Supporting Information

for

Assembly of Fused Indenes via Au(I)-Catalyzed C1-C5 Cyclization of Enediynes Bearing An Internal Nucleophile

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General information

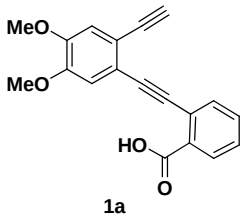
All melting points were determined without correction. All products were characterized by IR, ^{1}H NMR, ^{13}C NMR, EI-MS and element analysis. ^{1}H NMR and ^{13}C NMR spectra were recorded by using TMS or residue solvent as internal standards. Triphenylphosphinegold(I) bis(trifluoromethanesulfonyl)imidate was prepared according to the procedure reported by F. Gagosz (Mezailles, N.; Ricard, L.; Gagosz, F. *Org. Lett.* **2005**, *7*, 4133.).

General procedure for the preparation of 2-[(2-Ethynylphenyl)ethynyl]benzoic acid by a Sonogashira coupling

Under the protection of nitrogen, a THF solution (65 mL) including Et_3N (2.8 mL) and methyl 2-iodobenzoate (4 mmol) or (*Z*)-methyl 3-iodoacrylate (4 mmol) was added to a flask containing 1,2-diethynylarene (16 mmol), *trans*-dichlorobis(triphenylphosphine)palladium (II) (0.16 mmol) and CuI (0.08 mmol). The mixture was stirred overnight at room temperature (monitored by TLC). Then the solvent was removed under vacuum. The obtained residue was treated with a mixture of chloroform (60 mL) and water (60 mL). The separated organic layer was washed with brine (60 mL), dried with anhydrous $MgSO_4$. After filtration, the filtrate was concentrated and the residue was purified by column chromatography on silica gel (EtOAc-PE as eluent) to give methyl 2-[(2-ethynylphenyl)ethynyl]benzoate or (*Z*)-methyl-5-(2-ethynylphenyl)pent-2-en-4-ynoate.

The corresponding methyl 2-[(2-ethynylphenyl)ethynyl]benzoate (3 mmol) or (*Z*)-methyl-5-(2-ethynylphenyl)pent-2-en-4-ynoate (3 mmol) and sodium hydroxide (6 mmol) was dissolved in a solution involving THF (6 mL), H_2O (12 mL) and EtOH (6 mL). The mixture was stirred at room temperature for 4 hours (monitored by TLC). After extraction with CH_2Cl_2 (10 mL $\times$3), the solution was neutralized until pH = 1 at lower temperature (0- 5^oC) by concentrated HCl solution. The resultant acidic solution was extracted with CH_2Cl_2 (20 mL$\times$3), and the combined organic phase was dried with anhydrous $MgSO_4$. After filtration, the filtrate was concentrated to afford the acid.

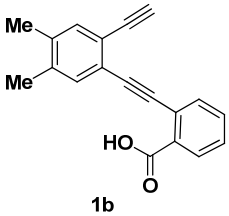
2-[(2-Ethynyl-4,5-dimethoxyphenyl)ethynyl]benzoic acid (1a).



1a

Compound **1a** was prepared in 60% yield according to the general procedure. White solids, mp 152-154 ^{o}C. R_f (EtOAc/PE 1: 4 (5 mL) + HOAc (one drop)) = 0.36; IR (KBr) ν_{max} 2205, 1696, 1597, 1512, 1357, 1250, 862 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.90 (d, J = 7.5 Hz, 1H), 7.65-7.57 (m, 2H), 7.49 (td, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.09 (s, 1H), 7.04 (s, 1H), 4.28 (s, 1H), 3.82 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 167.1, 149.2, 133.7, 132.9, 131.7, 130.1, 128.4, 122.4, 118.3, 117.0, 114.8, 114.2, 92.6, 90.8, 83.1, 82.1, 55.8, 55.7; ESI-MS m/z 305.2 [M-H^{+}]. Anal. Calcd for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.38; H, 4.74.

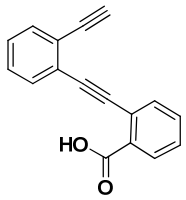
2-[(2-Ethynyl-4,5-dimethylphenyl)ethynyl]benzoic acid (1b).



1b

Compound **1b** was prepared in 64% yield according to the general procedure. White solids, mp 176-178 ^{o}C. R_f (EtOAc/PE 1: 4 (5 mL) + HOAc (one drop)) = 0.33; IR(KBr) ν_{max} 2207, 1671, 1494, 1305, 1271, 755 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.89 (d, J = 7.5 Hz, 1H), 7.64-7.57 (m, 2H), 7.52-7.47 (m, 1H), 7.36 (s, 1H), 7.33 (s, 1H), 4.31 (s, 1H), 2.24 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 167.1, 137.9, 133.8, 133.1, 133.0, 132.6, 131.7, 130.0, 128.6, 122.8, 122.3, 121.4, 92.3, 91.3, 83.7, 82.0, 19.1; ESI-MS m/z 273.8 [M^{+}]. Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.21, H, 5.24.

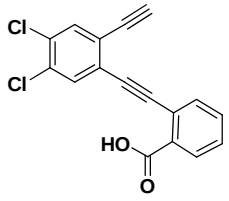
2-[(2-Ethynylphenyl)ethynyl]benzoic acid (1c).



1c

Compound **1c** was prepared in 53% yield according to the general procedure. White solids, mp 106-107 ^{o}C. R_f (EtOAc/PE 1: 4 (5 mL) + HOAc (one drop)) = 0.52; IR(KBr) ν_{max} 2217, 1700, 1470, 757 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.96 (d, *J* = 6.3 Hz, 1H), 7.67-7.41 (m, 7H), 4.42 (s, 1H); ^{13}CNMR (75 MHz, DMSO-d_6) δ 167.3, 133.9, 133.6, 132.5, 132.0, 131.6, 130.2, 129.0, 128.8, 125.6, 124.2, 122.2, 92.5, 92.1, 84.8, 81.9; ESI-MS m/z 245.8 [M^{+}]. Anal.Calcd for $C_{17}H_{10}O_2$: C, 82.91; H, 4.09. Found: C, 82.76, H, 4.16.

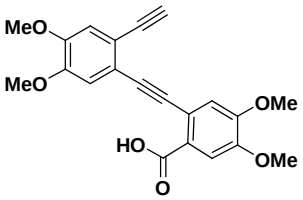
2-[(4,5-Dichloro-2-ethynylphenyl)ethynyl]benzoic acid (1d).



1d

Compound **1d** was prepared in 79% yield according to the general procedure. White solids, mp 196-198 ^{o}C. R_f (EtOAc/PE 1: 4 (5 mL) + HOAc (one drop)) = 0.30; IR(KBr) ν_{max} 2109, 1698, 1466, 887, 750 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.94 (d, *J* = 7.5 Hz, 1H), 7.90 (s, 1H), 7.80 (s, 1H), 7.69-7.61 (m, 2H), 7.58-7.53 (m, 1H), 4.65 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.8, 140.5, 133.8, 133.2, 133.1, 131.9, 130.3, 129.4, 128.1, 125.8, 124.2, 121.4, 94.3, 89.8, 87.2, 79.7; ESI-MS m/z 315.1 [M+H^{+}]. Anal. Calcd for $C_{17}H_8Cl_2O_2$: C, 64.79; H, 2.56. Found: C, 64.89; H, 2.61.

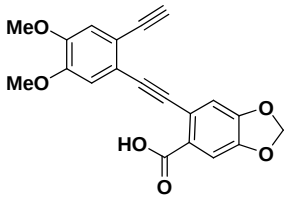
2-[(2-Ethynyl-4,5-dimethoxyphenyl)ethynyl]-4,5-dimethoxybenzoic acid (1e).



1e

Compound **1e** was prepared in 50% yield according to the general procedure. White solids, mp 157-159 ^{o}C. R_f (EtOAc/PE 1: 4 (5 mL) + HOAc (one drop)) = 0.10; IR (KBr) ν_{max} 2101, 1689, 1599, 1509, 1211, 864, 751 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.44 (s, 1H), 7.10 (s, 1H), 7.07 (s, 1H), 7.03 (s, 1H), 4.29 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.81 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.6, 151.1, 149.2, 148.9, 148.5, 125.2, 118.7, 116.8, 116.1, 115.8, 114.8, 114.0, 112.9, 91.4, 91.3, 83.0, 82.3, 55.8, 55.7, 55.63, 55.59; ESI-MS m/z 365.3 (M-H^{+}). Anal. Calcd for $C_{21}H_{18}O_6$: C, 68.85; H, 4.95. Found: C, 68.91; H, 4.96.

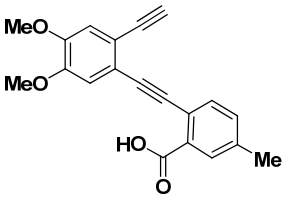
6-[(2-Ethynyl-4,5-dimethoxyphenyl)ethynyl]benzo[*d*][1,3]dioxole-5-carboxylic acid (1f).



1f

Compound **1f** was prepared in 65% yield according to the general procedure. White solids, mp 181-183 ^{o}C. R_f (EtOAc/PE 1: 4 (5 mL) + HOAc (one drop)) = 0.12; IR (KBr) ν_{max} 2207, 1686, 1511, 1495, 1229, 1028, 860 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.38 (s, 1H), 7.07 (s, 2H), 7.01 (s, 1H), 6.17 (s, 2H), 4.28 (s, 1H), 3.81 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 166.2, 150.1, 149.2, 149.1, 147.6, 127.3, 118.5, 117.7, 116.9, 114.7, 114.1, 112.5, 109.7, 102.6, 91.6, 91.0, 83.1, 82.2, 55.8, 55.7; ESI-MS m/z 349.2 [M-H^{+}]. Anal. Calcd for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03. Found: C, 68.65; H, 4.02.

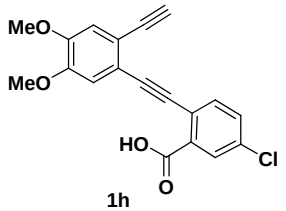
2-[(2-Ethynyl-4,5-dimethoxyphenyl)ethynyl]-5-methylbenzoic acid (1g).



1g

Compound **1g** was prepared in 54% yield according to the general procedure. White solids, mp 160-162 ^{o}C. R_f (EtOAc/PE 1: 4 (5 mL) + HOAc (one drop)) = 0.18; IR (KBr) ν_{max} 2207, 1686, 1511, 1248, 1217, 865 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.71 (s, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.08 (s, 1H), 7.02 (s, 1H), 4.27 (s, 1H), 3.81(s, 6H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 167.2, 149.2, 149.1, 138.3, 133.6, 132.8, 132.3, 130.5, 119.5, 118.5, 116.8, 114.8, 114.1, 91.8, 90.9, 83.0, 82.2, 79.1, 55.7, 55.6, 20.8; ESI-MS m/z 343.6 [M+Na^{+}]. Anal. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03. Found: C, 75.09; H, 5.12.

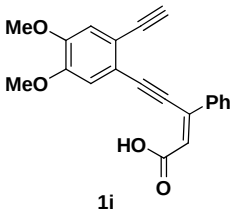
5-Chloro-2-[(2-ethynyl-4,5-dimethoxyphenyl)ethynyl]benzoic acid (1h).



1h

Compound **1h** was prepared in 60% yield according to the general procedure. White solids, mp 193-195 ^{o}C. R_f (EtOAc/PE 1: 4 (5 mL) + HOAc (one drop)) = 0.18; IR (KBr) ν_{max} 2211, 1692, 1509, 1245, 1214, 822 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.88 (d, *J* = 2.1 Hz, 1H), 7.70-7.62 (m, 2H), 7.09 (s, 1H), 7.05 (s, 1H), 4.28 (s, 1H), 3.81 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.9, 149.4, 149.2, 135.3, 134.6, 132.9, 131.7, 129.7, 121.3, 117.9, 117.1, 114.8, 114.2, 93.8, 89.6, 83.3, 82.0, 55.8, 55.7; ESI-MS m/z 339.7 [M^{+}]. Anal. Calcd for $C_{19}H_{13}ClO_4$: C, 66.97; H, 3.85. Found: C, 67.02; H, 3.92.

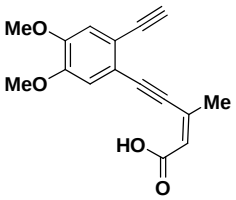
(*Z*)-5-(2-Ethynyl-4,5-dimethoxyphenyl)-3-phenylpent-2-en-4-ynoic acid (1i).



1i

Compound **1i** was prepared in 58% yield according to the general procedure. White solids, mp 181-183 ^{o}C. R_f (EtOAc/PE 1: 4 (5 mL) + HOAc (one drop)) = 0.14; IR (KBr) ν_{max} 2197, 1685, 1587, 1511, 1263, 762 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.03-7.99 (m, 2H), 7.49-7.47 (m, 3H), 7.13 (s, 1H), 7.05 (s, 1H), 6.77 (s, 1H), 4.47 (s, 1H), 3.83 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, DMSO- d_6) δ 166.1, 149.8, 149.3, 135.7, 133.9, 130.0, 128.7, 127.1, 123.6, 117.8, 117.5, 114.9, 114.4, 99.7, 89.1, 83.6, 82.4, 55.8, 55.6; ESI-MS m/z 331.0 [M-H^{+}]. Anal. Calcd for $C_{21}H_{16}O_4$: C, 75.89; H, 4.85. Found: C, 75.91; H, 4.85.

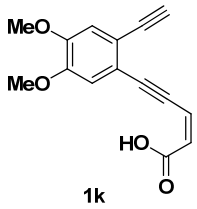
(*Z*)-5-(2-Ethynyl-4,5-dimethoxyphenyl)-3-methylpent-2-en-4-ynoic acid (1j).



1j

Compound **1j** was prepared in 50% yield according to the general procedure. White solids, mp 208-209 ^{o}C. R_f (EtOAc/PE 1: 4 (5 mL) + HOAc (one drop)) = 0.17; IR (KBr) ν_{max} 2189, 1682, 1591, 1511, 1254, 1210, 862 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.08 (s, 1H), 6.97 (s, 1H), 6.08 (s, 1H), 4.28 (s, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.7, 149.5, 149.1, 133.0, 125.4, 117.8, 117.4, 114.8, 114.2, 98.2, 91.1, 83.4, 81.9, 55.8, 55.6, 24.6; ESI-MS m/z 269.1 [M-H^{+}]. Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.96; H, 5.17.

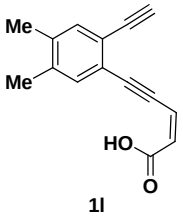
(*Z*)-5-(2-Ethynyl-4,5-dimethoxyphenyl)pent-2-en-4-ynoic acid (1k).



1k

Compound **1k** was prepared in 52% yield according to the general procedure. White solids, mp 144-146 ^{o}C. R_f (EtOAc/PE 1: 4 (5 mL) + HOAc (one drop)) = 0.14; IR (KBr) ν_{max} 2185, 1691, 1590, 1511, 1262, 1235, 863 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.07 (s, 1H), 7.00 (s, 1H), 6.52 (d, *J* = 11.1 Hz, 1H), 6.17 (d, *J* = 11.7 Hz, 1H), 4.24 (s, 1H), 3.81 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.5, 149.6, 149.2, 130.0, 121.9, 117.7, 117.1, 114.9, 114.5, 98.8, 89.1, 83.4, 81.9, 55.8, 55.7; ESI-MS m/z 255.3 [M-H^{+}]. Anal. Calcd for $C_{15}H_{12}O_4$: C, 70.31; H, 4.72. Found: C, 70.21; H, 4.90.

(*Z*)-5-(2-Ethynyl-4,5-dimethylphenyl)pent-2-en-4-ynoic acid (1l).



1l

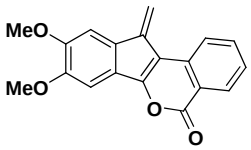
Compound **1l** was prepared in 62% yield according to the general procedure. White solids, mp 113-114 ^{o}C. R_f (EtOAc/PE 1: 4 (5 mL) + HOAc (one drop)) = 0.40; IR (KBr) ν_{max} 2181, 1697, 1674, 1590, 1439, 1246, 1219, 877, 816 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.34 (s, 1H), 7.29 (s, 1H), 6.53 (d, *J* = 11.4 Hz, 1H), 6.18 (d, *J* = 11.4 Hz, 1H), 4.26 (s, 1H), 2.22 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.5, 138.5, 138.0, 133.3, 133.0, 130.2, 122.2, 121.8, 121.4, 98.4, 89.3, 83.9, 81.8, 19.06, 19.03; ESI-MS m/z 225.2 [M+H^{+}]. Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.34; H, 5.30.

General procedure for Assembly of Fused Indenes via Au(I)-Catalyzed C1-C5 Cyclization of

Enediynes Bearing An Internal Nucleophile

Triphenylphosphinegold(I) bis(trifluoromethanesulfonyl)imidate (18.5 mg, 0.025 mmol) was added in one portion to a stirred solution of 2-[(2-ethynylphenyl)ethynyl]benzoic acid (0.5 mmol) or (*Z*)-methyl-5-(2-ethynylphenyl)pent-2-en-4-ynoic acid (0.5 mmol) in anhydrous CH_2Cl_2 (10 mL) at room temperature. After 15 minutes, the solution was concentrated under vacuum pressure and the residue was purified by chromatography with EtOAc-PE as eluent to give the pure indeno[1,2-*c*]isochromen-5(11*H*)-one or indeno[1,2-*b*]pyran-2(5*H*)-one.

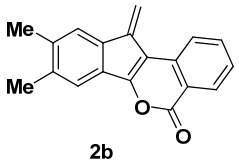
8,9-Dimethoxy-11-methyleneindeno[1,2-*c*]isochromen-5(11*H*)-one (2a).



2a

Compound **2a** was prepared in 85% yield according to the general procedure. Yellow solids, mp 231-233 ^{o}C. R_f (EtOAc/PE 1: 3) = 0.36; IR (KBr) ν_{max} 1732, 1607, 1488, 1271, 1012, 874, 712 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 7.10 (s, 1H), 7.00 (s, 1H), 6.16 (s, 1H), 6.09 (s, 1H), 3.94 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1, 157.6, 150.1, 150.0, 139.9, 135.4, 135.0, 131.3, 129.9, 126.3, 125.8, 121.6, 118.9, 112.2, 108.4, 103.6, 101.6, 56.21, 56.17; ESI-MS m/z 307.1 [M+H^{+}]. Anal. Calcd for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.37; H, 4.62.

8,9-Dimethyl-11-methyleneindeno[1,2-*c*]isochromen-5(11*H*)-one (2b).

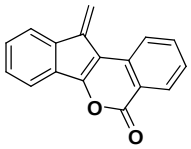


2b

Compound **2b** was prepared in 72% yield according to the general procedure. Yellow solids, mp 211-213 ^{o}C. R_f (EtOAc/PE 1: 3) = 0.84; IR (KBr) ν_{max} 1747, 1614, 1492, 1392, 1006, 769 cm^{-1}; ^{1}H

NMR (300 MHz, $CDCl_3$) δ 8.30 (dd, J_1 = 8.1 Hz, J_2 = 0.9 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.69 (td, J_1 = 7.7 Hz, J_2 = 1.2 Hz, 1H), 7.39 (td, J_1 = 7.5 Hz, J_2 = 0.6 Hz, 1H), 7.33 (s, 1H), 7.24 (s, 1H), 6.16 (s, 1H), 6.14 (s, 1H), 2.29 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0, 157.8, 140.0, 137.3, 137.2, 135.4, 135.0, 134.8, 131.3, 130.7, 126.5, 122.0, 121.1, 119.7, 119.5, 112.0, 109.2, 20.4, 20.1; ESI-MS m/z 275.2 [M+H$^+$]. Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.27; H, 5.15.

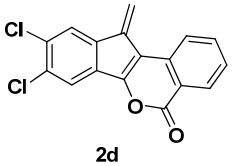
11-Methyleneindeno[1,2-*c*]isochromen-5(11*H*)-one (2c).



2c

Compound **2c** was prepared in 61% yield according to the general procedure. Yellow solids, mp 199-200 °C. R_f (EtOAc/PE 1: 3) = 0.84; IR (KBr) ν_{max} 1736, 1608, 1493, 1396, 744 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 8.02 (d, J = 8.7 Hz, 1H), 7.79 (td, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 7.72-7.69 (m, 1H), 7.62-7.59 (m, 1H), 7.49 (td, J_1 = 7.7 Hz, J_2 = 0.9 Hz, 1H), 7.41-7.38 (m, 2H) 6.37 (s, 1H), 6.34 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.9, 157.4, 139.9, 136.8, 135.2, 132.8, 131.4, 128.7, 128.4, 127.1, 122.2, 119.8, 119.7, 118.6, 113.2, 109.8; ESI-MS m/z 269.0 [M+Na$^+$]. Anal. Calcd for $C_{17}H_{10}O_2$: C, 82.91; H, 4.09. Found: C, 82.95; H, 4.14.

8,9-Dichloro-11-methyleneindeno[1,2-*c*]isochromen-5(11*H*)-one (2d).

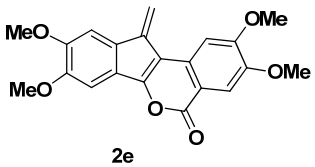


2d

Compound **2d** was prepared in 23% yield according to the general procedure. Yellow solids, mp

197-200 °C. R_f (EtOAc/PE 1: 3) = 0.80; IR (KBr) ν_{max} 1748, 1606, 1496, 1457, 1394, 1004, 872, 776 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.39 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.80 (td, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H), 7.72 (s, 1H), 7.63 (s, 1H), 7.52 (t, J = 6.9 Hz, 1H), 6.42 (s, 1H), 6.29 (d, J = 0.9 Hz, 1H); ^{13}C NMR (150MHz, $CDCl_3$) δ 161.3, 155.6, 138.5, 136.1, 135.4, 134.5, 133.0, 132.5, 132.4, 131.7, 127.9, 122.4, 122.1, 120.3, 120.1, 115.1, 111.3; ESI-MS m/z 338.3 ($M+Na^+$). Anal. Calcd for $C_{17}H_8Cl_2O_2$: C, 64.79; H, 2.56. Found: C, 64.67; H, 2.52.

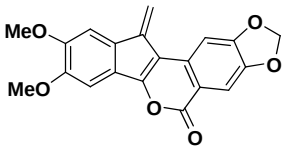
2,3,8,9-Tetramethoxy-11-methyleneindeno[1,2-*c*]isochromen-5(11*H*)-one (2e).



2e

Compound **2e** was prepared in 65% yield according to the general procedure. Yellow solids, mp 221-223 °C. R_f (EtOAc/PE 1: 3) = 0.36; IR (KBr) ν_{max} 1721, 1614, 1519, 1494, 1360, 1312, 1261, 1027, 777 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (s, 1H), 6.98 (s, 1H), 6.96 (s, 1H), 6.88 (s, 1H), 5.93 (s, 1H), 5.89 (s, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.92 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8, 156.7, 155.1, 149.9, 149.5, 148.0, 139.9, 131.0, 129.4, 126.0, 111.9, 111.1, 110.9, 108.3, 103.4, 102.4, 101.2, 56.12, 56.08, 56.0; ESI-MS m/z 366.2 [M^+]. Anal. Calcd for $C_{21}H_{18}O_6$: C, 68.85; H, 4.95. Found: C, 68.72; H, 4.95.

8,9-Dimethoxy-11-methylene-[1,3]dioxolo[4,5-*g*]indeno[1,2-*c*]isochromen-5(11*H*)-one (2f).

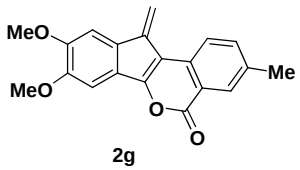


2f

Compound **2f** was prepared in 78% yield according to the general procedure. Yellow solids, mp >300 °C. R_f (EtOAc/PE 1: 3) = 0.36; IR (KBr) ν_{max} 1710, 1620, 1561, 1492, 1308, 1026, 842, 777

cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.33 (s, 1H), 7.21 (s, 1H), 7.12 (s, 1H), 6.17 (s, 2H), 6.12 (s, 2H), 3.98 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.8, 157.1, 154.2, 150.3, 149.9, 146.8, 140.1, 133.2, 129.8, 126.0, 113.6, 111.9, 109.4, 108.8, 103.9, 102.3, 101.8, 100.9, 56.4, 56.3; ESI-MS m/z 351.2 [$M+H^+$]. Anal. Calcd for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03. Found: C, 68.65; H, 4.06.

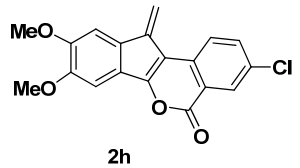
8,9-Dimethoxy-3-methyl-11-methyleneindeno[1,2-*c*]isochromen-5(11*H*)-one (2g).



2g

Compound **2g** was prepared in 85% yield according to the general procedure. Yellow solids, mp 240-243 °C. R_f (EtOAc/PE 1: 3) = 0.38; IR (KBr) ν_{max} 1718, 1616, 1512, 1309, 1204, 820, 778 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 7.01 (s, 1H), 6.16 (s, 1H), 6.09 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 2.43 (s, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 162.3, 156.9, 150.1, 149.8, 140.1, 136.5, 136.3, 133.0, 131.1, 129.8, 126.1, 118.9, 112.1, 108.6, 103.8, 101.6, 56.3, 56.2, 21.2; ESI-MS m/z 321.2 [$M+H^+$]. Anal. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03. Found: C, 75.04; H, 5.09.

3-Chloro-8,9-dimethoxy-11-methyleneindeno[1,2-*c*]isochromen-5(11*H*)-one (2h).

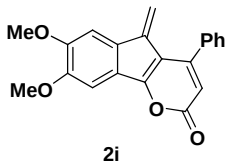


2h

Compound **2h** was prepared in 90% yield according to the general procedure. Yellow solids, mp 290-292 °C. R_f (EtOAc/PE 1: 3) = 0.38; IR (KBr)ν_{max} 1725, 1529, 1487, 1305, 1260, 822, 777 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, *J* = 2.4 Hz, 1H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.67 (dd, J_1

= 8.7 Hz, J_2 = 2.1 Hz, 1H), 7.21 (s, 1H), 7.11 (s, 1H), 6.23 (s, 1H), 6.20 (s, 1H), 3.99 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.2, 157.9, 150.3, 139.8, 135.5, 133.9, 132.0, 130.9, 130.1, 125.7, 123.2, 120.3, 112.7, 108.0, 103.8, 101.8, 56.31, 56.29; ESI-MS m/z 339.5 [M^+]. Anal. Calcd for $C_{19}H_{13}ClO_4$: C, 66.97; H, 3.85. Found: C, 67.01; H, 3.89.

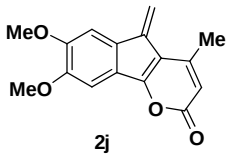
7,8-Dimethoxy-5-methylene-4-phenylindeno[1,2-*b*]pyran-2(5*H*)-one (2i).



2i

Compound **2i** was prepared in 80% yield according to the general procedure. Yellow solids, mp 164-166 °C. R_f (EtOAc/PE 1: 3) = 0.26; IR (KBr) ν_{max} 1717, 1708, 1504, 1489, 1370, 1271, 826, 764, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 5H), 7.21 (s, 1H), 7.19 (s, 1H), 5.98 (s, 1H), 5.89 (s, 1H), 5.27 (s, 1H), 3.98 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 162.0, 155.5, 151.2, 150.5, 137.8, 136.0, 131.4, 129.5, 128.5, 127.8, 125.1, 113.6, 111.3, 108.4, 103.6, 102.0, 56.3; ESI-MS m/z 333.2 [M+H^+]. Anal. Calcd for $C_{21}H_{16}O_4$: C, 75.89; H, 4.85. Found: C, 75.84; H, 4.86.

7,8-Dimethoxy-4-methyl-5-methyleneindeno[1,2-*b*]pyran-2(5*H*)-one (2j).

