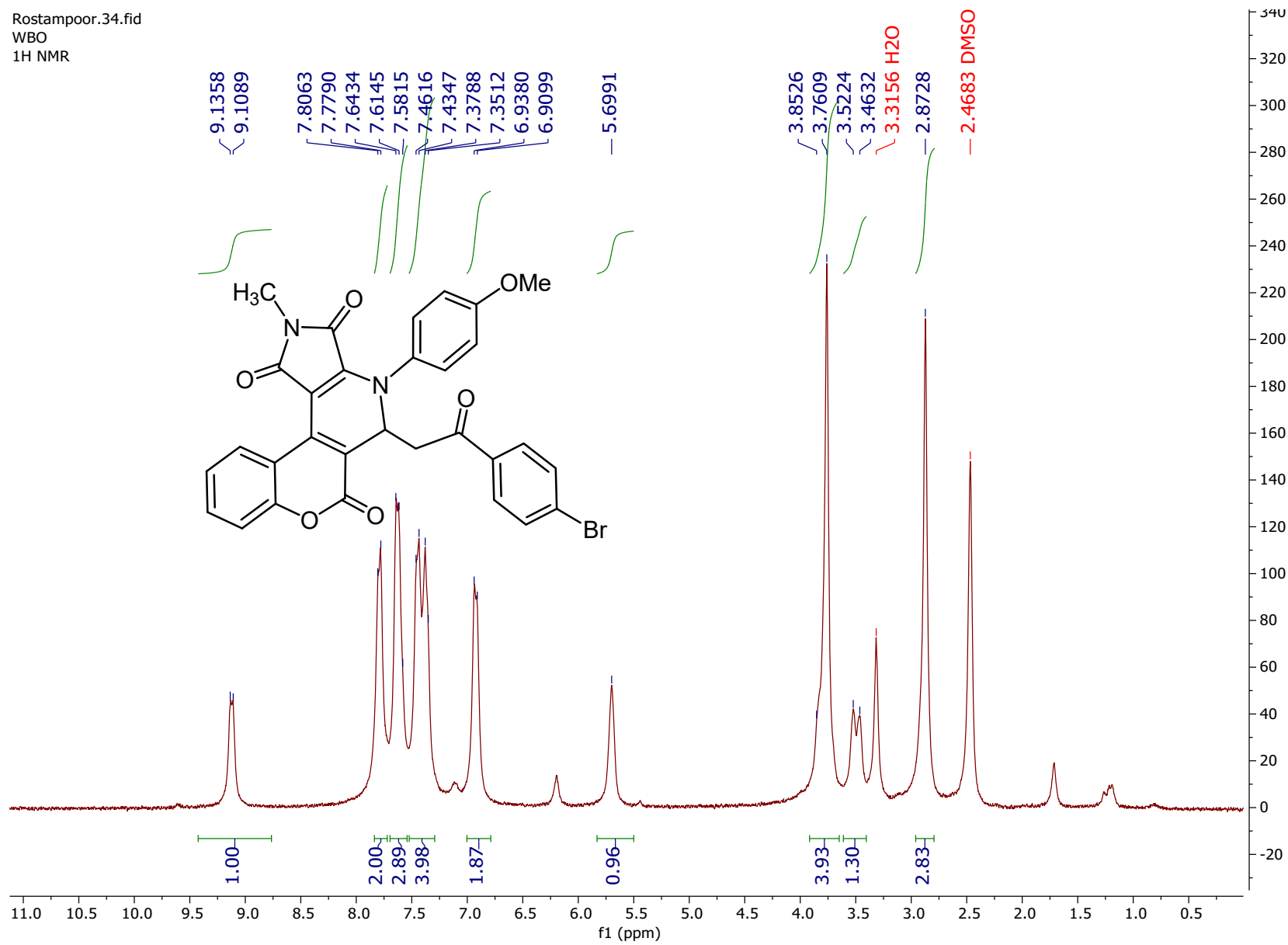
Mass spectrum of **3e**

S34

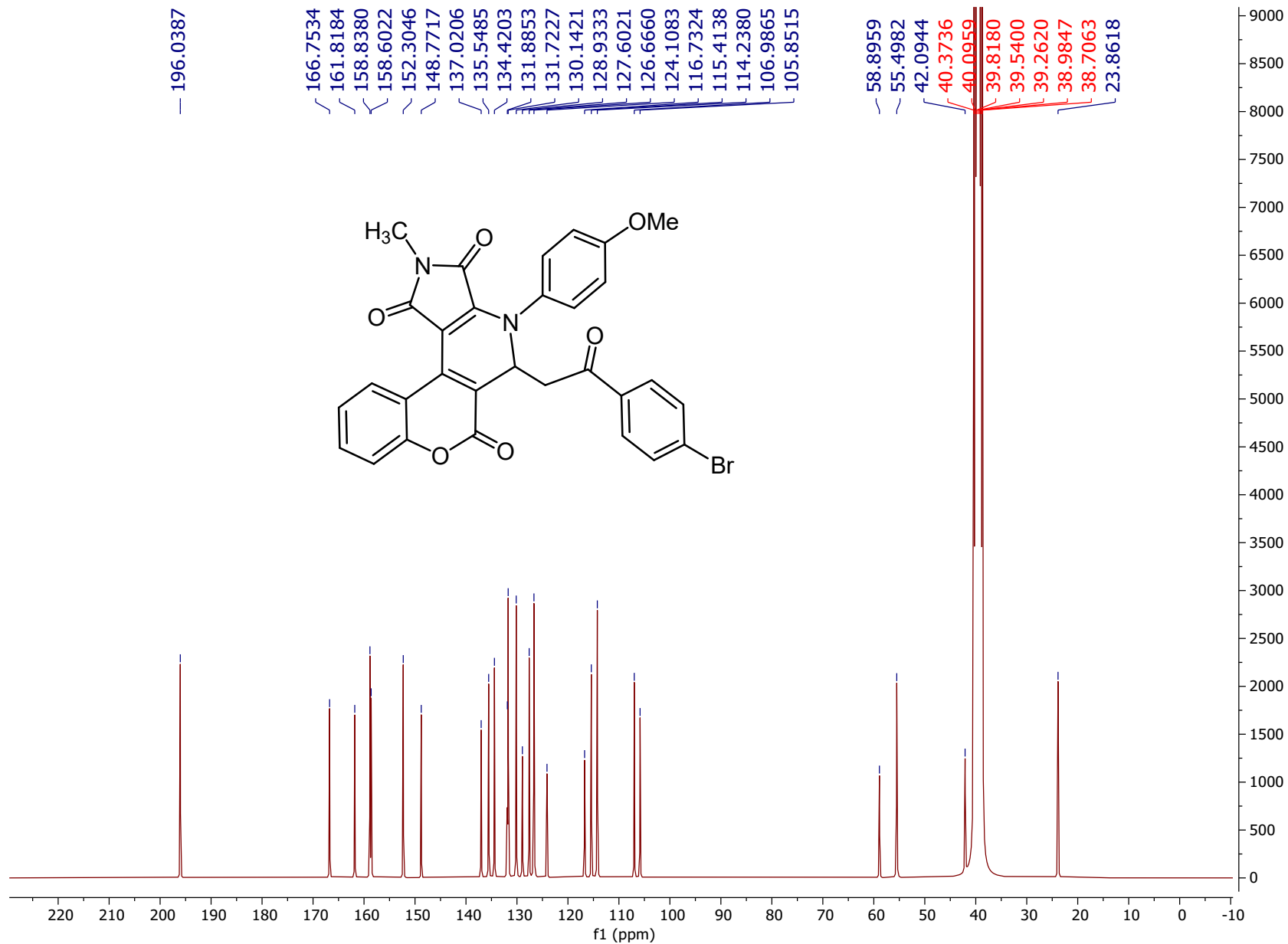


IR spectrum of 3f

Rostampoor.34.fid
WBO
1H NMR

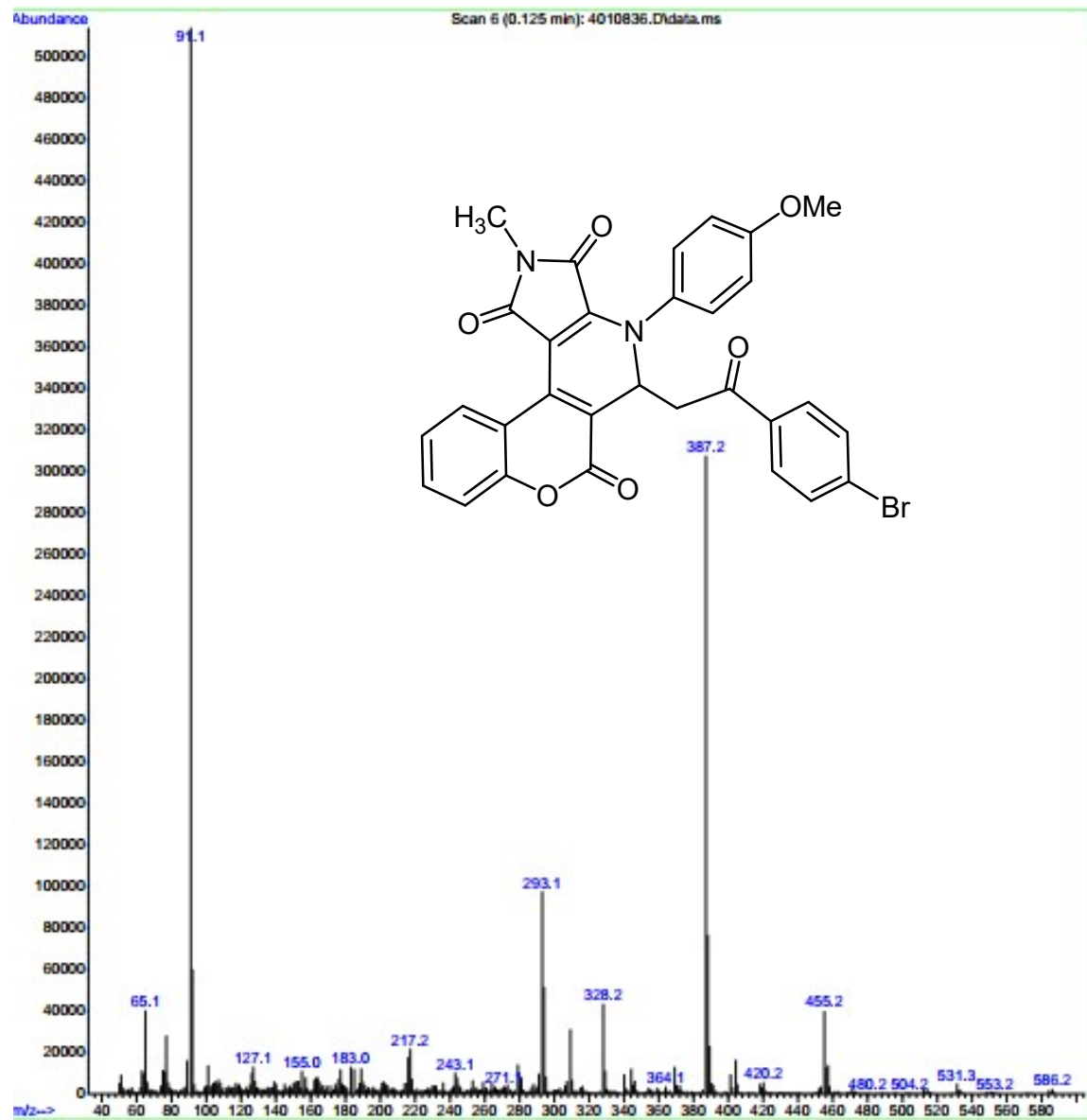


¹H NMR Spectrum of **3f**

