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Supplementary Information

σ-Bond initiated generation of aryl radicals from aryl diazonium salts

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General Experimental:

CAUTION: Although we had no incidents relating to the stability of the diazonium salts used in this work, care was taken to avoid the use of metal needles and spatulas.

All reactions were performed under air using plastic tubing, plastic syringes, and oven dried glassware. Dimethylsulfoxide (DMSO) was dried over 3 Å molecular sieves. All other solvents and reagents were used as received from commercial sources. Melting points were determined using a Stanford Research Systems Optimelt automated melting point system and are uncorrected. Infrared spectra were acquired on a Bruker ALPHA FT-IR spectrometer as thin films, or neat. Absorption maxima are expressed in wavenumbers (cm^{-1}). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, $(CD_3)_2CO$, CD_3CN, or $(CD_3)_2SO$ on a Bruker AVANCE III 500, a Bruker AVANCE III 400 and a Bruker AVANCE 300 spectrometer (^{1}H frequencies 500, 400, 300; ^{13}C frequencies 125, 100 and 75 MHz respectively). ^{1}H chemical shifts are expressed as parts per million (ppm) with residual chloroform (δ 7.26) as an internal reference and are reported as chemical shift (δ_H); relative integral; multiplicity (s = singlet, br = broad, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, m = multiplet); and coupling constants (*J*) reported in Hz. ^{13}C NMR chemical shifts are expressed as parts per million (ppm) with residual chloroform (δ 77.1) as internal reference and are reported as chemical shift (δ_C). High resolution mass spectra were recorded on a Bruker Apex II Fourier Transform Ion Cyclotron Resonance mass spectrometer with a 7.0 T magnet, fitted with an off-axis Analytica electrospray source. Column chromatography was performed using Grace Davison, Merck, or Scharlau 40-60 µm (230-400 mesh) silica gel using commercial solvents. Analytical thin layer chromatography was performed using preconditioned plates (Merck TLC silica gel 60 F_{254} on aluminium) and visualised using UV light (254 nm and 365 nm), ethanolic anisaldehyde solution.

General procedure A: Preparation of aryl diazonium tetrafluoroborates

To a solution of the requisite aniline (4.87 mmol) in water (1.1 mL) and aqueous tetrafluoroboric acid (35% w/w; 2.4 mL) at 0°C , was dropwise added a solution of sodium nitrite (353 mg, 5.12 mmol) in water (0.8 mL). The mixture was stirred for 40 min, then diethyl ether (10 mL) was added and precipitate was collected by filtration. The solid was washed with diethyl ether (20 mL) and dried under vacuum.

Benzenediazonium tetrafluoroborate (1) as a light-pink solid (94%). ^{1}H NMR (500 MHz; CD_3CN) δ: 8.51-8.53 (2H, m), 8.27-8.24 (1H, m), 7.96-7.91 (2H, m); ^{13}C NMR (126 MHz; CD_3CN) δ: 142.5, 133.0, 132.4; ^{19}F NMR (471 MHz; CD3CN) δ: -150.8 ; ν_{max}/cm^{-1}: 3106, 2306, 1540, 1356, 1037, 866,743, 525; LRMS (ESI+) m/z : 297.07. Data consistent with literature.[1]

2-(Methylthio)benzenediazonium tetrafluoroborate (37) as a yellow solid (90%). ^{1}H NMR (500 MHz; CD_3CN) δ: 8.43 (1H, dd, J_1 = 1.4 Hz, J_2 = 8.5 Hz), 8.11-8.15 (1H, m), 7.86 (1H, d, *J* = 8.2 Hz), 7.63-7.67 (1H, m), 2.83 (3H, s); ^{13}C NMR (126 MHz; CD_3CN) δ: 149.5, 141.8, 133.9, 130.0, 128.6, 16.3 ^{19}F NMR (471 MHz; CD3CN) δ: −151.4; ν_{max}/cm^{-1}: 2257, 1577, 1548, 1453, 1304, 1258, 1037, 764; LRMS (ESI+) m/z : 389.01, 151.01 Data consistent with literature.[2]

4-Methoxybenzenediazonium tetrafluoroborate as a purple solid (85%). ^{1}H NMR (500 MHz; CD_3CN) δ: 8.42–8.40 (2H, m), 7.35–7.34 (2H, m), 4.06 (3H, s); ^{13}C NMR (126 MHz; CD_3CN) δ: 171.2, 136.7, 118.8, 102.5, 58.4; ^{19}F NMR (471 MHz; CD3CN) δ: −151.7; ν_{max}/cm^{-1}: 3120, 2252, 1583, 1569, 1291, 1051, 1002; LRMS (ESI+) m/z : 357, 135 . Data consistent with literature.[1]

4-Nitrobenzenediazonium tetrafluoroborate (12) as a yellow solid (87%). ^{1}H NMR (500 MHz; $(CD_3)_2CO$) δ: 9.19–9.17 (2H, m), 8.87–8.84 (2H, m); ^{13}C NMR (126 MHz; $(CD_3)_2CO$) δ: 155.1, 135.9, 127.4, 122.5; ^{19}F NMR (471 MHz; $(CD_3)_2CO$) δ: −150.7; ν_{max}/cm^{-1}: 3119, 3106, 2307, 1539, 1359, 1317, 1040 LRMS (ESI+) m/z :387, 150 . Data consistent with literature.[1]

Biphenyl-2-diazonium tetrafluoroborate (44): as beige solid (86%). ^{1}H NMR (400 MHz; CD_3CN) δ: 8.62 (1H, d, *J* = 8.4 Hz), 8.34 (1H, t, *J* = 8.4 Hz), 8.00 (1H, d, *J* = 8.0 Hz), 7.96 (1H, t, *J* = 8.0 Hz); ^{13}C NMR (100 MHz; CD_3CN) δ: 147.1, 143.1, 134.4, 133.7, 133.6, 132.4, 131.7, 130.1, 129.7; ^{19}F NMR (377 MHz; CD3CN): -151.6; LRMS (ESI+) m/z : 150.03

4-Chlorobenzenediazonium tetrafluoroborate: Isolated as white solid (94%); ^{1}H NMR (400 MHz; CD_3CN) δ: 8.50 (2H, d, *J* = 8.8 Hz), 7.96 (2H, d, *J* = 9.2 Hz); ^{13}C NMR (100 MHz; CD_3CN) δ: 149.2, 133.9, 132.3, 112.9; ^{19}F NMR (377 MHz; CD3CN): -151.2; ν_{max}/cm^{-1}: 3109,, 2289, 1561, 1023, 834, 521; LRMS (ESI) m/z : 313.93 [M-]

General procedure B: Preparation of Hantzsch esters

To a mixture of ethyl, benzyl or allyl acetoacetate (80 mmol) and aldehyde (40 mmol) was added ammonium acetate (60 mmol). The mixture was stirred at 60°C for 1 hour, the cooled to room temperature. The precipitate was collected, washed with water (30 mL) and collected by filtration. The solid was recrystallised from ethanol to give corresponding Hantzsch ester.

General procedure C: Alternative preparation of Hantzsch esters

To a mixture of ethyl acetoacetate (20 mmol) and aldehyde (10 mmol) was added ammonium acetate (15 mmol). Mixture was stirred at 60°C for 17 hours. The reaction mixture was transferred to separating funnel and diluted with dichloromethane (20 mL) and water (50 mL), was added and extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum and the residue was purified by flash chromatography on silica gel, using hexanes/ethyl acetate as eluent.

Diethyl Hantzsch Ester (4): using general procedure B; as a yellow solid (91%). ^{1}H NMR (300 MHz; $CDCl_3$) δ: 5.36 (1H, brs), 4.17 (4H, q, *J* = 7.0 Hz), 3.27 (2H, s), 2.19 (6H, s), 1.29 (6H, t, *J* = 7.1 Hz); ^{13}C NMR (75 MHz; $CDCl_3$) δ: 168.0, 144.9, 99.5, 59.6, 24.8, 19.1, 14.4; ν_{max}/cm^{-1}: 3343, 2980, 1693, 1647, 1511, 1321, 1227, 1059; LRMS (ESI+) m/z : 276.12 $[M+Na]^+$. Data consistent with literature.[3]

Diethyl Hantzsch Ester-*d_2* (4a): using general procedure C; as a yellow solid (88%). m.p. 190-192 °C; ^{1}H NMR (400 MHz; $CDCl_3$) δ: 5.33 (1H, brs), 4.15 (4H, q, *J* = 7 Hz), 2.18 (6H, s), 1.27 (6H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz; $CDCl_3$) δ: 168.2, 145.0, 99.4, 59.7, 24.2 (t, *J* = 20 Hz), 19.2, 14.52; ν_{max}/cm^{-1}: 3344, 2986, 1693, 1646, 1500, 1367, 1326, 1180, 1099, 736; HRMS (ESI+) m/z: 278.13544 $[M+Na]^+$

Dibenzyl Hantzsch Ester (6): using general procedure B; as a yellow solid (90%). ^{1}H NMR (300 MHz; $CDCl_3$) δ: 7.38-7.34 (10H, m), 5.68 (1H, brs) 5.20 (4H, s), 3.44 (2H, s), 2.20 (6H, s), ^{13}C NMR (75 MHz; $CDCl_3$) δ: 167.7, 145.8, 136.9, 128.5, 127.8, 127.7, 99.2, 65.5, 25.0, 19.1 ; ν_{max}/cm^{-1} : 3347, 1676, 1505, 1246, 1123, 1013, 751, 719, 690; LRMS (APCI+) m/z: 378.15 $[M+H]^+$. : Data consistent with literature.[4]

Diallyl Hantzsch Ester (8): using general procedure B; as a yellow solid (92%). ^{1}H NMR (300 MHz; $CDCl_3$) δ: 6.03-5.90 (2H, m), 5.37- 5.19 (4H, m), 4.63 (4H, d, J = 5.4 Hz) 3.34 (2H, s), 2.21 (6H, s); ^{13}C NMR (75 MHz; $CDCl_3$) δ: 167.5, 145.3, 132.9, 117.2, 99.3, 64.4, 24.8, 19.2; ν_{max}/cm^{-1}: 3348, 1695, 1659, 1509, 1301, 1217, 1117, 1087, 998, 931, 752; LRMS (APCI+) m/z: 278.10 $[M+H]^+$. Data consistent with literature.[3b]

Diethyl 4-(2-furyl) Hantzsch ester (9): Using General procedure B; as beige solid (91%). ^{1}H NMR (500 MHz; $CDCl_3$) δ: 6.25 (1H, t, J = 2.0 Hz), 6.04 (1H, s), 5.98 (1H, d, J = 3.0 Hz), 5.25 (1H, s), 4.15-4.27 (4H, m), 2.37 (6H, s), 1.31 (6H, t, J = 7.0 Hz); ^{1}H NMR (500 MHz; $CDCl_3$) δ: 167.5, 158.7, 1145.2, 140.8, 110.0, 104.4, 100.7, 59.82, 33.4, 19.4, 14.3; ν_{max}/cm^{-1}:3343, 1698, 1645, 1476, 1202, 1116, 1094, 1006, 805, 729; LRMS (APCI+) m/z: 320.12 $[M+H]^+$.

Diethyl 2,6-dimethyl-4-(2-nitrophenyl) Hantzsch Ester (10): Isolated as yellow solid (65%); ^{1}H NMR (400 MHz; $CDCl_3$) δ: 7.72 (1H, d, J = 8.4 Hz), 7.52 (1H, d, J = 7.84 Hz), 7.45 (1H, t, J = 7.94 Hz), 7.24 (1H, t, J = 7.44 Hz), 5.84 (1H, s), 5.66 (1H, s), 4.14-4.10 (2H, m), 4.01-3.95 (2H, m), 2.32 (6H, s), 1.15 (6H, t, J = 7.1 Hz); ^{13}C NMR (100 MHz; $CDCl_3$) δ: 167.3, 144.4, 142.6, 132.8, 131.4, 127.0, 124.0 104.1, 60.1, 34.8, 19.7, 14.2; ν_{max}/cm^{-1} : 3327, 2977, 1671, 1526, 1487, 1276, 1207, 1096, 1018, 713; LRMS (ESI+) m/z : 397.12 $[M+Na]^+$.

Dibenzyl 4-(2'-Chloro-5'-nitrophenyl) Hantzsch Ester (11): using general procedure C; as a yellow solid (65%). m.p. 153–155 °C; ^{1}H NMR (500 MHz; $CDCl_3$) δ: 8.16 (1H, d, J = 2.5 Hz), 7.86 (1H, dd, J_1 = 2.5 Hz, , J_2 = 8.5 Hz), 7.30-7.7.18 (11 H, m), 5.98 (1H, s), 5.52 (1H, s), 5.08 (4H, dd, J_1 = 12Hz, J_2 = 12.5 Hz), 2.34 (6H, s); ^{13}C NMR (125 MHz; $CDCl_3$) δ: 166.8, 147.1, 146.6, 145.5, 139.8, 136.2, 130.3, 128.4, 128.3, 128.0, 126.8, 122.0, 102.5, 65.7, 38.6, 19.8; ν_{max}/cm^{-1}: 3348, 1579, 1459, 1344, 1297, 1199, 1106, 1096, 739, 695, 585; HRMS (ESI+) m/z: 555.12948 $[M+Na]^+$

General procedure D: preparation of N-Methyl Hantzsch Esters

In a round bottom flask Hantzsch ester (3.3 mmol) was dissolved in dry THF (30ml) and stirred under argon at 0^{o}C for 5 min. Sodium hydride was added and stirred for additional 10 min, followed by dropwise addition of iodomethane. The reaction mixture was allowed to warm to room temperature and stirred for 15 min. The reaction mixture was then refluxed overnight followed by addition of 30 ml of water and extraction with ethyl acetate (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, concentrated under vacuum and the product as purified by flash chromatography on silica gel, using hexanes/ethyl acetate as eluent.

***N*-Methyl diethyl Hantzsch Ester (5):** Isolated as an orange oil (86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.19 (4H, q, J = 7.0 Hz), 3.17 (5H, s), 2.39 (6H, s), 1.31 (6H, t, J = 7.2 Hz) ; ^{13}C NMR (101 MHz; $CDCl_3$): 168.0, 150.5, 101.6, 59.8, 33.8, 24.0, 15.9, 14.4; ν_{max}/cm^{-1}: 2981, 1686, 1642, 1582, 1384, 1307, 1286, 1196, 1164, 1136, 1106, 2053; LRMS (ESI+) m/z : 290.04 $[M+Na]^+$.

***N*-Methyl dibenzyl Hantzsch Ester (7):** as an orange oil (72%); ^{1}H NMR (300 MHz; $CDCl_3$) δ: 7.27-7.36 (10 H, m), 5.10 (4H, s), 3.28 (2H, s), 3.15 (3H, s), 2.40 (6H, s); ^{13}C NMR (75 MHz; $CDCl_3$) δ: 167.6, 151.3, 136.9, 128.4, 127.7, 127.6, 101.3, 65.5, 33.9, 23.9, 16.0; ν_{max}/cm^{-1}: 3031, 2953, 1682, 1638, 1576, 1381, 1302, 1285, 1193, 1154, 1132, 1102, 1043, 989, 733, 695, 511; HRMS (ESI+) m/z: 414.17061 $[M+Na]^+$

General procedure E: preparation of silyl enol ethers

A round bottom flask containing a mixture of ketone (20mmol) and sodium iodide (24mmol) was evacuated and filled with nitrogen, and dry acetonitrile (30ml) and pentane (20ml) were added and stirred for 5 min at room temperature. To the resulting solution, triethylamine (30mmol) was added, followed by chlorotrimethylsilane (24mmol). The reaction mixture was stirred for 40 min at room temperature, reaction completion was monitored by TLC. The reaction was quenched with cold saturated solution of ammonium chloride and extracted with cold pentane (3 × 100 mL). The residue was concentrated under reduced pressure and regenerated ketone was removed by filtration.

Trimethyl((1-(4-nitrophenyl)vinyl)oxy)silane (49): as a yellow oil (72%); NMR (300 MHz; $CDCl_3$) δ: 8.16 (2H, d, *J* = 9.0 Hz), 7.72 (2H, d, *J* = 9.0 Hz), 5.07 (1H, d, *J* = 2.4 Hz), 4.61 (1H, d, *J* = 2.1 Hz), 0.29 (9H, s); ^{13}C NMR (75 MHz; $CDCl_3$) δ: 153.8, 147.6, 143.7, 125.9, 123.5, 94.5, 0.0; ν_{max}/cm^{-1}: 2960, 1559, 1517, 1491, 1309, 1291, 1252, 1103, 1009, 841, 759, 701; LRMS (APCI+) m/z: 238.08$[M+H]^+$.

Trimethyl((1-(4-methoxyphenyl)vinyl)oxy)silane (51): as a yellow oil (80%); NMR (300 MHz; $CDCl_3$) δ: 7.39 (2H, d, *J* = 8.7 Hz), 6.70 (2H, d, *J* = 9.0 Hz), 4.67 (1H, d, *J* = 1.5 Hz), 4.21 (1H, d, *J* = 1.5 Hz), 3.63 (3H, s), 0.14 (9H, s); ^{13}C NMR (75 MHz; $CDCl_3$) δ: 159.7, 155.4, 130.2, 126.5, 113.3, 99.3, 55.1, 0.0; ν_{max}/cm^{-1}: 2958, 1606, 1509, 1291, 1248, 1174, 1108, 1033, 1008, 834, 691, 552; LRMS (APCI+) m/z: 223.13 $[M+H]^+$.

General procedure F: Gomberg-Bachmann-Hey arylation reactions

A solution of the heterocyclic compound (2.6 mmol) in dry DMSO (1 mL) was added to a round bottom flask equipped with stirrer bar. For the reaction of pyridine and quinolone, trifluoroacetic acid (26 mmol) was added to the flask. In the meantime, aryl diazonium tetrafluoroborate (0.39 mmol) and HE (0.26 mmol) were separately dissolved in dry DMSO (3 mL) and drawn up into 3 ml plastic syringes. Both syringes were placed in a syringe pump and the solutions were added to the round bottom flask (flow rate 1 mL/min). After addition, the reaction mixture was transferred to separating funnel, diluted with diethyl ether (10 mL) and washed with water (40 mL). The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexanes / diethyl ether /ethyl acetate as eluent.

2-(4'-Nitrophenyl)furan (14): Isolated as yellow solid (93%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (2H, d, *J* = 9.0 Hz), 7.79 (2H, d, *J* = 9.0 Hz), 7.57 (1H, d, *J* = 1.3 Hz), 6.87 (1H, d, *J* = 3.4 Hz), 6.55 (1H, dd, *J* = 3.4, 1.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.8, 146.5, 144.2, 136.4, 124.3, 123.9, 112.4, 108.9; ν_{max}/cm^{-1}:

2930, 2920, 2851, 1601, 1507, 1335, 1109, 1018; LRMS (ESI+) m/z: 212.02 $[M+Na]^+$ Data consistent with literature.[5]

2-Phenylfuran (15): Isolated as a colourless liquid (81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.54–7.57 (2H, m), 7.34 (1H, s), 7.25 (2H, t, J = 7.6 Hz), 7.10–7.15 (1H, m), 6.52 (1H, d, J = 3.0 Hz), 6.34–6.35 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 154.0, 142.1, 130.9, 128.7, 127.3, 123.8, 111.6, 104.9; ν_{max}/cm^{-1} : 3077, 3040, 1730, 1687, 1608, 1506, 1477, 1448, 1278; LRMS (APCI+) m/z: 145.07 $[M+H]^+$. Data consistent with literature.[5]

2-(4′-Methoxyphenyl)furan (16): Isolated as a white solid (86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.52–7.55 (2H, m), 7.36 (1H, d, J = 1.5 Hz,), 6.84–6.88 (2H, m), 6.44 (1H, d, J = 3.3 Hz), 6.37–6.38 (1H, m), 3.76(3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.0, 154.0, 141.4, 125.2, 124.1, 114.1, 111.5, 103.4, 55.3; ν_{max}/cm^{-1}: 3005, 2974, 2939, 1617, 1589, 1570, 1514, 1486, 1297, 1253: LRMS (APCI+) m/z: 175.06 $[M+H]^+$. Data consistent with literature.[5]

2-(4′-Nitrophenyl)thiophene (17): Isolated as a yellow solid (51%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.24 (2H, d, J = 8.7 Hz), 7.44 (2H, d, J = 8.7 Hz), 7.47 (1H, dd, J = 4.6, 1.0 Hz), 7.43 (1H, d, J = 5.1 Hz), 7.15 (1H, t, J = 4.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 146.6, 141.6, 140.6, 128.7, 127.7, 126.0, 125.7, 124.4; ν_{max}/cm^{-1}: 3106, 1592, 1515, 1491, 1341, 1300, 1286, 1181; LRMS (ESI+) m/z: 228.03 $[M+Na]^+$. Data consistent with literature.[5]

2-(4′-Methoxyphenyl)thiophene (18): Isolated as a white solid (25%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.53–7.56 (2H, m), 7.19–7.21 (2H, m), 7.05–7.07 (1H, m), 6.92 (2H, d, J = 8.7 Hz), 3.86 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 159.2, 144.4, 127.9, 127.2, 123.8, 122.1, 114.3, 55.4; ν_{max}/cm^{-1}: 1605, 1503, 1432, 1293, 1262, 1185, 1112, 1032; LRMS (APCI+) m/z: 191.04[$M+H]^+$. Data consistent with literature.[6]

2-(4′-Nitrophenyl)pyrrole (19): Isolated as an orange solid (35%). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 10.87 (1H, brs), 7.36 (2H, d, J = 8.8 Hz), 7.01 (2H, d, J = 8.8 Hz), 6.21 (1H, s), 6.00 (1H, s), 5.40 (1H, s); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 144.1, 139.2, 129.2, 124.3, 123.3, 122.5, 110.3, 109.8; ν_{max}/cm^{-1}: 1975, 1600, 1493, 1328, 1110, 1040; LRMS (APCI+) m/z: 189.05$[M+H]^+$. Data consistent with literature.[7]

2-(4′-Chlorophenyl)pyrrole (20): Isolated as a yellow solid (72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ:9.29 (1H, brs), 7.73 (2H, d, J = 8.4 Hz), 7.42 (2H, d, J = 8.8 Hz), 7.02 (1H, d, J = 3.2 Hz), 6.94(1H, s), 6.40 (1H, t, J = 3.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.2, 145.9, 135.3, 129.3, 123.4, 122.0, 116.0, 111.9; ; ν_{max}/cm^{-1}: 3434, 3222, 1360, 1122, 1084, 1029,736; LRMS (APCI+) m/z: 178.04$[M+H]^+$.

***N*-Boc-2-(4′-Nitrophenyl)pyrrole (21):** Isolated as a pale-yellow solid (84%).^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.40 (2H, d, J = 6.0 Hz), 6.81 (2H, d, J = 9.0 Hz), 6.64 (1H, s), 5.66 (1H, s), 5.53 (1H, s), 0.53 (9H, s); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 148.4, 146.0, 140.1, 132.3, 129.6, 124.5, 122.8, 116.7, 111.3, 84.3, 27.1; ν_{max}/cm^{-1}: 1745, 1598, 1516, 1372, 1343, 1312, 1146; LRMS (APCI+) m/z: 289.14$[M+H]^+$. Data consistent with literature.[5]

***N*-Boc-2-(4′-Methoxyphenyl)pyrrole (22):** Isolated as a yellow oil (77%). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.25–7.23 (1H, m), 7.19 (2H, d, J = 9.0 Hz), 6.81 (2H, d, J = 8.7 Hz), 6.13 (1H, t, J = 3.3 Hz), 6.06–6.05 (1H, m), 3.75 (3H, s), 1.31 (9H, s); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 158.9,154.9, 149.4, 134.9,

130.4, 126.9, 122.2, 114.0, 110.4, 83.4, 55.3, 27.7; ν_{max}/cm^{-1}: 1736, 1614, 1568, 1515, 1475, 1247; LRMS (APCI+) m/z: 274.16[M+H]$^+$. Data consistent with literature.[8]

2-(4'-Nitrophenyl)benzofuran (23): Isolated as a yellow solid (40%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.23 (2H, d, J = 9.0 Hz), 7.92 (2H, d, J = 9.0 Hz), 7.57 (1H, d, J = 7.5 Hz), 7.48 (1H, d, J = 8.1 Hz), 7.29–7.32 (1H, m), 7.16–7.27 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 155.5, 153.3, 147.3, 136.3, 128.7, 125.8, 125.2, 124.3, 123.6, 121.6, 111.5, 105.1; ν_{max}/cm^{-1}: 1572, 1514, 1489, 1448, 1336, 1301, 1279, 1251, 1203, 1181, 1168, 1146, 1109; LRMS (APCI+) m/z: 240.09 [M+H]$^+$. Data consistent with literature.[9]

2-(4'-Methoxyphenyl)benzofuran (24): Isolated as a white solid (16%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (2H, d, J = 8.8 HZ), 7.54-7.7.57 (1H, m), 7.49-7.51 (1H, m), 7.27-7.20 (2H, m), 6.98 (2H, d, J = 8.8 Hz), 6.89 (1H, s), 3.87 (3H, s) ; ^{13}C NMR (101 MHz, CDCl) δ: 160.0, 159.01, 154.7, 129.5, 126.4, 123.7, 123.4, 122.8, 120.6, 114.3, 111.0, 99.7, 55.4 ; ν_{max}/cm^{-1}: 2959, 2916, 2837, 1606, 1502, 1451, 1245, 1038, 1022, 835, 779, 744, 521; LRMS (APCI+) m/z: 225.05 [M+H]$^+$. Data consistent with literature.[9-10]

2-(4'-Nitrophenyl)indole (25): Isolated as a yellow oil (50%). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 11.06 (1H, s), 7.54 (2H, d, J = 8.9 Hz), 7.34 (2H, d, J = 8.9 Hz), 6.83 (1H, d, J = 7.6 Hz), 6.67 (1H, d, J = 7.9 Hz), 6.38–6.43(2H, m), 6.26 (1H, t, J = 7.5 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 145.8, 138.5, 137.9, 135.1, 128.3, 125.4, 124.3, 123.1, 120.8, 119.9, 111.7, 102.4; ν_{max}/cm^{-1}: 3398, 2164, 2032, 1966, 1957, 1599, 1511, 1338, 1310, 1112; LRMS (APCI+) m/z: 239.08 [M+H]$^+$. Data consistent with literature.[11]

2-(4'-Methoxyphenyl)indole (26): Isolated as a white solid (41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.24 (1H, brs), 7.61-7.59 (3H, m), 7.38 (1H, dd, J_1 = 0.5 Hz, J_2 = 8.0 Hz), 7.19-7.15 (1H, m), 7.13-7.10 (1H, m), 7.99 (2H, d, J = 8.5 Hz), 6.72 (1H, d, J = 1.5 Hz), 3.86 (3H, s) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ: 159.4, 138.0, 136.7, 129.5, 126.5, 125.2, 121.9, 120.4, 120.2, 114.5, 110.7, 98.9, 55.4 ; ν_{max}/cm^{-1}: 2368, 2118, 2000, 1500, 1431, 1248, 1026, 835, 785, 529; LRMS (APCI+) m/z: 224.09 [M+H]$^+$. Data consistent with literature.[12]

2-Phenylpyridine (27): Isolated as a brown oil (68%).^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.70 (1H, d, J = 4.7 Hz), 7.98–8.01 (2H, m), 7.71–7.75 (2H, m), 7.41–7.50 (3H, m), 7.20–7.25 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 157.5, 149.7, 139.4, 136.7, 128.9, 128.7, 126.9, 122.1, 120.6; ν_{max}/cm^{-1}: 1580, 1564, 1467, 1424, 1297, 1269, 1152; LRMS (APCI+) m/z: 156.08 [M+H]$^+$. Data consistent with literature.[13]

2-(4'-Methoxyphenyl)pyridine (28): Isolated as a brown oil (70%).^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.57 (1H, d, J = 3.9 Hz), 7.87 (2H, d, J = 8.5 Hz), 7.56–7.65 (2H, m), 7.08–7.10 (1H, m), 6.91 (2H, d, J = 8.7 Hz), 3.77 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.5, 157.1, 149.5, 136.7, 132.0, 128.2, 121.4, 119.8, 114.1, 55.3; ν_{max}/cm^{-1}: 1604, 1581, 1564, 1514, 1461, 1433, 1307, 1272, 1245, 1176; LRMS (APCI+) m/z: 186.10 [M+H]$^+$. Data consistent with literature.[14]

2-Phenylquinoline (29): Isolated as a beige solid (38%).^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.14–8.20 (4H, m), 7.79–7.87 (2H, m), 7.68–7.74 (1H, m), 7.42–7.54(4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 157.4, 148.3, 139.7, 136.7, 129.8, 129.7, 129.3, 128.9, 127.6, 127.5, 127.2, 126.3, 119.0; ; ν_{max}/cm^{-1}: 2043, 2021, 1965, 1491, 1448; LRMS (APCI+) m/z: 206.10 [M+H]$^+$. Data consistent with literature.[13b]

2-(4'-Methoxyphenyl)quinolone (30): Isolated as a beige solid (34%).^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.13–8.17 (4H, m), 7.80 (2H, t, J = 8.2 Hz), 7.70 (1H, t, J = 7.7 Hz), 7.49 (1H, t, J = 7.4 Hz), 7.05 (2H, d, J = 8.7 Hz), 3.87 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.8, 159.9, 148.3, 136.6, 132.2, 129.6, 128.9,

127.4, 126.9, 125.9, 118.5, 114.2, 55.4; ν_{max}/cm^{-1}: 1596, 1498, 1429, 1288, 1250, 1175; LRMS (APCI+) m/z: 236.12 $[M+H]^+$. Data consistent with literature.[13b]

2,5-(4'-Nitrophenyl)furan (31): Isolated as an orange solid (78%). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 8.32 (4H, d, J = 8.7 Hz), 8.13 (4H, d, J = 8.7 Hz), 7.54 (2H, s); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 152.3, 146.3, 135.2, 124.6, 124.5, 113.1; ν_{max}/cm^{-1}: 1595, 1505, 1486, 1326, 1303, 1286, 1185, 1106; LRMS (APCI+) m/z: 311.08 $[M+H]^+$. Data consistent with literature.[15]

2-(4'-Nitrophenyl)-5-phenylfuran (32): Isolated as a yellow solid (51%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.27 (2H, d, J = 9.0 Hz), 8.85 (2H, d, J = 9.0 Hz,), 7.78 (2H, d, J = 9.0 Hz), 7.44 (2H, t, J = 7.5Hz), 7.31–7.36 (1H, m), 6.97 (1H, d, J = 6.0 Hz), 6.81 (1H, d, J = 3.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 155.6, 151.0, 146.3, 135.9, 130.0, 128.9, 128.3, 124.4, 124.1, 123.7, 111.4, 107.9; ν_{max}/cm^{-1}: 3121, 2925, 1601, 1504, 1330, 1105, 845, 793, 747, 686; LRMS (APCI+) m/z: 266.07 $[M+H]^+$. Data consistent with literature.[16]

2-(4'-Methoxyphenyl)-5-(4'-nitrophenyl)furan (33): Isolated as an orange solid (45%). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.44 (2H, d, J = 9.0 Hz), 7.19 (2H, d, J = 9.0 Hz), 6.98 (2H, d, J = 9.0 Hz), 6.57 (1H, d, J = 3.0 Hz), 6.21 (3H, t, J = 3.0 Hz,), 2.98(3H, s); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 159.4, 155.1, 149.8, 145.5, 135.9, 125.6, 124.4, 123.7, 122.3, 114.5, 112.9, 107.3, 55.3; ν_{max}/cm^{-1}: 1600, 1518, 1497, 1459, 1342, 1294, 1250, 1179, 1108; LRMS (APCI+) m/z: 296.12 $[M+H]^+$. Data consistent with literature.[16]

3-Bromo-2(4'-nitrophenyl)furan (34): Isolated as a yellow solid (48%) as a 5:1 mixture of regioisomers. M.p: 79-81^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.28 (2H, d, J = 9.0 Hz), 8.16 (2H, d, J = 9.0 Hz), 7.52 (1H, d, J = 2.1 Hz), 6.62 (1H, d, J = 1.8Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 146.7, 146.6, 143.5, 142.2, 135.4, 125.5, 123.94, 117.2, 99.9; ν_{max}/cm^{-1}: 2150, 2005, 1599, 1518, 1341, 850, 785, 423; HRMS (APPI+) m/z: 266.95247 [$C_{10}H_6{}^{79}BrNO_3$], 268.95042 [$C_{10}H_6{}^{81}BrNO_3$]

3-Bromo-2(4'-methoxyphenyl)furan (35): Isolated as a light-yellow liquid (57%) as a 5:1 mixture of regioisomers. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.88 (2H, d, J = 9.0 Hz), 7.38 (1H, d, J = 1.8 Hz), 6.94 (2H, d, J = 8.7 Hz), 6.50 (1H, d, J = 1.8 Hz), 3.85 (3H, s); (75 MHz, $CDCl_3$) δ (ppm): 159.4, 149.1, 141.1, 127.1, 122.7, 116.0, 113.9, 94.8, 55.3; ν_{max}/cm^{-1}: 1668, 1598, 1511, 1258, 1176, 1028, 835; LRMS (APCI+) m/z: 252.97 [$C_{11}H_9{}^{79}BrO_2$], 254.98 [$C_{11}H_9{}^{81}BrO_2$], Data consistent with literature.[17]

3-Bromo-5-(furan-2-yl)pyridine (36): Isolated as a pale yellow oil (38%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.81 (1H, d, J = 1.1 Hz), 8.53 (1H, d, J = 1.6 Hz), 8.07 (1H, t, J = 2.0 Hz), 7.53 (1H, dd, J = 1.8, 0.7Hz), 6.77 (1H, dd, J = 3.5, 0.7 Hz), 6.51 (1H, dd, J = 3.4, 1.8 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.5, 149.0, 143.8, 143.4, 133.3, 128.4, 121.1, 112.2, 107.8; ν_{max}/cm^{-1}: 3045, 1722, 1597, 1565, 1544, 1492, 1430, 1155, 1098; HRMS: (APCI+) m/z: 223.97066 [$C_9H_6{}^{79}BrO+H]^+$, 225.96858 [$C_9H_6{}^{81}BrO+H]^+$. Data consistent with literature.[18]

General procedure G: Annulation reactions

A solution of alkyne or alkene (2.6 mmol) in dry DMSO (1 mL) was added to a round bottom flask equipped with stirrer bar. In the meantime, 2-(methylthio)benzenediazonium tetrafluoroborate (**37**) or biphenyl-2-diazonium tetrafluoroborate (**44**) (0.39 mmol) and the nucleophile (0.26 mmol) were dissolved in dry DMSO (3 mL) and drawn up into plastic syringes. Both syringes were placed in a

syringe pump and the solutions were added to the round bottom flask (flow rate 1 mL/min). After addition, reaction mixture was transferred to separating funnel, diluted with diethyl ether (40 mL) and washed with water (40 mL). The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexanes/ diethyl ether /ethyl acetate as eluent.

