Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Catalytic Highly Asymmetric 1,5(6)-Selective Cyclization Reaction of *α*-Hydroxyimino Cyclic Ketones: Direct Approach to Ring-Fused Hydroxyimino Dihydropyrans

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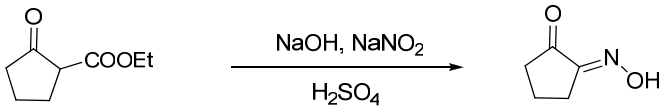
Supporting Information

Contents

1.0 General Methods for Procedure of Synthesis:

All solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC), column chromatography purifications were carried out using silica gel GF254. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Bruker 300 MHz spectrometer in $CDCl_3$ and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on 300 MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard unless otherwise noted. Data are presented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, cm = complex multiplet) and coupling constant in Hertz (Hz). Infrared (IR) spectra were recorded on a FT-IR spectrometer. Optical rotations were recorded on a Perkin-Elmer 341 polarimeter. HR-MS was measured with an APEX II 47e mass spectrometer. The ee values determination was carried out using chiral high-performance liquid chromatography (HPLC) with Daicel Chiracel AD-H column on Waters with a 2998 UV-detector and the dr values determined by 300 Hz ^{1}H NMR. Thiourea catalysts were synthesized according to the procedures.[1-3] β, γ-unsaturated α-keto esters were synthesized according to the procedures.[4]

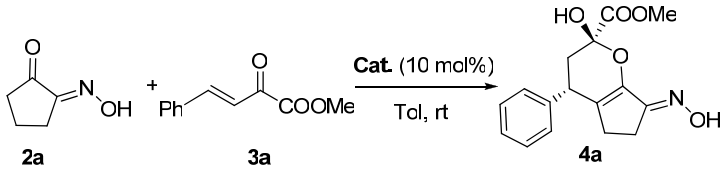
2.0 General Procedure for Substrates



A solution of sodium hydroxide (11.0 g) in water (200 mL) was added slowly to ethyl 2-oxocyclopentanecarboxylate (42.5 g) in a narrow-mouthed bottle. A solution of sodium nitrite (17.2 g) in water (50 mL) was added. The bottle was tightly sealed and shaken mechanically for 48 hours at room temperature. The pale yellow solution was cooled to 0 °C and a small excess of cold sulfuric acid (6 N, 100 mL) was added with shaking. A considerable amount of gas was evolved. The solution was allowed to stand for 30 minutes and then extracted with ten 50-mL portions of ether. The ether solution was dried over magnesium sulfate (20 minutes, with shaking) and the solvent re-moved at 40 °C, then the last traces being removed by raising the temperature to

70 °C and reducing the pressure to 20 mm for 5 minutes. The crude product was applied to silica gel for purification of the pure product.

3.0 General Procedure for Asymmetric 1,5(6)-Selective Cyclization

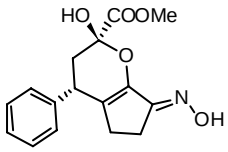


2a **3a** **4a**

Catalyst **1c** (0.02 mmol, 10 mol%), 2-(hydroxyimino) cyclopentanone **2a** (0.2 mmol, 1equiv) and (*E*)-methyl 2-oxo-4-phenylbut-3-enoate **3a** (0.24 mmol, 1.1 equiv), were dissolved in 1.0 mL toluene at room temperature. The reaction progress was monitored by TLC. After complete consumption of the **2a**, the mixture was applied to silica gel (CH_2Cl_2/EtOAc, 92:8) for purification of the desired product **4a**. The enantiomeric ratio was determined by HPLC on a chiral stationary phase, and the dr. was determined by ^{1}H NMR spectroscopy (300 Hz). **4b-q** were prepared using the same method.

4.0 Characterization Data

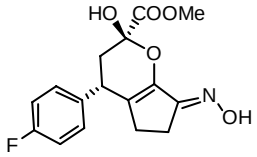
4a: (2*R*,4*S*,*E*)-methyl 2-hydroxy-7-(hydroxyimino)-4-phenyl-2,3,4,5,6,7-hexahydrocy clopenta[*b*]py ran-2-carboxylate



Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to afford **4a** in 82% yield; $[\alpha]^{20}_D$= 34 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19-7.36(m, 5 H), 3.81(br s, 4 H), 2.63-2.67(m, 2 H), 2.19-2.32(m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.8, 159.9, 144.4, 140.8, 129.8, 128.8, 128.1, 127.1, 95.8, 53.3, 37.6, 37.1, 26.0, 23.0. **HRMS-ESI** (*m/z*): calcd for $C_{16}H_{17}NO_5$+H^+: 304.1179; found: 304.1188, 2.7ppm. **IR**: 3329.8, 2924.9, 1746.1, 1653.4, 1451.5, 1290.0, 1243.4, 1135.4, 931.1, 844.2cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 30/70, 1.0mL/min, 255 nm.) Retention time: t_{minor} = 30.42 min, t_{major} = 18.53 min, ee = > 99%.

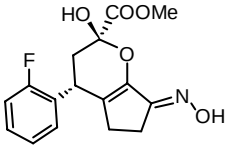
4b: (2*R*,4*S*,*E*)-methyl 4-(4-fluorophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7-

hexahydrocyclopenta[*b*]pyran-2-carboxylate



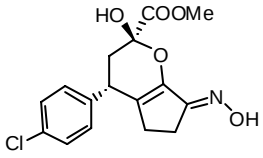
Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to afford **4b** in 86% yield; $[\alpha]^{20}_D$= 92 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.15-7.19(dd, *J* = 8.4 Hz, *J* = 5.1 Hz, 2 H), 7.00-7.06(t, *J* = 8.4 Hz, 2 H), 3.82(br s, 4 H), 2.61-2.69(m, 2 H), 2.05-2.32(m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.6, 159.9, 144.5, 136.4, 129.6, 129.5, 115.8, 115.5, 95.8, 53.4, 37.1, 36.9, 25.9, 23.0. **HRMS-ESI** (*m/z*): calcd for $C_{16}H_{16}FNO_5$+H^+: 322.1085; found: 322.1092, 2.0ppm. **IR**: 3336.3, 2927.3, 1749.0, 1707.5, 1654.1, 1509.6, 1441.3, 1292.4, 1227.6, 1136.4, 931.7, 844.7cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 30/70, 1.0mL/min, 255 nm.) Retention time: t_{minor} = 30.10 min, t_{major} = 22.14 min, ee = > 99%.

4c: (2*R*,4*S*,*E*)-methyl 4-(2-fluorophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate



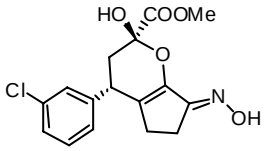
Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to afford **4c** in 99% yield; $[\alpha]^{20}_D$= 146 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.03-7.29(m, 4 H), 4.15-4.21(m, 1 H), 3.84(s, 3 H), 2.61-2.75(m, 2 H), 2.22-2.44(m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.6, 162.7, 160.0, 159.4, 144.4, 129.7, 129.6, 129.0, 128.8, 127.4, 127.2, 124.52, 124.47, 116.0, 115.7, 95.6, 53.5, 35.0, 31.0, 26.0, 23.0. **HRMS-ESI** (*m/z*): calcd for $C_{16}H_{16}FNO_5$+H^+: 322.1085; found: 322.1086, 0.2ppm. **IR**: 3331.2, 2926.3, 1749.1, 1708.0, 1755.3, 1491.3, 1452.8, 1290.7, 1231.2, 1137.5, 935.4, 761.34cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 40/60, 1.0mL/min, 260 nm.) Retention time: t_{minor} = 25.67 min, t_{major} = 16.22 min, ee = > 99%.

4d: (2*R*,4*S*,*E*)-methyl 4-(4-chlorophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate



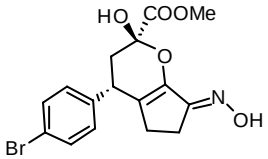
Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to afford **4d** in 99% yield; $[\alpha]^{20}_D$= 73 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.27-7.33(d, *J* = 8.1 Hz, 2 H), 7.13-7.16(d, *J* = 8.4 Hz, 2 H), 3.83(br s, 4 H), 2.62-2.72(m, 2 H), 2.18-2.29(m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.5, 159.8, 144.6, 139.3, 132.9, 129.4, 129.1, 129.0, 95.6, 53.5, 37.0, 36.9, 25.9, 23.0. **HRMS-ESI** (*m/z*): calcd for $C_{16}H_{16}ClNO_5$+H^+: 338.0790; found: 338.0794, 1.3ppm. **IR**: 3325.0, 2925.2, 2855.2, 1749.6, 1654.3, 1490.0, 1441.8, 1293.9, 1234.3, 1136.9, 931.4, 842.8cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 30/70, 1.0mL/min, 255 nm.) Retention time: t_{minor} = 37.50 min, t_{major} = 24.58 min, ee = > 99%.

4e: (2*R*,4*S*,*E*)-methyl 4-(3-chlorophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate



Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to afford **4e** in 99% yield; $[\alpha]^{20}_D$= 5 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.28-7.31(m, 1 H), 7.20-7.24(m, 2 H), 7.09-7.11(m, 1 H), 3.78-3.84(m, 4 H), 2.64-2.70(m, 2 H), 2.20-2.29(m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.5, 159.9, 144.6, 142.9, 134.6, 130.1, 128.9, 128.2, 127.4, 126.3, 95.6, 53.5, 37.4, 36.8, 25.9, 23.0. **HRMS-ESI** (*m/z*): calcd for $C_{16}H_{16}ClNO_5$+H^+: 338.0790; found: 338.0794, 1.2ppm. **IR**: 3312.6, 2924.6, 2854.9, 1747.0, 1653.2, 1436.4, 1287.0, 1236.2, 1135.9, 935.5, 788.8cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 40/60, 1.0mL/min, 255 nm.) Retention time: t_{minor} = 19.59 min, t_{major} = 13.63 min, ee = 99%.

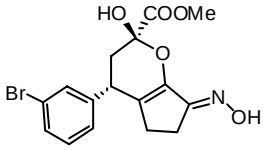
4f: (2*R*,4*S*,*E*)-methyl 4-(4-bromophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate



Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to afford **4f** in 92% yield; $[\alpha]^{20}_D$= 47 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.46-7.48(d, *J* = 8.1 Hz, 2 H), 7.07-7.10(d, *J* = 8.4 Hz, 2 H), 3.77-3.84(m, 4 H), 2.56-2.73(m, 2 H), 2.10-2.32(m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.5,

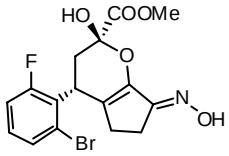
159.9, 144.6, 139.8, 132.0, 129.8, 129.0, 121.0, 95.6, 53.5, 37.1, 36.8, 25.9, 23.0. **HRMS-ESI** (*m/z*): calcd for $C_{16}H_{16}BrNO_5+H^+$: 382.0285; found: 382.0292, 1.9ppm. **IR**: 3313.2, 2925.1, 1747.0, 1709.7, 1654.4, 1486.7, 1442.6, 1291.5, 1241.4, 1136.6, 931.6cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 30/70, 1.0mL/min, 255 nm.) Retention time: t_{minor} = 39.42 min, t_{major} = 25.44 min, ee = 99%.

4g: (2*R*,4*S*,*E*)-methyl 4-(3-bromophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate



Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to afford **4g** in 99% yield; $[\alpha]^{20}_D$= 87 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ7.36-7.42(m, 2 H), 7.22-7.25(m, 1 H), 7.13-7.20(m, 1 H), 3.81-3.84(m, 4 H), 2.66-2.69(m, 2 H), 2.20-2.30(m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.5, 159.8, 144.7, 143.2, 131.1, 130.4, 130.3, 128.9, 126.8, 122.8, 95.6, 53.5, 37.3, 36.8, 25.9, 23.0. **HRMS-ESI** (*m/z*): calcd for $C_{16}H_{16}BrNO_5+H^+$: 382.0285; found: 382.0287, 0.5ppm. **IR**: 3330.9, 2927.2, 2855.4, 1750.1, 1709.4, 1654.1, 1436.0, 1288.4, 1232.2, 1137.1, 934.0, 824.2cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 40/60, 1.0mL/min, 255 nm.) Retention time: t_{minor} = 9.07 min, t_{major} = 6.29 min, ee = 97%.

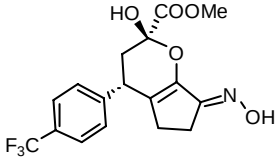
4h: (2*R*,4*S*,*E*)-methyl 4-(2-bromo-6-fluorophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate



Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to afford **4h** in 78% yield; $[\alpha]^{20}_D$= 59 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): 7.51-7.56(dd, *J* = 8.4 Hz, *J* = 5.1 Hz, 1 H), 6.84-6.91(m, 2 H), 4.37-4.43(m, 1 H), 3.82(s, 3 H), 2.61-2.78(m, 2 H), 2.02-2.45(m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.4, 159.6, 145.6, 142.2, 134.2, 127.7, 118.7, 116.1, 116.0, 115.7, 95.7, 53.5, 37.1, 35.6, 25.8, 23.0. **HRMS-ESI** (*m/z*): calcd for $C_{16}H_{15}BrNO_5+H^+$: 400.1090; found: 400.1093, 0.6ppm. **IR**: 3436.0, 2926.7, 1749.6, 1653.2, 1467.9, 1276.6, 1238.2, 1135.3, 1026.4, 922.1, 731.7cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-

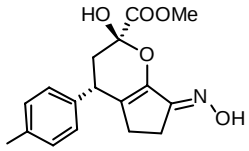
H, *i*-PrOH/ Hexane = 40/60, 1.0mL/min, 255 nm.) Retention time: t_{minor} = 8.29 min, t_{major} = 23.39 min, ee = 99%.

4i: (2*R*,4*S*,*E*)-methyl 2-hydroxy-7-(hydroxyimino)-4-(4-(trifluoromethyl)phenyl)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate



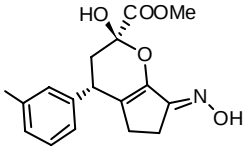
Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to afford **4i** in 99% yield; $[\alpha]^{20}_D$= 59 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.60-7.62(d, *J* = 7.8 Hz, 2 H), 7.32-7.35(d, *J* = 7.8 Hz, 2 H), 3.84-3.94(m,4 H), 2.59-2.76(m, 2 H), 2.18-2.31(m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.5, 159.7, 145.0, 144.9, 129.8, 129.3, 128.5, 125.9, 125.8, 95.6, 53.5, 37.5, 36.9, 25.9, 23.0. **HRMS-ESI** (*m/z*): calcd for $C_{17}H_{16}F_3NO_5$+H^+: 372.1053; found: 372.1063, 2.6ppm. **IR**: 3332.2, 2928.5, 1751.3, 1710.5, 1654.9, 1442.2, 1326.1, 1293.5, 1131.9, 1066.9, 932.8, 850.4cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 40/60, 1.0mL/min, 255 nm.) Retention time: t_{minor} = 17.08 min, t_{major} = 14.03 min, ee = > 99%.

4j: (2*R*,4*S*,*E*)-methyl 2-hydroxy-7-(hydroxyimino)-4-p-tolyl-2,3,4,5,6,7-hexahydro-cyclopenta[*b*]pyran-2-carboxylate



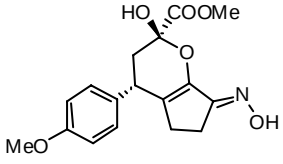
Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to afford **4j** in 65% yield; $[\alpha]^{20}_D$= 78 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.07-7.16(q, *J* = 8.4 Hz, 4 H), 3.82(m, 4 H), 2.61-2.68(m, 2 H), 2.34(s, 3 H), 2.18-2.29(m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.7, 160.1, 144.2, 137.7, 136.7, 130.3, 129.5, 127.9, 95.8, 53.3, 37.1, 26.0, 23.0, 21.0. **HRMS-ESI** (*m/z*): calcd for $C_{17}H_{19}NO_5$+H^+: 318.1336; found: 318.1336, 0.1ppm. **IR**: 3330.1, 2925.8, 2856.5, 1749.2, 1707.8, 1654.0, 1513.2, 1441.3, 1291.3, 1236.9, 1136.8, 932.1cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 50/50, 1.0mL/min, 258 nm.) Retention time: t_{minor} = 22.00 min, t_{major} = 15.03 min, ee = >99%.

4k: (2*R*,4*S*,*E*)-methyl 2-hydroxy-7-(hydroxyimino)-4-m-tolyl-2,3,4,5,6,7-hexahydro-cyclopenta[*b*]pyran-2-carboxylate



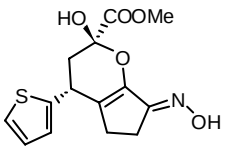
Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to afford **4k** in 66% yield; $[\alpha]^{20}_D$= 65 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.20-7.23(d, *J* = 7.8 Hz, 1 H), 7.07-7.09(d, *J* = 7.5 Hz, 1 H), 6.99-7.01(m, 2 H), 3.75-3.84(m, 4 H), 2.63-2.68(m, 2 H), 2.35(s, 3 H), 2.19-2.31(m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.7, 160.1, 144.3, 140.7, 138.5, 130.1, 128.8, 128.7, 127.9, 125.1, 95.6, 53.5, 37.4, 36.9, 26.0, 22.9, 21.4. **HRMS-ESI** (*m/z*): calcd for $C_{17}H_{19}NO_5$+H^+: 318.1336; found: 318.1345, 2.7ppm. **IR**: 3433.3, 2924.3, 2854.2, 1749.5, 1652.8, 1443.1, 1290.0, 1254.6, 1136.3, 915.5, 708.6cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 40/60, 1.0mL/min, 255 nm.) Retention time: t_{major} = 7.08 min, ee = > 99%.

4l: (2*R*,4*S*,*E*)-methyl2-hydroxy-7-(hydroxyimino)-4-(4-methoxyphenyl)-2,3,4,5,6,7-hexahydr-ocyclopenta[*b*]pyran-2-carboxylate



Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to afford **4l** in 70% yield; $[\alpha]^{20}_D$= 77 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.11-7.14(d, *J* = 8.7 Hz, 2 H), 6.87-6.90(dd, *J* = 6.6 Hz, *J* = 1.8 Hz,2 H), 3.85(s, 3 H), 3.81(br s, 4 H), 2.64-2.69(m, 2 H), 2.19-2.30(m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.8, 160.1, 158.6, 144.2, 132.7, 130.4, 129.0, 114.2, 95.8, 55.3, 53.4, 37.1, 36.7, 26.0, 23.0. **HRMS-ESI** (*m/z*): calcd for $C_{17}H_{19}NO_6$+H^+: 334.1285; found: 334.1286, 0.1ppm. **IR**: 3335.7 2928.7 1748.8, 1652.9 1612.1, 1512.2 1443.7 1295.2 1248.5, 1135.9, 931.2, 838.0cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 40/60, 1.0mL/min, 256 nm.) Retention time: t_{minor} = 28.18 min, t_{major} = 18.57 min, ee = 99%.

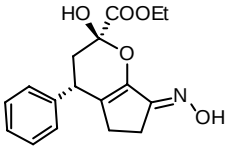
4m: (2*R*,4*S*,*E*)-methyl 2-hydroxy-7-(hydroxyimino)-4-(thiophen-2-yl)-2,3,4,5,6,7-hex-ahydrocyclopenta[*b*]pyran-2-carboxylate



Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to

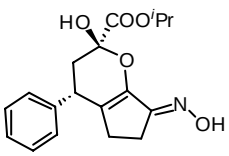
afford **4m** in 80% yield; $[\alpha]^{20}_D$= 83 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.21-7.23(d, *J* = 5.1 Hz, 1 H), 6.92-6.99(m, 2 H), 4.17-4.23(t, *J* = 8.7 Hz,1 H), 3.85(s, 3 H), 2.59-2.73(m, 2 H), 2.29-2.41(m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.5, 160.0, 143.6, 129.6, 126.9, 125.4, 124.2, 95.7, 53.5, 53.4, 37.1, 32.7, 26.0, 23.0. **HRMS-ESI** (*m/z*): calcd for $C_{14}H_{15}NO_5S+H^+$: 310.0744; found: 310.0753, 2.9ppm. **IR**: 3337.7, 2925.3, 1749.0, 1707.2, 1653.5, 1439.3, 1293.6, 1233.0, 1133.8, 928.9 704.4m^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 40/60, 1.0mL/min, 253 nm.) Retention time: t_{minor} = 36.86 min, t_{major} = 26.13 min, ee = > 99%.

4n: (2*R*,4*S*,*E*)-ethyl 2-hydroxy-7-(hydroxyimino)-4-phenyl-2,3,4,5,6,7-hexahydro-cyclopenta[*b*]pyran-2-carboxylate



Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to afford **4n** in 81% yield; $[\alpha]^{20}_D$= 10 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.28-7.38(m, 3 H), 7.21-7.23(m, 2 H), 4.24-4.33(qd, *J* = 11.7 Hz, *J* = 4.5 Hz, 2 H), 3.79-3.86(t, *J* = 9.3 Hz,, 1 H), 2.63-2.69(m, 2 H), 2.19-2.31(m, 4 H), 1.29-1.34(t, *J* = 14.4 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.2, 160.1, 144.5, 140.9, 129.9, 128.8, 128.1, 127.1, 95.6, 63.0, 37.6, 37.0, 26.0, 23.0, 13.9. **HRMS-ESI** (*m/z*): calcd for $C_{17}H_{19}NO_5+H^+$: 318.1336; found: 318.1338, 0.7ppm. **IR**: 3338.6, 2924.6, 2855.2, 1741.9, 1651.5, 1455.1, 1292.3, 1240.5, 1136.1, 1026.1, 934.9cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 30/70, 1.0mL/min, 254 nm.) Retention time: t_{minor} = 16.91 min, t_{major} = 9.55 min, ee = 99%.

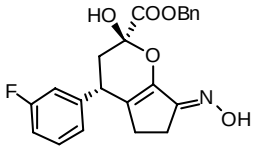
4o: (2*R*,4*S*,*E*)-isopropyl 2-hydroxy-7-(hydroxyimino)-4-phenyl-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate



Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to afford **4o** in 85% yield; $[\alpha]^{20}_D$= 99 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.20-7.38(m, 5 H), 5.06-5.14(m, 1 H), 3.79-3.85(t, *J* = 9 Hz, 1 H), 2.55-2.75(m, 2 H), 2.19-2.28(m, 4 H), 1.27-1.32(dd, *J* = 8.7 Hz, *J* = 6.3 Hz, 6 H); **^{13}C NMR** (75

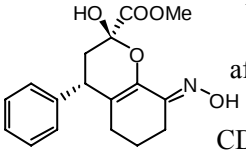
MHz, $CDCl_3$): δ168.8, 160.0, 144.7, 141.0, 129.7, 128.8, 128.1, 127.1, 95.6, 71.0, 37.7, 37.0, 26.0, 23.0, 21.51, 21.48. **HRMS-ESI** (*m/z*): calcd for $C_{18}H_{21}NO_5$+H^+: 332.1492; found: 347.1498, 1.6ppm. **IR**: 3276.5, 2927.7, 1740.2, 1654.3, 1454.5, 1291.7, 1236.1, 1141.4, 1103.5, 936.0, 845.9, 704.1cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 30/70, 1.0mL/min, 254 nm.) Retention time: t_{minor} = 16.72 min, t_{major} = 8.70 min, ee = 99%.

4p: (2*R*,4*S*,*E*)-benzyl 4-(3-fluorophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate



Prepared according to general procedure with CH_2Cl_2/EtOAc = 4/1 as to afford **4p** in 65% yield; $[\alpha]^{20}_D$= 110 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.33(br s, 5 H), 7.11-7.16(dd, *J* = 11.4 Hz, *J* = 8.4 Hz, 2 H), 6.98-7.04(t, *J* = 8.7 Hz, 2 H),5.18-5.29(q, *J* = 12.3 Hz, 2 H), 3.79-3.84(m, 1 H), 2.53-2.70(m, 2 H), 2.14-2.40(m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.0, 163.5, 160.2, 159.8, 144.5, 136.5, 134.7, 129.6, 129.5, 128.6, 128.5, 128.3, 128.1, 115.8, 115.5, 95.8, 68.2, 37.0, 336.9, 25.9, 23.0. **HRMS-ESI** (*m/z*): calcd for $C_{22}H_{20}FNO_5$+H^+: 398.1398; found: 398.1400, 0.4ppm. **IR**: 3434.1, 2926.8, 1746.6, 1652.4, 1509.6, 1288.3, 1226.4, 1136.0, 1092.8, 932.2, 734.2cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH / Hexane = 30/70, 1.0mL/min, 255 nm.) Retention time: t_{minor} = 27.90 min, t_{major} = 12.02 min, ee = 99%.

