

Supporting Information 1

***B*-Alkylcatecholborane-Mediated Tandem Radical Conjugated Addition-Aldol Cyclization**

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General remarks

Catecholborane was used distilled under reduced pressure (50 mmHg, 50 °C). Other reagents were obtained from commercial sources and used as received or made following the general procedures. Solvents for reactions (THF, CH₂Cl₂, Et₂O, benzene and toluene) were filtered through columns of dried alumina under a positive pressure of argon. Dioxane was distilled under CaH₂ prior to use. Solvents for extractions were of technical grade and were distilled prior to use. All reactions were performed under a nitrogen atmosphere in oven-dried (120 °C) flasks and standard precautions against moisture were taken. A dry ice/acetone bath was used to obtain a temperature of -78 °C. An ice bath was used to obtain 0 °C. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 analytical plates; visualization under UV (254 nm) then staining with a solution of KMnO₄ (3 g), K₂CO₃ (20 g) NaOH 5% (3 mL) in H₂O (300 mL) or with solution of anisaldehyde (1 mL), acid acetic (100 mL), H₂SO₄ conc. (2 mL) and subsequent heating. Silica gel 60 (40-63 μm, SDS) was used for flash column chromatography. ¹H and ¹³C NMR spectrum were recorded on a Bruker AVANCE-300 spectrometer operating at 300 MHz for ¹H and 75 MHz for ¹³C at rt unless otherwise stated. Some ¹H and ¹³C NMR spectrum, two-dimensional NMR spectrum and ¹H/¹H-COSY and NOE experiments were recorded on a Bruker DRX-400 spectrometer. Chemical shift data are reported in units of δ (ppm) using as internal standard either CHCl₃ (δ = 7.26 for ¹H NMR spectrum and δ = 77.00 for ¹³C NMR spectrum) or Si(CH₃)₄ (δ = 0 for ¹H NMR and ¹³C NMR spectrum). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), qt (quintet), m (multiple), and bs (broad singlet) for ¹H. Coupling constants, *J*, are reported in Hz. Infrared spectrum were recorded on an Jasco FT-IR- 460 Plus spectrometer equipped with a Specac MKII Golden Gate Single Reflection Diamond ATR System and are reported in wave numbers (cm⁻¹). Low and high-resolution mass spectrum were recorded on a Waters Micromass Autospec Q mass spectrometer in EI mode at 70 eV. GC-MS were recorded on a Finnigan Trace CG 200 gas chromatograph equipped with an autosampler and a Trace MS mass selective detector.

General procedure A (GP A): synthesis of *B*-cyclohexylcatecholborane **1**

Catecholborane (1 equiv) was heated with the cyclohexene (1.2 equiv) without solvent at 100 °C for 12 h to afford the **1** in 95% yield after evaporation of the excess of cyclohexene under reduced pressure.

General procedure B (GP B): synthesis of compounds 2, 5-11, 22, 32, 35

Cyclopentene, 1-methylcyclopentene, 1-phenylcyclopentene (prepared from cyclopentanone and phenylmagnesium bromide), 1-benzylcyclopentene (prepared from 2-chlorocyclopentanone and benzylmagnesium bromide) or 1-methylcyclohexene (1 equiv) dissolved in CH_2Cl_2 (0,2 M) are treated with ozone at $-78\text{ }^\circ\text{C}$ for 30 min. The solution was purged with O_2 , and triphenylphosphine (1 equiv) was added; the reaction mixture was allowed to stir for 2 h at $25\text{ }^\circ\text{C}$. At this point, the appropriate, commercially available or prepared, Wittig reagent (1 equiv) was added in portions over 5 min and the solution stirred until the reaction is complete. The crude product was purified by column chromatography (cyclohexane/t-BuOMe) (20% to 54% yield).

General procedure C (GP C): synthesis of compound 20

PCC (2 equiv) is dissolved in CH_2Cl_2 (0.2 M) with 5-hydroxy-2-pentanone (1 equiv) then stirred 3 h at rt. The solution is filtrated under silica gel then the filtrate is evaporated under reduced pressure to give yellowish oil which was purified by column chromatography (cyclohexane/t-BuOMe). The aldehyde obtained reacts with the appropriate, commercially available or prepared, Wittig reagent (1 equiv) added in portions over 5 min and the solution stirred until the reaction is complete. The crude product was purified by column chromatography (cyclohexane/t-BuOMe) (45% yield).

General procedure D (GP D): synthesis of compound 25

2-Methyl-1,3-cyclopentanedione (1 equiv) dissolved in aqueous solution of NaOH 1M (1 equiv) are stirred 15 min then allyl bromide solution is added (2 equiv). The mixture is stirred at $25\text{ }^\circ\text{C}$ for 24 h. The mixture is extracted with CH_2Cl_2 and the organic layer was washed with brine and dried on MgSO_4 . The solvent is evaporated to give yellowish oil which was purified by column chromatography (cyclohexane/t-BuOMe). After, a solution of this product in CH_2Cl_2 is treated with ozone at $-78\text{ }^\circ\text{C}$ for 30 min. The solution was purged with O_2 , and triphenylphosphine (1 equiv) was added; the reaction mixture was allowed to stir for 2 h at $25\text{ }^\circ\text{C}$. At this point, the appropriate, commercially available or prepared, Wittig reagent (1.5 equiv) was added in portions over 5 min and the solution was stirred in at rt 20 h (35% to 52% yield over 2 steps). The crude product was purified by column chromatography (cyclohexane/t-BuOMe).

General procedure E (GP E): synthesis of compounds 26, 27

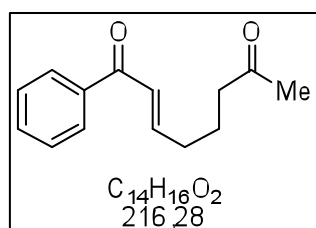
2-Methyl-1,3-cyclopentanedione or 2-methyl-1,3-cyclohexanedione (1 equiv) dissolved in H₂O (0.7 M) with acrolein (11.5 equiv) are stirred 20 h at rt. The solvent is removed under reduce pressure then the product is dissolved in CH₂Cl₂ during 30 min. The solid is filtered and the solution is evaporated under reduced pressure to give yellowish oil which was used in the second step without purifications. The appropriate, commercially available or prepared, Wittig reagent (1 equiv) was added in portions over 5 min and the solution was stirred in at rt 20 h (31% to 55% yield over 2 steps). The crude product was purified by column chromatography (cyclohexane/*t*-BuOMe).

General procedure F (GP F): tandem radical conjugate addition-aldol cyclization reaction

Under N₂, *B*-Alkylcatecholborane (4 equiv) and DMF (1.5 equiv) are added to a solution of the radical trap (1 equiv) in dioxane (0.35 M). The reaction mixture is heated at 50 °C and dry oxygen (CaCl₂) is slowly bubbled into the solution. Reaction takes up to 7 h to go to completion. The reaction mixture is then concentrated and the products are isolated and purified by flash chromatography (cyclohexane/*t*-BuOMe).

Physical data:

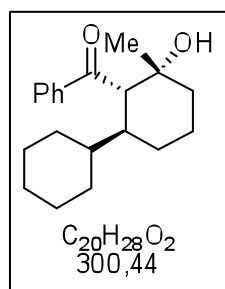
1-Phenyl-oct-2-ene-1,7-dione (2): Prepared according to GP B from 1-methylcyclopentene



(0.55 mL, 5.3 mmol) and (benzoylmethylene)triphenylphosphorane (2.0 g, 5.3 mmol). White solid is obtained in 40% yield. Physical and spectrum data were in accordance with literature data.¹

NMR ¹H (300 MHz, CDCl₃), δ: 1.80 (qu, *J* = 7.4 Hz, 2H), 2.13 (s, 3H), 2.32 (m, 2H), 2.48 (t, *J* = 7.2 Hz, 2H) ; 6.87 (m, 1H), 7.00 (m, 1H), 7.44 (m, 2H), 7.54 (m, 1H), 7.90 (m, 2H). **NMR** ¹³C (75 MHz, CDCl₃), δ: 21.9, 29.9, 31.8, 42.5, 126.3, 128.4, 128.5, 132.6, 137.7, 148.5, 190.6, 208.1. **IR** (neat) 2935, 2325, 1709, 1663, 1618, 1595, 1577, 1450, 1357, 1244, 982, 767, 699 cm⁻¹. **Mp**: 60.7°C. **EI-MS**: *m/z* (%): 216 (10) [M⁺], 198 (17), 159 (38), 146 (19), 105 (76), 91 (15), 84 (85), 77 (64), 73 (93), 56 (100), 41 (92). **HRMS-EI**: calcd. for C₁₄H₁₆O₂: 216.1149, found: 216.1150.

(3-hydroxy-3-methylbi(cyclohexan)-2-yl)-phenyl-methanone (3): Prepared according to

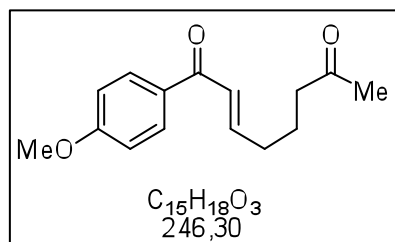


GP F from **2** (0.300 g, 1.4 mmol), cyclohexylcatecholborane (1.1 g, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). White crystals (311 mg, 74%) were obtained. M.p. 86-87 °C.

NMR 1H (300 MHz, $CDCl_3$), δ : 0.88-1.87 (several peaks, 20H), 2.17 (m, 1H), 3.47 (d, $J = 11.5$ Hz, 1H), 4.14 (bs, 1H), 7.47 (m, 2H), 7.58 (m, 1H), 7.98 (m, 2H). **NMR** ^{13}C (75 MHz, $CDCl_3$), δ : 21.1, 25.6, 26.5, 26.7, 26.8,

27.3, 30.6, 39.1, 40.2, 43.3, 54.0, 71.1, 128.1, 128.8, 133.5, 139.1, 209.8. **IR** (neat) 3481, 2924, 2853, 2361, 1646, 1595, 1450, 1394, 1347, 1260, 1212, 996, 760. 702 cm^{-1} . **Mp**: 86.8°C. **EI-MS**: m/z (%): 300 (21) [M^+], 282 (32), 260 (34), 242 (71), 217 (31), 175 (35), 120 (38), 105 (100), 91 (26), 77 (47), 43 (42). **HRMS** (+ESI) calcd. for $C_{20}H_{28}NaO_2$ ($[M + Na]^+$): 323.1979. Found: 323.1987.

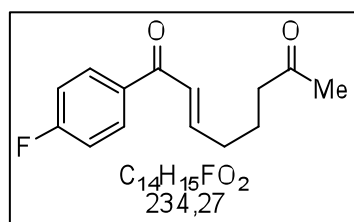
1-(4-Methoxy-phenyl)-oct-2-ene-1,7-dione (5): Prepared according to GP B from 1-



methylcyclopentene (0.55 mL, 5.3 mmol) and previously prepared Wittig reagent (2.2 g, 5.3 mmol) (prepared from 2-bromo-4'-methoxyacetophenone (2.3 g, 10 mmol) with triphenylphosphine (2.9 g, 11 mmol)). Yellowish oil is obtained in 44% yield.

NMR 1H (300 MHz, $CDCl_3$), δ : 1.80 (qu, $J = 7.1$ Hz, 2H), 2.14 (s, 3H), 2.17 (q, $J = 6.4$ Hz, 2H), 2.50 (t, $J = 7.3$ Hz, 2H), 3.86 (s, 3H), 6.01 (m, 1H), 6.87-7.04 (m, 4H), 7.93 (m, 2H). **NMR** ^{13}C (75 MHz, $CDCl_3$), δ : 22.0, 29.9, 31.8, 42.6, 55.4, 113.7, 126.0, 130.6, 130.8, 147.4, 163.3, 188.9, 208.2. **IR** (neat) 2936, 2365, 1711, 1664, 1616, 1596, 1573, 1510, 1419, 1354, 1256, 1168, 1114, 1023, 833, 678 cm^{-1} . **EI-MS**: m/z (%): 246 (8) [M^+], 235 (36), 213 (8), 203 (35), 189 (34), 176 (30), 163 (30), 150 (42), 135 (81), 121 (32), 113 (34), 107 (46), 99 (37), 92 (44), 77 (55), 64 (21), 43 (100). **HRMS** (+ESI) calcd. for $C_{15}H_{18}NaO_3Na$ ($[M + Na]^+$): 269.1150. Found: 269.1153.

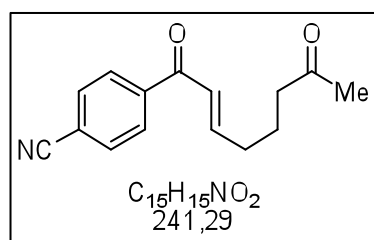
1-(4-Fluoro-phenyl)-oct-2-ene-1,7-dione (6): Prepared according to GP B from 1-



methylcyclopentene (0.55 mL, 5.3 mmol) and previously prepared Wittig reagent (2.1 g, 5.3 mmol) (prepared from 2-bromo-4'-fluoroacetophenone (2.2 g, 10 mmol) with triphenylphosphine (2.9 g, 11 mmol)). Yellowish oil is obtained in 43% yield.

NMR 1H (300 MHz, $CDCl_3$), δ : 1.80 (qu, $J = 7.3$ Hz, 2H), 2.14 (s, 3H), 2.17 (qd, $J = 1, 1$ Hz, $J = 7, 1$ Hz, 2H), 2.49 (t, $J = 7, 2$ Hz, 2H), 6.86 (dt, $J = 1, 1$ Hz, $J = 15, 3$ Hz, 1H), 7.00 (dt, $J = 6, 7$ Hz, $J = 15, 3$ Hz, 1H), 7.13 (m, 2H), 7.94 (m, 2H). **NMR ^{13}C** (75 MHz, $CDCl_3$), δ : 21.5, 29.1, 31.3, 41.9, 125.3, 130.5, 130.6, 131.8, 131.9, 133.6, 133.7, 148.2, 161.7, 174.8, 188.0, 207.3. **IR** (neat) 2941, 1709, 1596, 1507, 1410, 1364, 1228, 1156, 1011, 841, 605 cm^{-1} . **EI-MS**: m/z (%): 234 (23) [M^+], 216 (8), 191 (15), 177 (52), 165 (31), 149 (24), 140 (85), 123 (100), 113 (55), 95 (100), 75 (86), 55 (63), 39 (46). **HRMS** (+ESI): calcd. for $C_{14}H_{15}FNaO_2$ ($[M + Na]^+$): 257.0946, found: 257.0953.

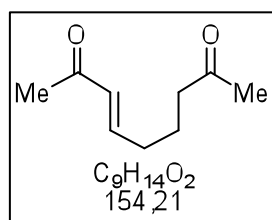
4-(7-Oxo-oct-2-enoyl)-benzonitrile (7): Prepared according to GP B from 1-



methylcyclopentene (0.55 mL, 5.3 mmol) and previously prepared Wittig reagent (2.1 g, 5.3 mmol) (prepared from 2-bromo-4'-cyanoacetophenone (2.2 g, 10 mmol) with triphenylphosphine (2.9 g, 11 mmol)). Yellowish oil is obtained in 47% yield.

NMR 1H (300 MHz, $CDCl_3$), δ : 1.80 (qu, $J = 7.3$ Hz, 2H), 2.13 (s, 3H), 2.33 (qd, $J = 1, 3$ Hz, $J = 6, 7$ Hz, 2H), 2.49 (t, $J = 7, 1$ Hz, 2H), 6.82 (dt, $J = 1, 3$ Hz, $J = 15, 4$ Hz, 1H), 7.04 (dt, $J = 6, 7$ Hz, $J = 15, 4$ Hz, 1H), 7.75 (m, 2H), 7.96 (m, 2H). **NMR ^{13}C** (75 MHz, $CDCl_3$), δ : 21.3, 29.4, 31.5, 42.0, 115.2, 117.5, 125.3, 128.4, 131.9, 140.5, 150.3, 188.8, 207.9. **IR** (neat) 2940, 2361, 2231, 1711, 1672, 1621, 1405, 1358, 1292, 1223, 1015, 908, 833, 725, 647 cm^{-1} . **EI-MS**: m/z (%): 241 (23) [M^+], 239 (33), 223 (26), 208 (12), 196 (19), 182 (41), 171 (24), 147 (48), 140 (24), 130 (100), 113 (54), 102 (85), 85 (46), 71 (45), 58 (47), 51 (48), 43 (77). **HRMS** (+ESI): calcd. for $C_{15}H_{15}NNaO_2$ ($[M + Na]^+$): 264.1009, found: 264.1000.

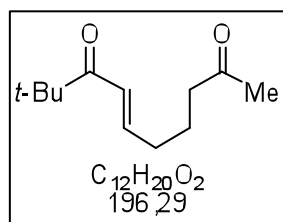
Non-3-ene-2,8-dione (8): Prepared according to GP B from 1-methylcyclopentene (0.55 mL,



5.3 mmol) and acetylmethylene-triphenylphosphorane (1.7 g, 5.3 mmol). Yellowish oil is obtained in 20% yield. Physical and spectrum data were in accordance with literature data.¹

NMR ¹H (300 MHz, CDCl₃), δ : 1.70 (qt, $J = 7.3$ Hz, 2H), 2.08 (s, 3H), 2.17 (m, 3H, 2H), 2.41 (t, $J = 7.3$ Hz, 2H); 6.01 (m, 1H), 6.70 (m, 1H). **NMR ¹³C** (75 MHz, CDCl₃), δ : 21.7, 26.7, 29.8, 31.5, 42.4, 131.6, 147.1, 198.3, 207.9. **IR** (neat) 2942, 2361, 1712, 1671, 1626, 1424, 1360, 1253, 1157, 980, 733 cm⁻¹. **EI-MS**: m/z (%): 154 (15) [M⁺], 136 (53), 121 (32), 111 (40), 97 (100), 93 (69), 84 (89), 81 (87), 69 (87), 58 (84), 55 (80), 53 (82), 43 (68), 77 (41), 39 (87). **HRMS** (+ESI): calcd. for C₉H₁₄NaO₂ ([M + Na]⁺): 177.0894, found: 177.0891.

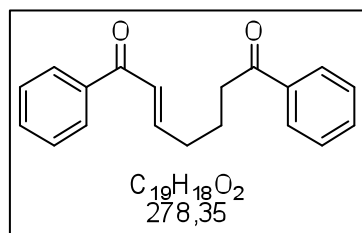
9,9-Dimethyl-dec-6-ene-2,8-dione (9): Prepared according to GP B from 1-



1-methylcyclopentene (0.55 mL, 5.26 mmol) and previously prepared Wittig reagent (1.9 g, 5.3 mmol) (prepared from 1-bromo-3,3-dimethyl-2-butanone (1.3 mL, 10 mmol) with triphenylphosphine (2.9 g, 11 mmol)). A yellowish oil is obtained in 43% yield.²

NMR ¹H (300 MHz, CDCl₃), δ : 1.09 (s, 3H), 1.70 (qu, $J = 7.5$ Hz, 2H), 2.09 (s, 3H), 2.17 (qd, $J = 1.5$ Hz, $J = 7.2$ Hz, 2H), 2.41 (t, $J = 7.3$ Hz, 2H), 6.45 (dt, $J = 1.5$ Hz, $J = 15.3$ Hz, 1H), 6.83 (dt, $J = 6.7$ Hz, $J = 15.3$ Hz, 1H). **NMR ¹³C** (75 MHz, CDCl₃), δ : 22.0, 26.1, 29.9, 31.5, 42.6, 42.8, 124.7, 146.3, 204.4, 208.6. **IR** (neat) 2967, 1713, 1687, 1622, 1478, 1395, 1365, 1158, 1077, 984 cm⁻¹. **EI-MS**: m/z (%): 196 (17) [M⁺], 179 (4), 155 (7), 139 (46), 127 (21), 111 (55), 99 (40), 93 (44), 81 (59), 71 (25), 57 (87), 43 (100). **HRMS-EI**: calcd. for C₁₂H₂₀O₂: 196.1463, found: 196.1463.

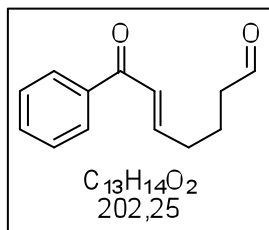
1,7-Diphenyl-hept-2-ene-1,7-dione (10): Prepared according to GP B from 1-



phenylcyclopentene (prepared from cyclopentanone (4.4 mL, 50 mmol) and phenylmagnesium bromide 2.8 M in Et₂O (23.2 mL, 65 mmol)) and (benzoylmethylene)triphenylphosphorane (2.0 g, 5.26 mmol). White powder is obtained in 54% yield.

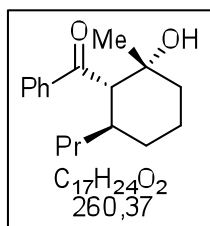
NMR ¹H (300 MHz, CDCl₃), δ : 2.01 (qt, $J = 7.3$ Hz, 2H), 2.44 (qd, $J = 0.9$ Hz, $J = 7.0$ Hz, 2H), 3.04 (t, $J = 7.2$ Hz, 2H); 7.46 (m, 4H), 7.55 (m, 2H), 7.92 (m, 4H). **NMR** ¹³C (75 MHz, CDCl₃), δ : 22.5, 32.1, 37.5, 126.5, 127.9, 128.4, 128.5, 128.6, 132.6, 133.1, 136.9, 137.9, 148.6. **IR** (neat) 3059, 2954, 2361, 1735, 1676, 1664, 1613, 1596, 1578, 1510, 1447, 1355, 1261, 1195, 1178, 964, 696, 687 cm⁻¹. **Mp**: 40.4 °C. **EI-MS**: m/z (%): 278 (4) [M⁺], 260 (27), 173 (6), 159 (56), 146 (23), 131 (11), 120 (25), 105 (100), 91 (13), 77 (87), 51 (21), 43 (10). **HRMS-EI**: calcd. for C₁₉H₁₈O₂: 278.1306, found: 278.1306.

7-Oxo-7-phenyl-hept-5-enal (11): Prepared according to GP B from cyclopentene (0.23 mL, 5.3 mmol) and (benzoylmethylene)triphenylphosphorane (2.0 g, 5.3 mmol). Yellowish oil is obtained in 32% yield.



NMR ¹H (300 MHz, CDCl₃), δ : 1.87 (qu, $J = 7.3$ Hz, 2H), 2.36 (qd, $J = 1.1$ Hz, $J = 15.2$ Hz, 2H), 2.50 (td, $J = 1.3$ Hz, $J = 7.3$ Hz, 2H), 6.89 (dt, $J = 1.7$ Hz, $J = 15.8$ Hz, 1H), 7.01 (dt, $J = 6.6$ Hz, $J = 15.2$ Hz, 1H), 7.46 (m, 2H), 7.53 (m, 1H), 7.90 (m, 2H), 9.78 (s, 1H). **NMR** ¹³C (75 MHz, CDCl₃), δ : 20.4, 31.7, 42.9, 126.5, 128.4, 128.5, 132.7, 137.6, 148.0, 190.6, 201.6. **IR** (neat) 2940, 2254, 1722, 1670, 1617, 1597, 1578, 1510, 1448, 1216, 1001, 907, 728, 690, 647 cm⁻¹. **EI-MS**: m/z (%): 202 (12) [M⁺], 184 (10), 159 (13), 146 (53), 131 (10), 122 (33), 115 (11), 105 (100), 97 (20), 91 (9), 81 (16), 77 (89), 67 (5), 55 (9), 51 (35), 43 (5), 39 (13). **HRMS-EI**: calcd. for C₁₃H₁₄O₂: 202.0992, found: 202.0994.

(2-hydroxy-2-methyl-6-propylcyclohexyl)(phenyl)methanone (12): Prepared according to

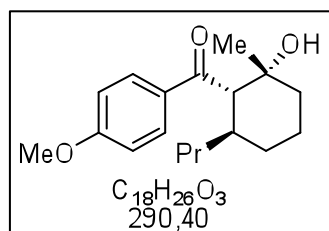


GP F from **2** (0.300g, 1.4 mmol), *B*-propylcatecholborane (0.9 mL, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). Colourless oil is obtained in 67% yield.

NMR ¹H (300 MHz, CDCl₃), δ : 0.69 (t, $J = 7.1$ Hz, 3H), 0.84-1.18 (several peaks, 6H), 1.27-1.35 (several peaks, 2H), 1.55 (m, 1H), 2.08 (m, 1H), 3.25 (d, $J = 11.1$ Hz, 1H), 4.13 (d, $J = 2.1$ Hz, 1H), 6.98 (m, 2H), 7.12 (m, 1H), 7.98 (m, 2H). **NMR** ¹³C (75 MHz, CDCl₃), δ : 13.9, 19.8, 20.8, 30.3, 30.8, 37.1, 37.2, 38.9, 56.8, 70.8,

128.2, 128.8, 133.6, 139.0, 209.2. **IR** (neat) 3484, 2957, 2930, 2870, 2844, 1652, 1596, 1447, 1374, 1262, 1206, 992, 946, 695, 669 cm^{-1} . **EI-MS**: m/z (%): 260 (21) $[\text{M}^+]$, 242 (42), 217 (36), 200 (47), 113 (68), 105 (44), 91 (58), 71 (65), 55 (27), 43 (100). **HRMS** (+ESI) calcd. for $\text{C}_{17}\text{H}_{24}\text{NaO}_2$ ($[\text{M} + \text{Na}]^+$): 283.1684. Found: 283.1673.

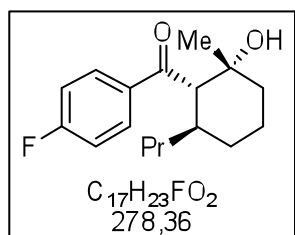
(2-Hydroxy-2-methyl-6-propyl-cyclohexyl)-(4-methoxy-phenyl)-methanone (13):



Prepared according to GP F from radical trap **5** (0.345 g, 1.4 mmol), propylcatecholborane (0.9 mL, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). White crystals are obtained in 54% yield.

NMR ^1H (300 MHz, CDCl_3), δ : 0.69 (t, $J = 7.1$ Hz, 3H), 1.02 (s, 3H), 0.84-1.40 (several peaks, 5H), 1.52-1.91 (several peaks, 5H), 2.10 (m, 1H), 3.16 (d, $J = 11.3$ Hz, 1H), 3.88 (s, 3H), 4.23 (bs, 1H), 6.96 (m, 2H), 7.98 (m, 2H). **NMR** ^{13}C (75 MHz, CDCl_3), δ : 14.0, 19.9, 20.9, 30.3, 30.9, 37.0, 37.2, 39.0, 55.5, 56.4, 70.7, 113.9, 130.7, 132.2, 164.0, 207.3. **IR** (neat) 3441, 2963, 2929, 2361, 1738, 1631, 1599, 1571, 1510, 1452, 1422, 1350, 1322, 1263, 1227, 1215, 1171, 1118, 1025, 847, 766, 690, 618 cm^{-1} . **Mp**: 80.3°C. **+ESI-MS**: m/z (%): 313 (85) ($[\text{M} + \text{Na}]^+$), 291 (25), 273 (20), 195 (1), 177 (1), 135 (147). **HRMS** (+ESI) calcd. for $\text{C}_{18}\text{H}_{26}\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$): 313.1786. Found: 313.1779.

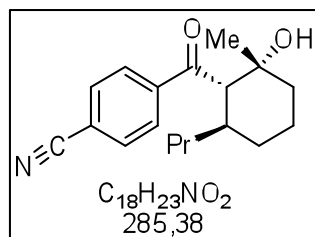
(4-Fluoro-phenyl)-(2-hydroxy-2-methyl-6-propyl-cyclohexyl)-methanone (14): Prepared



according to GP F from **6** (0.328g, 1.4 mmol), propylcatecholborane (0.9 mL, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). Colourless oil is obtained in 60% yield.

