A Formal Total Synthesis of Dysidiolide

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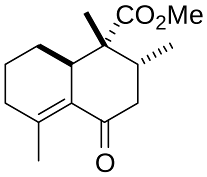
Experimental

General: ^{1}H- and ^{13}C-NMR: Bruker AC 250 and Bruker ARX 400; all spectra were recorded in $CDCl_3$; chemical shifts are calibrated to residual proton resonances in $CDCl_3$ (7.25 ppm and 77.00 ppm, respectively). IR: Jasco FT/IR-430 spectrometer. EI-MS: Flash chromatography: J. T. Baker silica gel 43-60 µm. Thin-layer chromatography: Merck Sil G/UV_{254}. Solvents were distilled prior to use; petroleum ether with a boiling range of 30-50 °C was used. The following abbreviations were used: ps pseudo, qu quintet, q quartet. The following compounds were prepared according to literature procedures: (3*E*)-4-(1-pyrrolidinyl)-3-buten-2-one (**8**),[1] 5-hexenal (**11**) from 5-hexenol,[2,3] methyl 2-(diethoxyphosphoryl)propanoate (**12**),[4] (3*E*)-4-methoxy-3-buten-2-one (**13**).[5]



2

***rac*-Methyl (1*S*,2*R*,8a*R*)-1,2,5-trimethyl-4-oxo-1,2,3,4,6,7,8,8a-octahydro-1-naphthalenecarboxylate** (**2**). To a solution of LDA [prepared at –78 °C from *i*Pr_2NH (410 µl, 2.90 mmol) in THF (2 ml) and *n*BuLi (1.81 ml, 2.90 mmol, 1.6 M in hexanes)] was added dropwise a solution of the diketone **17** (707 mg, 2.64 mmol) in THF (4 ml) at –78 °C. The mixture was stirred for 20 min, then the cooling bath was removed and stirring continued at room temperature for another 90 min. The reaction was quenched by adding 12 N HCl (10 ml) and extracted with Et_2O (3 × 20 ml). The organic extracts were neutralized ($NaHCO_3$), dried

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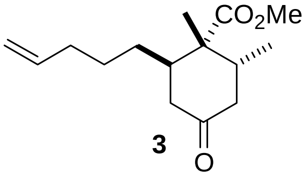
[1] Kozmin, S. A.; Janey, J. M.; Rawal, V. H. *J. Org. Chem.* **1999**, *64*, 3039-3052.

[2] Tufariello, J. J.; Trybulski, E. J. *J. Org. Chem.* **1974**, *39*, 3378-3384.

[3] Craig, D. C.; Edwards, G. L.; Muldoon, C. A. *Synlett* **1997**, 1318-1320.

[4] Gerlach, H.; Wetter, H. *Helv. Chim. Acta* **1974**, *57*, 2306-2321.

($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/Et_2O, 1:1) to provide **2** as a slightly yellow oil (382 mg, 58%). TLC (petroleum ether/Et_2O, 1:1): R_f = 0.63; IR (neat): 1102 (s), 1133 (s), 1254 (s), 1380 (m), 1435 (m), 1683 (s), 1733 (s), 2949 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.91 (d, ^3J=7.2 Hz, 3H, $CHCH_3$), 1.22-1.31 (m, 1H, H-7), 1.26 (s, 3H, CCH_3), 1.44-1.55 (m, 1H, H-8), 1.67-1.75 (m, 1H, H-8), 1.91 (d, J=2.4 Hz, 3H, $=CCH_3$), 2.08-2.13 (m, 3H, H-2, H-6), 2.27 (dd, ^2J=15.9, ^3J=4.5 Hz, 1H, H-3), 2.63 (dd, ^2J=15.3, ^3J=5.3 Hz, 1H, H-3), 3.06-3.10 (m, 1H, H-8a), 3.68 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.85, 19.61, 21.41, 22.62, 24.79, 34.25, 38.53, 38.79, 44.96, 48.89, 51.60, 130.6, 148.6, 176.3, 202.3; MS MS (EI): m/z (%) = 250 (75) [M^+], 191 (100), 175 (70), 135 (37), 121 (32), 91 (23), 79 (18); HRMS (ESI): calcd for $C_{15}H_{22}O_3$ 250.156881; found 250.157872.



3

***rac*-Methyl (1*R*,2*R*,6*R*)-1,2-dimethyl-4-oxo-6-(4-pentenyl)cyclohexanecarboxylate** (**3**). To a cooled (0 °C) suspension of CuI (275 mg, 1.44 mmol) in Et_2O (12 ml) was added methyllithium (2.00 ml, 1.6 M in Et_2O, 3.20 mmol) in a dropwise fashion. To the resulting colorless solution the cyclohexenone **4** (303 mg, 1.28 mmol), dissolved in Et_2O (1.5 ml), was added dropwise. Stirring was continued for 45 min and then the reaction was quenched with satd. NH_4Cl (20 ml). The copper salts were dissolved by adding concentrated NH_3 (15 ml). The mixture was extracted with Et_2O (2 × 25 ml), the combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure to yield 301 mg (93%) of **3** as a slightly yellow oil. TLC (petroleum ether/Et_2O, 2:1): R_f = 0.43; IR (neat): 734 (w), 912 (w), 1119 (w), 1214 (m), 1458 (w), 1719 (vs), 2950 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (d, ^3J=7.1 Hz, 3H, $CHCH_3$), 1.05-1.47 (m, 4H, H-1‘, H-2‘), 1.30 (s, 3H, CH_3), 2.03-2.11 (m, 4H, H-2, H-6, H-3‘), 2.34-2.49 (m, 4H, H-3, H-5), 3.68 (s, 3H, OCH_3), 4.91-4.99 (m, 2H, H-5‘), 5.70-5.78 (m, 1H, H-4‘); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.66, 18.21, 26.63, 31.07, 33.56, 38.50, 39.11, 42.23, 44.40, 48.63, 51.62, 114.6, 138.4, 176.2, 210.7; MS (EI): m/z (%) = 253 (77) [M^+ + H], 192 (50), 138 (88), 123 (72), 95 (72), 69 (67), 41 (100); HRMS (EI): calcd for $C_{15}H_{24}O_3$ 252.17253, found 252.17570.

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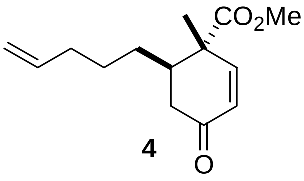
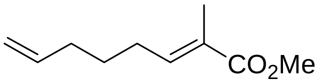
[5] Lienhard, U.; Fahrni, H.-P.; Neuenschwander, M. *Helv. Chim. Acta* **1978**, *61*, 16-09-1621.



4

***rac*-Methyl (1*S*,6*R*)-1-methyl-4-oxo-6-(4-pentenyl)-2-cyclohexene-1-carboxylate** (**4**). A solution of the Diels-Alder adduct **16** (204 mg, 516 μmol) in THF (3.5 ml) was treated with 1.2 N HCl (1.15 ml) and 40% aqueous HF (0.50 ml). The mixture was stirred for 12 h at room temperature before it was neutralized with satd. Na_2CO_3 and extracted with Et_2O (3 × 15 ml). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated to yield the enone **4** as a slightly yellow oil (122 mg, 100%). TLC (petroleum ether/Et_2O, 2:1): $R_f = 0.39$; IR (neat): 796 (w), 912 (w), 1097 (m) 1218 (m), 1263 (s), 1434 (w), 1683 (s), 1736 (s), 2938 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 3H, H-1‘‘), 1.28-1.49 (m, 4H, H-1‘, H-2‘), 1.98-2.04 (m, 2H, H-3‘), 2.16 (dd, ^{2}J=17.7, ^{3}J=13.4 Hz, 1H, H-5), 2.51-2.57 (m, 2H, H-5, H-6), 3.72 (s, 3H, OCH_3), 4.91-4.99 (m, 2H, H-5‘), 5.70-5.77 (m, 1H, H-4‘), 5.96 (d, ^{3}J=10.1 Hz, 1H, H-3), 6.73 (d, ^{3}J=10.1 Hz, 1H, H-2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.44, 25.96, 30.16, 33.43, 38.98, 39.59, 48.51, 52.59, 114.8, 127.9, 138.1, 152.4, 175.0, 198.4; MS (EI): *m/z* (%) = 236 (26) [M$^+$], 209 (38), 195 (100), 177 (93), 121 (98), 112 (86), 79 (67), 42 (93); HRMS (EI): calcd for $C_{14}H_{20}O_3$ 236.14123, found 236.14307.

