Platinum-Catalyzed 1,3-Acyloxy Migration / [1,5]-Hydride Transfer/ Cycloaddition Sequence: Synthesis of Ring-Fused Tetrahydroquinolines

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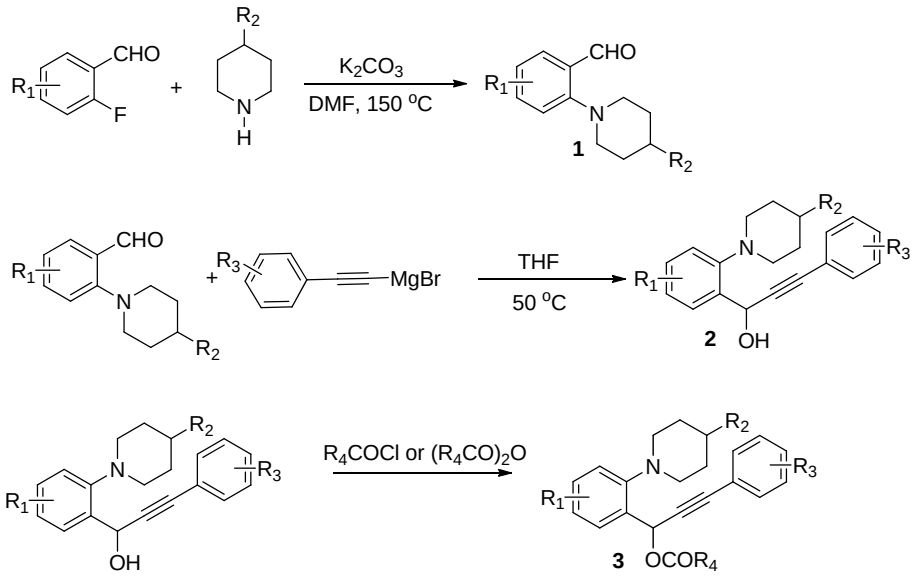
General Remarks:

Column chromatography was carried out on silica gel. Unless noted ^{1}H NMR spectra were recorded on 400 MHz or 300 MHz in $CDCl_3$, ^{13}C NMR spectra were recorded on 100 MHz or 75 MHz in $CDCl_3$ using TMS as internal standard. IR spectra were recorded on an FT-IR spectrometer and only major peaks are reported in cm^{-1}. Melting points were determined on a microscopic apparatus and were uncorrected. All products were further characterized by HRMS (high resolution mass spectra); copies of their ^{1}H NMR and ^{13}C NMR spectra are provided. Commercially available reagents and solvents were used without further purification.

Typical procedure for the preparation of propargylic esters derivatives



(i) To a stirred solution of potassium carbonate (3.0 g, 22.0 mmol) in 20 mL DMF was added 2-fluorobenzaldehyde (2.5 g, 20 mmol) and piperidine (1.9 g, 22.0 mmol). After heating the reaction mixture at reflux for 8 h, it was cooled and diluted with diethyl ether and water. The organic layer was extracted with diethyl ether (2 × 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel.

(ii) To a stirring solution of 2-(piperidin-1-yl)benzaldehyde (1 equiv) in THF (1.0 M) was added phenylethynylmagnesium bromide (1.0 M in THF, 2 equiv) at room temperature. After heating the reaction mixture at 50 °C for 6 h, the reaction mixture was quenched by addition of saturated aqueous ammonium chloride (40 mL) and

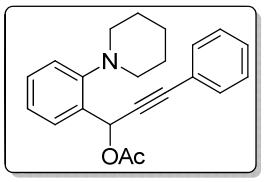
extracted with ethyl ether (2 × 40 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by flash column chromatography to obtain the pure product.

(**iii**) To a stirred solution of **2**, DMAP (5 %), and pyridine (10 equiv.) in 20 mL DCM was slowly added acyl chloride at 0 ^oC, or to a stirred solution of **2**, triethylamine (3 eq), DMAP (10 %) was slowly added acetic anhydride (1.3 eq) at 0 ^oC, when the reaction was finished, 5 ml water was added. The organic layer was extracted with DCM (2 × 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel.

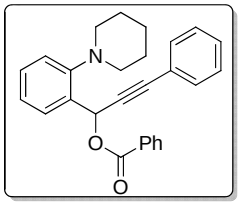
General procedure for the preparation of product 2a-2o

To a test tube, **propargylic esters derivatives** (0.20 mmol), $PtCl_2$ (15 mol %), LiCl (2eq) and CaO (4 eq) were added. The test tube was purged under vacuum and then refilled with argon 3 times. Toluene (2.0 mL) was then injected, and the mixture was allowed to stir at 110 °C. When the reaction was considered complete as determined by TLC analysis, ethyl acetate (20 mL) and water (20 mL) were then added to the reaction mixture. The organic layer was extracted with ethyl acetate (2 × 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The residue was purified by flash chromatography on alkalescence silica gel to afford corresponding products. The separated product was then treated with K_2CO_3 (3 eq) and methanol (2 ml). When the reaction was considered complete as determined by TLC analysis, ethyl acetate (10 mL) and water (5 mL) were then added to the reaction mixture. The organic layer was extracted with ethyl acetate (2 × 10 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The residue was purified by flash chromatography on alkalescence silica gel to afford corresponding products.

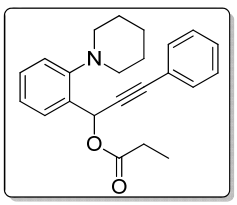
Characterization data of 1a-1t and D-1a



1a was obtained according to the above method. mp:62-63 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.80 (m, 1 H), 7.44-7.46 (m, 2 H), 7.33-7.37 (m, 1 H), 7.25-7.31 (m, 3 H), 7.17-7.20 (m, 3 H), 2.78-2.89 (m, 4 H), 2.11 (s, 3 H), 1.66-1.80 (m, 4 H), 1.55-1.60 (m 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 152.6, 133.1, 131.9, 129.8, 129.1, 128.5, 128.2, 124.3, 122.5, 121.2, 86.9, 85.9, 61.8, 54.8, 26.5, 24.2, 21.1; IR (neat, cm^{-1}) 2936, 2852, 2800, 1742, 1598, 1489, 1447, 1372, 1226, 1016, 951, 915, 759, 691, 535; HRMS (ESI) m/z: calcd for $C_{22}H_{23}NO_2$: M+H = 334.1802; found: 334.1798.

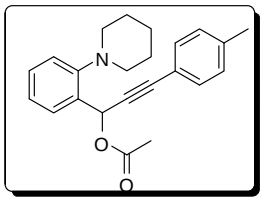


1b was obtained according to the above method. mp: 129-130 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.09 (m, 2 H), 7.89-7.92 (m, 1 H), 7.44-7.53 (m, 1 H), 7.34-7.43 (m, 6 H), 7.19-7.29 (m, 5 H), 2.79-2.92 (m, 4 H), 1.63-1.74 (m, 4 H), 1.53-1.58 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 152.8, 133.3, 132.9, 131.9, 130.2, 129.8, 129.7, 129.1, 128.5, 128.3, 128.2, 128.1, 124.4, 122.5, 121.3, 87.0, 86.1, 62.5, 54.9, 26.6, 26.5, 24.2; IR (neat, cm^{-1}) 2935, 2852, 2801, 1722, 1599, 1489, 1448, 1378, 1319, 1267, 1098, 1028, 918, 759, 712, 597; HRMS (ESI) m/z: calcd for $C_{27}H_{25}NO_2$: M+H = 396.1958; found: 396.1966.

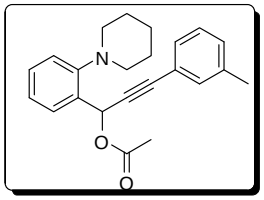


1c was obtained according to the above method as an oil. ^{1}H NMR (400 MHz, $CDCl_3$):

δ 7.69-7.72 (m, 1 H), 7.35-7.37 (m, 2 H), 7.23-7.27 (m, 1 H), 7.15-7.20 (m, 3 H), 7.08-7.13 (m, 3 H), 2.70-2.81 (m, 4 H), 2.21-2.38 (m, 2 H), 1.58-1.71 (m, 4 H), 1.46-1.48 (m, 2 H), 1.06-1.09 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 152.6, 133.3, 131.8, 129.7, 128.9, 128.4, 128.1, 124.3, 122.5, 121.1, 87.1, 85.8, 61.6, 54.8, 29.7, 27.7, 26.5, 24.2, 9.0; IR (neat, cm^{-1}) 2926, 2852, 1742, 1489, 1450, 1223, 1165, 1071, 1028, 919, 758, 691; HRMS (ESI) m/z: calcd for $C_{23}H_{25}NO_2$: M+H = 348.1958; found: 348.1952.

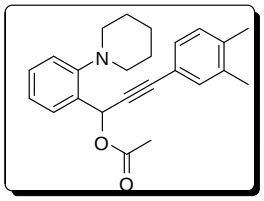


1d was obtained according to the above method. mp: 79-80 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.71 (m, 1 H), 7.21-7.24 (m, 3 H), 7.05-7.09 (m, 3 H), 6.95-6.98 (m, 2 H), 2.68-2.81 (m, 4 H), 2.21 (s, 3 H), 1.98 (s, 3 H), 1.55-1.68 (m, 4 H), 1.43-1.46 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 152.5, 138.5, 133.2, 131.7, 129.6, 128.9, 128.8, 124.3, 121.1, 119.4, 86.2, 86.0, 67.8, 61.8, 54.7, 26.4, 24.1, 21.3, 20.9; IR (neat, cm^{-1}) 2933, 2853, 2801, 1741, 1600, 1488, 1448, 1372, 1226, 1015, 951, 912, 818, 760, 554; HRMS (ESI) m/z: calcd for $C_{23}H_{25}NO_2$: M+H = 348.1958; found: 348.1948.

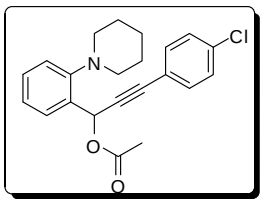


1e was obtained according to the above method as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.80 (m, 1 H), 7.31-7.35 (m, 1 H), 7.22-7.27 (m, 2 H), 7.14-7.18 (m, 4 H), 7.08-7.10 (m, 1 H), 2.78-2.88 (m, 4 H), 2.29 (s, 3 H), 2.09 (s, 3 H), 1.68-1.76 (m, 4 H), 1.55-1.56 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 152.6, 137.8, 133.1, 132.4, 129.7, 129.3, 129.0, 128.9, 128.0, 124.3, 122.2, 121.1, 86.5, 86.1, 61.8, 54.8, 26.5,

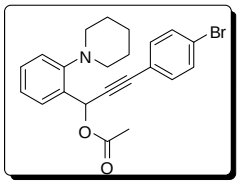
24.2, 21.1; IR (neat, cm^{-1}) 2934, 2255, 1735, 1601, 1448, 1374, 1244, 1046, 912, 734, 648, 608; HRMS (ESI) m/z: calcd for $C_{23}H_{25}NO_2$: M+H = 348.1958; found: 348.1949.



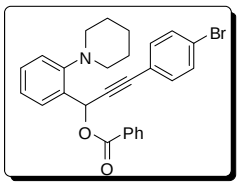
1f was obtained according to the above method. mp: 72-73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.80 (m, 1 H), 7.32-7.36 (m, 1 H), 7.16-7.25 (m, 5 H), 7.03-7.05 (m, 1 H), 2.78-2.89 (m, 4 H), 2.23 (s, 3 H), 2.21 (s, 3 H), 2.09 (s, 3 H), 1.67-1.76 (m, 4 H), 1.55-1.58 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 152.6, 137.4, 136.5, 133.3, 132.9, 129.7, 129.5, 129.3, 129.1, 124.3, 121.1, 119.7, 86.2, 85.9, 61.9, 54.8, 26.5, 24.2, 21.1, 19.7, 19.5; IR (neat, cm^{-1}) 2927, 2228, 1740, 1600, 1493, 1448, 1373, 1228, 1025, 952, 821, 758, 538; HRMS (ESI) m/z: calcd for $C_{24}H_{27}NO_2$: M+H = 362.2115; found: 362.2109.



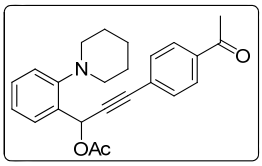
1g was obtained according to the above method. mp: 65-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.77 (m, 1 H), 7.33-7.38 (m, 3 H), 7.25-7.28 (m, 2 H), 7.16-7.20 (m, 3 H), 2.78-2.90 (m, 4 H), 2.10 (s, 3 H), 1.65-1.78 (m, 4 H), 1.54-1.57 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 152.6, 134.5, 133.1, 132.9, 129.9, 128.9, 128.5, 124.4, 121.3, 120.9, 87.9, 84.7, 61.7, 54.8, 26.5, 24.2, 21.1; IR (neat, cm^{-1}) 2933, 2852, 1742, 1597, 1489, 1448, 1372, 1226, 1092, 1016, 951, 915, 829, 763, 545; HRMS (ESI) m/z: calcd for $C_{22}H_{22}NClO_2$: M+H = 368.1412; found: 368.1409.



1h was obtained according to the above method. mp: 85-86 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.77 (m, 1 H), 7.41-7.43 (m, 2 H), 7.29-7.37 (m, 3 H), 7.16-7.20 (m, 3 H), 2.78-2.87 (m, 4 H), 2.10 (s, 3 H), 1.66-1.77 (m, 4 H), 1.55-1.56 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 152.6, 133.2, 132.8, 131.4, 129.8, 128.9, 124.4, 122.8, 121.4, 121.3, 88.1, 84.8, 77.2, 61.7, 54.8, 26.5, 24.1, 21.1; IR (neat, cm^{-1}) 2934, 2852, 2801, 1742, 1596, 1487, 1448, 1371, 1325, 1225, 1068, 1014, 951, 914, 825, 760, 544; HRMS (ESI) m/z: calcd for $C_{22}H_{22}NBrO_2$: M+H = 412.0907; found: 412.0916.

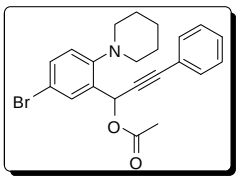


1i was obtained according to the above method as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.09 (m, 2 H), 7.86-7.88 (m, 1 H), 7.52-7.56 (m, 1 H), 7.37-7,44 (m, 6 H), 7.29-7.35 (m, 2 H), 7.19-7.31 (m, 2 H), 2.79-2.89 (m, 4 H), 1.67-1.69 (m, 4 H), 1.53-1.54 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 152.8, 133.3, 133.0, 132.9, 131.5, 131.4, 130.1, 129.9, 129.8, 129.1, 128.3, 124.4, 122.8, 121.5, 121.3, 88.2, 85.0, 62.4, 54.9, 26.5, 24.2; IR (neat, cm^{-1}) 2926, 2853, 1724, 1596, 1487, 1452, 1380, 1319, 1265, 1096, 1068, 1018, 924, 823, 759, 711, 601,547; HRMS (ESI) m/z: calcd for $C_{27}H_{24}NBrO_2$: M+H = 474.1063; found: 474.1068.

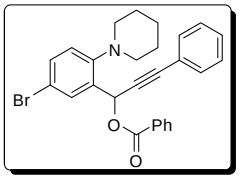


1j was obtained according to the above method as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.89 (m, 2 H), 7.76-7.78 (m, 1 H), 7.51-7.53 (m, 2 H), 7.33-7.37 (m, 1 H), 7.17-7.21 (m, 3 H), 2.79-2.91 (m, 4 H), 2.57 (s, 3 H), 2.11 (s, 3 H), 1.67-1.78 (m, 4 H), 1.54-1.57 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.0, 169.5, 152.6, 136.4, 132.6,

131.8, 129.9, 128.9, 128.0, 127.2, 124.4, 121.3, 90.3, 84.9, 61.6, 54.7, 26.4, 24.1, 20.9; IR (neat, cm^{-1}) 2935, 2801, 1742, 1685, 1600, 1488, 1444, 1366, 1261, 1224, 1016, 954, 837, 758, 669, 602; HRMS (ESI) m/z: calcd for $C_{24}H_{25}NO_3$: M+H = 376.1907; found: 376.1896.

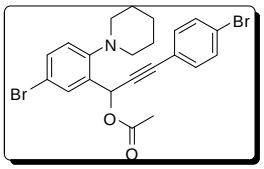


1k was obtained according to the above method. mp: 69-70 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1 H), 7.42-7.48 (m, 3 H), 7.26-7.38 (m, 3 H), 7.10 (s, 1 H), 7.03-7.05 (m, 1 H), 2.84-2.89 (m, 2 H), 2.74-2.79 (m, 2 H), 2.11 (s, 3 H), 1.65-1.78 (m, 4 H), 1.53-1.56 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 169.4, 151.9, 151.4, 135.4, 133.1, 132.6, 131.8, 131.7, 131.5, 128.6, 128.2, 123.0, 122.1, 121.7, 117.3, 116.2, 86.3, 86.2, 61.7, 61.1, 54.7, 54.3, 26.4, 24.1, 21.0, 20.9; IR (neat, cm^{-1}) 2935, 2852, 2803, 1744, 1484, 1447, 1372, 1327, 1227, 1108, 1021, 958, 914, 867, 820, 756, 691, 657, 533; HRMS (ESI) m/z: calcd for $C_{22}H_{22}NBrO_2$: M+H = 412.0907; found: 412.0897.

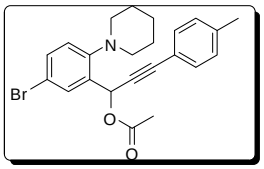


1l was obtained according to the above method as an oil. ^1H NMR (400 MHz, $CDCl_3$): δ 8.08-8.09 (m, 2 H), 7.99-8.07 (m, 1 H), 7.52-7.58 (m, 1 H), 7.36-7.46 (m, 6 H), 7.23-7.30 (m, 3 H), 7.05-7.07 (m, 1 H), 2.76-2.90 (m, 4 H), 1.68-1.71 (m, 4 H), 1.49-1.55 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 151.7, 135.5, 133.1, 132.7, 132.0, 131.9, 129.9, 129.8, 129.6, 128.6, 128.4, 128.3, 128.2, 123.1, 122.2, 117.3, 86.6, 86.2, 61.8, 54.7, 54.3, 26.4, 26.3, 24.0; IR (neat, cm^{-1}) 2936, 2852, 2804, 1723, 1596, 1484, 1317, 1264, 1175, 1097, 1028, 911, 821, 755, 733, 711, 651, 604, 535;

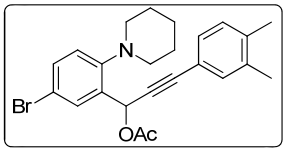
HRMS (ESI) m/z: calcd for $C_{27}H_{24}NBrO_2$: M+H = 474.1063; found: 474.1073.



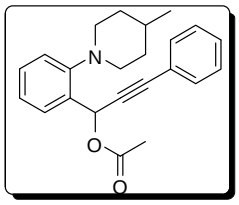
1m was obtained according to the above method. mp: 87-88 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.84 (m, 1 H), 7.41-7.45 (m, 3 H), 7.29-7.31 (m, 2 H), 7.03-7.08 (m, 2 H), 2.74-2.88 (m, 4 H), 2.12 (s, 3 H), 1.64-1.77 (m, 4 H), 1.53-1.56 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 151.4, 135.0, 133.2, 132.7, 131.7, 131.5, 123.1, 123.0, 121.1, 117.3, 87.4, 85.1, 61.0, 54.6, 26.3, 24.0, 20.9; IR (neat, cm^{-1}) 2935, 2853, 2804, 1745, 1483, 1372, 1328, 1225, 1069, 1015, 958, 913, 869, 823, 733, 656, 606, 538; HRMS (ESI) m/z: calcd for $C_{22}H_{21}NBr_2O_2$: M+H = 490.0012; found: 490.0020.



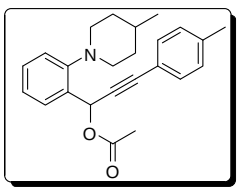
1n was obtained according to the above method as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 2.4 Hz, 1 H), 7.42 (dd, *J* = 6.0, 2.4 Hz, 1 H), 7.33-7.35 (m, 2 H), 7.08-7.10 (m, 3 H), 7.02 (d, *J* = 8.4 Hz, 1 H), 2.84-2.86 (m, 2 H), 2.74-2.79 (m, 2 H), 2.32 (s, 3 H), 2.10 (s, 3 H), 1.67-1.75 (m, 4 H), 1.52-1.55 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 151.4, 138.8, 135.5, 132.5, 131.8, 131.7, 128.9, 122.9, 119.0, 117.3, 86.5, 85.5, 61.2, 54.6, 26.4, 24.0, 21.4, 21.0; IR (neat, cm^{-1}) 2927, 2853, 1745, 1508, 1480, 1449, 1373, 1327, 1229, 1176, 1109, 1017, 957, 913, 870, 817, 733, 656, 549; HRMS (ESI) m/z: calcd for $C_{23}H_{24}NBrO_2$: M+H = 426.1063; found: 426.1070.



1o was obtained according to the above method as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1 H), 7.39-7.42 (m, 1 H), 7.23 (s, 1 H), 7.18 (d, *J* = 7.6 Hz, 1 H), 7.09 (s, 1 H), 7.00-7.04 (m, 2 H), 2.84-2.85 (m, 2 H), 2.75-2.77 (m, 2 H), 2.22 (s, 3 H), 2.19 (s, 3 H), 2.10 (s, 3 H), 1.67-1.75 (m, 4 H), 1.53-1.55 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 151.3, 137.5, 136.4, 135.4, 132.8, 132.5, 131.8, 129.4, 129.2, 122.9, 119.2, 117.2, 86.6, 85.2, 61.1, 54.6, 26.3, 23.9, 20.9, 19.6, 19.4; IR (neat, cm^{-1}) 2934, 2854, 2803, 1744, 1682, 1484, 1451, 1372, 1225, 1111, 1023, 958, 912, 821, 734, 656, 538; MS: m/z 439 (2.02), 441 (2.04).

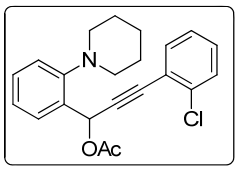


1p was obtained according to the above method. mp: 56-57 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.78 (m, 1 H), 7.43-7.45 (m, 2 H), 7.24-7.36 (m, 4 H), 7.16-7.19 (m, 3 H), 2.95-3.12 (m, 2 H), 2.65-2.73 (m, 2 H), 2.10 (s, 3 H), 1.67-1.70 (m, 2 H), 1.36-1.55 (m, 3 H), 0.99 (d, *J* = 5.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 152.3, 133.1, 131.8, 129.7, 129.0, 128.5, 128.1, 124.3, 122.5, 121.1, 86.9, 85.9, 61.8, 54.5, 53.9, 34.9, 34.8, 30.7, 21.9, 21.1; IR (neat, cm^{-1}) 2949, 2921, 2804, 1742, 1598, 1490, 1449, 1373, 1225, 1015, 950, 913, 759, 691, 659, 537; HRMS (ESI) m/z: calcd for $C_{23}H_{25}NO_2$: M+H = 348.1958; found: 348.1950.

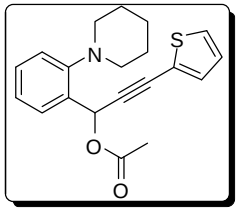


1q was obtained according to the above method. mp: 66-67 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.79 (m, 1 H), 7.27-7.31 (m, 3 H), 7.19 (s, 1 H), 7.12-7.16 (m, 2 H), 7.02-7.04 (m, 2 H), 3.06-3.09 (m, 1 H), 2.94-2.97 (m, 1 H), 2.61-2.69 (m, 2 H), 2.26 (s, 3 H), 2.04 (s, 3 H), 1.65-1.67 (m, 2 H), 1.38-1.53 (m, 3 H), 0.97 (d, *J* = 5.2 Hz, 3

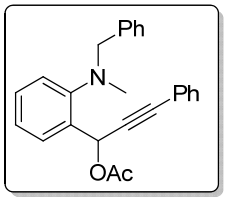
H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 152.1, 138.4, 133.1, 131.6, 129.5, 128.9, 128.8, 124.2, 120.9, 119.3, 86.2, 85.9, 61.7, 54.3, 53.7, 34.8, 34.7, 21.8, 21.2, 20.8; IR (neat, cm^{-1}) 2923, 2253, 1736, 1452, 1374, 1232, 1015, 952, 909, 818, 733, 650, 554; HRMS (ESI) m/z: calcd for $C_{24}H_{27}NO_2$: M+H = 362.2115; found: 362.2122.



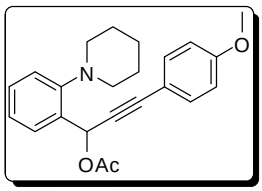
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 1.2 Hz, 1 H), 7.46 (dd, *J* = 5.6, 2.0 Hz, 1 H), 7.31-7.35 (m, 2 H), 7.12-7.24 (m, 5 H), 2.78-2.89 (m, 4 H), 2.08 (s, 3 H), 1.66-1.78 (m, 4 H), 1.53-1.56 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 152.6, 136.2, 133.4, 132.6, 129.8, 129.4, 129.2, 129.1, 126.2, 124.3, 122.4, 121.0, 92.1, 82.6, 61.7, 54.7, 26.4, 24.1, 20.9; IR (neat, cm^{-1}) 2935, 2804, 1741, 1599, 1490, 1474, 1368, 1230, 1064, 1033, 1013, 951, 922, 757, 535.



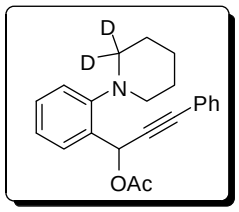
1r was obtained according to the above method as an oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.75 (m, 1 H), 7.31-7.36 (m, 1 H), 7.16-7.23 (m, 5 H), 6.92-6.94 (m, 1 H), 2.77-2.89 (m, 4 H), 2.09 (s, 3 H), 1.65-1.77 (m, 4 H), 1.53-1.56 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 152.6, 132.8, 132.6, 129.8, 128.9, 127.4, 126.8, 124.4, 122.3, 121.2, 90.8, 79.1, 61.9, 54.8, 26.5, 24.2, 22.6, 21.0, 14.1; IR (neat, cm^{-1}) 2928, 2853, 1736, 1218, 908, 760, 669, 539; HRMS (ESI) m/z: calcd for $C_{20}H_{21}NSO_2$: M+H = 340.1366; found: 340.1377.



1s ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76-7.79 (m, 1 H), 7.18-7.43 (m, 14 H), 4.07 (s, 2 H), 2.62 (s, 3 H), 2.07 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 151.6, 138.3, 133.5, 131.8, 129.6, 128.7, 128.6, 128.5, 128.3, 128.1, 127.1, 124.8, 122.3, 121.9, 86.9, 85.9, 61.9, 61.7, 42.6, 21.1; IR (neat, cm^{-1}) 3061, 2948, 2845, 2796, 1741, 1446, 1373, 1224, 1015, 950, 759, 694, 564. HRMS (ESI) m/z: calcd for $C_{25}H_{23}NO_2$: M+H = 370.1802; found: 370.1809.

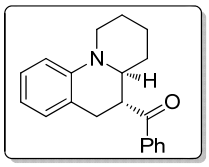


1t was obtained according to the above method. mp: 66-67 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.81 (m, 1 H), 7.32-7.41 (m, 3 H), 7.16-7.20 (m, 3 H), 6.79-6.83 (m, 2 H), 3.79 (s, 3 H), 2.78-2.89 (m, 4 H), 2.10 (s, 3 H), 1.67-1.78 (m, 4 H), 1.55-1.56 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 159.7, 152.6, 133.4, 133.2, 129.7, 129.0, 124.3, 121.1, 114.5, 113.7, 85.9, 85.5, 61.9, 55.2, 54.8, 26.5, 24.2, 21.2; IR (neat, cm^{-1}) 3017, 2936, 2847, 2802, 2225, 1738, 1604, 1509, 1448, 1372, 1288, 1239, 1175, 1109, 1031, 951, 833, 757, 664, 538; HRMS (ESI) m/z: calcd for $C_{23}H_{25}NO_3$: M+H = 364.1907; found: 364.1901.

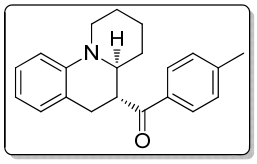


D-1a was obtained according to the above method as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78-7.81 (m, 1 H), 7.43-7.46 (m, 2 H), 7.27-7.37 (m, 4 H), 7.19-7.26 (m, 3 H), 2.77-2.93 (m, 2 H), 2.10 (s, 3 H), 1.66-1.75 (m, 4 H), 1.53-1.64 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 152.6, 133.1, 131.8, 129.6, 129.0, 128.5, 128.1, 124.3, 122.4, 121.2, 86.9, 85.9, 61.8, 54.7, 26.5, 26.3, 24.1, 21.1;

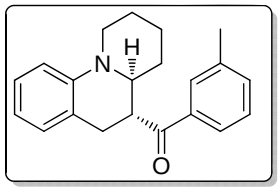
Characterization data of 2a-2o and D-2a.



2a was obtained according to the above method as an oil. major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-8.00 (m, 2 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.46-7.49 (m, 2 H), 7.12 (t, *J* = 7.6 Hz, 1 H), 6.94 (d, *J* = 7.2 Hz, 1 H), 6.86 (d, *J* = 8.4 Hz, 1 H), 6.65 (t, *J* = 7.2 Hz, 1 H), 3.99-4.02 (m, 1 H), 3.71-3.78 (m, 1 H), 3.35-3.40 (m, 1 H), 2.96-3.03 (m, 1 H), 2.80-2.86 (m, 2 H), 1.71-1.77 (m, 3 H), 1.36-1.65 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.2, 146.1, 136.9, 133.3, 128.7, 128.6, 128.5, 128.3, 127.5, 123.1, 117.2, 112.9, 58.9, 48.5, 46.9, 32.4, 31.6, 25.4, 24.3; IR (neat, cm^{-1}) 3399, 2920, 2852, 1677, 1585, 1450, 1057, 754, 705, 590; HRMS (ESI) m/z: calcd for $C_{20}H_{21}NO$: M+H = 292.1696; found: 292.1694. minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.2 Hz, 2 H), 7.52-7.56 (m, 1 H), 7.43 (t, *J* = 8.0 Hz, 2 H), 7.06-7.12 (m, 2 H), 6.65 (t, *J* = 7.2 Hz, 1 H), 6.49 (d, *J* = 7.6 Hz, 1 H), 3.84-3.89 (m, 1 H), 3.63-3.66 (m, 1 H), 3.38 (dd, *J* = 9.6, 8.0 Hz, 1 H), 3.27-3.32 (m, 1 H), 3.03 (dd, *J* = 11.6, 6.0 Hz, 1 H), 2.56-2.63 (m, 1 H), 1.84-1.86 (m, 1 H), 1.66-1.72 (m, 2 H), 1.34-1.59 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 151.5, 137.0, 133.1, 133.0, 128.5, 128.0, 127.7, 124.5, 118.1, 106.6, 67.5, 45.8, 39.1, 38.5, 26.3, 24.5, 24.4;

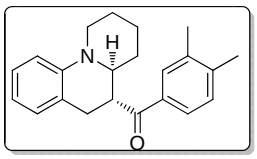


2b was obtained according to the above method as an oil. major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.0 Hz, 2 H), 7.25-7.29 (m, 2 H), 7.12 (t, *J* = 7.6 Hz, 1 H), 6.94 (d, *J* = 7.2 Hz, 1 H), 6.86 (d, *J* = 8.4 Hz, 1 H), 6.65 (t, *J* = 7.6 Hz, 1 H), 3.99-4.02 (m, 1 H), 3.69-3.75 (m, 1 H), 3.32-3.38 (m, 1 H), 2.96-3.02 (m, 1 H), 2.78-2.86 (m, 2 H), 2.42 (s, 3 H), 1.71-1.77 (m, 3 H), 1.56-1.62 (m, 1 H), 1.26-1.47 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 146.1, 144.2, 134.6, 129.5, 128.7, 128.5, 127.5, 123.2, 117.2, 112.9, 58.9, 48.5, 46.9, 32.6, 31.6, 25.5, 24.3, 21.6; IR (neat, cm^{-1}) 3434, 2925, 2852, 1673, 1604, 1494, 1451, 1377, 1255, 1225, 1177, 1113, 1061, 747, 574; HRMS (ESI) m/z: calcd for $C_{21}H_{23}NO$: M+H = 306.1852; found: 306.1848.

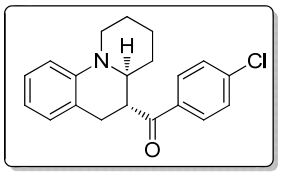


2c was obtained according to the above method as an oil. major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.80 (m, 2 H), 7.34-7.41 (m, 2 H), 7.12 (t, *J* = 7.6 Hz, 1 H), 6.94 (d, *J* = 7.2 Hz, 1 H), 6.86 (d, *J* = 8.4 Hz, 1 H), 6.65 (t, *J* = 7.2 Hz, 1 H), 3.99-4.02 (m, 1 H), 3.71-3.77 (m, 1 H), 3.33-3.39 (m, 1 H), 2.95-3.02 (m, 1 H),

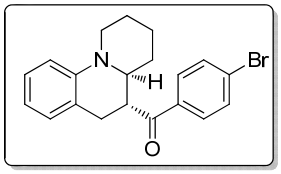
2.79-2.86 (m, 2 H), 2.41 (s, 3 H), 1.71-1.77 (m, 3 H), 1.55-1.65 (m, 1 H), 1.23-1.49 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.5, 146.1, 138.6, 137.1, 134.1, 128.9, 128.7, 128.6, 127.5, 125.6, 123.2, 117.2, 112.9, 58.9, 48.5, 47.1, 32.6, 31.6, 25.5, 24.3, 21.3; IR (neat, cm^{-1}) 3336, 2929, 2851, 1675, 1601, 1494, 1451, 1370, 1253, 1161, 1050, 744, 550; HRMS (ESI) m/z: calcd for $C_{21}H_{23}NO$: M+H = 306.1852; found: 306.1850.



2d was obtained according to the above method as an oil. major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.77 (m, 2 H), 7.14-7.26 (m, 1 H), 7.10-7.14 (m, 1 H), 6.94 (d, *J* = 7.6 Hz, 1 H), 6.87 (d, *J* = 8.4 Hz, 1 H), 6.63-6.67 (m, 1 H), 3.99-4.03 (m, 1 H), 3.69-3.76 (m, 1 H), 3.32-3.37 (m, 1 H), 2.96-3.02 (m, 1 H), 2.77-2.86 (m, 2 H), 2.33 (s, 3 H), 2.32 (s, 3 H), 1.71-1.77 (m, 3 H), 1.56-1.62 (m, 1 H), 1.24-1.47 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.1, 146.1, 143.0, 137.2, 135.0, 130.0, 129.5, 128.8, 127.4, 126.1, 123.3, 117.1, 112.9, 59.0, 48.5, 46.8, 32.6, 31.6, 25.6, 24.3, 20.0, 19.8; IR (neat, cm^{-1}) 3400, 2923, 2851, 1671, 1602, 1494, 1451, 1378, 1253, 1115, 1054, 793, 749, 708; HRMS (ESI) m/z: calcd for $C_{22}H_{25}NO$: M+H = 320.2009; found: 320.2006.

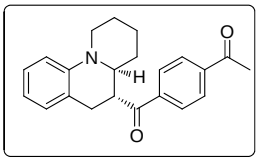


2e was obtained according to the above method as an oil. major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.94 (m, 2 H), 7.44-7.46 (m, 2 H), 7.12 (t, *J* = 7.6 Hz, 1 H), 6.93 (d, *J* = 7.6 Hz, 1 H), 6.85 (d, *J* = 8.4 Hz, 1 H), 6.66 (t, *J* = 7.2 Hz, 1 H), 3.98-4.01 (m, 1 H), 3.65-3.71 (m, 1 H), 3.32-3.38 (m, 1 H), 2.95-3.01 (m, 1 H), 2.78-2.86 (m, 2 H), 1.55-1.76 (m, 4 H), 1.38-1.49 (m, 1 H), 1.19-1.29 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.9, 146.0, 139.9, 135.3, 129.7, 129.1, 128.7, 127.6, 122.9, 117.3, 112.9, 58.8, 48.5, 47.1, 32.3, 31.6, 25.4, 24.3; IR (neat, cm^{-1}) 3436, 2929, 2851, 1677, 1590, 1493, 1451, 1253, 1092, 1008, 839, 747, 534; HRMS (ESI) m/z: calcd for $C_{20}H_{20}ClNO$: M+H = 326.1306; found: 326.1301.

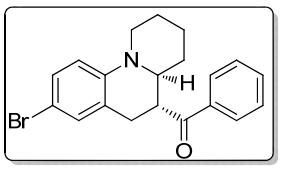


2f was obtained according to the above method as an oil. major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.4 Hz, 2 H), 7.62 (d, *J* = 8.4 Hz, 2 H), 7.12

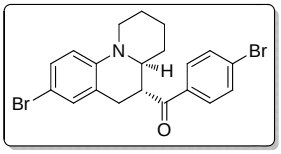
(t, J = 7.6 Hz, 1 H), 6.93 (d, J = 7.6 Hz, 1 H), 6.85 (d, J = 8.4 Hz, 1 H), 6.65 (t, J = 7.2 Hz, 1 H), 3.98-4.01 (m. 1 H), 3.64-3.69 (m, 1 H), 3.33-3.38 (m, 1 H), 2.95-3.01 (m, 1 H), 2.78-2.86 (m, 2 H), 1.56-1.76 (m, 4 H), 1.20-1.49 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 146.0, 135.7, 132.1, 129.8, 128.7, 128.6, 127.6, 122.9, 117.3, 112.9, 58.8, 48.5, 47.1, 32.3, 31.6, 25.4, 24.3; IR (neat, cm^{-1}) 3403, 2923, 2853, 1764, 1681, 1452, 1381, 1243, 1061, 913, 746; HRMS (ESI) m/z: calcd for $C_{20}H_{20}NOBr$: M+H = 370.0801; found: 370.0806.



2g was obtained according to the above method as an oil. major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (m, 4 H), 7.13 (t, J = 7.6 Hz, 1 H), 6.94 (d, J = 7.2 Hz, 1 H), 6.86 (d, J = 8.4 Hz, 1 H), 6.66 (t, J = 7.2 Hz, 1 H), 3.99-4.02 (m, 1 H), 3.72-3.78 (m, 1 H), 3.35-3.41 (m, 1 H), 2.96-3.03 (m, 1 H), 2.80-2.86 (m, 2 H), 2.65 (s, 3 H), 1.73-1.79 (m, 3 H), 1.28-1.69 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.7, 197.4, 146.0, 140.2, 140.1, 128.7, 128.6, 128.5, 127.6, 122.8, 117.3, 113.0, 58.8, 48.5, 47.6, 32.2, 31.6, 26.9, 25.3, 24.3; IR (neat, cm^{-1}) 2927, 2852, 1683, 1601, 1495, 1259, 910, 748; HRMS (ESI) m/z: calcd for $C_{22}H_{23}NO_2$: M+H = 334.1802; found: 334.1812.

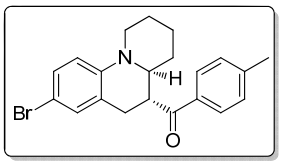


2h was obtained according to the above method as an oil. major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.98 (m, 2 H), 7.59 (t, J = 7.2 Hz, 1 H), 7.47-7.50 (m, 2 H), 7.17-7.19 (m, 1 H), 7.03 (d, J = 2.0 Hz, 1 H), 6.69 (d, J = 8.8 Hz, 1H); 3.89-3.93 (m, 1 H), 3.67-3.72 (m, 1 H), 3.34-3.39 (m, 1 H), 2.91-2.97 (m, 1 H), 2.76-2.86 (m, 2 H), 1.70-1.79 (m, 3 H), 1.54-1.63 (m, 1 H), 1.39-1.49 (m, 1 H), 1.20-1.30 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.6, 145.1, 136.8, 133.4, 130.9, 130.1, 128.8, 128.3, 125.3, 114.5, 108.8, 58.7, 48.4, 46.8, 31.8, 31.5, 25.2, 24.2; IR (neat, cm^{-1}) 3436, 2927, 2851, 1676, 1592, 1489, 1445, 1370, 1254, 1219, 793, 705, 546; HRMS (ESI) m/z: calcd for $C_{20}H_{20}NOBr$: M+H = 370.0801; found: 370.0795.

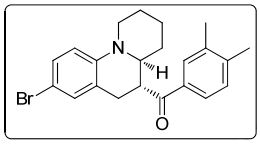


2i was obtained according to the above method as an oil. major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.4 Hz, 2 H), 7.63 (d, J = 8.8 Hz, 2 H),

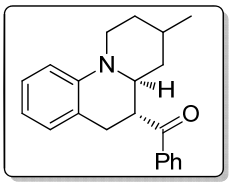
7.17-7.19 (m, 1 H), 7.03 (d, *J* = 2.0 Hz, 1 H), 6.69 (d, *J* = 8.8 Hz, 1 H), 3.89-3.93 (m, 1 H), 3.60-3.66 (m, 1 H), 3.31-3.36 (m, 1 H), 2.90-2.97 (m, 1 H), 2.74-2.85 (m, 2 H), 1.66-1.79 (m, 3 H), 1.28-1.63 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.6, 145.0, 135.4, 132.2, 130.9, 130.1, 129.8, 128.8, 125.0, 114.5, 108.9, 58.7, 48.4, 46.8, 31.7, 31.5, 25.1, 24.2; IR (neat, cm^{-1}) 3433, 2923, 2851, 1764, 1676, 1584, 1488, 1387, 1251, 1066, 1009, 746; HRMS (ESI) m/z: calcd for $C_{20}H_{19}NOBr_2$: M+H = 447.9906; found:447.9914.



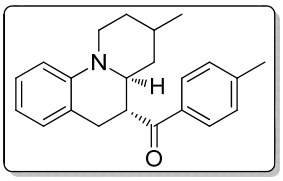
2j was obtained according to the above method as an oil. major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 7.18 (dd, *J* = 6.8, 2.0 Hz, 1 H), 7.03 (d, *J* = 2.0 Hz, 1 H), 6.70 (d, *J* = 8.8 Hz, 1 H), 3.90-3.93 (m, 1 H), 3.64-3.70 (m, 1 H), 3.32-3.38 (m, 1 H), 2.91-2.98 (m, 1 H), 2.74-2.86 (m, 2 H), 2.43 (s, 3 H), 1.69-1.79 (m, 3 H), 1.26-1.59 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2, 145.2, 144.4, 134.4, 130.9, 130.1, 129.5, 128.5, 125.4, 114.5, 108.8, 58.8, 48.5, 46.7, 31.9, 31.5, 25.2, 24.2, 21.6; IR (neat, cm^{-1}) 3400, 2922, 2852, 2332, 1764, 1674, 1489, 1380, 1248, 1058, 913, 771, 747, 669; HRMS (ESI) m/z: calcd for $C_{21}H_{22}NOBr$: M+H = 384.0958; found: 384.0962.



