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Supporting Information

An Atom-Economical and Stereoselective Domino Synthesis of Functionalised Dienes

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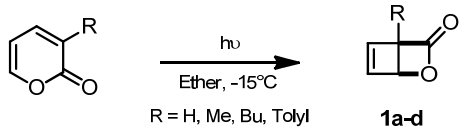
General Methods: All glassware was oven dried at 80 ºC before use and all reactions were performed under an atmosphere of argon unless otherwise stated. All solvents were distilled from appropriate drying agents prior to use. All reagents were used as received from commercial suppliers unless otherwise stated. Neat infra-red spectra were recorded using a Perkin-Elmer Spectrum 100 FT-FTIR spectrometer. Wavelengths (ν) are reported in cm^{-1}. Mass spectra were obtained using a Finnigan MAT 8200 or (70 eV) or an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI). Accurate mass determinations were obtained on a Brucker APEX III FT-MS (7 T magnet). All ^{1}H-NMR and ^{13}C-NMR experiments were recorded using Bruker DPX-300, AV-400, AV-500 and AV-600 spectrometers at 300 K. Chemical shifts (δ) are quoted in ppm and coupling constants (*J*) are quoted in Hz. The 7.27, 7.23, 5.99 and 2.05 ppm resonance of residual $CDCl_3$, $CDCl_2CHCl_2$, C_6D_5H and CD_3COCD_2H for proton spectra and 128.0, 77.16, 73.8 and 29.84 ppm resonance of C_6D_6, $CDCl_3$, $CDCl_2CDCl_2$, and CD_3COCD_3 for carbon spectra were used as internal references. Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminium plates coated with keiselgel F_{254} with 0.2 mm thickness. Visualisation was achieved by a combination of ultraviolet light (254 nm) and acidic potassium permanganate or anisaldehyde. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck and co.).

Microwave reactions were performed using a Discover SP CEM microwave.

All the reactions were performed using a stock ethereal solution of bicyclic lactone **1** prepared according to the literature in a concentration typically ranging from 0.15M to 0.25M. No significant change in yields depending on the concentration of **1** was noted in the reactions reported on this study (provided that the concentration is in the range 0.15-0.25M).

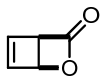
1. General procedure for lactone preparation:



2-pyrone (500 mg, 5.2 mmol) was dissolved in degassed Et_2O (150 mL) and the resulting solution was irradiated at – 10 ºC using a water-cooled mercury arc lamp (Hanovia, 450 W) with a quartz filter. The reaction progress was followed by ^{1}H-NMR and usually 24 to 36h was required to reach completion. After warming to room temperature, the solution was concentrated under vacuum in a cold bath to reach a volume of 5-10 mL and the concentration of **1** was repeatedly assayed by ^{1}H-NMR. Solutions of **1** were stored at 4 ºC and did not show any signs of decomposition after several weeks.

The synthesis of 3-substituted-2-pyrone was performed in accordance to the reported literature.[1]

2-oxabicyclo[2.2.0]hex-5-en-3-one (1a)

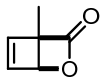


1a

Data of the ^{1}H-NMR spectra of **1a** matches those reported in the literature.[2] ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.73 (app. t, *J* 3.5, 1H), 6.54 (app. t, *J* 1.9, 1H), 5.29 (dd, *J* 4.5, 1.9, 1H), 4.39 (s, 1H).

[1] F. Frebault, M. T. Oliveira, E. Wostefeld, N. Maulide *J. Org. Chem.* **2010**, *75*, 7962-7965.
[2] E. J. Corey; J. Streith *J. Am. Chem. Soc.* **1964**, *86*, 950.

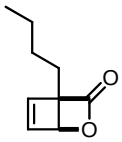
4-methyl-2-oxabicyclo[2.2.0]hex-5-en-3-one (1b)



1b

Data of the ^{1}H-NMR spectra of **1b** matches those reported in the literature.[3] ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.73 (dd, *J* 4.5, 2.5, 1H), 6.55 (d, *J* 2.5, 1H), 5.15 (d, *J* 4.5, 1H), 1.45 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.9, 145.9, 139.9, 76.0, 66.7, 11.4.

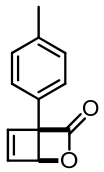
4-butyl-2-oxabicyclo[2.2.0]hex-5-en-3-one (1c)



1c

Compound **1c** was obtained as a yellow solution in diethyl ether in quantitative yield according to the general procedure. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 4.4, *J* = 2.4, 1H), 6.51 (d, *J* = 2.4, 1H), 5.13 (d, *J* = 4.4, 1H), 1.88-1.81 (m, 2H), 1.45-1.33 (m, 4H), 0.91 (t, *J* 7.1, 3H).

4-(p-tolyl)-2-oxabicyclo[2.2.0]hex-5-en-3-one (1d)



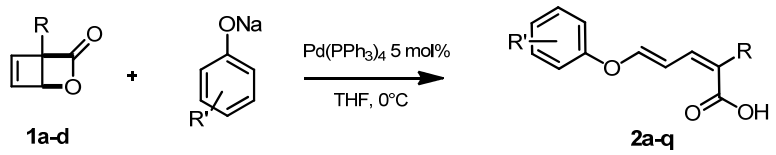
1d

Compound **1d** was obtained as a yellow solution in diethylether in quantitative yield according to the general procedure. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.22 (m, 4H), 6.97 (dd, *J*

[3] M. Luparia, M. T. Oliveira, D. Audisio, F. Frébault, R. Goddard, N. Maulide *Angew. Chem. Int. Ed.* **2011**, *50*, 12631-12635.

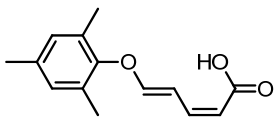
4.2, 2.7, 1H), 6.76 (d, *J* 2.7, 1H), 5.33 (d, *J* 4.2, 1H), 2.36 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.0, 144.8, 141.5, 138.6, 129.9 (2C), 128.2, 126.6 (2C), 73.2, 21.4; FTIR (neat) ν_{max} 3030, 1810, 830; HRMS (ESI) exact mass calculated for [M] ($C_{12}H_{10}O_2$) requires *m/z* 186.0679, found *m/z* 186.0681.

2. Preparation of (*E*,*Z*)-5-aryloxy-dienes:



To a stirred suspension of sodium hydride (60% in mineral oil, 6.5 mg, 0.16 mmol, 1.0 equiv) in THF (1.0 mL) was added dropwise a solution of the desired substituted phenol (0.17 mmol, 1.1 equiv) in THF (0.2 mL) at room temperature. In a schlenk flask, $Pd(PPh_3)_4$ (9.0 mg, 8 μmol, 5 mol%) was evacuated/backfilled with Ar three times and dissolved in THF (2.0 mL). The phenolate sodium salt solution was added to the solution of $Pd(PPh_3)_4$ and the mixture was cooled to 0 °C. After 5 min, an etheral solution of lactone (0.20 M in Et_2O, 0.8 mL, 0.16 mmol, 1.0 eq) was added dropwise and the mixture was stirred at 0 °C for 3 hours. The solution was quenched with H_2O (2 mL) and Et_2O (2 mL) was added to the mixture. The organic phase was extracted three times with saturated $NaHCO_3$. The combined aqueous phases were then acidified using 1M HCl and extracted three times with EtOAc. The combined organic phases were washed with brine, dried over $MgSO_4$ and the solvent was removed under vacuum to give the corresponding diene **2**.

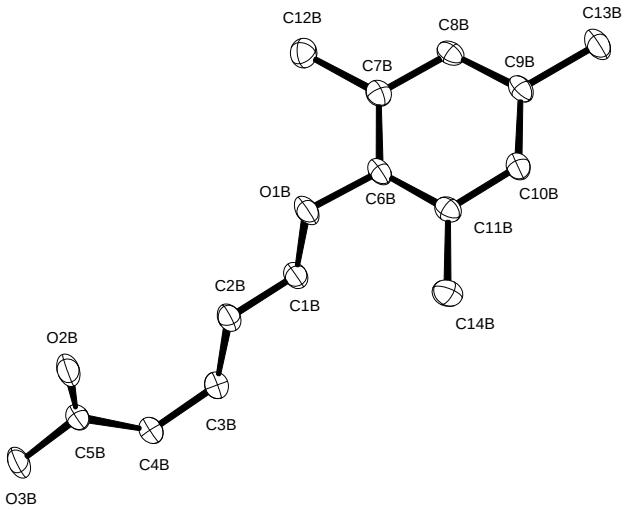
(2*Z*,4*E*)-5-(mesityloxy)penta-2,4-dienoic acid (2a)



2a

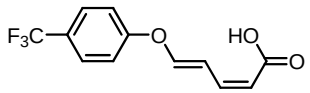
Compound **2a** was obtained as colourless crystals in 98% yield according to the general procedure. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.13 (d, *J* = 12.4, 1H), 6.86 (s, 2H), 6.83 (app.

t, J = 11.6, 1H), 6.88 (app. t, J = 11.6, 1H), 5.43 (d, J = 11.6, 1H), 2.20 (s, 3H), 2.01 (s, 6H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 168.1, 158.2, 150.6, 143.4, 135.6, 130.3 (2C), 130.2, 113.4, 107.1 (2C), 20.8, 16.1 (2C); FTIR (neat) ν_{max} 2923, 1684, 1621, 1592, 1445, 1193, 1162, 937, 823; HRMS (ESI) exact mass calculated for $[M-H]^-$ ($C_{14}H_{15}O_3$) requires *m/z* 231.1025, found *m/z* 231.1027. The structure of compound (*Z,E*)-**2a** was confirmed through single-crystal X-ray analysis (see below).



Crystal structure analysis of compound (*Z,E*)-**2a** crystallized from acetone (CCDC 878396)

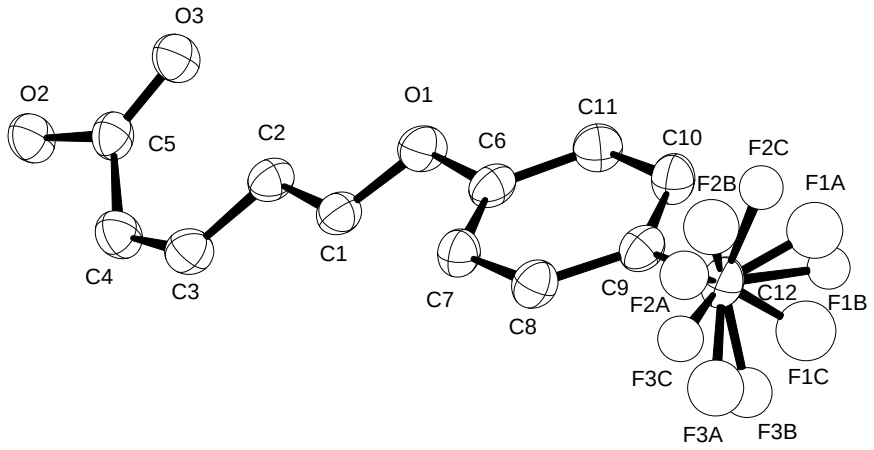
(2*Z*,4*E*)-5-(4-(trifluoromethyl)phenoxy)penta-2,4-dienoic acid (2b)



2b

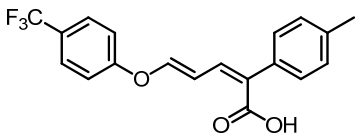
Compound **2b** was obtained as colourless crystals in 98% yield according to the general procedure. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.76 (d, J = 8.4, 2H), 7.54 (d, J = 11.9, 1H), 7.43 (app. t, J = 11.9, 1H), 7.36 (d, J = 8.4, 2H), 6.82 (app. t, J = 11.3, 1H), 5.66 (d, J = 11.3, 1H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 167.8, 159.8, 153.2, 141.8, 128.2 (q, J_{C-F} 4, 2C), 126.1 (q, J_{C-F} 33), 125.1 (q, J_{C-F} 270), 118.1 (2C), 116.3, 112.2; ^{19}F-NMR (376 MHz, CD_3COCD_3) δ -62.3; FTIR (neat) ν_{max} 2924, 1689, 1599, 1453, 1209, 1129, 1107, 1062, 927, 822; HRMS (ESI) exact mass calculated for $[M-H]^-$ ($C_{12}H_8O_3F_3$) requires *m/z* 257.0429,

found *m/z* 257.0431. The structure of compound (*Z,E*)-**2b** was confirmed through single-crystal X-ray analysis (see below).



Crystal structure analysis of compound (*Z,E*)-**2b** crystallized from acetone (disordered CF_3 group) (CDCC 878394)

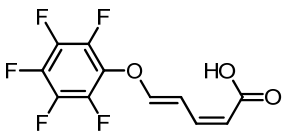
(2*Z*,4*E*)-2-(*p*-tolyl)-5-(4-(trifluoromethyl)phenoxy)penta-2,4-dienoic acid (2c)



2c

Compound **2c** was obtained as a yellow oil in 81% yield according to the general procedure. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.77 (d, J = 8.8, 2H), 7.55 (d, J = 11.8, 1H), 7.36 (d, J = 8.8, 2H), 7.33 (d, J = 8.1, 2H), 7.17 (d, J = 8.1, 2H), 7.02 (app. t, J = 11.8, 1H), 6.91 (d, J = 11.8, 1H), 2.32 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 168.9, 160.2, 151.3, 137.8, 136.6, 133.5, 132.3, 129.6 (2C), 128.4 (2C), 128.2 (q, $J_{C\text{-}F}$ 4, 2C), 125.8 (q, $J_{C\text{-}F}$ 33), 125.3 (q, $J_{C\text{-}F}$ 271), 117.9 (2C), 113.6, 21.1; ^{19}F-NMR (375 MHz, CD_3COCD_3) δ = -61.7; FTIR (neat) ν_{max} 2925, 1684, 1606, 1321, 1235, 1158, 1103, 1064, 839, 821; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{19}H_{15}F_3O_3Na$) requires *m/z* 371.0870, found *m/z* 371.0866.

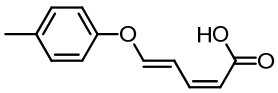
(2*Z*,4*E*)-5-(perfluorophenoxy)penta-2,4-dienoic acid (2d)



2d

Compound **2d** was obtained as a yellow oil in 51% yield according to the general procedure. ^{1}H-NMR (300 MHz, CD_3COCD_3); δ 7.39 (d, J = 12.3, 1H), 7.30 (app. t, J = 11.6, 1H), 6.77 (app. t, J = 11.3, 1H), 5.67 (d, J = 11.3, 1H); ^{13}C-NMR (75 MHz, CD_3COCD_3) δ 167.6, 155.7, 140.4, 117.4, 110.2; (C^{IV} from pentafluoro phenol not detected by ^{13}C-NMR); ^{19}F-NMR (375 MHz, CD_3COCD_3) δ -157.5 (2F), -162.3, -164.6 (2F); FTIR (neat) ν_{max} 2927, 1628, 1599, 1512, 1223, 1171, 1106, 997, 978, 927; HRMS (ESI) exact mass calculated for $[M-H]^-$ ($C_{11}H_4F_5O_3$) requires *m/z* 279.0083, found *m/z* 279.0086.

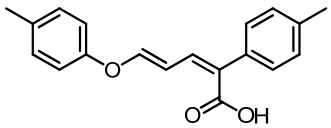
(2*Z*,4*E*)-5-(*p*-tolyloxy)penta-2,4-dienoic acid (2e)



2e

Compound **2e** was obtained as colourless crystals in 88% yield according to the general procedure. ^{1}H-NMR: (500 MHz, CD_3COCD_3) δ 7.37 (d, J = 11.9, 1H), 7.28 (dd, J = 11.9, J = 11.5, 1H), 7.20 (d, J = 8.3, 2H), 7.02 (d, J =8.3, 2H), 6.78 (dd, J = 11.9, J = 11.5, 1H), 5.57 (d, J = 11.5, 1H), 2.30 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 168.1, 155.7, 155.2, 142.8, 134.3, 131.1 (2C), 117.9 (2C), 114.6, 110.2, 20.5; FTIR (neat) ν_{max} 3028, 2925, 2569, 1677, 1630, 1591, 1501, 1443, 1206, 930; HRMS (ESI) exact mass calculated for $[M-H]^-$ ($C_{12}H_{11}O_3$) requires *m/z* 203.0715, found *m/z* 203.0714.

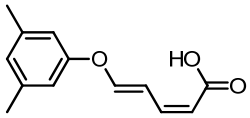
(2*Z*,4*E*)-2-(*p*-tolyl)-5-(*p*-tolyloxy)penta-2,4-dienoic acid (2g)



2g

Compound **2g** was obtained as a yellow oil in 49% yield according to the general procedure. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.39 (d, J = 11.6, 1H), 7.32 (d, J = 8.0, 2H), 7.20 (d, J = 8.4, 2H), 7.15 (d, J = 8.0, 2H), 7.03 (d, J = 8.4, 2H), 6.95-6.86 (m, 2H), 2.31 (s, 3H), 2.30 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 169.0, 155.4, 153.7, 137.5, 137.1, 135.2, 134.1, 131.1 (2C), 130.4, 129.5 (2C), 128.4 (2C), 117.7 (2C), 111.6, 21.1, 20.6; FTIR (neat) ν_{max} 2923, 1765, 1698, 1512, 1220, 819;HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{19}H_{18}O_3Na$) requires *m/z* 317.1149, found *m/z* 317.1148.

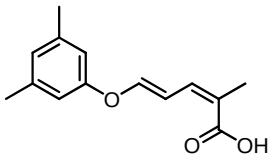
(2*Z*,4*E*)-5-(3,5-dimethylphenoxy)penta-2,4-dienoic acid (2h)



2h

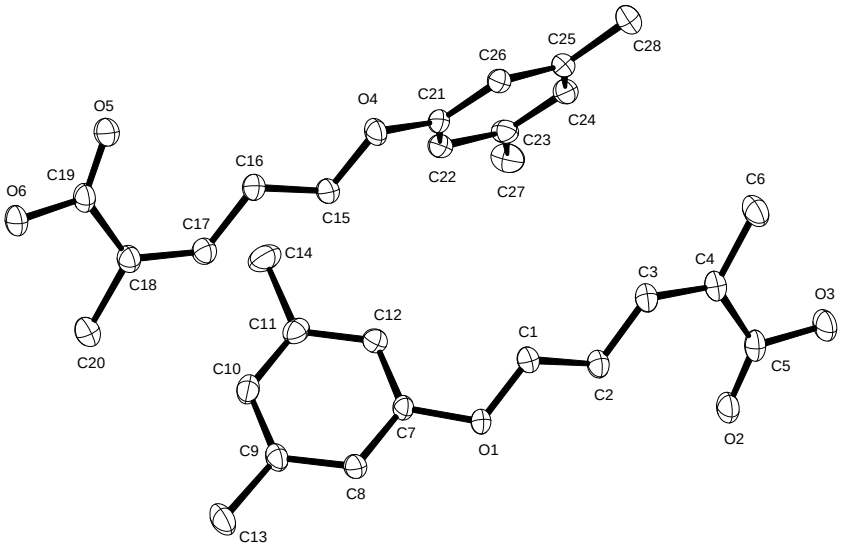
Compound **2h** was obtained as colourless crystals in 89% yield according to the general procedure. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.39 (d, J = 12.0, 1H), 7.30 (app. td, J = 12.0, J = 1.0, 1H), 6.81-6.75 (m, 4H), 5.57 (d, J = 11.3, 1H), 2.29 (s, 6H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 168.1, 157.3, 155.4, 142.9, 140.5 (2C), 126.5, 115.5 (2C), 114.7, 110.5, 21.2 (2C); FTIR (neat) ν_{max} 3029, 2923, 1632, 1584, 1446, 1174, 932; HRMS (ESI) exact mass calculated for $[M]^+$ ($C_{13}H_{14}O_3$) requires *m/z* 218.0942, found *m/z* 218.0943.

(2*Z*,4*E*)-5-(3,5-dimethylphenoxy)-2-methylpenta-2,4-dienoic acid (2i)



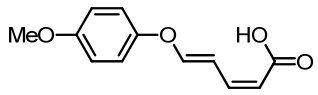
2i

Compound **2i** was obtained as colourless crystals in 97% yield according to the general procedure. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.22 (d, J = 12.1, 1H), 7.15 (app. t, J = 11.5, 1H), 6.78 (s, 1H), 6.72 (s, 2H), 6.72 (d, J = 11.5, 1H), 2.28 (s, 6H), 1.94 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 169.0, 157.6, 152.5, 140.5, 137.9, 126.1, 123.4, 115.3 (3C), 111.9, 21.3, 21.0 (2C); FTIR (neat) ν_{max} 2924, 2856, 1681, 1592, 1177, 947; HRMS (ESI) exact mass calculated for $[M]^+$ ($C_{14}H_{16}O_3$) requires *m/z* 232.1097, found *m/z* 232.1099. The structure of compound (*Z,E*)-**3i** was confirmed through single-crystal X-ray analysis (see below).



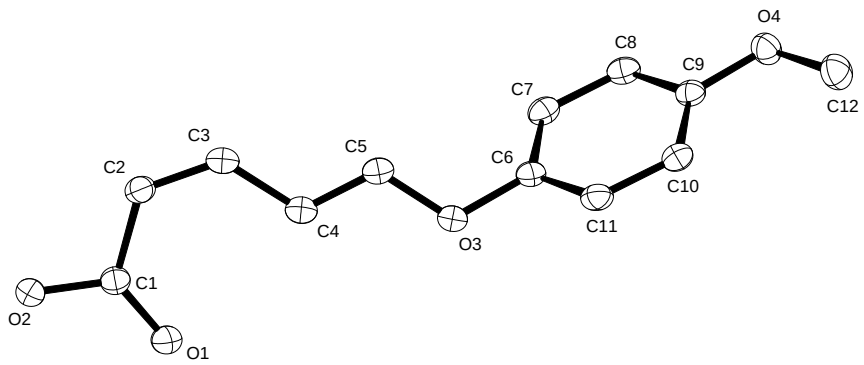
Crystal structure analysis of compound (*Z,E*)-**2i** crystallized from acetone (Cambridge Crystallographic Data Centre number: 878398).

(2*Z*,4*E*)-5-(4-methoxyphenoxy)penta-2,4-dienoic acid (2j)



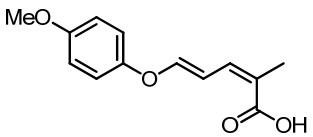
2j

Compound **2j** was obtained as colourless crystals in 64% yield according to the general procedure. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.32 (d, J = 12.2, 1H), 7.24 (dd, J = 12.2, J = 11.5, 1H), 7.07 (d, J = 9.1, 2H), 6.95 (d, J = 9.1, 2H), 6.76 (dd, J = 12.2, J = 11.5, 1H), 5.55 (d, J = 11.5, 1H), 3.78 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 168.1, 156.6 (2C), 142.8 (2C), 119.4 (2C), 115.9 (2C), 114.6, 109.9, 56.0; FTIR (neat) ν_{max} 2933, 2837, 1679, 1632, 1505, 1198, 1131, 930, 825; HRMS (ESI) exact mass calculated for $[M-H]^-$ ($C_{12}H_{11}O_4$) requires *m/z* 219.0664, found *m/z* 219.0663. The structure of compound (*Z,E*)-**2j** was confirmed through single-crystal X-ray analysis (see below).



Crystal structure analysis of compound (*Z,E*)-**2j** crystallized from acetone (Cambridge Crystallographic Data Centre number: 878394).

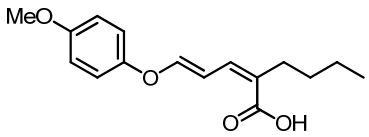
(2*Z*,4*E*)-5-(4-methoxyphenoxy)-2-methylpenta-2,4-dienoic acid (2k)



2k

Compound **2k** was obtained as colourless crystals in 71% yield according to the general procedure. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.18 (d, J = 12.1, 1H), 7.11 (app. t, J = 11.7, 1H), 7.07 (d, J = 9.1, 2H), 6.96 (d, J = 9.1, 2H), 6.61 (app. td, J = 11.7, J = 1.3, 1H), 3.80 (s, 3H), 1.96 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 168.8, 157.3, 153.8, 151.5, 138.2, 123.3, 119.3 (2C), 116.0 (2C), 111.3, 55.9, 21.0; FTIR (neat) ν_{max} 2957, 2931, 2836, 1671, 1627, 1505, 1214, 1176, 1103, 944; HRMS (ESI) exact mass calculated for $[M-H]^-$ ($C_{13}H_{13}O_4$) requires *m/z* 233.0820, found *m/z* 233.0819.

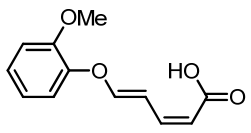
(*Z*)-2-((*E*)-3-(4-methoxyphenoxy)allylidene)hexanoic acid (2l)



2l

Compound **2l** was obtained as a yellow oil in 44% yield according to the general procedure. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.19 (d, J 12.1, 1H), 7.07-7.02 (m, 3H), 6.93 (d, J = 9.1, 2H), 6.56 (d, J = 11.5, 1H), 3.78 (s, 3H), 2.30 (t, J = 7.8, 2H), 1.49-1.43 (m, 2H), 1.37-1.29 (m, 2H), 0.91 (t, J = 7.1, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 168.9, 157.2, 153.8, 151.5, 138.4, 128.3, 119.3 (2C), 115.8 (2C), 111.4, 56.0, 35.2, 32.7, 23.1, 14.3; FTIR (neat) ν_{max} 2957, 2931, 2861, 1676, 1631, 1503, 1206, 1169, 1113, 1035, 952; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{16}H_{20}ONa$) requires *m/z* 299.1252, found *m/z* 299.1254.

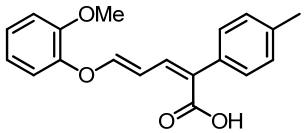
(2*Z*,4*E*)-5-(2-methoxyphenoxy)penta-2,4-dienoic acid (2m)



2m

Compound **2m** was obtained as yellow solid in 97% yield according to the general procedure. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.25 (d, J = 12.2, 1H), 7.21-7.19 (m, 2H), 7.13-7.10 (m, 2H), 6.96 (app. t, J = 7.7, 1H), 6.74 (app. t, J = 11.3, 1H), 5.53 (d, J = 11.3, 1H), 3.84 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 168.0, 157.6, 151.4, 146.0, 143.0, 126.4, 121.7, 120.4, 114.2, 114.0, 109.1, 56.1; FTIR (neat) ν_{max} 3036, 2924, 2573, 1691, 1633, 1590, 1497, 1199, 1179, 1103; HRMS (ESI) exact mass calculated for $[M-H]^-$ ($C_{12}H_{11}O_4$) requires *m/z* 219.0664, found *m/z* 219.0663.

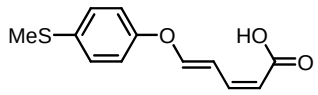
(2*Z*,4*E*)-5-(2-methoxyphenoxy)-2-(*p*-tolyl)penta-2,4-dienoic acid (2n)



2n

Compound **2n** was obtained as a yellow oil in 90% yield according to the general procedure. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.33-7.27 (m, 3H), 7.20-7.11 (m, 5H), 6.98 (ddd, J = 8.5, J = 6.7, J = 1.8, 1H), 6.85 (d, J = 4.9, 1H), 6.84 (d, J = 6.5, 1H) 3.86 (s, 3H), 2.33 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 168.9, 155.2, 151.1, 146.0, 137.1, 136.9, 135.0, 129.8, 129.2 (2C), 128.1 (2C), 125.8, 121.4, 119.7, 113.7, 110.2, 56.0, 20.8; FTIR (neat) ν_{max} 2923, 1678, 1627, 1583, 1499, 1257, 1212, 1137; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{19}H_{18}O_4Na$) requires *m/z* 333.1094, found *m/z* 333.1097.

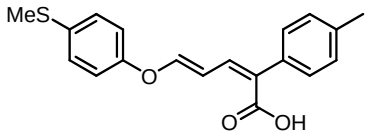
(2*Z*,4*E*)-5-(4-(methylthio)phenoxy)penta-2,4-dienoic acid (2o)



2o

Compound **2o** was obtained as a yellow solid in 67% yield according to the general procedure. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.36 (d, J = 12.5, 1H), 7.29-7.24 (m, 3H), 7.07 (d, J = 8.1, 2H), 6.74 (app. t, J = 11.4, 1H), 5.56 (d, J = 11.4, 1H), 2.44 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 167.9, 155.2, 142.6, 134.7, 129.3 (2C), 118.7 (3C), 115.1, 110.7, 16.4; FTIR (neat) ν_{max} 2916, 2573, 1627, 1490, 1213, 1137, 922; HRMS (ESI) exact mass calculated for $[M-H]^-$ ($C_{12}H_{11}O_3S$) requires *m/z* 235.0433, found *m/z* 235.0434.

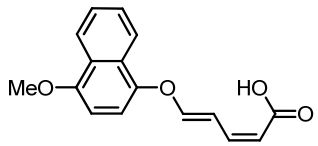
(2*Z*,4*E*)-5-(4-(methylthio)phenoxy)-2-(*p*-tolyl)penta-2,4-dienoic acid (2p)



2p

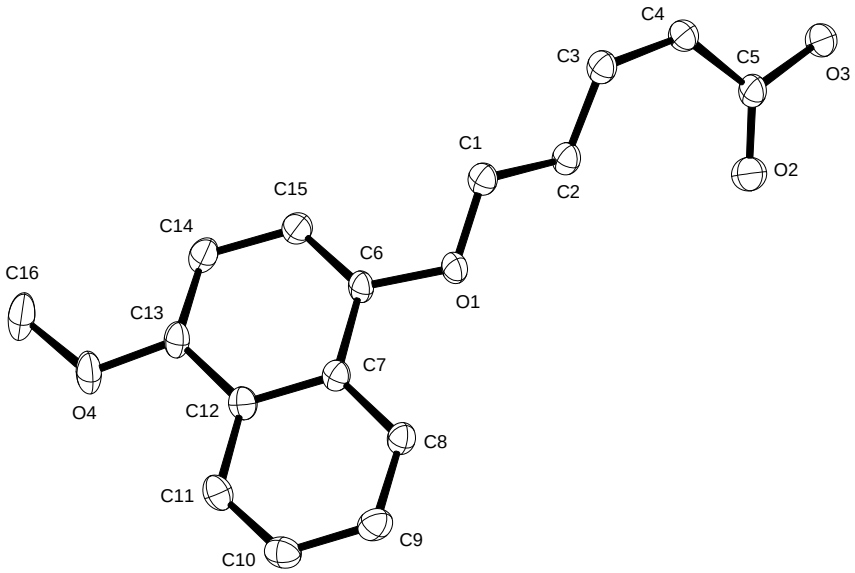
Compound **2p** was obtained as a yellow oil in 81% yield according to the general procedure. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.42 (d, J = 11.0, 1H), 7.35-7.31 (m, 4H), 7.16 (d, J = 8.3, 2H), 7.12 (d, J = 8.6, 2H), 6.95-6.88 (m, 2H), 2.48 (s, 3H), 2.32 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 169.0, 155.5, 153.2, 137.7, 137.0, 134.8, 134.4, 131.0, 129.6 (2C), 129.5 (2C), 128.5 (2C), 118.6 (2C), 112.1, 21.1, 16.5; FTIR (neat) ν_{max} 2922, 1678, 1628, 1583, 1488, 1219, 1158, 818;HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{19}H_{18}O_3S_1$) requires *m/z* 349.0870, found *m/z* 349.0869.

(2*Z*,4*E*)-5-((4-methoxynaphthalen-1-yl)oxy)penta-2,4-dienoic acid (2q)



2q

Compound **2q** was obtained as colourless crystals in 43% yield according to the general procedure. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 8.24 (d, J = 8.2, 1H), 8.07 (d, J = 8.2, 1H), 7.62-7.56 (m, 2H), 7.47 (d, J = 12.1, 1H), 7.37 (app. td, J = 11.9, J = 1.0, 1H), 7.17 (d, J = 8.2, 1H), 6.91 (d, J = 8.2, 1H), 6.81 (t, J = 11.6, 1H), 5.58 (d, J = 11.4, 1H), 4.02 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 167.9, 157.1, 153.2, 146.7, 142.9, 127.7, 127.4, 127.1, 127.0, 123.0, 122.0, 114.7, 113.2, 110.1, 104.1, 56.2; FTIR (neat) ν_{max} 2934, 2571, 1677, 1620, 1589, 1390, 1221, 1176, 1092, 922; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{16}H_{14}O_4Na$) requires *m/z* 293.0787, found *m/z* 293.0784. The structure of compound (*Z,E*)-**2q** was confirmed through single-crystal X-ray analysis (see below).



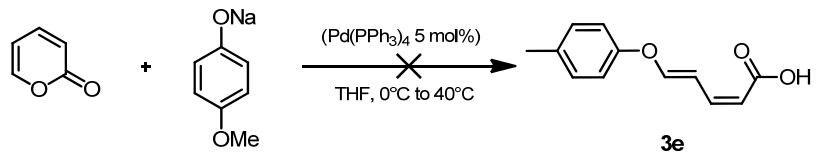
Crystal structure analysis of compound (*Z,E*)-**2q** crystallized from Acetone (Cambridge Crystallographic Data Centre number: 878397).

Background reaction on the lactone 1a:

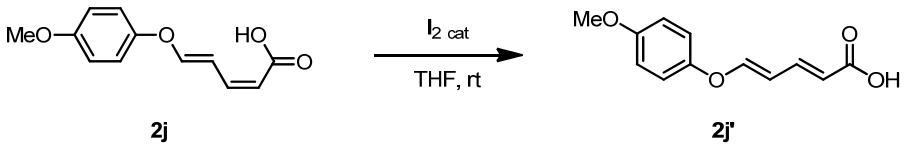
Diene **2i** was not observed when the reaction was performed in absence of Pd catalyst according to the general procedure (p. S4).

Background reaction on the 2-pyrone:

When 2-pyrone was submitted to the optimized reaction conditions reported on p. S4 (in presence of phenoxide anion, with and without Pd cat.), no reaction was observed.



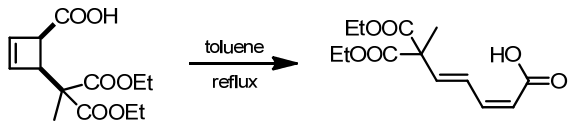
Procedure for isomerisation of (*Z*,*E*) diene (2j) to (*E*,*E*) diene (2*E*,4*E*)-5-(4-methoxyphenoxy)penta-2,4-dienoic acid (2j')



(2*Z*,4*E*)-5-(4-methoxyphenoxy)penta-2,4-dienoic acid (**2j**) was dissolved in THF (1 mL) and a catalytic amount of I_2 (10 mol%) was added to the solution. The mixture was stirred at room temperature for 2h. H_2O (5 mL) and EtOAc (5 mL) were added to the reaction mixture and the organic phase was extracted three times with saturated $NaHCO_3$. The combined aqueous phases were acidified to pH 1 using 1M HCl and extracted three times with EtOAc. Solvent was removed under vacuum to give the (*E,E*) diene **2j'** in 22% yield. ^{1}H-NMR (300 MHz, CD_3COCD_3) δ 7.40 (d, J = 11.8, 1H), 7.37 (dd, J = 15.3, J = 11.6, 1H), 7.08 (d, J = 9.0, 2H), 6.96 (d, J = 9.0, 2H), 6.06 (app. t, J = 11.9, 1H), 5.82 (d, J = 15.2, 1H), 3.79 (s, 3H); ^{13}C-NMR (75 MHz, CD_3COCD_3) δ 168.0, 157.2, 155.5, 151.0, 143.1, 119.4 (2C), 118.4, 115.8 (2C), 110.6, 56.0. HRMS (ESI) exact mass calculated for $[M]^+$ ($C_{12}H_{12}O_4$) requires *m/z* 220.0734, found *m/z* 293.0736.

3. Ring opening of cyclobutenes

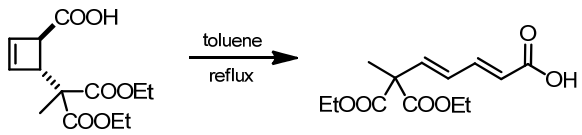
(2*Z*,4*E*)-7-ethoxy-6-(ethoxycarbonyl)-6-methyl-7-oxohepta-2,4-dienoic acid ((*Z*,*E*)-5)



cis-**4** (*Z,E*)-**5**

A stirred solution of cyclobutenes *cis*-**4** [4] (50.0 mg) was heated in toluene at 110 °C for 30 min. The solvent was removed under vacuum to give (*Z,E*)-**5** as a white solid in essentially quantitative yield (NMR internal standard yield). ^{1}H-NMR (400 MHz, CD_3COCD_3) δ 7.53 (ddd, J = 15.9, J = 11.1, J = 0.9, 1H), 6.76 (app.td, J = 11.1, J = 0.9, 1H), 6.51 (app. dt, J = 15.9, J = 0.9, 1H), 5.75 (app. dt, J = 11.1, J = 0.9, 1H), 4.19 (q, J = 7.1, 4H), 1.56 (s, 3H), 1.23 (t, J = 7.1, 6H); ^{13}C-NMR (100 MHz, CD_3COCD_3) δ 170.9 (2C), 167.3, 144.7, 141.3, 127.7, 119.5, 62.3 (2C), 56.9, 20.8, 14.3 (2C); FTIR (neat) ν_{max} 2985, 2939, 1728, 1692, 1253, 1107, 1016, 858.

(2*E*,4*E*)-7-ethoxy-6-(ethoxycarbonyl)-6-methyl-7-oxohepta-2,4-dienoic acid ((*E*,*E*)-5)



trans-**4** (*E,E*)-**5**

A stirred solution of cyclobutenes *cis*-**4** [3] (50.4 mg) was heated in toluene at 110 °C for 2 hours. The solvent was removed under vacuum to give (*E,E*)-**5** as a white solid in essentially quantitative yield (NMR internal standard yield). ^{1}H-NMR (400 MHz, CD_3COCD_3) δ 7.31 (ddd, J = 15.4, J = 10.6, J = 0.6, 1H), 6.60 (app.dt, J = 15.8, J = 0.6, 1H), 6.42 (ddd, J = 15.8, J = 10.6, J = 0.6, 1H), 6.00 (app. dt, J = 15.4, J = 0.6, 1H), 4.19 (q, J 7.1, 4H), 1.56 (s, 3H), 1.23 (t, J 7.1, 6H); ^{13}C-NMR (100 MHz, CD_3COCD_3) δ 170.7 (2C), 167.6, 144.7, 140.5, 129.6, 123.4, 62.3 (2C), 56.8, 20.5, 14.3 (2C); FTIR (neat) ν_{max} 2985, 2939, 1727, 1691, 1108, 1014, 858, 827The structure of compound (*E,E*)-**5** was confirmed through single-crystal X-ray analysis (see below).

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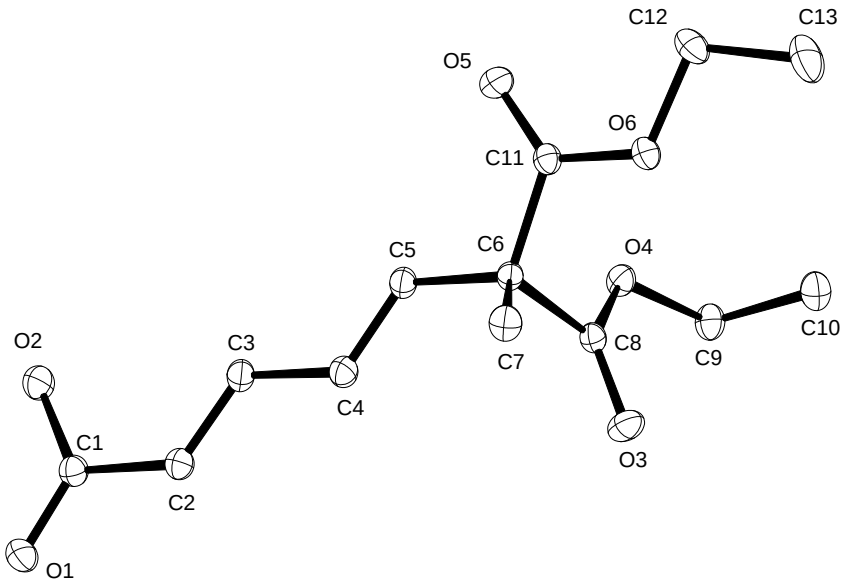
[4] F. Frébault, M. Luparia, M. T. Oliveira, R. Goddard, N. Maulide, *Angew. Chem. Int. Ed.* **2010**, *49*, 5672-5676.



Crystal structure analysis of compound (*E,E*)-**5** crystallized from CH_2Cl_2/Heptane (Cambridge Crystallographic Data Centre number: 887605).

4. Kinetic studies of electrocyclic ring opening of cyclobuenes.

Samples of cyclobutene *cis*-**4**, *cis*-**6**, *cis*-**8**, *trans*-**4**, trans-**6**, *trans*-**8** were dissolved in $CDCl_2CDCl_2$ (0.04 M) and heated to 90 °C in an Avance III 500 spectrometer (499.89MHz) equipped with a $BBFO_{plus}$ ^1H/BB (incl. ^{19}F) probehead with z-gradient from Bruker Biospin GmbH. The conversion of the cyclobutene starting material into the corresponding diene was monitored recording the ^1H-NMR spectra over time.

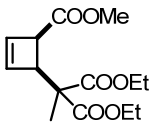
Preparation of the starting materials.

Compounds *cis*-**4**, *cis*-**8**, *trans*-**4**, *trans*-**8** were prepared following a procedure described in the literature and their spectroscopic properties match those reported.[3,4]

Compounds **6** were prepared starting from the corresponding free carboxylic acid **4** according to the following procedure: carboxylic acid **4** (100.0 mg, 0.37 mmol) was dissolved in dichlorometane (3.7 mL) and the resulting solution was cooled to 0 °C. DMF (1 drop) followed by oxalyl chloride (48 μL, 0.55 mmol, 1.5 equiv.) were added dropwise, the resulting mixture was stirred for 30 min and then dry MeOH (375 μL, 9.2 mmol, 25 equiv.)

was added dropwise. After 30 min at 0 °C, the solvent was removed under vacuum and the product was purified by column chromatography (pentane/EtOAc: 95/5) to give ester **6**.

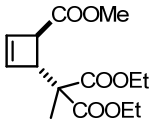
diethyl 2-(*cis*-4-(methoxycarbonyl)cyclobut-2-en-1-yl)-2-methylmalonate (*cis*-6)



cis-**6**

Compound *cis*-**6** was obtained in 80% yield according to the procedure. Spectroscopic properties in agreement with those reported in the literature.[4]

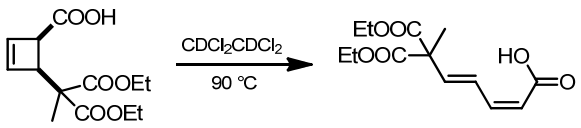
diethyl 2-(*trans*-4-(methoxycarbonyl)cyclobut-2-en-1-yl)-2-methylmalonate (*trans*-6)



trans-**6**

Compound *trans*-**6** was obtained in 84% yield according to the procedure. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 6.22 (d, J = 2.6, 1H), 6.13 (d, J = 2.6, 1H), 4.18-4.12 (m, 4H), 3.64 (s, 3H), 3.57 (s, 1H), 3.43 (s, 1H), 1.37 (s, 3H), 1.21 (t, J = 7.1, 6H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 172.8, 171.8, 171.5, 140.8, 136.3, 62.0 (2C), 55.3, 52.0, 51.5, 48.3, 17.6, 14.5 (2C).

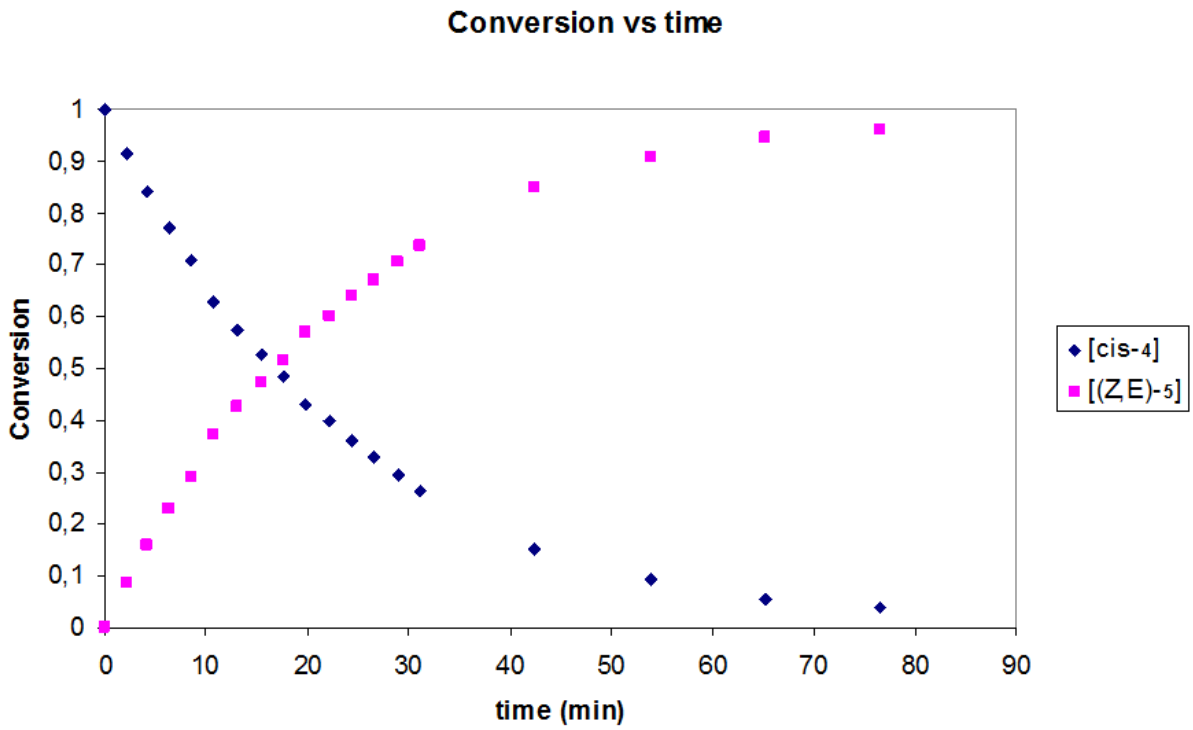
Kinetic data

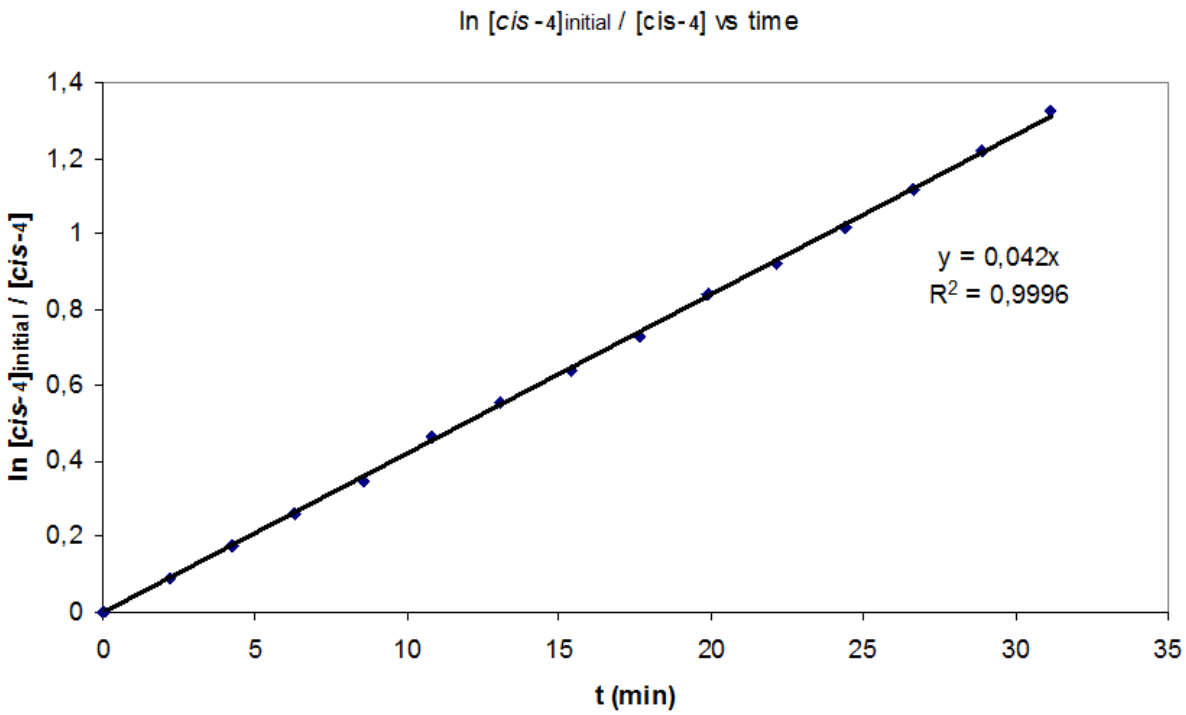


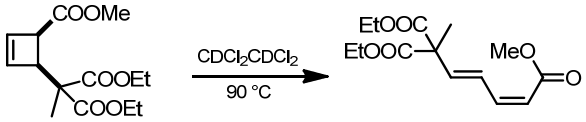
cis-**4** (*Z*,*E*)-**5**

Time (min)	Conversion
0	0
2,2	0,085
4,2	0,160
6,3	0,230
8,5	0,291
10,8	0,372
13,1	0,425
15,4	0,471
17,6	0,517
19,9	0,568
22,1	0,601
24,4	0,639
26,6	0,672
28,9	0,705
31,2	0,735
42,5	0,848
53,9	0,909
65,2	0,947
76,6	0,961
130,8	1.000
198,8	1.000
206,4	1.000

Calculated $t_{1/2}$ = 16.3 min


Conversion vs time
Conversion
time (min)
[cis-4]
[(Z,E)-5]

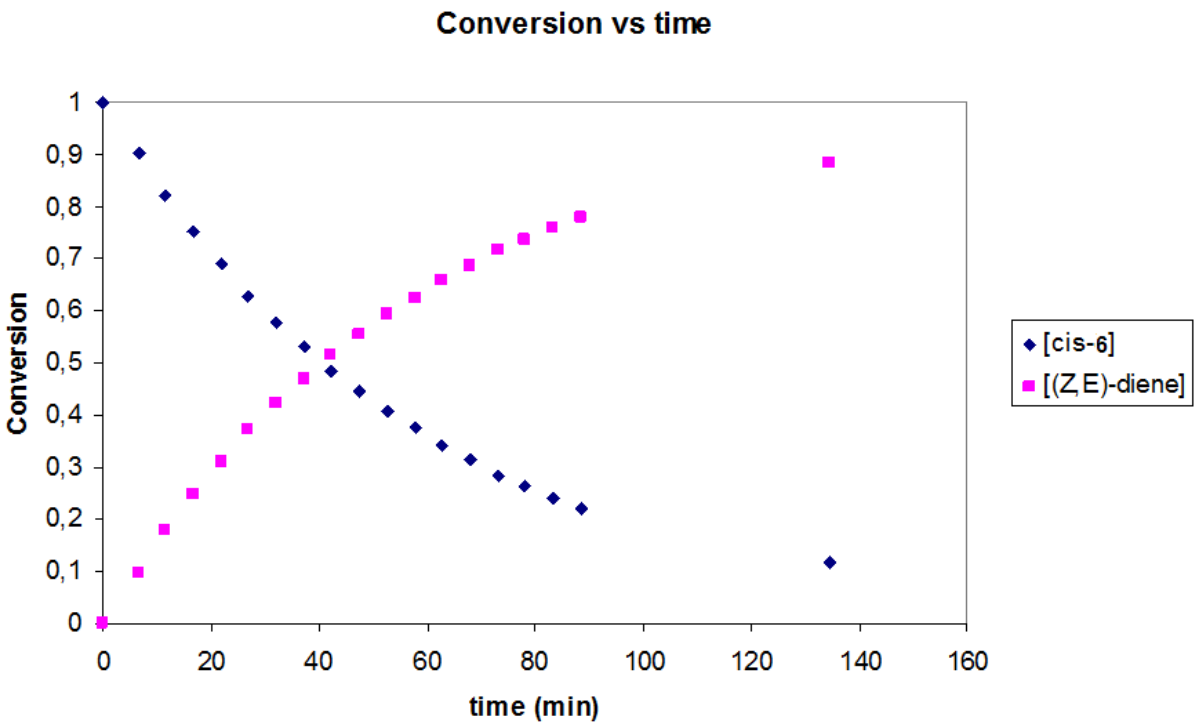

ln [cis-4]initial / [cis-4] vs time
ln [cis-4]initial / [cis-4]
t (min)
y = 0,042x
R2 = 0,9996

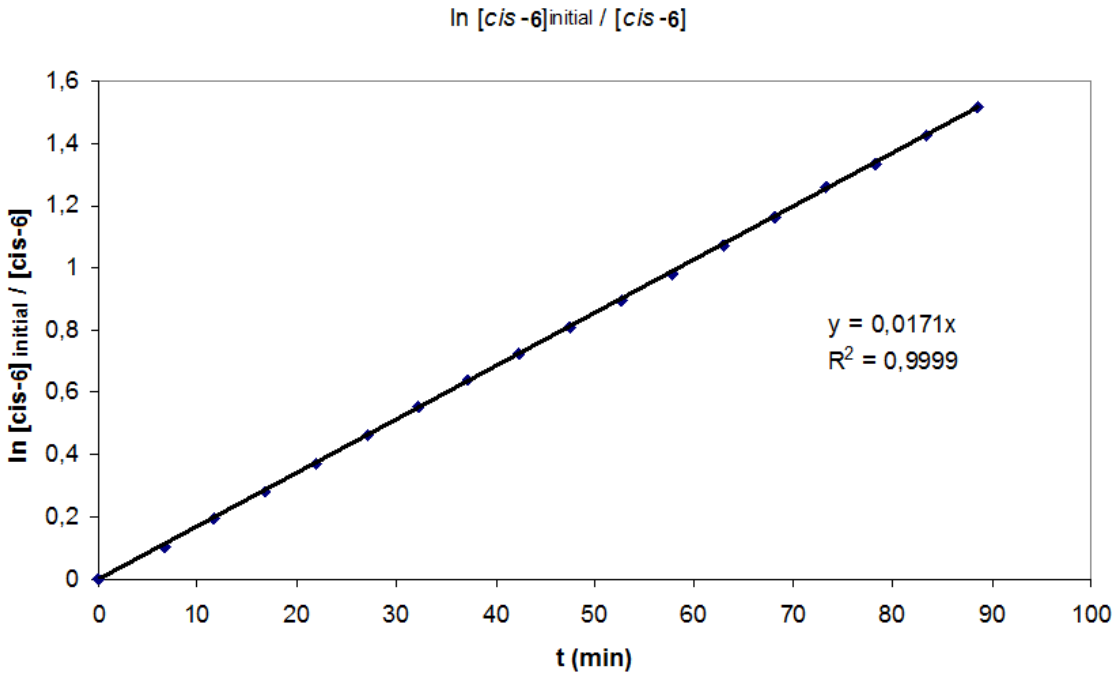


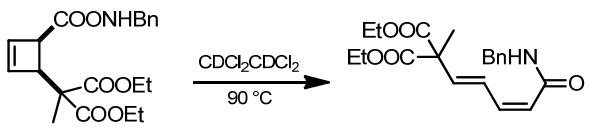
cis-**6** (*Z*,*E*)-**7**

time (min)	Conversion
0	0
6,6	0,097
11,7	0,177
16,8	0,246
21,9	0,311
27,1	0,372
32,2	0,424
37,3	0,471
42,4	0,515
47,6	0,555
52,7	0,591
57,8	0,624
62,9	0,657
68,1	0,687
73,2	0,717
78,3	0,737
83,4	0,759
88,6	0,780
134,7	0,882
201,3	0,966

Calculated $t_{1/2}$ = 40.6 min


Conversion vs time
Conversion
time (min)
[cis-6]
[(Z,E)-diene]

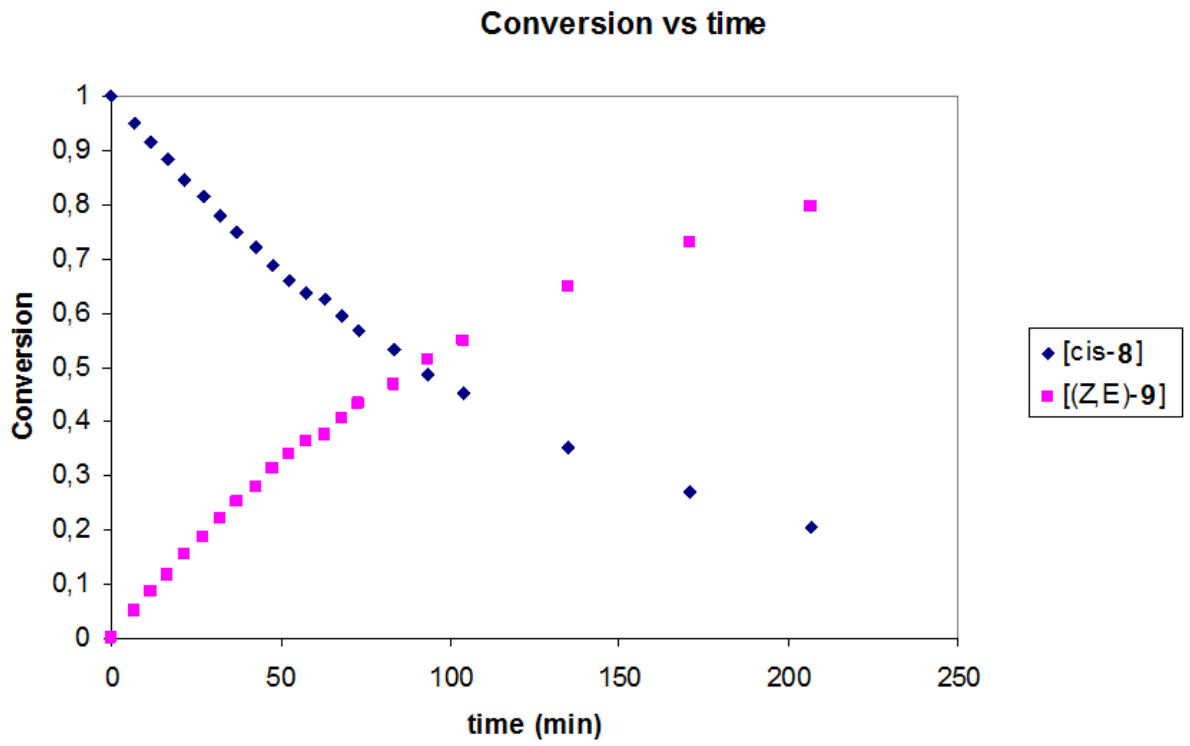

ln [cis-6]initial / [cis-6]
ln [cis-6] initial / [cis-6]
t (min)
y = 0,0171x
R2 = 0,9999

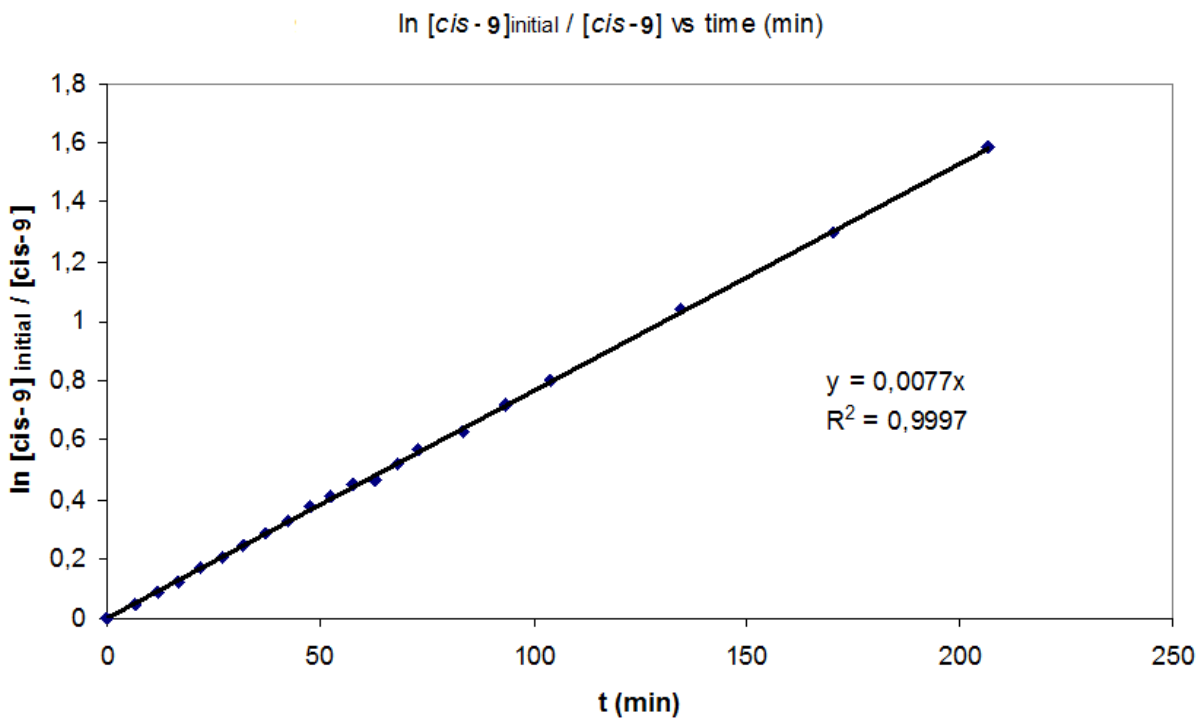


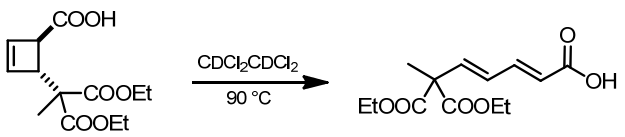
cis-**8** (*Z*,*E*)-**9**

time (min)	Conversion
0	0
6,6	0,049
11,7	0,084
16,8	0,116
21,9	0,156
27,1	0,185
32,2	0,218
37,3	0,249
42,4	0,279
47,6	0,311
52,7	0,339
58	0,365
62,9	0,373
68,1	0,404
73,2	0,432
83,4	0,466
93,7	0,513
103,9	0,550
134,7	0,648
170,5	0,728
206,4	0,795

Calculated $t_{1/2}$ = 90.0 min


Conversion vs time
Conversion
time (min)
[cis-8]
[(Z,E)-9]

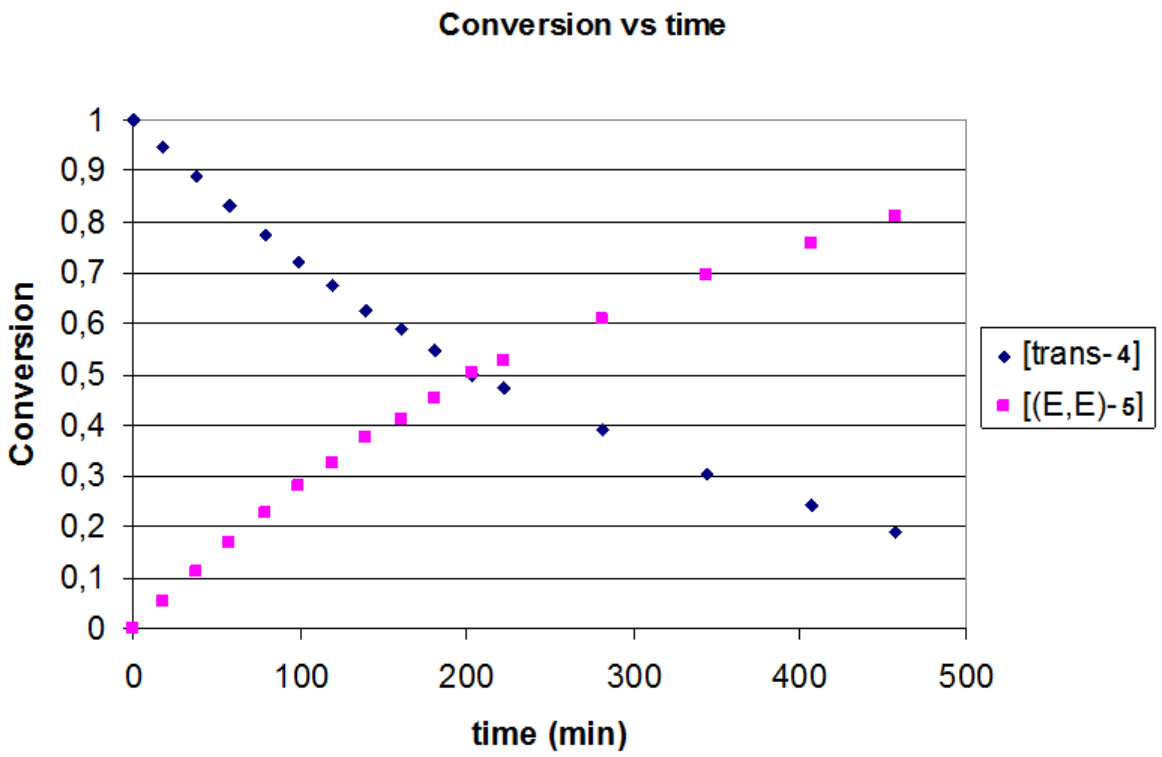

ln [cis-9]initial / [cis-9] vs time (min)
ln [cis-9] initial / [cis-9]
t (min)
y = 0,0077x
R2 = 0,9997

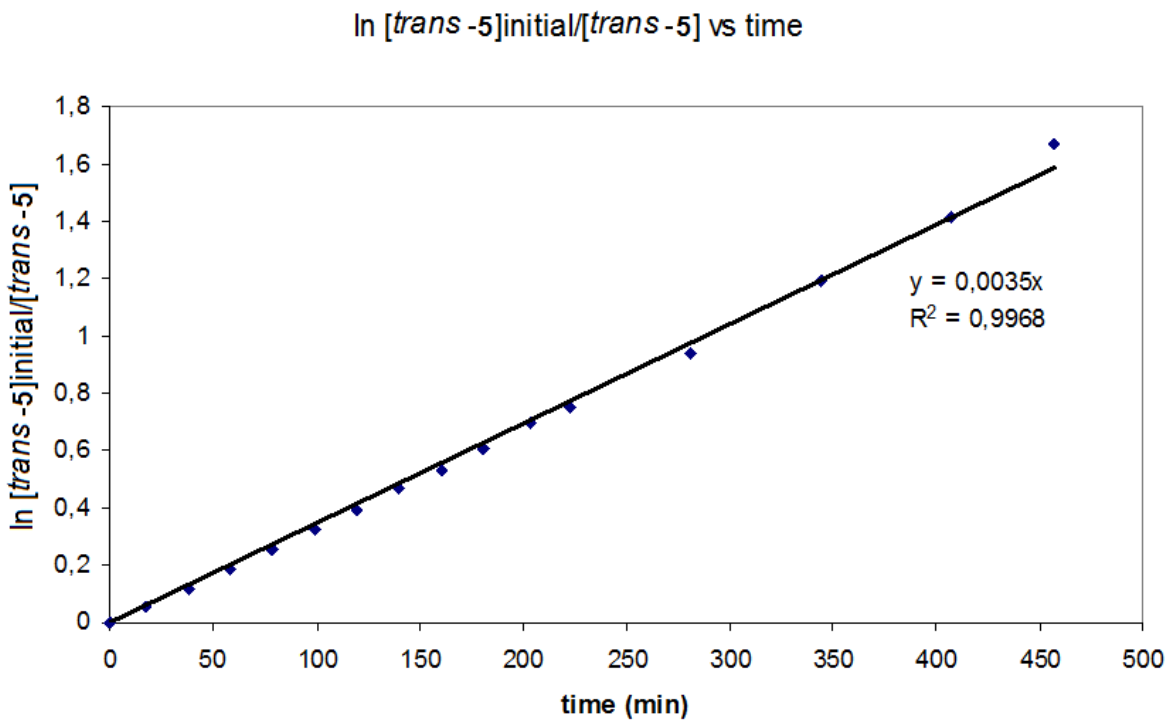


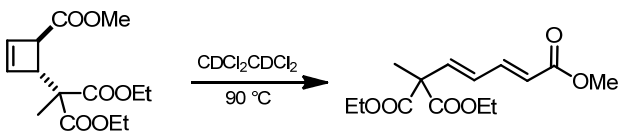
trans-**4** (*E*,*E*)-**5**

time (min)	Conversion
0	0
17,7	0,054
38,0	0,111
58,3	0,170
78,6	0,226
99,0	0,279
119,4	0,326
139,8	0,376
160,2	0,413
180,6	0,453
203,4	0,503
222,5	0,528
280,9	0,609
344,4	0,696
407,4	0,756
456,8	0,811

Calculated $t_{1/2}$ = 198.0 min


Conversion vs time
Conversion
time (min)
[trans-4]
[(E,E)-5]

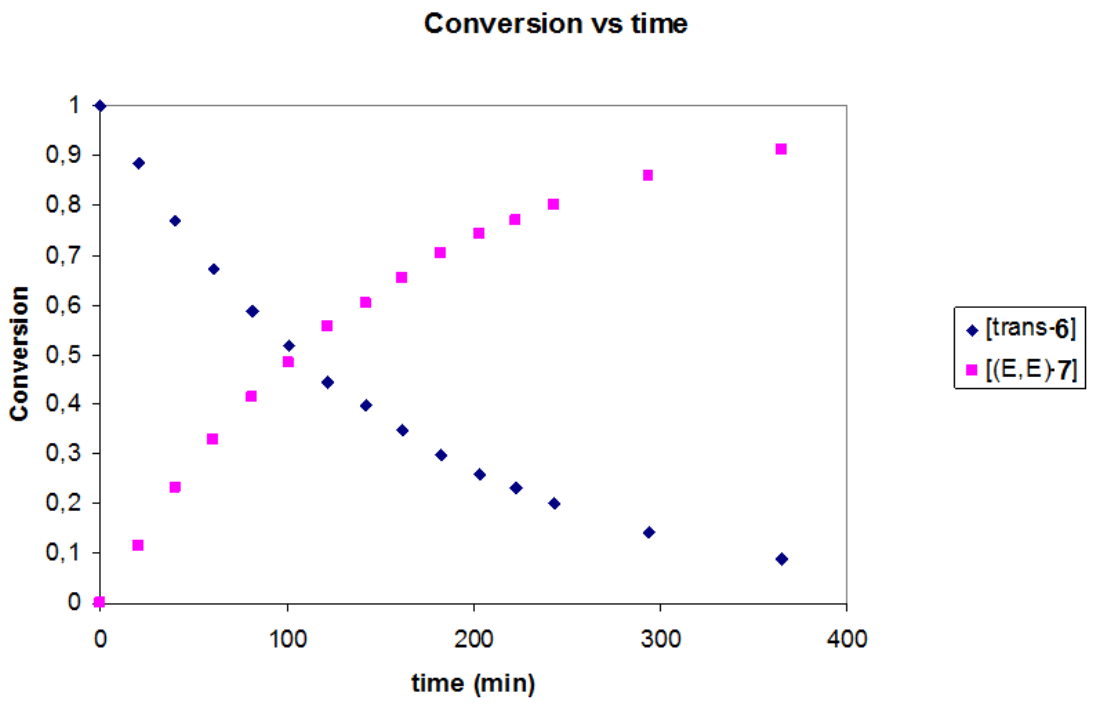

ln [trans -5]initial/[trans -5] vs time
ln [trans -5]initial/[trans -5]
time (min)
y = 0,0035x
R2 = 0,9968

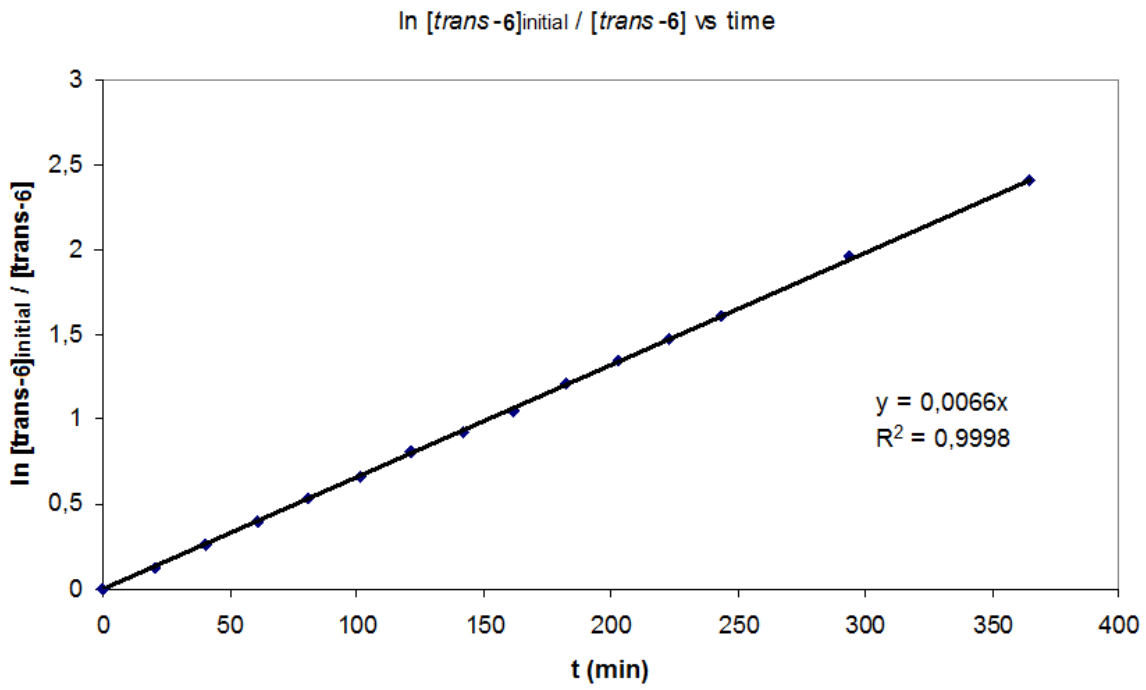


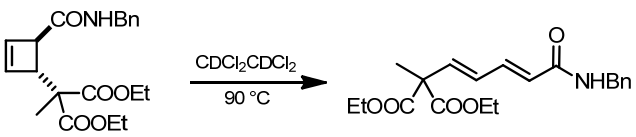
trans-**6** (*E*,*E*)-**7**

time (min)	Conversion
0	0
20,5	0,117
40,7	0,231
61	0,329
81,2	0,412
101,5	0,482
121,7	0,555
142	0,604
162,2	0,652
182,5	0,701
202,7	0,740
223	0,770
243,2	0,800
293,9	0,859
364,7	0,910
455,9	0,955

Calculated $t_{1/2}$ = 105.0 min


Conversion vs time
Conversion
time (min)
[trans-6]
[(E,E)-7]

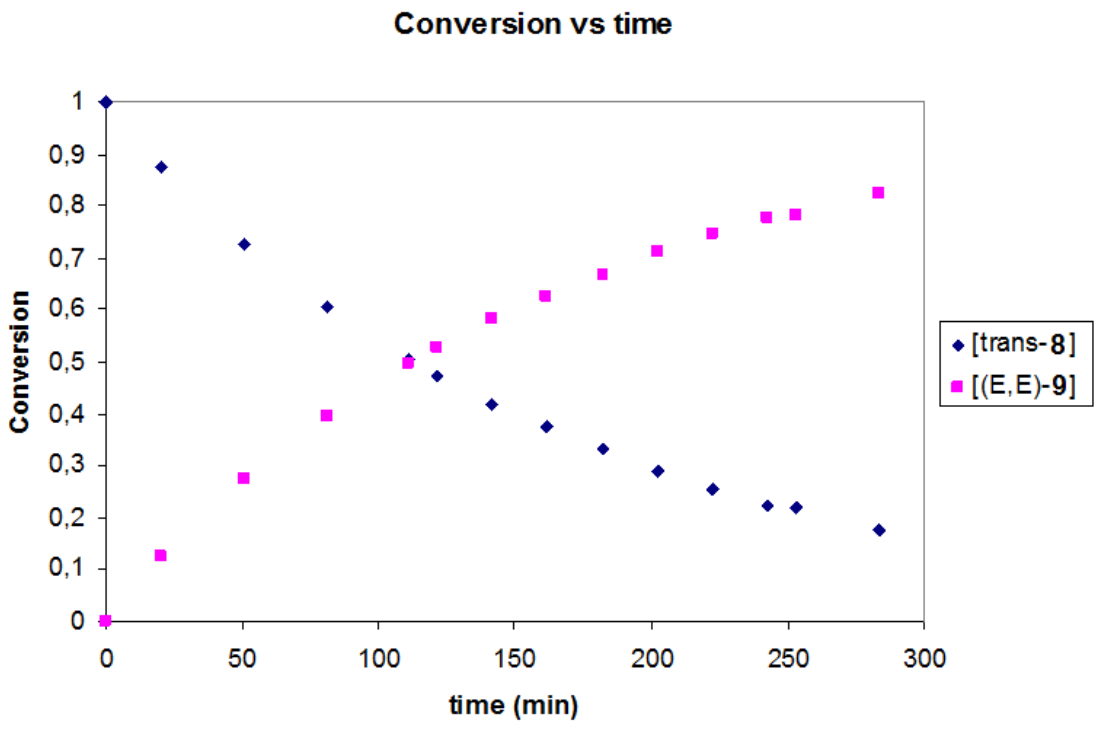

ln [trans-6]initial / [trans-6] vs time
ln [trans-6]initial / [trans-6]
t (min)
y = 0,0066x
R2 = 0,9998

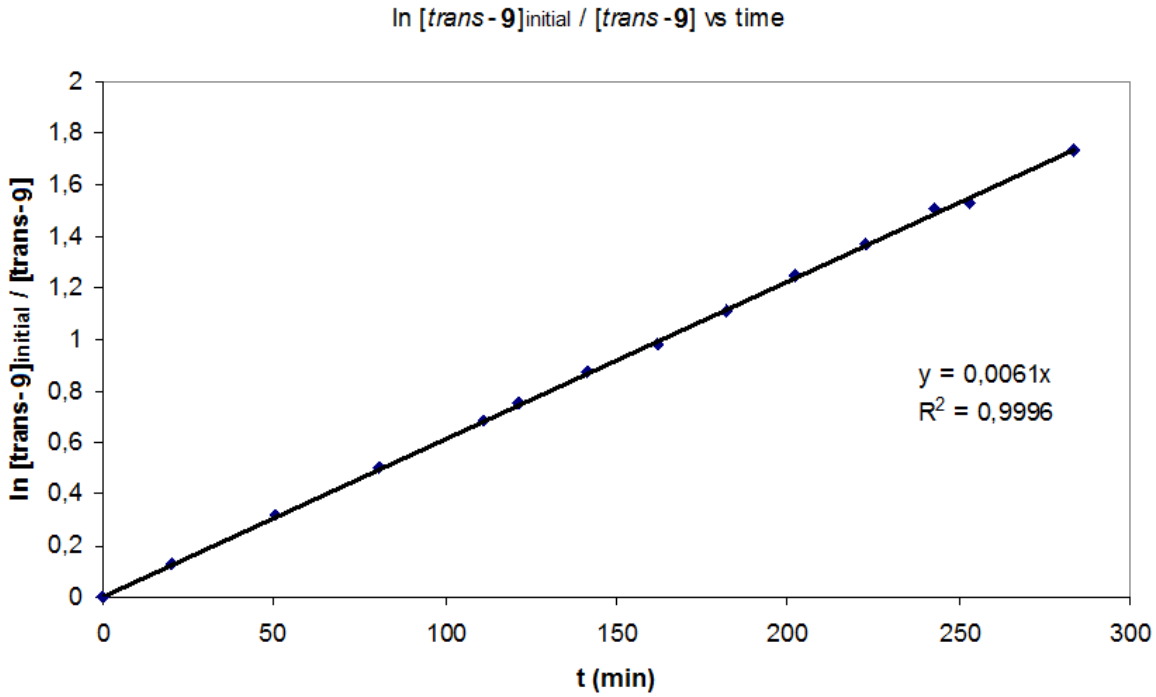


trans-**8** (*E*,*E*)-**9**

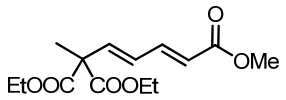
time (min)	Conversion
0	0
20,1	0,124
50,4	0,274
80,8	0,395
111,2	0,496
121,3	0,528
141,6	0,583
161,8	0,626
182,1	0,670
202,3	0,713
222,6	0,746
242,8	0,778
253	0,783
283,4	0,823
364,4	0,892
455,5	0,935

Calculated $t_{1/2}$ = 113.6 min


Conversion vs time
Conversion
time (min)
[trans-8]
[(E,E)-9]
0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1
0
50
100
150
200
250
300


ln [trans-9]initial / [trans-9] vs time
ln [trans-9]initial / [trans-9]
t (min)
y = 0,0061x
R2 = 0,9996
0
0,2
0,4
0,6
0,8
1
1,2
1,4
1,6
1,8
2
0
50
100
150
200
250
300

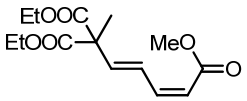
(1E,3E)-5,5-diethyl 1-methyl hexa-1,3-diene-1,5,5-tricarboxylate ((*E*,*E*)-7)



(*E*,*E*)-**7**

^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.31 (dd, J = 15.4, 10.8, 1H), 6.61 (d, J = 15.8, 1H), 6.69 (dd, J = 15.8, J = 10.8, 1H), 6.02 (d, J = 15.4, 1H), 4.19 (q, J = 7.1, 4H), 3.69 (s, 3H), 1.56 (s, 3H), 1.23 (t, J = 7.1, 6H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 170.8 (2C), 167.3, 144.6, 140.9, 129.6, 123.0, 62.4 (2C), 56.9, 51.8, 20.6, 14.4 (2C).