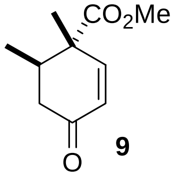


5

Methyl (2*E*)-2-methyl-2,7-octadienoate (**5**). To a suspension of sodium hydride (1.91 g, 47.9 mmol, 60 % in mineral oil) in THF (55 ml) was added methyl 2-(diethoxyphosphoryl)propanoate (**12**) (10.7 g, 47.9 mmol), dissolved in THF (28 ml), in a dropwise fashion. After the addition was complete, the mixture was refluxed for another 15 min. This was follwowed by the dropwise addition of 5-hexenal (**11**) (3.13 g, 31.9 mmol), dissolved in THF (10.0 ml). The resulting mixture was refluxed for additional 60 min. After being cooled to room temperature water (15 ml) was added carefully. The organic layer was dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/Et_2O, 10:1) to yield 3.93 g (71%) of the (*E*)-compound and 0.54 g of the (*Z*)-compound (10%) as colorless oils. (*E*)-compound: TLC (petroleum ether/Et_2O, 10:1): $R_f = 0.62$; IR (neat): 912 (s), 1099 (s), 1193 (s), 1258 (s), 1437 (s), 1648 (s), 1718 (s), 2930 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (ps-qu, ^{3}J=7.2 Hz, 2H, H-5), 1.72 (s, 3H, OCH_3), 1.98 (ps-q, ^{3}J=7.5 Hz, 2H, H-6), 2.09 (ps-q,

^3J=7.4 Hz, 2H, H-4), 3.66 (s, 3H, CCH_3), 4.90-4.99 (m, 2H, $CH{=}CH_2$), 5.70-5.80 (m, 1H, $CH{=}CH_2$), 6.73 (qt, ^4J=1.4, ^3J=7.6 Hz, 1H, H-3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.34, 27.71, 27.96, 33.25, 51.62, 114.9, 127.7, 138.1, 142.2, 168.24; MS (EI): *m/z* (%) = 168 (78) [M^+], 137 (70), 109 (100); HRMS (EI): calcd for $C_{10}H_{16}O_2$ 168.11502, found 163.11448.

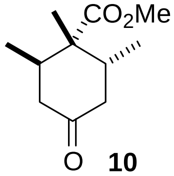
(*Z*)-compound: TLC (petroleum ether/Et_2O, 10:1): R_f = 0.72; IR (neat): 911 (m), 1145 (m), 1197 (m), 1241 (m), 1718 (s), 2927(m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36-1.44 (m, 2 H, H-5), 1.79 (s, 3H, CCH_3), 1.94-2.01 (m, 2H, H-6), 2.34-2.41 (m, 2H, H-4), 3.66 (s, 3H, OCH_3), 4.88-4.94 (m, 2H, $CH{=}CH_2$), 5.71-5.82 (m, 1H, $CH{=}CH_2$), 5.89 (qt, ^4J=1.8, ^3J=7.6 Hz, 1H, H-3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.60, 28.62, 29.02, 33.34, 51.14, 114.6, 127.0, 138.5, 143.1, 168.4; MS (EI): *m/z* (%) = 168 (50) [M^+], 136 (60), 127 (68), 109 (100), 95 (65); HRMS (EI): calcd for 168.11502, found 168.11462.



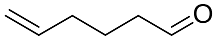
9

***rac*-Methyl (1*R*,6*S*)-1,6-dimethyl-4-oxo-2-cyclohexene-1-carboxylate** (**9**). To a solution of LDA [prepared at –78 °C from *i*Pr_2NH (1.02 ml, 7.18 mmol) in THF (5.5 ml) and *n*BuLi (2.60 ml, 7.18 mmol, 2.7 M in heptane)] was added dropwise the vinylogous amide **8** (1.00 g, 7.18 mmol). The dark yellow solution was stirred for 45 min at –78 °C before methyl tiglate (820 mg, 7.18 mmol) was added. The resulting red mixture was stirred for further 30 min, then the cooling bath was removed and stirring was continued for 4 h. The reaction was quenched with satd. NH_4Cl and the mixture extracted with Et_2O (3 × 25 ml). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. Purification of the residue by flash chromatography (petroleum ether/Et_2O, 1:1) yielded 693 mg (53%) of the enone **9** as a yellow liquid that crystallized at 0 °C, m.p. 57.8-58.5 °C. TLC (petroleum ether/Et_2O, 1:1): R_f = 0.49; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.97 (d, ^3J = 7.0 Hz, 3H, $CHCH_3$), 1.27 (s, 3H, CCH_3), 2.22 (dd, *J*=17.1, 11.6 Hz, 1H, H-5), 2.40 (dd, *J*=17.1, 4.6 Hz, 1H, H-5), 2.60-2.75 (m, 1H, H-6), 3.72 (s, 3H, OCH_3), 5.95 (d, ^3J=10.1 Hz, 1H, H-3), 6.76 (d, ^3J=10.1 Hz, 1H, H-2); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 16.28, 16.69, 34.89, 41.93, 48.08, 52.54, 127.9, 151.9, 174.9, 198.4; MS (EI): *m/z (%)* = 183 (6) [M^+ + H], 140 (30), 123 (52), 112 (60), 97 (46), 95 (74), 79 (90), 77 (61), 67 (100), 55 (57), 53 (89), 39 (58); HRMS (EI): calcd for $C_{10}H_{14}O_3$ 182.09429, found 182.09359.

X-ray structure determination of **9**: Crystal data: $C_{10}H_{14}O_3$, M_r = 182.21, a = 24.808(2), b = 5.9534(5), c = 13.2719(8) Å, α = 90, β = 96.887(6), γ = 90 °, Z = 8, $d_{calcd.}$ = 1.244 g cm^{-3}, monoclinic, space group C2/c. – Data collection: Enraf-Nonius CAD4 diffractometer, Cu-K_α = 1.54184 Å, graphite monochromator, crystal size: 0.80 × 0.25 x 0.10 mm, measurement temperature = 213 K, omega scan mode, Θ range = 6.72-64.93 deg, reflections collected = 3033, number of reflections observed, $I > 2\sigma$ = 1142, linear absorption coefficient = 0.748 mm^{-1}. – Structural analysis and refinement: full-matrix least squares on F^2, hydrogen positions were calculated, goodness of fit on F^2, S = 1.045, final R_1 value = 0.0599, wR_2 = 0.1519, programs SHELXS-97 and SHELXL-97.[6]


10

Methyl (2*R*,6*S*)-1,2,6-trimethyl-4-oxocyclohexanecarboxylate (**10**). To a cooled (0 °C) suspension of CuI (677 mg, 3.56 mmol) in Et_2O (29 ml) was added dropwise methyllithium (4.50 ml, 1.6 M in Et_2O, 7.12 mmol) to afford a clear, colorless solution. This was followed by the dropwise addition of the cyclohexenone **9** (575 mg, 3.16 mmol), dissolved in Et_2O (4 ml). The mixture was stirred for 90 min and then poured onto satd. NH_4Cl (30 ml). NH_3 (8 ml) conc. was added and the mixture extracted with Et_2O (3 × 30 ml). The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure to afford 466 mg (74%) of a yellow liquid. TLC (petroleum ether/Et_2O, 1:1): R_f = 0.55; IR (neat): 1123 (vs), 1350 (w), 1382 (m), 1444 (w), 1723 (w), 1736 (w), 2864 (s), 2977 (vs) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.88 (d, *J*=7.1 Hz, 3H, CH_3), 0.92 (d, *J*=7.0 Hz, 3H, CH_3), 1.29 (s, 3H, CCH_3), 2.02-2.66 (m, 6H, H-3, H-5, H-2, H-6), 3.67 (s, 3H, OCH_3); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 16.69, 16.82, 18.24, 33.80, 38.71, 44.50, 45.34, 48.13, 51.63, 176.1, 210.7; MS (EI): *m/z* (%) = 198 (14) [M^+], 138 (14), 128 (17), 84 (65), 69 (100), 55 (34), 41 (38); HRMS (EI): calcd for $C_{11}H_{18}O_3$ 198.12559, found 198.12989.


11

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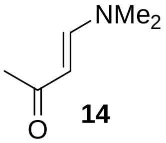
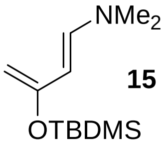
[6] Sheldrick, G. M. **1997**, *Universität Göttingen, Germany*.

5-Hexenal (**11**). To a cooled (–78 ºC) solution of $(COCl)_2$ (10.45 ml, 119.8 mmol) in CH_2Cl_2 (50 ml) was added dropwise DMSO in CH_2Cl_2 (20 ml). After the addition was complete, the mixture was stirred for another 20 min, then 5-hexen-1-ol (10.00 g, 99.84 mmol) in CH_2Cl_2 (40 ml) was added dropwise and the mixture stirred for 18 h at -78 °. This was followed by the addition of NEt_3 (61.0 ml, 439.3 mmol) and warming of the mixture to room temperature. It was washed with ice-cold 1 M $KHSO_4$ (250 ml) and satd. $NaHCO_3$ (250 ml). The organic layer was dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified by distillation to yield 7.198 g (74%) of **11** as a colorless liquid; b.p. 57-59 °C (80 mbar). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.65-1.77 (m, 2H, H-3), 2.03-2.12 (m, 2H, H-4), 2.43 (dt, ^3J=1.9, ^3J=7.4 Hz, 2H, H-2), 4.95-5.05 (m, 2H, H-6), 5.67-5.83 (m, 1H, H-5), 9.75 (t, ^3J=1.5 Hz, 1H, CHO); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.15, 32.93, 43.08, 115.5, 137.5, 202.4.