4q: (2*R*,4*S*,*E*)-methyl 2-hydroxy-8-(hydroxyimino)-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromene-2-carboxylate



Prepared according to general procedure with CH_2Cl_2/EtOAc = 1/2 as to afford **4q** in 70% yield; $[\alpha]^{20}_D$= 32 (*c*=1.0, $CHCl_3$). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.20-7.35(m, 5 H), 3.80-3.92(m, 3 H), 3.69-3.75(t, *J* = 10.5 Hz, 1 H), 2.85-2.94(m, 1 H), 2.23-2.45(m, 3 H), 1.85-1.87(d, *J* = 5.4 Hz, 2 H), 1.63-1.71m, 2 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 170.2, 151.6, 141.8, 139.6, 128.8, 128.6, 128.4, 127.0, 94.1, 53.3, 39.8, 37.6, 26.5, 23.0, 20.7. **HRMS-ESI** (*m/z*): calcd for $C_{17}H_{19}NO_5$+H^+: 318.1336; found: 318.1335,

0.2ppm. **IR**: 3313.0, 2926.5, 2857.1, 1748.3, 1452.0, 1295.2, 1235.1, 1140.2, 910.8, 733.6, 703.2 cm^{-1}. **HPLC**: ee of major diastereoisomer was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH / Hexane = 30/70, 1.0mL/min, 255 nm.) Retention time: t_{major} = 7.42 min, ee = >99%.

5.0 References

1. X. X. Jiang, Y. F. Zhang, A. S. C. Chan and R. Wang, *Org. Lett*., 2009, **11**, 153.

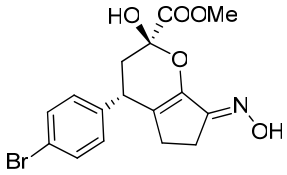
2. X. X. Jiang, Y. F. Zhang, X. Liu, G. Zhang, L. H. Lai, L. P. Wu, J. N. Zhang and R. Wang, *J. Org. Chem*., 2009, **74**, 5562.

3. X. X. Jiang, Y. F. Zhang, L. P. Wu, G. Zhang, X. Liu, H. L. Zhang, D. Fu and R. Wang, *Adv. Synth.Catal*., 2009, **351**, 2096.

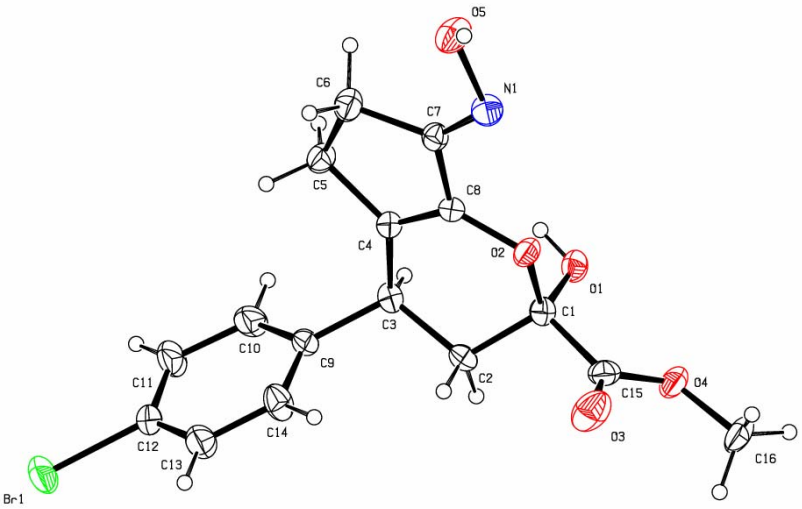
4. Y. C. Wu, L. Liu, H. J. Li, D. Wang and Y. J. Chen, *J. Org. Chem*. 2006, **71**, 6592.

6.0 Absolute Configuration and X-Ray Analysis Data

(2*R*,4*S*,*E*)-methyl 4-(4-bromophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7-hexahydro cyclopenta[b]pyran-2-carboxylate (4f):



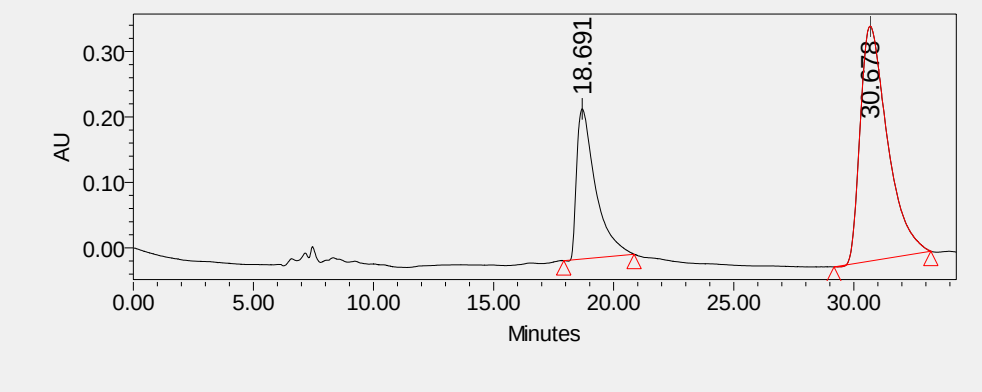
CCDC Number: 931435



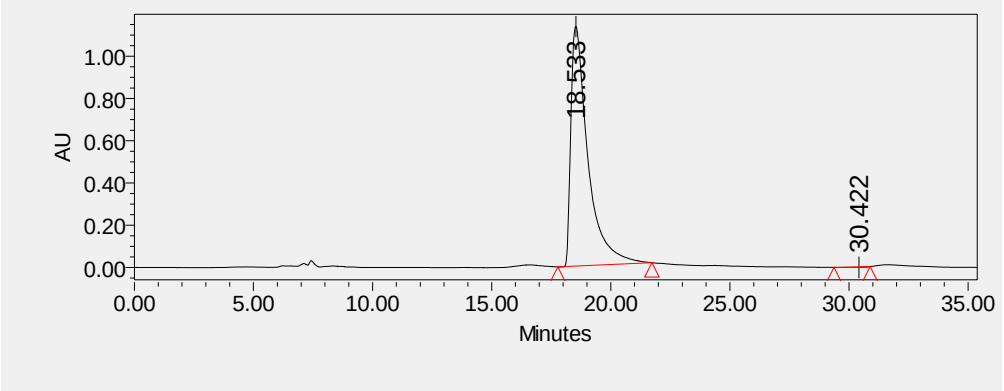
Bond precision: C-C = 0.0078 A			Wavelength=0.71073
Cell:	a=7.907(8)	b=8.093(8)	c=12.534(13)
	alpha=90	beta=101.397(9)	gamma=90
Temperature:	296 K		
	Calculated		Reported
Volume	786.3(14)		786.2(14)
Space group	P 21		P2(1)
Hall group	P 2yb		?
Moiety formula	C16 H16 Br N O5		?
Sum formula	C16 H16 Br N O5		C16 H16 Br N O5
Mr	382.20		382.21
Dx,g cm-3	1.614		1.614
Z	2		2
Mu (mm-1)	2.639		2.639
F000	388.0		388.0
F000’	387.62		
h,k,lmax	9,9,15		9,9,15
Nref	1572[2920]		2877
Tmin,Tmax	0.550,0.656		0.582,0.677
Tmin’	0.540		
Correction method= MULTI-SCAN			
Data completeness= 1.83/0.99			Theta(max)= 25.490
R(reflections)= 0.0489(2032)			wR2(reflections)= 0.1218(2877)
S = 1.009		Npar= 211	

7.0 Copies of HPLC Spectra of Racemic and Chiral Product

4a: (2*R*,4*S*,*E*)-methyl 2-hydroxy-7-(hydroxyimino)-4-phenyl-2,3,4,5,6,7-hexahydrocy clopenta[*b*]py ran-2-carboxylate

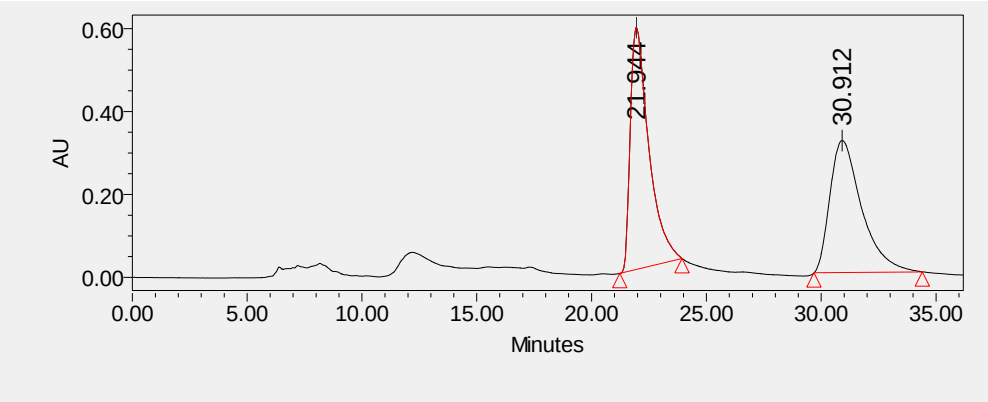


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	18.691	12551312	30.75	229293	bb	Unknown
2	30.678	28262353	69.25	358708	bb	Unknown

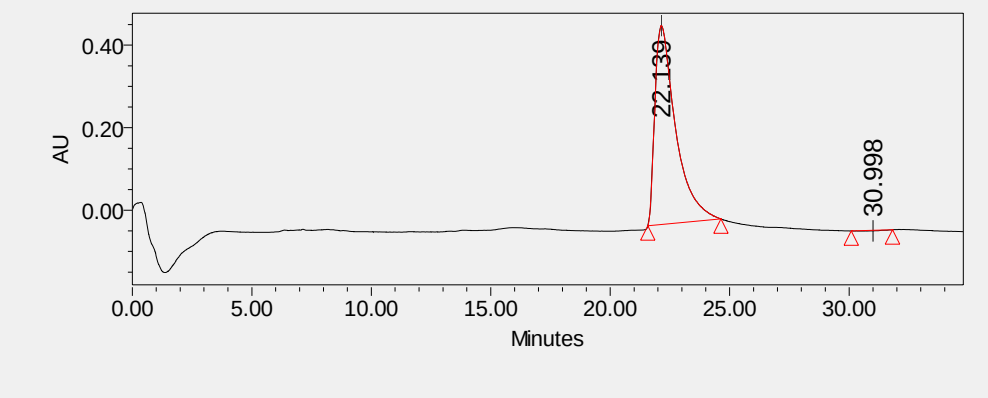


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	18.533	56514736	99.73	1134763	bb	Unknown
2	30.422	150657	0.27	-2574	bb	Unknown

4b: (2*R*,4*S*,*E*)-methyl 4-(4-fluorophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate

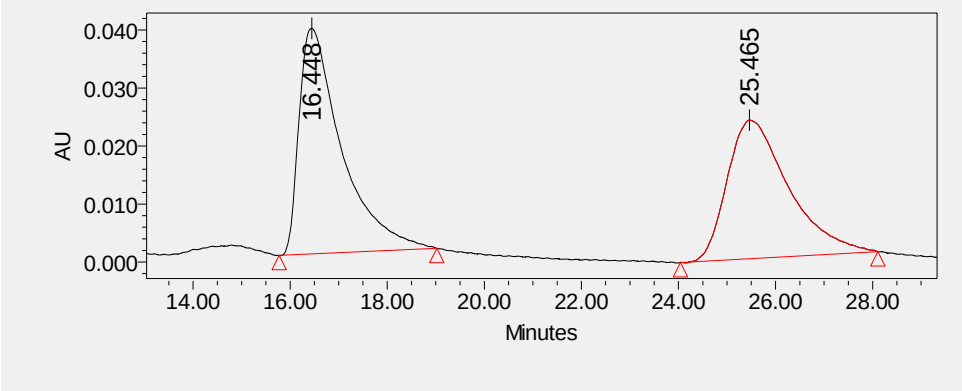


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	21.944	32830327	51.79	583453	bb	Unknown
2	30.912	30566687	48.21	318214	bb	Unknown



Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	22.139	29149594	99.71	481819	bb	Unknown
2	30.998	85790	0.29	-1438	bb	Unknown

4c: (2*R*,4*S*,*E*)-methyl 4-(2-fluorophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7 hexahydrocyclopenta[*b*]pyran-2-carboxylate



Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
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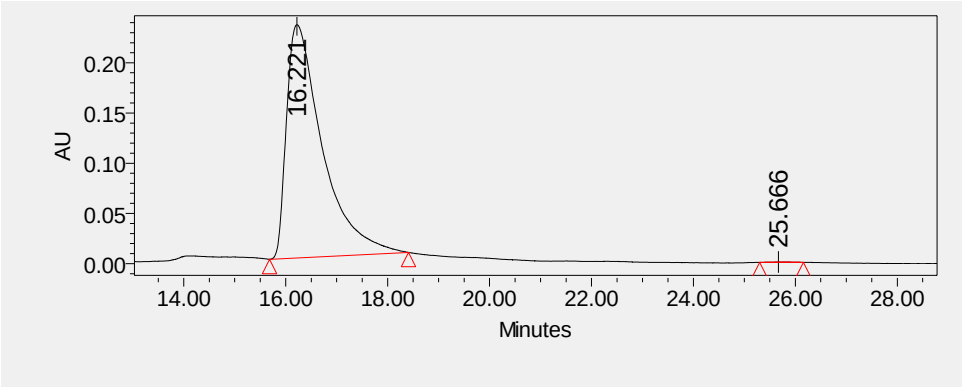
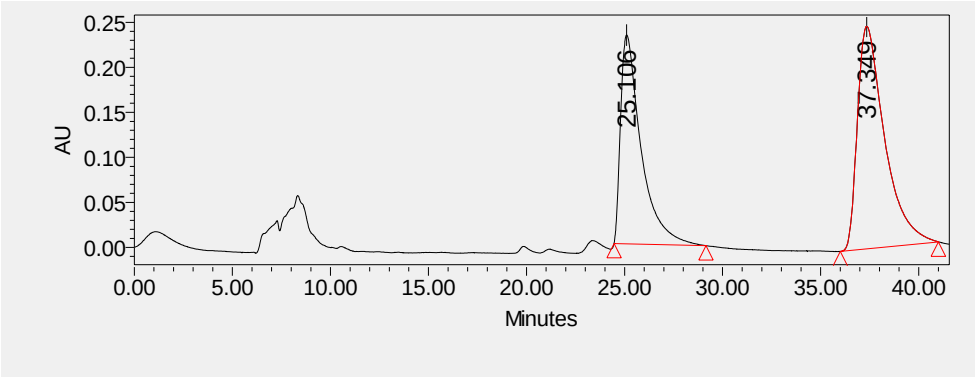
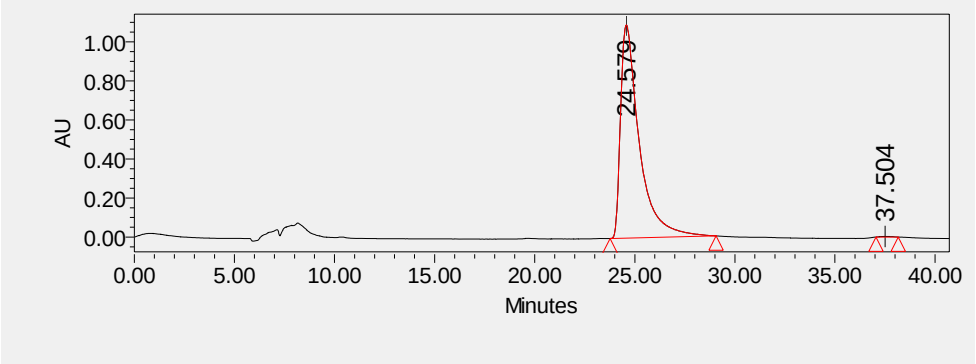


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	16.221	11334293	99.90	232126	bb	Unknown
2	25.666	10989	0.10	382	bb	Unknown

4d: (2*R*,4*S*,*E*)-methyl 4-(4-chlorophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate

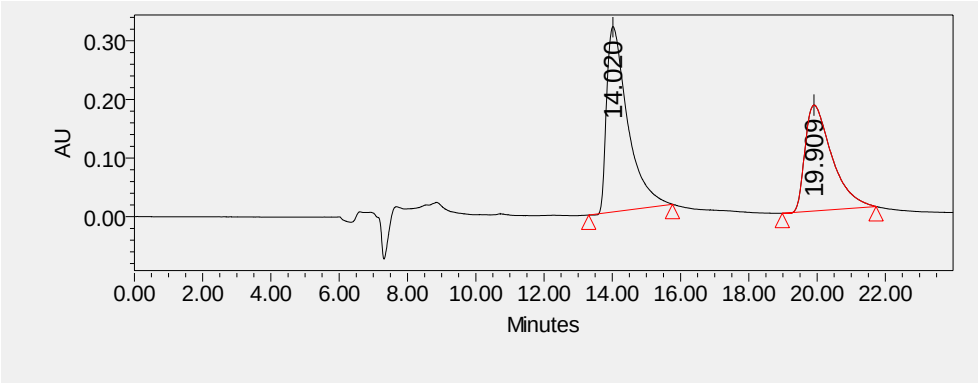


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	25.106	16826508	41.44	231787	bb	Unknown
2	37.349	23778914	58.56	247017	bb	Unknown



Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	24.579	70959052	99.83	1092141	bb	Unknown
2	37.504	118832	0.17	2901	bb	Unknown

4e: (2*R*,4*S*,*E*)-methyl 4-(3-chlorophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate



Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
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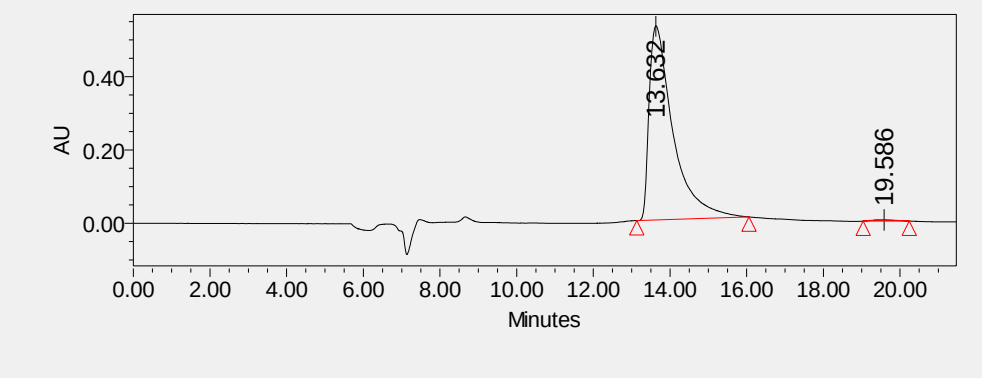
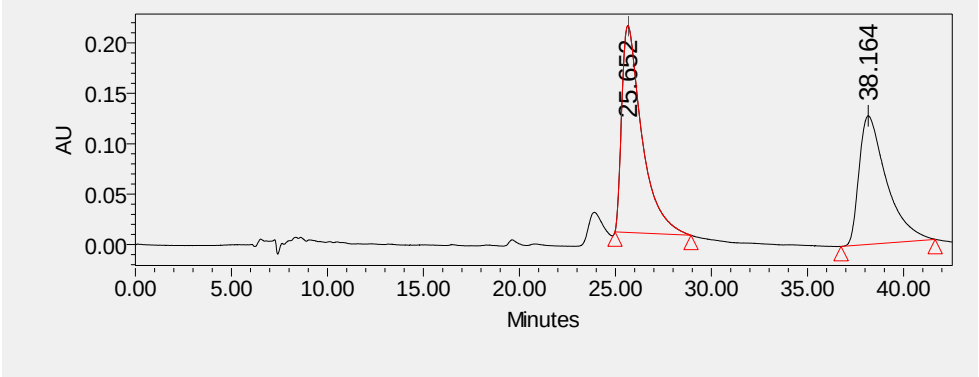


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	13.632	22906968	99.41	529428	bb	Unknown
2	19.586	135258	0.59	3211	bb	Unknown

4f: (2*R*,4*S*,*E*)-methyl 4-(4-bromophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate



Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
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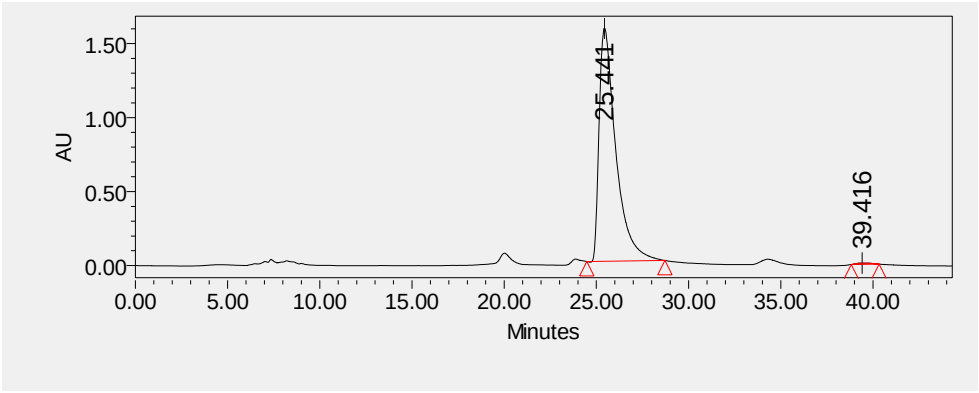
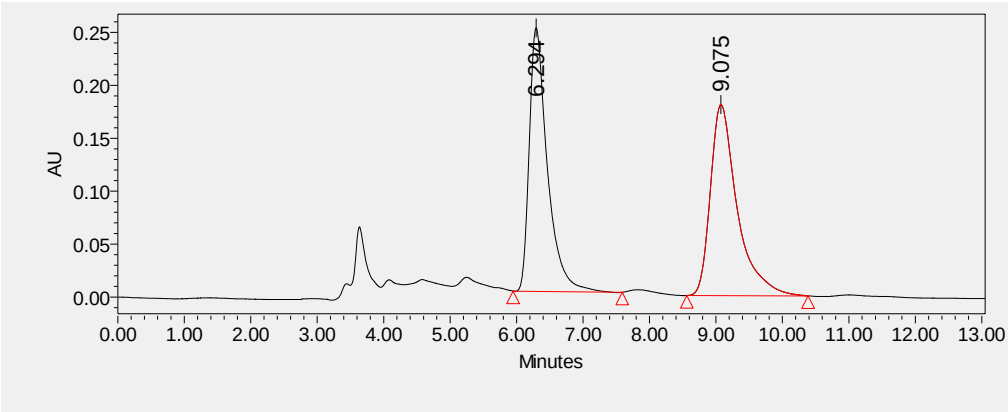
2	38.164	12624616	45.78	127547	bb	Unknown

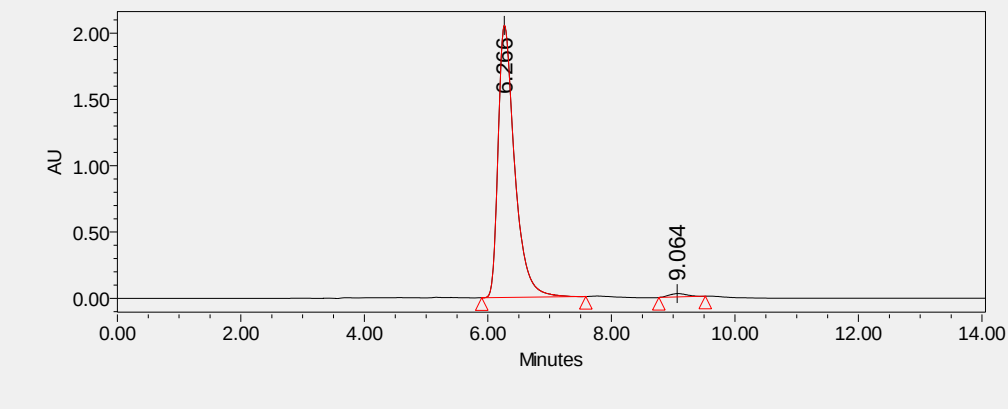


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	25.441	99095584	99.52	1576197	bb	Unknown
2	39.416	478307	0.48	8565	bb	Unknown

4g: (2*R*,4*S*,*E*)-methyl 4-(3-bromophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate

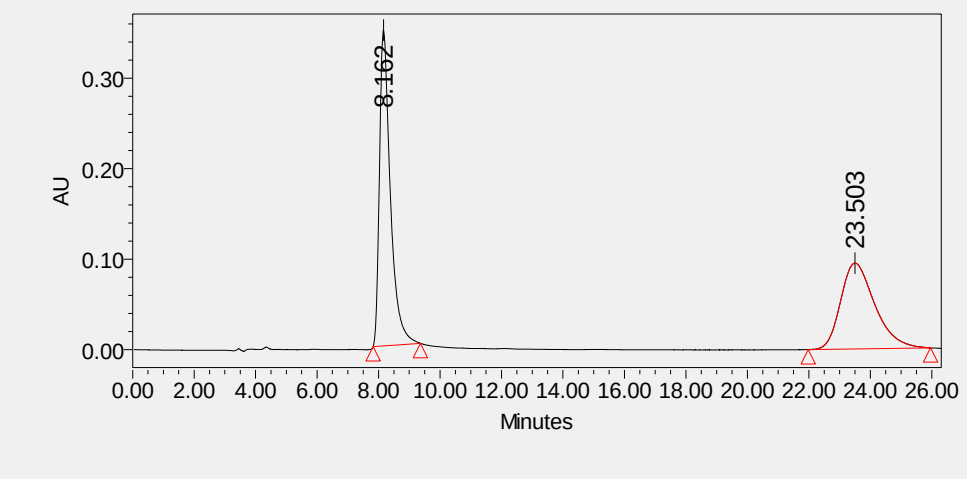


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	6.294	4718211	48.31	248972	bb	Unknown
2	9.075	5048773	51.69	180533	bb	Unknown

