

Supporting Information

DMAP mediated one-pot domino thienannulation: A versatile, regioselective and green mechanochemical route to naphtho[2,3-*b*]thiophenes

Gaurav Shukla,^a Girijesh Kumar Verma,^a Anugula Nagaraju ^a Rajiv Kumar Verma,^b Keshav Raghuvanshi,^c and Maya Shankar Singh*^a

^a Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi-221005, India. E-mail: mssinghbhu@yahoo.co.in

^b Institute of Scientific and Industrial Research, Osaka university, Osaka-567-0047, Japan

^c Institut für Organische und Biomolekulare Chemie, Georg-August-Universität, Tammannstrasse 2, 37077 Göttingen, Germany

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1. Experimental Section

1.1. General

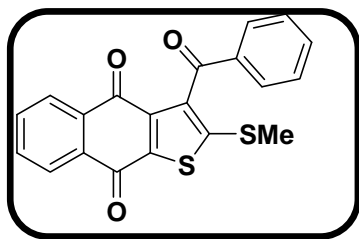
All reagents were commercial and purchased from Merck, Aldrich, and Fluka and were used as received. β -Oxodithioesters and β -Oxothioamides were prepared from literature procedure.¹ ^1H and ^{13}C NMR spectra were recorded on JEOL AL 300 FT-NMR spectrometer. Chemical shifts are given as δ value with reference to tetramethylsilane (TMS) as the internal standard, and coupling constants (J) are given in Hertz. The IR spectra were recorded on Varian 3100 FT-IR spectrophotometer. HRMS data were recorded on Waters-Q-ToF premier HAB 213 spectrometer from IIT Kanpur and Q-ToF micro (YA-105) spectrometer from IIT Bombay using electron spray ionization (ESI) technique. X-ray diffraction analysis was measured on X-calibur Oxford CCD Diffractometer. All the reactions were monitored by TLC using precoated sheets of silica gel G/UV-254 of 0.25 mm thickness (Merck 60F₂₅₄) using UV light for visualization. Melting points were determined with Büchi B-540 melting point apparatus and are uncorrected.

1.2. General procedure

In a mortar α -enolicdithioester/ β -oxothioamides **1** (1.0 mmol), 1,4-naphthoquinone **2** (0.158 g, 1.0 mmol) and DMAP (0.122 g, 1.0 mmol) was taken and to this 1-2 drops of ethanol was added to make paste. The pasty mixture was ground manually with a mortar and pestle for stipulated period of time (Table 2). After completion of the reaction (monitored by TLC), the whole reaction mixture was dissolved in dichloromethane (20 mL) and washed with water (3×15 mL). The organic layer was dried over anhydrous Na_2SO_4 and subsequently evaporated under reduced pressure. The residue thus obtained was purified by column chromatography on silica gel (100-200 mesh) using ethyl acetate-*n*-hexane mixture as eluent to afford the desired product **3**.

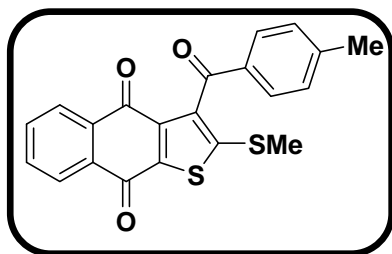
1.3. Experimental data of the naphtho[2,3-*b*]thiophene-4,9-dione derivatives:

3-Benzoyl-2-methylthio-naphtho[2,3-*b*]thiophene-4,9-dione (3a):



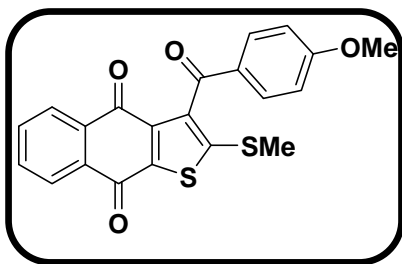
Red Solid, m.p. 224-226 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.19 (d, $J = 6.9$ Hz, 1H), 8.00 (d, $J = 7.2$ Hz, 1H), 7.85 (d, $J = 7.8$ Hz, 2H), 7.75-7.65 (m, 2H), 7.60-7.56 (m, 1H), 7.47-7.43 (m, 2H), 2.61 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 191.4, 178.2, 176.8, 150.3, 143.7, 141.4, 138.5, 136.4, 134.0, 133.9, 133.8, 133.0, 132.7, 129.2, 128.7, 127.4, 126.8, 20.0; **IR** (KBr, cm^{-1}): 2918, 1670, 1638, 1593, 1245, 720; **HRMS** [ESI, (M+H) $^+$]: $\text{C}_{20}\text{H}_{13}\text{O}_3\text{S}_2^+$, Calcd: 365.0306, Found: 365.0315.

3-(4-Methyl-benzoyl)-2-methylthio-naphtho[2,3-*b*] thiophene-4,9-dione (3b):



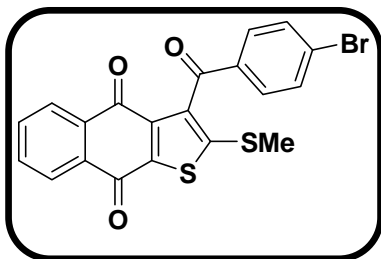
Orange Solid, m.p. 225-227 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.20 (d, $J = 6.9$ Hz, 1H), 8.02 (d, $J = 7.2$ Hz, 1H), 7.78-7.66 (m, 6H), 2.61 (s, 3H), 2.41 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 191.0, 178.3, 176.9, 150.0, 145.0, 143.7, 141.4, 138.8, 133.9, 133.0, 132.7, 129.5, 129.4, 127.4, 126.8, 21.8, 20.0; **IR** (KBr, cm^{-1}): 2925, 1678, 1643, 1590, 1253, 726.

3-(4-Methoxy-benzoyl)-2-methylthio-naphtho[2,3-*b*] thiophene-4,9-dione (3c):



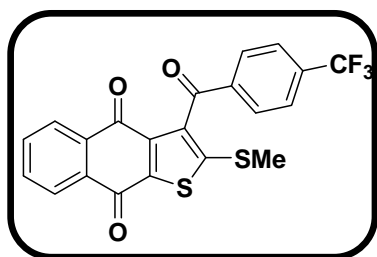
Red Solid, m.p. 220-222 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.20 (d, $J = 6.9$ Hz, 1H), 8.03 (d, $J = 8.4$ Hz, 1H), 7.84 (d, $J = 8.7$ Hz, 2H), 7.72 (d, $J = 7.2$ Hz, 2H), 6.94 (d, $J = 8.7$ Hz, 2H), 3.86 (s, 3H), 2.61 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 189.9, 178.3, 176.8, 164.2, 149.7, 143.7, 141.2, 138.9, 135.0, 133.9, 133.8, 133.7, 133.0, 132.7, 131.7, 129.4, 128.3, 127.4, 126.8, 55.4, 19.9; **IR** (KBr, cm^{-1}): 2928, 1675, 1643, 1591, 1255, 722; **HRMS** [ESI, (M+H) $^+$]: $\text{C}_{21}\text{H}_{15}\text{O}_4\text{S}_2^+$, Calcd: 395.0411, Found: 395.0429.

3-(4-Bromo-benzoyl)-2-methylthio-naphtho[2,3-*b*] thiophene-4,9-dione (3d):



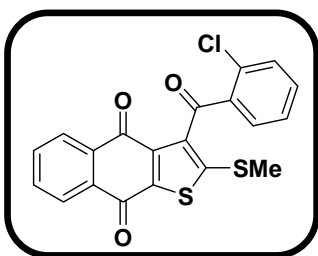
Orange Solid, m.p. 235-237 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.20 (d, $J = 6.9$ Hz, 1H), 8.02 (d, $J = 7.2$ Hz, 1H), 7.75-7.70 (m, 4H), 7.60 (d, $J = 8.4$ Hz, 2H), 2.63 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 190.4, 178.3, 176.8, 150.9, 141.4, 135.4, 134.0, 133.0, 132.7, 132.1, 130.6, 129.2, 127.5, 126.9, 20.0; **IR** (KBr, cm^{-1}): 2915, 1674, 1632, 1580, 1270, 710; **HRMS** [ESI, (M + H) $^+$]: $\text{C}_{20}\text{H}_{12}\text{BrO}_3\text{S}_2^+$, Calcd: 442.9411, Found: 442.9524.

2-Methylthio-3-(4-trifluoromethyl-benzoyl)-naphtho[2,3-b] thiophene-4,9-dione (3e):



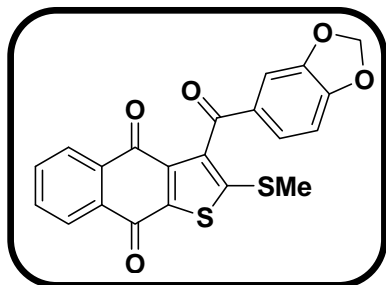
Red Solid, m.p. 240-242 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.16 (d, $J = 7.2$ Hz, 1H), 7.90-7.83 (m, 2H), 7.73-7.65 (m, 2H), 7.58 (d, $J = 8.1$ Hz, 1H), 7.51-7.46 (m, 1H), 7.39 (d, $J = 7.5$ Hz, 1H), 2.71 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 189.5, 178.0, 176.9, 142.5, 141.4, 138.4, 137.3, 135.0, 134.5, 134.4, 134.3, 133.9, 133.7, 130.2, 129.2, 128.4, 127.5, 127.3, 126.8, 126.5, 19.3; **IR** (KBr, cm^{-1}): 2925, 1667, 1655, 1592, 1269, 711.

3-(2-Chloro-benzoyl)-2-methylthio-naphtho[2,3-b] thiophene-4,9-dione (3f):



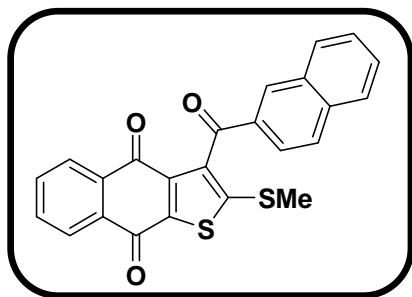
Red Solid, m.p. 210-212 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.18 (d, $J = 7.8$ Hz, 1H), 7.97 (d, $J = 7.2$ Hz, 1H), 7.69 (s, 3H), 7.41-7.34 (m, 3H), 2.68 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 189.3, 178.1, 176.8, 155.6, 142.8, 141.3, 136.99, 136.95, 134.3, 133.7, 132.94, 132.90, 132.7, 131.3, 130.8, 129.9, 129.5, 127.1, 126.6, 19.4; **IR** (KBr, cm^{-1}): 2925, 1668, 1643, 1588, 1265, 723. **HRMS** [ESI, (M+H) $^+$]: $\text{C}_{20}\text{H}_{12}\text{ClO}_3\text{S}_2^+$, Calcd.: 398.9911, Found: 398.9911.

3-(Benzo[1,3]dioxole-5-carbonyl)-2-methylthio-naphtho[2,3-b] thiophene-4,9-dione (3g):



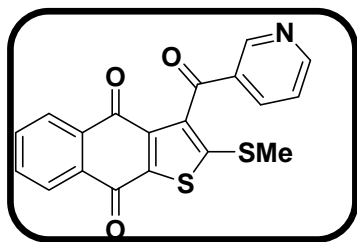
Red Solid, m.p. 218-220 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.19 (s, 1H), 8.03 (s, 1H), 7.81-7.73 (m, 2H), 7.32-7.23 (m, 2H), 6.81 (d, $J = 8.1$ Hz, 1H), 6.06 (s, 2H), 2.62 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 189.4, 178.3, 176.8, 152.6, 149.7, 148.5, 143.8, 141.3, 138.8, 133.99, 133.93, 133.0, 132.7, 131.4, 127.4, 126.8, 126.6, 108.3, 108.1, 102.0, 20.0; **IR** (KBr, cm^{-1}): 2950, 1640, 1620, 1560, 1235, 720.

2-Methylthio-3-(naphthalene-2-carbonyl)-naphtho[2,3-b] thiophene-4,9-dione (3h):



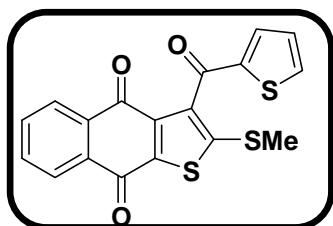
Red Solid, m.p. 208-210 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.22 (s, 2H), 8.07 (d, $J = 8.7$ Hz, 1H), 7.99-7.87 (m, 4H), 7.76-7.57 (m, 3H), 7.53-7.48 (m, 1H), 2.63 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 191.4, 178.3, 176.7, 150.3, 136.0, 134.0, 133.1, 132.8, 132.5, 131.6, 129.6, 128.8, 128.5, 127.8, 127.6, 127.4, 126.8, 124.1, 20.0; **IR** (KBr, cm^{-1}): 2952, 1668, 1639, 1592, 1267, 720; **HRMS** [ESI, (M+H) $^+$]: $\text{C}_{24}\text{H}_{15}\text{O}_3\text{S}_2^+$, Calcd.: 415.0462, Found: 415.0467.

2-Methylthio-3-(pyridine-3-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3i):



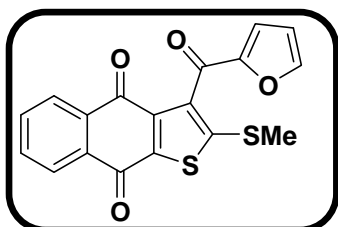
Red Solid, m.p. 222-224 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.90 (s, 1H), 8.78 (d, $J = 4.5$ Hz, 1H), 8.26-8.19 (m, 2H), 7.98 (d, $J = 7.2$ Hz, 1H), 7.77-7.70 (m, 2H), 7.48-7.44 (m, 1H), 2.66 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 190.0, 178.4, 176.7, 153.7, 152.2, 150.6, 143.8, 141.4, 136.5, 136.1, 134.1, 132.9, 132.6, 132.3, 127.4, 126.9, 123.8, 19.9; **IR** (KBr, cm^{-1}): 3745, 2924, 1670, 1640, 1582, 1267, 697. **HRMS** [ESI, (M+H) $^+$]: $\text{C}_{19}\text{H}_{12}\text{NO}_3\text{S}_2^+$, Calcd.: 366.0253, Found: 366.0256.

2-Methylthio-3-(thiophene-2-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3j):



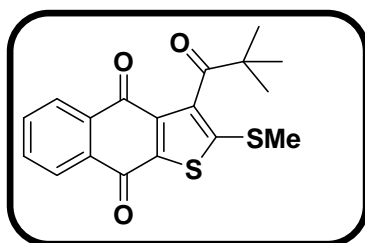
Red Solid, m.p. 205-207 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.22-8.19 (m, 1H), 8.07 (d, $J = 6.9$ Hz, 1H), 7.75-7.71 (m, 3H), 7.48 (d, $J = 3.0$ Hz, 1H), 7.12-7.09 (m, 1H), 2.64 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 183.1, 178.2, 176.8, 150.5, 143.8, 143.6, 141.1, 138.1, 135.4, 134.5, 134.0, 133.9, 132.9, 132.8, 128.3, 127.5, 126.8, 20.0; **IR** (KBr, cm^{-1}): 2923, 1674, 1642, 1590, 1269, 712; **HRMS** [ESI, (M+H) $^+$]: $\text{C}_{18}\text{H}_{11}\text{O}_3\text{S}_3^+$, Calcd.: 370.9870, Found: 370.9875.

3-(Furan-2-carbonyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3k):



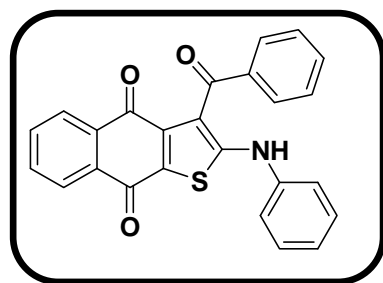
Red Solid, m.p. 215-217 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.21 (d, $J = 7.5$ Hz, 1H), 8.07 (d, $J = 6.6$ Hz, 1H), 7.73 (s, 3H), 7.56 (s, 2H), 2.65 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 192.5, 178.4, 178.1, 147.1, 134.2, 134.0, 133.8, 132.9, 127.4, 126.9, 126.8, 126.3, 119.3, 112.8, 19.8; **IR** (KBr, cm^{-1}): 2920, 1670, 1648, 1594, 1270, 710.

3-(2,2-Dimethyl-propionyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3l):



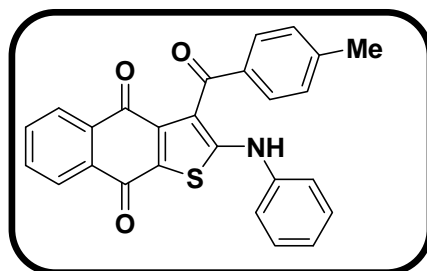
Red viscous liquid, $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.11 (d, $J = 7.5$ Hz, 2H), 7.74 (d, $J = 5.4$ Hz, 2H), 2.63 (s, 3H), 1.34 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 191.4, 178.3, 176.8, 158.9, 143.6, 134.46, 134.45, 133.0, 132.7, 132.1, 130.6, 128.3, 127.5, 126.9, 43.6, 26.6, 18.0; **IR** (KBr, cm^{-1}): 2962, 1650, 1647, 1598, 1258, 714.

3-Benzoyl-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3m):



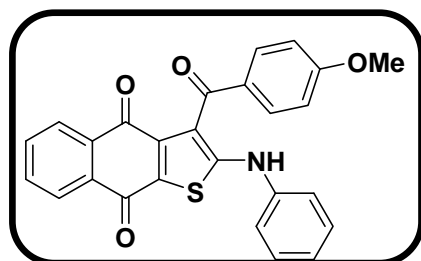
Red solid, m.p. 218-220 °C; $^1\text{H NMR}$ (300 MHz, DMSO): δ 9.82 (s, 1H), 8.03 (d, $J = 7.2$ Hz, 1H), 7.89-7.72 (m, 5H), 7.64-7.59 (m, 1H), 7.51-7.39 (m, 6H), 7.19-7.13 (m, 1H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 193.1, 179.0, 177.4, 163.5, 141.9, 140.2, 139.0, 133.6, 133.3, 133.2, 132.8, 132.1, 129.9, 129.2, 128.3, 128.2, 127.1, 125.9, 125.6, 120.5, 114.7; **IR** (KBr, cm^{-1}): 2926, 1648, 1630, 1590, 1247, 712; **HRMS** [ESI, (M+H) $^+$]: $\text{C}_{25}\text{H}_{16}\text{NO}_3\text{S}^+$, Calcd.: 410.0851, Found: 410.0859.

3-(4-Methyl-benzoyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3n):



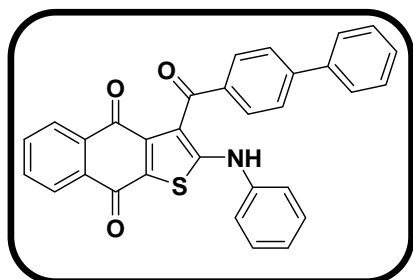
Red solid, m.p. 216-218 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 10.18 (s, 1H), 8.13 (d, $J=7.5$ Hz, 1H), 7.84 (d, $J=7.5$ Hz, 1H), 7.71-7.59 (m, 3H), 7.48-7.38 (m, 4H), 7.29-7.19 (m, 4H), 2.41 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 192.7, 179.0, 177.3, 163.0, 143.0, 141.8, 139.0, 137.3, 133.5, 133.3, 133.2, 132.8, 129.8, 129.2, 128.9, 128.6, 127.1, 125.9, 125.4, 120.3, 115.1, 21.6; **IR** (KBr, cm^{-1}): 2925, 1664, 1642, 1595, 1237, 717.

3-(4-Methoxy-benzoyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3o):



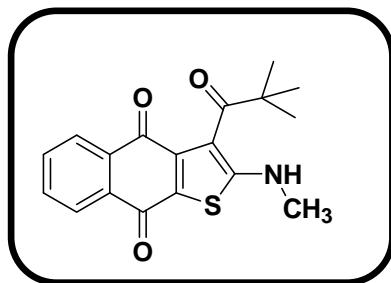
Red solid, m.p. 230-232 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 9.98 (s, 1H), 8.15-8.12 (m, 1H), 7.87-7.77 (m, 1H), 7.75-7.60 (m, 4H), 7.46-7.37 (m, 5H), 6.89 (d, $J=8.7$ Hz, 2H), 3.86 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 199.1, 179.2, 177.1, 150.8, 139.2, 139.1, 133.5, 133.4, 133.2, 133.0, 132.8, 130.9, 129.8, 129.5, 129.1, 129.0, 128.9, 128.5, 128.0, 127.6, 127.2, 127.1, 55.6; **IR** (KBr, cm^{-1}): 2925, 1662, 1639, 1598, 1247, 719. **HRMS** [ESI, (M+H) $^+$]: $\text{C}_{26}\text{H}_{18}\text{NO}_4\text{S}^+$, Calcd.: 440.0951, Found: 440.0952.

3-(Biphenyl-4-carbonyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3p):



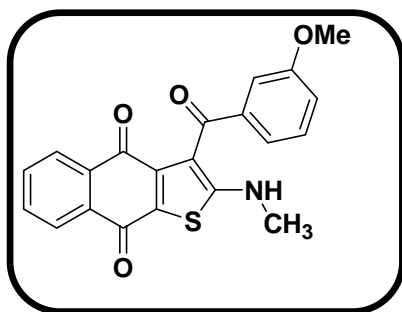
Orange solid, m.p. 212-214 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 10.27 (s, 1H), 8.14 (d, $J=7.2$ Hz, 1H), 7.83 (d, $J=8.4$ Hz, 3H), 7.71-7.58 (m, 7H), 7.48-7.38 (m, 7H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 192.5, 179.1, 177.3, 163.3, 144.7, 141.9, 139.9, 139.1, 138.9, 133.6, 133.4, 133.2, 132.9, 129.9, 129.2, 129.0, 128.8, 128.0, 127.2, 126.8, 125.9, 125.6, 120.4, 114.9; **IR** (KBr, cm^{-1}): 2925, 1665, 1642, 1595, 1260, 709; **HRMS** [ESI, (M+H) $^+$]: $\text{C}_{31}\text{H}_{20}\text{NO}_3\text{S}^+$, Calcd.: 486.1164, Found: 486.1165.

3-(2,2-Dimethyl-propionyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3q):



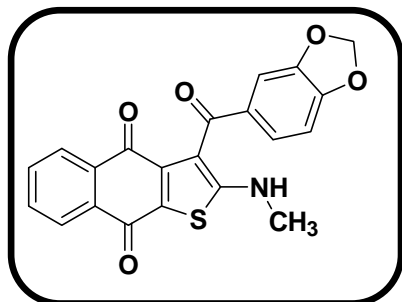
Red solid, m.p. 206-208 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.16-8.07 (m, 2H), 7.73-7.66 (m, 2H), 5.40 (s, 1H), 3.03 (s, 3H), 1.31 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 211.3, 180.4, 176.1, 163.5, 142.2, 133.8, 133.6, 132.7, 127.2, 126.8, 126.0, 115.2, 46.2, 34.0, 27.4; **IR** (KBr, cm^{-1}): 2962, 1650, 1647, 1598, 1258, 714. **HRMS** [ESI, (M+H) $^+$]: $\text{C}_{18}\text{H}_{18}\text{NO}_3\text{S}^+$, Calcd.: 328.1002, Found: 328.1007.

3-(3-Methoxy-benzoyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3r):



Red Solid, m.p. 220-222 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.48 (s, 1H), 8.12 (d, $J = 7.2$ Hz, 2H), 7.78 (d, $J = 7.2$ Hz, 2H), 7.66-7.58 (m, 2H), 7.02 (d, $J = 7.2$ Hz, 2H), 3.81 (s, 3H), 3.17 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 192.5, 179.4, 177.0, 170.8, 159.5, 133.7, 133.3, 133.1, 132.9, 129.4, 128.9, 127.0, 125.8, 122.5, 121.1, 120.2, 118.2, 114.3, 112.6, 55.4, 33.9; **IR** (KBr, cm^{-1}): 2928, 1670, 1643, 1596, 1255, 720.

3-(Benzo[1,3]dioxole-5-carbonyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3s) :



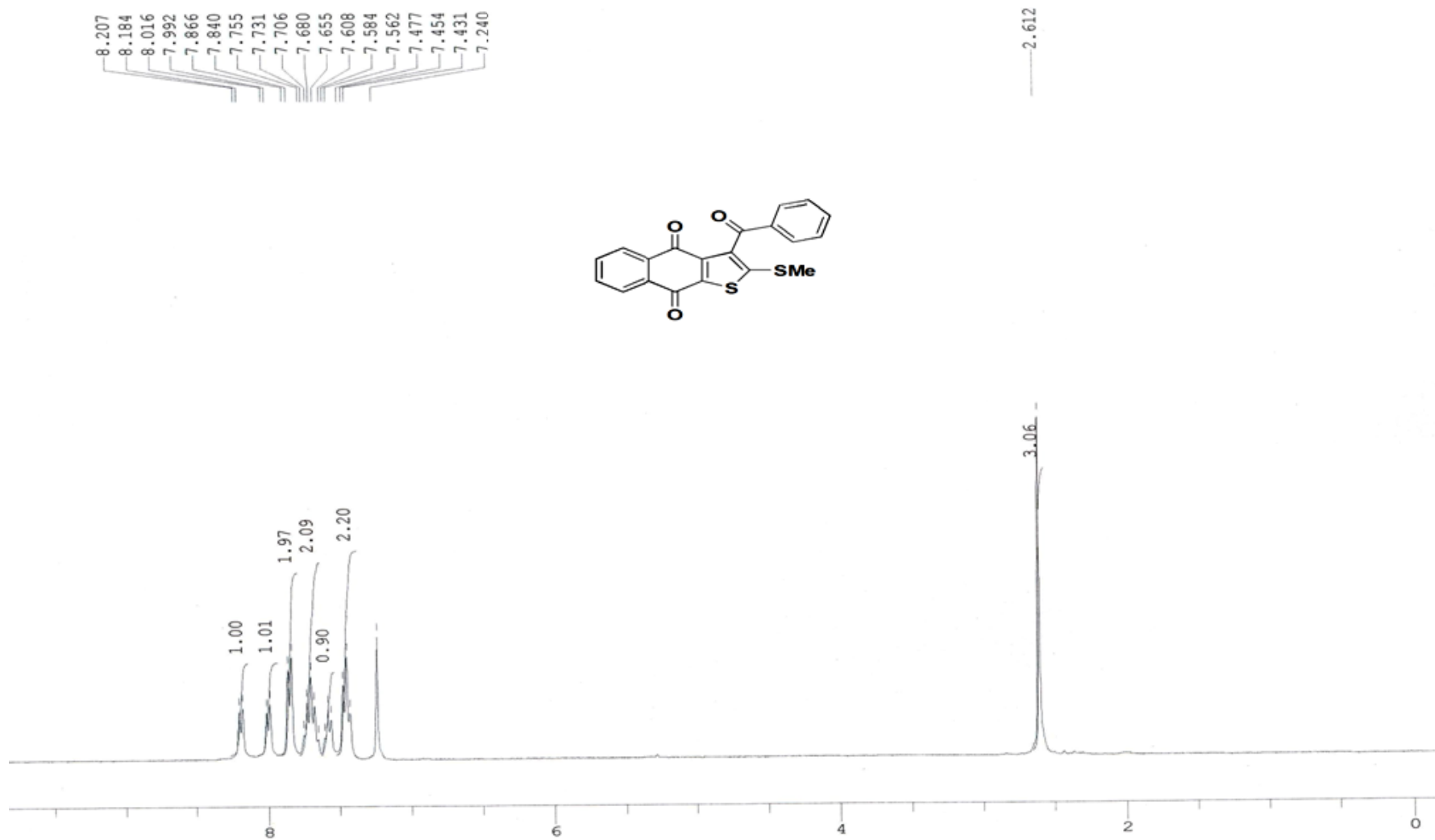
Red solid, m.p. 232-234 °C; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.12 (d, $J = 7.5$ Hz, 2H), 7.84 (d, $J = 7.5$ Hz, 1H), 7.67-7.60 (m, 2H), 7.17 (d, $J = 8.4$ Hz, 1H), 6.71 (d, $J = 8.1$ Hz, 1H), 6.03 (s, 2H), 5.15 (s, 1H), 3.15 (s, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): 191.1, 179.6, 177.0, 170.3, 150.9, 147.9, 143.0, 135.1, 133.7, 133.4, 133.1, 133.0, 128.4, 127.1, 125.9, 124.5, 111.8, 108.4, 107.5, 101.7, 33.9; **IR** (KBr, cm^{-1}): 2927, 1658, 1636, 1594, 1255, 711.