2-Phenylbenzo[*b*]thiophene (39): Isolated as a white solid (80%). ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.84 (1H, d, *J* = 10 Hz), 7.79 (1H, d, *J* = 5.0 Hz), 7.73 (2H, d, *J* = 10 Hz), 7.56 (1H, s), 7.44 (2H, t, *J* = 7.5 Hz), 7.26–7.38(3H, m); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 144.3, 140.7, 139.5, 134.3, 129.0, 128.3, 126.5, 126.4, 126.3, 124.5, 124.3, 123.6, 122.3, 119.5; ν_{max}/cm^{-1}: 2166, 2017, 1456, 756, 744, 724,686, 462; LRMS (APCI+) m/z: 211.02 $[M+H]^+$.Data consistent with literature.[2]

Methyl benzo[*b*]thiophene-2-carboxylate (41): Isolated as an orange solid (59%). ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.06 (1H, s), 7.87 (2H, t, *J* = 7.5 Hz), 7.45 (1H, t, *J* = 7.5 Hz), 7.40 (1H, t, *J* = 7.5 Hz), 3.95 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 163.3, 142.2, 138.7, 133.3, 130.6, 127.0, 125.6, 124.9, 122.8, 52.5; ν_{max}/cm^{-1}: 2959, 2930, 1715, 1520, 1437, 1288, 1246, 1153, 1059, 760; LRMS (APCI+) m/z: 193.01 $[M+H]^+$.Data consistent with literature.[2]

Diethyl benzo[*b*]thiophene-2,3-dicarboxylate (43): Isolated as a white solid (44%). ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 7.94 (1H, d, *J* = 5.0 Hz), 7.85 (1H, d, *J* = 5.0 Hz), 7.44–7.50 (2H, m), 4.50 (2H, q , *J* = 6.7 Hz), 4.41 (2H, q, *J* = 8.3 Hz), 1.44 (3H, t, *J* = 7.5 Hz), 1.40 (3H, t, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) *δ*: 164.5, 161.8, 140.4, 136.9, 133.5, 133.3, 127.3, 125.6, 124.4, 122.5, 62.1, 62.0, 14.2; ν_{max}/cm^{-1}: 1730, 1704, 1531, 1284, 1255, 1216, 1099, 1021, 757; LRMS (APCI+) m/z: 279.05 $[M+H]^+$.Data consistent with literature.[2]

Methyl 9,10-dihydrophenanthrene-9-carboxylate (46): Isolated as yellow oil (34%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.70 (1H, d, *J* = 5.0 Hz), 7.66 (1H, d, *J* = 5.0 Hz), 7.27–7.30 (1H, m), 7.17–7.24 (4H, m), 3.81 (1H, t, *J* = 7.5Hz), 3.53 (3H, s), 3.23 (1H, dd, *J* = 10.0, 5.0 Hz), 3.03 (1H, dd, *J* = 10.0, 5.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 173.6, 134.5, 134.2, 133.8, 133.7, 128.7, 128.5, 128.2, 127.9, 127.7, 127.4, 124.1, 123.7, 52.1, 44.7, 31.8;

9-Phenylphenanthrene (48): Isolated as white solid (40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.80 (1H, d, *J* = 10 Hz), 8.75 (1H, d, *J* = 5.0 Hz), 7.93 (2H, dd, *J* = 10, 5.0 Hz), 7.65–7.95 (3H, m), 7.64 (1H, t, *J* = 7.5 Hz), 7.48–7.57 (5H, m), 7.47 (1H, t, *J* = 5.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 140.8, 138.8, 131.6, 131.2, 130.7, 130.1, 123.0, 128.7, 128.3, 127.5, 127.4, 127.09, 126.9, 126.6, 126.52, 126.47, 122.9, 122.6.

General procedure H: Reaction onto silyl enol ethers

A solution of silyl enol ether (3.12 mmol) in dry DMSO (1 mL) was added to a round bottom flask equipped with stirrer bar. In the meantime, 4-nitrobenzenediazonium tetrafluoroborate (**12**) (0.39 mmol) and the nucleophile (0.26 mmol) were dissolved in dry DMSO (3 mL) and drawn up into plastic syringes. Both syringes were placed in a syringe pump and the solutions were added to the round bottom flask (flow rate 1 mL/min). After addition, reaction mixture was transferred to separating funnel, diluted with diethyl ether (40 mL) and washed with water (40 mL). The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over

Na_2SO_4, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexanes/ diethyl ether /ethyl acetate as eluent.

1,2-bis(4-Nitrophenyl)ethan-1-one (50): Isolated as an orange solid (95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.35 (2H, d, J = 8.7Hz), 8.23 (2H, d, J = 8.7 Hz), 8.16 (2H, d, J = 8.7 Hz), 7.43 (2H, d, J = 8.4 Hz), 4.46 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 194.6, 150.6, 147.3, 140.8, 140.6, 130.7, 129.5, 124.1, 123.9, 45.3 ; ν_{max}/cm^{-1}: 1692, 1601, 1518, 1348, 1201, 855, 741; LRMS (APCI+) m/z: 287.04 $[M+H]^+$. Data consistent with literature.[19]

1-(4-Methoxyphenyl)-2-(4-nitrophenyl)ethan-1-one (52): Isolated as a yellow solid (99%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.18 (2H, d, J = 8.7 Hz), 7.99 (2H, d, J = 8.7 Hz), 7.43 (2H, d, J = 8.7 Hz), 6.91 (2H, d, J = 9.0 Hz), 4.35 (2H, s), 3.88 (3H, s) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 194.6, 164.0, 147.0, 142.6, 130.8, 130.6, 129.2, 123.7, 114.0, 55.6, 44.6 ; ν_{max}/cm^{-1}; 2163, 1680, 1601, 1512, 1262, 1169, 991, 822, 592, 569; LRMS (APCI+) m/z: 272.07 $[M+H]^+$. Data consistent with literature.[20]

Mechanistic Studies:

Reaction in the dark

The following experiment was conducted in the dark room until purification. A solution of furan (2.6 mmol) in dry DMSO (1 mL) was added to a round bottom flask equipped with stirrer bar. In the meantime, 4-nitrobenzenediazonium tetrafluoroborate (0.39 mmol) and dibenzyl Hantzsch ester (0.26 mmol) were separately dissolved in dry DMSO (3 mL) and drawn up into 3 ml plastic syringes. Both syringes were placed in a syringe pump and the solutions were added to the round bottom flask (flow rate 1 mL/min). After addition, the reaction mixture was transferred to separating funnel, diluted with diethyl ether (10 mL) and washed with water (40 mL). The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. 4-(Nitrophenyl)furan was isolated by flash chromatography on silica gel using hexanes /ethyl acetate as eluent. Isolated yield 70%.

Iodine abstraction reaction from molecular iodine

A solution of the iodine (0.46 mmol) in dry DMSO (1 mL) was added to a round bottom flask equipped with stirrer bar. In the meantime, aryl diazonium tetrafluoroborate (0.39 mmol) and dibenzyl Hantzsch ester (0.26 mmol) were separately dissolved in dry DMSO (3 mL) and drawn up into 3 ml plastic syringes. Both syringes were placed in a syringe pump and the solutions were added to the round bottom flask (flow rate 1 mL/min). After addition, the reaction mixture was transferred to separating funnel, diluted with diethyl ether (10 mL) and washed with sodium thiosulfate solution (10% sol; 40 mL). The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexanes / diethyl ether /ethyl acetate as eluent.

Radical trap reactions

A solution of the TEMPO (0.26 mmol) in dry DMSO (1 mL) was added to a round bottom flask equipped with stirrer bar. In the meantime, aryl diazonium tetrafluoroborate (0.39 mmol) and dibenzyl Hantzsch ester (0.26 mmol) were separately dissolved in dry DMSO (3 mL) and drawn up

into 3 ml plastic syringes. Both syringes were placed in a syringe pump and the solutions were added to the round bottom flask (flow rate 1 mL/min). After addition, the reaction mixture was transferred to separating funnel, diluted with diethyl ether (10 mL) and washed with sodium thiosulfate solution (10% sol; 40 mL). The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexanes / diethyl ether /ethyl acetate as eluent.

Gomberg-Bachmann-Hey arylation in the presence of TEMPO

A solution of the furan (**13**) (2.6 mmol) and TEMPO (2.6 mmol) in dry DMSO (1 mL) was added to a round bottom flask equipped with stirrer bar. In the meantime, 4-nitrobenzenediazonium tetrafluoroborate (**12**) (0.39 mmol) and dibenzyl Hantzsch ester (**6**) (0.26 mmol) were separately dissolved in dry DMSO (3 mL) and drawn up into 3 ml plastic syringes. Both syringes were placed in a syringe pump and the solutions were added to the round bottom flask (flow rate 1 mL/min). During this experiment arylated furan was not detected by TLC analysis. The reaction mixture was transferred to separating funnel, diluted with diethyl ether (40 mL) and washed with water (40 mL). The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexanes / diethyl ether /ethyl acetate as eluent.

2,2,6,6-Tetramethyl-1-(4-nitrophenoxy)piperidine (57): Isolated as a yellow solid (77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.13 (2H, d, J = 9.0), 7.27-7.31 (2H, m), 1,59-1.65 (5H, m), 1.42-1.46 (1H, m), 1.24 (6H, s), 0.98 (6H, s) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 168.7, 141.2, 125.5, 114.2, 60.9, 39.7, 32.3, 20.5, 16.9; ν_{max}/cm^{-1}: 1586, 1505, 1484, 1331, 1252, 1227, 1109, 922, 854, 753, 654; LRMS (APCI+) m/z: 279.15 $[M+H]^+$. Data consistent with literature.[21]

2,2,6,6-Tetramethyl-1-phenoxypiperidine (62)*:* Isolated as yellow solid (82%); ^{1}H NMR (400 MHz; $CDCl_3$) δ: 2.24-7.29 (2H, m), 7.08-7.01 (2H, m), 6.85-6.90 (1H, m), 1.61-1.68 (5H, m), 1.45-1.48 (m, 1H), 1.28 (6H, s), 1.07 (6H, s); ^{13}C NMR (100 MHz; $CDCl_3$) δ: 163.6, 128.7, 119.9, 113.9, 60.3, 39.8, 32.6, 20.5, 17.1; ν_{max}/cm^{-1} : 2975, 2930, 1591, 1486, 1363, 1183, 1152, 1131, 750, 692; LRMS (APCI+) m/z: 234.19 $[M+H]^+$.

Effect of degassing reaction mixtures

The following experiment was conducted as quickly as possible to minimize exposure to the air. A solution of furan (2.6 mmol) in dry DMSO (1 mL) was added to a round bottom flask equipped with stirrer bar and sparged with argon via a balloon. In the meantime, 4-nitrobenzenediazonium tetrafluoroborate (0.39 mmol) and dibenzyl Hantzsch ester (0.26 mmol) were separately dissolved in dry DMSO (3 mL) and sparged with argon before being drawn up into 3 ml plastic syringes. Both syringes were placed in a syringe pump and the solutions were added to the round bottom flask (flow rate 1 mL/min). After addition, the reaction mixture was transferred to separating funnel, diluted with diethyl ether (10 mL) and washed with water (40 mL). The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, and concentrated under vacuum. 4-(Nitrophenyl)furan was isolated by flash chromatography on silica gel using hexanes /ethyl acetate as eluent. Isolated yield 38%.

Effect of water content on reaction

Deionised water was added to DMSO to give solutions of known composition. These were employed in the general procedure F using 4-nitrobenzenediazonium tetrafluoroborate (**12**) and dibenzyl Hantzsch ester (**6**). 4-(Nitrophenyl)furan (**14**) was isolated by flash chromatography on silica gel using hexanes /ethyl acetate as eluent, and the yields were calculated.

Effect of deuterated solvent

General procedure F was repeated with the same amounts of 4-nitrobenzenediazonium (**12**) and dibenzyl Hantzsch ester (**6**). The reaction mixture was subjected to mass spectrometric analysis, then 4-(nitrophenyl)furan (**14**) was isolated by flash chromatography on silica gel using hexanes /ethyl acetate as eluent.

Competition reaction between HE 4 and deuterated HE 4a

General procedure F was repeated with the same amounts of 4-nitrobenzenediazonium (**12**) and a 1:1 mixture of **4** and **4a**. The reaction mixture was subjected to mass spectrometric analysis, then 4-(nitrophenyl)furan (**14**) and the mixture of unreacted HEs (**4** and **4a**) were isolated by flash chromatography on silica gel using hexanes /ethyl acetate as eluent.

Furan-2-carboxylic-*d_3* acid: Furoic acid (320 mg) was added to a solution of sodium deuteroxide (1 M in D_2O; 4 mL) under an argon atmosphere and the resulting mixture was refluxed for 36 h. Consumption of the starting material was monitored by mass spectrometry. After completion of the reaction, the mixture was acidified with 5 N HCl and extracted with ethyl acetate (3 × 20 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under vacuum to give furan-2-carboxylic-*d_3* acid (310 mg, 97%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.25 (1H, brs); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.6, 147.2 (t, = 31 Hz), 143.7 (d, J = 5 Hz), 120.2–119.7 (m), 112.1–111.6 (m); ν_{max}/cm^{-1}: 3200, 1677, 1559, 1434, 1403, 1295, 1183, 867, 785; LRMS (ESI+) m/z : 138.01 $[M+Na]^+$

Furfuryl alcohol-*d_3* (59a): Furan-2-carboxylic-*d_3* acid (310 mg, 2.7 mmol) was dissolved in diethyl ether (20 mL) under an argon atmosphere and the mixture was cooled to 0° C. Lithium aluminium hydride (72 mg, 19 mmol) was added portion wise. The reaction mixture was left to warm to room temperature and then heated to reflux for two hours. Saturated aqueous Rochelle salt (15 mL) was added and stirred vigorously until disappearance of the grey colour. The mixture was extracted with diethyl ether (3 × 20 mL), the combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under vacuum to give **59a** (223 mg, 82%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.60 (2H, s), 1.81 (1H, brs); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153. 9 (d, J = 7 Hz), 142.3 (t, J = 31 Hz), 110.7–109.7 (m), 107.7–107.2 (m); ν_{max}/cm^{-1}: 3338, 1449, 1106, 1015, 988, 975, 869, 781, 599, 501; LRMS (ESI+) m/z : 224.05 $[M+Na]^+$

Competition reaction between furfuryl alcohols 59 and 59a

General procedure F was repeated with the same amounts of 4-nitrobenzenediazonium tetrafluoroborate and dibenzyl Hantzsch ester but with 1:1 mixture of **59** and **59a**. The reaction

mixture was subjected to mass spectrometric analysis, then (5-(4-nitrophenyl)furan-2-yl)methanol-H_3/d_3 was isolated by flash chromatography as 2.1:1 mixture.

(5-(4-Nitrophenyl)furan-2-yl-3,4-d_2)methanol: Isolated as an orange solid (64%). M.p: 113-115 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (2H, d, J = 11.2 Hz), 8.79 (2H, d, J = 11.2 Hz), 4.71 (2H, s), 1.81 (1H, brs); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.79 (d, J = 6 Hz), 151.61, 146.49, 136.24, 124.33, 123.93, 110.57-110.30 (m), 109.73-109.47 (m); ν_{max}/cm^{-1}: 2926, 1713, 1599, 1511, 1330, 1108, 1090, 852; LRMS (ESI+) m/z : 244.01 $[M+Na]^+$

(5-(4-Nitrophenyl)furan-2-yl)methanol: Isolated as an orange solid (69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (2H, d, J = 11.2 Hz), 8.79 (2H, d, J = 11.2 Hz), 6.83 (1H, s), 6.46 (1H, s), 4.71(2H, s), 1.81 (1H, brs); ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.85, 151.66, 146.49, 136.24, 124.39, 124.00, 110.63, 109.74, 57.61; ν_{max}/cm^{-1} : 3318, 1509, 1329, 1106, 998, 966, 851, 794, 752, 690; LRMS (ESI+) m/z : 242.01 $[M+Na]^+$

Reaction between deuterated HE 4a and biphenyldiazonium salt 44

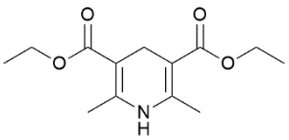
Dry DMSO (1 mL) was added to a round bottom flask equipped with stirrer bar. In the meantime, biphenyl-2-diazonium tetrafluoroborate (**44**) (0.39 mmol) and d_2-dibenzyl Hantzsch ester (**4a**) (0.26 mmol) were separately dissolved in dry DMSO (3 mL) and drawn up into 3 ml plastic syringes. Both syringes were placed in a syringe pump and the solutions were added to the round bottom flask (flow rate 1 mL/min). After addition, the reaction mixture was transferred to separating funnel, diluted with diethyl ether (10 mL) and washed with water (40 mL). The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexanes / diethyl ether /ethyl acetate as eluent.

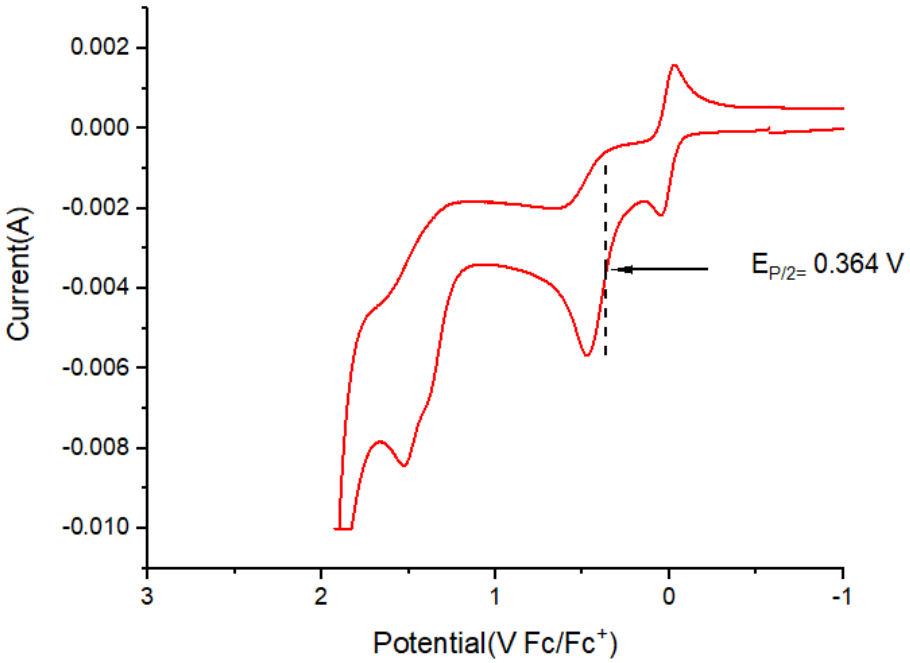
1,1'-Biphenyl-2-*d*: Isolated as white solid (87%); ^{1}H NMR (400 MHz; $CDCl_3$) δ: 7.62-7.64 (3H, m), 7.45-7.49 (4H, m), 7.36-7.40 (m, 2H); ^{13}C NMR (100 MHz; $CDCl_3$) δ: 141.3 (t, J = 6.5 Hz), 128.7, 127.3, 127.2; ν_{max}/cm^{-1} : 3060, 3034, 1466, 1427, 907, 727, 691 ;LRMS (APCI+) m/z: 155.09 $[M+H]^+$.

Cyclic Voltammetry

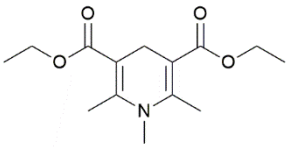
Electrochemical potentials were obtained according to the method of Nicewicz and co-workers,[22] using a Pine WaveNow Potentiostat. Samples consisted of the nucleophile (0.05 mmol) in a solution of tetrabutylammonium hexafluorophosphate (0.1 M in CH_3CN; 5 mL). Ferrocene was added as an internal reference. The $E_{p/2}$ was calculated at half the current maximum and was converted to SCE according to the method of Addison and co-worker.[23]

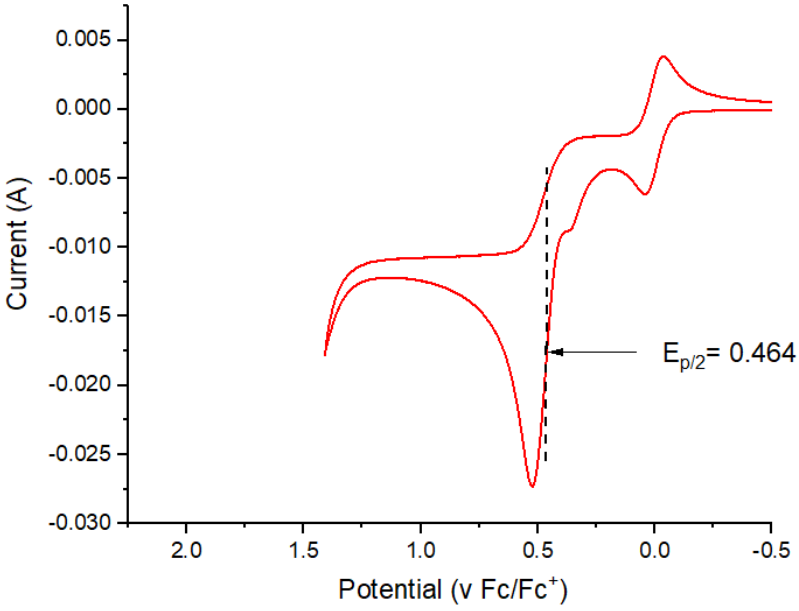
Diethyl Hantzsch ester (4)



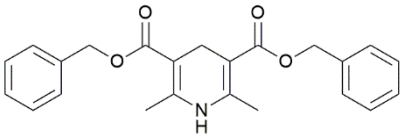


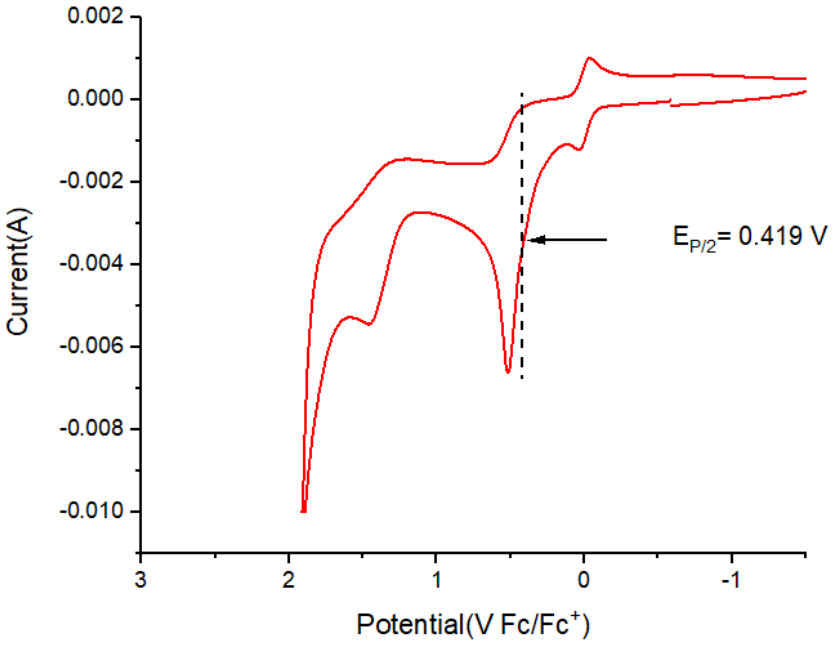
***N*-Methyldiethyl Hantzsch ester (5)**



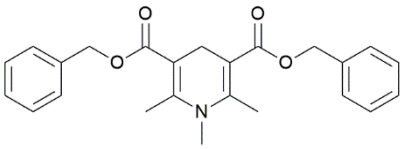


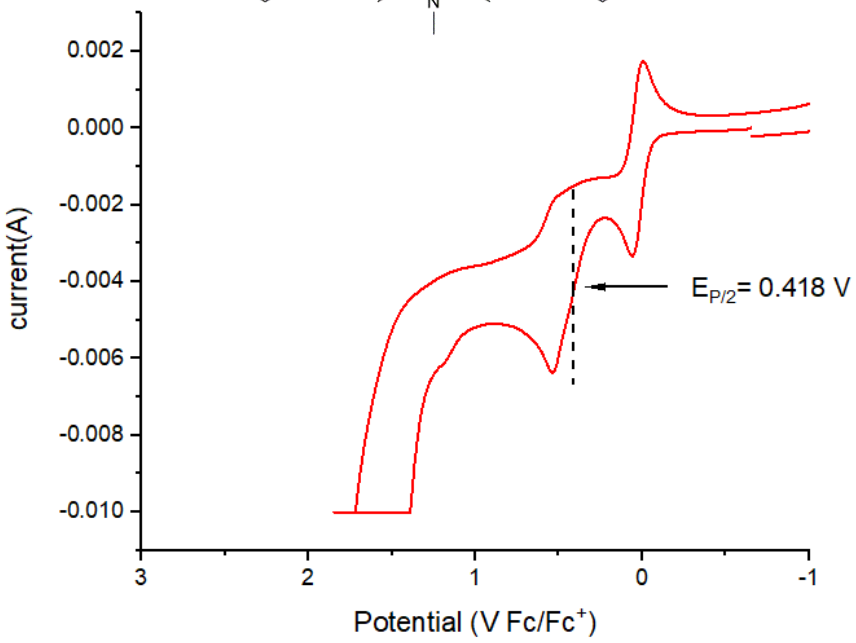
Dibenzyl Hantzsch ester (6)





***N*-Methyldibenzyl Hantzsch ester (7)**





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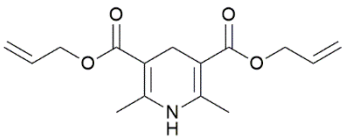
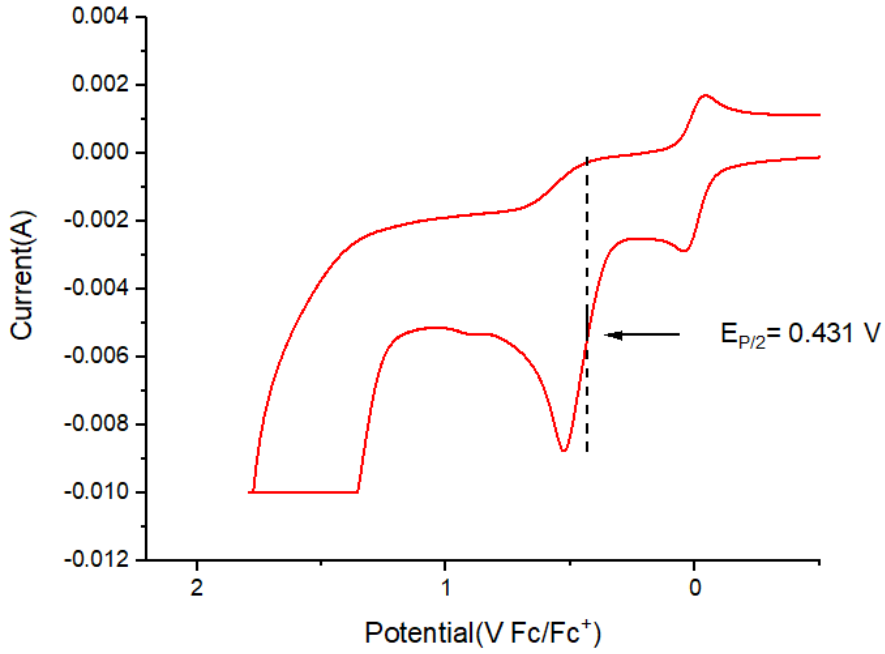
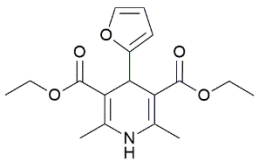




4-(2′-furanyl)diethyl Hantzsch ester (9)



