Supplementary Material (ESI) for Chemical Communications

Supporting information

Pd^0-Catalyzed Carbonylation of 1,1-Dichloro-1-Alkenes, a New Selective Access to *Z*-α-Chloroacrylates

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General Experimental Procedures

^{1}H NMR-Spectra (300 or 500 MHz), **^{13}C NMR-spectra** (75 MHz) spectra were recorded on Brüker spectrometers. Chemical shifts are given in ppm (δ) and were referenced to the internal solvent signal or to TMS used as an internal standard (^{1}H and ^{13}C NMR). Multiplicities are declared as follow: *s* (singlet), *br s* (broad singlet), *d* (doublet), *t* (triplet), *q* (quadruplet), *quint* (quintuplet), *sept* (septet), *dd* (doublet of doublet), *ddd* (doublet of doublet of doublet), *dt* (doublet of triplet), *m* (multiplet). Coupling constants *J* are given in Hz.

Infrared spectra (IR) were recorded on a Perkin-Elmer FT-IR system using diamond window Dura SamplIR II and the data are reported in reciprocal centimetres (ν, cm^{-1}).

Mass spectra were recorded on a Micromass LCT (ESI) or on a thermo finnigan map95xl (CI).

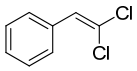
Reactions were performed using oven dried glasswares under an atmosphere of dry argon. Silica gel 60 (35-70 μm) was used for flash chromatography. Silica gel (5 μm) was used for HPLC. TLC plates (Merck 60 F_{254} aluminum sheets) were rendered visible by ultraviolet and/or spraying with phosphomolybdic acid (5%) in MeOH or vanillin (1%) + sulfuric acid (5%) in EtOH followed by heating.

Solvents: Tetrahydrofuran was distilled under Argon on sodium-benzophenone. Dichloromethane was distilled under Argon on CaH_2. Unless otherwise noted, all reagent-grade chemicals and solvents were obtained from commercial suppliers (Sigma-Aldrich, Acros Organics and Avocado) and were used as received.

CAUTION: CO is a highly toxic odorless and colorless gas. Reactions involving Carbone Monoxide must be performed in a well ventilated hood with a Carbon Monoxide detector nearby.

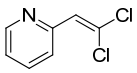
1,1-dichloro-1-alkene, general procedure[1]

Diethyl 1,1,1-trichloromethylphosphonate (1.2 equiv. In THF) was added dropwise to a solution of *n*-BuLi (1.25 equiv in THF) at -100°C and stirred for 10 min. The aldehyde (1 equiv. in THF) was then added dropwise at -100 °C. The reaction mixture was slowly warm to room temperature and stirred overnight before being quenched by a 1/1 mixture of ice/2N HCl and extracted with CH_2Cl_2 (three times). The organic layers were dried over $MgSO_4$, filtered concentrated under *vacuum* and purified by flash column chromatography on silica gel to furnish the title compound.



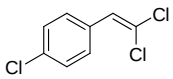
(2,2-dichlorovinyl)benzene[2] **(1a):**

The product (10.97 g, 87%) as a colorless oil was prepared according to the general procedure described above. Spectroscopic and analytical data were in accordance with those reported in the literature. R*f* 0.66 (heptanes/ethylacetate 9/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 6.86 (s, 1H), 7.31 (t, *J*= 7.1 Hz, 1H), 7.37 (t, *J*= 7.4 Hz, 2H), 7.53 (d, *J*= 7.4 Hz, 2H).



2-(2,2-dichlorovinyl)pyridine[3] **(1e):**

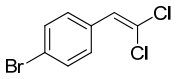
The product (680 mg, 78%) as a colorless oil was prepared according to the general procedure described above. R*f* 0.44 (heptanes/ethylacetate 7/3), IR (neat) υ_{max}/cm^{-1} 3053, 1608, 1580, 1567, 1460, 1433, 990, 912, 829, 768, 739, 670, 626; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 7.04 (s, 1H), 7.21 (ddd, *J*= 6.8, 4.7, 1.5 Hz, 1H), 7.71 (td, *J*= 7.6, 1.7 Hz, 1H), 7.74 (t, *J*= 7.6 Hz, 1H), 8.63 (d, *J*= 4.8 Hz, 1H); ^{13}C (75 MHz, $CDCl_3$) δ_C 123.0 (1), 123.8(1) , 124.8 (0), 129.4 (1), 136.5 (1), 149.8 (1), 152.6 (0); MS (EI) m/z 173, 175.



1-chloro-4-(2,2-dichlorovinyl)benzene[4] **(1f):**

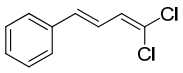
[1] Villieras, J.; Perriot, P.; Normant, J. F. *Synthesis*, **1975**, 458-461
[2] Liron, F.; Fosse, C.; Pernolet, A.; Roulland, E. *J. Org. Chem.* **2007,** *72*, 2220-2223
[3] Jubault, P.; Feasson, C.; Collignon N. *Bull. Soc. Chim. Fr.* **1994**, *131*, 1001-1006.
[4] Krabbenhoft, H. O. *J. Org. Chem.* **1978,** 43, 1305-1311.

The product (670 mg, 65%) as a colorless oil was prepared according to the general procedure described above. Spectroscopic and analytical data were in accordance with those reported in the literature. R*f* 0.57 (heptanes/ethylacetate 97/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 6.81 (s, 1H), 7.34 (d, *J*= 8.6 Hz, 2H), 7.47 (d, *J*= 8.7 Hz, 2H).



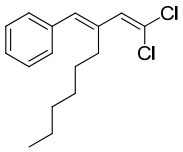
1-bromo-4-(2,2-dichlorovinyl)benzene[5] (1g):

The product (1.04 g, 80%) as a colorless oil that crystallized at 4°C was prepared according to the general procedure described above. Spectroscopic and analytical data were in accordance with those reported in the literature. R*f* 0.51 (heptanes/ethylacetate 97/3); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 6.79 (s, 1H), 7.40 (d, *J*= 8.6 Hz, 2H), 7.50 (d, *J*= 8.7 Hz, 2H).



(*E*)-(4,4-dichlorobuta-1,3-dienyl)benzene[6] (1h):

The product (600 mg, 60%) as a yellow oil that crystallized at 4 °C was prepared according to the general procedure described above. Spectroscopic and analytical data were in accordance with those reported in the literature. R*f* 0.75 (heptanes/ethylacetate 9/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 6.58 (d, *J*= 10.5 Hz, 1H), 6.65 (d, *J*= 15.7 Hz, 1H), 6.89 (dd, *J*= 15.7, 10.5 Hz, 1H), 7.29 (d, *J*= 7.5 Hz, 1H), 7.34 (t, *J*= 7.4 Hz, 2H), 7.44 (d, *J*= 7.4 Hz, 1H).

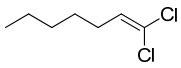


(*E*)-(2-(2,2-dichlorovinyl)oct-1-enyl)benzene (1i):

The product (1.219 g, 86 %) as a colorless oil was prepared according to the general procedure described above. R*f* 0.77 (heptanes/ethylacetate 9/1), IR (neat) υ_{max}/cm^{-1} 2954, 2925, 2854, 1598, 1492, 1456, 1377, 1073, 861, 746, 695; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.86 (t, *J*= 6.8 Hz, 3H), 1.22-1.32 (m, 6H); 1.45-1.51 (m, 2H), 2.40 (m, 2H), 6.43 (d, *J*= 1.3 Hz, 1H), 6.68 (s, 1H), 7.24-7.26 (m, 3H), 7.34 (t, *J*= 7.5 Hz, 2H); ^{13}C (75 MHz, $CDCl_3$) δ_C 14.1 (3), 22.6 (2), 28.9 (2), 29.1 (2), 30.1 (2), 31.5 (2), 119.8 (0), 127.1 (1), 128.3 (1), 128.8

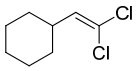
[5] Shastin, A. V.; Korotchenko, V. N.; Nenajdenko, V. G.; Balenkova E. S. *Tetrahedron*, **2000**, *56*, 6557-6564
[6] Brady, W. T.; Saidi, K. *J. Org. Chem.* **1979,** 44, 733-737.

(1), 131.7 (1), 132.7 (1), 136.6 (0), 136.9 (0), MS (CI) *m/z* 247, 249, 283, 285 HRMS (CI) *m/z* calcd for $C_{16}H_{21}Cl_2$ 283.1020, found 283.1020.



1,1-dichlorohept-1-ene[2] (1j):

The product (650 mg, 86%) as a colorless oil was prepared according to the general procedure described above and purified by distillation. Spectroscopic and analytical data were in accordance with those reported in the literature. R*f* 0.66 (heptanes/ethylacetate 97/3), ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.90 (t, *J*= 6.8 Hz, 3H), 1.30 (m, 4H), 1.41 (quint, *J*= 7.1 Hz, 2H), 2.16 (q, *J*= 7.3 Hz, 2H), 5.85 (t, *J*= 7.4 Hz, 1H).

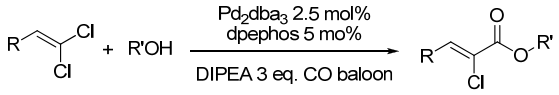


(2,2-dichlorovinyl)cyclohexane[1] (1l):

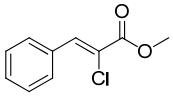
The product (800 mg, 89%) as a colorless oil was prepared according to the general procedure described above. Spectroscopic and analytical data were in accordance with those reported in the literature. R*f* 0.55 (heptanes 100%), ^{1}H NMR (500 MHz, $CDCl_3$) δH 1.06-1.22 (m, 3H), 1.26-1.34 (m, 2H), 1.63-1.66 (m, 1H), 1.69-1.73 (m, 4H), 2.33-2.39 (m, 1H), 5.70 (d, *J*= 9.2 Hz, 1H).

1,1-dichloro-1-alkene **1k** is commercially available, 1,1-dichloro-1-alkenes **1b**, **1c**, **1d** were previously prepared in our laboratory following Liron *et al*. procedure.[2]

Carbonylation of 1,1-dichloro-1-alkene, general procedure

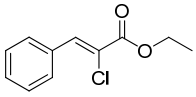


A flask was charged with Pd_2dba_3 (22.9 mg, 0.025 mmol), dpephos (26.9 mg, 0.05mmol) and purged with argon. Dichloroalkene (1 mmol, in 6 ml of degassed alcohol) and DIPEA (522 µl, 3 mmol) were added. The mixture was stirred for 5 min and purged and backfilled with carbon monoxide (balloon), heated at the appropriate temperature for the indicated time. After cooling at room temperature, the mixture was directly purified by column chromatography on silica gel (for BnOH and MPMOH) or concentrated under vacuum, partitioned between ethylacetate and water, extracted (twice with ethylacetate), dried over $MgSO_4$, filtered, concentrated under vacuum and purified by column chromatography (other alcohol) to afford the desired chloroacrylate.



(*Z*)-methyl 2-chloro-3-phenylacrylate[7] (2aa):

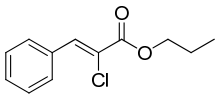
Acrylate **2aa** was prepared according to the general procedure described above (60°C, 70h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 95/5) provides the title compound as colorless oil witch solidifies at 4 °C (133 mg, 68 %). Spectroscopic and analytical data were in accordance with those reported in the literature. R*f* 0.30 (heptanes/ethylacetae 9/1), IR (neat) υ_{max}/cm^{-1}; 2951, 1721, 1615, 1446, 1433, 1242, 4498, 1038, 764; ^1H NMR (500 MHz, $CDCl_3$) δ_H 3.91 (s, 3H), 7.41-7.45 (m, 3H), 7.84 (d, *J*= 7.8 Hz, 2H), 7.91 (s, 1H); MS (CI) *m/z* 197, 199 HRMS (CI) *m/z* calcd for $C_{10}H_{10}ClO_2$ 197.0369, found 197.0368.



(*Z*)-ethyl 2-chloro-3-phenylacrylate[8] (2ab):

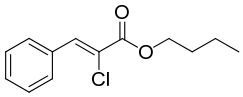
[7] Barma, D. K. ; Kundu, A., Zhang, H. Mioskowski, C. Falck, J. R. *J. Am. Chem. Soc*. **2003**, *125*, 3218-3219
[8] Concellon, J. M., Huerta, M. *J. Org. Chem*, **2005**, *70*, 4714-4719.

Acrylate **2ab** was prepared according to the general procedure described above (70°C, 65h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 98/2) provides the title compound as colorless oil (184 mg, 87 %). Spectroscopic and analytical data were in accordance with those reported in the literature. R*f* 0.30 (heptanes/ethylacetate 9/1); IR (neat) υ_{max}/cm^{-1} 2980, 1713, 1614, 1492, 1446, 1366, 1237, 1196, 1037; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 1.39 (t, *J*= 7.0 Hz, 3H), 4.36 (q, *J*= 7.0 Hz, 2H), 7.41-7.45 (m, 3H), 7.84 (d, *J*= 7.5 Hz, 2H), 7.91 (s, 1H); ^{13}C (75 MHz, $CDCl_3$) δ_C 14.2 (3), 62.3 (2), 122.2 (0), 128.5 (1), 130.2 (1), 130.6 (1), 133.0 (0), 136.9 (1), 163.4 (0); MS (CI) *m/z* 211, 213 HRMS (CI) m/z calcd for $C_{11}H_{12}ClO_2$ 211.0526, found 211.0525.



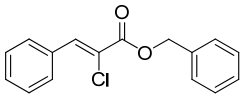
(*Z*)-propyl 2-chloro-3-phenylacrylate (2ac):

Acrylate **2ac** was prepared according to the general procedure described above (85°C, 65h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 98/2) provides the title compound as a pale yellow oil (145 mg, 65 %). R*f* 0.36 (heptanes/ethylacetate 9/1); IR (neat) υ_{max}/cm^{-1} 2969, 1716, 1615, 1492, 1446, 1236, 1196, 1023, 763; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 1.02 (t, *J*= 7.5 Hz, 3H), 1.78 (m, 2H), 4.26 (t, *J*= 6.7 Hz, 2H), 7.40-7.45 (m, 3H), 7.84 (d, *J*= 7.6 Hz, 2H), 7.91 (s, 1H); ^{13}C (75 MHz, $CDCl_3$) δ_C 10.4 (3), 22.0 (2), 68.1 (2), 122.3 (0), 128.6 (1), 130.2 (1), 130.7 (1), 133.0 (0), 136.9 (1), 163.5 (0); MS (CI) *m/z* 225, 227; HRMS (CI) *m/z* calcd for $C_{12}H_{14}ClO_2$ 225.0682, found 225.0682.



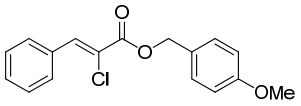
(*Z*)-butyl 2-chloro-3-phenylacrylate (2ad):

Acrylate **2ad** was prepared according to the general procedure described above (105 °C, 65h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 100/0 to 97/3) provides the title compound as colorless oil (164 mg, 69 %). R*f* 0.42 (heptanes/ethylacetate 9/1); IR (neat) υ_{max}/cm^{-1} 2958, 1716, 1616, 1492, 1447, 1239, 1196, 1031; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.98 (t, *J*= 7.4 Hz, 3H), 1.47 (h, *J*= 7.3 Hz, 2H), 1.75 (q, *J*= 7.2 Hz, 2H), 4.30 (t, *J*= 6.7 Hz, 2H), 7.41-7.45 (m, 3 H), 7.84 (d, *J*= 7.5 Hz, 2H), 7.90 (s, 1H); ^{13}C (75 MHz, $CDCl_3$) δ_C 13.7 (3), 19.2 (2), 30.6 (2), 66.4 (2), 122.3 (0), 128.5 (1), 130.2 (1), 130.6 (1), 133.0 (0), 136.9 (1), 163.5 (0); MS (CI) *m/z* 239, 241 HRMS (CI) m/z calcd for $C_{13}H_{16}ClO_2$ 239.0839, found 239.0837.



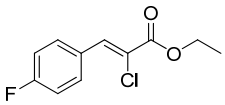
(*Z*)-benzyl 2-chloro-3-phenylacrylate (2ae):

Acrylate **2ae** was prepared according to the general procedure described above (70°C, 24h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 97/3) provides the title compound as colorless oil witch solidifies at 4 °C (237 mg, 87 %). R*f* 0.37 (heptanes/ethylacetate 9/1); IR (neat) υ_{max}/cm^{-1} 3030, 2966, 1713, 1616, 1491, 1447, 1372, 1232, 1207, 1018; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 5.33 (s, 2H), 7.36-7.45 (m, 8 H), 7.83 (d, *J*= 8.0 Hz, 2H), 7.94 (s, 1H); ^{13}C (75 MHz, $CDCl_3$) δ_C 13.7 (3), 19.2 (2), 30.6 (2), 66.4 (2), 122.3 (0), 128.5 (1), 130.2 (1), 130.6 (1), 133.0 (0), 136.9 (1), 163.5 (0); MS (CI) *m/z* 273, 275; HRMS (CI) m/z calcd for$C_{16}H_{14}ClO_2$ 273.0682, found 273.0680.



(*Z*)-4-methoxybenzyl 2-chloro-3-phenylacrylate (2af):

Acrylate **2af** was prepared according to the general procedure described above (70°C, 24h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 95/5) provides the title compound as colorless oil witch solidifies at 4 °C (274 mg, 91 %). R*f* 0.25 (heptanes/ethylacetate 9/1); IR (neat) υ_{max}/cm^{-1} 2962, 2845, 1702, 1609, 1511, 1446, 1378, 1233, 1176, 1024; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 3.82 (s, 3H), 5.26 (s, 2H), 6.93 (d, *J*= 9.0 Hz, 2H), 7.37-7.43 (m, 5H), 7.82 (d, *J*= 9.0Hz, 2H), 7.90 (s, 1H); ^{13}C (75 MHz, $CDCl_3$) δ_C 55.3 (3), 68.0 (2), 114.1 (1), 122.1 (0), 127.5 (0), 128.6 (1), 130.2 (1), 130.3 (1), 130.7 (1), 132.9 (0), 137.3 (1), 159.9 (0), 163.4 (0); MS (ESI) *m/z* 325, 327 $[M+Na]^+$; HRMS (ESI) *m/z* calcd for $C_{17}H_{15}O_3NaCl$ 325.0607, found 325.0621.

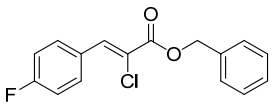


(*Z*)-ethyl 2-chloro-3-(4-fluorophenyl)acrylate[9] (2bb):

Acrylate **2bb** was prepared according to the general procedure described above (70°C, 84h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 97/3) provides the title compound as a pale yellow oil (125 mg, 55 %). R*f* 0.30 (heptanes/ethylacetate 9/1); IR (neat) υ_{max}/cm^{-1} 2980, 1717, 1617, 1599, 1506, 1411, 1366, 4563, 1225, 1194, 1160, 1039; ^{1}H

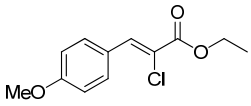
[9] Tay, M. K.; About-Jaudet, E.; Collignon, N.; Teulade, M. P.; Savignac, Ph. *Synth.Commun.* **1988**, *18*, 1349.

NMR (500 MHz, $CDCl_3$) δ_H 1.39 (t, *J*= 7.2 Hz, 3H), 4.35 (q, *J*= 7.2 Hz, 2H), 7.12 (t, *J*= 8.6 Hz, 2H), 7.85-7.88 (m, 3H); ^{13}C (75 MHz, $CDCl_3$) δ_C 14.3 (3), 62.7 (2), 115.8 (1, *J*= 21.8 Hz), 122.0 (0), 129.3 (0, *J*= 3.3 Hz), 132.9 (1, *J*= 8.7 Hz), 135.7 (1), 163.4 (0), 163.6 *J*= 247.6 Hz (0); MS (CI) *m/z* 229, 231; HRMS (CI) *m/z* calcd for $C_{11}H_{11}ClFO_2$ 229.0432, found 229.0431.



(*Z*)-benzyl 2-chloro-3-(4-fluorophenyl)acrylate (2be):

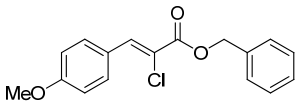
Acrylate **2be** was prepared according to the general procedure described above (70°C, 24h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 95/5) provides the title compound as white solid (238 mg, 82 %). R*f* 0.31 (heptanes/ethylacetate 9/1); Mp: 42°C; IR (neat) υ_{max}/cm^{-1} 3037, 1704, 1618, 1597, 1504, 1454, 1407, 1256, 1227, 1191, 1154, 1100; ^1H NMR (500 MHz, $CDCl_3$) δ_H 5.33 (s, 2H), 7.11 (t, *J*= 8.7 Hz, 2H), 7.36-7.44 (m, 5H), 7.84-7.87 (m, 2H), 7.89 (s, 1H); ^{13}C (75 MHz, $CDCl_3$) δ_C 68.2 (2), 115.8 (1, J = 21.8 Hz), 121.6 (0), 128.4 (1), 128.6 (1), 128.7 (1), 129.1 (0, d, J = 3.3 Hz), 132.9 (1, J = 7.6 Hz), 135.4 (0), 136.1 (1), 163.2 (0), 163.3 (0, *J* = 252 Hz); MS (CI) *m/z* 291, 293; HRMS (CI) *m/z* calcd for $C_{16}H_{13}ClFO_2$ 291.0588, found 291.0585.



(*Z*)-ethyl 2-chloro-3-(4-methoxyphenyl)acrylate[10] (2cb):

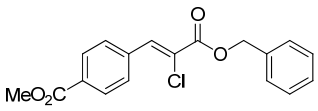
Acrylate **2cb** was prepared according to the general procedure described above (70°C, 84h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 95/5) provides the title compound as colorless oil (108 mg, 45%). R*f* 0.25 (heptanes/ethylacetate 9/1); IR (neat) υ_{max}/cm^{-1} 2976, 2838, 1712, 1598, 1508, 1461, 1421, 1365, 1241, 1170, 1028; ^1H NMR (500 MHz, $CDCl_3$) δ_H 1.38 (t, *J*= 7.2 Hz, 3H), 4.33 (q, *J*= 7.2 Hz, 2H), 6.95 (d, *J*= 8.8 Hz, 2H), 7.85 (s, 1H), 7.86 (d, *J*= 8.8 Hz, 2H); ^{13}C (75 MHz, $CDCl_3$) δ_C 14.3 (3), 55.4 (3), 62.4 (2), 114.1 (1), 119.6 (0), 125.6 (0), 132.7 (1), 136.5 (1), 161.1 (0), 163.7 (0); MS (CI) *m/z* 241, 243; HRMS (CI) *m/z* calcd for $C_{12}H_{14}ClO_3$ 241.0631, found 241.0632.

[10] Thomas, O.; Reinhard, B. *Synthesis* **2004**, 2135.



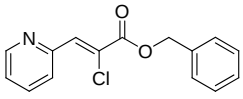
(*Z*)-benzyl 2-chloro-3-(4-methoxyphenyl)acrylate (2ce):

Acrylate **2ce** was prepared according to the general procedure described above (70°C, 24h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 97/3) provides the title compound as pale yellow solid (243 mg, 80 %). R*f* 0.37 (heptanes/ethylacetate 9/1); Mp : 48°C; IR (neat) υ_{max}/cm^{-1} 3030, 2952, 2894, 2835, 1696, 1598, 1507, 1456, 1420, 1239, 1200, 1169, 1023; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 3.85 (s, 3H), 5.32 (s, 2H), 6.94 (d, *J*= 9.0 Hz, 2H), 7.36-7.45 (m, 5 H), 7.86 (d, *J*= 8.9 Hz, 2H), 7.89 (s, 1H); ^{13}C (75 MHz, $CDCl_3$) δ_C 55.4 (3), 67.9 (2), 114.1 (1), 119.3 (0), 125.6 (0), 128.3 (1), 128.5 (1), 128.7 (1), 132.8 (1), 135.6 (0), 137.0 (1), 161.2 (0), 163.6 (0); MS (CI) *m/z* 303, 305 HRMS (CI) *m/z* calcd for $C_{17}H_{16}ClO_3$ 303.0788, found 303.0788.



(Z)-methyl 4-(3-(benzyloxy)-2-chloro-3-oxoprop-1-enyl)benzoate (2de):

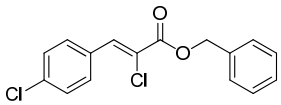
Acrylate **2de** was prepared according to the general procedure described above (70°C, 24h). Purification by flash chromatography on silica gel (toluene/ethylacetate 100/1) provides the title compound as a white solid (260 mg, 78%). R*f* 0.30 (heptanes/ethylacetate 7/3); Mp: 94°C; IR (neat) υ_{max}/cm^{-1} 3030, 2953, 2893, 2836, 1696, 1598, 1507, 1456, 1420, 1238, 1169, 1022; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 3.93 (s, 3H), 5.34 (s, 2H), 7.36-7.45 (m, 5H), 7.87 (d, *J*= 8.2 Hz, 2H), 7.95 (s, 1H), 8.07 (d, *J*= 8.3 Hz, 2H); ^{13}C (75 MHz, $CDCl_3$) δ_C 52.5 (3), 68.5 (2), 124.3 (0), 128.6 (1), 128.8 (1), 128.9(1), 129.8 (1), 130.6 (1), 131.4 (0), 135.4 (0), 136.3 (1), 137.3 (0), 163.1 (0), 166.6 (0); MS (CI) *m/z* 331, 333; HRMS (CI) *m/z* calcd for $C_{18}H_{16}ClO_4$ 331.0737, found 331.0736.



(*Z*)-benzyl 2-chloro-3-(pyridin-3-yl)acrylate (2ee):

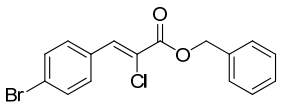
Acrylate **2ee** was prepared according to the general procedure described above (70°C, 24h). Benzyl alcohol was distilled under vacuum (2.10^{-2} Torr, 95 °C) before purification by flash chromatography on silica gel (heptanes/ethylacetate 2/2) that provides the title compound as a colorless oil (172 mg, 63%). R*f* 0.23 (heptanes/ethylacetate 7/3); IR (neat) υ_{max}/cm^{-1} 3049,

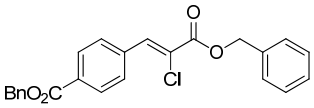
1719, 1618, 1581, 1457, 1374, 1233, 1199, 1093, 1022; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 5.33 (s, 1H), 7.29 (dd, *J*= 7.6, 5.0 Hz, 1H), 7.35-7.44 (m, 5H), 7.78 (td, *J*= 7.8, 1.7 Hz, 1H), 8.07 (s, 1H), 8.15 (d, *J*= 8.0 Hz, 1H), 8.70 (d, *J*= 5.0 Hz); ^{13}C (75 MHz, $CDCl_3$) δ_C 68.4 (2), 124.0 (1), 124.8 (0), 125.4 (1), 128.4 (1), 128.6 (1), 128.7 (1), 135.1 (0), 136.3 (1), 137.5 (1), 149.9 (1), 152.9 (0), 162.8 (0); MS (ESI) *m/z* 274, 276; HRMS (ESI) *m/z* calcd for$C_{15}H_{13}NO_2Cl$ 274.0635, found 274.0616.



(*Z*)-benzyl 2-chloro-3-(4-chlorophenyl)acrylate (2fe);

Acrylate **2fe** was prepared according to the general procedure described above (70°C, 24h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 95/5) provides the title compound as pale yellow needles (227 mg, 74%). R*f* 0.37 (heptanes/ethylacetate 9/1); Mp: 72°C; IR (neat) υ_{max}/cm^{-1} 3065, 3032, 1707, 1617, 1586, 1486, 1253, 1193, 1083, 1009; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 5.32 (s, 2H), 7.34-7.45 (m, 7 H), 7.77 (d, *J*= 8.5 Hz, 2H), 7.87 (s, 1H); ^{13}C (75 MHz, $CDCl_3$) δ_C 68.3 (2), 122.5 (0), 128.4 (1), 128.5 (1), 128.6 (1), 128.7 (1), 128.9 (1), 131.3 (0), 131.9 (1), 136.3 (0), 163.1 (0); MS (CI) *m/z* 307, 309; HRMS (CI) *m/z* calcd for$C_{16}H1_6Cl_2O_2$ 307.0293, found 307.0293.





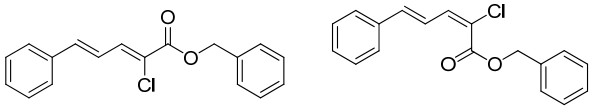
Acrylate **2ge** and **2gee** were prepared according to the general procedure described above (70°C, 72h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 95/5) provides the mono ester **2ge** as colorless solid (70 mg, 20%) and diester **2gee** as a colorless oil (151mg, 37 %).

(*Z*)-benzyl 2-chloro-3-(4-bromophenyl)acrylate (2ge):

R*f* 0.33 (heptanes/ethylacetate 9/1); Mp: 90°C IR (neat) υ_{max}/cm^{-1} 2959, 1708, 1610, 1581, 1488, 1454, 1446, 1397, 1361, 1253, 1194, 1073, 1024, 1008; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 5.33 (s, 2H), 7.35-7.46 (m, 5 H), 7.55 (d, *J*= 8.6 Hz, 2H), 7.70 (d, *J*= 8.6 Hz, 2H), 7.86 (s, 1H); ^{13}C (75 MHz, $CDCl_3$) δ_C 68.3 (2), 122.7 (0), 124.7 (0), 128.4 (1), 128.6 (1), 128.7 (1), 131.7 (0), 131.9 (1), 132.1 (1), 136.1 (0), 163.1 (0); MS (CI) *m/z* 351, 353, 355 HRMS (CI) *m/z* calcd for $C_{16}H_{13}BrO_2Cl$ 350.9788, found 350.9786.

(*Z*)-benzyl 4-(3-(benzyloxy)-2-chloro-3-oxoprop-1-enyl)benzoate (2gee):

R*f* 0.20 (heptanes/ethylacetate 9/1); IR (neat) υ_{max}/cm^{-1} 3031, 1731, 1615, 1497, 1454, 1409, 1375, 1255, 1235, 1195, 1098, 1016; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H, 5.33 (s, 2H), 5.38 (s, 2H), 7.39-7.44 (m, 10 H), 7.87 (d, *J*= 8.1 Hz), 7.94 (s, 1H), 8.11 (d, *J*= 8.1 Hz, 2H); ^{13}C (75 MHz, $CDCl_3$) δ_C, 67.0 (2), 68.4 (2), 124.2 (0), 128.3 (1, 2C), 128.4 (1, 3C), 128.6 (1, 1C), 128.7 (1, 2C), 128.8 (1, 2C), 129.8 (1, 2C), 130.5 (1, 2C), 131.2 (0), 135.2 (0), 135.9 (0), 136.2 (1), 137.2 (0), 162.9 (0), 165.7 (0); MS (CI) *m/z* 407, 409; HRMS (CI) *m/z* calcd for $C_{24}H2_0ClO_4$ 407.1050, found 407.1046.



Benzyl 2-chloro-5-phenylpenta-2,4-dienoate **2he**

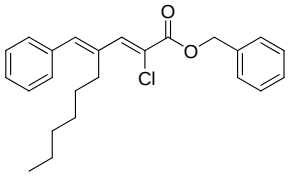
Acrylate XX was prepared according to the general procedure described above (70°C, 24h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 95/5) provides the *Z,E*-**2he** with solid (137 mg, 46 %) and *E,E*-**2he** as a colorless oil (75 mg, 25 %).

(2*Z*,4*E*)-benzyl 2-chloro-5-phenylpenta-2,4-dienoate (2he):

R*f* 0.24 (heptanes/ethylacetate 9/1); Mp: 58 °C IR (neat) υ_{max}/cm^{-1} 3022, 1708, 1613, 1588, 1495, 1448, 1380, 1257, 1231, 1147, 1021, 965; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 5.29 (s, 2H), 7.00 (d, *J*= 15.7 Hz), 7.21 (dd, *J*= 15.7, 10.8 Hz, 1H), 7.31-7.44 (m, 8H), 7.52 (d, *J*= 7.4 Hz), 7.64 (d, *J*= 10.8 Hz); ^{13}C (75 MHz, $CDCl_3$) δ_C 67.9 (2), 122.4 (0), 122.9 (1), 127.6 (1), 128.4 (1), 128.5 (1), 128.7 (1), 128.9 (1), 129.6 (1), 135.5 (0), 135.9 (0), 138.2 (1), 142.4 (1), 162.9 (0); MS (CI) *m/z* 299, 301; HRMS (CI) *m/z* calcd for $C_{18}H_{16}ClO_2$ 299.0839, found 299.0838.

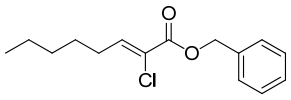
(2*E*,4*E*)-benzyl 2-chloro-5-phenylpenta-2,4-dienoate (2he):

R*f* 0.30 (heptanes/ethylacetate 9/1); IR (neat) υ_{max}/cm^{-1} 3030, 1711, 1609, 1577, 1447, 1378, 1350, 1315, 1300, 1259, 1197, 1143, 1003, 971; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 5.31 (s, 2H), 6.78 (d, *J*= 15.6 Hz), 7.07 (d, *J*= 11.5 Hz, 1H), 7.29-7.48 (m, 10H), 7.79 (dd, *J*= 15.6, 11.5 Hz, 1H); ^{13}C (75 MHz, $CDCl_3$) δ_C 67.8 (2), 121.1 (0), 124.2 (1), 127.5 (1), 128.4 (1), 128.5 (1), 128.77 (1), 128.80 (1), 129.3 (1), 135.3 (0), 136.1 (0), 141.4 (1), 142.5 (1), 162.6 (0); MS (CI) *m/z* 299, 301; HRMS (CI) *m/z* calcd for $C_{18}H_{16}ClO_2$ 299.0839, found 299.0837.



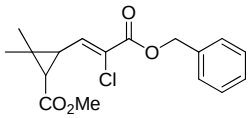
(2*Z*,4*E*)-benzyl 4-benzylidene-2-chlorodec-2-enoate (2ie):

Acrylate **2ie** was prepared according to the general procedure described above (70°C, 30h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 95/5) provides the title compound a pale yellow oil (292 mg, 76%). R*f* 0.35 (heptanes/ethylacetate 9/1); IR (neat) υ_{max}/cm^{-1} 2924, 2854, 1714, 1586, 1495, 1454, 1376, 1229, 1025; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.86 (t, *J*= 6.8 Hz, 3H), 1.22-1.34 (m, 6H), 1.47-1.53 (m, 2H), 2.60 (t, *J*= 7.9 Hz, 2H), 5.30 (s, 2H), 7.00 (s, 1H), 7.25-7.44 (m, 10 H), 7.57 (s, 1H); ^{13}C (75 MHz, $CDCl_3$) δ_C 14.2(3), 22.7 (2), 29.2 (2), 29.4 (2), 29.7 (2), 31.6 (2), 68.0 (2), 120.8(0), 127.8 (1), 128.3 (1), 128.4 (1), 128.5 (1), 128.7 (1), 129.1 (1), 135.6(0) 136.6 (0), 137.5 (0),138.4 (1), 141.4 (1), 163.5 (0); MS (CI) *m/z* 383, 385; HRMS (CI) *m/z* calcd for $C_{24}H_{28}ClO_2$ 383.1778, found 383.1787.



