Supporting Information

Intermolecular C-O Addition of Carboxylic Acids to Arynes

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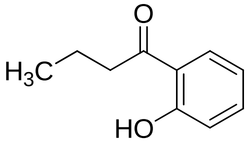
General Information. The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz or 400 and 100 MHz respectively. Thin layer chromatography was performed using 60 mesh silica gel plates, and visualization was effected by short wavelength UV light (254 nm). All melting points are uncorrected. All high resolution mass spectra (except for compound **25**) were recorded using EI at 70 eV. All reagents were used directly as obtained commercially, unless otherwise noted.

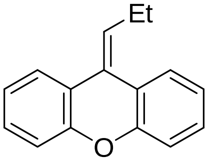
Procedure for the reaction of carboxylic acids with arynes.
The aryne precursor (1.5 equiv) was added to a mixture of the carboxylic acid (0.25 mmol) and CsF (4.0 equiv) in 15 mL of freshly distilled THF, and the reaction mixture was then stirred in a closed vial at 125 ºC for 18 h. After the reaction mixture was allowed to cool to room temperature, it was eluted through a plug of silica gel with ethyl acetate and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/EtOAc as the eluent to afford the desired *o*-hydroxyaryl ketone.

1-(2-Hydroxyphenyl)-1-butanone (8)



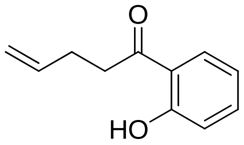
This compound was obtained as a pale yellow oil in a 77% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (t, J = 7.4 Hz, 3H), 1.72-1.82 (m, 2H), 2.95 (t, J = 7.3 Hz, 2H), 6.88 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 12.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 18.2, 40.4, 118.7, 119.0, 119.6, 130.2, 136.4, 162.7, 207.0; HRMS (EI) calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0839. The ^{1}H NMR spectral data are in good agreement with the literature data.[1]

9-Propylidene-9*H*-xanthene (11)



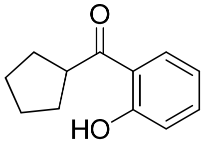
This compound was obtained as a pale amorphous solid in a 50% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (t, J = 7.4 Hz, 3H), 2.56 (m, 2H), 5.87 (t, J = 7.2 Hz, 1H), 7.07-7.18 (m, 4H), 7.21-7.32 (m, 2H), 7.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 23.4, 116.6, 116.8, 122.8, 123.1, 123.6, 123.9, 125.9, 126.1, 128.1, 128.2, 128.6, 128.9, 151.5, 153.1; HRMS (EI) calcd for $C_{16}H_{14}O$ 222.1045, found 222.1048.

1-(2-Hydroxyphenyl)-4-penten-1-one (19)



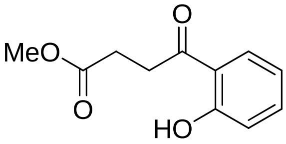
This compound was obtained as a pale yellow oil in a 72% yield: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 2.43-2.52 (m, 2H), 3.09 (t, *J* = 7.4 Hz, 2H), 5.02 (dd, *J* = 17.1, 1.3 Hz, 1H), 5.09 (dd, *J* = 10.2, <1 Hz, 1H), 5.82-5.94 (m, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 12.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 28.3, 37.6, 115.9, 118.7, 119.1, 119.5, 130.0, 136.5, 137.0, 162.6, 205.8; HRMS (EI) calcd for $C_{11}H_{12}O_2$ 176.0837, found 176.0840. The ^{1}H NMR spectral data are in good agreement with the literature data.[1]

Cyclopentyl(2-hydroxyphenyl)methanone (20)



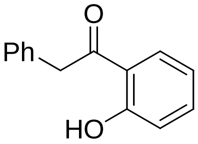
This compound was obtained as a pale yellow oil in a 68% yield: ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 1.66-1.74 (m, 4H), 1.89-1.96 (m, 4H), 3.73 (m, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.0 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 12.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 26.5, 30.5, 46.2, 118.7, 118.9, 119.2, 130.4, 136.2, 163.1, 209.4; HRMS (EI) calcd for $C_{12}H_{14}O_2$ 190.0994, found 190.0993.

Methyl 4-(2-hydroxyphenyl)-4-oxobutanoate (21)



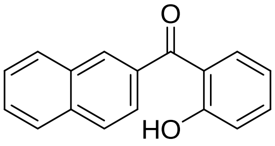
This compound was obtained as a pale yellow semisolid in a 58% yield: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 2.74 (t, *J* = 7.4 Hz, 2H), 3.36 (t, *J* = 7.4 Hz, 2H), 3.70 (s, 3H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 7.46 (t, *J* = 7.1 Hz, 1H), 7.78 (d, *J* = 7.1 Hz, 1H), 12.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 27.9, 33.3, 52.2, 118.7, 119.2, 119.4, 129.9, 136.7, 162.5, 173.2, 204.1; HRMS (EI) calcd for $C_{11}H_{12}O_4$ 208.0736, found 208.0740.

1-(2-Hydroxyphenyl)-2-phenylethanone (22)



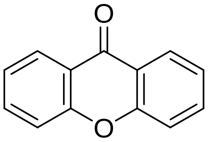
This compound was obtained as a pale yellow oil in a 62% yield: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 4.31 (s, 2H), 6.91 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 7.26-7.30 (m, 3H), 7.34-7.37 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 12.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 45.4, 118.9, 119.2, 127.4, 129.0, 129.6, 130.6, 134.1, 136.8, 163.0, 204.1; HRMS (EI) calcd for $C_{14}H_{12}O_2$ 212.0837, found 212.0842. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[2]

(2-Hydroxyphenyl)-2-naphthyl ketone (23)



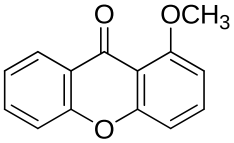
This compound was obtained as a pale yellow semisolid in a 44% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.49-7.64 (m, 3H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.90-7.97 (m, 3H), 8.17 (s, 1H), 12.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.7, 118.9, 119.6, 125.5, 127.2, 128.1, 128.4, 128.6, 129.4, 130.7, 132.4, 133.9, 135.1, 135.3, 136.5, 163.4, 201.7; HRMS (EI) calcd for $C_{17}H_{12}O_2$ 248.0837, found 248.0834. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[3]

Xanthone (24)



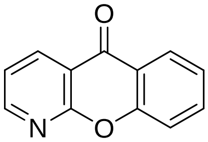
This compound was obtained as white crystals in an 80% yield: mp 176-177 ºC (lit. mp[4] 176-177 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 8.31 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.1, 122.0, 124.1, 126.9, 135.0, 156.3, 177.4; HRMS (EI) calcd for $C_{13}H_8O_2$ 196.0524, found 196.0527. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[4]

1-Methoxyxanthone (25)



This compound was obtained as white crystals in a 71% yield: mp 128-129 ºC (lit. mp[5] 128.5 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (s, 3H), 6.78 (d, *J* = 8.3 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.58 (t, *J* = 8.4 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 8.29 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.7, 105.6, 110.2, 112.8, 117.5, 123.2, 124.0, 127.0, 134.4, 135.1, 155.2, 158.3, 160.9, 176.7; APCI calcd for $C_{14}H_{11}O_3$ [M+H] 227.0703, found 227.0705. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[6]

4-Azaxanthone (26)

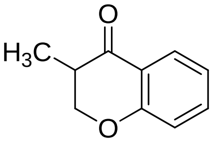


This compound was obtained as a light brown solid in a 22% yield: mp 177-181 ºC (lit. mp[7] 178-182 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.48 (m, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 8.31 (t, *J* = 7.9 Hz, 1H), 8.72 (t, *J* = 7.7 Hz, 1H), 8.75 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.0, 118.7, 121.3, 121.7, 124.9, 126.9, 135.9, 137.6, 154.4, 155.9, 160.5, 177.8; HRMS (EI) calcd for $C_{12}H_7NO_2$ 197.0477, found 197.0479. The ^{1}H NMR spectral data are in good agreement with the literature data.[8]

General procedure for the reaction of 2-alkenoic acids with arynes.

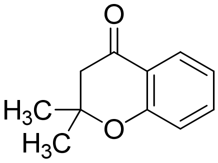
The aryne precursor (1.5 equiv) was added to a mixture of the 2-alkenoic acid (0.25 mmol) and CsF (4.0 equiv) in 15 mL of freshly distilled THF, and the reaction mixture was then stirred in a closed vial at 125 ºC for 18 h. After allowing the reaction mixture to cool, additional aryne precursor (0.5 equiv) and CsF (1.0 equiv) was quickly added and the heating was continued at 125 ºC for 6 h. After the reaction mixture was allowed to cool to room temperature, it was eluted through a plug of silica gel with ethyl acetate and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/EtOAc as the eluent to afford the desired 4-chromanones.

3-Methylchroman-4-one (37)



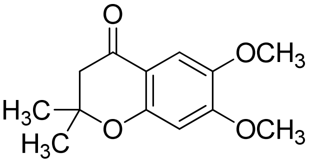
This compound was obtained as a colorless oil in an 84% yield: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.20 (d, J = 7.0 Hz, 3H), 2.75-2.95 (m, 1H), 4.13 (t, J = 11.1 Hz, 1H), 4.48 (dd, J = 11.3, 5.0 Hz, 1H), 6.94 (d, J = 8.3 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 10.9, 41.0, 72.4, 117.9, 120.8, 121.5, 127.6, 135.9, 161.9, 195.0; HRMS (EI) calcd for $C_{10}H_{10}O_2$ 162.0681, found 162.0683. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[9]

2,2-Dimethylchroman-4-one (38)



This compound was obtained as white crystals in a 77% yield: mp 87-89 ºC (lit. mp[10] 86-88 ºC); ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.44 (s, 6H), 2.70 (s, 2H), 6.90 (d, J = 8.3 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 26.8, 49.1, 79.4, 118.5, 120.4, 120.9, 126.7, 136.3, 160.1, 192.8; HRMS (EI) calcd for $C_{11}H_{12}O_2$ 176.0837, found 176.0833. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[11]

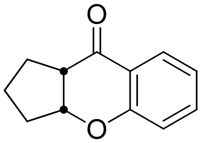
6,7-Dimethoxy-2,2-dimethylchroman-4-one (39)



This compound was obtained as a pale yellow solid in a 53% yield: mp 97-100 ºC (lit. mp[12] 98-100 ºC); ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.42 (s, 6H), 2.63 (s, 2H), 3.84 (s, 3H), 3.87 (s, 3H), 6.37 (s, 1H), 7.23 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 26.8, 48.6, 56.4, 56.4, 79.8, 100.7, 106.5, 112.5, 144.2, 156.5, 156.5, 191.2; HRMS (EI) calcd for

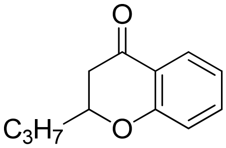
$C_{13}H_{16}O_4$ 236.1049, found 236.1048. The ^{13}C NMR spectral data are in good agreement with the literature data.[13]

cis-2,3,3a,9a-Tetrahydrocyclopenta[*b*][1]benzopyran-9(1*H*)-one (40)



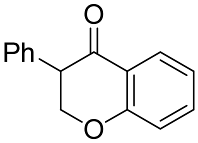
This compound was obtained as a pale yellow solid in a 68% yield: mp 48-49 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 1.75-2.20 (m, 6H), 2.66-2.74 (m, 1H), 4.91 (s, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6, 27.8, 33.2, 51.3, 83.5, 118.2, 119.3, 121.4, 127.2, 136.2, 160.8, 194.7; HRMS (EI) calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0841. The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[14]

2-Propylchroman-4-one (41)



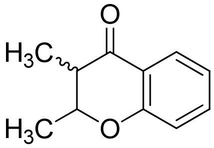
This compound was obtained as a pale yellow oil in an 82% yield: ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.3 Hz, 3H), 1.42-1.73 (m, 3H), 1.78-1.96 (m, 1H), 2.66 (d, *J* = 8.2 Hz, 2H), 4.39-4.47 (m, 1H), 6.93-7.05 (m, 2H), 7.44 (td, *J* = 8.9, 1.8 Hz, 1H), 7.85 (dd, *J* = 7.8, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 18.4, 37.2, 43.2, 77.9, 118.1, 121.2, 121.3, 127.1, 136.1, 161.9, 192.9; HRMS (EI) calcd for $C_{12}H_{14}O_2$ 190.0994, found 190.0992.

Isoflavanone (42)



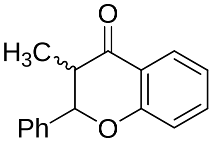
This compound was obtained as a yellow solid in a 56% yield: mp 67-70 ºC (lit. mp[15] 72 ºC); ^1H NMR (400 MHz, $CDCl_3$) δ 4.01 (t, *J* = 7.2 Hz, 1H), 4.67-4.69 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 7.26-7.39 (m, 5H), 7.51 (td, *J* = 6.8, 2.0 Hz, 1H), 7.97 (dd, *J* = 7.9, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.5, 71.7, 118.1, 121.3, 121.8, 128.0, 128.8, 129.1, 135.2, 136.2, 161.8, 192.3; HRMS (EI) calcd for $C_{15}H_{12}O_2$ 224.0837, found 224.0844. The ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[16]

2,3-Dimethylchroman-4-one (43)



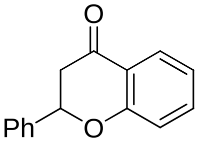
This compound was obtained in a 76% yield as a mixture of isomers (*E/Z* = 1.8). The *E* isomer was further purified and isolated as a colorless semisolid solid using flash chromatography (hexanes/EtOAc): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, J = 7.4 Hz, 3H), 1.50 (t, J = 7.4 Hz, 3H), 2.51-2.60 (m, 1H), 4.19-4.27 (m, 1H), 6.93 (d, J = 8.3 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 7.44 (td, J = 7.6, 1.6 Hz, 1H), 7.85 (td, J = 7.8, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.5, 20.0, 47.1, 79.4, 117.9, 120.5, 121.3, 127.4, 135.9, 161.4, 194.9; HRMS (EI) calcd for $C_{11}H_{12}O_2$ 176.0837, found 176.0841.

3-Methyl-2-phenylchroman-4-one (44)



This compound was obtained in a 67% yield as a mixture of isomers (*E/Z* = ~5.1). The *E* isomer was further purified and isolated as a pale yellow solid using flash chromatography (hexanes/EtOAc): mp 68-70 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (d, J = 6.9 Hz, 3H), 2.99-3.08 (m, 1H), 5.06 (d, J = 12.4 Hz, 1H), 7.00 (d, J = 8.3 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 7.38-7.52 (m, 6H), 7.94 (t, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.5, 46.6, 85.9, 115.6, 118.1, 120.6, 121.7, 127.5, 127.6, 129.0, 136.1, 138.2, 161.5, 194.6; HRMS (EI) calcd for $C_{16}H_{14}O_2$ 238.0994, found 238.0998.

Flavanone (45)

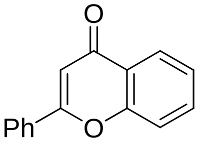


Flash chromatography on silica gel using hexanes/EtOAc as the eluent afforded the desired flavanone as a yellow solid in a 54% yield and a mixture which primarily contained the uncyclized *o*-hydroxyaryl ketone. The latter was dissolved in 5 mL of THF, then 10 mL of water and 10 µL of piperidine was added, and the mixture was stirred for 2 h at 40 ºC. After allowing the reaction mixture to cool to room temperature, the mixture was extracted with EtOAc (20 mL × 2), the organic fractions were combined and the solvent was evaporated under reduced pressure. Flash chromatography on silica gel using hexanes/EtOAc as the eluent afforded an additional 20% of the desired flavanone: mp 69-72 ºC (lit. mp[17] 72-73 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.88 (dd, J = 16.9, 2.9 Hz, 1H), 3.07 (dd, J = 16.9, 13.4 Hz, 1H), 5.46 (dd, J = 13.3, 2.8 Hz, 1H), 7.00-7.08 (m, 2H), 7.35-7.54 (m, 6H), 7.93 (dd, J = 8.0, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.9, 79.8, 118.3, 121.1, 121.8, 126.3, 127.3, 129.0, 129.1, 136.4, 138.9, 161.8, 192.1; HRMS (EI) calcd for $C_{15}H_{12}O_2$ 224.0837, found 224.0842. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[16]

Procedure for the reaction of 2-alkynoic acids with arynes.

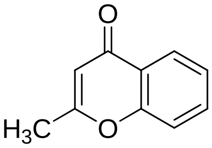
The aryne precursor (1.5 equiv) was added to a mixture of the 2-alkynoic acid (0.25 mmol) and TBAT (2.0 equiv) in 5 mL of anhydrous toluene, and the reaction mixture was then stirred in a closed vial at 60 ºC for 24 h. After the reaction mixture was allowed to cool to room temperature, the reaction mixture was then poured into brine (15 mL) and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (2 x 15 mL) and the organic layers were combined and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel using hexanes/EtOAc as the eluent to afford the desired chromone derivatives.

Flavone (46)



This compound was obtained as a yellow solid in a 56% yield: mp 96-97 ºC (lit. mp[18] 96-97 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.46-7.58 (m, 4H), 7.68 (t, J = 7.0 Hz, 1H), 7.87-7.94 (m, 2H), 8.22 (d, J = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.8, 118.3, 124.2, 125.4, 125.9, 126.5, 129.2, 131.8, 132.0, 134.0, 156.5, 163.6, 178.6; HRMS (EI) calcd for $C_{15}H_{10}O_2$ 222.0681, found 222.0686. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[19]

2-Methylchromone (47)

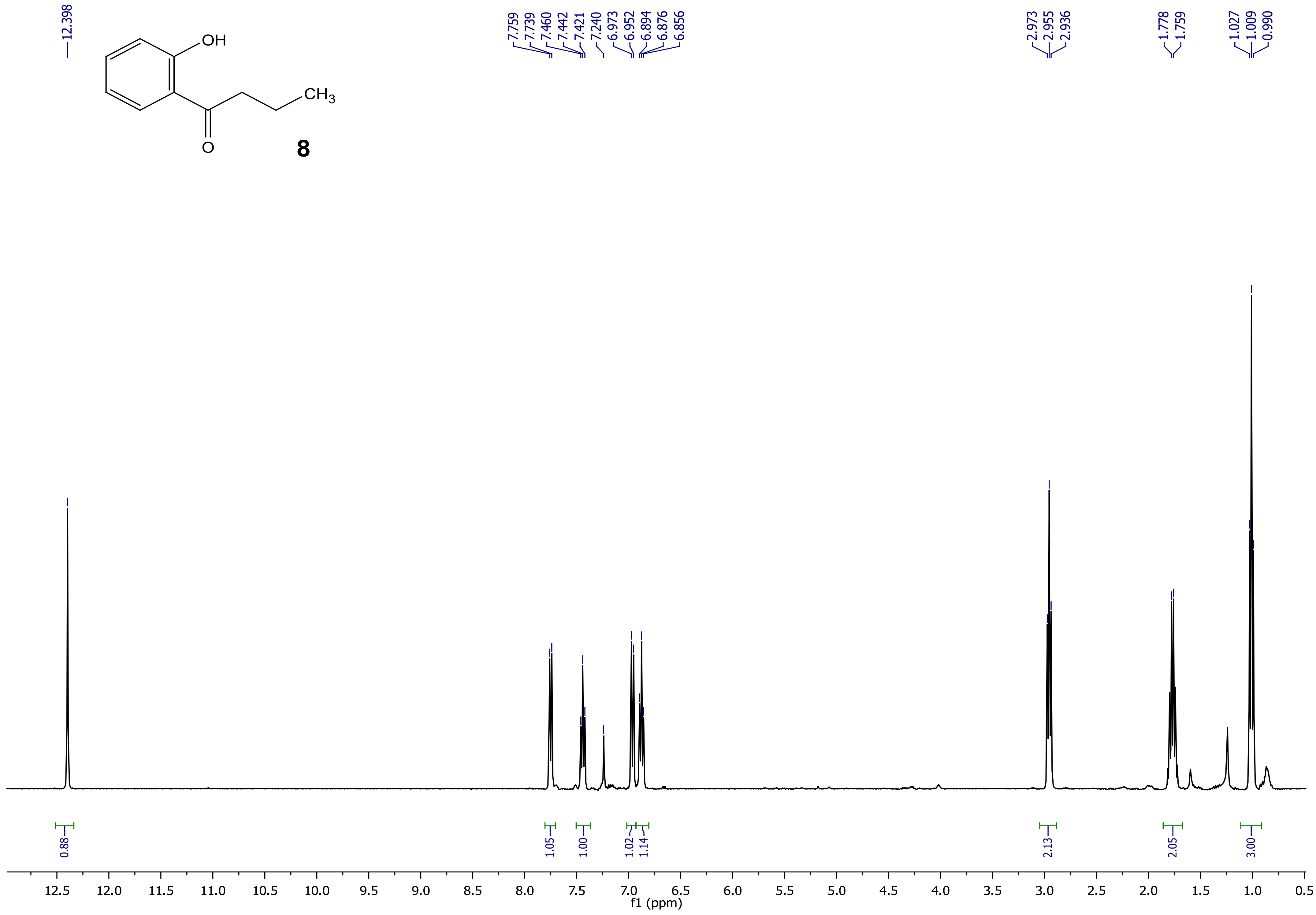


This compound was obtained as a pale yellow solid in a 64% yield: mp 69-71 ºC (lit. mp[20] 69-70 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 6.14 (s, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.38 (d, J = 7.4 Hz, 1H), 7.61 (td, J = 8.1, 1.7 Hz, 1H), 8.15 (dd, J = 7.9, 1.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 110.7, 118.0, 123.7, 125.1, 125.8, 133.6, 156.6, 166.3, 178.4; HRMS (EI) calcd for $C_{10}H_8O_2$ 160.0524, found 160.0548. The ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[21]

References

1. Palmieri, G.; Cimarelli, C. *Tetrahedron* **1998**, *54*, 15711.
2. Park, J. Y.; Ullapu, P. R.; Choo, H.; Lee, J. K.; Min, S.-J.; Pae, A. N.; Kim, Y.; Baek, D.-J.; Cho, Y. S. *Eur. J. Org. Chem.* **2008**, 5461.
3. Sandulache, A.; Silva, A. M. S.; Cavaleiro, J. A. S. *Tetrahedron* **2002**, *58*, 105.
4. Dohi, T. *J. Org. Chem.* **2008**, *73*, 7365.
5. Charlton, J. L.; Sayeed, V. A.; Koh, K.; Lau, W. F.; Lai, H. K.; Bell, A. R. *J. Agric. Food Chem.* **1990**, *38*, 1719.
6. Zhao, Z.; Larock, R. C. *J. Org. Chem.* **2007**, *72*, 583.
7. Villani, F. J. *J. Med. Chem.* **1975**, *18*, 1.
8. Trécourt, F.; Marsais, F.; Güngör, T.; Quéguiner, G. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2409.
9. Hirano, K.; Biju, A. T.; Piel, I.; Glorius, F. *J. Am. Chem. Soc.* **2009**, *131*, 14190.
10. Banerji, A. *Tetrahedron Lett.* **1979**, *38*, 3685.
11. Deagostino, A.; Farina, V.; Prandi, C.; Zavattaro, C.; Venturello, P. *Eur. J. Org. Chem.* **2006**, 3451.
12. Ayoub, M. T. *J. Iraqi Chem. Soc.* **1985**, *10*, 131.