NMR ^1H (300 MHz, CDCl_3), δ : 0.69 (t, $J = 7.1$ Hz, 3H), 1.02 (s, 3H), 0.80-1.20 (several peaks, 4H), 1.21-1.37 (several peaks, 2H), 1.57 (m, 1H), 1.73-1.97 (m, 3H), 2.11 (m, 1H), 3.18 (d, $J = 11.1$ Hz, 1H), 3.98 (bs, 1H), 7.16 (m, 2H), 7.98 (m, 2H). **NMR** ^{13}C (75 MHz, CDCl_3), δ : 14.0, 19.9, 20.8, 30.3, 30.9, 37.2, 37.3, 38.9, 56.9, 70.9, 130.9, 116.1, 130.9, 131.0, 135.5-135.6 (d, 1C_{IV}), 164.4-167.8 (d, 1C_{IV}), 207.4. **IR** (neat) 3488, 2960, 2931, 2872, 2361, 1653, 1597, 1507, 1374, 1225, 1205, 1155, 993, 943, 908, 857, 811, 730, 613 cm^{-1} . **ESI-MS**: m/z (%): 301 (92) ($[\text{M} + \text{Na}]^+$), 279 (3), 261 (6), 215 (1), 209 (26), 193 (4), 171 (1), 137 (1), 123 (68), 102 (6). **HRMS** (+ESI) calcd. for $\text{C}_{17}\text{H}_{23}\text{FNaO}_2$ ($[\text{M} + \text{Na}]^+$): 301.1570. Found: 301.1579.

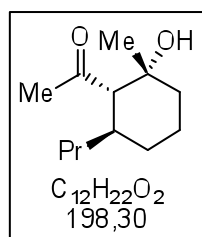
4-(2-Hydroxy-2-methyl-6-propyl-cyclohexanecarbonyl)-benzonitrile (15): Prepared



according to the GP F from **7** (0.338g, 1.4 mmol), propylcatecholborane (0.9 mL, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). Colourless oil is obtained in 70% yield (contaminated with catecholborane).

NMR ^1H (300 MHz, CDCl_3), δ : 0.71 (t, $J = 7.1$ Hz, 3H), 1.21 (s, 3H), 0.84-1.40 (several peaks, 4H), 1.11-1.34 (several peaks, 4H), 1.81 (m, 2H), 2.98 (m, 1H), 2.15 (m, 1H), 2.23 (d, $J = 11.3$ Hz, 1H), 4.36 (bs, 1H), 7.82 (m, 2H), 8.09 (m, 2H). **NMR** ^{13}C (75 MHz, CDCl_3), δ : 13.9, 19.8, 20.7, 30.1, 30.7, 37.3, 37.6, 38.7, 57.5, 77.3, 117.9, 117.0, 128.6, 132.8, 143.6, 208.1. **IR** (neat) 3369, 2933, 2361, 2235, 1660, 1604, 1511, 1468, 1362, 1255, 1207, 1095, 1030, 946, 918, 851, 769, 742, 682 cm^{-1} . **+ESI-MS**: m/z (%): 308 (85) ($[\text{M} + \text{Na}]^+$), 288 (3), 268 (100), 226 (20), 219 (9), 207 (3), 148 (2), 137 (21), 120 (1), 102 (27). **HRMS** (+ESI) calcd. for $\text{C}_{18}\text{H}_{23}\text{NNaO}_2$ ($[\text{M} + \text{Na}]^+$): 308.1624. Found: 308.1626.

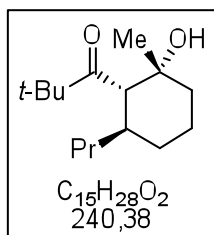
1-(2-Hydroxy-2-methyl-6-propyl-cyclohexyl)-ethanone (16): Prepared according to GP F



from **8** (0.216 g, 1.4 mmol), propylcatecholborane (0.9 mL, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). Colourless oil in 16% yield.

NMR ^1H (300 MHz, CDCl_3), δ : 0.81 (t, $J = 7.0$ Hz, 3H), 1.10 (s, 3H), 0.98-1.23 (several peaks, 4H), 1.30-1.50 (several peaks, 3H), 1.60-1.95 (several peaks, 4H), 2.23 (s, 3H), 2.31 (d, $J = 11.3$ Hz, 1H), 3.43 (bs, 1H). **NMR** ^{13}C (75 MHz, CDCl_3), δ : 14.1, 19.6, 20.7, 29.7, 30.4, 35.3, 36.3, 36.9, 38.7, 63.5, 70.1, 218.0. **IR** (neat) 3491, 2931, 1690, 1456, 1357, 1226, 1173, 1121, 1052, 947, 915, 889, 808, 731, 625 cm^{-1} . **EI-MS**: m/z (%): 198 (26) $[\text{M}]^+$, 183 (48), 155 (51), 137 (64), 113 (72), 97 (67), 85 (60), 71 (75), 55 (67), 43 (100). **HRMS** (+ESI) calcd. for $\text{C}_{12}\text{H}_{22}\text{NaO}_2$ ($[\text{M} + \text{Na}]^+$): 221.1524. Found: 221.1517.

1-(2-Hydroxy-2-methyl-6-propyl-cyclohexyl)-2,2-dimethyl-propan-1-one (17): Prepared

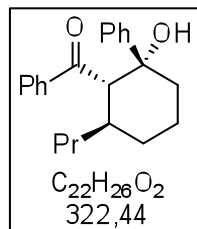


according to the GP F from **9** (0.275 g, 1.4 mmol), propylcatecholborane (0.9 mL, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). Colourless oil is obtained in 17% yield.

NMR ^1H (300 MHz, CDCl_3), δ : 0.80 (t, $J = 7.0$ Hz, 3H), 1.06 (s, 3H), 1.16 (s, 9H), 1.00-2.00 (several peaks, 11H), 2.77 (d, $J = 10.7$ Hz, 1H), 3.81 (bs, 1H). **NMR** ^{13}C (75 MHz, CDCl_3), δ : 14.1, 20.2, 20.8, 26.3, 27.7, 30.5, 37.6, 37.8, 39.0, 44.8, 57.8, 70.7, 227.5. **IR** (neat) 3489, 2957, 2872, 2361, 1706, 1670, 1462, 1366, 1225,

1154, 1061, 995, 734 cm^{-1} . **EI-MS:** m/z (%): 240 (23) [M^+], 225 (11), 197 (17), 183 (75), 165 (62), 155 (55), 137 (83), 123 (39), 109 (24), 95 (77), 81 (80), 57 (95), 43 (100). **HRMS-EI** calcd. for $\text{C}_{15}\text{H}_{28}\text{O}_2$ ($[\text{M}]^+$): 240.2085. Found: 240.2089.

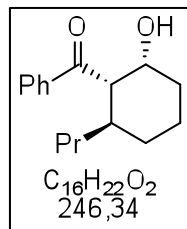
(2-Hydroxy-2-phenyl-6-propyl-cyclohexyl)-phenyl-methanone (18): Prepared according to



the GP F from **10** (0.390 g, 1.4 mmol), propylcatecholborane (0.9 mL, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). Colourless oil is obtained in 63% yield.

NMR ^1H (300 MHz, CDCl_3), δ : 0.72 (t, $J = 7.1$ Hz, 3H), 0.87-1.48 (several peaks, 5H), 1.71 (m, 1H), 1.85 (m, 2H), 2.09 (m, 2H), 2.32 (m, 1H), 3.72 (d, $J = 11.1$ Hz, 1H), 4.97 (bs, 1H), 6.98 (m, 1H), 7.10 (m, 2H), 7.28 (m, 2H), 7.39 (m, 3H), 7.63 (m, 2H). **NMR ^{13}C** (75 MHz, CDCl_3), δ : 13.9, 19.9, 21.2, 30.9, 37.3, 37.6, 39.3, 57.3, 75.2, 124.8, 126.4, 127.8, 127.9, 128.2, 133.1, 138.6, 147.1, 208.6. **IR** (neat) 3466, 3058, 2939, 2860, 2361, 1644, 1597, 1447, 1214, 1071, 986, 758, 697, 645 cm^{-1} . **Mp:** 83.2°C. **EI-MS:** m/z (%): 322 (17) [M^+], 304 (13), 203 (30), 184 (19), 175 (29), 159 (11), 133 (20), 120 (35), 105 (100), 91 (11), 77 (51), 57 (9), 43 (16). **HRMS-EI** calcd. for $\text{C}_{22}\text{H}_{26}\text{O}_2$ ($[\text{M}]^+$): 322.1932. Found: 322.1933.

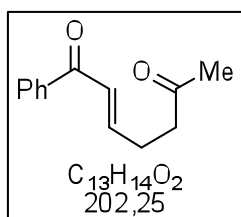
(2-Hydroxy-6-propyl-cyclohexyl)-phenyl-methanone (19): Prepared according to GP F



from **11** (0.283g, 1.4 mmol), propylcatecholborane (0.9 mL, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). Colourless oil is obtained in 36% yield.

NMR ^1H (300 MHz, CDCl_3), δ : 0.73 (t, $J = 7.1$ Hz, 3H), 0.84-1.70 (several peaks, 8H), 1.76-1.98 (several peaks, 3H), 2.19 (m, 1H), 3.34 (dd, $J = 1.9$ Hz, $J = 11.1$ Hz, 1H), 4.05 (d, $J = 2.6$ Hz, 1H), 7.46 (m, 2H), 7.52 (m, 1H), 7.98 (m, 2H). **NMR ^{13}C** (75 MHz, CDCl_3), δ : 13.9, 19.2, 19.7, 26.8, 30.8, 31.9, 33.9, 37.1, 37.2, 53.5, 66.5, 128.3, 128.7, 133.5, 137.4, 206.4. **IR** (neat) 3250, 2930, 2867, 2360, 1675, 1598, 1581, 1444, 1371, 1334, 1310, 1266, 1201, 1166, 1136, 1065, 1032, 1004, 991, 936, 905, 836, 793, 770, 730, 688, 661 cm^{-1} . **EI-MS:** m/z (%): 246 (12) [M^+], 228 (10), 175 (35), 149 (8), 133 (11), 120 (16), 105 (100), 91 (6), 82 (23), 77 (51), 67 (9), 55 (17), 51 (9), 41 (14). **HRMS-EI:** calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_2$: 246.1620, found: 246.1620.

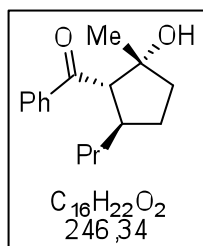
1-Phenyl-hept-2-ene-1,6-dione (20): Prepared according to GP C from 5-hydroxy-2-



pentanone (7.4 mL, 72.6 mmol), PCC (31.5 g, 145 mmol) and (Benzoylmethylene)triphenylphosphorane (27.6g, 72.6 mmol). Yellowish oil is obtained in 38% yield. Physical and spectrum data were in accordance with literature data.¹

NMR 1H (300 MHz, $CDCl_3$), δ : 2.09 (s, 3H), 2.49 (m, 2H), 2.57 (m, 2H), 6.82 (dt, $J = 1,1$ Hz, $J = 15,3$ Hz, 1H), 6.93 (dt, $J = 6,4$ Hz, $J = 15,4$ Hz, 1H), 7.38 (m, 2H), 7.47 (m, 1H), 7.84 (m, 2H). **NMR ^{13}C** (75 MHz, $CDCl_3$), δ : 26.4, 29.8, 41.4, 126.4, 128.3, 128.4, 132.6, 137.6, 147.3, 190.4, 206.6. **IR** (neat) 3057, 2936, 2360, 1713, 1668, 1618, 1446, 1354, 1274, 1219, 1168, 976, 769, 691 cm^{-1} . **EI-MS**: m/z (%): 202 (53) [M^+], 184 (6), 159 (82), 141 (32), 131 (46), 115 (26), 105 (91), 91 (50), 77 (88), 51 (28), 43 (100). **HRMS-EI**: calcd. for $C_{13}H_{14}O_2$: 202.0995, found: 202.0994.

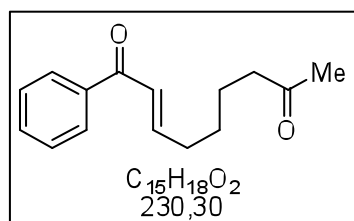
(2-Hydroxy-2-methyl-5-propyl-cyclopentyl)-phenyl-methanone (21): Prepared according



to GP F from **20** (0.283 g, 1.4 mmol), propylcatecholborane (0.9 mL, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). Colourless oil is obtained in 31% yield (contaminated with catecholborane).

NMR 1H (300 MHz, $CDCl_3$), δ : 0.74 (t, $J = 7.1$ Hz, 3H), 1.24 (s, 3H), 1.02-1.43 (several peaks, 5H), 1.77 (m, 1H), 1.87 (m, 1H), 2.13 (m, 1H), 2.64 (m, 1H), 3.39 (d, $J = 11.1$ Hz, 1H), 3.84 (bs, 1H), 7.44 (m, 2H), 7.58 (m, 1H), 7.98 (m, 2H). **NMR ^{13}C** (75 MHz, $CDCl_3$), δ : 13.9, 21.3, 27.3, 29.2, 37.9, 40.9, 44.3, 60.4, 81.7, 128.3, 128.6, 133.4, 138.4, 205.9. **IR** 3495, 2955, 2928, 2870, 2360, 1713, 1683, 1597, 1580, 1447, 1361, 1265, 1212, 1160, 1001, 753, 690, 602 cm^{-1} . **EI-MS**: m/z (%): 246 (6) [M^+], 228 (17), 188 (48), 175 (50), 145 (49), 137 (67), 126 (70), 120 (80), 105 (89), 97 (59), 81 (55), 77 (84), 57 (62), 43 (100). **HRMS-EI** calcd. for $C_{16}H_{22}O_2$ ($[M]^+$): 246.1620. Found: 246.1620.

1-Phenyl-non-2-ene-1,8-dione (22): Prepared according to GP B from 1-methylcyclohexene

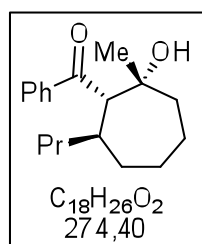


(5.8 mL, 60 mmol) and methyl(triphenylphosphoranylidene)acetate (22.8 g, 60 mmol). Yellowish oil is obtained in 43% yield.³

NMR 1H (300 MHz, $CDCl_3$), δ : 1.55 (m, 4H), 2.10 (s, 3H), 2.29 (m, 2H), 2.43 (t, $J = 6.9$ Hz, 2H); 6.87 (d, $J = 15.5$ Hz, 1H), 7.00 (dt, $J = 6.1$ Hz, $J = 15.1$ Hz, 1H), 7.42 (m, 2H), 7.51 (m, 1H), 7.89 (m, 2H). **NMR ^{13}C** (75 MHz, $CDCl_3$), δ : 23.2, 27.6, 29.8, 32.5, 43.2, 126.1, 128.4, 128.5, 132.5, 137.8, 149.0,

190.7, 208.5. **IR** (neat) 2936, 1712, 1668, 1617, 1447, 1354, 1284, 1220, 1176, 1158, 1074, 981, 847, 730, 693, 661 cm^{-1} . **EI-MS**: m/z (%): 230 (13) $[\text{M}^+]$, 202 (8), 172 (20), 159 (20), 145 (5), 131 (7), 122 (31), 105 (100), 84 (47), 77 (76), 43 (64). **HRMS-EI**: calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_2$: 230.1307, found: 230.1307.

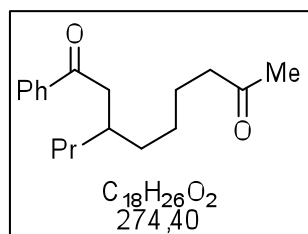
(2-Hydroxy-2-methyl-7-propyl-cycloheptyl)-phenyl-methanone (23): Prepared according



to GP F from **22** (0.322g, 1.4 mmol), propylcatecholborane (0.9 mL, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). Colourless oil is obtained in 12% yield.

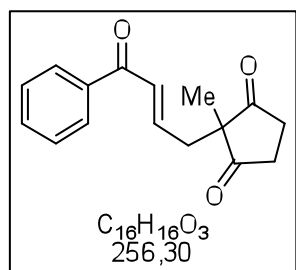
NMR ^1H (300 MHz, CDCl_3), δ : 0.70 (t, $J = 7.3$ Hz, 3H), 0.82-2.19 (several peaks, 13H), 1.04 (s, 3H), 3.25 (d, $J = 11.3$ Hz, 1H), 4.11 (d, $J = 2.2$ Hz, 1H), 7.50 (m, 2H), 7.62 (m, 1H), 7.98 (m, 2H). **NMR ^{13}C** (75 MHz, CDCl_3), δ : 14.0, 19.9, 20.9, 30.3, 30.9, 37.2, 37.3, 39.0, 56.9, 70.9, 128.3, 128.8, 133.6, 139.1, 209.3. **IR** (neat) 3487, 2927, 2870, 1717, 1654, 1596, 1579, 1447, 1374, 1261, 1225, 1207, 1180, 1159, 1025, 992, 945, 888, 873, 800, 760, 695, 669 cm^{-1} . **+ESI-MS**: m/z (%): 297 (15) $[\text{M} + \text{Na}]^+$, 283 (100), 275 (5), 243 (10), 215 (5), 142 (5). **HRMS** (+ESI) calcd. for $\text{C}_{18}\text{H}_{26}\text{NaO}_2$ $[\text{M} + \text{Na}]^+$: 297.1841. Found: 297.1830.

1-Phenyl-3-propyl-nonane-1,8-dione (24): Colourless oil is obtained in 60% yield.



NMR ^1H (300 MHz, CDCl_3), δ : 0.85 (m, 3H), 1.28 (m, 8H), 1.51 (m, 2H), 2.08 (m, 4H), 2.37 (t, $J = 7.4$ Hz, 2H), 2.80 (dd, $J = 6.8$ Hz, $J = 16.2$ Hz, 1H), 2.87 (dd, $J = 6.6$ Hz, $J = 16.2$ Hz, 1H), 7.42 (m, 2H), 7.52 (m, 1H), 7.90 (m, 2H). **NMR ^{13}C** (75 MHz, CDCl_3), δ : 14.2, 19.7, 23.9, 26.1, 29.7, 33.7, 33.8, 36.3, 43.2, 43.5, 127.9, 128.4, 132.7, 137.4, 200.4, 208.9. **IR** (neat) 2953, 2928, 2869, 1713, 1679, 1597, 1447, 1360, 1210, 1002, 753, 691 cm^{-1} . **+ESI-MS**: m/z (%): 297 (100) $[\text{M} + \text{Na}]^+$, 275 (20), 215 (18), 193 (10). **HRMS** (+ESI) calcd. for $\text{C}_{18}\text{H}_{27}\text{O}_2$ $[\text{M} + \text{H}]^+$: 275.2015. Found: 275.2011.

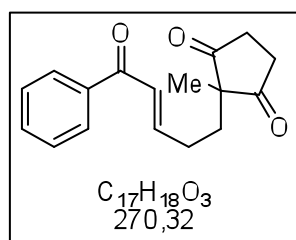
2-Methyl-2-(4-oxo-4-phenyl-but-2-enyl)-cyclopentane-1,3-dione (25): Prepared according



to GP D from 2-methyl-1,3-cyclopentanedione (1.1 g, 9.9 mmol), allylmagnesium bromide (1.7 mL, 19.7 mmol) and (benzoylmethylene)triphenylphosphorane (3.78 g, 9.9 mmol). White powder is obtained in 31% yield. Physical and spectrum data were in accordance with literature data.¹

NMR 1H (300 MHz, $CDCl_3$), δ : 1.21 (s, 3H), 2.60-2.82 (m, 6H), 6.74 (m, 1H); 6.89 (m, 1H), 7.46 (m, 2H), 7.55 (m, 1H), 7.90 (m, 2H). **NMR ^{13}C** (75 MHz, $CDCl_3$), δ : 20.1, 35.2, 37.6, 56.4, 128.5, 128.6, 128.5, 129.8, 133.0, 137.3, 141.1, 189.8, 215.3. **IR** (neat) 3048, 2937, 2361, 1764, 1719, 1659, 1619, 1577, 1449, 1322, 1287, 1015, 985, 918, 851, 789, 768, 705 cm^{-1} . **Mp**: 90.5°C. **EI-MS**: m/z (%): 256 (25) [M^+], 171 (6), 157 (6), 144 (7), 123 (8), 105 (100), 91 (6), 77 (49), 51 (12), 41 (19). **HRMS-EI**: calcd. for $C_{16}H_{16}O_3$: 256.1098, found: 256.1099.

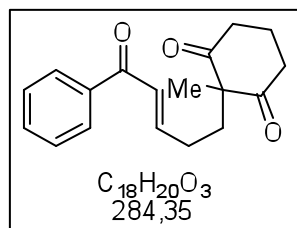
2-Methyl-2-(5-oxo-5-phenyl-pent-3-enyl)-cyclopentane-1,3-dione (26): Prepared according



to GP E from 2-methyl-1,3-cyclopentanedione (2.0 g, 17.5 mmol), acroleine (2.0 mL, 30 mmol) and (benzoylmethylene)triphenylphosphorane (6.7 g, 17.5 mmol). White powder is obtained in 49% yield. Physical and spectrum data were in accordance with literature data.¹

NMR 1H (300 MHz, $CDCl_3$), δ : 1.17 (s, 3H), 1.87 (m, 2H), 2.21 (m, 2H), 2.78 (m, 4), 6.85 (m, 2H); 7.45 (m, 2H), 7.55 (m, 1H), 7.89 (m, 2H). **NMR ^{13}C** (75 MHz, $CDCl_3$), δ : 19.9, 27.1, 32.8, 35.0, 56.1, 126.7, 128.5, 128.6, 132.8, 137.6, 147.2, 190.4, 215.8. **IR** (neat) 2971, 2361, 1766, 1720, 1668, 1610, 1594, 1577, 1510, 1447, 1420, 1371, 1332, 1304, 1277, 1219, 1192, 1042, 823, 685 cm^{-1} . **Mp**: 97.4 °C. **EI-MS**: m/z (%): 270 (25) [M^+], 232 (36), 215 (62), 204 (16), 186 (45), 170 (54), 157 (77), 133 (72), 120 (67), 105 (100), 77 (97), 67 (26), 51 (65), 41 (32). **HRMS-EI**: calcd. for $C_{17}H_{18}O_3$: 270.1248, found: 270.1256.

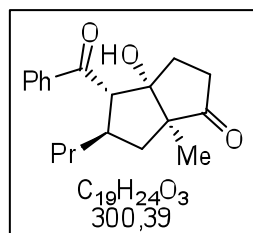
2-Methyl-2-(5-oxo-5-phenyl-pent-3-enyl)-cyclohexane-1,3-dione (27): Prepared according



to the GP E from 2-methyl-1,3-cyclohexanedione (2.2g, 17.5 mmol), acroleine (2.0 mL, 30 mmol) and (Benzoylmethylene) triphenylphosphorane (6.7g, 17.5 mmol). White powder is obtained in 55% yield.

NMR 1H (300 MHz, $CDCl_3$), δ : 1.28 (s, 3H), 1.94 (m, 4H), 2.11 (m, 2H), 2.66 (td, $J = 2.6$ Hz, $J = 6.6$ Hz, 4H), 6.82 (d, $J = 15.4$ Hz, 1H), 6.93 (dt, $J = 6.0$ Hz, $J = 15.2$ Hz, 1H), 7.44 (m, 2H), 7.52 (m, 1H), 7.88 (m, 2H). **NMR ^{13}C** (75 MHz, $CDCl_3$), δ : 17.5, 21.2, 28.0, 34.1, 37.9, 64.8, 126.4, 128.4, 128.5, 132.6, 137.7, 147.8, 190.5, 209.8. **IR** (neat) 2934, 1724, 1691, 1667, 1618, 1597, 1578, 1447, 1311, 1278, 1221, 1178, 1130, 1023, 988, 842, 768, 735, 692 cm^{-1} . **Mp**: 49.9 $^{\circ}C$. **EI-MS**: m/z (%): 284 (7) [M^+], 164 (43), 159 (95), 146 (47), 131 (34), 115 (34), 111 (63), 105 (96), 98 (39), 91 (45), 77 (100), 55 (72), 41 (97). **HRMS-EI**: calcd. for $C_{18}H_{20}O_3$: 284.1409, found: 284.1412.

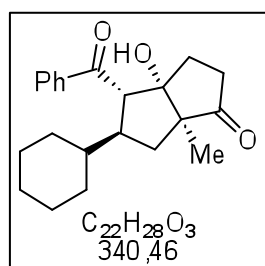
4-Benzoyl-3a-hydroxy-6a-methyl-5-propyl-hexahydro-pentalen-1-one (28): Prepared



according to GP F from **25** (0.359 g, 1.4 mmol), propylcatecholborane (0.9 mL, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). Colourless oil is obtained in 58% yield.

NMR 1H (300 MHz, $CDCl_3$), δ : 0.77 (t, $J = 6.8$ Hz, 3H), 1.17 (s, 3H), 1.10-1.32 (several peaks, 4H), 1.71-2.21 (several peaks, 4H), 2.40-2.79 (several peaks, 3H), 3.47 (d, $J = 10.7$ Hz, 1H), 4.26 (bs, 1H), 7.52 (m, 2H), 7.65 (m, 1H), 7.94 (m, 2H). **NMR ^{13}C** (75 MHz, $CDCl_3$), δ : 14.0, 16.3, 21.2, 31.0, 35.4, 37.4, 40.2, 43.5, 58.4, 60.3, 89.0, 128.4, 129.0, 134.2, 137.8, 204.2, 221.9. **IR** (neat) 3370, 2957, 2872, 2362, 1722, 1654, 1596, 1511, 1468, 1363, 1254, 1095, 1030, 910, 851, 735, 689 cm^{-1} . **+ESI-MS**: m/z (%): 323 (32) ($[M + Na]^+$), 301 (3), 283 (3), 254 (1), 237 (1), 187 (1), 147 (1). **HRMS (+ESI)** calcd. for $C_{19}H_{24}NaO_3$ ($[M + Na]^+$): 323.1617. Found: 323.1623.

4-Benzoyl-5-cyclohexyl-3a-hydroxy-6a-methyl-hexahydro-pentalen-1-one (29): Prepared

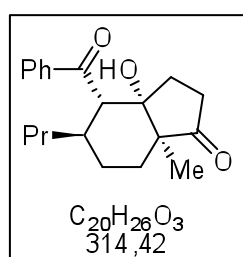


according to GP F from **25** (0.359 g, 1.4 mmol), cyclohexylcatecholborane (1.1 g, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). Colourless oil is obtained in 69% yield (contaminated with catecholborane).