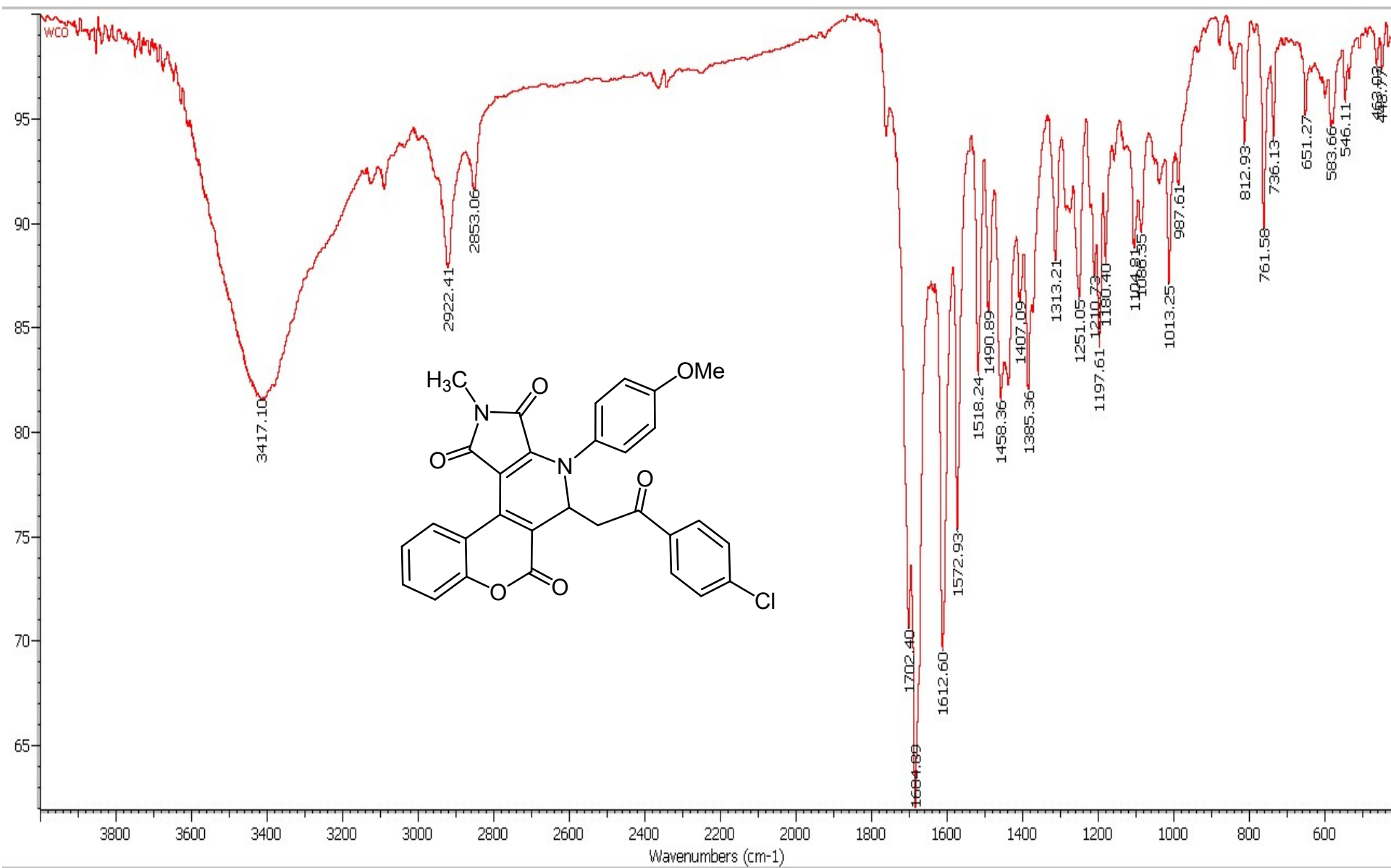


^{13}C NMR Spectrum of **3f**

S37

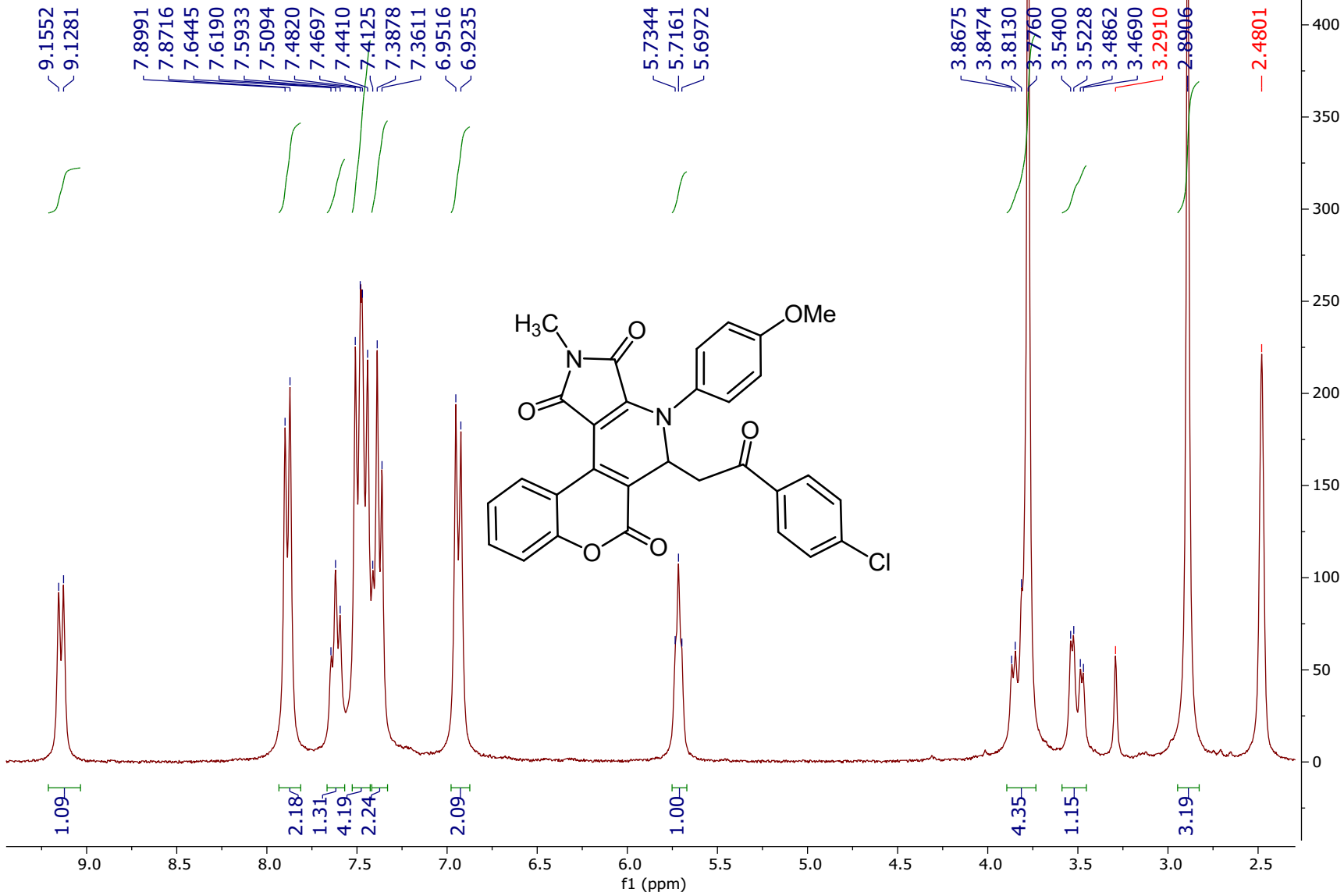


Mass spectrum of 3f

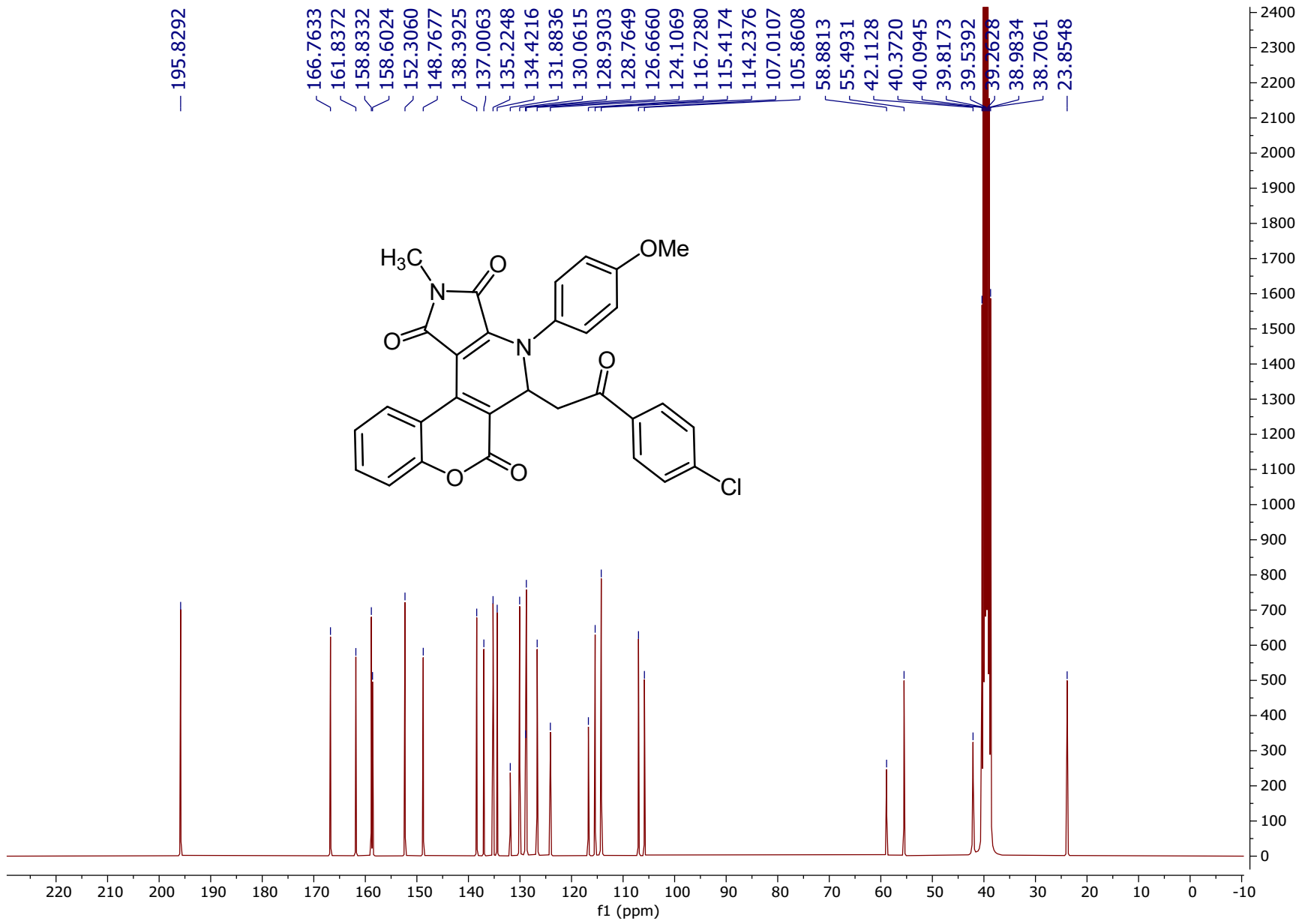


IR spectrum of **3g**

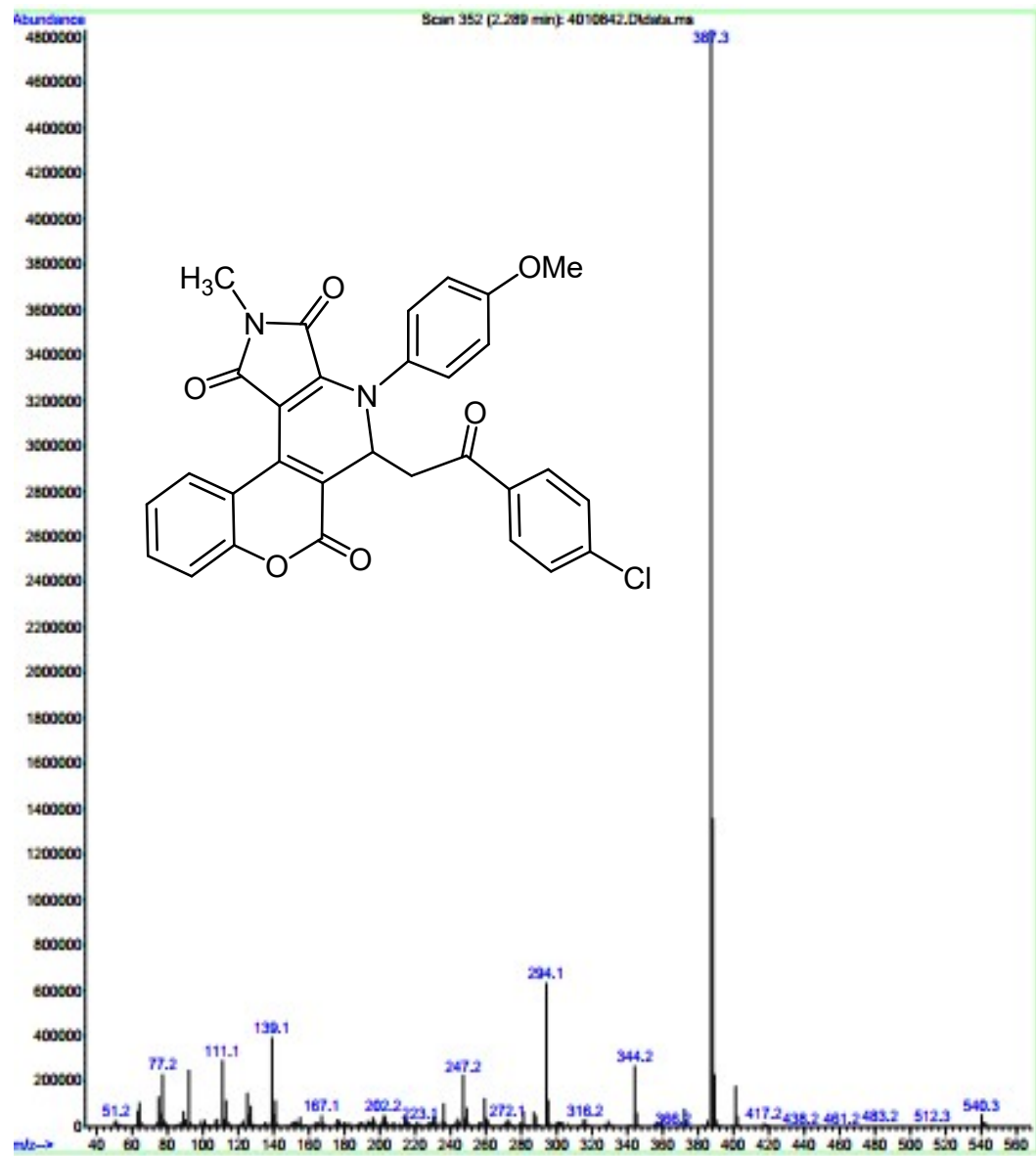
Rostampoor.22.fid
