Reactivity of Substrates with Multiple Competitive Reactive Sites toward NBS under Neat Reaction Conditions Promoted by Visible Light

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Supporting Information

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Experimental

General information

Reagents and solvents were obtainted from commercial sources. NBS was recrystallized from a mixture of CH_2Cl_2/petroleum ether, solvents were used as received. All ketones were prepared by the method of the classical *Friedel-Crafts* acylation (Vogel's 1989). **14** was prepared according to the published procedure (Coan et al 1955).

Reactions were performed in closed flasks without inert atmosphere. The experimental procedure was the same for liquid and solid ketones: NBS was added to the substrate and the reaction mixture was stirred with a small stirring bar under solvent-free-reaction conditions (SFRC). Reaction mixtures with solid ketones turned into a molten state and the reaction proceeded as efficiently as the reactions with liquid substrates. An 8 W energy-saving lamp was used throughout all the experiments, and the average reaction temperature was 27 °C. The experiments in the dark were carried out at 27 °C. The progress of the reactions was monitored by thin-layer chromatography (TLC). Light source: Philips Genie 8 W energy-saving light bulb. Column chromatography (CC): silica gel 60 (63–200 mm, 70–230 mesh ASTM; Fluka); CH_2Cl_2/ petroleum ether (1:3). Preparative thin-layer chromatography (TLC): Merck-60-F_{254} plates; mixtures of light petroleum ether (b.p. 40–60 °C) and CH_2Cl_2. NMR spectra: Bruker DPX 300 (300 MHz) and Bruker AVANCE III (500 MHz) instruments; in $CDCl_3$; δ in ppm relative to TMS as internal standard for ^{1}H NMR and to the central line of $CDCl_3$ (δ = 77.00 ppm) for ^{13}C NMR, J in Hz. IR spectra: Bruker Alpha FT-IR spectrometer; in cm^{-1}. HRMS: Agilent 6224 Accurate Mass TOF LC/MS system spectrometer; electrospray ionization; in m/z. Elemental analysis: Perkin Elmer CHNS/O Analyzer 2400 Series II elemental analyzer. Melting points: Büchi 535 melting point apparatus; uncorrected.

General Procedure for Photoinduced Reactions with NBS under SFRC

To a ketone (0.3 mmol), NBS (0.33 or 0.66 mmol, 20 or 39 mg) was added and the resulted reaction mixture was stirred under illumination with an 8 W energy-saving light bulb for 19-29h. At the end of the reaction, conversions and the product distribution were determined by ^{1}H NMR spectroscopy of the crude reaction mixture. Pure products were obtained after separation either by CC or preparative TLC and were analyzed by ^{1}H NMR, ^{13}C NMR, IR, HRMS and melting point when solid. Copies of ^{1}H and ^{13}C NMR spectra of products are provided. Spectroscopic data of all known compounds were in accordance with literature data.

Characterization of the known products

2-Bromo-1-(4-methylphenyl)ethanone **2a** (Song et al 2010)

1a (0.040 g, 0.3 mmol), NBS (0.059 g, 0.33 mmol). Preparative TLC (R_f = 0.55, CH_2Cl_2/petroleum ether 1:3). Colorless solid (0.008 g, 13%). M.p. 51–52 °C (lit. 51–53 °C). IR (neat): ν 2951, 1690, 1607, 1572, 1390, 1283, 1193, 1178, 994, 798, 683 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.43 (s, 3H), 4.43 (s, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 30.9, 129.0, 129.5, 131.5, 145.0, 190.9. HRMS (ESI-TOF, *m/z*): found 212.9908 ([*M* + H]$^+$, $C_9H_{10}BrO^+$; calc. 212.9910).

2-Bromo-1-(4-ethylphenyl)ethanone **2b** (Jacobs et al 1915)

1b (0.044 g, 0.3 mmol), NBS (0.059 g, 0.33 mmol). Preparative TLC (R_f = 0.61, CH_2Cl_2/petroleum ether 1:3). Brownish solid (0.010 g, 15%). M.p. 33–35 °C (lit. 33–34 °C). IR (neat): ν 2962, 1691, 1604, 1570, 1413, 1388, 1282, 1210, 1193, 1180, 1115, 1052, 989, 818, 681 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.27 (t, *J* = 7.6 Hz, 3H), 2.73 (q, *J* = 7.6 Hz, 2H), 4.43 (s, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.0, 29.0, 30.9, 128.4, 129.2, 131.7, 151.1, 190.9. HRMS (ESI-TOF, *m/z*): found 227.0066 ([*M* + H]$^+$, $C_{10}H_{12}BrO^+$; calc. 227.0066).

2-Bromo-1-(4-(cyclohexyl)phenyl)ethanone **2d** (Roman et al 2010)

1d (0.061 g, 0.3 mmol), NBS (0.059 g, 0.33 mmol). Column chromatography on silica gel (R_f = 0.61, CH_2Cl_2/petroleum ether 1:3 → 2:1). Brownish solid (0.030 g, 36%). M.p. 35–37 °C (lit. 44–45 °C). IR (neat): ν 2922, 2851, 1671, 1602, 1567, 1455, 1426, 1311, 1280, 1186, 1110, 1021, 1006, 853, 835, 764, 708, 608 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.20–1.33 (m, 1H), 1.35–1.49 (m, 4H), 1.74–1.80 (m, 1H), 1.82–1.93 (m, 4H), 2.53–2.62 (m, 1H), 4.44 (s, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.0, 26.7, 31.0, 34.0, 44.8, 127.4, 129.2, 131.7, 154.8, 190.9. HRMS (ESI-TOF, *m/z*): found 281.0533 ([*M* + H]$^+$, $C_{14}H_{18}BrO^+$; calc. 281.0536).

2-Bromo-1-(4-(bromomethyl)phenyl)ethanone **3a** (Salama et al 2011)

1a (0.040 g, 0.3 mmol), NBS (0.059 g, 0.33 mmol). Preparative TLC (R_f = 0.42, CH_2Cl_2/petroleum ether 1:3). Colorless solid (0.002 g, 4%). M.p. 107–109 °C. IR (neat): ν 2923, 1694, 1603, 1571, 1414, 1384, 1275, 1227, 1190, 1177, 987, 833, 817, 732, 685, 635 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 4.43 (s, 2H), 4.50 (s, 2H), 7.49–7.55 (m, 2H), 7.94–8.00 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 30.6, 31.8, 129.5, 129.5, 133.7, 143.7, 190.6. HRMS (ESI-TOF, *m/z*): found 290.9013 ([*M* + H]$^+$, $C_9H_9Br_2O^+$; calc. 290.9015).

2,2-Dibromo-1-(4-methylphenyl)ethanone **4a** (Terent'ev et al 2006)

1a (0.040 g, 0.3 mmol), NBS (0.059 g, 0.33 mmol). Column chromatography on silica gel (R_f = 0.61, CH_2Cl_2/petroleum ether 1:3 → 2:1). Colorless solid (0.013 g, 26%). M.p. 94–96 °C (lit. 97–98 °C). IR (neat): ν 3028, 1683, 1602, 1570, 1273, 1224, 1194, 1139, 977, 833, 750, 697 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.45 (s, 3H), 6.69 (s, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.98 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.8, 39.8, 128.2, 129.6, 129.8, 145.7, 185.6. HRMS (ESI-TOF, *m/z*): found 290.9013 ([*M* + H]$^+$, $C_9H_9Br_2O^+$; calc. 290.9015).

122.8, 127.6, 130.1, 132.2, 162.9, 184.9. HRMS (ESI-TOF, *m/z*): found 320.9117 ([*M* + H]$^+$, $C_{10}H_{11}Br_2O_2^+$; calc. 320.9120).

2-Bromo-1-(4-methylphenyl)propan-1-one **6a** (Santali et al 2011)

5a (0.044 g, 0.3 mmol), NBS (0.059 g, 0.33 mmol). Preparative TLC (R_f = 0.64, CH_2Cl_2/petroleum ether 1:3). Colorless solid (0.021 g, 30%). M.p. 77–78.5 °C (lit. 76–77 °C). IR (neat): ν 2923, 1673, 1604, 1440, 1347, 1240, 1213, 1163, 991, 945, 833, 746 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.90 (d, *J* = 6.6 Hz, 3H), 2.43 (s, 3H), 5.28 (q, *J* = 6.6 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.2, 21.7, 41.5, 129.0, 129.4, 131.5, 144.7, 193.0. HRMS (ESI-TOF, *m/z*): found 227.0067 ([*M* + H]$^+$, $C_{10}H_{12}BrO^+$; calc. 227.0066).

2-Bromo-1-(4-methoxyphenyl)propan-1-one **6b** (Ghosh et al 2003)

5b (0.164 g, 1.0 mmol), NBS (0.267 g, 1.5 mmol). Column chromatography on silica gel (R_f = 0.29, CH_2Cl_2/hexane 1:2 → 2:1). Colorless solid (0.164 g, 68%). M.p. 65–67 °C (lit. 66 °C). IR (neat): ν 2975, 1665, 1598, 1570, 1508, 1421, 1352, 1243, 1164, 1023, 947, 843, 816, 762, 603 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.89 (d, *J* = 6.6 Hz, 3H), 3.88 (s, 3H), 5.26 (q, *J* = 6.6 Hz, 1H), 6.92–6.99 (m, 2H), 7.97– 8.05 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.3, 41.4, 55.5, 114.0, 126.9, 131.3, 163.9, 192.0. HRMS (ESI-TOF, *m/z*): 243.0008 ([*M* + H]$^+$, $C_{10}H_{12}BrO_2^+$; calc. 243.0015). Anal. calc. for $C_{10}H_{11}BrO_2$: C 49.41, H 4.56; found: C 49.21, H 4.41.

2-Bromo-1-(4-methoxyphenyl)-2-methylpropan-1-one **9c** (Maier et al 1985)

8c (0.178 g, 1.0 mmol), NBS (0.267 g, 1.5 mmol). Column chromatography on silica gel (R_f = 0.39, CH_2Cl_2/hexane 1:1 → 2:1). Pale yellowish solid (0.201 g, 78%). M.p. 38–40 °C (lit. 33 °C). IR (neat): ν 2931, 1666, 1597, 1572, 1508, 1458, 1309, 1252, 1157, 1104, 1029, 978, 886, 839, 762 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.04 (s, 6H), 3.87 (s, 3H), 6.89–6.95 (m, 2H), 8.18–8.25 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 31.9, 55.4, 60.5, 113.3, 126.9, 132.8, 162.9, 194.9. HRMS (ESI-TOF, *m/z*): found 257.0178 ([*M* + H]$^+$, $C_{11}H_{14}BrO_2^+$; calc. 257.0172).

$C_{11}H_{13}Br_2O^+$; calc. 318.9328).

2-Bromo-1-(4-methylphenyl)-2-phenylethan-1-one **12a** (Ali et al 2007)

11a (0.063 g, 0.3 mmol), NBS (0.059 g, 0.33 mmol). Column chromatography on silica gel (R_f = 0.65, CH_2Cl_2/petroleum ether 1:3 → 2:1). Colorless solid (0.031 g, 35%). M.p. 82–84 °C (lit. 86–87 °C). IR (neat): ν 3011, 1675, 1602, 1493, 1455, 1282, 1222, 1197, 1179, 1157, 994, 839, 765, 729, 697, 671, 632 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.39 (s, 3H), 6.37 (s, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.29–7.39 (m, 3H), 7.50–7.54 (m, 2H), 7.89 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.7, 51.1, 129.0, 129.0, 129.1, 129.2, 129.5, 131.6, 136.1, 144.7, 190.6. HRMS (ESI-TOF, *m/z*): found 289.0219 ($[M + H]^+$, $C_{15}H_{14}BrO^+$; calc. 289.0223).

2-Bromo-2-phenylacetonitrile **18** (Donslund et al 2019)

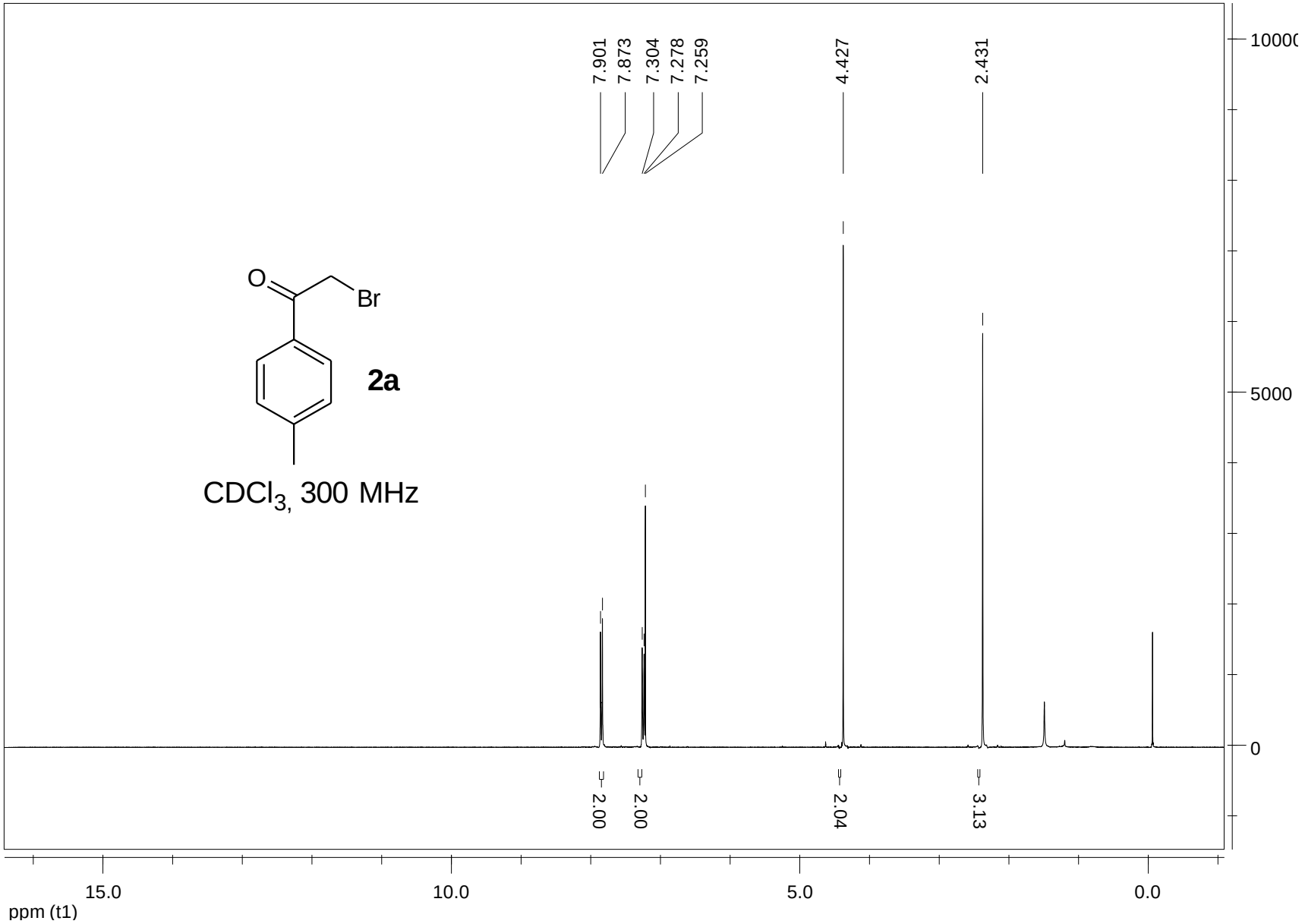
16 (0.048 g, 0.3 mmol), NBS (0.059 g, 0.33 mmol). Preparative TLC (R_f = 0.35, CH_2Cl_2/petroleum ether 1:3) Yellowish oil (0.031 g, 53%). IR (neat): 2971, 1496, 1455, 1188, 1138, 971, 817, 763, 690, 653, 621 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.49 (s, 1H), 7.39–7.48 (m, 3H), 7.52–7.60 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.4, 116.2, 127.8, 129.5, 130.3, 133.5.

2,4-Dibromo-1-methoxynaphthalene **20** (Lash et al 2011)

19a (0.200 g, 1.0 mmol), NBS (0.356 g, 2.0 mmol). Column chromatography on silica gel (R_f = 0.65, CH_2Cl_2/petroleum ether 1:3 → 2:1). Colorless solid (0.249 g, 79%). M.p. 49–52 °C (lit. 51–52 °C). IR (neat): ν 3062, 2934, 1572, 1448, 1363, 1248, 1212, 1068, 981, 908, 833, 751, 711, 679, 651 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.00 (s, 3H), 7.54–7.67 (m, 2H), 7.91 (s, 1H), 8.09–8.22 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 61.6, 112.1, 118.0, 122.5, 127.5, 127.6, 127.8, 129.8, 132.2, 133.0, 153.1. Anal. calc. for $C_{11}H_8Br_2O$: C 41.81, H 2.55; found: C 41.78, H 2.50.