2. References

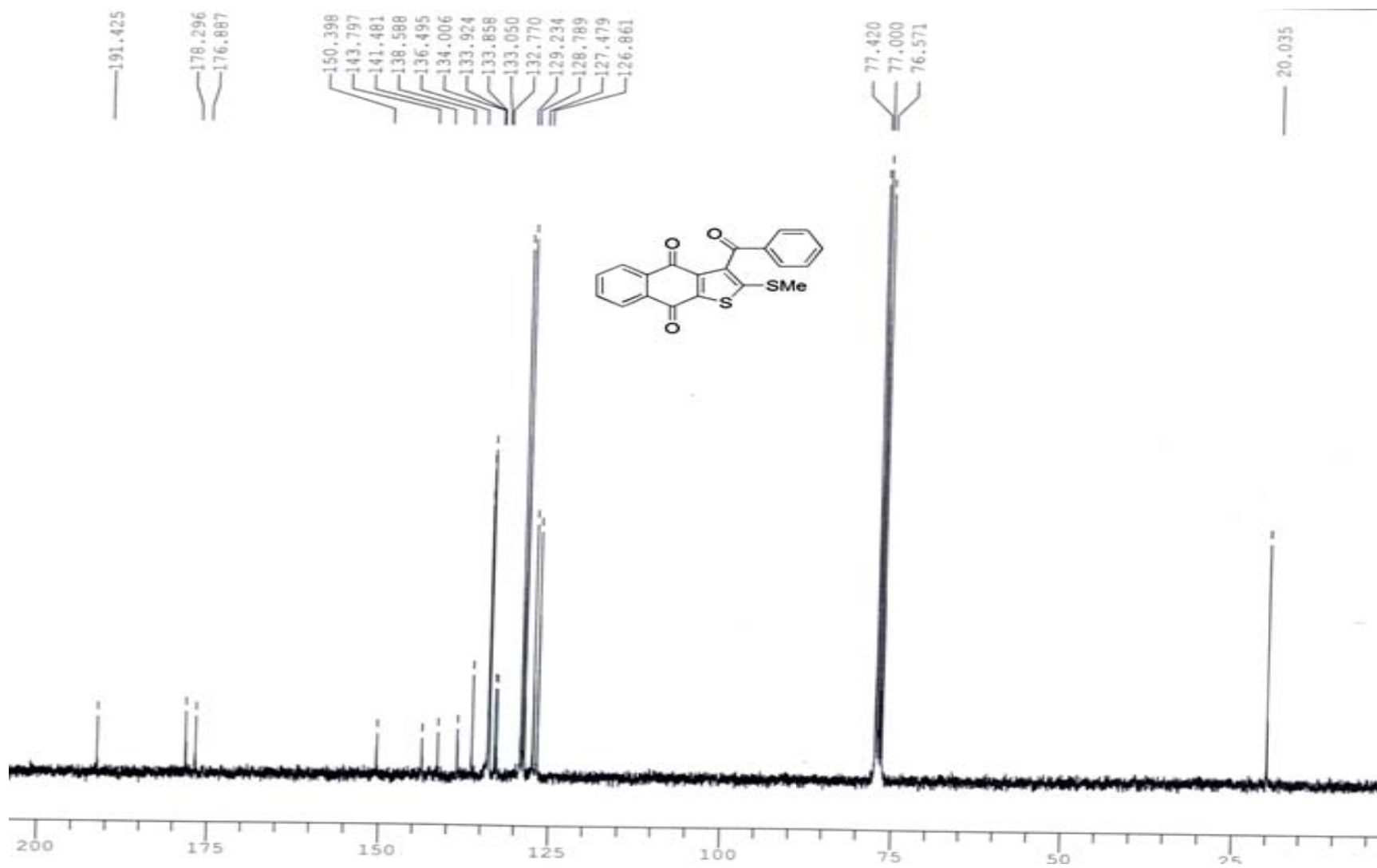
1. (a) R. Samuel, C. V. Asoken, S. Suma, P. Chandran, S. Retnamma and E. R. Anabha, *Tetrahedron Lett.*, 2007, **48**, 8376; (b) G. C. Nandi, M. S. Singh, H. Ila and H. Junjappa, *Eur. J. Org. Chem.*, 2012, 967.

3. ^1H and ^{13}C NMR spectra of Compounds

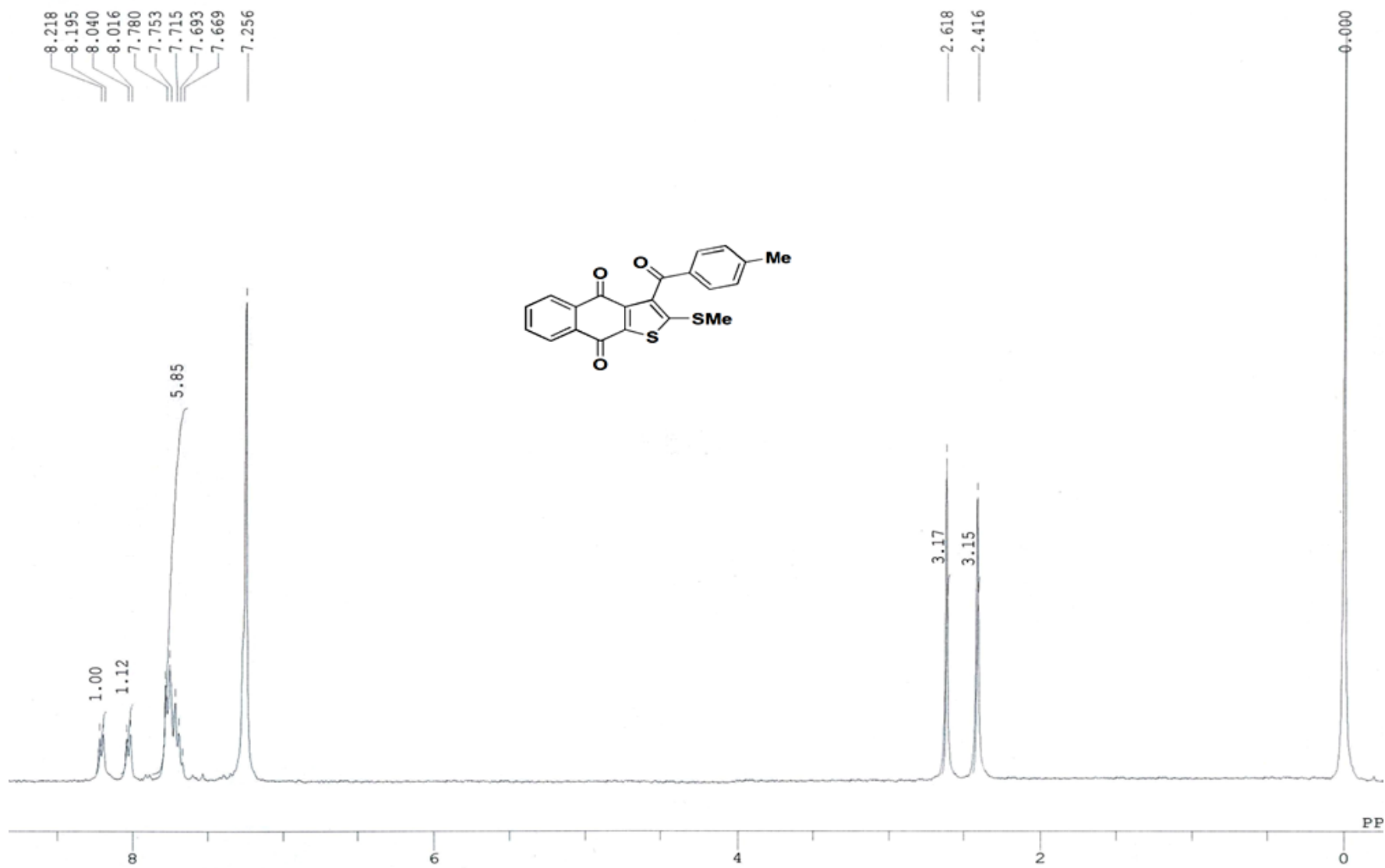
^1H NMR of 3-Benzoyl-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3a)



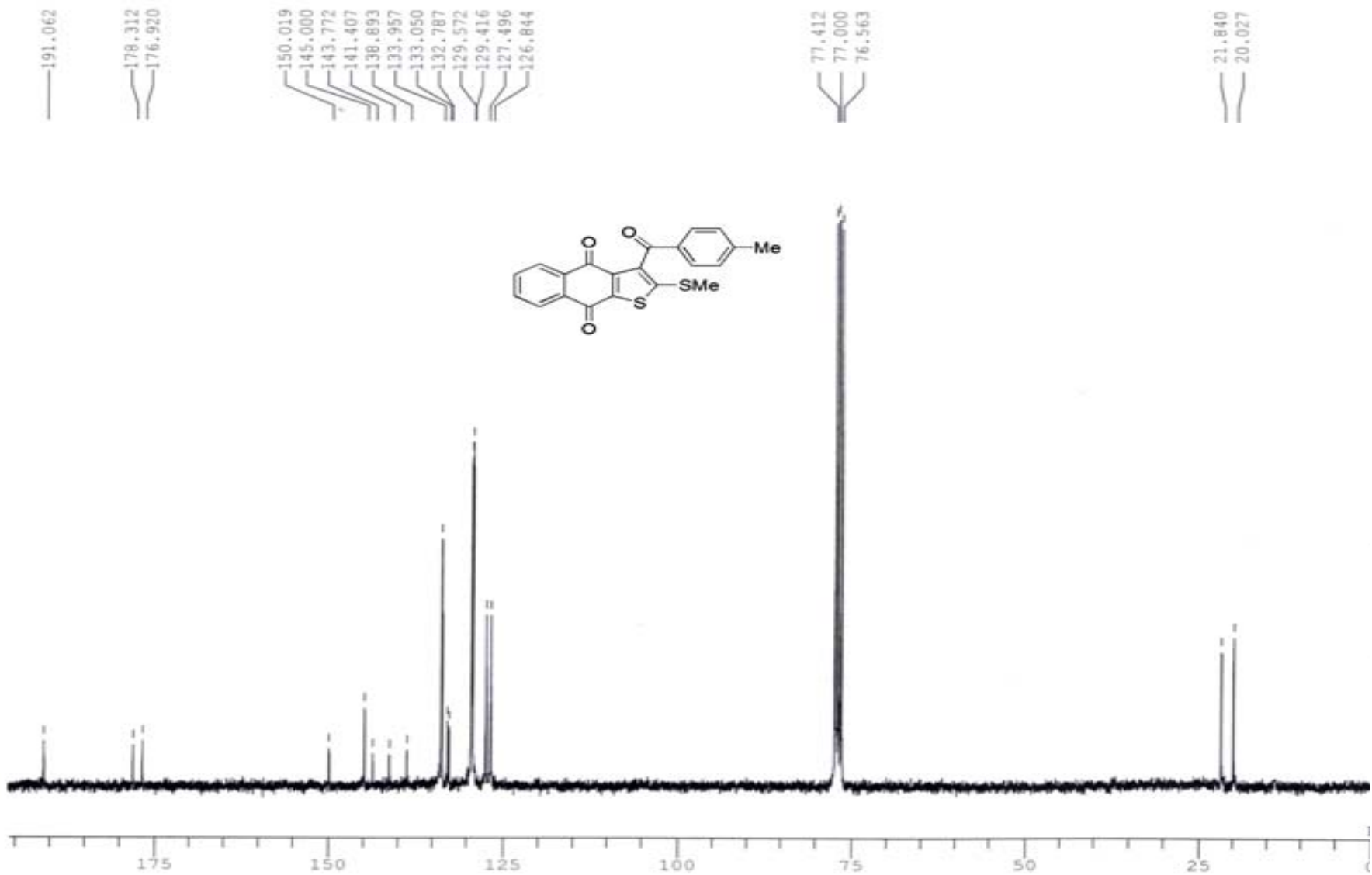
^{13}C NMR of 3-Benzoyl-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3a)



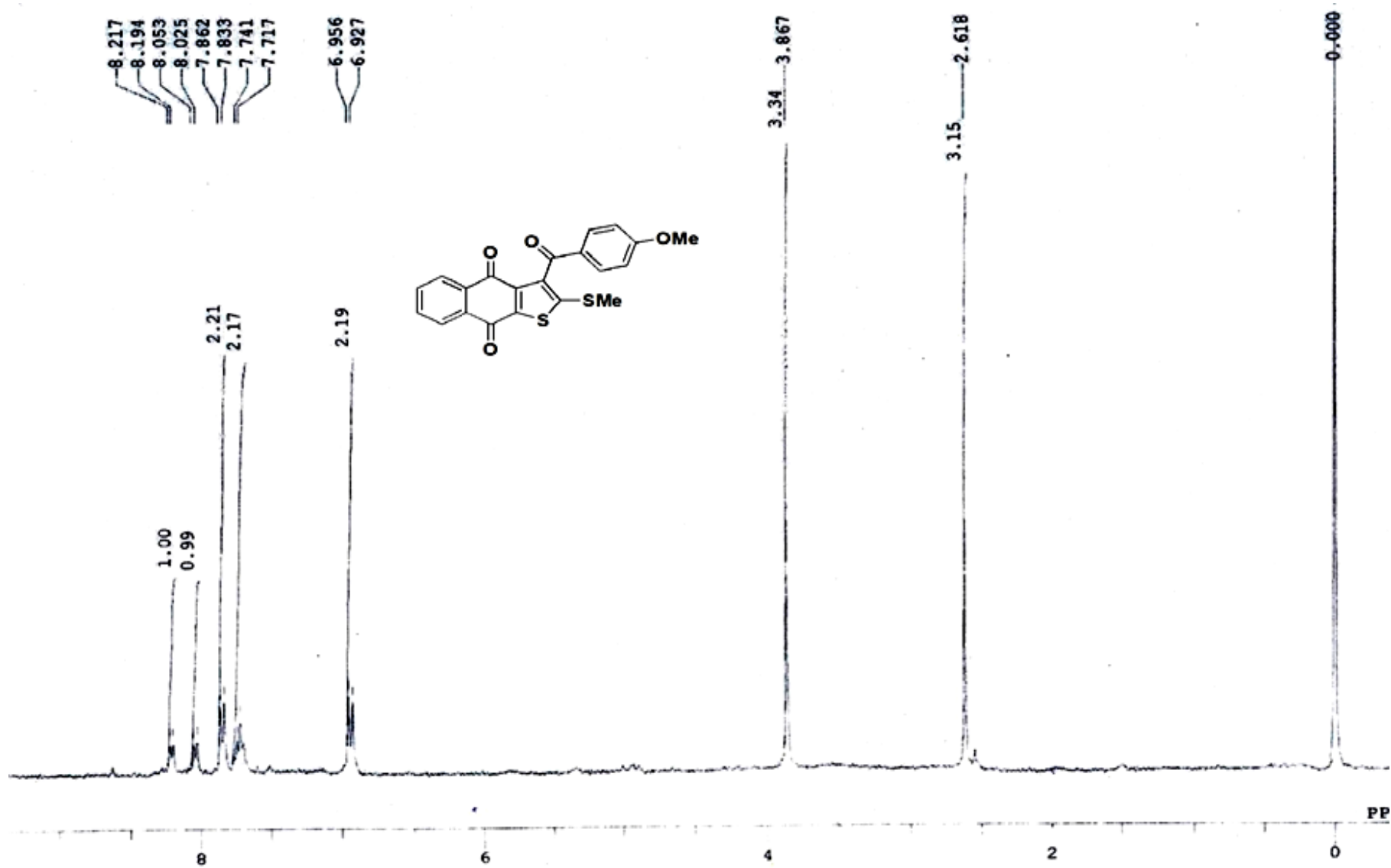
¹H NMR of 3-(4-Methylbenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3b)



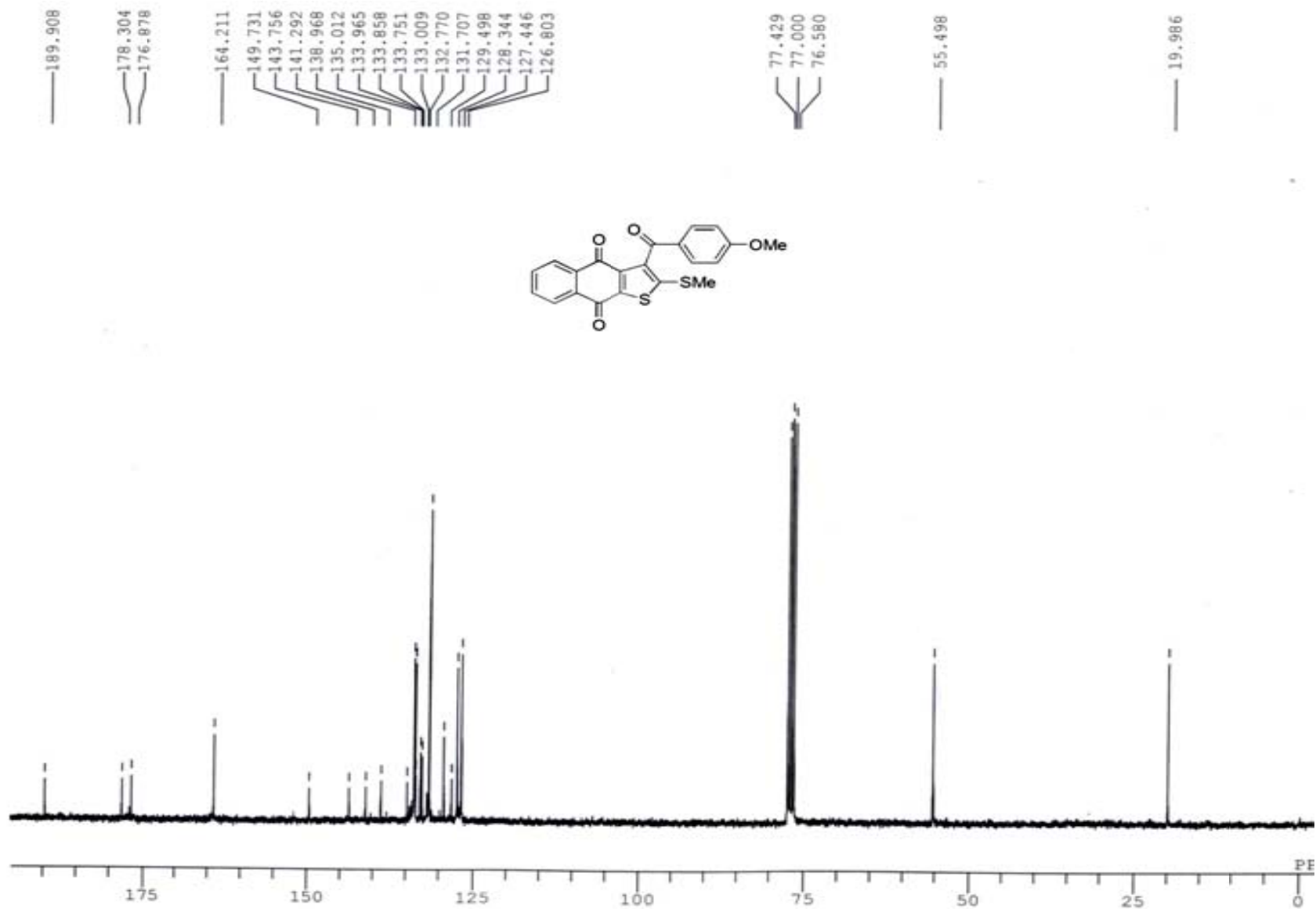
^{13}C NMR of 3-(4-Methylbenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3b)



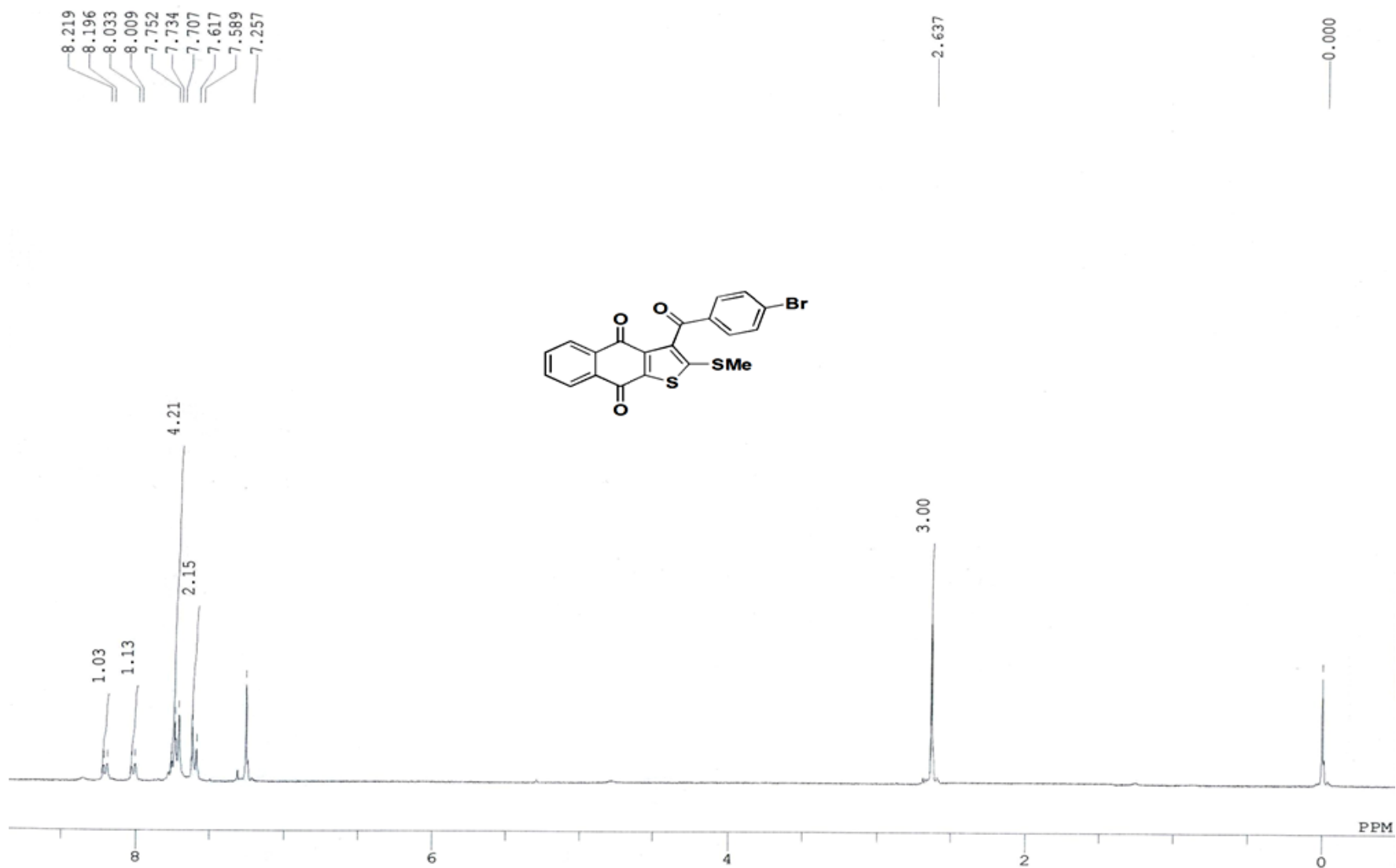
¹H NMR of 3-(4-Methoxybenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3c)



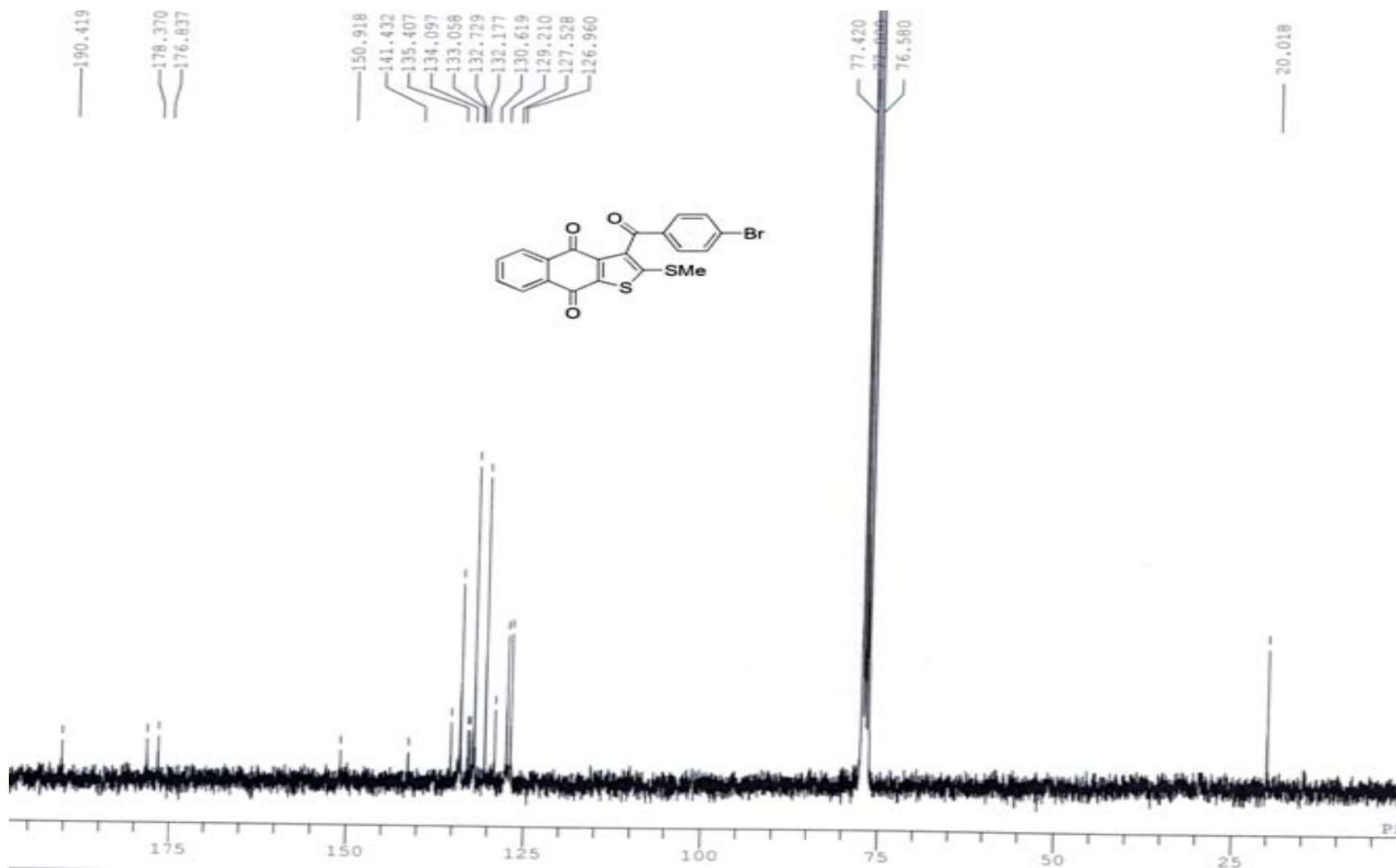
^{13}C NMR of 3-(4-Methoxybenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3c)