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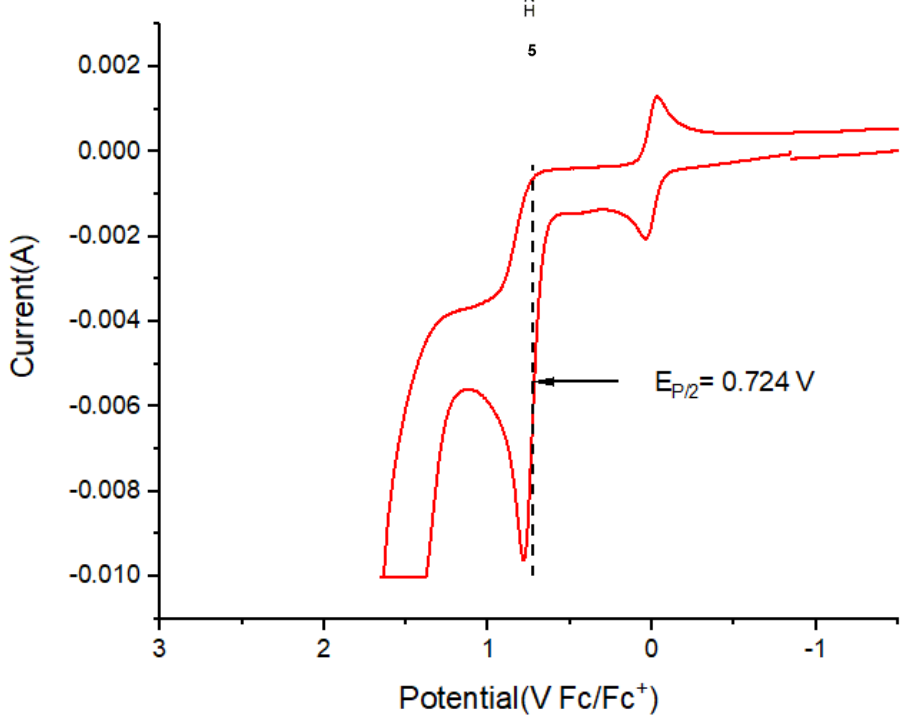
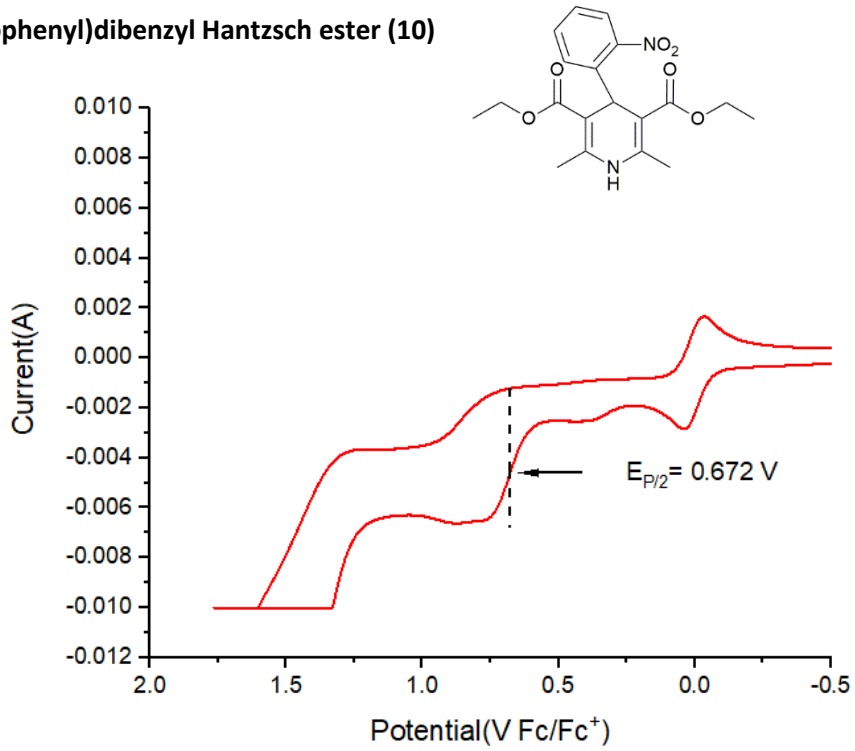
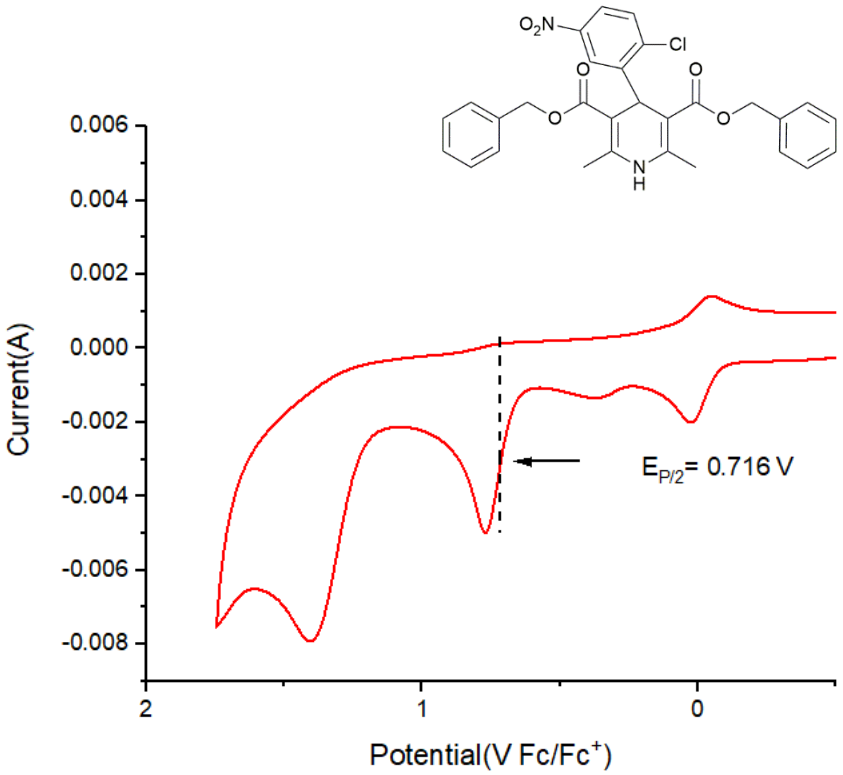


4-(2′-Nitrophenyl)dibenzyl Hantzsch ester (10)

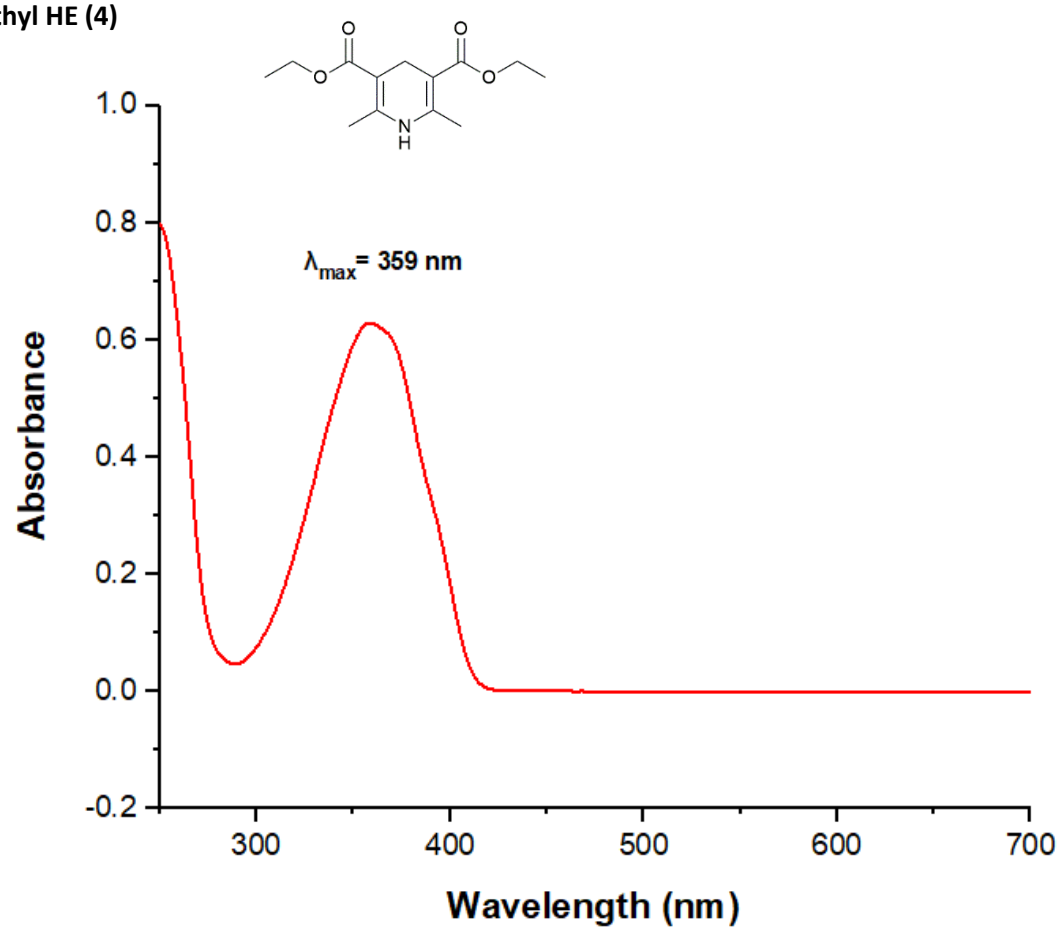


4-(2′-Chloro-5′-nitrophenyl)dibenzyl Hantzsch ester (11)



UV-vis absorbance

Diethyl HE (4)



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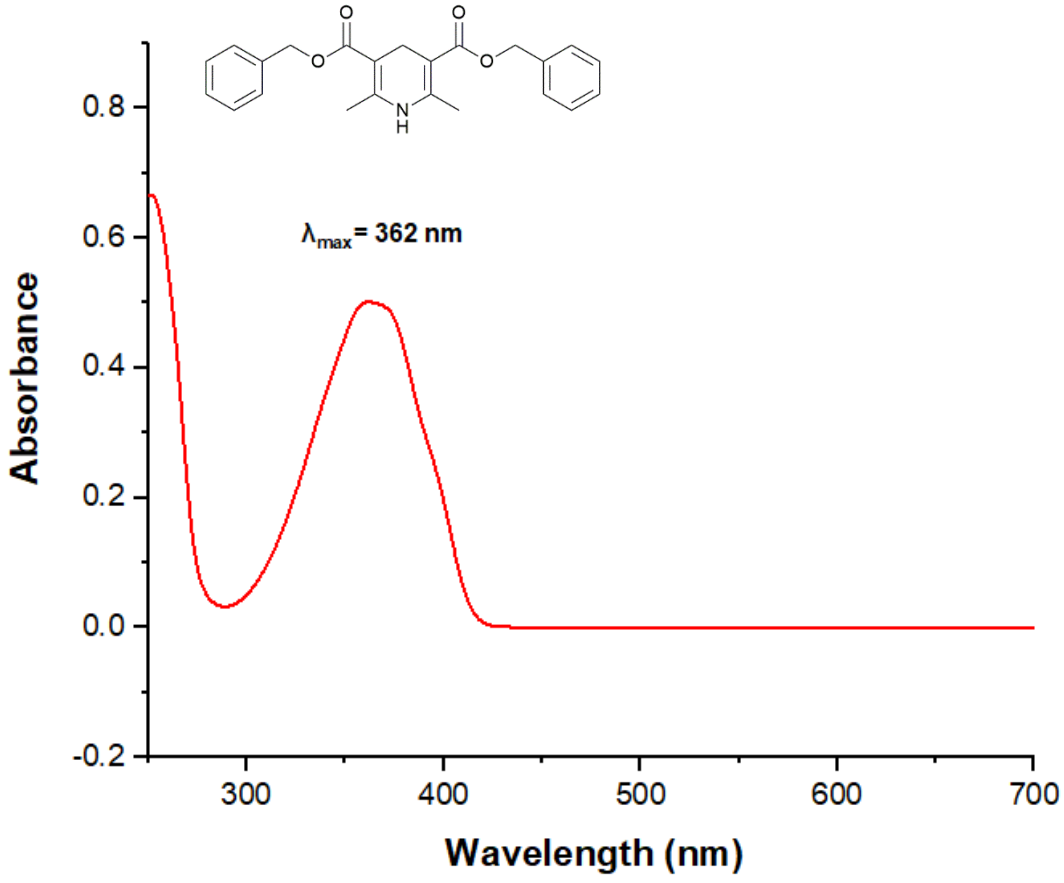
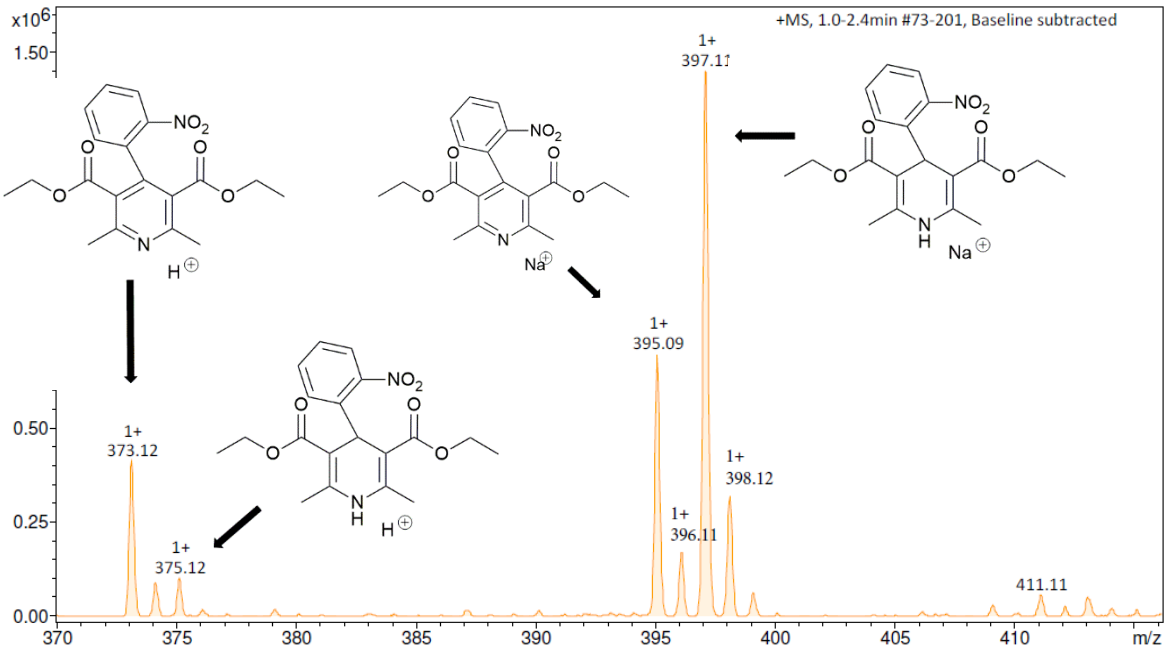


Mass spectroscopic analysis of GBH reaction using HE 10



Computational details

Standard computational chemistry calculations were carried out with Gaussian 16.[24] Geometries were optimized using the N12/6-31G(d) procedure.[25] The choice of this level of theory is based on the our previous studies into the use of efficient computational chemistry methods for obtaining reliable molecular geometries and thermochemical quantities related to vibrational frequencies.[26] To obtain zero-point vibrational energies (ZPVEs) and thermal corrections to 298 K free energies, we used N12/6-31G(d) frequencies scaled by 0.9849, 1.0205, and 1.0351, respectively. For the calculation of single-point energies, we used the higher-level MN15-L functional[27] in conjunction with the larger 6-311+G(3df,2p) basis set. The effect of solvation was applied in all computations using the SMD continuum model[28] with densities obtained at the M05-2X/6-31G(d) level.[29] and solvent parameters for tetrahydrofuran. Computed relative energies in the text are given as MN15-L/6-311+G(3df,2p) 298 K free energies in kJ mol^{-1}.

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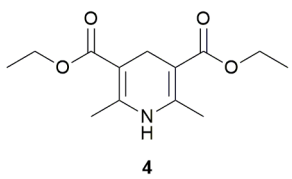

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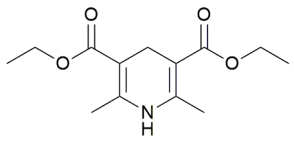

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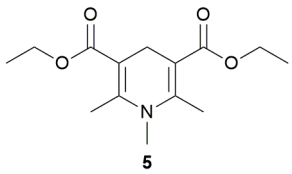

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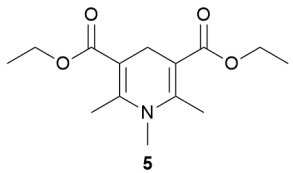

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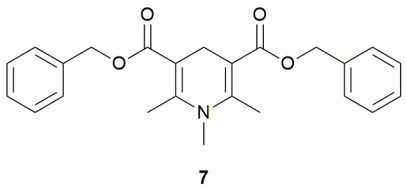

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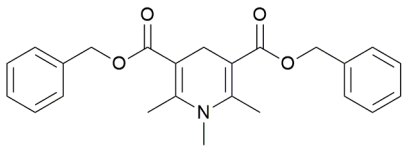

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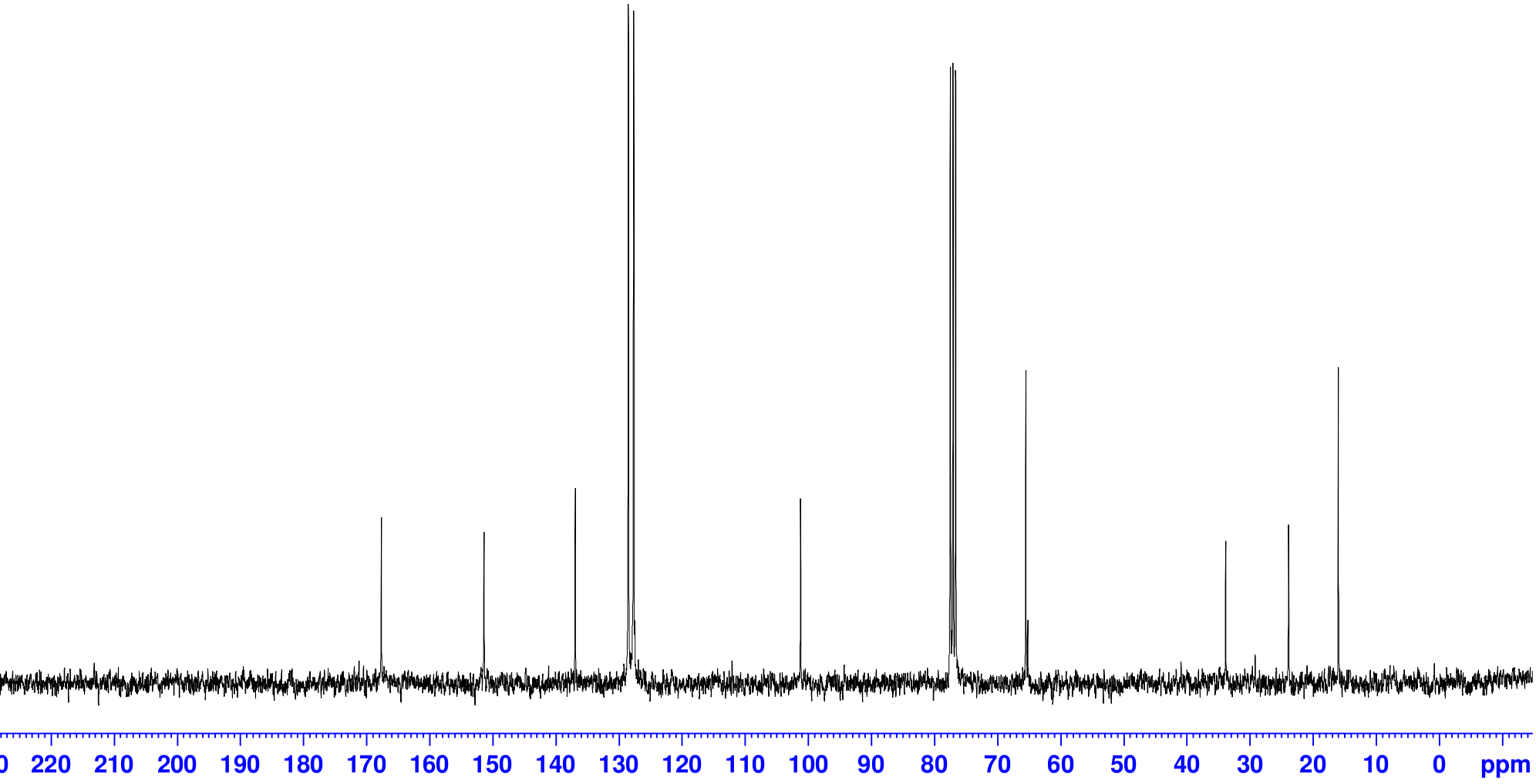

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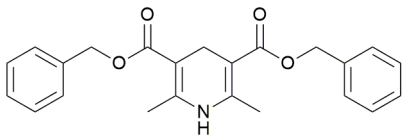

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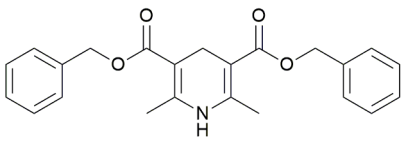

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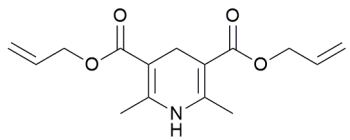
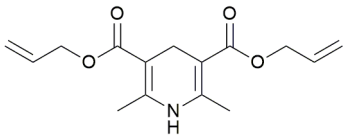


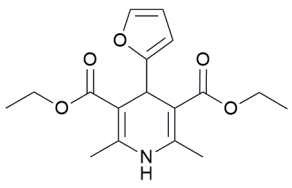
8

diallyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate



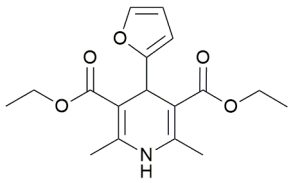
8

diethyl 4-(furan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate



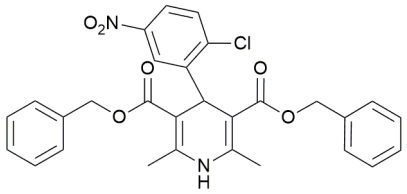
9

diethyl 4-(furan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate



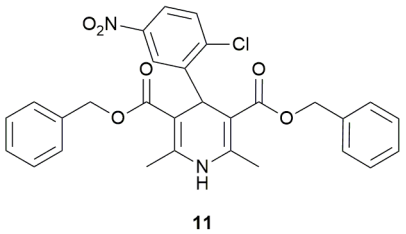
9

dibenzyl 4-(2-chloro-5-nitrophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarb



11

dibenzyl 4-(2-chloro-5-nitrophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarb

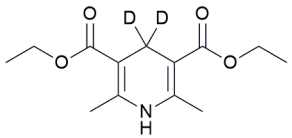


11

166.77
147.11
146.64
145.52
139.83
136.21
130.27
128.38
128.25
128.01
126.79
121.95
102.54
77.30
77.05
76.80
65.74
38.57
19.75

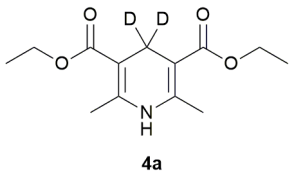
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate-4,4-d2



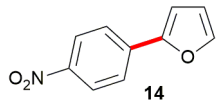
4a

diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate-4,4-d2

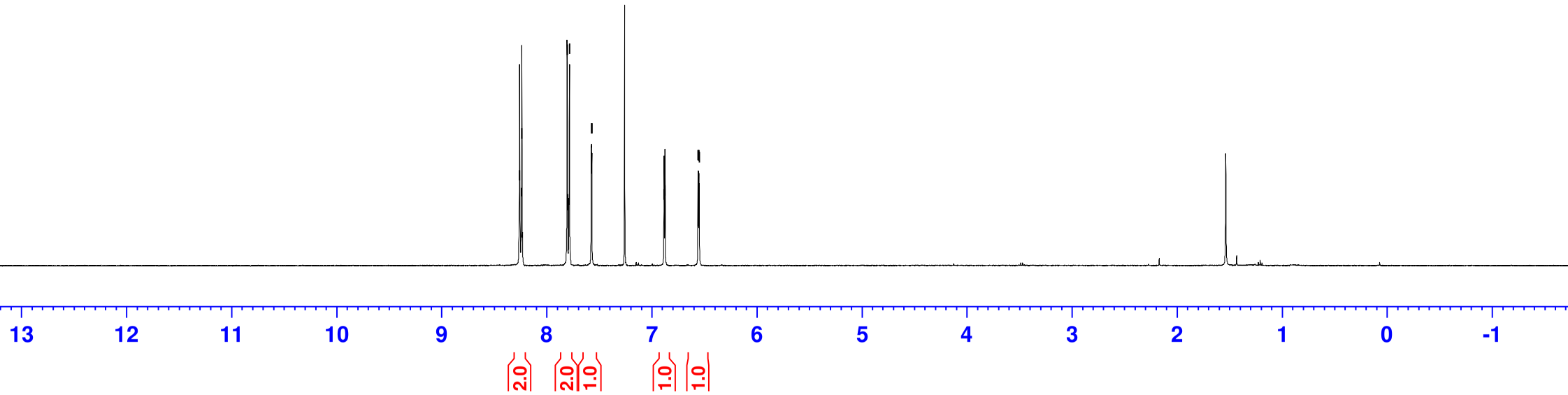


4a

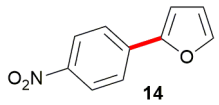
2-(4-nitrophenyl)-furan



8.260
8.237
7.806
7.783
7.575
7.572
6.883
6.875
6.560
6.555
6.551
6.547

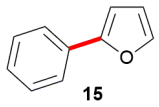


2-(4-nitrophenyl)-furan

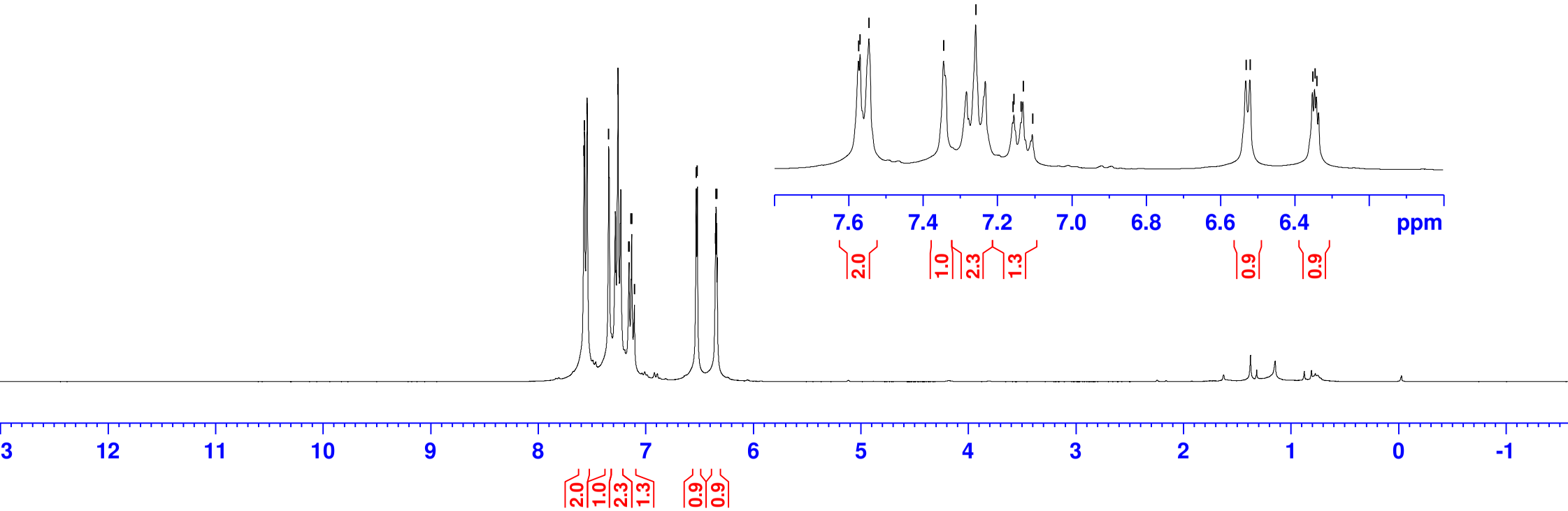


14

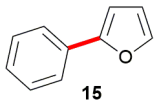
2-Phenyl-furan



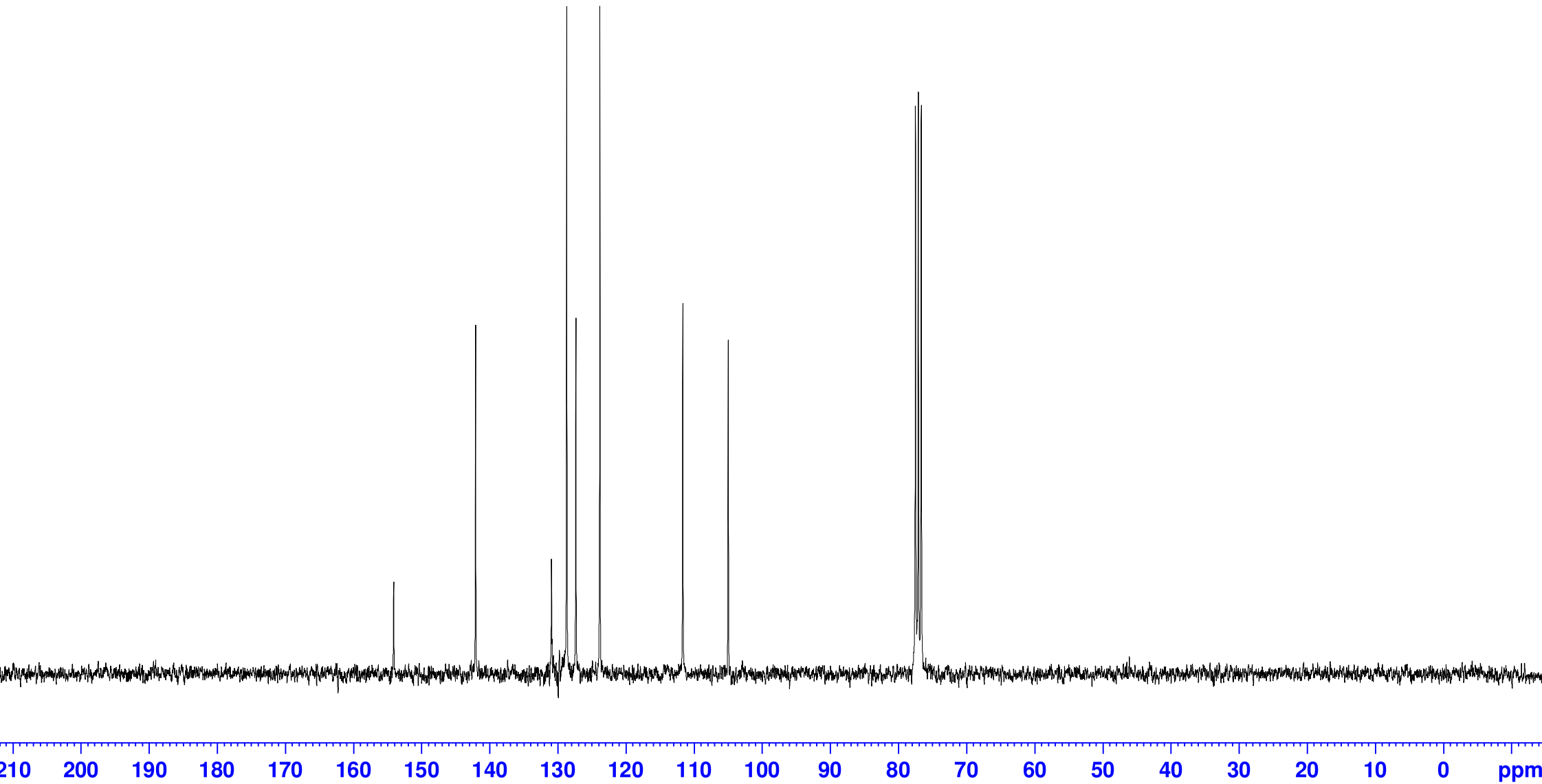
7.574
7.570
7.546
7.345
7.258
7.159
7.156
7.137
7.131
7.106
6.531
6.521
6.352
6.346
6.341