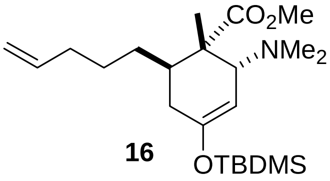
14

(3*E*)-4-Dimethylamino-3-buten-2-one (**14**)[1]. To a solution of (3*E*)-4-methoxy-3-buten-2-one (**13**) (8.08 g, 80.7 mmol) in CH_2Cl_2 (20 ml) was slowly added dimcarb (5.17 ml, 40.4 mmol) at room temperature and the mixture was stirred for 12 h. The solvent was removed under reduced pressure and the residue distilled to give 7.97 g (87%) of the vinylogous amide **14** as a yellow liquid, b.p. 53 °C (0.25 mbar); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.99 (s, 3H, $C(O)CH_3$), 2.82 (s, br, 6 H, $N(CH_3)_2$), 4.93 (d, J=12.8 Hz, 1H, C(O)CH), 7.36 (d, J=12.8 Hz, 1H, Me_2NCH); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 27.2, 36.6, 44.4, 96.6, 152.5, 194.9.



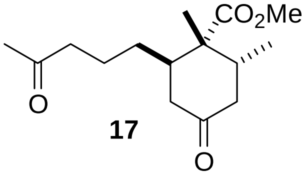
15

(1*E*)-3-{[*tert*-Butyl(dimethyl)silyl]oxy}-*N*,*N*-dimethyl-1,3-butadien-1-amine (**15**). This compound was prepared after a slightly modified procedure according to Rawal et al.: To a cooled (-78 ^{o}C) solution of $KN(SiMe_3)_2$ (42.0 ml, 21.0 mmol, 0.5 M in toluene) was added the ketone **14** (2.26 g, 20.0 mmol), dissolved in THF (17 ml) over a period of 20 min. The solution was allowed to warm to -30 ^{o}C over 2 h, then it was recooled to -78 ^{o}C. At this point, a solution of tBuMe$_2$SiCl (3.32 g, 22.0 mmol) in THF (15 ml) was added dropwise within 20 min. After 30 min the cooling bath was removed and the mixture allowed to reach room temperature. Most of the solvent was removed under reduced pressure. The mixture was treated with Et_2O (200 ml), 2 spoons of dry celite were added, and the slurry filtered through a pad of celite. The filtrate was concentrated under reduced pressure and the resulting residue purified by vacuum distillation to yield 2.41 g (53%) of a pale yellow liquid, b.p. 49-50 ^{o}C (0.5 mbar). The spectral data are identical to those reported in the literature.[1]



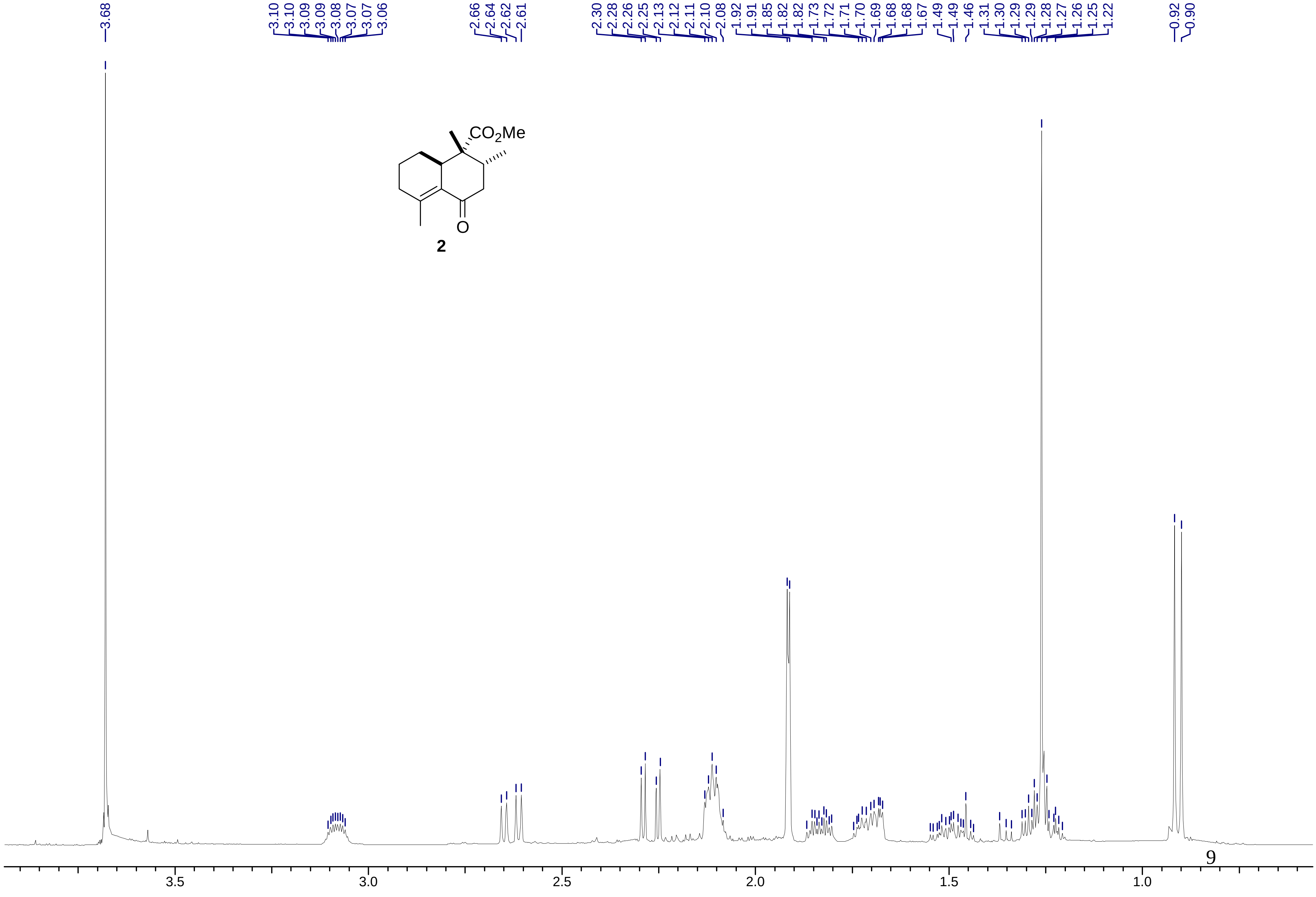
16

***rac*-Methyl (1*R*,2*S*,6*S*)-4-{[*tert*-butyl(dimethyl)silyl]oxy}-2-(dimethylamino)-1-methyl-6-(4-pentenyl)-3-cyclohexene-1-carboxylate** (**16**). A solution of 1-(dimethylamino)-3-(*tert*-butyldimethylsiloxy)-1,3-butadiene (**15**) (2.47 g, 10.8 mmol) and methyl (2*E*)-2-methyl-2,7-octadienoate (**5**) (2.74 g, 16.3 mmol) in toluene (22 ml) was stirred for 5 days at 115 °C. The solvent was removed under reduced pressure and the residue purified by flash chromatography (petroleum ether/Et_2O, 4:1) to yield 1.67 g (49%) of the cyclohexene **16** as a slightly yellow oil. TLC (petroleum ether/Et_2O, 4:1): R_f = 0.20; IR (neat): 780 (m), 838 (s), 914 (s), 1181 (s), 1195 (s), 1252 (m), 1672 (w), 1737 (s), 2859 (m), 2931 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 0.14, 0.15 (2 s, 3H each, $Si(CH_3)_2$), 0.92 (s, 9H, *t*Bu), 1.05 (s, CCH_3), 1.31-1.62 (m, 5H, H-6,CH_2 side-chain), 1.98-2.10 (m, 2H, allylic CH_2 side-chain), 2.20 (s, 6H, $N(CH_3)_2$), 2.24-2.37 (m, 2H, H-5), 3.04 (d, ^3J=4.9 Hz, 1H, H-2), 3.65 (s, 3H, OCH_3), 4.79 (d, ^3J=5.3 Hz, H-3), 4.90-5.01 (m, 2H, alkenyl-H), 5.75-5.85 (m, 1H, alkenyl-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = -4.38, -4.30, 17.06, 17.99, 25.69, 27.41, 33.06, 33.15, 33.95, 34.56, 43.68, 51.05, 51.22, 68.62, 97.74, 114.2, 139.0, 152.3, 176.1; MS (EI): *m/z* (%) = 395 (25) [M^+], 351 (23), 308 (38), 156 (100), 73 (30); HRMS (EI): calcd for $C_{22}H_{41}NO_3$ 395.28556, found 395.28375.