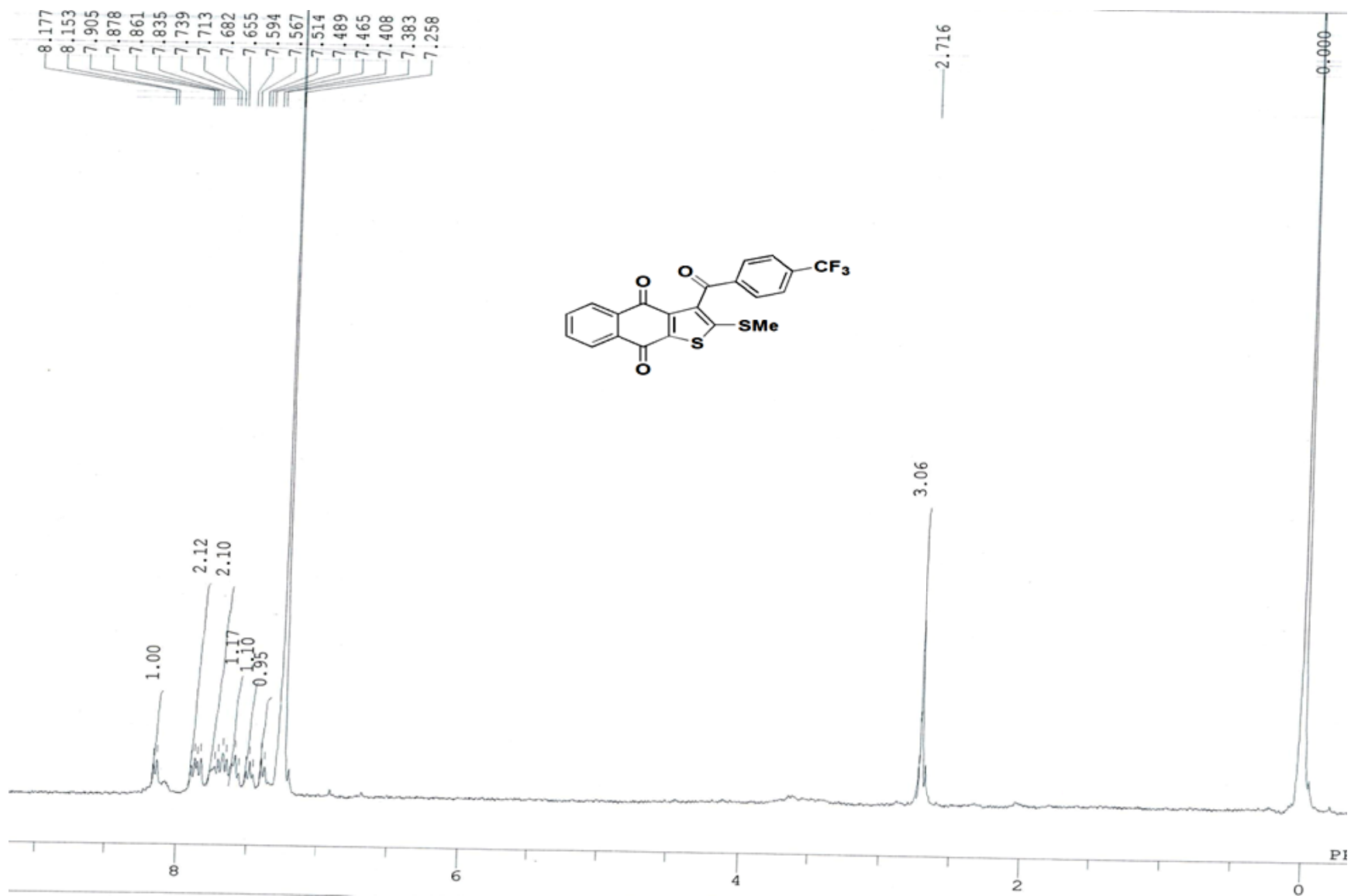
¹H NMR of 3-(4-Bromobenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3d)



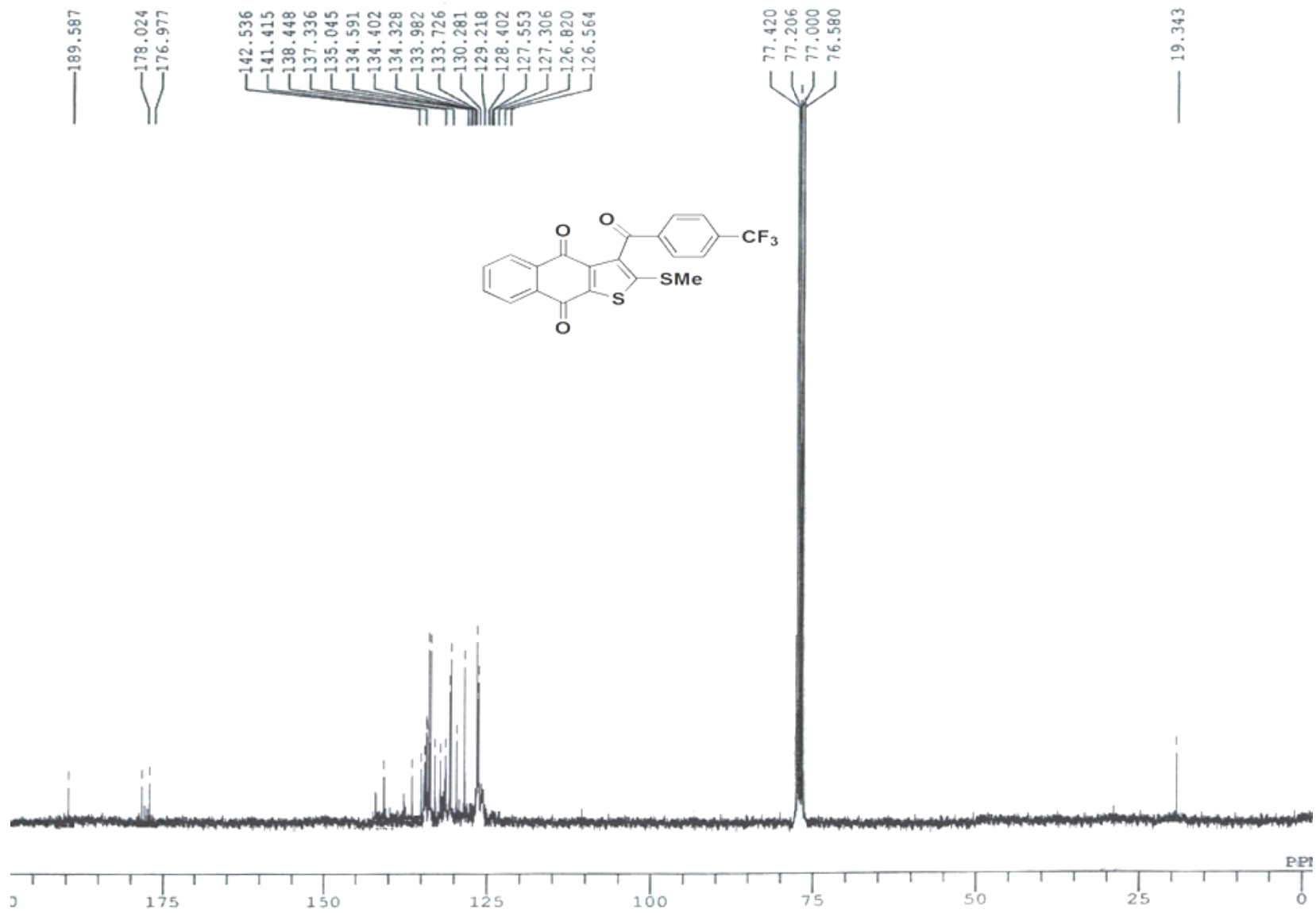
^{13}C NMR of 3-(4-Bromobenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3d)



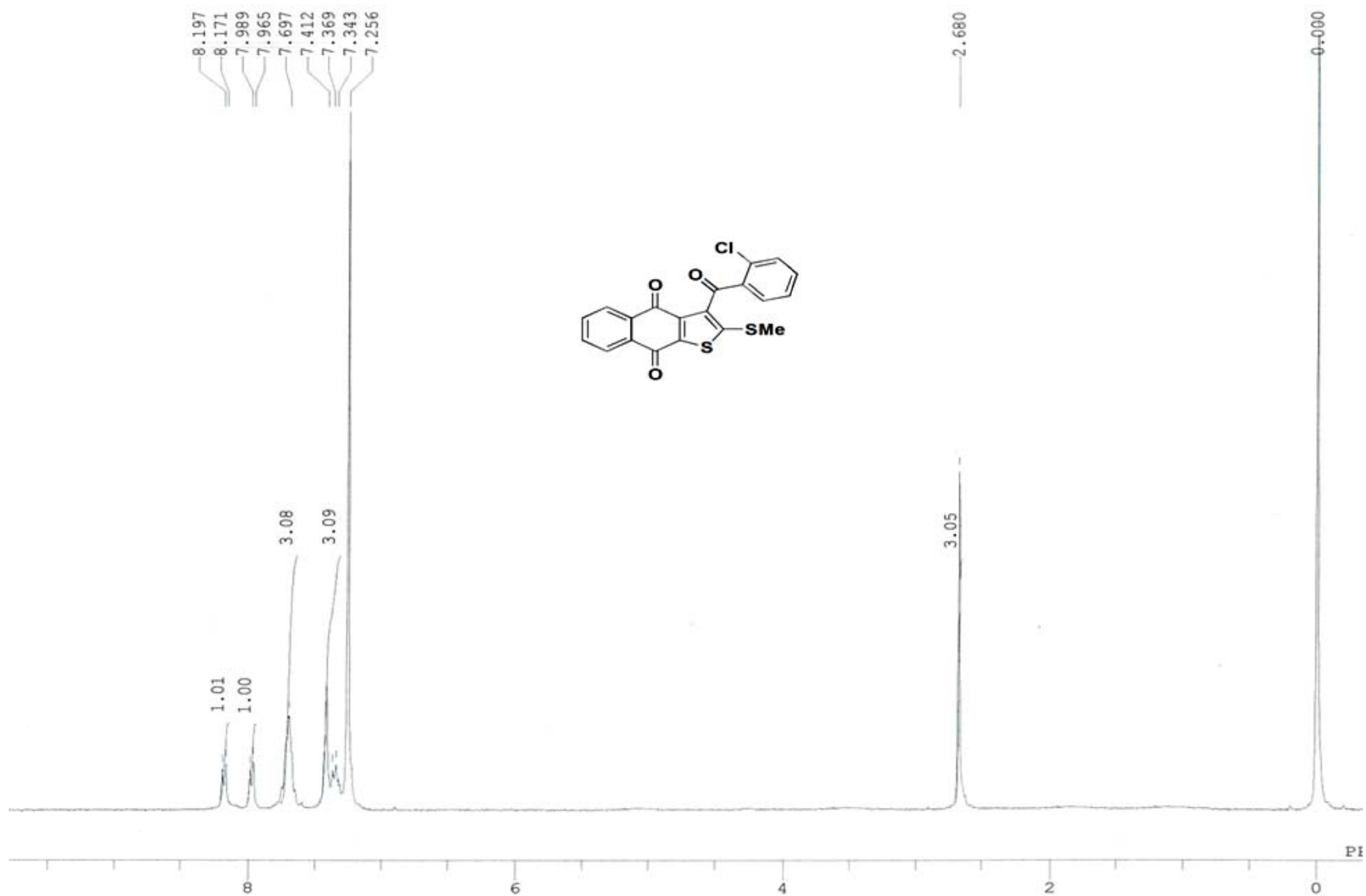
¹H NMR of 2-Methylthio-3-(4-trifluoromethylbenzoyl)-naphtho[2,3-b]thiophene-4,9-dione (3e)



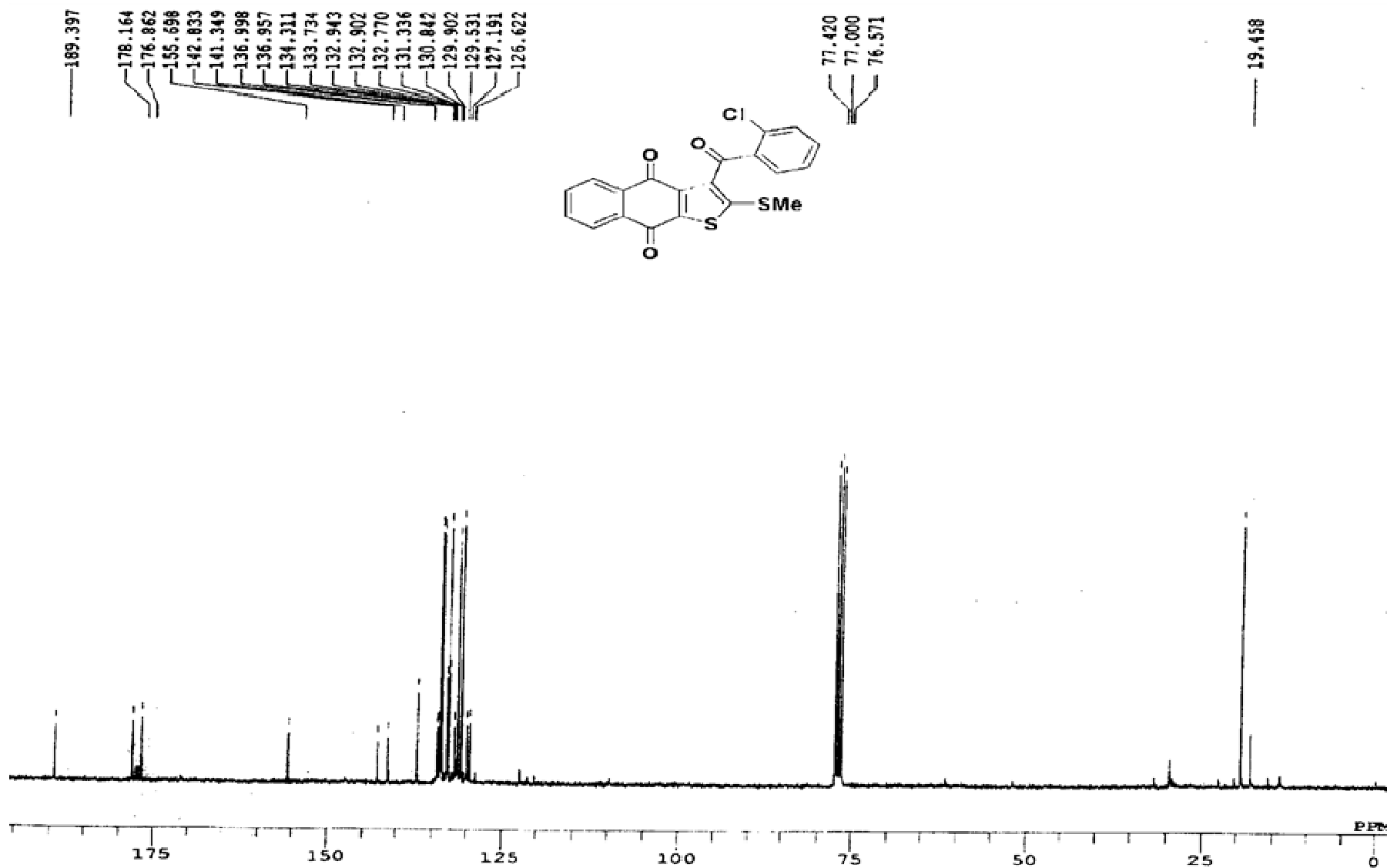
^{13}C NMR of 2-Methylthio-3-(4-trifluoromethylbenzoyl)-naphtho[2,3-b]thiophene-4,9-dione (3e)



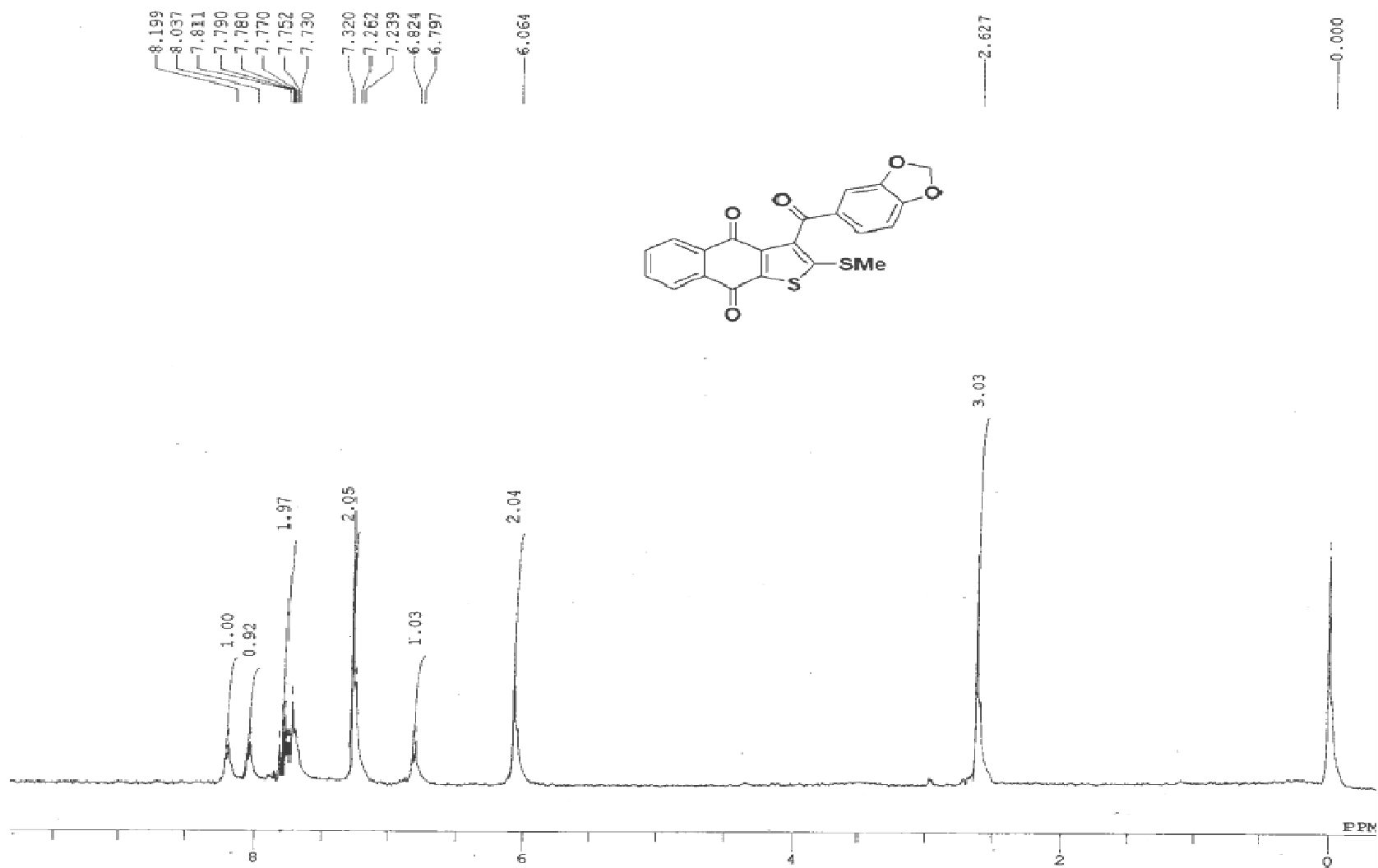
¹H NMR of 3-(2-Chlorobenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3f)



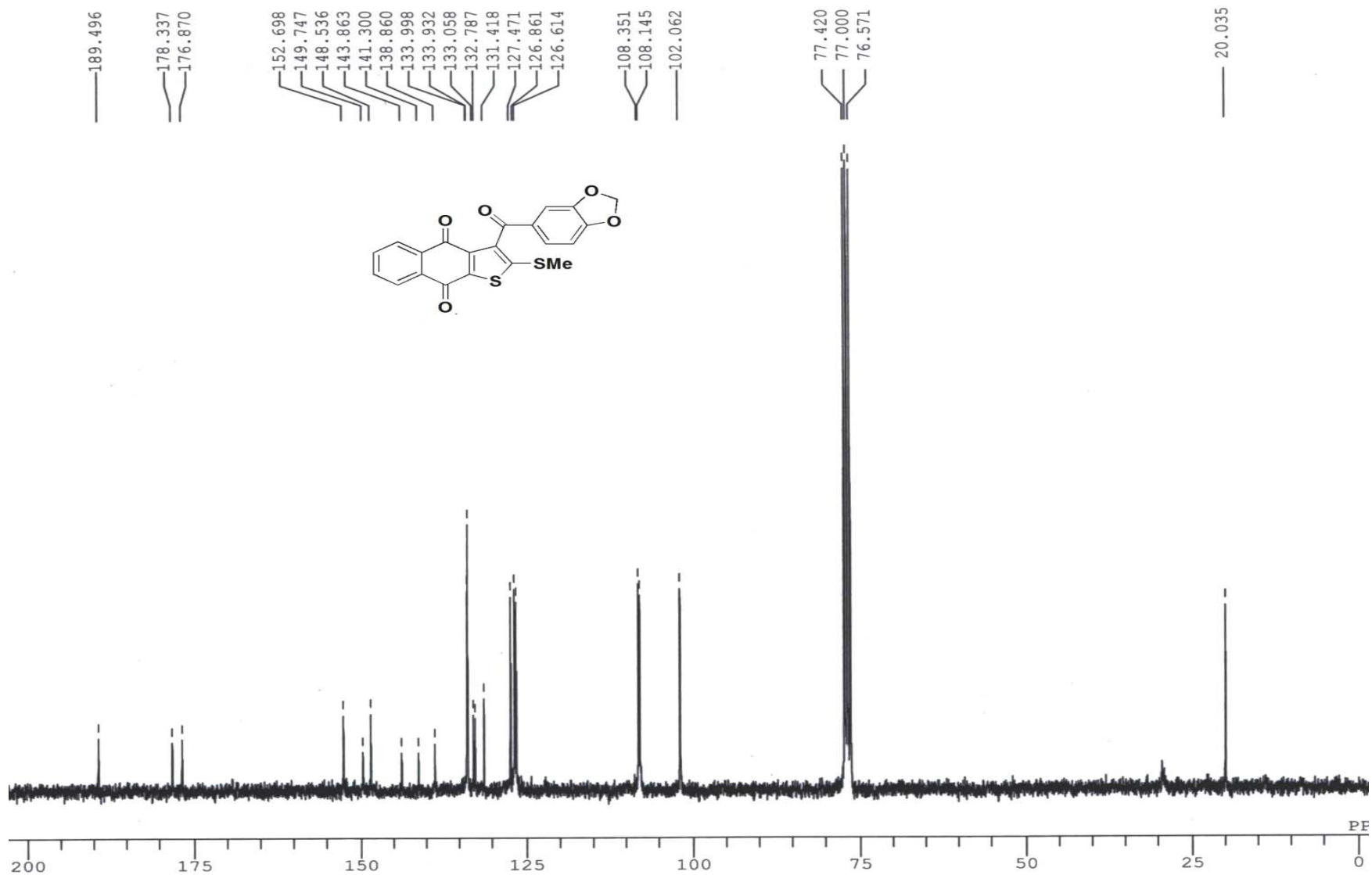
^{13}C NMR of 3-(2-Chlorobenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3f)



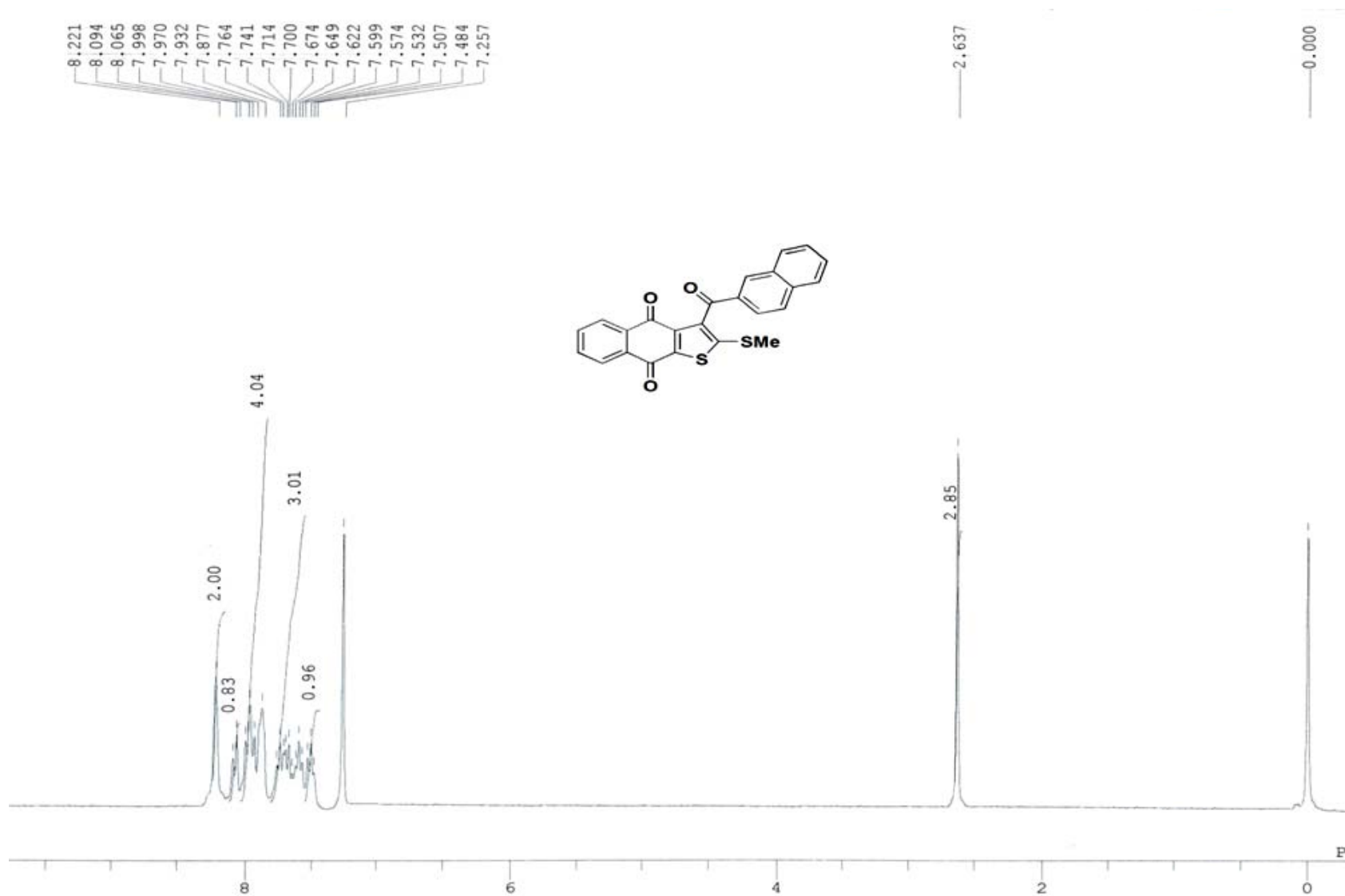
¹H NMR of 3-(Benzo[1,3]dioxole-5-carbonyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3g)