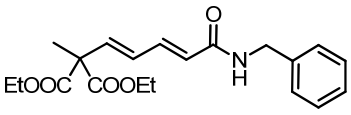
(1Z,3E)-5,5-diethyl 1-methyl hexa-1,3-diene-1,5,5-tricarboxylate ((*Z*,*E*)-7)



(*Z*,*E*)-**7**

^{1}H-NMR (500 MHz, $CDCl_2CDCl_2$) δ 7.46 (dd, J = 15.8, J = 11.1, 1H), 6.64 (app. t, J = 11.3, 1H), 6.46 (d, J = 15.8, 1H), 5.73 (d, J = 11.3, 1H), 4.20 (q, J = 7.1, 4H), 3.71 (s, 3H), 1.62 (s, 3H), 1.25 (t, J = 7.1, 6H); ^{13}C-NMR (125 MHz, $CDCl_2CDCl_2$) δ 170.4 (2C), 166.5, 143.8, 140.3, 126.9, 118.1, 62.0 (2C), 56.0, 51.4, 19.7, 14.0 (2C).

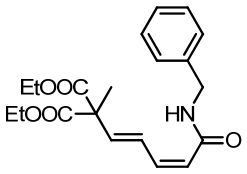
diethyl 2-((1E,3E)-5-(benzylamino)-5-oxopenta-1,3-dienyl)-2-methylmalonate ((*E*,*E*)-9)



(*E*,*E*)-**9**

^{1}H-NMR (500 MHz, $CDCl_2CDCl_2$) δ 7.36-7.33 (m, 2H), 7.31-7.27 (m, 3H), 7.25 (dd, J 15.0, 10.9, 1H), 6.48 (d, J = 15.7, 1H), 6.23 (dd, J = 15.7, J = 10.9, 1H), 5.91 (d, J = 15.0, 1H), 5.86 (t, J = 5.7, 1H), 4.50 (d, J = 5.7, 2H), 4.19 (q, J = 7.1, 4H), 1.58 (s, 3H), 1.25 (t, J = 7.1, 6H); ^{13}C-NMR (125 MHz, $CDCl_2CDCl_2$) δ 170.3 (2C), 165.3, 140.2, 138.3, 138.0, 128.7 (2C), 128.5, 127.6 (2C), 127.5, 124.5, 62.0 (2C), 55.8, 43.5, 19.9, 14.0 (2C).

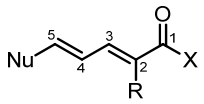
diethyl 2-((1E,3Z)-5-(benzylamino)-5-oxopenta-1,3-dienyl)-2-methylmalonate ((*Z*,*E*)-9)



(*Z*,*E*)-**9**

^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.86 (dd, J = 16.0, J = 11.0, 1H), 7.71 (br s, 1H), 7.31 (app.d, J = 4.3, 1H), 7.23 (m, 1H), 6.51 (dd, J = 11.2, J = 11.0, 1H), 6.36 (d, J = 16.0, 1H), 5.88 (d, J = 11.2, 1H), 4.43 (d, J = 6.0, 2H), 4.19 (q, J = 7.1, 4H), 1.55 (s, 3H), 1.23 (t, J = 7.1, 6H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 171.1 (2C), 166.3, 140.5, 138.9, 129.3 (2C), 128.6, 128.6 (2C), 127.8, 122.9, 119.5, 62.3 (2C), 56.8, 43.4, 20.8, 14.3 (2C).

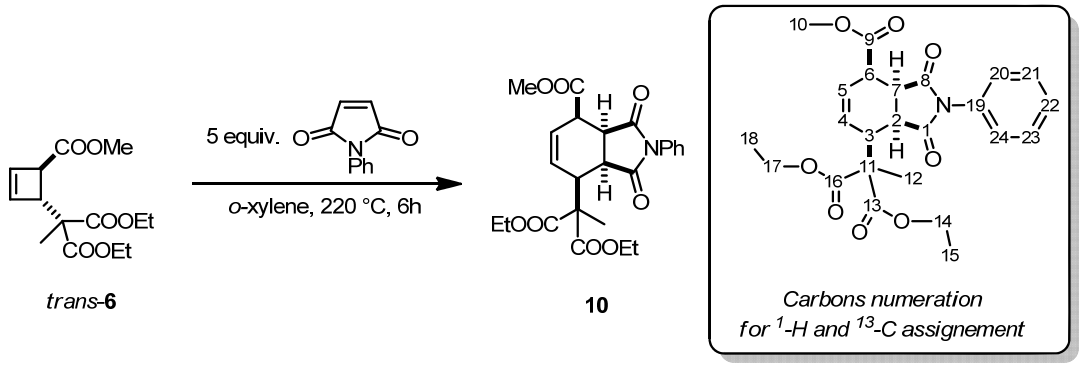
5. Comparison of ^{1}H-NMR data for dienes



Diene	X	R	Nu	Solvent	$\delta(H_2)$ (ppm)	$\delta(H_3)$ (ppm)	$\delta(H_4)$ (ppm)	$\delta(H_5)$ (ppm)	$^{3}J(H_3H_2)$ (Hz)	$^{3}J(H_4H_3)$ (Hz)	$^{3}J(H_5H_4)$ (Hz)	Geometry
2a	-OH	-H	-OAr	Acetone	5.4	6.8	6.9	7.1	11.6	11.6	12.4	Z,E
2b	-OH	-H	-OAr	Acetone	5.7	6.8	7.4	7.5	11.5	11.5	12.1	Z,E
2c	-OH	-Tolyl	-OAr	Acetone	--	6.9	7.0	7.6	--	11.8	11.8	Z,E
2d	-OH	-H	-OAr	Acetone	5.7	6.8	7.3	7.4	11.3	11.6	12.3	Z,E
2e	-OH	-H	-OAr	Acetone	5.6	6.8	7.3	7.4	11.5	11.5	11.9	Z,E
2f	-OH	-Bu	-OAr	Acetone	--	6.6	7.1	7.2	--	11.9	12.3	Z,E
2g	-OH	-Tolyl	-OAr	Acetone	--	6.9	7.0	7.4	--	ND	11.6	Z,E
2h	-OH	-H	-OAr	Acetone	5.6	6.8	7.3	7.4	ND	12.0	12.0	Z,E
2i	-OH	-Me	-OAr	Acetone	--	6.7	7.2	7.2	--	11.5	12.2	Z,E
2j	-OH	-H	-OAr	Acetone	5.6	6.8	7.2	7.3	11.5	11.5	12.2	Z,E
2k	-OH	-Me	-OAr	Acetone	--	6.6	7.1	7.2	--	11.7	12.1	Z,E
2l	-OH	-Bu	-OAr	Acetone	--	6.6	7.1	7.2	--	11.5	12.1	Z,E
2m	-OH	-H	-OAr	Acetone	5.5	6.7	7.2	7.3	11.3	11.3	12.2	Z,E
2n	-OH	-Tolyl	-OAr	Acetone	--	6.8	7.2	7.3	--	11.9	12.1	Z,E
2o	-OH	-H	-OAr	Acetone	5.6	6.7	7.2	7.4	11.4	11.4	12.5	Z,E
2p	-OH	-Tolyl	-OAr	Acetone	--	6.9	7.3	7.4	--	ND	ND	Z,E
2q	-OH	-H	-OAr	Acetone	5.6	6.8	7.4	7.5	11.4	11.9	12.1	Z,E
2j'	-OH	-H	-OAr	Acetone	5.8	7.4	6.1	7.4	15.2	11.5	11.8	E,E
(*E,E*)-**5**	-OH	-H	Malonate	Acetone	6.0	7.3	6.4	6.6	15.4	10.6	15.8	E,E
(*E,E*)-**7**	-OMe	-H	Malonate	Acetone	6.0	7.3	6.7	6.6	15.4	10.8	15.4	E,E
(*E,E*)-**9**	-NHBz	-H	Malonate	Tetrachloroethane	5.9	7.3	6.2	6.5	15.0	10.9	15.7	E,E
(*Z,E*)-**5**	-OH	-H	Malonate	Acetone	5.8	6.5	6.8	7.5	11.1	11.1	15.9	Z,E
(*Z,E*)-**7**	-OMe	-H	Malonate	Tetrachloroethane	5.7	6.6	6.5	7.5	11.3	11.1	15.8	Z,E
(*Z,E*)-**9**	-NHBz	-H	Malonate	Tetrachloroethane	5.7	6.6	6.5	7.5	11.3	11.1	15.8	Z,E

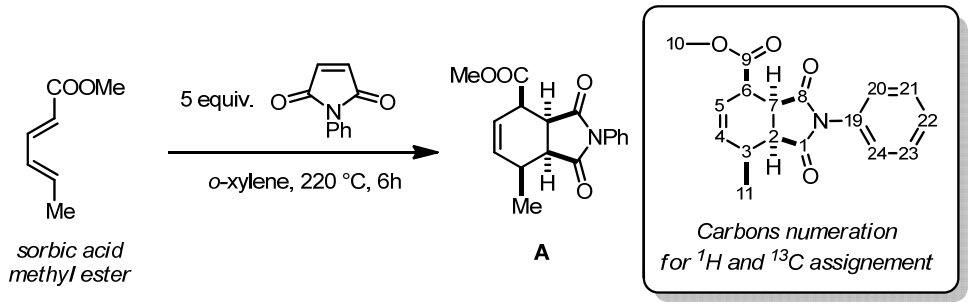
6. Domino electrocyclic ring opening / Diels-Alder cycloaddition

Cyloadduct 10

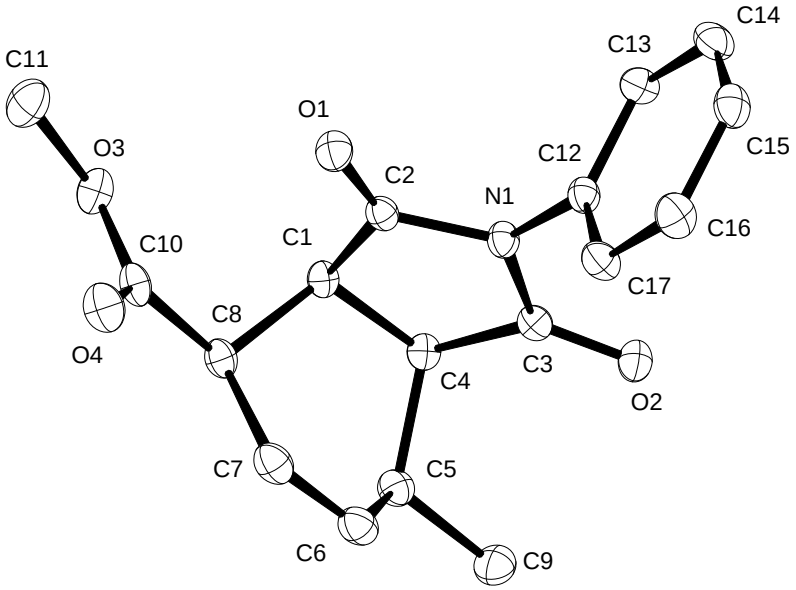


A microwave tube containing *trans*-**6** (70.8 mg, 0.25 mmol, 1 equiv.), *o*-xylene (2.5 mL) and *N*-phenylmaleimide (215.6 mg, 1.25 mmol, 5 equiv.) was purged with Ar and heated at 220 °C for 6 hours in a microwave oven (200 W). The solvent was removed under vacuum and the product was purified by column chromatography (pentane/EtOAc: 75/25) to afford cycloadduct **10** (87 mg,76%). FTIR (neat) ν_{max} 3063, 2985, 2953, 1709, 1500, 1384, 1185, 1105, 1019, 733, 699;^{1}H-NMR (600 MHz, CD_3COCD_3) δ 7.45-7.41 (m, H_{21}, H_{23}), 7.36 (m, H_{22}), 7.29-7.25 (m, H_{20}, H_{24}), 6.34 (dt, J = 9.7, J = 3.1, H_5), 6.30 (dt, J = 9.7, J = 3.1, H_4), 4.19 (q, J = 7.1, $2H_{17}$), 4.15 (ddd, J = 9.1, J = 4.9, J = 0.7, H_7), 4.12-4.02 (m, $2H_{14}$), 3.80 (ddd, J = 8.9, J = 8.2, J = 0.5, H_2), 3.76 (s, $3H_{10}$), 3.36 (m, H_6), 3.01 (m, H_3), 1.82 (s, $3H_{12}$), 1.22 (t, J = 7.1, $3H_{18}$), 1.20 (t, J = 7.1, $3H_{18}$); ^{13}C-NMR (150 MHz, CD_3COCD_3) δ 177.1 (C_1), 177.0 (C_8), 173.0 (C_{16}), 171.7 (C_9), 171.1 (C_{13}), 133.5 (C_{19}), 131.7 (C_4), 129.4 (C_{21}, C_{23}), 128.9 (C_{22}), 127.8 (C_{20}, C_{24}), 125.9 (C_5), 62.4 (C_{17}), 61.3 (C_{14}), 55.3 (C_{11}), 52.2 (C_{10}), 45.5 (C_7), 44.2 (C_3), 41.0 (C_2), 39.7 (C_6), 20.5 (C_{12}), 14.2 (C_{15}), 14.2 (C_{18}); HRMS exact mass calculated for $[M+Na]^+$ ($C_{24}H_{27}NO_8Na$) requires *m*/*z* 480.1629, found *m*/*z* 480.1635.

The relative stereochemistry of compound **10** was determined by analogy with compound **A** synthesized in an analogous way starting from sorbic acid methyl ester (*o*-xylene, 5 equiv. and *N*-phenylmaleimide, 2 hours, 220 °C, 82% yield). In particular the almost identical diagnostic coupling constant of protons 2 and 7 in compound **10** and **A** as well as similar NOE effects clearly indicate that these two compounds have the same relative stereochemistry. The structure of **A** was unambiguously determined by single-crystal X-ray analysis (see below).



Following the same procedure, compound **A** was isolated in 79% yield. FTIR (neat) ν_{max} 2993, 1725, 1701, 1392, 1198, 1053, 759, 716, 706, 695, 685; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.44-7.39 (m, H_{21}, H_{23}), 7.35 (m, H_{22}), 7.20-7.19 (m, H_{20}, H_{24}), 6.45 (dt, J = 9.4, J = 3.3, H_5), 5.85 (dt, J = 9.4, J = 3.3, H_4), 3.88 (dd, J = 8.9, J = 5.8, H_7), 3.83 (s, $3H_{10}$), 3.28 (dd, J = 8.9, J = 7.5, H_2), 3.21 (m, H_6), 2.51 (m, H_3), 1.47 (d, J = 7.4, $3H_{11}$); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 176.3 (C_1), 175.9 (C_8), 171.2 (C_9), 134.8 (C_4), 131.6 (C_{19}), 129.2 (C_{21}, C_{23}), 128.8 (C_{22}), 126.5 (C_5, C_{20}, C_{24}), 52.5 (C_{10}), 44.0 (C_2), 43.9 (C_7), 40.6 (C_6), 31.7 (C_3), 16.8 (C_{11}); HRMS exact mass calculated for $[M+Na]^+$ ($C_{17}H_{17}NO_4Na$) requires m/z 322.1050, found m/z 322.1050.

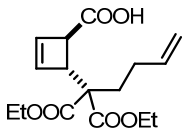


Crystal structure analysis of compound **A** crystallized from CH_2Cl_2/Heptane (Cambridge Crystallographic Data Centre number: 866301).

Synthesis of the cyclobutenes starting material for intramolecular domino electrocyclic ring opening / Diels-Alder cycloaddition

Compound *trans*-**11a** and *trans*-**11b** were synthesized according to literature procedure.[3]

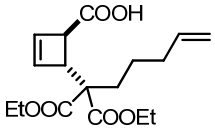
4-(1-ethoxy-2-(ethoxycarbonyl)-1-oxohex-5-en-2-yl)cyclobut-2-enecarboxylic acid (*trans*-11a)



trans-**11a**

Compound *trans*–**11a** was obtained in 66% isolated yield. FTIR (neat) ν_{max} 2983, 1727, 1373, 1238, 1045, 915, 719; ^{1}H-NMR (300 MHz, CD_3COCD_3) δ 6.28 (dt, J = 2.8, J = 1.1, 1H), 6.12 (dt, J = 2.8, J = 0.9, 1H), 5.81 (m, 1H), 5.03 (m, 1H), 4.95 (m, 1H), 4.24-4.14 (m, 4H), 3.66 (m, 1H), 3.54 (m, 1H), 2.16-1.95 (m, 4H), 1.25 (t, J = 7.1, 3H), 1.24 (t, J = 7.1, 3H); ^{13}C-NMR (75 MHz, CD_3COCD_3) δ 173.2, 171.0, 170.8, 141.1, 138.7, 135.6, 115.4, 61.8, 61.8, 59.6, 49.4, 48.4, 32.7, 29.5, 14.4, 14.4; HRMS exact mass calculated for $[M+Na]^+$ ($C_{16}H_{22}O_6Na$) requires m/z 333.1308, found m/z 333.1308.

4-(1-ethoxy-2-(ethoxycarbonyl)-1-oxohept-6-en-2-yl)cyclobut-2-enecarboxylic acid (*trans*-11b)



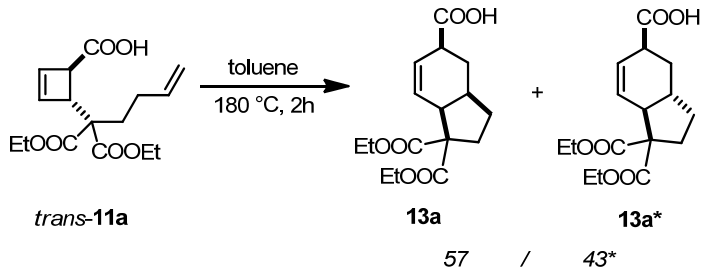
trans-**11b**

Compound *trans*-**11b** was obtained in 70% isolated yield. FTIR (neat) ν_{max} 2982, 1726, 1371, 1238, 1045, 914, 718; ^{1}H-NMR (300 MHz, CD_3COCD_3) δ 6.26 (dt, J = 2.8, J = 1.1, 1H), 6.10 (dt, J = 2.8, J = 0.9, 1H), 5.78 (m, 1H), 5.00 (m, 1H), 4.93 (m, 1H), 4.22-4.12 (m, 4H), 3.63 (m, 1H), 3.52 (m, 1H), 2.09-2.01 (m, 2H), 1.99-1.87 (m, 2H), 1.44 (m, 1H), 1.31 (m, 1H), 1.23 (t, J = 7.1, 3H), 1.22 (t, J = 7.1, 3H); ^{13}C-NMR (75 MHz, CD_3COCD_3) δ 173.2, 171.2,

170.9, 141.2, 139.1, 135.5, 115.3, 61.7, 61.7, 59.8, 49.4, 48.4, 34.6, 32.7, 24.5, 14.4, 14.4; HRMS exact mass calculated for $[M+Na]^+$ ($C_{17}H_{24}O_6Na$) requires *m/z* 347.1471, found *m/z* 347.1433.

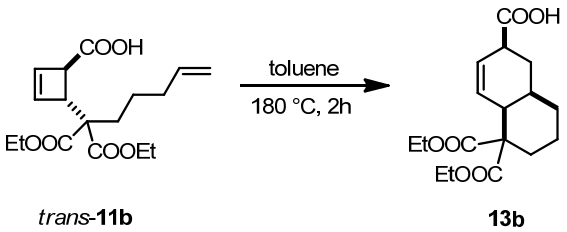
Intramolecular domino electrocyclic ring opening / Diels-Alder cycloaddition

Cycloadduct 13a/13a*

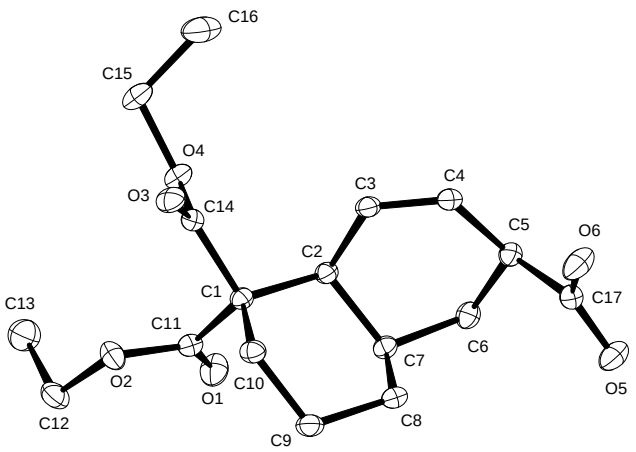


A microwave tube containing *trans*-**11a** (81.5 mg, 0.26 mmol) and toluene (5.2 mL) was purged with Ar and heated at 180 °C for 2 hours in a microwave oven (200 W). The solvent was removed under vacuum and the product was purified by column chromatography (toluene/EtOAc/CH_3COOH: 80/20/0.5) to afford the desired cycloadduct **13a** in 63% yield as a whitish solid (57/43* mixture of diastereisomers). FTIR (neat) ν_{max} 2982, 2934, 2872, 1720, 1695, 1252, 1231, 1094, 1014, 912, 723; ^{1}H-NMR (600 MHz, C_6D_6) δ 6.05 (dt, J = 10.0, J = 2.0, 1H*), 5.89 (tdt, J = 10.2, J = 2.3, J = 1.0, 1H), 5.79 (ddd, J = 10.2, J = 4.1, J = 2.8, 1H), 5.74 (dddd, J = 10.2, J = 4.4, J = 3.0, J = 1.1, 1H*), 4.22-4.05 (m, 4H, 4H*), 3.25 (m, 1H), 3.19 (m, 1H*), 3.00 (m, 1H), 2.55 (m, 1H), 2.49 (dt, J = 14.0, J = 8.6 1H*), 2.45 (m, 1H*), 2.34 (m, 1H*), 2.33 (m, 1H), 2.02 (ddd, J = 14.0, J = 10.4, J = 2.5, 1H*), 1.95-1.80 (m, 3H, 2H*), 1.63 (m, 1H), 1.48 (dt, J = 12.6, J = 7.0, 1H*), 1.45 (dt, J = 12.8, J = 11.2, 1H), 1.26 (m, 1H*), 1.19 (t, J = 7.1, 3H*), 1.18 (t, J = 7.1, 3H), 1.16 (t, J = 7.1, 3H), 1.14 (t, J = 7.1, 3H*); ^{13}C-NMR (150 MHz, CD_3COCD_3) δ 175.1, 174.7*, 172.5, 172.4*, 171.4, 171.3*, 130.1*, 127.9, 127.8, 126.4*, 64.3, 61.8, 61.6*, 61.6*, 61.5, 61.1*, 50.6*, 44.9, 41.8*, 41.7, 38.3*, 37.5, 34.1, 32.9*, 31.0*, 30.2, 29.1*, 14.4*, 14.3, 14.3, 14.3*; HRMS exact mass calculated for $[M+Na]^+$ ($C_{16}H_{22}O_6Na$) requires *m/z* 333.1308, found *m/z* 333.1306.

Cycloadduct 13b



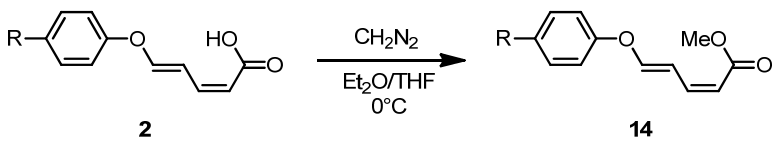
A microwave tube containing *trans*-**11b** (56.5 mg, 0.17 mmol) and toluene (3.5 mL) was purged with Ar and heated at 180 °C for 2 hours in a microwave oven (200 W). The solvent was removed under vacuum and the product was purified by column chromatography (toluene/EtOAc/CH_3COOH: 90/10/0.5) to afford the desired cycloadduct **13b** (43.3 mg, 77% contamined with 10% of an unidentified by-product). This material was cristalized from pentane to afford pure compound **13b** as a white solid (33.7 mg, 60%, single diastereisomer). FTIR (neat) ν_{max} 2978, 2934, 1723, 1696, 1446, 1249, 1016, 921, 764; ^{1}H-NMR (600 MHz, C_6D_6) δ 5.97 (dddd, J = 10.4, J = 4.0, J = 3.0, J = 1.3, 1H), 5.57 (d, J = 10.4, 1H), 3.98-3.89 (m, 4H), 3.40 (m, 1H), 2.65 (m, 1H), 2.42 (m, 1H), 2.35-2.30 (m, 2H), 1.87 (td, J = 13.7, J = 3.5, 1H), 1.72 (ddd, J = 14.3, J = 8.6, J = 3.8, 1H), 1.44 (dt, J = 13.5, J = 3.6, 1H), 1.35 (qd, J = 12.6, J = 3.6, 1H), 1.31 (m, 1H), 1.07 (m, 1H), 0.89 (t, J = 7.1, 3H), 0.87 (t, J = 7.1, 3H); ^{13}C-NMR (150 MHz, C_6D_6) δ 180.9, 170.8, 170.6, 128.3, 126.0, 61.2, 61.0, 59.0, 39.4, 37.9, 30.6, 29.0, 27.6, 25.8, 22.5, 14.0, 14.0; HRMS: exact mass calculated for $[M+Na]^+$ ($C_{17}H_{24}O_6Na$) requires m/z 347.1471, found m/z 347.1433. The structure of **13b** was confirmed by single-crystal X-ray analysis (see below).



Crystal structure analysis of compound **13b** crystallized from CH_2Cl_2/Heptanes (Cambridge Crystallographic Data Centre number: 866302).

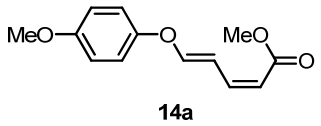
7. Diels-Alder reactions of push-pull aryloxy-dienes

General procedure for methyl ester formation:



An ethereal solution of diazomethane[5] was added dropwise to a stirred solution of crude acid **2** in THF until complete consumption of the starting material was observed by TLC. Excess CH_2N_2 was quenched by addition of a few drops of acetic acid and the solvent was removed under vacuum. The product was then purified by column chromatography (pentane/EtOAc: 95/5) to afford the methyl esters **14**.

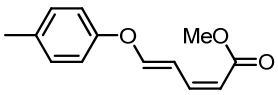
(2*Z*,4*E*)-methyl 5-(4-methoxyphenoxy)penta-2,4-dienoate (14a)



Compound **14a** was obtained as a colourless oil in 50% yield. ^{1}H-NMR (300 MHz, CD_3COCD_3) δ 7.34 (d, J = 12.0, 1H), 7.21 (td, J = 11.7, J = 0.9, 1H), 7.08 (d, J = 9.2, 2H), 6.95 (d, J = 9.2, 2H), 6.75 (app. t, J = 11.7, 1H), 5.53 (d, J = 11.2, 1H), 3.79 (s, 3H), 3.65 (s, 3H); ^{13}C-NMR (75 MHz, CD_3COCD_3) δ 167.3, 157.0, 142.9, 119.5 (2C), 118.4, 115.8 (2C), 115.5, 114.0, 109.7, 56.0, 51.0; FTIR (neat) ν_{max} 3076, 2942, 2838, 1702, 1634, 1504, 1439, 1164, 1130, 833; HRMS (DE) exact mass calculated for $[M+H]^+$ ($C_{13}H_{15}O_4$) requires *m/z* 235.0968, found *m/z* 235.0970.

[5] Arndt, F. *Org. Synth., Coll. Vol. 2*, **1943**, 165.

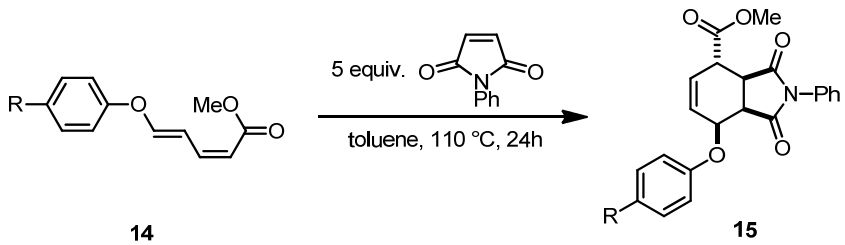
(2*Z*,4*E*)-methyl 5-(*p*-tolyloxy)penta-2,4-dienoate (14b)



14b

Compound **14b** was obtained as a colourless oil in 50% yield. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.40 (d, J = 12.0, 1H), 7.26 (app. td, J = 11.7, J = 1.0, 1H), 7.21 (d, J = 8.3, 2H), 7.03 (d, J = 8.3, 2H), 6.77 (app. t, J = 11.7, 1H), 5.55 (d, J = 11.4, 1H), 3.65 (s, 3H), 2.31 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 167.6, 156.2, 143.0, 134.7, 131.4 (2C), 118.1 (2C), 117.1, 114.4, 110.3, 51.1, 20.7; FTIR (neat) ν_{max} 2945, 1701, 1636, 1604, 1501, 1440, 1221, 1162, 926;HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{13}H_{15}O_3Na$) requires *m/z* 241.0831, found *m/z* 241.0835.

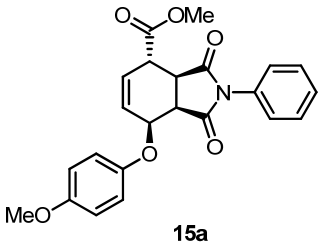
General procedure for Diels-Alder reactions of 4-aryloxy-dienyl methyl esters:



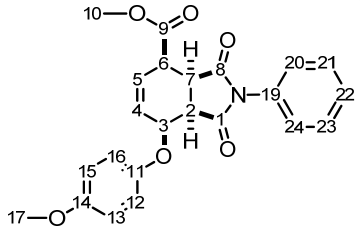
14 **15**

Diene methyl ester **14** (0.07 mmol) and *N*-Phenyl maleimide (0.36 mmol, 5.0 equiv.) in toluene (2 mL) were heated under reflux for 24h. Solvents were removed under vacuum and the product was purified by column chromatography on silica gel (pentane/EtOAc: 9/1) to afford cycloadduct **15**.

methyl-7-(4-methoxyphenoxy)-1,3-dioxo-2-phenyl-2,3,3a,4,7,7a-hexahydro-1*H*-isoindole-4-carboxylate (15a)



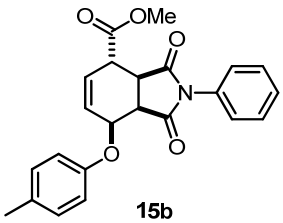
15a



Carbons numeration for ^{1}-H and ^{13}-C assignement

Compound **15a** (single diastereoisomer) was obtained as a pale yellow oil in 98% yield. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.50-7.37 (m, H_{21}, H_{23}), 7.44-7.37 (m, H_{22}), 7.32 (d, J = 7.7, H_{20}, H_{24}), 6.90 (d, J = 8.9, H_{12}, H_{16}), 6.83 (d, J = 8.9, H_{13}, H_{15}), 6.51 (m, H_4), 6.20 (dd, J = 9.5, 1.9, H_5), 5.27 (t, J = 4.6, H_3), 4.09 (dd, J = 9.8, J = 6.8, H_7), 3.80 (s, $3H_{10}$), 3.75 (m, H_6), 3.74 (s, $3H_{17}$), 3.45 (dd, J 10.2, 3.7, H_2); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 179.0 (C_8), 175.9 (C_1), 173.8 (C_9), 155.8 (C_{14}), 152.0 (C_{11}), 133.9 (C_8), 132.1 (C_5), 129.9 (C_4), 129.8 (C_{21}, C_{23}), 129.1 (C_{22}), 127.9 (C_{20}, C_{24}), 118.2 (C_{12}, C_{16}), 115.5 (C_{13}, C_{15}), 70.3 (C_3), 55.9 (C_{17}), 53.1 (C_{10}), 45.4 (C_2), 41.1 (C_6), 39.7 (C_7). MS (EI) *m/z* (%) = 252 (35), 124 (100), 119 (39); FTIR (neat) ν_{max} 2954, 1710, 1504, 1383, 1196, 1212, 1172, 1030, 822, 753, 691; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{23}H_{21}NO_6Na$) requires *m/z* 430.1263, found *m/z* 430.1261.

methyl-1,3-dioxo-2-phenyl-7-(*p*-tolyloxy)-2,3,3a,4,7,7a-hexahydro-1*H*-isoindole-4-carboxylate (15b)



15b

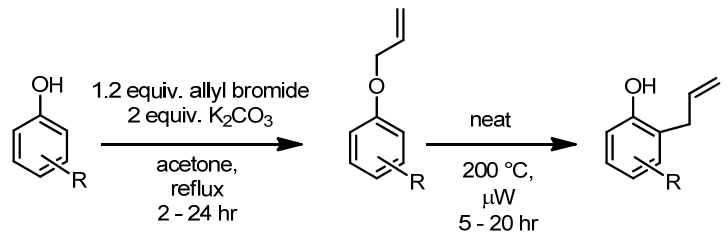
Compound **15b** (dr = 85:15) was obtained as a pale yellow oil in 80%. Data for major isomer: ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.50-7.36 (m, 3H), 7.33-7.31 (m, 2H), 7.07 (d, J 8.2, 2H), 6.85 (d, J 8.8, 2H), 6.55 (qd, J 5.3, 3.7, 1H), 6.19 (dd, J 9.6, 2.6, 1H), 5.34 (dd, J 6.0, 4.1,

1H), 4.10 (dd, J = 10.8, J = 6.9, 1H), 3.80 (s, 3H), 3.72 (m, 1H), 3.46 (dd, J = 10.8, J = 4.1, 1H), 2.23 (s, 3H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 178.9, 175.8, 173.7, 155.8, 133.9, 132.1, 131.6, 130.8 (2C), 129.9, 129.8 (2C), 129.1, 127.8 (2C), 116.6 (2C), 69.5, 53.1, 45.3, 41.1, 39.7, 20.6; FTIR (neat) ν_{max} 3029, 2953, 1710, 1499, 1507, 1382, 1224, 1173; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{23}H_{21}NO_5Na$) requires *m/z* 414.1310, found *m/z* 414.1312.

8. Intramecular Diels-Alder reactions of 4-aryloxy-dienyl methyl esters

Preparation of *O*-allyl-phenol

o-allyl phenol and 2-allyl-6-methoxyphenol were purchased from Aldrich. Methyl 3-allyl-4-hydroxybenzoate, 2-allyl-3,5-dimethoxyphenol and (3-allyl-4-hydroxyphenyl)(phenyl) methanone were synthesized according to the scheme below:



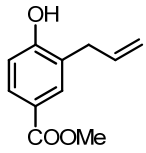
General procedure for *O*-allylation of phenols:

The desired phenol (1 equiv.) was dissolved in acetone (0.2 M), K_2CO_3 (2 equiv.) and allyl bromide (1.2 equiv.) were added. The resulting mixture was heated at reflux untill complete consumption of the starting material was detected by TLC (3 – 24 hours). The reaction mixture was allowed to cool to room temperature and the solid was filtered off. The solvent was removed under vacuum to afford a crude residue which was used in the next step withouth further purification.

General procedure for Claisen rearrangement:

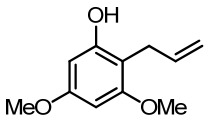
The desired *O*-allyl phenol was poured in a microwave tube, purged with Ar and heated in a microwave oven (200 W) at 200 °C. The product was purified by column chromatography or cristalized to afford the *O*-allyl phenols.

methyl 3-allyl-4-hydroxybenzoate



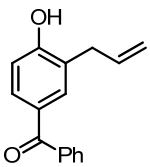
The reaction was stopped after 10h, although the starting material was not completely consumed. The product was purified by cristalization from pentane to afford methyl 3-allyl-4-hydroxybenzoate (65% yield).[6]

2-allyl-3,5-dimethoxyphenol



The reaction was stopped after 5h and the product was purified by column chromatography (pentane/EtOAc: 97/3 to 95/5) to afford 2-allyl-3,5-dimethoxyphenol (76% yield). ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 8.11 (s, 1H), 6.11 (d, J = 2.2, 1H), 6.09 (d, J = 2.2, 1H), 5.88 (m, 1H), 4.93 (d, J = 16.6, 1H), 4.83 (d, J = 9.9, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.30 (d, J = 6.4, 2H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 160.4, 160.1, 157.0, 138.2, 113.8, 107.6, 94.5, 90.9, 55.8, 55.3, 27.6.

(3-allyl-4-hydroxyphenyl)(phenyl)methanone



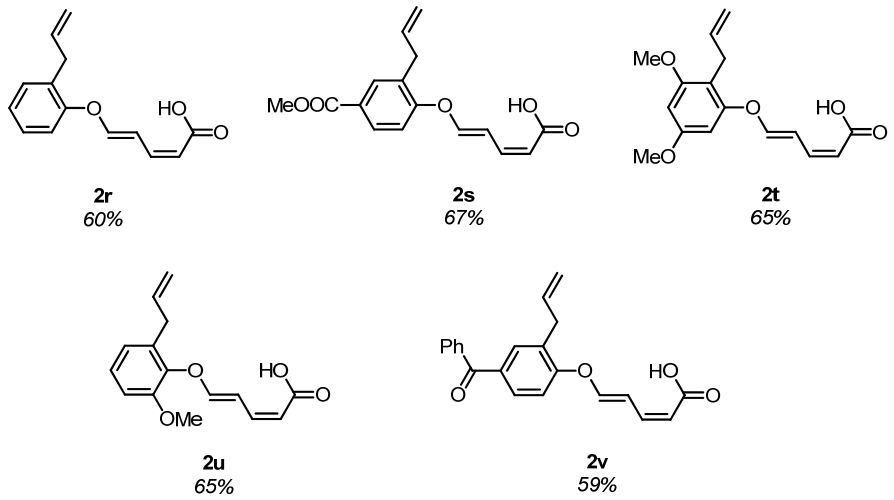
The reaction was stopped after 20h, although the starting material was not completely consumed. The product was purified by column chromatography (pentane/EtOAc: 9/1) to afford (3-allyl-4-hydroxyphenyl)(phenyl)methanone (62% yield). ^{1}H-NMR (500 MHz,

[6] J. A. Burlison, L. Neckers, A. B. Smith, A. Maxwell, B. S. J. Blagg, *J. Am. Chem. Soc.* **2006**, *128*, 15529-15536.

CD_3COCD_3) δ 9.25 (br s, 1H), 7.73-7.71 (m, 2H), 7.66 (d, J = 2.2, 1H), 7.61 (ddd, J = 7.4, J = 6.6, J = 2.0, 1H), 7.56 (dd, J = 8.2, J = 2.2, 1H), 7.54-7.51 (m, 2H), 6.98 (d, J = 8.2, 1H), 6.03 (m, 1H), 5.09 (d, J = 17.3, 1H), 5.03 (d, J = 10.0, 1H), 3.44 (d, J = 6.7, 2H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 195.3, 160.3, 139.6, 137.3, 133.3, 132.5, 131.4, 130.2 (2C), 130.1, 129.1 (2C), 127.6, 116.1, 115.4, 34.8.

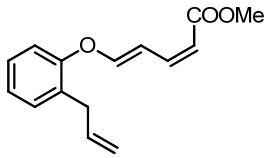
Preparation of dienes 2r-v

Dienes **2r-v** were synthesized according to the general procedure reported at page S5. After work-up the crude material was carried to the next step withouth any further purification. The ^{1}H-NMR internal standard yields (internal standard = 1,3,5-trimethoxybenzene) are listed below:



Crude carboxylic acid **2** was dissolved in dichlorometane (0.1 M) and the resulting solution was cooled to 0 °C. DMF (1 drop) followed by oxalyl chloride (2 equiv. assuming a quantitative yield of formation of the carboxylic acids **2r-v** in the Tsuji-Trost reaction) were added dropwise and the resulting mixture was stirred for 30 min at 0 °C. MeOH (25 equiv.) was added dropwise and after 30 min at 0 °C, the reaction mixture was quenched with a saturated solution of $NaHCO_3$ and diluted with CH_2Cl_2. The layers were separated and the aqueous phase was exctracted 3 times with CH_2Cl_2. The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under vacuum and the product was purified by column chromatography (pentane/EtOAc: 98/2) to give ester **16a-e**.

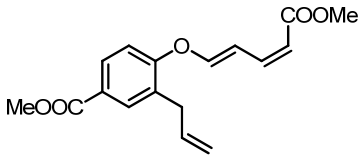
(2*Z*,4*E*)-methyl 5-(2-allylphenoxy)penta-2,4-dienoate (16a)



16a

Compound **16a** was obtained in 33% isolated yield over 2 steps (Tsuji-Trost allylation and ester formation). ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.37 (d, J = 12.1, 1H), 7.32-7.22 (m, 3H), 7.18-7.10 (m, 2H), 6.78 (app. t, J = 11.5, 1H), 5.97 (m, 1H), 5.56 (d, J = 11.2, 1H), 5.05 (d, J = 16.5, 1H), 5.03 (d, J = 9.2, 1H), 3.65 (s, 3H), 3.41 (d, J = 6.5, 2H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 167.4, 156.5, 155.0, 142.7, 137.3, 131.4, 131.1, 128.7, 125.4, 118.1, 116.2, 114.2, 110.1, 51.0, 34.7; FTIR (neat) ν_{max} 1708, 1635, 1488, 1439, 1165, 1146, 930;HRMS exact mass calculated for $[M+Na]^+$ ($C_{15}H_{16}O_3Na$) requires *m*/*z* 267.0992, found *m*/*z* 267.0989.

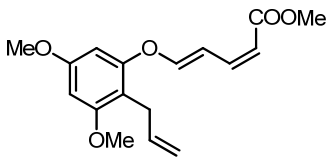
methyl 3-allyl-4-(((1*E*,3*Z*)-5-methoxy-5-oxopenta-1,3-dien-1-yl)oxy)benzoate (16b)



16b

Compound **16b** was obtained in 46% isolated yield over 2 steps (Tsuji-Trost allylation and ester formation). ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.95-7.90 (m, 2H), 7.49 (d, J = 12.0, 1H), 7.37 (app. t, J = 11.7, 1H), 7.25 (d, J 8.4, 1H), 6.81 (app. t, J = 11.7, 1H), 5.99 (m, 1H), 5.62 (d, J = 11.2, 1H), 5.10 (d, J = 15.9, 1H), 5.08 (d, J 8.7, 1H), 3.86 (s, 3H), 3.67 (s, 3H), 3.48 (d, J = 6.7, 2H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 167.3, 166.5, 158.5, 154.4, 142.0, 136.7, 132.6, 131.0, 130.4, 126.8, 116.8, 116.7, 115.4, 111.6, 52.3, 51.1, 34.5; FTIR (neat) ν_{max} 1710, 1638, 1604, 1437, 1165, 1140; HRMS exact mass calculated for $[M+Na]^+$ ($C_{17}H_{18}O_5Na$) requires *m*/*z* 325.1046, found *m*/*z* 325.1047.

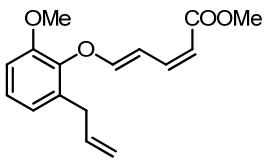
(2*Z*,4*E*)-methyl 5-(2-allyl-3,5-dimethoxyphenoxy)penta-2,4-dienoate (16c)



16c

Compound **16c** was obtained in 43% isolated yield over 2 steps (Tsuji-Trost allylation and ester formation). ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.33 (d, J = 12.2, 1H), 7.25 (app. t, J = 11.9, 1H), 6.75 (app. t, J = 11.9, 1H), 6.42 (d, J = 2.2, 1H), 6.35 (d, J = 2.2, 1H), 5.86 (m, 1H), 5.55 (d, J = 11.2, 1H), 4.91 (d, J = 17.1, 1H), 4.88 (d, J = 9.9, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.65 (s, 3H), 3.30 (d, J = 6.2, 2H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 167.4, 160.8, 160.0, 156.5, 156.2, 142.8, 137.4, 114.7, 114.1, 111.4, 110.0, 96.1, 95.5, 56.2, 55.8, 51.0, 27.7; FTIR (neat) ν_{max} 1709, 1581, 1604, 1438, 1416, 1145, 1065, 993, 932, 816; HRMS exact mass calculated for $[M+Na]^+$ ($C_{17}H_{20}O_5Na$) requires *m*/*z* 327.1208, found *m*/*z* 327.1211.

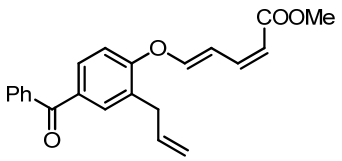
(2*Z*,4*E*)-methyl 5-(2-allyl-6-methoxyphenoxy)penta-2,4-dienoate (16d)



16d

Compound **16d** was obtained in 44% isolated yield over 2 steps (Tsuji-Trost allylation and ester formation). ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.19-7.13 (m, 2H), 7.04-6.97 (m, 2H), 6.86 (d, J = 7.9, 1H), 6.69 (app. t, J = 11.5, 1H), 5.93 (m, 1H), 5.47 (d, J = 11.2, 1H), 5.05 (d, J = 18.7, 1H), 5.01 (d, J = 11.8, 1H), 3.82 (s, 3H), 3.61 (s, 3H), 3.34 (d, J = 6.6, 2H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 167.5, 159.6, 152.4, 143.3, 143.2, 137.2, 134.0, 126.9, 122.7, 116.3, 113.0, 112.0, 107.3, 56.3, 50.9, 34.6; FTIR (neat) ν_{max} 1708, 1632, 1476, 1439, 1274, 1162, 994, 928, 815, 757; HRMS exact mass calculated for $[M+Na]^+$ ($C_{16}H_{18}O_4Na$) requires *m*/*z* 297.1097, found *m*/*z* 297.1099.

(2*Z*,4*E*)-methyl 5-(2-allyl-6-methoxyphenoxy)penta-2,4-dienoate (16e)



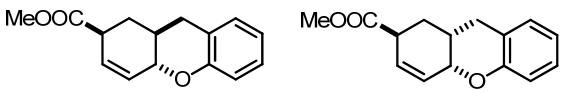
16e

Compound **16e** was obtained in 65% isolated yield over 2 steps (Tsuji-Trost allylation and ester formation). ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.77-7.75 (m, 3H), 7.73 (dd, J = 8.2, 2.2, 1H), 7.66 (m, 1H), 7.57-7.52 (m, 3H), 7.41 (dd, J = 12.0, 1.0, 1H), 7.30 (d, J = 8.4, 1H), 6.83 (app. t, J = 11.6, 1H), 6.01 (m, 1H), 5.63 (d, J = 11.2, 1H), 5.13-5.06 (m, 2H), 3.68 (s, 3H), 3.51 (d, J = 6.6, 2H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 195.4, 167.5, 158.3, 154.6, 142.2, 138.8, 136.7, 134.3, 133.3, 133.2 (2C), 131.2, 131.1, 130.5 (2C), 129.3 (2C), 116.9, 115.5, 111.8, 51.3, 34.8. FTIR (neat) ν_{max} 3080, 2949, 1637, 1192, 1162, 1135;

General procedure for intramolecular Diels-Alder reaction

A microwave tube containing diene **16a-e** and toluene (0.1 M) was purged with Ar and heated at 180 °C for 20 hours in a microwave oven (200 W). The solvent was removed under vacuum and the product was purified by column chromatography. All intramolecular Diels-alder reactions described in this section were performed on a 0.5 mmol scale.

Cycloadducts 17a/17a*

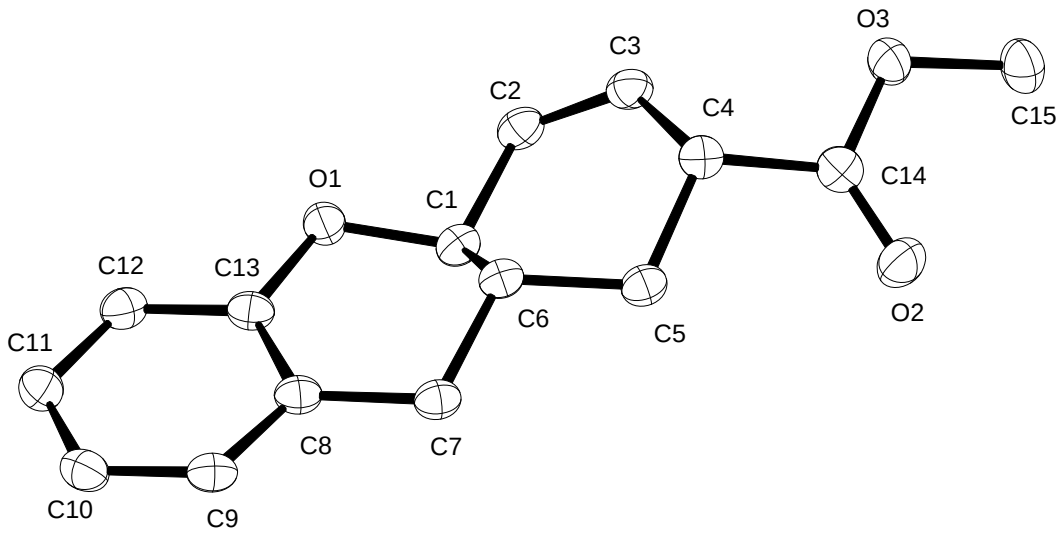


17a **17a***

Some unreacted diene was observed in the ^{1}H-NMR of the crude reaction mixture. The product was purified by column chromatography (pentane/EtOAc from 98/2 to 95/5) to afford cycloadducts **17a/17a*** (79/21* mixture of diastereomers, 52%). The product was obtaines in 60% isolated yield based on the recovered starting material. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.13-7.03 (m, 2H, 2H*), 6.89-6.83 (m, 2H, 1H*), 6.81 (d, J = 8.2, 1H*), 6.10 (ddd, J = 10.0, J = 4.3, J = 2.2, 1H*), 6.04 (dd, J = 10.0, J = 4.1, 1H*), 6.01 (dm, J = 10.2, 1H), 5.96 (dm, J = 10.2, 1H), 4.53 (t, J = 3.9, 1H*), 4.27 (dm, J = 9.6, 1H), 3.74 (s, 3H), 3.73 (s, 3H*), 3.39 (m, 1H), 3.30 (m, 1H*), 3.02 (dd, J = 16.6, J = 6.6, 1H*), 2.78 (dd, J = 16.0, J = 4.9, 1H),

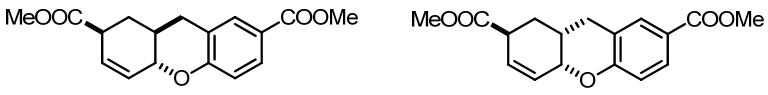
2.64 (dd, J = 16.0, J = 12.0, 1H), 2.62 (dd, J = 16.5, J = 4.4, 1H*), 2.40 (m, 1H*), 2.26 (dddd, J = 13.4, J = 5.7, J = 2.9, J = 1.3, 1H), 2.03-1.94 (m, 1H, 2H*), 1.68 (dt, J = 13.1, J = 11.5, 1H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 173.9, 173.8*, 155.1, 153.4*, 129.9, 129.8*, 129.5, 129.2*, 128.7*, 127.5, 127.3*, 127.2, 122.3, 120.7, 120.5*, 120.4*, 117.0, 116.6*, 76.0, 69.8, 52.3 (1C+1C*), 42.5, 40.2*, 34.2, 32.1, 29.9, 28.8*, 28.4*, 25.9*; FTIR (neat) ν_{max} 1736, 1579, 1488, 1454, 1440, 1236, 1176, 1051, 931; HRMS exact mass calculated for $[M+Na]^+$ ($C_{15}H_{16}O_3Na$) requires m/z 267.0992, found m/z 267.0990.

A mixture of diastereomers **17a** and **17a*** was repetedly purified by column chromatograpy and crystalization to yield an analitycally pure sample of the main diastereomer **17a**. Crystals suitable for X-ray crystallographic analysis were prepared by crystallization from dichloromethane/heptane.



Crystal structure analysis of the major isomer **17a** crystallized from CH_2Cl_2/Heptanes (Cambridge Crystallographic Data Centre number: 887606).

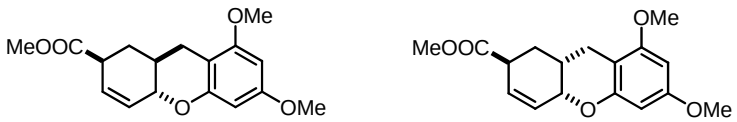
Cycloadducts 17b/17b*



17b **17b***

Some unreacted diene was observed in the ^{1}H-NMR of the crude reaction mixture. The product was purified by column chromatography (toluene/EtOAc from 98/2 to 95/5) to afford cycloadducts **17b/17b*** (78/22* mixture of diastereomers, 42%). The product was obtaines in 54% isolated yield based on the recovered starting material. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.81-7.75 (m, 2H, 2H*), 6.85 (d, J = 8.7, 1H), 6.80 (d, J = 9.1, 1H*), 6.10-6.03 (m, 2H*), 6.03-5.95 (m, 2H), 4.61 (m, 1H*), 4.32 (dm, J = 9.8, 1H), 3.87 (s, 3H), 3.86 (s, 3H*), 3.74 (s, 3H), 3.73 (s, 3H*), 3.38 (m, 1H), 3.29 (m, 1H*), 3.02 (dd, J = 16.7, J = 6.5, 1H*), 2.81 (dd, J = 16.1, J = 4.9, 1H), 2.64 (dd, J = 16.4, J = 12.2, 1H, 1H*), 2.43 (m, 1H*), 2.29 (m, 1H), 2.03-1.87 (m, 1H, 2H*), 1.69 (app q, J = 12.0 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.7, 173.6*, 167.1*, 167.0, 159.2, 157.6*, 132.0, 131.9*, 129.4, 129.0, 128.9*, 128.7*, 127.6 (1C+1C*), 122.5, 122.3*, 122.2, 120.1*, 117.0, 116.5*, 76.7, 70.6*, 52.3 (1C+1C*), 52.0, 51.0*, 42.4, 40.1*, 34.0, 31.9, 29.8, 28.6*, 28.1*, 25.7*; FTIR (neat) ν_{max} 2957, 2924, 1729, 1707, 1613, 1578, 1494, 1437, 1319, 1161, 1094, 1034, 837, 767, 699; HRMS exact mass calculated for $[M+Na]^+$ ($C_{17}H_{18}O_5Na$) requires m/z 325.1046, found m/z 325.1044.

Cycloadducts 17c/17c*

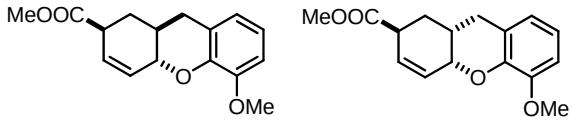


17c **17c***

The product was purified by column chromatography (toluene/EtOAc from 98/2 to 95/5) to afford cycloadducts **17c/17c*** (78/22* mixture of diastereomers, 65%). ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 6.10 (d, J = 2.2, 1H), 6.07 (d, J = 2.2, 1H*), 6.00 (d, J = 2.2, 1H), 5.98-5.94 (m, 3H*), 5.94-5.88 (m, 2H), 4.48 (m, 1H*), 4.15 (dd, J = 9.6, J = 3.3, 1H), 3.78 (s, 3H), 3.77 (s, 3H*), 3.72 (s, 3H), 3.71 (s, 3H*), 3.69 (s, 3H), 3.68 (s, 3H*), 3.41 (m, 1H), 3.33 (m, 1H*), 2.71 (dd, J = 16.4, J = 5.2, 1H), 2.69 (m, 1H*), 2.38 (dd, J = 16.7, J = 5.3, 1H*), 2.31 (m, 1H*), 2.23 (dddd, J = 13.2, J = 5.7, J = 2.6, 1H), 2.16 (dd, J = 16.2, J = 12.0, 1H), 1.98-1.88

(m, 2H*), 1.80 (m, 1H), 1.63 (app q, J = 12.0 1H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 174.0, 173.9*, 160.5, 160.3*, 159.5*, 159.5, 157.2, 155.3*, 129.9, 129.9*, 129.3*, 128.3, 104.4, 102.2*, 94.3, 94.1*, 92.0, 91.7*, 76.6, 70.5*, 55.7, 55.7*, 55.5, 55.4*, 52.1 (C, C*), 43.1, 40.6*, 34.7, 30.6, 28.6*, 27.0*, 26.9, 22.9*; FTIR (neat) ν_{max} 2942, 2927, 1735, 1618, 1586, 1494, 1213, 1197, 1142, 1117, 1054, 806; HRMS exact mass calculated for $[M+Na]^+$ ($C_{17}H_{20}O_5Na$) requires *m/z* 327.1205, found *m/z* 327.1203.

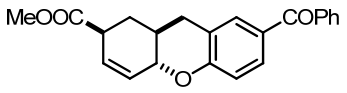
Cycloadducts 17d/17d*



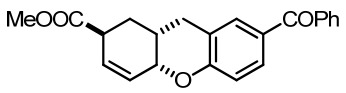
17d **17d***

Some unreacted diene was observed in the ^{1}H-NMR of the crude reaction mixture. The product was purified by column chromatography (toluene/EtOAc from 98/2 to 95/5) to afford cycloadducts **17d/17d*** (79/21* mixture of diastereomers, 57%). The product was obtaines in 67% isolated yield based on the recovered starting material. Data for **17d**: ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 6.78-6.74 (m, 2H), 6.66 (t, J = 4.6, 1H), 5.98 (dm, J = 10.4, 1H), 5.93 (dm, J = 10.4, 1H), 4.23 (dm, J = 9.5, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 3.44 (m, 1H), 2.77 (dd, J = 16.0, J = 5.1, 1H), 2.63 (dd, J = 16.0, J = 12.3, 1H), 2.25 (m, 1H), 1.92 (m, 1H), 1.65 (app q, J = 13.0, 1H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 174.0, 149.7, 145.7, 130.0, 128.2, 124.0, 122.4, 120.8, 110.7, 76.8, 56.0, 52.2, 43.0, 34.9, 32.5, 30.5; FTIR (neat) ν_{max} 2925, 2839, 1733, 1583, 1481, 1259, 1089, 1036, 926, 763, 729;HRMS exact mass calculated for $[M+Na]^+$ ($C_{16}H_{18}O_4Na$) requires *m/z* 297.1097, found *m/z* 297.1100.