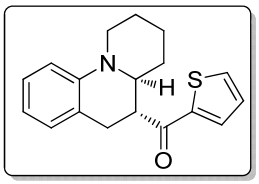
2k was obtained according to the above method as an oil. major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.76 (m, 2 H), 7.10-7.25 (m, 3 H), 6.28-6.34 (m, 1 H), 3.81-3.87 (m, 1 H), 3.59-3.56 (m, 1 H), 3.23-3.37 (m, 2 H), 2.95-3.01 (m, 1 H), 2.57-2.64 (m, 1 H), 2.32 (s, 3 H), 2.31 (s, 3 H), 1.83-1.85 (m, 1 H), 1.31-1.69 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 150.5, 142.7, 136.9, 135.6, 134.7, 130.2, 129.9, 129.8, 129.2, 127.5, 127.1, 125.8, 125.7, 109.5, 107.8, 67.5, 45.7, 38.9, 38.1, 26.0, 24.2, 24.1, 20.0, 19.8; IR (neat, cm^{-1}) 2930, 2852, 1679, 1602, 1477, 1448, 1382, 1249, 1122, 803; HRMS (ESI) m/z: calcd for $C_{22}H_{24}BrNO$: M+H = 398.1114; found: 398.1111.



2l was obtained according to the above method as an oil. major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99-8.01 (m, 2 H), 7.59 (t, *J* = 7.6 Hz, 1 H), 7.49 (t, *J* = 7.6 Hz, 2 H), 7.12 (t, *J* = 7.8 Hz, 1 H), 6.94 (d, *J* = 7.2 Hz, 1 H), 6.86 (d, *J* = 8.4 Hz, 1 H),6.65 (t, *J* = 7.2 Hz, 1 H), 3.99-4.04 (m, 1 H), 3.70-3.76 (m, 1 H), 3.38-3.43 (m, 1 H), 2.94-3.00 (m, 1 H), 2.81-2.88 (m, 2 H), 1.70-1.76 (m, 2 H), 1.21-1.64 (m, 3 H), 0.87 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.2, 145.9, 136.9, 133.3, 128.8, 128.6, 128.4, 127.5, 123.1, 117.2, 112.9, 58.3, 48.0, 47.1, 39.9, 33.8, 32.6, 30.9, 21.9; IR (neat, cm^{-1}) 3440, 2923, 2849, 1677, 1600, 1495, 1452, 1373, 1239, 1210, 750, 702, 665; HRMS (ESI) m/z: calcd for $C_{21}H_{23}NO$: M+H = 306.1852; found: 306.1855.

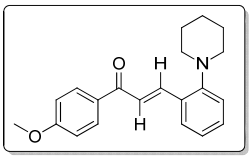


2m was obtained according to the above method as an oil. major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.92 (m, 2 H), 7.25-7.30 (m, 2 H), 7.12 (t, *J* = 7.8 Hz, 1 H), 6.94 (d, *J* = 7.2 Hz, 1 H), 6.86 (d, *J* = 8.4 Hz, 1 H), 6.65 (t, *J* = 7.2 Hz, 1 H), 3.99-4.04 (m, 1 H), 3.68-3.74 (m, 1 H), 3.36-3.41 (m, 1 H), 2.94-3.01 (m, 1 H), 2.79-2.88 (m, 2 H), 2.43 (s, 3 H), 1.69-1.77 (m, 2 H), 1.53-1.63 (m, 2 H), 1.24-1.28 (m, 1 H), 0.87 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 145.9, 144.3, 134.5, 129.5, 128.7, 128.5, 127.5, 123.2, 117.2, 112.9, 58.4, 48.1, 46.9, 39.9, 33.9, 32.7, 30.9, 21.9, 21.6; IR (neat, cm^{-1}) 3399, 2019, 2850, 1672, 1603, 1494, 1453, 1374, 1241, 1045, 748, 610; HRMS (ESI) m/z: calcd for $C_{22}H_{25}NO$: M+H = 320.2009; found: 320.2001.



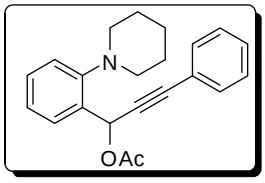
2n was obtained according to the above method as an oil. major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 3.6 Hz, 1 H), 7.68 (d, *J* = 4.8 Hz, 1 H), 7.10-7.17 (m, 2 H), 6.96 (d, *J* = 7.2 Hz, 1 H), 6.87 (d, *J* = 8.4 Hz, 1 H), 6.67 (t, *J* = 7.2 Hz, 1 H), 3.99-4.02 (m, 1 H), 3.50-3.56 (m, 1 H), 3.28-3.34 (m, 1 H) 3.05-3.12 (m, 1 H), 2.78-2.87 (m, 2 H), 1.76-1.78 (m, 3 H), 1.57-1.66 (m, 1 H), 1.28-1.47 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 146.1, 144.9, 134.5, 132.2, 128.6, 128.4, 127.5, 123.0, 117.3, 113.1, 58.8, 49.1, 48.5, 32.6, 31.6, 25.5, 24.1; IR (neat, cm^{-1}) 3399, 2925, 2851, 1653, 1494, 1413, 1253, 1057, 789, 744, 661; HRMS (ESI) m/z: calcd for

$C_{18}H_{19}NOS$: M+H = 298.1260; found:298.1254.



2o ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 15.6 Hz, 1 H), 8.05 (d, *J* = 8.8 Hz, 2 H), 7.66 (d, *J* = 8.4 Hz, 1 H), 7.52 (d, *J* = 16.0 Hz, 1 H), 7.32-7.37 (m, 1 H), 7.05 (d, *J* = 7.6 Hz, 2 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 3.89 (s, 3 H), 2.91-2.94 (m, 4 H), 1.73-1.78 (m, 4 H), 1.57-1.60 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 163.2, 154.4, 142.0, 131.4, 130.9, 130.8, 130.7, 129.2, 127.9, 122.3, 121.4, 119.0, 113.7, 113.6, 55.4, 54.4, 26.4, 24.2; IR (neat, cm^{-1}): 2928, 1655, 1599, 1449, 1380, 1332, 1257, 1219, 1167, 1021, 835, 757, 575; HRMS (ESI) m/z: calcd for $C_{21}H_{23}NO_2$: M+H = 322.1802; found:322.1808.

D-2a ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.2 Hz, 2 H), 7.59 (t, *J* = 7.6 Hz, 1 H), 7.49 (t, *J* = 8.0 Hz, 2 H), 7.13 (t, *J* = 7.6 Hz, 1 H), 6.94 (d, *J* = 7.2 Hz, 1 H), 6.86 (d, *J* = 8.0 Hz, 1 H), 6.65 (t, *J* = 7.2 Hz, 1 H), 3.99-4.02 (m, 0.3 H), 3.71-3.78 (m, 1 H), 3.35-3.40 (m, 0.7 H), 2.96-3.03 (m, 1 H), 2.80-2.88 (m, 1.2 H), 1.38-1.79 (m, 6 H); ^{13}C NMR (100 MHz, CDCl3): δ 202.2, 146.1, 137.1, 133.3, 128.8, 128.7, 128.4, 127.5, 123.1, 117.2, 112.9, 58.9, 47.1, 32.5, 31.6, 25.3, 24.3; HRMS (ESI) m/z: calcd for $C_{20}H_{19}NOD_2$: M+H = 294.1821; found:294.1825.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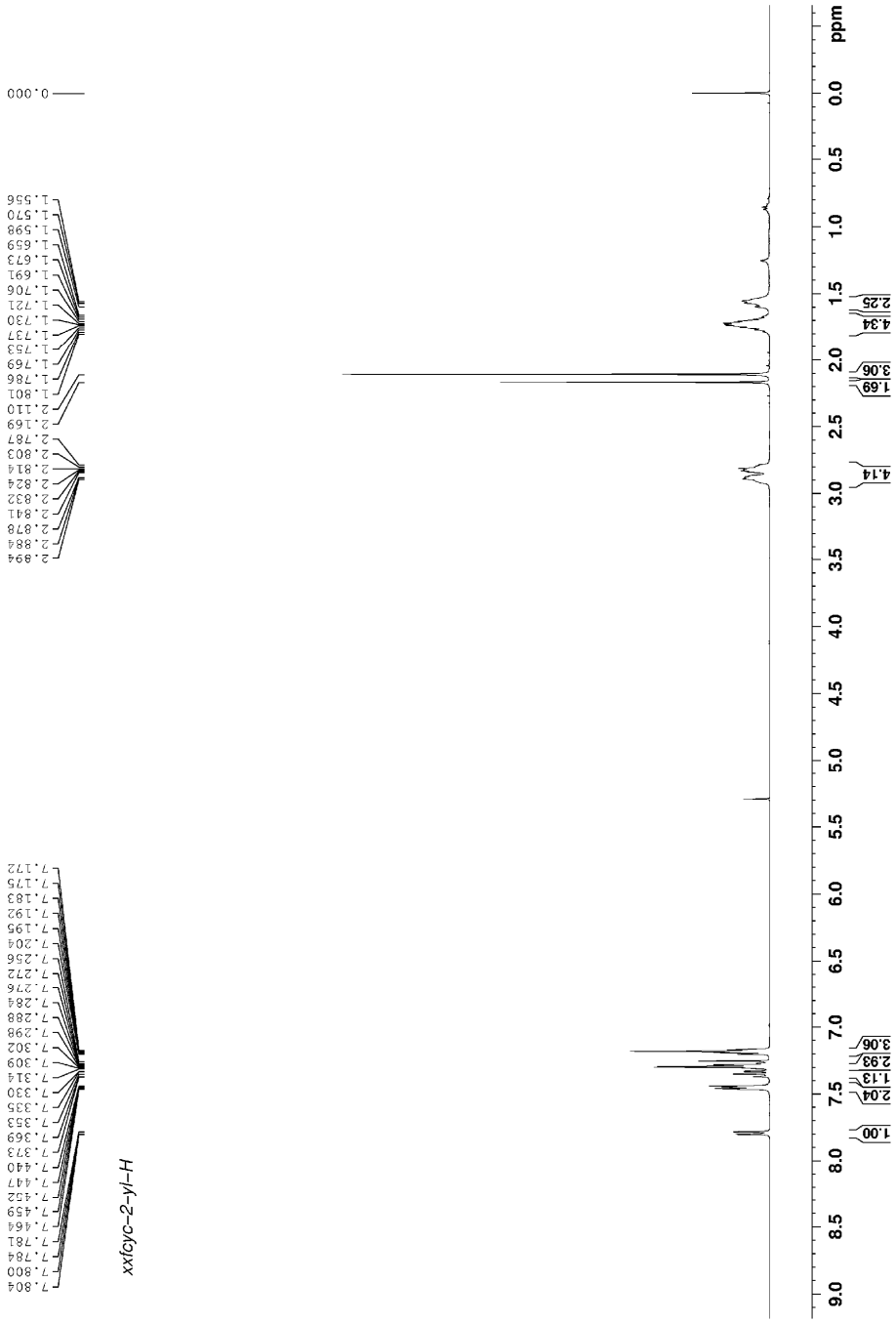
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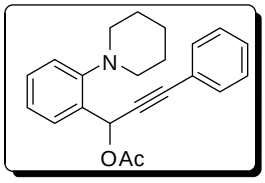

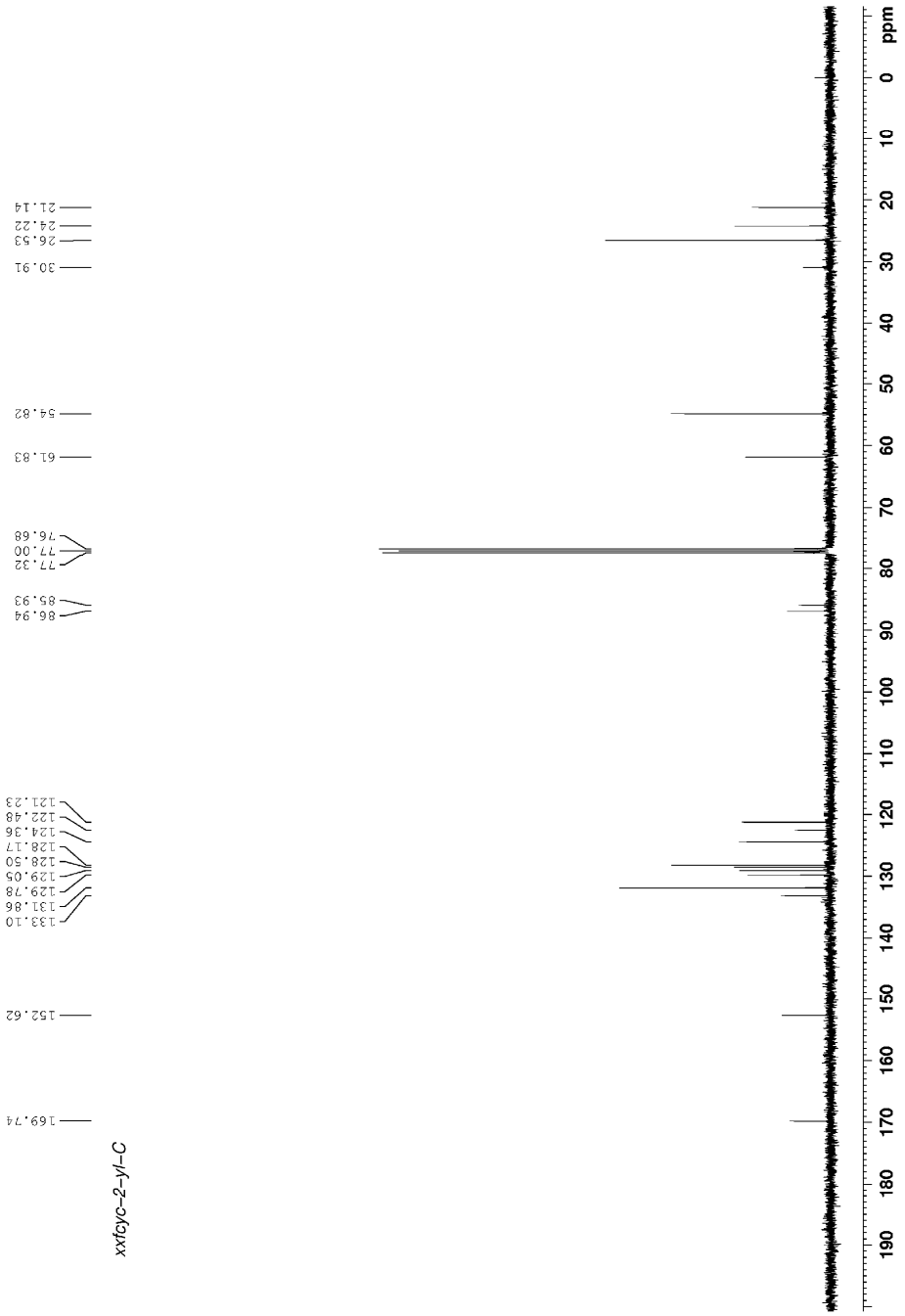

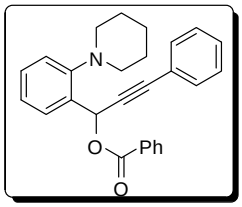
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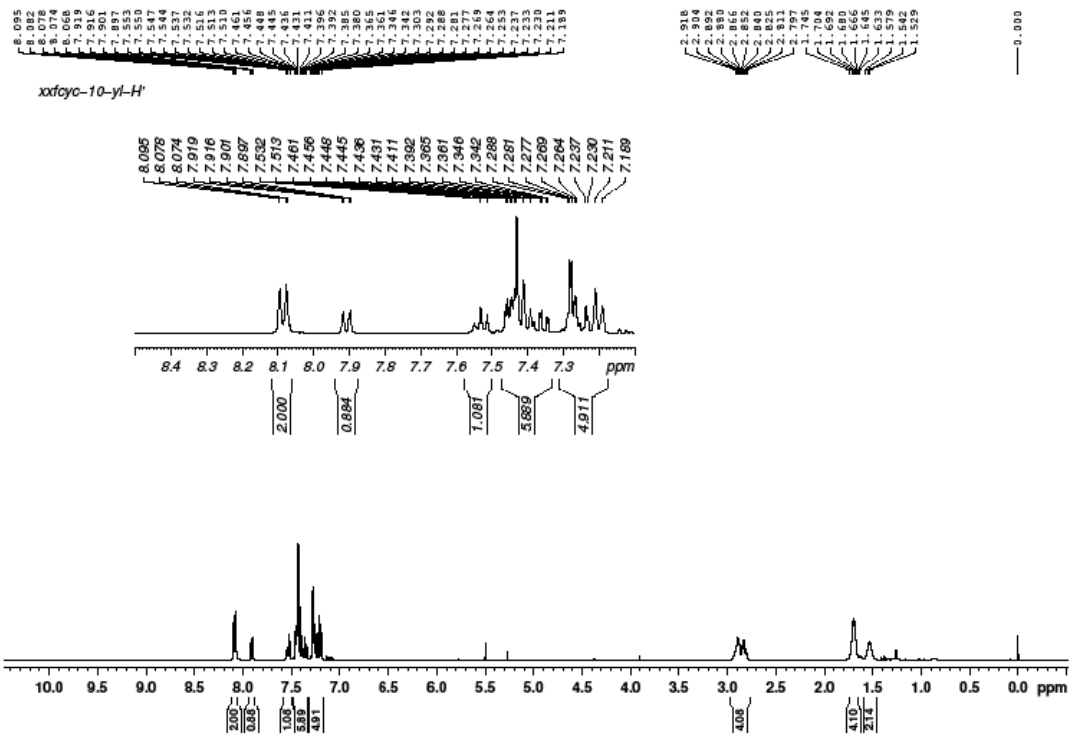
O
Ph
O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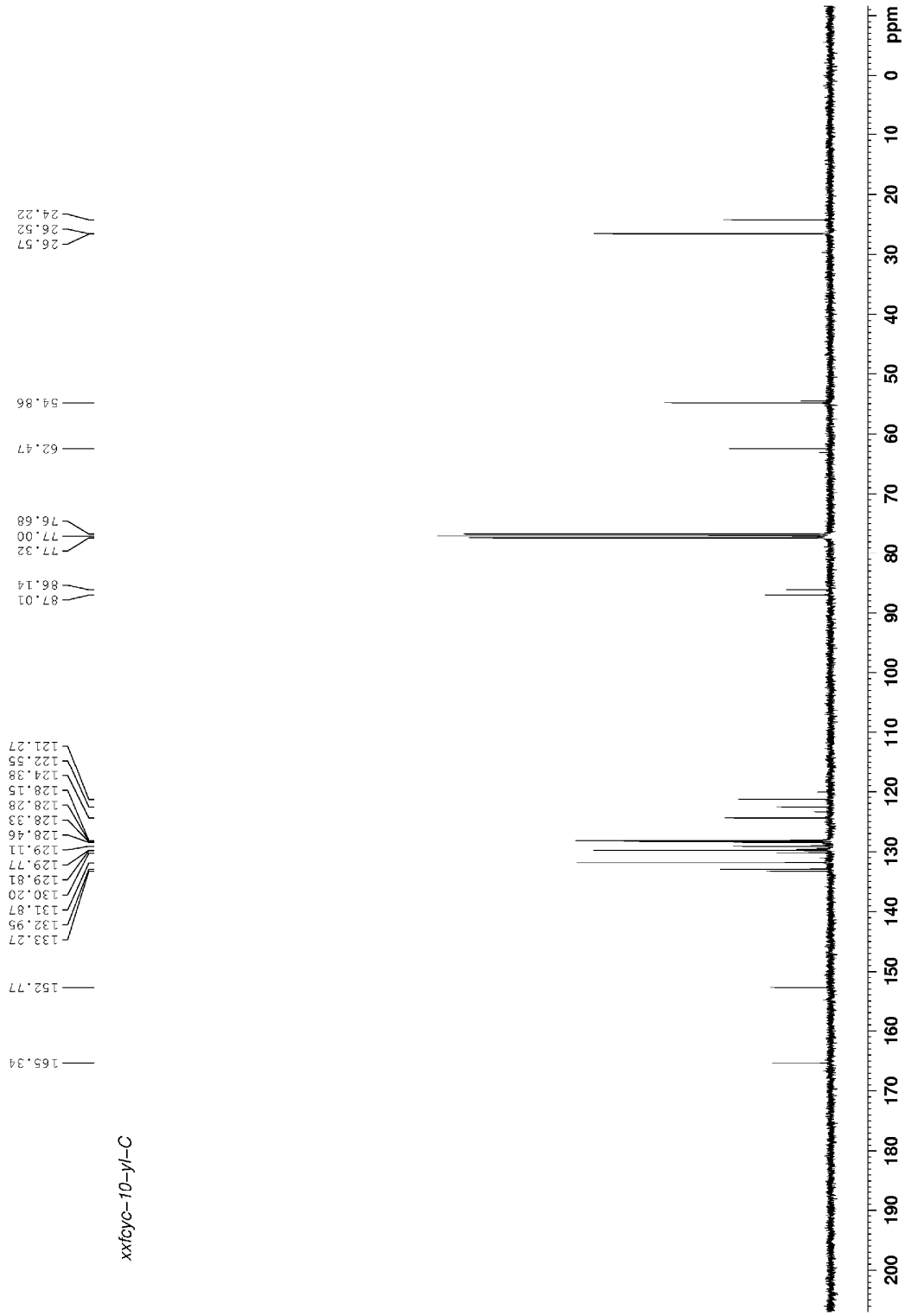
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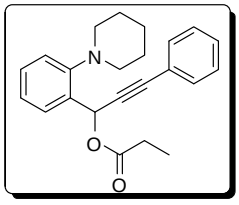
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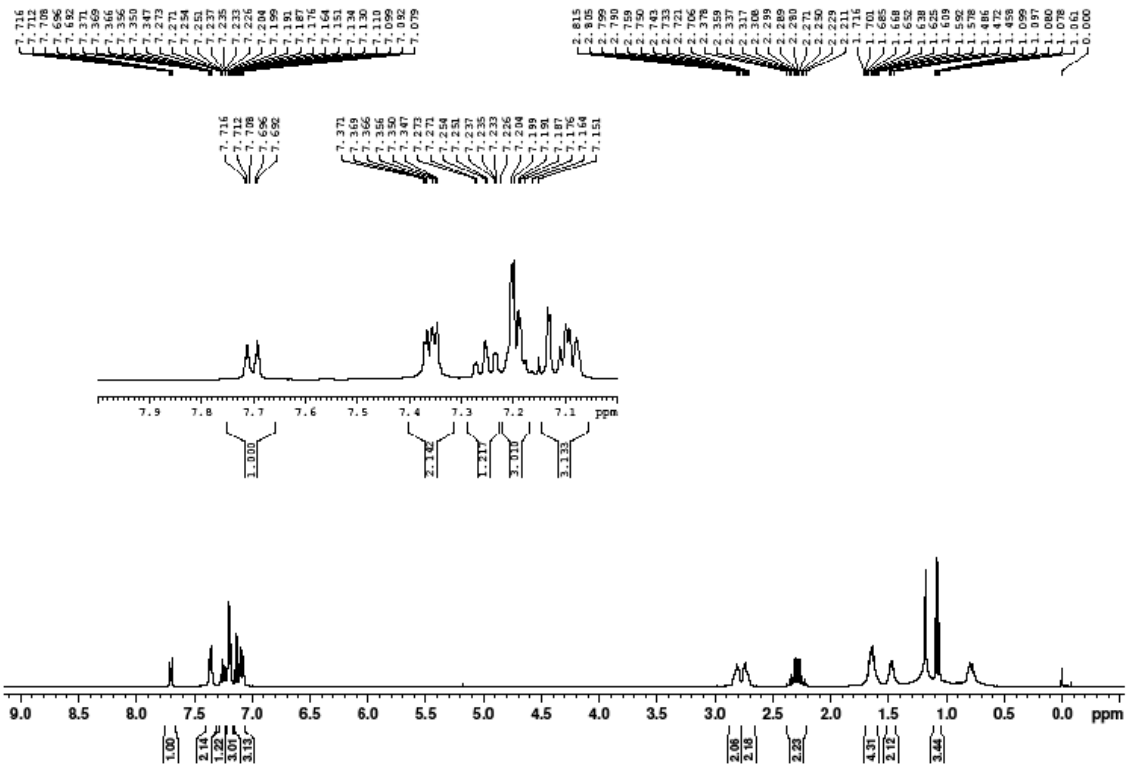
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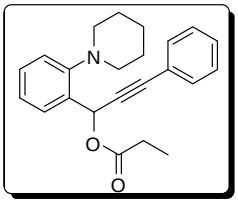

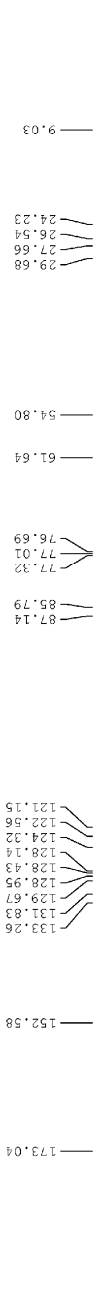

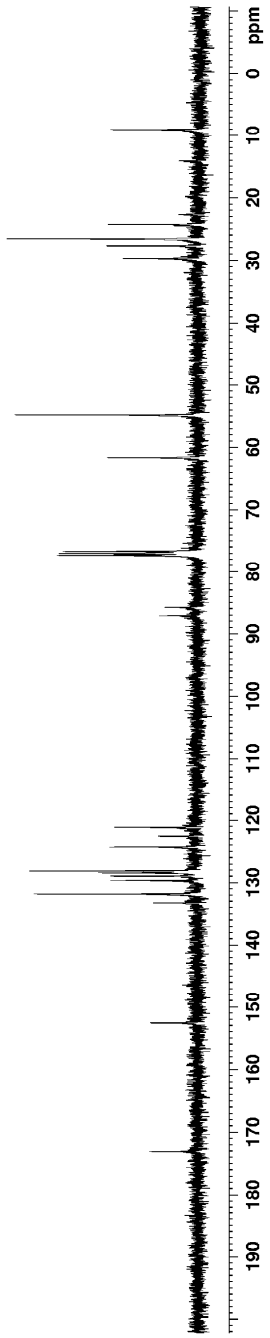

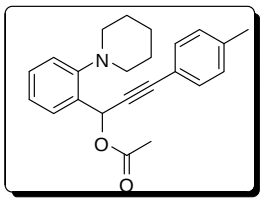
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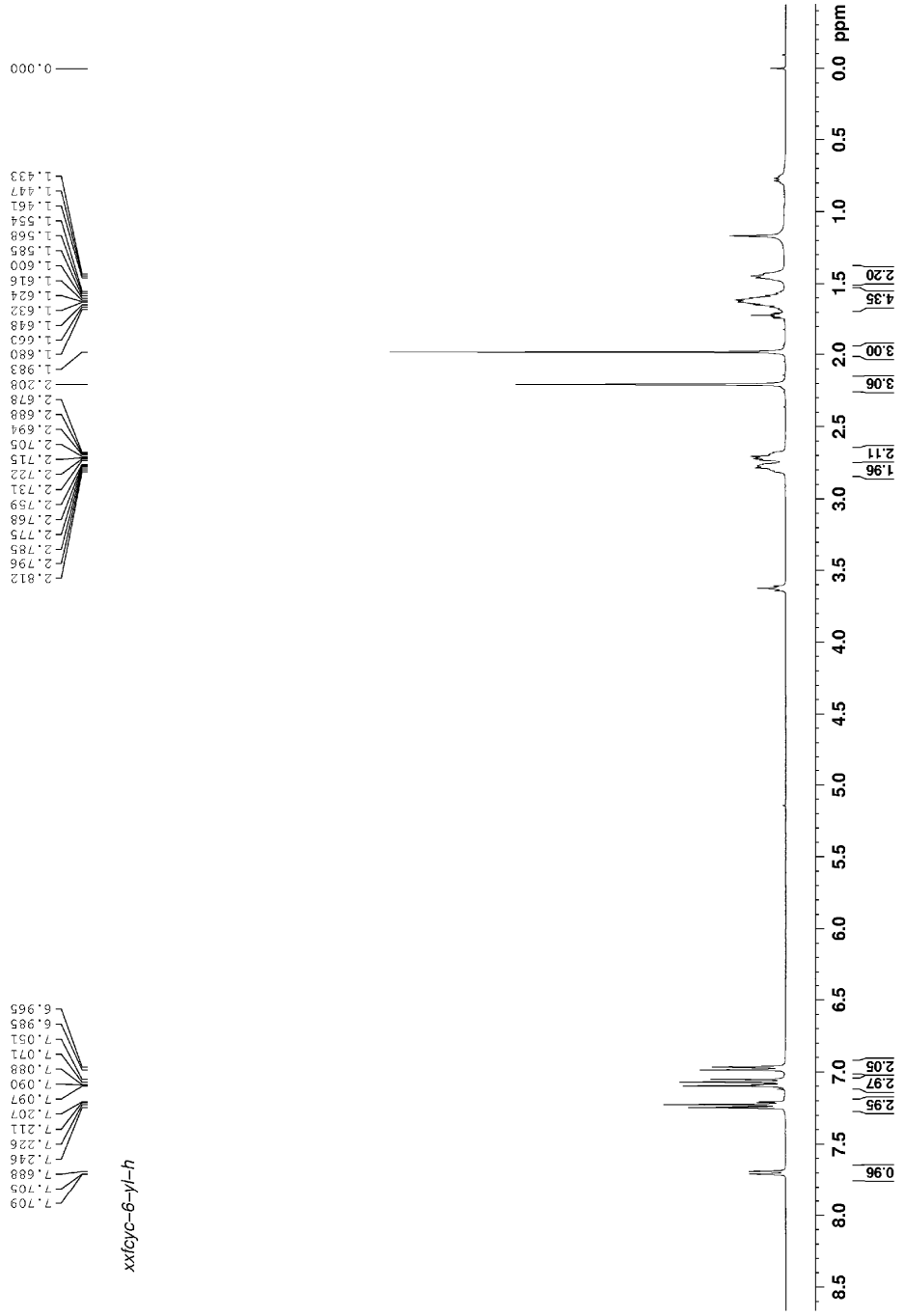
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2.775
2.785
2.796
2.812
6.965
6.985
7.051
7.071
7.088
7.090
7.097
7.207
7.211
7.226
7.246
7.688
7.705
7.709
xxlcyc-6-yl-h
ppm
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1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
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6.0
6.5
7.0
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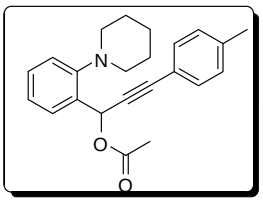
2.05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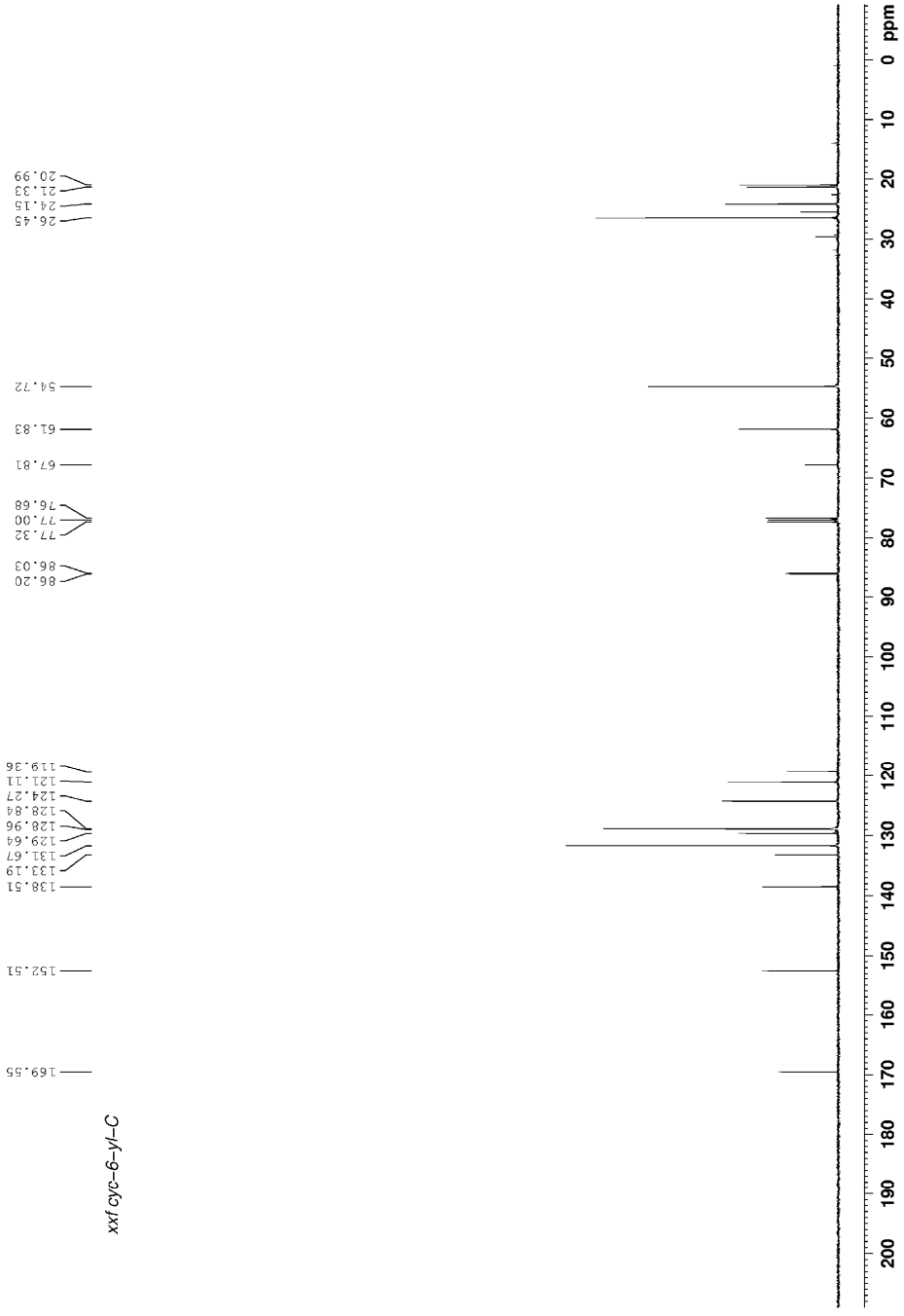
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67.81
76.68
77.00
77.32
86.03
86.20
119.36
121.11
124.27
128.84
128.96
129.64
131.67
133.19
138.51
152.51
169.55
xxf cyc-6-yl-C
0 ppm
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20
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50
60
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90
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170
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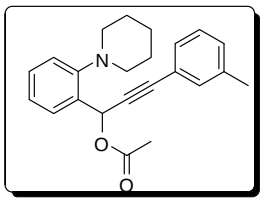
190
200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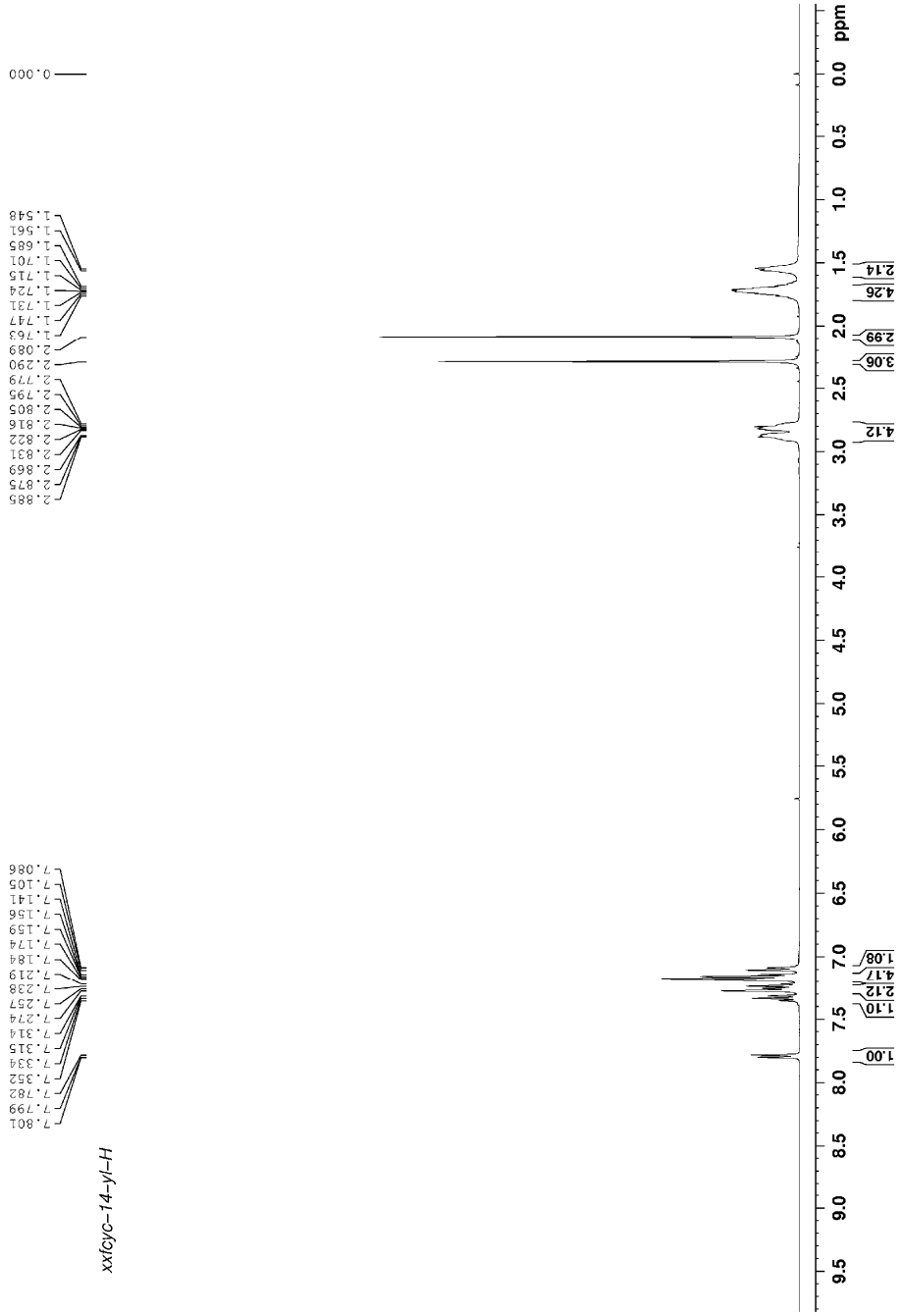
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2.290
2.779
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2.805
2.816
2.822
2.831
2.869
2.875
2.885
7.086
7.105
7.141
7.156
7.159
7.174
7.184
7.219
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7.257
7.274
7.314
7.315
7.334
7.352
7.782
7.799
7.801
xxfcyc-14-yl-H
ppm
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1.5
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3.0
3.5
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5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
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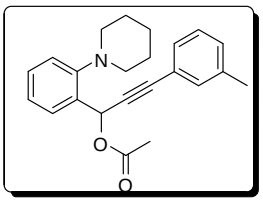
1.08
4.17
2.12
1.10
1.00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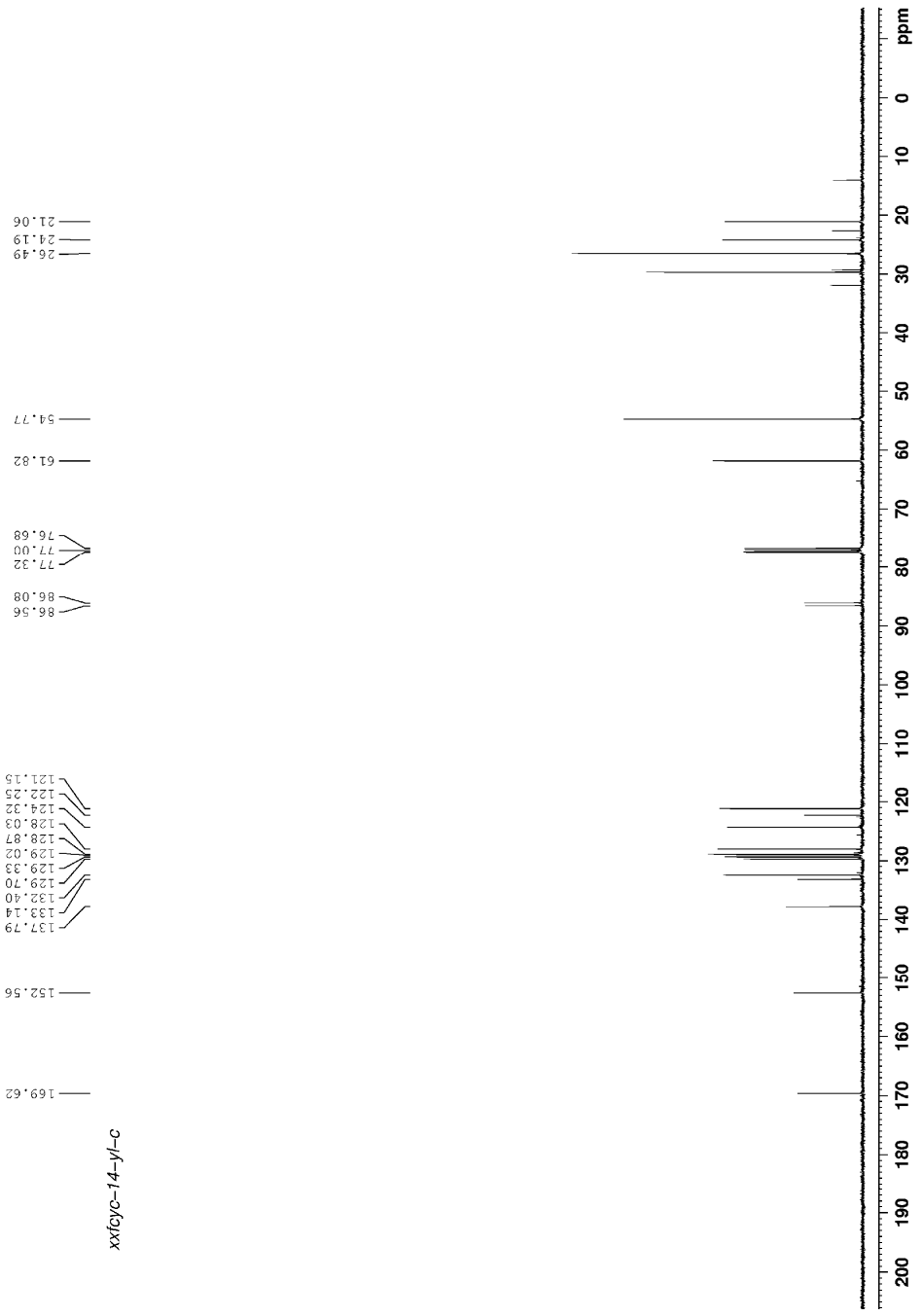
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122.25
124.32
128.03
128.87
129.02
129.33
129.70
132.40
133.14
137.79
152.56
169.62
xxfcyc-14-yl-c
ppm
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50
60
70
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90
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130
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170
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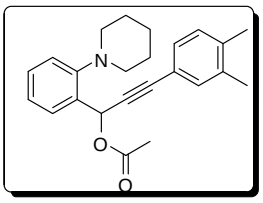
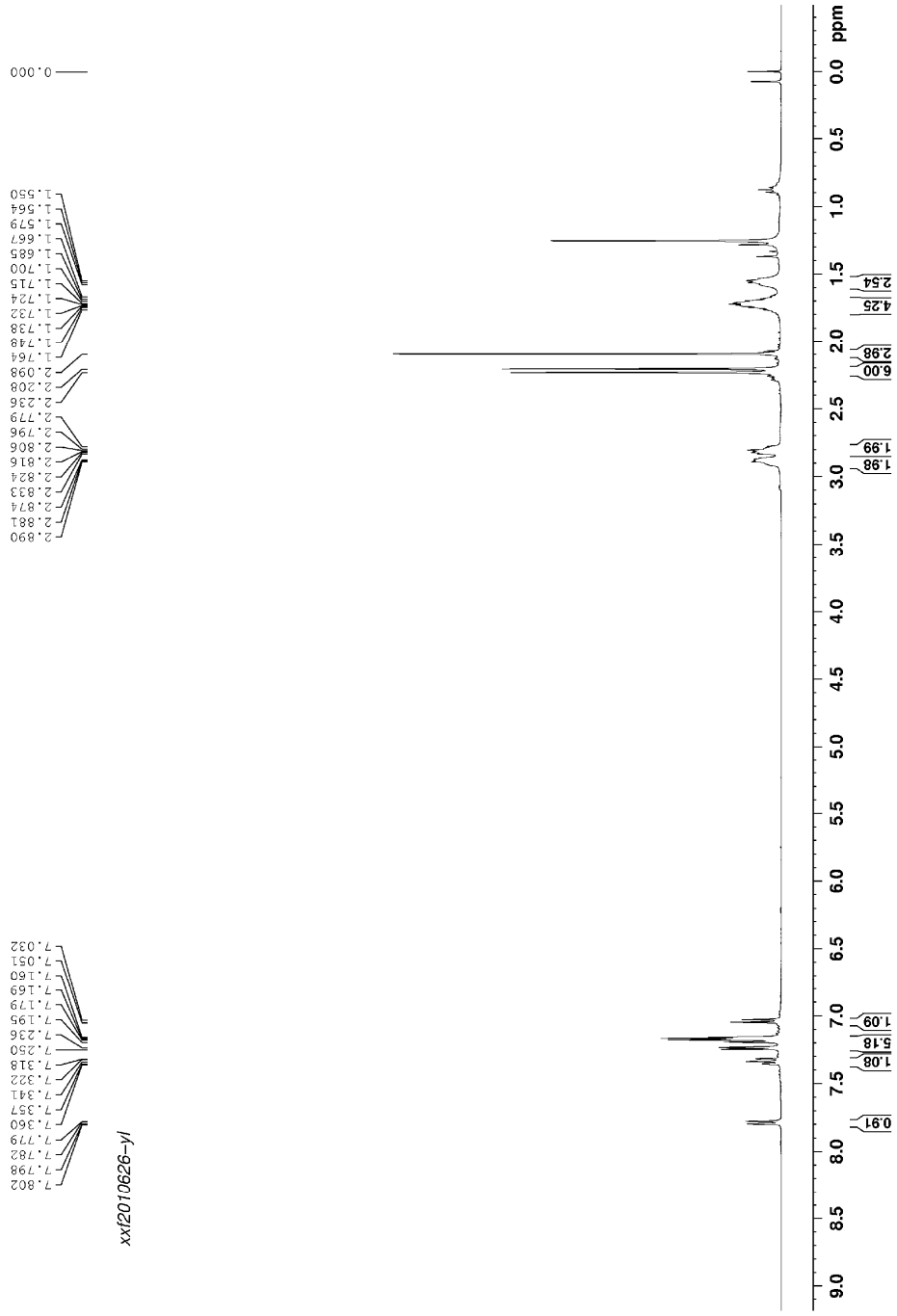
200