WCO
1H NMR



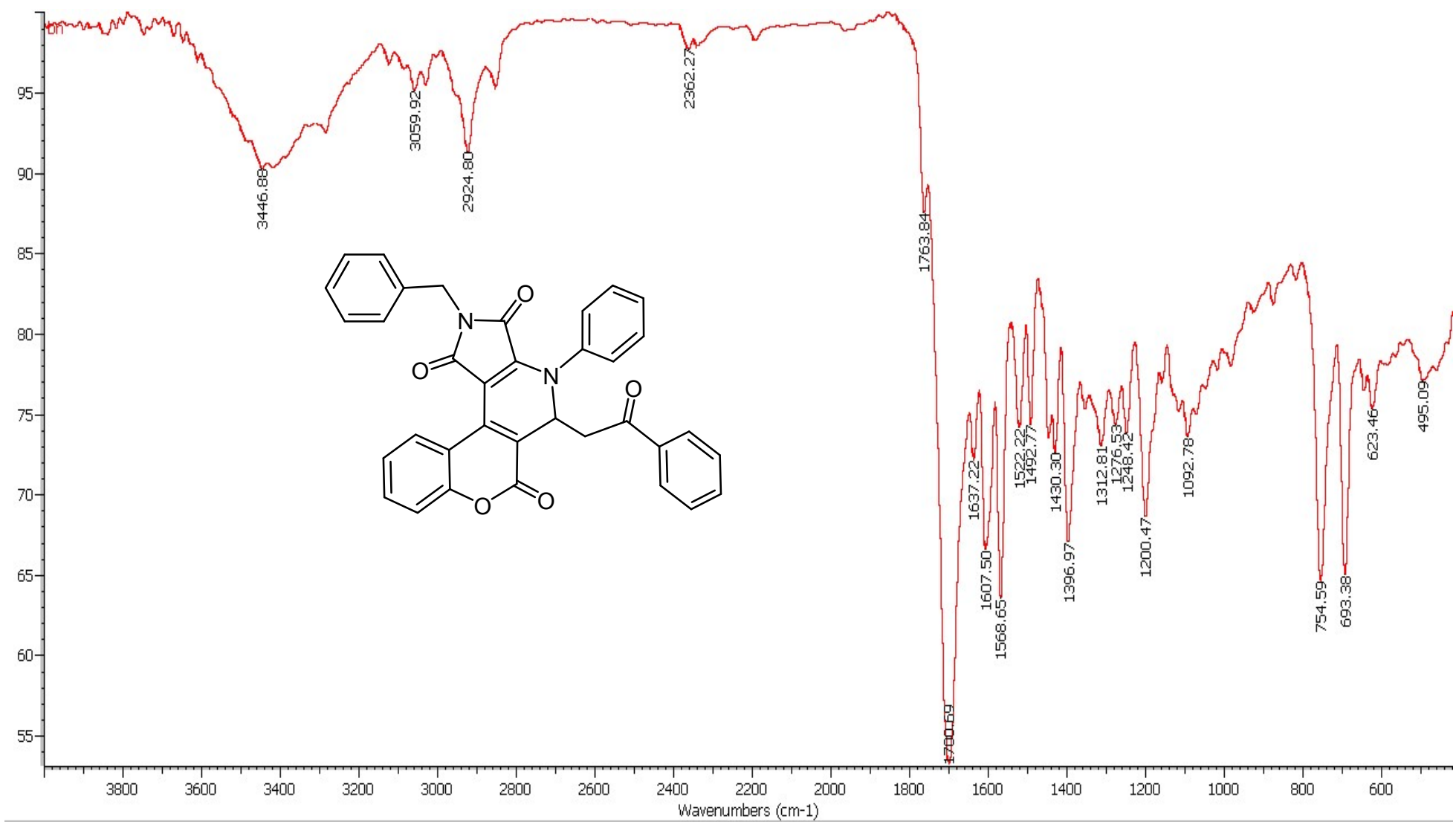
¹H NMR Spectrum of 3g



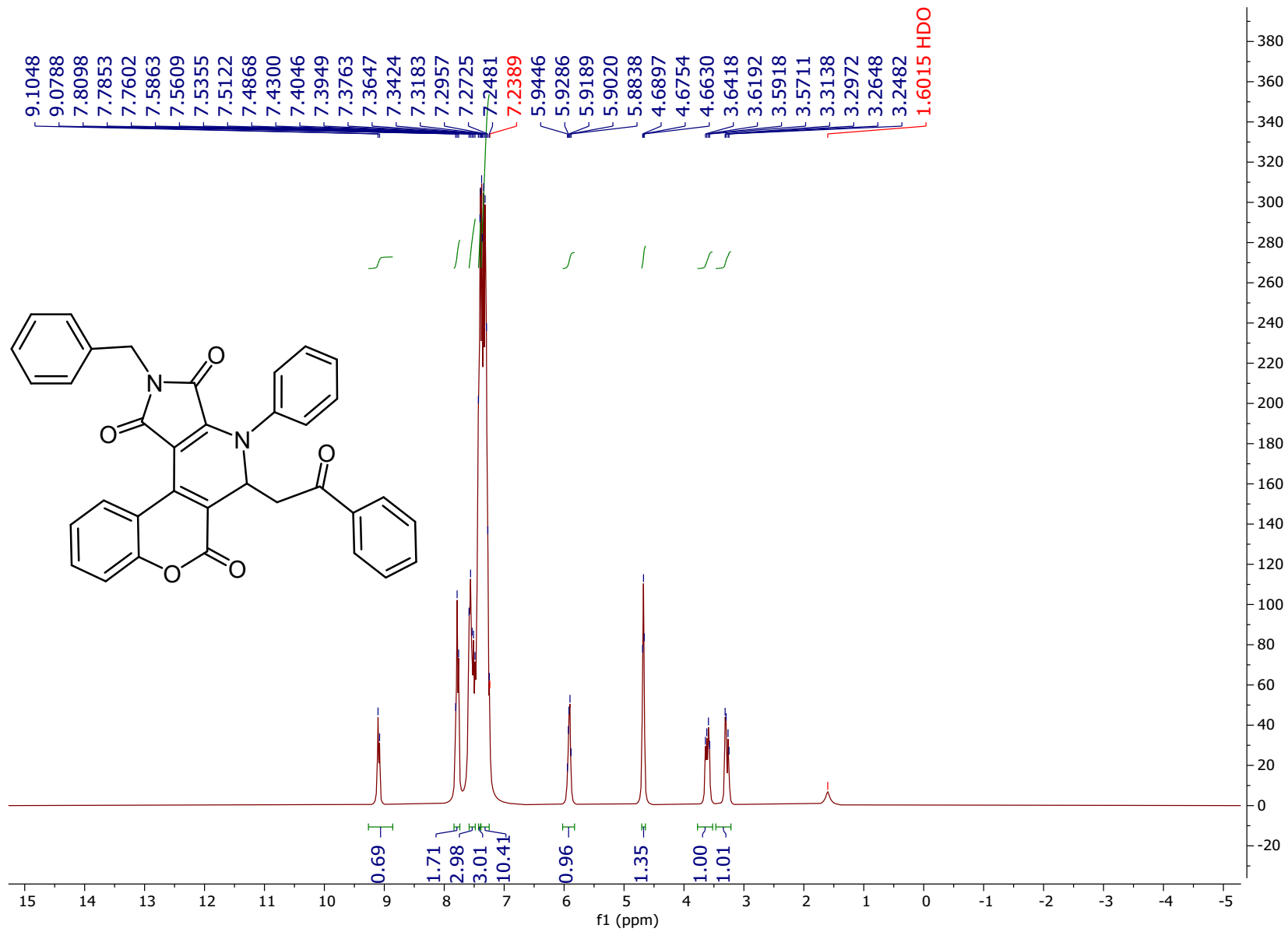
¹³C NMR Spectrum of **3g**



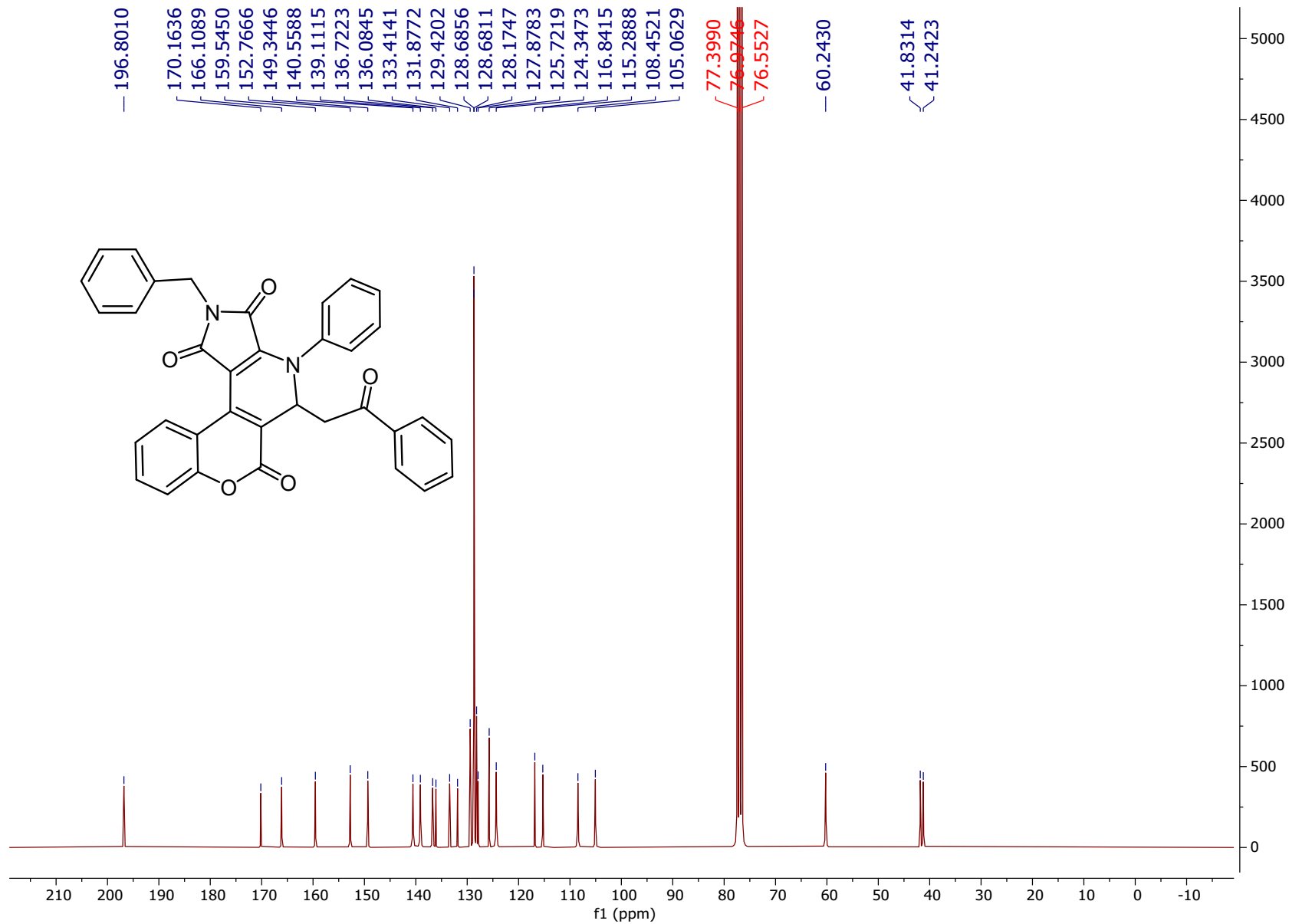
Mass spectrum of 3g



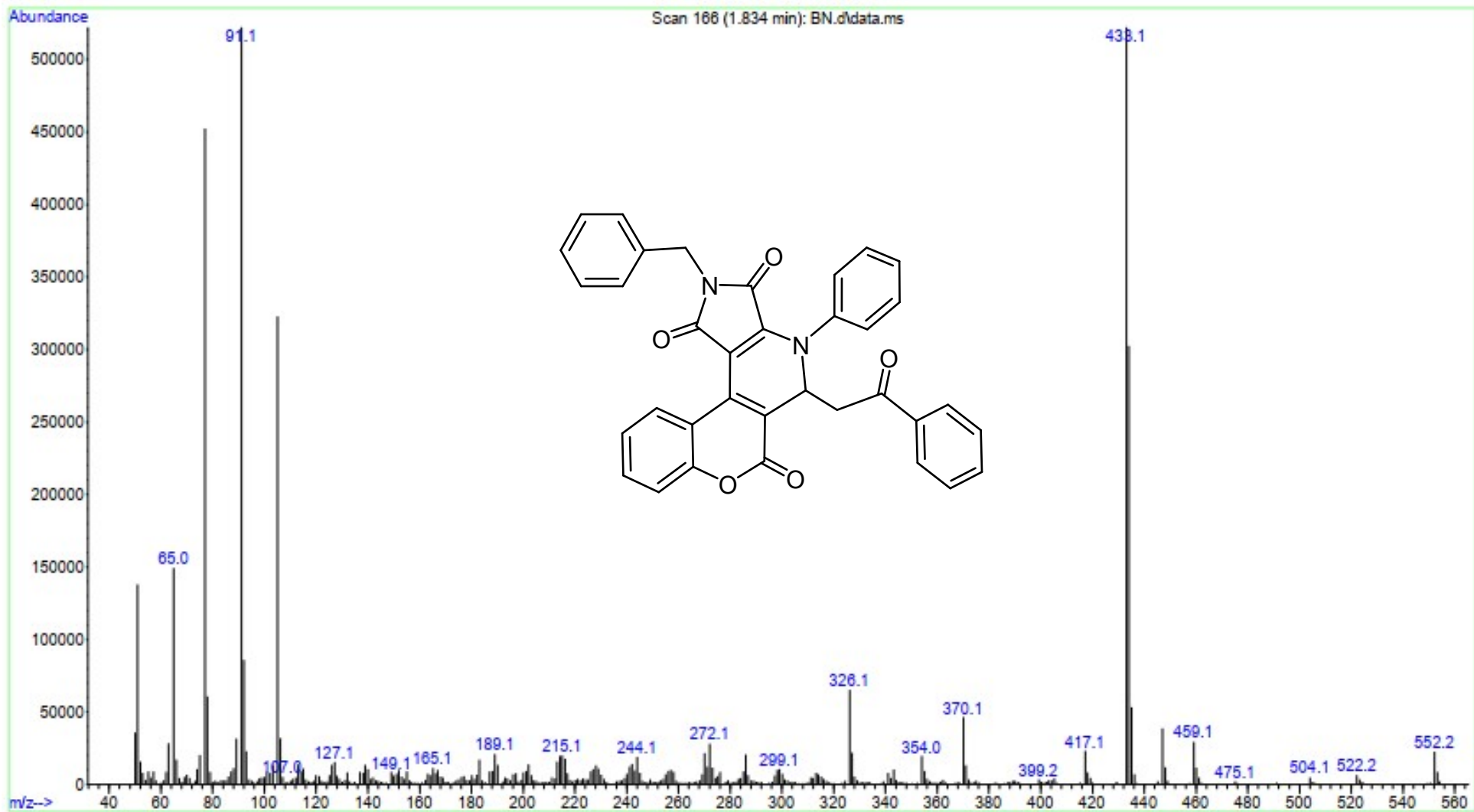