Cycloadducts 17e/17e*

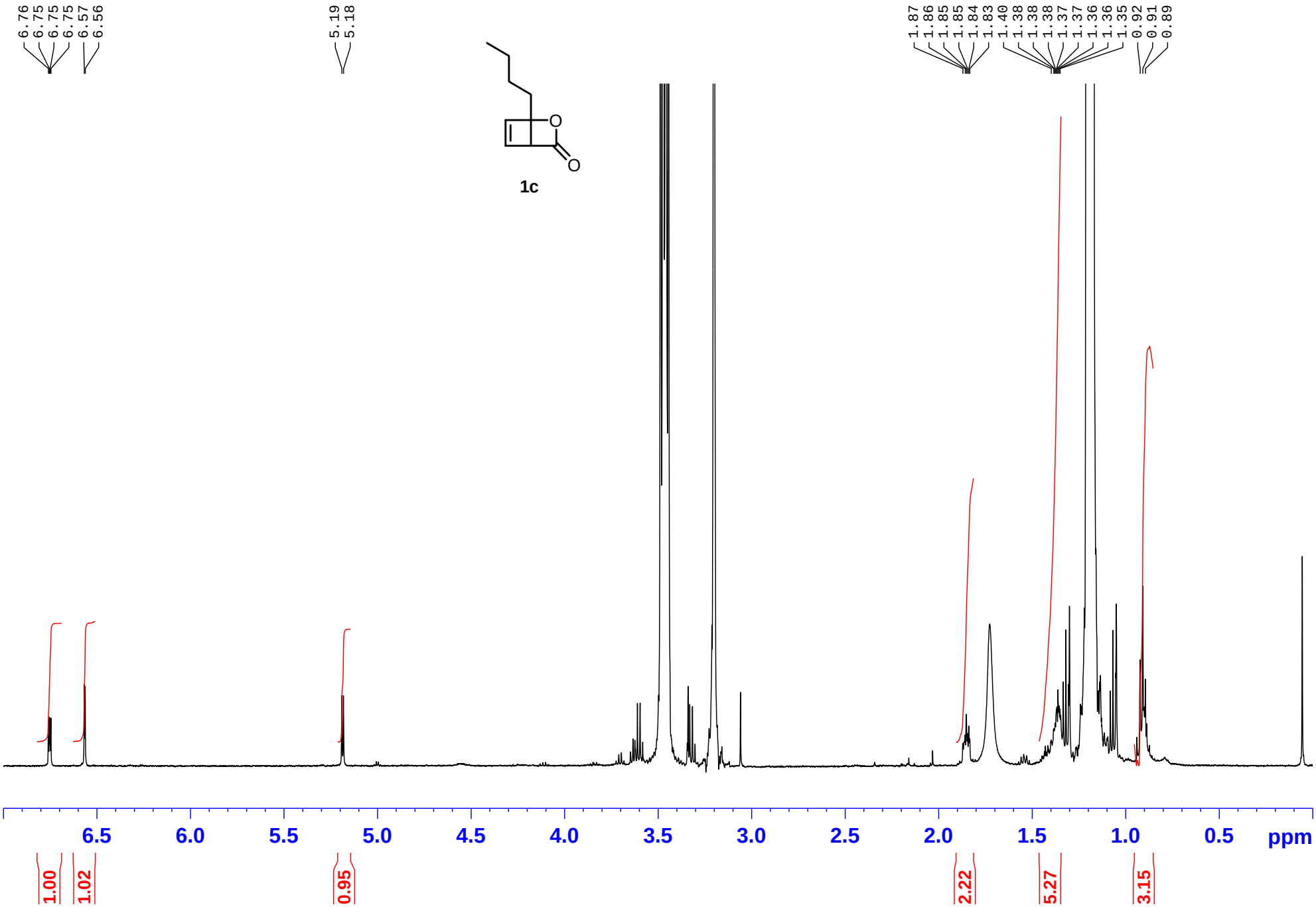


17e



17e*

Some unreacted diene was observed in the ^{1}H-NMR of the crude reaction mixture. The product was purified by column chromatography (toluene/EtOAc from 98/2 to 95/5) to afford cycloadducts **17e/17e*** (79/21* mixture of diastereomers, 48%). The product was obtaines in 55% isolated yield based on the recovered starting material. ^{1}H-NMR (500 MHz, CD_3COCD_3) δ 7.75-7.70 (m, 2H, 3H*), 7.68-7.50 (m, 5H, 4H*), 6.92 (d, J = 8.4, 1H), 6.86 (d, J = 8.4, 1H*), 6.05-6.00 (m, 2H*), 6.00-5.95 (m, 2H), 4.74 (m, 1H*), 4.41 (dd, J = 9.6, J = 3.6, 1H), 3.70 (s, 3H), 3.69 (s, 3H*), 3.46 (m, 1H), 3.36 (m, 1H*), 3.04 (dd, J = 16.6, J = 6.2, 1H*), 2.87 (dd, J = 16.1, J = 4.8, 1H), 2.77-2.68 (m, 1H, 1H*), 2.45 (m, 1H*), 2.28 (m, 1H), 2.04-1.87 (m, 1H, 2H*), 1.69 (app q, J = 12.9, 1H); ^{13}C-NMR (125 MHz, CD_3COCD_3) δ 195.2, 195.2*, 173.8, 173.7*, 159.9, 158.5*, 139.4*, 139.3, 133.4, 133.2*, 132.6, 132.5*, 130.8*, 130.7*, 130.6, 130.2 (2C), 130.2* (2C), 129.6*, 129.4, 129.2*, 129.1 (3C), 129.1 (2C)*, 128.7, 123.6, 121.5*, 117.4, 116.9*, 77.5, 71.7*, 52.2*, 52.2, 43.0, 40.3*, 34.8, 32.3, 30.3, 29.0*, 28.6*, 26.6*. FTIR (neat) ν_{max} 3044, 2951, 1732, 1648, 1602, 1572, 1236, 1118; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{22}H_{20}O_4Na$) requires *m/z* 371.1253, found *m/z* 371.1253.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0.91
0.89
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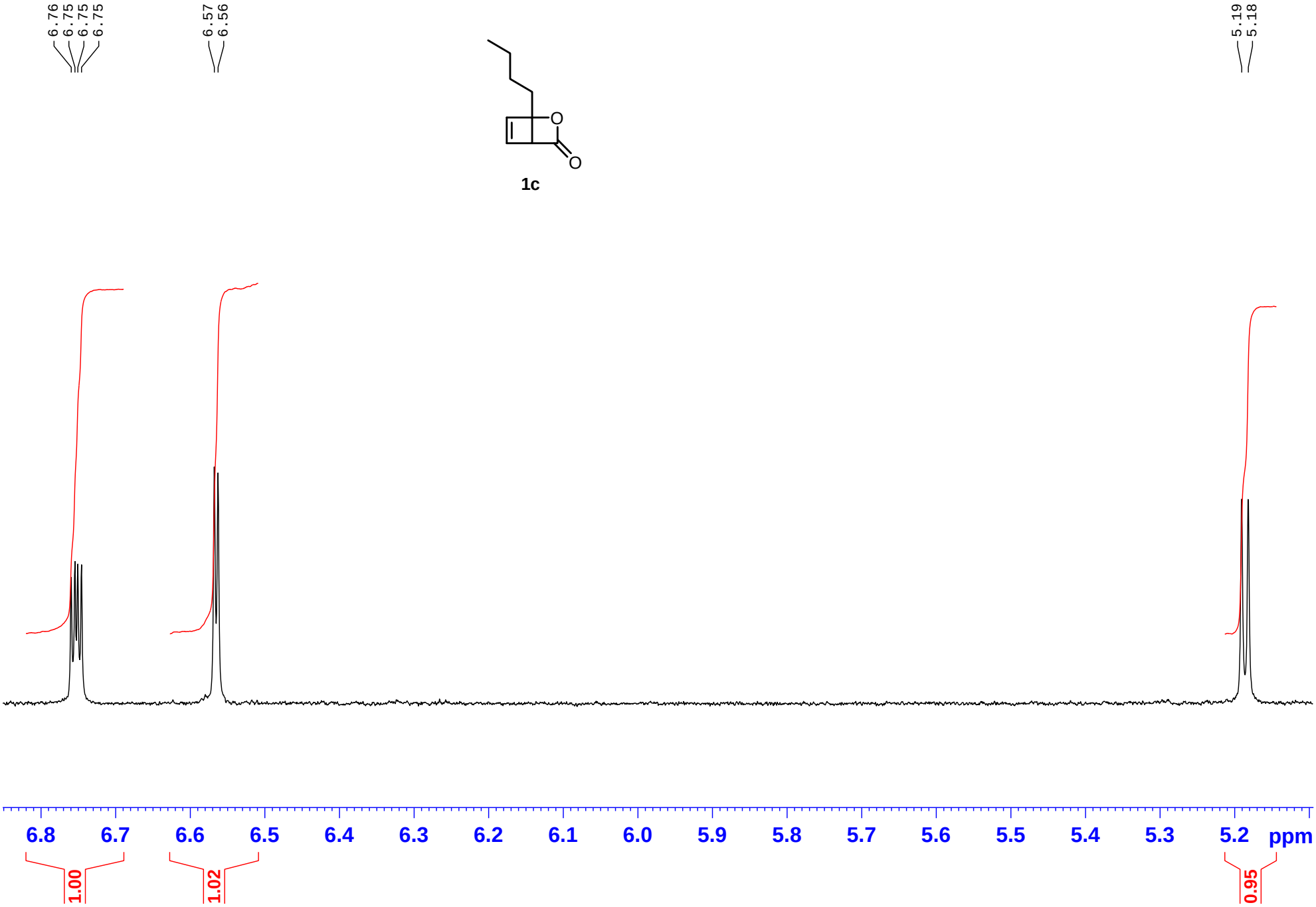
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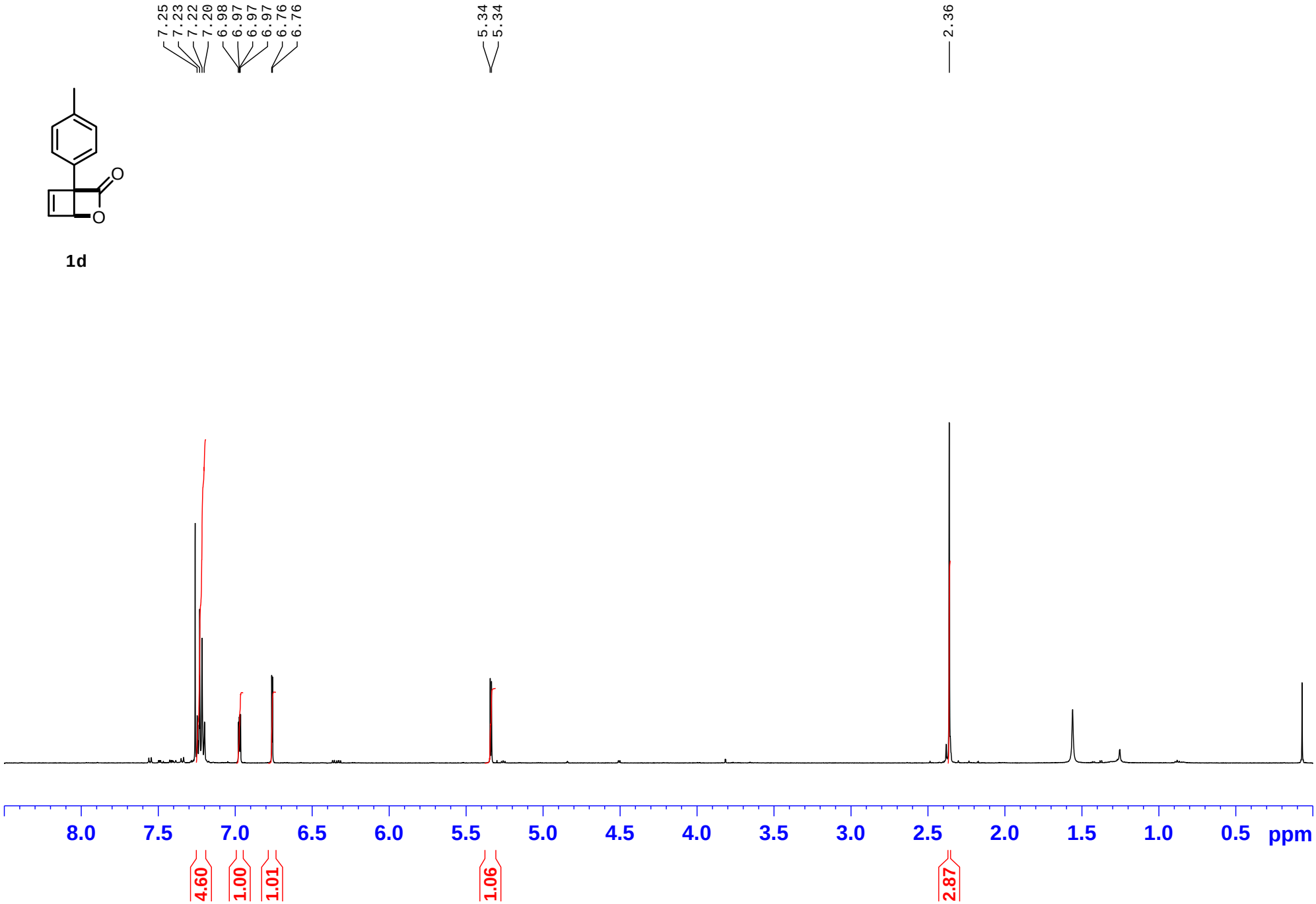
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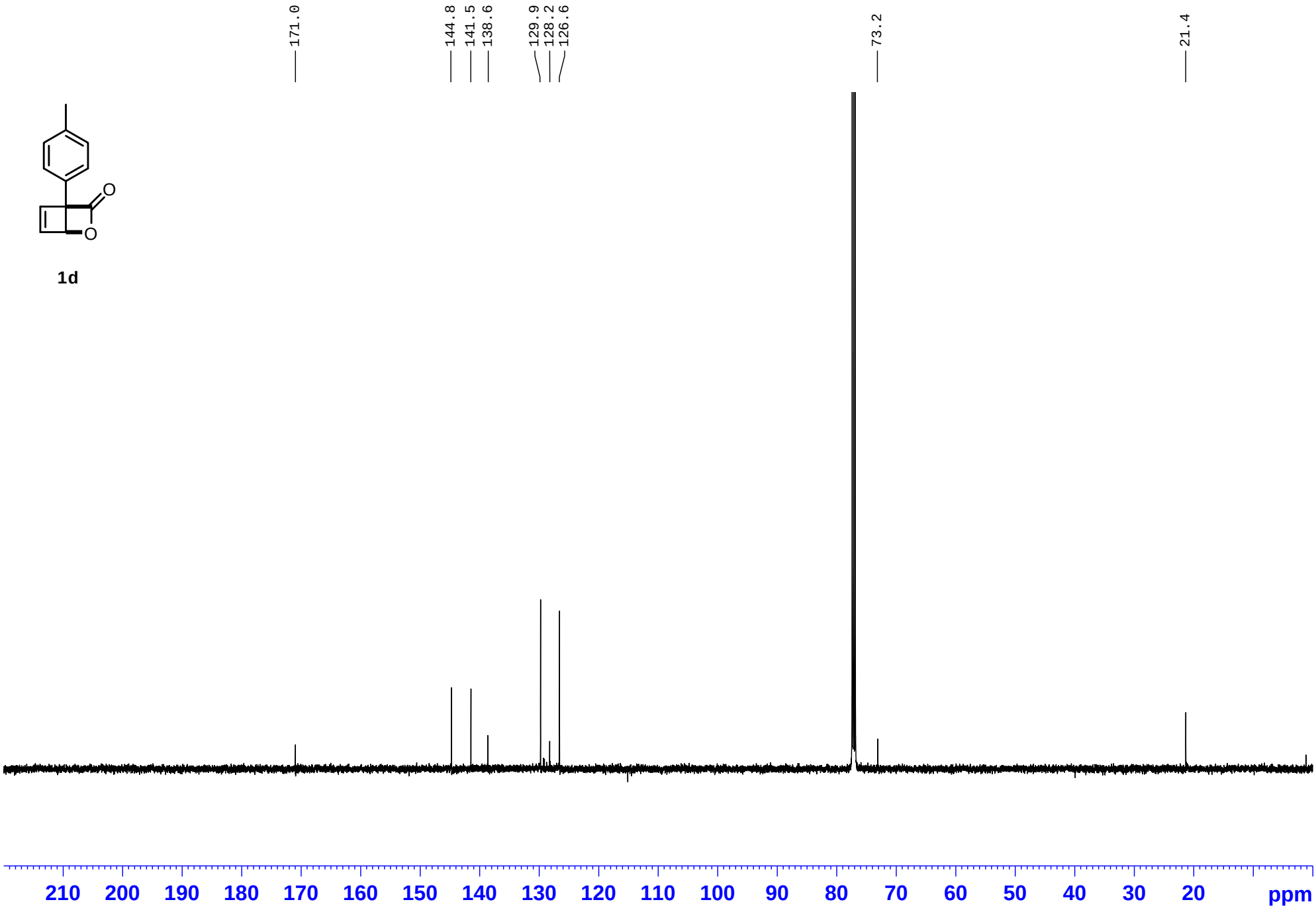
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30
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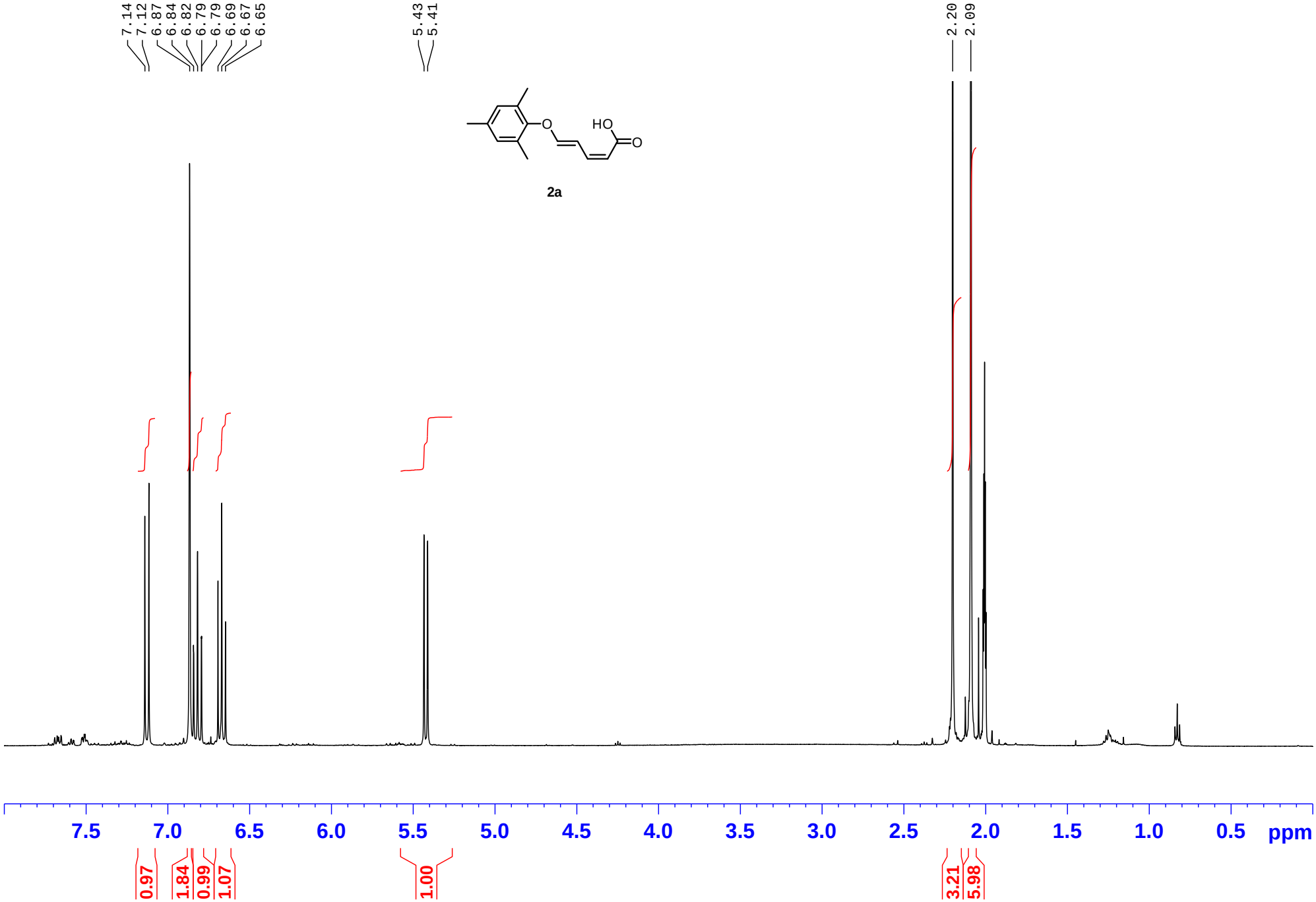
ppm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6.67
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5.41
2.20
2.09
HO
O
O
2a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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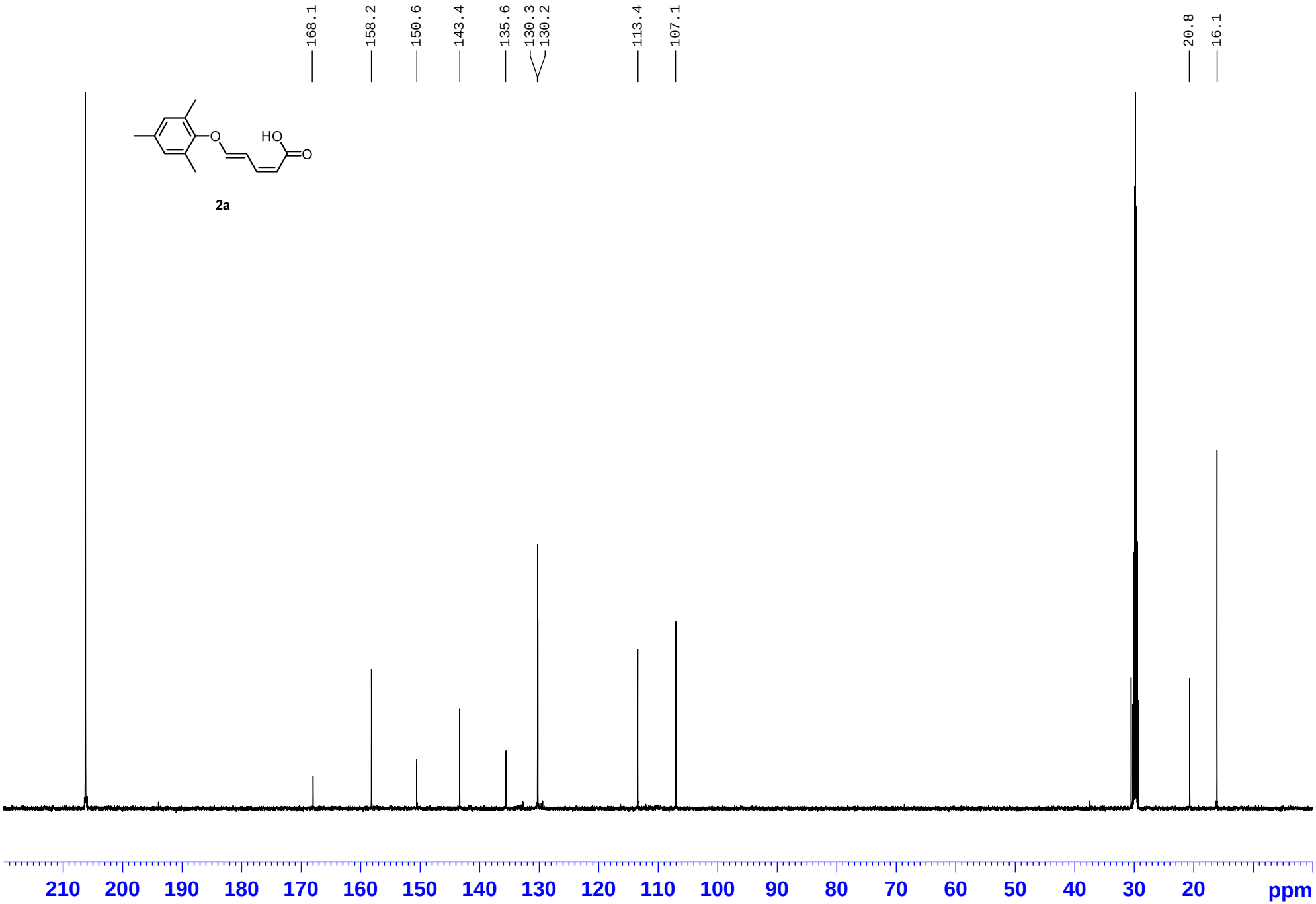
3.21
5.98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113.4
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16.1
HO
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O
2a
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150
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80
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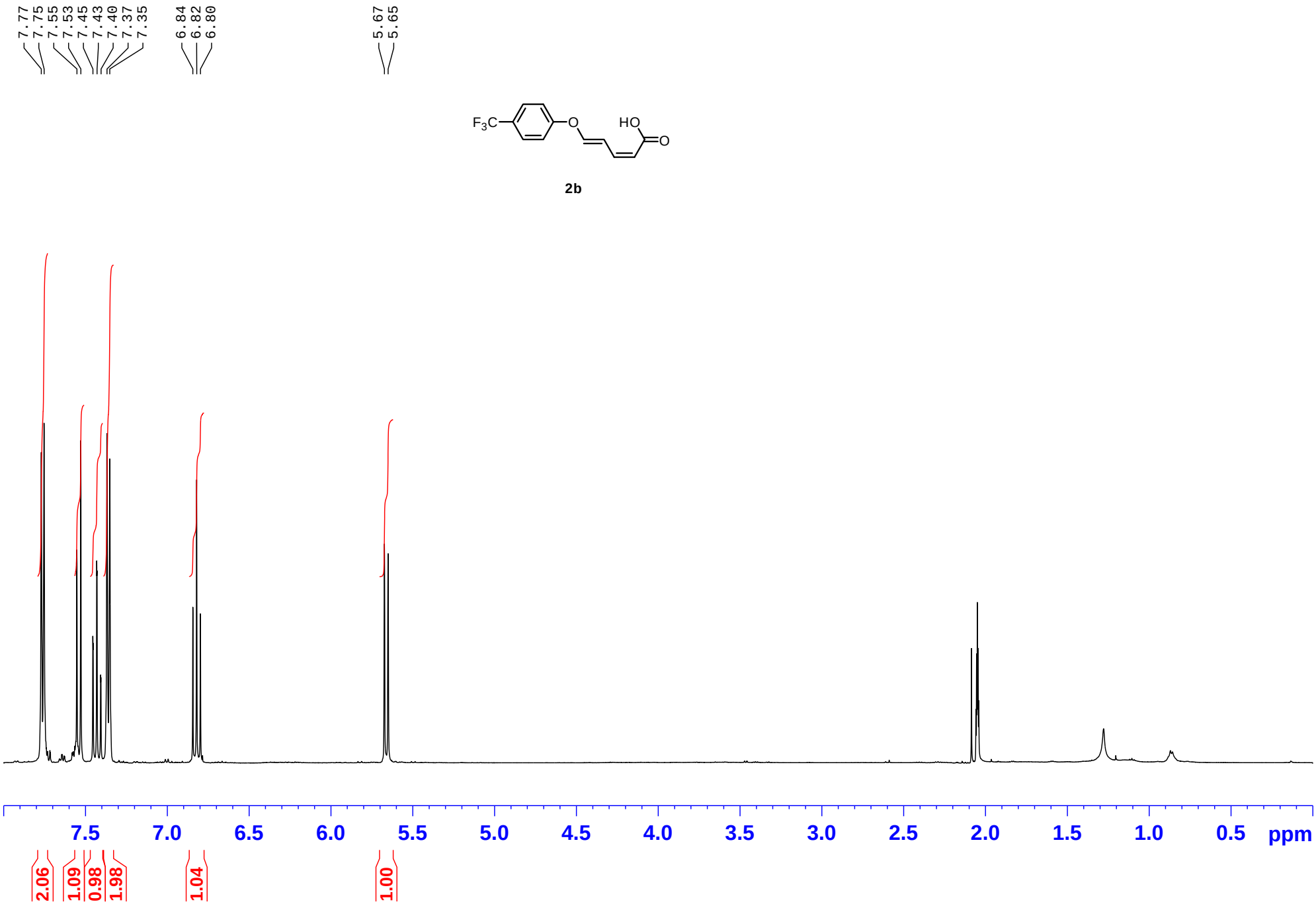
40
30
20
ppm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7.37
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6.82
6.80
5.67
5.65
F3C
O
HO
O
2b
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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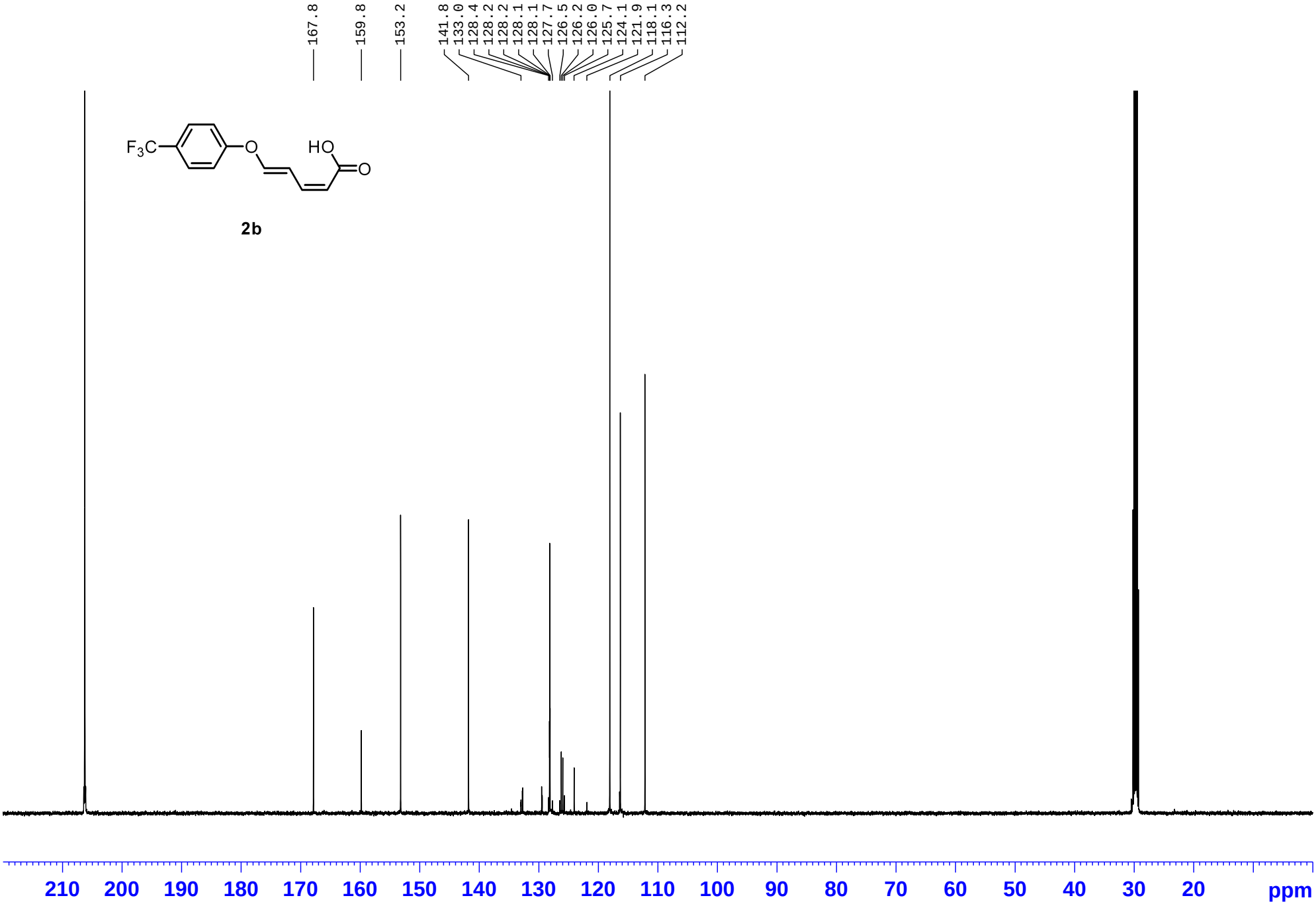
1.04
1.00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126.2
126.0
125.7
124.1
121.9
118.1
116.3
112.2
F3C
O
HO
O
2b
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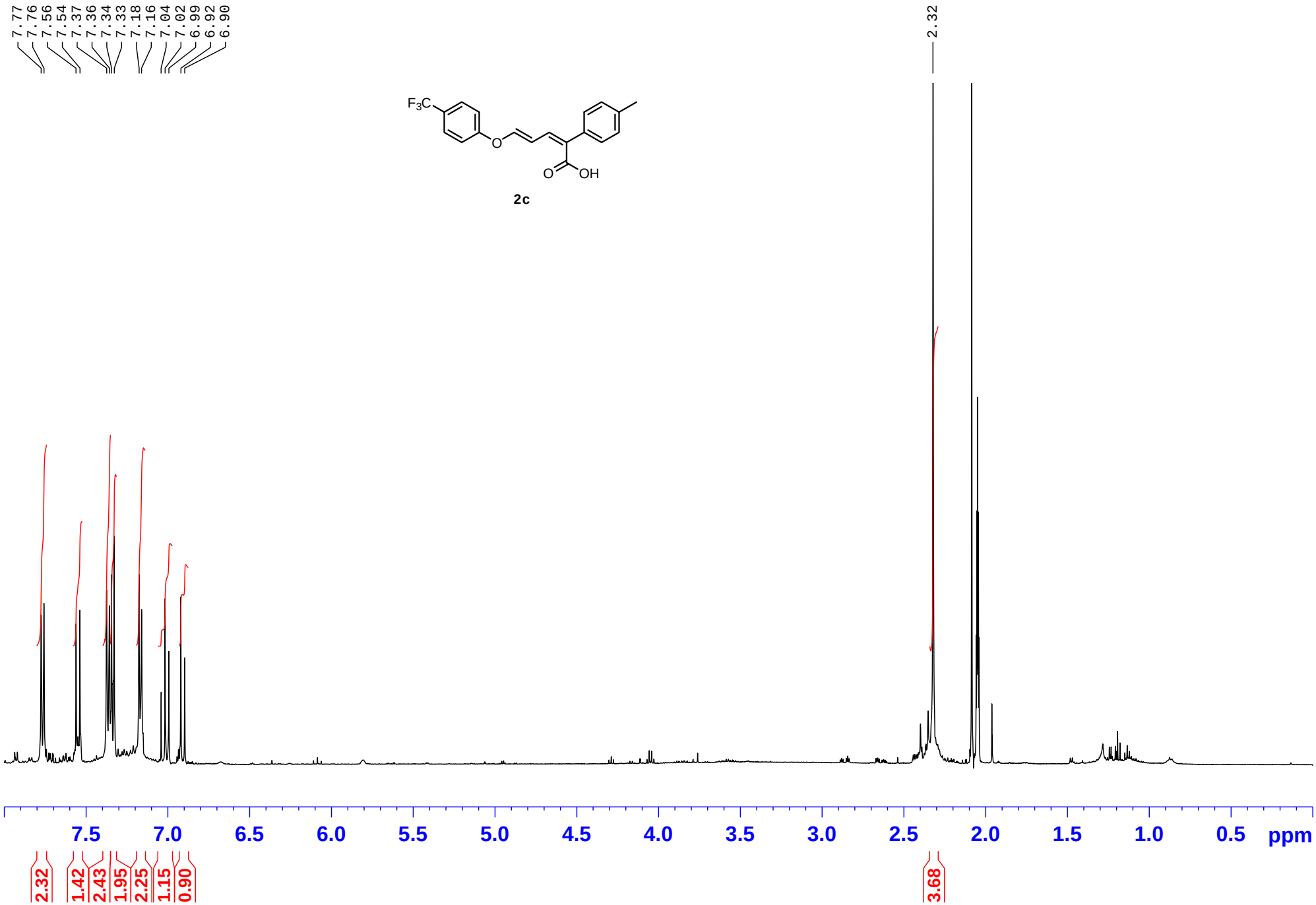
40
30
20
ppm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7.36
7.34
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7.16
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7.02
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6.92
6.90
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O
O
OH
2c
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.95
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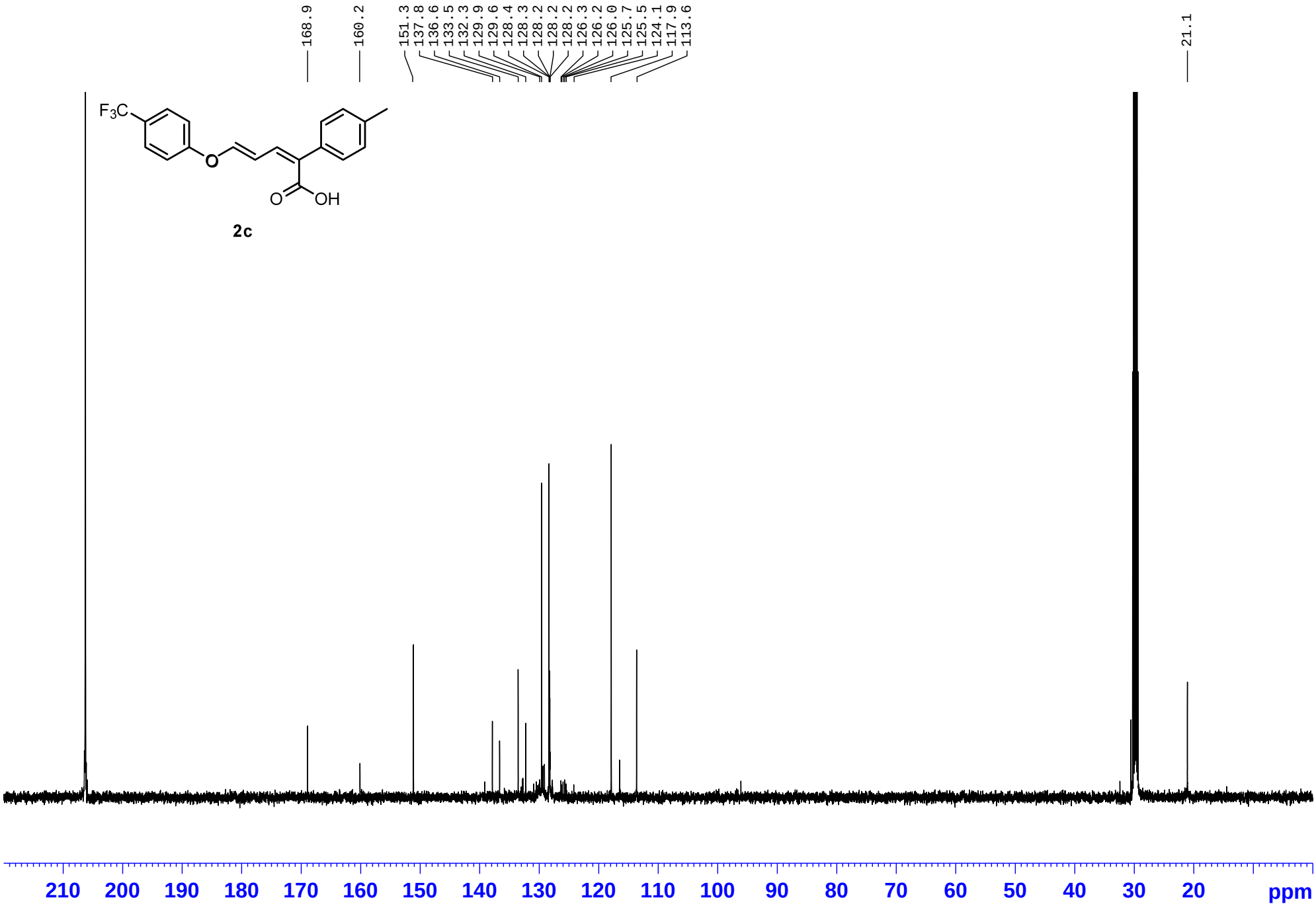
3.68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128.2
128.2
128.2
126.3
126.2
126.0
125.7
125.5
124.1
117.9
113.6
21.1
F3C
O
O
OH
2c
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200
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160
150
140
130
120
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100
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80
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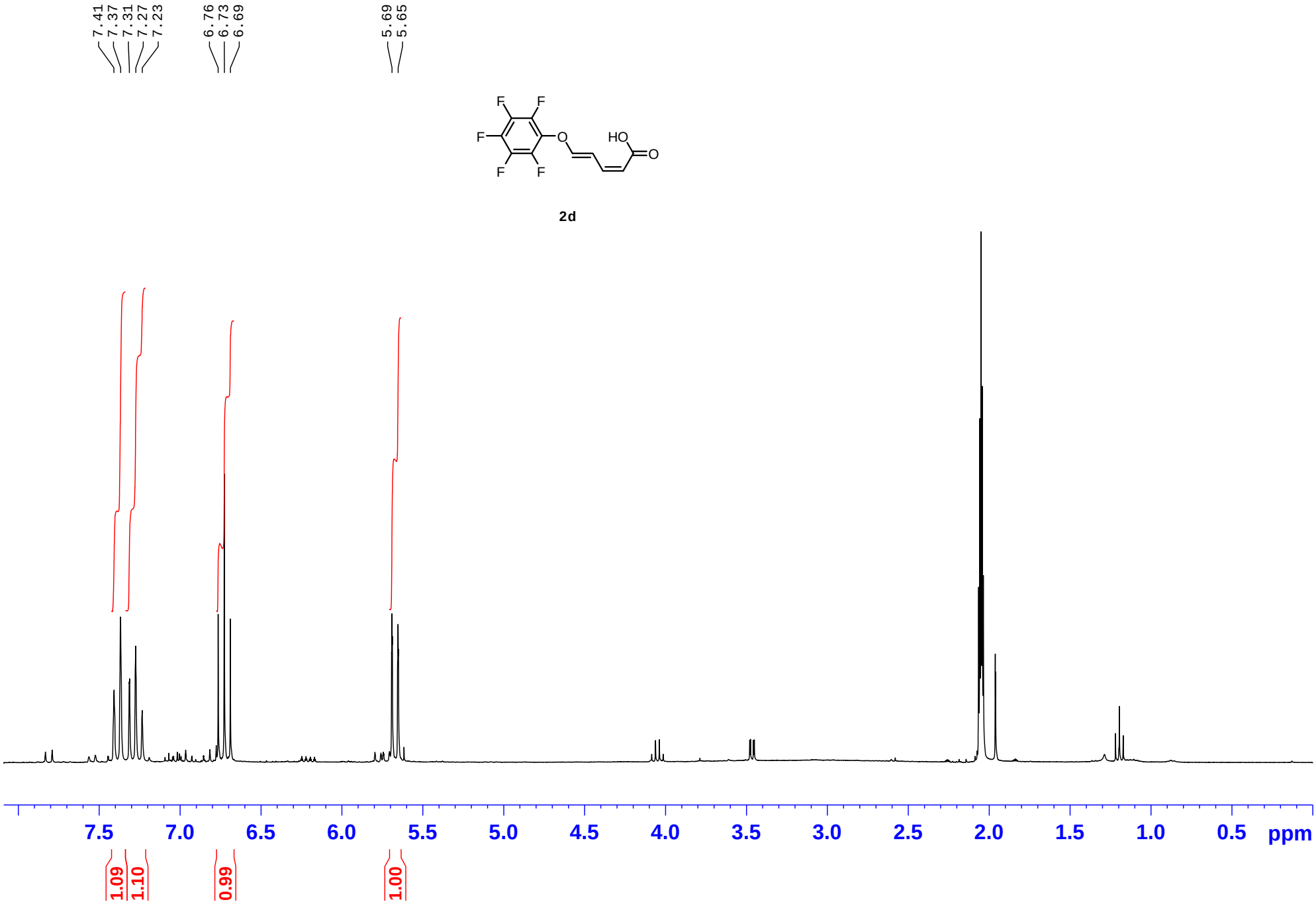
40
30
20
ppm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6.69
5.69
5.65
F
F
F
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HO
O
F
F
2d
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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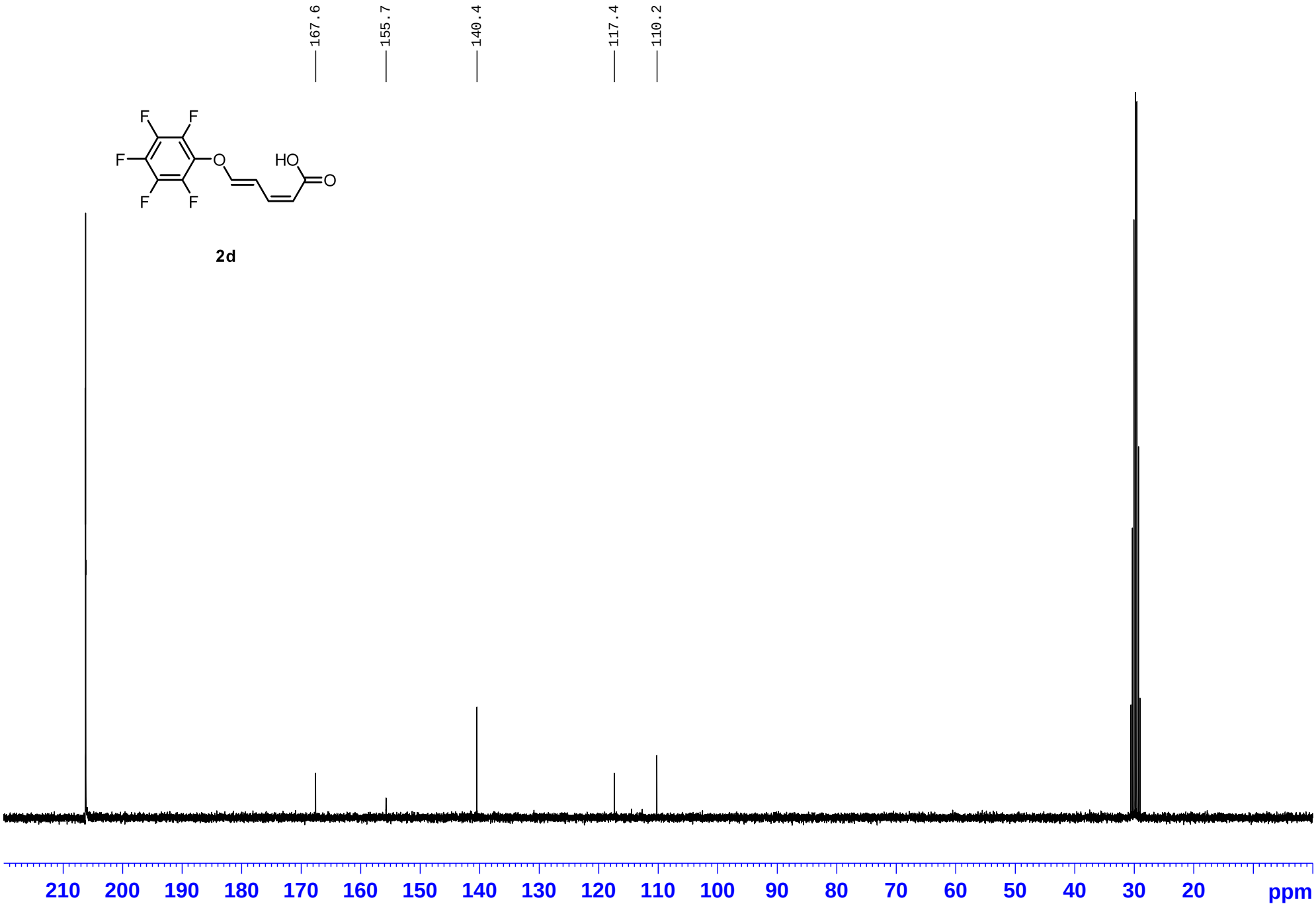
1.10
0.99
1.00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117.4
110.2
F
F
F
F
F
O
HO
O
2d
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200
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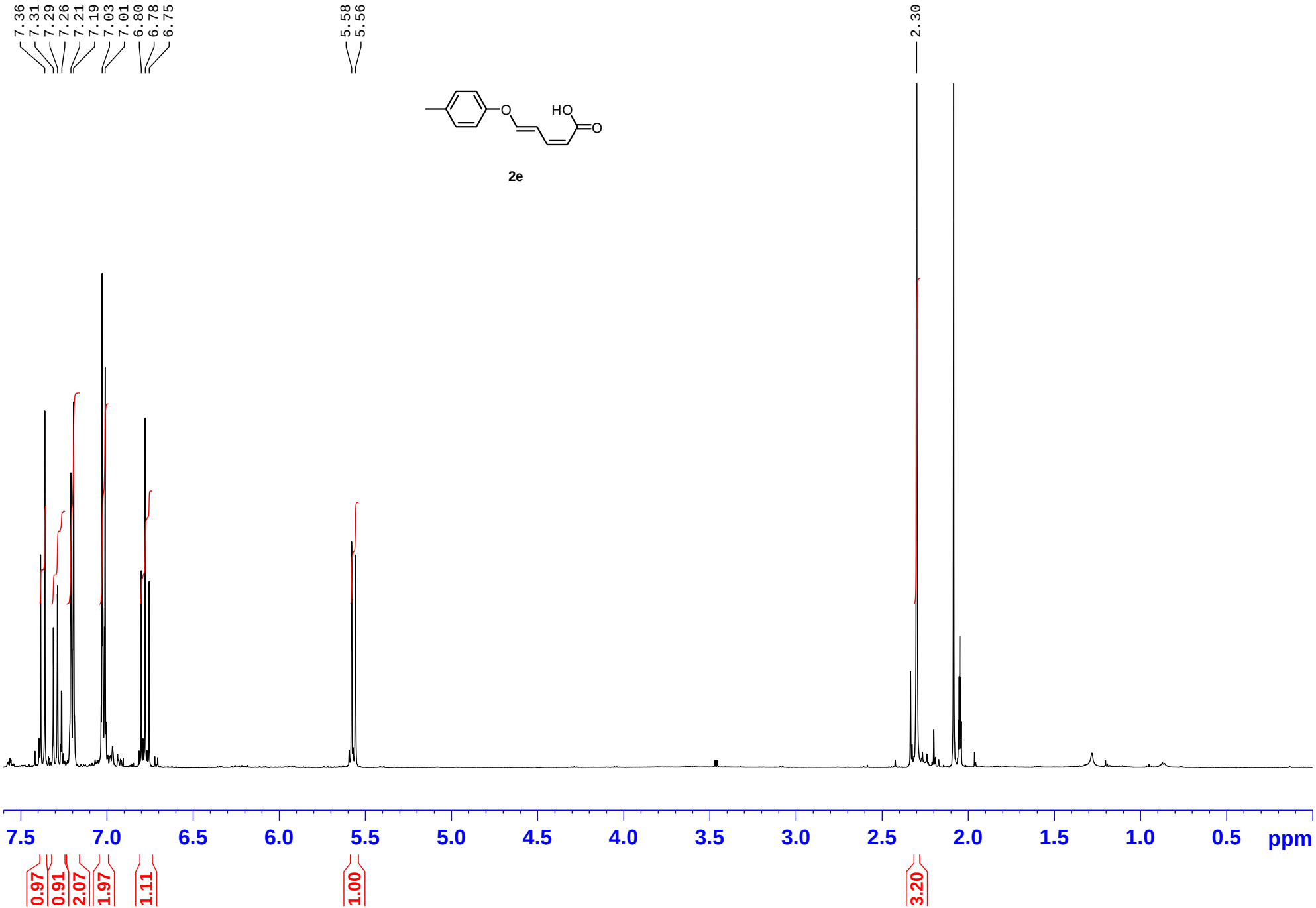
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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6.78
6.75
5.58
5.56
2.30
HO
O
O
2e
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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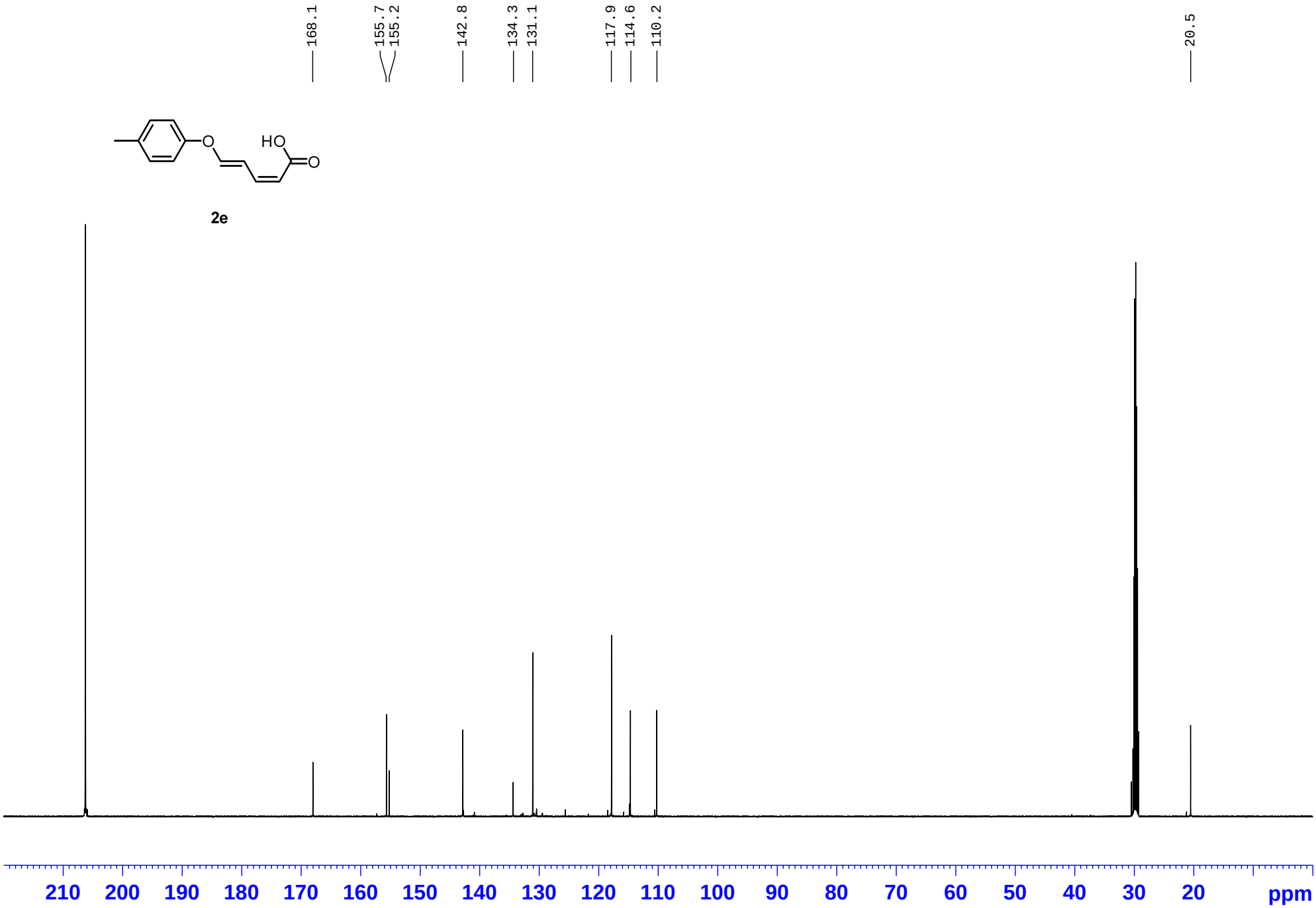
0.91
2.07
1.97
1.11
1.00
3.20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155.2
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134.3
131.1
117.9
114.6
110.2
20.5
HO
O
O
2e
210
200
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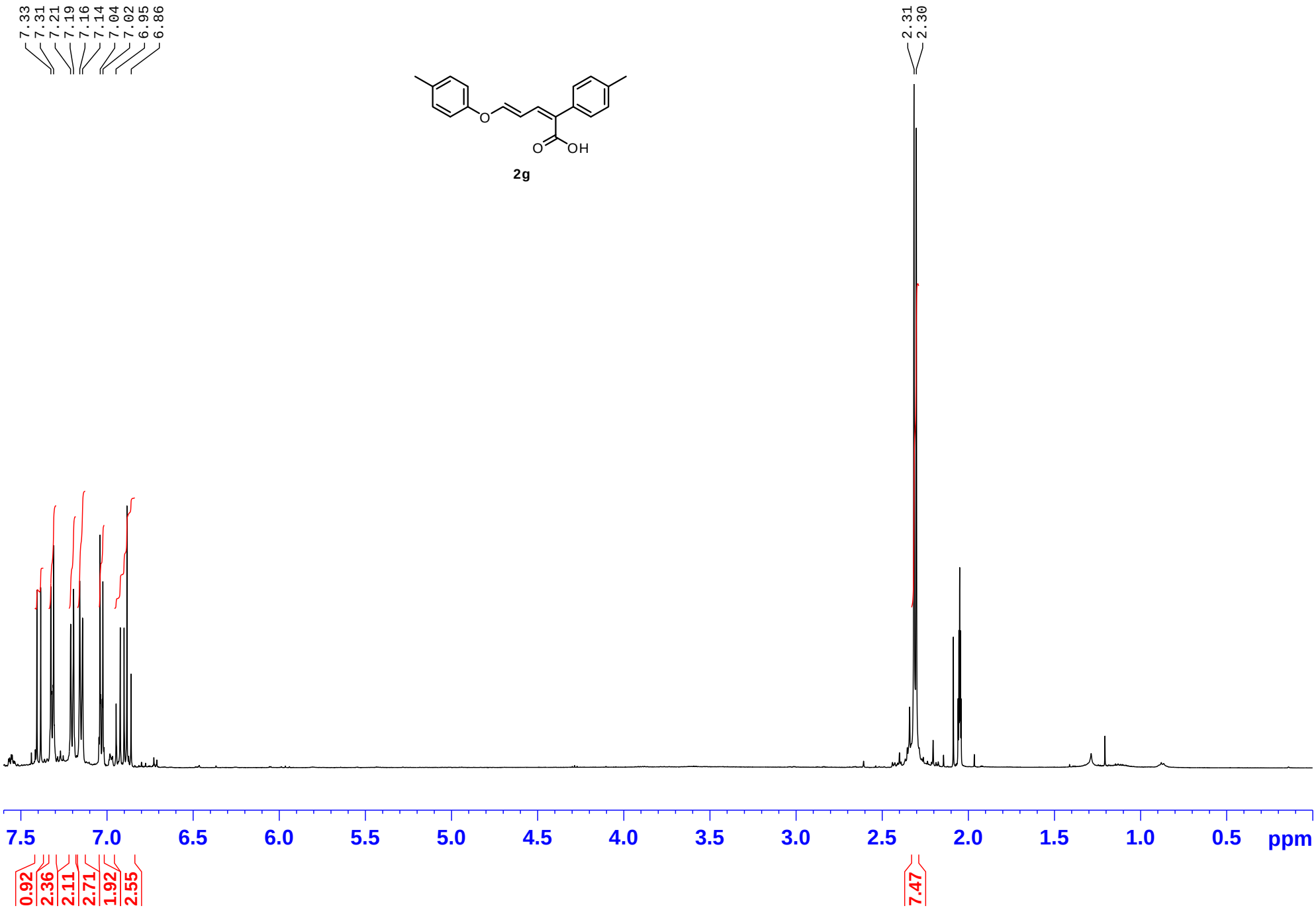
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.14
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7.02
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6.86
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2.30
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O
OH
2g
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.0
0.5
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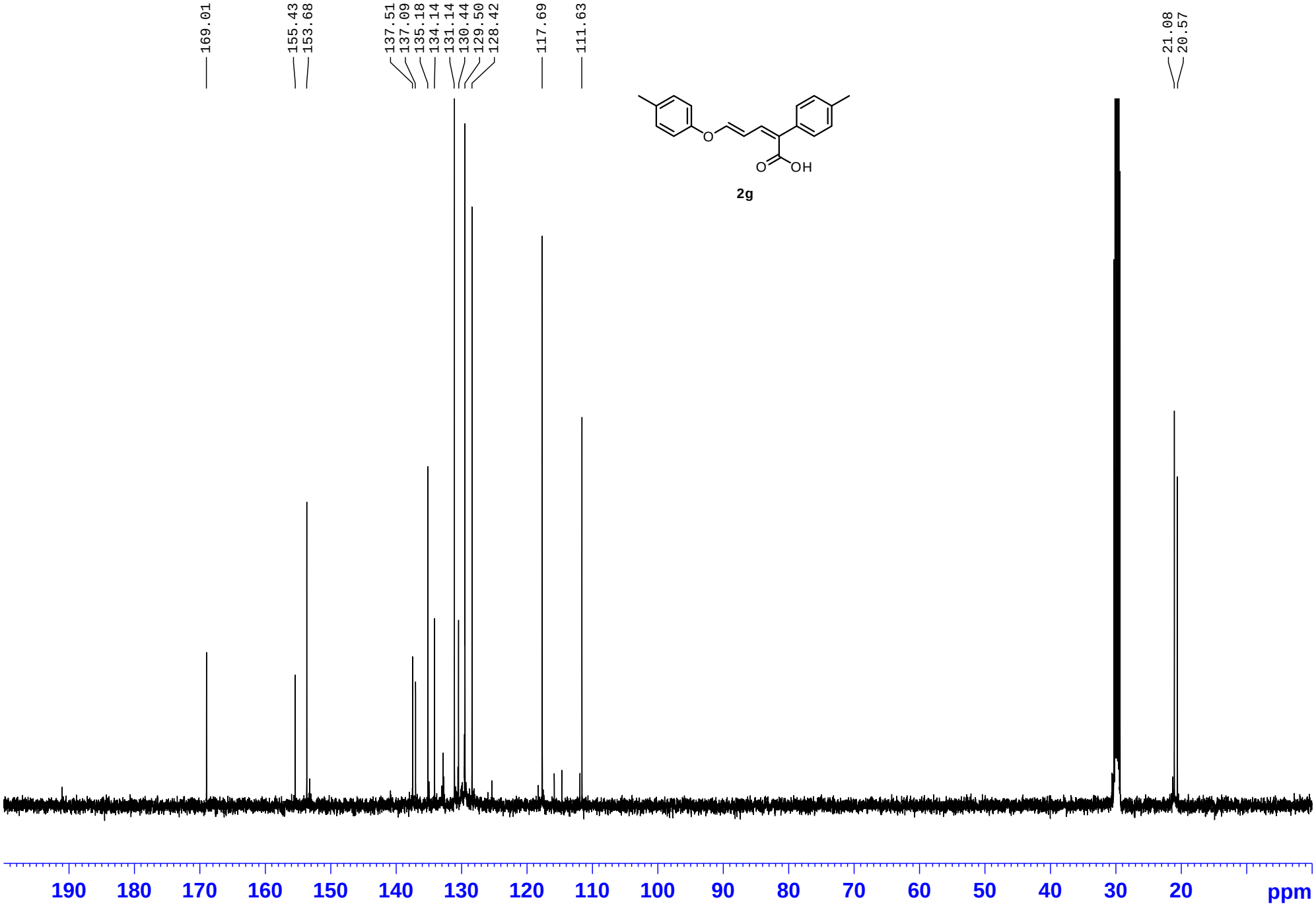
2.55
7.47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131.14
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129.50
128.42
117.69
111.63
21.08
20.57
O
O
OH
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160
150
140
130
120
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90
80
70
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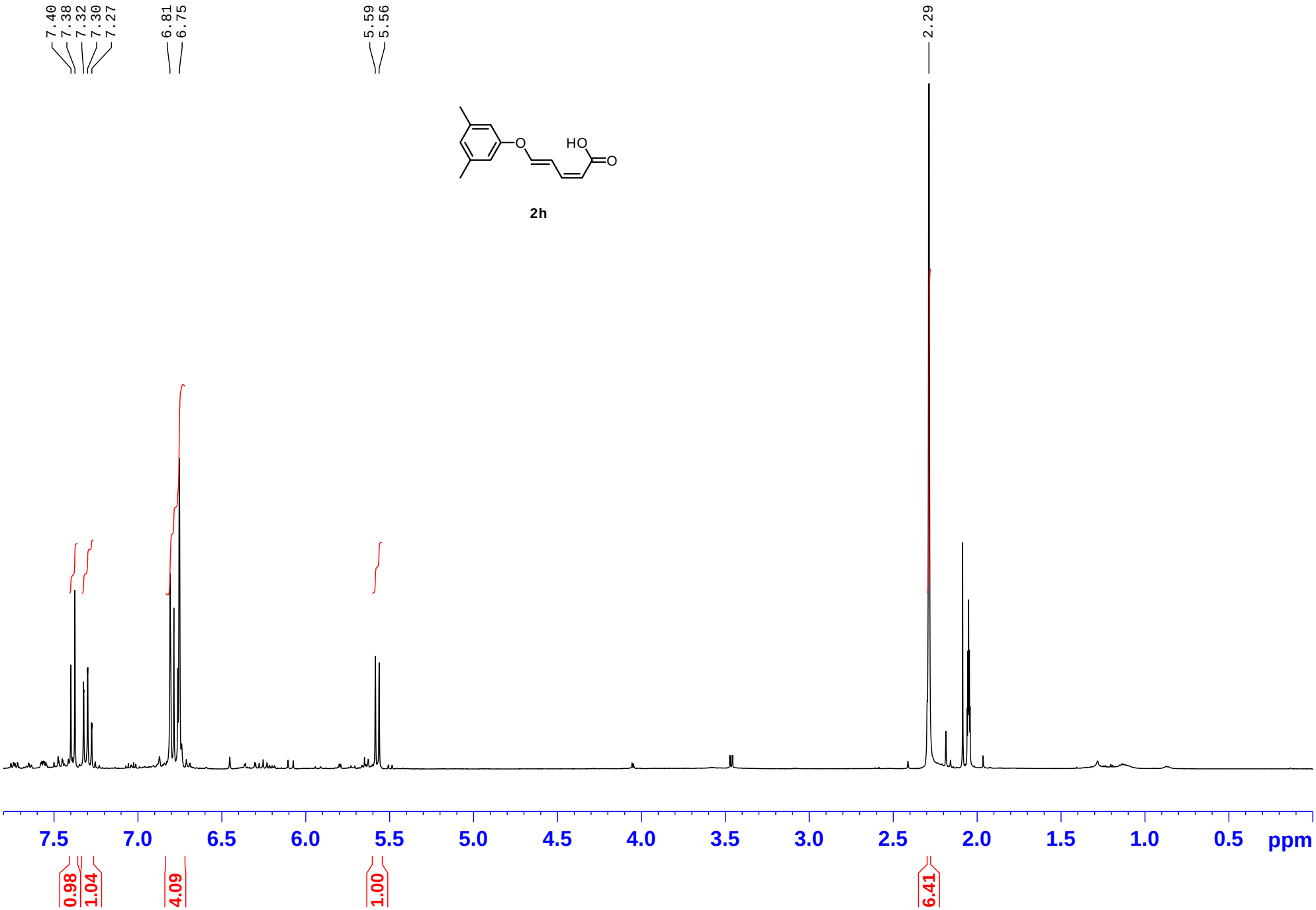
50
40
30
20
ppm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5.56
2.29
O
HO
O
2h
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.0
1.5
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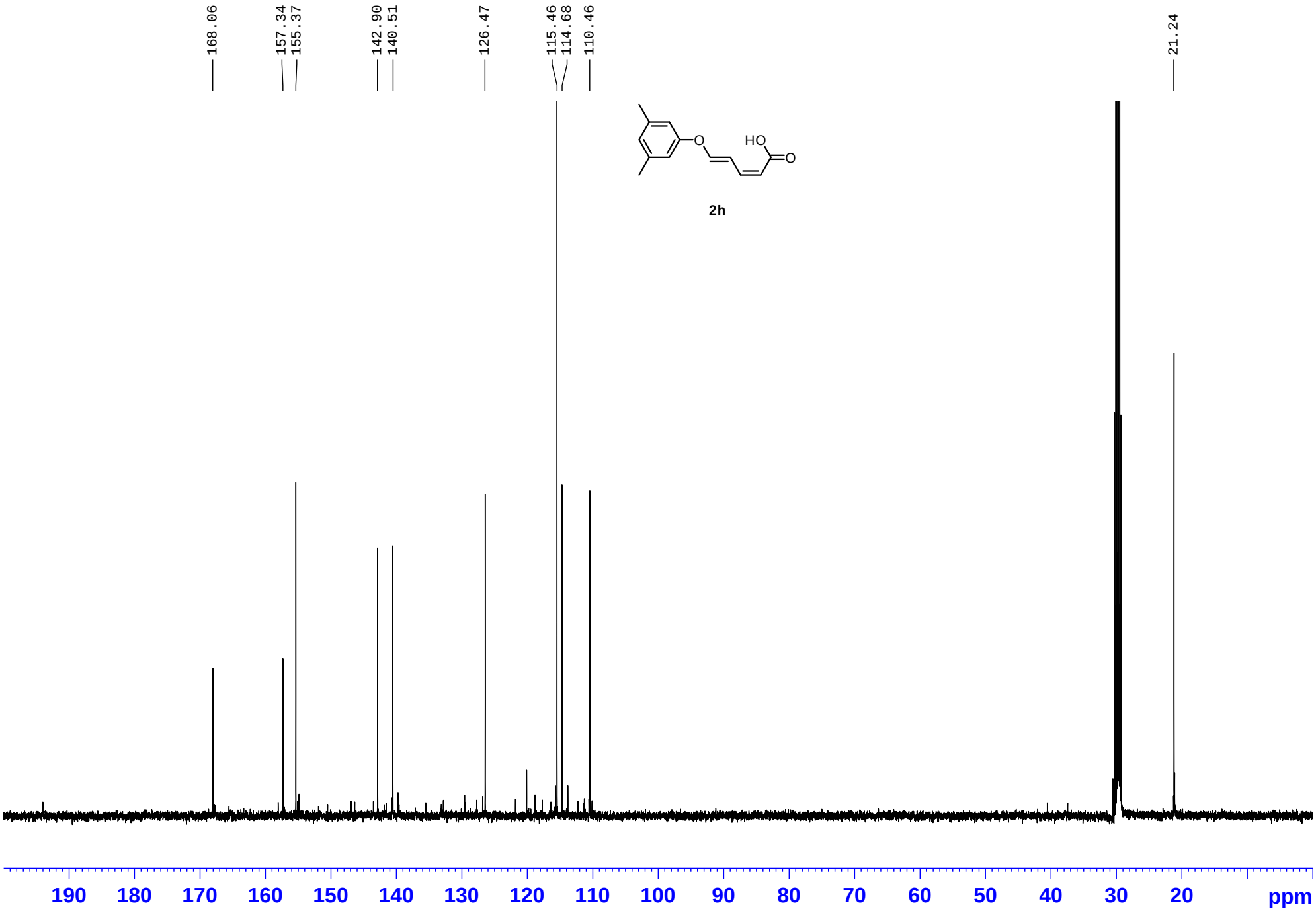
4.09
1.00
6.41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140.51
126.47
115.46
114.68
110.46
21.24
O
HO
O
2h
190
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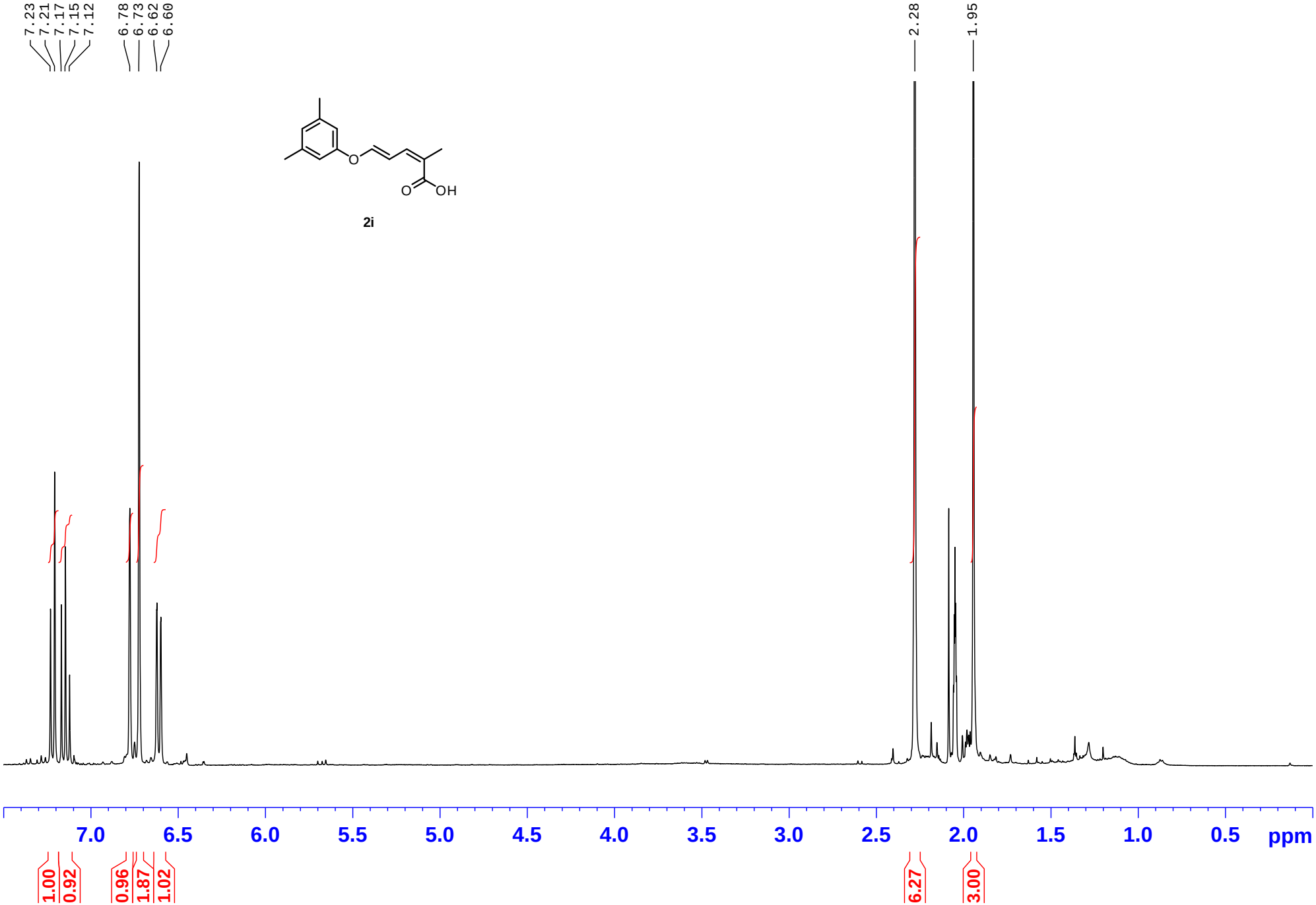
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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6.62
6.60
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1.95
O
O
OH
2i
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
0.5
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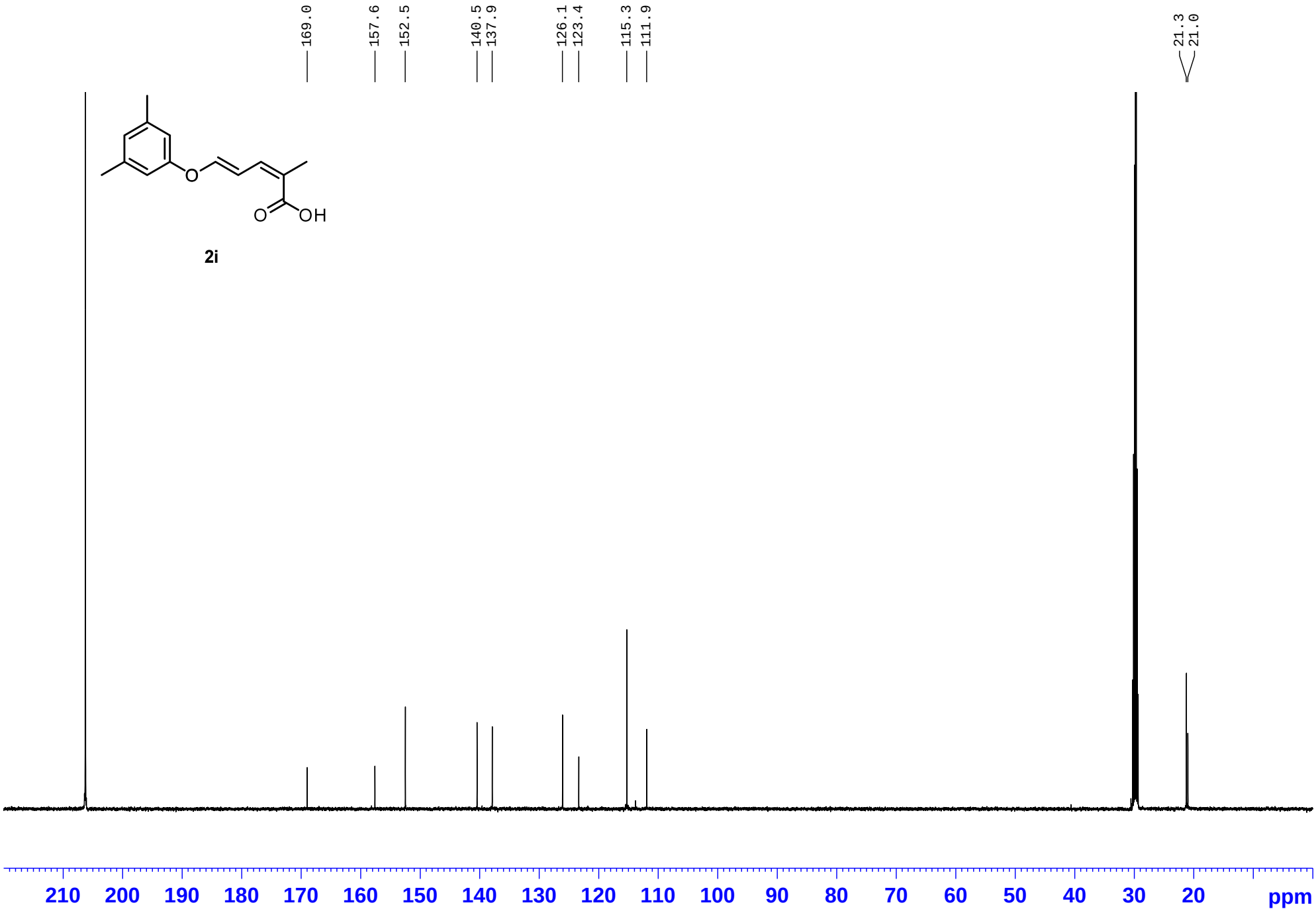
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140.5
137.9
126.1
123.4
115.3
111.9
21.3
21.0
O
O
OH
2i
210
200
190
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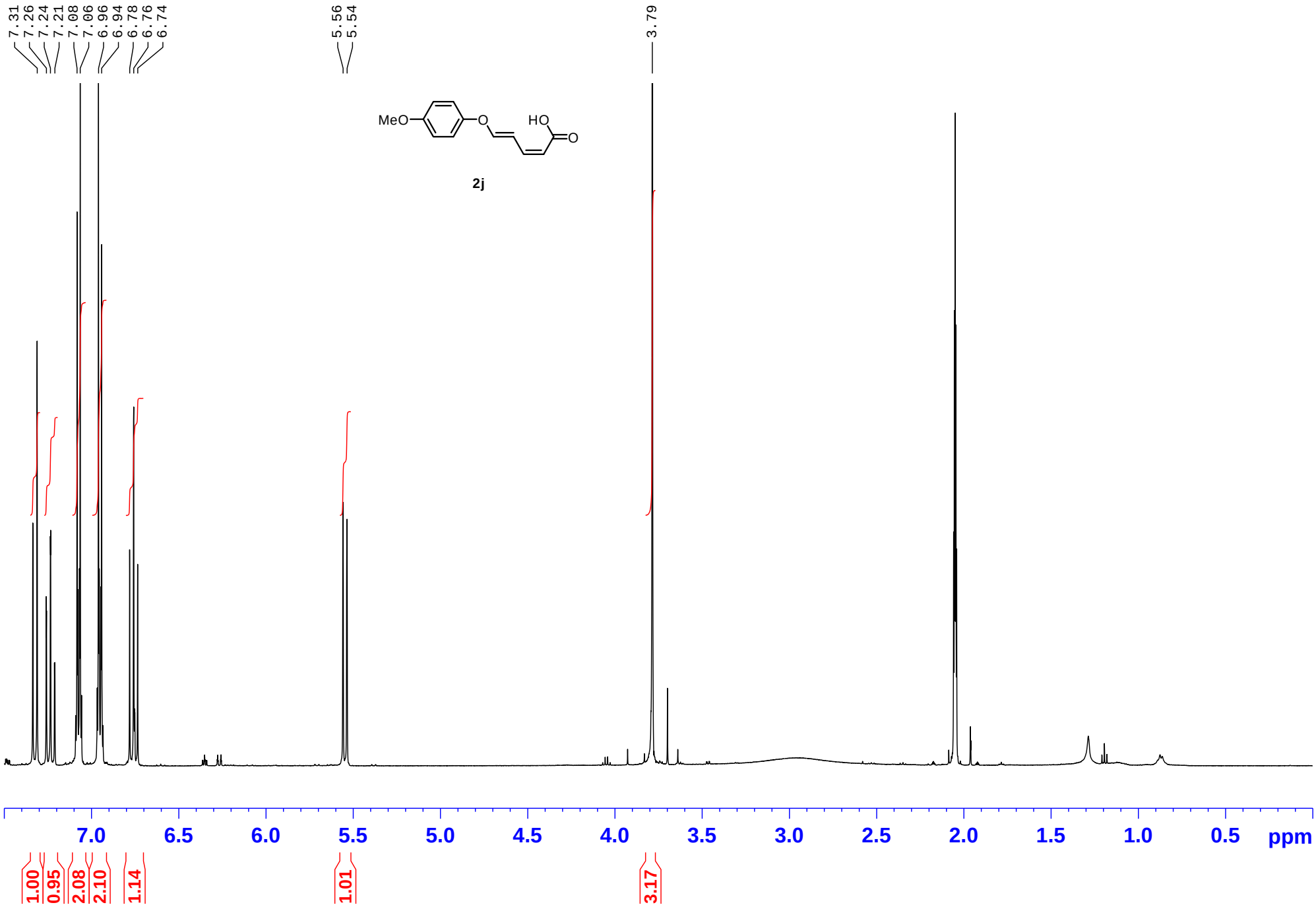
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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6.78
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6.74
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5.54
3.79
MeO
O
HO
O
2j
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
0.5
ppm
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2.08
2.10
1.14
1.01
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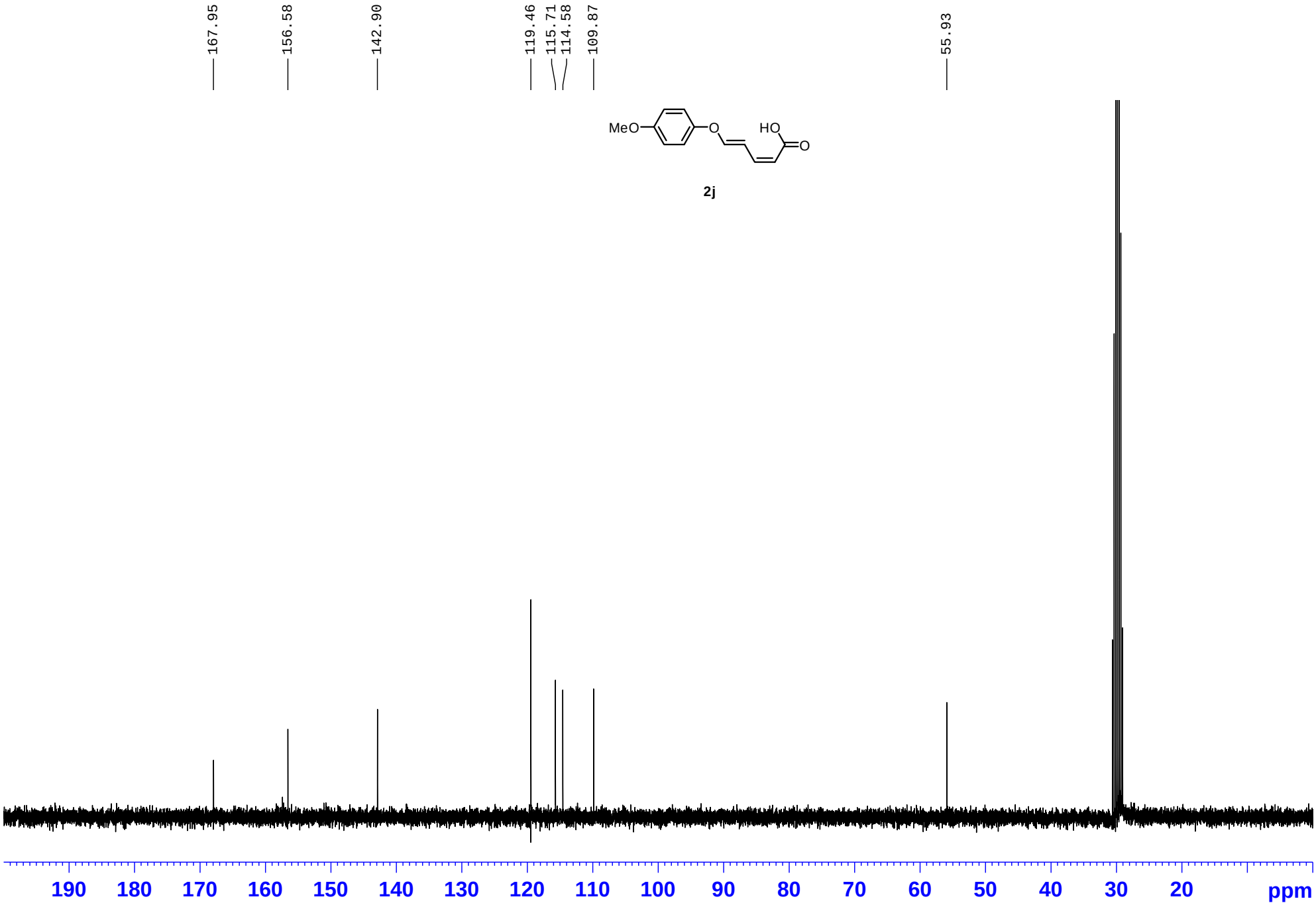
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O
HO
O
2j
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160
150
140
130
120
110
100
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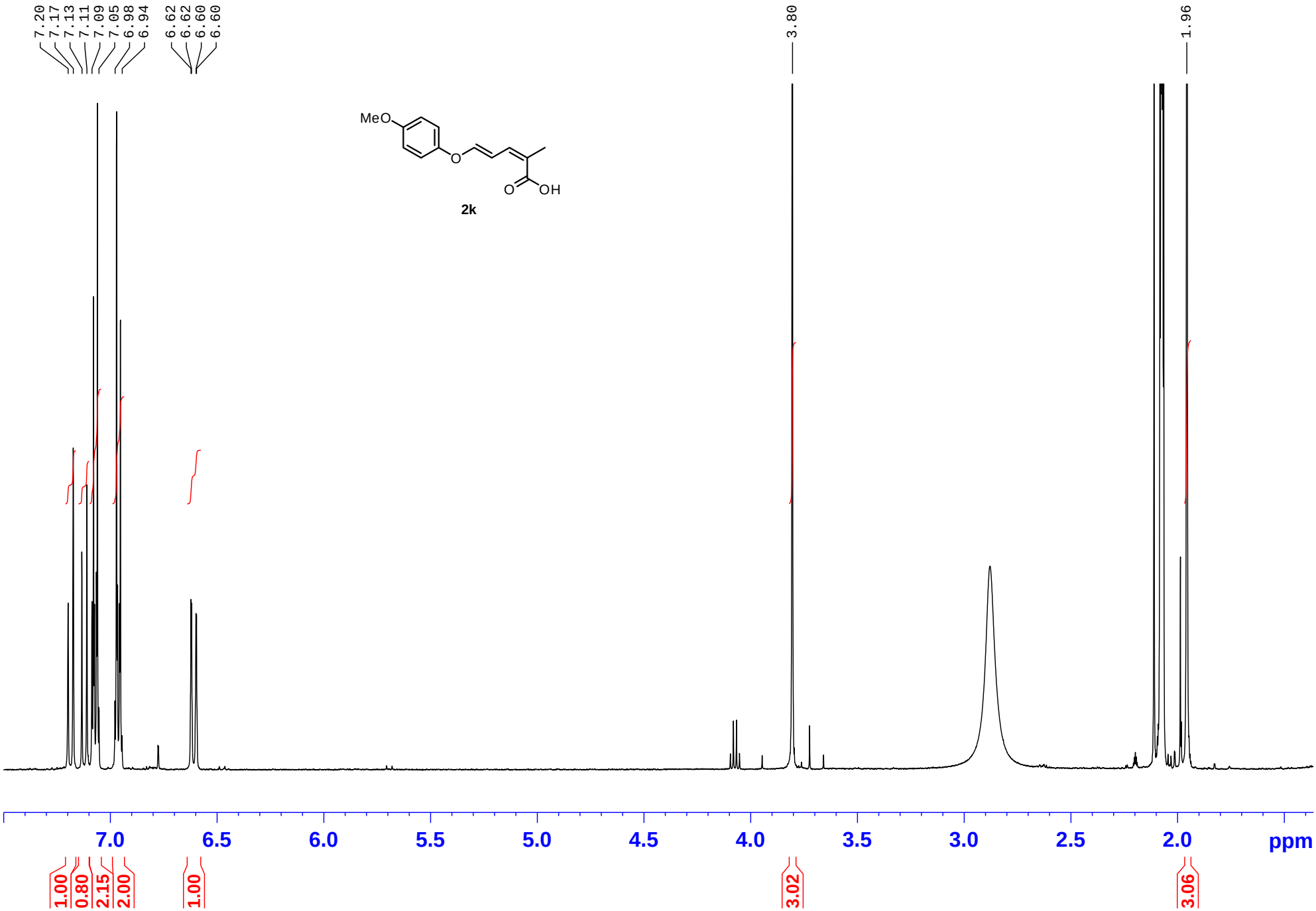
80
70
60
50
40
30
20
ppm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6.62
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6.60
6.60
3.80
1.96
MeO
O
O
OH
2k
7.0
6.5
6.0
5.5
5.0
4.5
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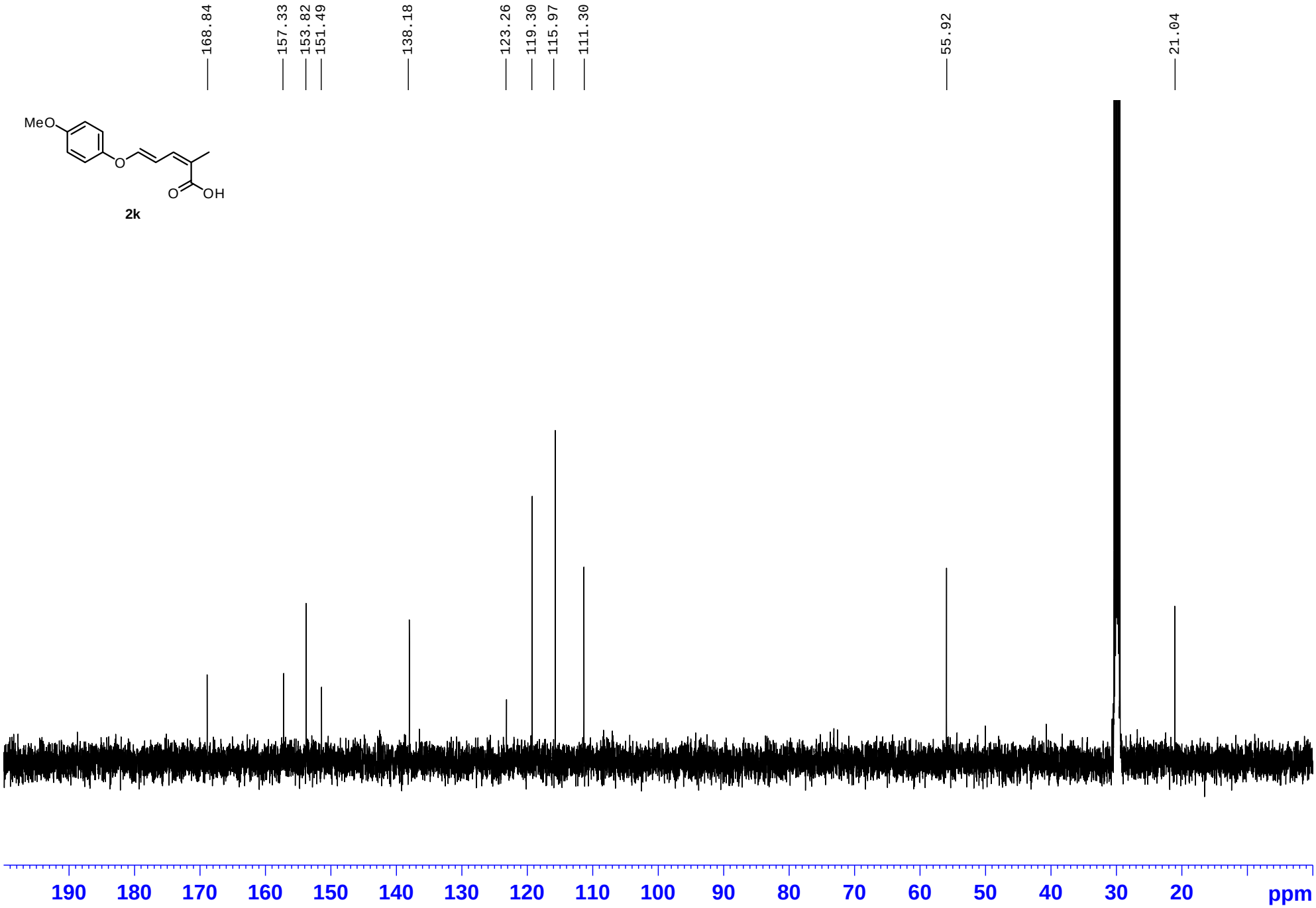
3.06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55.92
21.04
MeO
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O
OH
2k
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160
150
140
130
120
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100
90
80
70
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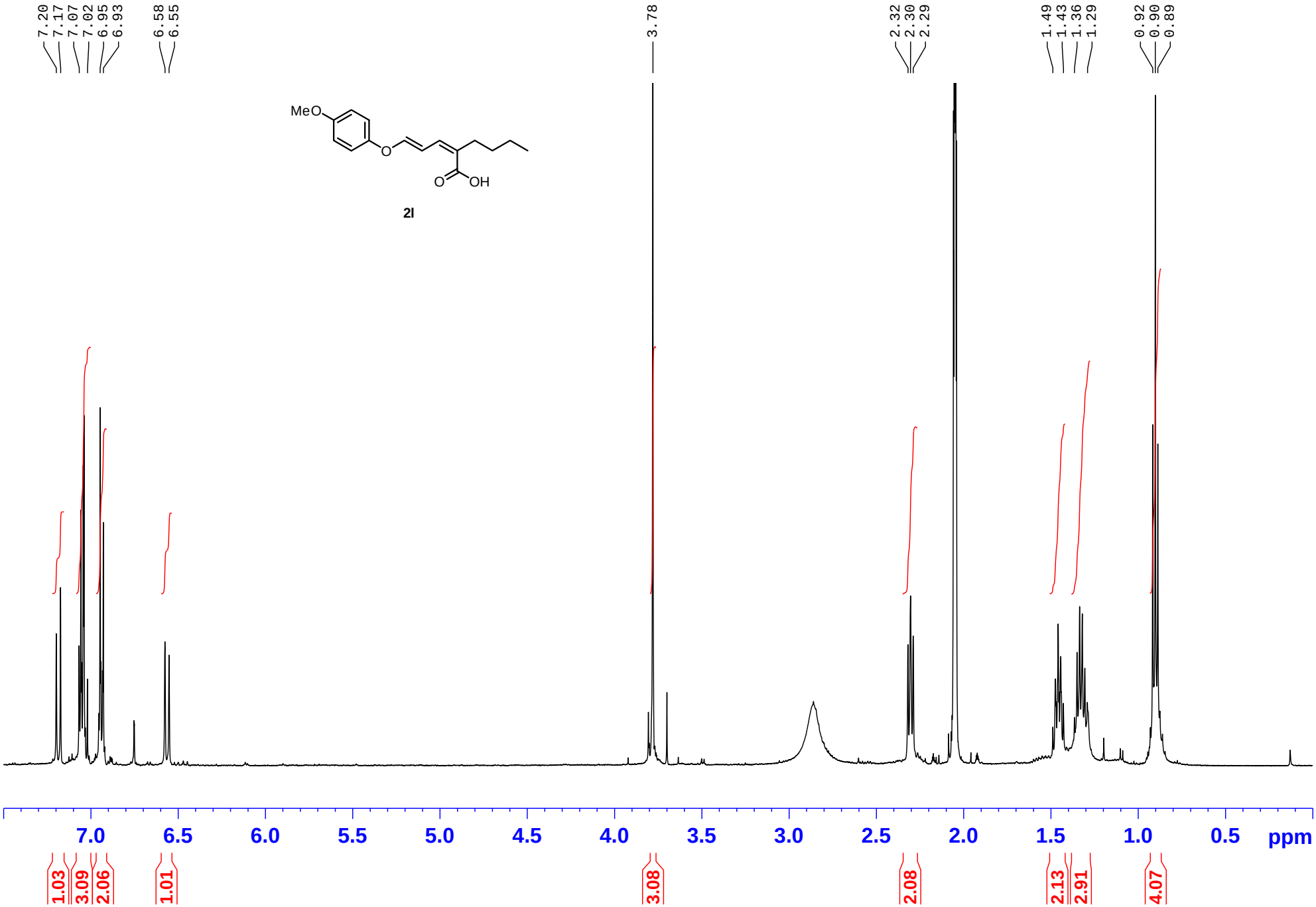
50
40
30
20
ppm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6.55
3.78
2.32
2.30
2.29
1.49
1.43
1.36
1.29
0.92
0.90
0.89
MeO
O
O
OH
2l
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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ppm
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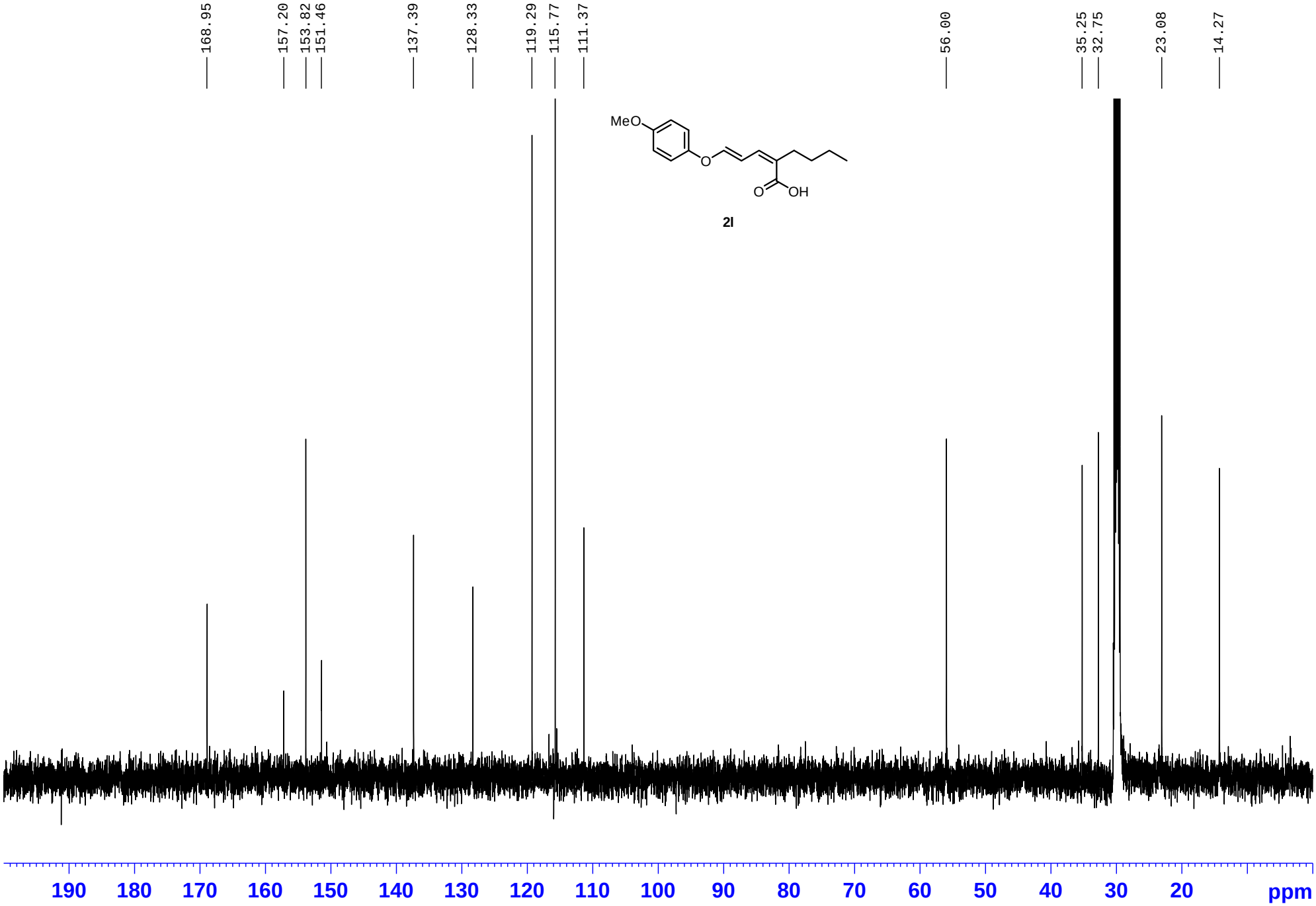
3.08
2.08
2.13
2.91
4.07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56.00
35.25
32.75
23.08
14.27
MeO
O
O
OH
2l
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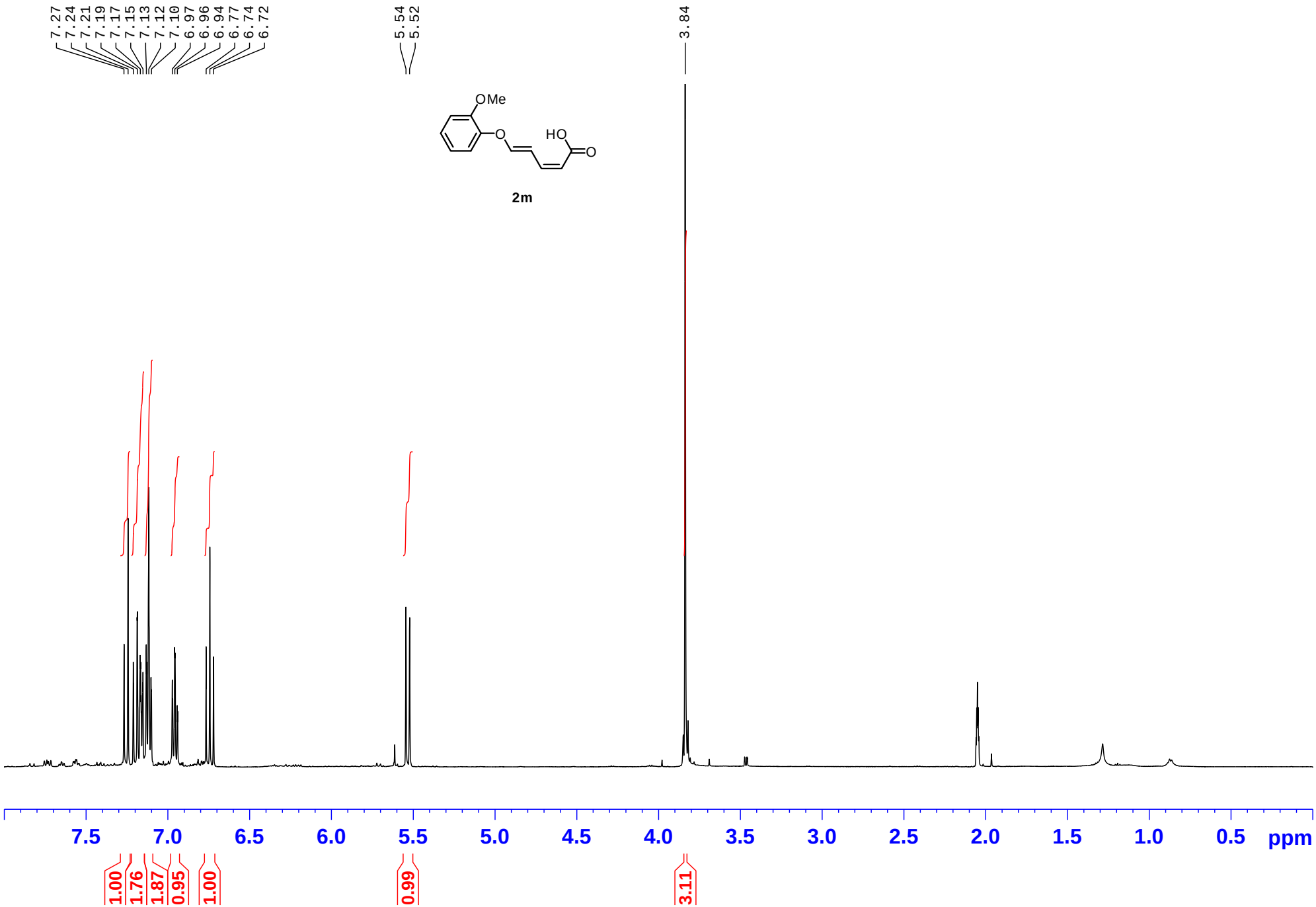
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.13
7.12
7.10
6.97
6.96
6.94
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5.52
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O
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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0.5
ppm
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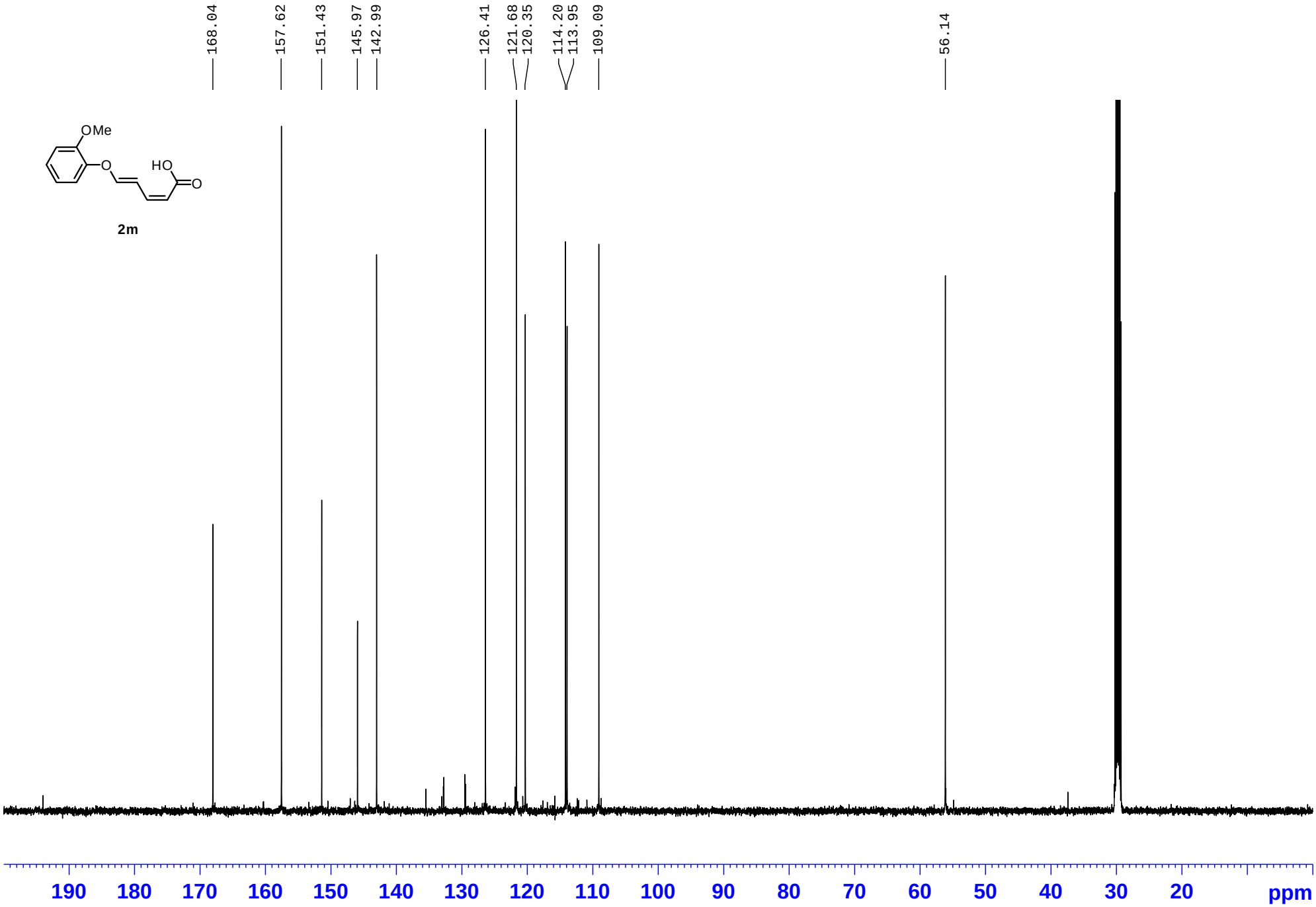
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142.99
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121.68
120.35
114.20
113.95
109.09
56.14
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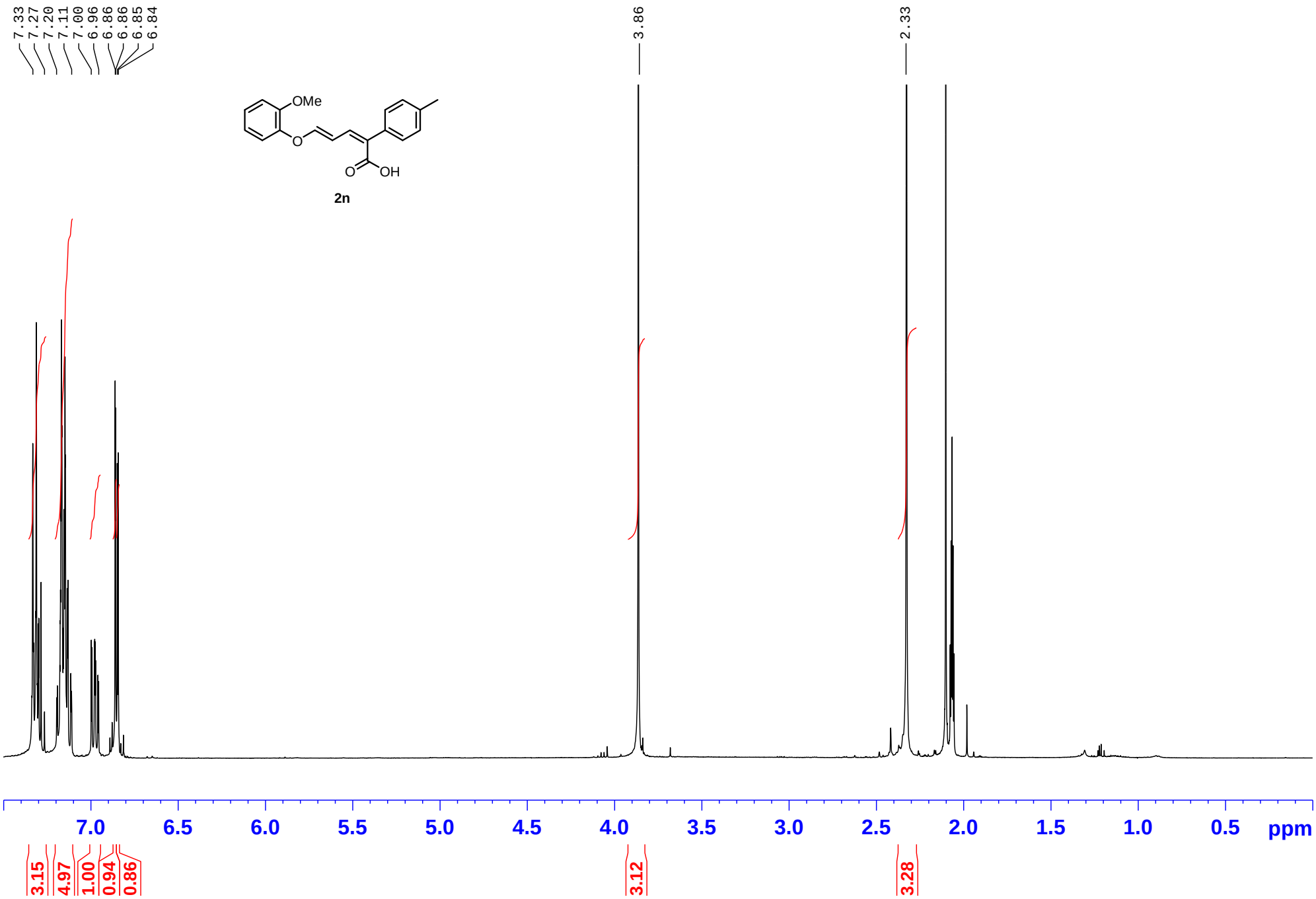
O
HO
O
2m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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6.86
6.85
6.84
3.86
2.33
OMe
O
O
OH
2n
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
0.5
ppm
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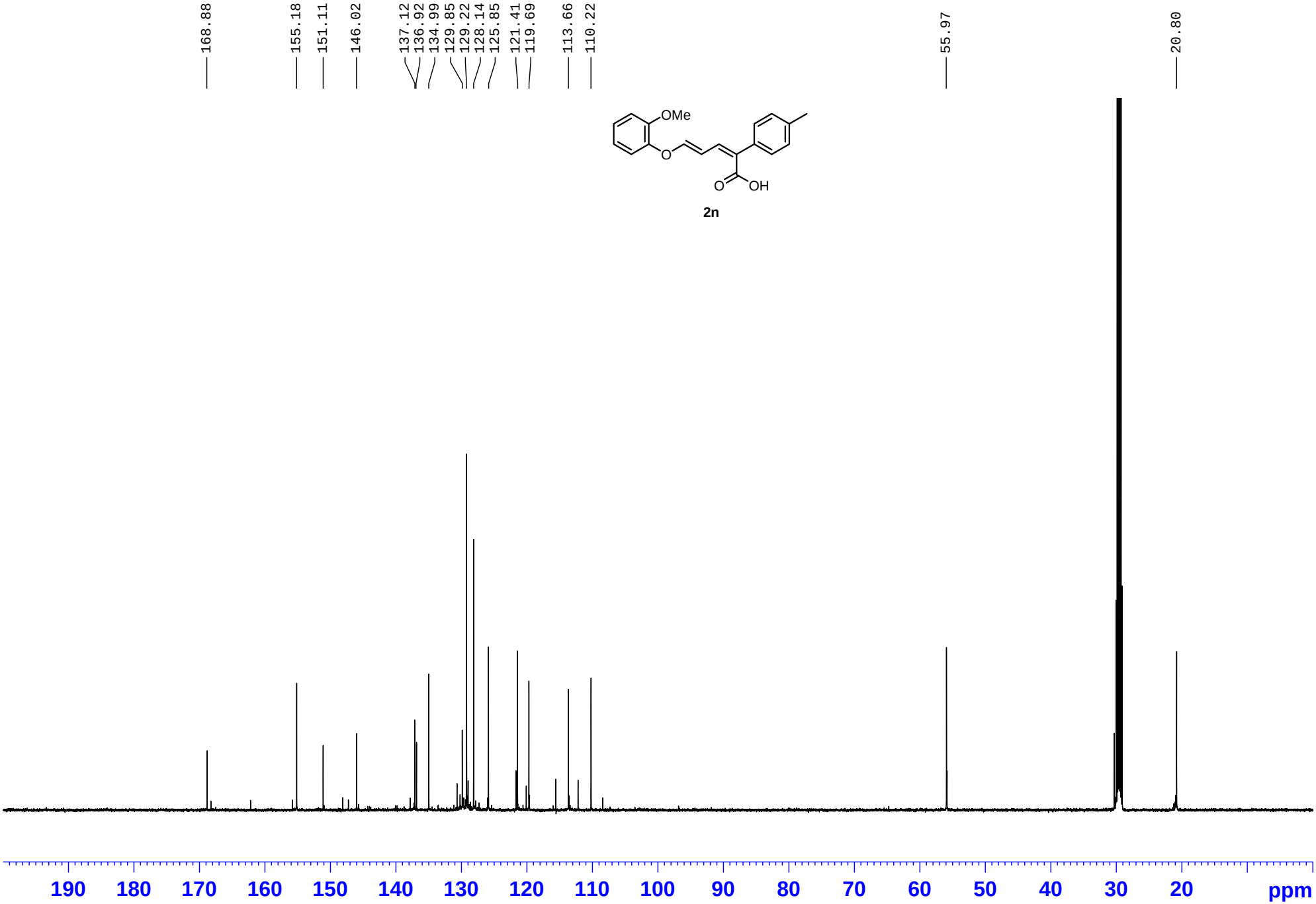
1.00
0.94
0.86
3.12
3.28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134.99
129.85
129.22
128.14
125.85
121.41
119.69
113.66
110.22
55.97
20.80
OMe
O
O
OH
2n
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180
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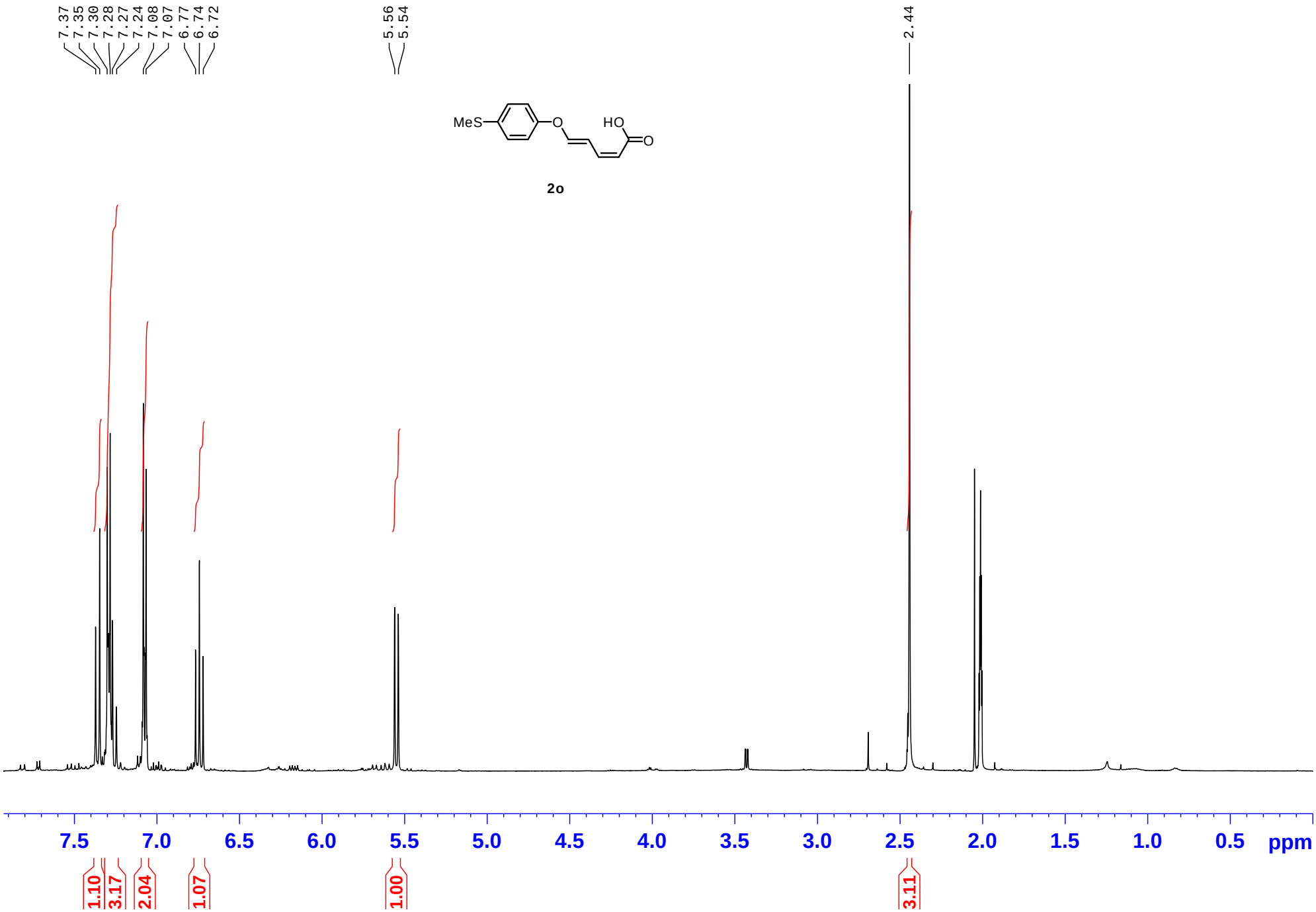
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.28
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7.24
7.08
7.07
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6.74
6.72
5.56
5.54
2.44
MeS
O
HO
O
2o
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.5
1.0
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ppm
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3.17
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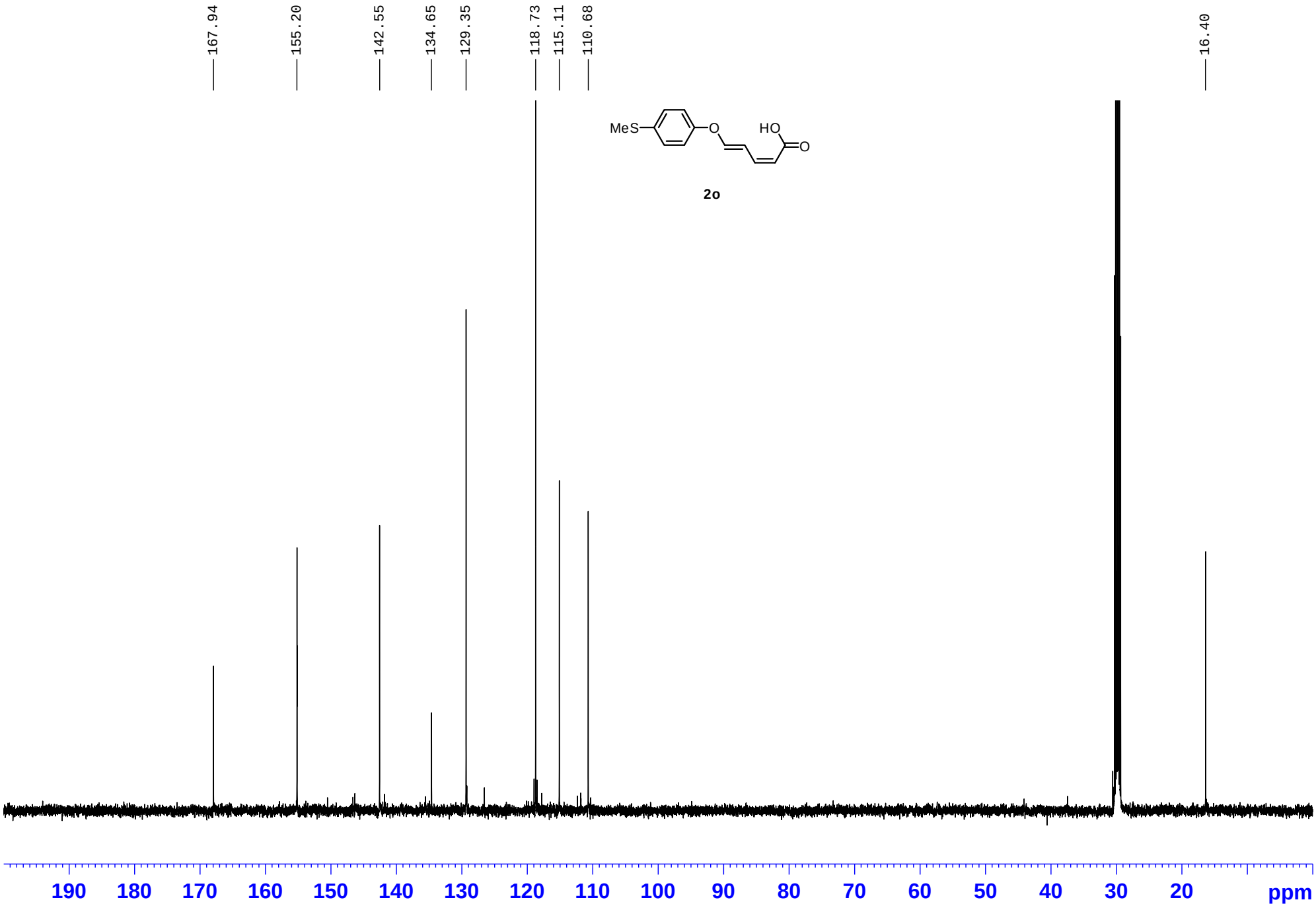
1.07
1.00
3.11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129.35
118.73
115.11
110.68
16.40
MeS
O
HO
O
2o
190
180
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160
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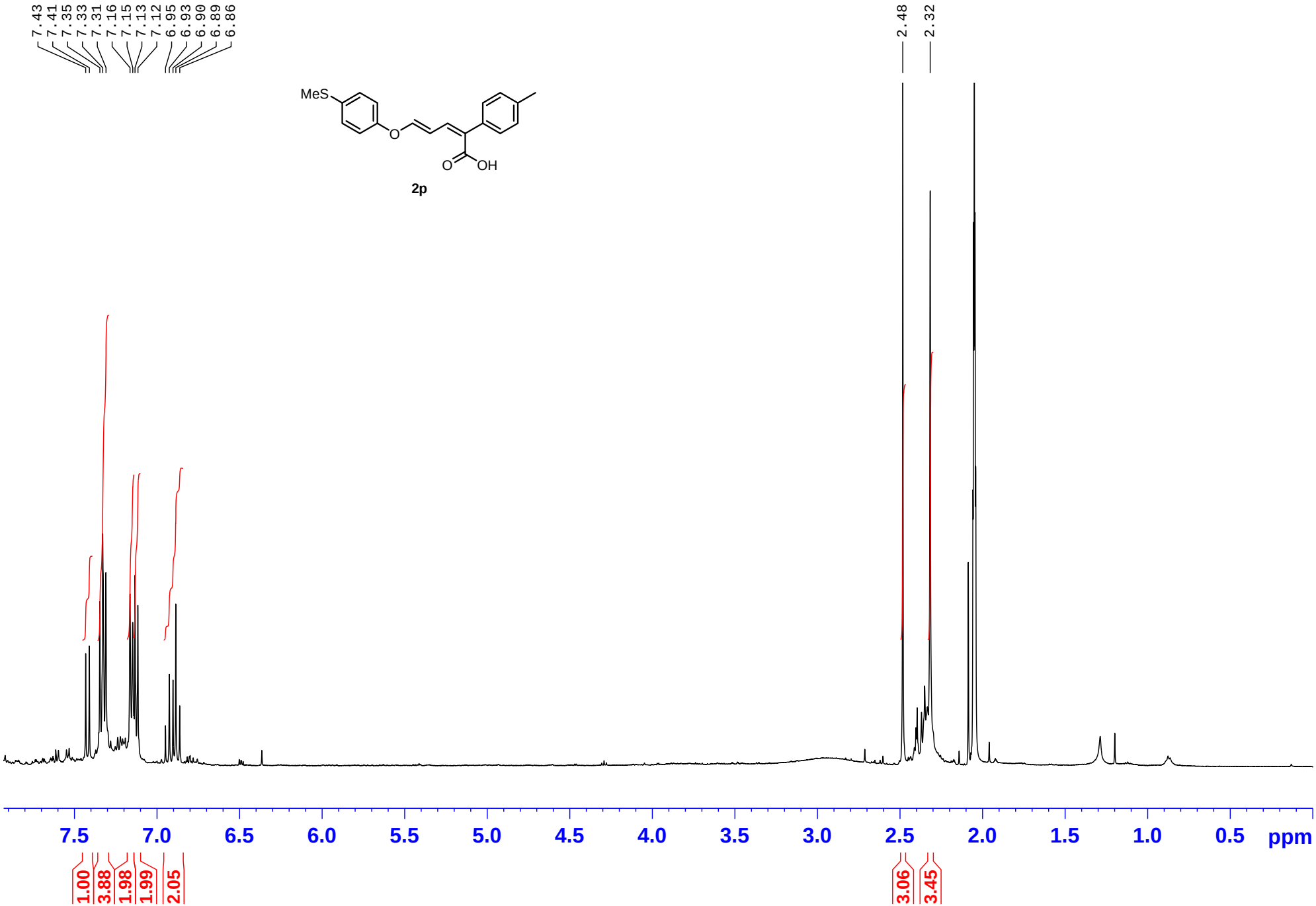
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7.13
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6.93
6.90
6.89
6.86
2.48
2.32
MeS
O
O
OH
2p
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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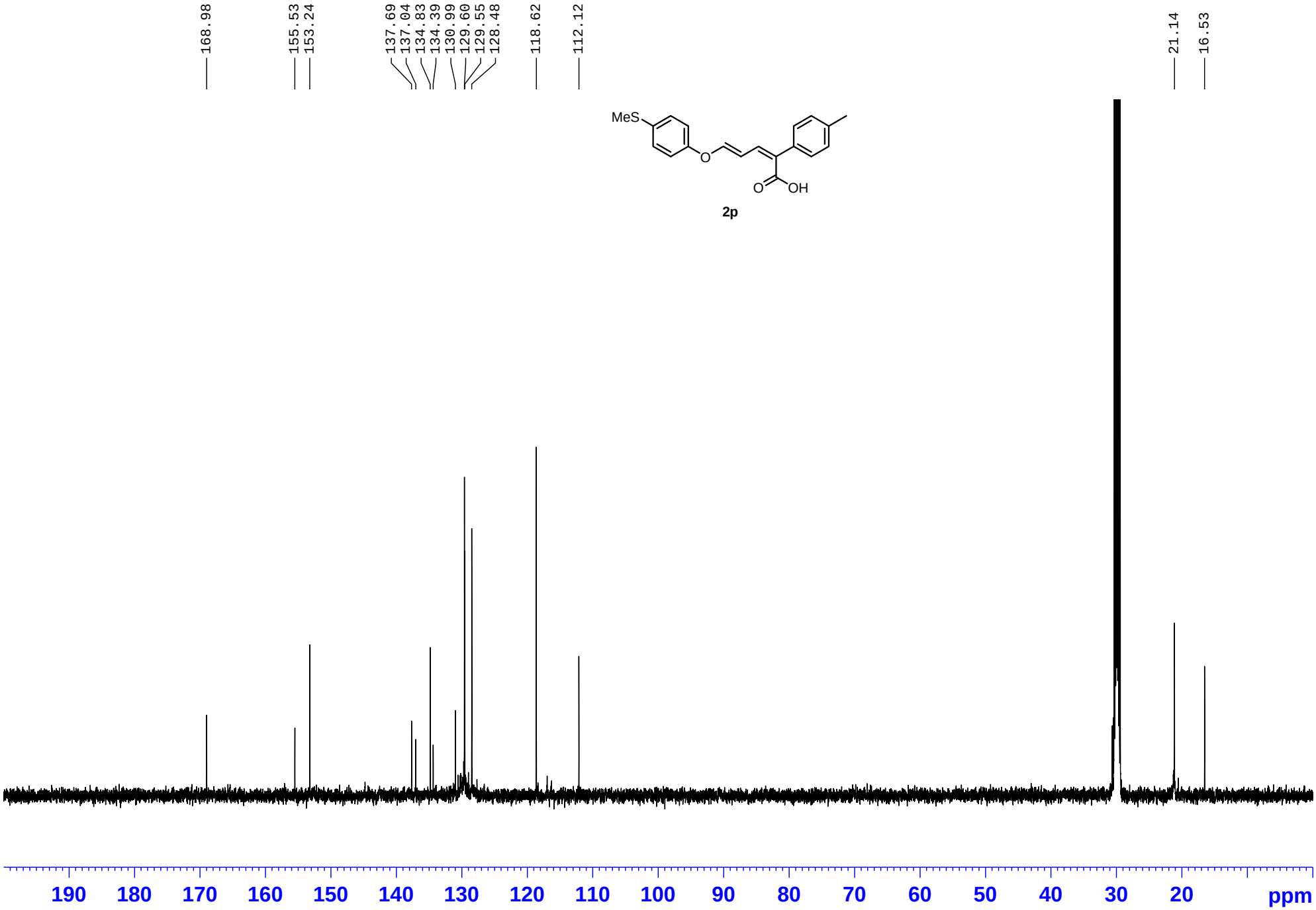
3.06
3.45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137.04
134.83
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130.99
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128.48
118.62
112.12
21.14
16.53
MeS
O
O
OH
2p
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160
150
140
130
120
110
100
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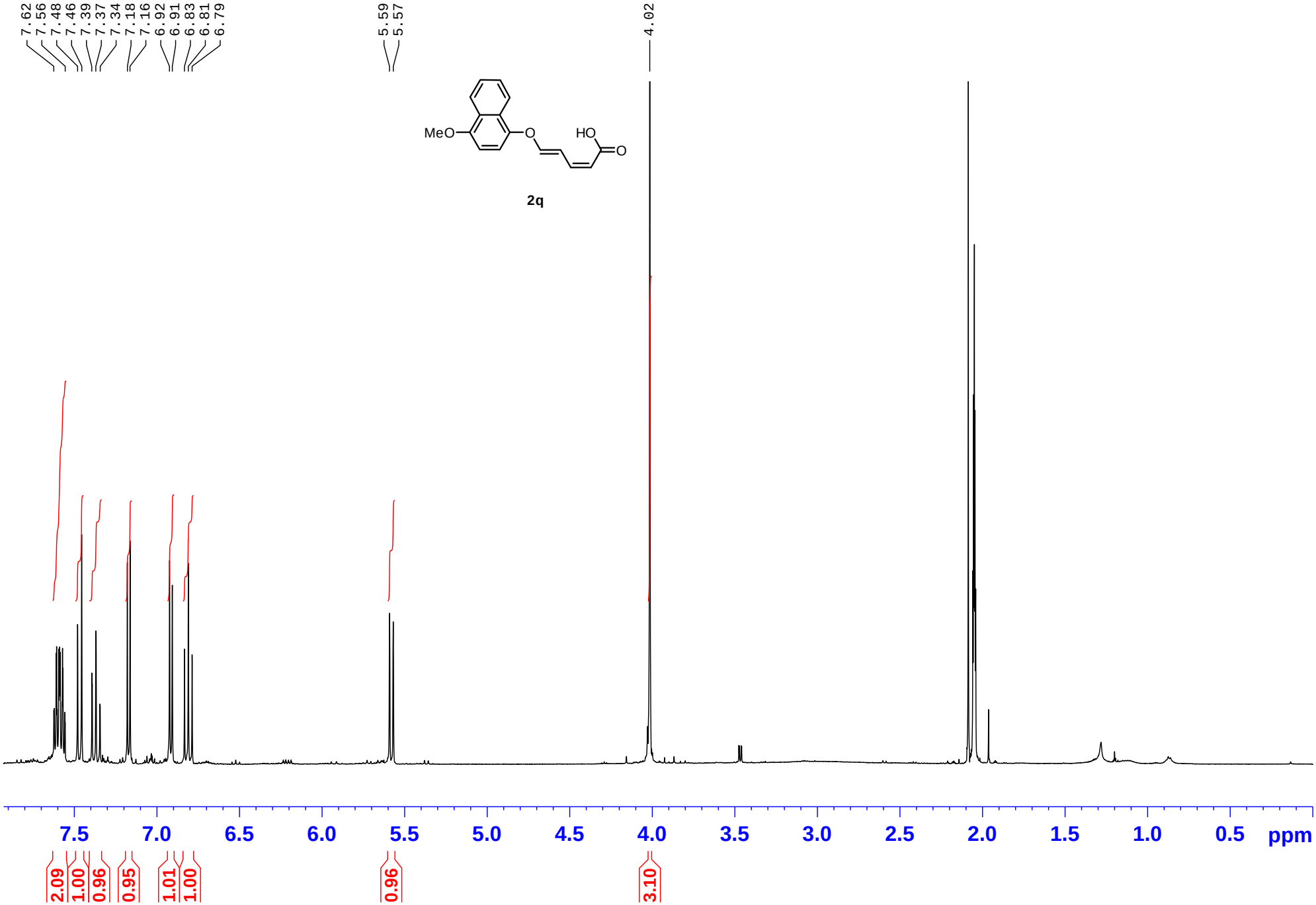
80
70
60
50
40
30
20
ppm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7.34
7.18
7.16
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6.81
6.79
5.59
5.57
4.02
MeO
O
HO
O
2q
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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0.5
ppm
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0.95
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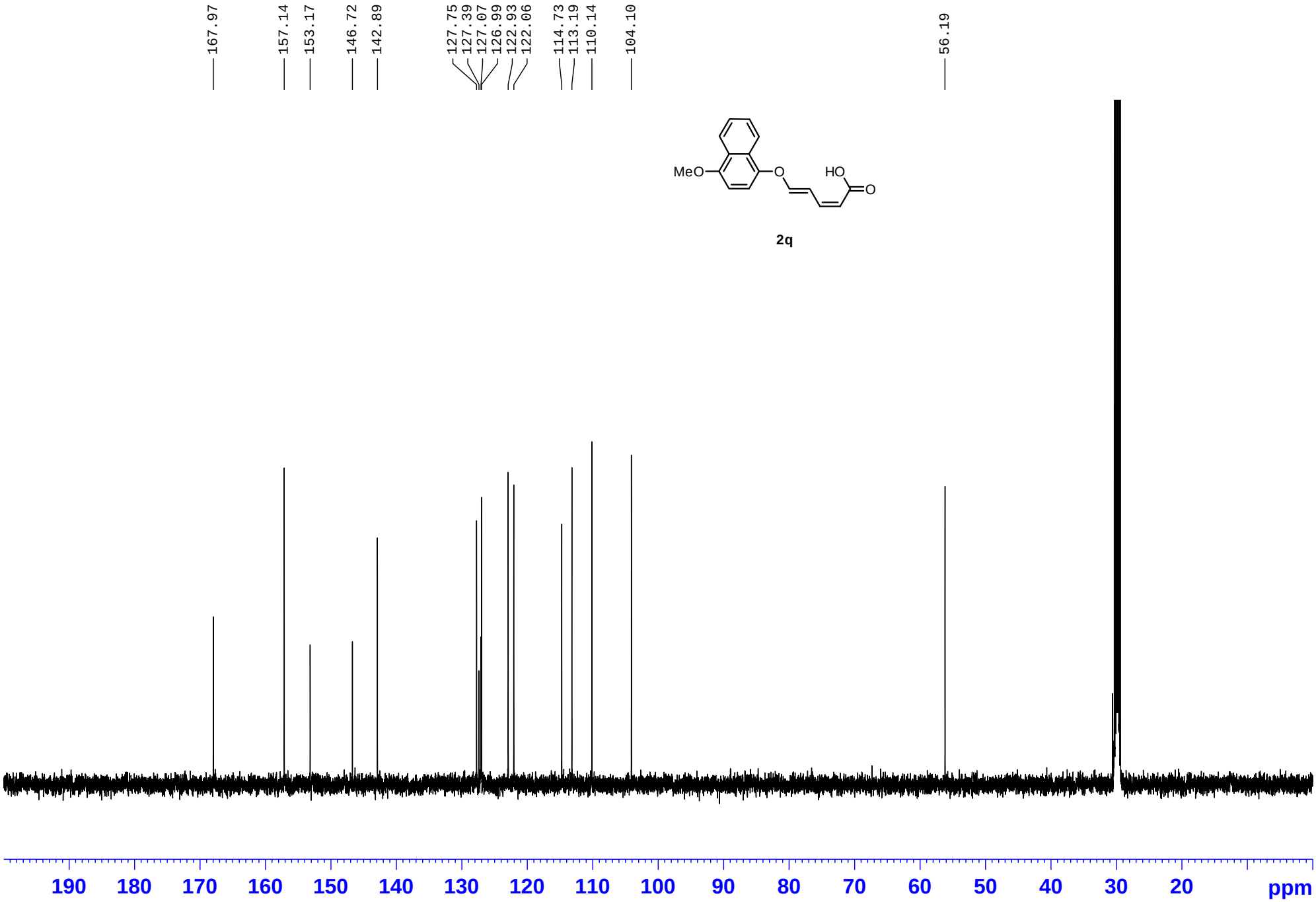
1.00
0.96
3.10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127.39
127.07
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122.93
122.06
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113.19
110.14
104.10
56.19
MeO
O
HO
O
2q
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160
150
140
130
120
110
100
90
80
70
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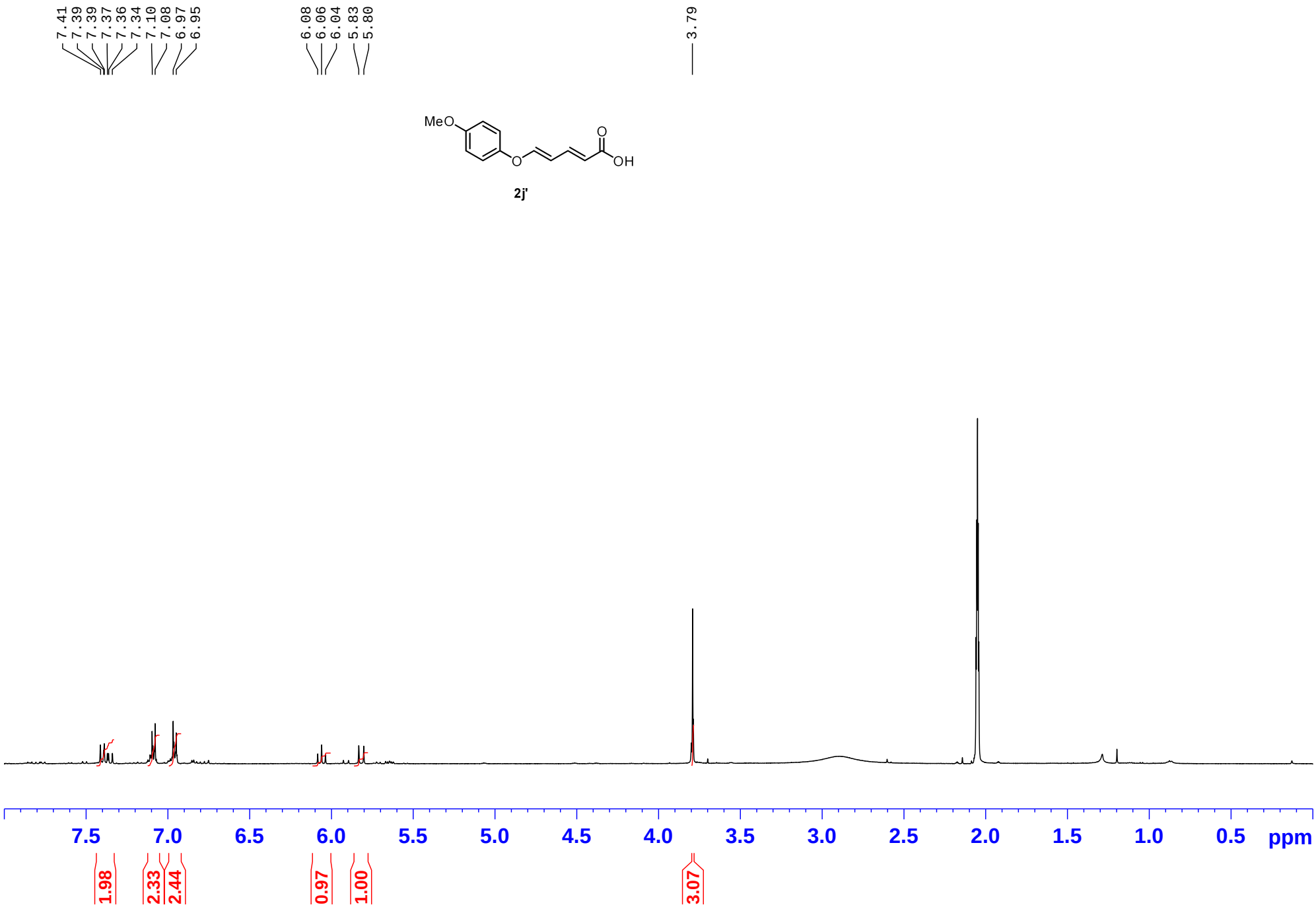
50
40
30
20
ppm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7.37
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7.10
7.08
6.97
6.95
6.08
6.06
6.04
5.83
5.80
3.79
MeO
O
O
OH
2j'
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.5
1.0
0.5
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2.33
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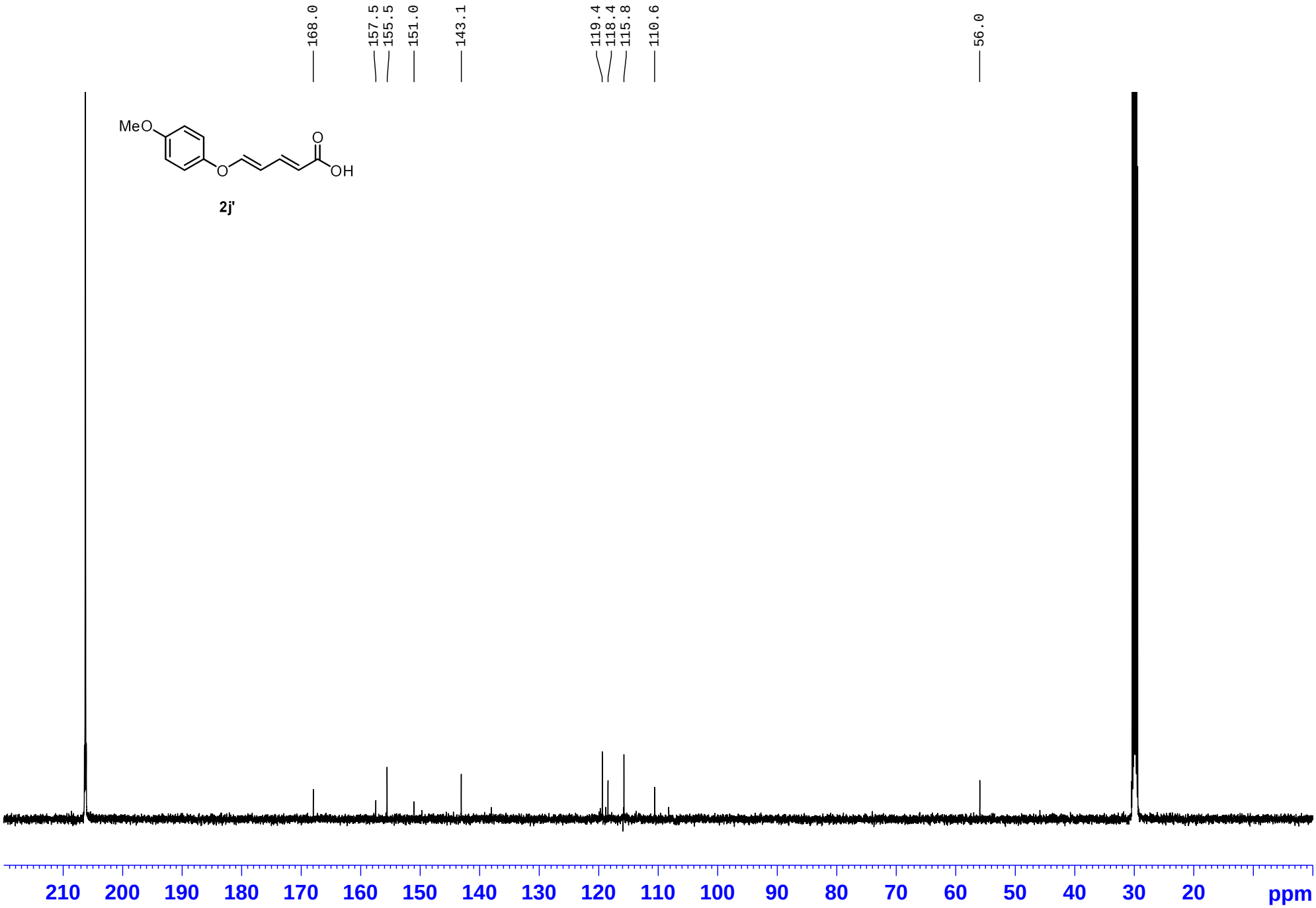
1.00
3.07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155.5
151.0
143.1
119.4
118.4
115.8
110.6
56.0
MeO
O
O
OH
2j'
210
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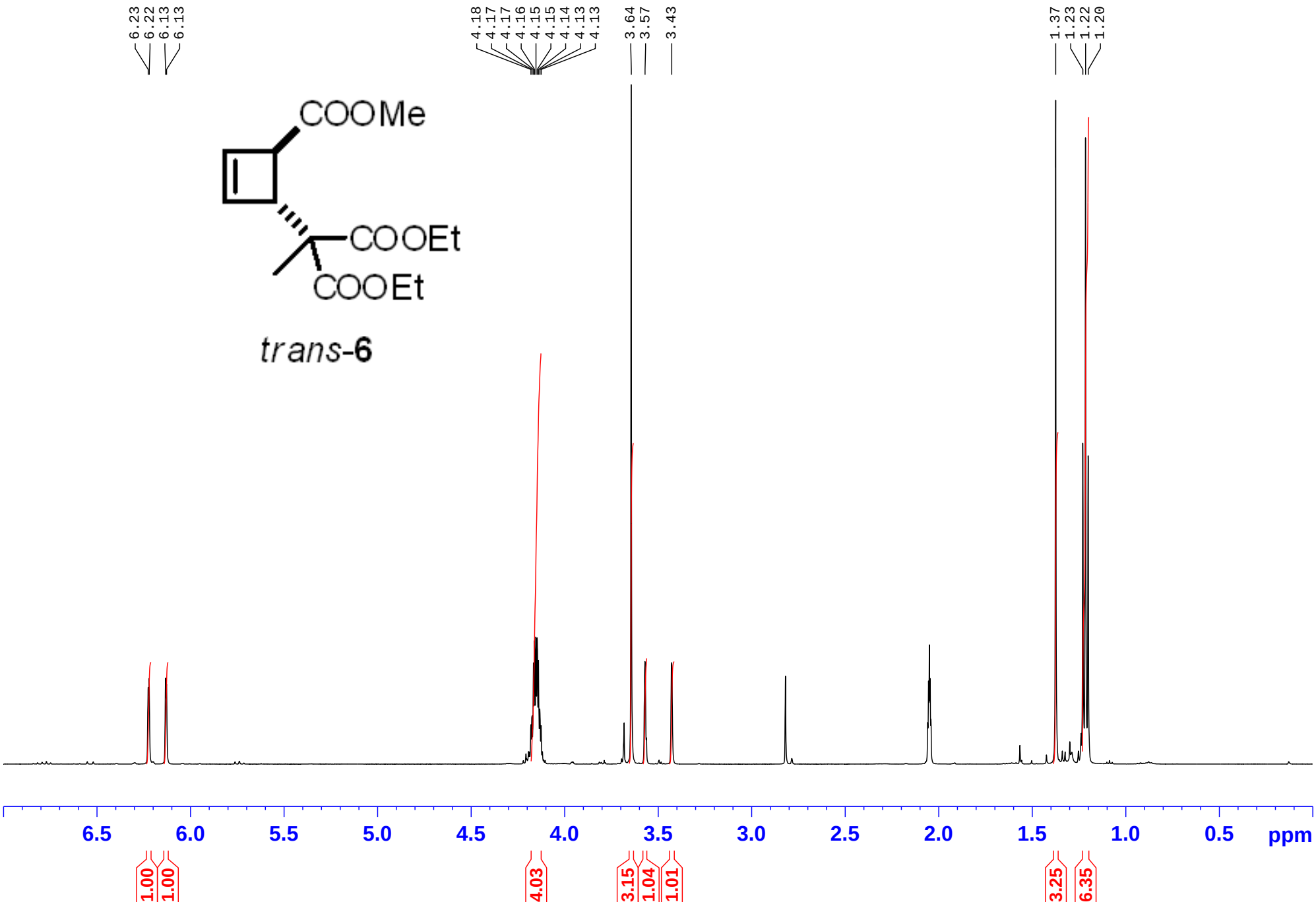
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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6.13
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4.17
4.16
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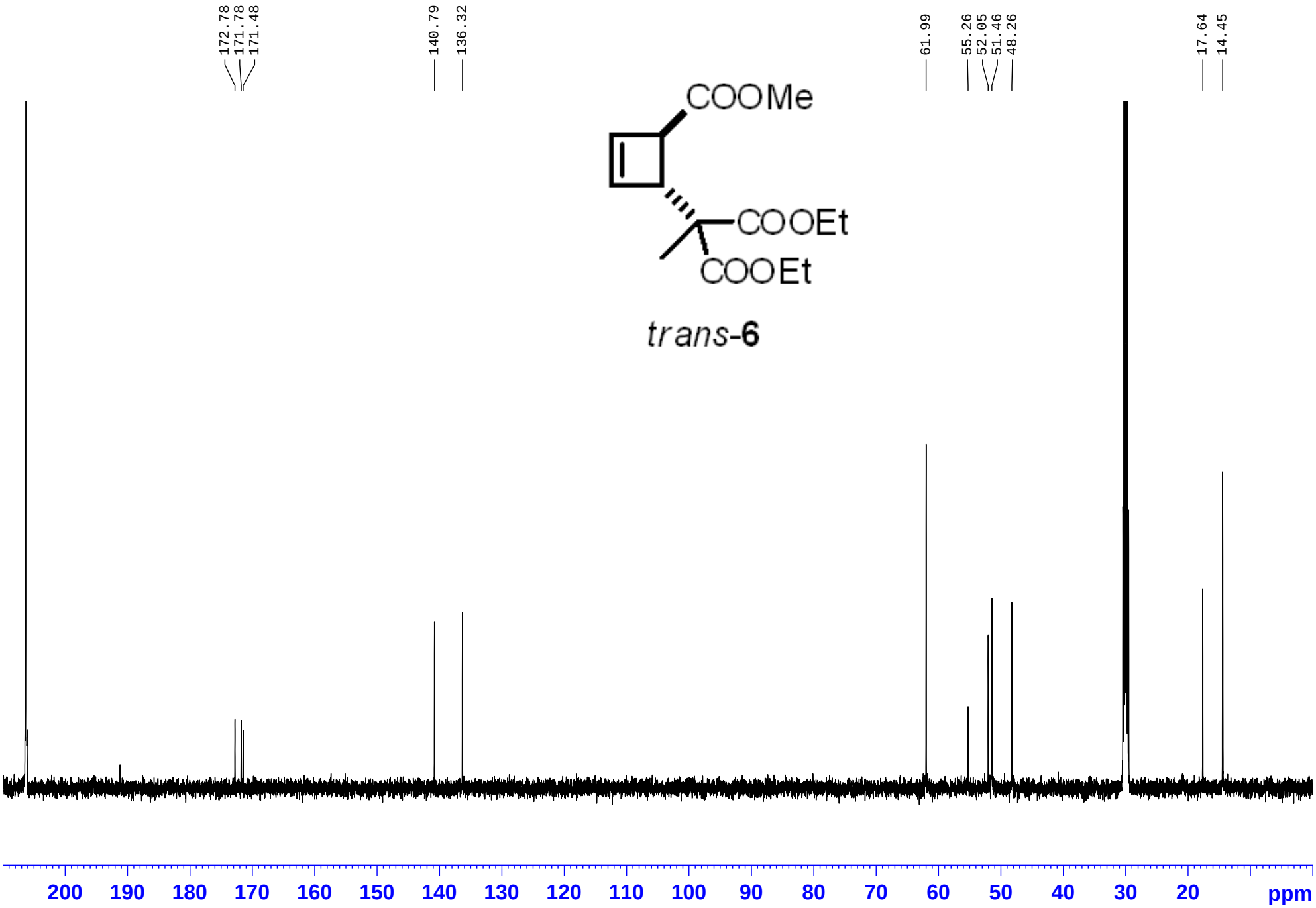
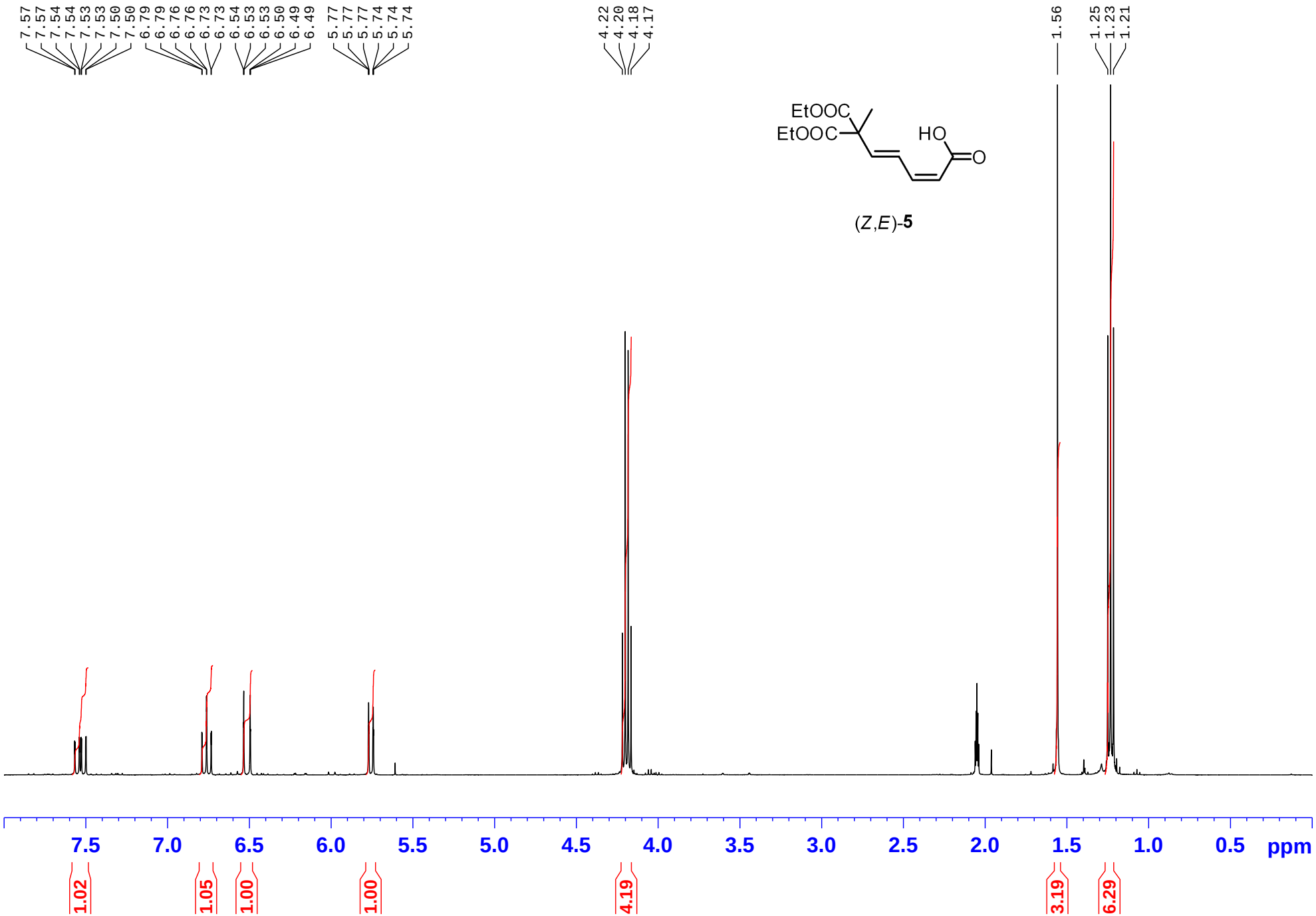
4.15
4.14
4.13
4.13
3.64
3.57
3.43
1.37
1.23
1.22
1.20
COOMe
COOEt
COOEt
trans-6
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.00
4.03
3.15
1.04
1.01
3.25
6.35


