Supporting Information

Triphenylphosphine Oxide-Catalyzed Stereoselective Poly- and Dibromination of Unsaturated Compounds

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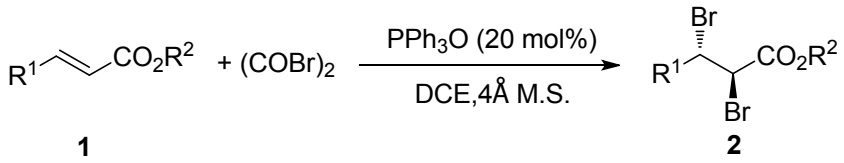
1. General Information

Chemicals and solvents were either purchased from commercial suppliers or purified by standard procedures as specified in *Purification of Laboratory Chemicals*, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997). Analytical thin-layer chromatography (TLC) was performed on silica gel plates with F-254 indicator and compounds were visualized by irradiation with UV light. Flash column chromatography was carried out using silica gel (200–300 mesh) at increased pressure. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C). The spectra were recorded in $CDCl_3$ as the solvent at room temperature. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to either the residual solvent peak (^{13}C) or TMS (^{1}H) as an internal standard. IR spectra were recorded using Nicolet NEXUS 670 FT-IR instrument. HRMS were performed on Thermo ORBITRAP ELITE (ESI). GC-MS (EI) was performed on SHIMADZU GCMS-QP2010. The substrates were prepared according to the literature procedures.[1-5]

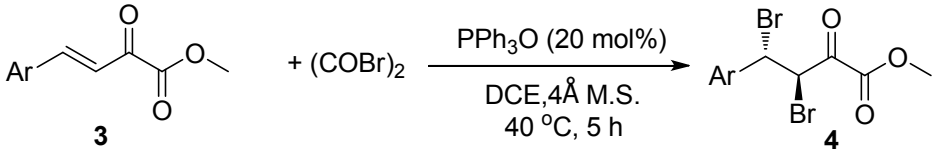
2.General Procedure for the Preparation of Compounds 2a-2o



1 **2**

α,β-unsaturated ester **1** (0.10 mmol), Ph_3PO (5.6 mg, 0.02 mmol) and 4Å molecular sieve (40.0 mg) were added to a flame-dried Schlenk tube. The vessel was placed under vacuum and the atmosphere was exchanged with argon three times before adding dry DCE (0.5 ml).Then oxalyl bromide (29 μL, 0.3 mmol) was added to the stirred reaction mixture. The reaction mixture was stirred at a proper temperature for 24h or 36h. After the reaction was complete, the reaction mixture was purified by flash column chromatography using petroleum ether/EtOAc (70:1) to obtain the desired product **2**.

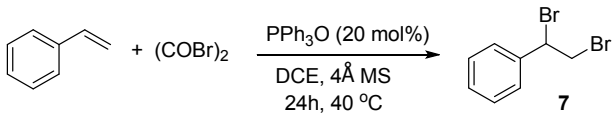
3. General Procedure for the Preparation of Compounds 4a-4g



β,γ-unsaturated α-ketoester **3** (0.10 mmol), Ph_3PO (5.6 mg, 0.02 mmol) and 4Å molecular sieve (40.0 mg) were added to a flame-dried Schlenk tube. The vessel was placed under vacuum and the atmosphere was exchanged with argon three times before adding dry DCE (0.5 ml). Then oxalyl bromide (29 μL, 0.3 mmol) was added to the stirred reaction mixture. The reaction mixture was stirred at 40 °C for 5h. After the reaction was complete, the reaction mixture was purified by flash column chromatography using petroleum ether/EtOAc (30:1) to obtain the desired product **4**.

4. Preparation of Compounds 6-7

5 (18.8 mg, 0.10 mmol), Ph_3PO (5.6 mg, 0.02 mmol) and 4Å molecular sieve (40.0 mg) were added to a flame-dried Schlenk tube. The vessel was placed under vacuum and the atmosphere was exchanged with argon three times before adding dry DCE (0.5 ml). Then oxalyl bromide (29 μL, 0.3 mmol) was added to the stirred reaction mixture. The reaction mixture was stirred at 40 °C for 48h. After the reaction was complete, the reaction mixture was purified by flash column chromatography using petroleum ether/EtOAc (30:1) to obtain the desired product **6**, the yield was 69% and d.r. = 10:1.

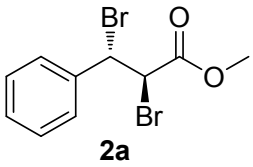


Styrene (11.5 μL, 0.10 mmol), Ph_3PO (5.6 mg, 0.02 mmol) and 4Å molecular sieve (40.0 mg) were added to a flame-dried Schlenk tube. The vessel was placed under vacuum and the atmosphere was exchanged with argon three times before adding dry DCE (0.5 ml). Then oxalyl bromide (29 μL, 0.3 mmol) was added to the stirred reaction mixture. The reaction mixture was stirred at 40 °C for 24h. The reaction mixture was purified by flash column chromatography using petroleum ether to obtain the desired product **7**, the yield was 49%.

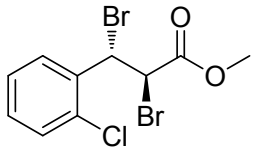
5. Control experiment

1a (16.2 mg, 0.10 mmol), Ph_3P (5.2 mg, 0.02 mmol) and 4Å molecular sieve (40.0 mg) were added to a flame-dried Schlenk tube. The vessel was placed under vacuum and the atmosphere was exchanged with argon three times before adding dry DCE (0.5 ml). Then oxalyl bromide (29 μL, 0.3 mmol) was added to the stirred reaction mixture. The reaction mixture was stirred at 40 °C for 24h. The reaction mixture was purified by flash column chromatography using petroleum ether/EtOAc (30:1) to obtain the desired product **2a**, the yield was 81% and d.r. >19:1.

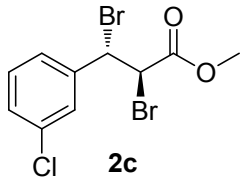
6. Analytical data


2a

(*trans*)-methyl 2,3-dibromo-3-phenylpropanoate (2a): a white solid (29.0 mg, 90%, d.r. >19 :1), m.p. 108-109 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 3.90 (s, 3H), 4.85 (d, *J* = 11.6 Hz, 1H), 5.34 (d, *J* = 11.6 Hz, 1H), 7.36-7.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 137.5, 129.4, 128.9, 128.0, 53.4, 50.6, 46.7; IR (KBr): 3456, 3064, 3009, 2950, 2847, 1961, 1737, 1497, 1454, 1434, 1380, 1273, 1219, 1149, 981, 699, 587 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{10}H_{10}Br_2NaO_2$) requires *m/z* 342.8940, found *m/z* 342.8944.

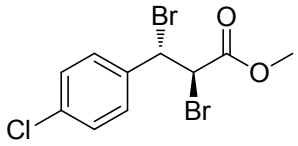

2b

(*trans*)-methyl2,3-dibromo-3-(2-chlorophenyl)-propanoate (2b): a white solid (32.4mg, 91%, d.r. > 19:1), m.p. 80-81 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 3.91 (s, 3H), 4.93 (s, 1H), 5.92 (s, 1H), 7.26-7.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 135.1, 134.0, 130.3, 130.2, 128.8, 127.6, 53.5, 45.4; IR (KBr): 3448, 3026, 3006, 2325, 1737, 1591, 1480, 1433, 1288, 1276, 1230, 1036, 1013, 764, 735, 604, 487 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{10}H_9Br_2ClNaO_2$) requires *m/z* 376.8550, found *m/z* 376.8557.


2c

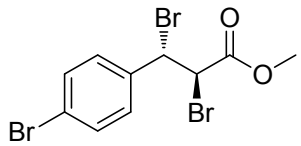
(*trans*)-methyl 2,3-dibromo-3-(3-chlorophenyl)propanoate (2c): a white solid (34.2 mg, 96%, d.r. > 19:1), m.p. 61-62 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 3.90 (s, 3H), 4.78 (d, *J* = 12.0 Hz, 1H), 5.28 (d, *J* = 12.0 Hz, 1H), 7.27-7.35 (m, 3H), 7.40 (s, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 168.1, 139.5, 134.7, 130.1, 129.6, 128.2, 126.3, 53.5, 49.2, 46.3; IR (KBr): 3463, 3101, 3021, 2064, 1743, 1595, 1574, 1480, 1435, 1370, 1303, 1268, 1214, 1155, 1141, 1079, 978, 921, 891, 795, 700, 684, 608, 576, 482 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{10}H_9Br_2ClNaO_2$) requires *m/z* 376.8550, found *m/z* 376.8556.



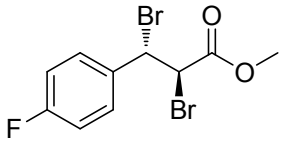
2d

(*trans*)-methyl 2,3-dibromo-3-(4-chlorophenyl)propanoate (2d): a white solid (32.8 mg, 92%, d.r. > 19:1), m.p. 96-97 °C; ^1H NMR(400 MHz, $CDCl_3$): δ 3.90 (s, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 5.31 (d, *J* = 11.6 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 136.1, 135.2, 129.4, 129.2, 53.5, 49.5, 46.4; IR (KBr): 3454, 3089, 3049, 3009, 2359, 1920, 1745, 1593, 1494, 1439, 1414, 1279, 1231, 1152, 1012, 838, 726, 713, 590, 511 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{10}H_9Br_2ClNaO_2$) requires *m/z* 376.8550, found *m/z* 376.8557.



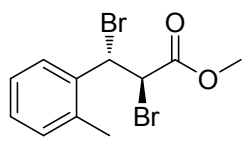
2e

***(trans)*-methyl 2,3-dibromo-3-(4-bromophenyl)propanoate (2e) :** a white solid (37.0 mg, 92%, d.r. > 19:1), m.p. 105-106 °C; 3.90 (s, 3H), 4.78 (d, *J* = 11.6 Hz, 1H), 5.30 (d, *J* = 11.6 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 136.6, 132.1, 129.6, 123.4, 53.5, 49.5, 46.3; IR (KBr): 3452, 3008, 2591, 1744, 1590, 1491, 1438, 1277, 1231, 1152, 1072, 1010, 835, 587, 509 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{10}H_9Br_3NaO_2$) requires *m/z* 420.8045, found *m/z* 420.8054.



2f

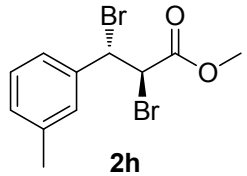
(*trans*)-methyl 2,3-dibromo-3-(4-fluorophenyl)propanoate (2f): a white solid (31.0 mg, 91%, d.r. > 19 :1), m.p. 61-63 °C; ^1H NMR(400 MHz, $CDCl_3$): δ 3.90 (s, 3H), 4.80 (d, *J* = 12 Hz, 1H), 5.34 (d, *J* = 11.6 Hz, 1H), 7.09 (t, *J* = 8.4 Hz, 2H), 7.39 (dd, *J* = 5.4 Hz, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 162.9 (d, *J* = 249.0 Hz), 133.5 (d, *J* = 3.0 Hz), 129.9 (d, *J* = 8.0 Hz), 116.0 (d, *J* = 22.0 Hz), 53.5, 49.7, 46.8; IR (KBr): 3451, 3014, 2958, 2452, 1739, 1602, 1511, 1436, 1276, 1229, 1157, 1011, 861, 841, 591, 510 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{10}H_9Br_2FNaO_2$) requires *m/z* 360.8846, found *m/z* 360.8852.



2g

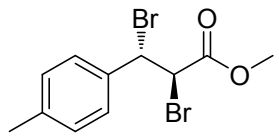
(*trans)*-methyl 2,3-dibromo-3-(*o*-tolyl)propanoate (2g): a white solid (30.9 mg, 92%, d.r. > 19 :1), m.p. 81-82 °C; ^1H NMR(400 MHz, $CDCl_3$):

δ 2.45 (s, 3H), 3.91 (s, 3H), 4.93 (d, *J* = 11.6 Hz, 1H), 5.65 (d, *J* = 12.0 Hz, 1H), 7.18-7.29 (m, 3H), 7.40-7.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 136.5, 135.6, 130.8, 129.2, 126.9, 126.7, 53.5, 46.2, 19.4; IR (KBr): 3454, 3022, 2848, 2349, 1735, 1464, 1436, 1382, 1313, 1274, 1210, 1145, 982, 918, 771, 729, 600, 498 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{11}H_{12}Br_2NaO_2$) requires *m/z* 356.9096, found *m/z* 356.9099.



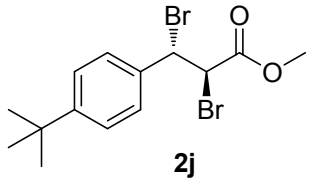
2h

(*trans*)-methyl 2,3-dibromo-3-(*m*-tolyl)propanoate (2h): a white solid (28.0 mg, 83%, d.r. > 19:1), m.p. 68-69 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 3.90 (s, 3H), 4.85 (d, *J* = 12.0 Hz, 1H), 5.31 (d, *J* = 11.6 Hz, 1H), 7.16-7.30 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 138.7, 137.4, 130.2, 128.8, 128.6, 125.1, 53.4, 50.8, 46.6, 21.4; IR (KBr): 3463, 3018, 2948, 1739, 1605, 1436, 1373, 1306, 1248, 1198, 1148, 978, 799, 701, 615, 579, 483 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{11}H_{12}Br_2NaO_2$) requires *m/z* 356.9096, found *m/z* 356.9098.



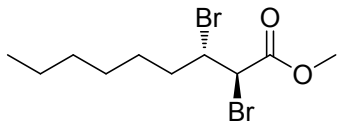
2i

(*trans*)-methyl 2,3-dibromo-3-(*p*-tolyl)propanoate (2i): a white solid (32.0 mg, 95%, d.r. > 19:1), m.p. 96-98 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 3.90 (s, 3H), 4.85 (d, *J* = 12.0 Hz, 1H), 5.34 (d, *J* = 12.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 139.5, 134.6, 129.6, 127.9, 53.4, 50.8, 46.8, 21.3; IR (KBr): 3469, 3007, 2919,2308, 1746, 1610, 1514, 1434, 1374, 1322, 1266, 1187, 1141, 1009, 979, 700, 512 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{11}H_{12}Br_2NaO_2$) requires *m/z* 356.9096, found *m/z* 356.9100.



2j

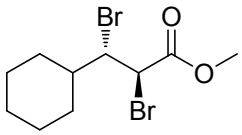
(*trans*)-methyl 2,3-dibromo-3-(4-(*tert*-butyl)phenyl)propanoate (2j): a white solid (35.9mg, 95%, d.r. > 19:1), m.p. 105-106 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 1.32 (s, 9H), 3.89 (s, 3H), 4.86 (d, *J* = 12.0 Hz, 1H), 5.35 (d, *J* = 12.0 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 152.6, 134.4, 127.7, 125.8, 53.4, 50.8, 46.7, 34.7, 31.2; IR (KBr): 3468, 3001, 2954, 2867, 1917, 1747, 1609, 1436, 1365, 1275, 1145, 1020, 834, 654, 589 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{14}H_{18}Br_2NaO_2$) requires *m/z* 398.9566, found *m/z* 398.9574.



2k

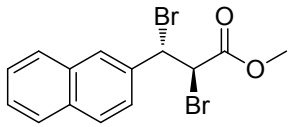
(*trans*)-methyl 2,3-dibromononanoate (2k) : a colorless oil (30.2 mg, 91%, d.r. > 19:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.9 (t,

J = 6.4 Hz, 3H), 1.32-1.60 (m, 8H), 1.77-1.86 (m, 1H), 2.20-2.28 (m, 1H), 3.83 (s, 3H), 4.35-4.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 53.2, 52.8, 47.7, 35.0, 31.5, 28.4, 26.2, 22.5, 14.0; IR (KBr): 3381, 3052, 2956, 2923, 2857, 2309, 1750, 1458, 1438, 1266, 1150, 1022, 740, 565 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{10}H_{18}Br_2NaO_2$) requires *m/z* 350.9566, found *m/z* 350.9574.



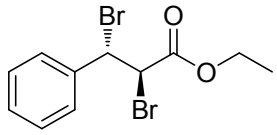
2l

(*trans*)-methyl 2,3-dibromo-3-cyclohexylpropanoate (2l): a colorless oil (31.0 mg, 95%, d.r. = 11:1); ^{1}H NMR(400 MHz, $CDCl_3$): δ 1.10-1.60 (m, 7H), 1.70 (d, *J* = 12.8 Hz, 1H), 1.79-1.82 (m, 2H), 1.95-2.02 (m, 1H), 3.83 (s, 3H), 4.39 (dd, *J* = 2.0 Hz, 11.6 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 59.9, 53.2, 45.4, 39.0, 32.1, 25.9, 25.9, 25.5, 25.4; IR (KBr): 3482, 3007, 2929, 2855, 1752, 1449, 1437, 1369, 1301, 1276, 1214, 1158, 1018, 988, 569 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{10}H_{16}Br_2NaO_2$) requires *m/z* 348.9409, found *m/z* 348.9420.



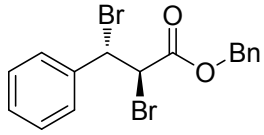
2m

(*trans*)-methyl 2,3-dibromo-3-(naphthalen-2-yl)propanoate (2m): a white solid (36.5 mg, 98%, d.r. > 19 : 1), m.p. 92-93 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 3.92 (s, 3H), 4.98 (d, *J* = 11.6 Hz, 1H), 5.54 (d, *J* = 11.6 Hz, 1H), 7.48-7.54 (m, 3H), 7.83-7.90 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 134.5, 133.5, 132.8, 129.2, 128.2, 128.0, 127.8, 127.1, 126.8, 124.3, 53.5, 51.2, 46.5; IR (KBr): 3467, 3050, 3003, 2849, 1747, 1599, 1437, 1377, 1280, 1267, 1197, 1145, 1024, 747, 575, 476 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{14}H_{12}Br_2NaO_2$) requires *m/z* 392.9096, found *m/z* 392.9097.



2n

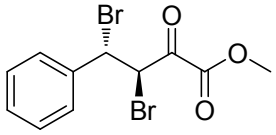
(*trans*)-ethyl 2,3-dibromo-3-phenylpropanoate (2n): a white solid (29.5 mg, 88%, d.r. > 19 :1), m.p. 71-72 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 1.38 (t, *J* = 7.2 Hz, 3H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.83 (d, *J* = 11.6 Hz, 1H), 5.35 (d, *J* = 12.0 Hz, 1H), 7.35-7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 137.6, 129.4, 128.9, 128.0, 62.6, 50.7, 47.0, 13.9; IR (KBr): 3455, 3007, 2988, 2939, 2902, 1974, 1739, 1455, 1394, 1274, 1217, 1149, 1018, 772, 694, 620, 605, 560 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{11}H_{12}Br_2NaO_2$) requires *m/z* 356.9096, found *m/z* 356.9104.



2o

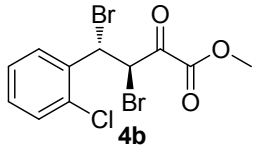
(*trans*)-benzyl 2,3-dibromo-3-phenylpropanoate (2o): a white solid (34.7 mg, 87%, d.r. > 19 :1) 95-96 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ

4.89 (d, J = 12.0 Hz, 1H), 5.31 (d, J = 4.0 Hz, 2H), 5.35 (d, J = 12.0 Hz, 1H), 7.36-7.45 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 137.5, 134.7, 129.4, 128.9, 128.6, 128.4, 128.0, 68.2, 50.6, 46.9; IR (KBr): 3469, 3061, 3011, 2348, 1954, 1746, 1584, 1495, 1454, 1438, 1387, 1212, 1143, 981, 732, 694, 732, 694, 609, 592 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{16}H_{14}Br_2NaO_2$) requires *m/z* 418.9253, found *m/z* 418.9259.



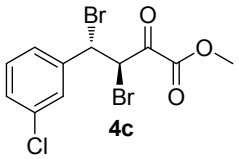
4a

(*trans*)-methyl 3,4-dibromo-2-oxo-4-phenylbutanoate (4a):a white solid (32.2 mg, 92%, d.r. = 8:1), m.p. 109-110 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 4.00 (s, 3H), 5.48 (d, J = 12.0 Hz, 1H), 5.77 (d, J = 11.6 Hz, 1H), 7.38-7.48 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.4, 159.4, 137.3, 129.6, 129.0, 128.2, 53.9, 48.1, 47.5; IR (KBr): 3458, 3062, 3015, 2850, 1962, 1733, 1689, 1453, 1438, 1310, 1293, 1239, 1208, 1146, 918, 732, 698, 595, 572, 471 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{11}H_{10}Br_2NaO_3$) requires *m/z* 370.8889, found *m/z* 370.8895.



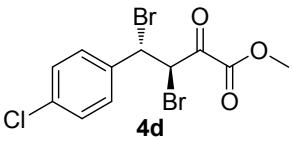
4b

(*trans*)-methyl 3,4-dibromo-4-(2-chlorophenyl)-2-oxobutanoate (4b): a white solid (31.1 mg, 81%, d.r. = 7:1), m.p. 70-71 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 4.01 (s, 3H), 5.88 (s, 1H), 6.06 (s, 1H), 7.30-7.44 (m, 3H), 7.57-7.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.0, 159.5, 134.9, 134.0, 130.5, 130.2, 129.3, 127.7, 53.9, 46.1, 43.2; IR (KBr): 3449, 3005, 2991, 1727, 1695, 1479, 1441, 1321, 1286, 1239, 1207, 1139, 1086, 1063, 1037, 763, 731, 678, 589, 450 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{11}H_9Br_2ClNaO_3$) requires *m/z* 404.8499, found *m/z* 404.8503.



4c

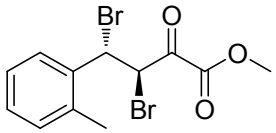
(*trans*)-methyl 3,4-dibromo-4-(3-chlorophenyl)-2-oxobutanoate (4c) : a white solid (36.2 mg, 94%, d.r. = 11:1), m.p. 95-96 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 4.00 (s, 3H), 5.42 (d, J = 12.0 Hz, 1H), 5.71 (d, J = 11.6 Hz, 1H), 7.34-7.37 (m, 3H), 7.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.1, 159.3, 139.3, 134.8, 130.2, 129.7, 128.3, 126.4, 53.9, 47.1, 46.7; IR (KBr): 3458, 3029, 3007, 2949, 1736, 1597, 1572, 1479, 1447, 1435, 1312, 1281, 1245, 1204, 1145, 1043, 847, 798, 699, 686, 583, 447 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{11}H_9Br_2ClNaO_3$) requires *m/z* 404.8499, found *m/z* 404.8504.



4d

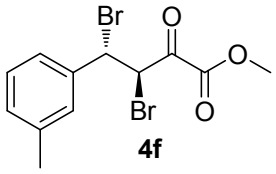
(*trans*)-methyl 3,4-dibromo-4-(4-chlorophenyl)-2-oxobutanoate (4d): a white solid (36.9 mg, 96%, d.r. = 9:1), m.p. 94-96 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 4.00 (s, 3H), 5.45 (d, J = 11.6 Hz, 1H),

5.72 (d, J = 12.0 Hz, 1H), 7.38-7.43 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.1, 159.3, 135.9, 135.4, 129.5, 129.2, 53.9, 47.1, 47.0; IR (KBr): 3458, 2997, 2953, 1732, 1686, 1592, 1492, 1439, 1413, 1375, 1318, 1300, 1279, 1242, 1205, 1092, 1041, 832, 746, 563 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{11}H_9Br_2ClNaO_3$) requires *m/z* 404.8499, found *m/z* 404.8503.



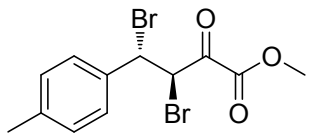
4e

(*trans)*-methyl 3,4-dibromo-2-oxo-4-(*o*-tolyl)butanoate (4e): a white solid (30.0 mg, 82%, d.r.= 7:1), m.p. 61-62 ^{o}C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 2.46 (s, 3H), 4.00 (s, 3H), 5.81 (d, J = 11.6 Hz, 1H), 5.86 (d, J = 11.6 Hz, 1H), 7.19-7.33 (m, 3H), 7.52-7.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.4, 159.5, 136.5, 135.4, 130.9, 129.3, 127.2, 127.0, 53.9, 46.9, 43.8, 19.4; IR (KBr): 3452, 3015, 3000, 2952, 1734, 1604, 1493, 1463, 1449, 1434, 1322, 1288, 1239, 1191, 1163, 1145, 1079, 1042, 789, 770, 725, 599 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{12}H_{12}Br_2NaO_3$) requires *m/z* 384.9045, found *m/z* 384.9053.



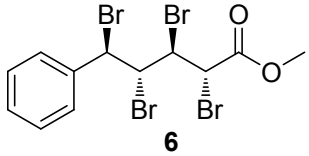
4f

(*trans*)-methyl 3,4-dibromo-2-oxo-4-(*m*-tolyl)butanoate (4f) : a white solid (33.3 mg, 92%, d.r. = 12:1), m.p. 106-108 ^{o}C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 4.00 (s, 3H), 5.45 (d, J = 11.6 Hz, 1H), 5.77 (d, J = 12.0 Hz, 1H), 7.19 (d, J = 7.2 Hz, 1H), 7.25-7.32 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.4, 159.4, 138.8, 137.1, 130.4, 128.8, 128.7, 125.2, 53.9, 48.2, 47.4, 21.4; IR (KBr): 3453, 3017, 3000, 2952, 2923, 1734, 1691, 1602, 1590, 1487, 1435, 1287, 1231, 1055, 800, 704, 590 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{12}H_{12}Br_2NaO_3$) requires *m/z* 384.9045, found *m/z* 384.9052.



4g

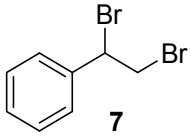
(*trans*)-methyl 3,4-dibromo-2-oxo-4-(*p*-tolyl)butanoate (4g) : a white solid (33.9 mg, 93%, d.r. = 9:1), m.p. 81-82 ^{o}C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 2.38 (s,, 3H), 4.00 (s, 3H), 5.48 (d, J = 11.6 Hz, 1H), 5.77 (d, J = 11.6 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.4, 159.4, 139.7, 134.4, 129.7, 128.0, 53.8, 48.3, 47.5, 21.3; IR (KBr): 3445, 3015, 2955, 2927, 1915, 1727, 1685, 1610, 1513, 1450, 1306, 1288, 1241, 1213, 1187, 1036, 820, 718, 601, 501 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{12}H_{12}Br_2NaO_3$) requires *m/z* 384.9045, found *m/z* 384.9052.



