Supplementary Material (ESI) for Chemical Communications

Supporting Information

A New Catalytic Oxidative Cleavage Reaction to Furnish Lactones

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Content

1. General information

All reagents were used as purchased from commercial suppliers. Solvents were purified by conventional methods prior to use. Column chromatography: Merck silica gel 60, 0.040-0.063 mm (230-400 mesh). TLC: *pre*-coated aluminium sheets, Merck silica gel 60, F254; detection by UV, cerium/molybdenum solution [phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot H_2O$ (10 g), concd. H_2SO_4 (60 mL), H_2O (940 mL)] or by vanillin solution [vanillin (1.0 g), methanol (170 mL), glacial acetic acid (20 mL), concd. H_2SO_4 (10 mL)]. ^1H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ with a Bruker AC 500. Chemical shifts δ are given relative to TMS as internal standard or relative to the resonance of the solvent (^1H: $CDCl_3$, δ= 7.24 ppm; ^{13}C: $CDCl_3$, δ= 77.0 ppm). Mass spectra were recorded with a Varian MAT 771, MAT 112 S (EI), an Agilent 6210 ESI-TOF, Agilent Technologies, Santa Clara, CA, USA or an Ionspec QFT-7, Varian Inc., Lake Forest, CA, USA. FT-IR spectra were recorded with a Nicolet 5 SXC with DTGS detector. Elemental analysis was performed using elemental analyzer Vario EL. Melting points were recorded with a „Büchi 510 Melting Point" apparatus and are uncorrected.

2. General reaction procedure

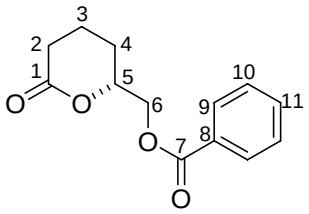
2.0 mmol periodic acid (4 eq., 456 mg) are suspended in 8.0 mL acetonitrile and cooled to 0 °C. To this suspension 1.0 mol% PCC (as a 0.01 M stock solution in acetonitrile, 0.5 mL) is added under vigorous stirring. After 5 mins 0.5 mmol of the tertiary alcohol (1 eq.) is added as a solution in 2.0 mL acetonitrile. After complete consumption of the starting material (TLC control, usually 10-20 mins), 10 mL of dichloromethane (precipitation of iodate) are added followed by 0.2 mL of ethanol (quenching of PCC). The solvent is removed *in vacuo* and the crude mixture is *re*-dissolved in dichloromethane (~ 2 mL). This suspension is then filtered through a short pad of sodium thiosulfate adsorbed on silica to remove inorganic salts. The solvent is evaporated and in most cases, the purity of the resulting lactone after drying in high vacuum is >99 % (determined by GC-analysis).

Preparation of $Na_2S_2O_3$ on silica:

50 mL of a saturated sodium thiosulfate solution are added under vigorous stirring to 50 g of silica. After evaporation of water in high vacuum (no heat, decomposition of thiosulfate), a homogenous powder is obtained.

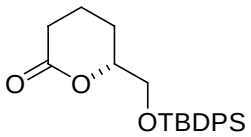
3. Experimental Data

a) Benzoic acid-6-oxotetrahydro-pyran-2-yl methyl ester (**2**)



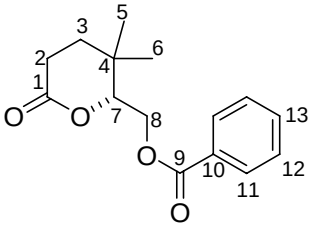
^{1}H-NMR (500 MHz): δ = 7.94 (m, 2 H, H-9), 7.47 (m, 1 H, H-11), 7.34 (m, 2 H, H-10), 4.57 (dddd, ^{3}J = 11.9, 5.6, 3.8, 3.5 Hz, 1 H, H-5), 4.38 (dd, ^{3}J = 3.8 Hz, ^{2}J = 11.9 Hz, 1 H, H-6a), 4.34 (dd, ^{3}J = 5.6 Hz, ^{2}J = 11.9 Hz, 1 H, H-6b), 2.53 (dddd, ^{4}J = 1.2 Hz, ^{3}J = 6.7, 5.1 Hz, ^{2}J = 17.7 Hz, 1 H, H-2a), 2.39 (ddd, ^{3}J = 9.1, 6.9 Hz, ^{2}J = 17.7 Hz, 1 H, H-2b), 1.90 (m, 2 H, H-3), 1.81 (m, 1 H, H-4a), 1.64 ppm (m, 1 H, H-4b); ^{13}C-NMR (125 MHz): δ = 170.5 (C-7), 165.8 (C-1), 133.0 (C-11), 129.4 (C-9), 129.2 (C-8), 128.1 (C-10), 77.4 (C-5), 65.7 (C-6), 29.1 (C-2), 24.0 (C-4), 17.9 ppm (C-3); MS (EI, 120 °C): *m/z* = 234 (<1 %, $[M]^{+\bullet}$), 216 (<1 %, $[M - H_2O]^{+}$), 135 (1 %, $[CH_2OBz]^{+}$), 112 (82 %, $[C_6H_8O_2]^{+}$), 135 (<1 %, $[CH_2OBz]^{+}$), 123 (31 %, $[M - CH_2OBz - H_2O - CH_3]^{+}$), 105 (100 %, $[C_7H_5O]^{+}$), 99 (81 %, $[C_5H_7O_2]^{+}$), 43 (31 %, $[CH_3CO]^{+}$); HRMS (EI): calculated for $C_{13}H_{14}O_4$ ($[M]^{+\bullet}$): *m/z* = 234.0892, found: *m/z* = 234.0886; IR (KBr): 3462, 3064, 2956, 1738, 1720, 1451, 1276, 1234, 1175, 1070, 713 cm^{-1}; elemental analysis: calculated for $C_{13}H_{14}O_4$: C: 66.66 %, H: 6.02 %, found: C: 66.46 %, H: 6.09 %.

b) 6-((*tert*-Butyldiphenylsilyloxy)methyl)-tetrahydropyran-2-one (**4**)



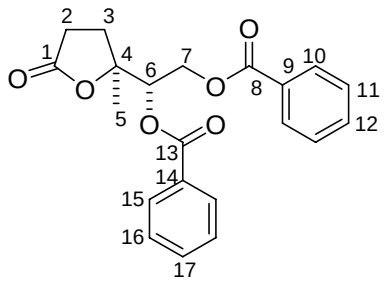
Analytical data for lactone **4** were in full accord with those previously published: Taylor, R. J. K;. Wiggins, K.; Robinson, D. H. *Synthesis* 1990, 589-590.

c) Benzoic acid (3,3-dimethyl-6-oxotetrahydro-pyran-2-yl)-methyl ester (**6**)



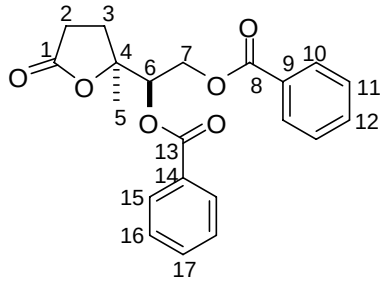
Mp.: 57 – 59 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.03 (dd, ^{4}J = 1.2 Hz, ^{3}J = 7.4 Hz, 2 H, H-11), 7.54 (tt, ^{4}J = 1.2 Hz, ^{3}J = 7.4 Hz, 1 H, H-13), 7.41 (d, ^{3}J = 7.4 Hz, 2 H, H-12), 4.61 (dd, ^{3}J = 11.7, 2.2 Hz, 1 H, H-7), 4.37 (dd, ^{3}J = 2.2 Hz, ^{2}J = 7.7 Hz, 1 H, H-8a), 4.31 (dd, ^{3}J = 11.7 Hz, ^{2}J = 7.7 Hz, 1 H, H-8b), 2.59 (dd, ^{3}J = 8.0, 5.5 Hz, 1 H, H-2a), 2.58 (dd, ^{3}J = 8.8, 6.9 Hz, 1 H, H-2b), 1.78 (ddd, ^{3}J = 8.8, 8.0 Hz, ^{2}J = 13.8 Hz, 1 H, H-3a), 1.66 (ddd, ^{3}J = 6.9, 5.8 Hz, ^{2}J = 13.8 Hz, 1 H, H-3b), 1.15 (s, 3 H, H-5), 1.06 ppm (s, 3 H, H-6); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 170.7 (C-1), 166.4 (C-9), 133.2 (C-13), 129.7 (C-11), 129.5 (C-10), 128.4 (C-12), 84.8 (C-7), 64.0 (C-8), 34.5 (C-3), 31.3 (C-4), 27.3 (C-2), 26.5 (C-5), 20.1 ppm (C-6); MS (ESI-TOF): *m/z* = 547 (47 %, $[2M + Na]^+$), 301 (10 %, $[M + K]^+$), 285 (100 %, $[M + Na]^+$), 263 (52 %, $[M + H]^+$) ; HRMS (ESI-TOF): calculated for $C_{15}H_{18}O_4Na$ ($[M + Na]^+$): *m/z* = 285.1097, found: *m/z* = 285.1105 ; IR (KBr): 2964, 2933, 1741, 1722, 1451, 1275, 1250, 1113, 1068, 713 cm^{-1}; elemental analysis: calculated for $C_{15}H_{18}O_4$: C: 68.68 %, H: 6.92 %, found: C: 68.55 %, H: 7.67 %.

d) Benzoic acid-2-benzoyloxy-2-(2-methyl-5-oxotetrahydro-furan-2-yl)-ethyl ester (**8**)



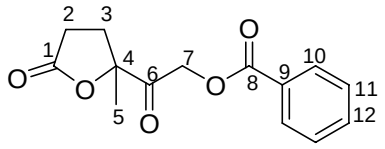
Mp.:116 – 118 °C; ^{1}H-NMR (500 MHz): δ = 8.01 (dd, ^{4}J = 1.2 Hz, ^{3}J = 7.8 Hz, 2 H, H-15), 7.89 (dd, ^{4}J = 1.2 Hz, ^{3}J = 7.7 Hz, 2 H, H-10), 7.56 (tt, ^{4}J = 1.2 Hz, ^{3}J = 7.8 Hz, 1 H, H-17), 7.48 (tt, ^{4}J = 1.2 Hz, ^{3}J = 7.7 Hz, 1 H, H-12), 7.43 (t, ^{3}J = 7.8 Hz, 2 H, H-16), 7.33 (t, ^{3}J = 7.7 Hz, 2 H, H-11), 5.63 (dd, ^{3}J = 8.2, 3.2 Hz, 1 H, H-6), 4.81 (dd, ^{3}J = 3.2 Hz, ^{2}J = 12.1 Hz, 1 H, H-7a), 4.50 (dd, ^{3}J = 8.2 Hz, ^{2}J = 12.1 Hz, 1 H, H-7b), 2.57 (dd, ^{3}J = 9.2, 7.4 Hz, 2 H, H-2), 2.33 (td, ^{3}J = 7.4 Hz, ^{2}J = 13.5 Hz, 1 H, H-3a), 2.05 (td, ^{3}J = 9.2 Hz, ^{2}J = 13.5 Hz, 1 H, H-3b), 1.62 ppm (s, 3 H, H-5); ^{13}C-NMR (125 MHz): δ = 176.0 (C-1), 166.1 (C-13), 165.4 (C-8), 133.6 (C-17), 133.1 (C-12), 129.8 (C-15), 129.6 (C-10), 129.3 (C-14), 128.9 (C-9), 128.6 (C-16), 128.3 (C-11), 85.1 (C-4), 75.5 (C-6), 62.7 (C-7), 31.4 (C-3), 28.8 (C-2), 24.0 ppm (C-5); MS (ESI-QFT): *m/z* = 386 (12 %, $[M + NH_4]^+$), 369 (46 %, $[M + H]^+$); HRMS (ESI-QFT): calculated for $C_{21}H_{21}O_6$ ($[M + H]^+$): m/z = 369.1333, found: m/z = 369.1338; IR (KBr): 2970, 1770, 1725, 1707, 1449, 1290, 1277, 1266, 1126, 1070, 717, 710 cm^{-1}; elemental analysis calculated for $C_{21}H_{20}O_6$: C: 68.47 %, H: 5.47 %, found: C: 68.22 %, H: 5.89 %.

e) Benzoic acid-2-benzoyloxy-2-(2-methyl-5-oxotetrahydro-furan-2-yl)-ethyl ester (**10**)



