DMF as Carbon Source: Rh-Catalyzed α-Methylation of Ketones

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Contents

1. General Information

Flash chromatography was performed with freshly distilled solvents. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using $CDCl_3$ as solvent. Chemical shifts (δ) are reported in ppm, using TMS as an internal standard. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Solvents were purified by using the following method: DMF and DMSO were dried over CaH_2 for 24 h and distilled under reduced pressure. Toluene and dioxane were dried over sodium for 4 h, and distilled under N_2 atmosphere. $Cu(OAc)_2$ was refluxed in acetic anhydride for 5 h before using. The reactions were carried out in oven-dried glassware sealed with Teflon srew caps using the vacuum line technique. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using thermostat-controlled silicone oil baths.

2. General method for the synthesis of ketones

Ketone (0.5 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $(NH_4)_2S_2O_8$ (1.5 mmol), H_2O (2 mmol) and DMF (2 mL) were added to an oven-dried 25 ml pressure tube (with a Teflon cap). The reaction tube was evacuated and refilled with N_2 three times. The sealed tube was then placed in a 110 °C oil bath and stirred for 3 h. After completion, the reaction mixture was cooled down to room temperature, quenched by water and extracted with ethyl acetate (3 x 15 mL). The combined organic layer was washed with brine (1 x 45 mL), and dried over $MgSO_4$. After the evaporation, the residue was purified with silica gel chromatography with petroleum ether/ethyl acetate as eluent to afford the products.

3. Deuterium labeling experiments

3.1 Deuterium labeling experiments by using D_2O

Ketone (0.5 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $(NH_4)_2S_2O_8$ (1.5 mmol), D_2O (2 mmol), DMF (2 mL) and a stir bar were added to an oven-dried 25 mL pressure tube (with a Teflon cap). The reaction tube was degassed and refilled with N_2 for 3 times. Tube was then sealed and placed in a 110 °C oil bath and stirred for 3 h. After completion, the reaction mixture was cooled down to room temperature, diluted with

water and extracted with ethyl acetate (3 x 15 mL). The combined organic layer was washed with brine (1 x 45 mL), and dried over $MgSO_4$. After the evaporation of solvent, the residue was purified with silica gel chromatography with petroleum ether/ethyl acetate as eluent to afford the product **4a.**

3.2 Deuterium labeling experiments by using d_7-DMF

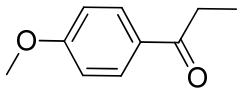
Ketone (0.5 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $(NH_4)_2S_2O_8$ (1.5 mmol), H_2O (2 mmol), d_7-DMF (0.7 mL) and a stir bar were added to an oven-dried 25 ml pressure tube (with a Teflon cap). The reaction tube was degassed and refilled with N_2 for 3 times. Tube was then sealed and placed in a 110 °C oil bath and stirred for 3 h. After completion, the reaction mixture was cooled down to room temperature, diluted with water and extracted with ethyl acetate (3 x 15 mL). The combined organic layer was washed with brine (1 x 45 mL), and dried over $MgSO_4$. After the evaporation of solvent, the residue was purified with silica gel chromatography with petroleum ether/ethyl acetate as eluent to afford the product **4b.**

4. Preparation of aryl vinyl ketone 4c

A 0.7 M solution of vinylmagnesium bromide (22 mL, 15.4 mmol) in THF was added via syringe pump to a solution of 4-methoxybenzaldehyde (14.0 mmol) in THF (45 mL) at -78 ºC over 30 min. Upon complete addition, the reaction solution was warmed to room temperature and stirred overnight, then quenched with saturated aqueous NH_4Cl (25 mL), stirred for 20 min, and extracted with diethyl ether (3 x 30 mL). The combined organic layer was washed with brine (25 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue was then dissolved in DMSO (10 mL), and IBX (5.096 g, 18.2 mmol) was added in two equal portions over 5 min at room temperature. The reaction solution was stirred for 1.3 h at room temperature, and then water (30 mL) and diethyl ether (30 mL) were added. The biphasic mixture was filtered through a pad of Celite and rinsed with diethyl ether (40 mL), and the organic layer was separated. The aqueous layer was then extracted with diethyl ether (2 x 25 mL), and the combined organic layer was washed with water (3 x 25 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2) eluting with hexanes and ethyl acetate to afford the products **4c.**

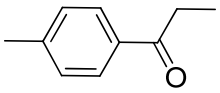
5. Analytic data for products

1-(4-Methoxyphenyl)propan-1-one (2a)



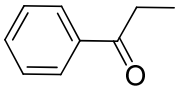
Colorless oil. R_f = 0.4 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.95 (d, 2H, *J* = 7.6 Hz), 6.93 (d, 2H, *J* = 7.6 Hz), 3.86 (s, 3H), 2.96 (q, 2H, *J* = 7.2 Hz), 1.22 (t, 3H, *J* = 7.6 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 199.5, 163.3, 130.2, 130.0, 113.7, 55.4, 31.4, 8.4; IR (KBr):3065, 2976, 1681, 1571, 1451, 1311, 1228, 1099, 950 cm^{-1} ; HRMS (ESI): calc. for ($M + Na^+$) 187.0730; found: 187.0732.

1-(p-tolyl)propan-1-one (2b)



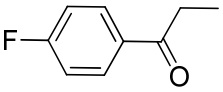
Colorless oil. R_f = 0.5 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.79 (d, 2H, *J* = 8.0 Hz), 7.17 (d, 2H, *J* = 8.0 Hz), 2.90 (q, 2H, *J* = 7.2 Hz), 2.33 (s, 3H), 1.14 (t, 3H, *J* = 7.6 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 200.5, 143.6, 134.5, 129.2, 128.1, 31.6, 21.6, 8.3; IR (KBr):3031, 2938, 1685, 1573, 1454, 1371, 1225, 1111, 952 cm^{-1} ; HRMS (ESI): calc. for ($M + H^+$) 149.0966; found: 149.0961.

Propiophenone (2c)



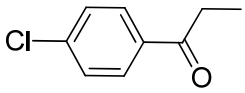
Colorless oil. R_f = 0.5 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.50-7.46 (m, 2H), 7.40-7.36 (m, 2H), 2.93 (q, 2H, *J* = 7.2 Hz), 1.15 (t, 3H, *J* = 7.2 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 200.8, 137.0, 132.9, 128.5, 128.0, 31.8, 8.2; IR (KBr):3063, 2978, 1682, 1583, 1464, 1301, 1225, 1105, 937 cm^{-1} ; HRMS (ESI): calc. for ($M + Na^+$) 157.0624; found: 157.0629.

1-(4-Fluorophenyl)propan-1-one (2d)



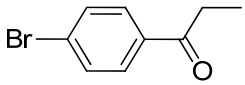
Colorless oil. R_f = 0.5 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.99 (q, 2H, *J* = 8.8 Hz), 7.13 (m, 2H), 2.98 (q, 2H, *J* = 7.2 Hz), 1.23 (t, 3H, *J* = 7.2 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 199.2, 165.6 (d, *J* = 252.8 Hz), 133.7 (d, *J* = 3 Hz), 130.6 (d, *J* = 9 Hz), 115.6 (d, *J* = 21.8 Hz), 31.7, 8.2; IR (KBr): 2925, 1693, 1601, 1507, 1463, 1357, 1227, 1160, 960, 855, 805 cm^{-1} ; HRMS (ESI): calc. for (M + Na^+) 175.0530; found: 175.0536.

1-(4-Chlorophenyl)propan-1-one (2e)



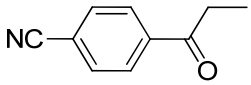
Colorless oil. R_f = 0.5 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.90 (d, 2H, *J* = 8.8 Hz), 7.43 (d, 2H, *J* = 8.8 Hz), 2.98 (q, 2H, *J* = 7.2 Hz), 1.23 (t, 3H, *J* = 7.6 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 199.5, 139.2, 135.2, 129.3, 128.9, 31.8, 8.1; IR (KBr):2975, 2931, 1693, 1463, 1385, 1277, 1041, 885, 738 cm^{-1} ; HRMS (ESI): calc. for (M + Na^+) 191.0234; found: 191.0236.

1-(4-Bromophenyl)propan-1-one (2f)



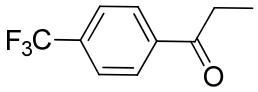
White solid. mp = 47-48 ℃. R_f = 0.5 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.84-7.81(d, 2H, *J* = 8.4 Hz), 7.60 (d, 2H, *J* = 8.4 Hz), 2.97(q, 2H, *J* = 7.2 Hz), 1.22 (t, 3H, *J* = 7.2 Hz), ^{13}CNMR (100 MHz, $CDCl_3$) δ 199.7, 135.6, 131.9, 129.5, 128.0, 31.8, 8.1; IR (KBr): 3059, 3009, 1685, 1579, 1357, 1224, 1071, 1013, 955, 796 cm^{-1} ; HRMS (ESI): calc. for (M + Na^+) 234.9729; found: 234.9722.

4-Propionylbenzonitrile (2g)



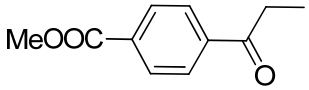
Colorless oil. R_f = 0.2 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.05 (d, 2H, *J* = 8.4 Hz), 7.77 (d, 2H, *J* = 8.4 Hz), 3.03 (q, 2H, *J* = 7.2 Hz), 1.25 (t, 3H, *J* = 7.6 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ 199.3, 139.8, 132.5, 128.4, 118.0, 116.2, 32.2, 7.9; IR (KBr): 3050, 3003, 1696, 1465, 1404, 1365, 1227, 955, 802 cm^{-1} ; HRMS (ESI): calc. for (M + Na^+) 182.0576; found: 182.0576.

1-(4-(Trifluoromethyl)phenyl)propan-1-one (2h)



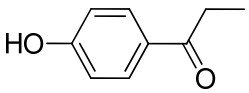
Colorless oil. R_f = 0.5 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.07 (d, 2H, *J* = 8.4 Hz), 7.73 (d, 2H, *J* = 8 Hz), 3.04 (q, 2H, *J* = 7.2 Hz), 1.25 (t, 3H, *J* = 7.2 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 199.7, 139.6, 134.2 (q, *J* = 275.5 Hz), 128.3, 125.6 (d, *J* = 3.8 Hz), 123.6 (d, *J* = 270.6 Hz), 32.1, 8.0; IR (KBr): 2967, 2928, 1682, 1599, 1460, 1327, 1260, 1174, 1030, 955 cm^{-1} ; HRMS (ESI): calc. for (M + Na^+) 225.0498; found: 225.0496.

Methyl 4-propionylbenzoate (2i)



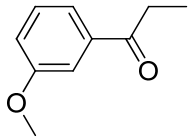
White solid. R_f = 0.2 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.12 (d, 2H, *J* = 8.4 Hz), 8.01 (d, 2H, *J* = 8.8 Hz), 3.95 (s, 3H), 3.04 (q, 2H, *J* = 7.2 Hz), 1.25 (t, 3H, *J* = 7.2 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 200.2, 166.3, 140.2, 133.7, 129.8, 127.9, 52.4, 32.2, 8.1; IR (KBr): 2967, 1726, 1679, 1446, 1288, 1224, 1113, 960, 758 cm^{-1} ; HRMS (ESI): calc. for (M + Na^+) 215.0679; found: 215.0681.

1-(4-Hydroxyphenyl)propan-1-one (2j)



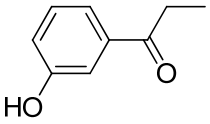
White solid. R_f = 0.2 (petroleum ether/ethyl acetate 5:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.92 (d, 2H, *J* = 8.8 Hz), 6.90 (d, 2H, *J* = 8.8 Hz), 5.96 (s, 1H), 2.97 (q, 2H, *J* = 7.4 Hz), 1.22 (t, 3H, *J* = 7.2 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 199.8, 159.9, 130.6, 130.2, 115.3, 31.4, 8.5; IR (KBr): 3039, 2989, 1660, 1596, 1457, 1377, 1288, 1235, 1160, 988, 849 cm^{-1} ; HRMS (ESI): calc. for (M + H^+) 151.0759; found: 151.0756.

1-(3-Methoxyphenyl)propan-1-one (2k)



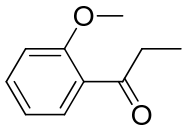
Colorless oil. R_f = 0.4 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.52 (d, 1H, *J* = 12.0 Hz), 7.49 (s, 1H), 7.36 (t, 2H, *J* = 8.0 Hz), 3.85 (s, 3H), 2.99 (q, 2H, *J* = 7.2 Hz), 1.22 (t, 3H, *J* = 7.2 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 200.6, 159.8, 138.3, 129.5, 120.6, 119.2, 112.3, 55.4, 31.9, 8.3; IR (KBr):2975, 2936, 1687, 1596, 1463, 1340, 1260, 1046, 783 cm^{-1} ; HRMS (ESI): calc. for (M + Na^+) 187.0730; found: 187.0735.

1-(3-Hydroxyphenyl)propan-1-one (2l)



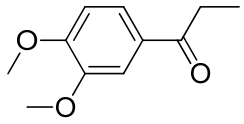
Colorless oil. R_f = 0.2 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.57-7.52 (m, 2H), 7.34 (t, 1H, *J* = 8.0 Hz), 7.10-7.07 (m, 2H), 5.95 (s, 1H), 3.00 (q, 2H, *J* = 7.2 Hz), 1.23 (t, 3H, *J* = 7.2 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 201.3, 156.2, 138.3, 129.9, 120.6, 120.3, 114.5, 32.0, 8.2; IR (KBr):2975, 1679, 1590, 1454, 1374, 1274, 1043, 877, 780 cm^{-1} ; HRMS (ESI): calc. for (M + H^+) 151.0759; found: 151.0756.

1-(2-Methoxyphenyl)propan-1-one (2m)



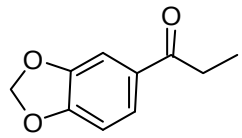
Colorless oil. R_f = 0.2 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.68-7.66 (m, 1H, *J* = 9.0 Hz), 7.46-7.42 (m, 1H), 7.01-6.95 (m, 2H), 3.89 (S, 3H), 2.99 (q, 2H, *J* = 7.2 Hz), 1.17 (t, 3H, *J* = 7.6 Hz), ^{13}CNMR (100 MHz, $CDCl_3$) δ 203.5, 158.4, 133.1, 130.2, 128.6, 120.6, 111.5, 55.5, 37.0, 8.4; IR (KBr):3067, 2997, 1682, 1596, 1468, 1288, 1246, 1027, 760 cm^{-1} ; HRMS (ESI): calc. for (M + Na^+) 187.0730; found: 187.0735

1-(3,4-Dimethoxyphenyl)propan-1-one (2n)



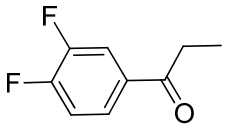
Colorless oil. R_f = 0.3 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.60-7.59 (m, 1H), 7.55 (s, 1H), 6.89 (d, 2H, *J* = 8.4 Hz), 3.94 (s, 3H), 2.98 (q, 2H, *J* = 7.2 Hz), 1.23(t, 3H, *J* = 7.2 Hz). ^{13}CNMR (100 MHz, $CDCl_3$) δ 199.5, 153.1, 149.0, 130.2, 122.5, 110.2, 110.0, 56.0, 55.9, 31.3, 8.6. IR (KBr): 3086, 2975, 1682, 1590, 1513, 1457, 1265, 1160, 1030, 871 cm^{-1} ; HRMS (ESI): calc. for ($M + Na^+$) 217.0835; found: 217.0843.

1-(Benzo[d][1,3]dioxol-5-yl)propan-1-one (2o)



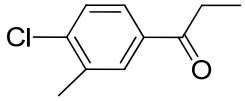
Colorless oil. R_f = 0.3 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.48 (t, 2H, *J* = 8.4 Hz), 7.36 (s, 1H), 6.76 (d, 2H, *J* = 8.0 Hz), 2.85 (q, 2H, *J* = 7.2 Hz), 1.13 (t, 3H, *J* = 7.4 Hz). ^{3}CNMR (100 MHz) δ 198.9, 151.5, 148.1, 131.8, 124.1, 107.9, 107.8, 101.8, 31.5, 8.5. IR (KBr):2978, 2906, 1679, 1610, 1493, 1446, 1249, 1038, 802 cm^{-1} ; HRMS (ESI): calc. for ($M + Na^+$) 201.0522; found: 201.0529.

1-(3,4-Difluorophenyl)propan-1-one (2p)



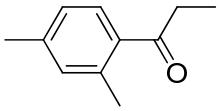
Colorless oil. R_f = 0.5 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.76-7.72 (m, 2H), 7.28-7.21 (m, 1H), 2.96 (q, 2H, *J* = 7.2 Hz), 1.22 (t, 3H, *J* = 7.2 Hz). ^{13}CNMR (100 MHz) δ 198.1, 154.8 (d, *J* = 13 Hz), 153.3 (dd, *J* = 356.8, 13 Hz), 149.1(d, *J* = 12 Hz), 134.0, 124.9 (q, *J* = 4 Hz), 117.4 (m), 31.7, 8.1. IR (KBr): 3057, 2989, 1696, 1612, 1515, 1429, 1283, 1171, 791 cm^{-1}; HRMS (ESI): calc. for ($M + Na^+$) 201.0522; found: 201.0528

1-(4-Chloro-3-methylphenyl)propan-1-one (2q)



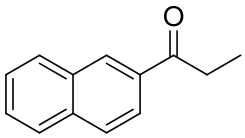
White solid. mp = 40-41℃. R_f = 0.2 (petroleum ether/ethyl acetate 5:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.83 (d, 1H, *J* =2.0 Hz), 7.72 (dd, 2H, *J* = 8.4, 2.0 Hz), 7.42(d, 1H, *J* = 8.4 Hz), 2.97 (q, 2H, *J* = 7.2 Hz), 2.43 (s, 3H), 1.22 (t, 3H, *J* =7.2 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 199.9, 139.4, 136.5, 135.4, 130.4, 129.3, 126.7, 31.8, 20.1, 8.2; IR (KBr):2978, 2837, 1621, 1562, 1457, 1363, 1271, 1118, 885 cm^{-1} ; HRMS (ESI): calc. for ($M + H^+$) 205.0390; found: 205.0396.

1-(2,4-Dimethylphenyl)propan-1-one (2r)



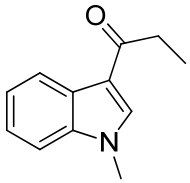
Colorless oil. R_f = 0.4 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.58 (d, 1H, *J* = 8.4 Hz), 7.05 (m, 2H), 2.91 (q, 2H, *J* = 7.2 Hz), 2.49 (s, 3H), 2.35 (s, 3H), 1.28 (t, 3H, *J* = 7.2 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 204.3, 141.6, 138.5, 135.0, 132.8, 128.9, 126.2, 34.4, 21.5, 21.3, 8.5; IR (KBr):3038, 2954, 1680, 1553, 1468, 1379, 1246, 1176, 950 cm^{-1} ; HRMS (ESI): calc. for ($M + H^+$) 163.1123; found: 163.1121.

1-(Naphthalen-2-yl)propan-1-one (2s)



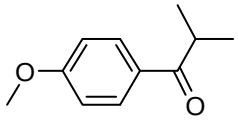
White solid. mp = 64-65℃. R_f = 0.2 (petroleum ether/ethyl acetate 5:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.05 (d, 1H, *J* = 1 Hz), 8.03 (d, 1H, *J* = 1 Hz), 7.87 (d, 2H, *J* = 1 Hz), 7.57 (m, 2H), 3.14 (q, 2H, *J* = 7.2 Hz), 1.29 (t, 3H, *J* = 7.2 Hz). ^{13}CNMR (100 MHz) δ 199.7, 134.5, 133.3, 131.6, 128.5, 128.5, 127.4, 127.3, 126.7, 125.7, 122.9, 30.8, 7.4; IR (KBr): 2978, 2931, 1687, 1465, 1374, 1193, 1129, 805, 755 cm^{-1} ; HRMS (ESI): calc. for ($M + H^+$) 185.0961; found: 185.0964.

1-(1-Methyl-1H-indol-3-yl)propan-1-one (2t)



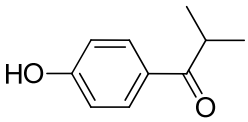
Colorless oil. R_f = 0.4 (petroleum ether/ethyl acetate 5:1); ^{1}HNMR (400 MHz) δ 8.36 (d, 2H, *J* = 8 Hz), 7.71 (s, 1H), 7.34-7.29 (m, 3H), 3.84 (s, 3H), 2.88 (q, 2H, *J* = 7.6 Hz), 1.26 (t, 3H, *J* = 7.4 Hz). ^{13}CNMR (100 MHz) δ 196.3, 137.5, 135.0, 126.4, 123.2, 122.6, 122.5, 116.3, 109.5, 33.5, 32.9, 9.0; IR (KBr): 3420, 2360, 1685, 1569, 1417, 1285, 1052, 795 cm^{-1}; HRMS (ESI): calc. for (M + Na$^+$) 210.0889; found: 210.0882.

1-(4-Methoxyphenyl)-2-methylpropan-1-one (3a)



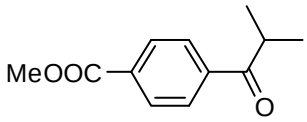
Colorless oil. R_f = 0.35 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.95 (d, 2H, *J* = 8.8 Hz), 6.94 (d, 2H, *J* = 9.2 Hz), 3.87 (s, 3H), 3.55-3.48 (m, 1H), 1.21 (d, 6H, *J* = 6.8 Hz). ^{13}CNMR (100 MHz) δ 203.1, 163.3, 130.6, 129.2, 113.7, 113.4, 55.4, 34.9, 19.2. IR (KBr): 2978, 1643, 1385, 1166, 1088, 880, 699 cm^{-1} ; HRMS (ESI): calc. for (M + Na$^+$) 201.0886; found: 201.0889.

1-(4-Hydroxyphenyl)-2-methylpropan-1-one (3b)



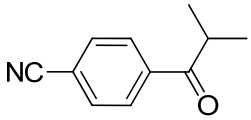
Colorless oil. R_f = 0.35 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz) δ 7.92(d, 2H, *J* = 8.8 Hz), 6.91 (d, 2H, *J* = 8.4 Hz), 3.56-3.50 (m, 1H), 1.21(d, 6H, *J* = 6.8 Hz). ^{13}CNMR (100 MHz) δ 203.8, 160.1, 131.0, 129.1, 115.4, 35.0, 19.3; IR (KBr): 3056, 2920, 1643, 1582, 1460, 1315, 1249, 1141, 916, 749 cm^{-1} ; HRMS (ESI): calc. for (M + Na$^+$) 187.0729; found: 187.0734.

Methyl 4-isobutyrylbenzoate (3c)



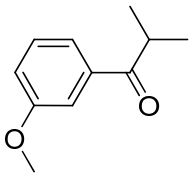
Colorless oil. R_f = 0.35 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz) δ 8.13 (d, 2H, *J* = 8.4 Hz), 8.00（d, 2H, *J* = 8.8 Hz), 3.95 (s, 3H), 3.59-3.52 (m, 1H), 1.23 (d, 2H, *J* = 6.8 Hz). ^{13}CNMR (100 MHz) δ 204.0, 166.3, 139.6, 133.6, 129.8, 128.2, 52.4, 35.8, 19.0; IR (KBr): 2970, 2931, 1729, 1687, 1576, 1449, 1288, 1116, 977, 730 cm^{-1} ; HRMS (ESI): calc. for (M + Na$^+$) 229.0835; found: 2229.0839.

4-Isobutyrylbenzonitrile (3d)



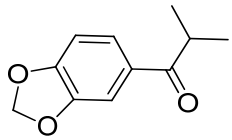
Colorless oil. R_f = 0.4 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz) δ 8.03 (s, 2H, *J* = 8.4 Hz), 7.78 (d, 2H, *J* = 8.4 Hz), 3.53-3.50 (m, 1H), 1.23 (d, 6H, *J* = 7.2 Hz). ^{13}CNMR (100 MHz) δ 203.0, 139.4, 132.5, 128.7, 118.0, 116.1, 35.9, 18.9; IR (KBr): 2992, 2989, 1685, 1463, 1379, 1224, 988, 857, 744 cm^{-1} ; HRMS (ESI): calc. for (M + H$^+$) 174.0913; found: 174.0916.

1-(3-Methoxyphenyl)-2-methylpropan-1-one (3e)



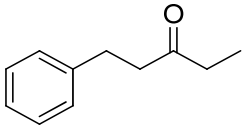
Colorless oil. R_f = 0.35 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz) δ 7.46 (d, 1H, *J* = 7.6 Hz), 7.42 (s, 1H), 7.30 (t, 1H, *J* = 8.0 Hz), 7.03 (m, 1H), 3.79 (s, 3H), 3.50-3.43 (m, 1H), 1.15 (d, 6H, *J* = 6.8 Hz); ^{13}CNMR (100 MHz) δ 204.3, 159.9, 137.7, 129.5, 120.8, 119.2, 112.8, 55.4, 35.5, 19.2; IR (KBr):3075, 2992, 1690, 1590, 1468, 1263, 1010, 816, 744 cm^{-1} ; HRMS (ESI): calc. for (M + Na$^+$) 201.0886; found: 201.0889.

1-(Benzo[d][1,3]dioxol-5-yl)-2-methylpropan-1-one (3f)



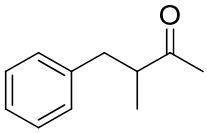
Colorless oil. R_f = 0.31 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz) δ 7.58-7.56 (m, 1H), 7.45 (s, 1H), 6.85 (d, 2H, *J* = 8.0 Hz), 3.50-3.43 (m, 1H), 1.20 (d, 6H, *J* = 6.8 Hz); ^{13}CNMR (100 MHz) δ 202.6, 151.5, 148.2, 131.0, 124.3, 108.3, 107.9, 101.8, 35.1, 19.4; IR (KBr): 3075, 3000, 1679, 1499, 1449, 1260, 1041, 935, 819 cm^{-1} ; HRMS (ESI): calc. for (M + Na$^+$) 201.0886; found: 201.0889.