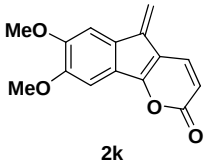


2j

Compound **2j** was prepared in 51% yield according to the general procedure. Yellow solids, mp 174-176 °C. R_f (EtOAc/PE 1: 3) = 0.15; IR (KBr) ν_{max} 1704, 1518, 1278, 1217, 823 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (s, 1H), 7.08 (s, 1H), 6.07 (s, 1H), 5.95 (s, 1H), 5.86 (d, J = 1.2 Hz, 1H), 3.96 (s, 3H), 3.92 (s, 3H), 2.42 (d, J = 0.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 162.0, 153.4, 150.9, 150.4, 139.1, 130.9, 125.2, 112.6, 112.3, 108.3, 103.5, 102.0, 56.23, 56.19,

20.5; ESI-MS m/z 271.2 [M+H$^+$]. Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.97; H, 5.23.

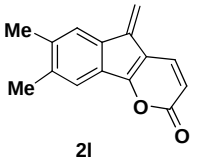
7,8-Dimethoxy-5-methyleneindeno[1,2-*b*]pyran-2(5*H*)-one (2k).



2k

Compound **2k** was prepared in 80% yield according to the general procedure. Yellow solids, mp 191-193 ^{o}C. R_f (EtOAc/PE 1: 3) = 0.15; IR (KBr) ν_{max} 1714, 1537, 1375, 1295, 840 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.03 (d, *J* = 9.3 Hz, 1H), 7.59 (s, 1H), 7.12 (s, 1H), 6.35 (s, 1H), 6.14-6.11 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.5, 161.3, 150.8, 150.2, 139.1, 137.4, 130.2, 124.8, 112.7, 108.5, 105.5, 101.9, 56.0, 55.8; ESI-MS m/z 257.1 [M+H$^+$]. Anal. Calcd for $C_{15}H_{12}O_4$: C, 70.31; H, 4.72. Found: C, 70.43; H, 4.81.

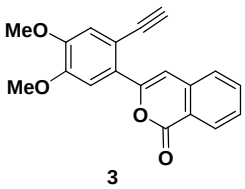
7,8-Dimethyl-5-methyleneindeno[1,2-*b*]pyran-2(5*H*)-one (2l).



2l

Compound **2l** was prepared in 75% yield according to the general procedure. Yellow solids, mp 145-147 ^{o}C. R_f (EtOAc/PE 1: 3) = 0.80; IR (KBr) ν_{max} 1708, 1533, 1371, 875, 823 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 9.3 Hz, 1H), 7.44 (s, 1H), 7.32 (s, 1H), 6.15 (d, *J* = 9.0 Hz, 1H), 6.04 (s, 1H), 5.76 (s, 1H), 2.33 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 162.2, 138.5, 138.0, 134.8, 130.5, 122.0, 120.3, 113.4, 110.4, 109.7, 109.5, 20.5, 20.2; ESI-MS m/z 225.2 [M+H$^+$]. Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.33; H, 5.38.

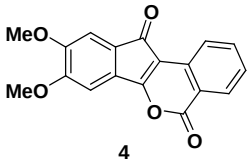
3-(2-Ethynyl-4,5-dimethoxyphenyl)-1*H*-isochromen-1-one (3).



3

Compound **3** was prepared in 80% yield according to the general procedure using 10 mol% $AuCl_3$ as catalyst. R_f (EtOAc/PE 1: 3) = 0.42; White solids, mp 161-162 ^oC. IR (KBr) ν_{max} 1717, 1515, 1265, 1210, 1017, 839, 764 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.33-8.30 (m, 1H), 7.72 (td, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H), 7.53-7.47 (m, 2H), 7.45 (s, 1H), 7.33 (s, 1H), 7.07 (s, 1H), 3.98 (s, 3H), 3.93 (s, 3H), 3.33 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5, 151.6, 149.8, 149.4, 137.4, 134.8, 129.5, 128.2, 127.8, 126.1, 120.5, 116.6, 111.9, 110.3, 106.0, 82.7, 81.4, 56.2, 56.1; ESI-MS m/z 329.2 [M+Na^+]. Anal. Calcd for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.64; H, 4.68.

8,9-Dimethoxyindeno[1,2-*c*]isochromene-5,11-one (4).

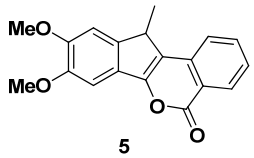


4

To a solution of **2a** (30.6 mg, 0.1 mmol) in mixed solvents including THF (0.6 mL), H_2O (0.4 mL) and CH_2Cl_2 (1.0 mL) was added $K_2Os_2O_4{\cdot}2H_2O$ (1.1 mg). The mixture was stirred at room temperature for 20 min and $NaIO_4$ (85.6 mg) was then added in portions. After 6 h, the reaction was quenched and diluted by the addition of CH_2Cl_2 (10 ml). The formed solution was washed with saturated aqueous $NaHCO_3$ solution (10 mL), dried over anhydrous $MgSO_4$. After filtration, the solvent was distilled under reduced pressure. The residue was purified through column chromatography to afford **4** as a yellow solid in 90% yield. mp 280-281 ^oC ($CHCl_3$). R_f (EtOAc/PE 1: 3) = 0.15; IR (KBr): 1736, 1702, 1692, 1608, 1493, 1389, 1364, 965, 784 cm^{-1}; ^1H NMR (300 MHz, CF_3CO_2D) δ 8.26 (d, J = 8.1 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.85 (t, J = 8.1

Hz, 1H), 7.57-7.53 (m, 1H), 7.28 (s, 1H), 7.03 (s, 1H), 4.02 (s, 3H), 3.98 (s, 3H); ^{13}C NMR (75 MHz, CF_3CO_2D) δ 191.8, 169.2, 163.4, 152.1, 149.5, 136.1, 131.3, 129.5, 127.4, 123.8, 121.3, 115.8, 115.7, 106.5, 103.3, 54.3; ESI-MS m/z 308.1 [M+1]. Anal. Calcd for $C_{18}H_{12}O_5$: C, 70.13; H, 3.92. Found: C, 69.89; H, 4.17.

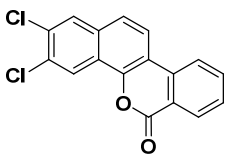
8,9-Dimethoxy-11-methylindeno[1,2-*c*]isochromen-5(11*H*)-one (5).



5

To a solution of **2a** (61.2 mg, 0.2 mmol) in HOAc (8.0 mL) was added 10% Pd/C (12 mg) in one portion. The mixture was exposed to an atmosphere of H_2 at 100 °C. After 10 h, the resulting mixture was filtered and concentrated to give crude product, which was purified by column chromatography to afford **5** in 75% yield. mp 195-196 °C (EA). R_f (EtOAc/PE 1: 3) = 0.26; IR (KBr): 1738, 1613, 1491, 1269, 1216, 774 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.16 (s, 1H), 7.03 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.83 (q, *J* = 6.9 Hz, 1H), 1.54 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0, 153.2, 149.7, 149.0, 141.3, 136.0, 134.9, 131.2, 127.1, 126.3, 121.8, 119.1, 118.8, 107.1, 101.9, 56.2, 56.1, 38.7, 17.8; ESI-MS m/z 309.2 [M+1]. Anal. Calcd for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 74.11; H, 5.42.

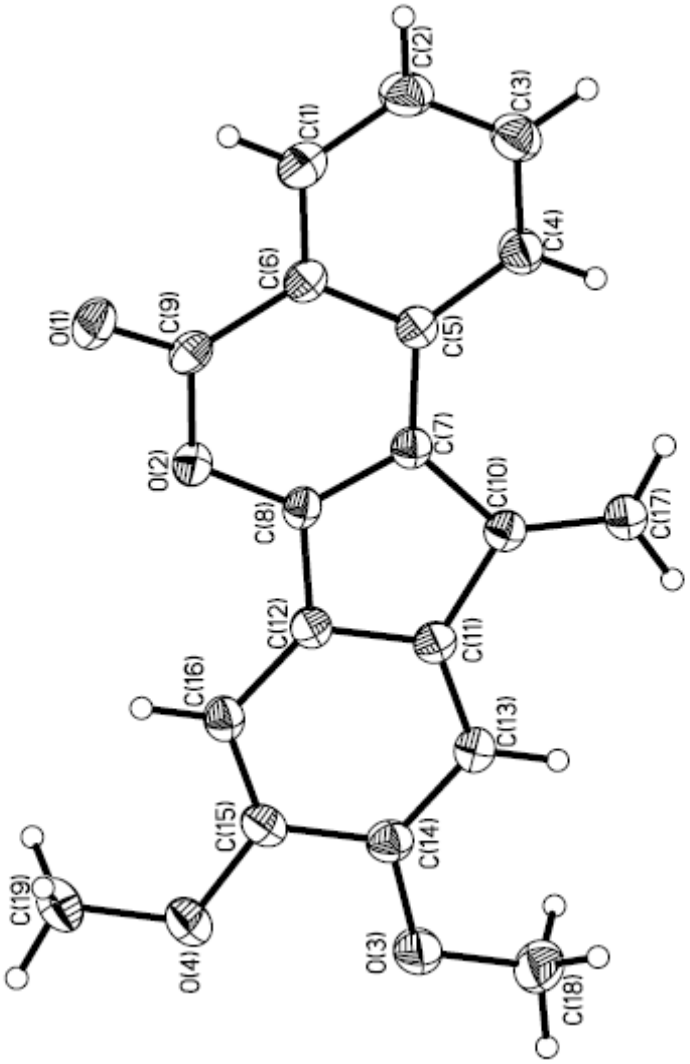
2,3-Dichloro-6*H*-dibenzo[*c*,*h*]chromen-6-one



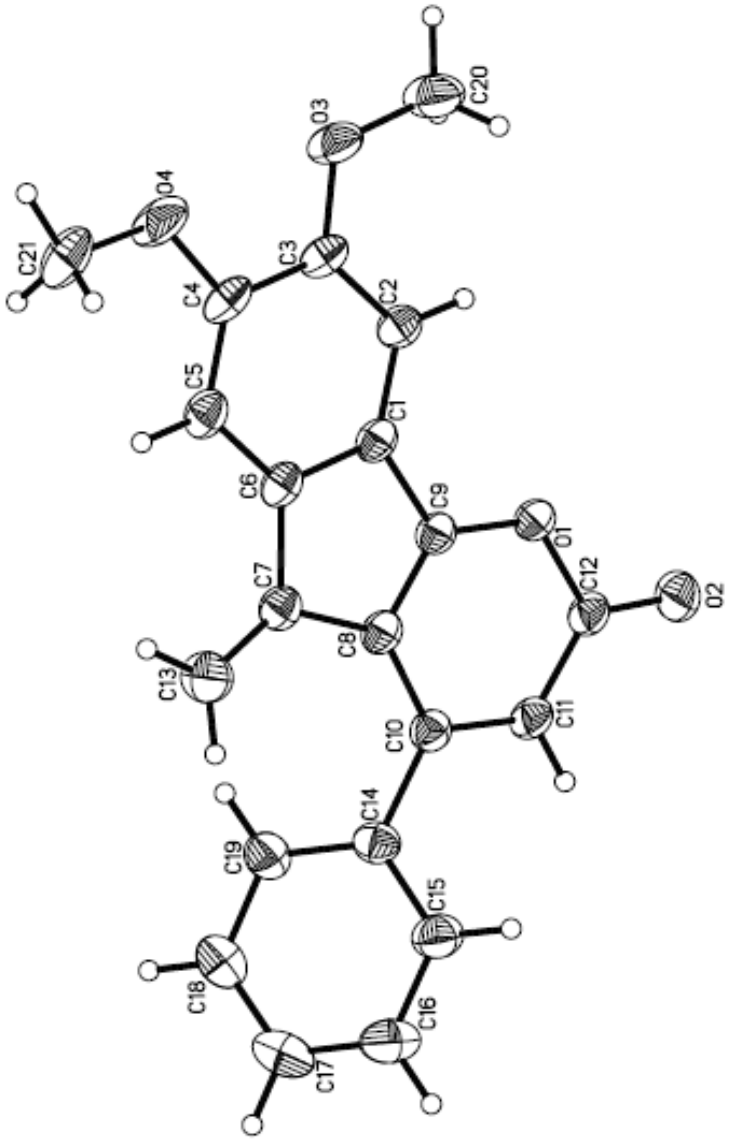
This compound was isolated in 17% yield in the preparation of compound **2d** according to the general procedure. Yellow solids, mp 269-271 °C. R_f (EtOAc/PE 1: 3) = 0.85; IR(KBr) ν_{max} 1783,

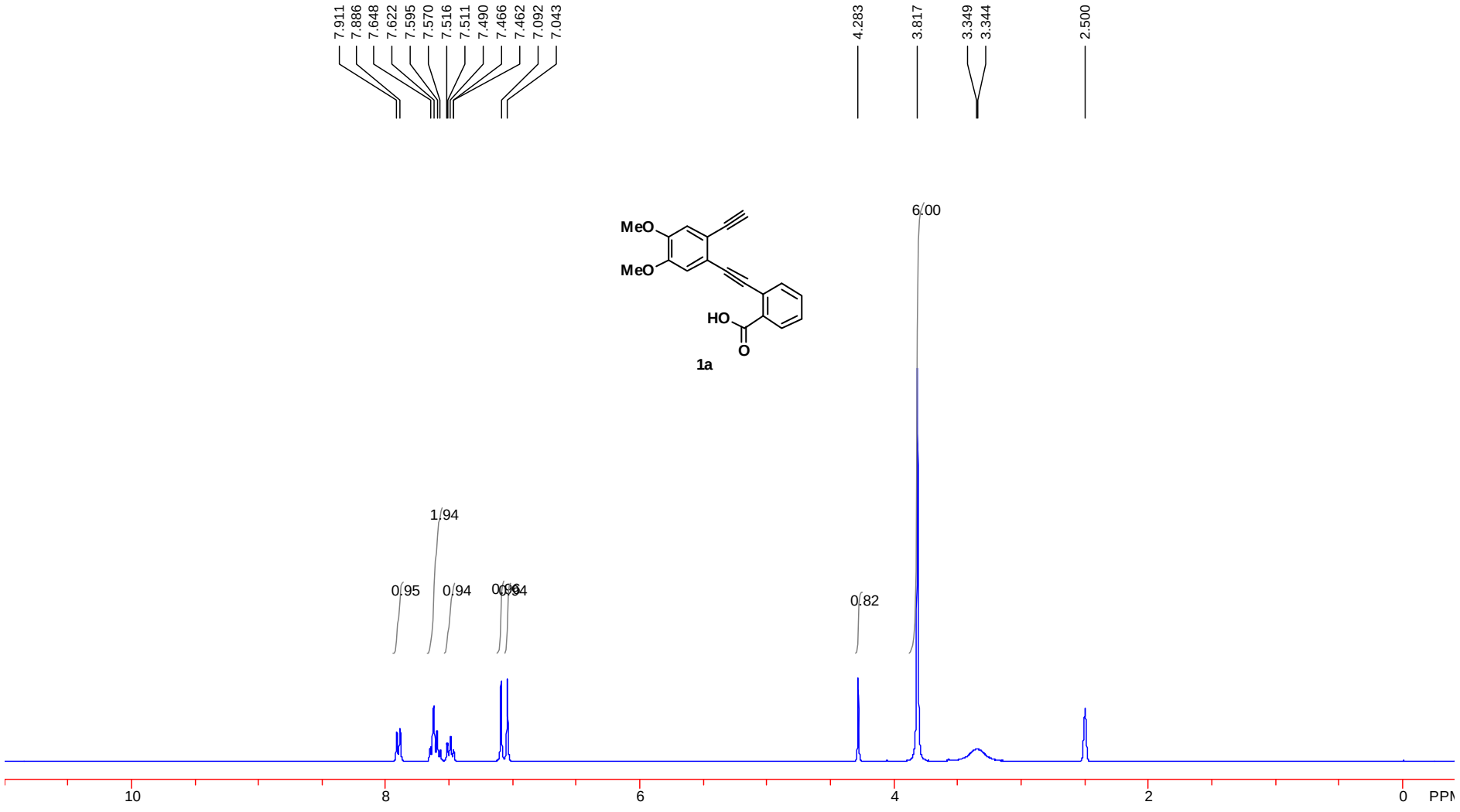
1647, 1267, 993, 693 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.04 (t, *J* = 7.5 Hz, 2H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.37 (s, 1H), 7.19 (d, *J* = 5.4 Hz, 1H), 6.92 (d, *J* = 5.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.6, 146.4, 141.4, 138.4, 135.1, 133.9, 133.0, 132.0, 131.4, 130.0, 127.6, 126.5, 125.6, 125.5, 124.0, 122.9, 121.4; ESI-MS m/z 338.1 [$M+Na^+$]. Anal. Calcd for $C_{17}H_8Cl_2O_2$: C, 64.79; H, 2.56. Found: C, 64.67; H, 2.55.

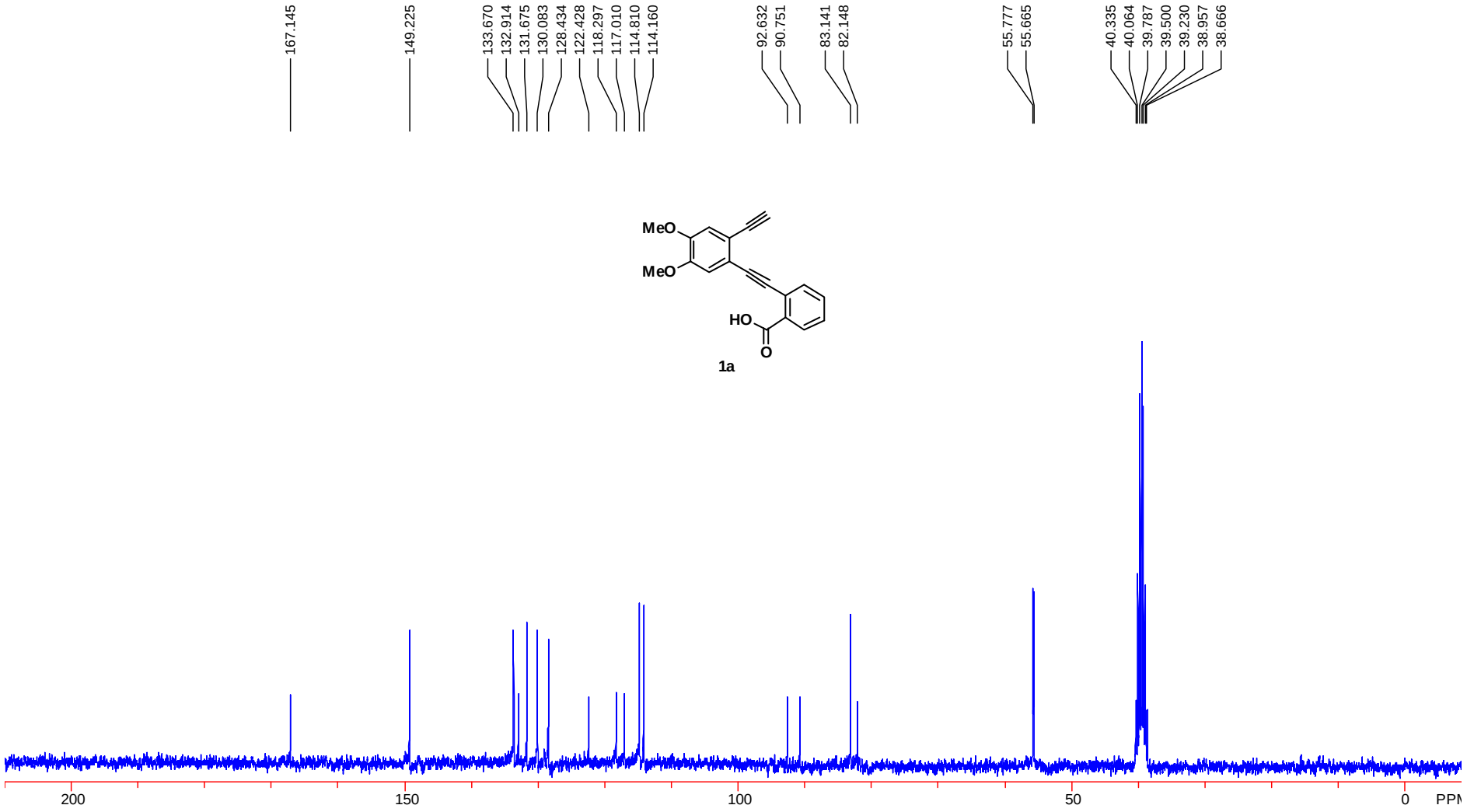
X-Ray Crystal Structure of Indeno[1,2-*c*]isochromen-5(11*H*)-one 2a

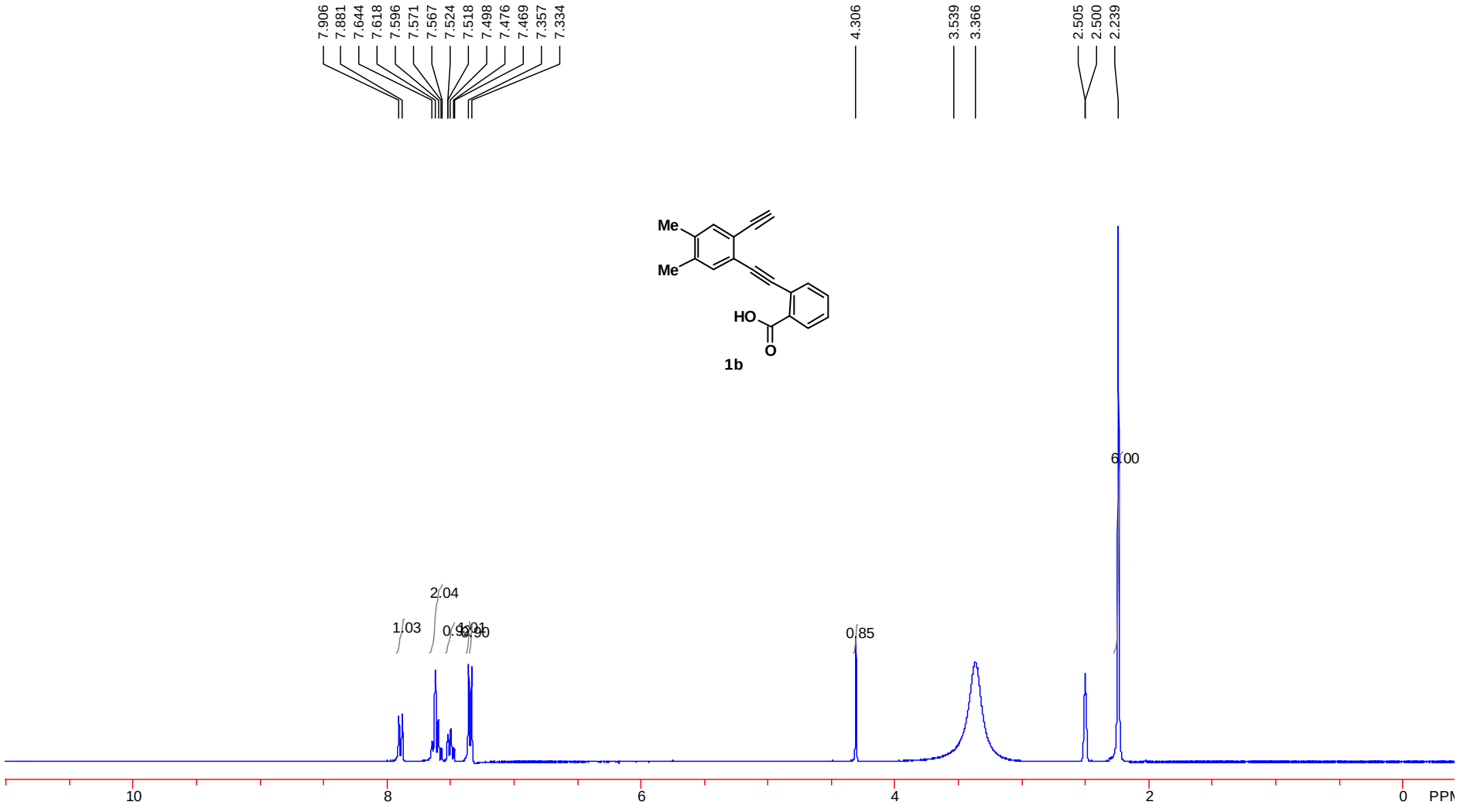


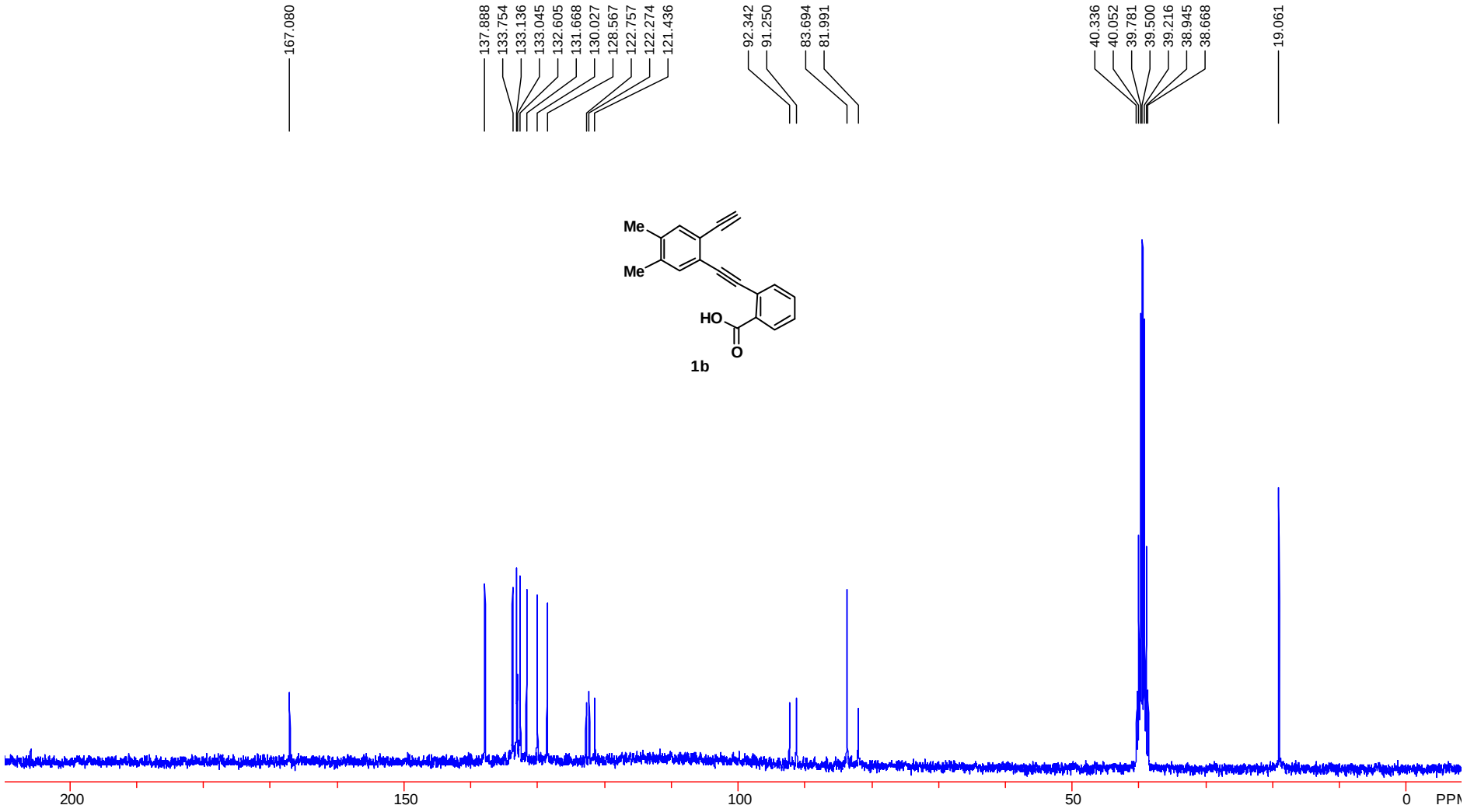
X-Ray Crystal Structure of Inden[1,2-b]pyran-2(5H)-one 2i