NMR 1H (300 MHz, $CDCl_3$), δ : 1.13 (s, 3H), 0.60-1.15 (several peaks,

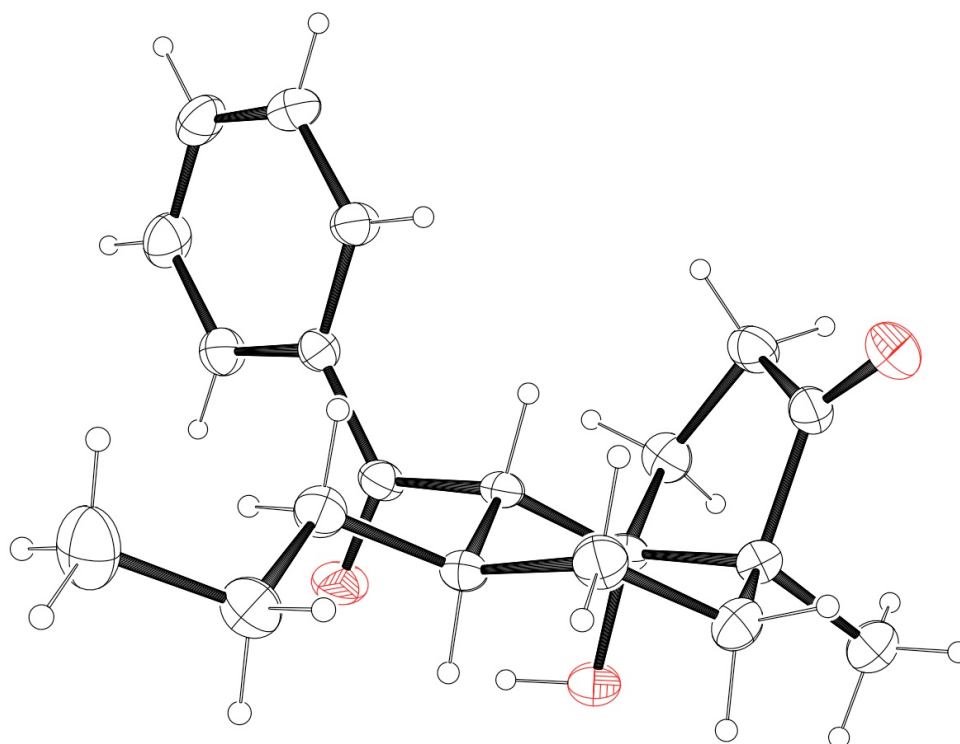
5H), 1.26 (m, 2H), 1.51 (m, 2H), 1.63 (m, 2H), 1.79 (dd, $J = 1.3$ Hz, $J = 10.0$ Hz, 2H), 1.96 (m, 1H), 2.08 (m, 1H), 2.49 (m, 2H), 2.70 (m, 1H), 3.10 (bs, 1H), 3.63 (d, $J = 10.2$ Hz, 1H), 7.46 (m, 2H), 7.64 (m, 1H), 7.94 (m, 2H). **NMR** ^{13}C (75 MHz, CDCl_3), δ : 15.5, 25.8, 25.9, 26.0, 30.4, 31.4, 32.1, 37.4, 42.4, 48.3, 53.4, 56.9, 59.8, 88.5, 128.0, 128.7, 133.4, 137.7, 202.3, 220.0. **IR** (neat) 3326, 2920, 2797, 1723, 1602, 1510, 1469, 1368, 1272, 1252, 1185, 1094, 916, 850, 769, 742, 709, 672 cm^{-1} . **+ESI-MS**: m/z (%): 363 (75) ($[\text{M} + \text{Na}]^+$), 353 (65), 341 (35), 323 (37), 313 (3), 277 (3), 227 (3), 215 (22), 185 (11), 157 (19), 149 (6). **HRMS** (+ESI) calcd. for $\text{C}_{22}\text{H}_{28}\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$): 363.1945. Found: 363.1936.

4-Benzoyl-3a-hydroxy-7a-methyl-5-propyl-octahydro-inden-1-one (30): Prepared



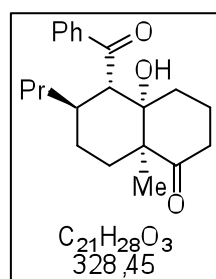
according to GP F from **26** (0.378 g, 1.4 mmol), propylcatecholborane (0.9 mL, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). Colorless oil is obtained in 57% yield. Crystallization in CH_2Cl_2 gave colorless crystals. The relative configuration of **30** was determined by X-ray crystallography.

NMR ^1H (300 MHz, CDCl_3), δ : 0.62 (s, 3H), 1.00 (s, 1H), 0.80-1.13 (several peaks, 4H), 1.22 (m, 1H), 1.49, (m, 2H), 1.74 (m, 1H), 2.00 (m, 3H), 2.02 (m, 1H), 2.49 (m, 1H), 3.09 (d, $J = 11.1$ Hz, 1H), 4.94 (s, 1H), 7.48 (m, 2H), 7.60 (m, 1H), 7.90 (m, 2H). **NMR** ^{13}C (75 MHz, CDCl_3), δ : 13.7, 19.3, 19.6, 27.8, 28.2, 31.2, 34.5, 36.0, 36.4, 52.4, 53.5, 78.3, 128.0, 129.0, 134.2, 138.7, 207.9, 217.7. **IR** (neat) 3425, 3068, 2962, 2933, 2875, 2841, 2361, 1734, 1647, 1595, 1579, 1449, 1402, 1365, 1302, 1231, 1216, 1199, 1058, 999, 887, 788, 723, 689, 650 cm^{-1} . **Mp** 132.9°C. **EI-MS**: m/z (%): 314 (53) ($[\text{M}]^+$), 296 (6), 271 (17), 209 (19), 191 (57), 175 (89), 133 (31), 120 (43), 105 (100), 77 (67), 41 (22). **HRMS-EI**: calcd. for $\text{C}_{20}\text{H}_{26}\text{O}_2$: 314.1881, found: 314.1881.



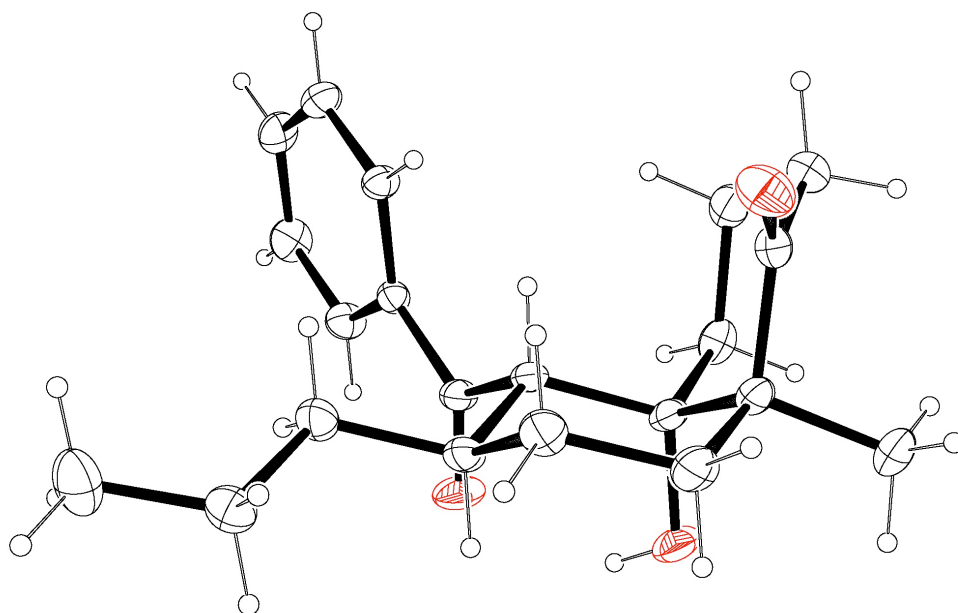
X-ray crystal structure analysis of **30**

5-Benzoyl-4a-hydroxy-8a-methyl-6-propyl-octahydro-naphthalen-1-one (31): Prepared



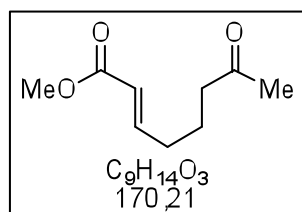
according to GP F from **27** (0.398g, 1.4 mmol), propylcatecholborane (0.9 mL, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). Colorless oil is obtained in 45% yield. Crystallization in CH_2Cl_2 gave colorless crystals. The relative configuration of **31** was determined by X-ray crystallography.

NMR 1H (300 MHz, $CDCl_3$), δ : 0.69 (s, 3H), 1.26, (s, 3H), 0.97-1.49 (m, 7H), 1.70 (m, 3H), 2.12 (m, 4H), 2.58 (m, 1H), 3.28 (d, $J = 11.1$ Hz, 1H), 4.78 (s, 1H), 7.51 (m, 2H), 7.63 (m, 1H), 7.95 (m, 2H). **NMR** ^{13}C (75 MHz, $CDCl_3$), δ : 13.9, 19.3, 19.9, 22.6, 27.6, 29.0, 32.6, 36.4, 37.1, 37.2, 52.1, 54.6, 77.2, 128.4, 129.0, 134.1, 138.6, 208.6, 213.8. **IR** (neat) 3435, 3072, 2939, 2877, 2839, 1703, 1648, 1596, 1579, 1450, 1393, 1344, 1313, 1228, 1212, 1139, 1013, 999, 988, 953, 885, 832, 821, 791, 788, 722, 695, 639 cm^{-1} . **Mp**: 148.5°C. **EI-MS**: m/z (%): 328 (20) [M^+], 310 (4), 285 (10), 223 (5), 205 (12), 175 (72), 159 (17), 133 (17), 124 (22), 105 (100), 77 (55), 41 (30). **HRMS-EI**: calcd. for $C_{21}H_{28}O_3$: 328.2033, found: 328.2038.



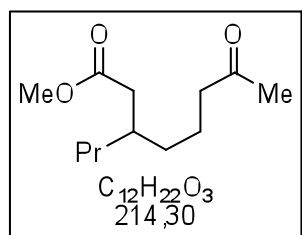
X-Ray crystal structure analysis of **31**

1-Phenyl-hept-2-ene-1,6-dione (32): Prepared according to GP B from 1-methylcyclopentene (0.55 mL, 5.3 mmol) and methyl(triphenylphosphoranylidene)acetate (1.8 g, 5.3 mmol). Yellowish oil is obtained in 25% yield.



NMR ^1H (300 MHz, CDCl_3), δ : 1.65 (qu, $J = 7.5$ Hz, 2H), 2.04 (s, 3H), 2.13 (qd, $J = 1.5$ Hz, $J = 7.1$ Hz, 2H), 2.37 (t, $J = 7.3$ Hz, 2H), 3.63 (s, 3H), 6.01 (dt, $J = 1.7$ Hz, $J = 15.8$ Hz, 1H), 6.70 (dt, $J = 6.7$ Hz, $J = 15.6$ Hz, 1H). **NMR ^{13}C** (75 MHz, CDCl_3), δ : 21.7, 26.7, 29.7, 31.1, 42.3, 51.1, 121.4, 148.1, 166.6, 207.7. **IR** (neat) 2950, 1711, 1656, 1436, 1358, 1315, 1270, 1197, 1172, 1141, 1041, 982, 857, 719 cm^{-1} . **EI-MS**: m/z (%): 170 (12) [M^+], 155 (20), 138 (67), 120 (12), 113 (70), 100 (64), 81 (76), 68 (55), 58 (66), 43 (100). **HRMS** (+ESI): calcd. for $\text{C}_9\text{H}_{14}\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$): 193.0838, found: 193.0840.

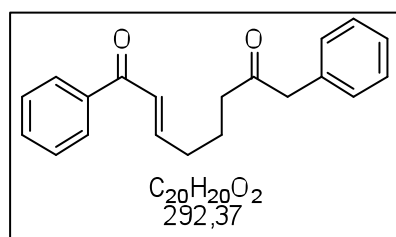
7-Oxo-3-propyl-octanoic acid methyl ester (34): Prepared according to GP F from **32** (0.238 g, 1.4 mmol), propylcatecholborane (0.9 mL, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). Colourless oil is obtained in 44% yield (contaminated with catecholborane).



NMR ^1H (300 MHz, CDCl_3), δ : 0.88 (m, 3H), 1.28 (m, 6H), 1.57 (m, 2H), 1.87 (m, 1H), 2.05 (s, 3H), 2.27 (m, 2H), 2.44 (t, $J = 7.3$ Hz, 2H), 6.01 (s, 3H). **NMR ^{13}C** (75 MHz, CDCl_3), δ : 14.2, 19.6, 20.7, 29.9, 33.2, 34.6, 36.0,

38.8, 43.8, 51.6, 174.6, 210.7. **IR** (neat) 1618, 1596, 1511, 1467, 1360, 1277, 1254, 1238, 1184, 1163, 1093, 1040, 937, 916, 848, 768, 738, 720, 624, 613 cm^{-1} . **+ESI-MS**: m/z (%): 237 (100) ($[\text{M} + \text{Na}]^+$), 226 (35). **HRMS** (+ESI) calcd. for $\text{C}_{12}\text{H}_{22}\text{NaO}_3$ ($[\text{M} + \text{Na}]^+$): 237.1460. Found: 237.1466.

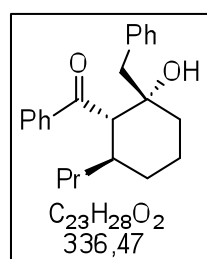
1,8-Diphenyl-oct-2-ene-1,7-dione (35): Prepared according to GP B from previously prepared 1-benzylcyclopentene (2.2 g, 5.3 mmol) and (Benzoylmethylene)- triphenylphosphorane (2.0 g, 5.3 mmol). Yellowish oil is obtained in 51% yield.



NMR ^1H (300 MHz, CDCl_3), δ : 1.79 (qu, $J = 7.2$ Hz, 2H), 2.26 (qd, $J = 1.1$ Hz, $J = 7.2$ Hz, 2H), 2.52 (t, $J = 7.0$ Hz,

2H), 3.68 (s, 2H) 6.81 (dt, $J = 1.3$ Hz, $J = 15.4$ Hz, 1H), 6.96 (dt, $J = 7.0$ Hz, $J = 15.5$ Hz, 1H), 7.18-7.34 (m, 5H), 7.46 (m, 2H), 7.56 (m, 1H), 7.90 (m, 2H). **NMR ^{13}C** (75 MHz, CDCl_3), δ : 21.9, 31.8, 40.8, 50.3 126.5, 127.1, 128.5, 128.7, 129.3, 132.6, 134.1, 137.9, 148.4, 190.6, 207.5. **IR** (neat) 2933, 2360, 1710, 1667, 1617, 1597, 1577, 1495, 1447, 1345, 1285, 1224, 1179, 1074, 974, 913, 730, 694 cm^{-1} . **EI-MS**: m/z (%): 292 (7) [M^+], 277 (8), 201 (23), 183 (6), 173 (18), 155 (25), 146 (8), 129 (6), 115 (12), 105 (100), 99 (8), 91 (72), 84 (36), 77 (55), 65 (17), 55 (35), 51 (15), 39 (11). **HRMS-EI**: calcd. for $\text{C}_{20}\text{H}_{20}\text{O}_2$: 292.1463, found: 292.1463.

(2-Benzyl-2-hydroxy-6-propyl-cyclohexyl)-phenyl-methanone (36): Prepared according to the GP F from **35** (0.409 g, 1.4 mmol), propylcatecholborane (0.9 mL, 5.6 mmol) and DMF (0.17 mL, 2.1 mmol). Colourless oil is obtained in 51% yield.



NMR ^1H (300 MHz, CDCl_3), δ : 0.70 (t, $J = 7.3$ Hz, 3H), 0.84-1.85 (several peaks, 4H), 1.94 (m, 1H), 2.18 (m, 1H), 2.46 (d, $J = 13.3$ Hz, 1H), 2.63 (d, $J = 13.3$ Hz, 1H), 3.34 (d, $J = 11.1$ Hz, 1H), 4.39 (d, $J = 2.5$ Hz, 1H), 7.05

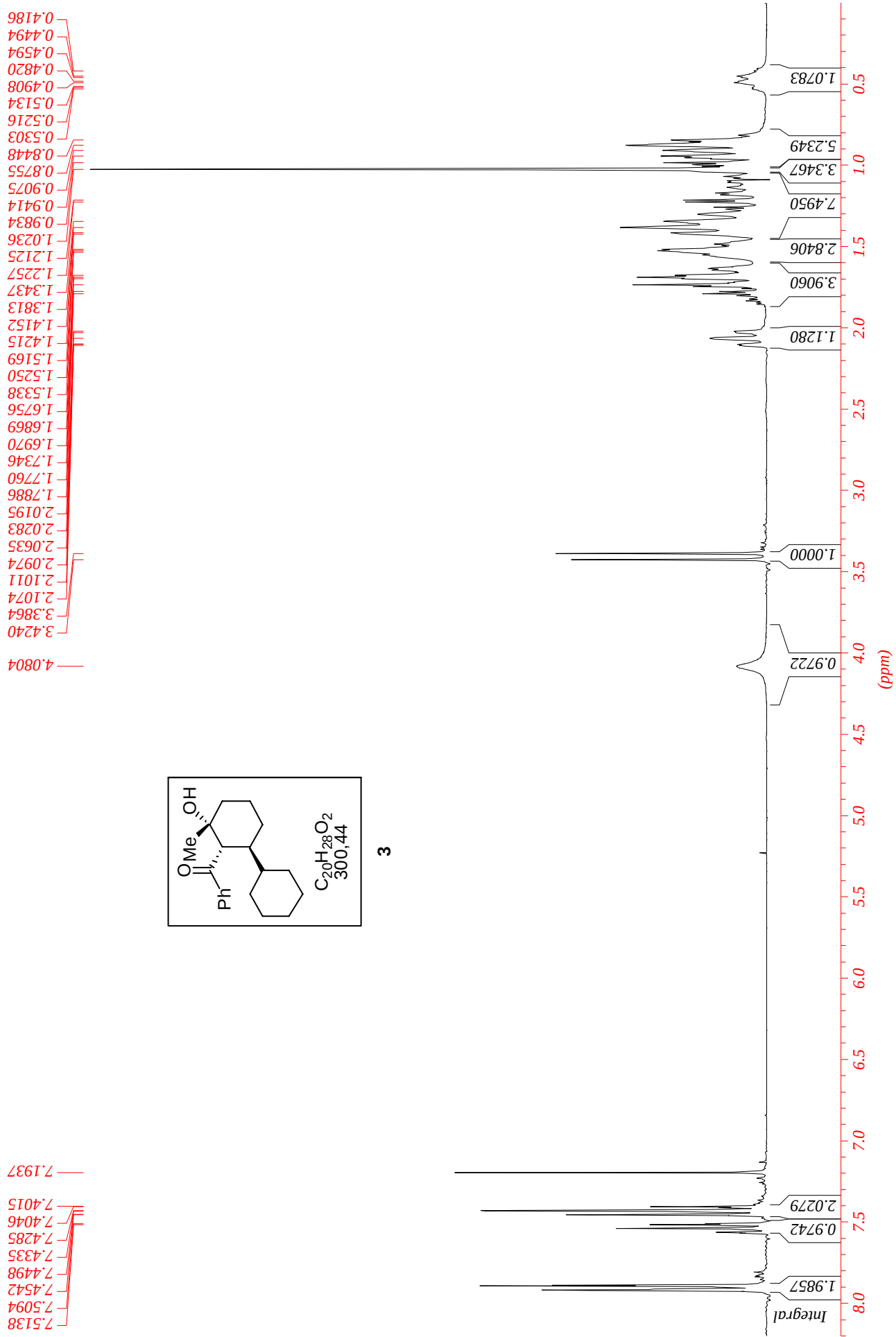
(m, 2H), 7.16 (m, 3H), 7.52 (m, 2H), 7.63 (m, 1H), 8.01 (m, 2H). **NMR ^{13}C** (75 MHz, CDCl_3), δ : 13.9, 19.9, 20.6, 31.0, 35.4, 37.3, 37.7, 49.2, 56.4, 73.9, 126.2, 127.7, 128.5, 128.8, 130.6, 133.8, 136.8, 139.1, 209.7. **IR** (neat) 3436, 2934, 2870, 1639, 1595, 1578, 1496, 1449, 1409, 1358, 1343, 1262, 1228, 1181, 1096, 1015, 982, 899, 873, 787, 750, 698, 684, 676, 640, 617 cm^{-1} . **Mp**: 106.6°C. **EI-MS**: m/z (%): 336 (12) [M^+], 318 (5), 245 (67), 227 (28), 213 (22), 199 (64), 175 (6), 167 (8), 157 (14), 143 (17), 129 (17), 120 (17), 105 (100), 91 (83), 77

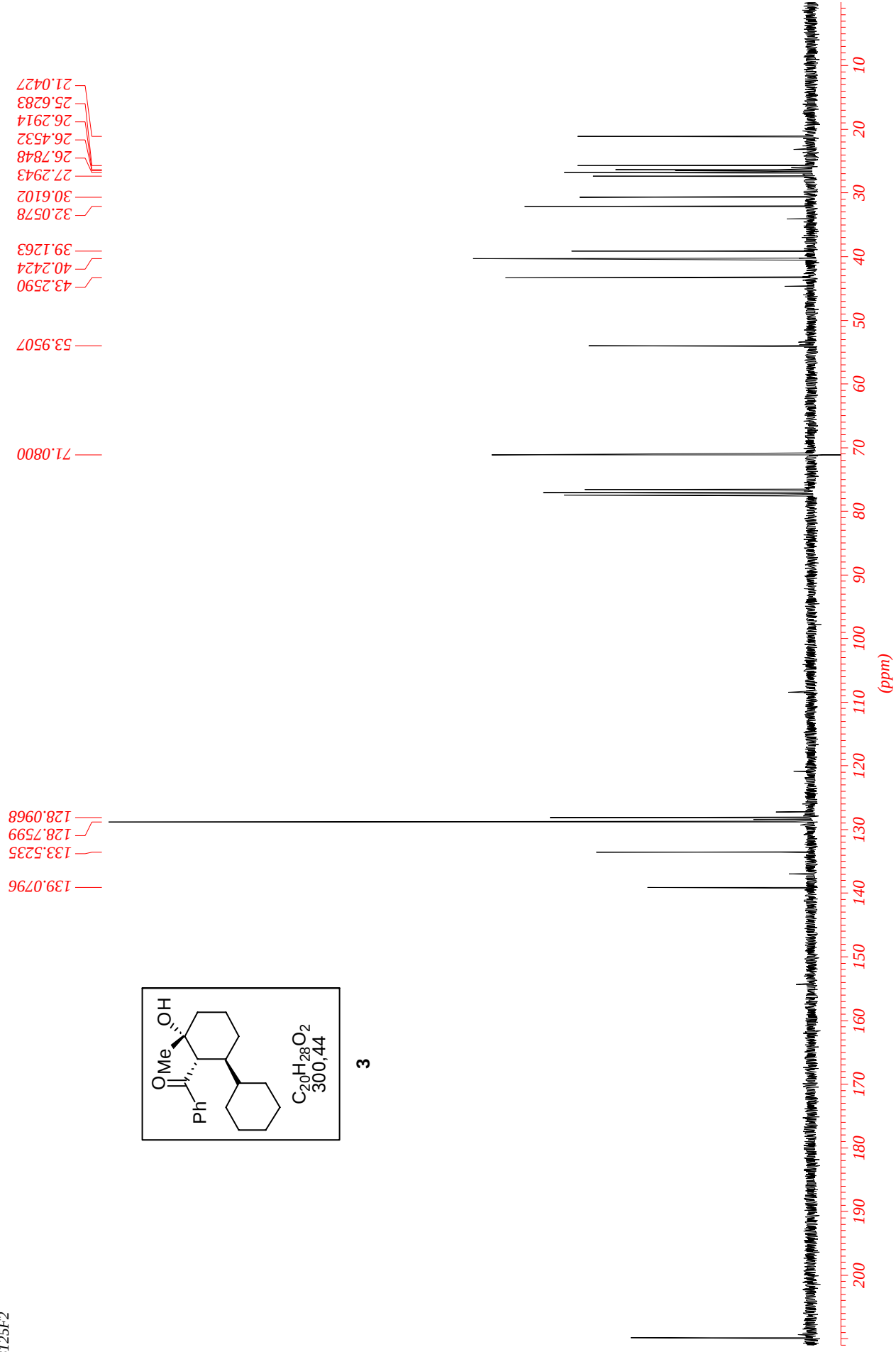
(74), 65 (14), 55 (36), 51 (11), 41 (23). **HRMS-EI** calcd. for C₂₃H₂₈O₂: 336.2088. Found: 336.2089.

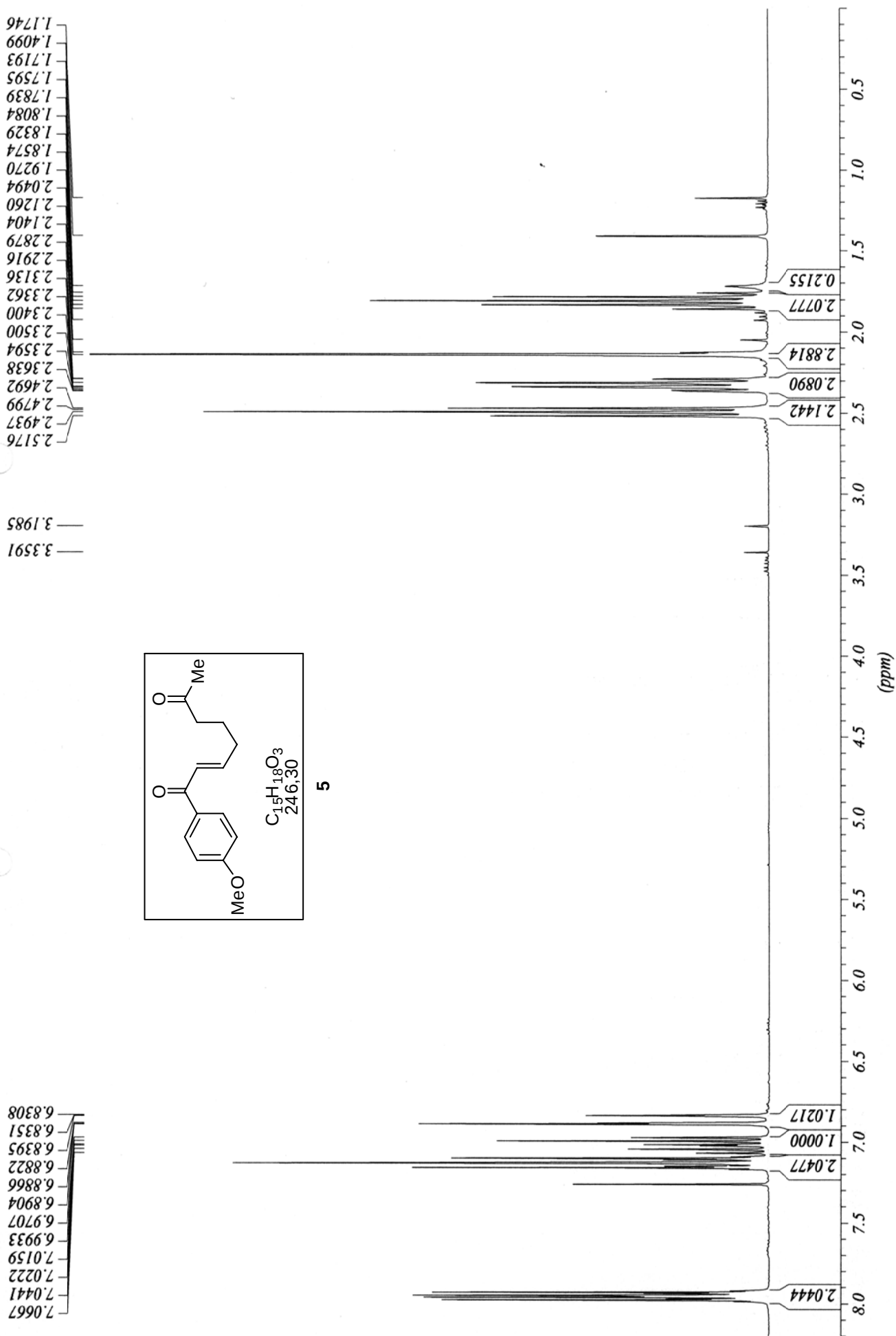
(1) Cauble, D. F.; Gipson, J. D.; Krische, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 1110.