1-Phenylpentan-3-one (3g-a)



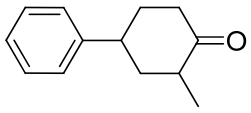
Colorless oil. R_f = 0.35 (petroleum ether/ethyl acetate 20:1); ^{1}HNMR (400 MHz) δ 7.22-7.19 (m, 2H), 7.13-7.10 (m, 3H), 2.83(t, 2H, *J* = 7.6 Hz), 2.66 (t, 2H, *J* = 7.6 Hz), 2.33 (q, 2H, *J* = 7.3 Hz), 0.97 (t, 3H, *J* = 7.4 Hz). ^{13}CNMR (100 MHz) δ 209.6, 140.2, 127.5, 127.3, 125.1, 42.9, 35.1, 28.9, 6.7; IR (KBr): 3056, 2917, 1646, 1582, 1460, 1232, 821, 749 cm^{-1} ; HRMS (ESI): calc. for (M + Na$^+$) 185.0939; found: 185.0939.

3-Methyl-4-phenylbutan-2-one (3g-b)



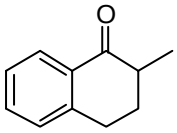
Colorless oil. R_f = 0.36 (petroleum ether/ethyl acetate 20:1); ^{1}HNMR (400 MHz) δ 7.26-7.21 (m, 2H), 7.20-7.14 (m, 3H), 3.02-2.97 (m, 1H), 2.86-2.80 (m, 1H), 2.59-2.54 (m, 1H), 2.09 (s, 3H), 1.09 (d, 3H, *J* = 6.8 Hz). ^{13}CNMR (100 MHz) δ 212.1, 139.7, 128.9, 128.4, 126.2, 48.8, 38.9, 28.8, 16.2; IR (KBr): 3059, 2959, 1654, 1587, 1463, 1329, 1171, 1124, 1068 cm^{-1} ; HRMS (ESI): calc. for (M + Na$^+$) 185.0936; found: 185.0939.

2-Methyl-4-phenylcyclohexanone (3h)



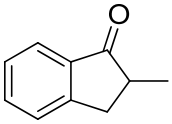
Colorless oil. R_f = 0.32 (petroleum ether/ethyl acetate 20:1); ^{1}HNMR (400 MHz) δ 7.33-7.20 (m, 5H), 3.16-3.10 (m, 1H), 2.62-2.59 (m, 1H), 2.52-2.50 (m, 2H), 2.27-2.22 (m, 2H), 1.95-1.90 (m, 1H), 1.72-1.65 (m, 1H), 1.06 (d, 3H, *J* = 8.4 Hz).^{13}CNMR (100 MHz) δ 212.5, 144.8, 128.6, 126.7, 126.6, 44.8, 43.5, 43.4, 41.5, 35.0, 14.4; IR (KBr): 3059, 2923, 1646, 1579, 1468, 1388, 1249, 1132, 744 cm^{-1} ; HRMS (ESI): calc. for (M + Na$^+$) 211.1093; found: 211.1097.

2-Methyl-3,4-dihydronaphthalen-1(2H)-one (3i)



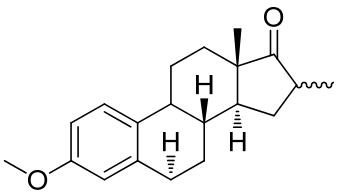
Colorless oil. R_f = 0.4 (petroleum ether/ethyl acetate 5:1); ^{1}HNMR (400 MHz) δ 8.04 (d, 1H, *J* = 7.6 Hz). 7.47-7.43 (m, 1H), 7.32-7.22 (m, 2H), 3.04-2.95 (m, 2H), 2.62-2.56 (m, 1H), 2.24-2.17 (m, 1H), 1.94-1.85 (m, 1H), 1.27 (d, 3H, *J* = 6.8 Hz). ^{13}CNMR (100 MHz) δ 200.7, 144.2, 133.1, 132.4, 128.7, 127.4, 126.5, 42.6, 31.4, 28.8, 15.4; IR (KBr): 2934, 2867, 1737, 1610, 1507, 1460, 1257, 1043 cm^{-1} ; HRMS (ESI): calc. for (M + Na$^+$) 183.0780; found: 183.0781.

2-Methyl-2,3-dihydro-1H-inden-1-one (3j)



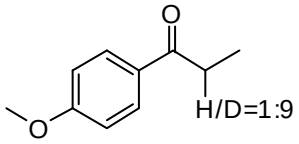
Colorless oil. R_f = 0.3 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz) δ 7.76 (d, 1H, *J* = 7.6 Hz), 7.59 (t, 1H, *J* = 7.2 Hz), 7.45 (d, 1H, *J* = 7.6 Hz), 7.37 (t, 1H, *J* = 7.2 Hz). 3.40 (q, 1H, *J* = 2.2 Hz), 2.76-2.70 (m, 2H), 1.32(d, 3H, *J* = 7.2 Hz). ^{13}CNMR (100 MHz) δ 209.4, 153.5, 136.4, 134.7, 127.4, 126.5, 124.0, 42.0, 35.0, 16.3; IR (KBr): 2925, 2864, 1740, 1612, 1504, 1460, 1254, 1041 cm^{-1}; HRMS (ESI): calc. for (M + Na$^+$) 169.0623; found: 169.0628.

(8R,13S,14S)-3-methoxy-13,16-dimethyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one



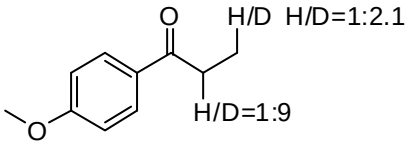
Colorless oil. R_f = 0.3 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz) δ 7.20 (d, 1H, *J* = 8.8 Hz), 6.73-6.70 (m, 1H), 6.65-6.64 (m, 1H), 3.78 (s, 3H), 2.90-2.89 (m,2H), 2.37-2.36 (m, 1H), 2.29-2.16 (m, 6H), 1.99-1.95 (m, 2H), 1.24 (d, 3H, *J* = 7.2 Hz),1.14 (d, 1H, *J* = 7.2 Hz), 0.94 (s, 1H), 0.87 (s, 3H); ^{13}CNMR (100 MHz) δ 223.2, 157.6, 137.8, 132.1, 126.3, 113.9, 111.6, 55.2, 49.1, 48.6, 48.4, 47.7, 44.1, 38.2, 32.0, 30.7, 30.0, 26.8, 25.9, 17.0, 15.3; IR (KBr): 2934, 2867, 1740, 1610, 1499, 1457, 1254, 1043 cm^{-1}; HRMS (ESI): calc. for (M + Na^+) 321.1825; found: 321.1829.

4a



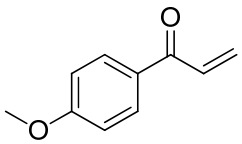
Colorless oil. R_f = 0.4 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.94 (d, 2H, *J* = 9.2 Hz), 6.92 (d, 2H, *J* = 9.2 Hz), 3.86 (s, 3H), 2.95 (q, 1.8 H, *J* = 7.2 Hz), 1.21 (t, 3H, *J* = 7.6 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 199.4, 163.3, 130.2, 130.1, 113.7, 55.4, 31.4-30.8 (m), 8.4.

4b



Colorless oil. R_f = 0.4 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.95 (d, 2H, *J* = 8.8 Hz), 6.93 (d, 2H, *J* = 8.8 Hz), 3.87 (s, 3H), 2.94 (d, 1.8 H, *J* = 7.2 Hz), 1.20-1.18 (m, 0.98 H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 199.5, 163.3, 130.2, 130.0, 113.7, 55.4, 31.4-30.8 (m), 8.3-7.7(m).

1-(4-methoxyphenyl)prop-2-en-1-one(4c)



Colorless oil. R_f = 0.4 (petroleum ether/ethyl acetate 9:1); ^{1}HNMR (400 MHz, $CDCl_3$)

δ 7.97 (d, 2H, *J* = 8.8 Hz), 7.17 (q, 1H, *J* = 10.4 Hz), 6.96 (d, 2H, *J* = 9.2 Hz), 6.42 (dd, 1H, *J* = 1.6, 16.8Hz), 5.87 (dd, 1H, *J* = 1.6, 10.4 Hz), 3.88 (s, 3H), *J* = 7.2 Hz).

6. References for known products

Entry	Products	Reference
1	2a	[S1]
2	2b	[S2]
3	2c	[S3]
4	2d	[S4]
5	2e	[S5]
6	2f	[S6]
7	2g	[S7]
8	2h	[S8]
9	2i	[S9]
10	2j	[S10]
11	2k	[S11]
12	2l	[S12]
13	2m	[S 13]
14	2n	[S 14]
15	2o	[S 15]
16	2p	[S 16]
17	2q	[S 17]
18	2r	[S 18]
19	2s	[S 19]
20	2t	[S 20]
21	3a	[S 21]
22	3b	[S 22]
23	3c	[S 23]
24	3d	[S 24]

25	3e	[S 25]
26	3f	[S 26]
27	3g	[S 27]
28	3h	[S 28]
29	3i	[S 29]
30	3j	[S 30]
31	3k	[S 31]

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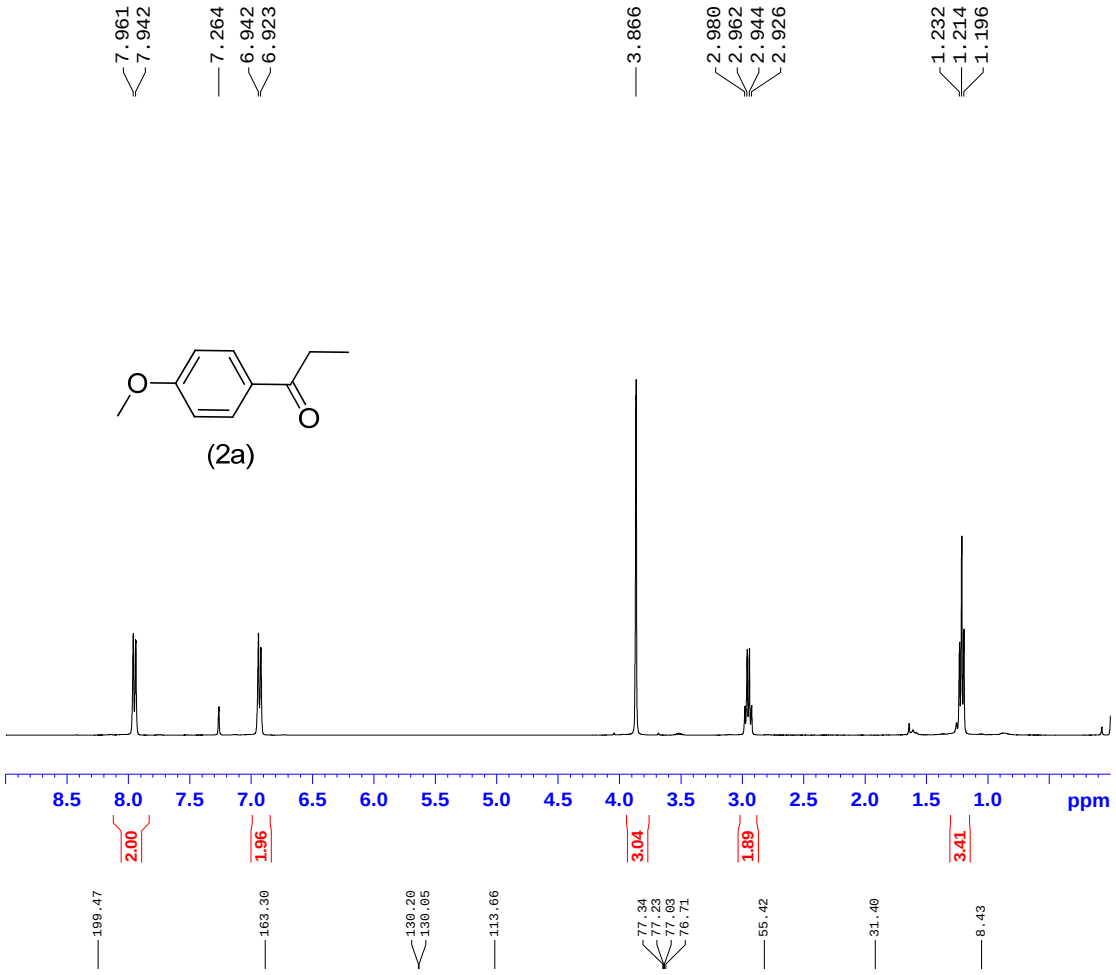
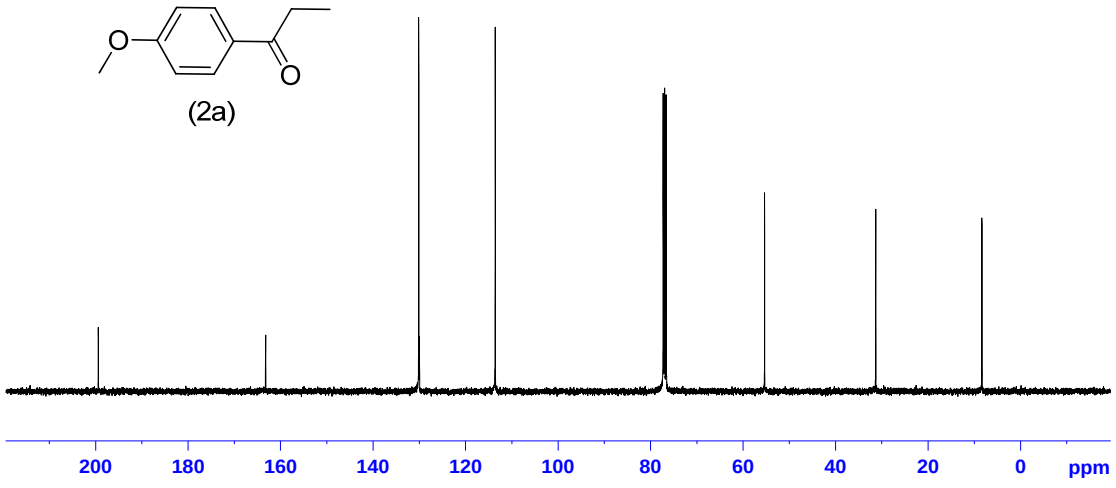
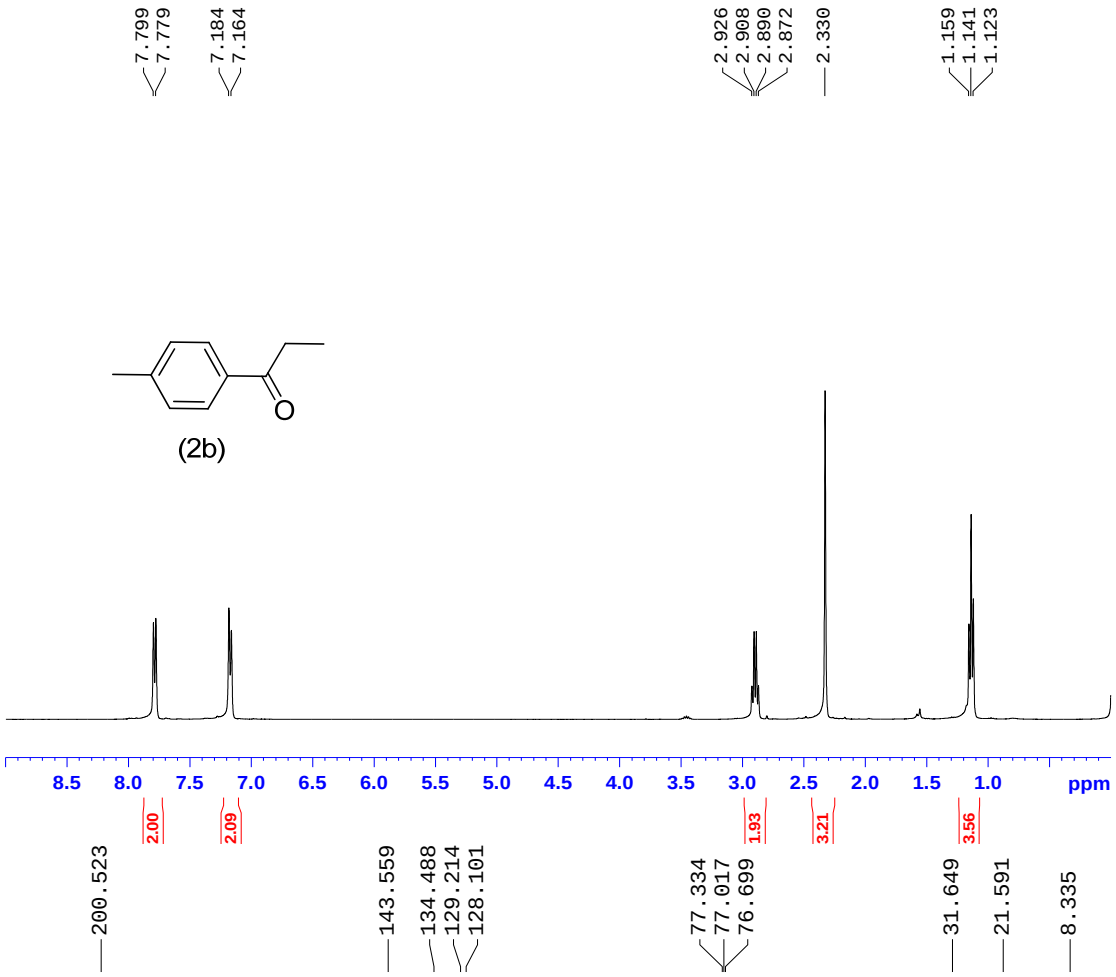
7. Copies of the ^{1}H NMR and ^{13}C NMR spectra of products



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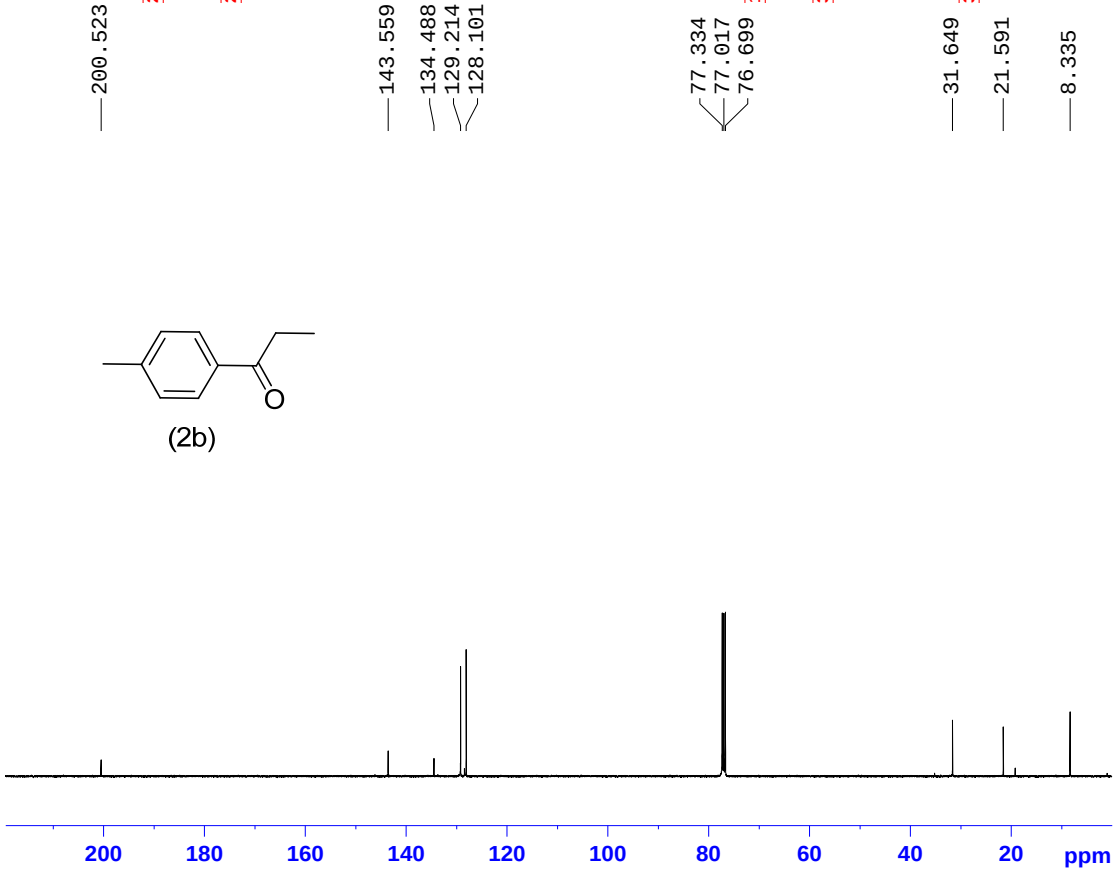
2.926
2.908
2.890
2.872
2.330
1.159
1.141
1.123
O
(2b)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
2.09
1.93
3.21
3.56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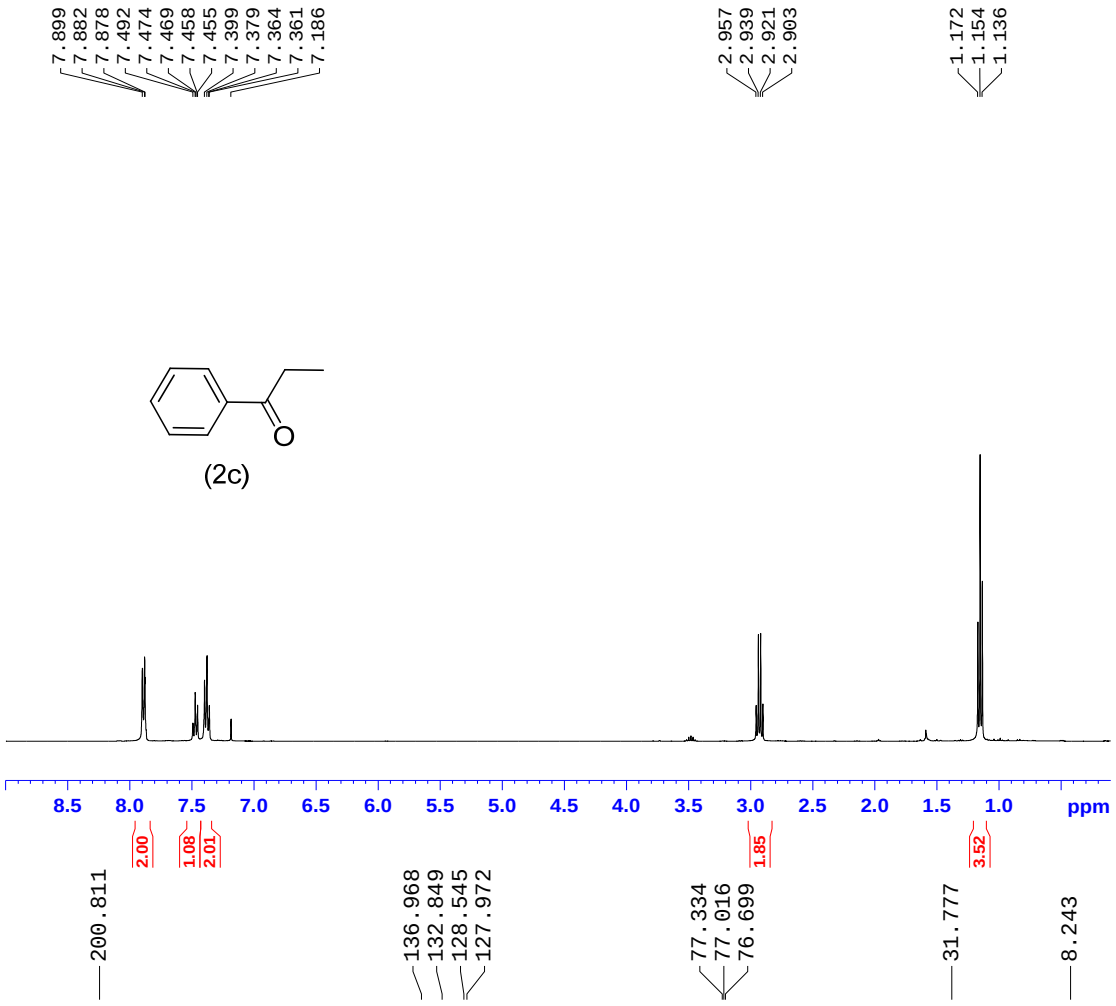
143.559
134.488
129.214
128.101
77.334
77.017
76.699
31.649
21.591
8.335
O
(2b)
200
180
160
140
120
100
80
60
40
20
ppm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7.882
7.878
7.492
7.474
7.469
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7.455
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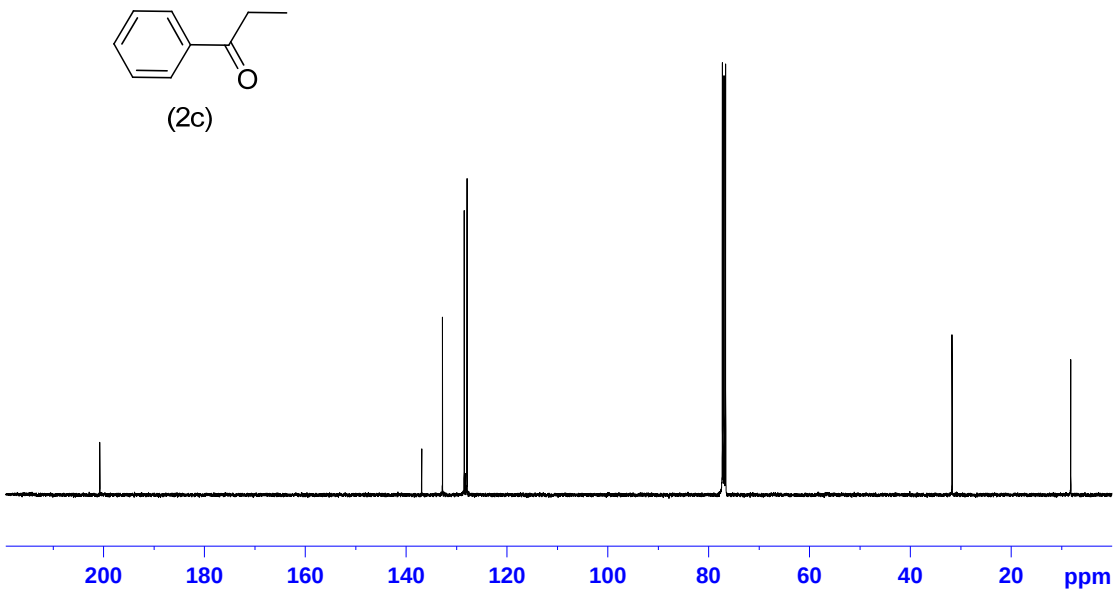
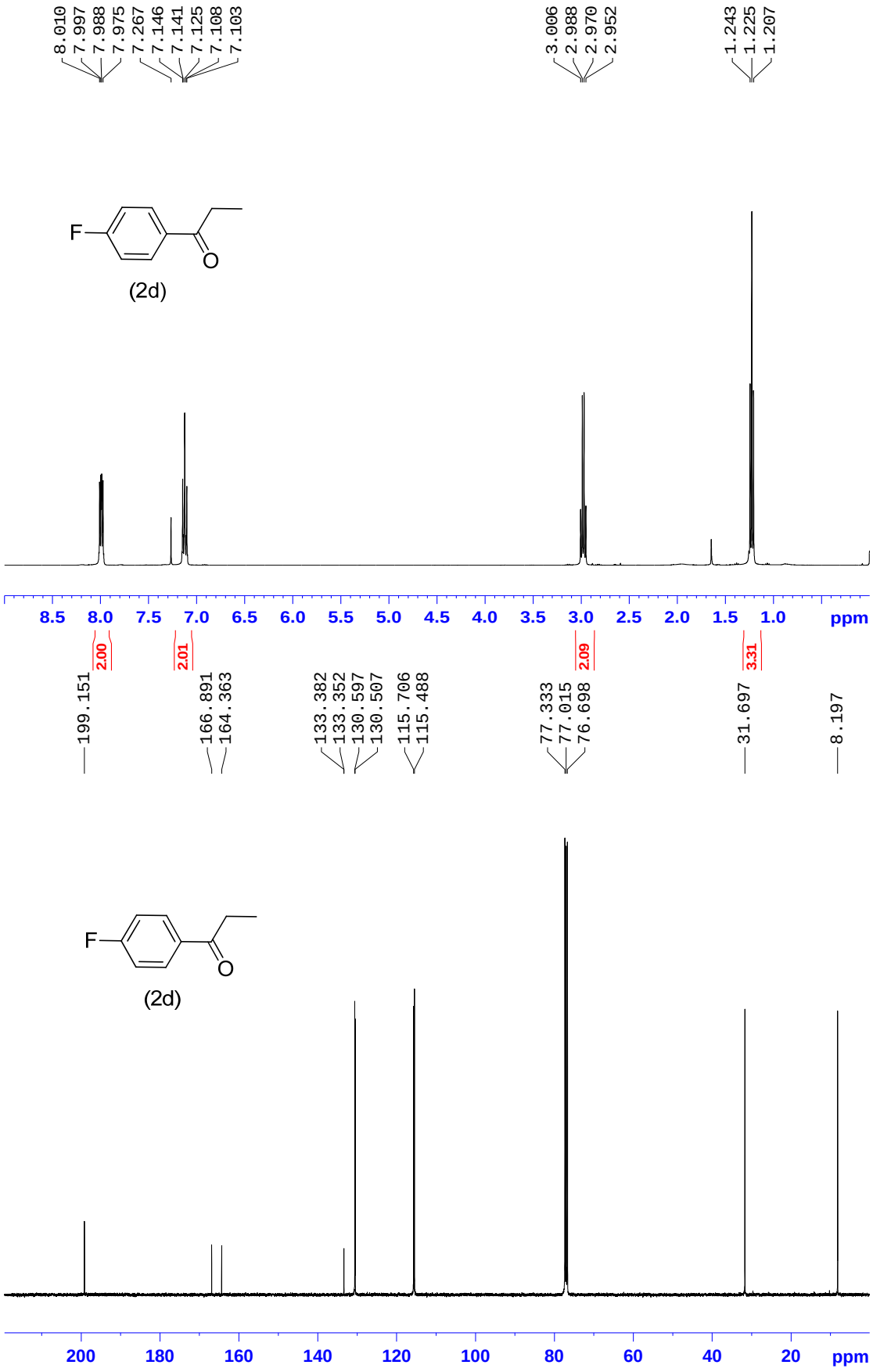
7.379
7.364
7.361
7.186
2.957
2.939
2.921
2.903
1.172
1.154
1.136
(2c)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
1.08
2.01
1.85
3.52