17

***rac*-Methyl (1*R*,2*R*,6*R*)-1,2-dimethyl-4-oxo-6-(4-oxopentyl)cyclohexanecarboxylate** (**17**). In a schlenk flask fitted with an oxygen filled balloon a suspension of $PdCl_2$ (24.5 mg, 138 μmol) and CuCl (137 mg, 1.38 mmol) in DMF/H_2O 7:1 (0.8 ml) was stirred for 60 min. Afterwards, the alkene **3** (348 mg, 1.38 mmol), dissolved in DMF/H_2O 7:1 (0.3 ml), was added and the mixture stirred for 48 h under an oxygen atmosphere. The reaction was then quenched by adding ice-cold 3 N HCl (4 ml). The mixture was extracted with Et_2O (2 × 10 ml), the combined organic extracts were dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/Et_2O, 1:1) to yield 241 mg (65%) of **17** a slightly yellow oil. TLC (petroleum ether/Et_2O, 1:1): R_f = 0.13; IR (neat): 1119 (w), 1213 (w), 1273 (w), 1718 (vs), 2952 (w) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 0.84 (d, ^3J=7.0 Hz, 3H, C(H)CH_3), 0.99-1.69 (m, 4H, H-1‘, H-2‘), 1.27 (s, 3H, CCH_3), 1.97-2.15 (m, 2H, H-2, H-6), 2.07 (s, 3H, $C(O)CH_3$), 2.19-2.54 (m, 6H, H-3, H-5, H-3‘); ^{13}C-NMR (63 MHz, $CDCl_3$): δ = 16.65, 17.95, 21.38, 29.73, 31.16, 38.07, 39.24, 42.09, 43.15, 44.22, 48.54, 51.65, 176.1, 208.4, 210.3; MS (EI): *m/z* (%) = 269 (16) [M^+ + H], 208 (34), 151 (22), 123 (21), 69 (18), 43 (100); HRMS (EI): calcd for $C_{15}H_{24}O_4$ 268.16744, found 268.17050.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2.61
2.30
2.28
2.26
2.25
2.13
2.12
2.11
2.10
2.08
1.92
1.91
1.85
1.82
1.73
1.72
1.71
1.70
1.69
1.68
1.68
1.67
1.49
1.49
1.46
1.31
1.30
1.29
1.29
1.28
1.27
1.26
1.25
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0.90
CO2Me
O
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2.5
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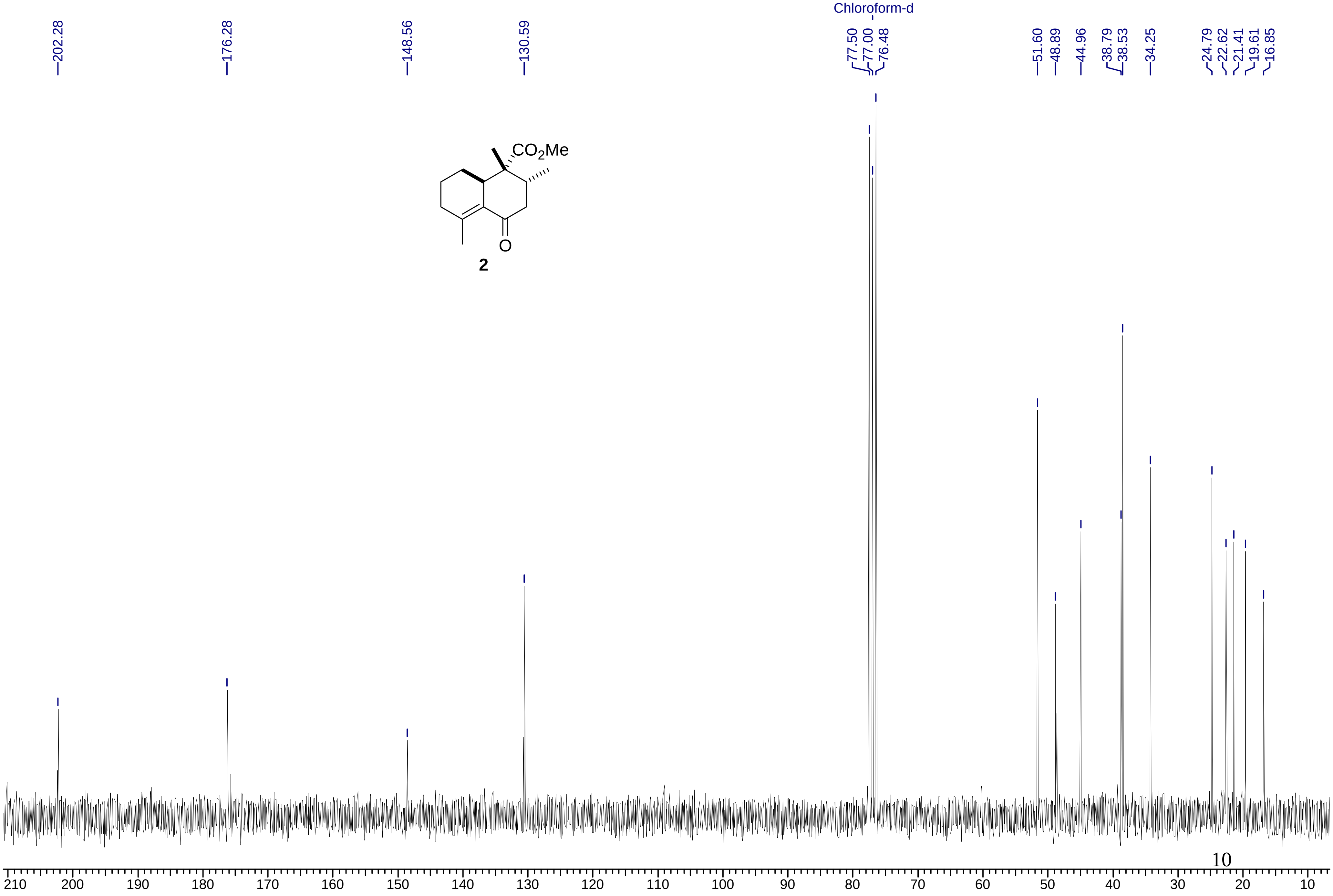
1.5
1.0