6

(*anti*)-methyl 2,3,4,5-tetrabromo-5-phenylpentanoate (6), white solid (35.0 mg, 69%, d.r. = 10 :1), m.p. 145-146 ^{o}C; ^{1}H NMR(400

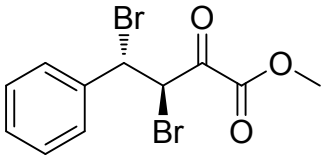
MHz, $CDCl_3$): δ 3.89 (s, 3H), 4.72 (d, *J* = 10.8 Hz, 1H), 5.06 (d, *J* = 10.8 Hz, 1H), 5.23 (d, *J* = 11.2 Hz, 1H), 5.31 (d, *J* = 11.2 Hz, 1H), 7.38-7.41 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 139.0, 129.3, 128.9, 128.1, 57.0, 55.0, 54.7, 53.6, 47.2; IR (KBr): 3470, 3001, 2952, 2290, 2126, 1957, 1878, 1749, 1435, 1269, 1144, 1023, 691, 603, 509 cm^{-1}; HRMS (ESI+) exact mass calculated for $[M+Na]^+$ ($C_{12}H_{12}Br_4NaO_2$) requires *m/z* 526.7463, found *m/z* 526.7463.



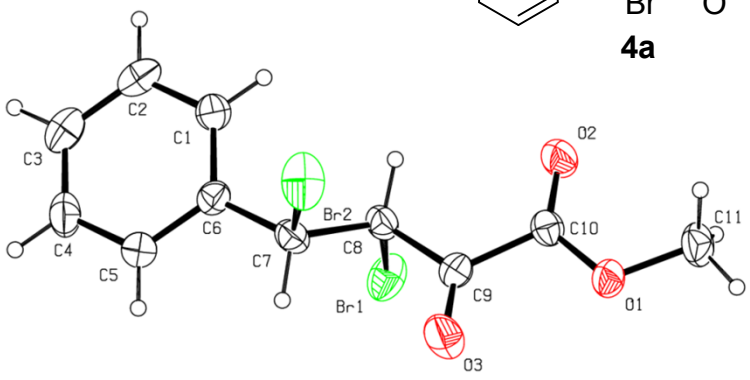
7

(1,2-dibromoethyl)benzene (7), white solid (13.0 mg, 49%), m.p. 69-71 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ 4.02 (t, *J* = 10.4 Hz, 1H), 4.08 (dd, *J* = 5.6, 10.2 Hz, 1H), 5.14 (dd, *J* = 5.2, 10.6 Hz, 1H), 7.33-7.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 129.2, 128.9, 127.7, 50.9, 35.0; IR (KBr):3365, 3032, 2923, 2854, 1455, 1433, 1265, 1134, 908, 769, 739, 693, 591 cm^{-1}; GC/MS *m/z* (rel. intensity): 104 (100), 183 (48), 185 (46), 262 (0.9), 264 (1.8), 266 (0.9).

7. X-Ray structure of 4a



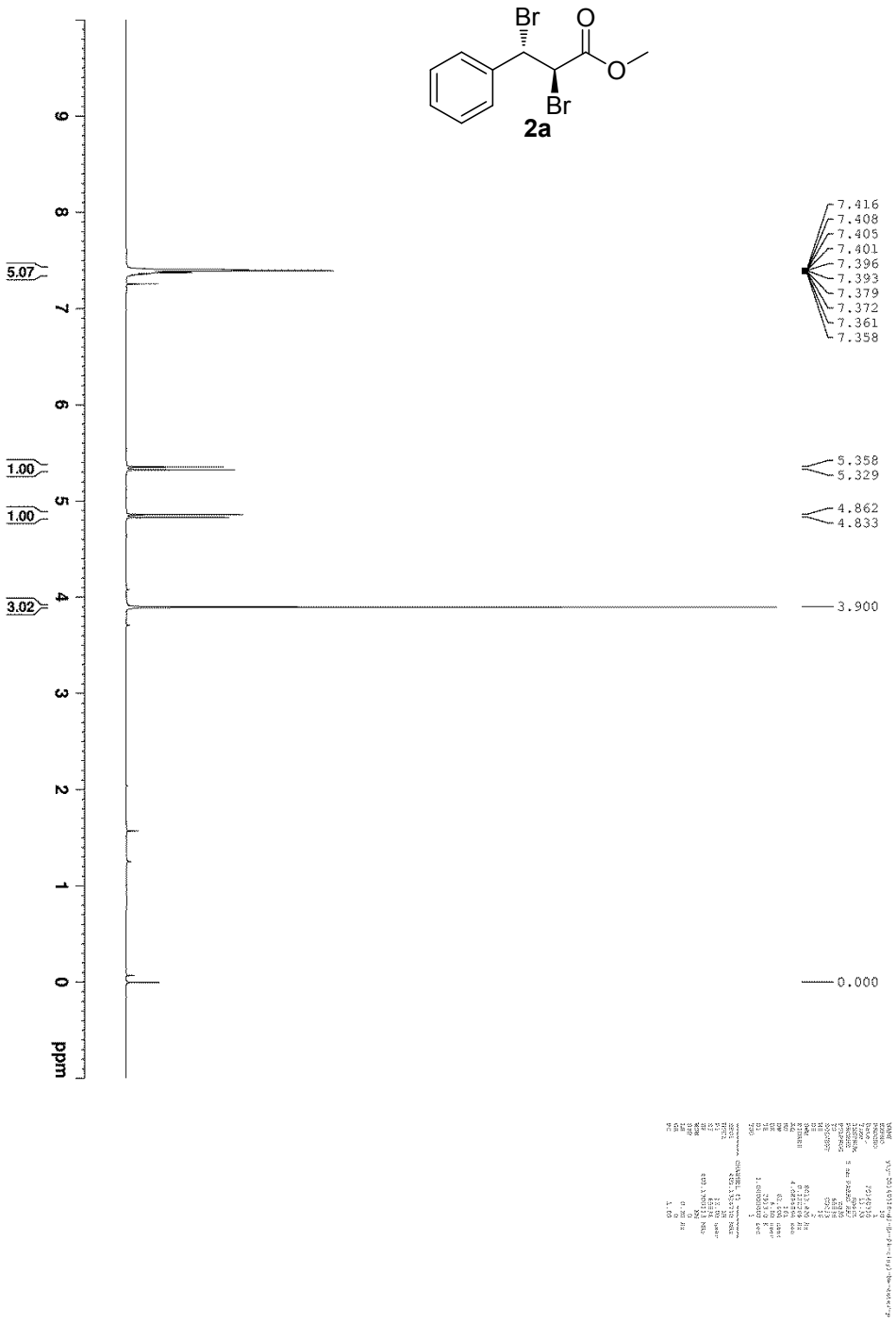
4a



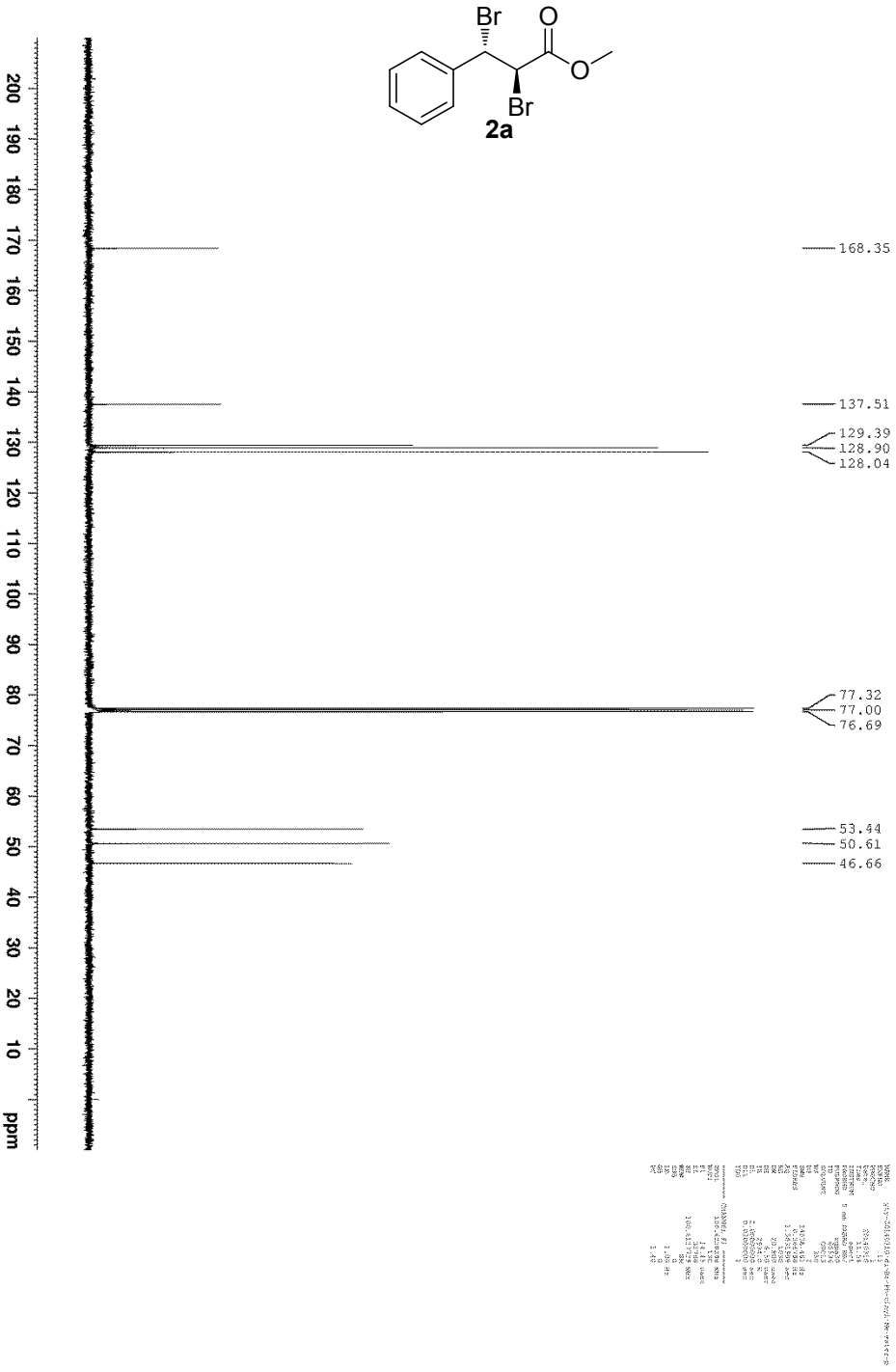
CCDC 992325 (**4a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

8. NMR Spectra

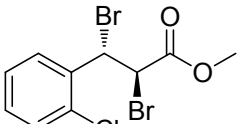
^{1}H NMR spectrum of compound **2a** ($CDCl_3$, 400MHz)

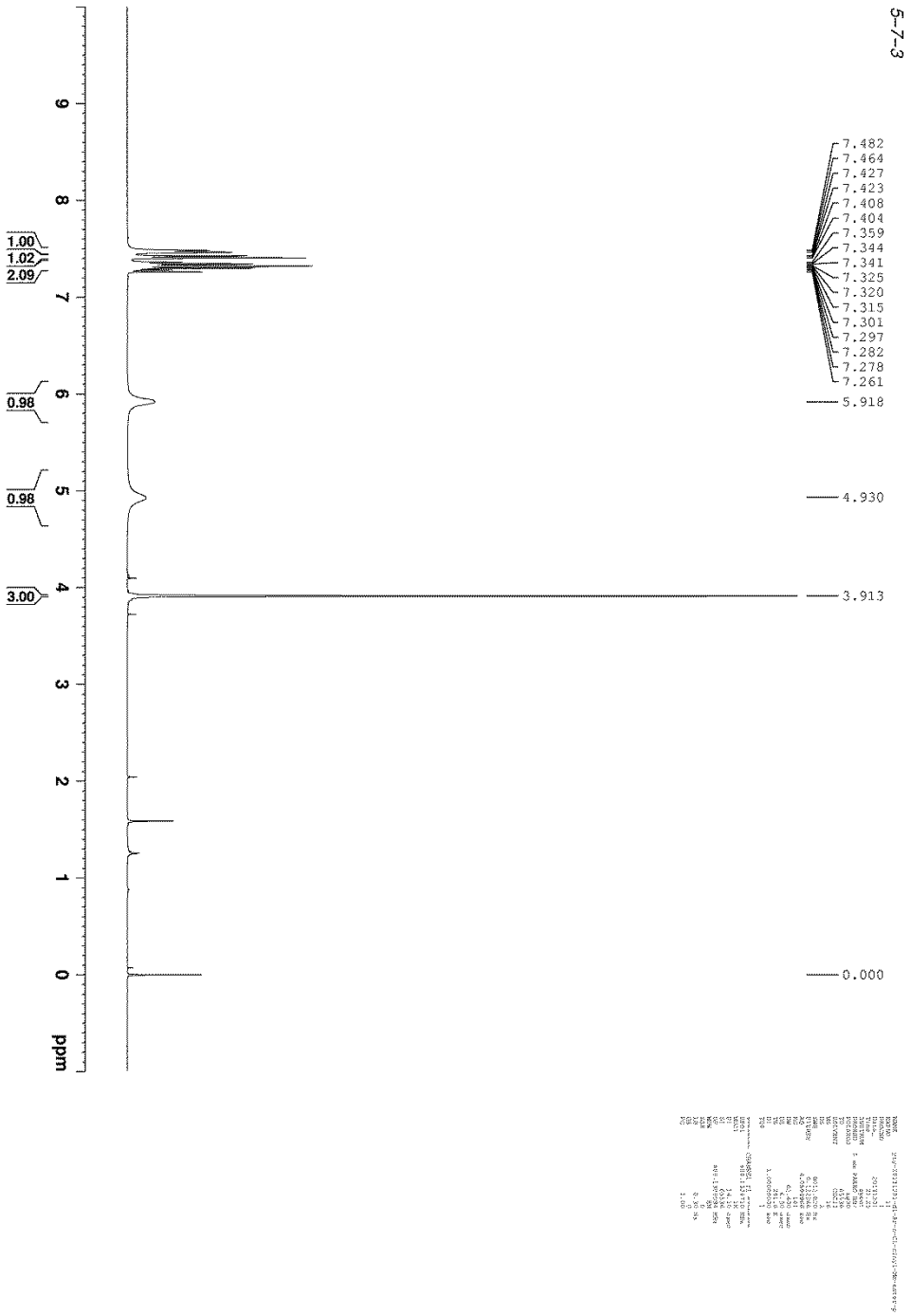


^{13}C NMR spectrum of compound **2a** ($CDCl_3$, 100MHz)

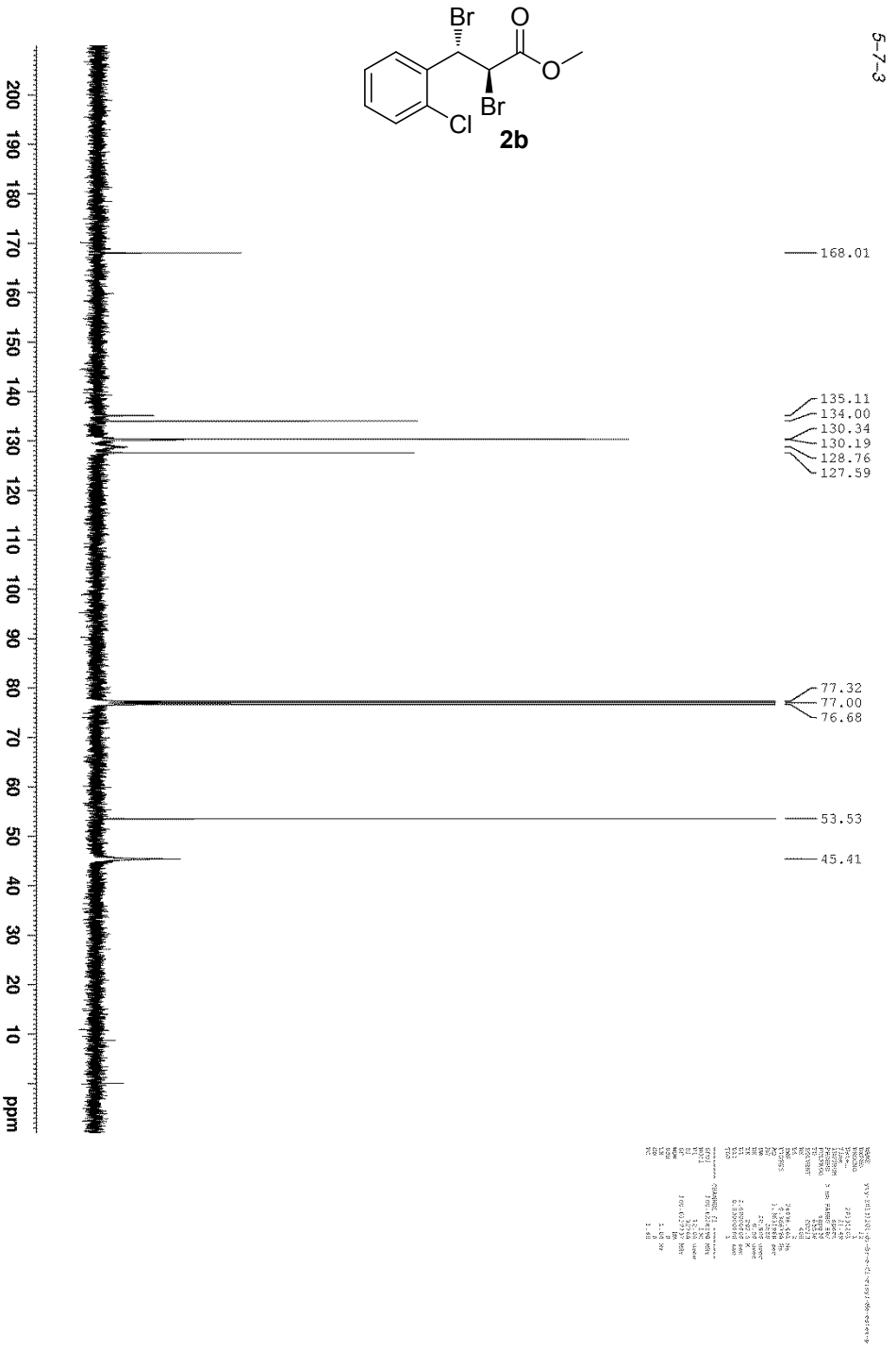


^{1}H NMR spectrum of compound **2b** ($CDCl_3$, 400MHz)

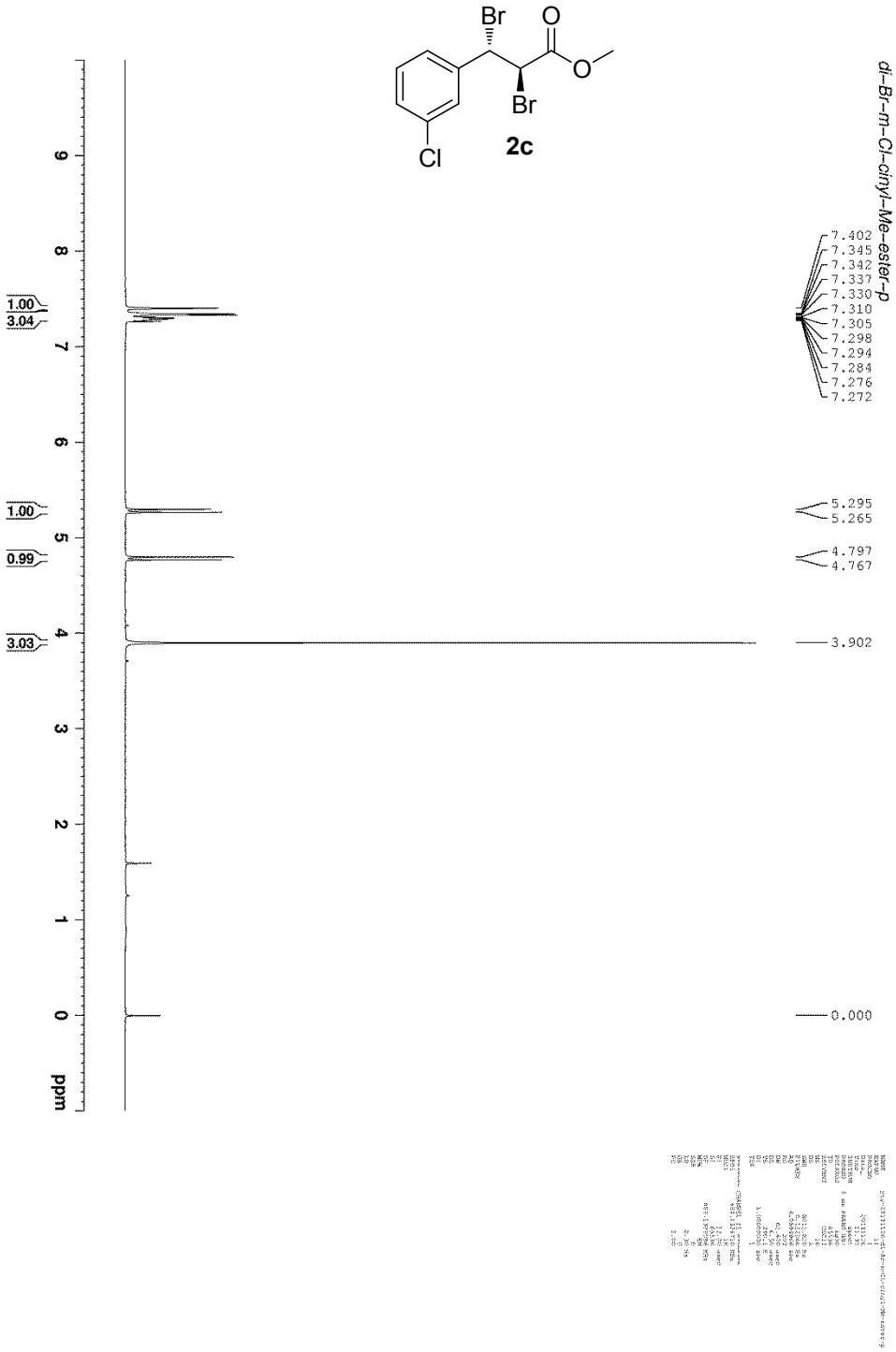




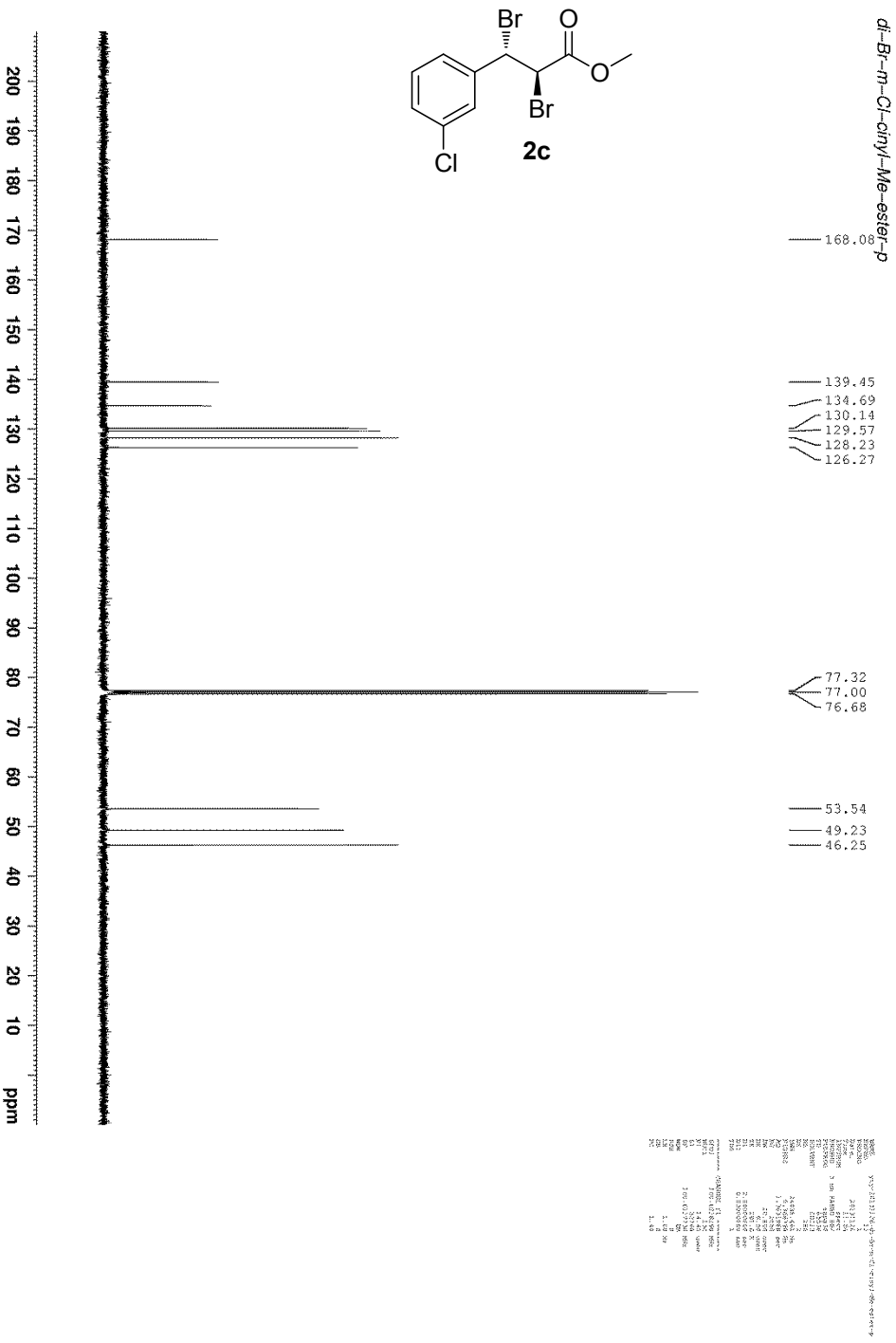
^{13}C NMR spectrum of compound **2b** ($CDCl_3$, 100MHz)