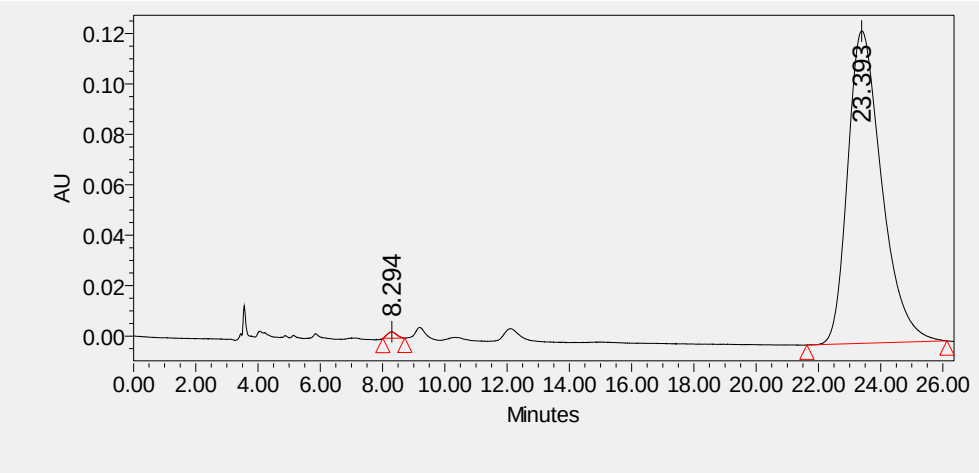


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	6.266	38179262	98.71	2051778	bb	Unknown
2	9.064	500898	1.29	25237	bb	Unknown

4h: (2*R*,4*S*,*E*)-methyl 4-(2-bromo-6-fluorophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4, 5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate

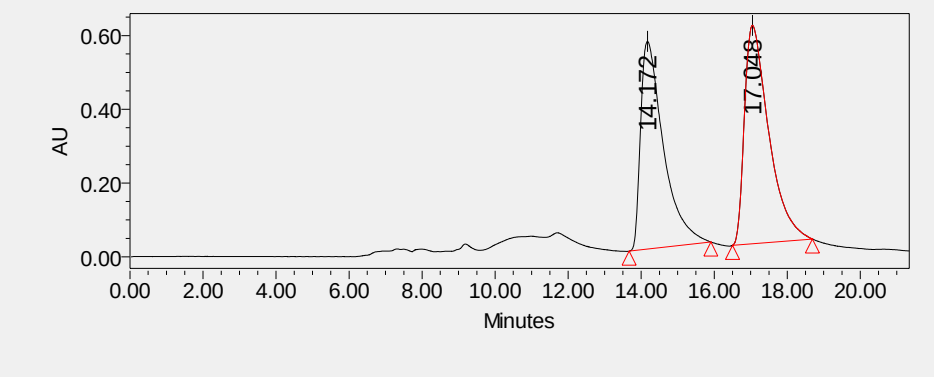


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	8.162	8591819	54.04	348916	bb	Unknown
2	23.503	7305840	45.96	94822	bb	Unknown

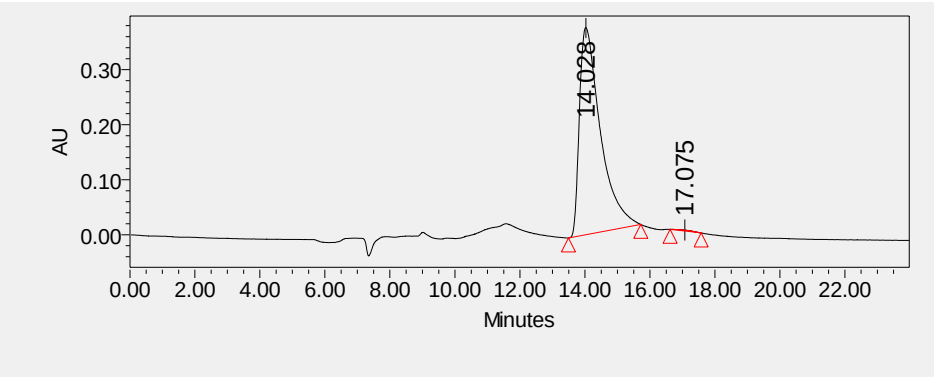


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	8.294	52706	0.56	2534	bb	Unknown
2	23.393	9408449	99.44	123923	bb	Unknown

4i: (2*R*,4*S*,*E*)-methyl 2-hydroxy-7-(hydroxyimino)-4-(4-(trifluoromethyl)phenyl)-2,3,4, 5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate

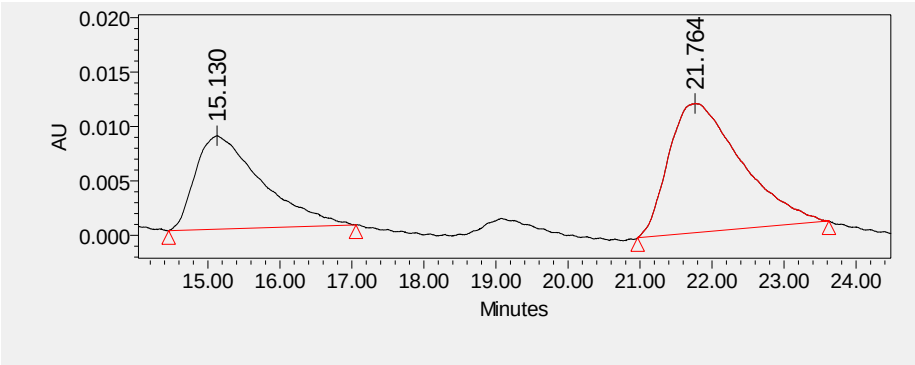


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	14.172	24485420	47.15	563199	bb	Unknown
2	17.048	27442332	52.85	592481	bb	Unknown

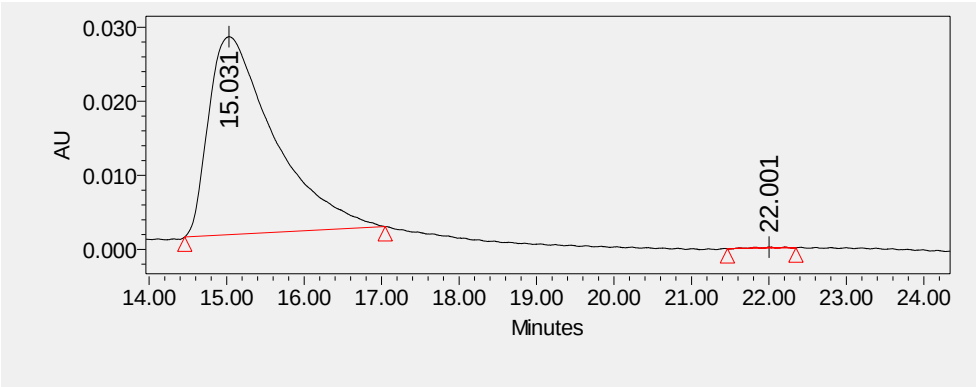


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	14.028	16844860	99.63	376386	bb	Unknown
2	17.075	62655	0.37	1897	bb	Unknown

4j: (2*R*,4*S*,*E*)-methyl 2-hydroxy-7-(hydroxyimino)-4-p-tolyl-2,3,4,5,6,7-hexahydro-cyclopenta[*b*]pyran-2-carboxylate

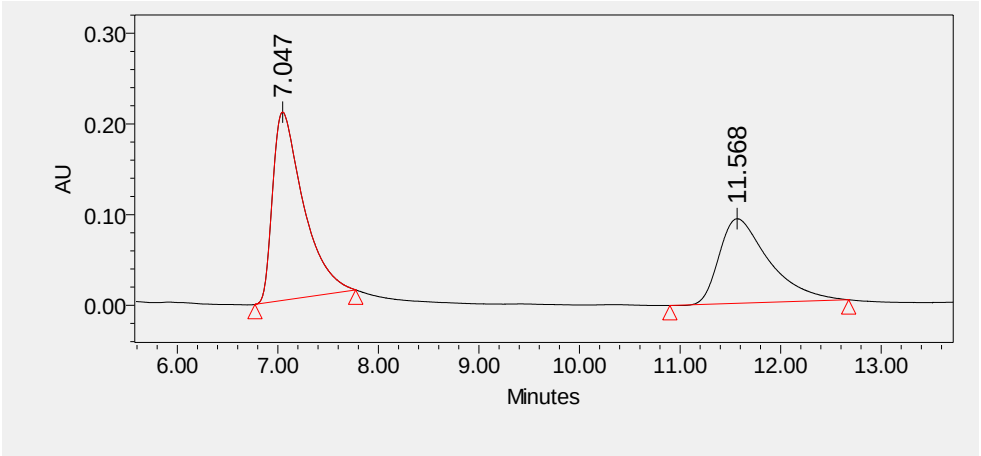


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	15.130	548792	39.77	8584	bb	Unknown
2	21.764	831144	60.23	11863	bb	Unknown

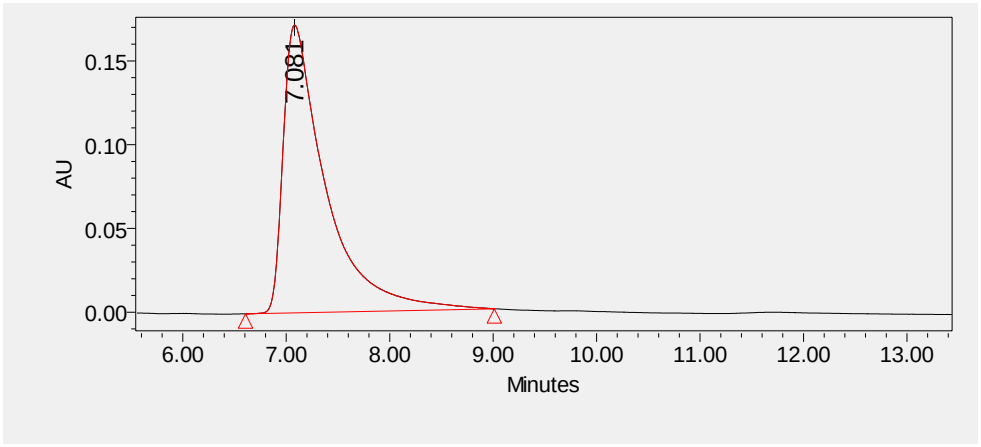


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	15.031	1566934	99.81	26768	bb	Unknown
2	22.001	2961	0.19	132	bb	Unknown

4k: (2*R*,4*S*,*E*)-methyl 2-hydroxy-7-(hydroxyimino)-4-m-tolyl-2,3,4,5,6,7-hexahydro-cyclopenta[*b*]pyran-2-carboxylate

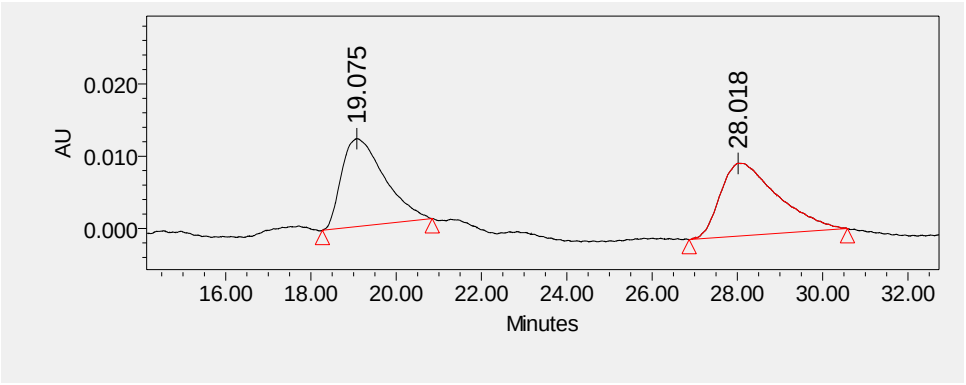


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	7.047	4422071	57.95	207758	bb	Unknown
2	11.568	3208114	42.05	93339	bb	Unknown

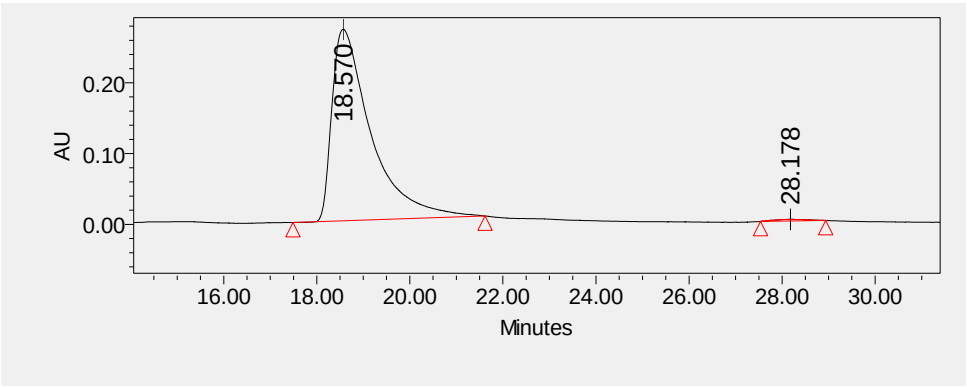


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	7.081	4901204	100.00	171710	bb	Unknown

4l: (2*R*,4*S*,*E*)-methyl 2-hydroxy-7-(hydroxyimino)-4-(4-methoxyphenyl)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate

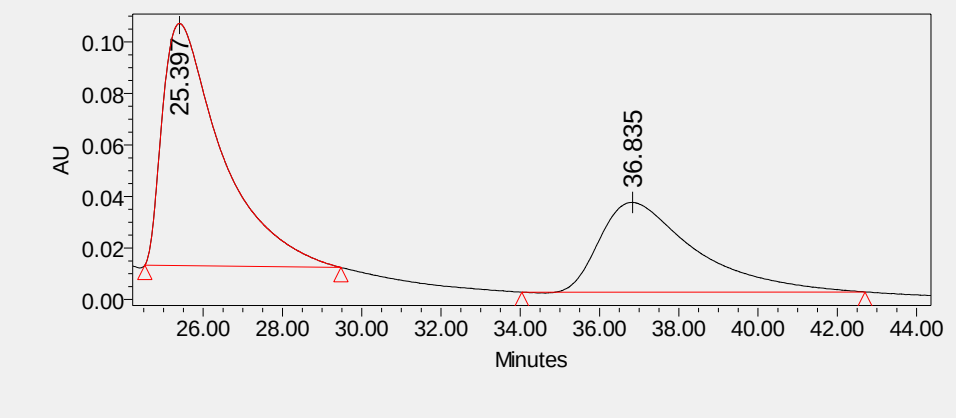


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	19.075	847831	47.49	12163	bb	Unknown
2	28.018	937280	52.51	10060	bb	Unknown

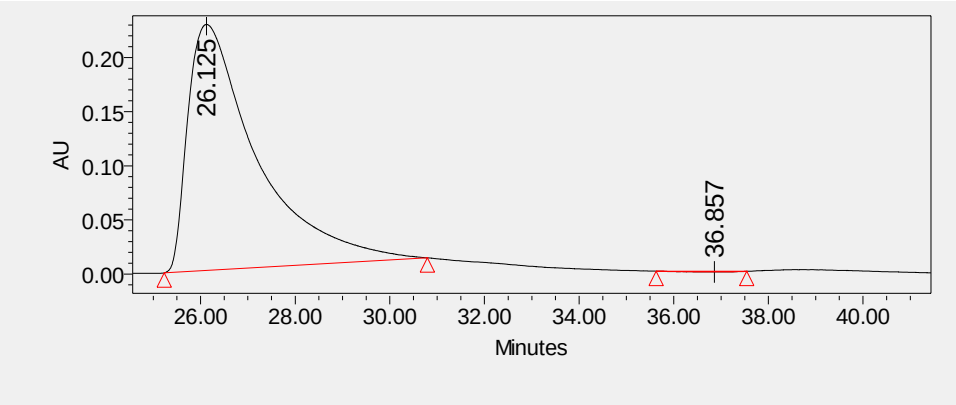


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	18.570	15755350	99.29	270483	bb	Unknown
2	28.178	112583	0.71	2272	bb	Unknown

4m: (2*R*,4*S*,*E*)-methyl 2-hydroxy-7-(hydroxyimino)-4-(thiophen-2-yl)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate

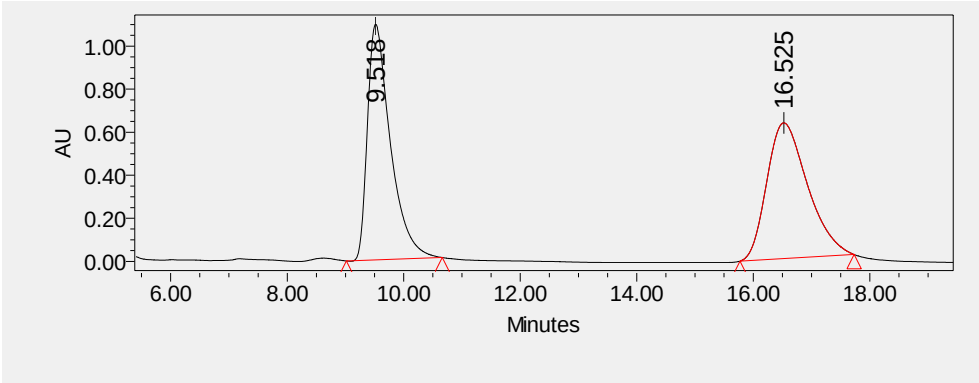


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	25.397	9782852	62.60	94019	bb	Unknown
2	36.835	5844782	37.40	34825	bb	Unknown

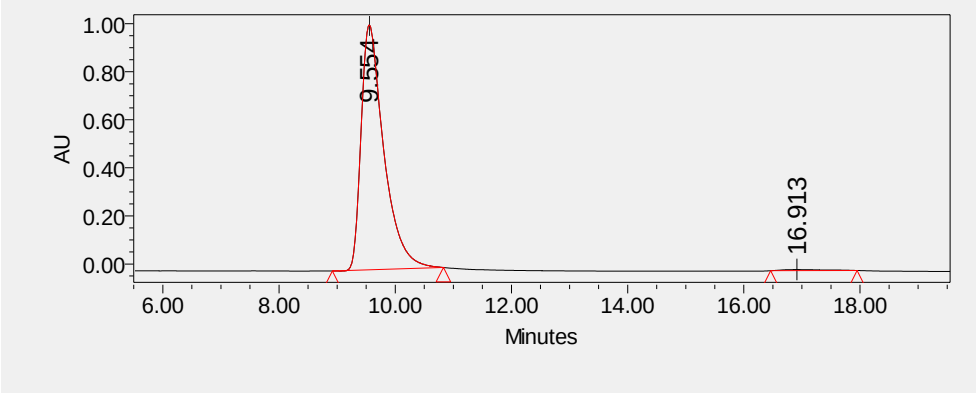


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	26.125	23063370	99.80	227138	bb	Unknown
2	36.857	45760	0.20	-655	bb	Unknown

4n: (2*R*,4*S*,*E*)-ethyl 2-hydroxy-7-(hydroxyimino)-4-phenyl-2,3,4,5,6,7-hexahydro-cyclopenta[*b*]pyran-2-carboxylate

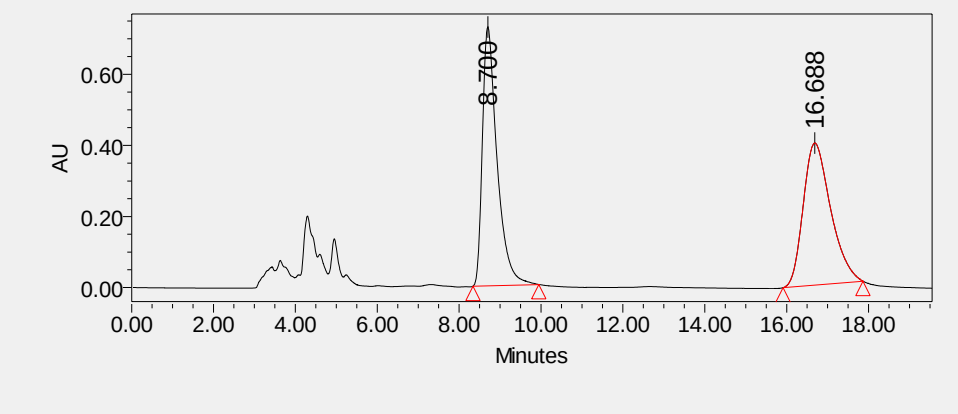


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	9.518	30010714	49.49	1095213	bb	Unknown
2	16.525	30627396	50.51	630396	bb	Unknown

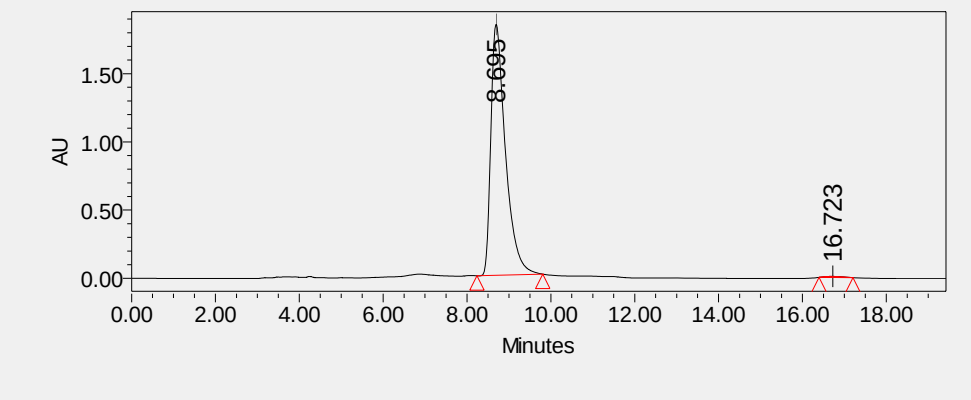


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	9.554	27592621	99.21	1018769	bb	Unknown
2	16.913	221000	0.79	4584	bb	Unknown

4o: (2*R*,4*S*,*E*)-isopropyl 2-hydroxy-7-(hydroxyimino)-4-phenyl-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate

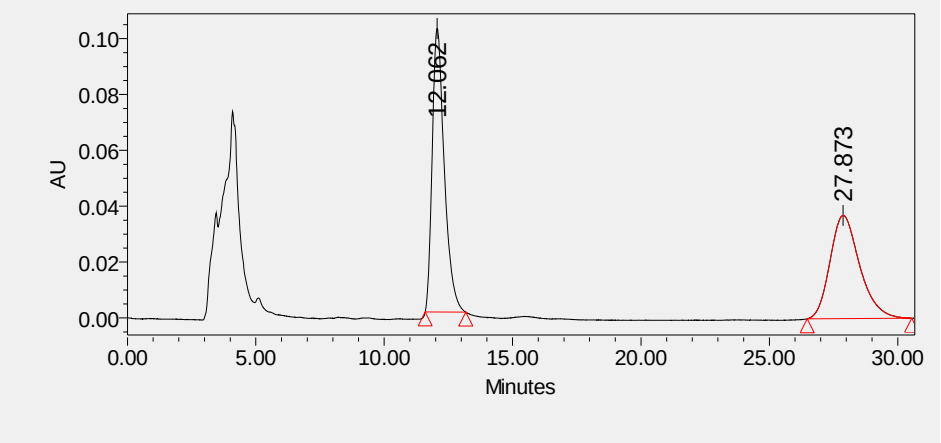


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	8.700	18112666	49.32	728007	bb	Unknown
2	16.688	18611418	50.68	399604	bb	Unknown

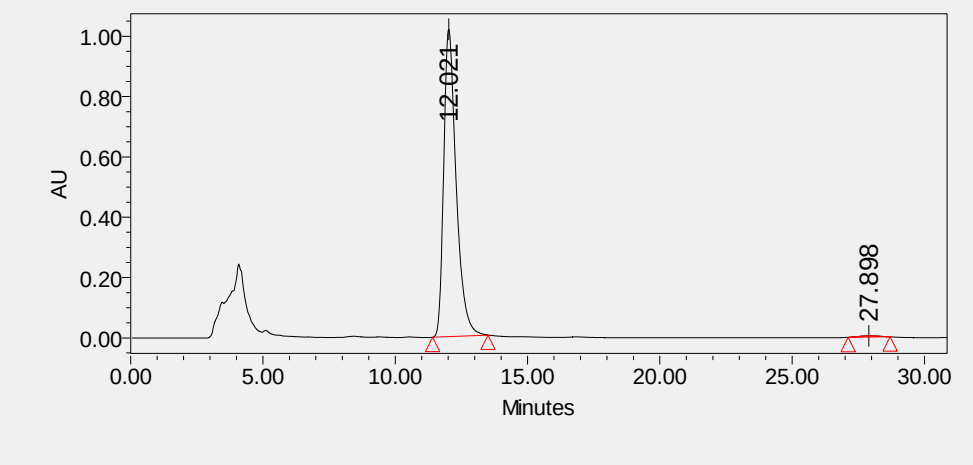


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	8.695	44387200	99.48	1838861	bb	Unknown
2	16.723	230581	0.52	7936	bb	Unknown

4p: (2*R*,4*S*,*E*)-benzyl 4-(3-fluorophenyl)-2-hydroxy-7-(hydroxyimino)-2,3,4,5,6,7-hexahydrocyclopenta[*b*]pyran-2-carboxylate