200.811
136.968
132.849
128.545
127.972
77.334
77.016
76.699
31.777
8.243


(2c)
200
180
160
140
120
100
80
60
40
20
ppm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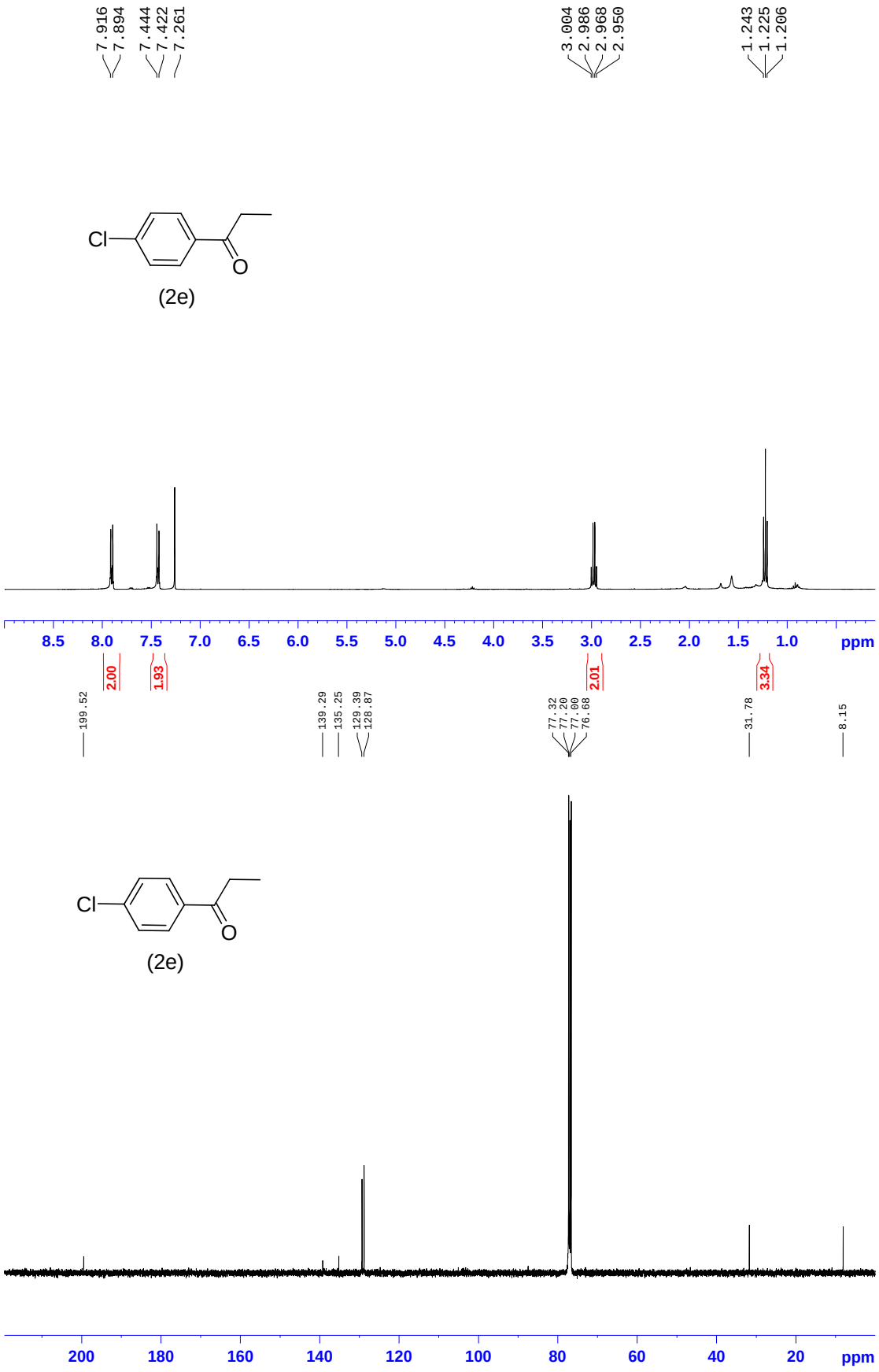
7.997
7.988
7.975
7.267
7.146
7.141
7.125
7.108
7.103
3.006
2.988
2.970
2.952
1.243
1.225
1.207
F
O
(2d)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
2.01
2.09
3.31
199.151
166.891
164.363
133.382
133.352
130.597
130.507
115.706
115.488
77.333
77.015
76.698
31.697
8.197
F
O
(2d)
200
180
160
140
120
100
80
60
40
20
ppm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7.444
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7.261
3.004
2.986
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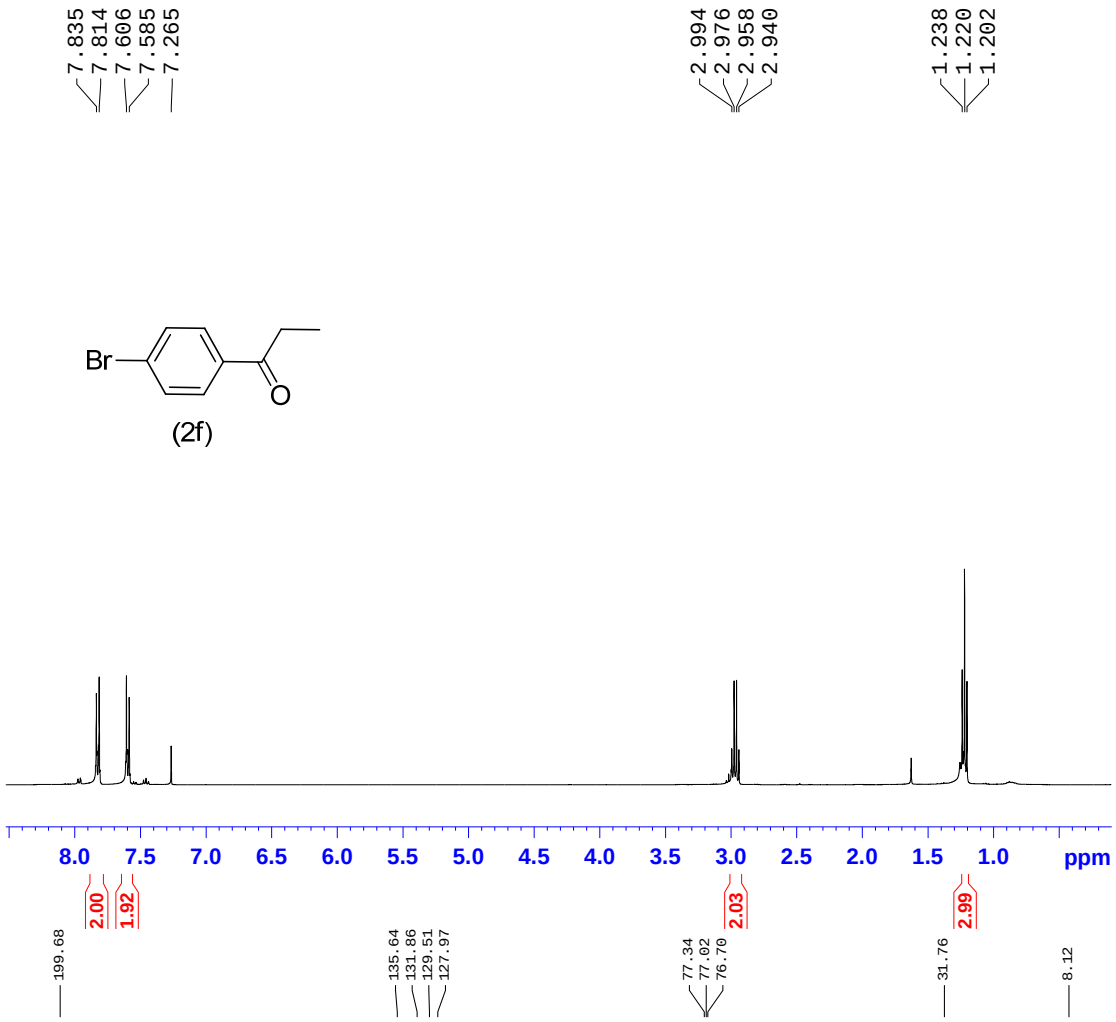
2.950
1.243
1.225
1.206
Cl
O
(2e)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
1.93
2.01
3.34
199.52
139.29
135.25
129.39
128.87
77.32
77.20
77.00
76.68
31.78
8.15
Cl
O
(2e)
200
180
160
140
120
100
80
60
40
20
ppm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7.606
7.585
7.265
2.994
2.976
2.958
2.940
1.238
1.220
1.202
Br
O
(2f)
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
ppm
2.00
1.92
2.03
2.99
199.68
135.64
131.86
129.51
127.97
77.34
77.02
76.70
31.76
8.12
Br
O
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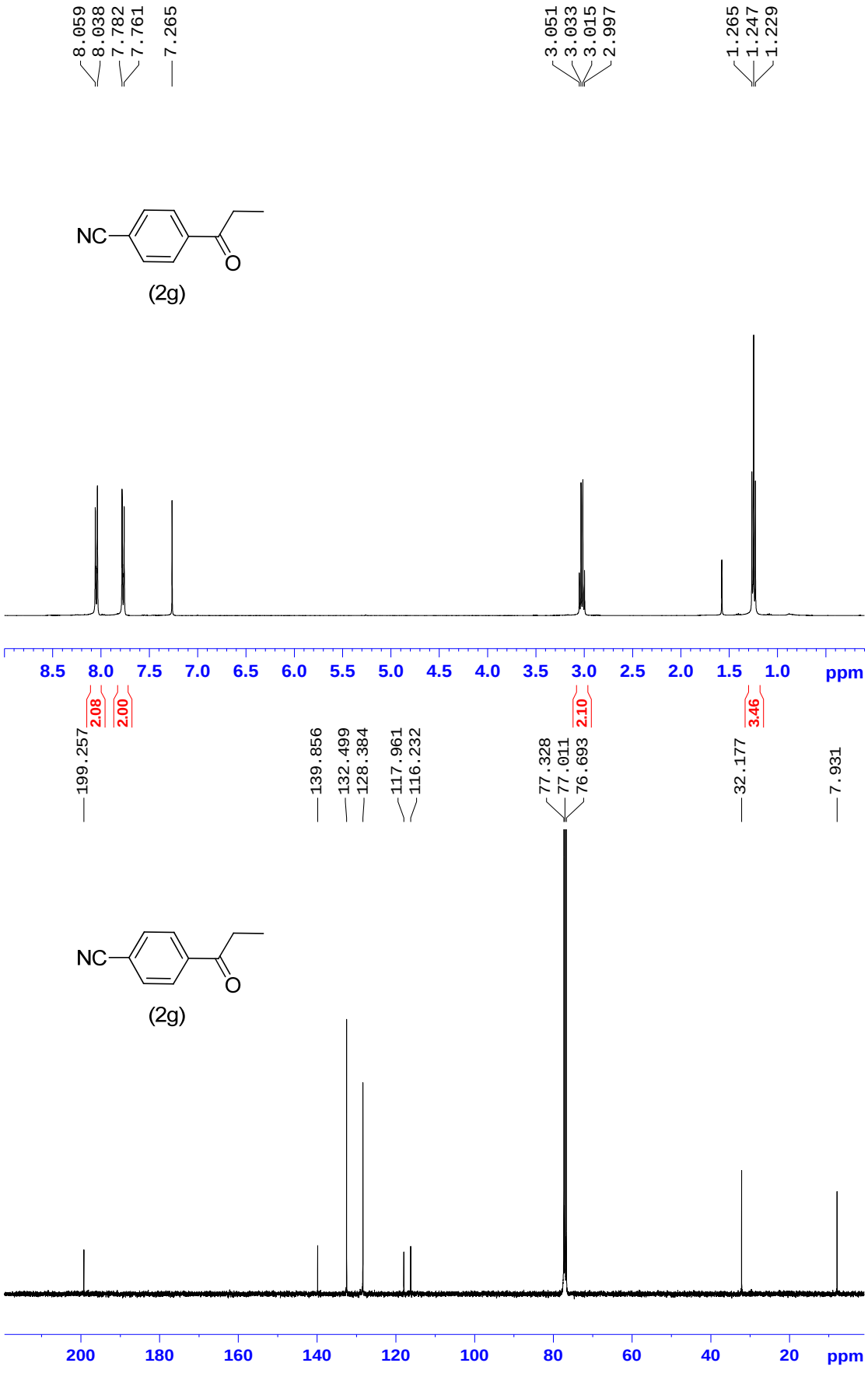
200
180
160
140
120
100
80
60
40
20
ppm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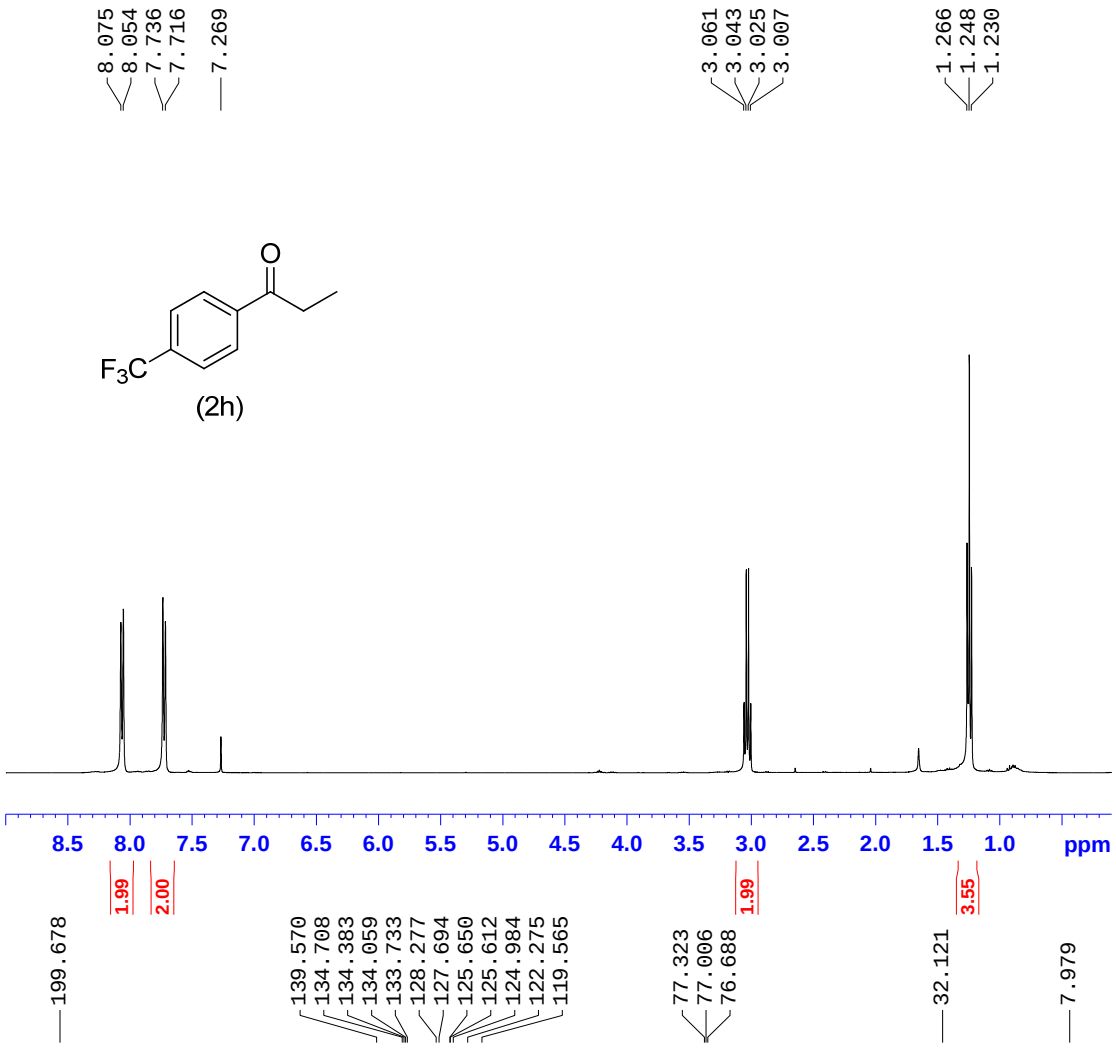
8.038
7.782
7.761
7.265
3.051
3.033
3.015
2.997
1.265
1.247
1.229
NC
O
(2g)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.08
2.00
2.10
3.46
199.257
139.856
132.499
128.384
117.961
116.232
77.328
77.011
76.693
32.177
7.931
NC
O
(2g)
200
180
160
140
120
100
80
60
40
20
ppm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7.736
7.716
7.269
3.061
3.043
3.025
3.007
1.266
1.248
1.230
O
F3C
(2h)
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
ppm
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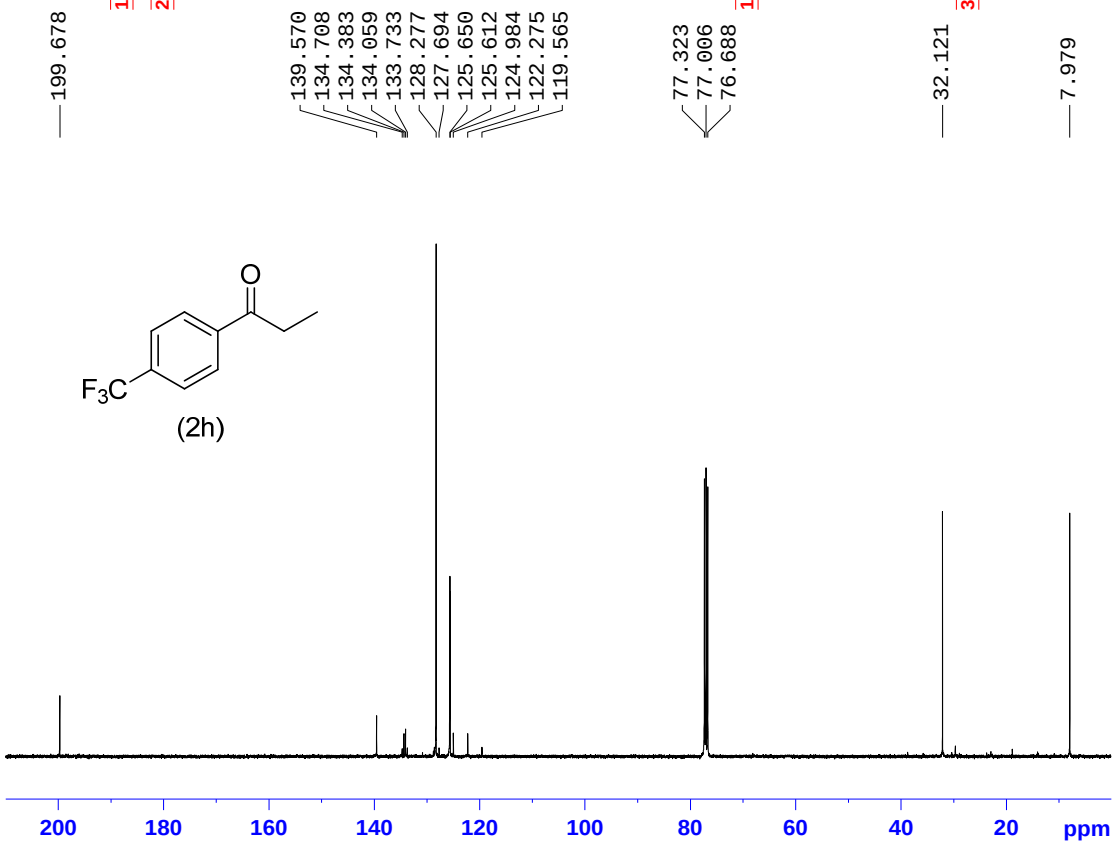
2.00
1.99
3.55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127.694
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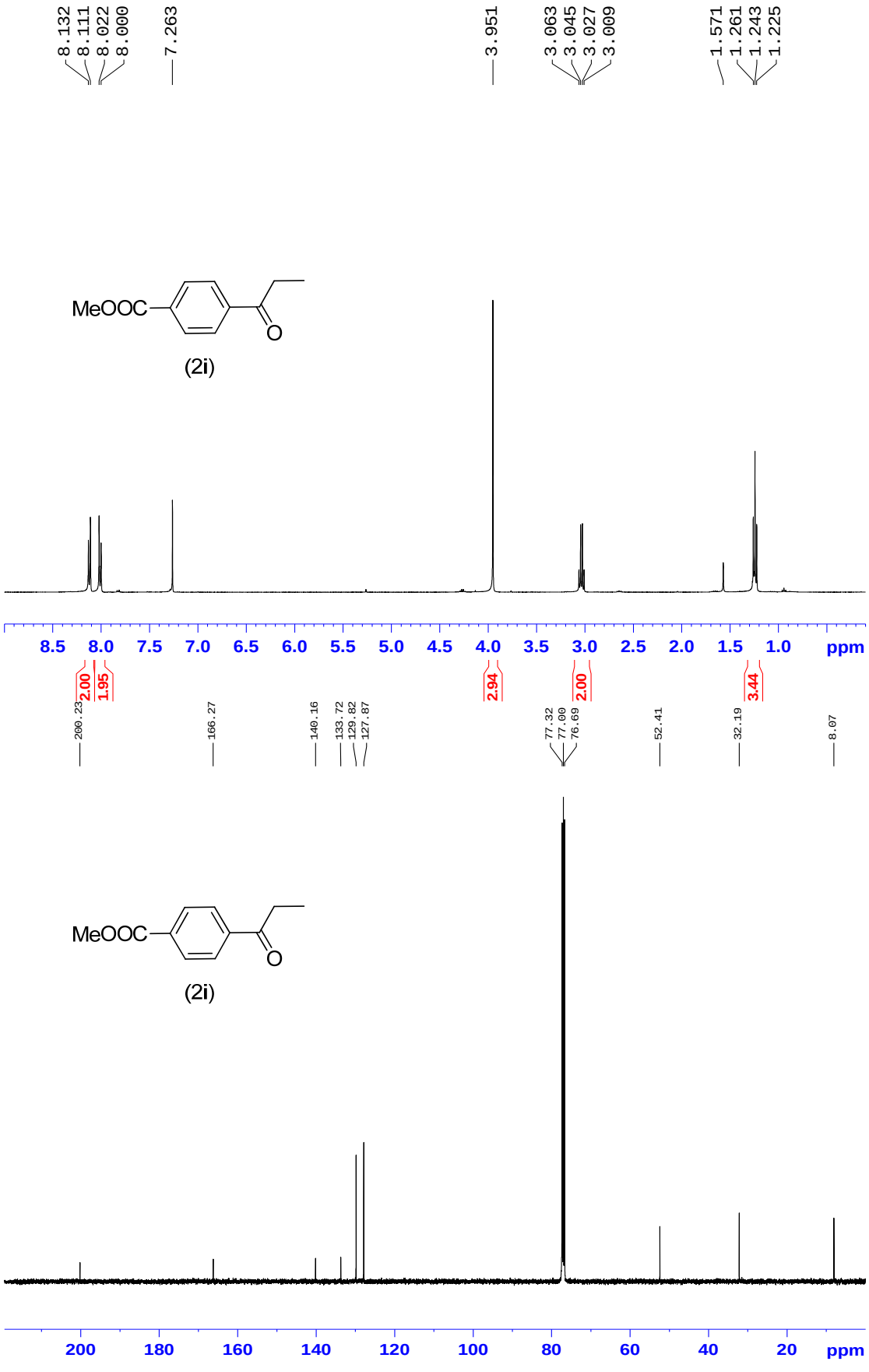
125.612
124.984
122.275
119.565
77.323
77.006
76.688
32.121
7.979
O
F3C
(2h)
200
180
160
140
120
100
80
60
40
20
ppm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7.263
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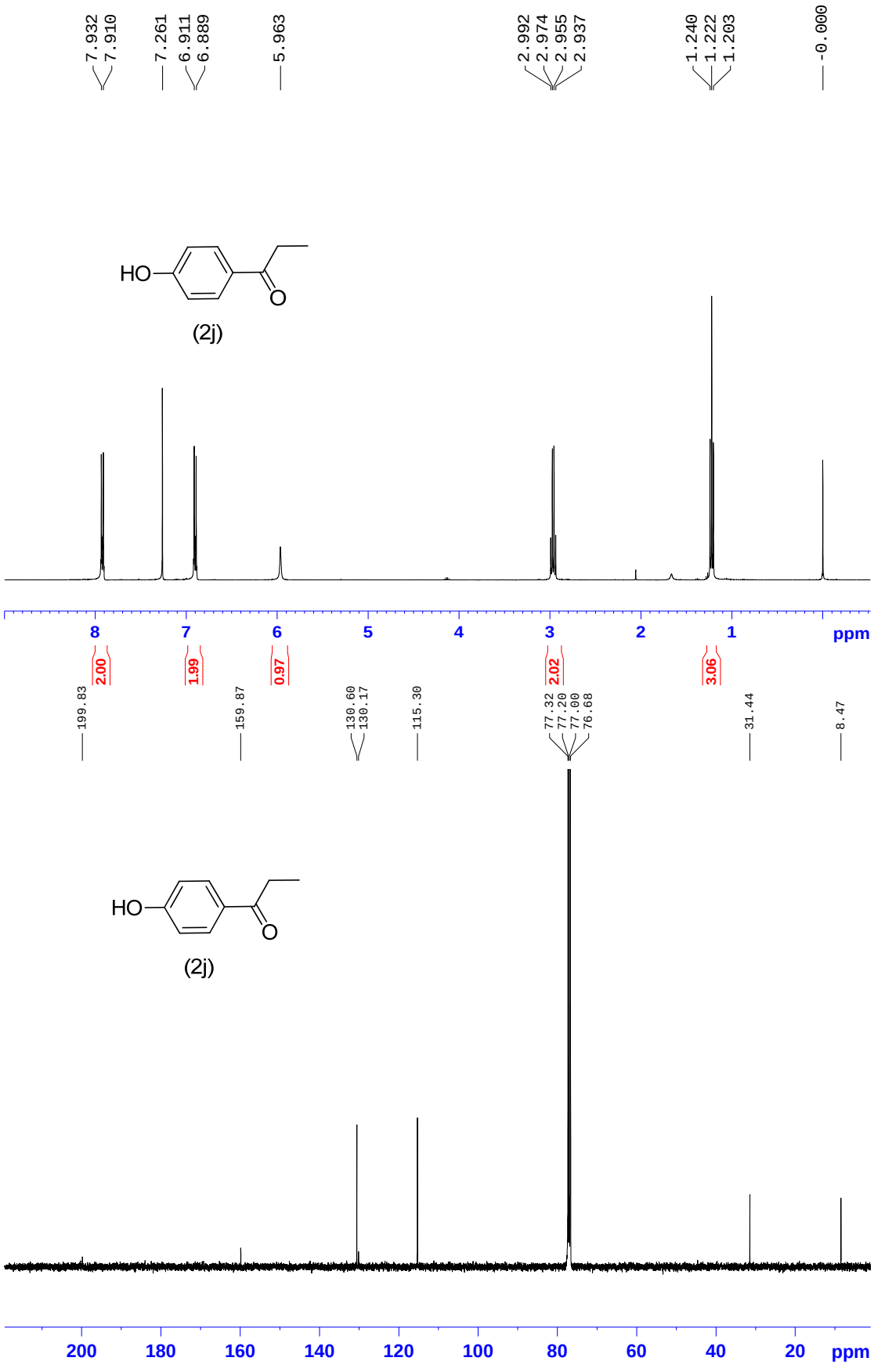
3.045
3.027
3.009
1.571
1.261
1.243
1.225
MeOOC
O
(2i)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
1.95
2.94
2.00
3.44
200.23
166.27
140.16
133.72
129.82
127.87
77.32
77.00
76.69
52.41
32.19
8.07
MeOOC
O
(2i)
200
180
160
140
120
100
80
60
40
20
ppm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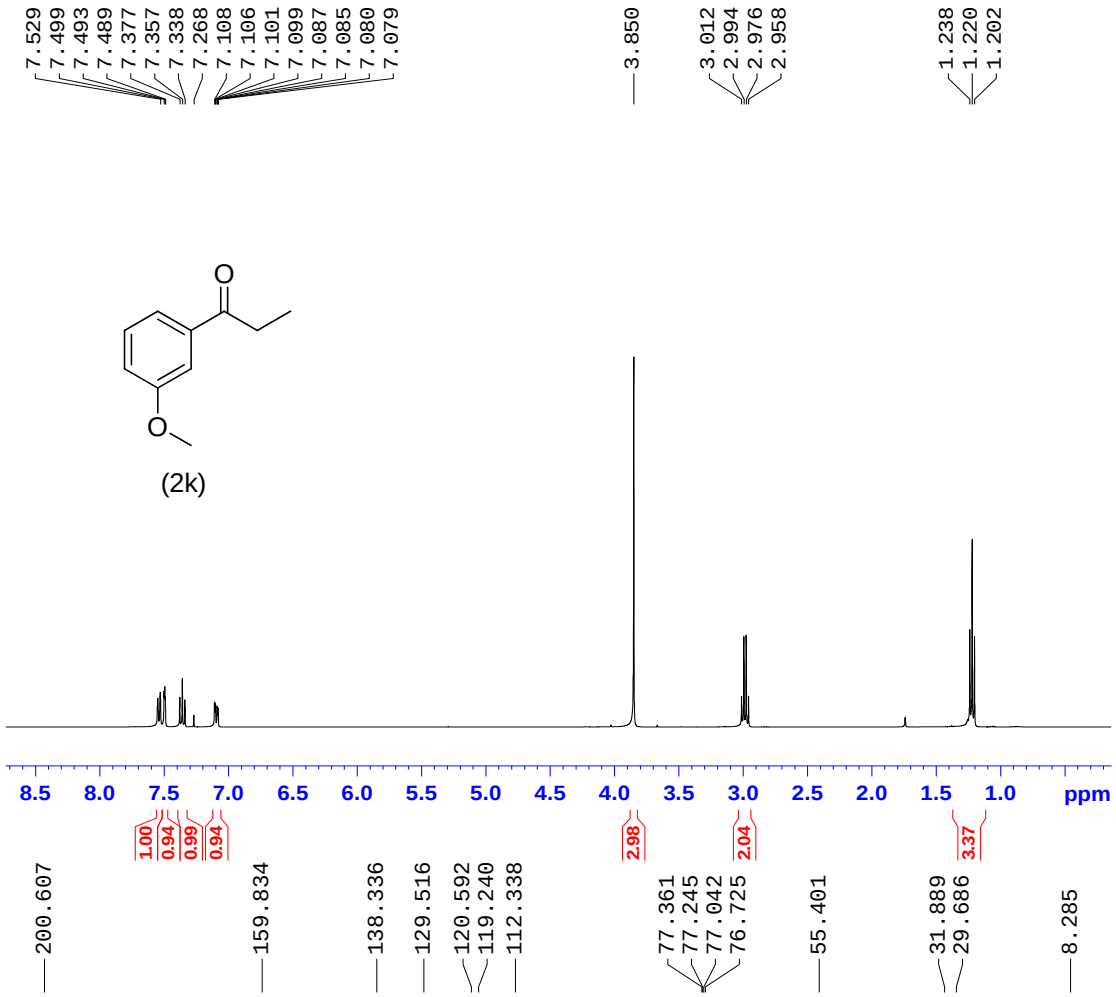
7.910
7.261
6.911
6.889
5.963
2.992
2.974
2.955
2.937
1.240
1.222
1.203
-0.000
HO
O
(2j)
8
7
6
5
4
3
2
1
ppm
2.00
1.99
0.97
2.02
3.06
199.83
159.87
130.60
130.17
115.30
77.32
77.20
77.00
76.68
31.44
8.47
HO
O
(2j)
200
180
160
140
120
100
80
60
40
20
ppm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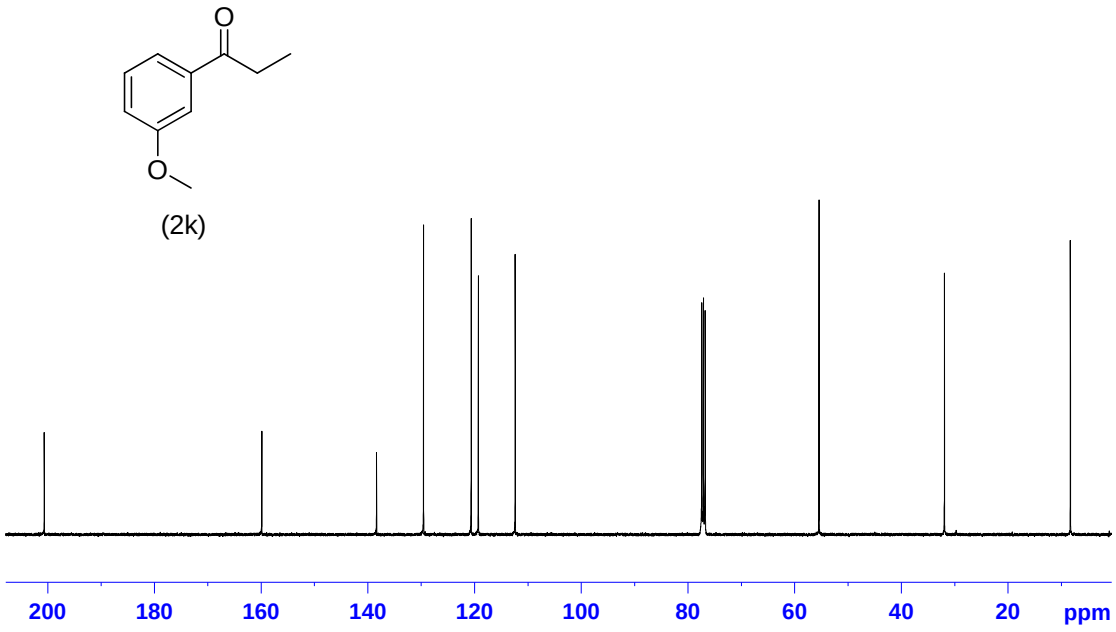
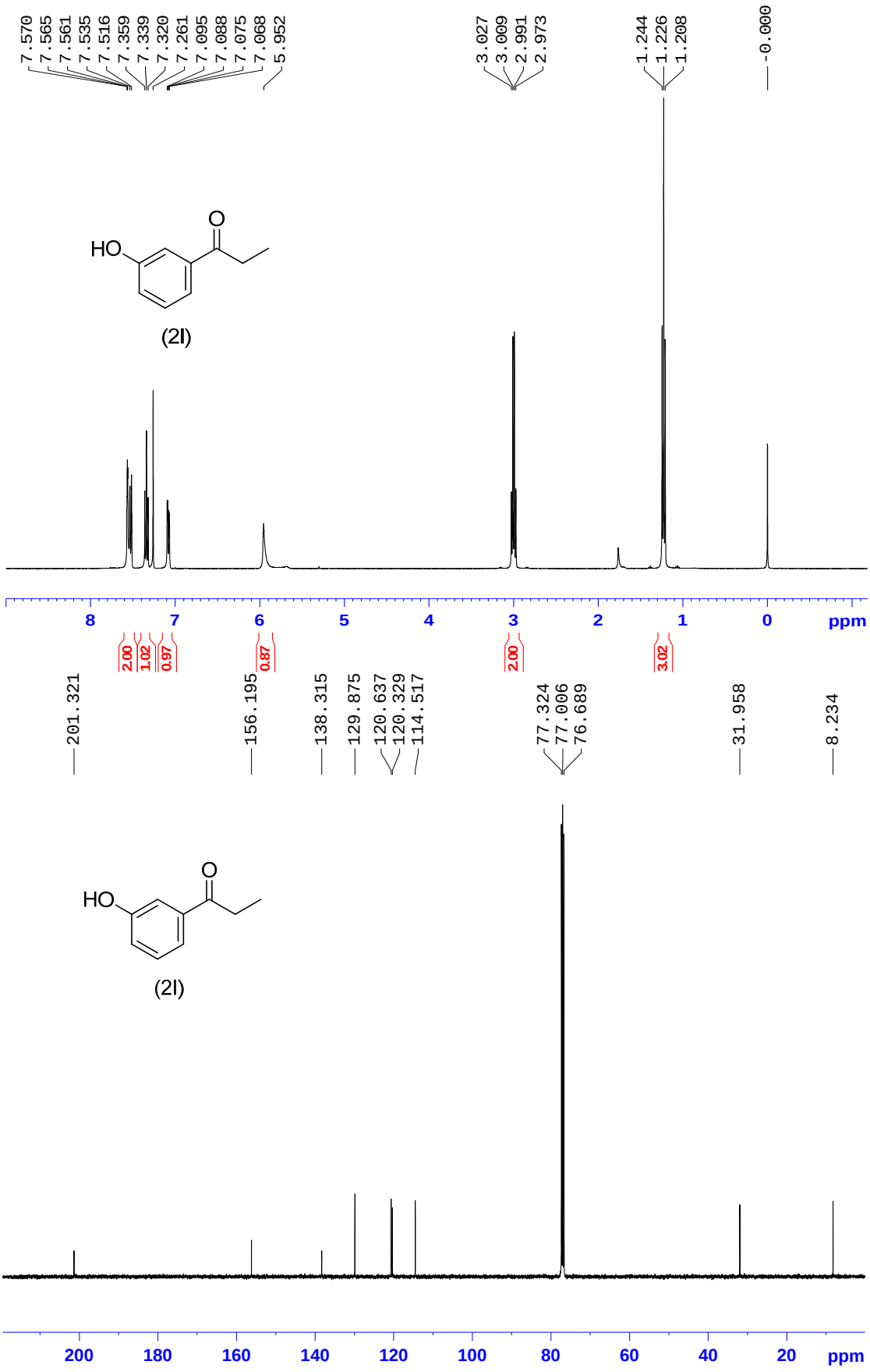
7.489
7.377
7.357
7.338
7.268
7.108
7.106
7.101
7.099
7.087
7.085
7.080
7.079
3.850
3.012
2.994
2.976
2.958
1.238
1.220
1.202
O
O
(2k)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
0.94
0.99
0.94
2.98
2.04
3.37