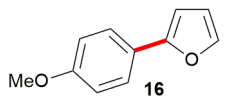
ET 1-19 final carbon



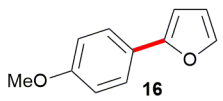
154.04
142.07
130.94
128.69
127.35
123.83
111.65
104.97
77.48
77.06
76.63



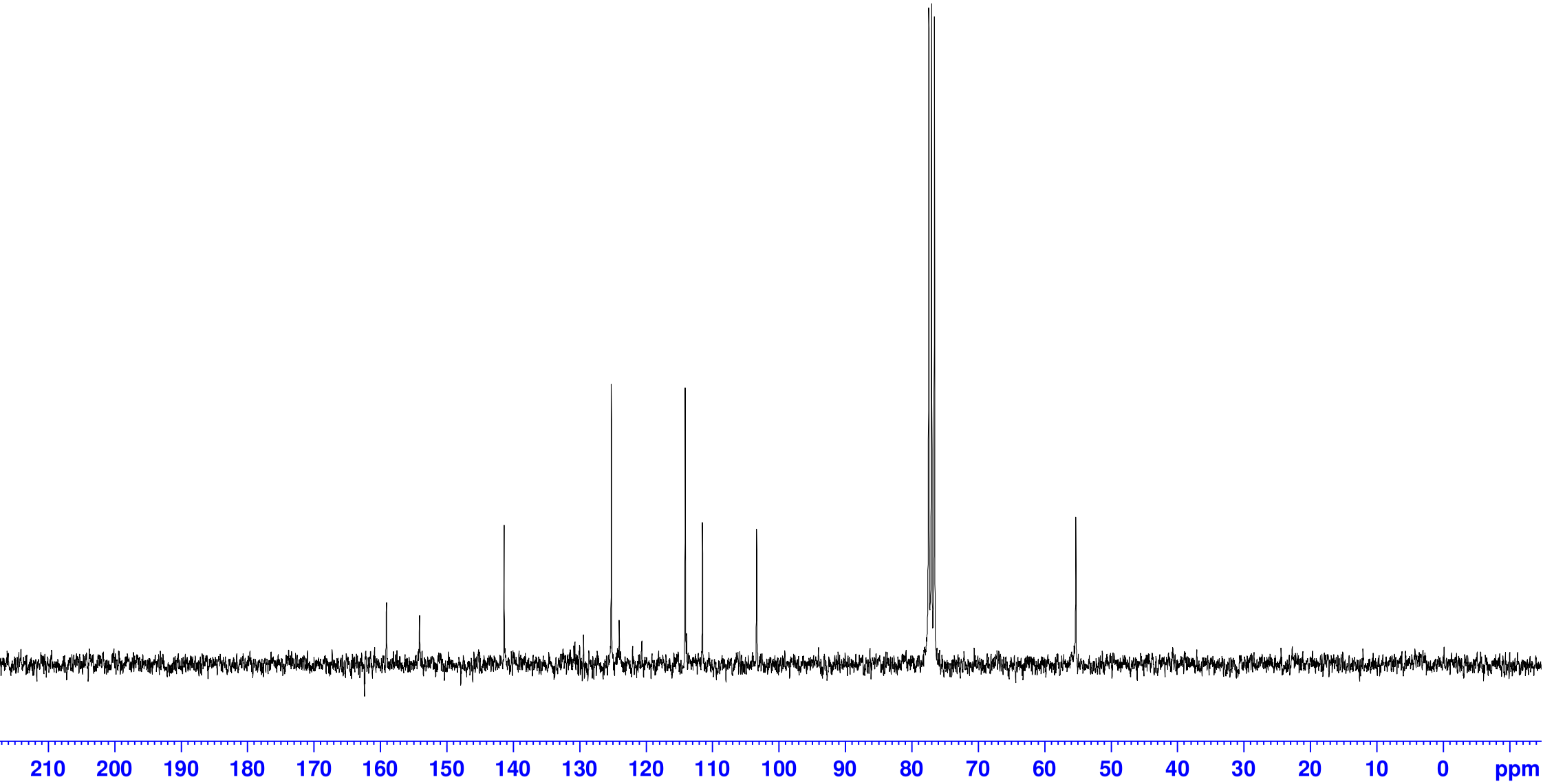
2-(4-methoxyphenyl)-furan



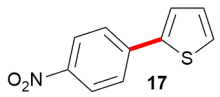
2-(4-methoxyphenyl)-furan



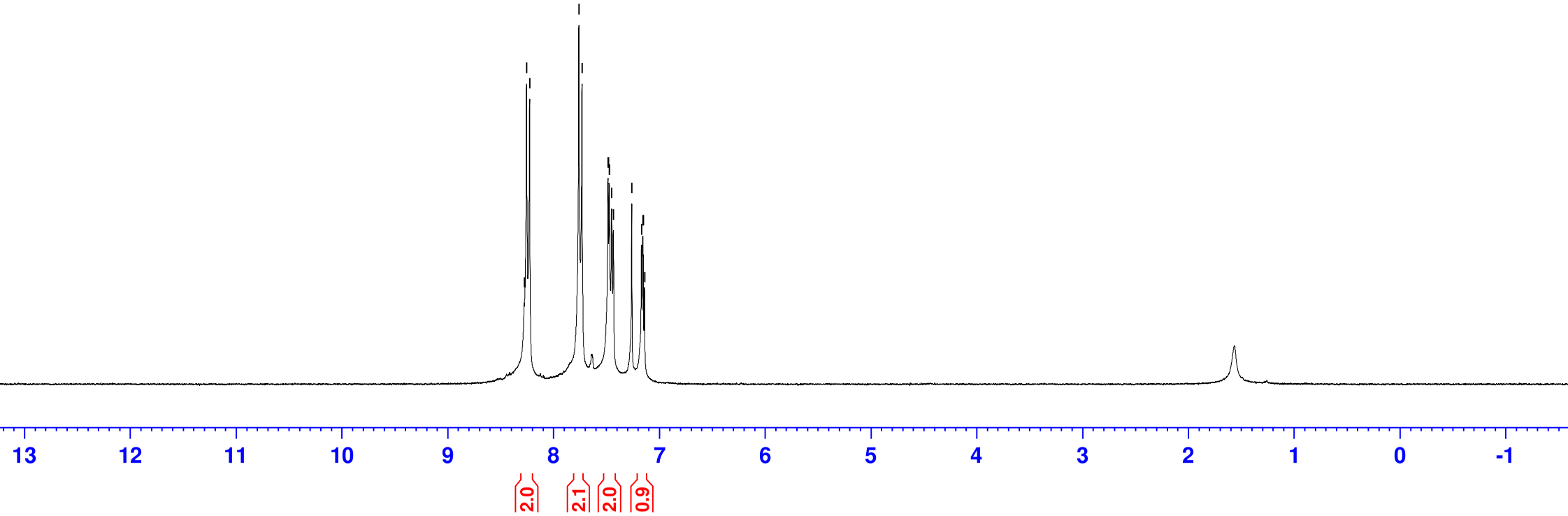
159.03
154.06
141.38
125.24
124.06
114.13
111.53
103.37
77.45
77.02
76.60
55.32



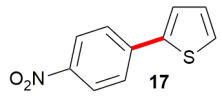
2-(4-nitrophenyl)-thiophene



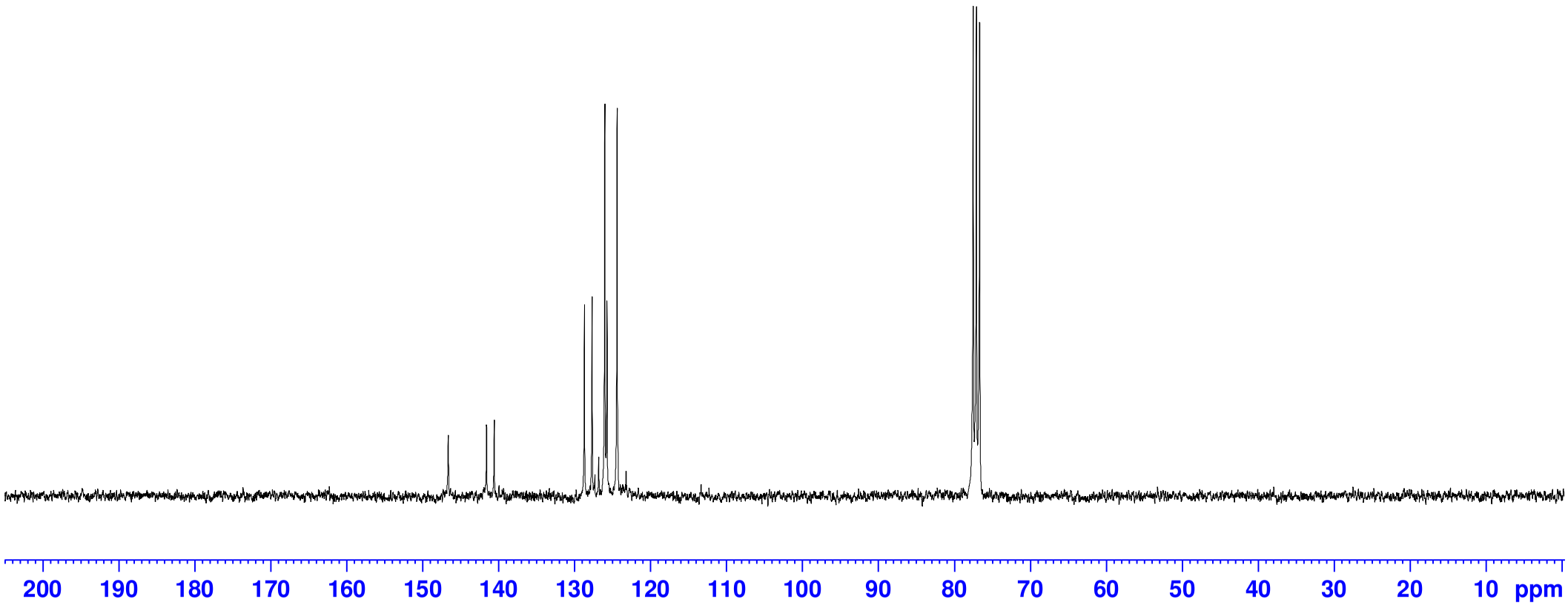
8.278
8.255
8.226
7.760
7.731
7.485
7.483
7.473
7.471
7.451
7.434
7.260
7.168
7.156
7.152
7.139



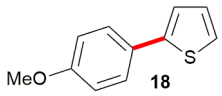
2-(4-nitrophenyl)-thiophene



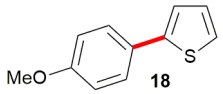
146.64
141.59
140.58
128.70
127.69
126.02
125.72
124.40
77.49
77.07
76.64



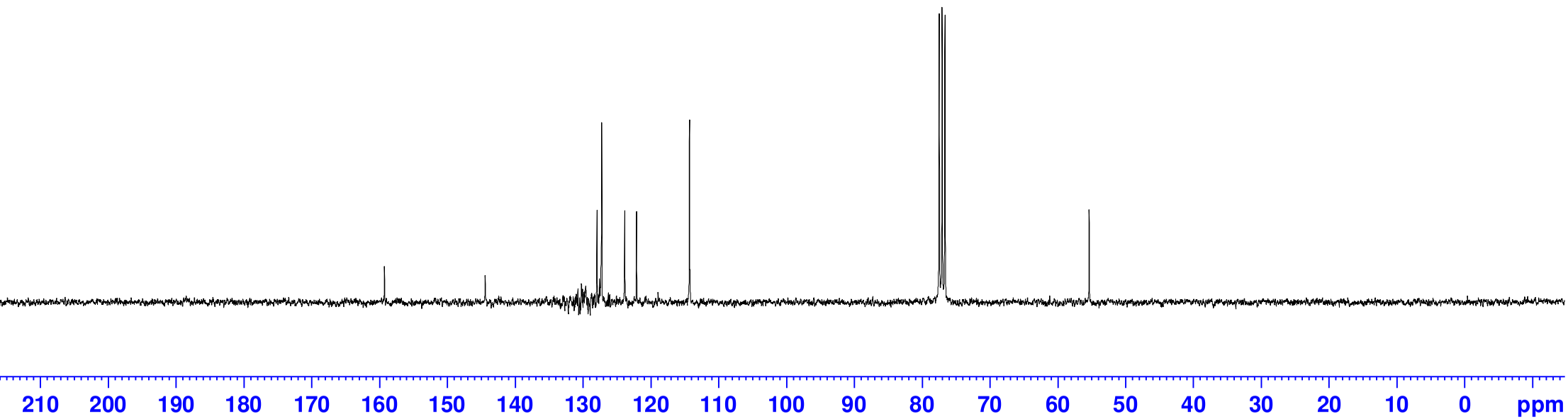
2-(4-methoxyphenyl)-thiophene



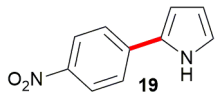
2-(4-methoxyphenyl)-thiophene



159.21
144.36
127.93
127.24
123.84
122.10
114.30
77.47
77.04
76.62
55.36

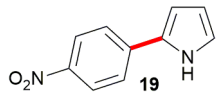


2-(4-nitrophenyl)-1H-pyrrole

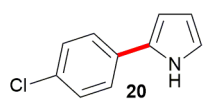


11.694
8.201
8.172
7.855
7.826
7.039
6.830
6.223
3.370
2.498

2-(4-nitrophenyl)-pyrrole

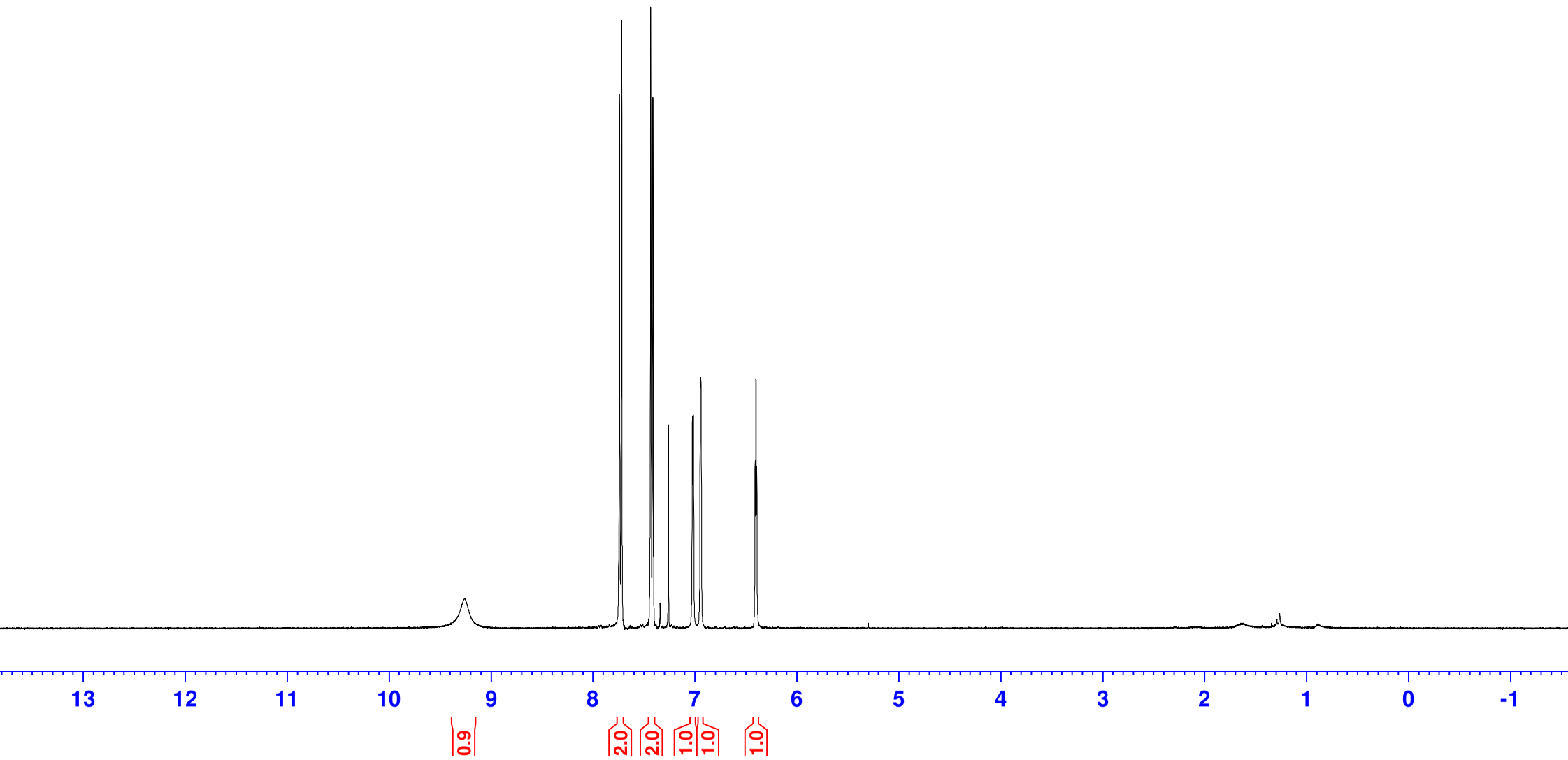


2-(4-chlorophenyl)pyrrole

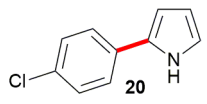


9.260

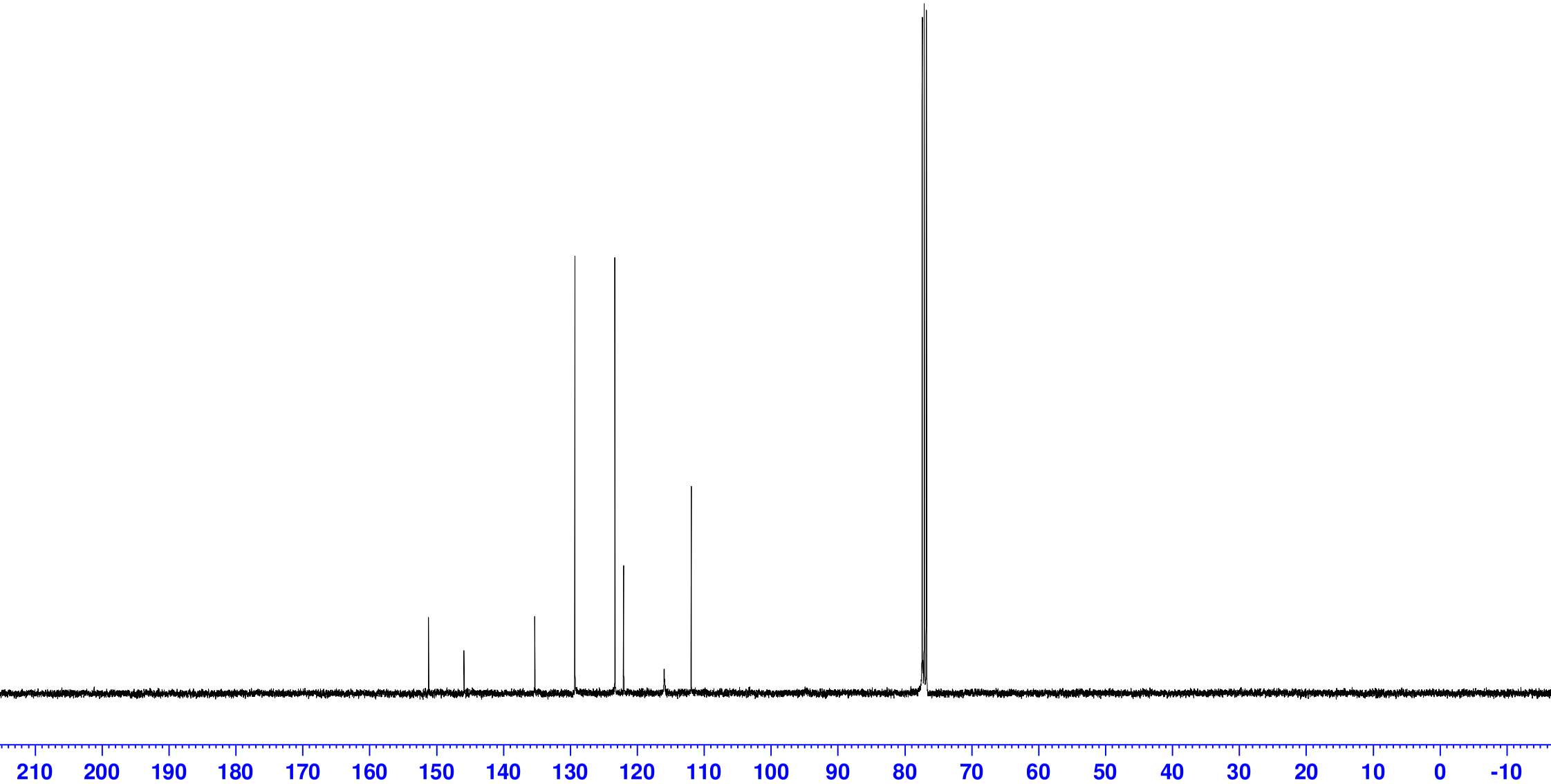
7.739
7.718
7.433
7.411
7.022
7.014
6.941
6.408
6.400
6.392



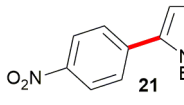
2-(4-chlorophenyl)pyrrole



151.15
145.86
135.26
129.33
123.36
122.05
116.01
111.94

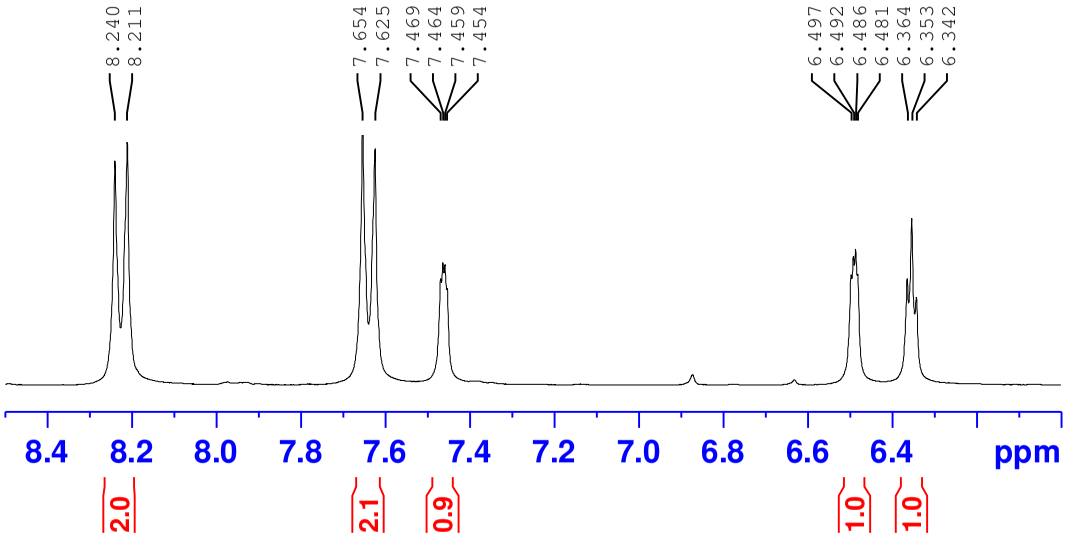


tert-butyl 2-(4-nitrophenyl)-1H-pyrrole-1-carboxylate

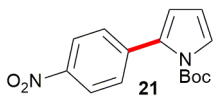


21

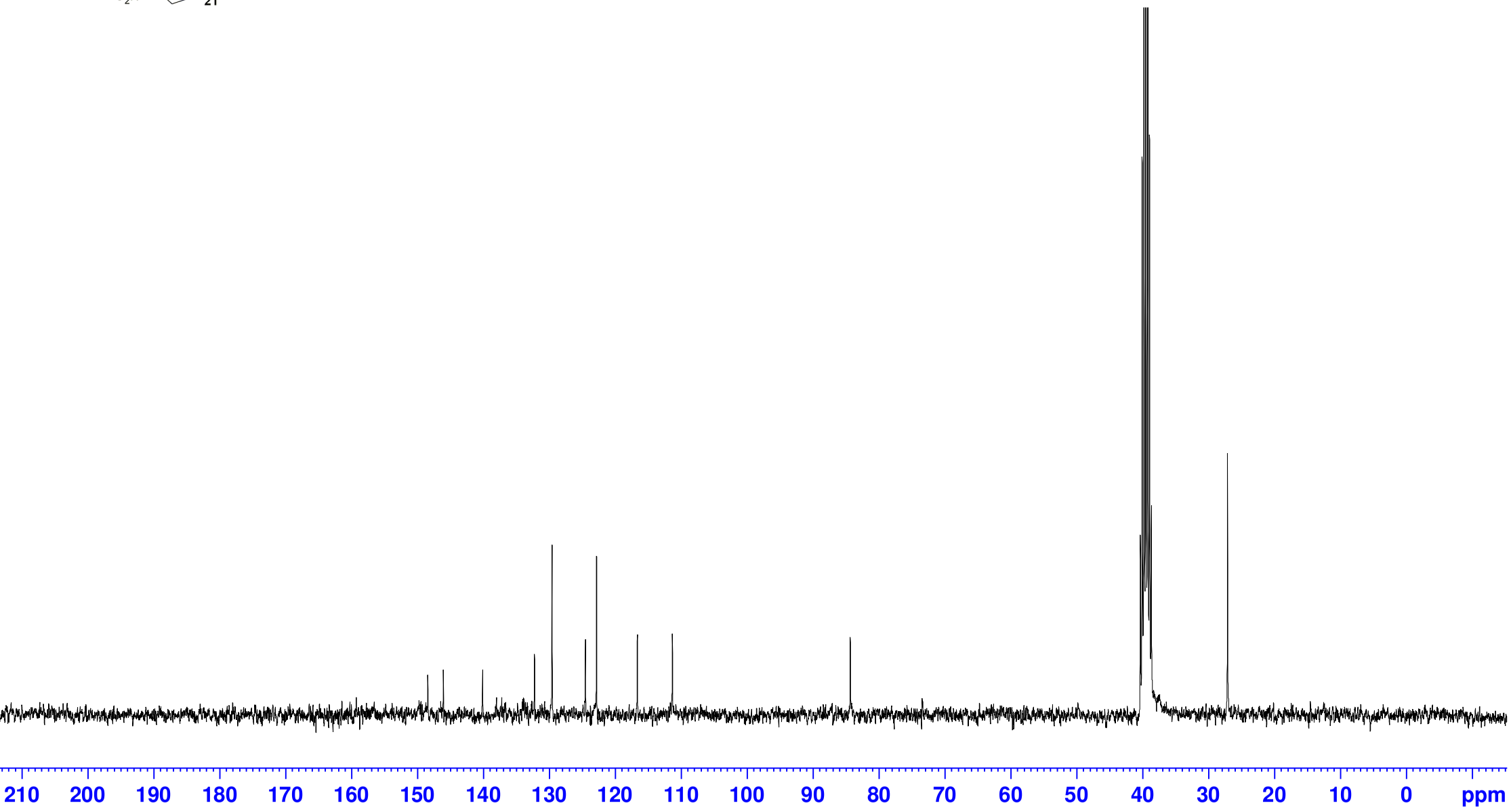
8.240
8.211
7.654
7.625
7.469
7.464
7.459
7.454
6.497
6.492
6.486
6.481
6.364
6.353
6.342
3.318
2.504
1.367



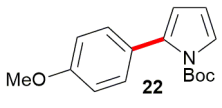
ET 2-(4-nitrophenyl)-pyrrole-1-carboxylic acid tert-butyl ester



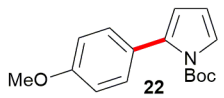
148.38
146.03
140.12
132.26
129.59
124.53
122.84
116.65
111.34
84.35
40.34
40.06
39.79
39.51
39.23
38.95
38.67
27.12



2-(4-methoxyphenyl)-pyrrole-1-carboxylic acid tert-butyl ester



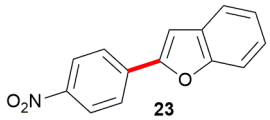
2-(4-methoxy-phenyl)-pyrrole-1-carboxylic acid tert-butyl ester



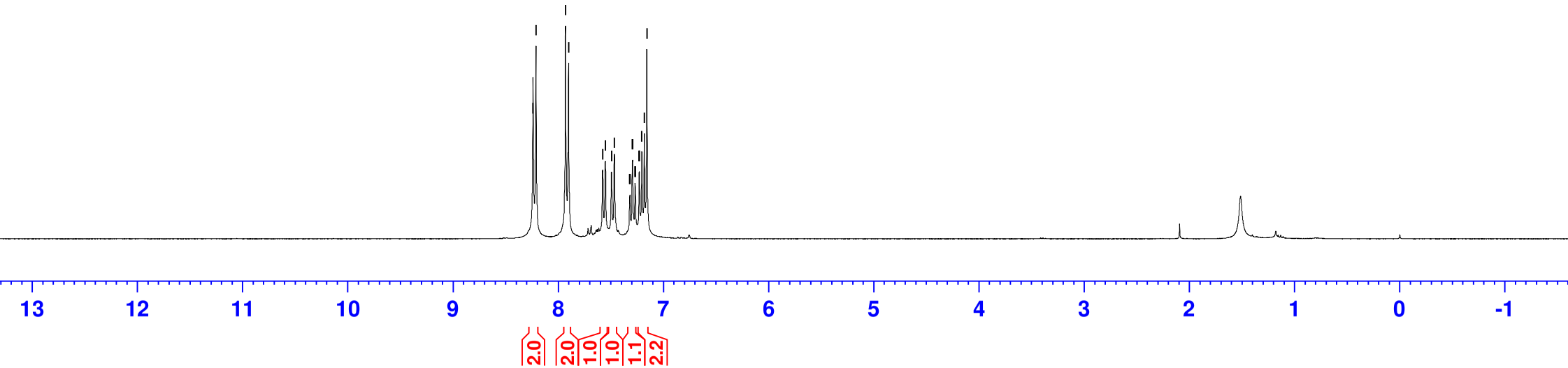
158.91
154.91
149.41
134.87
130.40
126.91
122.16
113.98
113.04
110.44
83.40
77.43
77.01
76.59
55.28
27.70

220 200 180 160 140 120 100 80 60 40 20 0 ppm

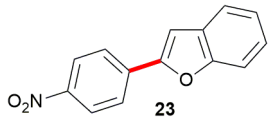
2-(4-nitrophenyl)-benzofuran



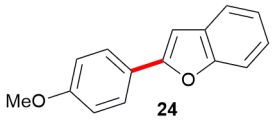
8.241
8.211
7.932
7.902
7.578
7.553
7.494
7.467
7.322
7.318
7.297
7.294
7.271
7.266
7.231
7.228
7.206
7.182
7.158



