Bifunctional Organocatalysis with Squaramide-Containing Dawson Organo-Polyoxotungstates

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Content

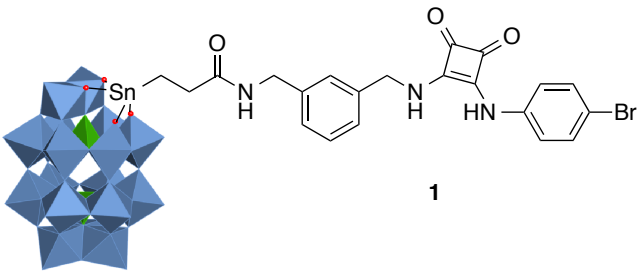
Reagents and chemicals were purchased from commercial sources and used as received. Unless otherwise noted, reactions were carried out under argon atmosphere with magnetic stirring in redistilled solvents when necessary. Solvents were purified and dried by standard procedures. Merck 60F254 silica gel was used for thin-layer chromatography (TLC) and Merck Geduran SI 60 Å silica gel 60 (40-63 µM) was used for flash column chromatography.

Melting points were measured on a Stuart Scientific Melting Point SMP3 apparatus in open capillaries. IR spectra were recorded from a Bruker Tensor 27 ATR diamond PIKE spectrophotometer. NMR ^{1}H, ^{31}P, ^{13}C spectra were recorded at 400, 162, and 100 MHz, respectively, using a Bruker AVANCE 400 spectrometer equipped with a BBFO probe. Chemical shifts are reported in ppm, using, for ^{1}H and ^{13}C, solvent residual peak as internal standard references. Coupling constants (*J*) are given in Hertz (Hz), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet).

Mass spectrometry experiments have been carried out on an electrospray-ion trap instrument (Bruker, Esquire 3000). The 50 µmol·L^{-1} solutions of POMs were infused using a syringe pump (160 µL·h^{-1}). The negative ion mode was used with capillary high voltage 3500 V. The orifice/skimmer voltage difference was set to 45 V to avoid decomposition of the POMs. The low-mass-cutoff (LMCO) of the ion trap was set to 80 Th. Elemental analyses were carried out at ICSN (CNRS, Gif, France).

General procedure for POM functionalization :

To a solution of $TBA_6[\alpha_2\text{-}P_2W_{17}O_{61}SnCH_2CH_2C(=O)]$ (0.026 mmol, 150 mg) in acetonitrile (3 mL) was added squaramide ligand (0.052 mmol, 2 equiv) and triethylamine (0.031 mmol, 1.2 equiv). The mixture was stirred at rt for 4 hours. A cation-exchange resin (Amberlyst 15, 16-50 mesh, TBA form) was added, followed by acetone (10 mL) and the mixture was stirred for 1 hour. The resin was filtered off and the filtrate was concentrated *in vacuo*. The oil which was obtained was dissolved in acetone (2 mL), and precipitated upon addition of EtOH/Et_2O (2 mL/30 mL). The solid was isolated by centrifugation, washed with Et_2O and dried *in vacuo* to afford the desired POM.

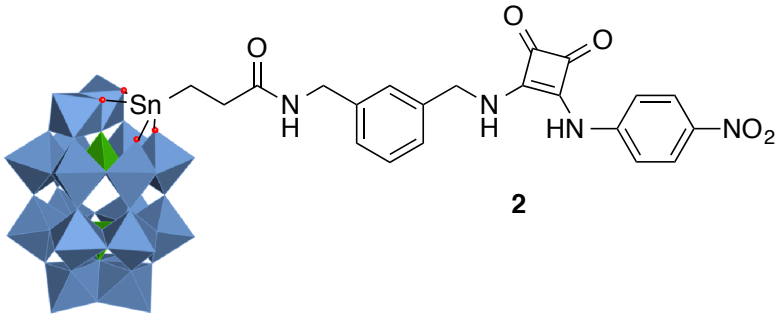


1

1 : Prepared according to the general procedure from $TBA_6[\alpha_2\text{-}P_2W_{17}O_{61}SnCH_2CH_2C(=O)]$ (139 mg, 24 µmol). Organo-POM **1** was isolated as a orange powder (142 mg, 22 µmol, 92% yield). IR: υ = 2960, 2872, 1790, 1626, 1599, 1556, 1481, 1452, 1327, 1295, 1087, 945, 894, 764 cm^{-1}. ^1H NMR (300 MHz, CD_3CN): δ = 11.12 (s, 1H, NH), 8.66 (br s, 1H, NH), 7.99 (br s, 1H, NH), 7.85 (d, *J* = 8.4 Hz, 2H, arom.), 7.79 (s, 1H, arom.), 7.43 (d, *J* = 8.5 Hz 2H, arom.), 7.23-7.19 (m, 2H, arom.), 7.06-7.05 (m, 1H, arom.), 5.03 (d, *J* = 6.3 Hz, 2H, NCH_2), 4.31 (d, *J* = 6.2 Hz, 2H, NCH_2), 3.19-3.15 (m, 56H, $N(CH_2CH_2CH_2Me)_4$), 2.65-2.63 (m, 2H, $CH_2C=O$), 1.67-1.61 (m, 56H, $N(CH_2CH_2CH_2Me)_4$), 1.45-1.37 (m, 56H, $N(CH_2CH_2CH_2Me)_4$), 0.99-0.96 (m, 86H, $N(CH_2CH_2CH_2Me)_4$ + $SnCH_2$). ^{13}C NMR (75 MHz, CD_3CN): δ = 185.2 (C=O), 181.9 (C=O), 175.4 (C=O or =CN), 171.1 (C=O or =CN), 165.3 (C=O or =CN), 142.0 (C arom.), 141.6 (C arom.), 140.9 (C arom.), 132.9 (CH arom.), 128.6 (CH arom.), 126.5 (CH arom.), 121.8 (CH arom.), 115.1 (C arom.), 59.3 ($N(CH_2CH_2CH_2Me)_4$), 48.7 (NCH_2), 43.8 (NCH_2), 32.1 ($CH_2C=O$), 24.5 ($N(CH_2CH_2CH_2Me)_4$), 20.5 ($N(CH_2CH_2CH_2Me)_4$), 19.4 ($SnCH_2$), 14.1 ($N(CH_2CH_2CH_2Me)_4$). ^{31}P NMR (122 MHz, CD_3CN): δ = –10.7 (s, 1P, s+d, 1 P, J_{SnP} = 26.5 Hz), –13.6 (s, 1P). Anal. calc. for $TBA_7C_{21}H_{19}N_3O_{64}P_2W_{17}SnBr$ (6420.76 $g.mol^{-1}$) : C 24.88, H 4.25, N 2.18; found : C 25.28, H 4.41, N 2.20.

Electrospray mass spectrometry see below for full details :

Entry	Charge	Simulated m/z	Observed m/z	Composition
1	3-	1897.0	1895.2	$TBA_4[P_2W_{17}O_{64}C_{21}H_{19}N_3SnBr]$
2	4-	1362.2	1360.1	$TBA_3[P_2W_{17}O_{64}C_{21}H_{19}N_3SnBr]$
3	4-	1212.2	1210.5	$H_3(CH_3CN)_3[P_2W_{17}O_{64}C_{21}H_{19}N_3SnBr]$
4	5-	1041.4	1041.8	$TBA_2[P_2W_{17}O_{64}C_{21}H_{19}N_3SnBr]$

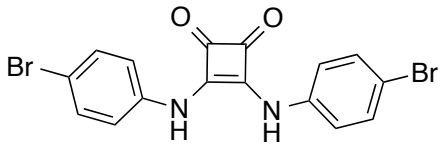


2

2 : Prepared according to the general procedure from $TBA_6[\alpha_2\text{-}P_2W_{17}O_{61}SnCH_2CH_2C(=O)]$ (80 mg, 13.8 µmol). Organo-POM **2** was isolated as a yellow powder (78.2 mg, 12.3 µmol, 89% yield). IR: υ = 2961, 2872, 1788, 1626, 1599, 1556, 1483, 1452, 1327, 1296, 1087, 945, 894, 762 cm^{-1}. ^1H NMR (300 MHz, CD_3CN): δ = 11.87 (br s, 1H, NH), 8.84 (br s, 1H, NH), 8.17 (d, *J* = 8.8 Hz, 2H, arom.), 8.08 (d, *J* = 8.9 Hz, 2H, arom.), 7.96 (br s, 1H, NH), 7.82 (s, 1H, arom.), 7.24-7.19 (m, 2H, arom.), 7.07-7.06 (m, 1H, arom.), 5.06 (d, *J* = 6.0 Hz, 2H, NCH_2), 4.30 (d, *J* = 6.2 Hz, 2H, NCH_2), 3.18-3.14 (m, 56H, $N(CH_2CH_2CH_2Me)_4$), 2.66-2.64 (m, 2H, $CH_2C=O$), 1.67-1.61 (m, 56H, $N(CH_2CH_2CH_2Me)_4$), 1.44-1.36 (m, 56H, $N(CH_2CH_2CH_2Me)_4$), 0.99-0.96 (m, 86H, $N(CH_2CH_2CH_2Me)_4$ + $SnCH_2$). ^{13}C NMR (75 MHz, CD_3CN): δ = 186.3 (C=O), 181.7 (C=O), 175.4 (C=O or =CN), 172.0 (C=O or =CN), 164.5 (C=O or =CN), 147.7 (C arom.), 142.7 (C arom.), 142.1 (C arom.), 141.5 (C arom.), 128.6 (CH arom.), 126.5 (CH arom.), 119.6 (CH arom.), 59.4 ($N(CH_2CH_2CH_2Me)_4$), 48.9 (NCH_2), 43.9 (NCH_2), 32.1 ($CH_2C=O$), 24.5 ($N(CH_2CH_2CH_2Me)_4$), 20.5 ($N(CH_2CH_2CH_2Me)_4$), 19.4 ($SnCH_2$), 14.0 ($N(CH_2CH_2CH_2Me)_4$). ^{31}P NMR (202 MHz, CD_3CN): δ = –11.0 (s+d, 1P, J_{SnP} = 26.5 Hz), –13.9 (s, 1P). Anal. calc. for $TBA_7C_{21}H_{19}N_4O_{66}P_2W_{17}Sn$ (6387.84 $g.mol^{-1}$) : C 25.01, H 4.28, N 2.41; found: C 25.45, H 4.25, N 2.25. Electrospray mass spectrometry see below for full details :

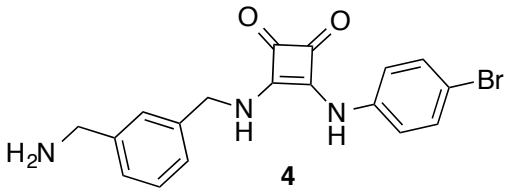
Entry	Charge	Simulated m/z	Observed m/z	Composition
1	3-	1885.7	1884.8	$TBA_4[P_2W_{17}O_{66}C_{21}H_{19}N_4Sn]$
2	4-	1353.7	1353.3	$TBA_3[P_2W_{17}O_{66}C_{21}H_{19}N_4Sn]$
3	5-	1051.0	1051.0	$TBA_2(CH_3CN)_2[P_2W_{17}O_{66}C_{21}H_{19}N_4Sn]$
4	6-	862.8	862.8	$TBA(CH_3CN)_6[P_2W_{17}O_{66}C_{21}H_{19}N_4Sn]$

*Ligands **3**, **4** and **4'** :*



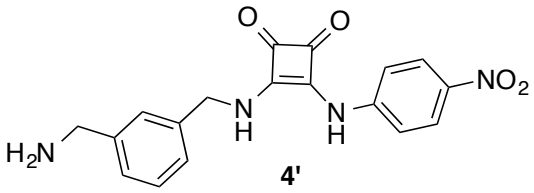
3

3,4-bis((4-bromophenyl)amino)cyclobut-3-ene-1,2-dione : Ligand **3** was isolated as a yellow powder (88% yield). IR: υ = 3461, 2252, 2119, 1053, 1026, 1006, 820, 758 cm^{-1}. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ = 9.96 (br s, 2H, NH), 7.56 (d, *J* = 8.8 Hz, 4H, arom.), 7.42 (d, *J* = 8.8 Hz, 4H, arom.). ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ = 181.9 (C=O), 165.5 (C=C–N), 137.9 (C arom.), 132.1 (CH arom.), 120.7 (CH arom.), 115.3 (C arom.). HRMS (ESI-TOF) calc. for $C_{16}H_9Br_2N_2O_2$ $[M-H]^+$: 418.9031; found: 418.9034.



4

3-((3-(aminomethyl)benzyl)amino)-4-((4-bromophenyl)amino)cyclobut-3-ene-1,2-dione : Ligand **4** was isolated as a white powder (81% yield). IR: υ = 3244, 3177, 3038, 2988, 2634, 1796, 1664, 1609, 1564, 1539, 1494, 1463, 1440, 1380, 1346, 1203, 1179, 1135, 1077, 1010, 958, 886, 867, 834, 820, 797, 753, 722, 701 cm^{-1}. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ = 10.01-9.96 (br s, 1H, NH), 8.33-8.29 (br s, 1H, NH), 8.16-8.14 (br s, 2H, NH_2), 7.51-7.45 (m, 2H, arom.), 7.43-7.39 (m, 6H, arom.), 4.85-4.83 (m, 2H, NCH_2), 4.04-4.03 (m, 2H, NCH_2). ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ = 184.2 (C=O), 180.4 (C=O squaramide), 169.1 (C=C–N), 163.5 (C=C–N), 139.1 (C arom.), 138.6 (C arom.), 134.6 (C arom.), 132.1 (CH arom.), 129.1 (CH arom.), 128.1 (CH arom.), 127.9 (CH arom.), 127.7 (CH arom.), 120.2 (CH arom.), 114.5 (C arom.), 46.9 (NCH_2), 42.2 (NCH_2). HRMS (ESI-TOF) calc. for $C_{18}H_{17}BrN_3O_2$ $[M+H]^+$: 386.0504; found: 386.0482.

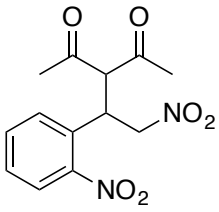


4'

3-((3-(aminomethyl)benzyl)amino)-4-((4-nitrophenyl)amino)cyclobut-3-ene-1,2-dione : Ligand **4'** was isolated as a yellow powder (75% yield). IR: υ = 3213, 1793, 1669, 1621, 1579, 1555, 1508, 1440, 1336, 1311, 1292, 1185, 976, 846, 806, 749, 686 cm^{-1}. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ = 10.52 (br s, 1H, NH), 8.57 (br s, 1H, NH), 8.21-8.19 (m, 4H, arom. or NH_2), 7.66 (br s, 2H, m, 4H, arom. or NH_2), 7.44-7.41 (m, 4H, m, 4H, arom. or NH_2), 4.86 (m, 2H, NCH_2), 4.04 (m, 2H, NCH_2). ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ = 185.2 (C=O), 180.2 (C=O), 169.9 (C=C–N), 162.5 (C=C–N), 145.3 (C arom.), 141.5 (C arom.), 138.8 (C arom.), 134.5 (C arom.), 129.0 (CH arom.), 128.0 (CH arom.), 127.8 (CH arom.), 127.6 (CH arom.), 125.6 (CH arom.), 177.7 (CH arom.), 47.0 (NCH_2), 42.2 (NCH_2). HRMS (ESI-TOF) calc. for $C_{18}H_{17}N_4O_4$ $[M+H]^+$: 353.1250; found: 353.1240.

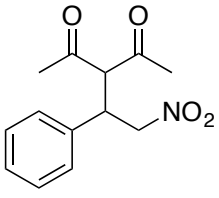
General procedure for the conjugate addition reactions :

To a solution of nitroolefin (1 equiv) in DCM (0.5 mL) was added squaramide POM **1** (1.8 mol%) and 1,3-dicarbonyl compound (2 equiv). The reaction mixture was stirred at reflux overnight and the solvent was removed under reduced pressure. The residue was purified on silica gel to afford the conjugate addition product.