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3.5
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4.5
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5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
0.91
1.08
5.18
1.09
1.99
1.98
6.00
2.98
4.25
2.54
0.000
1.550
1.564
1.579
1.667
1.685
1.700
1.715
1.724
1.732
1.738
1.748
1.764
2.098
2.208
2.236
2.779
2.796
2.806
2.816
2.824
2.833
2.874
2.881
2.890
7.032
7.051
7.160
7.169
7.179
7.195
7.236
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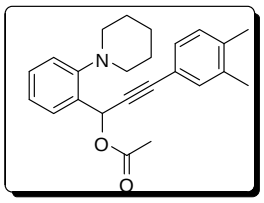
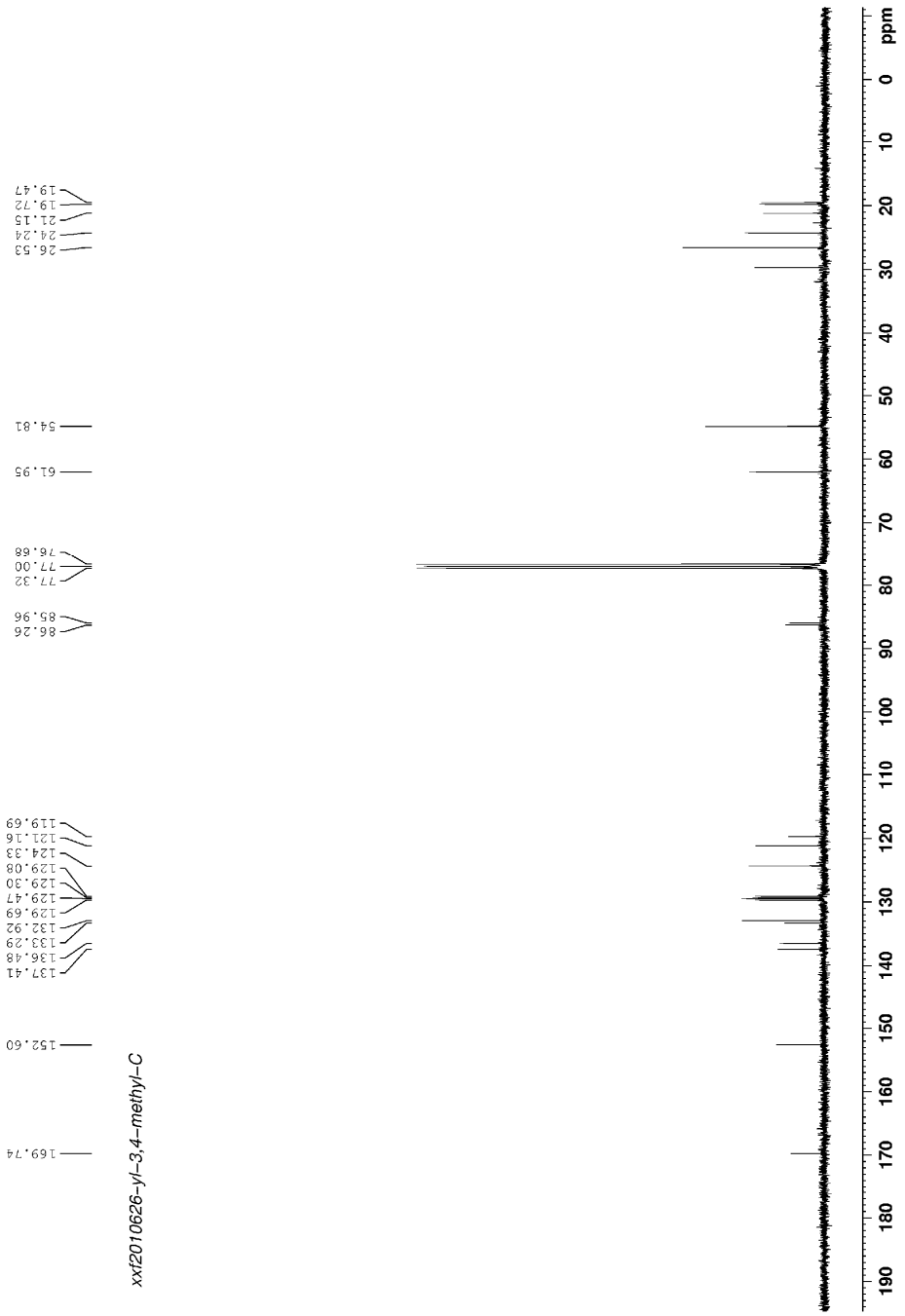
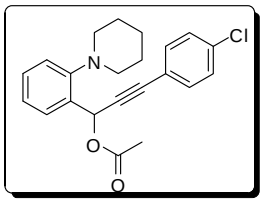
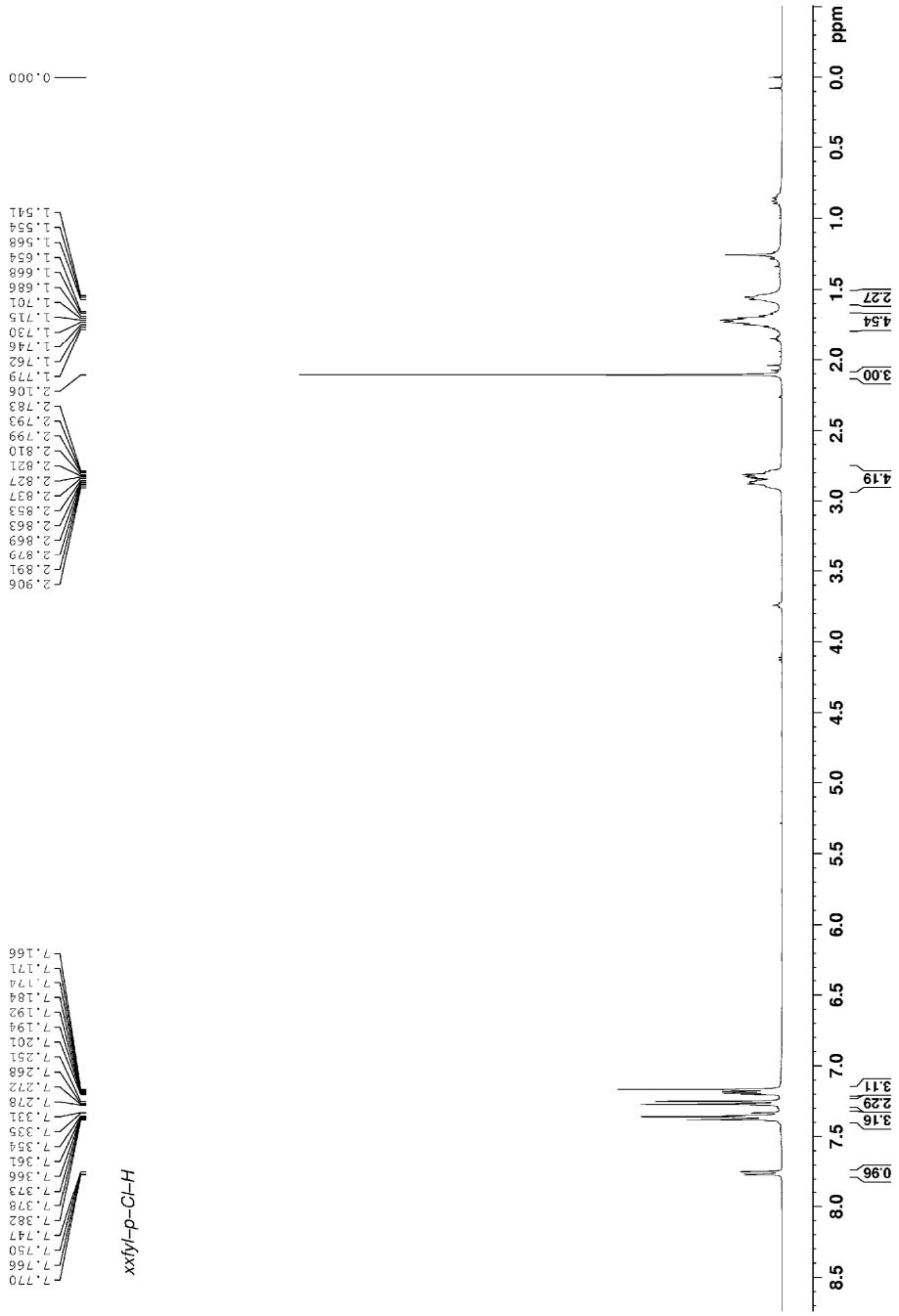
7.322
7.341
7.357
7.360
7.779
7.782
7.798
7.802
xxl2010626-yl






Cl
N
O
O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3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
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3.00
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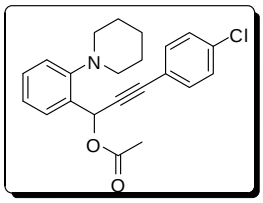
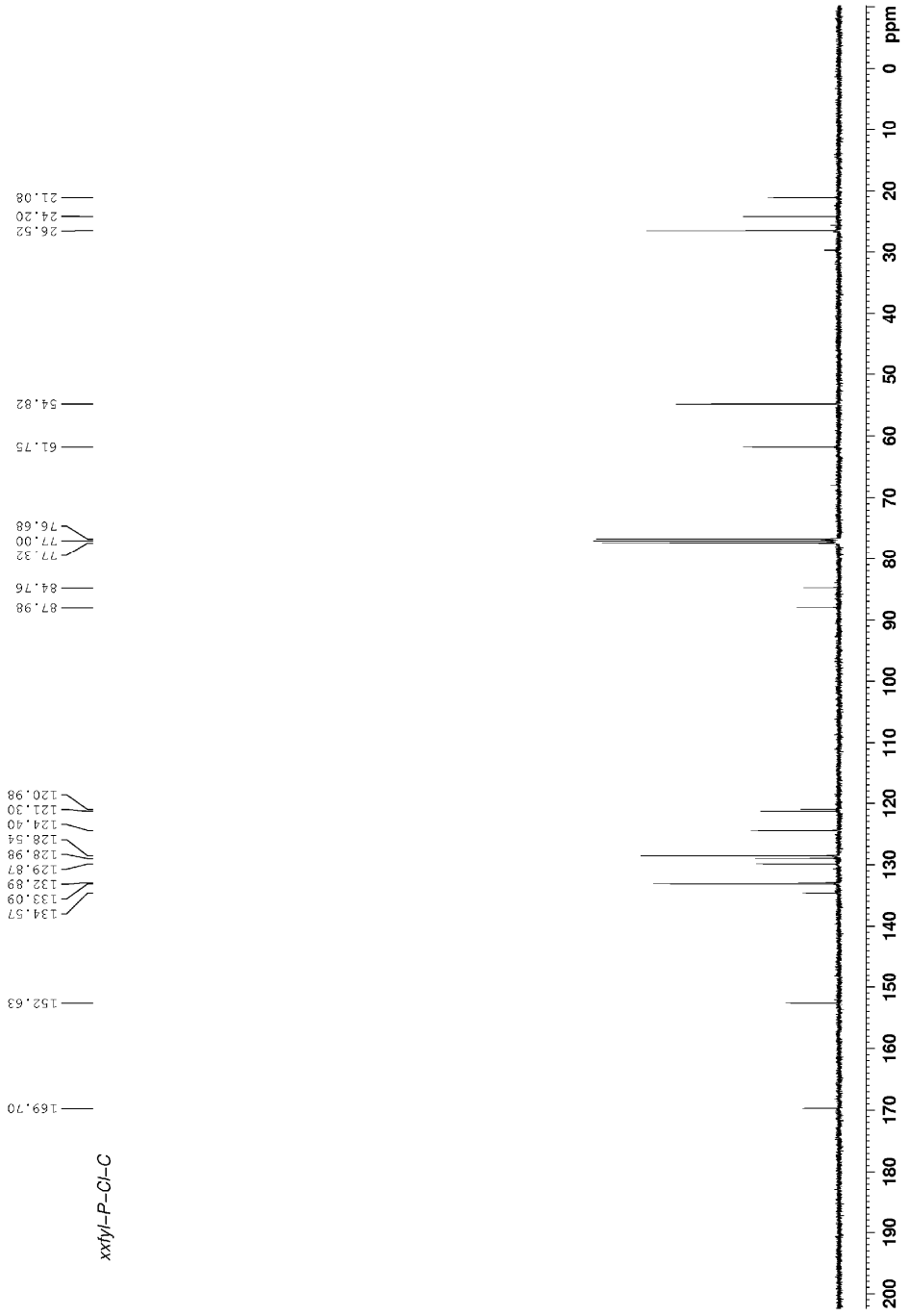
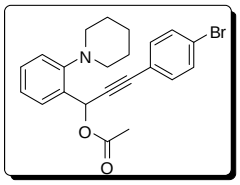
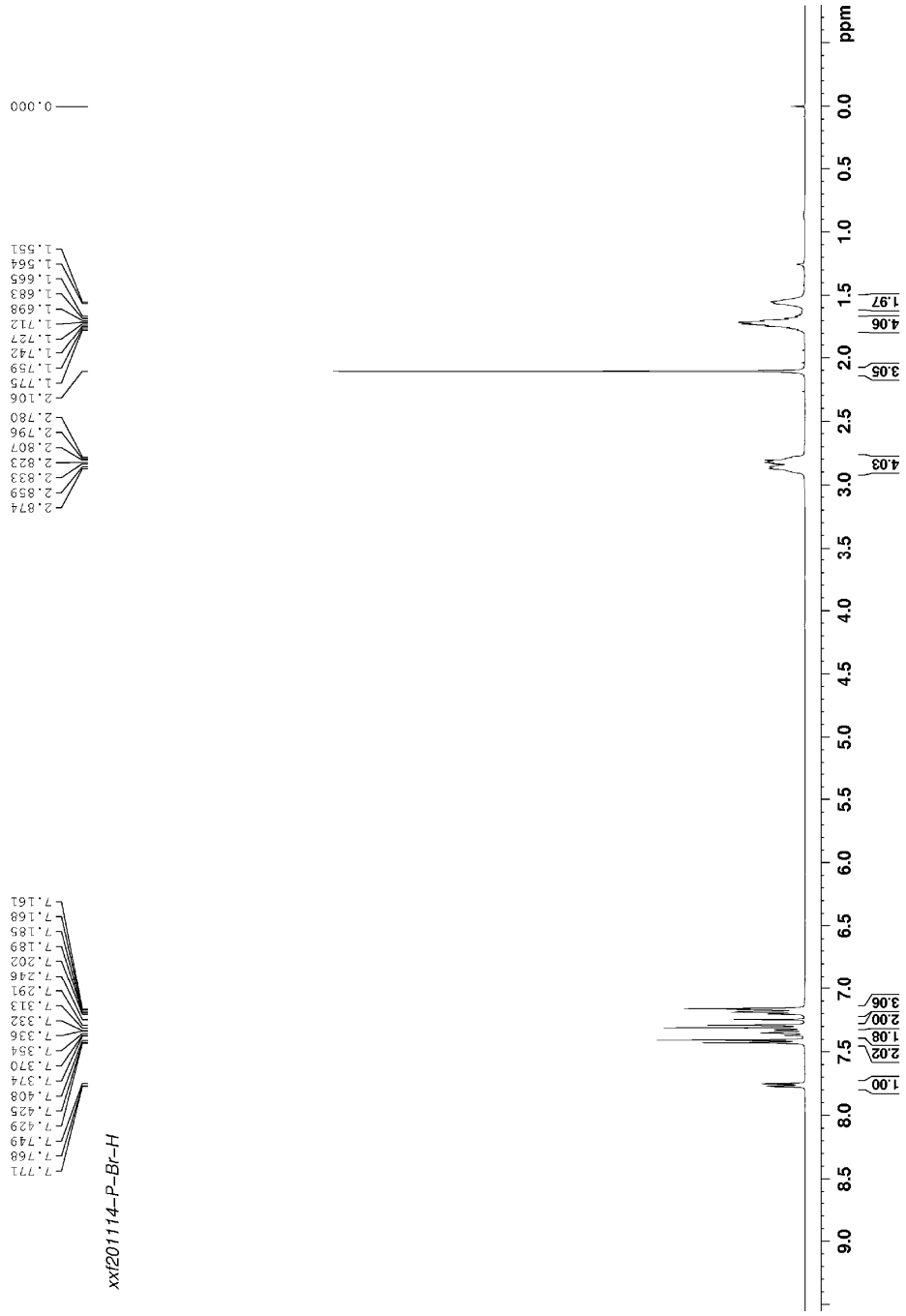
2.29
3.16
0.96






Br
N
O
O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2.780
2.796
2.807
2.823
2.833
2.859
2.874
7.161
7.168
7.185
7.189
7.202
7.246
7.291
7.313
7.332
7.336
7.354
7.370
7.374
7.408
7.425
7.429
7.749
7.768
7.771
xxi201114-P-Br-H
ppm
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1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
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4.03
3.06
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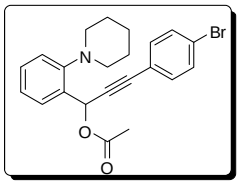
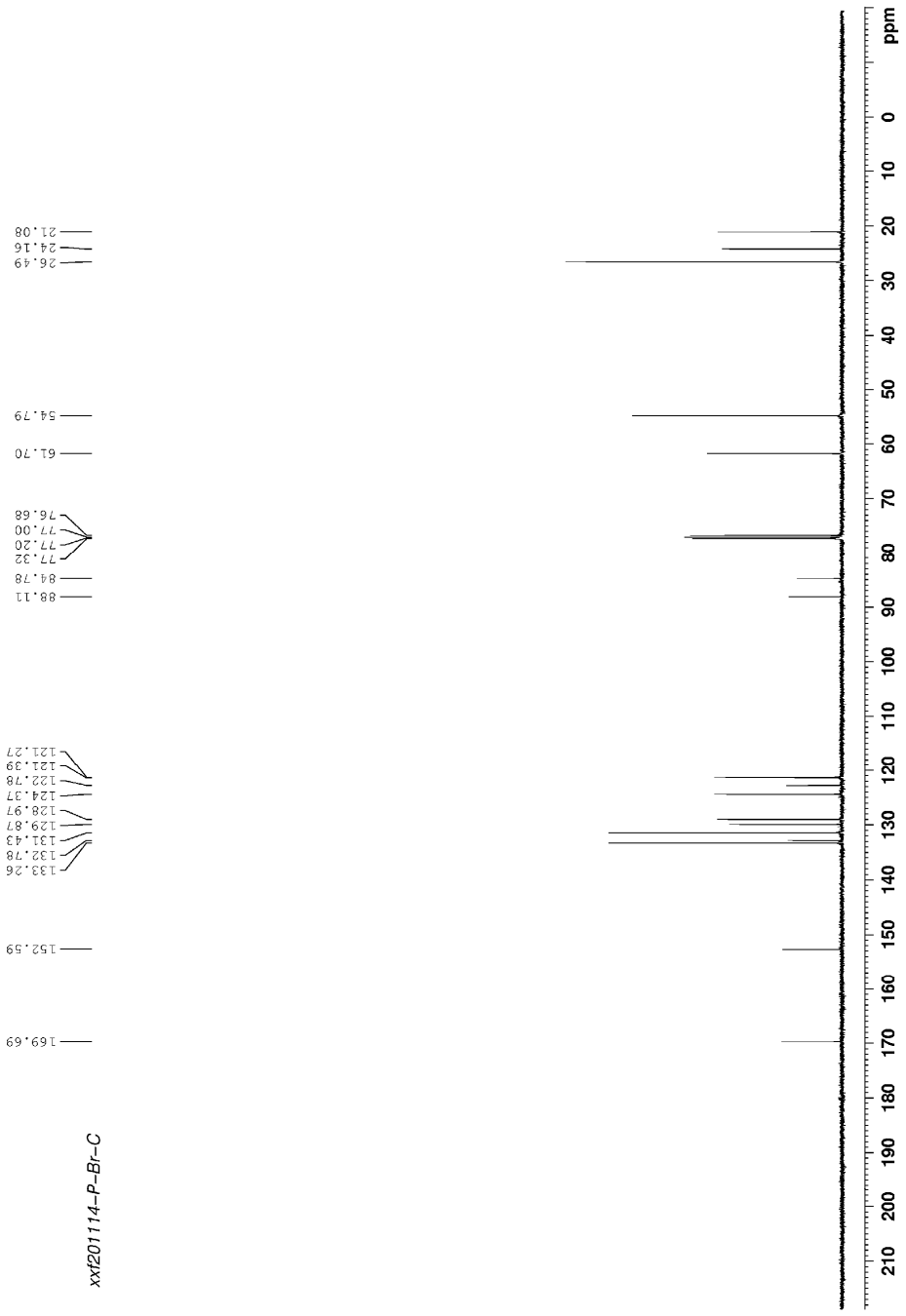
1.08
2.02
1.00


Br
N
O
O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54.79
61.70
76.68
77.00
77.20
77.32
84.78
88.11
121.27
121.39
122.78
124.37
128.97
129.87
131.43
132.78
133.26
152.59
169.69
xxf201114-P-Br-C
ppm
0
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30
40
50
60
70
80
90
100
110
120
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140
150
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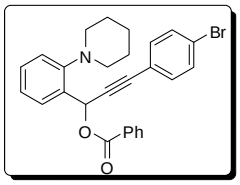
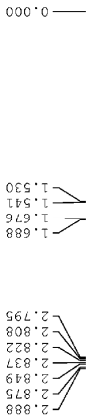
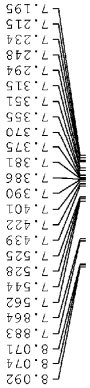
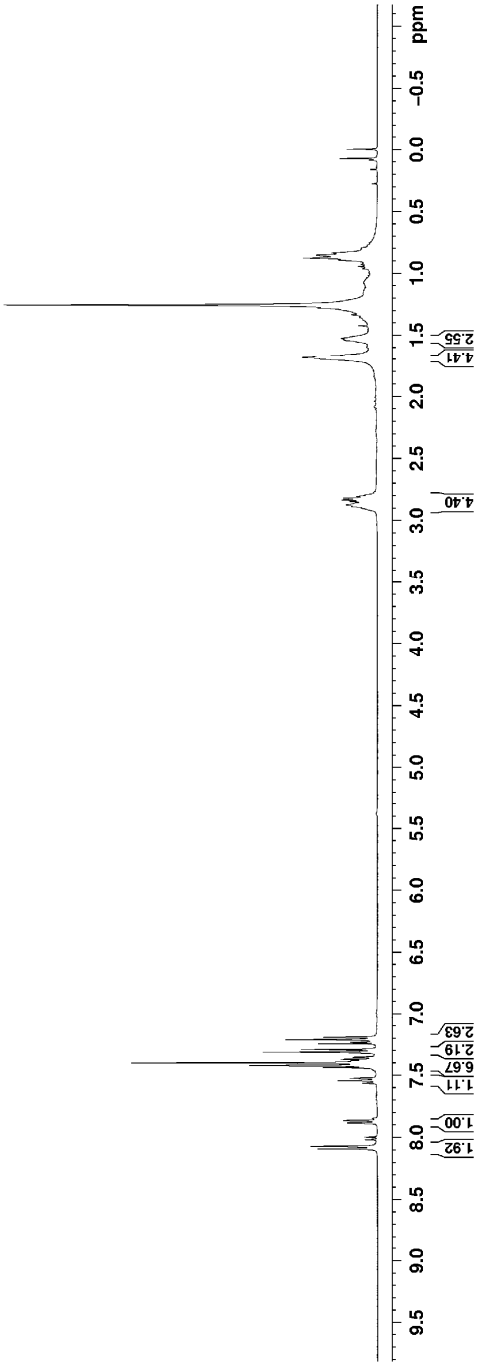
180
190
200
210

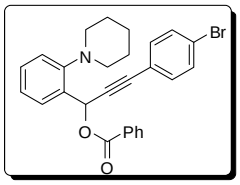






XXFCYC-24-YL-H

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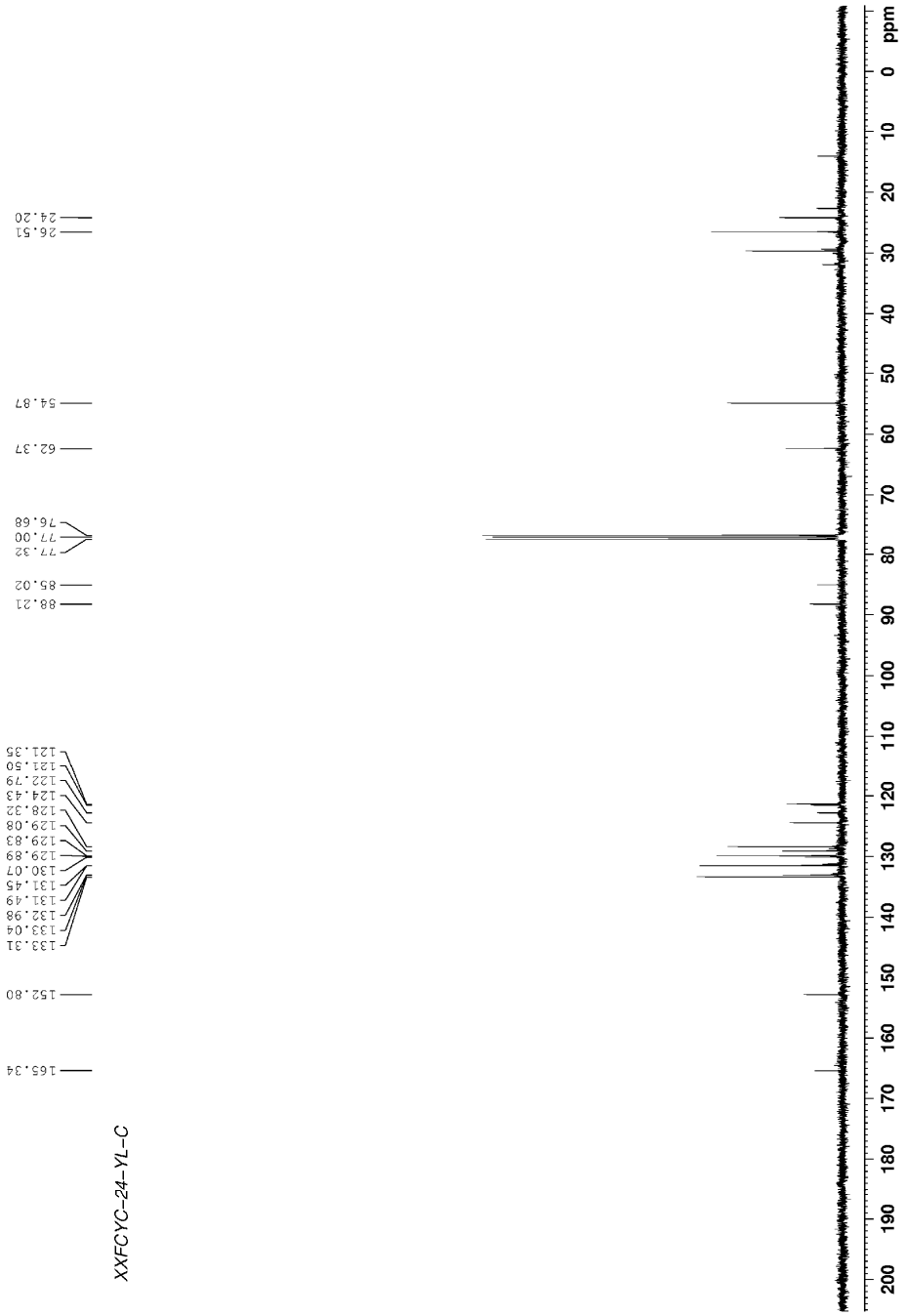
O
Ph
O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85.02
88.21
121.35
121.50
122.79
124.43
128.32
129.08
129.83
129.89
130.07
131.45
131.49
132.98
133.04
133.31
152.80
165.34
XXFCYC-24-YL-C
ppm
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50
60
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130
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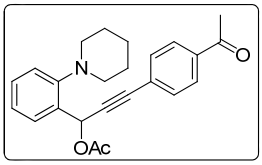
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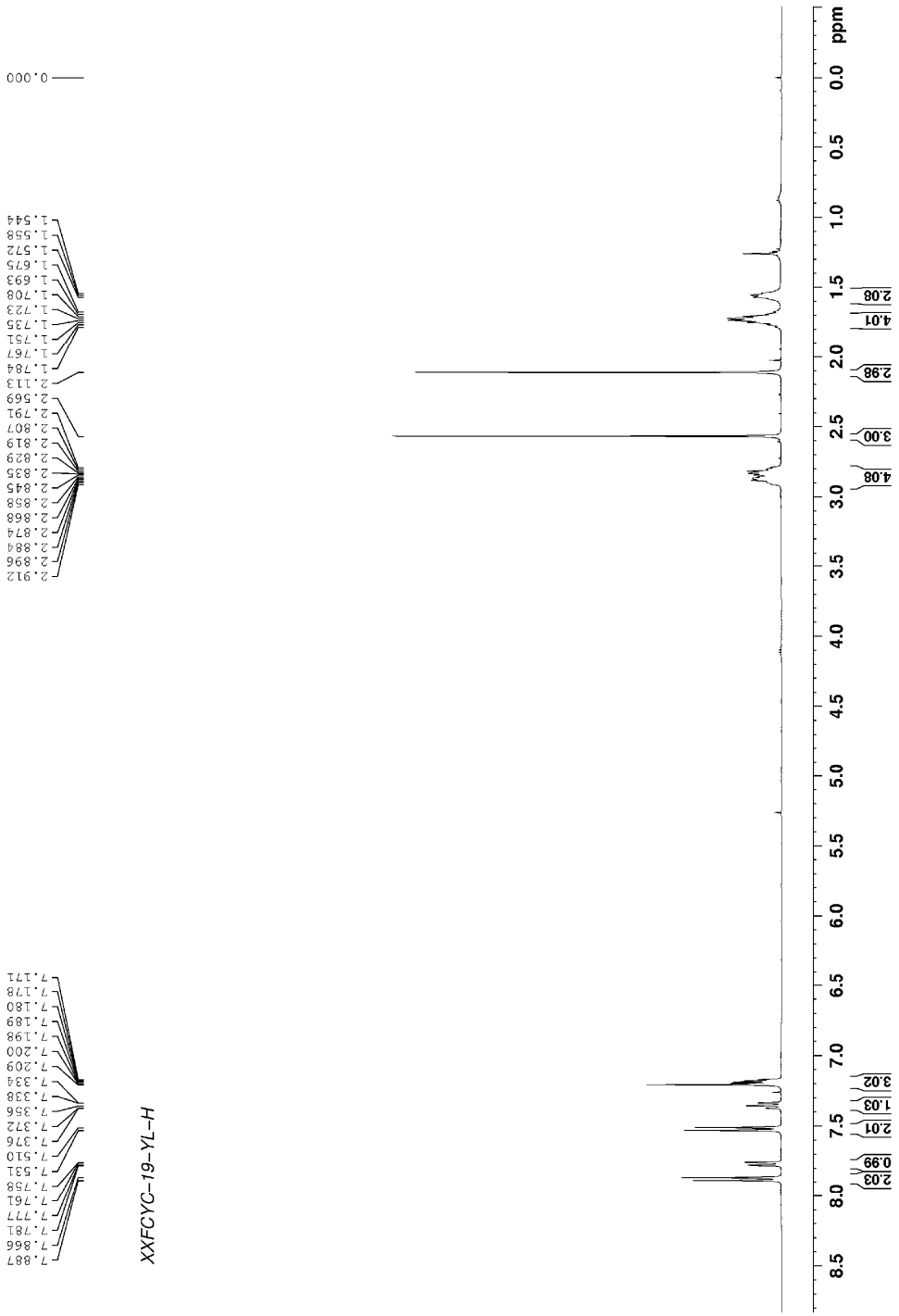
OAc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2.569
2.791
2.807
2.819
2.829
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2.845
2.858
2.868
2.874
2.884
2.896
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7.171
7.178
7.180
7.189
7.198
7.200
7.209
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7.338
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7.376
7.510
7.531
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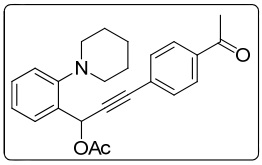
2.03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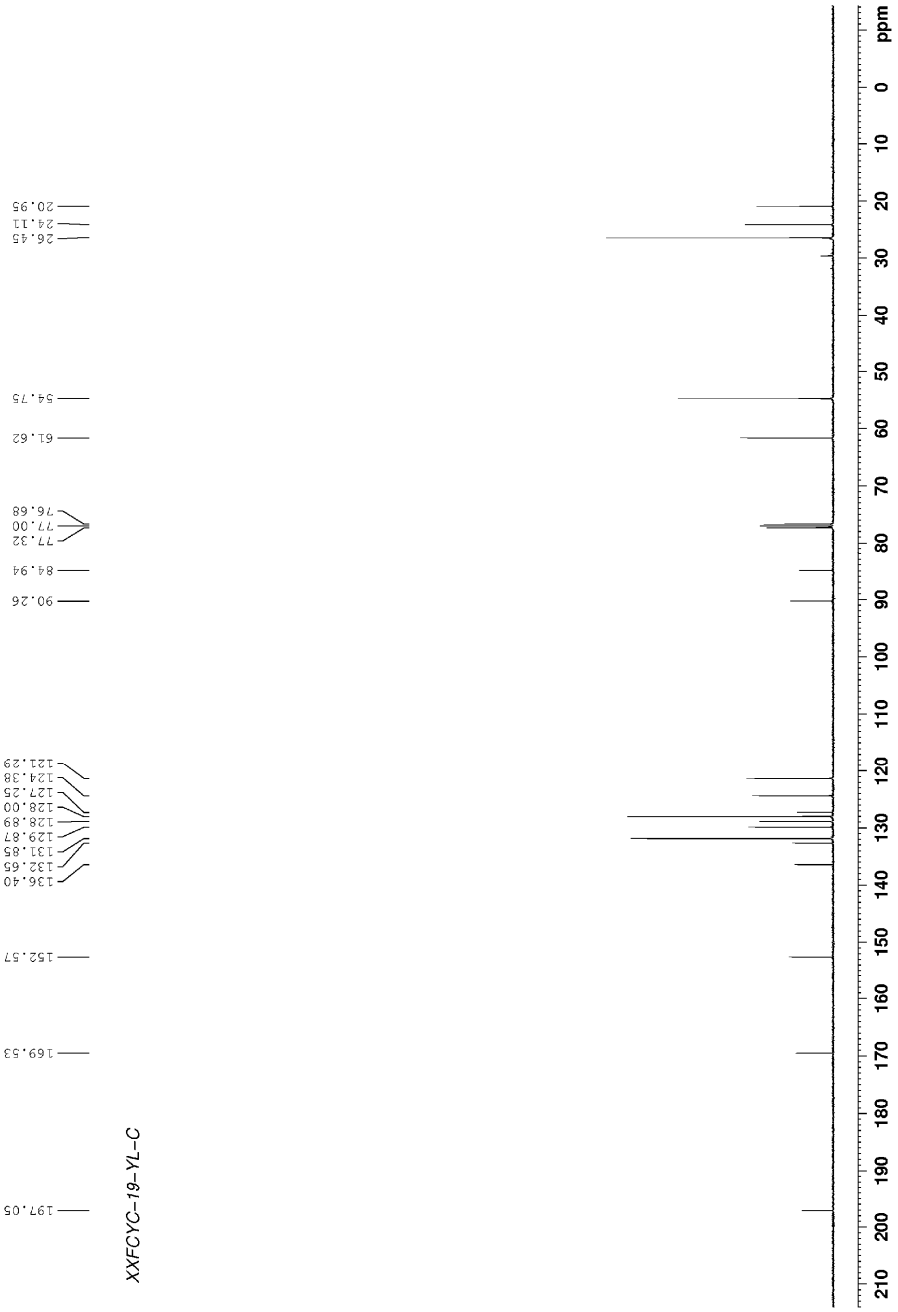
OAc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124.38
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128.00
128.89
129.87
131.85
132.65
136.40
152.57
169.53
197.05
XXFCYC-19-YL-C
ppm
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60
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80
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100
110
120
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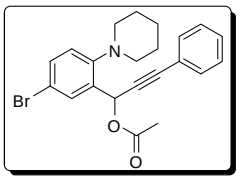
180
190
200
210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Br
O
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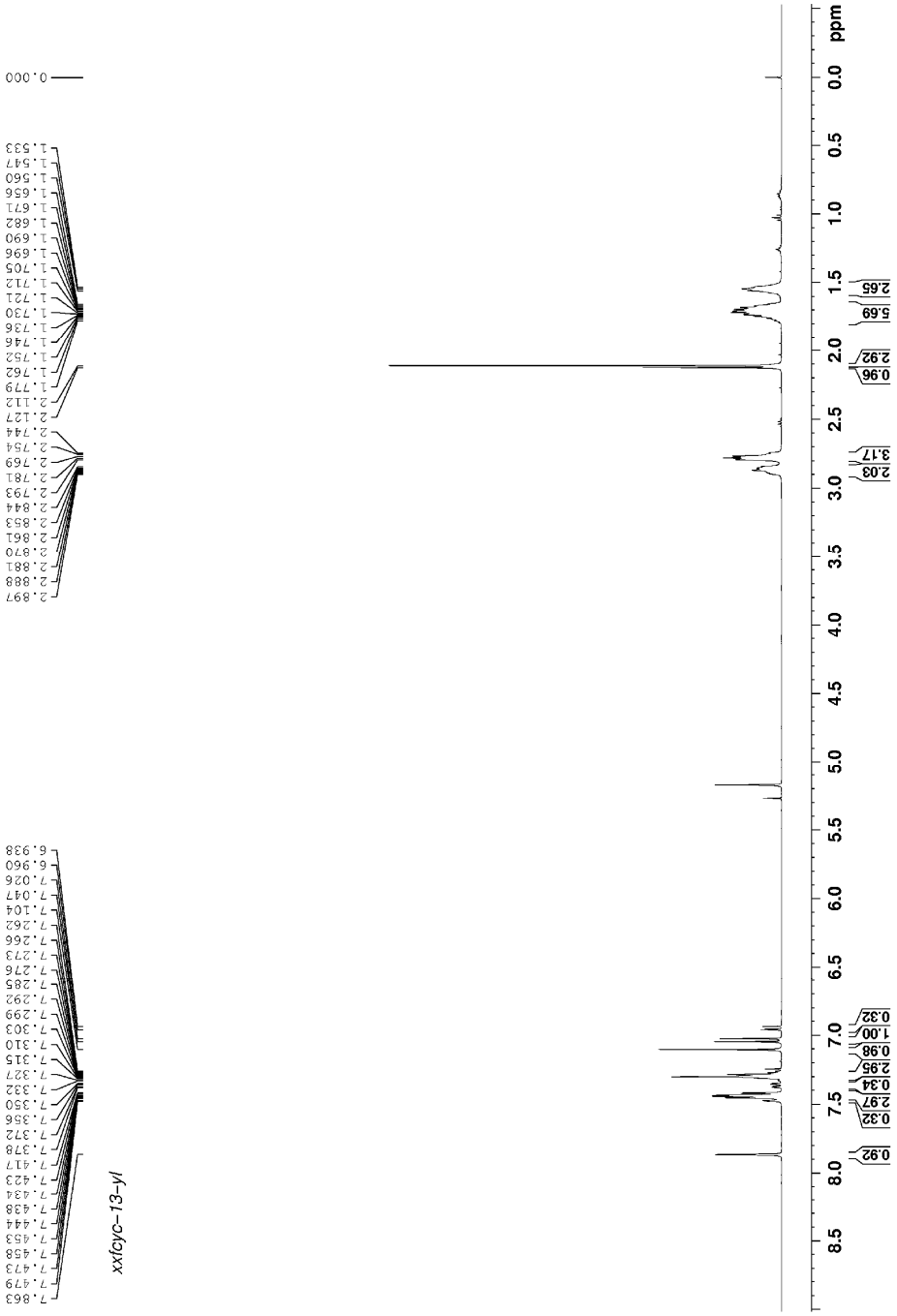
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1.736
1.746
1.752
1.762
1.779
2.112
2.127
2.744
2.754
2.769
2.781
2.793
2.844
2.853
2.861
2.870
2.881
2.888
2.897
6.938
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7.262
7.266
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2.5
3.0
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4.0
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5.5
6.0
6.5
7.0
7.5
8.0
8.5
0.92
0.32
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2.95
0.98
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0.32
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2.03
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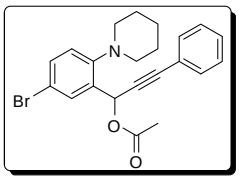
0.96
5.69
2.65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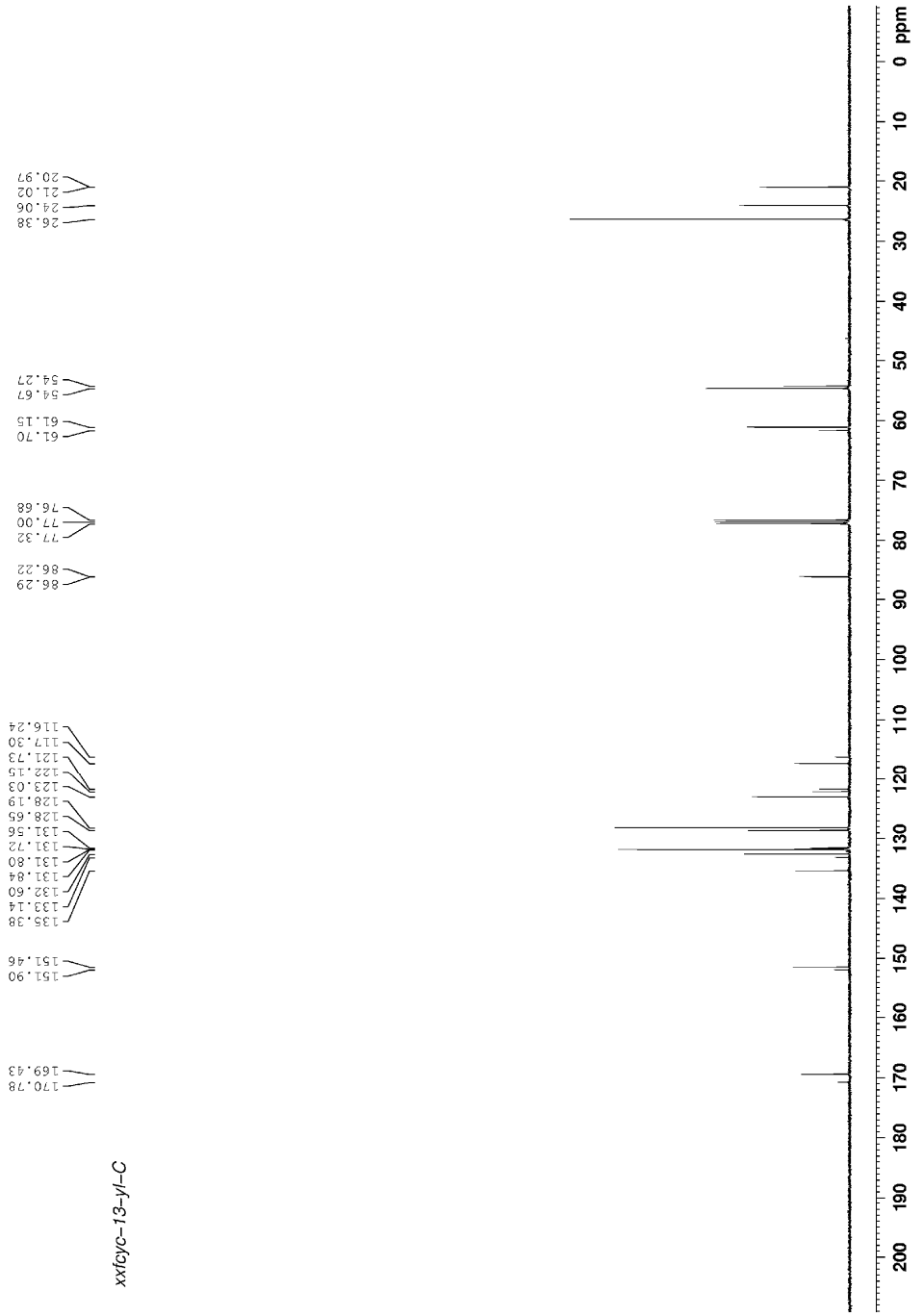
Br
O
O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61.70
76.68
77.00
77.32
86.22
86.29
116.24
117.30
121.73
122.15
123.03
128.19
128.65
131.56
131.72
131.80
131.84
132.60
133.14
135.38
151.46
151.90
169.43
170.78
xxfcyc-13-yl-C
0 ppm
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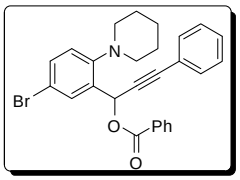
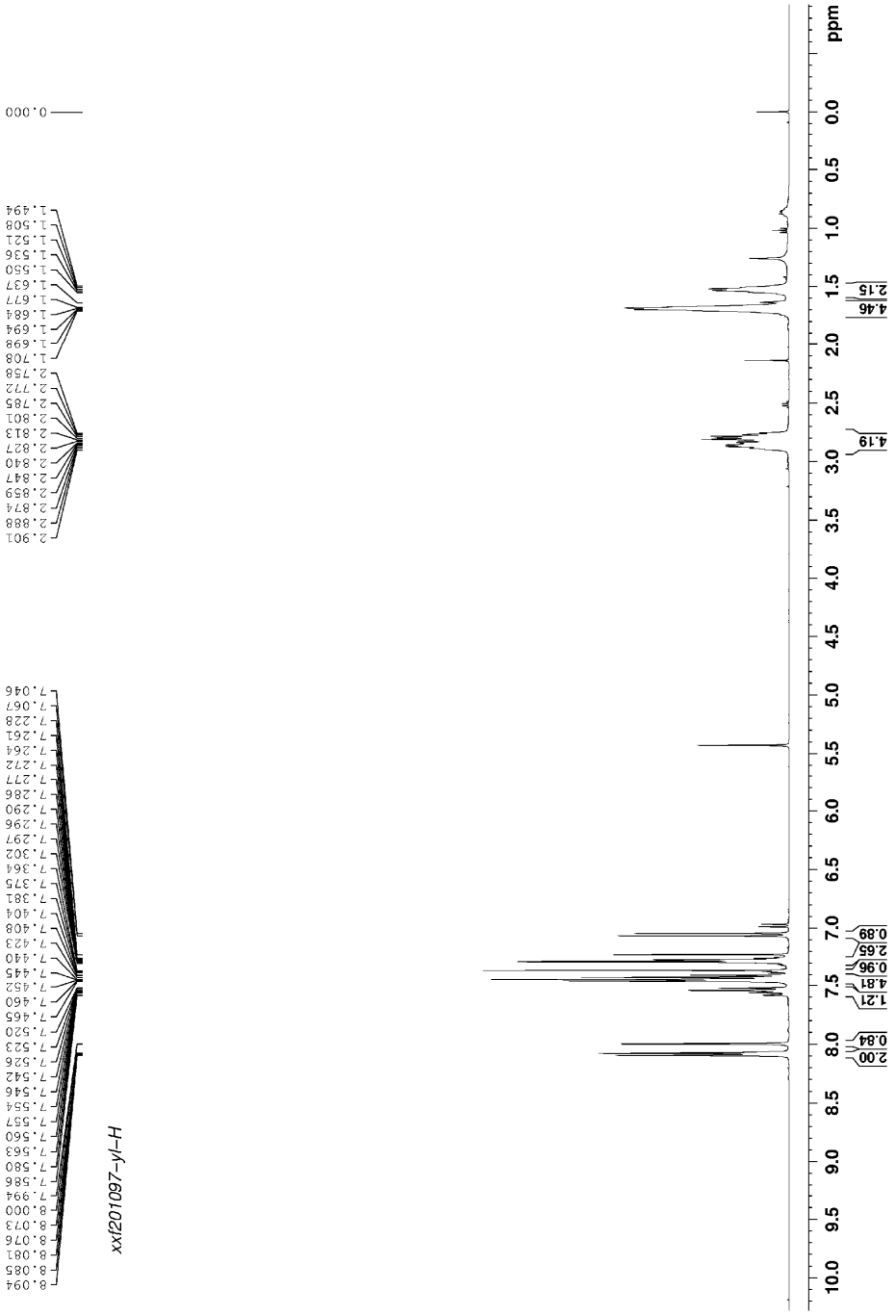