Mp.: 116 – 118 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.99 (dd, ^{4}J = 1.2 Hz, ^{3}J = 7.8 Hz, 2 H, H-15), 7.91 (dd, ^{4}J = 1.2 Hz, ^{3}J = 7.8 Hz, 2 H, H-10), 7.54 (tt, ^{4}J = 1.2 Hz, ^{3}J = 7.8 Hz, 1 H, H-17), 7.49 (tt, ^{4}J = 1.2 Hz, ^{3}J = 7.8 Hz, 1 H, H-12), 7.40 (m, 2 H, H-16), 7.35 (m, 2 H, H-11), 5.63 (dd, ^{3}J = 8.3, 2.9 Hz, 1 H, H-6), 4.72 (dd, ^{3}J = 2.9 Hz, ^{2}J = 12.2 Hz, 1 H, H-7a), 4.56 (dd, ^{3}J = 8.3 Hz, ^{2}J = 12.2 Hz, 1 H, H-7b), 2.67 (m, 2 H, H-2), 2.52 (ddd, ^{3}J = 10.2, 7,3 Hz, ^{2}J = 13.2 Hz, 1 H, H-3a), 2.05 (ddd, ^{3}J = 9.9, 6.6 Hz, ^{2}J = 13.2 Hz, 1 H, H-3b), 1.56 ppm (s, 3 H, H-5); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 175.6 (C-1), 166.0 (C-13), 165.4 (C-8), 133.5 (C-17), 133.2 (C-12), 129.6 (C-15), 129.5 (C-10), 129.5 (C-14), 129.3 (C-9), 128.5 (C-16), 128.3 (C-11), 84.9 (C-4), 74.2 (C-6), 62.7 (C-7), 30.4 (C-3), 28.3 (C-2), 22.9 ppm (C-5); MS (EI, 180 °C): *m/z* = 368 (<1 %, $[M]^{+\bullet}$), 325 (13 %, $[M - C_2H_3O]^{+}$), 269 (1 %, $[C_{16}H_{13}O_4]^{+}$), 105 (100 %, $[PhCO]^{+}$), 99 (66 %, $[C_5H_7O_2]^{+}$); HRMS (EI): calculated for $C_{21}H_{20}O_6$ ($[M]^{+\bullet}$): *m/z* = 368.1260, found: *m/z* = 368.1265; IR (KBr): 1783, 1714, 1280, 1256, 1098, 934, 715 cm^{-1}.

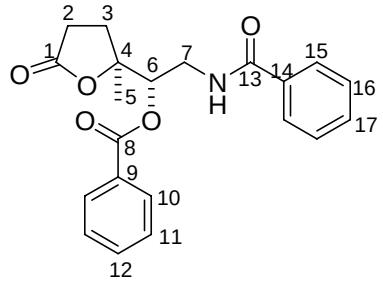
f) Benzoic acid-2-(2-methyl-5-oxotetrahydro-furan-2-yl)-2-oxo ethyl ester (**12**)



Mp.: 98 – 100 °C. ^{1}H-NMR (500 MHz): δ = 8.02 (dd, ^{4}J = 1.3 Hz, ^{3}J = 8.0 Hz, 2 H, H-10), 7.53 (tt, ^{4}J = 1.3 Hz, ^{3}J = 8.0 Hz, 1 H, H-12), 7.41 (t, ^{3}J = 8.0 Hz, 2 H, H-11), 5.14 (s, 2 H, H-7), 2.59 (m, 3 H, H-2, H-3a), 2.10 (m, 1 H, H-3b), 1.57 ppm (s, 3 H, H-5); ^{13}C-NMR (125 MHz): δ = 203.0 (C-6), 175.3 (C-1), 165.8 (C-8), 133.4 (C-12), 129.7 (C-10), 128.8 (C-9), 128.4 (C-11), 88.6 (C-4), 65.5 (C-7), 31.1 (C.2), 27.7 (C-3), 23.5 ppm (C-5); MS (EI, 95 °C): *m/z* = 262 (<1 %, $[M]^{+\bullet}$), 163 (24 %, $[M - C_5H_7O_2]^{+}$), 105 (31 %, $[C_7H_5O]^{+}$), 99 (100 %, $[C_5H_7O_2]^{+}$), 77 (26 %, $[C_6H_5]^{+}$), 43 (46 %, $[CH_3CO]^{+}$); HRMS (EI): calculated for $C_{14}H_{14}O_5$ ($[M]^{+\bullet}$): *m/z* = 262.0841, found: *m/z* = 262.0834; IR (KBr): 2997,

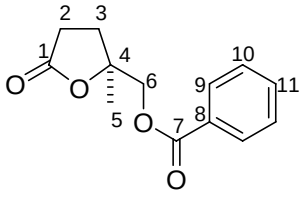
2952, 1793, 1786, 1746, 1720, 1599, 1452, 1417, 1277, 1095, 898, 710 cm^{-1}; elemental analysis calculated for $C_{14}H_{14}O_5$: C: 64.12 %, H: 5.38 %, found: C: 64.00 %, H: 5.10 %.

g) Benzoesäure-2-benzamido-1-(2-methyl-5-oxotetrahydrofuran-2-yl)-ethylester (**14**)



Mp.: 67 – 69 °C; ^{1}H-NMR (500 MHz): δ = 7.98 (dd, ^4J = 1.4 Hz, ^3J = 7.6 Hz, 2 H, H-10), 7.67 (m, 2 H, H-15), 7.55 (tt, ^4J = 1.4 Hz, ^3J = 7.6 Hz, 1 H, H-12), 7.42 (m, 3 H, H-11, H-17), 7.35 (t, ^3J = 7.6 Hz, 2 H, H-16), 6.82 (m, 1 H, NH), 5.40 (dd, ^3J = 7.6, 2.6 Hz, 1 H, H-6), 4.11 (ddd, ^3J = 6.5, 2.7 Hz, ^2J = 14.6 Hz, 1 H, H-7a), 3.62 (ddd, ^3J = 7.6, 4.9 Hz, ^2J = 14.6 Hz, 1 H, H-7b), 2.56 (ddd, ^3J = 9.9, 7.4 Hz, ^2J =4.0 Hz, 2 H, H-2), 2.30 (ddd, ^3J = 9.3, 7.4 Hz, ^2J = 13.4 Hz, 1 H, H-3a), 2.03 (ddd, ^3J = 9.9, 7.7 Hz, ^2J = 13.4 Hz, 1 H, H-3b), 1.60 ppm (s, 3 H, H-5); ^{13}C-NMR (125 MHz): δ = 176.0 (C-1), 167.8 (C-13), 166.1 (C-8), 133.9 (C-14), 133.7 (C-12), 131.5 (C-17), 129.8 (C-10), 128.9 (C-9), 128.7 (C-16), 128.5 (C-11), 126.9 (C-15), 85.9 (C-4), 77.0 (C-6), 40.2 (C-7), 31.4 (C-3), 28.8 (C-2), 23.6 ppm (C-5); MS (ESI-TOF): *m/z* = 757 (39 %, $[2M + Na]^+$), 735 (17 %, $[2M + H]^+$), 406 (13 %, $[M + K]^+$), 390 (100 %, $[M + Na]^+$), 368 (84 %, $[M + H]^+$), 246 (9 %, $[M – PhCO_2]^+$), 105 (14 %, $[PhCO]^+$); HRMS (ESI-TOF): calculated for $C_{21}H_{22}NO_5$ ($[M + H]^+$): *m/z* = 368.1492, found: *m/z* = 368.1503; IR (KBr): 3341, 1775, 1723, 1646, 1538, 1269, 1110, 712 cm^{-1}.

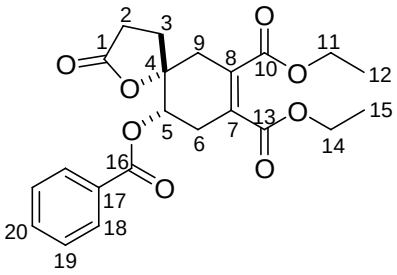
h) Benzoic acid-2-methyl-5-oxotetrahydro-furan-2-yl-methyl ester (**16**)



^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.95 (m, 2 H, H-9), 7.53 (tt, ^4J = 1.4 Hz, ^3J = 7.6 Hz, 1 H, H-11), 7.41 (m, 2 H, H-10), 4.35 (d, ^2J = 11.8 Hz, 1 H, H-6a), 4.30 (d, ^2J = 11.8 Hz, 1 H, H-6b), 2.67 (ddd, ^3J = 10.0, 7.8 Hz, ^2J = 18.1 Hz, 1 H, H-2a), 2.61 (ddd, ^3J = 10.2, 6.1 Hz, ^2J = 18.1 Hz, 1 H, H-2b), 2.29 (ddd, ^3J = 10.0, 6.1 Hz, ^2J = 13.2 Hz, 1 H, H-3a), 2.04 (ddd, ^3J = 10.2, 7.8 Hz, ^2J = 13.2 Hz, 1 H, H-3b), 1.48 ppm (s, 3 H, H-5); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 176.2 (C-1), 165.8 (C-7), 133.3 (C-11),

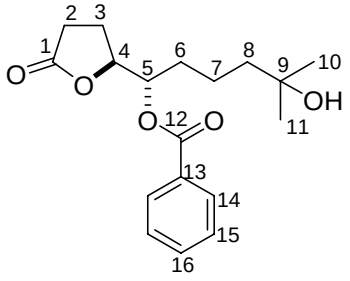
129.5 (C-9), 129.2 (C-8), 128.5 (C-10), 83.9 (C-4), 69.1 (C-6), 30.3 (C-3), 29.1 (C-2), 23.7 ppm (C-5); MS (EI, 50 °C): *m/z* = 234 (3 %, $[M]^{+\bullet}$), 137 (12 %, $[PhCO_2CH_4]^+$), 105 (44 %, $[C_7H_5O]^+$), 99 (100 %, $[M - CH_2O_2CPh]^+$), 77 (35 %, $[C_6H_5]^+$), 43 (43 %, $[CH_3CO]^+$); HRMS (EI): calculated for $C_{13}H_{14}O_4$ ($[M]^{+\bullet}$): *m/z* = 234.0892, found: *m/z* = 234.0886; IR (KBr): 3531, 3063, 2980, 2952, 1776, 1723, 1273, 1113, 945, 712 cm^{-1}: elemental analysis: calculated for $C_{13}H_{14}O_4$: C: 66.66 %, H: 6.02 %, found: C: 66.41 %, H: 6.48 %.

i) 10-Benzoyloxy-2-oxo-1-oxaspiro[4.5]dec-7-en-7,8-dicarboxylic acid diethyl ester (**18**)



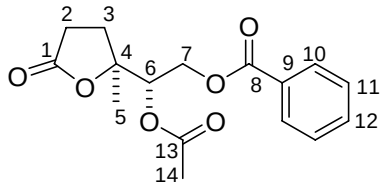
Mp.: 99 – 101 °C; ^{1}H-NMR (500 MHz): δ = 7.95 (m, 2 H, H-18), 7.56 (m, 1 H, H-20), 7.42 (m, 2 H, H-19), 5.29 (dd, ^3J = 8.9, 6.3 Hz, 1 H, H-5), 4.18 (m, 4 H, H-11, H-14), 2.91 (m, 2 H, H-6a, H-9a), 2.76 (m, 2 H, H-6b, H-9b), 2.59 (m, 2 H, H-2), 2.28 (m, 1 H, H-3a), 2.10 (m, 1 H, H-3b), 1.24 ppm (m, 6 H, H-12, H-15); ^{13}C-NMR (125 MHz): δ = 175.8 (C-1), 166.4, 166.3 (C-10, C-13), 165.3 (C-16), 133.7 (C-20), 133.1 (C-8), 130.6 (C-7), 129.6 (C-18), 128.9 (C-17), 128.7 (C-19), 82.6 (C-4), 72.3 (C-5), 61.5, 61.4 (C-11, C-14), 38.1 (C-9), 29.8 (C-3), 29.4 (C-6), 28.8 (C-2), 13.9 ppm (C-12, C-15); MS (EI, 160 °C): m/z = 416 (2 %, $[M]^{+\bullet}$), 371 (4 %, $[M - C_2H_5O]^+$), 311 (1 %, $[M - C_7H_5O]^+$), 294 (19 %, $[M - PhCO_2H]^+$), 248 (31 %, $[M - PhCO_2H - EtOH]^+$), 220 (15 %, $[M - PhCO_2H - EtOH - C_2H_4]^+$), 105 (100 %, $[PhCO]^+$), 77 (32 %, $[C_6H_5]^+$); HRMS (EI): calculated for $C_{22}H_{24}O_8$ ($[M]^{+\bullet}$): *m/z* = 416.1471, found: *m/z* = 416.1466; IR (KBr): 2982, 1782, 1726, 1268, 1191, 1178, 1112, 1068, 714 cm^{-1}.