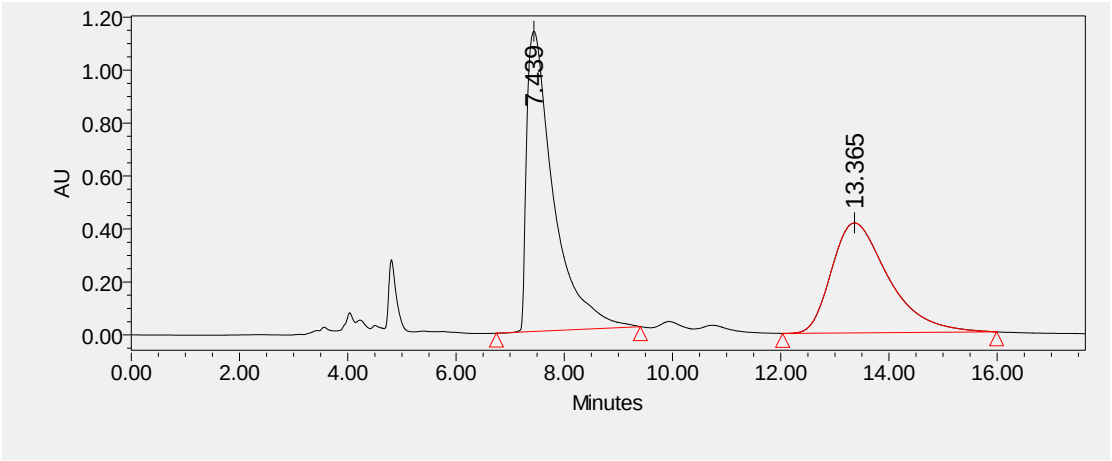


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	12.062	3319305	52.85	101558	bb	Unknown
2	27.873	2960890	47.15	36906	bb	Unknown

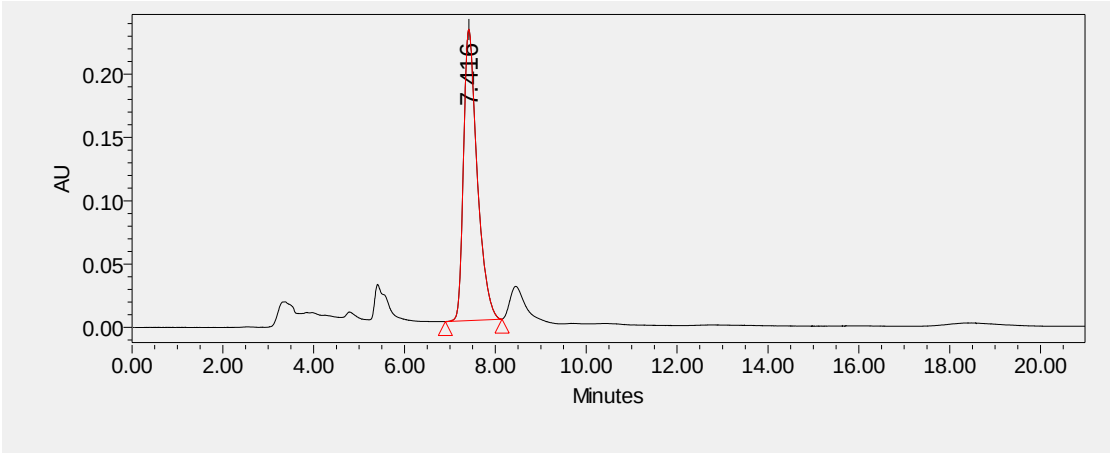


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	12.021	33284421	99.29	1019062	bb	Unknown
2	27.898	238905	0.71	4386	bb	Unknown

4q: (2*R*,4*S*,*E*)-methyl 2-hydroxy-8-(hydroxyimino)-4-phenyl-3,4,5,6,7,8-hexahydro-2H-chromene-2-carboxylate

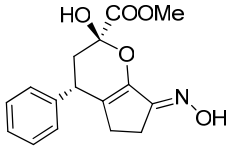


Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	7.439	39030246	56.33	1133680	bb	Unknown
2	13.365	30260847	43.67	415243	bb	Unknown



Entry	Retention Time	Area	Area (%)	Height	Int Type	Peak Type
1	7.416	4799397	100.00	229860	bb	Unknown

8.0 Copies of NMR Spectra of Products



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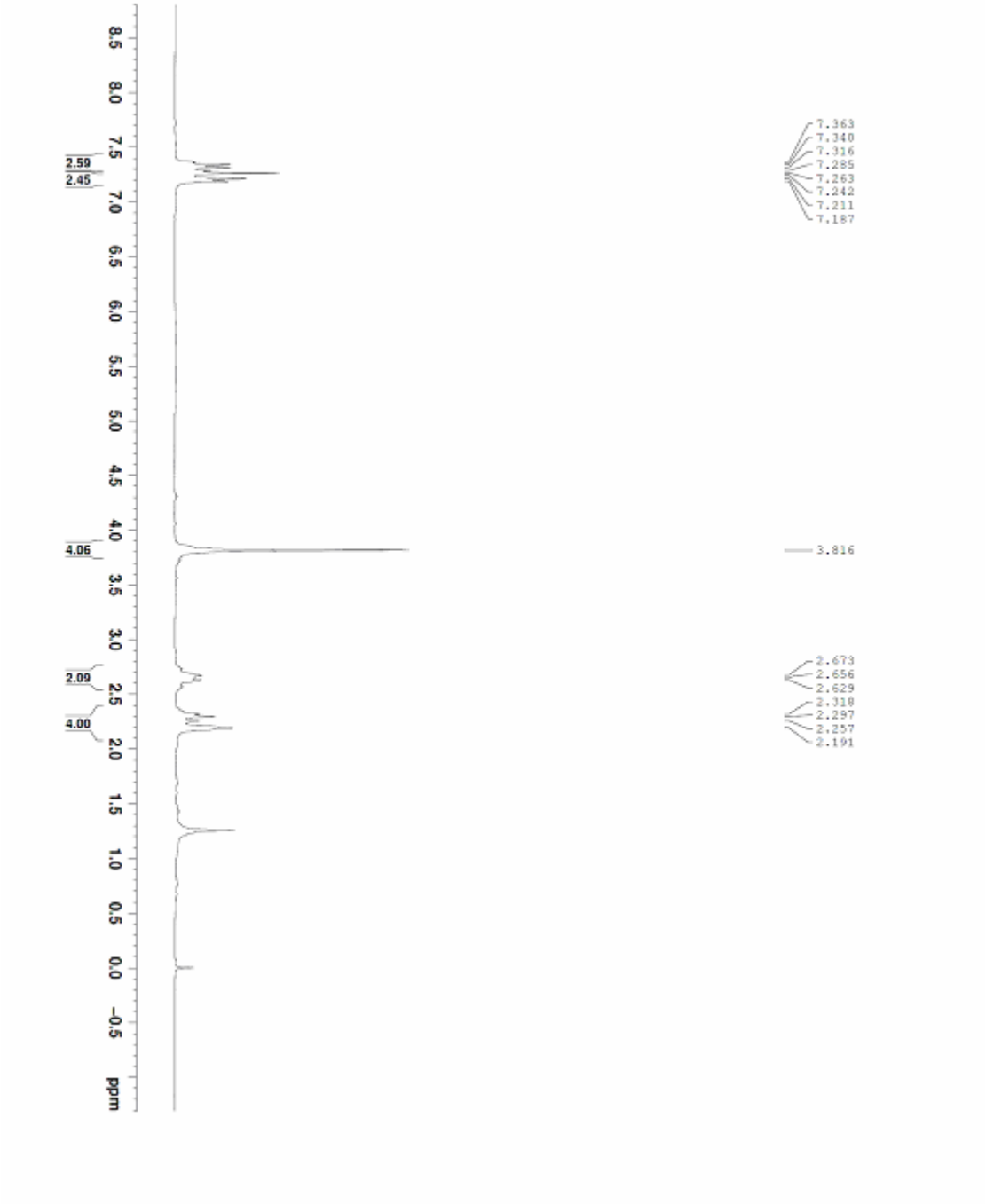

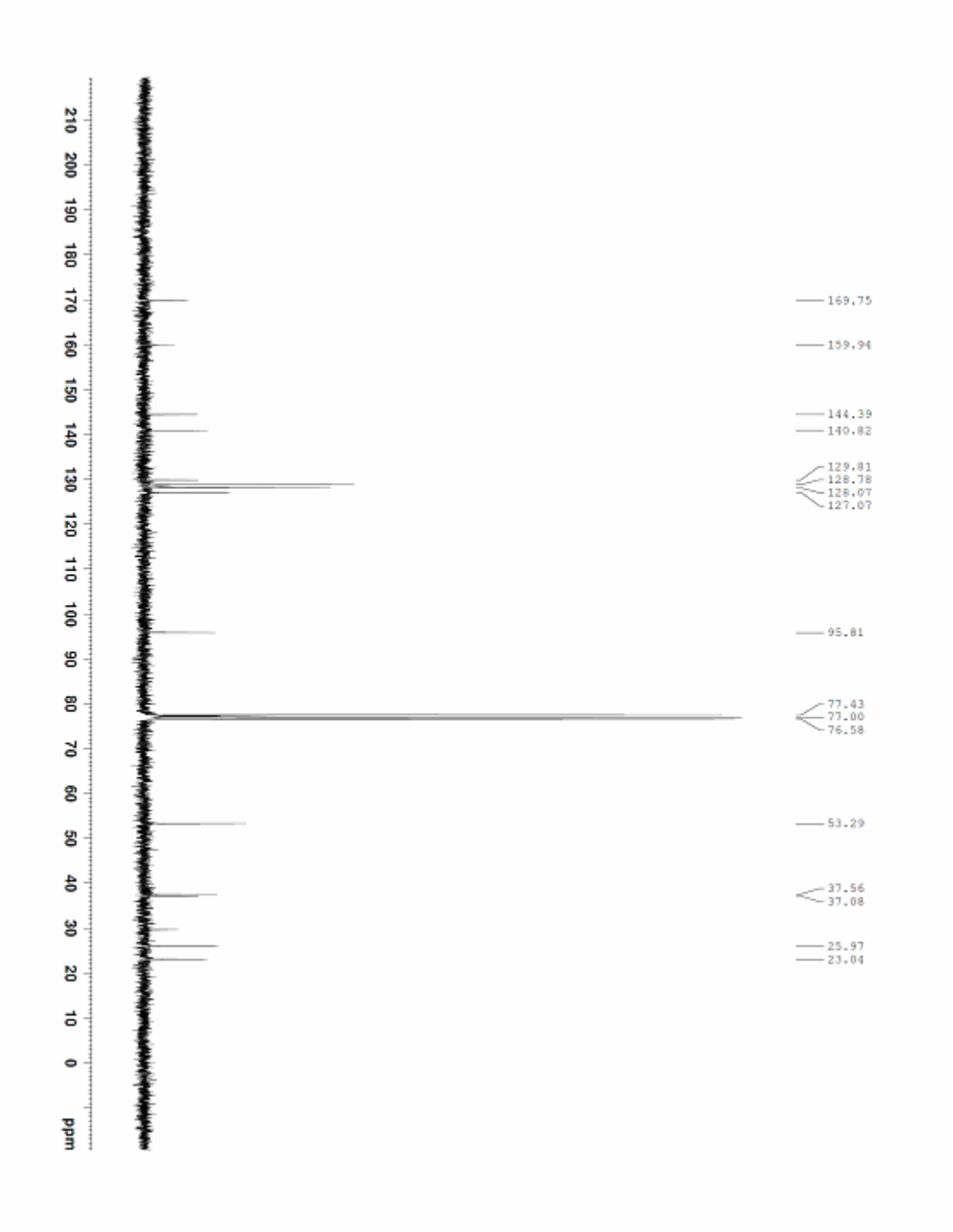

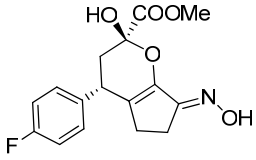

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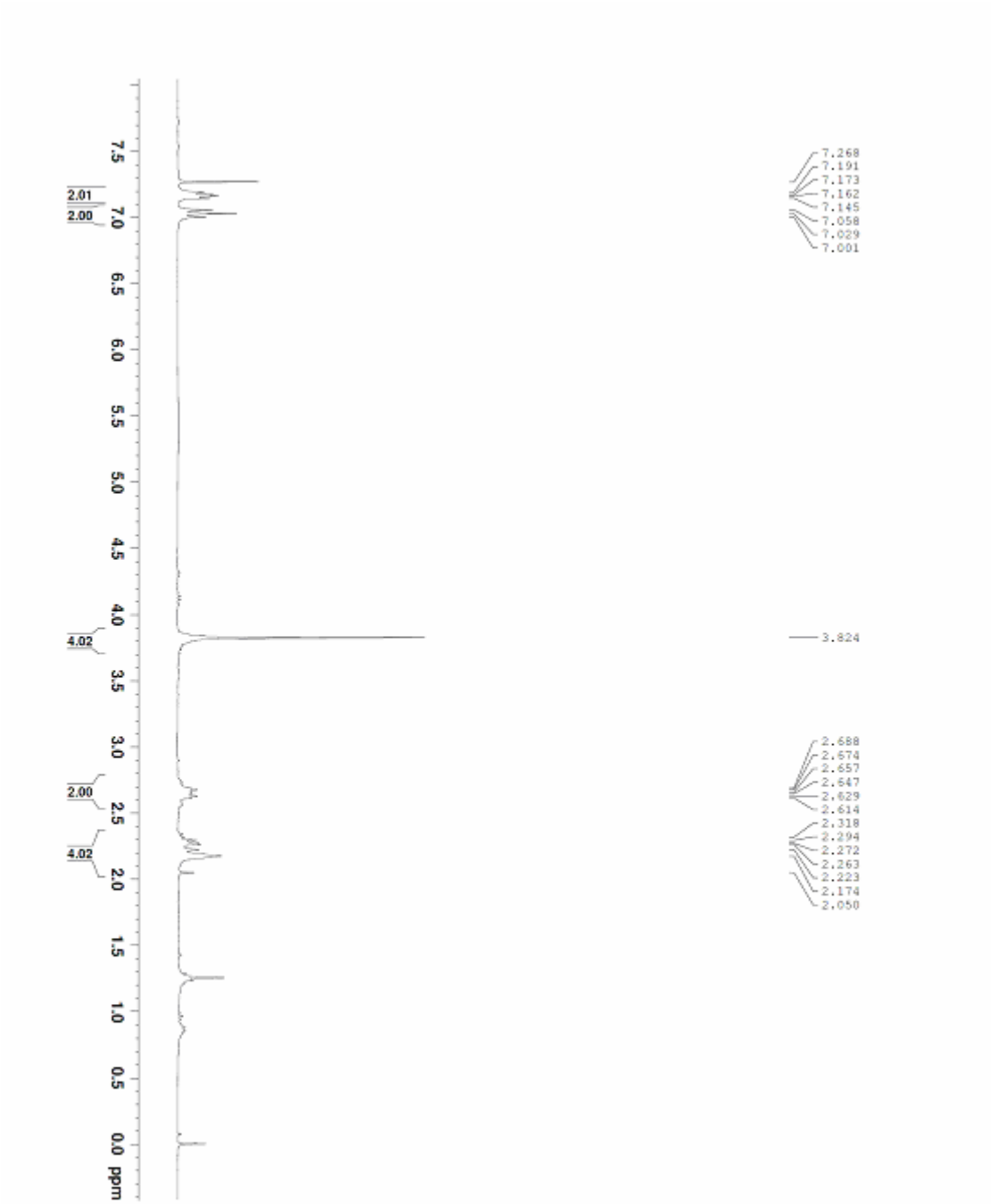

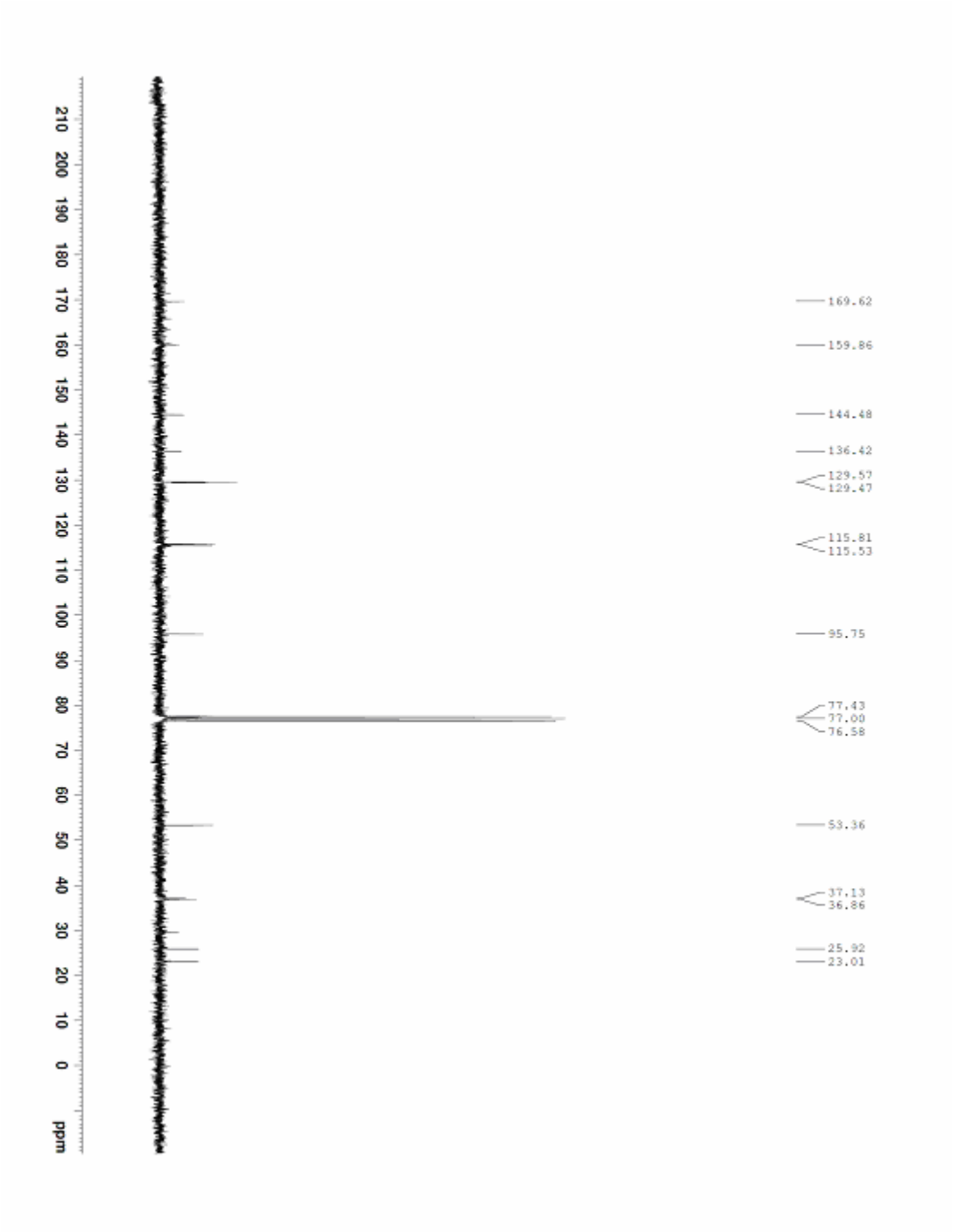
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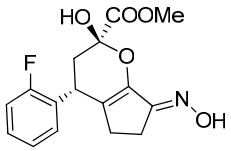
23.01



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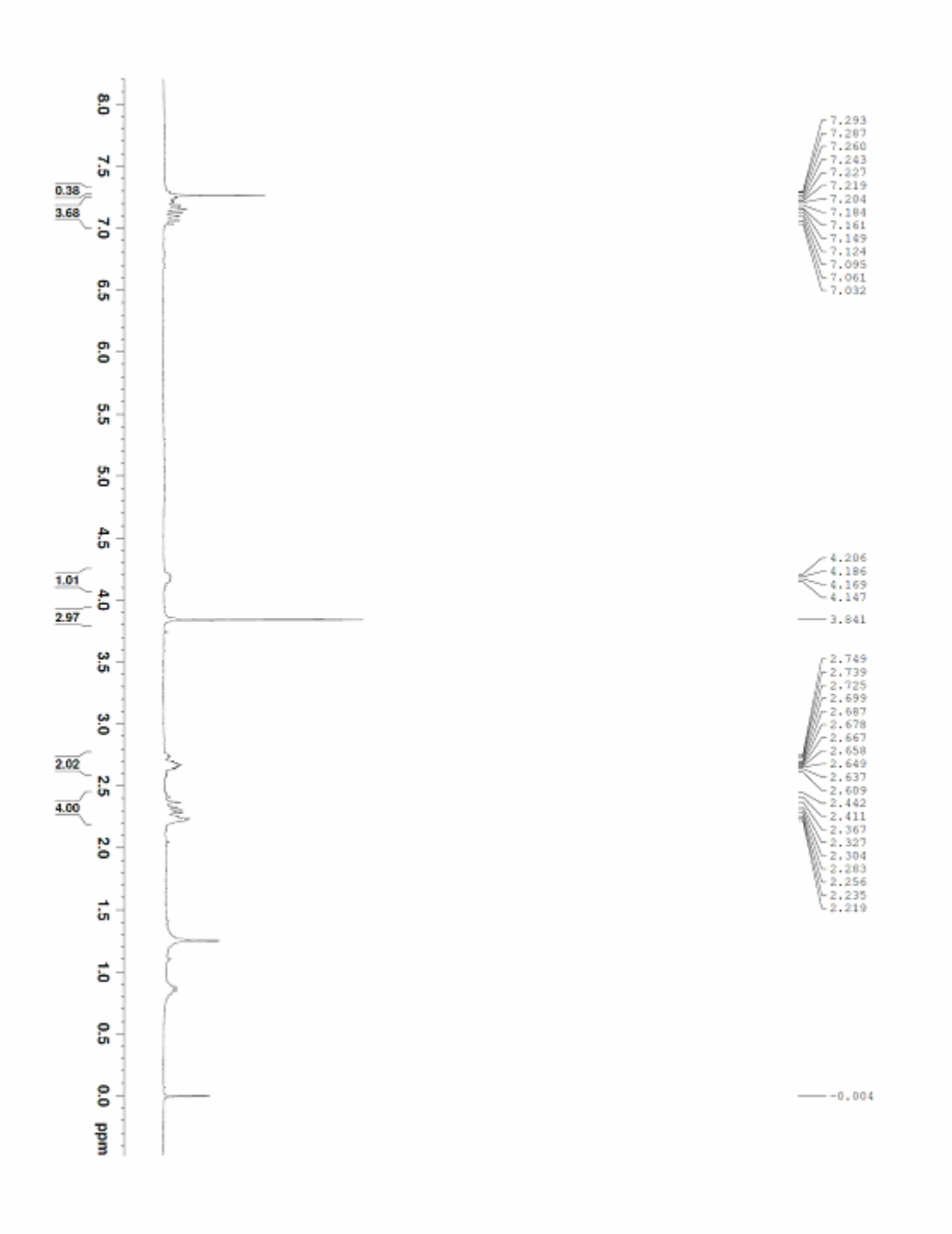