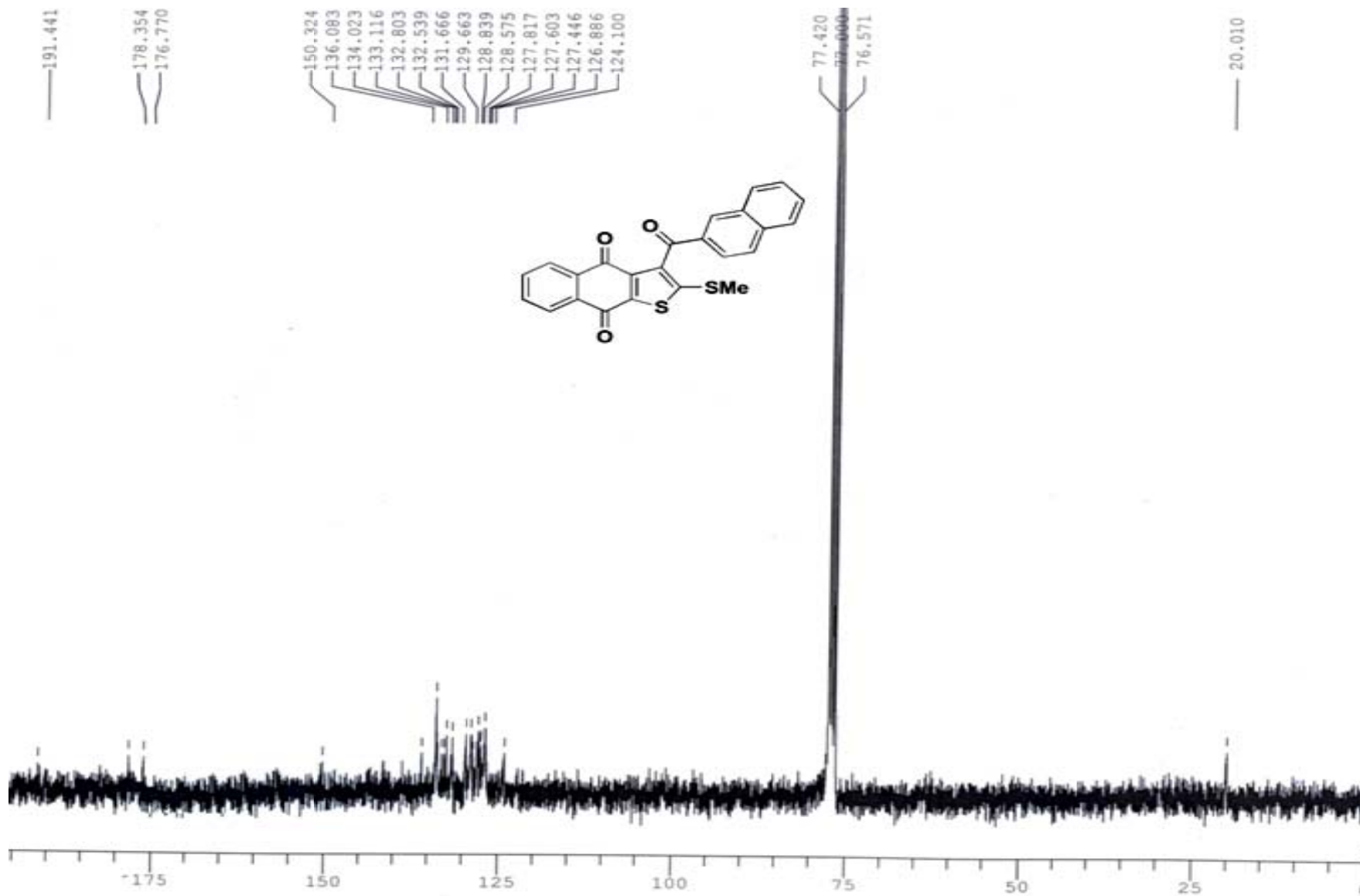
^{13}C NMR of 3-(Benzo[1,3]dioxole-5-carbonyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3g)



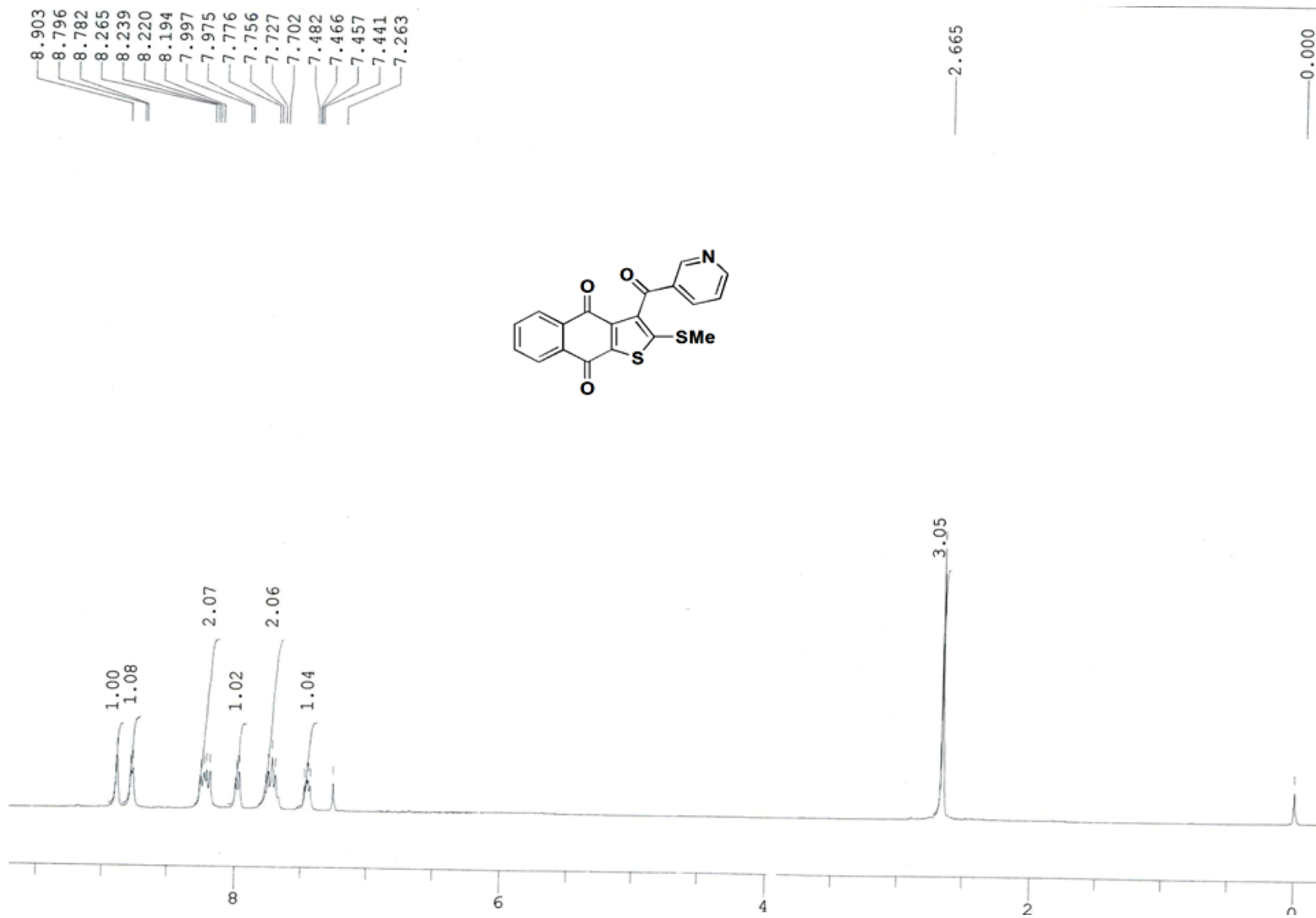
¹H NMR of 2-Methylthio-3-(naphthalene-2-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3h)



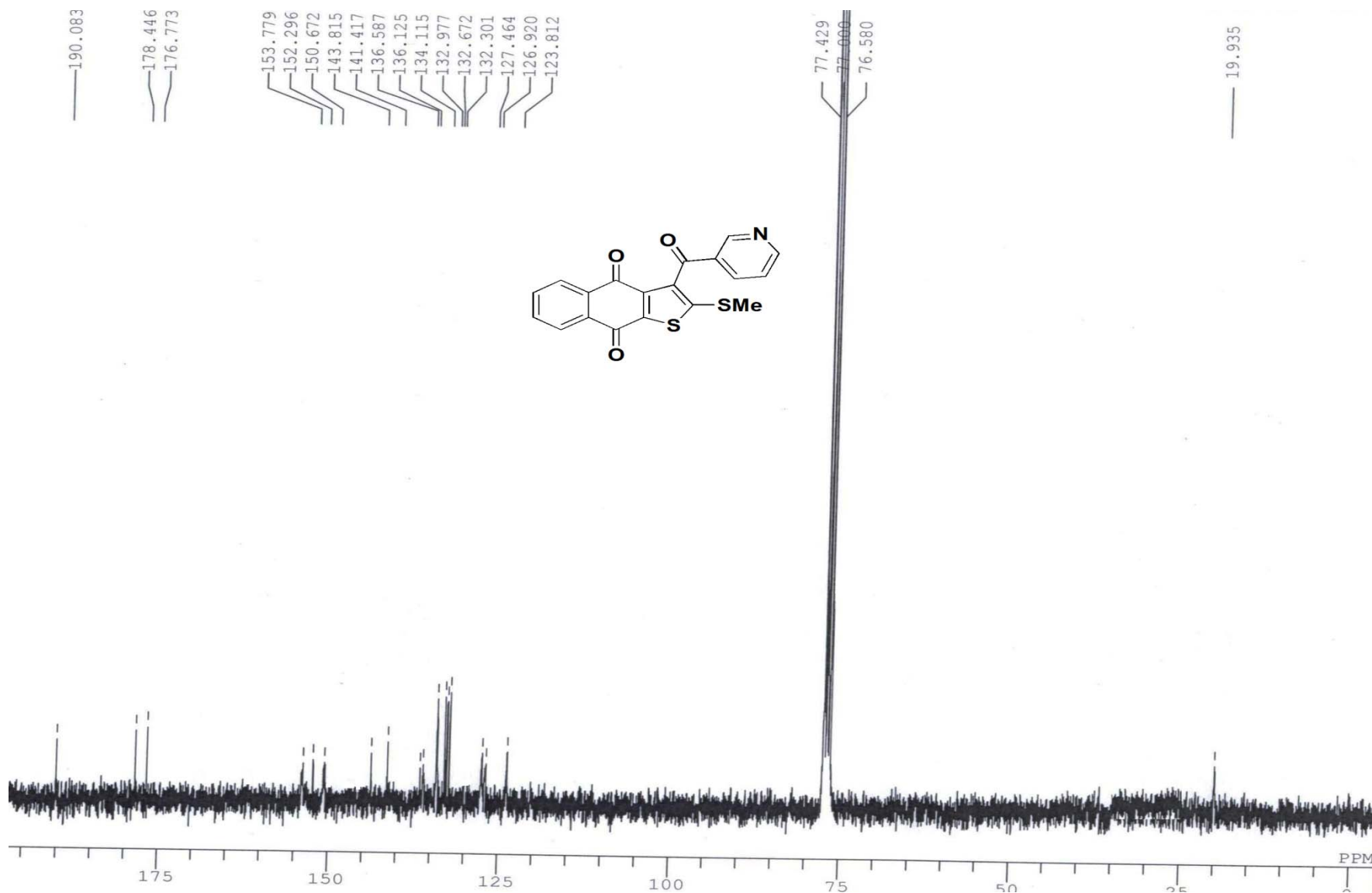
^{13}C NMR of 2-Methylthio-3-(naphthalene-2-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3h)



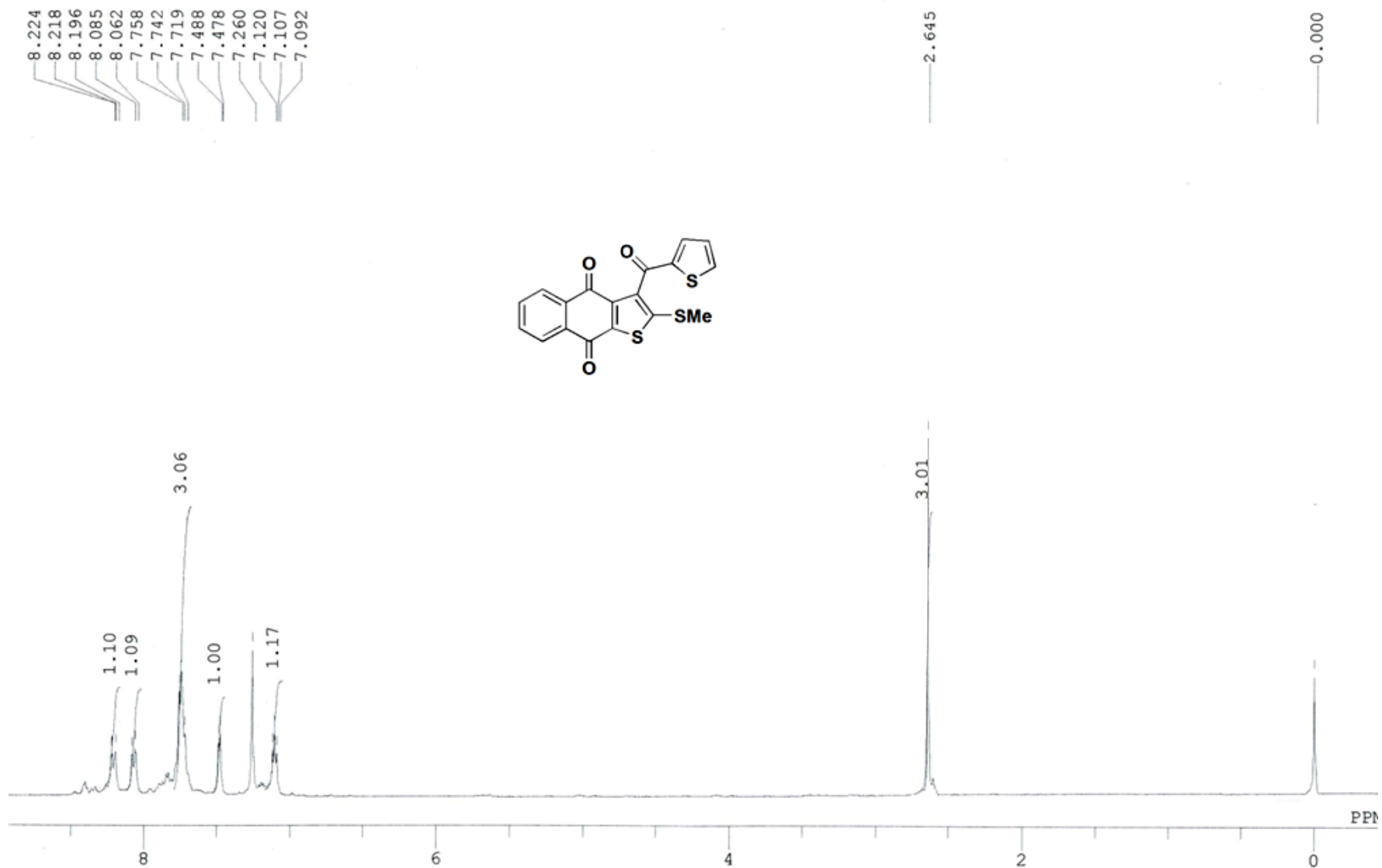
¹H NMR of 2-Methylthio-3-(pyridine-3-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3i)



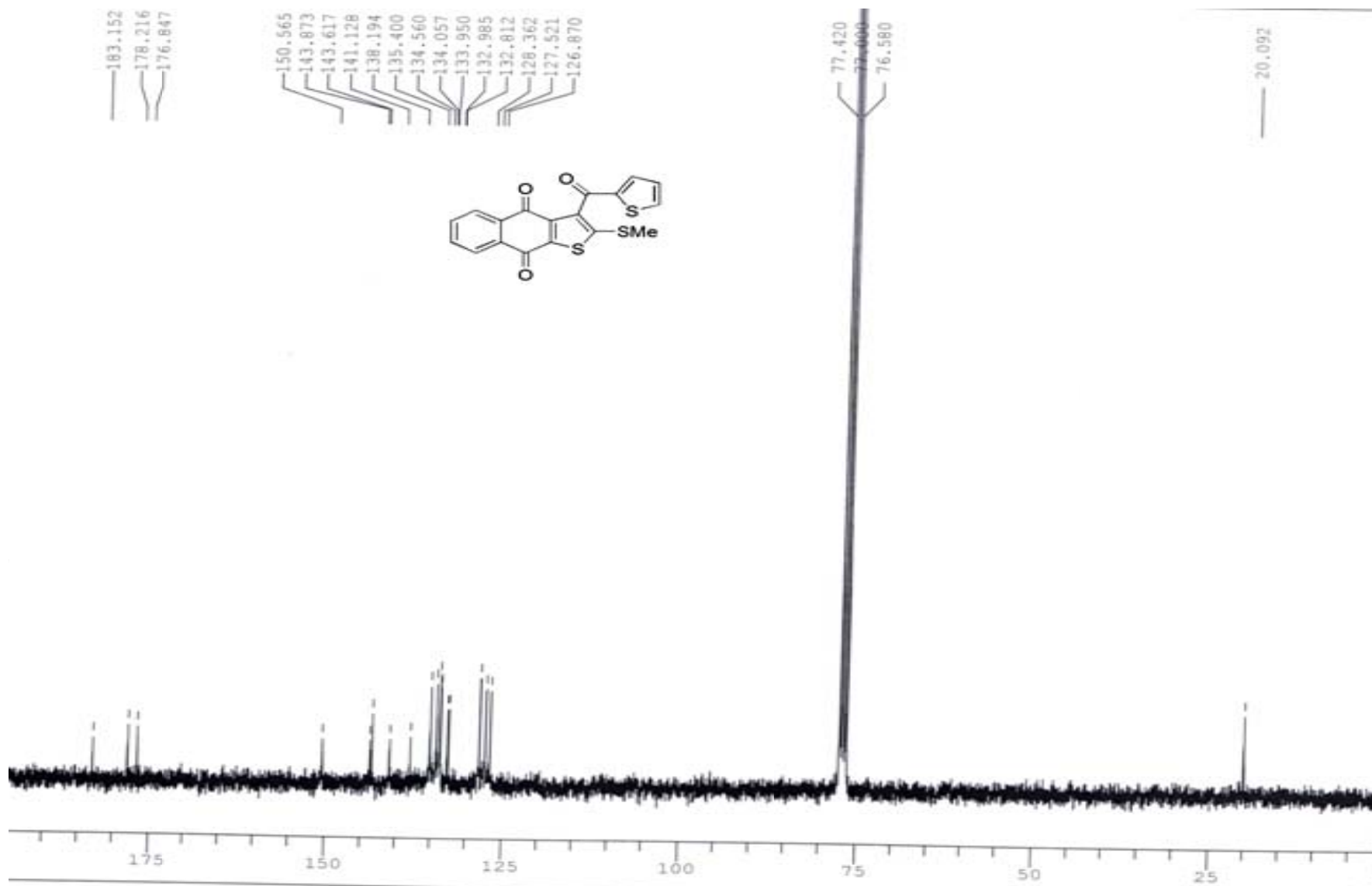
^{13}C NMR of 2-Methylthio-3-(pyridine-3-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3i)



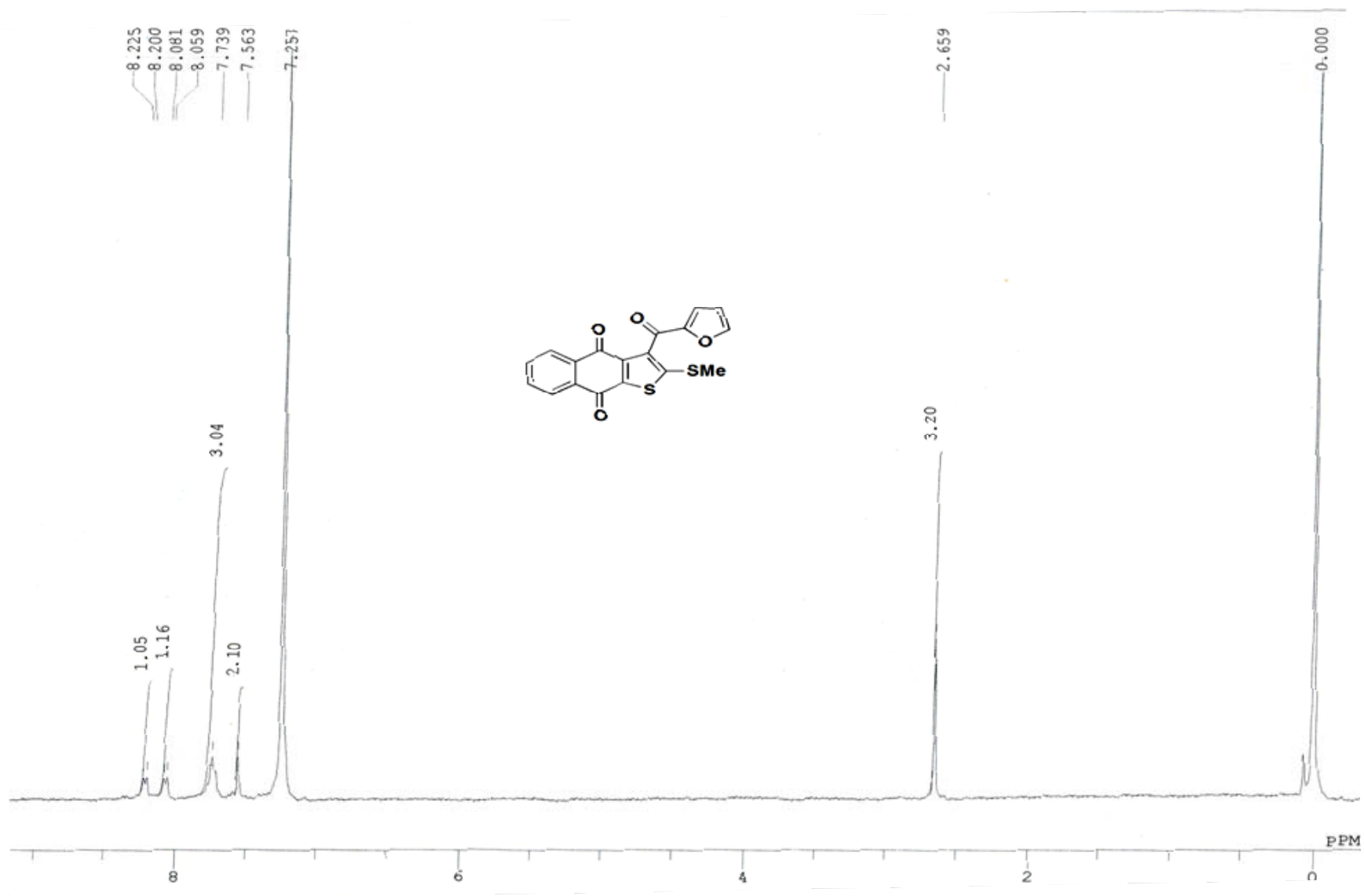
¹H NMR of 2-Methylthio-3-(thiophene-2-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3j)



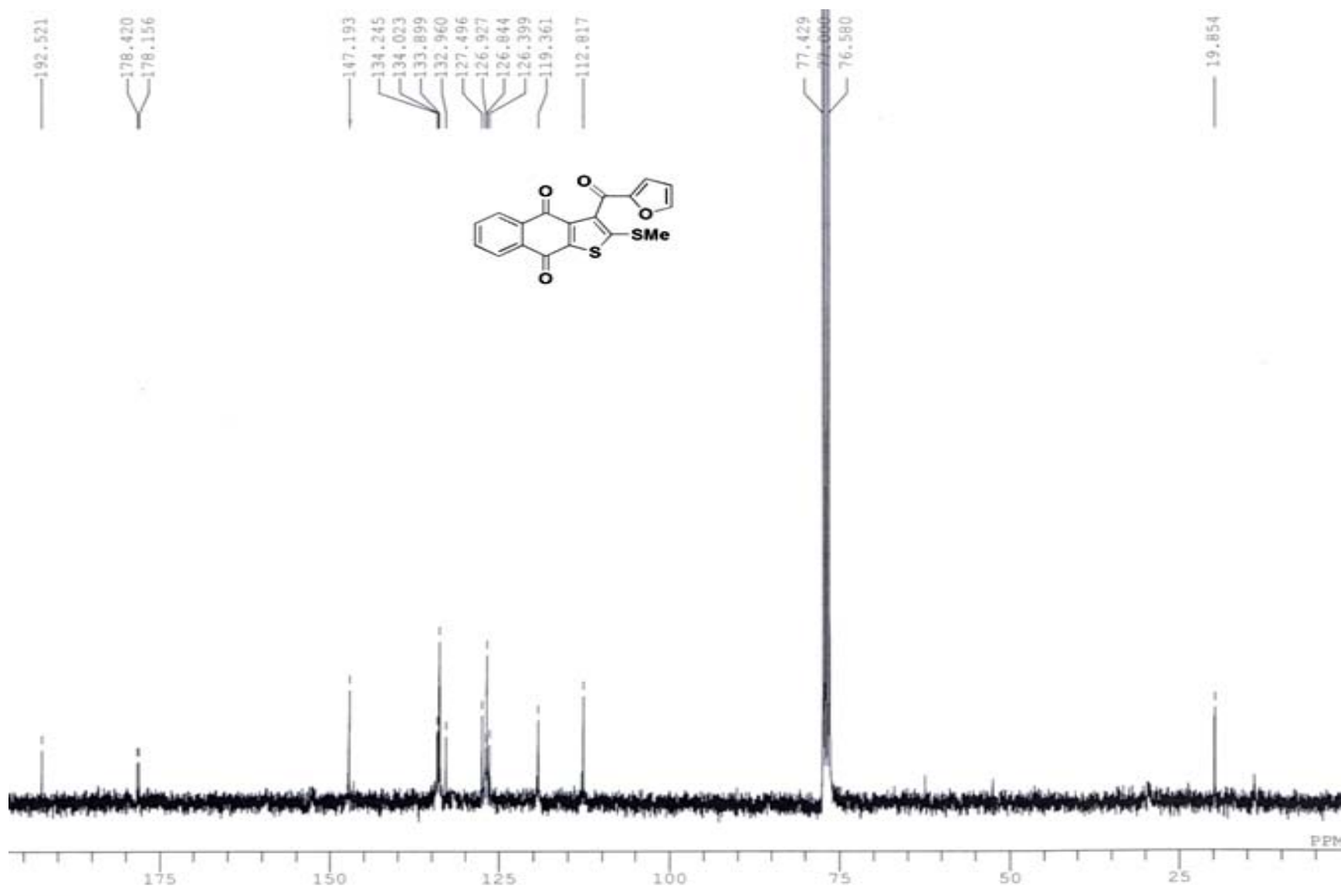
^{13}C NMR of 2-Methylthio-3-(thiophene-2-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3j)