200.607
159.834
138.336
129.516
120.592
119.240
112.338
77.361
77.245
77.042
76.725
55.401
31.889
29.686
8.285


O
O
(2k)
200
180
160
140
120
100
80
60
40
20
ppm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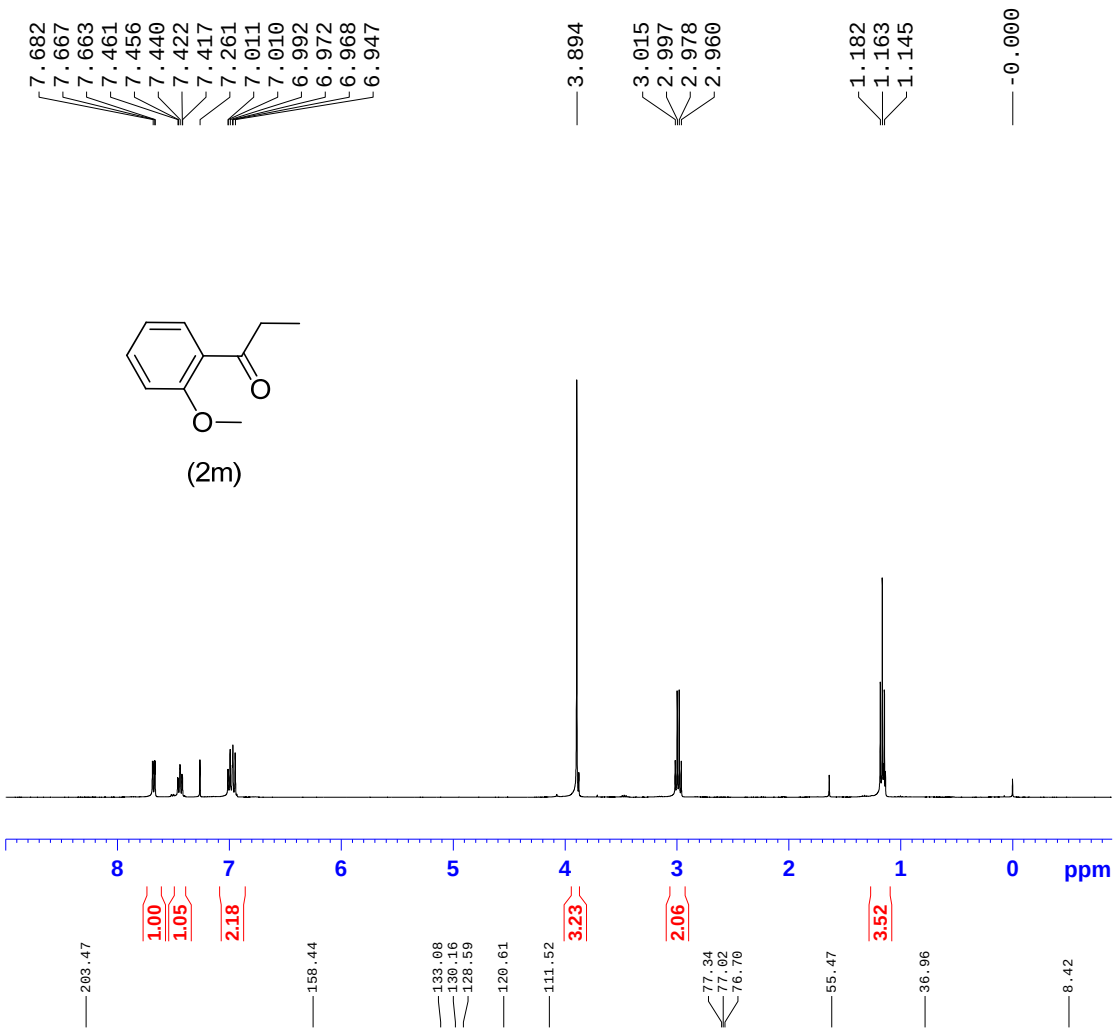
7.565
7.561
7.535
7.516
7.359
7.339
7.320
7.261
7.095
7.088
7.075
7.068
5.952
3.027
3.009
2.991
2.973
1.244
1.226
1.208
-0.000
HO
O
(2l)
8
7
6
5
4
3
2
1
0
ppm
2.00
1.02
0.97
0.87
2.00
3.02
201.321
156.195
138.315
129.875
120.637
120.329
114.517
77.324
77.006
76.689
31.958
8.234
HO
O
(2l)
200
180
160
140
120
100
80
60
40
20
ppm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7.663
7.461
7.456
7.440
7.422
7.417
7.261
7.011
7.010
6.992
6.972
6.968
6.947
3.894
3.015
2.997
2.978
2.960
1.182
1.163
1.145
-0.000
O
O—
(2m)
8
7
6
5
4
3
2
1
0
ppm
1.00
1.05
2.18
3.23
2.06
3.52
203.47
158.44
133.08
130.16
128.59
120.61
111.52
77.34
77.02
76.70
55.47
36.96
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O
O—
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140
120
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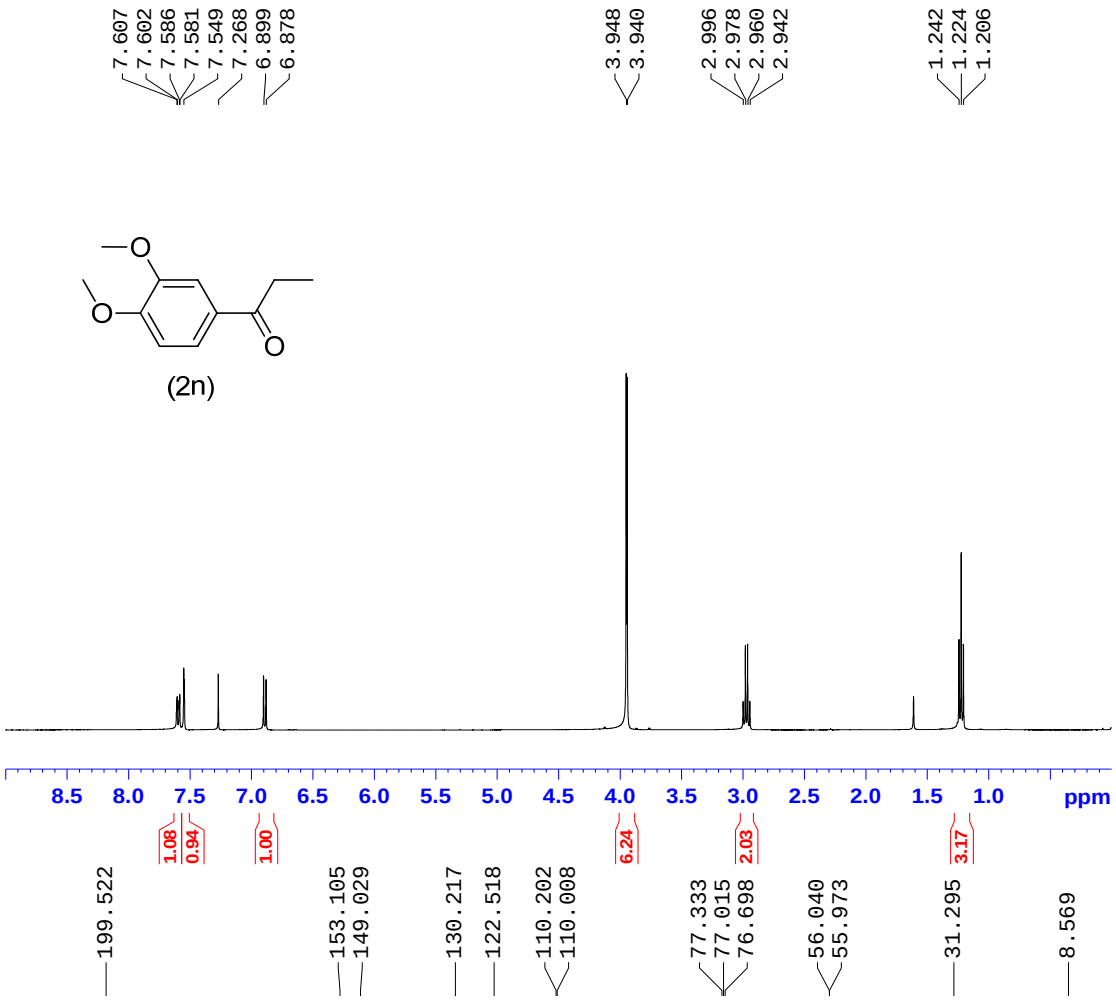
80
60
40
20
ppm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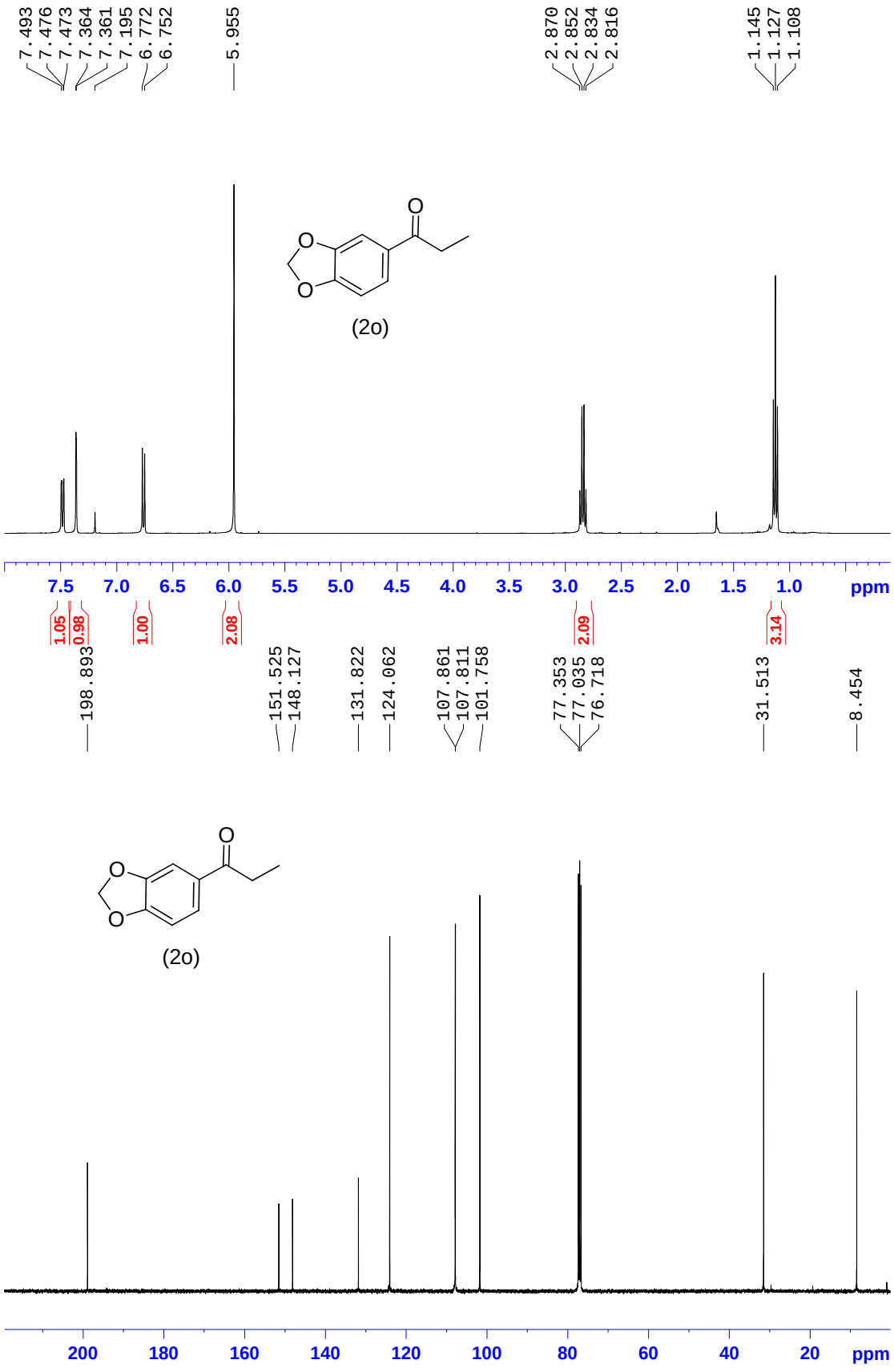
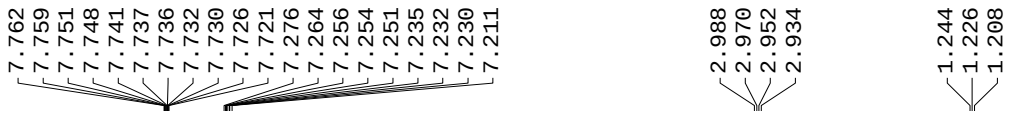
7.268
6.899
6.878
3.948
3.940
2.996
2.978
2.960
2.942
1.242
1.224
1.206
(2n)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.08
0.94
1.00
6.24
2.03
3.17
199.522
153.105
149.029
130.217
122.518
110.202
110.008
77.333
77.015
76.698
56.040
55.973
31.295
8.569
(2n)
200
180
160
140
120
100
80
60
40
20
ppm