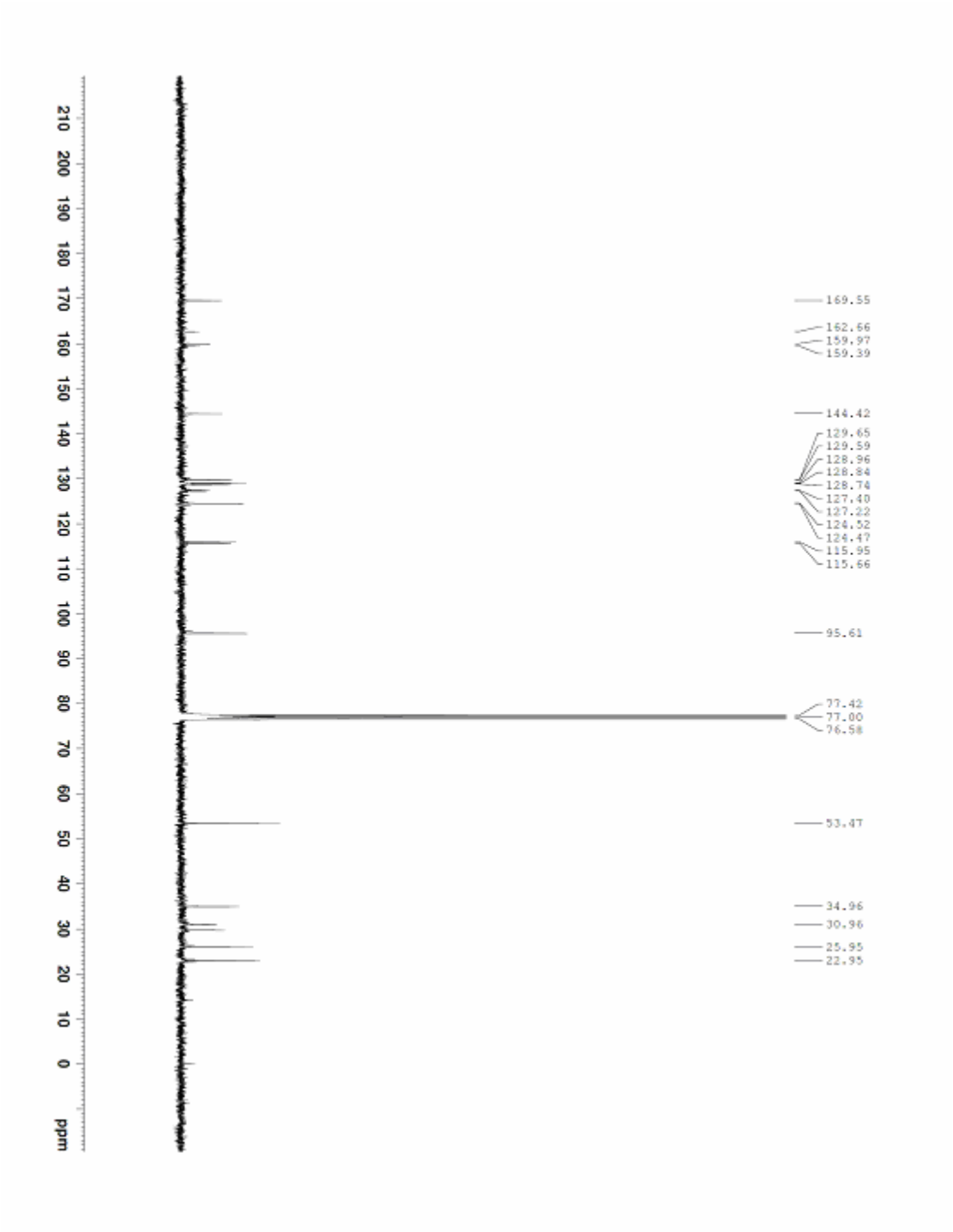

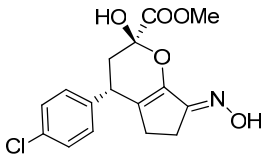

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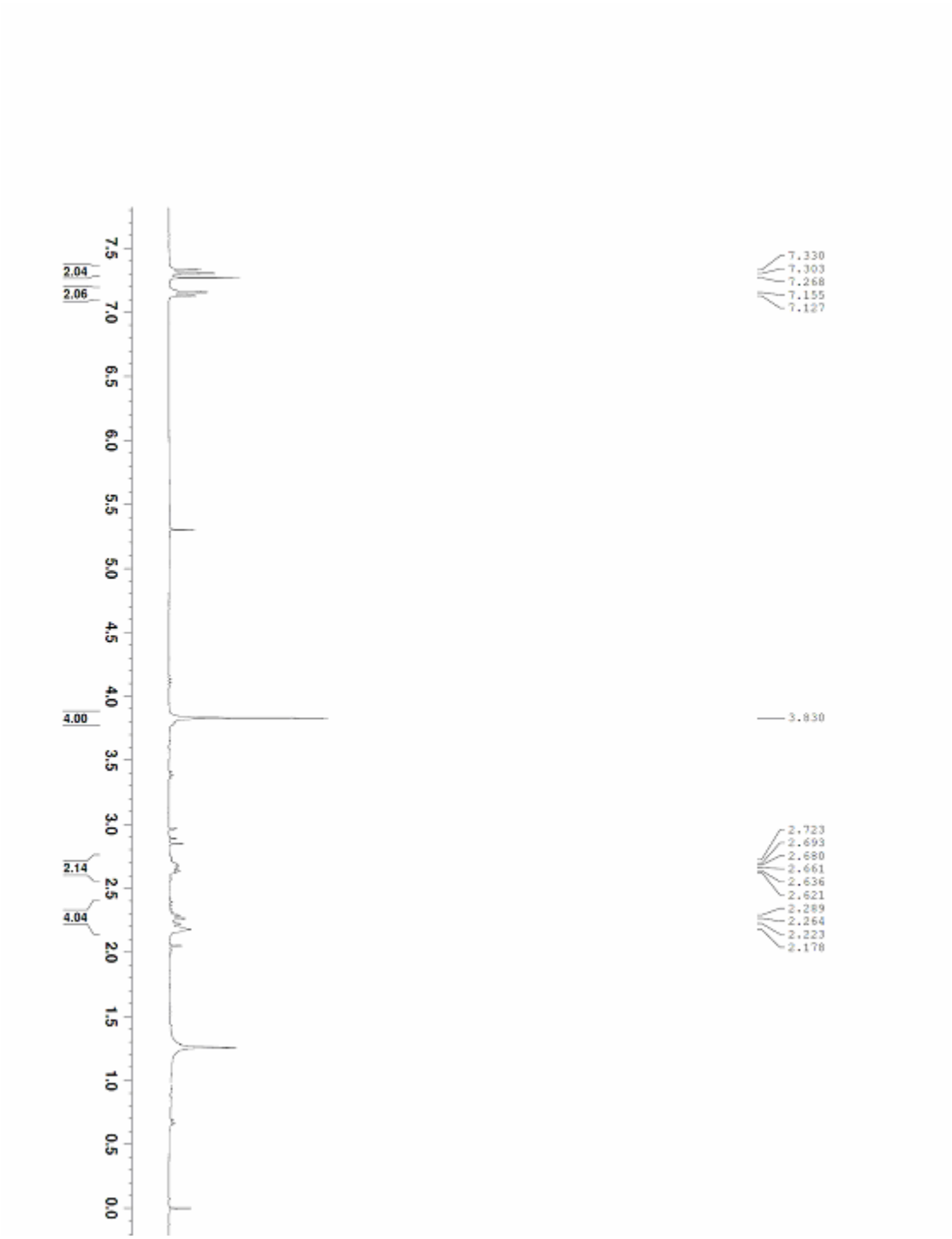

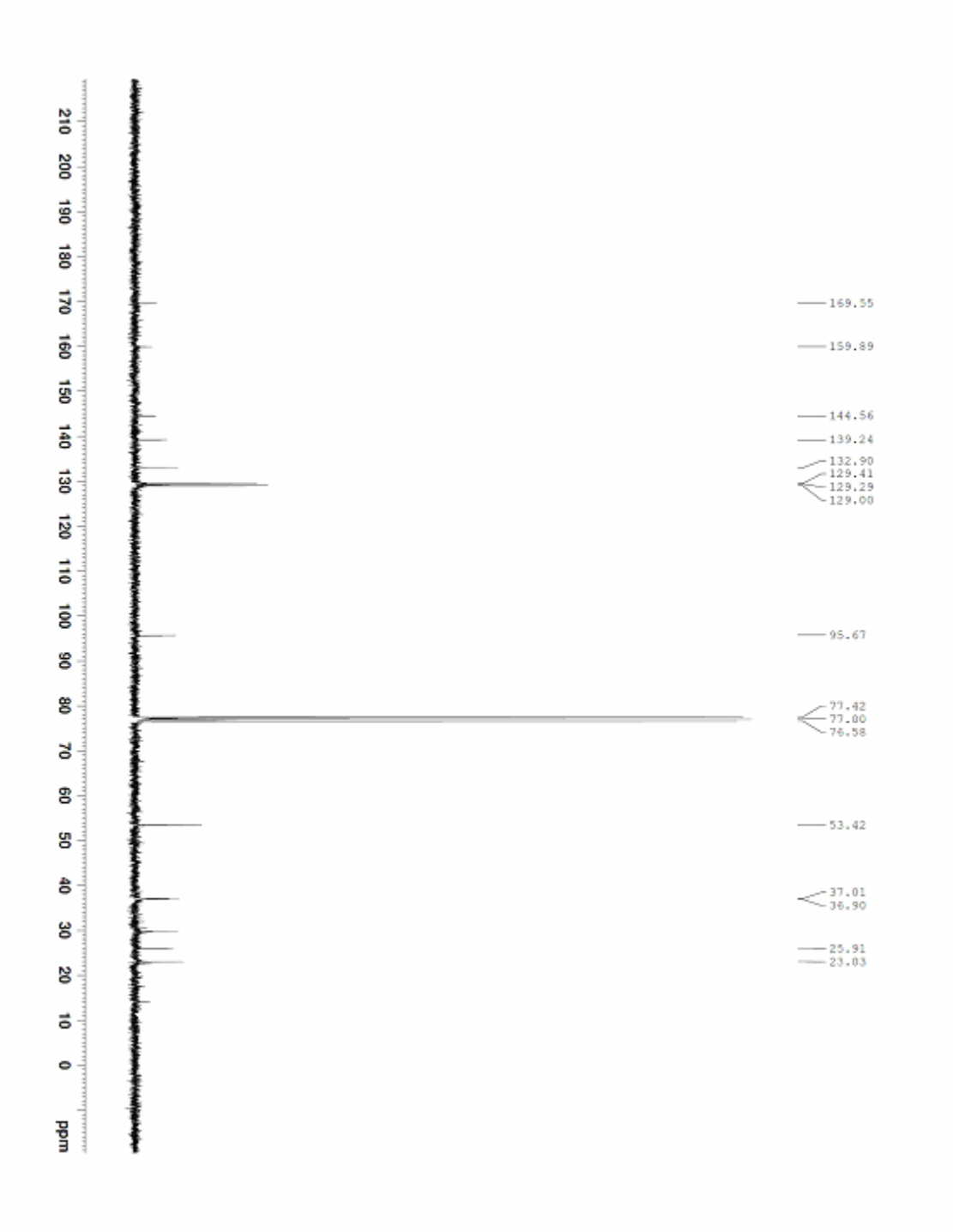

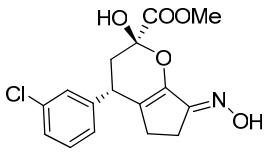

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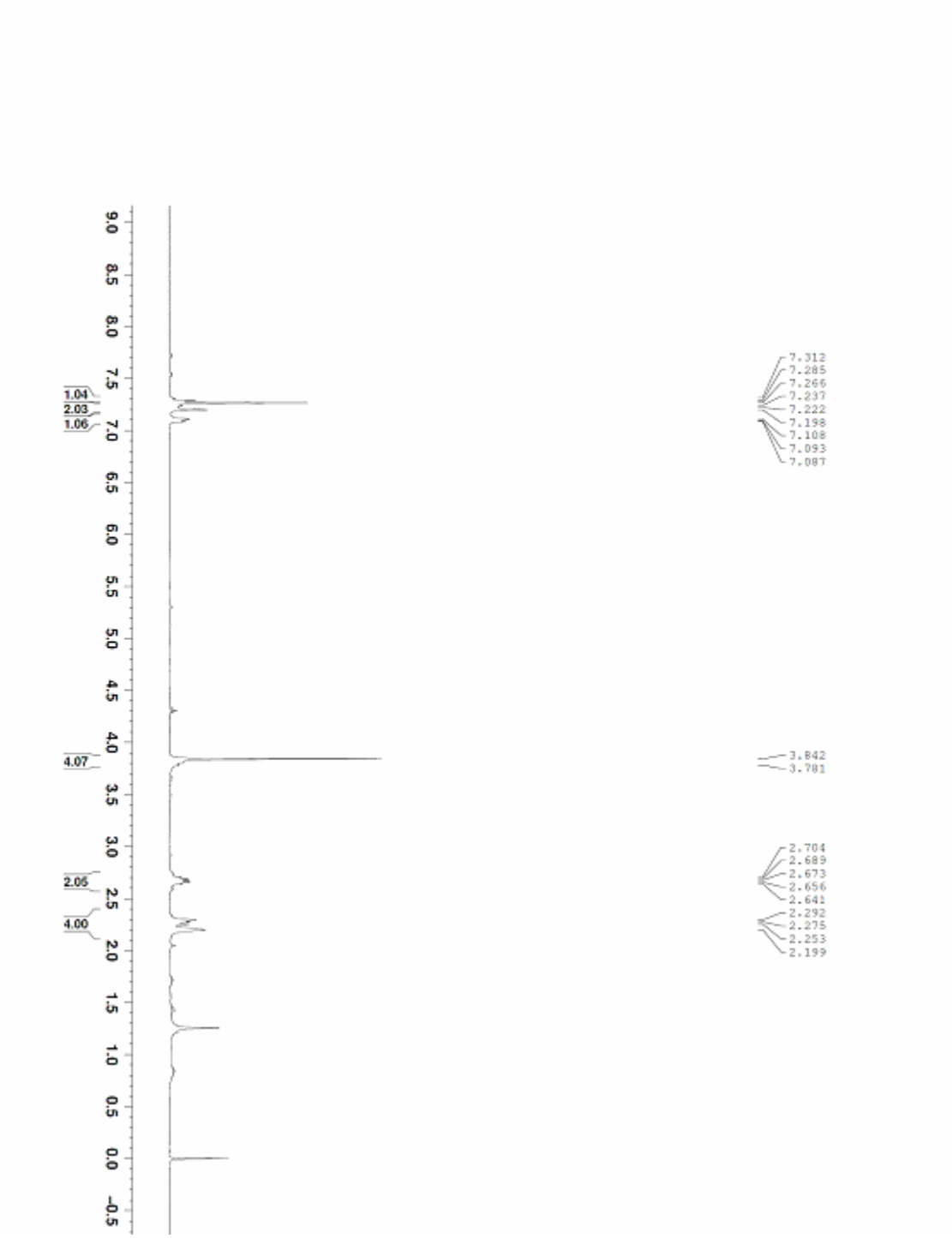

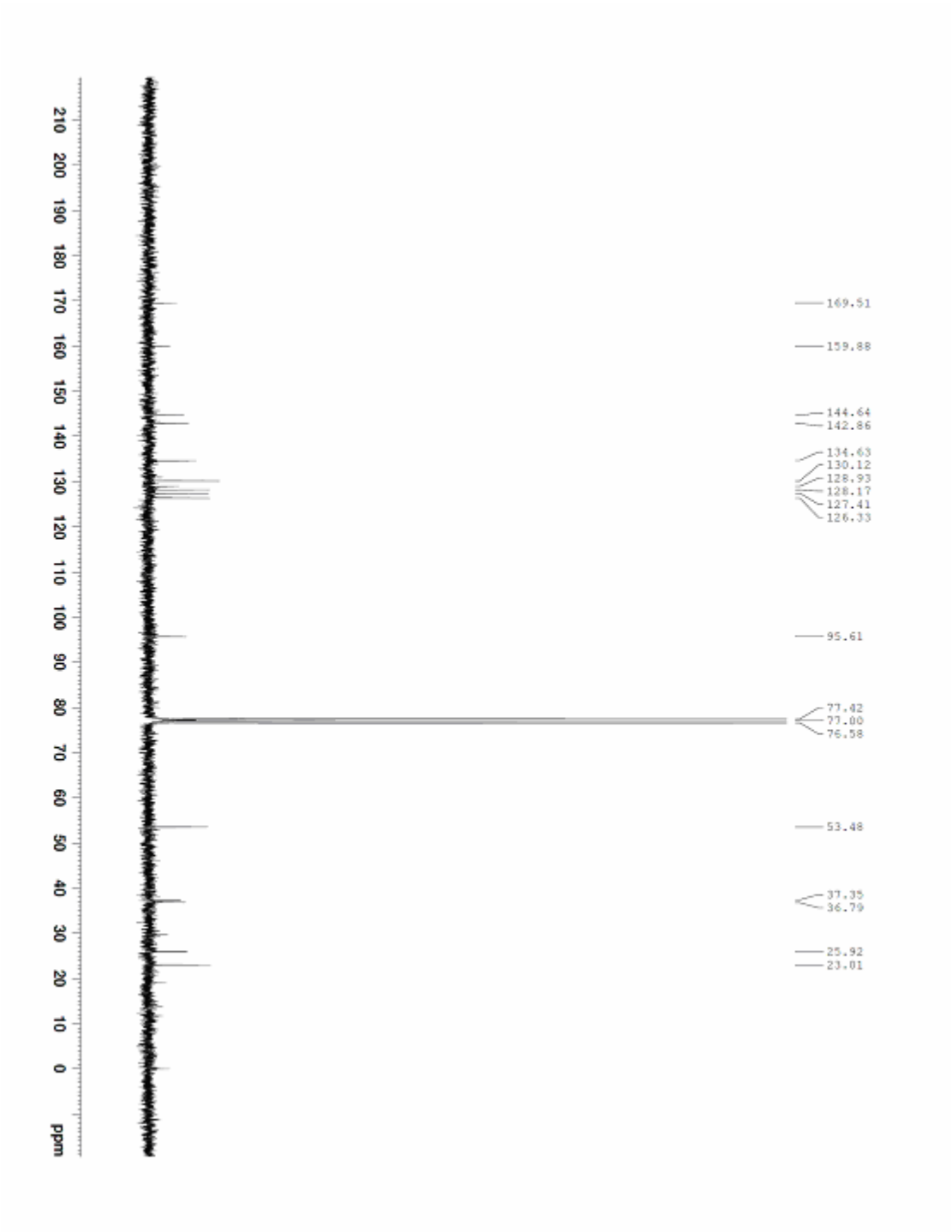

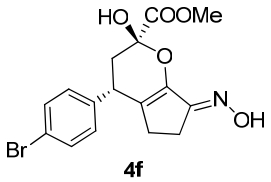
HO
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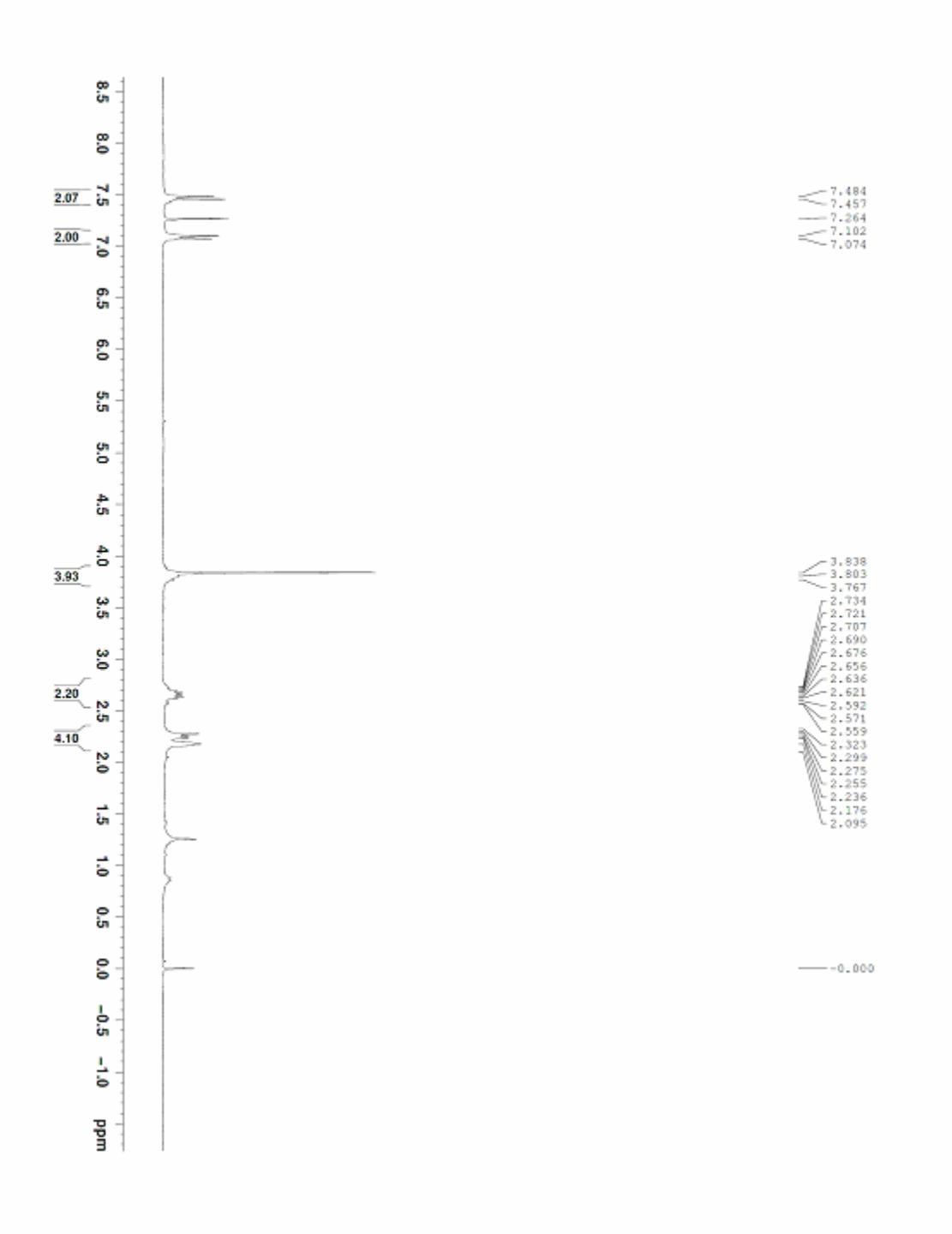
4f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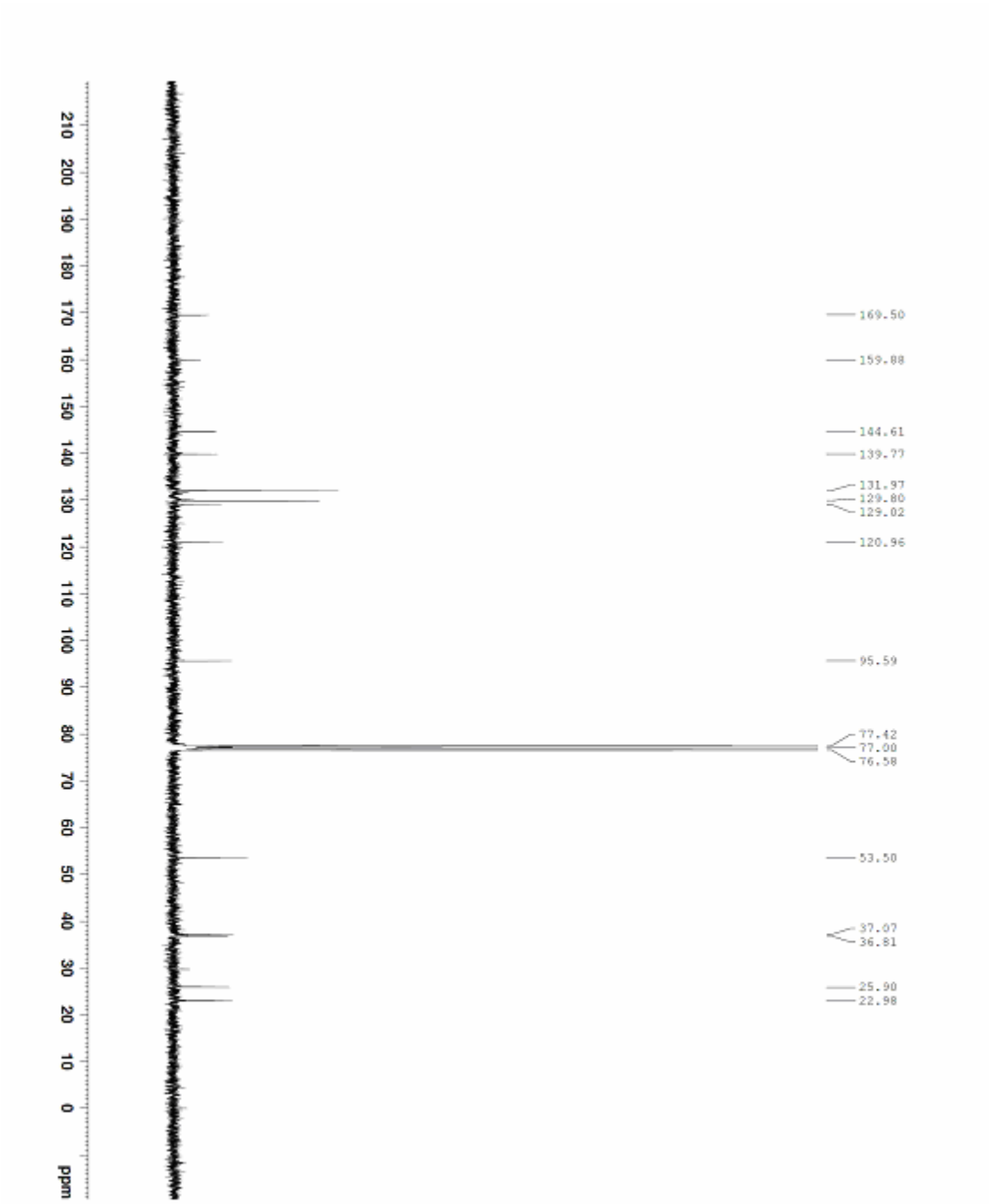
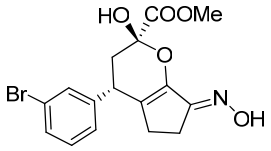
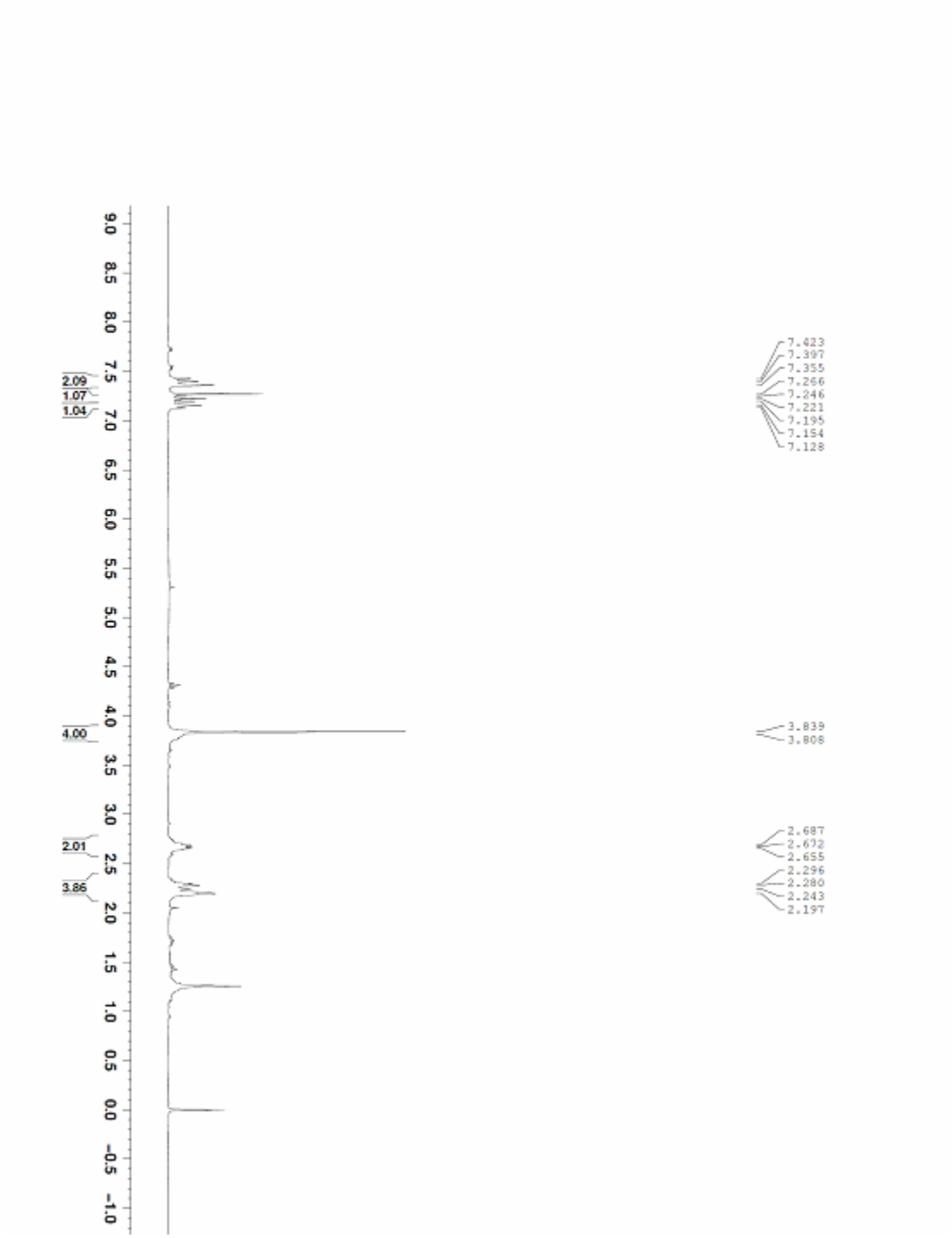
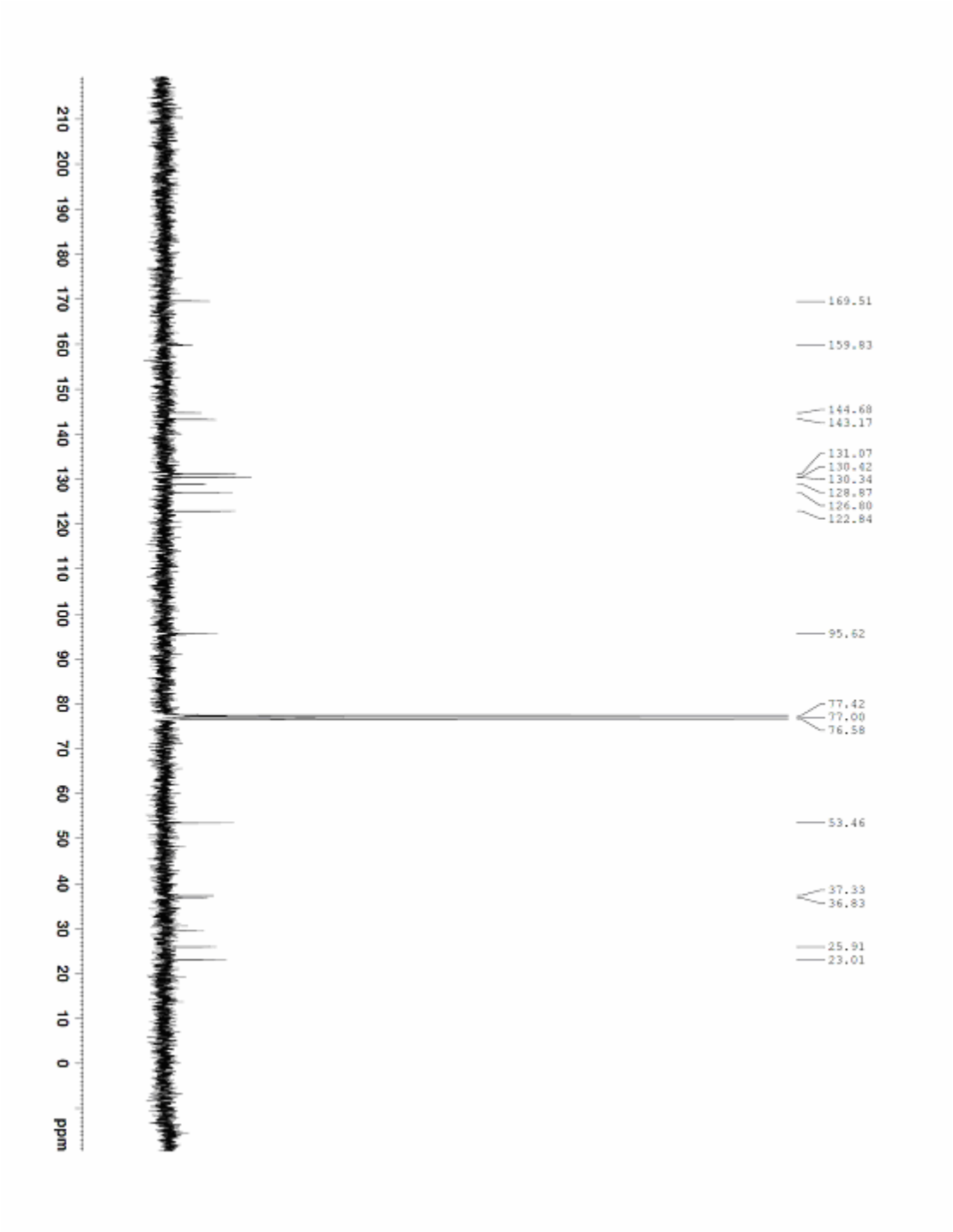