13. Brown, P. E.; Lewis, R. A.; Waring, M. A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2979.
14. Ranu, B. C.; Jana, U. *J. Org. Chem.* **1999**, *64*, 6380.
15. Ferrino, S. A. *Synth. Commun.* **1980**, *10*, 717.
16. Ibrahim, A. R.; Abul-Hajj, Y. J. *J. Nat. Prod.* **1990**, *53*, 644.
17. Litkei, G. *Acta Chim. Hungarica* **1983**, *114*, 47.
18. Jin, C. *J. Chem. Res.* **2009**, *1*, 27.
19. Blaskó, G.; Xun, L.; Cordell, J. A. *J. Nat. Prod.* **1988**, *51*, 60.
20. Hirao, I. *Synthesis* **1984**, 1076.
21. Shaw, A. Y.; Chang, C.-Y.; Liau, H.-H.; Lu, P.-J.; Chen, H.-L.; Yang, C.-N.; Li, H.-Y. *Eur. J. Med. Chem.* **2009**, *44*, 2552.



8

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7.739
7.460
7.442
7.421
7.240
6.973
6.952
6.894
6.876
6.856
2.973
2.955
2.936
1.778
1.759
1.027
1.009
0.990
OH
CH3
O
0.88
1.05
1.00
1.02
1.14
2.13
2.05
3.00
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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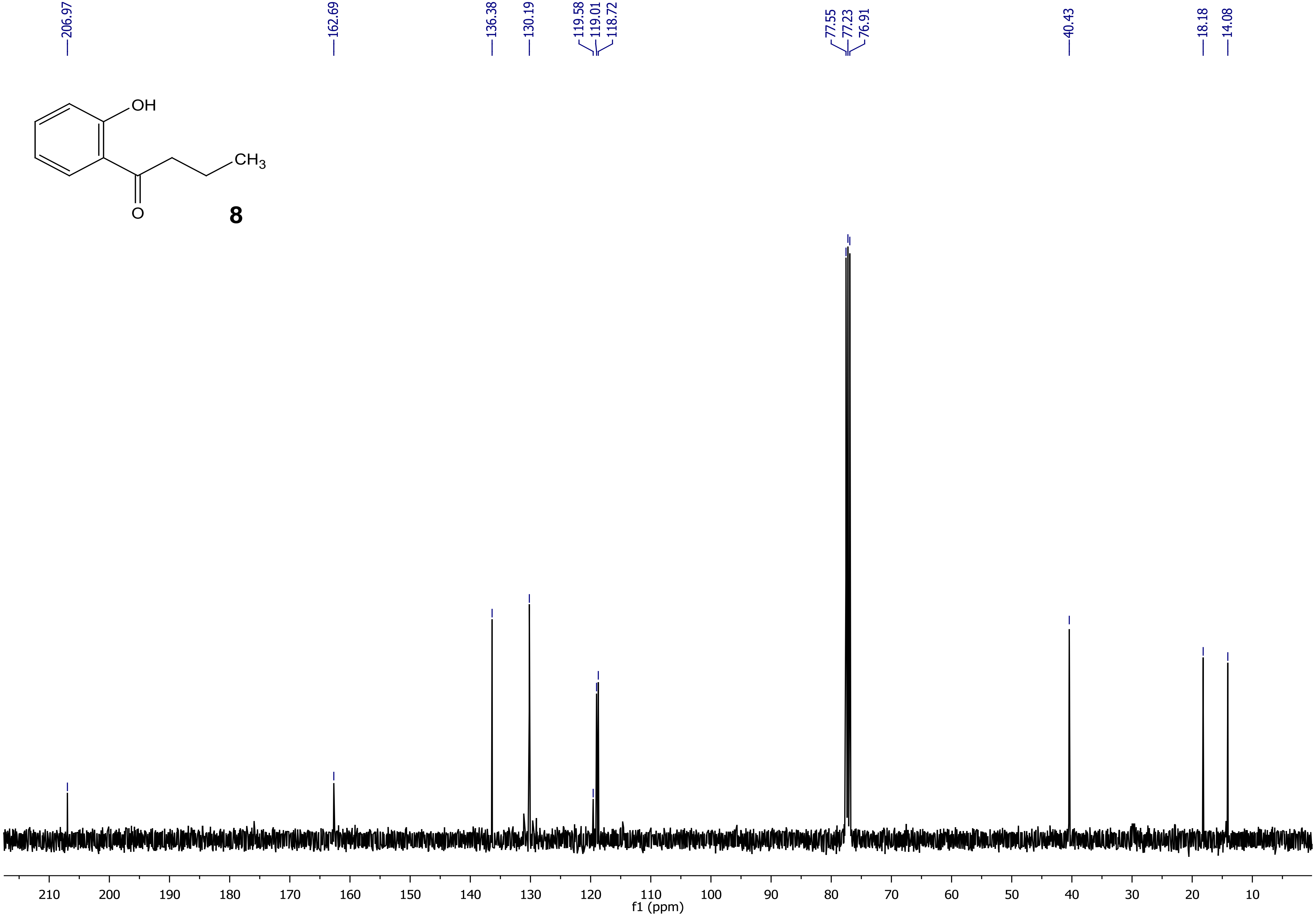
f1 (ppm)



8

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119.58
119.01
118.72
77.55
77.23
76.91
40.43
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14.08
OH
CH3
O
210
200
190
180
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160
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140
130
120
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100
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40
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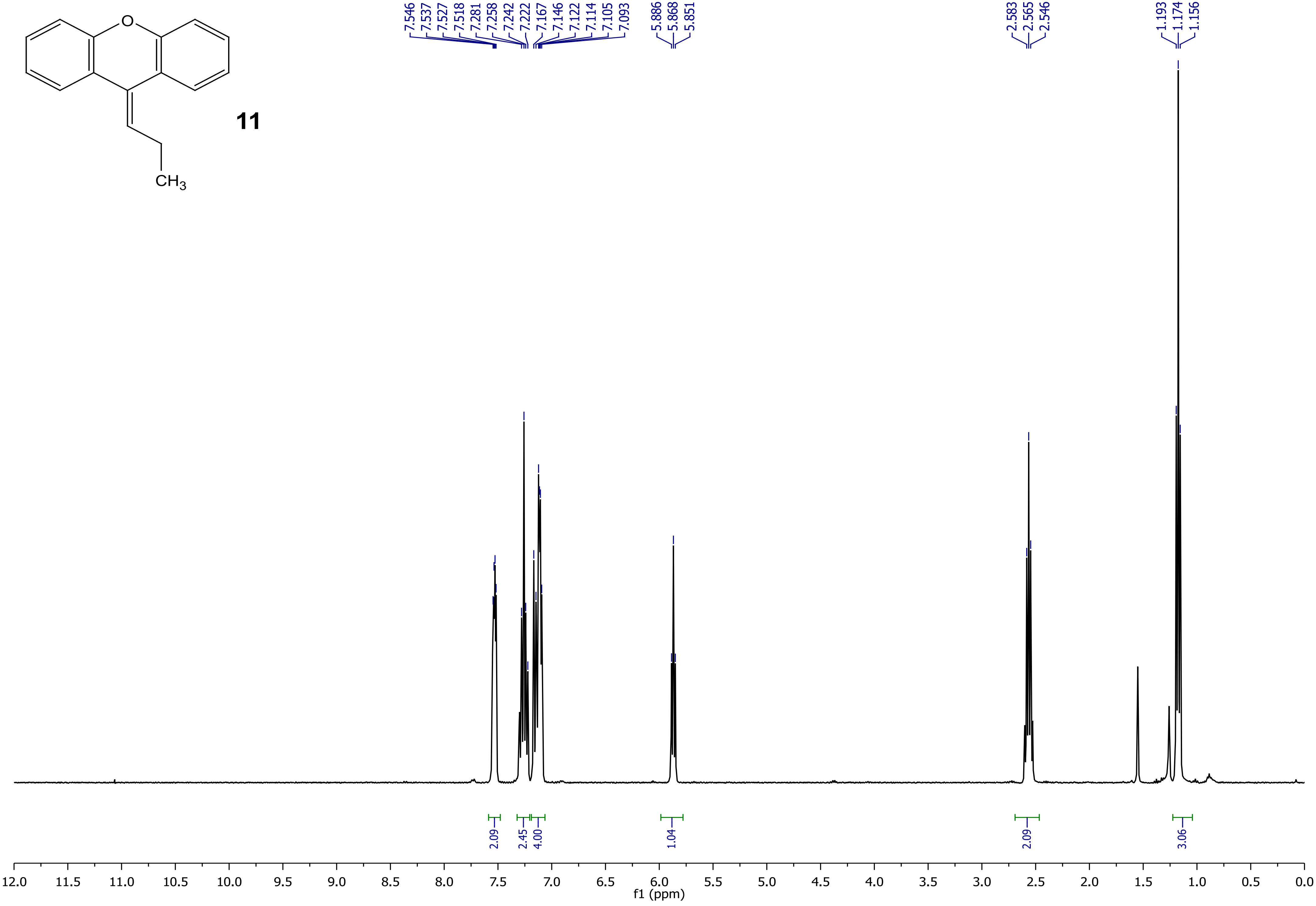
20
10
f1 (ppm)



11

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7.242
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7.114
7.105
7.093
5.886
5.868
5.851
2.583
2.565
2.546
1.193
1.174
1.156
O
CH3
2.09
2.45
4.00
1.04
2.09
3.06
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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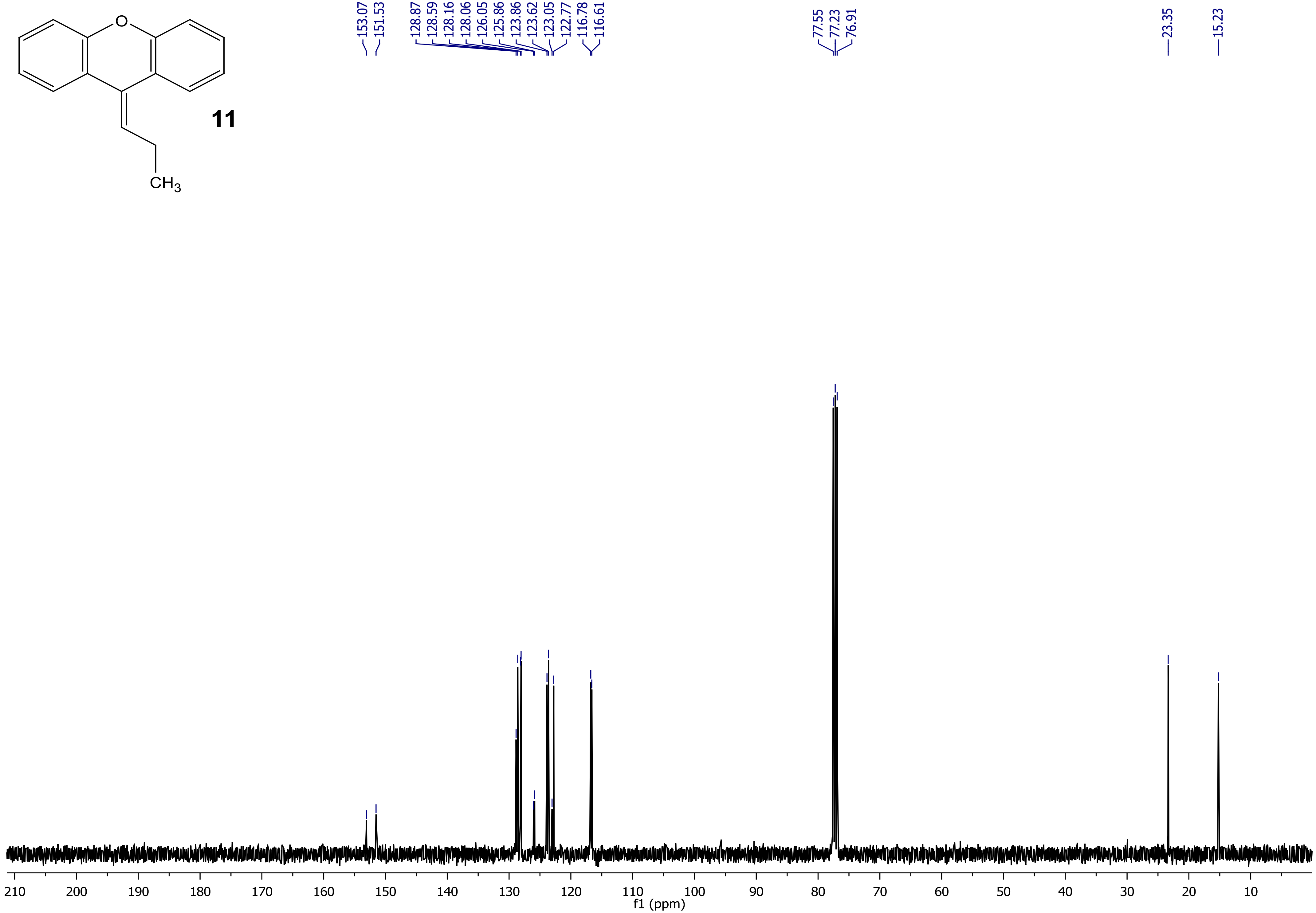
f1 (ppm)


11

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128.16
128.06
126.05
125.86
123.86
123.62
123.05
122.77
116.78
116.61
77.55
77.23
76.91
23.35
15.23
O
CH$_3$
210
200
190
180
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140
130
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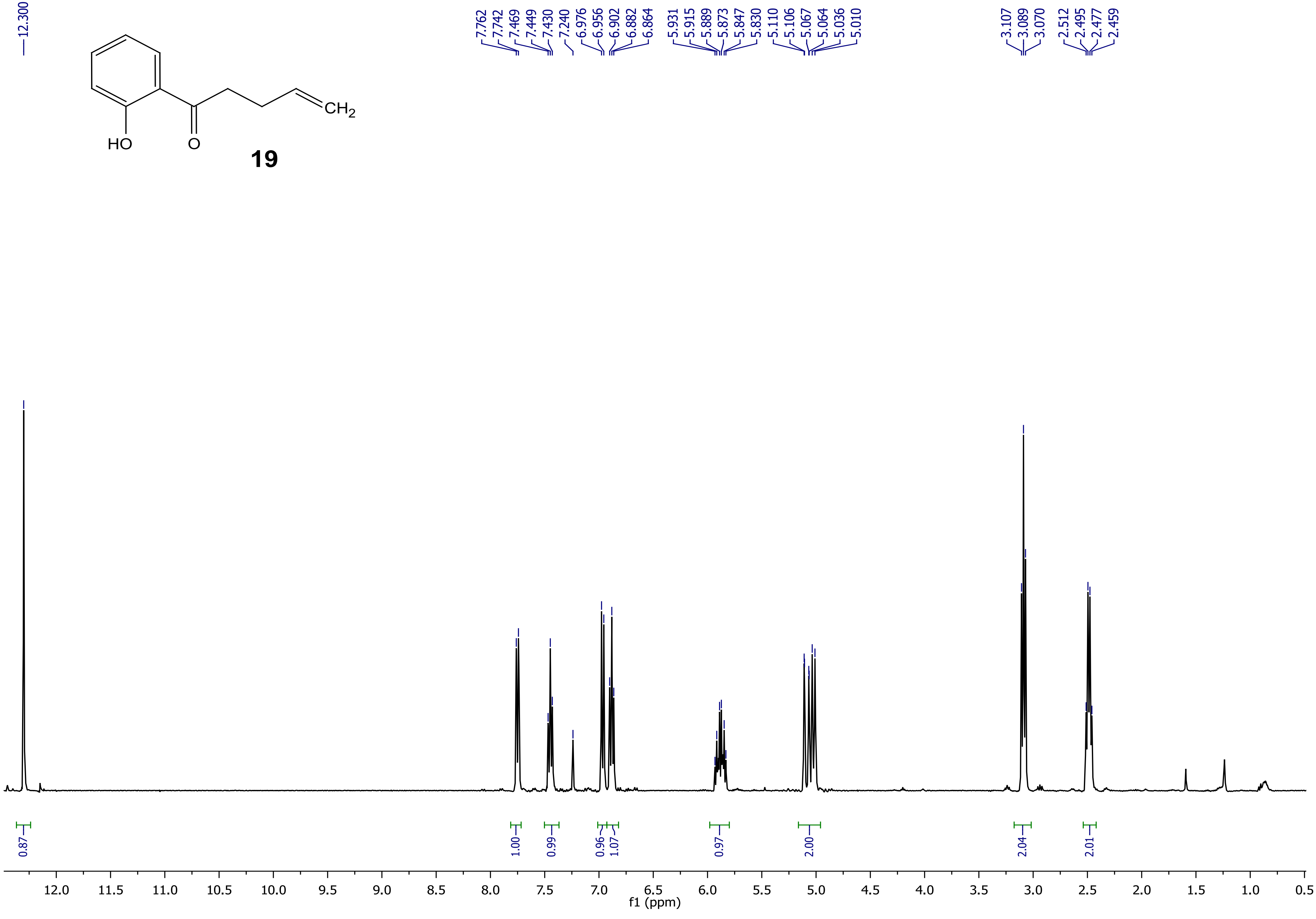
10
f1 (ppm)



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6.864
5.931
5.915
5.889
5.873
5.847
5.830
5.110
5.106
5.067
5.064
5.036
5.010
3.107
3.089
3.070
2.512
2.495
2.477
2.459
HO
O
CH2
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0.99
0.96
1.07
0.97
2.00
2.04
2.01
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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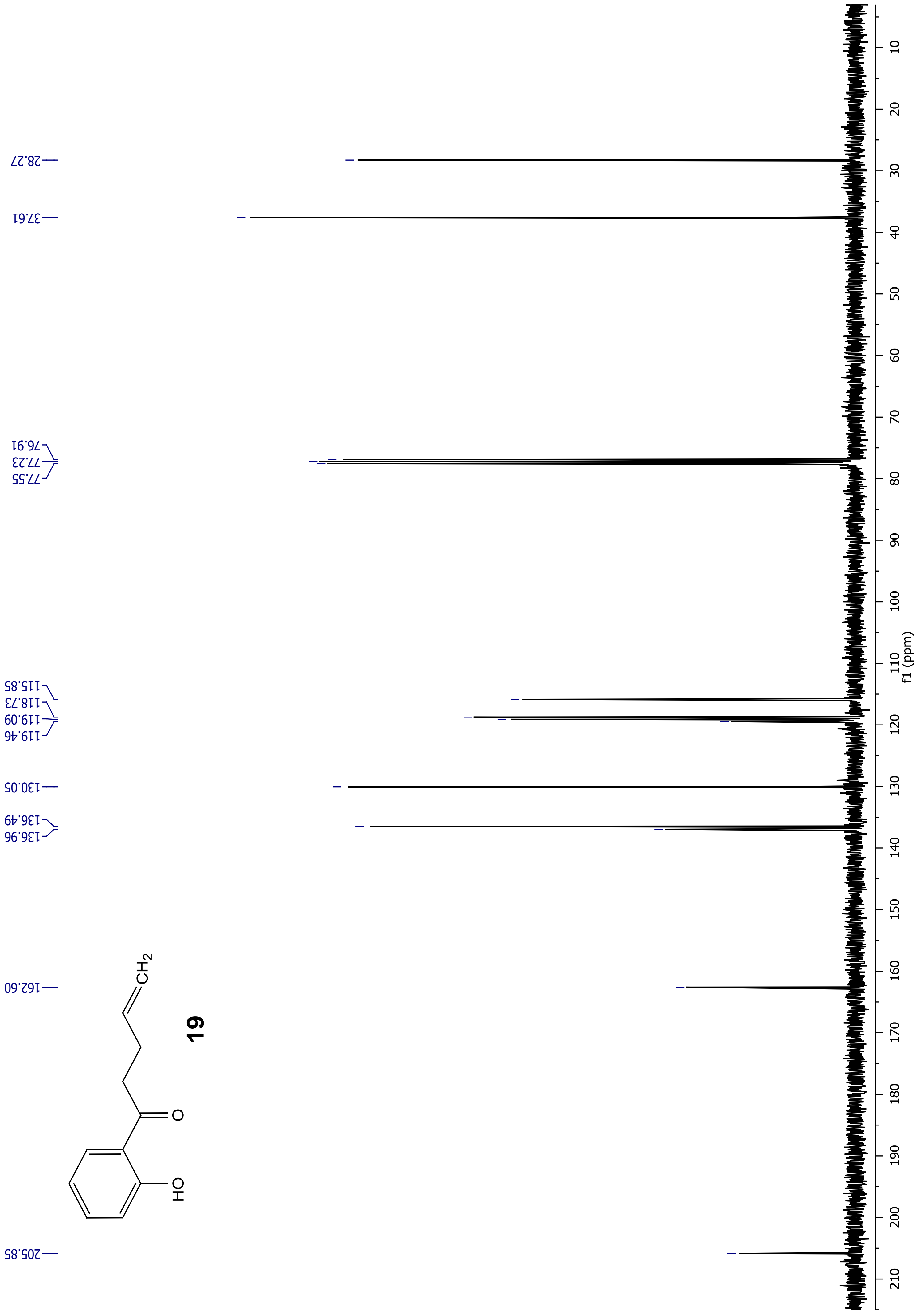
0.5
f1 (ppm)