(Z)-benzyl 2-chlorooct-2-enoate (2je):

Acrylate **2je** was prepared according to the general procedure described above (100°C, 17h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 97/3) provides the title compound as colorless oil (135 mg, 50%). R*f* 0.55 (heptanes/ethylacetate 9/1); IR (neat) υ_{max}/cm^{-1} 2927, 2858, 1718, 1628, 1497, 1455, 1375, 1235, 1025; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 0.89 (t, *J*= 6.3 Hz, 3H), 1.28-1.34 (m, 4H), 1.45-1.51 (m, 2H), 2.35 (q, *J*= 7.4 Hz, 2H), 5.25 (s, 2H), 7.11 (t, *J*= 7.2 Hz, 1H), 7.34-7.40 (m, 5H); ^{13}C (75 MHz, $CDCl_3$) δ_C 13.9 (3), 22.4 (2), 27.2 (2), 29.5 (2), 31.5 (2), 67.7 (2), 124.5 (0), 128.2 (1), 128.4 (1), 128.6 (1), 135.5 (0), 143.1 (1), 162.5 (0); HRMS (ESI) *m/z* calcd for $C_{15}H_{19}ClNaO_2$ 289.0971, found 289.0972.



methyl-3-((Z)-3-(benzyloxy)-2-chloro-3-oxoprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate (2ke):

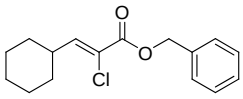
Acrylate **2ke** was prepared according to the general procedure described above (100°C, 17h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 95/5) provides *cis/trans* (3/7) cyclopropyle derivative as colorless oil (275 mg, 62%)

Cis

R*f* 0.54 (heptanes/ethylacetate 9/1); IR (neat) υ_{max}/cm^{-1} 2954, 1721, 1619, 1436, 1377, 1242, 1195, 1142, 1087, 1026; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 1.29 (s, 3H), 1.33 (s, 3H), 2.04 (d, *J*= 8.4 Hz, 1H), 2.29 (dd, *J*= 9.7, 8.5 Hz, 1H), 3.67 (s, 3H), 5.25 (d, *J*=, 12.0 Hz, 1H), 5.29 (d, *J*= 12.0 Hz, 1H), 7.32-7.41 (m, 5H), 7.55 (d, *J*= 9.7 Hz, 1H); ^{13}C (75 MHz, $CDCl_3$) δ_C 15.2 (3), 28.5 (3), 29.5 (0), 32.6 (1), 33.9 (1), 51.7 (3), 67.5 (2), 125.1 (0), 128.1 (1), 128.3 (1), 128.6 (1), 135.6 (0), 128.4 (1), 162.1 (0), 170.6 (0); MS (CI) *m/z* 323, 325; HRMS (CI) *m/z* calcd for $C_{17}H_{20}ClO_4$ 323.1050, found 323.1046.

trans

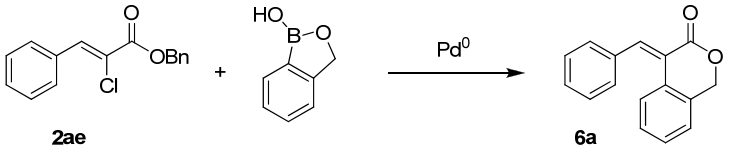
R*f* 0.46 (heptanes/ethylacetate 9/1); IR (neat) υ_{max}/cm^{-1} 2953, 1720, 1621, 1438, 1253, 1216, 1170, 1111, 1089, 1036; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H 1.25 (s, 3H), 1.34 (s, 3H), 1.84 (d, *J*= 5.2 Hz, 1H), 2.52 (dd, *J*= 9.7, 5.2 Hz, 1H), 3.70 (s, 3H), 5.23 (d, *J*= 12.5 Hz, 1H), 5.27 (d, *J*= 12.0 Hz, 1H), 6.79 (d, *J*= 9.7 Hz, 1H), 7.34-7.37 (m, 5H); ^{13}C (75 MHz, $CDCl_3$) δ_C 20.3 (3), 22.7 (3), 30.8 (0), 33.3 (1), 36.3 (1), 51.9 (3), 67.7 (2), 125.5 (0), 128.2 (1), 128.4 (1), 128.6 (1), 135.4 (0), 140.3 (1), 162.1 (0), 171.0 (0); MS (CI) *m/z* 323, 325; HRMS (CI) *m/z* calcd for $C_{17}H_{20}ClO_4$ 323.1050, found 323.1049.



(*Z*)-benzyl 2-chloro-3-cyclohexylacrylate (2le):

Acrylate **2le** was prepared according to the general procedure described above (100°C, 24h). Purification by flash chromatography on silica gel (heptanes/ethylacetate 97/3) provides the title compound a colorless oil (175 mg, 63%). R*f* 0.47 (heptanes/ethylacetate 95/5); IR (neat) υ_{max}/cm^{-1} 2925, 2851, 1720, 1625, 1448, 1252, 1216, 1142, 1020; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 1.10-1.40 (m, 5H), 1.66-1.77 (m, 5H), 2.56-2.66 (m, 1H), 5.24 (s, 2H), 6.93 (d, *J*= 9.4 Hz, 1H), 7.34-7.41(m, 5H); ^{13}C (75 MHz, $CDCl_3$) δ_C 25.4 (2), 25.7 (2), 30.9 (2), 38.7 (1), 67.7 (2), 122.7 (0), 128.3 (1), 128.4 (1), 128.6 (1), 135.5 (0), 147.4 (1), 162.7 (0); MS (CI) *m/z* 279, 281; HRMS (CI) *m/z* calcd for $C_{16}H_{20}ClO_2$ 279.1152, found 279.1151.

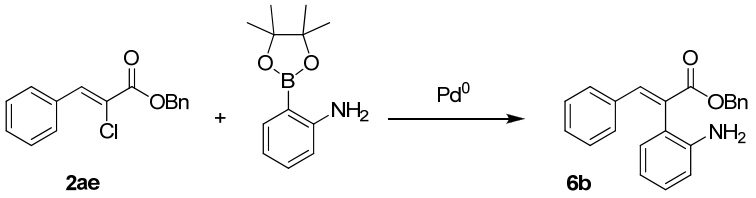
Suzuki-Miyaura rection with Z-α-chloroacrylates



2ae **6a**

(E)-4-benzylideneisochroman-3-one (6a):

Z-α-chloroacrylate **2ae** (64 mg, 0.235 mmol), benzo[c][1,2]oxaborol-1(3H)-ol (38 mg, 0.281 mmol), $Pd_2(dba)_3$ (5.4 mg, 0.0058 mmol), Ruphos (11.0 mg, 0.0235 mmol), Cs_2CO_3 (229 mg, 0.70 mmol), CsF (107 mg, 0.70 mmol) were introduced in a Schlenk tube flushed with argon. Then THF (1.9 mL) and H_2O (0.19 mL) were introduced, the tube was sealed and put in an oil bath at 80 °C. After 22 h of reaction, anhydrous Na_2SO_4 and EtOAc were added to the reaction medium, filtered, and the solvents were removed. The crude was purified by chromatography (heptanes/EtOAc : 4/1) affording lactone **6a** as a colorless solid (42.2 mg, 76%). Mp : 141 °C, R*f*= 0.29 (heptanes/ EtOAc : 10/1). IR (neat) υ_{max}/cm^{-1} 3023, 2919, 1724, 1618, 1387, 1149; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 5.32 (s, 2H), 7.14 (ddd, 1H, *J*= 7.5, 6.8, 1.9 Hz), 7.30 (m, 5H), 7.39 (d, 1H, *J*= 8.1 Hz), 7.46 (d, 2H, *J*= 6.4 Hz), 7.84 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 69.4, 125.2, 125.4, 127.6, 128.1, 128.6, 128.8, 129.5, 129.7, 130.6, 132.6, 134.5, 139.0, 168.8. MS (ESI): m/z= 259.1 ($M+Na^+$). HRMS (ESI) calcd for $C_{16}H_{12}O_2Na$: 259.0735. Found: 259.0739.

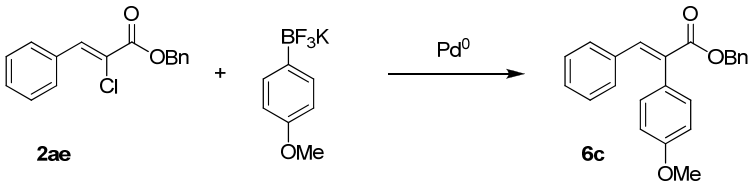


2ae **6b**

((E)-benzyl 2-(4-methoxyphenyl)-3-phenylacrylate (6b):

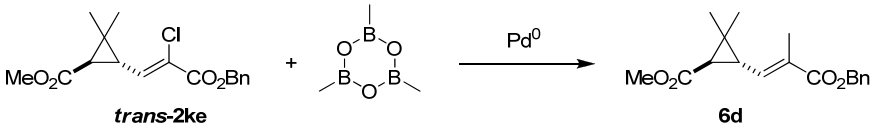
Z-α-chloroacrylate **2ae** (117.3 mg, 0.430 mmol), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (113 mg, 0.516 mmol), $Pd_2(dba)_3$ (9.8 mg, 0.0105 mmol), Ruphos (20.1 mg, 0.0430 mmol), Cs_2CO_3 (420 mg, 1.290 mmol) and CsF (196 mg, 1.290 mmol) were introduced in a Schlenk tube flushed with argon. Then THF (3.5 mL) and H_2O (0.35 mL) were introduced, the tube was sealed and put in an oil bath at 80 °C. After 22 h of reaction, anhydrous Na_2SO_4 and EtOAc were added to the reaction medium, filtered, and the solvents were removed. The crude was purified by chromatography (heptanes/EtOAc : 4/1) affording aniline **6b** as a yellow solid (104.7 mg, 75%). Mp= 112 °C, R*f*= 0.18 (heptanes/ EtOAc : 5/1). IR (neat) υ_{max}/cm^{-1} 3458, 3370, 3020, 1677, 1610, 1252; ^{1}H NMR (500 MHz, $CDCl_3$):

δ_H 5.26 (s, 2 H), 6.82 (t, 2H, *J*= 7.2 Hz), 7.01 (dd, 1H, *J*= 7.5, 1.6 Hz), 7.19 (m, 6H), 7.32 (m, 4H), 7.94 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 66.8, 116.0, 119.1, 121.6, 127.8, 128.1, 128.6, 129.2, 129.4, 129.8, 130.5, 134.4, 136.4, 142.3, 144.2, 167.8. HRMS (ESI) calcd for $C_{22}H_{19}NO_2Na$: 352.1313. Found: 352.1315.



((E)-benzyl 2-(4-methoxyphenyl)-3-phenylacrylate (6c):

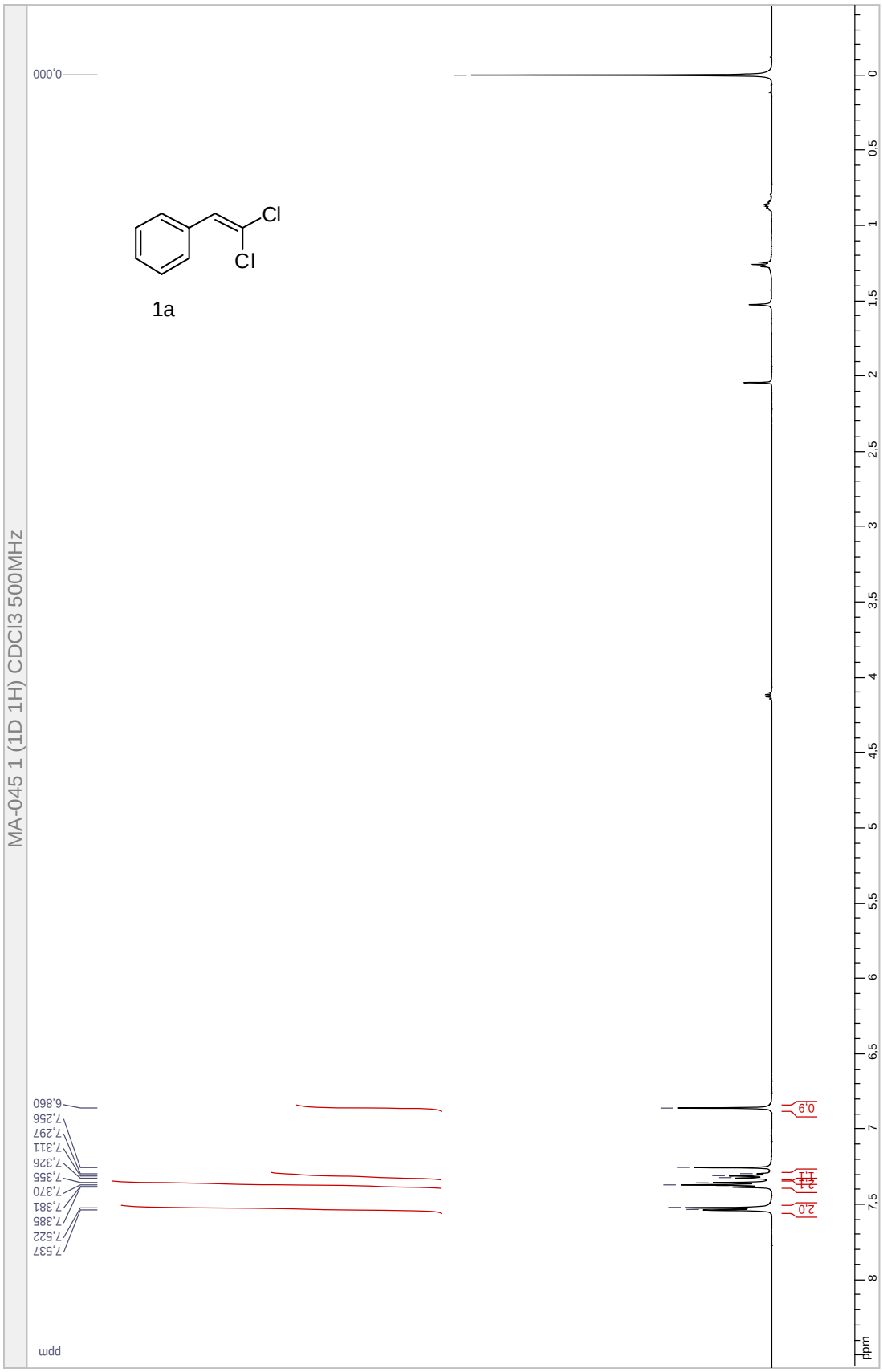
Z-α-chloroacrylate **2ae** (100.3 mg, 0.368 mmol), potassium 4-methoxyphenyltrifluoroborate (95 mg, 0.441 mmol), $Pd_2(dba)_3$ (8.4 mg, 0.0091 mmol), Ruphos (17.2 mg, 0.0368 mmol) and Cs_2CO_3 (360 mg, 1.103 mmol), were introduced in a Schlenk tube flushed with argon. Then THF (3.0 mL) and H_2O (0.30 mL) were introduced, the tube was sealed and put in an oil bath at 80 °C. After 19 h of reaction, anhydrous Na_2SO_4 and EtOAc were added to the reaction medium, filtered, and the solvents were removed. The crude was purified by chromatography twice (heptanes/EtOAc : 10/1, then PhMe/EtOAc : 100/2) affording ester **6c** as a colorless oil (124.5 mg, 98%). R*f*= 0.27 (heptanes/ EtOAc : 10/1). IR (neat) υ_{max}/cm^{-1} 3030, 2955, 2835, 1703, 1510, 1229, 1162; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.83 (s, 3H), 5.26 (s, 2H), 6.89 (d, 2H, *J*= 9.0 Hz), 7.08 (d, 2H, *J*= 7.3 Hz), 7.15 (d, 2H, *J*= 8.5 Hz), 7.17 (m, 2H), 7.31 (m, 2H), 7.34 (s, 4H), 7.82 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 55.3, 66.9, 114.2, 127.9, 128.0, 128.1, 128.3, 128.6, 128.8, 129.1, 130.7, 131.2, 132.2, 135.0, 136.4, 140.4, 159.3, 168.0. HRMS (ESI) calcd for $C_{23}H_{20}O_3Na$: 367.1310. Found: 367.1305.



Methyl 3-((E)-3-(benzyloxy)-2-methyl-3-oxoprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate (6d):

$Pd_2(dba)_3$ (6.4 mg, 0.0070 mmol), Ruphos (20.1 mg, 0.028 mmol) and Cs_2CO_3 (273 mg, 0.838 mmol) were introduced in a Schlenk tube flushed with argon. Then a solution of Z-α-chloroacrylate ***trans*-2ke** (90.2 mg, 0.279 mmol) and trimethylboroxine (50 wt% THF solution, 80 μL, 0.280 mmol) in THF (3.5 mL), were introduced, the tube was sealed and put