172.78
171.78
171.48
140.79
136.32
61.99
55.26
52.05
51.46
48.26
17.64
14.45
COOMe
COOEt
COOEt
trans-6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.50
7.50
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6.79
6.76
6.76
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6.73
6.54
6.53
6.53
6.50
6.49
6.49
5.77
5.77
5.77
5.74
5.74
5.74
4.22
4.20
4.18
4.17
1.56
1.25
1.23
1.21
EtOOC
EtOOC
HO
O
(Z,E)-5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
0.5
ppm
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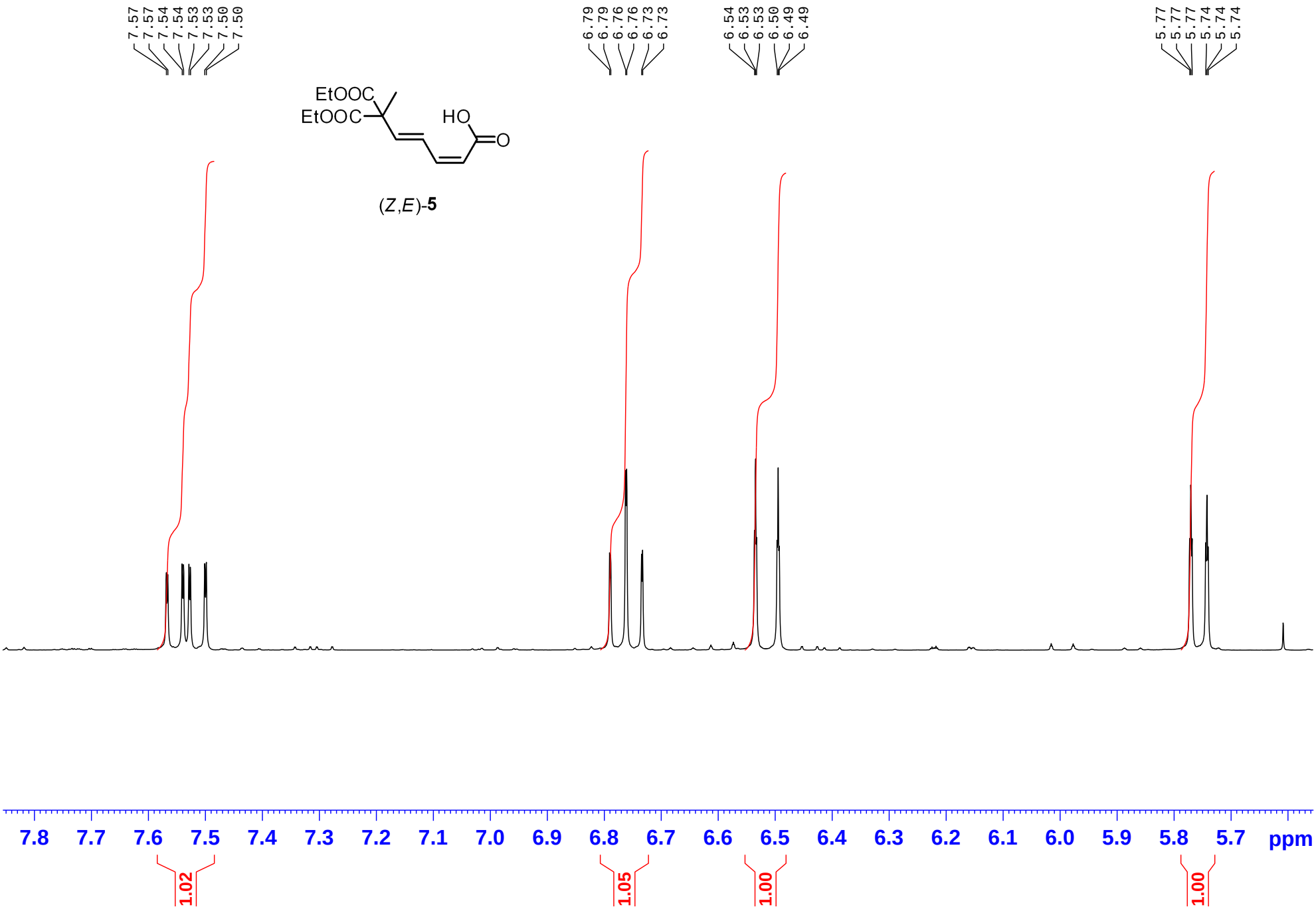
1.05
1.00
1.00
4.19
3.19
6.29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7.54
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7.53
7.50
7.50
6.79
6.79
6.76
6.76
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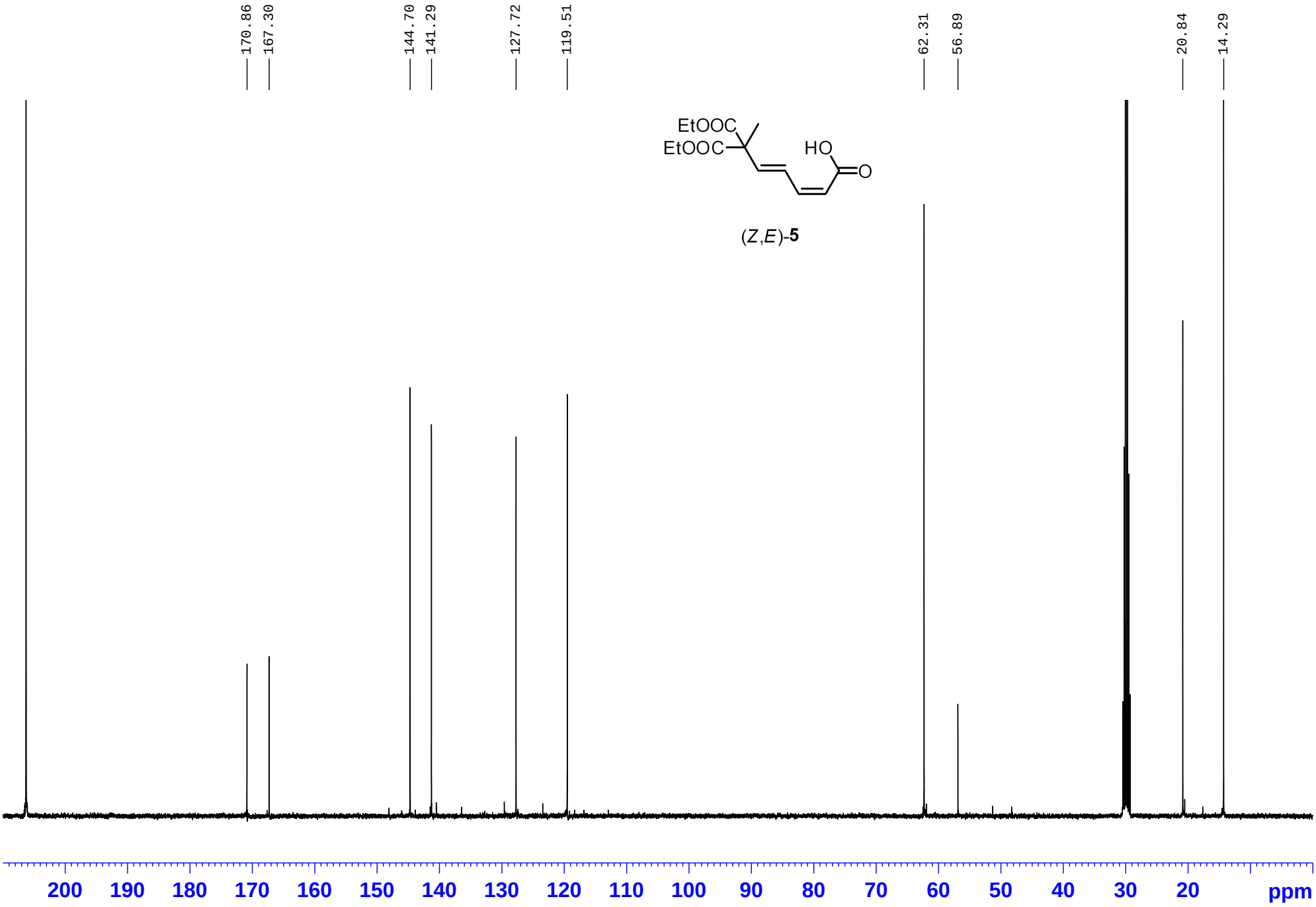
6.73
6.54
6.53
6.53
6.50
6.49
6.49
5.77
5.77
5.77
5.74
5.74
5.74
EtOOC
EtOOC
HO
O
(Z,E)-5
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
ppm
1.02
1.05
1.00
1.00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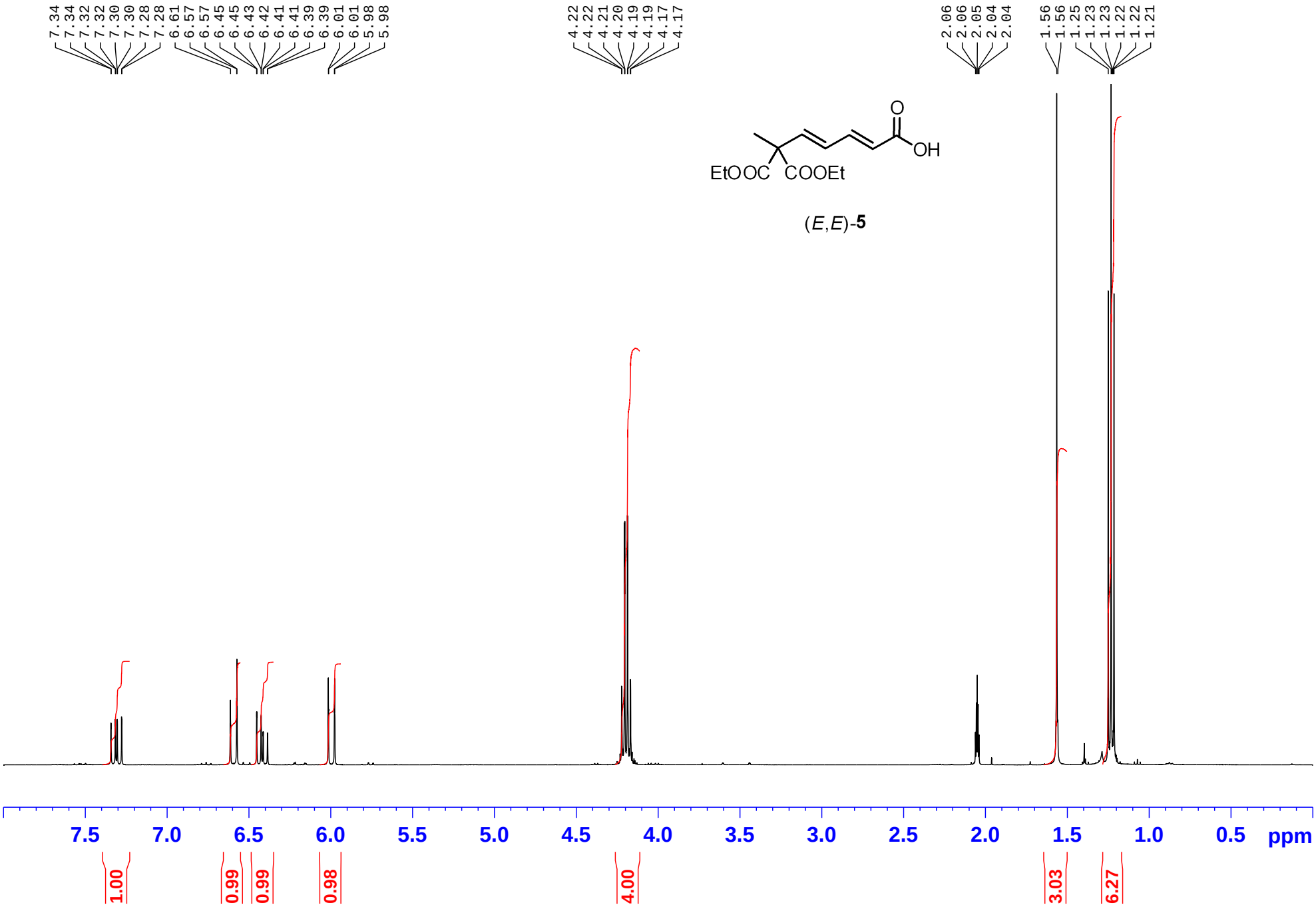
167.30
144.70
141.29
127.72
119.51
62.31
56.89
20.84
14.29
EtOOC
EtOOC
HO
O
(Z,E)-5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.34
7.32
7.32
7.30
7.30
7.28
7.28
6.61
6.57
6.57
6.45
6.45
6.43
6.42
6.41
6.41
6.39
6.39
6.01
6.01
5.98
5.98
4.22
4.22
4.21
4.20
4.19
4.19
4.17
4.17
2.06
2.06
2.05
2.04
2.04
1.56
1.56
1.25
1.23
1.23
1.22
1.22
1.21
O
OH
EtOOC
COOEt
(E,E)-5
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
0.5
ppm
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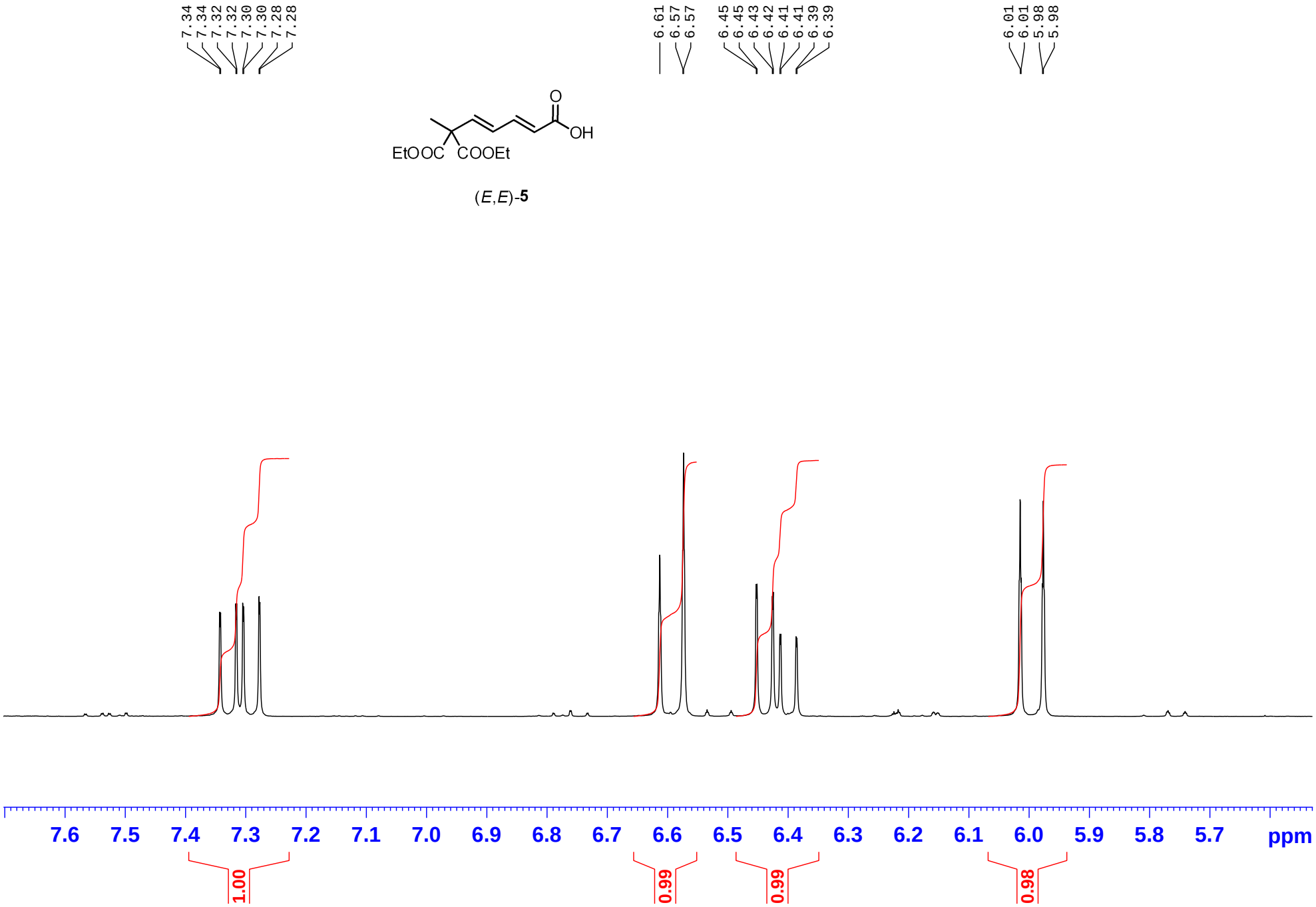
0.99
0.98
4.00
3.03
6.27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7.34
7.32
7.32
7.30
7.30
7.28
7.28
6.61
6.57
6.57
6.45
6.45
6.43
6.42
6.41
6.41
6.39
6.39
6.01
6.01
5.98
5.98
O
OH
EtOOC
COOEt
(E,E)-5
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
ppm
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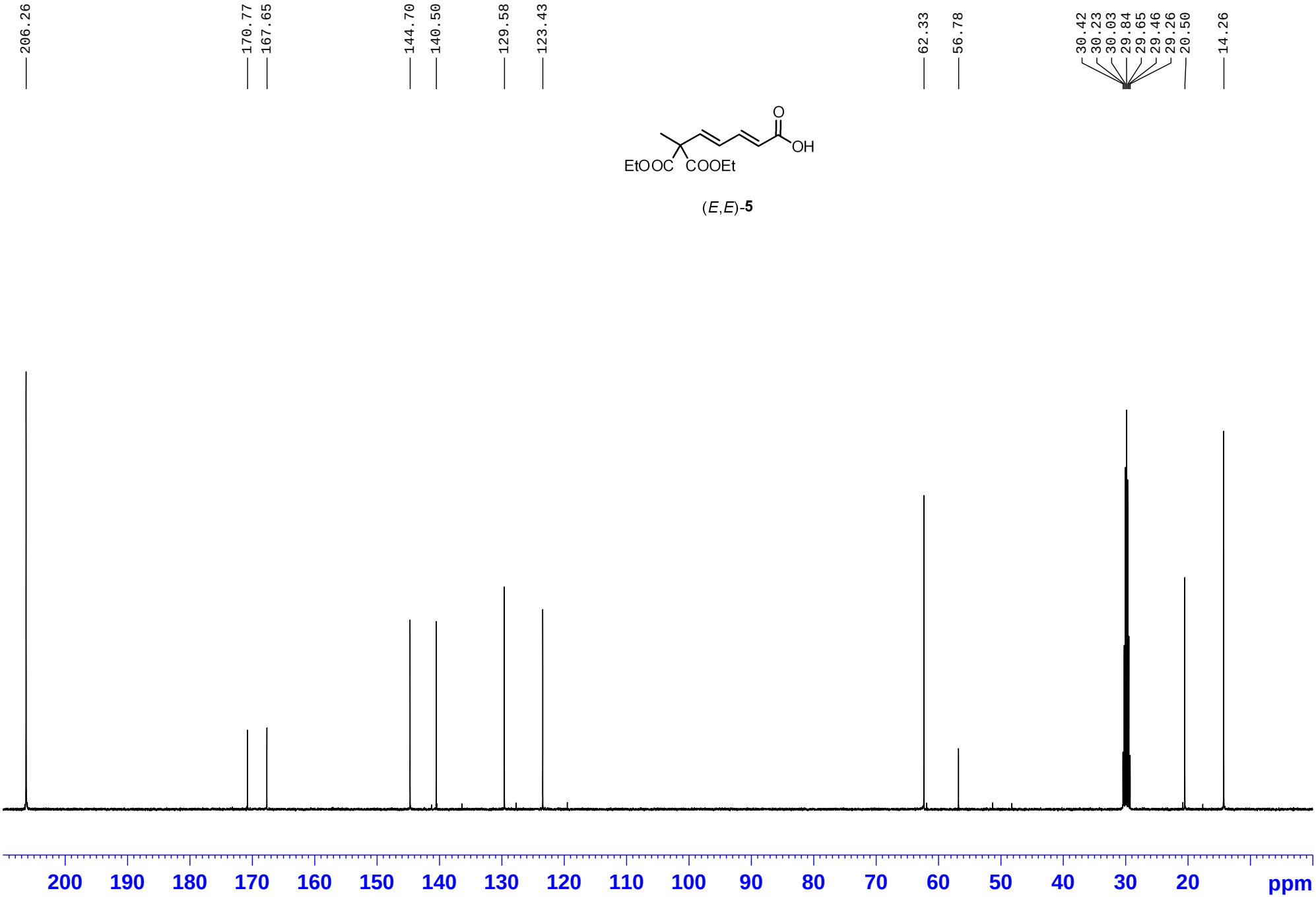
0.99
0.99
0.98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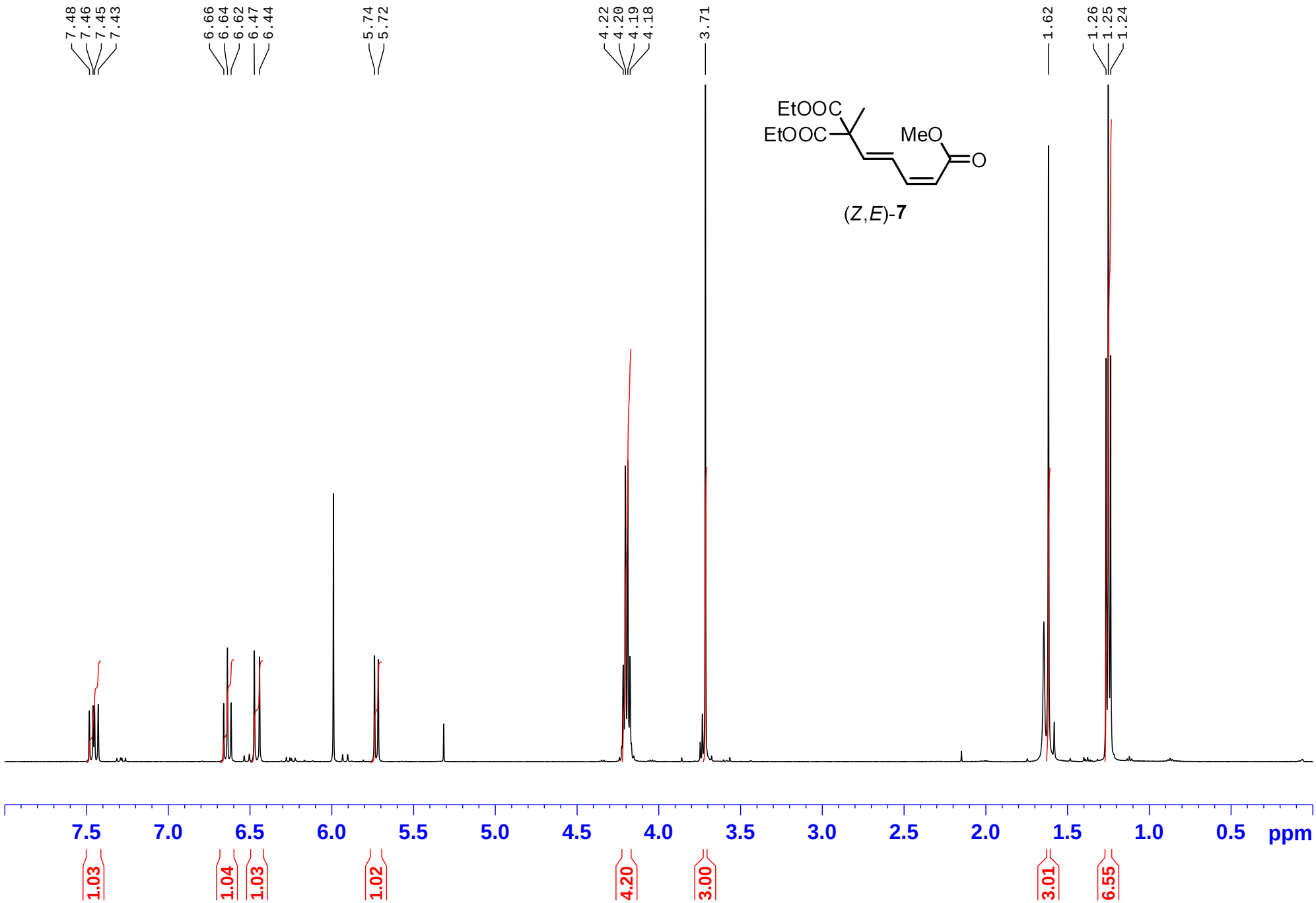
140.50
129.58
123.43
62.33
56.78
30.42
30.23
30.03
29.84
29.65
29.46
29.26
20.50
14.26
O
OH
EtOOC COOEt
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