2-(4-nitrophenyl)-benzofuran



2-(4-methoxyphenyl)-benzofuran



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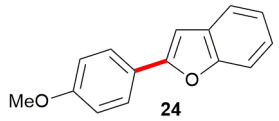
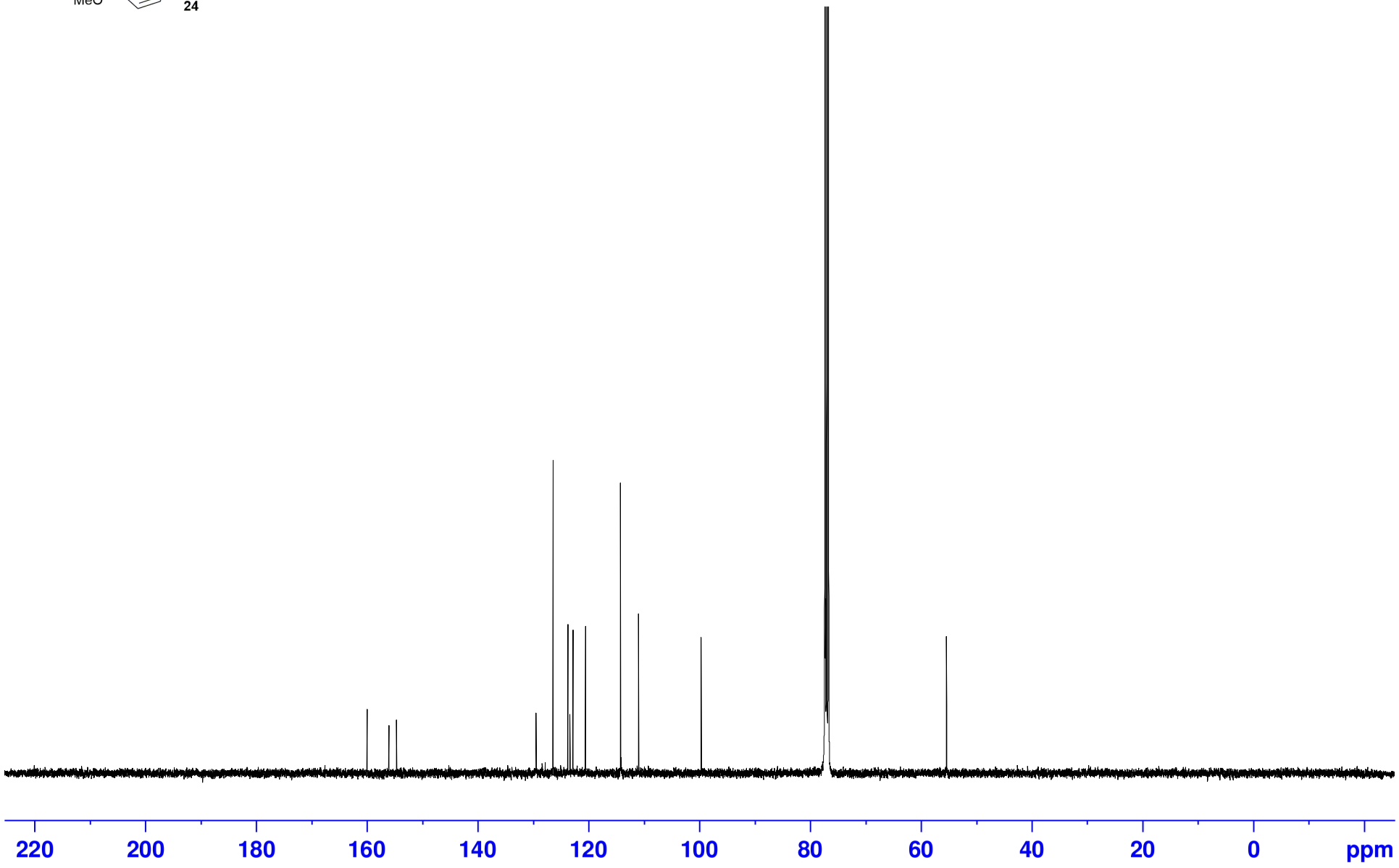
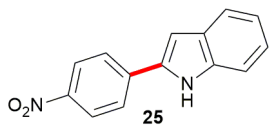
2-(4-methoxyphenyl)-benzofuran



159.99
156.06
154.71
129.50
126.43
123.74
123.37
122.83
120.57
114.26
110.99
99.68
77.34
77.02
76.70
55.39



2-(4-nitrophenyl)-1H-indole

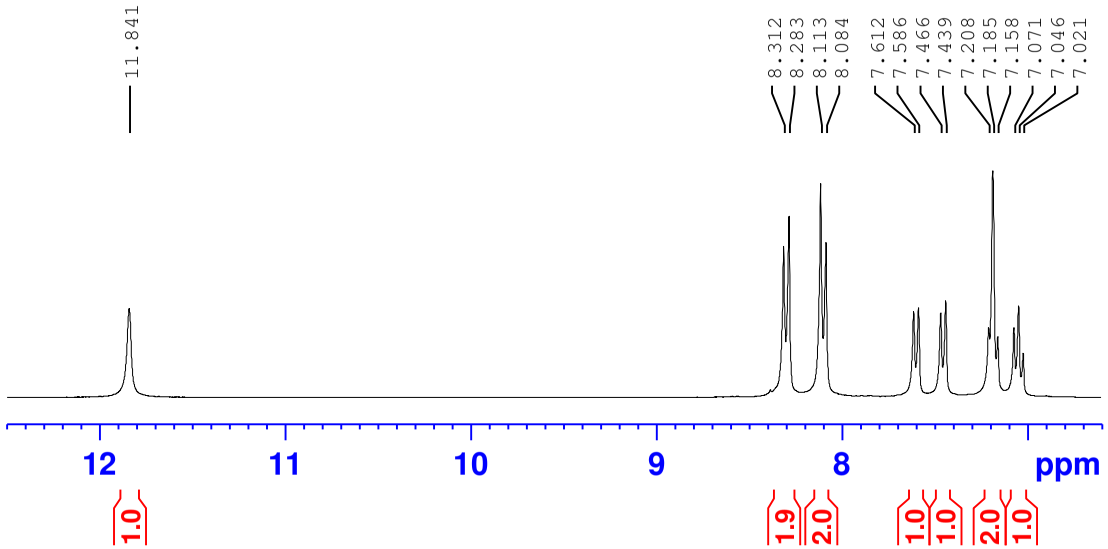


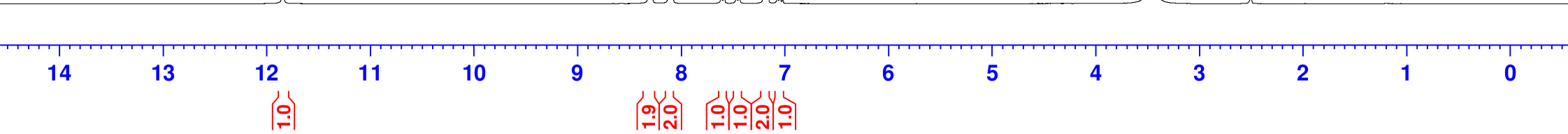
11.841

8.312
8.283
8.113
8.084
7.612
7.586
7.466
7.439
7.208
7.185
7.158
7.071
7.046
7.021

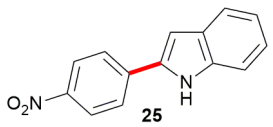
3.452

2.503

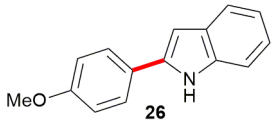


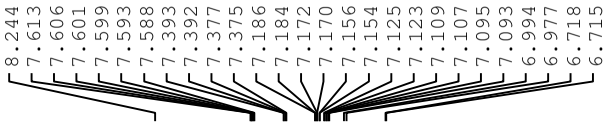


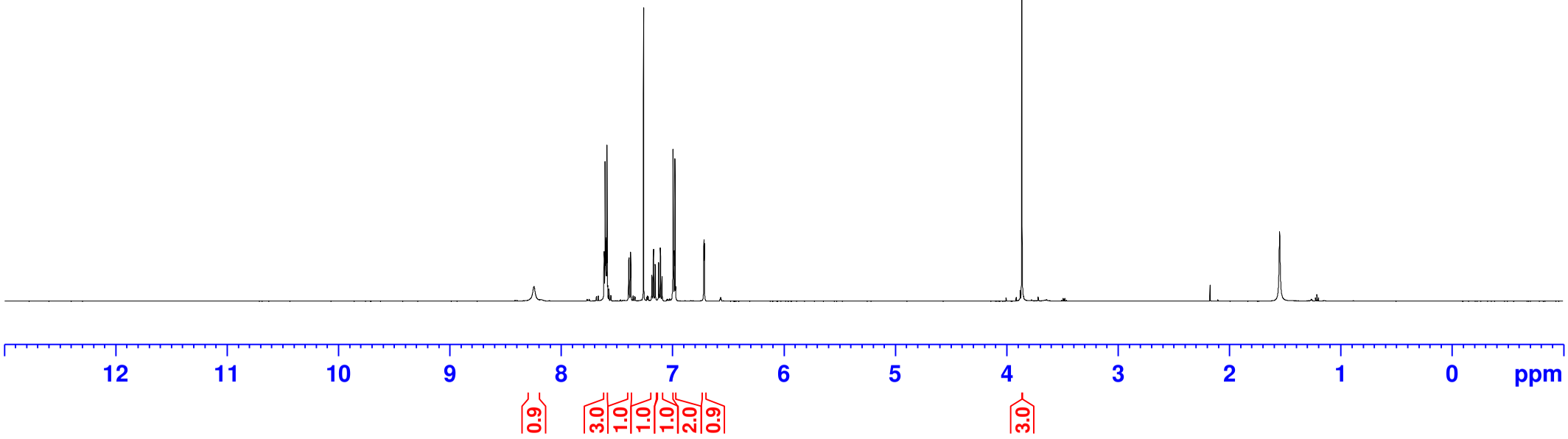
2-(4-nitrophenyl)-indole



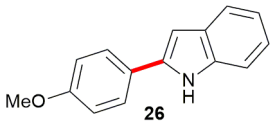
2-(4-methoxyphenyl)-indole



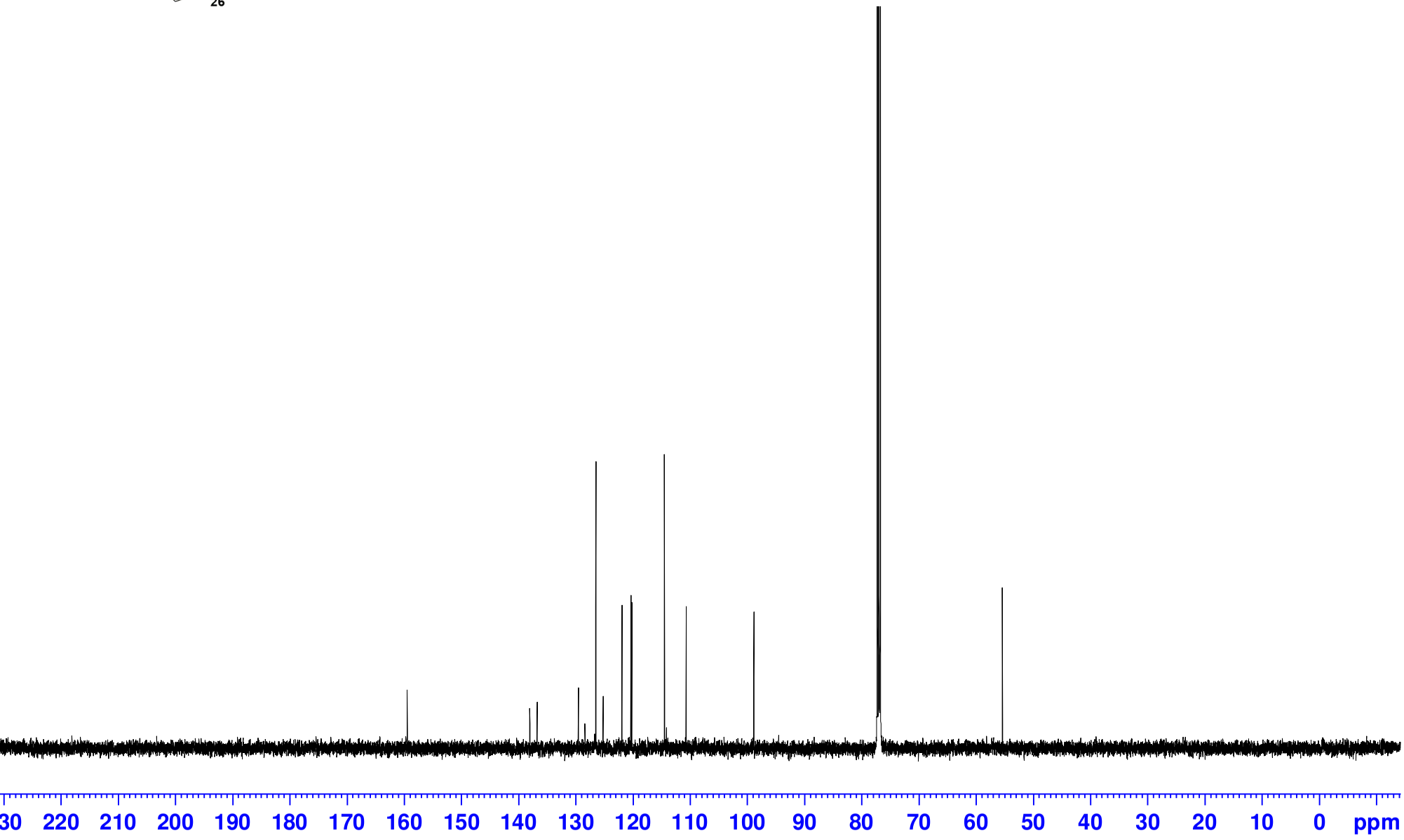




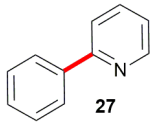
2-(4-methoxyphenyl)-indole



159.40
137.97
136.67
129.45
126.50
125.23
121.93
120.37
120.19
114.50
110.71
98.87
77.27
77.01
76.76
55.40



2-Phenyl-pyridine



8.711
8.695
8.011
8.006
7.983
7.505
7.482
7.457
7.442
7.437
7.433
7.414
7.259
7.252
7.244
7.235
7.231
7.227
7.223
7.216
7.207

8.711
8.695
8.011
8.006
7.983
7.505
7.482
7.457
7.442
7.437
7.433
7.414
7.259
7.252
7.244
7.235
7.231
7.227
7.223
7.216
7.207

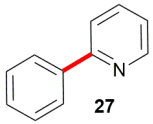
8.5 8.0 7.5 7.0 6.5 ppm

1.0 2.2 2.2 3.3 1.3

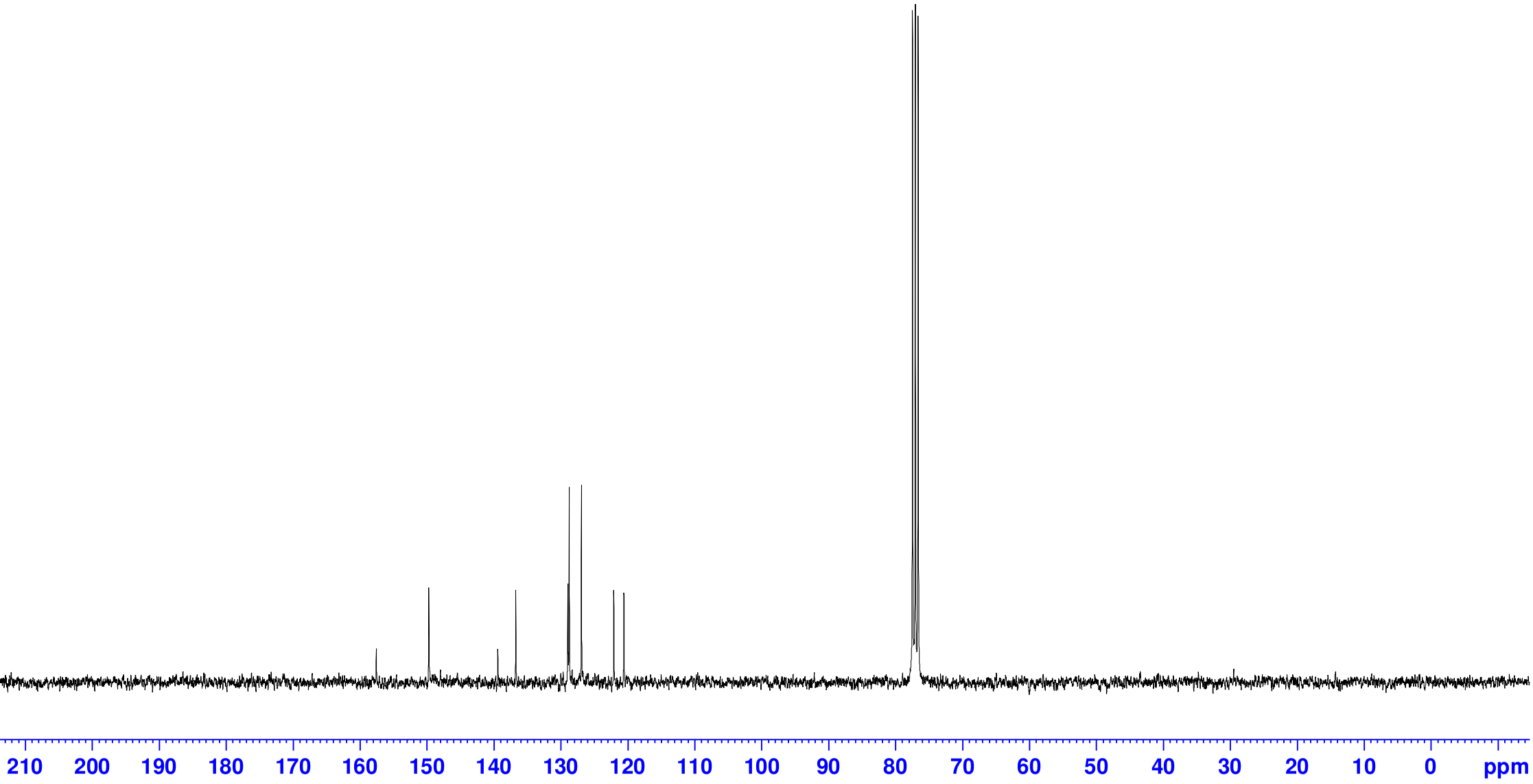
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1

1.0 2.2 2.2 3.3 1.3

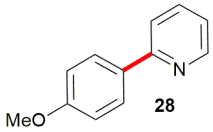
2-Phenyl-pyridine



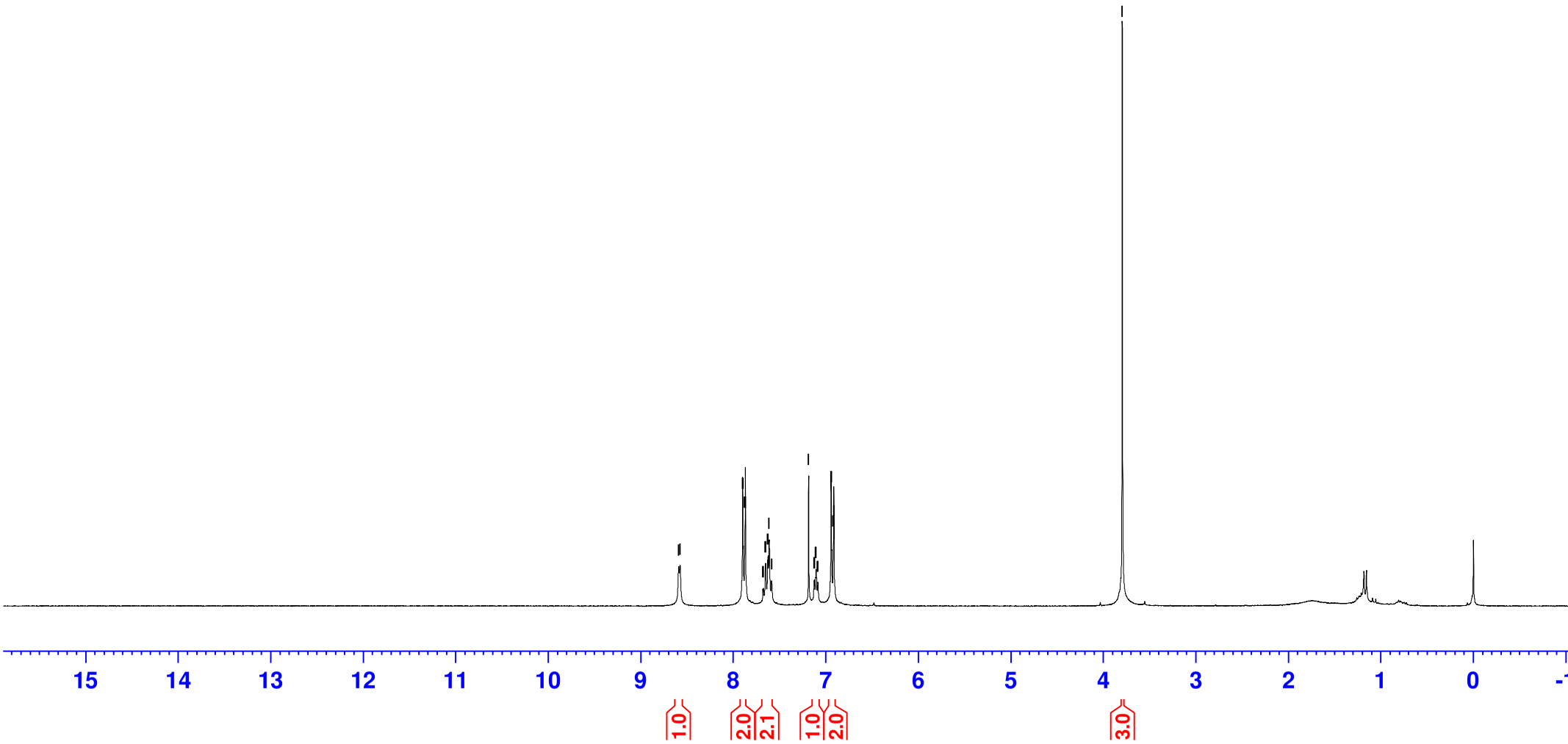
157.51
149.68
139.42
136.74
128.95
128.74
126.92
122.09
120.57
77.45
77.02
76.60



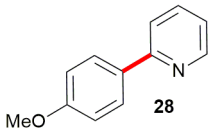
2-(4-methoxyphenyl)-pyridine



8.593
8.578
7.902
7.895
7.879
7.872
7.682
7.676
7.655
7.650
7.632
7.626
7.614
7.588
7.188
7.129
7.125
7.113
7.107
7.090
7.086
6.945
6.939
6.922
6.916
3.797

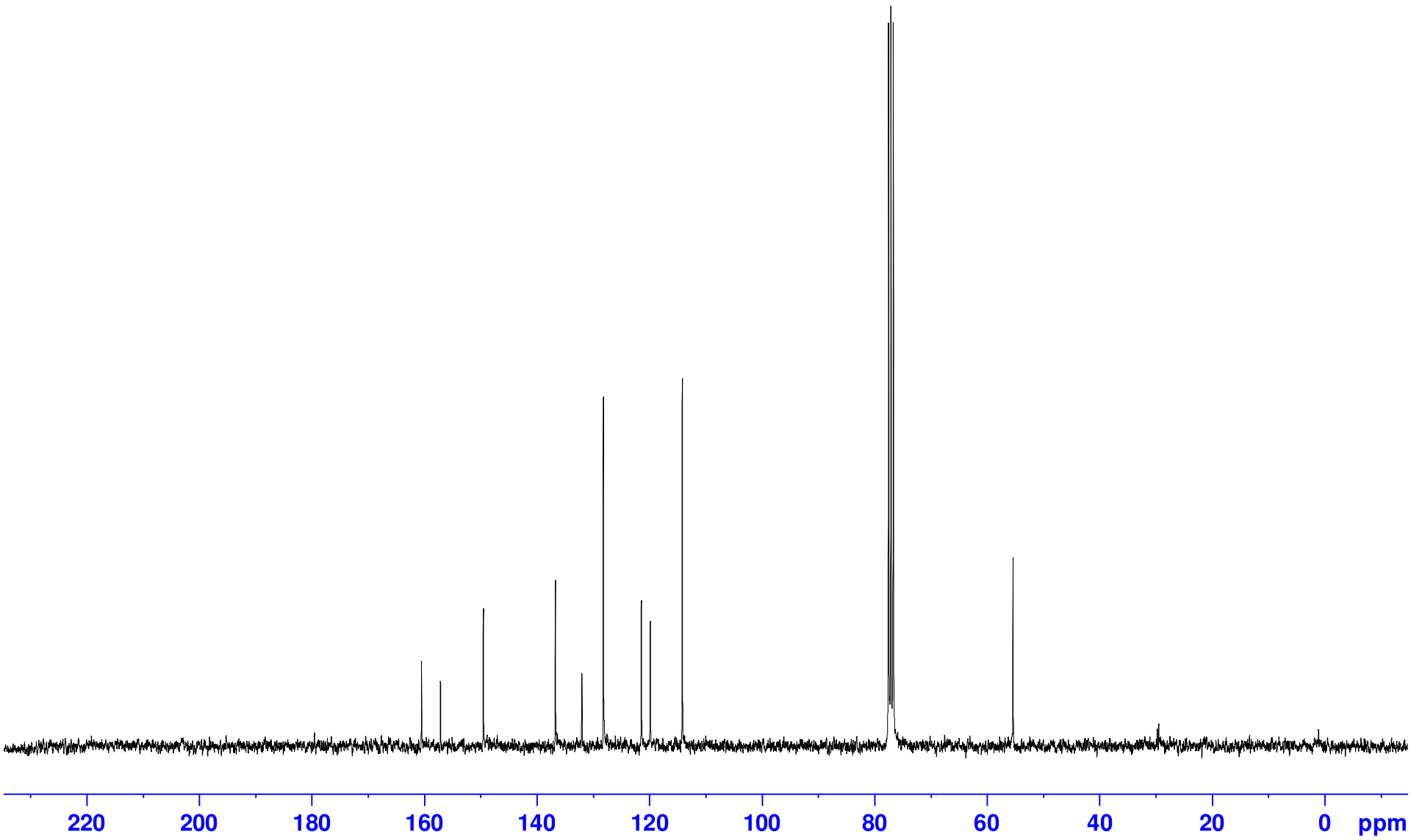


2-(4-methoxyphenyl)-pyridine

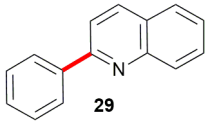


28

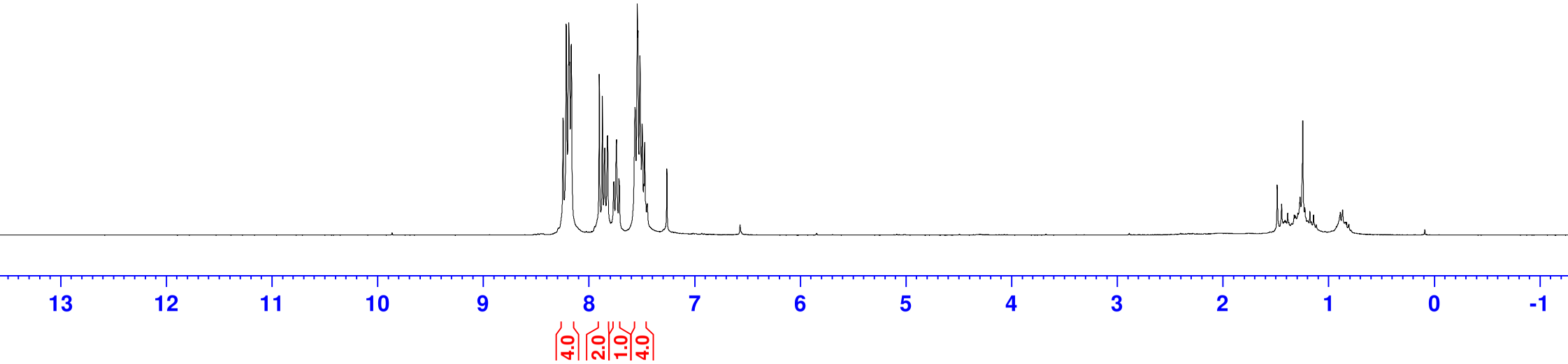
160.48
157.11
149.49
136.68
132.00
128.17
121.41
119.82
114.13
77.47
77.04
76.62
55.34



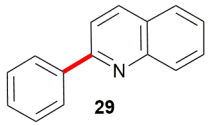
2-phenyl-quinoline



8.244
8.215
8.195
8.190
8.184
8.167
7.901
7.873
7.850
7.823
7.766
7.762
7.739
7.715
7.711
7.563
7.542
7.536
7.517
7.495
7.480
7.472
7.462
7.448
7.262

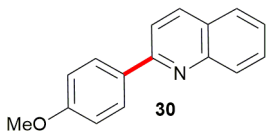


2-Phenyl-quinoline



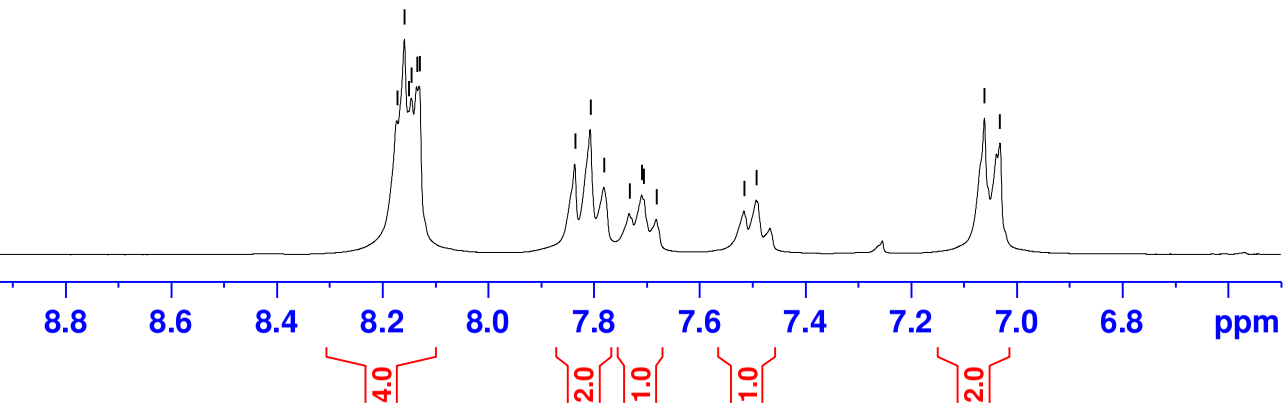
29

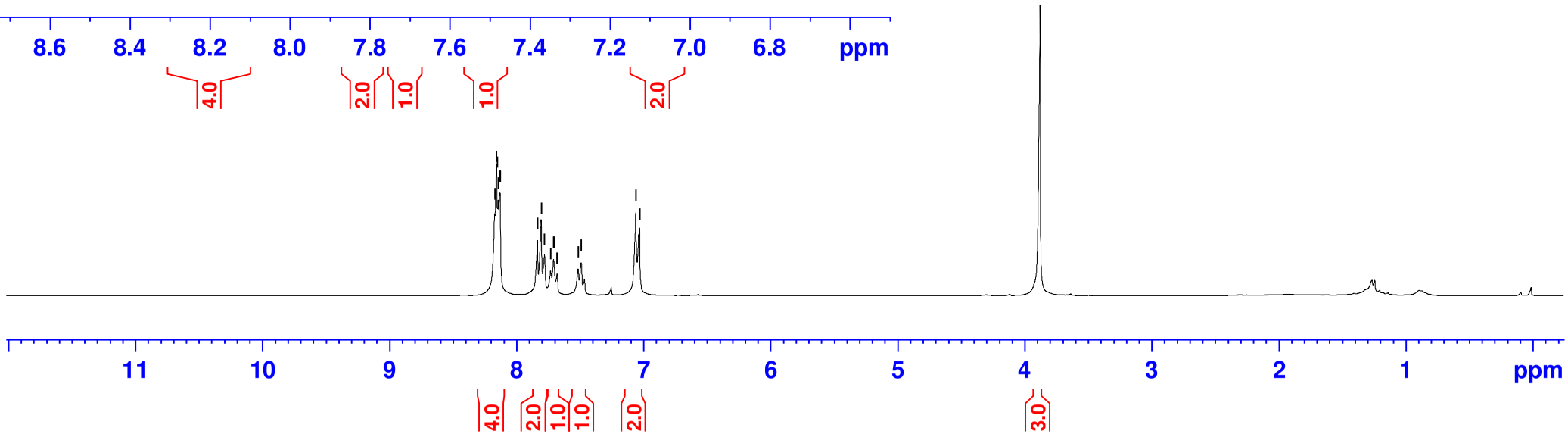
2-(4-methoxyphenyl)-quinoline



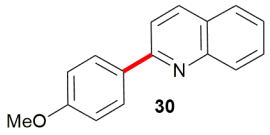
8.173
8.158
8.150
8.145
8.135
8.130
7.836
7.807
7.781
7.733
7.709
7.705
7.682
7.516
7.492
7.061
7.032