IR spectrum of 3h



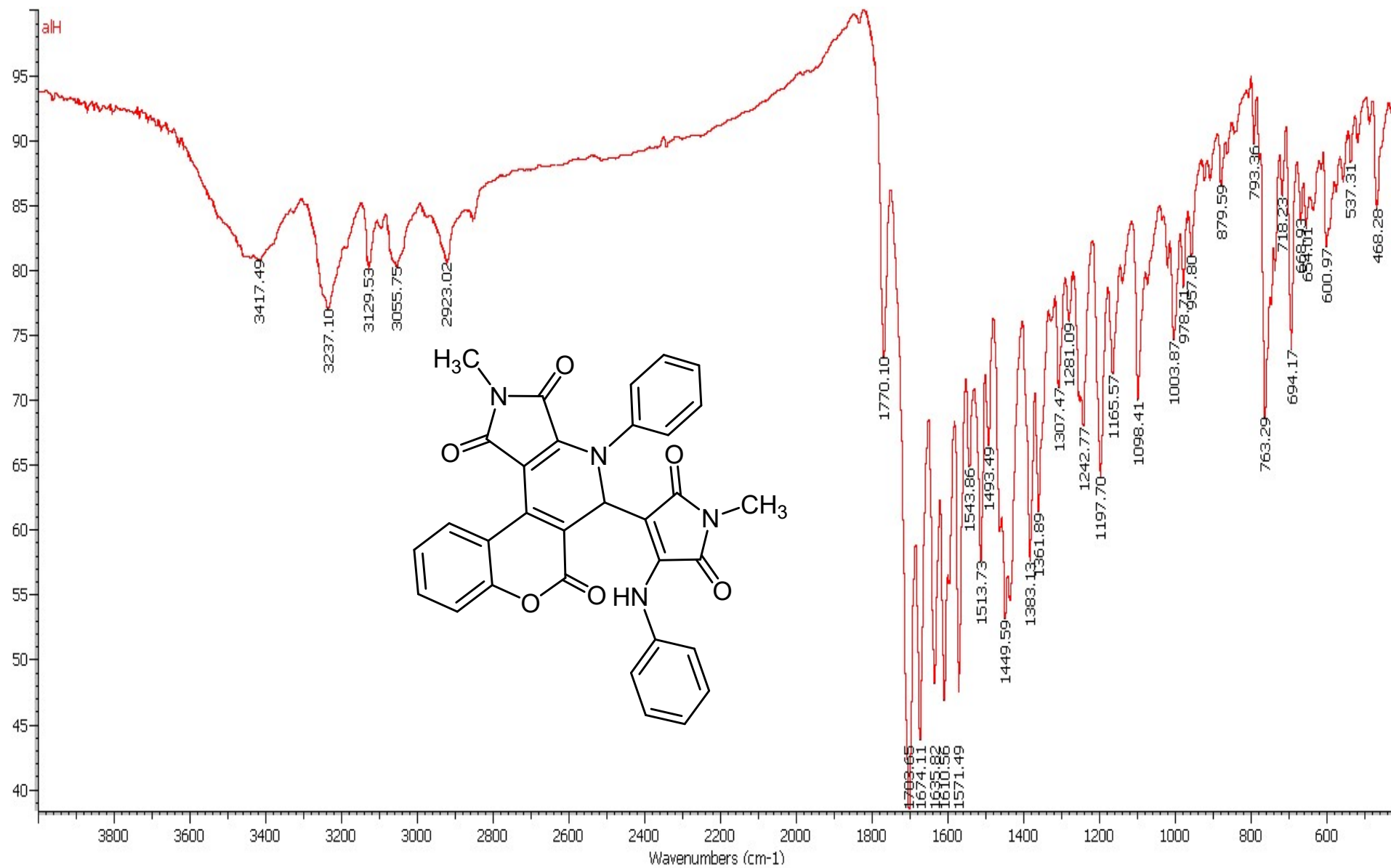
¹H NMR Spectrum of **3h**



¹³C NMR Spectrum of **3h**

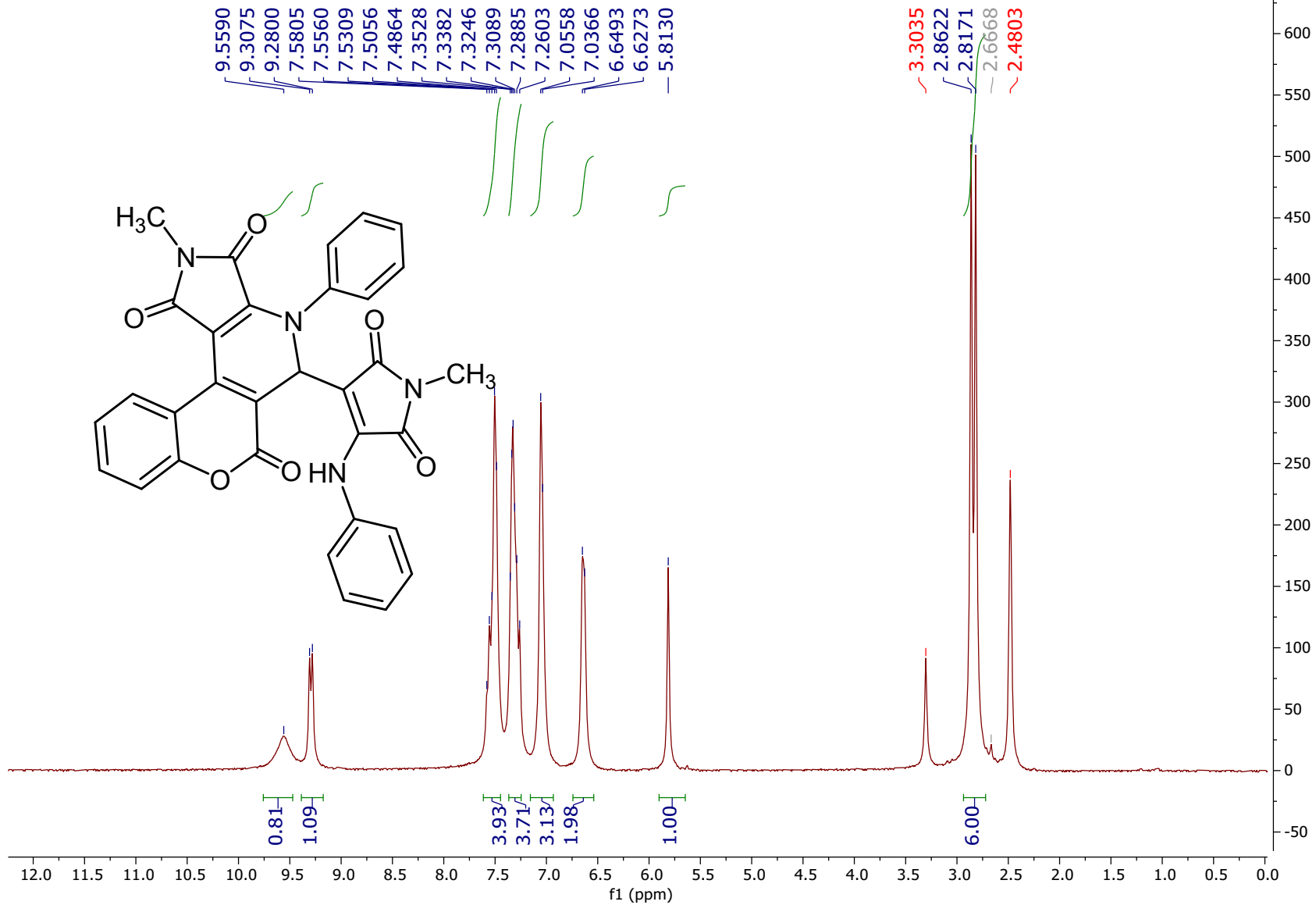


Mass spectrum of **3h**

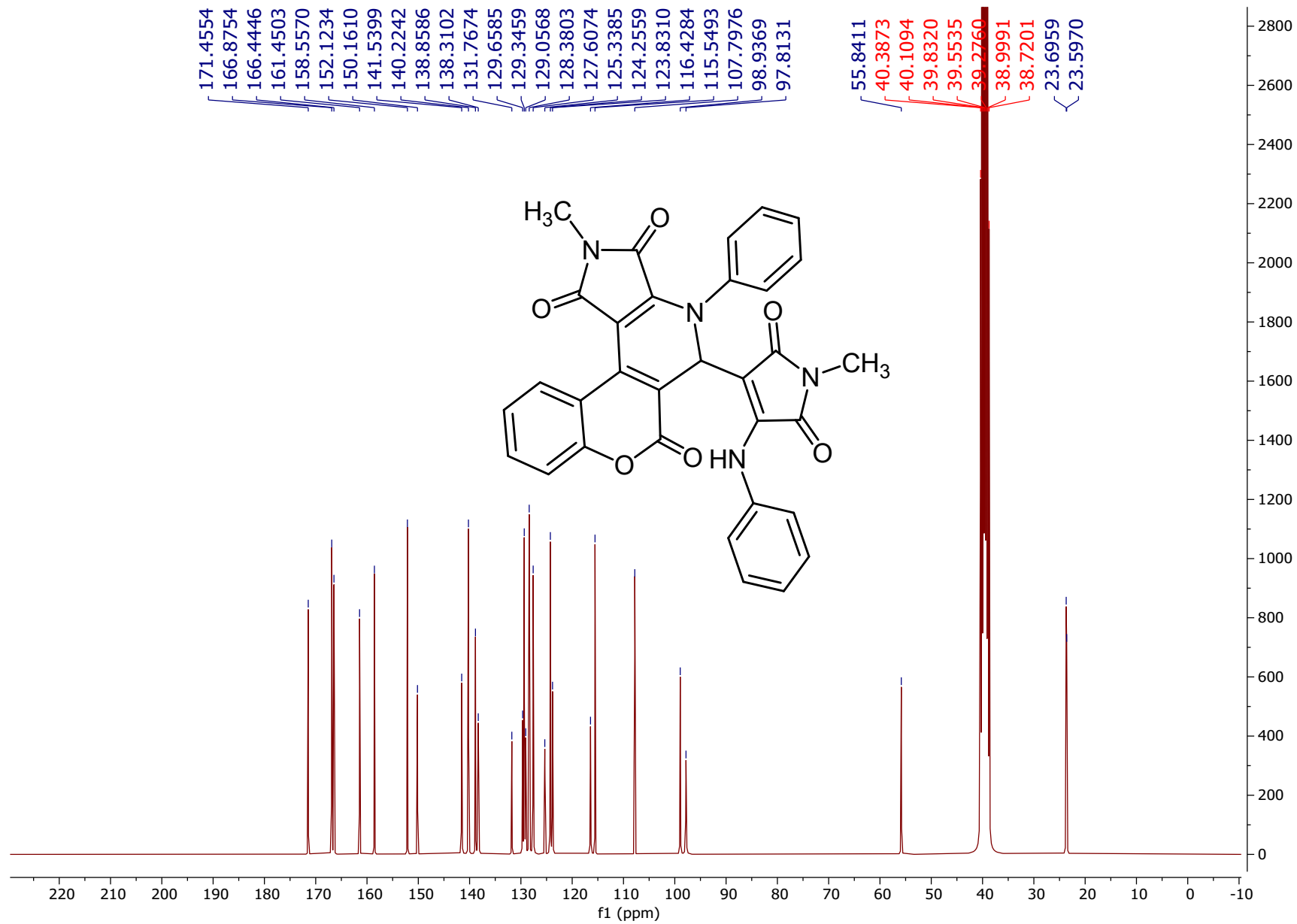