in an oil bath at 80 °C. After 18 h of reaction, EtOAc were added to the reaction medium, filtered through a 1cm silice pad, and the solvents were removed. The crude was purified by HPLC (heptanes/EtOAc: 10/1) affording diester **6d** as a yellow oil (65.6 mg, 78%). R*f*= 0.22 (heptanes/ EtOAc: 10/1). IR (neat) υ_{max}/cm^{-1} 2951, 1724, 1706, 1640, 1438, 1217; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.22 (s, 3H), 1.31 (s, 3H), 1.73 (d, 1H, *J*= 5.1 Hz), 1.97 (s, 3H), 2.21 (dd, *J*= 5.2, 9.6 Hz), 3.69 (s, 3H), 5.17 (d, 1H, *J*= 12.7 Hz), 5.20 (d, 1H, *J*= 12.7 Hz), 6.52 (d, 1H, *J*= 9.73 Hz), 7.32 (m, 1H), 7.35 (d , 4H *J*= 4.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 13.0, 20.6, 22.5, 30.3, 33.0, 36.1, 51.9, 66.4, 128.1, 128.2, 128.6, 129.6, 136.5, 140.0, 167.6, 171.9. HRMS (ESI) calcd for $C_{18}H_{22}O_4Na$: 325.1416. Found: 325.1423.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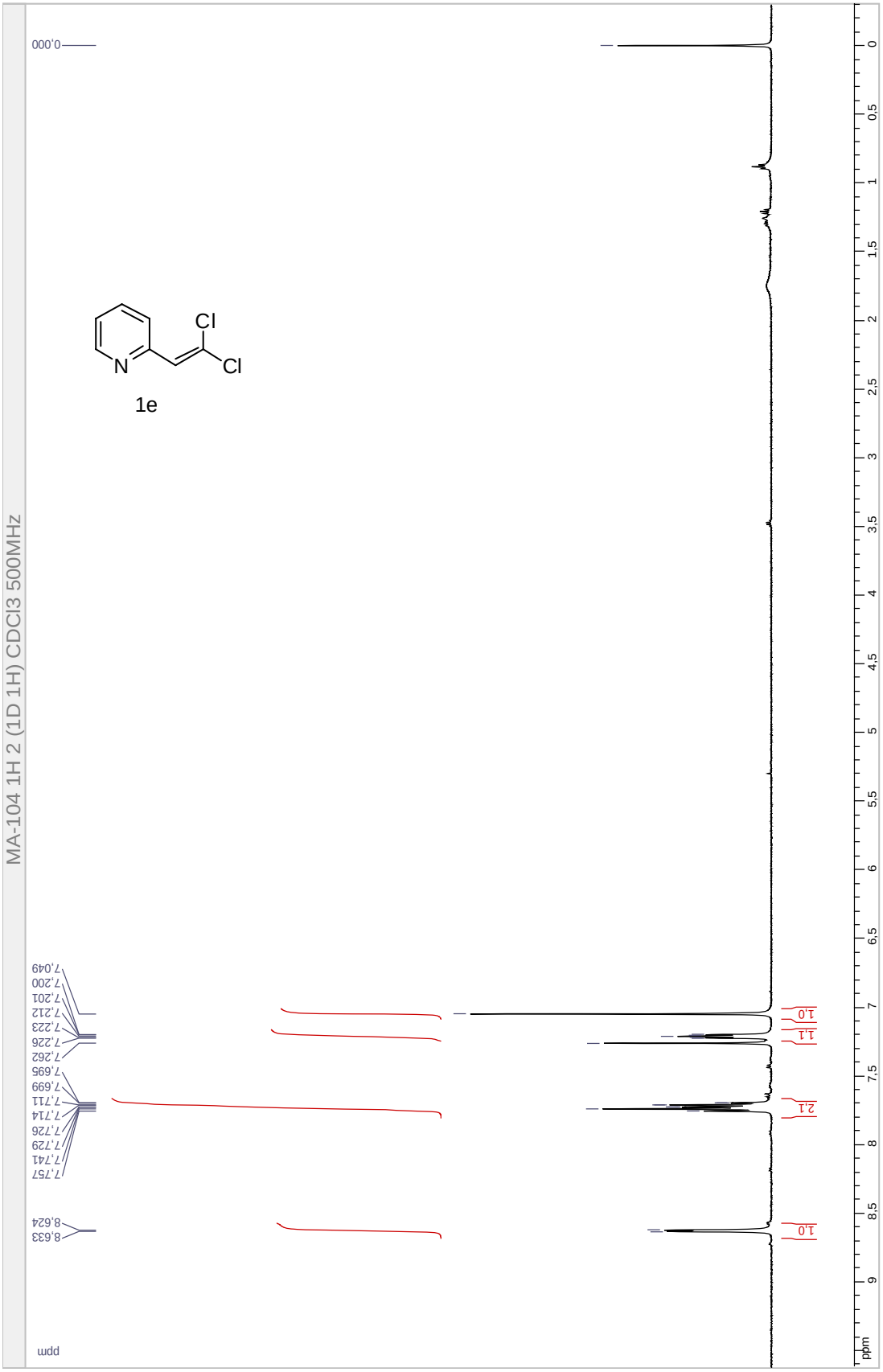
2,0
ppm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7,201
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7,226
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7,711
7,714
7,726
7,729
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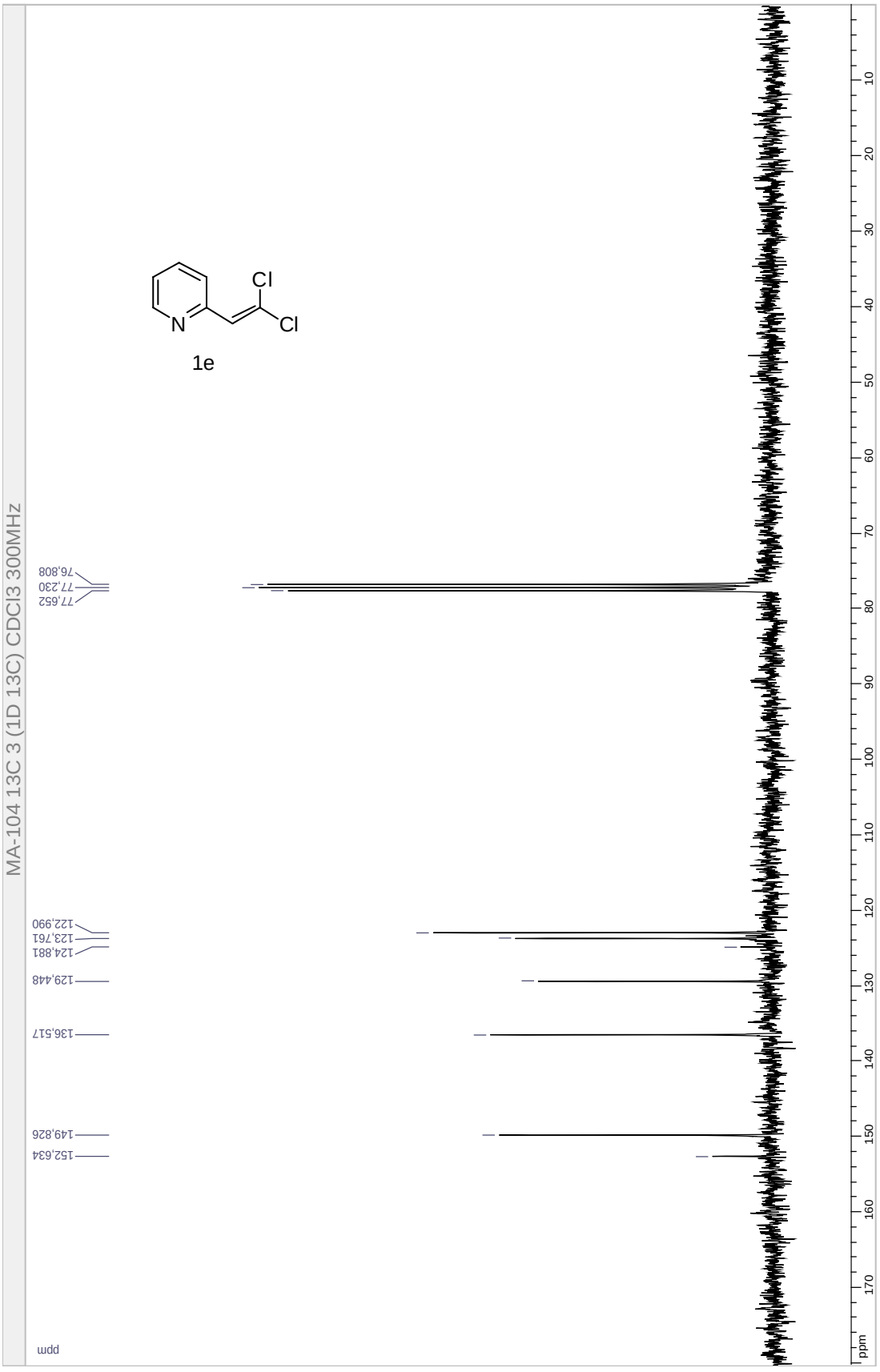
ppm
Cl
Cl
N
1e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Cl
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123.761
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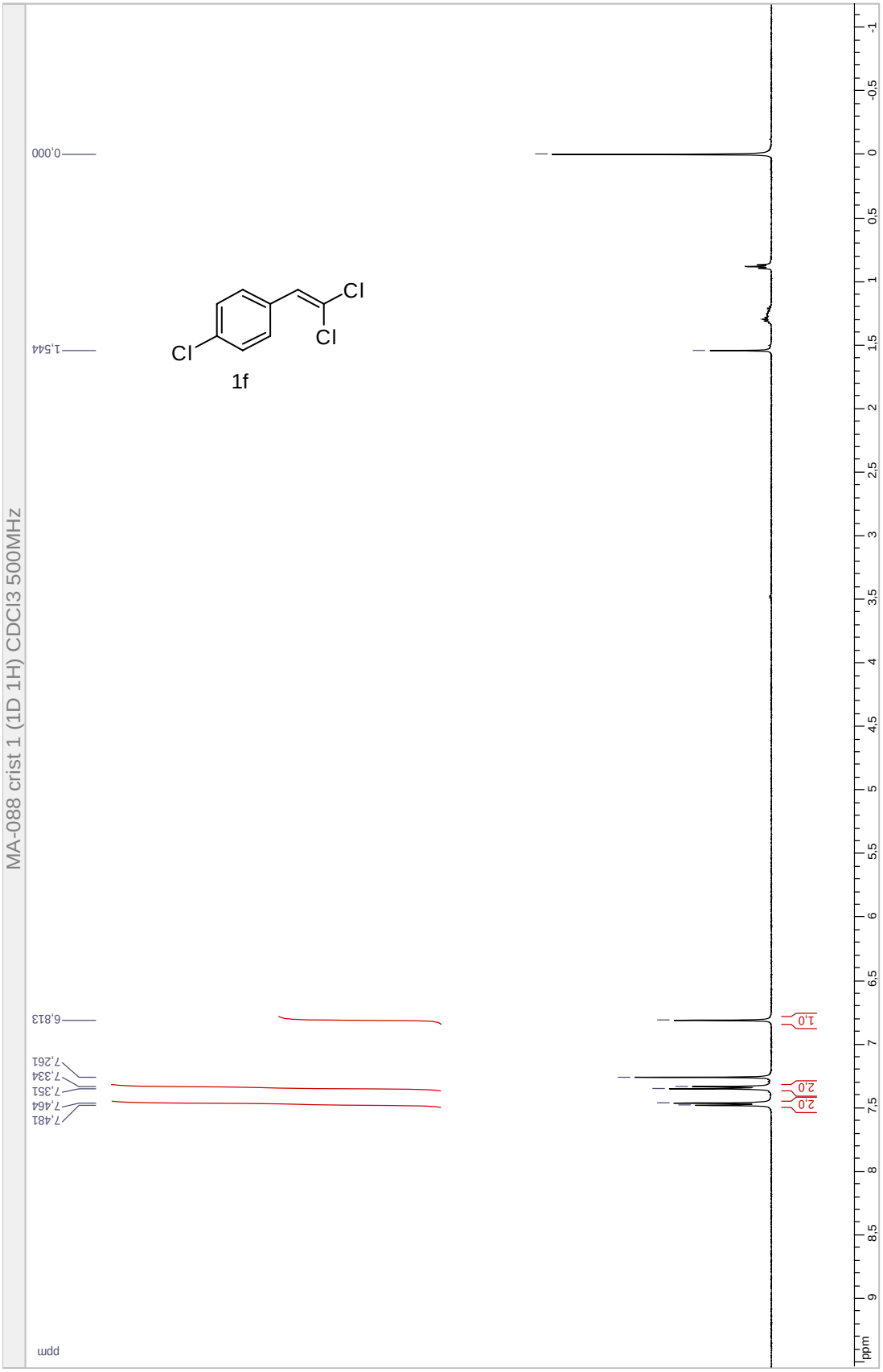
152.634
ppm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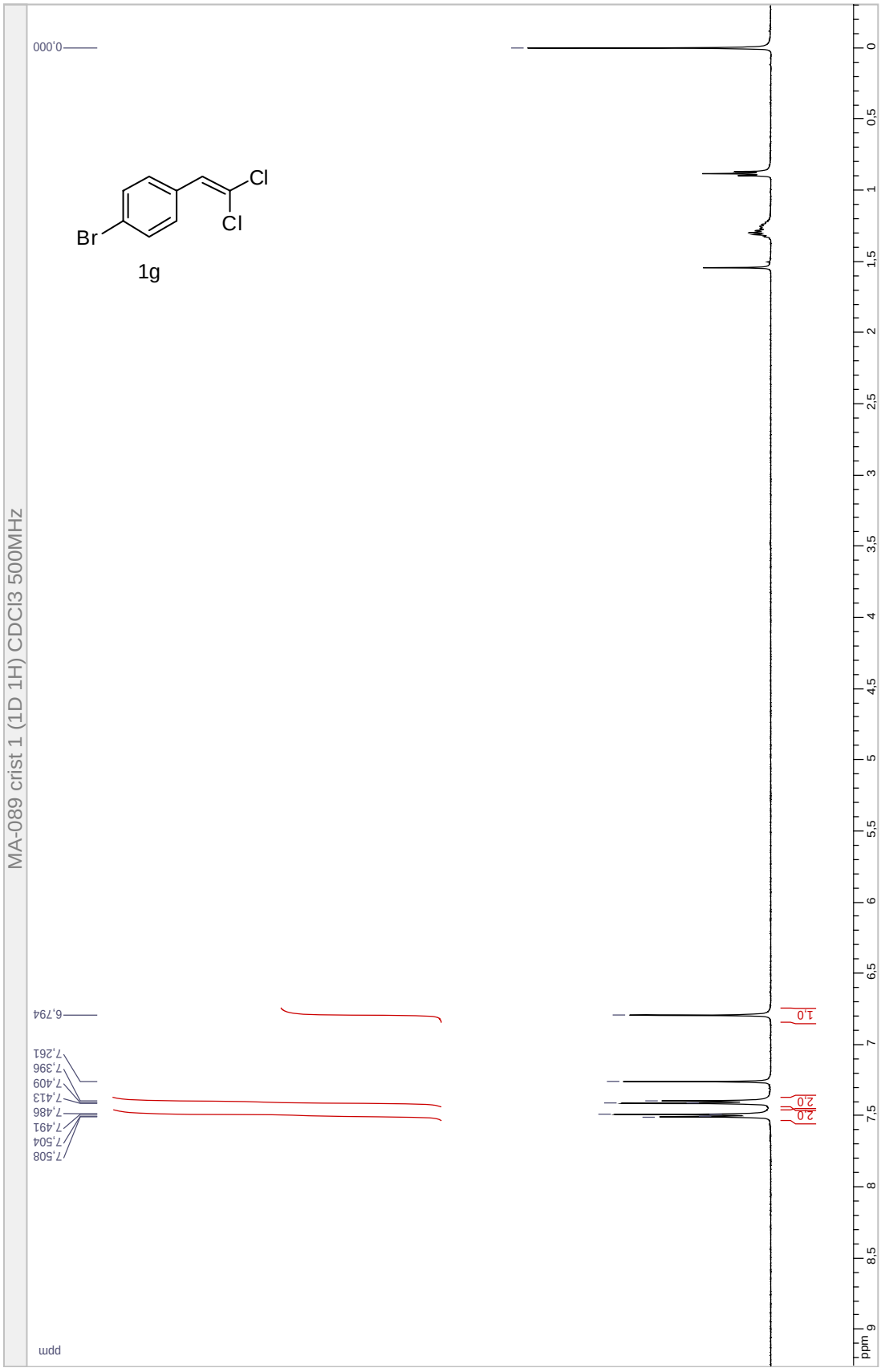
Cl
Cl
1f
ppm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7,508
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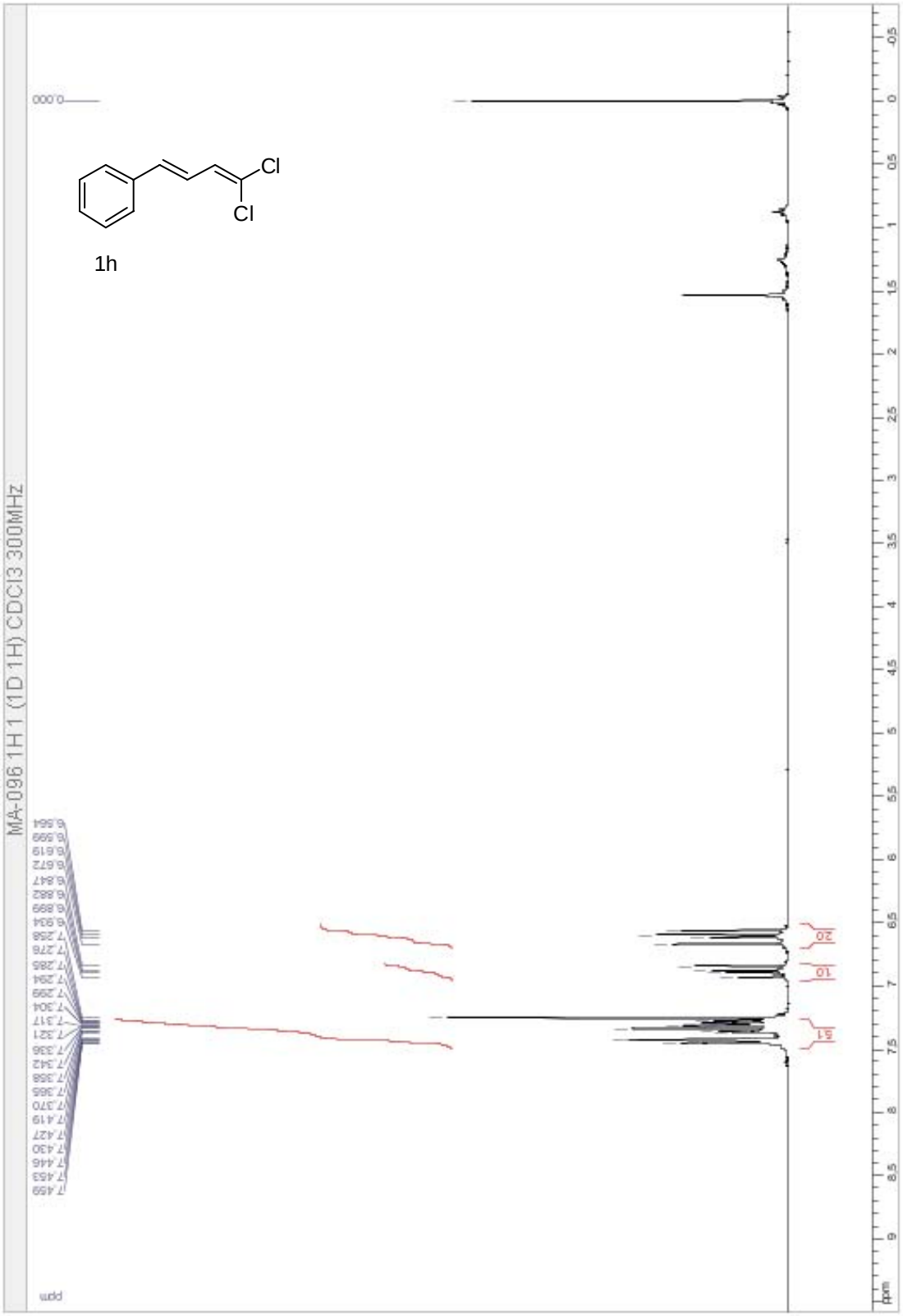
2,0
ppm
Br
Cl
Cl
1g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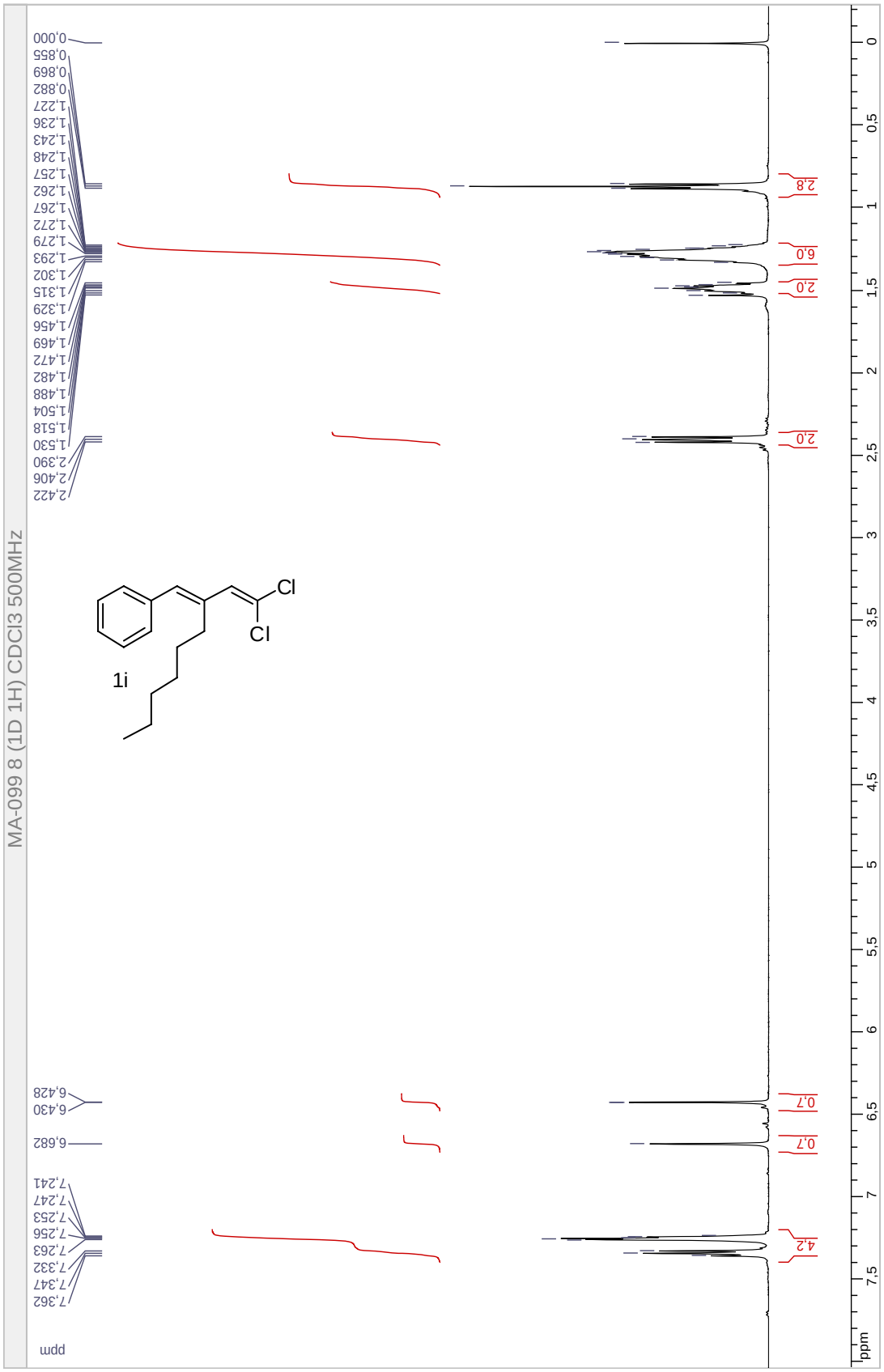
Cl
1h
ppm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1,262
1,267
1,272
1,279
1,293
1,302
1,315
1,329
1,456
1,469
1,472
1,482
1,488
1,504
1,518
1,530
2,390
2,406
2,422
6,428
6,430
6,682
7,241
7,247
7,253
7,256
7,263
7,332
7,347
7,362
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6,0
2,0
2,0
0,7
0,7
4,2
Cl
Cl
1i
ppm
0
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2
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3,5
4
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5
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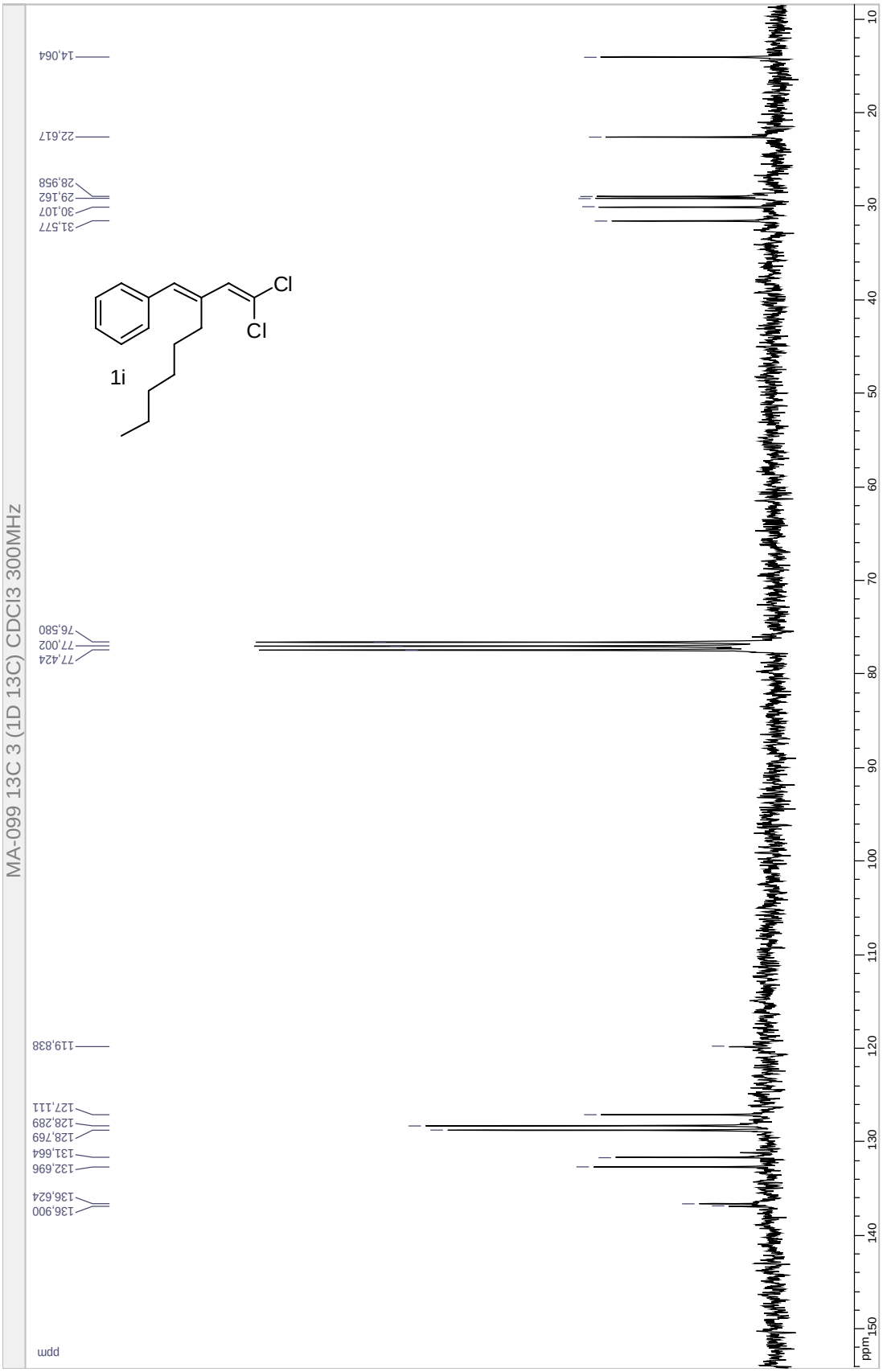
6
6,5
7
7,5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31,577
Cl
Cl
1i
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77,424
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127,111
128,289
128,769
131,664
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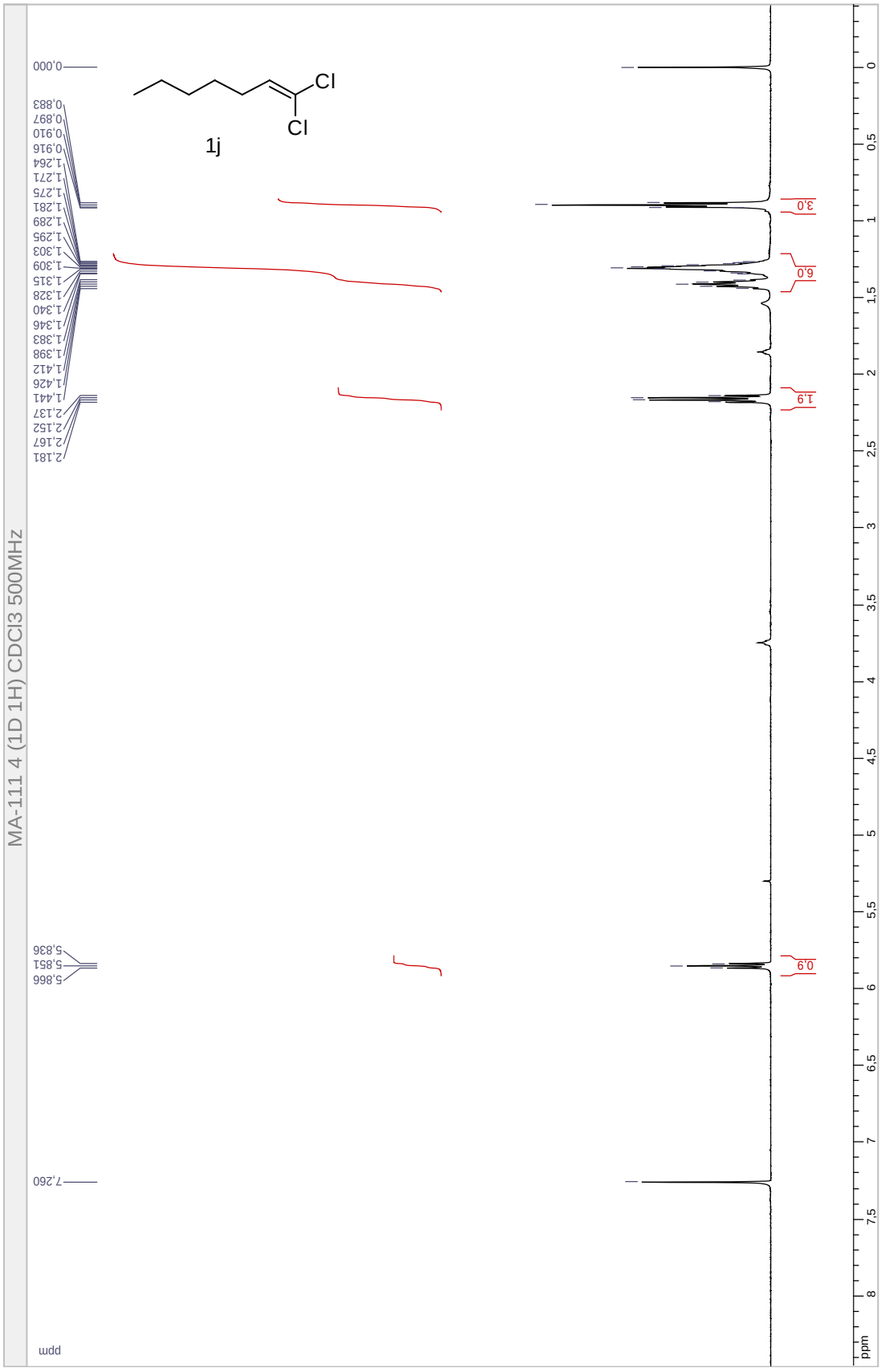
136,900
ppm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0,916
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1,275
1,281
1,289
1,295
1,303
1,309
1,315
1,328
1,340
1,346
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1,441
2,137
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5,851
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1,9
0,9
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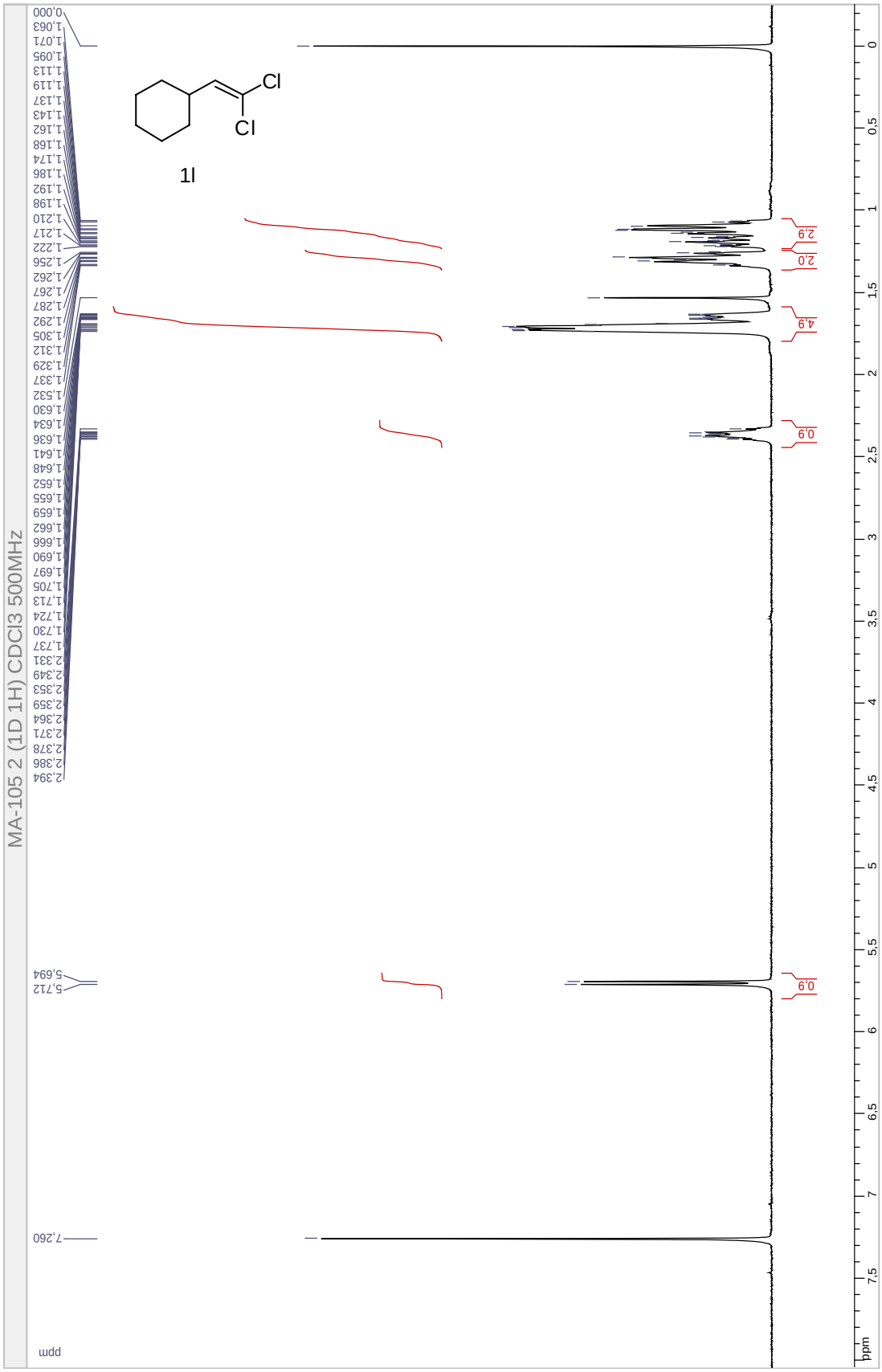
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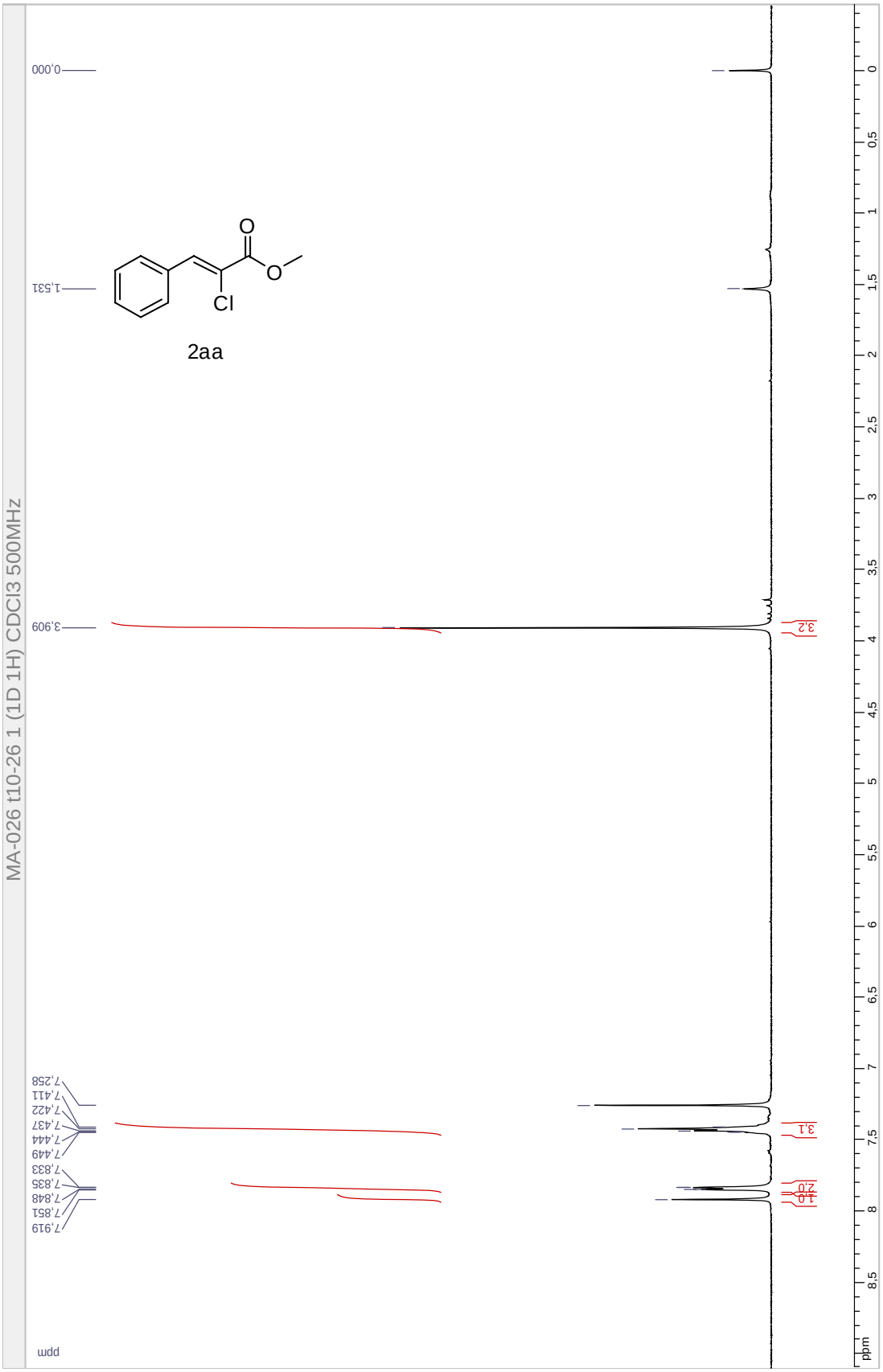
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7,444
7,449
7,833
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7,851
7,919
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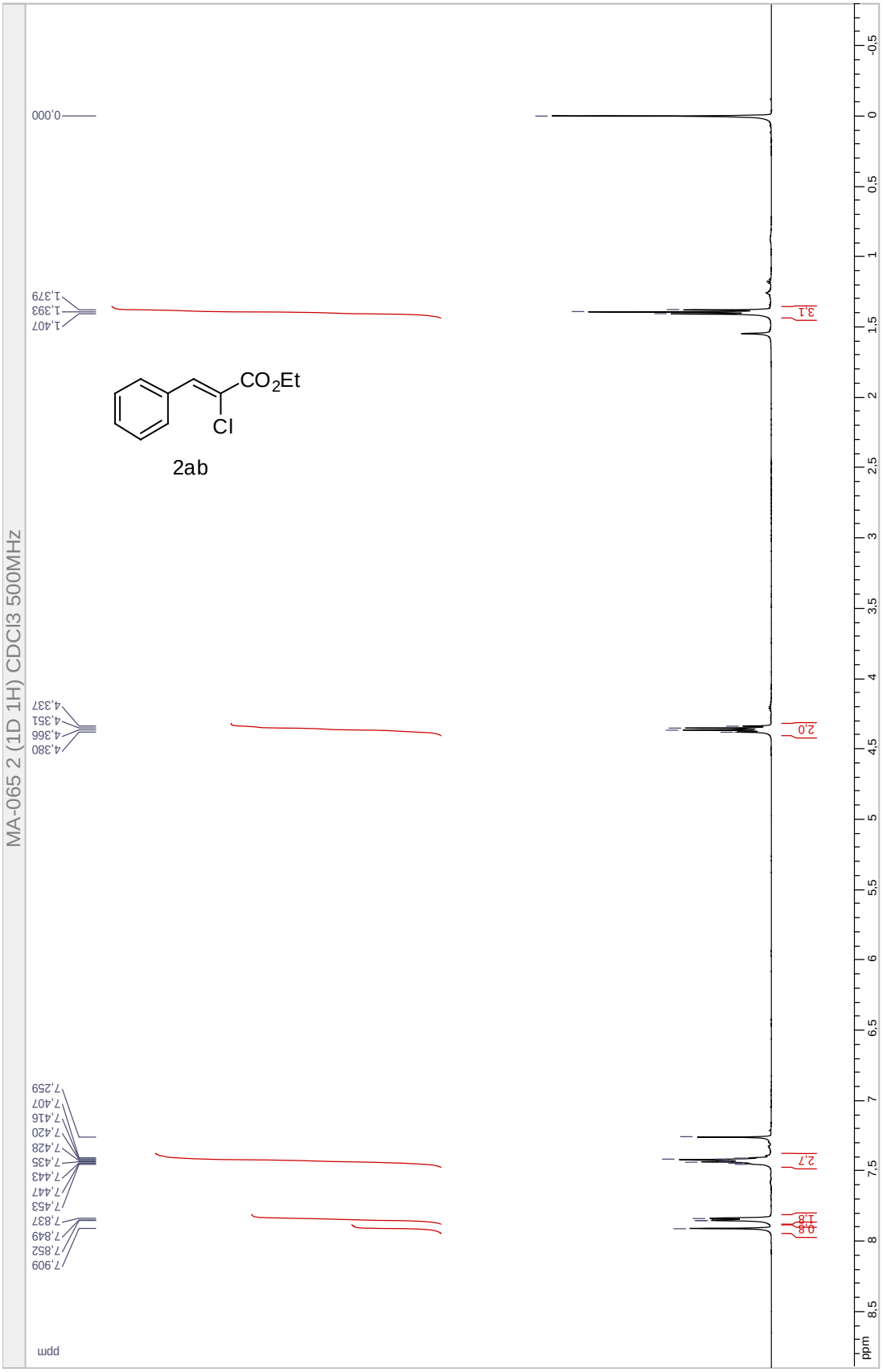
2,0
1,0
ppm
O
O
Cl
2aa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7,420
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7,435
7,443
7,447
7,453
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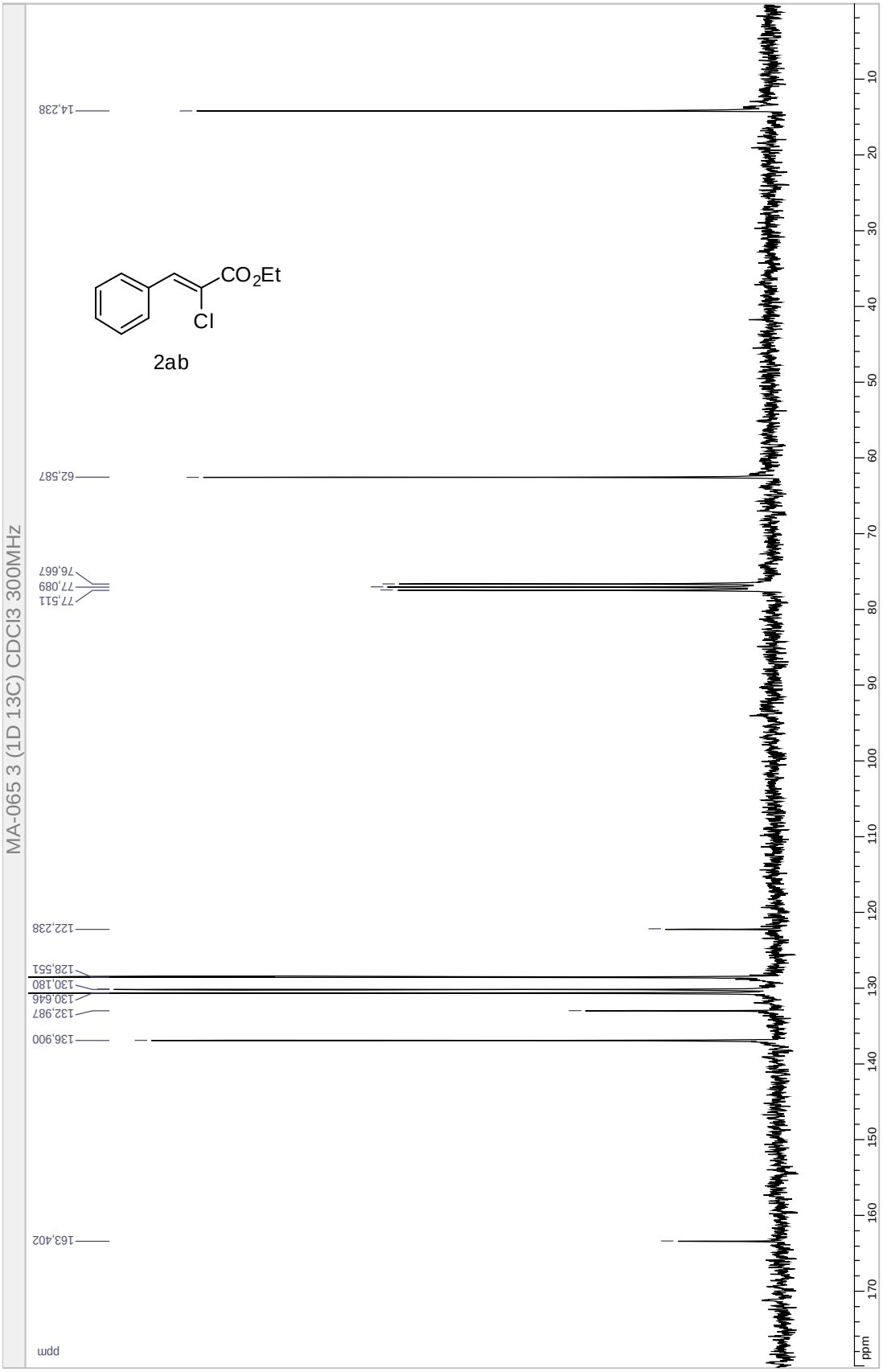
Cl
2ab
ppm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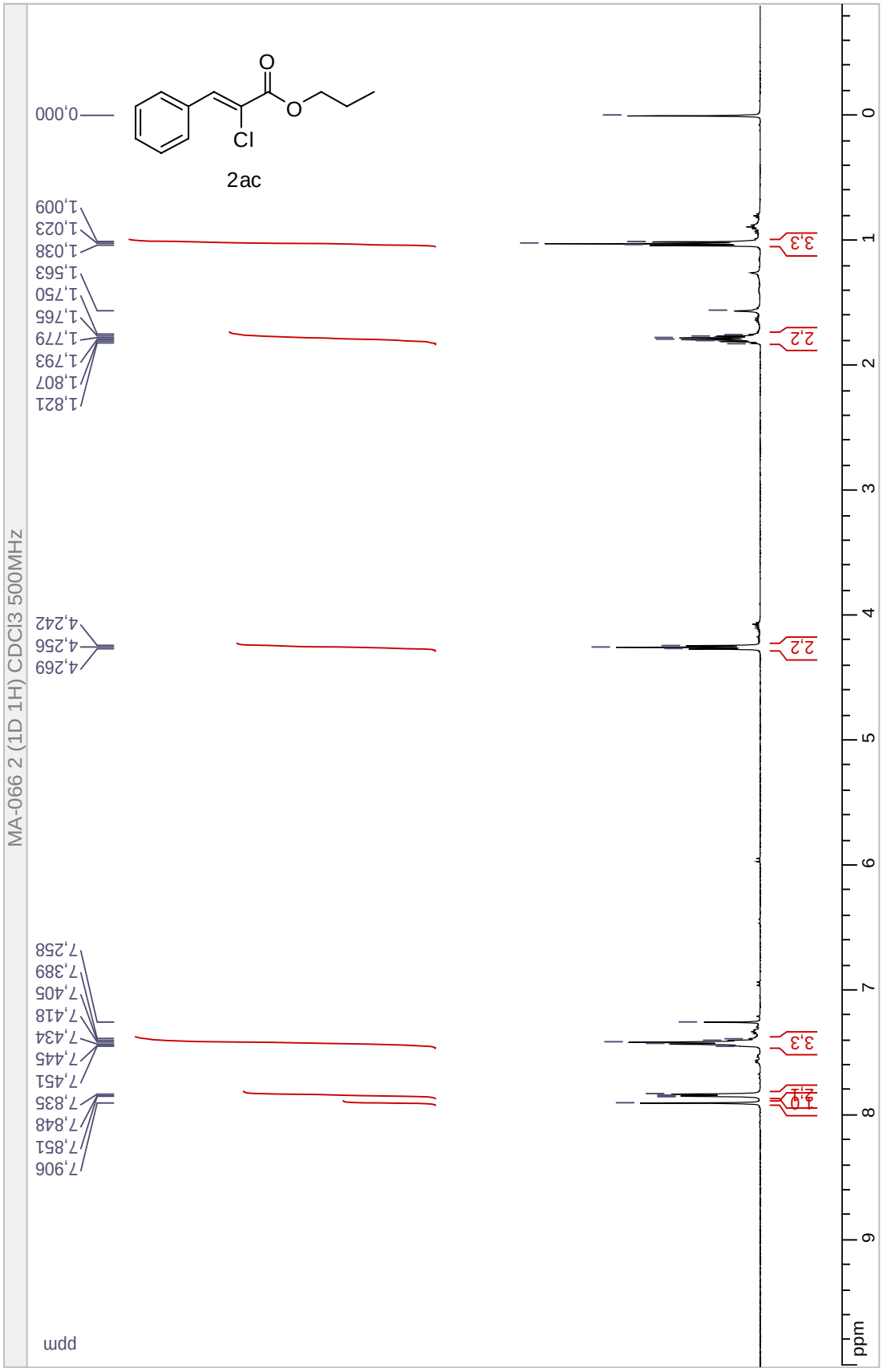
Cl
2ab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7,451
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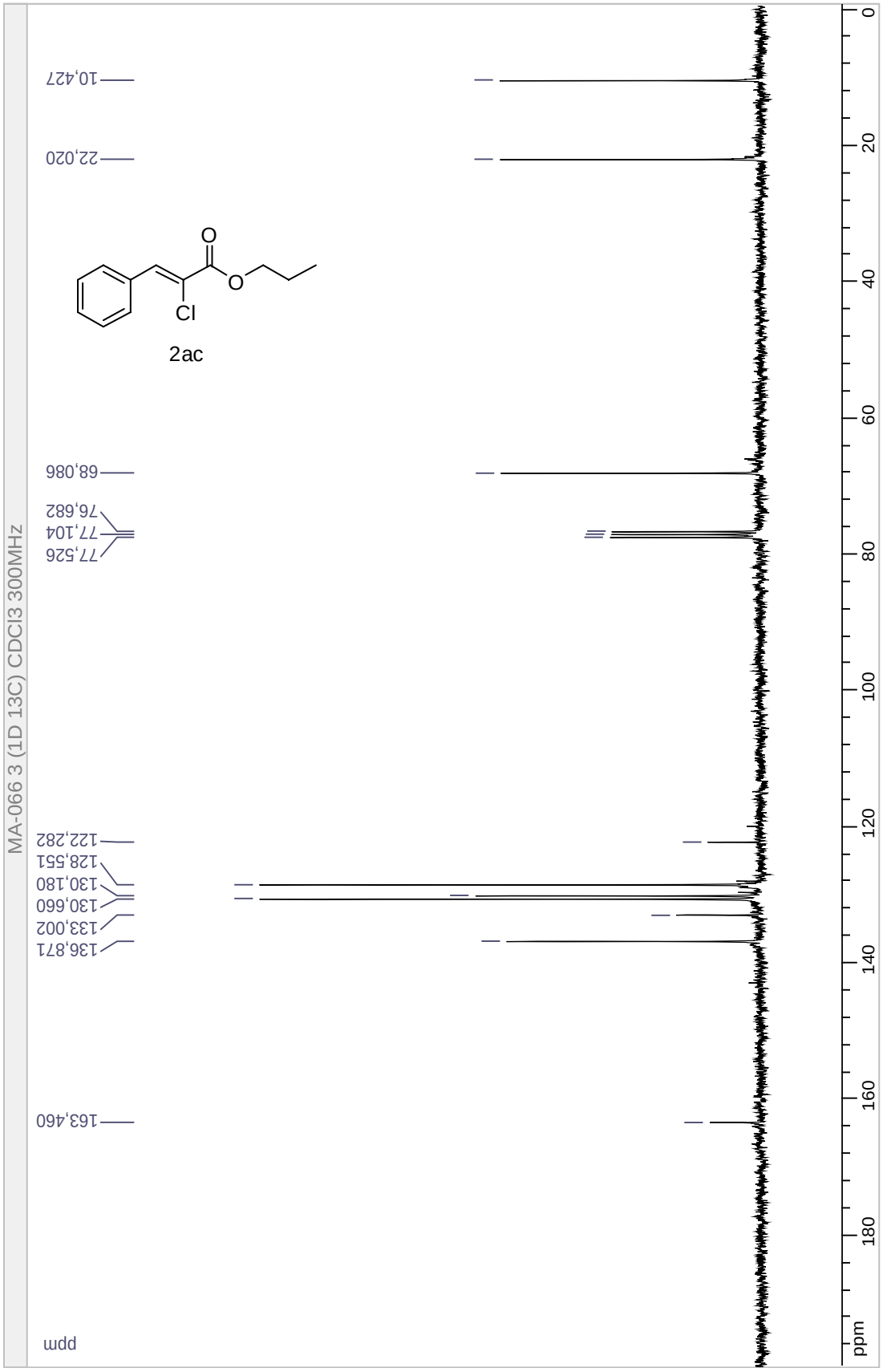
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120
140
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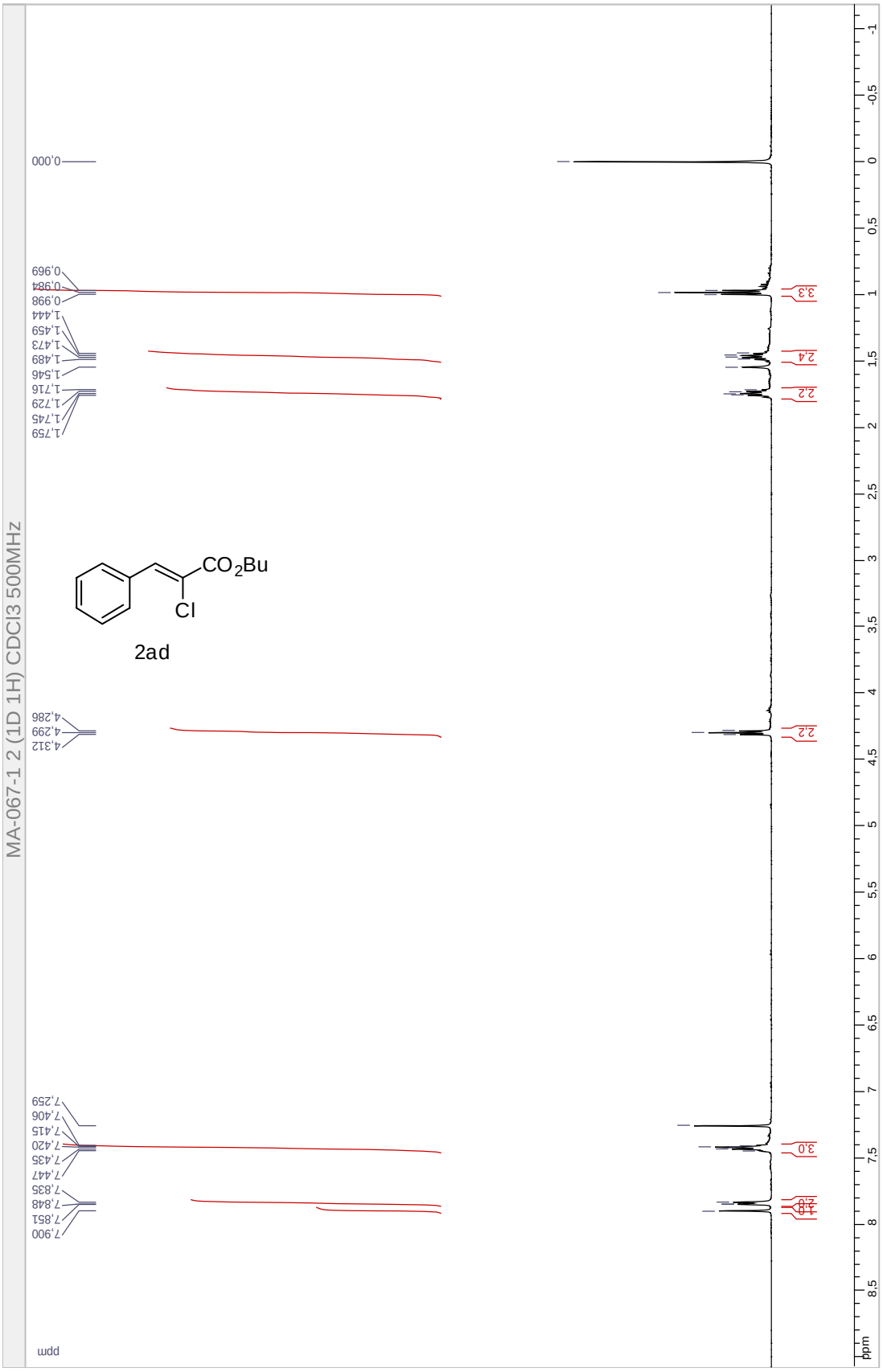
Cl
2ac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1,716
1,729
1,745
1,759
4,286
4,299
4,312
7,259
7,406
7,415
7,420
7,435
7,447
7,835
7,848
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2,0
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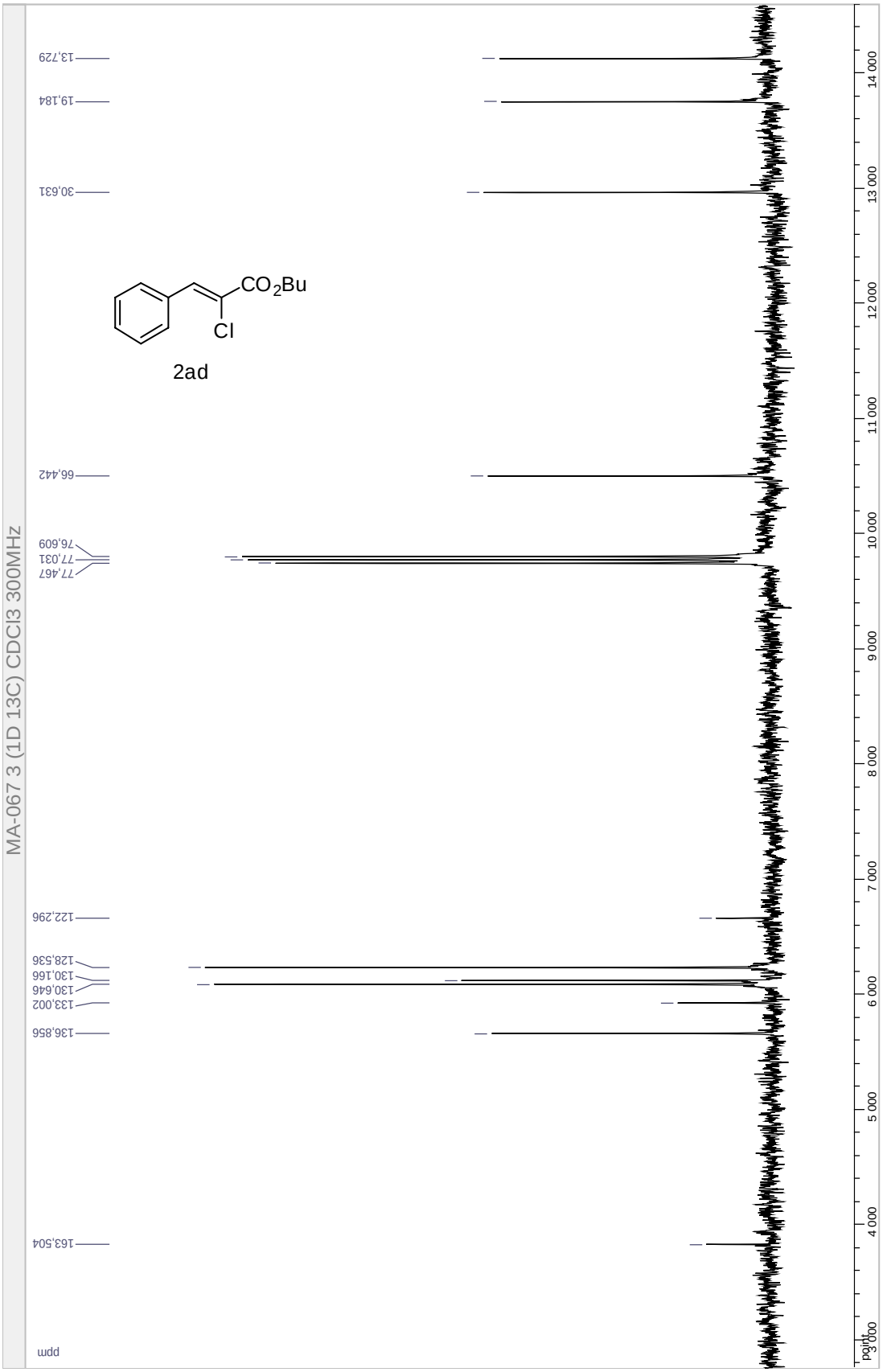
CO2Bu
Cl
2ad
ppm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136,856
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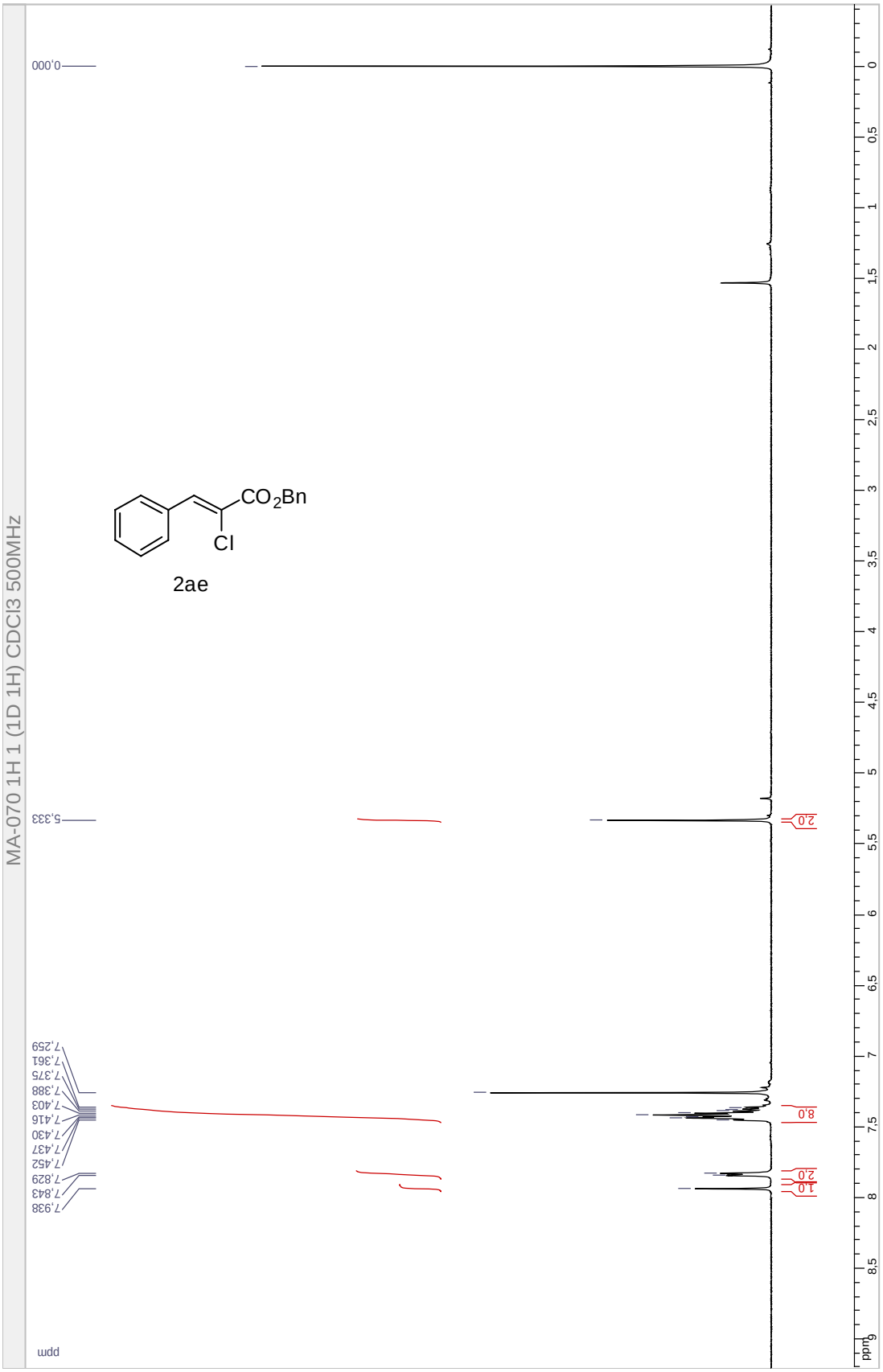
CO2Bu
Cl
2ad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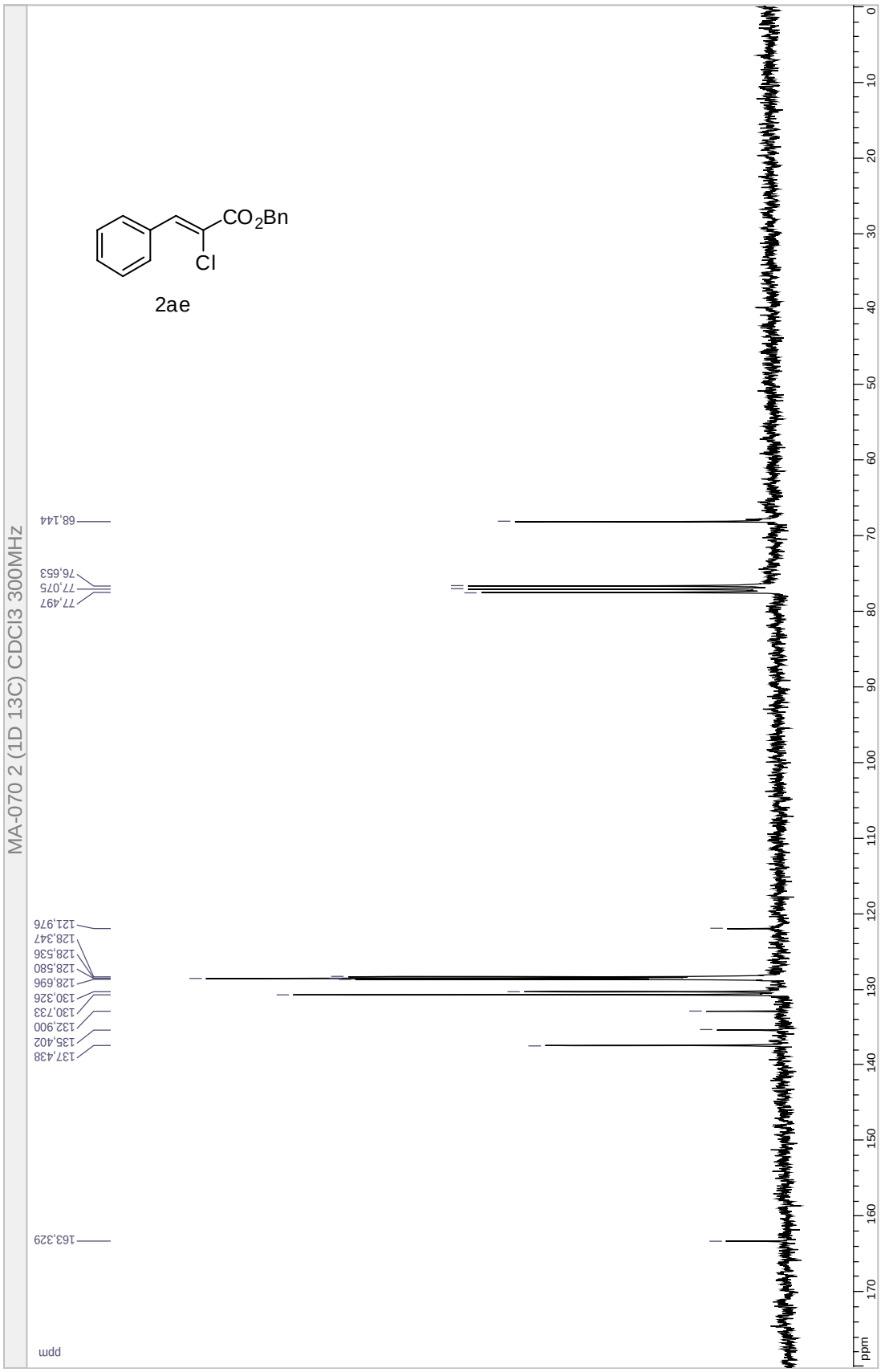
1,0
ppm
CO2Bn
Cl
2ae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CO2Bn
Cl
2ae
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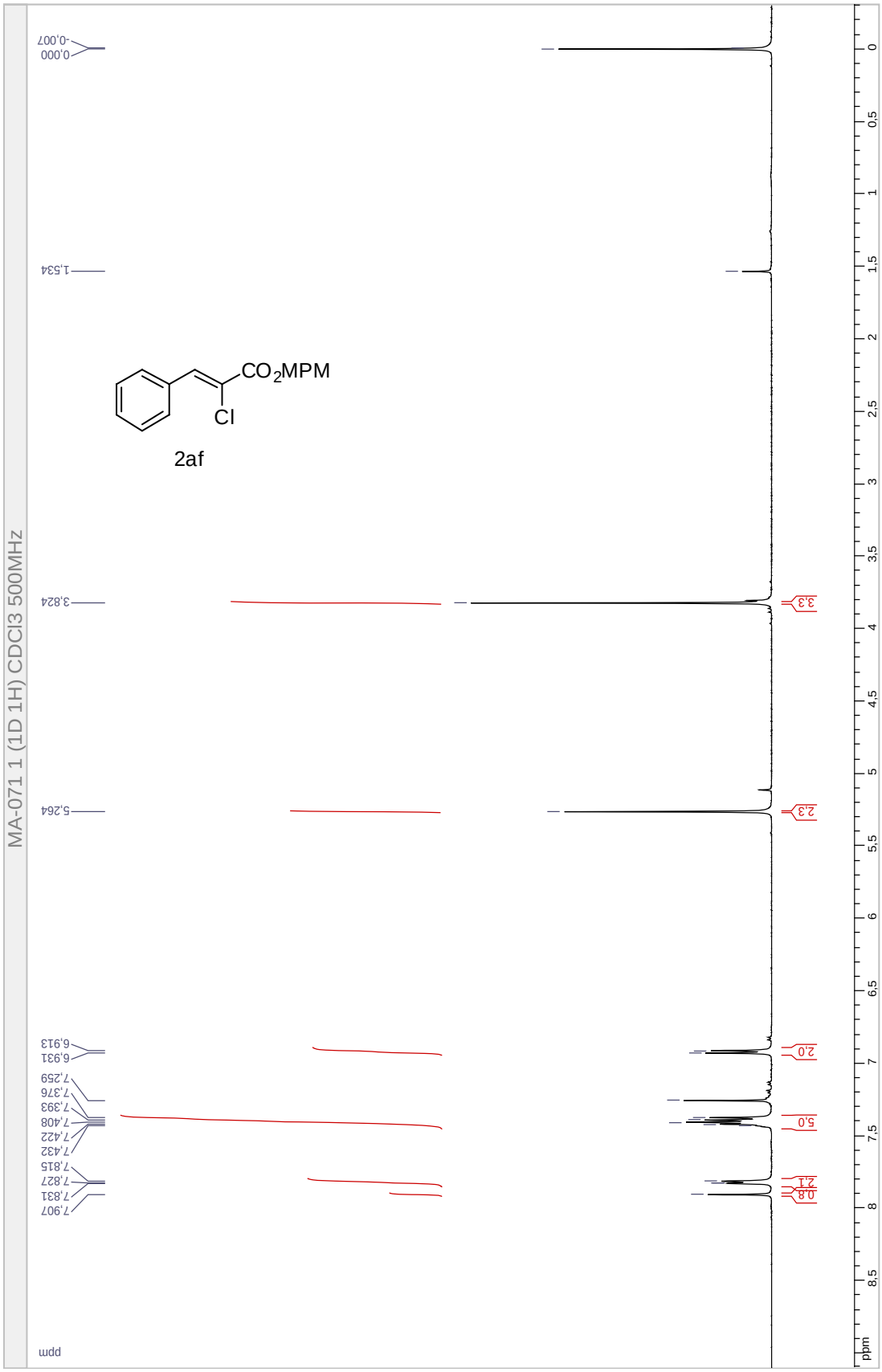
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7,422
7,432
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7,831
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CO2MPM
Cl
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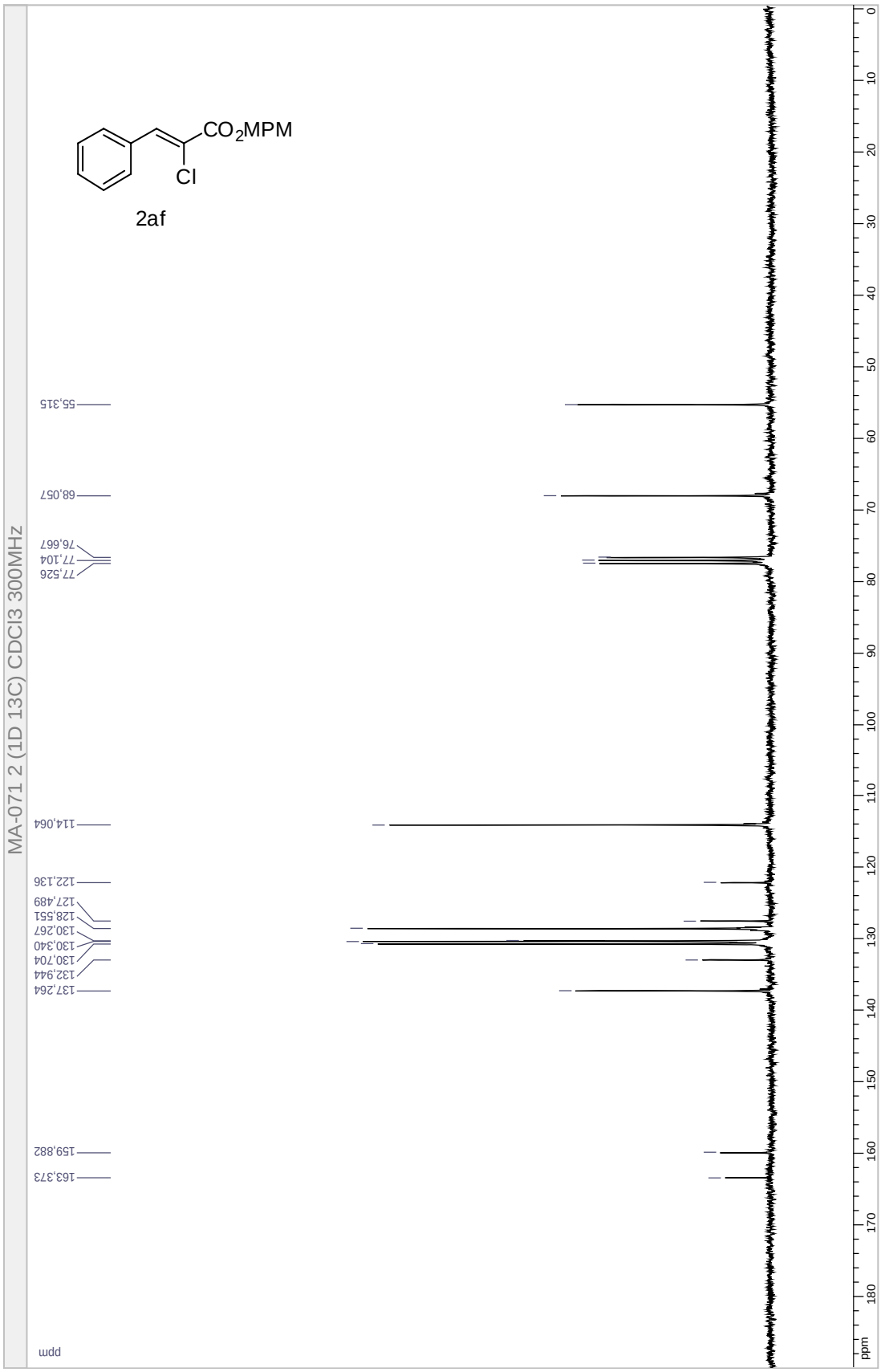
CO2MPM
Cl
2af
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77,526
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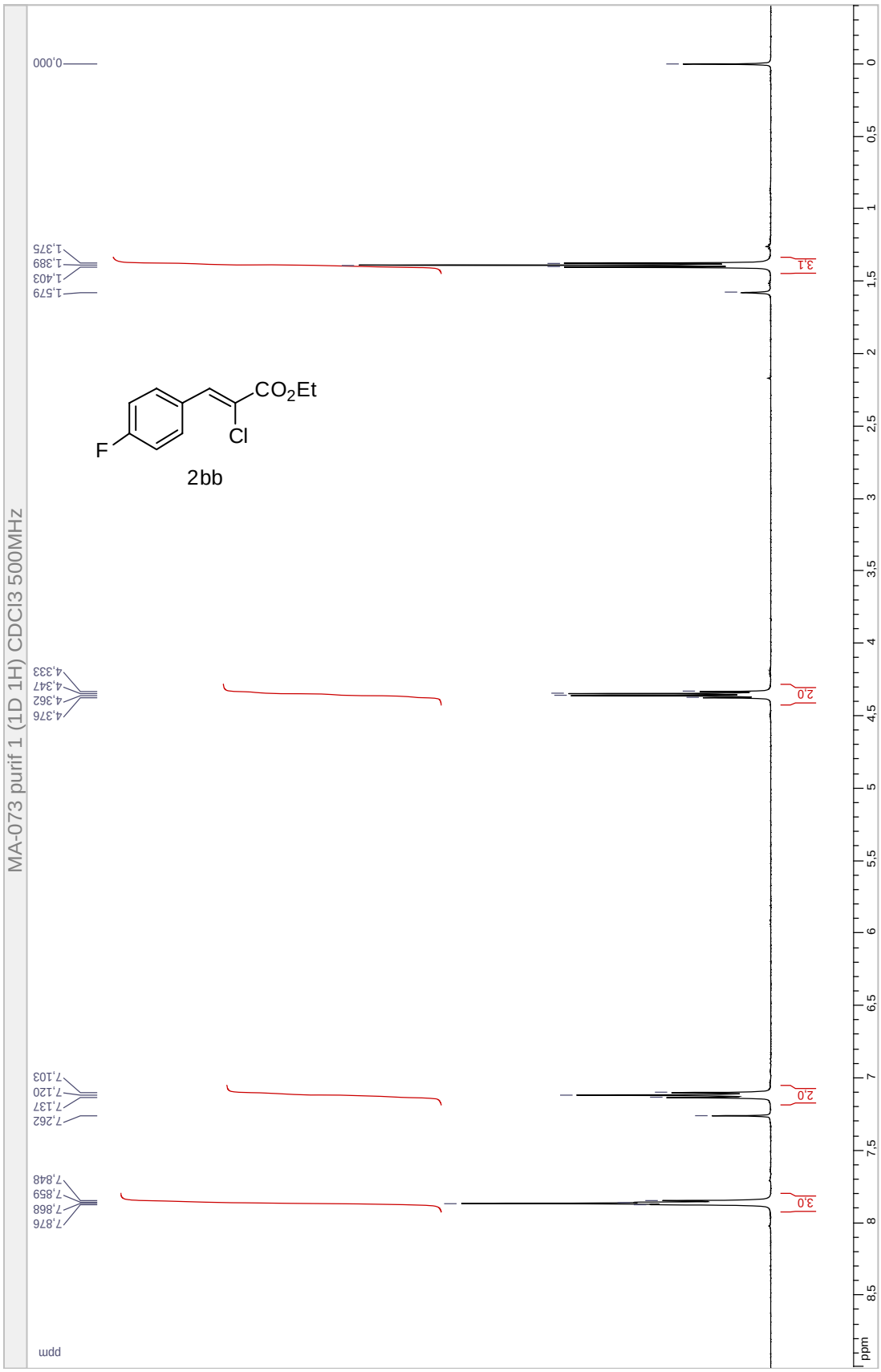
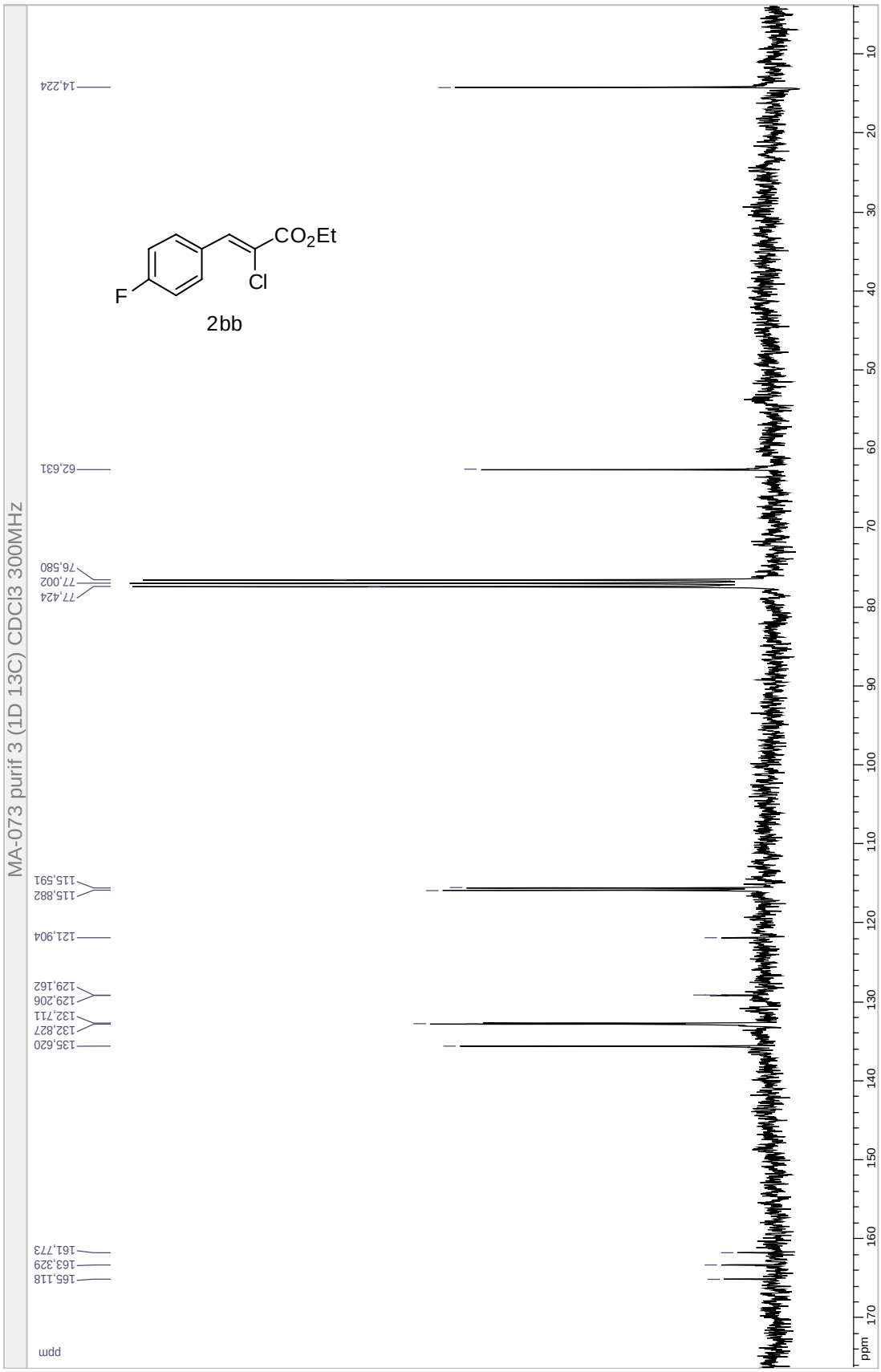
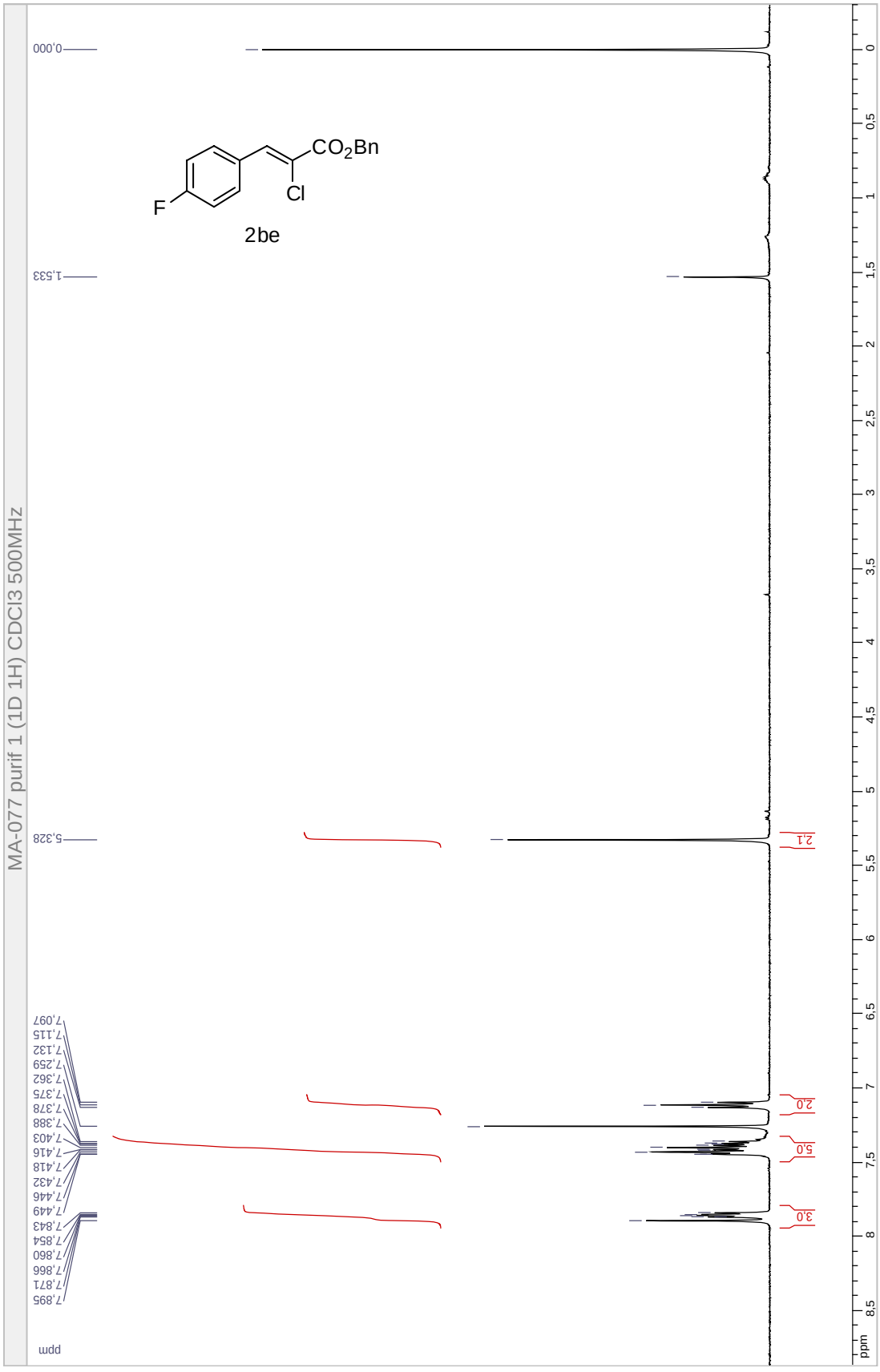
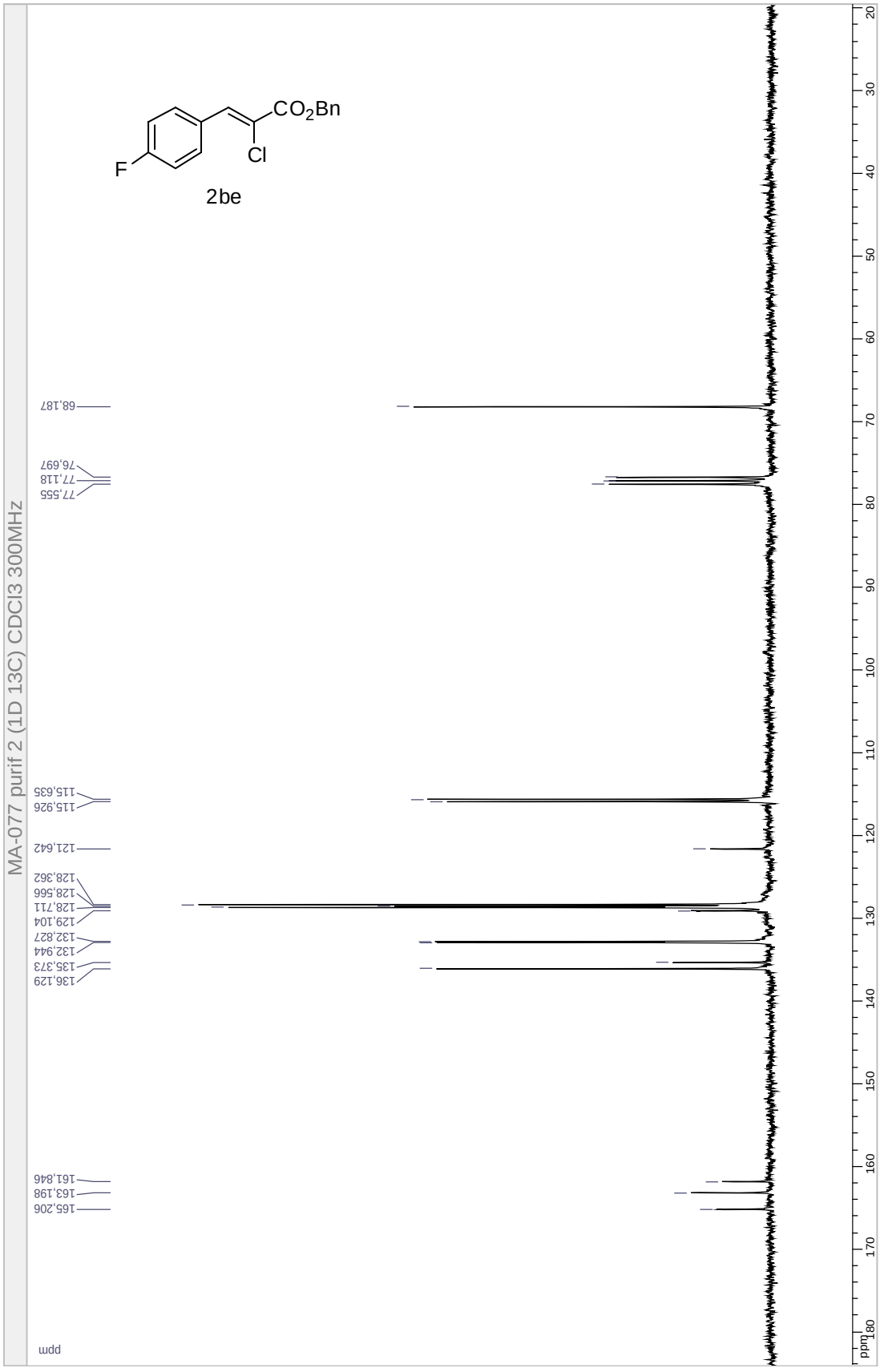
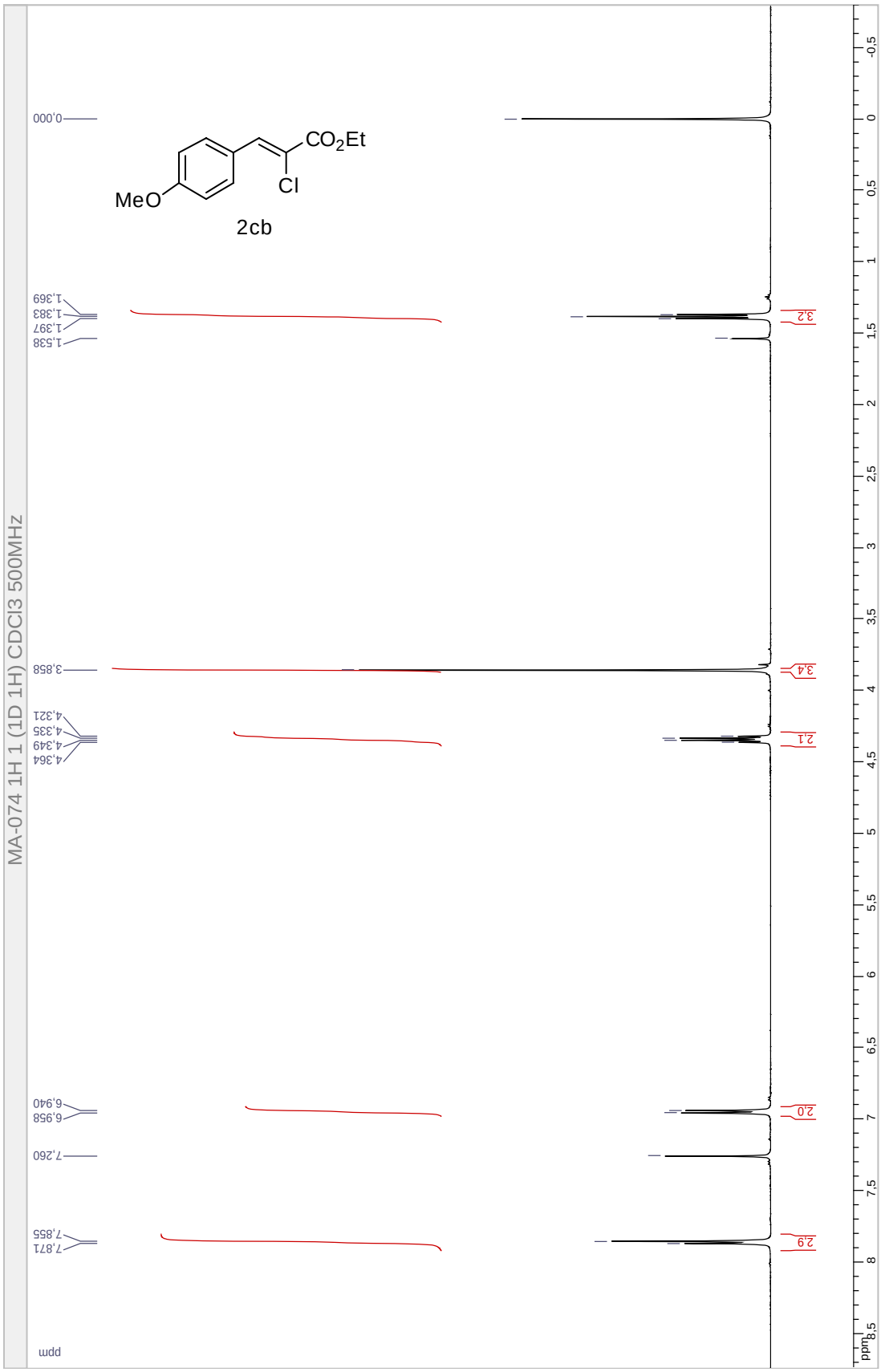
122,136
127,489
128,551
130,267
130,340
130,704
132,944
137,264
159,882
163,373
ppm