19

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130.05
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119.09
118.73
115.85
77.55
77.23
76.91
37.61
28.27
OH
O
CH_2
f1 (ppm)
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200
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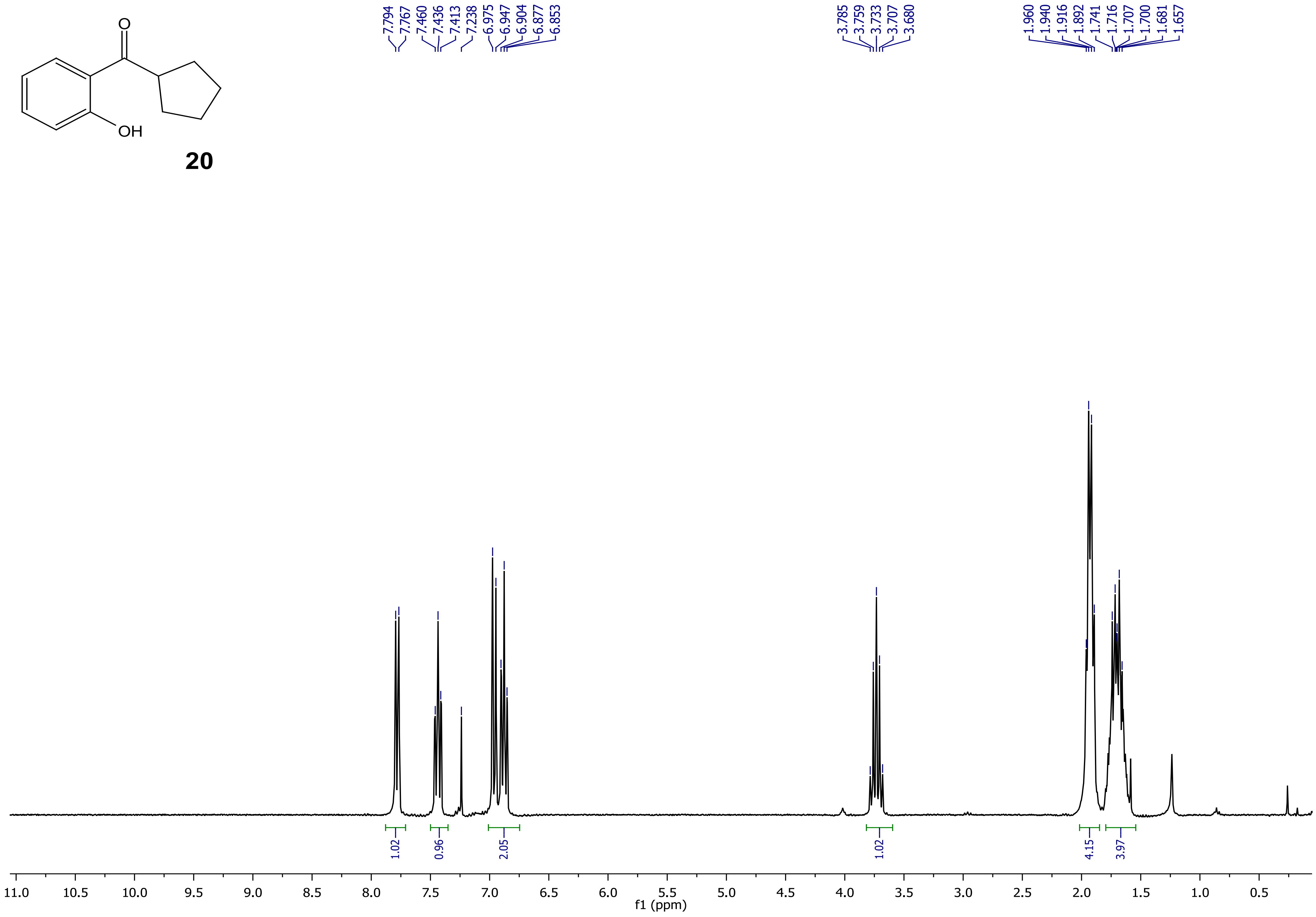
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10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OH
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7.238
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6.877
6.853
3.785
3.759
3.733
3.707
3.680
1.960
1.940
1.916
1.892
1.741
1.716
1.707
1.700
1.681
1.657
1.02
0.96
2.05
1.02
4.15
3.97
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10.5
10.0
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9.0
8.5
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6.5
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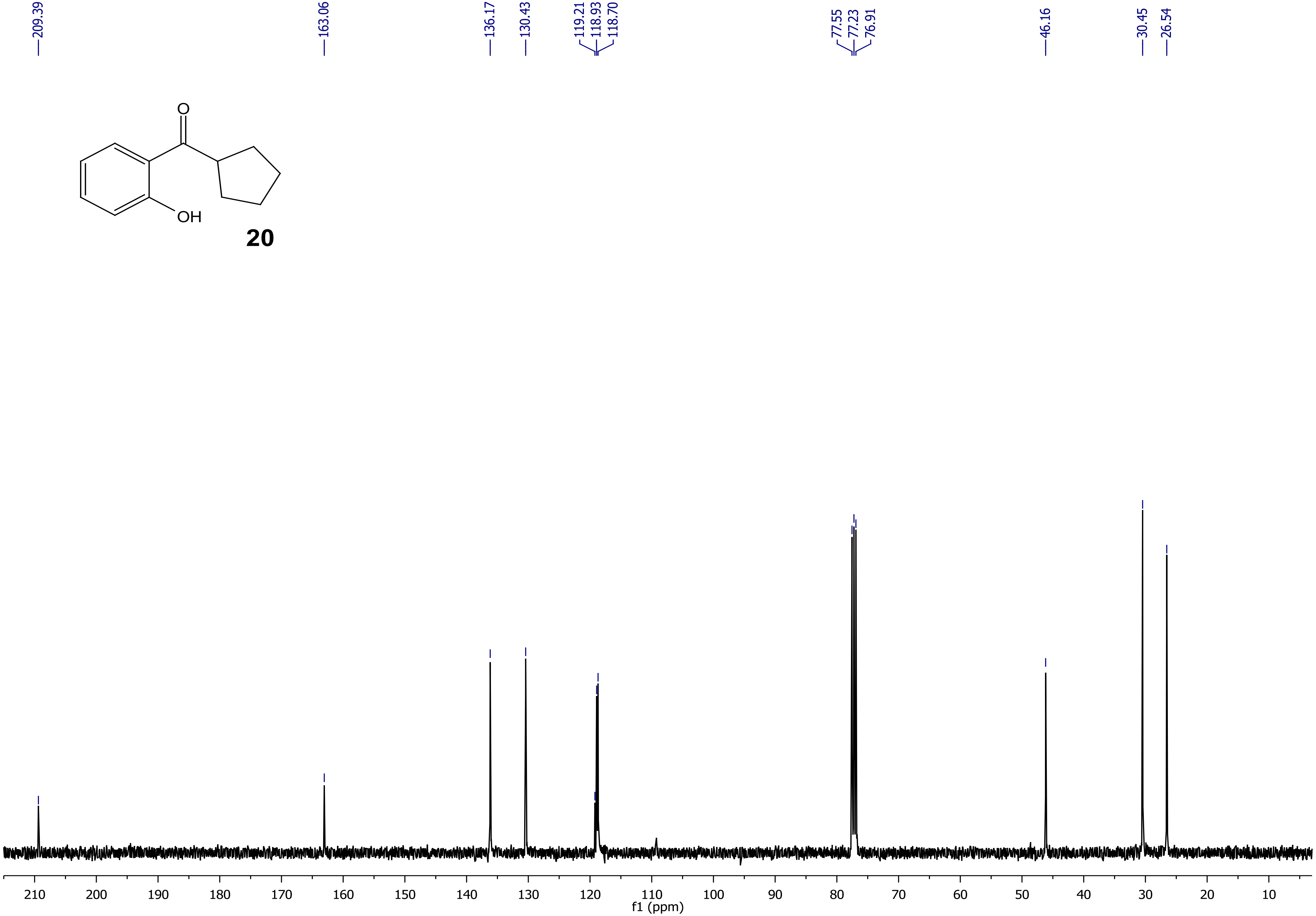
f1 (ppm)



20

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76.91
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26.54
O
OH
210
200
190
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140
130
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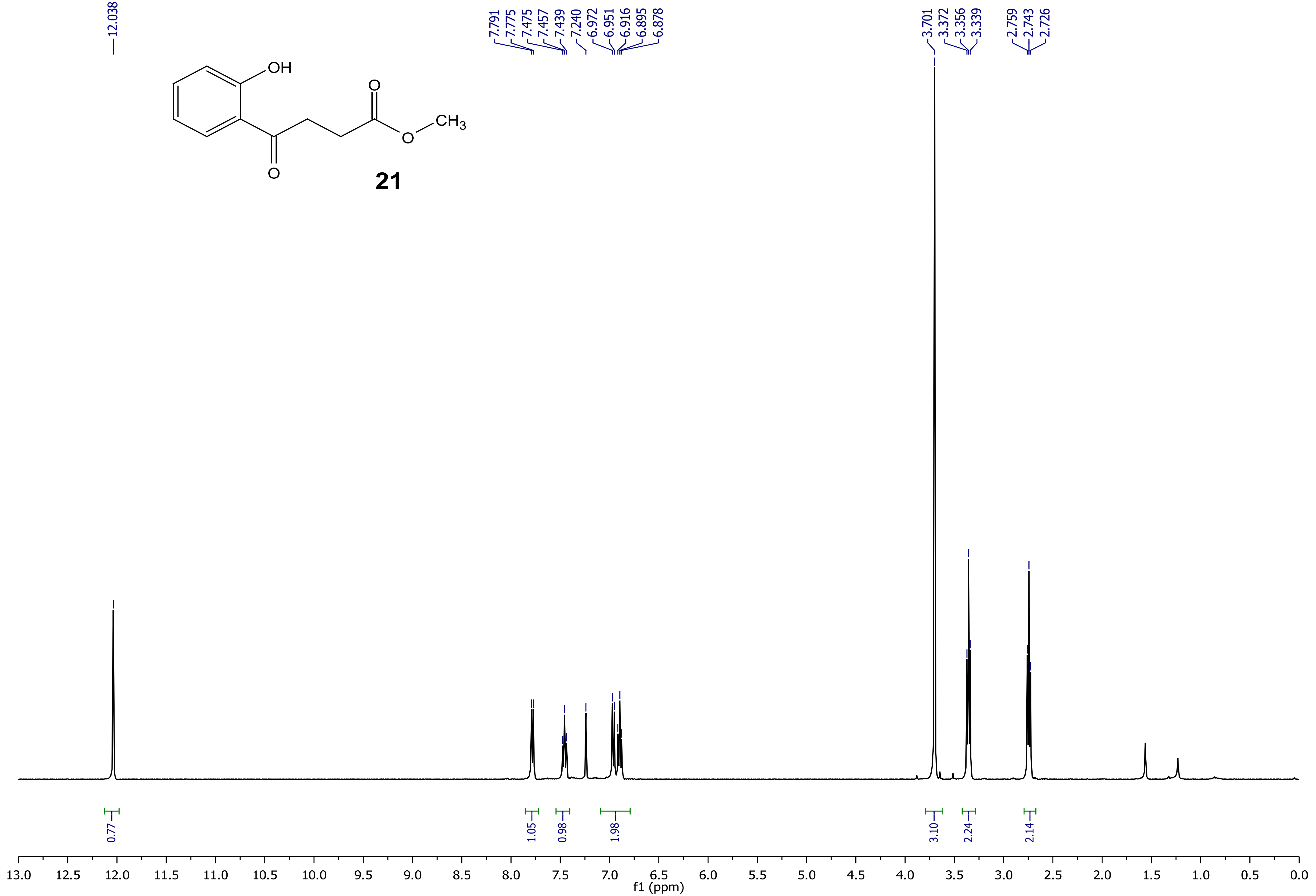
60
50
40
30
20
10
f1 (ppm)



21

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3.372
3.356
3.339
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2.743
2.726
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O
O
O
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1.98
3.10
2.24
2.14
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12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
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6.5
6.0
5.5
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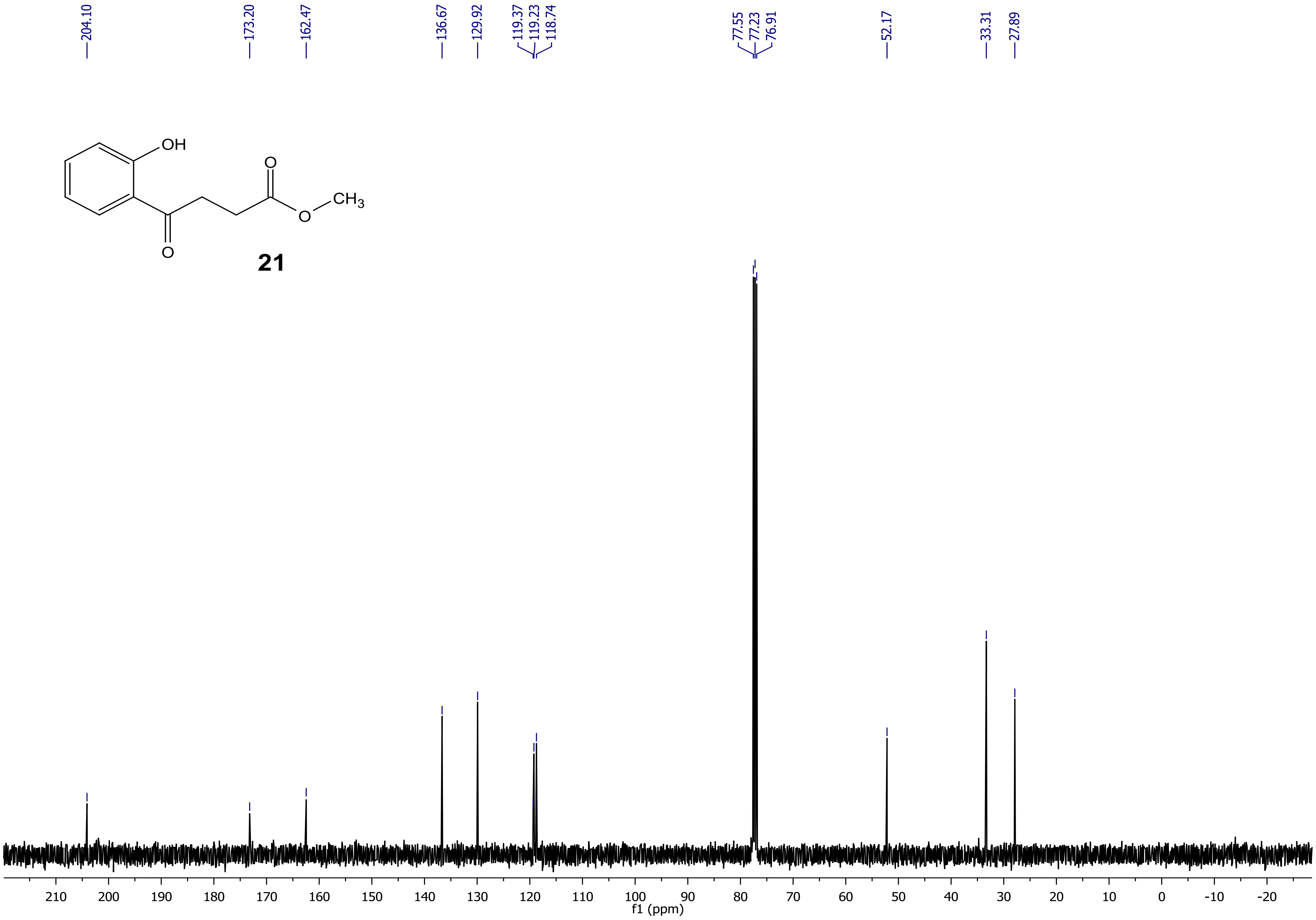
f1 (ppm)



21

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118.74
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77.23
76.91
52.17
33.31
27.89
OH
O
O
O
CH3
210
200
190
180
170
160
150
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20
10
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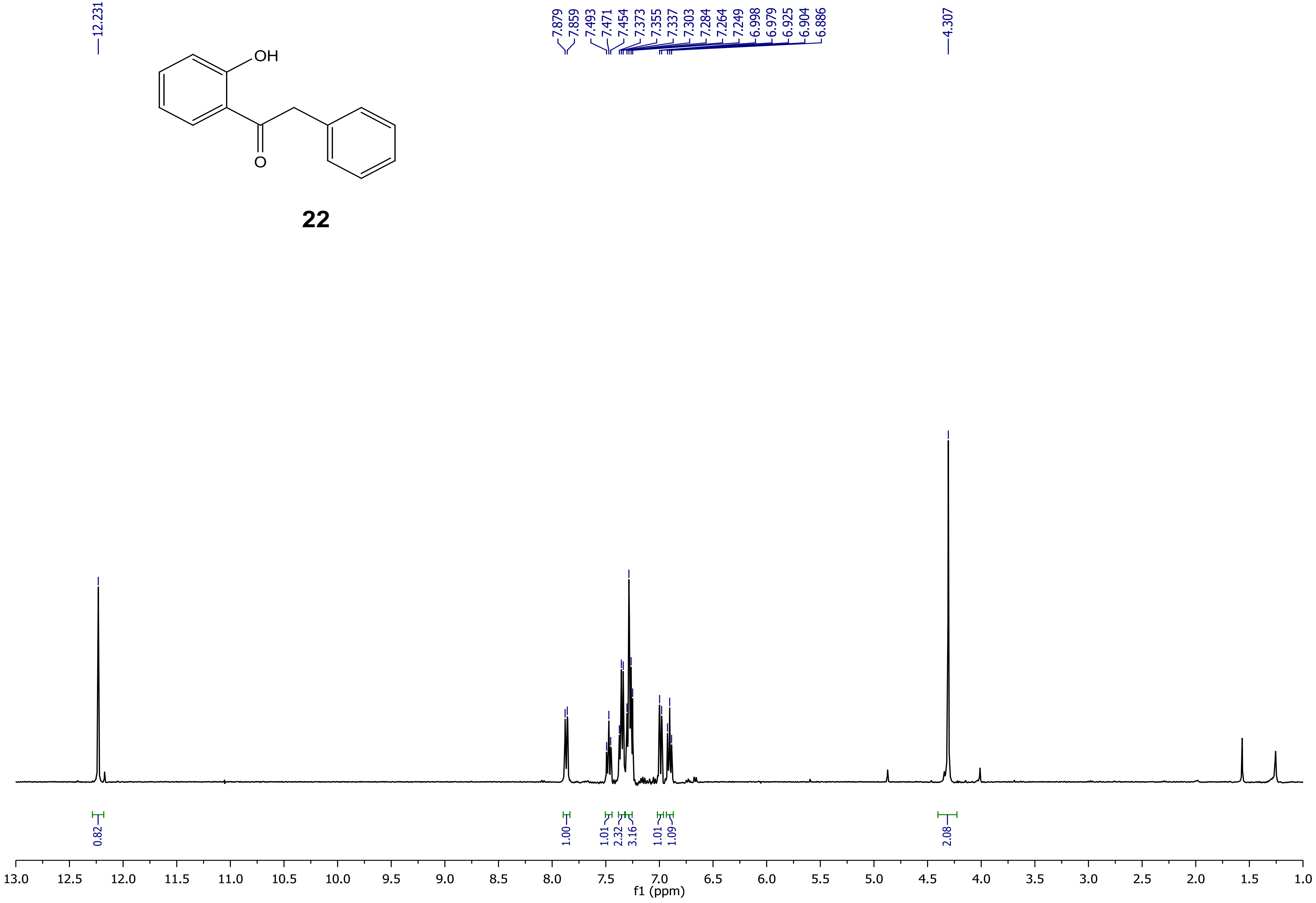
f1 (ppm)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7.249
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6.979
6.925
6.904
6.886
4.307
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1.01
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1.01
1.09
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10.5
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7.0
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

22

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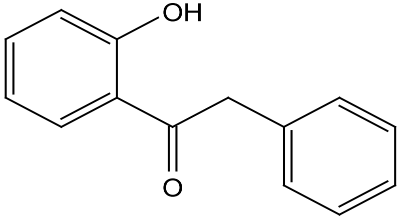
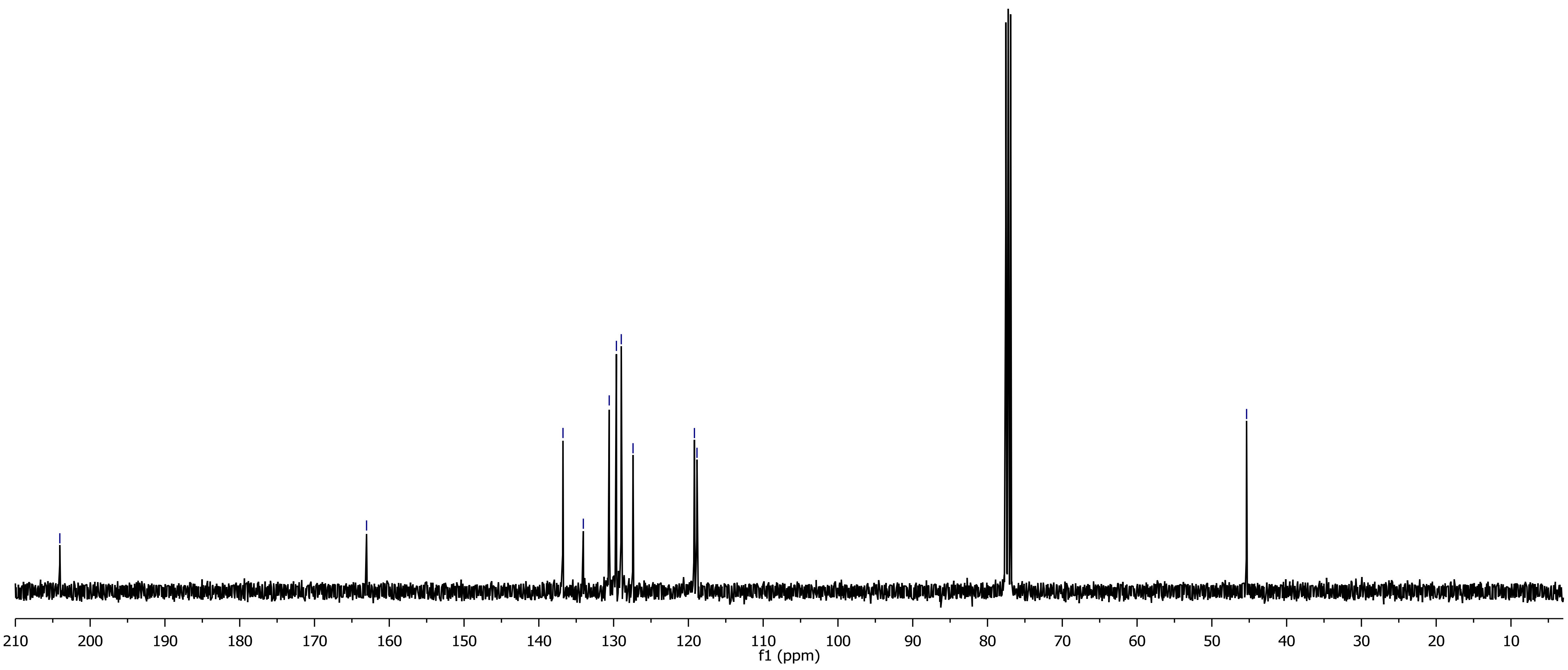
119.20
118.85
45.36


OH
O

22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200
190
180
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150
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120
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100
90
80
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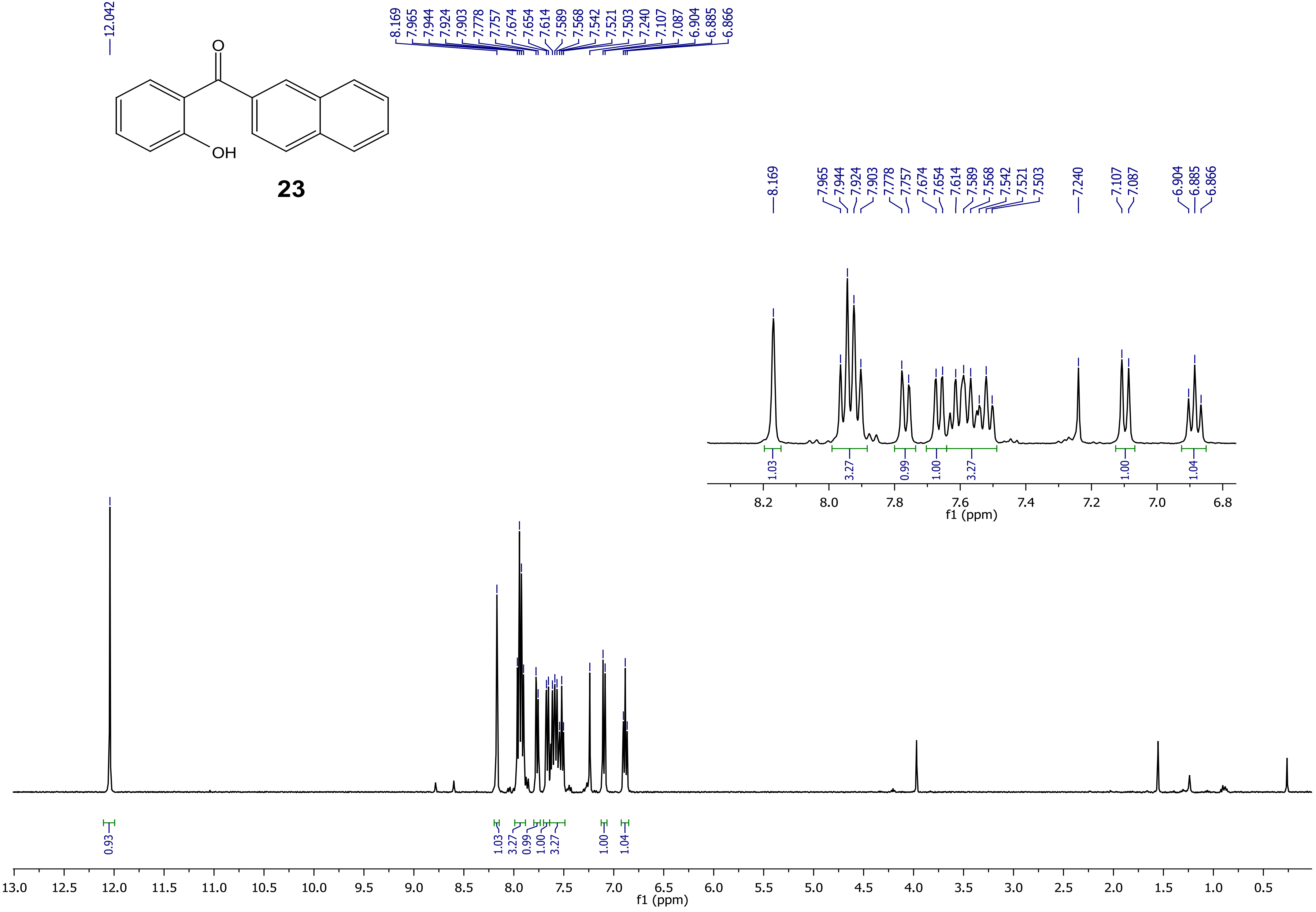
60
50
40
30
20
10
f1 (ppm)