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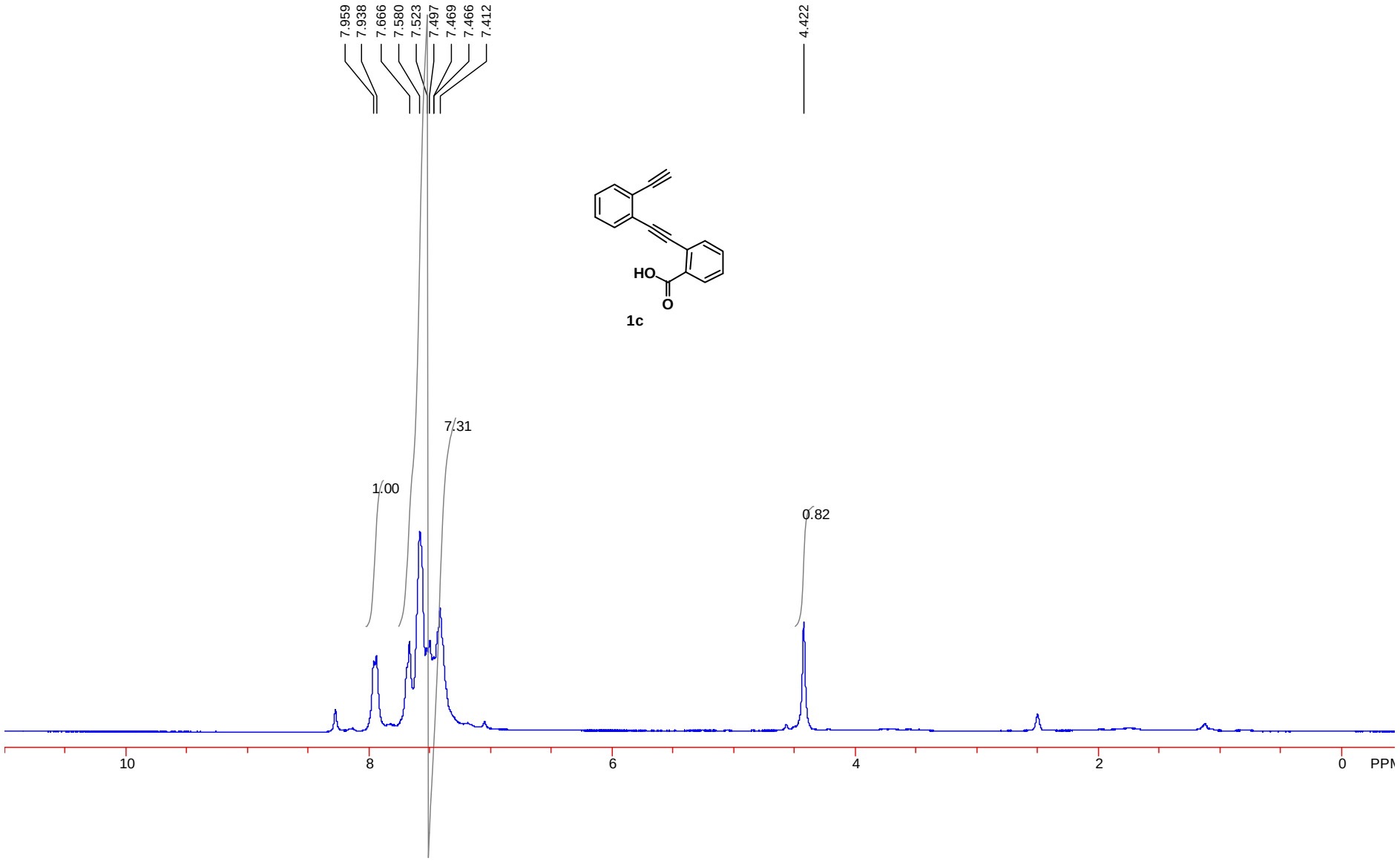

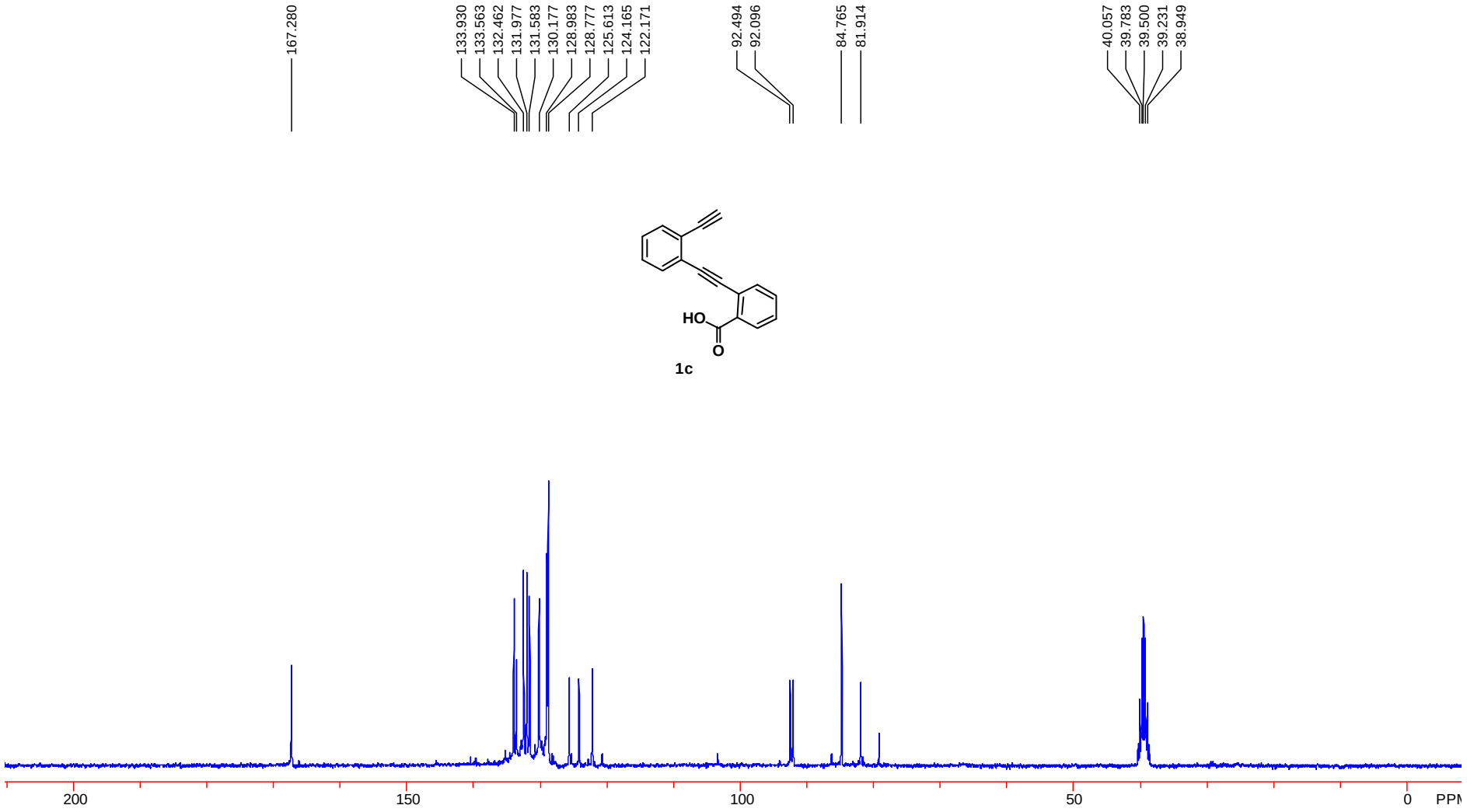

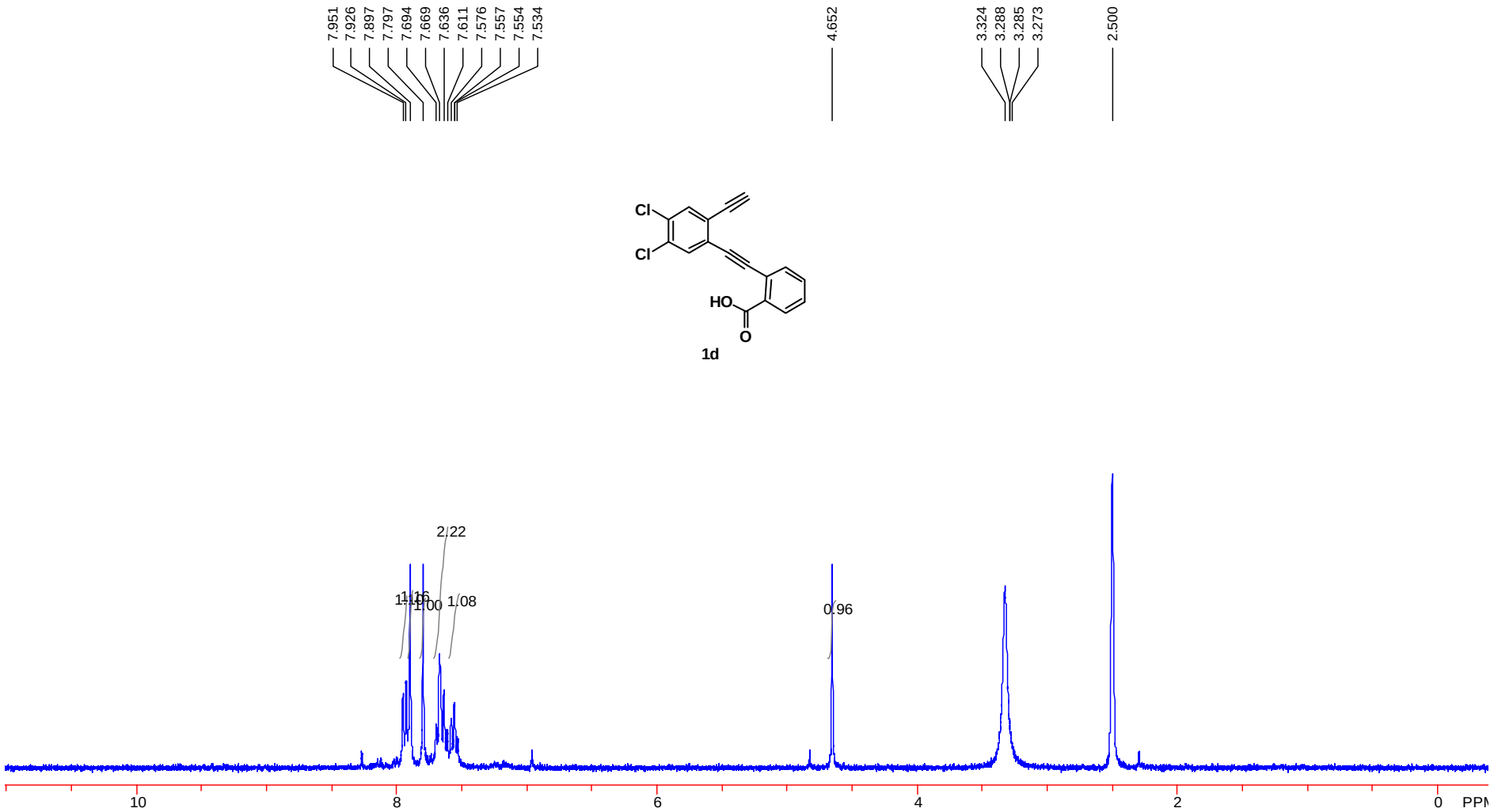

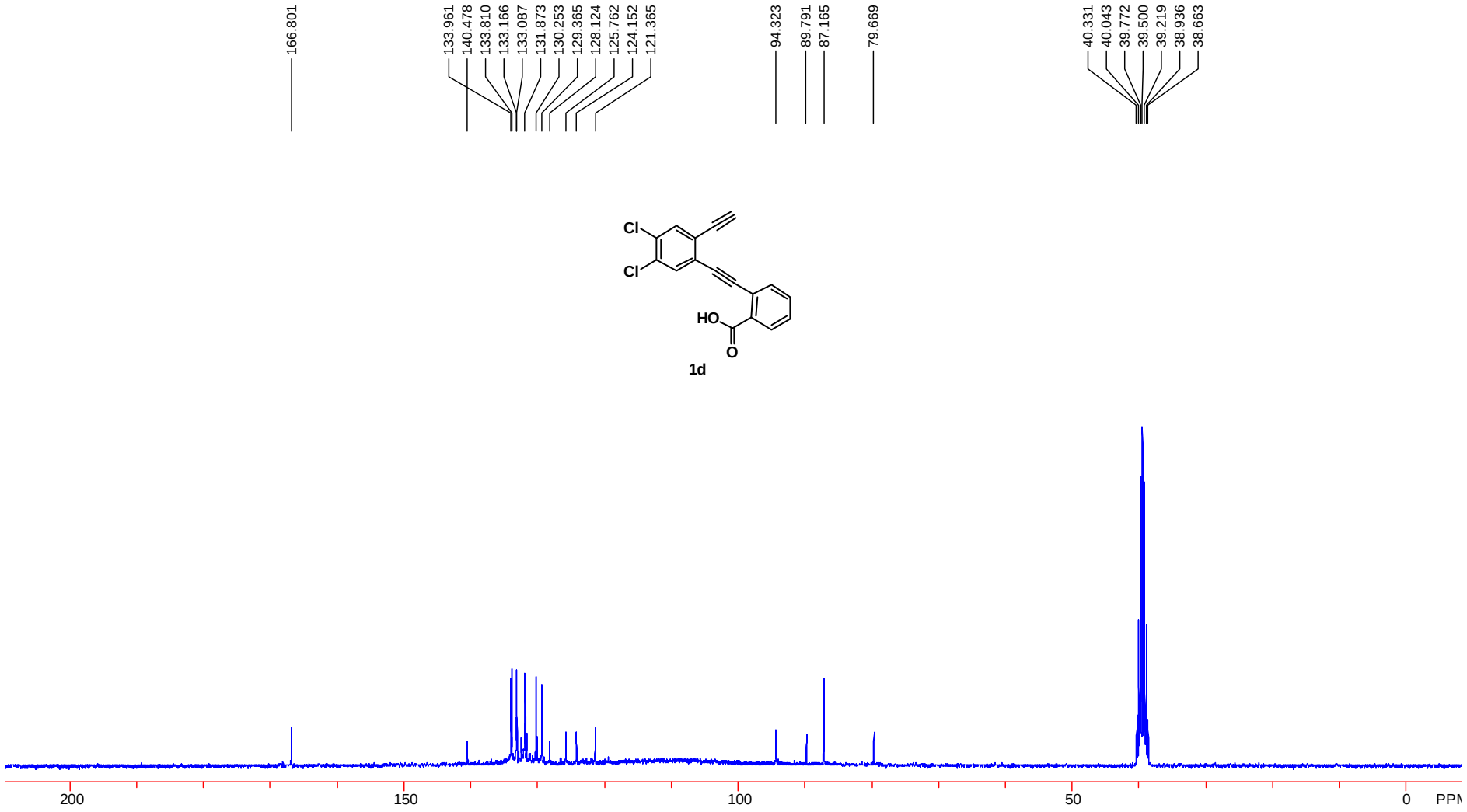
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121.365
94.323
89.791
87.165
79.669
40.331
40.043
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38.936
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Cl
Cl
HO
O
1d
200
150
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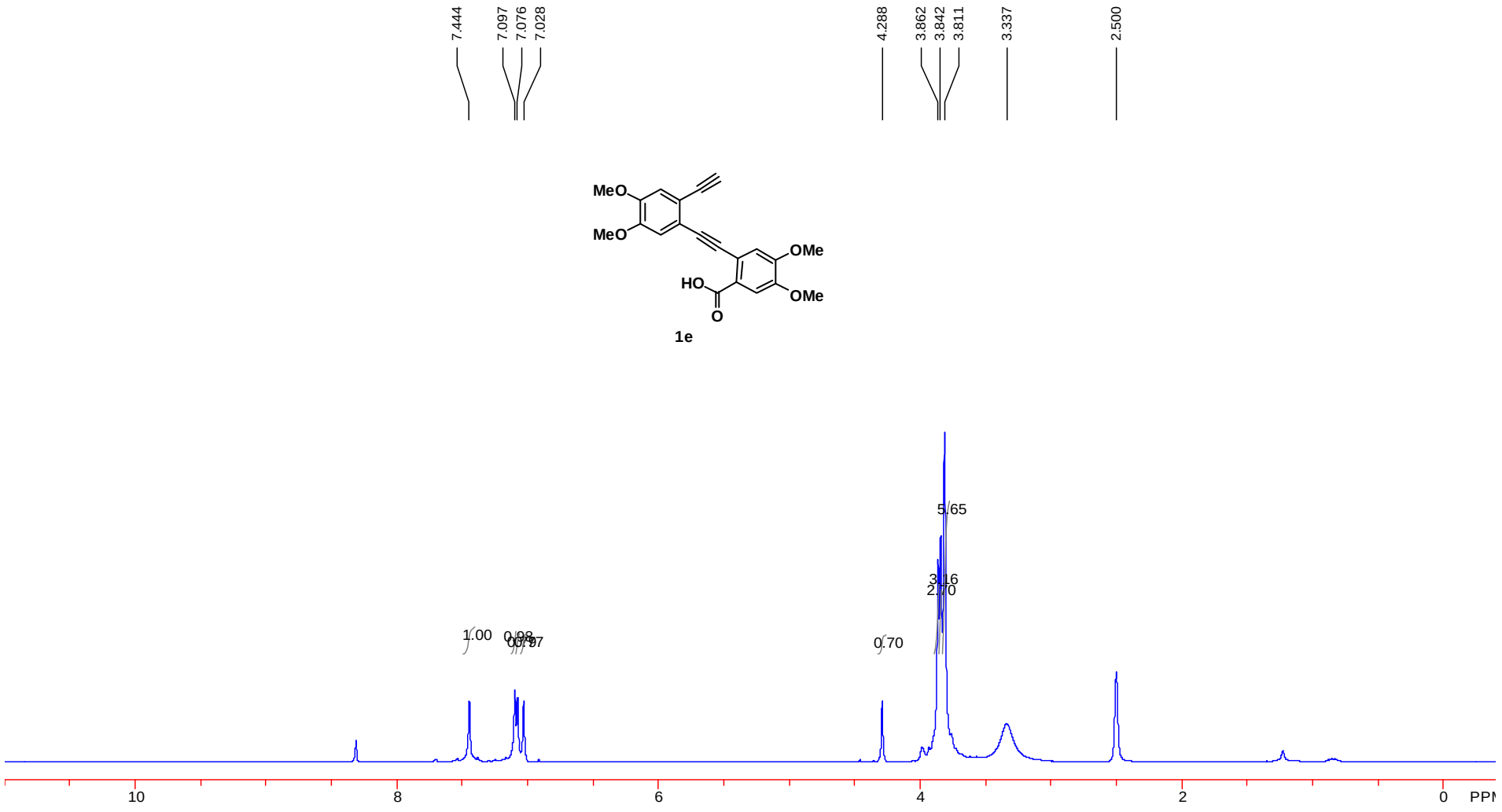
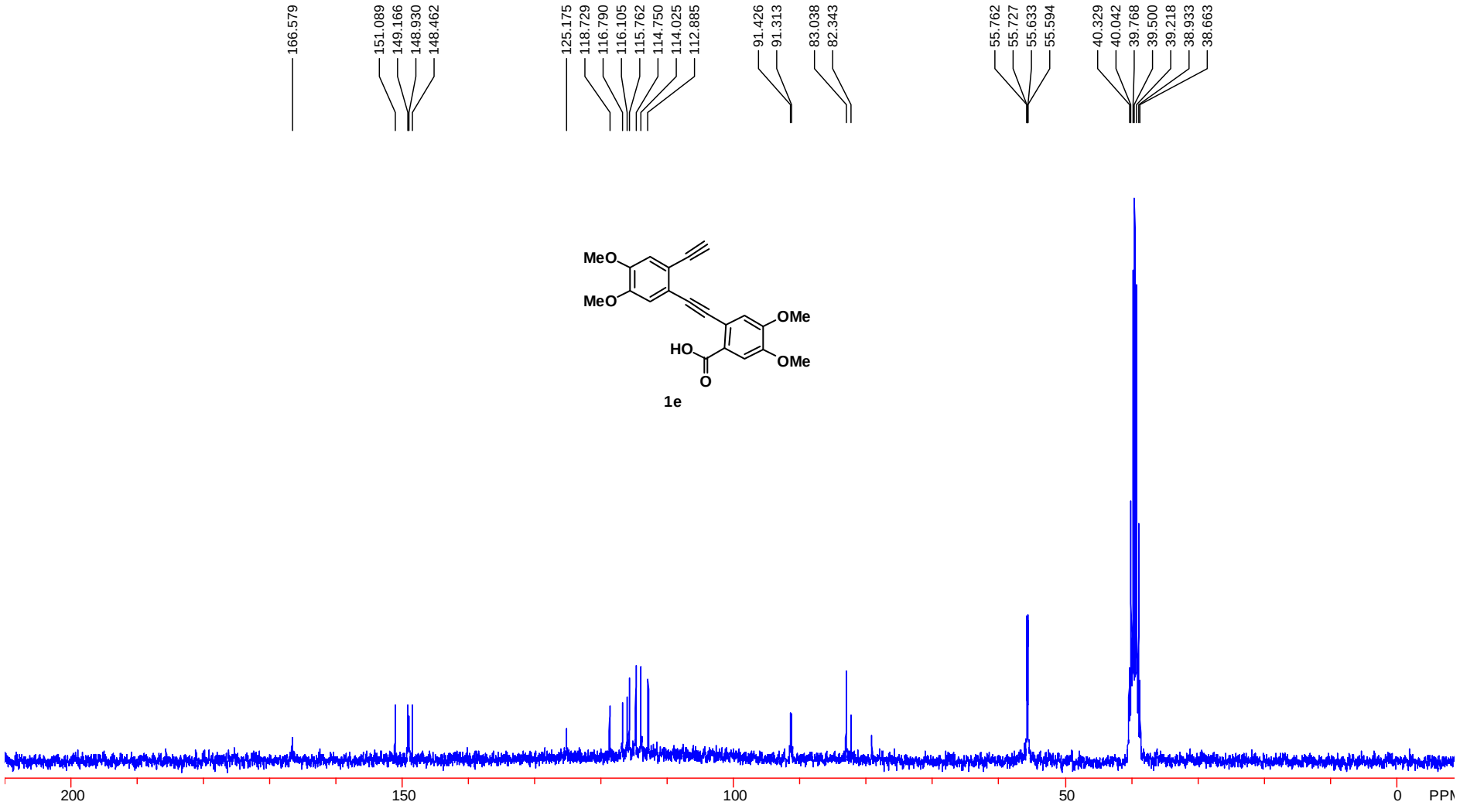
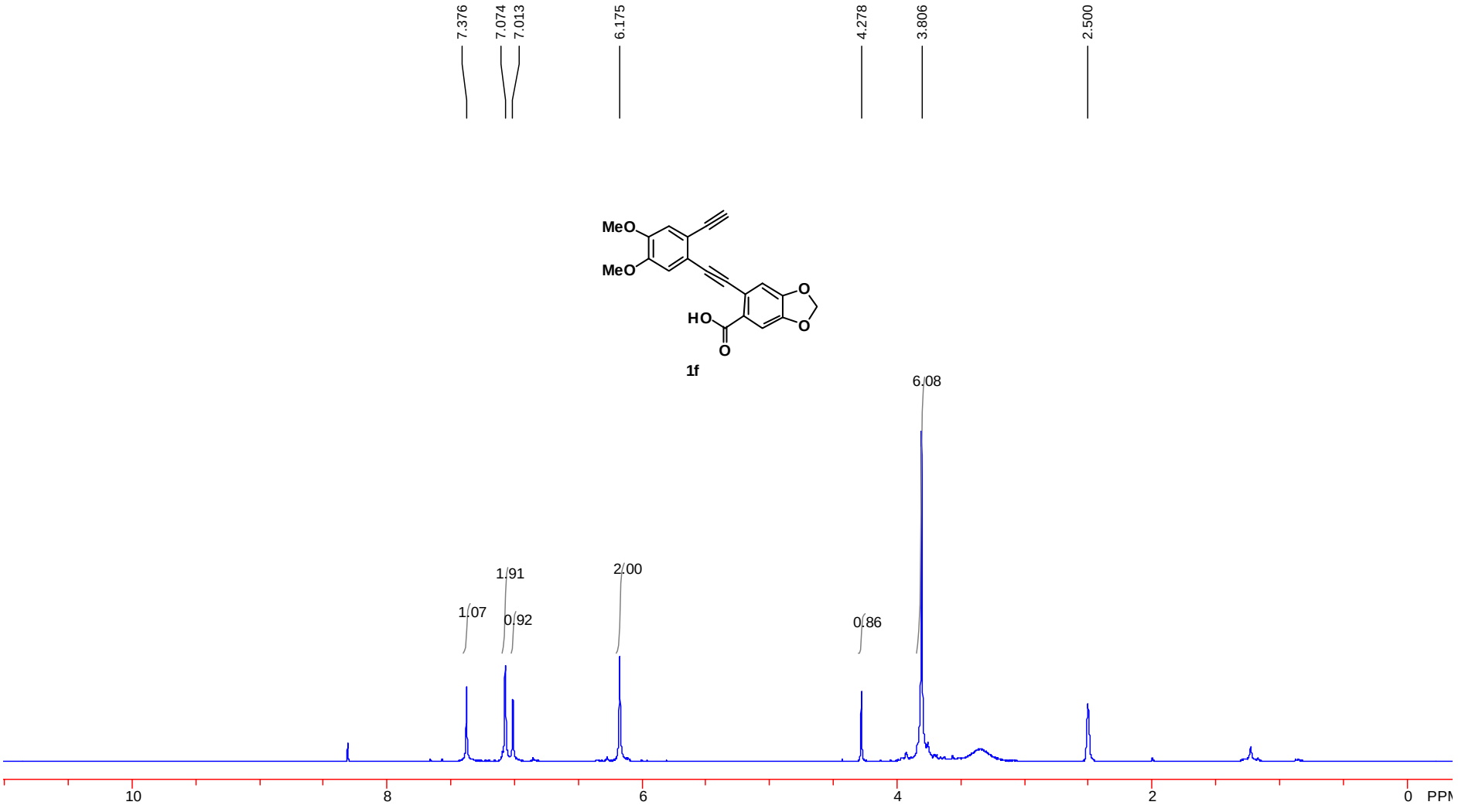
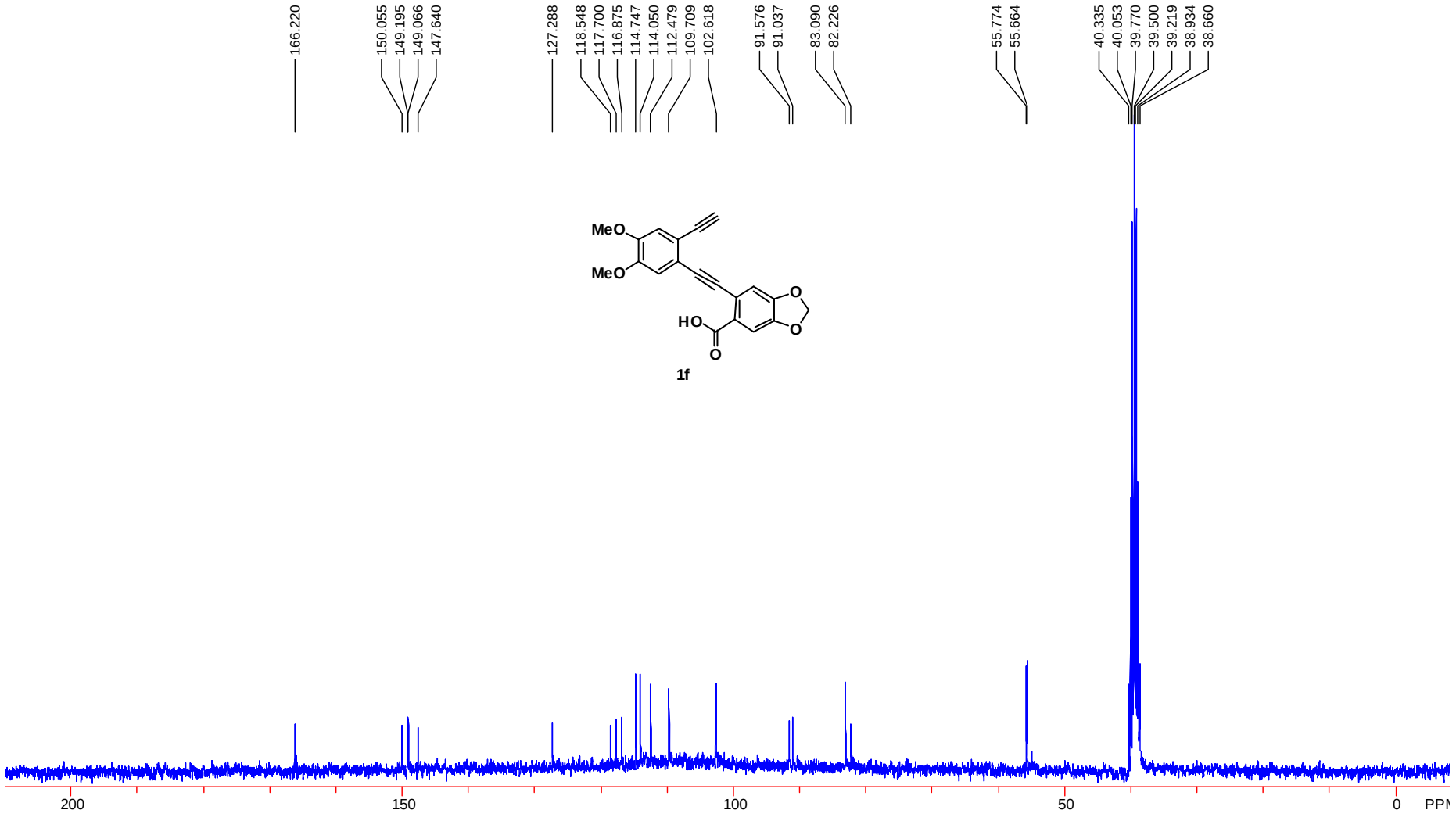
50
0
PPM