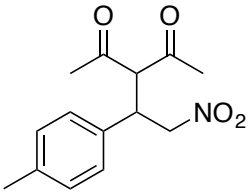
7

3-(2-nitro-1-(2-nitrophenyl)ethyl)pentane-2,4-dione. Flash column chromatography (7:3 Petroleum ether : EtOAc) afforded **7** (15.1 mg, 51.3 μmol, 99%) as colorless oil. IR: υ = 2924, 1731, 1703, 1555, 1496, 1431, 1358, 1240, 1142, 955, 856, 789, 710 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.1 Hz, 1H, arom.), 7.58 (t, *J* = 7.7 Hz, 1H, arom.), 7.48 (t, *J* = 7.8 Hz, 1H, arom.), 7.36 (d, *J* = 7.8 Hz, 1H, arom.), 4.97 (dd, *J* = 13.4, 7.1 Hz, 1H, C*H*HNO_2), 4.84 (dd, *J* = 13.3, 3.8 Hz, 1H, CH*H*NO_2), 4.76-4.72 (m, 1H, C*H*Ar), 4.67 (d, *J* = 8.7 Hz, 1H, CH–C=O), 2.31 (s, 3H, Me), 2.13 (s, 3H, Me). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.8 (C=O), 200.7 (C=O), 133.7 (CH arom.), 131.4 (C arom.), 129.6 (CH arom.), 129.5 (C arom.), 125.8 (CH arom.), 76.8 (CH_2NO_2), 69.3 (*CH*–C=O), 37.3 (*CH*Ar), 31.5 (Me), 29.5 (Me). HRMS (ESI-TOF) calc. for $C_{13}H_{13}N_2O_6$ $[M-H]^+$: 293.0774; found: 293.0760.



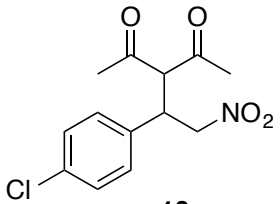
8

3-(2-nitro-1-phenylethyl)pentane-2,4-dione. Flash column chromatography (7:3 Petroleum ether : EtOAc) afforded **8** (12.8 mg, 51.4 μmol, 99%) as colorless oil. IR: υ = 2922, 1725, 1700, 1590, 1496, 1427, 1380, 1357, 1240, 1142, 1092, 953, 764, 702 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36-7.28 (m, 3H, arom.), 7.21-7.19 (m, 2H, arom.), 4.69-4.61 (m, 2H, CH_2NO_2), 4.39 (d, *J* = 10.6 Hz, 1H, CH–C=O), 4.28-4.24 (m, 1H, C*H*Ph), 2.31 (s, 3H, Me), 1.96 (s, 3H, Me). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 202.0 (C=O), 201.2 (C=O), 136.2 (C arom.), 129.6 (CH arom.), 128.8 (CH arom.), 128.1 (CH arom.), 78.4 (CH_2NO_2), 70.9 (*CH*–C=O), 43.0 (*CH*Ph), 30.7 (Me), 29.8 (Me). HRMS (ESI-TOF) calc. for $C_{13}H_{14}NO_4$ $[M-H]^+$: 248.0923; found: 248.0922.



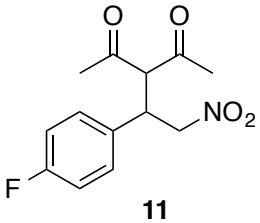
9

3-(2-nitro-1-(*p*-tolyl)ethyl)pentane-2,4-dione. Flash column chromatography (7:3 Petroleum ether : EtOAc) afforded **9** (13.0 mg, 49.4 μmol, 96%) as colorless oil. IR: υ = 2993, 1724, 1701, 1552, 1516, 1430, 1379, 1358, 1257, 1154, 954, 818, 719 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.12 (d, *J* = 7.6 Hz, 2H, arom.), 7.06 (d, *J* = 7.7 Hz, 2H, arom.), 4.63-4.57 (m, 2H, CH_2NO_2), 4.35 (d, *J* = 10.8 Hz, 1H, CH–C=O), 4.22-4.18 (m, 1H, C*H*Ar), 2.30 (s, 3H, Me), 2.28 (s, 3H, Me), 1.94 (s, 3H, Me). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.1 (C=O), 201.3 (C=O), 138.6 (C arom.), 133.3 (C arom.), 130.2 (CH arom.), 128.0 (CH arom.), 78.6 (CH_2NO_2), 71.0 (*CH*–C=O), 42.7 (*CH*Ar), 30.6 (Me), 29.7 (Me), 21.3 (*Me*Ar). HRMS (ESI-TOF) calc. for $C_{14}H_{16}NO_4$ $[M-H]^+$: 262.1079; found: 262.1094.



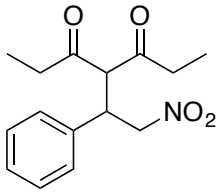
10

3-(1-(4-chlorophenyl)-2-nitroethyl)pentane-2,4-dione. Flash column chromatography (7:3 Petroleum ether : EtOAc) afforded **10** (14.0 mg, 49.5 μmol, 96%) as colorless oil. IR: υ = 2918, 2850, 1731, 1702, 1553, 1495, 1415, 1379, 1360, 1238, 1142, 1015, 955, 910, 825, 732, 670 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8.5 Hz, 2H, arom.), 7.13 (d, *J* = 8.4 Hz, 2H, arom.), 4.62-4.60 (m, 2H, CH_2NO_2), 4.32 (d, *J* = 10.6 Hz, 1H, *CH*–C=O), 4.25-4.22 (m, 1H, C*H*Ar), 2.29 (s, 3H, Me), 1.97 (s, 3H, Me). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 201.6 (C=O), 200.8 (C=O), 134.8 (C arom.), 129.8 (CH arom.), 129.5 (CH arom.), 78.1 (CH_2NO_2), 70.7 (*CH*–C=O), 42.3 (*CH*Ar), 30.7 (Me), 29.9 (Me). HRMS (ESI-TOF) calc. for $C_{13}H_{13}ClNO_4$ $[M-Na]^+$: 282.0533; found: 282.00539.



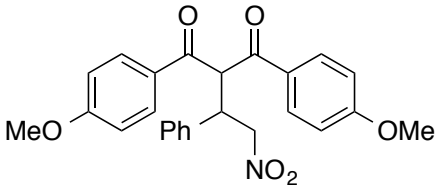
11

3-(1-(4-fluorophenyl)-2-nitroethyl)pentane-2,4-dione. Flash column chromatography (7:3 Petroleum ether : EtOAc) afforded **11** (13.7 mg, 51.3 μmol, 99%) as colorless oil. IR: υ = 2922, 1728, 1701, 1607, 1551, 1511, 1379, 1359, 1226, 1161, 1105, 1016, 953, 913, 838, 733 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20-7.15 (m, 2H, arom.), 7.05-6.99 (m, 2H, arom.), 4.62-4.59 (m, 2H, CH_2NO_2), 4.33 (d, *J* = 10.8 Hz, 1H, CH–C=O), 4.27-4.20 (m, 1H, C*H*Ar), 2.29 (s, 3H, Me), 1.96 (s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.7 (C=O), 200.9 (C=O), 162.7 (*J* = 246.4 Hz, C–F), 134.6 (C arom.), 132.0 (d, *J* = 8.2 Hz, CH arom. γ to F), 116.5 (d, *J* = 21.8 Hz, CH arom. β to F), 78.4 (CH_2NO_2), 70.9 (*CH*–C=O), 42.3 (*CH*Ar), 30.6 (Me), 29.8 (Me). HRMS (ESI-TOF) calc. for $C_{13}H_{13}FNO_4$ $[M-H]^+$: 266.0829; found: 266.0819.



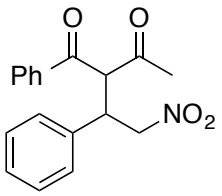
12

4-(2-nitro-1-phenylethyl)heptane-3,5-dione. Flash column chromatograpphy (9:1 Petroleum ether : EtOAc) afforded **12** (5.8 mg, 20.9 μmol, 35%) as colorless oil. IR: υ = 2925, 1728, 1702, 1553, 1493, 1456, 1379, 1097, 763, 702 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35-7.26 (m, 3H, arom.), 7.18-7.15 (m, 2H, arom.), 4.67-4.64 (m, 2H, CH_2NO_2), 4.35-4.27 (m, 2H, CH–C=O + C*H*Ph), 2.59-2.50 (m, 2H, CH_2Me), 2.36-2.25 (m, 1H, CH_2Me), 2.20-2.11 (m, 1H, CH_2Me), 1.07 (t, *J* = 7.2 Hz, 3H, Me), 0.78 (t, *J* = 7.1 Hz, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.7 (C=O), 204.1 (C=O), 136.1 (C arom.), 129.5 (CH arom.), 128.6 (CH arom.), 128.1 (CH arom.), 78.2 (CH_2NO_2), 69.4 (*CH*–C=O), 43.2 (*CH*Ph), 37.0 (CH_2Me), 36.6 (CH_2Me), 29.9 (Me), 7.6 (Me). HRMS (ESI-TOF) calc. for $C_{15}H_{18}NO_4$ $[M-H]^+$: 276.1236; found: 276.1239.



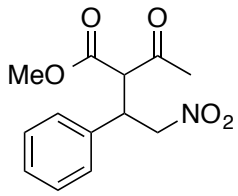
13

1,3-bis(4-methoxyphenyl)-2-(2-nitro-1-phenylethyl)propane-1,3-dione. Flash column chromatography (7:3 Petroleum ether : EtOAc) afforded **13** (4.2 mg, 9.7 μmol, 19%) as a colorless oil. IR: υ = 2924, 2854, 1682, 1600, 1553, 1511, 1457, 1261, 1172, 1028, 838, 702 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.8 Hz, 2H, arom.), 7.80 (d, *J* = 8.9 Hz, 2H, arom.), 7.24-7.15 (m, 5H, arom.), 6.89-6.82 (m, 4H arom.), 5.65 (d, *J* = 8.1 Hz, 1H, CH–C=O), 5.01-4.92 (m, 2H, CH_2NO_2), 4.64-4.60 (m, 1H, C*H*Ph), 3.84 (s, 3H, OMe), 3.82 (s, 3H, OMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.8 (C=O), 192.2 (C=O), 164.4 (*C*–OMe), 164.2 (*C*–OMe), 137.3 (C arom.), 131.5 (CH arom.), 131.3 (CH arom.), 129.4 (C arom.), 129.1 (CH arom.), 129.0 (C arom.), 128.5 (CH arom.), 128.2 (CH arom.), 114.3 (CH arom.), 114.2 (CH arom.), 77.8 (CH_2NO_2), 60.0 (*CH*–C=O), 55.8 (OMe), 44.3 (*CH*Ph). HRMS (ESI-TOF) calc. for $C_{25}H_{22}NO_6$ $[M-H]^+$: 432.1447; found: 432.1447. $C_{25}H_{23}NO_6Na$ $[M+Na]^+$: 456.1423; found: 456.1410.



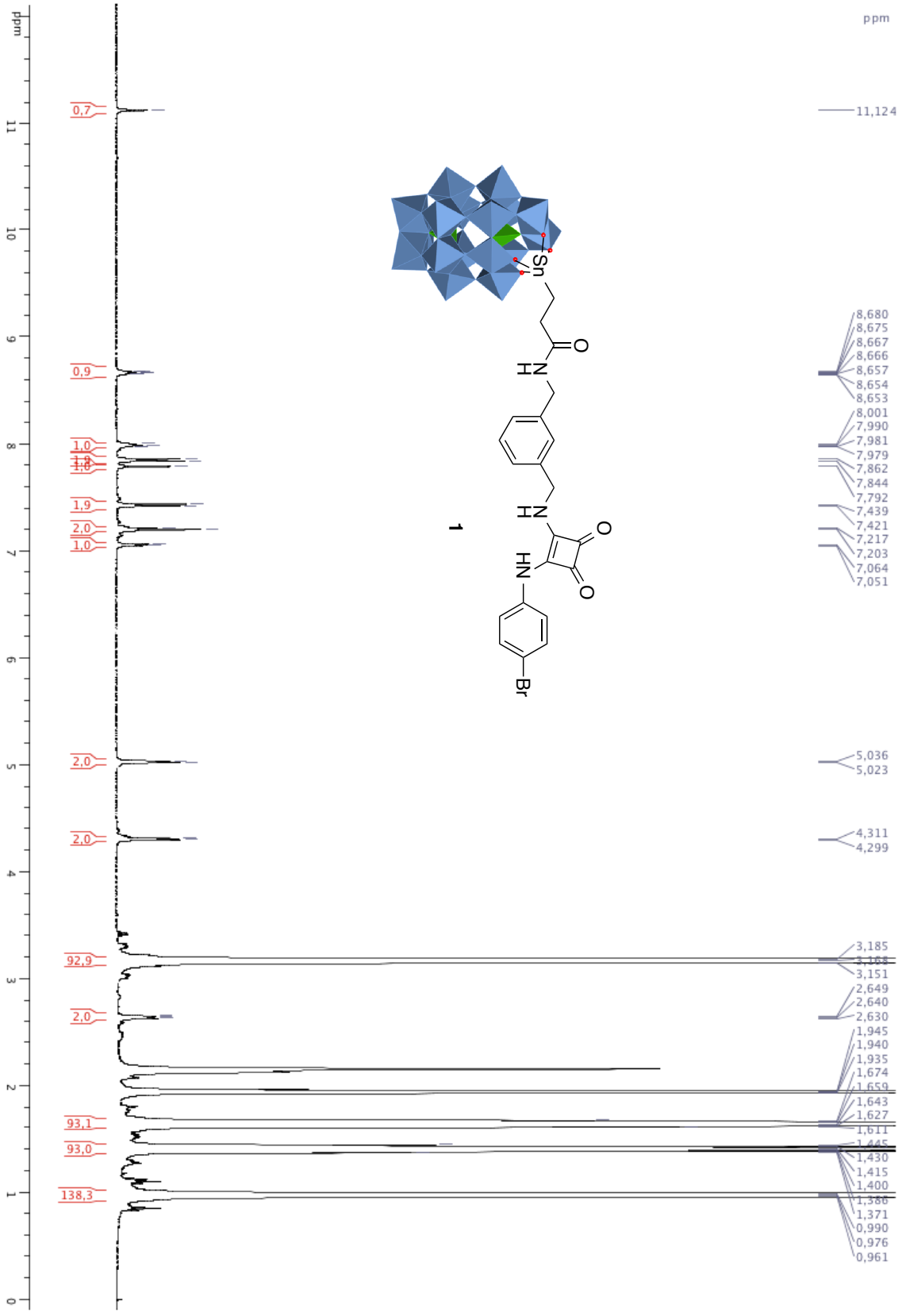
14

2-(2-nitro-1-phenylethyl)-1-phenylbutane-1,3-dione. Flash column chromatography (85:15 Petroleum ether/EtOAc) afforded **14** (16.9 mg, 54.3 μmol, 99%) as a colorless oil and a mixture of diastereomers. The spectral data of **14** corresponded to those described in the literature (Kasaplar, P.; Riente, P.; Hartmann, C.; Pericàs, M. A. *Adv. Synth. Catal.* **2012**, *354*, 2905-2912). HRMS (ESI-TOF) calc. for $C_{18}H_{16}NO_4$ $[M-H]^+$: 310.1079; found: 310.1078.