23

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7.674
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7.589
7.568
7.542
7.521
7.503
7.240
7.107
7.087
6.904
6.885
6.866
O
OH
1.03
3.27
0.99
1.00
3.27
1.00
1.04
0.93
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
f1 (ppm)
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12.5
12.0
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6.5
6.0
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4.0
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3.0
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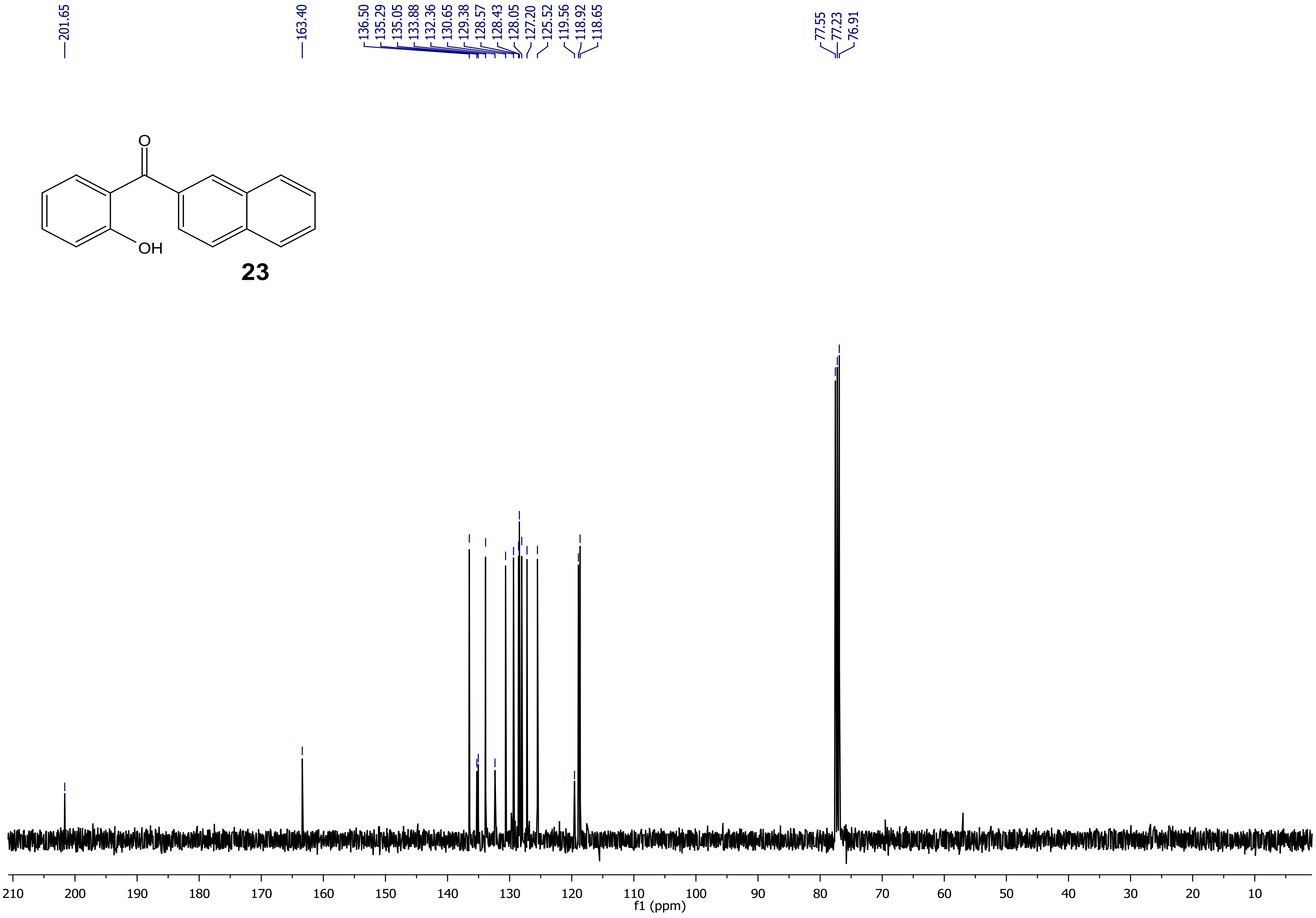
1.0
0.5
f1 (ppm)



23

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135.05
133.88
132.36
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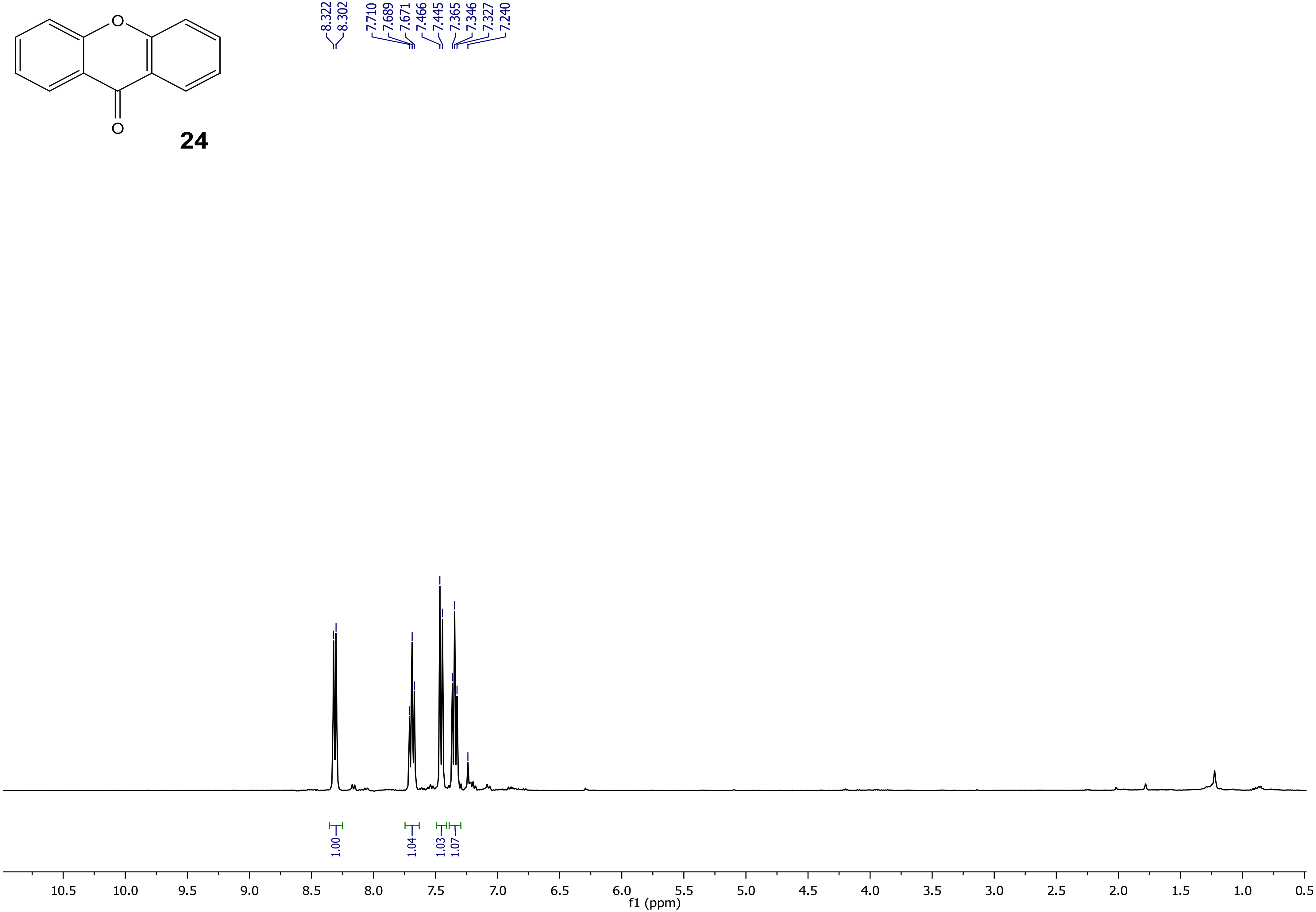
129.38
128.57
128.43
128.05
127.20
125.52
119.56
118.92
118.65
77.55
77.23
76.91
O
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


24

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1.00
1.04
1.03
1.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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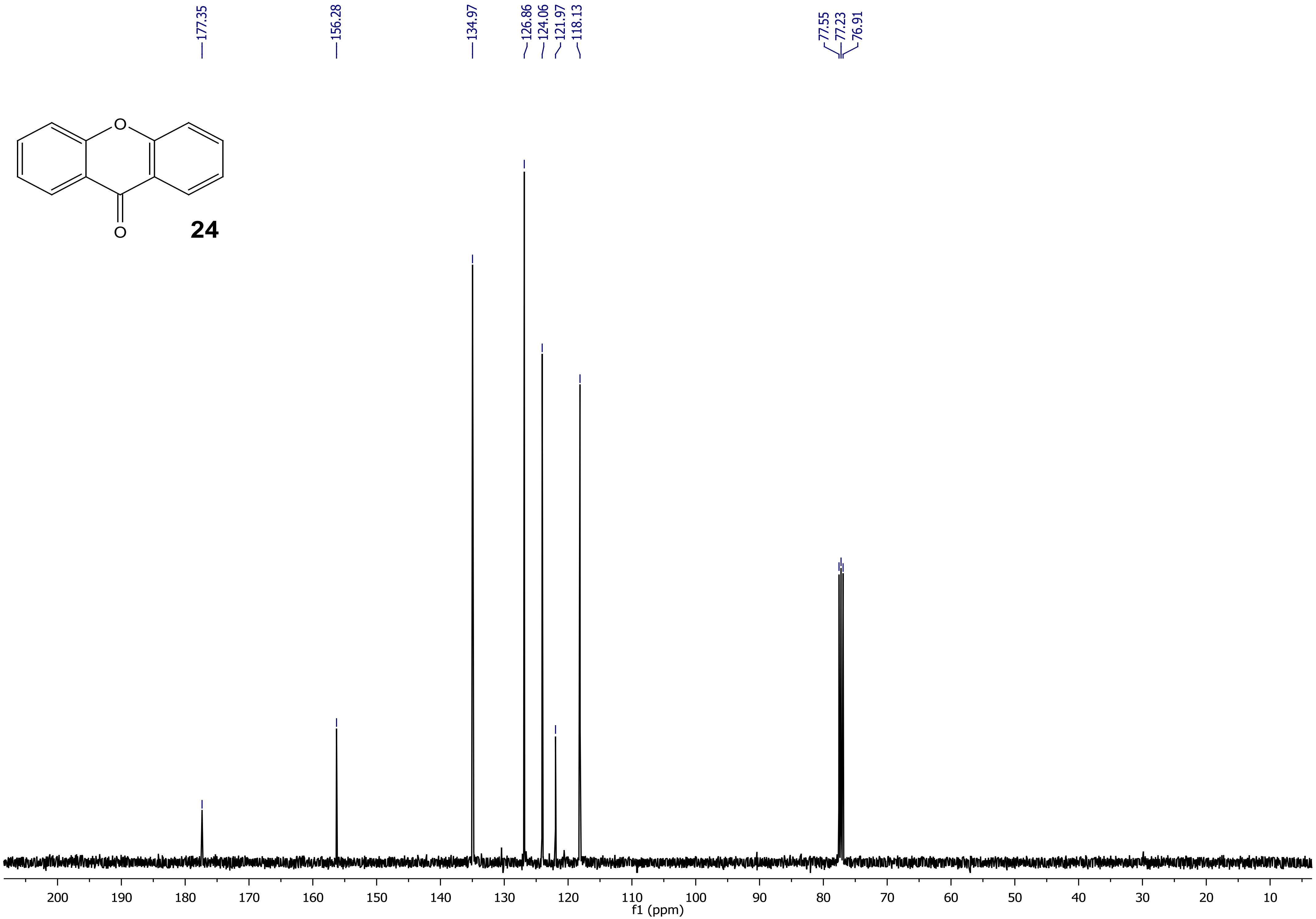
0.5
f1 (ppm)
O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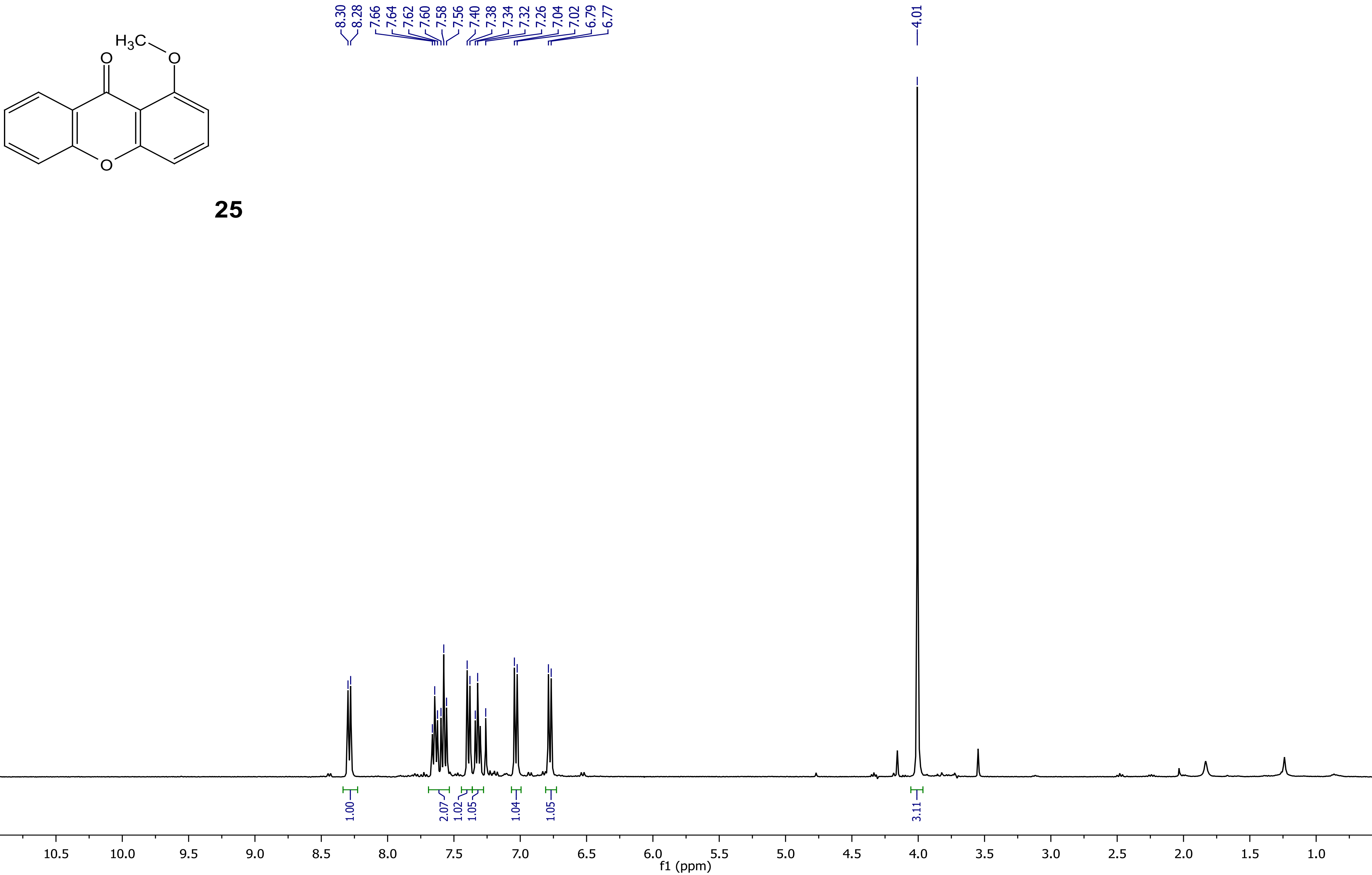
124.06
121.97
118.13
77.55
77.23
76.91
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

24



25

H3C
O
O
O
8.30
8.28
7.66
7.64
7.62
7.60
7.58
7.56
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7.38
7.34
7.32
7.26
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7.02
6.79
6.77
4.01
1.00
2.07
1.02
1.05
1.04
1.05
3.11
10.5
10.0
9.5
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8.5
8.0
7.5
7.0
6.5
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4.5
4.0
3.5
3.0
2.5
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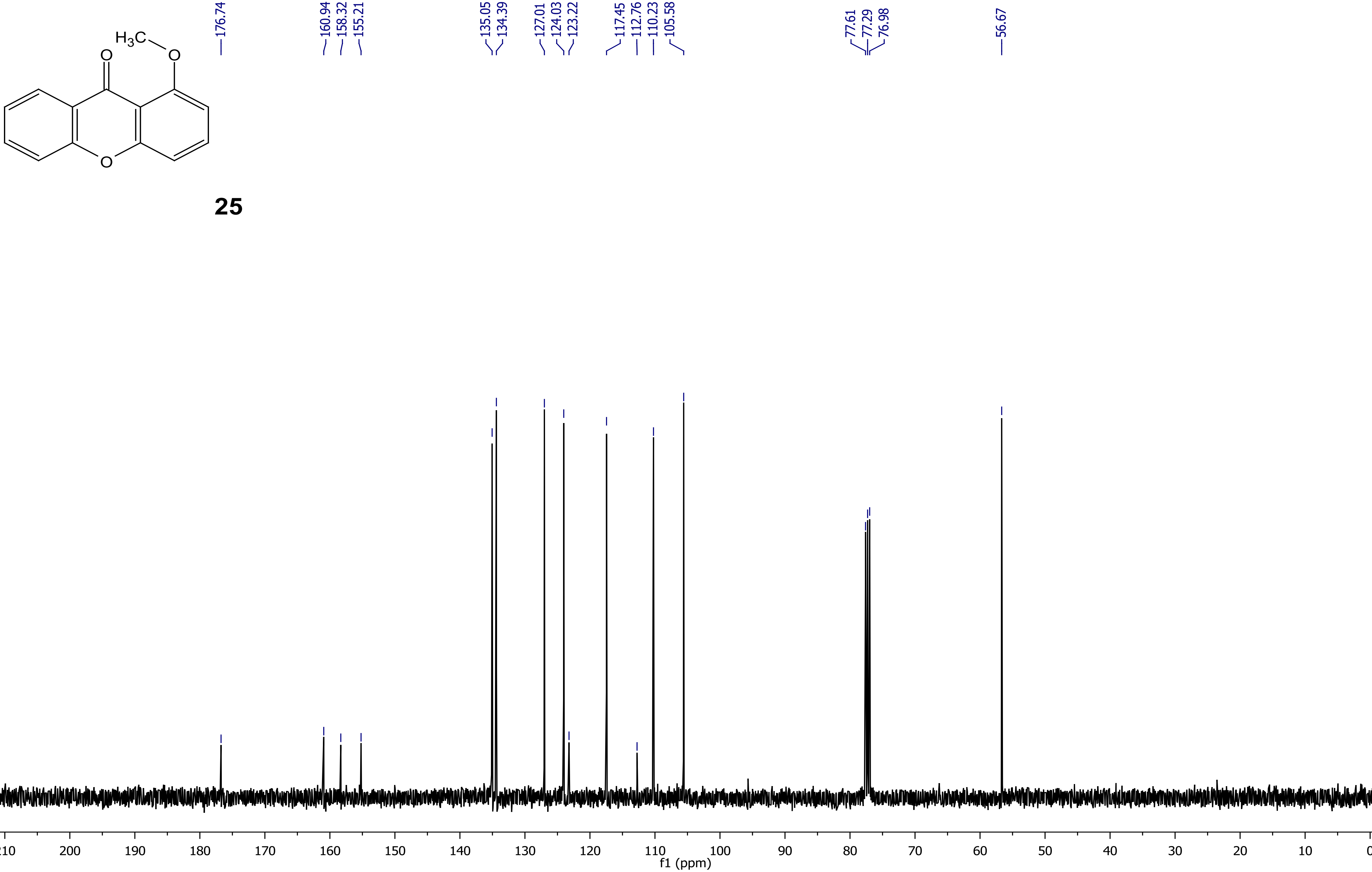
1.5
1.0
f1 (ppm)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O
O
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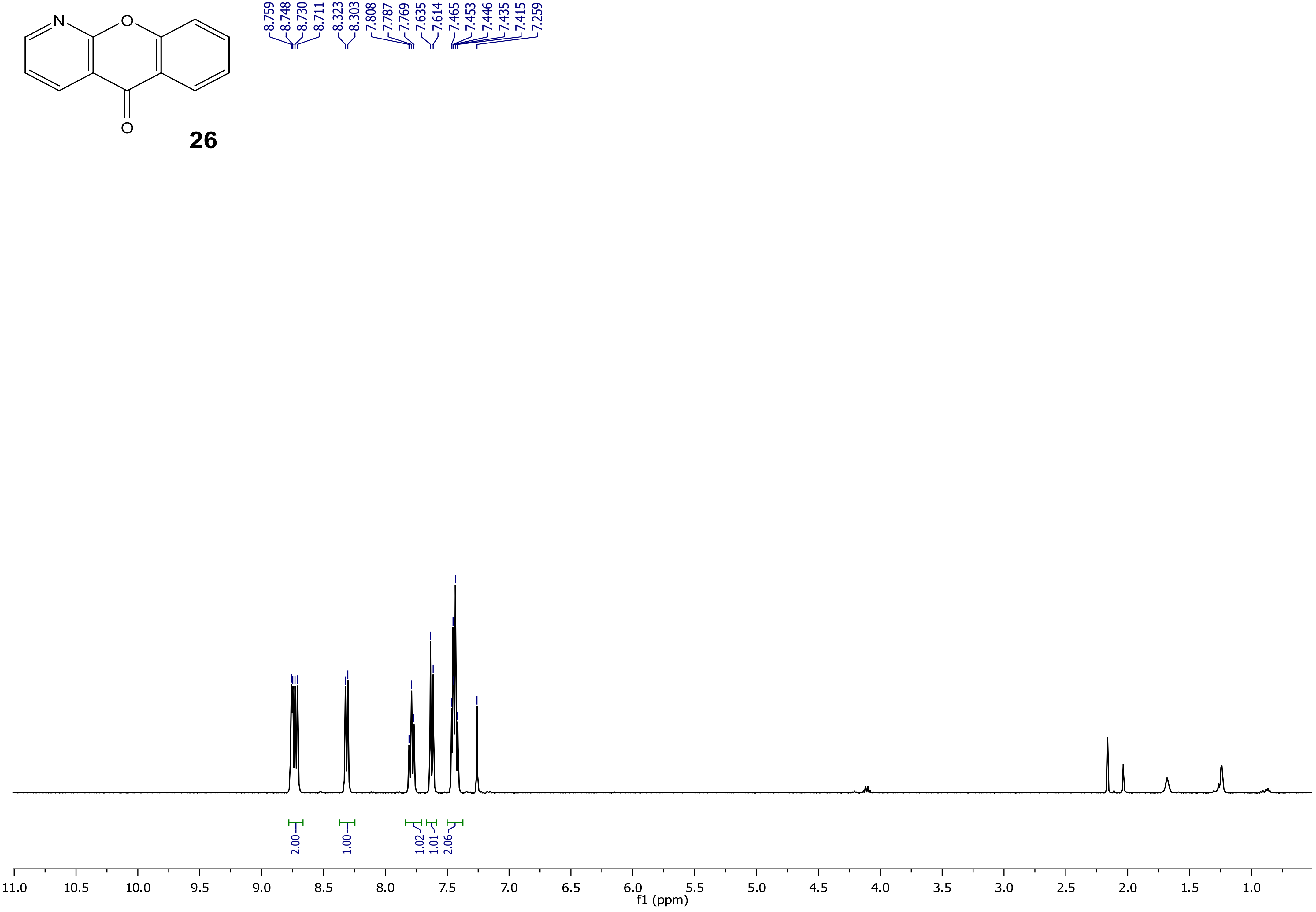
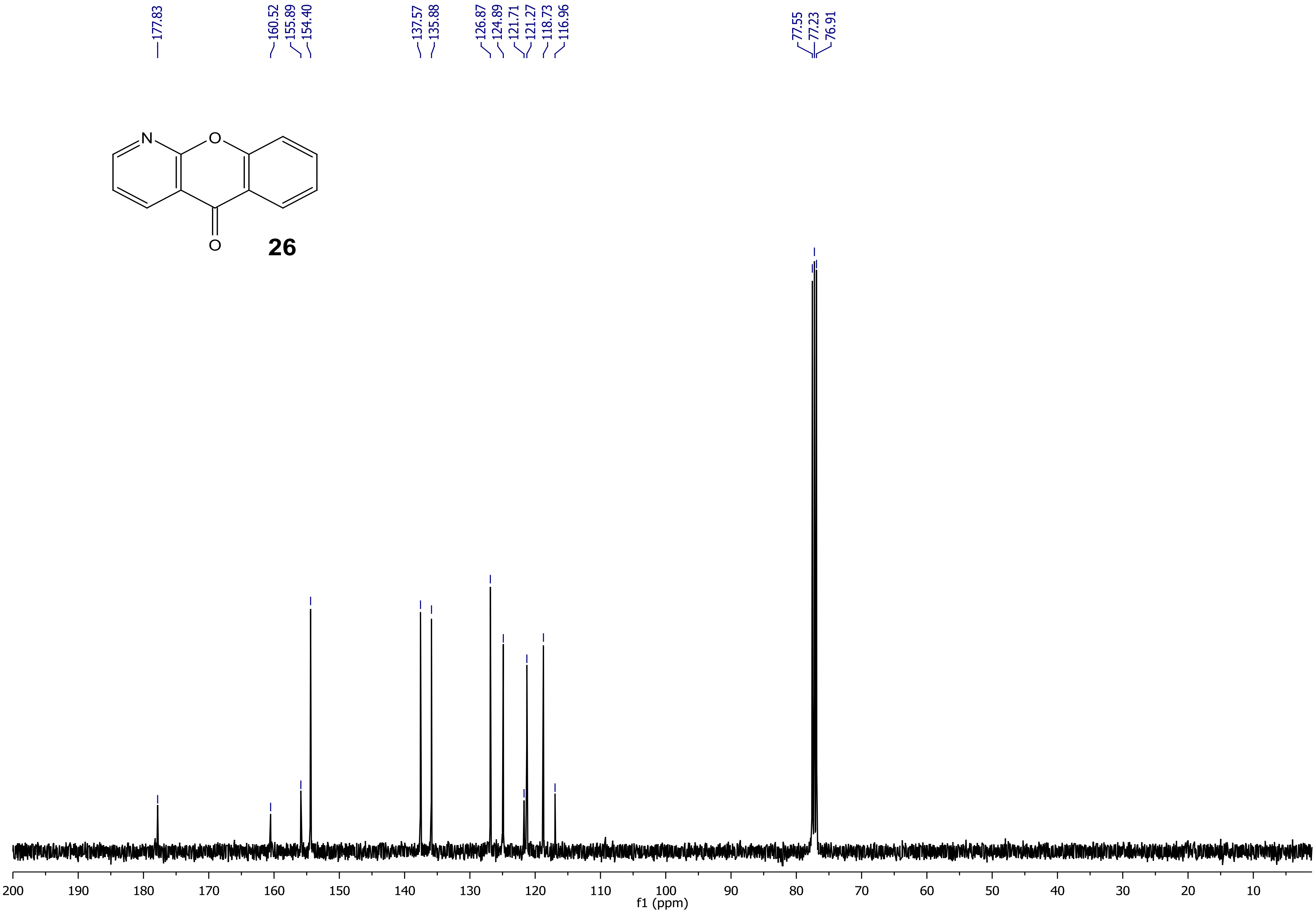
117.45
112.76
110.23
105.58
77.61
77.29
76.98
56.67
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