N
Br
O
Ph
O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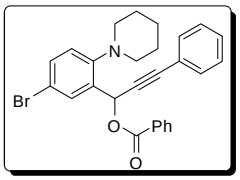
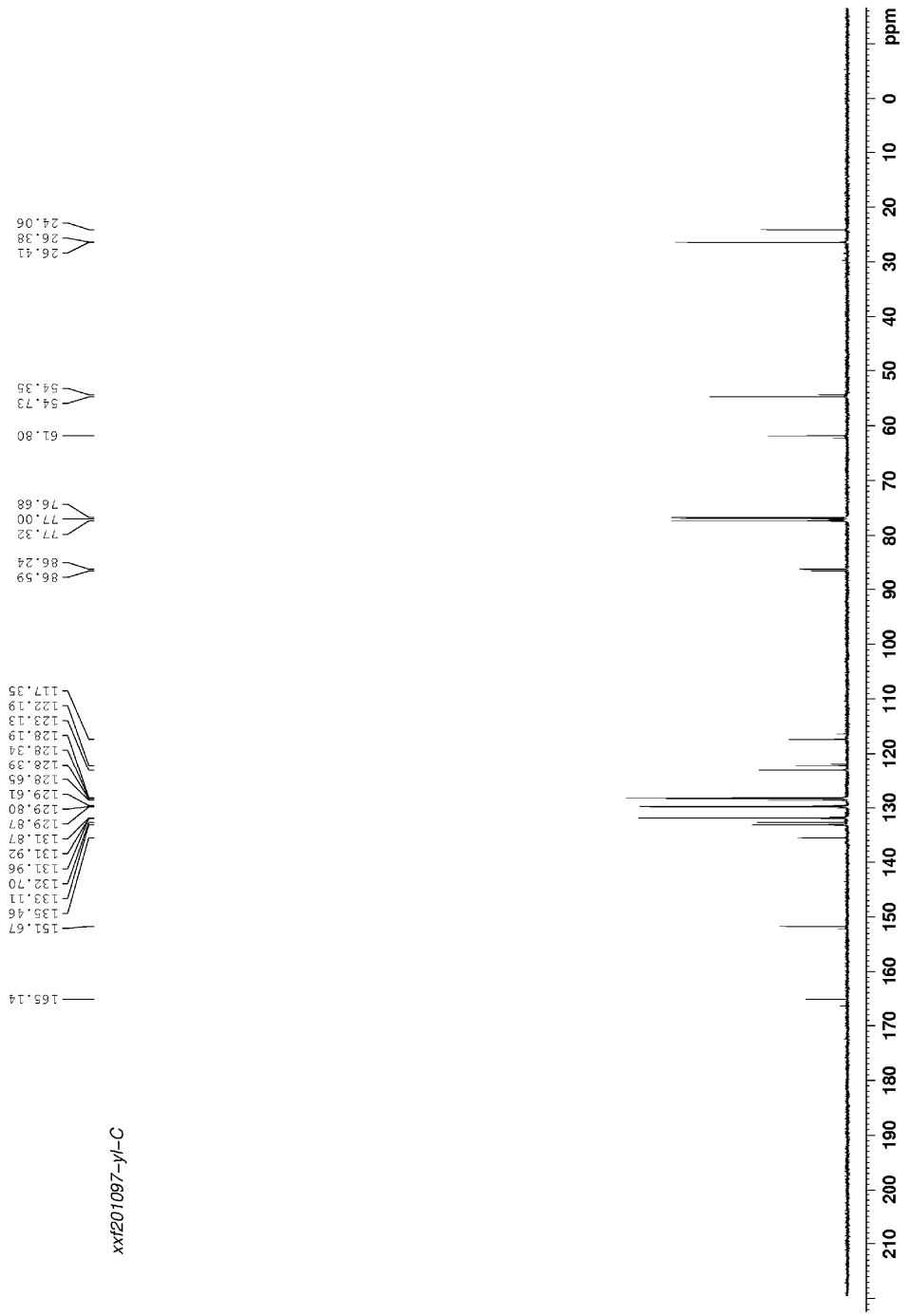
0.96
4.81
1.21
0.84
2.00


N
Br
O
Ph
O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26.41
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76.68
77.00
77.32
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86.59
117.35
122.19
123.13
128.19
128.34
128.39
128.65
129.61
129.80
129.87
131.87
131.92
131.96
132.70
133.11
135.46
151.67
165.14
xxf201097-yl-C
ppm
0
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100
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140
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190
200
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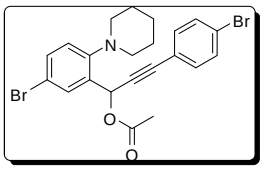
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Br
O
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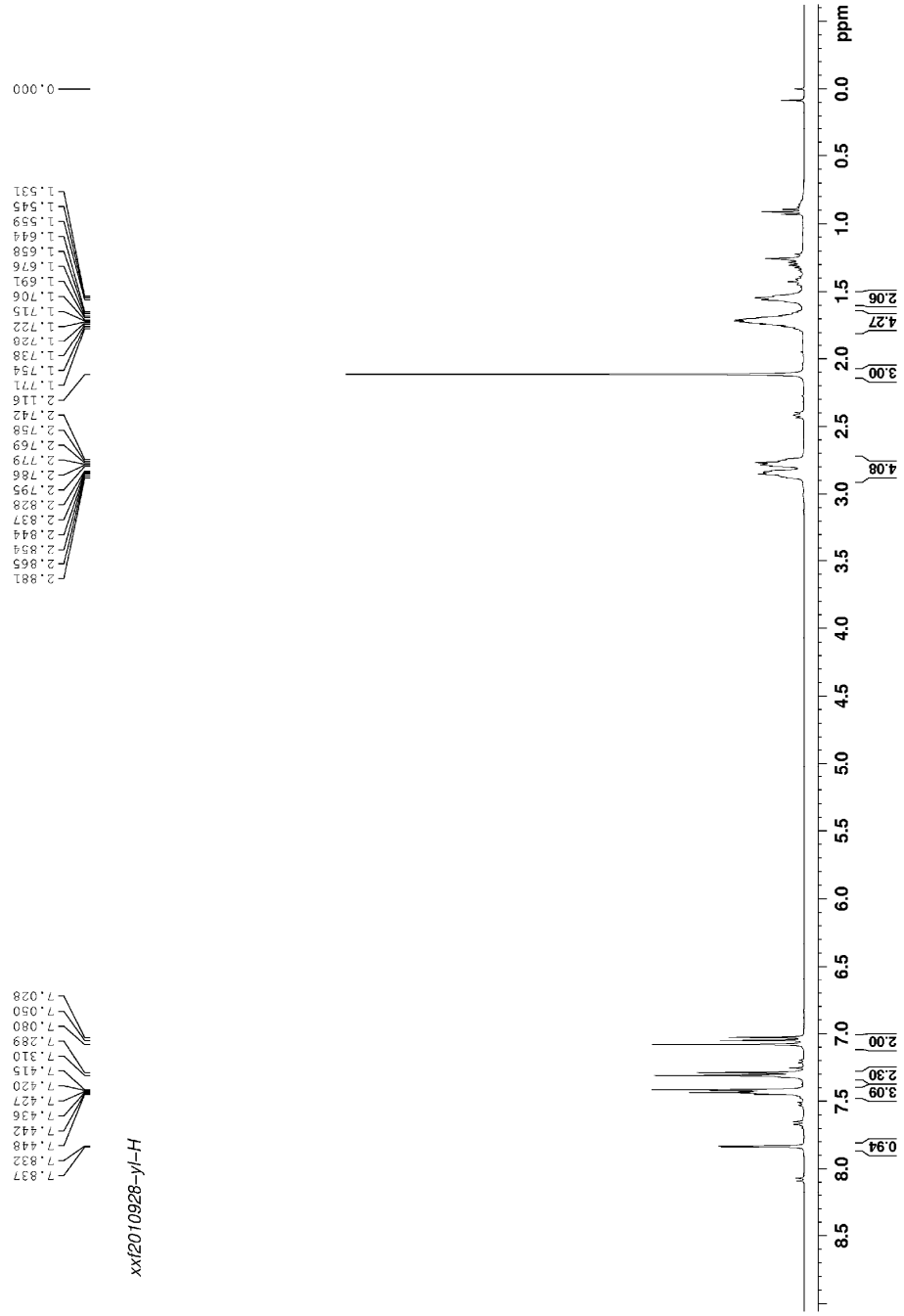
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1.715
1.722
1.729
1.738
1.754
1.771
2.116
2.742
2.758
2.769
2.779
2.786
2.795
2.828
2.837
2.844
2.854
2.865
2.881
7.028
7.050
7.080
7.289
7.310
7.415
7.420
7.427
7.436
7.442
7.448
7.832
7.837
xxl20100926-yl-H
ppm
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1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
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4.27
3.00
4.08
2.00
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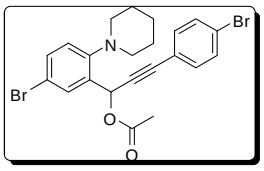
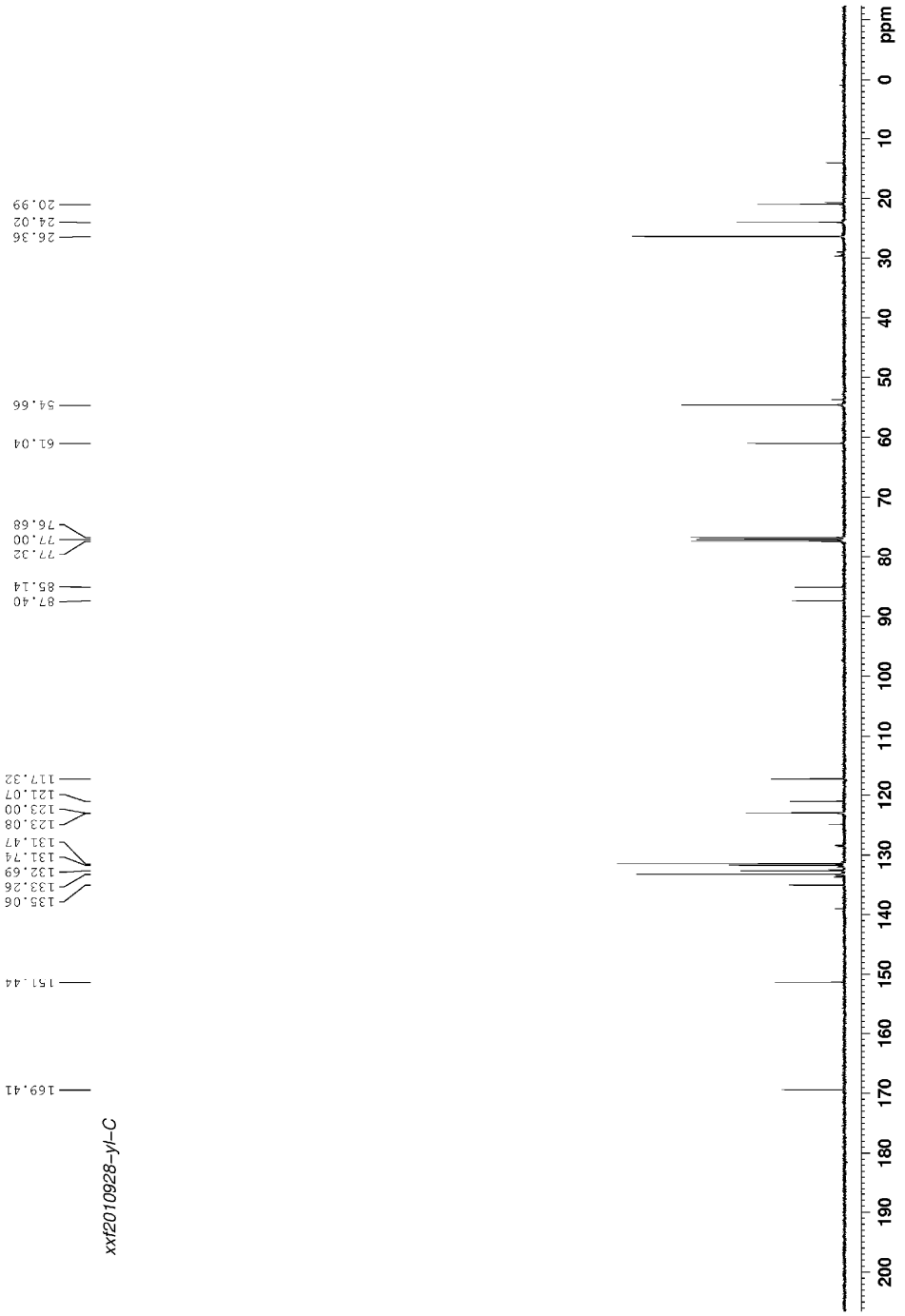
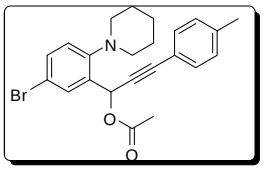
3.09
0.94



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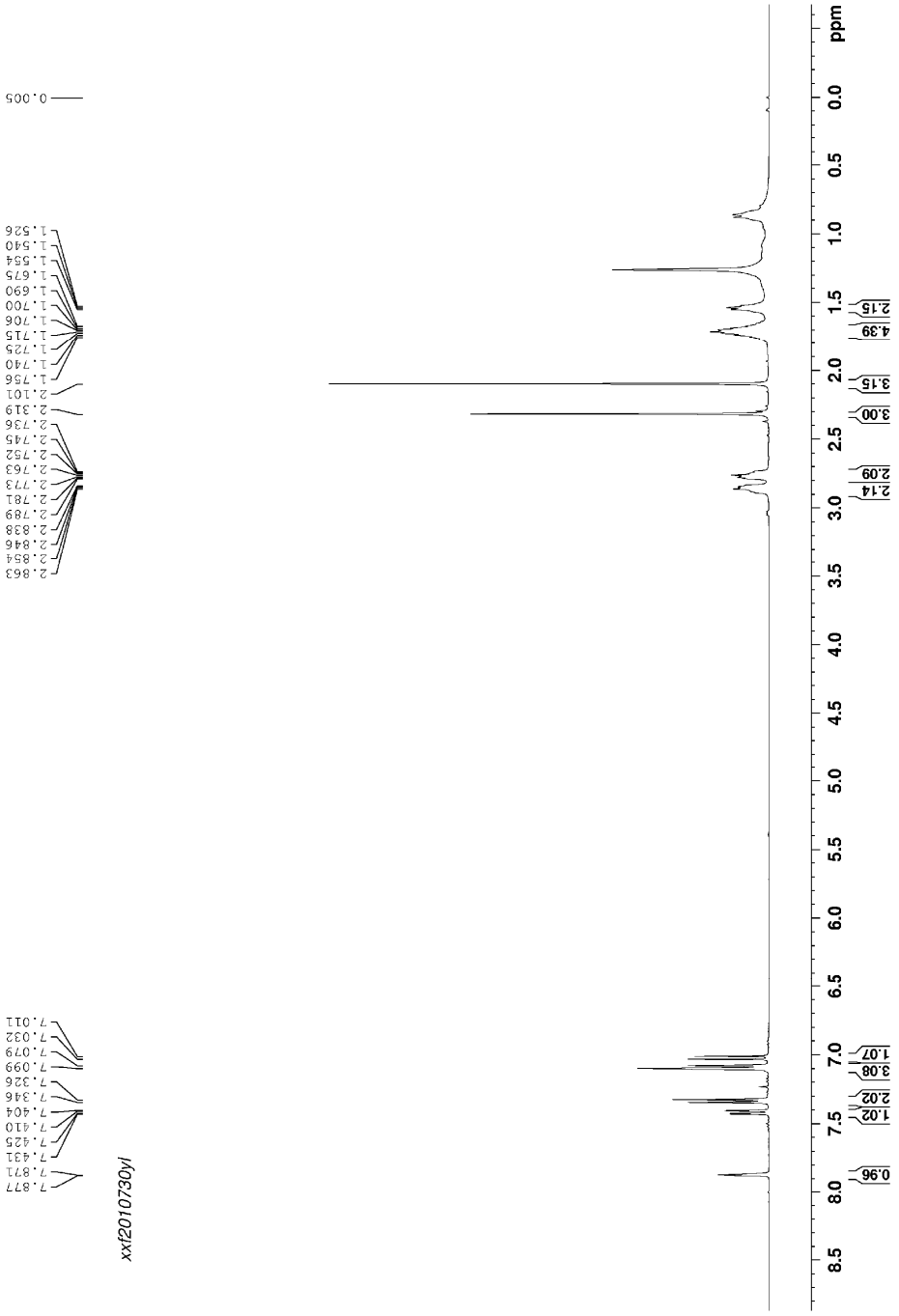
Br
O
O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7.011
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2.854
2.846
2.838
2.789
2.781
2.773
2.763
2.752
2.745
2.736
2.319
2.101
1.756
1.740
1.725
1.715
1.706
1.700
1.690
1.675
1.554
1.540
1.526
0.005
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
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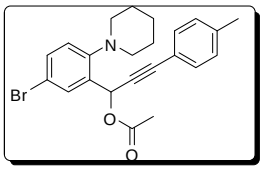
1.02
3.08
1.07
2.14
2.09
3.00
3.15
4.39
2.15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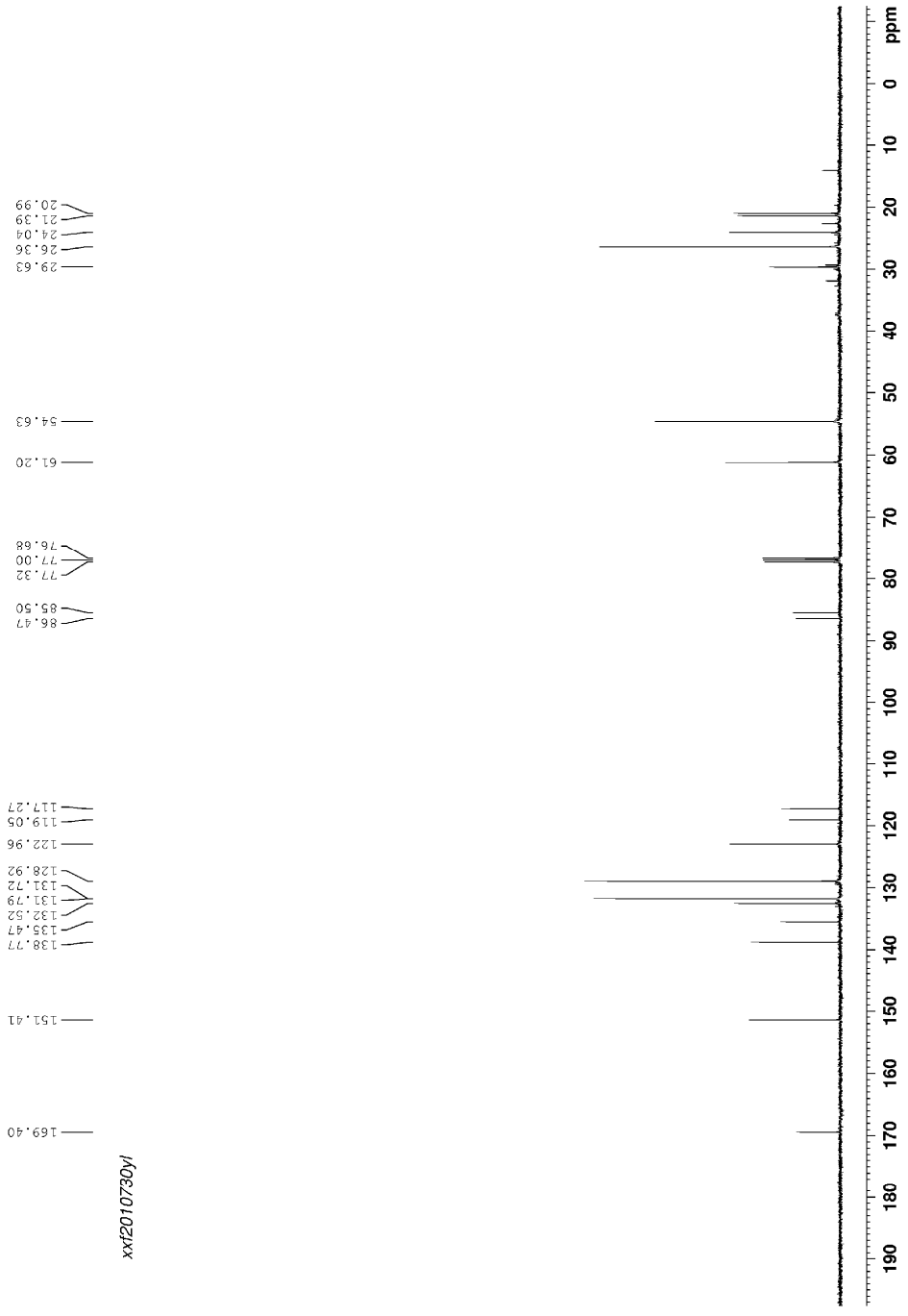
Br
O
O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24.04
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54.63
61.20
76.68
77.00
77.32
85.50
86.47
117.27
119.05
122.96
128.92
131.72
131.79
132.52
135.47
138.77
151.41
169.40
xxf2010730yl
ppm
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20
30
40
50
60
70
80
90
100
110
120
130
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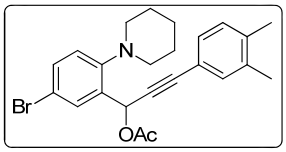
150
160
170
180
190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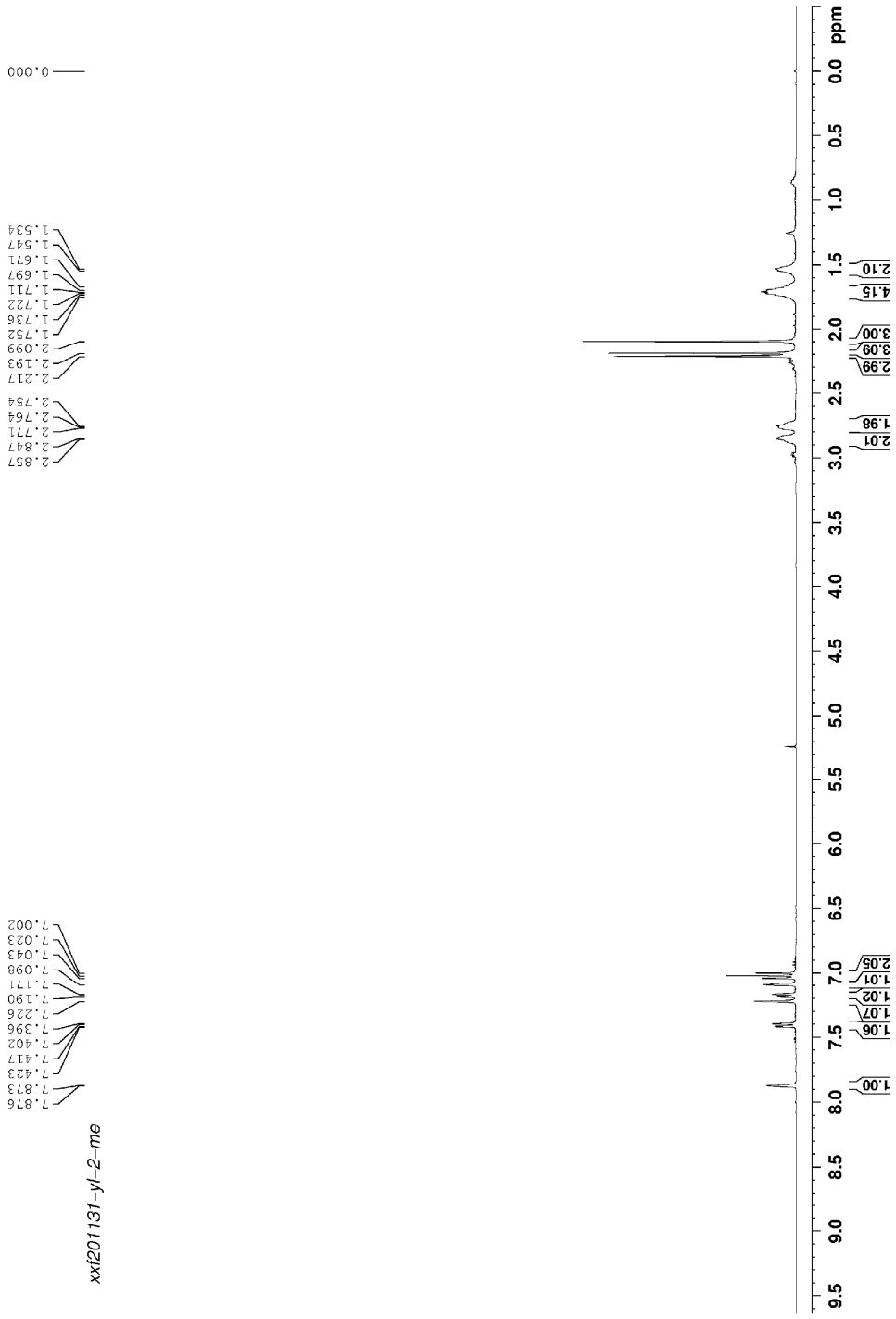
Br
OAc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1.697
1.711
1.722
1.736
1.752
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2.193
2.217
2.754
2.764
2.771
2.847
2.857
7.002
7.023
7.043
7.098
7.171
7.190
7.226
7.396
7.402
7.417
7.423
7.873
7.876
xxf201131-yl-2-me
ppm
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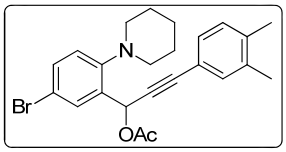
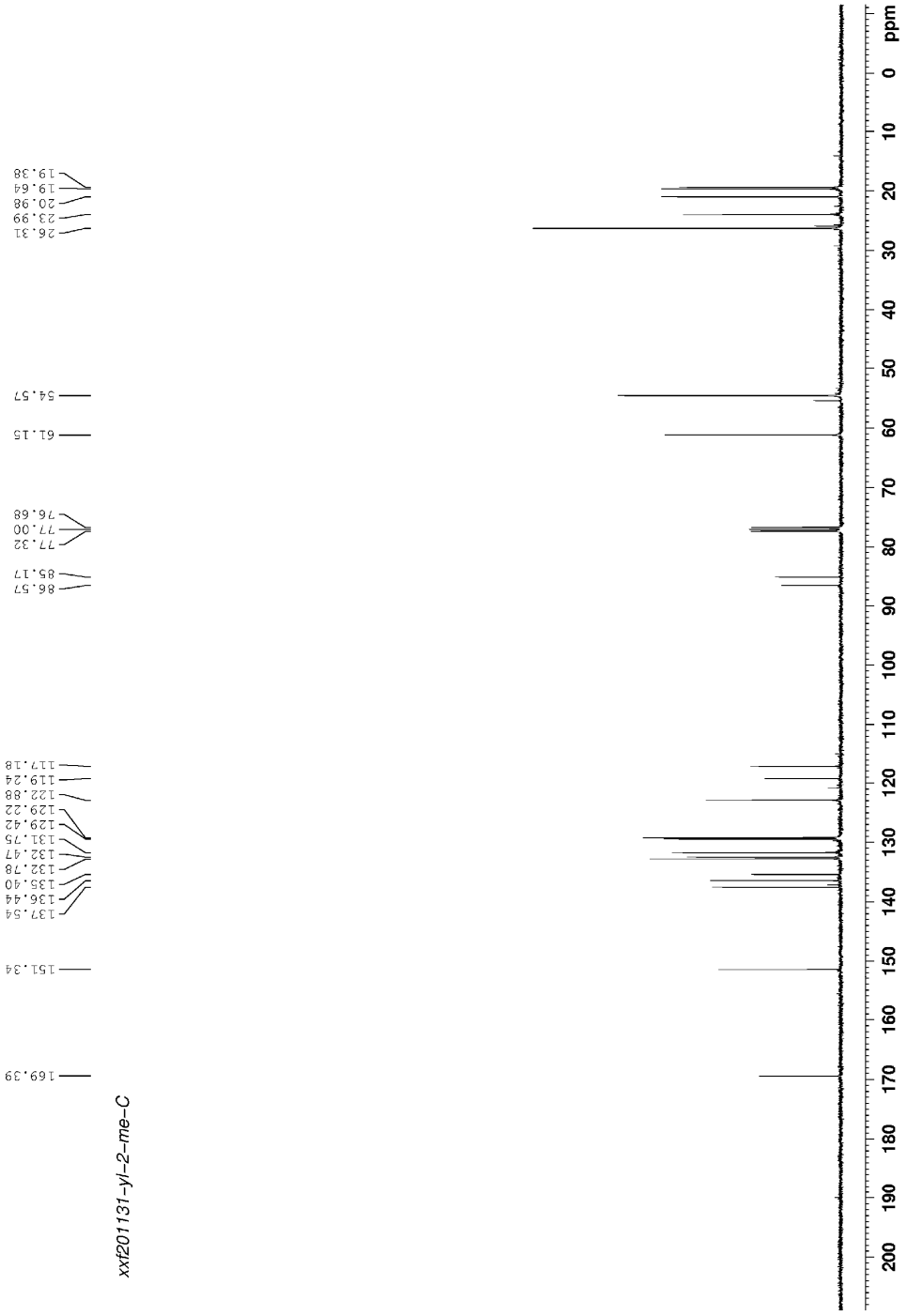
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
2.10
4.15
3.00
3.09
2.99
1.98
2.01
2.05
1.01
1.02
1.07
1.06
1.00


N
Br
OAc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26.31
54.57
61.15
76.68
77.00
77.32
85.17
86.57
117.18
119.24
122.88
129.22
129.42
131.75
132.47
132.78
135.40
136.44
137.54
151.34
169.39
xxf201131-yl-2-me-C
ppm
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10
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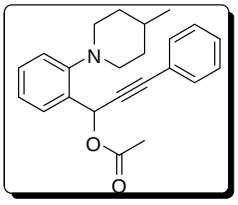
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200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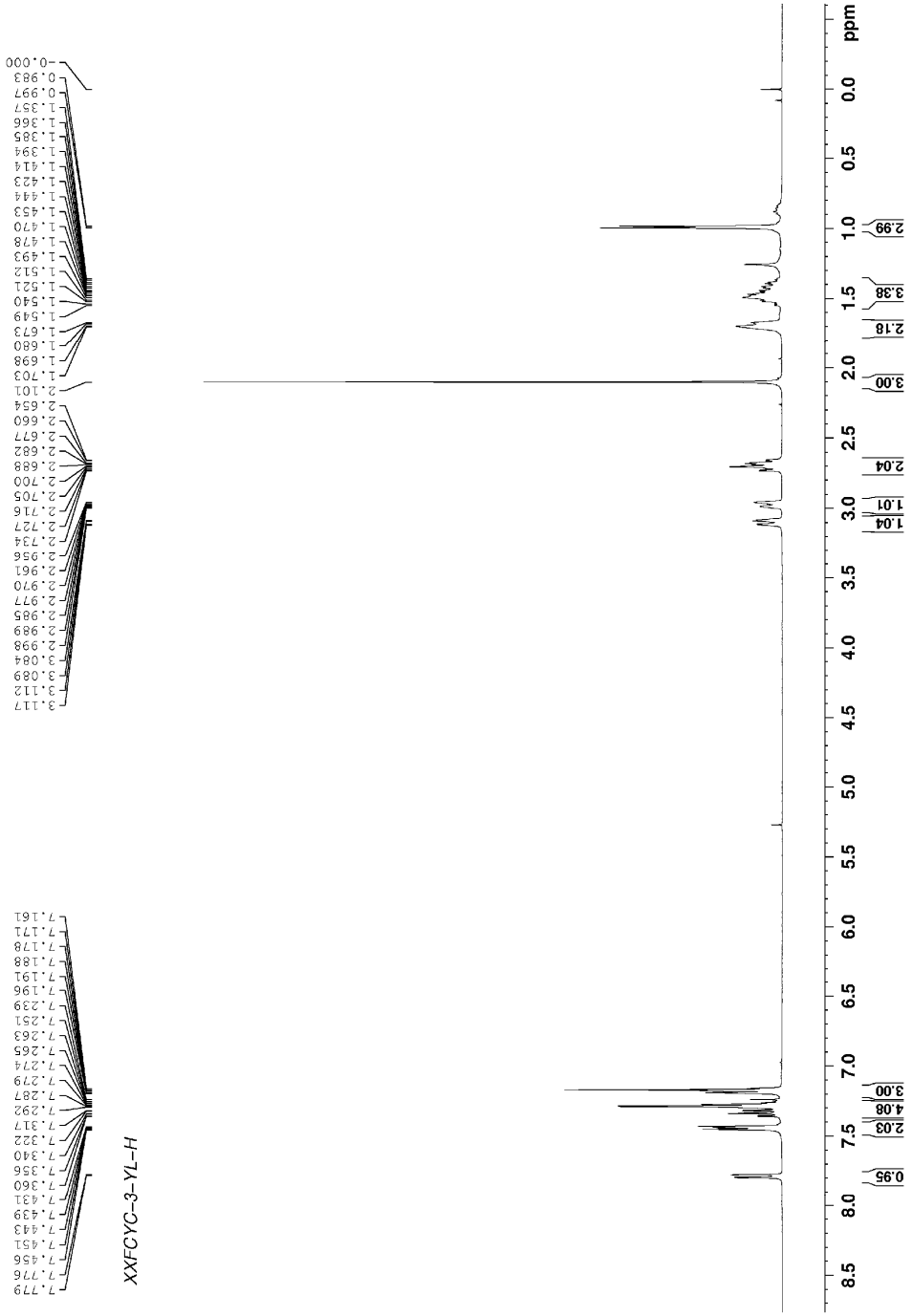
O