(*E*,*E*)-**5**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6.64
6.62
6.47
6.44
5.74
5.72
4.22
4.20
4.19
4.18
3.71
1.62
1.26
1.25
1.24
EtOOC
EtOOC
MeO
O
(Z,E)-7
7.5
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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ppm
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1.04
1.03
1.02
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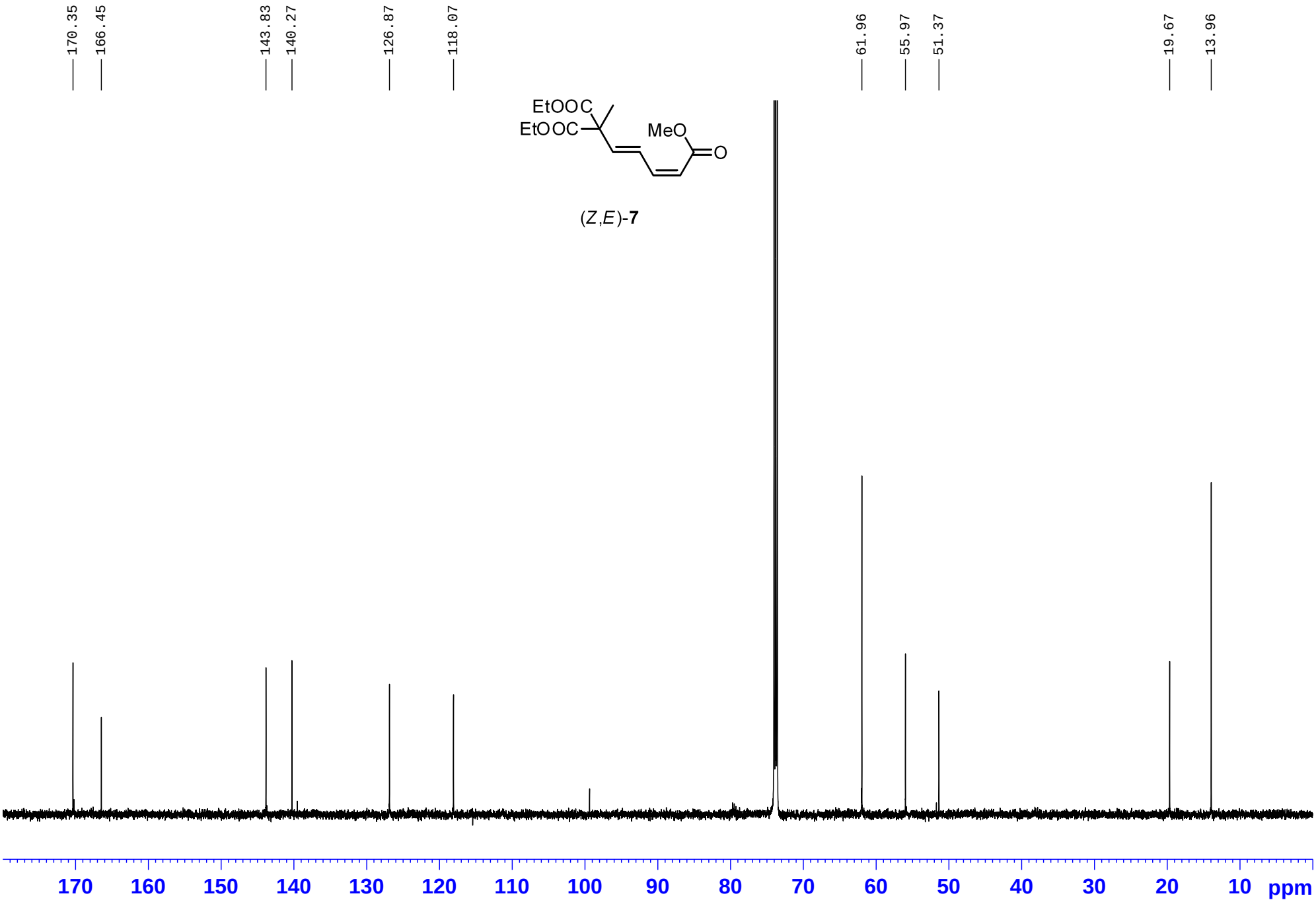
3.01
6.55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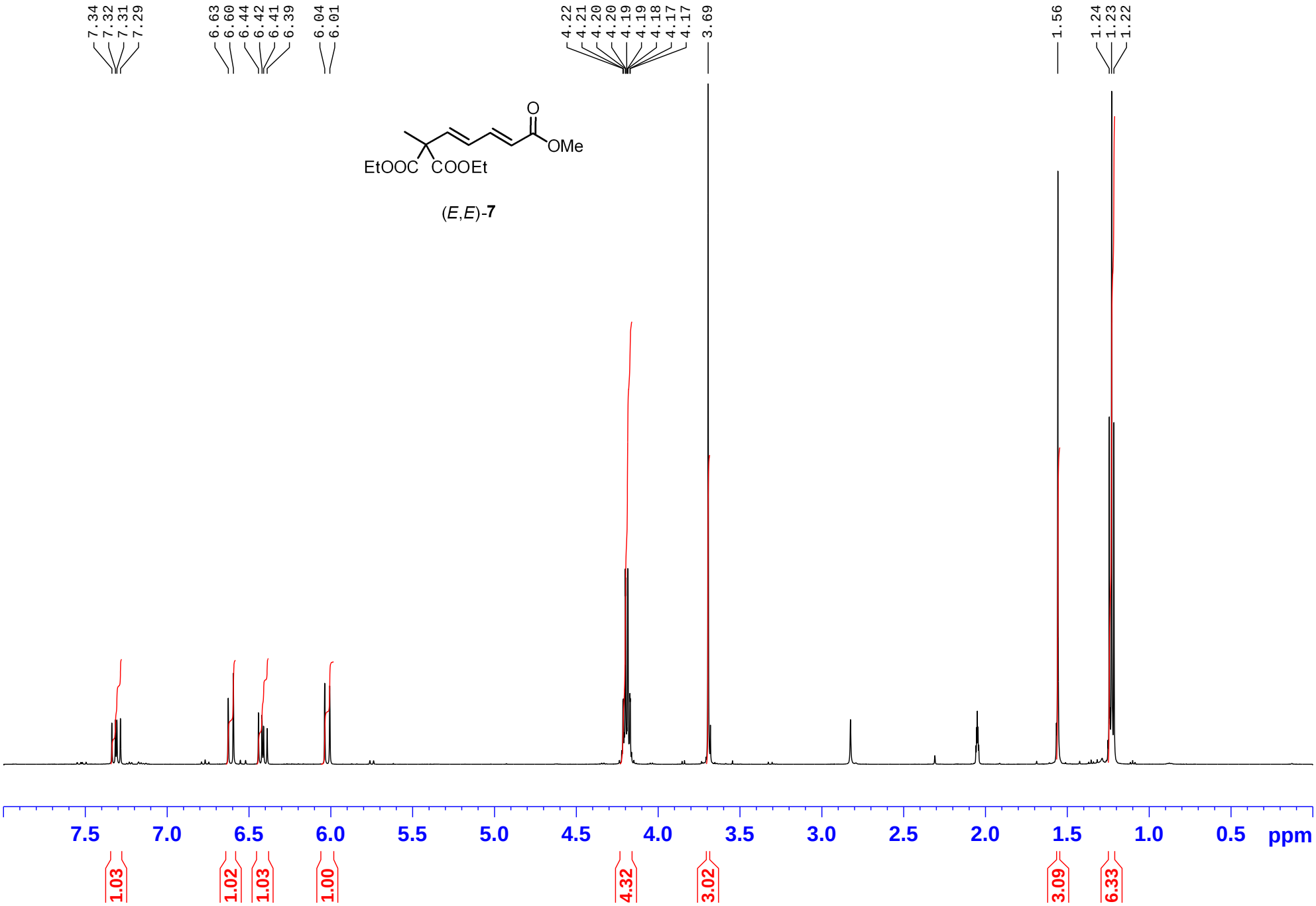
166.45
143.83
140.27
126.87
118.07
61.96
55.97
51.37
19.67
13.96
EtOOC
EtOOC
MeO
O
(Z,E)-7
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.32
7.31
7.29
6.63
6.60
6.44
6.42
6.41
6.39
6.04
6.01
4.22
4.21
4.20
4.20
4.19
4.19
4.18
4.17
4.17
3.69
1.56
1.24
1.23
1.22
O
OMe
EtOOC COOEt
(E,E)-7
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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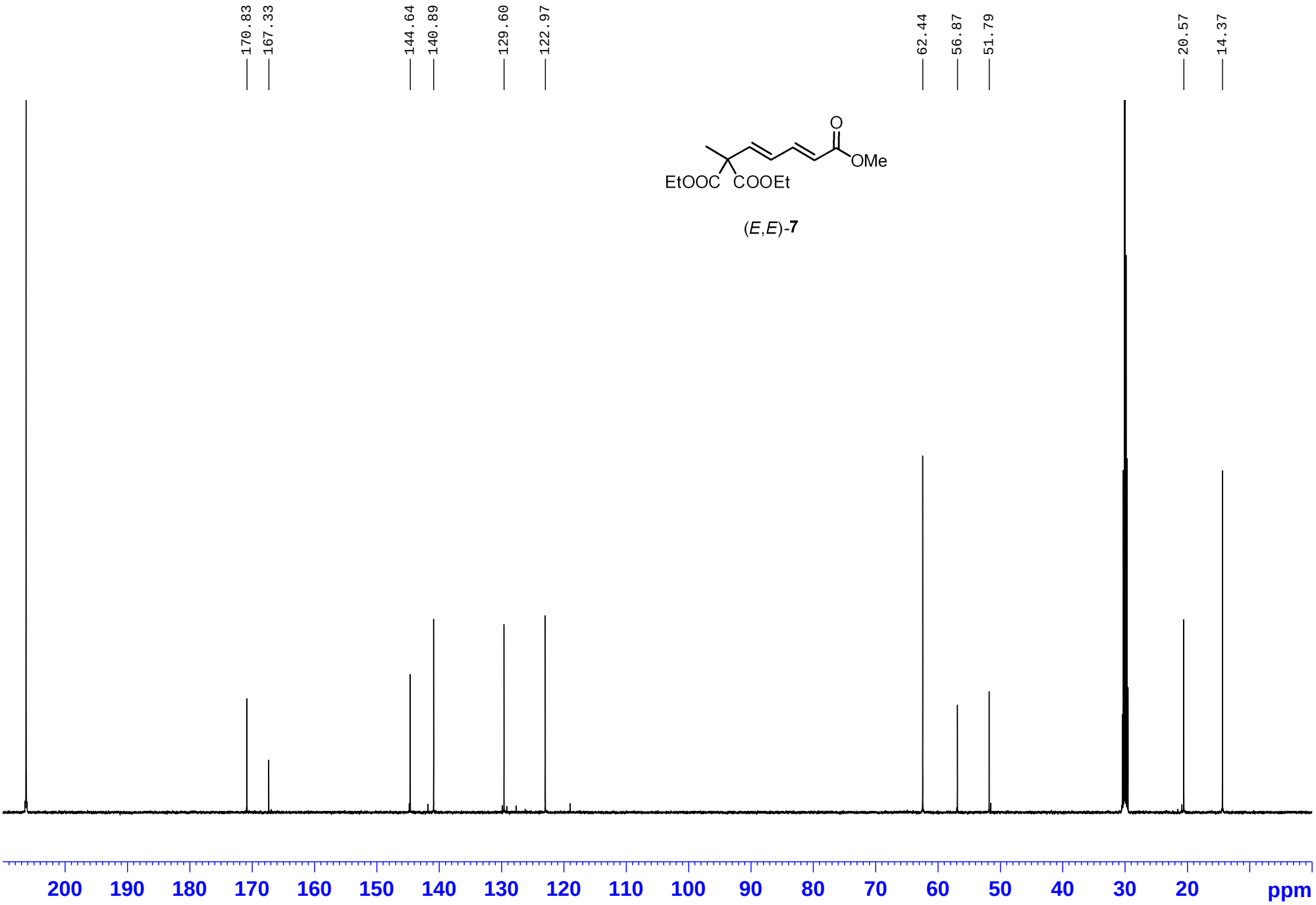
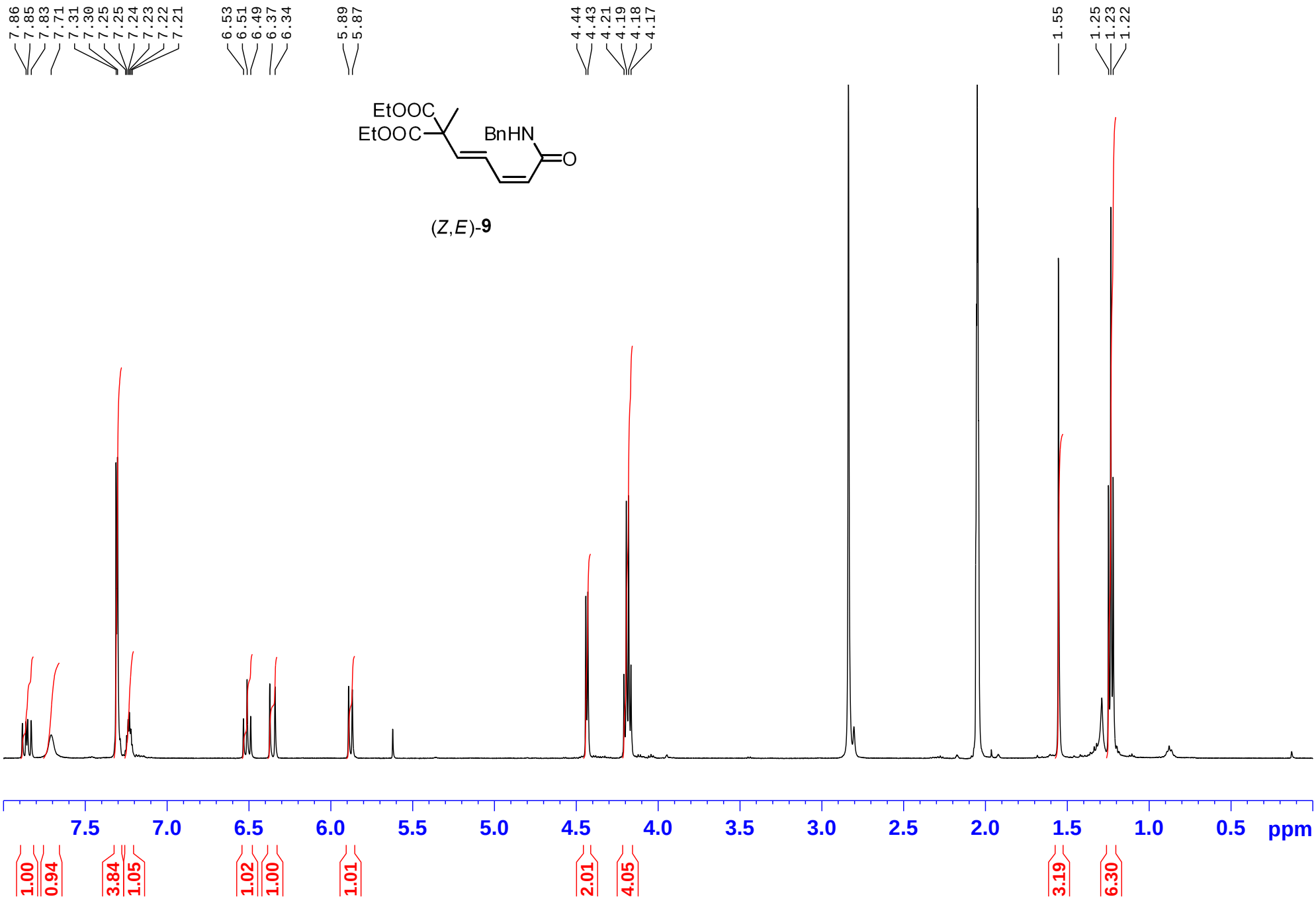
1.02
1.03
1.00
4.32
3.02
3.09
6.33


170.83
167.33
144.64
140.89
129.60
122.97
62.44
56.87
51.79
20.57
14.37
O
OMe
EtOOC
COOEt
(E,E)-7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.85
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7.71
7.31
7.30
7.25
7.25
7.24
7.23
7.22
7.21
6.53
6.51
6.49
6.37
6.34
5.89
5.87
4.44
4.43
4.21
4.19
4.18
4.17
1.55
1.25
1.23
1.22
EtOOC
EtOOC
BnHN
O
(Z,E)-9
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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0.94
3.84
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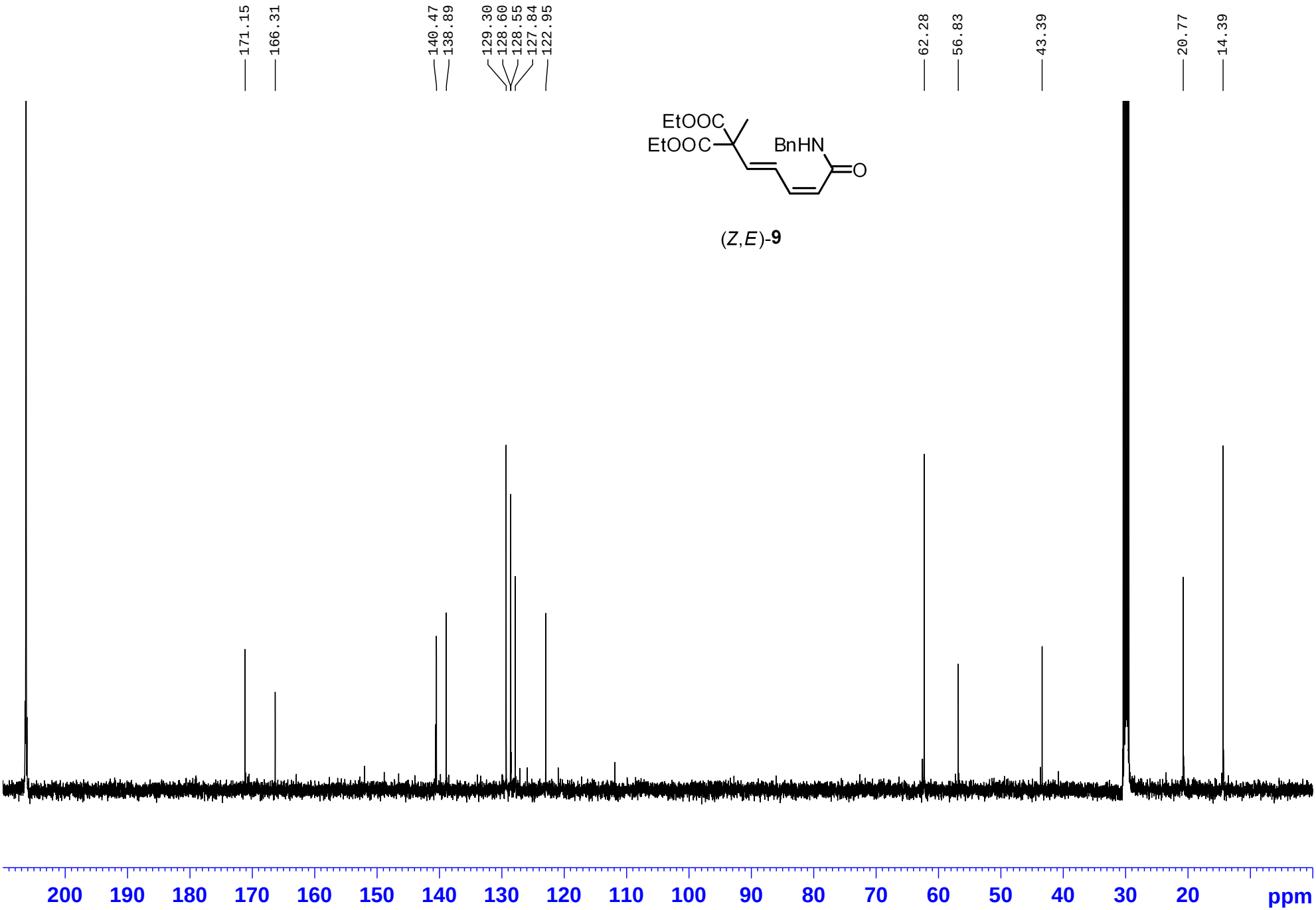
1.02
1.00
1.01
2.01
4.05
3.19
6.30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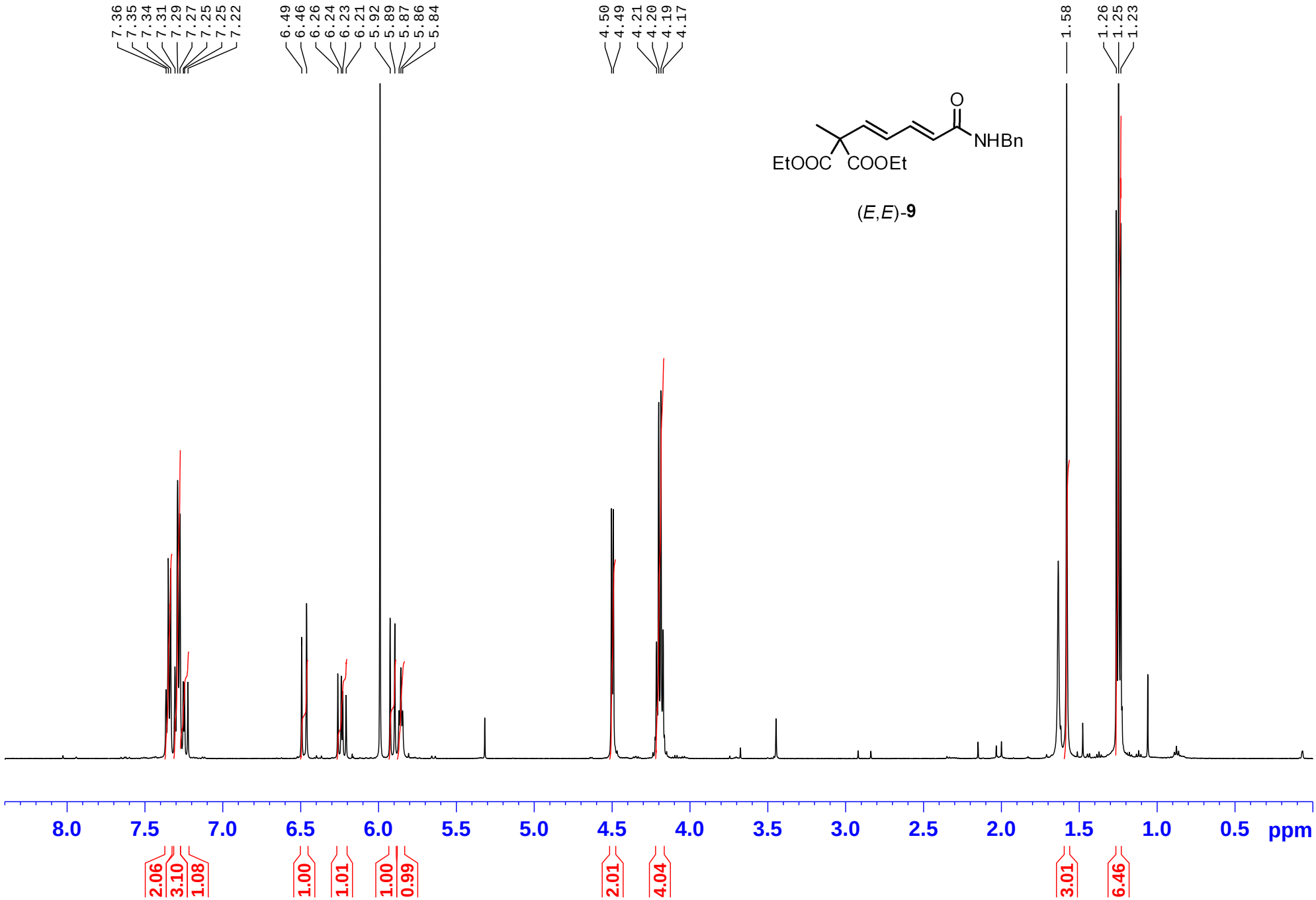
166.31
140.47
138.89
129.30
128.60
128.55
127.84
122.95
62.28
56.83
43.39
20.77
14.39
EtOOC
EtOOC
BnHN
O
(Z,E)-9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.34
7.31
7.29
7.27
7.25
7.25
7.22
6.49
6.46
6.26
6.24
6.23
6.21
5.92
5.89
5.87
5.86
5.84
4.50
4.49
4.21
4.20
4.19
4.17
1.58
1.26
1.25
1.23
O
NHBn
EtOOC
COOEt
(E,E)-9
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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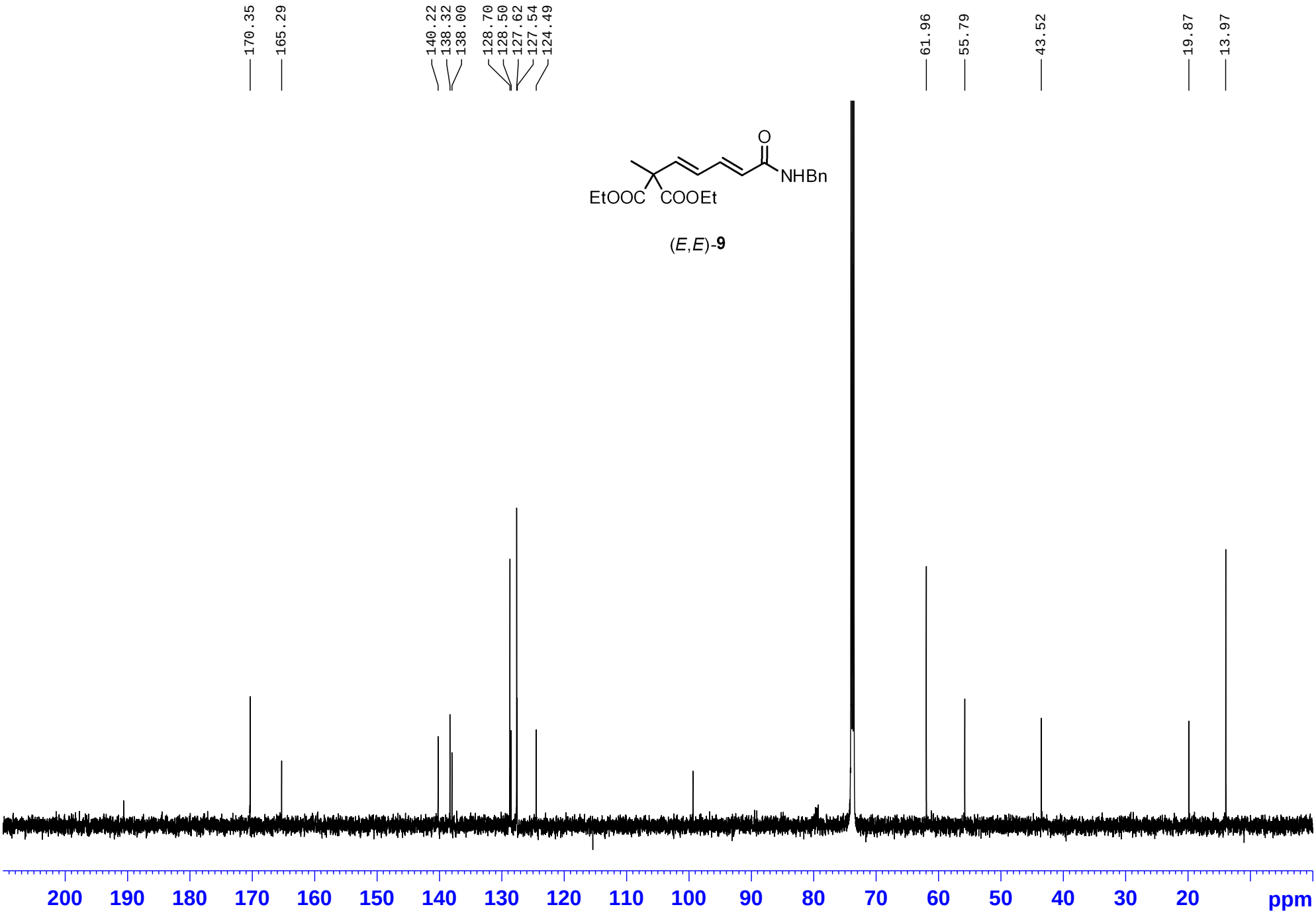
3.10
1.08
1.00
1.01
1.00
0.99
2.01
4.04
3.01
6.46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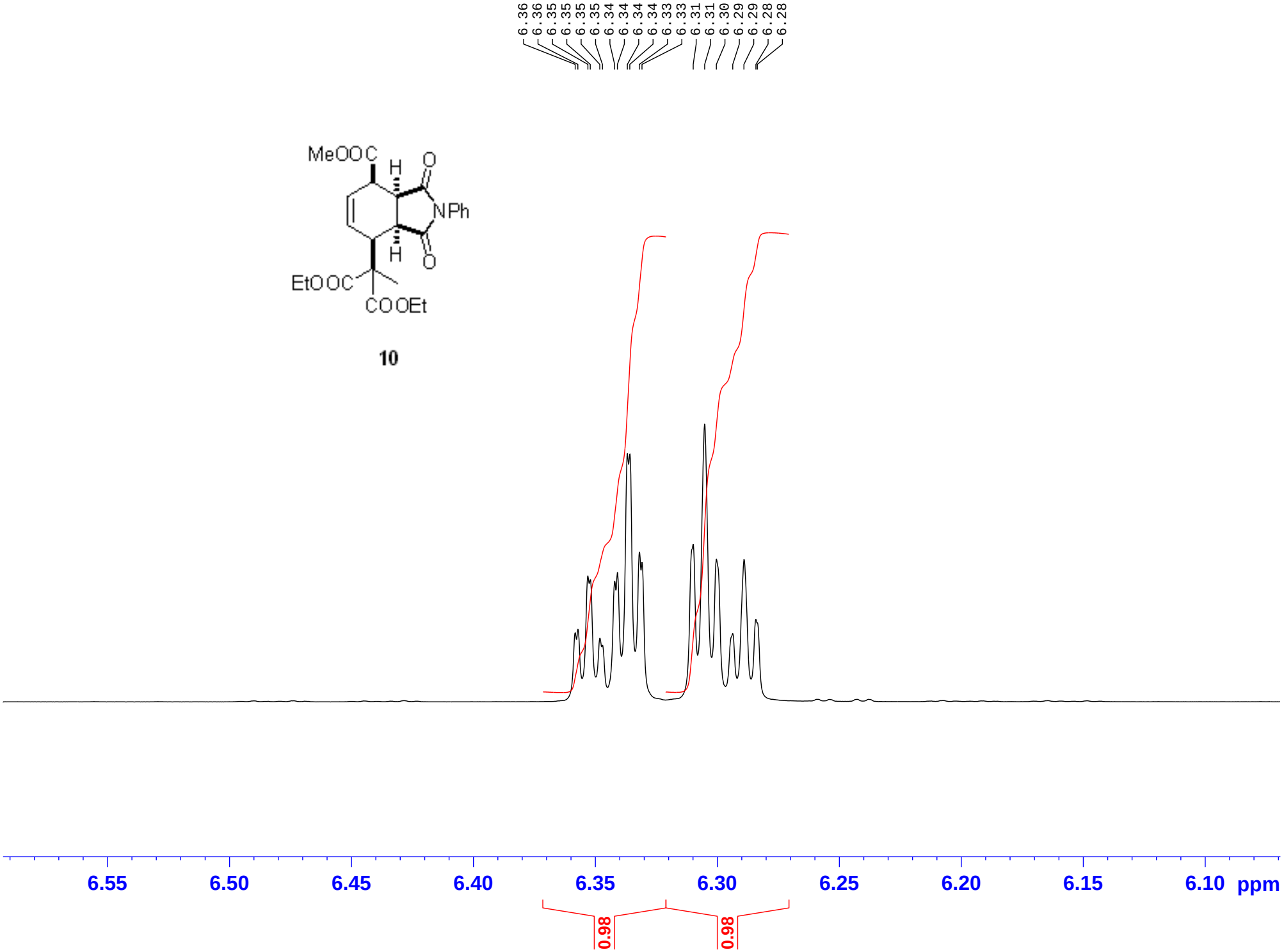
165.29
140.22
138.32
138.00
128.70
128.50
127.62
127.54
124.49
61.96
55.79
43.52
19.87
13.97
O
NHBn
EtOOC
COOEt
(E,E)-9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


6.36
6.36
6.35
6.35
6.35
6.34
6.34
6.34
6.33
6.33
6.31
6.31
6.30
6.29
6.29
6.28
6.28
MeOOC
H
O
NPh
H
O
EtOOC
COOEt
10
6.55
6.50
6.45
6.40
6.35
6.30
6.25
6.20
6.15
6.10
ppm
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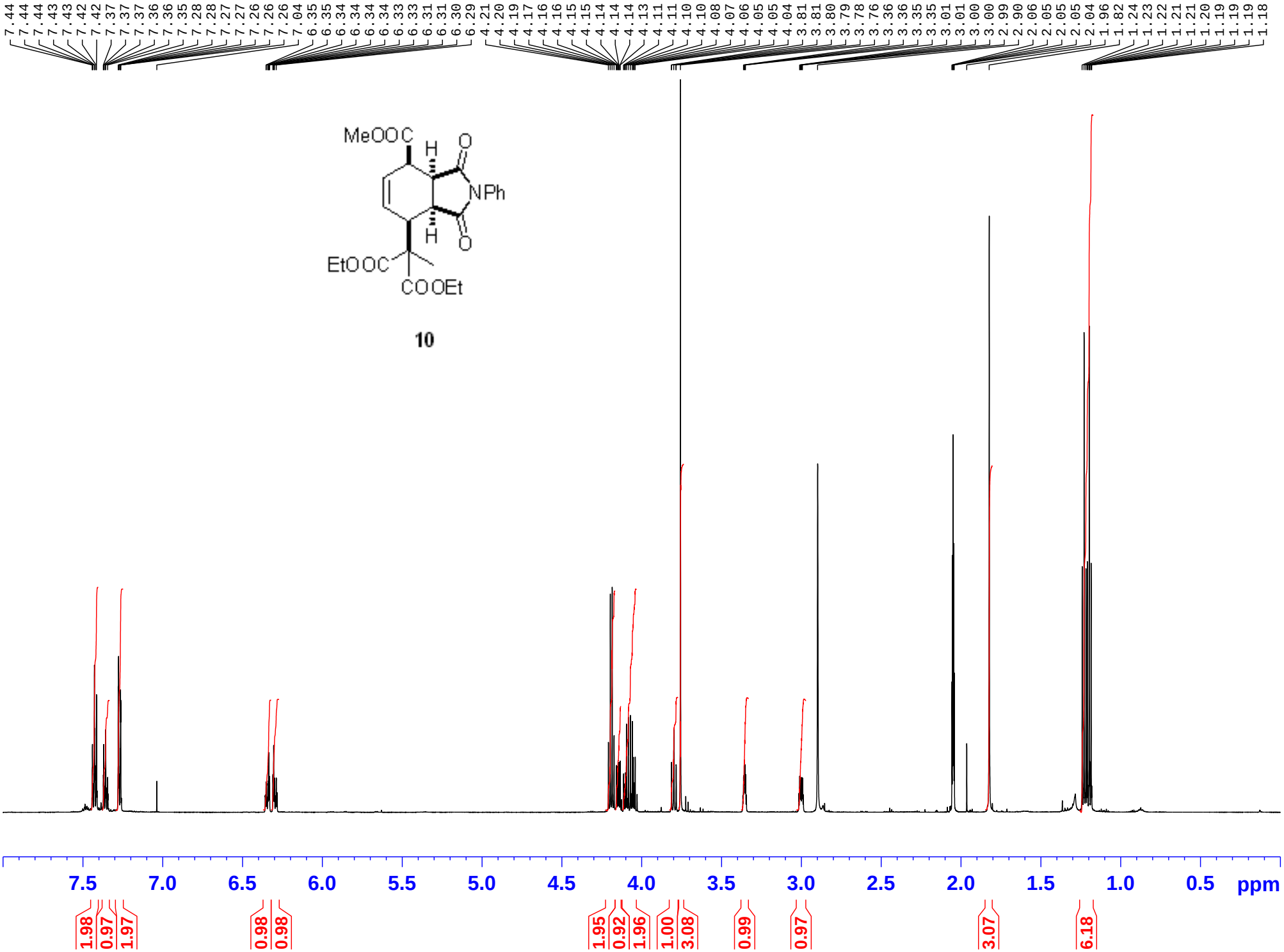
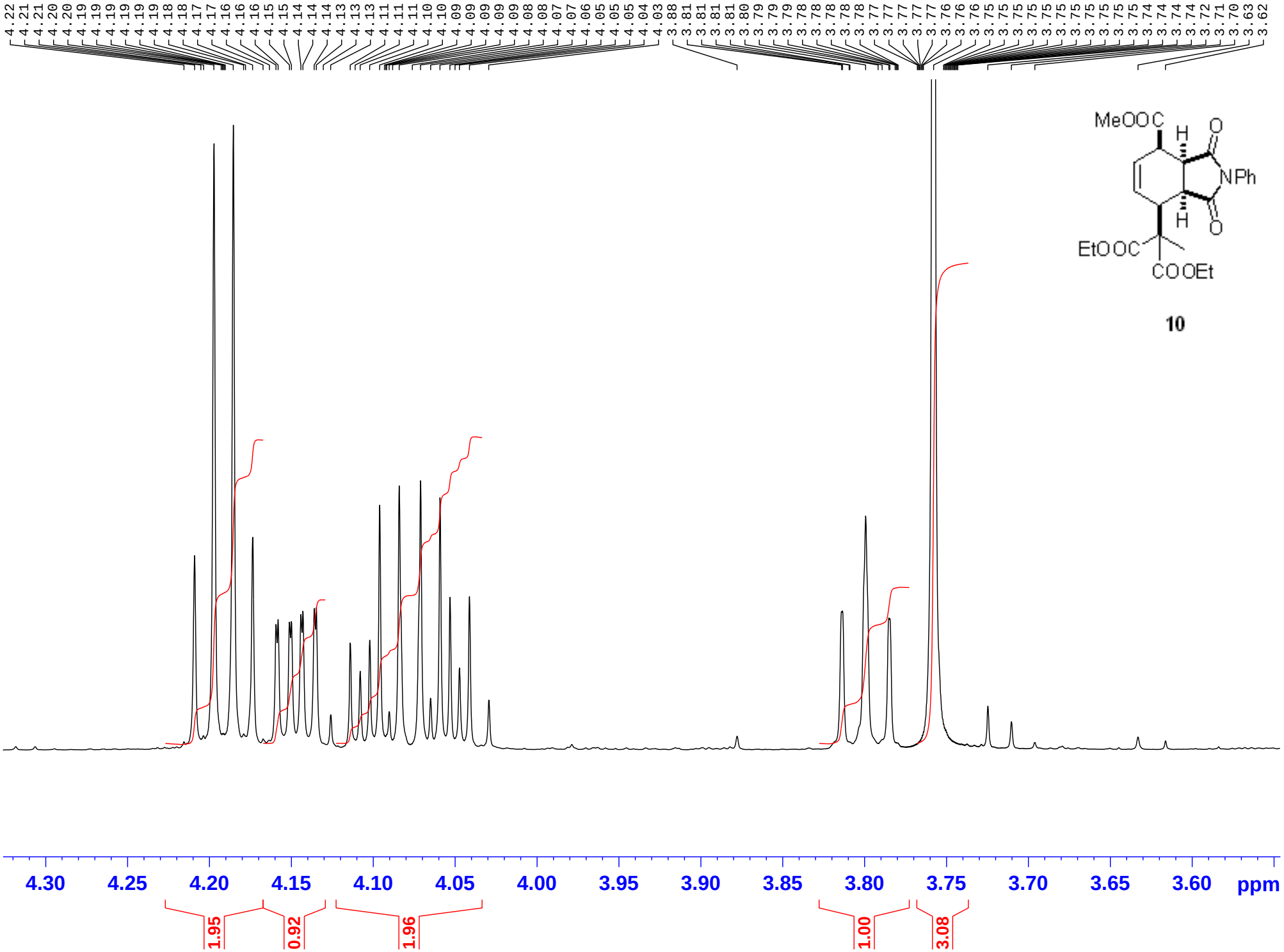
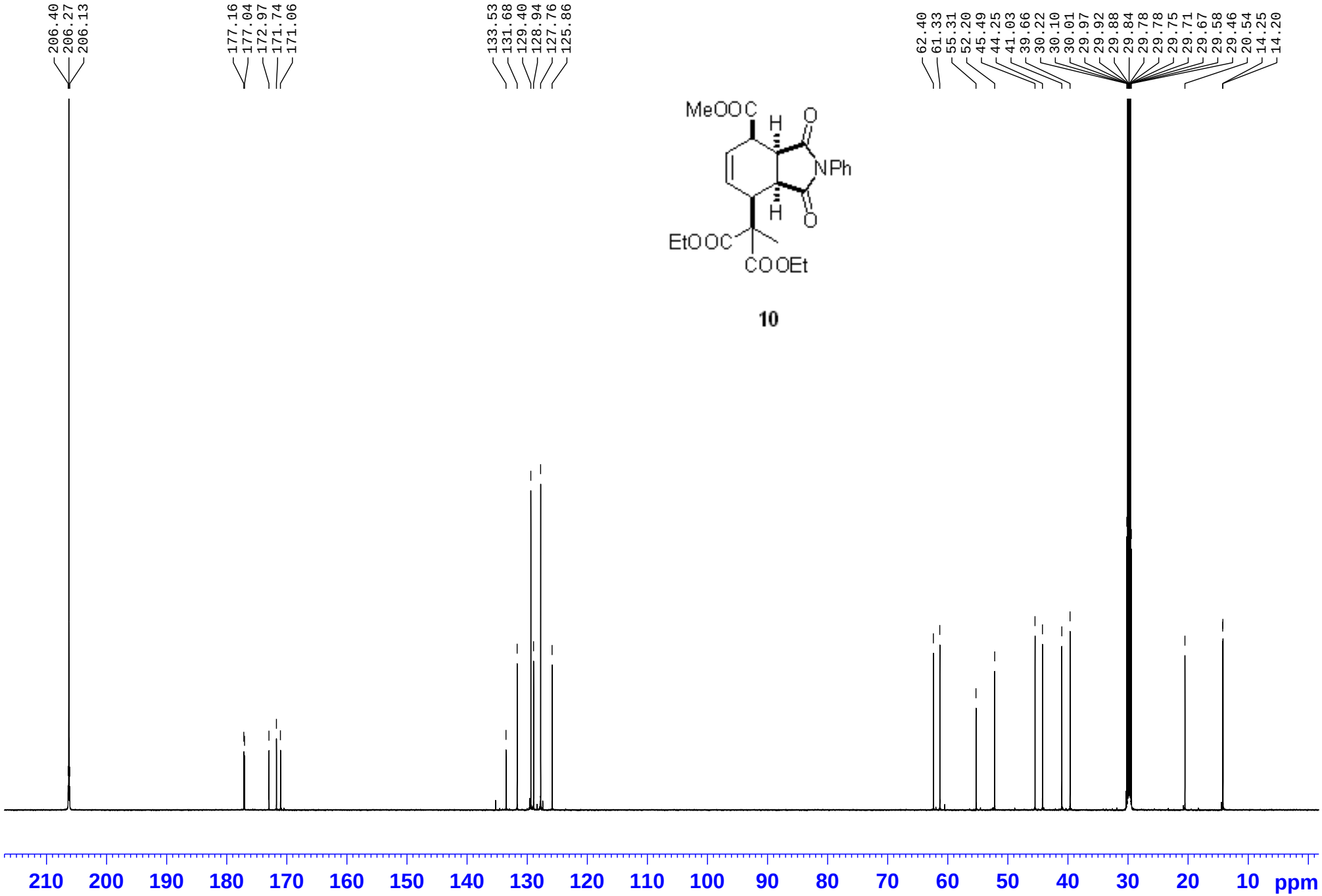
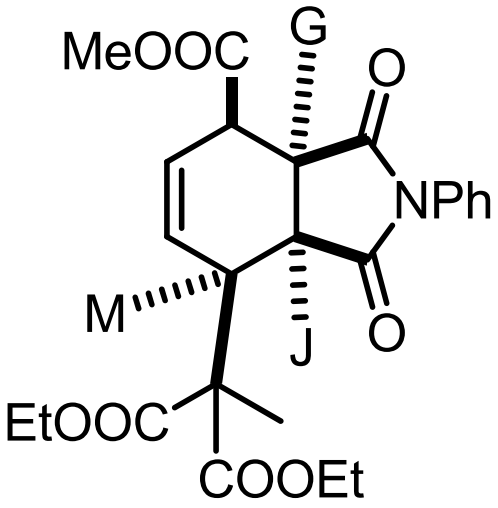
0.98


MeOOC
H
O
NPh
H
O
EtOOC
COOEt
10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.98
0.97
1.97
0.98
0.98
1.95
0.92
1.96
1.00
3.08
0.99
0.97
3.07
6.18

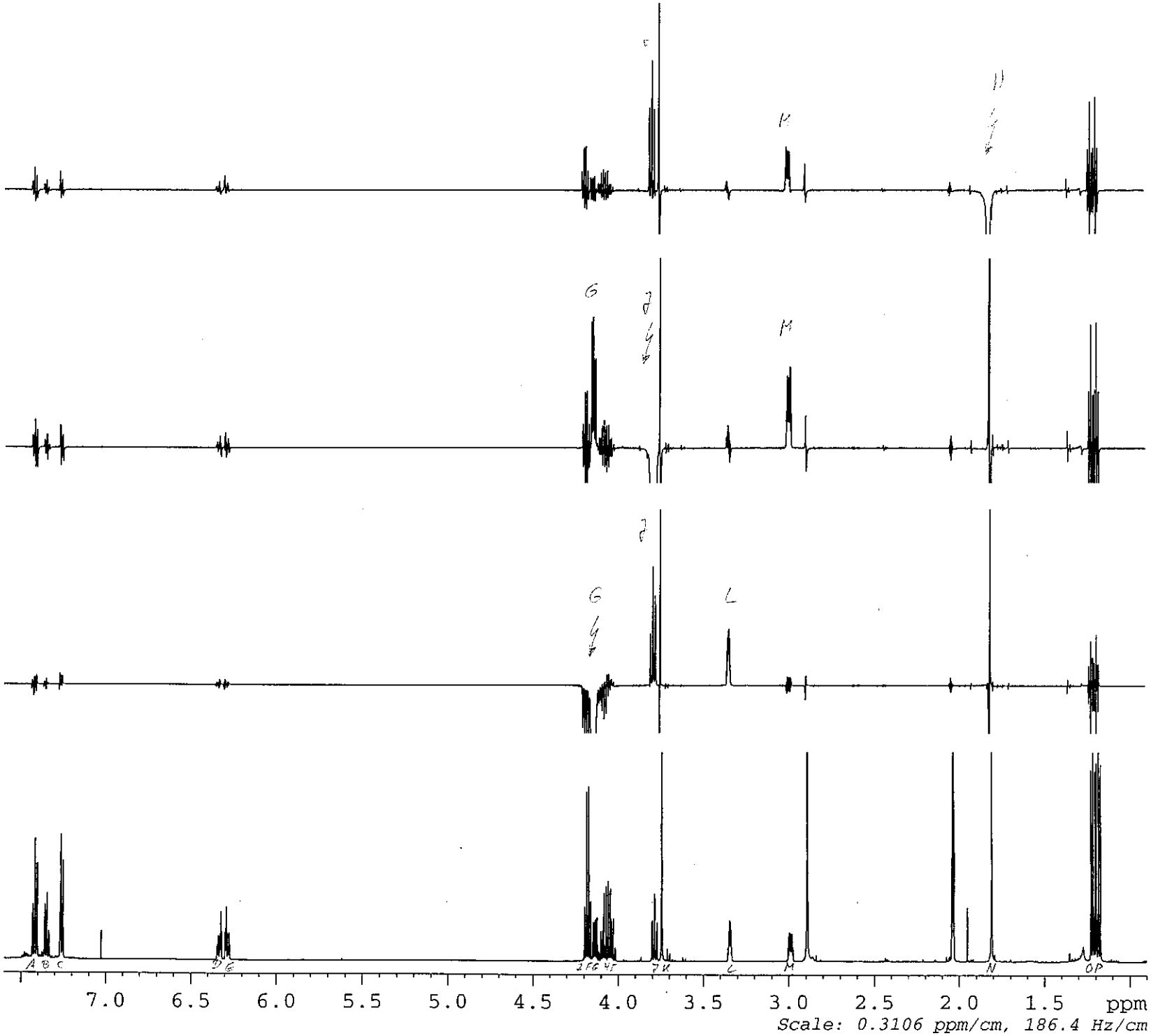

MeOOC
H
O
NPh
H
O
EtOOC
COOEt
10
4.30
4.25
4.20
4.15
4.10
4.05
4.00
3.95
3.90
3.85
3.80
3.75
3.70
3.65
3.60
ppm
1.95
0.92
1.96
1.00
3.08


206.40
206.27
206.13
177.16
177.04
172.97
171.74
171.06
133.53
131.68
129.40
128.94
127.76
125.86
62.40
61.33
55.31
52.20
45.49
44.25
41.03
39.66
30.22
30.10
30.01
29.97
29.92
29.88
29.84
29.78
29.78
29.75
29.71
29.67
29.58
29.46
20.54
14.25
14.20
MeOOC
H
O
NPh
H
O
EtOOC
COOEt
10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