2-Bromo-4,5-dimethoxytoluene **24** (Fukuda et al 2007)

23 (0.058 g, 0.3 mmol), NBS (0.059 g, 0.33 mmol). Column chromatography on silica gel (R_f = 0.51, CH_2Cl_2/petroleum ether 1:3 → 2:1). Colorless solid (0.042 g, 61%). M.p. 30–32 °C. IR (neat): ν 2933, 1503, 1437, 1371, 1327, 1253, 1211, 1161, 1032, 953, 848, 792 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 3H), 3.84 (s, 3H), 3.85 (s, 3H), 6.73 (s, 1H), 7.00 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.3, 56.0, 56.2, 113.6, 114.4, 115.4, 129.6, 147.7, 148.2. HRMS (ESI-TOF, *m/z*): found 231.0014 ($[M + H]^+$, $C_9H_{12}BrO_2^+$; calc. 231.0015).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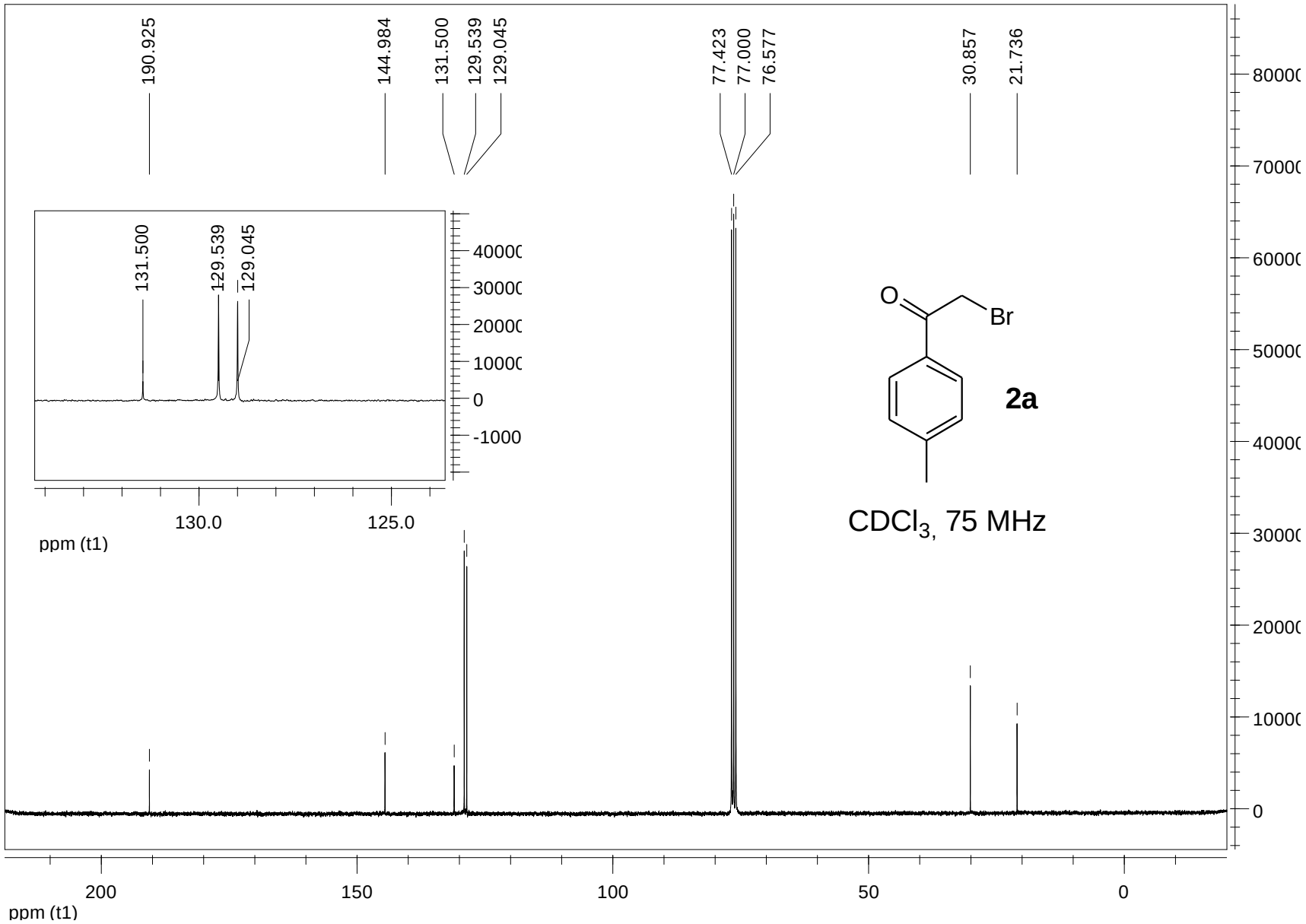