j) Benzoic acid 5-hydroxy-5-methyl-1-(5-oxotetrahydro-furan-2-yl)-hexyl ester (**20**)

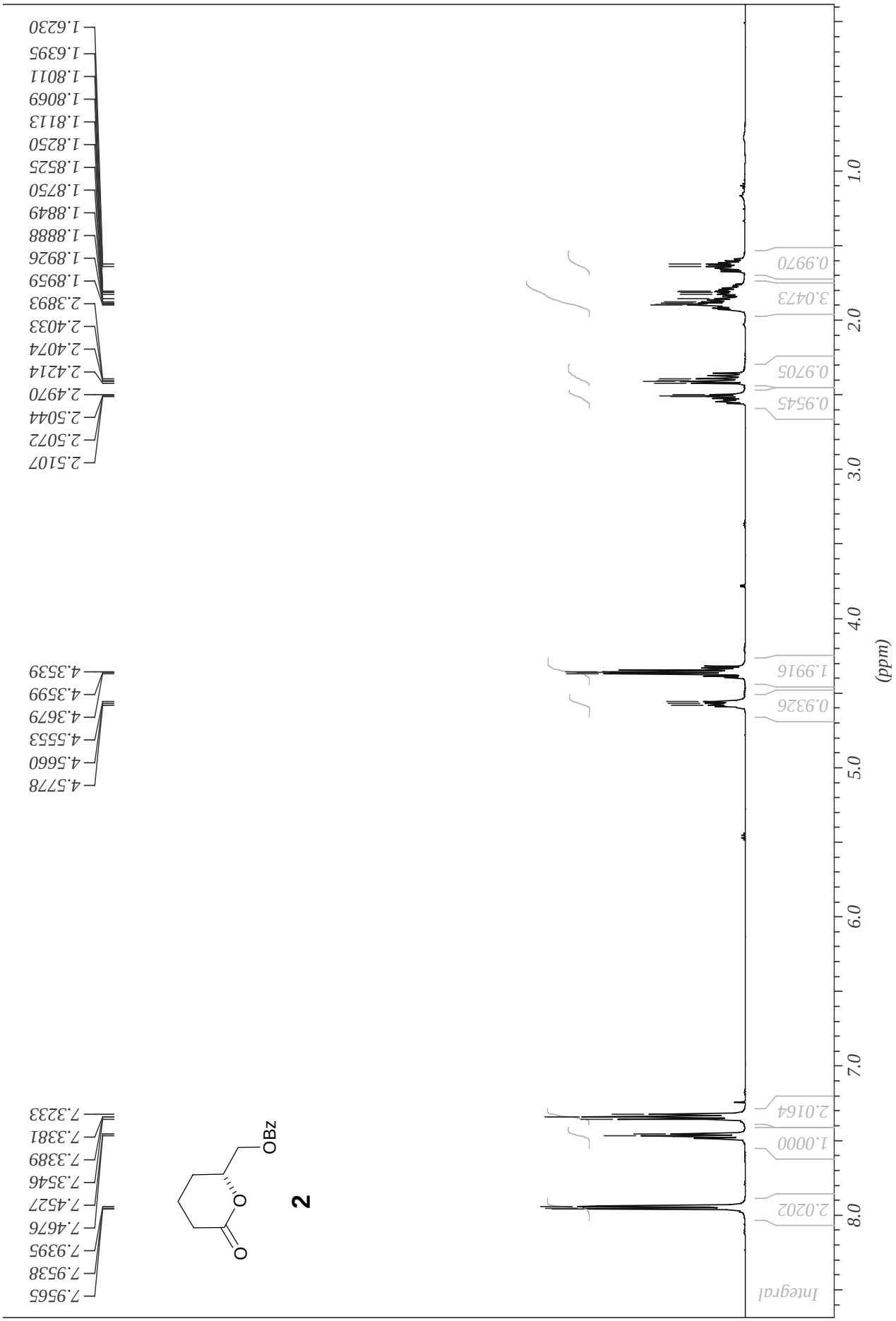


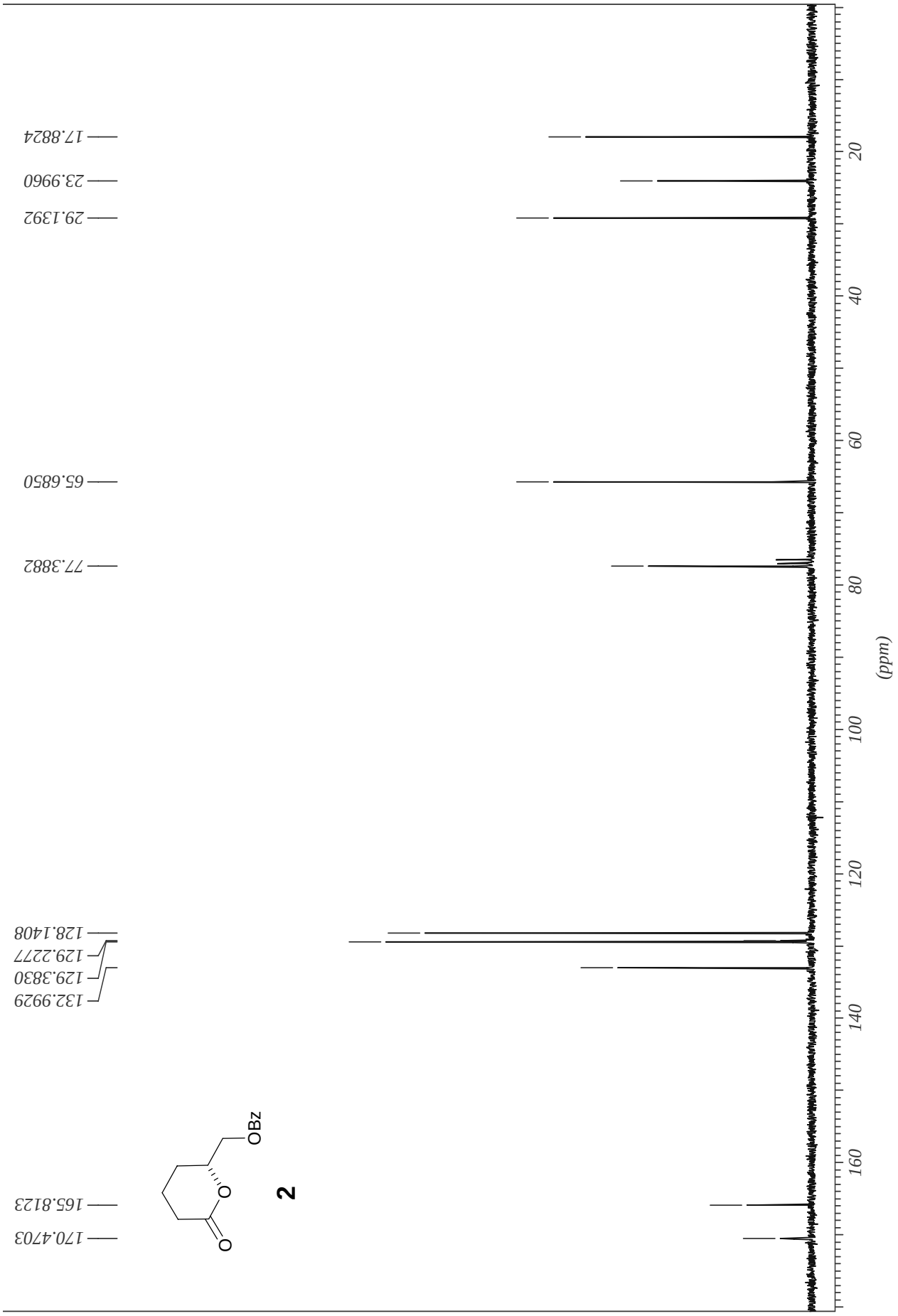
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.00 (dd, ^4J = 1.2 Hz, ^3J = 7.8 Hz, 2 H, H-14), 7.56 (tt, ^4J = 1.2 Hz, ^3J = 7.8 Hz, 1 H, H-16), 7.43 (t, ^3J = 7.8 Hz, 2 H, H-15), 5.27 (ddd, ^3J = 8.4, 5.4, 3.0 Hz, 1 H, H-5), 4.73 (ddd, ^3J = 8.2, 5.4, 2.9 Hz, 1 H, H-4), 2.47 (t, ^3J = 8.5 Hz, 2 H, H-2), 2.32 (m, 1 H, H-3a), 2.02 (m, 1 H, H-3b), 1.87 (m, 1 H, H-6a), 1.77 (m, 1 H, H-6b), 1.51 (m, 1 H, H-8a), 1.44 (m, 3 H, H-8b, H-7), 1.15 ppm (s, 6 H, H-10, H-11); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 176.8 (C-1), 166.0 (C-12), 133.5 (C-16), 129.7 (C-14), 128.6 (C-15), 79.9 (C-4), 74.7 (C-5), 70.7 (C-9), 43.3 (C-8), 31.2 (C-6), 29.2 (C-10, C-11), 28.1 (C-2), 24.0 (C-3), 19.9 ppm (C-7); MS (ESI-TOF): *m/z* = 359 (36 %, $[M + K]^+$), 343 (100 %, $[M + Na]^+$), 303 (39 %, $[M - OH]^+$); HRMS (ESI-TOF): calculated for $C_{18}H_{24}O_5Na$ ($[M + Na]^+$): *m/z* = 343.1516, found: *m/z* = 343.1518; IR (KBr): 3491, 2967, 2933, 1778, 1718, 1451, 1271, 1179, 1112, 920, 714 cm^{-1}.

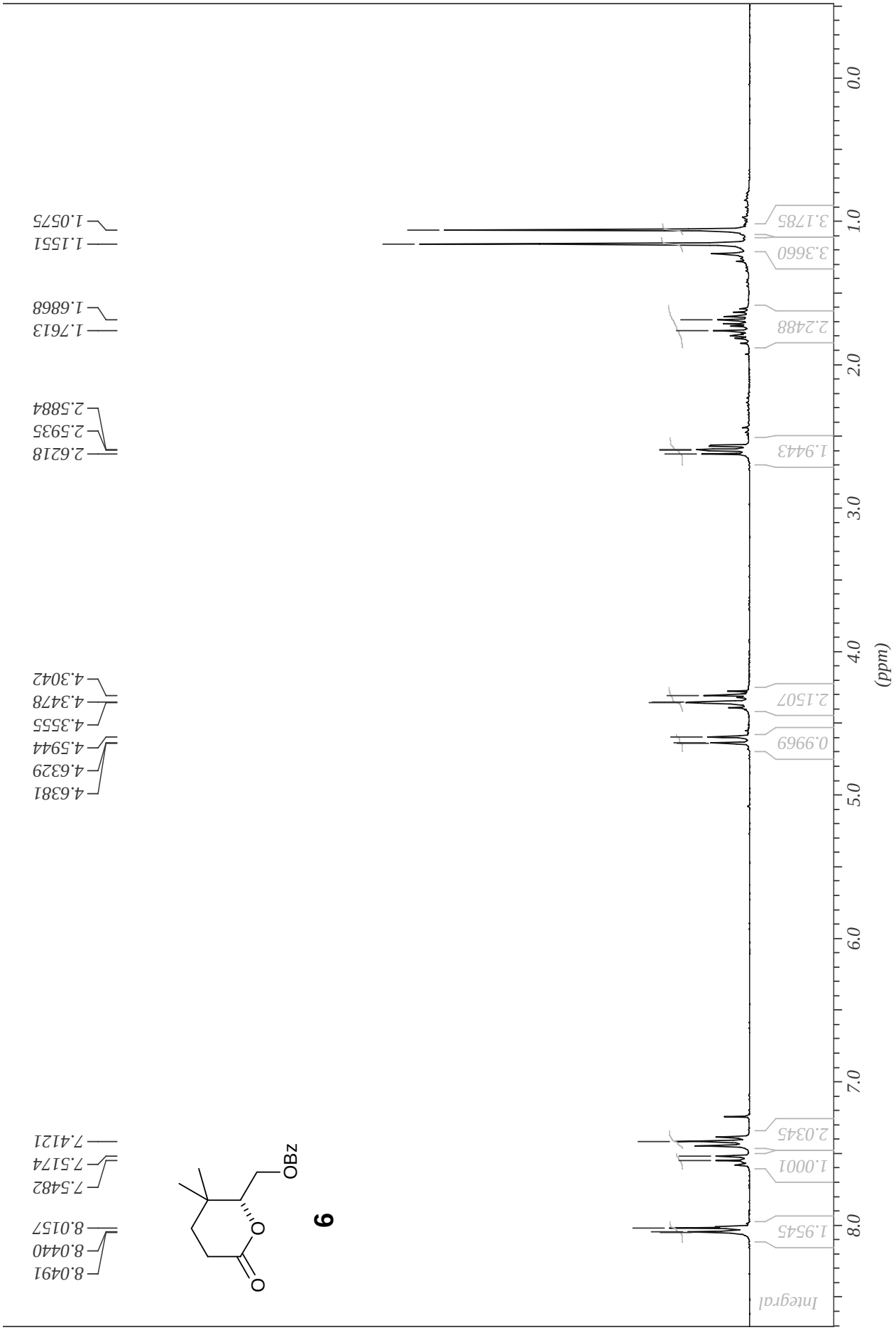
k) Benzoesäure-2-acetoxy-2-(2-methyl-5-oxotetrahydrofuran-2-yl)-ethylester (**22**)