XXFCYC-3-YL-H
ppm
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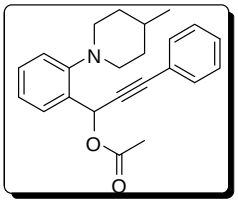
3.00
2.04
1.04
1.01
3.00
4.08
2.03
0.95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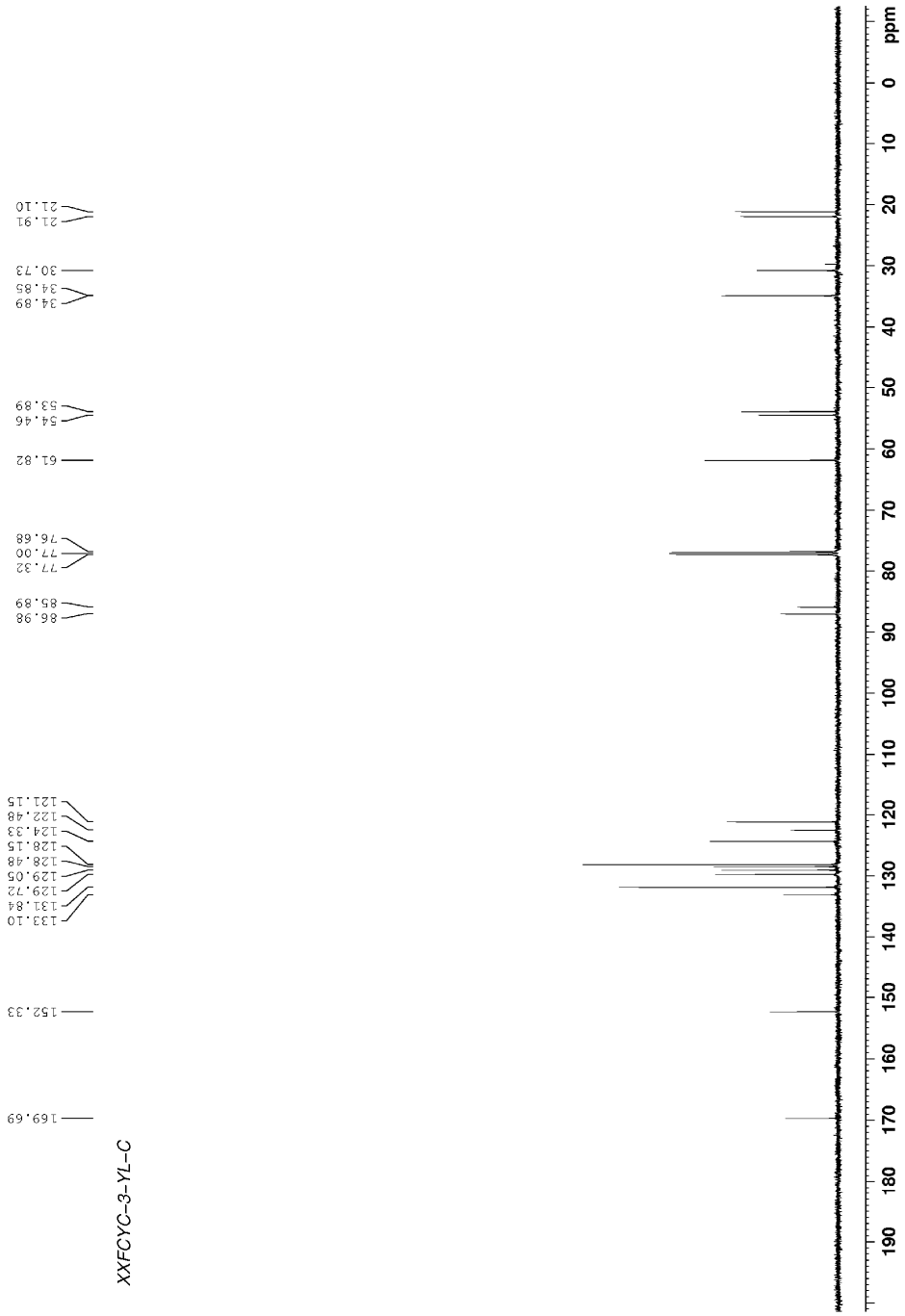
O
O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34.89
53.89
54.46
61.82
76.68
77.00
77.32
85.89
86.98
121.15
122.48
124.33
128.15
128.48
129.05
129.72
131.84
133.10
152.33
169.69
XXFCYC-3-YL-C
ppm
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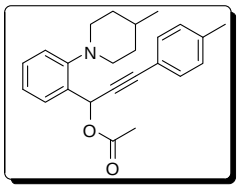
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190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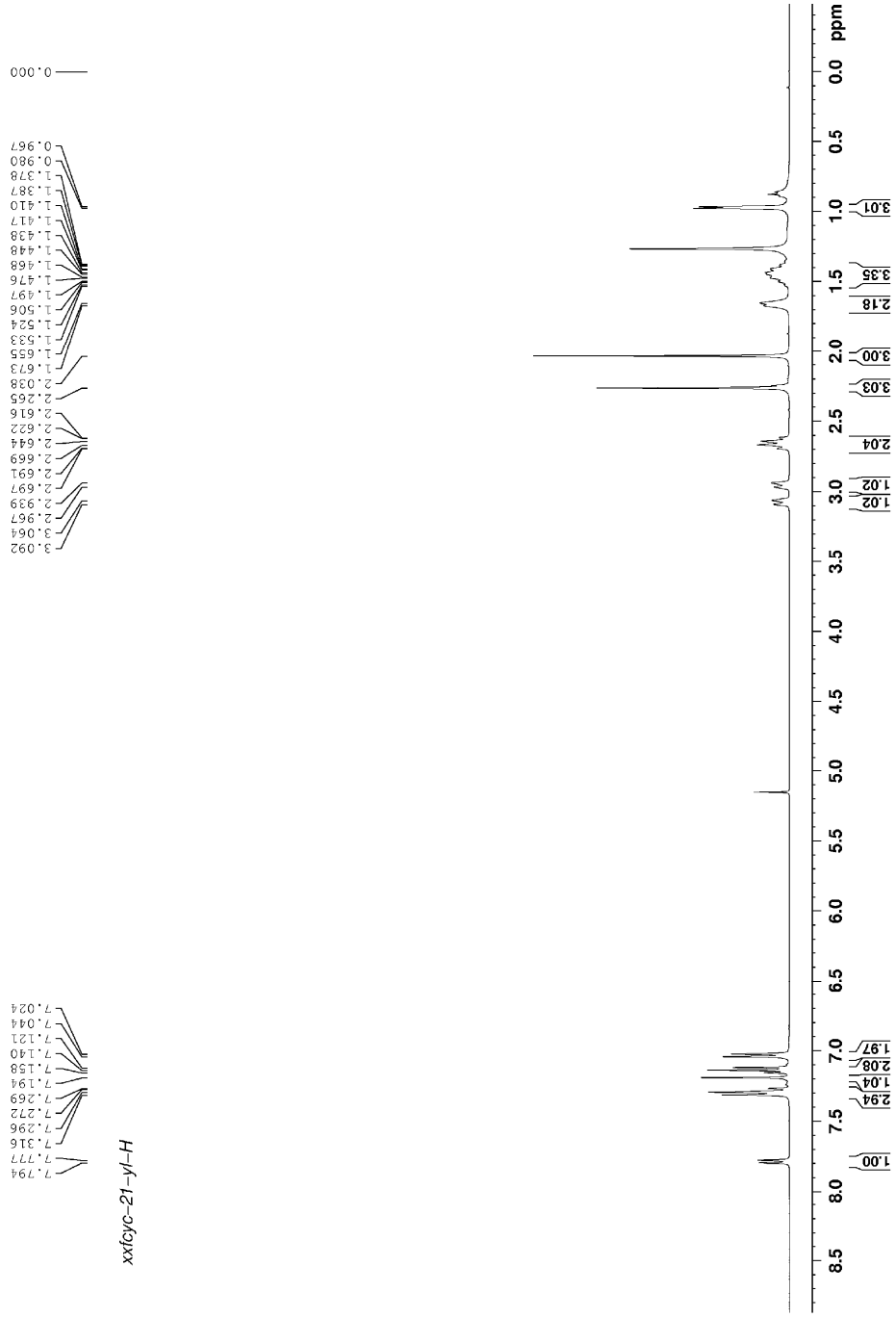
O
O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1.438
1.448
1.468
1.476
1.497
1.506
1.524
1.533
1.555
1.673
2.038
2.265
2.616
2.622
2.644
2.669
2.691
2.697
2.939
2.967
3.064
3.092
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7.121
7.140
7.158
7.194
7.269
7.272
7.296
7.316
7.777
7.794
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
3.01
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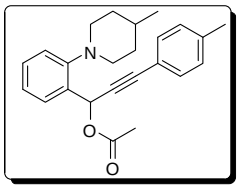
3.00
3.03
2.04
1.02
1.02
1.97
2.08
1.04
2.94
1.00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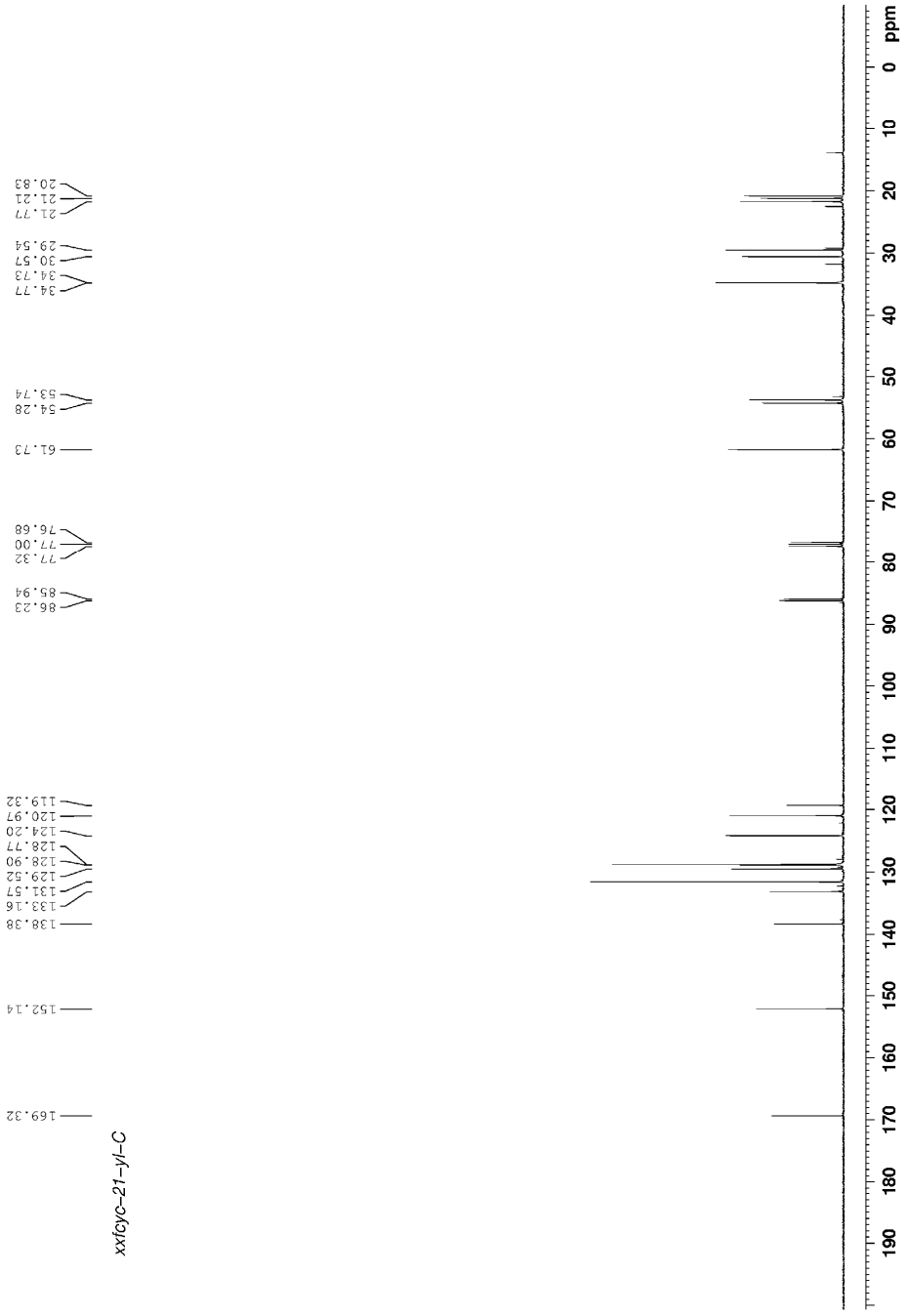
O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61.73
76.68
77.00
77.32
85.94
86.23
119.32
120.97
124.20
128.77
128.90
129.52
131.57
133.16
138.38
152.14
169.32
xxfcyc-21-yl-C
ppm
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40
50
60
70
80
90
100
110
120
130
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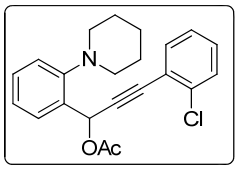
160
170
180
190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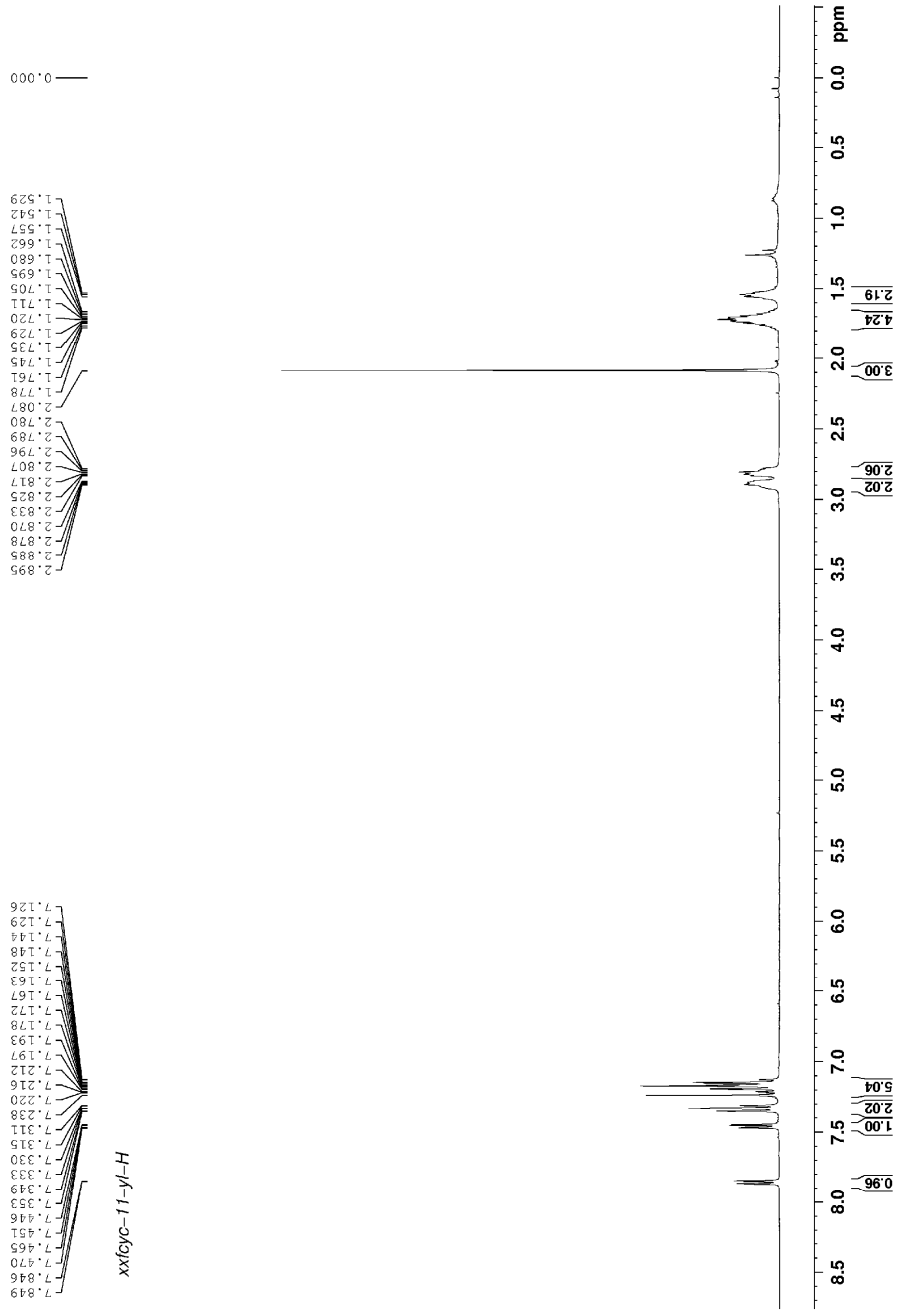
Cl
OAc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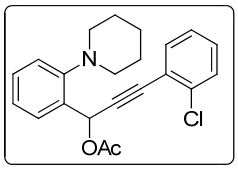
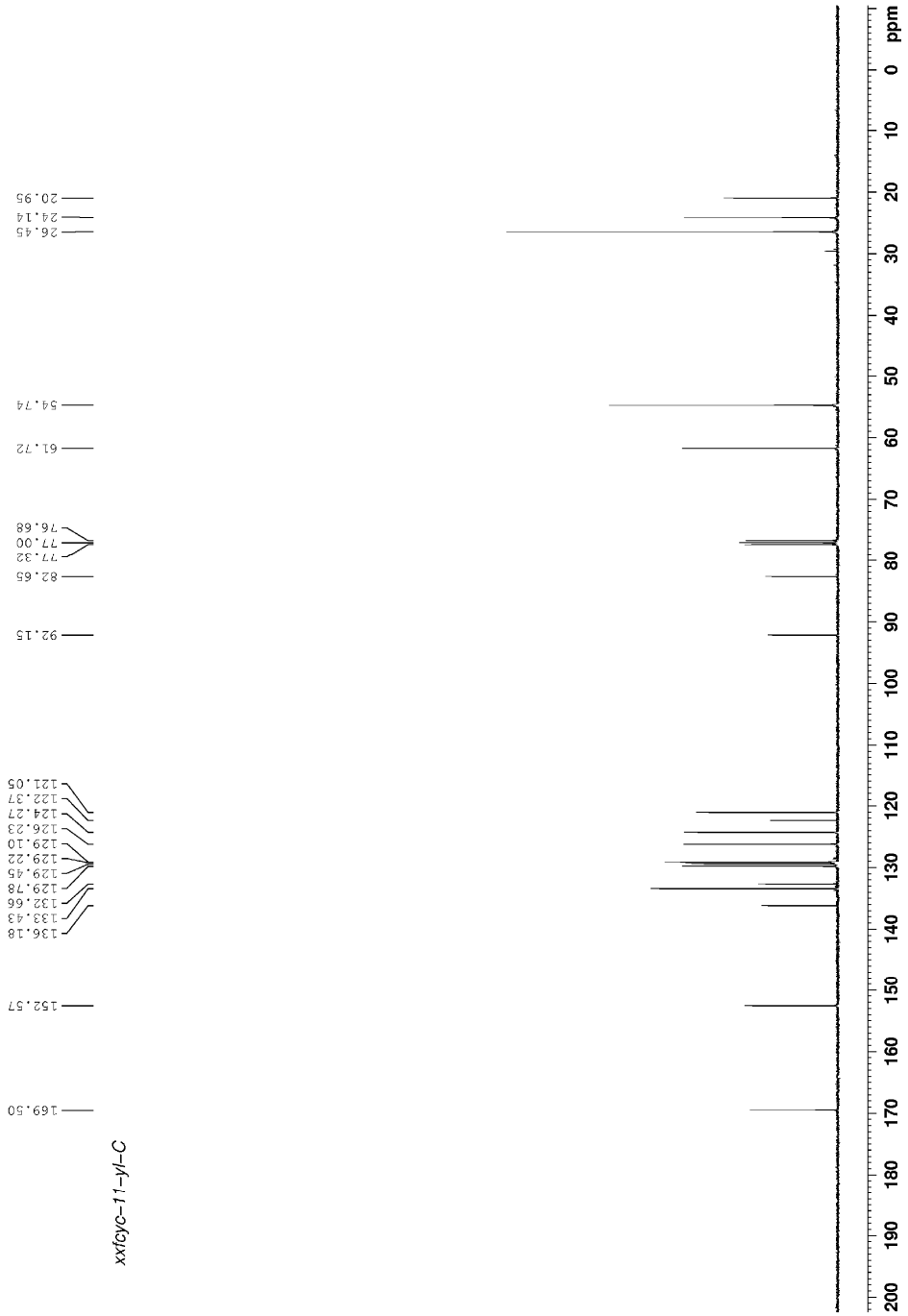
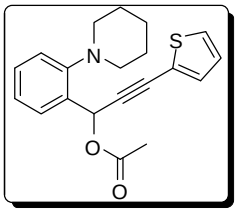
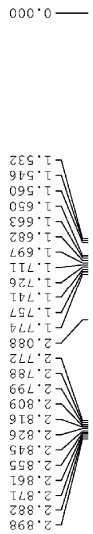
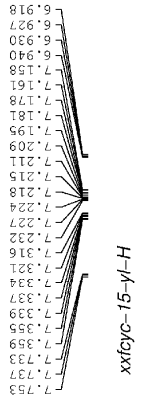
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
2.19
4.24
3.00
2.06
2.02
5.04
2.02
1.00
0.96



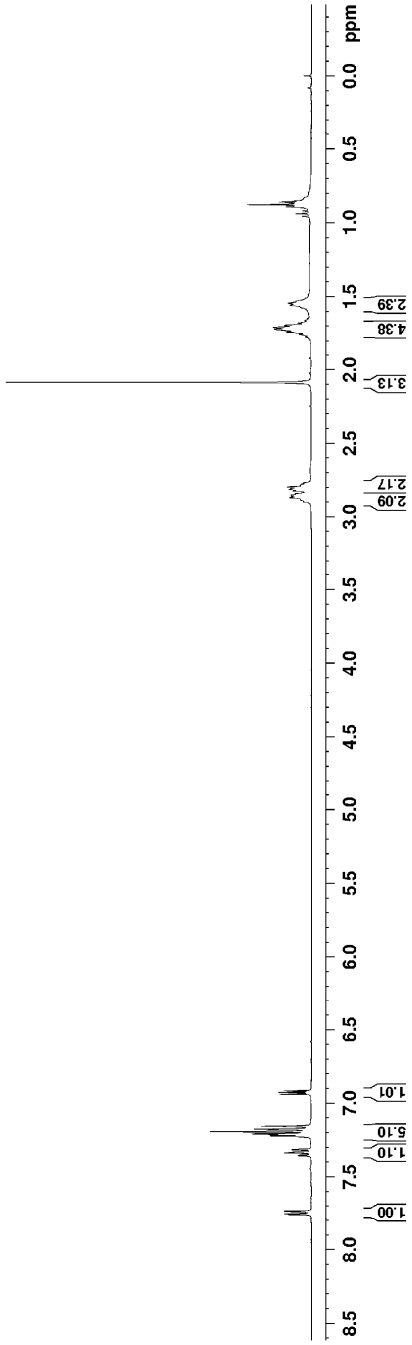


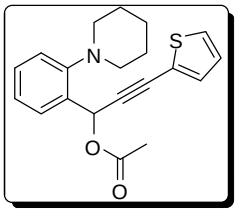


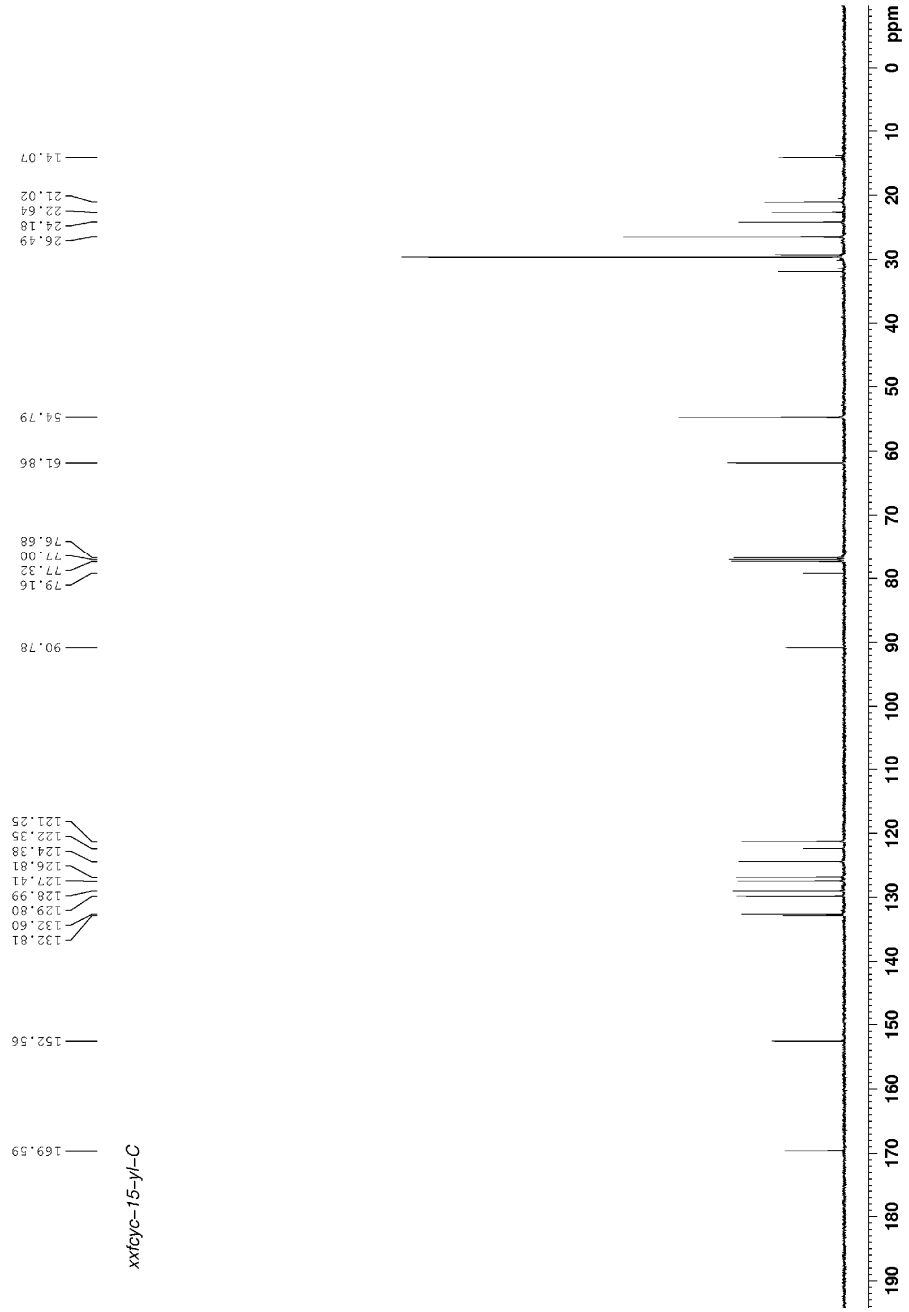


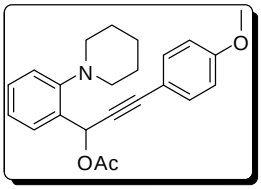


xxfcyc-15-yl-H





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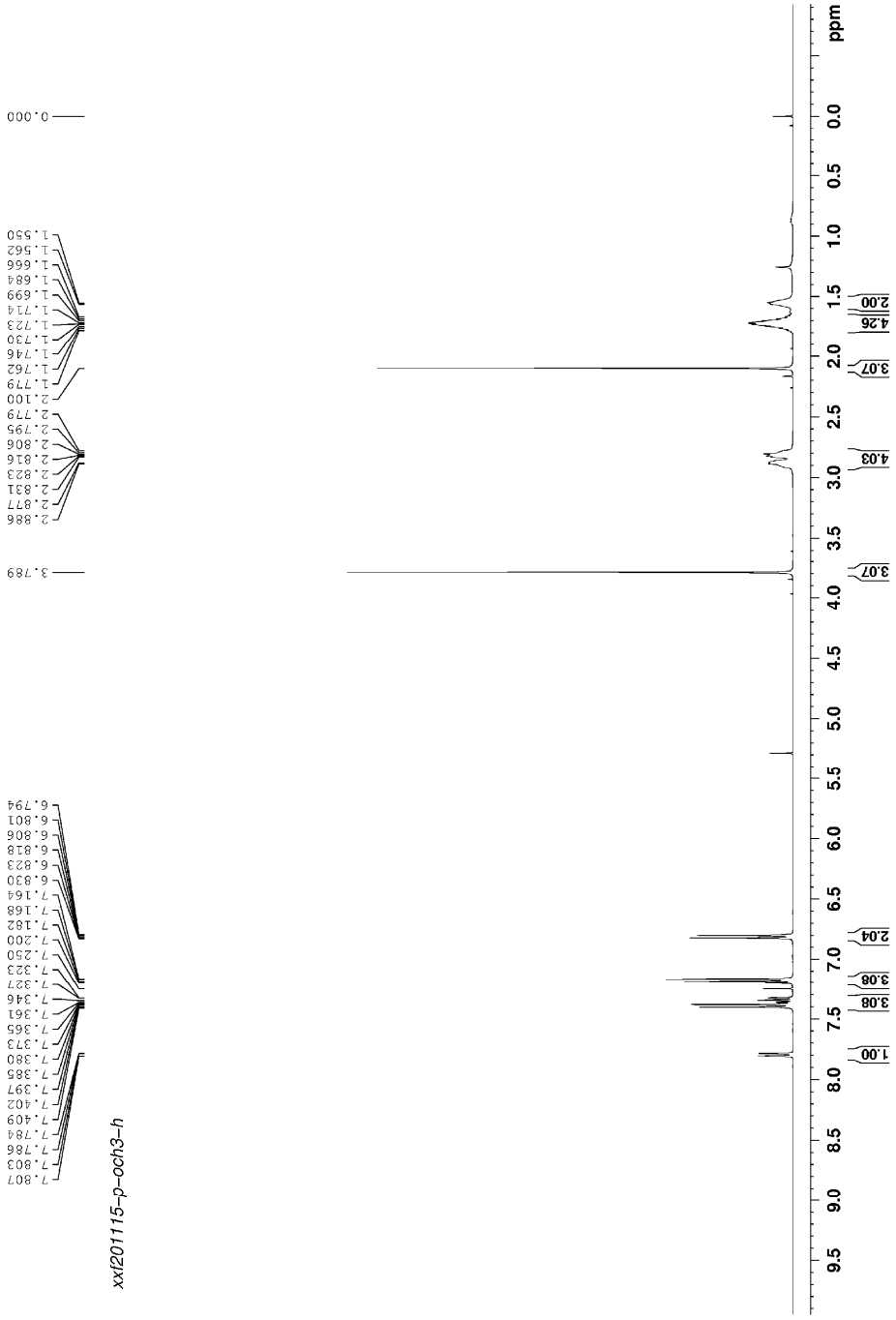
OAc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1.746
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1.779
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2.779
2.795
2.806
2.816
2.823
2.831
2.877
2.886
3.789
6.794
6.801
6.806
6.818
6.823
6.830
7.164
7.168
7.182
7.200
7.250
7.323
7.327
7.346
7.361
7.365
7.373
7.380
7.385
7.397
7.402
7.409
7.784
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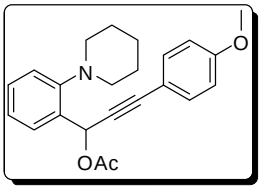
3.07
2.04
3.08
3.08
1.00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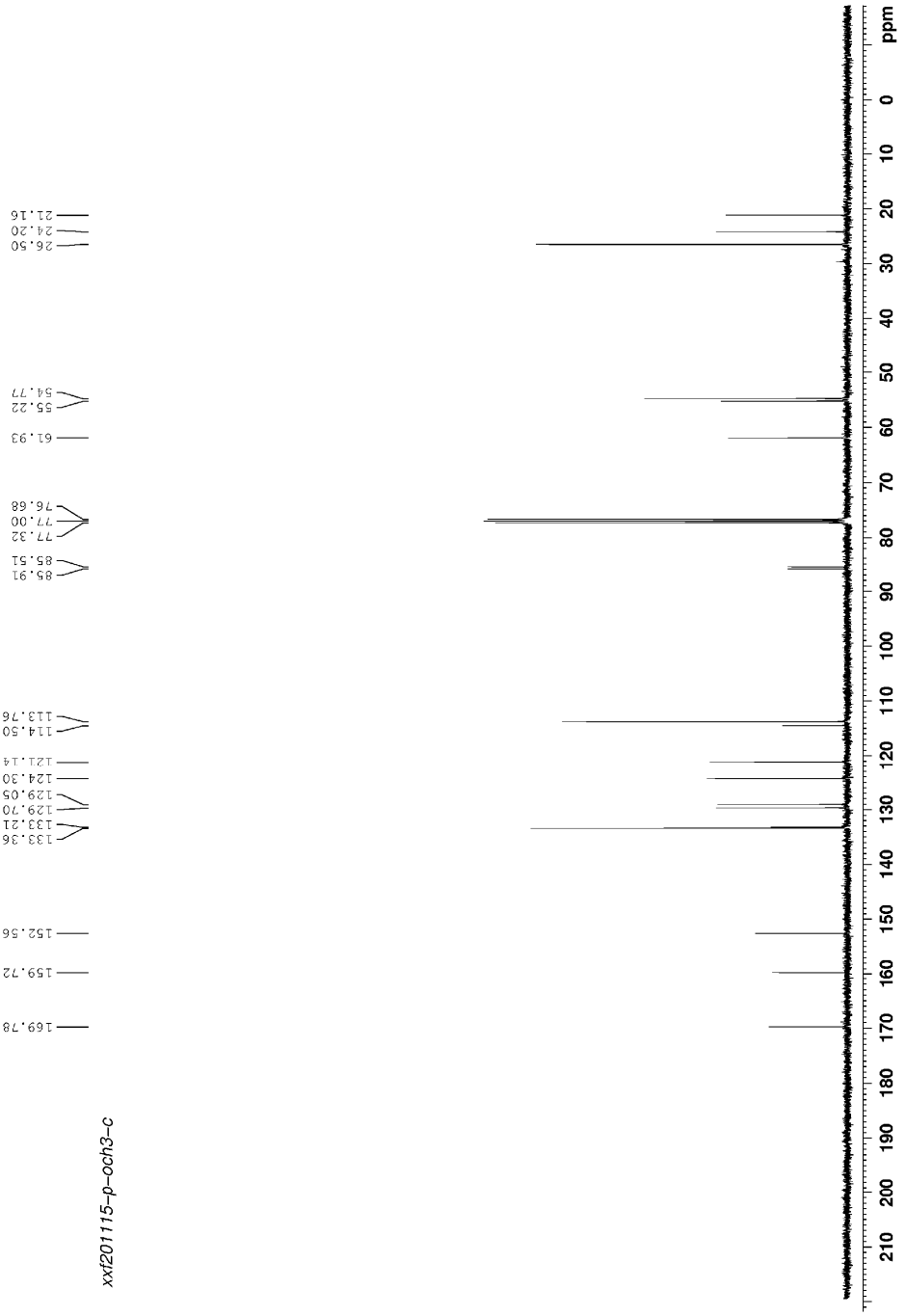
O
OAc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77.00
77.32
85.51
85.91
113.76
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121.14
124.30
129.05
129.70
133.21
133.36
152.56
159.72
169.78
xxf201115-p-och3-c
ppm
0
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30
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60
70
80
90
100
110
120
130
140
150
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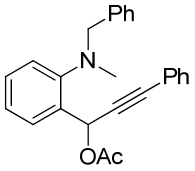
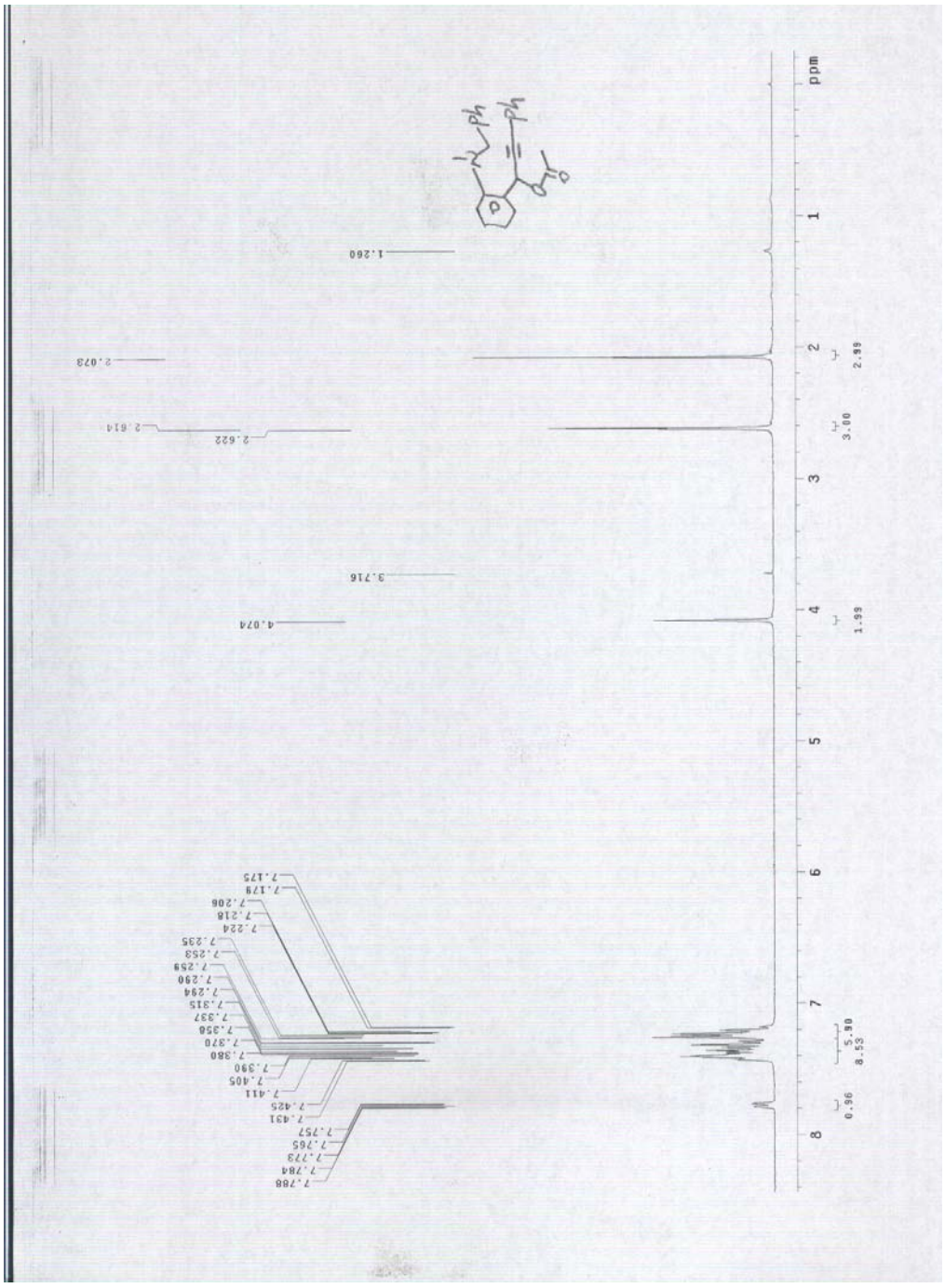
180
190
200
210


Ph
N
Ph
OAc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3
4
5
6
7
8
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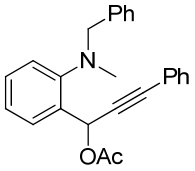
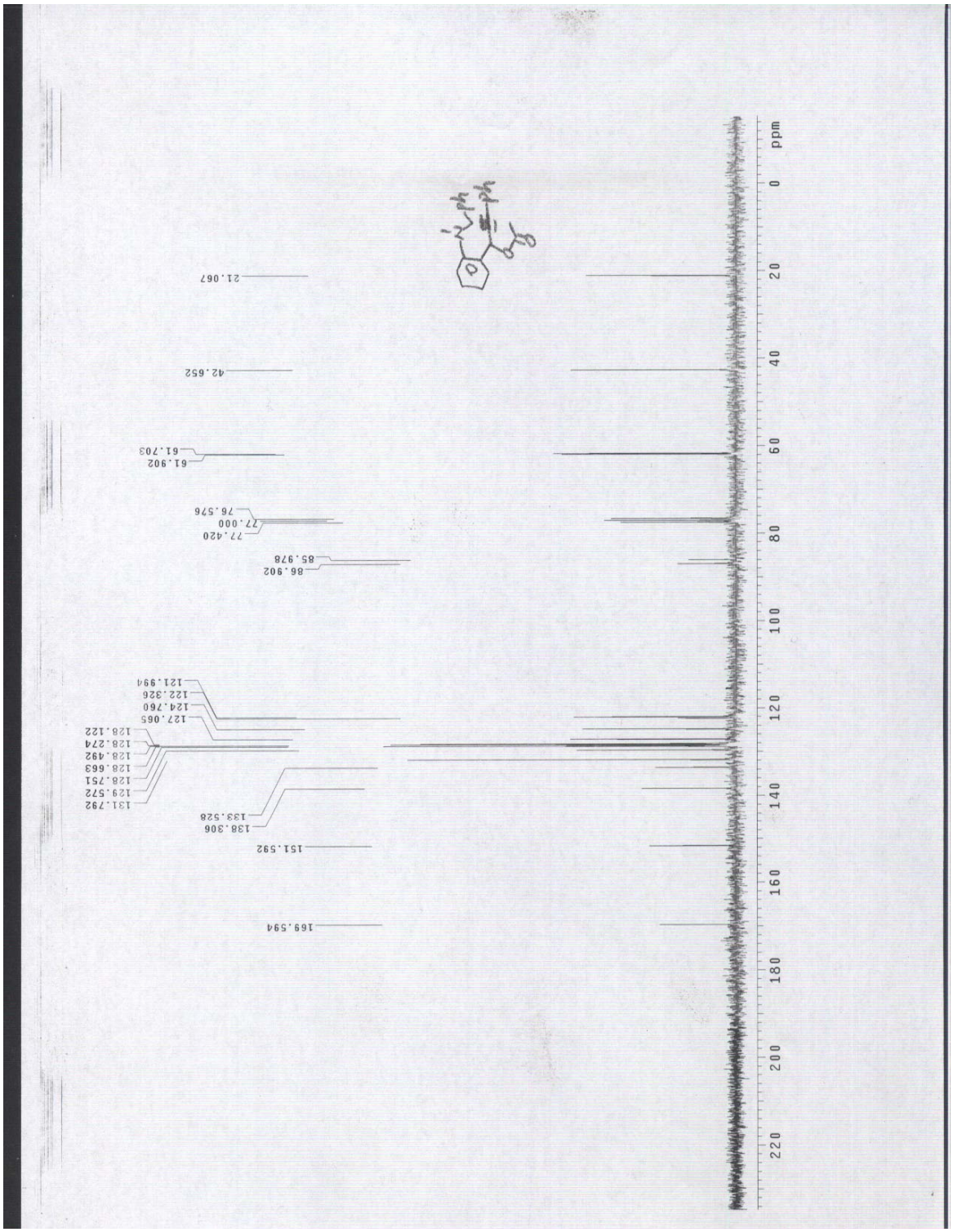
2.073
2.614
2.622
3.716
4.074
7.173
7.179
7.206
7.218
7.224
7.235
7.253
7.259
7.290
7.294
7.315
7.337
7.350
7.370
7.380
7.390
7.405
7.411
7.425
7.431
7.757
7.765
7.773
7.784
7.788
2.99
3.00
1.99
5.98
8.53
0.96