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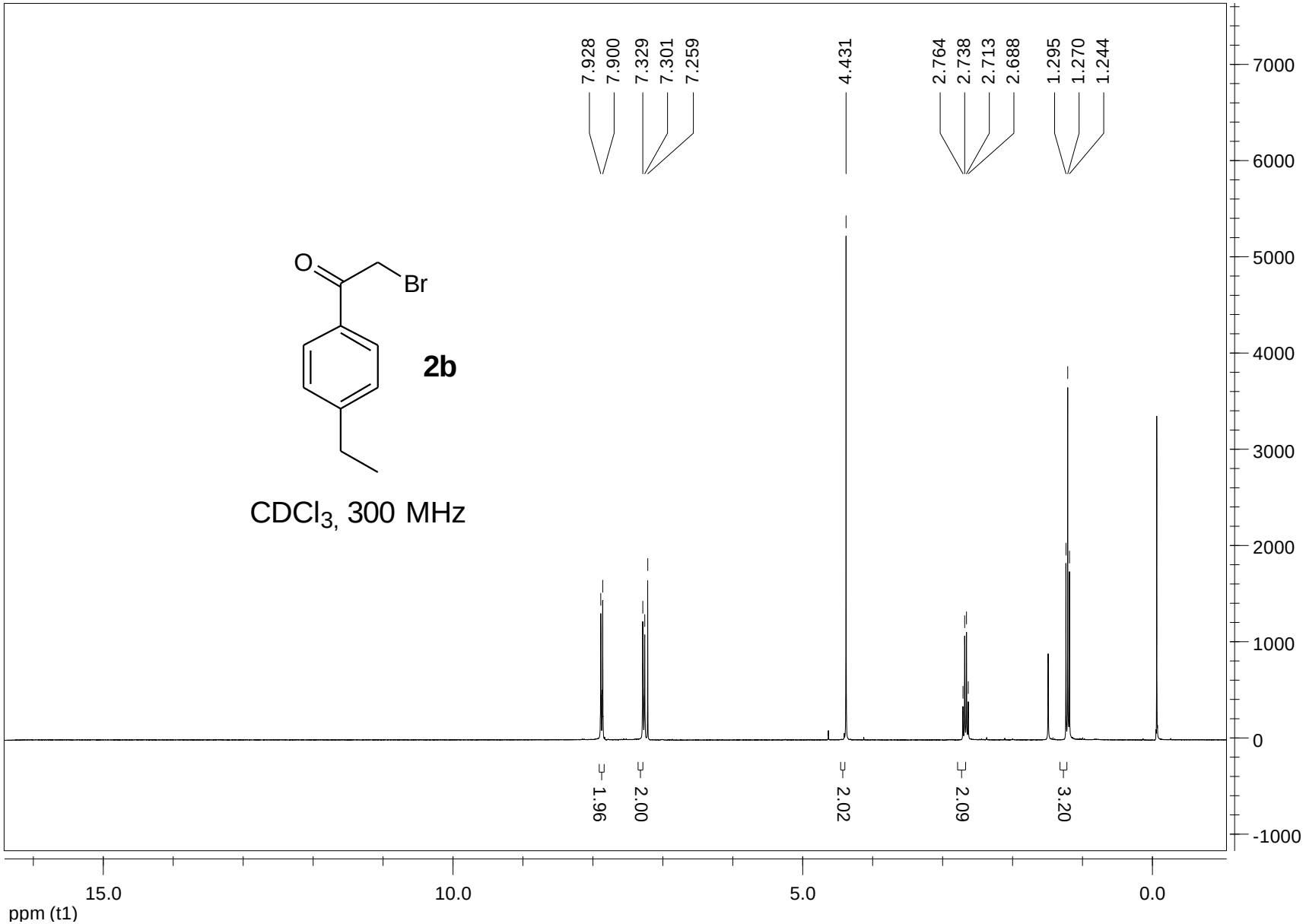
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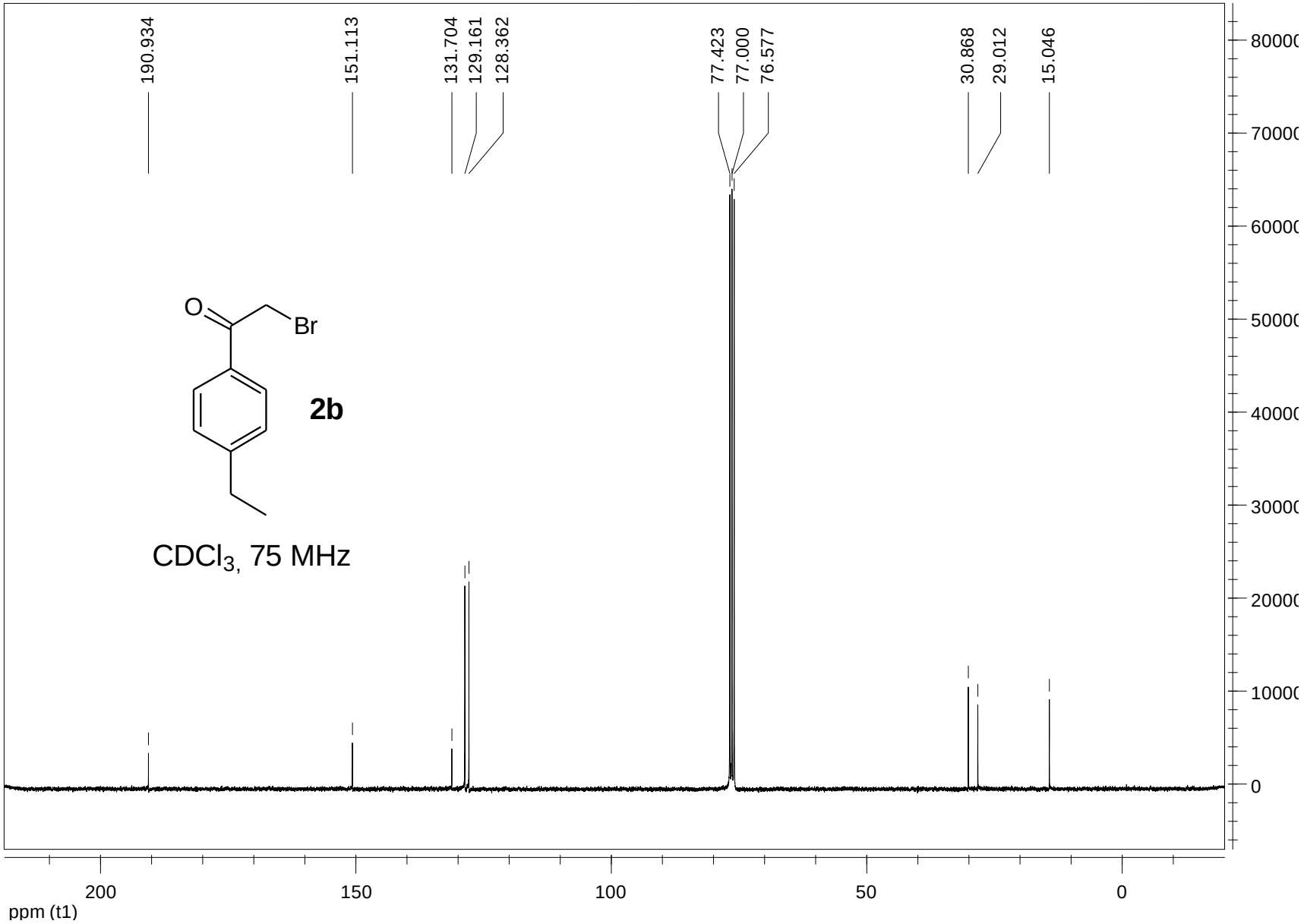
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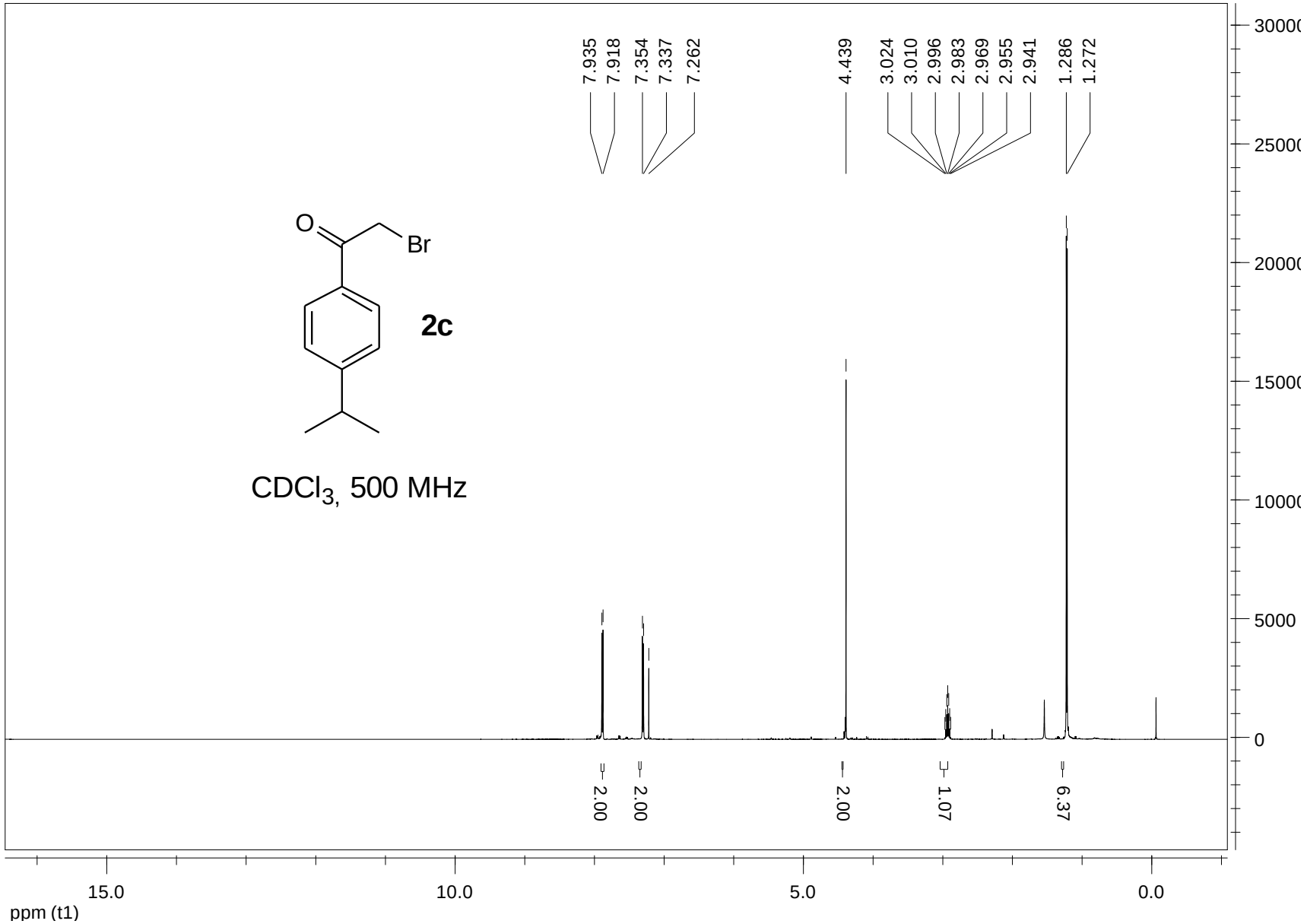
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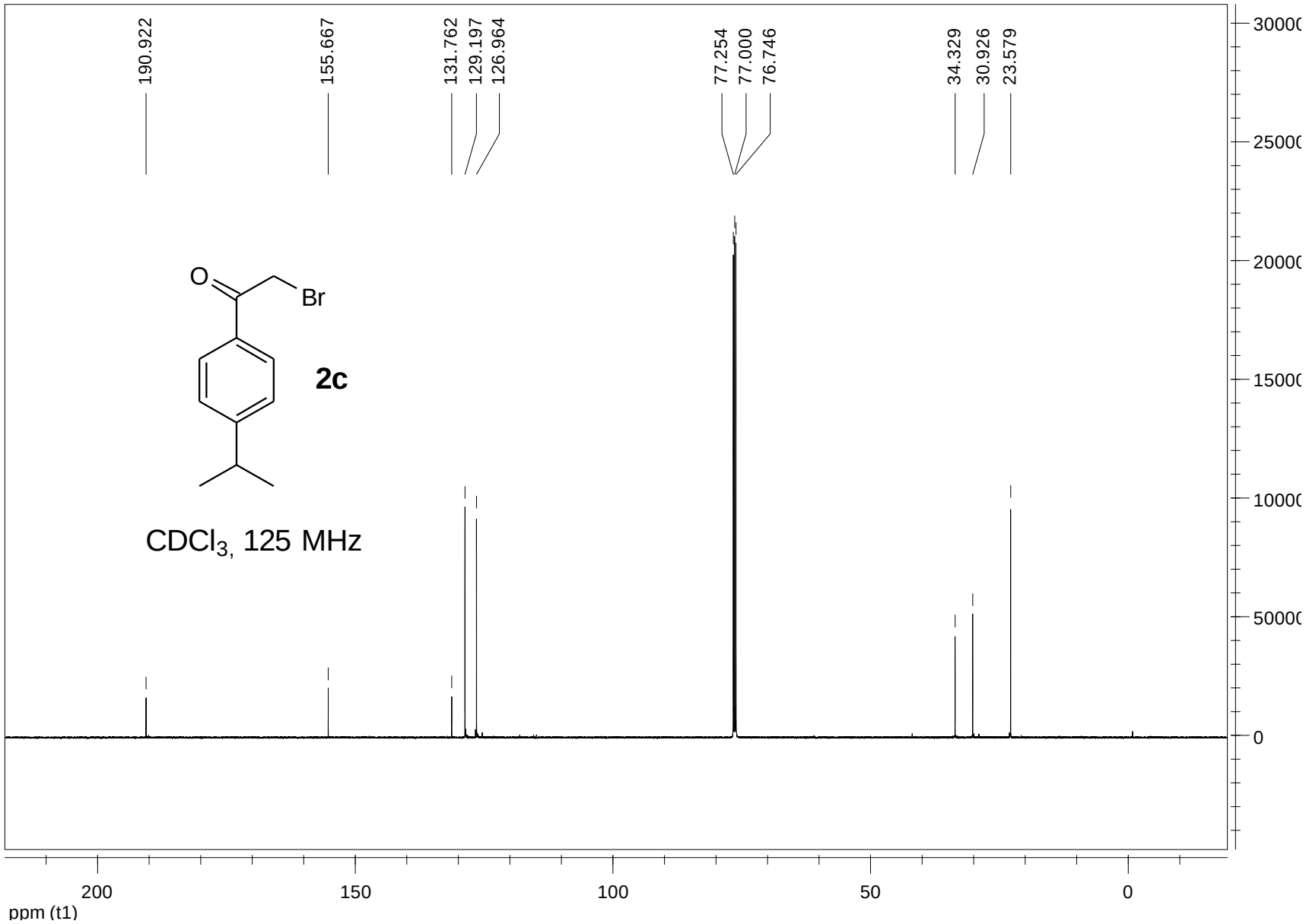
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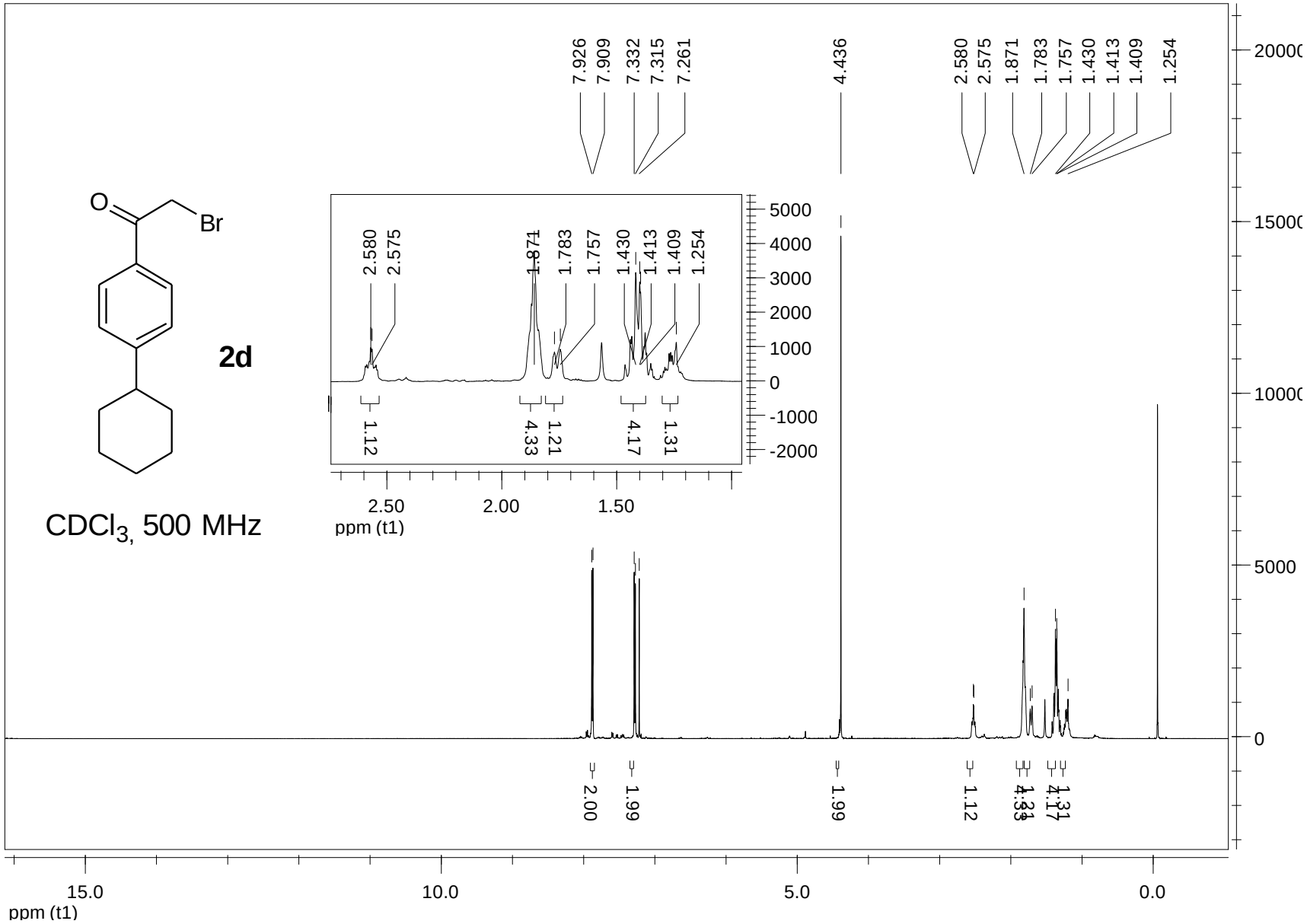
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1.254
1.12
4.33
1.21
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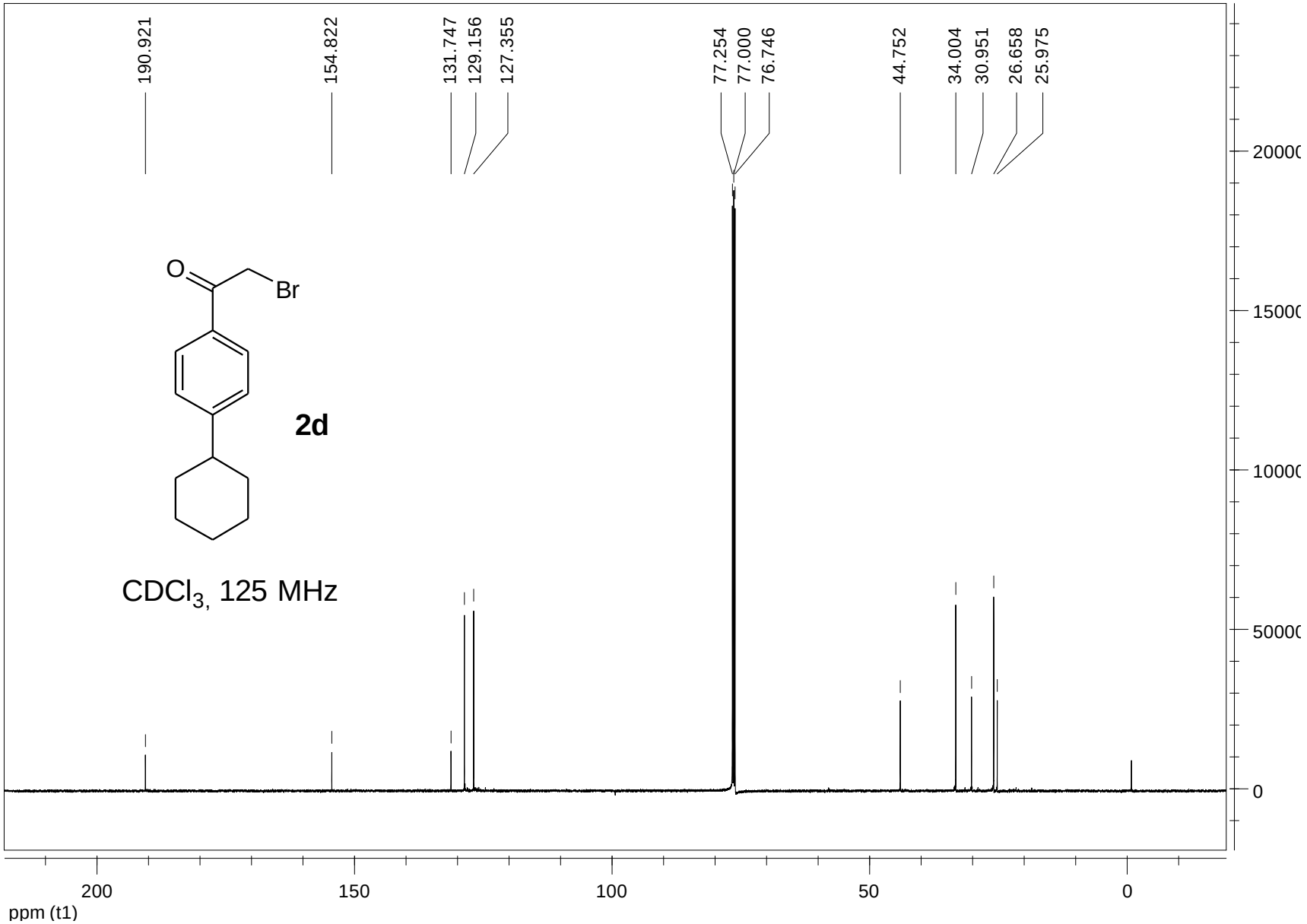
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50
0