4g

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144.68
143.17
131.07
130.42
130.34
128.87
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95.62
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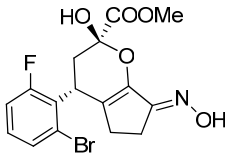
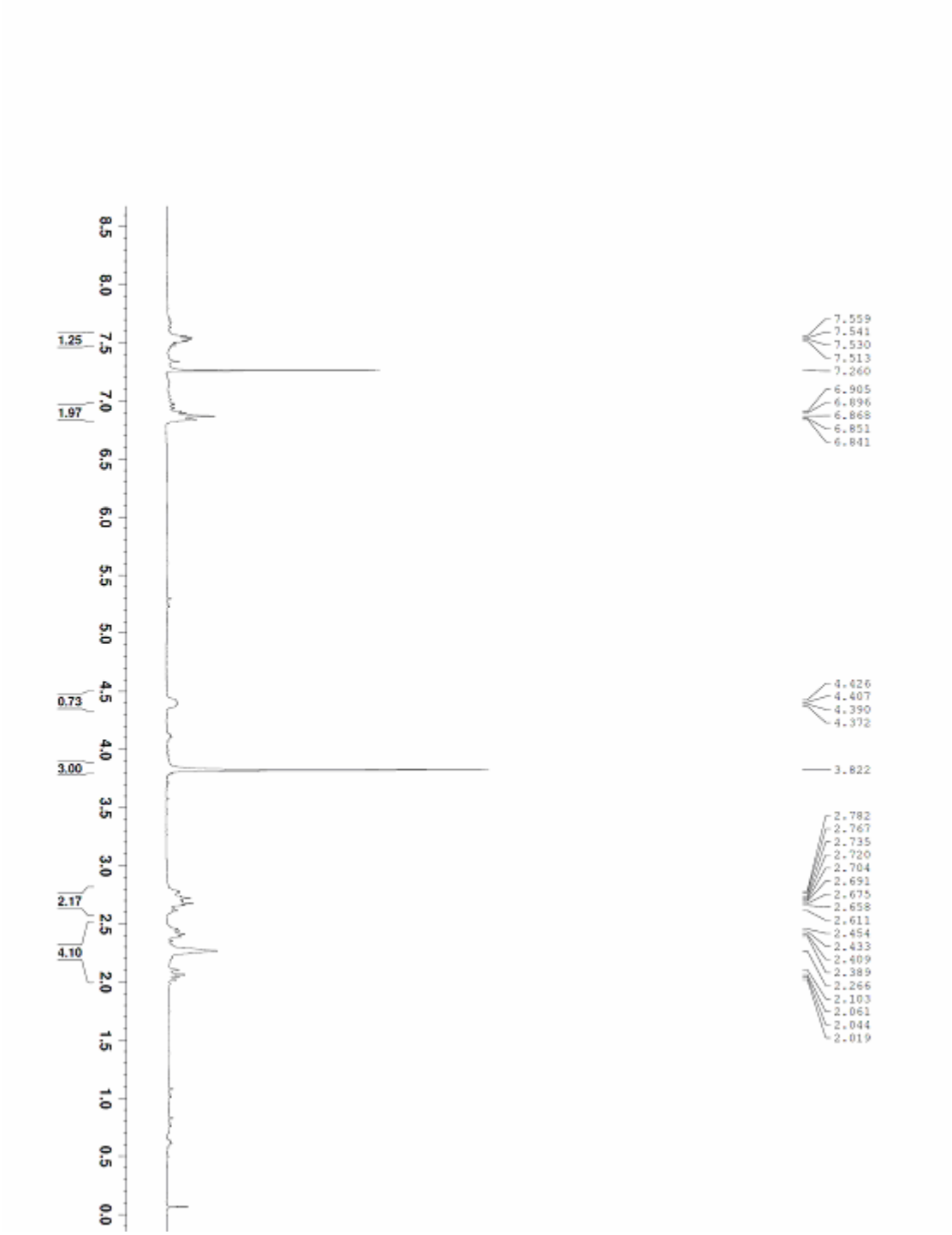
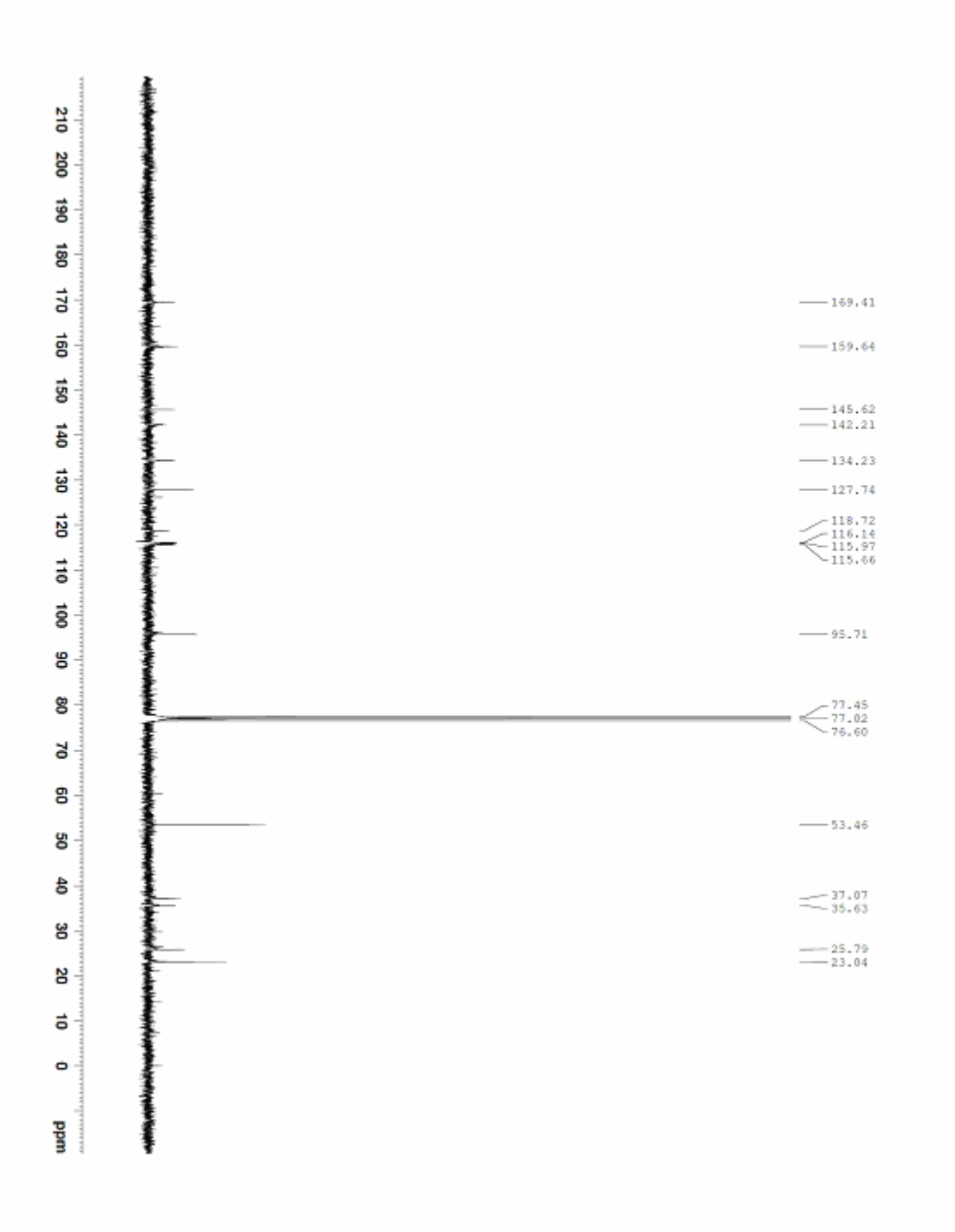
77.00
76.58
53.46
37.33
36.83
25.91
23.01
ppm



4h

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200
190
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170
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150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
169.41
159.64
145.62
142.21
134.23
127.74
118.72
116.14
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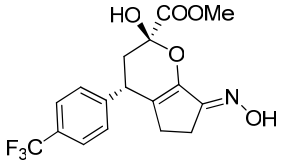
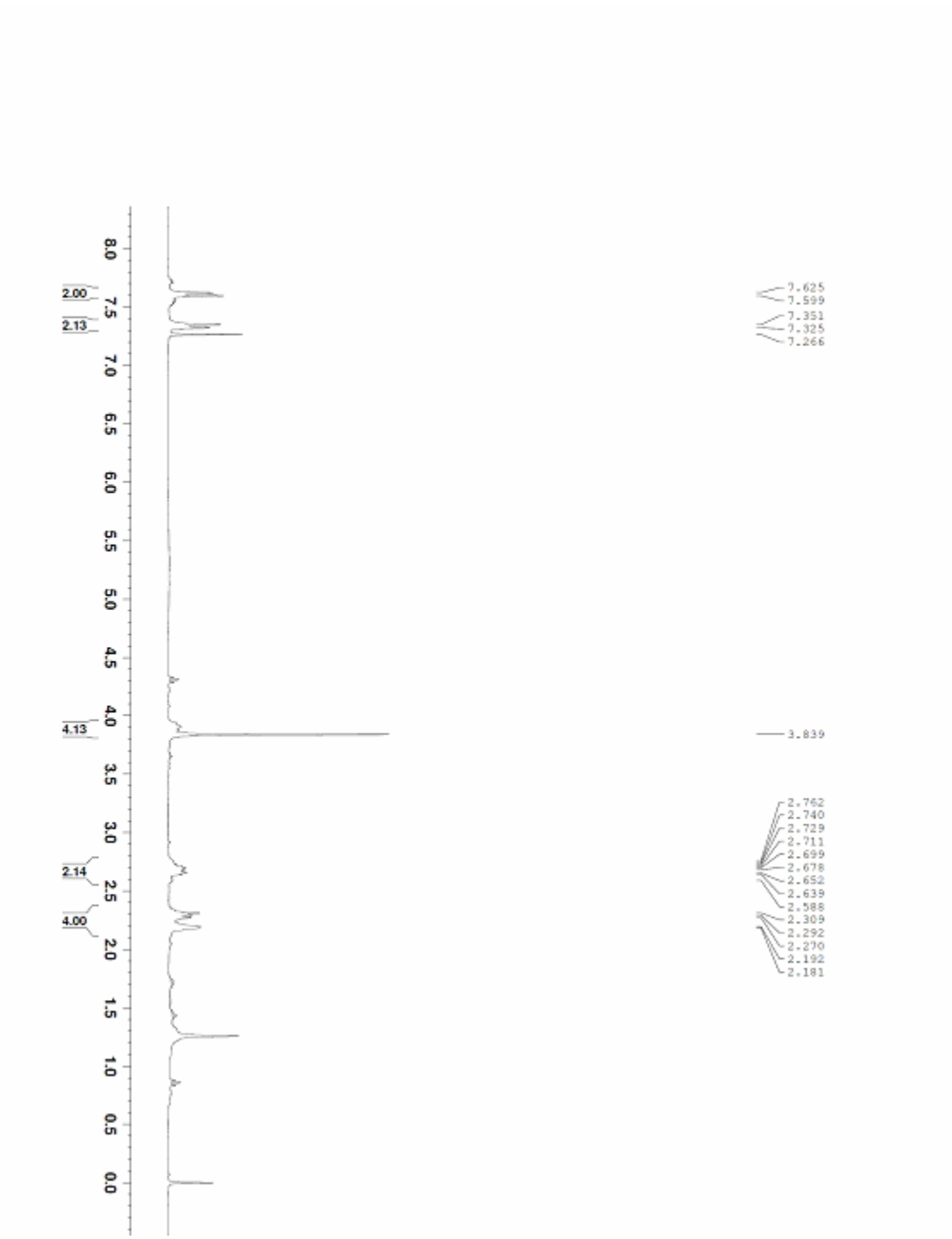
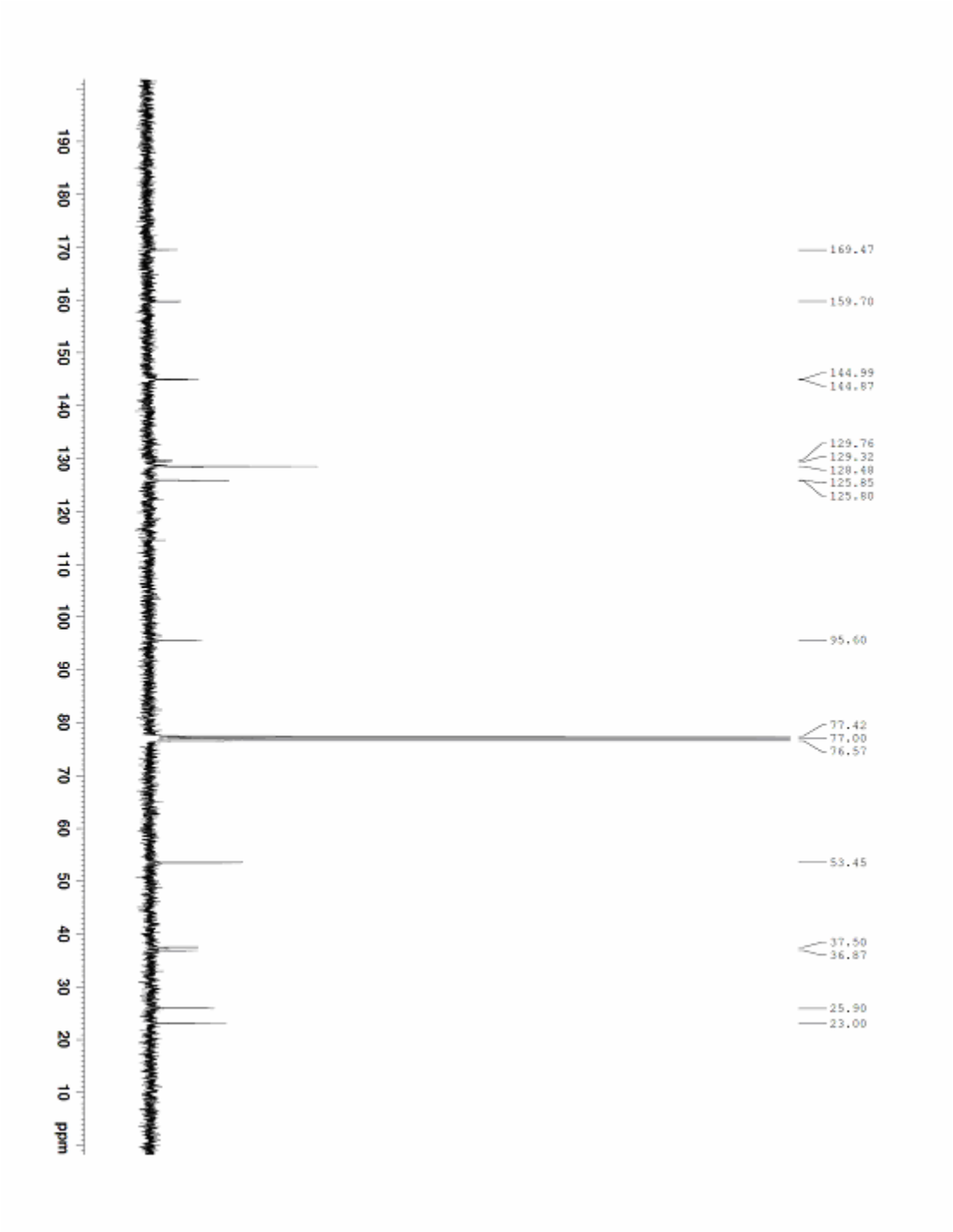
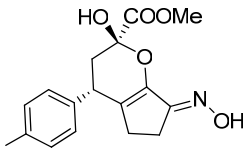
115.66
95.71
77.45
77.02
76.60
53.46
37.07
35.63
25.79
23.04