10

Relevant NOE interaction



H615812

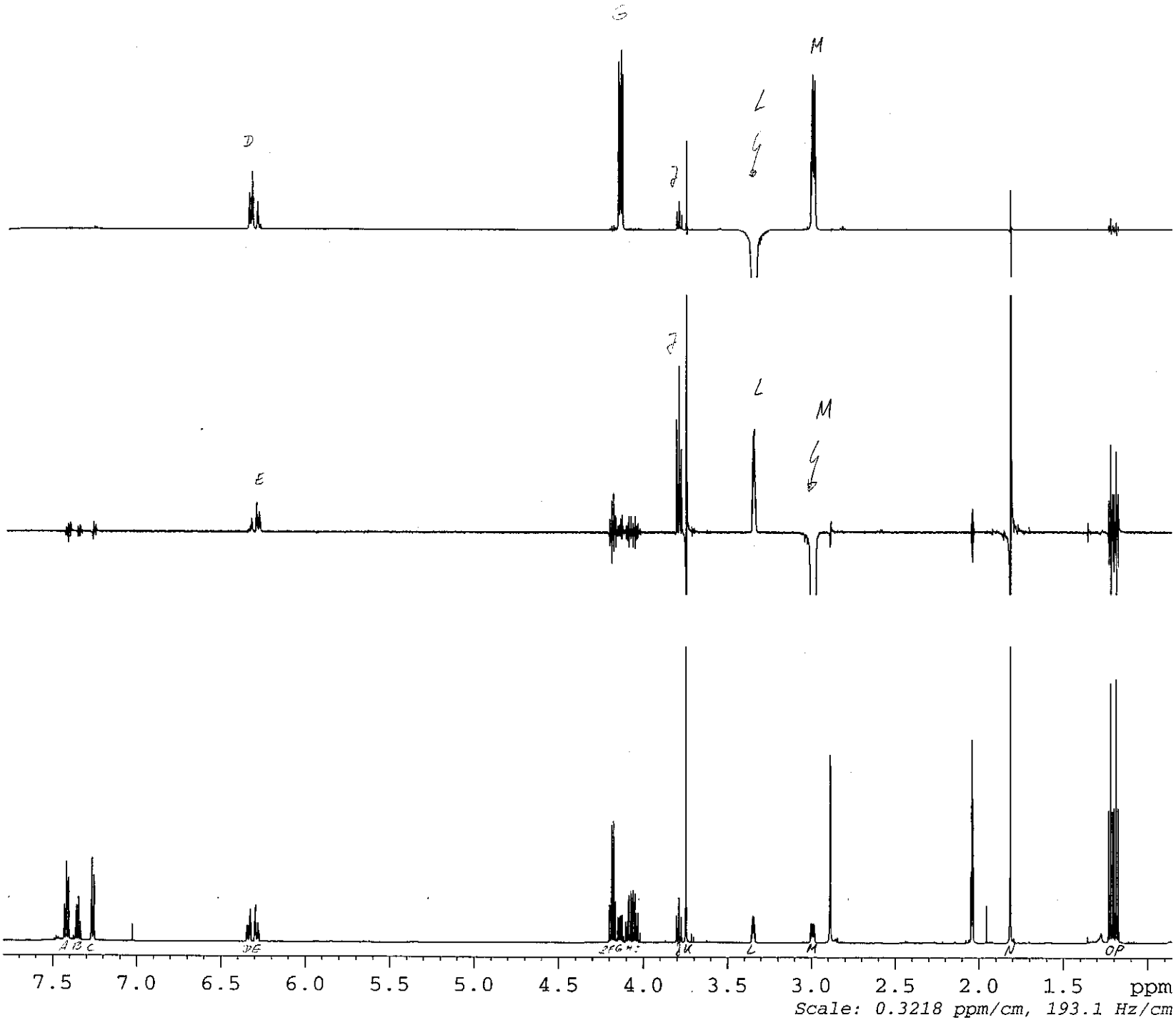
NAME lupic25403
EXPNO 110
PROCNO 1
Date_ 20110926
Time 9.47
INSTRUM av600
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 32
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 9
DW 41.600 usec
DE 10.00 usec
TE 287.5 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 8.50 usec
PL1 4.20 dB
PL1W 5.30020905 W
SFO1 600.2242403 MHz
SI 131072
SF 600.2200093 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
SR 9.30 Hz

LUP-LC-254-03

1D-NOESY

av600



H615810

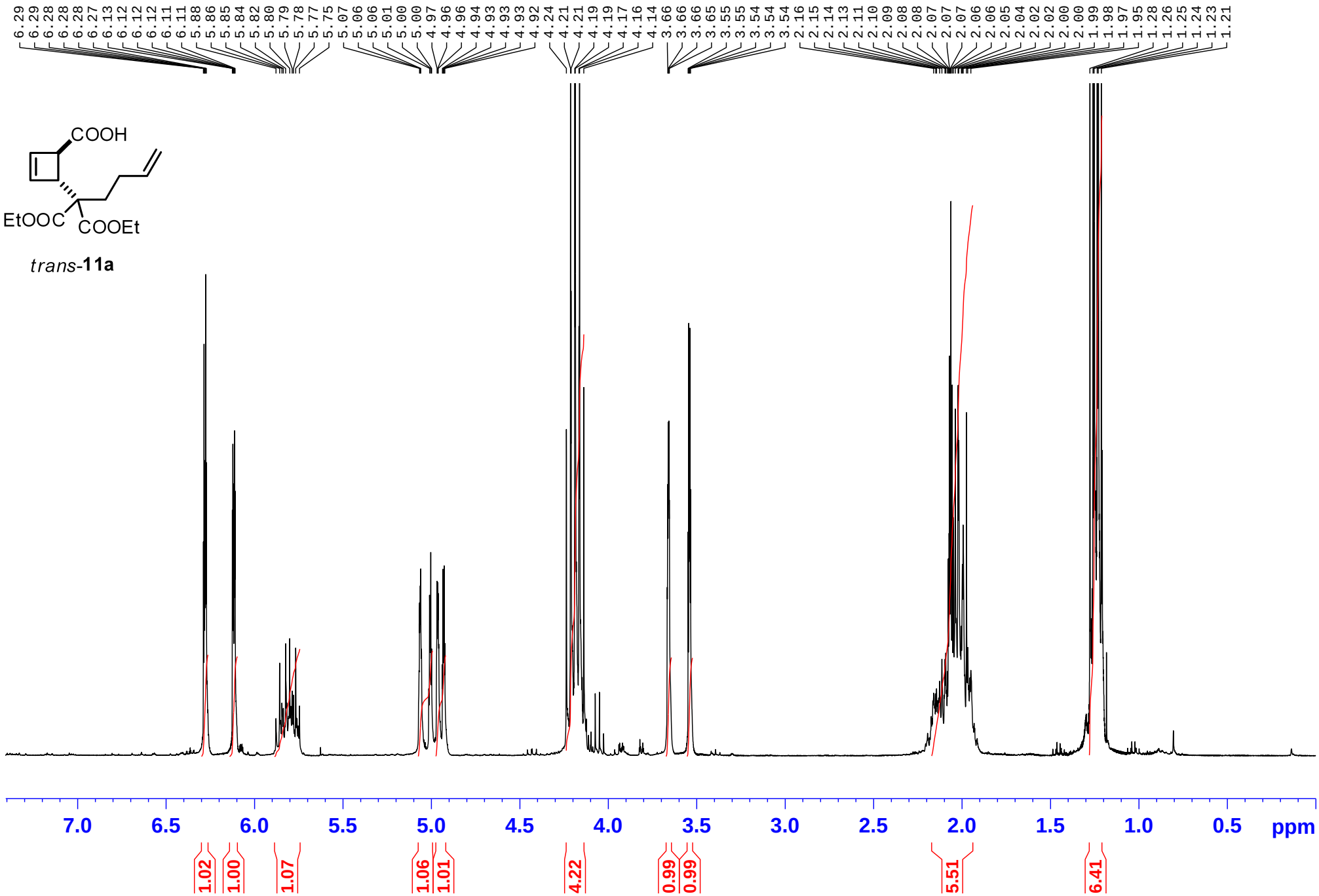
NAME lupic25403
EXPNO 10
PROCNO 1
Date_ 20110920
Time 13.58
INSTRUM av600
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 32
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 9
DW 41.600 usec
DE 10.00 usec
TE 287.9 K
D1 1.00000000 sec
TD0 1

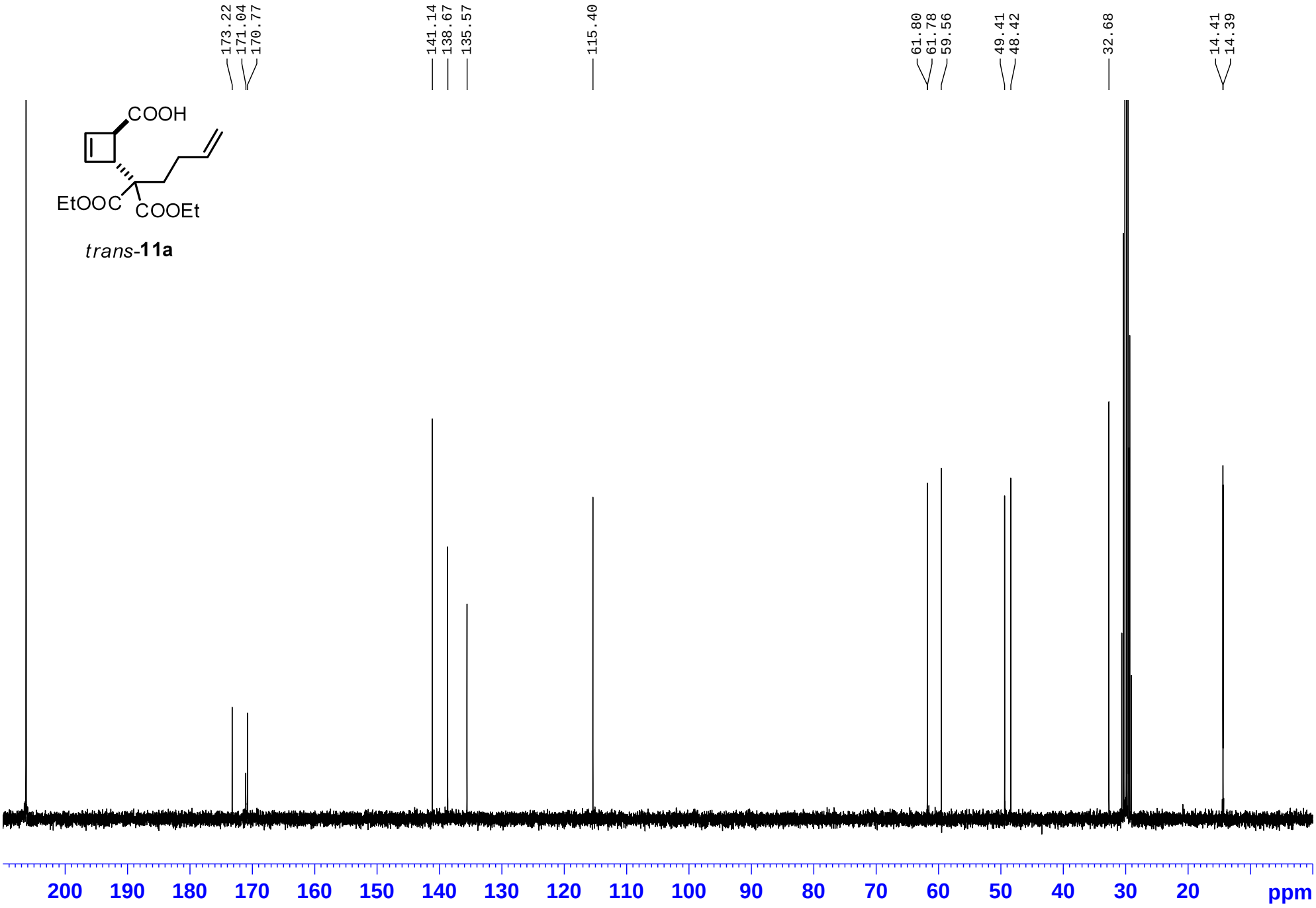
======== CHANNEL f1 ========
NUC1 1H
P1 8.50 usec
PL1 4.20 dB
PL1W 5.30020905 W
SFO1 600.2242403 MHz
SI 131072
SF 600.2200093 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
SR 9.30 Hz

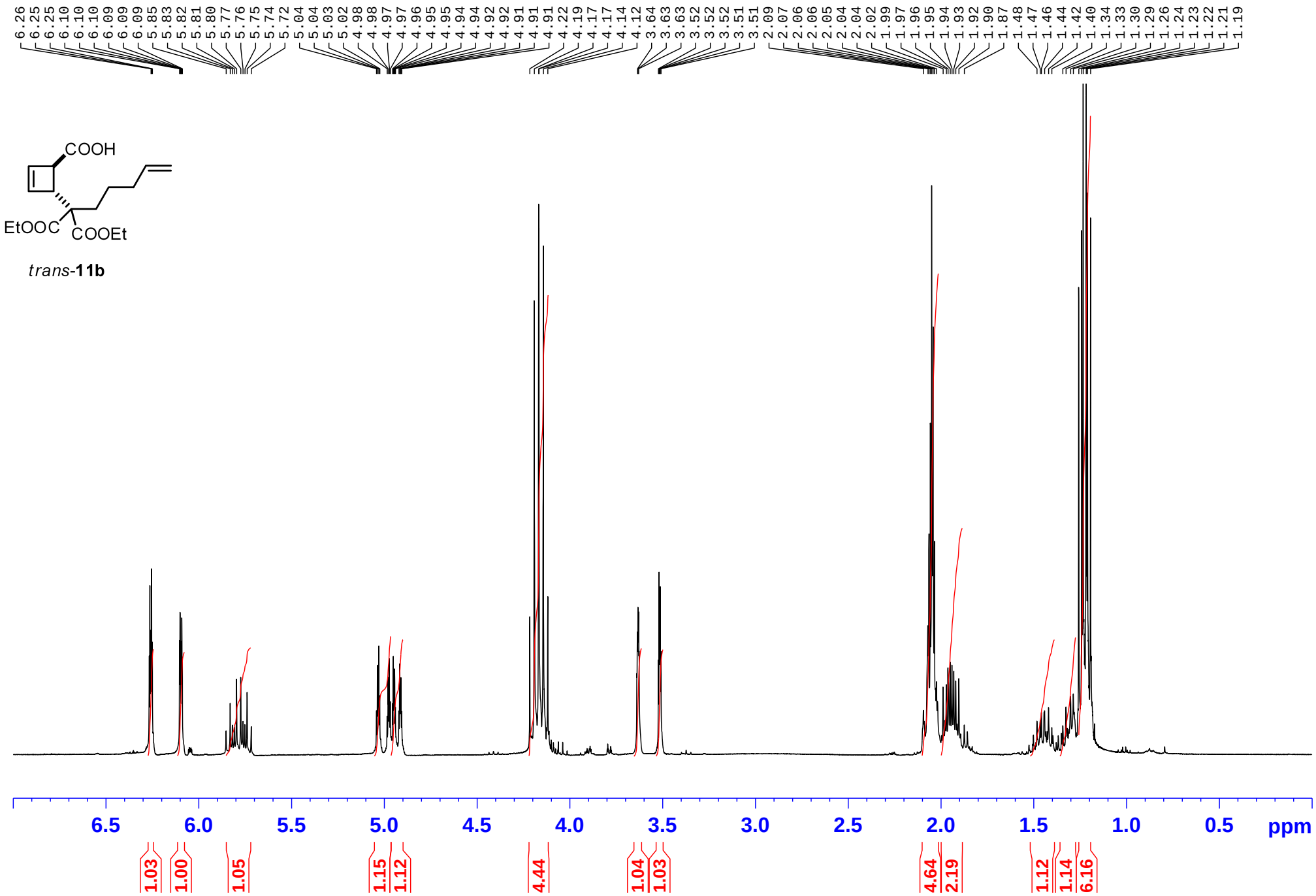
LUP-LC-254-03

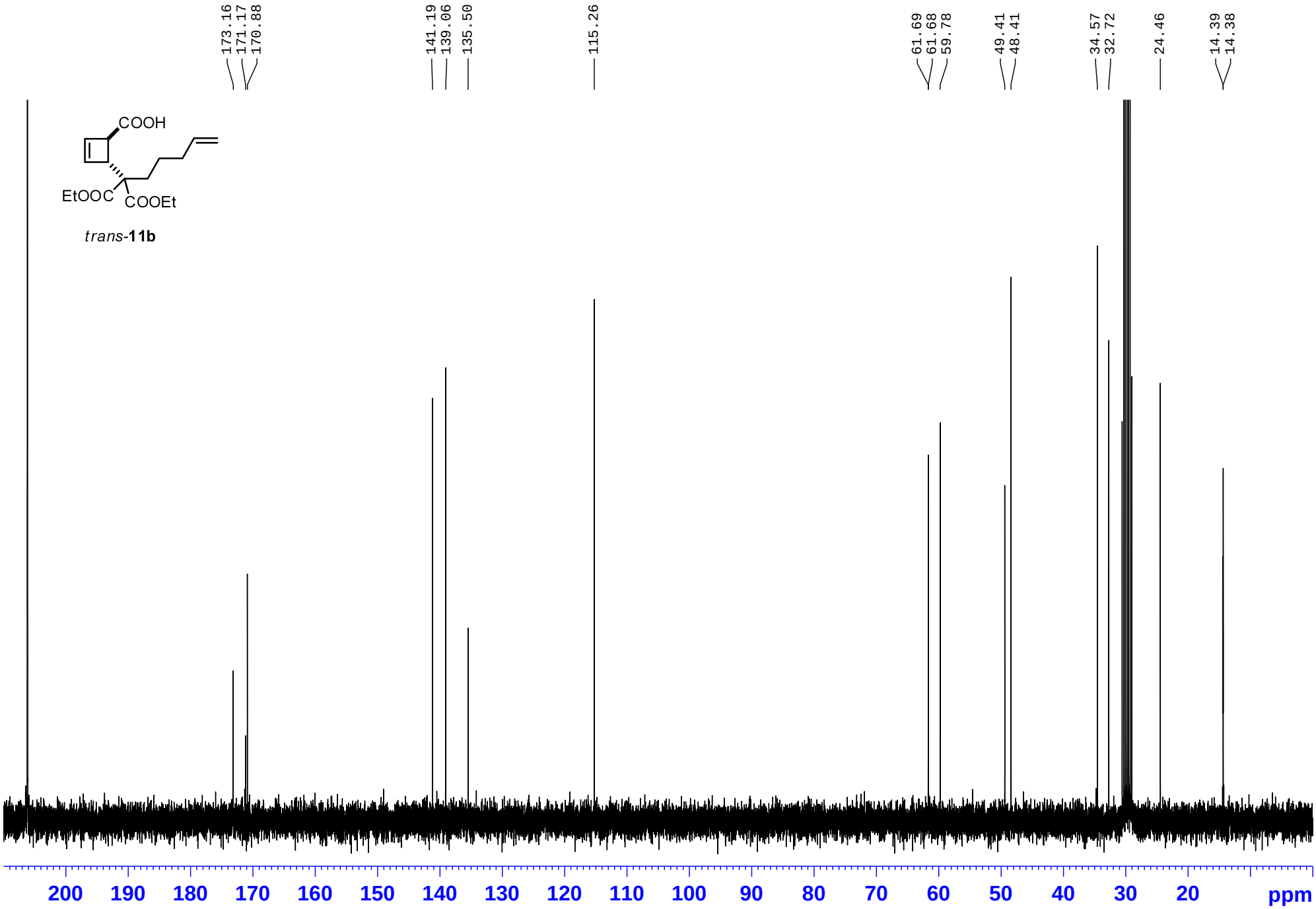
1D-NOESY

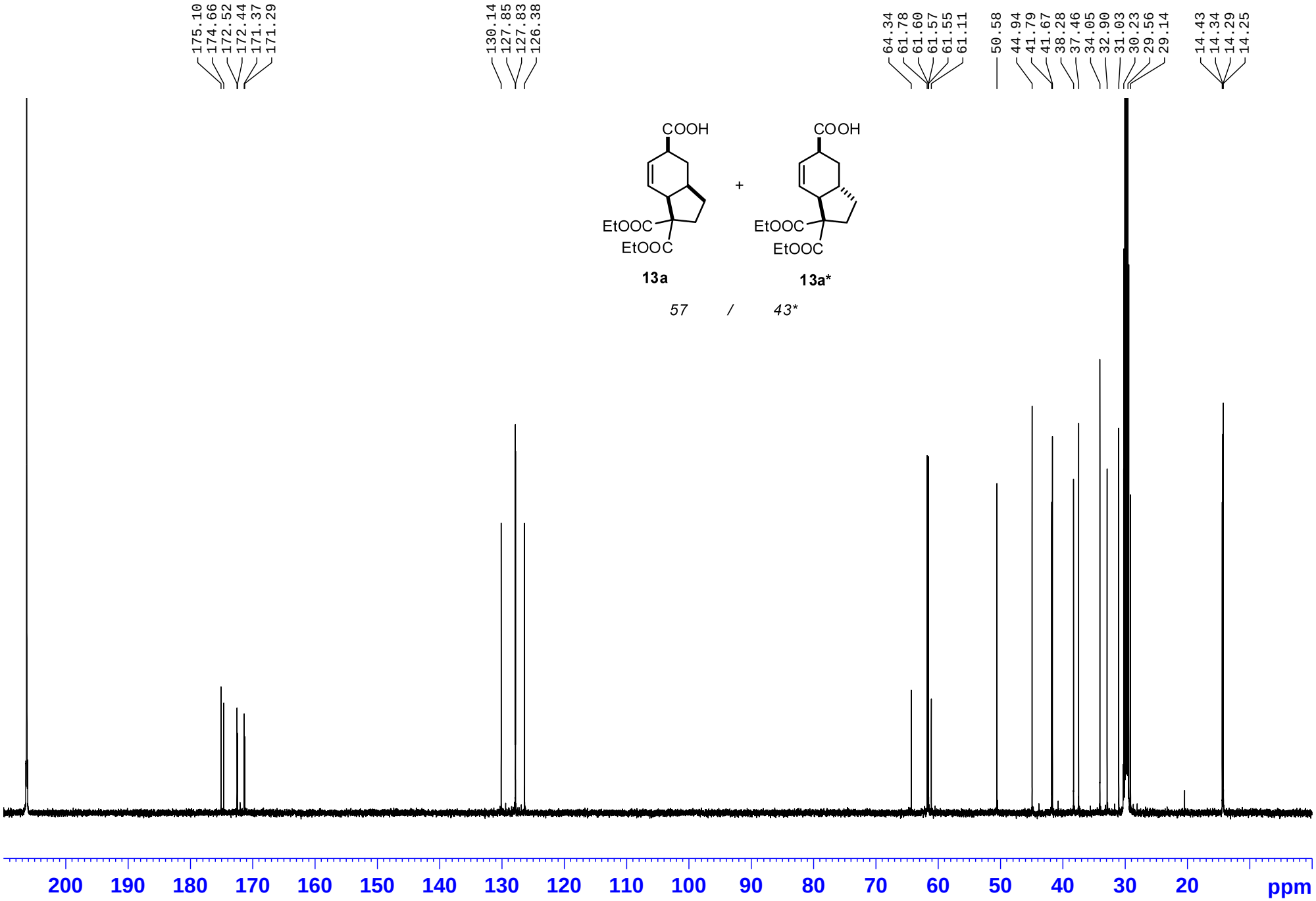
av600

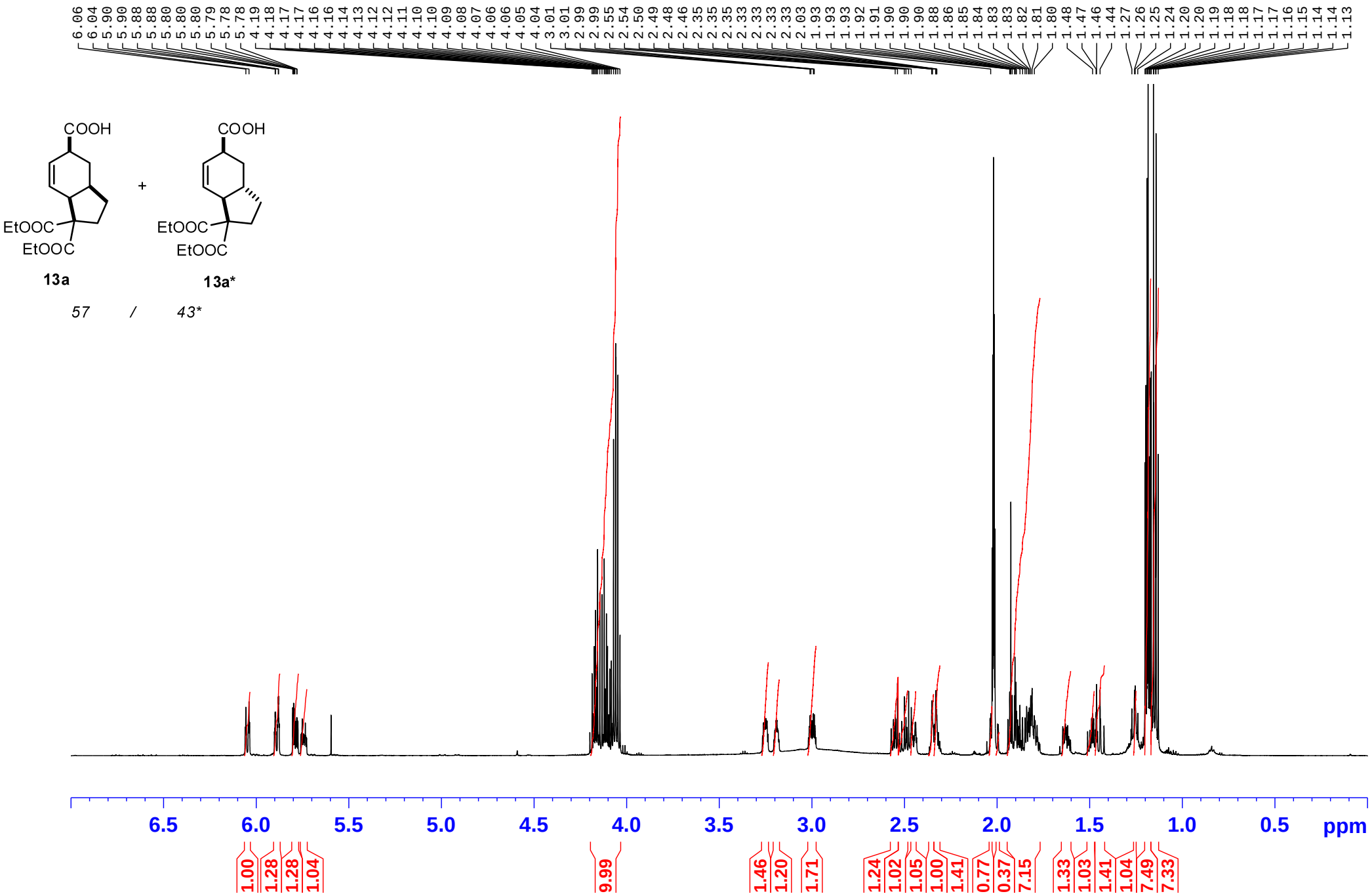

COOH
EtOOC
COOEt
trans-11a
6.29 6.29 6.28 6.28 6.27 6.13 6.12 6.12 6.11 6.11 5.88 5.86 5.85 5.84 5.82 5.80 5.79 5.78 5.77 5.75 5.07 5.06 5.06 5.01 5.00 5.00 4.97 4.96 4.96 4.94 4.93 4.93 4.93 4.92 4.24 4.21 4.21 4.19 4.19 4.17 4.16 4.14 3.66 3.66 3.66 3.65 3.55 3.55 3.54 3.54 3.54 2.16 2.15 2.14 2.13 2.11 2.10 2.09 2.08 2.08 2.07 2.07 2.07 2.06 2.06 2.05 2.04 2.02 2.02 2.00 2.00 1.99 1.98 1.97 1.95 1.28 1.26 1.25 1.24 1.23 1.21
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.02 1.00 1.07 1.06 1.01 4.22 0.99 0.99 5.51 6.41

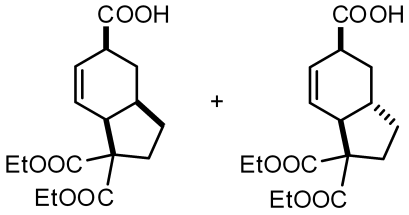

173.22
171.04
170.77
141.14
138.67
135.57
115.40
61.80
61.78
59.56
49.41
48.42
32.68
14.41
14.39
COOH
EtOOC
COOEt
trans-11a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


COOH
EtOOC
COOEt
trans-11b
6.26 6.25 6.25 6.10 6.10 6.09 6.09 6.09 5.85 5.83 5.82 5.81 5.80 5.77 5.76 5.75 5.74 5.72 5.04 5.04 5.03 5.02 4.98 4.98 4.97 4.97 4.96 4.95 4.95 4.94 4.94 4.92 4.92 4.91 4.91 4.22 4.19 4.17 4.17 4.14 4.12 3.64 3.63 3.63 3.52 3.52 3.52 3.51 3.51 2.09 2.07 2.06 2.06 2.05 2.04 2.04 2.02 1.99 1.97 1.96 1.95 1.94 1.93 1.92 1.90 1.87 1.48 1.47 1.46 1.44 1.42 1.40 1.34 1.33 1.30 1.29 1.26 1.24 1.23 1.22 1.21 1.19
6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.03 1.00 1.05 1.15 1.12 4.44 1.04 1.03 4.64 2.19 1.12 1.14 6.16


173.16
171.17
170.88
141.19
139.06
135.50
115.26
61.69
61.68
59.78
49.41
48.41
34.57
32.72
24.46
14.39
14.38
COOH
EtOOC
COOEt
trans-11b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

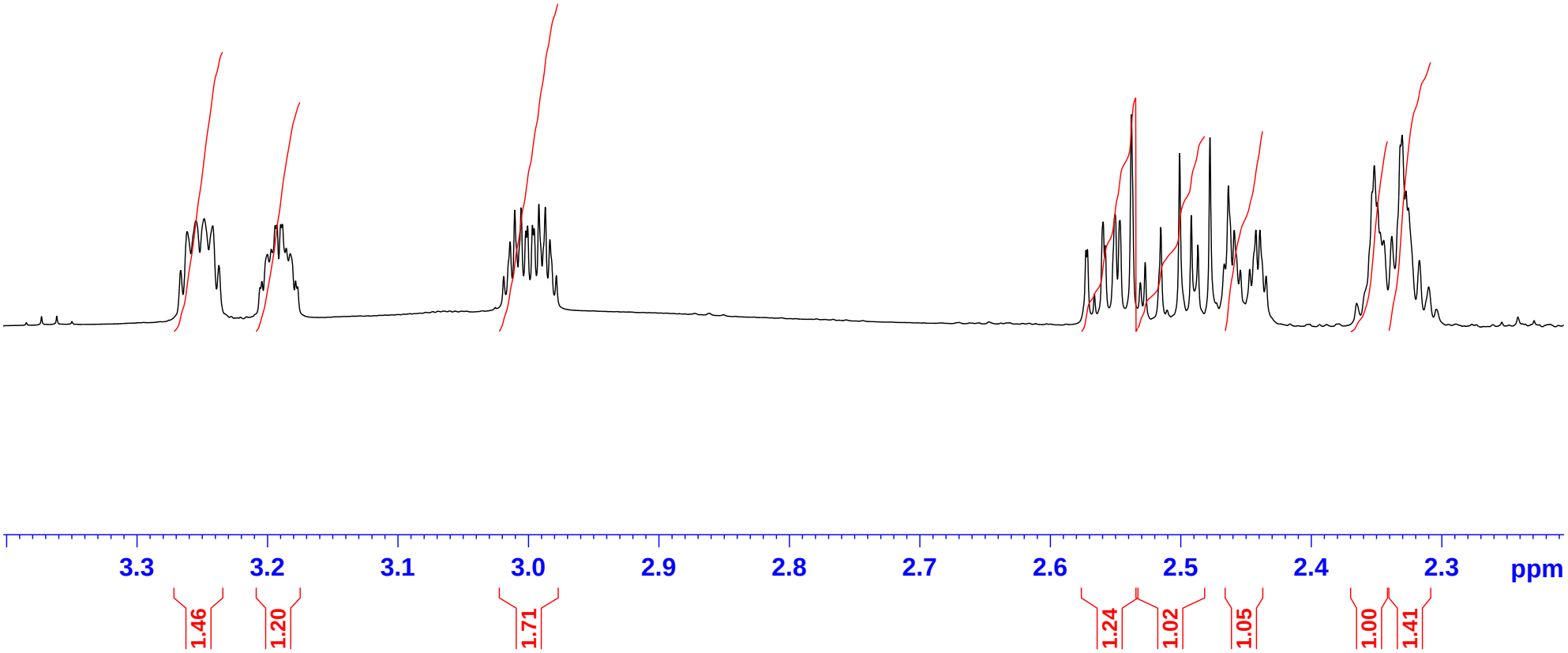

175.10
174.66
172.52
172.44
171.37
171.29
130.14
127.85
127.83
126.38
64.34
61.78
61.60
61.57
61.55
61.11
50.58
44.94
41.79
41.67
38.28
37.46
34.05
32.90
31.03
30.23
29.56
29.14
14.43
14.34
14.29
14.25
COOH
EtOOC
EtOOC
13a
+
COOH
EtOOC
EtOOC
13a*
57 / 43*
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

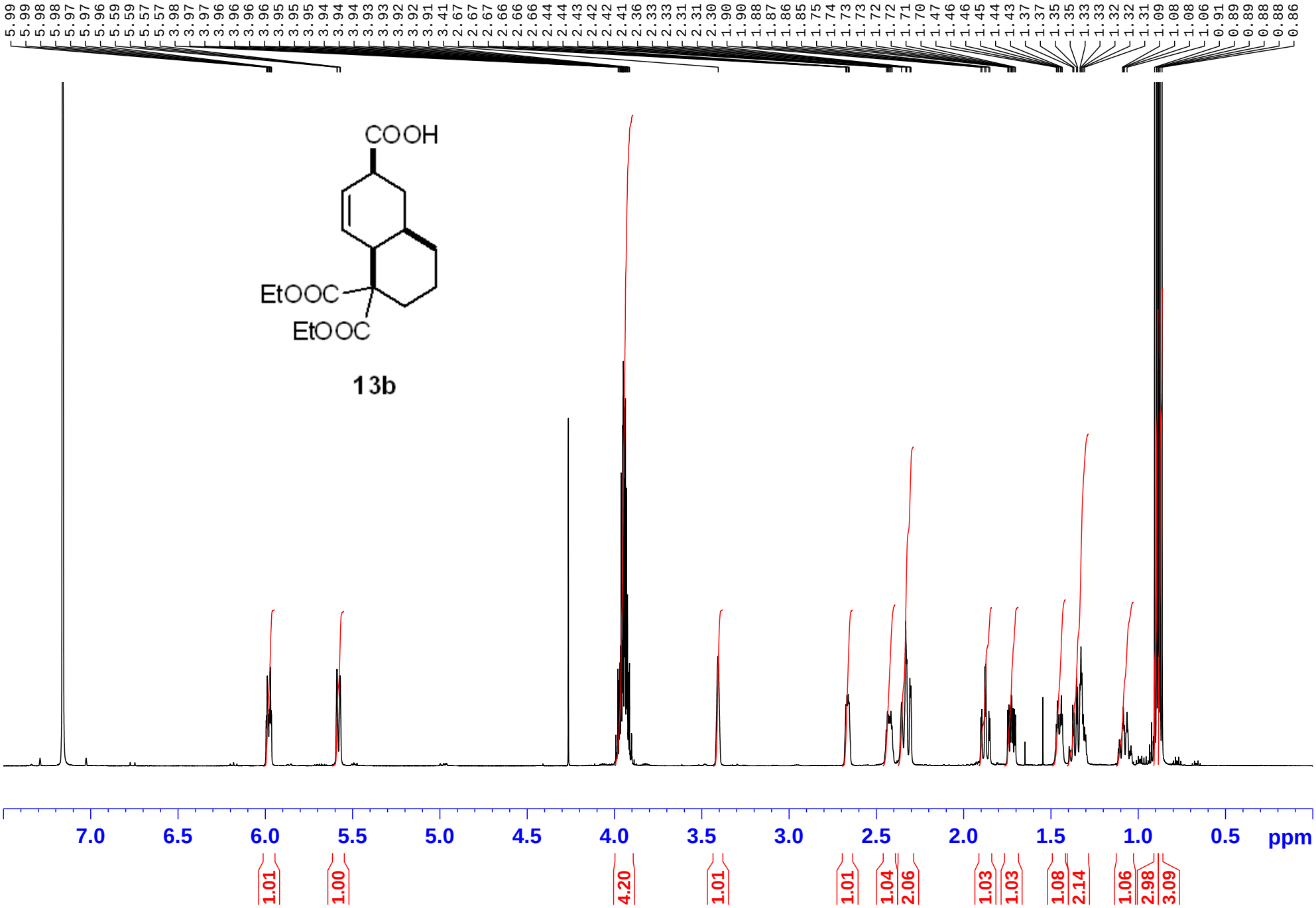

COOH
EtOOC
EtOOC
13a
+
COOH
EtOOC
EtOOC
13a*
57 / 43*
6.06 6.04 5.90 5.90 5.88 5.88 5.80 5.80 5.80 5.79 5.78 5.78 4.19 4.18 4.17 4.17 4.16 4.16 4.14 4.13 4.12 4.12 4.11 4.10 4.10 4.09 4.08 4.07 4.06 4.06 4.05 4.04 3.01 3.01 2.99 2.99 2.55 2.54 2.50 2.49 2.48 2.46 2.35 2.35 2.35 2.33 2.33 2.33 2.03 1.93 1.93 1.93 1.92 1.91 1.90 1.90 1.90 1.88 1.86 1.85 1.84 1.83 1.83 1.82 1.81 1.80 1.48 1.47 1.46 1.44 1.27 1.26 1.25 1.24 1.20 1.20 1.19 1.18 1.18 1.17 1.17 1.16 1.15 1.14 1.14 1.13
6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.28 1.28 1.04 9.99 1.46 1.20 1.71 1.24 1.02 1.05 1.00 1.41 0.77 0.37 7.15 1.33 1.03 1.41 1.04 7.49 7.33


COOH
EtOOC
EtOOC
+
COOH
EtOOC
EtOOC

13a / **13a***

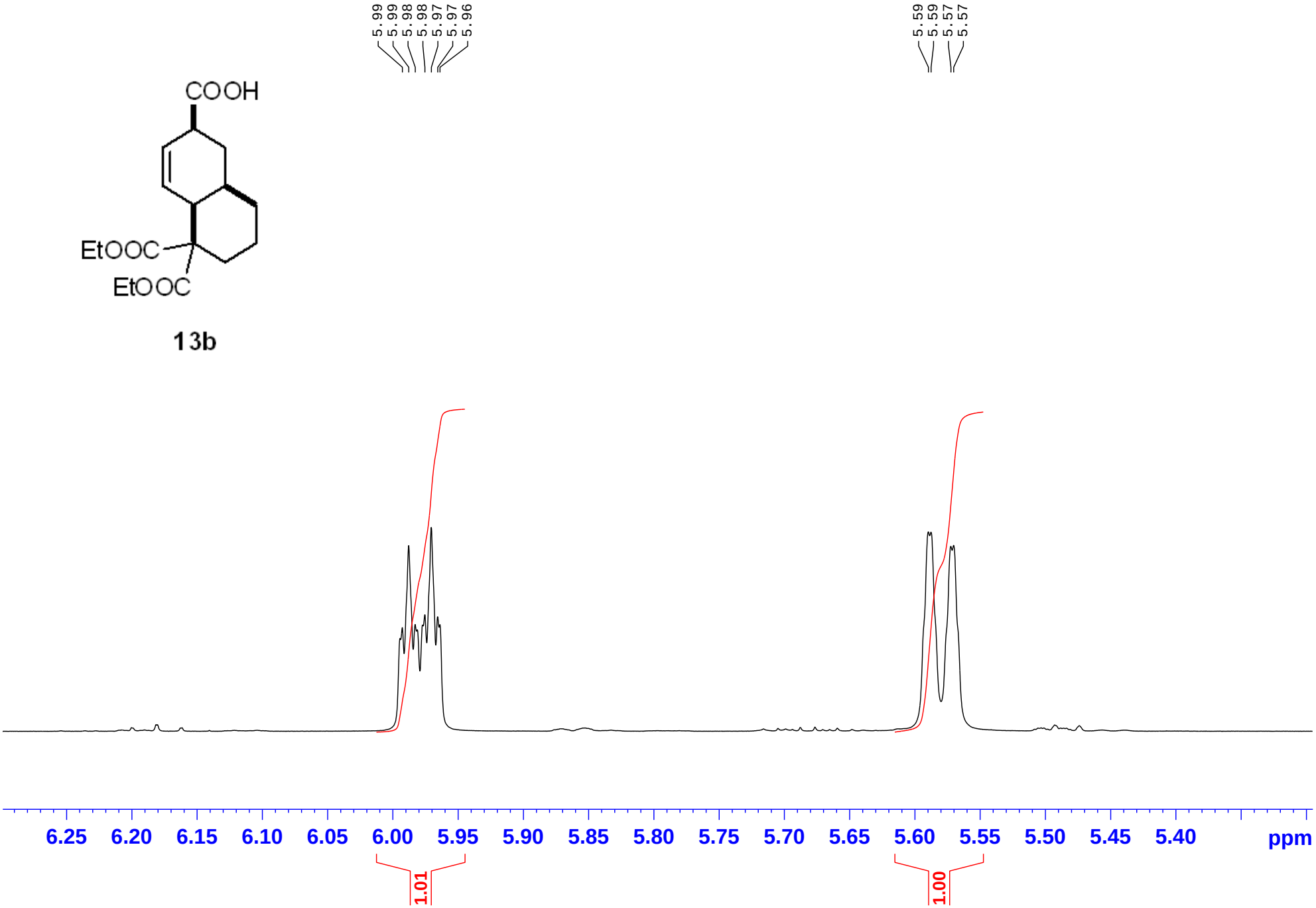
*57 / 43**

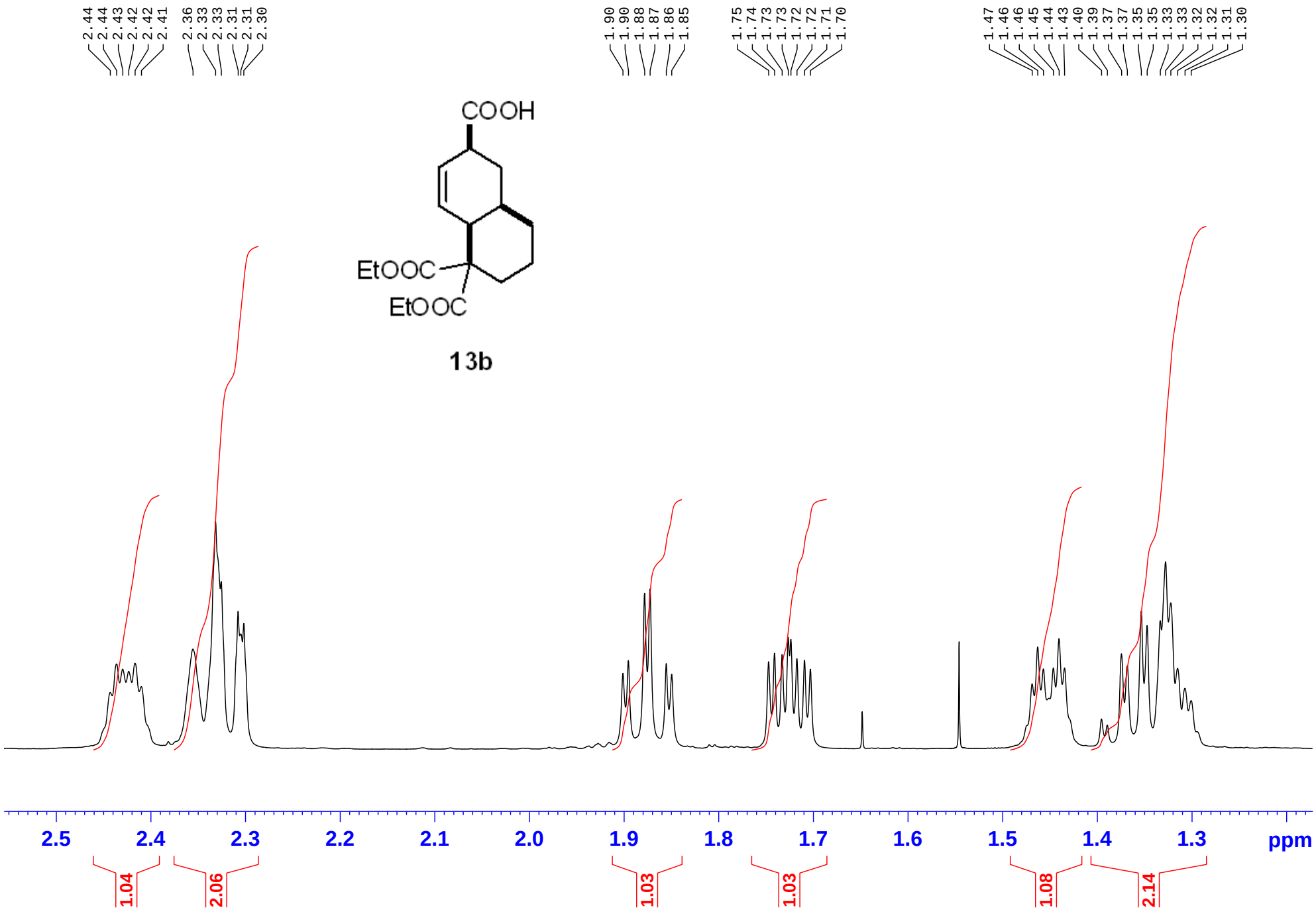

3.27 3.26 3.25 3.25 3.24 3.24 3.21 3.20 3.20 3.20 3.19 3.19 3.19 3.19 3.19 3.18 3.18 3.18
3.01 3.01 3.01 3.00 3.00 3.00 3.00 2.99 2.99 2.98
2.57 2.57 2.56 2.56 2.55 2.55 2.54 2.53 2.53 2.52 2.50 2.49 2.49 2.48 2.47 2.46 2.46 2.45 2.45 2.44 2.44 2.43 2.35 2.35 2.35 2.35 2.34 2.34 2.33 2.33 2.33 2.33 2.32
3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 ppm
1.46
1.20
1.71
1.24
1.02
1.05
1.00
1.41


COOH
EtOOC
EtOOC
13b
ppm

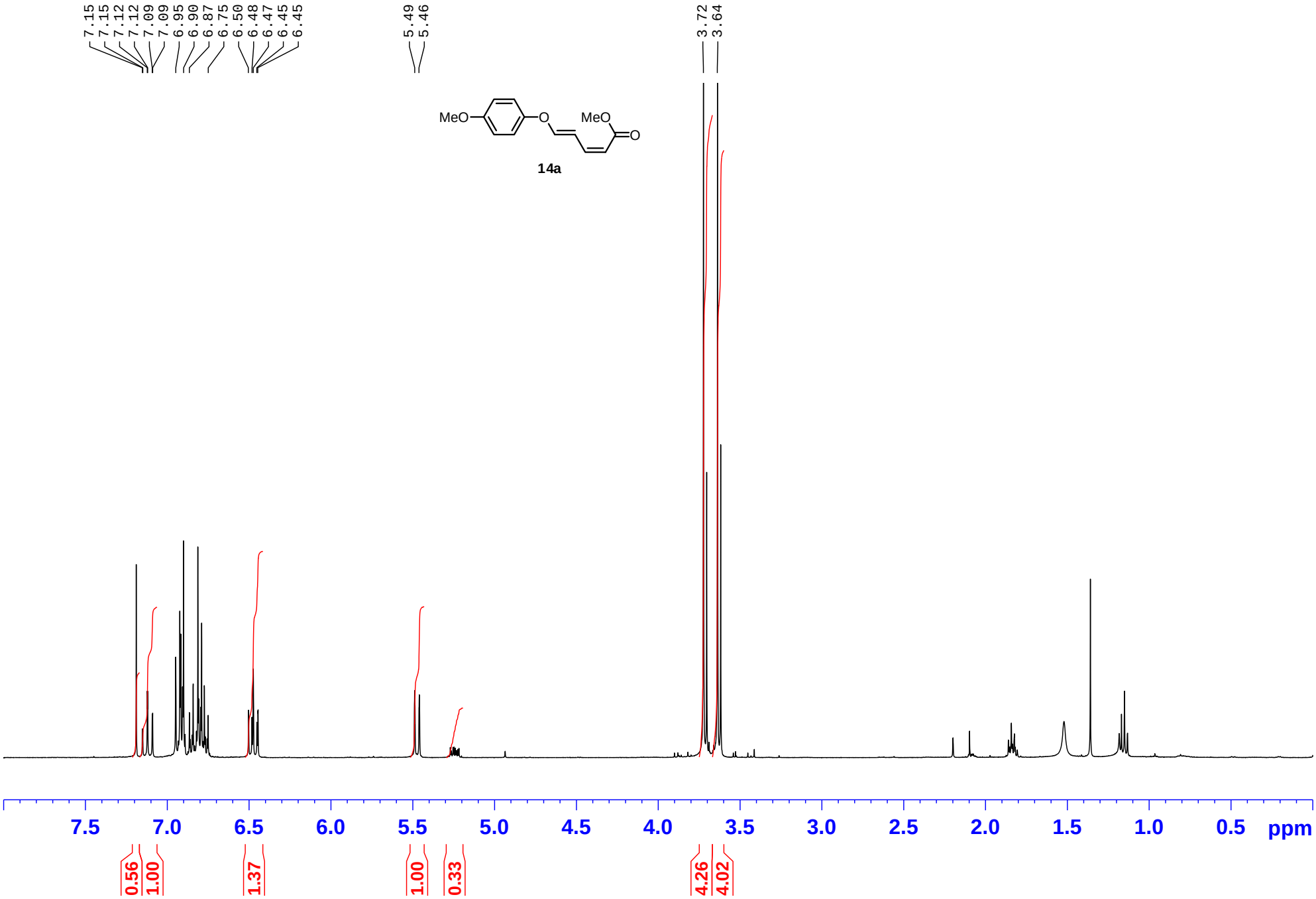
COOH
EtOOC
EtOOC

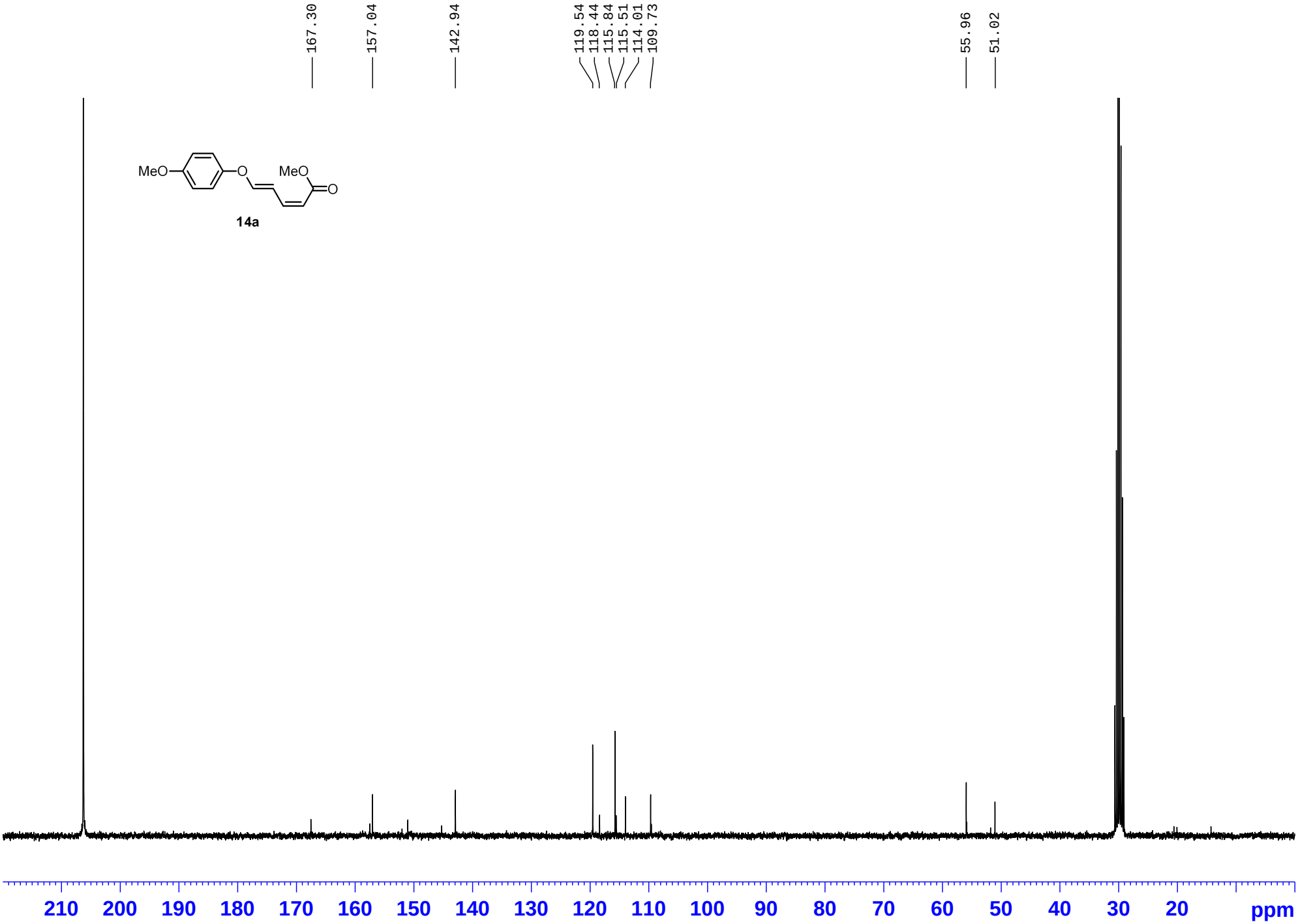
13b

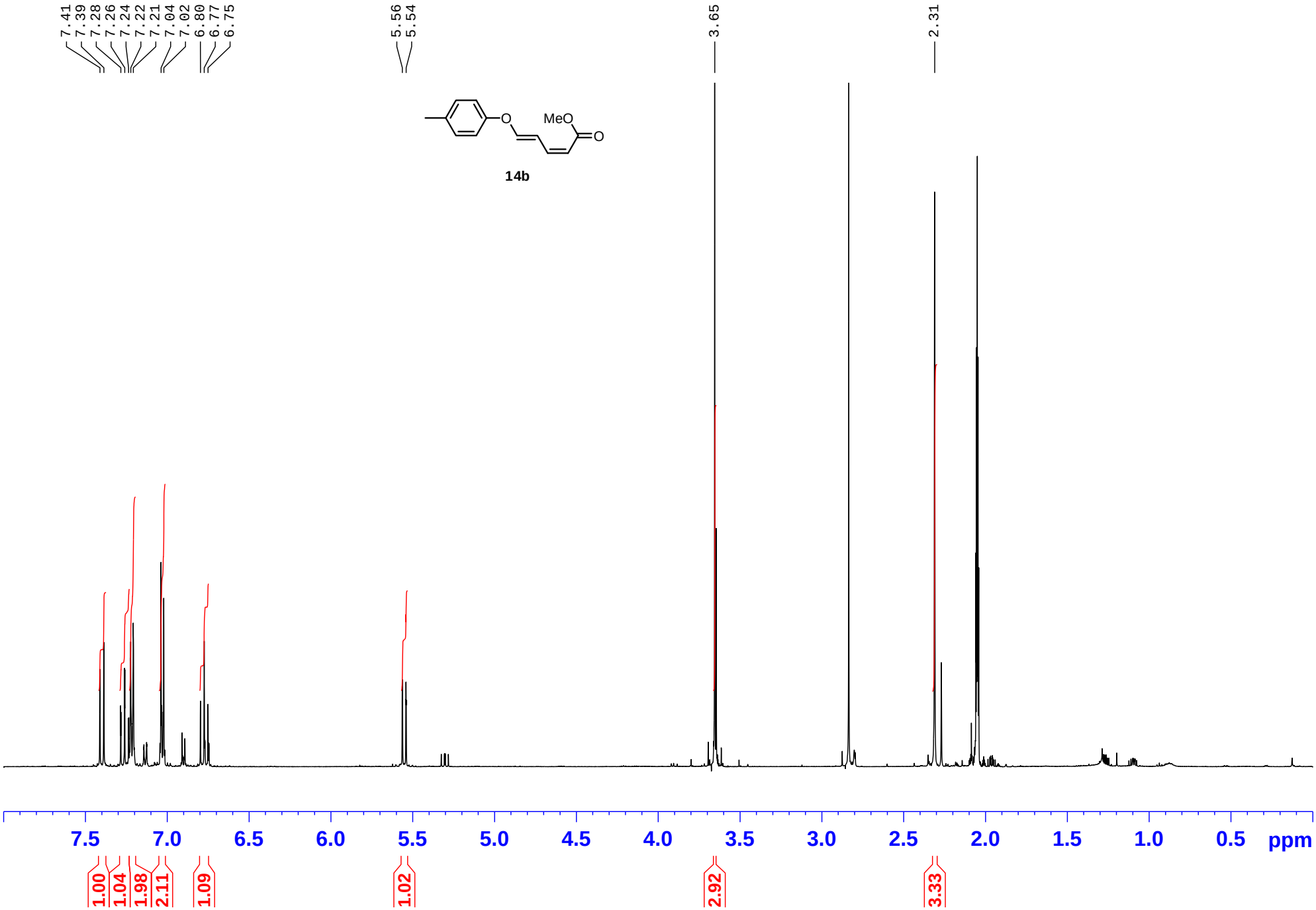

5.99
5.99
5.98
5.98
5.97
5.97
5.96
5.59
5.59
5.57
5.57
6.25
6.20
6.15
6.10
6.05
6.00
5.95
5.90
5.85
5.80
5.75
5.70
5.65
5.60
5.55
5.50
5.45
5.40
ppm
1.01
1.00


2.44
2.44
2.43
2.42
2.42
2.41
2.36
2.33
2.33
2.31
2.31
2.30
1.90
1.90
1.88
1.87
1.86
1.85
1.75
1.74
1.73
1.73
1.72
1.72
1.71
1.70
1.47
1.46
1.46
1.45
1.44
1.43
1.40
1.39
1.37
1.37
1.35
1.35
1.33
1.33
1.32
1.32
1.31
1.30
COOH
EtOOC
EtOOC
13b
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
ppm
1.04
2.06
1.03
1.03
1.08
2.14


180.86
170.79
170.61
128.29
126.03
61.15
61.09
59.03
39.44
37.90
30.62
28.99
27.64
25.82
22.52
13.98
13.95
COOH
EtOOC
EtOOC
13b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

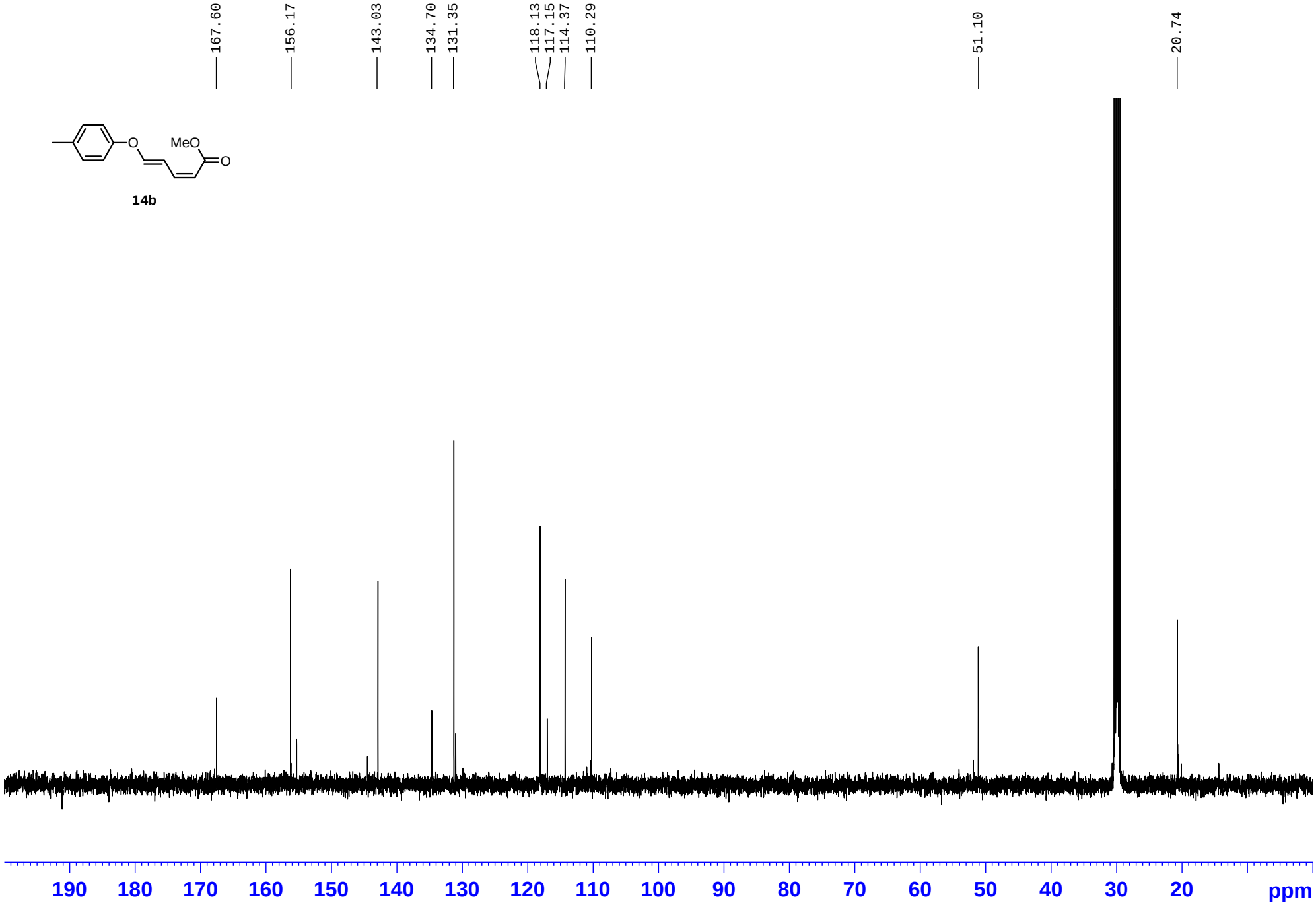

7.15
7.15
7.12
7.12
7.09
7.09
6.95
6.90
6.87
6.75
6.50
6.48
6.47
6.45
6.45
5.49
5.46
3.72
3.64
MeO
O
MeO
O
14a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.56
1.00
1.37
1.00
0.33
4.26
4.02

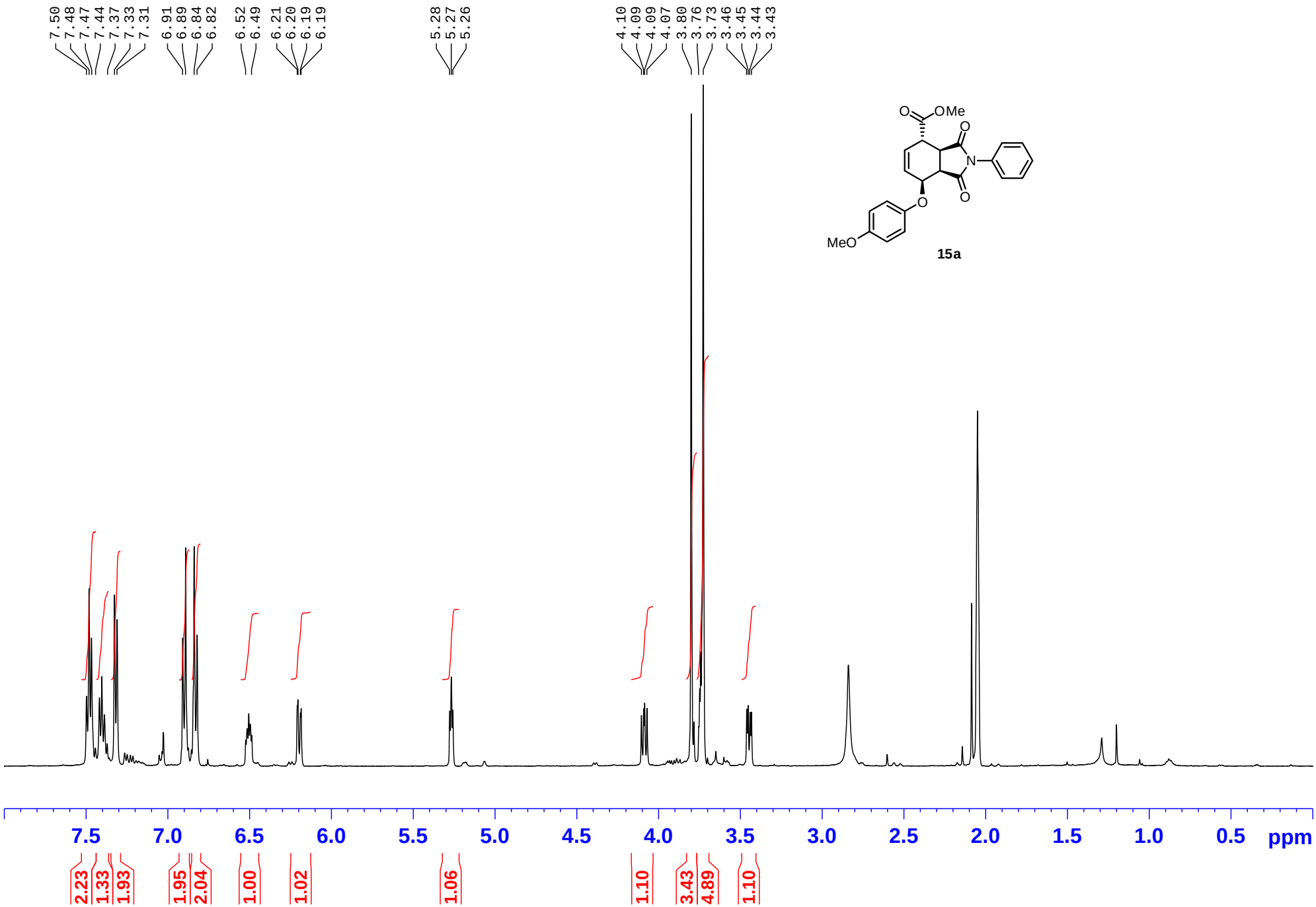

167.30
157.04
142.94
119.54
118.44
115.84
115.51
114.01
109.73
55.96
51.02
MeO
O
MeO
O
14a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

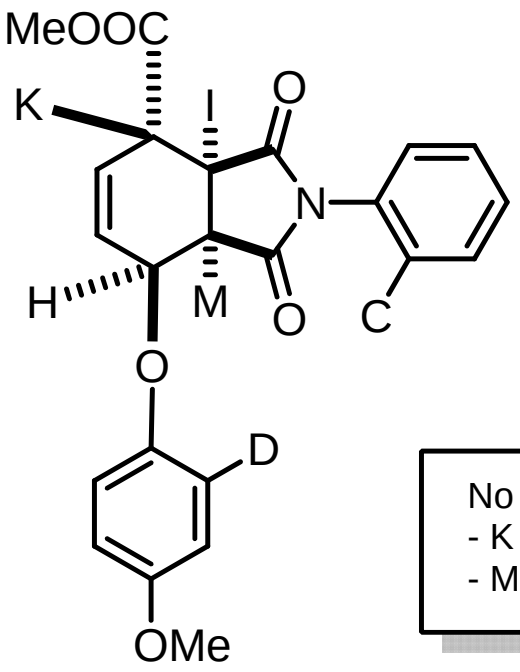

7.41
7.39
7.28
7.26
7.24
7.22
7.21
7.04
7.02
6.80
6.77
6.75
5.56
5.54
3.65
2.31
O
MeO
O
14b
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.04
1.98
2.11
1.09
1.02
2.92
3.33

O
MeO
O

14b


167.60
156.17
143.03
134.70
131.35
118.13
117.15
114.37
110.29
51.10
20.74
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

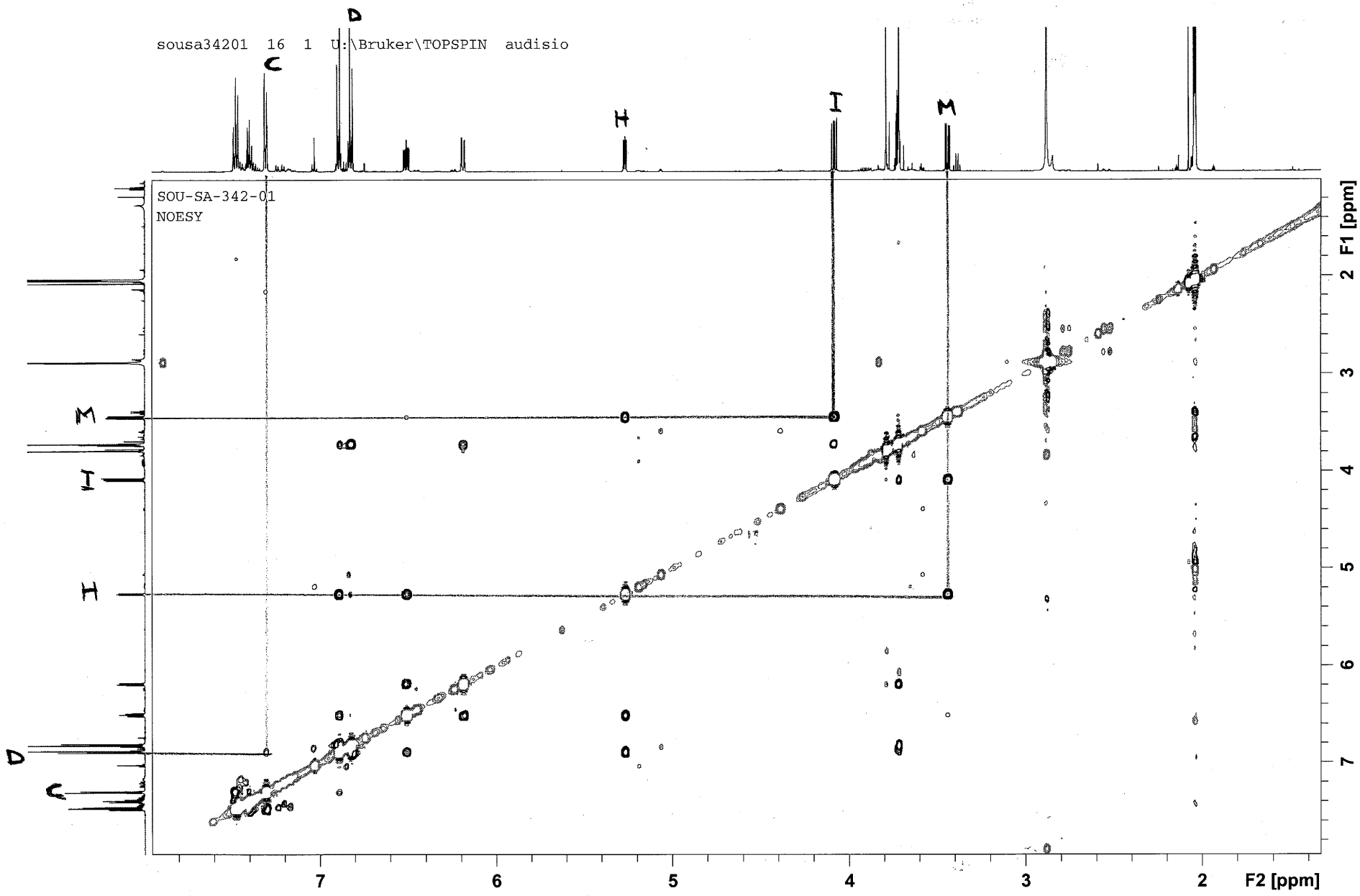

7.50
7.48
7.47
7.44
7.37
7.33
7.31
6.91
6.89
6.84
6.82
6.52
6.49
6.21
6.20
6.19
6.19
5.28
5.27
5.26
4.10
4.09
4.09
4.07
3.80
3.76
3.73
3.46
3.45
3.44
3.43
O
OMe
O
N
O
O
MeO
15a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.23
1.33
1.93
1.95
2.04
1.00
1.02
1.06
1.10
3.43
4.89
1.10