3.879

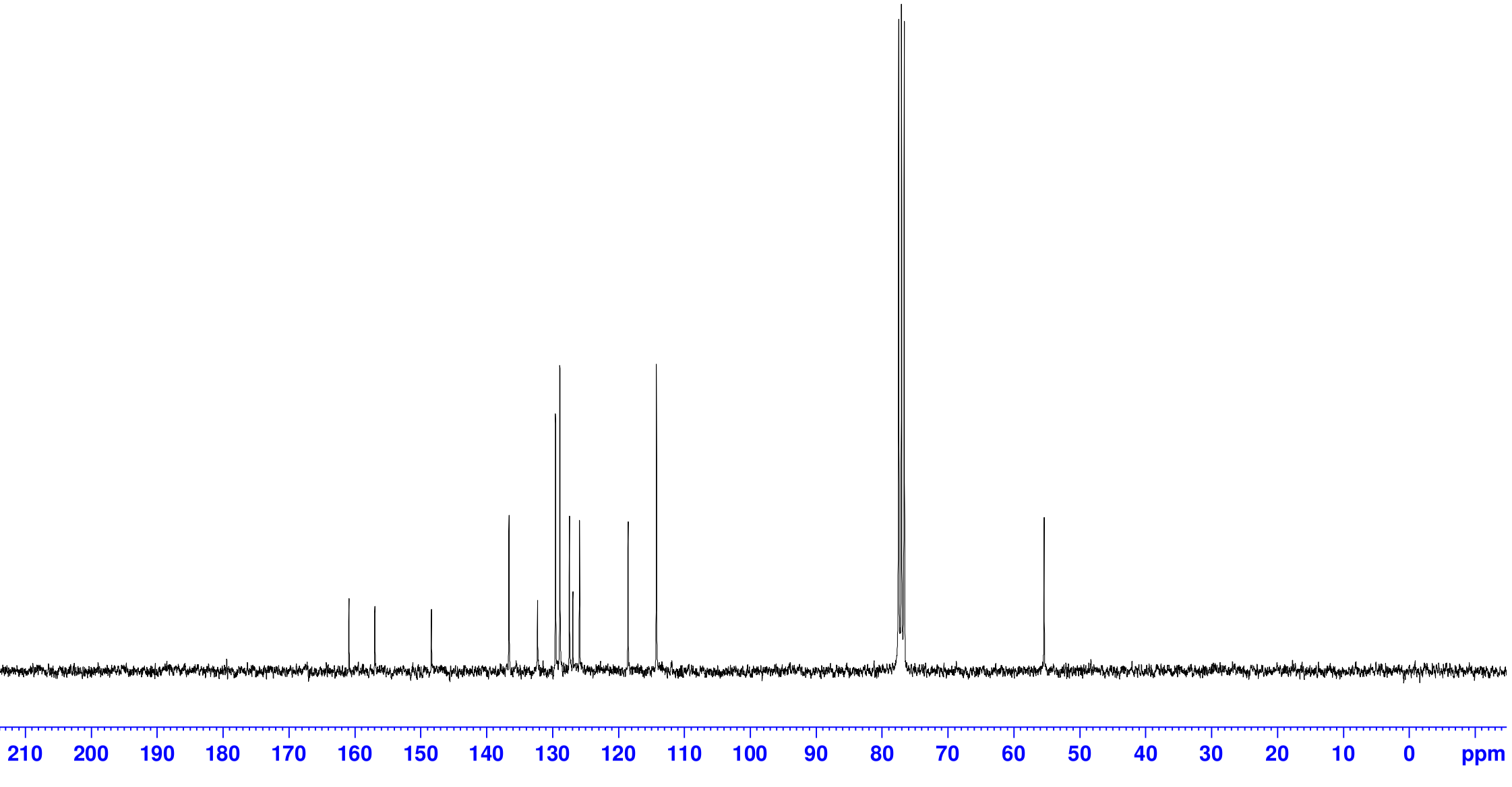




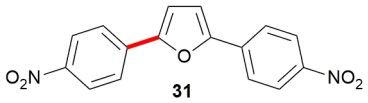
2-(4-methoxyphenyl)-quinoline



160.84
156.91
148.31
136.62
132.28
129.55
128.89
127.44
126.92
125.91
118.54
114.24
77.47
77.05
76.63
55.40

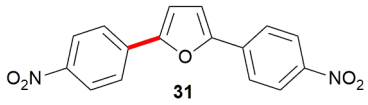


2,5 bis(4-nitrophenyl)-furan

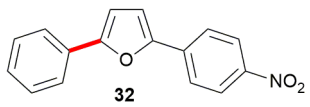


31

2,5 bis(4-nitrophenyl)-furan

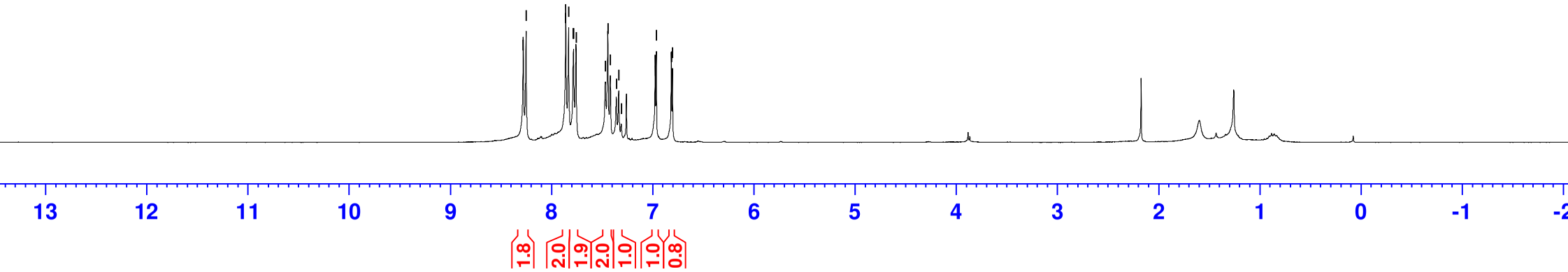


2-(4-nitrophenyl)-5-phenylfuran

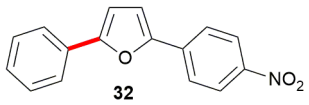


32

8.28
8.25
7.86
7.83
7.79
7.78
7.76
7.47
7.44
7.42
7.36
7.33
7.31
6.98
6.96
6.81
6.80

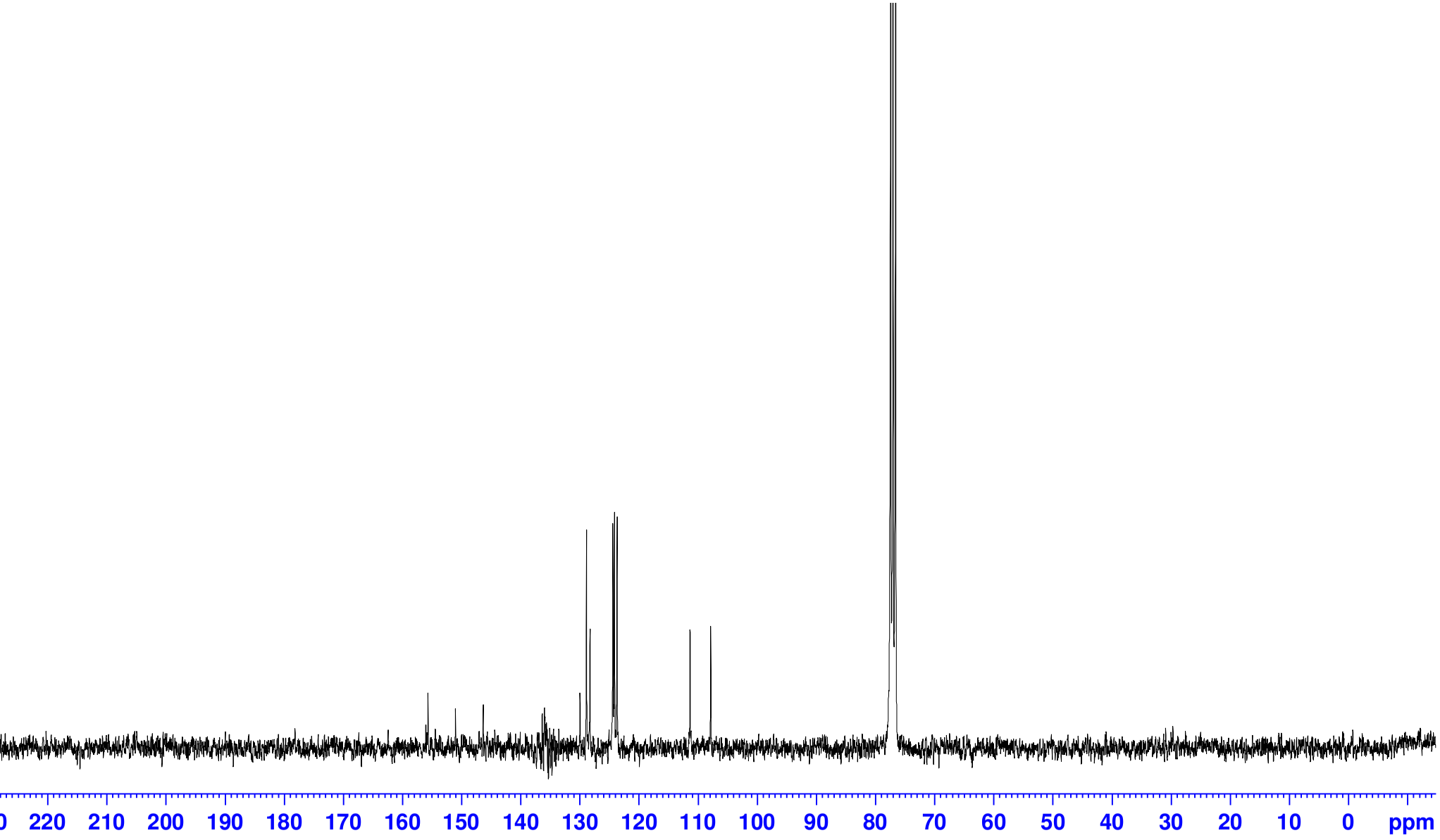


2-(4-nitrophenyl)-5-phenylfuran

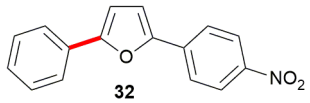


32

155.62
150.98
146.27
135.93
129.98
128.89
128.29
124.42
124.14
123.71
111.37
107.88
77.45
77.02
76.60

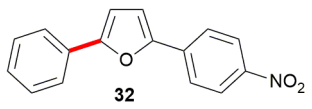


2-(4-methoxyphenyl)-5-(4-nitrophenyl)furan



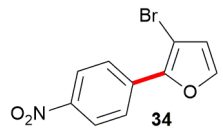
32

2-(4-methoxyphenyl)-5-(4-nitrophenyl)-furan

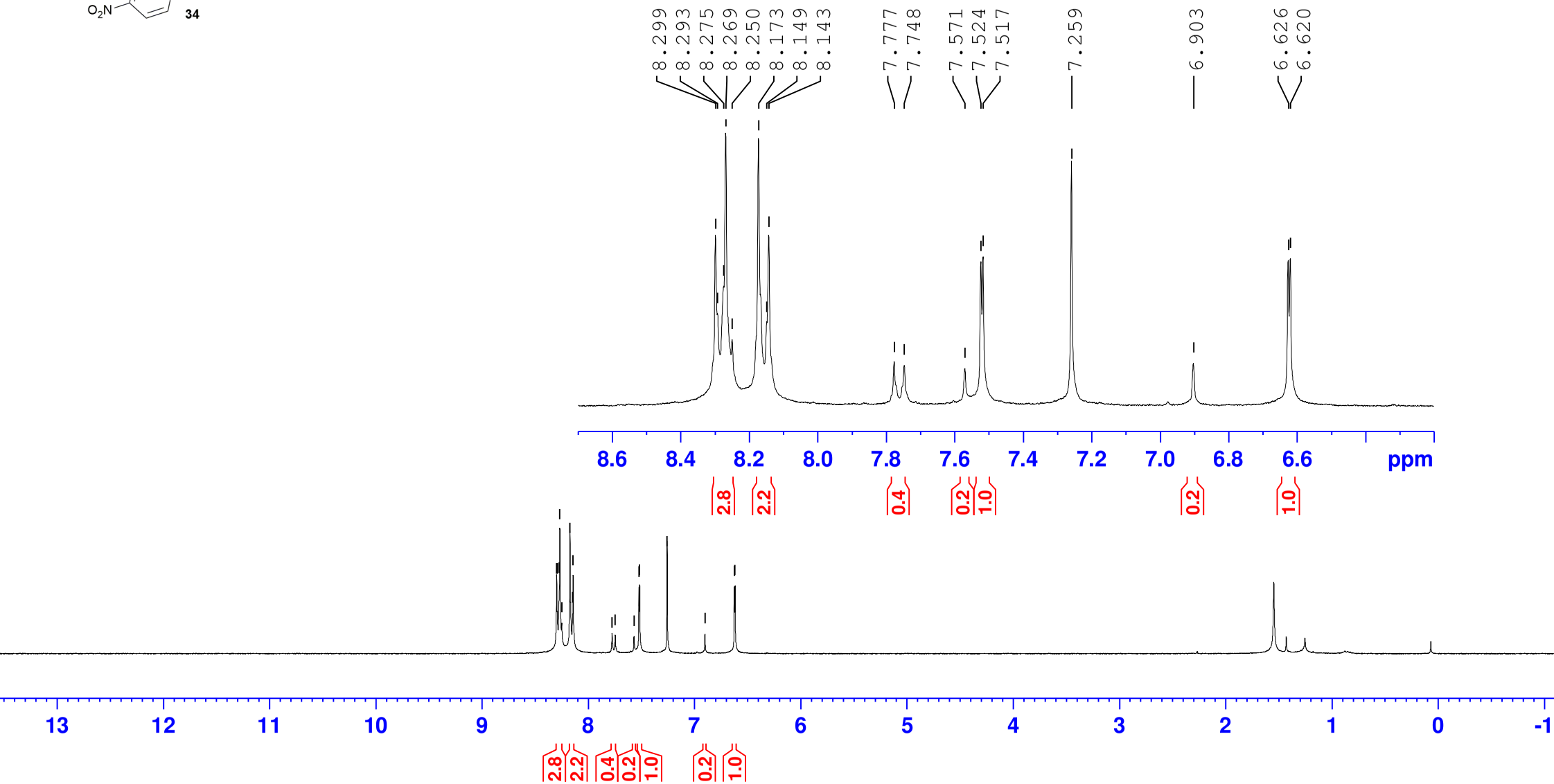


32

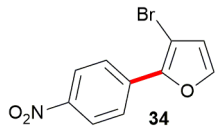
3-bromo-2-(4-nitrophenyl)-furan
4-bromo-2-(4-nitrophenyl)-furan



8.299
8.293
8.275
8.269
8.250
8.173
8.149
8.143
7.777
7.748
7.571
7.524
7.517
7.259
6.903
6.626
6.620

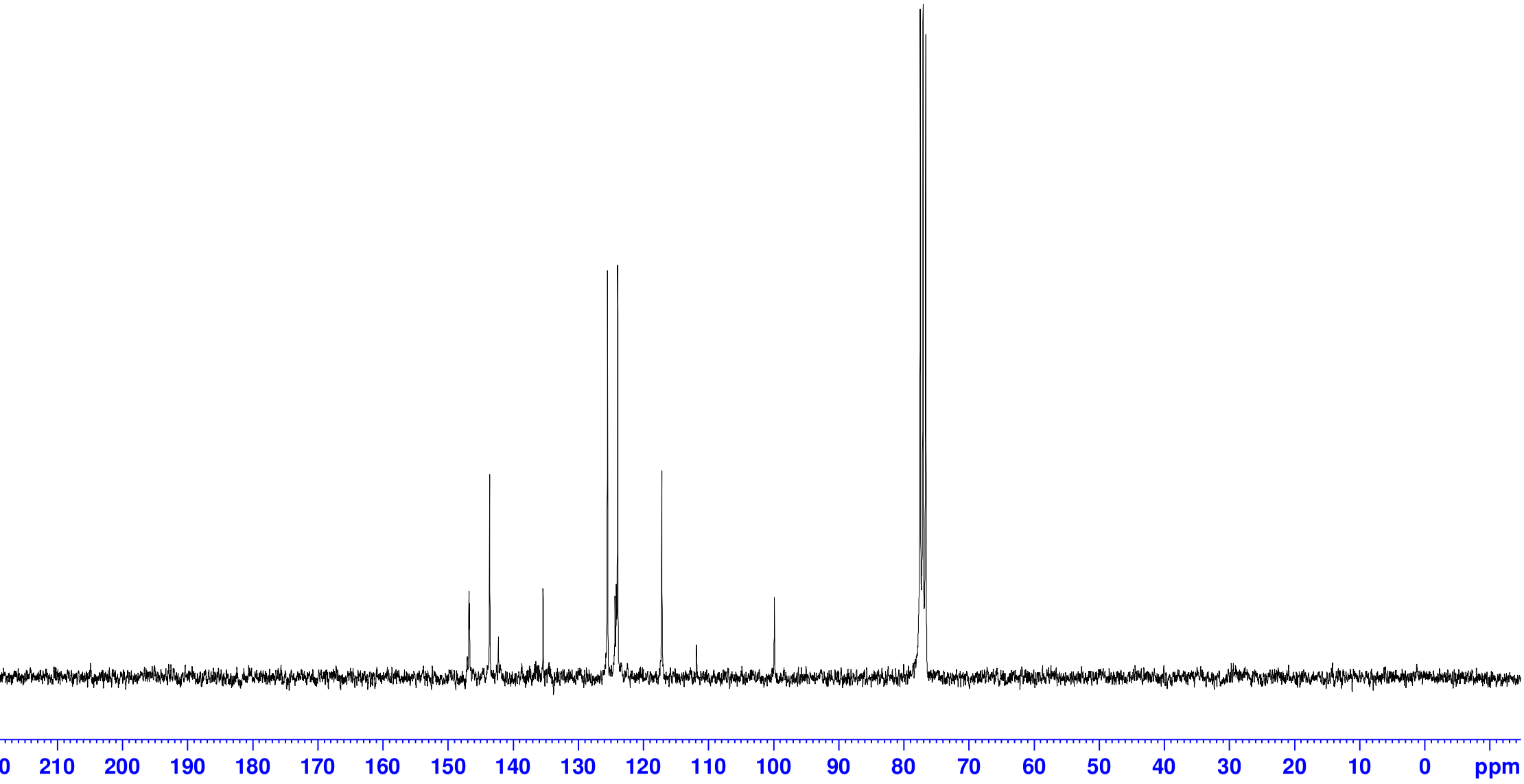


3-bromo-2-(4-nitrophenyl)-furan
4-bromo-2-(4-nitrophenyl)-furan

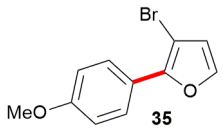


34

146.72
146.64
143.54
142.18
135.41
125.51
124.36
124.16
123.94
117.16
111.84
99.88
77.47
77.05
76.62

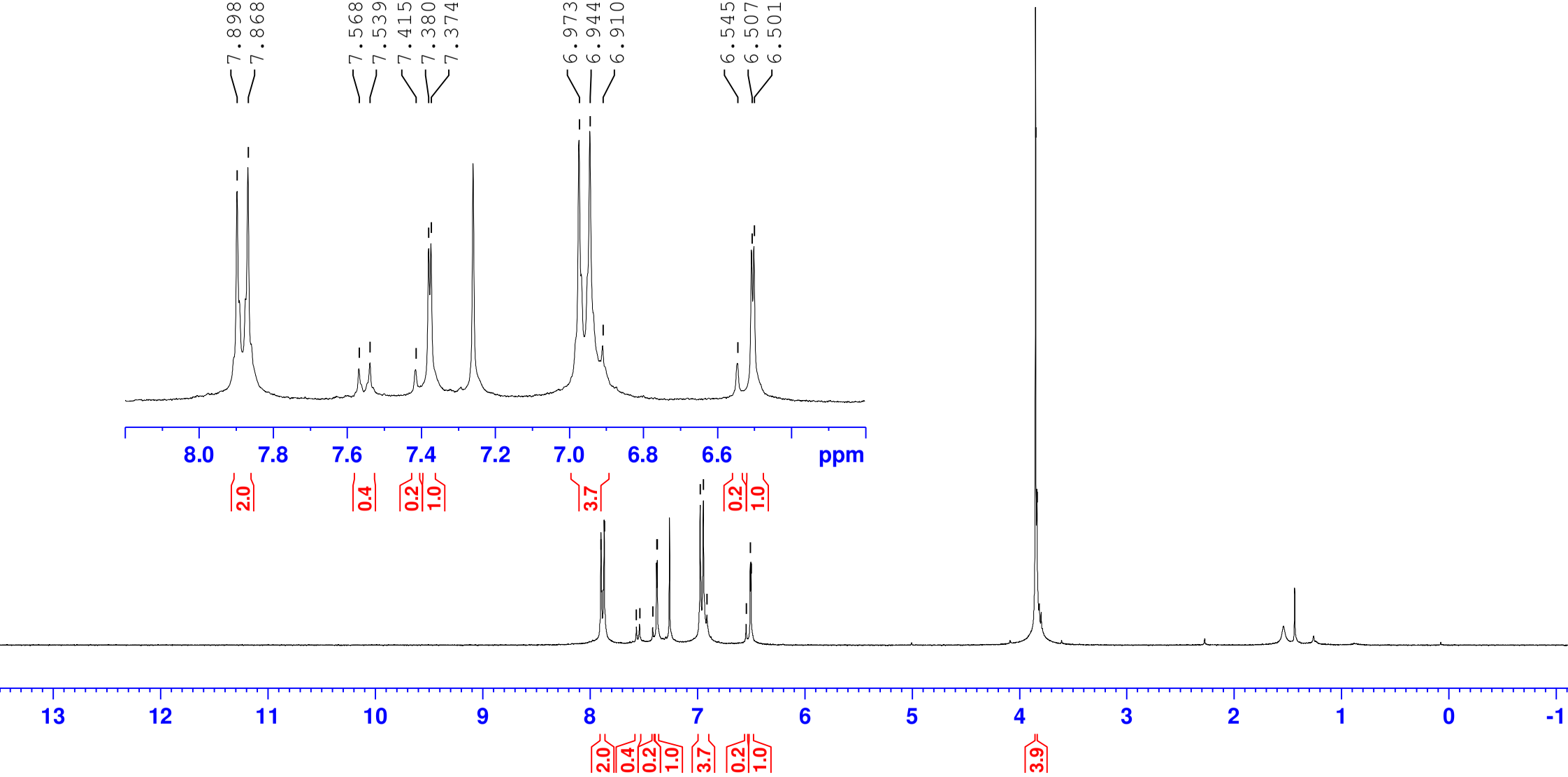


3-bromo-2-(4-methoxyphenyl)-furan
4-bromo-2-(4-methoxyphenyl)-furan

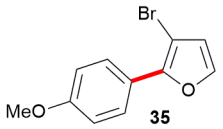


7.898 7.868 7.568 7.539 7.415 7.380 7.374 6.973 6.944 6.910 6.545 6.507 6.501

3.848 3.836

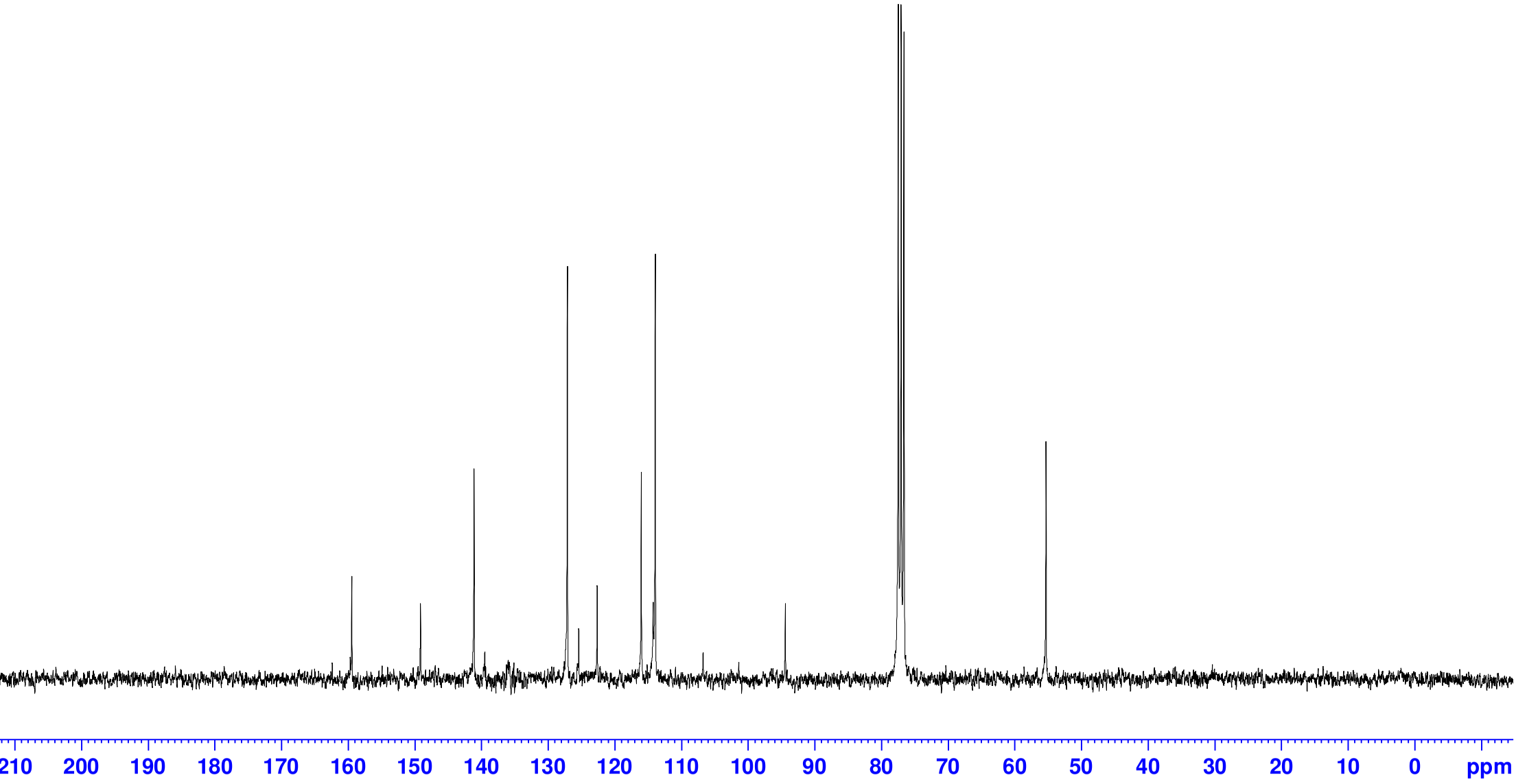


3-bromo-2-(4-methoxyphenyl)-furan
4-bromo-2-(4-methoxyphenyl)-furan

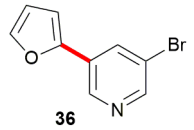


35

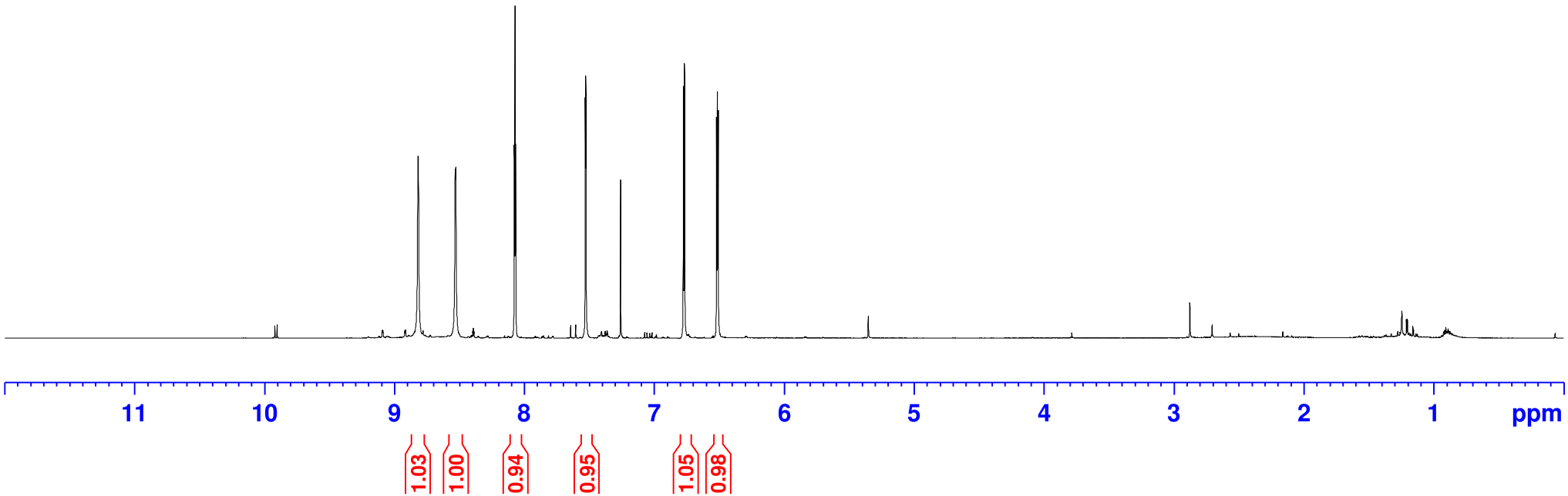
159.39
149.09
141.13
139.52
127.12
125.42
122.65
116.03
114.24
113.93
106.76
101.19
94.42
77.47
77.05
76.62
55.31