7.493
7.476
7.473
7.364
7.361
7.195
6.772
6.752
5.955
2.870
2.852
2.834
2.816
1.145
1.127
1.108
(2o)
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
1.05
0.98
1.00
2.08
2.09
3.14
198.893
151.525
148.127
131.822
124.062
107.861
107.811
101.758
77.353
77.035
76.718
31.513
8.454
(2o)
200
180
160
140
120
100
80
60
40
20
ppm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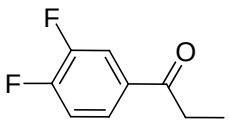
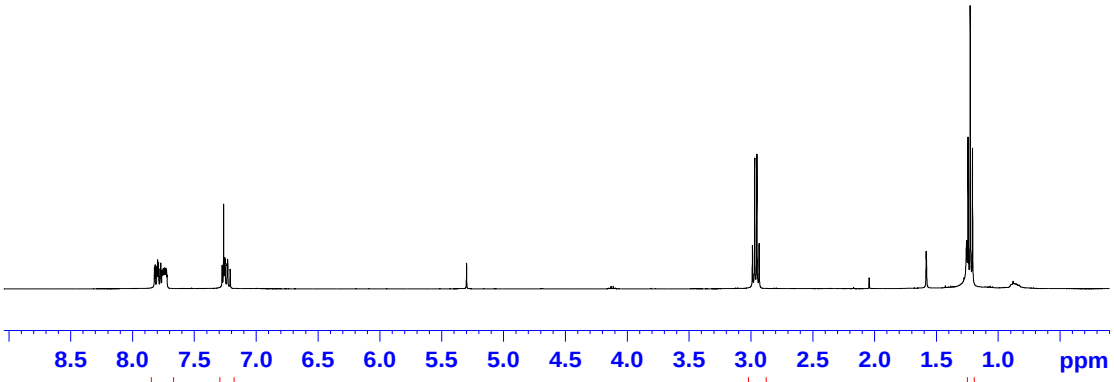
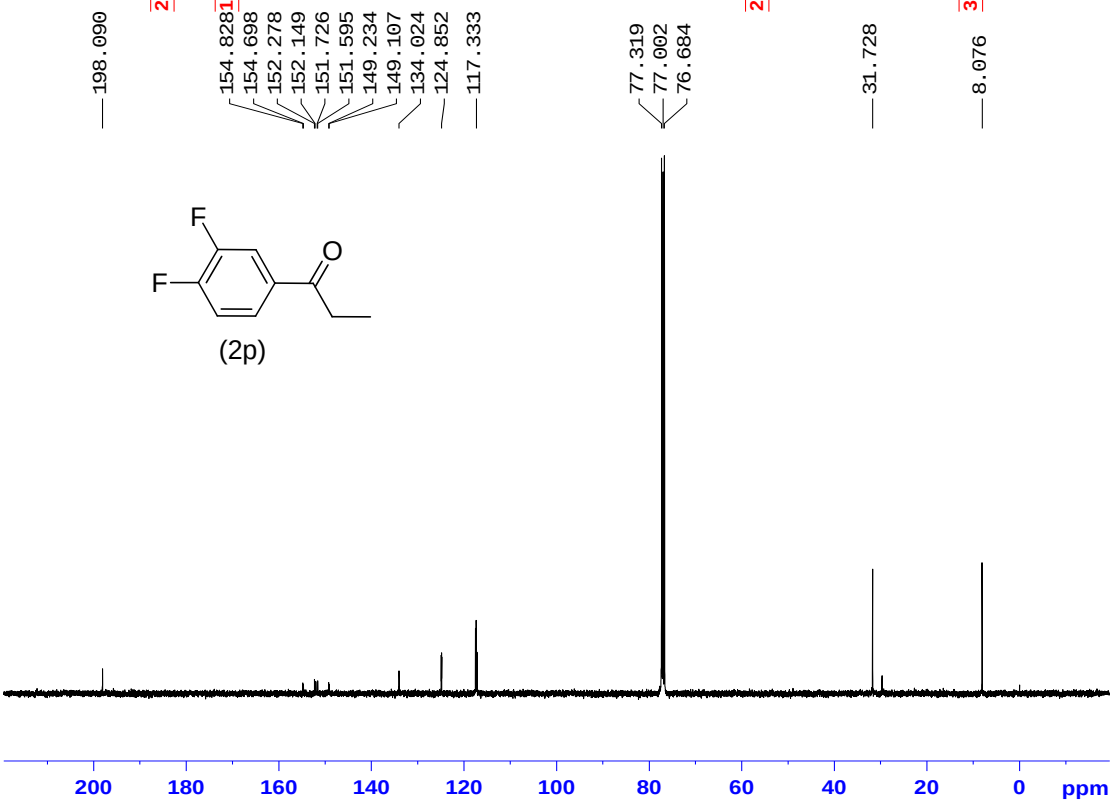
7.759
7.751
7.748
7.741
7.737
7.736
7.732
7.730
7.726
7.721
7.276
7.264
7.256
7.254
7.251
7.235
7.232
7.230
7.211
2.988
2.970
2.952
2.934
1.244
1.226
1.208


F
F
O

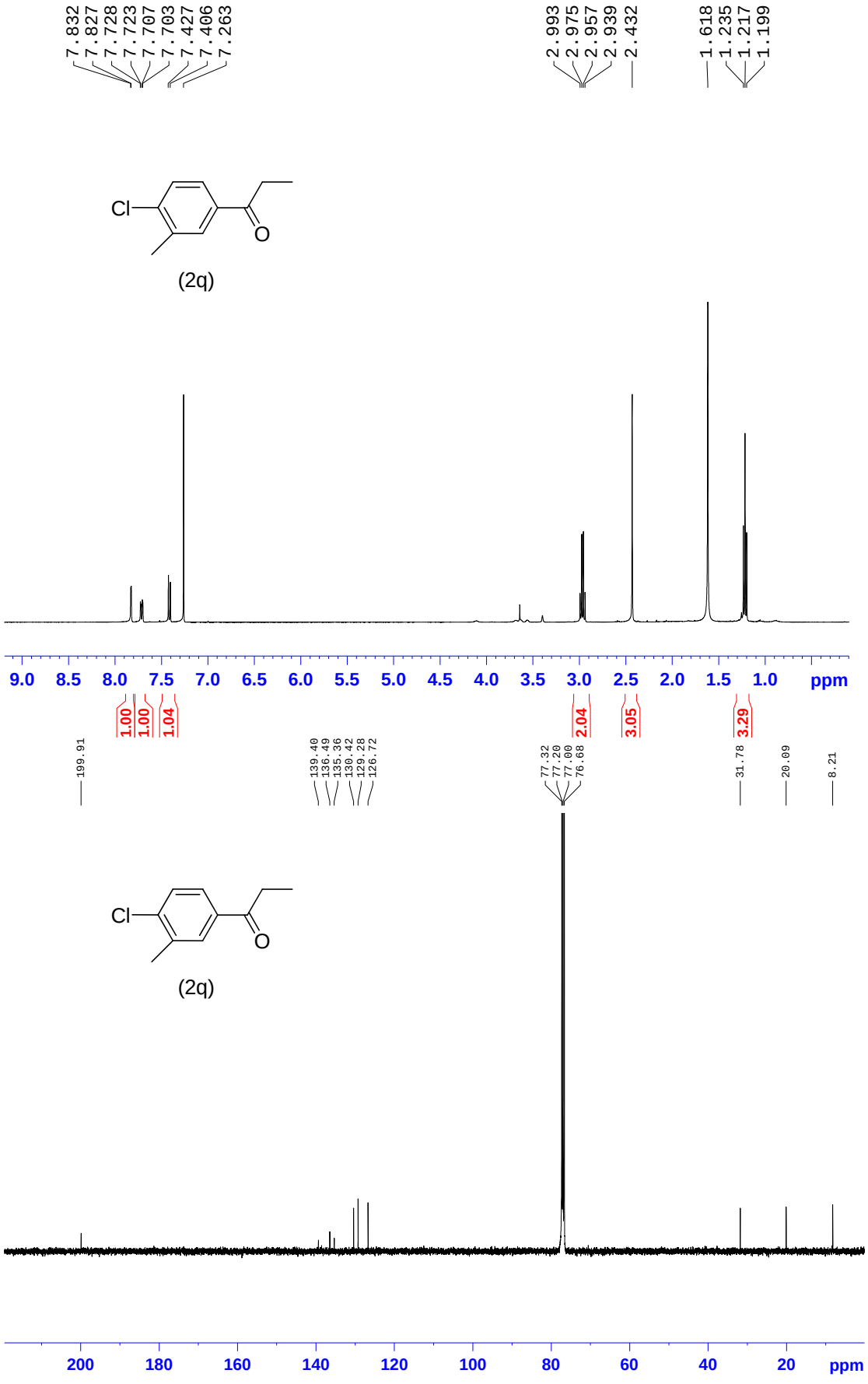
(2p)

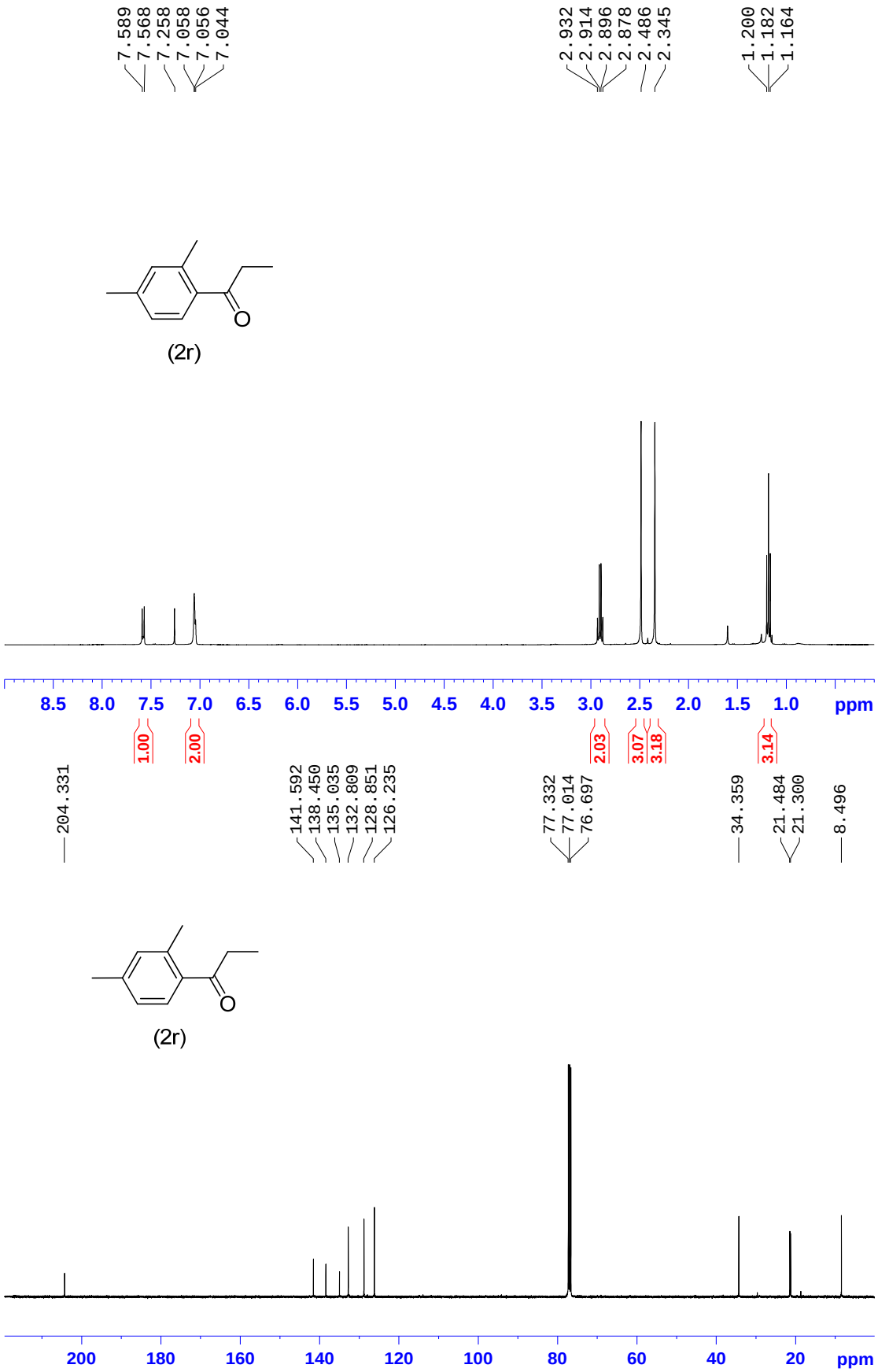

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
1.39
2.06
3.23

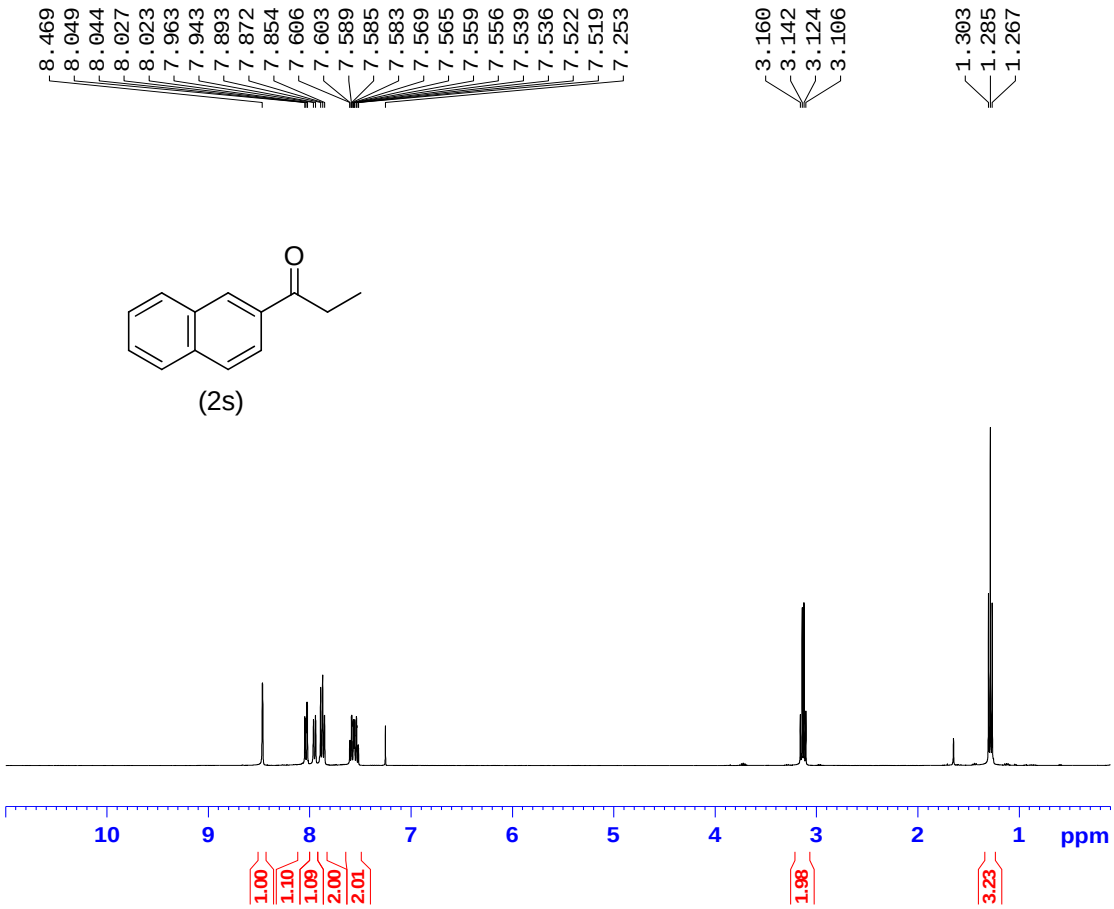

198.090
154.828
154.698
152.278
152.149
151.726
151.595
149.234
149.107
134.024
124.852
117.333
77.319
77.002
76.684
31.728
8.076
200
180
160
140
120
100
80
60
40
20
0
ppm

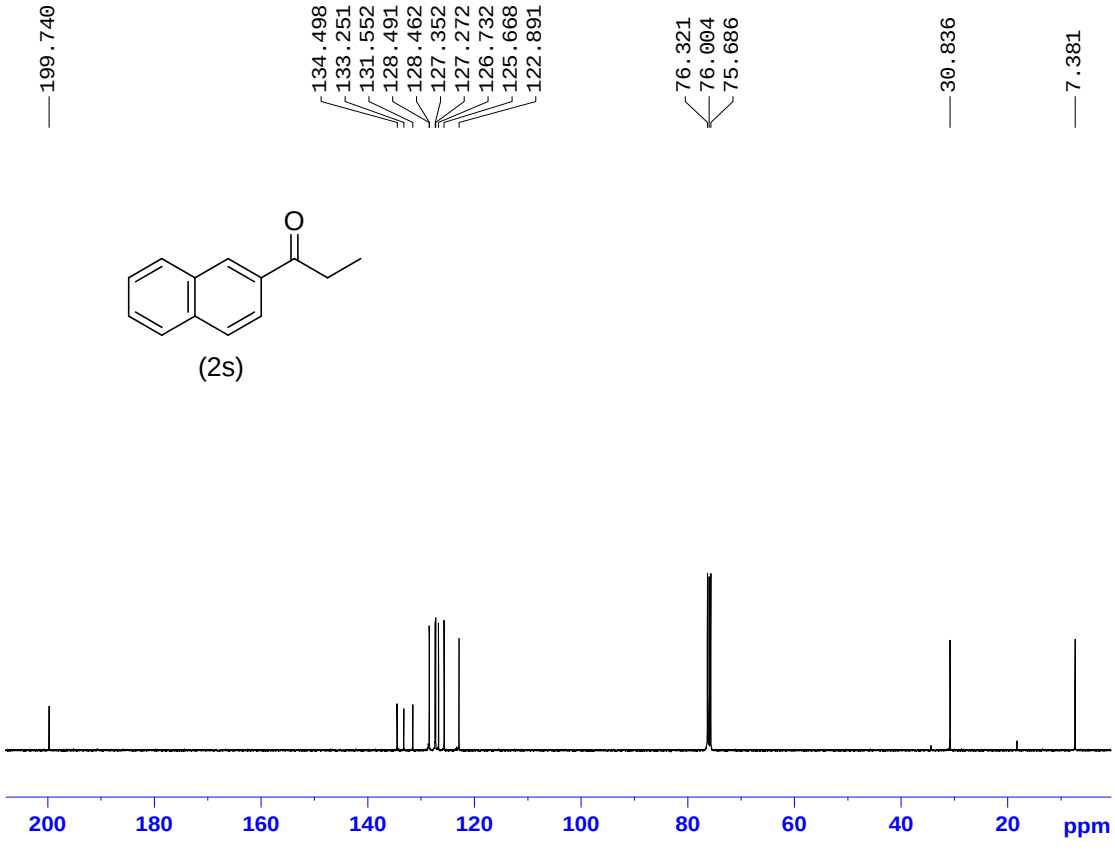
F
F
O

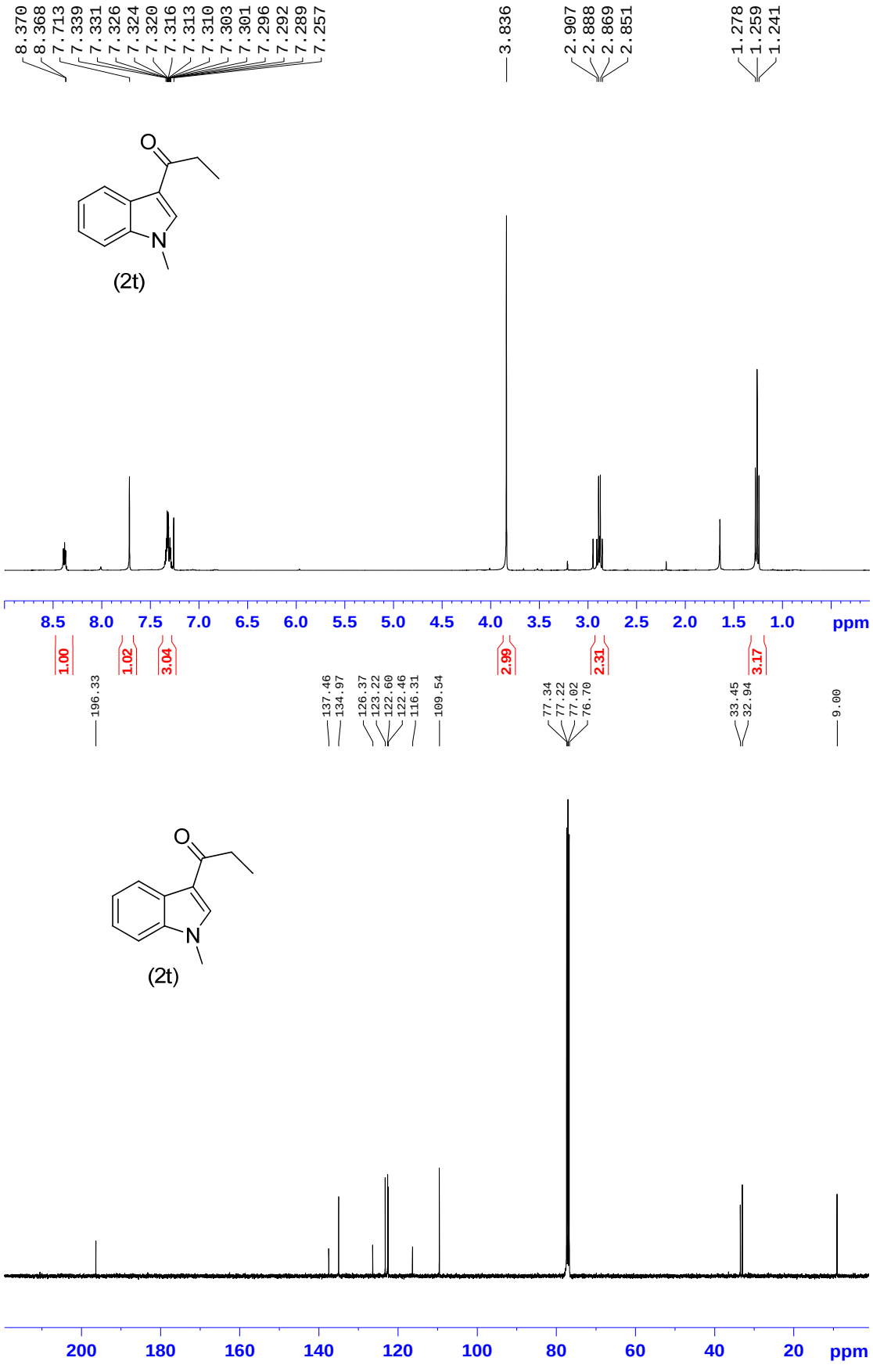
(2p)