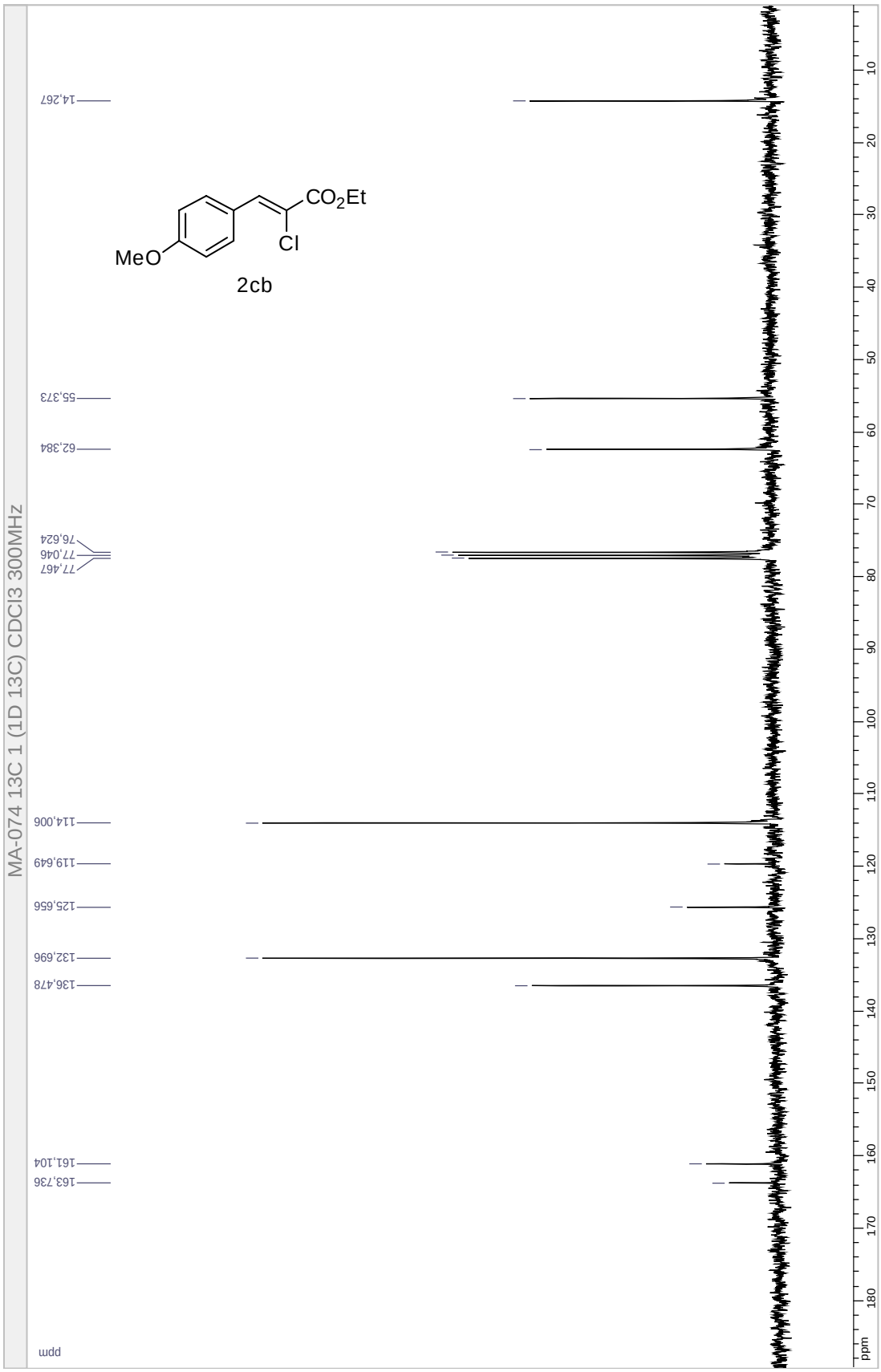

MA-073 purif 1 (1D 1H) CDCl3 500MHz
0,000
1,375
1,389
1,403
1,579
4,333
4,347
4,362
4,376
7,103
7,120
7,137
7,262
7,848
7,859
7,868
7,876
3,1
2,0
2,0
3,0
CO2Et
Cl
F
2bb
ppm