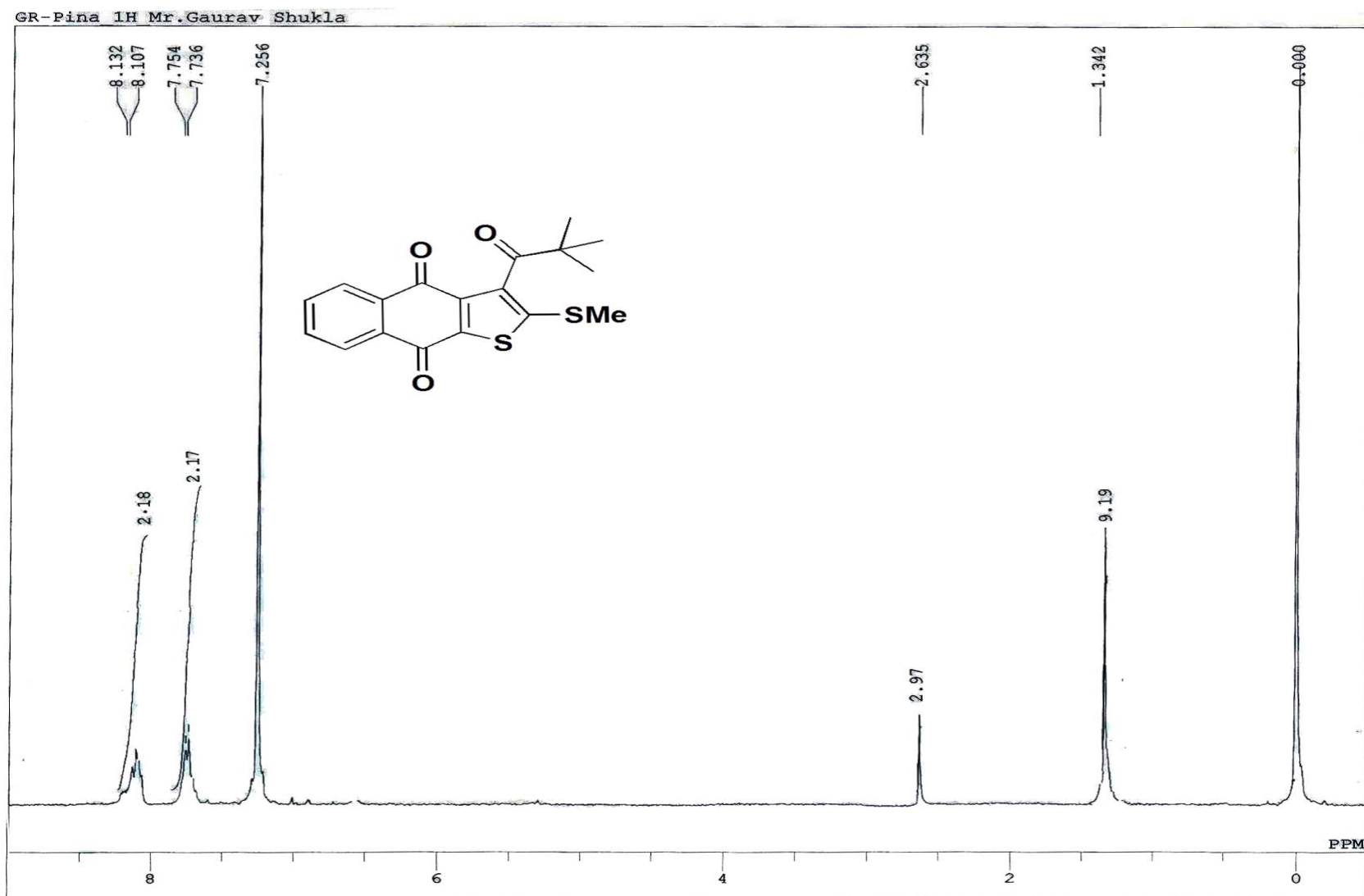
¹H NMR of 3-(Furan-2-carbonyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3k)



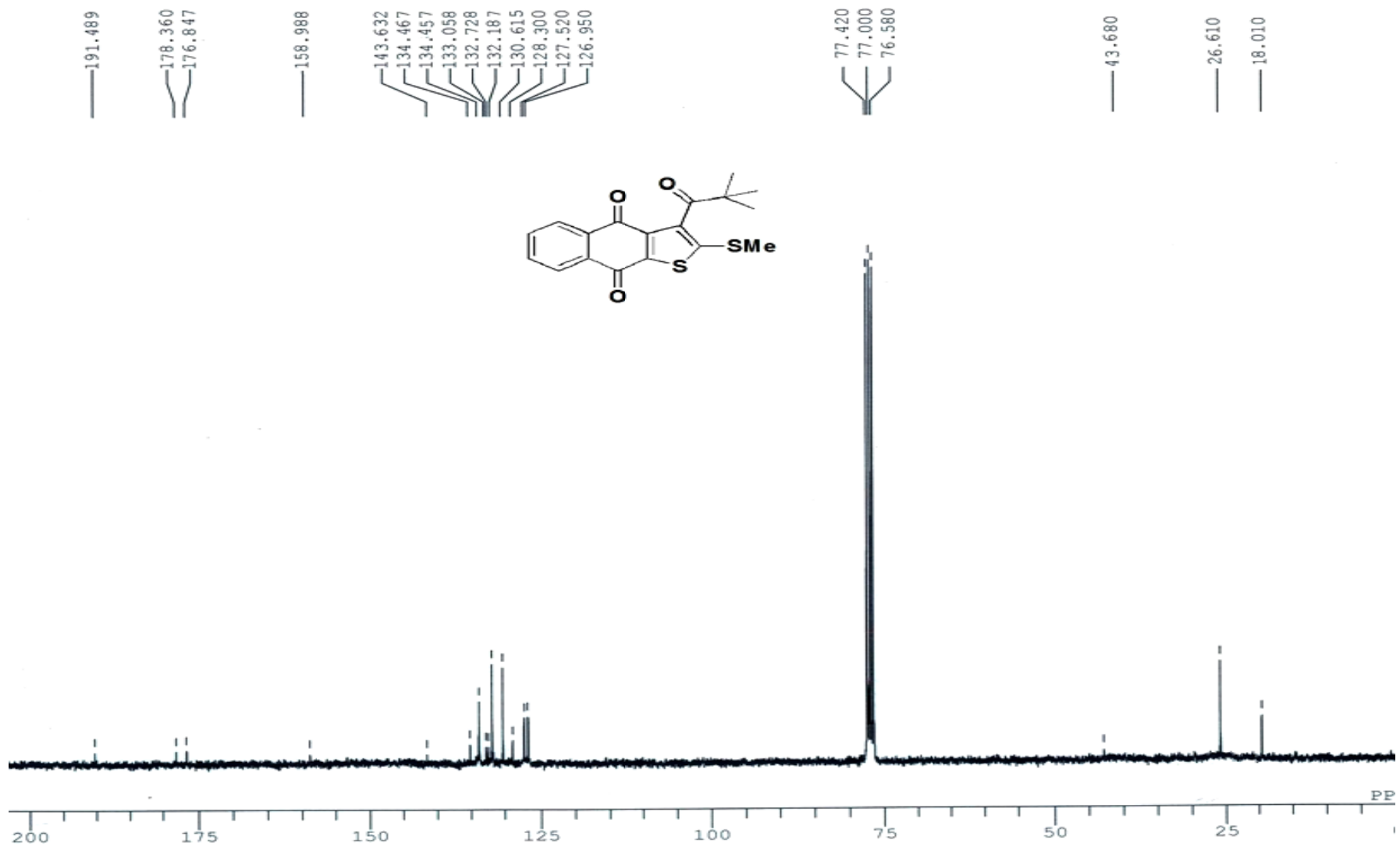
^{13}C NMR of 3-(Furan-2-carbonyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3k)



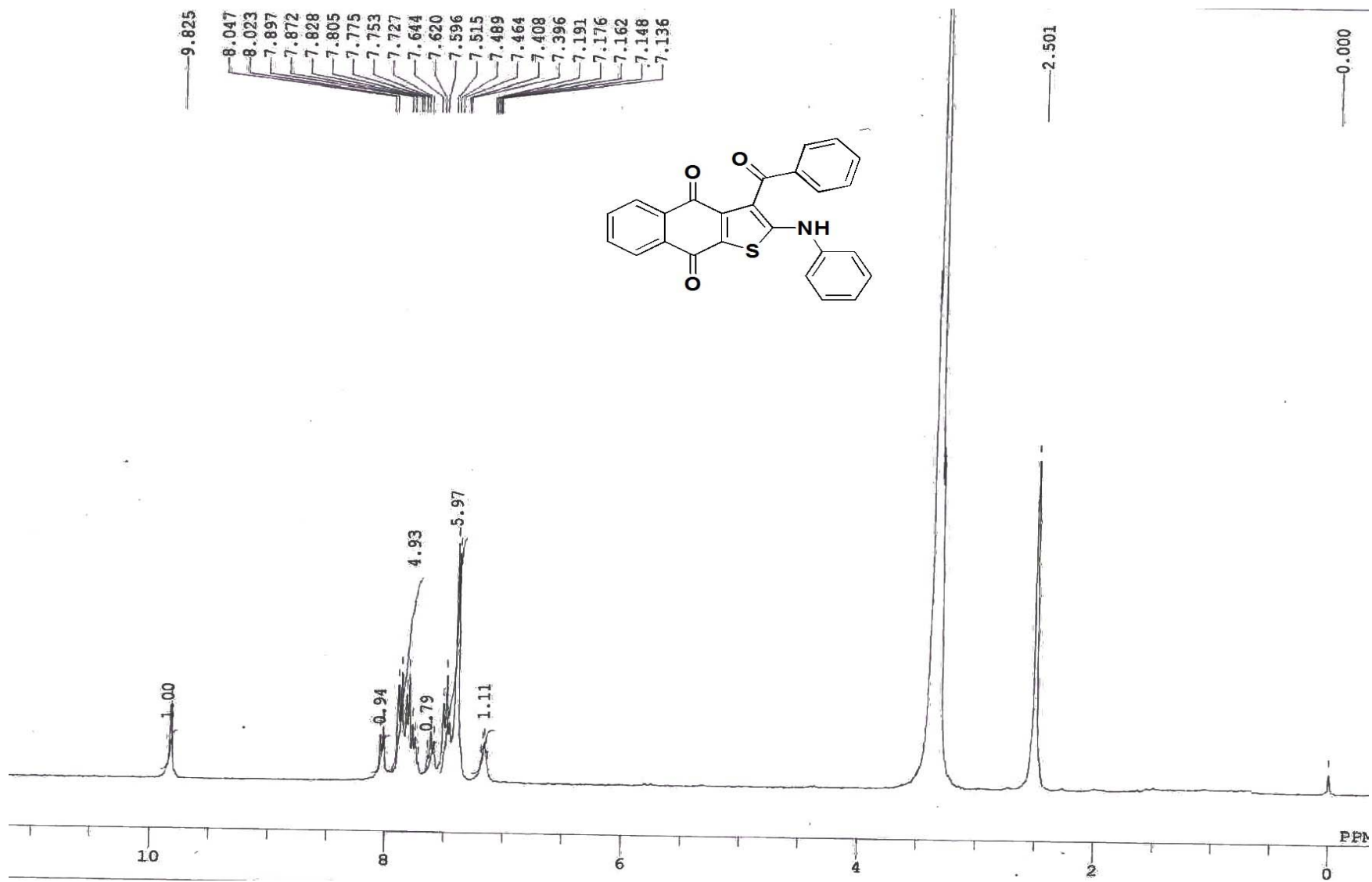
¹H NMR of 3-(2,2-Dimethylpropionyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3l)



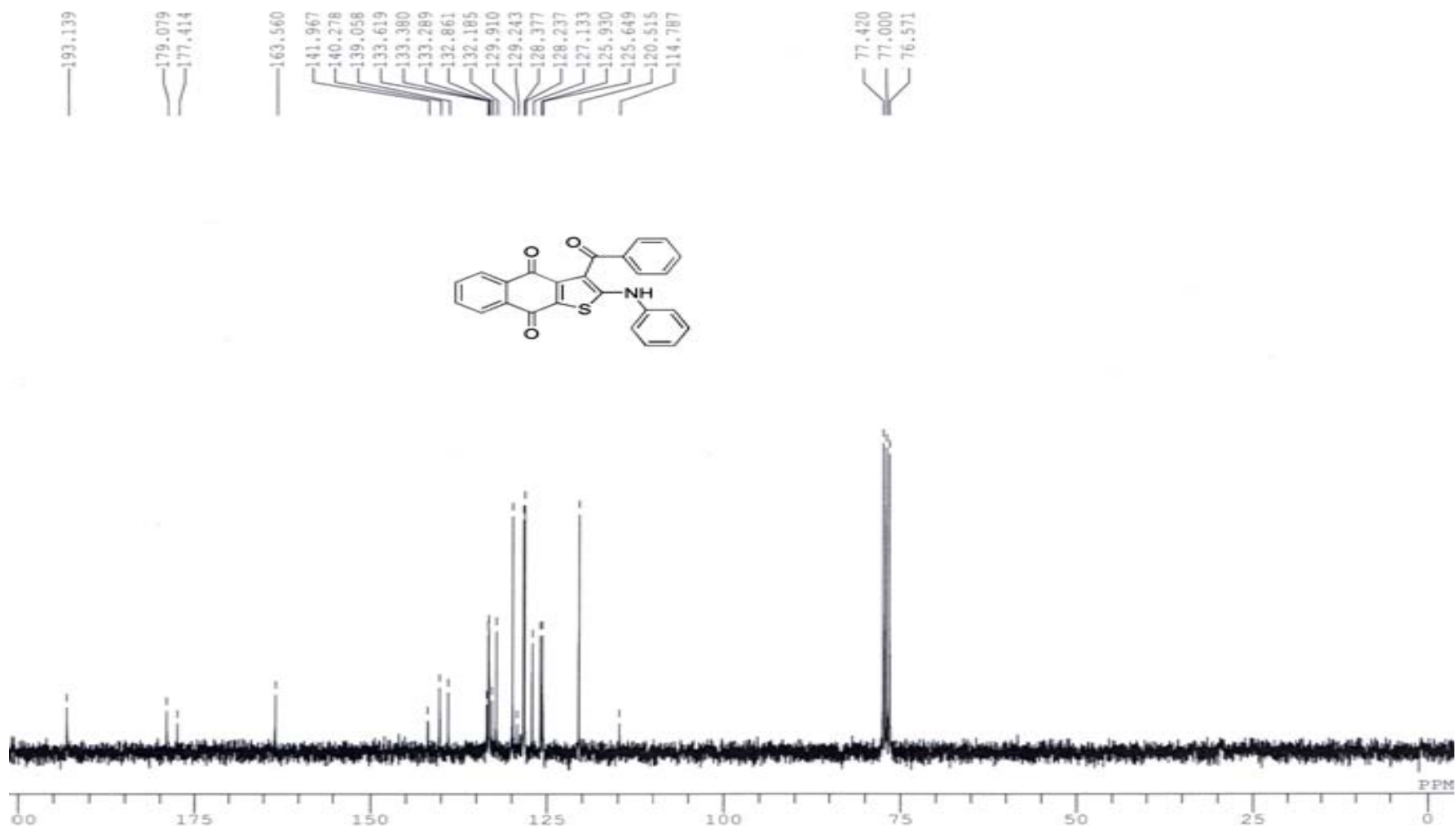
¹³C NMR of 3-(2,2-Dimethylpropionyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3l)



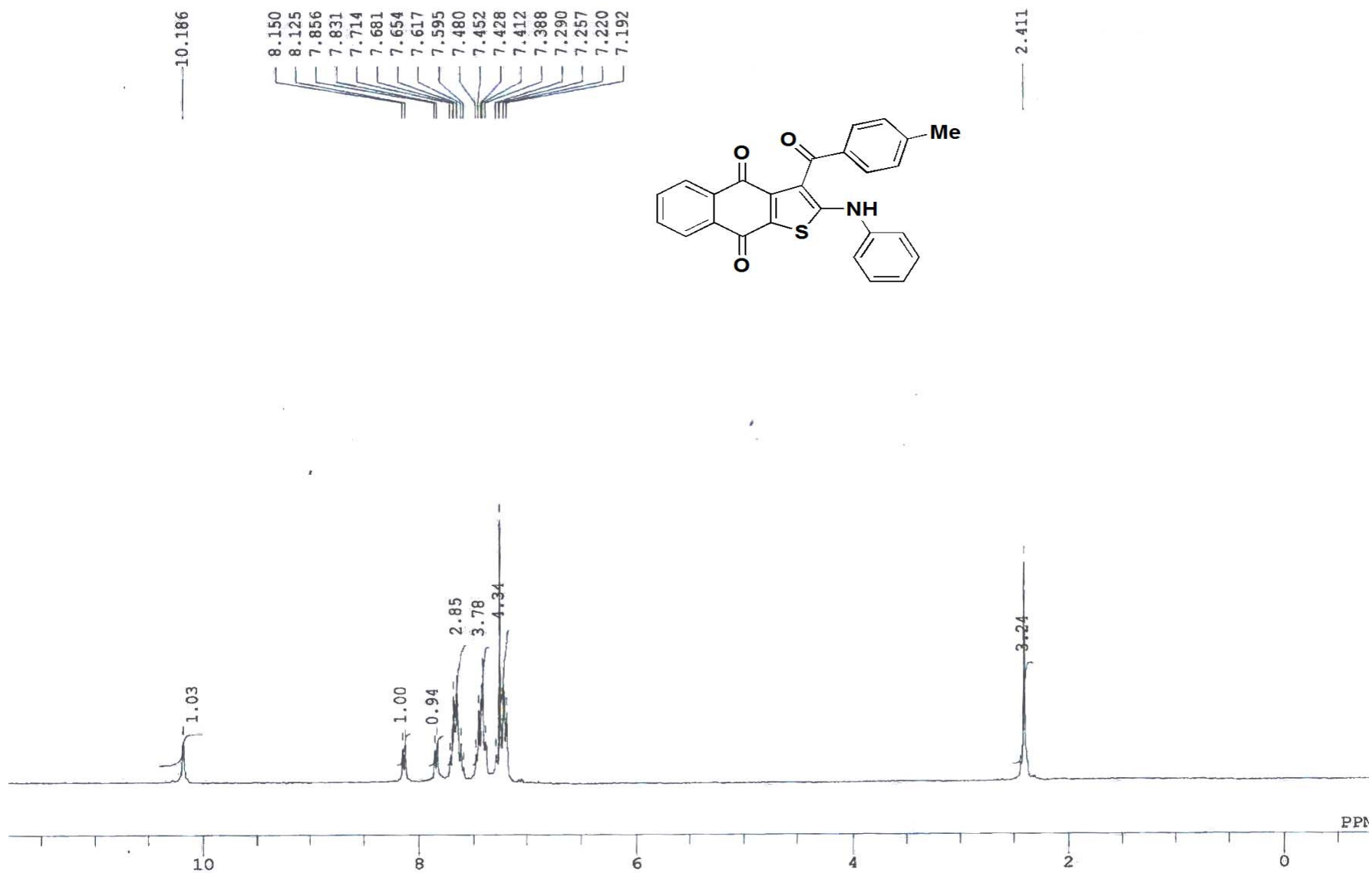
¹H NMR of 3-Benzoyl-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3m)



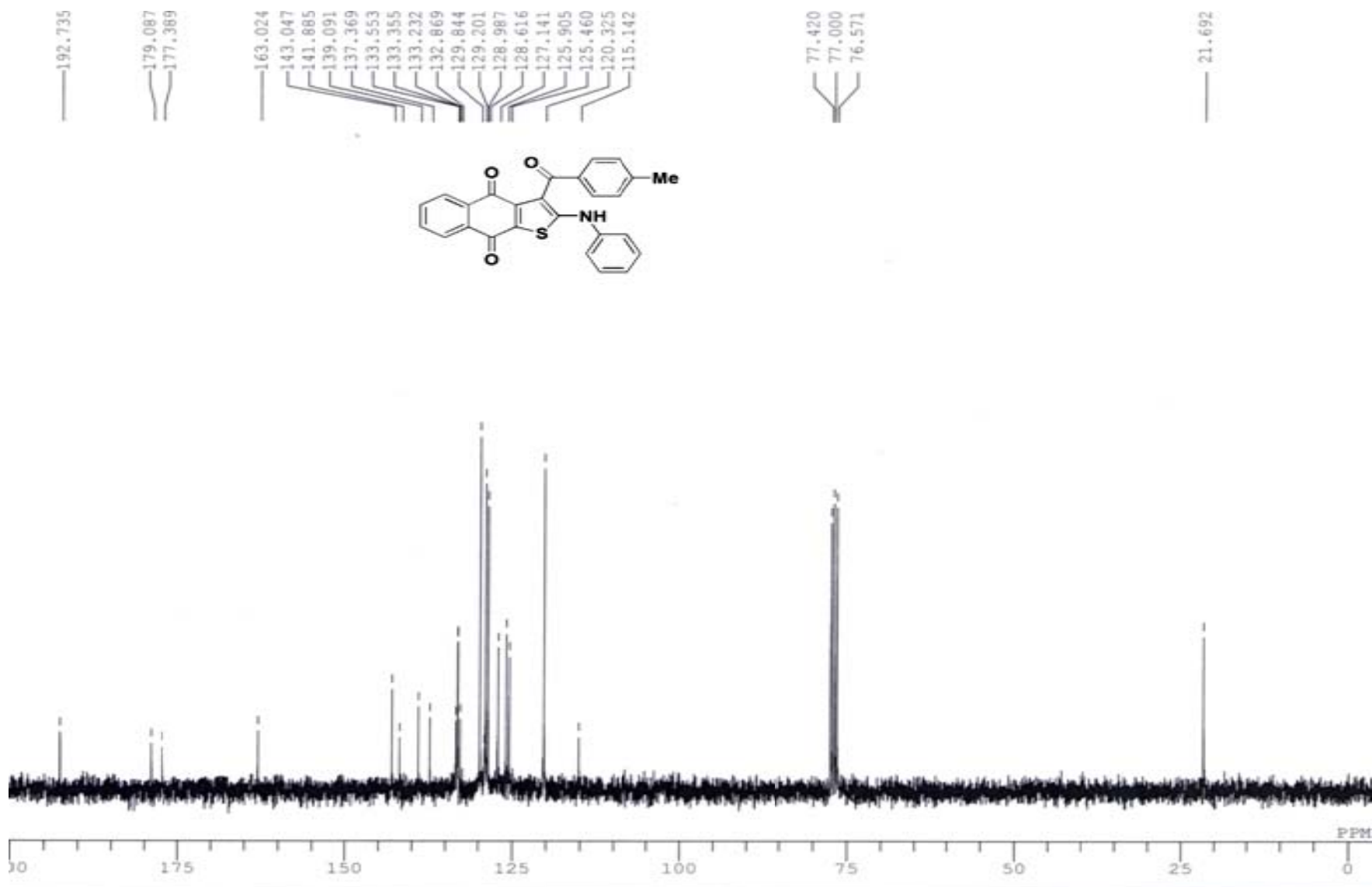
¹³C NMR of 3-Benzoyl-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3m)



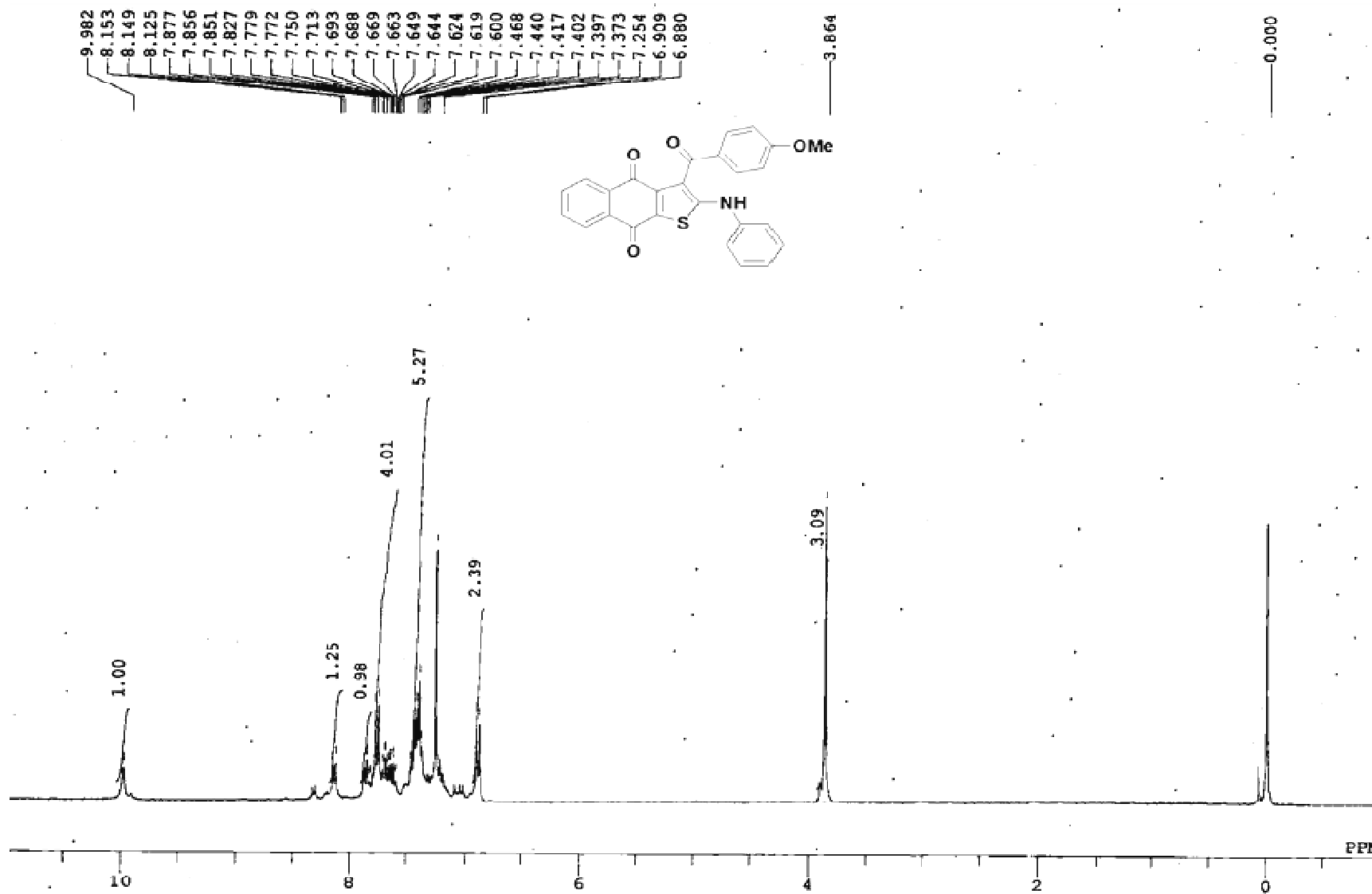
¹H NMR of 3-(4-Methyl-benzoyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3n)