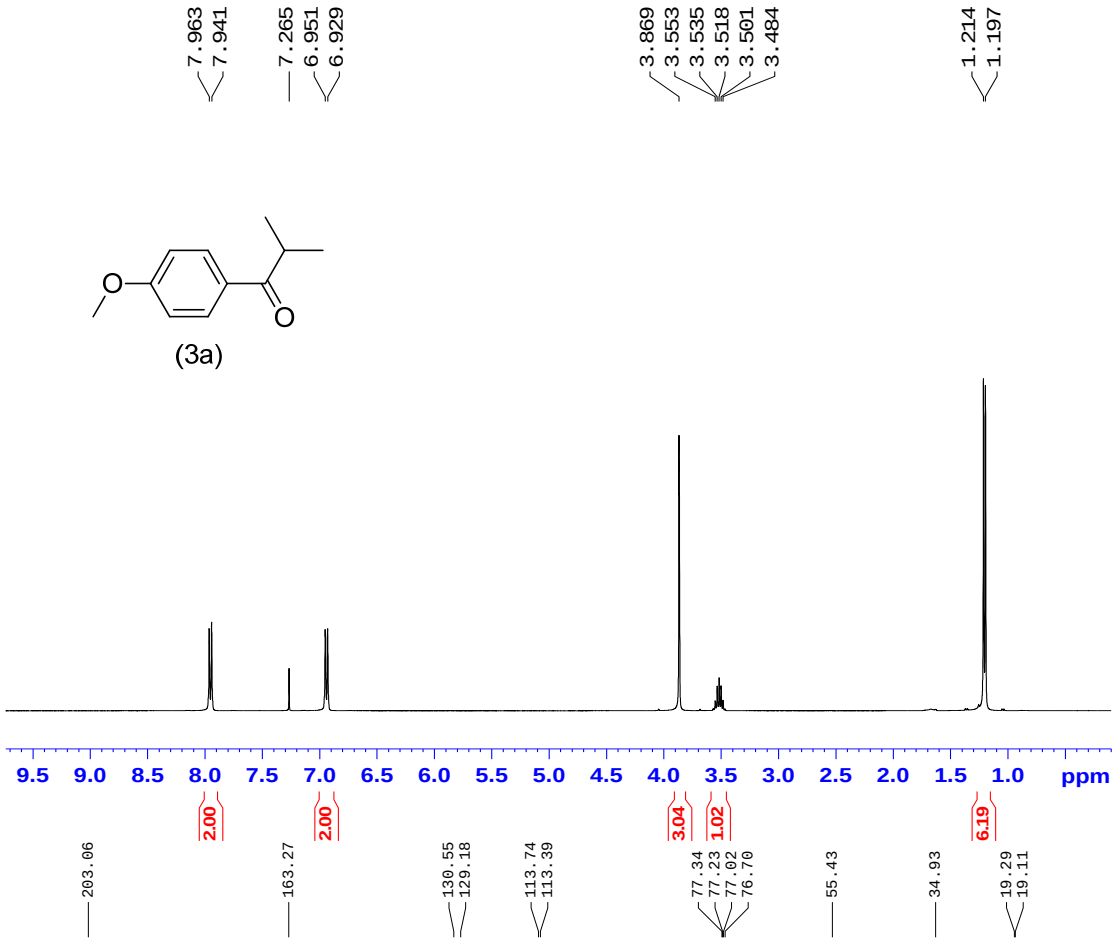

7.832
7.827
7.728
7.723
7.707
7.703
7.427
7.406
7.263
2.993
2.975
2.957
2.939
2.432
1.618
1.235
1.217
1.199
Cl
O
(2q)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.00
1.04
2.04
3.05
3.29
199.91
139.40
136.49
135.36
130.42
129.28
126.72
77.32
77.20
77.00
76.68
31.78
20.09
8.21
Cl
O
(2q)
200 180 160 140 120 100 80 60 40 20 ppm

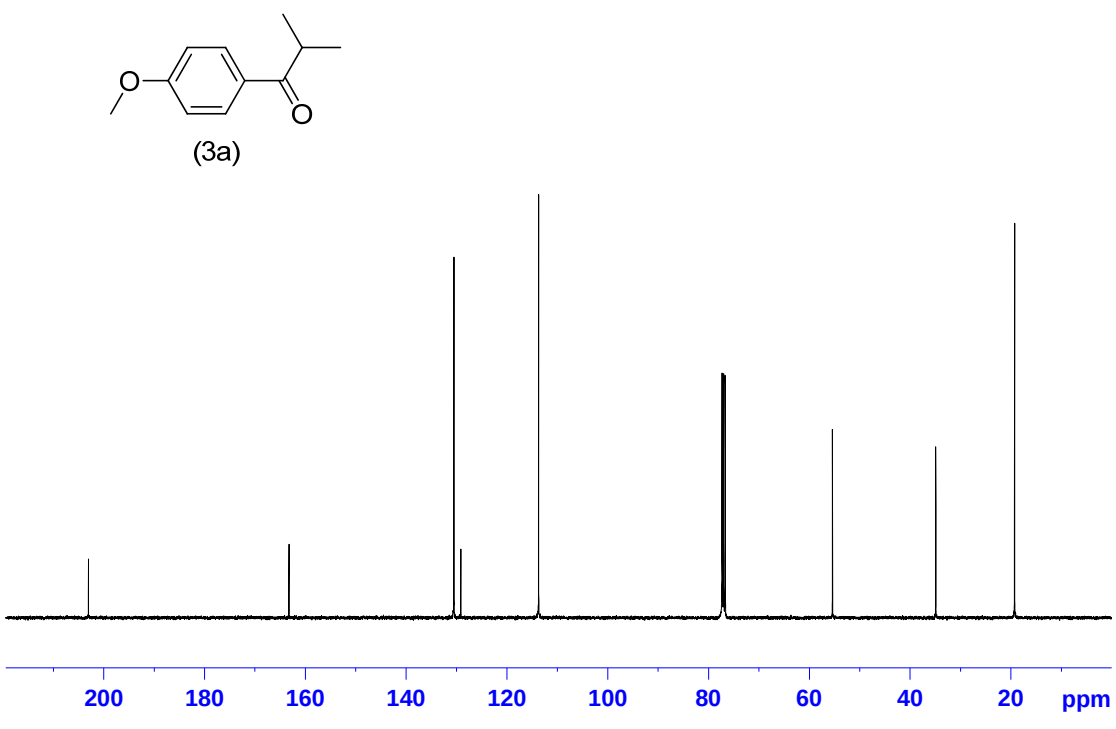

7.589
7.568
7.258
7.058
7.056
7.044
2.932
2.914
2.896
2.878
2.486
2.345
1.200
1.182
1.164
O
(2r)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
2.00
2.03
3.07
3.18
3.14
204.331
141.592
138.450
135.035
132.809
128.851
126.235
77.332
77.014
76.697
34.359
21.484
21.300
8.496
O
(2r)
200 180 160 140 120 100 80 60 40 20 ppm

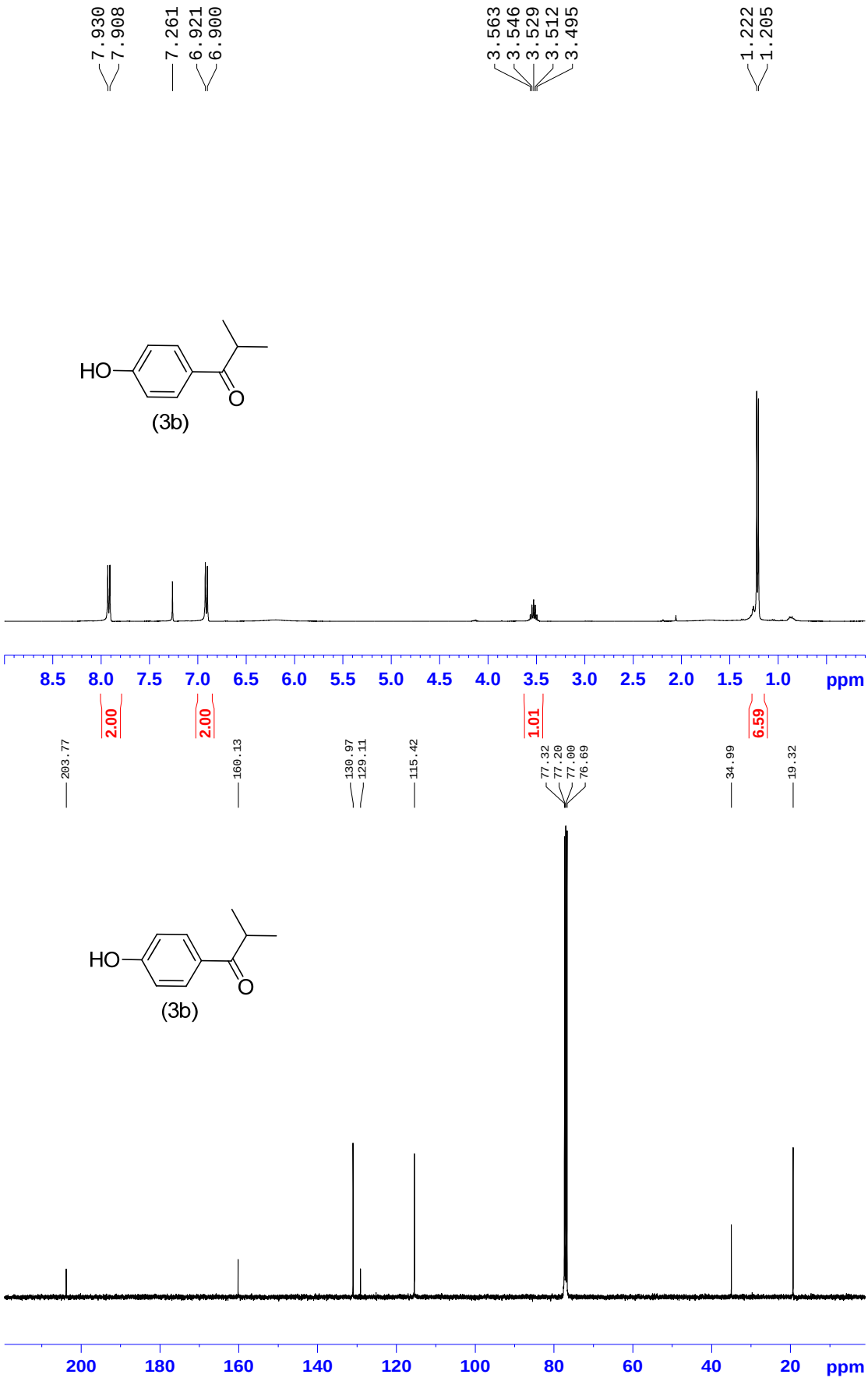

8.469
8.049
8.044
8.027
8.023
7.963
7.943
7.893
7.872
7.854
7.606
7.603
7.589
7.585
7.583
7.569
7.565
7.559
7.556
7.539
7.536
7.522
7.519
7.253
3.160
3.142
3.124
3.106
1.303
1.285
1.267
O
(2s)
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.10
1.09
2.00
2.01
1.98
3.23

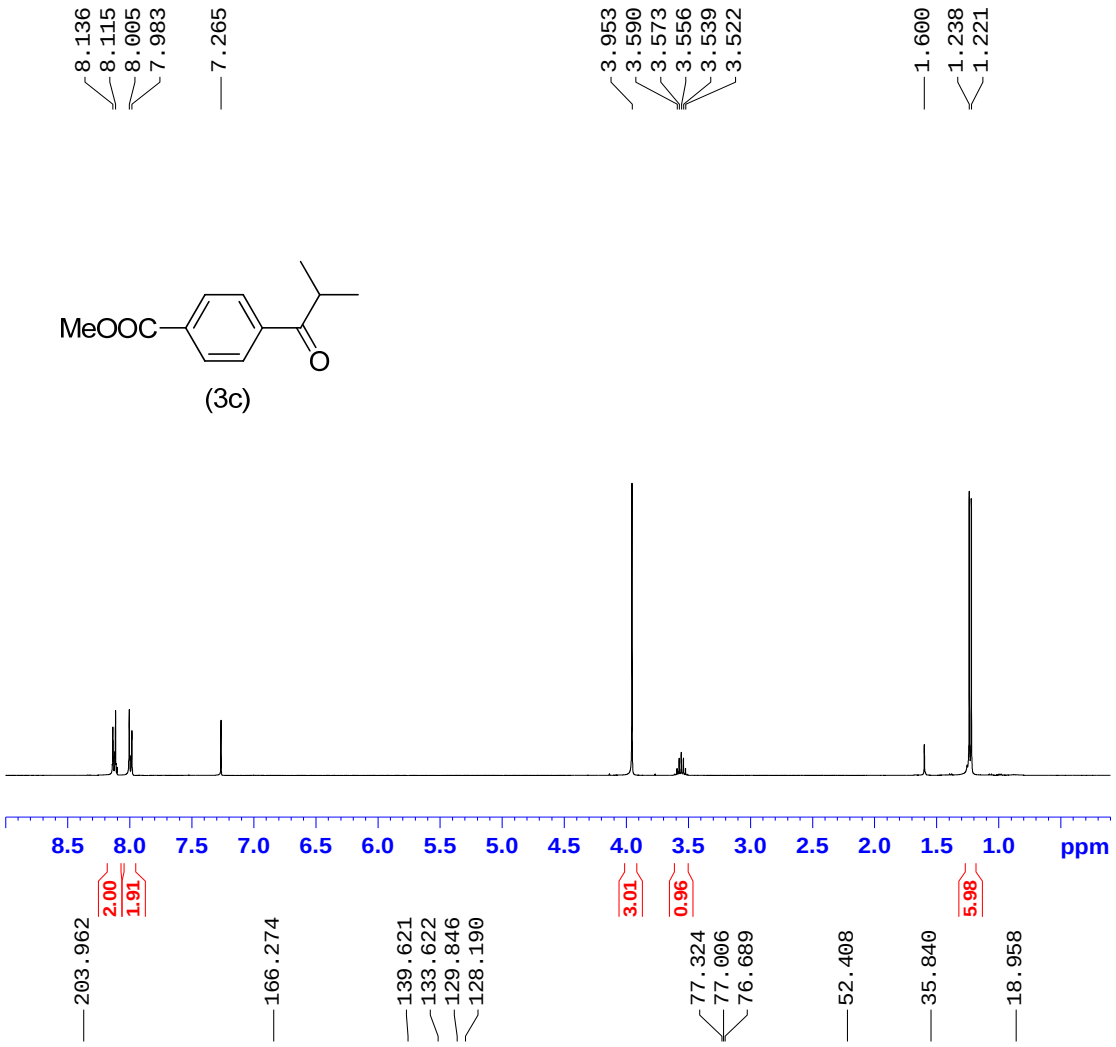

199.740
134.498
133.251
131.552
128.491
128.462
127.352
127.272
126.732
125.668
122.891
76.321
76.004
75.686
30.836
7.381
O
(2s)
200
180
160
140
120
100
80
60
40
20
ppm

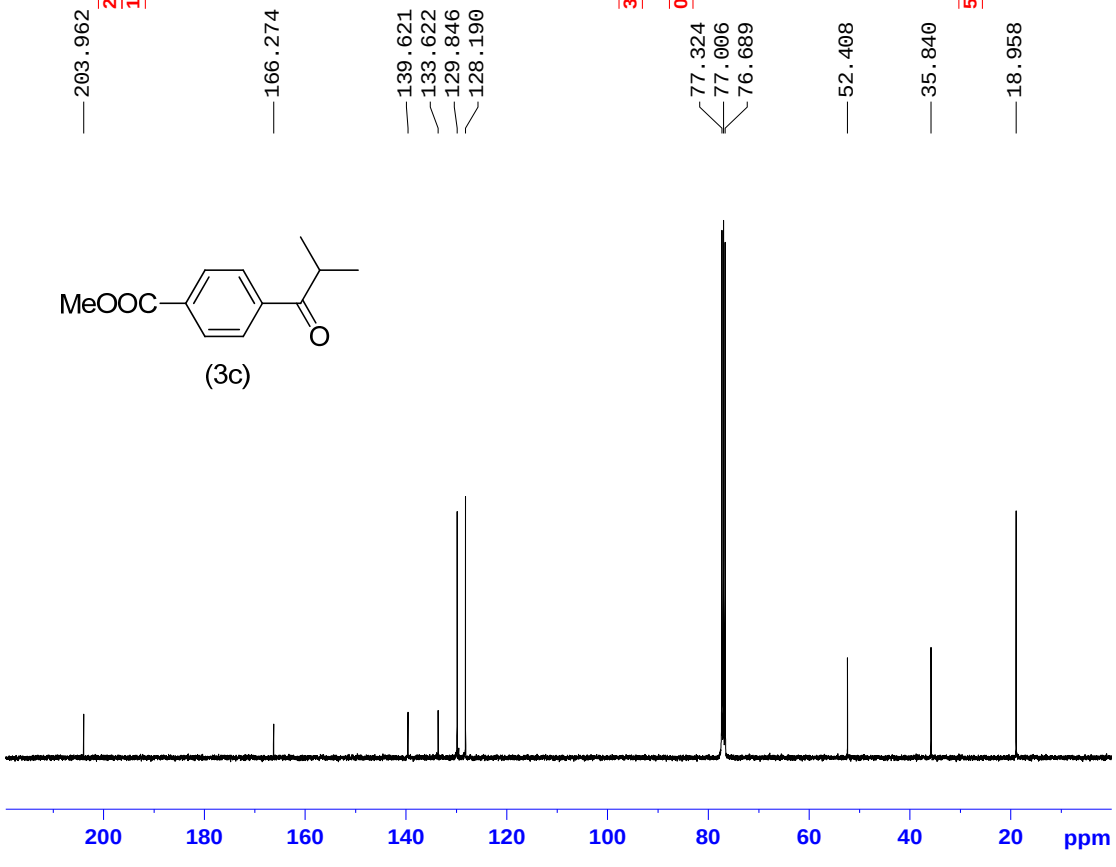

8.370
8.368
7.713
7.339
7.331
7.326
7.324
7.320
7.316
7.313
7.310
7.303
7.301
7.296
7.292
7.289
7.257
3.836
2.907
2.888
2.869
2.851
1.278
1.259
1.241
O
N
(2t)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.02
3.04
2.99
2.31
3.17
196.33
137.46
134.97
126.37
123.22
122.60
122.46
116.31
109.54
77.34
77.22
77.02
76.70
33.45
32.94
9.00
O
N
(2t)
200
180
160
140
120
100
80
60
40
20
ppm

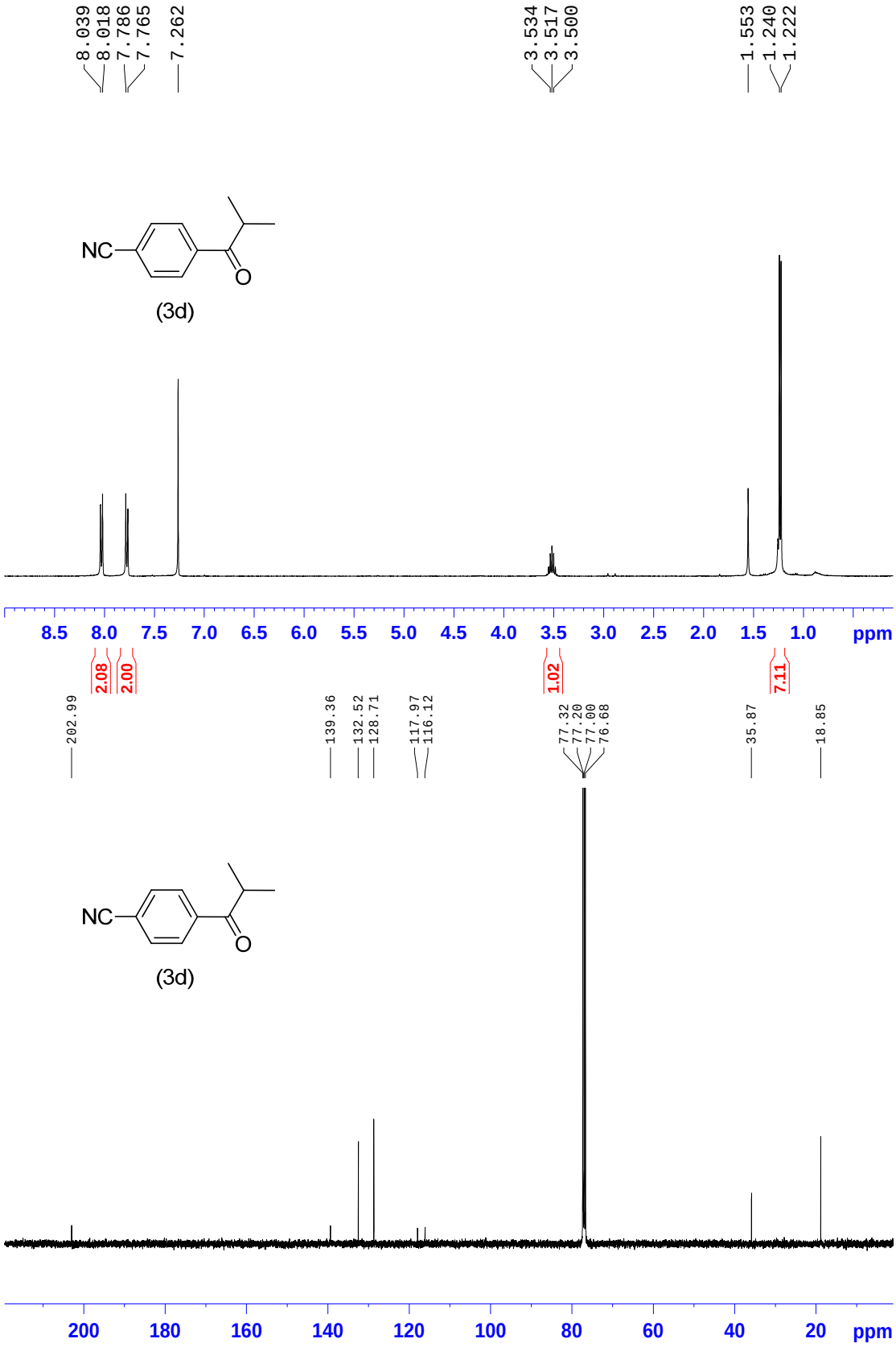

7.963
7.941
7.265
6.951
6.929
3.869
3.553
3.535
3.518
3.501
3.484
1.214
1.197
O
O
(3a)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.00
2.00
3.04
1.02
6.19

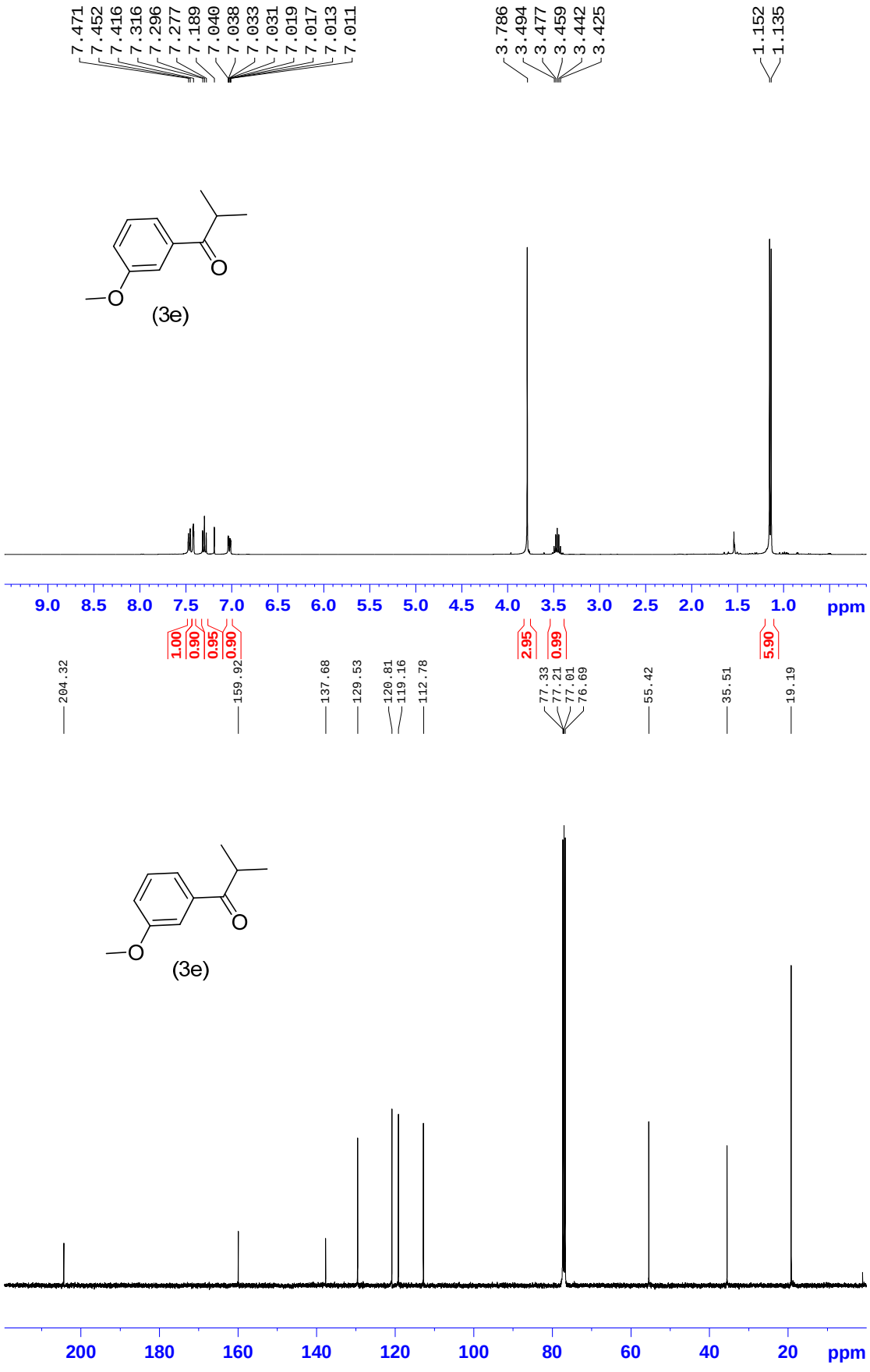

203.06
163.27
130.55
129.18
113.74
113.39
77.34
77.23
77.02
76.70
55.43
34.93
19.29
19.11
O
O
(3a)
200 180 160 140 120 100 80 60 40 20 ppm