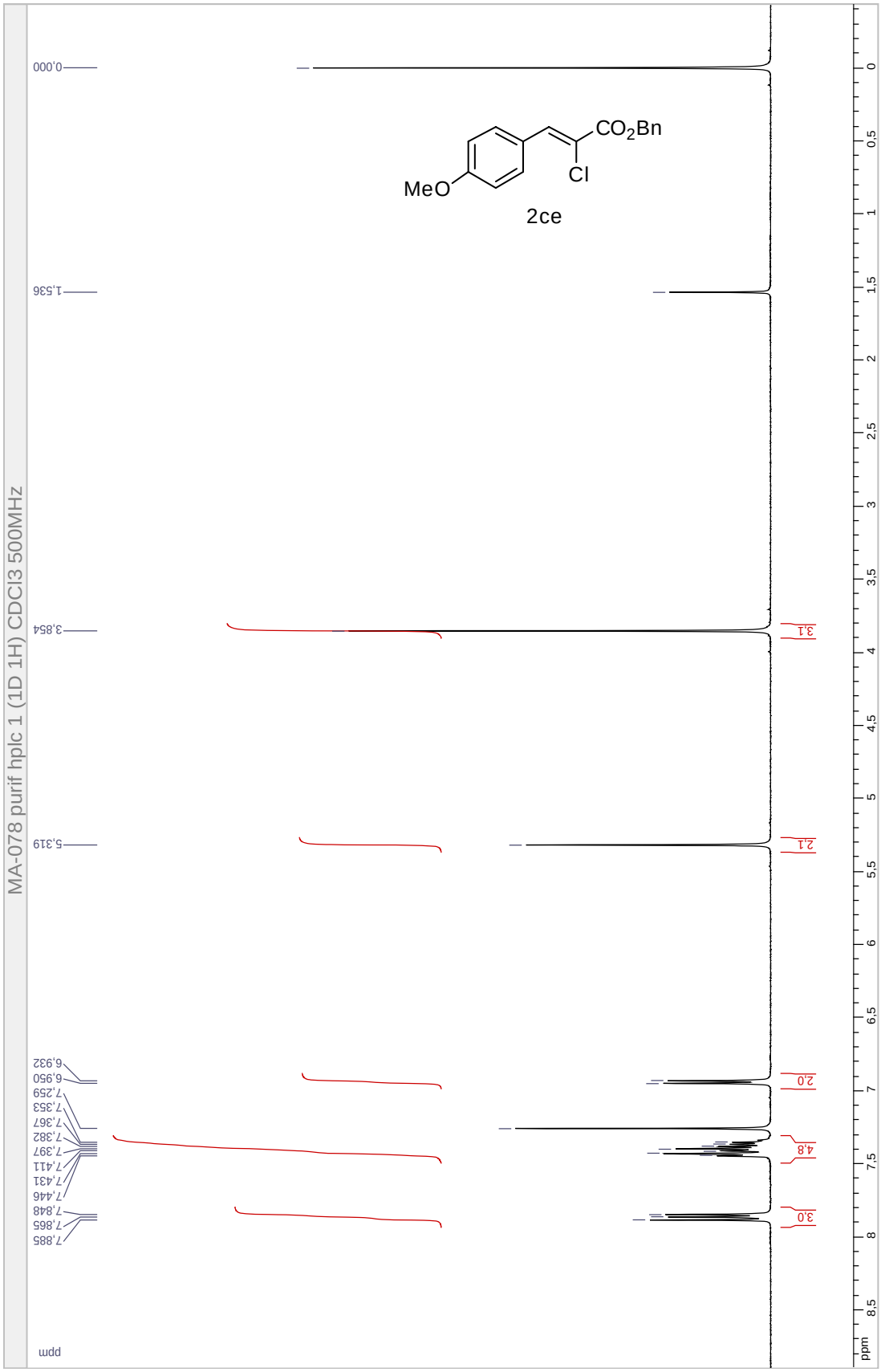

MA-073 purif 3 (1D 13C) CDCl3 300MHz
14,224
62,631
76,580
77,002
77,424
115,591
115,882
121,904
129,162
129,206
132,711
132,827
135,620
161,773
163,329
165,118
ppm
CO2Et
Cl
F
2bb

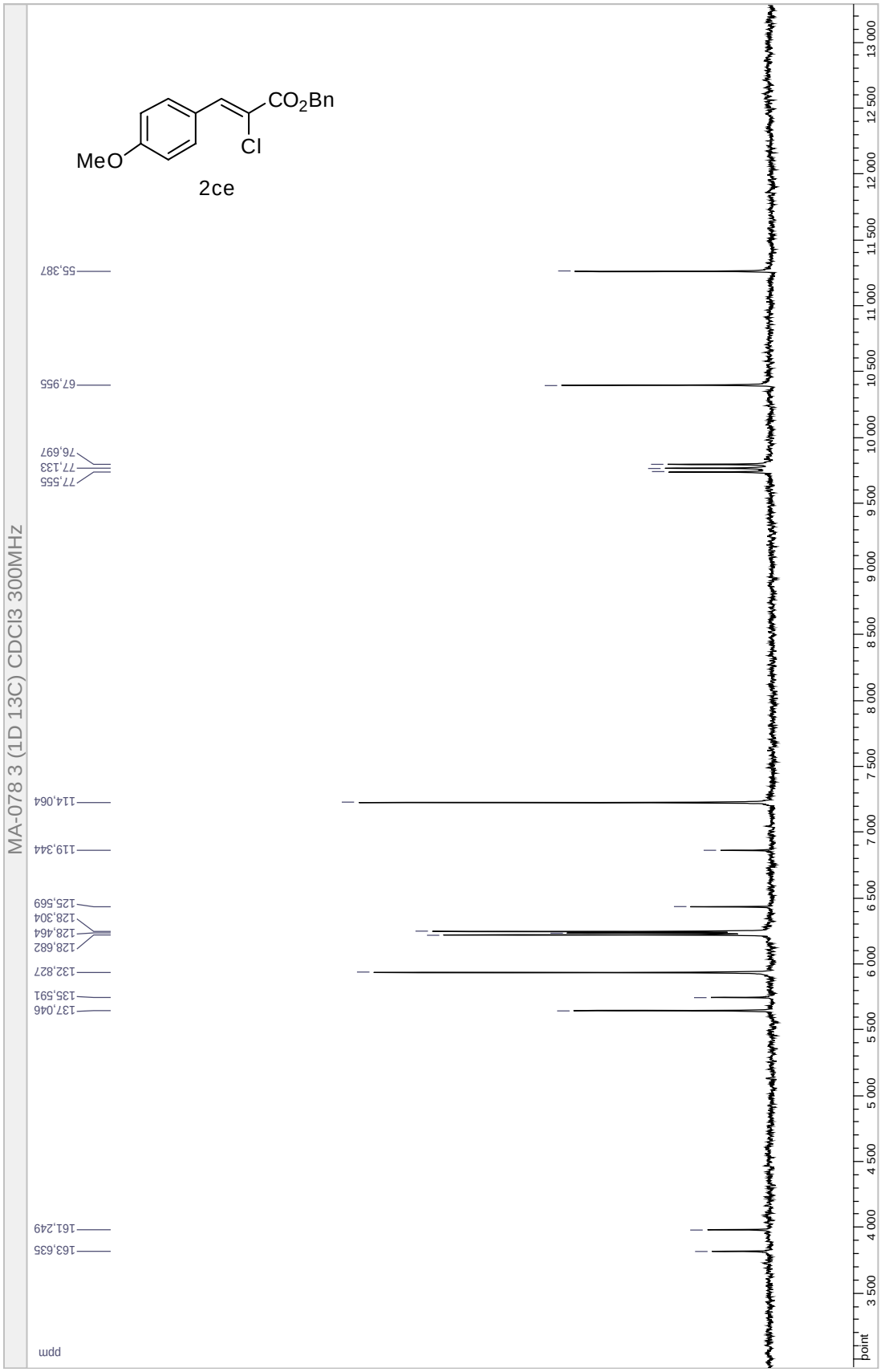

MA-077 purif 1 (1D 1H) CDCl3 500MHz
0,000
1,533
5,328
7,097
7,115
7,132
7,259
7,362
7,375
7,378
7,388
7,403
7,416
7,418
7,432
7,446
7,449
7,843
7,854
7,860
7,866
7,871
7,895
ppm
2,1
2,0
5,0
3,0
CO2Bn
Cl
F
2be

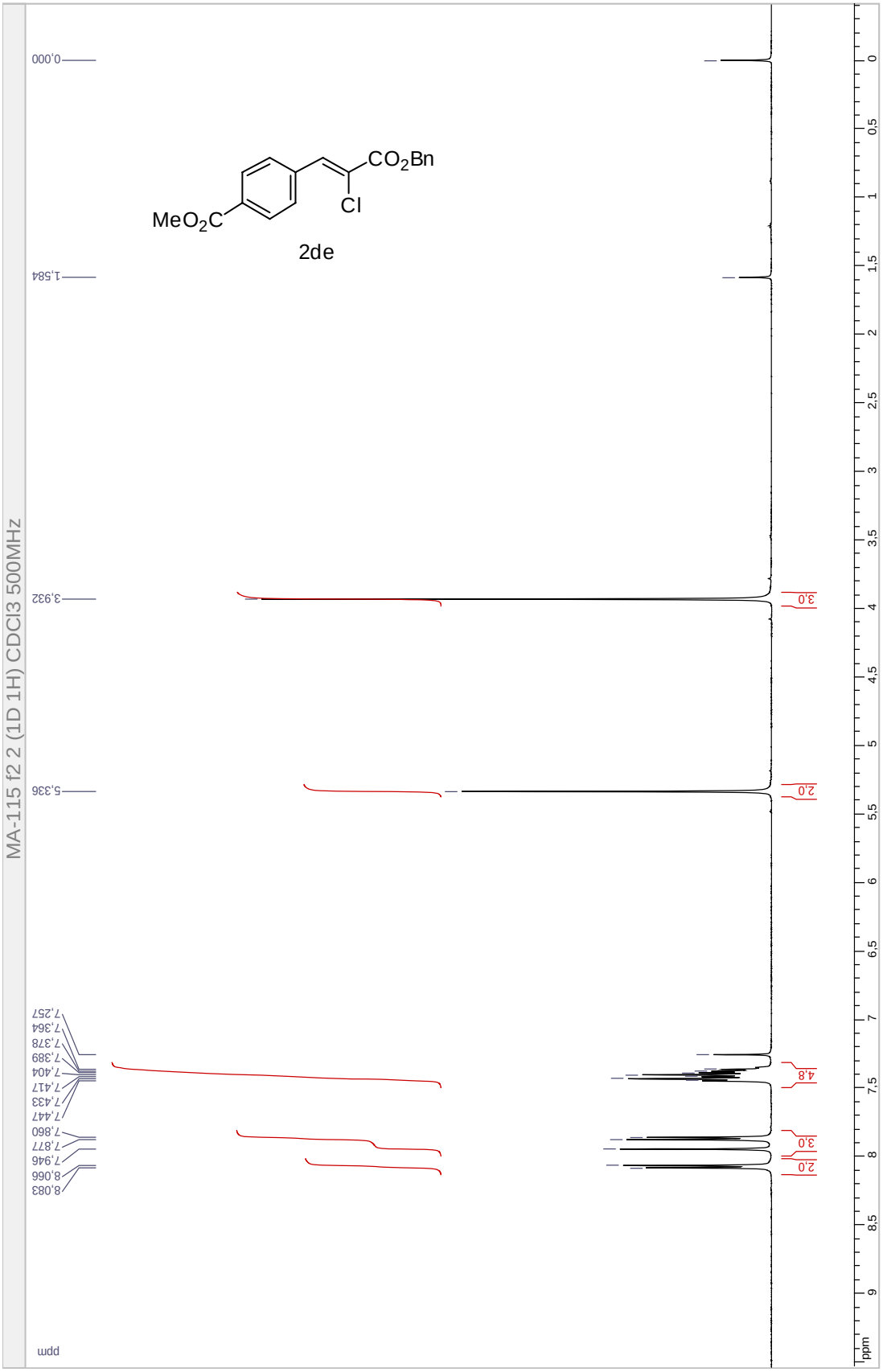

MA-077 purif 2 (1D 13C) CDCl3 300MHz
CO2Bn
Cl
F
2be
68,187
76,697
77,118
77,555
115,635
115,926
121,642
128,362
128,566
128,711
129,104
132,827
132,944
135,373
136,129
161,846
163,198
165,206
ppm

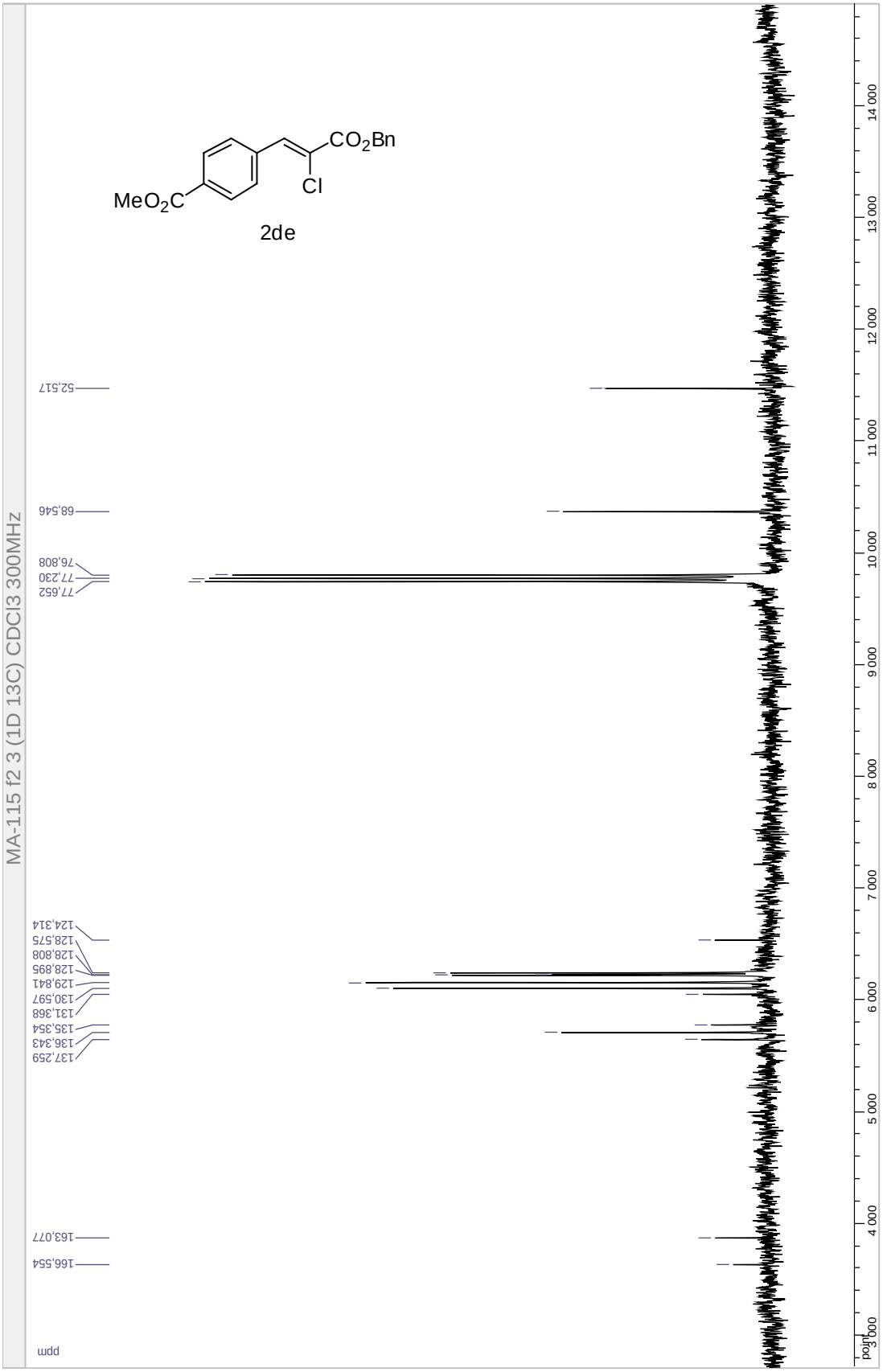

MA-074 1H 1 (1D 1H) CDCl3 500MHz
0,000
1,369
1,383
1,397
1,538
3,858
4,321
4,335
4,349
4,364
6,940
6,958
7,260
7,855
7,871
3,2
3,4
2,1
2,0
2,9
MeO
CO2Et
Cl
2cb
ppm

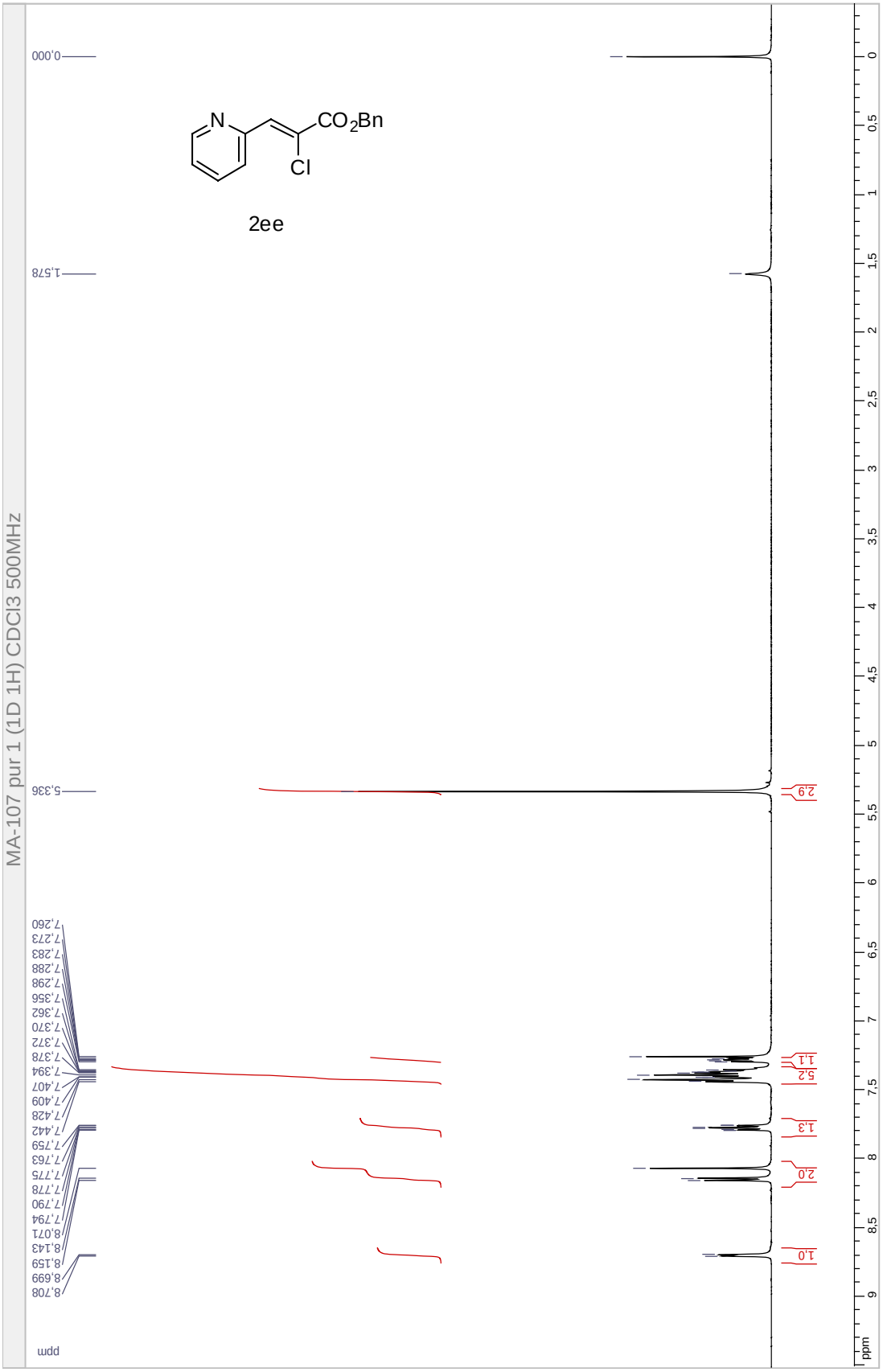

MA-074 13C 1 (1D 13C) CDCl3 300MHz
14,267
55,373
62,384
76,624
77,046
77,467
114,006
119,649
125,656
132,696
136,478
161,104
163,736
ppm
CO2Et
Cl
MeO
2cb

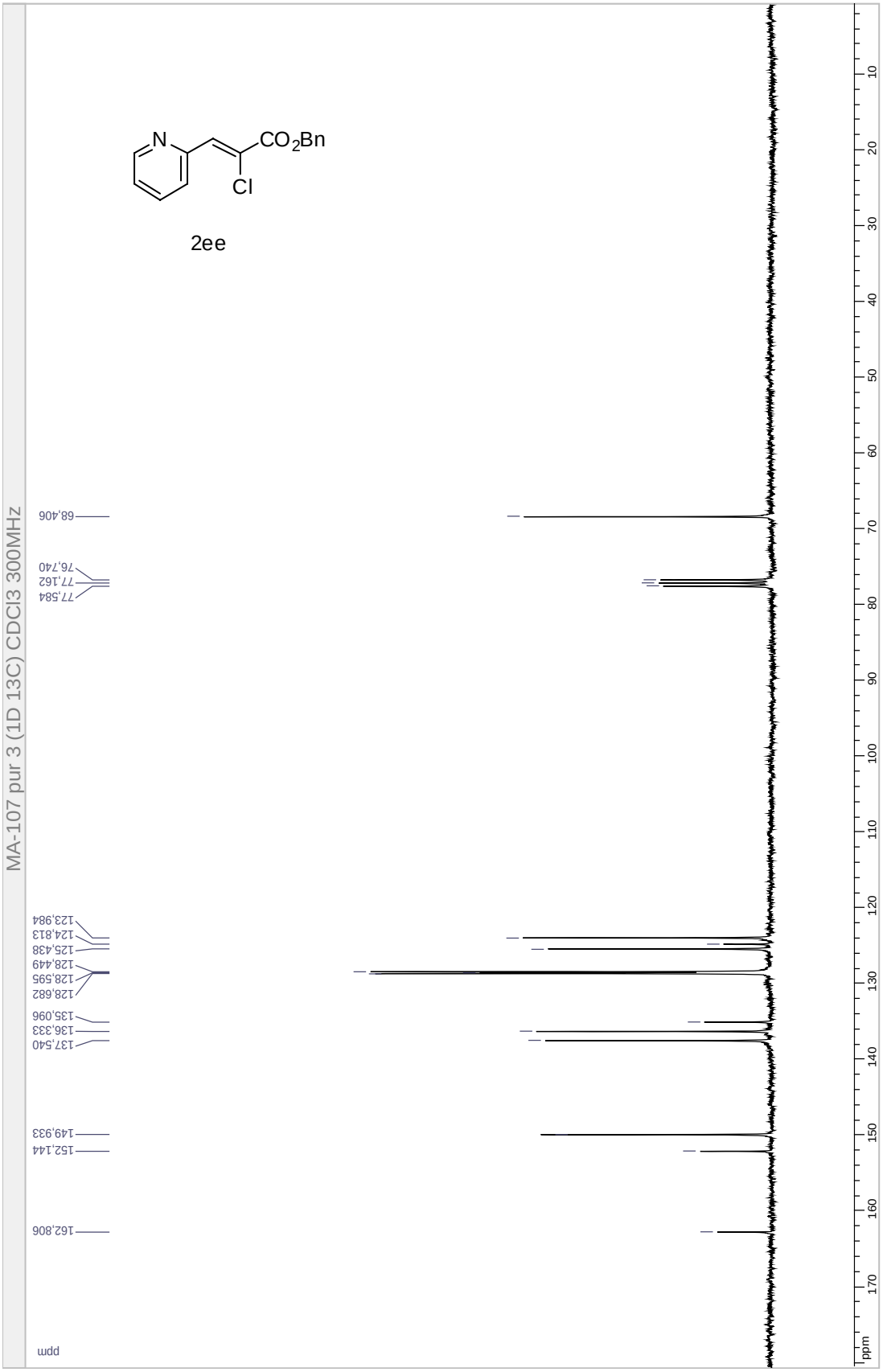

MA-078 purif hplc 1 (1D 1H) CDCl3 500MHz
0,000
1,536
3,854
5,319
6,932
6,950
7,259
7,353
7,367
7,382
7,397
7,411
7,431
7,446
7,848
7,865
7,885
3,1
2,1
2,0
4,8
3,0
MeO
CO2Bn
Cl
2ce
ppm

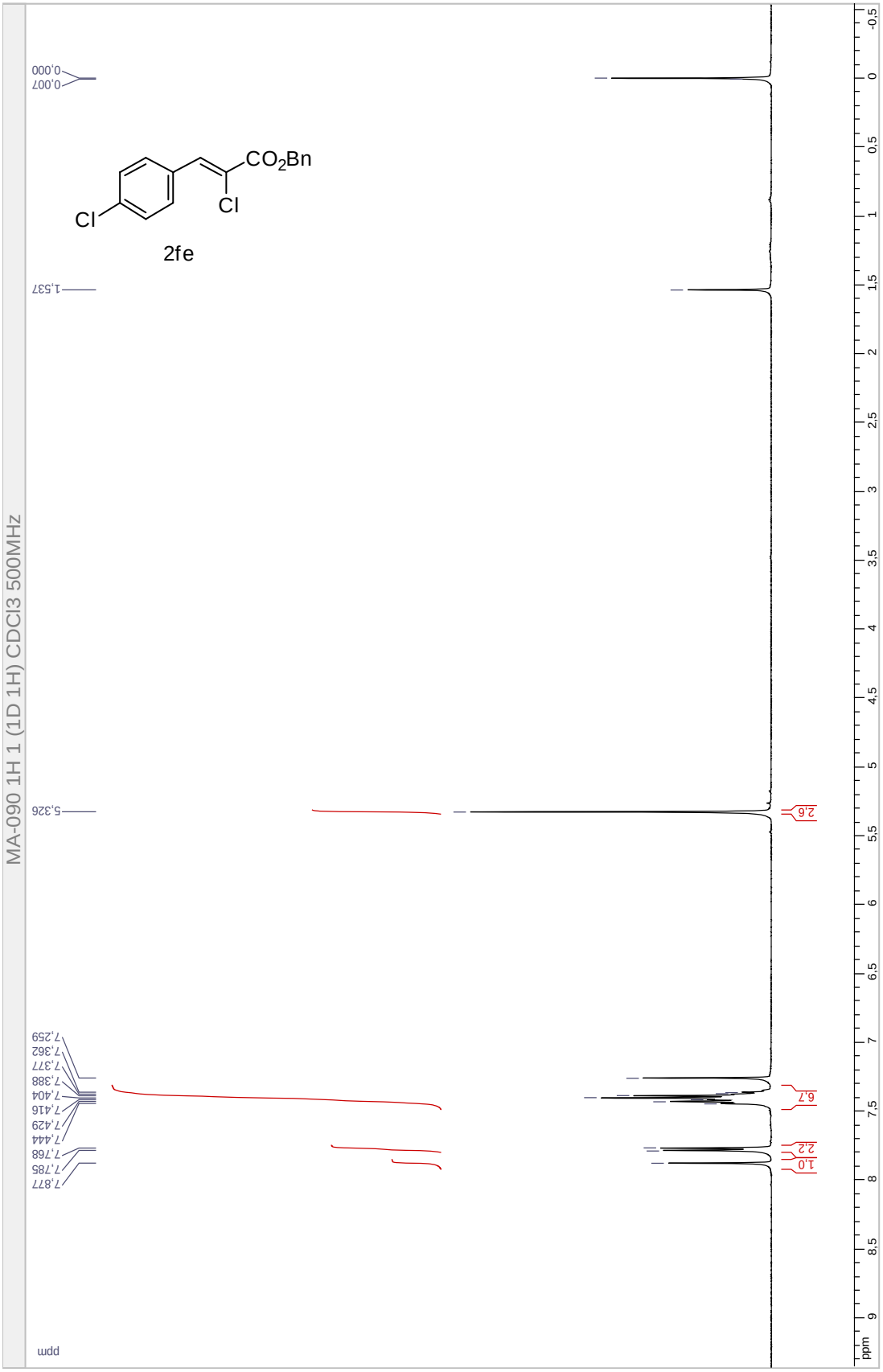

MA-078 3 (1D 13C) CDCl3 300MHz
MeO
CO2Bn
Cl
2ce
55,387
67,955
76,697
77,133
77,555
114,064
119,344
125,569
128,304
128,464
128,682
132,827
135,591
137,046
161,249
163,635
ppm
point

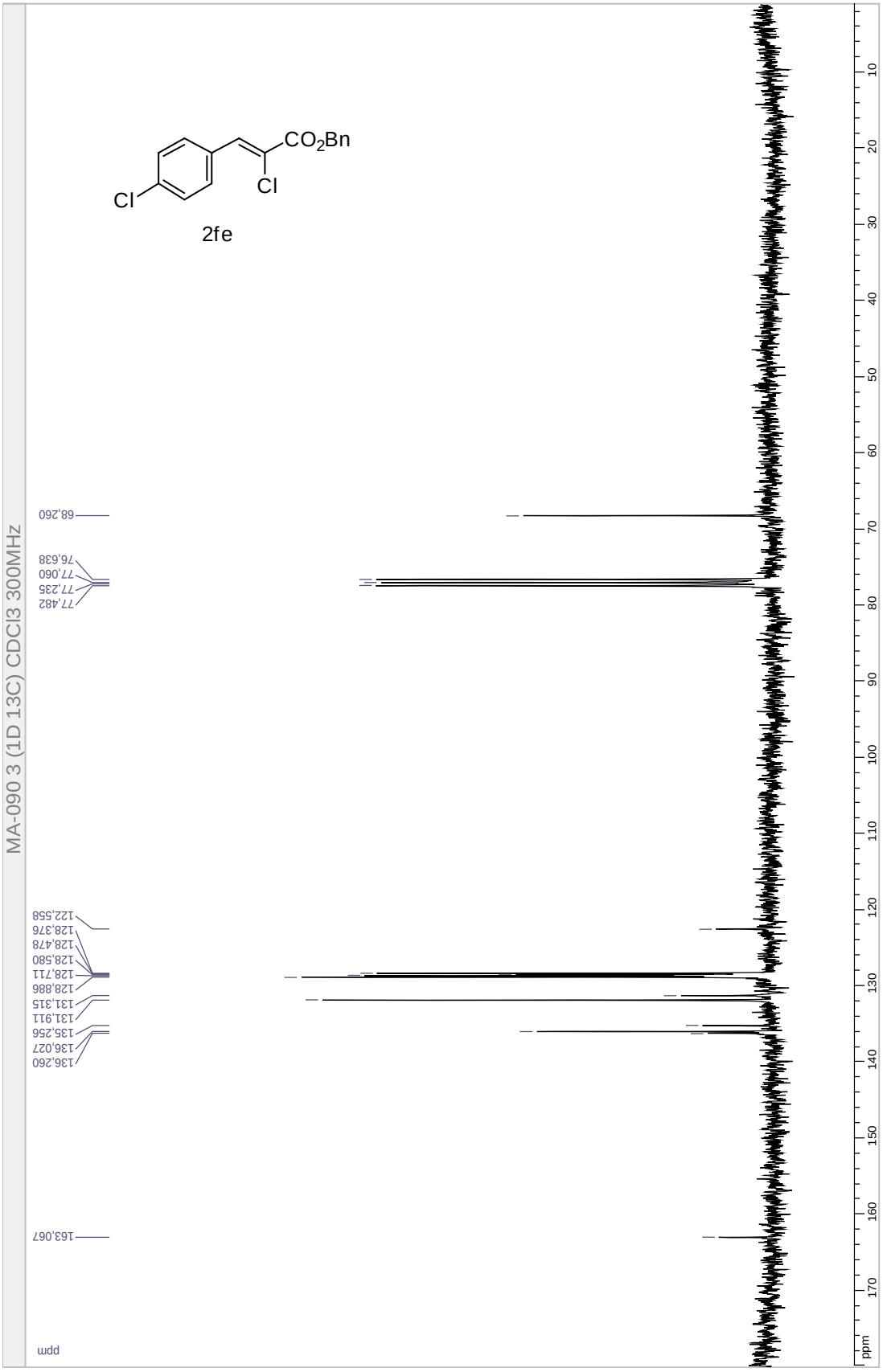

MA-115 f2 2 (1D 1H) CDCl3 500MHz
0,000
1,584
3,932
5,336
7,257
7,364
7,378
7,389
7,404
7,417
7,433
7,447
7,860
7,877
7,946
8,066
8,083
3,0
2,0
4,8
3,0
2,0
ppm
CO2Bn
Cl
MeO2C
2de