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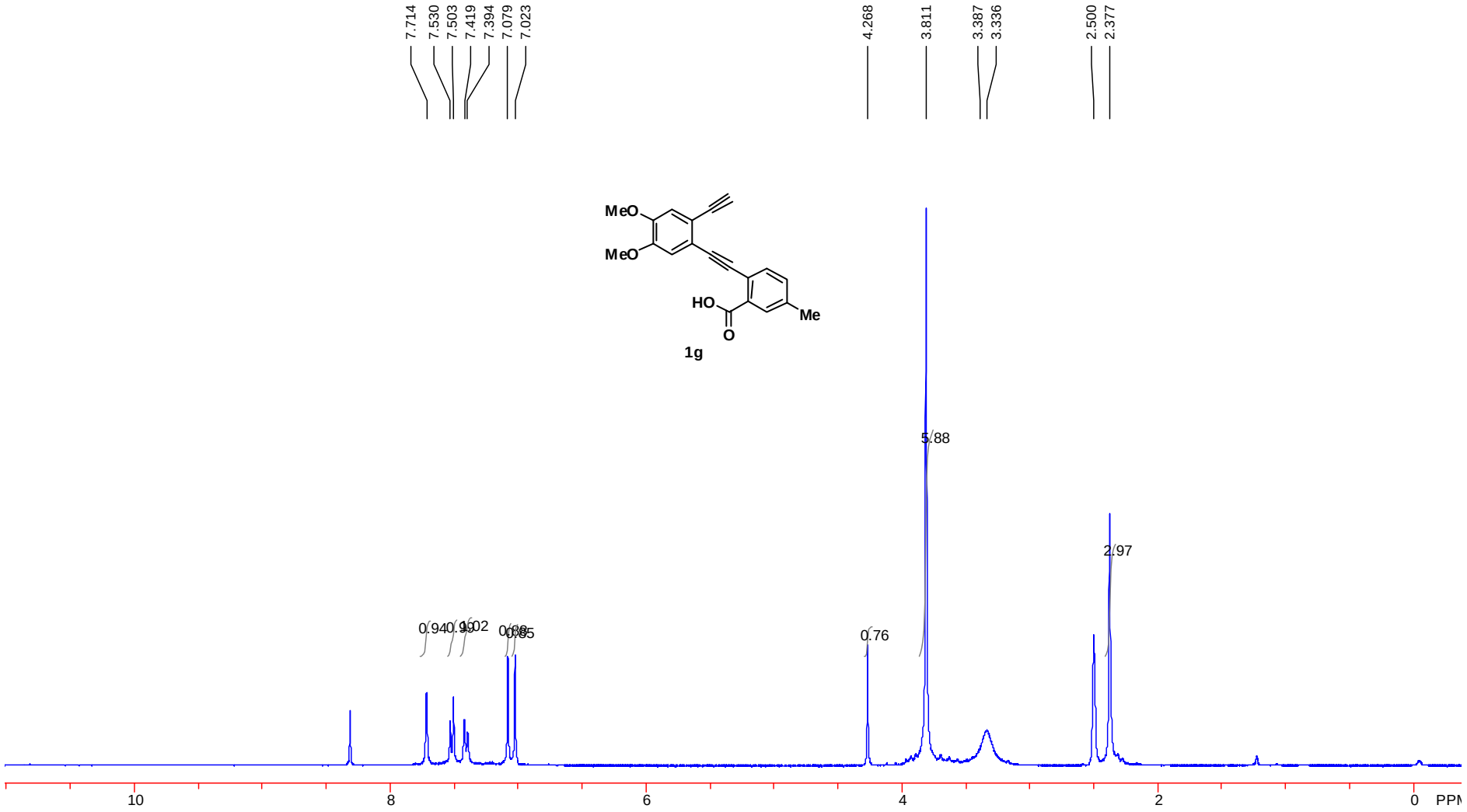