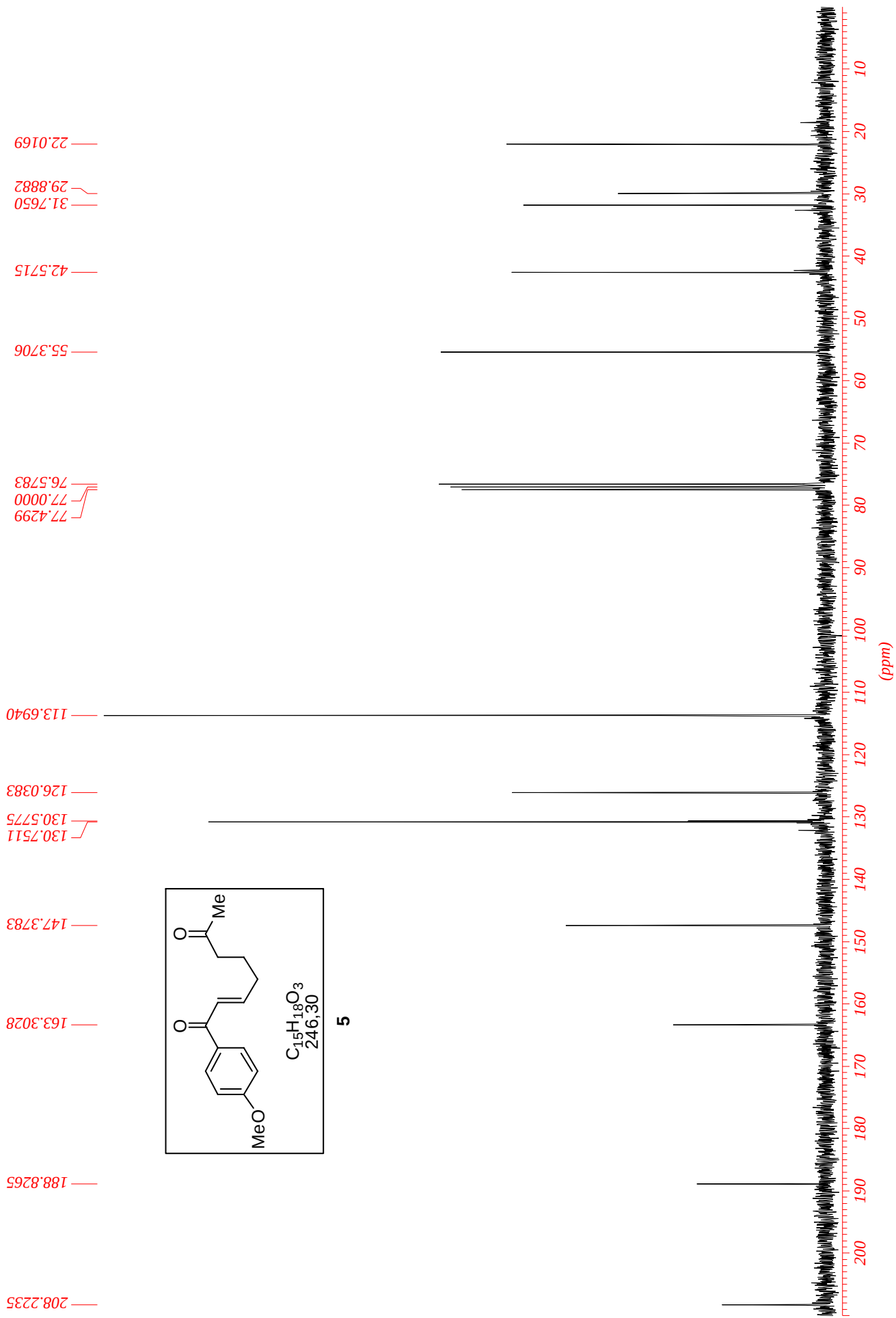
(2) Rodney, S.; Mukaiyama, T. *Chem. Lett.* **1985**, 851.

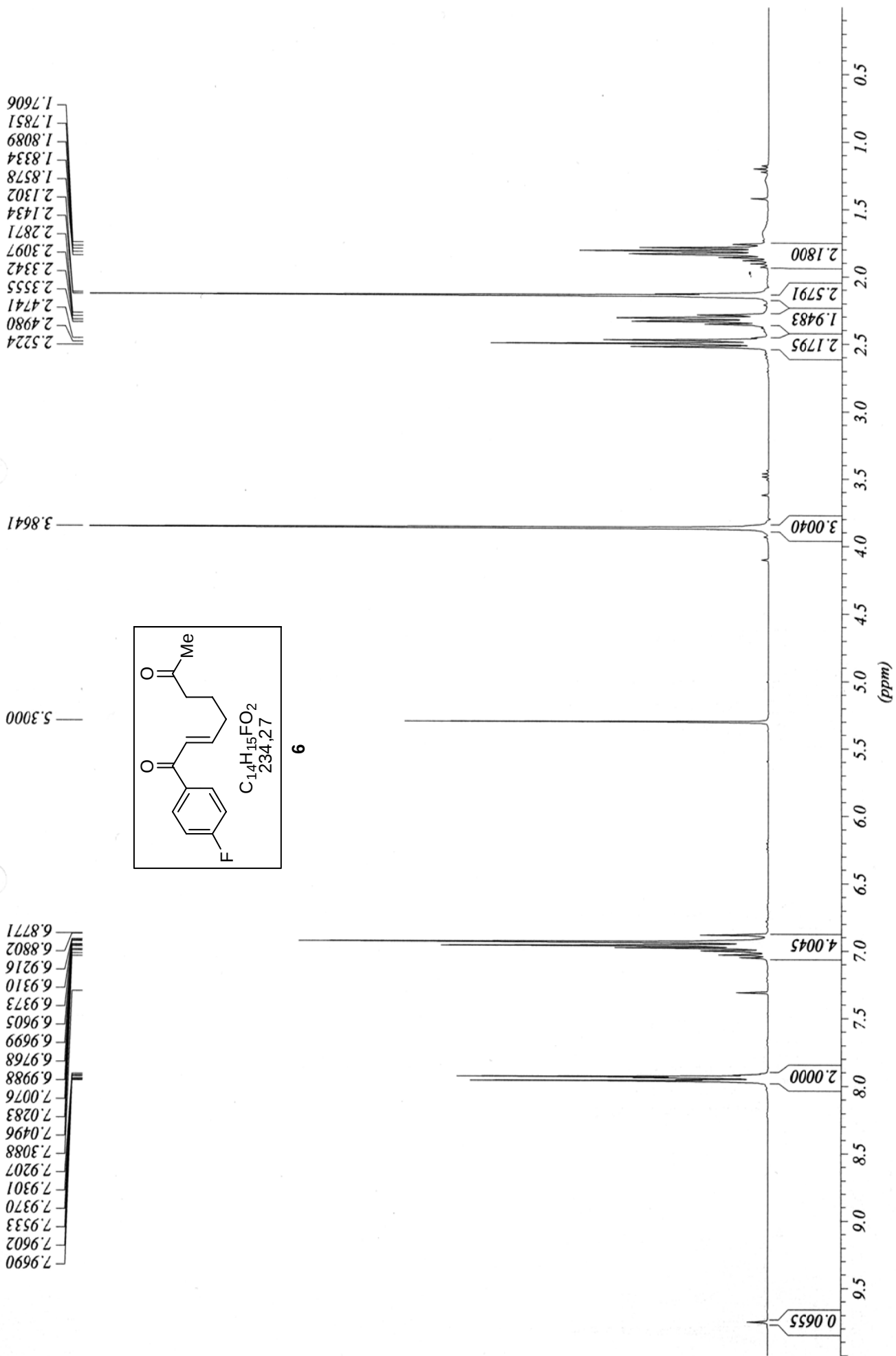
(3) Weinstein, R.; Lerner, R. A.; Barbas, C. F. III.; Shabat, D. *J. Am. Chem. Soc.* **2005**, *127*, 13104.

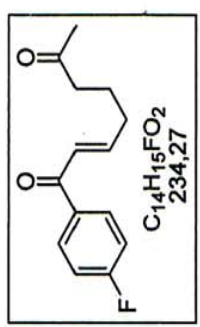
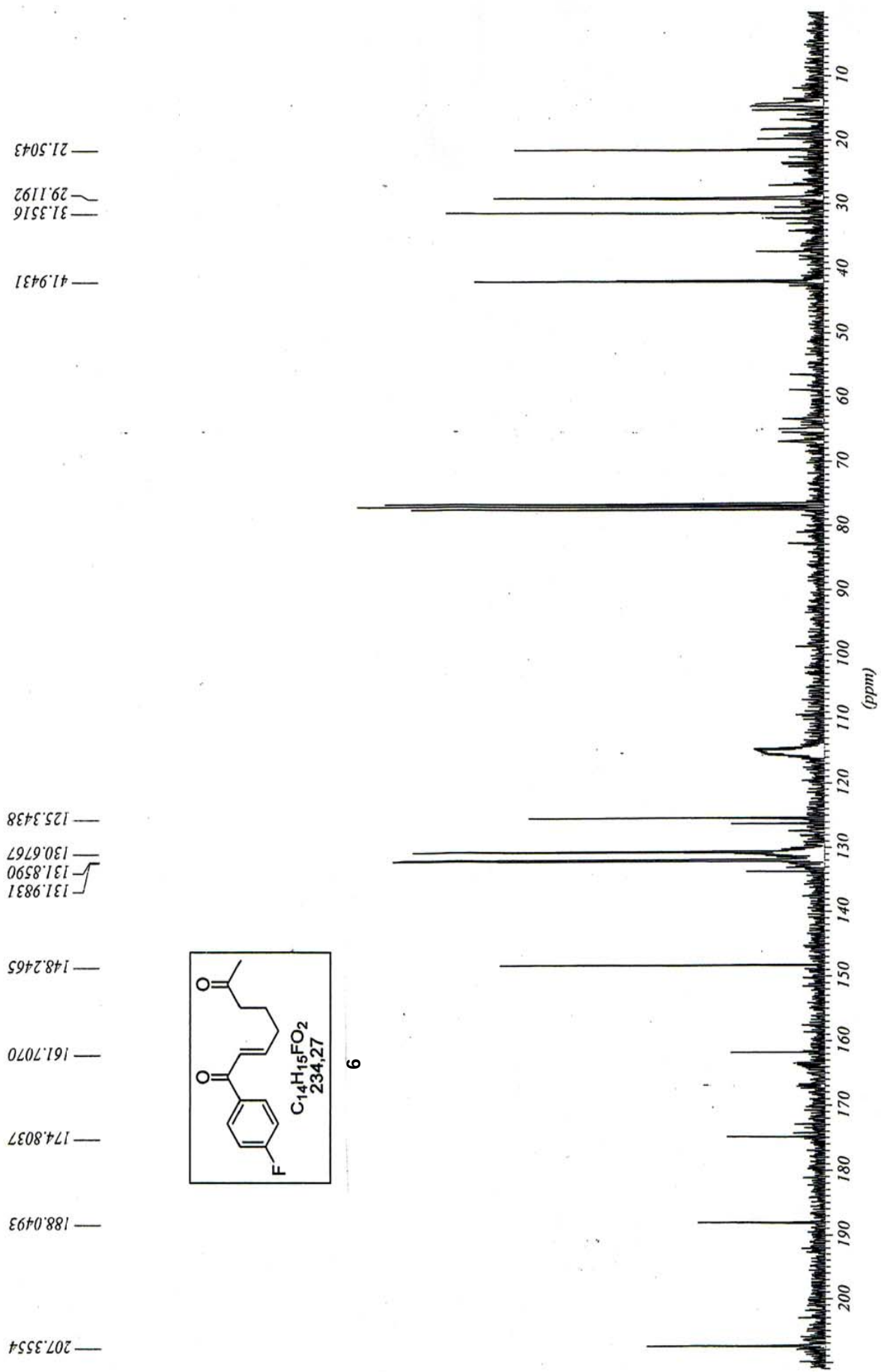




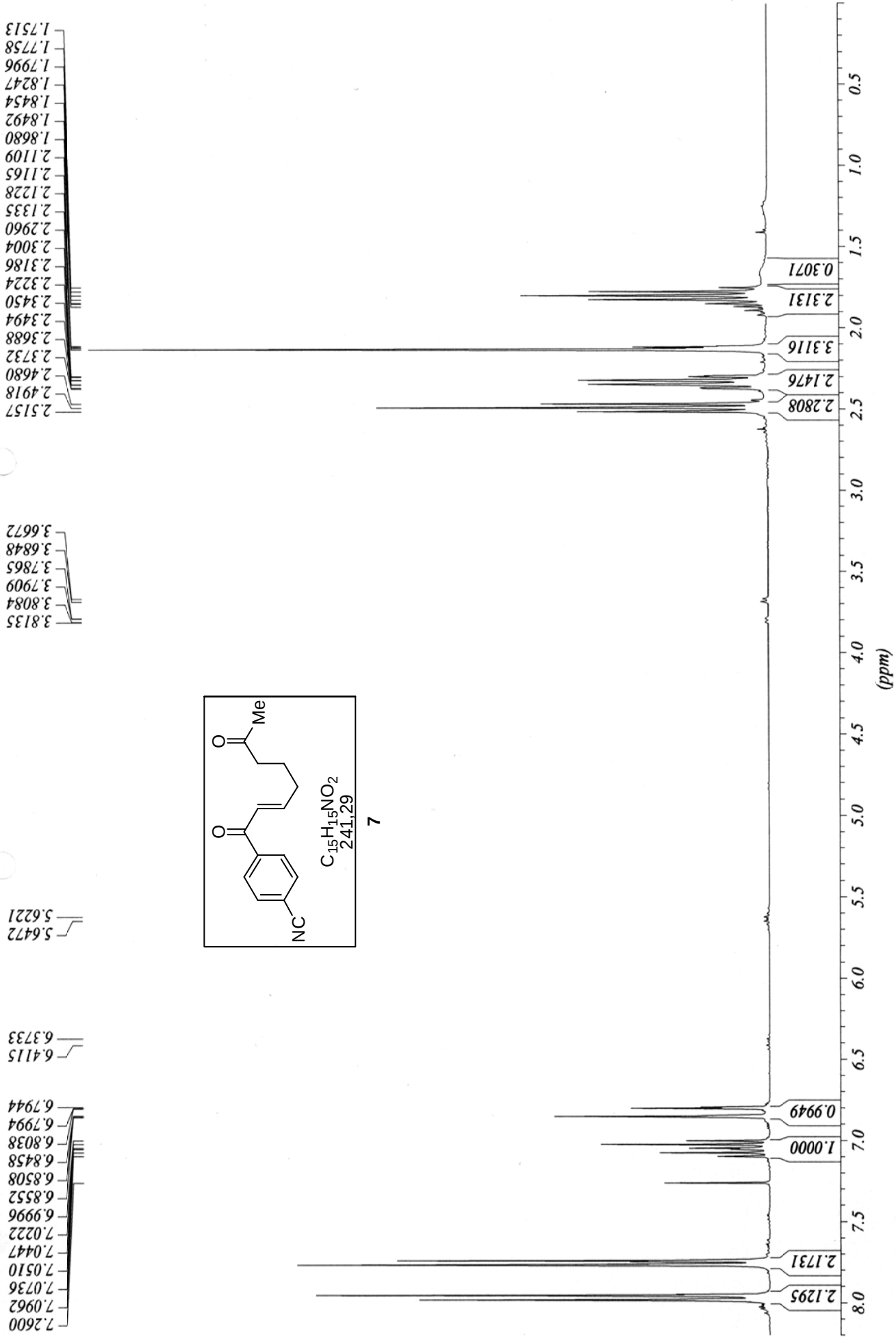


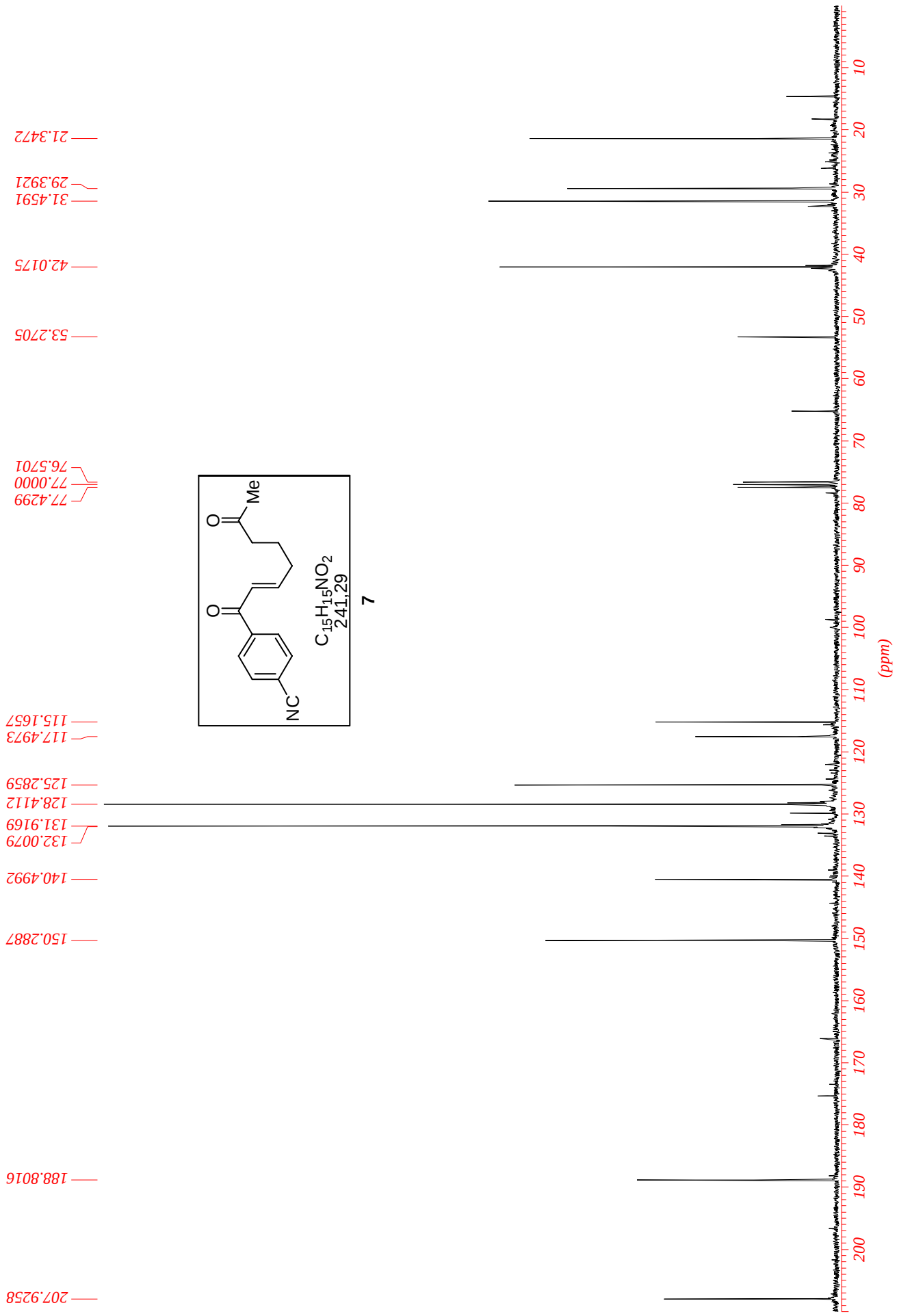


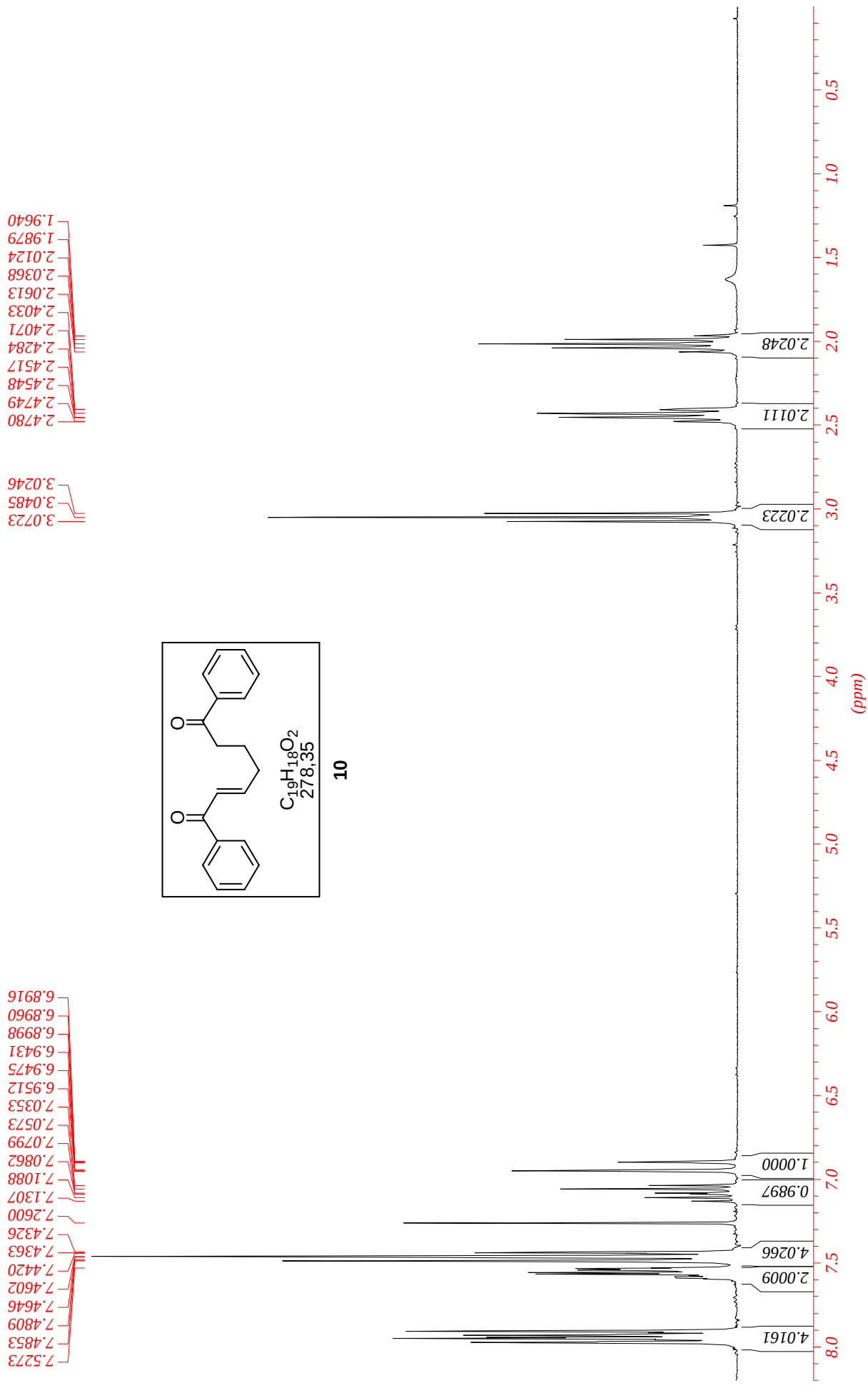




6

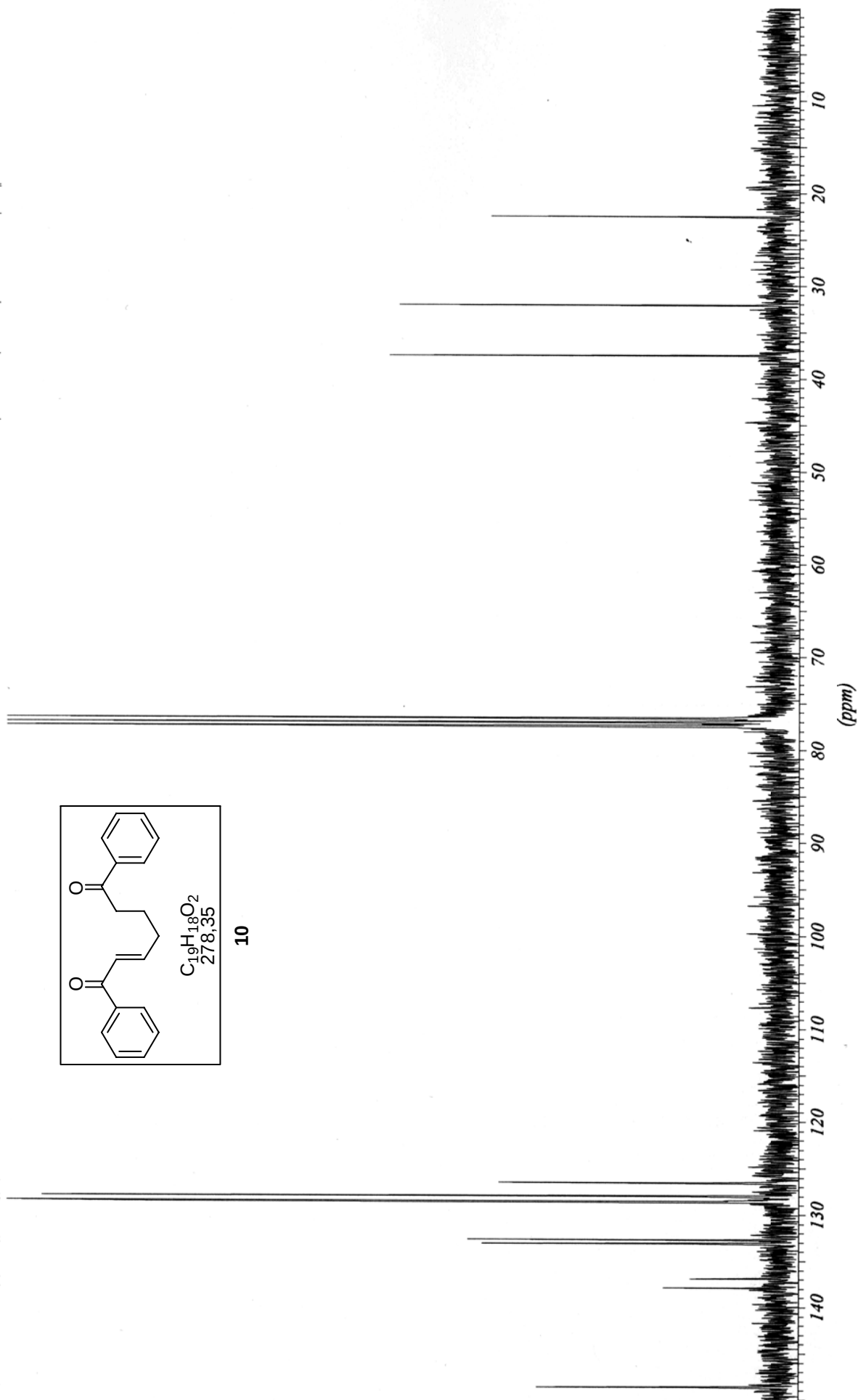
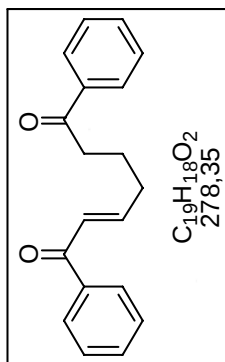