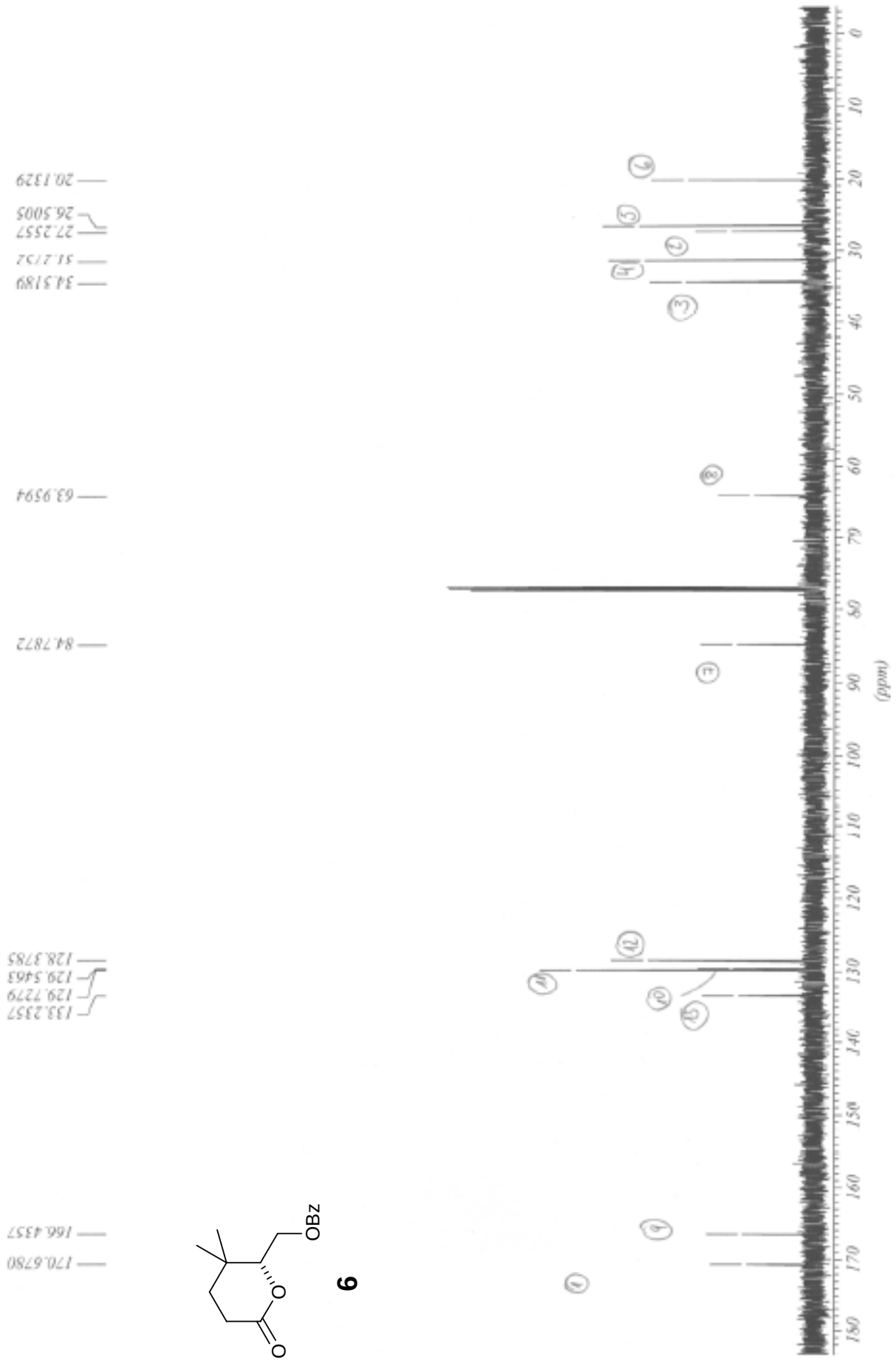


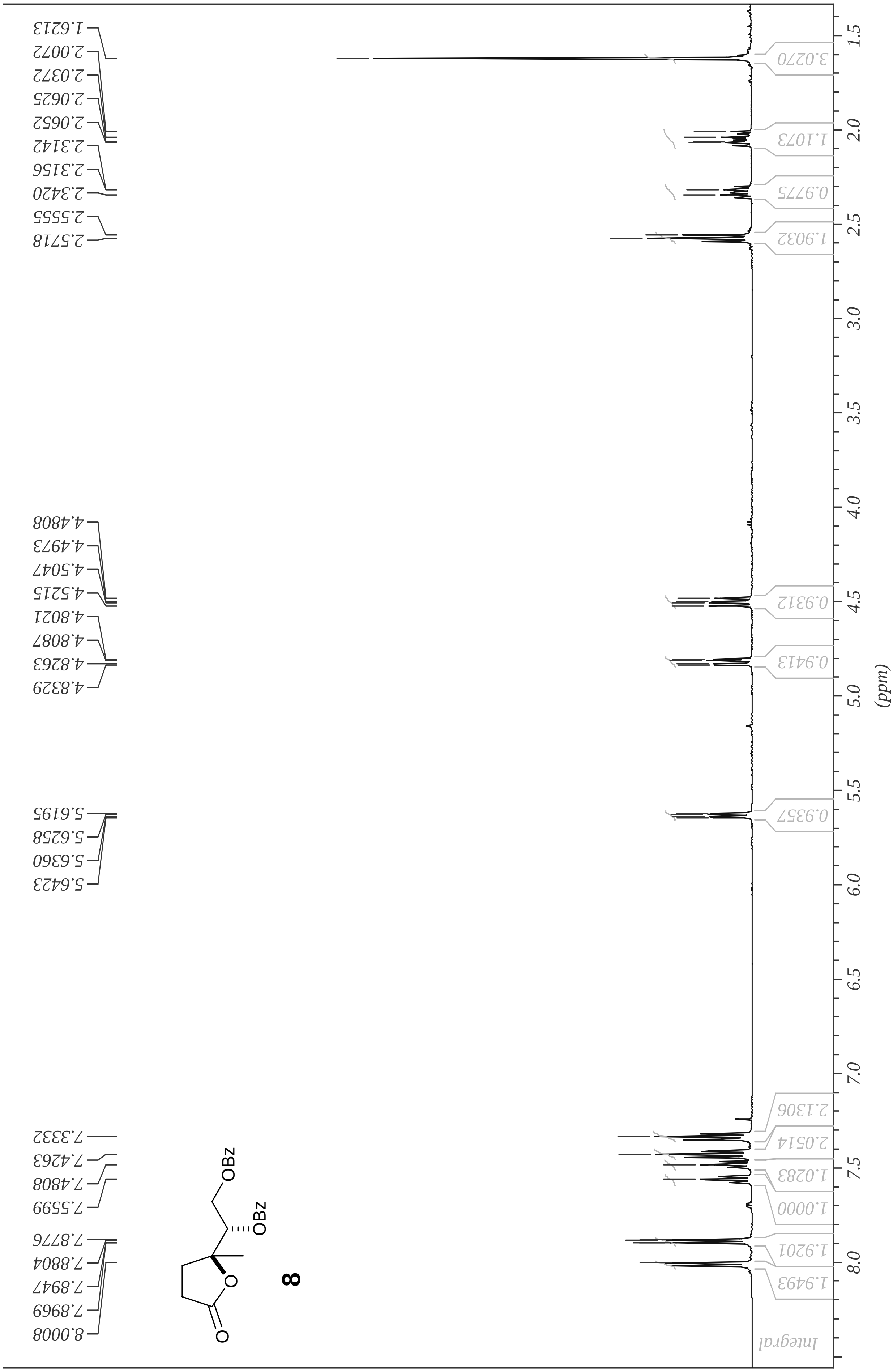
^{1}H-NMR (500 MHz): δ = 7.90 (m, 2 H, H-10), 7.50 (tt, ^4J = 1.4 Hz, ^3J = 7.4 Hz, 1 H, H-12), 7.37 (m, 2 H, H-11), 5.32 (dd, ^3J = 8.2, 3.2 Hz, 1 H, H-6), 4.62 (dd, ^3J = 3.2 Hz, ^2J = 12.0 Hz, 1 H, H-7a), 4.30 (dd, ^3J = 8.2 Hz, ^2J = 12.0 Hz, 1 H, H-7b), 2.56 (dd, ^3J = 10.0, 8.5 Hz, 2 H, H-2), 2.22 (ddd, ^3J = 10.0, 10.0 Hz, ^2J = 19.0 Hz, 1 H, H-3a), 2.05 (s, 3 H, H-14), 1.92 (m, 1 H, H-3b), 1.48 ppm (s, 3 H, H-5); ^{13}C-NMR (125 MHz): δ = 175.7 (C-1), 169.8 (C-13), 165.9 (C-8), 133.1 (C-12), 129.6 (C-9), 129.4 (C-10), 128.3 (C-11), 84.8 (C-4), 74.7 (C-6), 62.5 (C-7), 30.9 (C-3), 28.6 (C-2), 23.4 (C-5), 20.6 ppm (C-14); MS (ESI-TOF): *m/z* = 651 (15 %, $[2M + K]^+$), 635 (40 %, $[2M + Na]^+$), 345 (25 %, $[M + K]^+$), 329 (100 %, $[M + Na]^+$), 307 (74 %, $[M + H]^+$); HRMS (ESI-TOF) calculated for $C_{16}H_{19}O_6$ ($[M + H]^+$): *m/z* = 307.1176, found: *m/z* = 307.1178; IR (KBr): 2981, 1780, 1747, 1723, 1451, 1374, 1277, 1236, 1117, 948, 714 cm^{-1}.