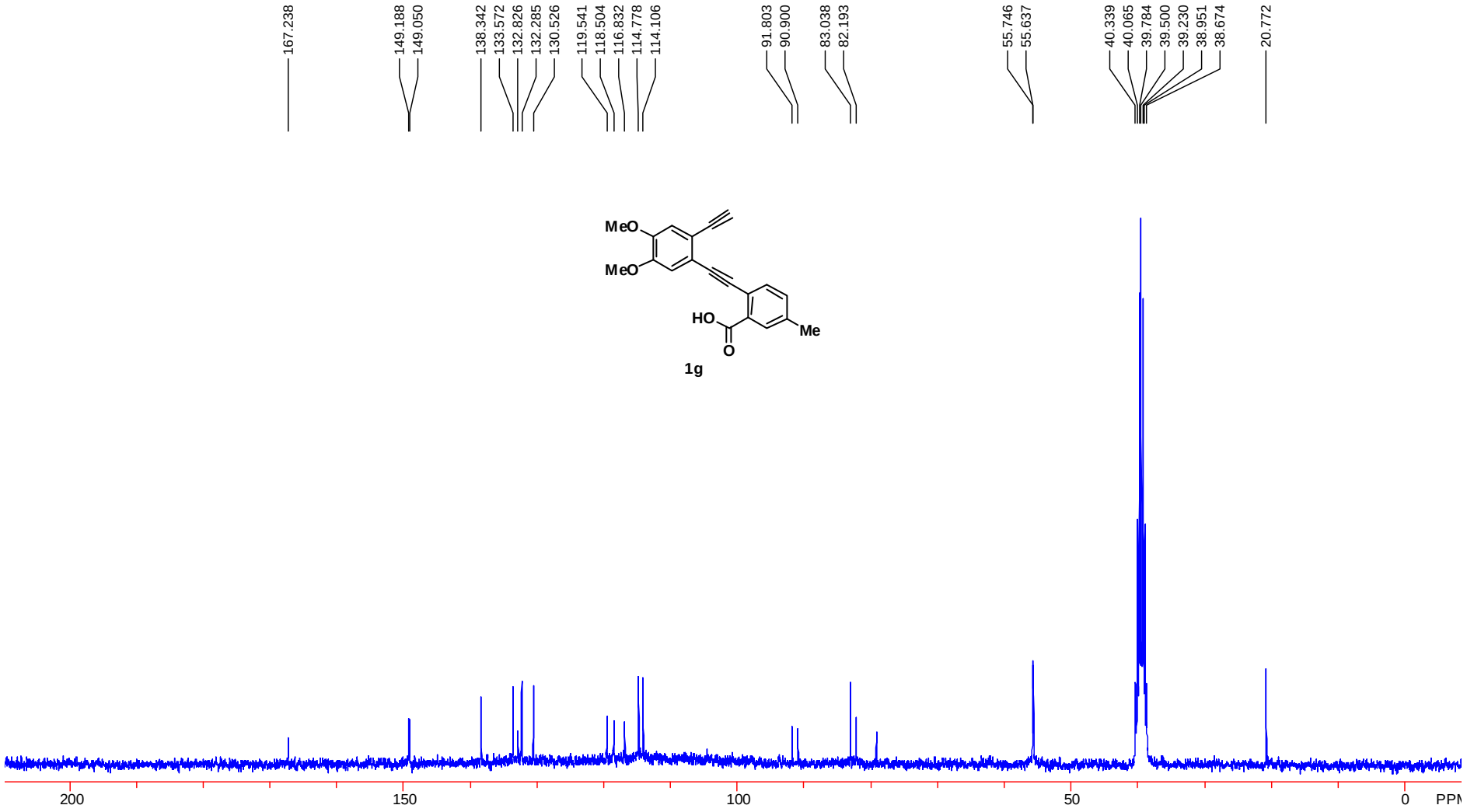

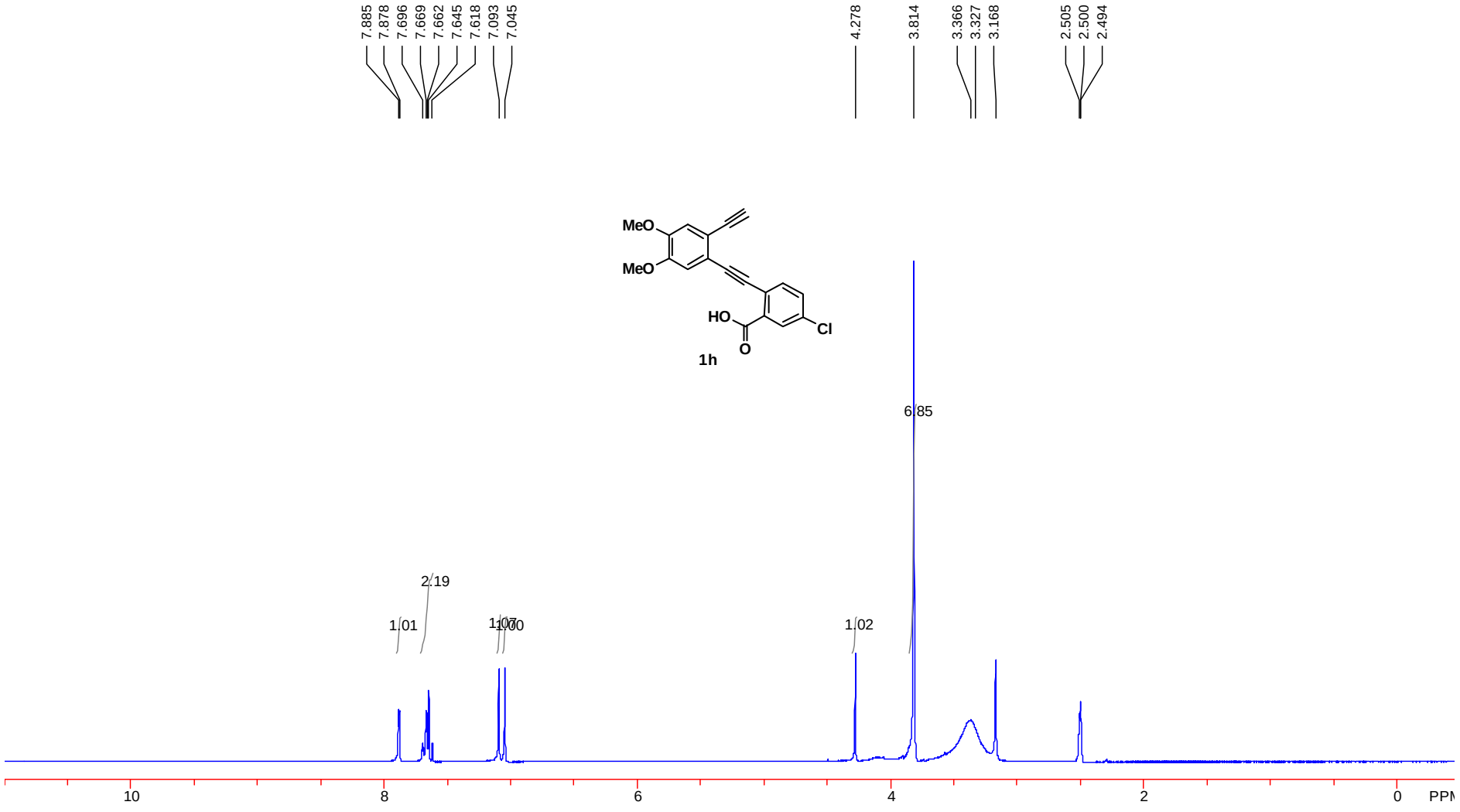

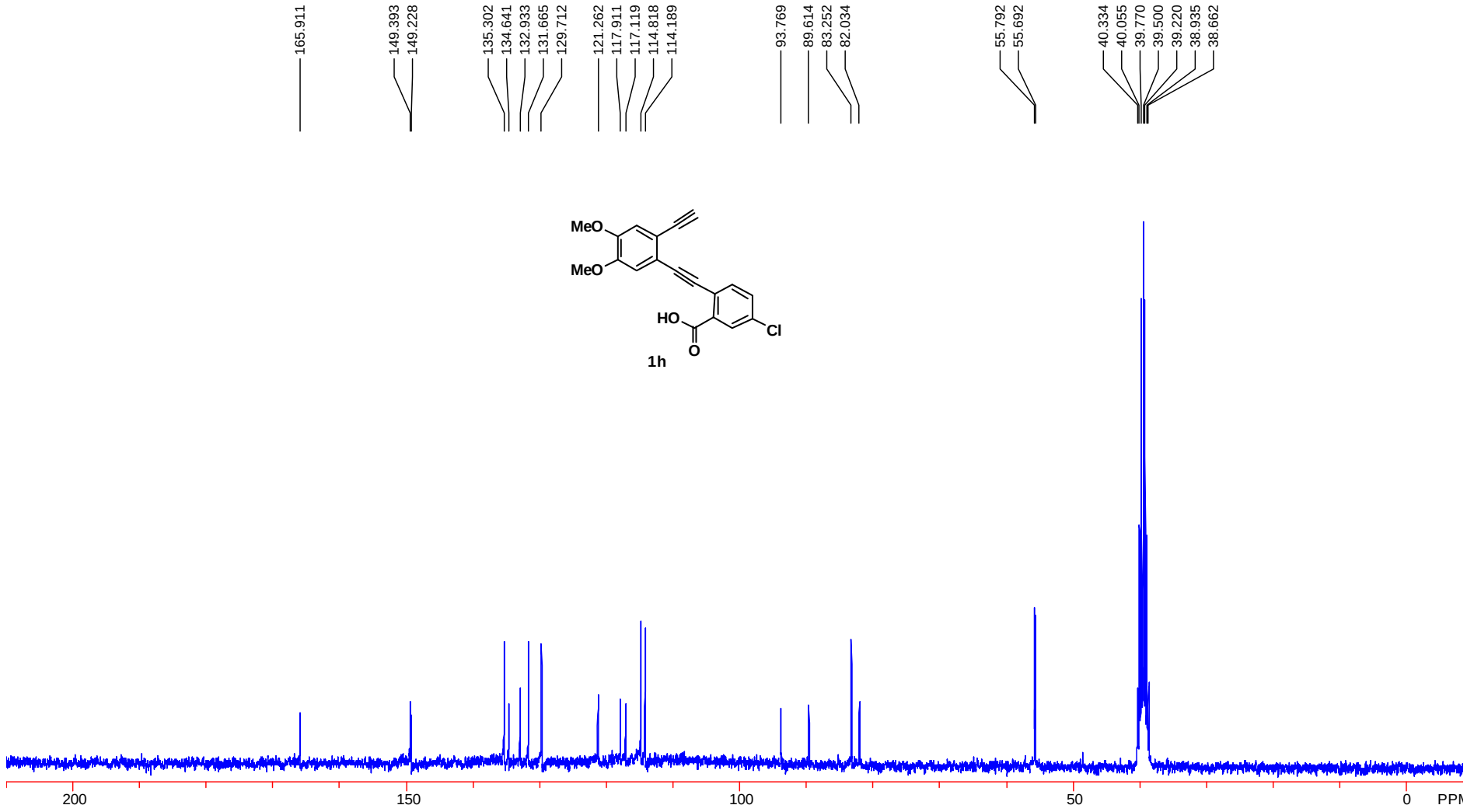

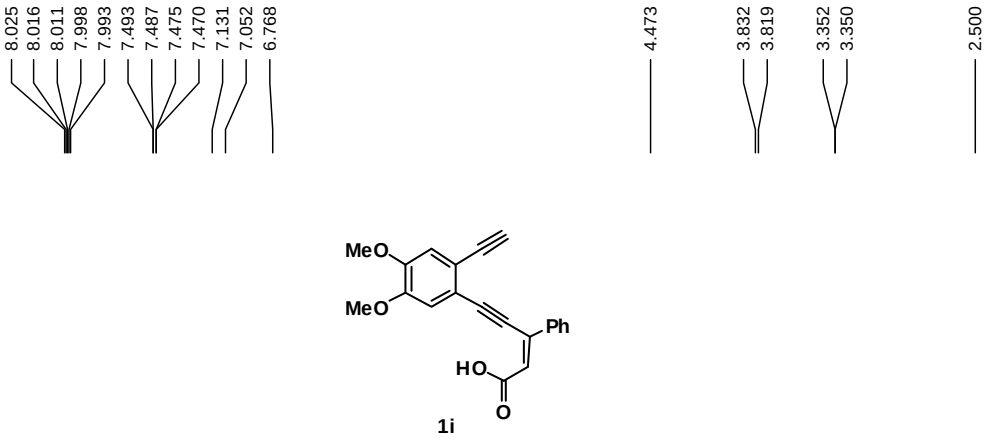

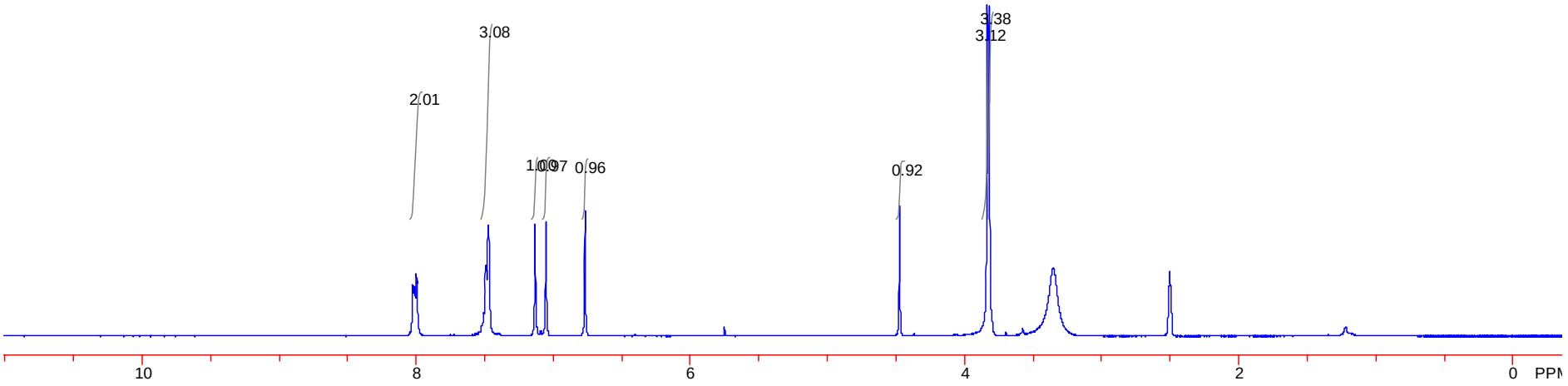

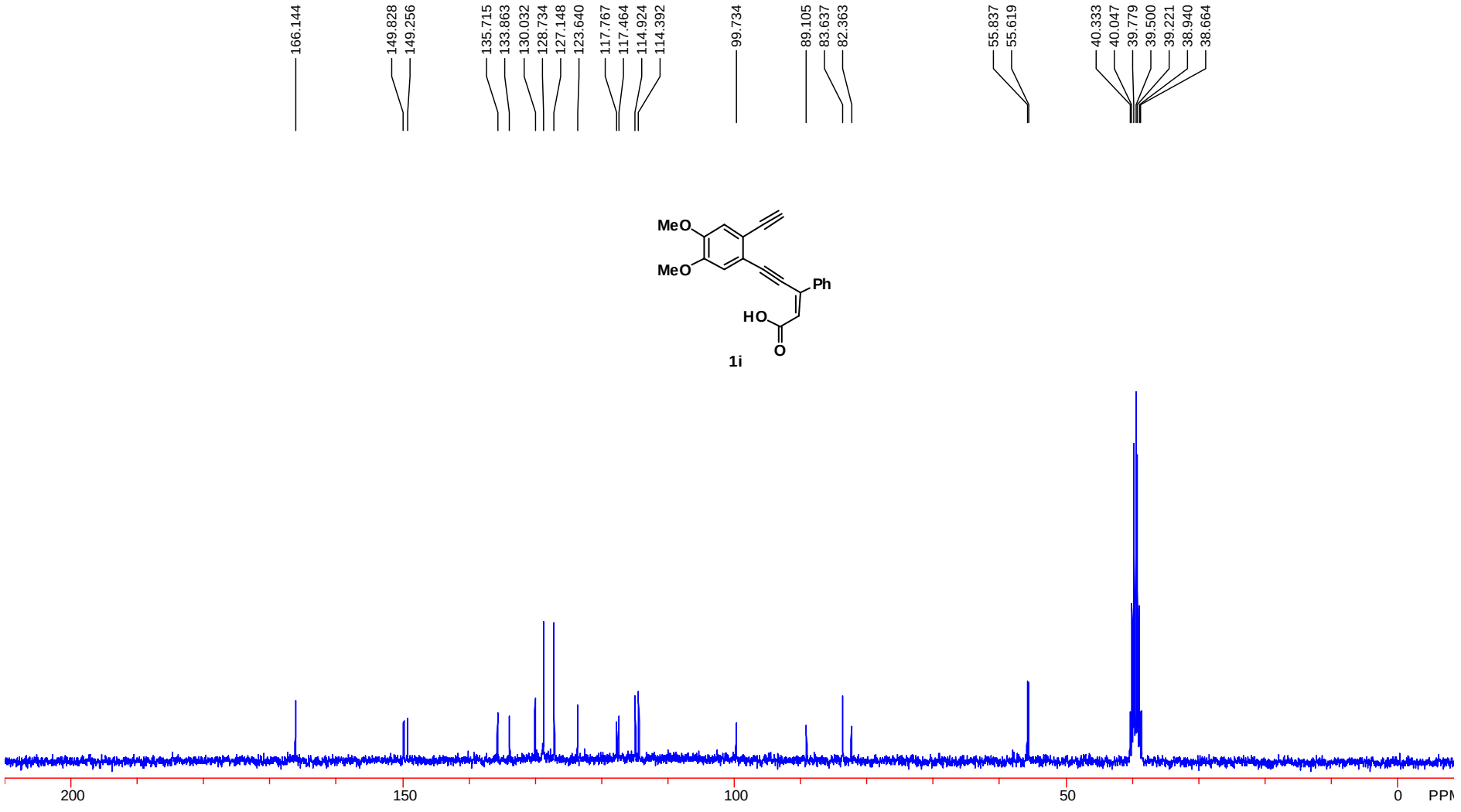

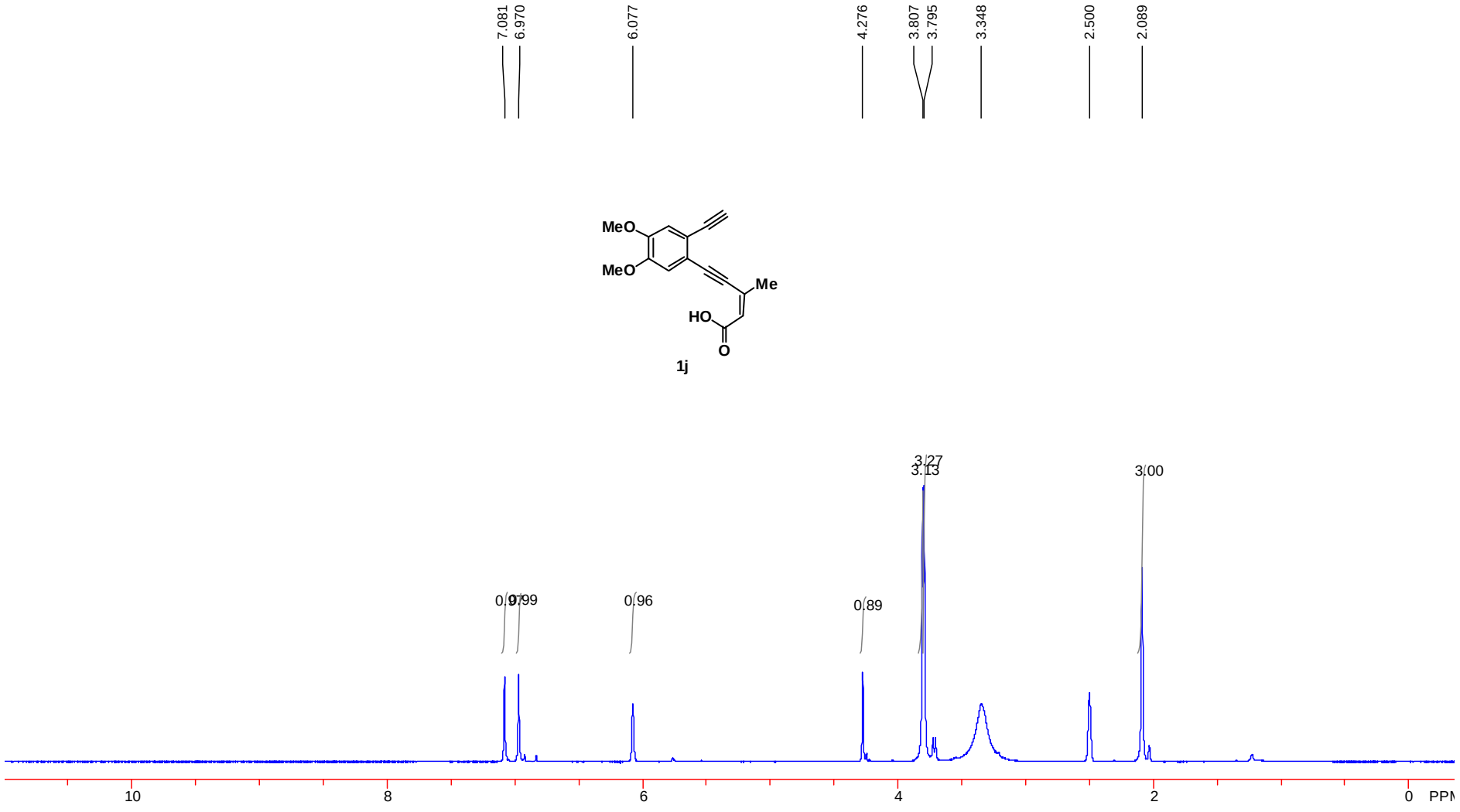

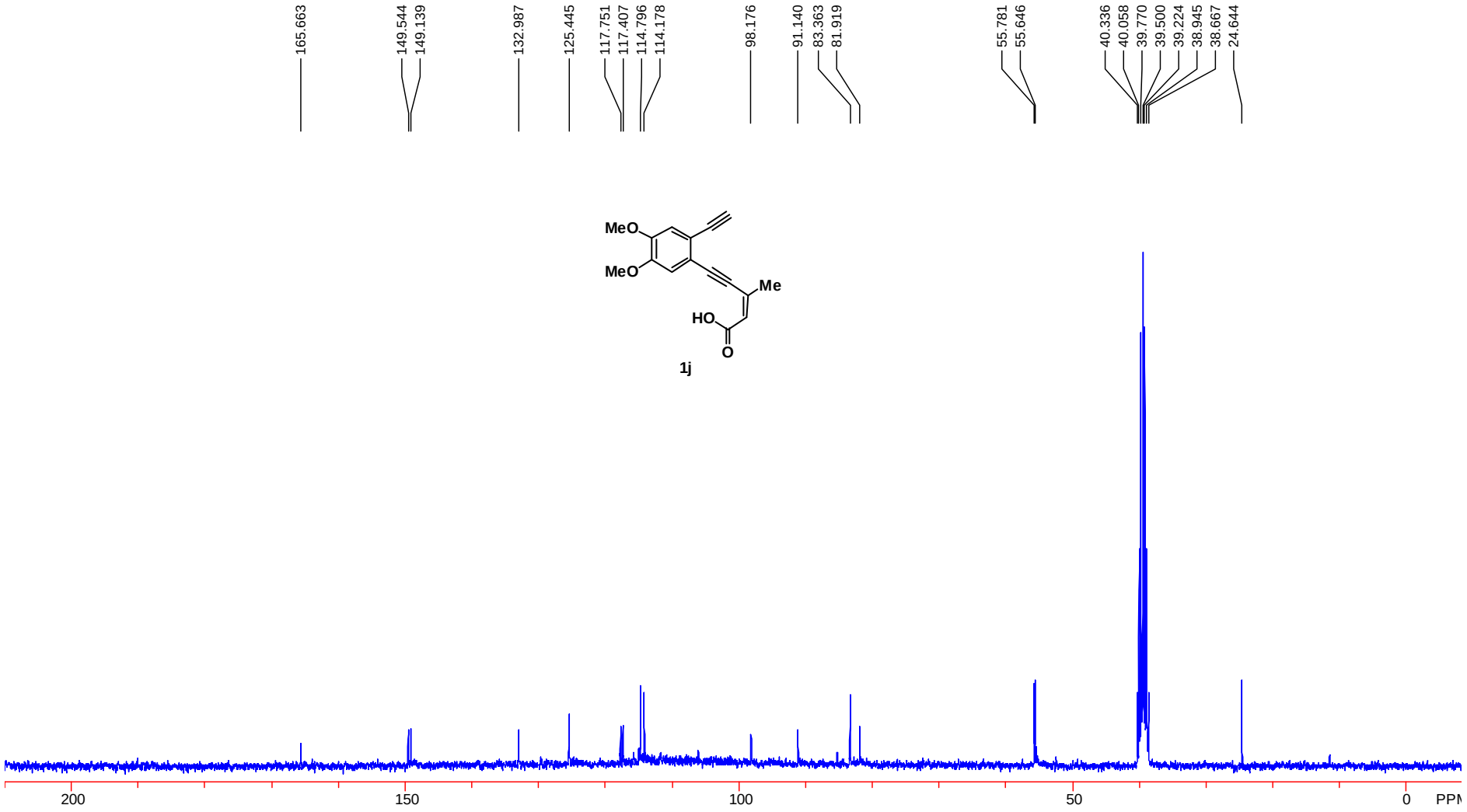

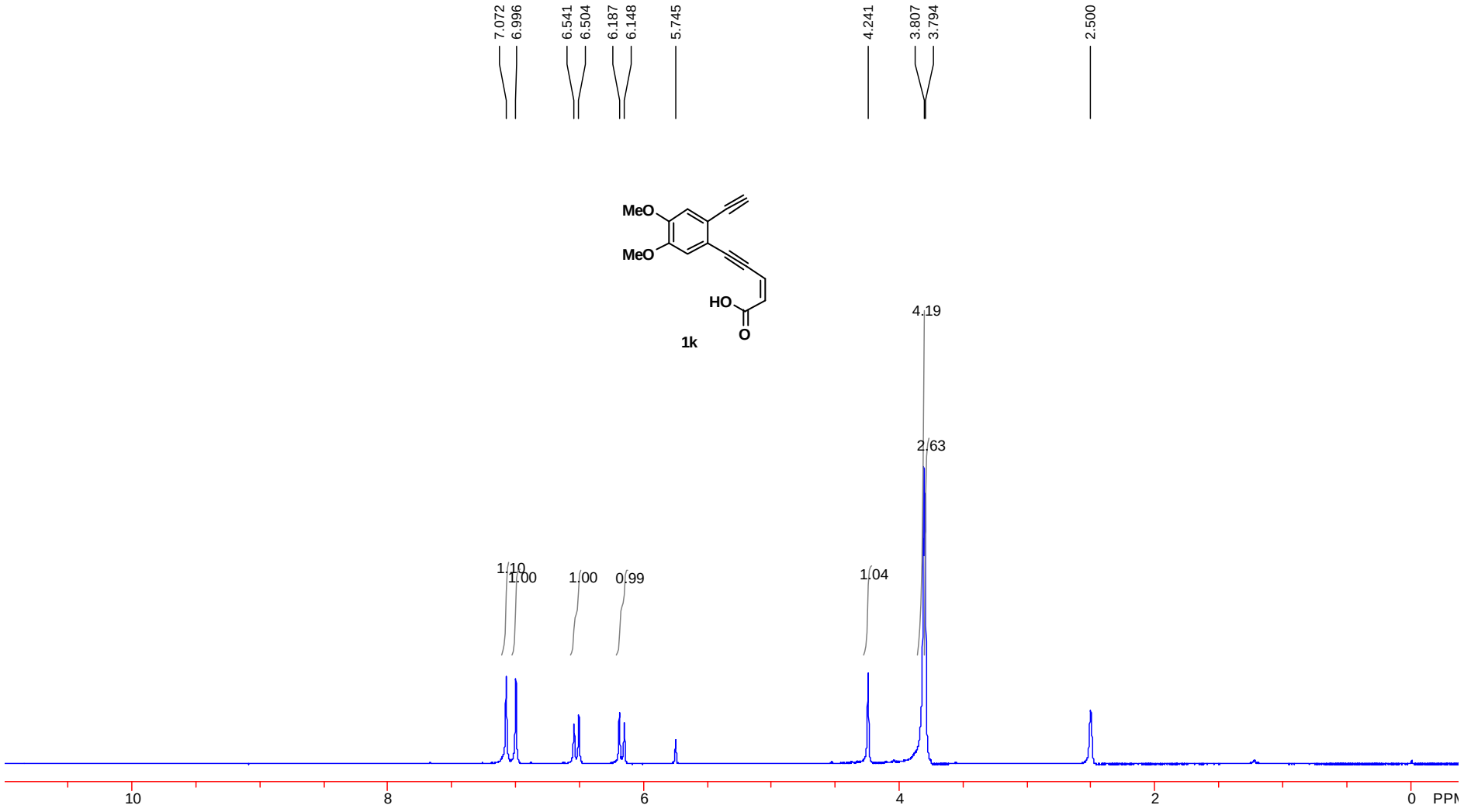

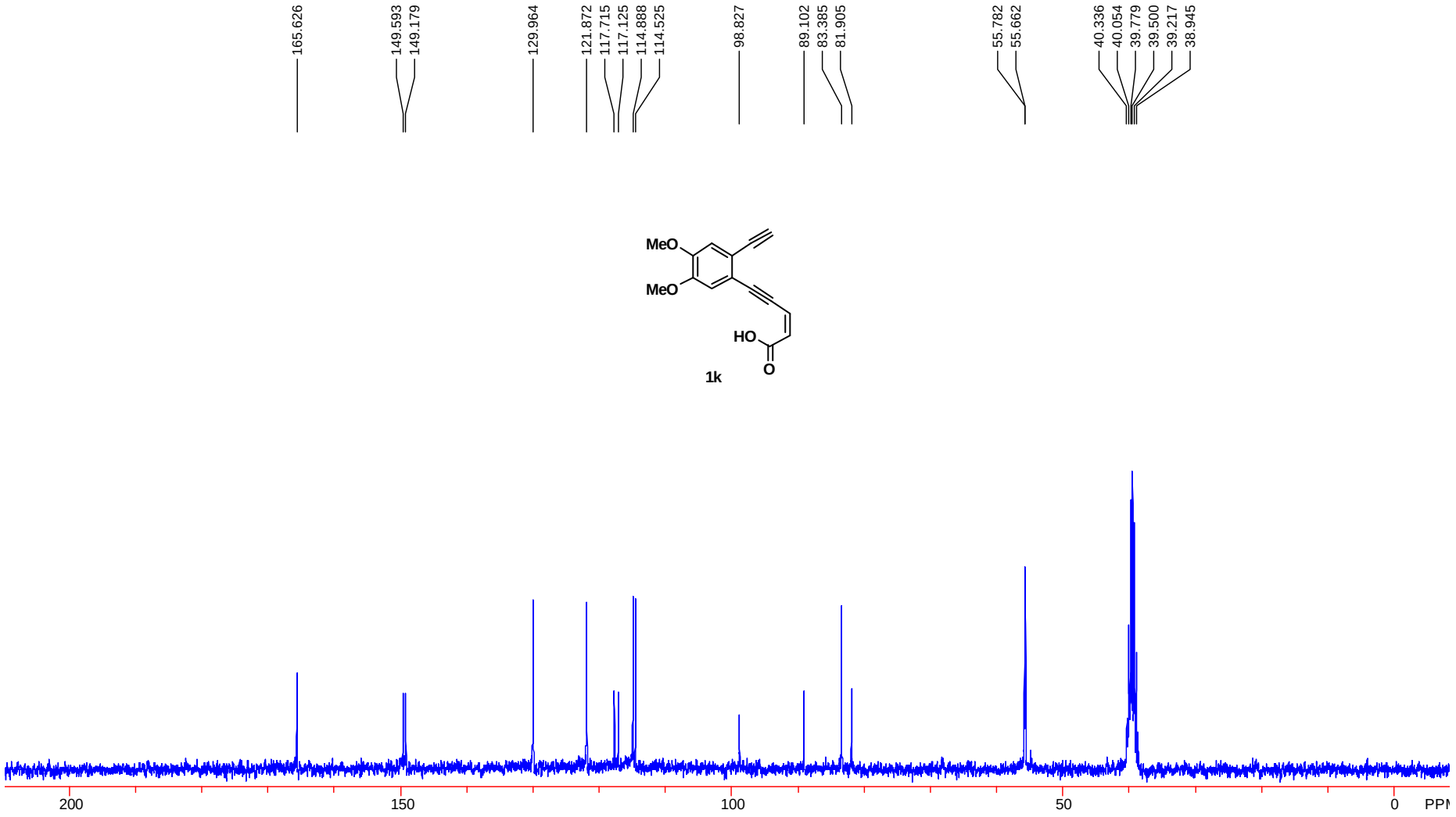

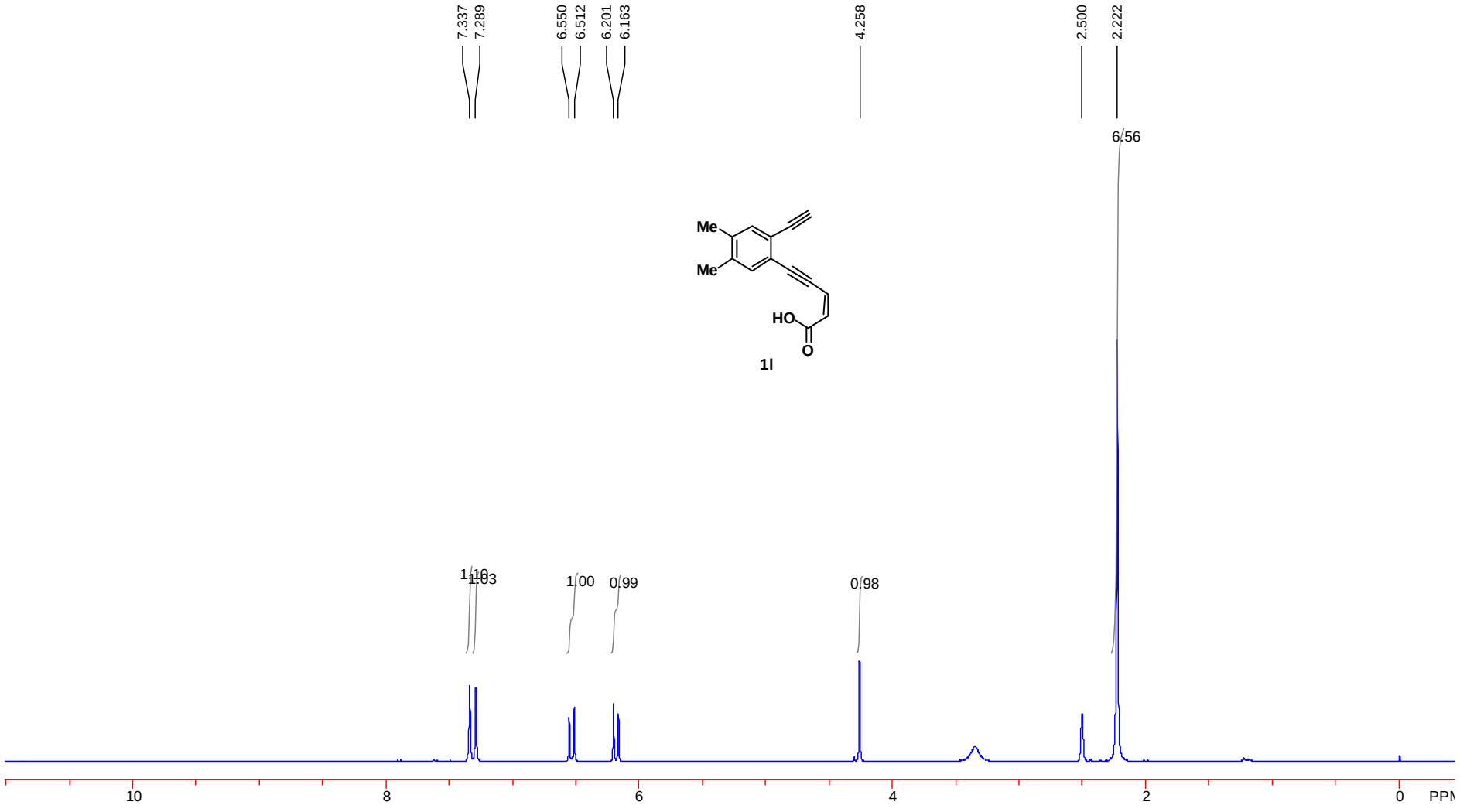

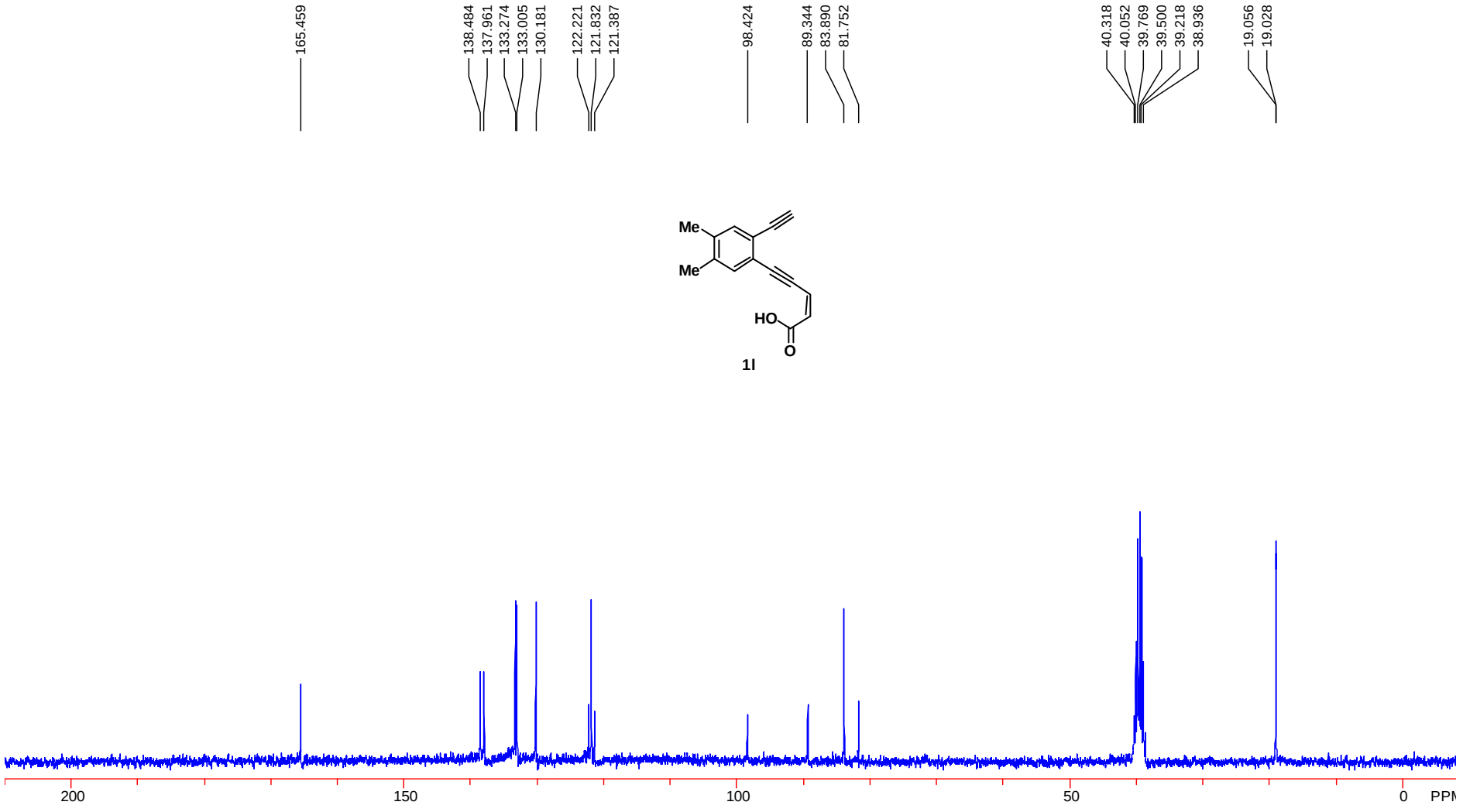

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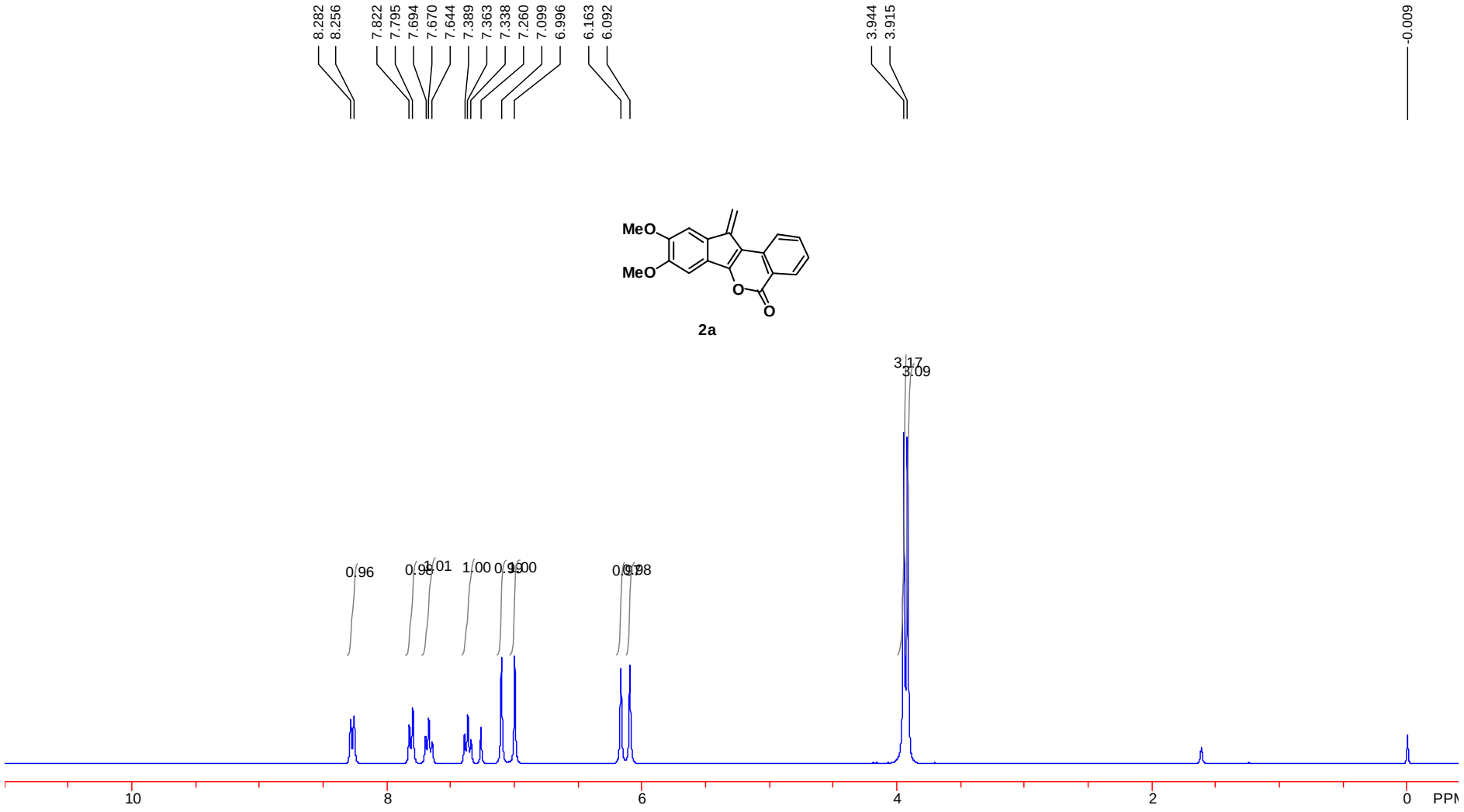

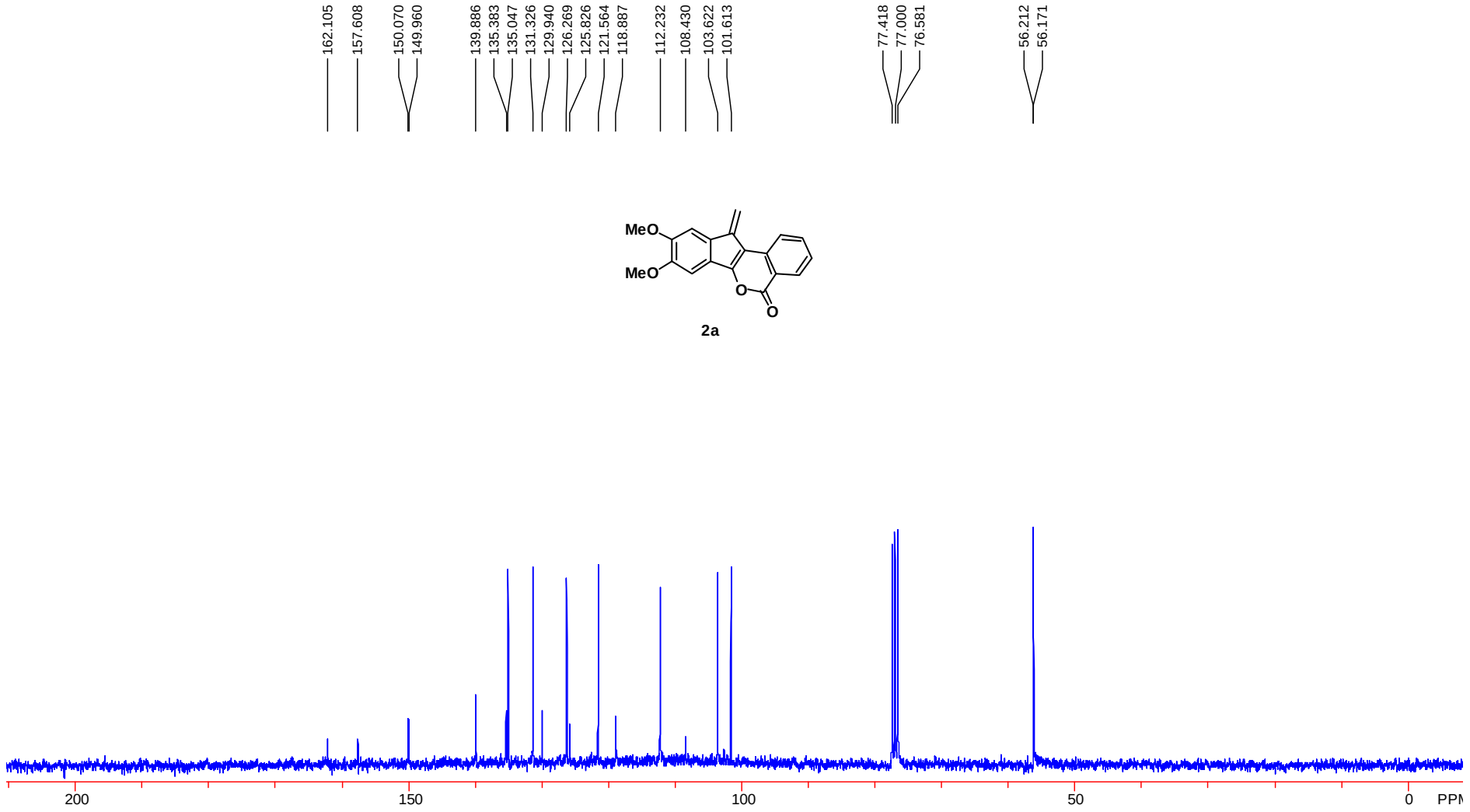

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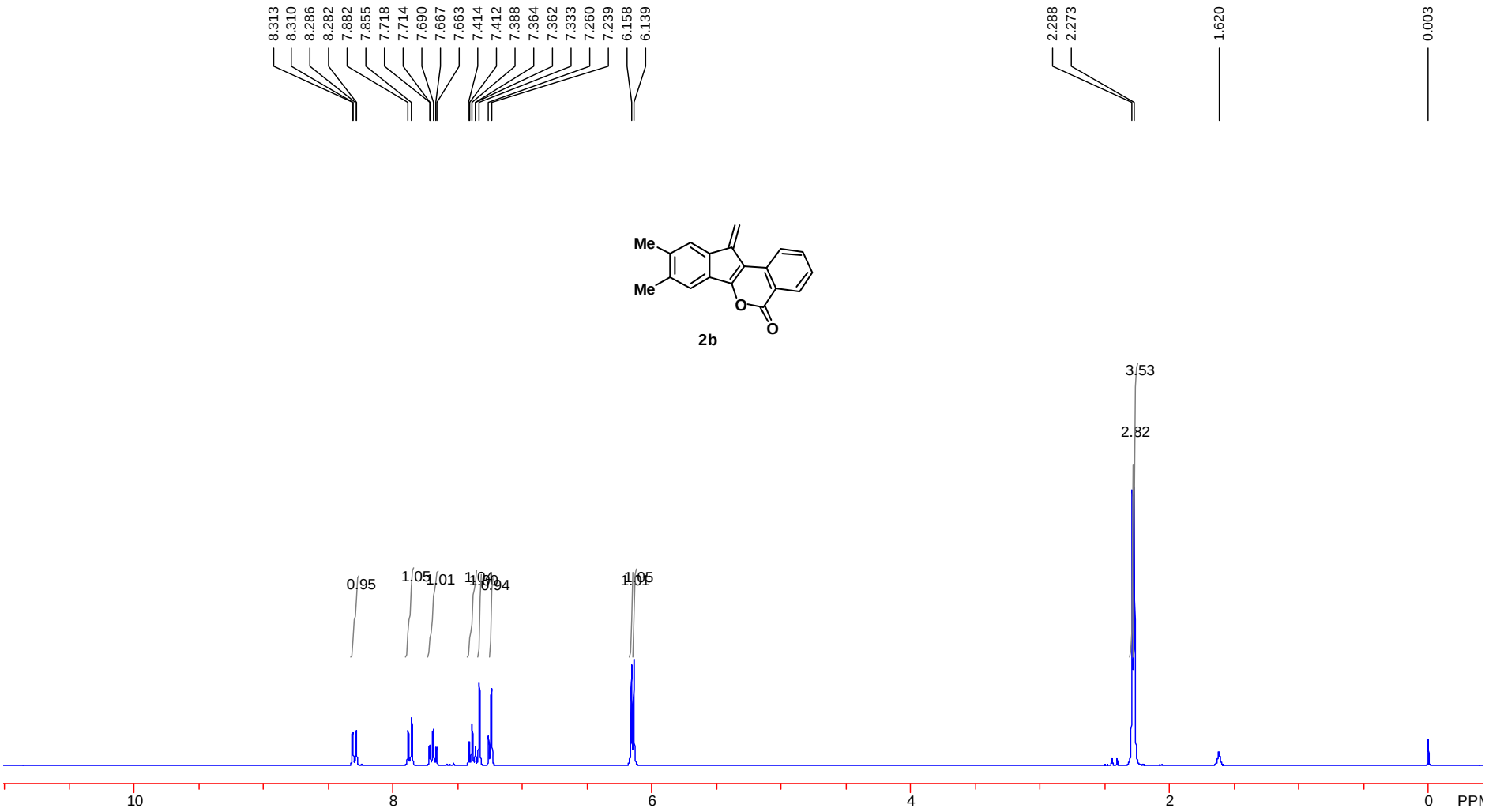