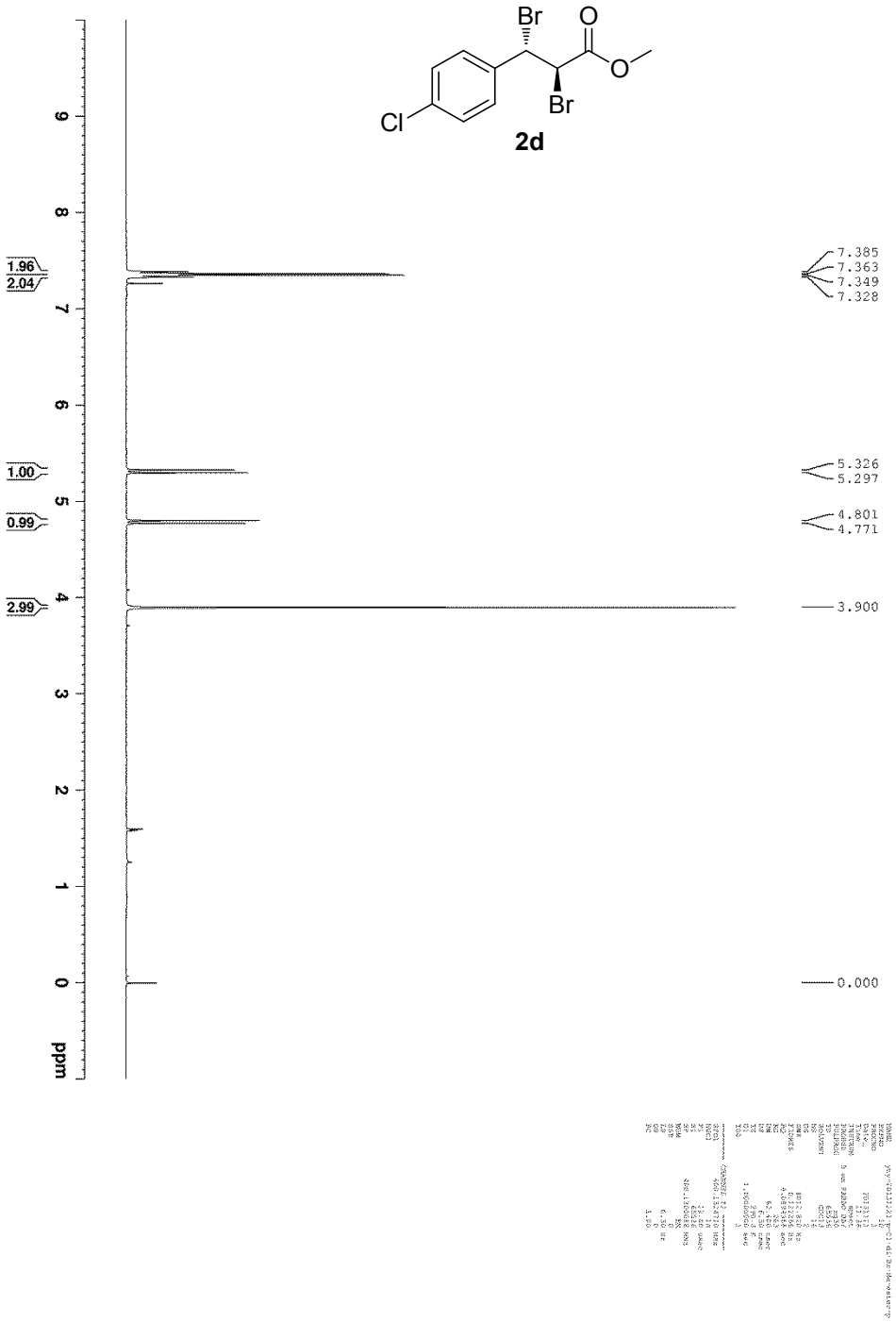
^{1}H NMR spectrum of compound **2c** ($CDCl_3$, 400MHz)



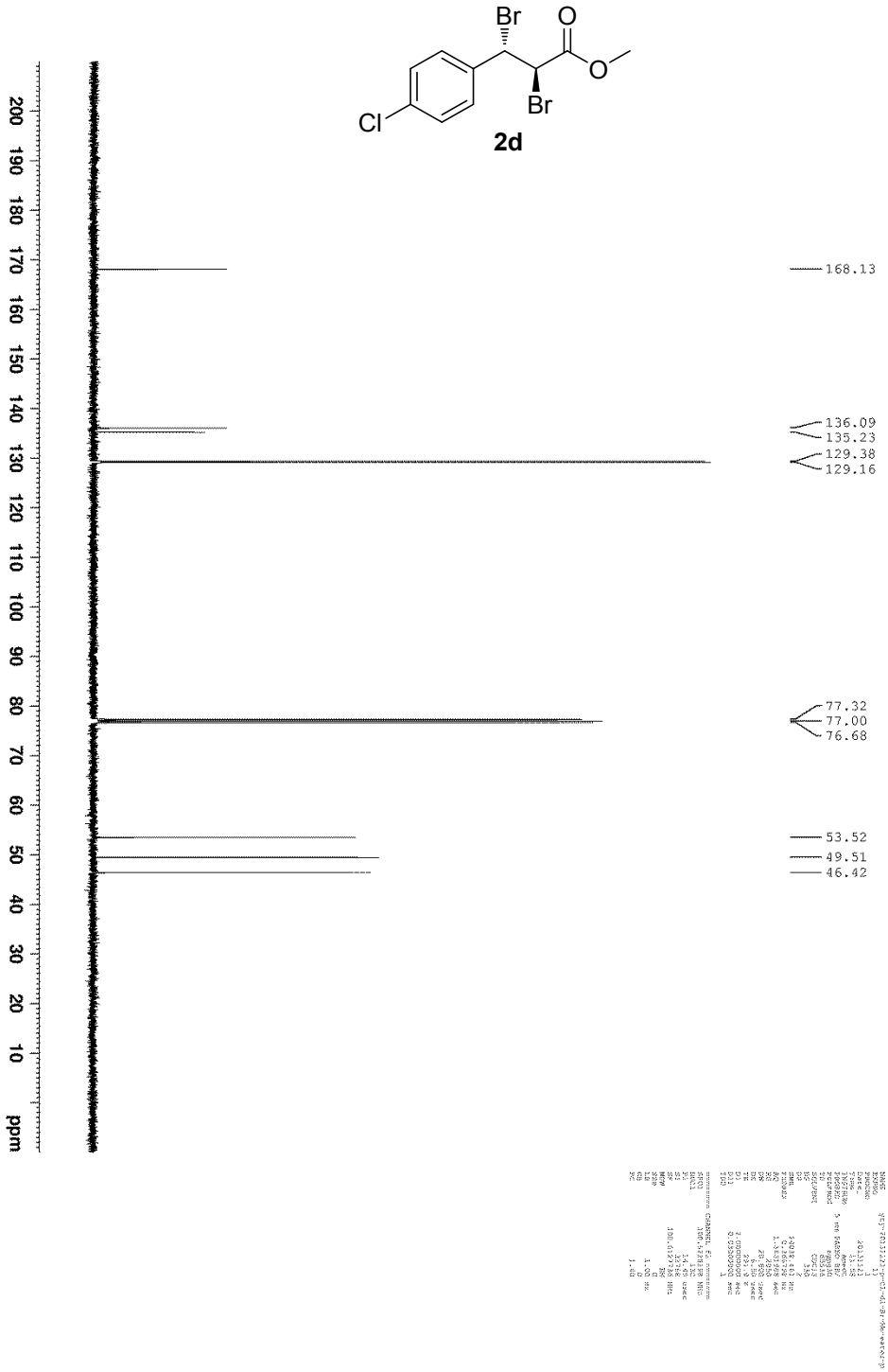
^{13}C NMR spectrum of compound **2c** ($CDCl_3$, 100MHz)



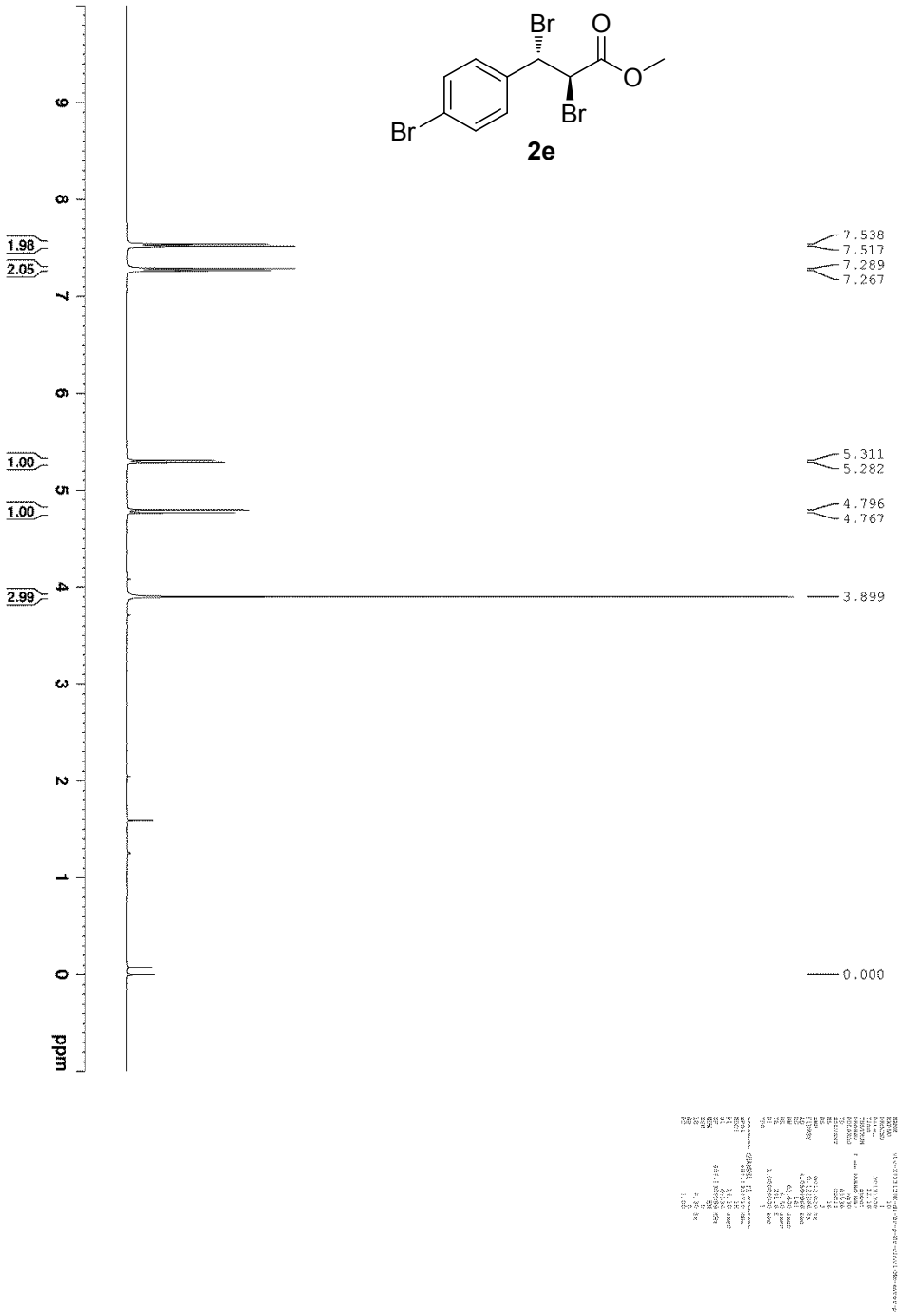
^{1}H NMR spectrum of compound **2d** ($CDCl_3$, 400 MHz)



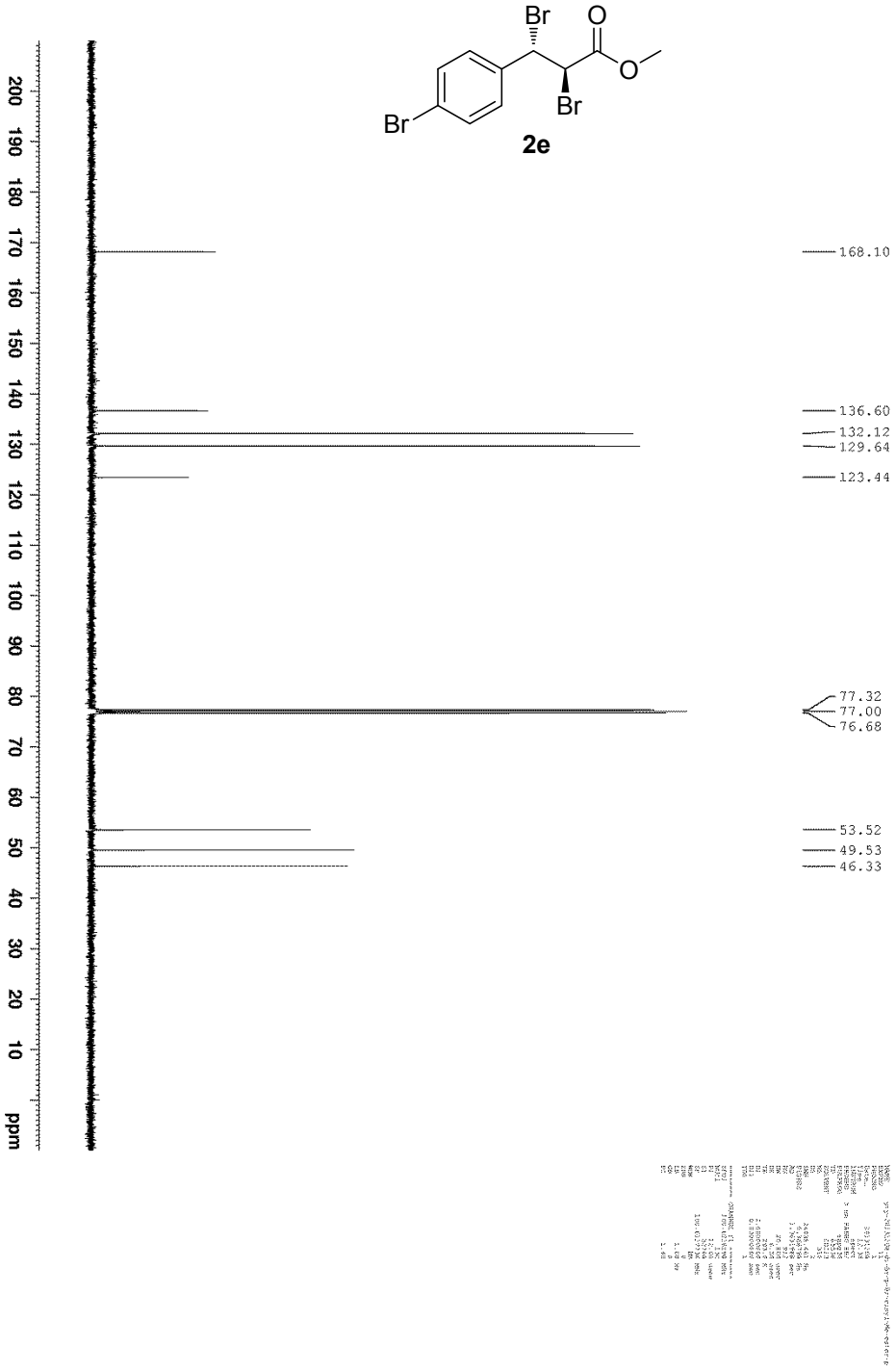
^{13}C NMR spectrum of compound **2d** ($CDCl_3$, 100 MHz)



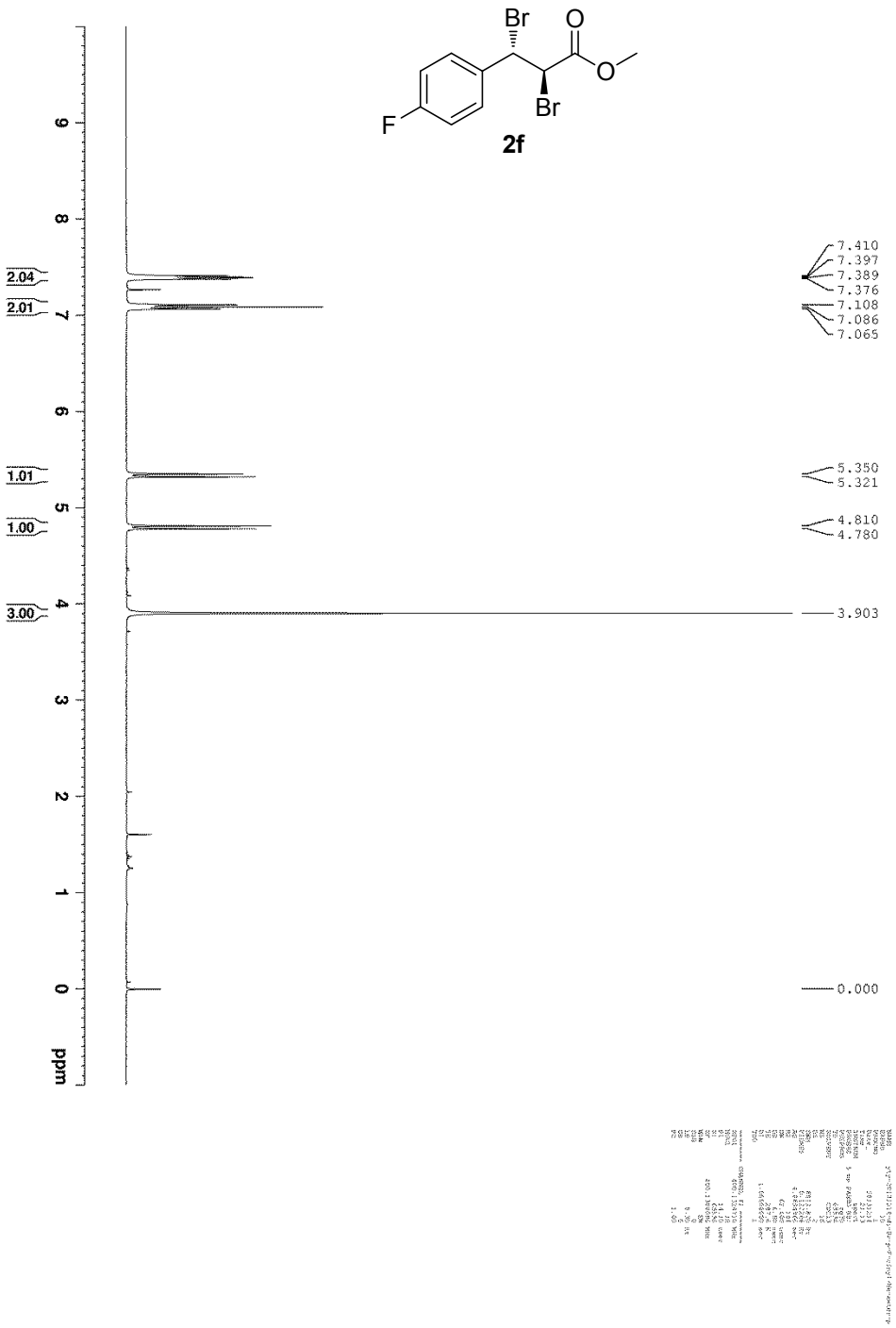
^{1}H NMR spectrum of compound **2e** ($CDCl_3$, 400 MHz)



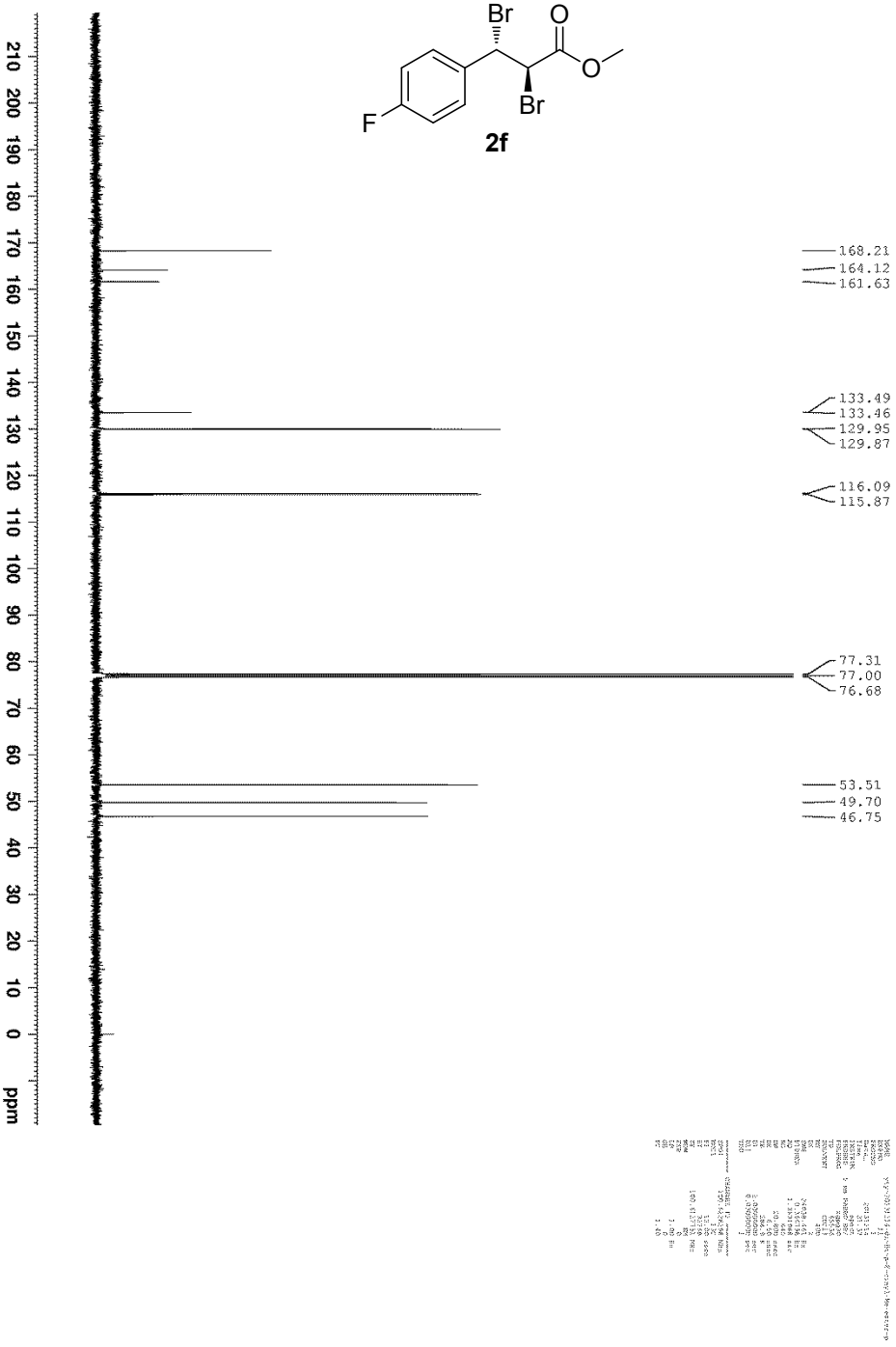
^{13}C NMR spectrum of compound **2e** ($CDCl_3$, 100 MHz)



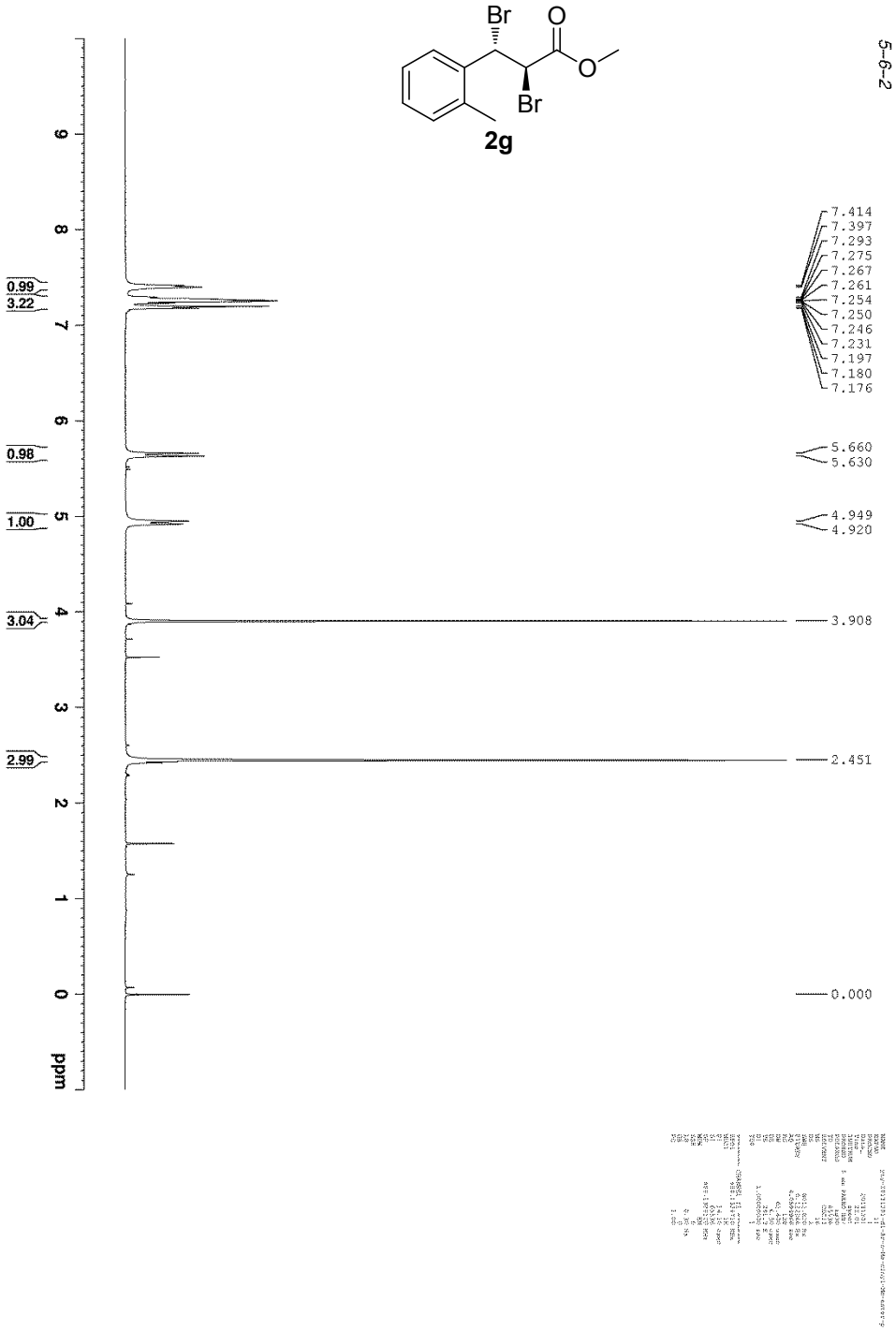
^{1}H NMR spectrum of compound **2f** ($CDCl_3$, 400 MHz)