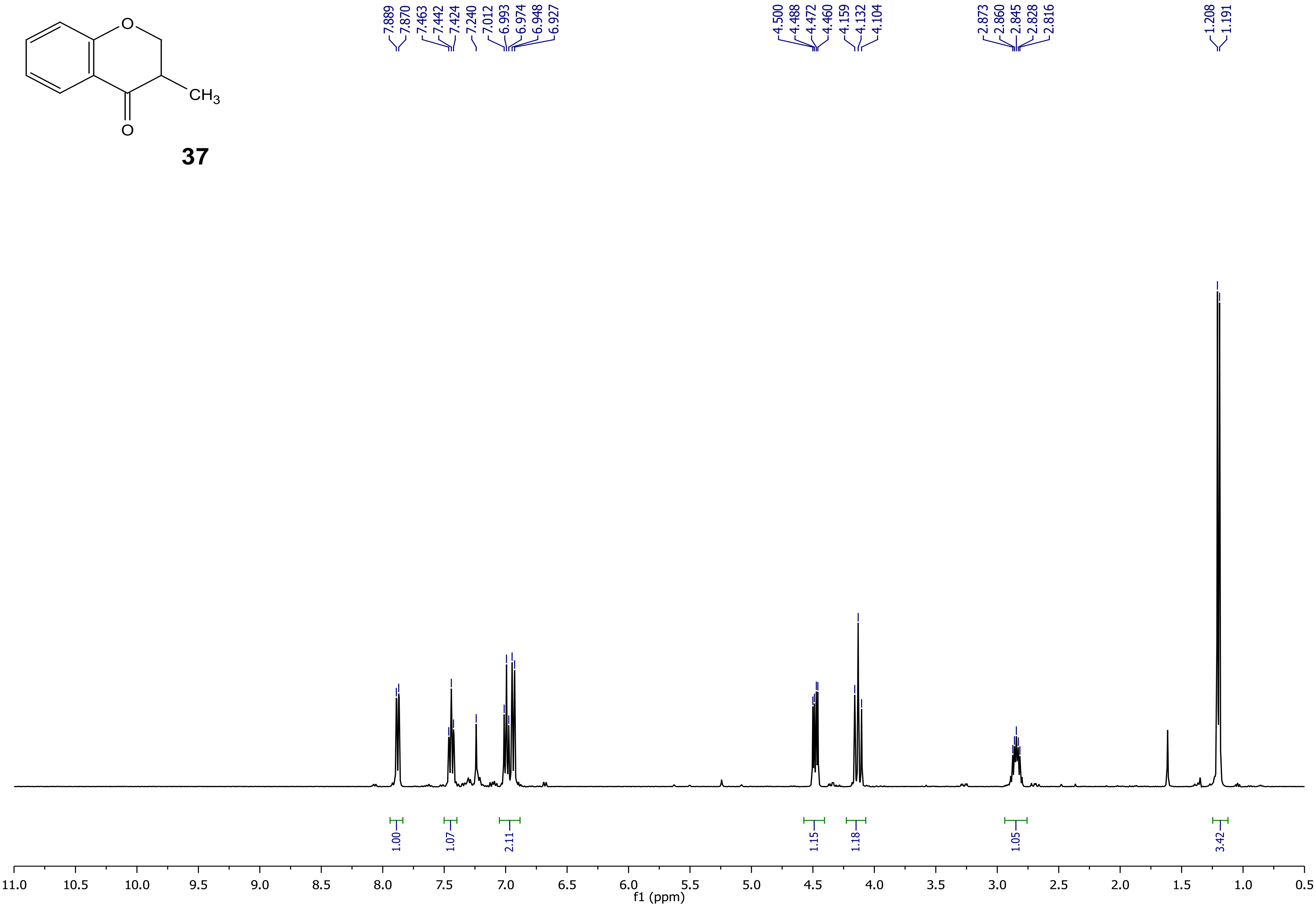
25


26
8.759
8.748
8.730
8.711
8.323
8.303
7.808
7.787
7.769
7.635
7.614
7.465
7.453
7.446
7.435
7.415
7.259
2.00
1.00
1.02
1.01
2.06
11.0
10.5
10.0
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
2.0
1.5
1.0
f1 (ppm)
N
O
O

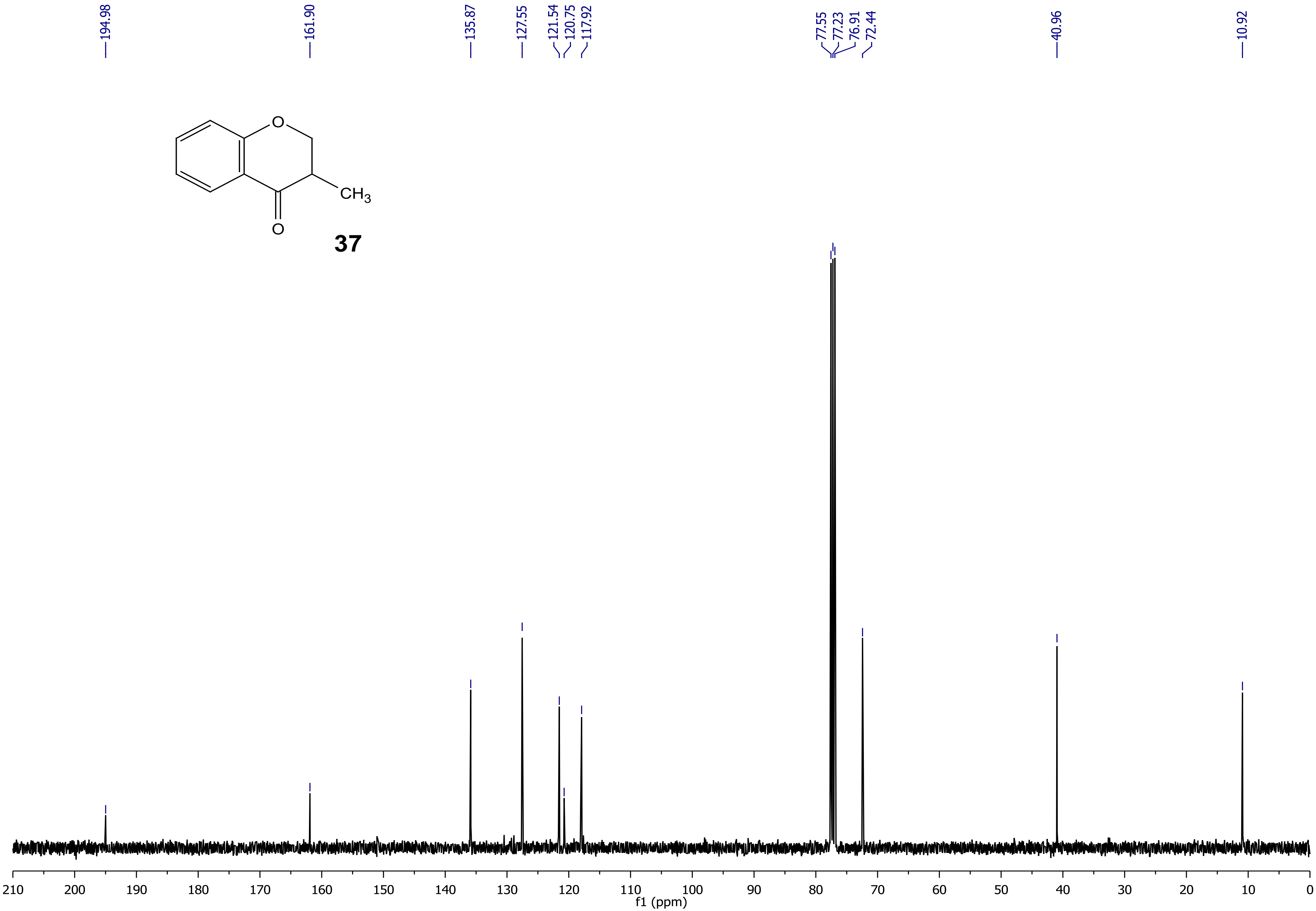


26

177.83
160.52
155.89
154.40
137.57
135.88
126.87
124.89
121.71
121.27
118.73
116.96
77.55
77.23
76.91
N
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

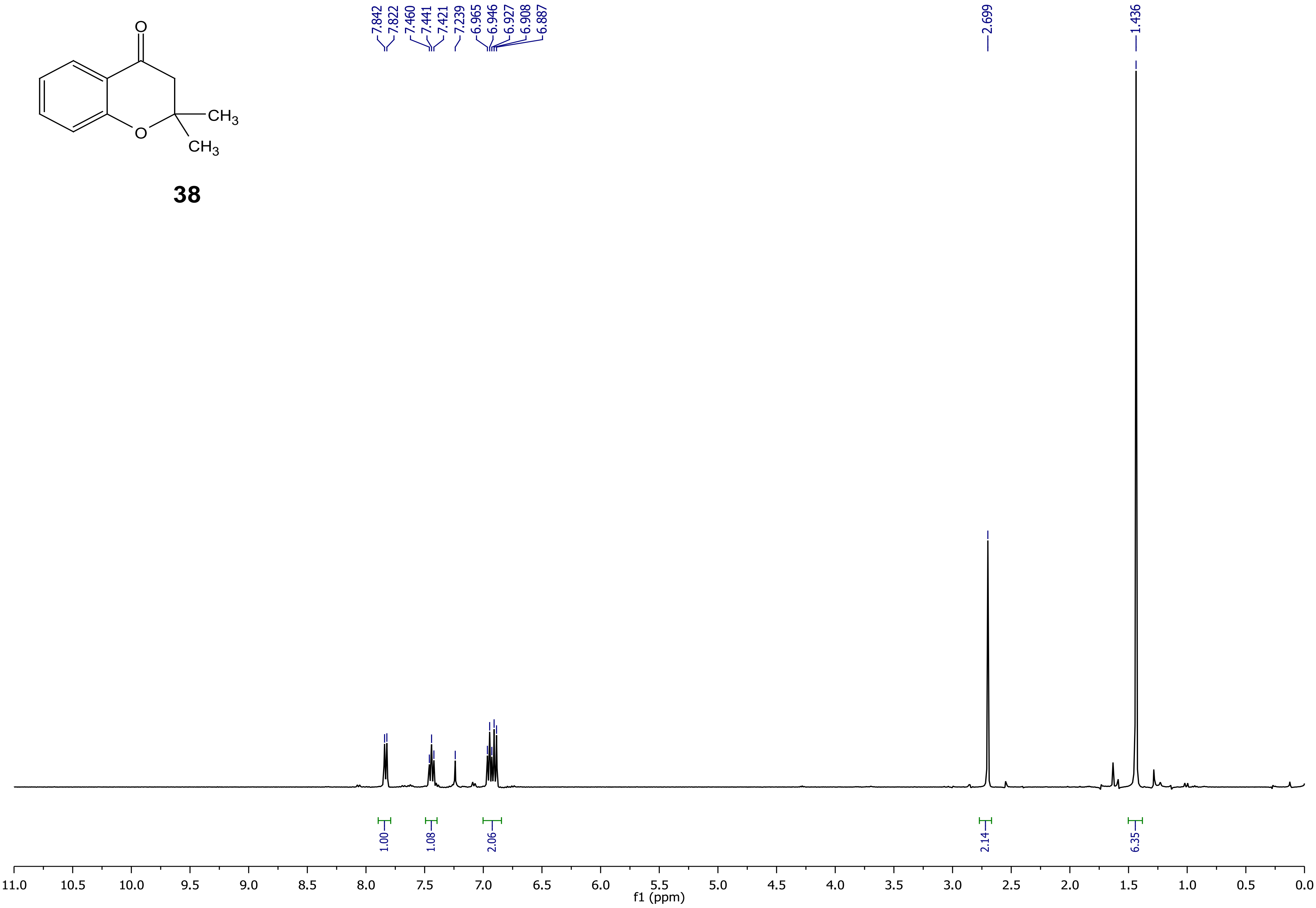

37

CH3
O
O
7.889
7.870
7.463
7.442
7.424
7.240
7.012
6.993
6.974
6.948
6.927
4.500
4.488
4.472
4.460
4.159
4.132
4.104
2.873
2.860
2.845
2.828
2.816
1.208
1.191
1.00
1.07
2.11
1.15
1.18
1.05
3.42
11.0
10.5
10.0
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
2.0
1.5
1.0
0.5
f1 (ppm)



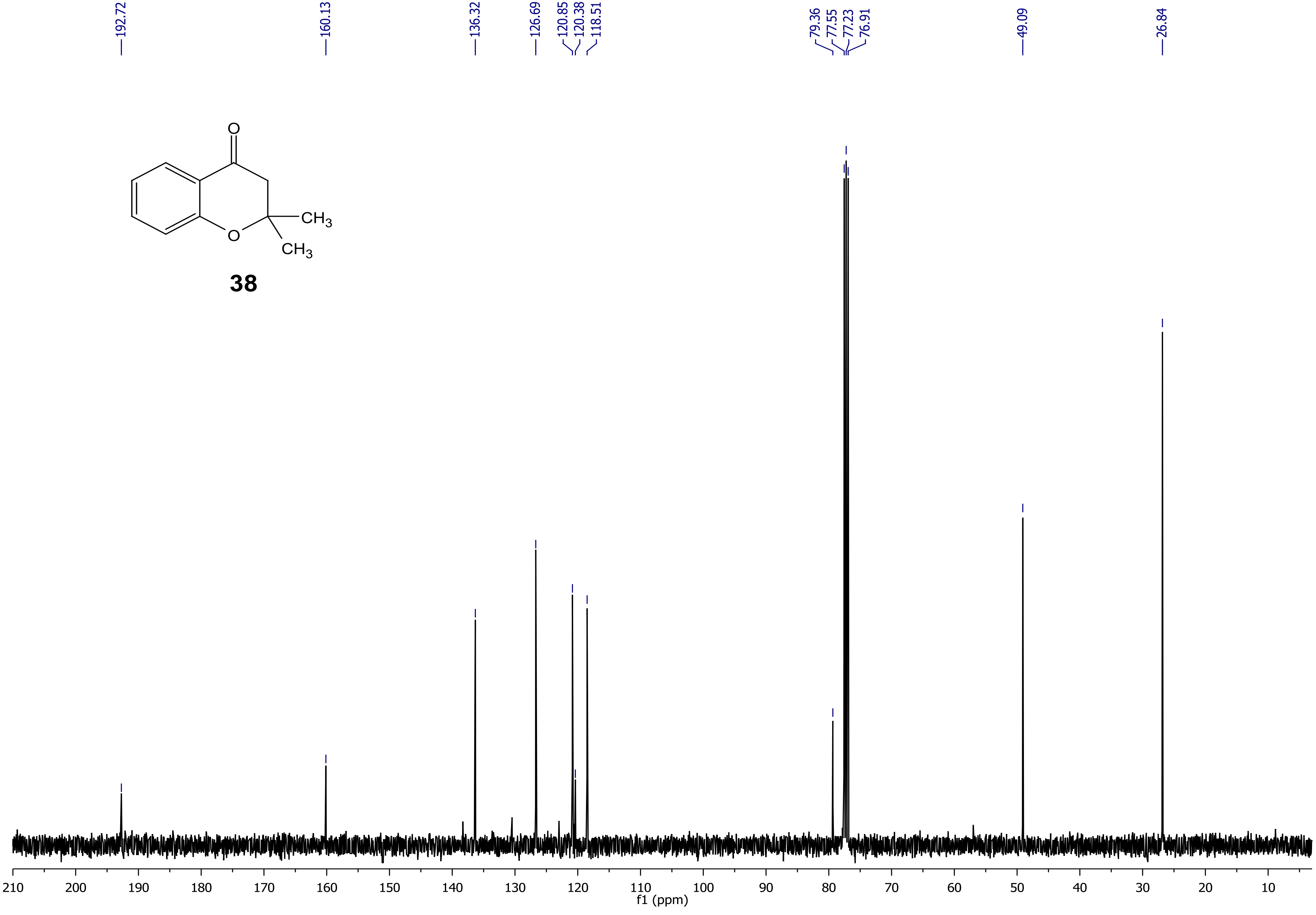
37

194.98
161.90
135.87
127.55
121.54
120.75
117.92
77.55
77.23
76.91
72.44
40.96
10.92
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

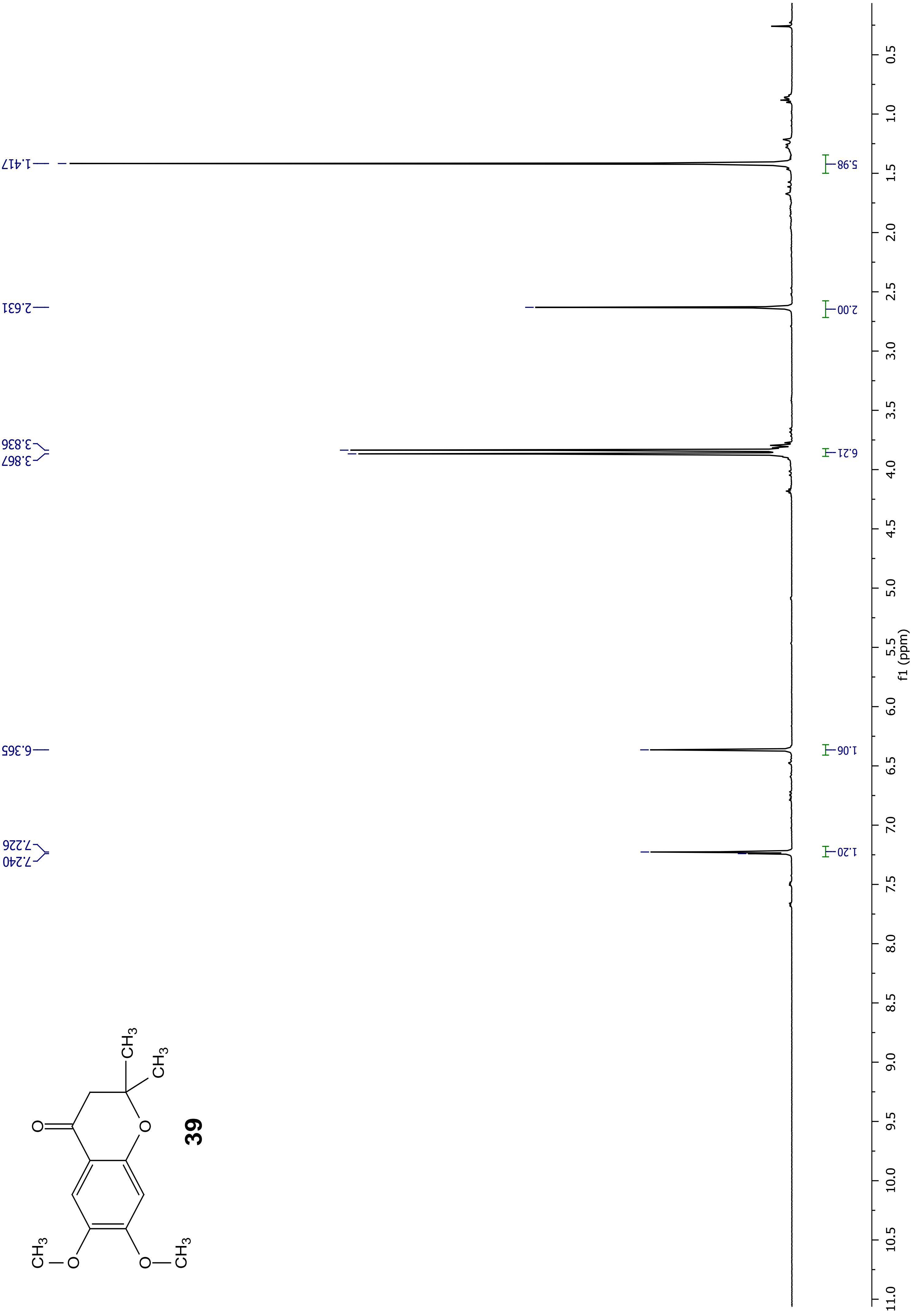


38

O
O
CH3
CH3
7.842
7.822
7.460
7.441
7.421
7.239
6.965
6.946
6.927
6.908
6.887
2.699
1.436
1.00
1.08
2.06
2.14
6.35
11.0
10.5
10.0
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
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