15

Methyl 2-acetyl-4-nitro-3-phenylbutanoate. Flash column chromatography (9:1 Petroleum ether : EtOAc) afforded **15** (13.5 mg, 50.9 μmol, 97%) as a colorless oil and a mixture of diastereomers. The spectral data of **15** corresponded to those described in the literature (Kasaplar, P.; Riente, P.; Hartmann, C.; Pericàs, M. A. *Adv. Synth. Catal.* **2012**, *354*, 2905-2912). HRMS (ESI-TOF) calc. for $C_{13}H_{14}NO_5$ $[M-H]^+$: 248.0872; found: 264.0863.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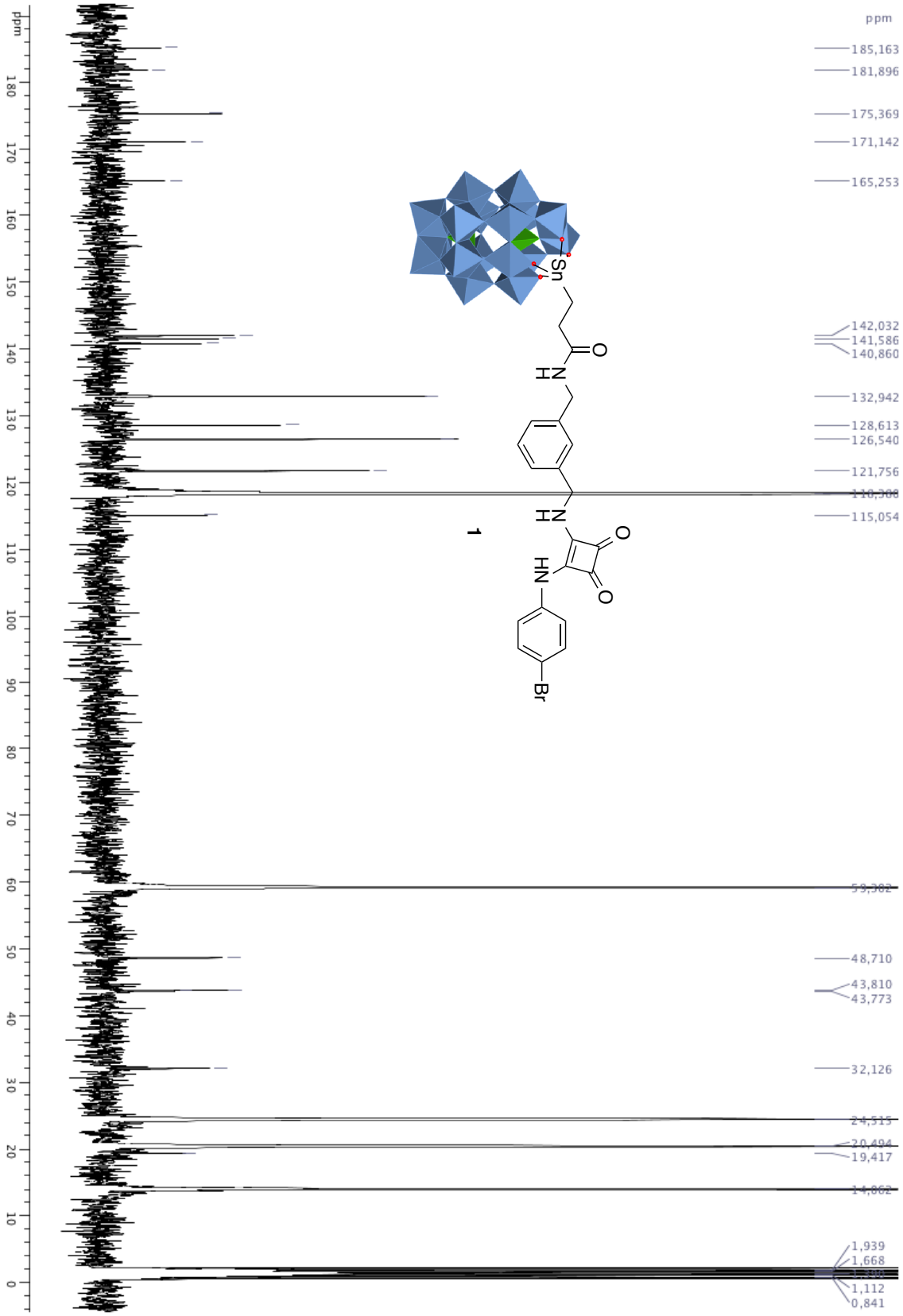
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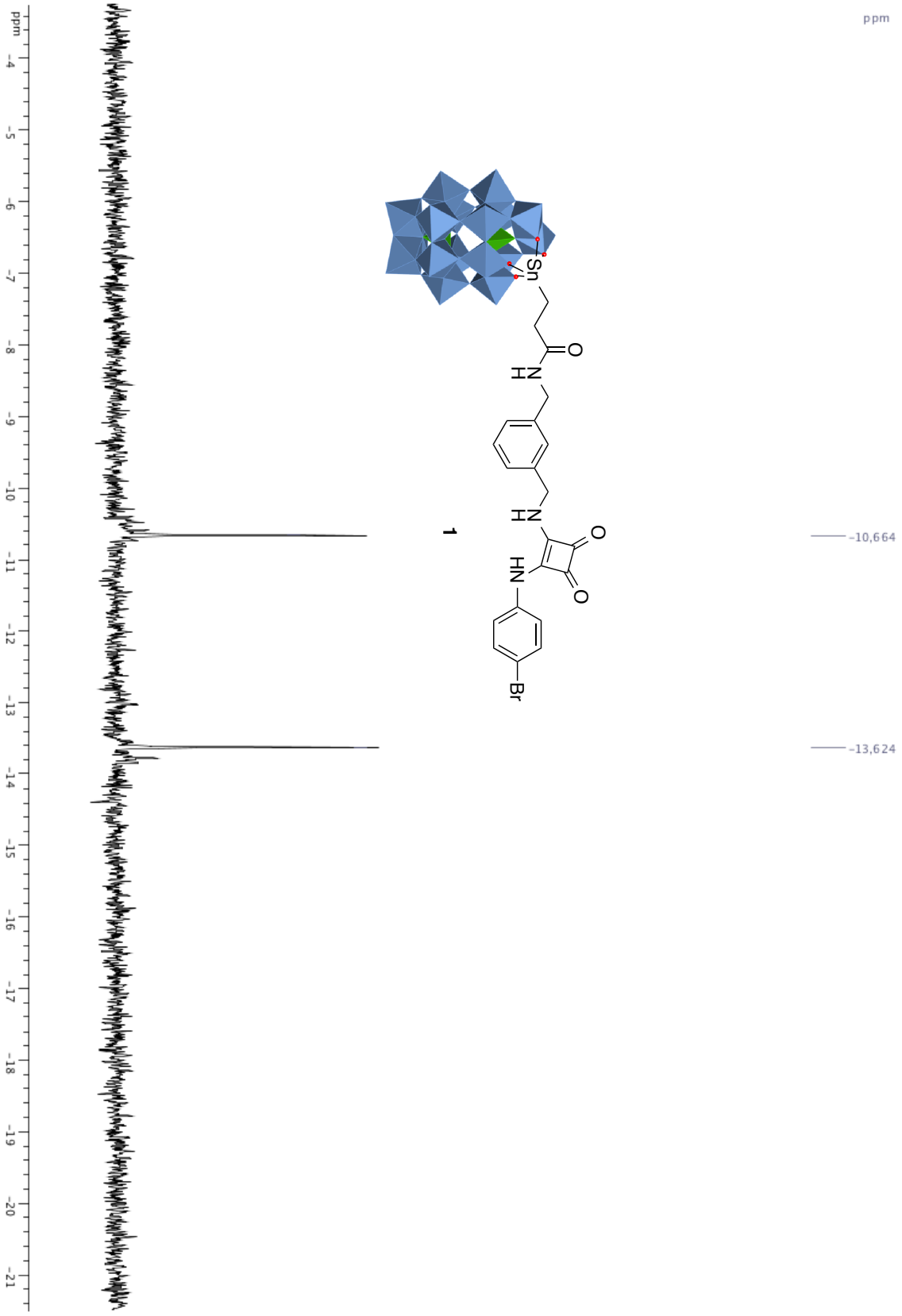
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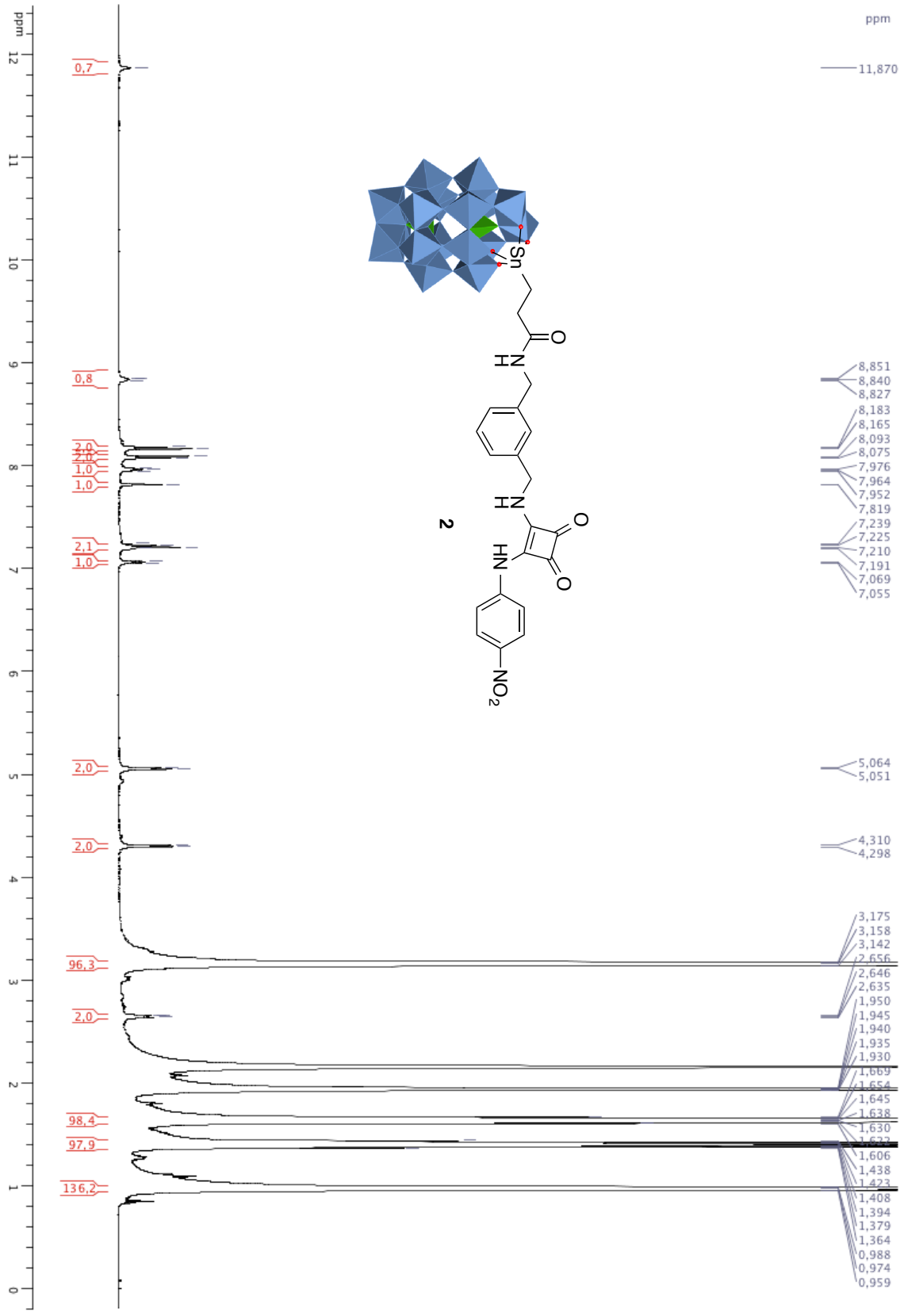
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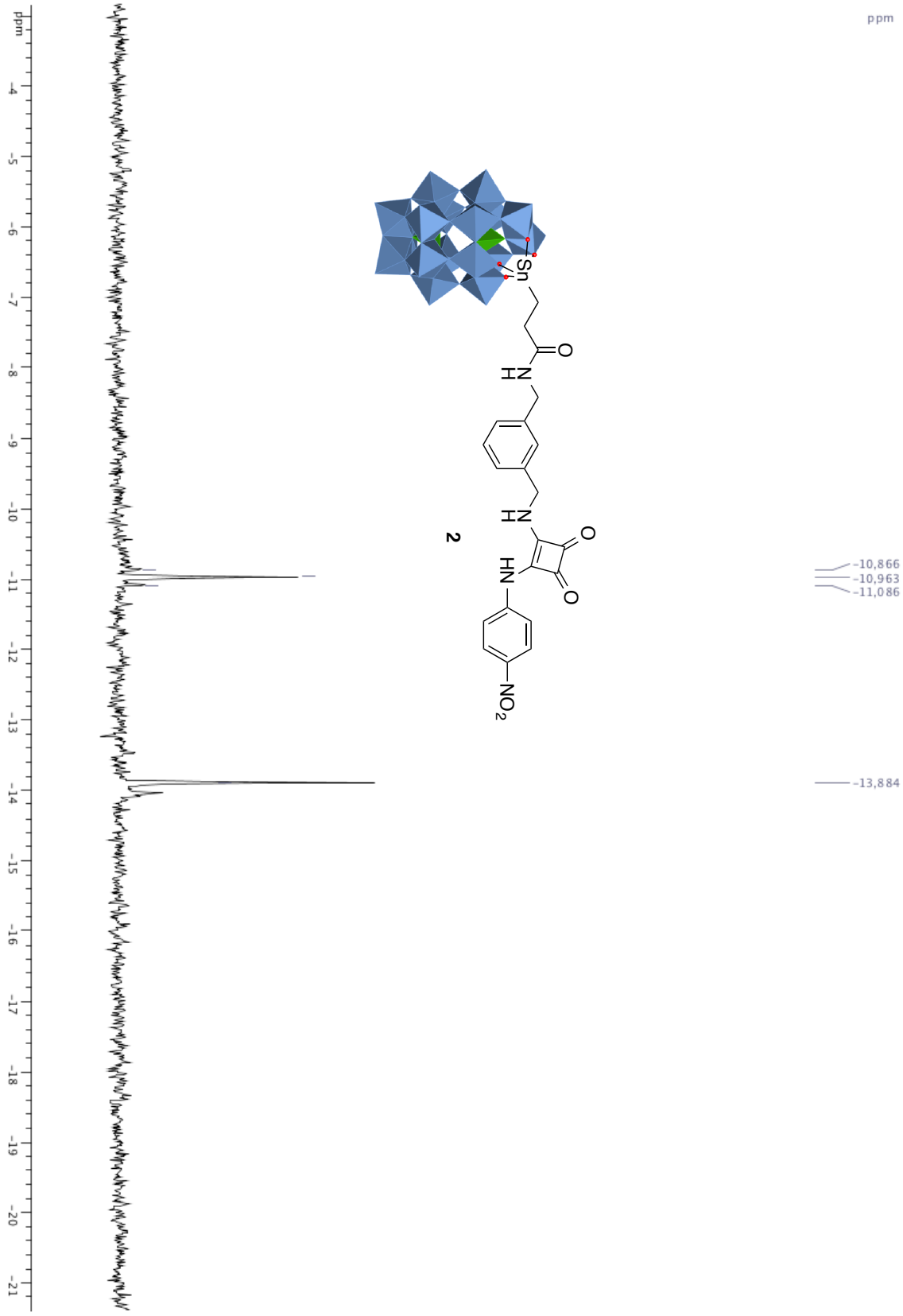