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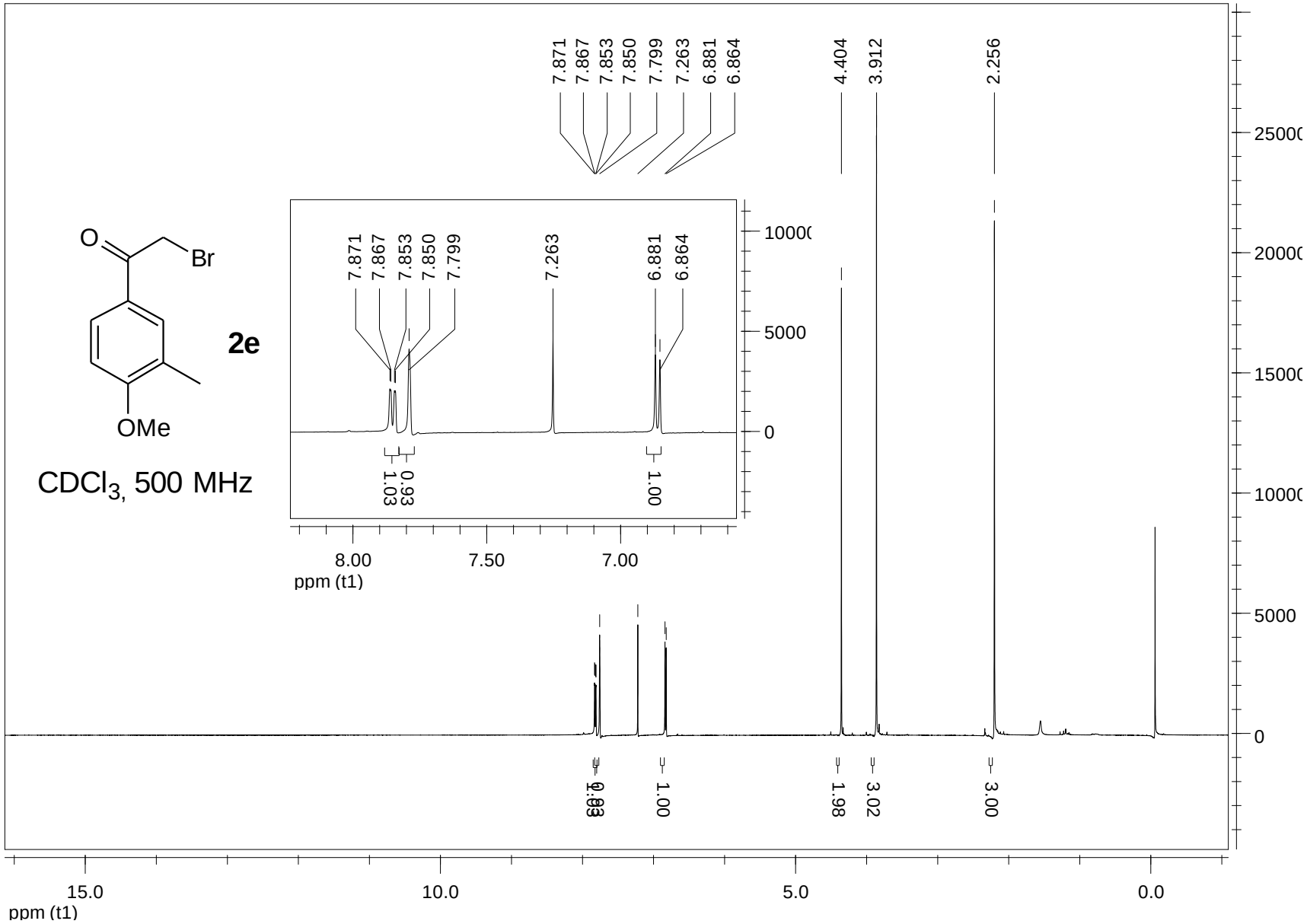
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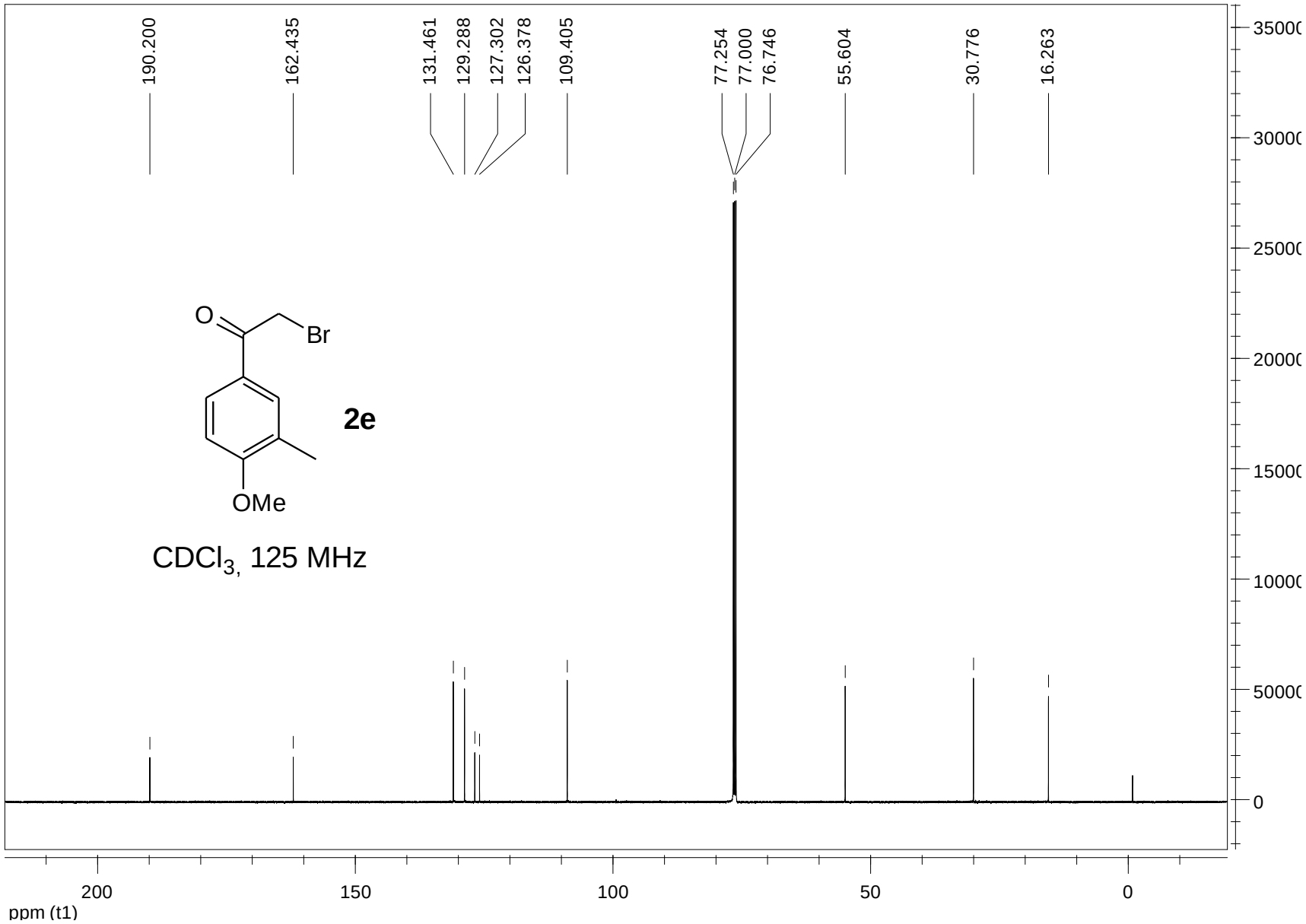
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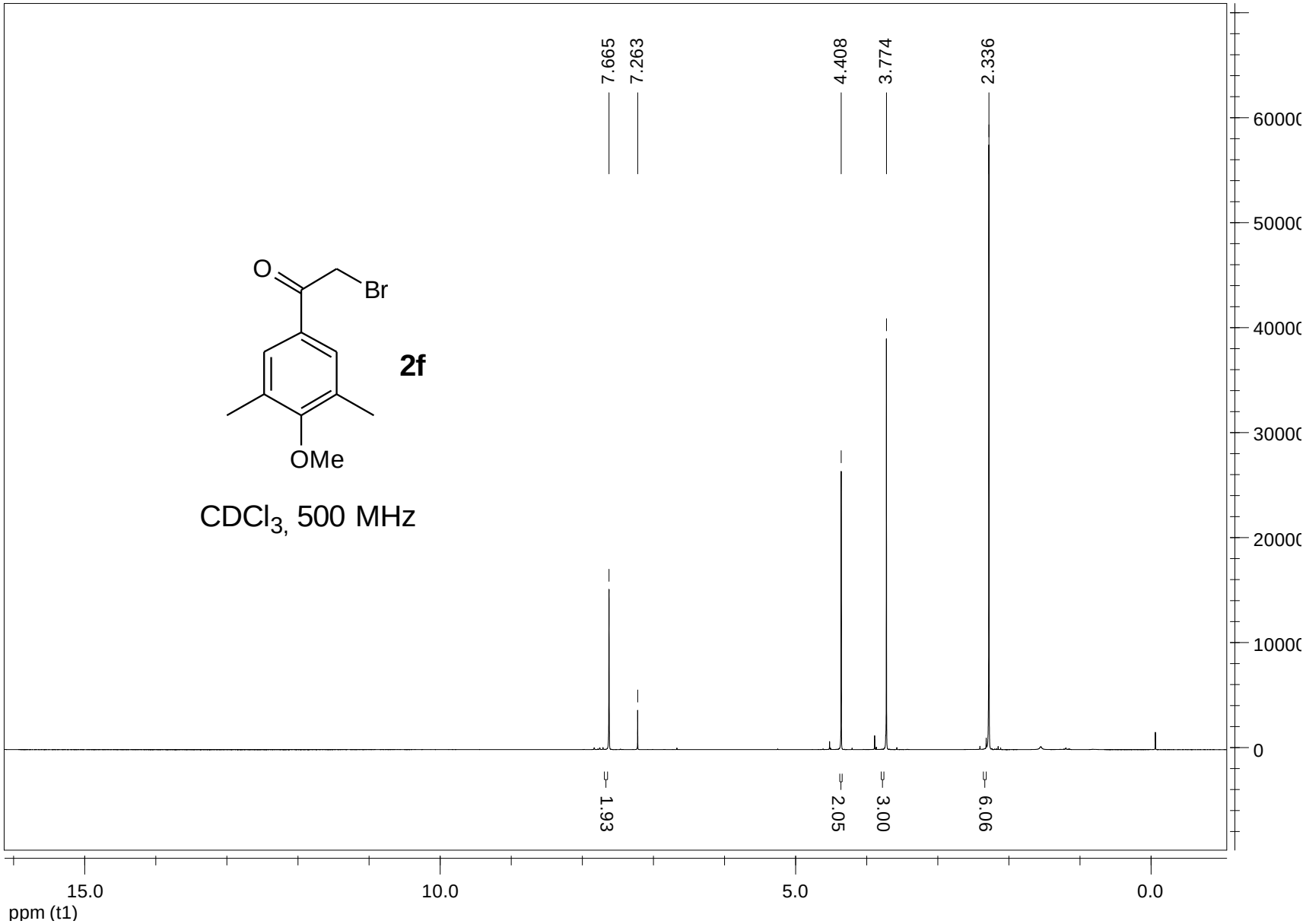
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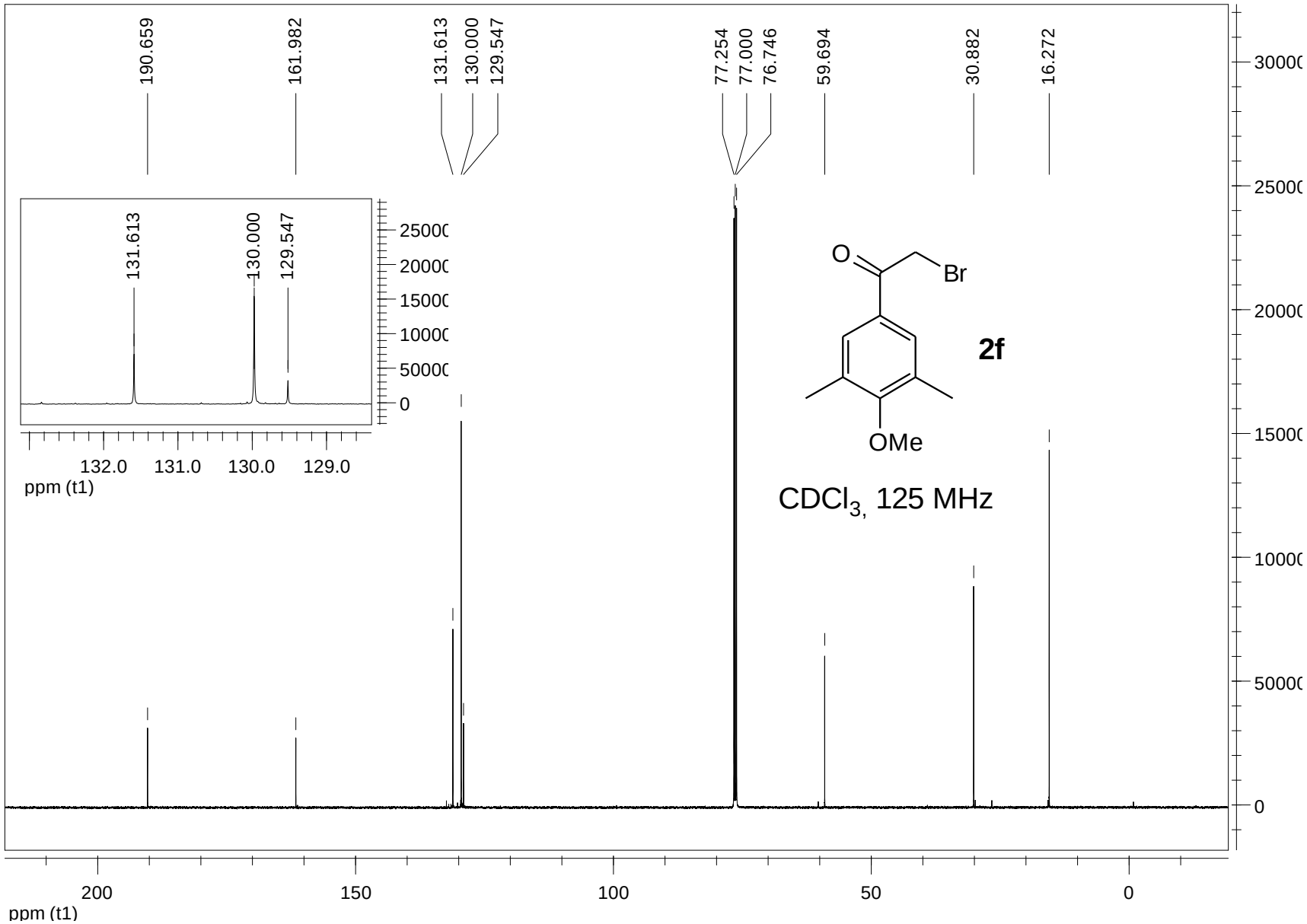
ppm (t1)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132.0
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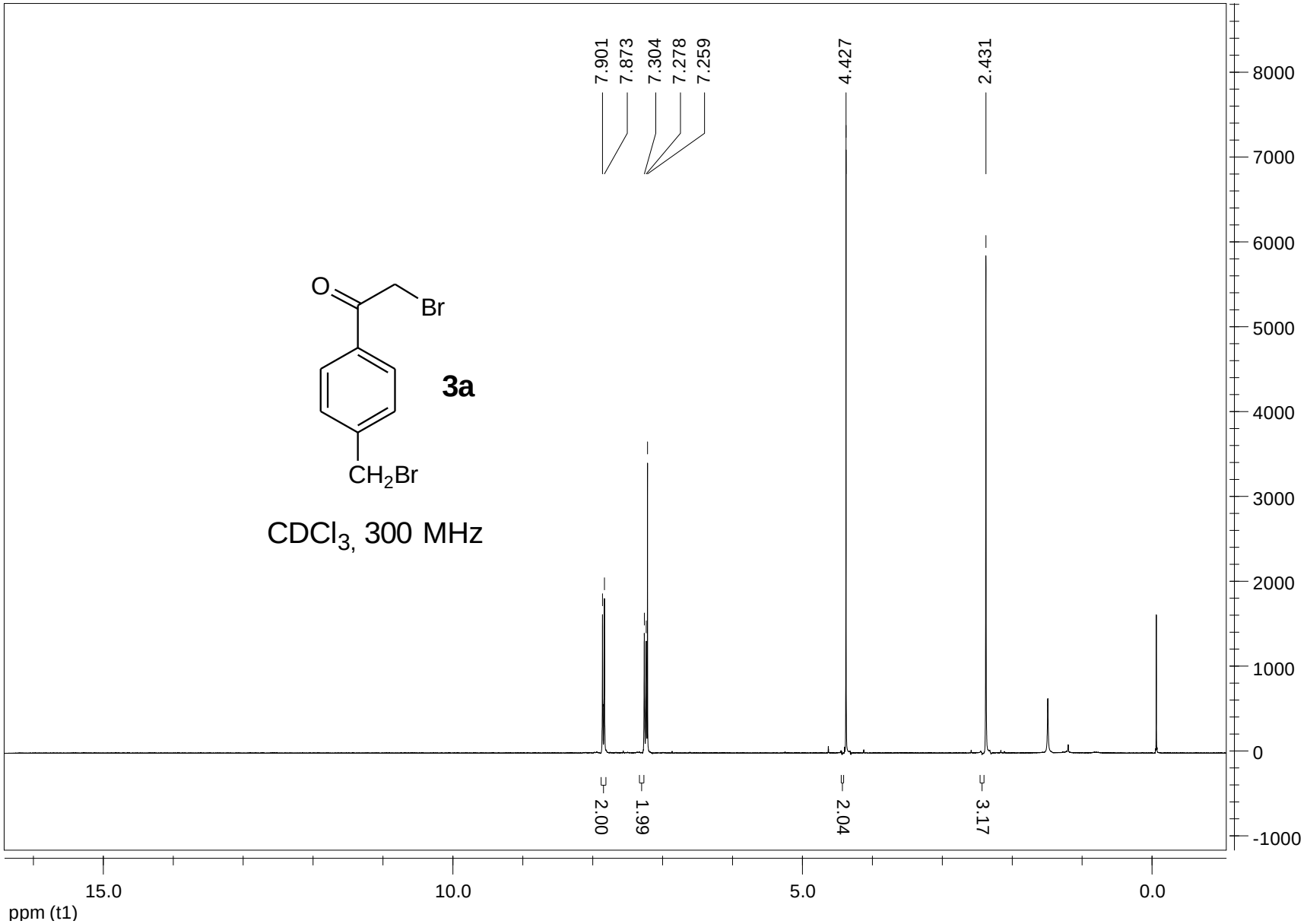
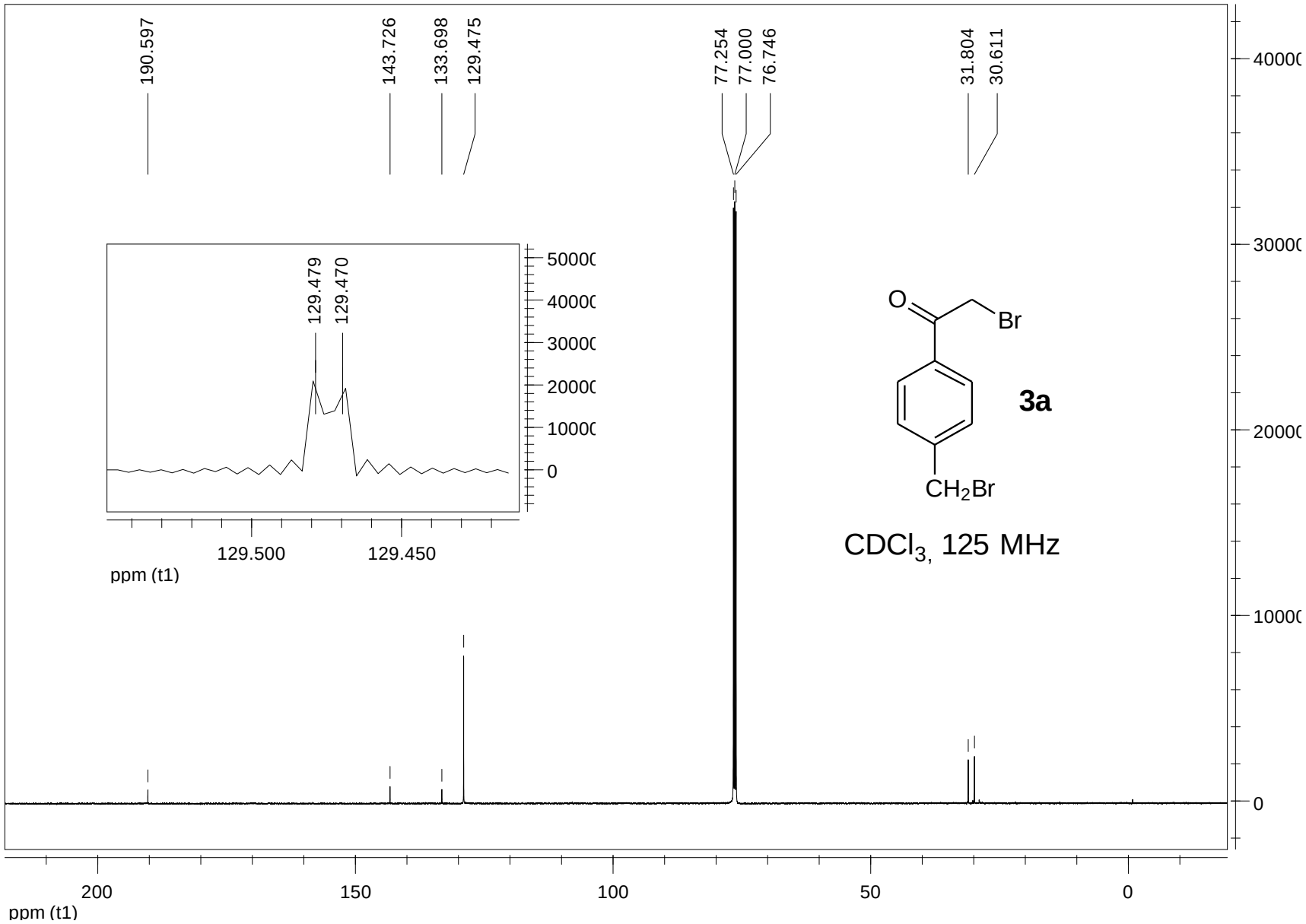
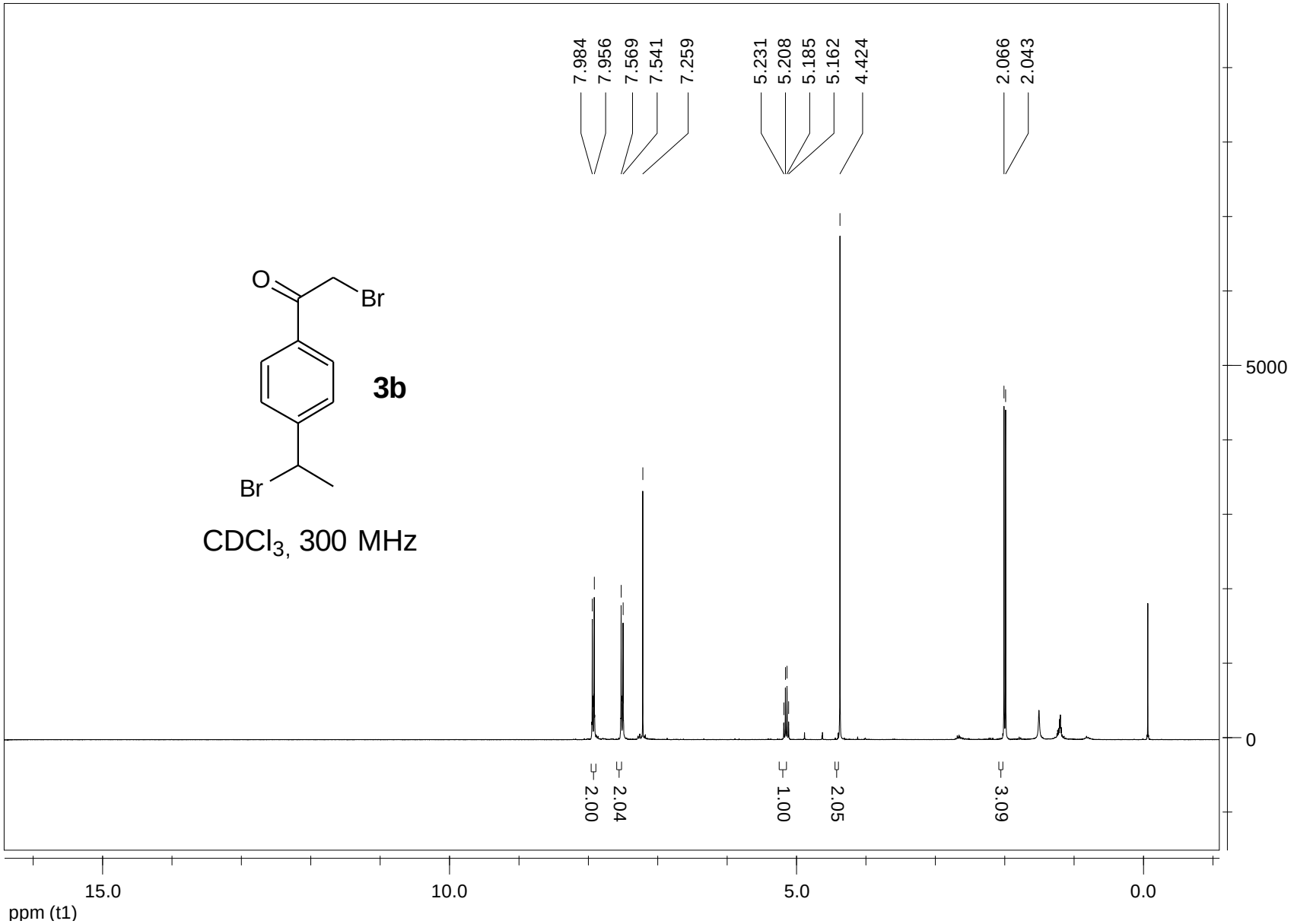
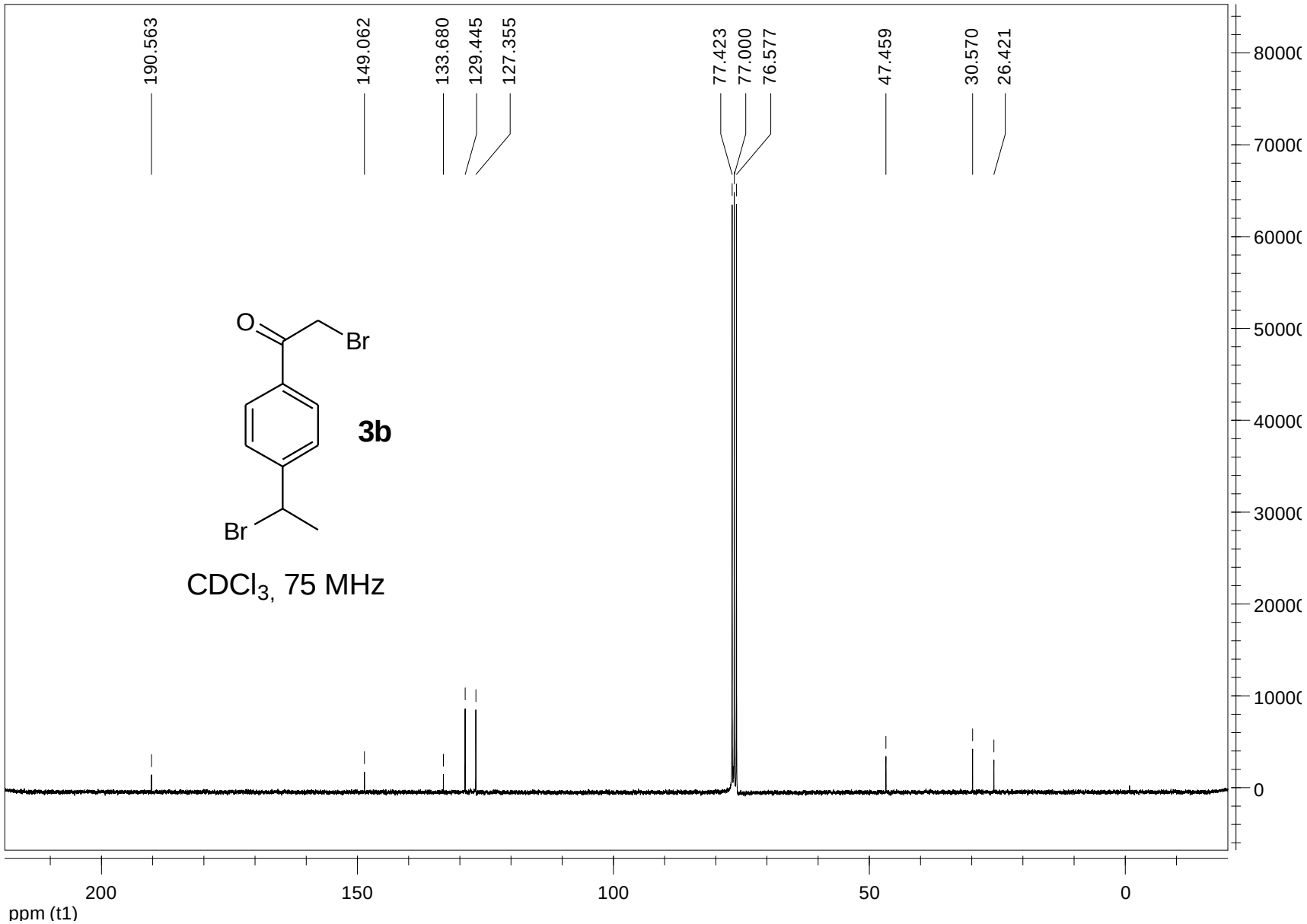
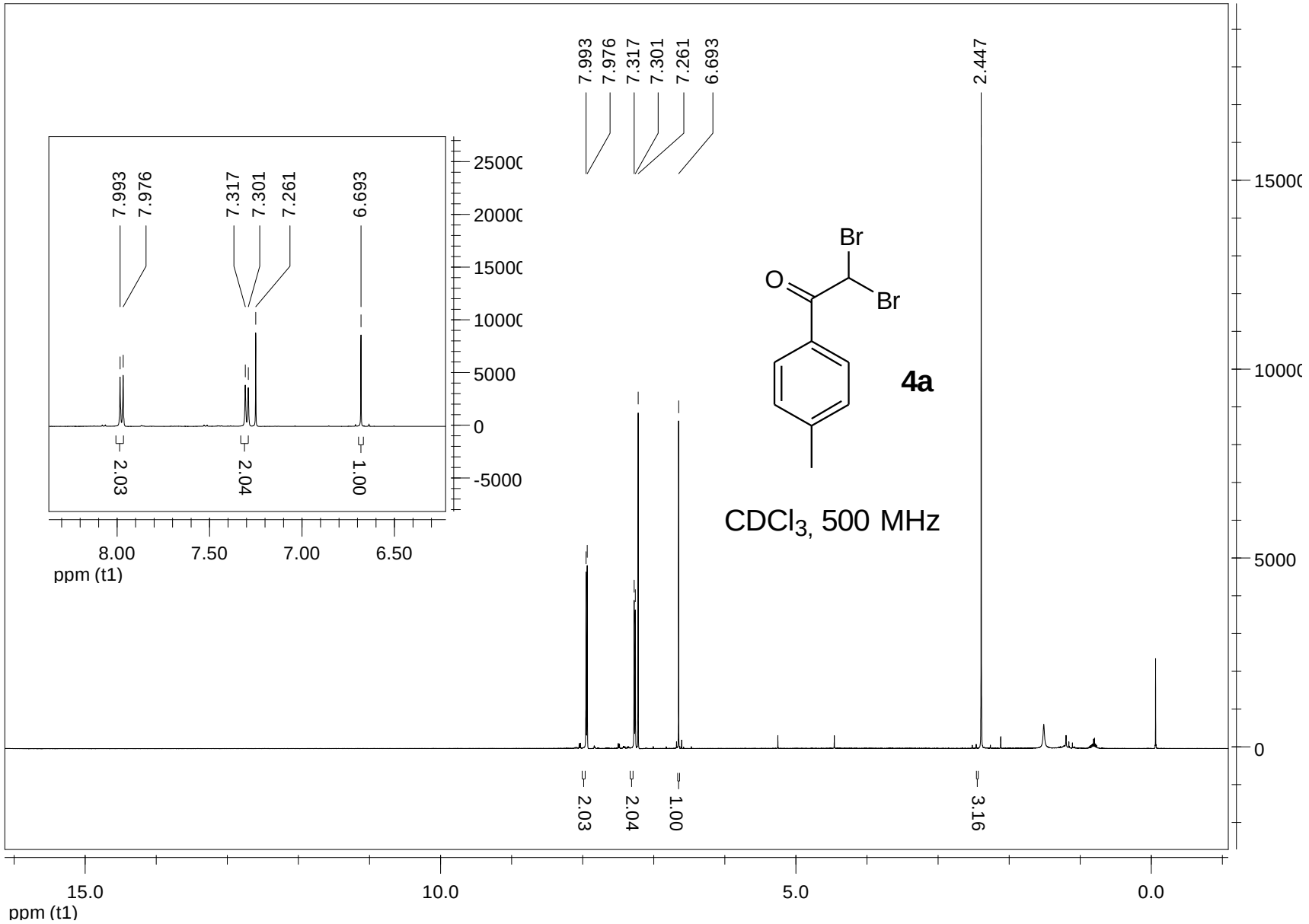
130.0
129.0
ppm (t1)
O
Br
OMe
2f
CDCl3, 125 MHz
200
150
100
50
0
ppm (t1)