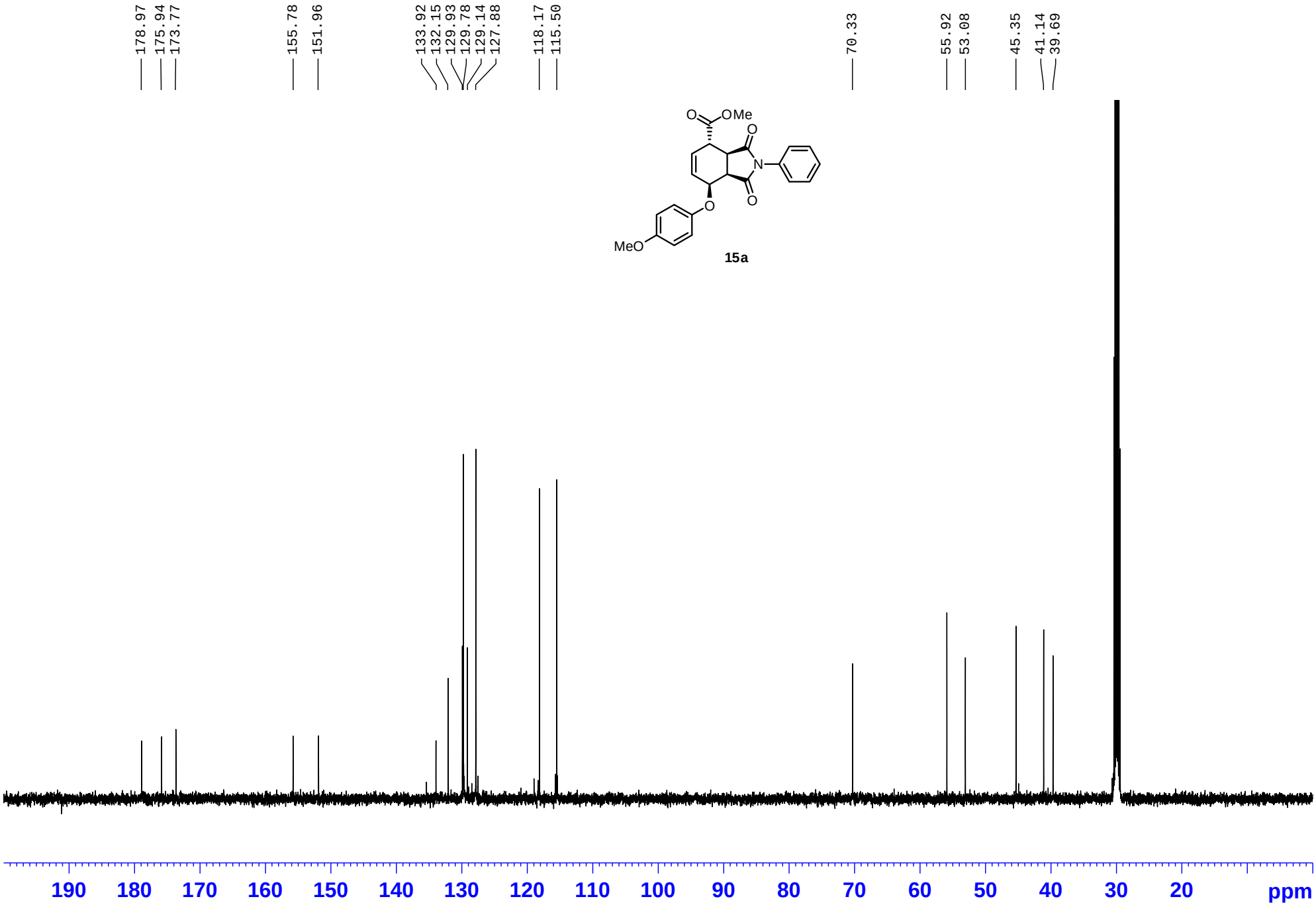


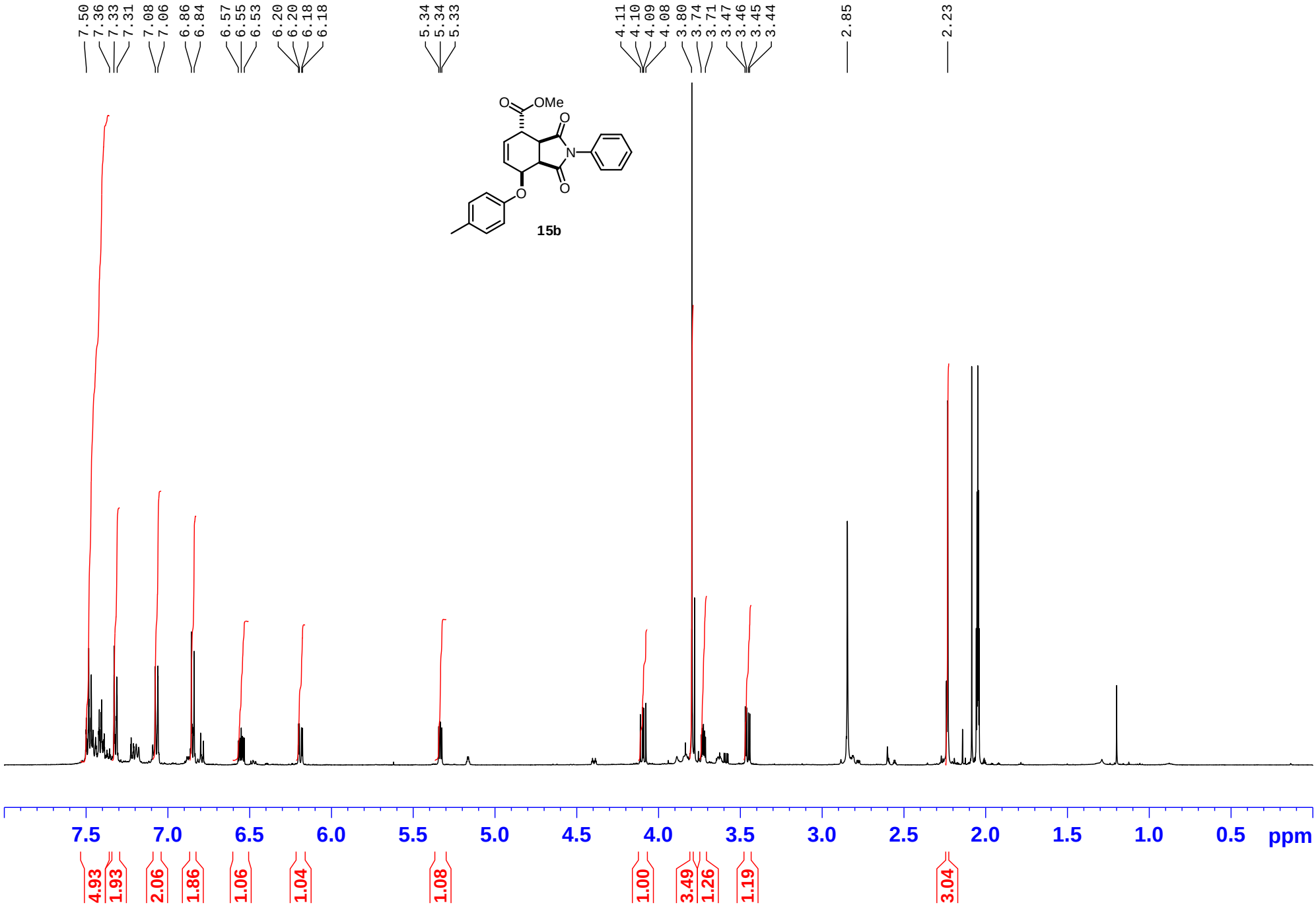
No NOE observed between:
- K and H;
- M and D

15a

Relevant NOE interaction


sousa34201 16 1 U:\Bruker\TOPSPIN audisio
SOU-SA-342-01
NOESY
F1 [ppm]
F2 [ppm]
2
3
4
5
6
7


178.97
175.94
173.77
155.78
151.96
133.92
132.15
129.93
129.78
129.14
127.88
118.17
115.50
70.33
55.92
53.08
45.35
41.14
39.69
O
OMe
O
N
O
O
MeO
15a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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6.84
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6.20
6.18
6.18
5.34
5.34
5.33
4.11
4.10
4.09
4.08
3.80
3.74
3.71
3.47
3.46
3.45
3.44
2.85
2.23
O
OMe
O
N
O
O
15b
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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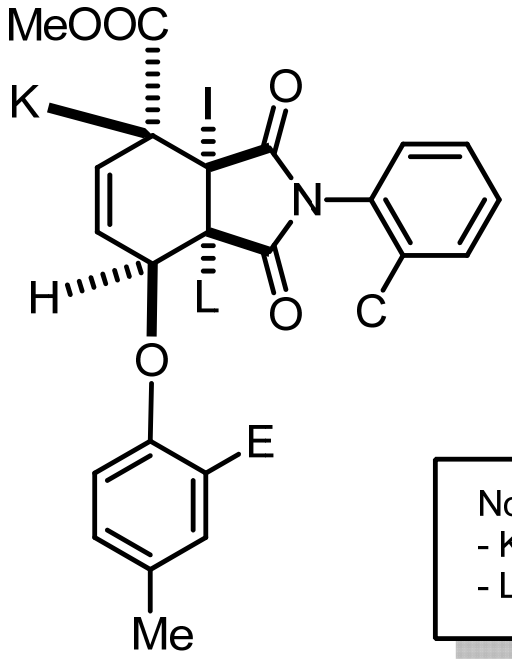
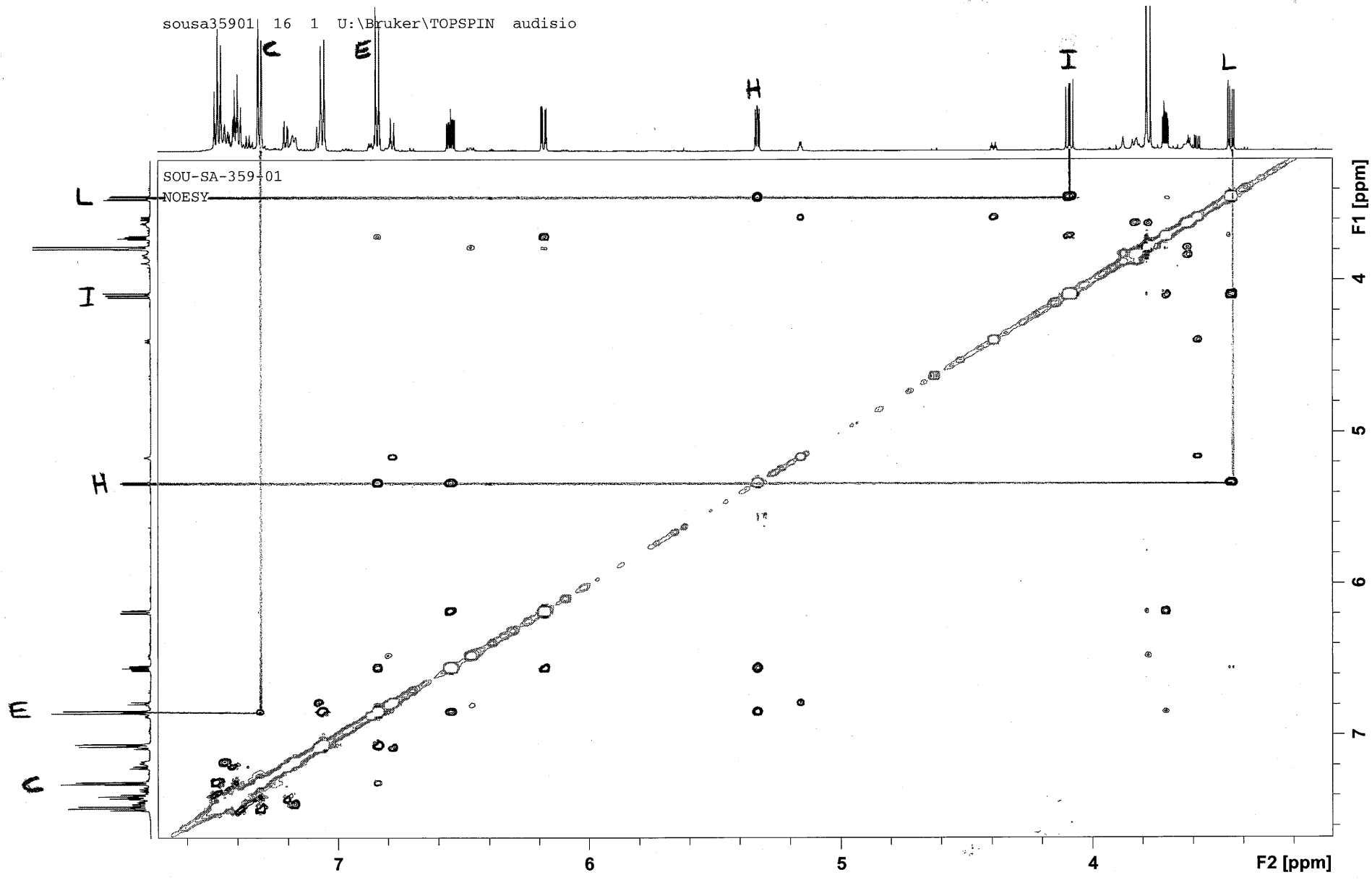
2.06
1.86
1.06
1.04
1.08
1.00
3.49
1.26
1.19
3.04

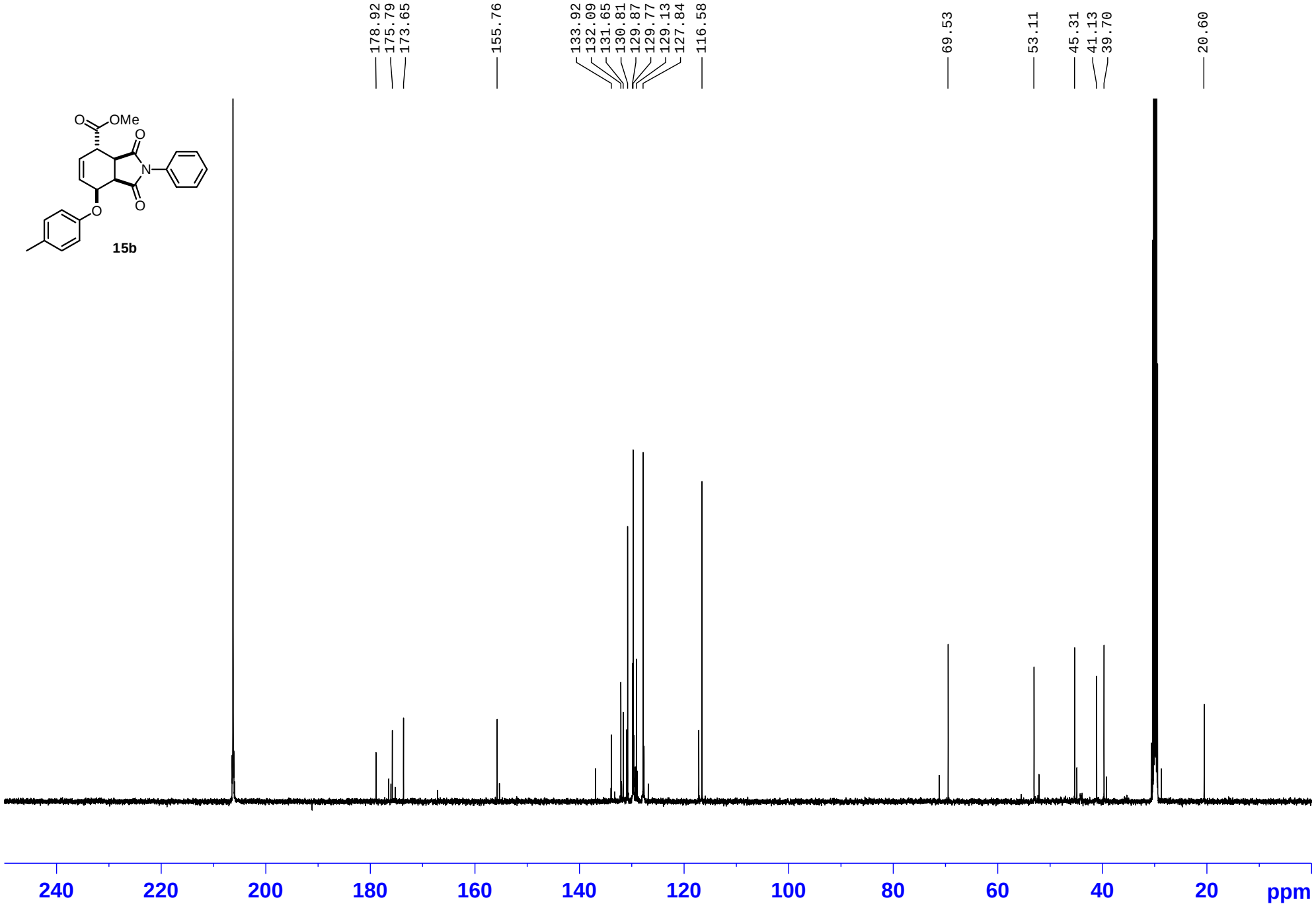


No NOE observed between:
- K and H;
- L and E

15b

Relevant NOE interaction


sousa35901 16 1 U:\Bruker\TOPSPIN audisio
SOU-SA-359-01
NOESY
C
E
H
I
L
F1 [ppm]
F2 [ppm]
4
5
6
7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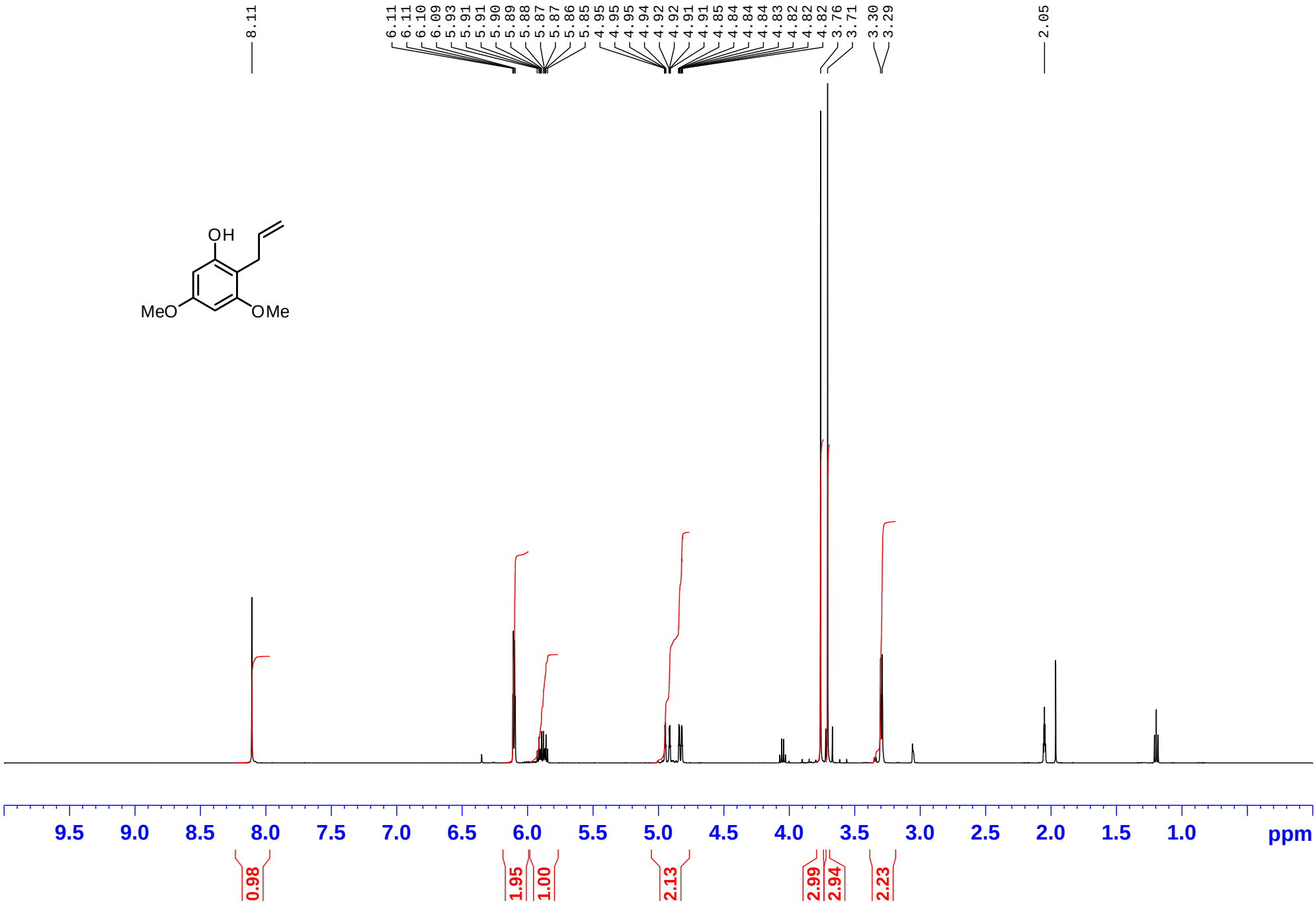
175.79
173.65
155.76
133.92
132.09
131.65
130.81
129.87
129.77
129.13
127.84
116.58
69.53
53.11
45.31
41.13
39.70
20.60
OMe
O
N
15b
240
220
200
180
160
140
120
100
80
60
40
20
ppm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6.11
6.11
6.10
6.09
5.93
5.91
5.91
5.90
5.89
5.88
5.87
5.87
5.86
5.85
4.95
4.95
4.95
4.94
4.92
4.92
4.91
4.91
4.85
4.84
4.84
4.84
4.83
4.82
4.82
4.82
3.76
3.71
3.30
3.29
2.05
OH
MeO
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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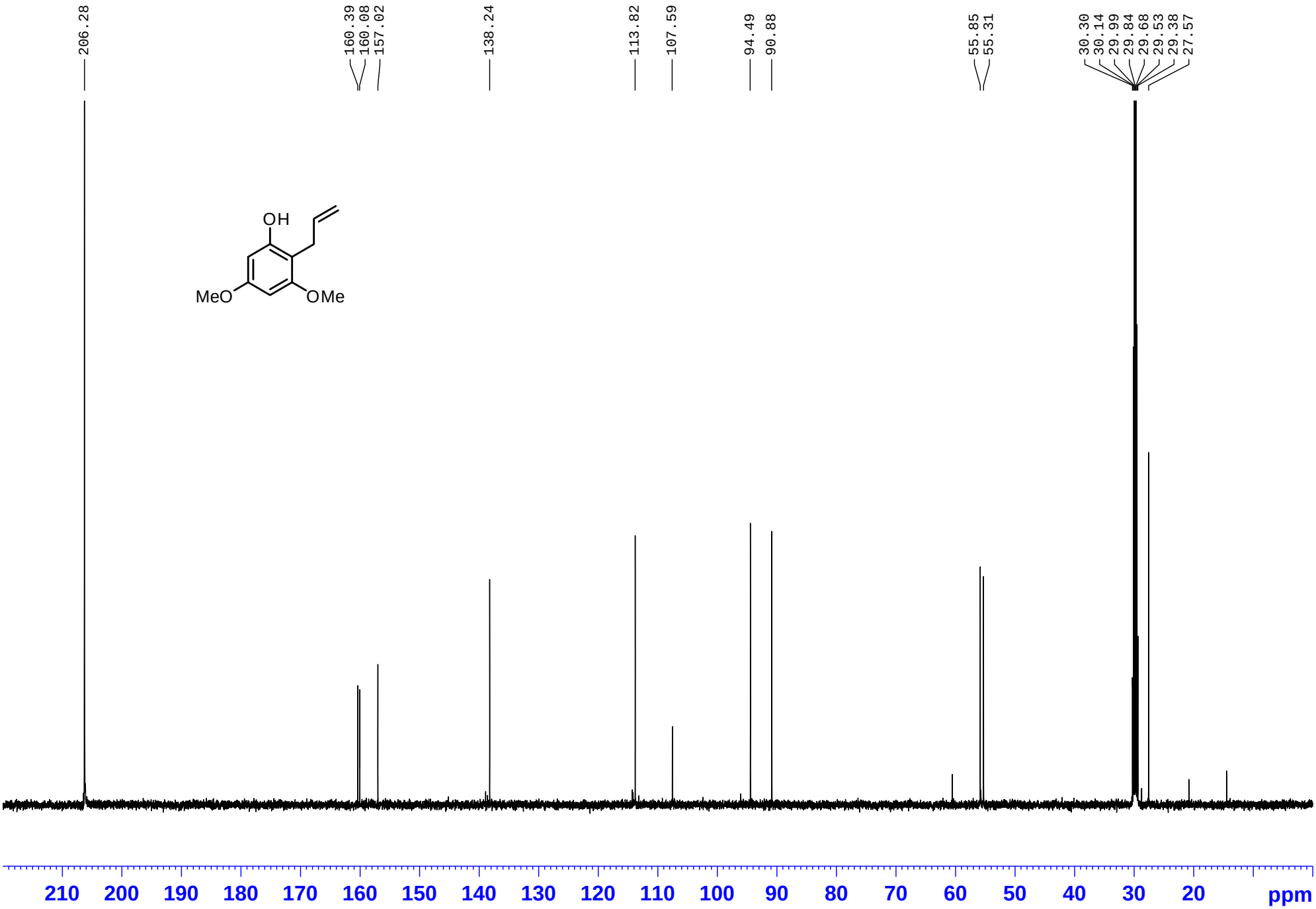
1.5
1.0
ppm
0.98
1.95
1.00
2.13
2.99
2.94
2.23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160.08
157.02
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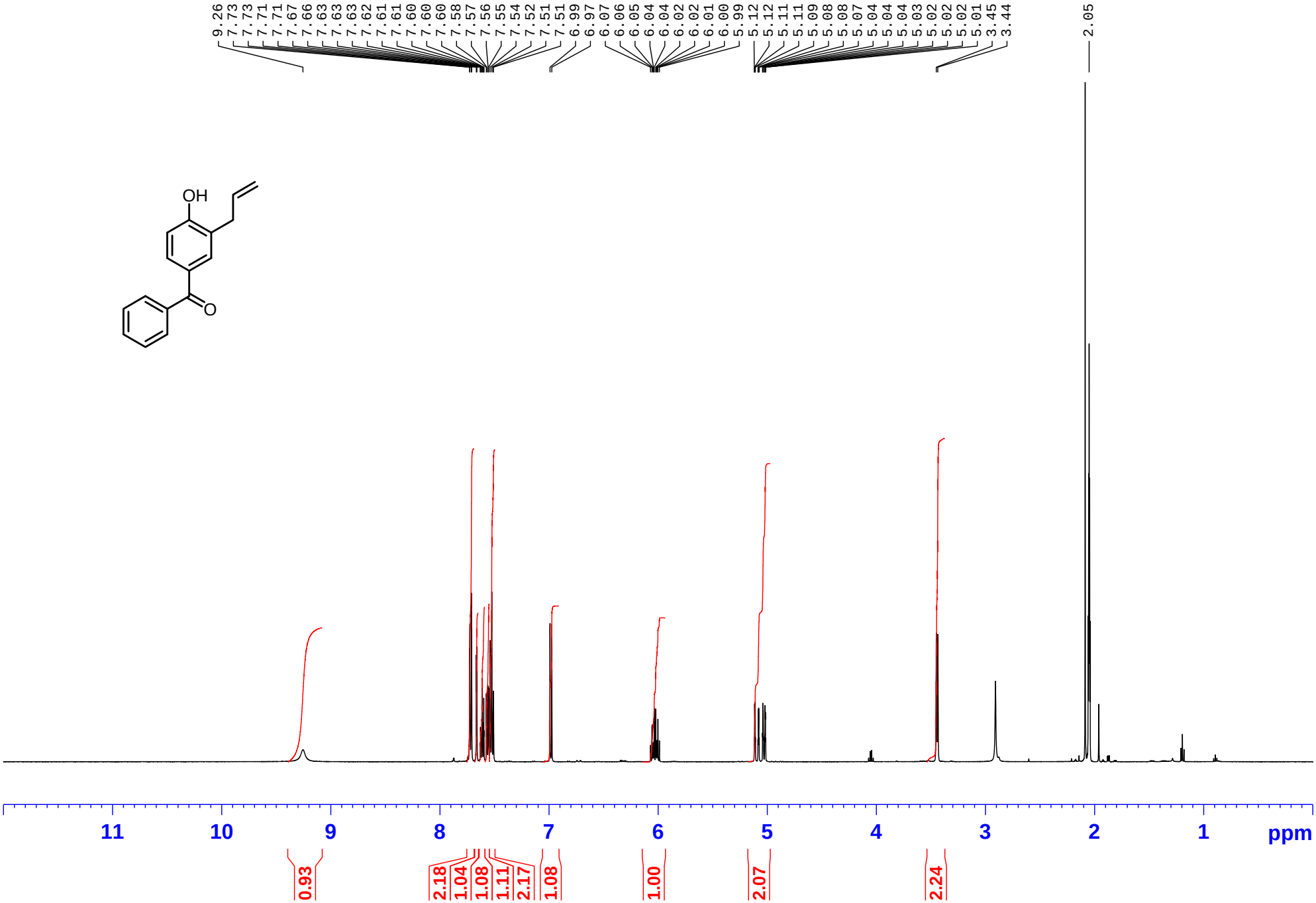
94.49
90.88
55.85
55.31
30.30
30.14
29.99
29.84
29.68
29.53
29.38
27.57
OH
MeO
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.73
7.71
7.71
7.67
7.66
7.63
7.63
7.63
7.62
7.61
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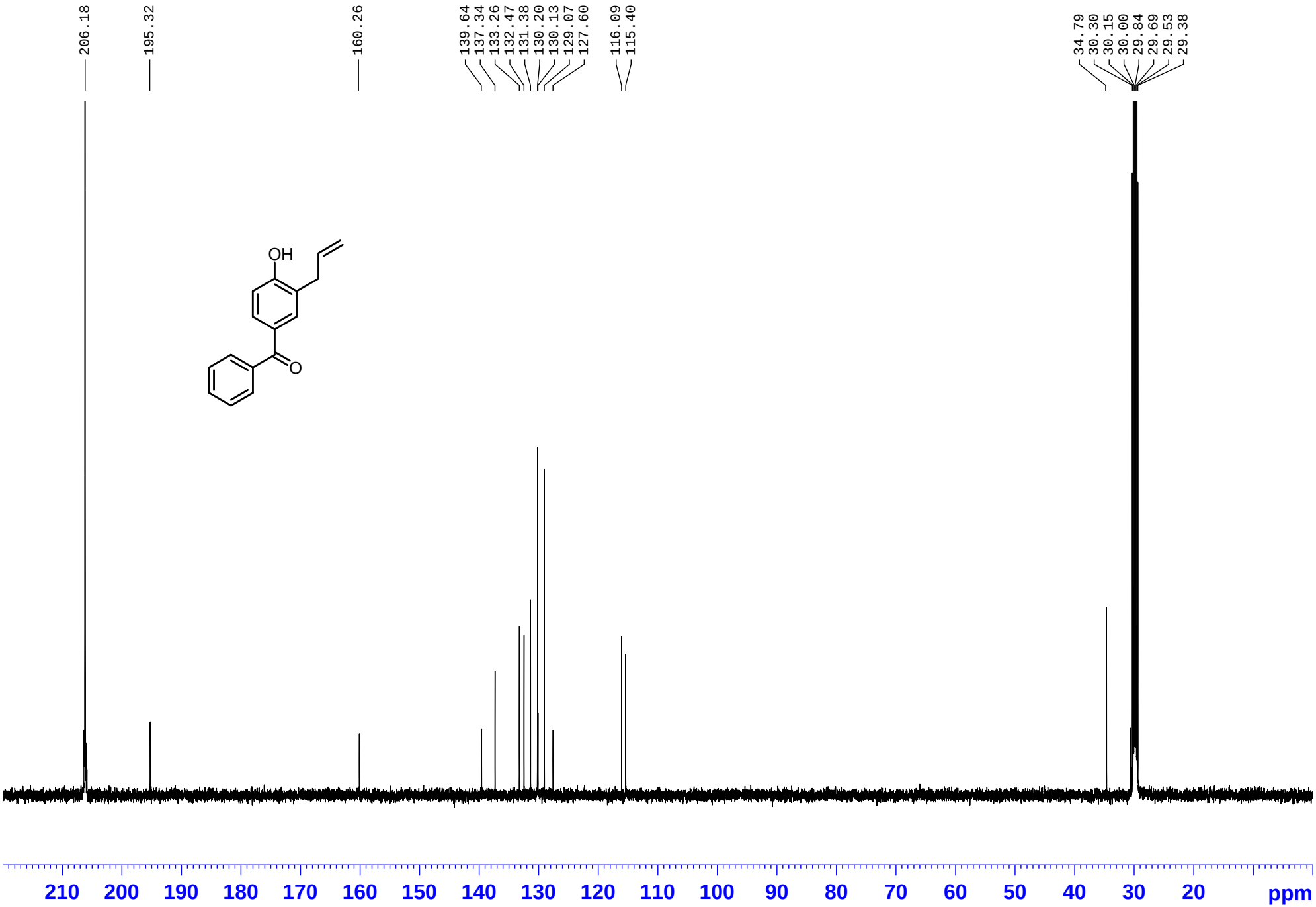
7.60
7.60
7.60
7.58
7.57
7.56
7.55
7.54
7.52
7.51
7.51
6.99
6.97
6.07
6.06
6.05
6.04
6.04
6.02
6.02
6.01
6.00
5.99
5.12
5.12
5.11
5.11
5.09
5.08
5.08
5.07
5.04
5.04
5.04
5.03
5.02
5.02
5.02
5.01
3.45
3.44
2.05
OH
O
11
10
9
8
7
6
5
4
3
2
1
ppm
0.93
2.18
1.04
1.08
1.11
2.17
1.08
1.00
2.07
2.24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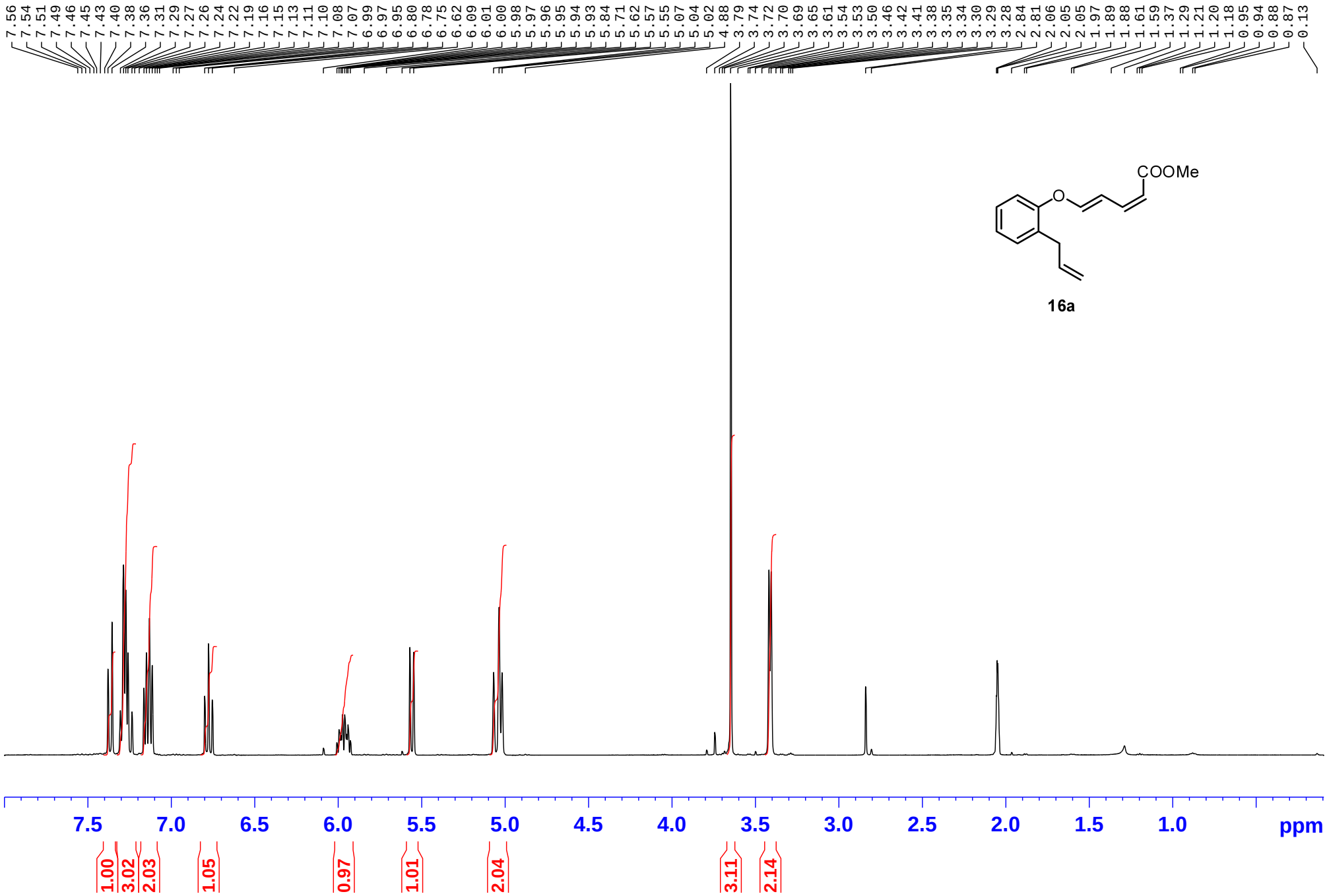
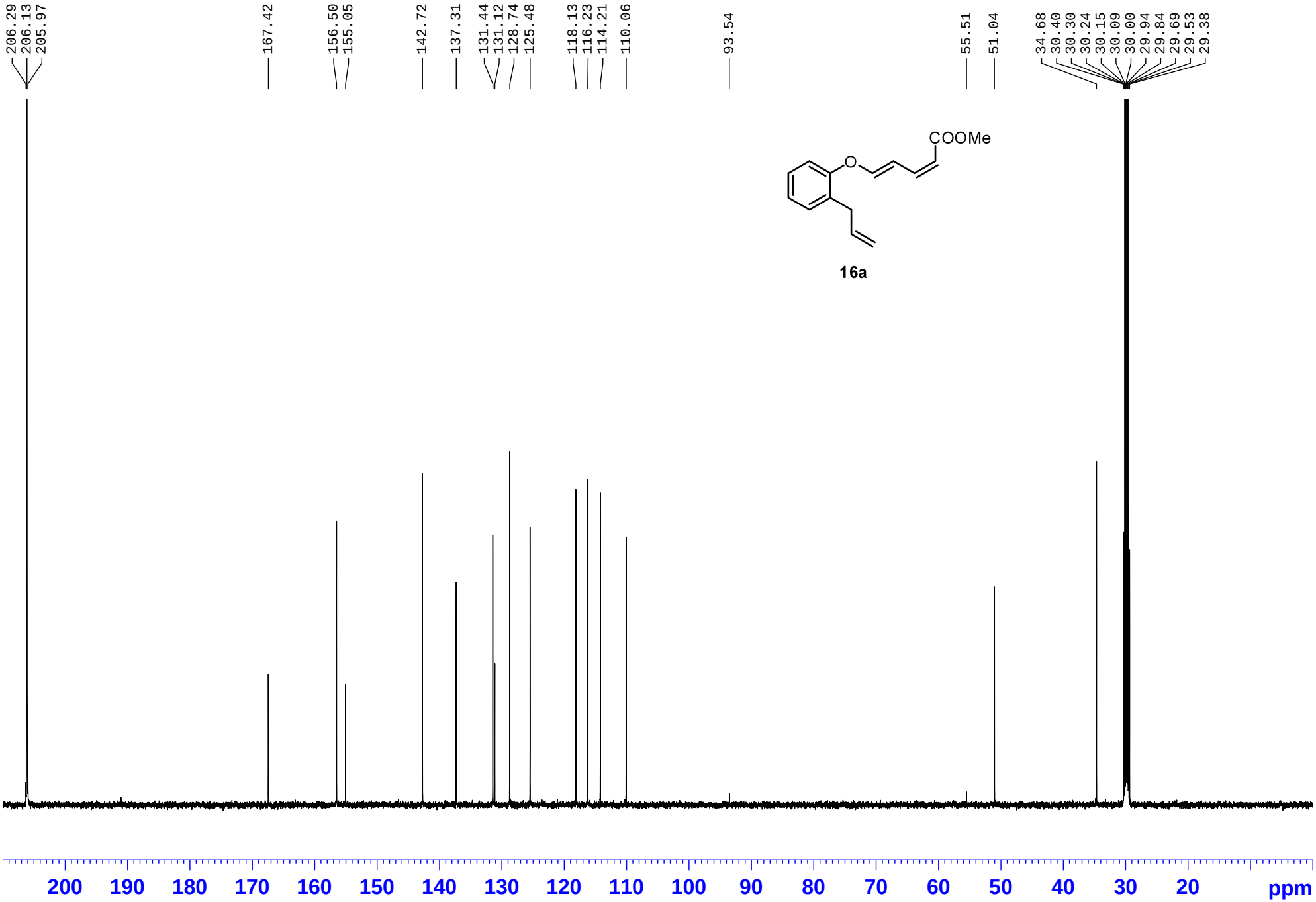
131.38
130.20
130.13
129.07
127.60
116.09
115.40
34.79
30.30
30.15
30.00
29.84
29.69
29.53
29.38
OH
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.56 7.54 7.51 7.49 7.46 7.45 7.43 7.40 7.38 7.36 7.31 7.29 7.27 7.26 7.24 7.22 7.19 7.16 7.15 7.13 7.11 7.10 7.08 7.07 6.99 6.97 6.95 6.80 6.78 6.75 6.62 6.09 6.01 6.00 5.98 5.97 5.96 5.95 5.94 5.93 5.84 5.71 5.62 5.57 5.55 5.07 5.04 5.02 4.88 3.79 3.74 3.72 3.70 3.69 3.65 3.61 3.54 3.53 3.50 3.46 3.42 3.41 3.38 3.35 3.34 3.30 3.29 3.28 2.84 2.81 2.06 2.05 2.05 1.97 1.89 1.88 1.61 1.59 1.37 1.29 1.21 1.20 1.18 0.95 0.94 0.88 0.87 0.13
COOMe
O
16a
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00 3.02 2.03 1.05 0.97 1.01 2.04 3.11 2.14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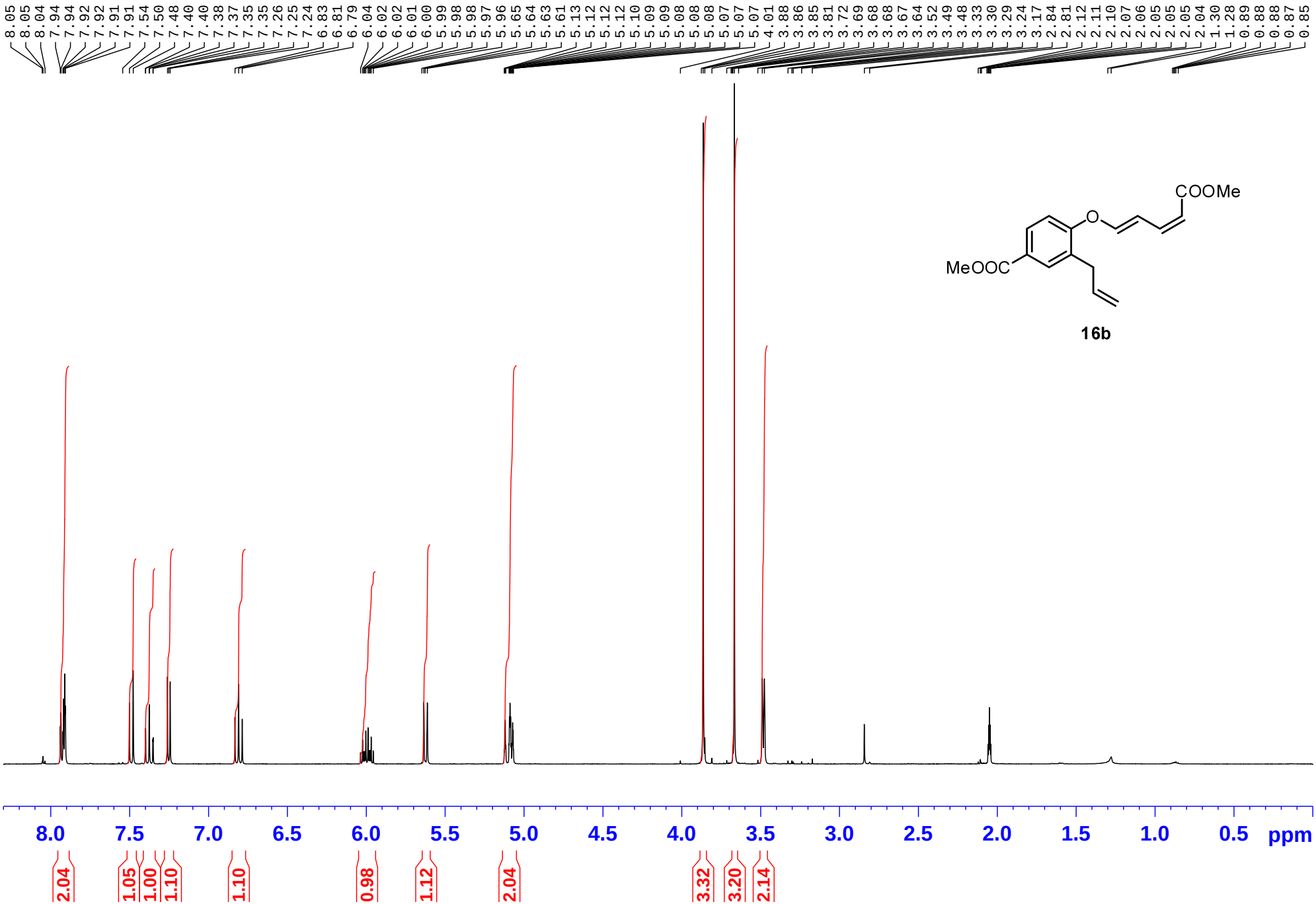
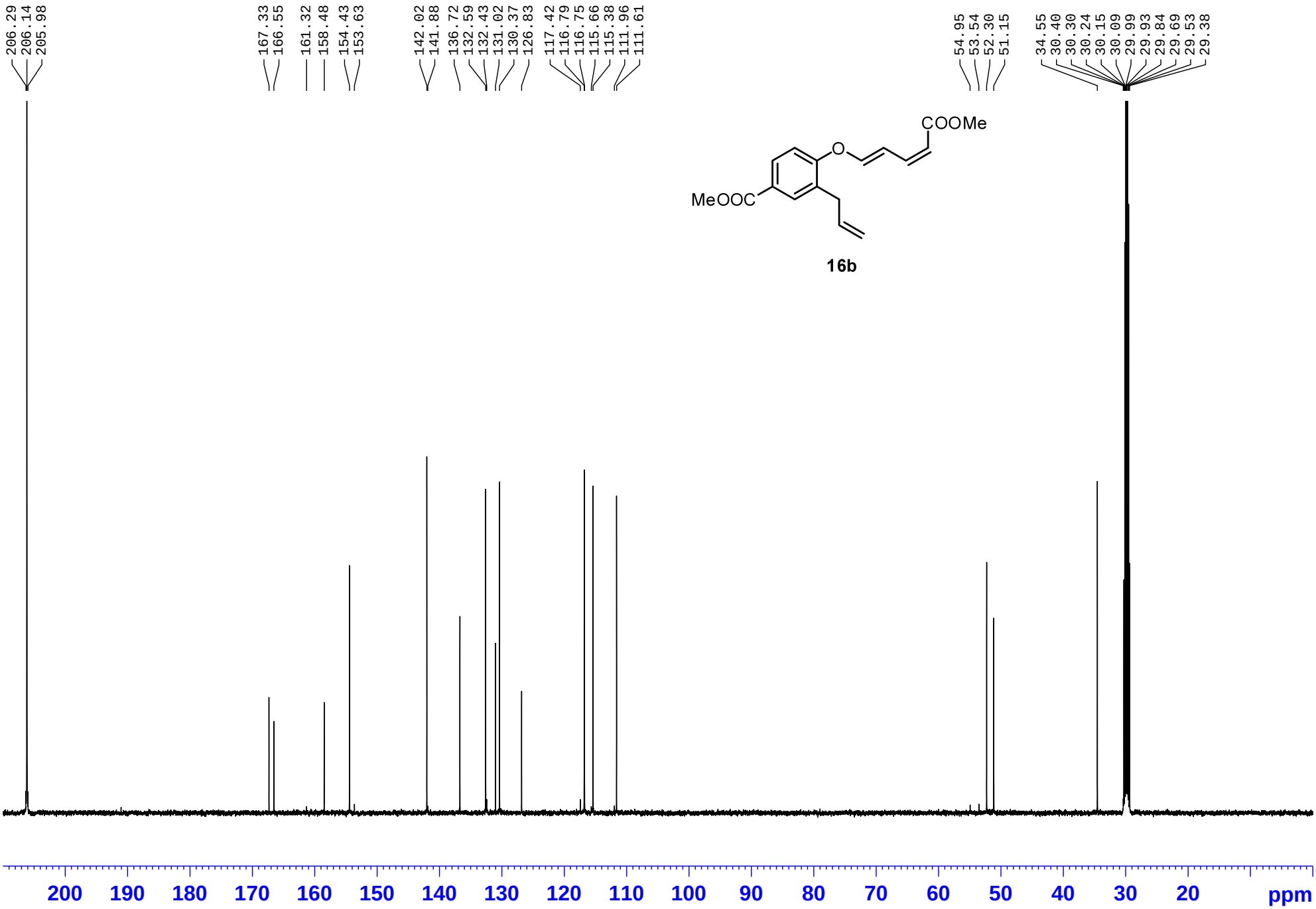
205.97
167.42
156.50
155.05
142.72
137.31
131.44
131.12
128.74
125.48
118.13
116.23
114.21
110.06
93.54
55.51
51.04
34.68
30.40
30.30
30.24
30.15
30.09
30.00
29.94
29.84
29.69
29.53
29.38
COOMe
O
16a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.05 8.05 8.04 7.94 7.94 7.92 7.92 7.91 7.91 7.54 7.50 7.48 7.40 7.40 7.38 7.37 7.35 7.35 7.26 7.25 7.24 6.83 6.81 6.79 6.04 6.02 6.02 6.01 6.00 5.99 5.98 5.98 5.97 5.96 5.65 5.64 5.63 5.61 5.13 5.12 5.12 5.12 5.10 5.09 5.09 5.08 5.08 5.08 5.07 5.07 5.07 4.01 3.88 3.86 3.85 3.81 3.72 3.69 3.68 3.68 3.67 3.64 3.52 3.49 3.48 3.33 3.30 3.29 3.24 3.17 2.84 2.81 2.12 2.11 2.10 2.07 2.06 2.05 2.05 2.05 2.04 1.30 1.28 0.89 0.88 0.88 0.87 0.85
COOMe
O
MeOOC
16b
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.04 1.05 1.00 1.10 1.10 0.98 1.12 2.04 3.32 3.20 2.14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206.14
205.98
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161.32
158.48
154.43
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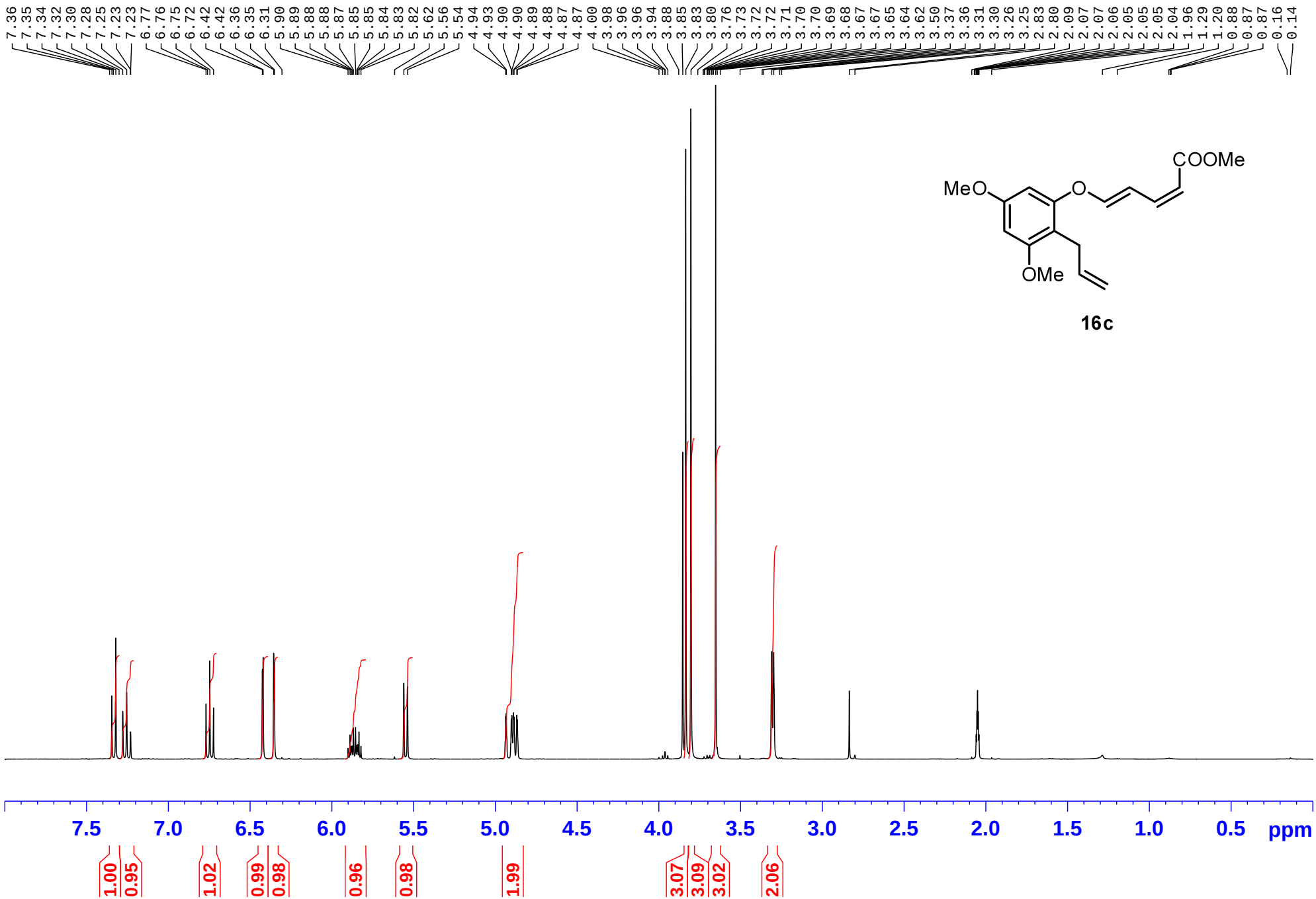
141.88
136.72
132.59
132.43
131.02
130.37
126.83
117.42
116.79
116.75
115.66
115.38
111.96
111.61
54.95
53.54
52.30
51.15
34.55
30.40
30.30
30.24
30.15
30.09
29.99
29.93
29.84
29.69
29.53
29.38
COOMe
O
MeOOC
16b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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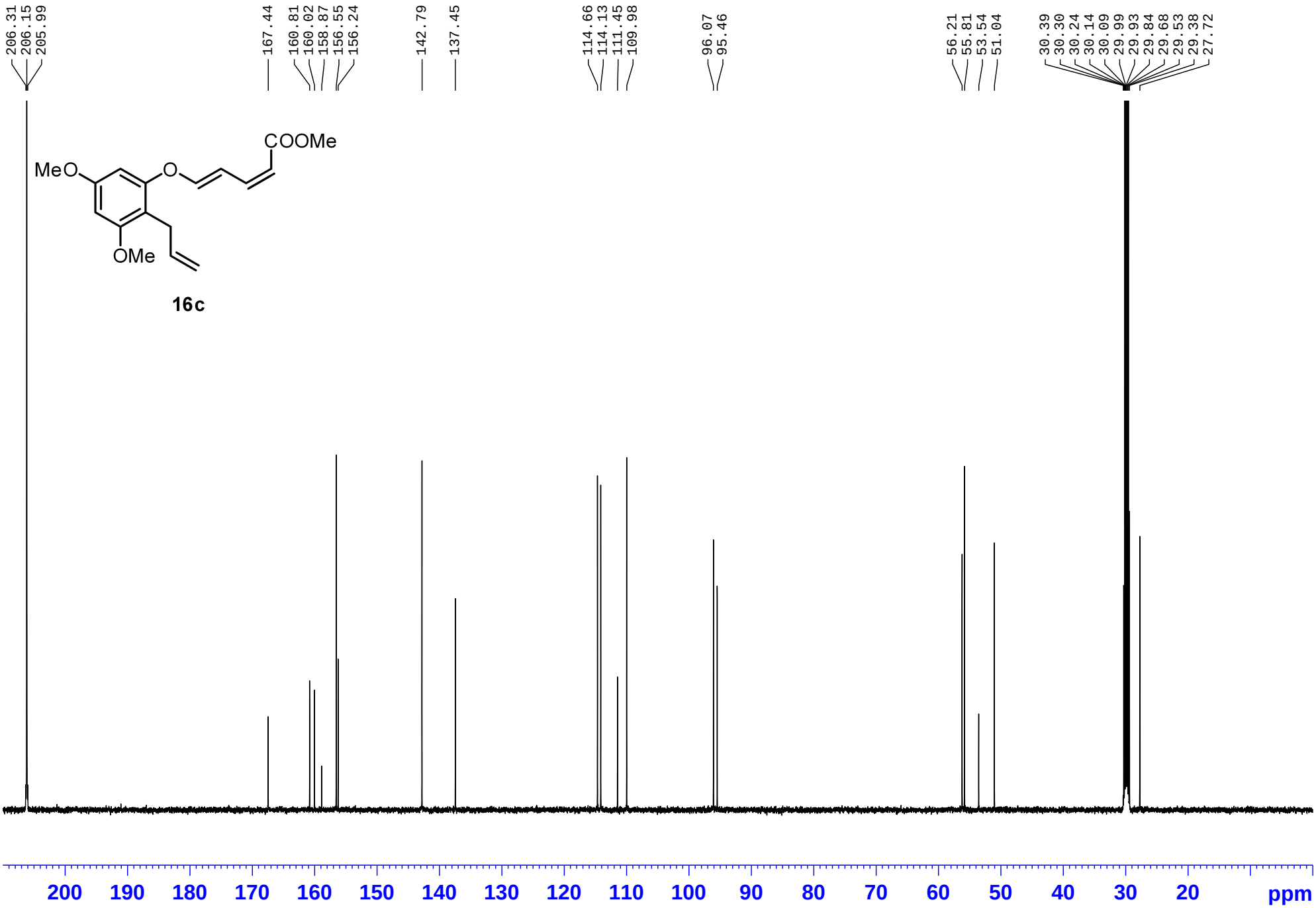
COOMe
MeO
O
OMe
16c
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 0.95 1.02 0.99 0.98 0.96 0.98 1.99 3.07 3.09 3.02 2.06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206.15
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160.02
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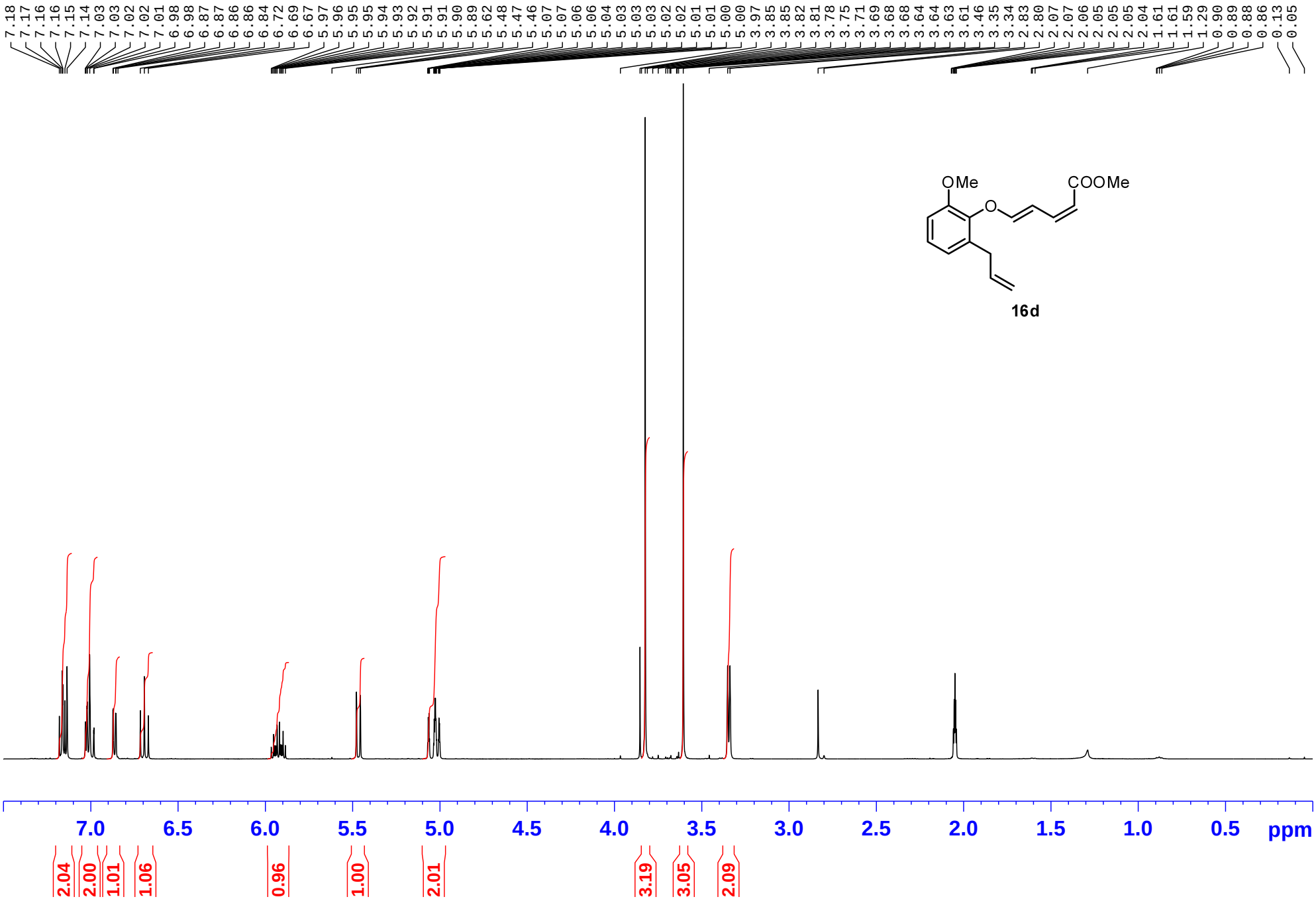
156.24
142.79
137.45
114.66
114.13
111.45
109.98
96.07
95.46
56.21
55.81
53.54
51.04
30.39
30.30
30.24
30.14
30.09
29.99
29.93
29.84
29.68
29.53
29.38
27.72
COOMe
MeO
O
OMe
16c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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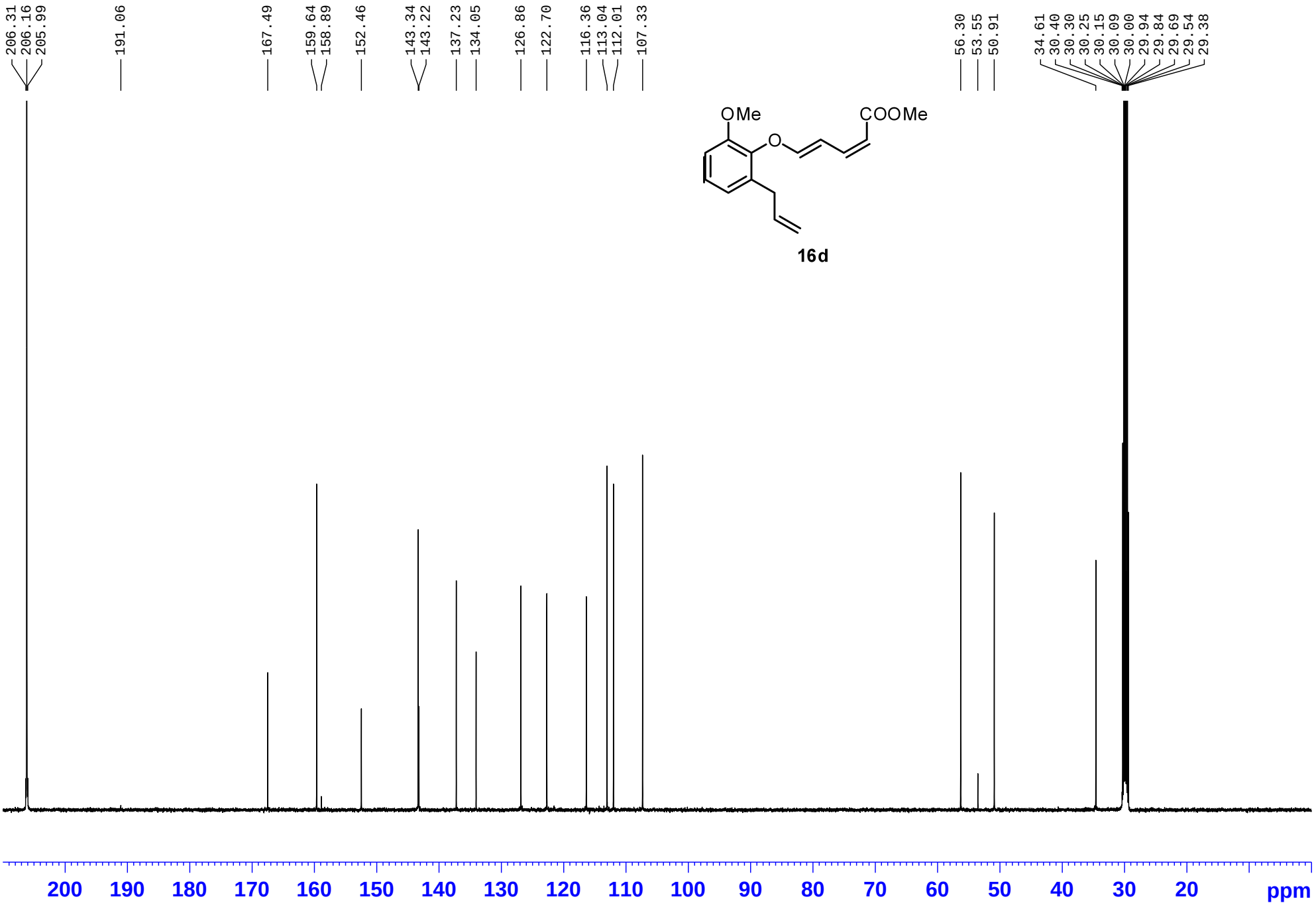
OMe
COOMe
O
16d
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.04 2.00 1.01 1.06 0.96 1.00 2.01 3.19 3.05 2.09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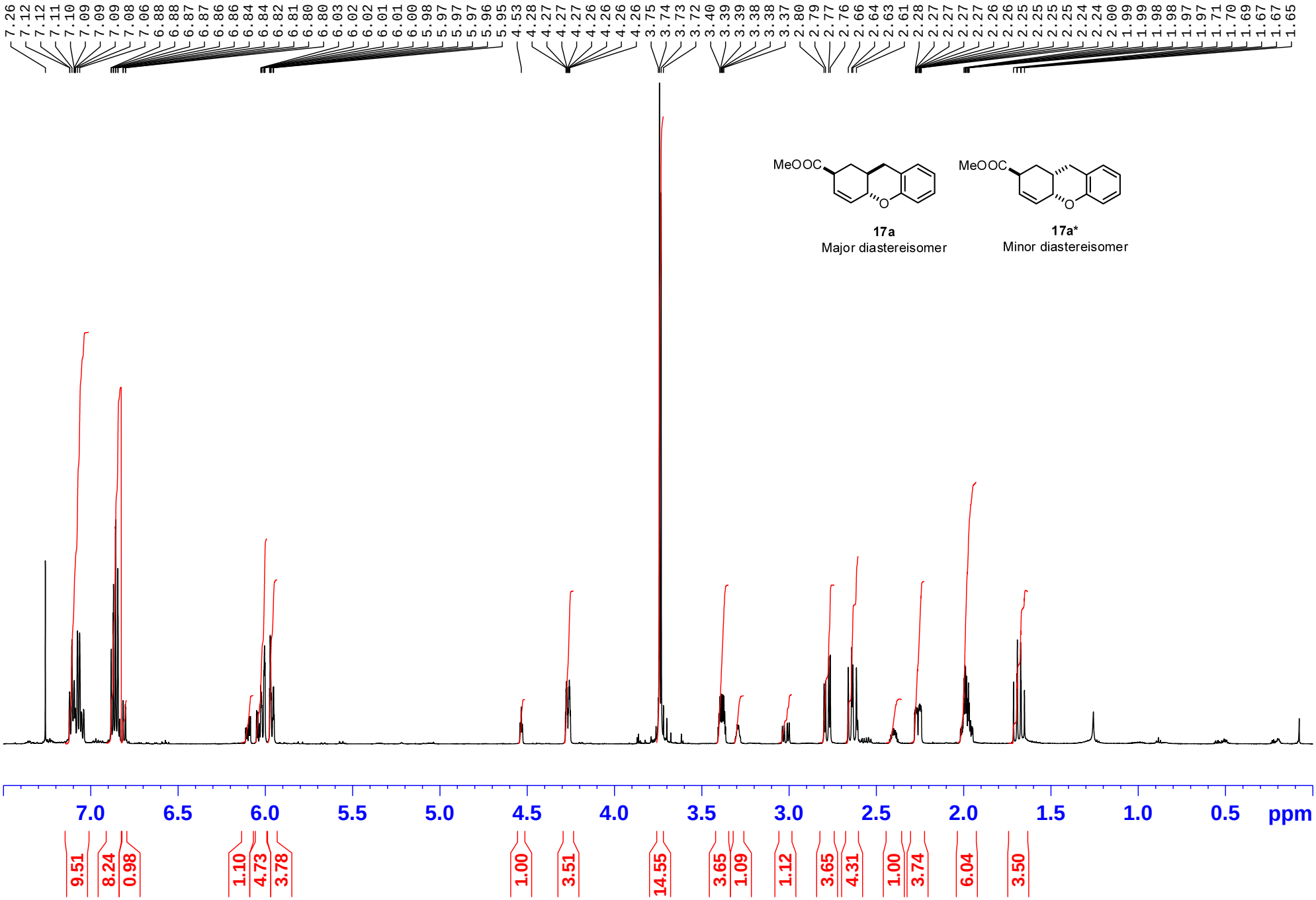
205.99
191.06
167.49
159.64
158.89
152.46
143.34
143.22
137.23
134.05
126.86
122.70
116.36
113.04
112.01
107.33
56.30
53.55
50.91
34.61
30.40
30.30
30.25
30.15
30.09
30.00
29.94
29.84
29.69
29.54
29.38
OMe
COOMe
O
16d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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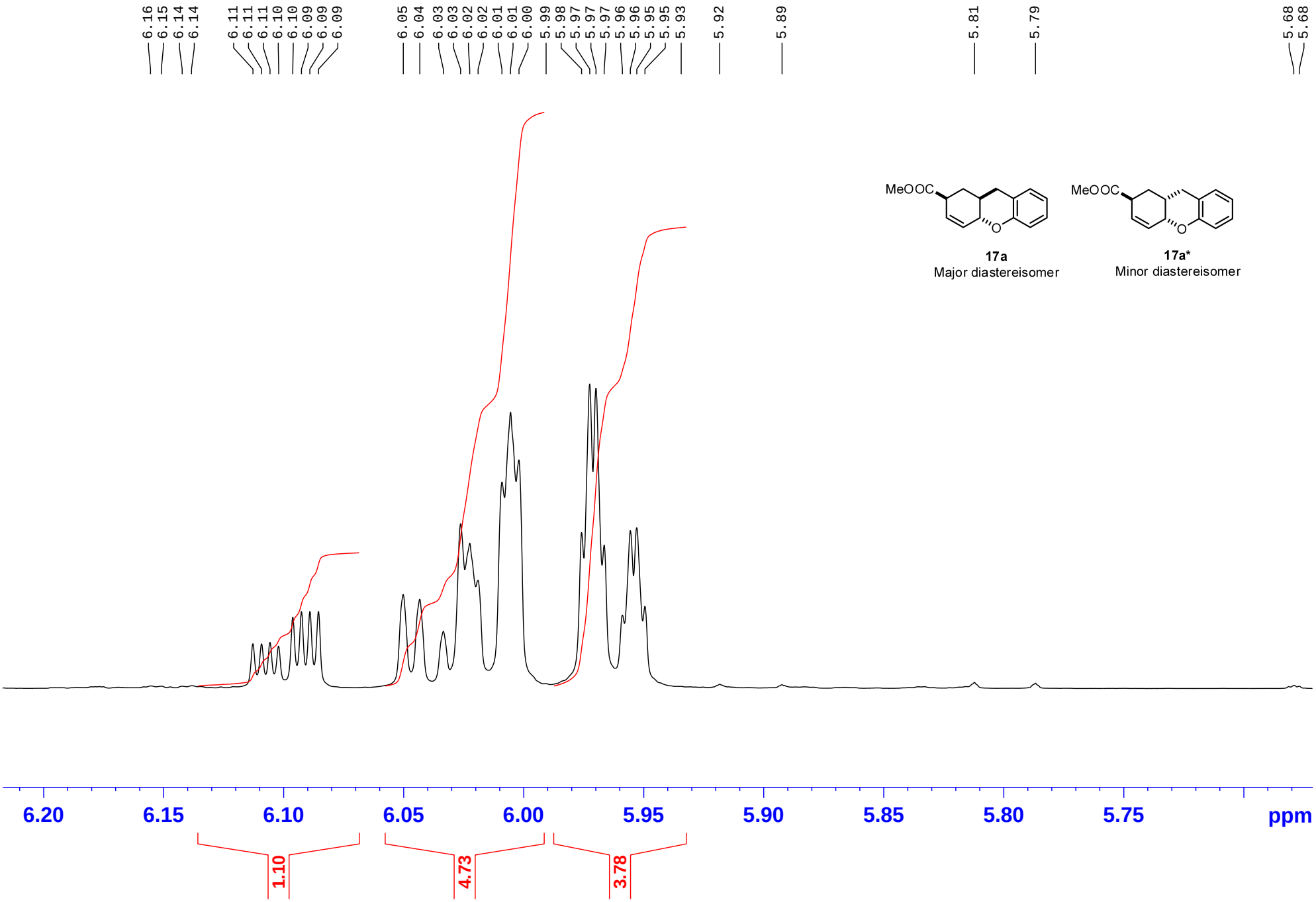
MeOOC
O
17a
Major diastereisomer
MeOOC
O
17a*
Minor diastereisomer
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
9.51 8.24 0.98 1.10 4.73 3.78 1.00 3.51 14.55 3.65 1.09 1.12 3.65 4.31 1.00 3.74 6.04 3.50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6.15
6.14
6.14
6.11
6.11
6.11
6.10
6.10
6.09
6.09
6.09
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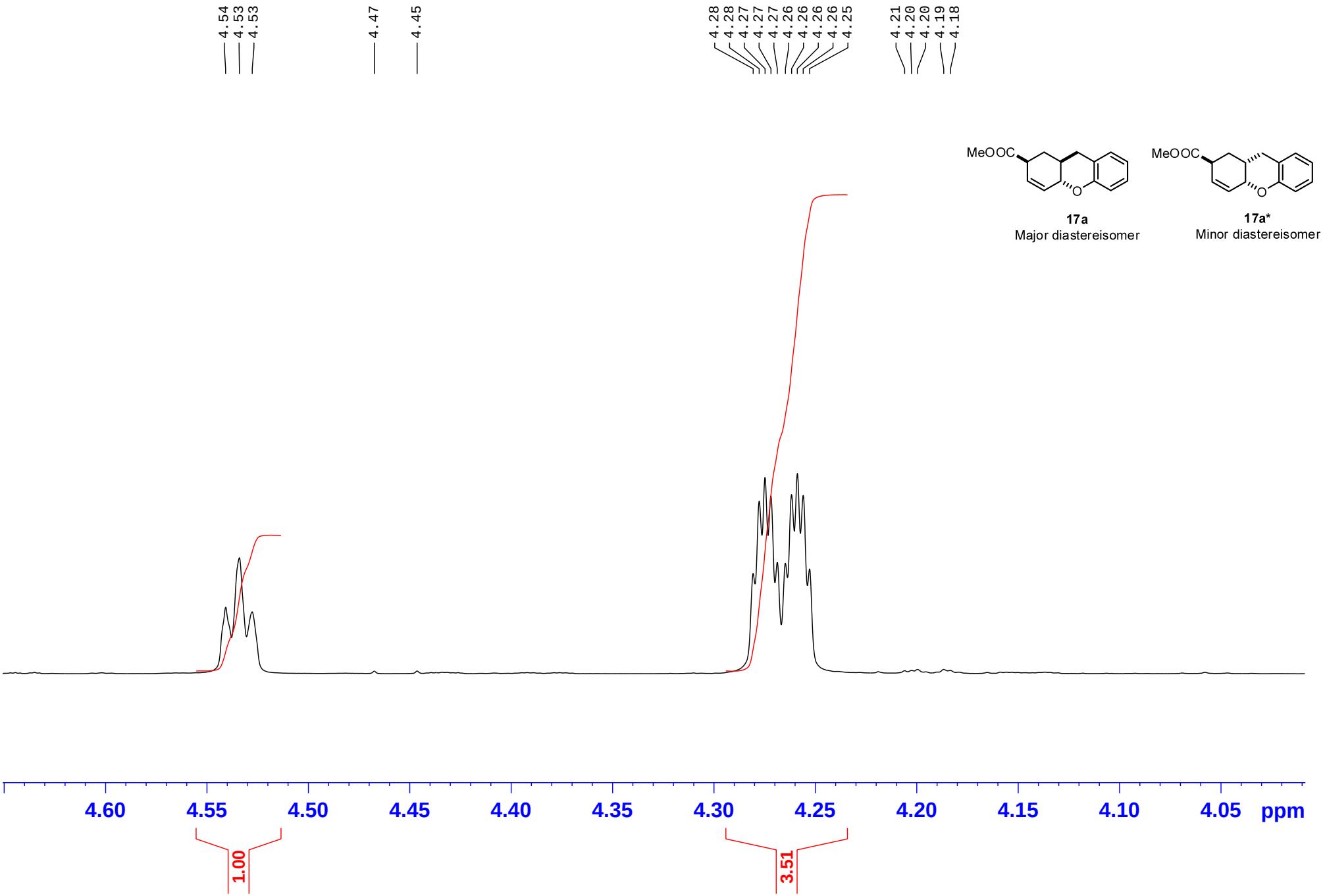
6.04
6.03
6.03
6.02
6.02
6.01
6.01
6.00
5.99
5.98
5.97
5.97
5.97
5.96
5.96
5.95
5.95
5.93
5.92
5.89
5.81
5.79
5.68
5.68
MeOOC
O
17a
Major diastereisomer
MeOOC
O
17a*
Minor diastereisomer
6.20
6.15
6.10
6.05
6.00
5.95
5.90
5.85
5.80
5.75
ppm
1.10
4.73
3.78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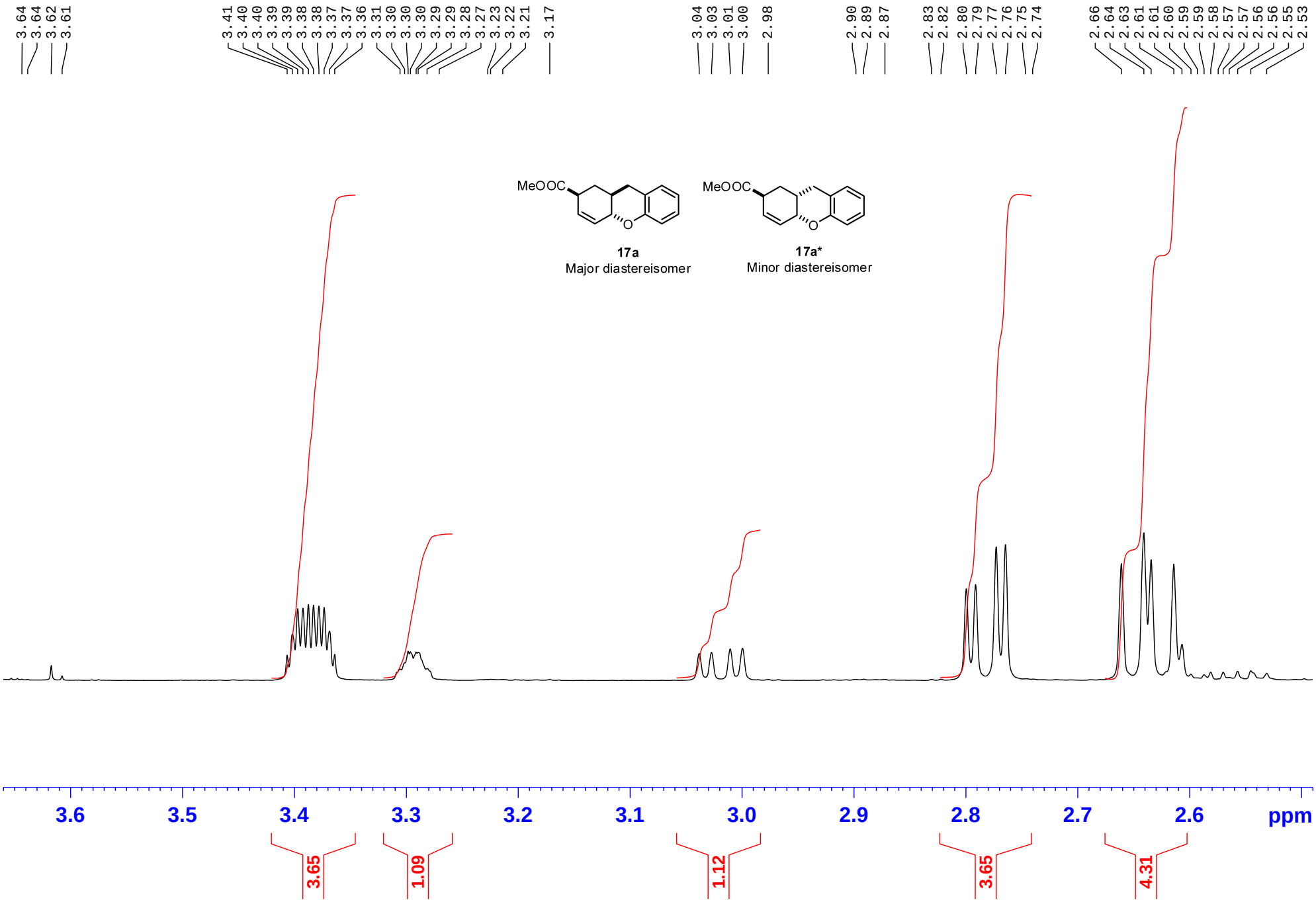
4.53
4.53
4.47
4.45
4.28
4.28
4.27
4.27
4.27
4.26
4.26
4.26
4.25
4.21
4.20
4.20
4.19
4.18
MeOOC
O
17a
Major diastereisomer
MeOOC
O
17a*
Minor diastereisomer
4.60
4.55
4.50
4.45
4.40
4.35
4.30
4.25
4.20
4.15
4.10
4.05
ppm
1.00
3.51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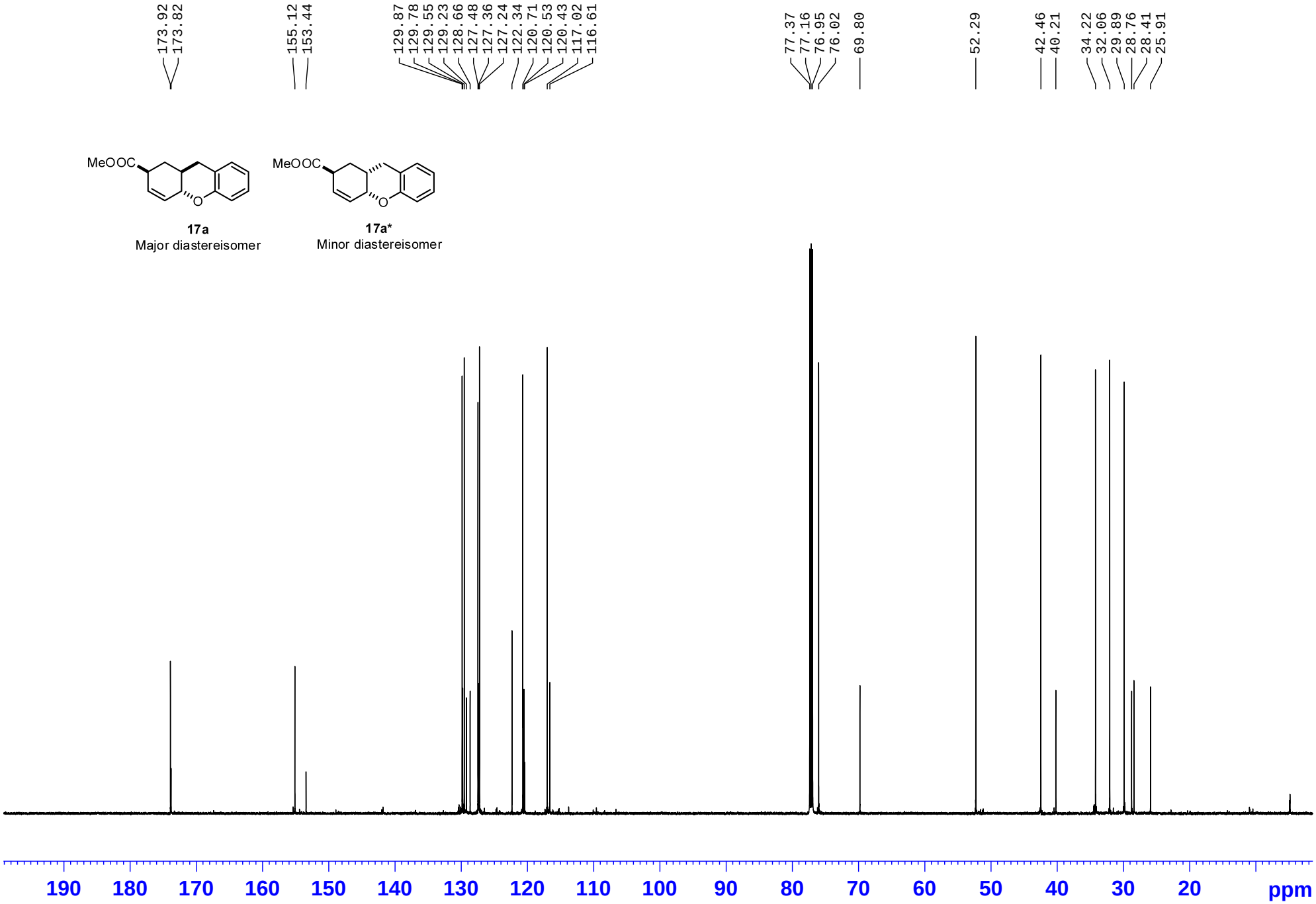
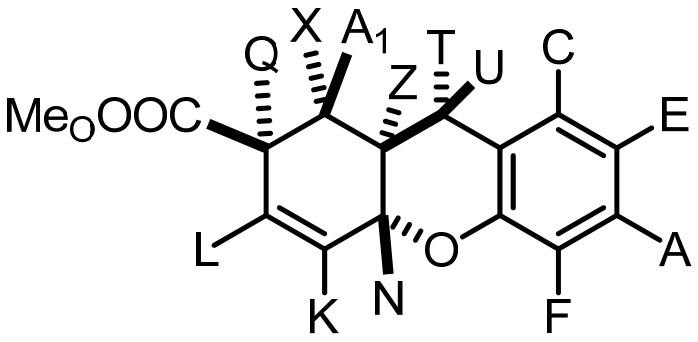
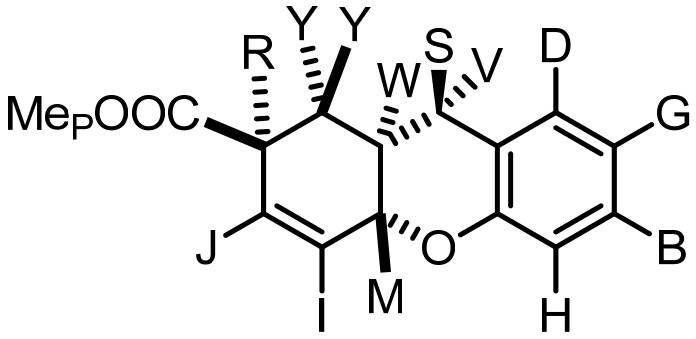
3.41 3.40 3.40 3.39 3.39 3.38 3.38 3.37 3.37 3.36 3.31 3.30 3.30 3.30 3.29 3.29 3.28 3.27 3.23 3.22 3.21 3.17
3.04 3.03 3.01 3.00 2.98
2.90 2.89 2.87
2.83 2.82 2.80 2.79 2.77 2.76 2.75 2.74
2.66 2.64 2.63 2.61 2.61 2.60 2.59 2.59 2.58 2.57 2.57 2.56 2.56 2.55 2.53
MeOOC
O
17a
Major diastereisomer
MeOOC
O
17a*
Minor diastereisomer
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
ppm
3.65
1.09
1.12
3.65
4.31