IR spectrum of 3'a

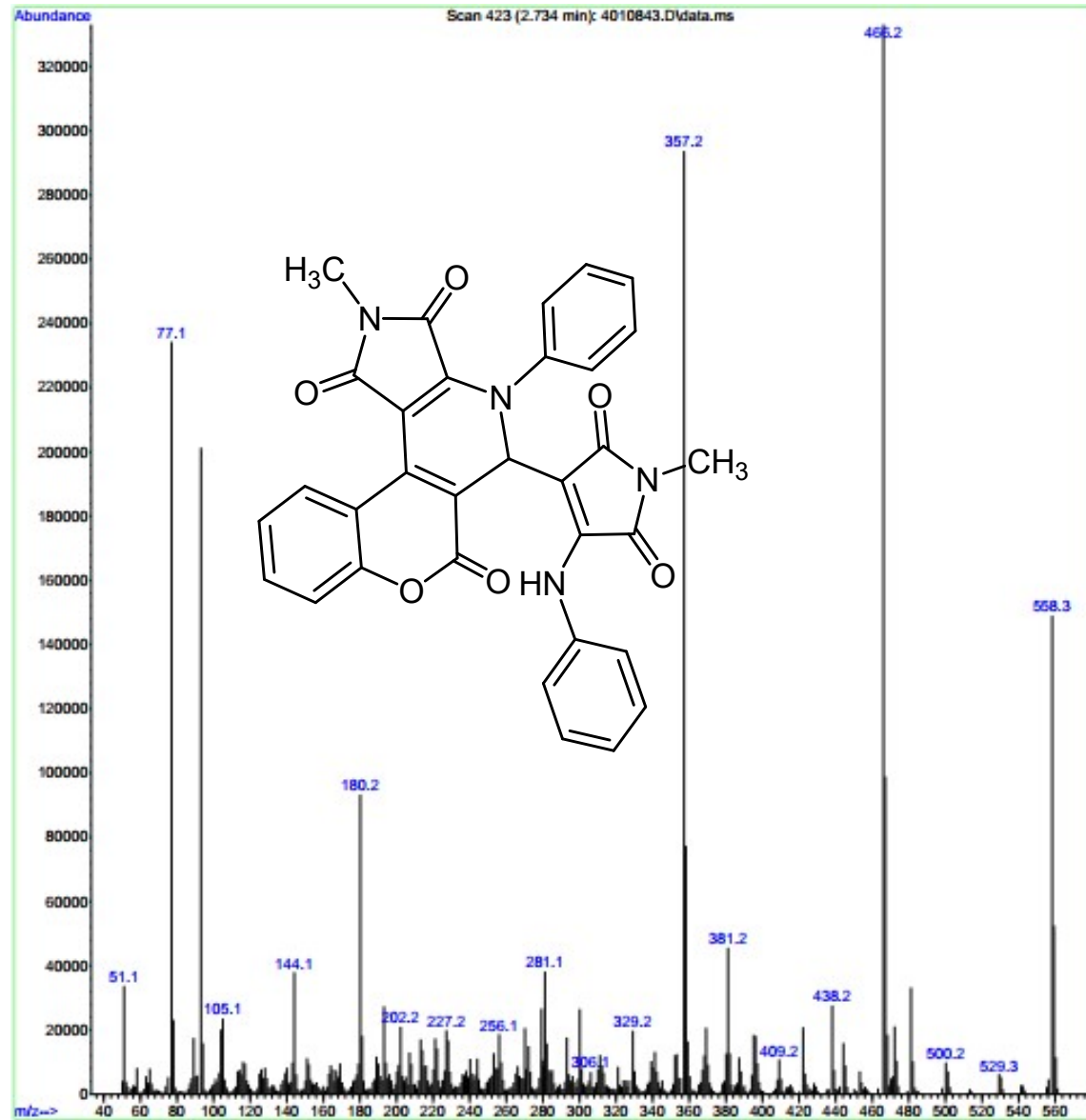
rostampoor.40.fid
ALH
1H NMR



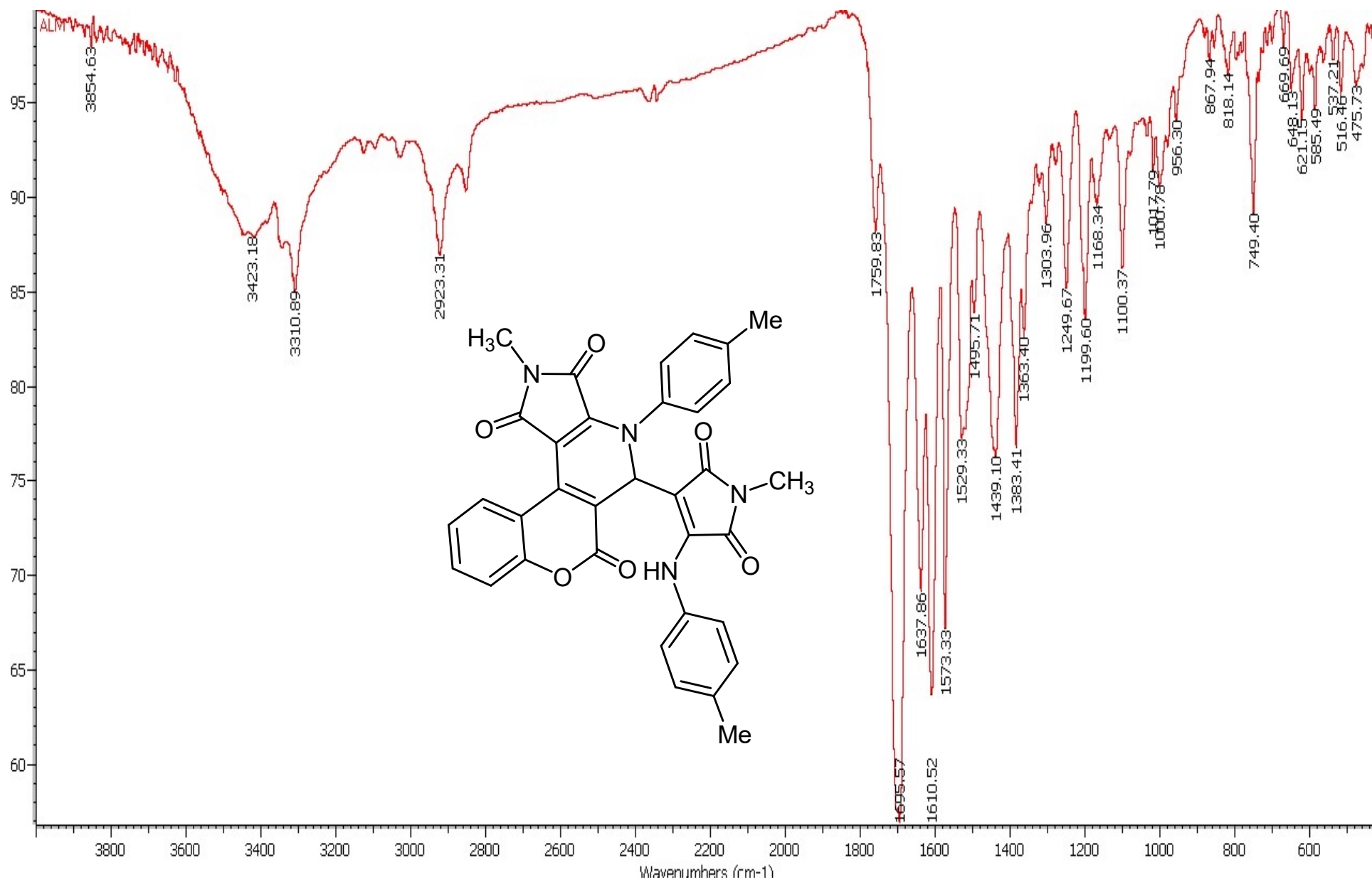
¹H NMR Spectrum of 3'a
S48



^{13}C NMR Spectrum of **3'a**



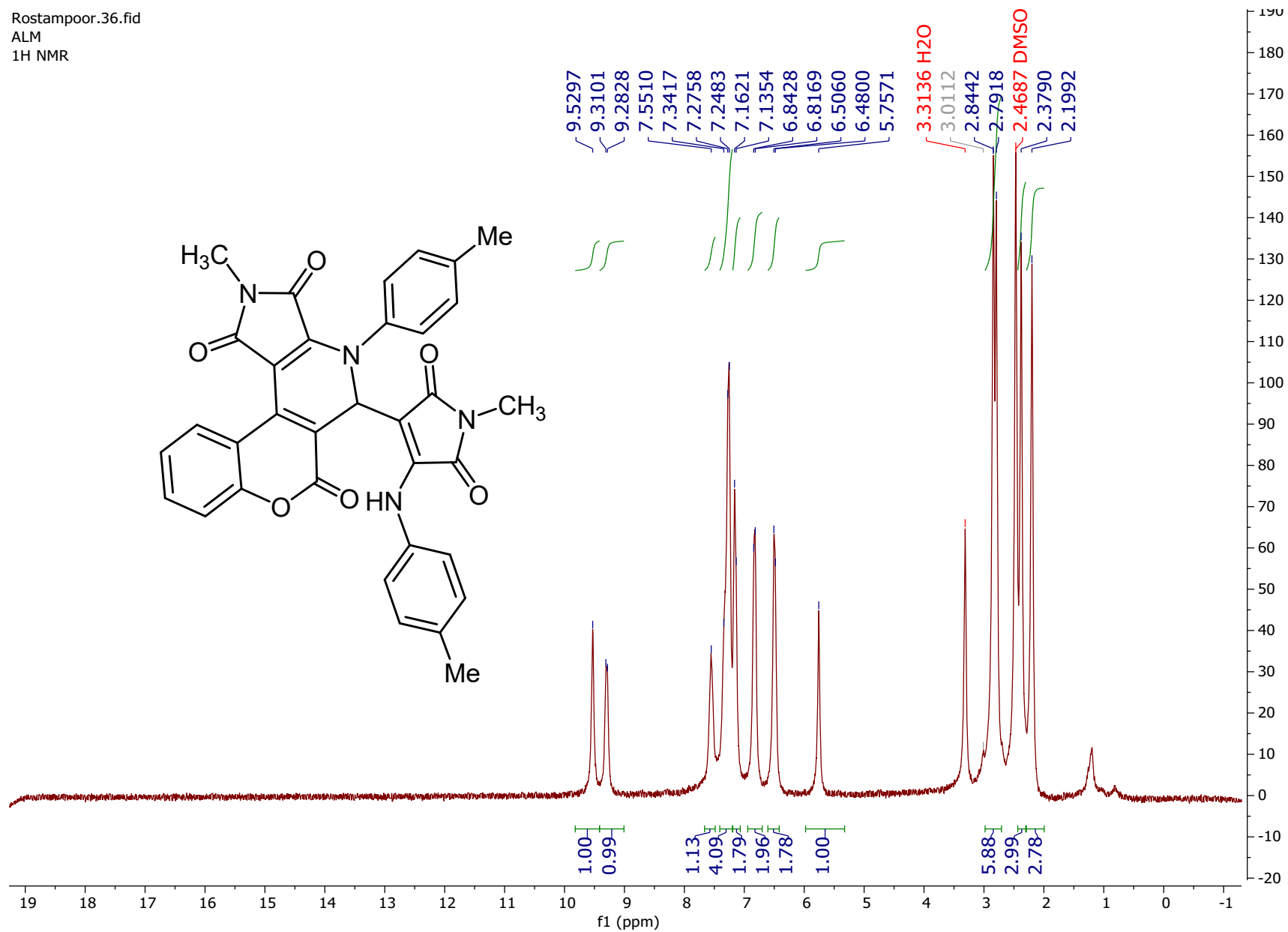