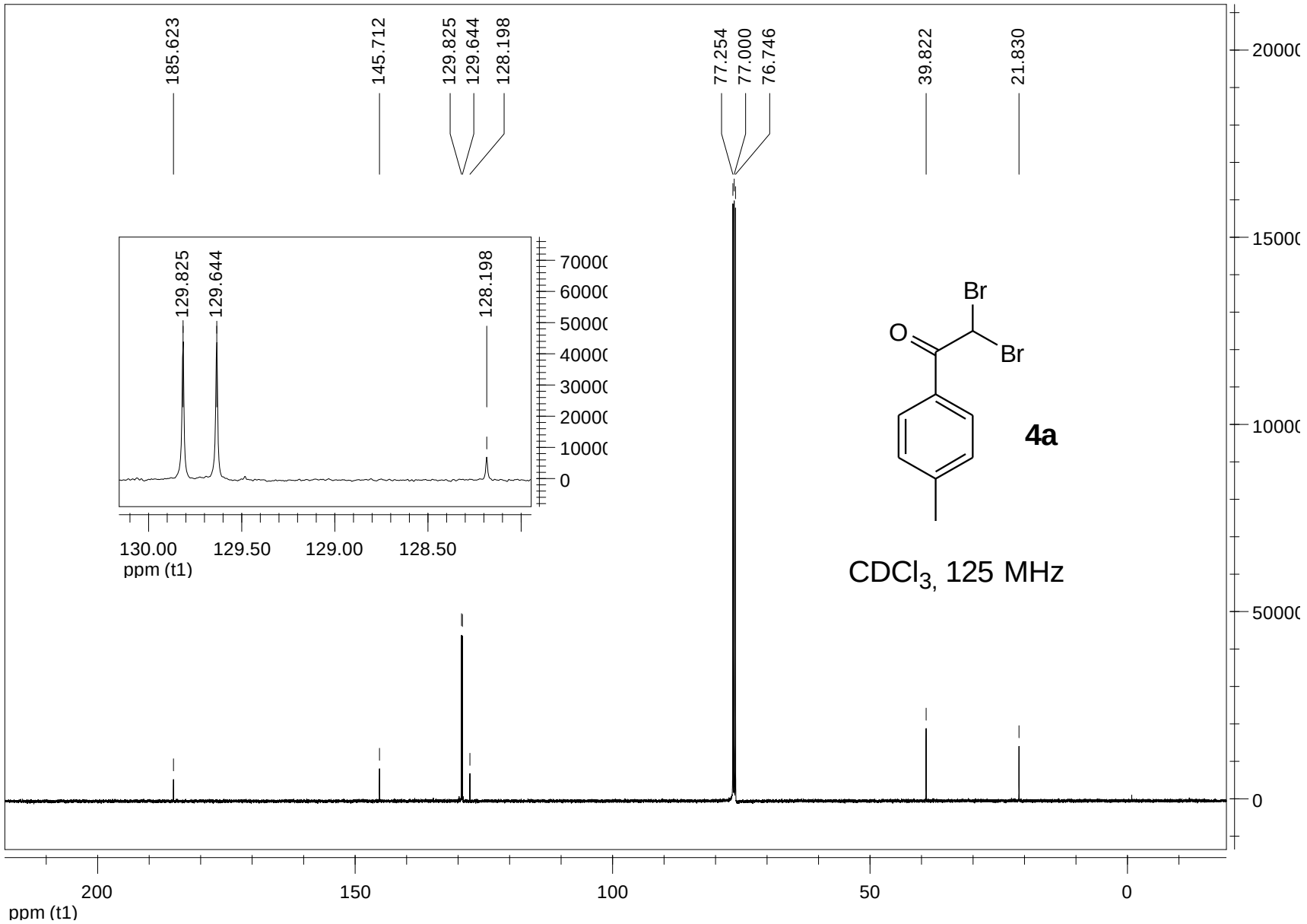

7.901
7.873
7.304
7.278
7.259
4.427
2.431
O
Br
CH2Br
3a
CDCl3, 300 MHz
2.00
1.99
2.04
3.17
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
15.0
10.0
5.0
0.0
ppm (t1)

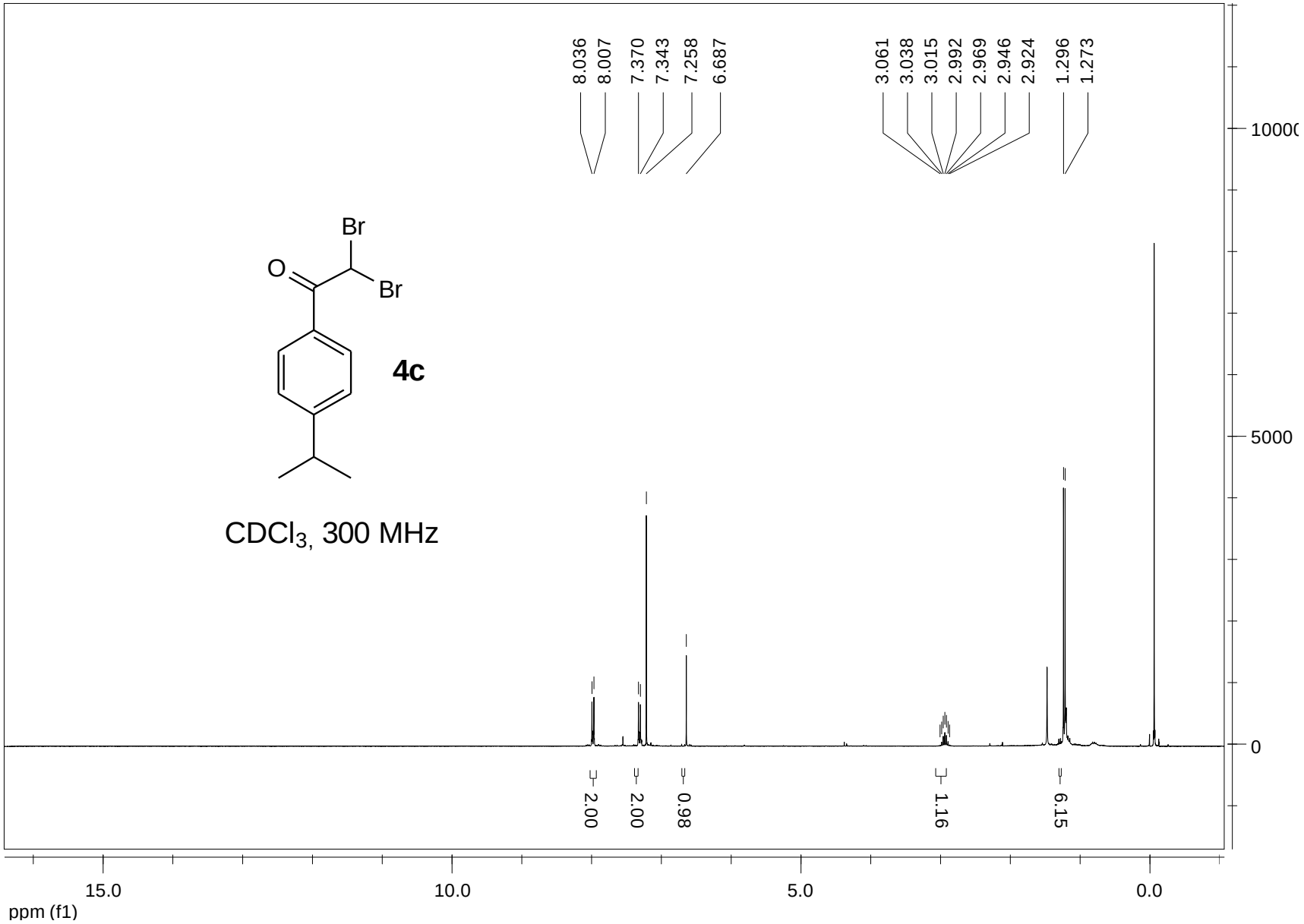

190.597
143.726
133.698
129.475
77.254
77.000
76.746
31.804
30.611
129.479
129.470
129.500
129.450
ppm (t1)
O
Br
CH2Br
3a
CDCl3, 125 MHz
200
150
100
50
0
ppm (t1)