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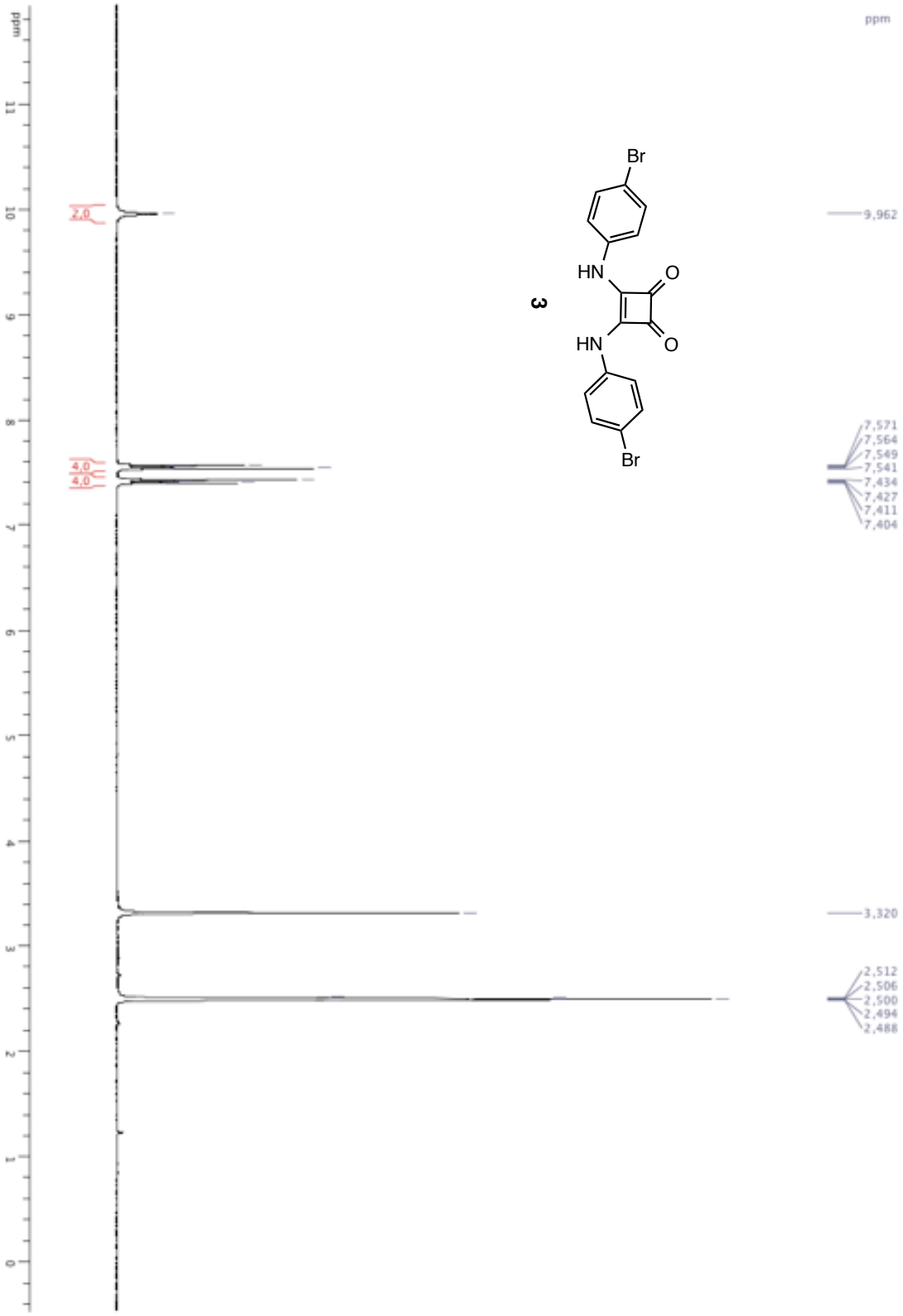
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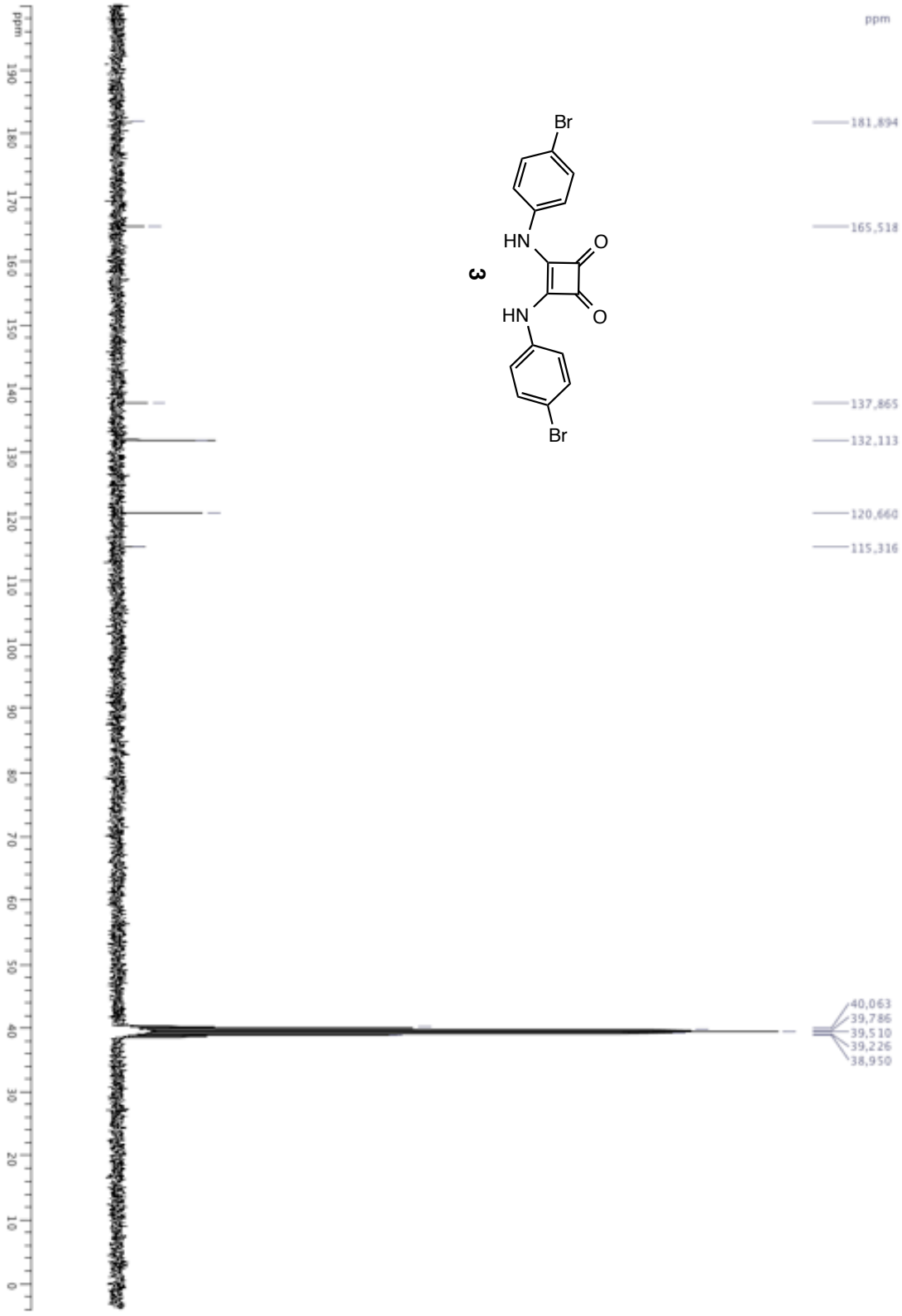
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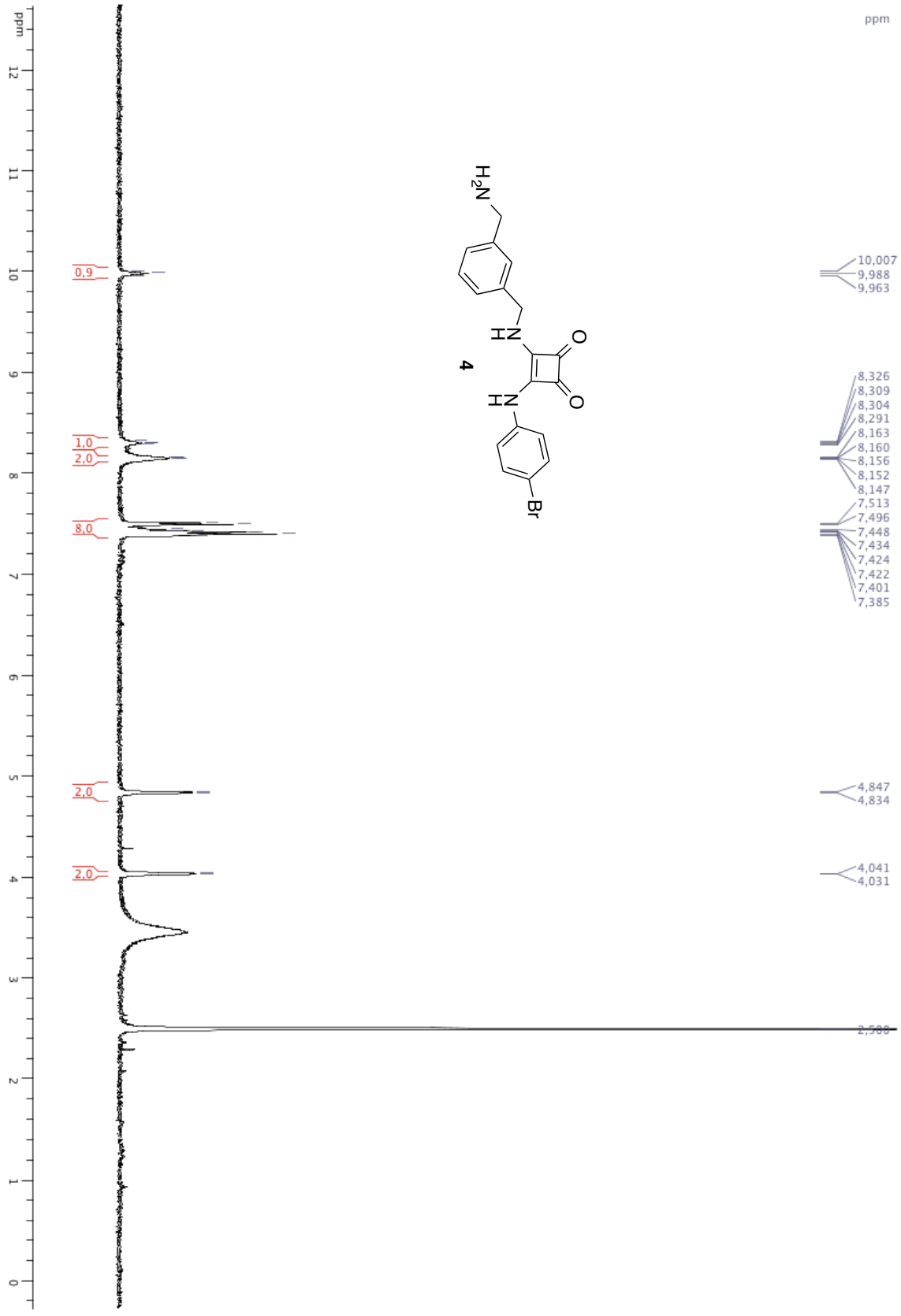
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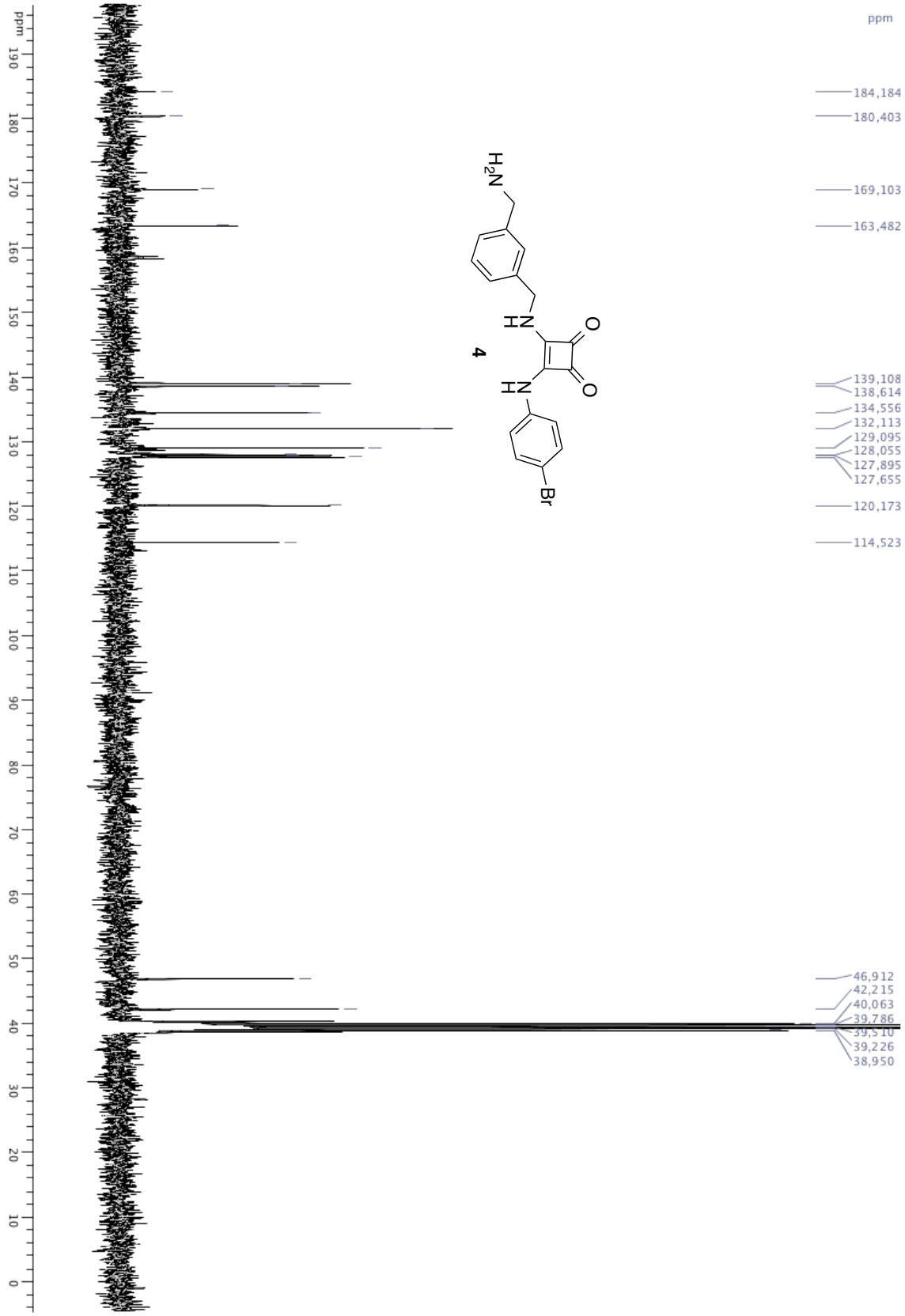
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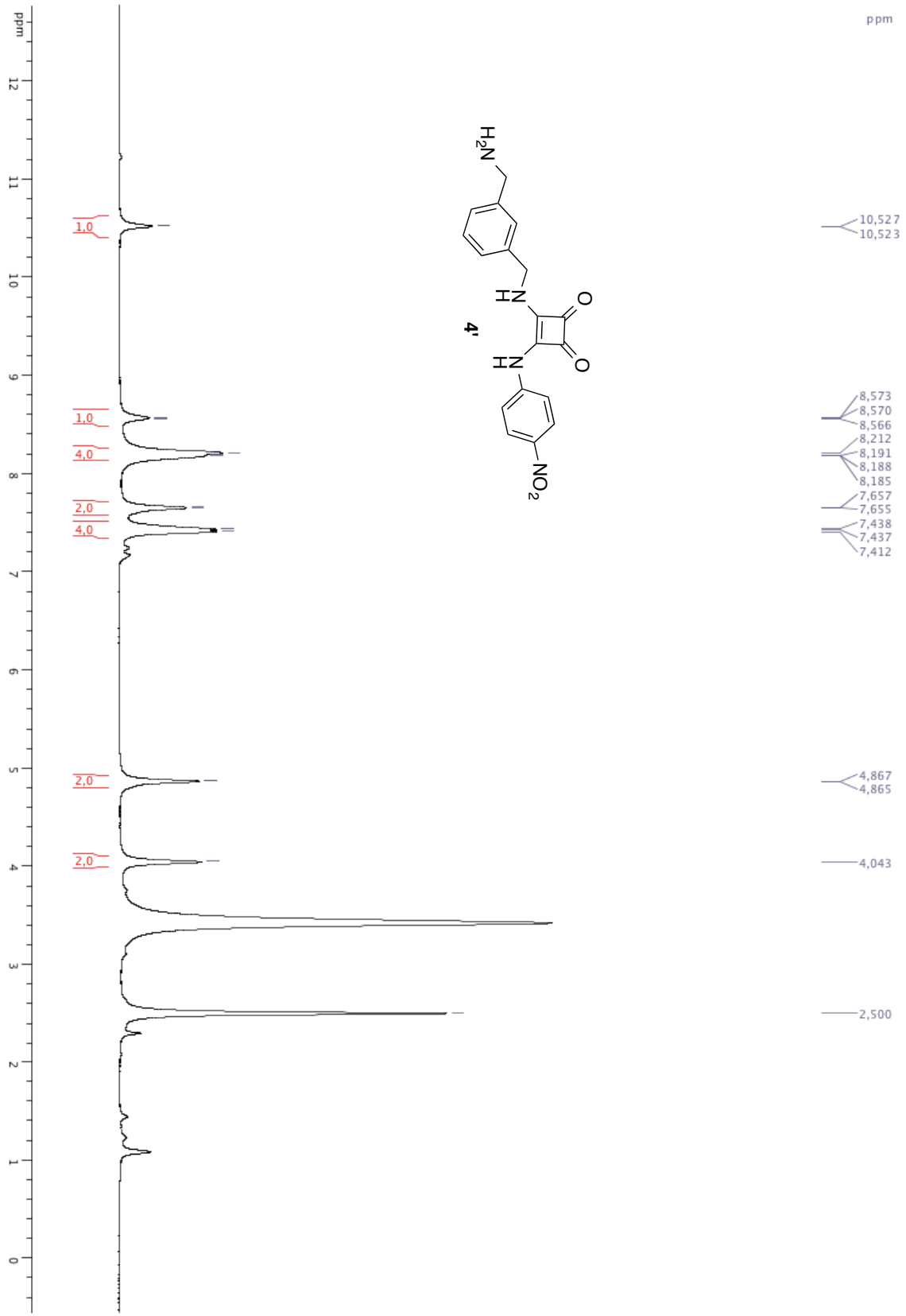
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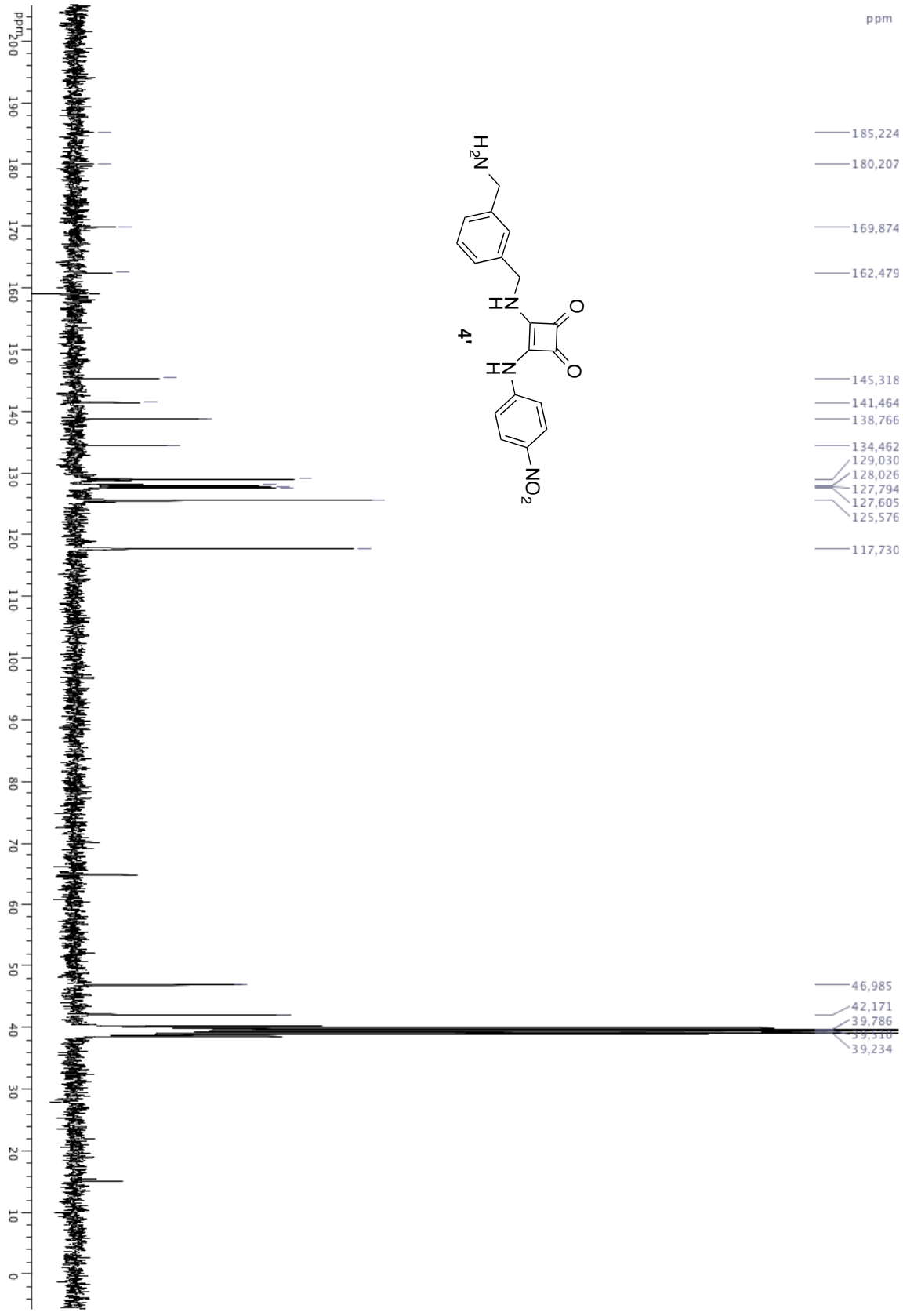
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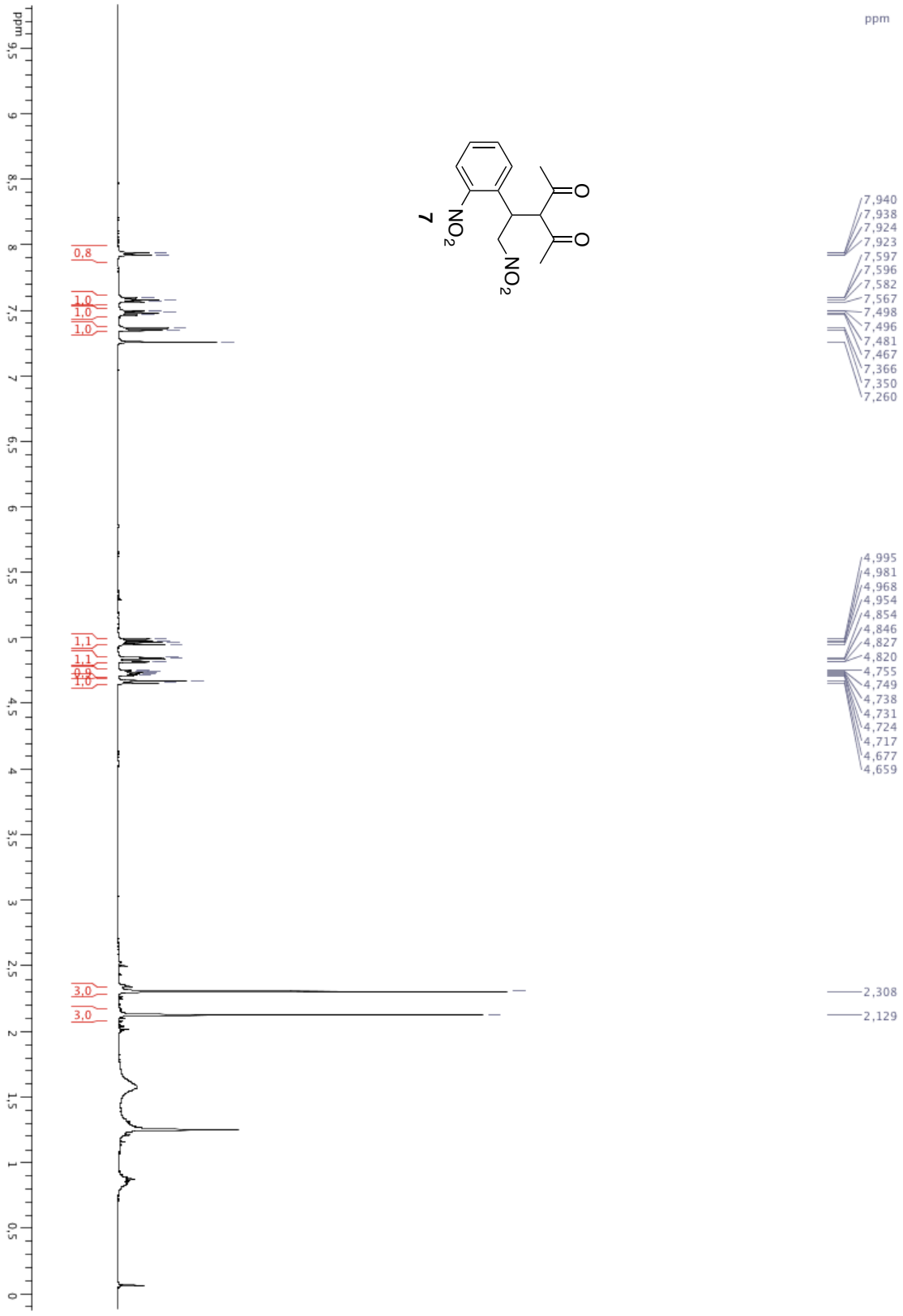
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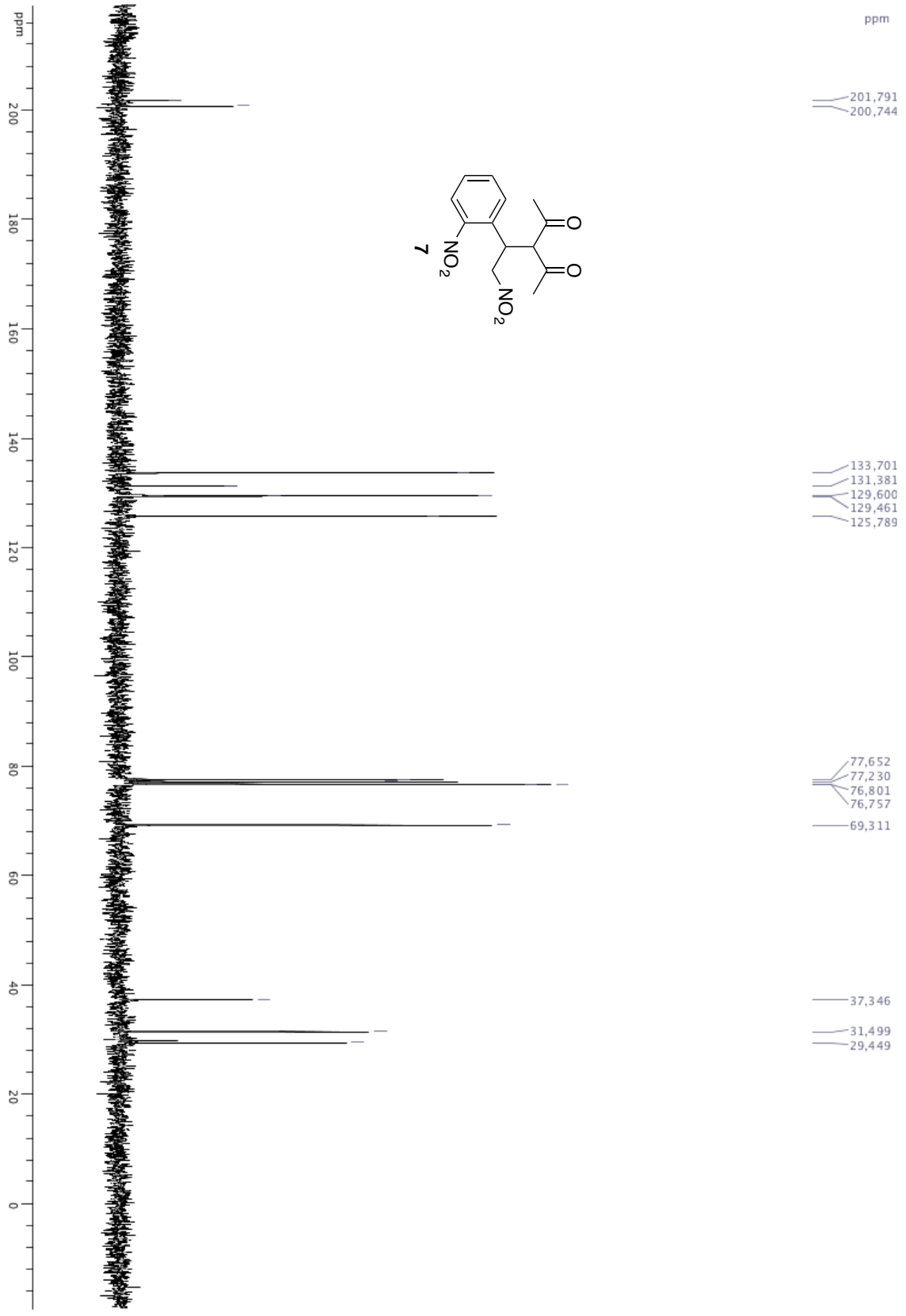
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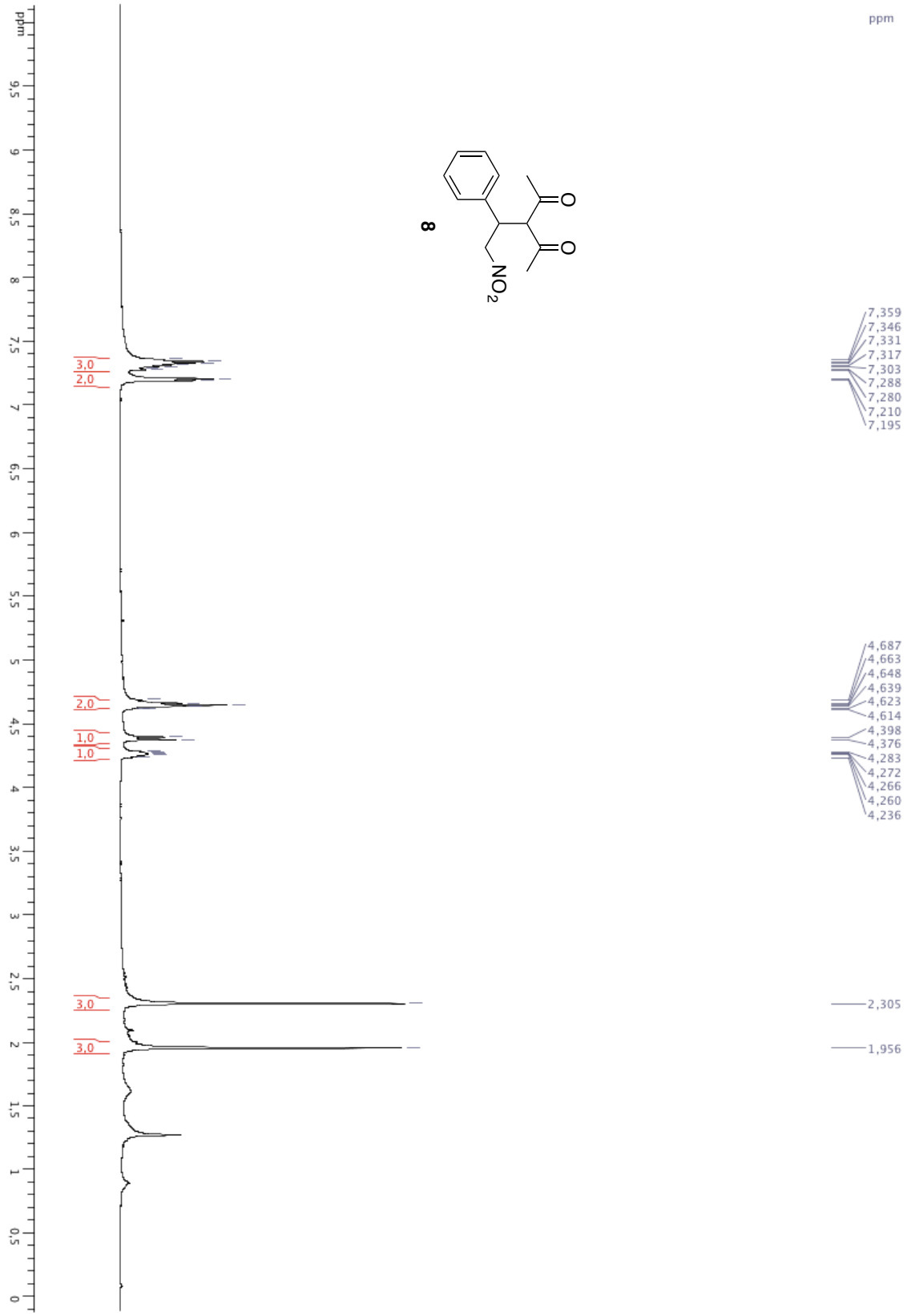