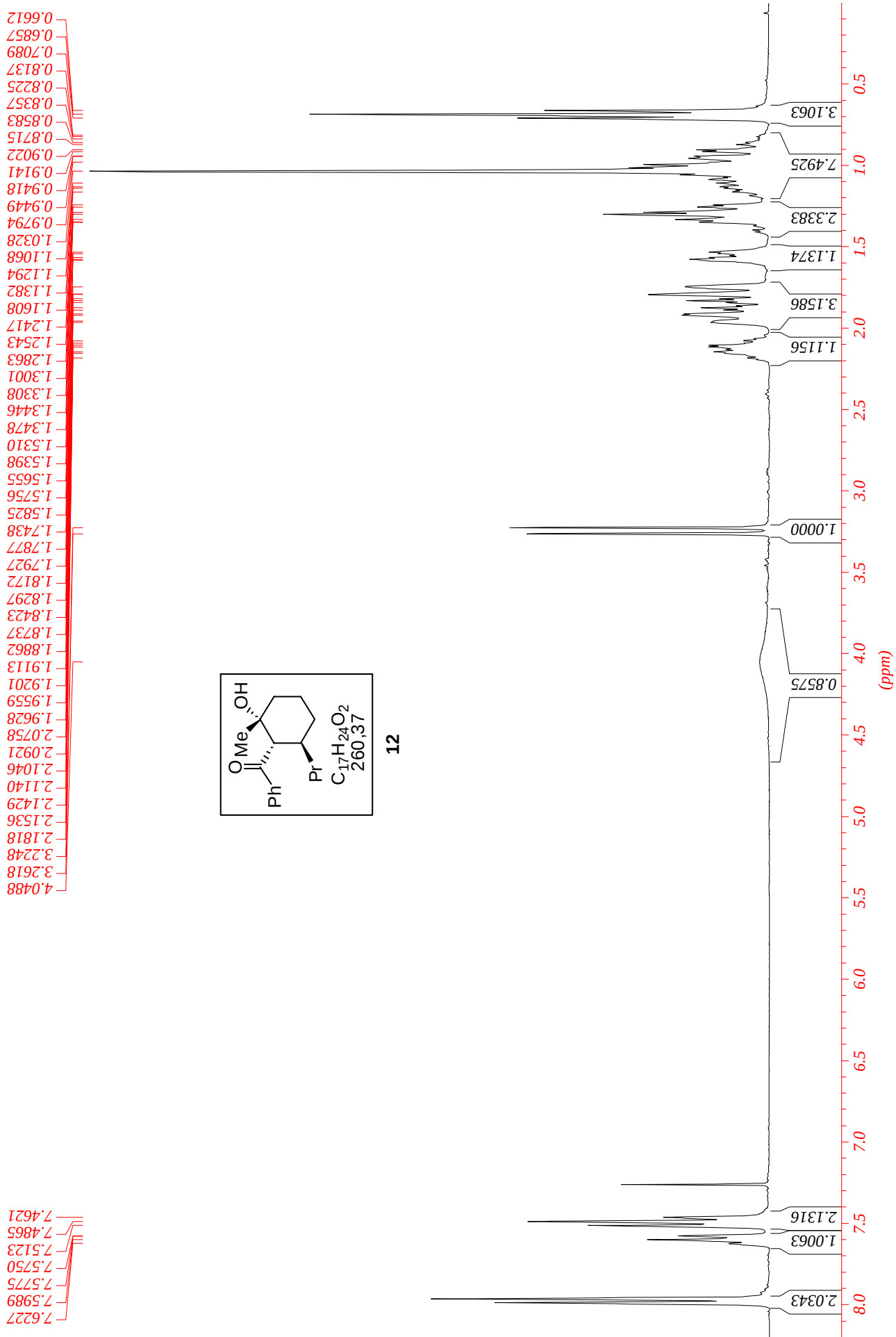




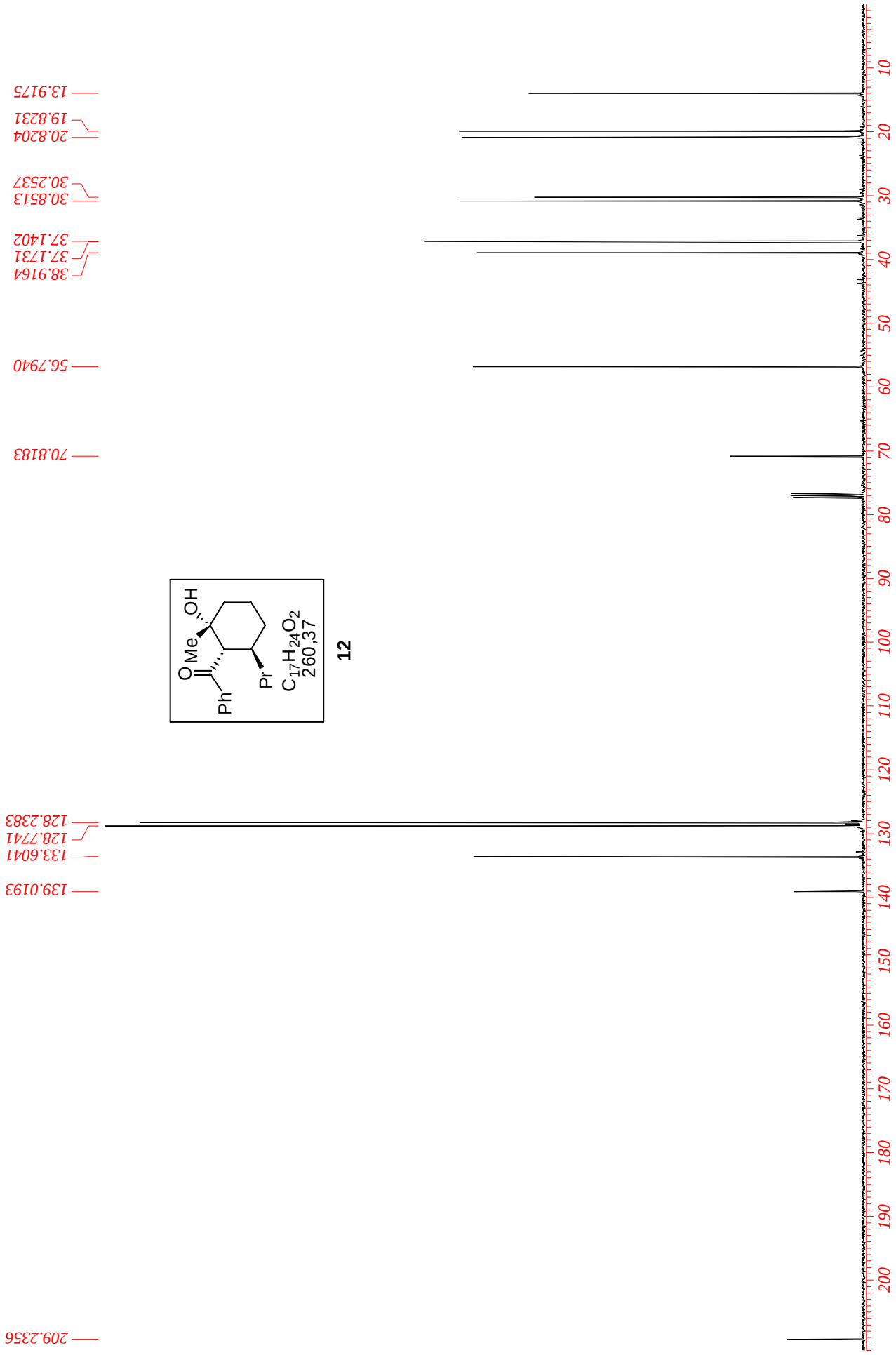
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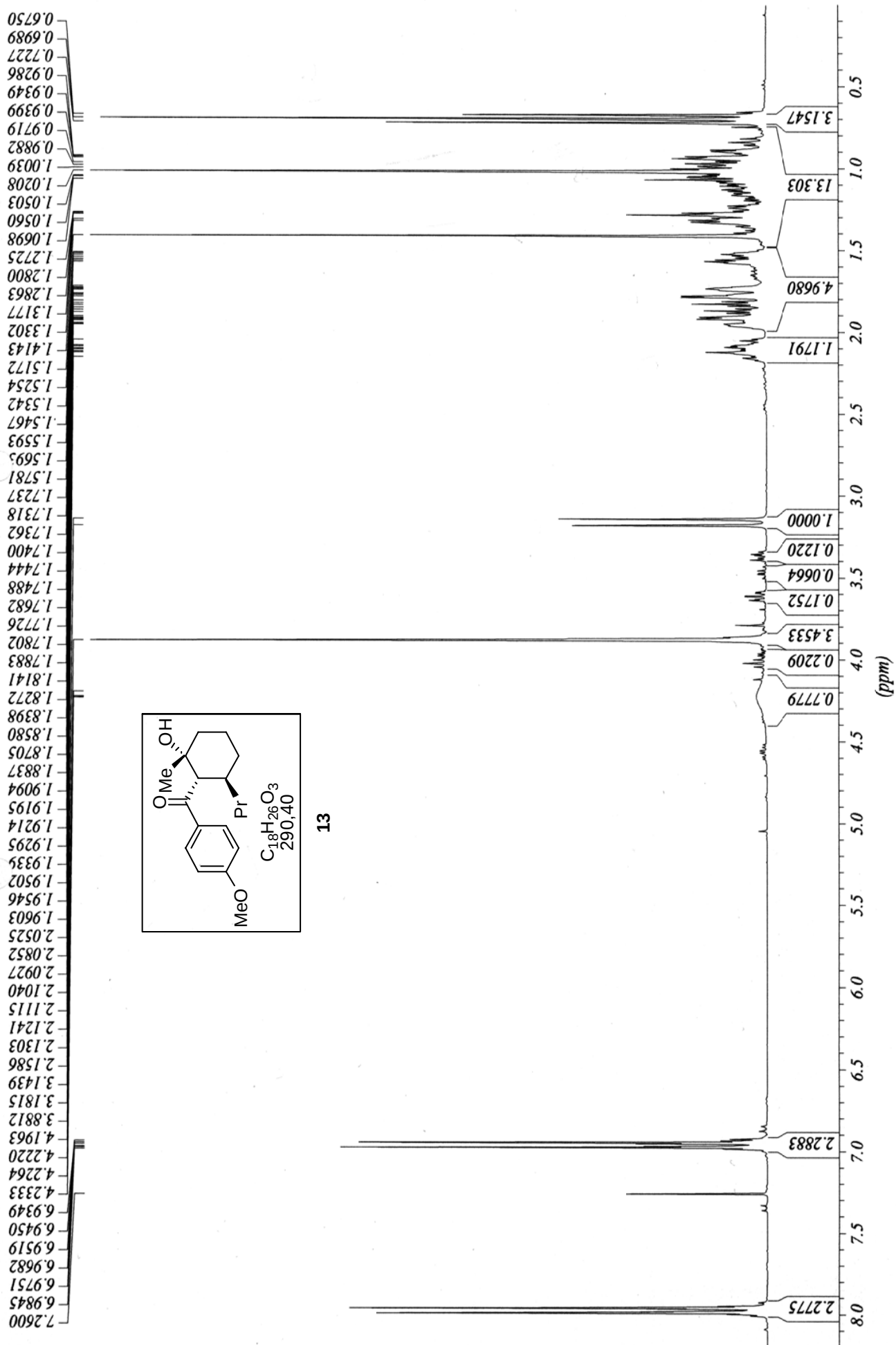
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19.3698



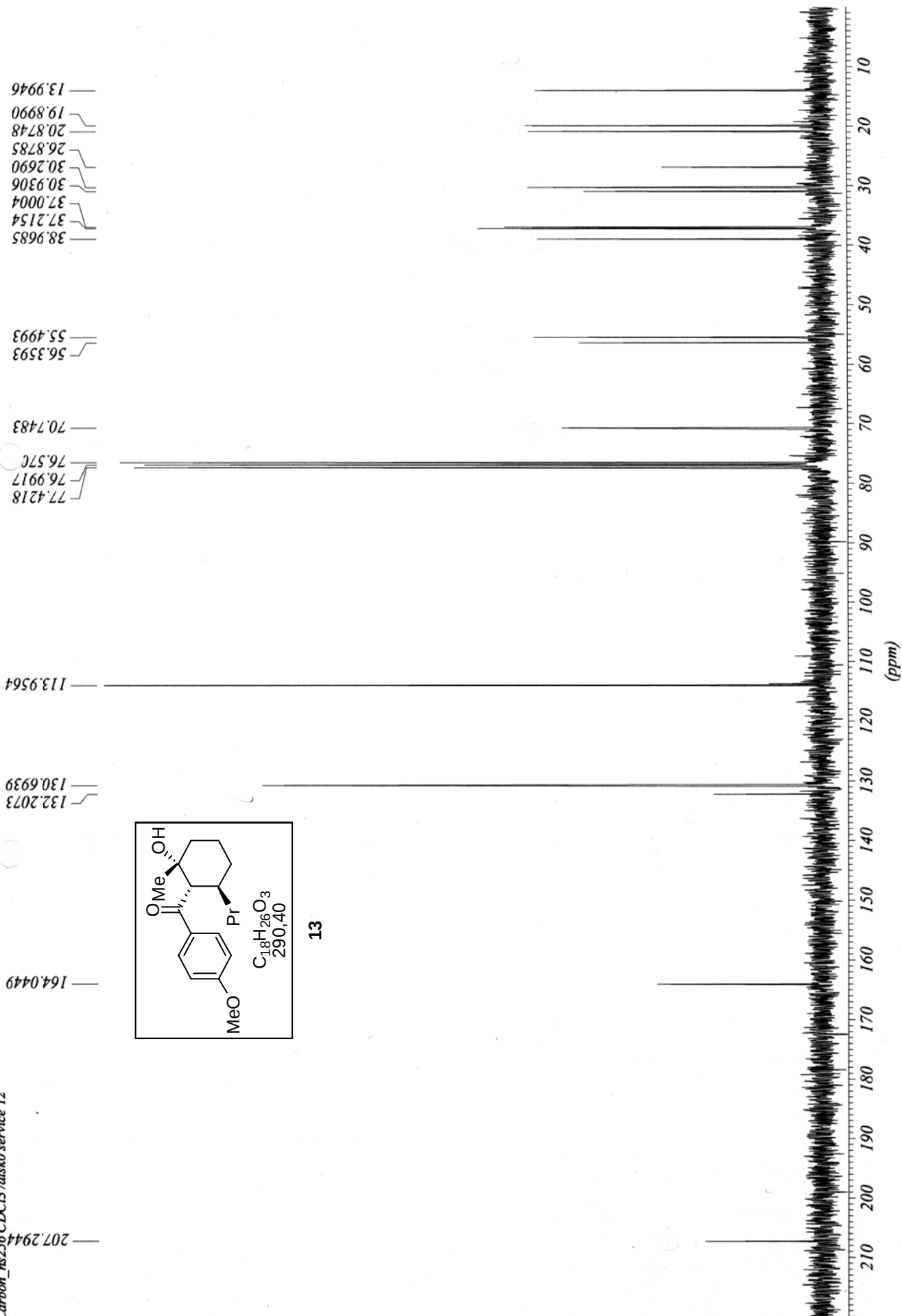


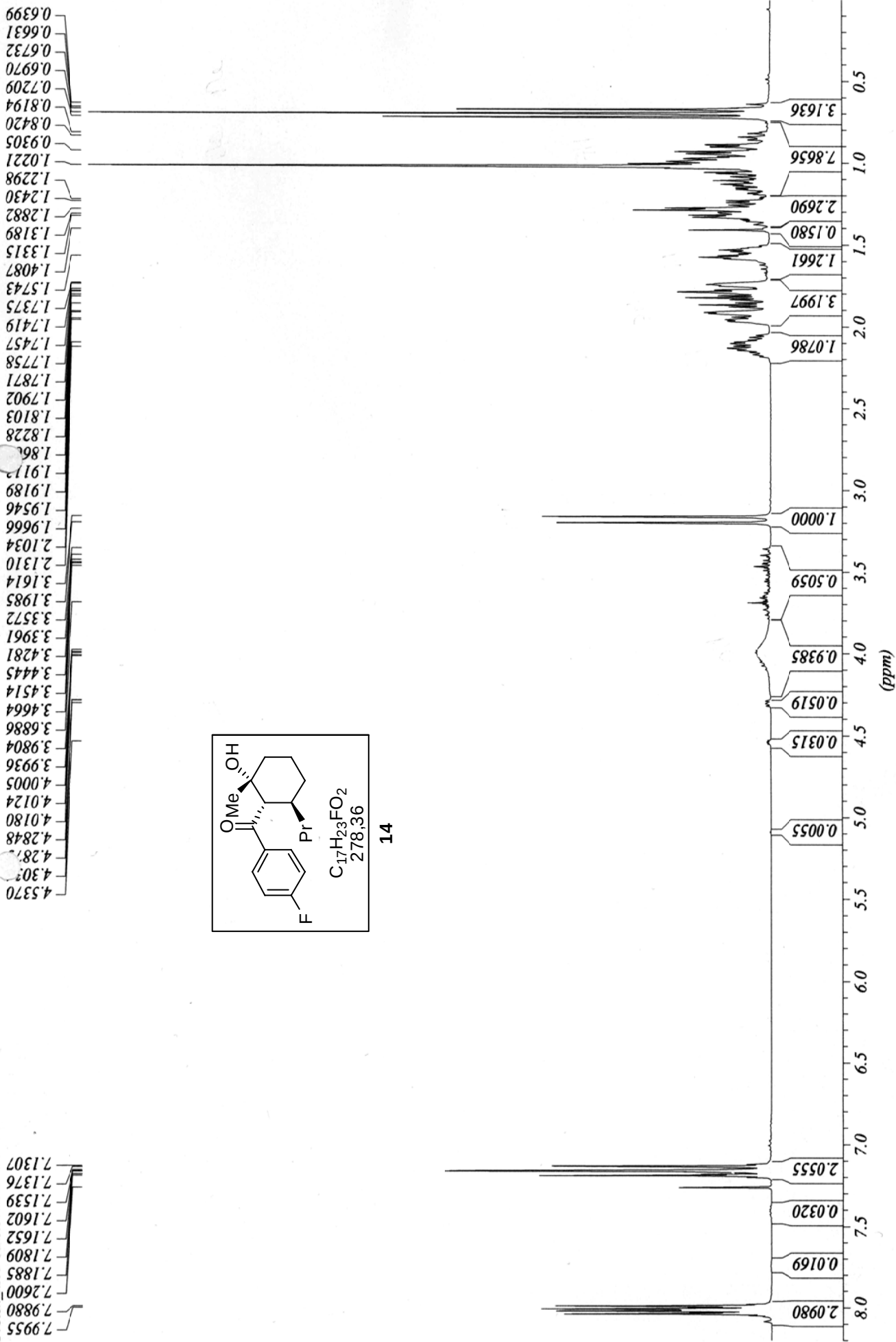
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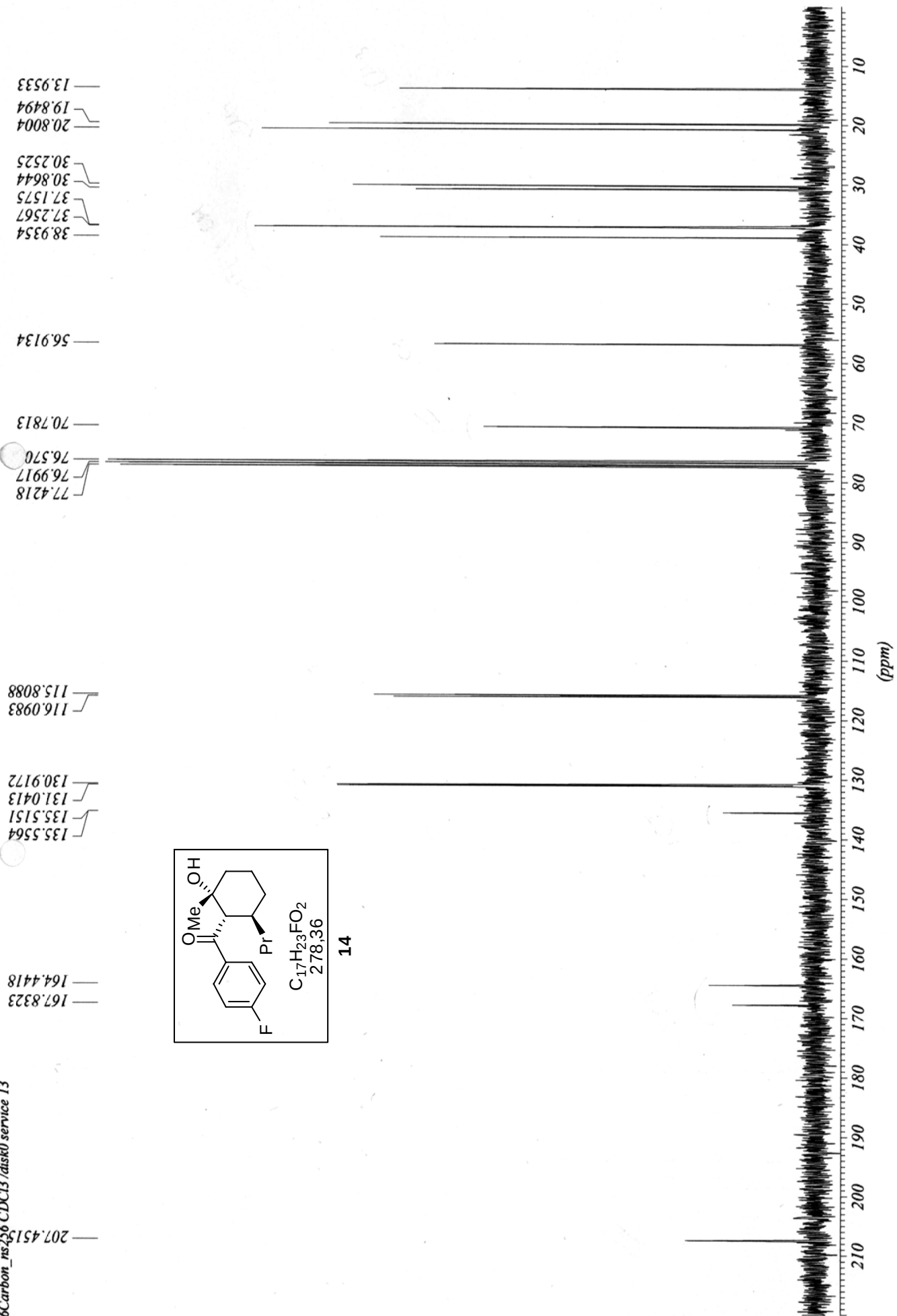