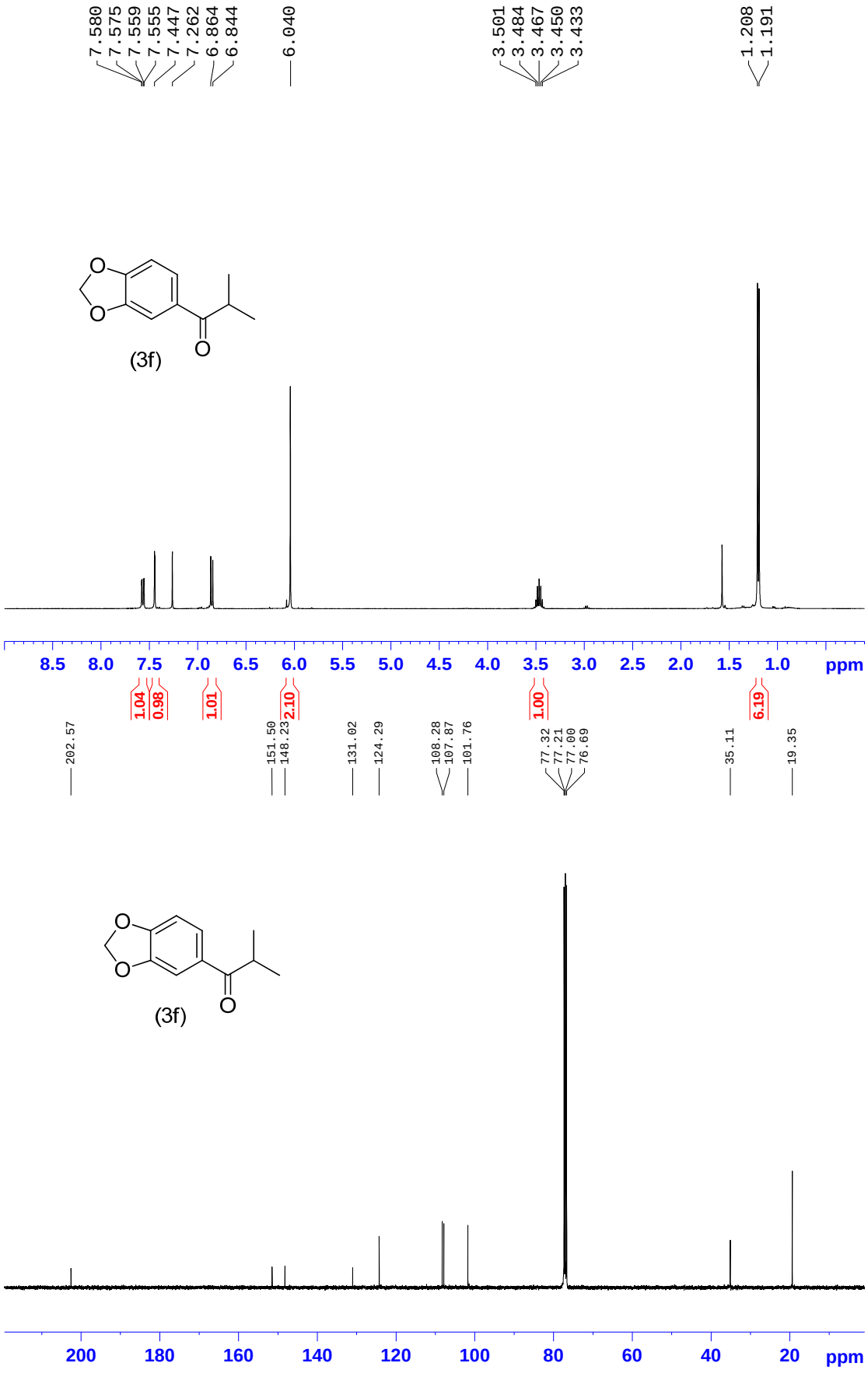

7.930
7.908
7.261
6.921
6.900
3.563
3.546
3.529
3.512
3.495
1.222
1.205
HO
O
(3b)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
2.00
1.01
6.59
203.77
160.13
130.97
129.11
115.42
77.32
77.20
77.00
76.69
34.99
19.32
HO
O
(3b)
200
180
160
140
120
100
80
60
40
20
ppm

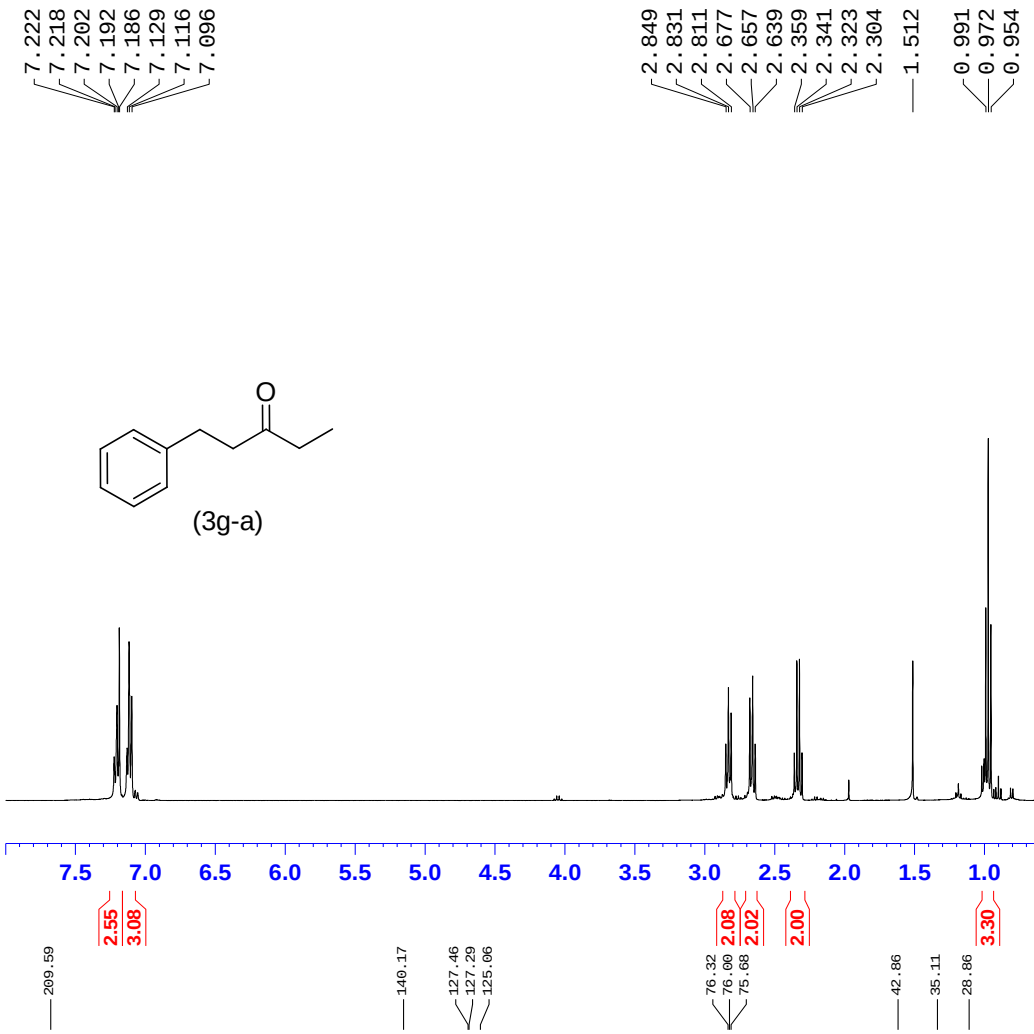

8.136
8.115
8.005
7.983
7.265
3.953
3.590
3.573
3.556
3.539
3.522
1.600
1.238
1.221
MeOOC
O
(3c)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
1.91
3.01
0.96
5.98

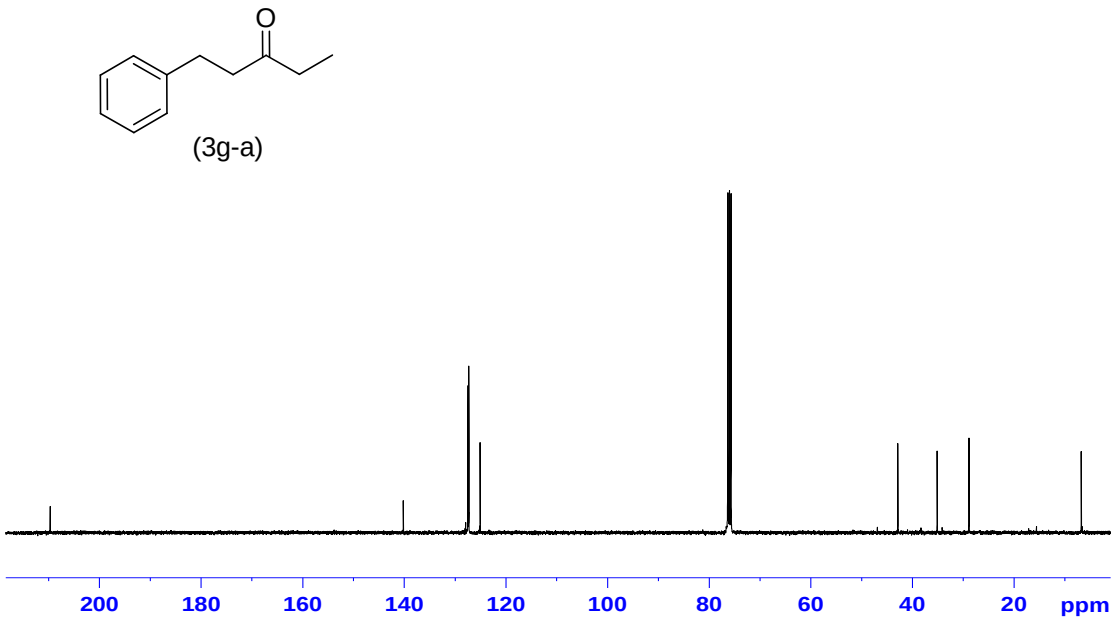

203.962
166.274
139.621
133.622
129.846
128.190
77.324
77.006
76.689
52.408
35.840
18.958
MeOOC
O
(3c)
200
180
160
140
120
100
80
60
40
20
ppm

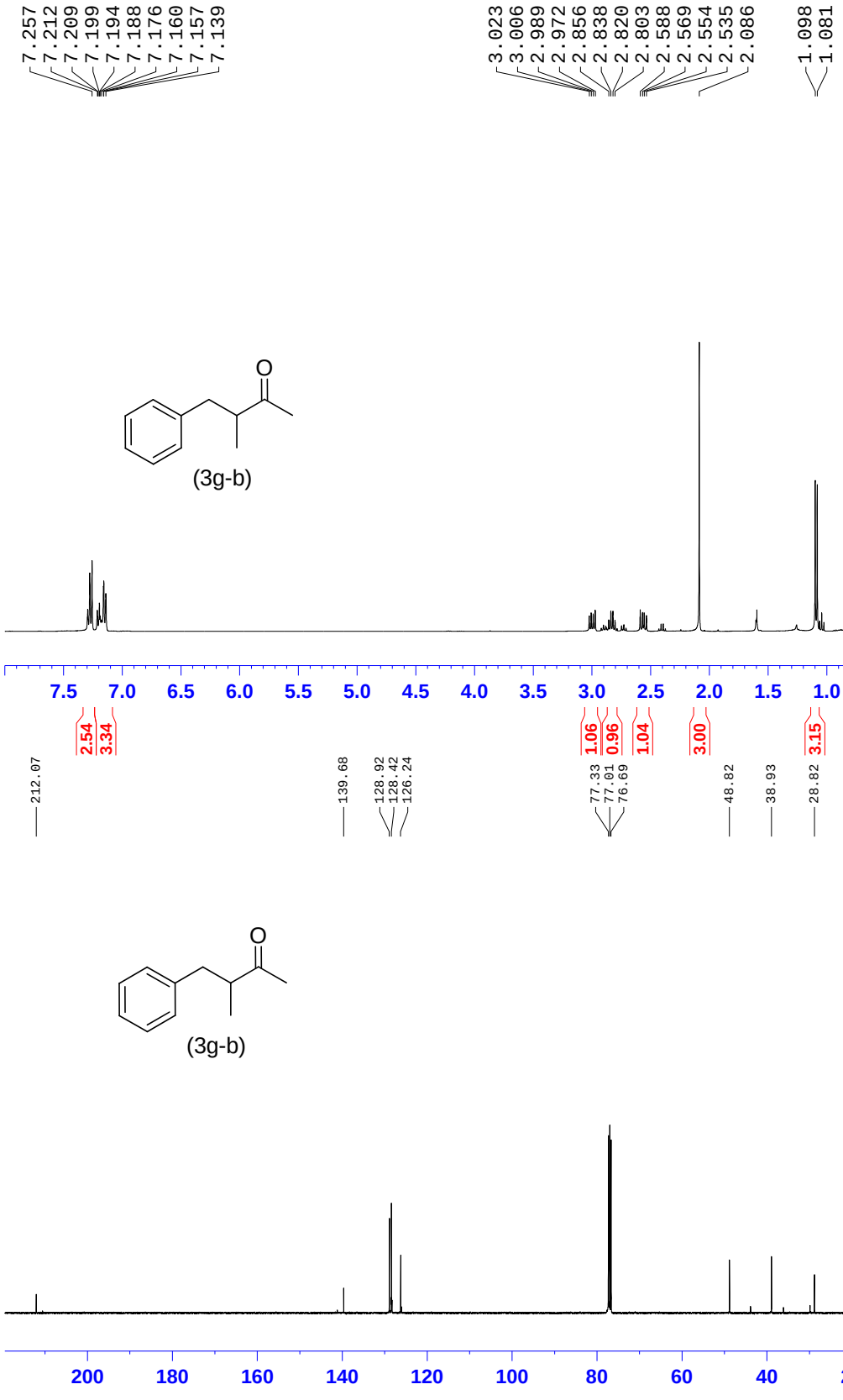

8.039
8.018
7.786
7.765
7.262
3.534
3.517
3.500
1.553
1.240
1.222
NC
O
(3d)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.08
2.00
1.02
7.11
202.99
139.36
132.52
128.71
117.97
116.12
77.32
77.20
77.00
76.68
35.87
18.85
NC
O
(3d)
200 180 160 140 120 100 80 60 40 20 ppm

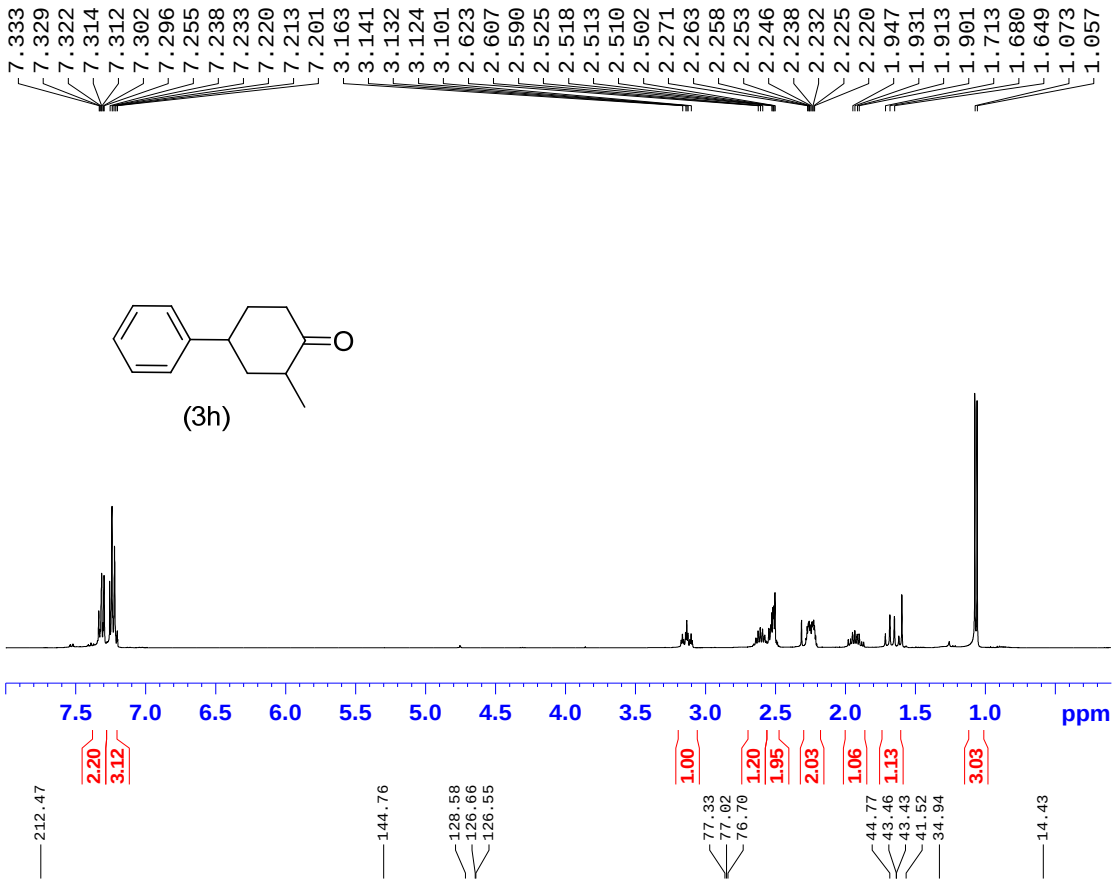

7.471
7.452
7.416
7.316
7.296
7.277
7.189
7.040
7.038
7.033
7.031
7.019
7.017
7.013
7.011
3.786
3.494
3.477
3.459
3.442
3.425
1.152
1.135
(3e)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
0.90
0.95
0.90
2.95
0.99
5.90
204.32
159.92
137.68
129.53
120.81
119.16
112.78
77.33
77.21
77.01
76.69
55.42
35.51
19.19
(3e)
200
180
160
140
120
100
80
60
40
20
ppm

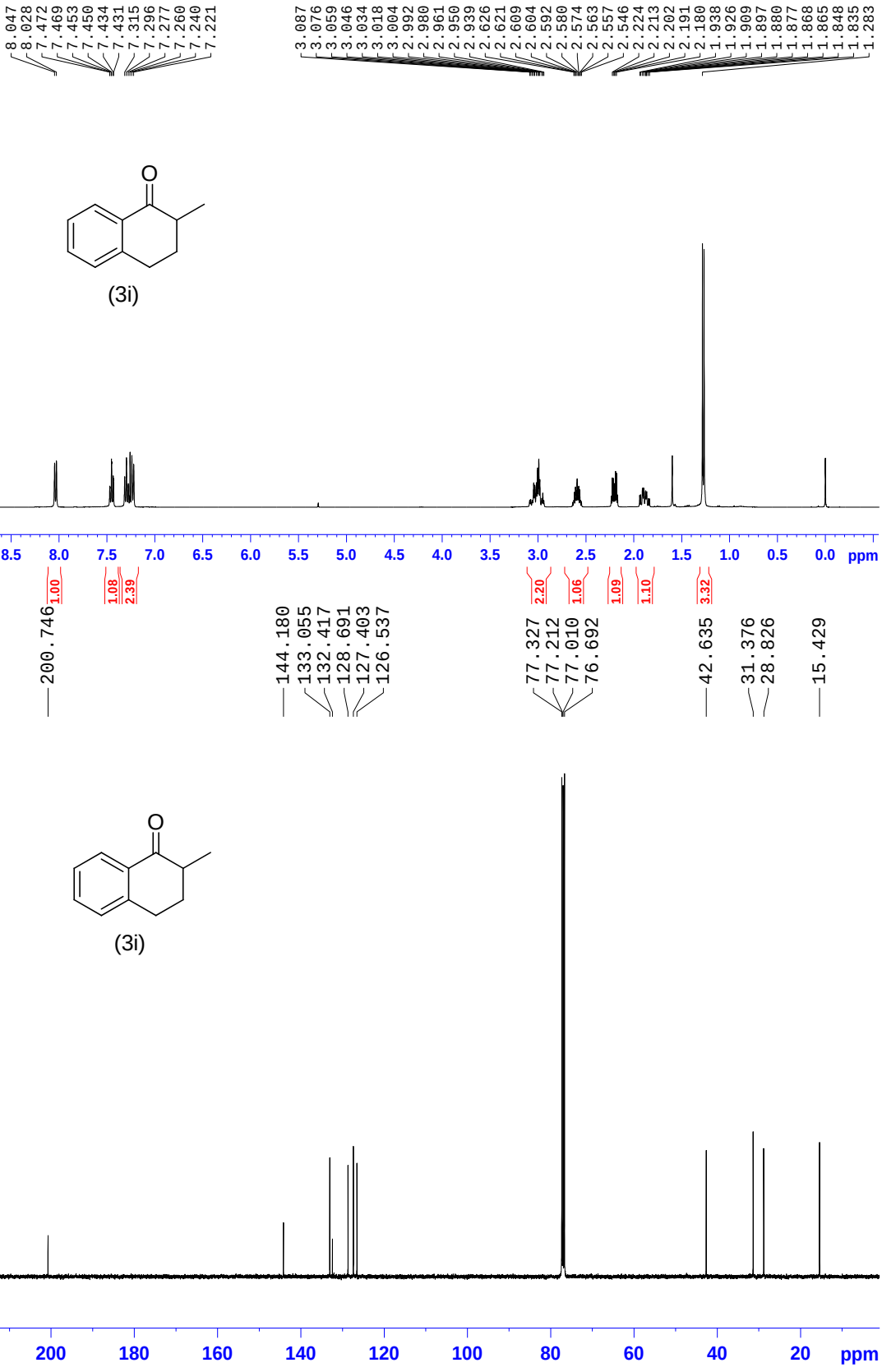

7.580
7.575
7.559
7.555
7.447
7.262
6.864
6.844
6.040
3.501
3.484
3.467
3.450
3.433
1.208
1.191
(3f)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.04
0.98
1.01
2.10
1.00
6.19
202.57
151.50
148.23
131.02
124.29
108.28
107.87
101.76
77.32
77.21
77.00
76.69
35.11
19.35
(3f)
200 180 160 140 120 100 80 60 40 20 ppm

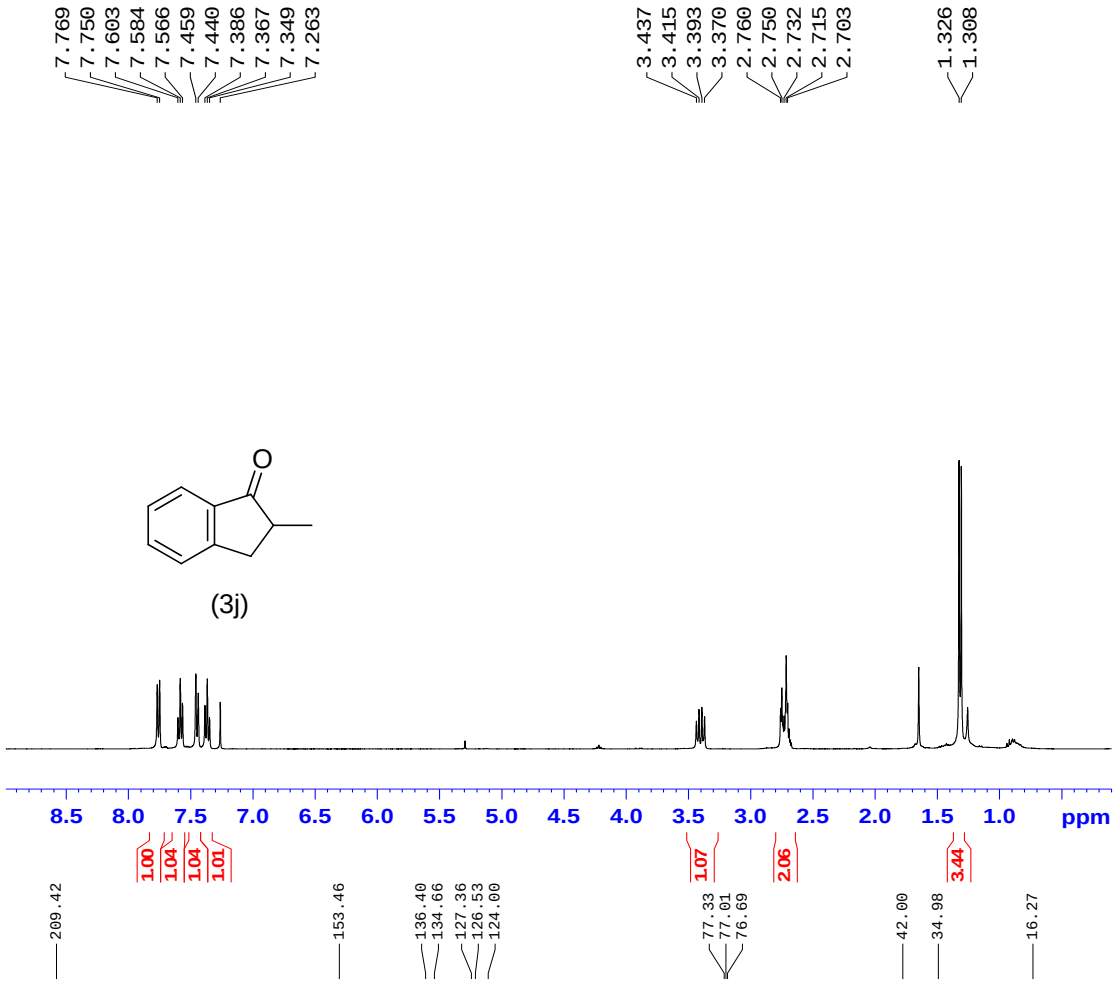

7.222
7.218
7.202
7.192
7.186
7.129
7.116
7.096
2.849
2.831
2.811
2.677
2.657
2.639
2.359
2.341
2.323
2.304
1.512
0.991
0.972
0.954
O
(3g-a)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.55
3.08
2.08
2.02
2.00
3.30
209.59
140.17
127.46
127.29
125.06
76.32
76.00
75.68
42.86
35.11
28.86
6.74