Mass spectrum of 3'a



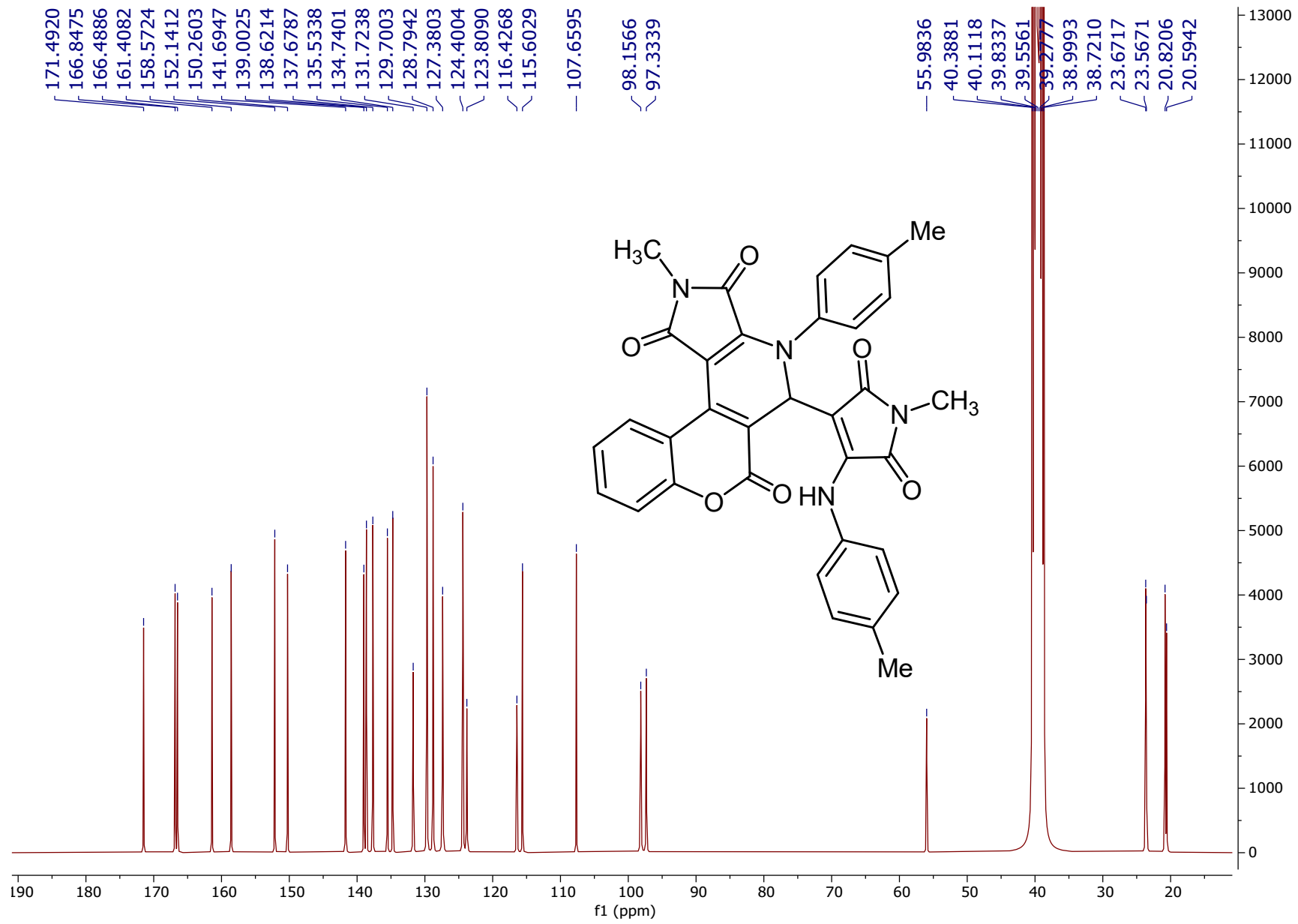
IR spectrum of 3'b

S51

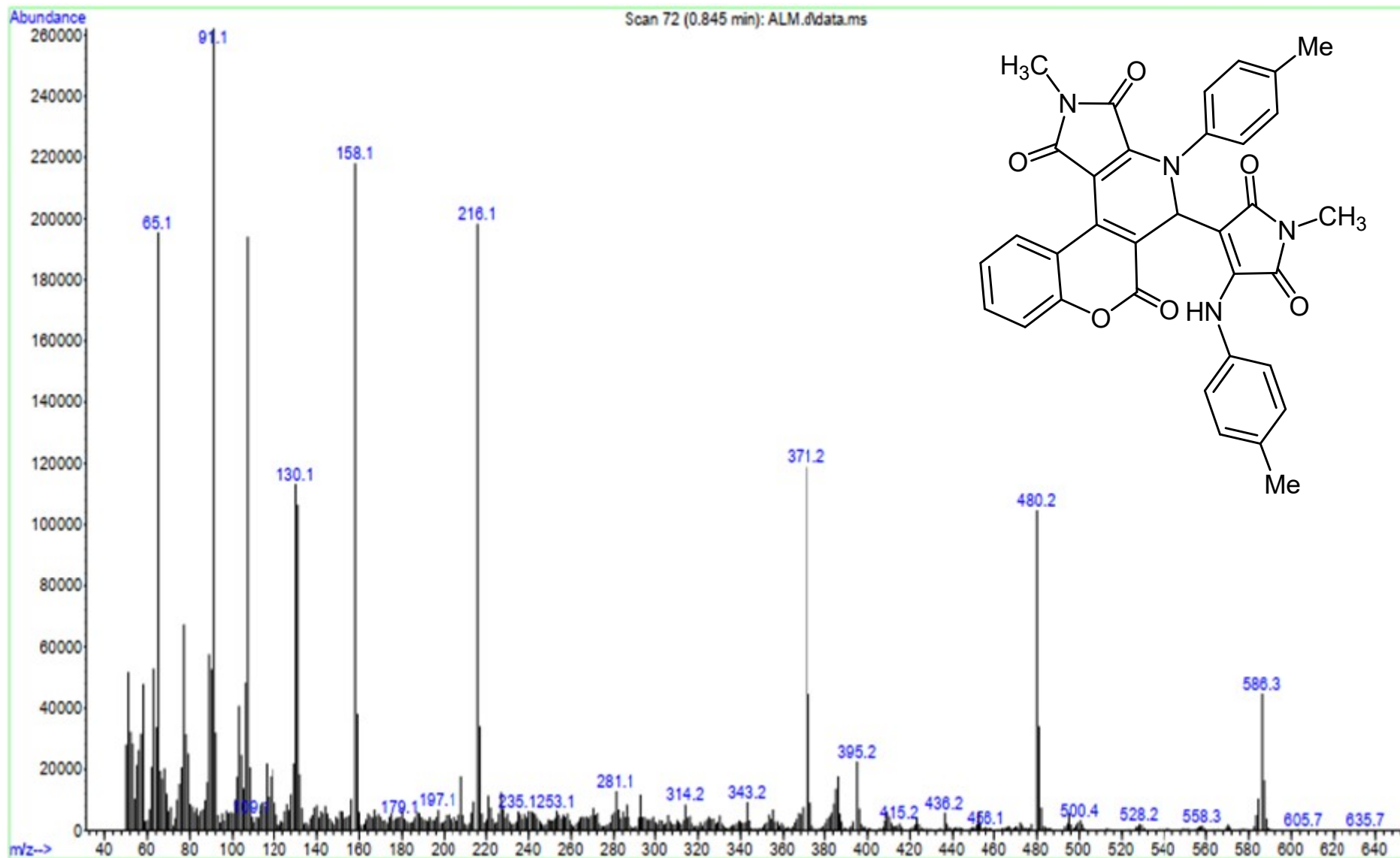
Rostampoor.36.fid
ALM
1H NMR



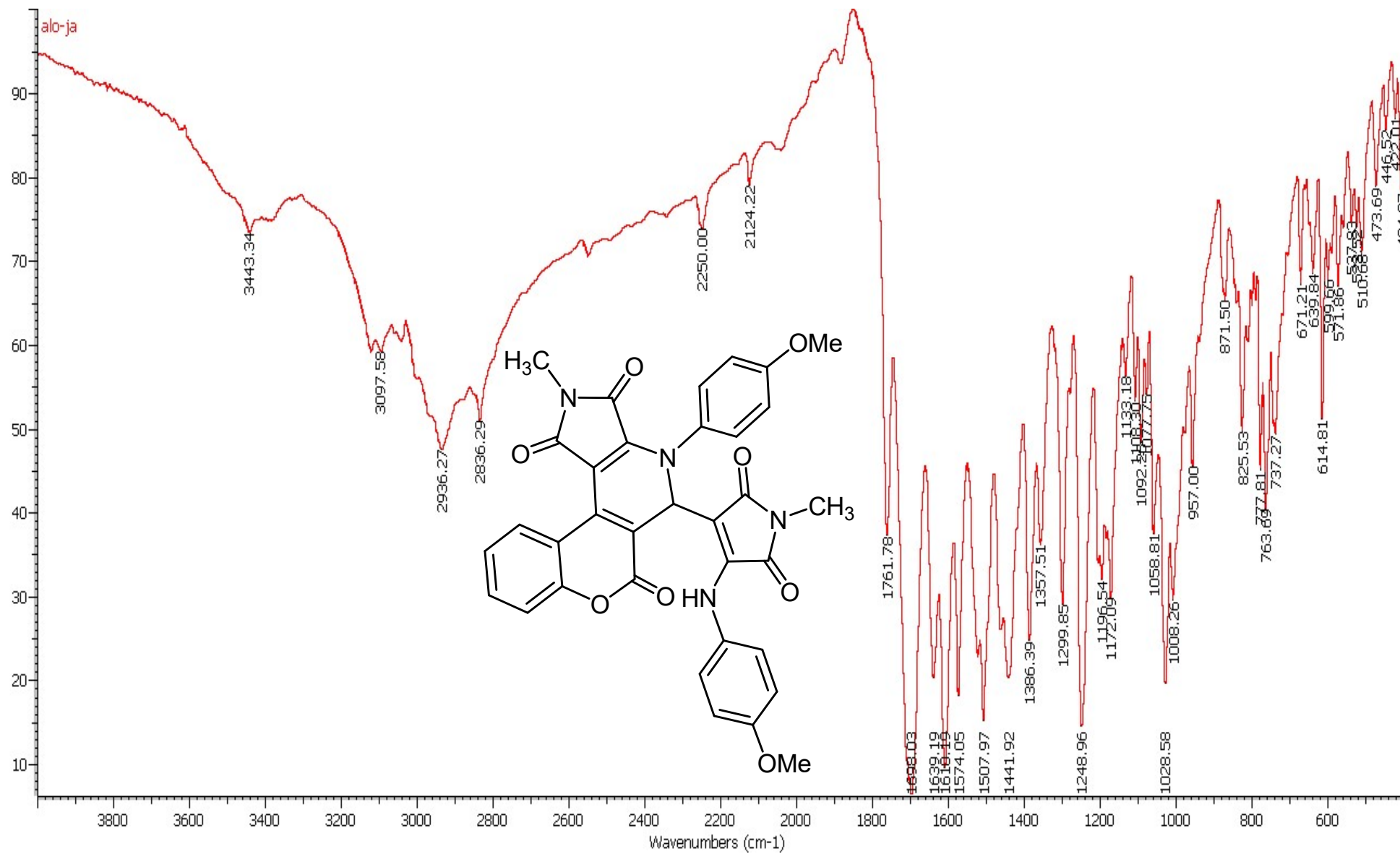
¹H NMR Spectrum of 3'b
S52



¹³C NMR Spectrum of **3'b**