Ph
N
Ph
OAc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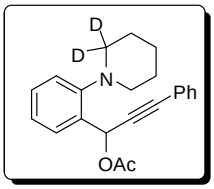
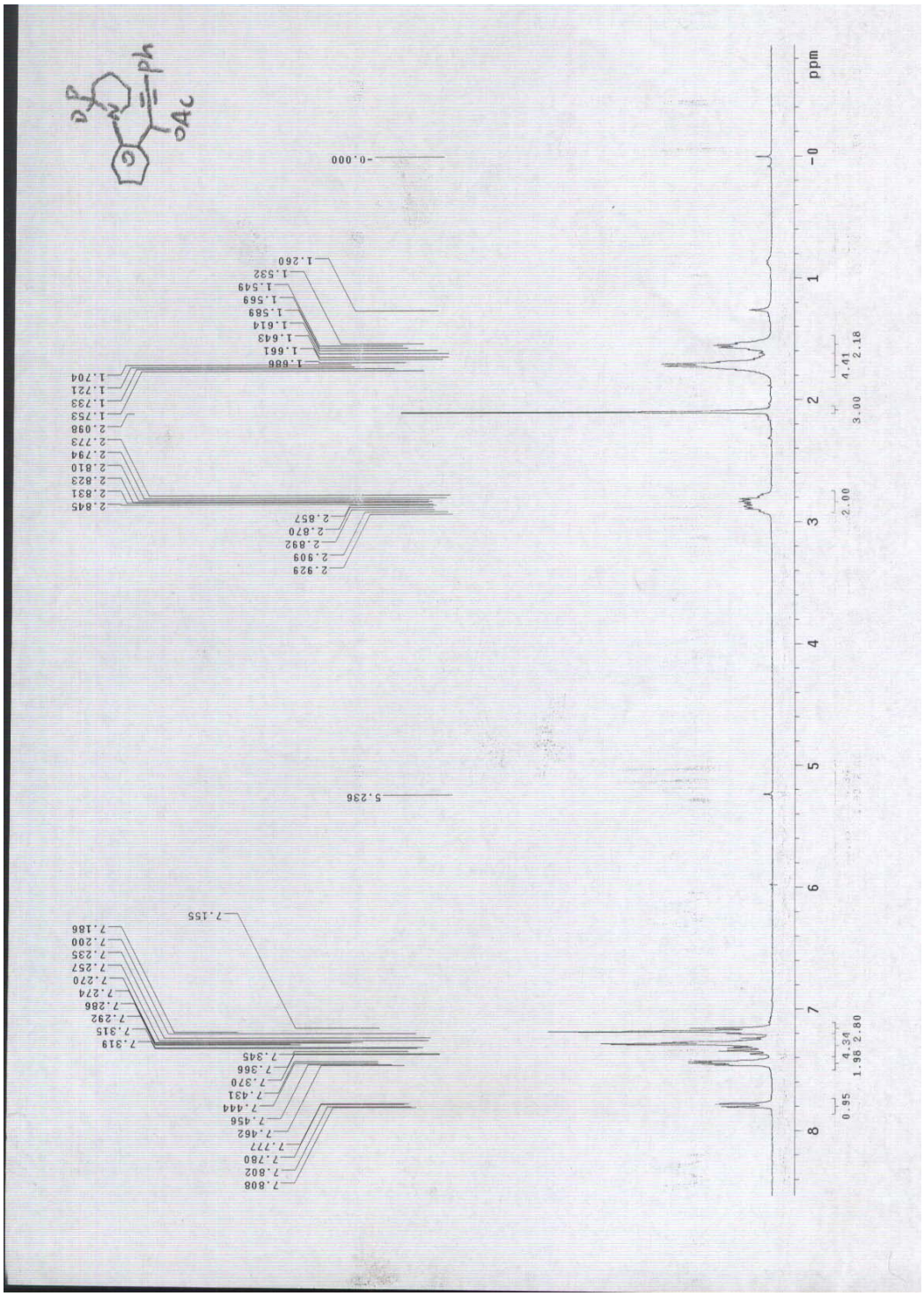
76.576
77.000
77.420
85.978
86.902
121.994
122.326
124.760
127.065
128.122
128.274
128.492
128.663
128.751
129.572
131.792
133.528
138.306
151.592
169.594
ppm
0
20
40
60
80
100
120
140
160
180
200
220


D
D
N
Ph
OAc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1.704
1.721
1.733
1.753
2.098
2.773
2.794
2.810
2.823
2.831
2.845
2.857
2.870
2.892
2.909
2.929
5.236
7.155
7.186
7.200
7.235
7.257
7.270
7.274
7.286
7.292
7.315
7.319
7.345
7.366
7.370
7.431
7.444
7.456
7.462
7.777
7.780
7.802
7.808
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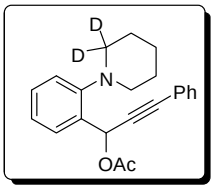
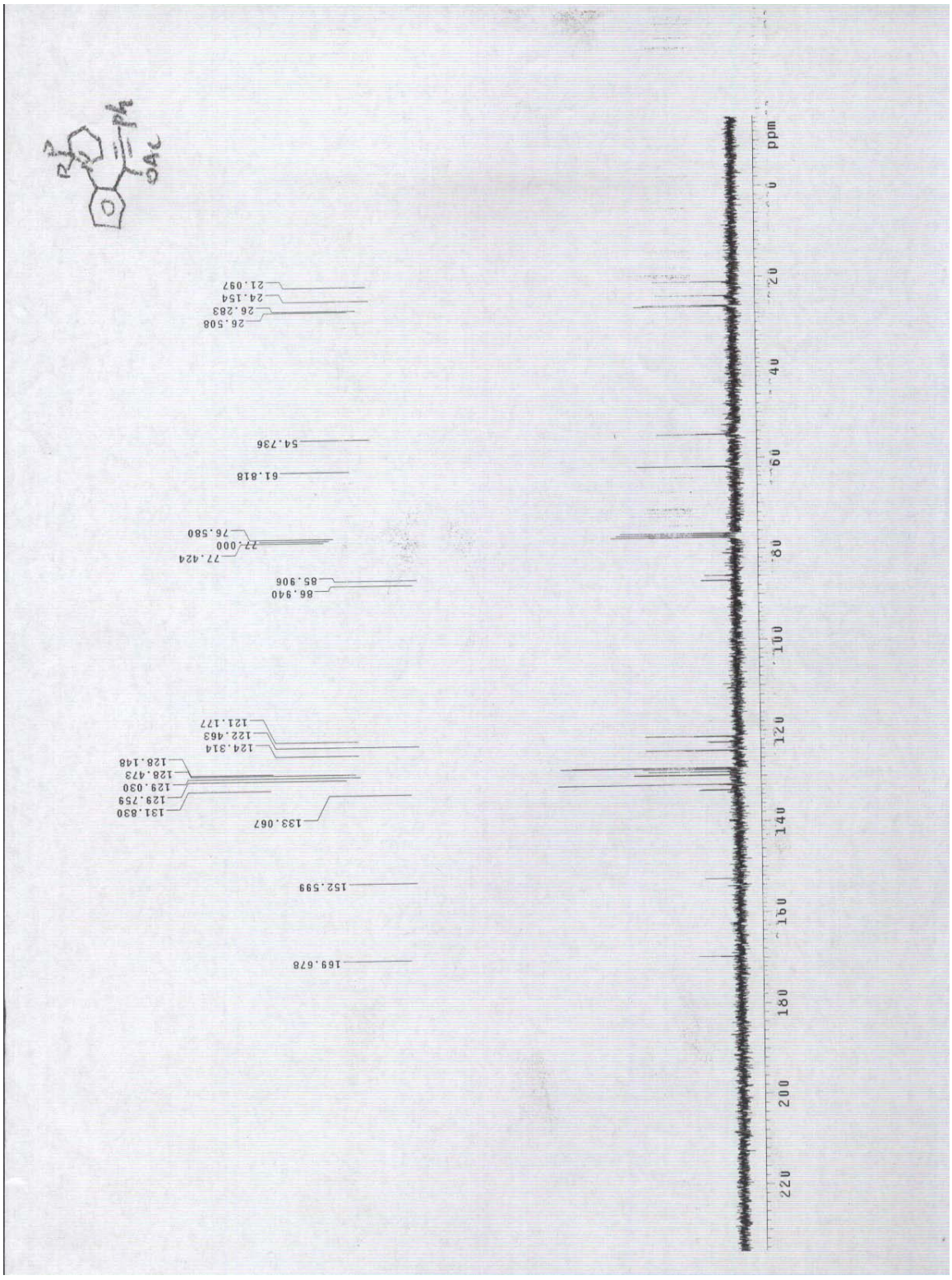
2.18
3.00
2.00
4.34
2.80
1.98
0.95


D
D
N
Ph
OAc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26.283
26.508
54.736
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76.580
77.000
77.424
85.906
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121.177
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124.314
128.148
128.473
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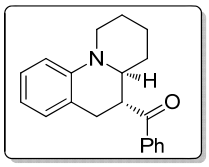
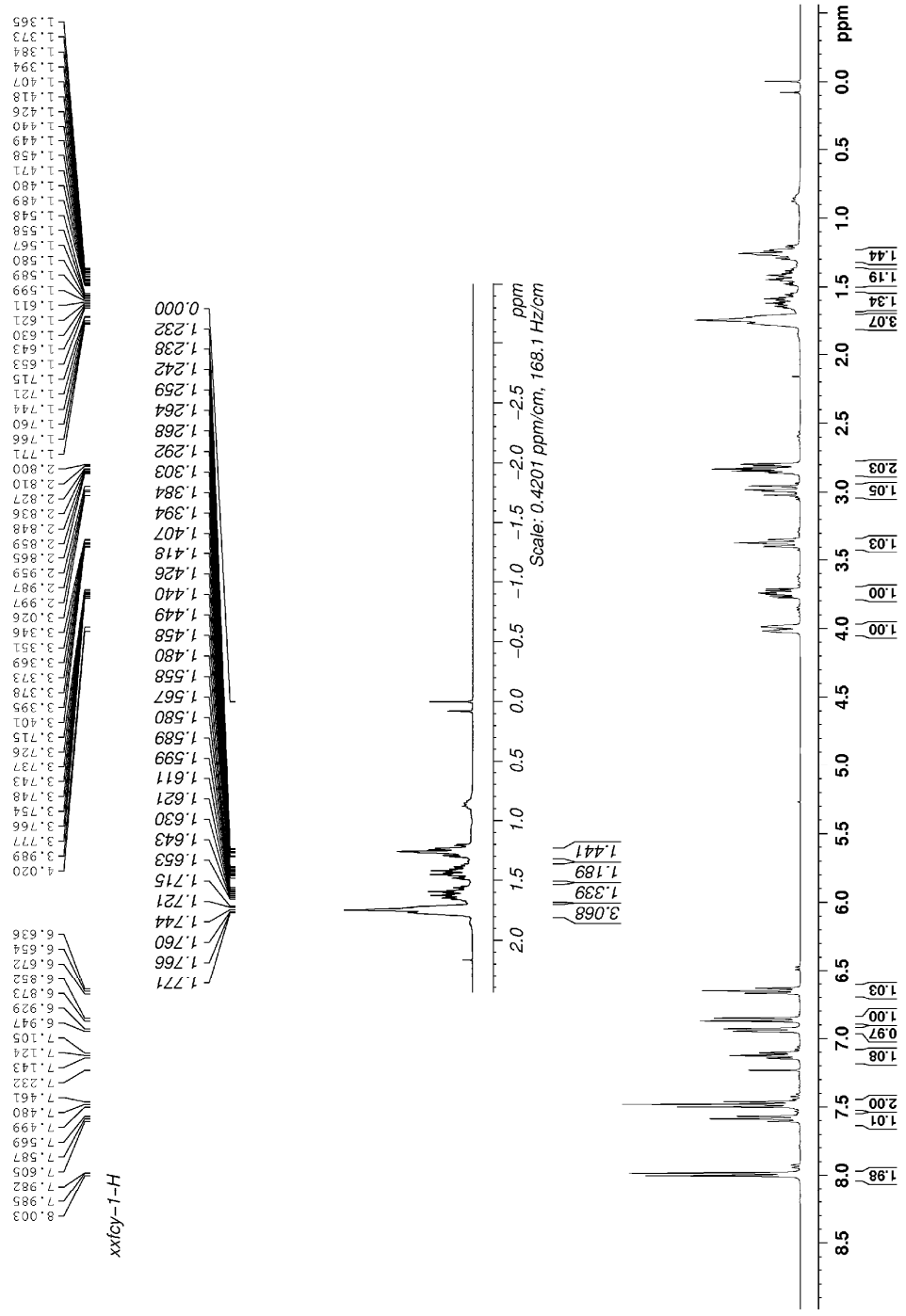
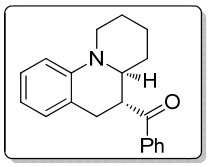
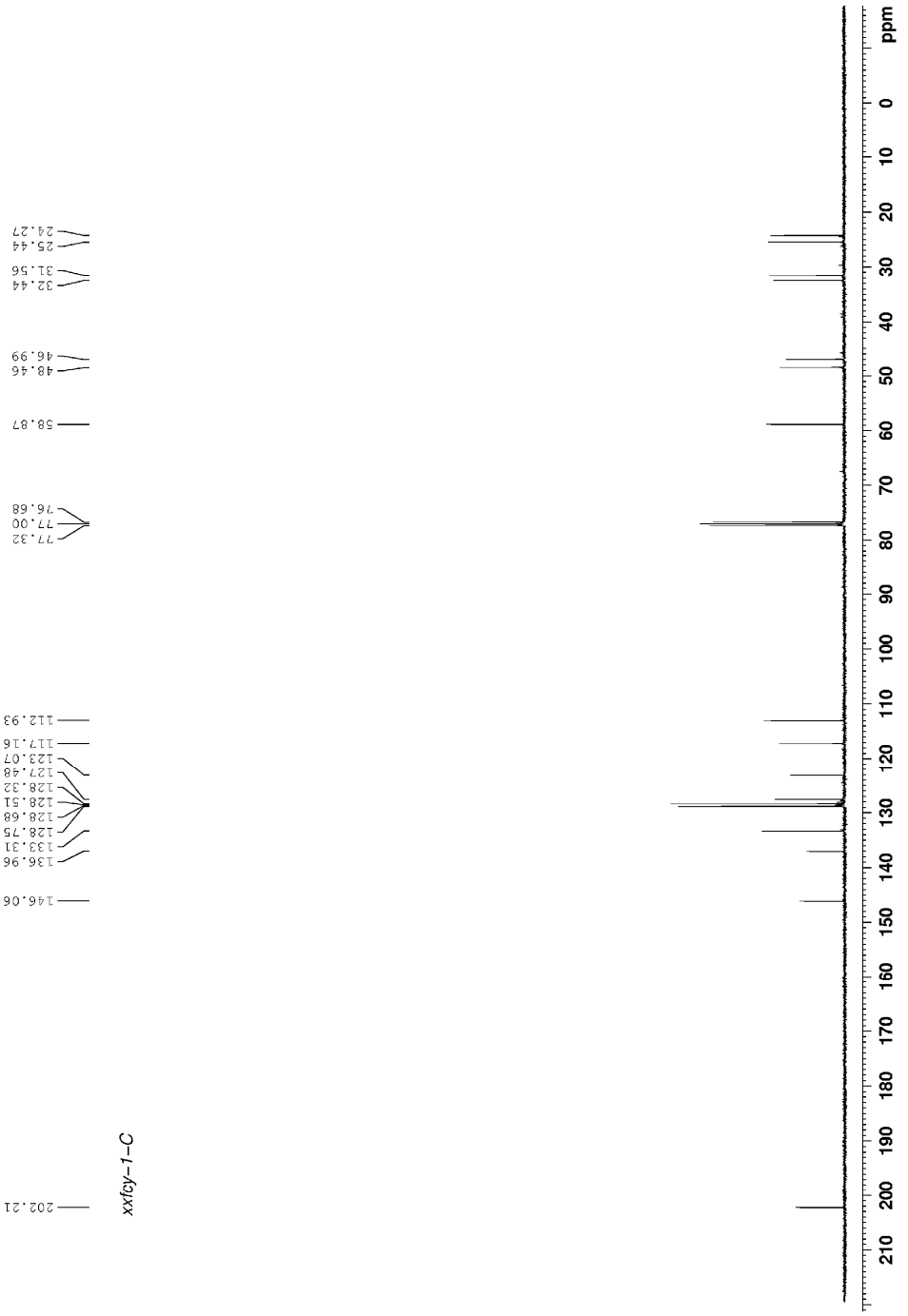
129.759
131.830
133.067
152.599
169.678
ppm


N
H
O
Ph


xxfcy-1-H
Scale: 0.4201 ppm/cm, 168.1 Hz/cm
ppm


N
H
O
Ph


xxf/cy-1-C
202.21
146.06
136.96
133.31
128.75
128.68
128.51
128.32
127.48
123.07
117.16
112.93
77.32
77.00
76.68
58.87
48.46
46.99
32.44
31.56
25.44
24.27
ppm
0
10
20
30
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50
60
70
80
90
100
110
120
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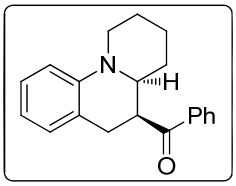
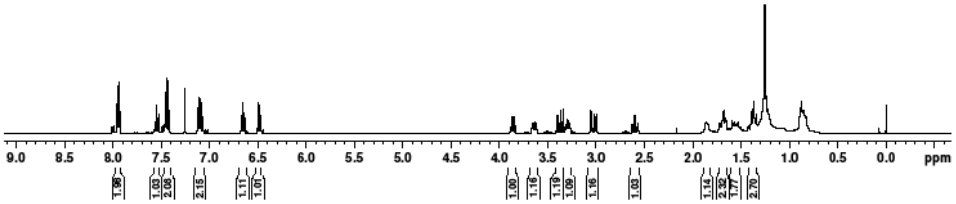
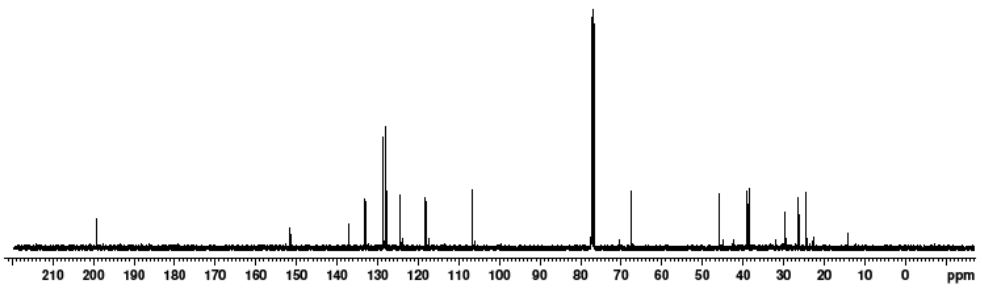
140
150
160
170
180
190
200
210

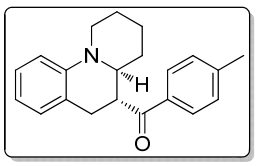


xxf2011322-1-H



xxf2011322-1-C

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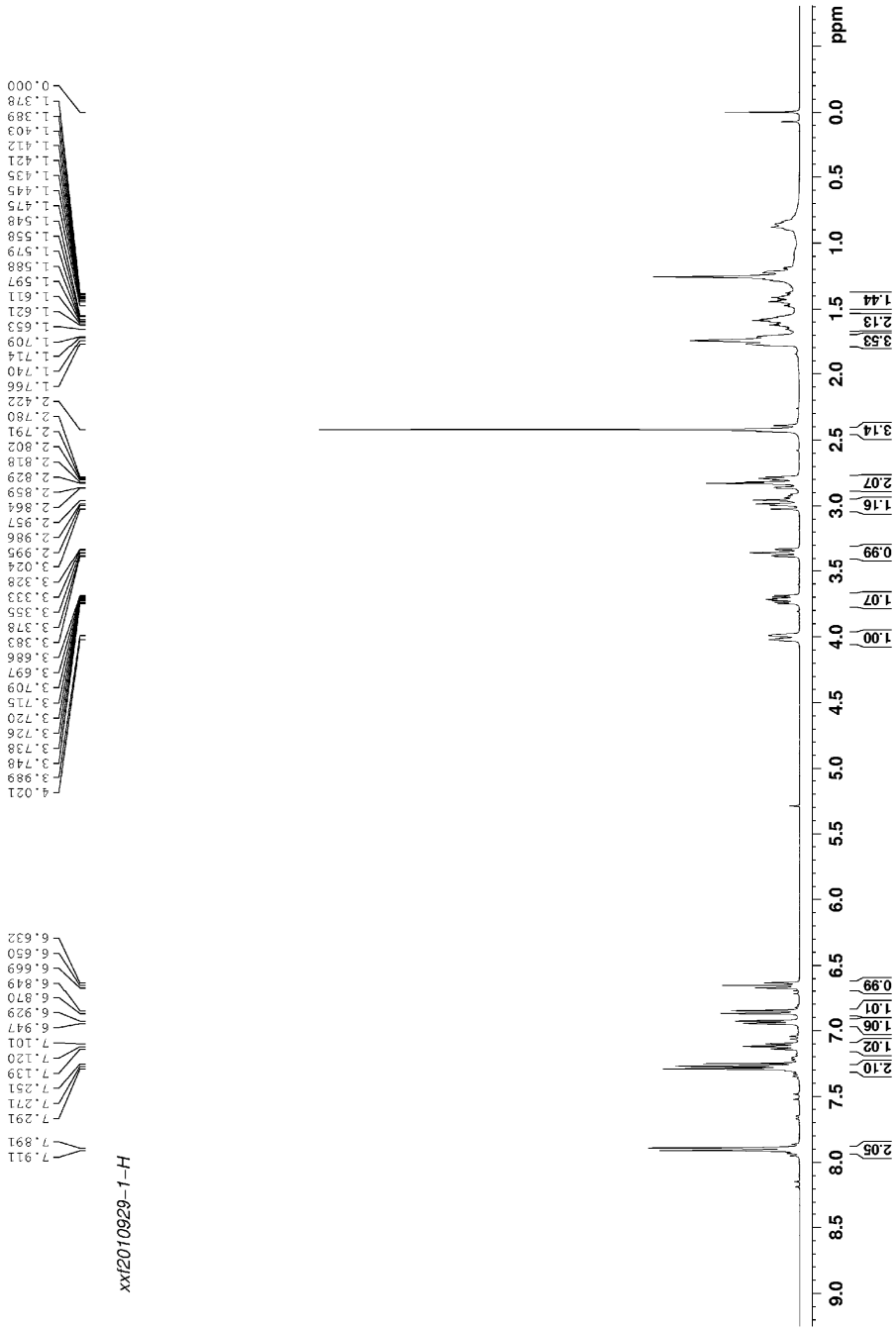
H
O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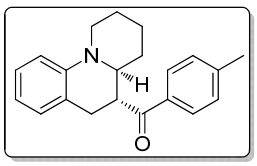
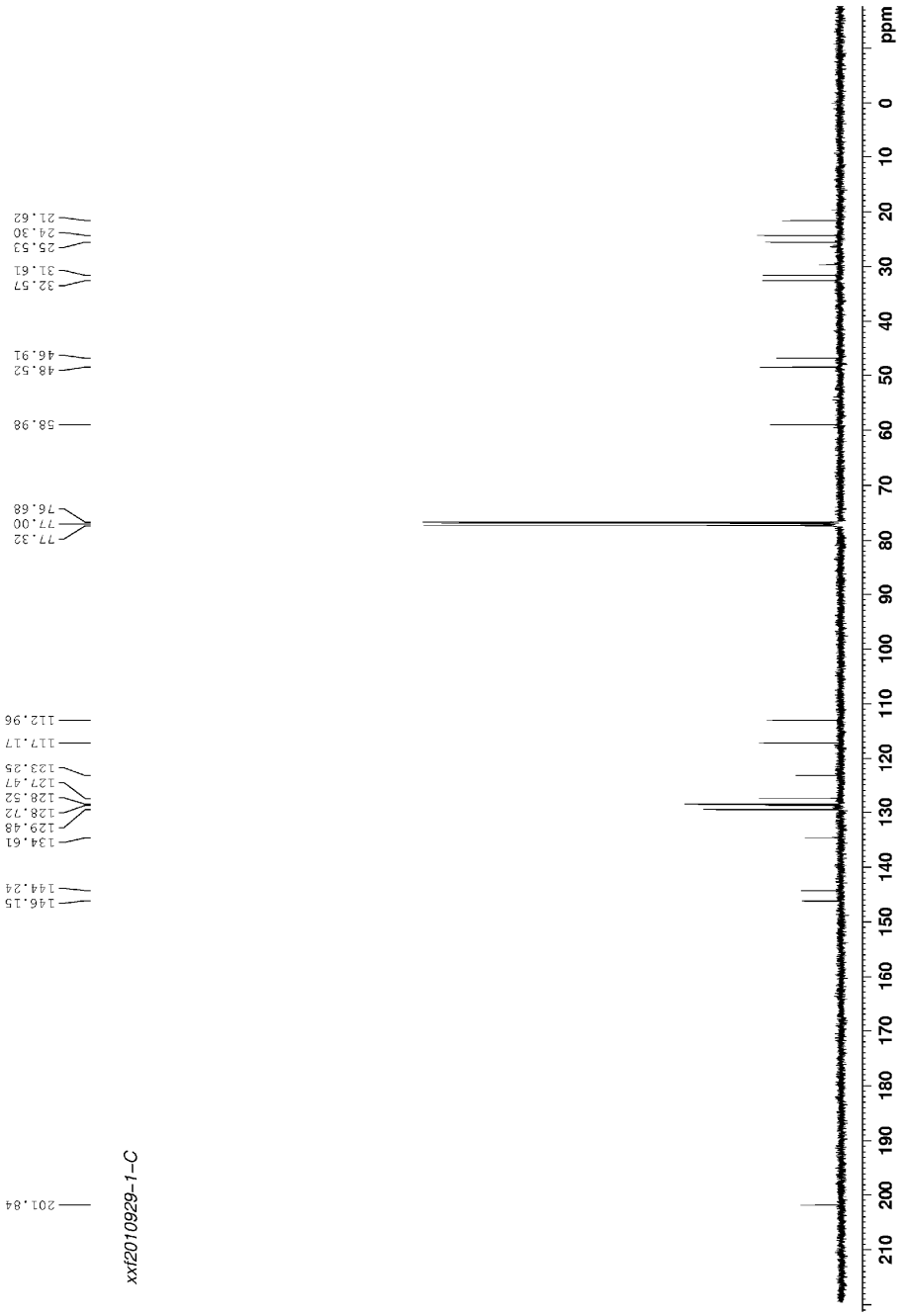
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
1.44
2.13
3.53
3.14
2.07
1.16
0.99
1.07
1.00
0.99
1.01
1.06
1.02
2.10
2.05


N
H
O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32.57
46.91
48.52
58.98
76.68
77.00
77.32
112.96
117.17
123.25
127.47
128.52
128.72
129.48
134.61
144.24
146.15
201.84
xxf20110929-1-C
ppm
0
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20
30
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50
60
70
80
90
100
110
120
130
140
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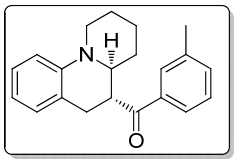
170
180
190
200
210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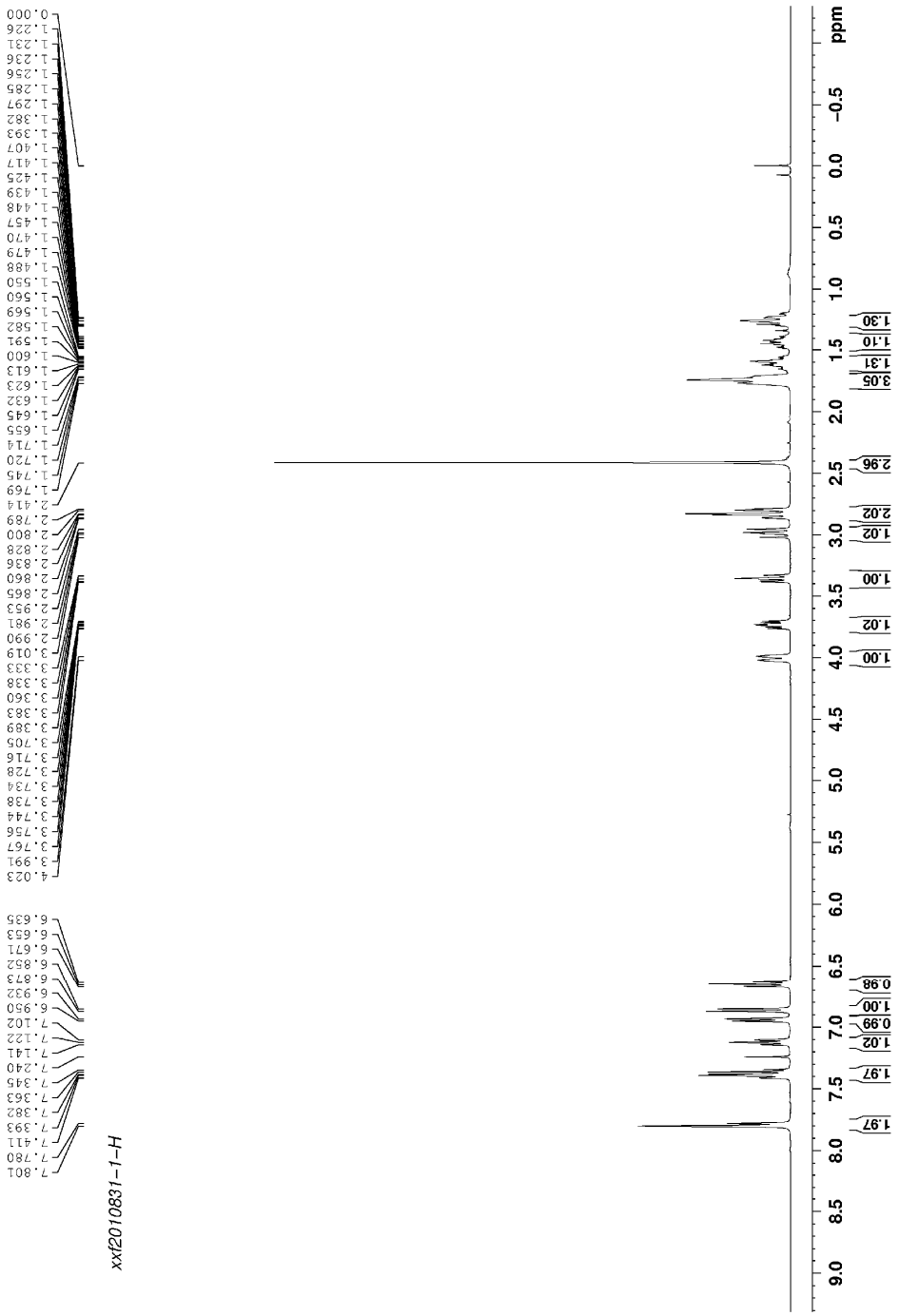
H
O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1.31
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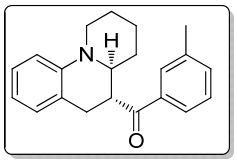
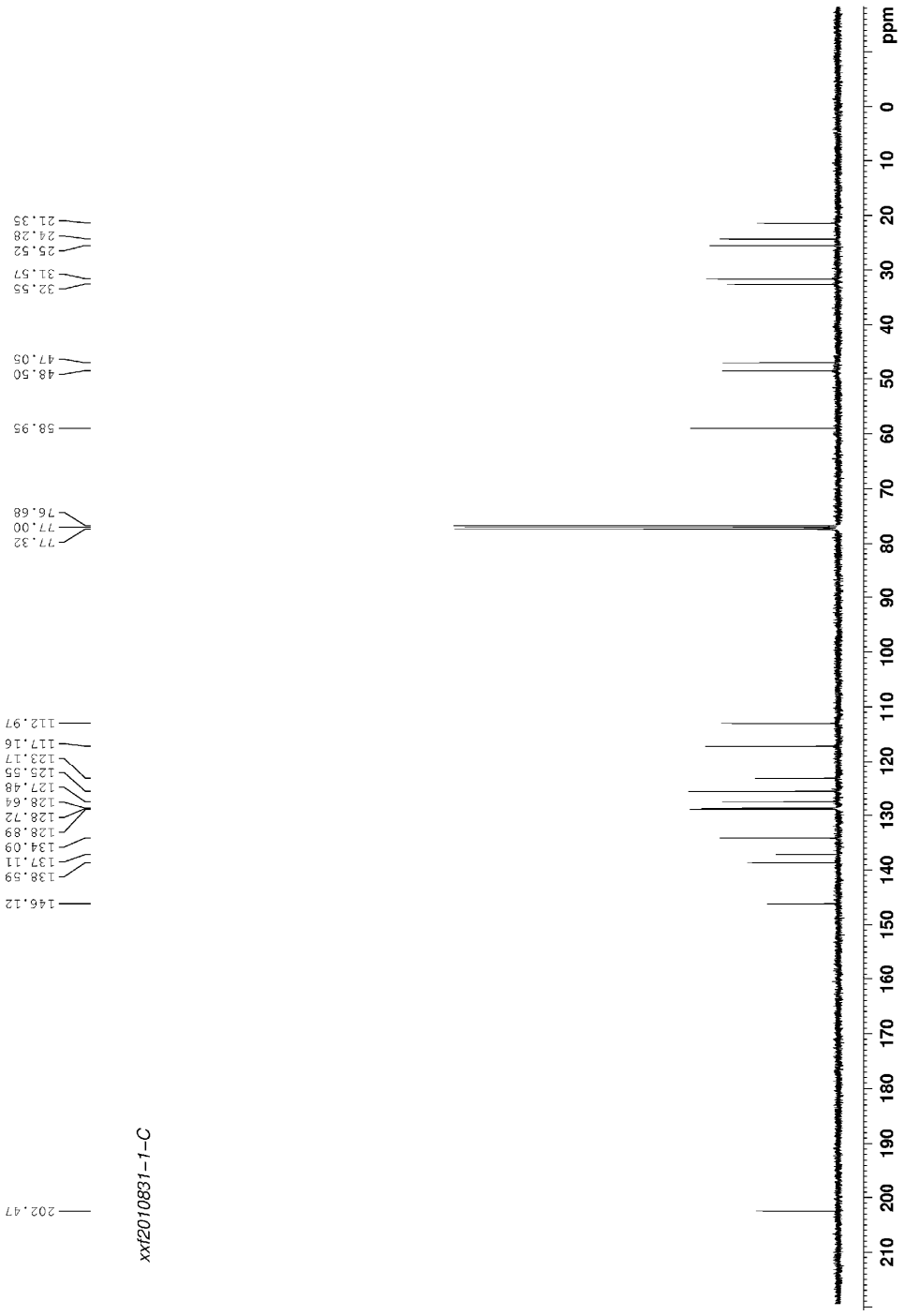
2.96
1.02
2.02
1.00
1.02
1.00
0.98
1.00
0.99
1.02
1.97
1.97


N
H
O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32.55
47.05
48.50
58.95
76.68
77.00
77.32
112.97
117.16
123.17
125.55
127.48
128.64
128.72
128.89
134.09
137.11
138.59
146.12
202.47
xxf20100831-1-C
ppm
0
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70
80
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140
150
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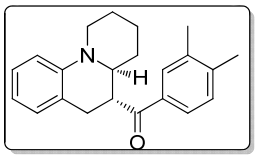
170
180
190
200
210



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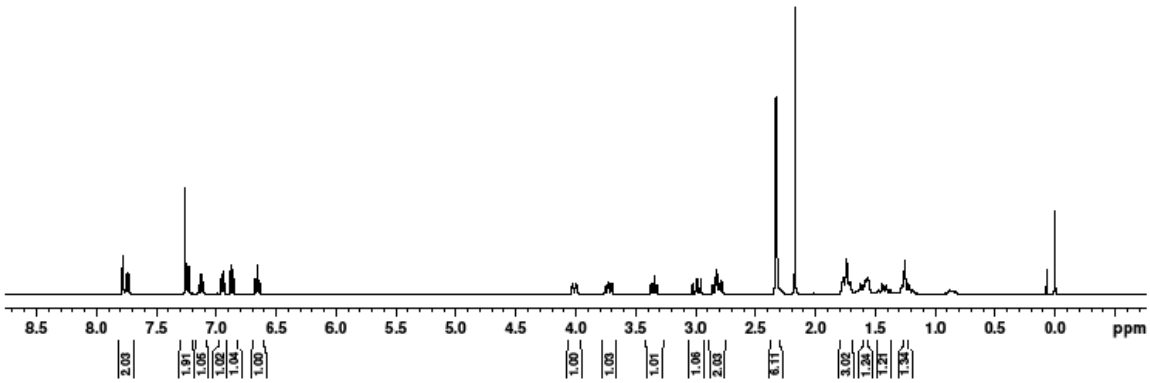
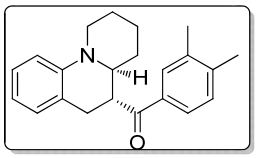
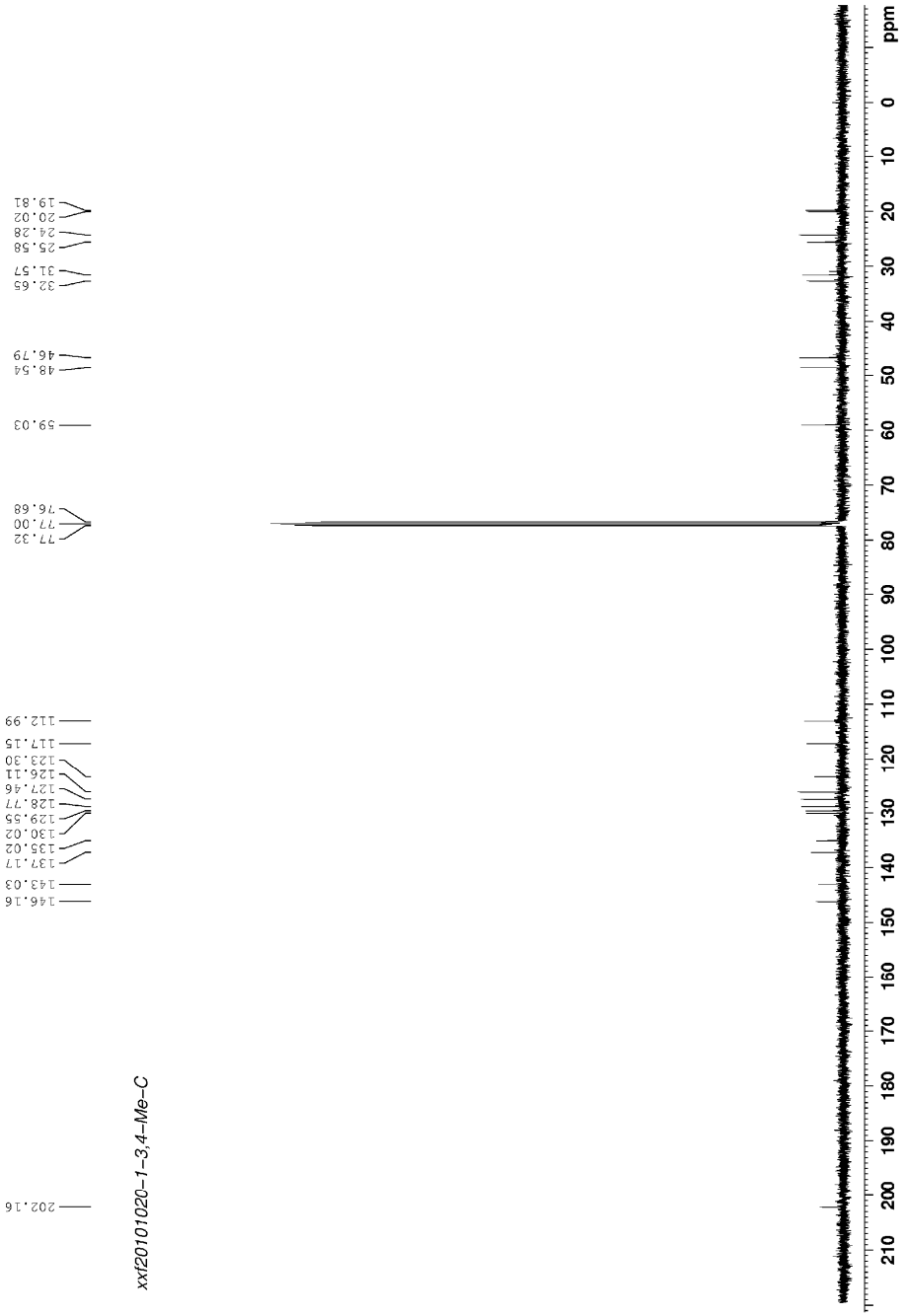