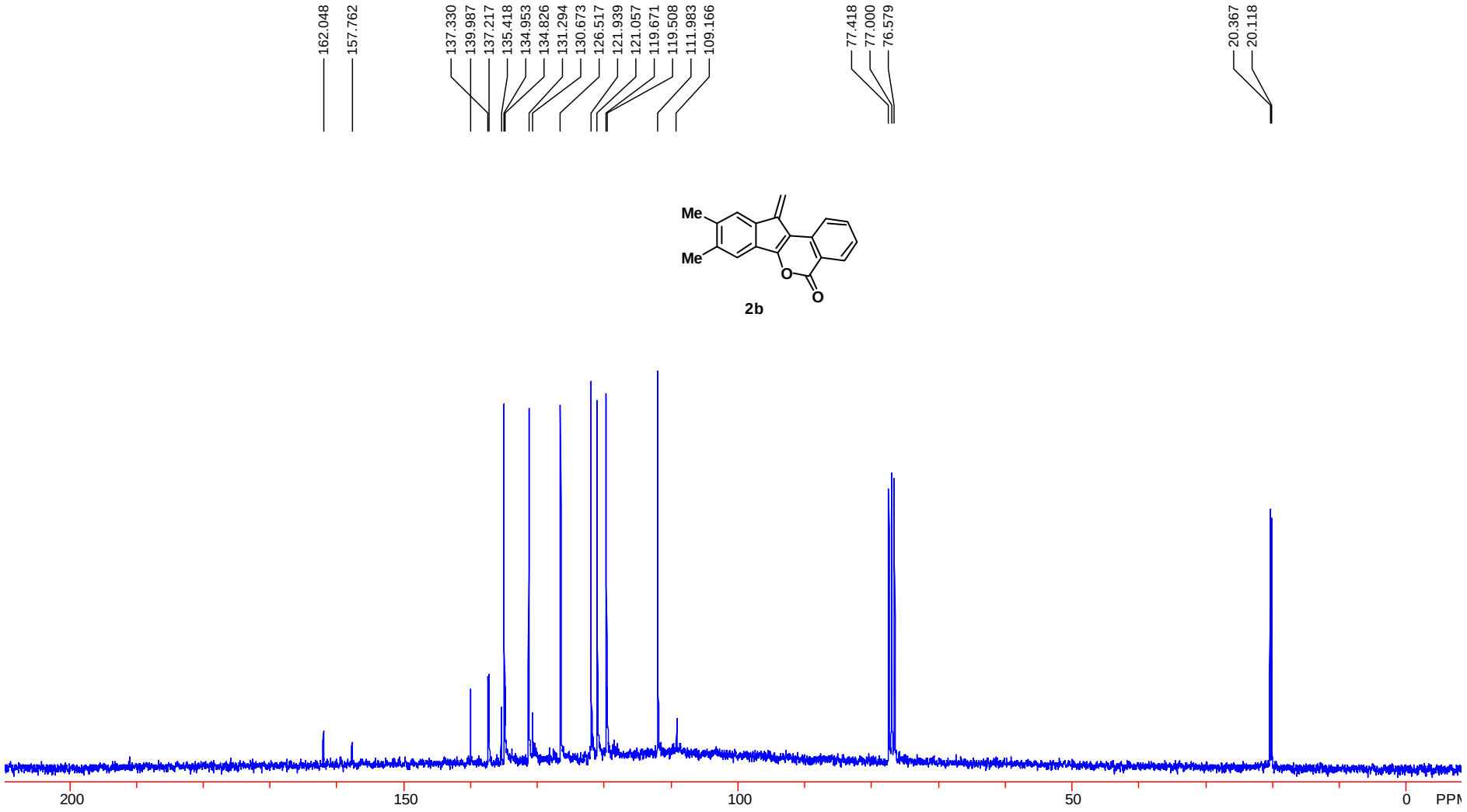

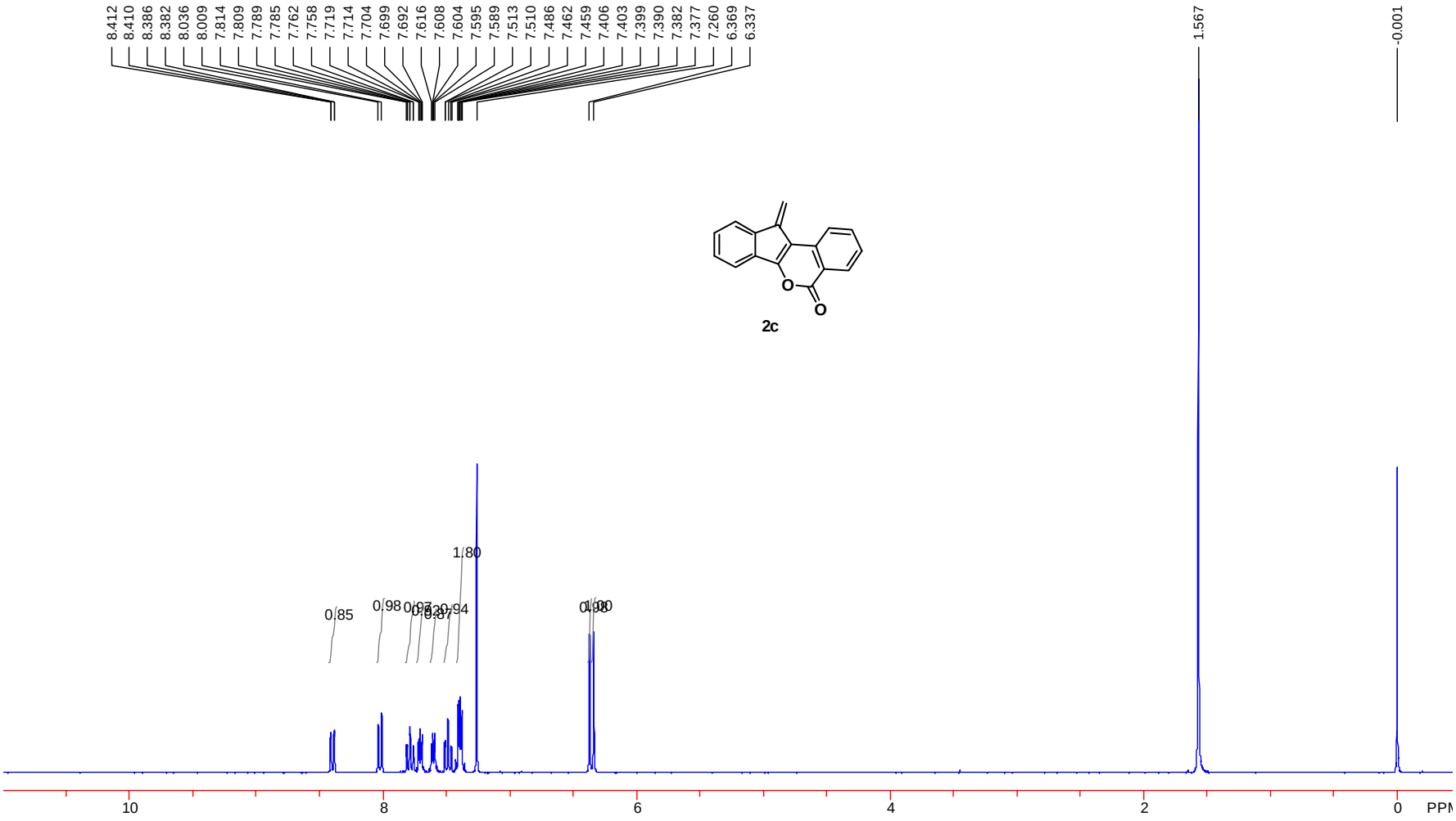

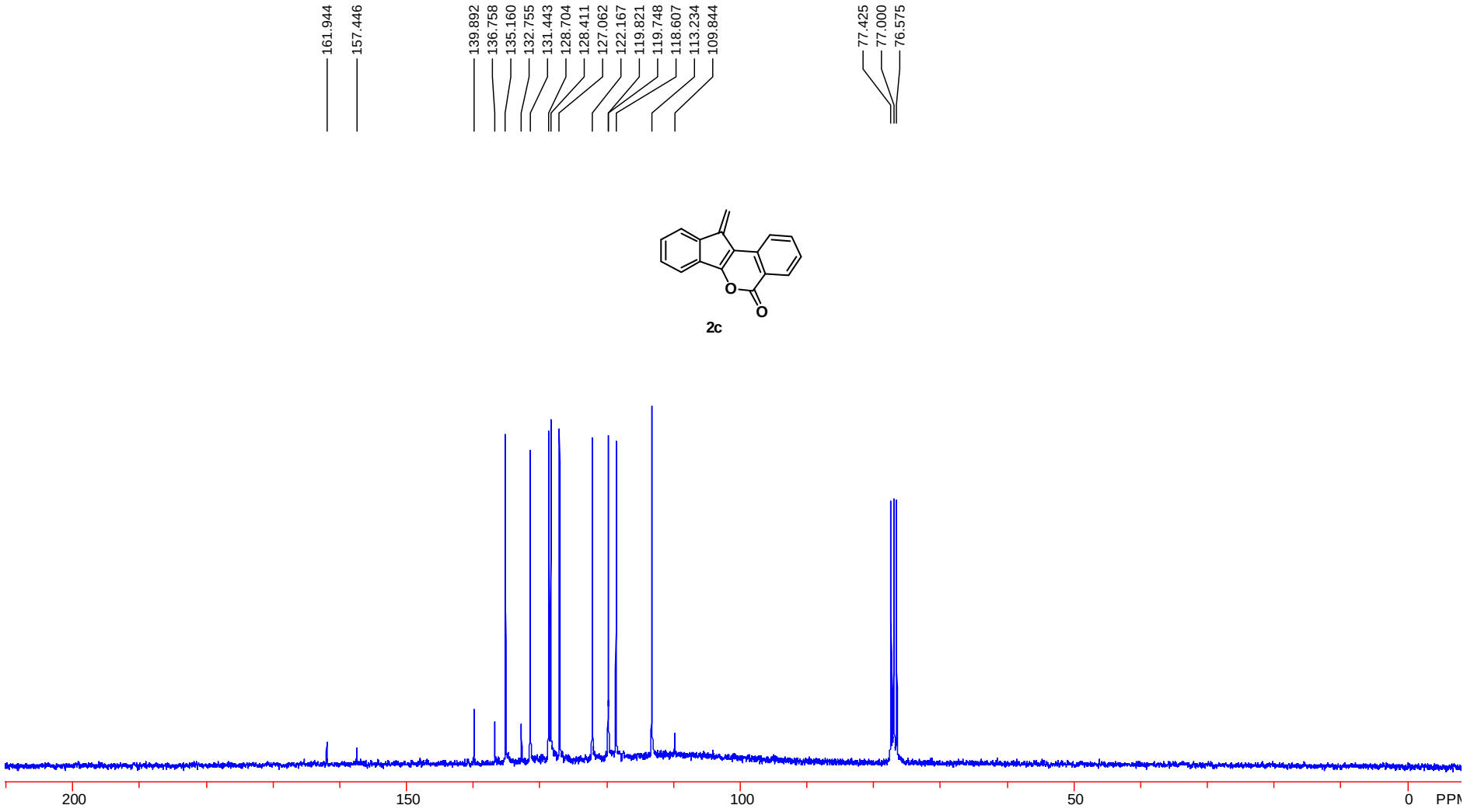

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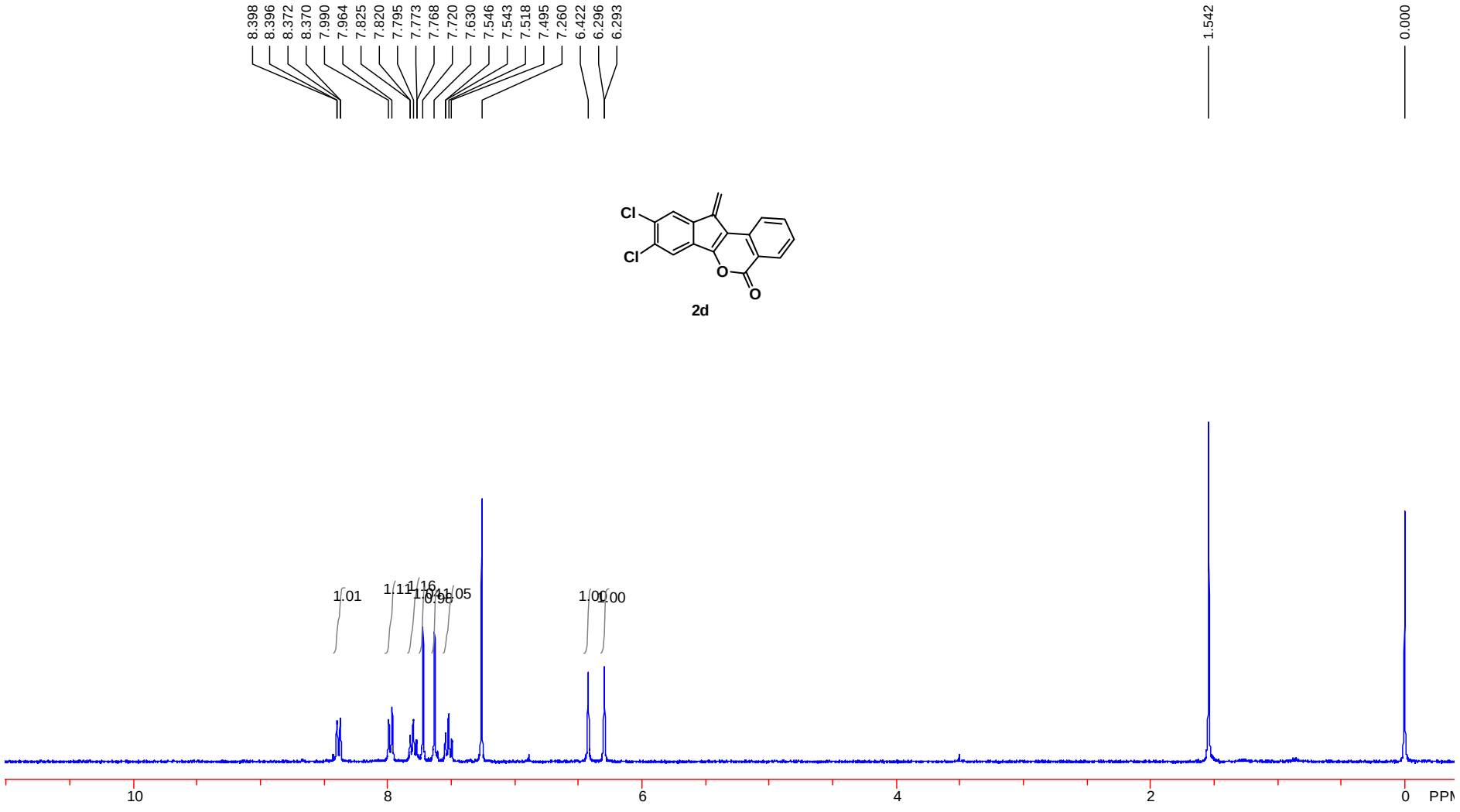
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7.630
7.546
7.543
7.518
7.495
7.260
6.422
6.296
6.293
1.542
0.000
Cl
Cl
O
O
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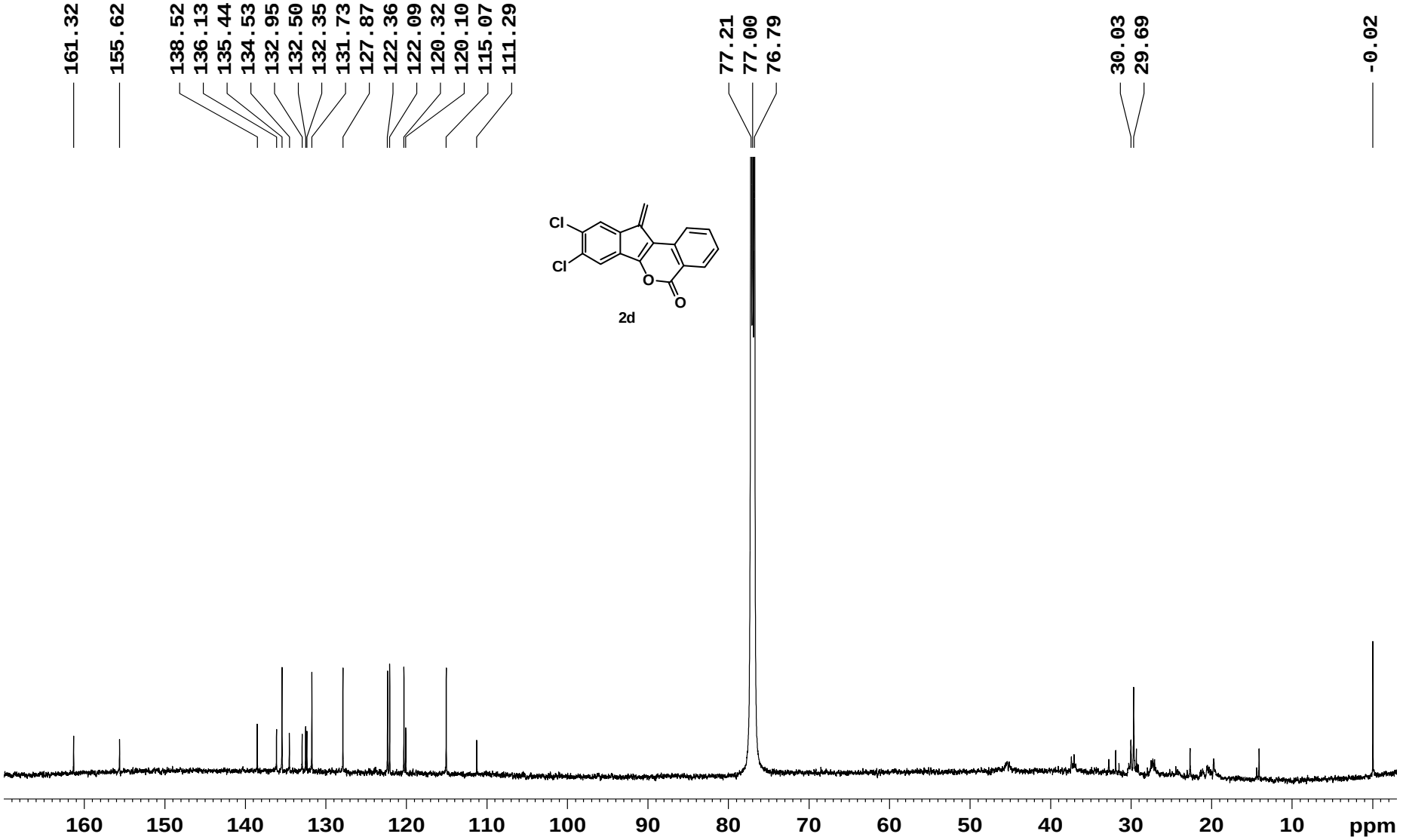