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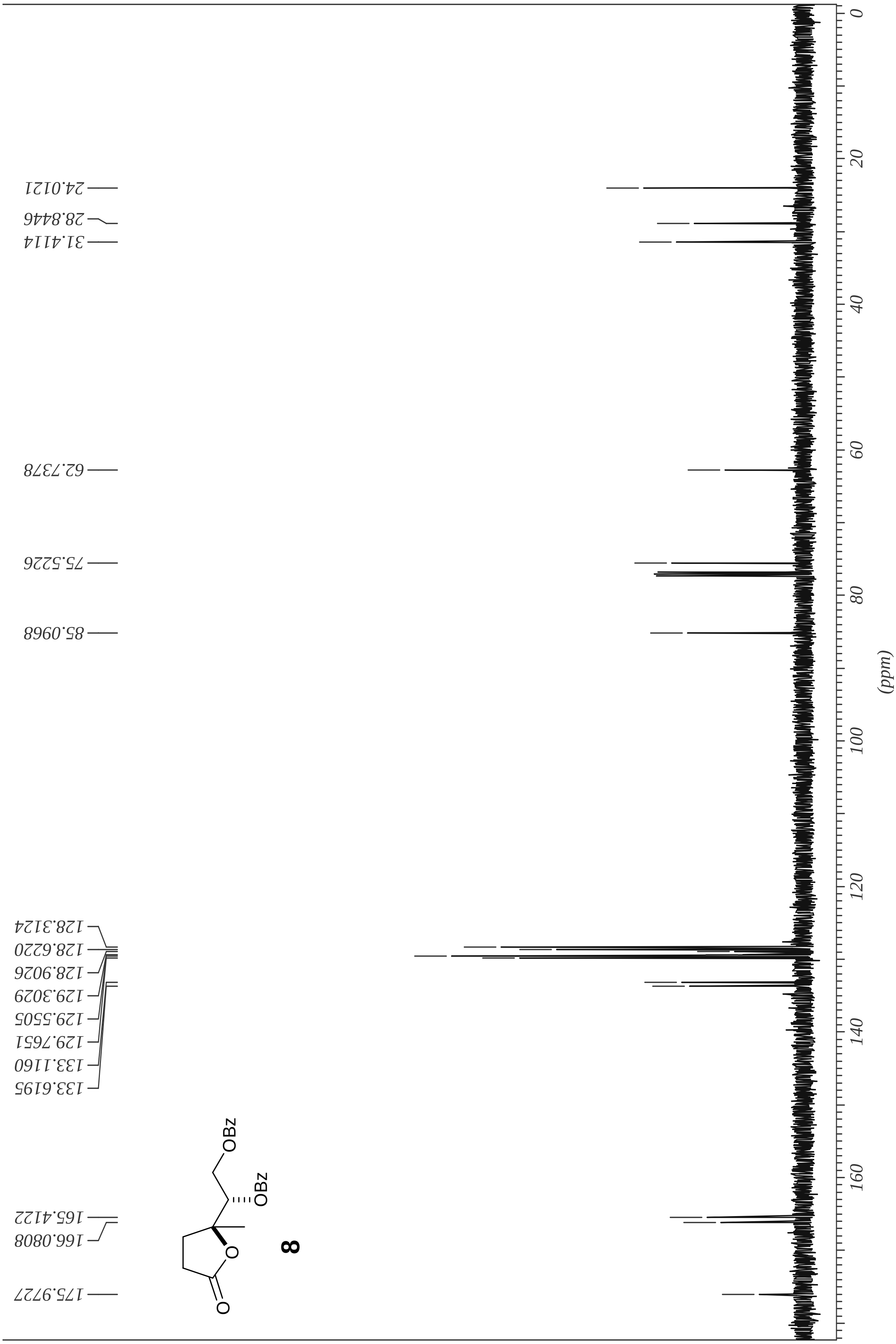
4.4973
4.5047
4.5215
4.8021
4.8087
4.8263
4.8329
5.6195
5.6258
5.6360
5.6423
7.3332
7.4263
7.4808
7.5599
7.8776
7.8804
7.8947
7.8969
8.0008
OBz
OBz
O
O
8
3.0270
1.1073
0.9775
1.9032
0.9312
0.9413
0.9357
2.1306
2.0514
1.0283
1.0000
1.9201
1.9493
Integral