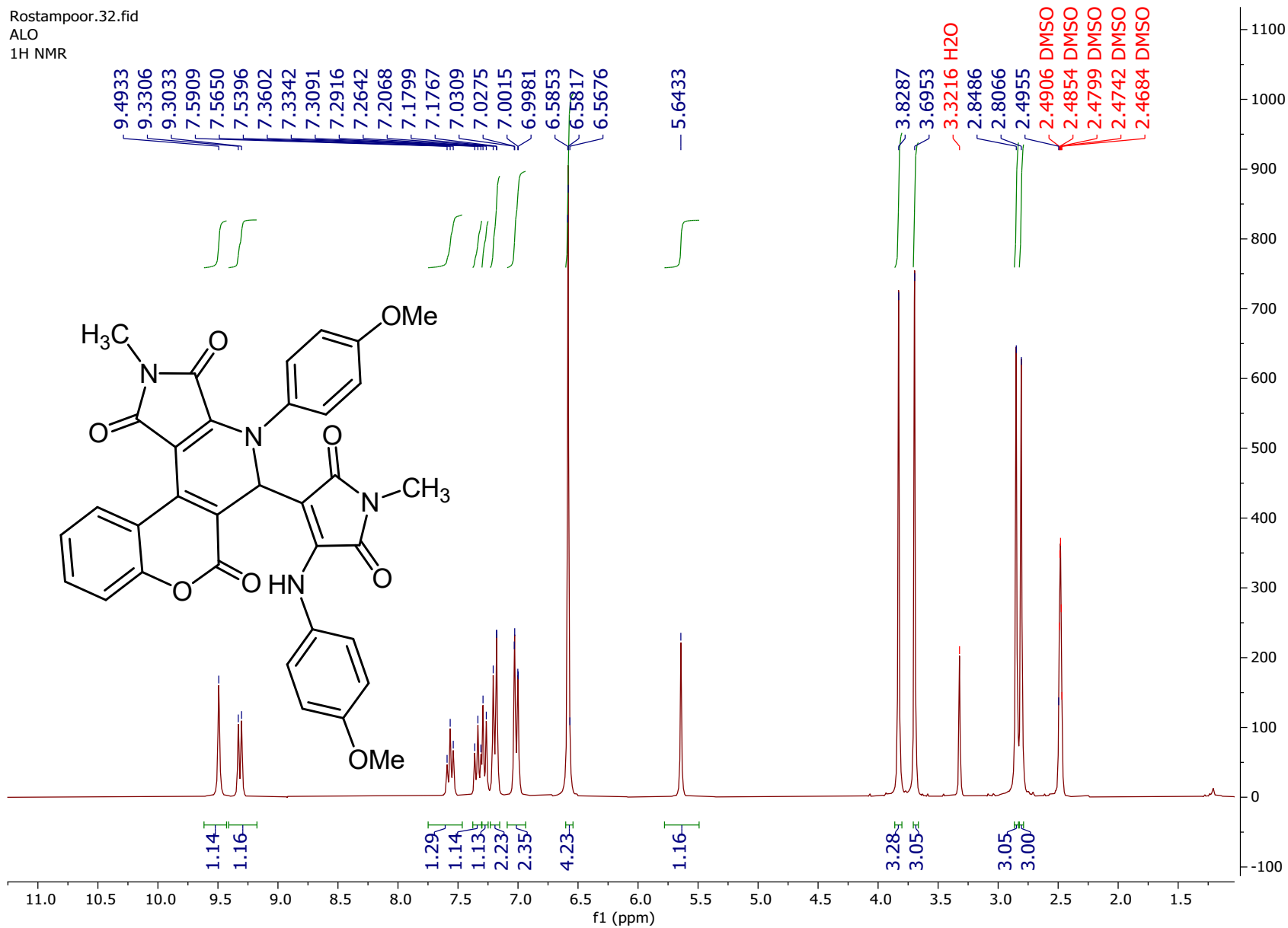


Mass spectrum of **3'b**

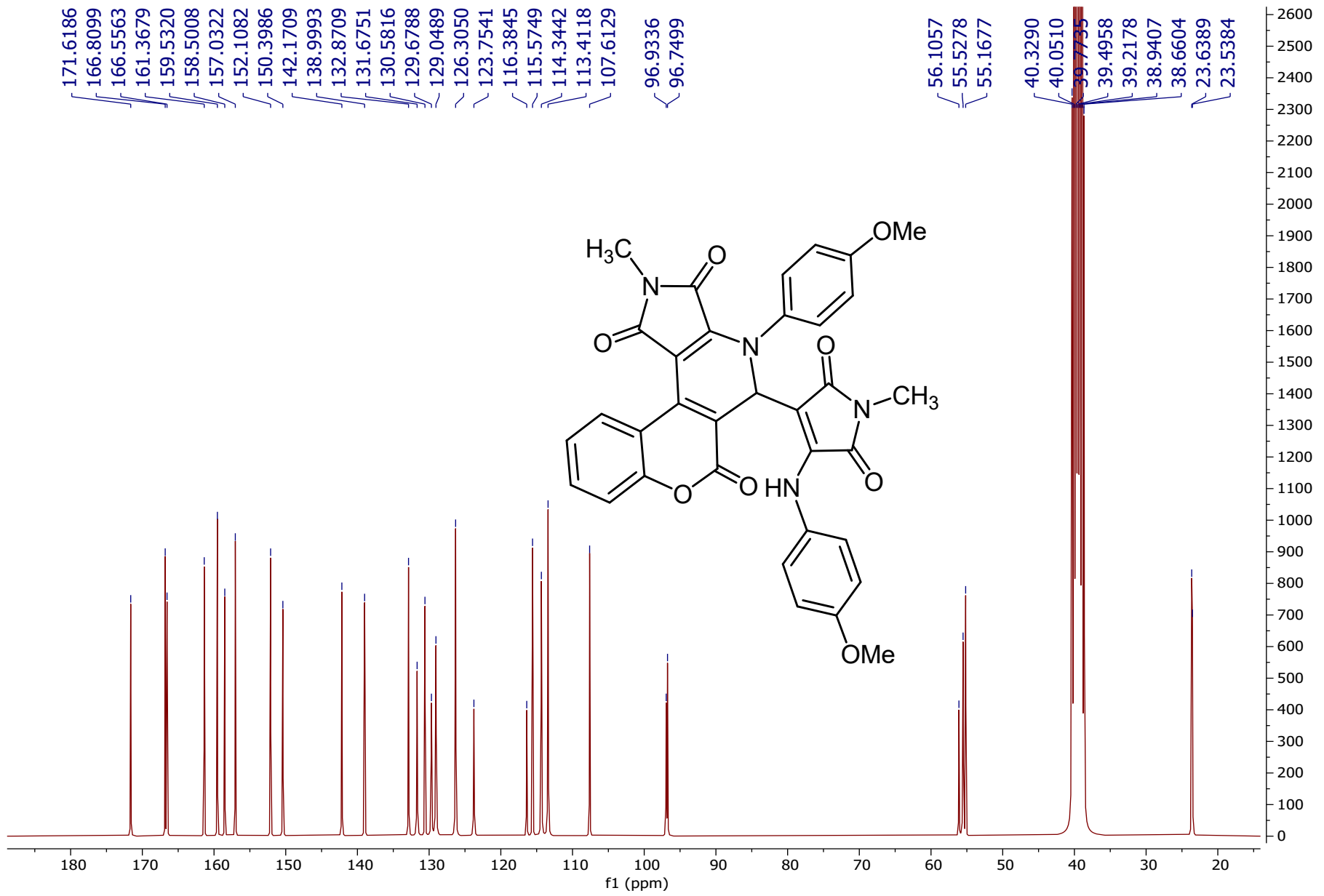


IR spectrum of 3'c

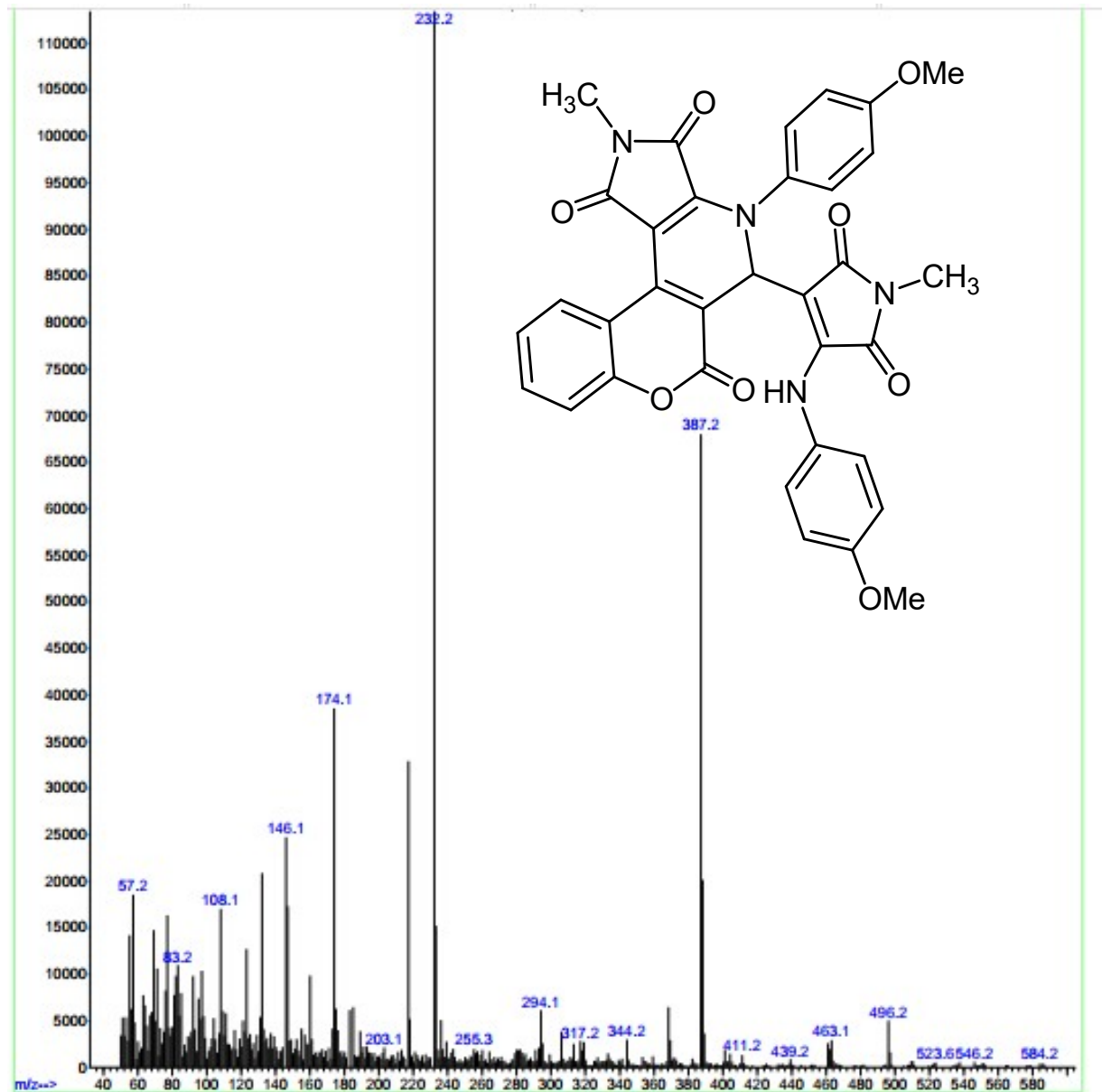
Rostampoor.32.fid
ALO
1H NMR



¹H NMR Spectrum of 3'c