4i







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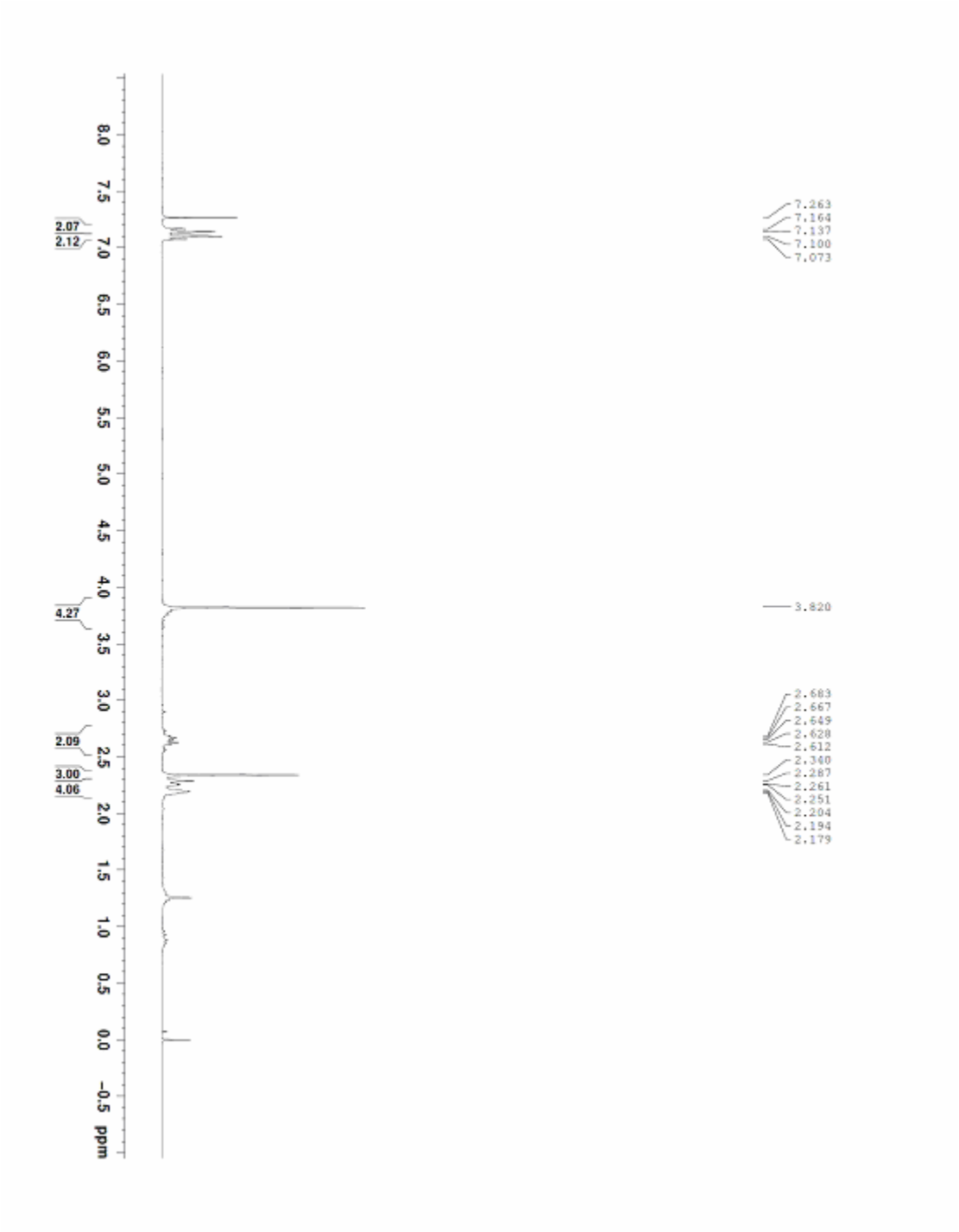
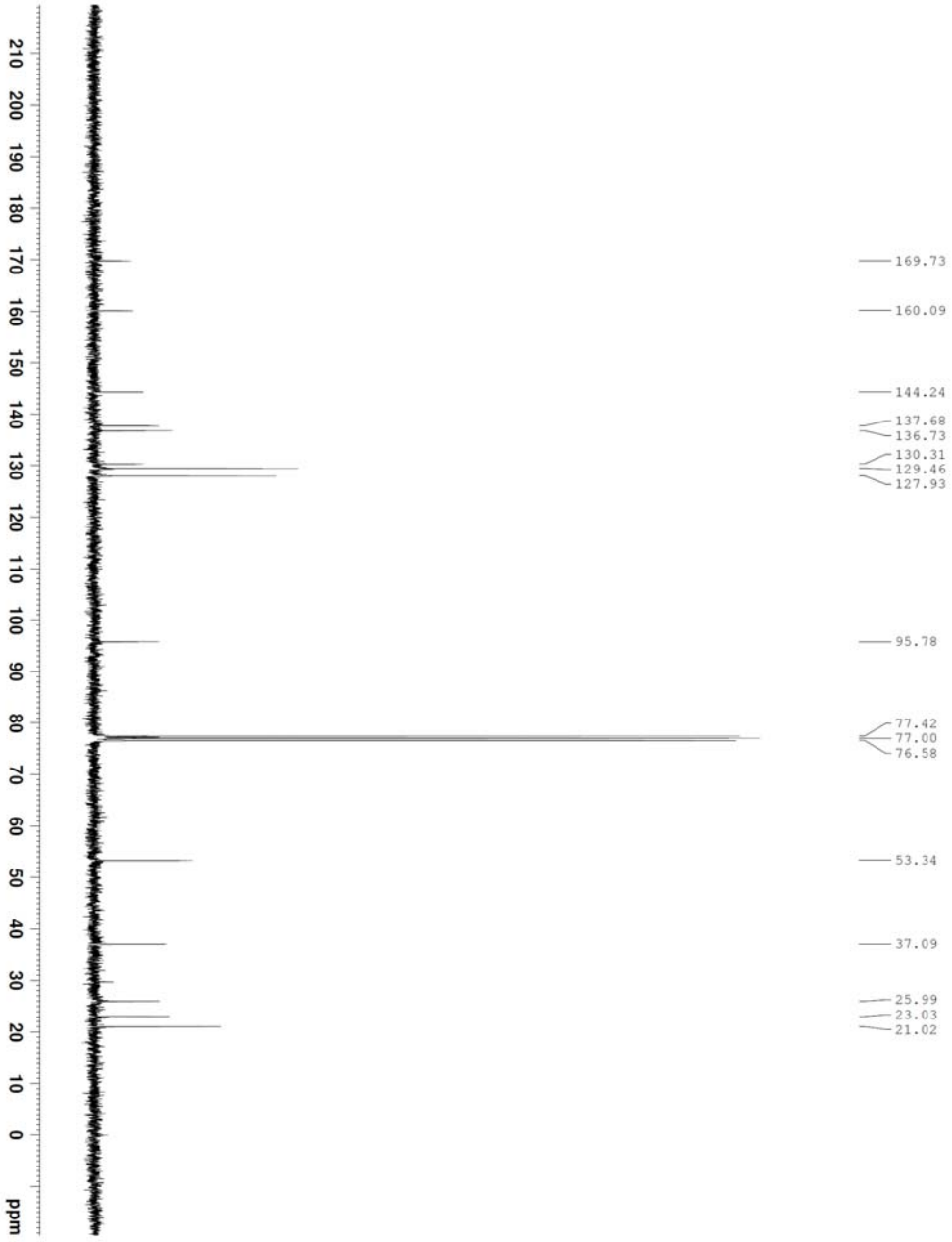
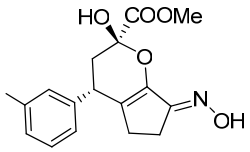
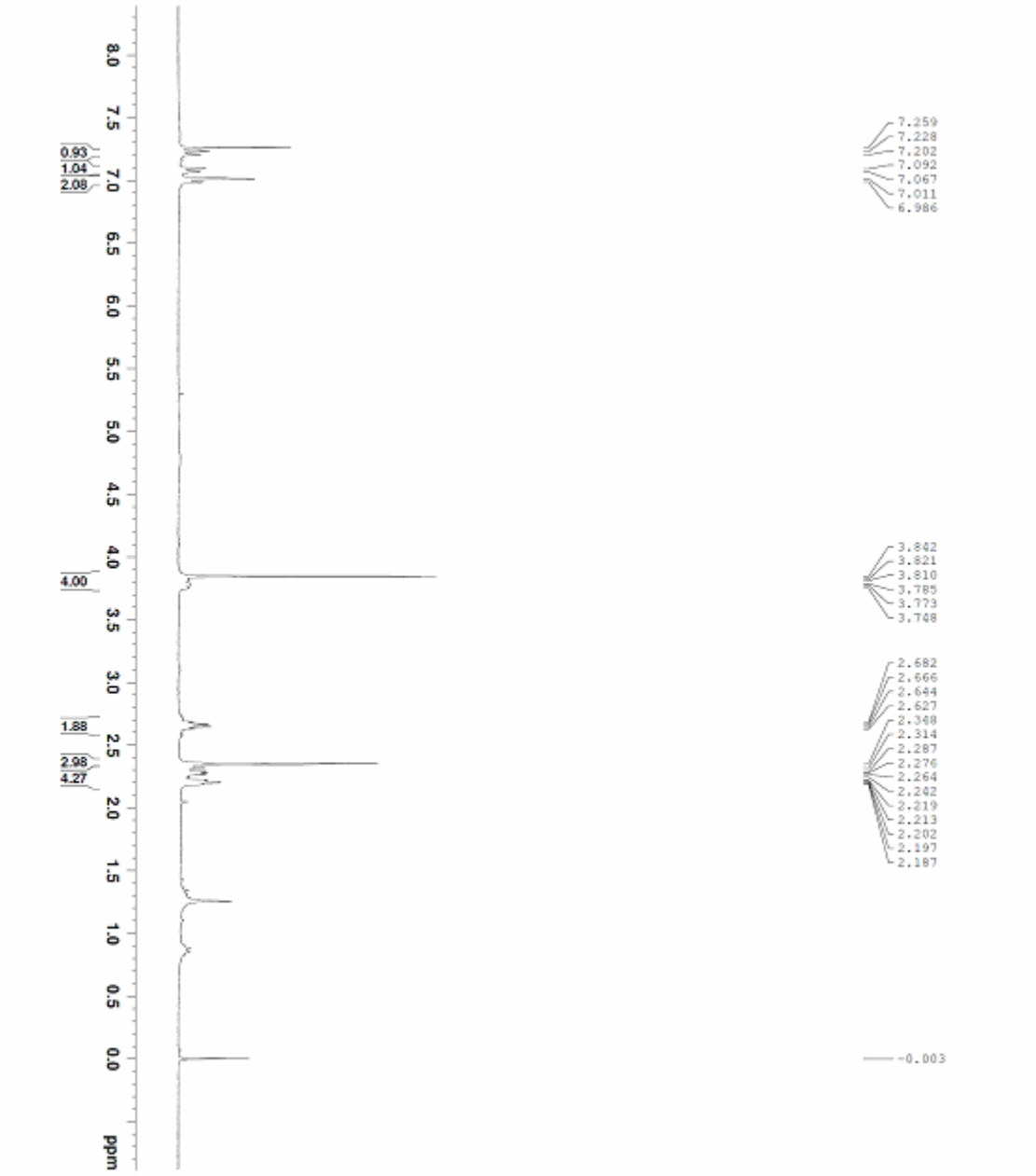





HO
COOMe
O
N
OH

4k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2.98
4.27
ppm
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7.092
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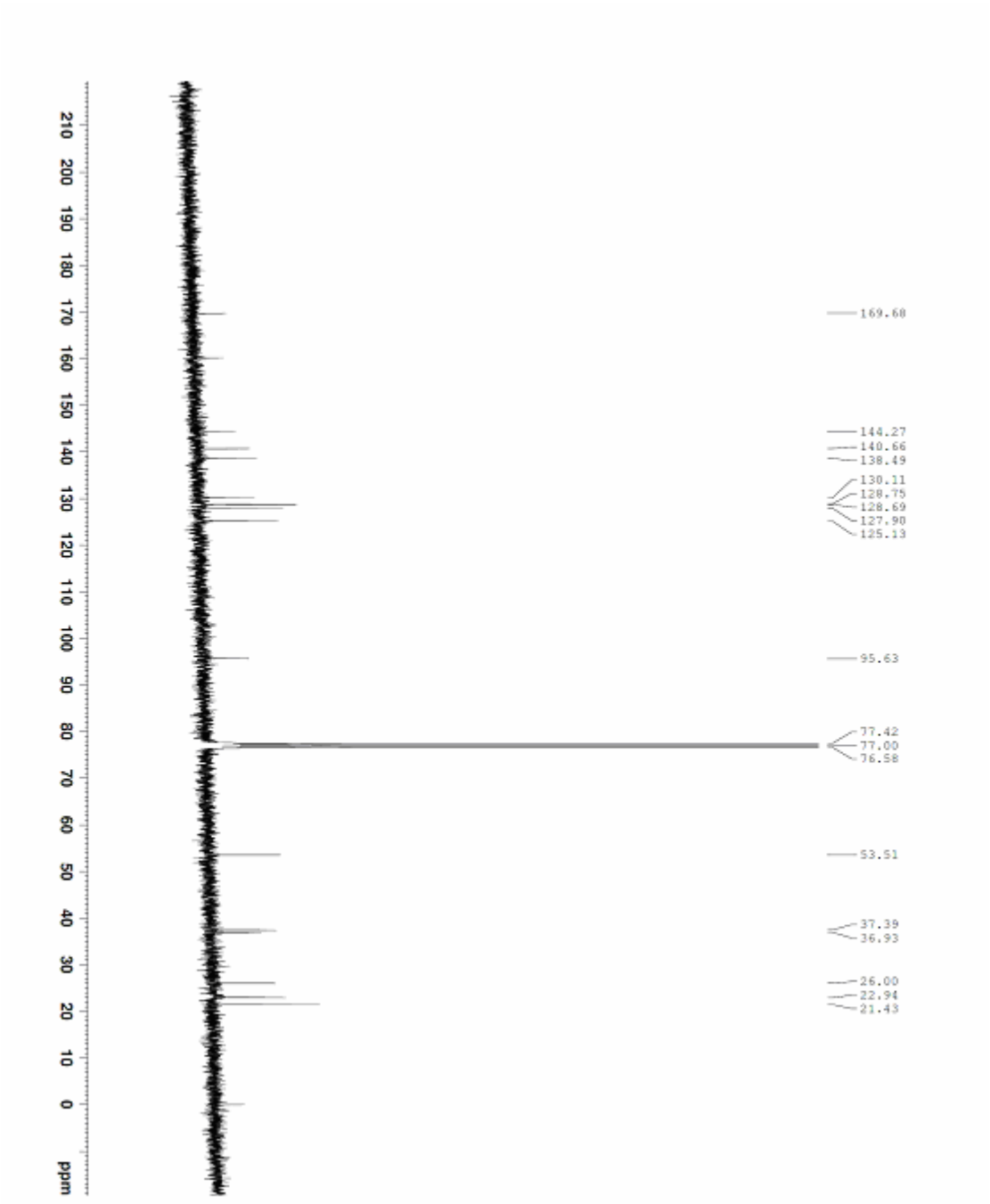
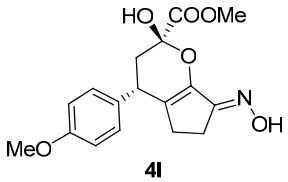
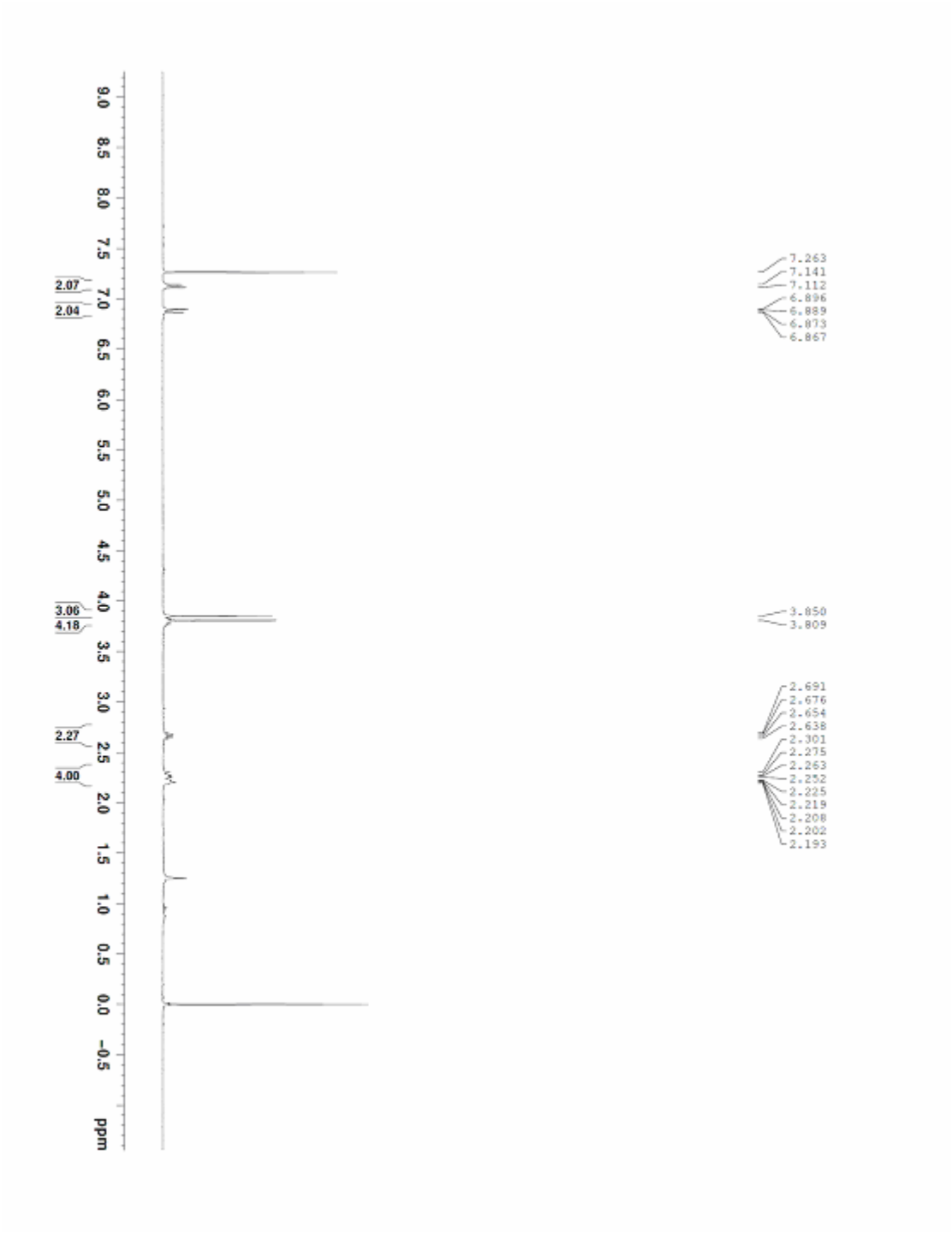
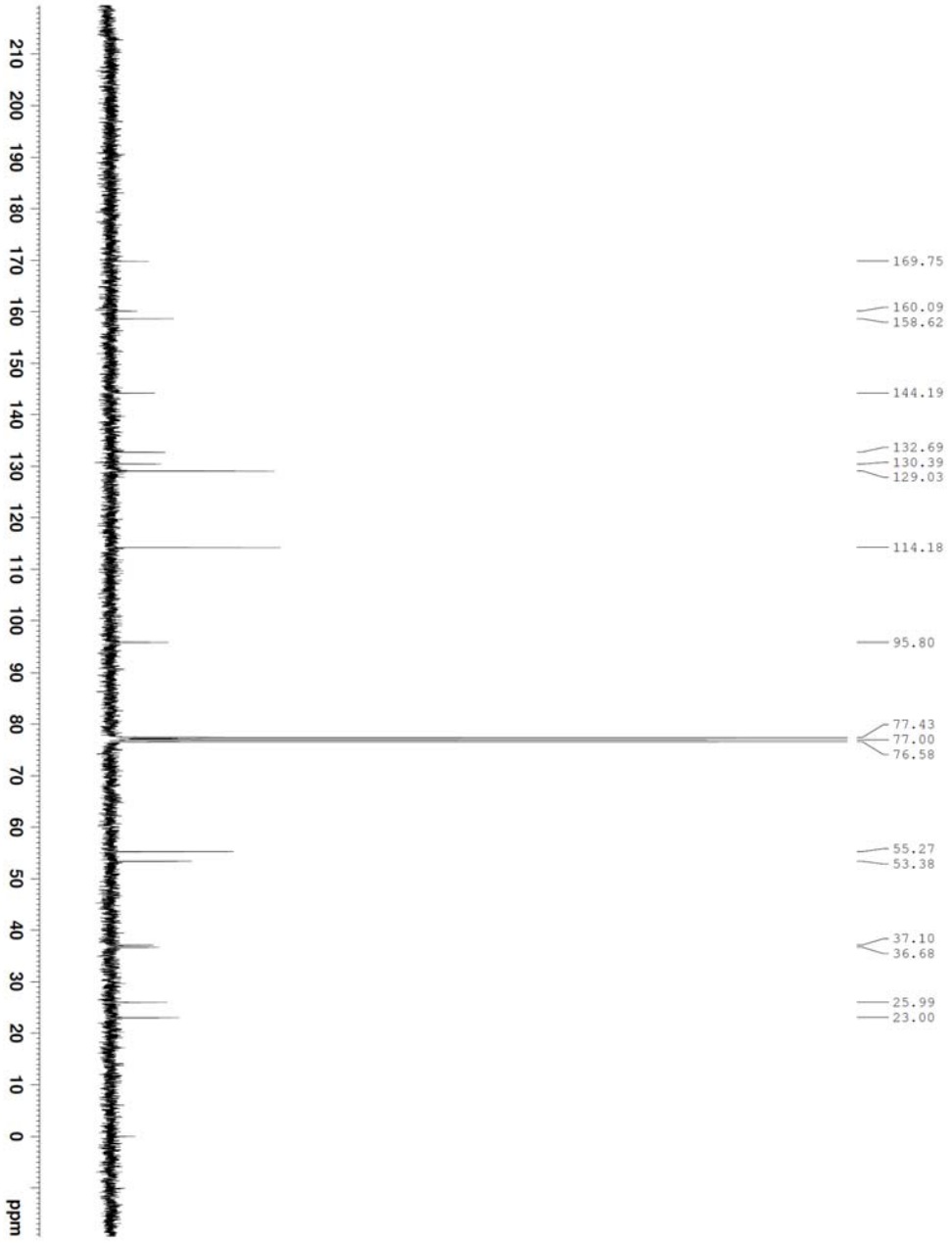
6.986
3.842
3.821
3.810
3.785
3.773
3.748
2.682
2.666
2.644
2.627
2.348
2.314
2.287
2.276
2.264
2.242
2.219
2.213
2.202
2.197
2.187
-0.003