(ppm)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129.7651
133.1160
133.6195
165.4122
166.0808
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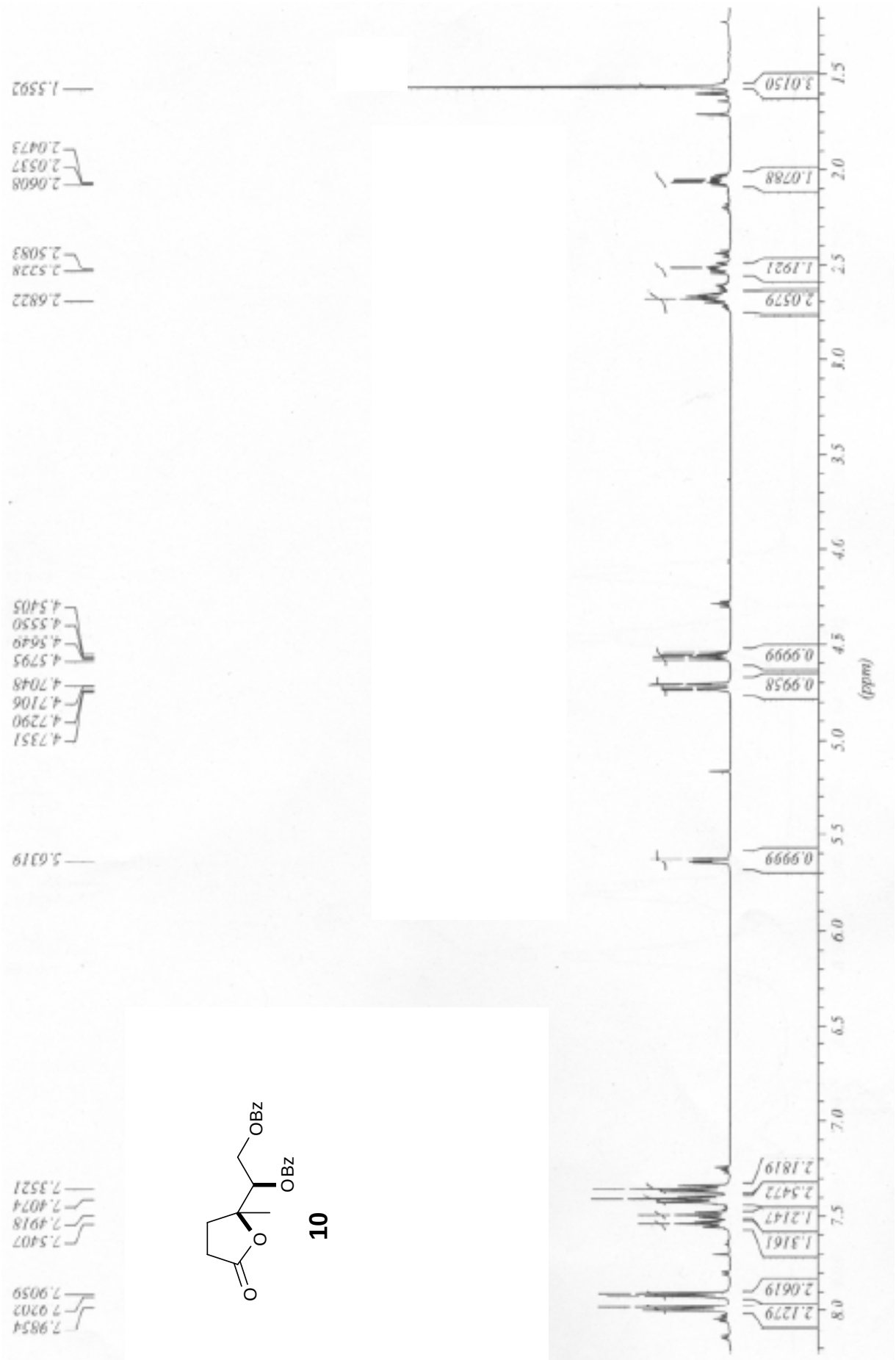
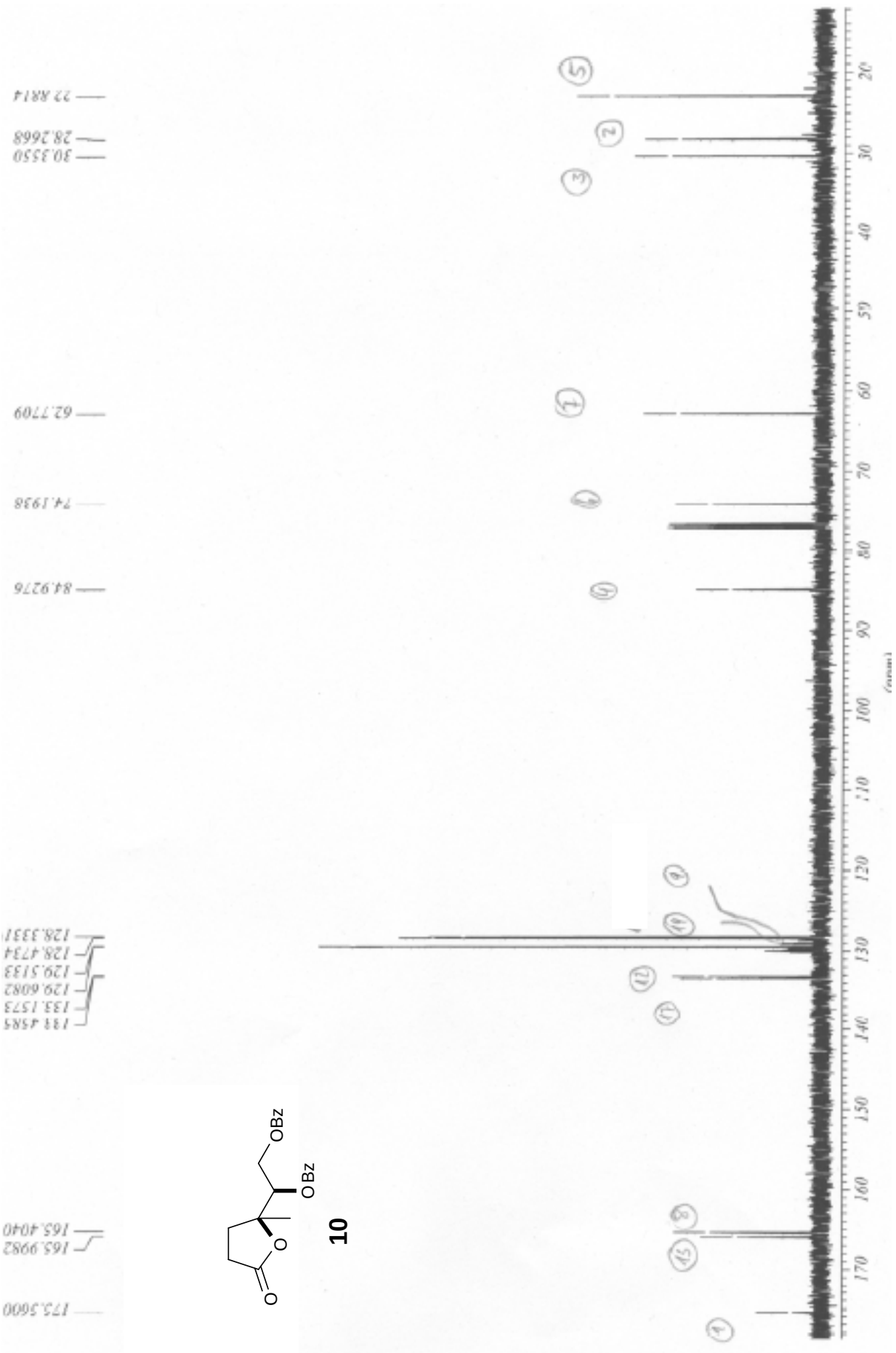
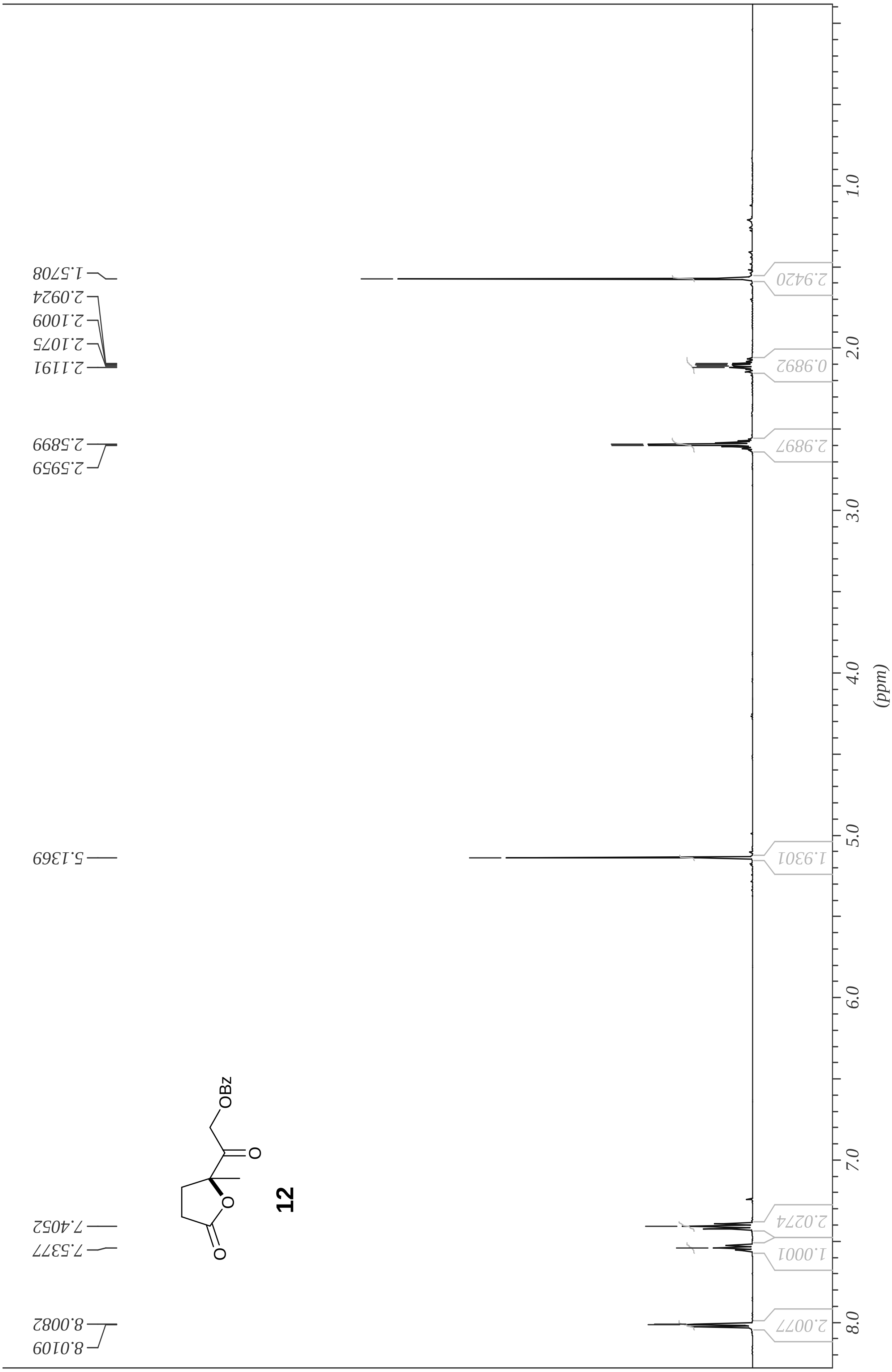
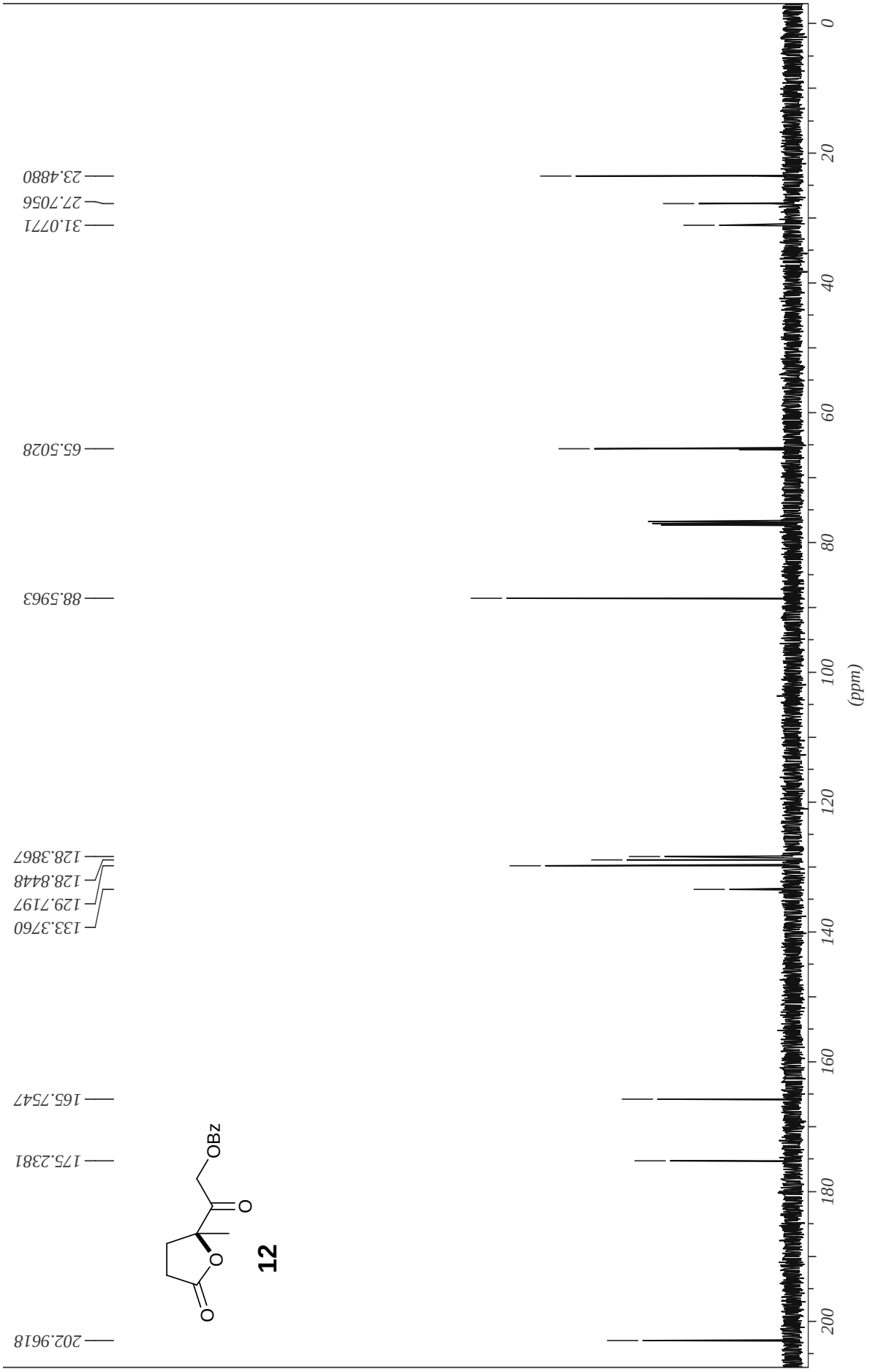
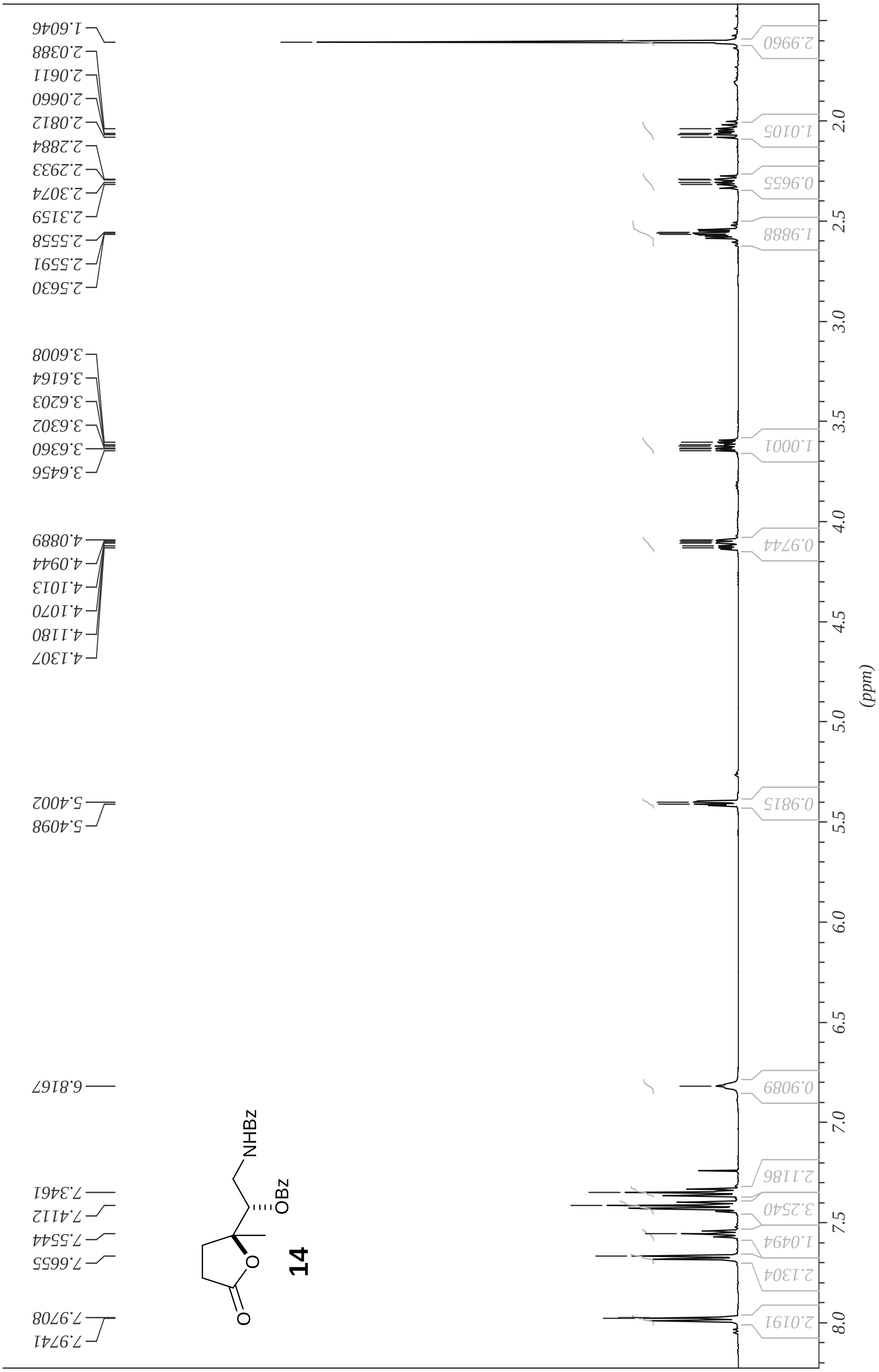
OBz
OBz
O
O
8
0
20
40
60
80
100
120
140
160
(ppm)