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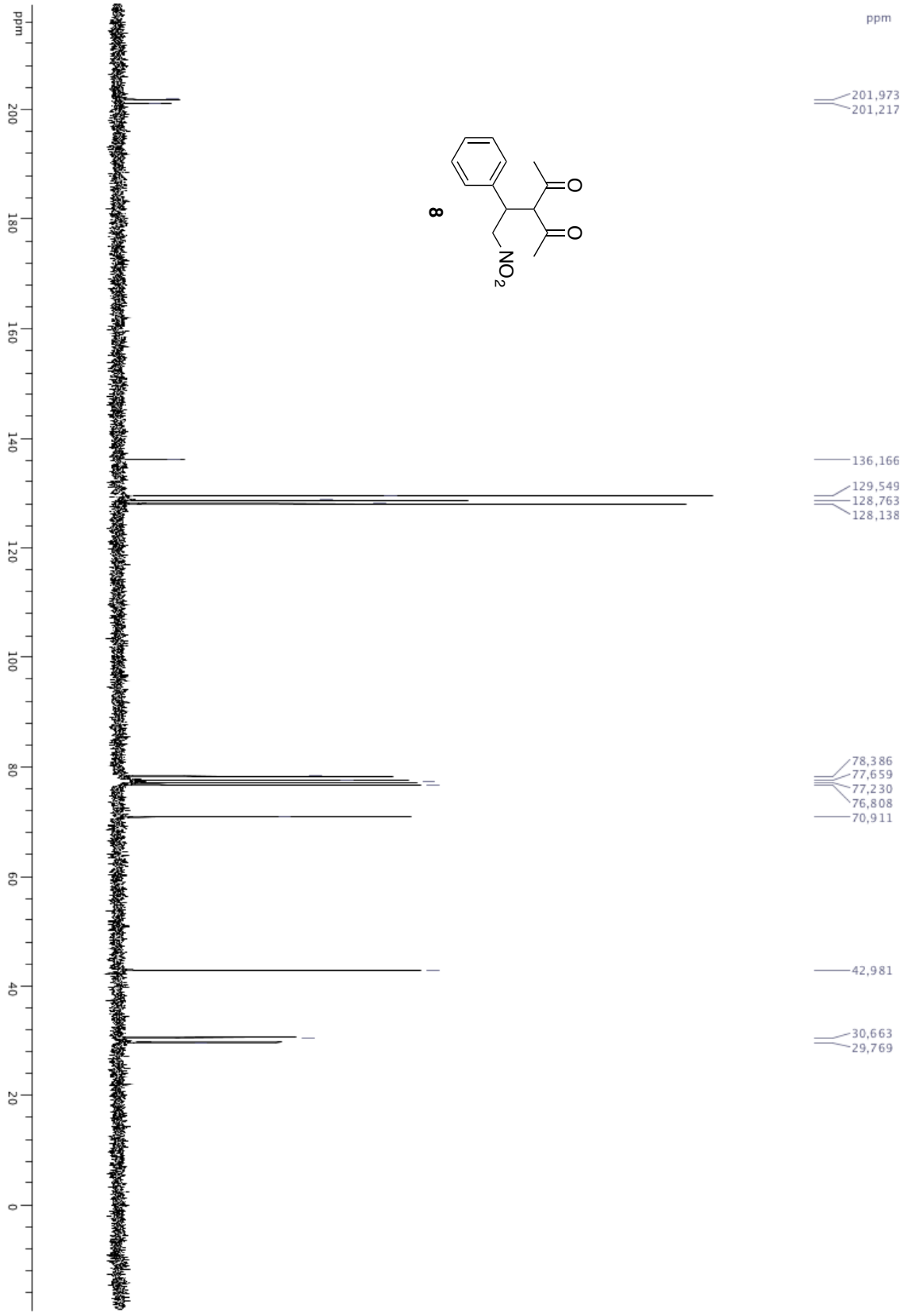
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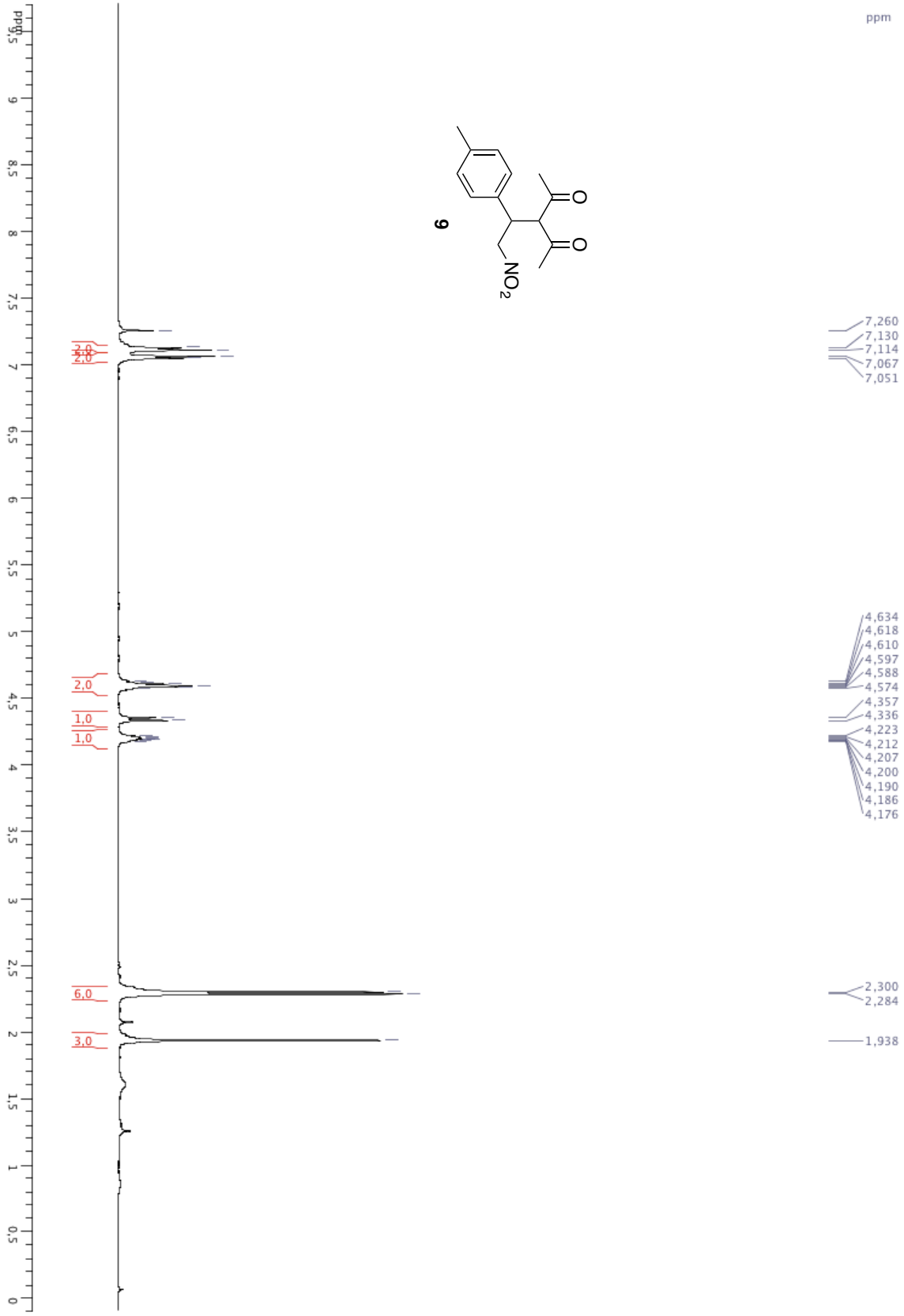
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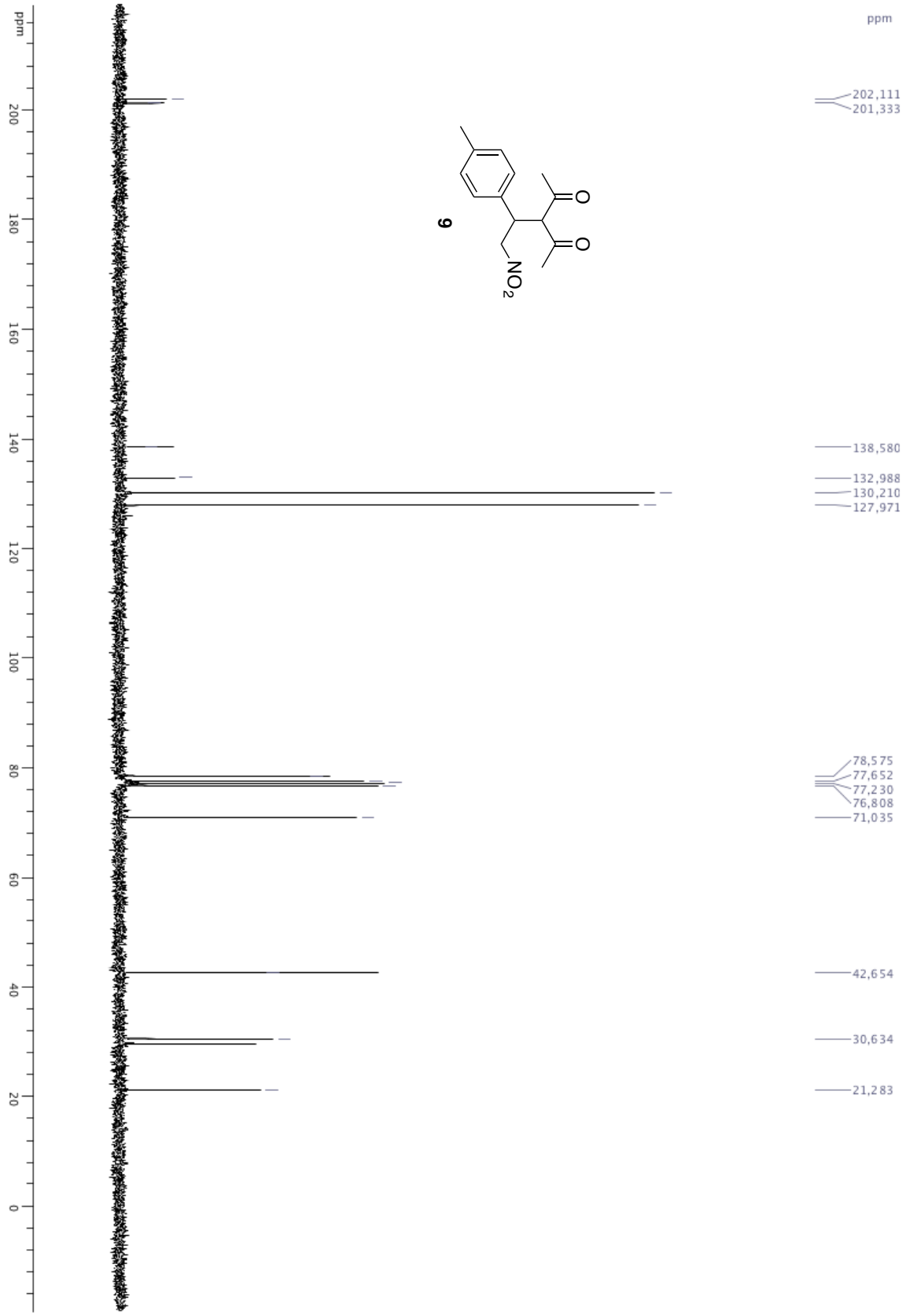
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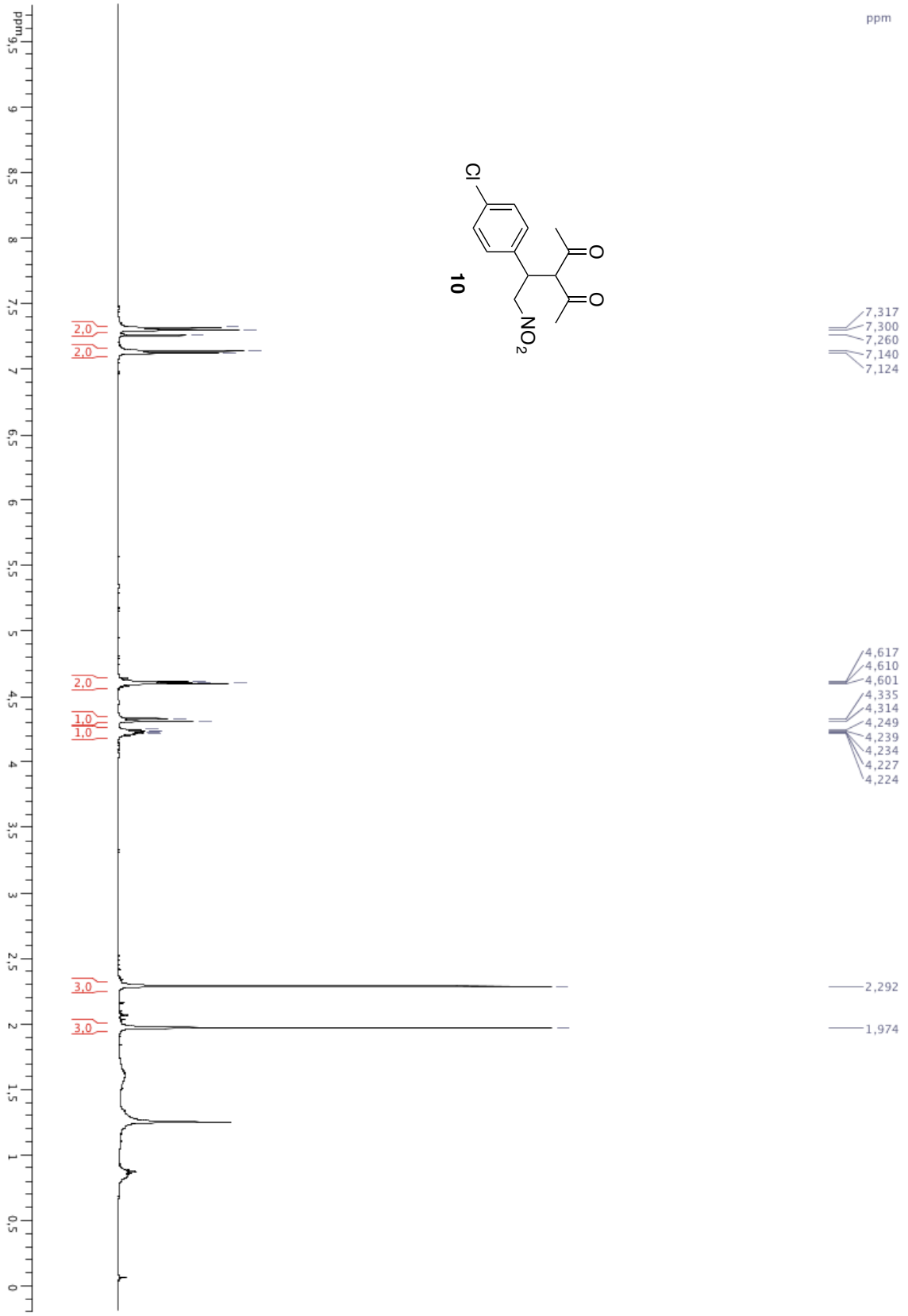
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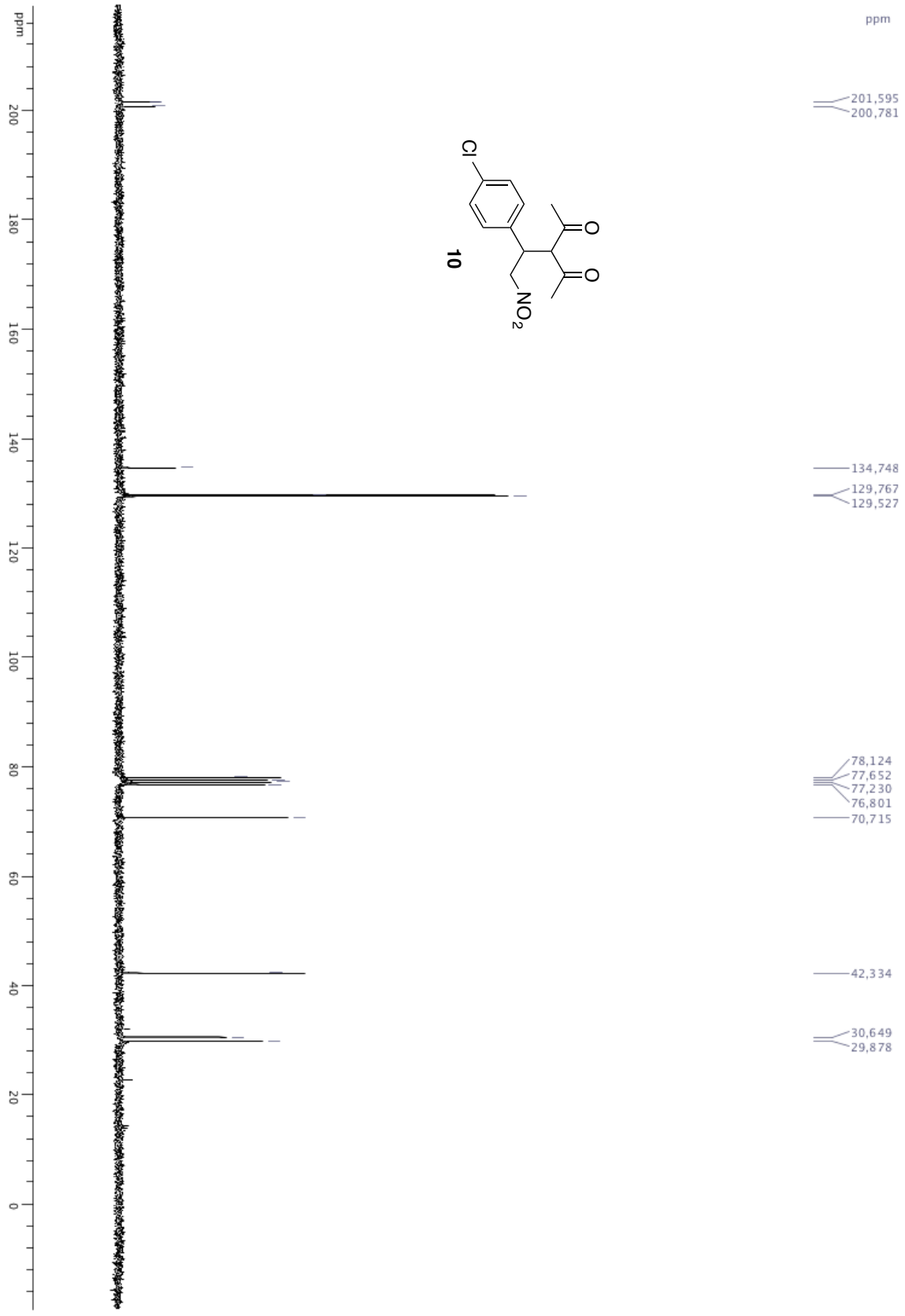
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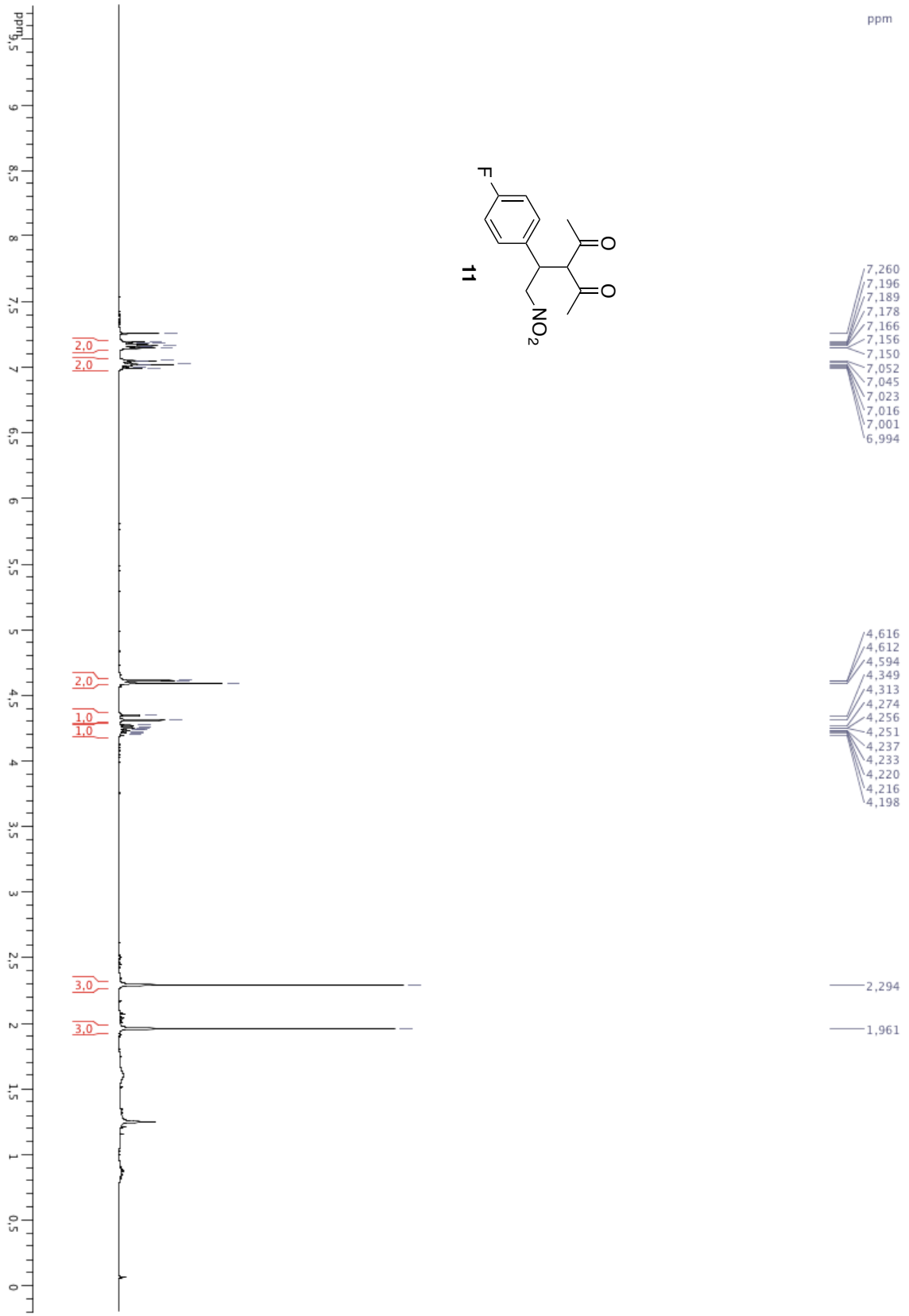
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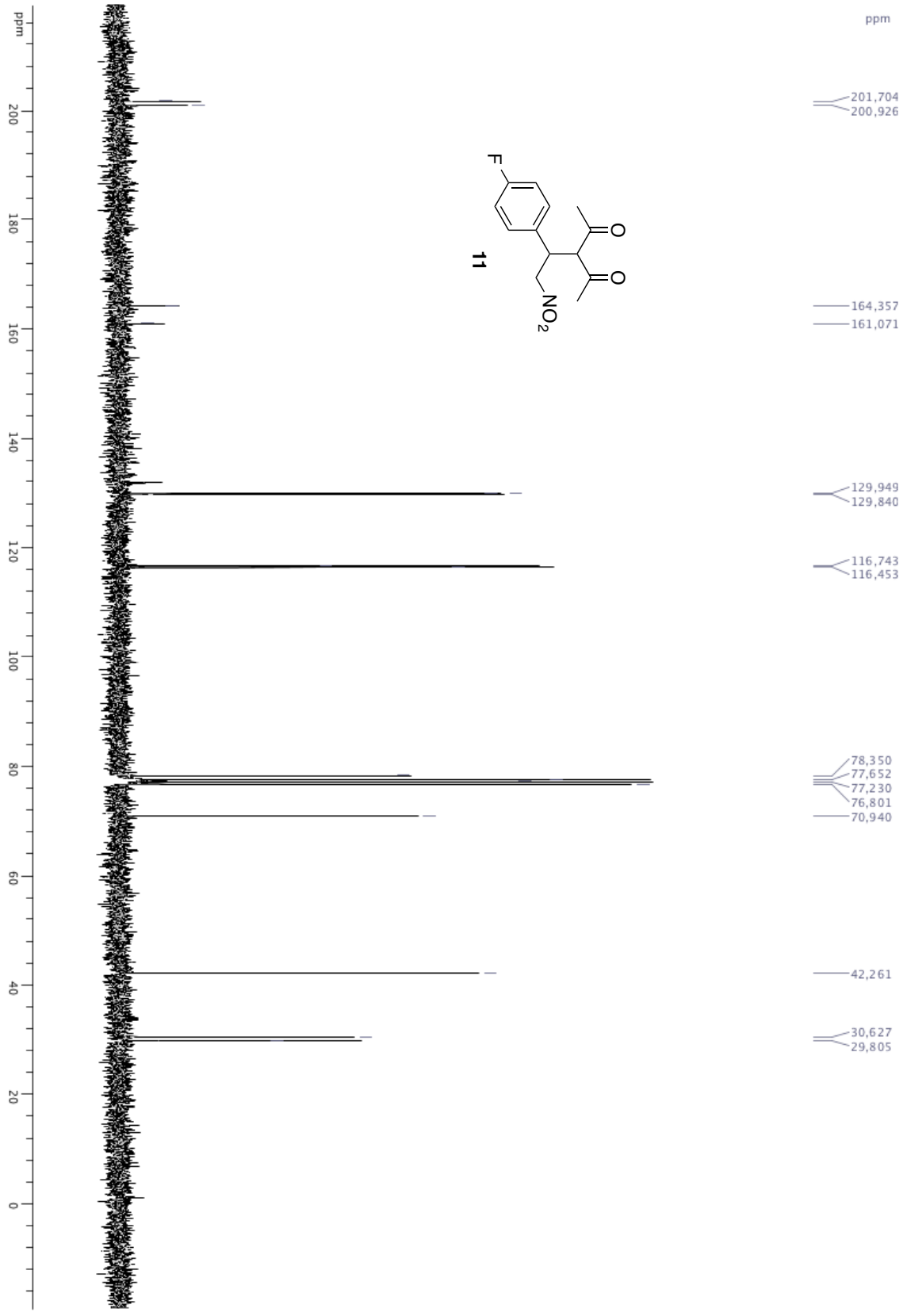
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O
NO2
11
ppm
201,704
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161,071