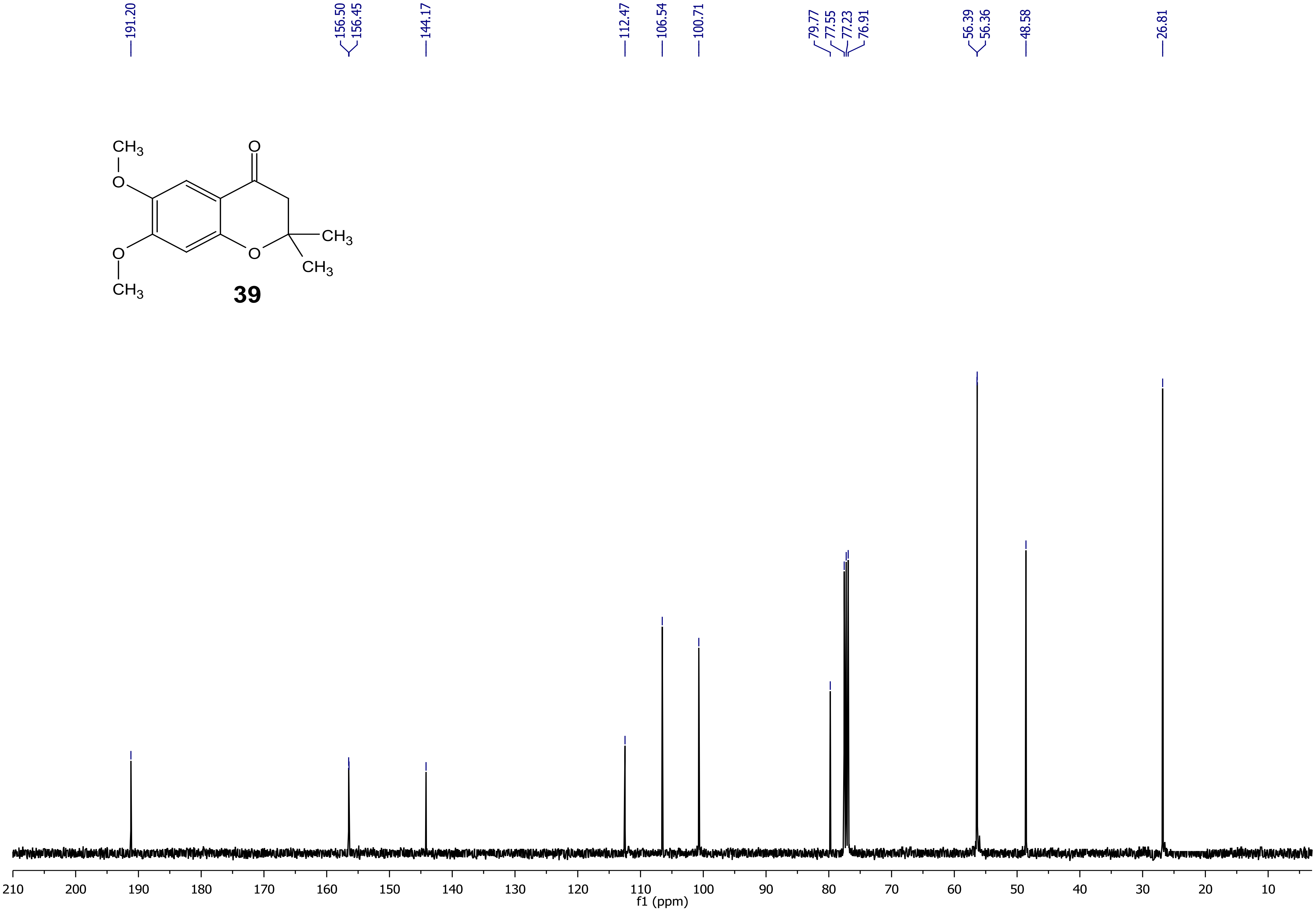

192.72
160.13
136.32
126.69
120.85
120.38
118.51
79.36
77.55
77.23
76.91
49.09
26.84
O
O
CH$_3$
CH$_3$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

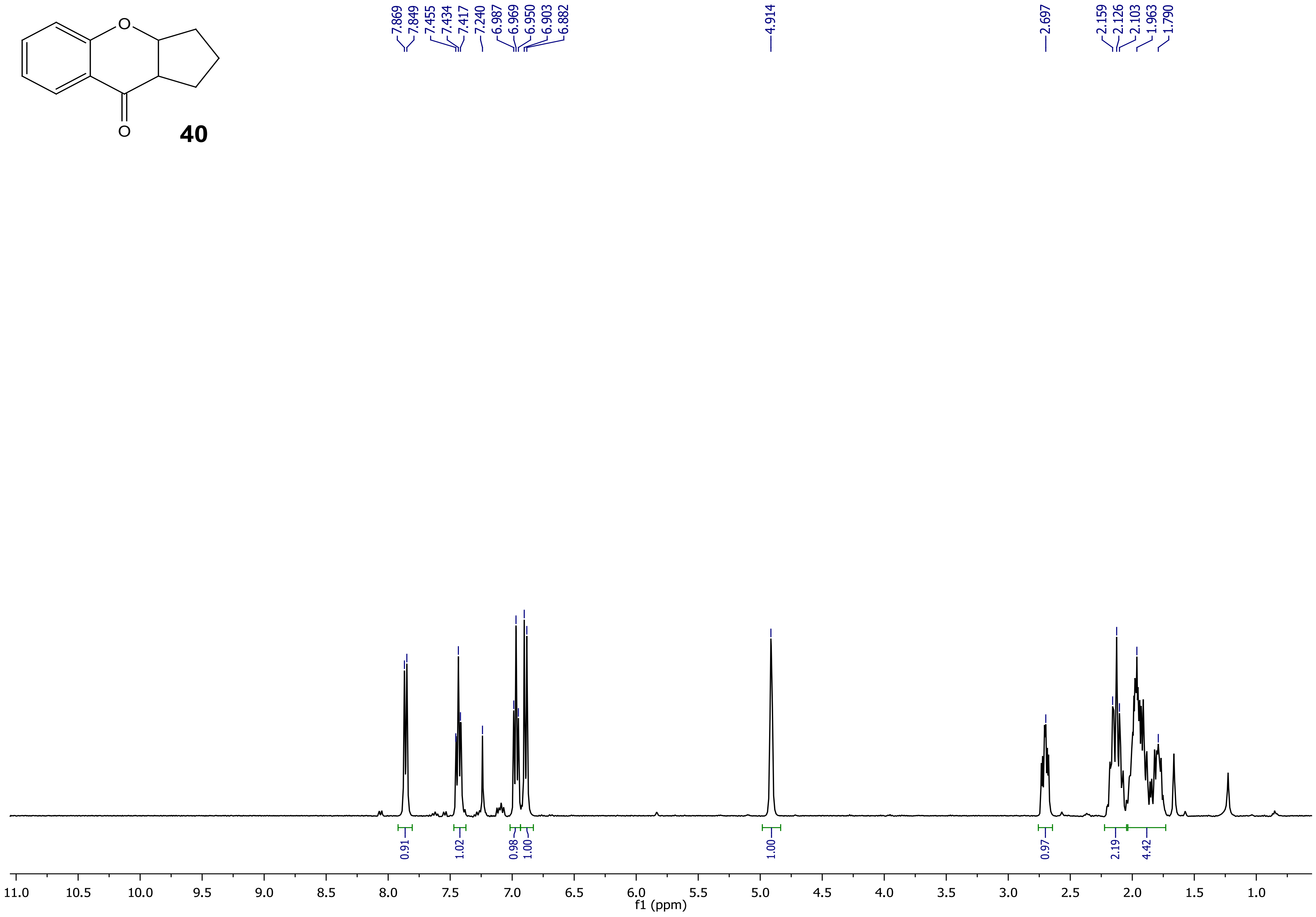
38



39

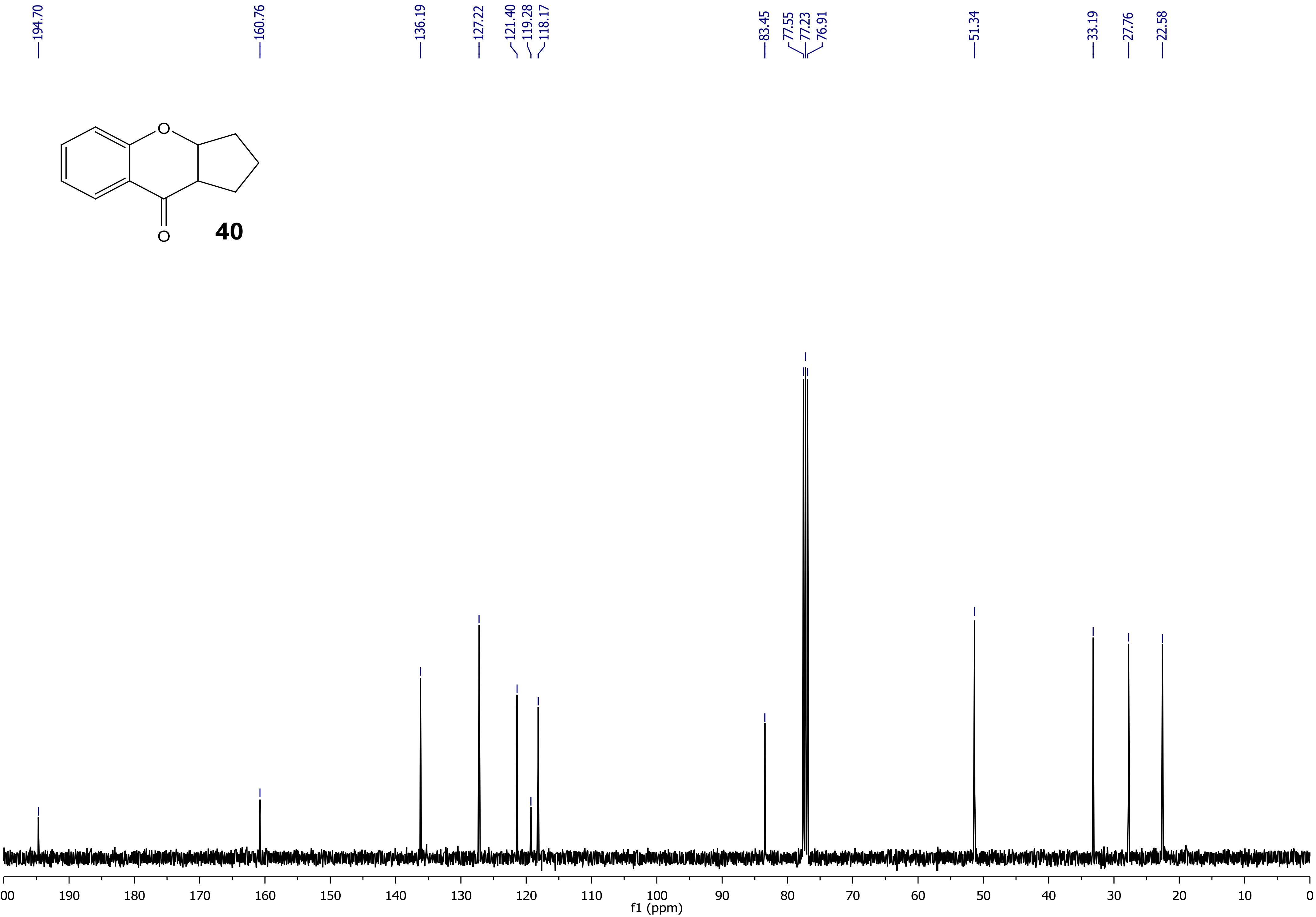
1.417
2.631
3.836
3.867
6.365
7.226
7.240
5.98
2.00
6.21
1.06
1.20
f1 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
O
CH3
CH3
O
CH3
O
O
CH3


39
191.20
156.50
156.45
144.17
112.47
106.54
100.71
79.77
77.55
77.23
76.91
56.39
56.36
48.58
26.81
CH3
O
CH3
CH3
O
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



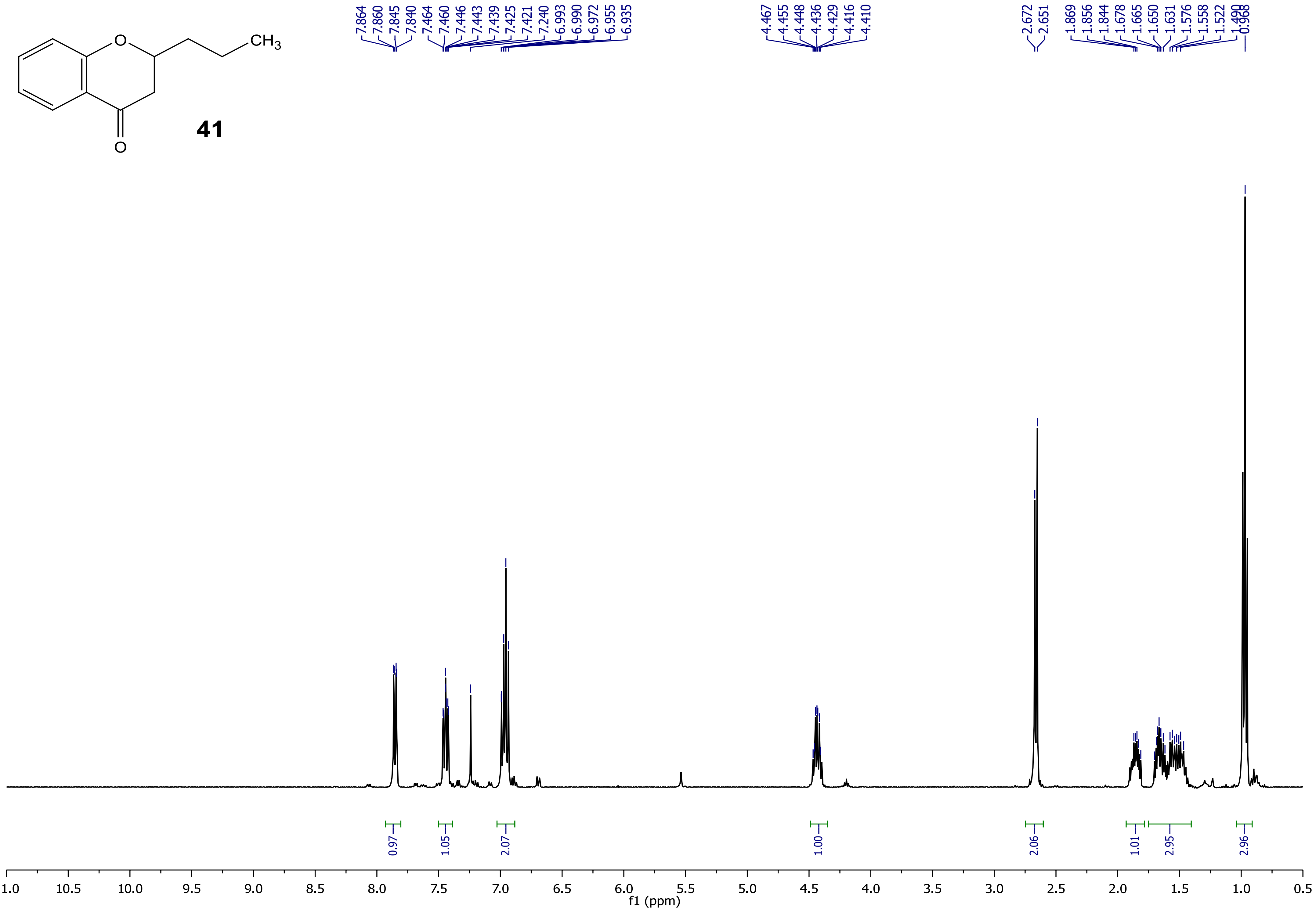
40

7.869
7.849
7.455
7.434
7.417
7.240
6.987
6.969
6.950
6.903
6.882
4.914
2.697
2.159
2.126
2.103
1.963
1.790
0.91
1.02
0.98
1.00
1.00
0.97
2.19
4.42
11.0
10.5
10.0
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
2.0
1.5
1.0
f1 (ppm)
O



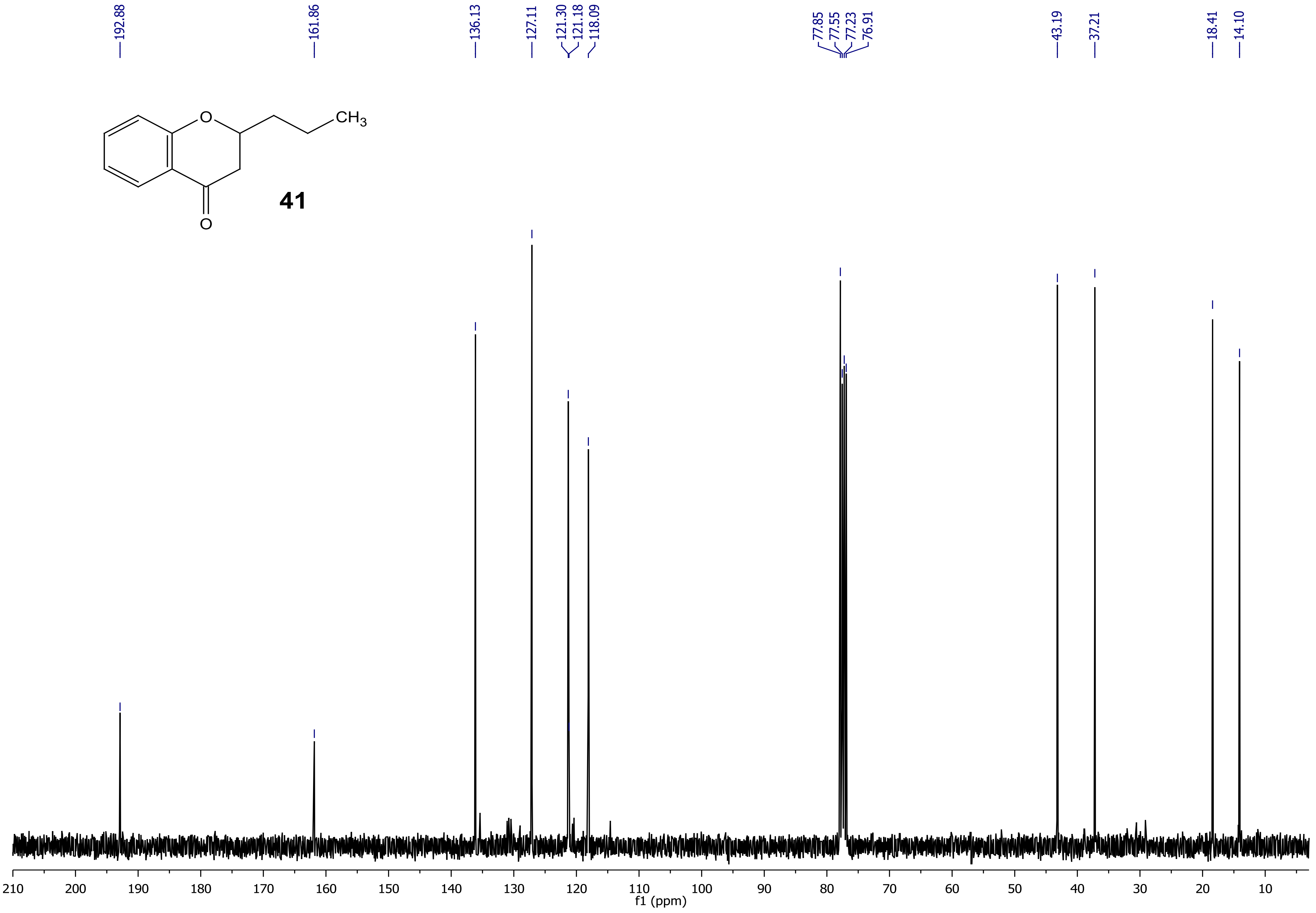
40

194.70
160.76
136.19
127.22
121.40
119.28
118.17
83.45
77.55
77.23
76.91
51.34
33.19
27.76
22.58
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

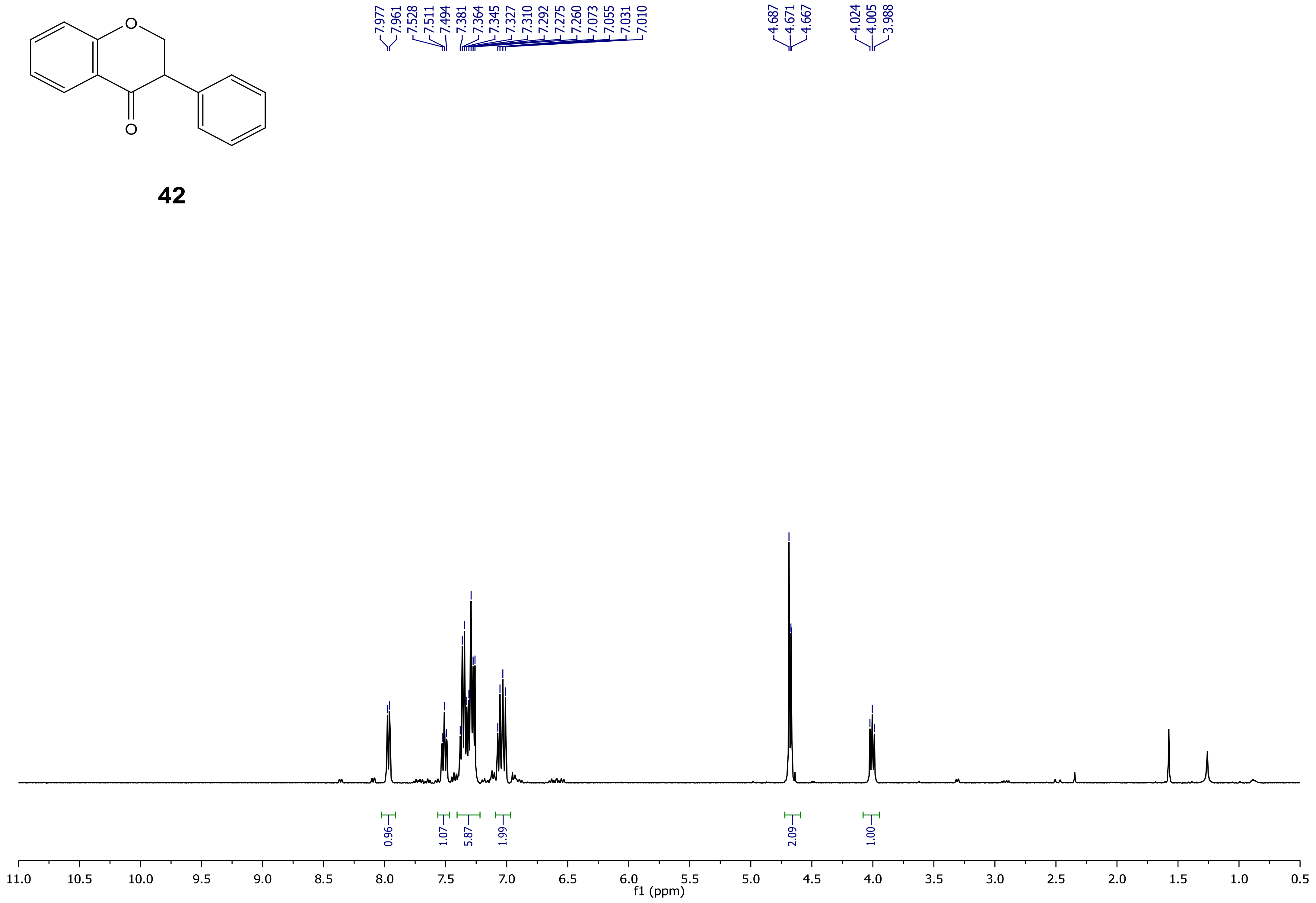


41

CH3
O
O
7.864
7.860
7.845
7.840
7.464
7.460
7.446
7.443
7.439
7.425
7.421
7.240
6.993
6.990
6.972
6.955
6.935
4.467
4.455
4.448
4.436
4.429
4.416
4.410
2.672
2.651
1.869
1.856
1.844
1.678
1.665
1.650
1.631
1.576
1.558
1.522
1.490
0.968
0.97
1.05
2.07
1.00
2.06
1.01
2.95
2.96
11.0
10.5
10.0
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
2.0
1.5
1.0
0.5
f1 (ppm)