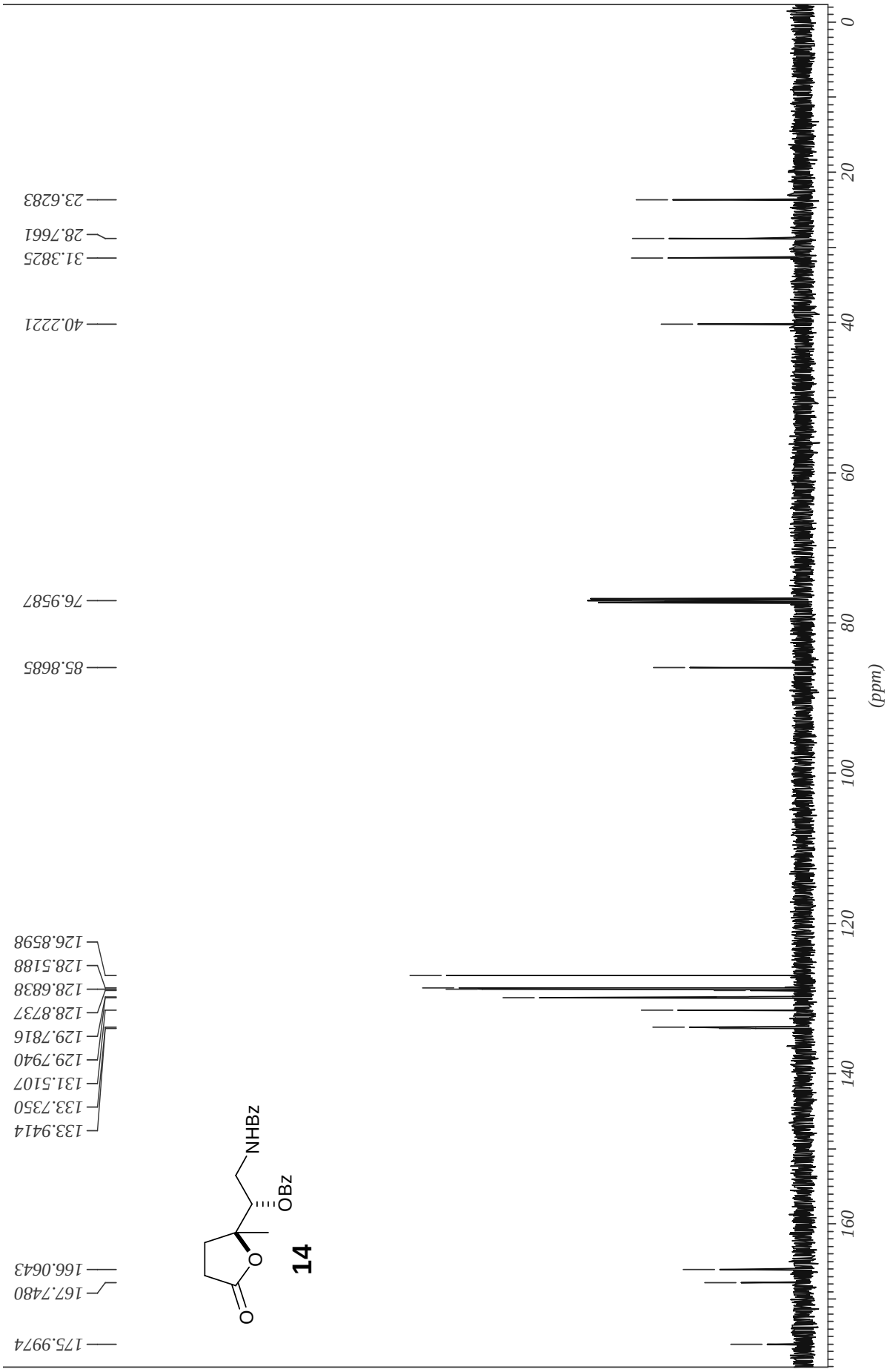









(ppm)
NHBz
OBz
O
14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126.8598
85.8685
76.9587
40.2221
31.3825
28.7661
23.6283
NHBz
OBz
O
O
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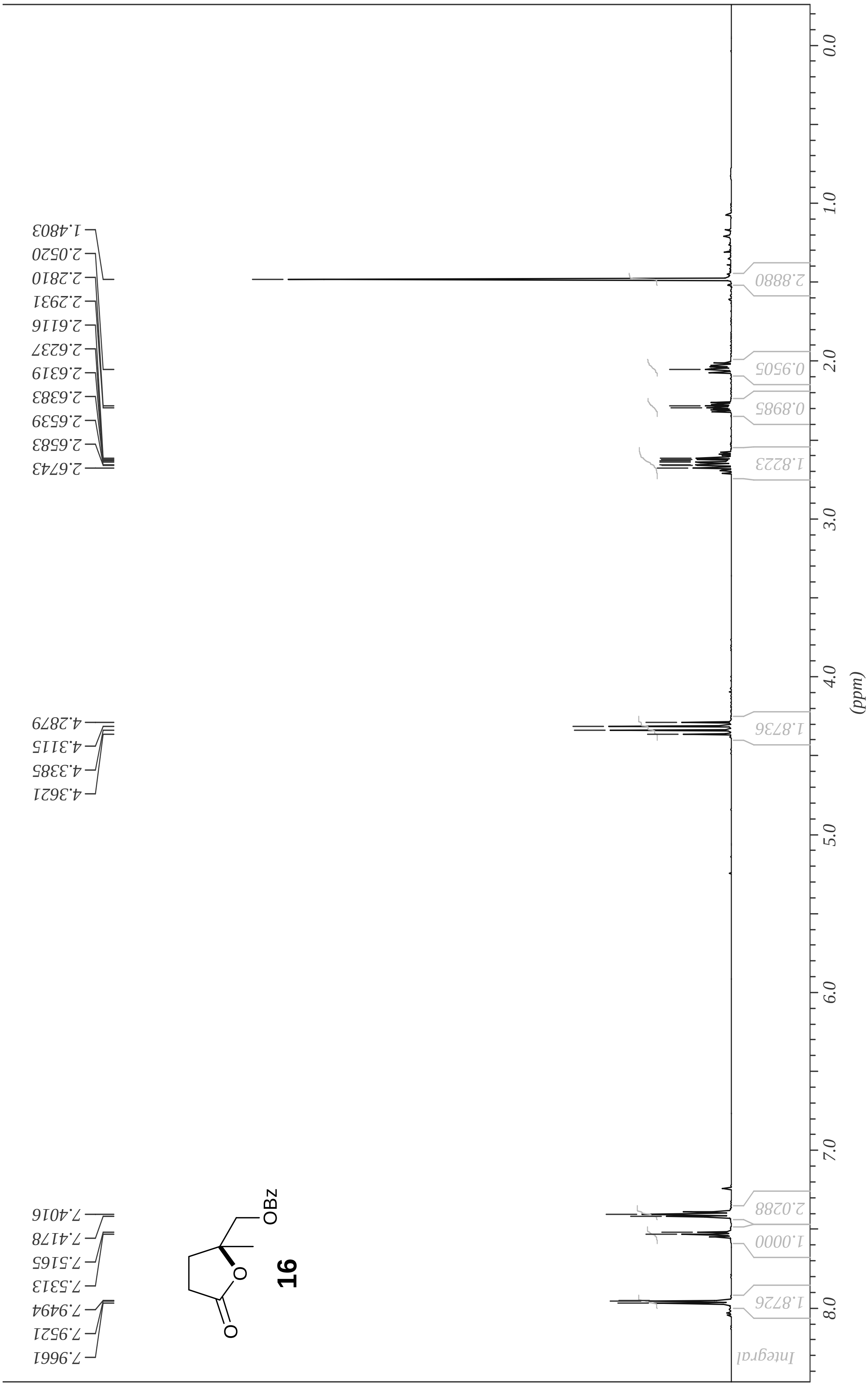
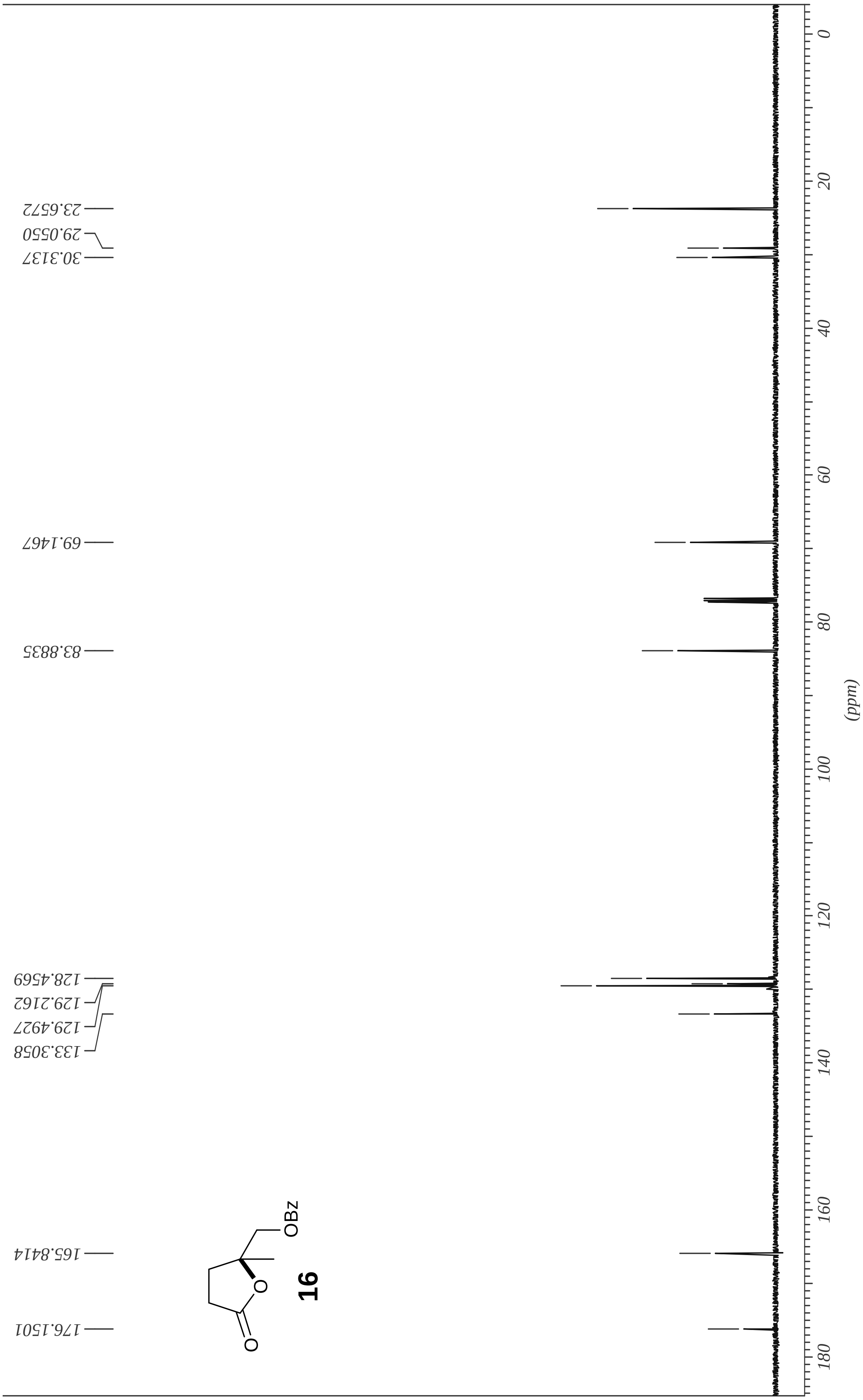
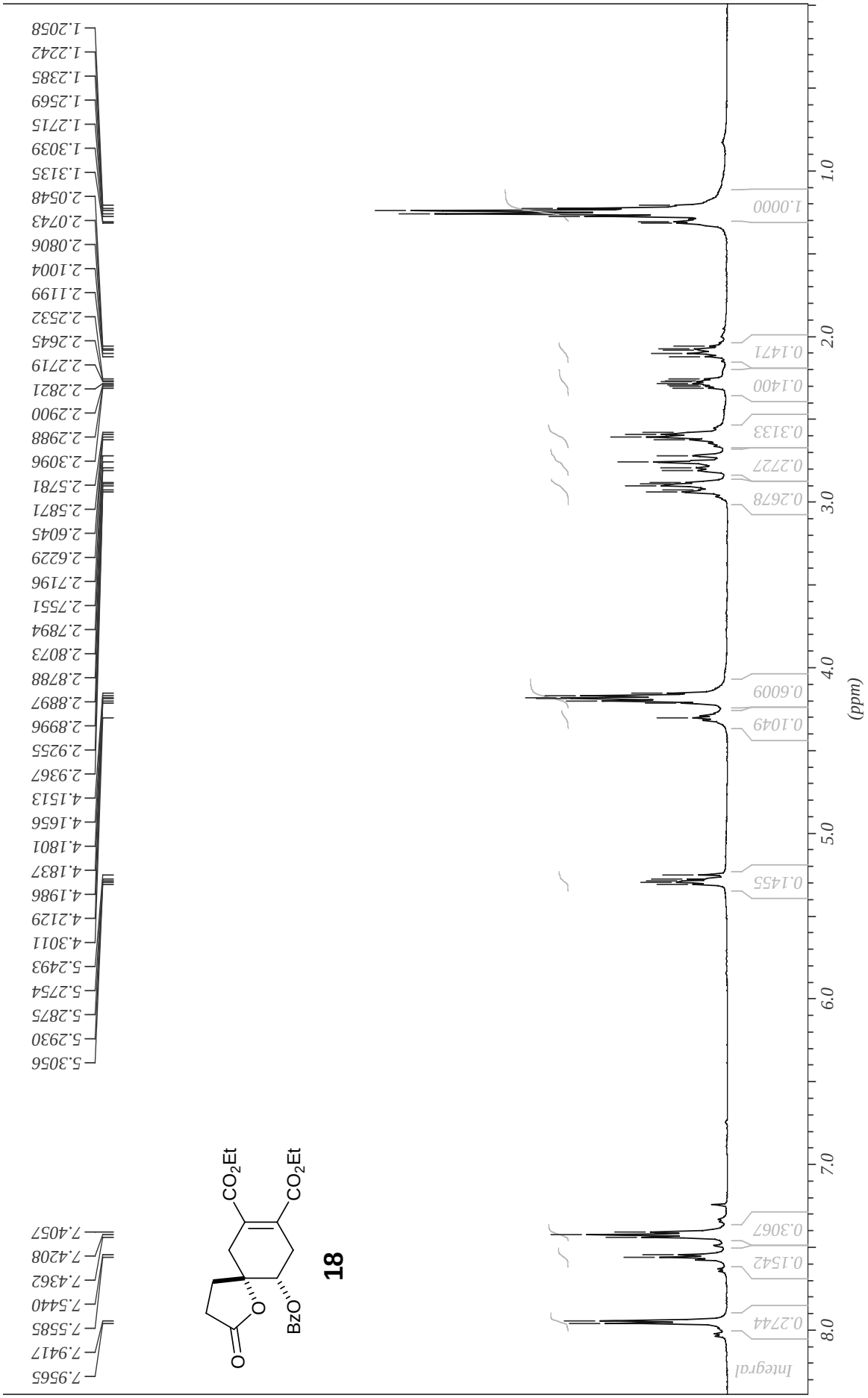
20
40
60
80
100
120
140
160
(ppm)