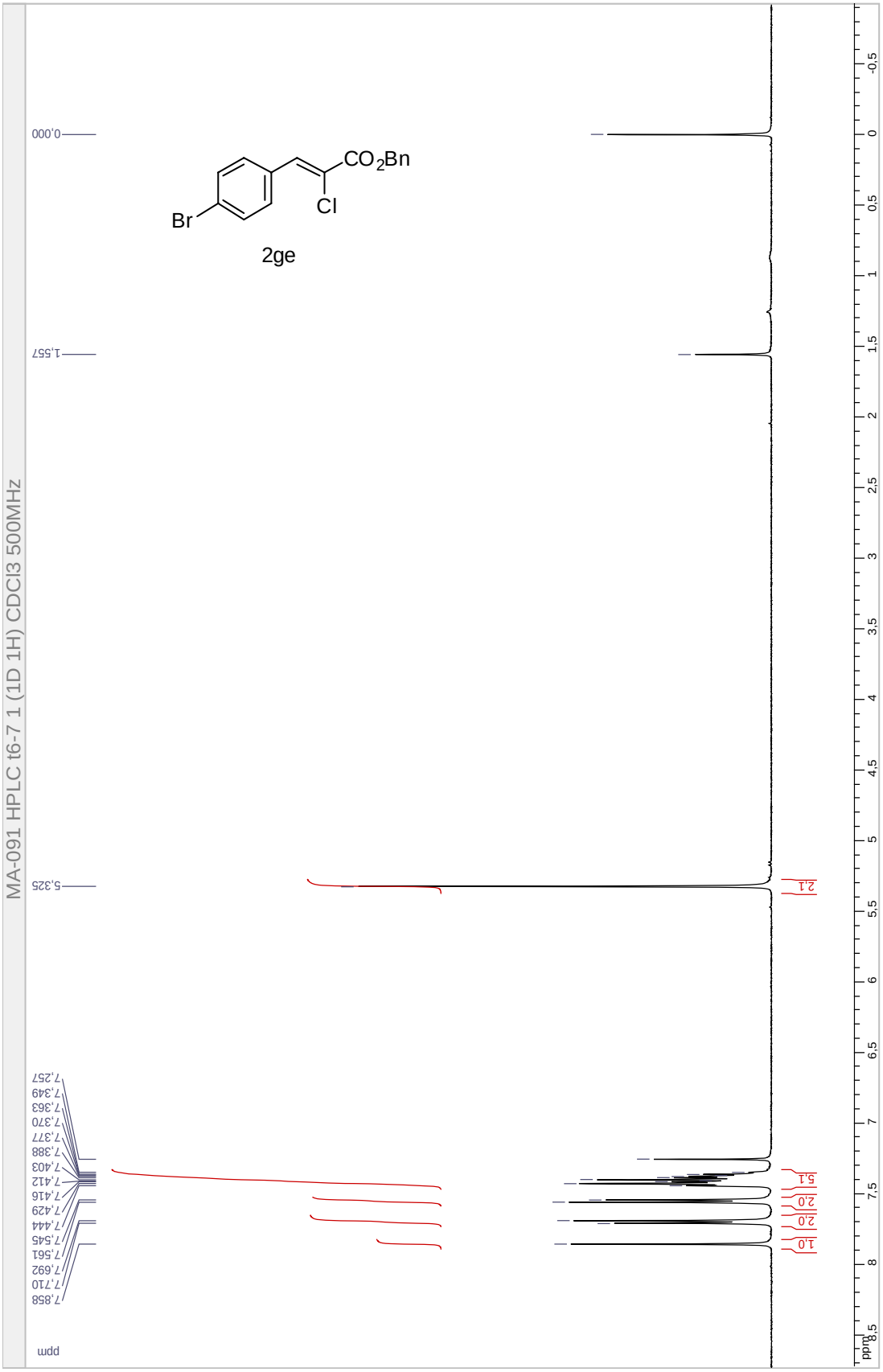

MA-115 f2 3 (1D 13C) CDCl3 300MHz
CO_2Bn
Cl
MeO_2C
2de
52,517
68,546
76,808
77,230
77,652
124,314
128,575
128,808
128,895
129,841
130,597
131,368
135,354
136,343
137,259
163,077
166,554
ppm
14 000
13 000
12 000
11 000
10 000
9 000
8 000
7 000
6 000
5 000
4 000
3 000
point

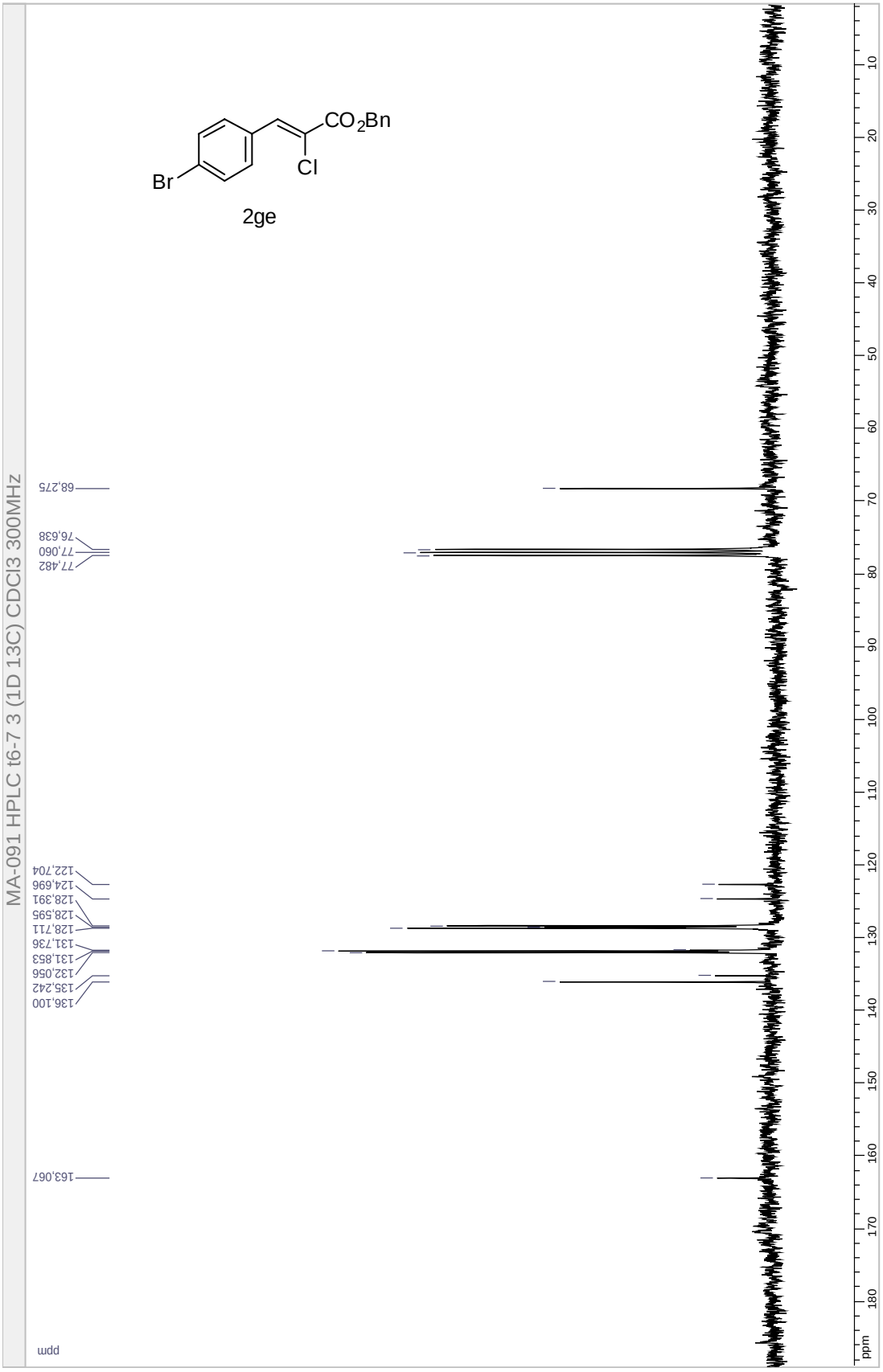

MA-107 pur 1 (1D 1H) CDCl3 500MHz
N
CO2Bn
Cl
2ee
0,000
1,578
5,336
2,9
1,1
5,2
1,3
2,0
1,0
7,260
7,273
7,283
7,288
7,298
7,356
7,362
7,370
7,372
7,378
7,394
7,407
7,409
7,428
7,442
7,759
7,763
7,775
7,778
7,790
7,794
8,071
8,143
8,159
8,699
8,708
ppm

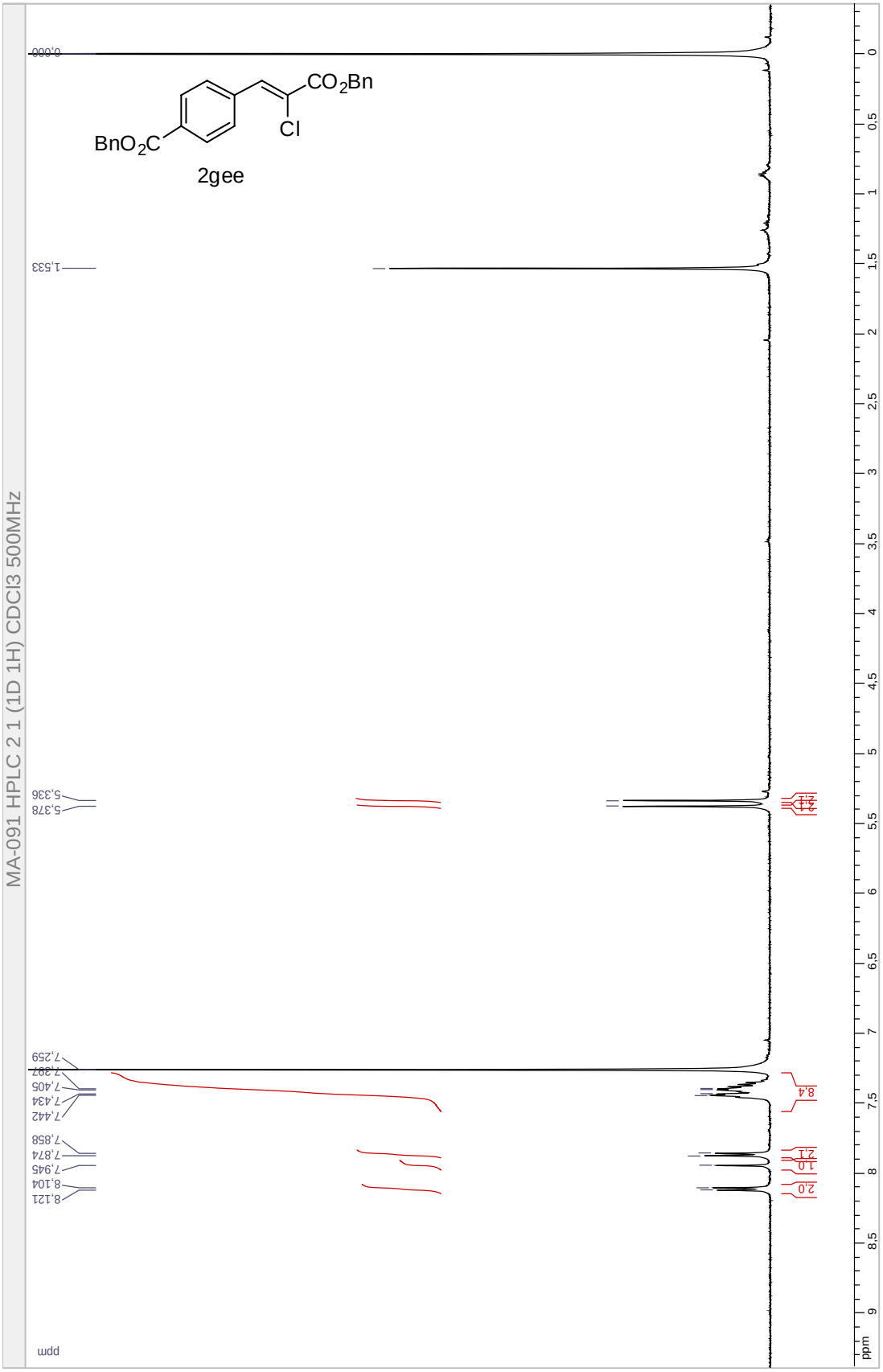

N
CO2Bn
Cl
2ee
MA-107 pur 3 (1D 13C) CDCl3 300MHz
68,406
76,740
77,162
77,584
123,984
124,813
125,438
128,449
128,595
128,682
135,096
136,333
137,540
149,933
152,144
162,806
ppm

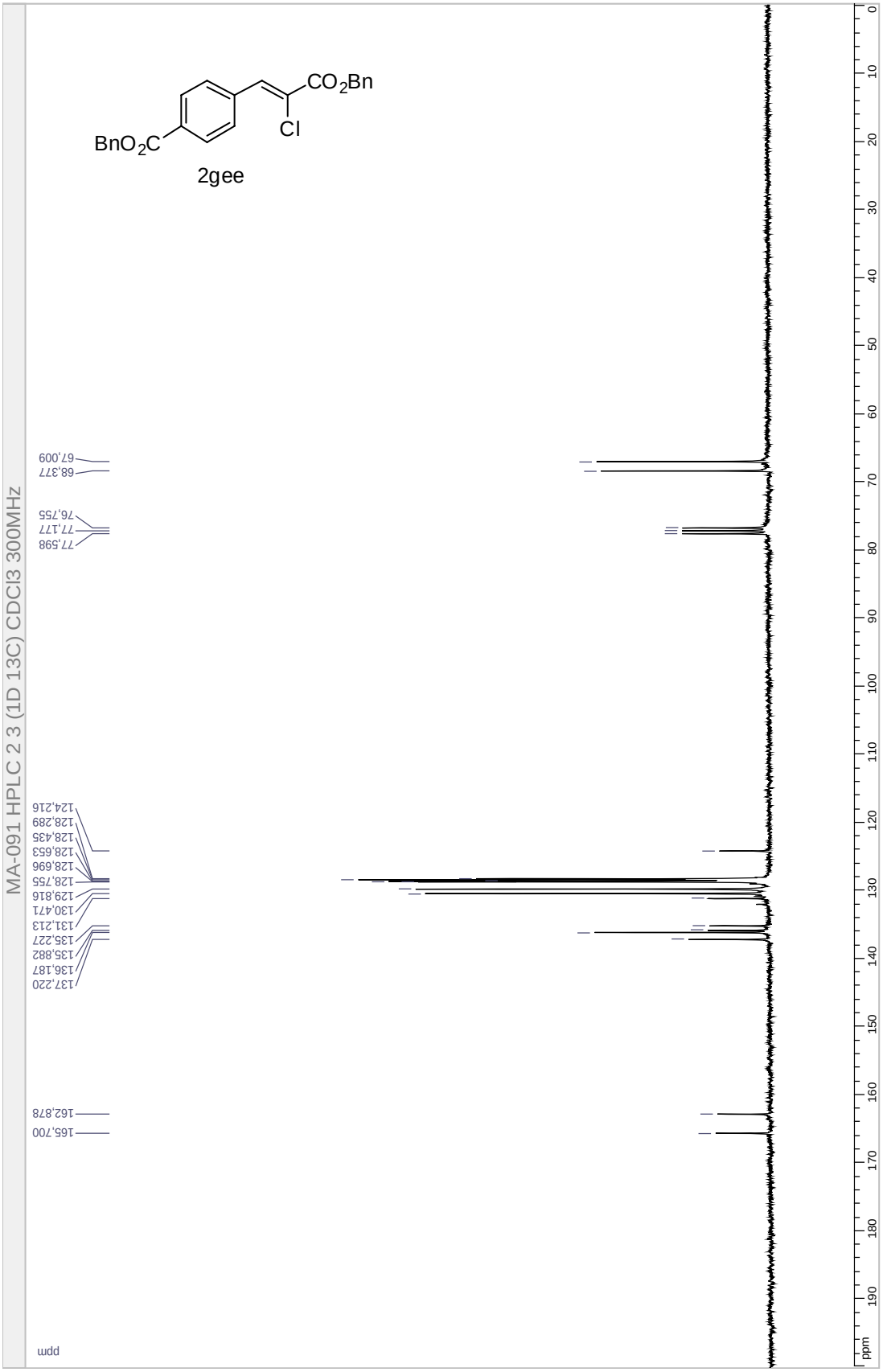

MA-090 1H 1 (1D 1H) CDCl3 500MHz
0,007
0,000
1,537
5,326
7,259
7,362
7,377
7,388
7,404
7,416
7,429
7,444
7,768
7,785
7,877
2,6
6,7
2,2
1,0
CO2Bn
Cl
Cl
2fe
ppm

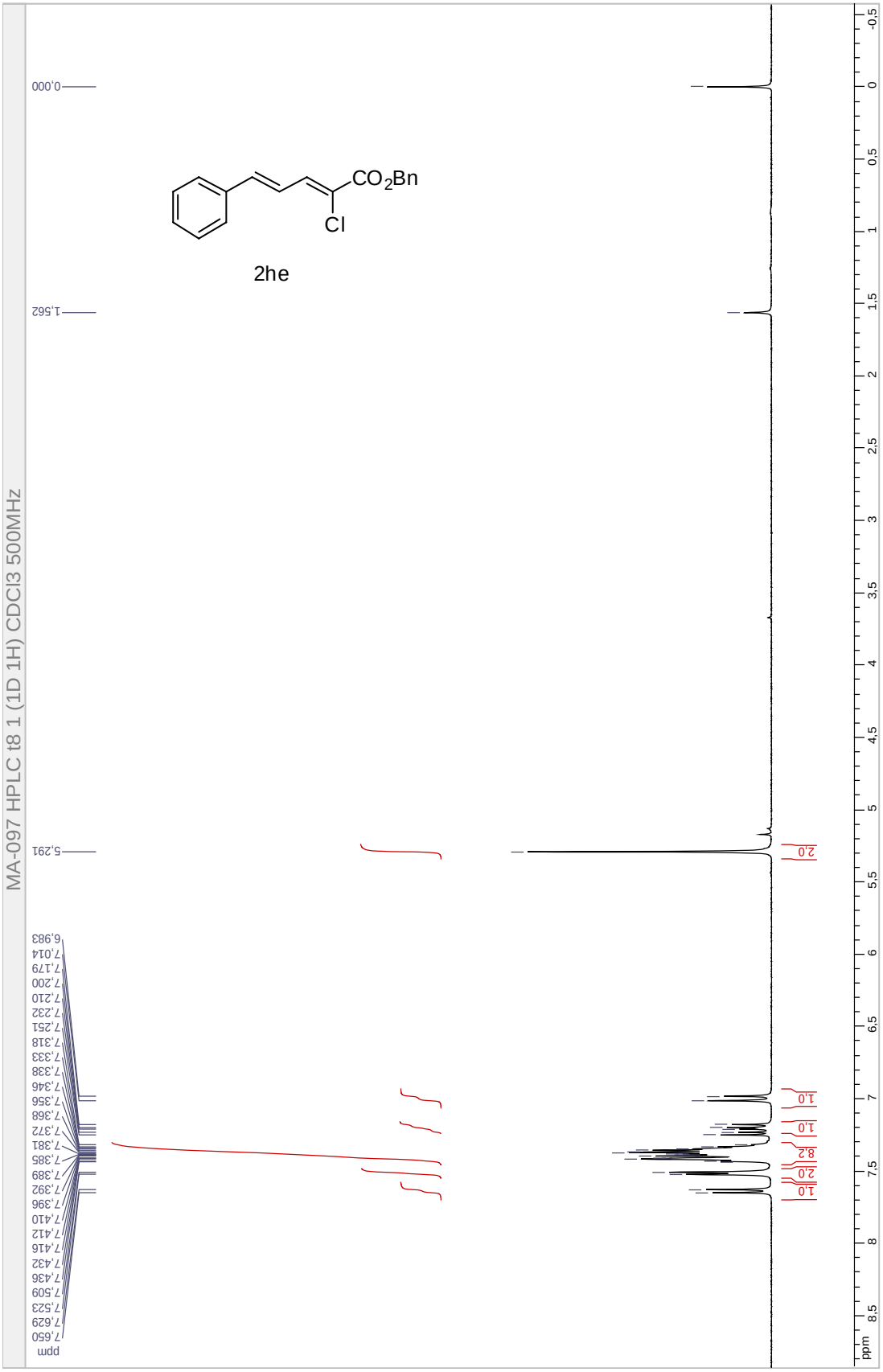

MA-090 3 (1D 13C) CDCl3 300MHz
CO2Bn
Cl
Cl
2fe
68,260
76,638
77,060
77,235
77,482
122,558
128,376
128,478
128,580
128,711
128,886
131,315
131,911
135,256
136,027
136,260
163,067
ppm

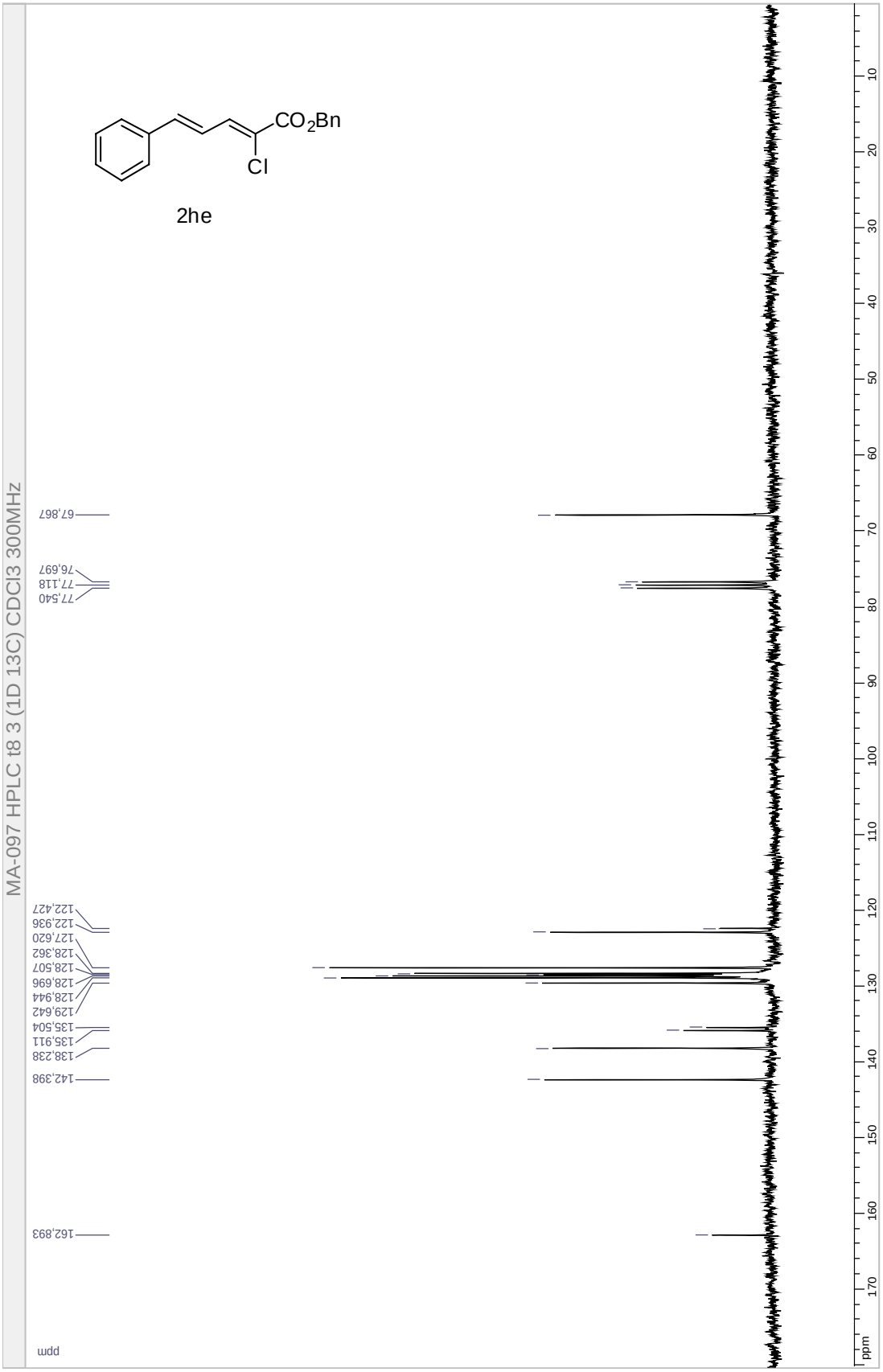

MA-091 HPLC t6-7 1 (1D 1H) CDCl3 500MHz
Br
CO2Bn
Cl
2ge
0,000
1,557
5,325
7,858
7,710
7,692
7,561
7,545
7,444
7,429
7,416
7,412
7,403
7,388
7,377
7,370
7,363
7,349
7,257
2,1
5,1
2,0
2,0
1,0
ppm

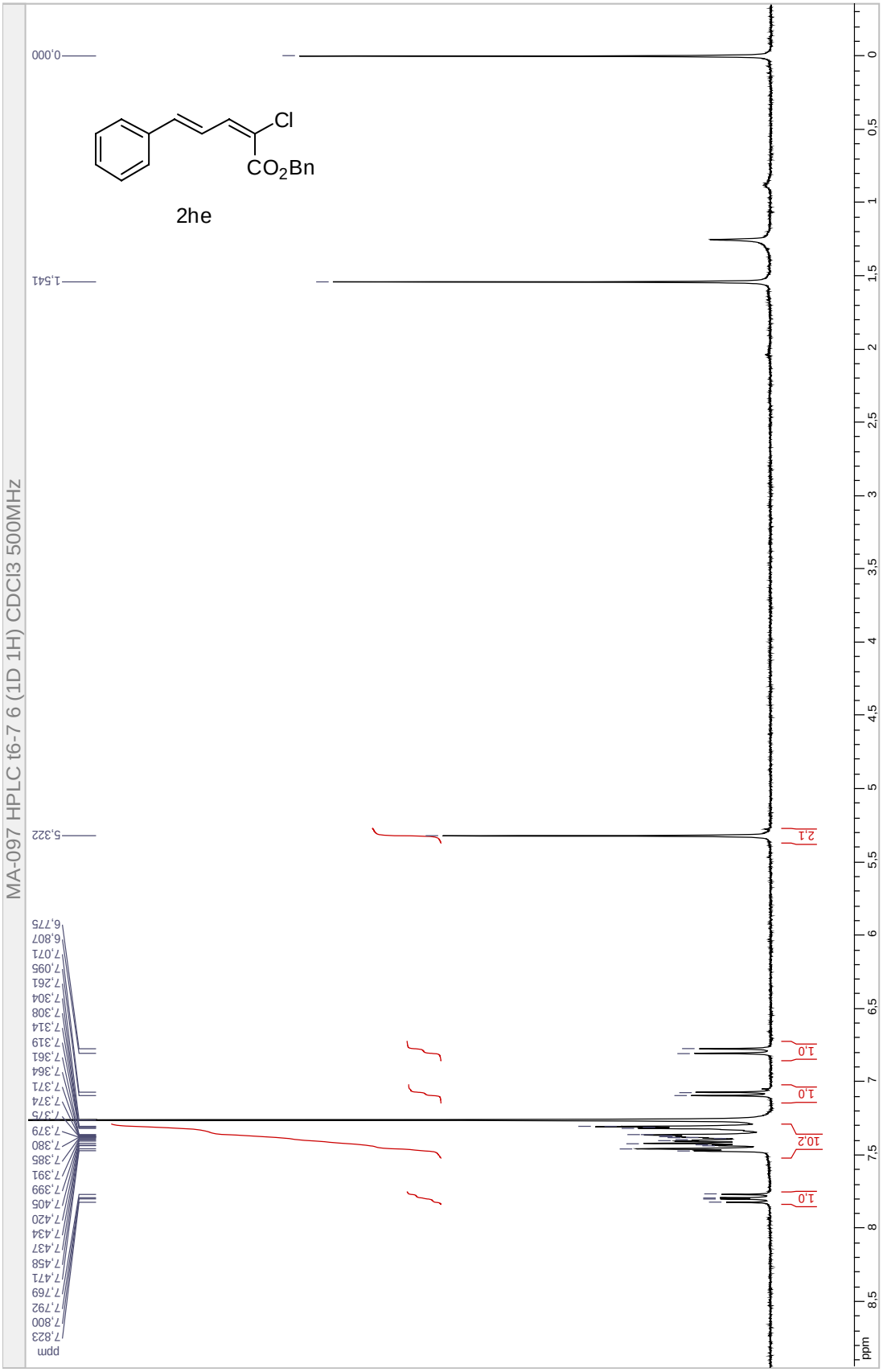

MA-091 HPLC t6-7 3 (1D 13C) CDCl3 300MHz
Br
CO2Bn
Cl
2ge
68,275
76,638
77,060
77,482
122,704
124,696
128,391
128,595
128,711
131,736
131,853
132,056
135,242
136,100
163,067
ppm

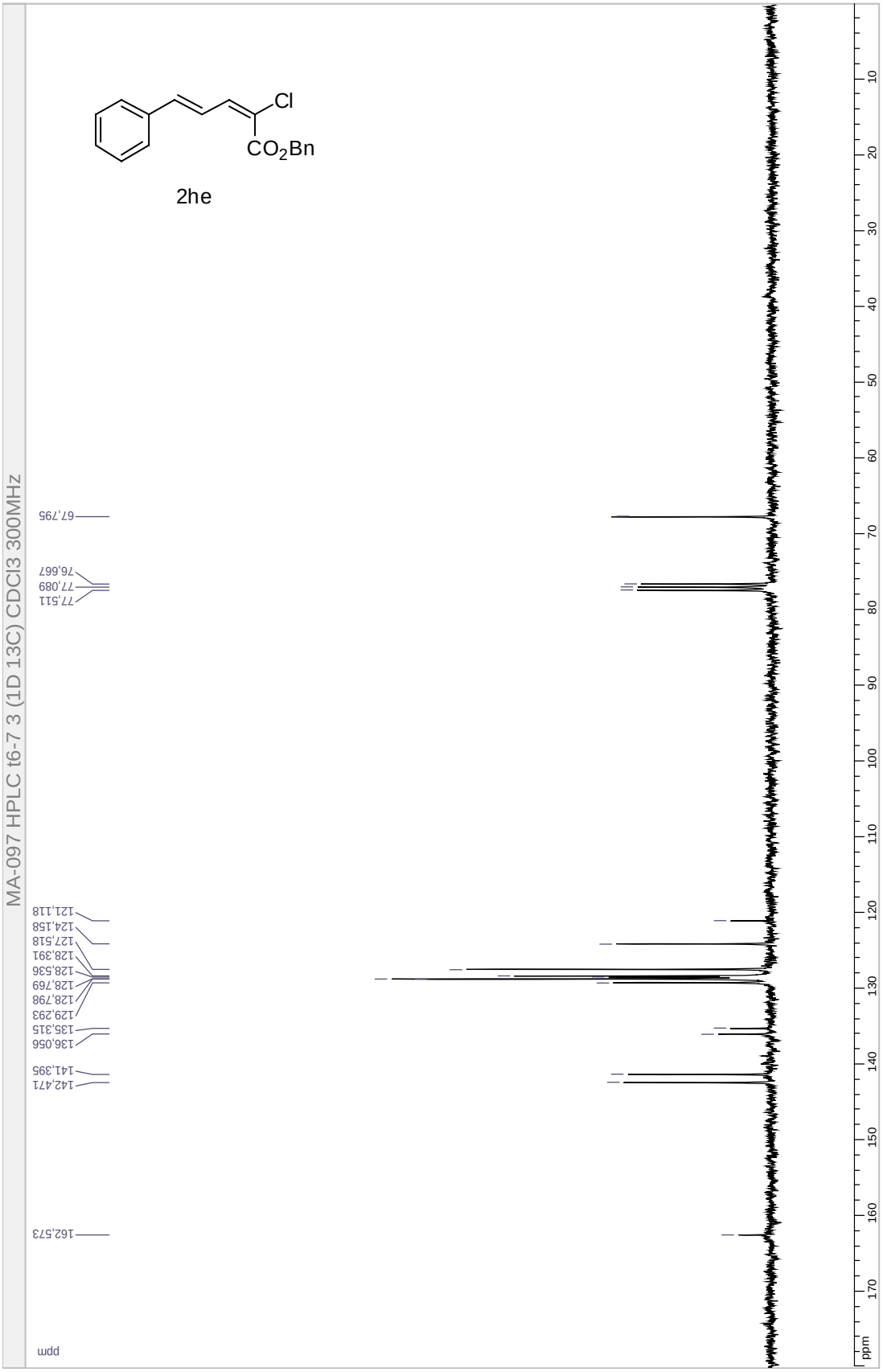

MA-091 HPLC 2 1 (1D 1H) CDCl3 500MHz
2gee
CO_2Bn
Cl
BnO_2C
0,000
1,533
5,336
5,378
7,259
7,397
7,405
7,434
7,442
7,858
7,874
7,945
8,104
8,121
2,1
8,4
2,1
1,0
2,0
ppm

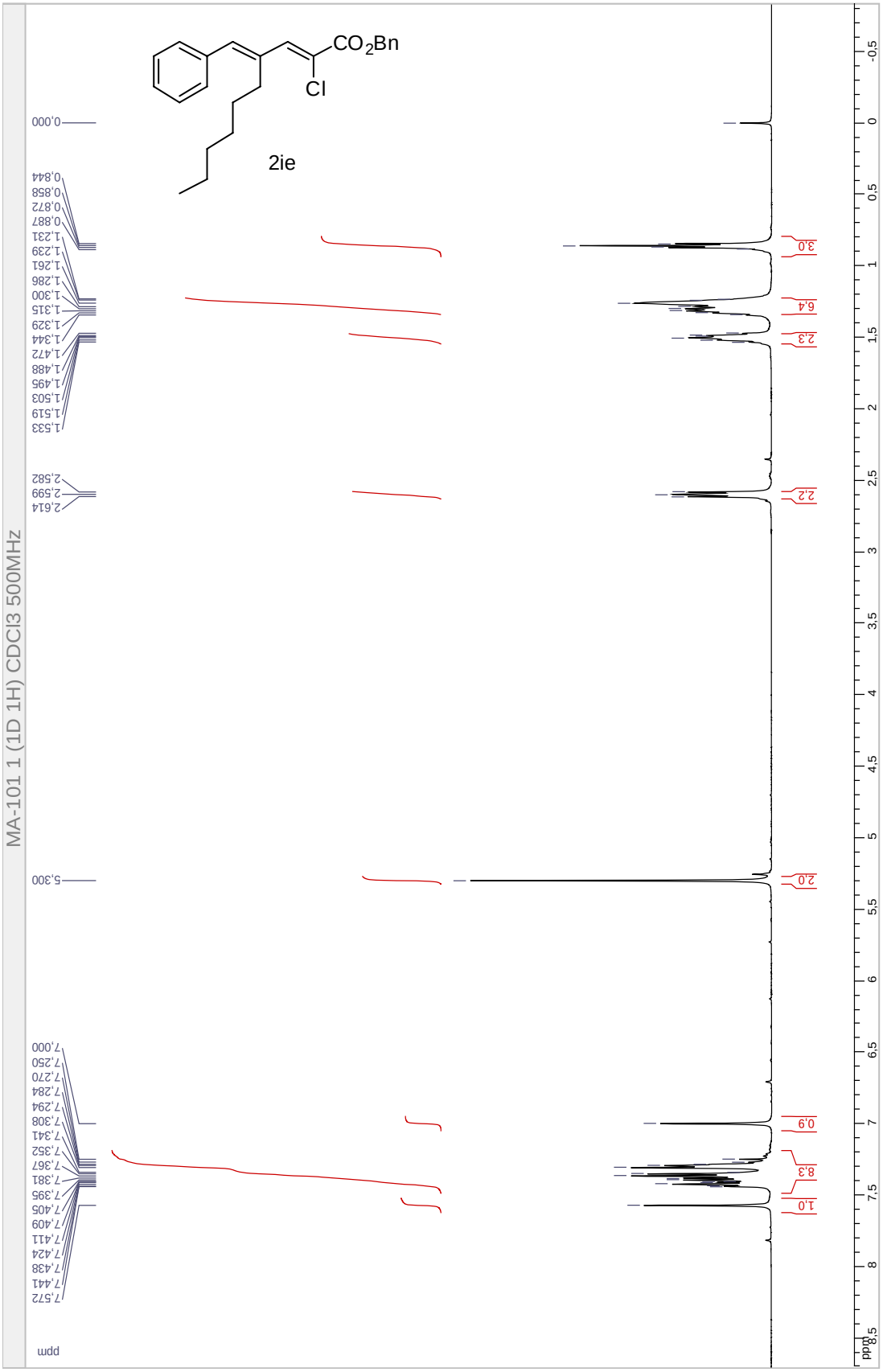

MA-091 HPLC 2 3 (1D 13C) CDCl3 300MHz
CO_2Bn
Cl
BnO_2C
2gee
67,009
68,377
76,755
77,177
77,598
124,216
128,289
128,435
128,653
128,696
128,755
129,816
130,471
131,213
135,227
135,882
136,187
137,220
162,878
165,700
ppm