2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38.53
34.25
24.79
22.62
21.41
19.61
16.85
CO$_2$Me
O
2
210
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80
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50
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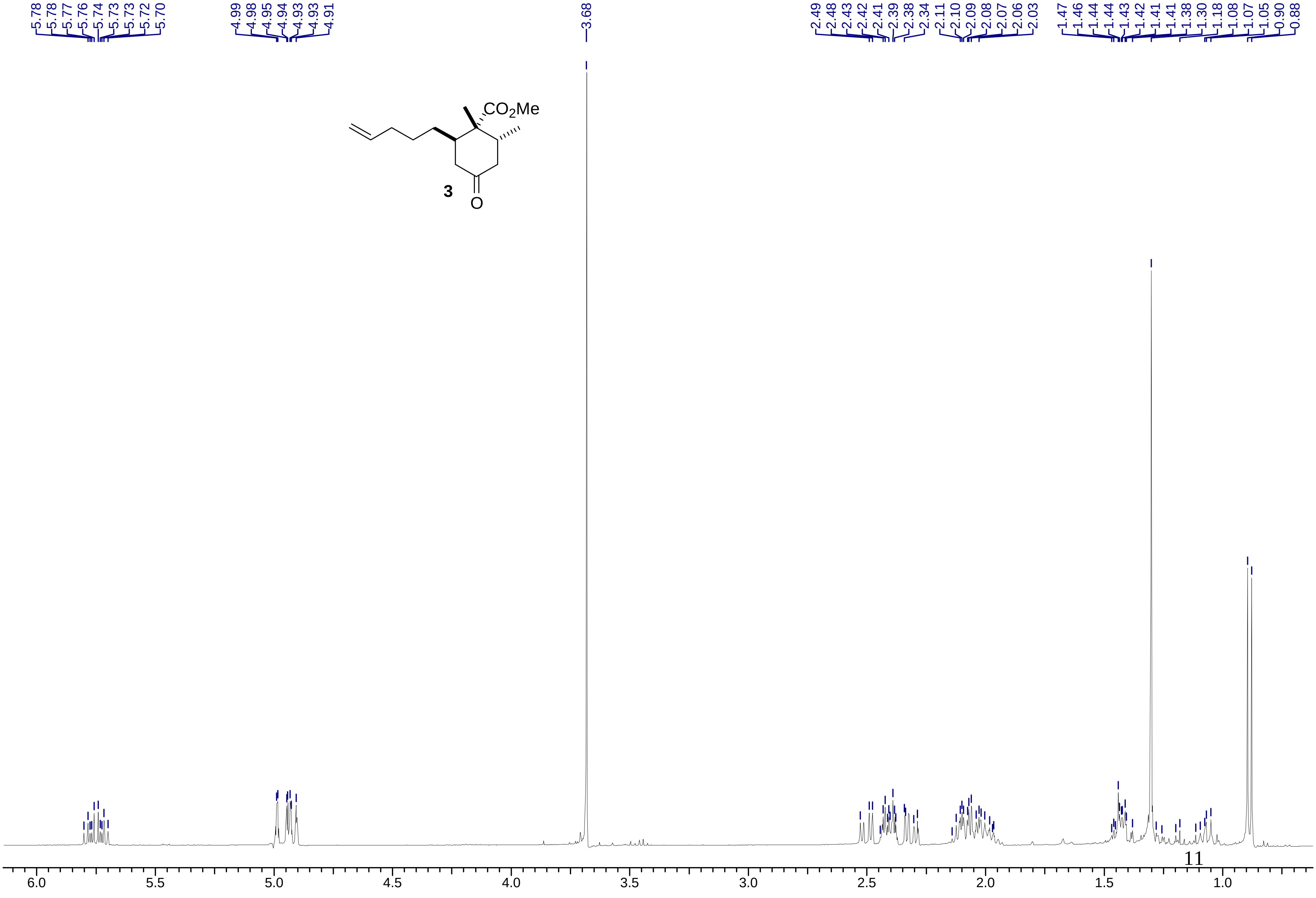
30
20
10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4.93
4.93
4.91
3.68
2.49
2.48
2.43
2.42
2.41
2.39
2.38
2.34
2.11
2.10
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2.08
2.07
2.06
2.03
1.47
1.46
1.44
1.44
1.43
1.42
1.41
1.41
1.38
1.30
1.18
1.08
1.07
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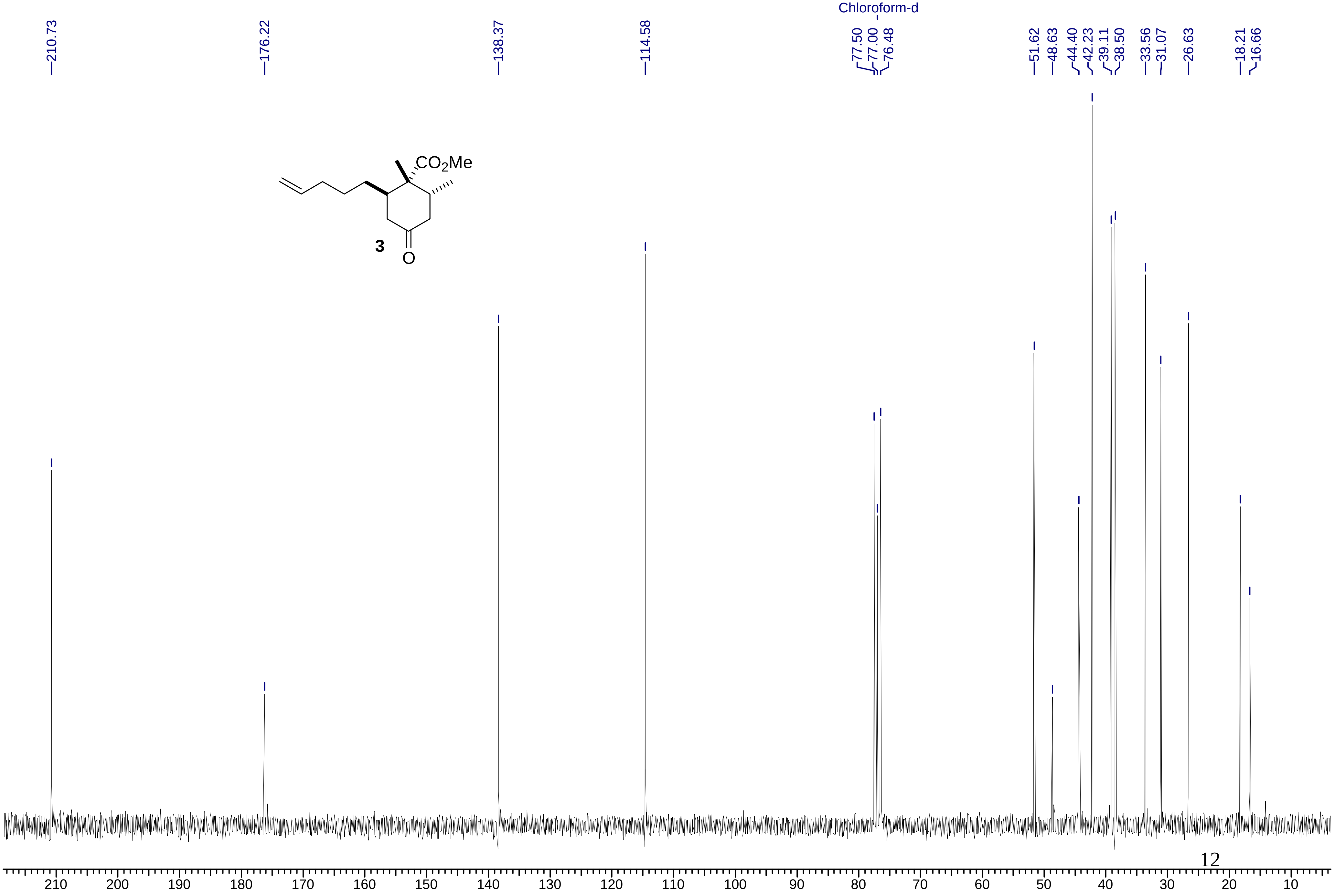
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38.50
33.56
31.07
26.63
18.21
16.66
CO_2Me
O
3
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20
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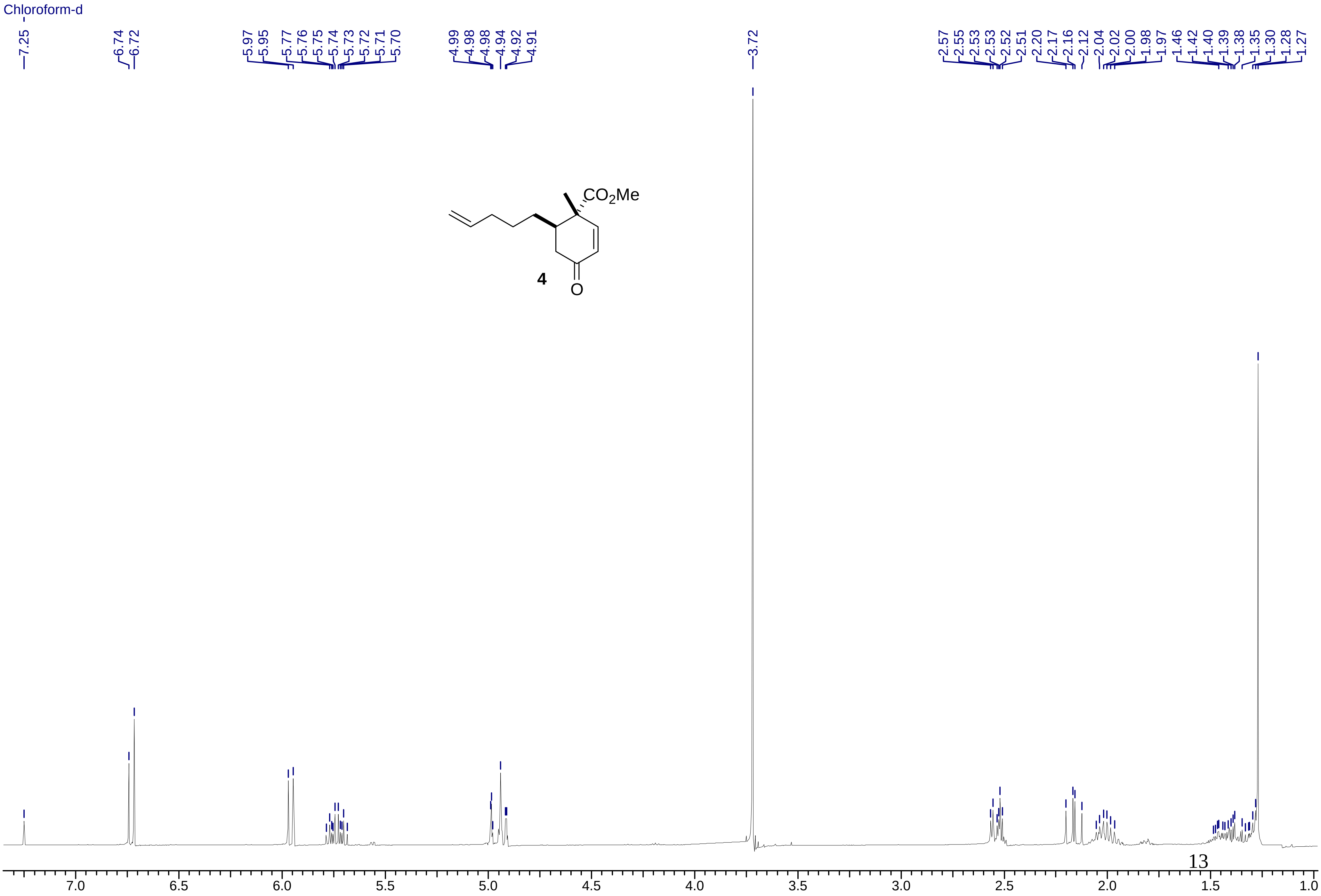
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5.71
5.70
4.99
4.98
4.98
4.94
4.92
4.91
3.72
2.57
2.55
2.53
2.53
2.52
2.51
2.20
2.17
2.16
2.12
2.04
2.02
2.00
1.98
1.97
1.46
1.42
1.40
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1.38
1.35
1.30
1.28
1.27
CO_2Me
O
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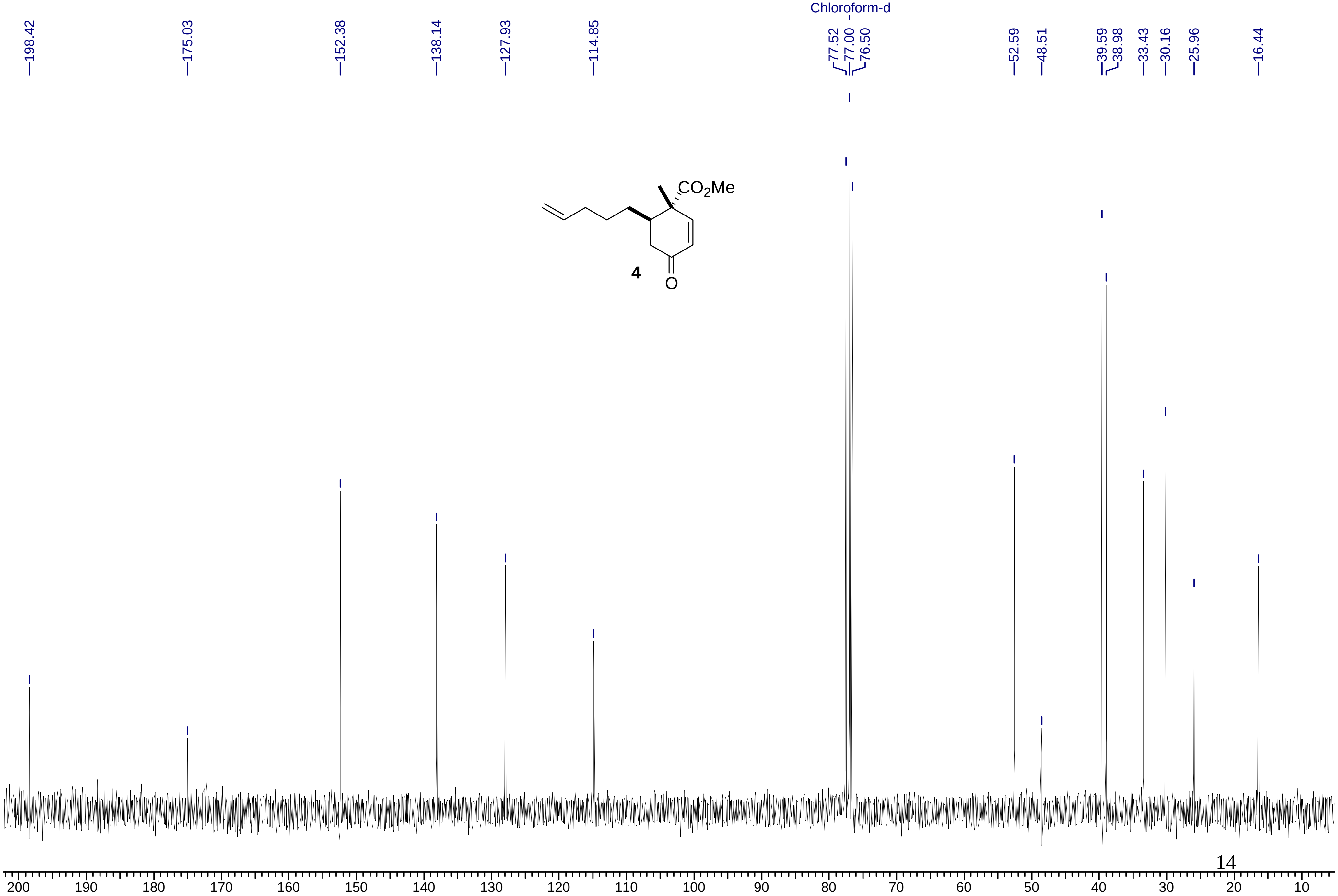
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48.51
39.59
38.98
33.43
30.16
25.96
16.44
CO2Me
O
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160
150
140
130
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80
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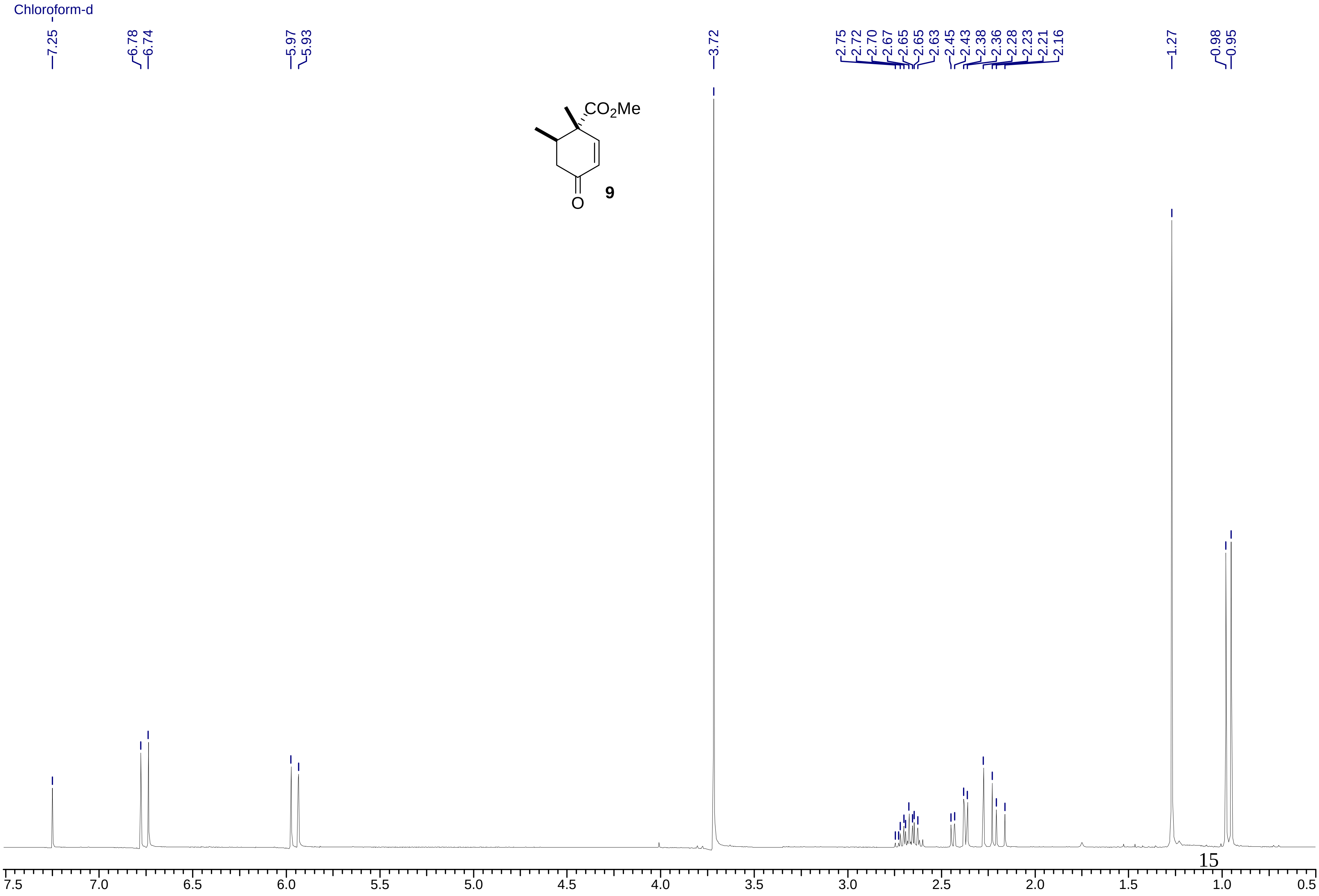