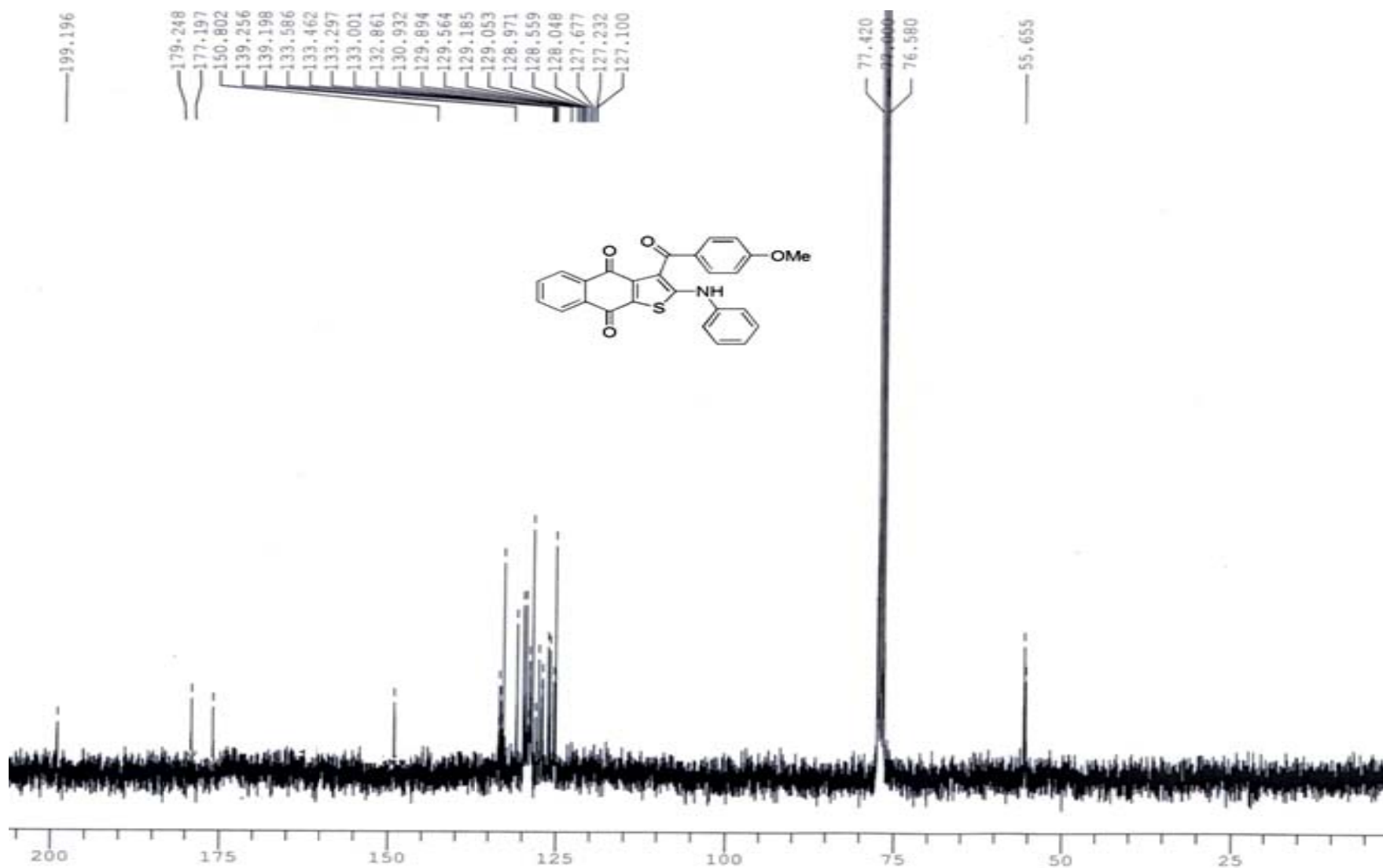
^{13}C NMR of 3-(4-Methyl-benzoyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3n)



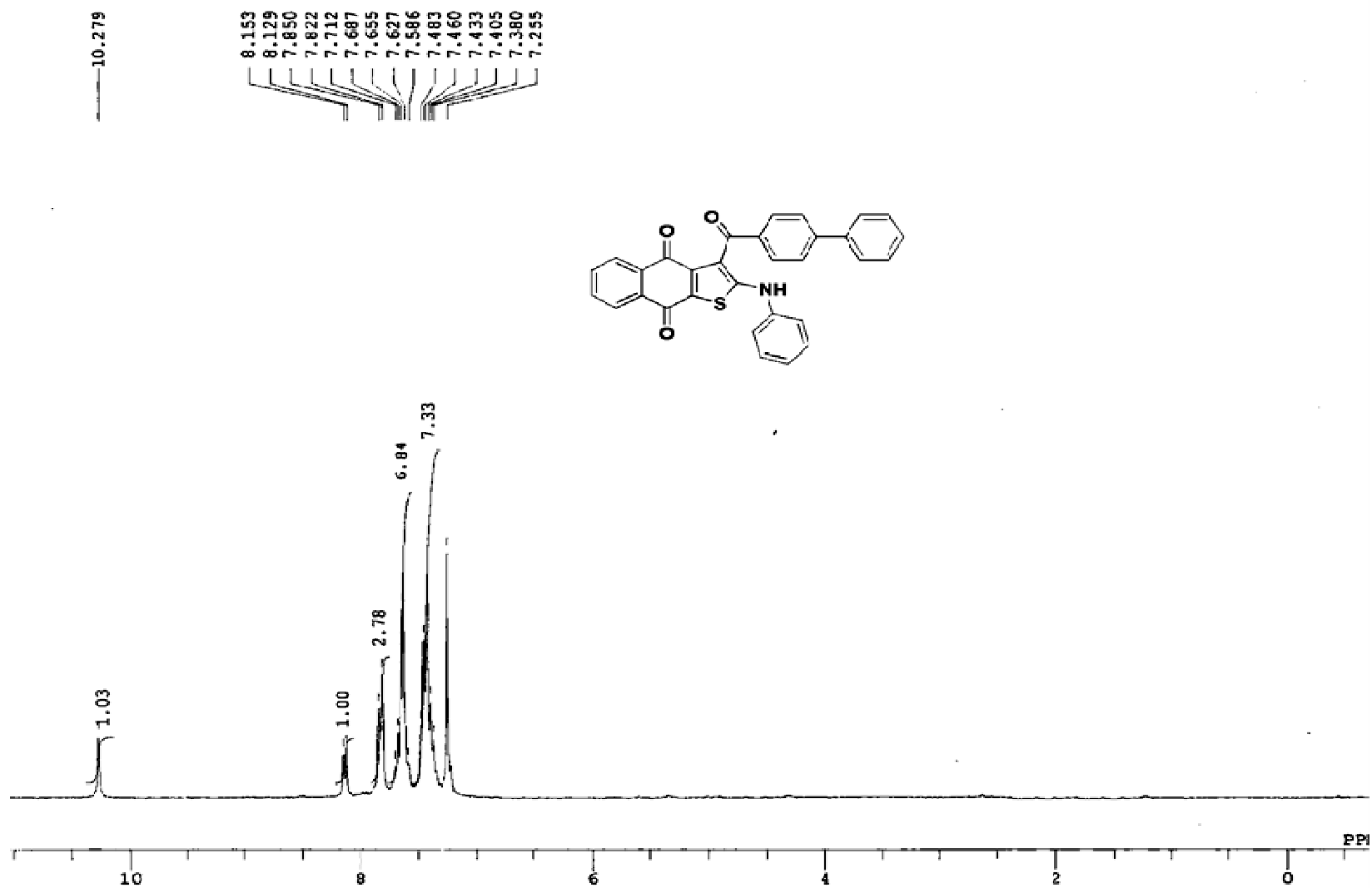
¹H NMR of 3-(4-Methoxy-benzoyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3o)



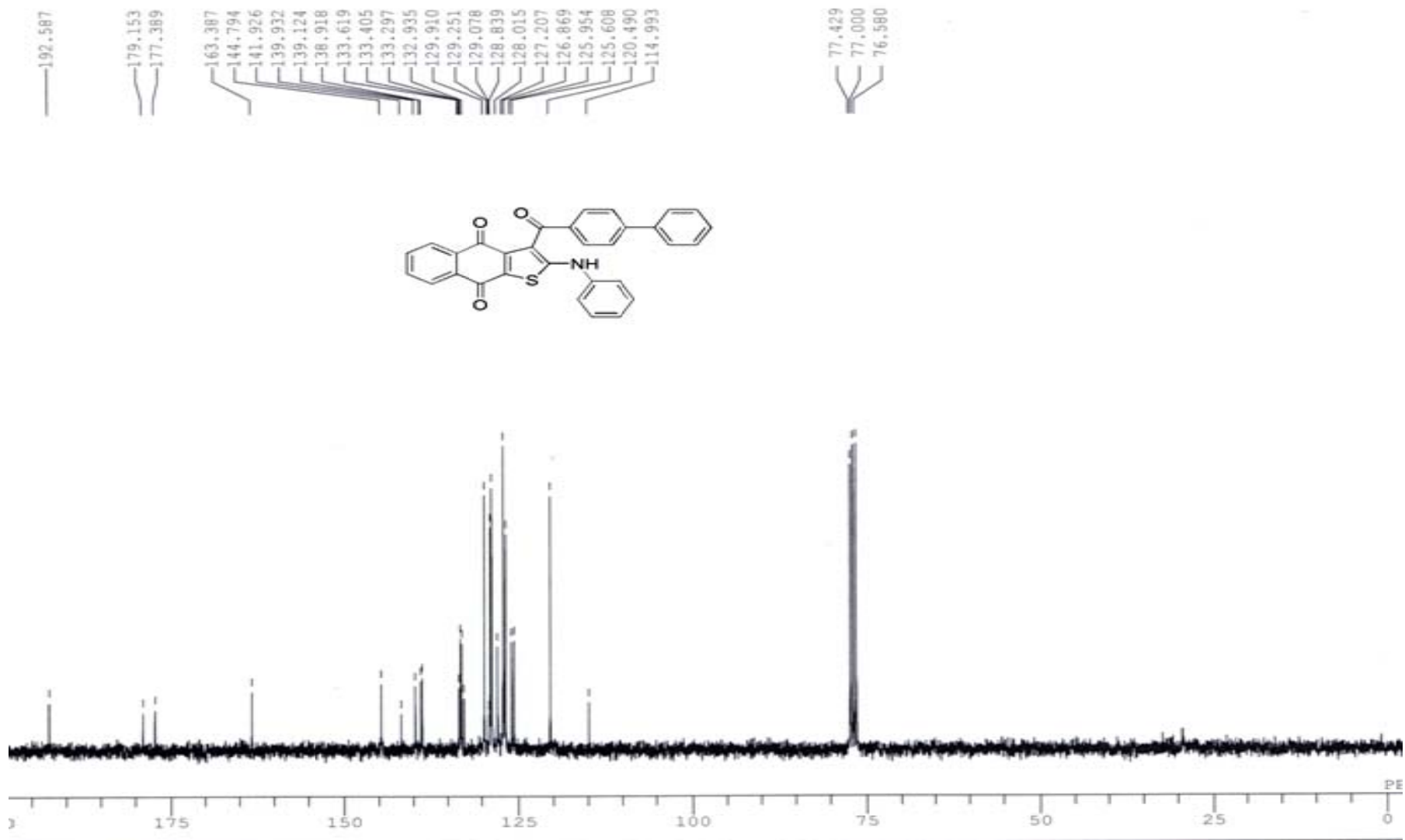
^{13}C NMR of 3-(4-Methoxy-benzoyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3o)



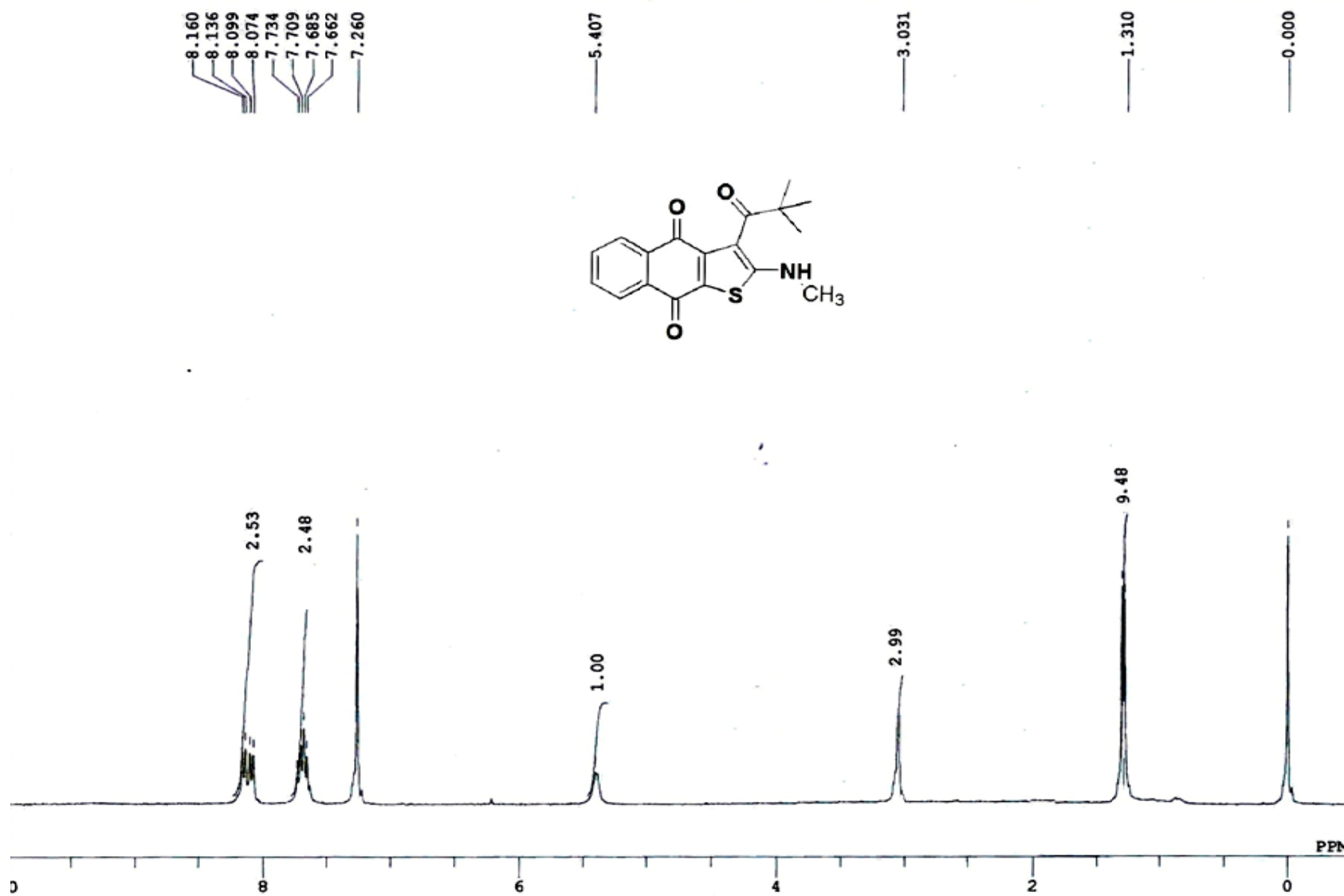
¹H NMR of 3-(Biphenyl-4-carbonyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3p)



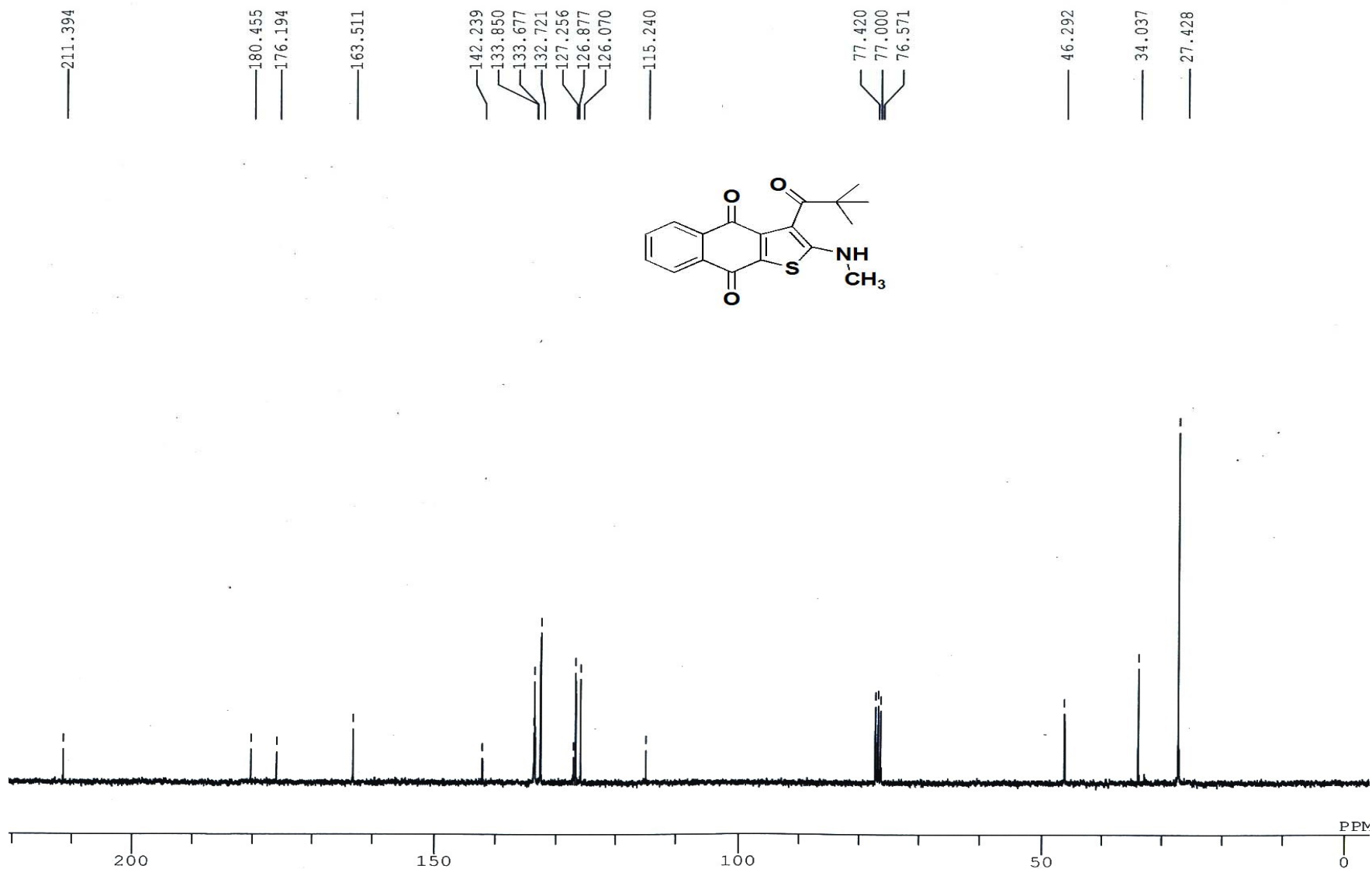
¹³C NMR of 3-(Biphenyl-4-carbonyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3p)



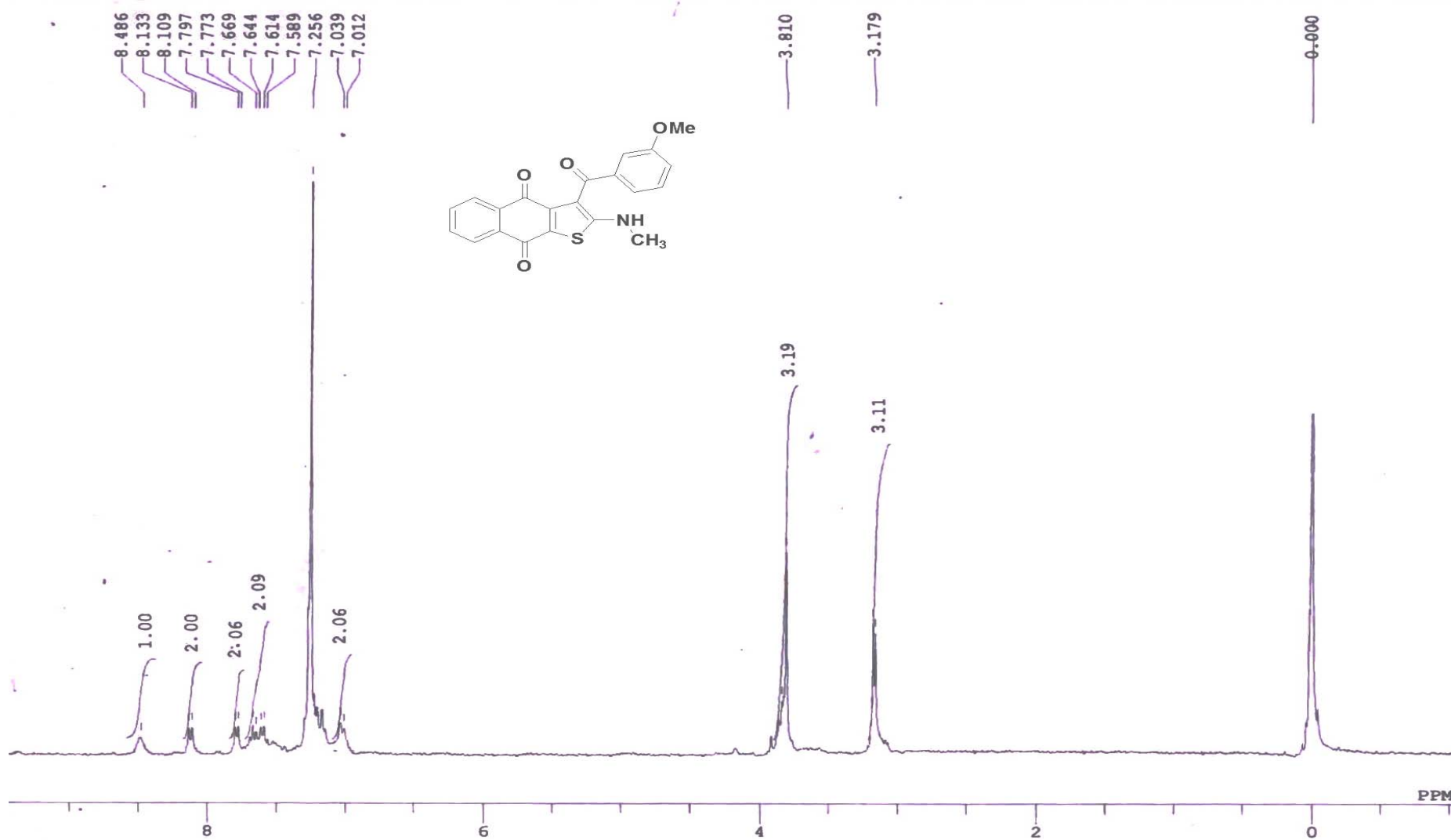
¹H NMR of 3-(2,2-Dimethyl-propionyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3q)



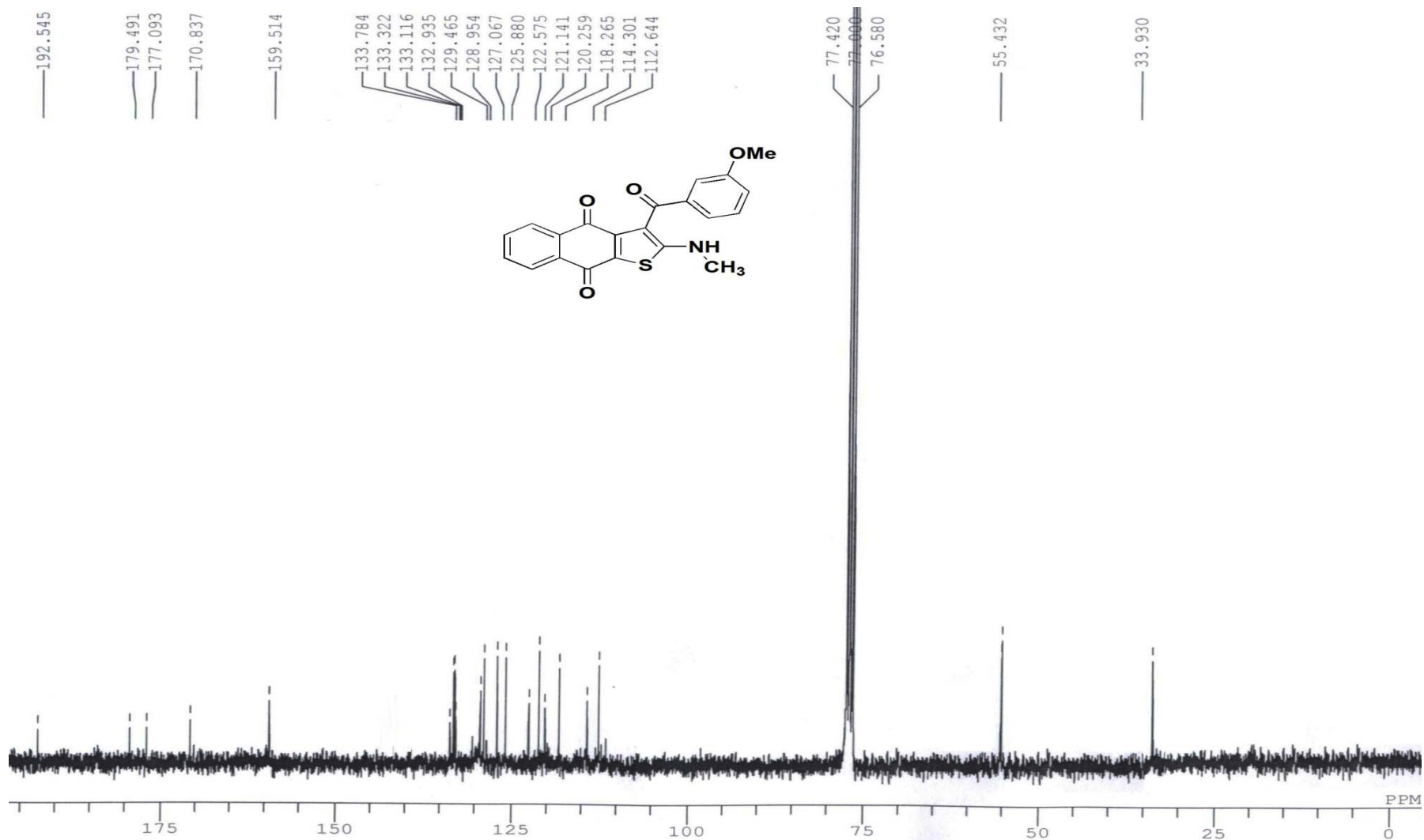
¹³C NMR of 3-(2,2-Dimethyl-propionyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3q)