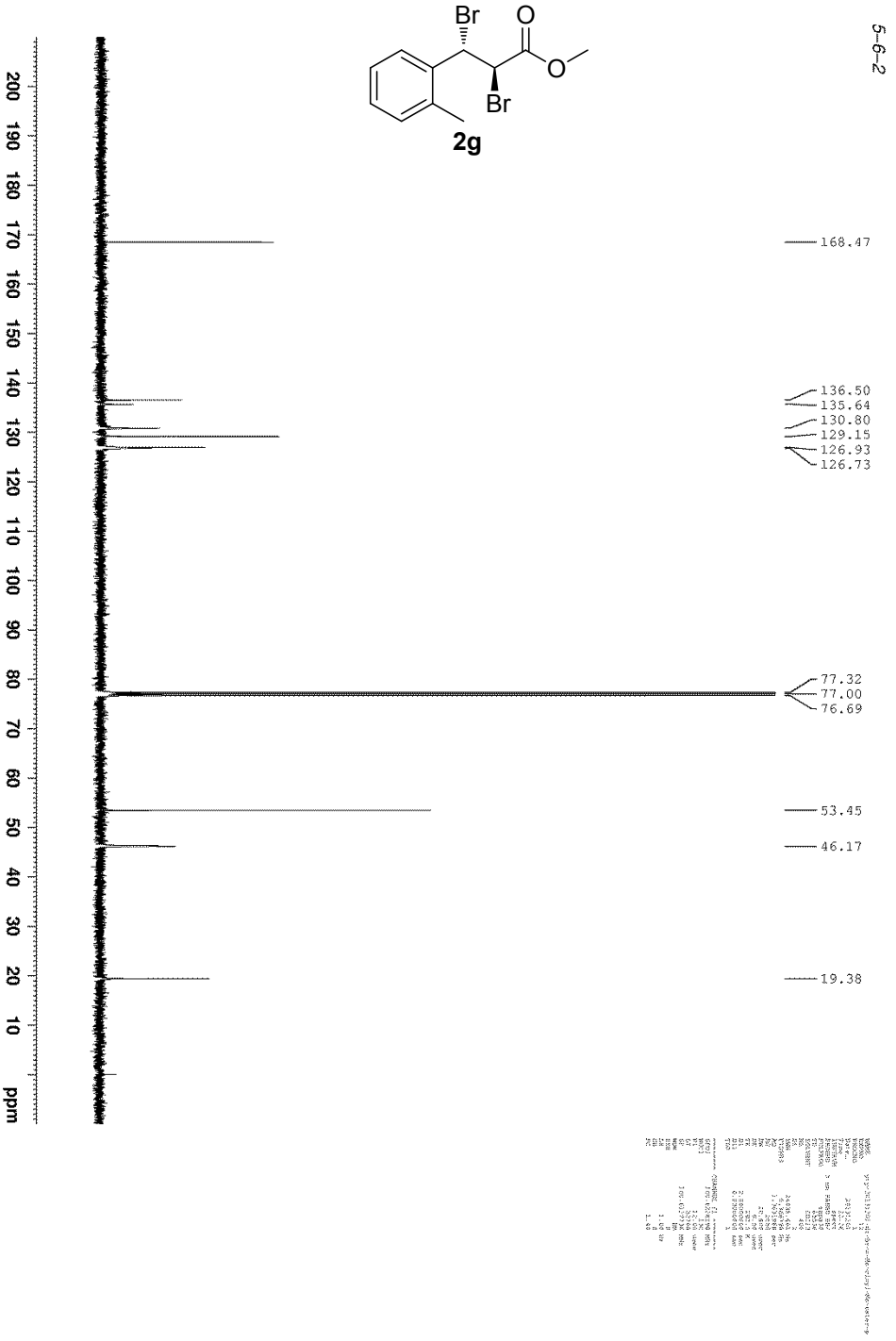
^{13}C NMR spectrum of compound **2f** ($CDCl_3$, 100 MHz)



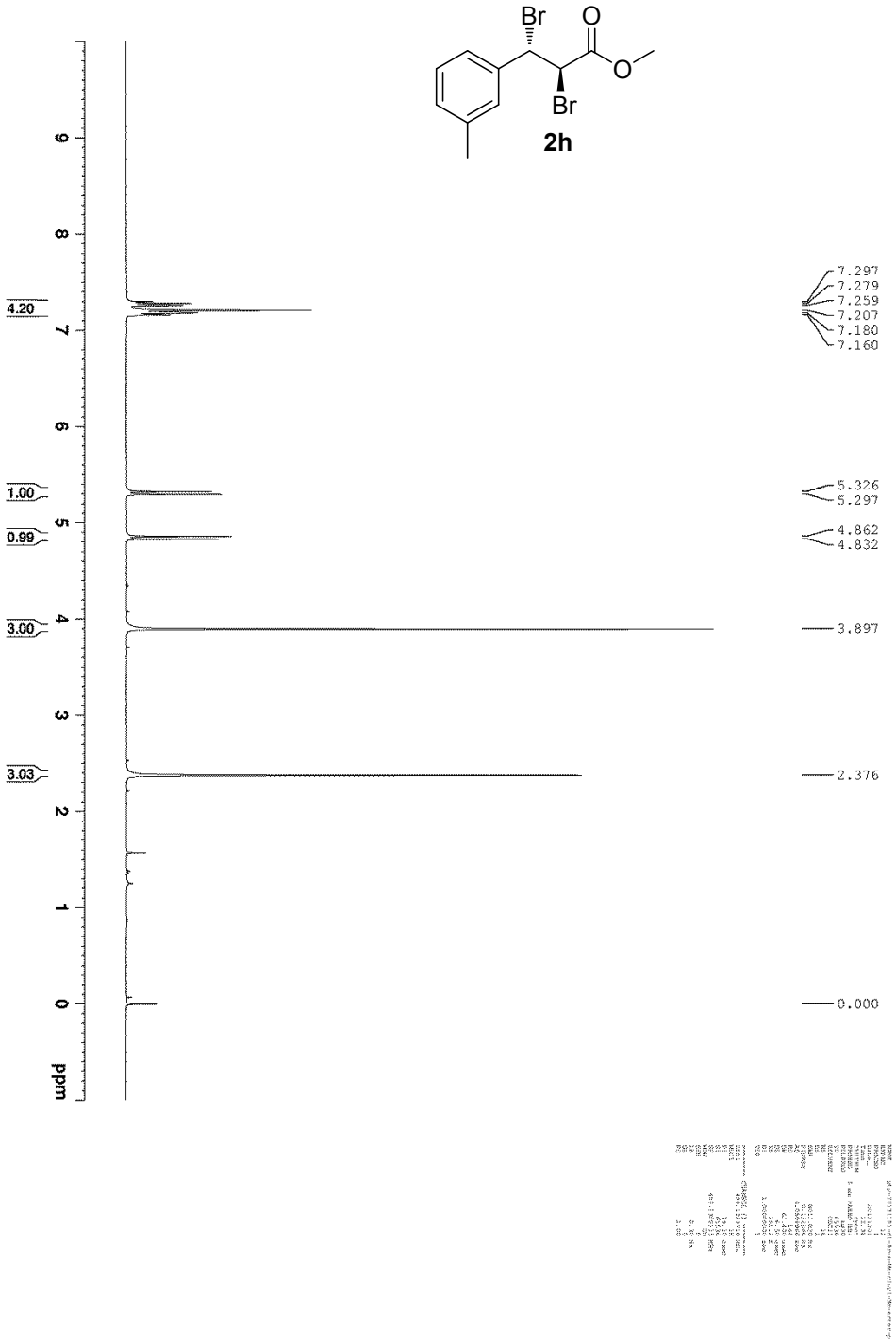
^{1}H NMR spectrum of compound **2g** ($CDCl_3$, 400 MHz)



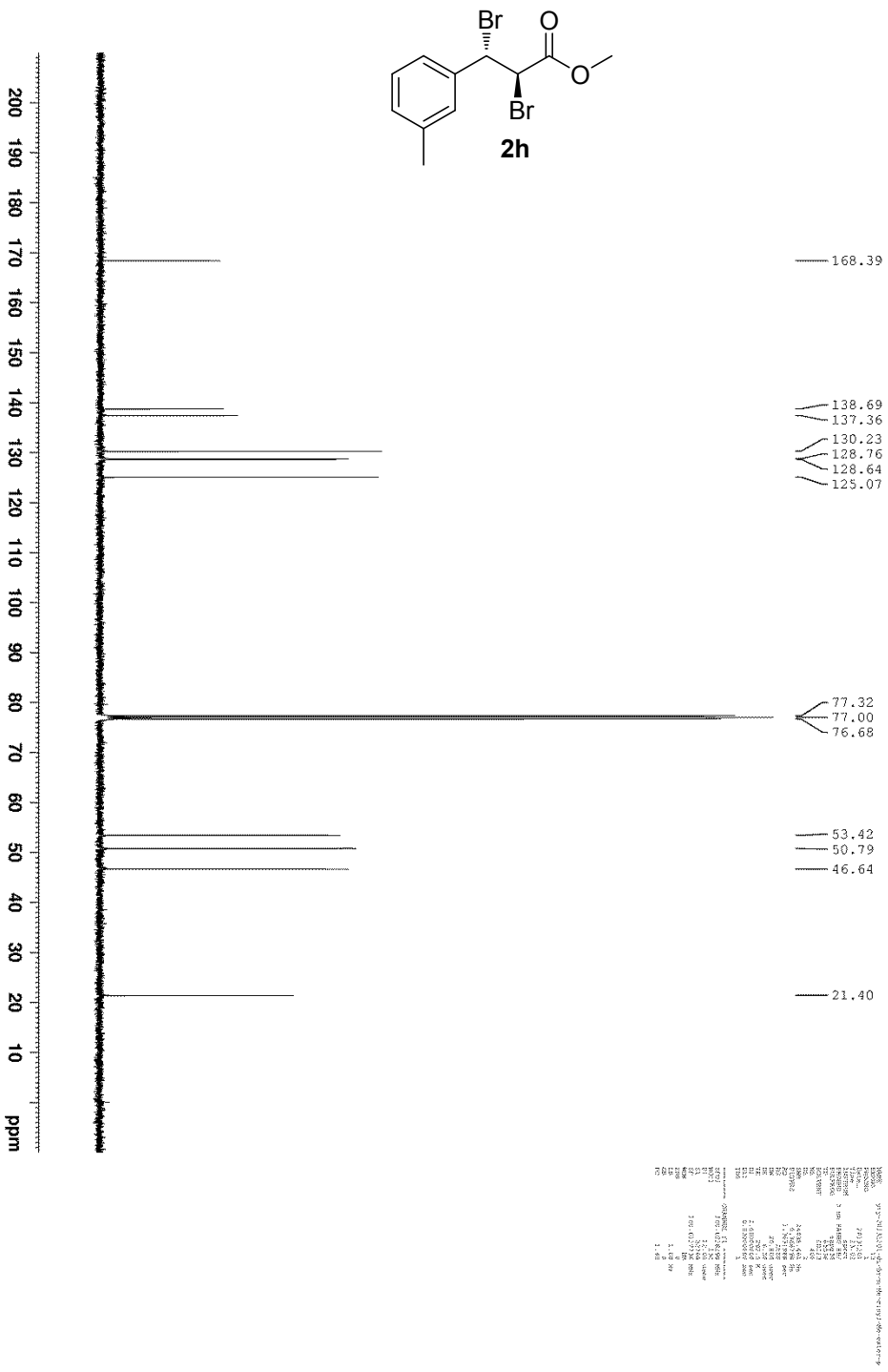
^{13}C NMR spectrum of compound **2g** ($CDCl_3$, 100 MHz)



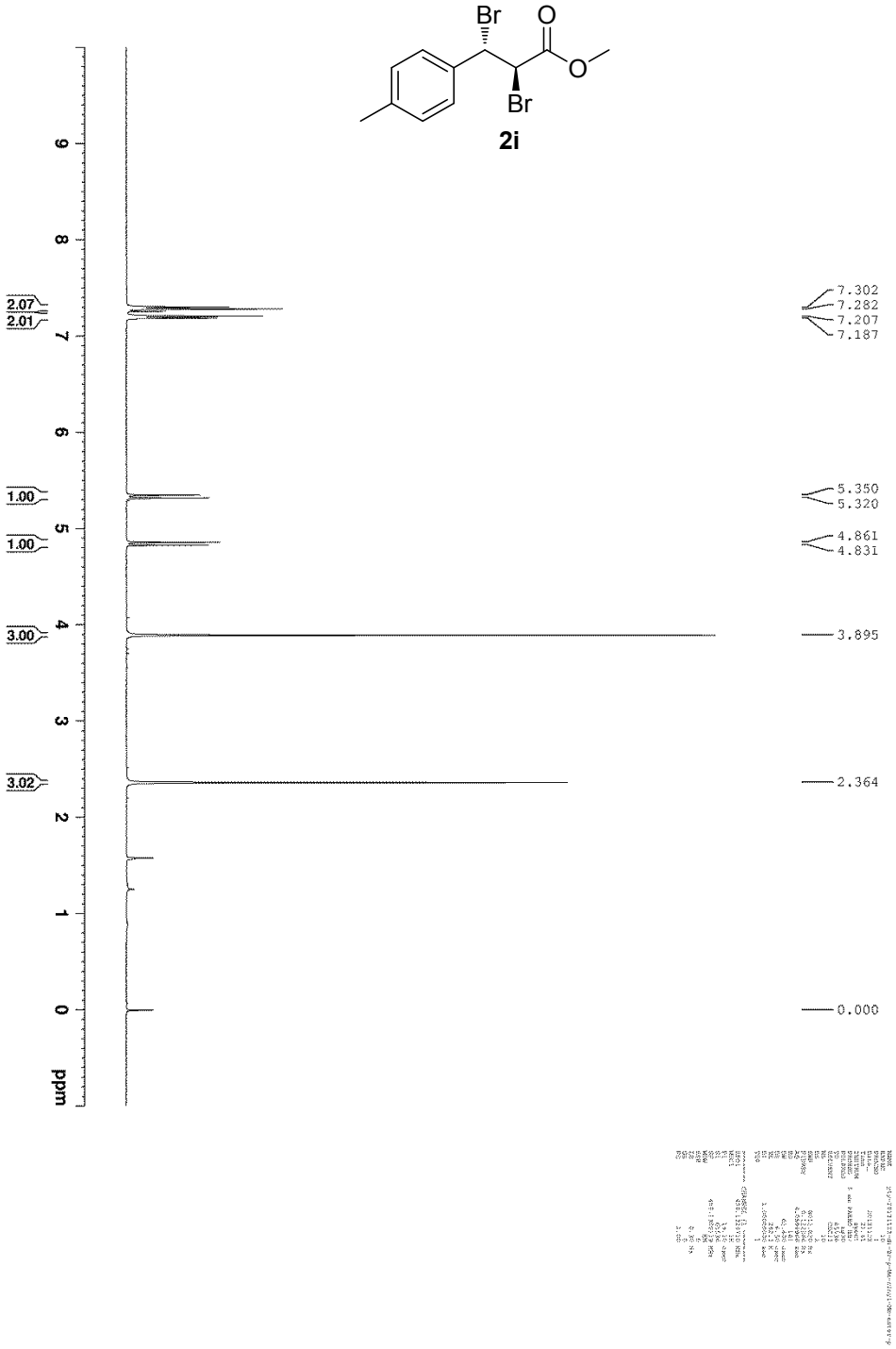
^{1}H NMR spectrum of compound **2h** ($CDCl_3$, 400 MHz)



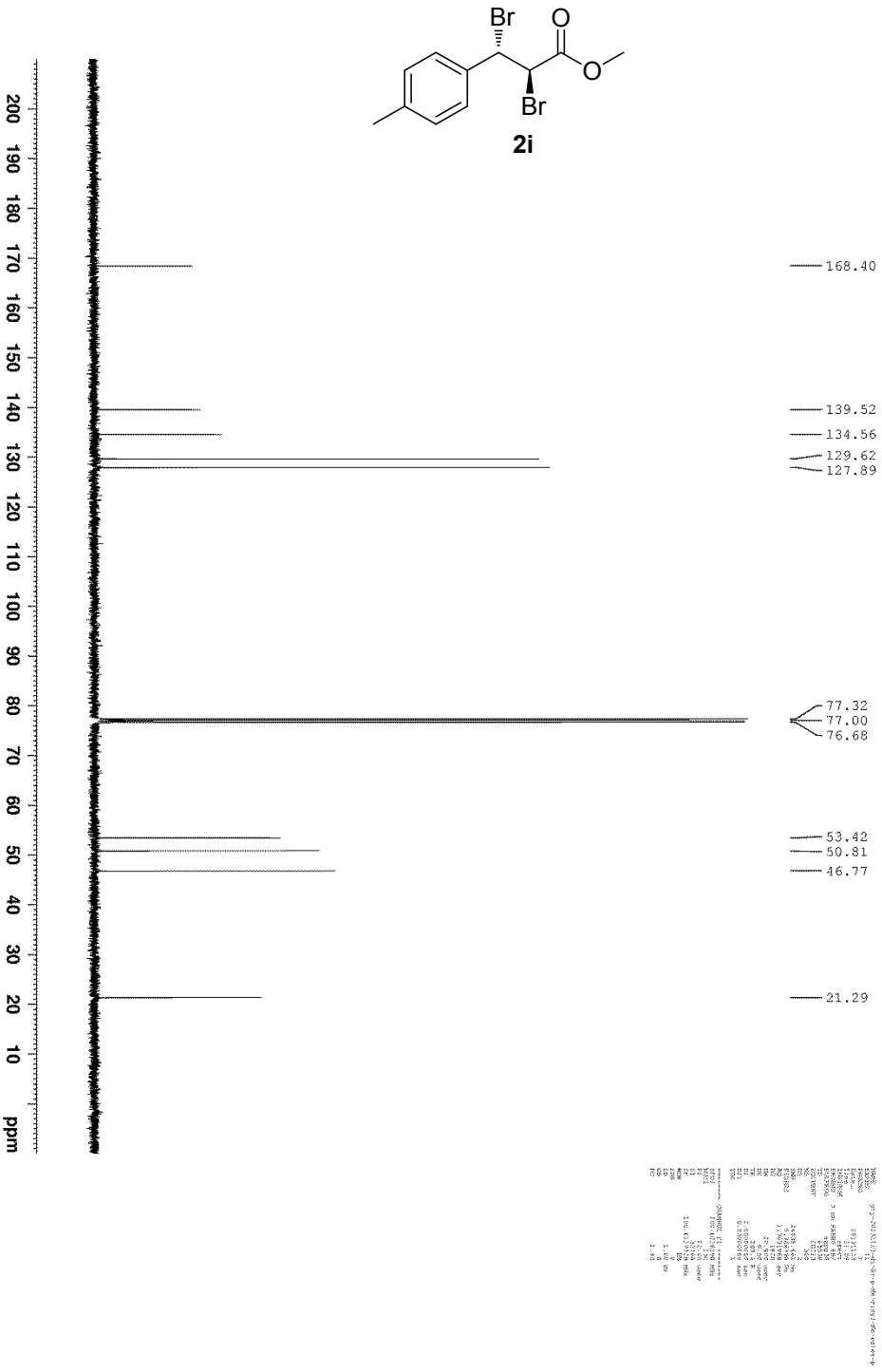
^{13}C NMR spectrum of compound **2h** ($CDCl_3$, 100 MHz)



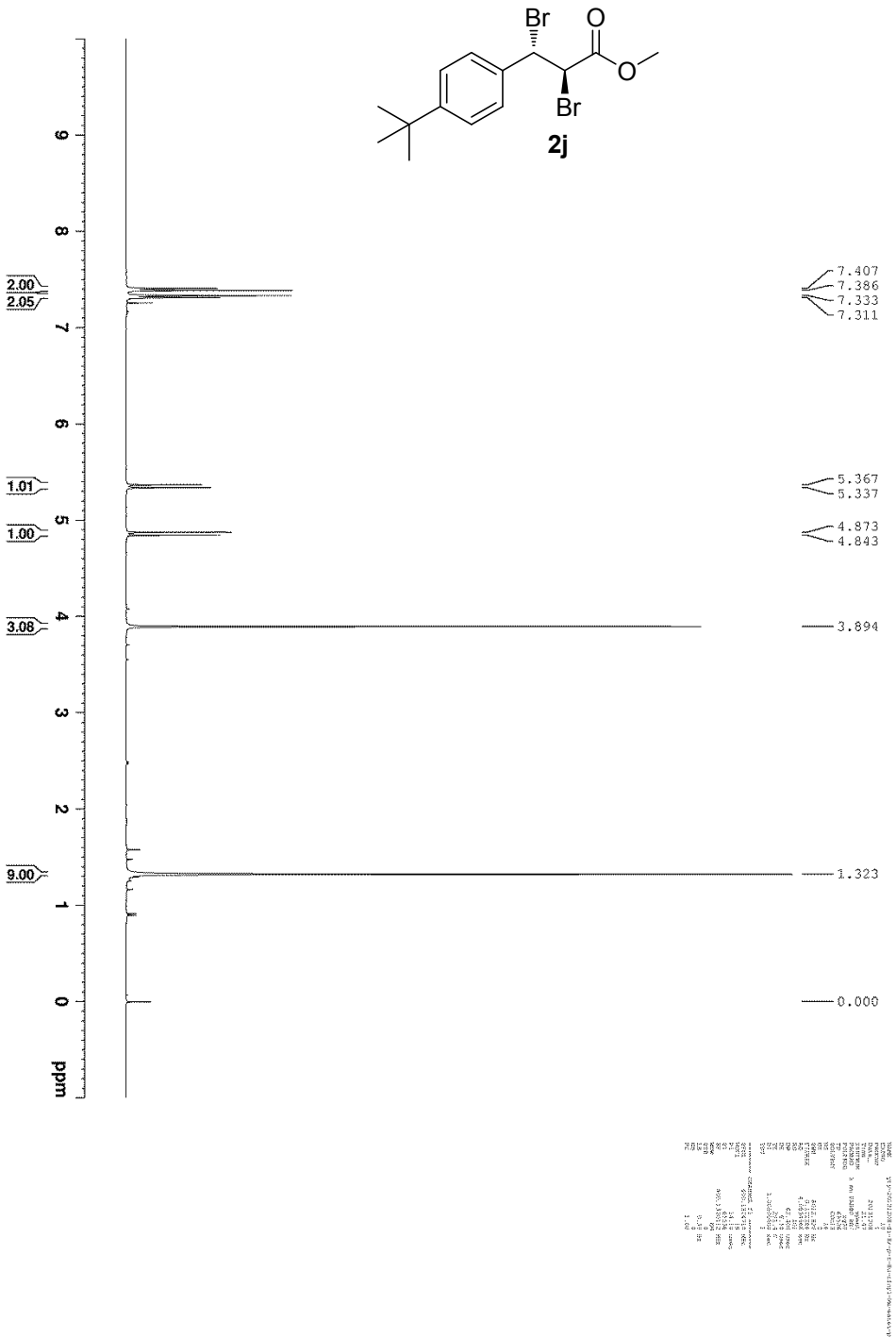
^{1}H NMR spectrum of compound **2i** ($CDCl_3$, 400 MHz)



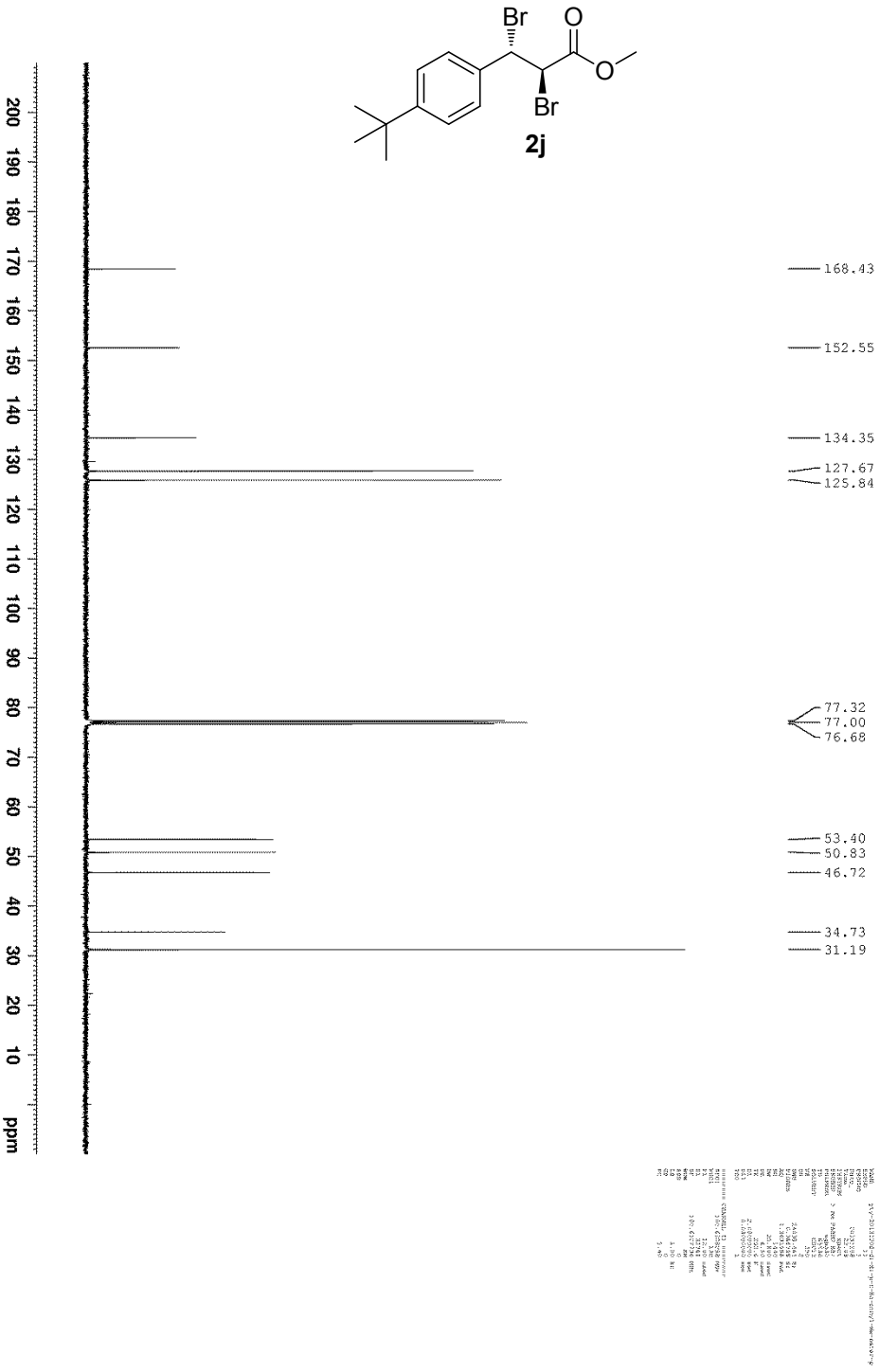
^{13}C NMR spectrum of compound **2i** ($CDCl_3$, 100 MHz)