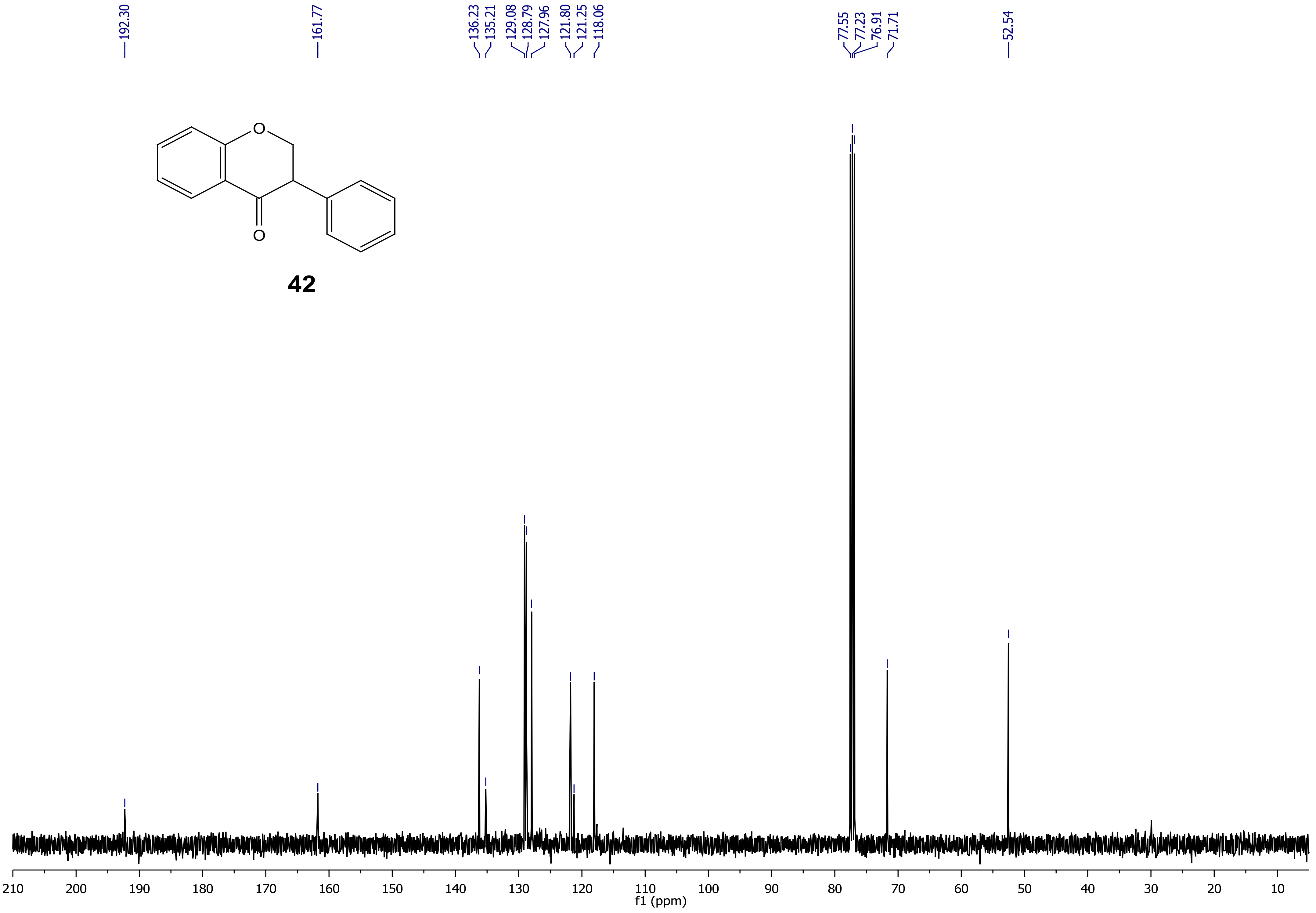


192.88
161.86
136.13
127.11
121.30
121.18
118.09
77.85
77.55
77.23
76.91
43.19
37.21
18.41
14.10
O
CH$_3$
O
41
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



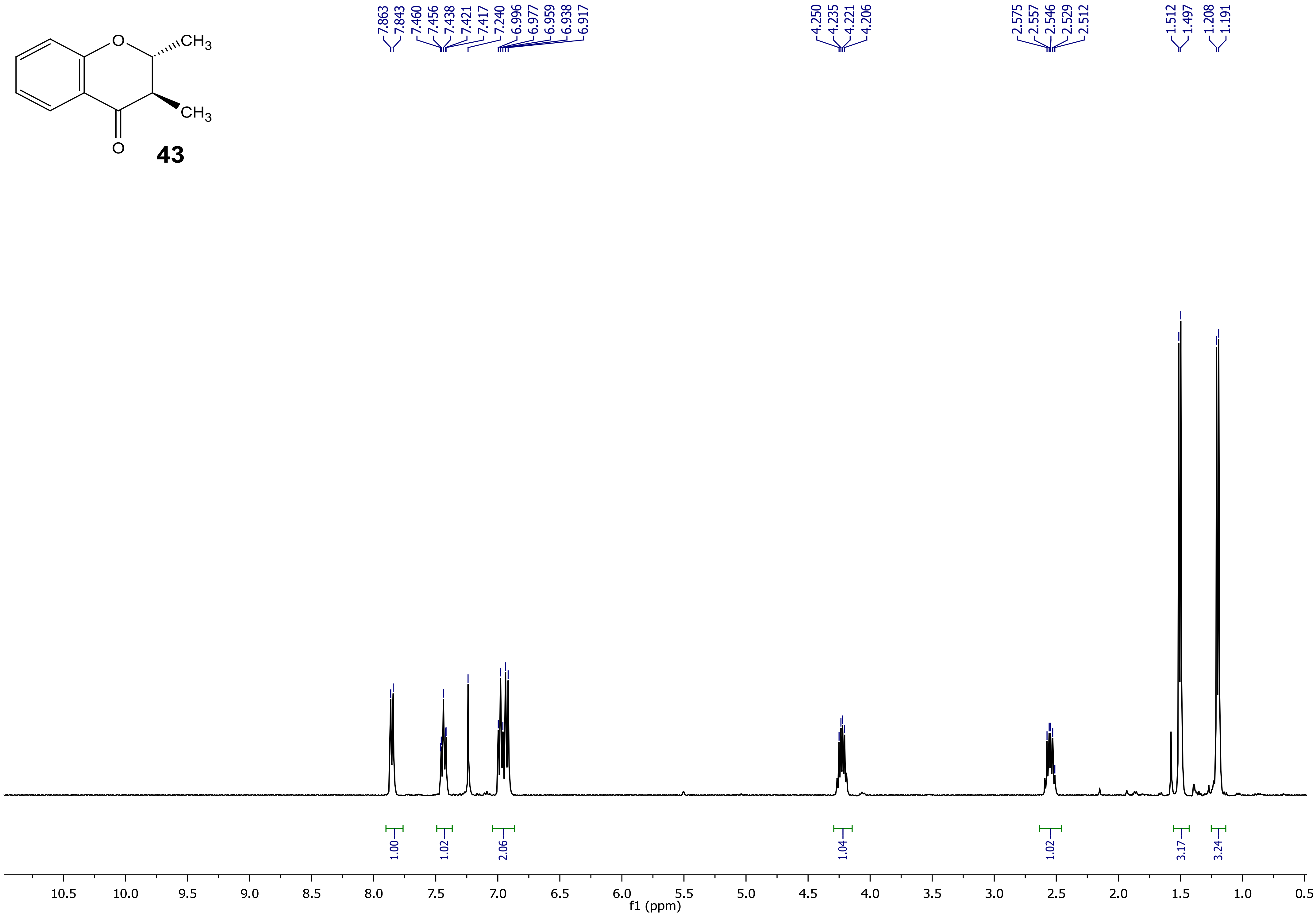
42

7.977
7.961
7.528
7.511
7.494
7.381
7.364
7.345
7.327
7.310
7.292
7.275
7.260
7.073
7.055
7.031
7.010
4.687
4.671
4.667
4.024
4.005
3.988
0.96
1.07
5.87
1.99
2.09
1.00
11.0
10.5
10.0
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
2.0
1.5
1.0
0.5
f1 (ppm)
O
O



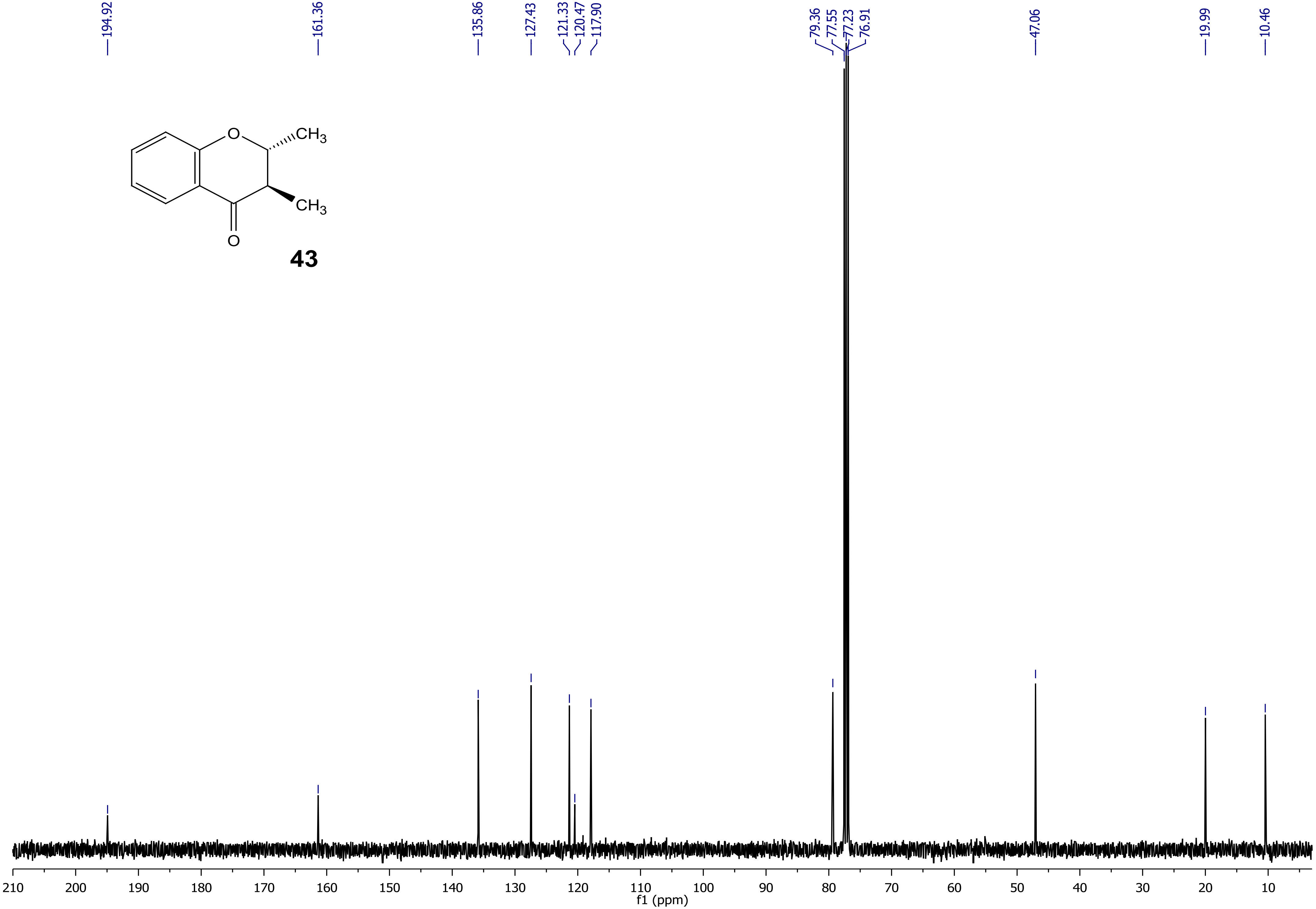
42

192.30
161.77
136.23
135.21
129.08
128.79
127.96
121.80
121.25
118.06
77.55
77.23
76.91
71.71
52.54
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



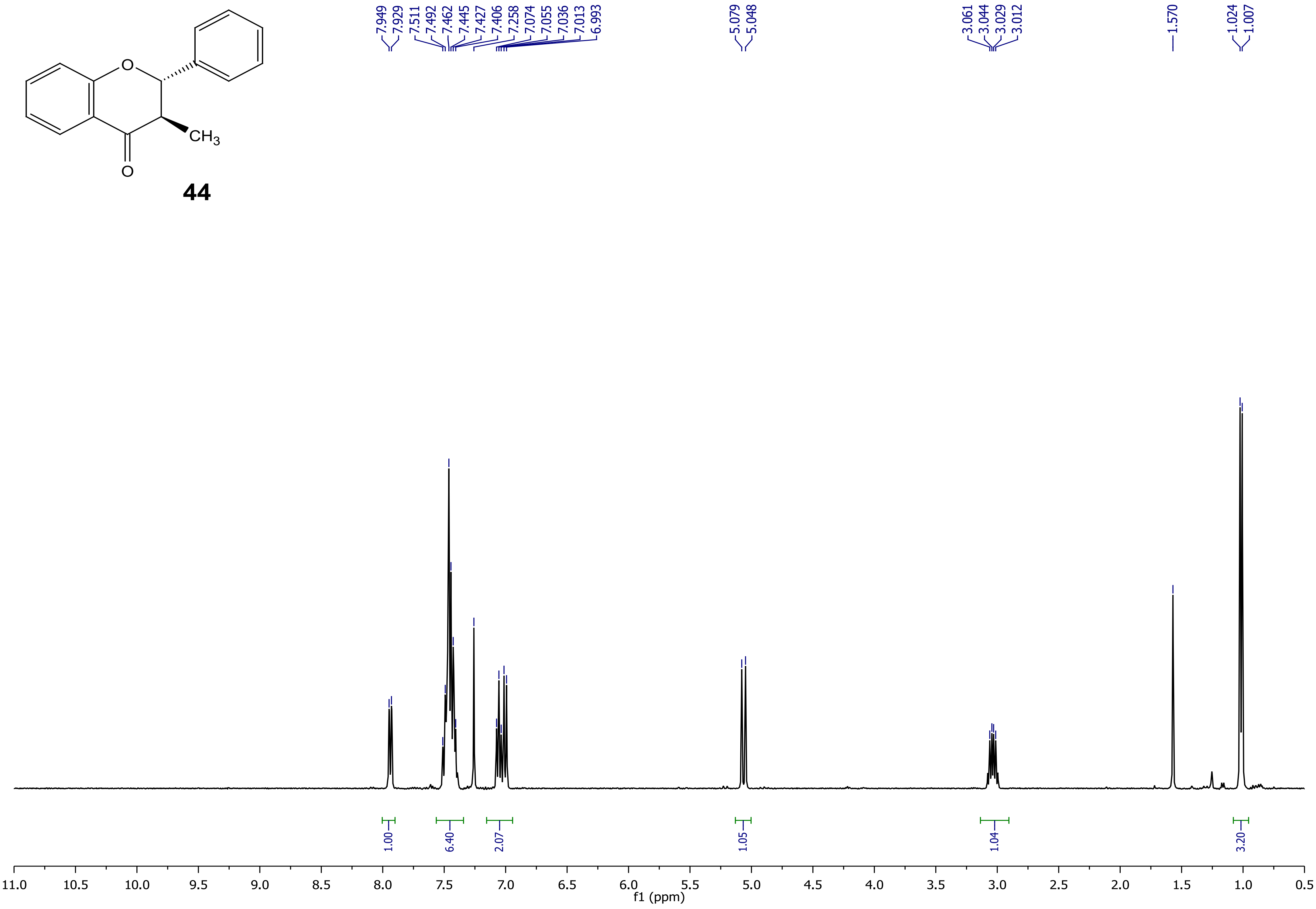
43

7.863
7.843
7.460
7.456
7.438
7.421
7.417
7.240
6.996
6.977
6.959
6.938
6.917
4.250
4.235
4.221
4.206
2.575
2.557
2.546
2.529
2.512
1.512
1.497
1.208
1.191
O
CH3
CH3
O
1.00
1.02
2.06
1.04
1.02
3.17
3.24
10.5
10.0
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
2.0
1.5
1.0
0.5
f1 (ppm)



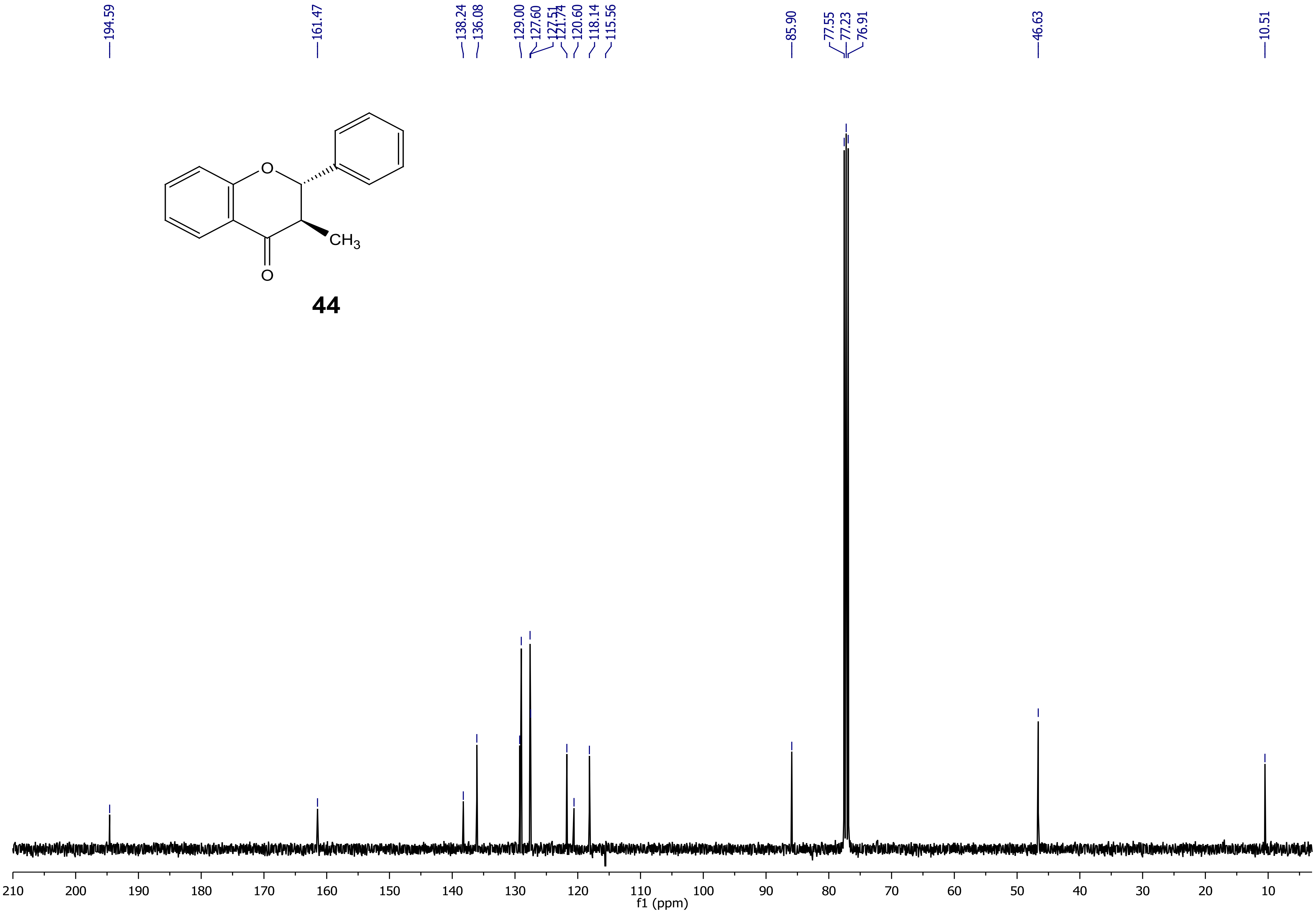
43

194.92
161.36
135.86
127.43
121.33
120.47
117.90
79.36
77.55
77.23
76.91
47.06
19.99
10.46
O
CH3
CH3
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