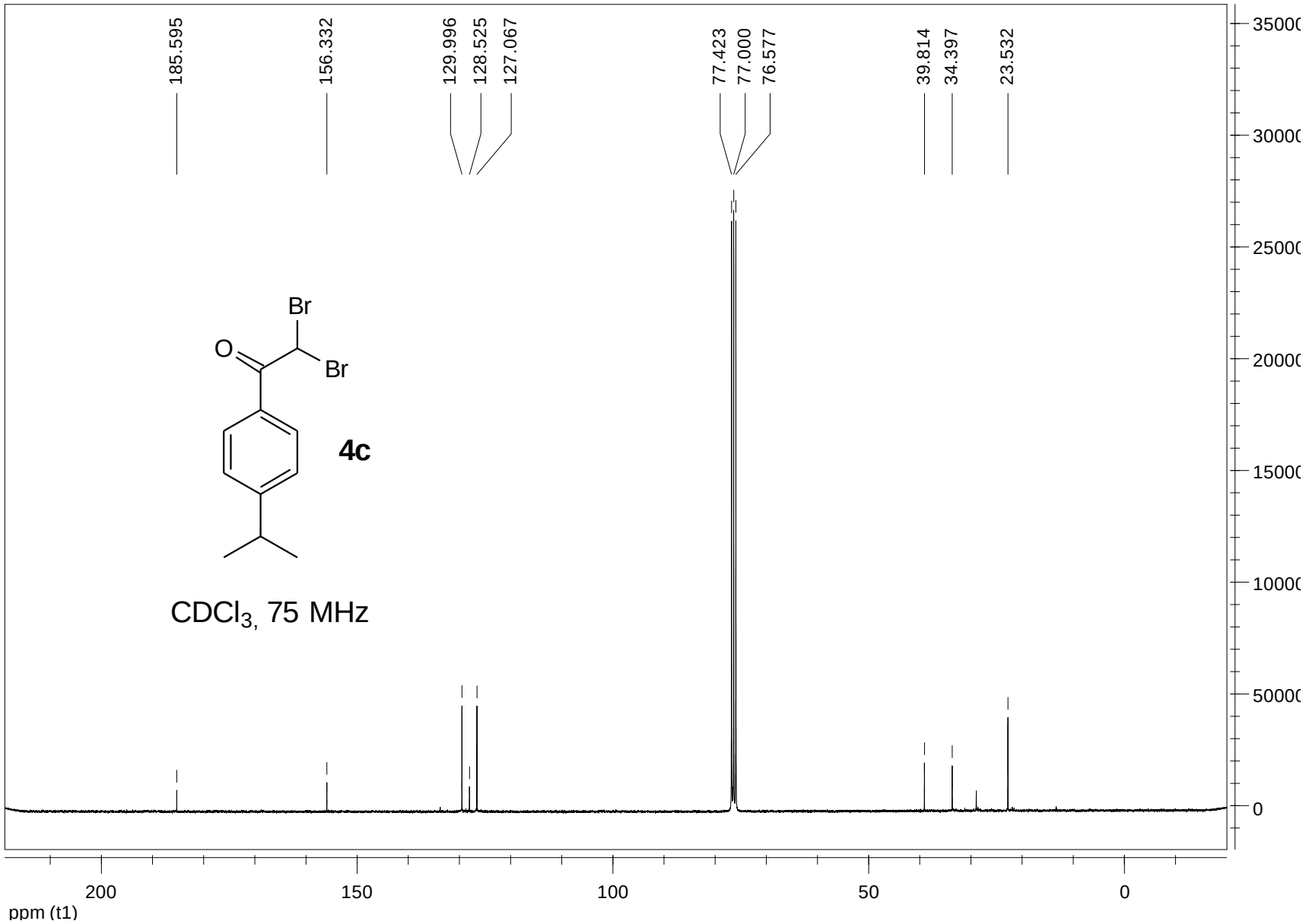

7.984
7.956
7.569
7.541
7.259
5.231
5.208
5.185
5.162
4.424
2.066
2.043
O
Br
Br
3b
CDCl3, 300 MHz
2.00
2.04
1.00
2.05
3.09
5000
0
15.0
10.0
5.0
0.0
ppm (t1)

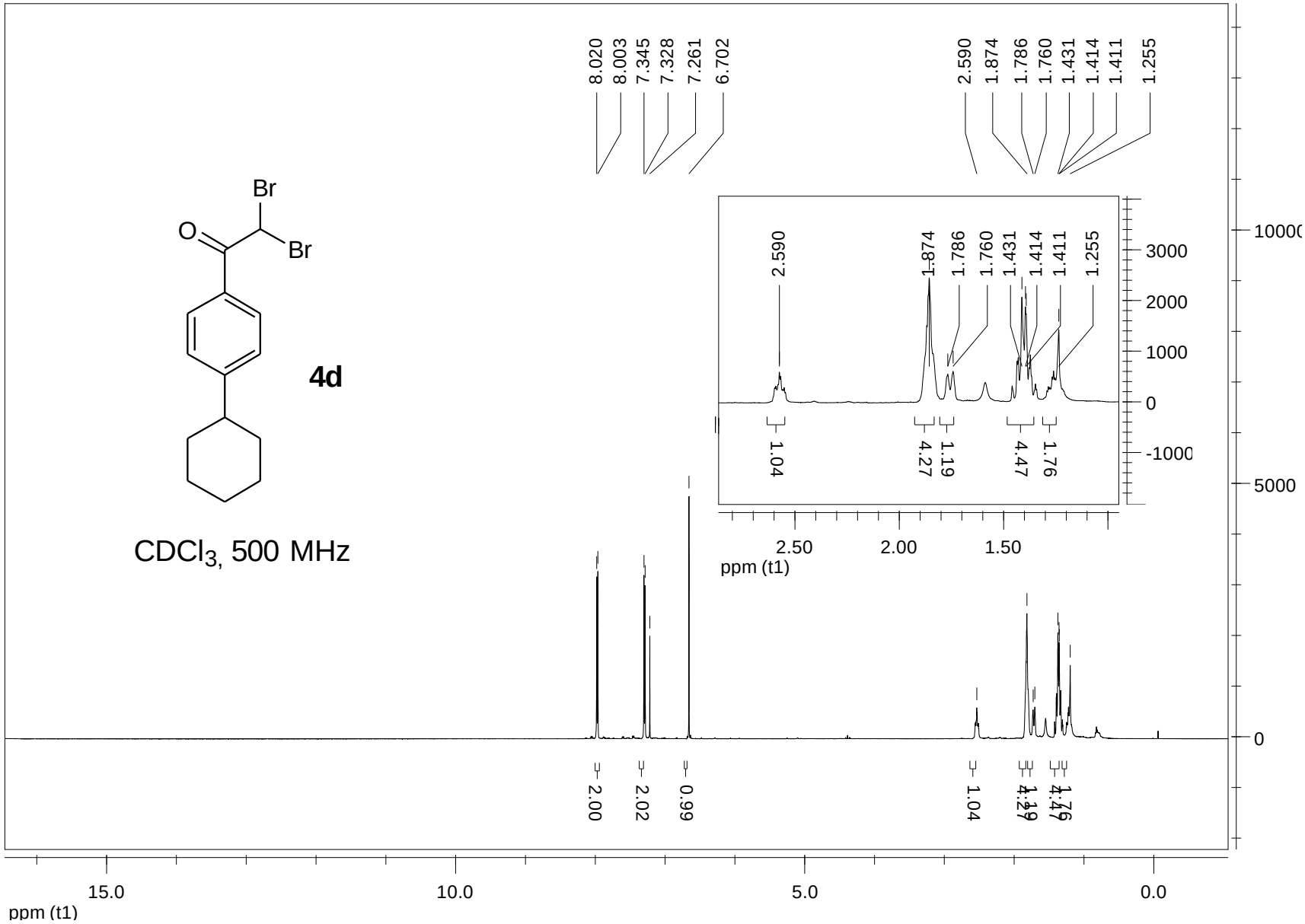

190.563
149.062
133.680
129.445
127.355
77.423
77.000
76.577
47.459
30.570
26.421
O
Br
Br
3b
CDCl3, 75 MHz
80000
70000
60000
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)

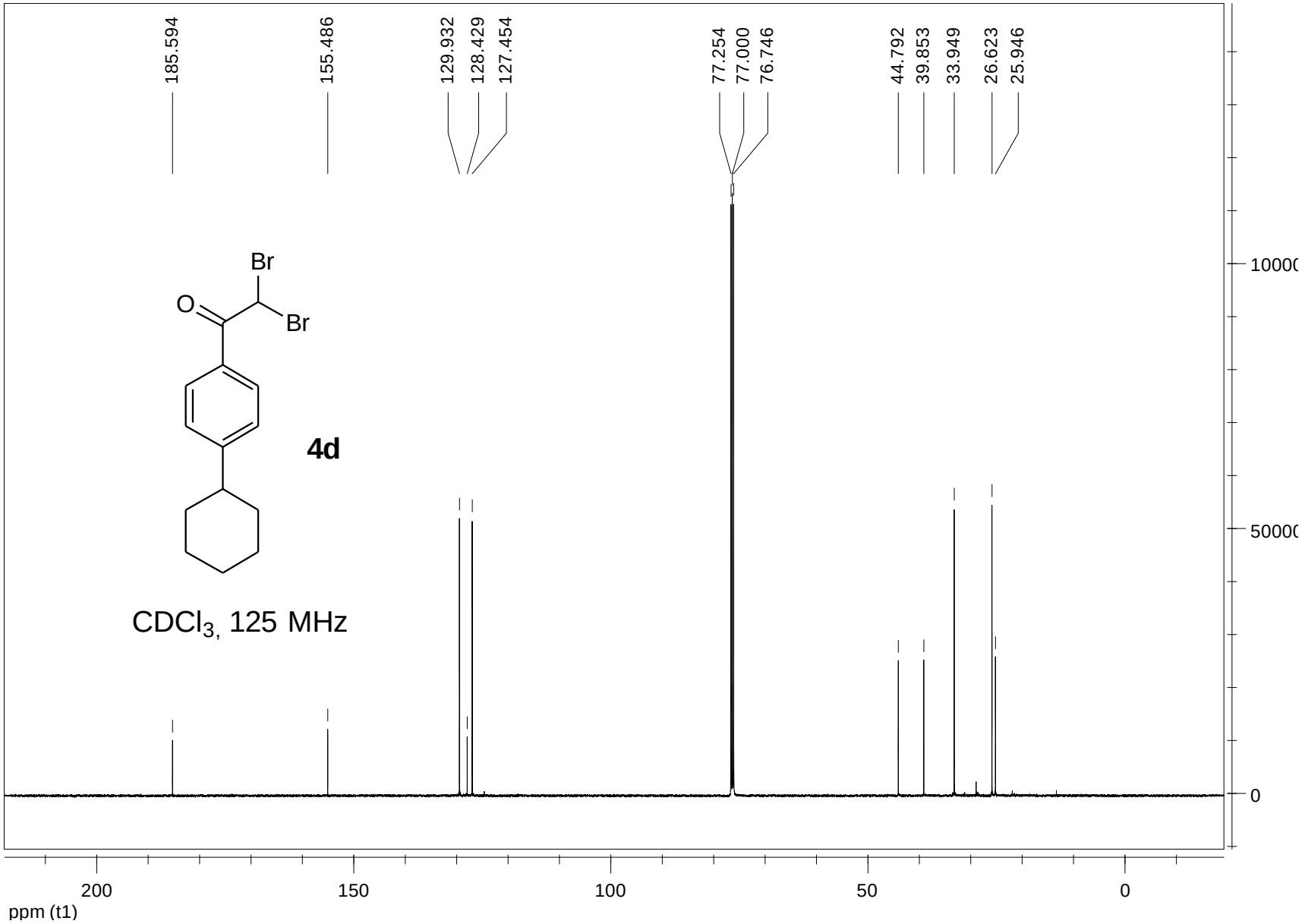

7.993
7.976
7.317
7.301
7.261
6.693
2.447
Br
O
Br
4a
CDCl3, 500 MHz
2.03
2.04
1.00
3.16
ppm (t1)

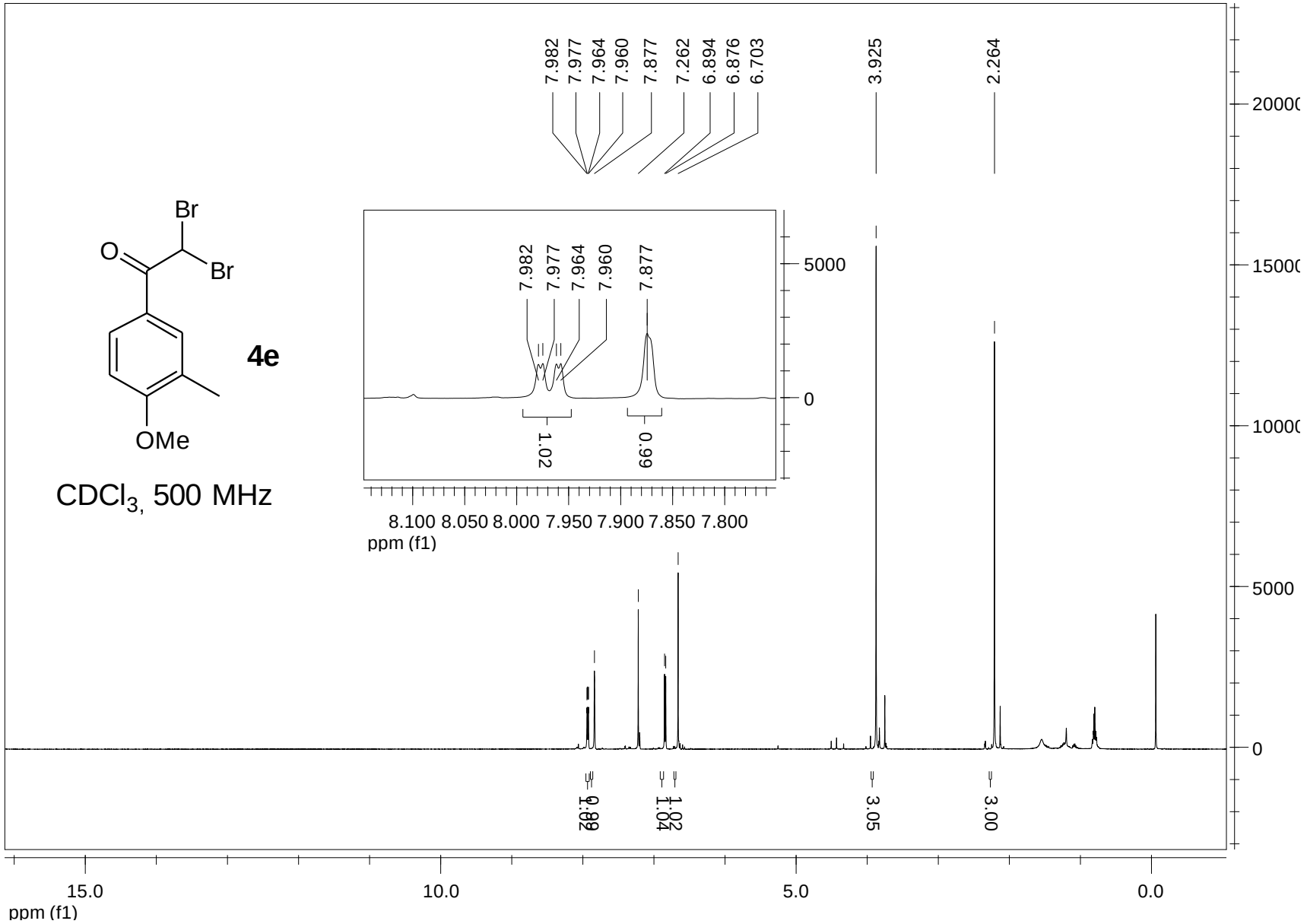

185.623
145.712
129.825
129.644
128.198
77.254
77.000
76.746
39.822
21.830
129.825
129.644
128.198
130.00
129.50
129.00
128.50
ppm (t1)
Br
O
Br
4a
CDCl3, 125 MHz
200
150
100
50
0
ppm (t1)