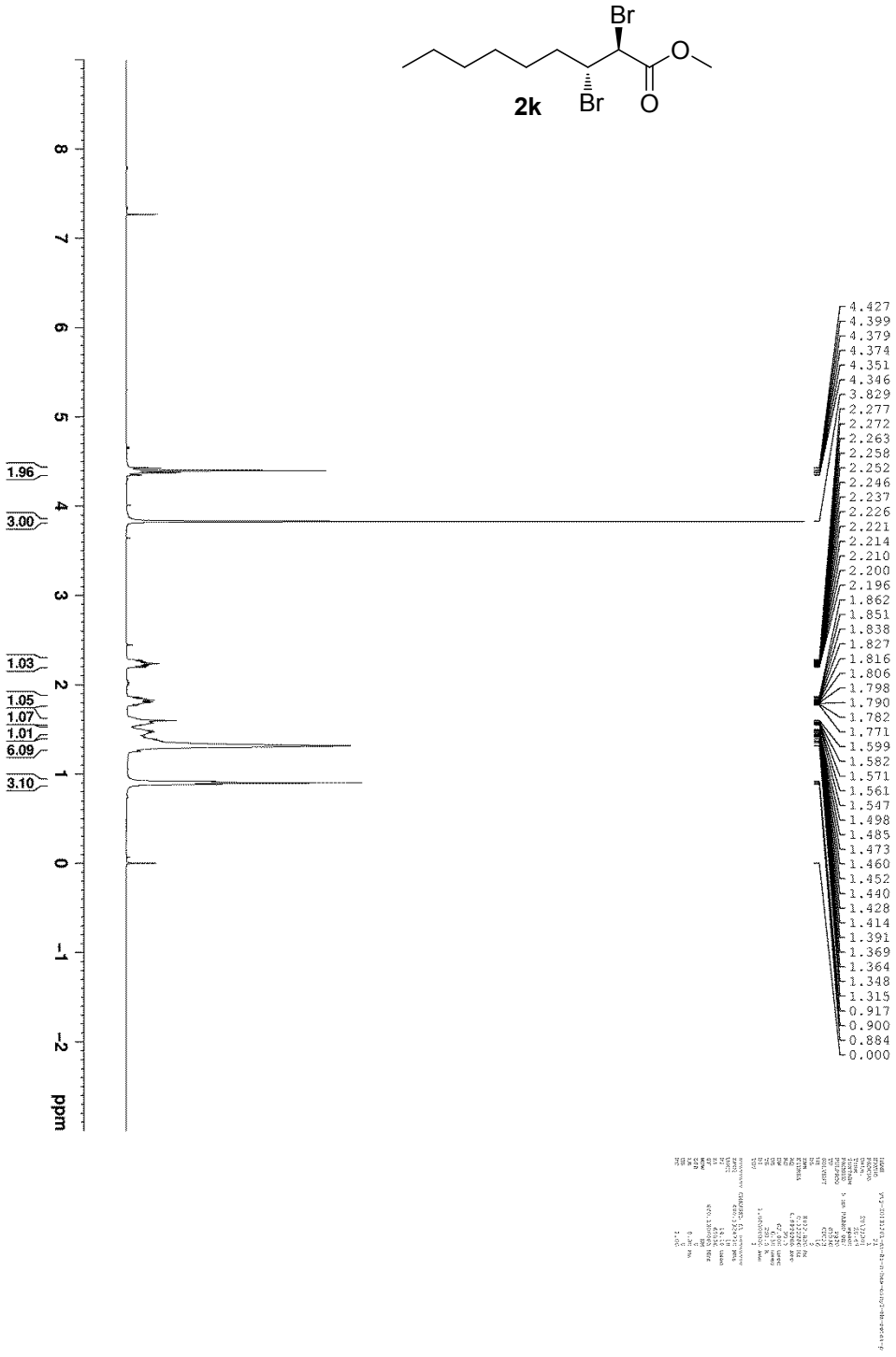
^{1}H NMR spectrum of compound **2j** ($CDCl_3$, 400 MHz)



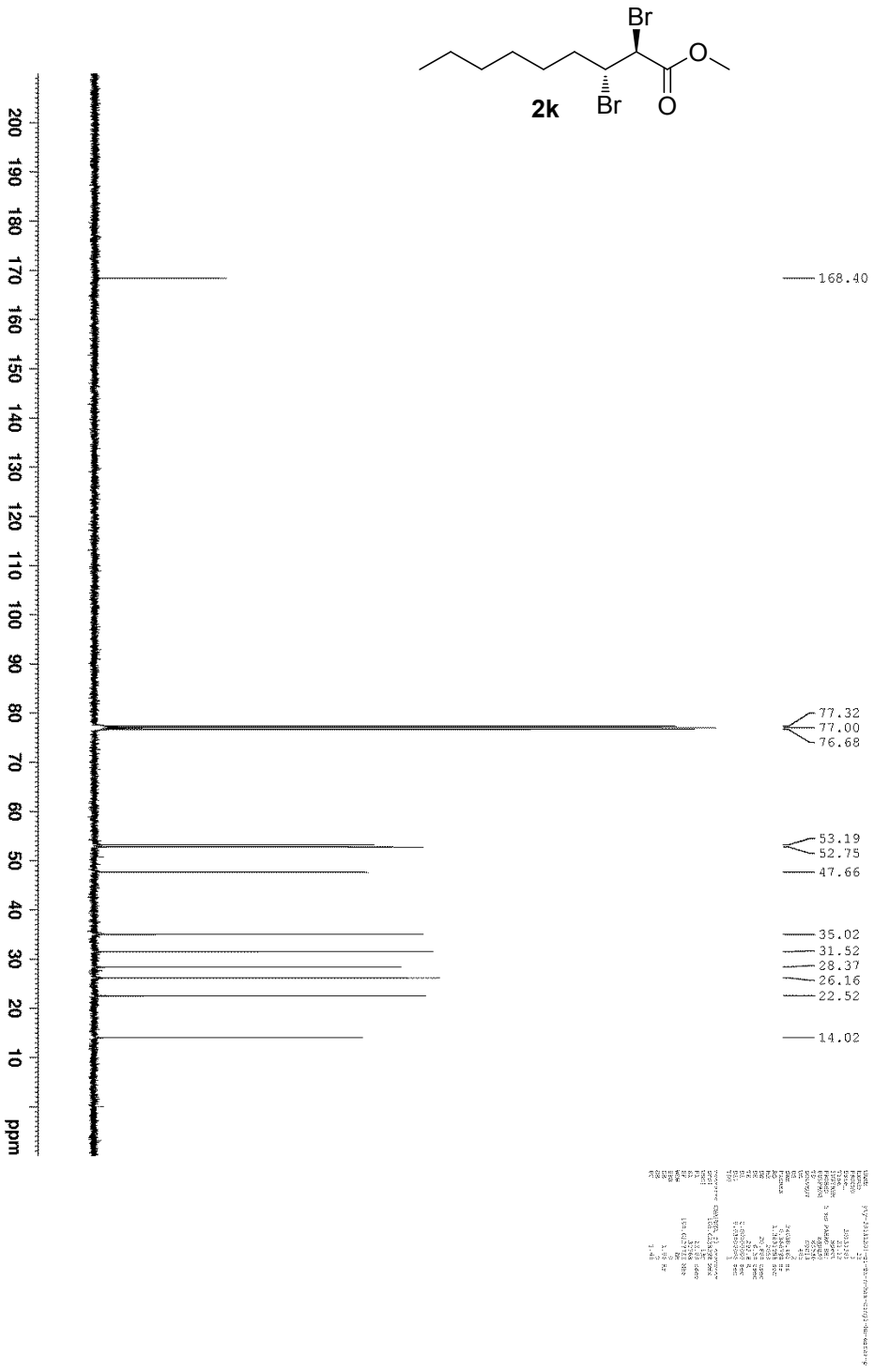
^{13}C NMR spectrum of compound **2j** ($CDCl_3$, 100 MHz)



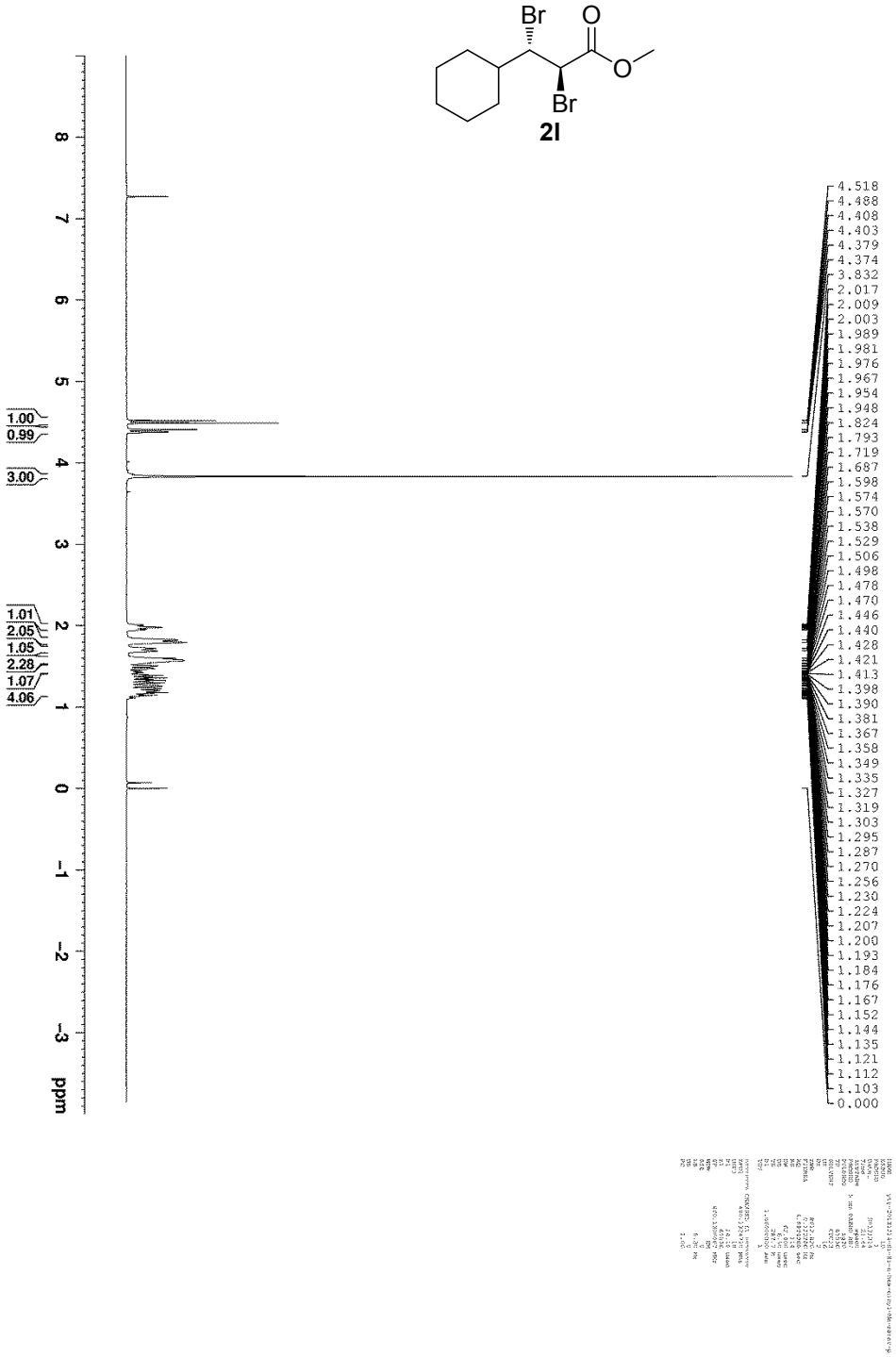
^{1}H NMR spectrum of compound **2k** ($CDCl_3$, 400 MHz)



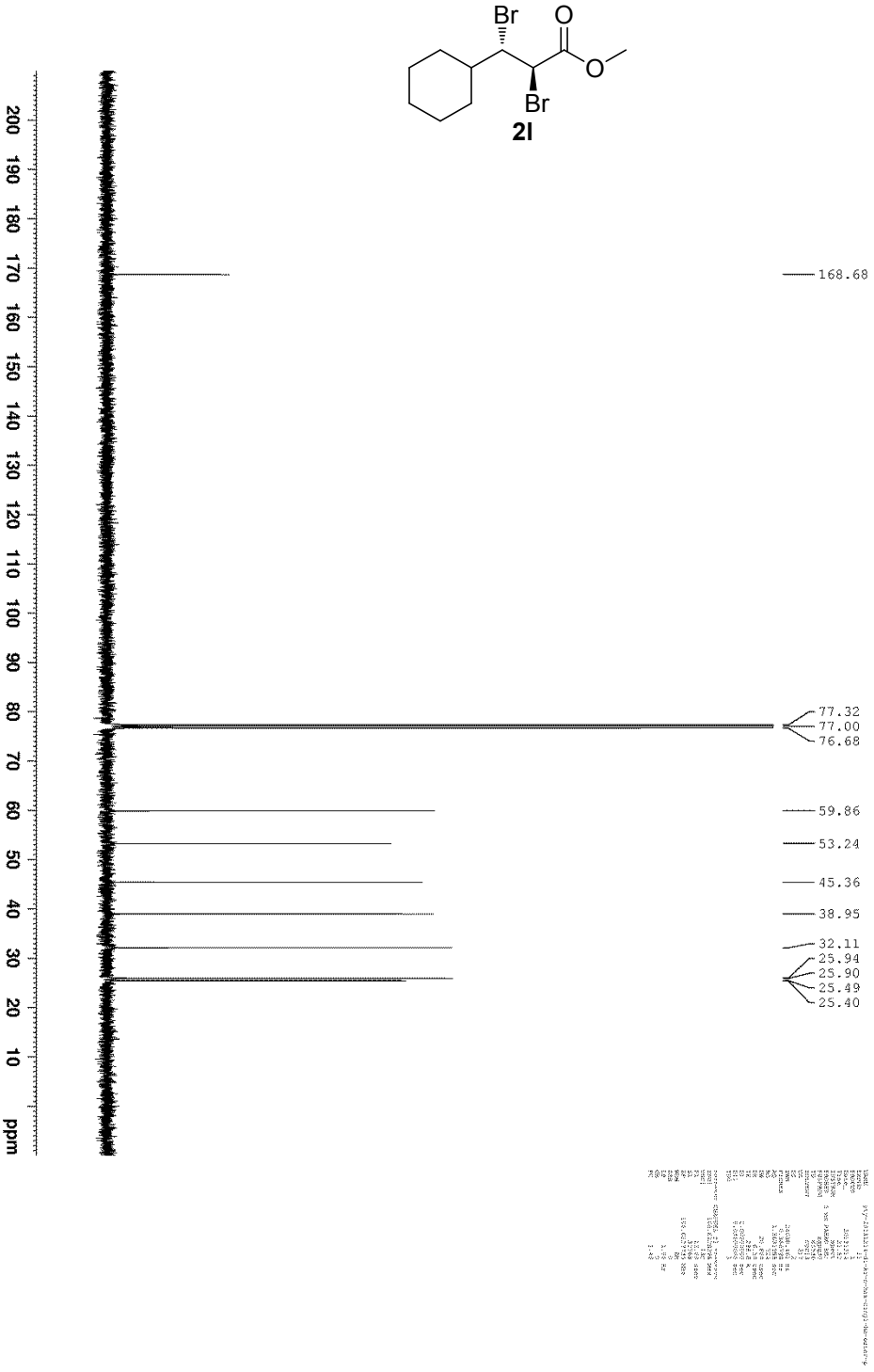
^{13}C NMR spectrum of compound **2k** ($CDCl_3$, 100 MHz)



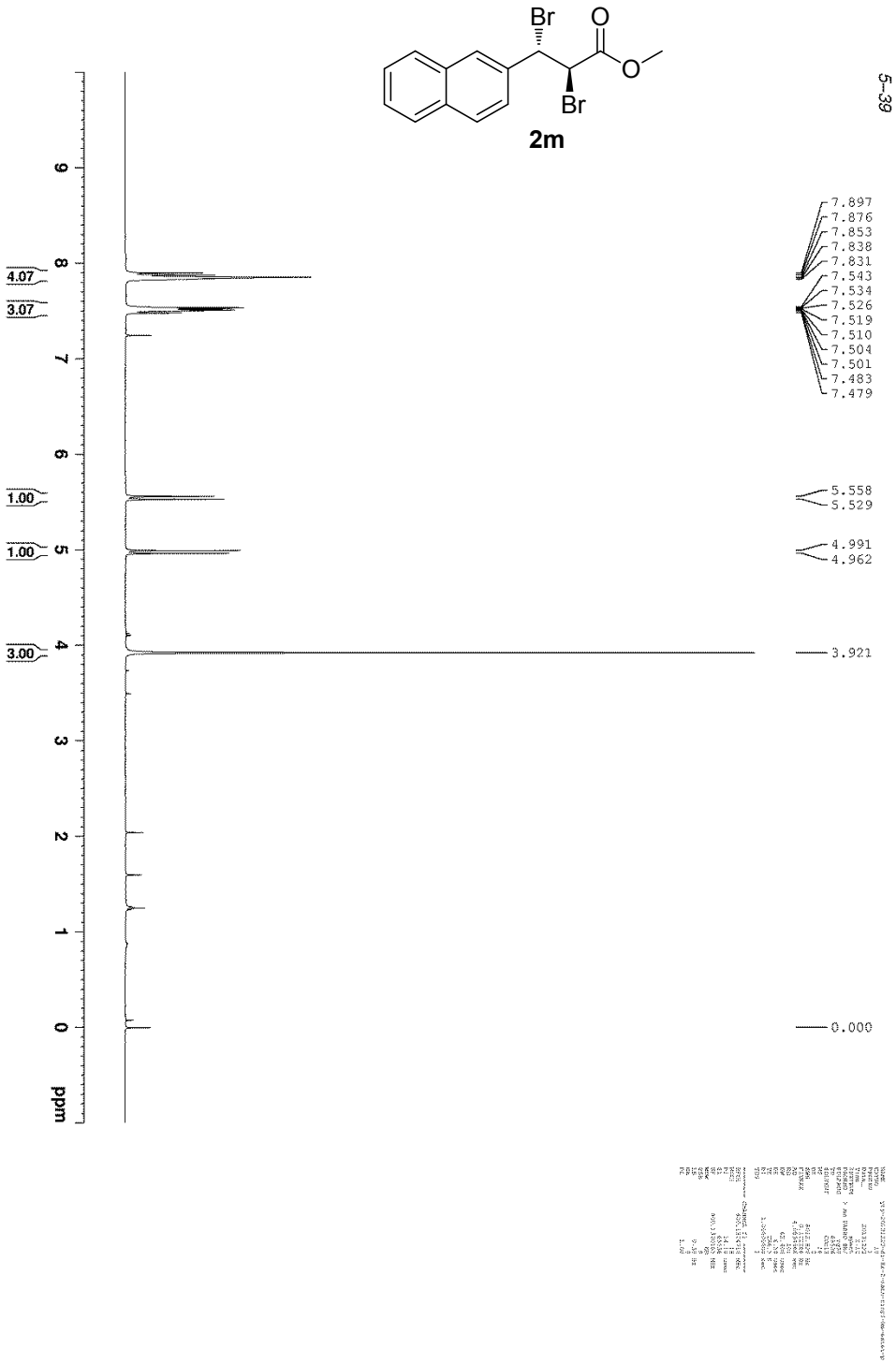
^{1}H NMR spectrum of compound **2l** ($CDCl_3$, 400 MHz)



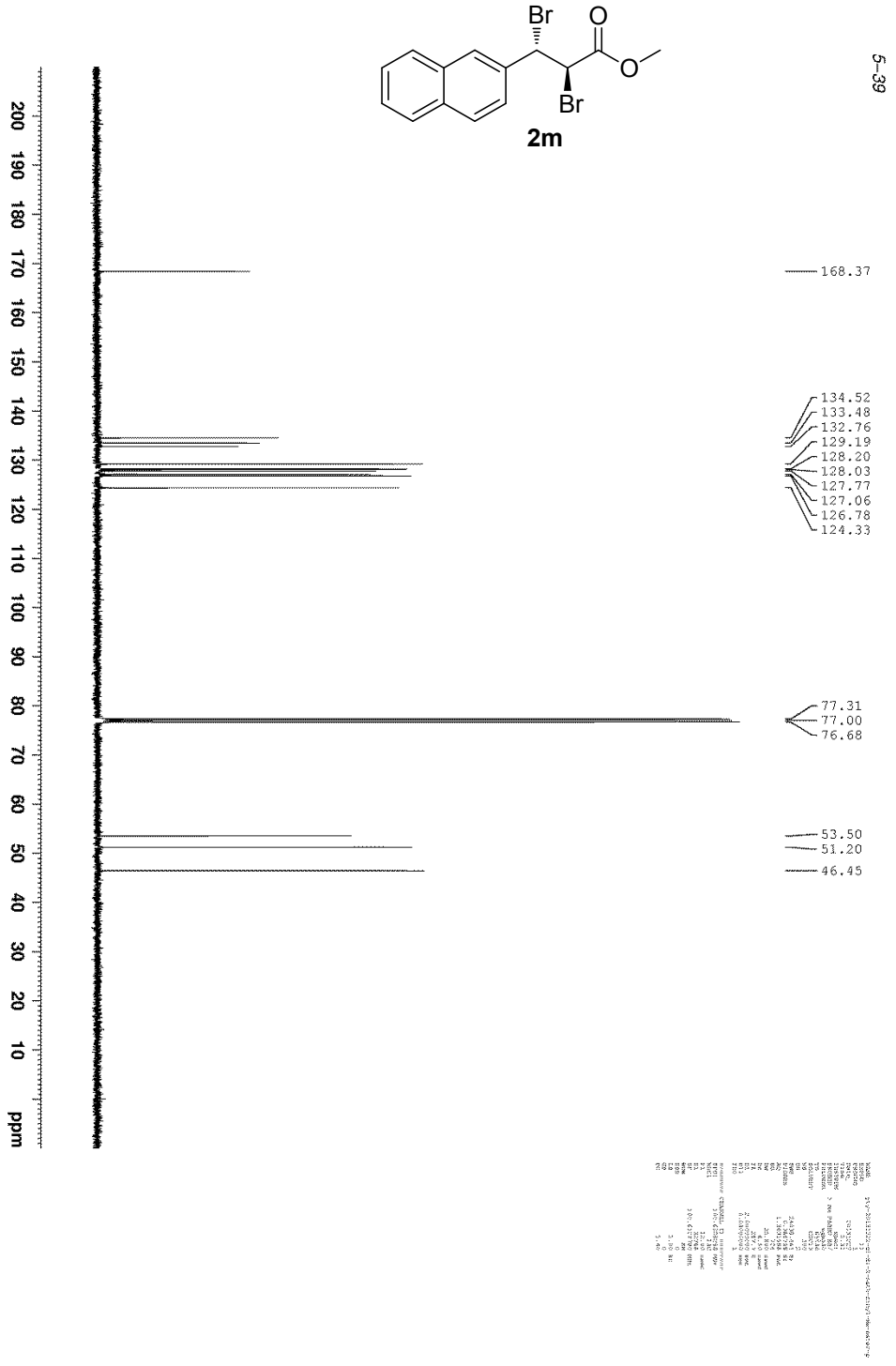
^{13}C NMR spectrum of compound **2l** ($CDCl_3$, 100 MHz)



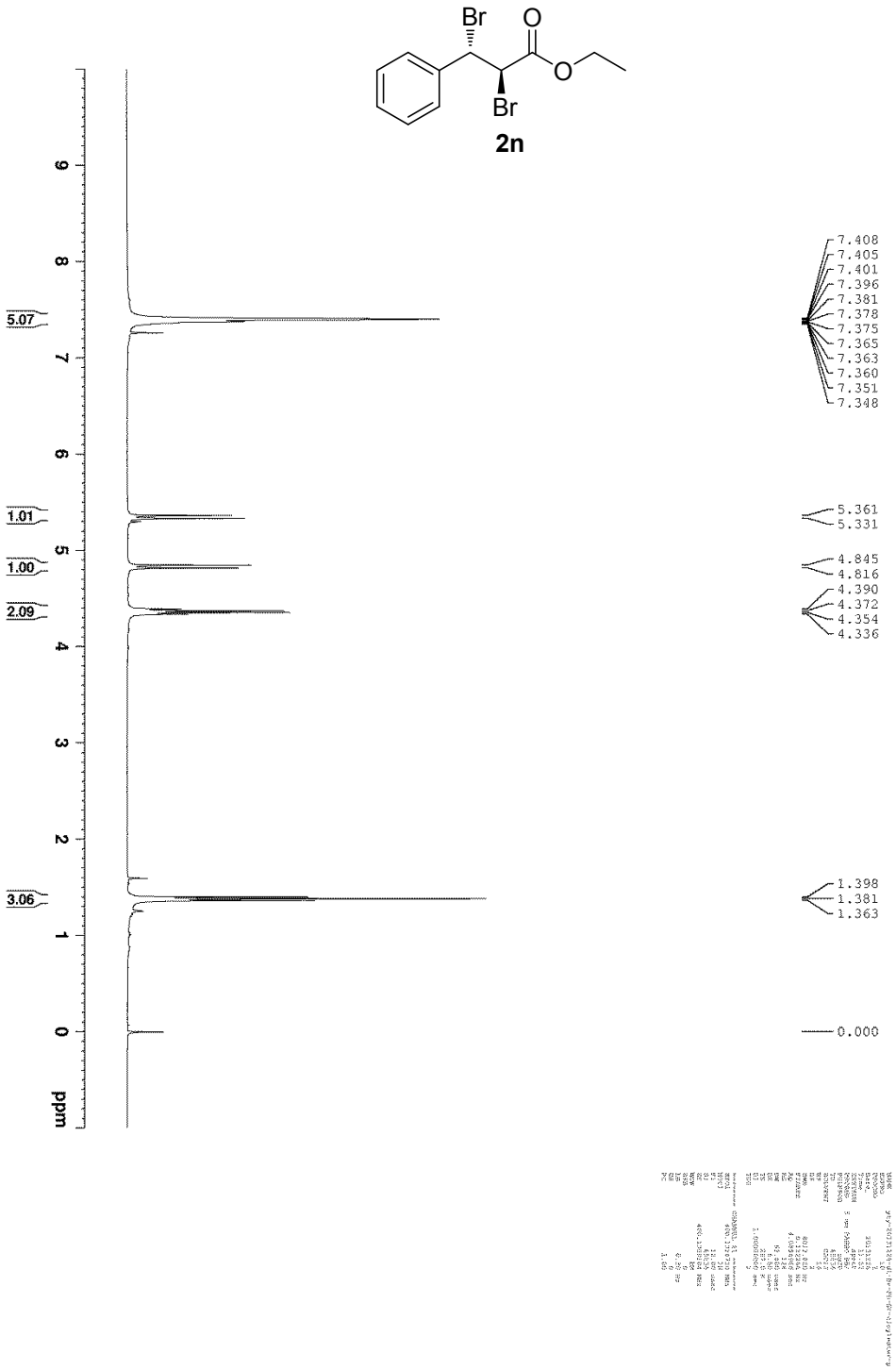
^{1}H NMR spectrum of compound **2m** ($CDCl_3$, 400 MHz)