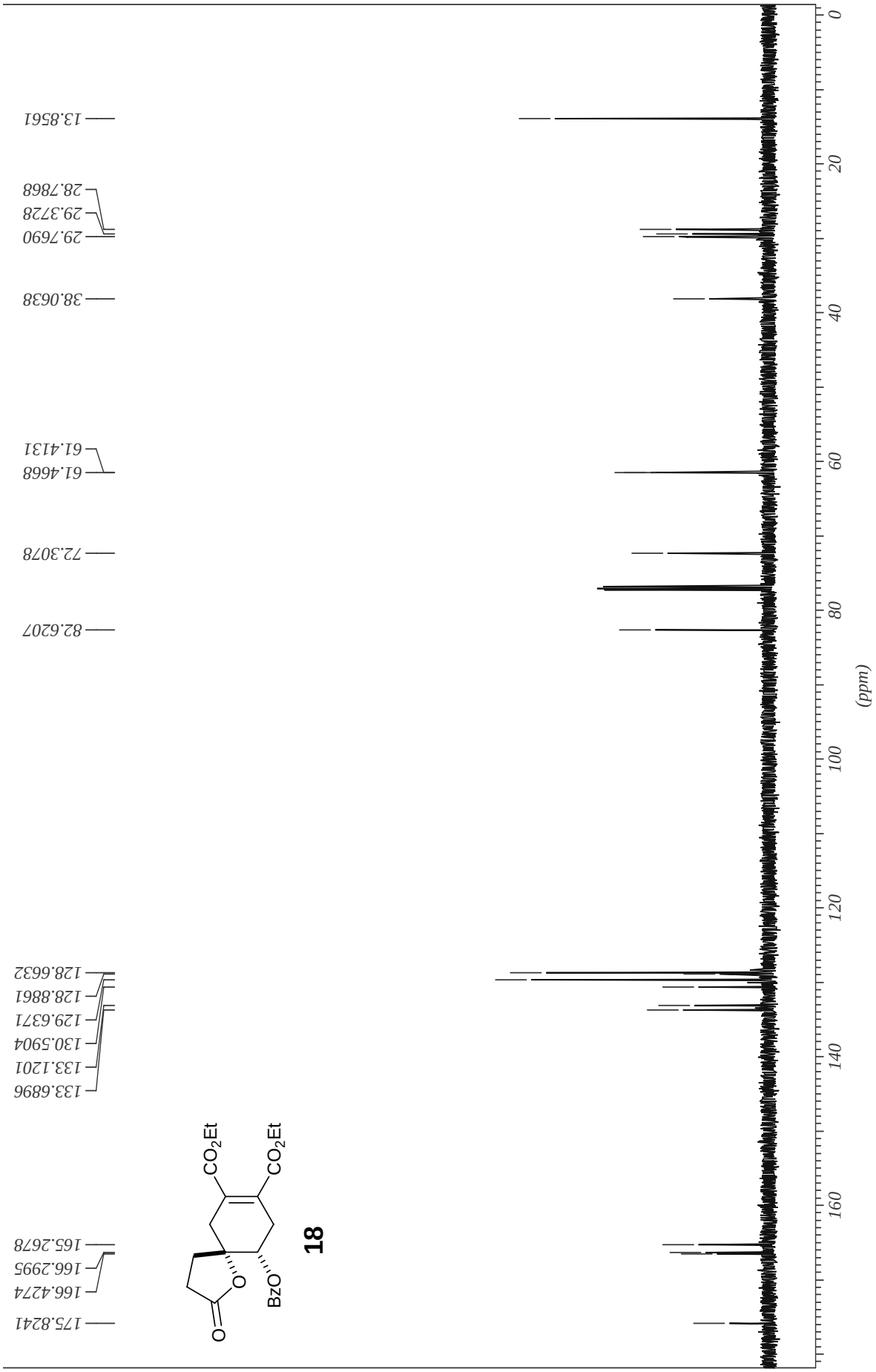
Supplementary Material (ESI) for Chemical Communications



Supplementary Material (ESI) for Chemical Communications







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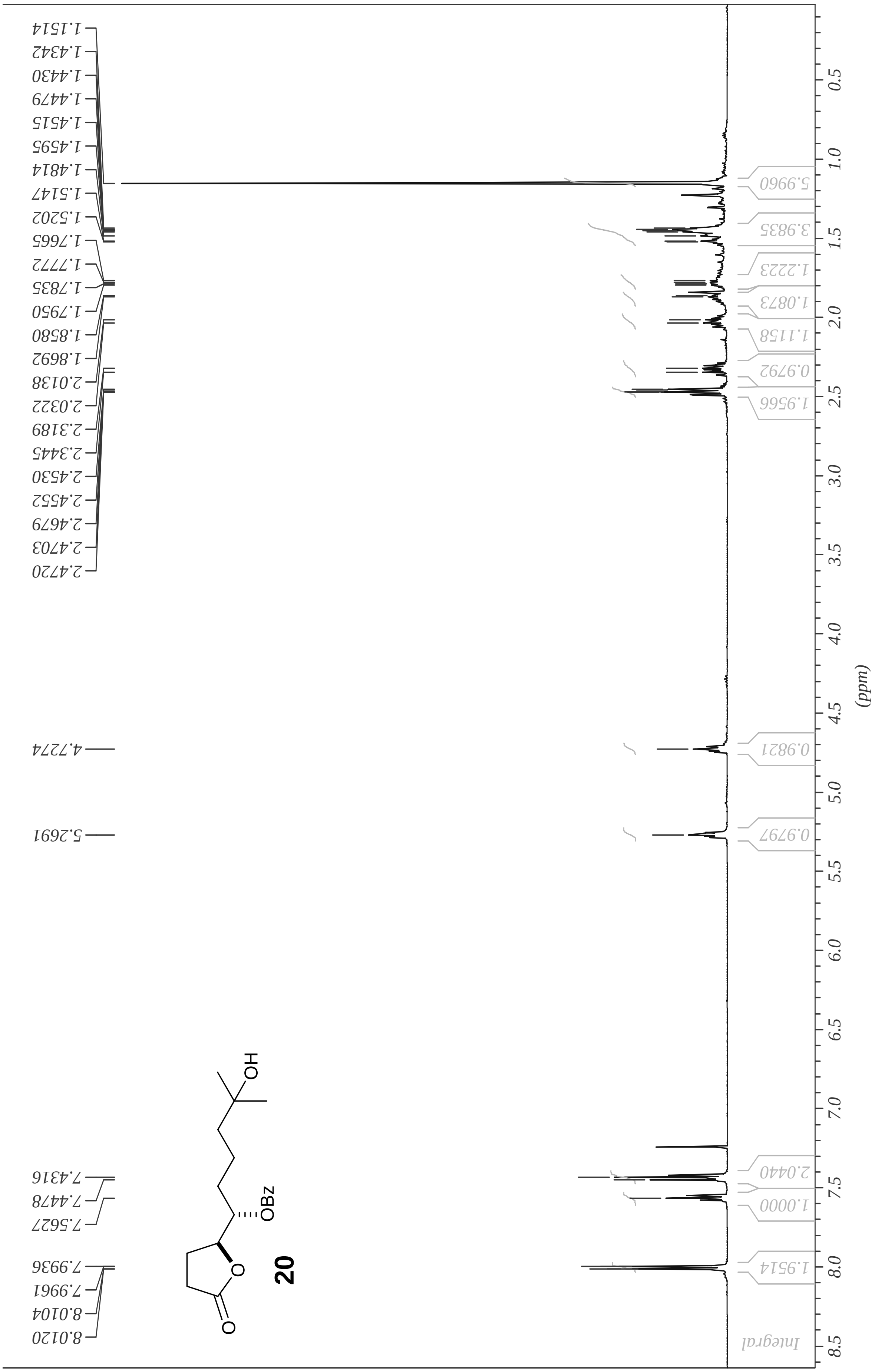

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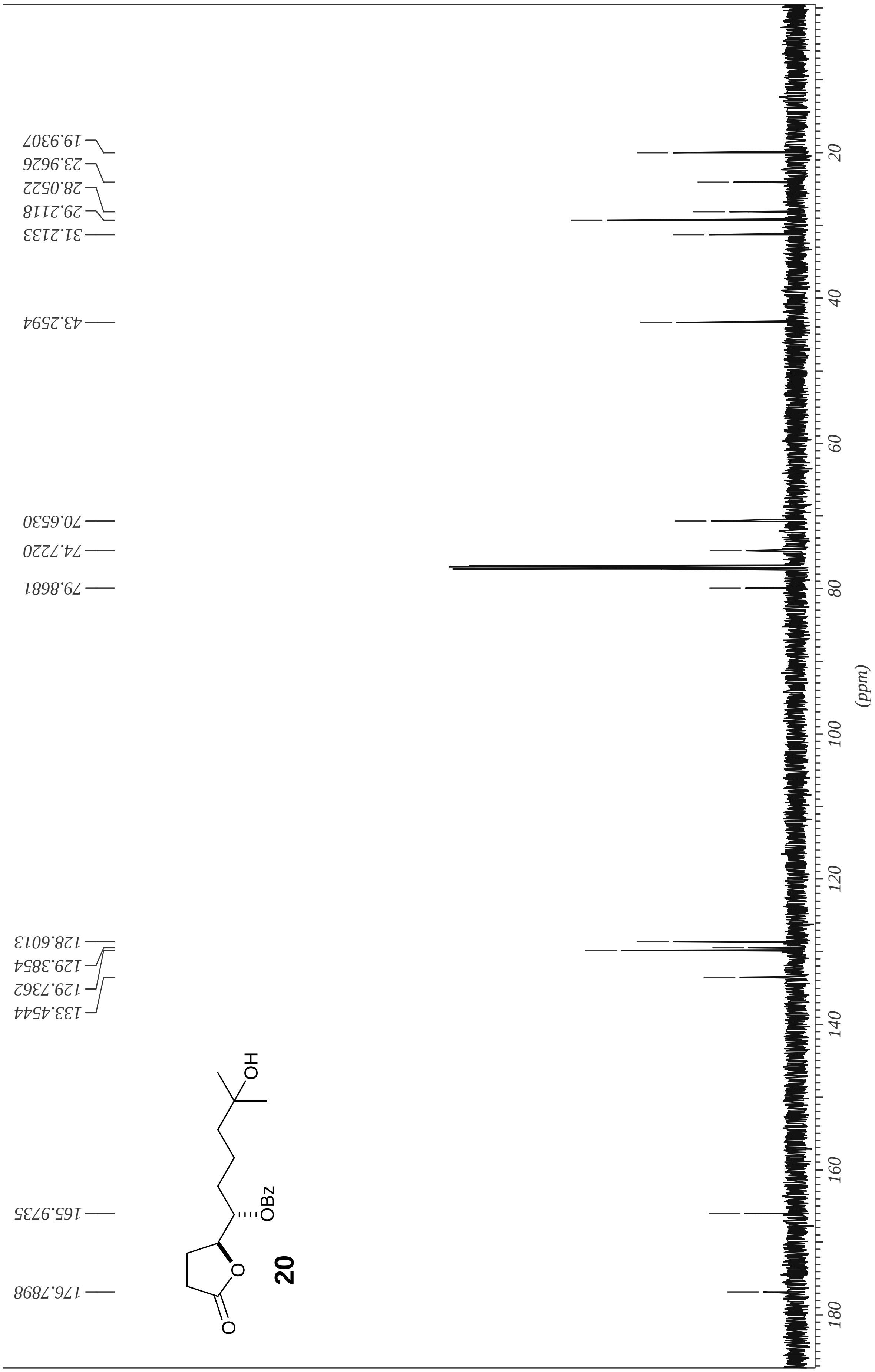

Supplementary Material (ESI) for Chemical Communications