Chloroform-d
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6.74
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5.93
3.72
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2.65
2.63
2.45
2.43
2.38
2.36
2.28
2.23
2.21
2.16
1.27
0.98
0.95
CO2Me
O
9
7.5
7.0
6.5
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4.5
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2.5
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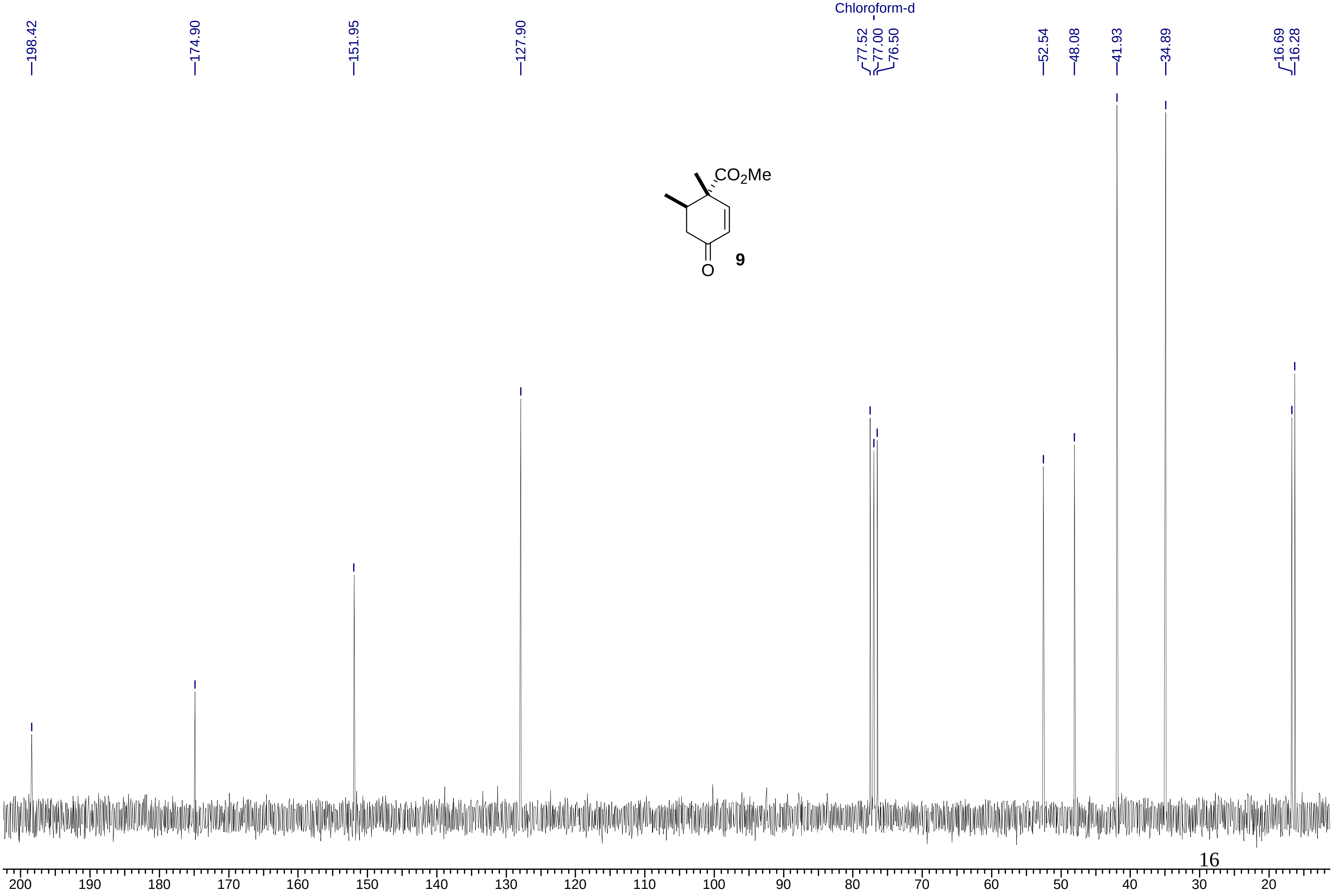