173.92
173.82
155.12
153.44
129.87
129.78
129.55
129.23
128.66
127.48
127.36
127.24
122.34
120.71
120.53
120.43
117.02
116.61
77.37
77.16
76.95
76.02
69.80
52.29
42.46
40.21
34.22
32.06
29.89
28.76
28.41
25.91
MeOOC
O
17a
Major diastereisomer
MeOOC
O
17a*
Minor diastereisomer
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



Major diastereomer
17a

Relevant NOE interaction

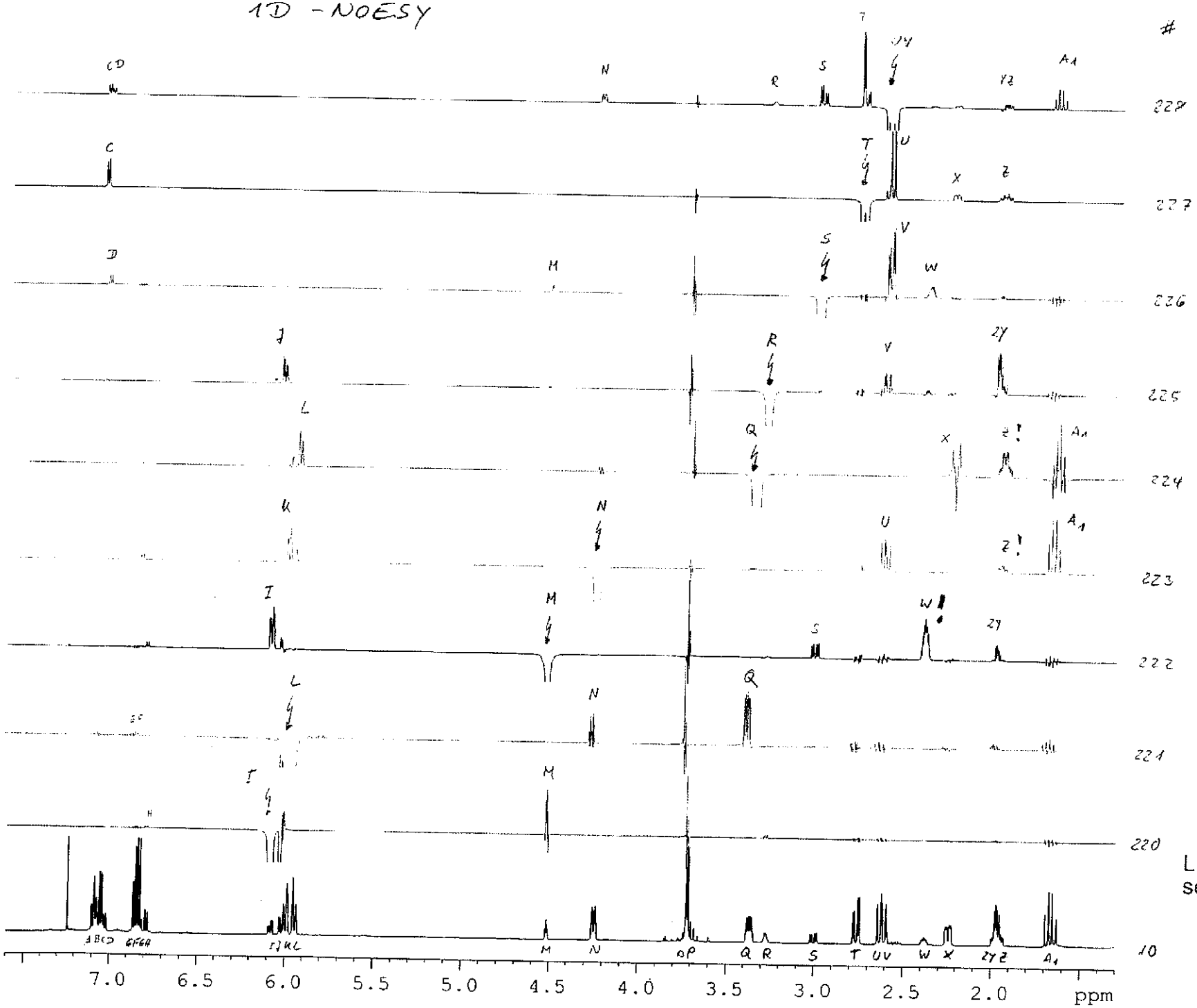


Minor diastereomer
17a*

Relevant NOE interaction

1D - NOESY

H616018



! R – V weak NOE
R – W
R – M

! Q – Z

! N – Z "trans"

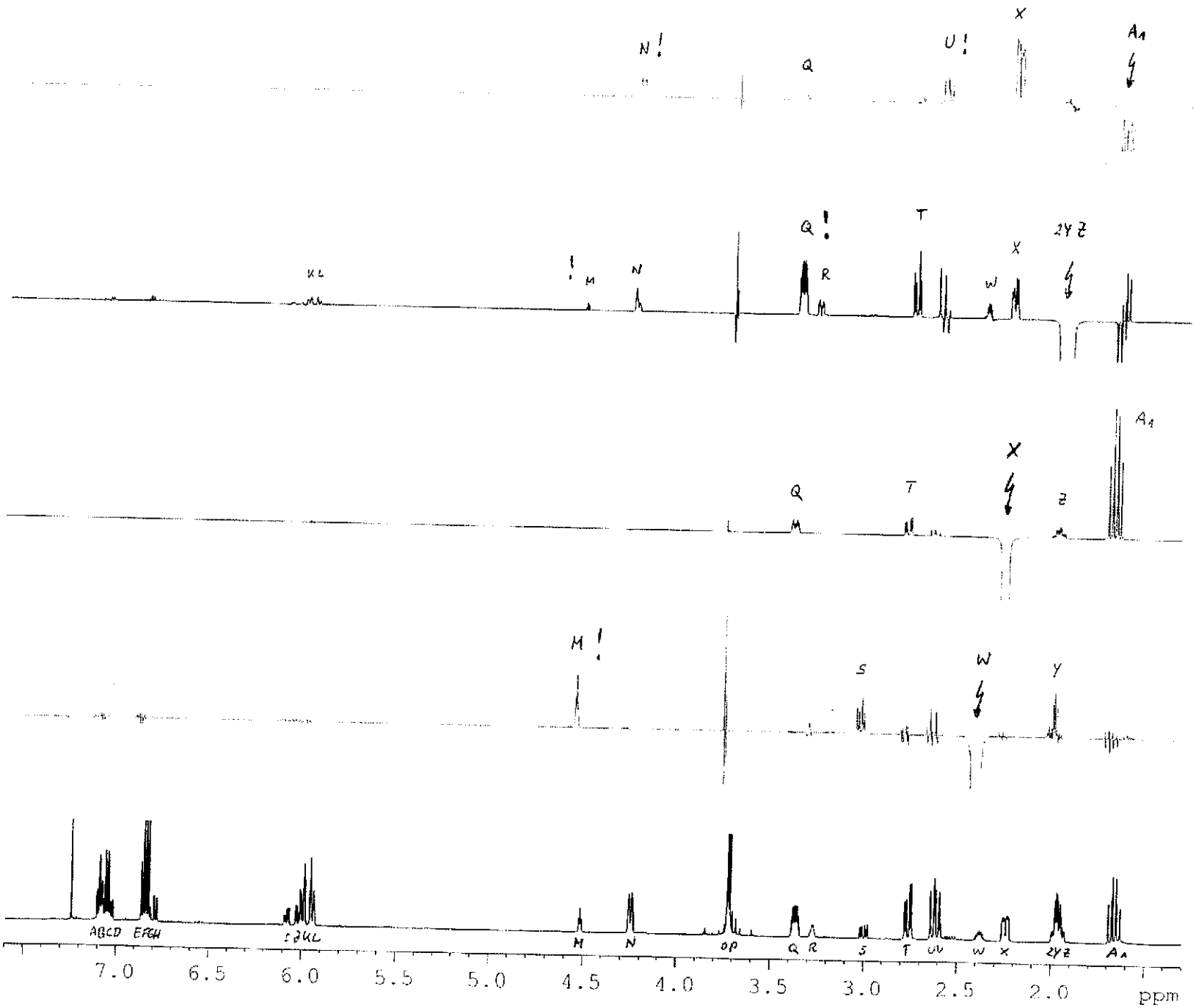
! M – W "cis"
M ⇔ R

LUP-LC-278-05
selnogp

dmx600

1D – NOESY

H616018



$A_1 \longleftrightarrow$ UN

$A_1 \longleftrightarrow$ Q schwach

$A_1 \not\longleftrightarrow$ Z

Z $\longleftrightarrow$ Q!

Y $\longleftrightarrow$ M schwach, aber da

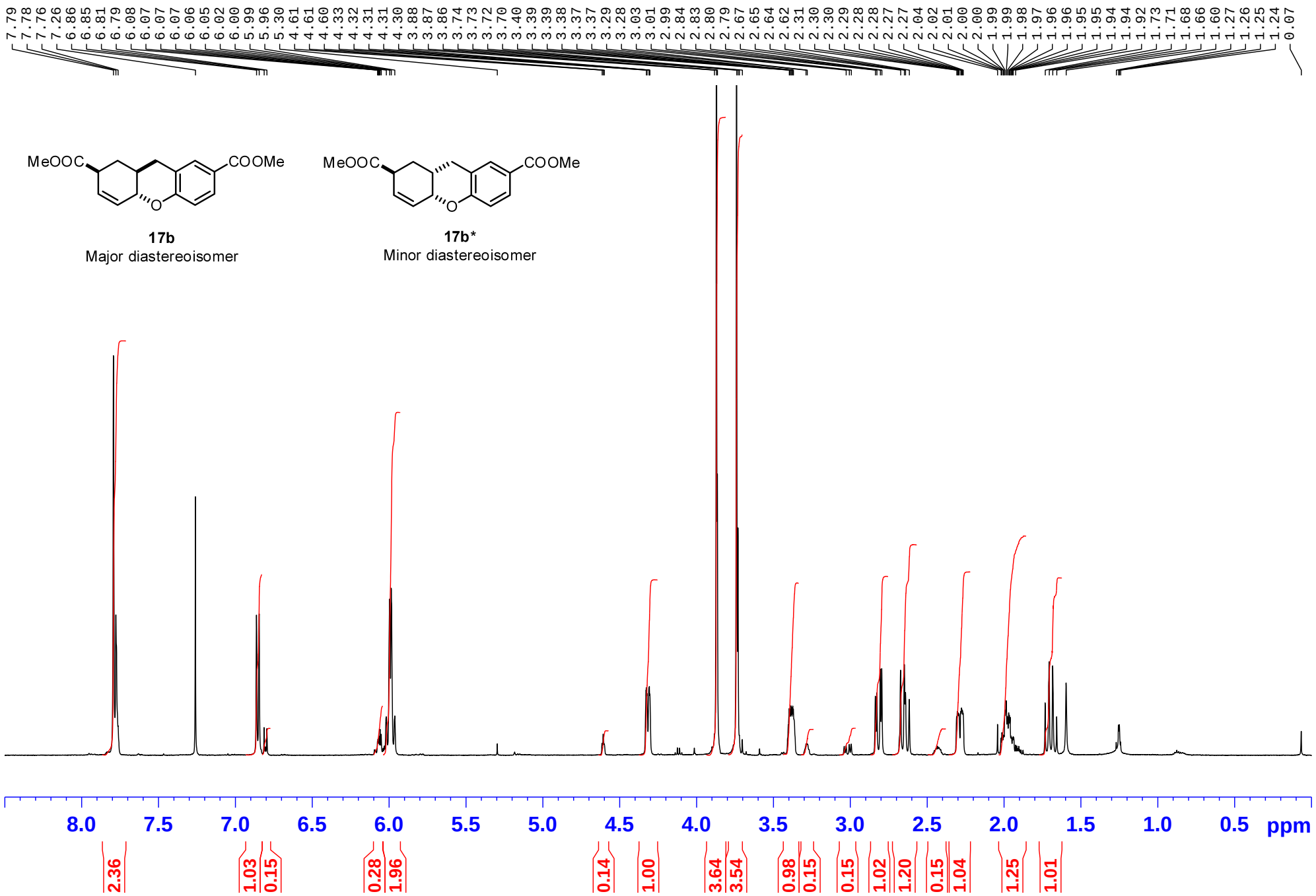
X $\longleftrightarrow$ QTZ A_1

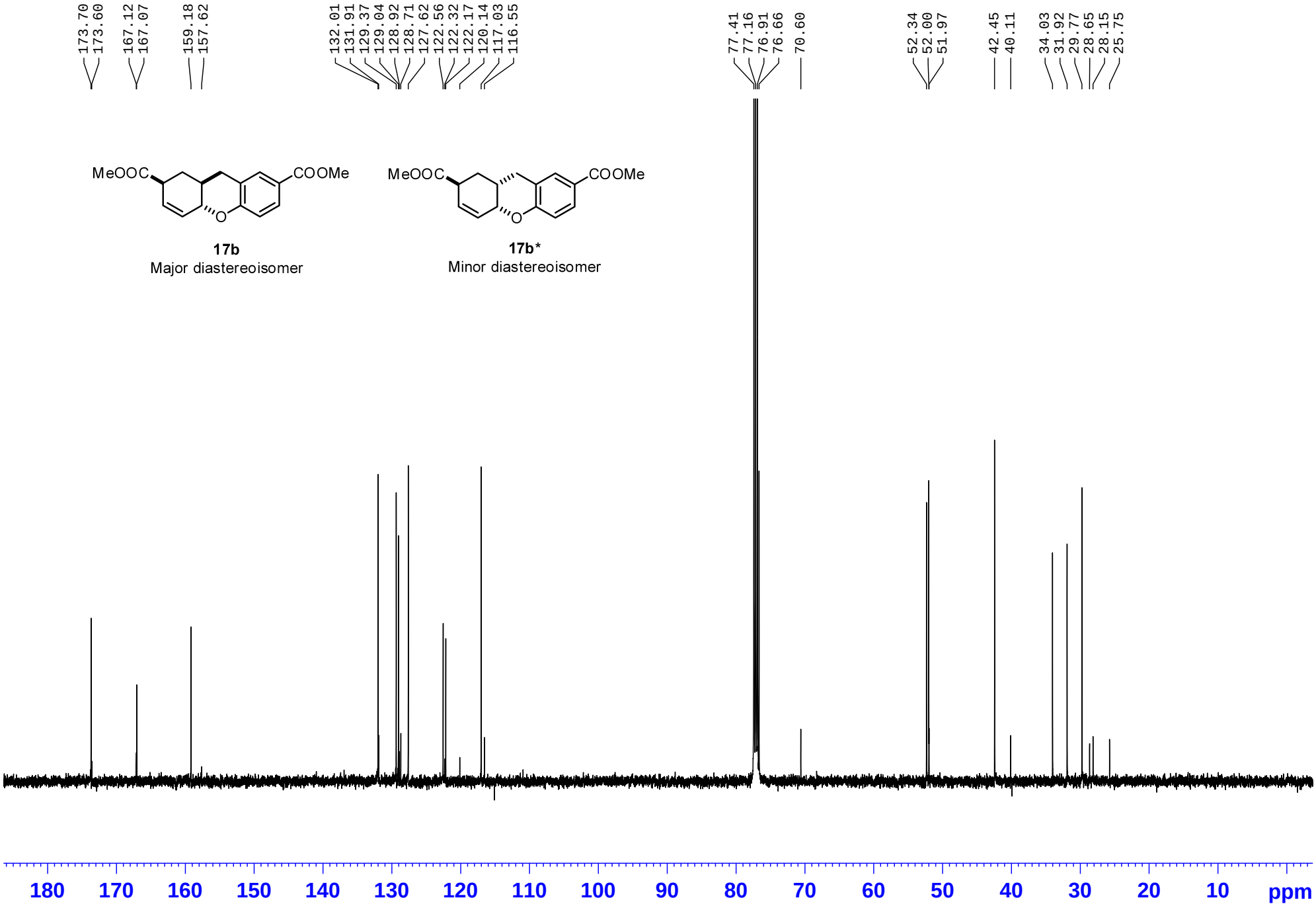
W $\longleftrightarrow$ M! S Y

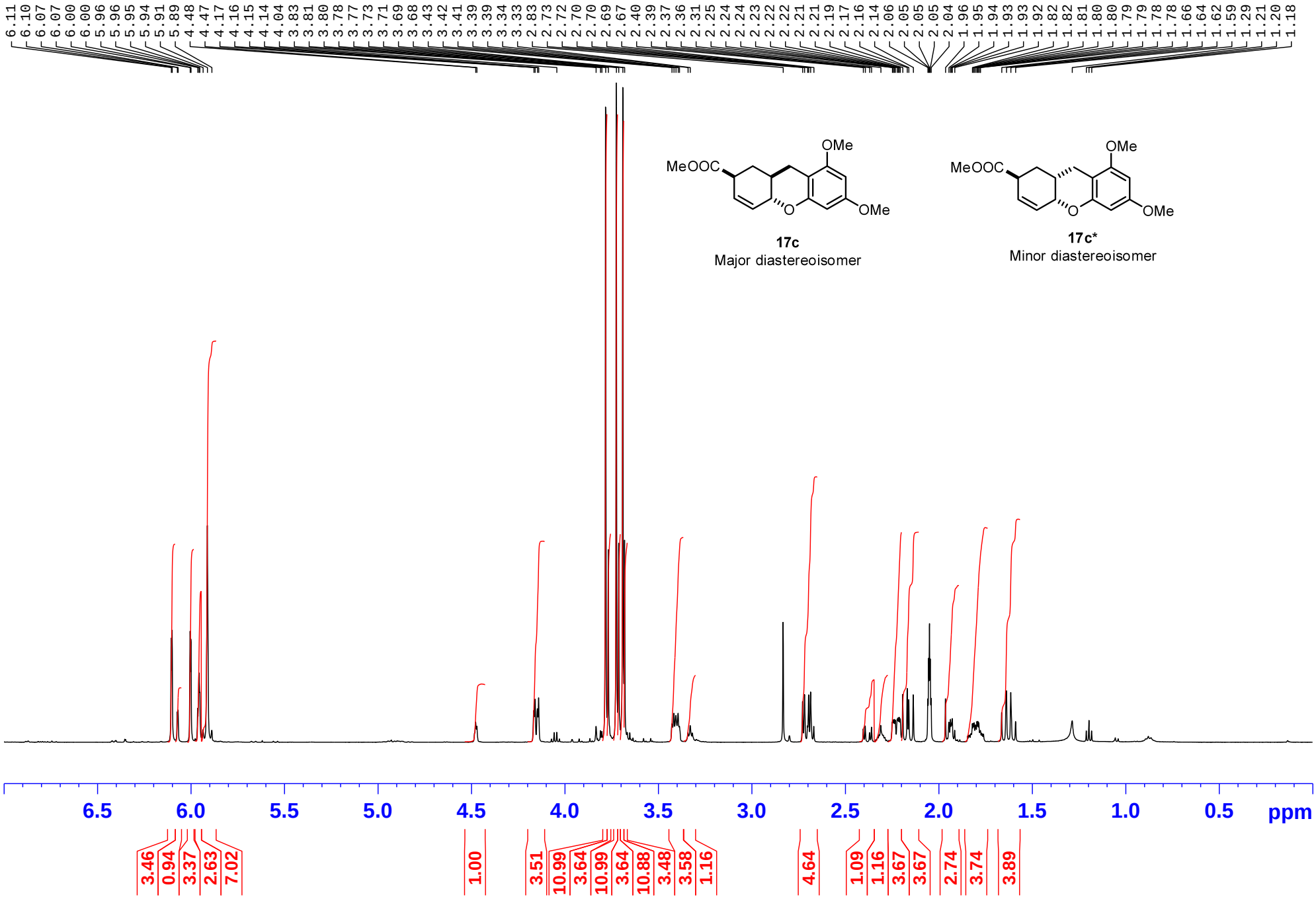
W $\not\longleftrightarrow$ R

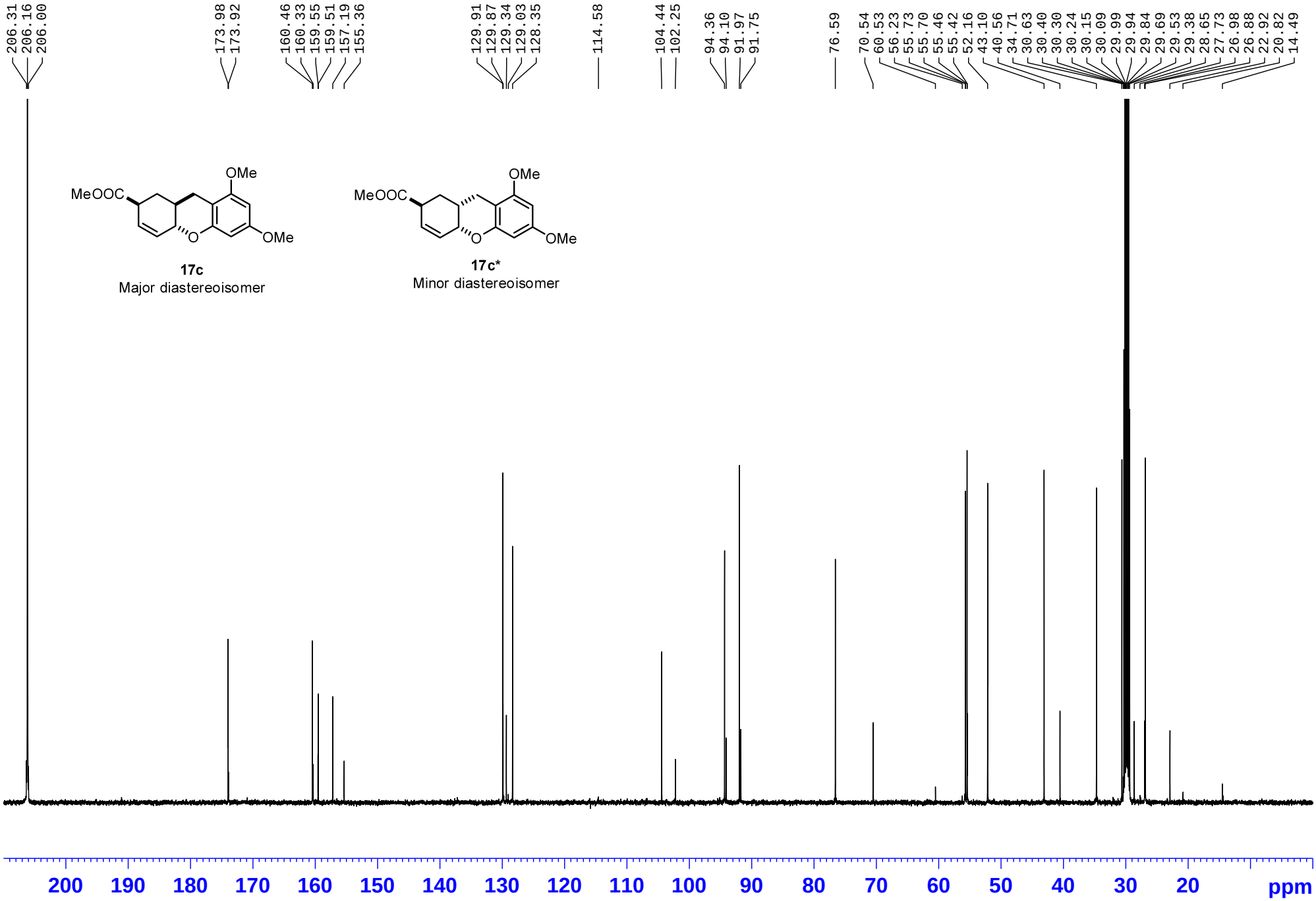
LUP-LC-278-05

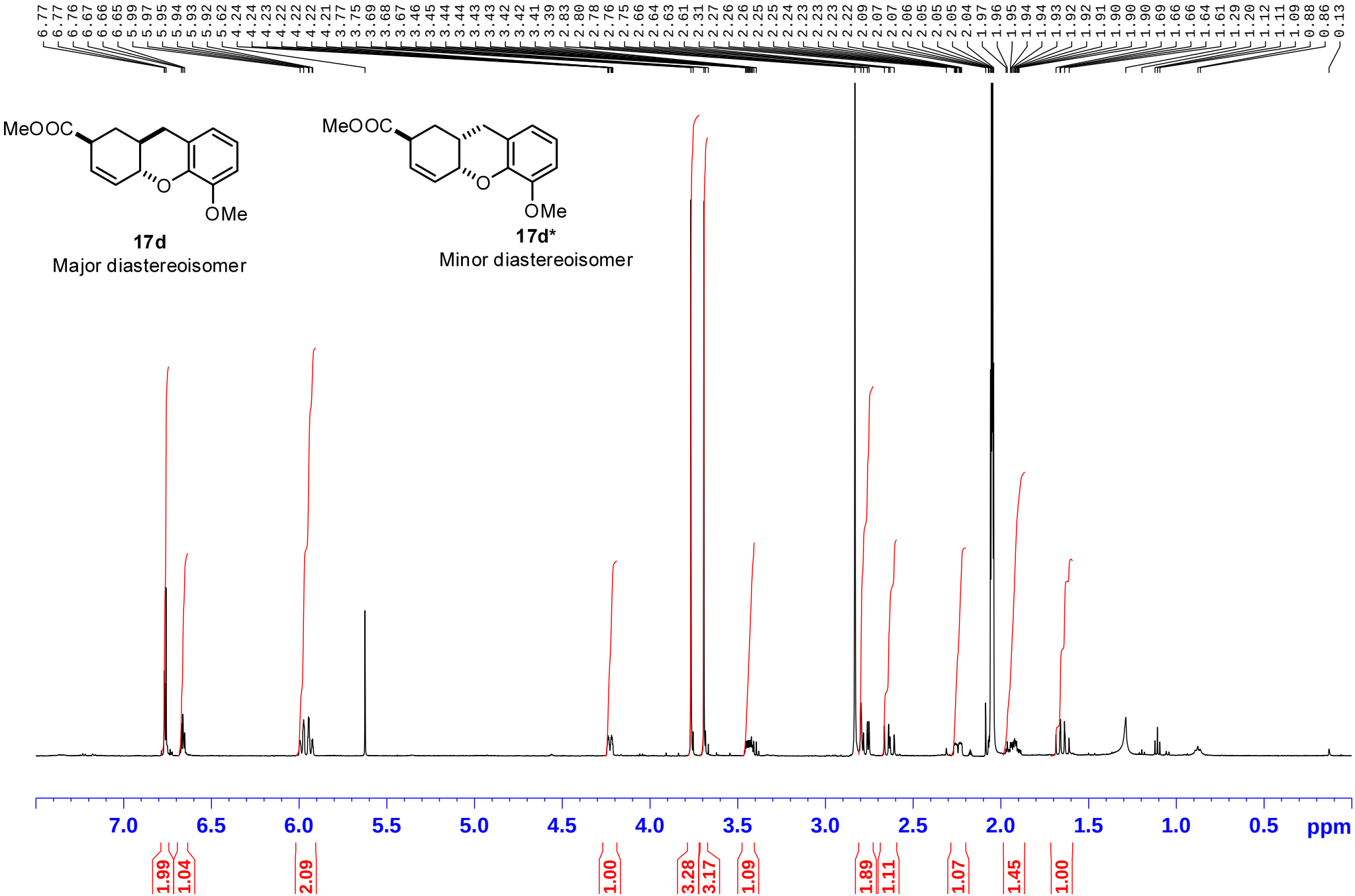
dmx600

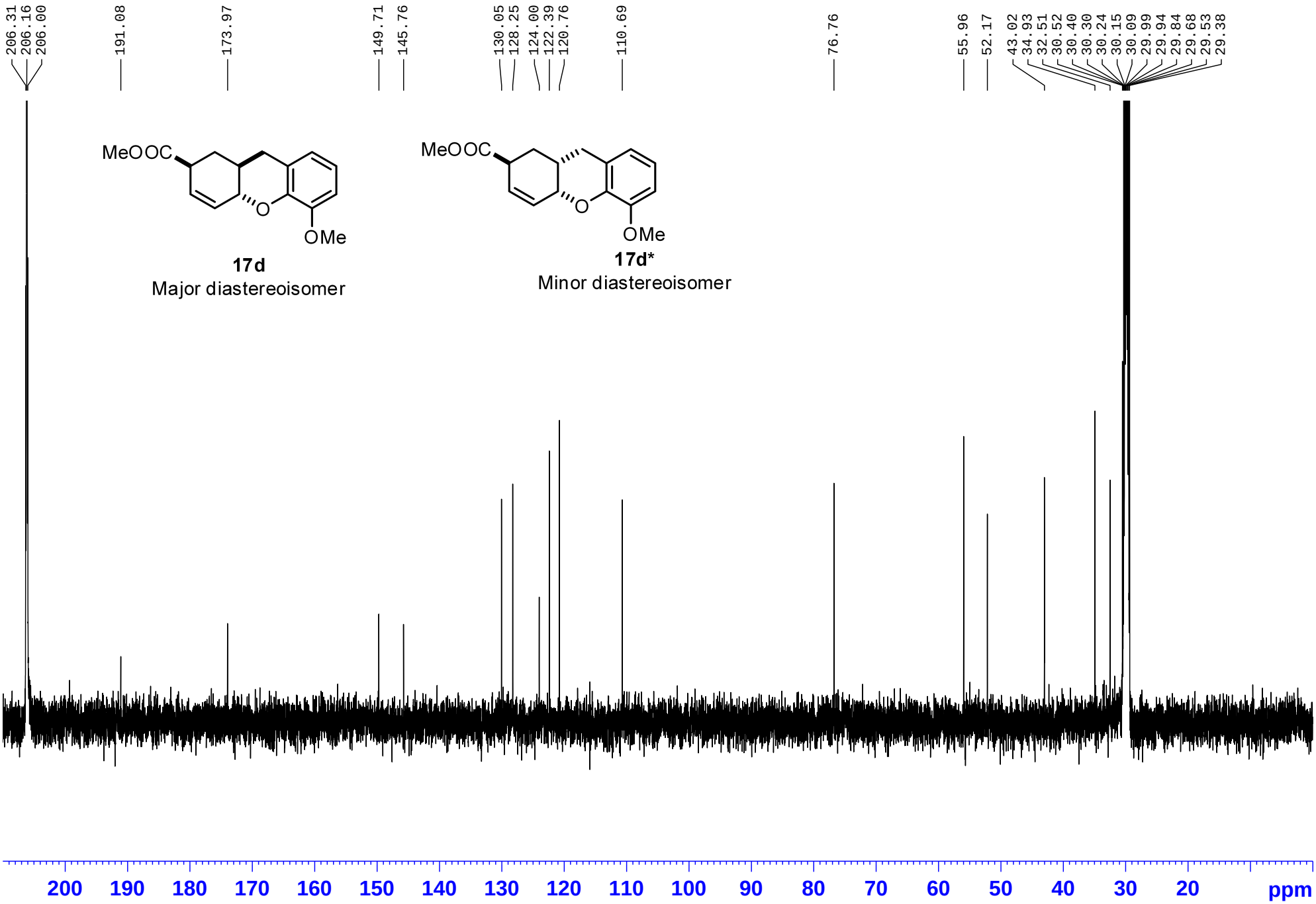

7.79 7.78 7.76 7.26 6.86 6.85 6.81 6.79 6.08 6.07 6.07 6.06 6.05 6.02 6.00 5.99 5.96 5.30 4.61 4.61 4.60 4.33 4.32 4.31 4.31 4.30 3.88 3.87 3.86 3.74 3.73 3.72 3.70 3.40 3.39 3.39 3.38 3.37 3.37 3.29 3.28 3.03 3.01 2.99 2.84 2.83 2.80 2.79 2.67 2.65 2.64 2.62 2.31 2.30 2.30 2.29 2.28 2.28 2.27 2.27 2.04 2.02 2.01 2.00 2.00 1.99 1.99 1.98 1.97 1.96 1.96 1.95 1.95 1.94 1.94 1.92 1.73 1.71 1.68 1.66 1.60 1.27 1.26 1.25 1.24 0.07
MeOOC
COOMe
O
17b
Major diastereoisomer
MeOOC
COOMe
O
17b*
Minor diastereoisomer
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.36
1.03
0.15
0.28
1.96
0.14
1.00
3.64
3.54
0.98
0.15
0.15
1.02
1.20
0.15
1.04
1.25
1.01

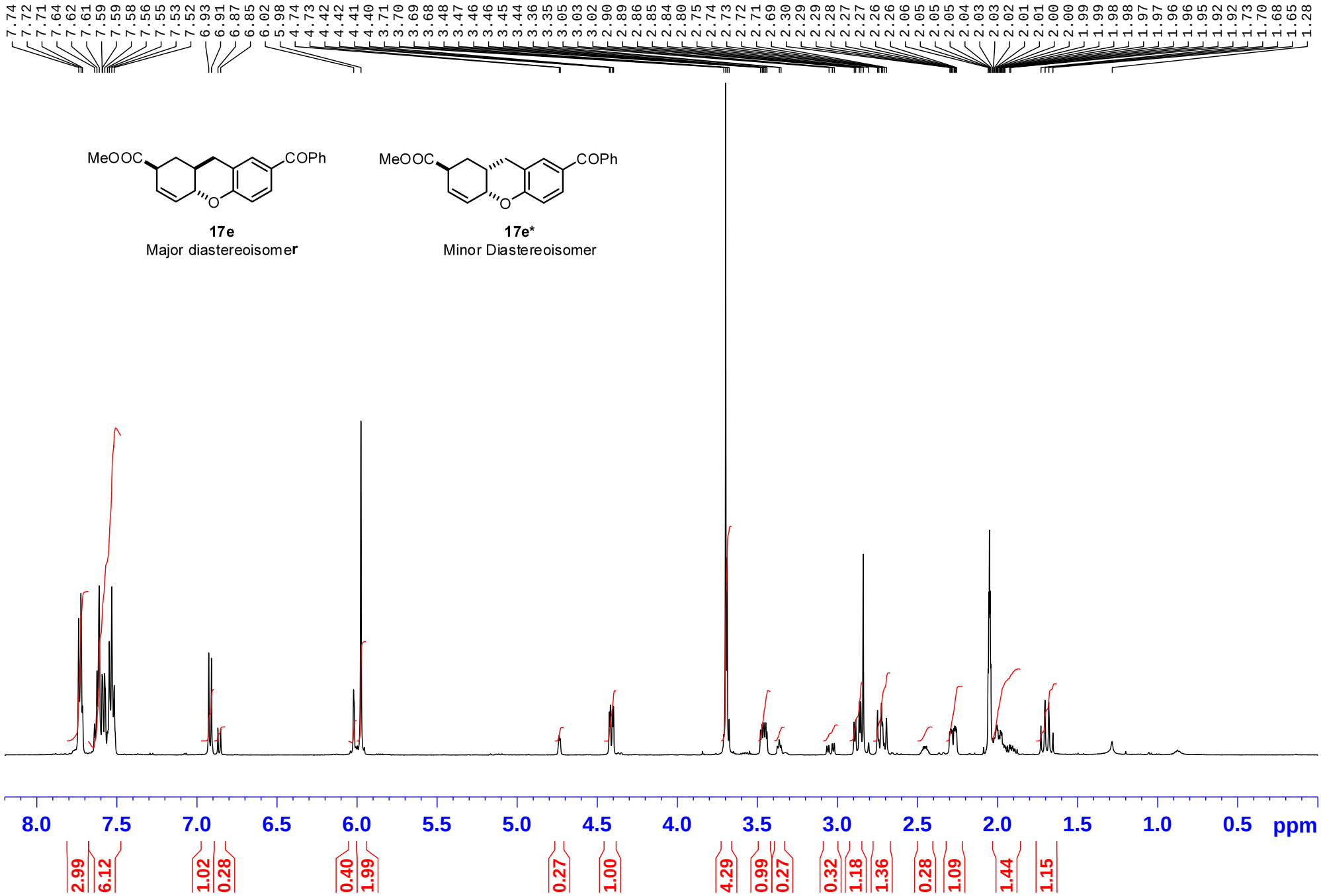

173.70
173.60
167.12
167.07
159.18
157.62
132.01
131.91
129.37
129.04
128.92
128.71
127.62
122.56
122.32
122.17
120.14
117.03
116.55
77.41
77.16
76.91
76.66
70.60
52.34
52.00
51.97
42.45
40.11
34.03
31.92
29.77
28.65
28.15
25.75
MeOOC
COOMe
O
17b
Major diastereoisomer
MeOOC
COOMe
O
17b*
Minor diastereoisomer
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

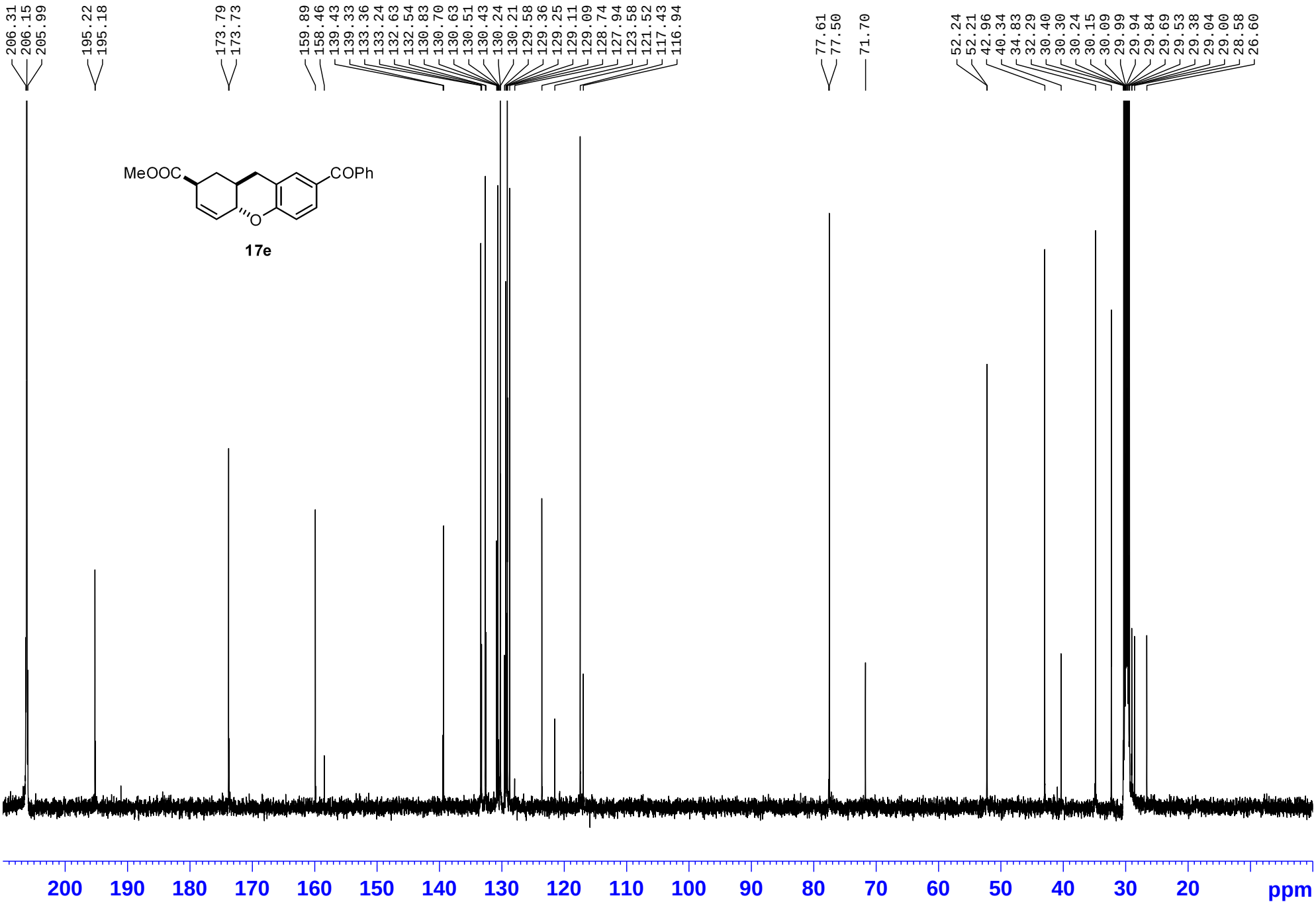

6.11 6.10 6.07 6.07 6.00 6.00 5.96 5.96 5.95 5.94 5.91 5.89 4.48 4.47 4.17 4.16 4.15 4.14 4.04 3.83 3.81 3.80 3.78 3.77 3.73 3.71 3.69 3.68 3.43 3.42 3.41 3.39 3.39 3.34 3.33 2.83 2.73 2.72 2.70 2.70 2.69 2.67 2.40 2.39 2.37 2.36 2.31 2.25 2.24 2.24 2.23 2.22 2.22 2.21 2.21 2.19 2.17 2.16 2.14 2.06 2.05 2.05 2.05 2.04 1.96 1.95 1.94 1.93 1.92 1.82 1.82 1.81 1.80 1.80 1.79 1.79 1.78 1.78 1.66 1.64 1.62 1.59 1.29 1.21 1.20 1.18
MeOOC
OMe
OMe
O
17c
Major diastereoisomer
MeOOC
OMe
OMe
O
17c*
Minor diastereoisomer
6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.46 0.94 3.37 2.63 7.02
1.00
3.51 10.99 3.64 10.99 3.64 10.88 3.48 3.58 1.16
4.64
1.09 1.16 3.67 3.67 2.74 3.74 3.89


206.31
206.16
206.00
173.98
173.92
160.46
160.33
159.55
159.51
157.19
155.36
129.91
129.87
129.34
129.03
128.35
114.58
104.44
102.25
94.36
94.10
91.97
91.75
76.59
70.54
60.53
56.23
55.73
55.70
55.46
55.42
52.16
43.10
40.56
34.71
30.63
30.40
30.30
30.24
30.15
30.09
29.99
29.94
29.84
29.69
29.53
29.38
28.65
27.73
26.98
26.88
22.92
20.82
14.49
MeOOC
OMe
OMe
O
17c
Major diastereoisomer
MeOOC
OMe
OMe
O
17c*
Minor diastereoisomer
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


MeOOC
OMe
17d
Major diastereoisomer
MeOOC
OMe
17d*
Minor diastereoisomer
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.99
1.04
2.09
1.00
3.28
3.17
1.09
1.89
1.11
1.07
1.45
1.00

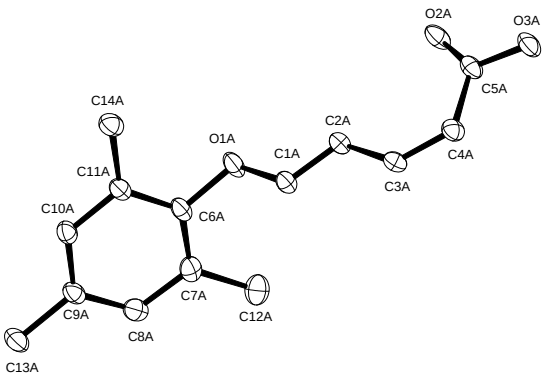

206.31
206.16
206.00
191.08
173.97
149.71
145.76
130.05
128.25
124.00
122.39
120.76
110.69
76.76
55.96
52.17
43.02
34.93
32.51
30.52
30.40
30.30
30.24
30.15
30.09
29.99
29.94
29.84
29.68
29.53
29.38
MeOOC
O
OMe
17d
Major diastereoisomer
MeOOC
O
OMe
17d*
Minor diastereoisomer
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


MeOOC
COPh
O
17e
Major diastereoisomer
MeOOC
COPh
O
17e*
Minor Diastereoisomer
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.99
6.12
1.02
0.28
0.40
1.99
0.27
1.00
4.29
0.99
0.27
0.32
1.18
1.36
0.28
1.09
1.44
1.15


206.31
206.15
205.99
195.22
195.18
173.79
173.73
159.89
158.46
139.43
139.33
133.36
133.24
132.63
132.54
130.83
130.70
130.63
130.51
130.43
130.24
130.21
129.58
129.36
129.25
129.11
129.09
128.74
127.94
123.58
121.52
117.43
116.94
77.61
77.50
71.70
52.24
52.21
42.96
40.34
34.83
32.29
30.40
30.30
30.24
30.15
30.09
29.99
29.94
29.84
29.69
29.53
29.38
29.04
29.00
28.58
26.60
MeOOC
COPh
O
17e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

Crystallographic data

(2*Z*,4*E*)-5-(mesityloxy)penta-2,4-dienoic acid (2a) CDCC 878396



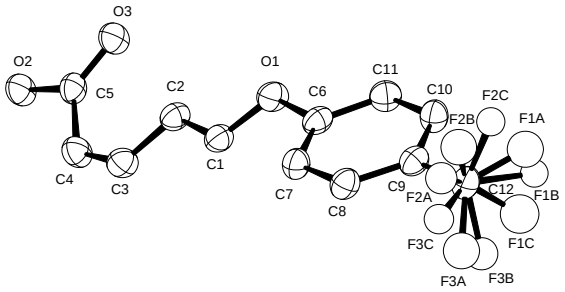
Crystal structure analysis of **2a** crystallized from acetone.

Crystal data and structure refinement.

Identification code	7417	
Empirical formula	$C_{14}H_{16}O_3$	
Color	colourless	
Formula weight	232.27 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	**P$\bar{1}$, (no. 2)**	
Unit cell dimensions	a = 8.2022(9) Å	α= 90.033(2)°.
	b = 11.0487(12) Å	β= 94.313(2)°.
	c = 28.058(3) Å	γ = 99.031(2)°.
Volume	2503.9(5) Å^3	
Z	8	
Density (calculated)	1.232 Mg · m^{-3}	
Absorption coefficient	0.086 mm^{-1}	
F(000)	992 e	
Crystal size	0.18 x 0.08 x 0.08 mm^3	
θ range for data collection	1.46 to 34.65°.	
Index ranges	$-13 \le h \le 13$, $-17 \le k \le 17$, $-44 \le l \le 44$	
Reflections collected	90815	
Independent reflections	21317 [R_{int} = 0.0561]	
Reflections with I>2σ(I)	13153	
Completeness to θ = 27.50°	100.0 %	
Absorption correction	Gaussian	

Max. and min. transmission	1.00 and 0.997	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21317 / 0 / 629	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2σ(I)]	R_1 = 0.0529	wR^2 = 0.1261
R indices (all data)	R_1 = 0.1024	wR^2 = 0.1485
Largest diff. peak and hole	0.457 and -0.266 e · $Å^{-3}$	

(2*Z*,4*E*)-5-(4-(trifluoromethyl)phenoxy)penta-2,4-dienoic acid (2b) CDCC 878394



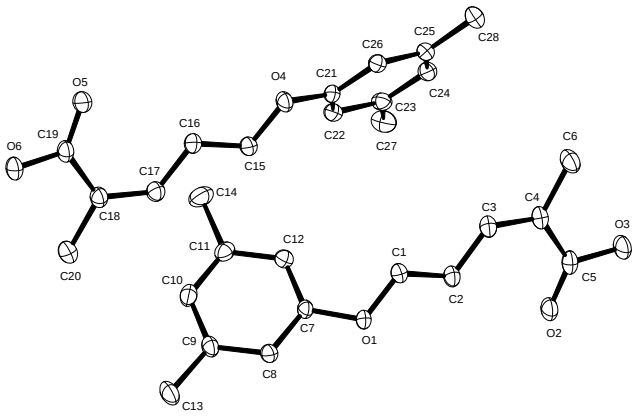
Crystal structure analysis of **2b** crystallized from acetone.

Crystal data and structure refinement.

Identification code	7364	
Empirical formula	$C_{12} H_9 F_3 O_3$	
Color	colourless	
Formula weight	258.19 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	1.54184 Å	
Crystal system	MONOCLINIC	
Space group	$P2_1/c$, (no. 14)	
Unit cell dimensions	a = 7.8605(3) Å	α= 90°.
	b = 13.6495(5) Å	β= 91.990(2)°.
	c = 10.5353(4) Å	γ = 90°.
Volume	1129.67(7) $Å^3$	
Z	4	
Density (calculated)	1.518 $Mg \cdot m^{-3}$	
Absorption coefficient	1.236 mm^{-1}	
F(000)	528 e	
Crystal size	0.28 x 0.09 x 0.08 mm^3	
θ range for data collection	5.31 to 67.10°.	
Index ranges	$-9 \leq h \leq 9$, $-15 \leq k \leq 16$, $-12 \leq l \leq 12$	
Reflections collected	24991	
Independent reflections	2000 [R_{int} = 0.0450]	
Reflections with $I>2\sigma(I)$	1793	
Completeness to θ = 67.10°	98.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.91 and 0.77	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	2000 / 0 / 174	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2σ(I)]	R_1 = 0.0641	wR^2 = 0.1453
R indices (all data)	R_1 = 0.0698	wR^2 = 0.1493
Extinction coefficient	0.0015(4)	
Largest diff. peak and hole	0.661 and -0.492 e · $Å^{-3}$	

(2*Z*,4*E*)-5-(3,5-dimethylphenoxy)-2-methylpenta-2,4-dienoic acid (2i) CDCC 878398



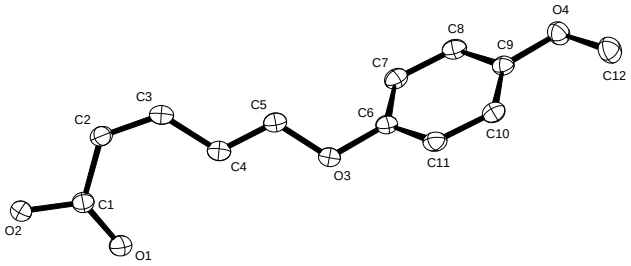
Crystal structure analysis of **2i** crystallized from acetone.

Crystal data and structure refinement.

Identification code	7401	
Empirical formula	$C_{13}H_{14}O_4$	
Color	colourless	
Formula weight	234.24 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 14.1580(12) Å	α= 90°.
	b = 10.4838(5) Å	β= 105.598(7)°.
	c = 8.1386(7) Å	γ = 90°.
Volume	1163.52(15) Å^3	
Z	4	
Density (calculated)	1.337 Mg · m^{-3}	
Absorption coefficient	0.099 mm^{-1}	
F(000)	496 e	
Crystal size	0.46 x 0.33 x 0.16 mm^3	
θ range for data collection	2.99 to 37.00°.	
Index ranges	$-23 \le h \le 23$, $-17 \le k \le 17$, $-13 \le l \le 13$	
Reflections collected	45164	
Independent reflections	5898 [R_{int} = 0.0489]	
Reflections with I>2σ(I)	4669	
Completeness to θ = 27.50°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98 and 0.95	

Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5898 / 0 / 157	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2σ(I)]	R_1 = 0.0427	wR^2 = 0.1086
R indices (all data)	R_1 = 0.0603	wR^2 = 0.1193
Largest diff. peak and hole	0.643 and -0.260 e · $Å^{-3}$	

(2*Z*,4*E*)-5-(4-methoxyphenoxy)penta-2,4-dienoic acid (2j) CDCC 878395



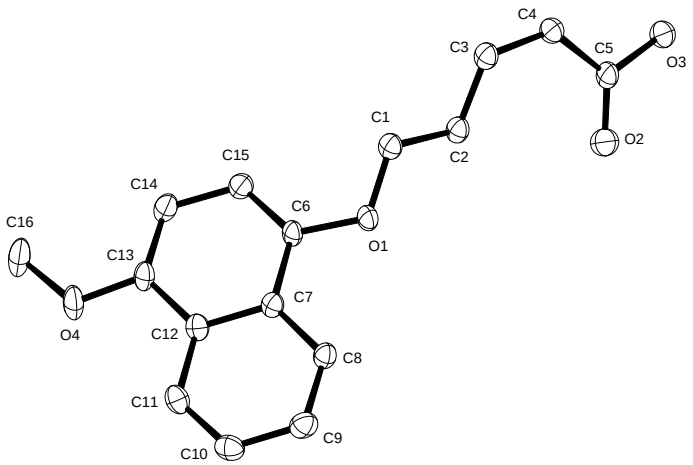
Crystal structure analysis of **2j** crystallized from acetone.

Crystal data and structure refinement.

Identification code	7373	
Empirical formula	$C_{12}H_{12}O_4$	
Color	colourless	
Formula weight	220.22 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	ORTHORHOMBIC	
Space group	**Pbcn, (no. 60)**	
Unit cell dimensions	a = 29.196(7) Å	α= 90°.
	b = 9.3405(15) Å	β= 90°.
	c = 7.9764(14) Å	γ = 90°.
Volume	2175.2(7) Å^3	
Z	8	
Density (calculated)	1.345 Mg · m^{-3}	
Absorption coefficient	0.101 mm^{-1}	
F(000)	928 e	
Crystal size	0.3 x 0.19 x 0.14 mm^3	
θ range for data collection	2.79 to 32.11°.	
Index ranges	$-43 \le h \le 43$, $-13 \le k \le 13$, $-11 \le l \le 11$	
Reflections collected	43914	
Independent reflections	3802 [R_{int} = 0.0611]	
Reflections with I>2σ(I)	2626	
Completeness to θ = 31.00°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.991 and 0.98	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	3802 / 0 / 147	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2σ(I)]	R_1 = 0.0455	wR^2 = 0.0999
R indices (all data)	R_1 = 0.0794	wR^2 = 0.1159
Largest diff. peak and hole	0.290 and -0.265 e · $Å^{-3}$	

(2*Z*,4*E*)-5-((4-methoxynaphthalen-1-yl)oxy)penta-2,4-dienoic acid (2q) CDCC 878397



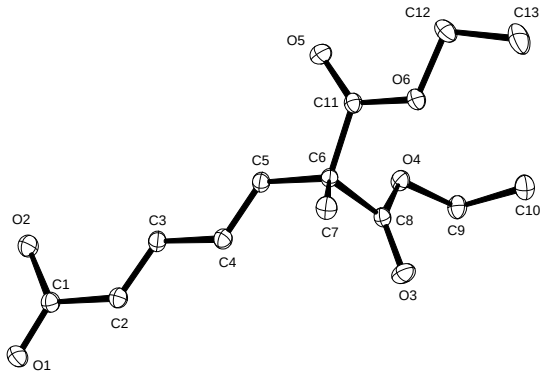
Crystal structure analysis of **2q** crystallized from acetone.

Crystal data and structure refinement.

Identification code	7418	
Empirical formula	$C_{16}H_{14}O_4$	
Color	colourless	
Formula weight	270.27 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/n$, (no. 14)**	
Unit cell dimensions	a = 8.6390(18) Å	α= 90°.
	b = 4.8905(13) Å	β= 96.394(18)°.
	c = 31.875(8) Å	γ = 90°.
Volume	1338.3(6) Å^3	
Z	4	
Density (calculated)	1.341 Mg · m^{-3}	
Absorption coefficient	0.096 mm^{-1}	
F(000)	568 e	
Crystal size	0.66 x 0.13 x 0.06 mm^3	
θ range for data collection	2.89 to 31.75°.	
Index ranges	$-12 \le h \le 12$, $-7 \le k \le 4$, $-41 \le l \le 46$	
Reflections collected	10747	
Independent reflections	4178 [R_{int} = 0.0439]	
Reflections with I>2σ(I)	2799	
Completeness to θ = 27.50°	98.7 %	
Absorption correction	Gaussian	

Max. and min. transmission	0.99 and 0.98	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4178 / 0 / 183	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2σ(I)]	R_1 = 0.0659	wR^2 = 0.1589
R indices (all data)	R_1 = 0.1048	wR^2 = 0.1830
Largest diff. peak and hole	0.411 and -0.366 e · $Å^{-3}$	

(2*E*,4*E*)-7-ethoxy-6-(ethoxycarbonyl)-6-methyl-7-oxohepta-2,4-dienoic acid ((*E*,*E*)-5)



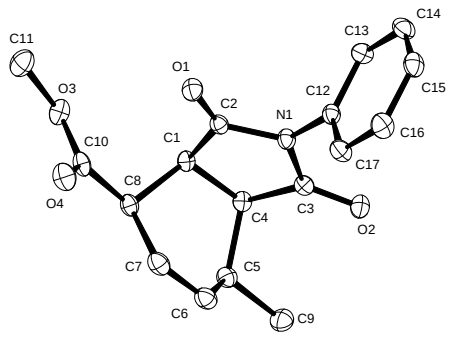
Crystal structure analysis of **(*E*,*E*)-5** crystallized from DCM/Heptane.

Crystal data and structure refinement.

Identification code	7505	
Empirical formula	$C_{13}H_{18}O_6$	
Color	colourless	
Formula weight	270.27 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 12.1829(16) Å	α= 90°.
	b = 9.3750(12) Å	β= 91.501(2)°.
	c = 12.2675(16) Å	γ = 90°.
Volume	1400.6(3) Å^3	
Z	4	
Density (calculated)	1.282 Mg · m^{-3}	
Absorption coefficient	0.102 mm^{-1}	
F(000)	576 e	
Crystal size	0.30 x 0.19 x 0.02 mm^3	
θ range for data collection	1.67 to 30.55°.	
Index ranges	$-17 \le h \le 17$, $-13 \le k \le 13$, $-17 \le l \le 17$	
Reflections collected	38377	
Independent reflections	4280 [R_{int} = 0.0354]	
Reflections with I>2σ(I)	3667	
Completeness to θ = 27.50°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.00 and 0.97	

Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4280 / 0 / 176	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2σ(I)]	R_1 = 0.0347	wR^2 = 0.0951
R indices (all data)	R_1 = 0.0424	wR^2 = 0.1014
Largest diff. peak and hole	0.470 and -0.182 e · $Å^{-3}$	

(**A) CDCC 866301**



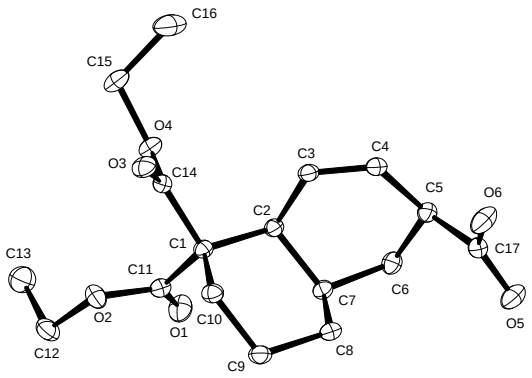
Crystal structure analysis of **A** crystallized from DCM/Heptane.

Crystal data and structure refinement.

Identification code	7585	
Empirical formula	$C_{17}H_{17}NO_4$	
Color	colorless	
Formula weight	299.32 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 9.845(2) Å	α= 90°.
	b = 15.130(4) Å	β= 95.633(4)°.
	c = 9.818(2) Å	γ = 90°.
Volume	1455.4(6) Å^3	
Z	4	
Density (calculated)	1.366 Mg · m^{-3}	
Absorption coefficient	0.098 mm^{-1}	
F(000)	632 e	
Crystal size	0.25 x 0.08 x 0.06 mm^3	
θ range for data collection	2.08 to 30.51°.	
Index ranges	$-14 \leq h \leq 14$, $-21 \leq k \leq 21$, $-14 \leq l \leq 14$	
Reflections collected	39991	
Independent reflections	4431 [R_{int} = 0.0796]	
Reflections with I>2σ(I)	4027	
Completeness to θ = 27.50°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.00 and 0.89	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4431 / 0 / 201	
Goodness-of-fit on F^2	1.131	

Final R indices [I>2σ(I)]	R_1 = 0.0434	wR^2 = 0.1068
R indices (all data)	R_1 = 0.0471	wR^2 = 0.1096
Largest diff. peak and hole	0.415 and -0.236 e · $Å^{-3}$	

Cycloadduct 13b CDCC 866302



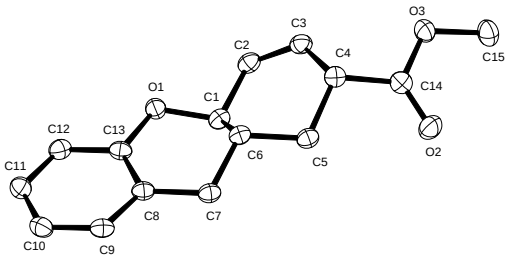
Crystal structure analysis of **13b** crystallized from DCM/Heptane.

Crystal data and structure refinement.

Identification code	7633	
Empirical formula	$C_{17}H_{24}O_6$	
Color	colourless	
Formula weight	324.36 g · mol^{-1}	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	**P$\bar{1}$, (no. 2)**	
Unit cell dimensions	a = 8.269(2) Å	α= 100.932(4)°.
	b = 10.113(3) Å	β= 101.789(4)°.
	c = 10.652(3) Å	γ = 100.590(4)°.
Volume	832.9(4) Å^3	
Z	2	
Density (calculated)	1.293 Mg · m^{-3}	
Absorption coefficient	0.097 mm^{-1}	
F(000)	348 e	
Crystal size	0.30 x 0.14 x 0.08 mm^3	
θ range for data collection	2.01 to 30.51°.	
Index ranges	$-11 \leq h \leq 11$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$	
Reflections collected	23194	
Independent reflections	5081 [R_{int} = 0.0337]	
Reflections with I>2σ(I)	4242	
Completeness to θ = 27.50°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.98	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	5081 / 0 / 211	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2σ(I)]	R_1 = 0.0370	wR^2 = 0.0942
R indices (all data)	R_1 = 0.0470	wR^2 = 0.1003
Largest diff. peak and hole	0.405 and -0.190 e · $Å^{-3}$	

Cycloadduct 17a CDCC 887606



Crystal structure analysis of **17a** crystallized from DCM/Heptane.

Crystal data and structure refinement.

Identification code	7640	
Empirical formula	$C_{15}H_{16}O_3$	
Color	colorless	
Formula weight	244.28 g · mol^{-1}	
Temperature	100 K	
Wavelength	1.54184 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1/c$, (no. 14)**	
Unit cell dimensions	a = 10.2678(4) Å	α= 90°.
	b = 13.6678(5) Å	β= 103.345(2)°.
	c = 8.7688(3) Å	γ = 90°.
Volume	1197.37(8) Å^3	
Z	4	
Density (calculated)	1.355 Mg · m^{-3}	
Absorption coefficient	0.759 mm^{-1}	
F(000)	520 e	
Crystal size	0.254 x 0.252 x 0.187 mm^3	
θ range for data collection	4.43 to 62.38°.	
Index ranges	$-11 \leq h \leq 11$, $-15 \leq k \leq 15$, $-10 \leq l \leq 10$	
Reflections collected	25643	
Independent reflections	1893 [R_{int} = 0.0461]	
Reflections with $I>2\sigma(I)$	1779	
Completeness to θ = 62.38°	99.4 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.32 and 0.14	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	1893 / 0 / 164	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2σ(I)]	R_1 = 0.0327	wR^2 = 0.0873
R indices (all data)	R_1 = 0.0345	wR^2 = 0.0887
Largest diff. peak and hole	0.200 and -0.172 e · $Å^{-3}$	