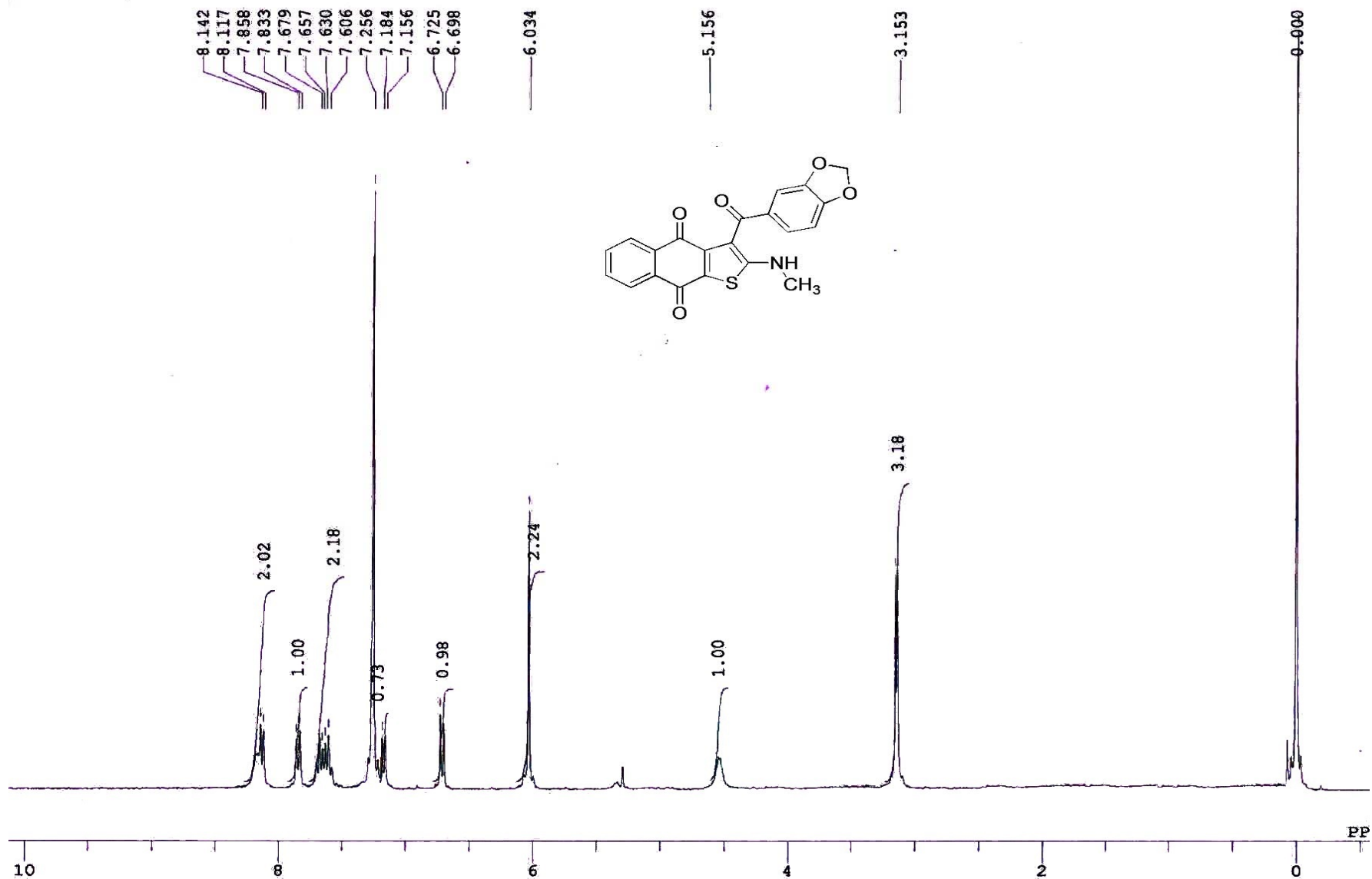
¹H NMR of 3-(3-Methoxy-benzoyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3r)



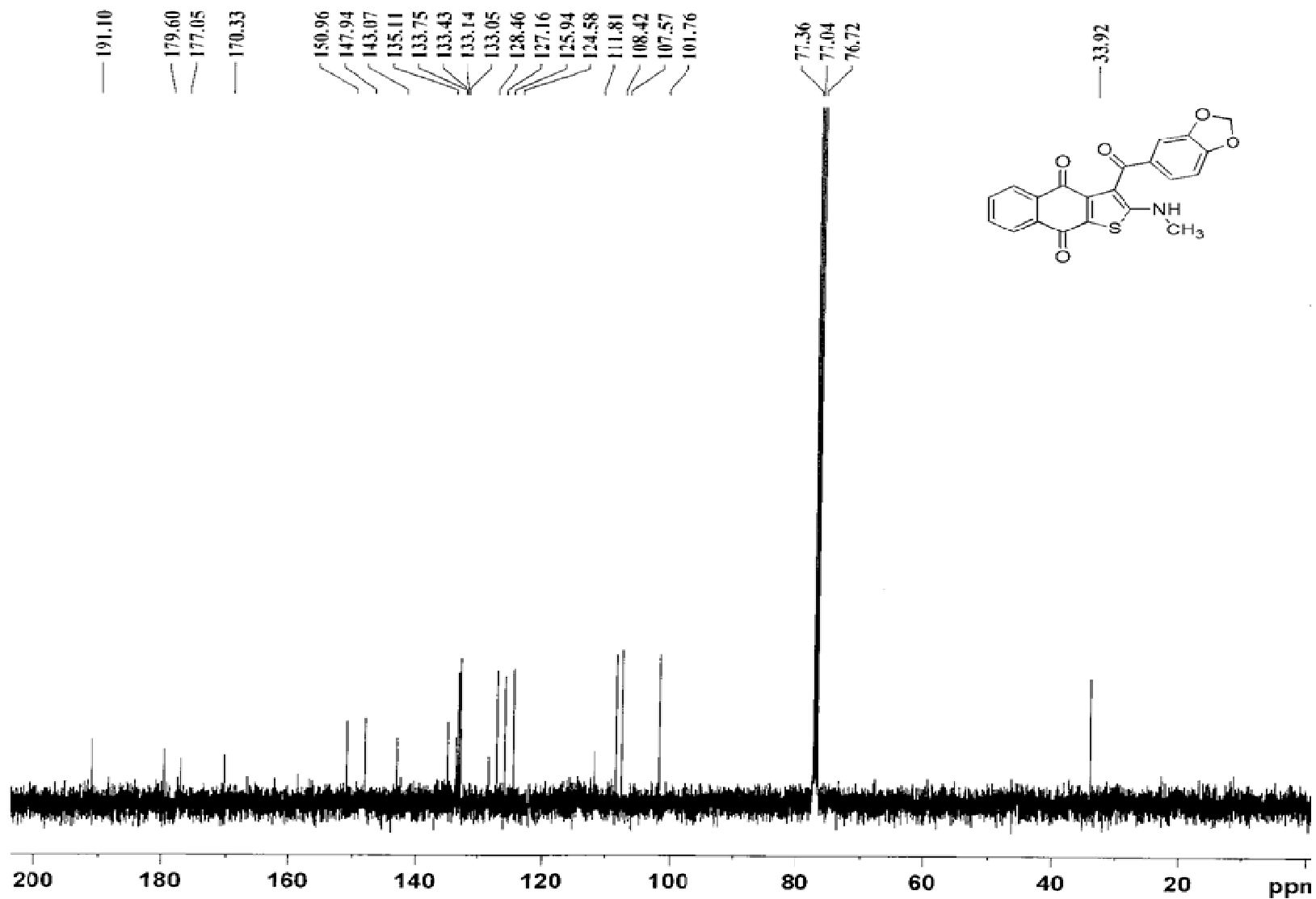
¹³C NMR of 3-(3-Methoxy-benzoyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3r)



¹H NMR of 3-(Benzo[1,3]dioxole-5-carbonyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3s)

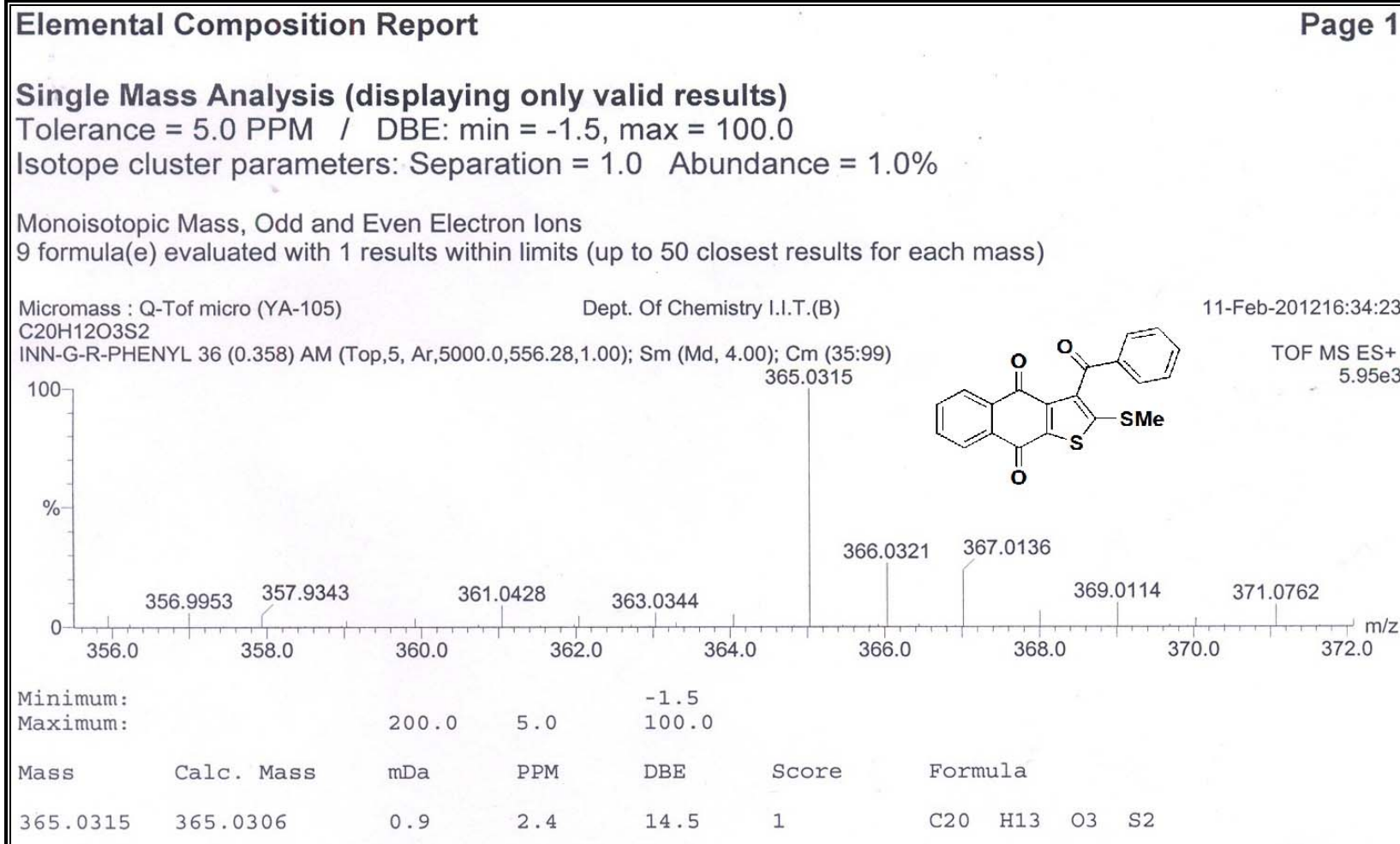


^{13}C NMR of 3-(Benzo[1,3]dioxole-5-carbonyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3s)

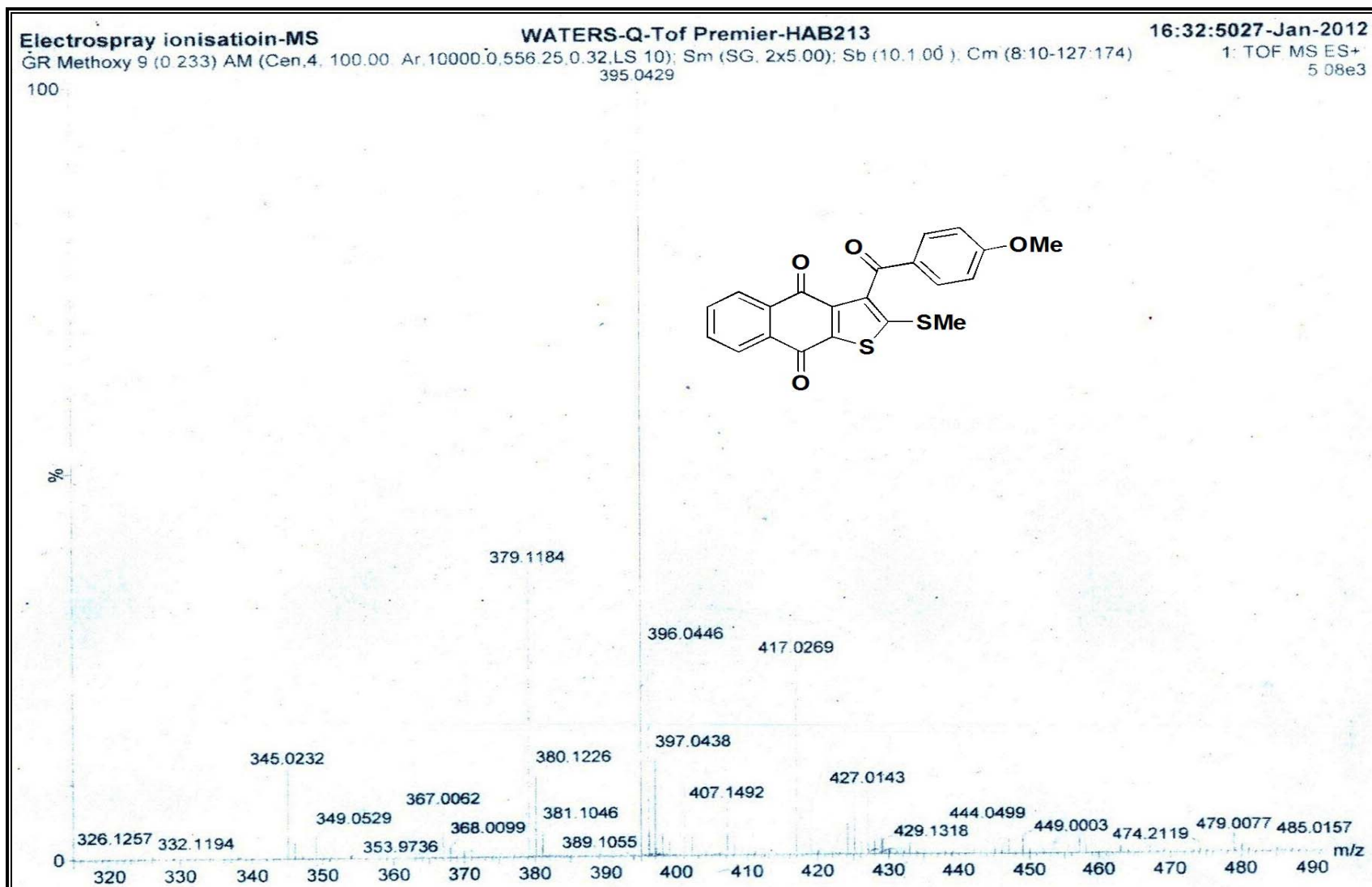


4. HRMS data of some selected compounds

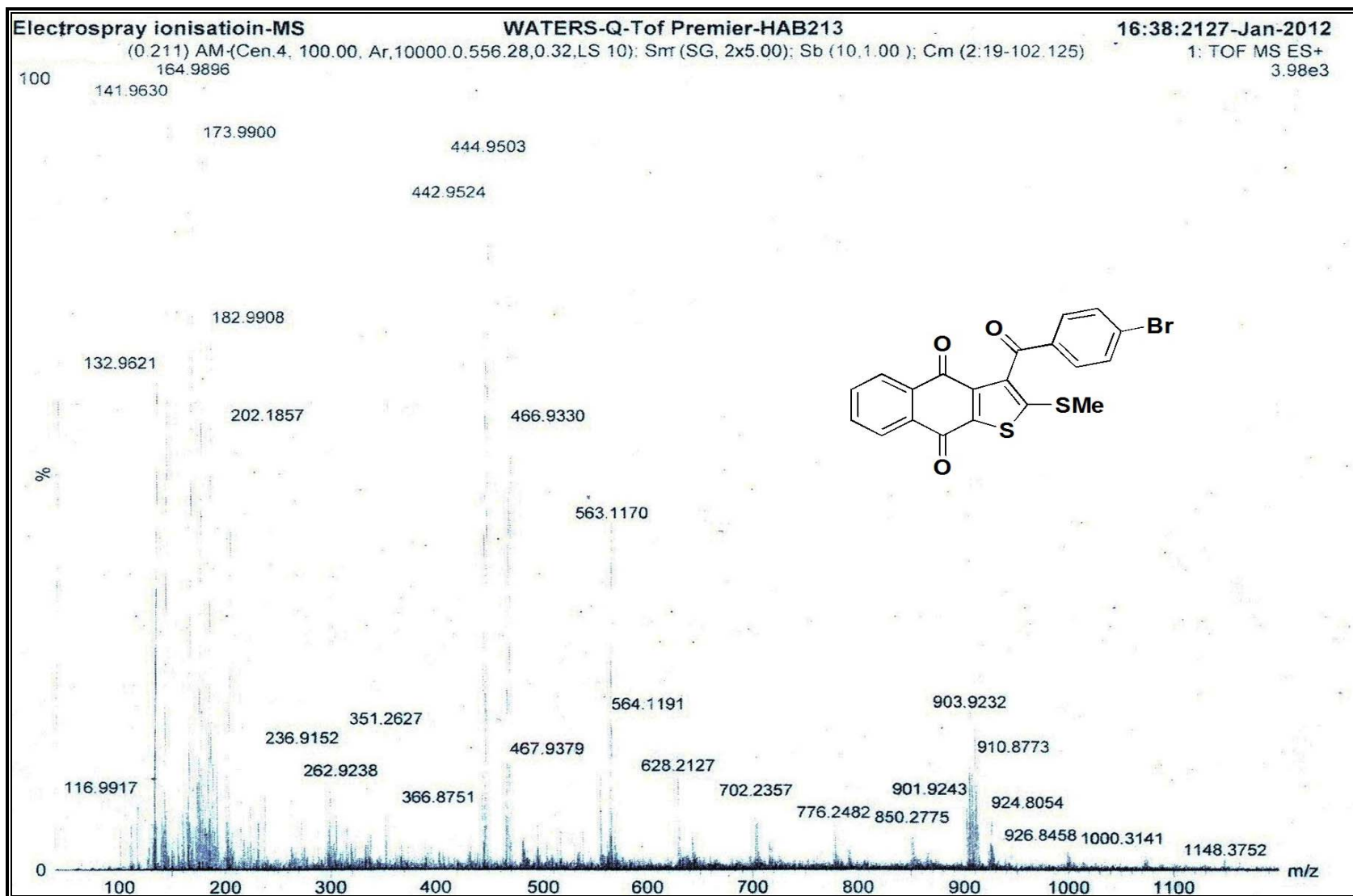
HRMS data of 3-Benzoyl-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3a)



HRMS data of 3-(4-Methoxybenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3c)



HRMS data of 3-(4-Bromobenzoyl)-2-methylthio-naphtho[2,3-b]thiophene-4,9-dione (3d)



HRMS data of 3-(2-Chloro-benzoyl)-2-methylthio-naphtho[2,3-b] thiophene-4,9-dione (3f)

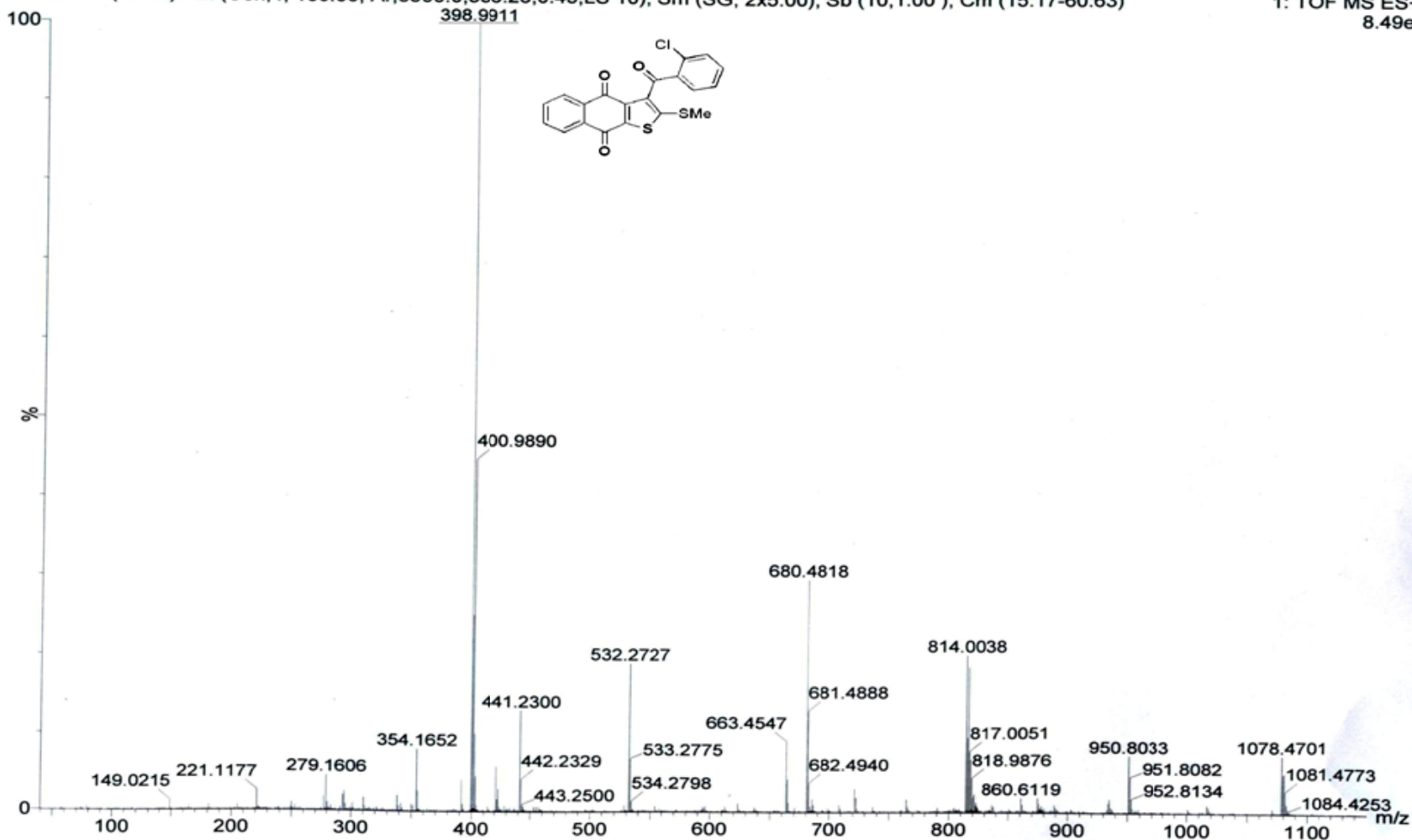
Electrospray ionisation-MS

WATERS-Q-ToF Premier-HAB213

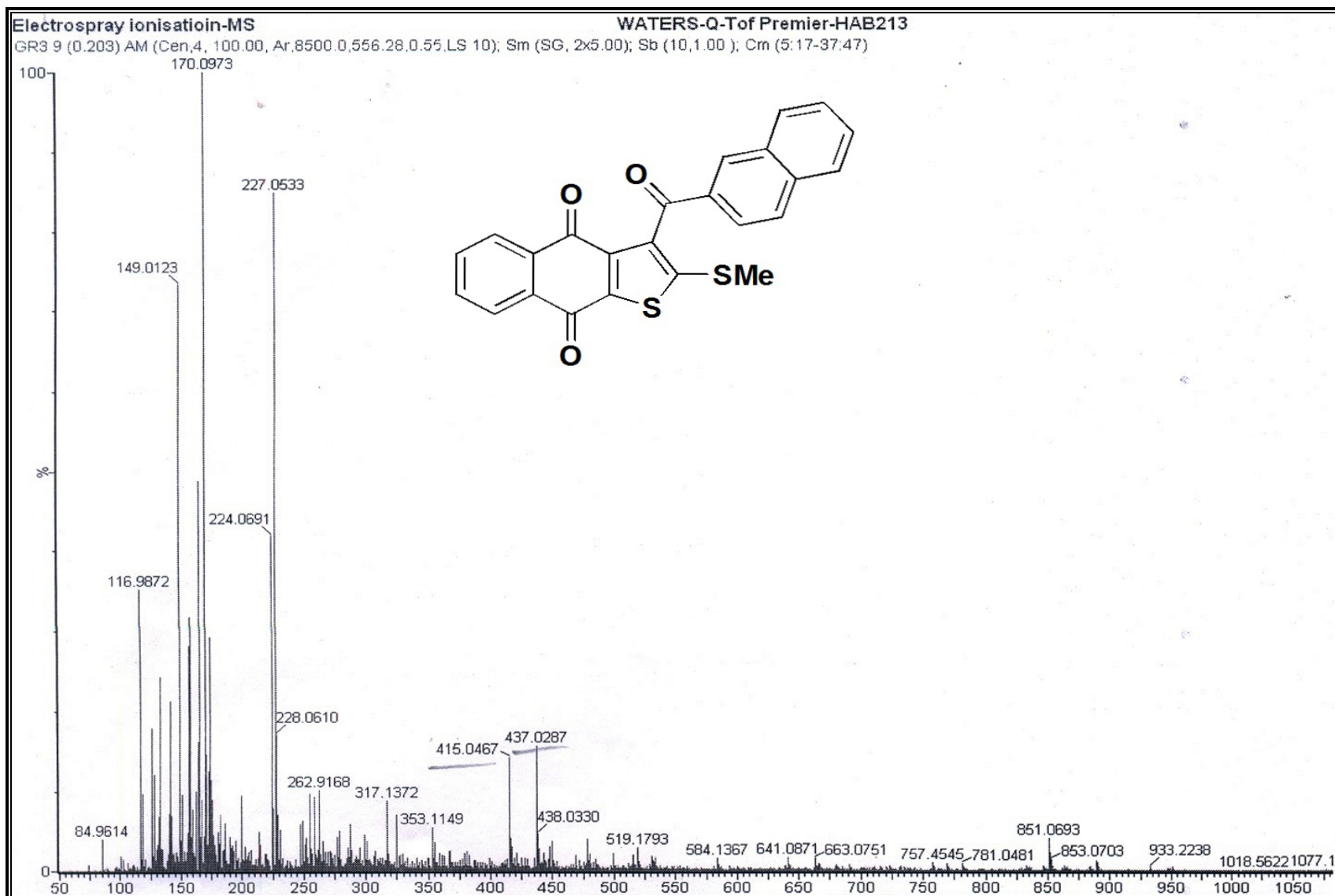
14:36:3517-Apr-2013

GR-101 15 (0.314) AM (Cen,4, 100.00, Ar,8500.0,556.28,0.45,LS 10); Sm (SG, 2x5.00); Sb (10,1.00); Cm (15:17-60:63)

1: TOF MS ES+
8.49e3



HRMS data of 2-Methylthio-3-(naphthalene-2-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3h)