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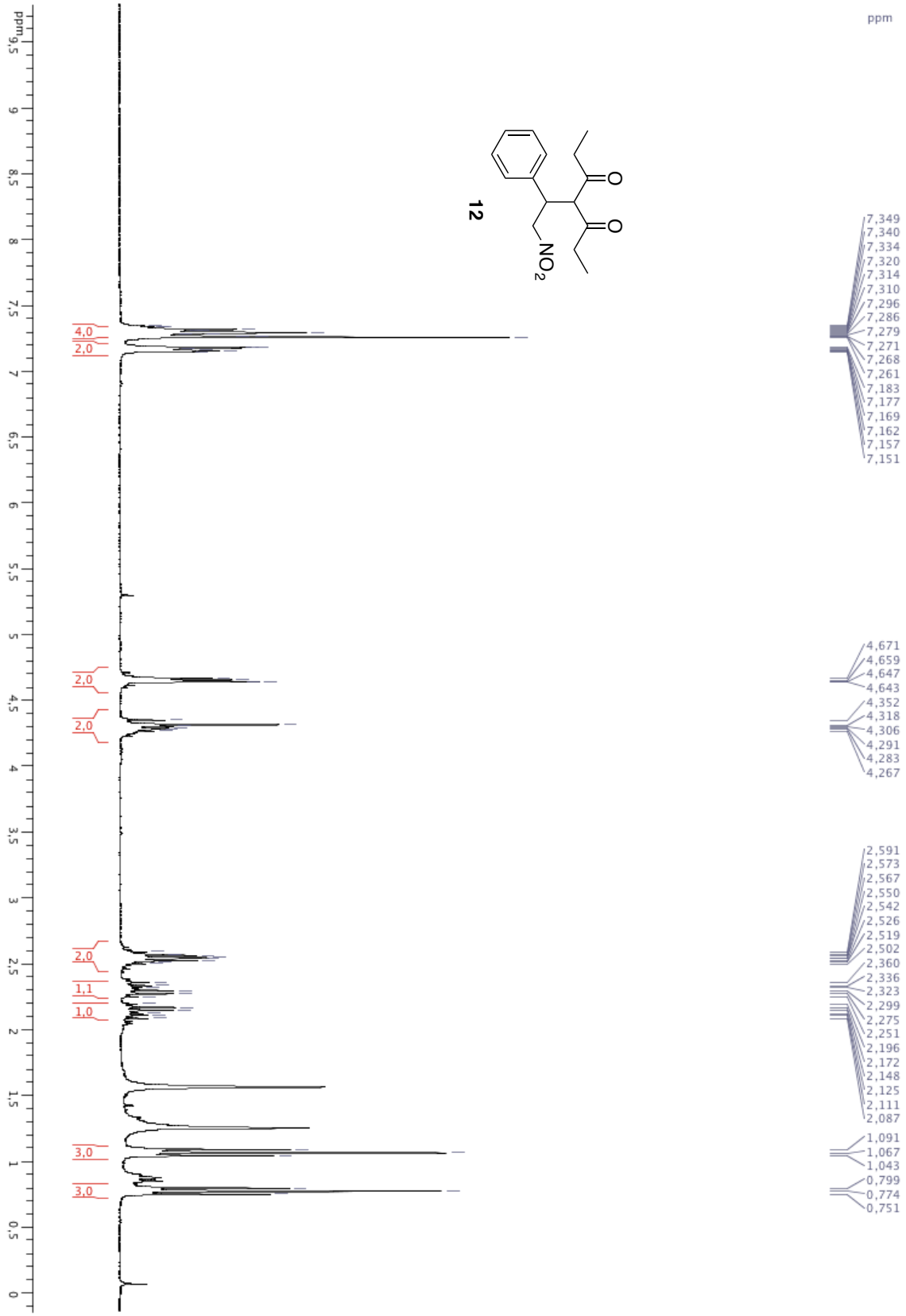
30,627
29,805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7,271
7,268
7,261
7,183
7,177
7,169
7,162
7,157
7,151
4,671
4,659
4,647
4,643
4,352
4,318
4,306
4,291
4,283
4,267
2,591
2,573
2,567
2,550
2,542
2,526
2,519
2,502
2,360
2,336
2,323
2,299
2,275
2,251
2,196
2,172
2,148
2,125
2,111
2,087
1,091
1,067
1,043
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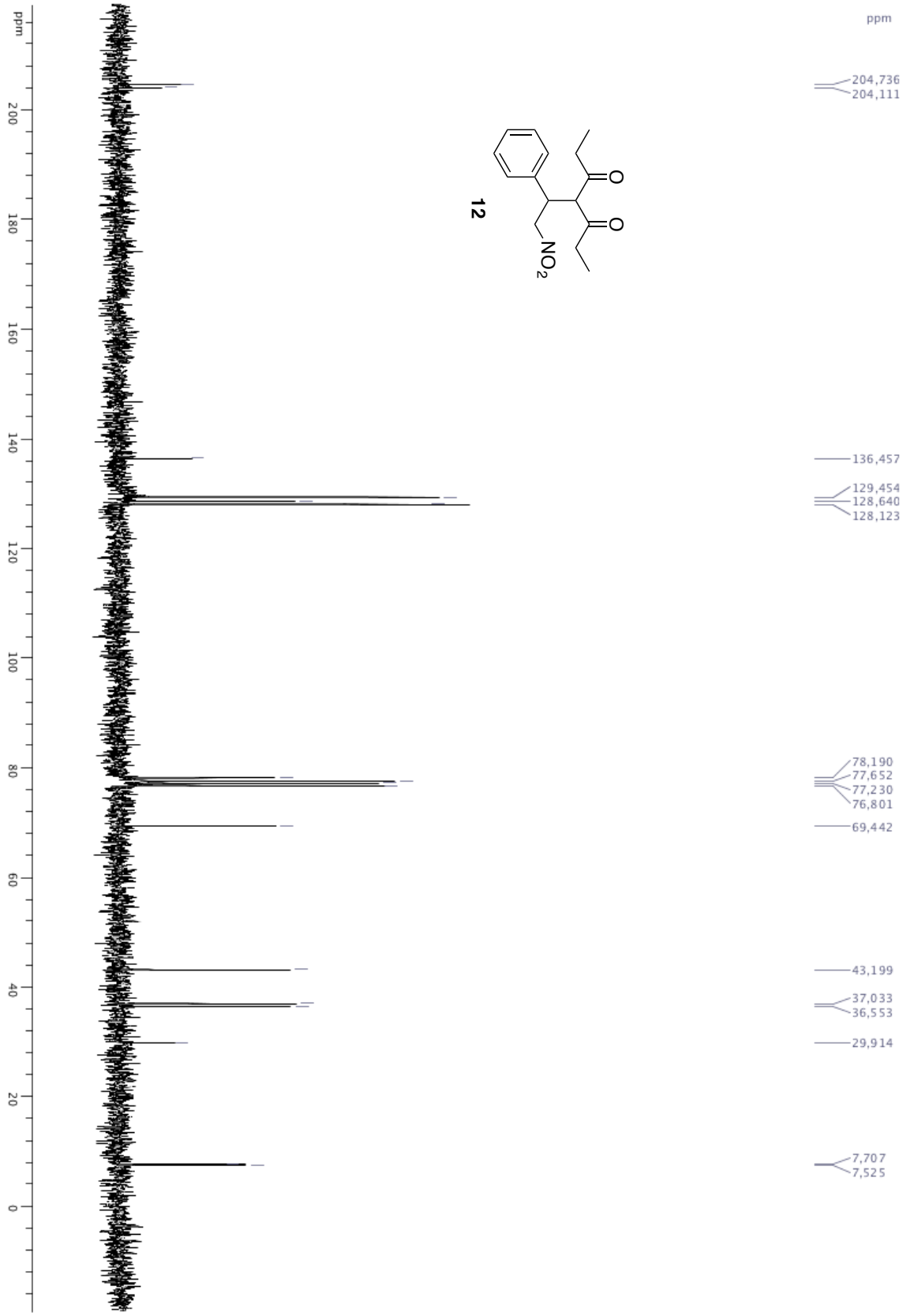
3,0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140
120
100
80
60
40
20
0
O
O
NO2
12
ppm
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204,111
136,457
129,454
128,640
128,123
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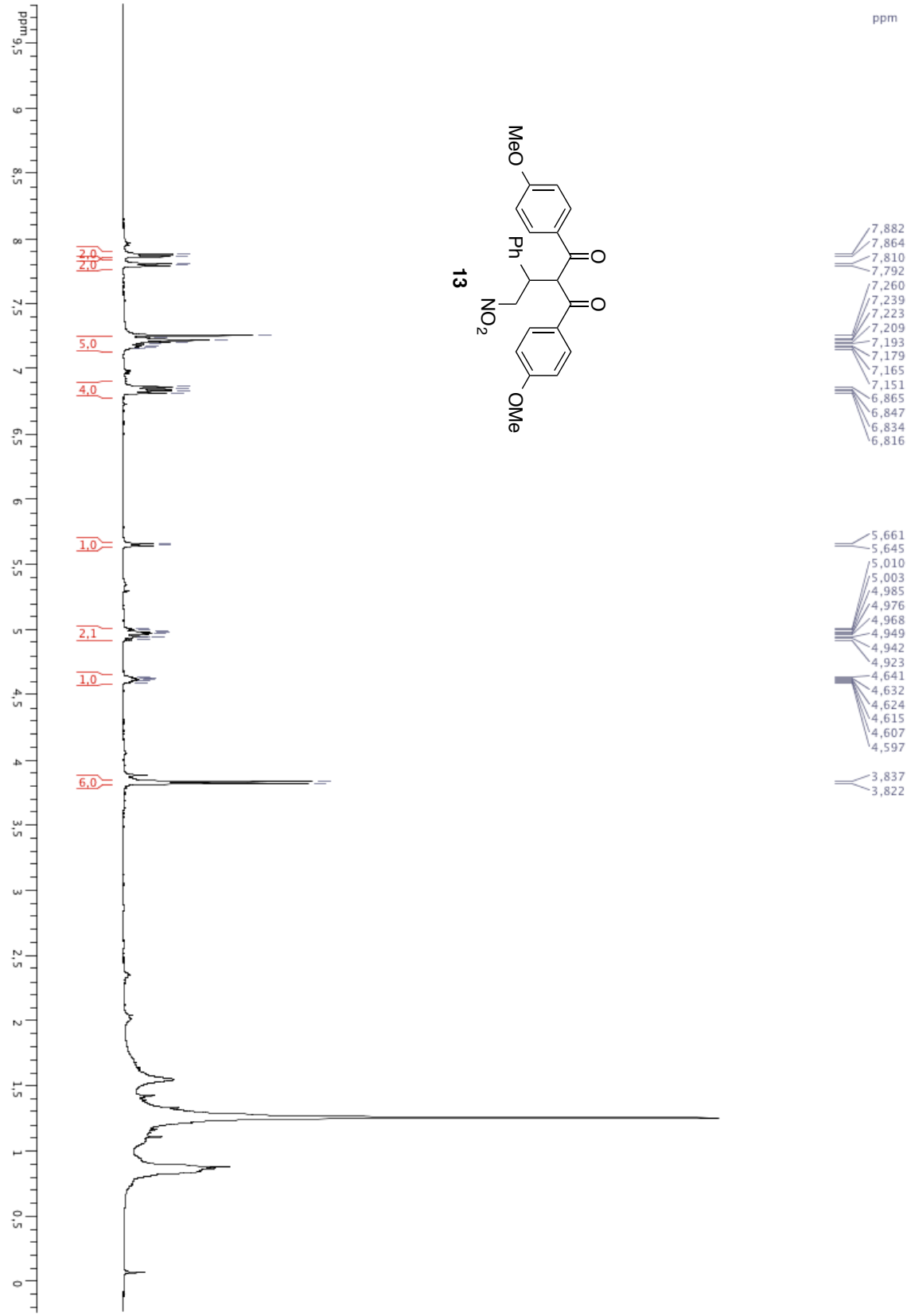
77,230
76,801
69,442
43,199
37,033
36,553
29,914
7,707
7,525