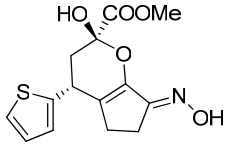




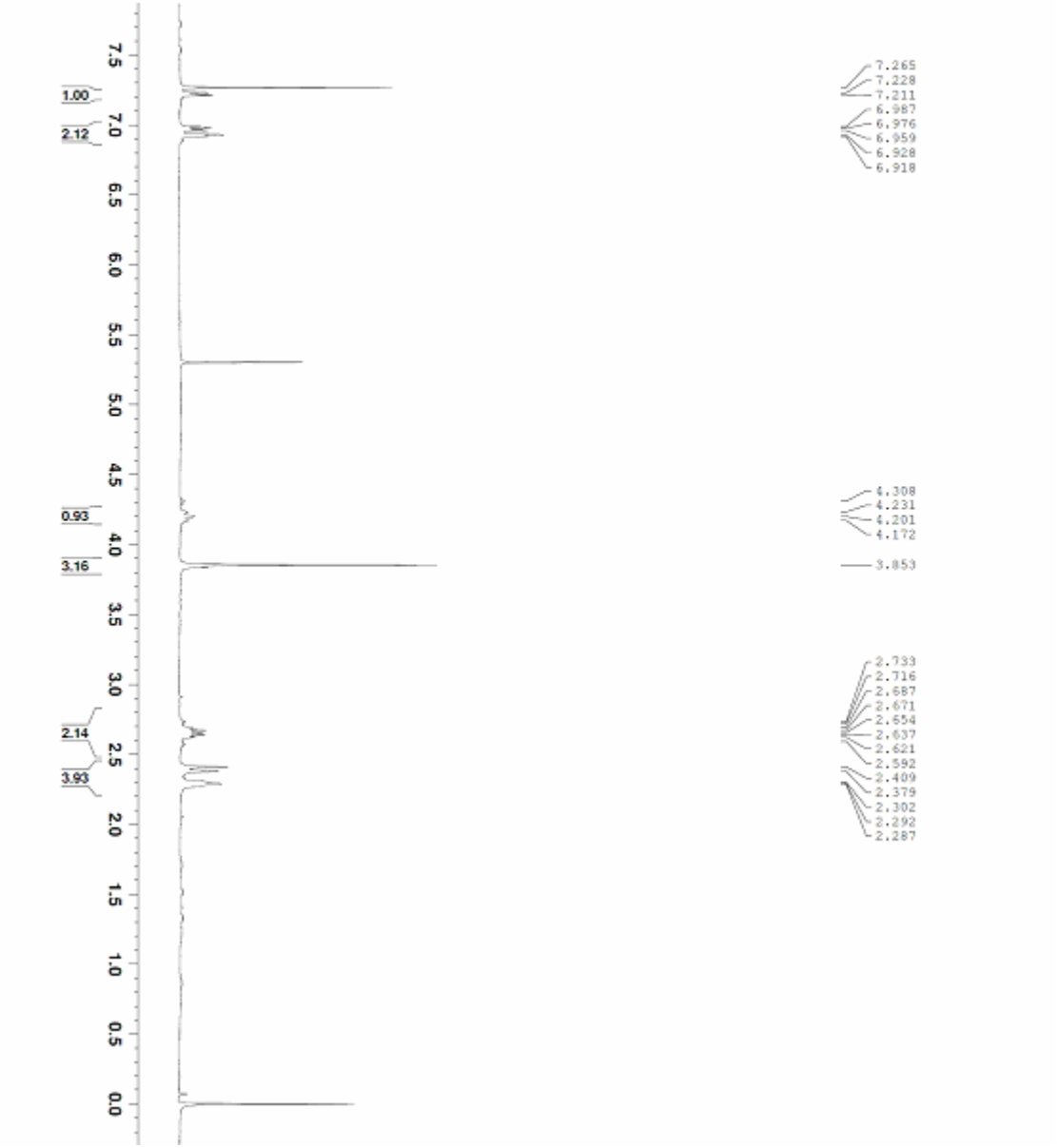
4l

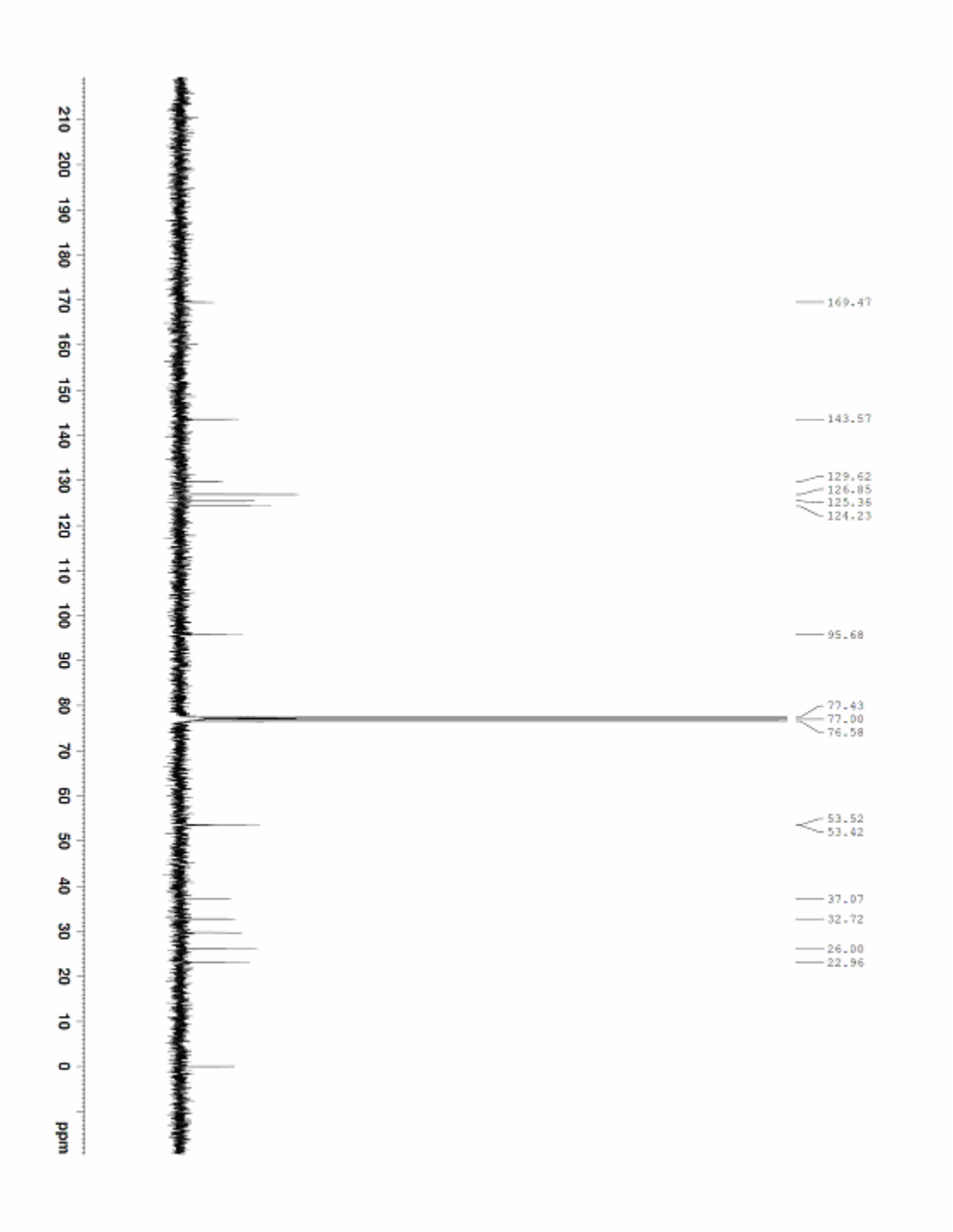


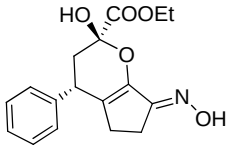




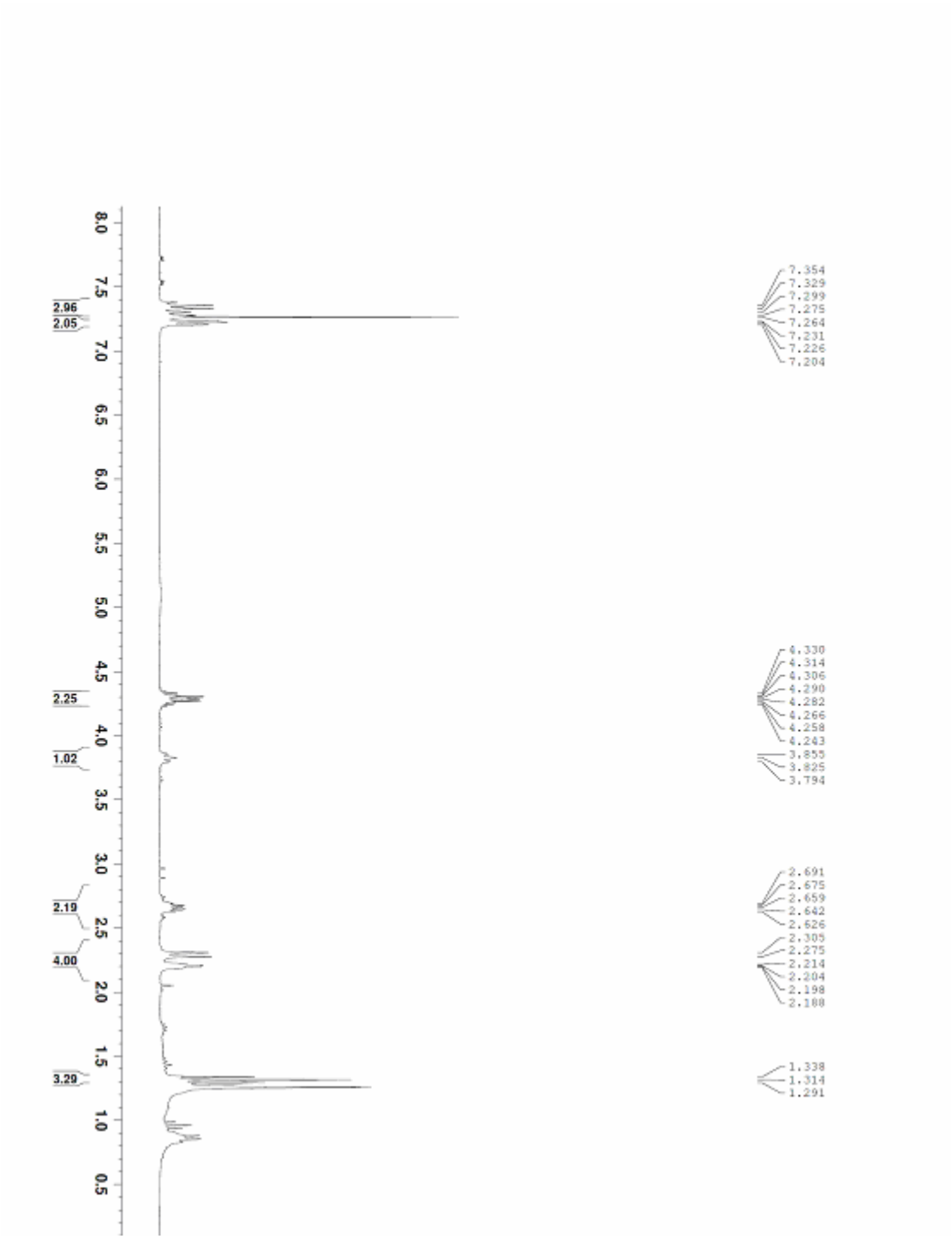
4m

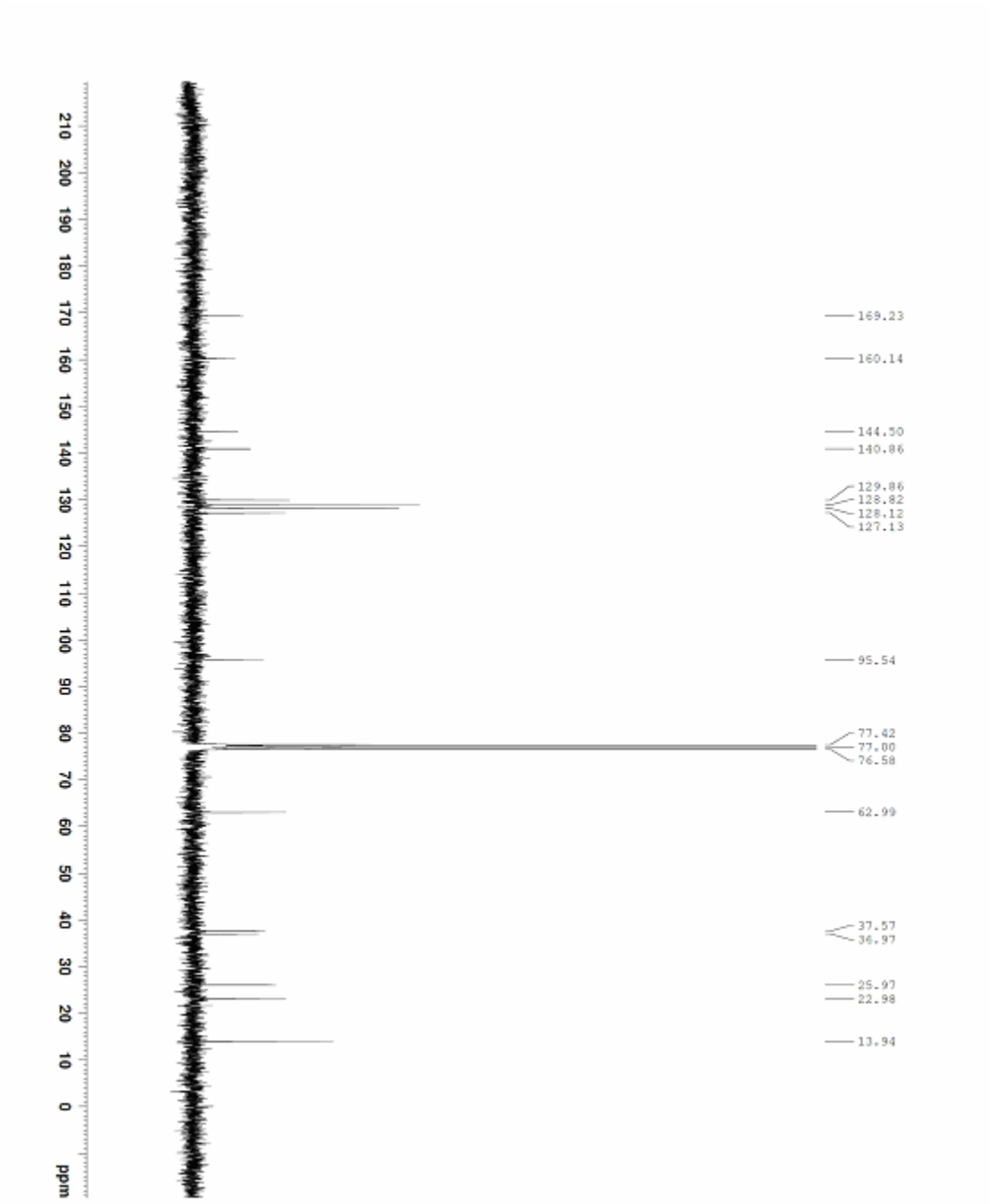


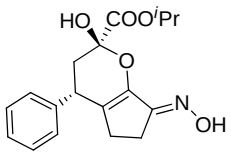




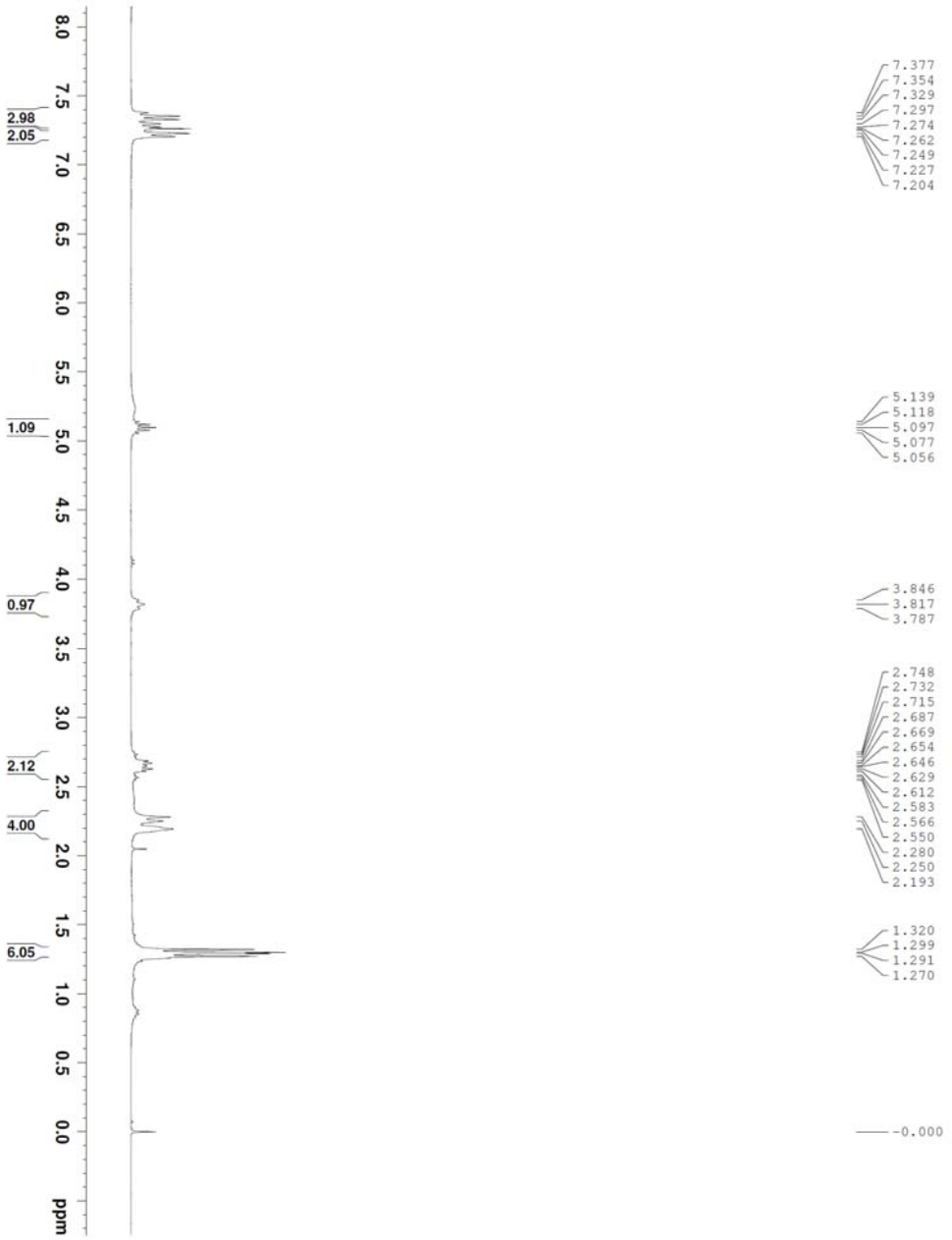
4n






HO
COO^{i}Pr
O
N
OH

4o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3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.98
2.05
1.09
0.97
2.12
4.00
6.05
7.377
7.354
7.329
7.297
7.274
7.262
7.249
7.227
7.204
5.139
5.118
5.097
5.077
5.056
3.846
3.817
3.787
2.748
2.732
2.715
2.687
2.669
2.654
2.646
2.629
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2.550
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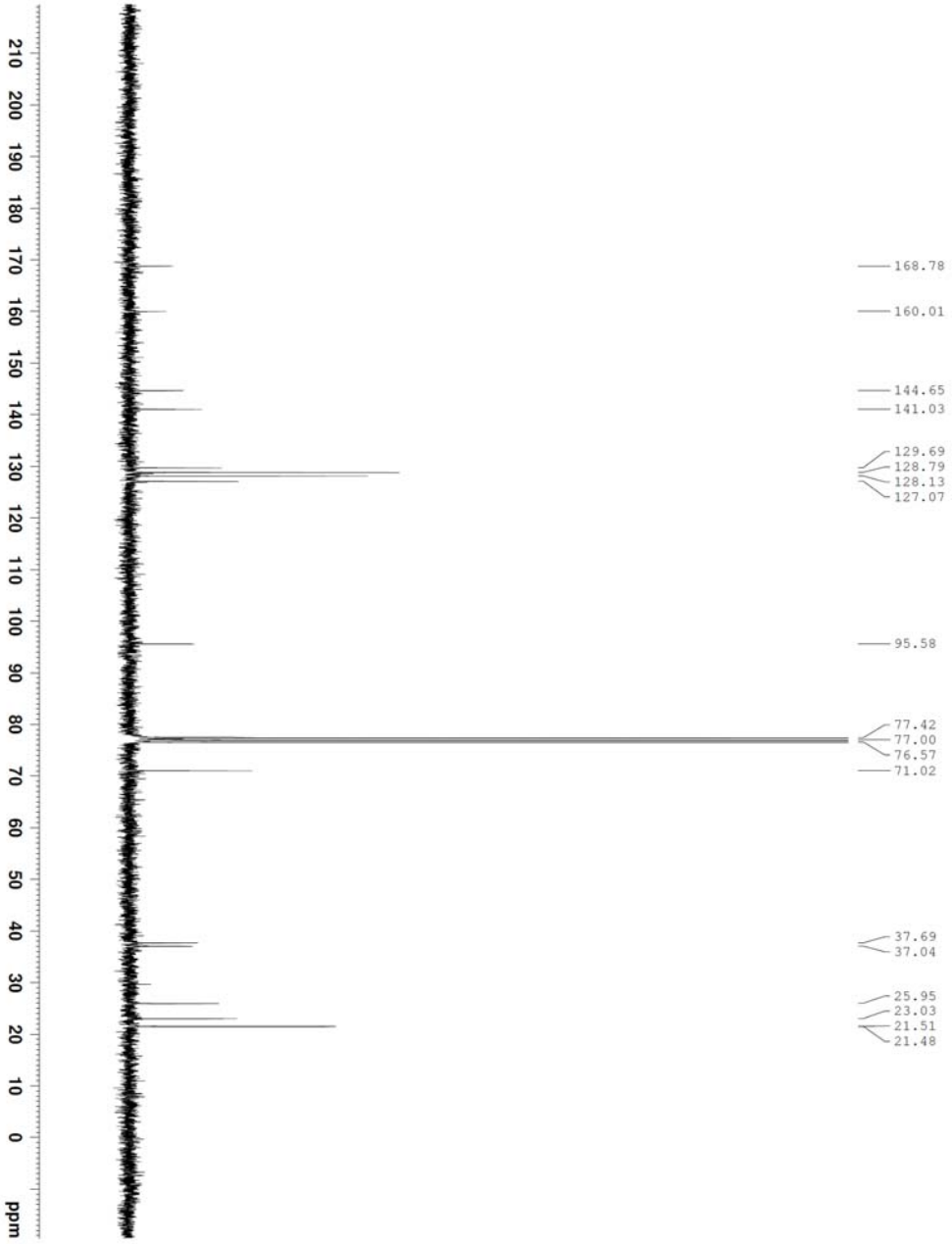
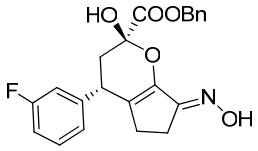
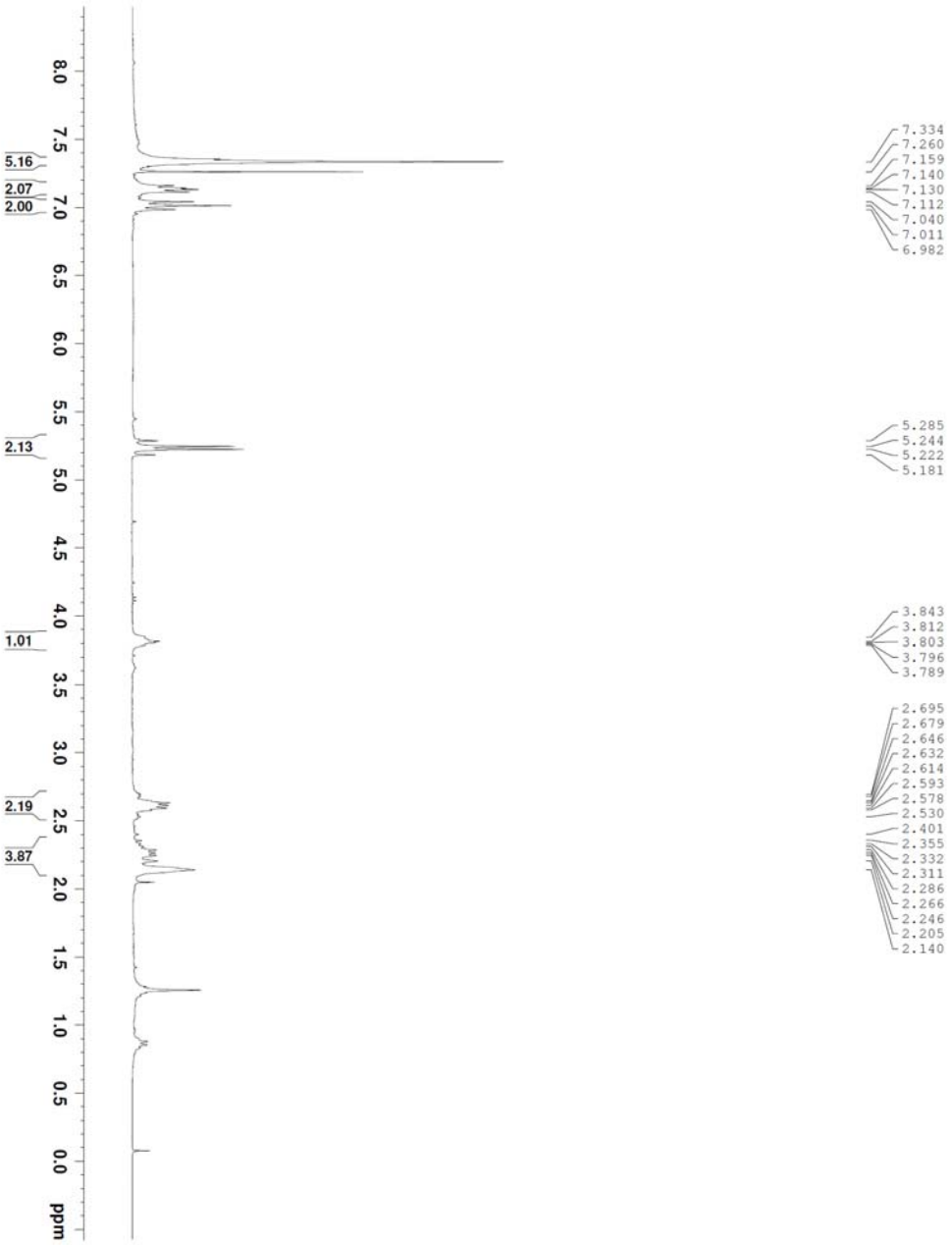
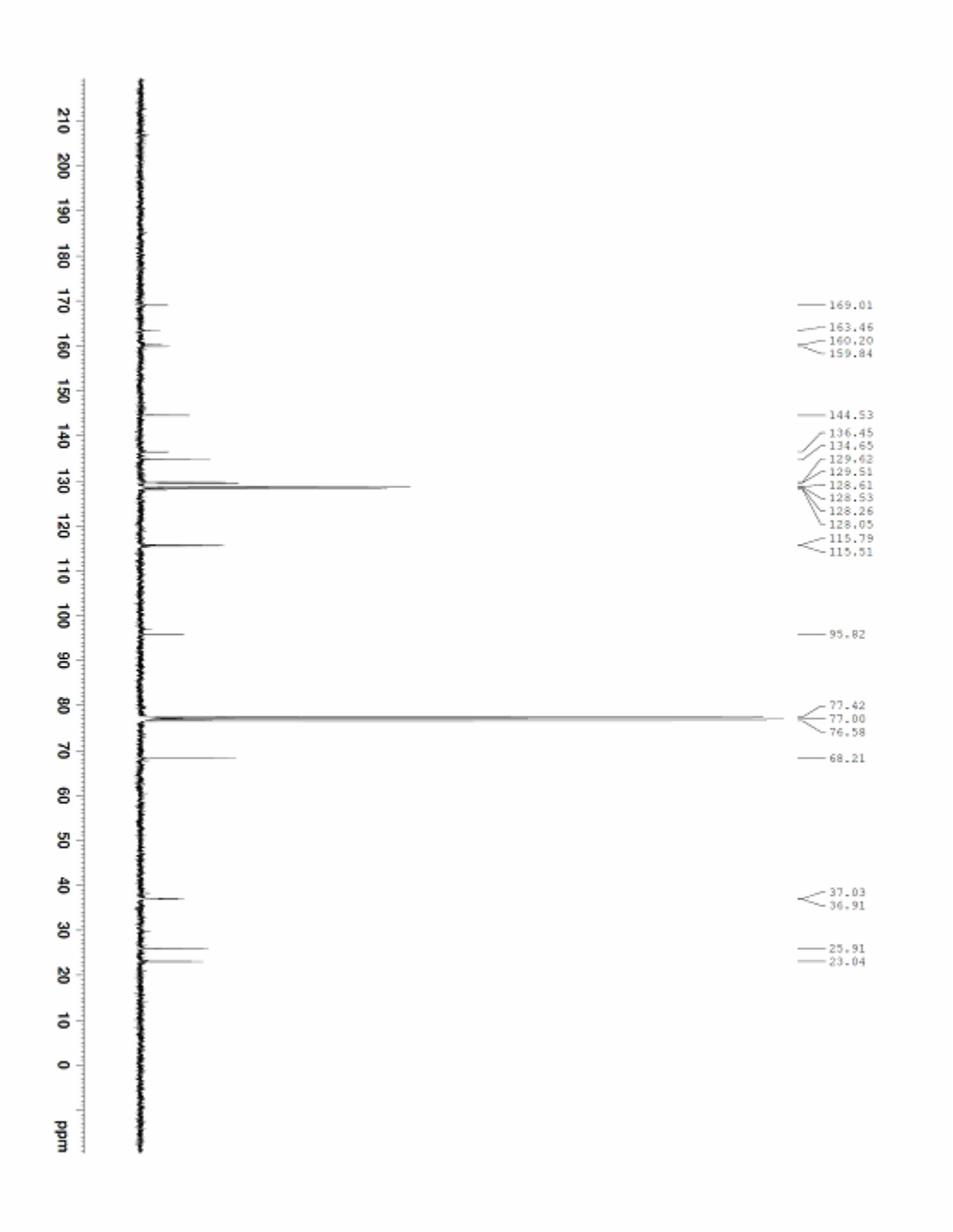
1.320
1.299
1.291
1.270
-0.000

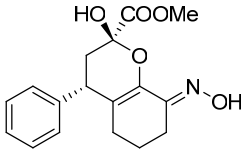




4p







4q