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174.90
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127.90
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76.50
52.54
48.08
41.93
34.89
16.69
16.28
CO$_2$Me
O
200
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150
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120
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80
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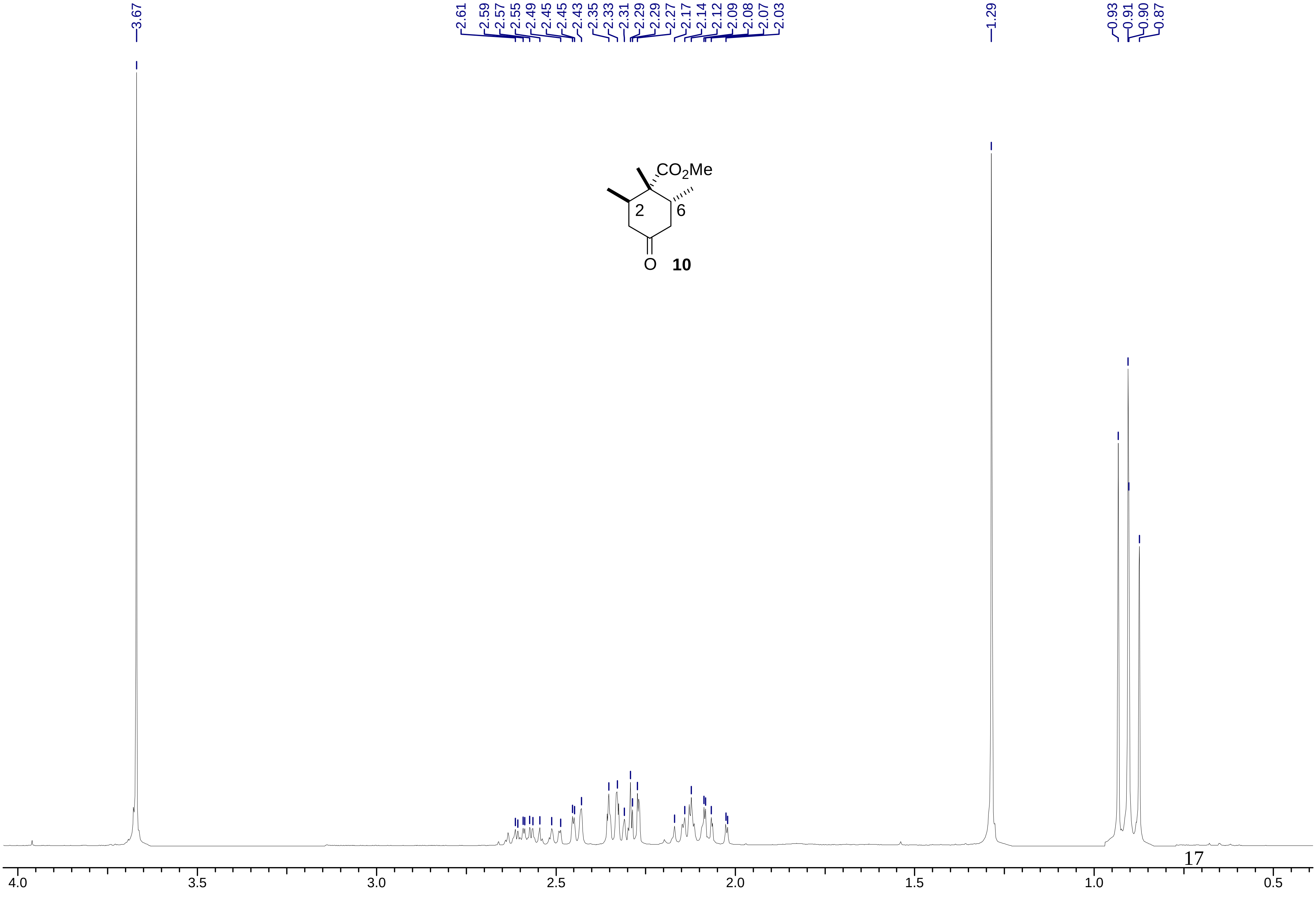
50
40
30
20

9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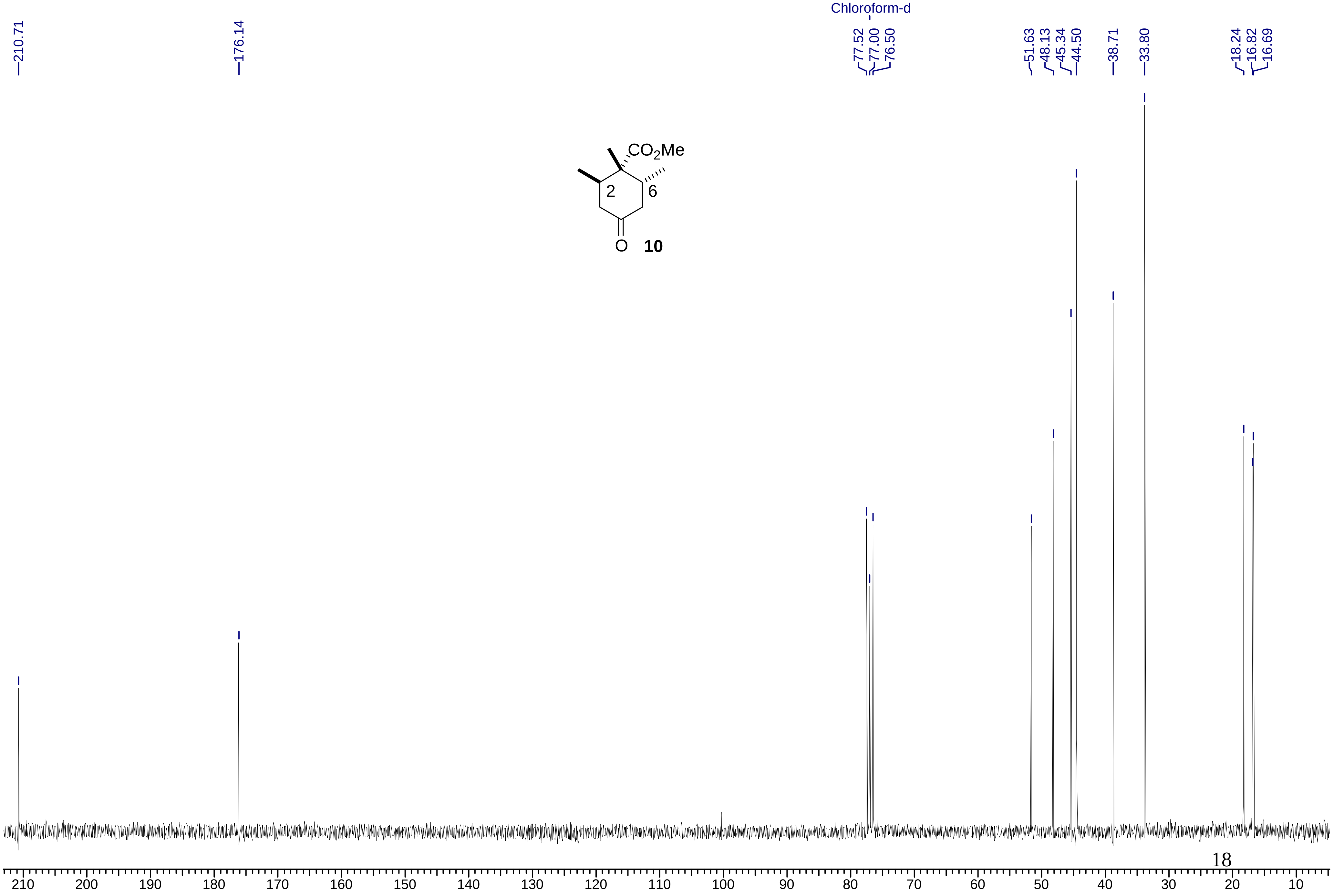