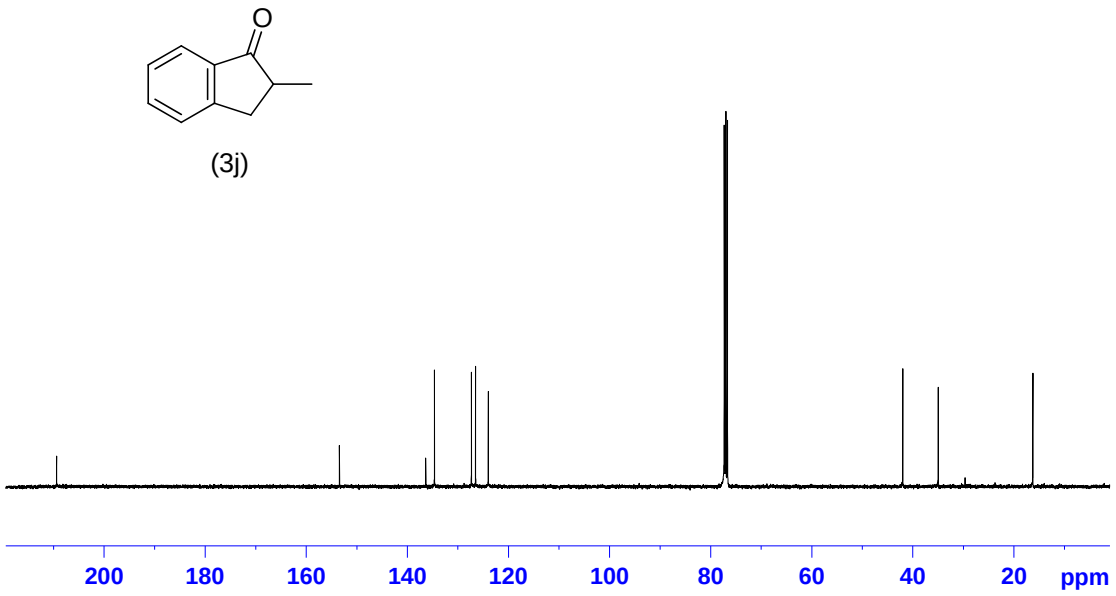

O
(3g-a)
200
180
160
140
120
100
80
60
40
20
ppm

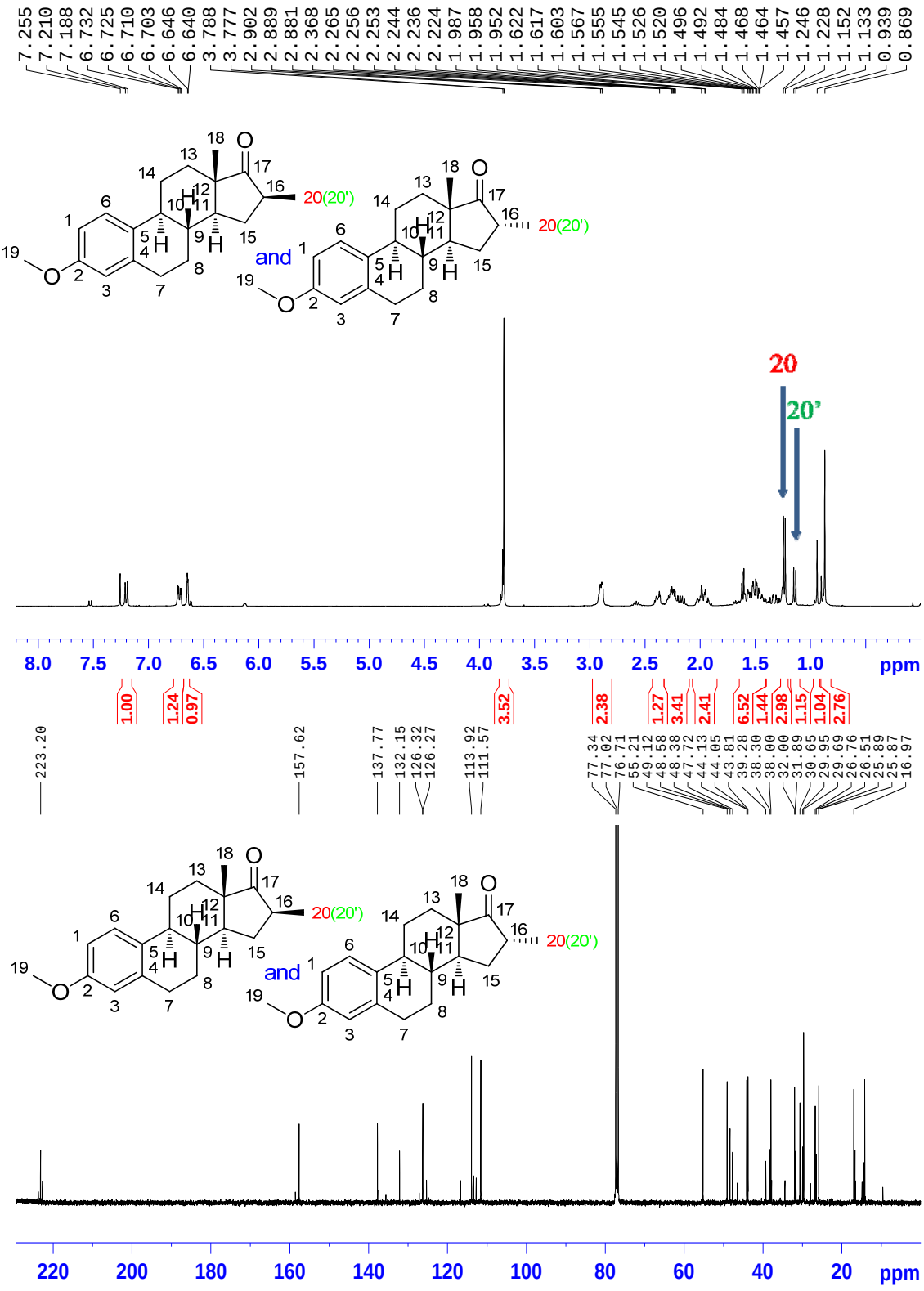

7.257
7.212
7.209
7.199
7.194
7.188
7.176
7.160
7.157
7.139
3.023
3.006
2.989
2.972
2.856
2.838
2.820
2.803
2.588
2.569
2.554
2.535
2.086
1.098
1.081
O
(3g-b)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.54
3.34
1.06
0.96
1.04
3.00
3.15
212.07
139.68
128.92
128.42
126.24
77.33
77.01
76.69
48.82
38.93
28.82
16.23
O
(3g-b)
200
180
160
140
120
100
80
60
40
20
ppm


7.333
7.329
7.322
7.314
7.312
7.302
7.296
7.255
7.238
7.233
7.220
7.213
7.201
3.163
3.141
3.132
3.124
3.101
2.623
2.607
2.590
2.525
2.518
2.513
2.510
2.502
2.271
2.263
2.258
2.253
2.246
2.238
2.232
2.225
2.220
1.947
1.931
1.913
1.901
1.713
1.680
1.649
1.073
1.057
O
(3h)
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
2.20
3.12
1.00
1.20
1.95
2.03
1.06
1.13
3.03
212.47
144.76
128.58
126.66
126.55
77.33
77.02
76.70
44.77
43.46
43.43
41.52
34.94
14.43
O
(3h)
200
180
160
140
120
100
80
60
40
20
ppm


8.047
8.028
7.472
7.469
7.453
7.450
7.434
7.431
7.315
7.296
7.277
7.260
7.240
7.221
3.087
3.076
3.059
3.046
3.034
3.018
3.004
2.992
2.980
2.961
2.950
2.939
2.626
2.621
2.609
2.604
2.592
2.580
2.574
2.563
2.557
2.546
2.224
2.213
2.202
2.191
2.180
1.938
1.926
1.909
1.897
1.880
1.877
1.868
1.865
1.848
1.835
1.283
O
(3i)
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
ppm
1.00
1.08
2.39
2.20
1.06
1.09
1.10
3.32
200.746
144.180
133.055
132.417
128.691
127.403
126.537
77.327
77.212
77.010
76.692
42.635
31.376
28.826
15.429
O
(3i)
200
180
160
140
120
100
80
60
40
20
ppm


7.769
7.750
7.603
7.584
7.566
7.459
7.440
7.386
7.367
7.349
7.263
3.437
3.415
3.393
3.370
2.760
2.750
2.732
2.715
2.703
1.326
1.308
O
(3j)
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
ppm
1.00
1.04
1.04
1.01
1.07
2.06
3.44


209.42
153.46
136.40
134.66
127.36
126.53
124.00
77.33
77.01
76.69
42.00
34.98
16.27
O
(3j)
200
180
160
140
120
100
80
60
40
20
ppm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7.210
7.188
6.732
6.725
6.710
6.703
6.646
6.640
3.788
3.777
2.902
2.889
2.881
2.368
2.265
2.256
2.253
2.244
2.236
2.224
1.987
1.958
1.952
1.622
1.617
1.603
1.567
1.555
1.545
1.526
1.520
1.496
1.492
1.484
1.468
1.464
1.457
1.246
1.228
1.152
1.133
0.939
0.869
20(20')
and
20
20'
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
ppm
1.00
1.24
0.97
3.52
2.38
1.27
3.41
2.41
6.52
1.44
2.98
1.15
1.04
2.76
223.20
157.62
137.77
132.15
126.32
126.27
113.92
111.57
77.34
77.02
76.71
55.21
49.12
48.58
48.38
47.72
44.13
44.05
43.81
39.28
38.30
38.00
32.00
31.89
30.65
29.95
29.69
26.76
26.51
25.89
25.87
16.97
220
200
180
160
140
120
100
80
60
40
20
ppm

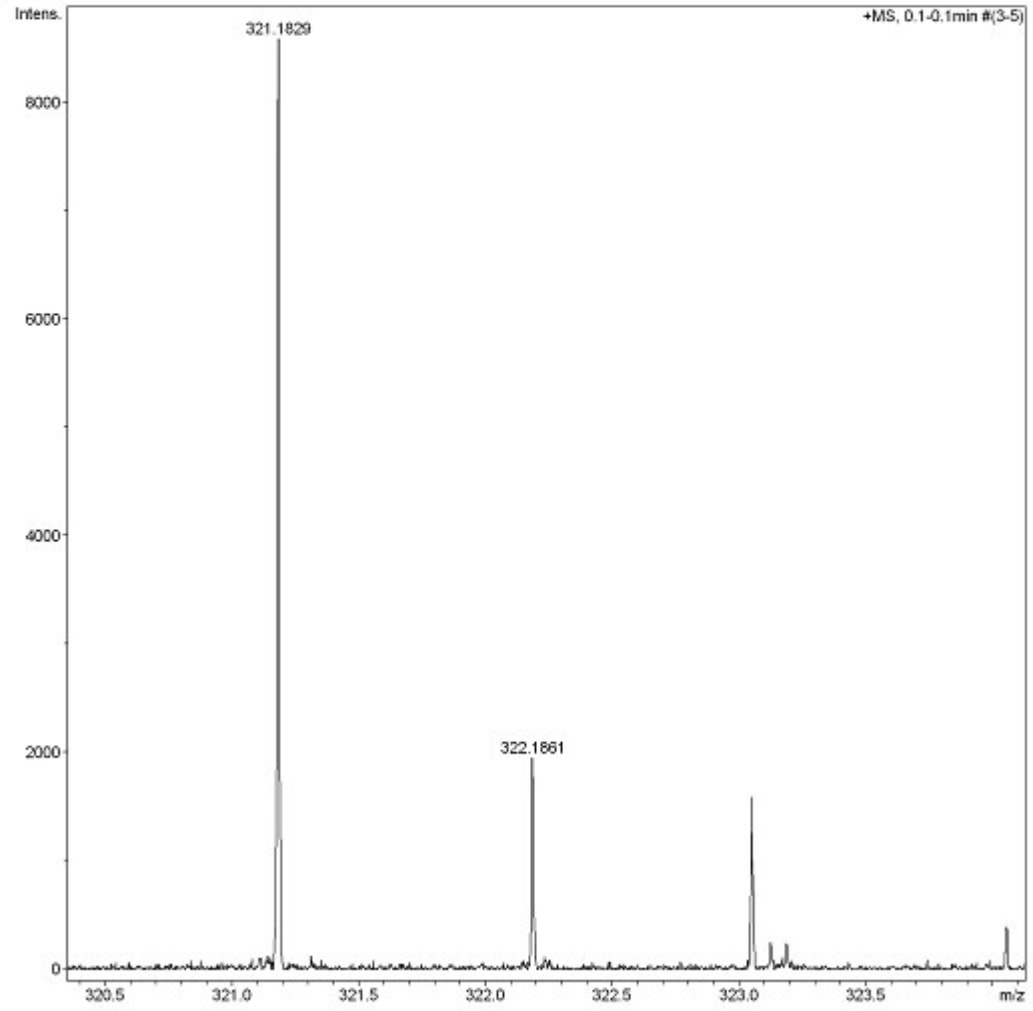
Display Report

Analysis Info

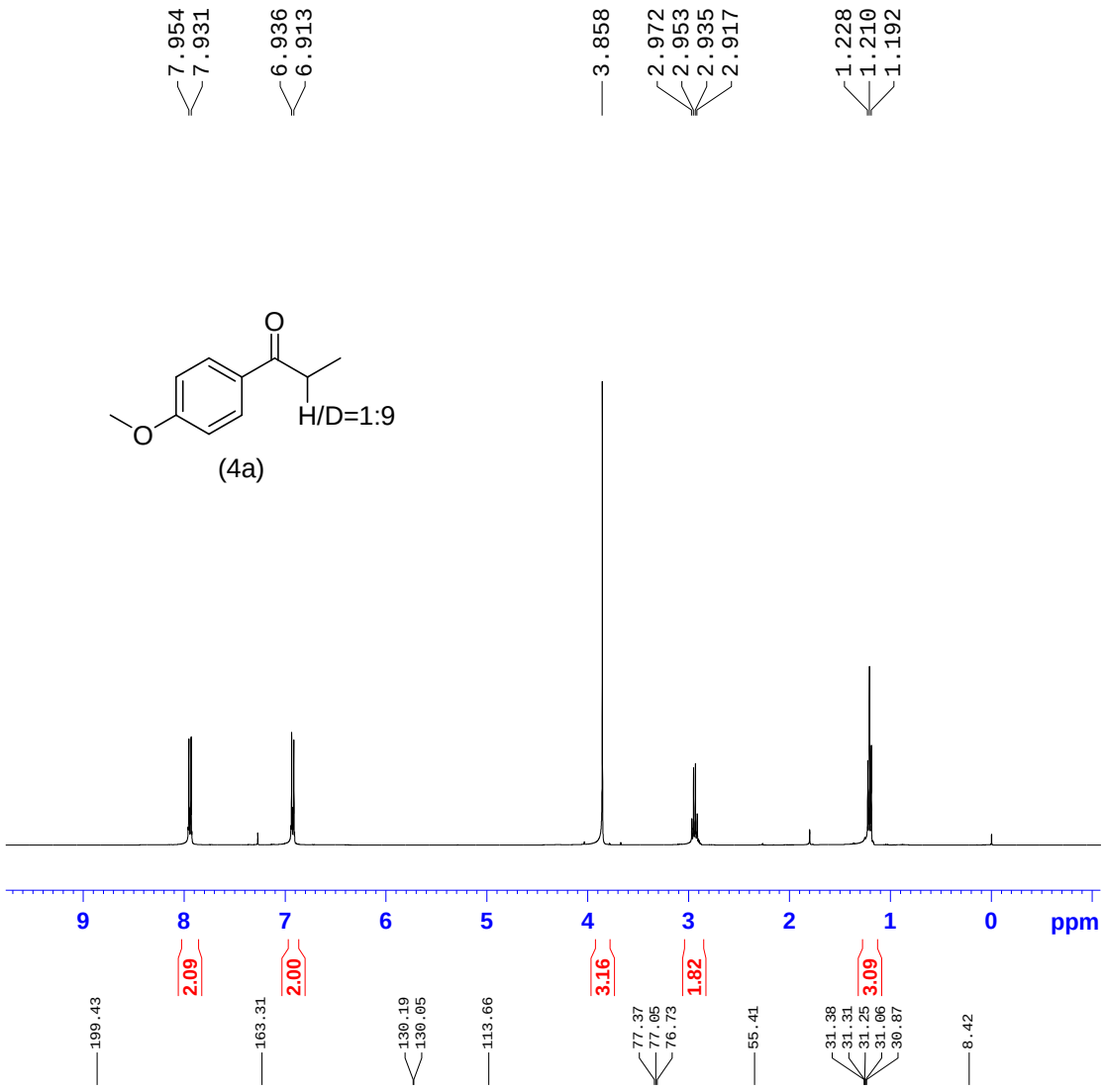
Analysis Name	D:\Data\FAN\data\2013\0820\ly1.d	Aoquisition Date	8/20/2013 9:32:32 AM
Method	pos_low_1000_0531.m	Operator	Fan
Sample Name	liyang	Instrument	maXis 10103
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	80.0 Vpp	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 8/20/2013 9:34:34 AM Page 1 of 1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7.931
6.936
6.913
3.858
2.972
2.953
2.935
2.917
1.228
1.210
1.192
O
O
H/D=1:9
(4a)
9
8
7
6
5
4
3
2
1
0
ppm
2.09
2.00
3.16
1.82
3.09
199.43
163.31
130.19
130.05
113.66
77.37
77.05
76.73
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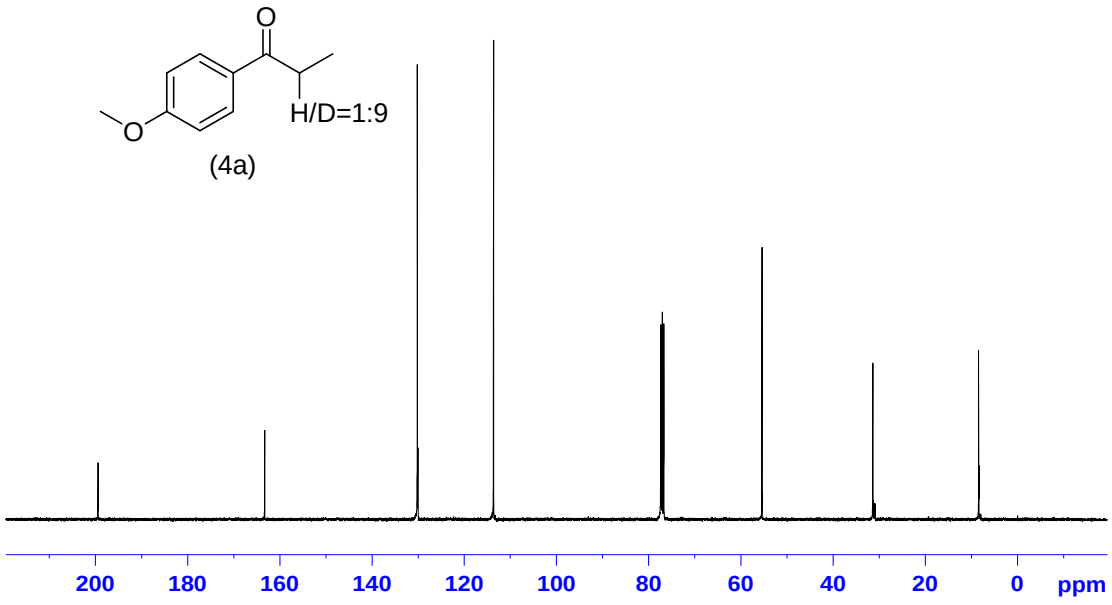
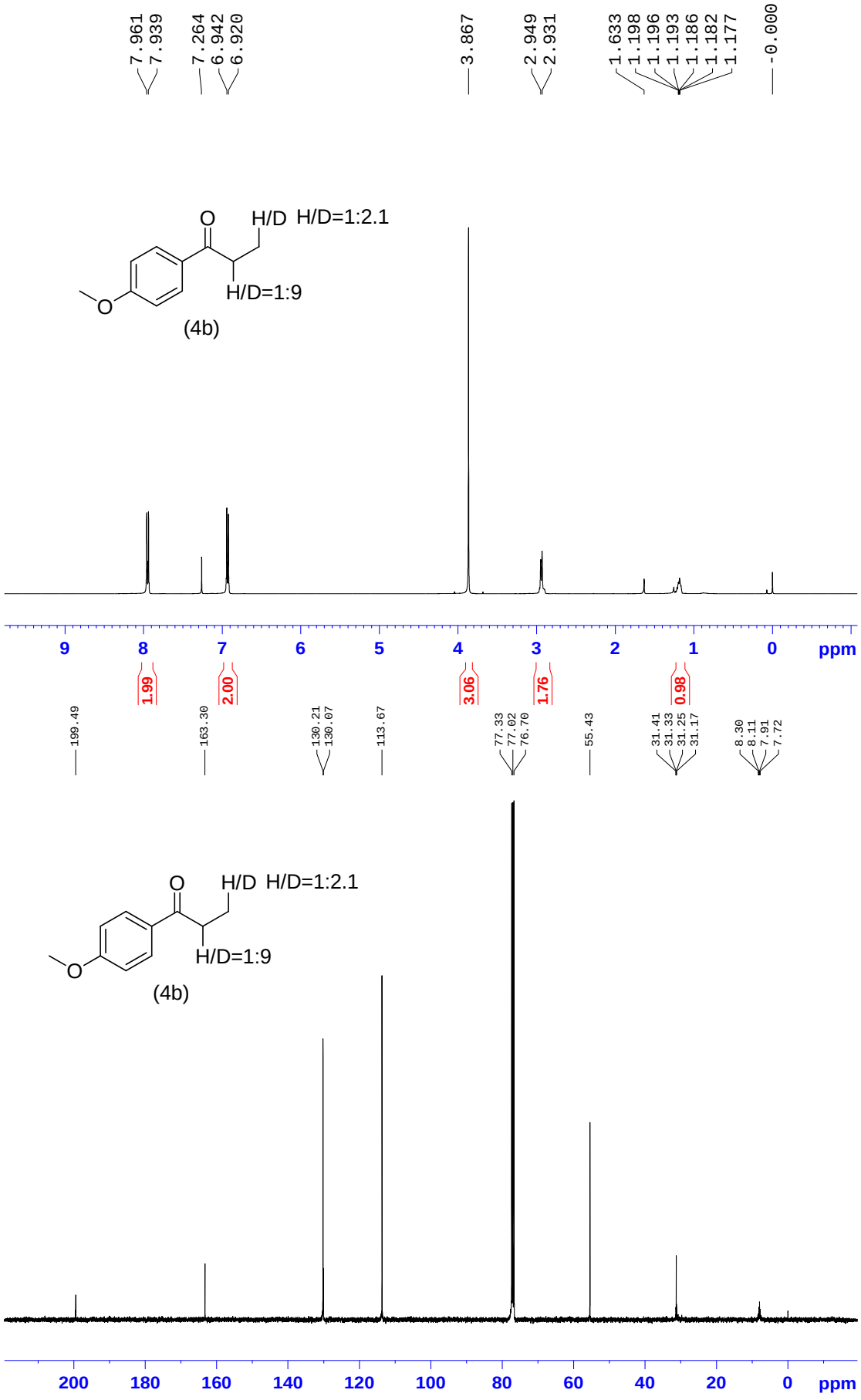
31.38
31.31
31.25
31.06
30.87
8.42


O
O
H/D=1:9
(4a)
200
180
160
140
120
100
80
60
40
20
0
ppm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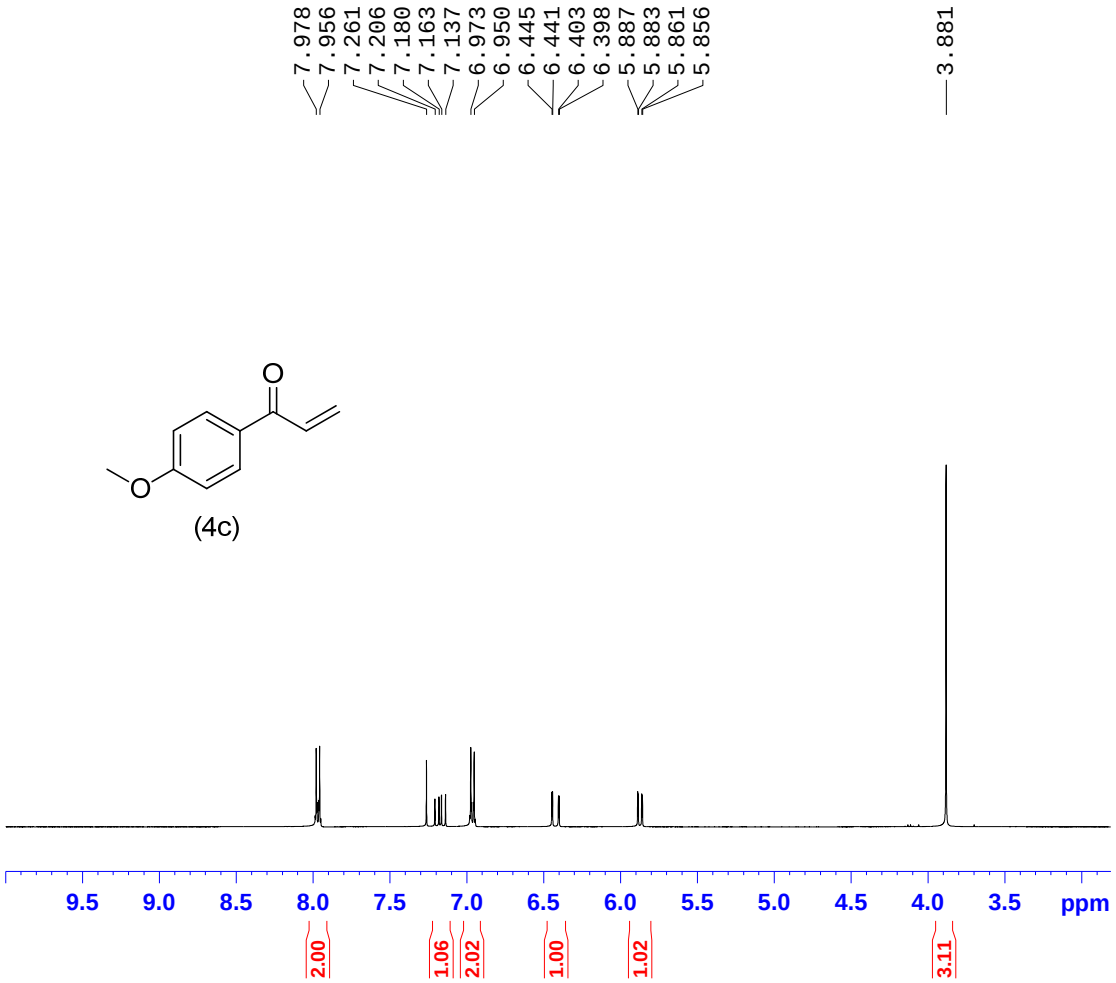
7.939
7.264
6.942
6.920
3.867
2.949
2.931
1.633
1.198
1.196
1.193
1.186
1.182
1.177
-0.000
O
H/D
H/D=1:2.1
H/D=1:9
O
(4b)
9
8
7
6
5
4
3
2
1
0
ppm
1.99
2.00
3.06
1.76
0.98
199.49
163.30
130.21
130.07
113.67
77.33
77.02
76.70
55.43
31.41
31.33
31.25
31.17
8.30
8.11
7.91
7.72
O
H/D
H/D=1:2.1
H/D=1:9
O
(4b)
200
180
160
140
120
100
80
60
40
20
0
ppm


7.978
7.956
7.261
7.206
7.180
7.163
7.137
6.973
6.950
6.445
6.441
6.403
6.398
5.887
5.883
5.861
5.856
3.881
O
O
(4c)
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
ppm
2.00
1.06
2.02
1.00
1.02
3.11