MeO
Ph
NO2
O
O
OMe
13
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7,810
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7,209
7,193
7,179
7,165
7,151
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6,847
6,834
6,816
5,661
5,645
5,010
5,003
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4,615
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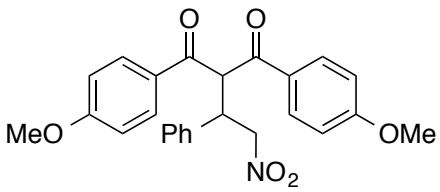
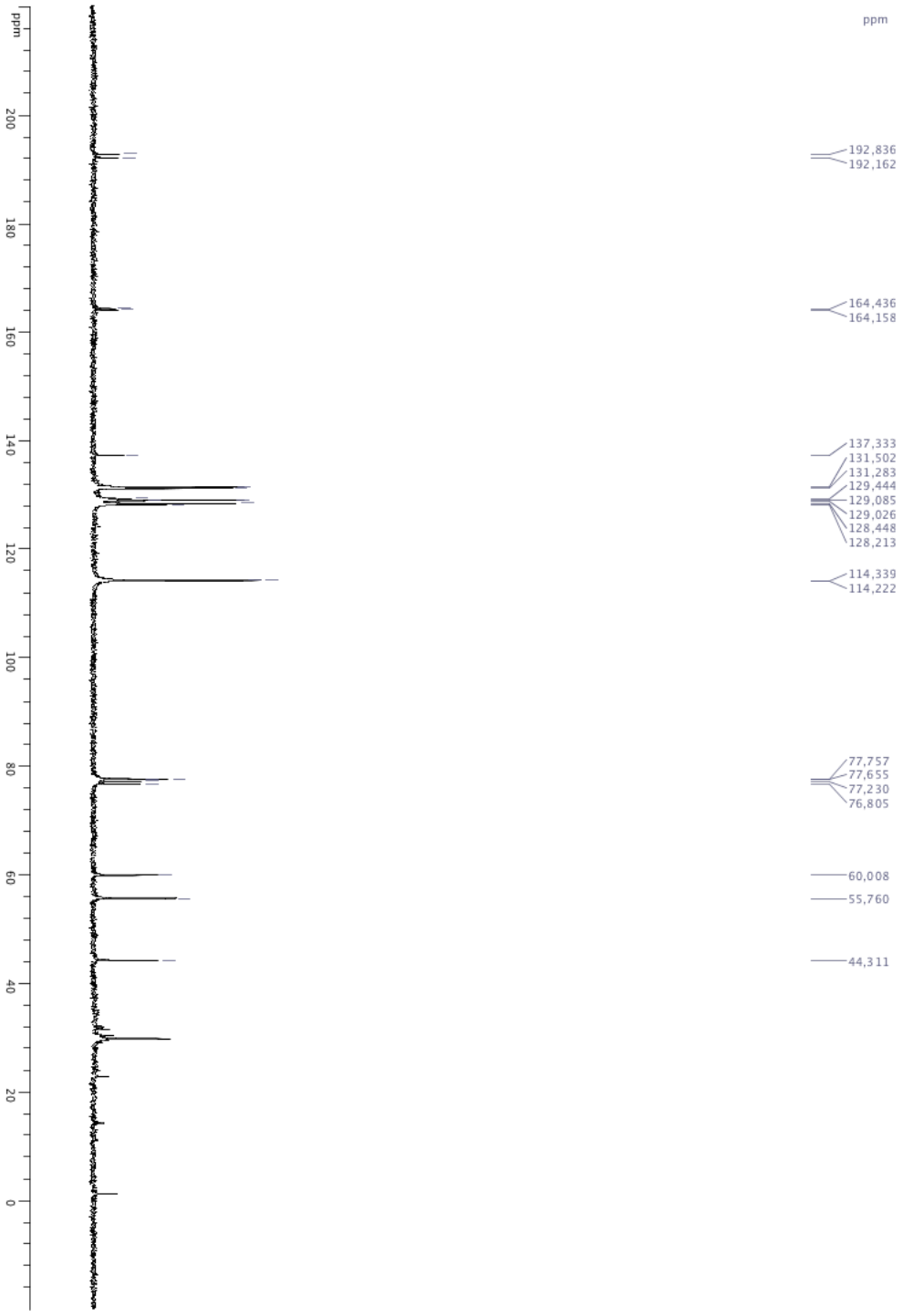