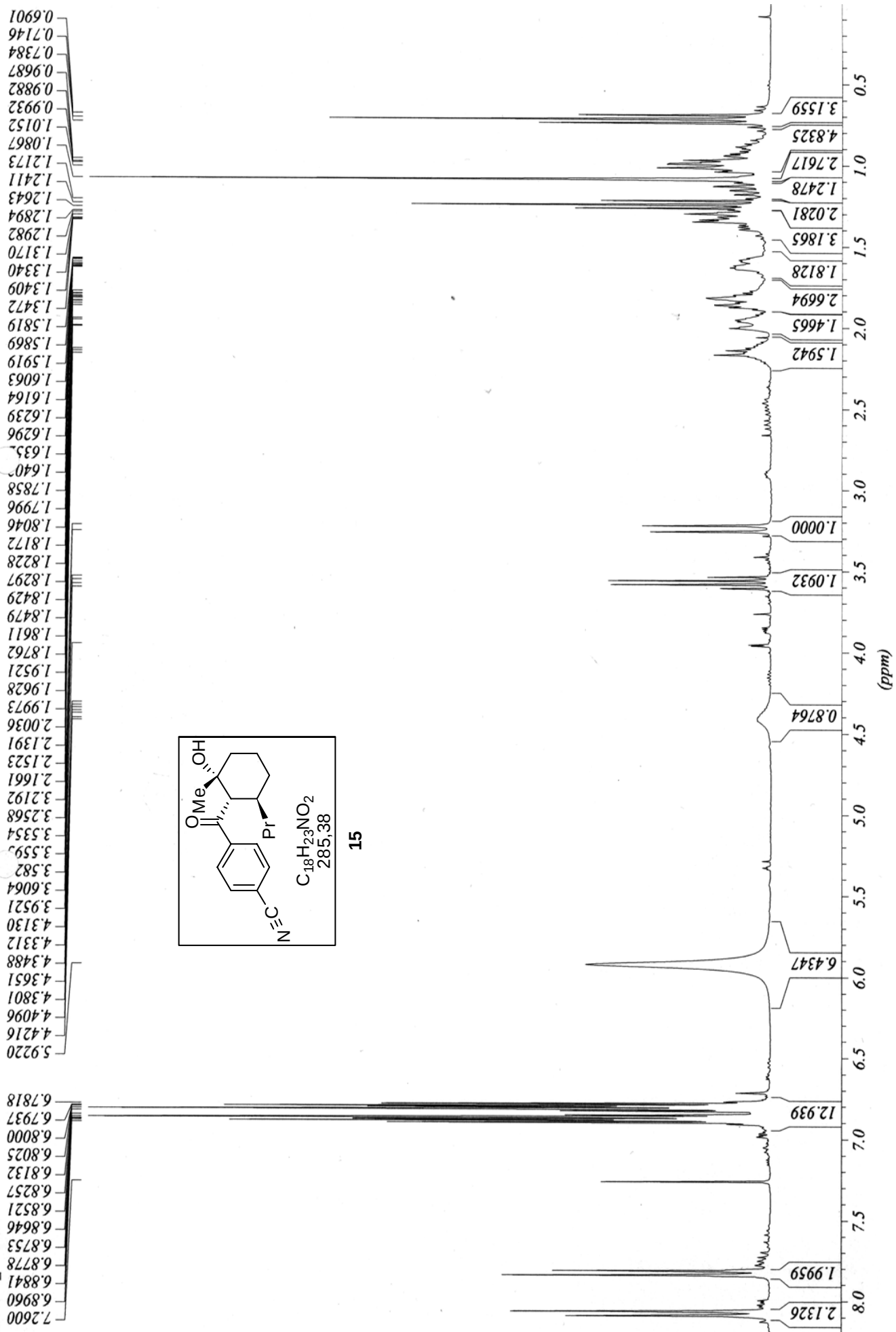


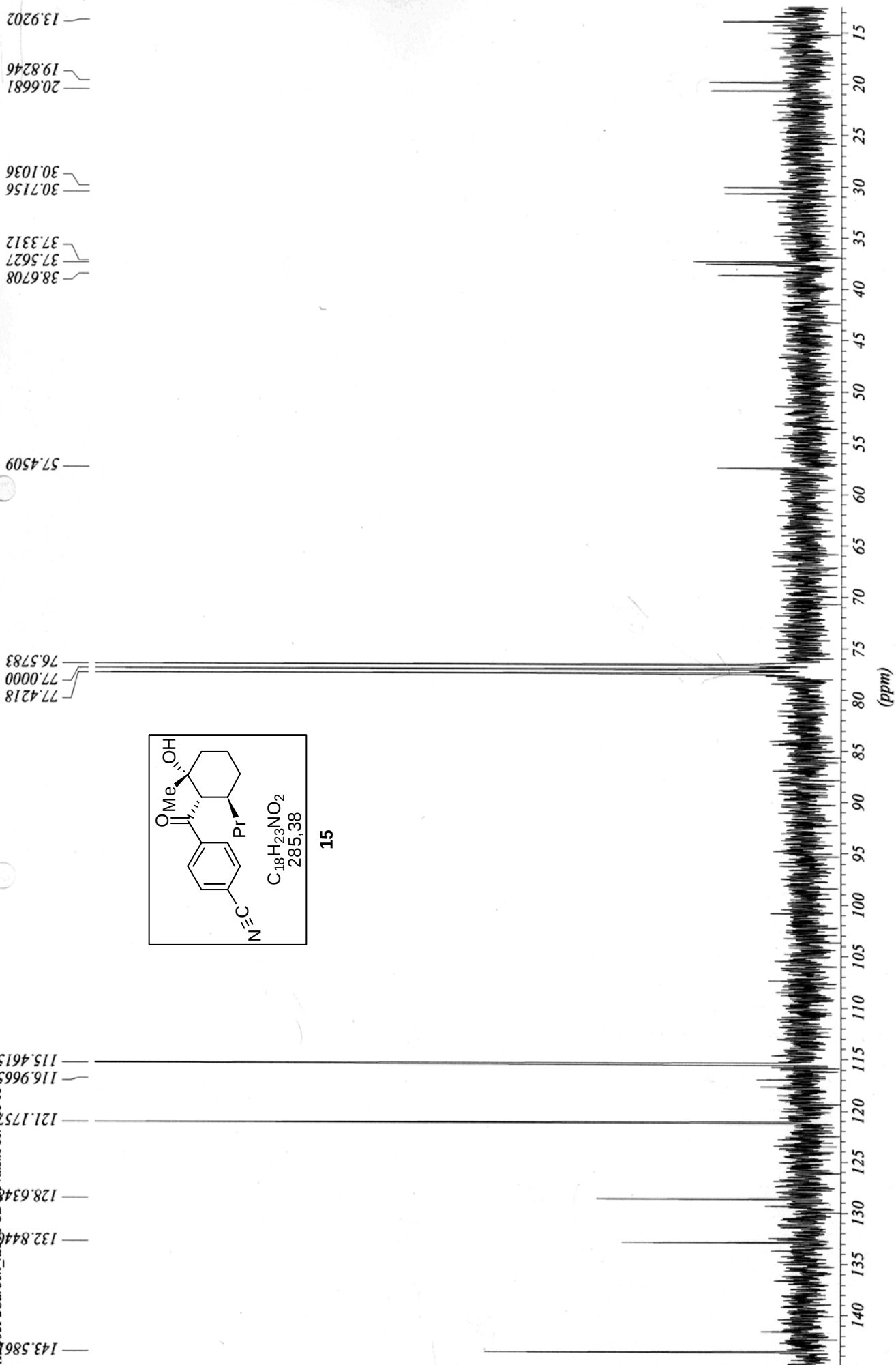
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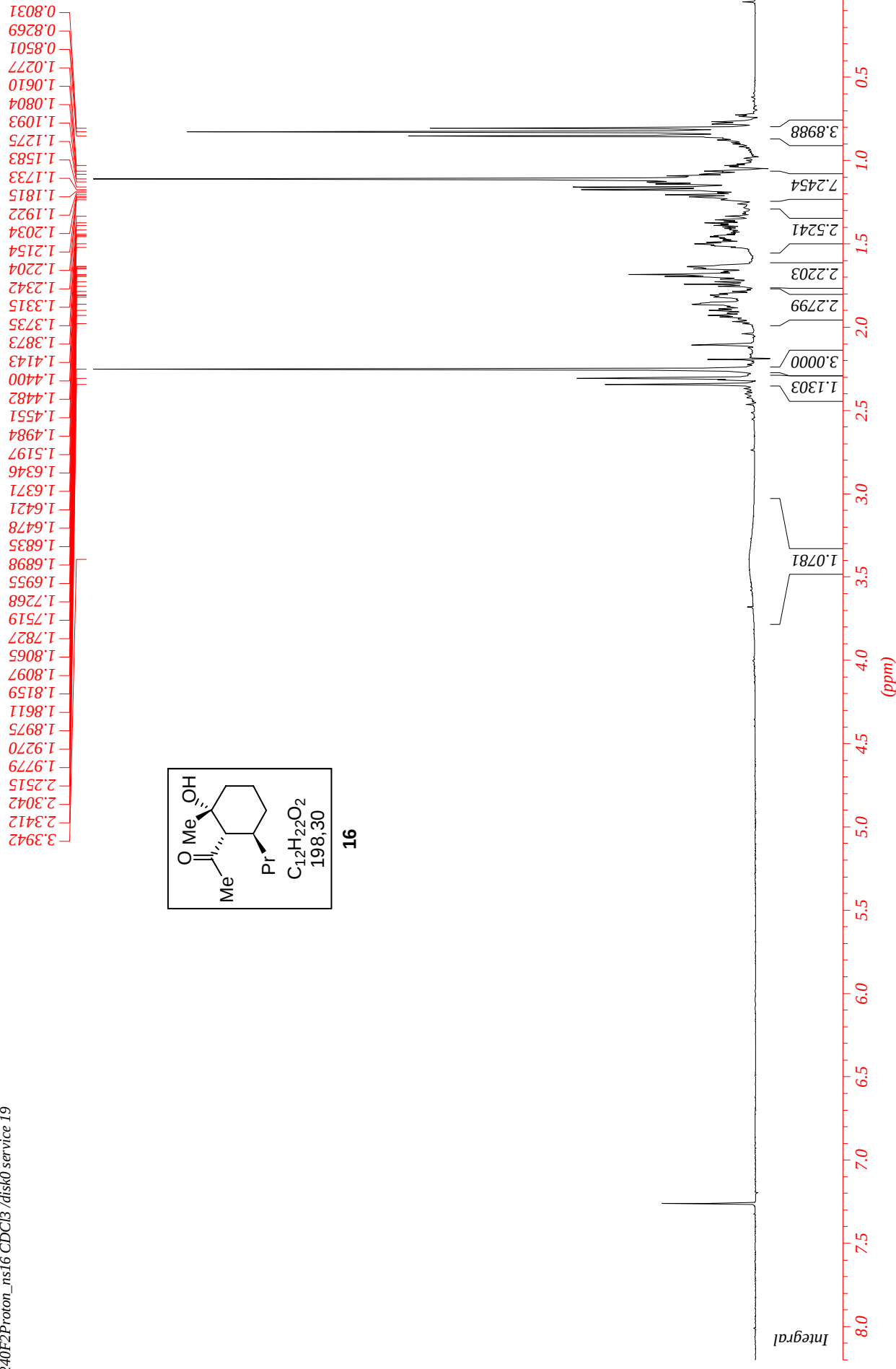


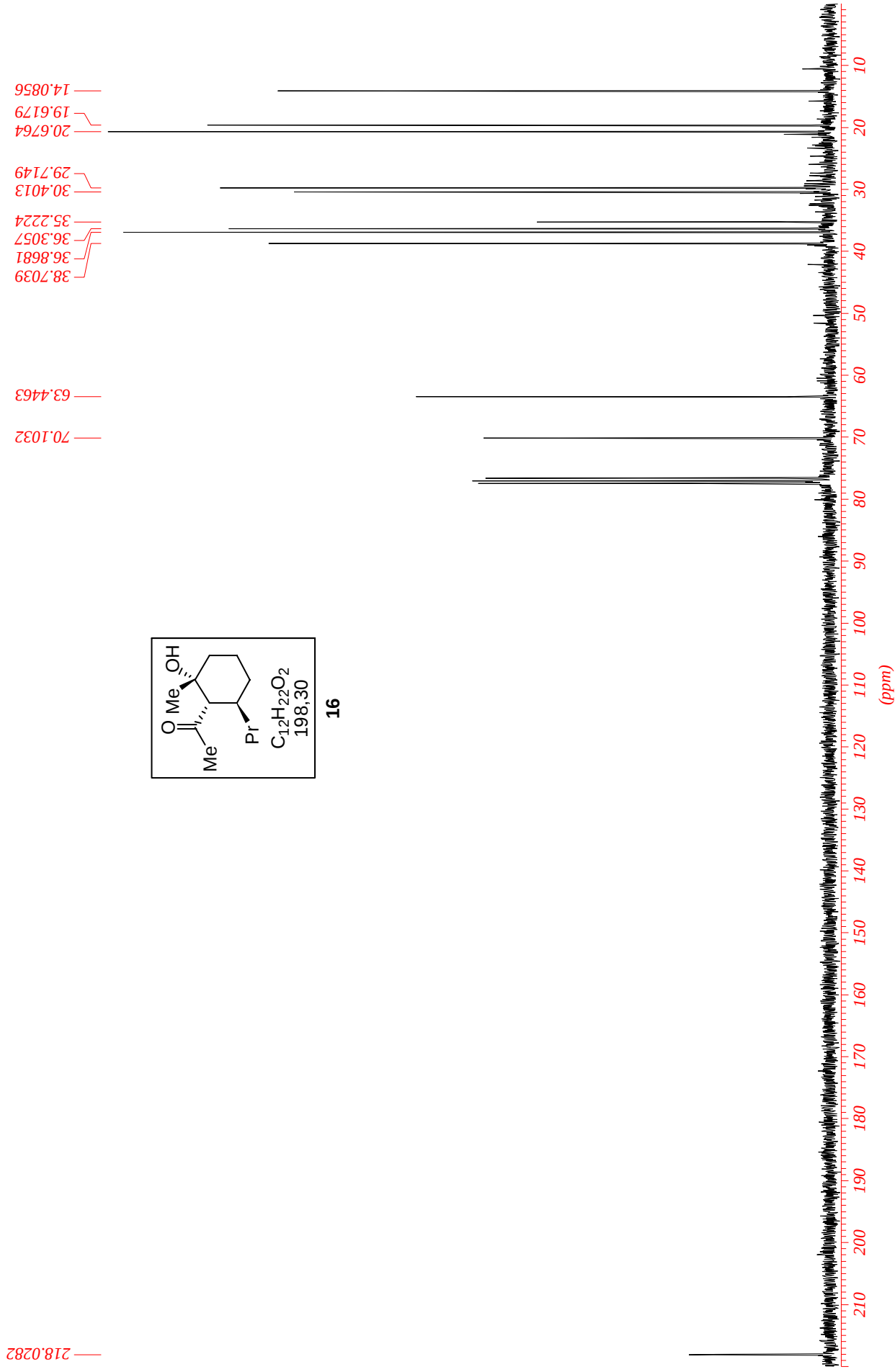




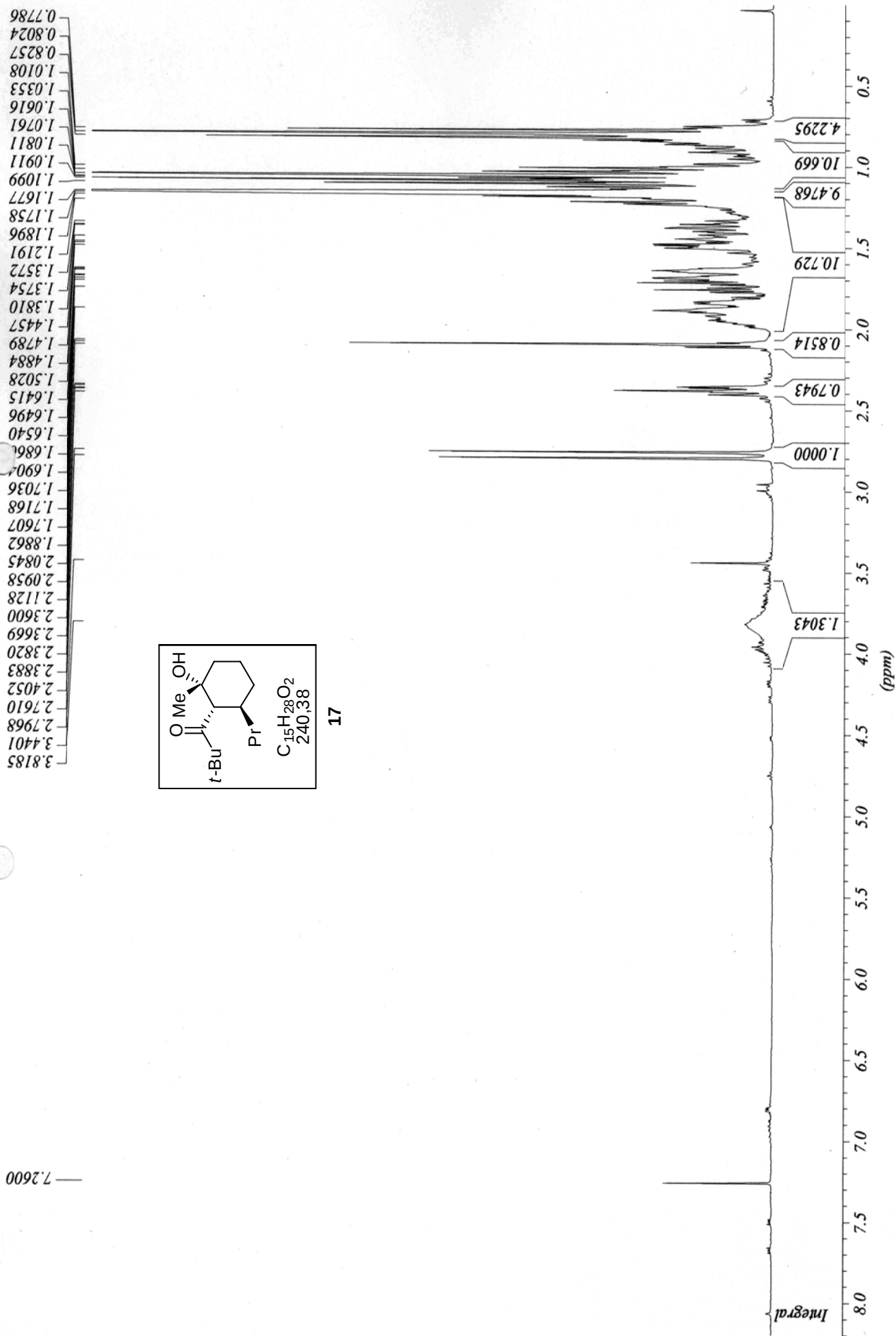




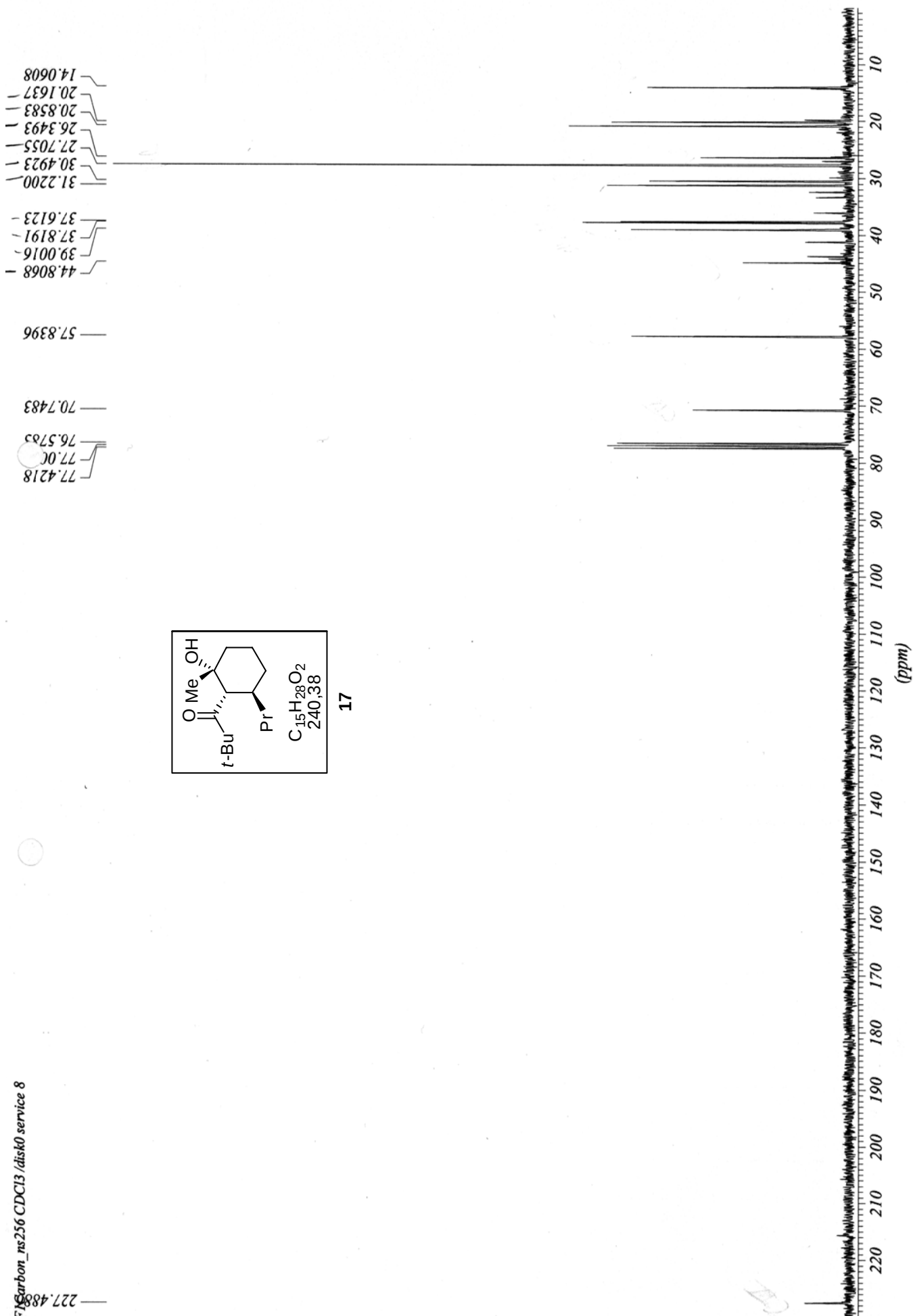


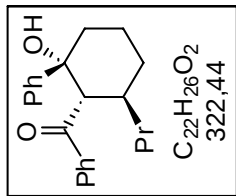
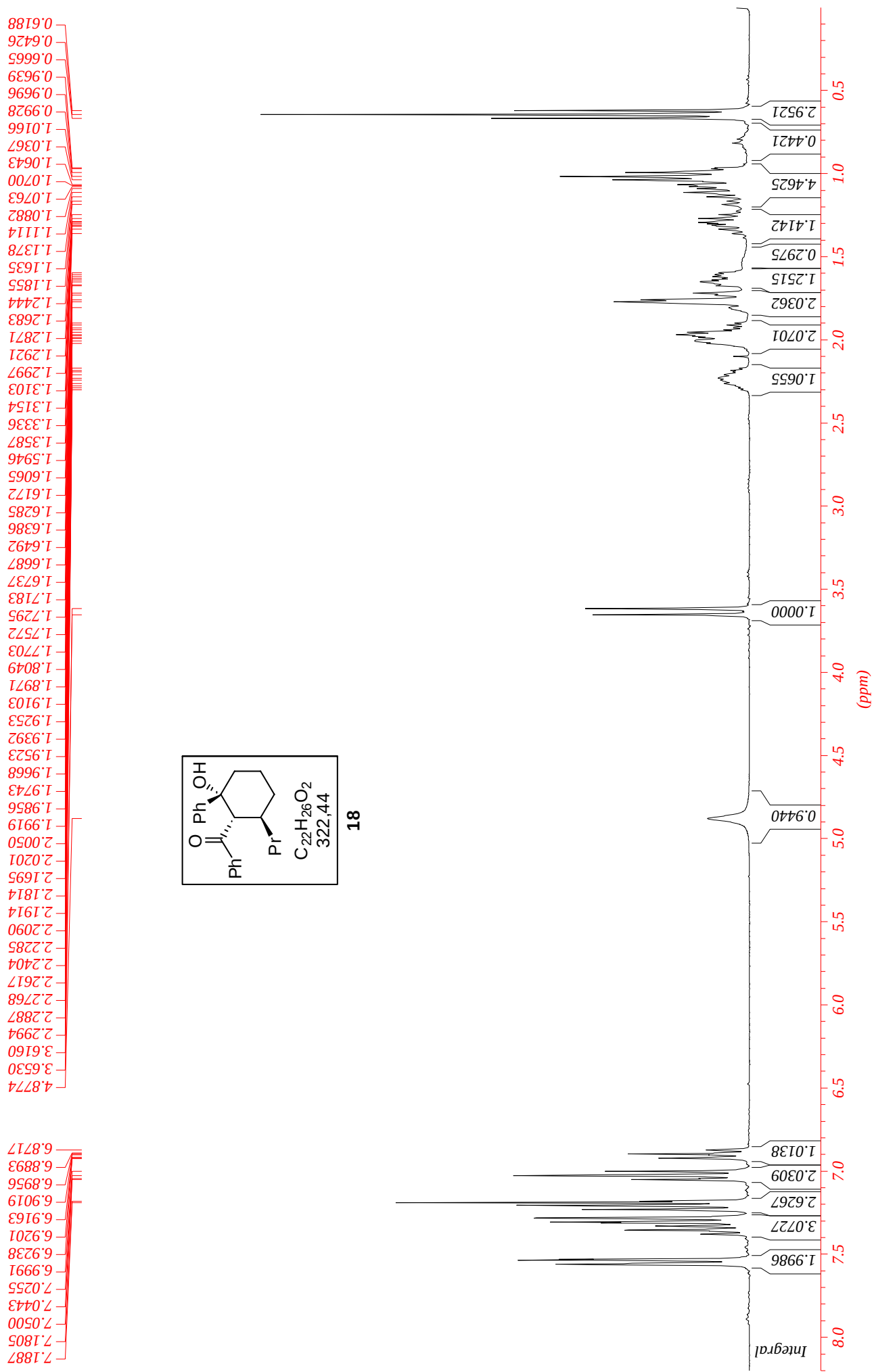


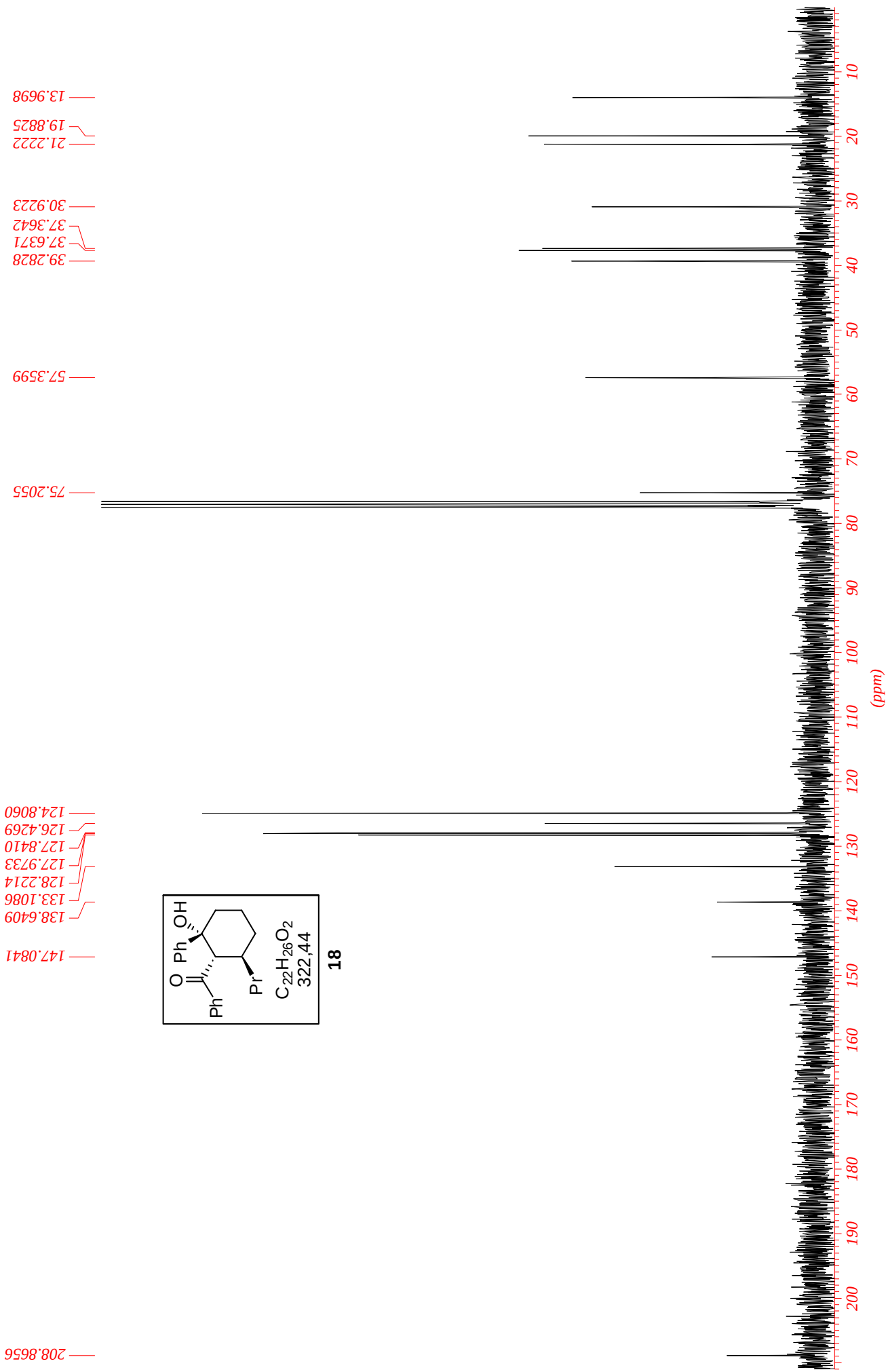
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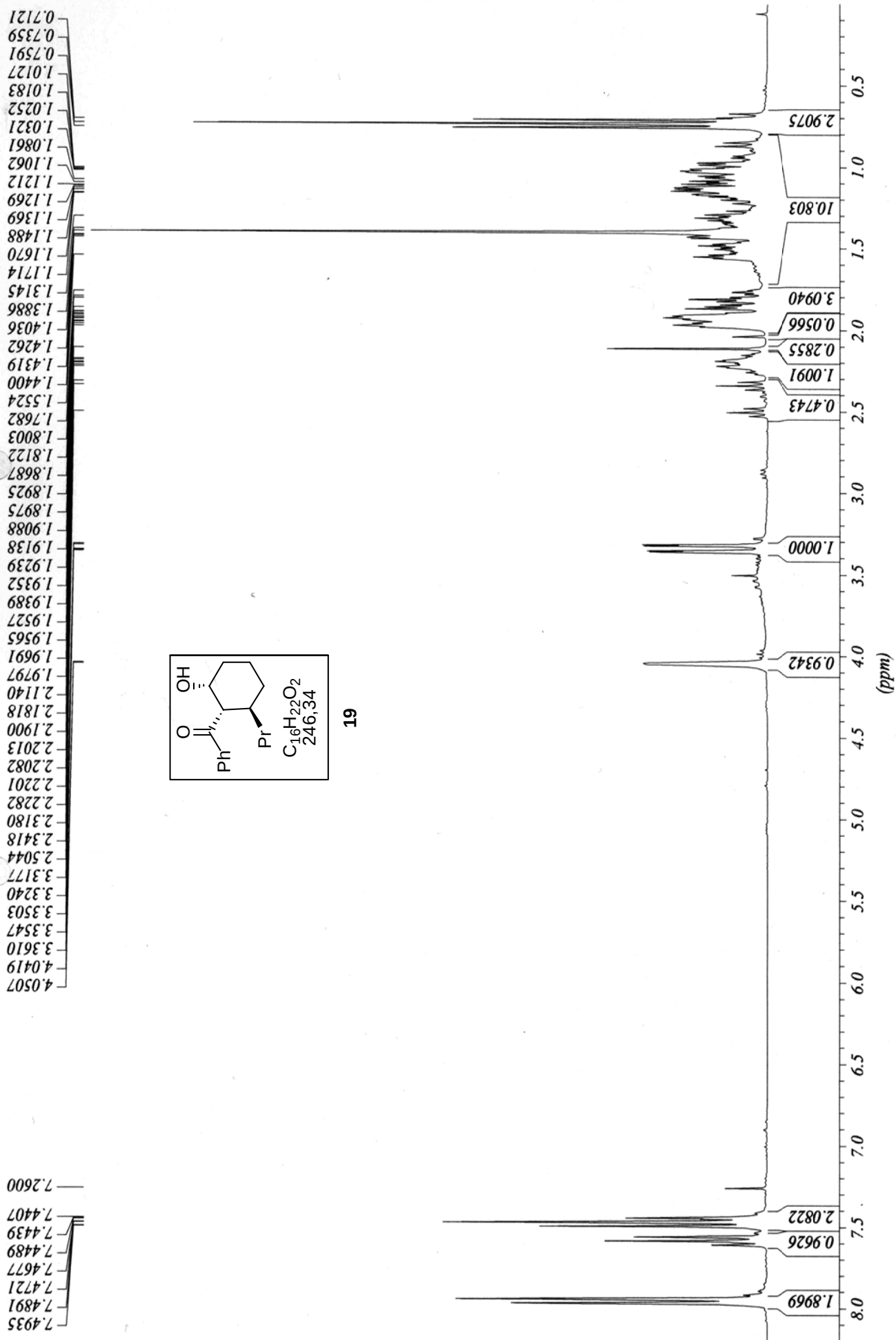