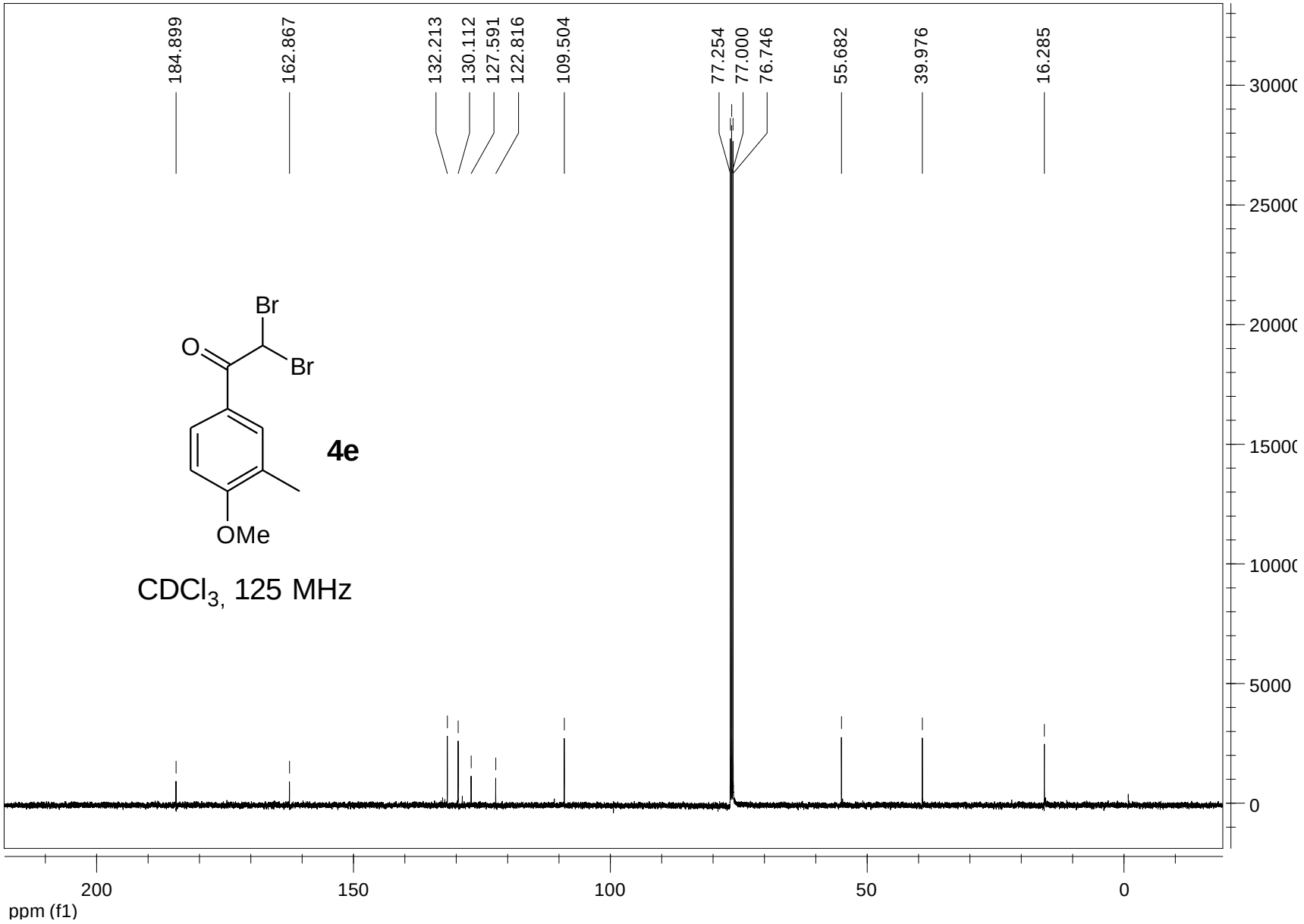

8.036
8.007
7.370
7.343
7.258
6.687
3.061
3.038
3.015
2.992
2.969
2.946
2.924
1.296
1.273
Br
O
Br
4c
CDCl3, 300 MHz
2.00
2.00
0.98
1.16
6.15
10000
5000
0
15.0
10.0
5.0
0.0
ppm (f1)

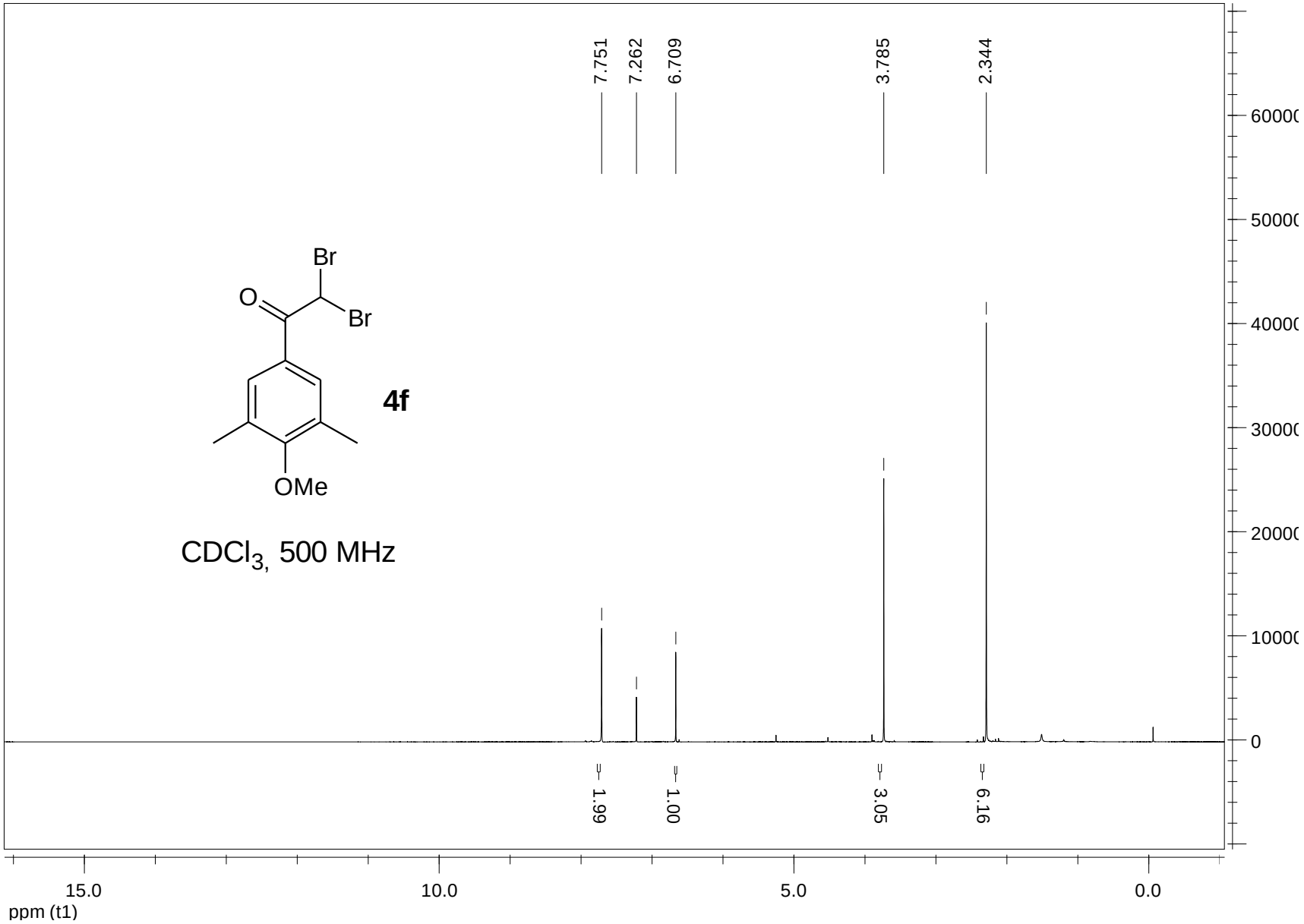

185.595
156.332
129.996
128.525
127.067
77.423
77.000
76.577
39.814
34.397
23.532
Br
O
Br
4c
CDCl3, 75 MHz
35000
30000
25000
20000
15000
10000
50000
0
200
150
100
50
0
ppm (t1)

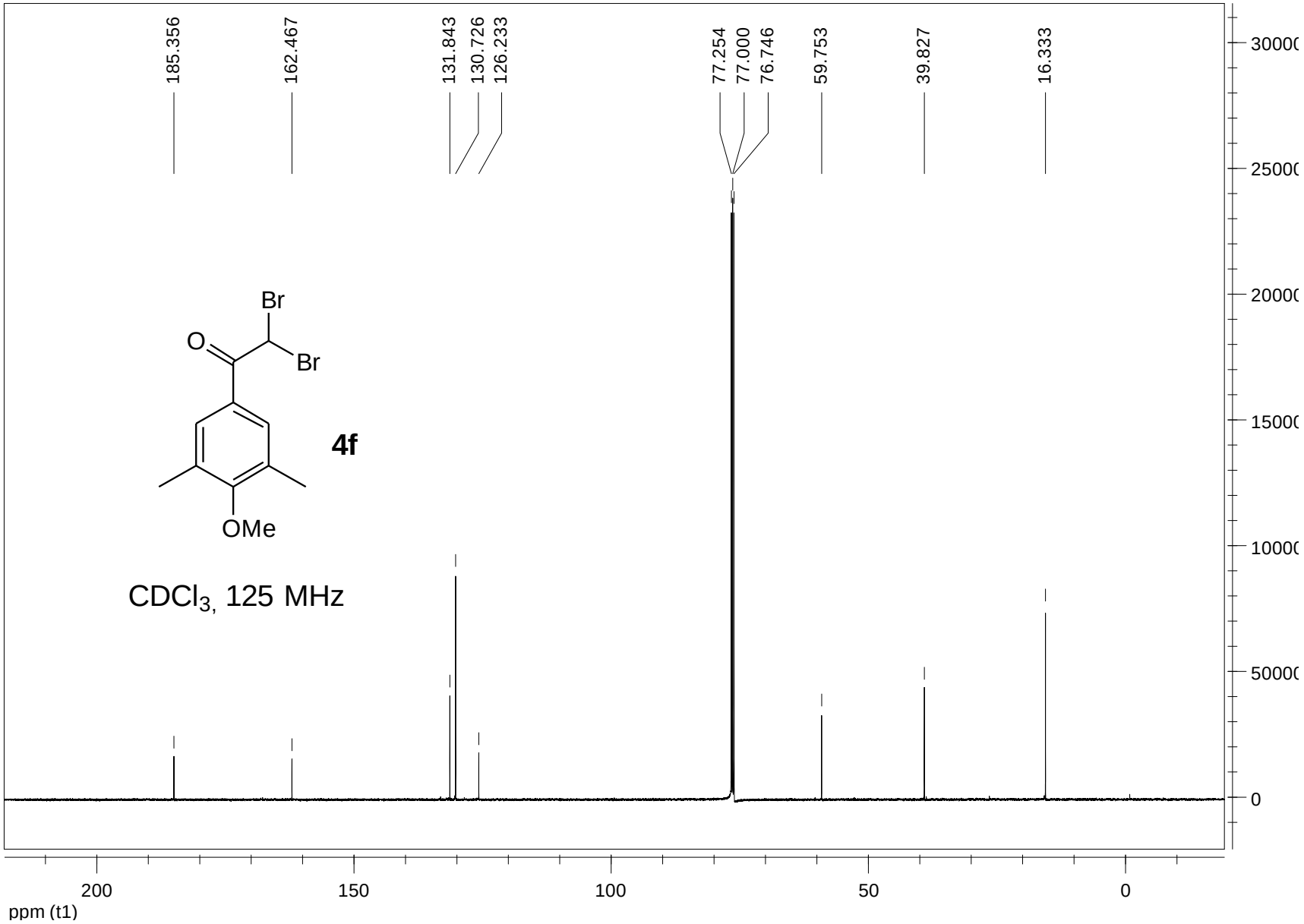

8.020
8.003
7.345
7.328
7.261
6.702
2.590
1.874
1.786
1.760
1.431
1.414
1.411
1.255
Br
O
Br
4d
CDCl3, 500 MHz
1.04
4.27
1.19
4.47
1.76
2.00
2.02
0.99
1.04
4.19
4.47
1.76
2.50
2.00
1.50
ppm (t1)
15.0
10.0
5.0
0.0
ppm (t1)
10000
5000
0
3000
2000
1000
0
-1000

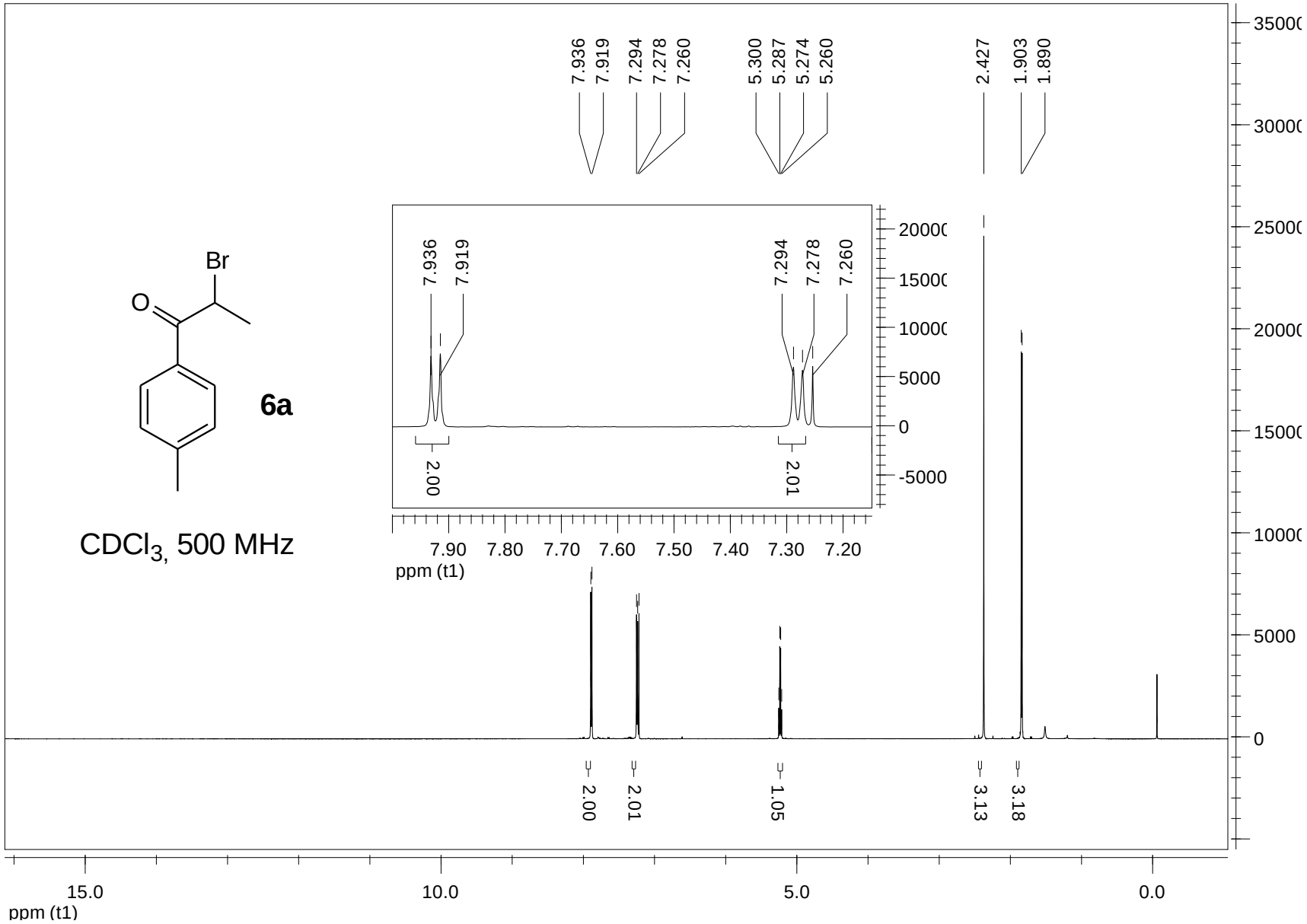

185.594
155.486
129.932
128.429
127.454
77.254
77.000
76.746
44.792
39.853
33.949
26.623
25.946
Br
O
Br
4d
CDCl3, 125 MHz
10000
50000
0
200
150
100
50
0
ppm (t1)