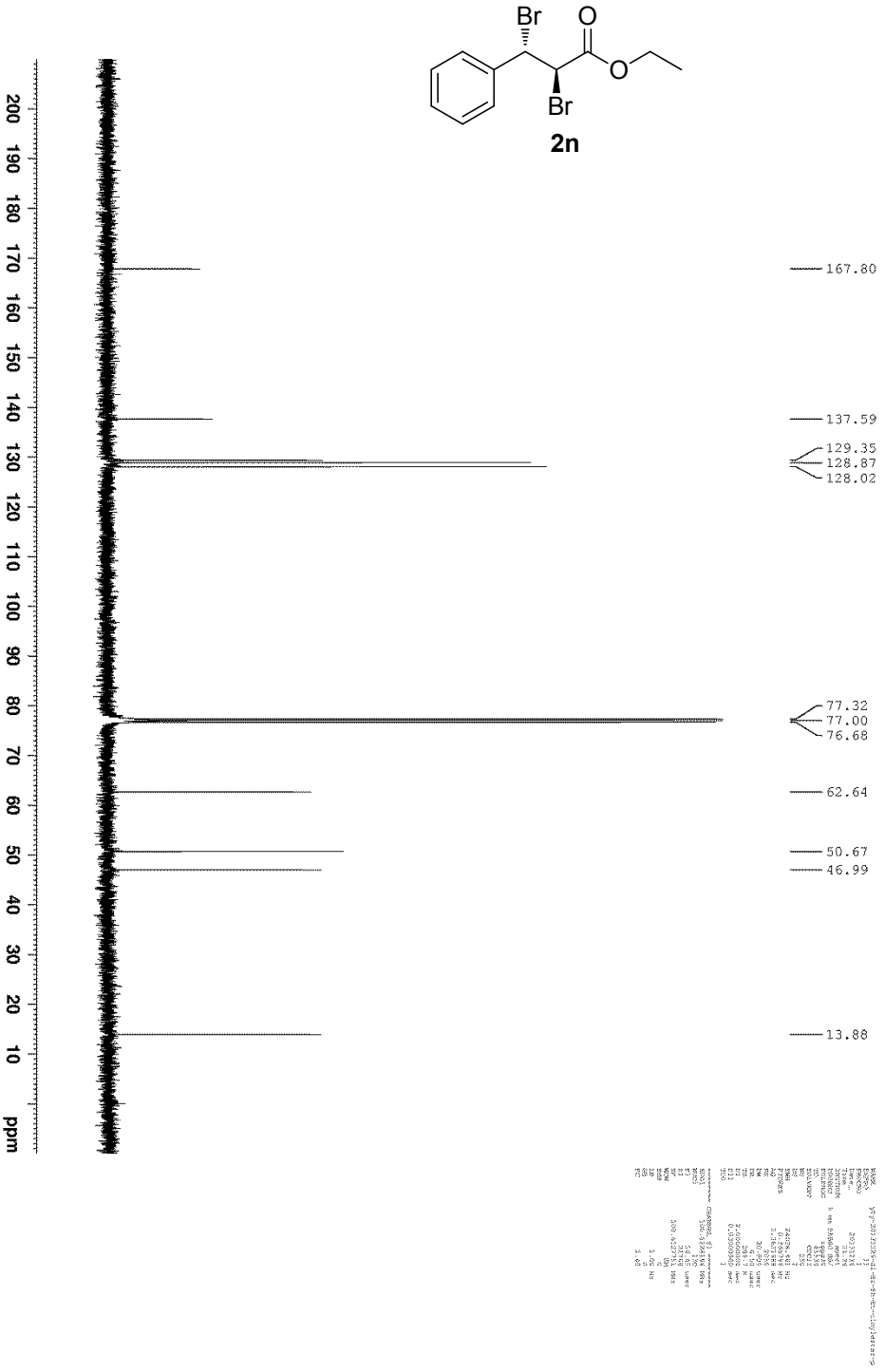
^{13}C NMR spectrum of compound **2m** ($CDCl_3$, 100 MHz)



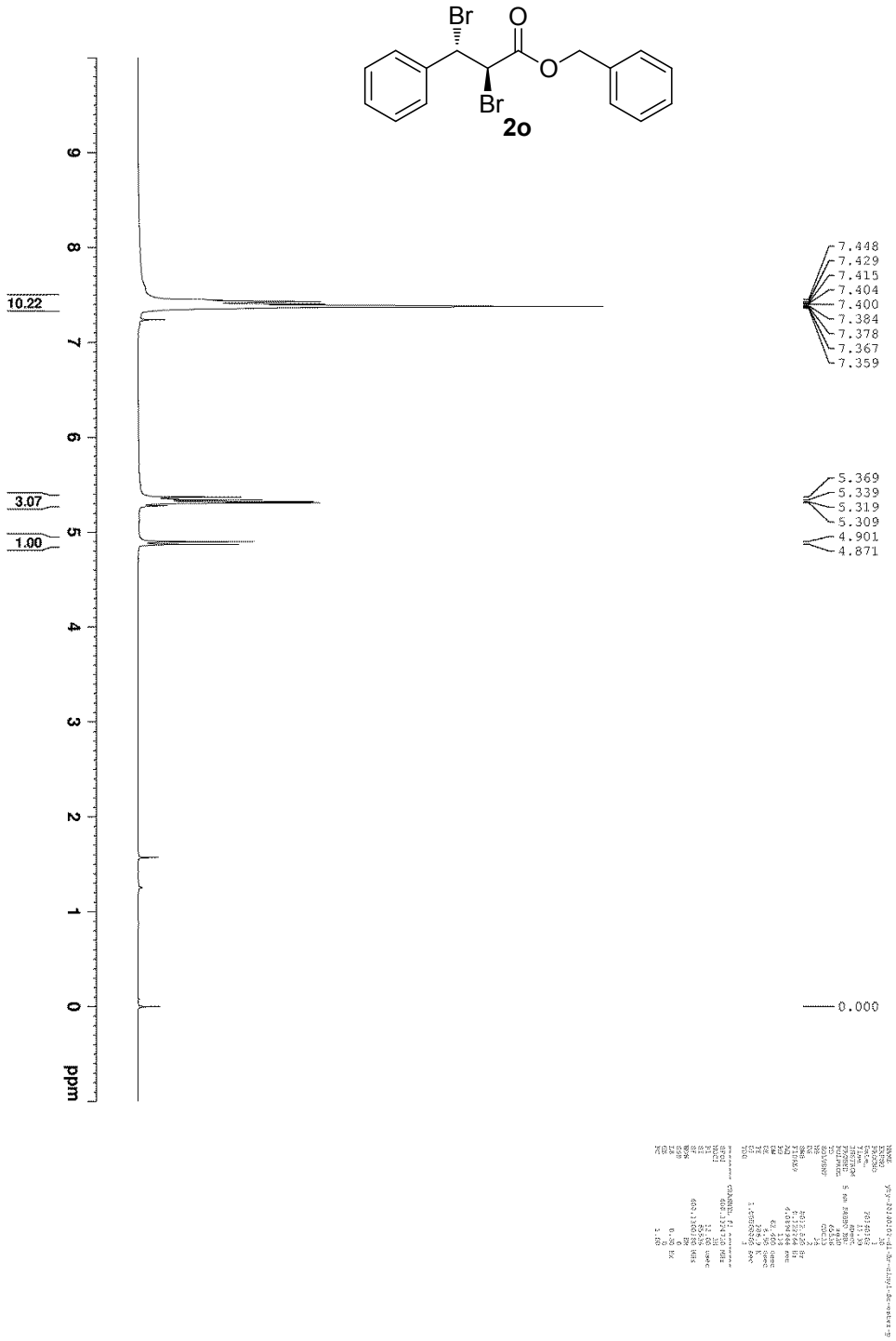
^{1}H NMR spectrum of compound **2n** ($CDCl_3$, 400 MHz)



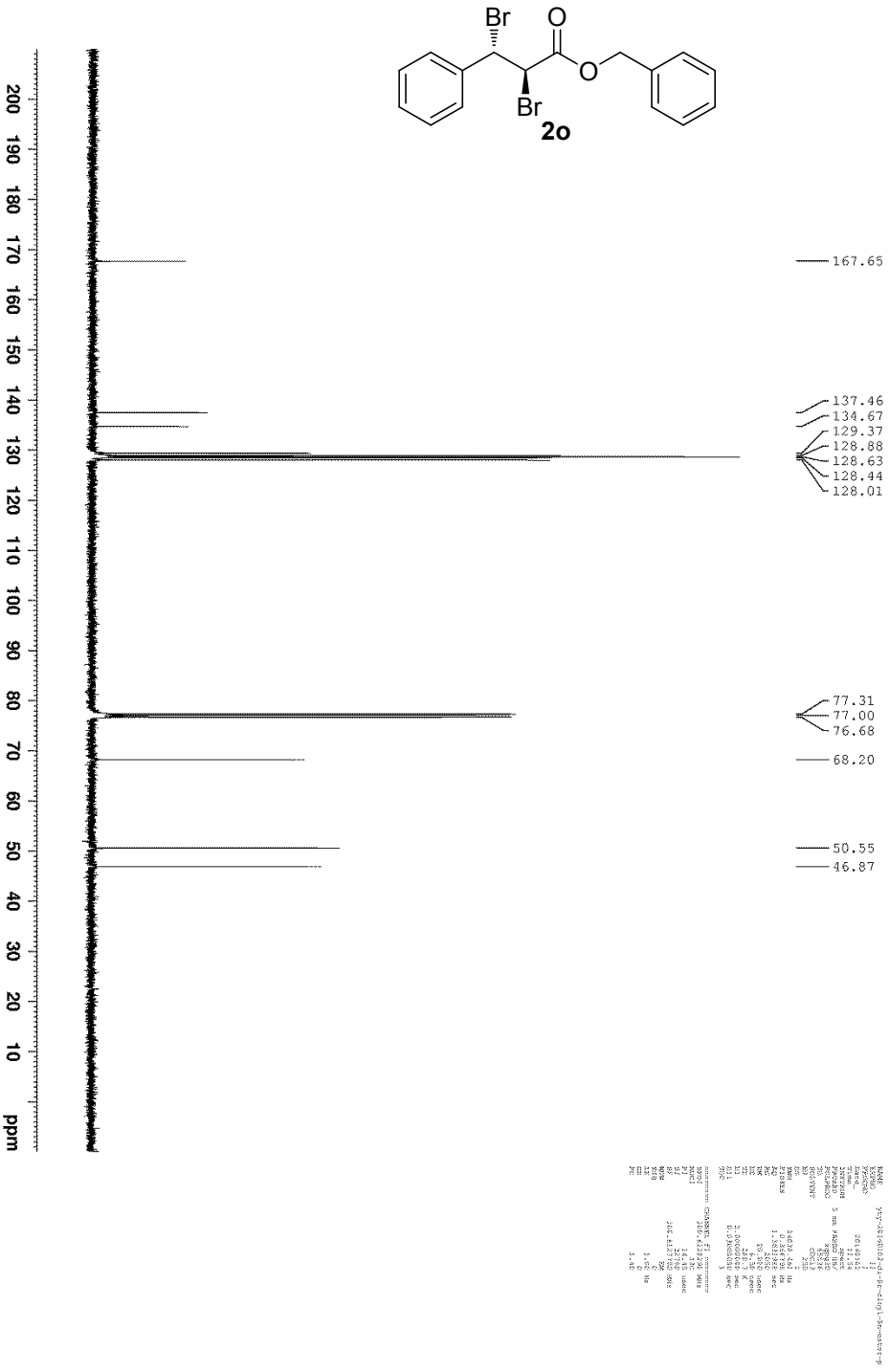
^{13}C NMR spectrum of compound **2n** ($CDCl_3$, 100 MHz)



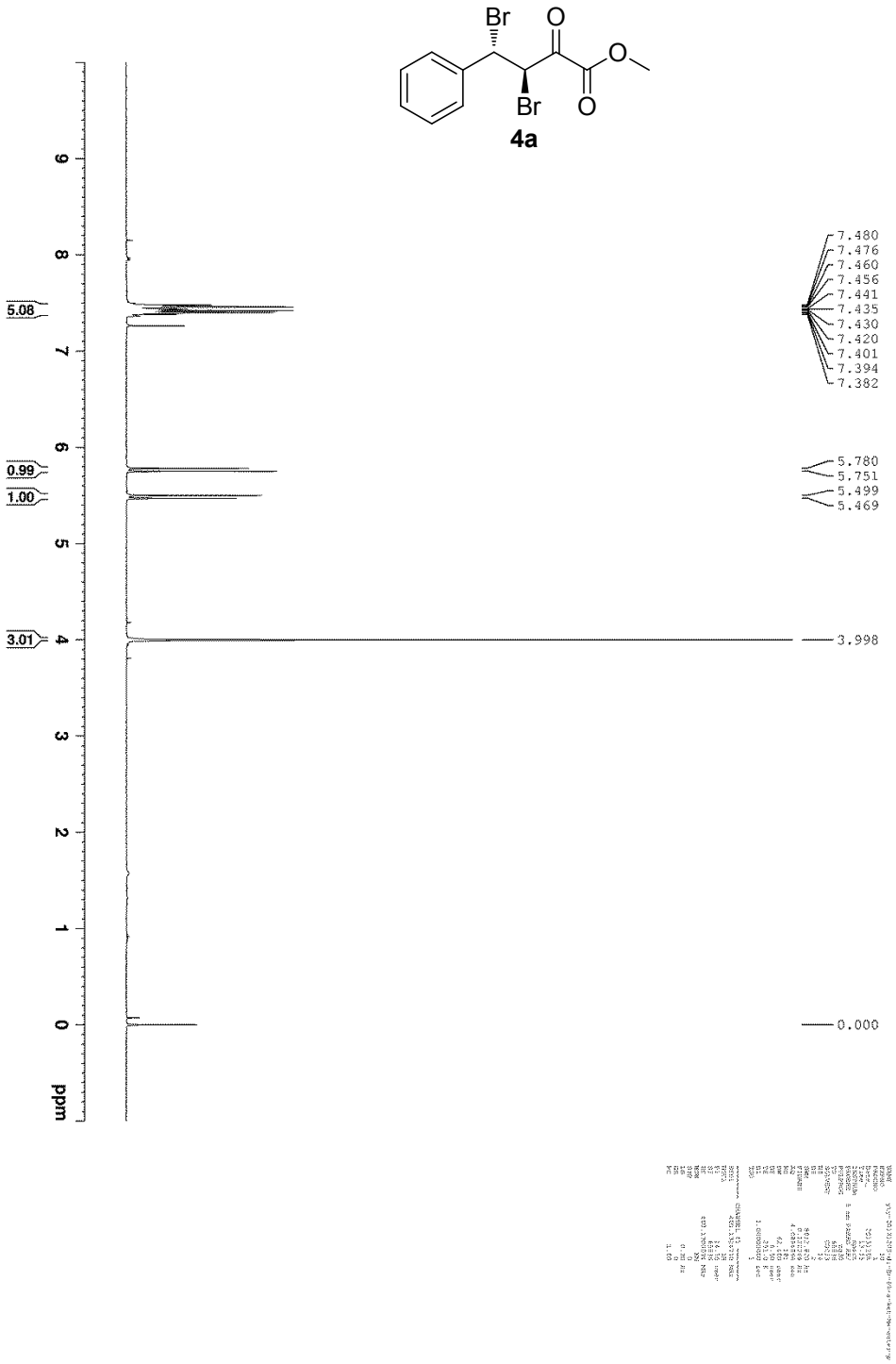
^{1}H NMR spectrum of compound **2o** ($CDCl_3$, 400 MHz)



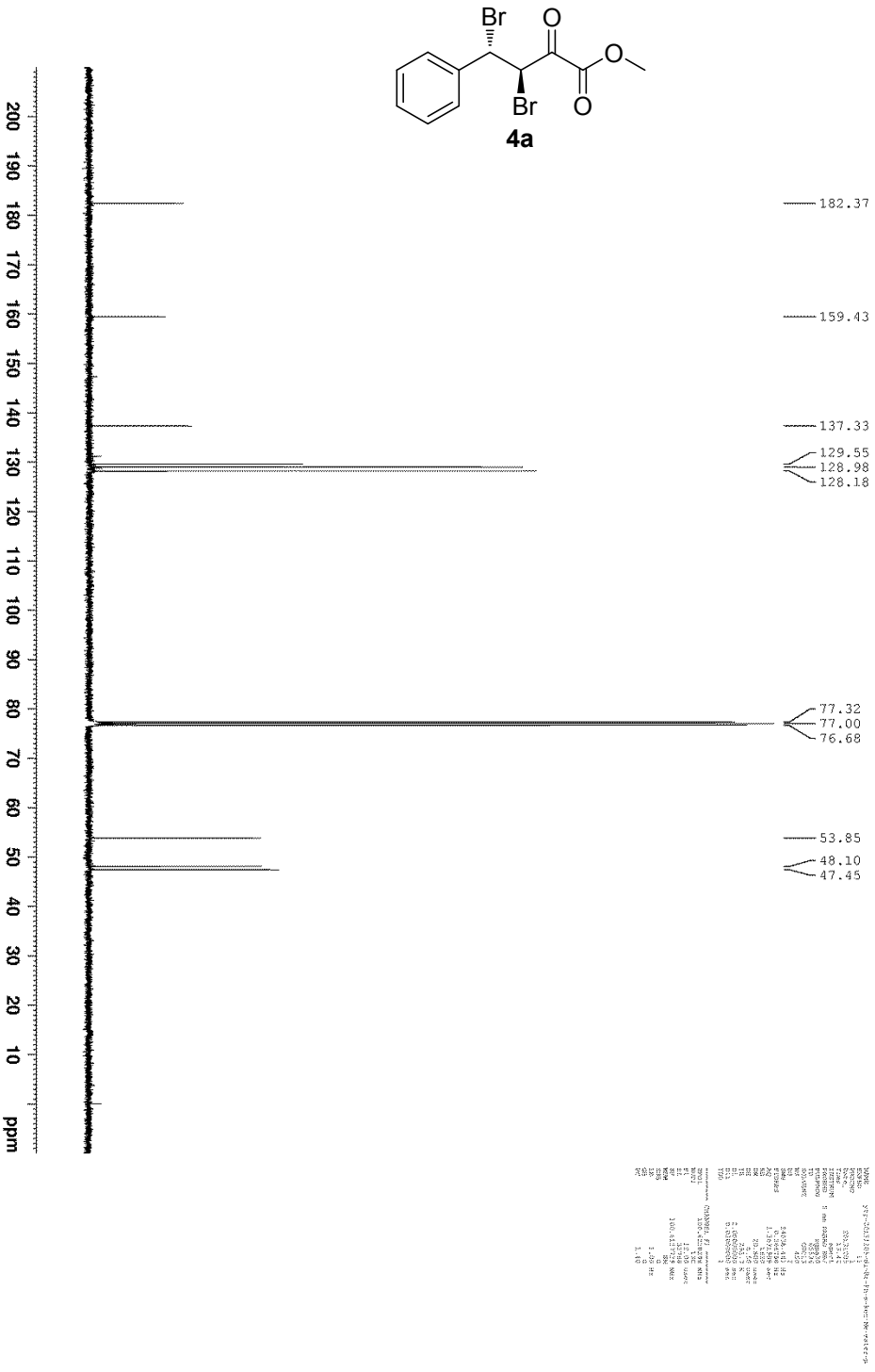
^{13}C NMR spectrum of compound **2o** ($CDCl_3$, 100 MHz)



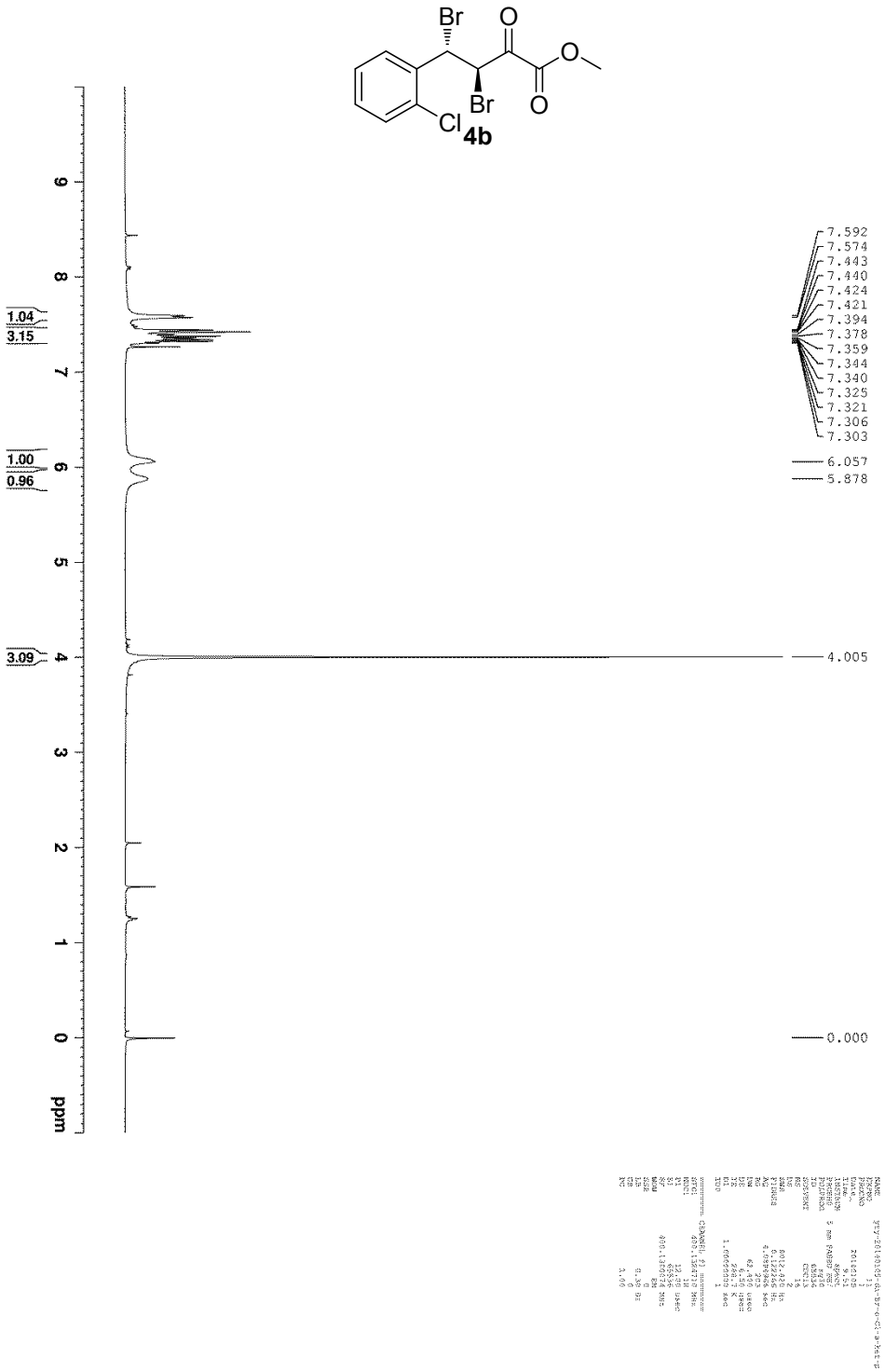
^{1}H NMR spectrum of compound **4a** ($CDCl_3$, 400 MHz)



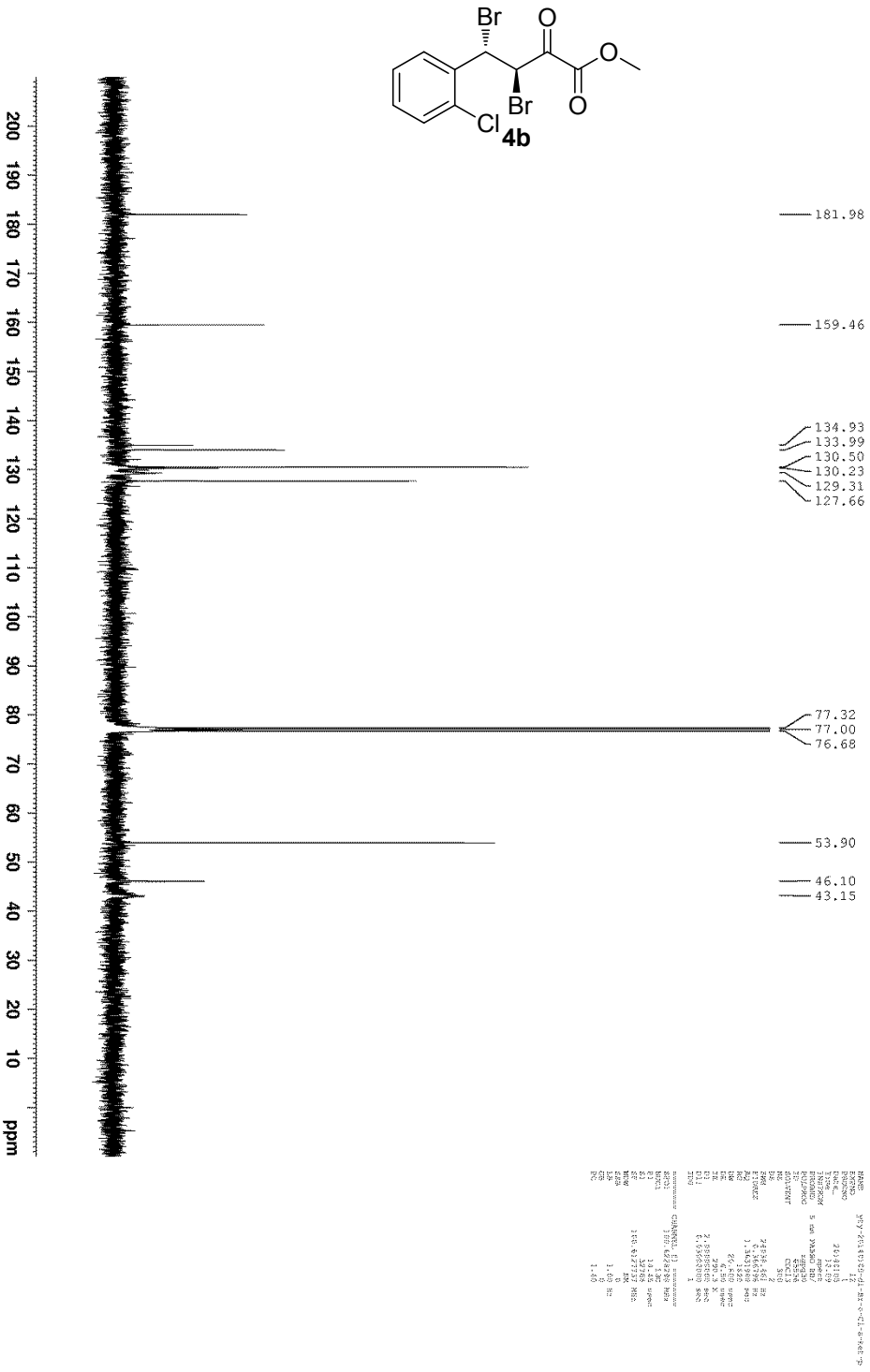
^{13}C NMR spectrum of compound **4a** ($CDCl_3$, 100 MHz)