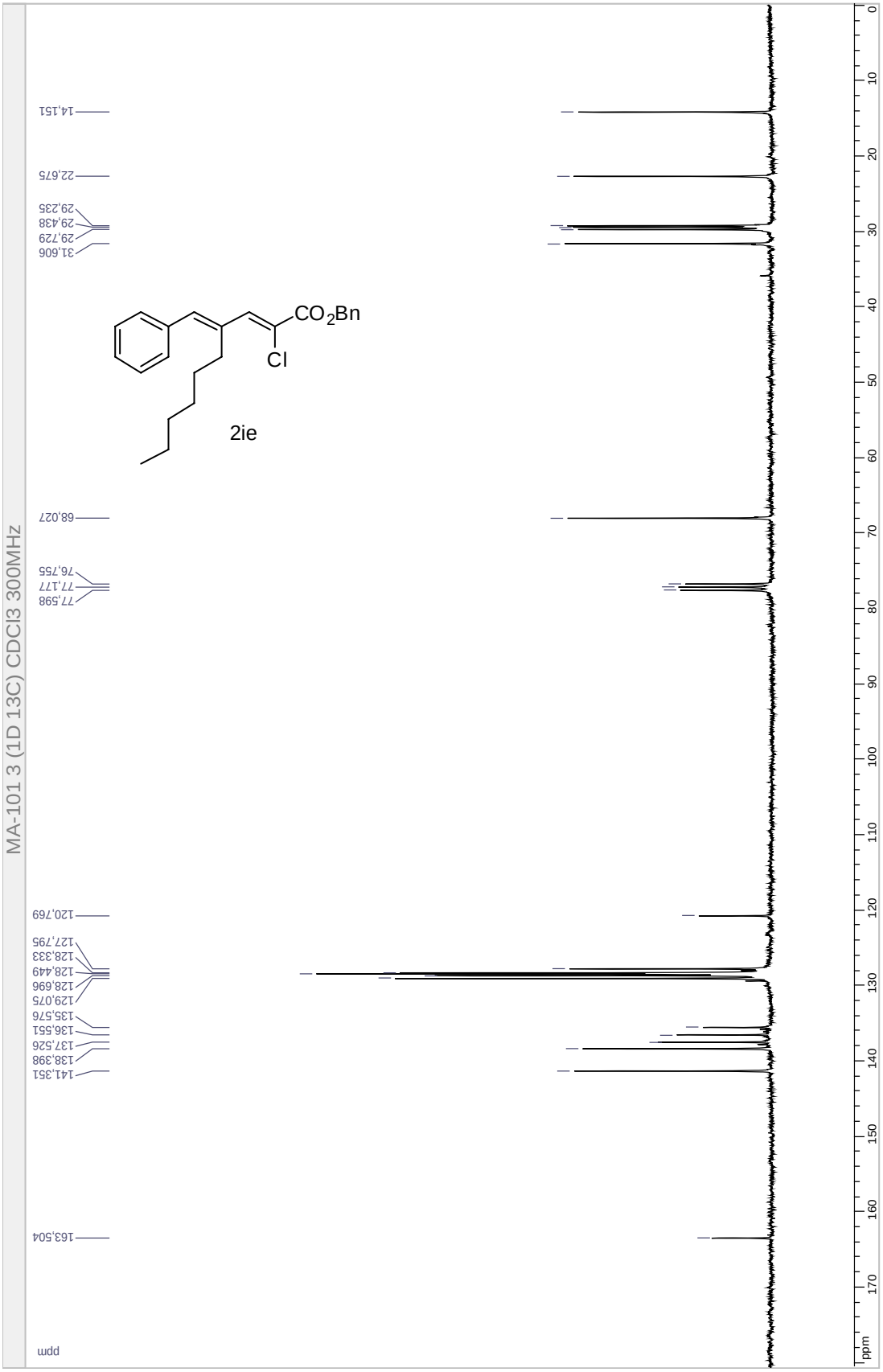

MA-097 HPLC t8 1 (1D 1H) CDCl3 500MHz
CO_2Bn
Cl
2he
0,000
1,562
5,291
2,0
1,0
1,0
8,2
2,0
1,0
ppm

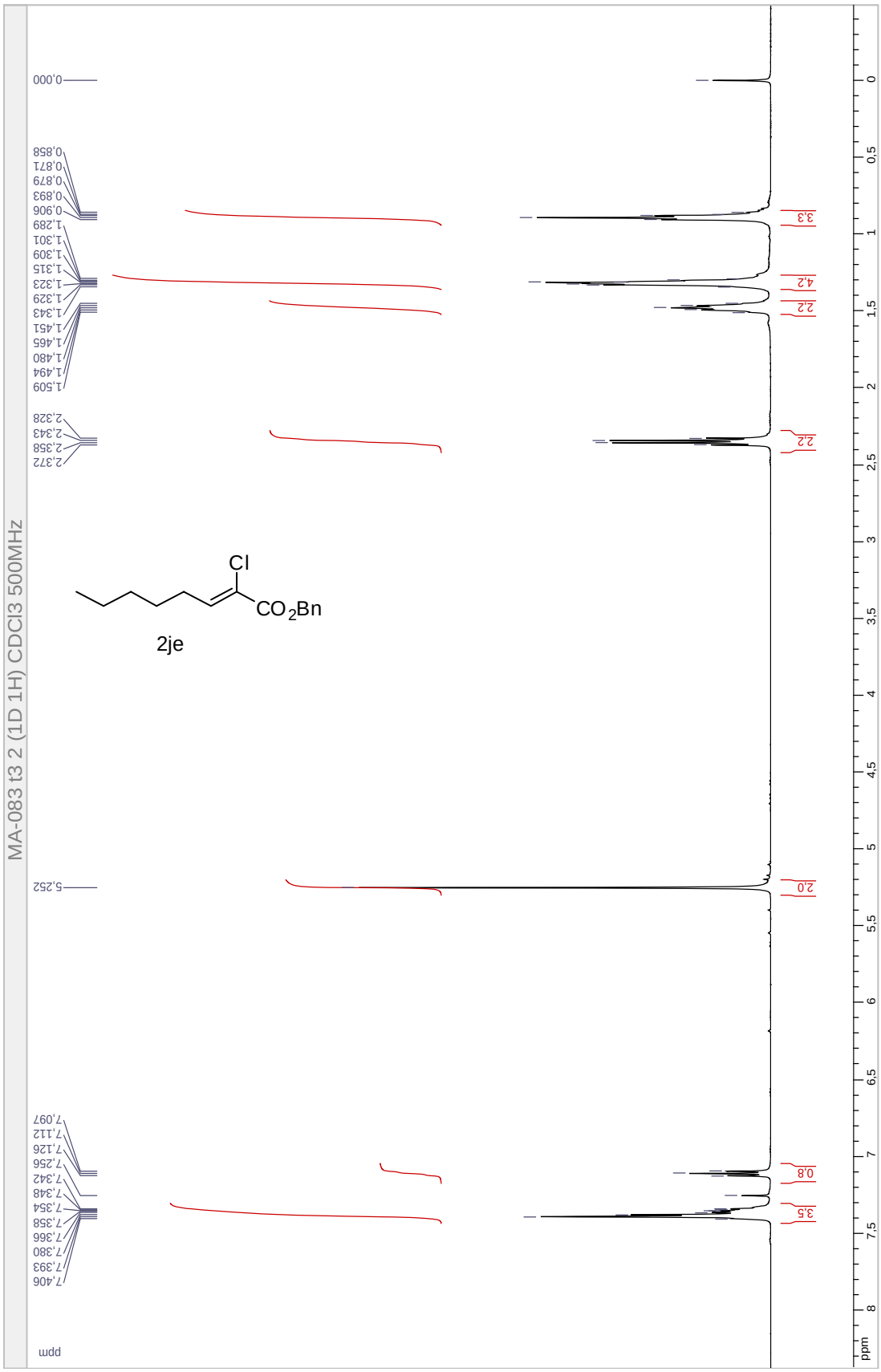

MA-097 HPLC t8 3 (1D 13C) CDCl3 300MHz
CO2Bn
Cl
2he
67,867
76,697
77,118
77,540
122,427
122,936
127,620
128,362
128,507
128,696
128,944
129,642
135,504
135,911
138,238
142,398
162,893
ppm

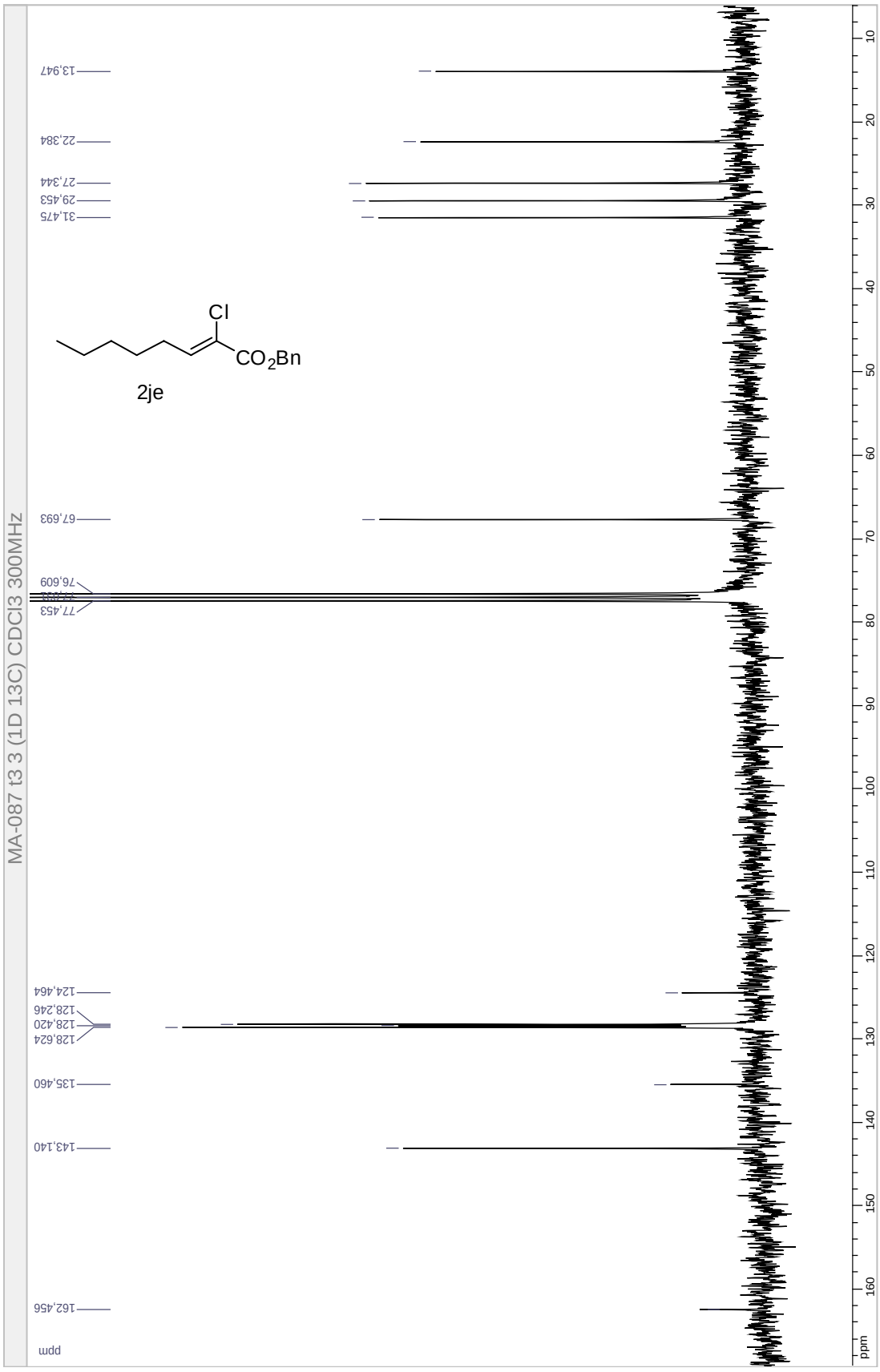

MA-097 HPLC t6-7 6 (1D 1H) CDCl3 500MHz
Cl
CO2Bn
2he
0,000
1,541
5,322
2,1
1,0
1,0
10,2
1,0
ppm

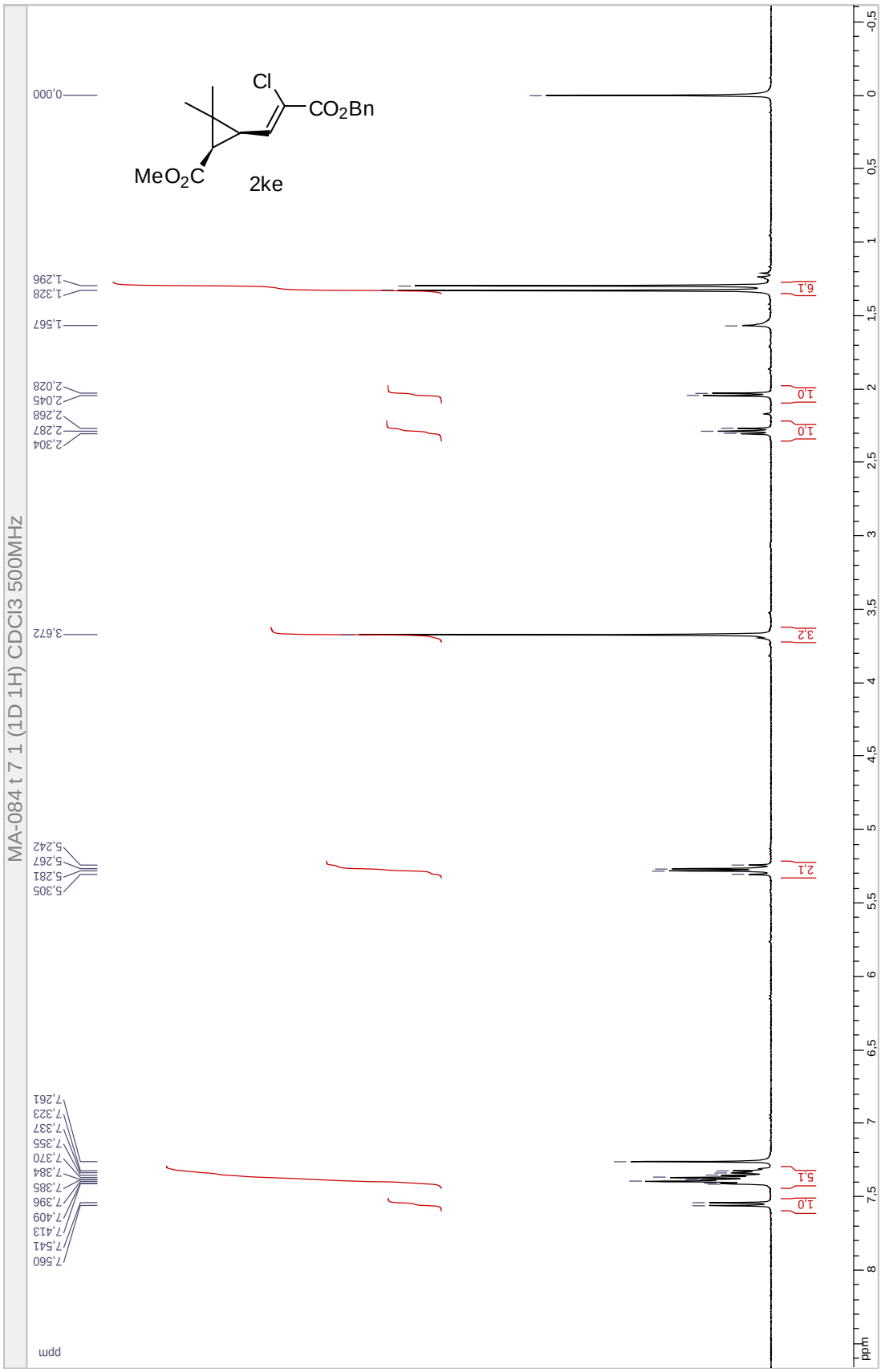

Cl
CO2Bn
2he
MA-097 HPLC t6-7 3 (1D 13C) CDCl3 300MHz
67,795
76,667
77,089
77,511
121,118
124,158
127,518
128,391
128,536
128,769
128,798
129,293
135,315
136,056
141,395
142,471
162,573
ppm

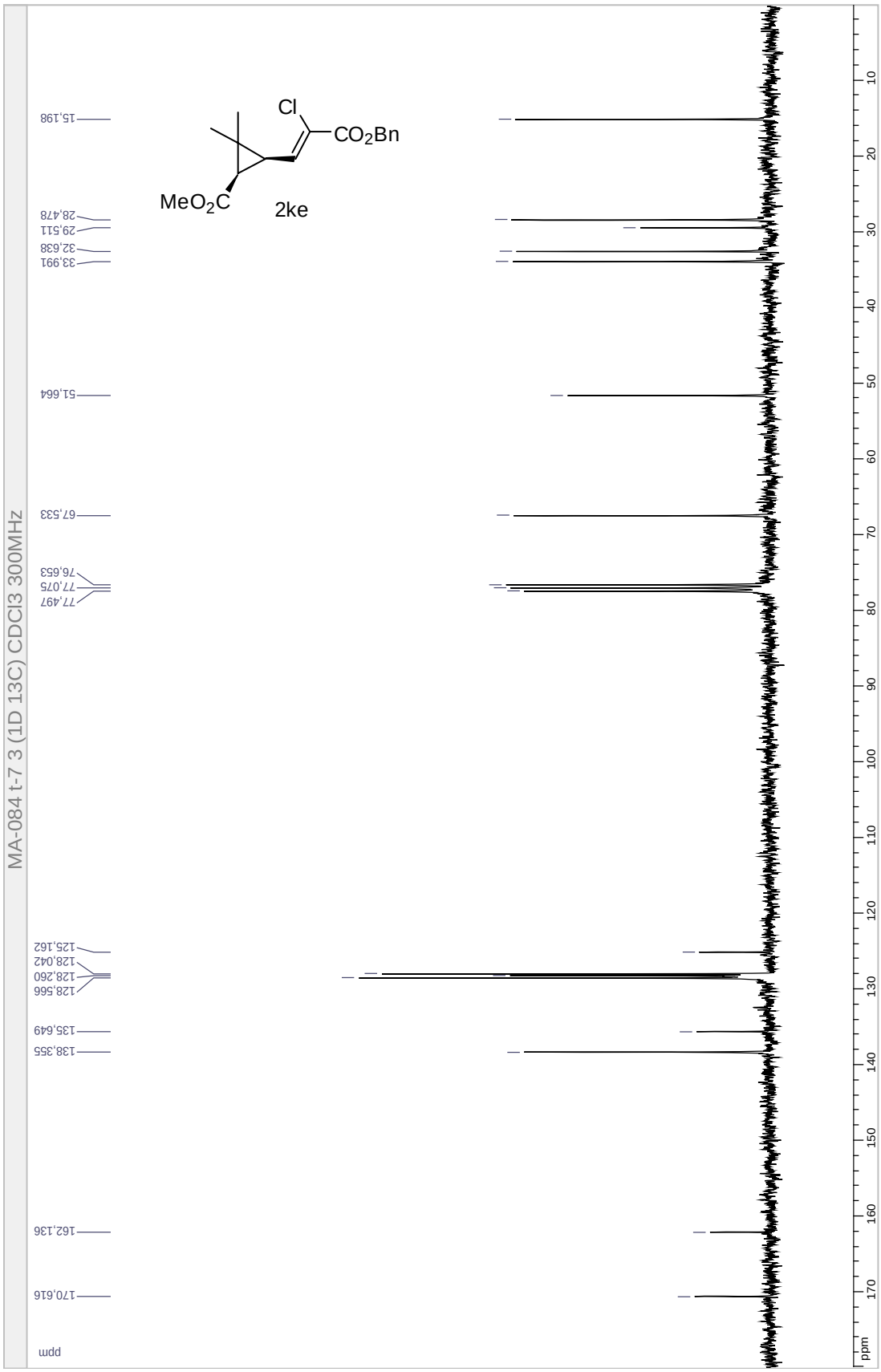

MA-101 1 (1D 1H) CDCl3 500MHz
CO2Bn
Cl
2ie
ppm

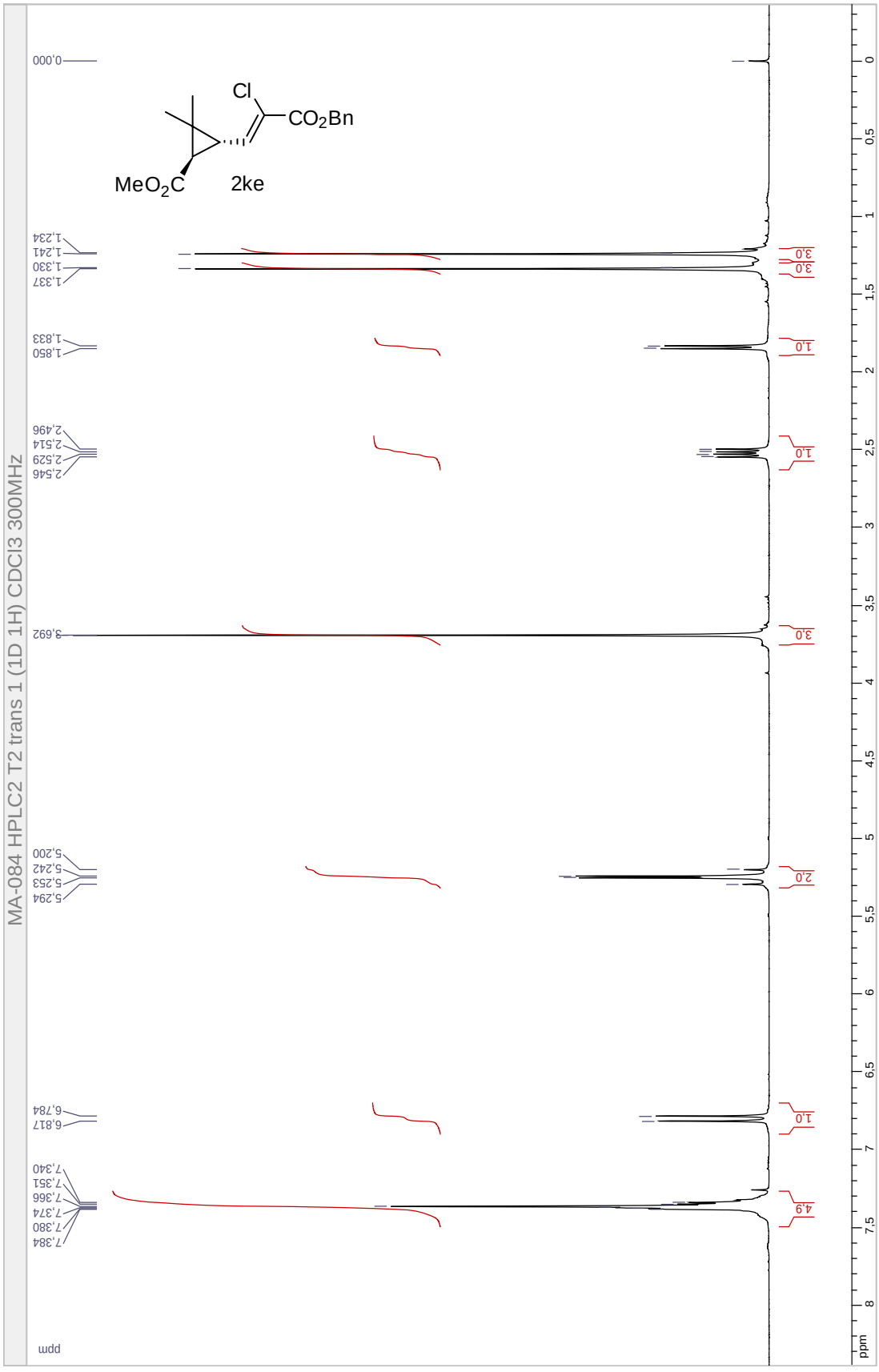

MA-101 3 (1D 13C) CDCl3 300MHz
14.151
22.675
29.235
29.438
29.729
31.606
68.027
76.755
77.177
77.598
120.769
127.795
128.333
128.449
128.696
129.075
135.576
136.551
137.526
138.398
141.351
163.504
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
CO2Bn
Cl
2ie

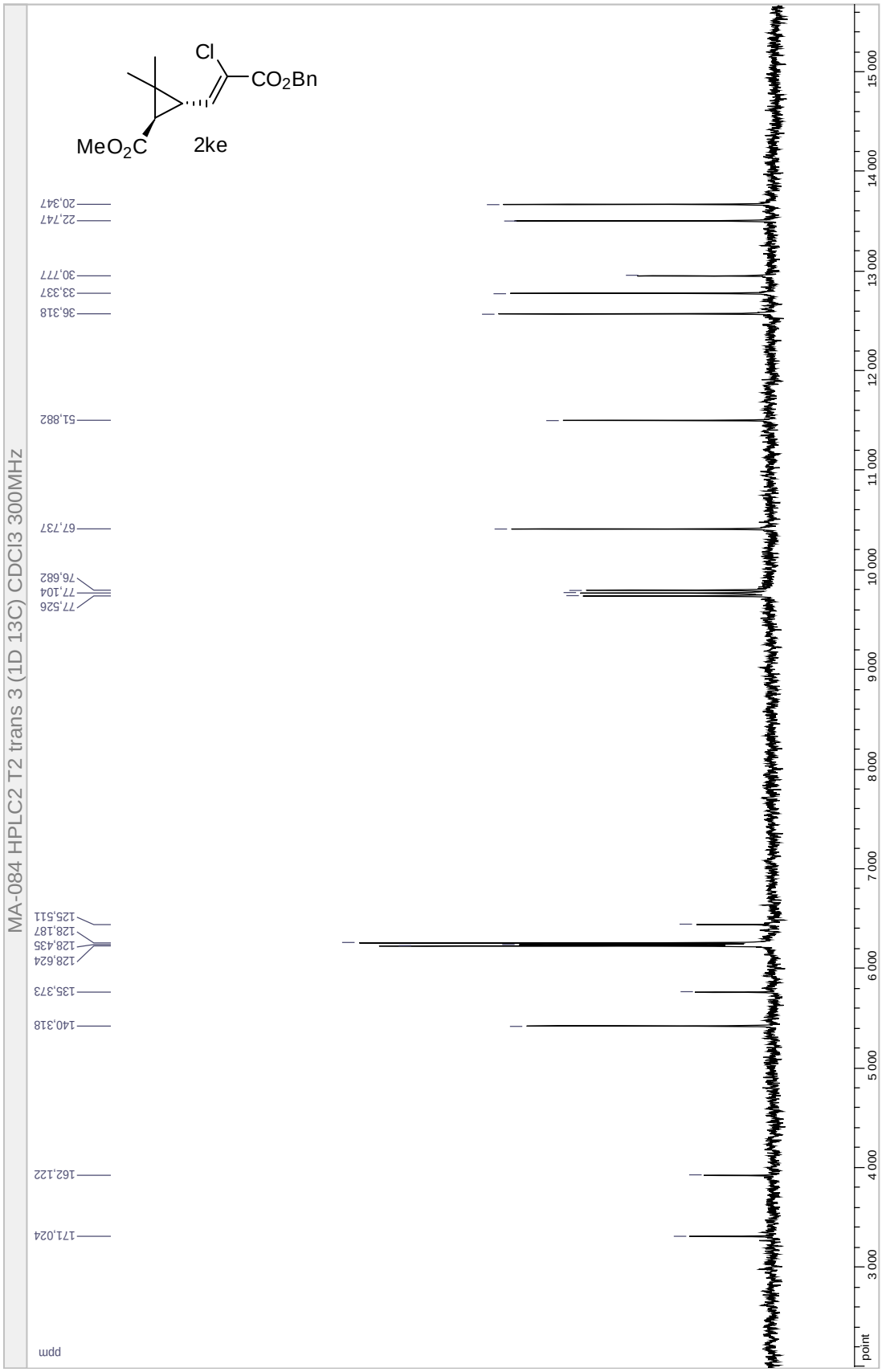

MA-083 t3 2 (1D 1H) CDCl3 500MHz
Cl
CO2Bn
2je
ppm

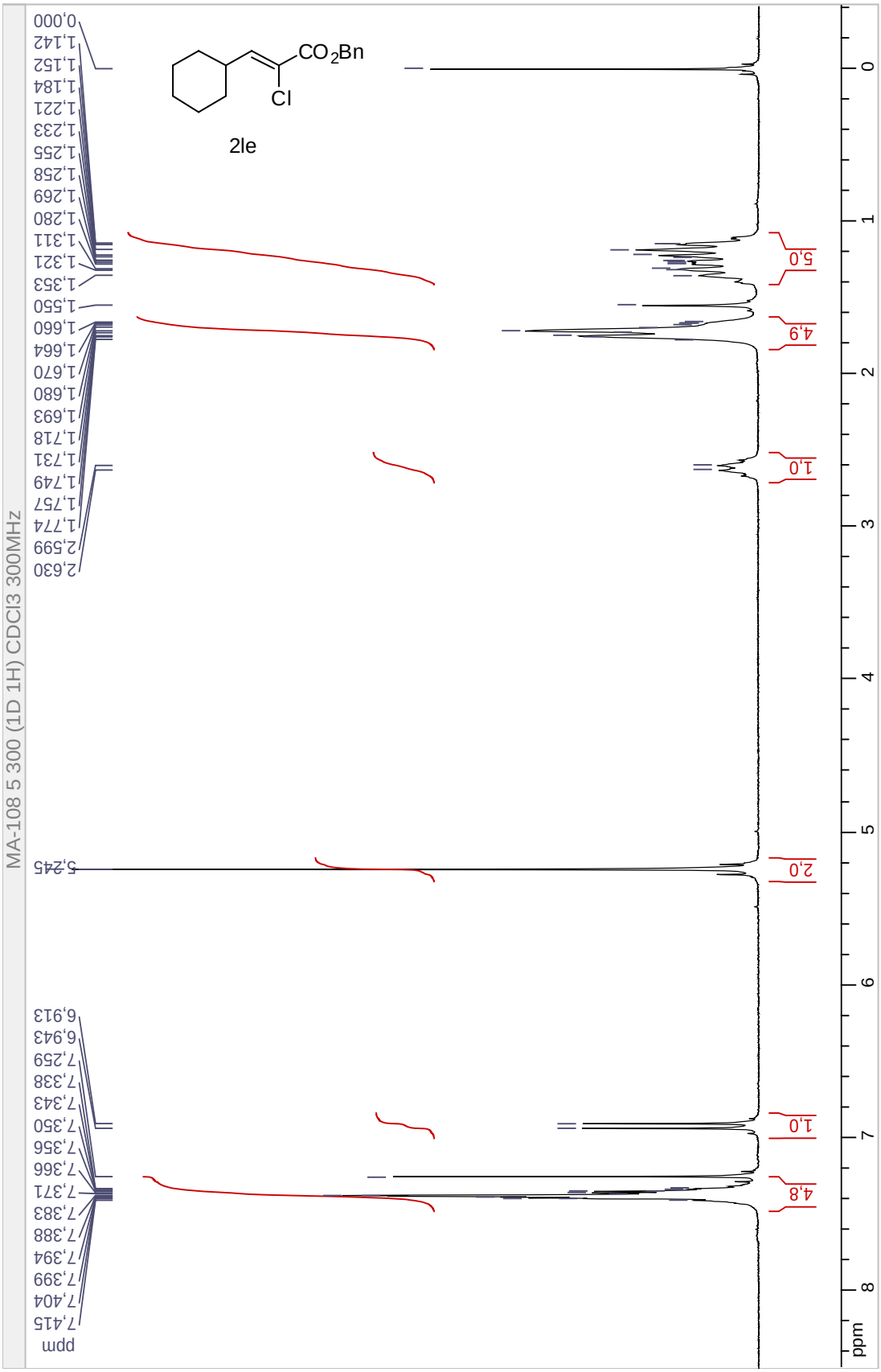

MA-087 t3 3 (1D 13C) CDCl3 300MHz
13,947
22,384
27,344
29,453
31,475
67,693
76,609
77,453
124,464
128,246
128,420
128,624
135,460
143,140
162,456
ppm
Cl
CO2Bn
2je

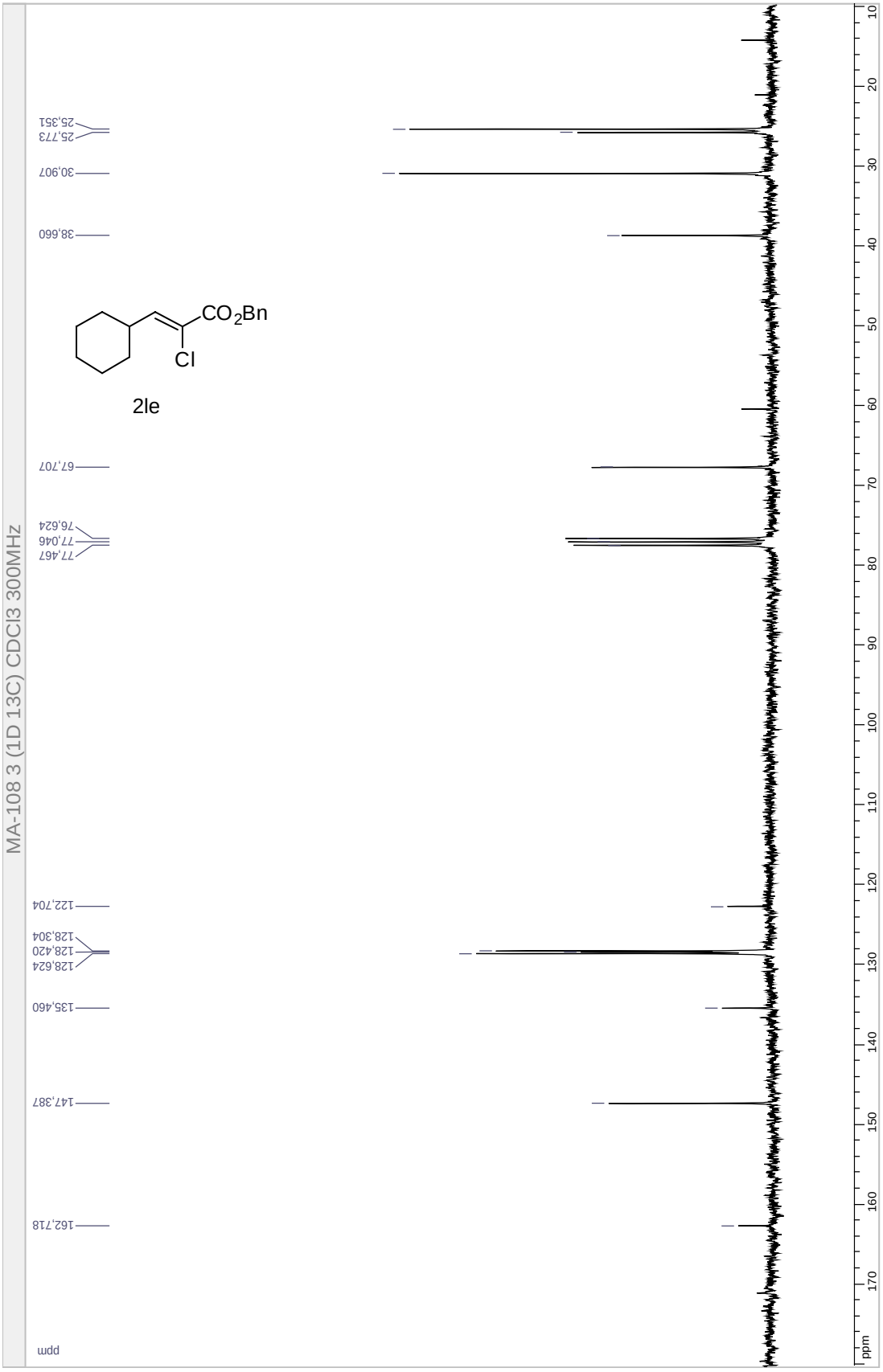

MA-084 t 7 1 (1D 1H) CDCl3 500MHz
Cl
CO2Bn
MeO2C
2ke
0,000
1,296
1,328
1,567
2,028
2,045
2,268
2,287
2,304
3,672
5,242
5,267
5,281
5,305
7,261
7,323
7,337
7,355
7,370
7,384
7,385
7,396
7,409
7,413
7,541
7,560
6,1
1,0
1,0
3,2
2,1
5,1
1,0
ppm

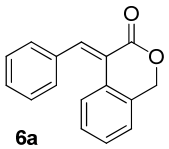

MA-084 t-7 3 (1D 13C) CDCl3 300MHz
Cl
CO2Bn
MeO2C
2ke
15.198
28.478
29.511
32.638
33.991
51.664
67.533
76.653
77.075
77.497
125.162
128.042
128.260
128.566
135.649
138.355
162.136
170.616
ppm


MA-084 HPLC2 T2 trans 1 (1D 1H) CDCl3 300MHz
Cl
CO2Bn
MeO2C
2ke
0,000
1,234
1,241
1,330
1,337
1,833
1,850
2,496
2,514
2,529
2,546
3,692
5,200
5,242
5,253
5,294
6,784
6,817
7,340
7,351
7,366
7,374
7,380
7,384
3,0
3,0
1,0
1,0
3,0
2,0
1,0
4,9
ppm