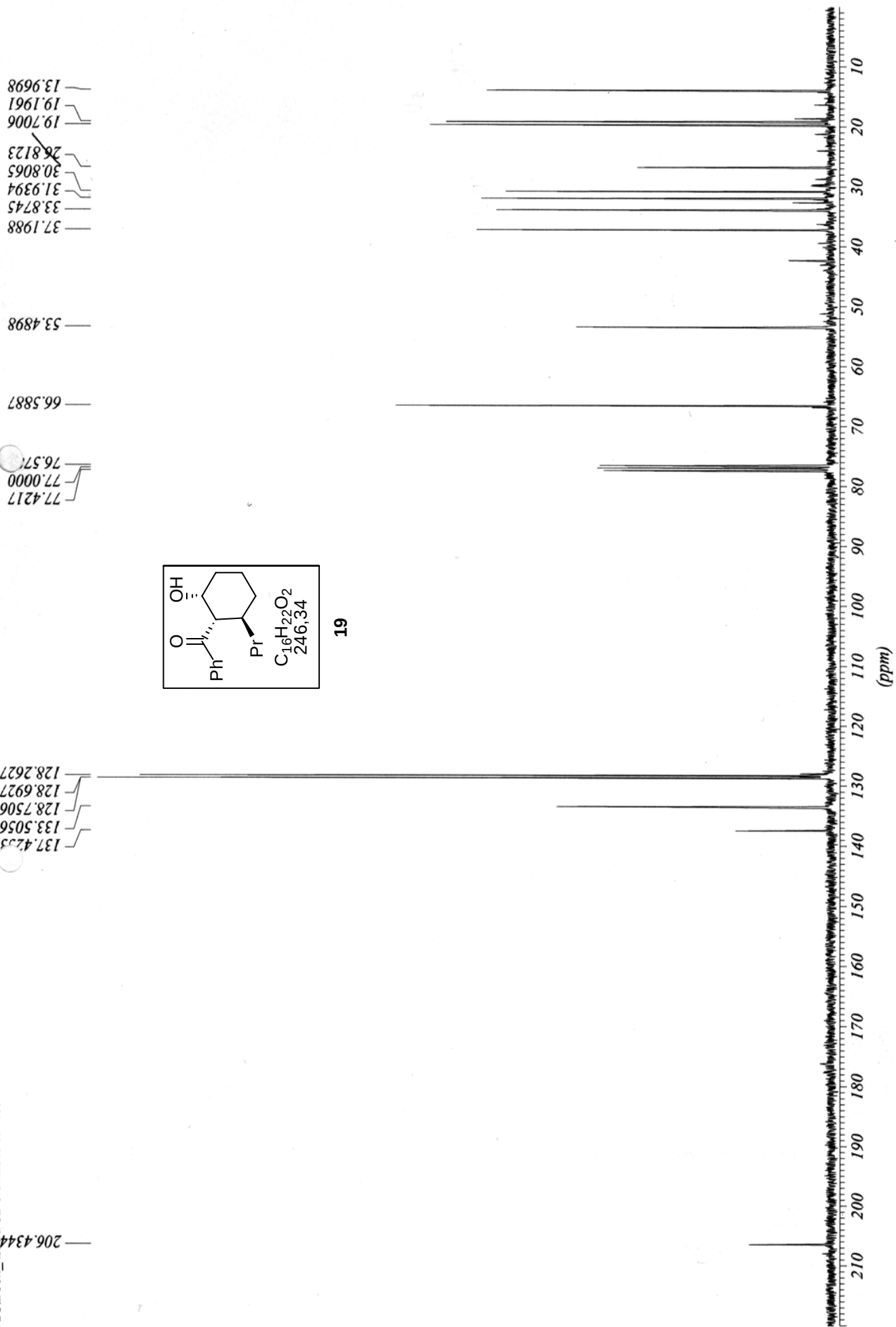
17

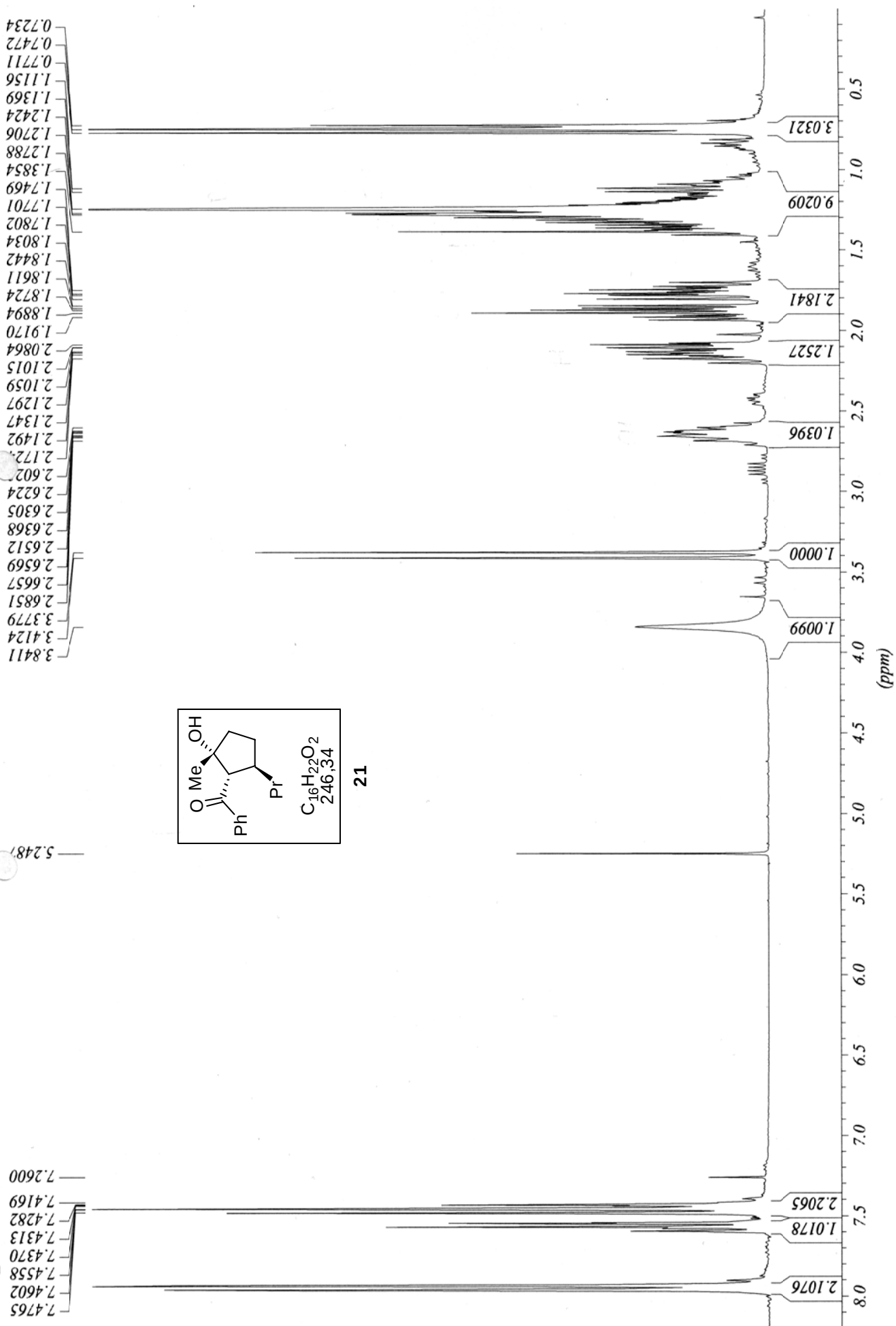


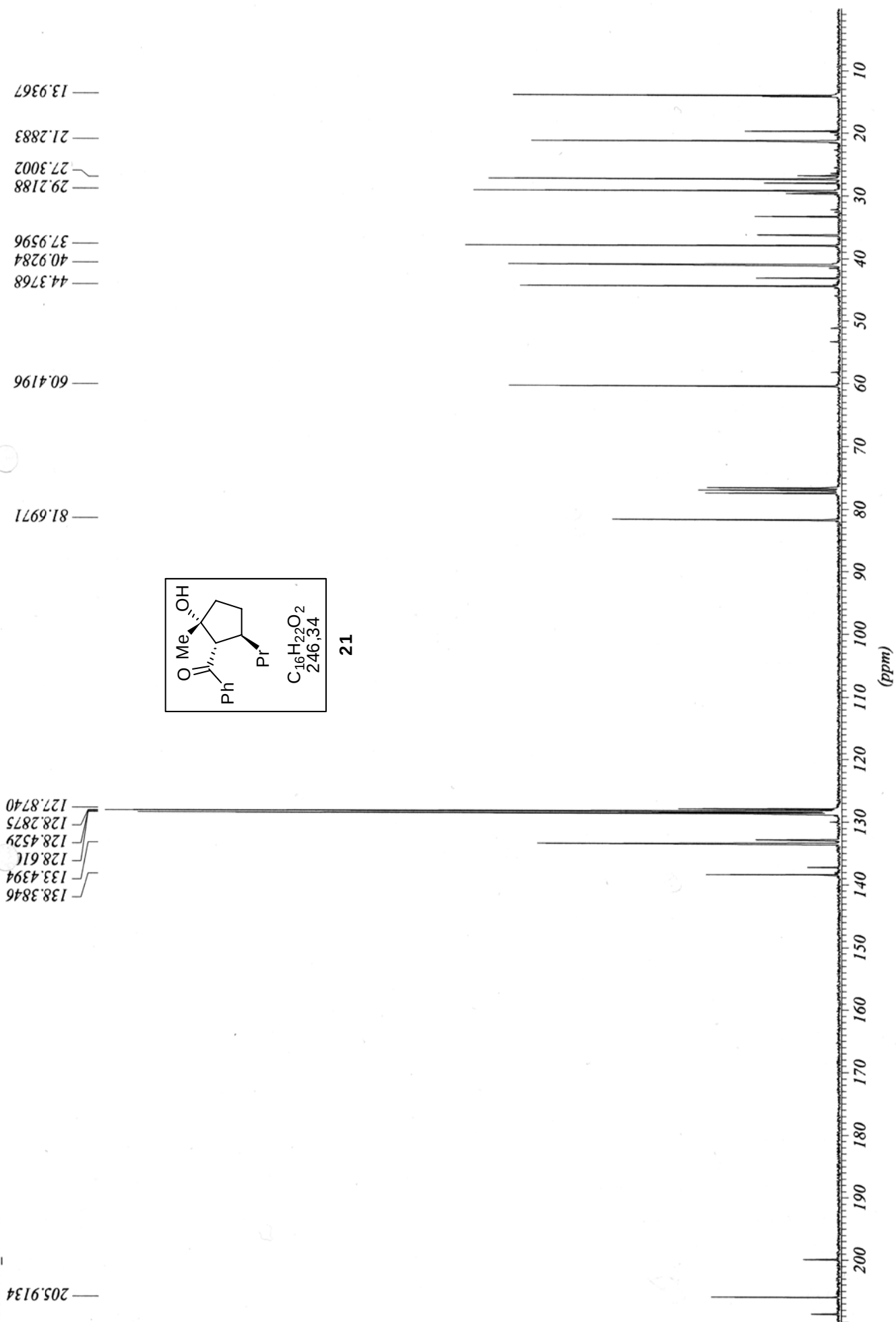


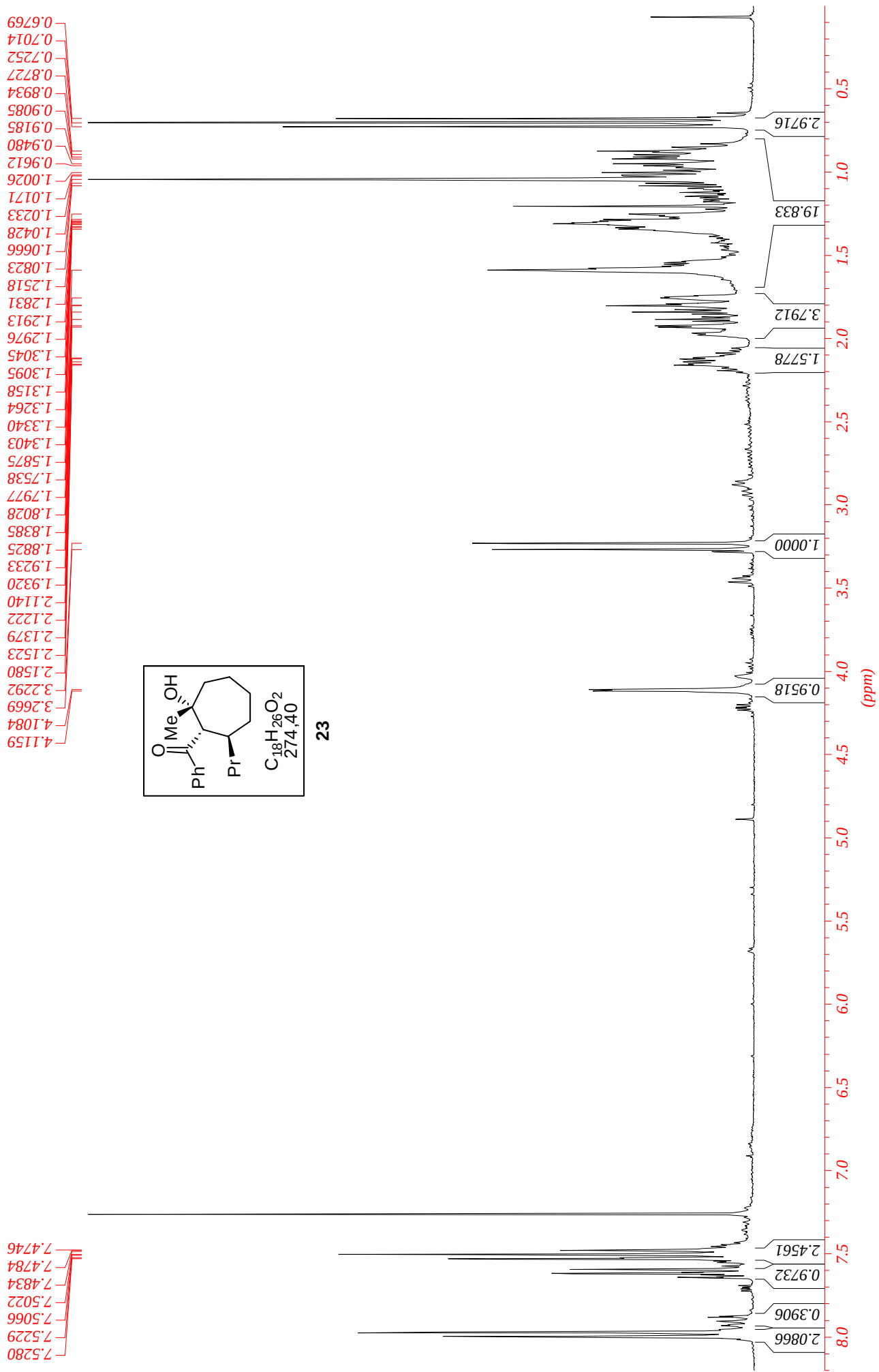


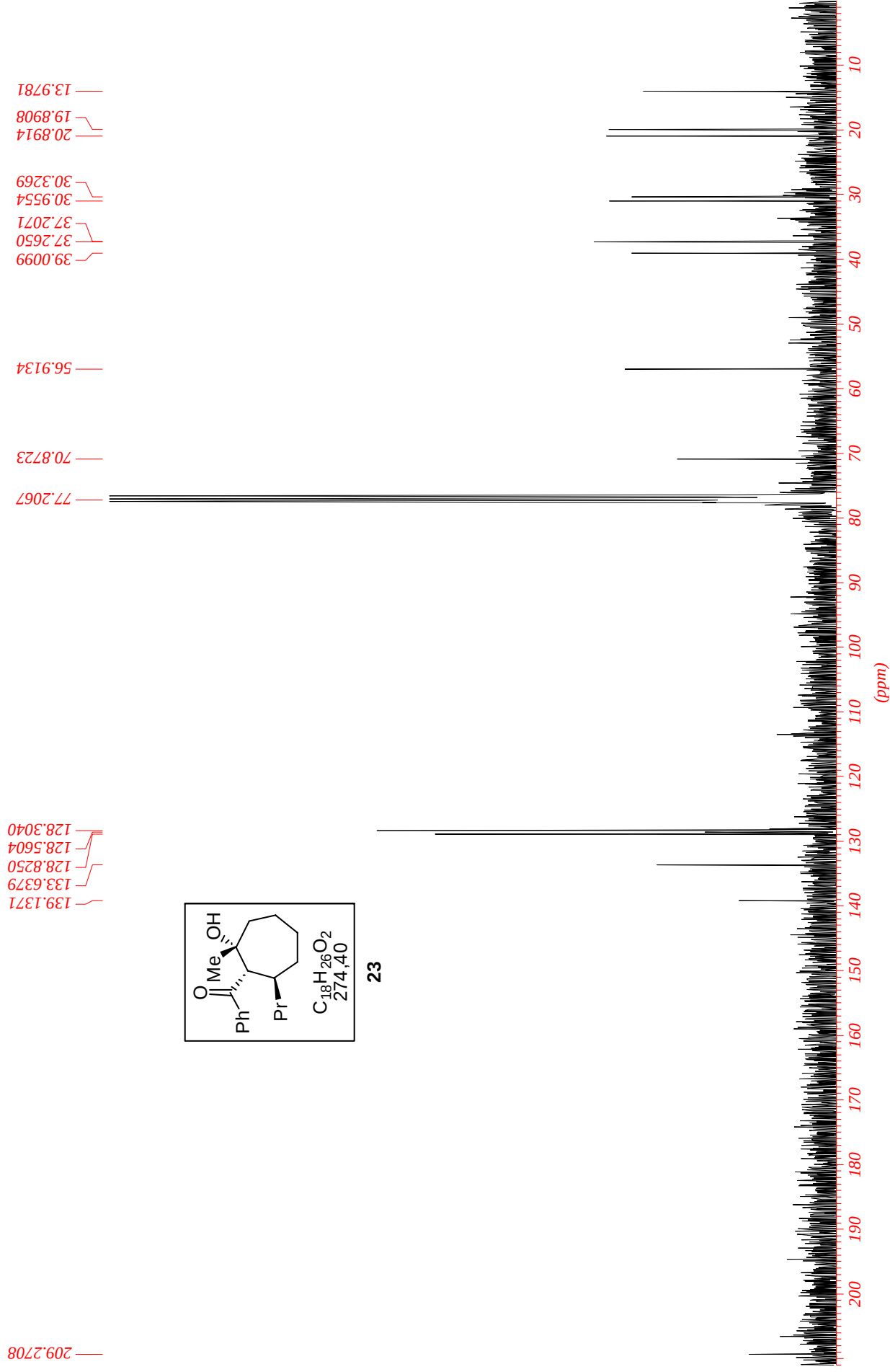


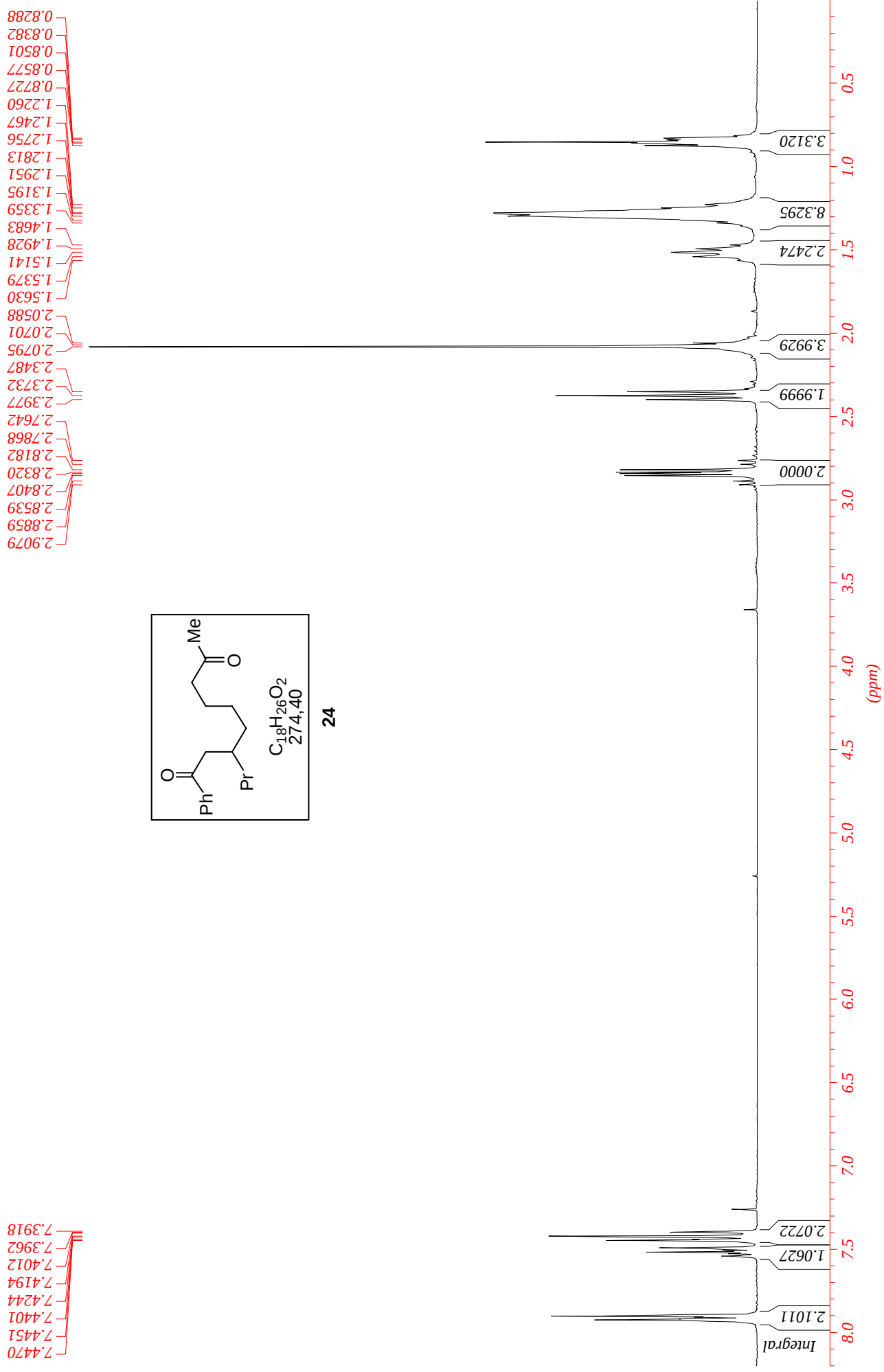


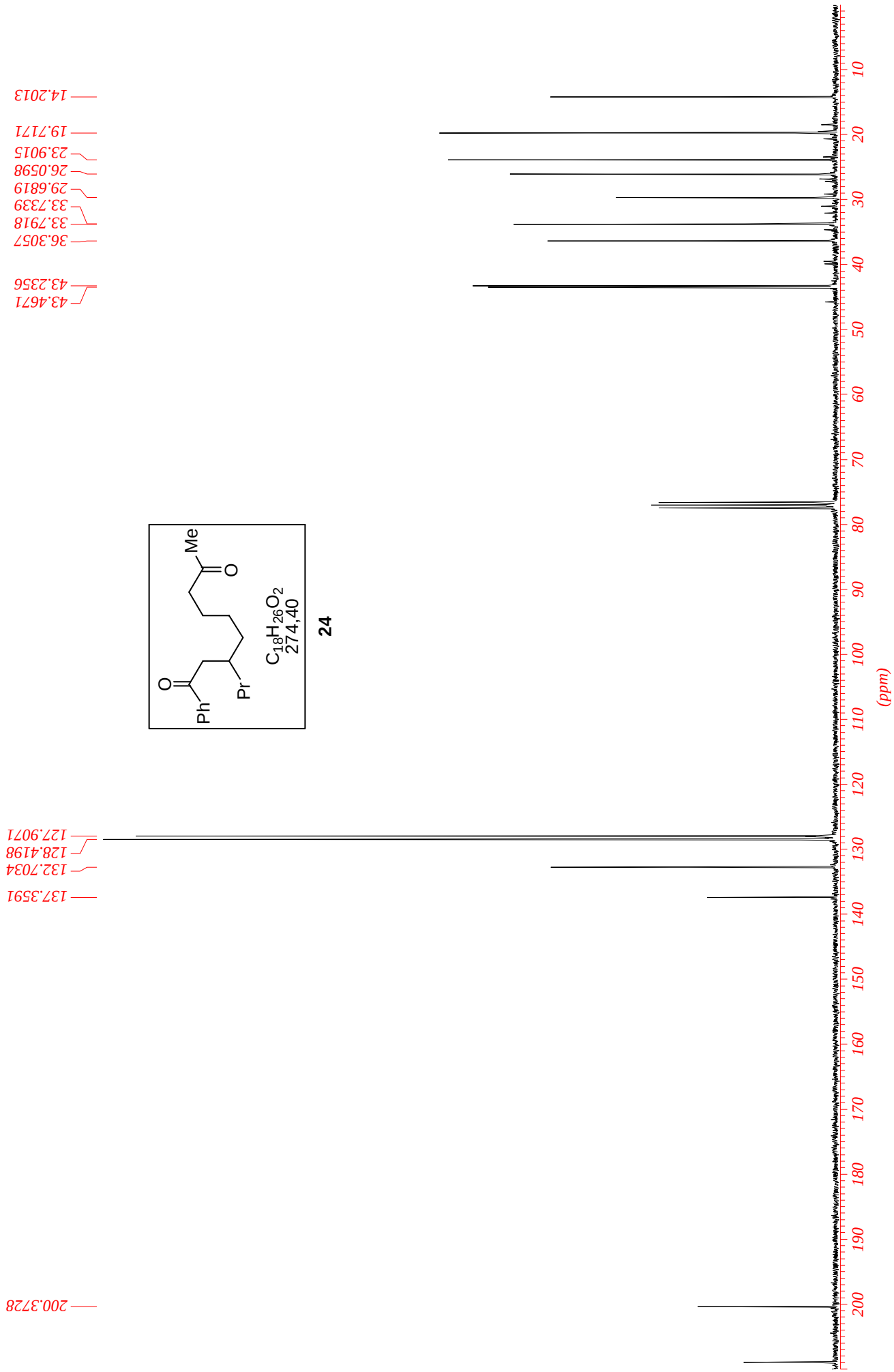


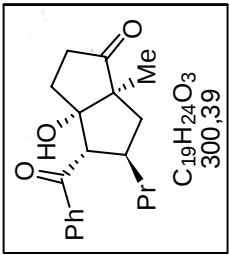


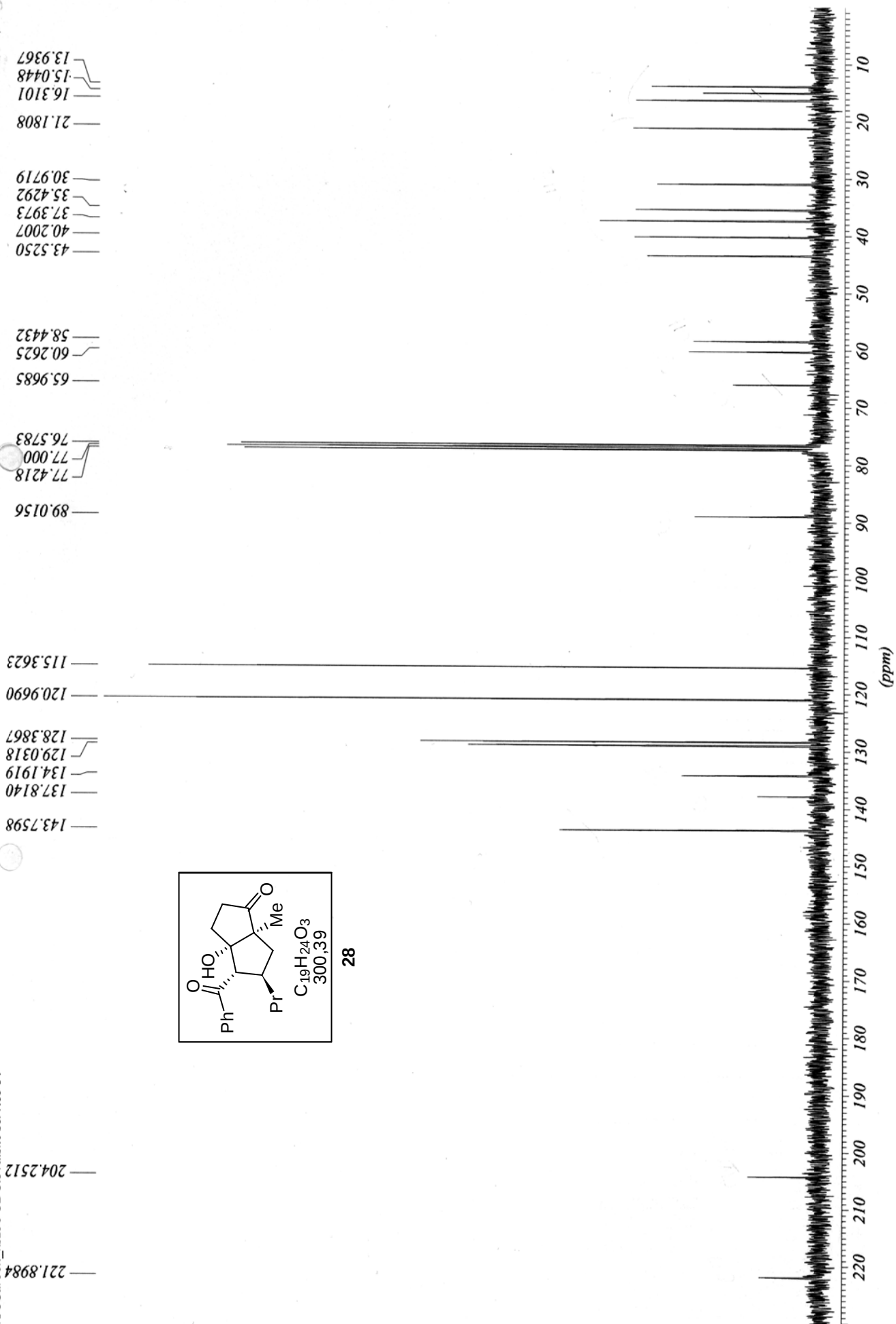


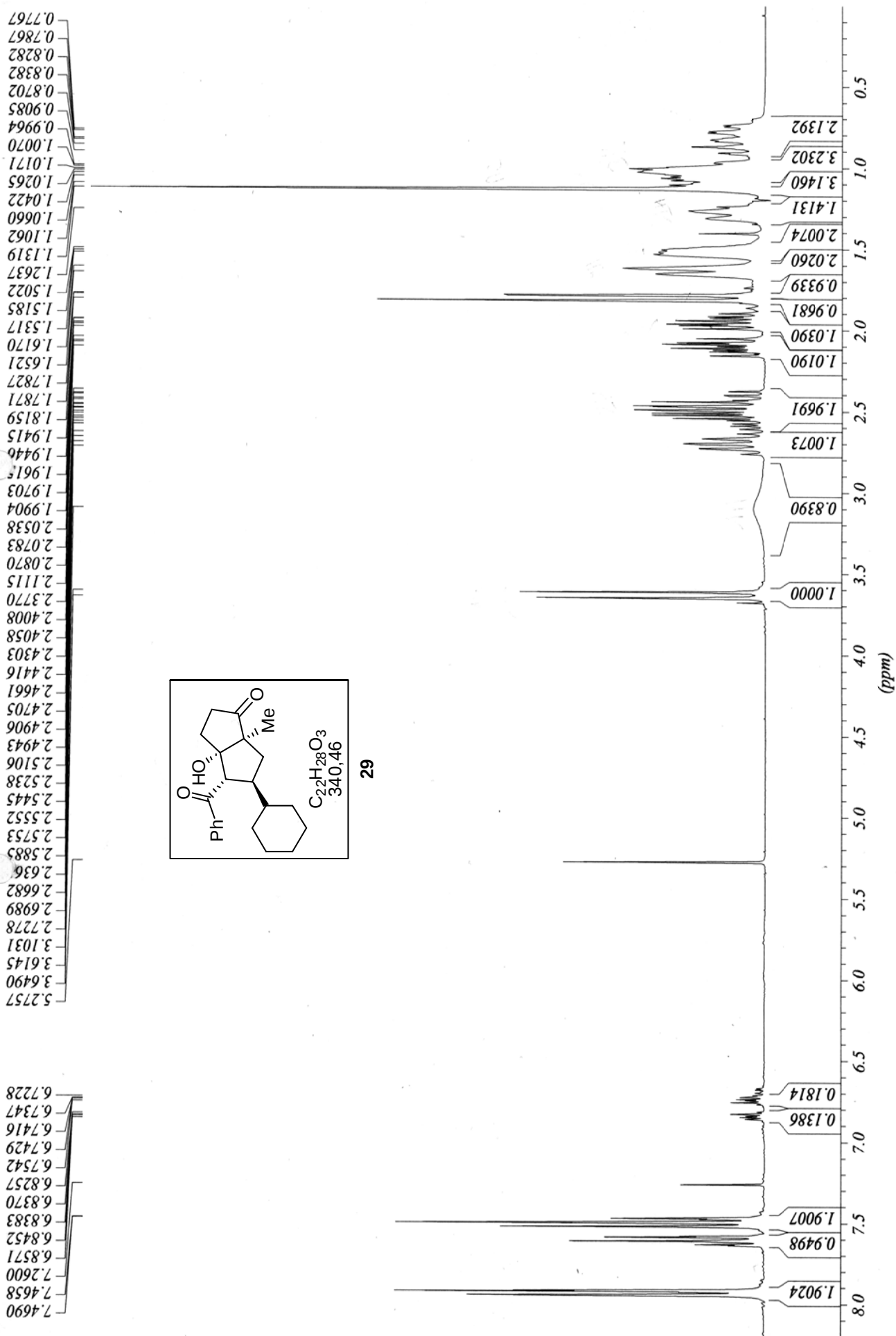




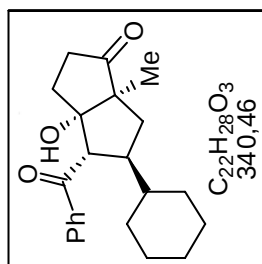




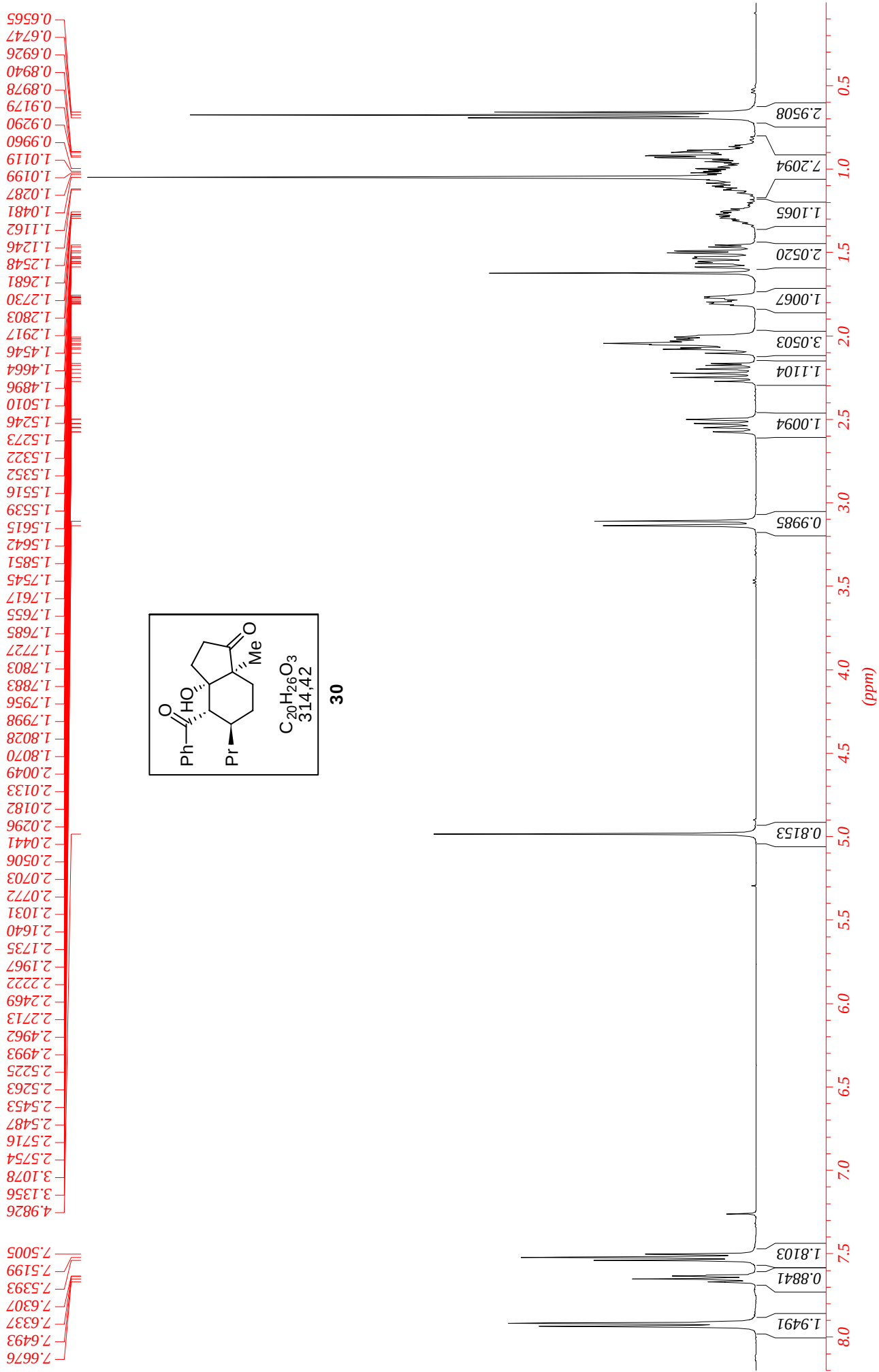




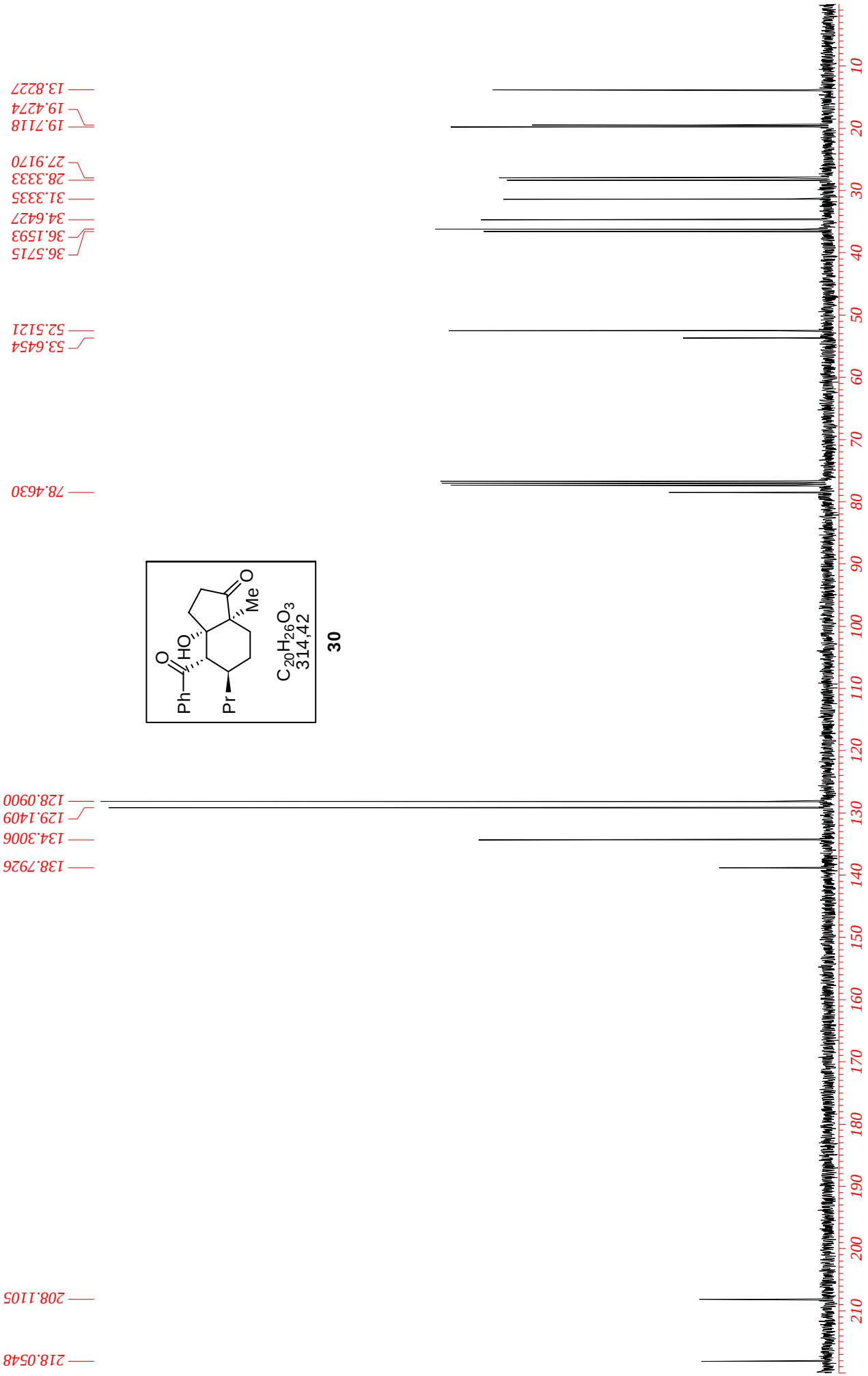
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25.9937
26.0102
30.4344