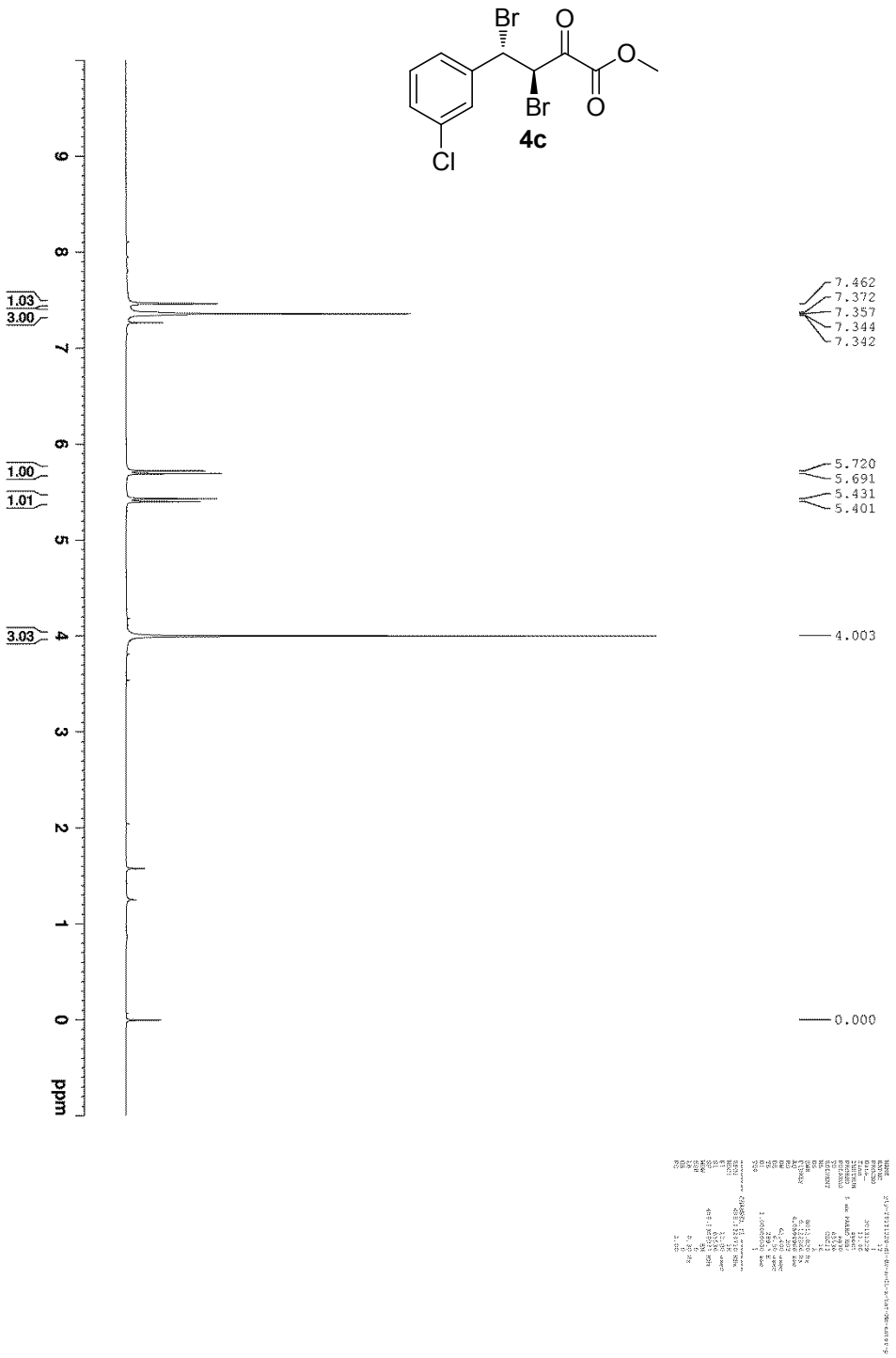
^{1}H NMR spectrum of compound **4b** ($CDCl_3$, 400 MHz)



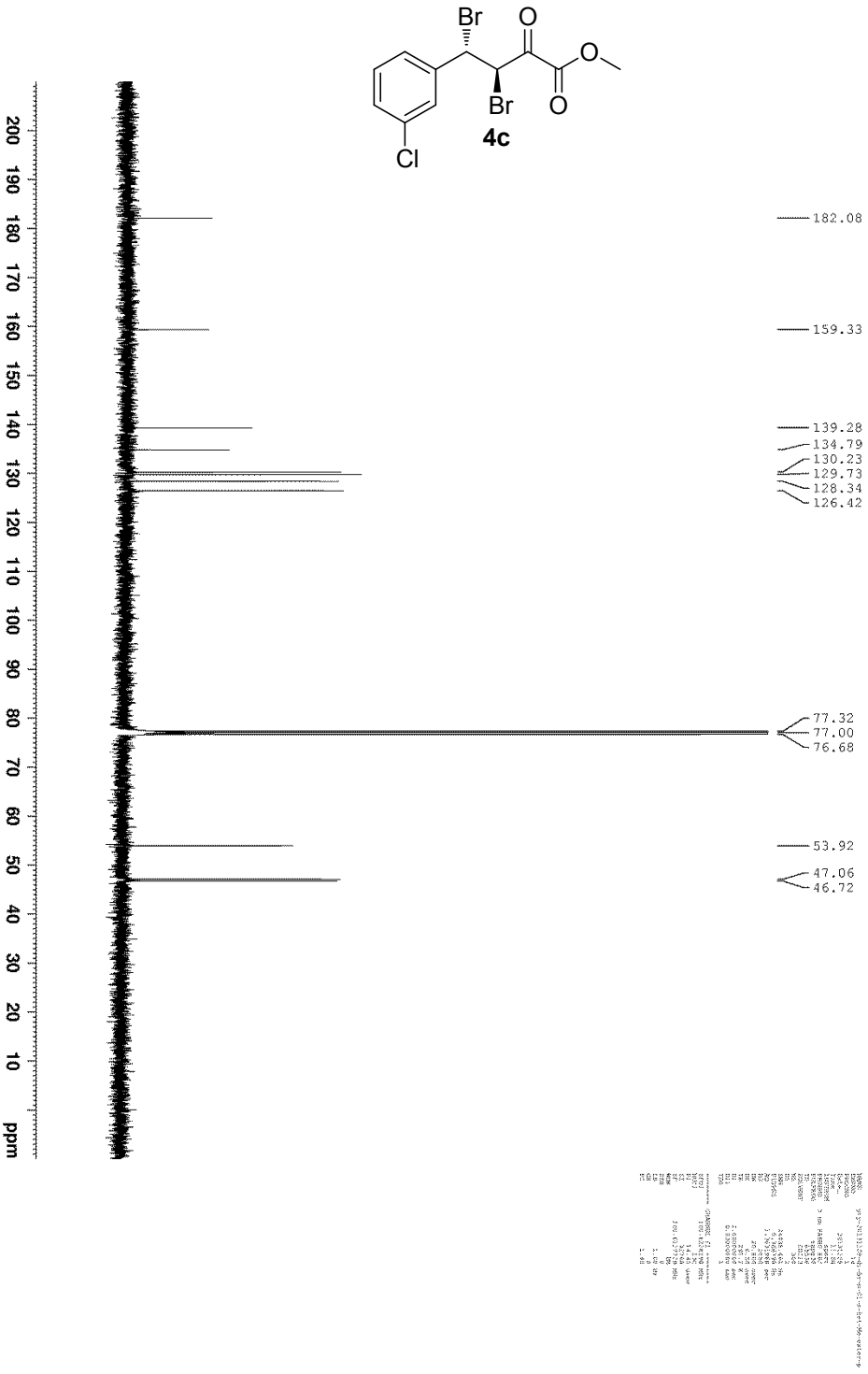
^{13}C NMR spectrum of compound **4b** ($CDCl_3$, 100 MHz)



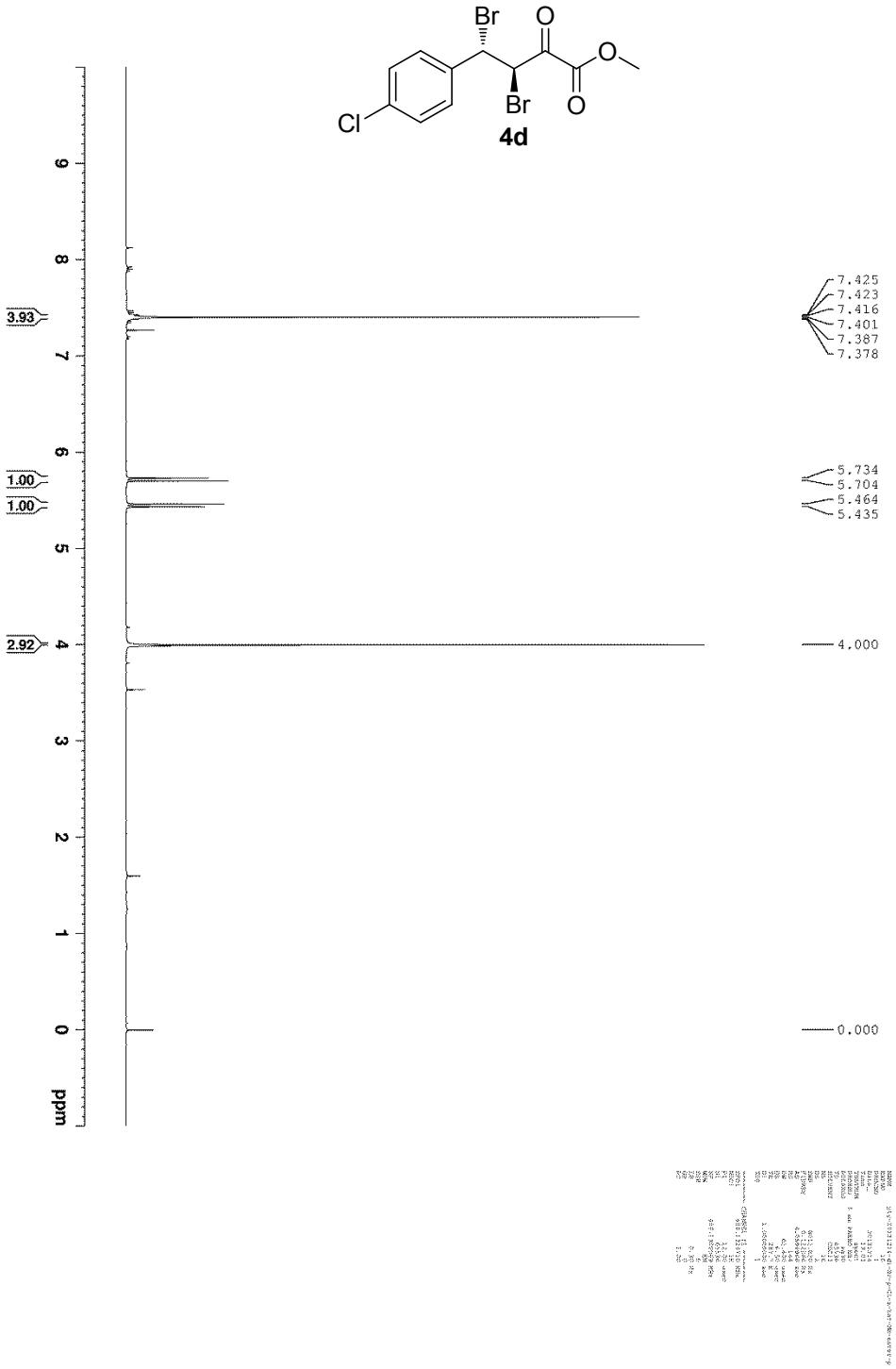
^{1}H NMR spectrum of compound **4c** ($CDCl_3$, 400 MHz)



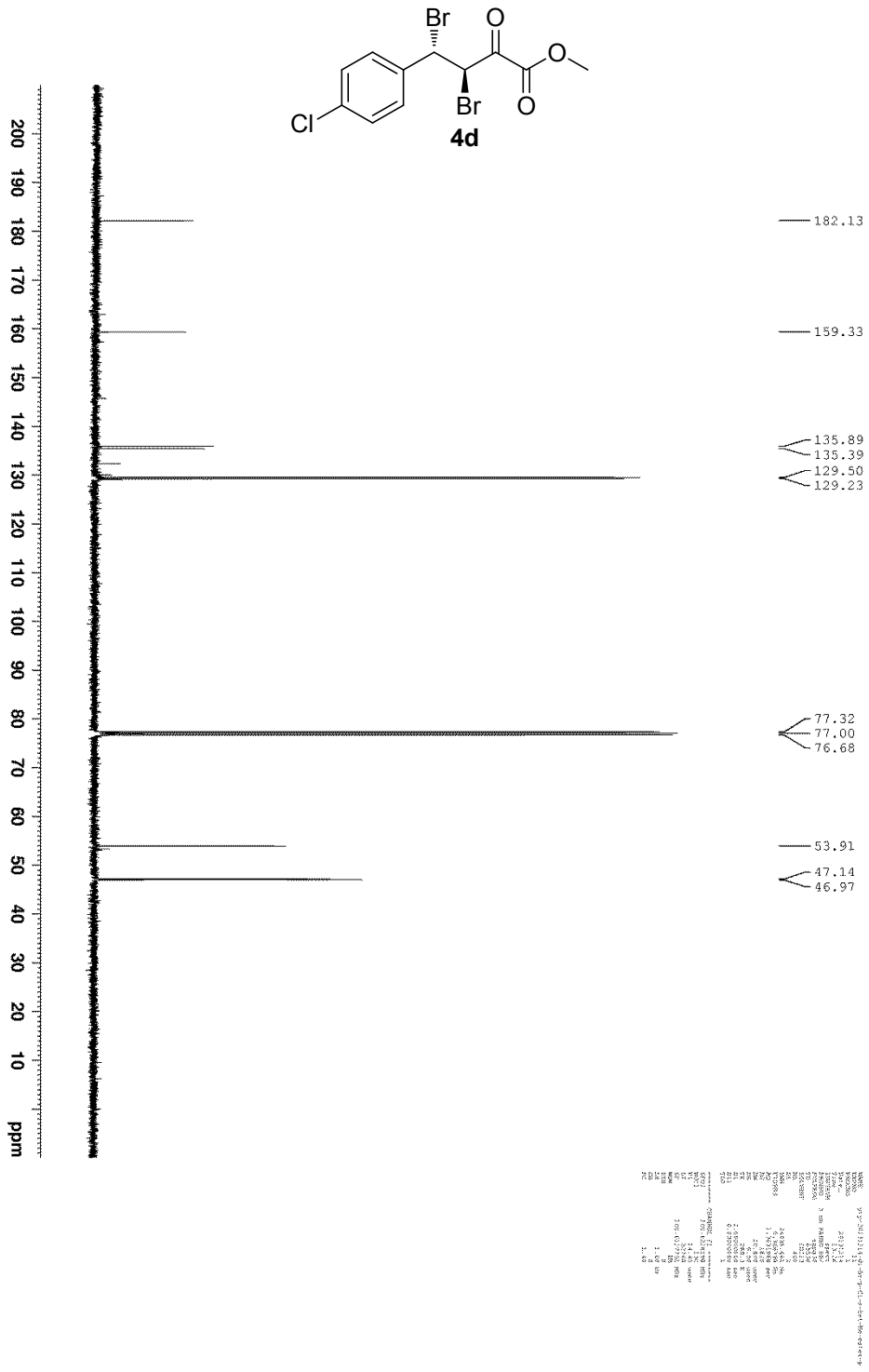
^{13}C NMR spectrum of compound **4c** ($CDCl_3$, 100 MHz)



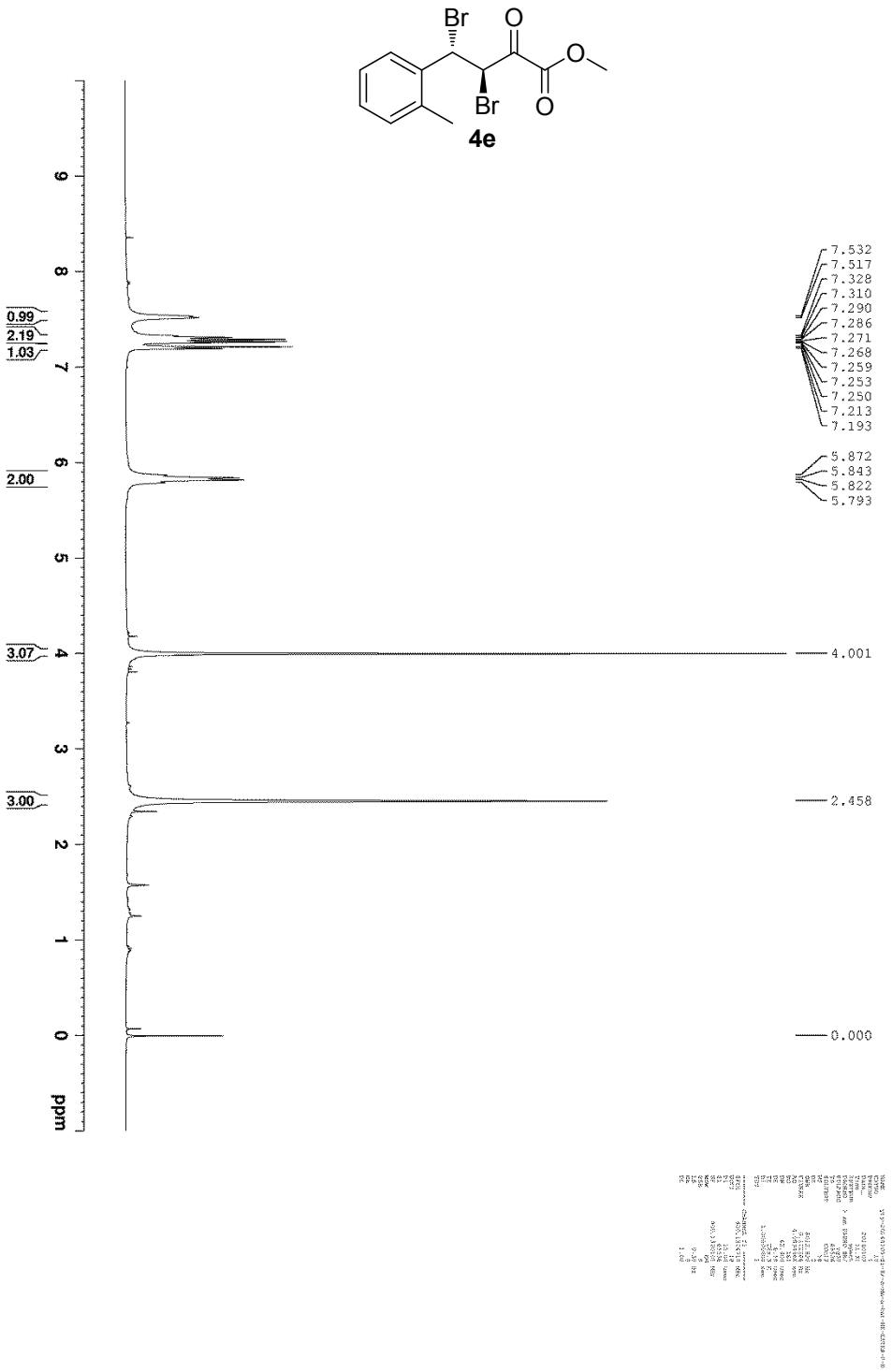
^{1}H NMR spectrum of compound **4d** ($CDCl_3$, 400 MHz)



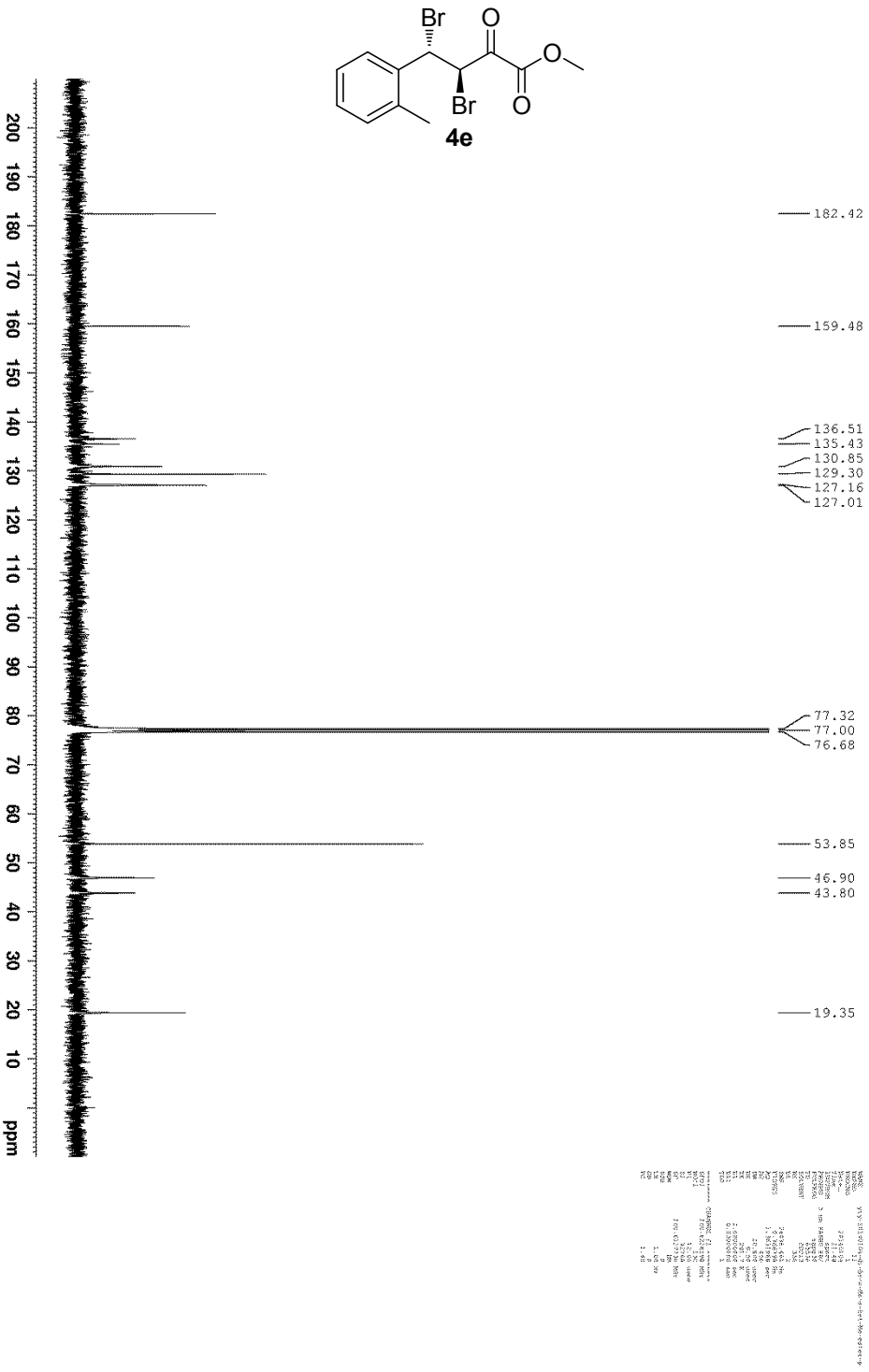
^{13}C NMR spectrum of compound **4d** ($CDCl_3$, 100 MHz)



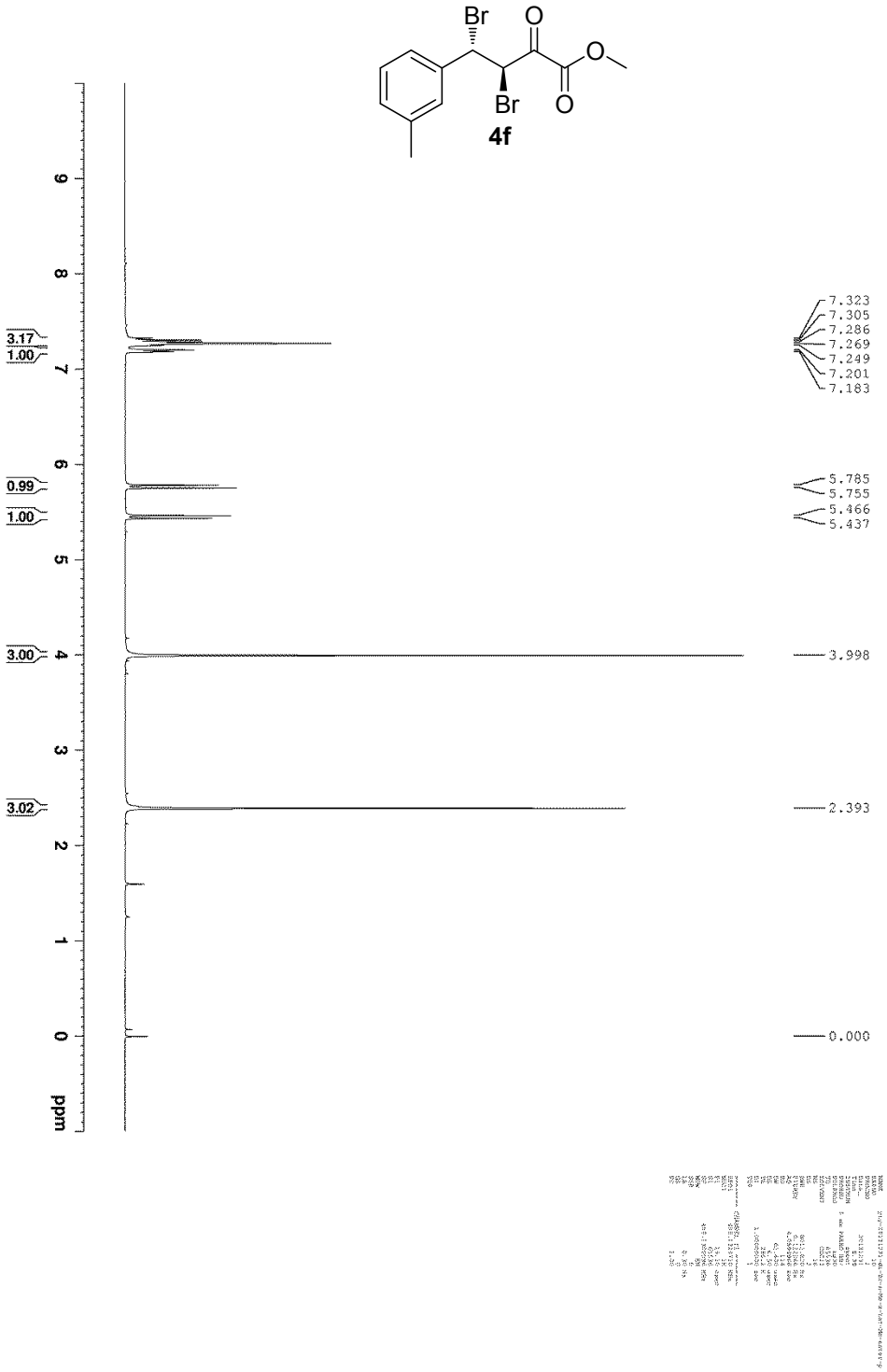
^{1}H NMR spectrum of compound **4e** ($CDCl_3$, 400 MHz)