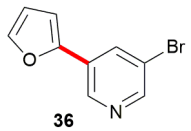
3-bromo-5-(furan-2-yl)pyridine



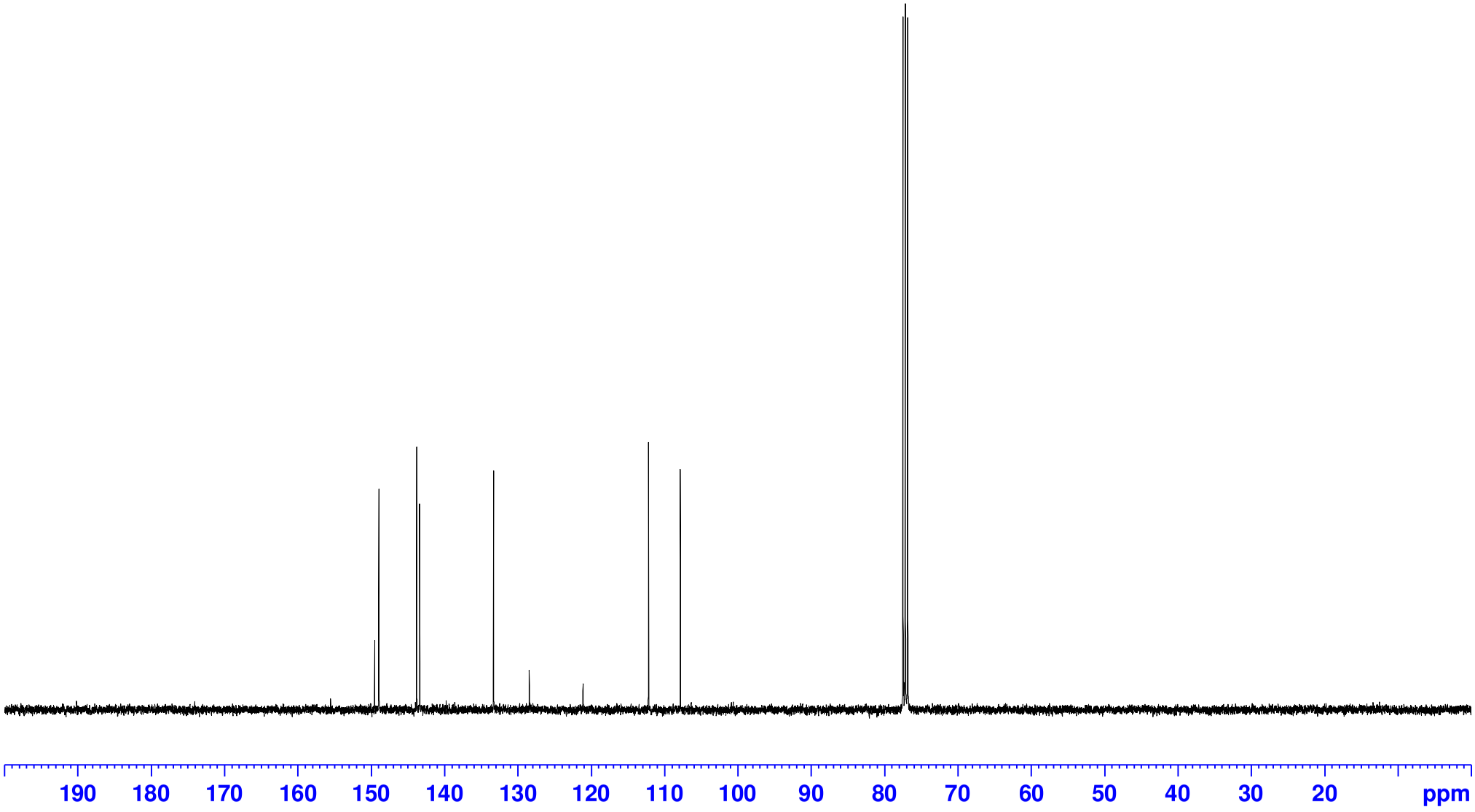
8.820
8.817
8.533
8.529
8.078
8.073
8.068
7.532
7.531
7.528
7.527
6.777
6.776
6.769
6.767
6.522
6.517
6.513
6.509



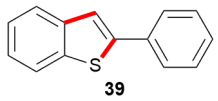
3-bromo-5-(furan-2-yl)pyridine



149.53
148.97
143.80
143.39
133.32
128.45
121.11
112.19
107.84

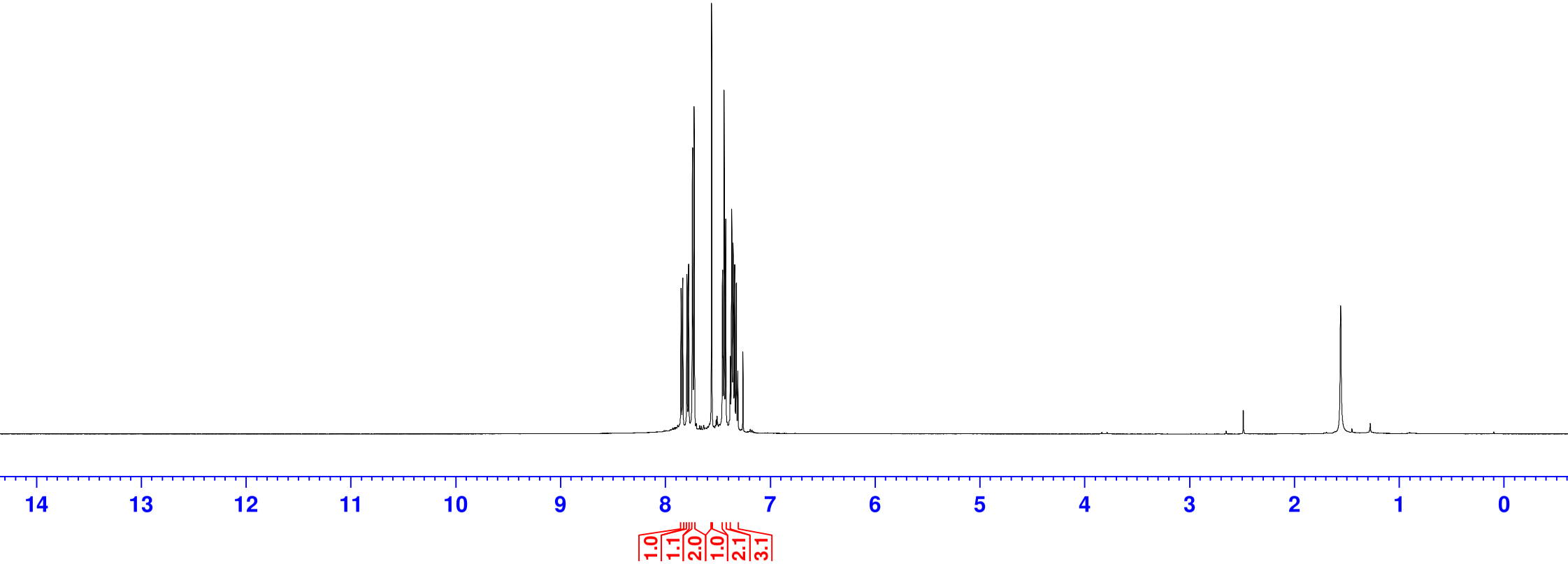


2-phenylbenzo[b]thiophene

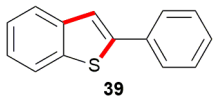


39

7.850
7.834
7.793
7.778
7.740
7.725
7.558
7.454
7.439
7.424
7.380
7.366
7.353
7.351
7.338
7.322
7.308
7.259

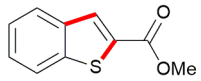


2-phenylbenzo[b]thiophene



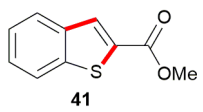
39

methyl benzo[b]thiophene-2-carboxylate



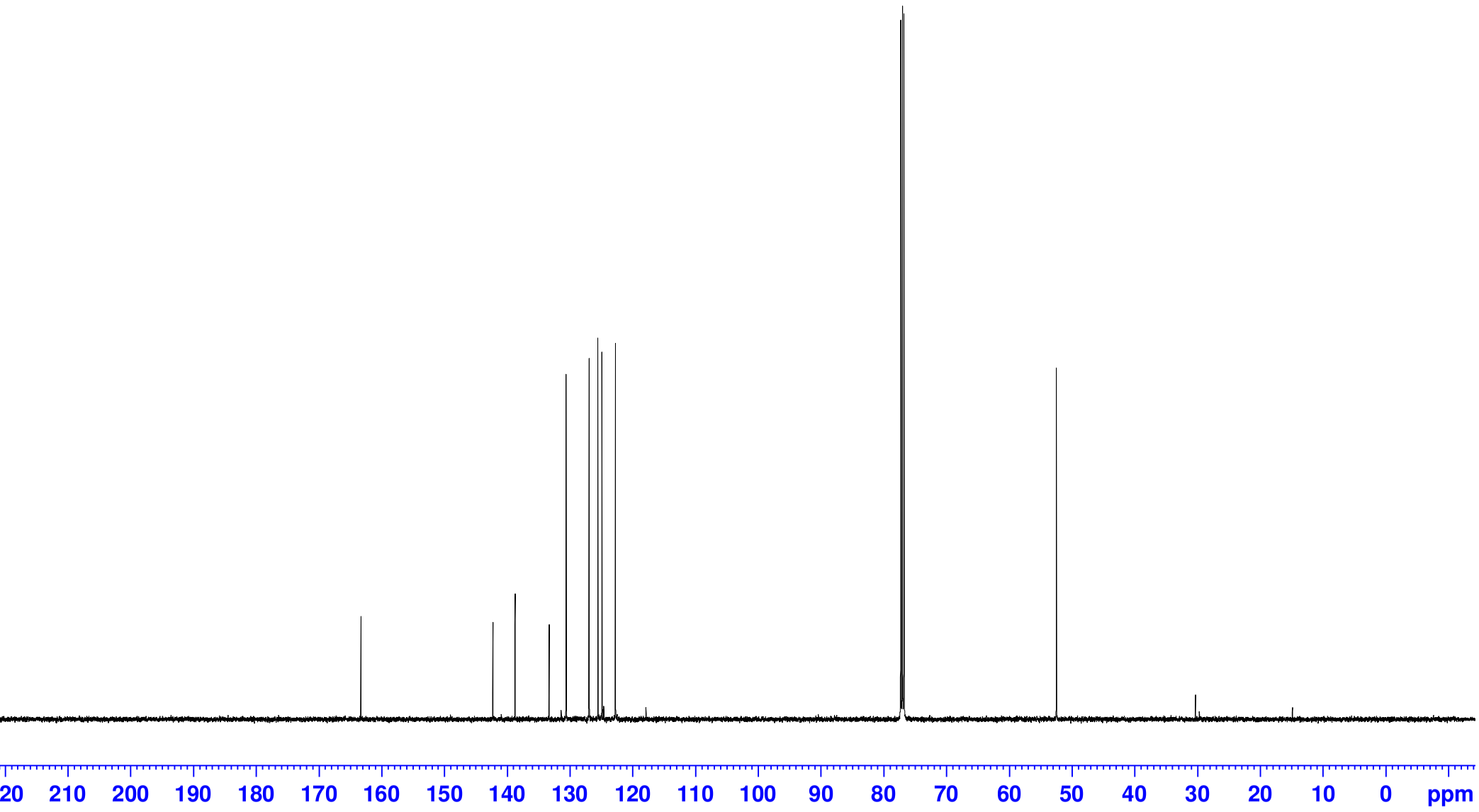
41

methyl benzo[b]thiophene-2-carboxylate

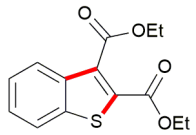


41

163.27
142.24
138.70
133.34
130.64
126.96
125.56
124.92
122.77
77.29
77.04
76.78
52.50

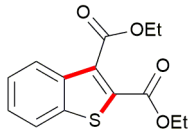


diethyl benzo[b]thiophene-2,3-dicarboxylate



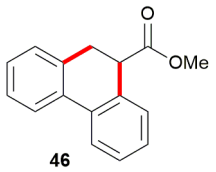
43

diethyl benzo[b]thiophene-2,3-dicarboxylate

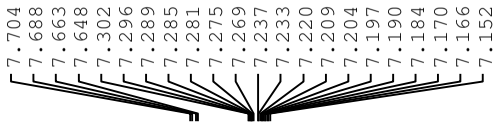


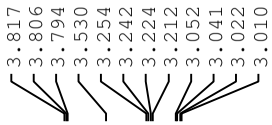
43

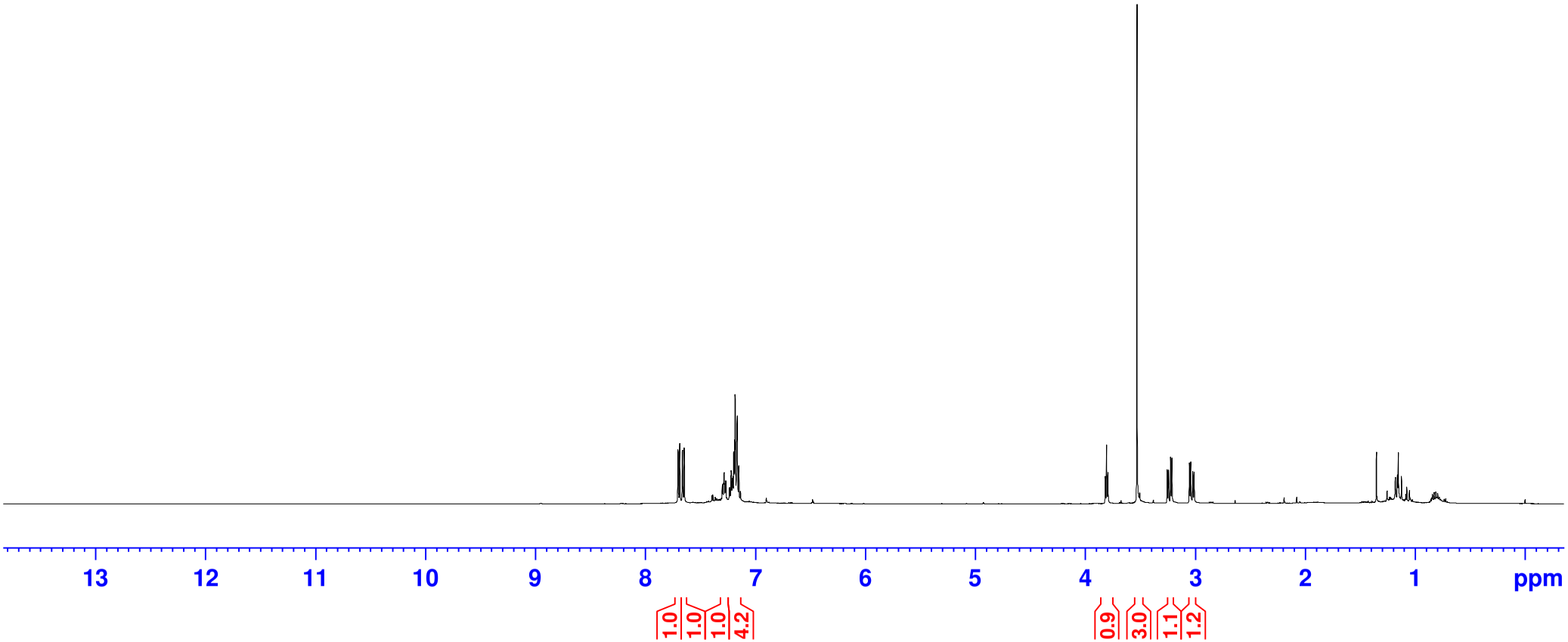
methyl 9,10-dihydrophenanthrene-9-carboxylate



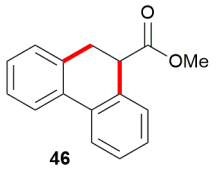
46







methyl 9,10-dihydrophenanthrene-9-carboxylate



46

173.55

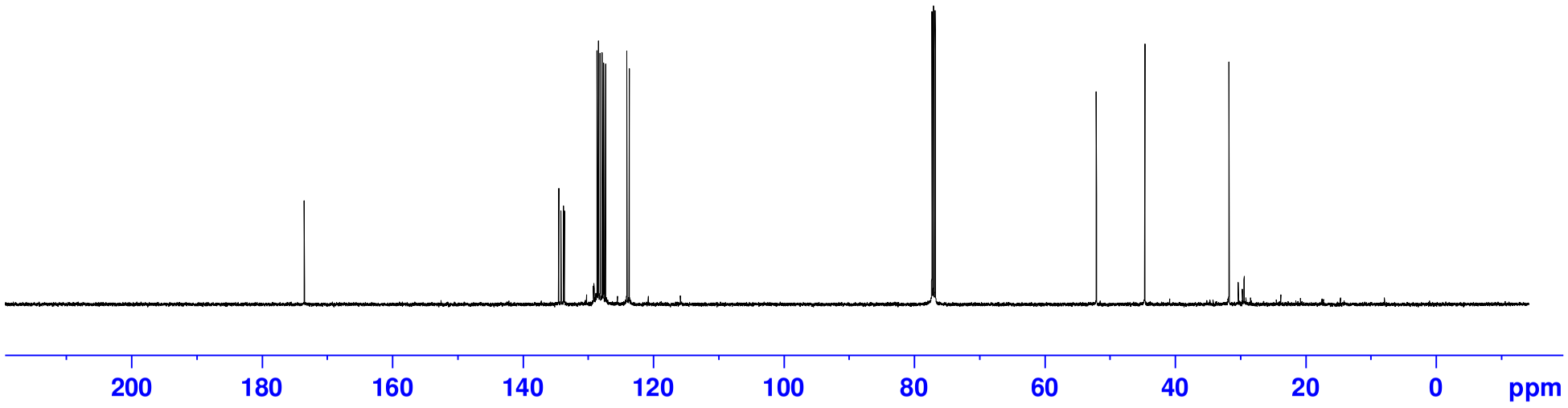
134.54
134.19
133.80
133.66
128.66
128.46
128.19
127.86
127.65
127.36
124.10
123.73

77.31
77.06
76.81

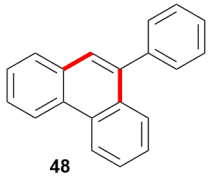
52.11

44.67

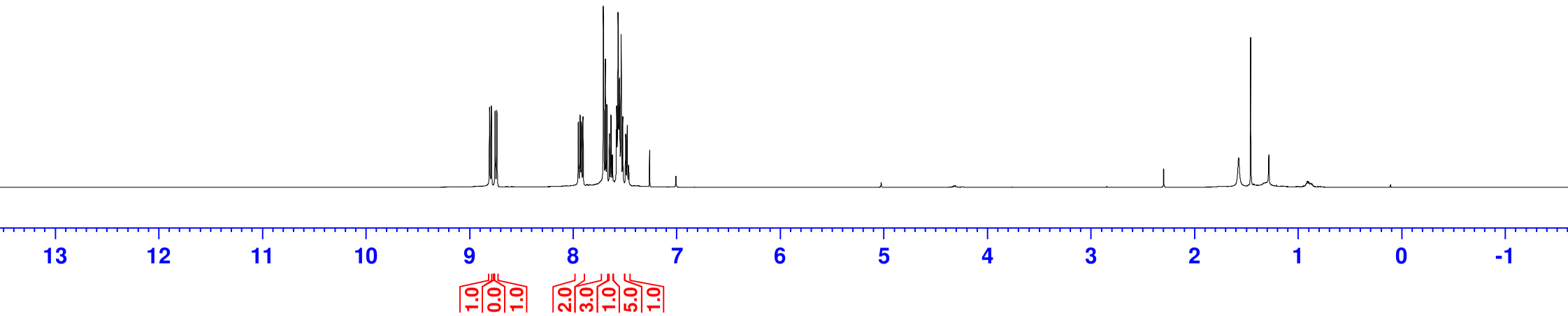
31.78



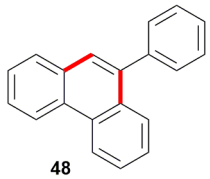
9-phenylphenanthrene



8.807
8.791
8.754
8.737
7.950
7.934
7.922
7.907
7.709
7.704
7.689
7.675
7.673
7.651
7.650
7.636
7.622
7.584
7.580
7.567
7.556
7.553
7.552
7.537
7.522
7.493
7.490
7.483
7.479
7.474
7.464

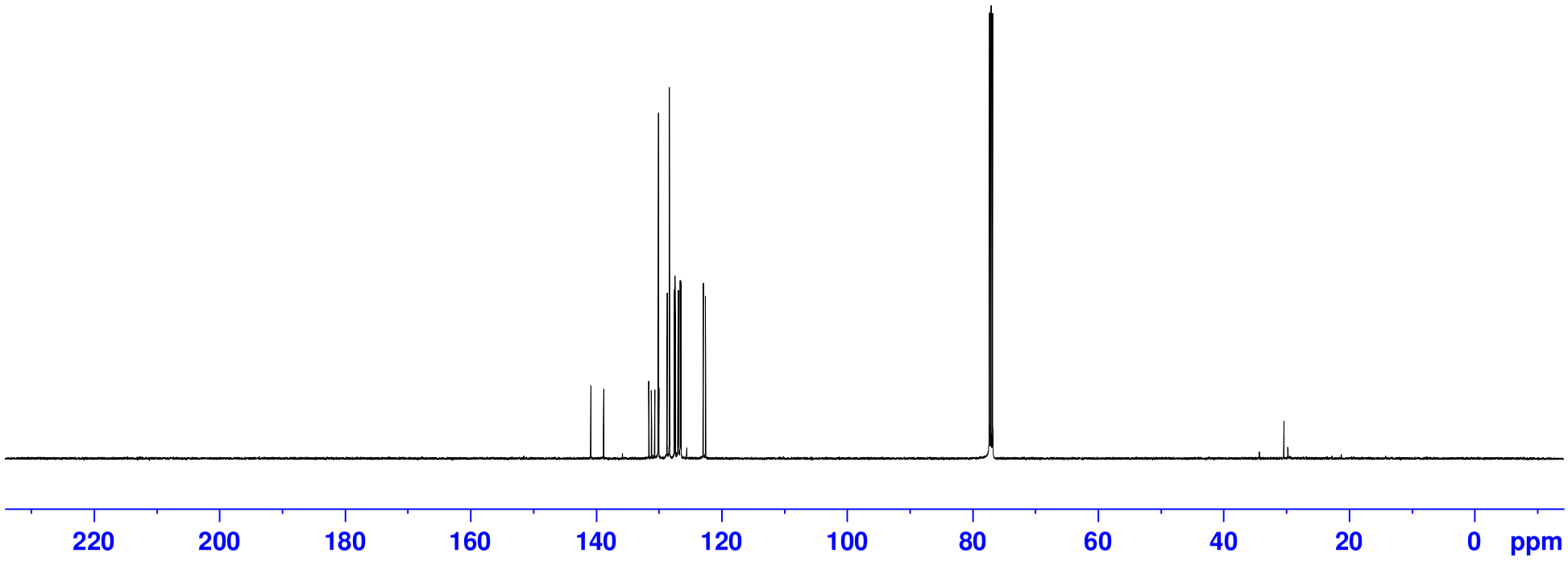


9-phenylphenanthrene

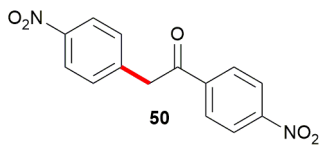


140.83
138.81
131.59
131.17
130.65
130.09
129.99
128.69
128.33
127.53
127.39
126.95
126.87
126.60
126.52
126.47
122.92
122.56

77.30
77.04
76.79

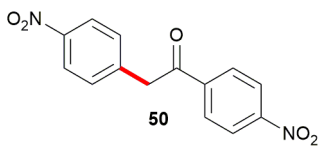


1,2-bis(4-nitrophenyl)ethan-1-one



50

1,2-bis(4-nitrophenyl)ethan-1-one

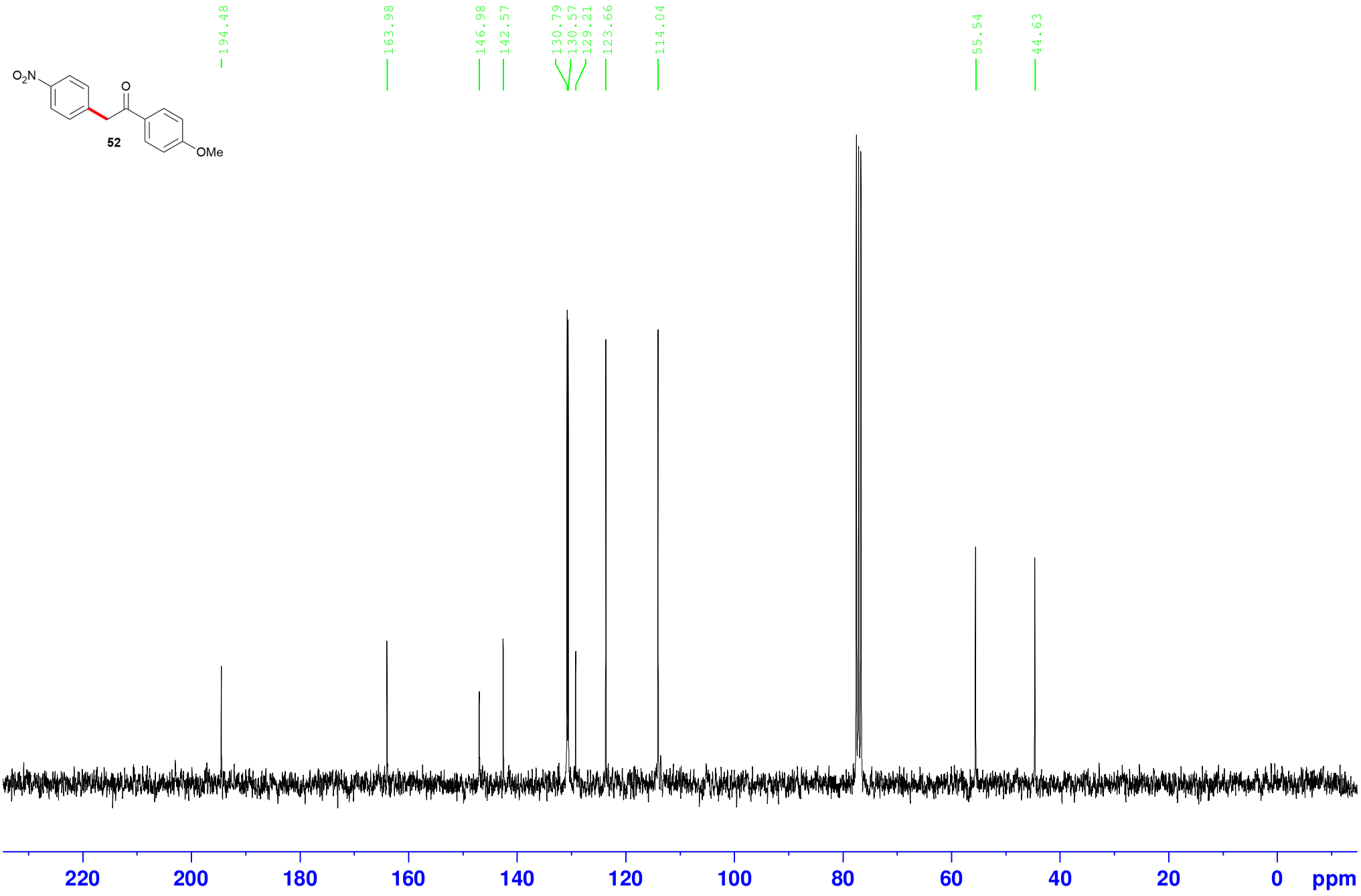


50

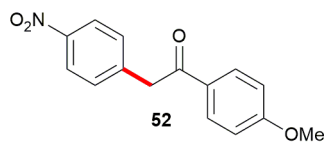
194.51
150.64
147.32
140.75
140.54
130.66
129.45
124.08
123.89
45.34

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

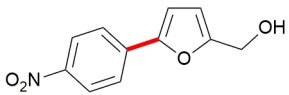
2-(4-methoxyphenyl)-1-(4-nitrophenyl)ethan-1-one



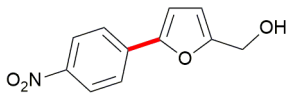
2-(4-methoxyphenyl)-1-(4-nitrophenyl)ethan-1-one