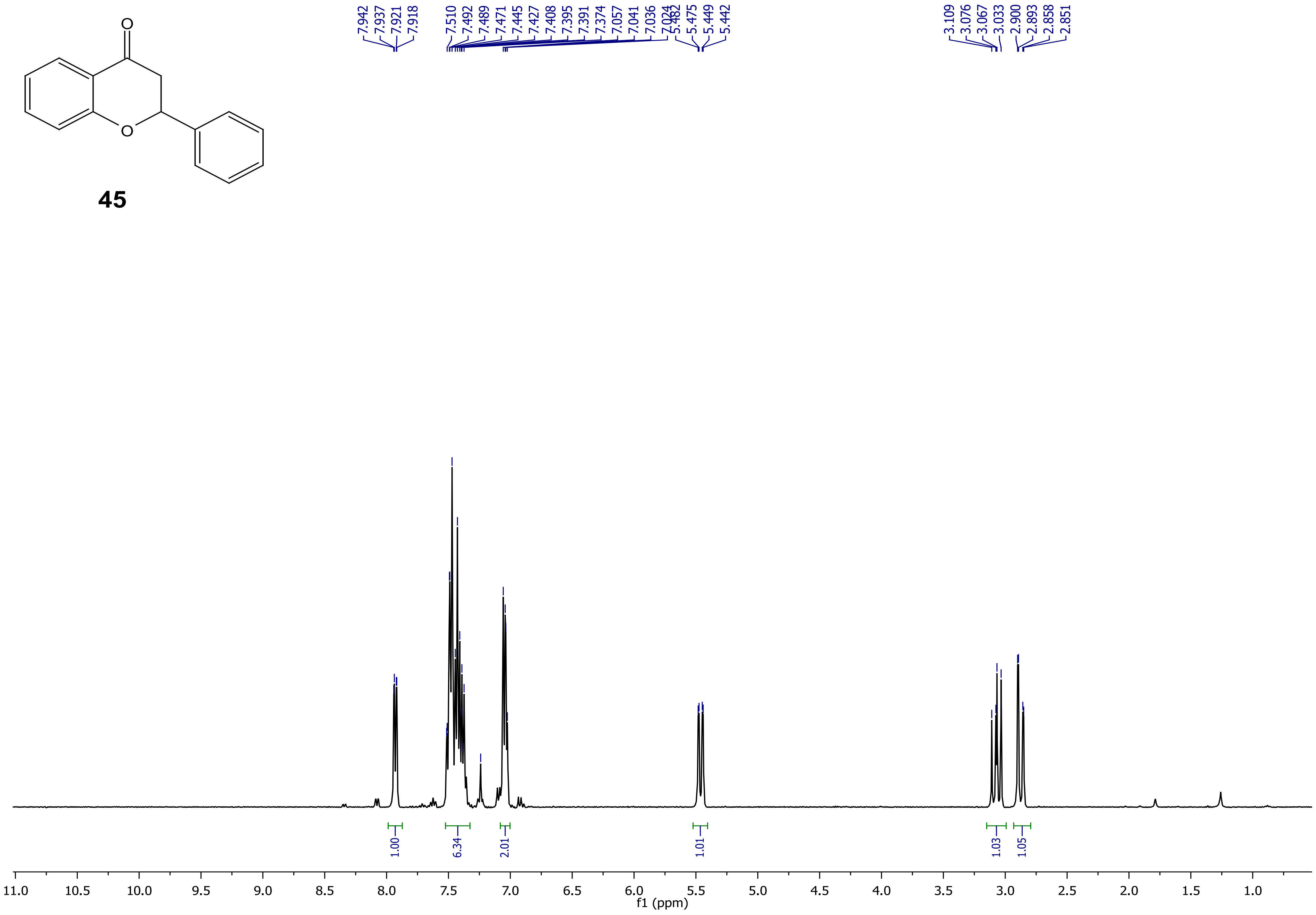
44

CH3
O
O
7.949
7.929
7.511
7.492
7.462
7.445
7.427
7.406
7.258
7.074
7.055
7.036
7.013
6.993
5.079
5.048
3.061
3.044
3.029
3.012
1.570
1.024
1.007
1.00
6.40
2.07
1.05
1.04
3.20
11.0
10.5
10.0
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
2.0
1.5
1.0
0.5
f1 (ppm)



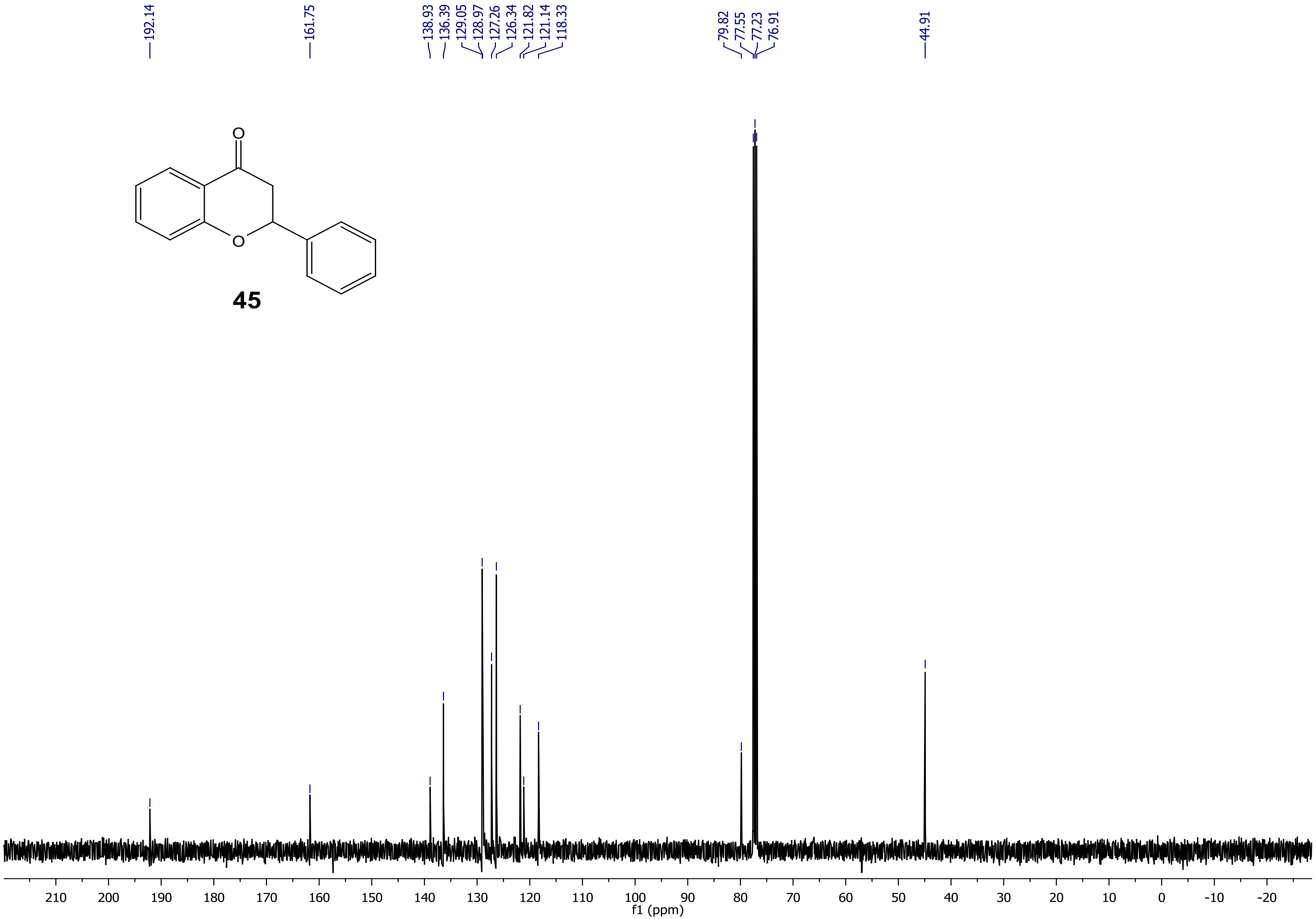
44

194.59
161.47
138.24
136.08
129.00
127.60
127.51
121.74
120.60
118.14
115.56
85.90
77.55
77.23
76.91
46.63
10.51
O
CH3
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



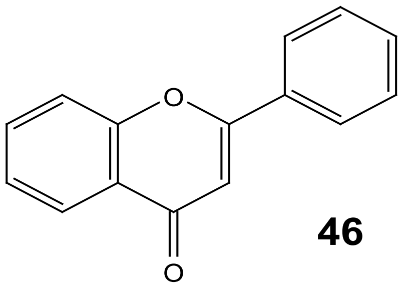
45

7.942
7.937
7.921
7.918
7.510
7.492
7.489
7.471
7.445
7.427
7.408
7.395
7.391
7.374
7.057
7.041
7.036
7.024
5.482
5.475
5.449
5.442
3.109
3.076
3.067
3.033
2.900
2.893
2.858
2.851
1.00
6.34
2.01
1.01
1.03
1.05
11.0
10.5
10.0
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
2.0
1.5
1.0
f1 (ppm)
O

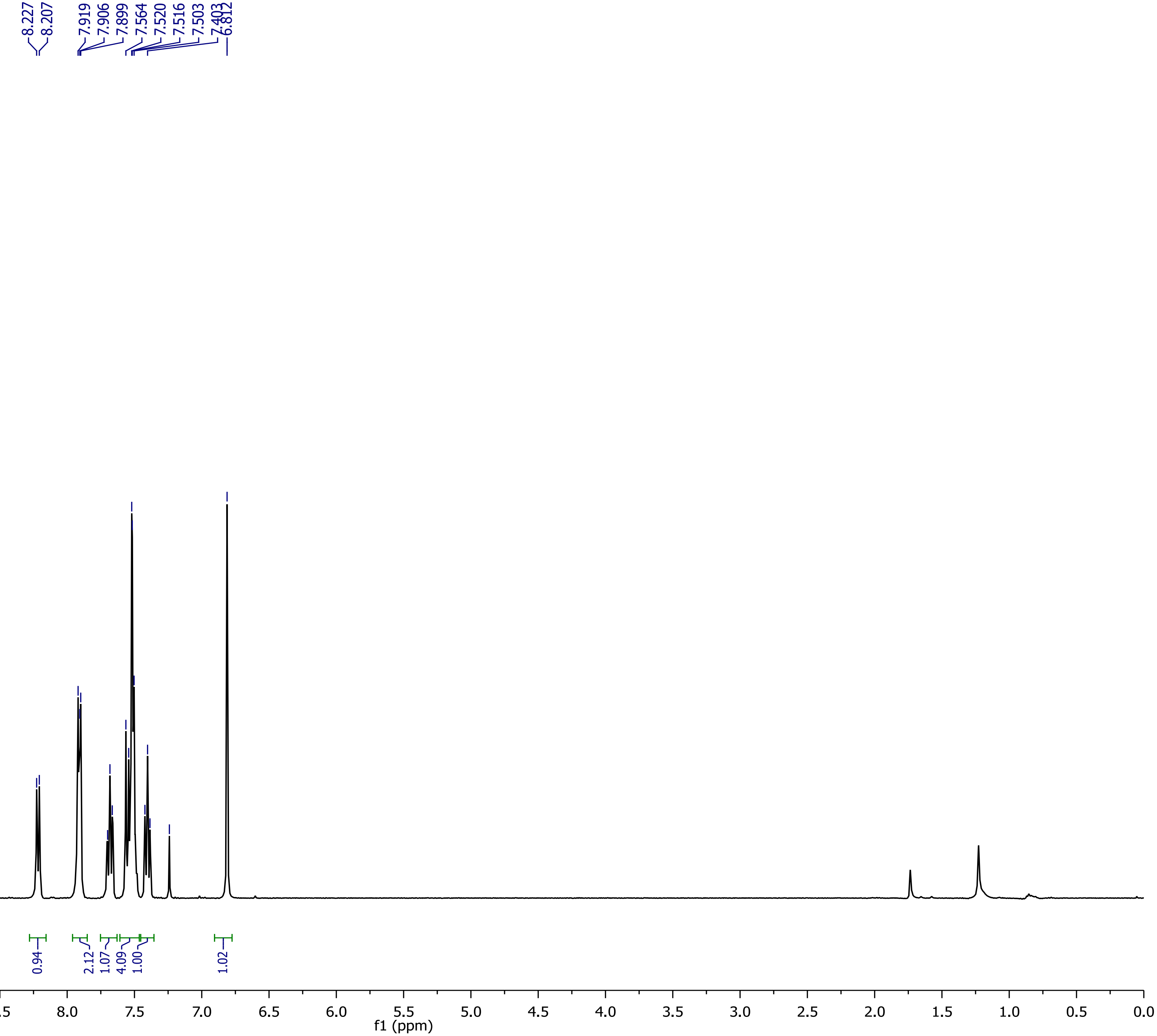


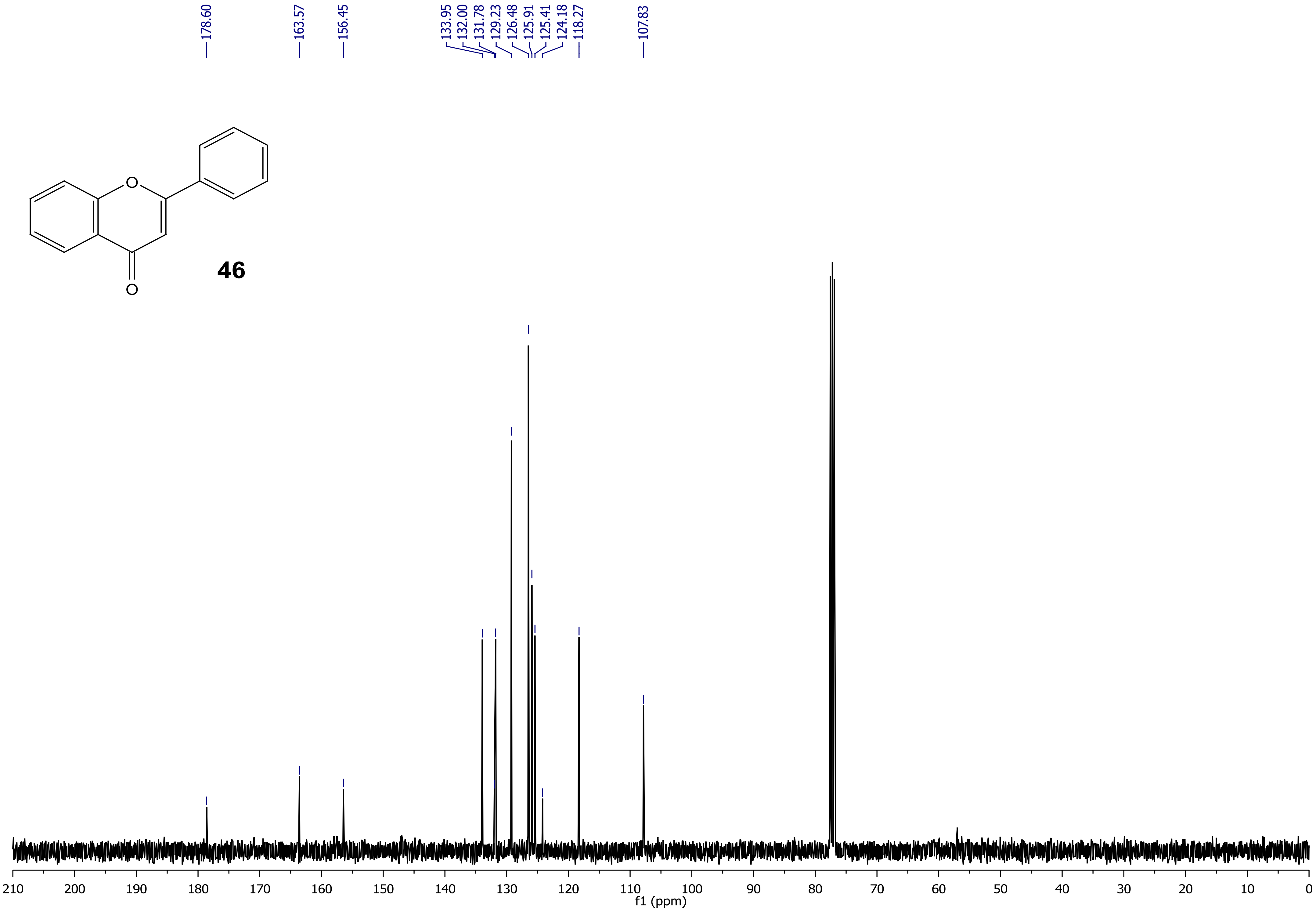
45

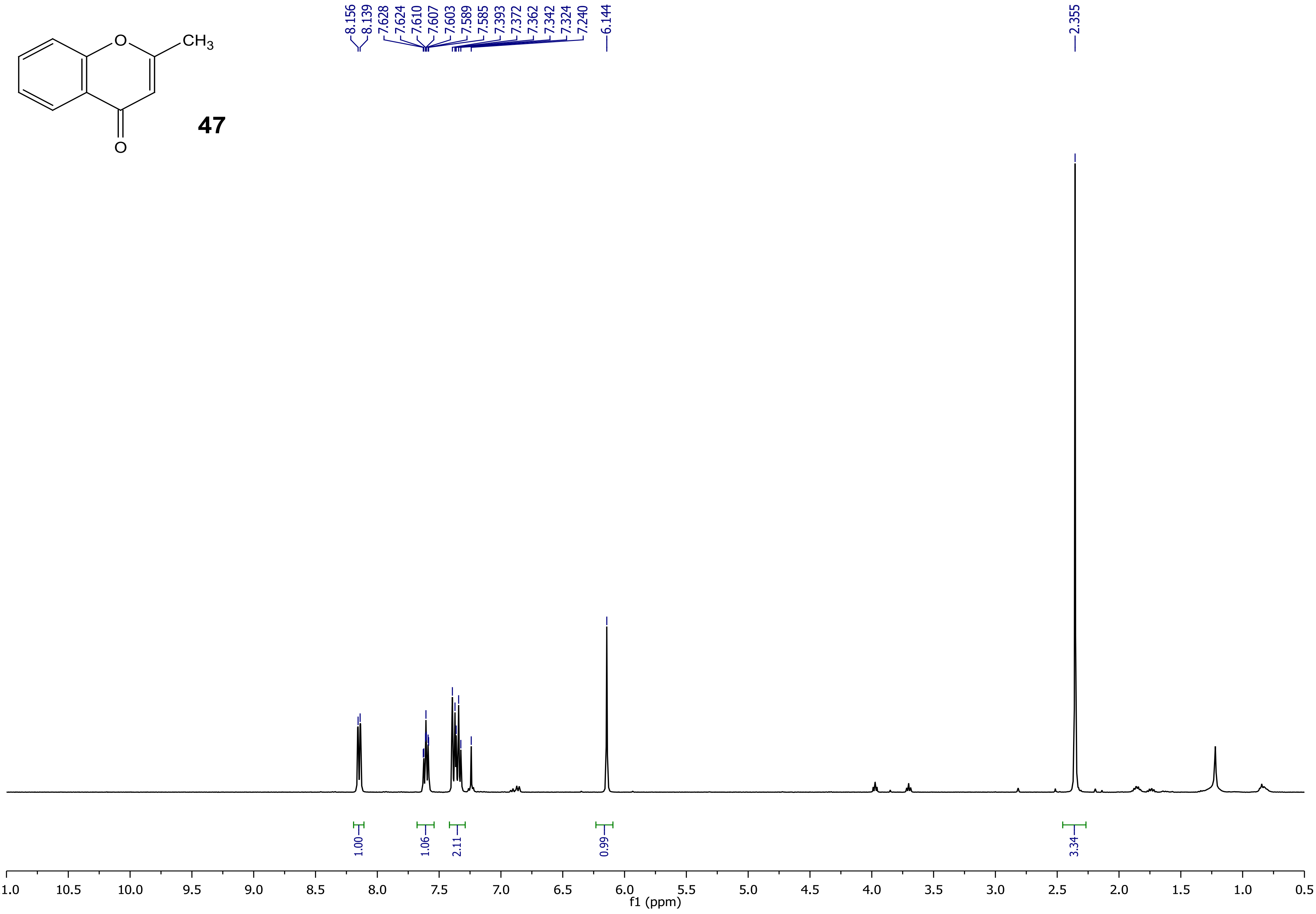
192.14
161.75
138.93
136.39
129.05
128.97
127.26
126.34
121.82
121.14
118.33
79.82
77.55
77.23
76.91
44.91
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



46

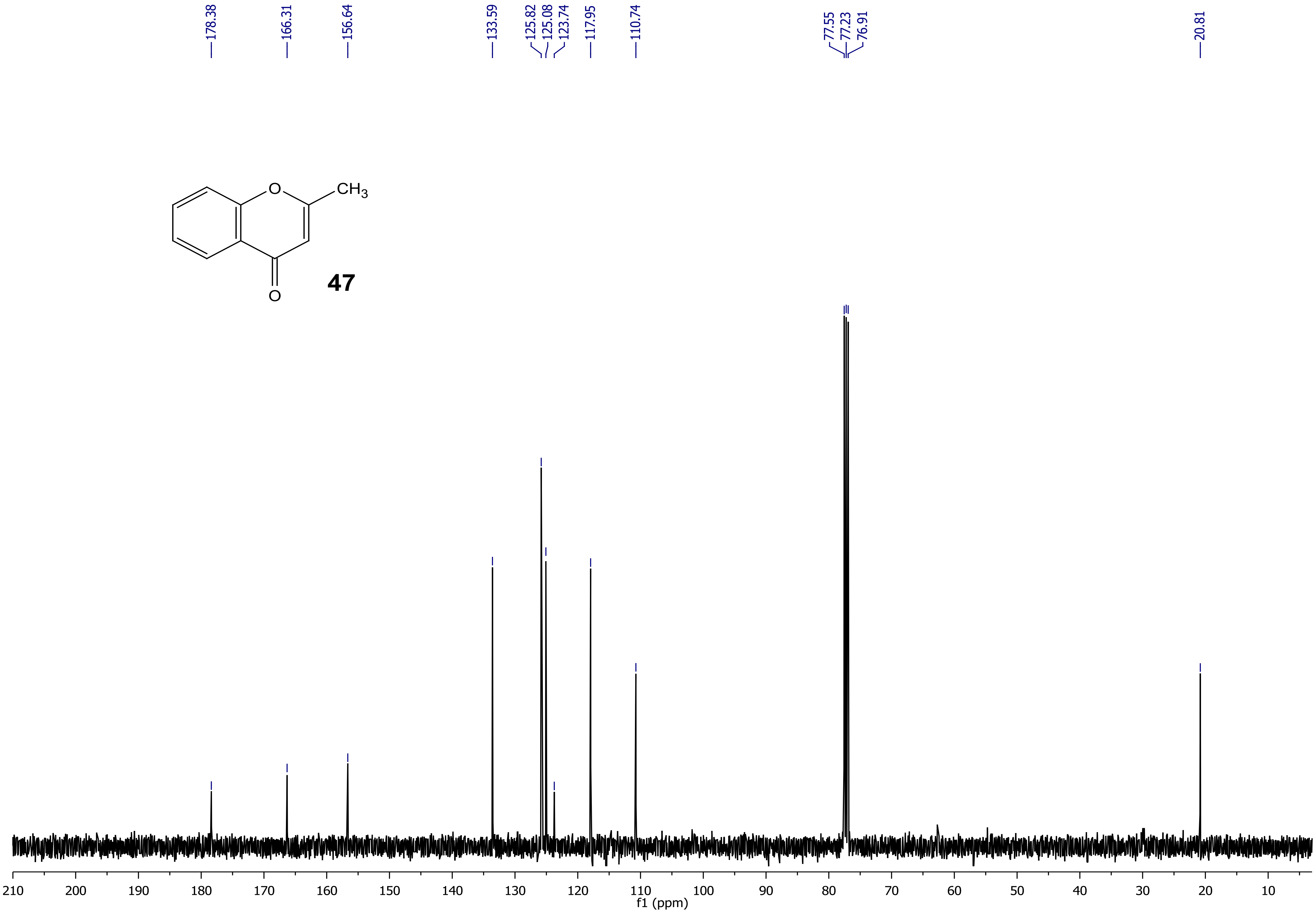

8.227
8.207
7.919
7.906
7.899
7.564
7.520
7.516
7.503
7.403
6.812
0.94
2.12
1.07
4.09
1.00
1.02
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


46
178.60
163.57
156.45
133.95
132.00
131.78
129.23
126.48
125.91
125.41
124.18
118.27
107.83
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



47

CH3
O
O
8.156
8.139
7.628
7.624
7.610
7.607
7.603
7.589
7.585
7.393
7.372
7.362
7.342
7.324
7.240
6.144
2.355
1.00
1.06
2.11
0.99
3.34
11.0
10.5
10.0
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
2.0
1.5
1.0
0.5
f1 (ppm)


178.38
166.31
156.64
133.59
125.82
125.08
123.74
117.95
110.74
77.55
77.23
76.91
20.81
O
CH3
O
47
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)