O
O
MeO
Ph
OMe
NO2

13


ppm
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180
160
140
120
100
80
60
40
20
0
ppm
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192,162
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164,158
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131,502
131,283
129,444
129,085
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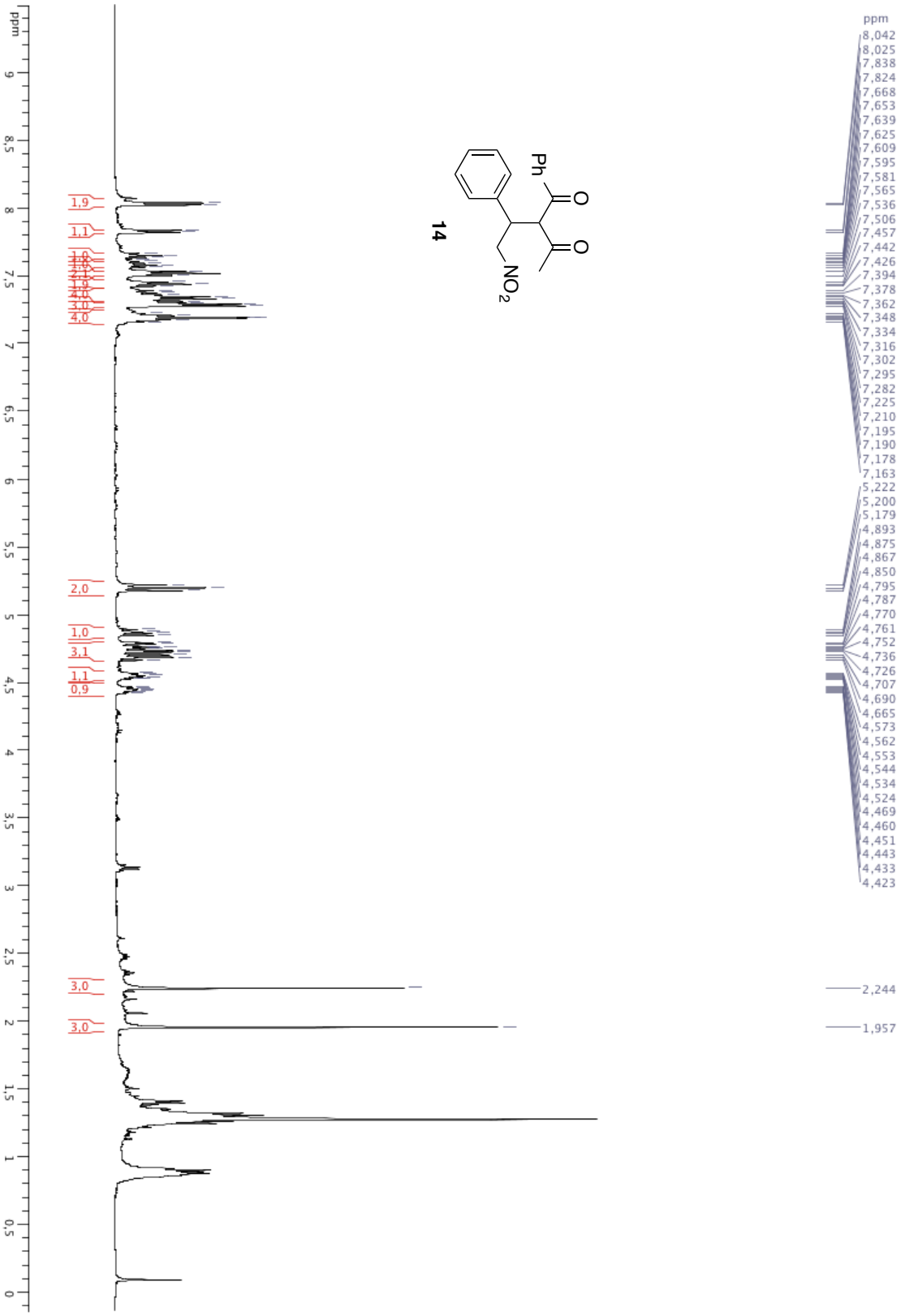
128,213
114,339
114,222
77,757
77,655
77,230
76,805
60,008
55,760
44,311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8
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6,5
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2
1,5
1
0,5
0
1,9
1,1
4,0
2,0
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3,1
1,1
0,9
3,0
3,0
Ph
O
O
NO2
14
ppm
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7,824
7,668
7,653
7,639
7,625
7,609
7,595
7,581
7,565
7,536
7,506
7,457
7,442
7,426
7,394
7,378
7,362
7,348
7,334
7,316
7,302
7,295
7,282
7,225
7,210
7,195
7,190
7,178
7,163
5,222
5,200
5,179
4,893
4,875
4,867
4,850
4,795
4,787
4,770
4,761
4,752
4,736
4,726
4,707
4,690
4,665
4,573
4,562
4,553
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4,524
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4,460
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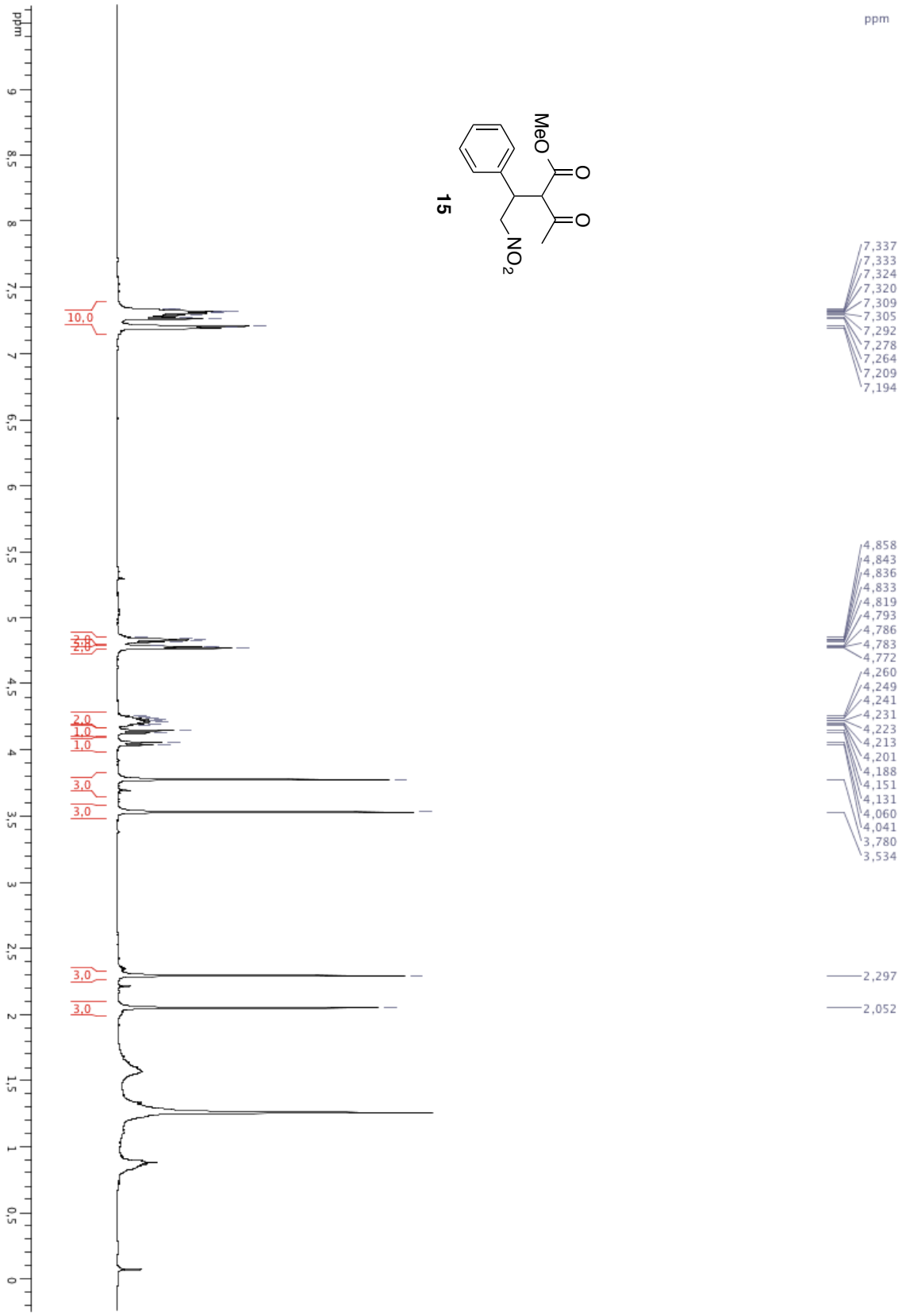
1,957


ppm
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O
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7,264
7,209
7,194
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4,843
4,836
4,833
4,819
4,793
4,786
4,783
4,772
4,260
4,249
4,241
4,231
4,223
4,213
4,201
4,188
4,151
4,131
4,060
4,041
3,780
3,534
2,297
2,052
10,0
2,0
2,0
2,0
1,0
1,0
3,0
3,0
3,0
3,0