HRMS data of 2-Methylthio-3-(pyridine-3-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3i)

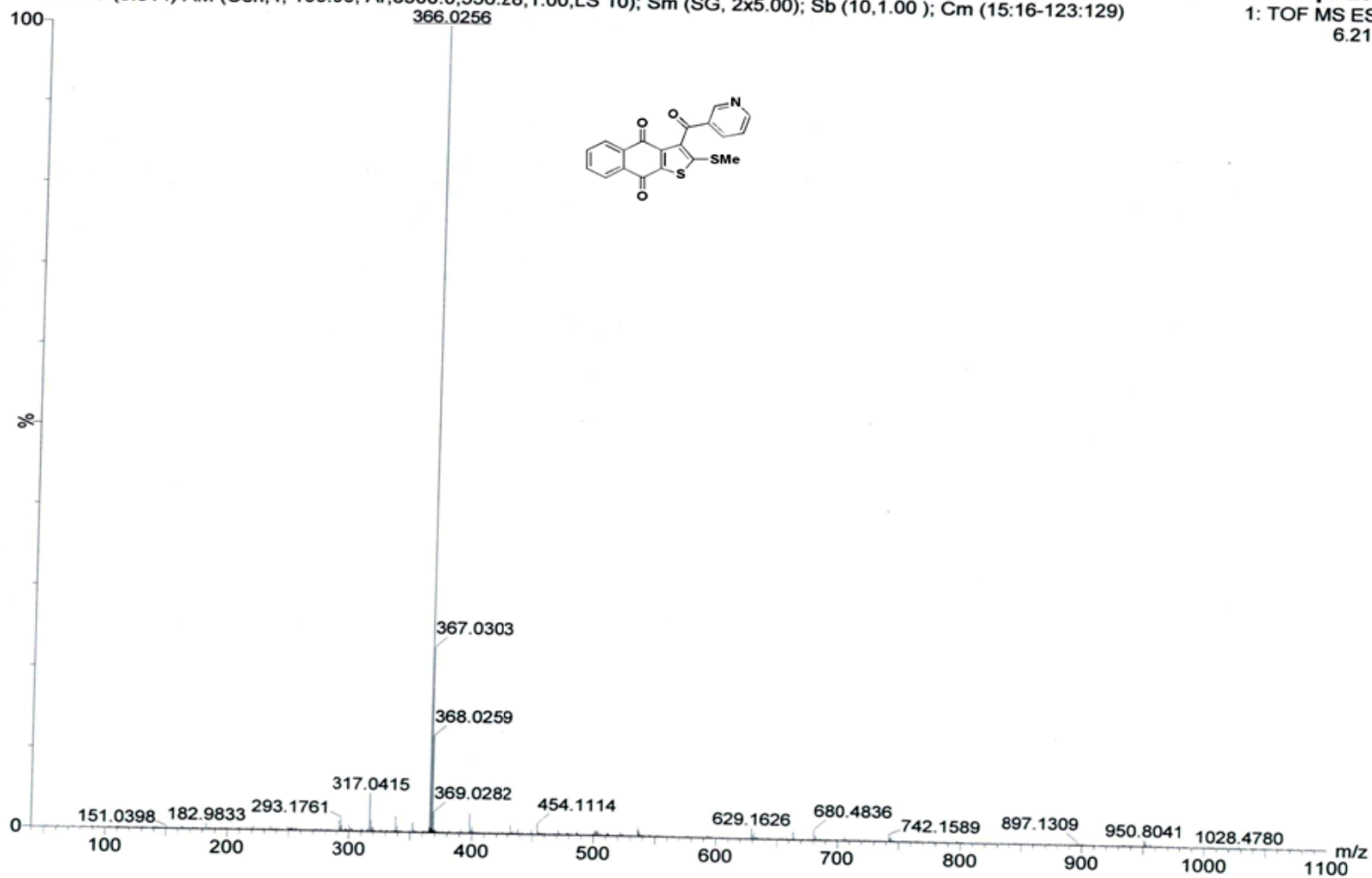
Electrospray ionisation-MS

WATERS-Q-ToF Premier-HAB213

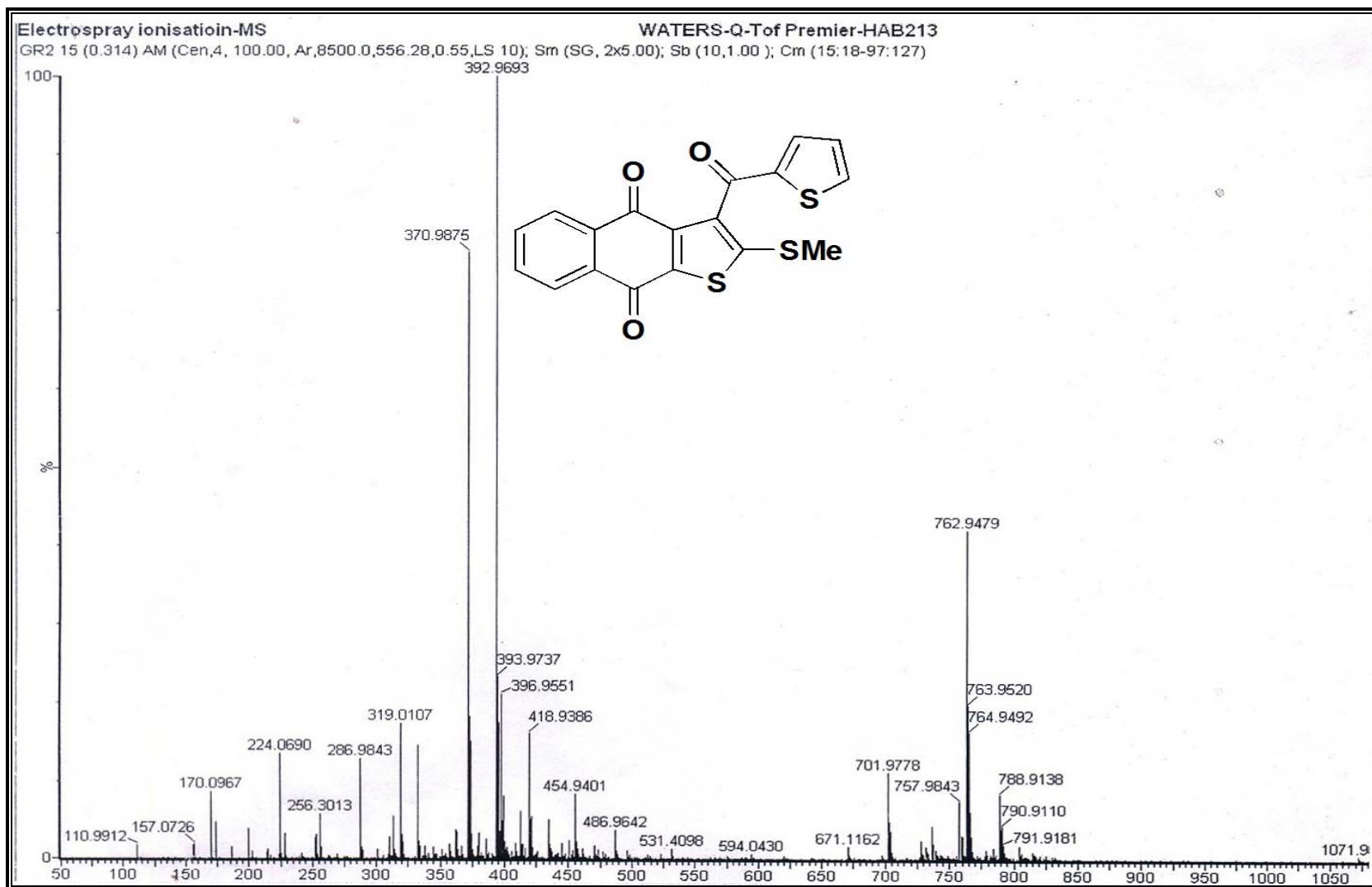
16:34:3217-Apr-2013

GR-102 15 (0.314) AM (Cen,4, 100.00, Ar,8500.0,556.28,1.00,LS 10); Sm (SG, 2x5.00); Sb (10,1.00); Cm (15:16-123:129)

1: TOF MS ES+
6.21e3



HRMS data of 2-Methylthio-3-(thiophene-2-carbonyl)-naphtho[2,3-b]thiophene-4,9-dione (3j)



HRMS data of 3-Benzoyl-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3m)

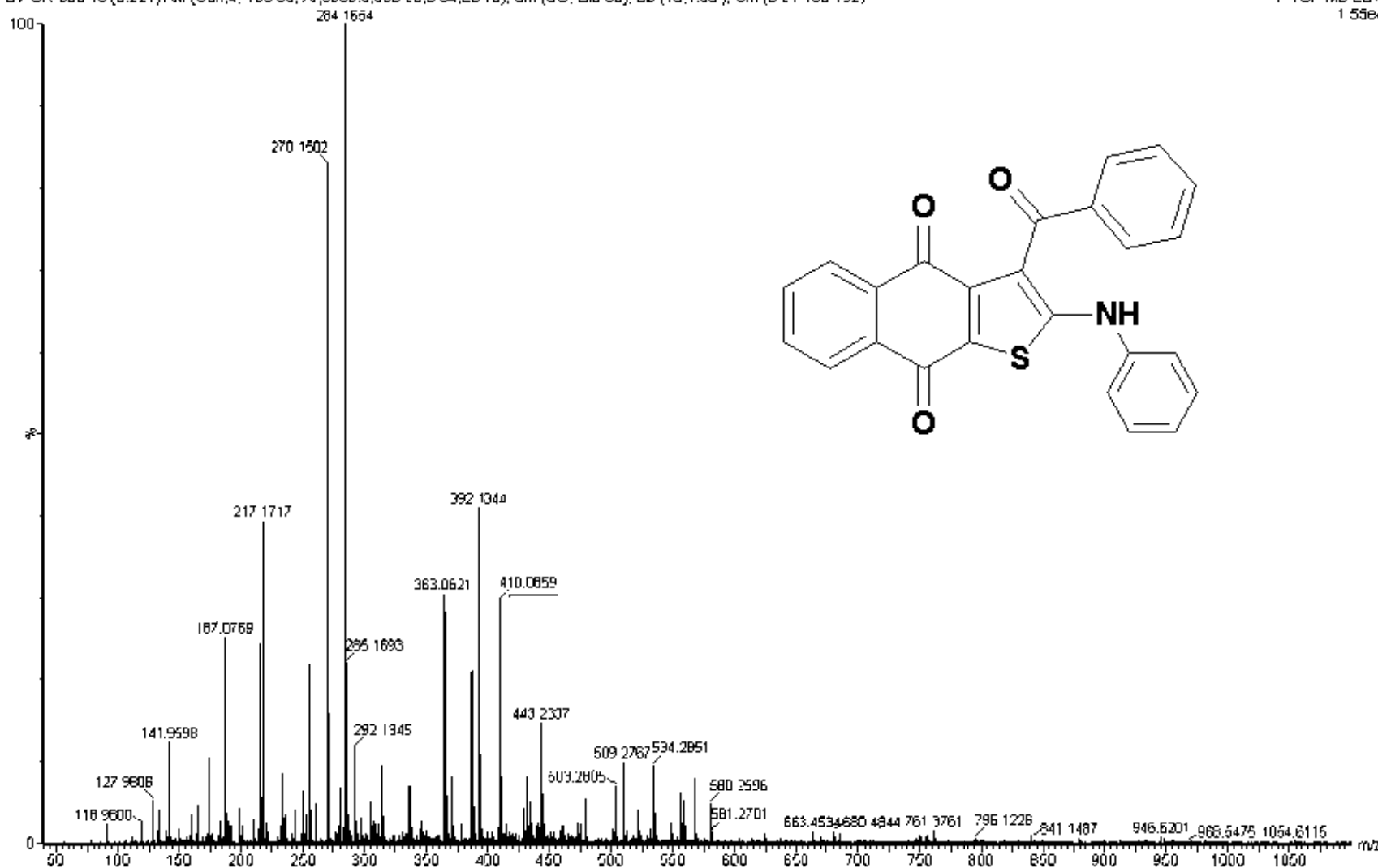
Electrospray ionisation-MS

WATERS-Q-ToF Premier-HAB213

01:18:4514-Dec-2012

SV-GR-500 10 (0.221) AM (Cen.4, 100.00, Ar, 8500.0, 556.28, 0.34, LS 10); Sm (SG, 2x5.00); Sb (10, 1.00); Cm (6.21-138.192)

1 TOF MS ES+
1.55e4



HRMS data of 3-(4-Methoxy-benzoyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3o)

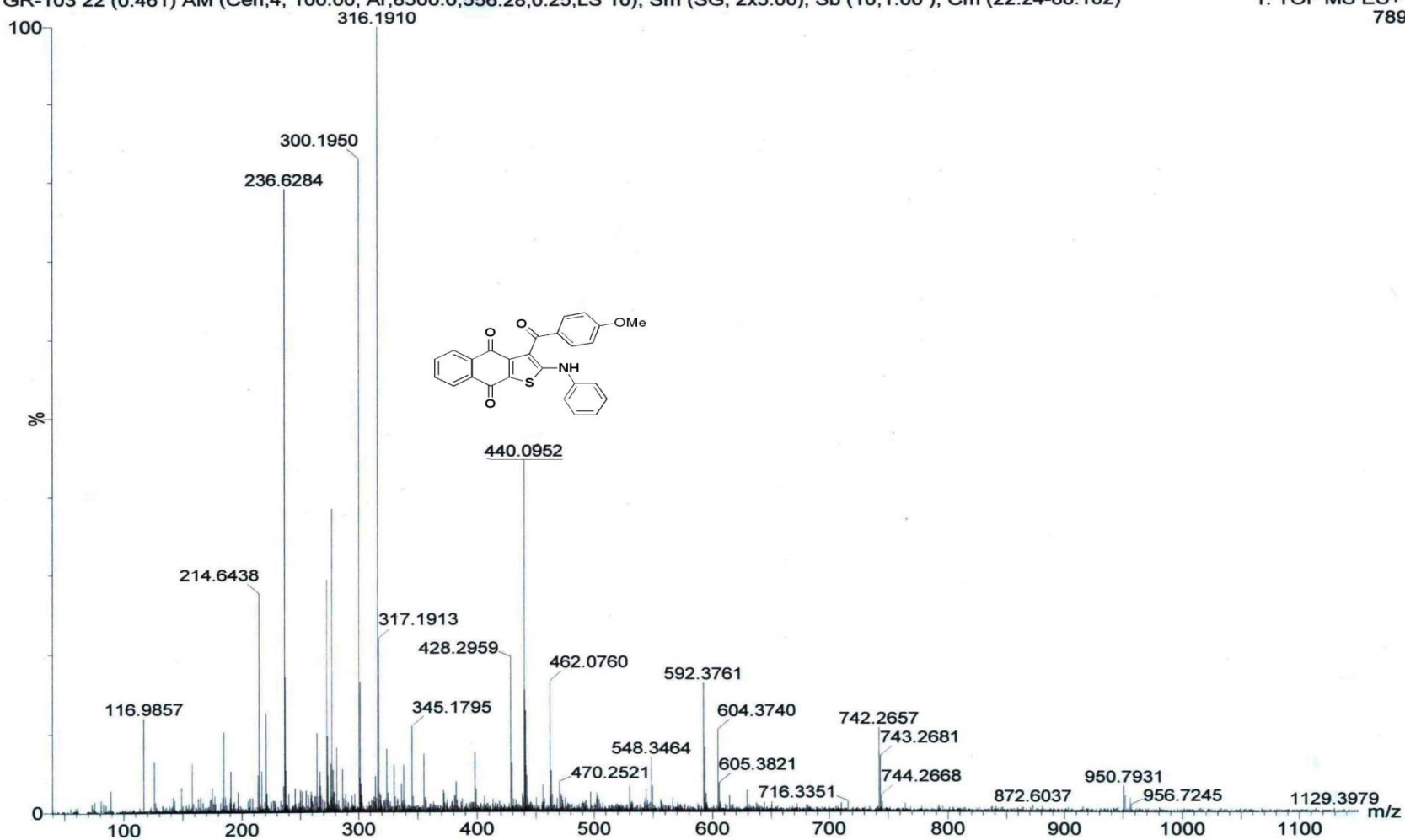
Electrospray ionisation-MS

WATERS-Q-ToF Premier-HAB213

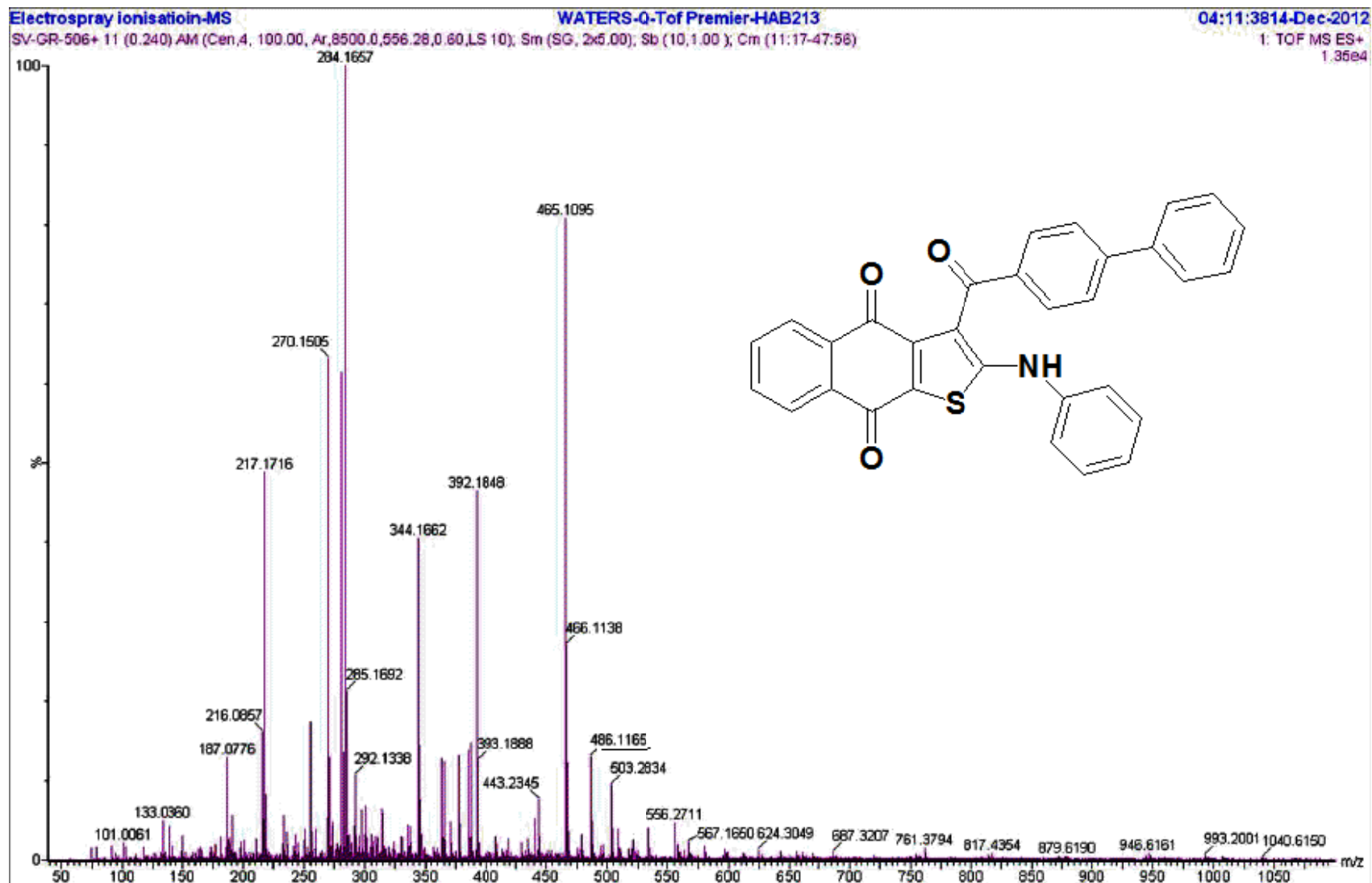
14:30:0517-Apr-2013

GR-103 22 (0.461) AM (Cen,4, 100.00, Ar,8500.0,556.28,0.25,LS 10); Sm (SG, 2x5.00); Sb (10,1.00); Cm (22:24-88:102)

1: TOF MS ES+
789



HRMS data of 3-(Biphenyl-4-carbonyl)-2-phenylamino-naphtho[2,3-b]thiophene-4,9-dione (3p)



HRMS data of 3-(2,2-Dimethyl-propionyl)-2-methylamino-naphtho[2,3-b]thiophene-4,9-dione (3q)

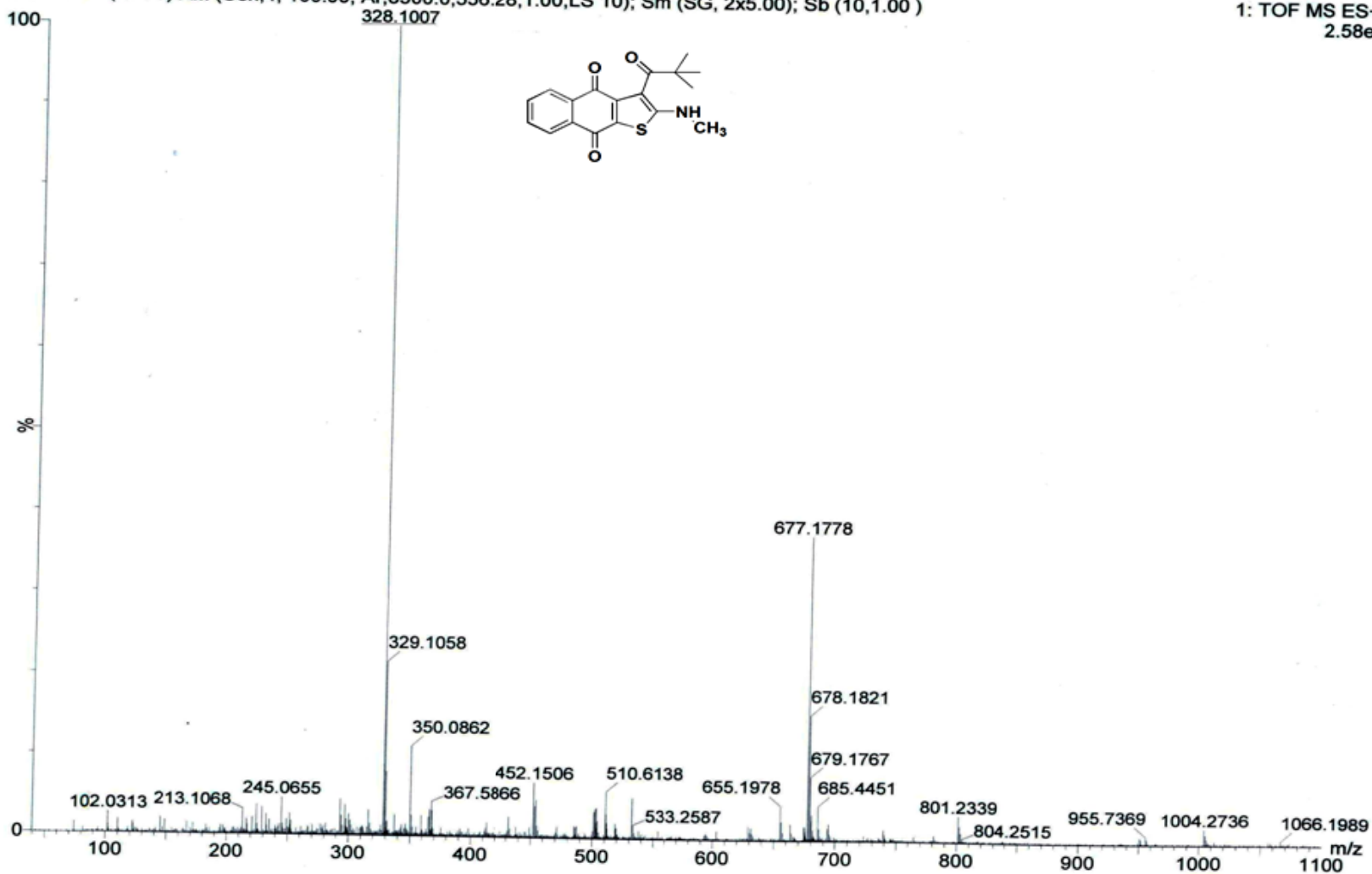
Electrospray ionisation-MS

WATERS-Q-ToF Premier-HAB213

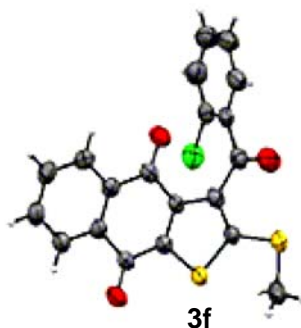
16:38:2717-Apr-2013

GR-104 12 (0.258) AM (Cen.4, 100.00, Ar,8500.0,556.28,1.00,LS 10); Sm (SG, 2x5.00); Sb (10,1.00)

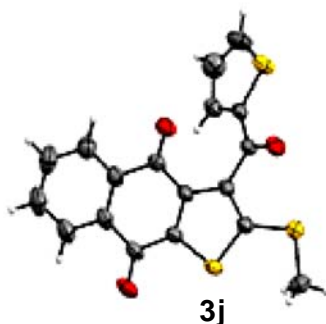
1: TOF MS ES+
2.58e3



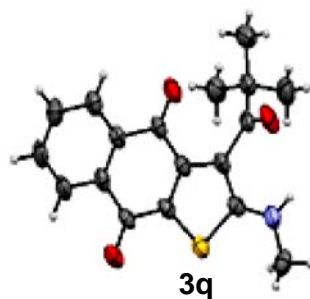
5. Crystallography data of 3f, 3j and 3q



Crystal data for **3f**: $C_{20}H_{11}ClO_3S_2$, Red, $M = 397.98$, Monoclinic, space group $P 1 21/n 1$, $a = 9.1727(12)$, $b = 12.4922(14)$, $c = 15.7956(17)$ Å, $V = 1749.4(3)$ Å³, $\mu = 0.475$ mm⁻¹, $Z = 4$, $T = 293$ K, $F_{000} = 816$, $R = 0.0636$, $wR^2 = 0.1954$. The CCDC deposition number: **CCDC 881391**.



Crystal data for **3j**: $C_{18}H_{10}O_3S_3$, Red, $M = 370.46$, Triclinic, space group $P-1$, $a = 8.245(5)$, $b = 8.504(5)$, $c = 12.515(5)$ Å, $V = 795.2(7)$ Å³, $\mu = 0.480$ mm⁻¹, $Z = 2$, $T = 293$ K, $F_{000} = 380$, $R = 0.0439$, $wR^2 = 0.1285$. The CCDC deposition number: **CCDC 881392**.



Crystal data for **3q**: $C_{18}H_{17}NO_3S$, Red, $M = 327.40$, Triclinic, space group $P -1$, $a = 6.1217(14)$, $b = 11.429(3)$, $c = 11.589(3)$ Å, $V = 793.3(3)$ Å³, $\mu = 0.219$ mm⁻¹, $Z = 2$, $T = 293$ K, $F_{000} = 344$, $R = 0.1058$, $wR^2 = 0.3071$. The CCDC deposition number: **CCDC 915292**.