N
H
O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77.32
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128.77
129.55
130.02
135.02
137.17
143.03
146.16
202.16
xxf20101020-1-3,4-Me-C
ppm
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100
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140
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180
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200
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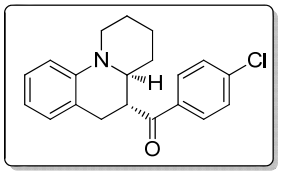
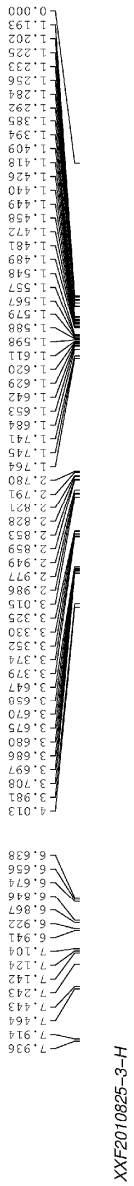
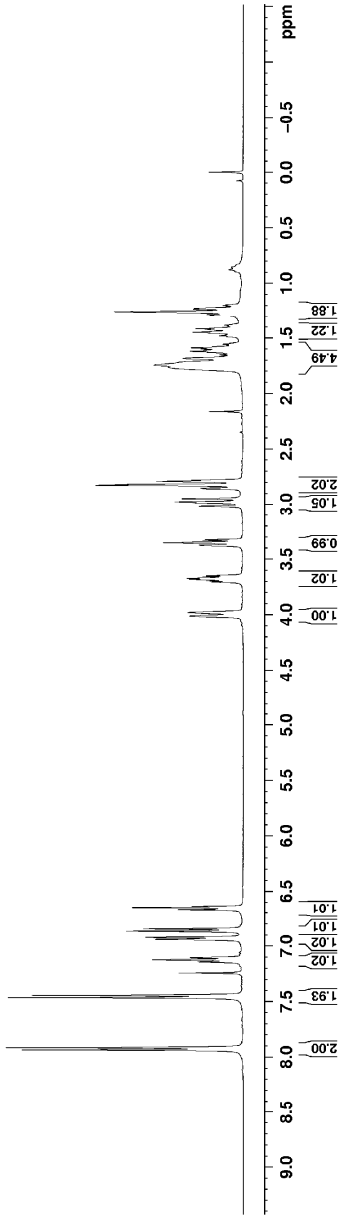
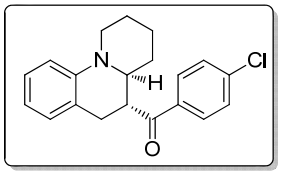
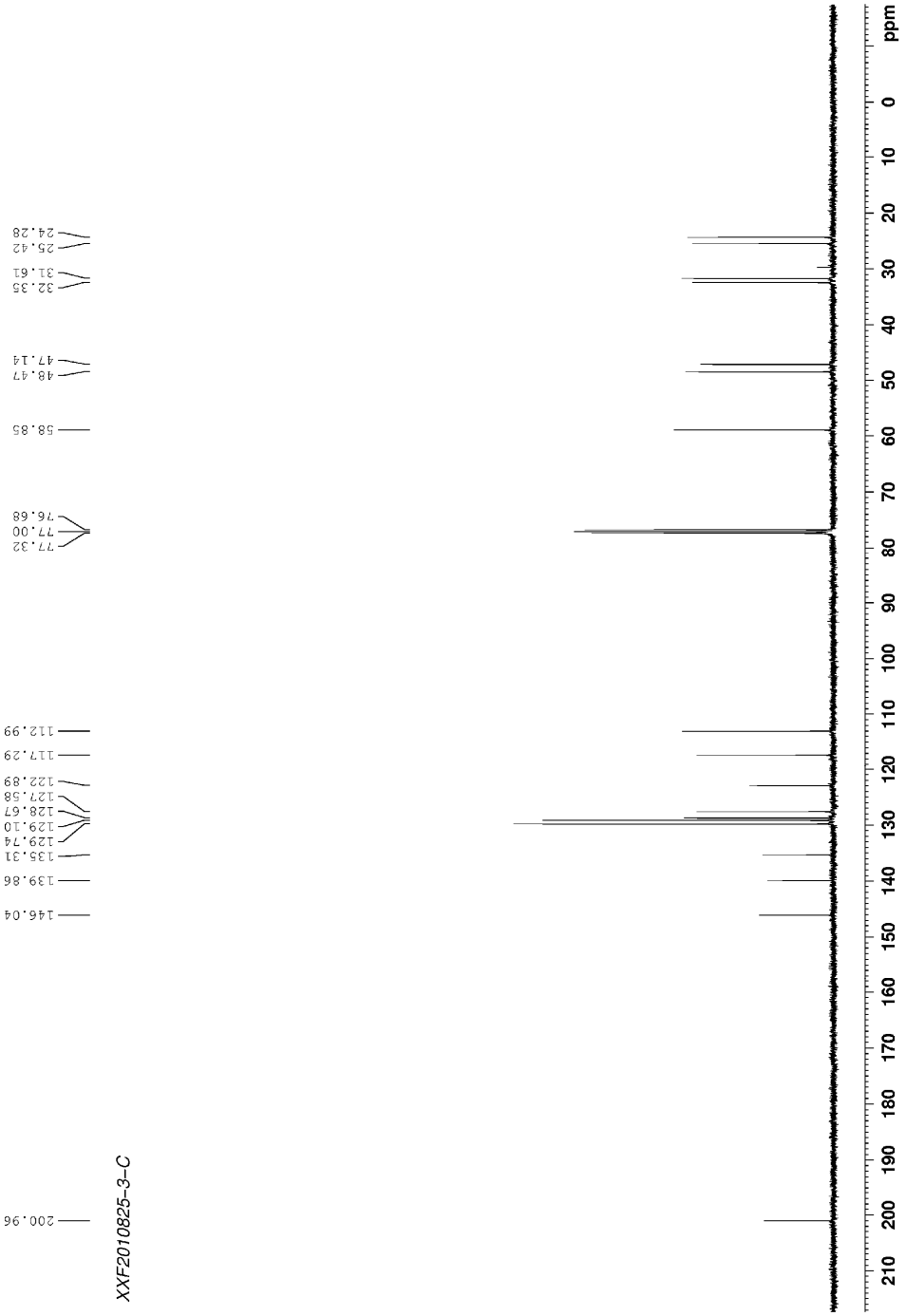







N
H
Cl
O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77.32
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127.58
128.67
129.10
129.74
135.31
139.86
146.04
200.96
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ppm
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140
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200
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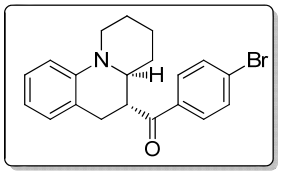

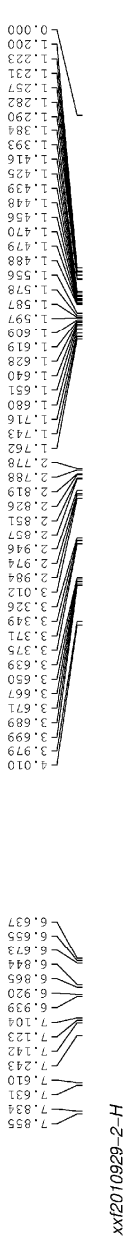

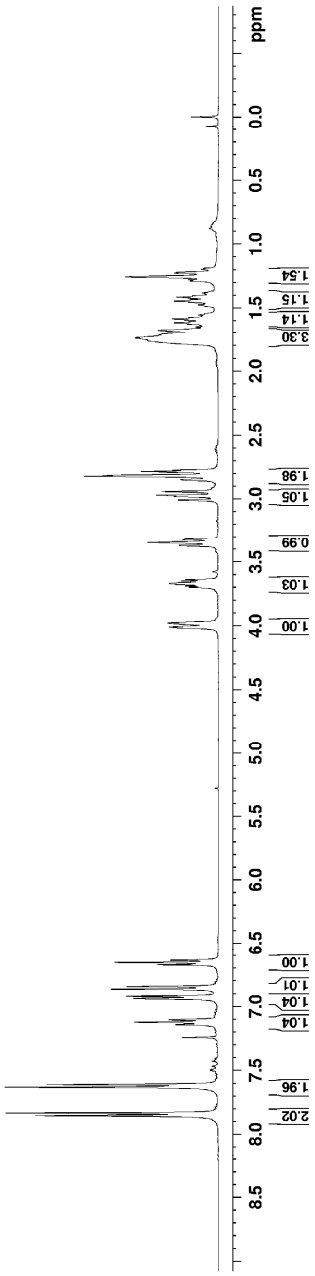

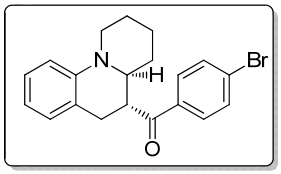
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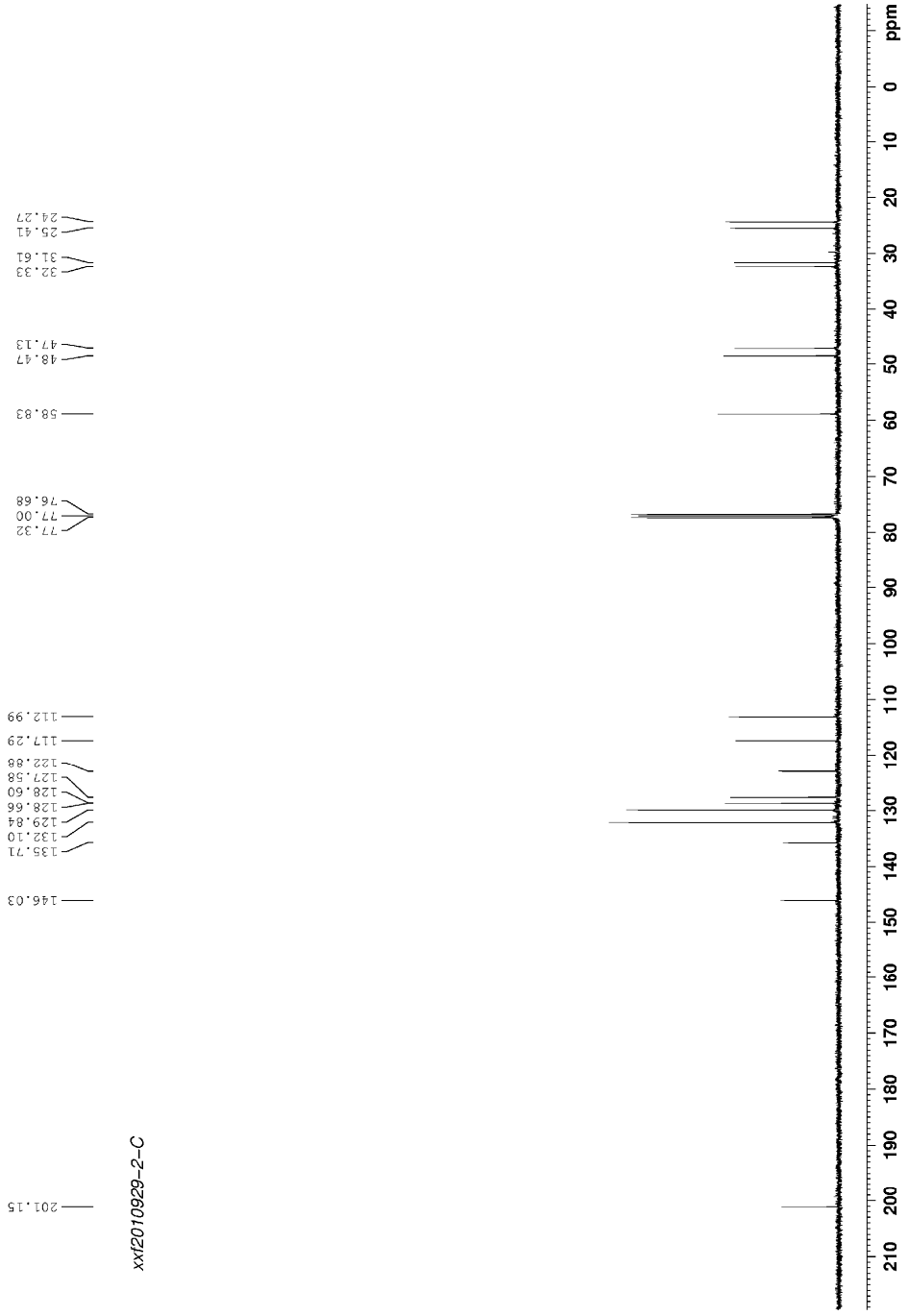
H
Br
O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48.47
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76.68
77.00
77.32
112.99
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122.88
127.58
128.60
128.66
129.84
132.10
135.71
146.03
201.15
xxf2010929-2-C
ppm
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70
80
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140
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200
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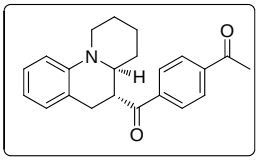
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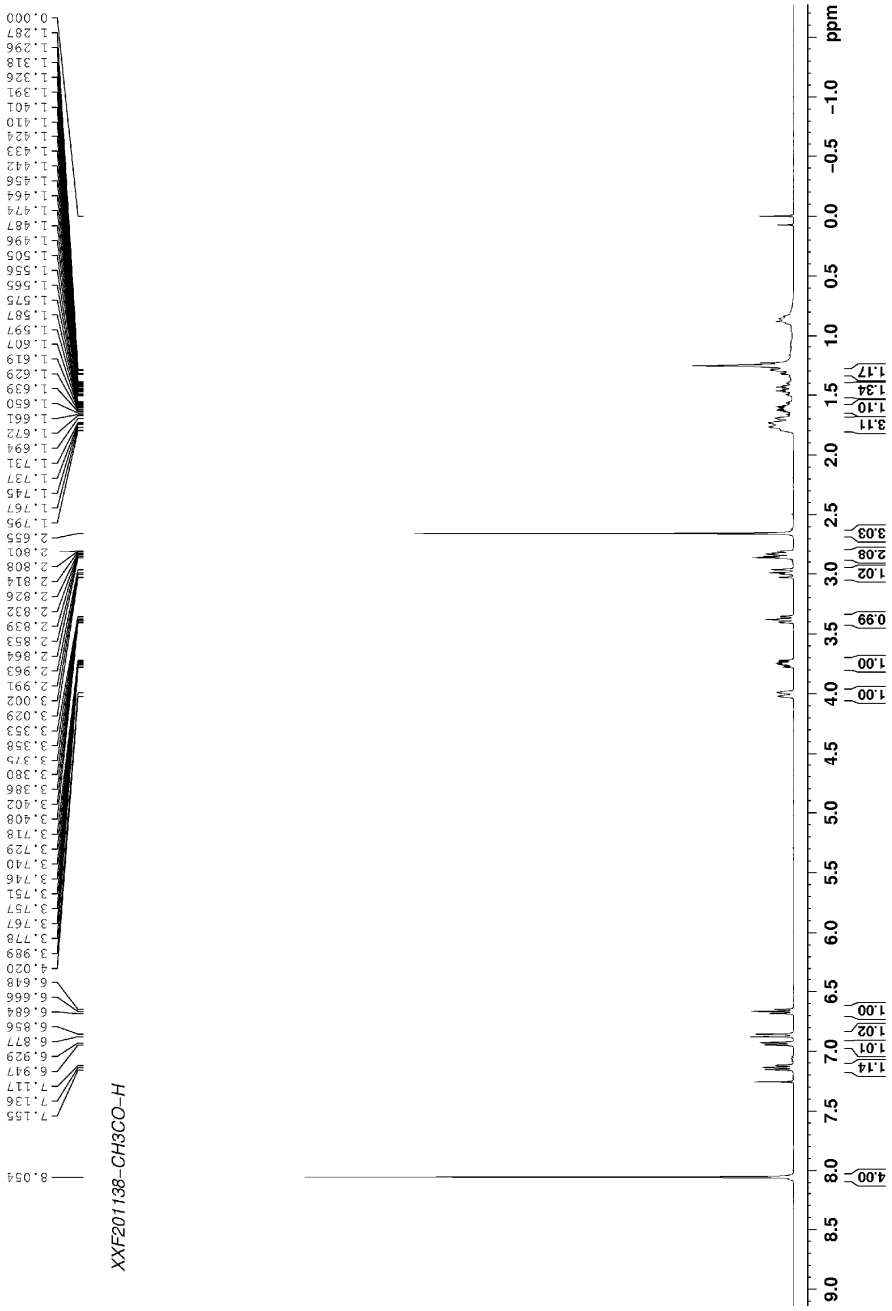
H
O
O


XXF201138-CH3CO-H
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
4.00
1.14
1.01
1.02
1.00
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0.99
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1.02
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3.03
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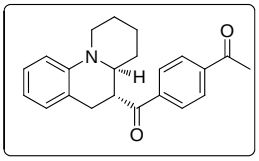
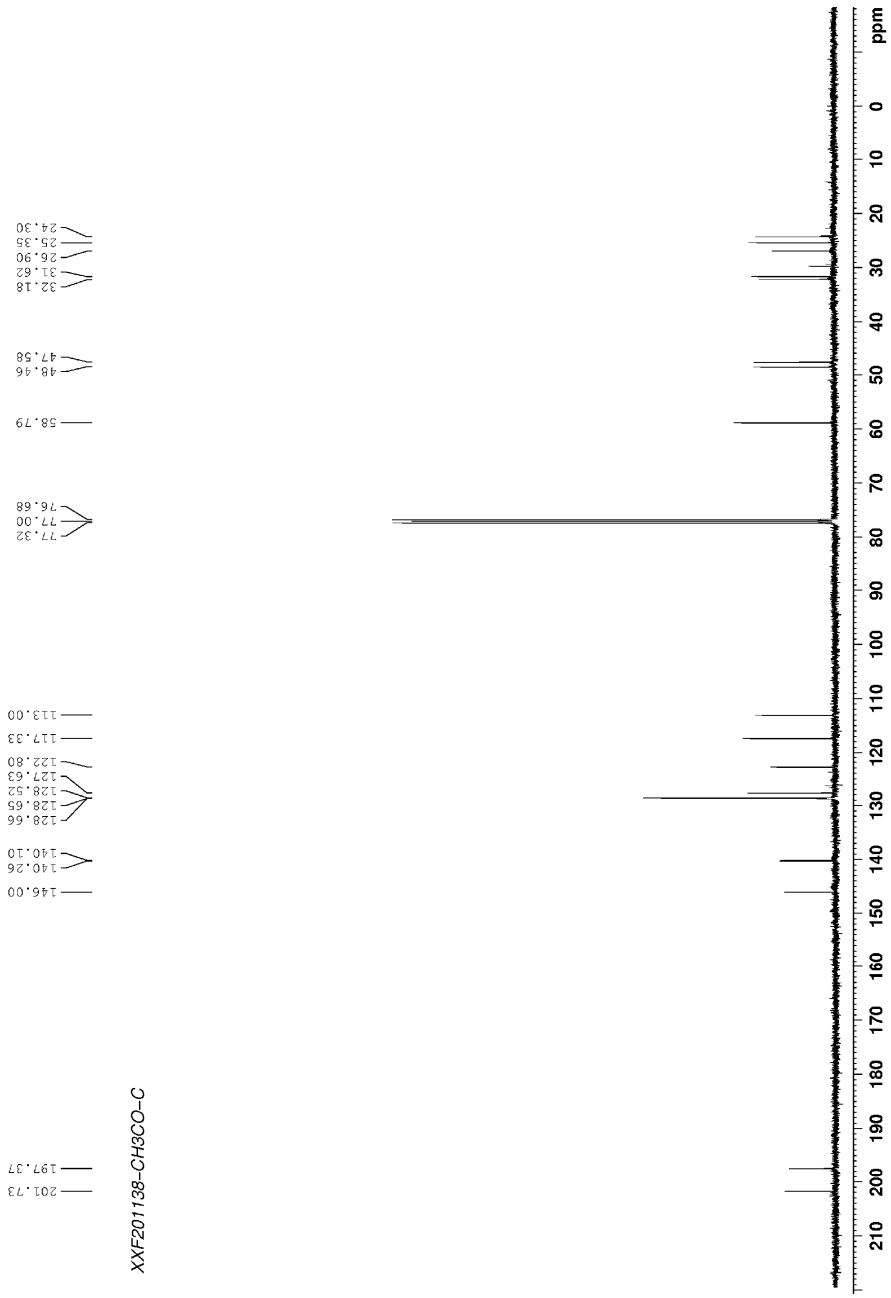
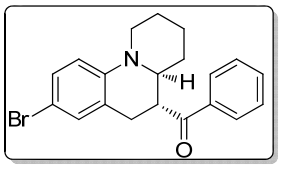
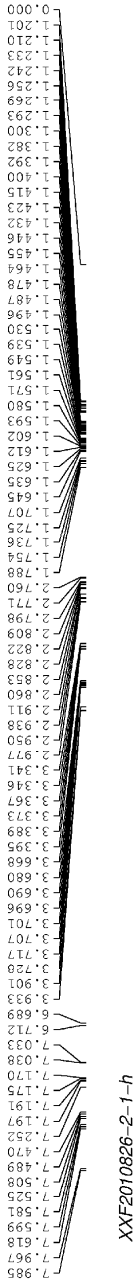
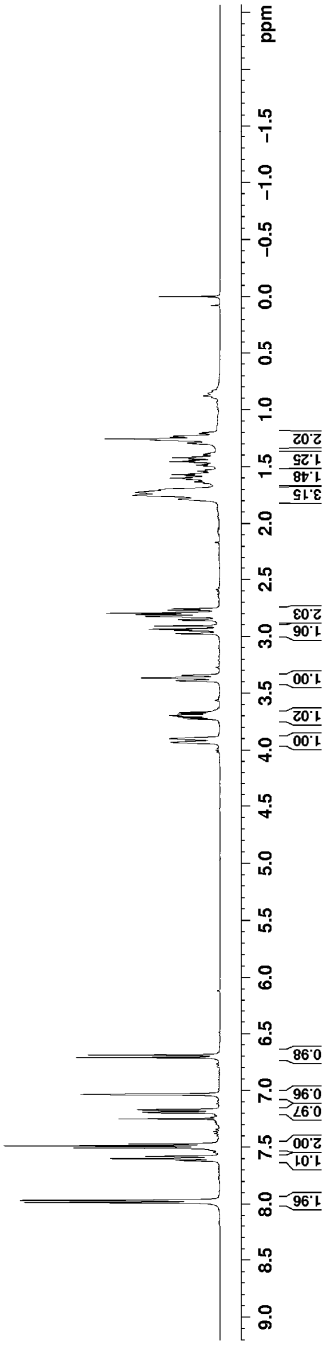
1.17






N
H
Br
O


XXF2010826-2-1-h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2.5
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1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
2.02
1.25
1.48
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1.02
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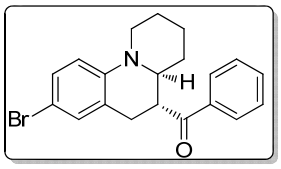
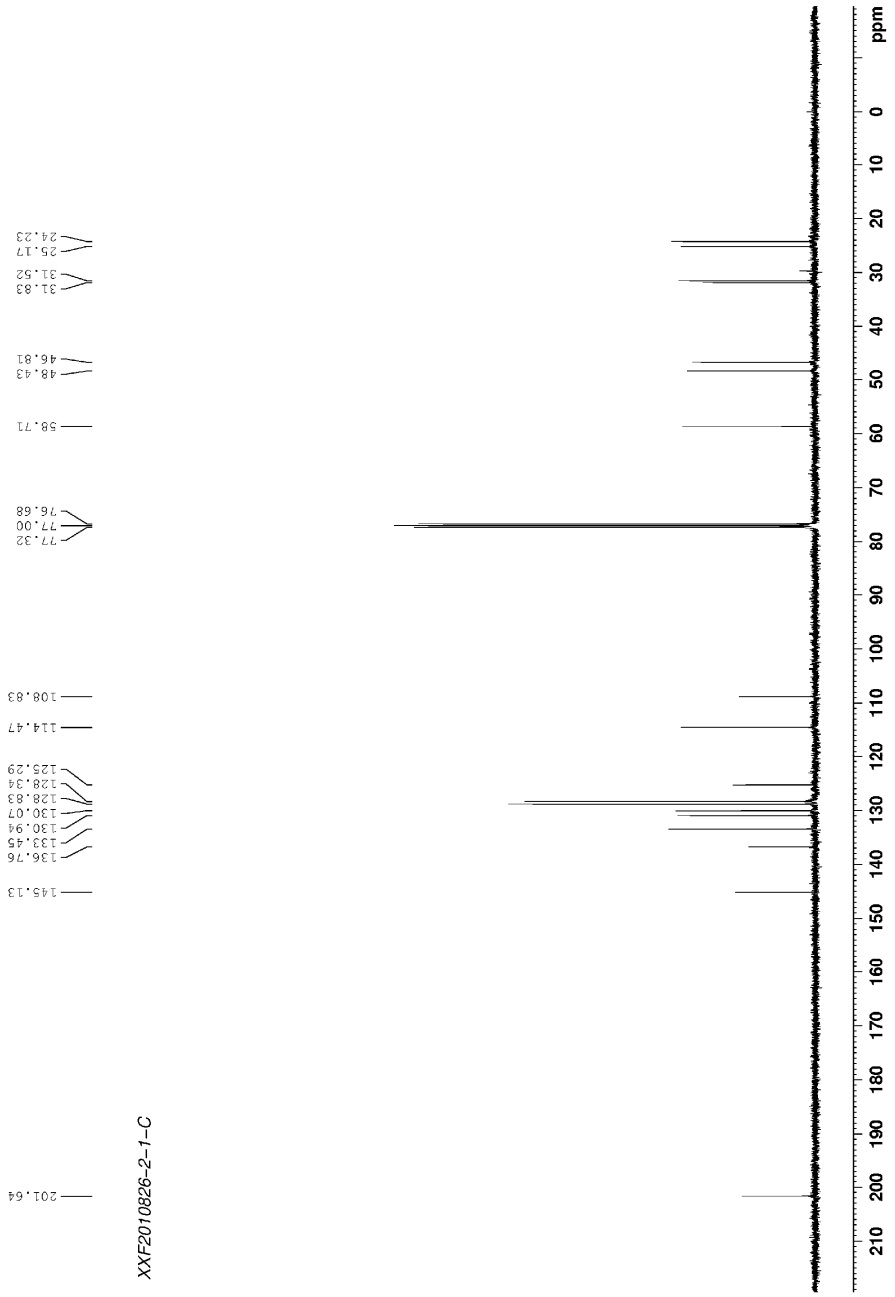
1.96


N
H
Br
O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128.34
128.83
130.07
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133.45
136.76
145.13
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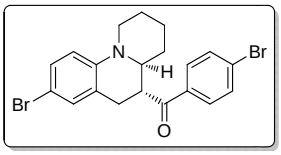

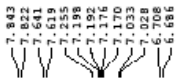

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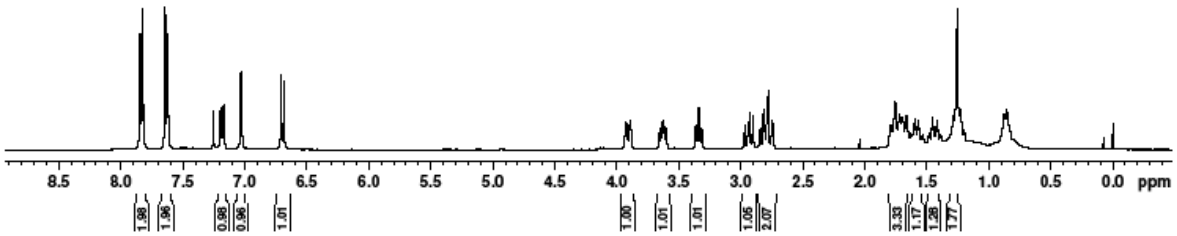

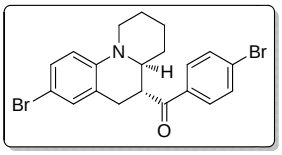
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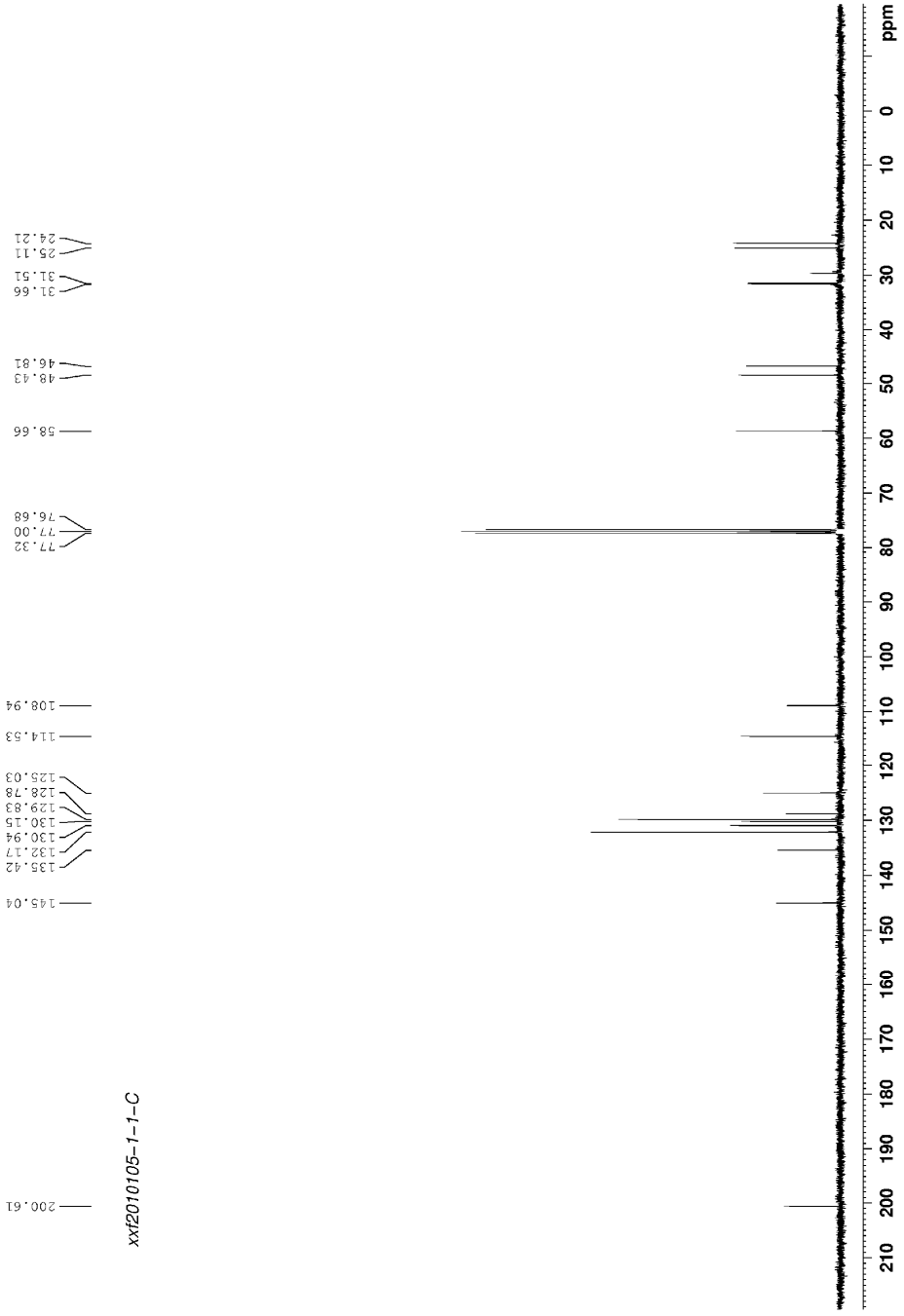
H
Br
Br
O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130.94
132.17
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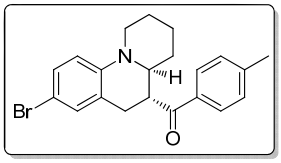
N
H
Br
O


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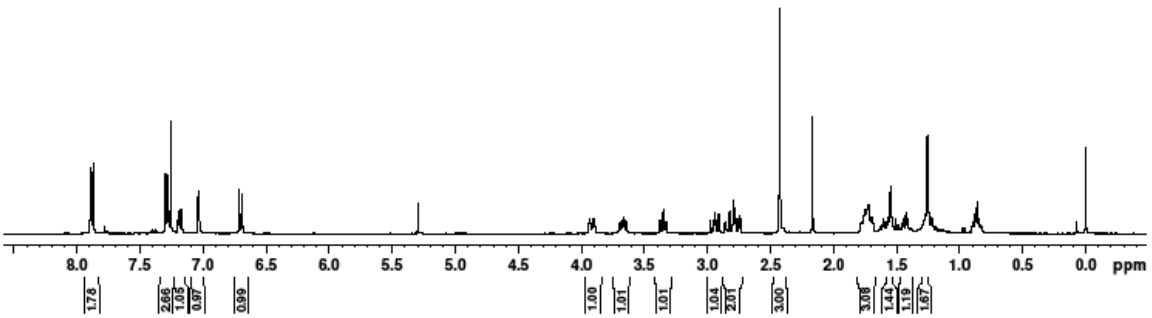
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0.0
ppm
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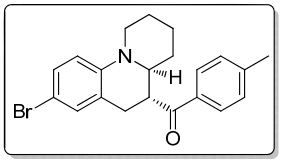

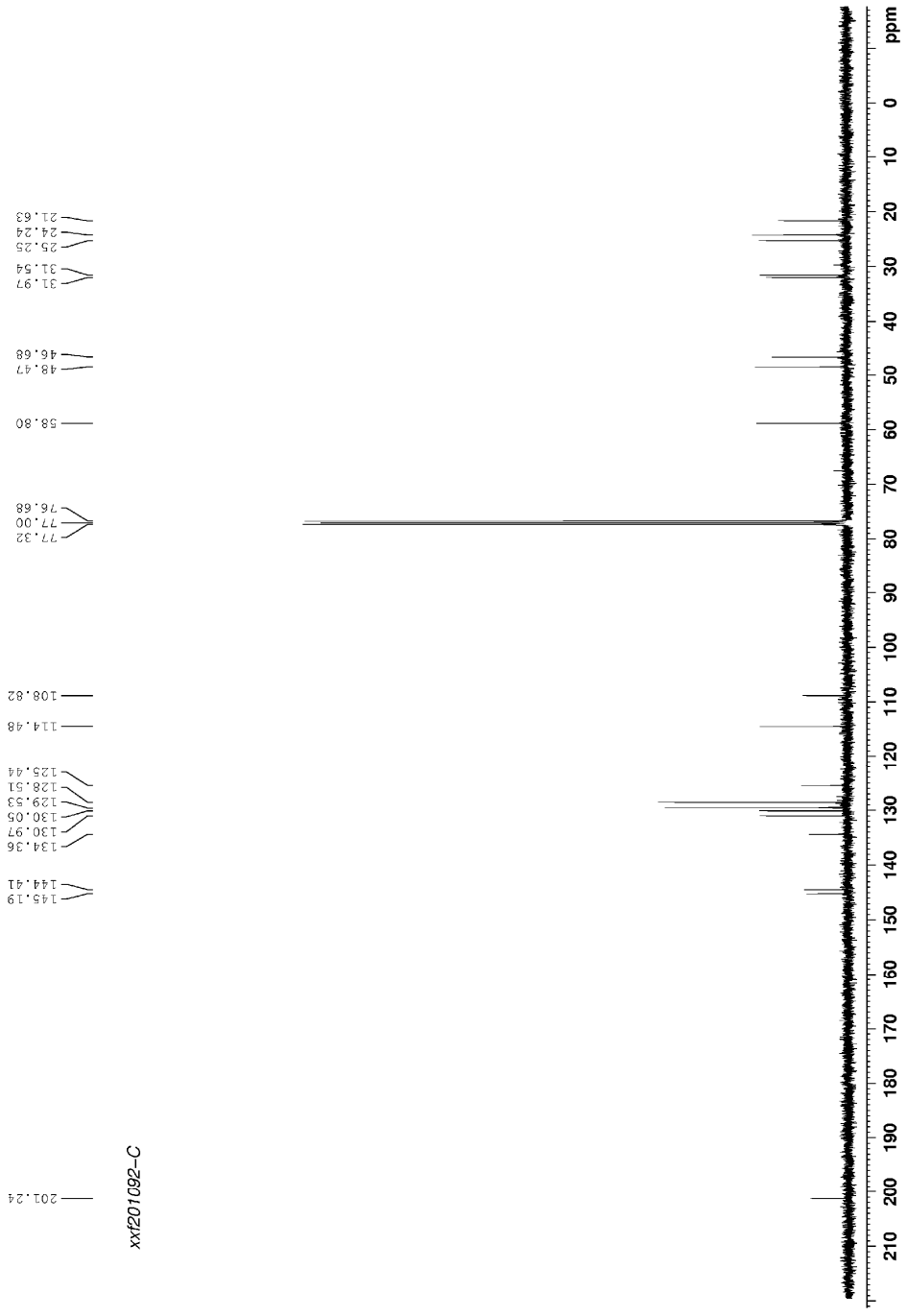

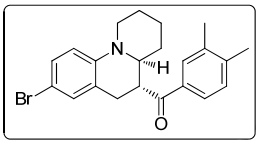
N
H
Br
O


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2.996
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3.322
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6.317
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7.164
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7.187
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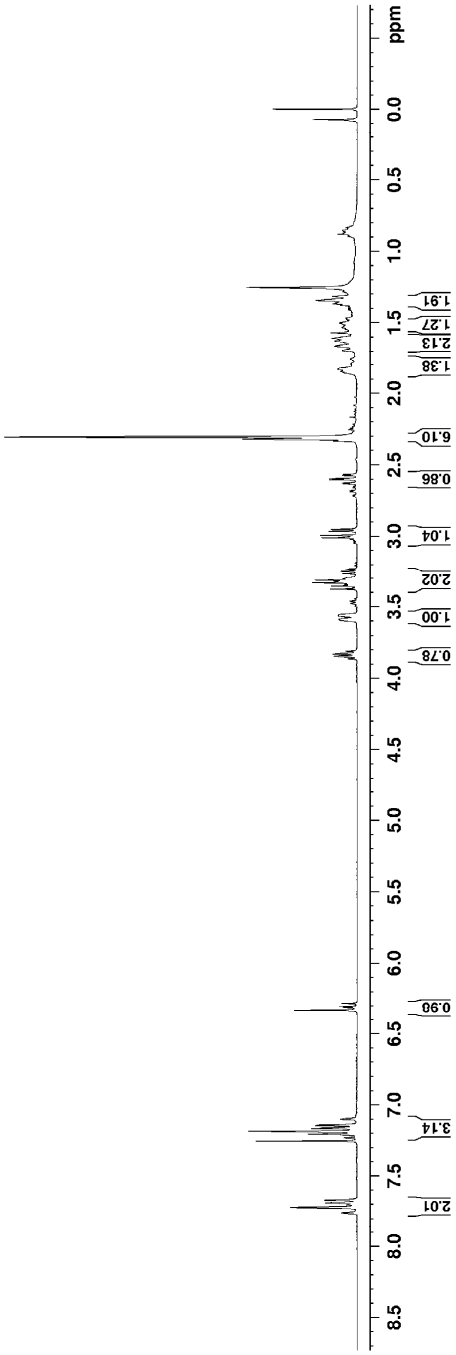
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7.5
8.0
8.5
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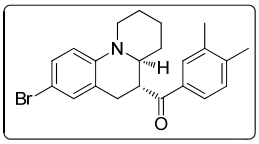

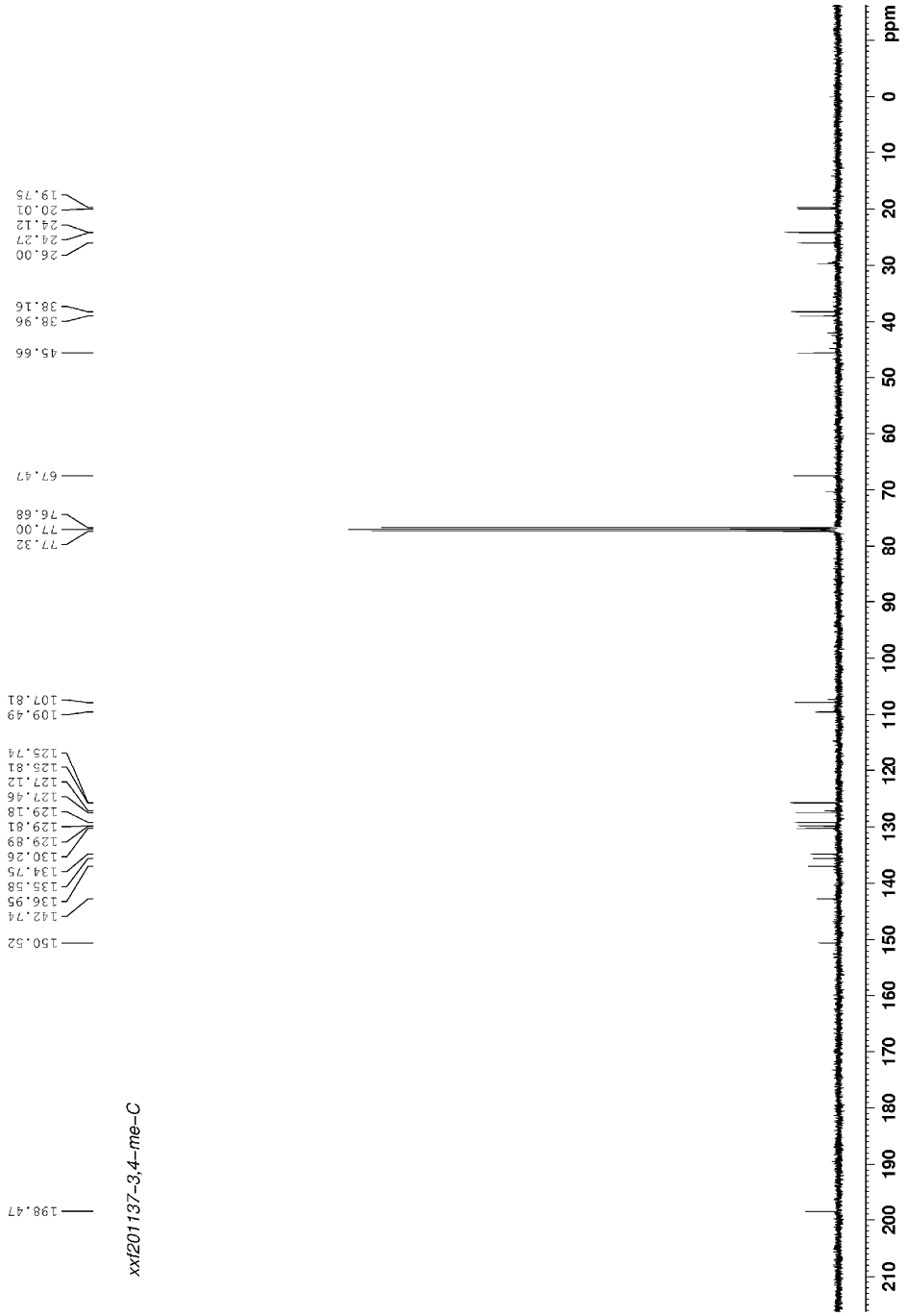

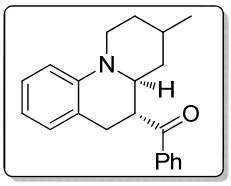
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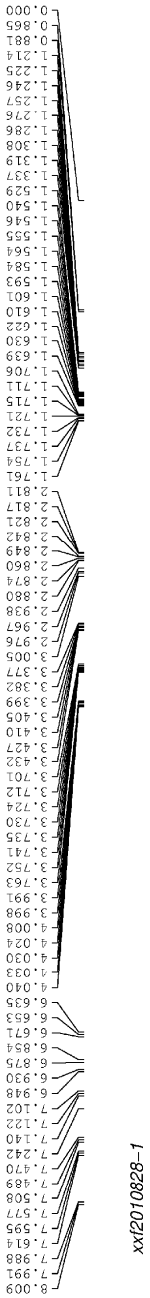
H
O
Ph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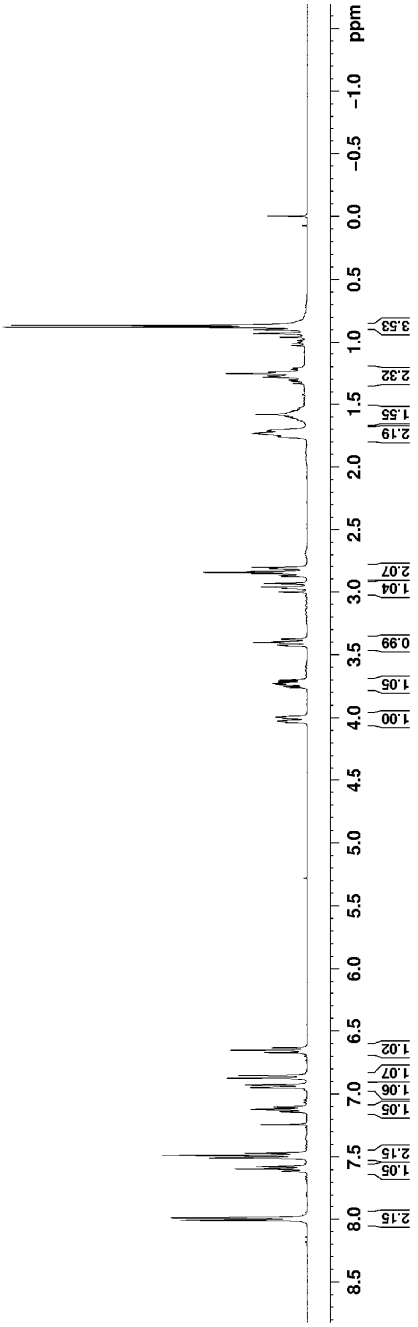
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1.00
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1.07
1.06
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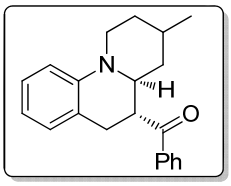
2.15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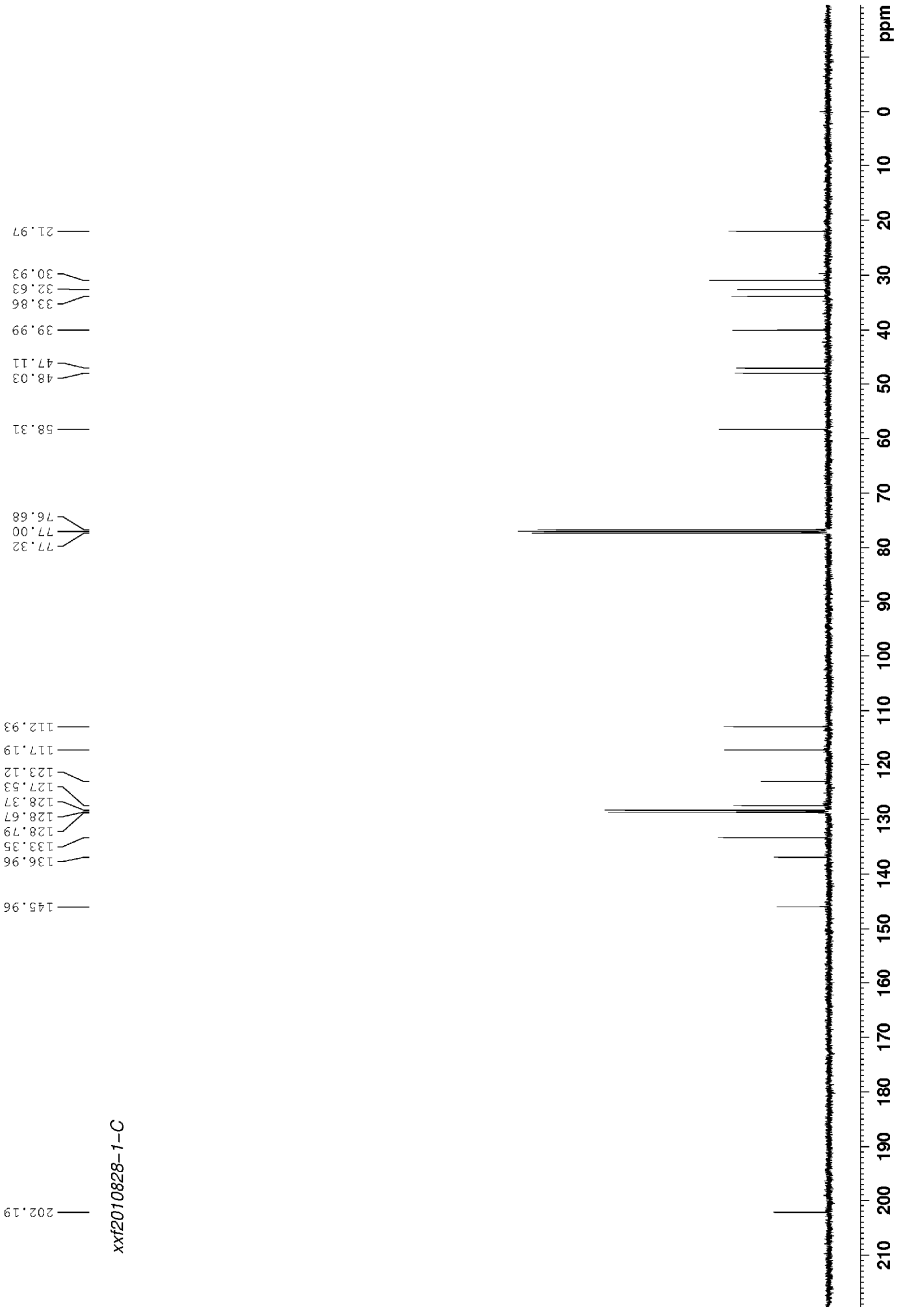
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128.67
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136.96
145.96
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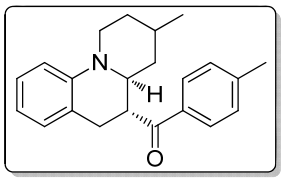
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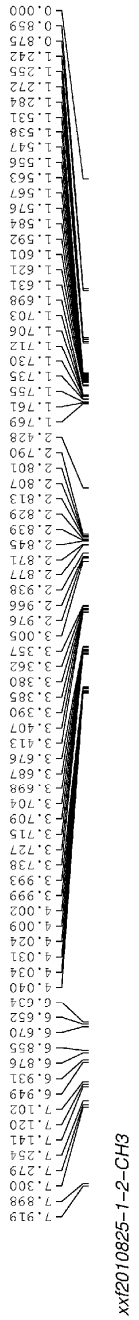
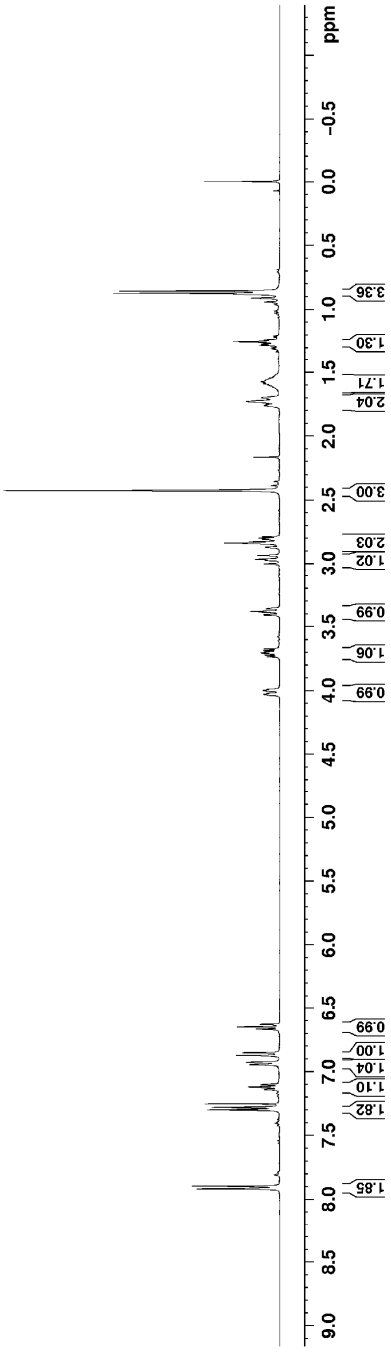
O