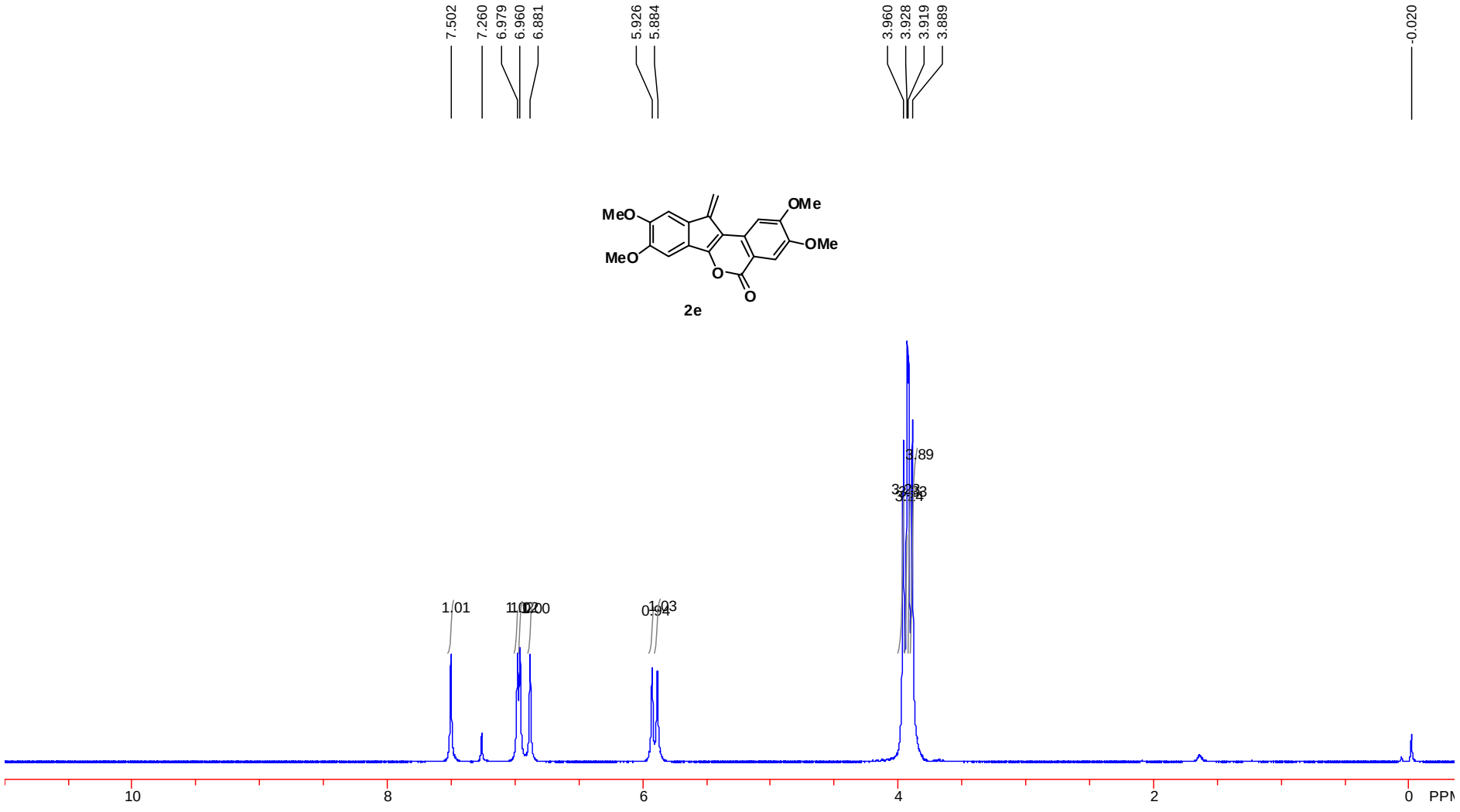

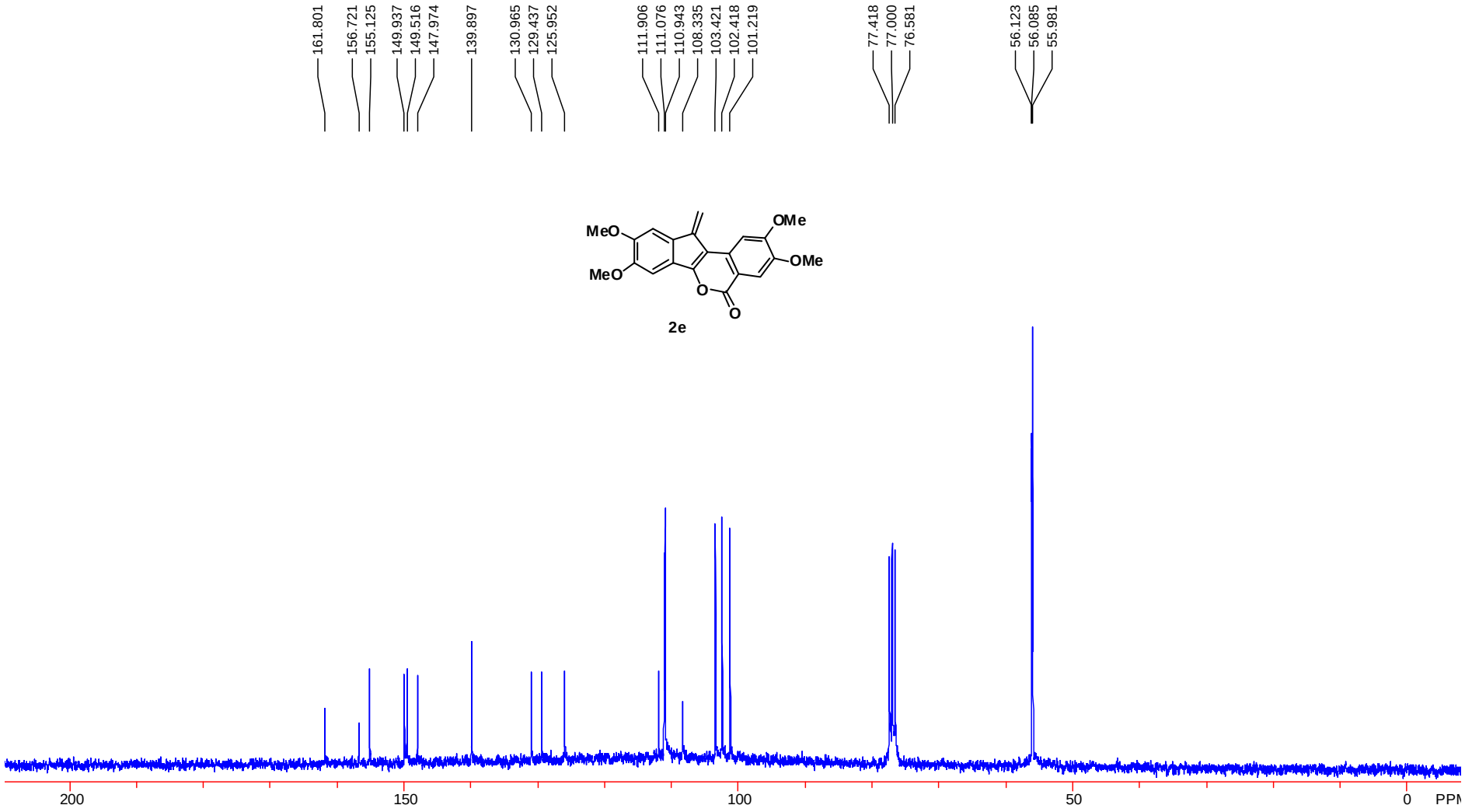

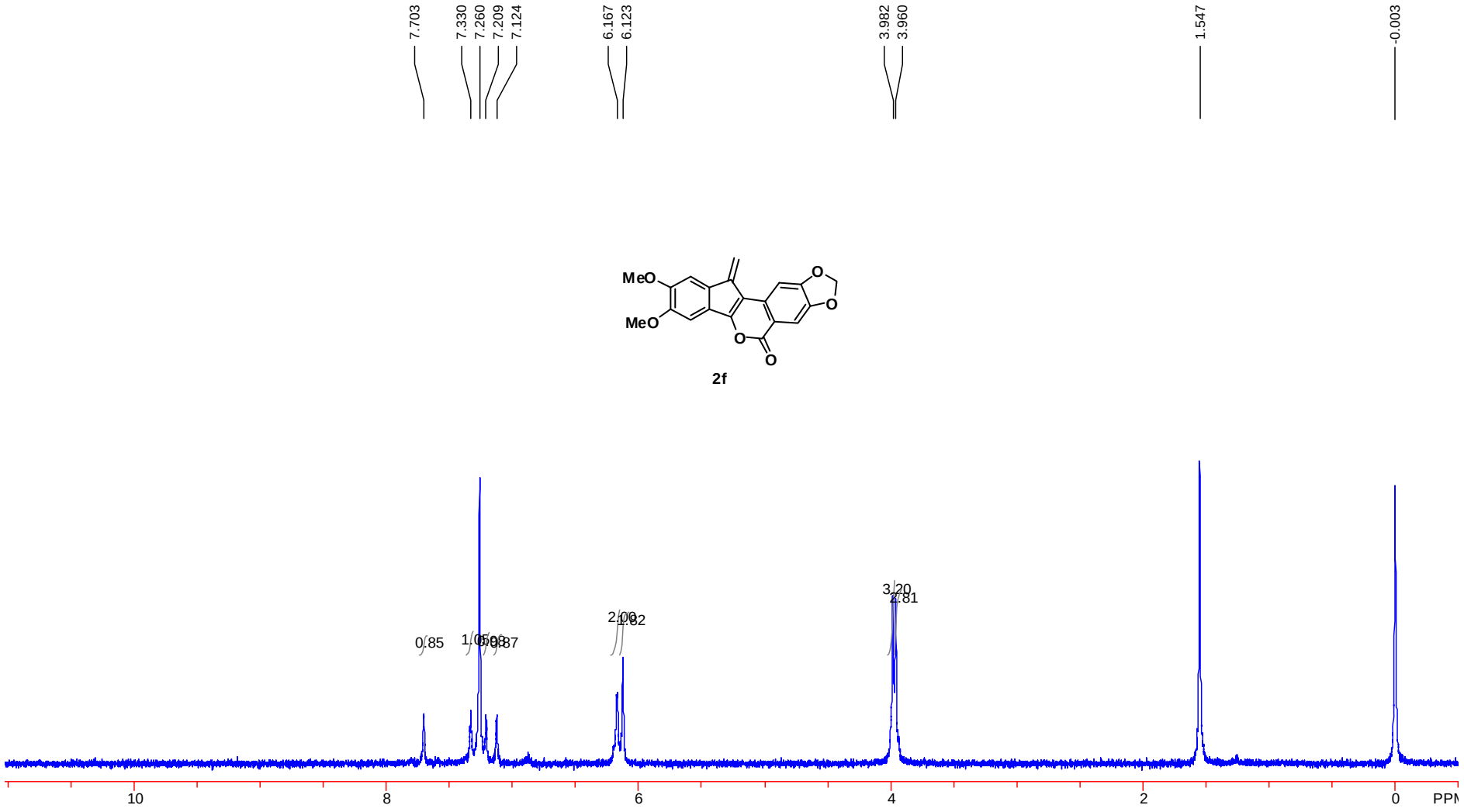

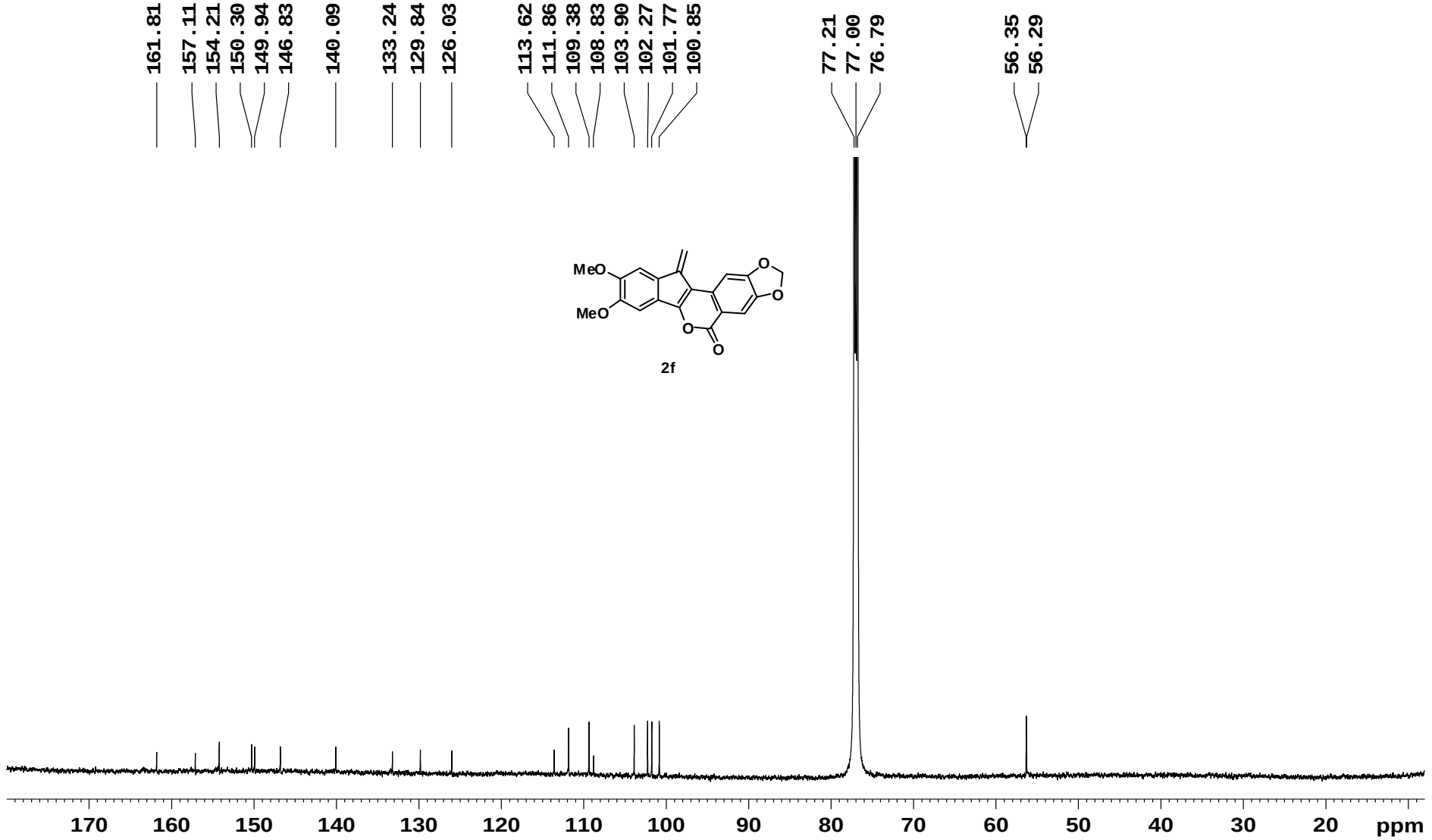

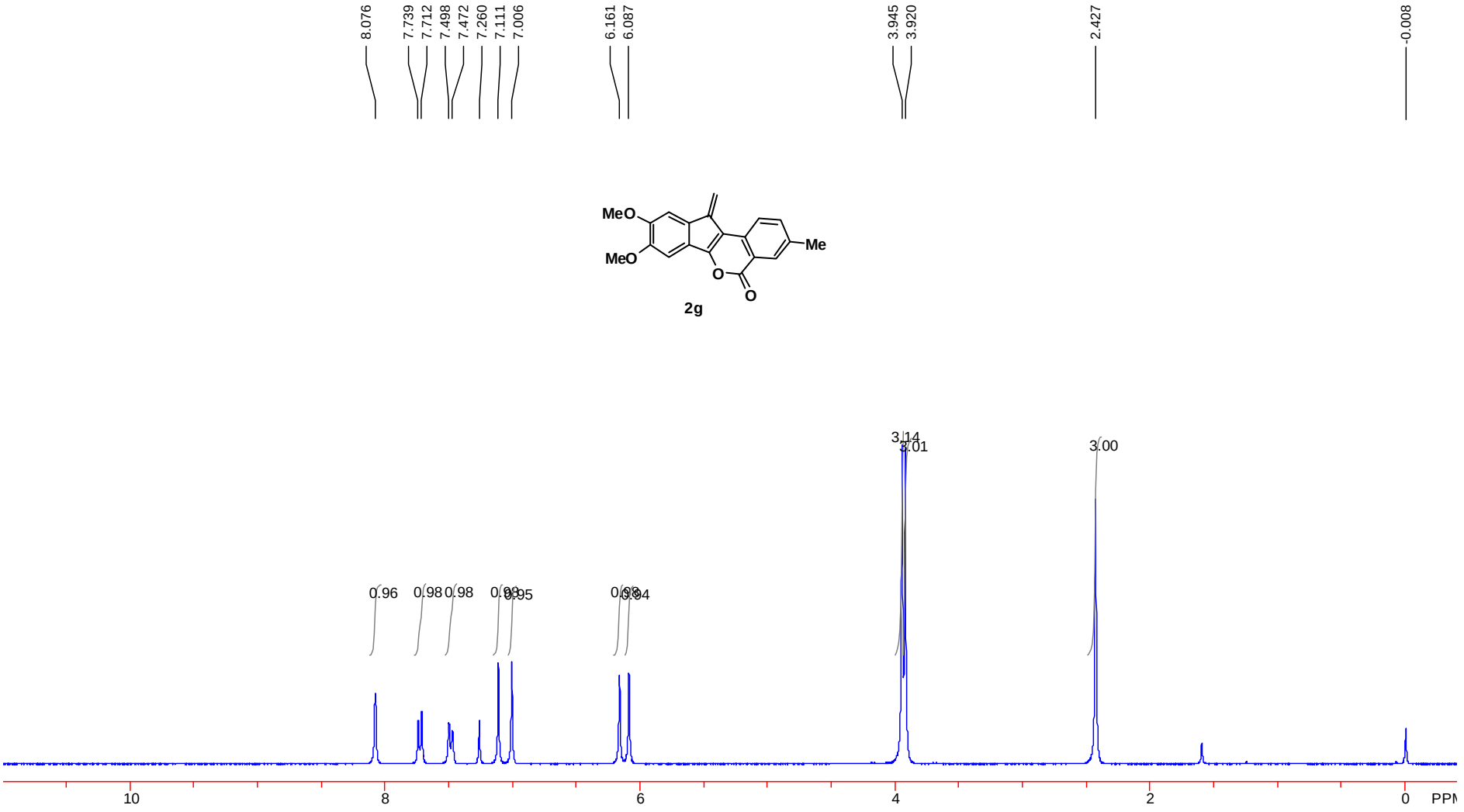

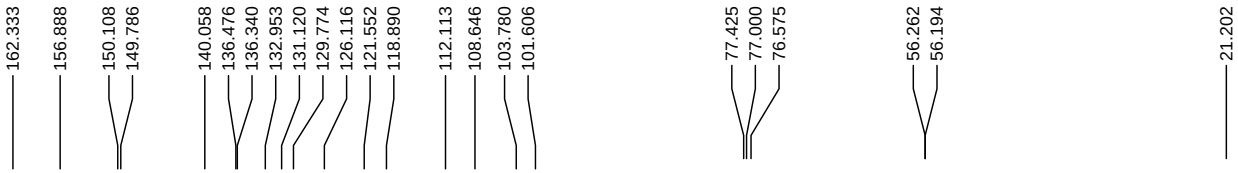

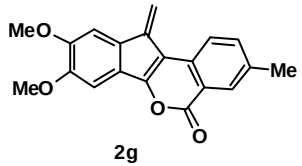

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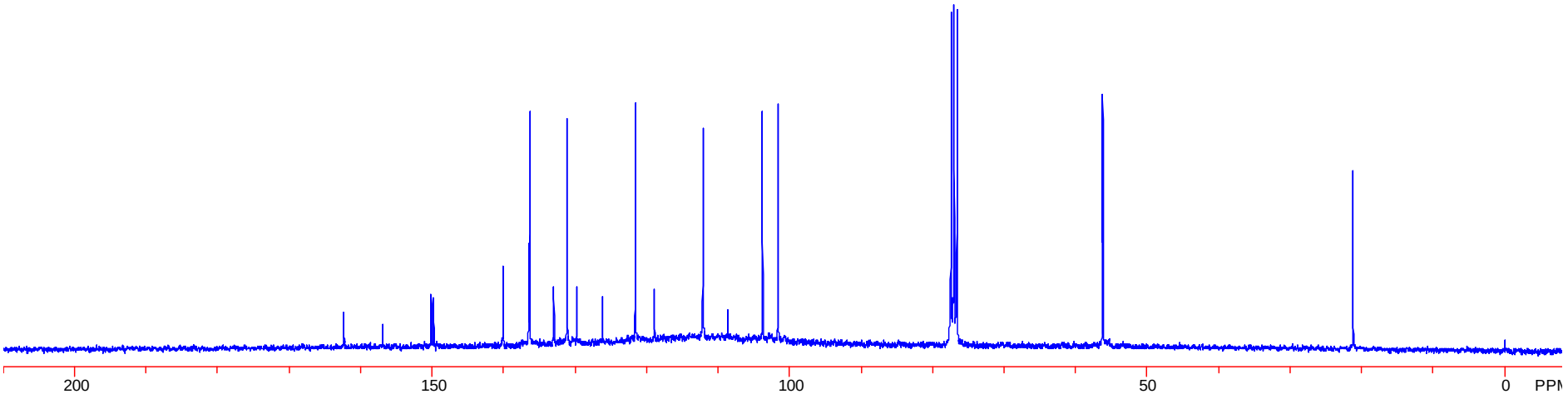