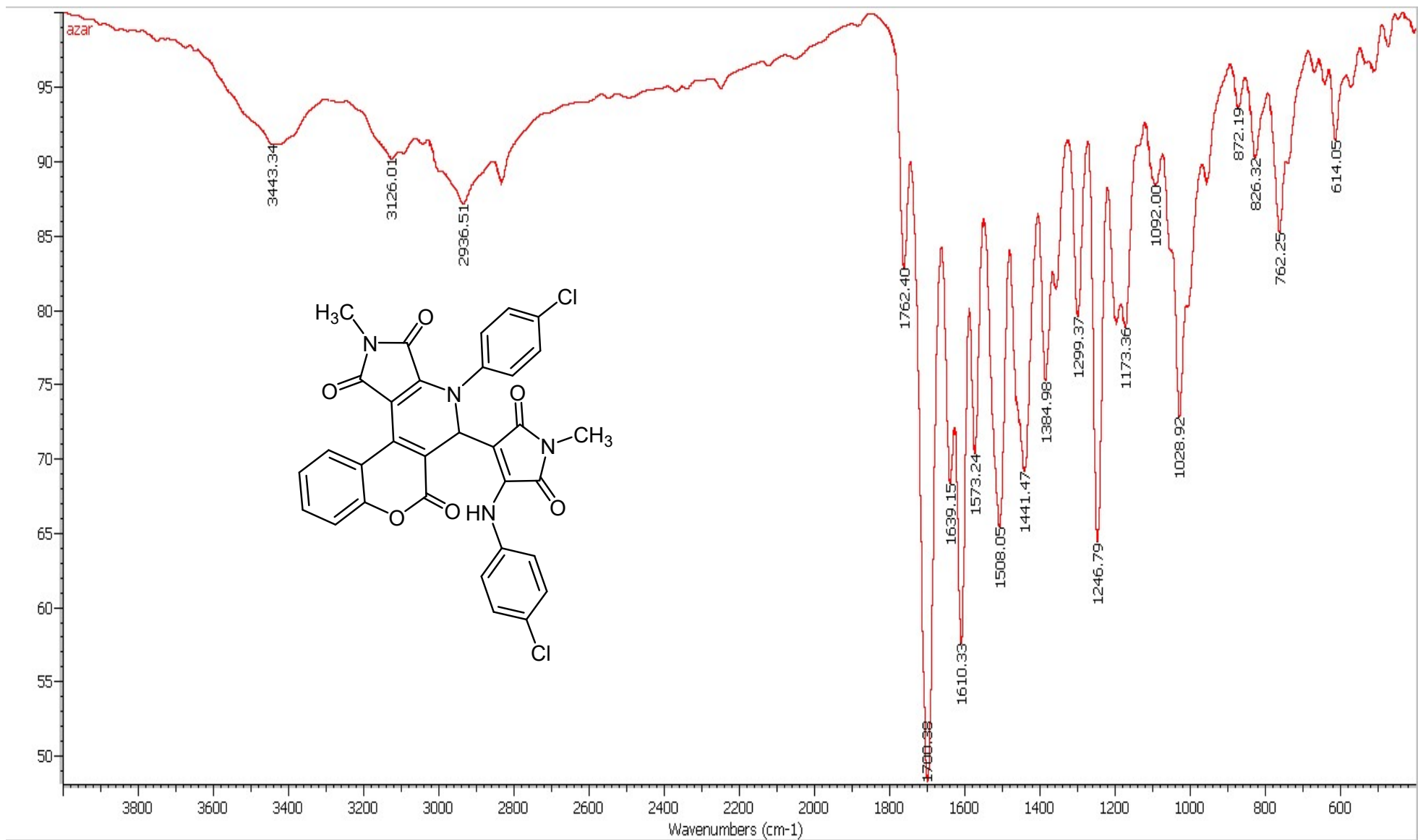


¹³C NMR Spectrum of 3'c

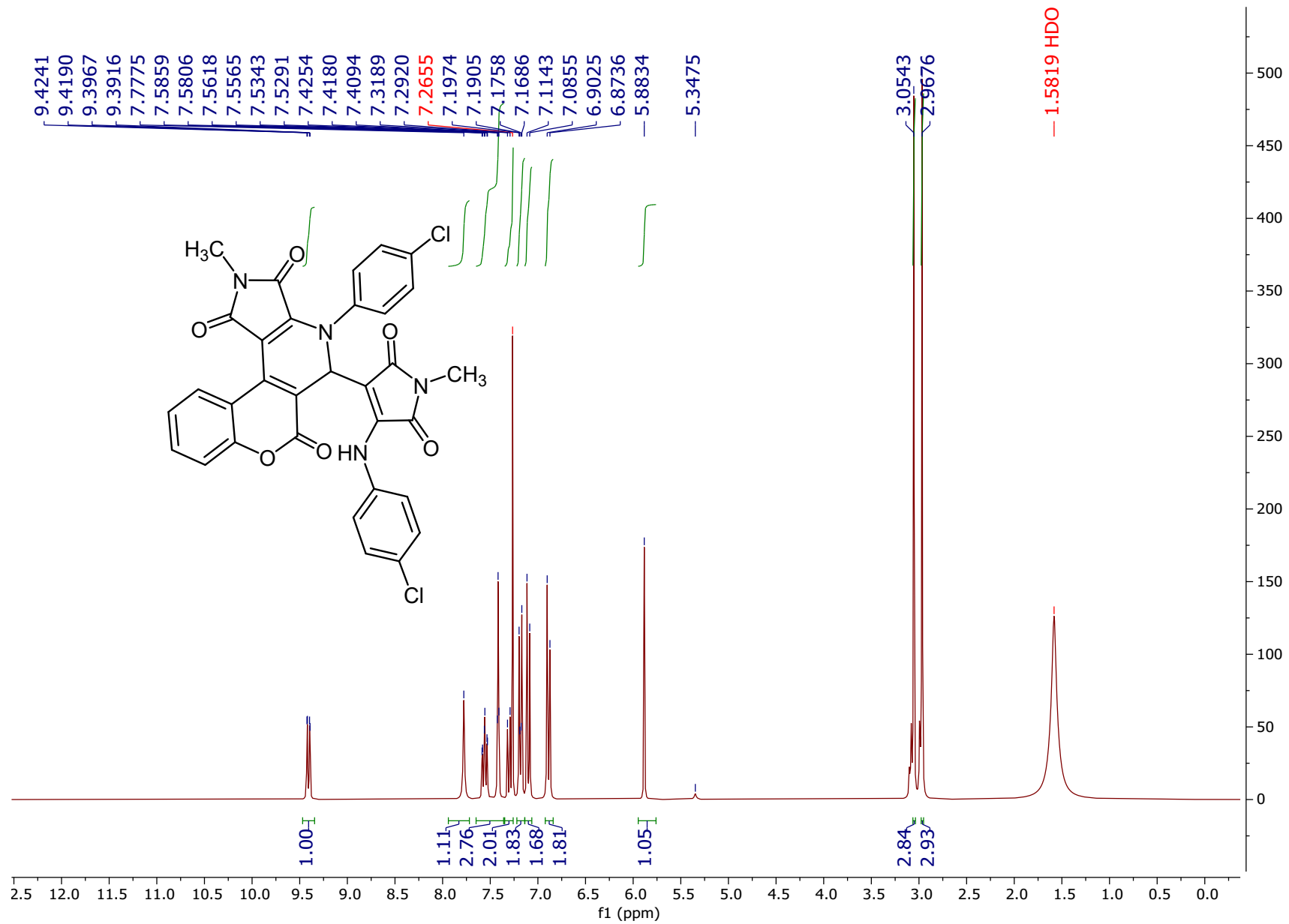


Mass spectrum of 3'c

S58

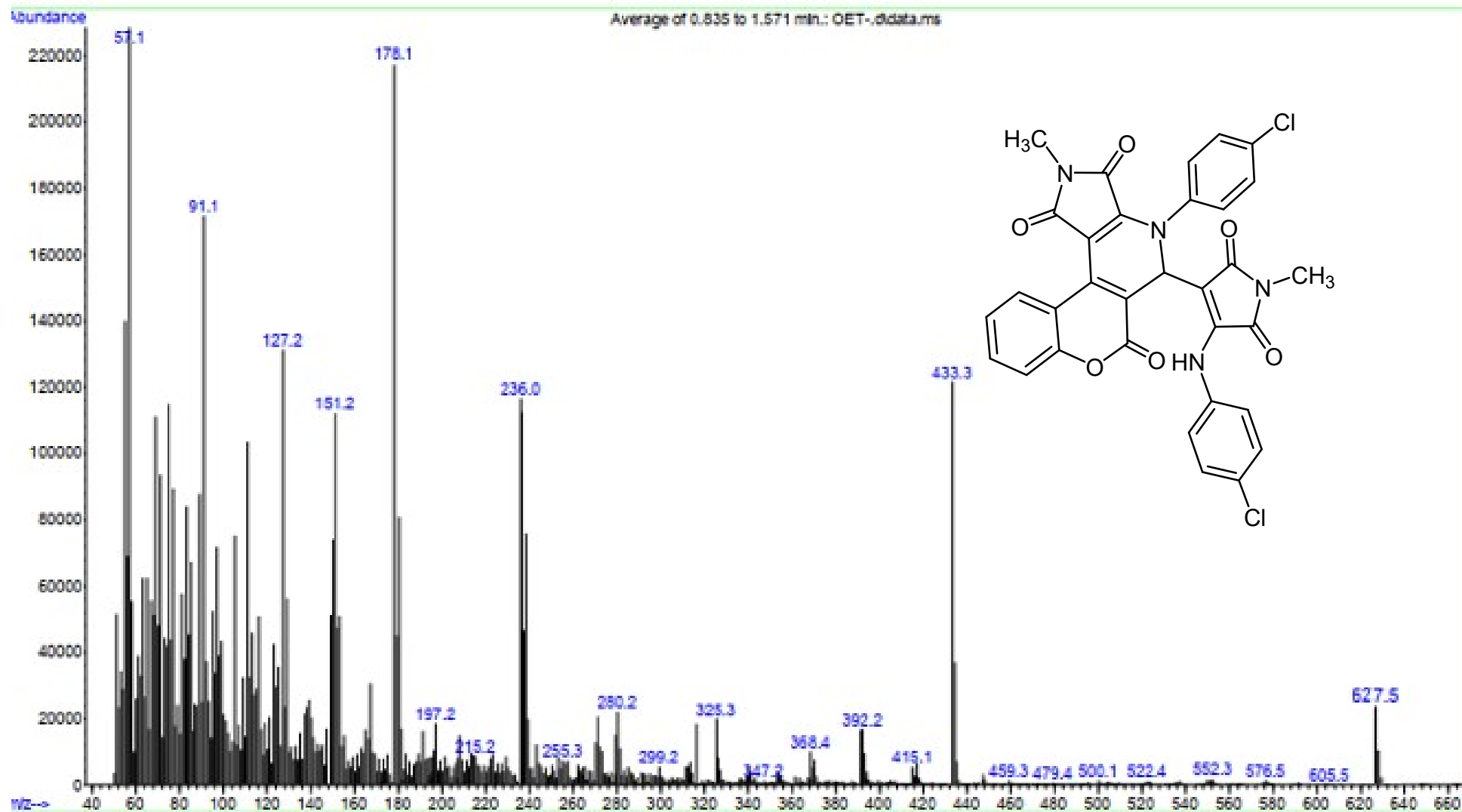


IR spectrum of 3'd



¹H NMR Spectrum of 3'd

S60



Mass Spectrum of 3'd