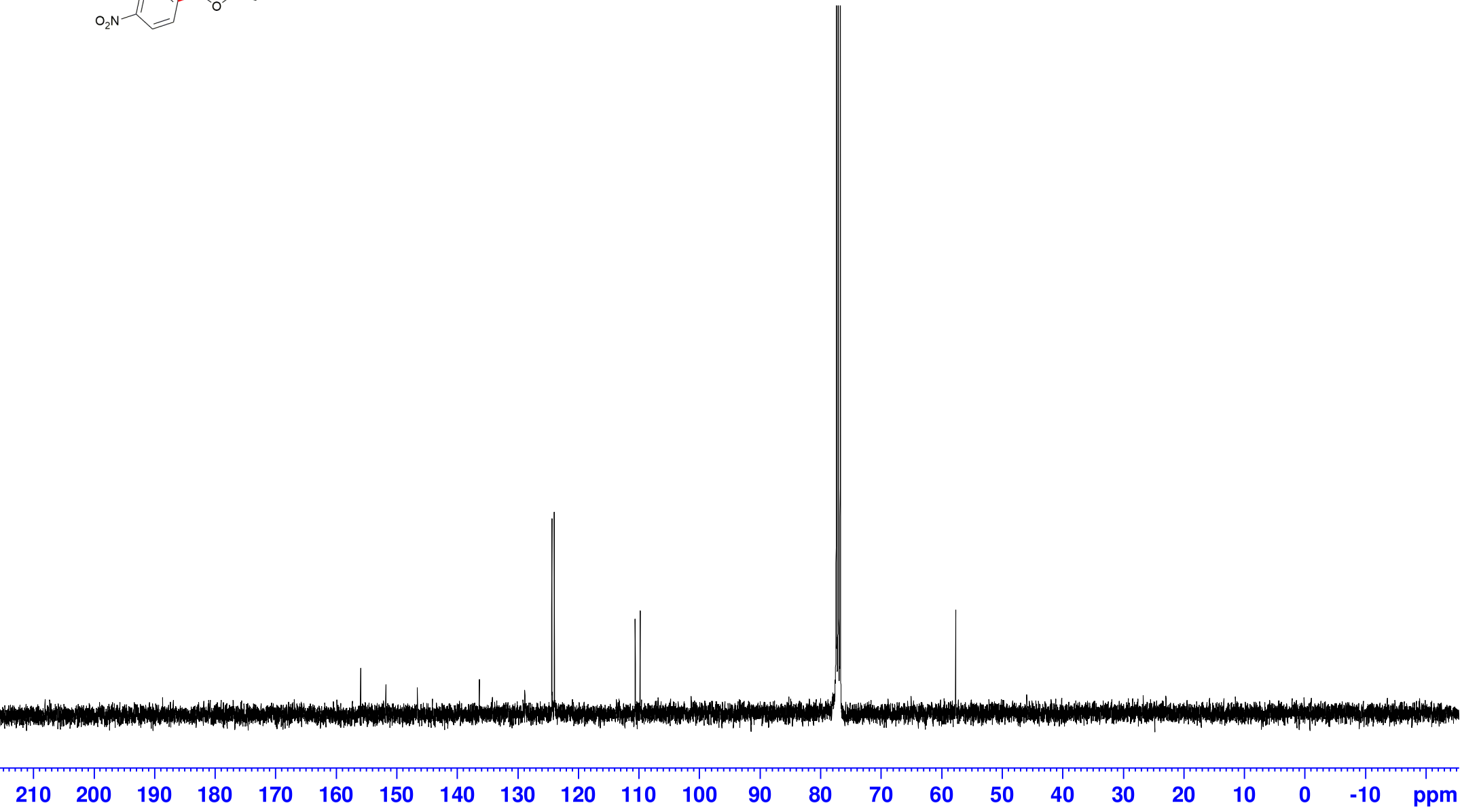
(5-(4-nitrophenyl)furan-2-yl)methanol



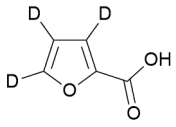
(5-(4-nitrophenyl)furan-2-yl)methanol



155.89
151.73
146.56
136.30
124.39
124.00
110.63
109.80
57.68



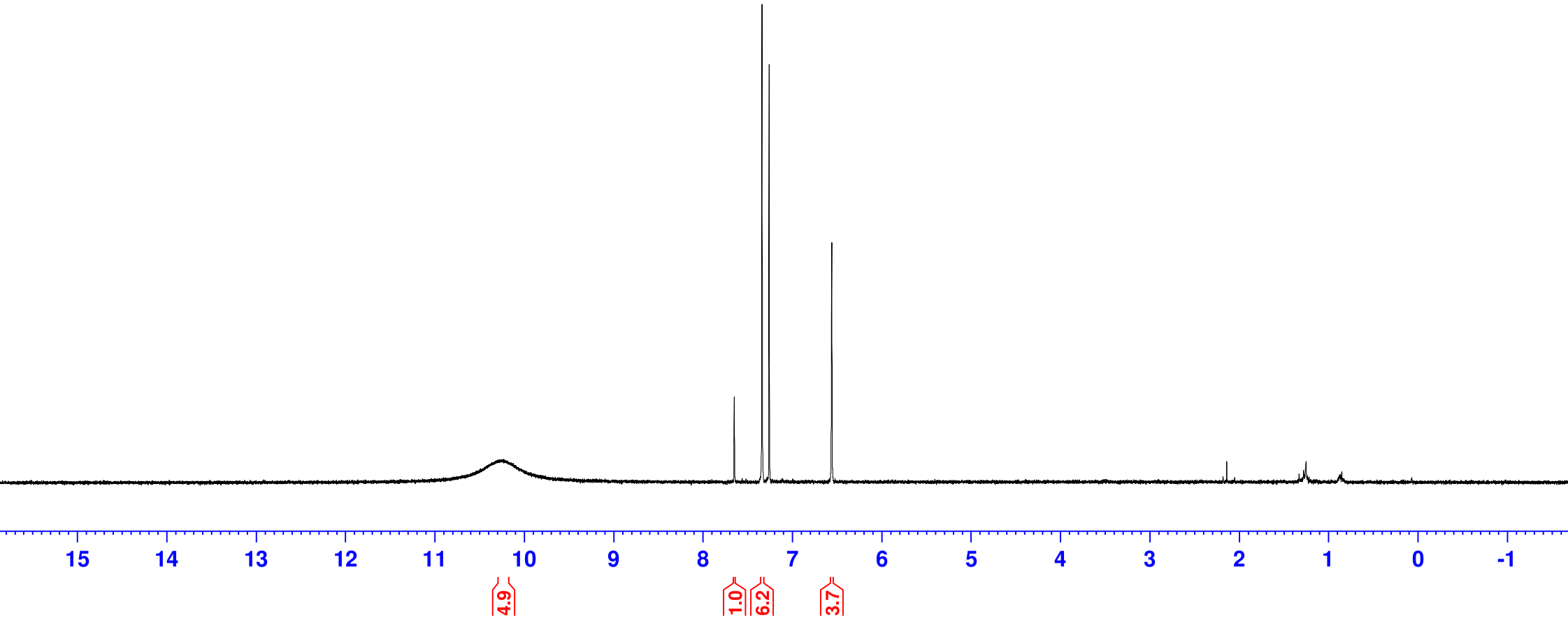
d3-furoic-acid

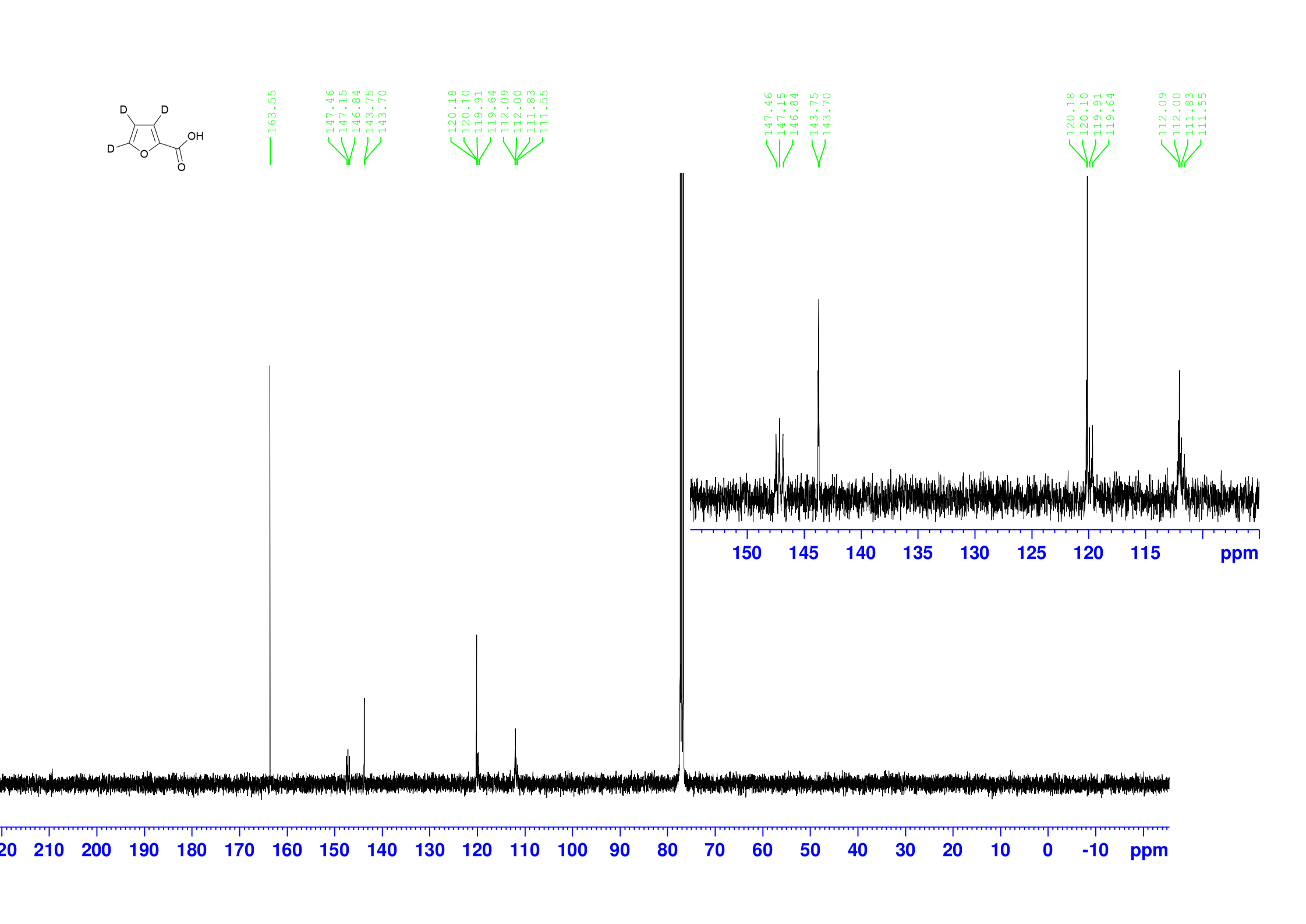


10.259

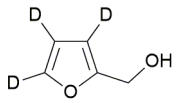
7.649
7.338
7.259

6.558

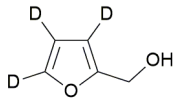



D
D
D
O
OH
O
163.55
147.46
147.15
146.84
143.75
143.70
120.18
120.10
119.91
119.64
112.09
112.00
111.83
111.55
150
145
140
135
130
125
120
115
ppm
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

d3-furfuryl alcohol



d3-furfuryl alcohol



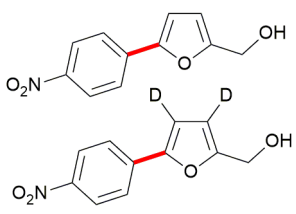
153.93
153.86
142.58
142.28
141.96
110.07
109.91
109.65
107.74
107.67
107.48
107.22
57.43

155 150 145 140 ppm

114 112 110 108 106 104 ppm

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

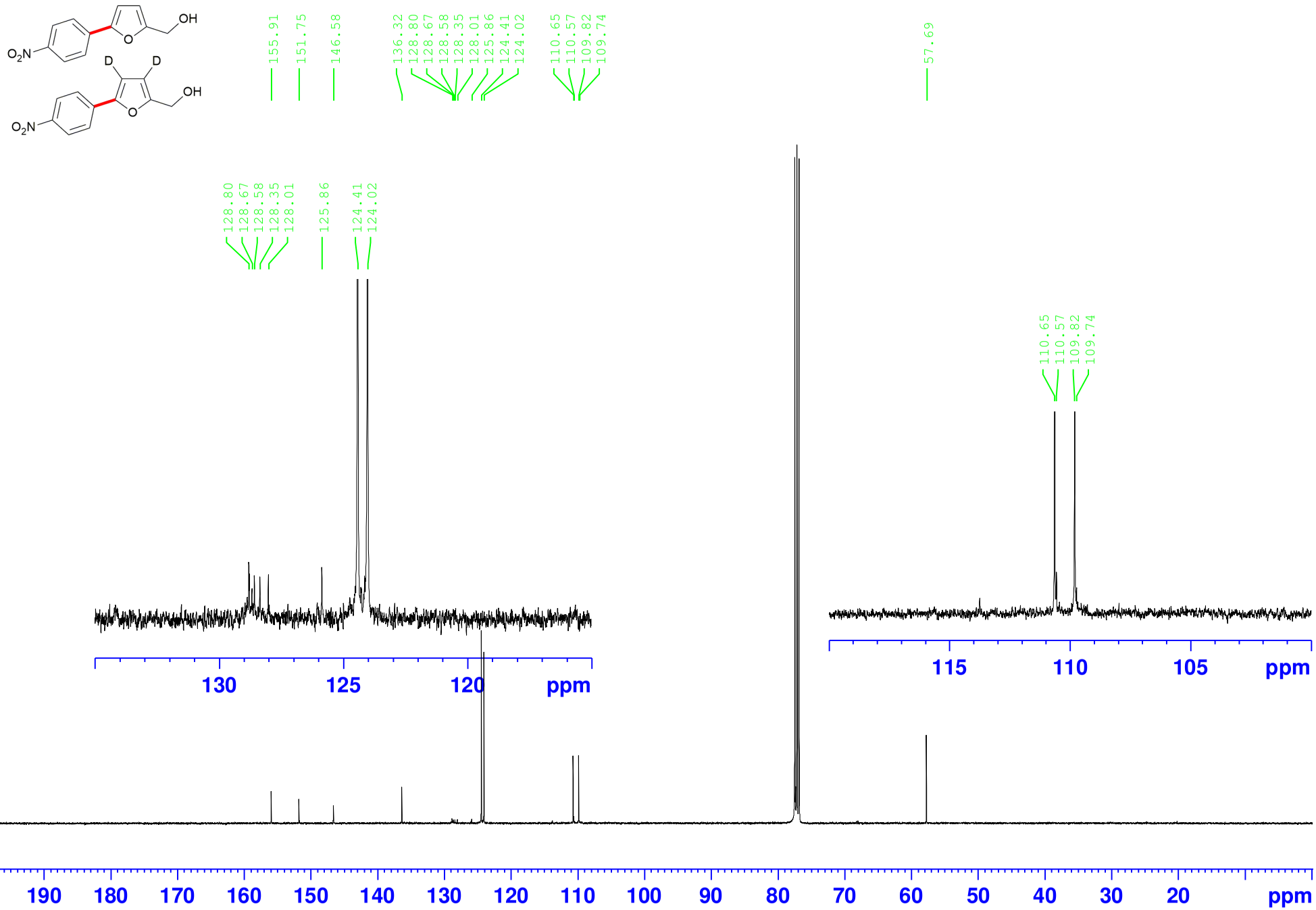
H2/d2-furfuryl alcohol-competition reaction



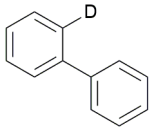
8.250
8.228
7.797
7.776
7.257
6.834
6.826
6.463
6.456
4.708
1.808

14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1

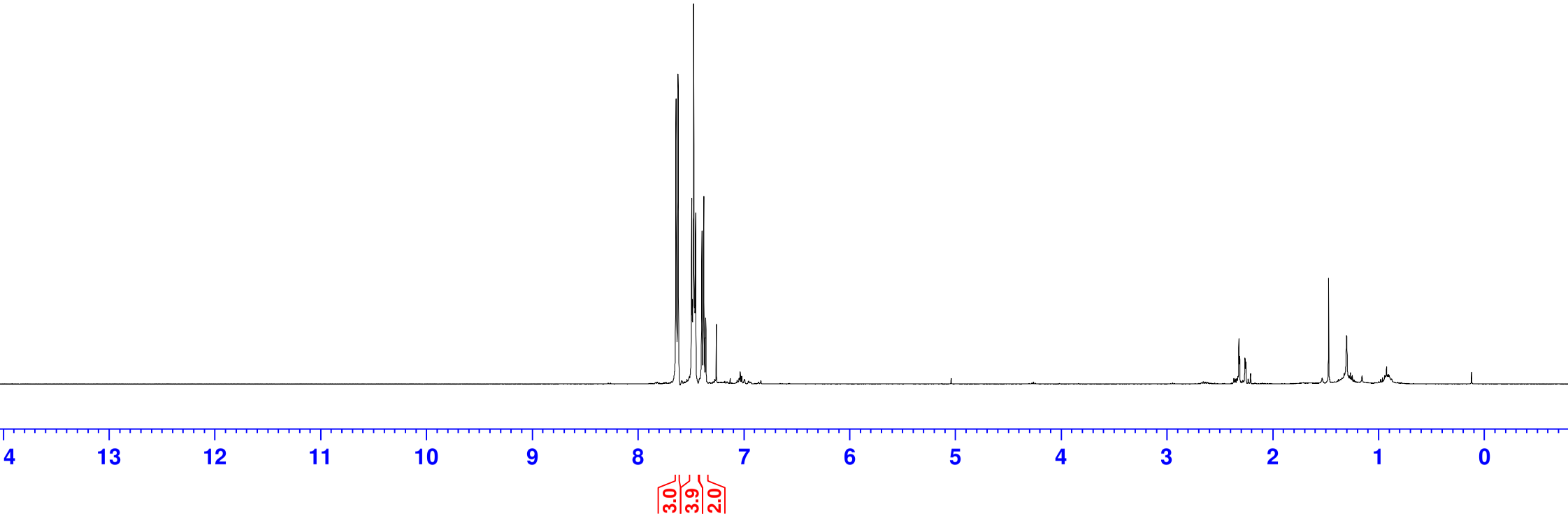
2.8 2.7 1.0 1.0 2.6 1.9


155.91
151.75
146.58
136.32
128.80
128.67
128.58
128.35
128.01
125.86
124.41
124.02
110.65
110.57
109.82
109.74
57.69
OH
OH
D
D
O_2N
O_2N
O
O
130
125
120
115
110
105
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

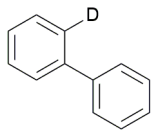
biphenyl-d



7.642
7.639
7.634
7.621
7.619
7.493
7.491
7.487
7.473
7.465
7.464
7.462
7.455
7.454
7.398
7.396
7.393
7.382
7.377
7.372
7.361
7.359

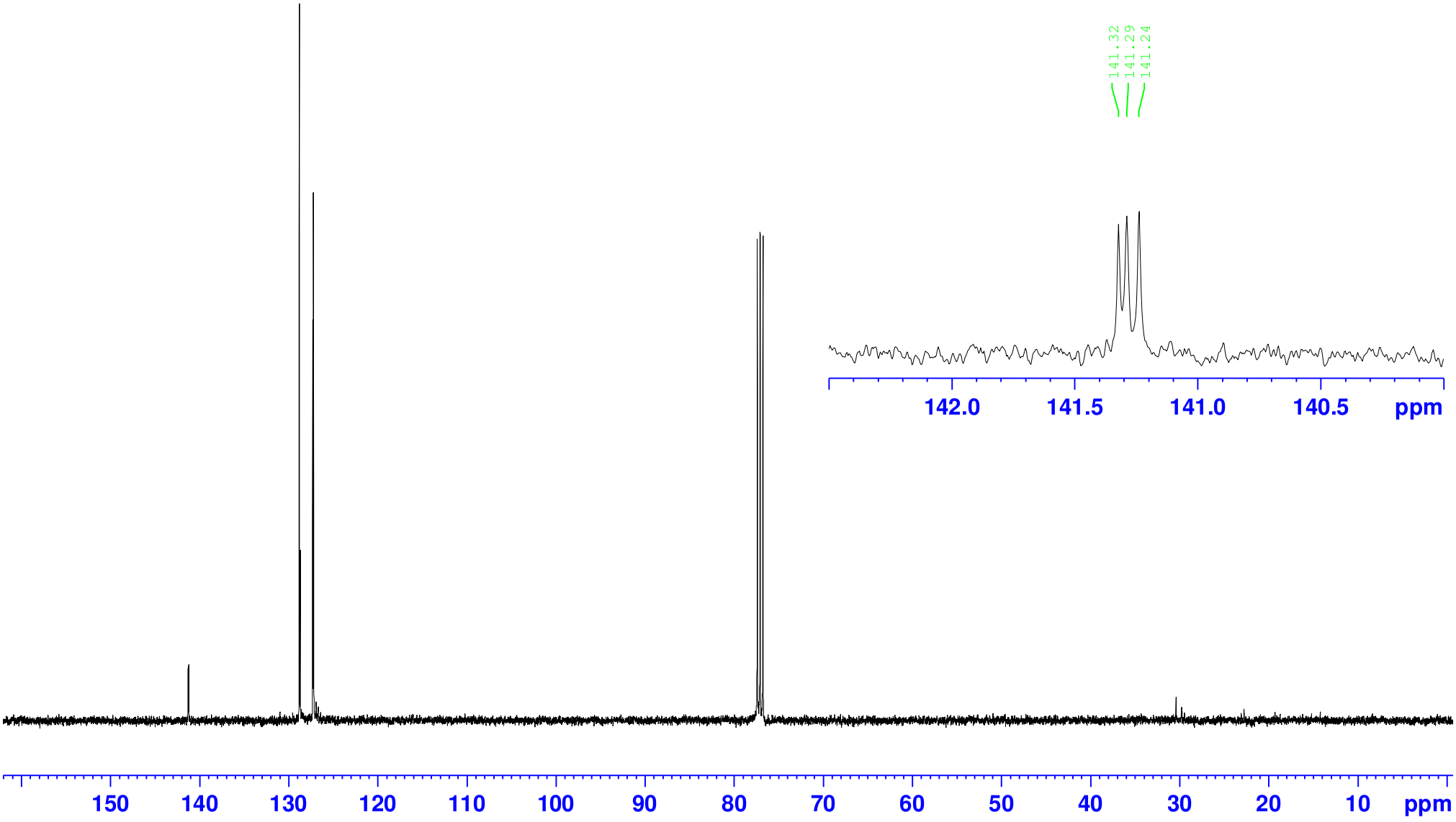


d-Biphenyl



141.32
141.29
141.24

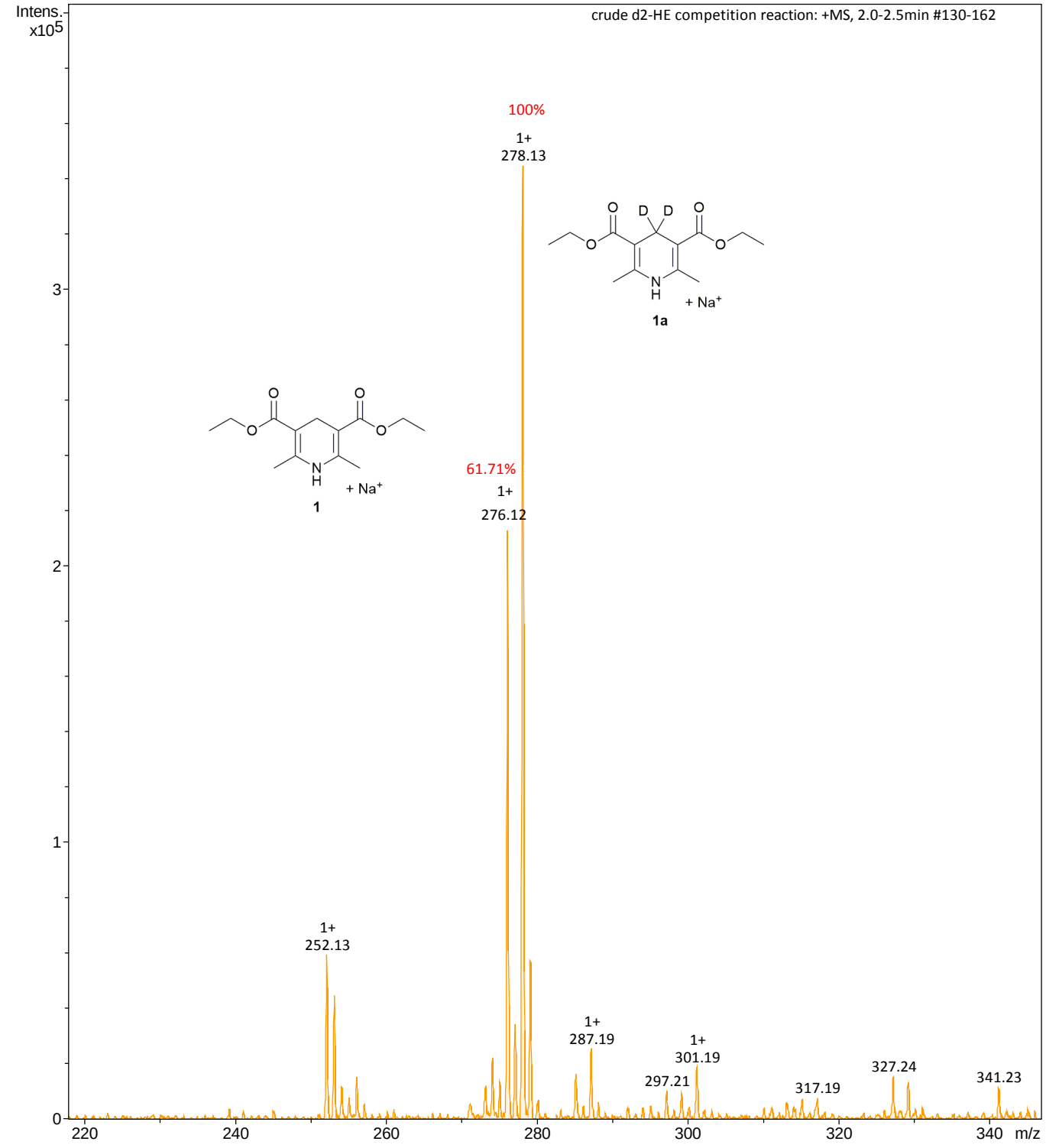
128.71
127.32
127.23



Generic Display Report

Analysis Info

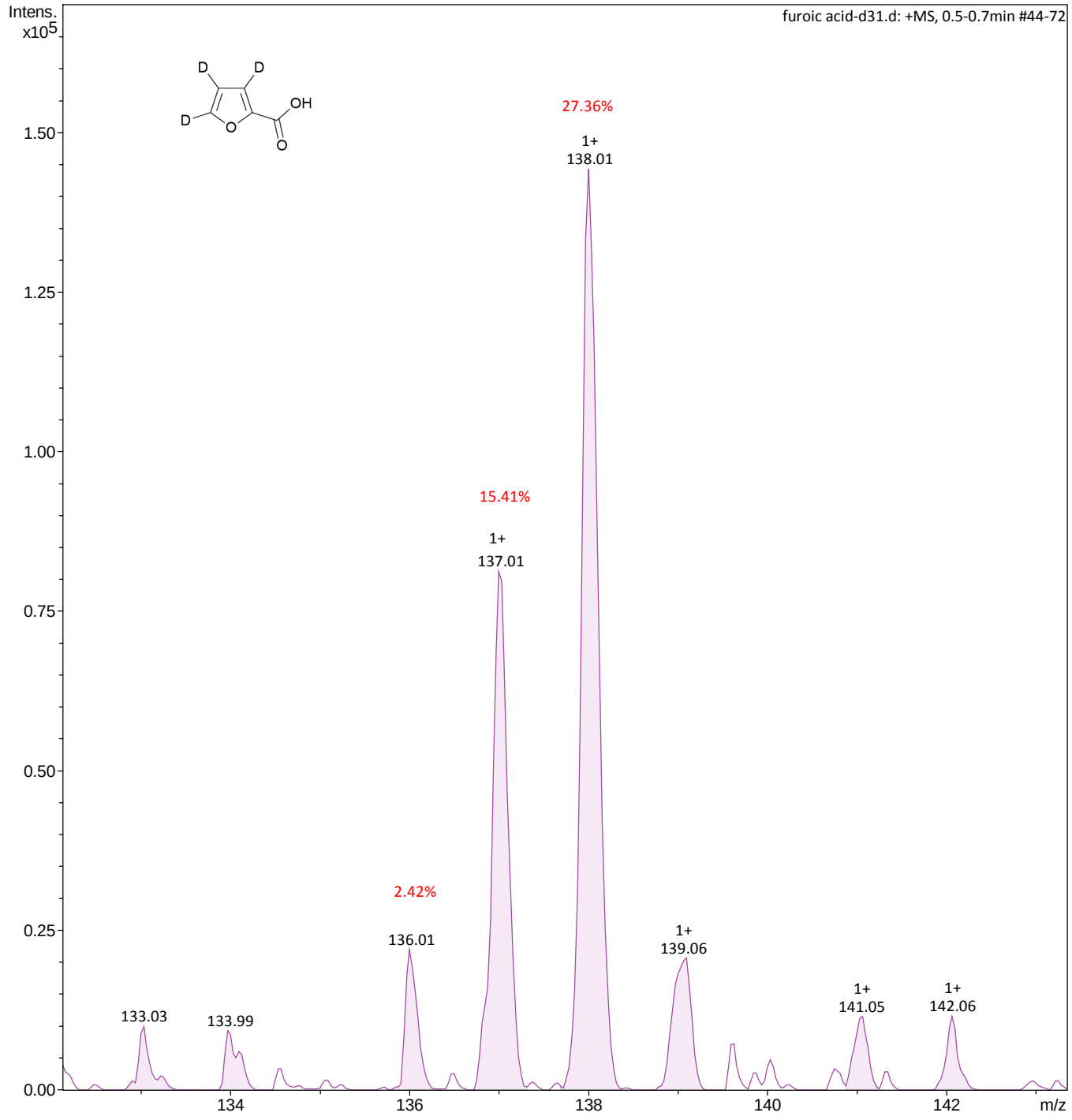
Analysis Name	D:\Data\CSPM\Elene\New folder\crude d2-HE	Acquisition Date	27-Jun-19 4:03:35 PM
Method	DEF_MS-NP.M	Operator	NICK
Sample Name	crude d2 - HE competition reaction	Instrument	amaZon SL
Comment	MeOH		



Generic Display Report

Analysis Info

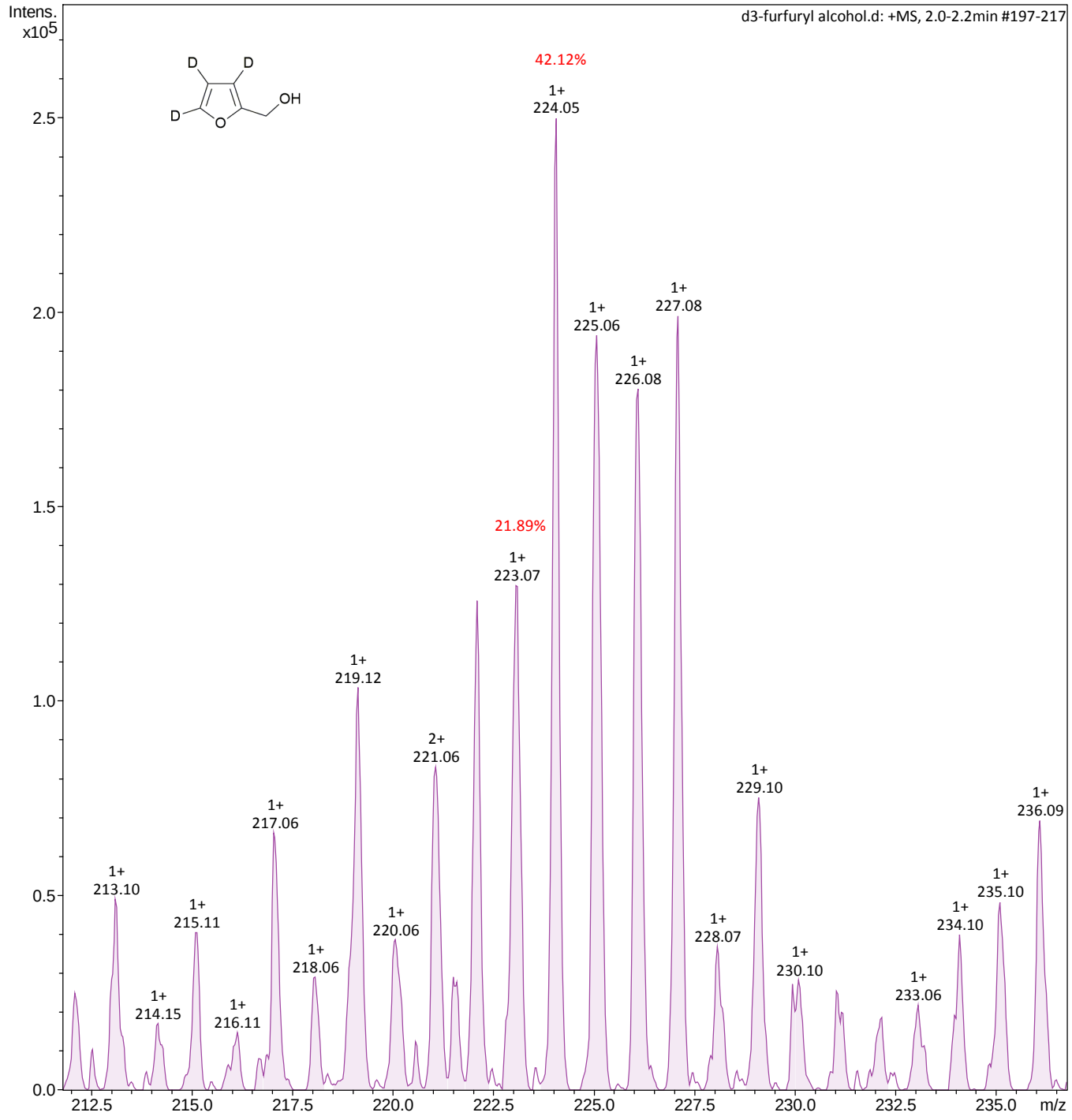
Analysis Name	D:\Data\CSPM\Elene\16-07-19\furoic acid.d	Acquisition Date	16-Jul-19 4:35:16 PM
Method	DEF_MS-NP.M	Operator	NICK
Sample Name	furoic acid	Instrument	amaZon SL
Comment	MeOH		



Generic Display Report

Analysis Info

Analysis Name	D:\Data\CSPM\Elene\16-07-19\d3-furfuryl alcohol.d	Acquisition Date	16-Jul-19 3:05:02 PM
Method	DEF_MS-NP.M	Operator	NICK
Sample Name	d3-furfuryl alcohol	Instrument	amaZon SL
Comment	MeOH		



Generic Display Report

Analysis Info

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Method	DEF_MS-NP.M	Operator	NICK
Sample Name	competition reaction	Instrument	amaZon SL
Comment	MeOH