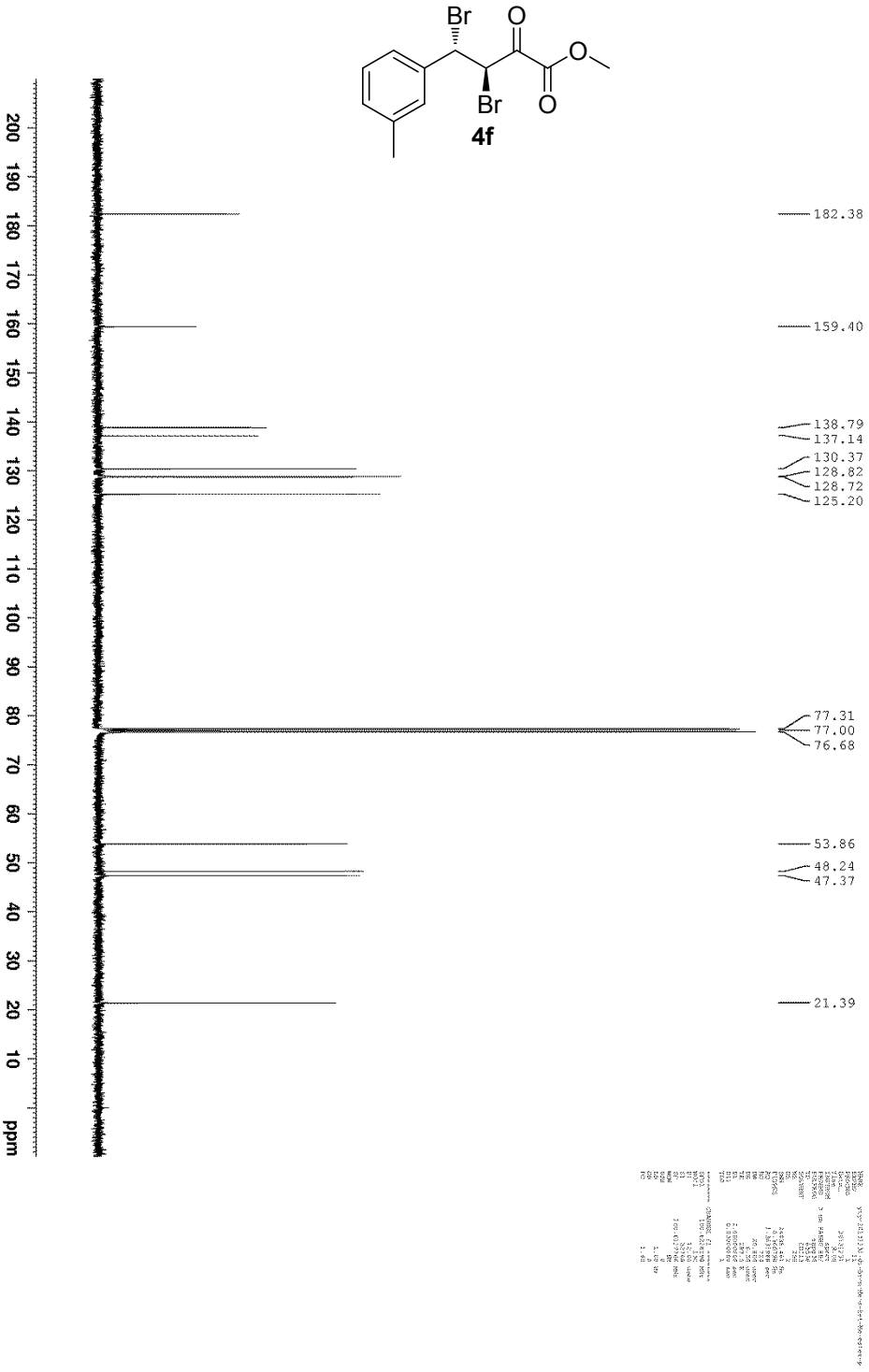
^{13}C NMR spectrum of compound **4e** ($CDCl_3$, 100 MHz)



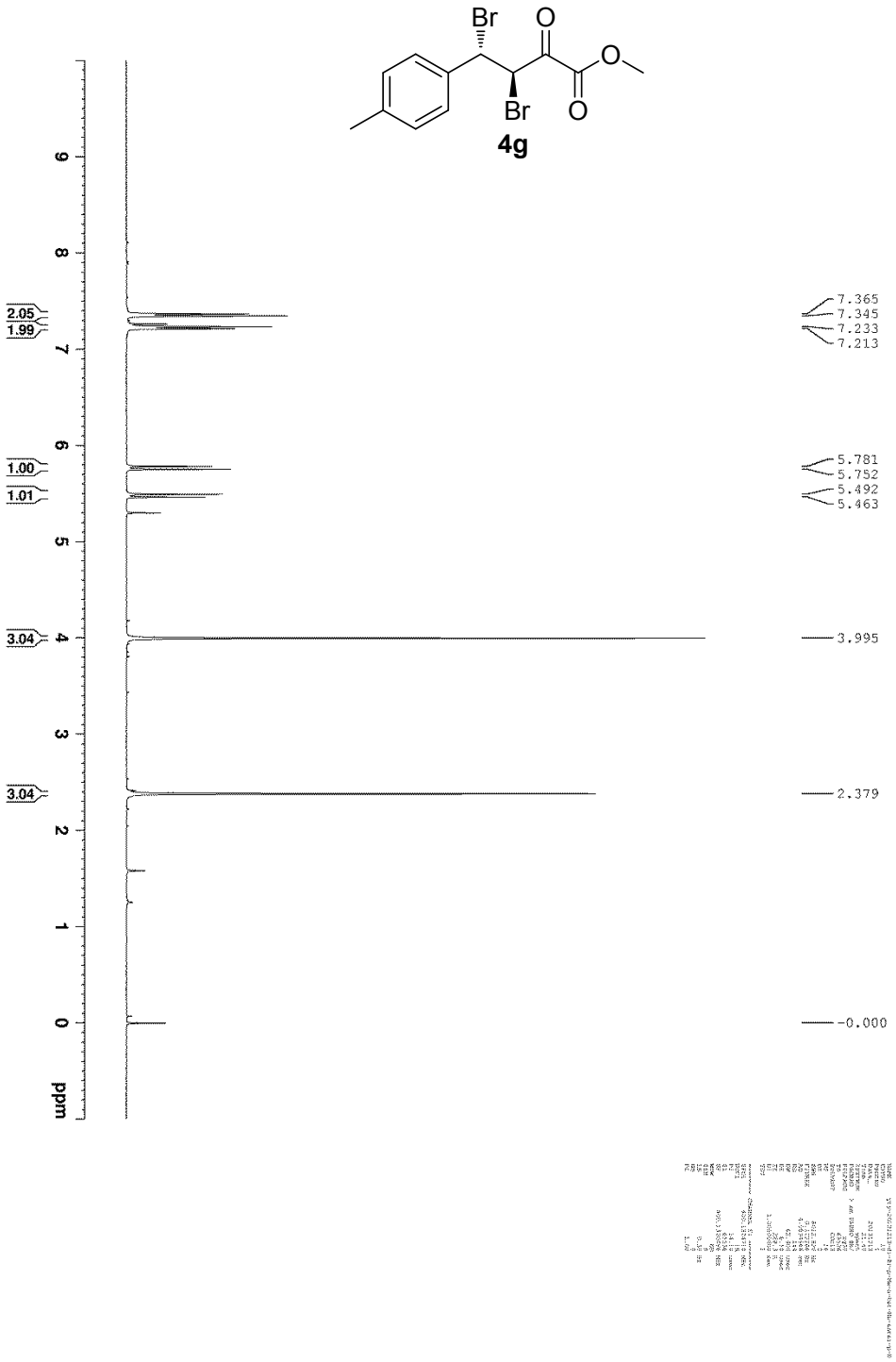
^{1}H NMR spectrum of compound **4f** ($CDCl_3$, 400 MHz)



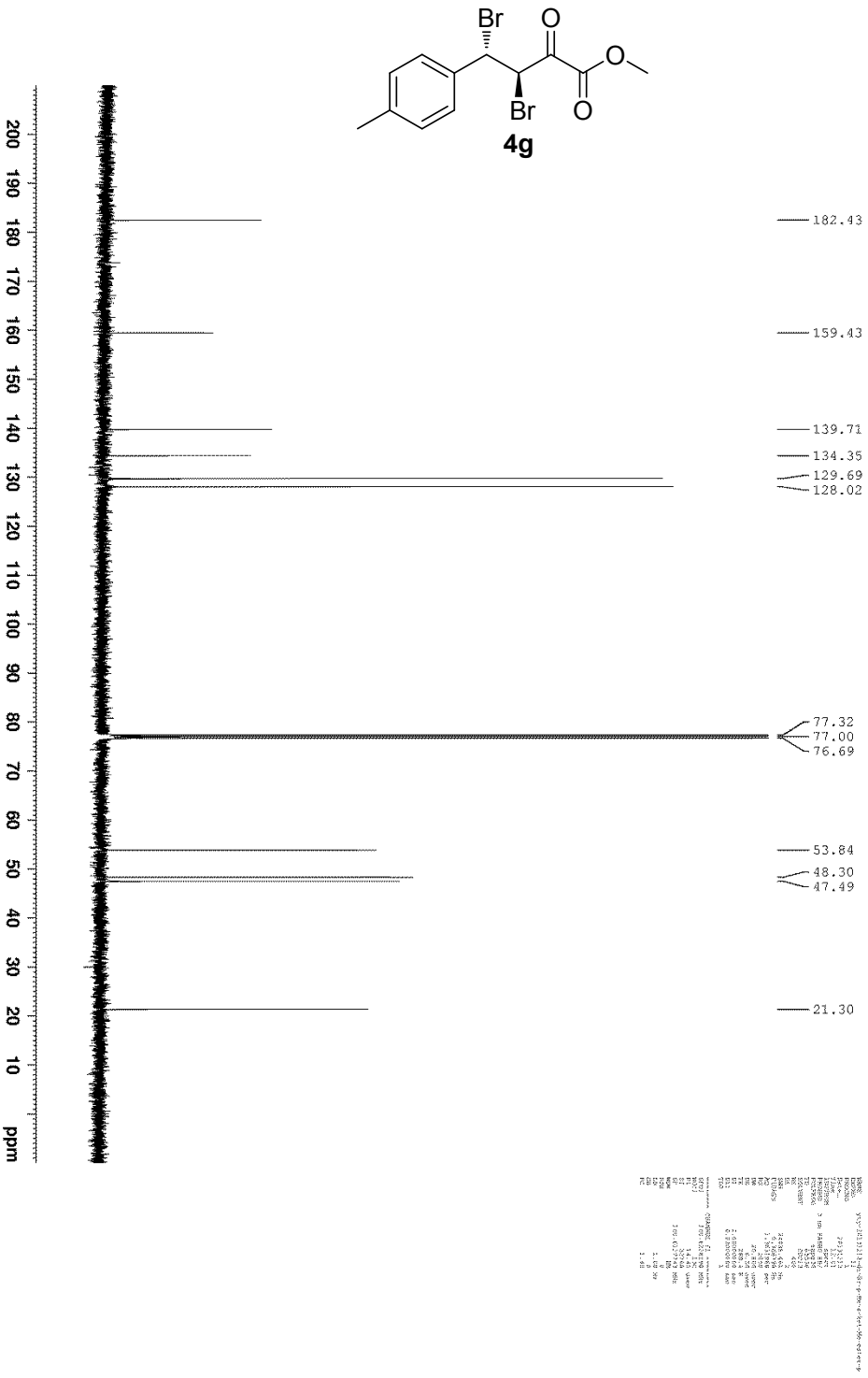
^{13}C NMR spectrum of compound **4f** ($CDCl_3$, 100 MHz)



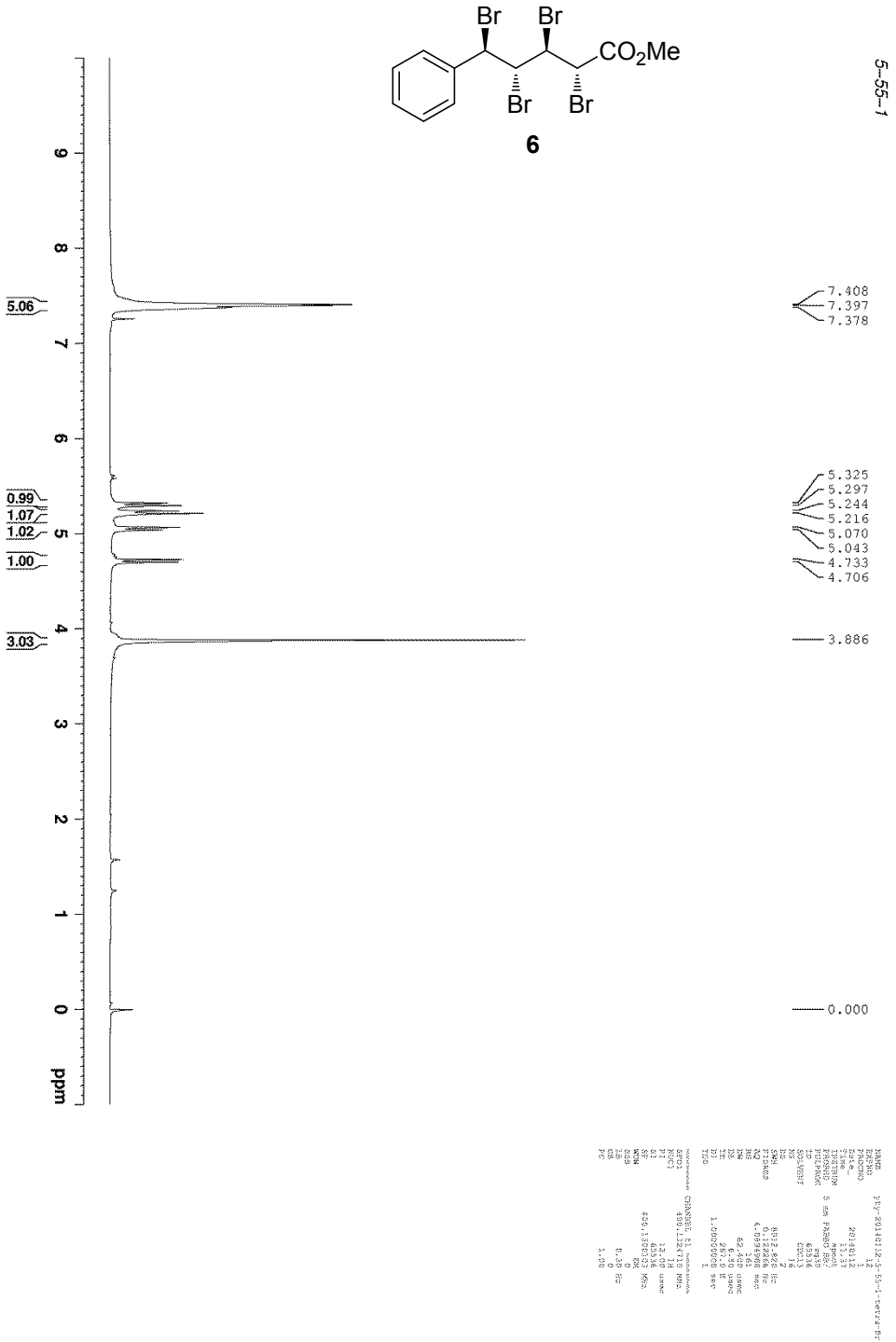
^{1}H NMR spectrum of compound **4g** ($CDCl_3$, 400 MHz)



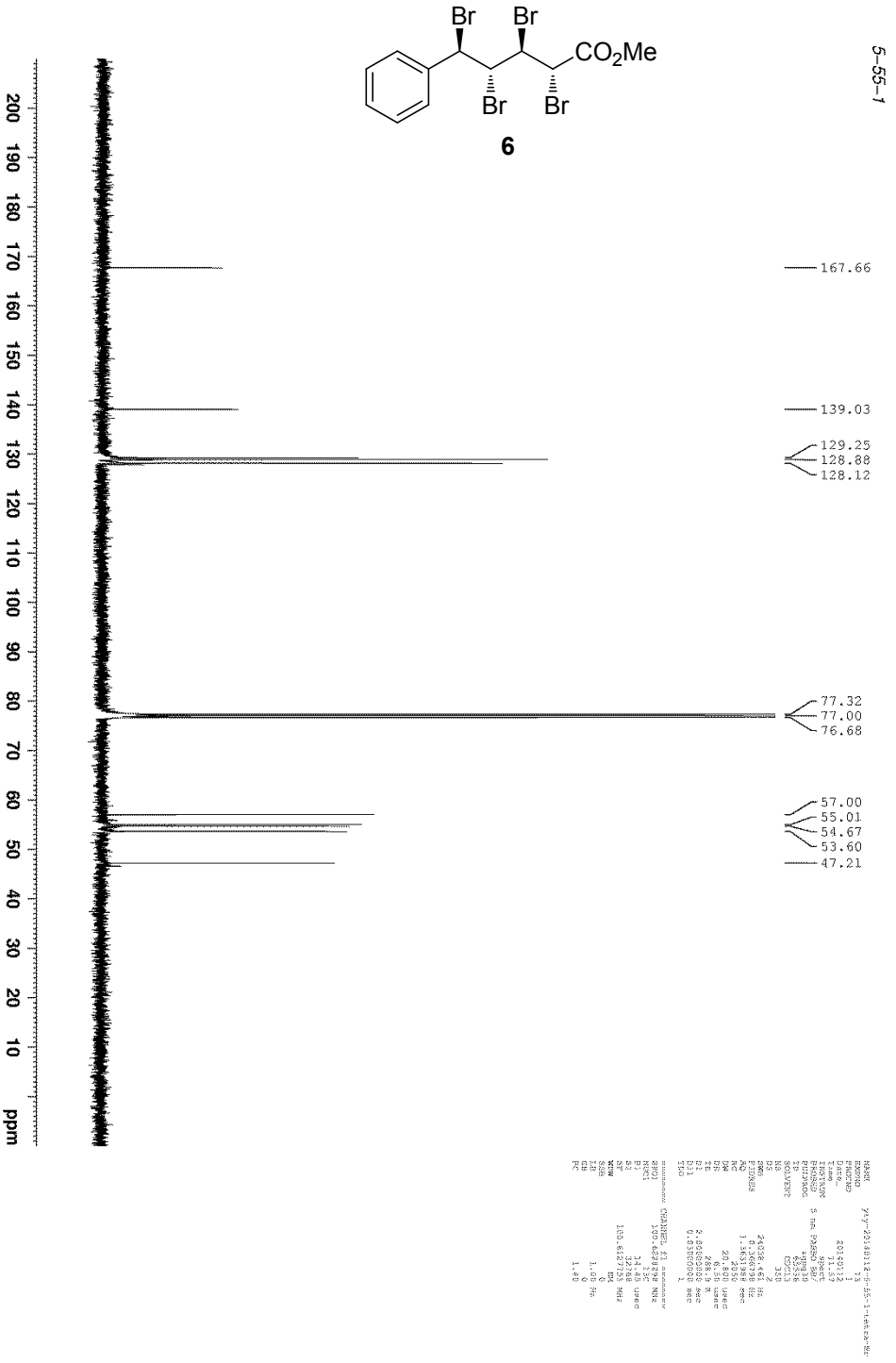
^{13}C NMR spectrum of compound **4g** ($CDCl_3$, 100 MHz)



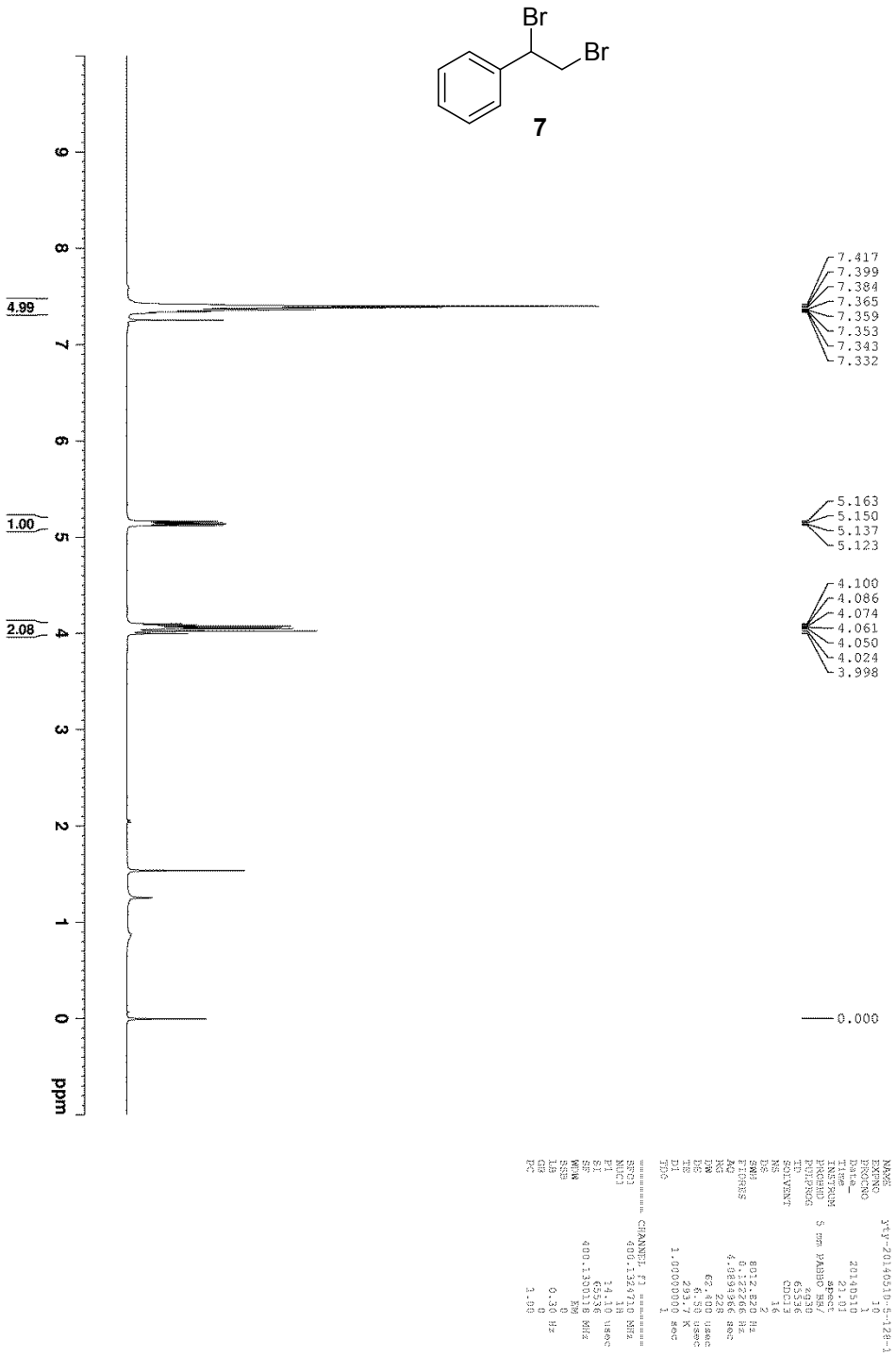
^{1}H NMR spectrum of compound **6** ($CDCl_3$, 400 MHz)



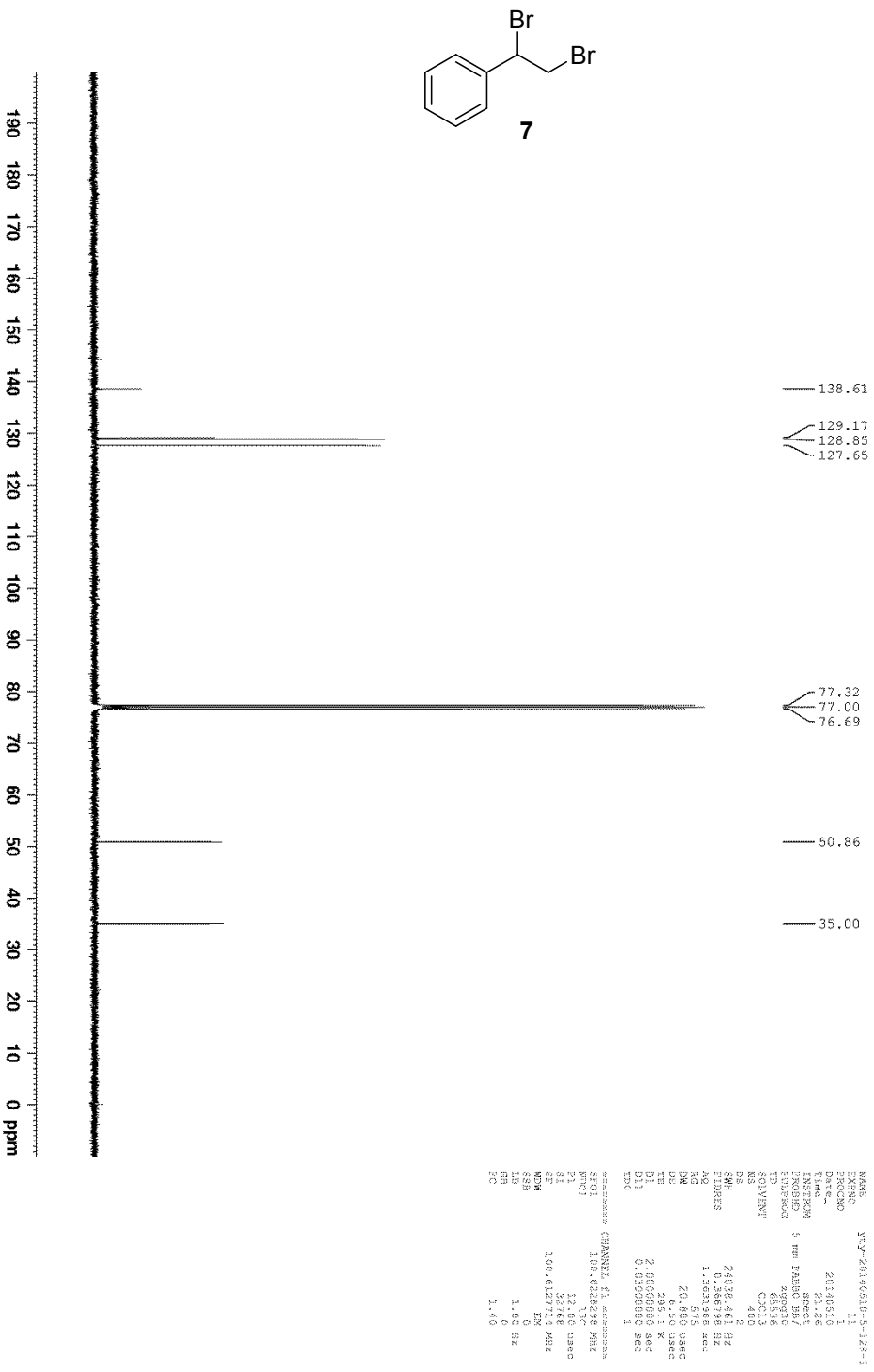
^{13}C NMR spectrum of compound **6** ($CDCl_3$, 100 MHz)



^{1}H NMR spectrum of compound **7** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of compound **7** ($CDCl_3$, 100 MHz)


Br
Br
7
138.61
129.17
128.85
127.65
77.32
77.00
76.69
50.86
35.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

9. Reference

1. L. Gremaud and A. Alexakis, *Angew. Chem.* 2012, **124**, 818; *Angew. Chem. Int. Ed.*, 2012, **51**, 794.
2. D. Belmessieri, L. C. Morrill, C. Simal, A. M. Z. Slawin and A. D. Smith, *J. Am. Chem. Soc.,* 2011, **133**, 2714.
3. Y. Ruland, P. Noereuil and M. Baltas, *Tetrahedron,* 2005, **61**, 8895.
4. H. Sugimura, M. Miura and N. Yamada, *Tetrahedron: Asymmetry,* 1997, **8**, 4089.
5. W. Cao, X. Liu, R. Peng, P. He, L. Lin and X. Feng, *Chem. Commun.*, 2013, **49**, 3470.