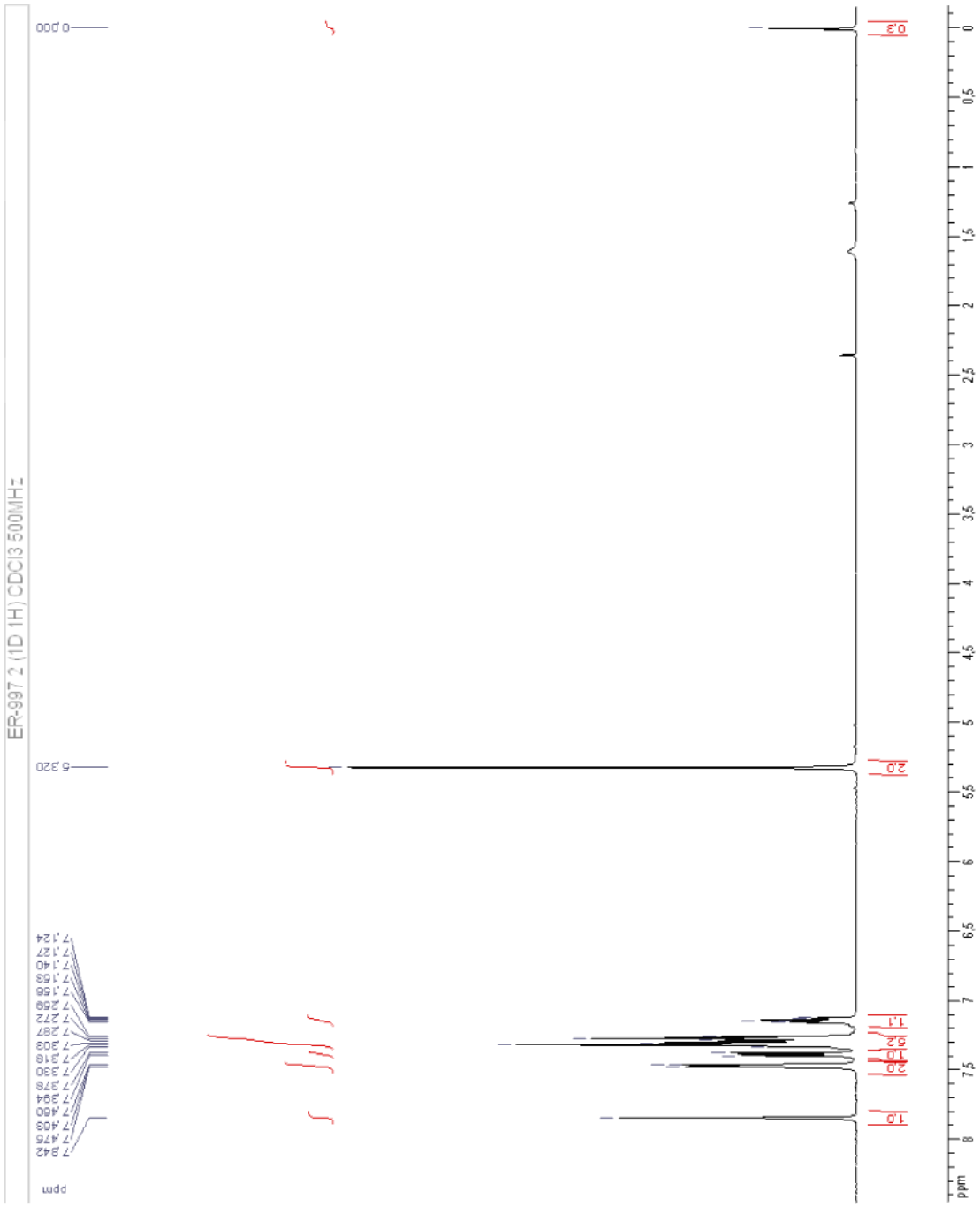

Cl
CO2Bn
MeO2C
2ke
MA-084 HPLC2 T2 trans 3 (1D 13C) CDCl3 300MHz
20,347
22,747
30,777
33,337
36,318
51,882
67,737
76,682
77,104
77,526
125,511
128,187
128,435
128,624
135,373
140,318
162,122
171,024
ppm
point
15 000
14 000
13 000
12 000
11 000
10 000
9 000
8 000
7 000
6 000
5 000
4 000
3 000

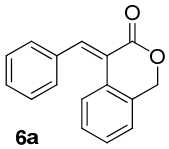

MA-108 5 300 (1D 1H) CDCl3 300MHz
ppm
0,000
1,142
1,152
1,184
1,221
1,233
1,255
1,258
1,269
1,280
1,311
1,321
1,353
1,550
1,660
1,664
1,670
1,680
1,693
1,718
1,731
1,749
1,757
1,774
2,599
2,630
5,245
6,913
6,943
7,259
7,338
7,343
7,350
7,356
7,366
7,371
7,383
7,388
7,394
7,399
7,404
7,415
CO2Bn
Cl
2le
5,0
4,9
1,0
2,0
1,0
4,8
0
1
2
3
4
5
6
7
8
ppm


MA-108 3 (1D 13C) CDCl3 300MHz
25,351
25,773
30,907
38,660
67,707
76,624
77,046
77,467
122,704
128,304
128,420
128,624
135,460
147,387
162,718
ppm
CO2Bn
Cl
2le

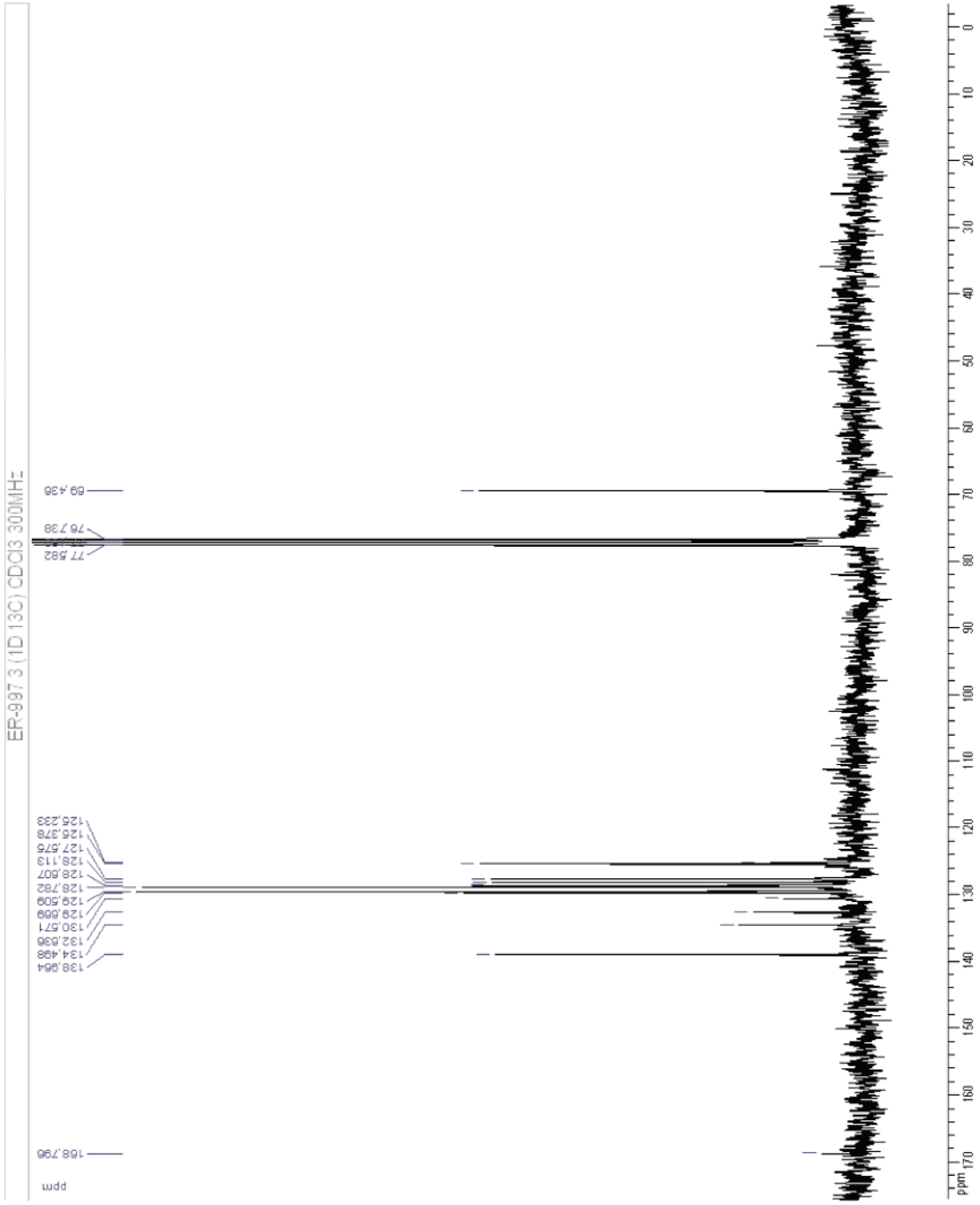


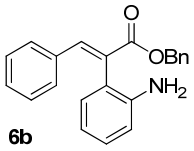
6a



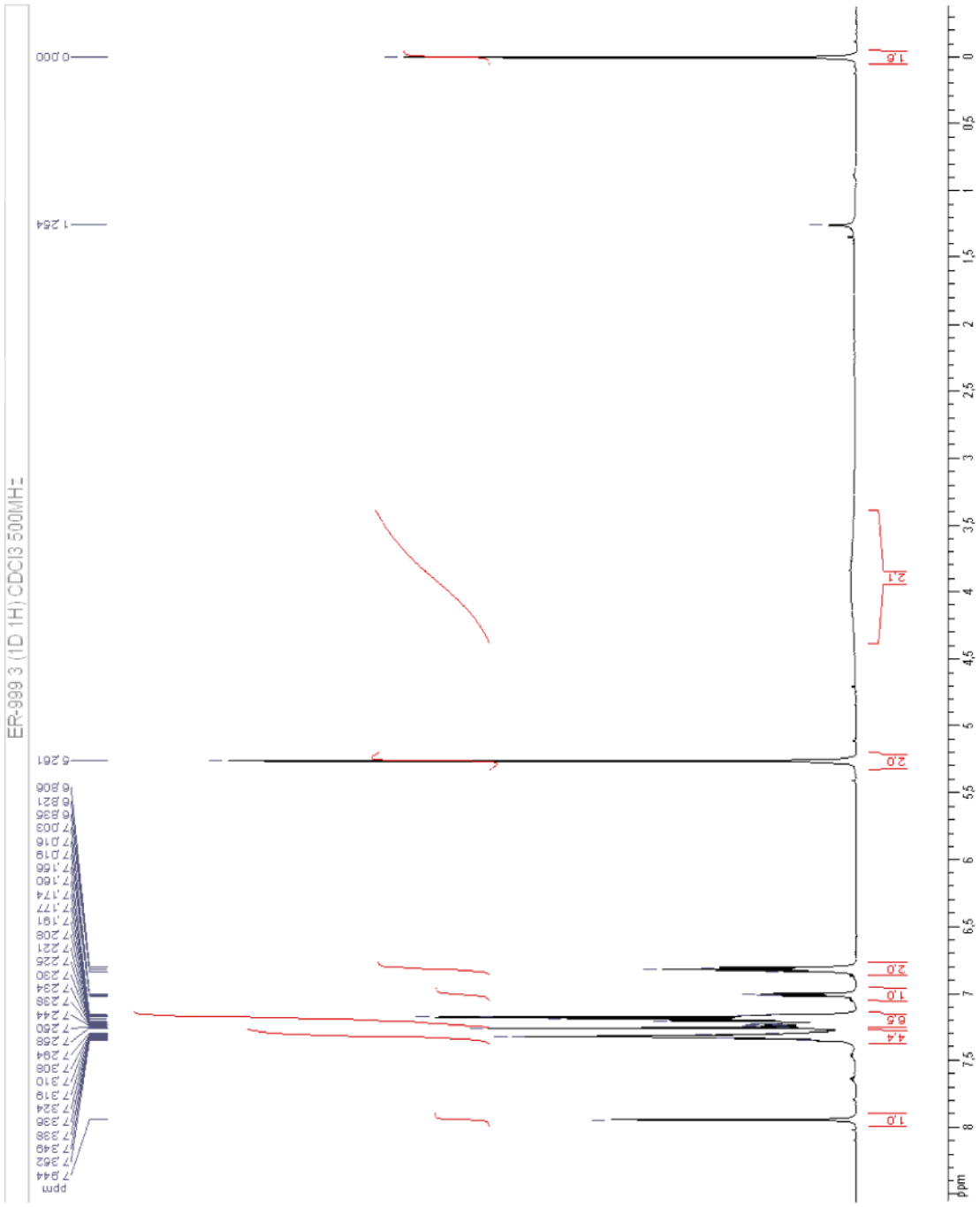


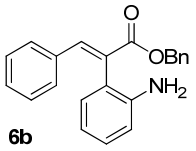
6a


ER-997 3 (1D 13C) CDCl3 300MHz
89.436
76.738
77.582
125.233
125.378
127.576
128.113
128.807
128.782
129.509
129.669
130.571
132.636
134.498
138.864
168.796
ppm

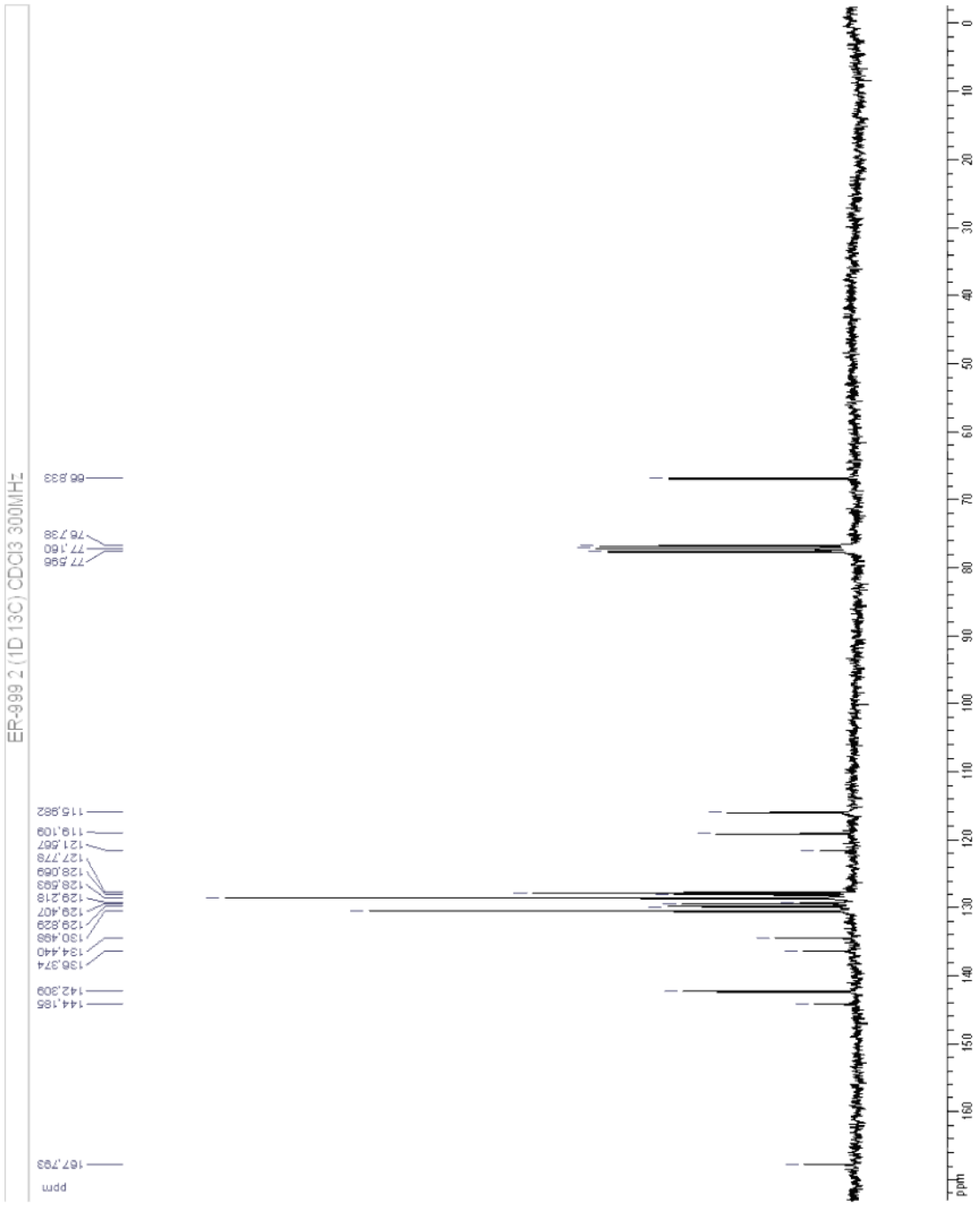


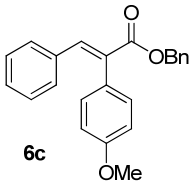
6b



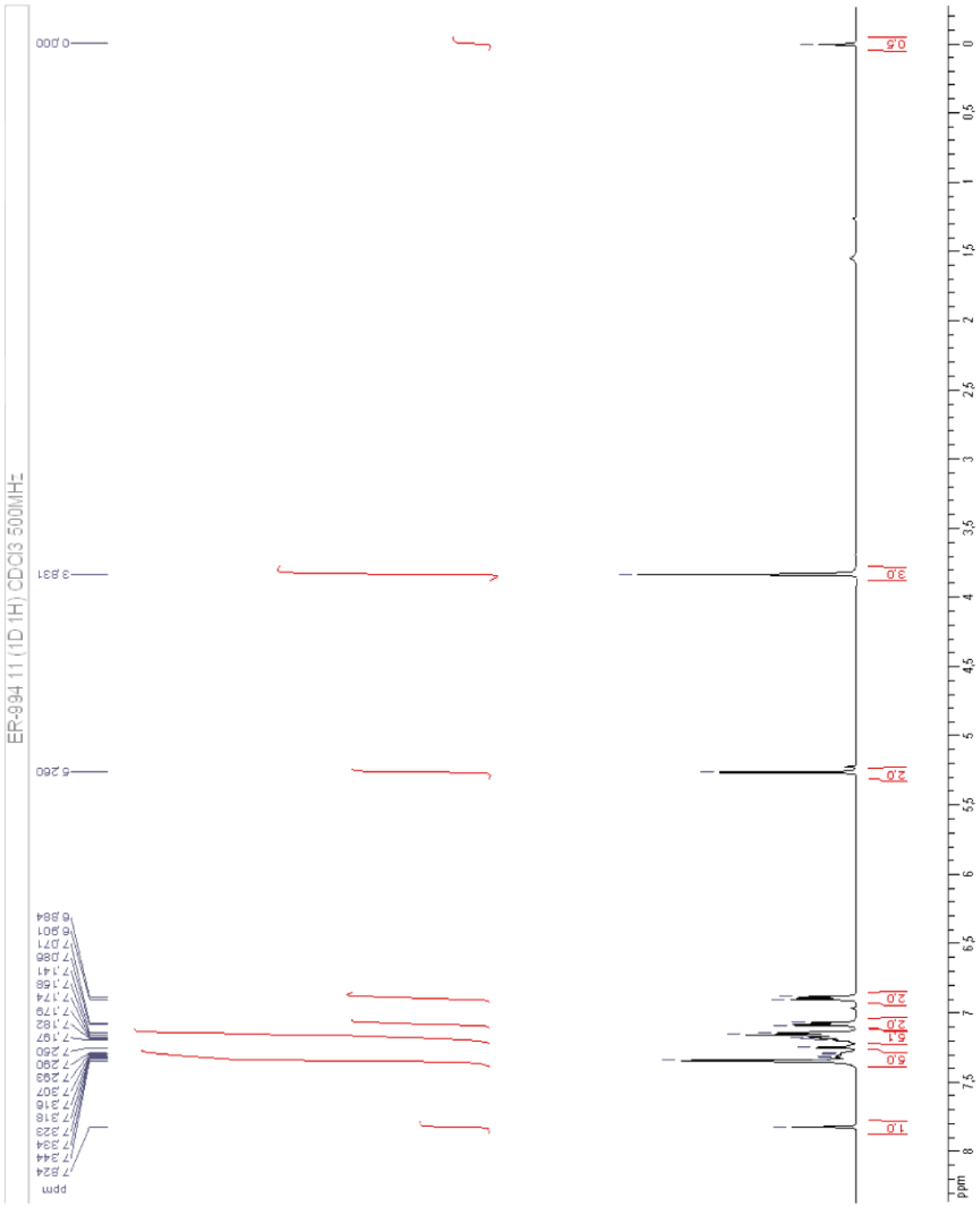

O
OBn
NH2

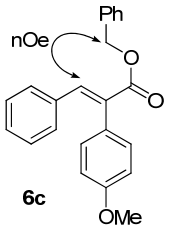
6b


ER-999 2 (1D 13C) CDCl3 300MHz
66.833
76.738
77.160
77.598
115.982
119.109
121.567
127.778
128.069
128.583
129.218
129.407
129.829
130.498
134.440
136.374
142.309
144.185
167.793
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
ppm

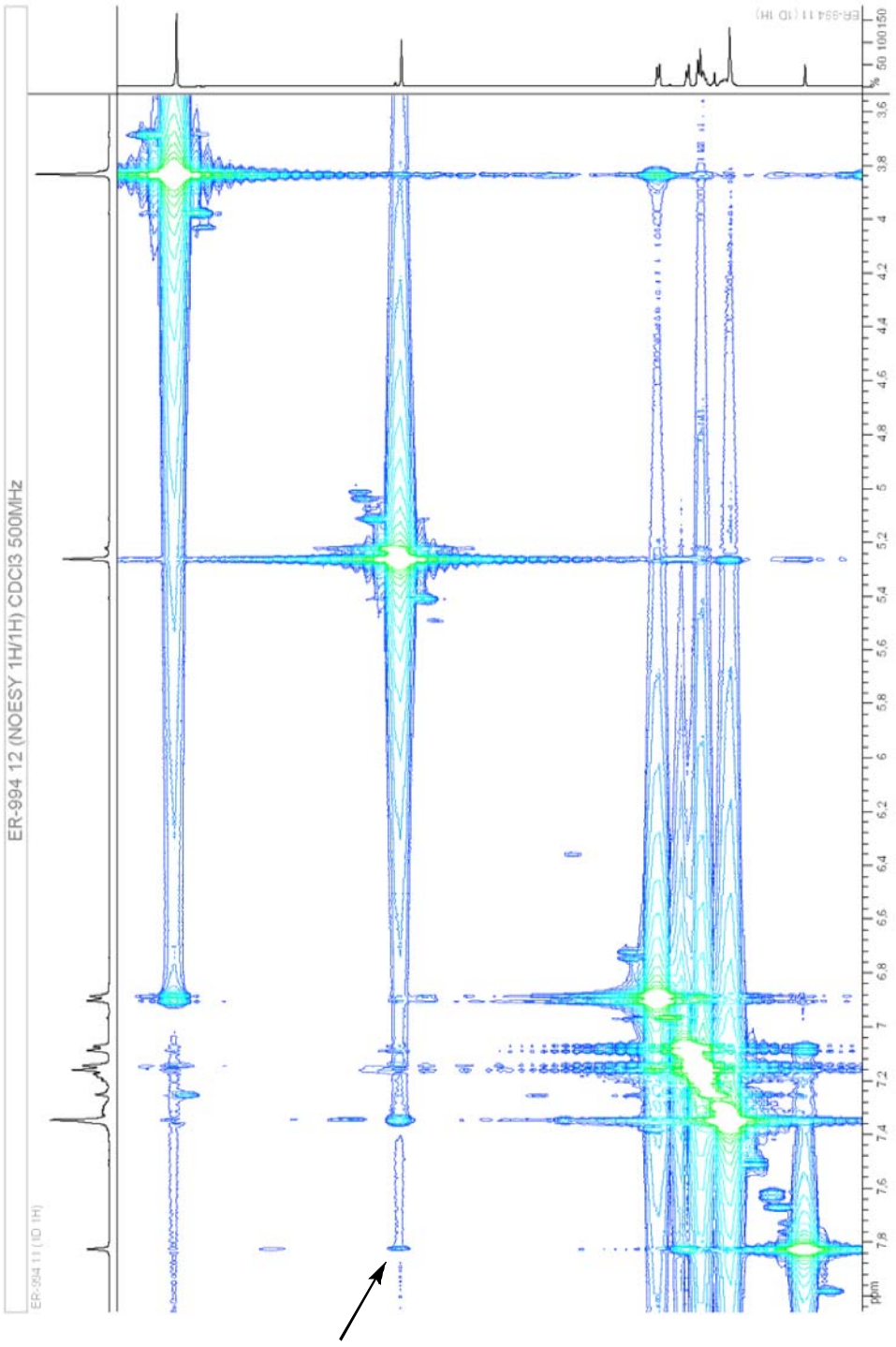


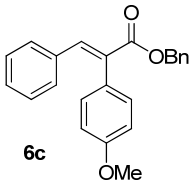
6c



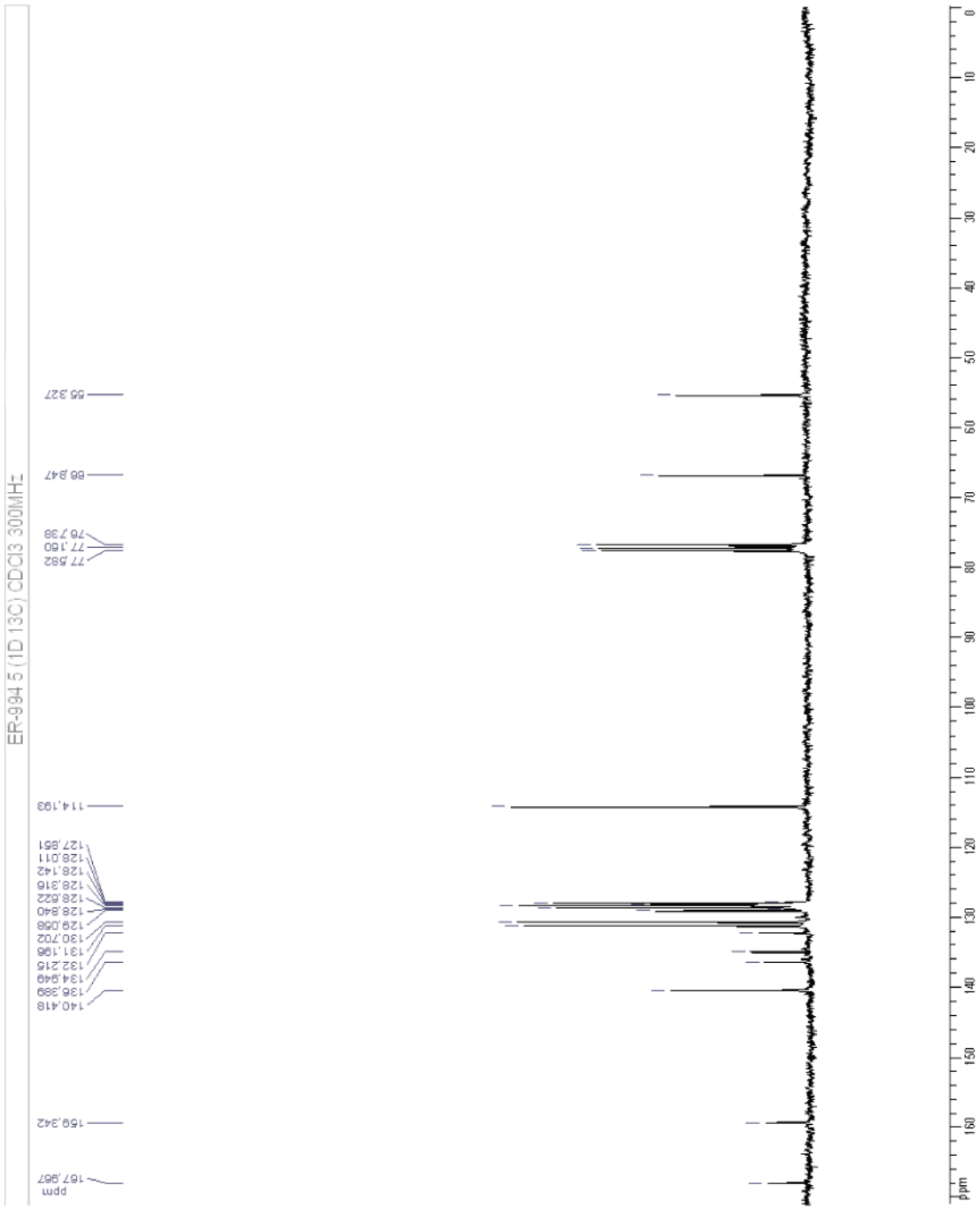


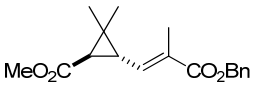
6c



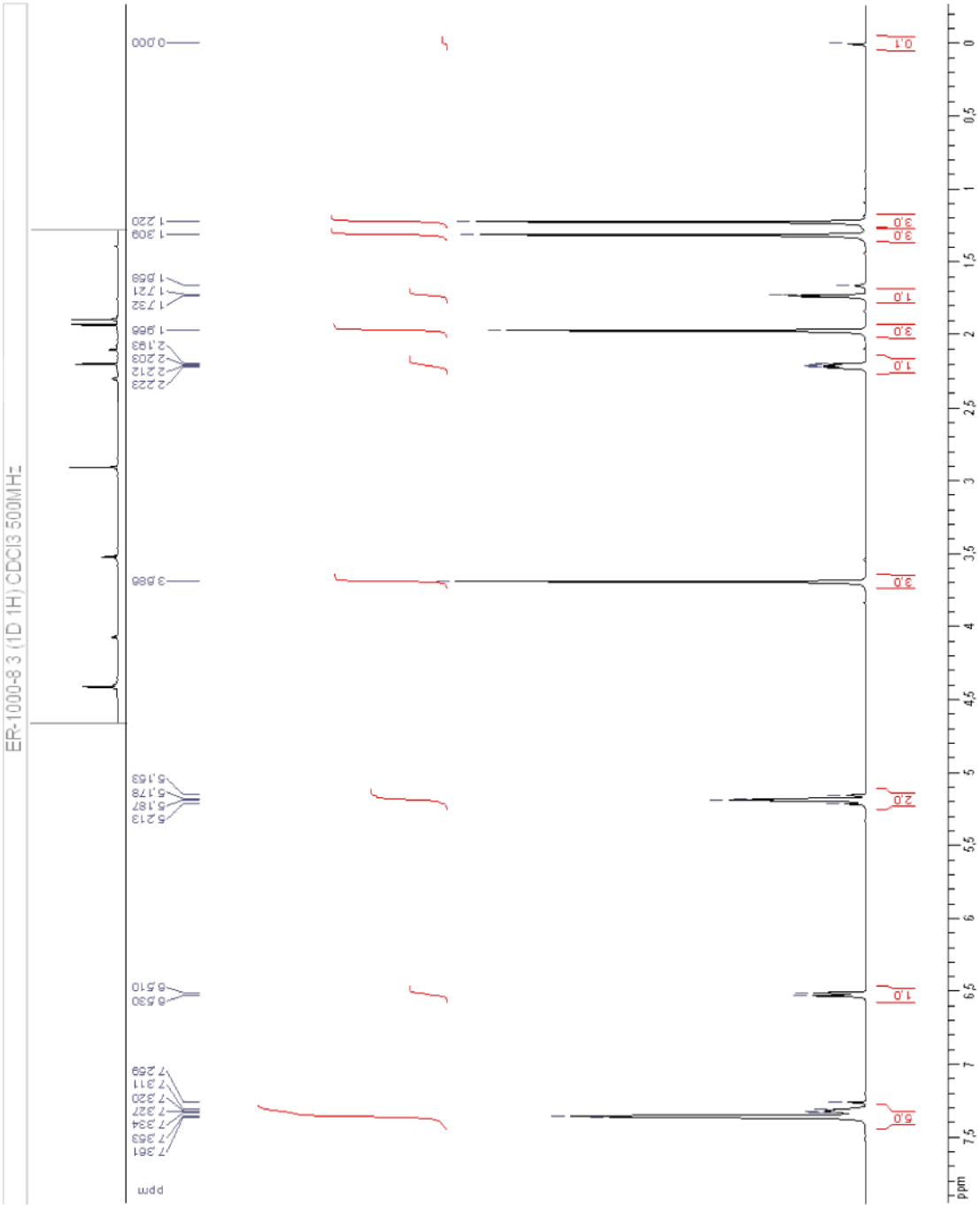

O
OBn
OMe

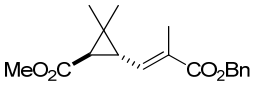
6c


ER-994 5 (1D 13C) CDCl3 300MHz
55.327
66.847
76.738
77.160
77.582
114.193
127.851
128.011
128.142
128.316
128.622
128.840
129.058
130.702
131.196
132.215
134.949
136.389
140.418
159.342
167.967
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
ppm

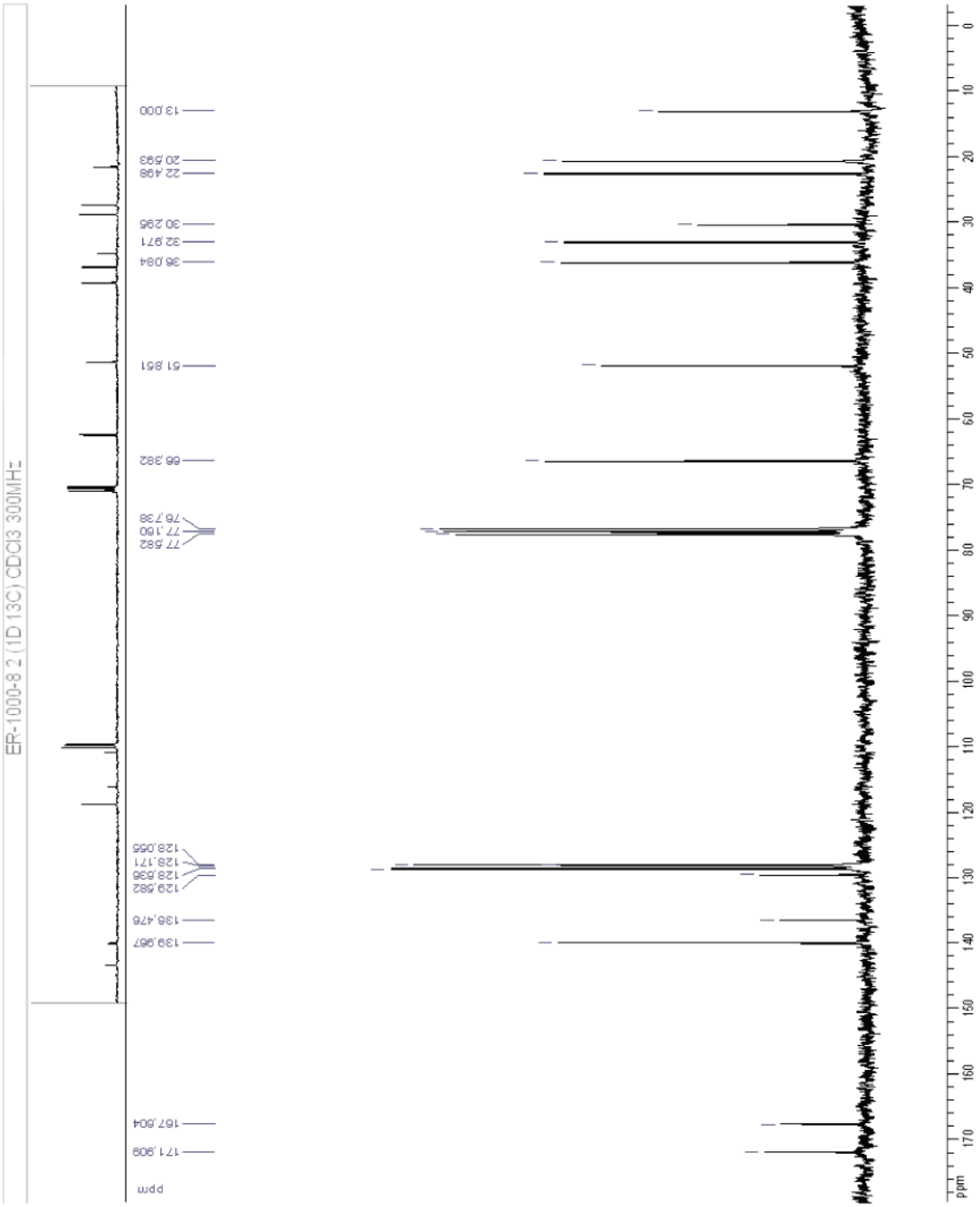

MeO2C
CO2Bn

6d


ER-1000-8 3 (1D 1H) CDCl3 500MHz
0.000
1.220
1.309
1.858
1.721
1.732
1.966
2.183
2.203
2.212
2.223
3.866
5.153
5.178
5.187
5.213
6.510
6.530
7.259
7.311
7.320
7.327
7.334
7.353
7.361
ppm


MeO2C
CO2Bn

6d


ER-1000-8 2 (1D 13C) CDCl3 300MHz
13.000
20.593
22.498
30.295
32.971
36.084
51.851
66.382
76.738
77.160
77.582
128.055
128.171
128.536
129.582
136.476
139.967
167.604
171.909
ppm