xxf2010825-1-2-CH3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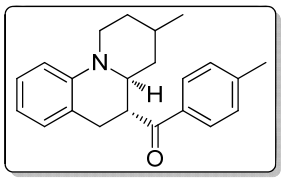
N
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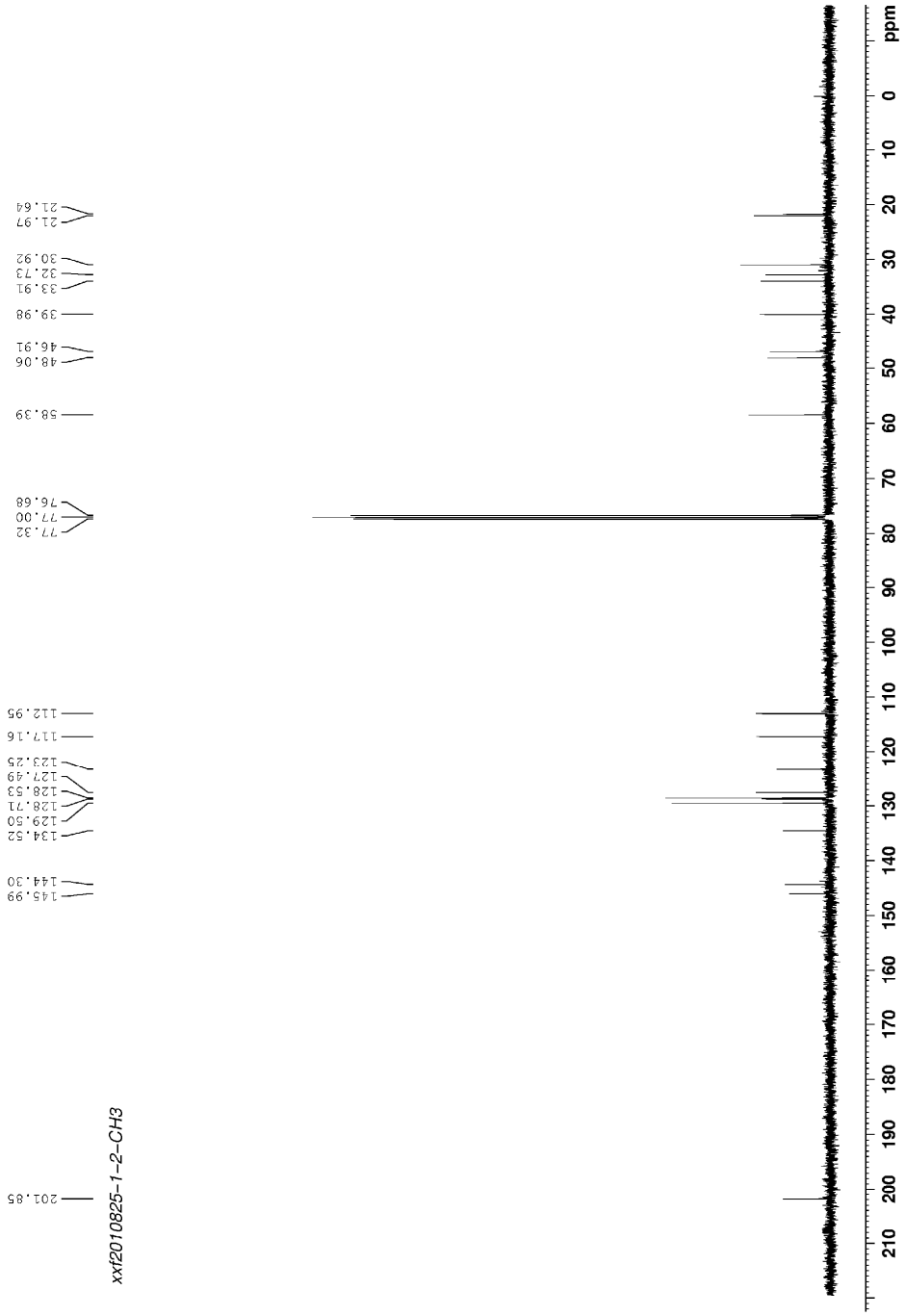
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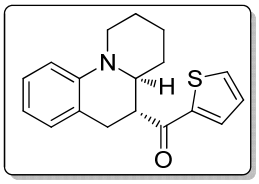
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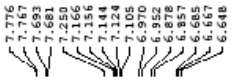
S
O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6.648


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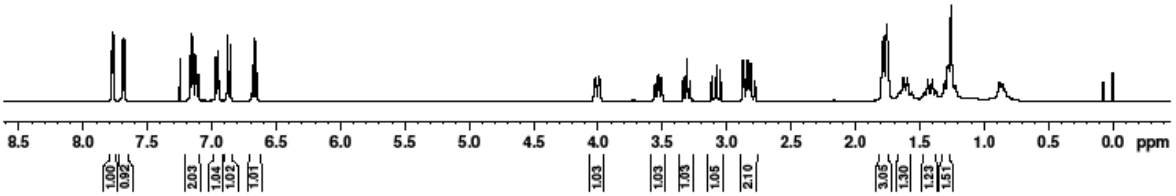
xxf201094'–H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0.0
ppm
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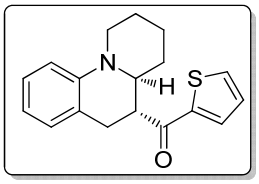
1.51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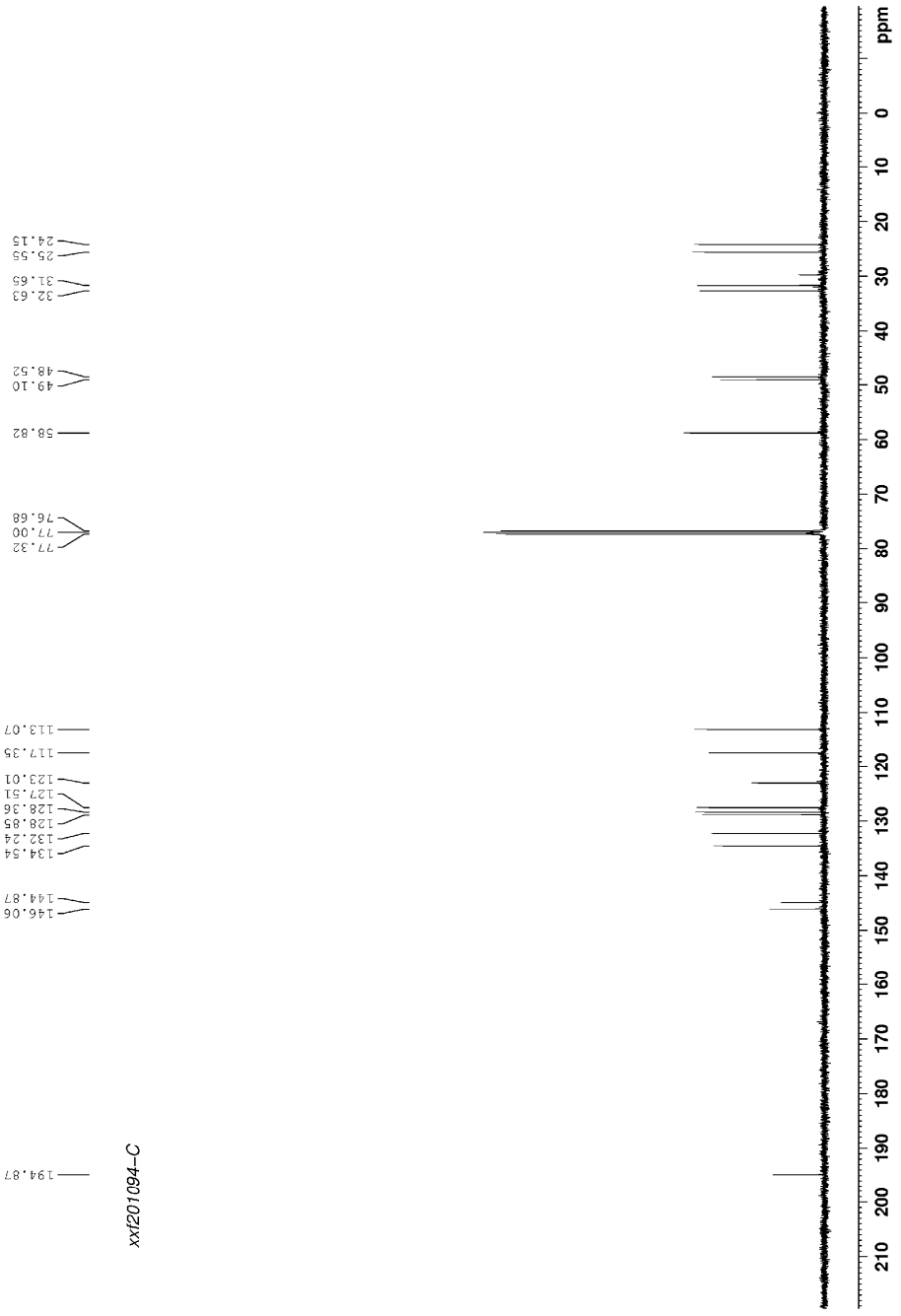
S
O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128.85
132.24
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146.06
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xx1201094-C
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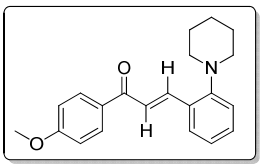
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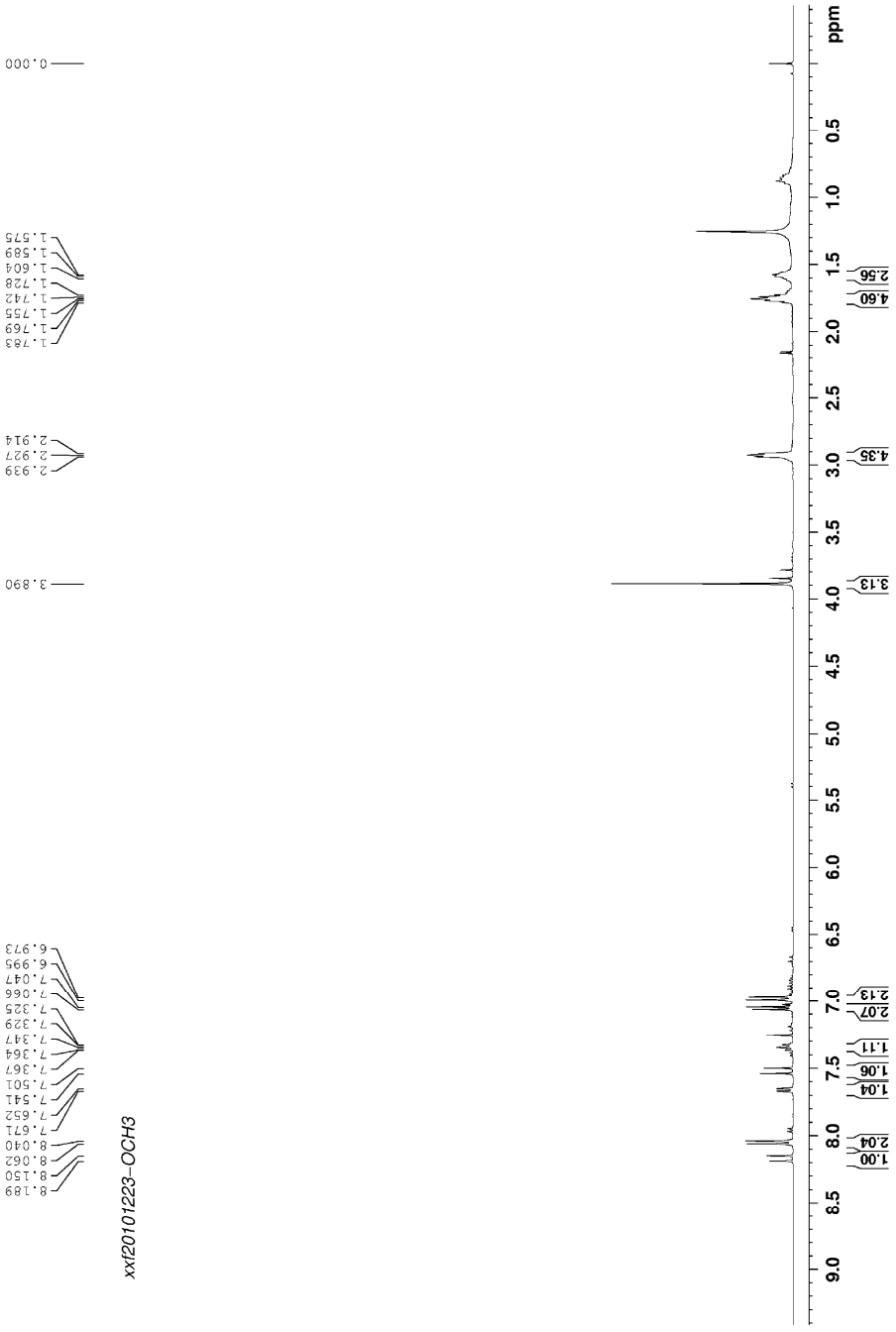
H
O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6.973
6.995
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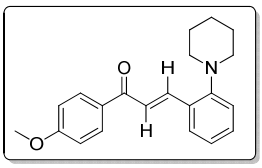
1.00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H
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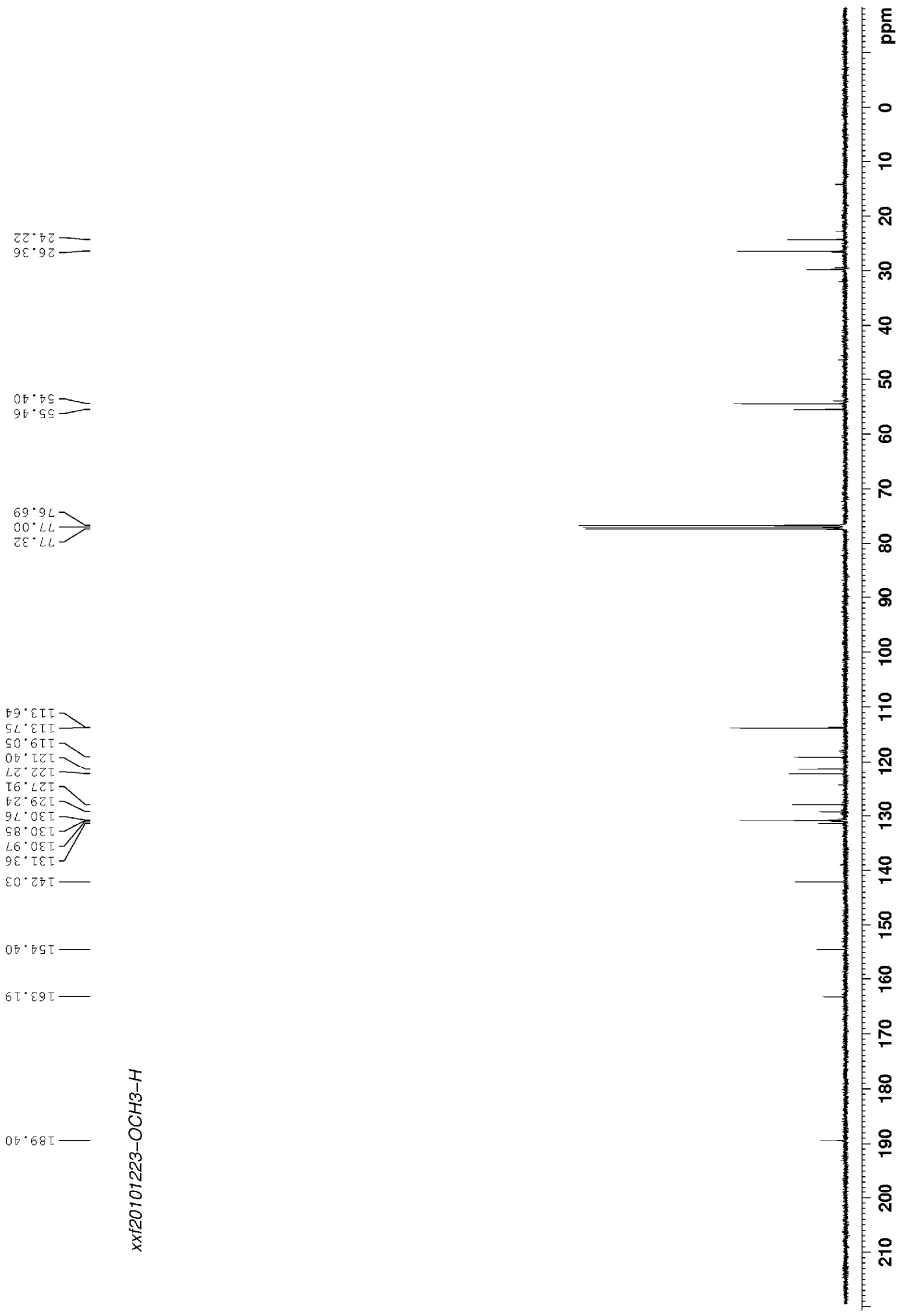
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130.85
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142.03
154.40
163.19
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xxl20101223-OCH3-H
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
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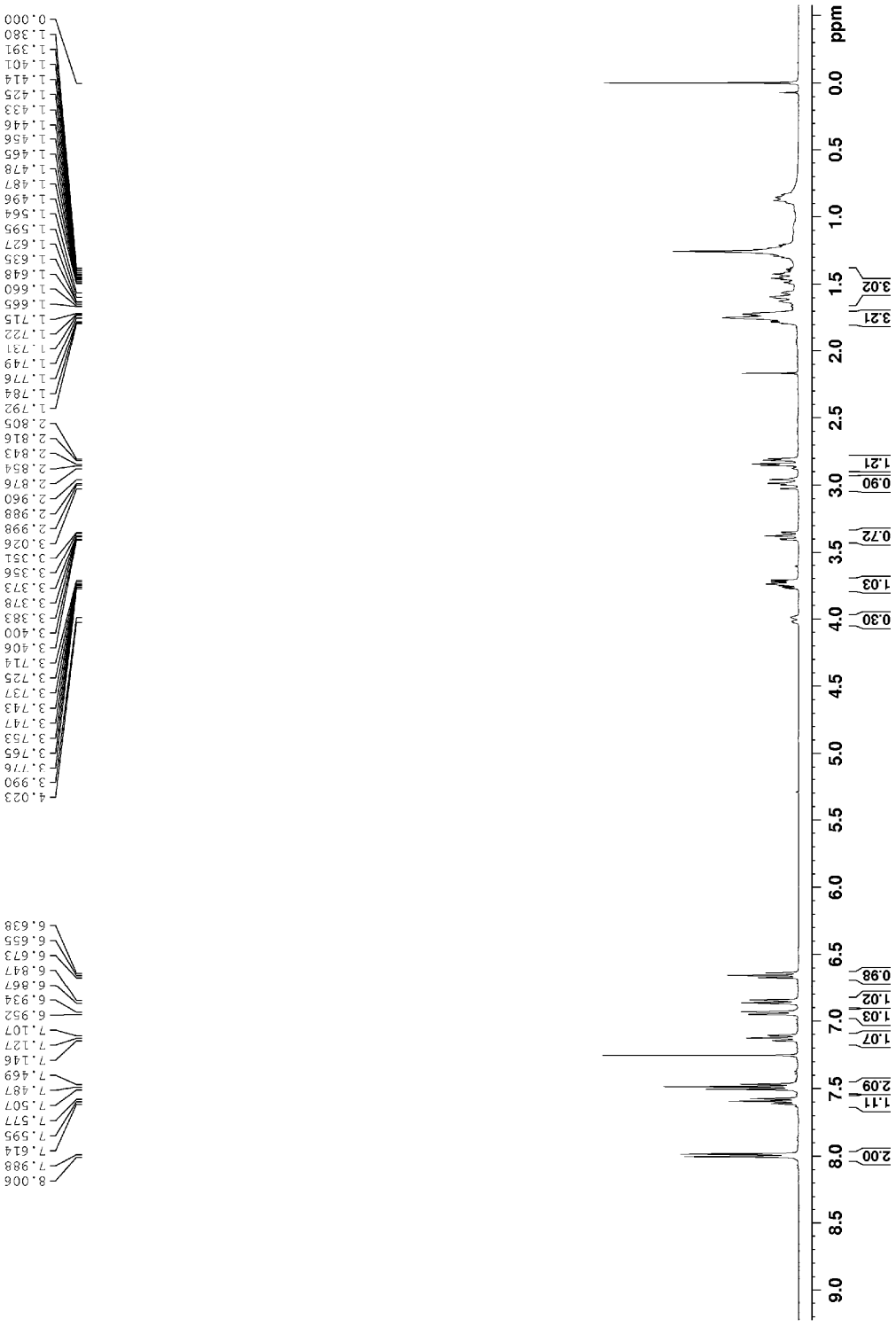
140
150
160
170
180
190
200
210

D-2a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1.380
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1.401
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1.496
1.564
1.595
1.627
1.635
1.648
1.660
1.665
1.715
1.722
1.731
1.749
1.776
1.784
1.792
2.805
2.816
2.843
2.854
2.876
2.960
2.988
2.998
3.026
3.351
3.356
3.373
3.378
3.383
3.400
3.406
3.714
3.725
3.737
3.743
3.747
3.753
3.765
3.776
3.990
4.023
6.638
6.655
6.673
6.847
6.867
6.934
6.952
7.107
7.127
7.146
7.469
7.487
7.507
7.577
7.595
7.614
7.988
8.006
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
3.02
3.21
1.21
0.90
0.72
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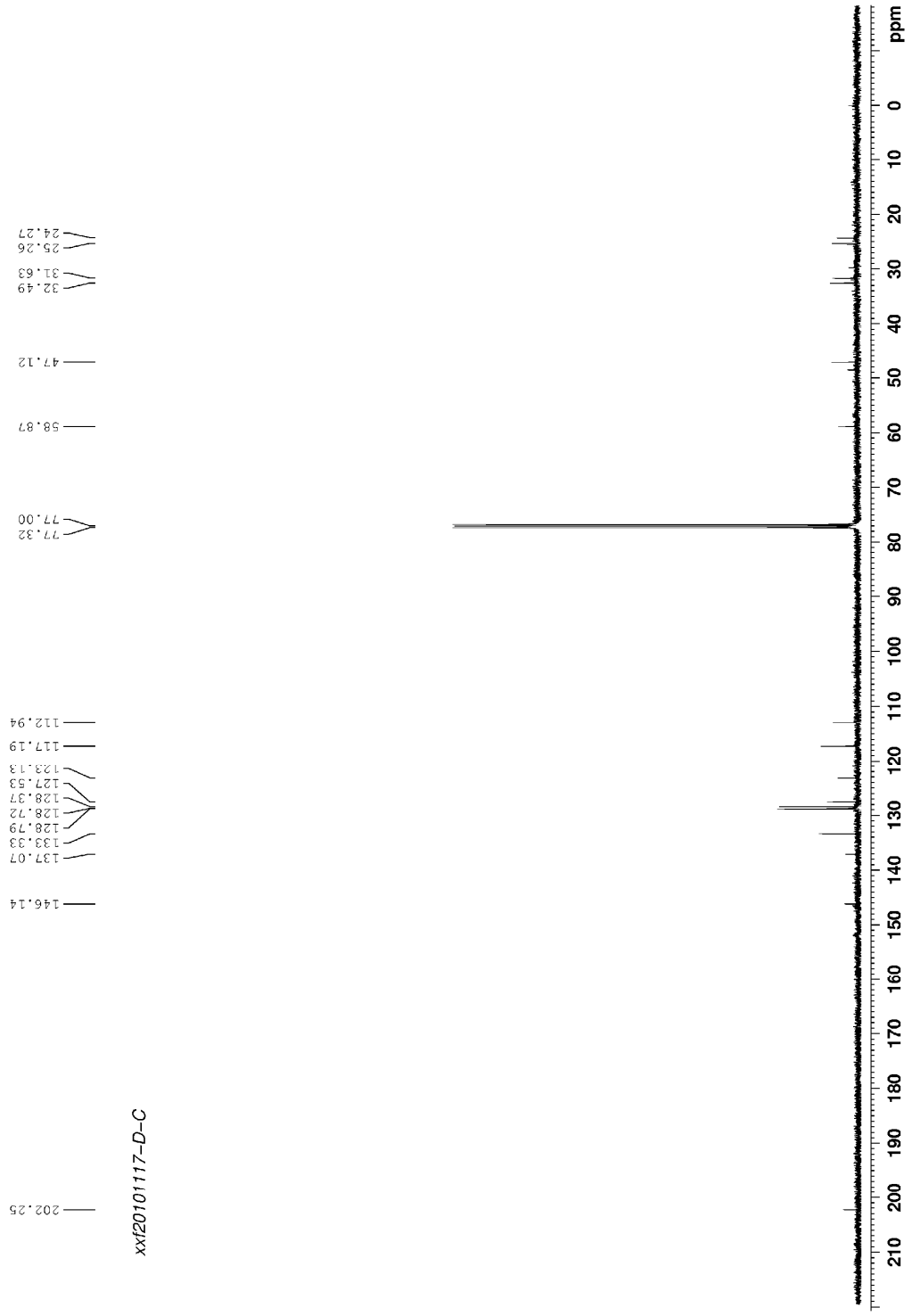
0.30
0.98
1.02
1.03
1.07
2.09
1.11
2.00

D-2a


24.27
25.26
31.63
32.49
47.12
58.87
77.00
77.32
112.94
117.19
123.13
127.53
128.37
128.72
128.79
133.33
137.07
146.14
202.25
xxf20101117-D-C
ppm
0
10
20
30
40
50
60
70
80
90
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110
120
130
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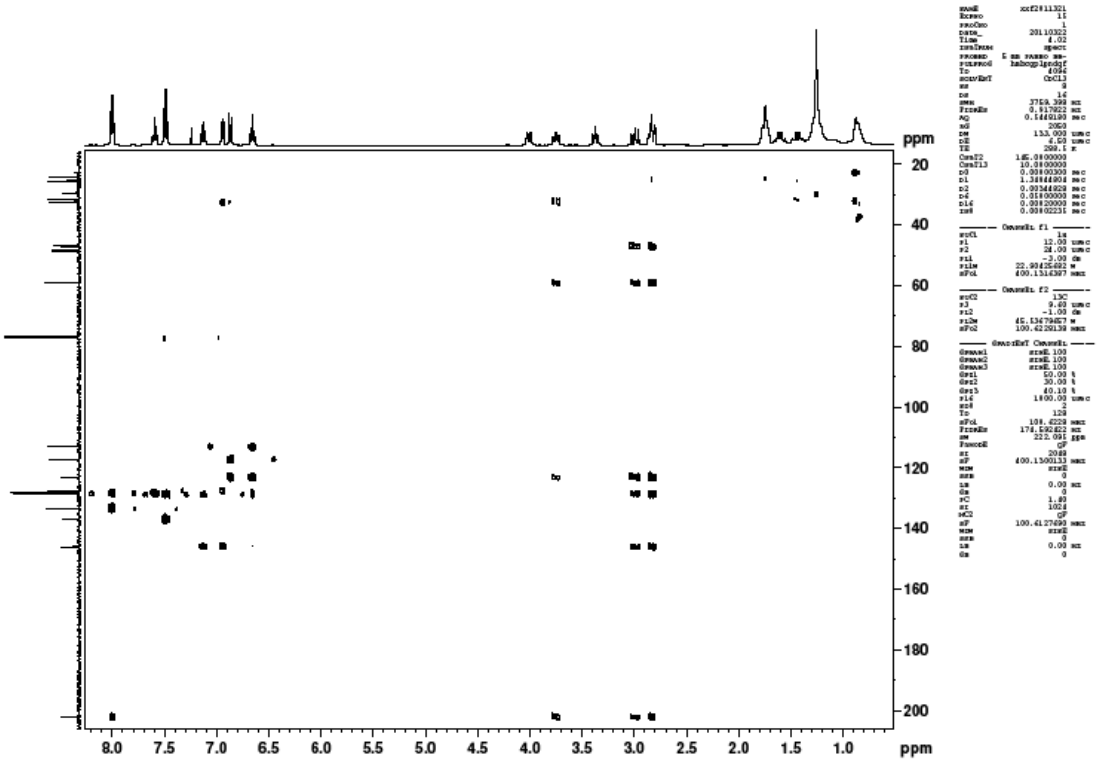
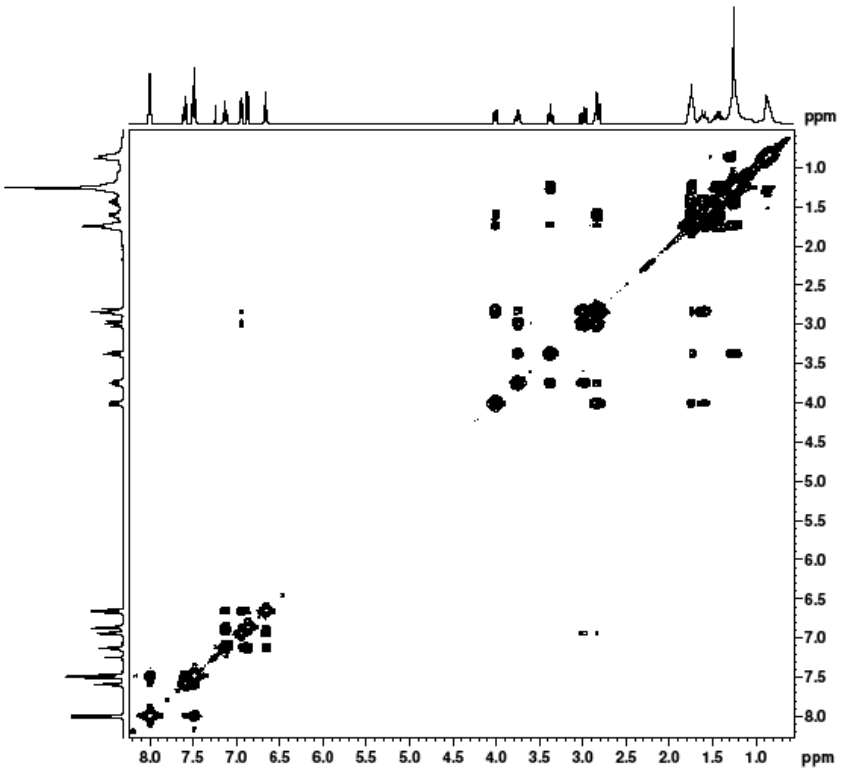
150
160
170
180
190
200
210

2D NMR of product **2a**

HMBC

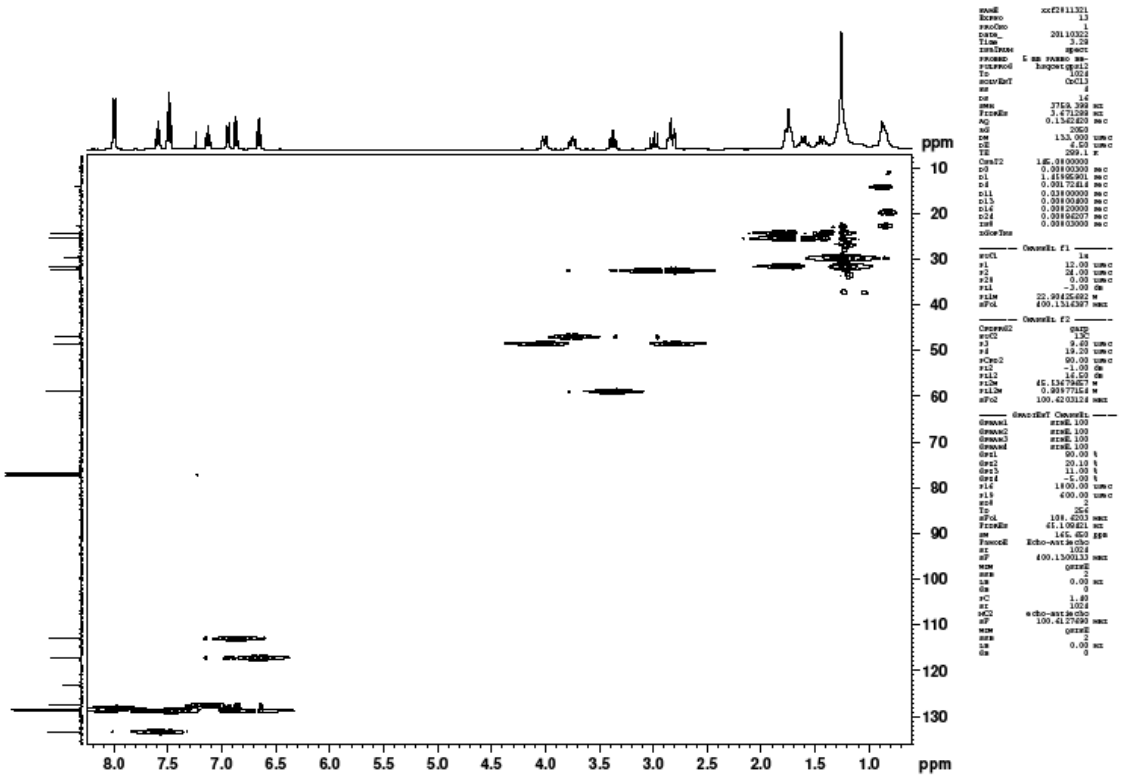


H-H cosy

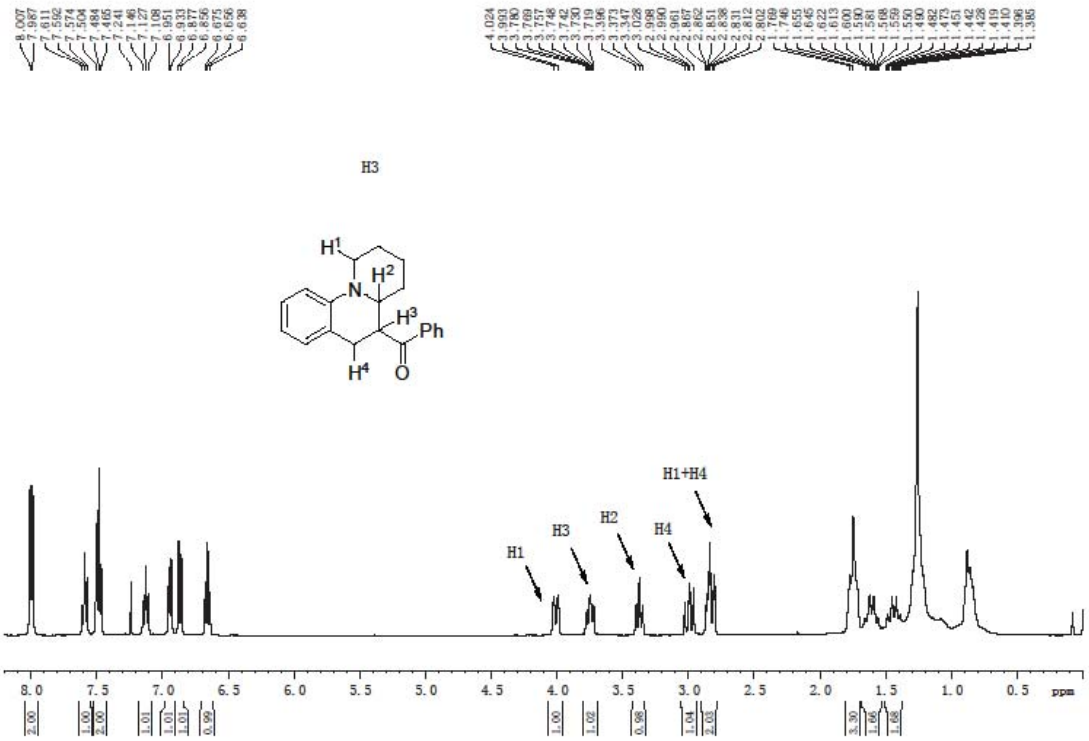



```
NAME            xxf2011321
EXPNO                   14
PROCNO                   1
Date_             20110322
Time                 3.57
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG          cosygpqf
TD                    2048
SOLVENT               CDCl3
NS                       1
DS                       8
SWH              3759.398 Hz
FIDRES           1.835644 Hz
AQ               0.2724240 sec
RG                    40.3
DW                133.000 usec
DE                  6.50 usec
TE                288.7 K
D0               0.00000300 sec
D1               1.40620100 sec
D13              0.00000400 sec
D16              0.00020000 sec
IN0              0.00026600 sec

======== CHANNEL f1 ========
NUC1                    1H
P0                   12.00 usec
P1                   12.00 usec
PL1                  -3.00 dB
PLW1            22.90425682 W
SFO1           400.1316387 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPZ1                10.00 %
P16               1000.00 usec
NE0                      1
TD                     128
SFO1           400.1316 MHz
FIDRES           29.370300 Hz
SW                   9.395 ppm
FnMODE                  QF
SI                     1024
SF             400.1300133 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.40
SI                     1024
MC2                     QF
SF             400.1300133 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
```

HMQC



From the 2D NMR of product 2a, we can identify the site of the hydrogen atom in 2a, see below:


H3
H1
H2
H3
H4
N
Ph
O
H1
H3
H2
H4
H1+H4
ppm