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42.3838
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53.4071
56.8968
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202.3497
219.9300

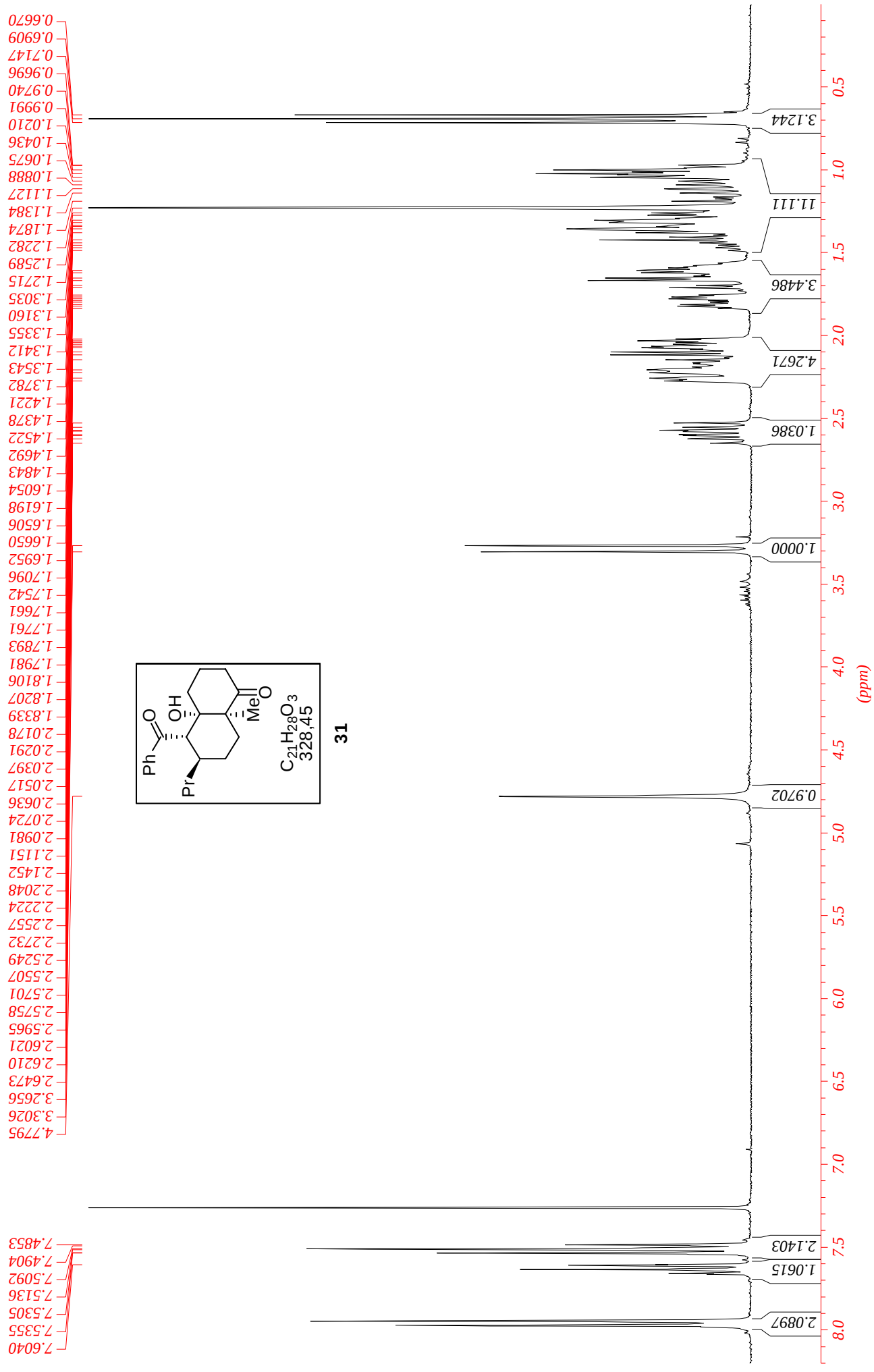


(ppm)

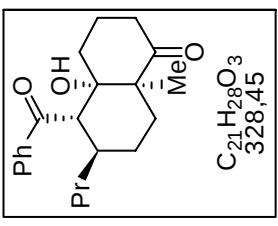
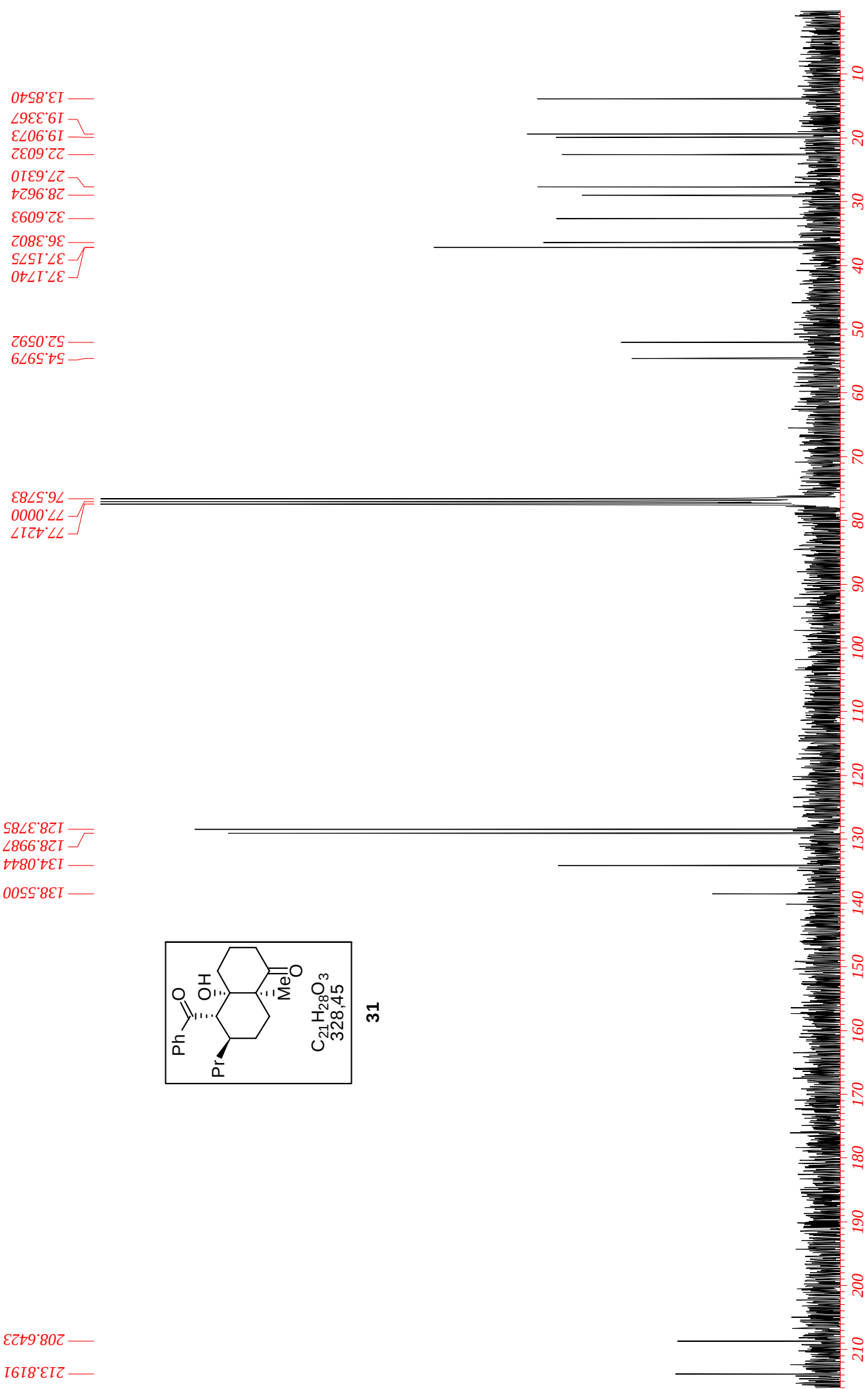


(ppm)

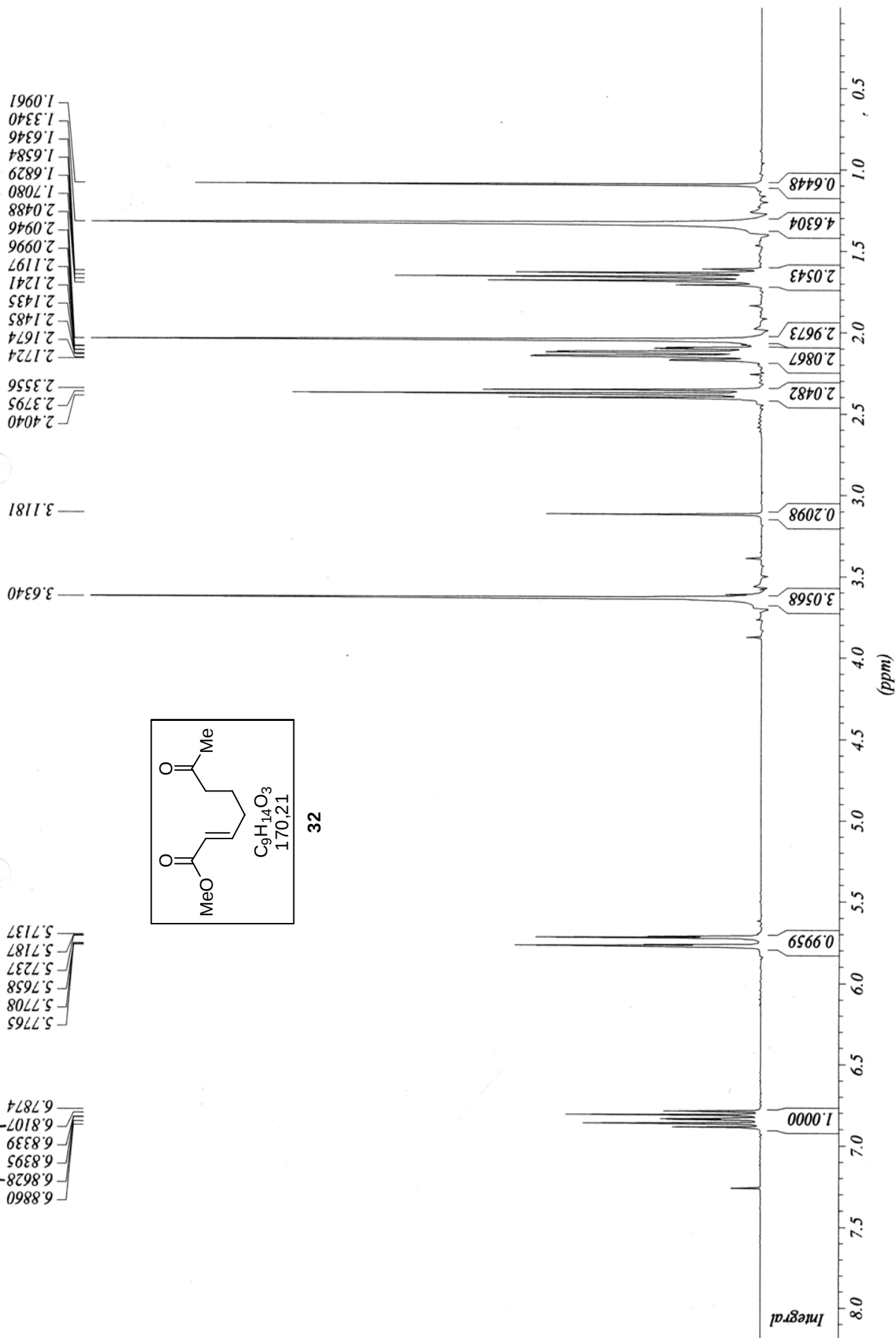




(ppm)



Integral



207.6831

166.6415

148.1343

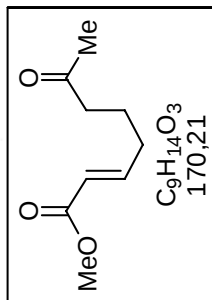
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77.0000
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51.1578

42.3011

31.1208
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26.7048
21.6852



32

(ppm)