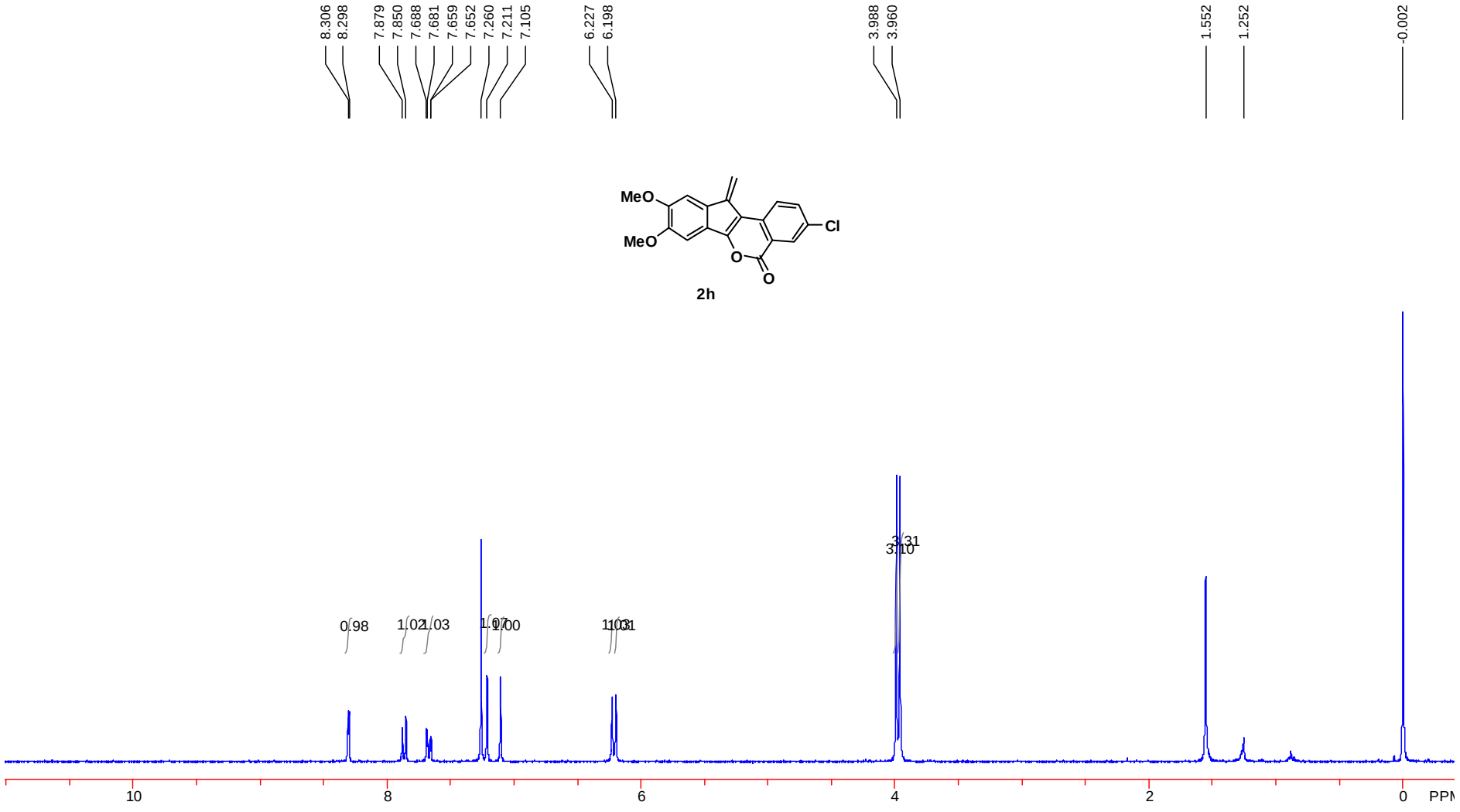

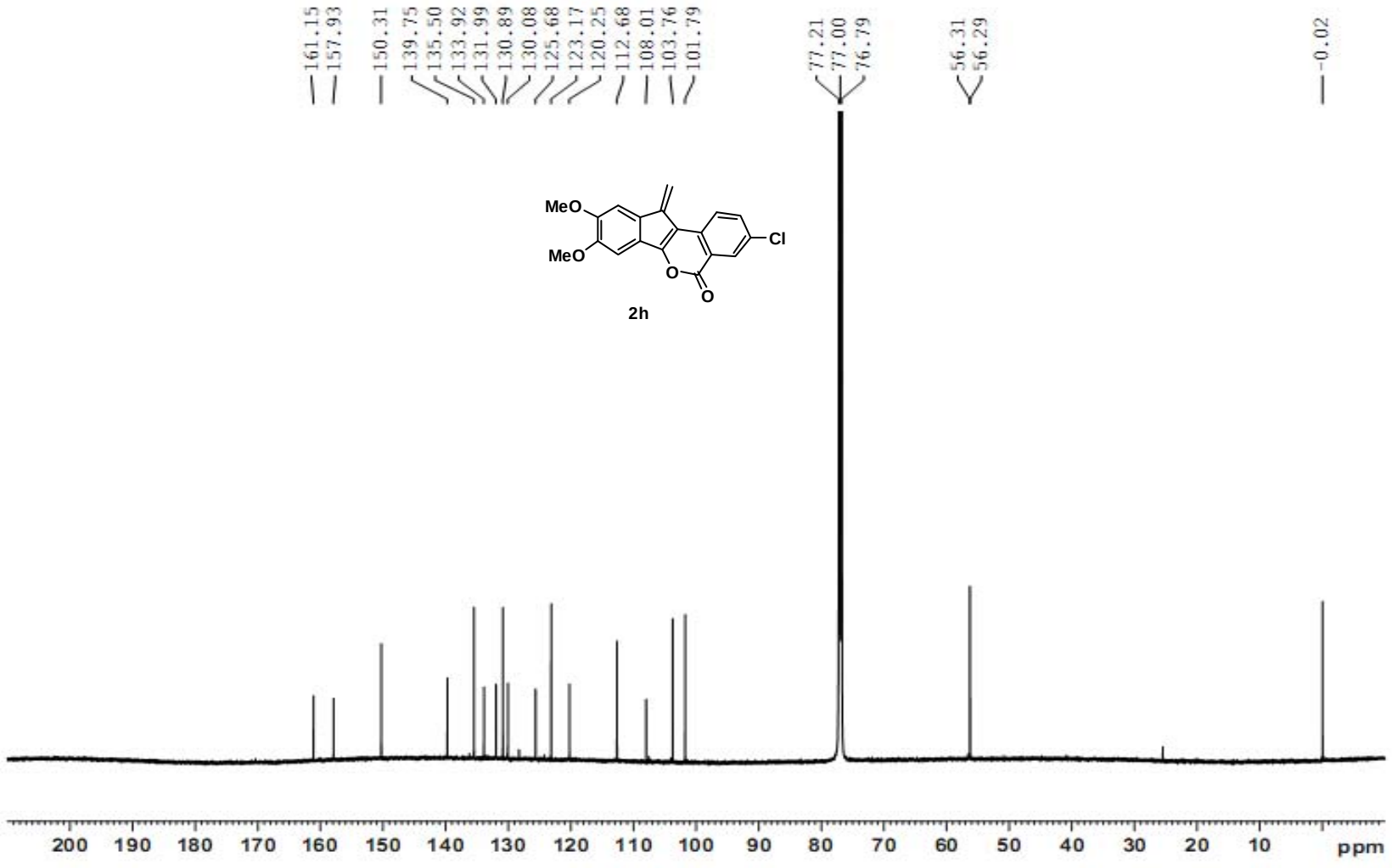

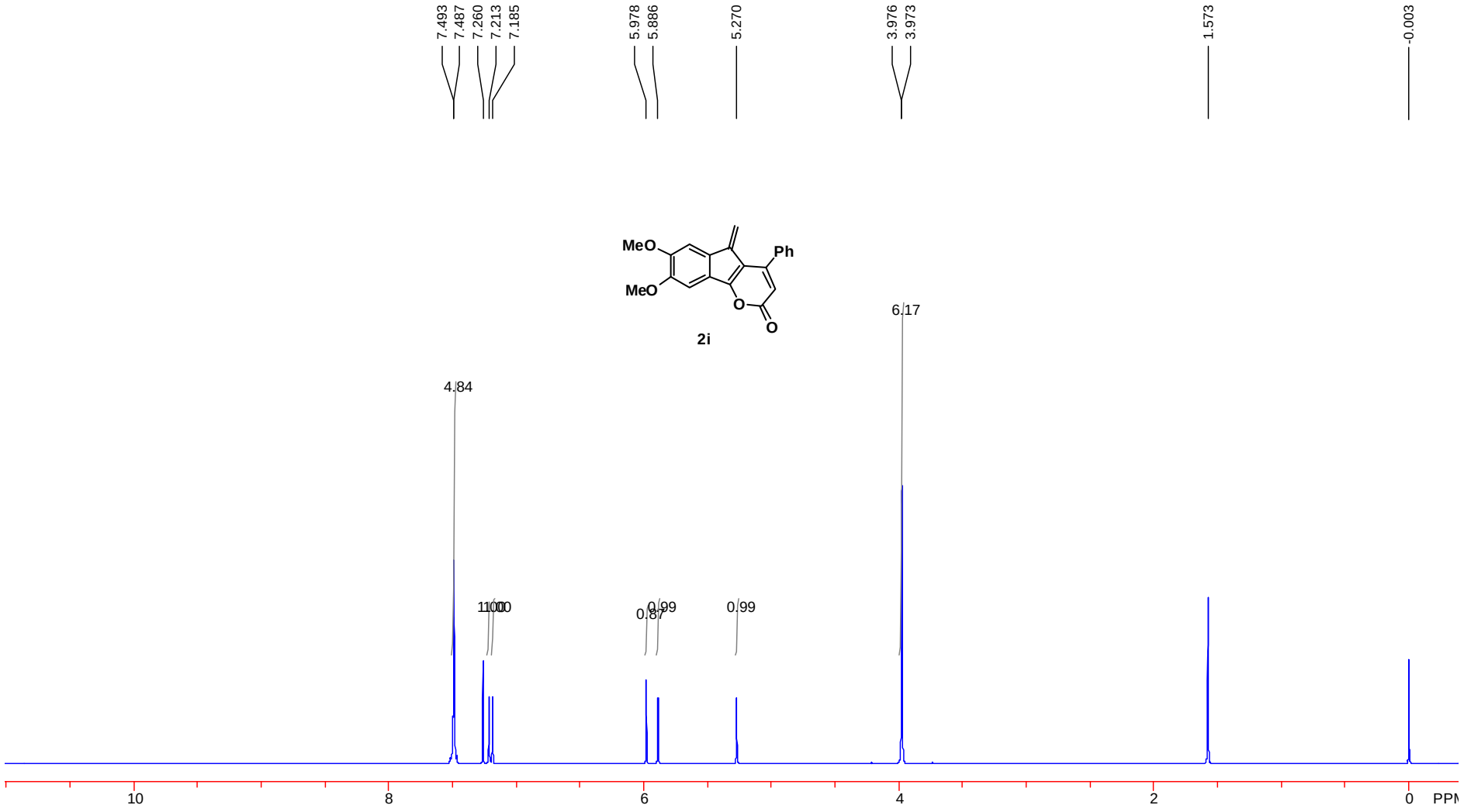

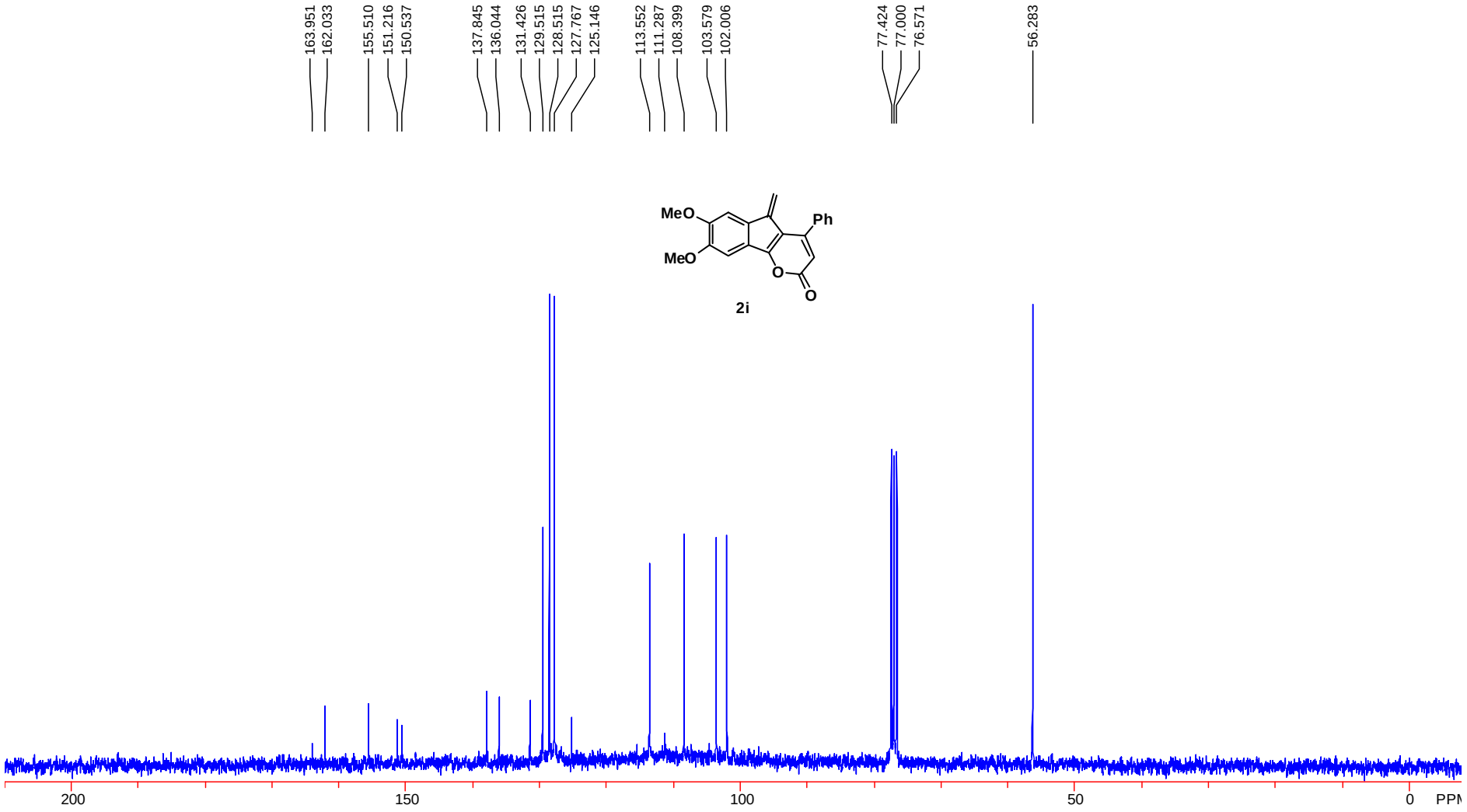

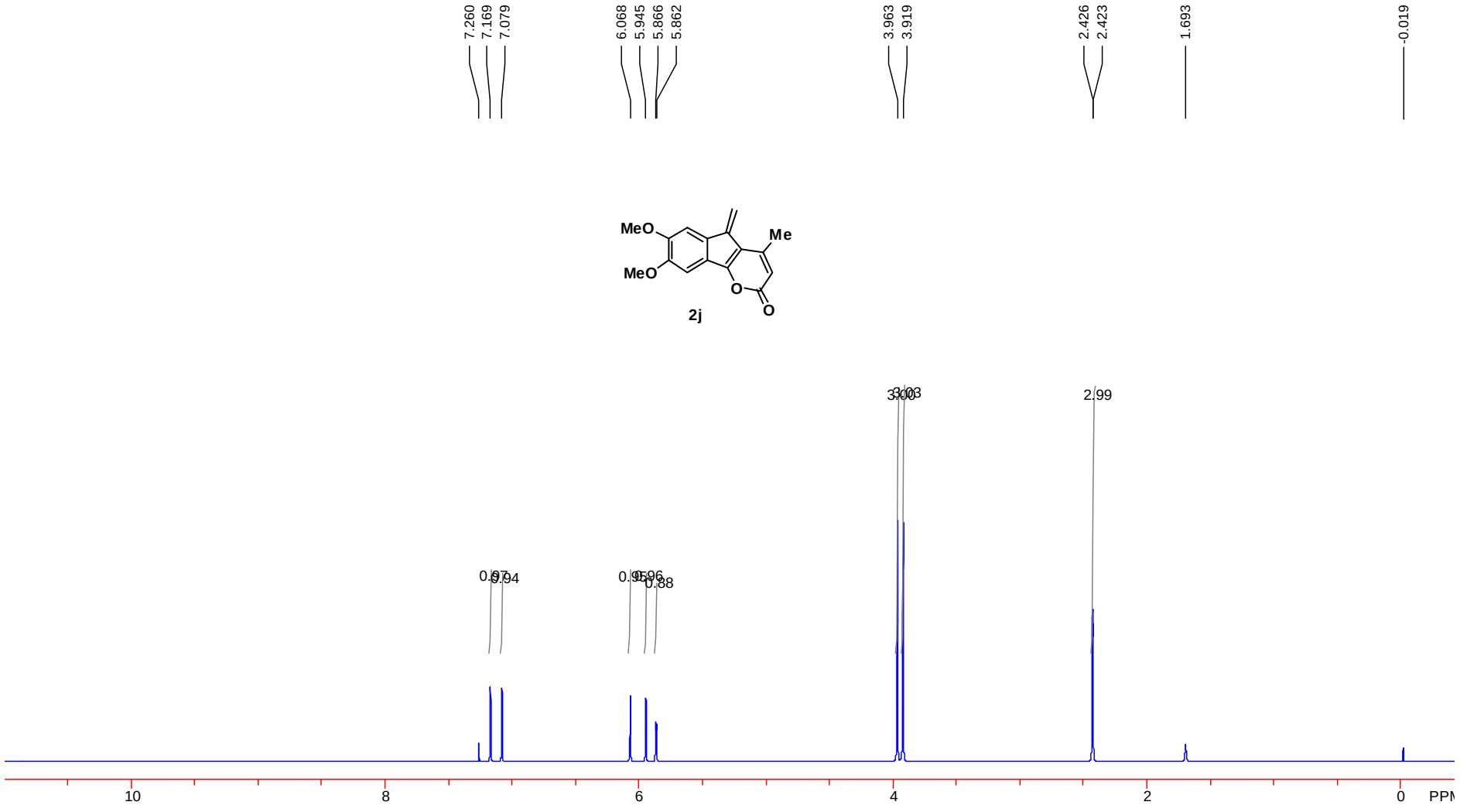
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MeO
Me
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O
2j
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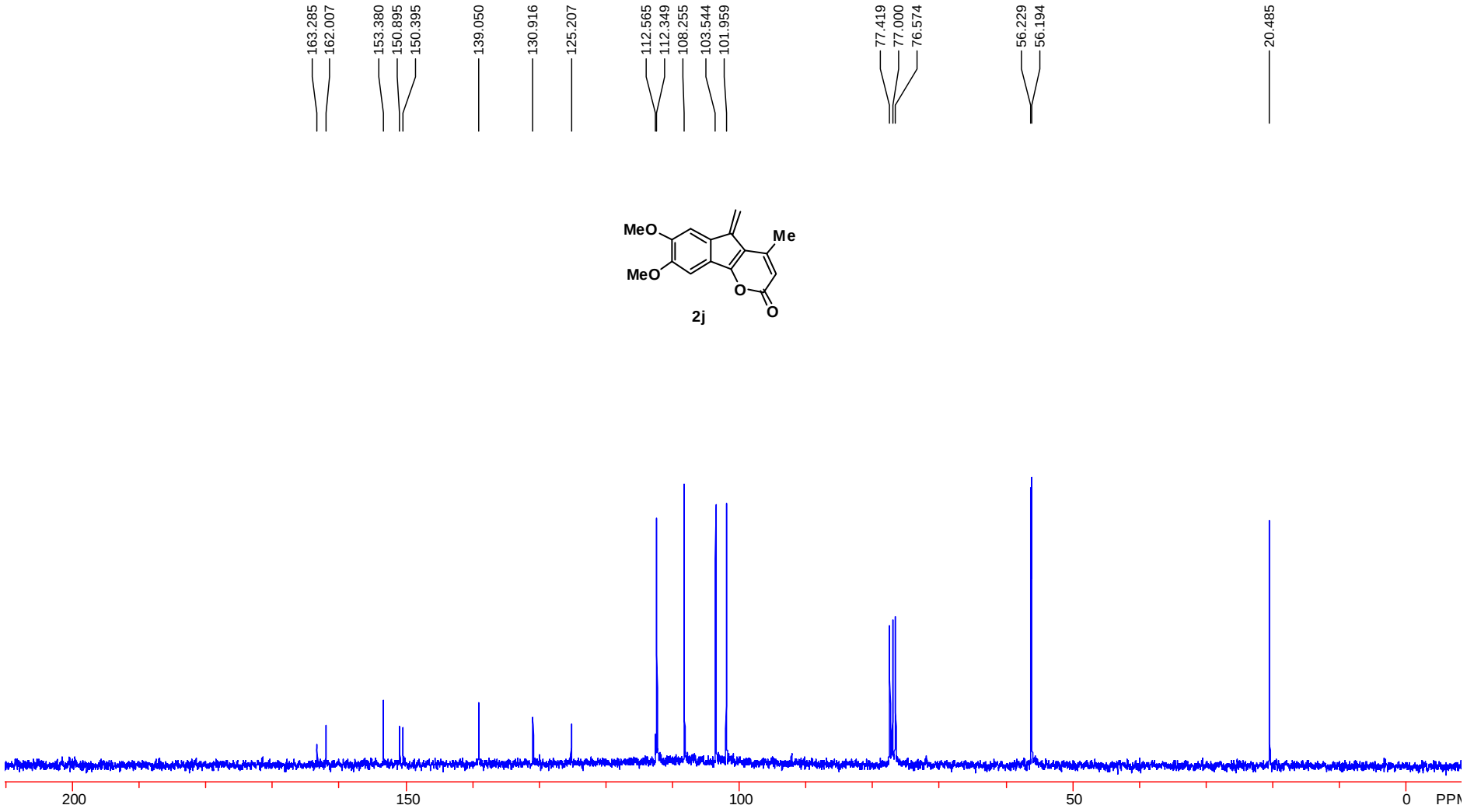
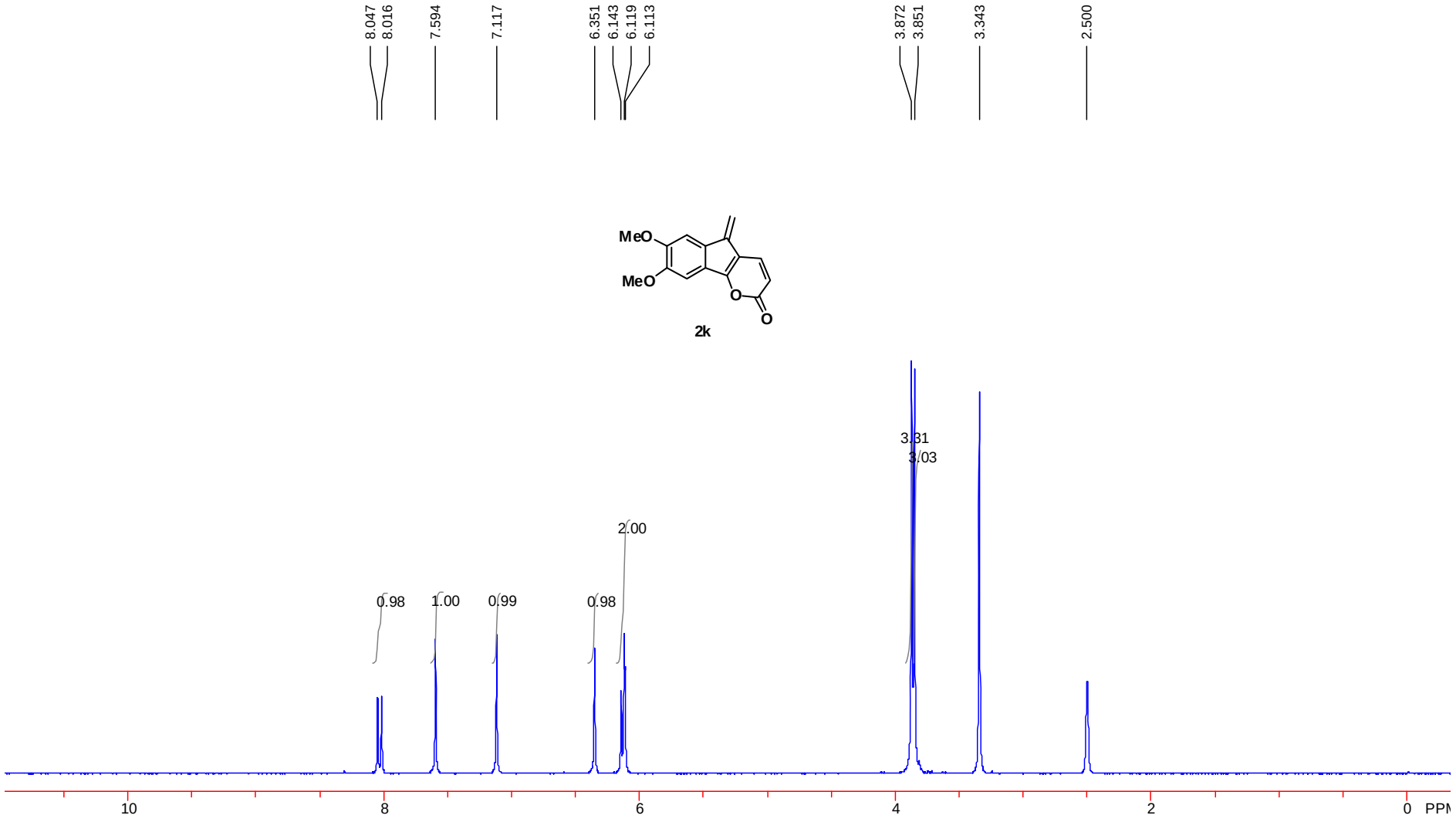
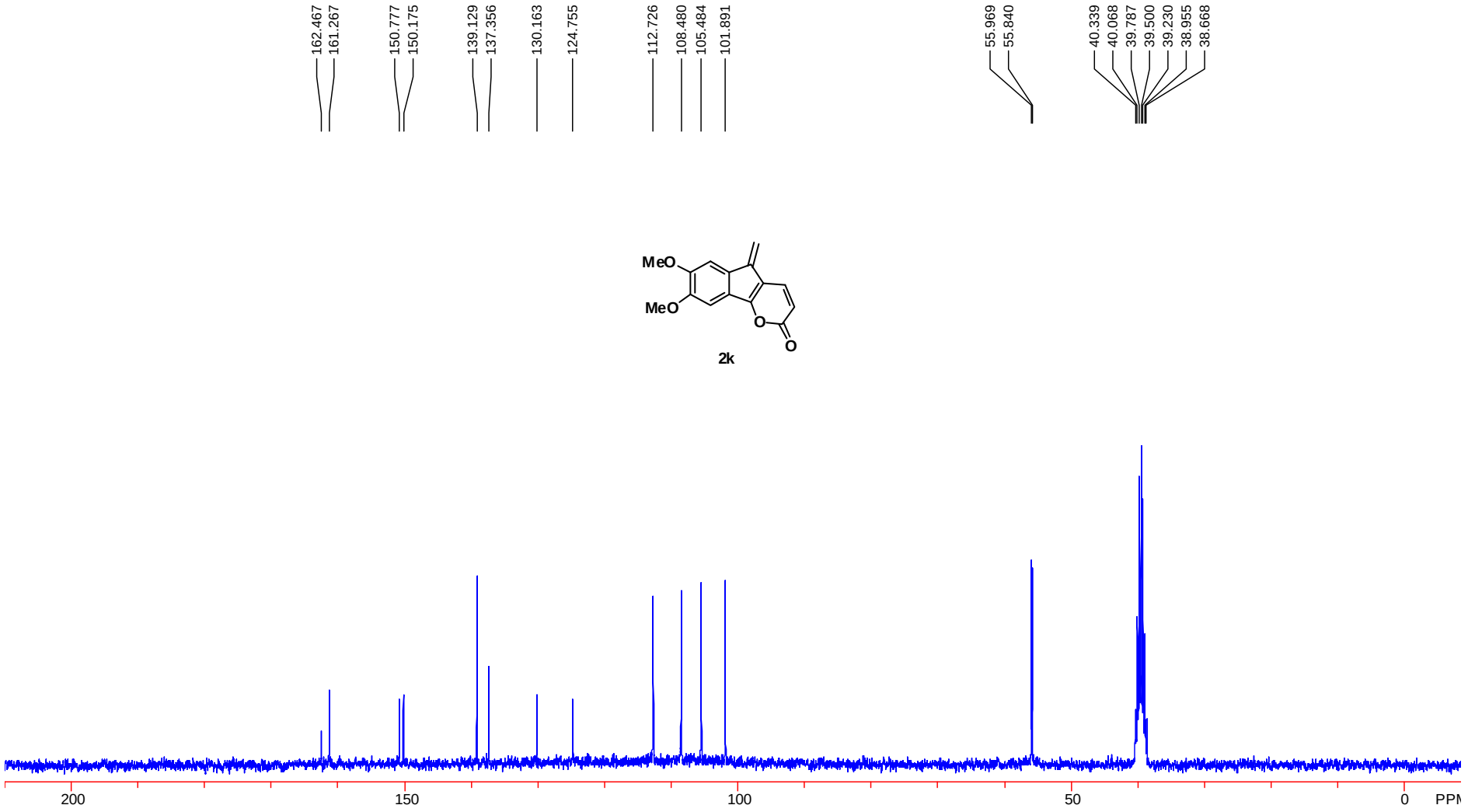
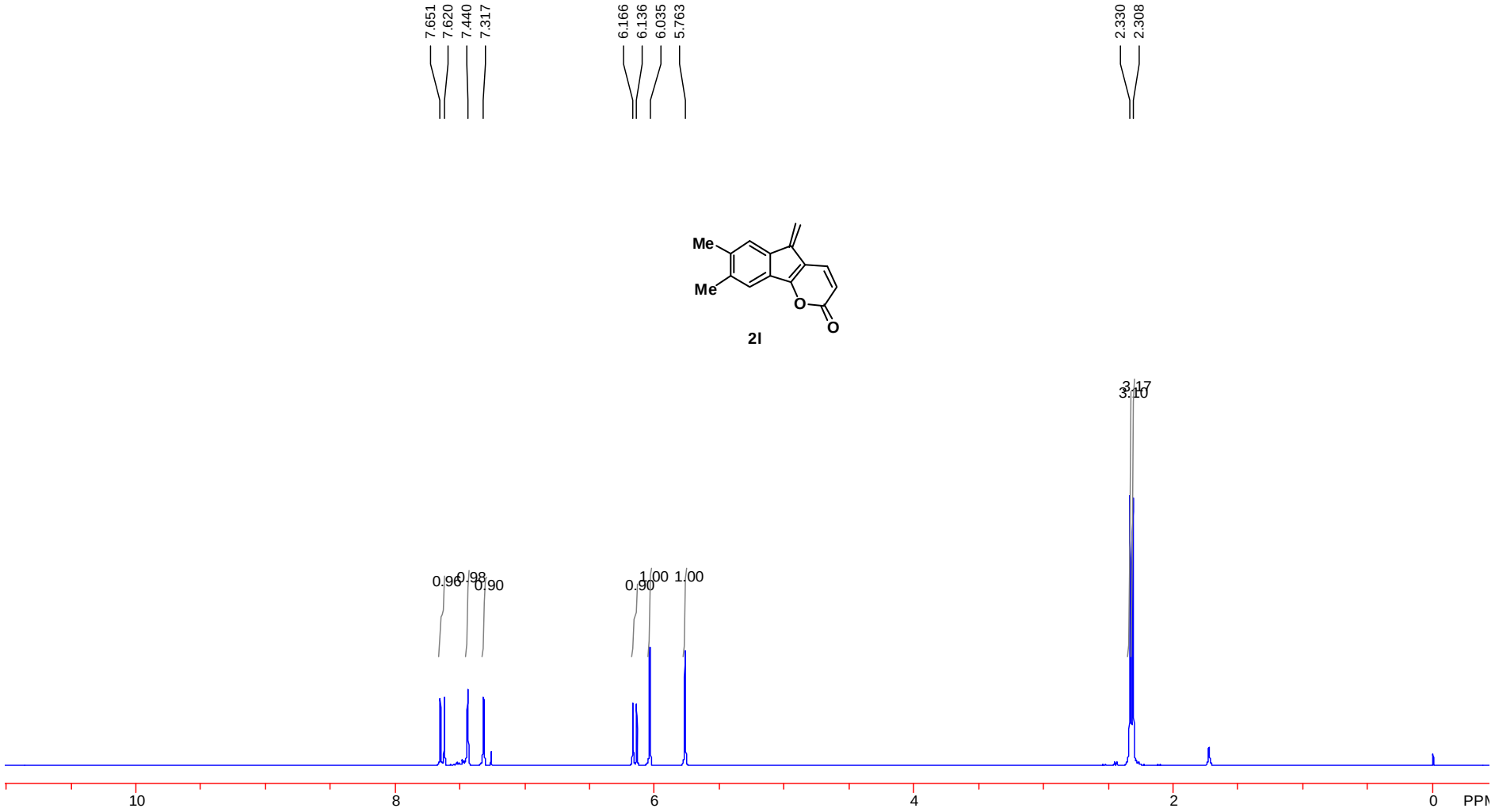
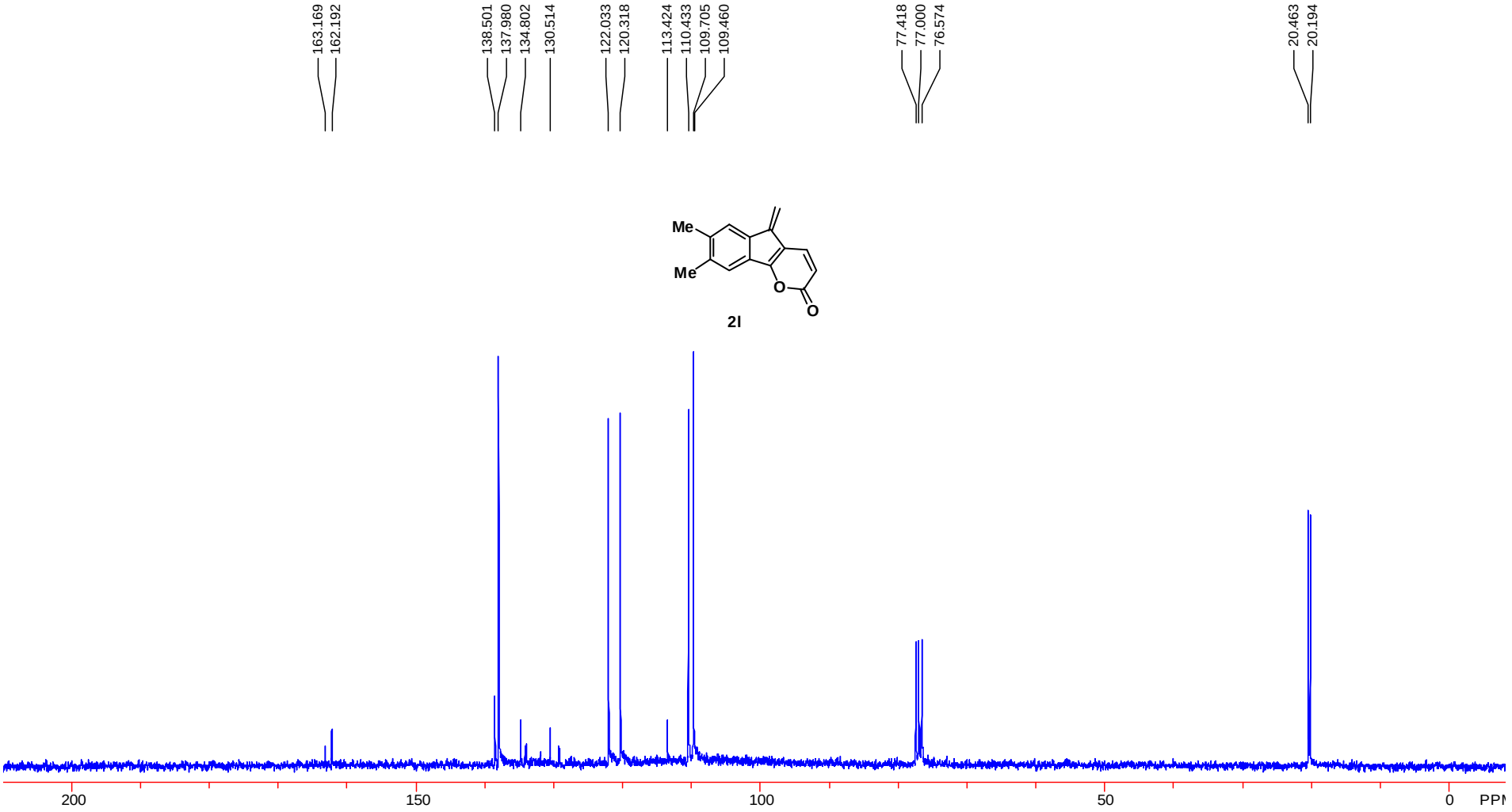
PPM











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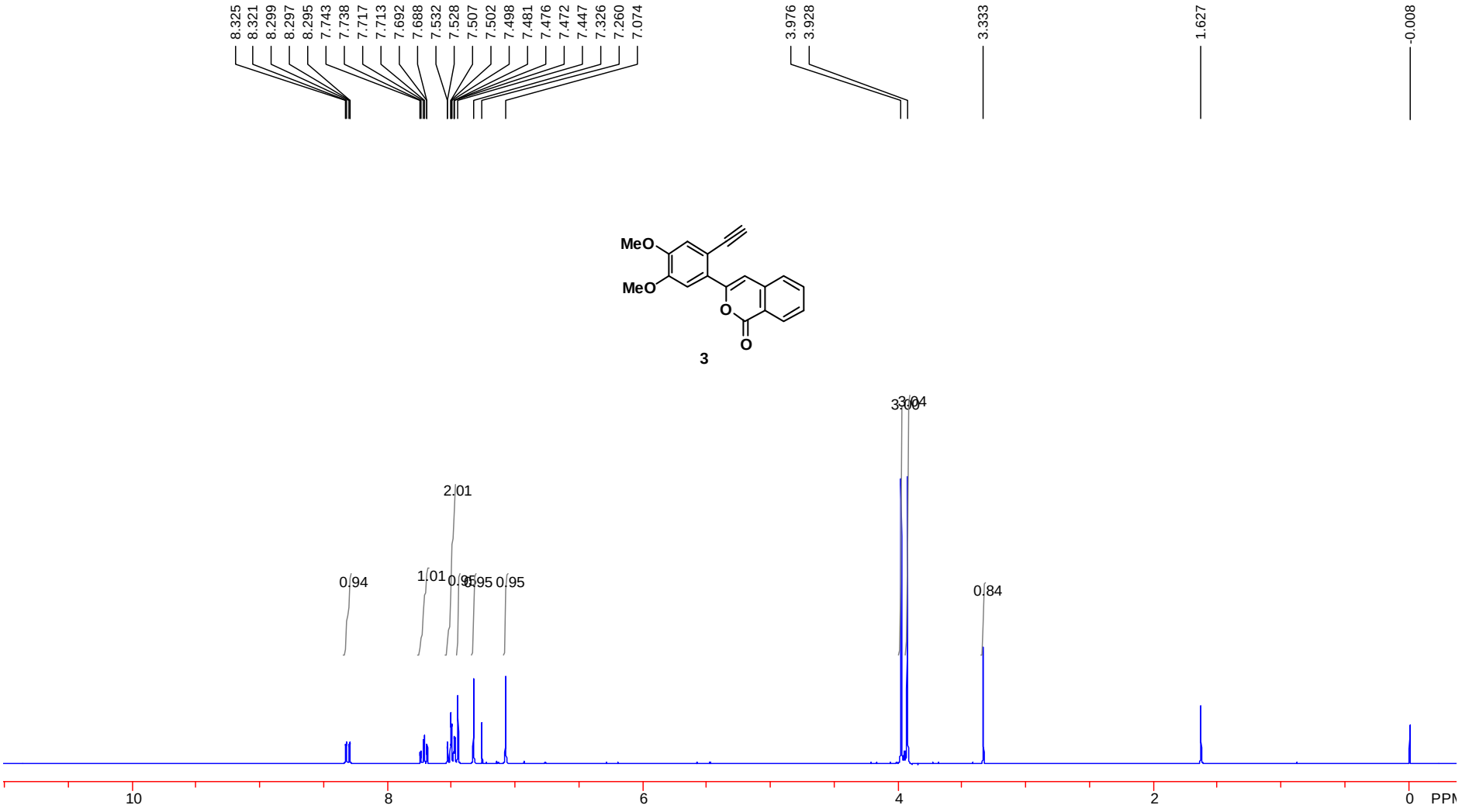

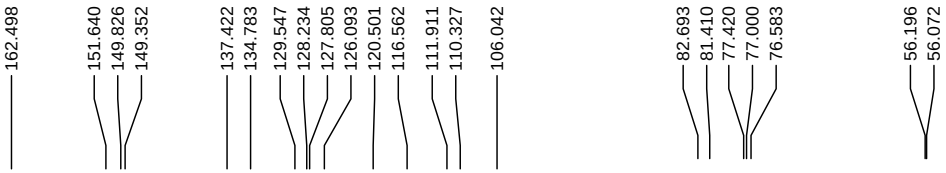

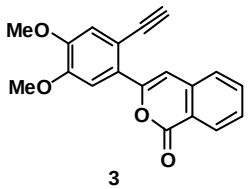

3