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O
10
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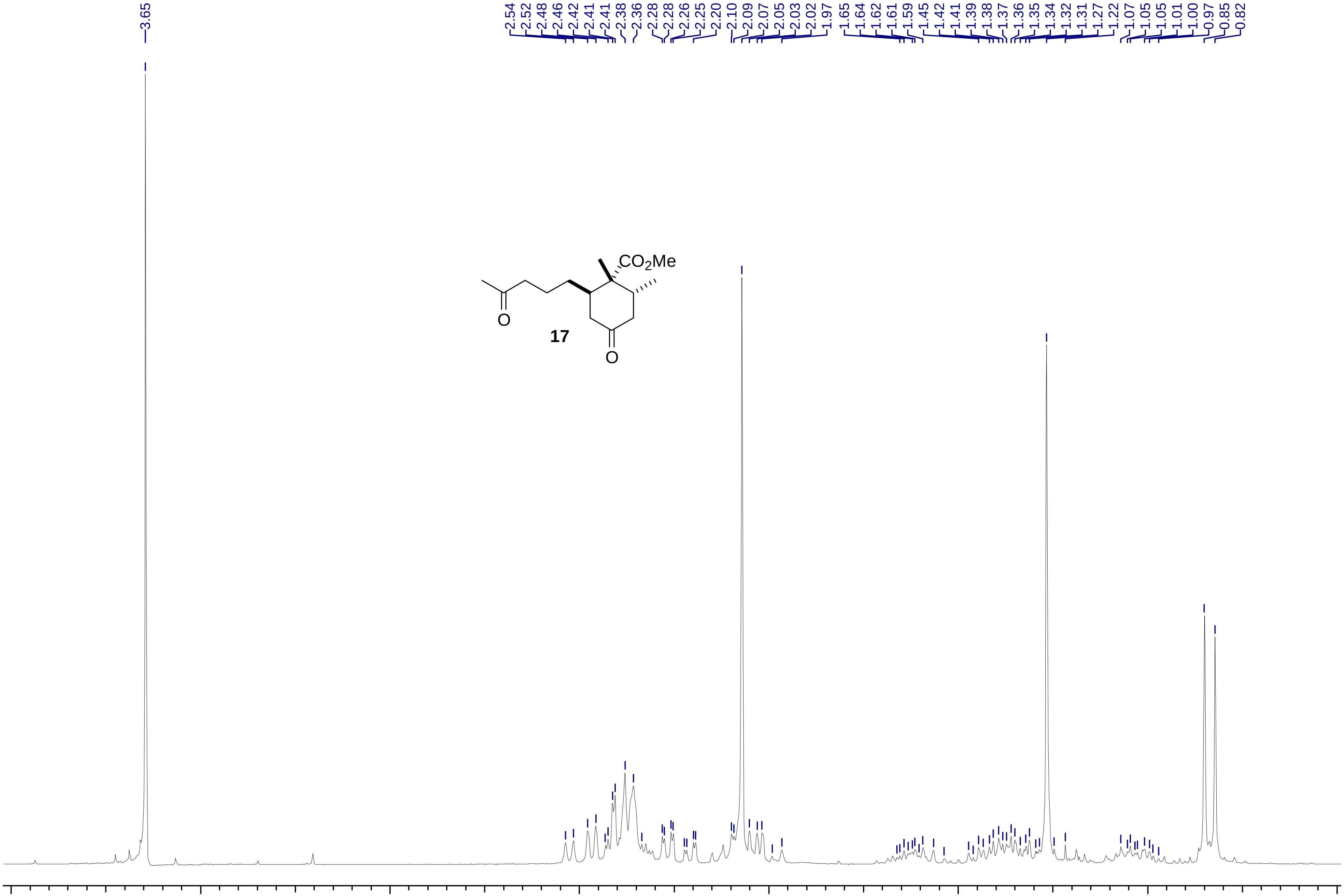
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1.05
1.01
1.00
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0.85
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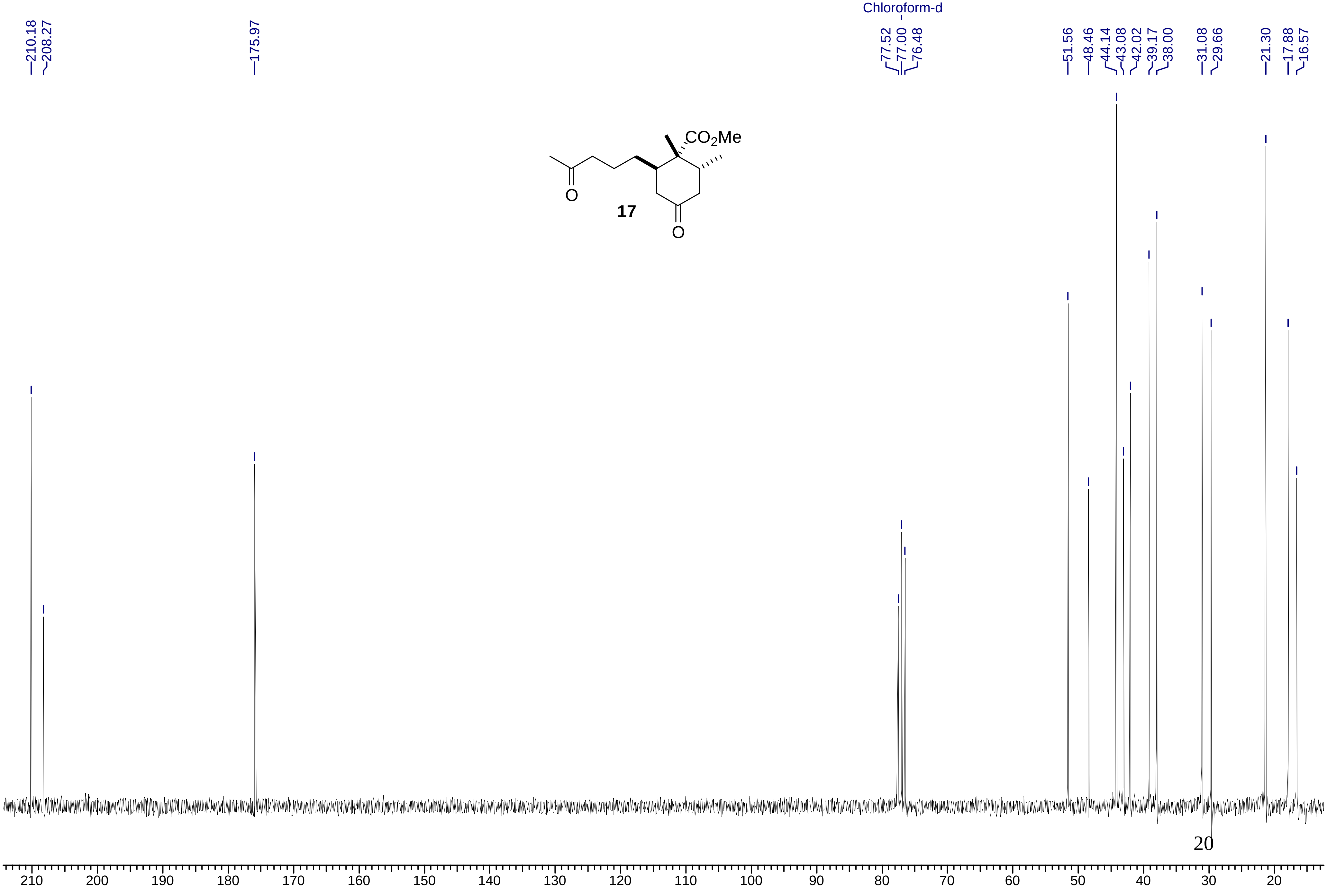

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CO$_2$Me
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