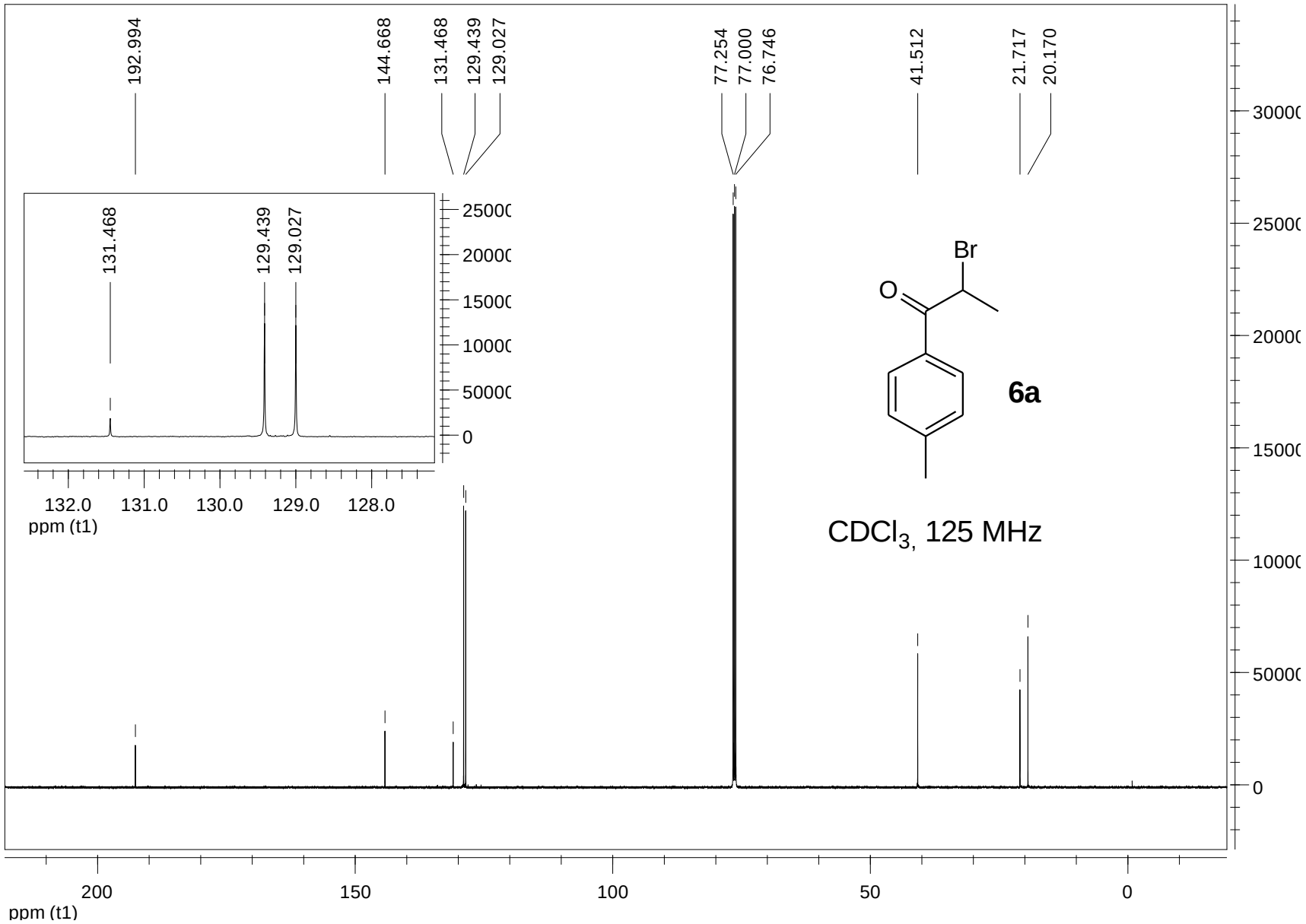

Br
O
Br
OMe
4e
CDCl3, 500 MHz
7.982
7.977
7.964
7.960
7.877
7.262
6.894
6.876
6.703
3.925
2.264
1.02
0.99
8.100 8.050 8.000 7.950 7.900 7.850 7.800
ppm (f1)
0.80
1.02
1.04
3.05
3.00
15.0
10.0
5.0
0.0
ppm (f1)

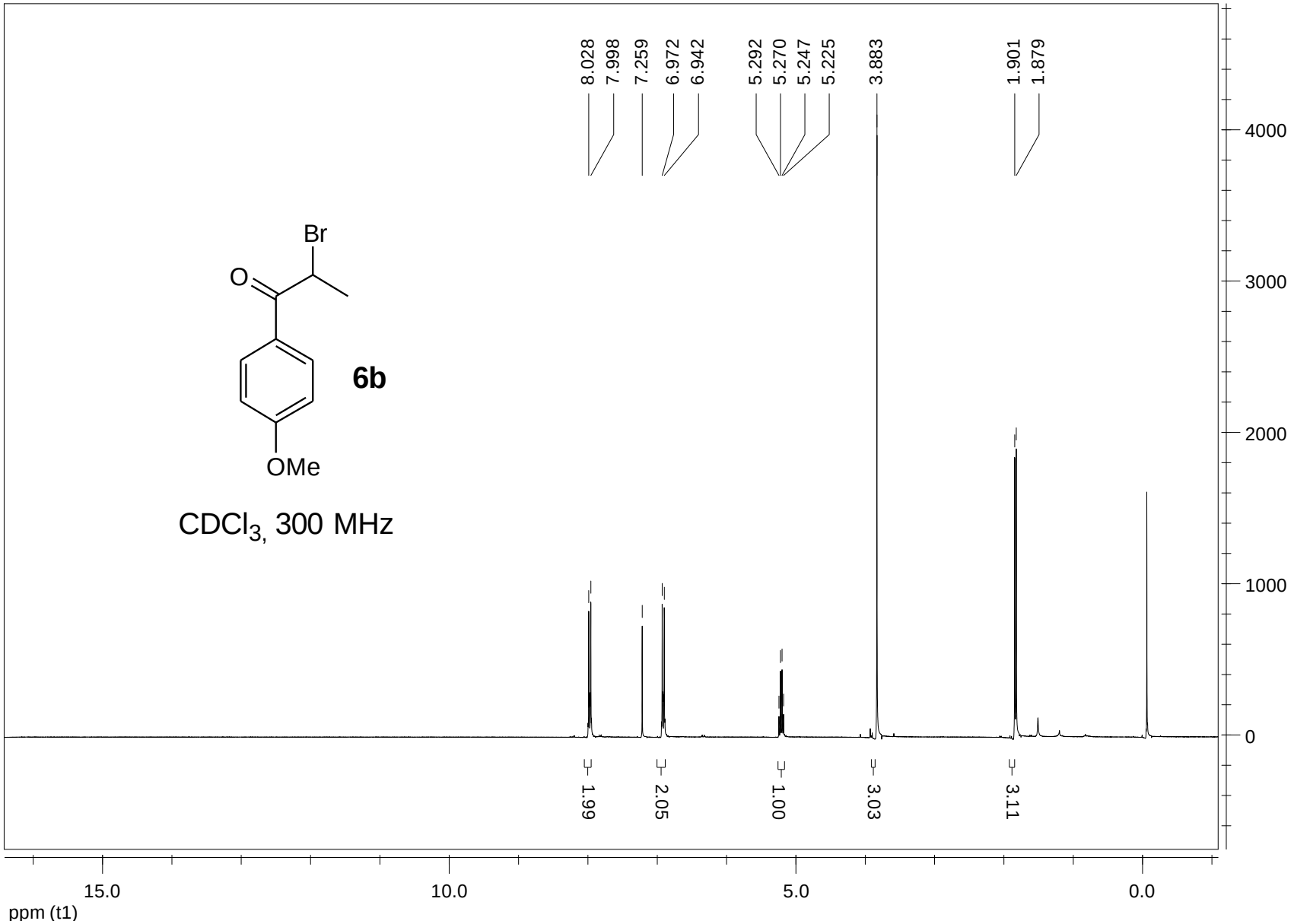

184.899
162.867
132.213
130.112
127.591
122.816
109.504
77.254
77.000
76.746
55.682
39.976
16.285
Br
O
Br
OMe
4e
CDCl3, 125 MHz
30000
25000
20000
15000
10000
5000
0
200
150
100
50
0
ppm (f1)

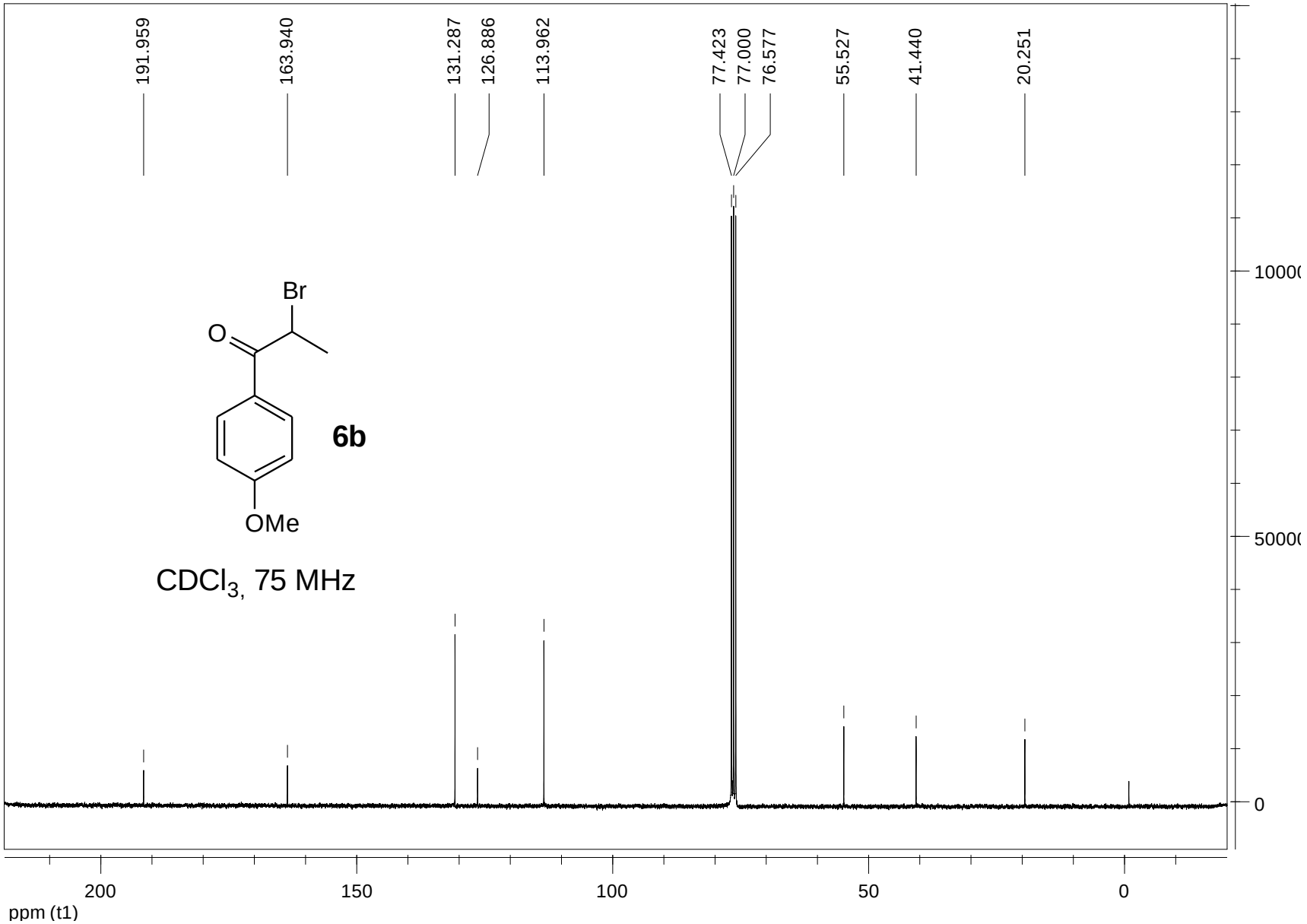

7.751
7.262
6.709
3.785
2.344
Br
O
Br
OMe
4f
CDCl3, 500 MHz
1.99
1.00
3.05
6.16
60000
50000
40000
30000
20000
10000
0
15.0
10.0
5.0
0.0
ppm (t1)

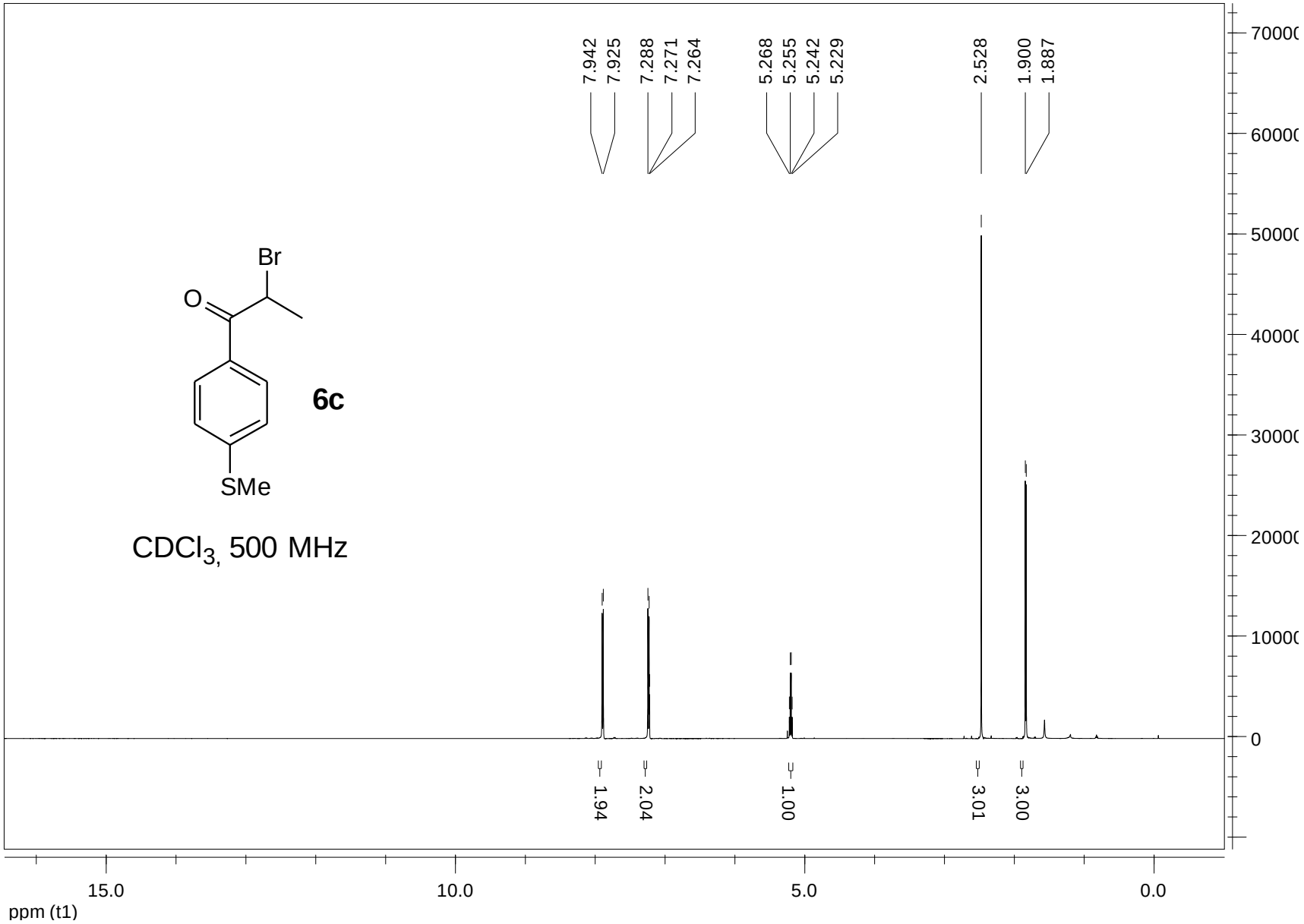

185.356
162.467
131.843
130.726
126.233
77.254
77.000
76.746
59.753
39.827
16.333
Br
O
Br
OMe
4f
CDCl3, 125 MHz
200
150
100
50
0
ppm (t1)

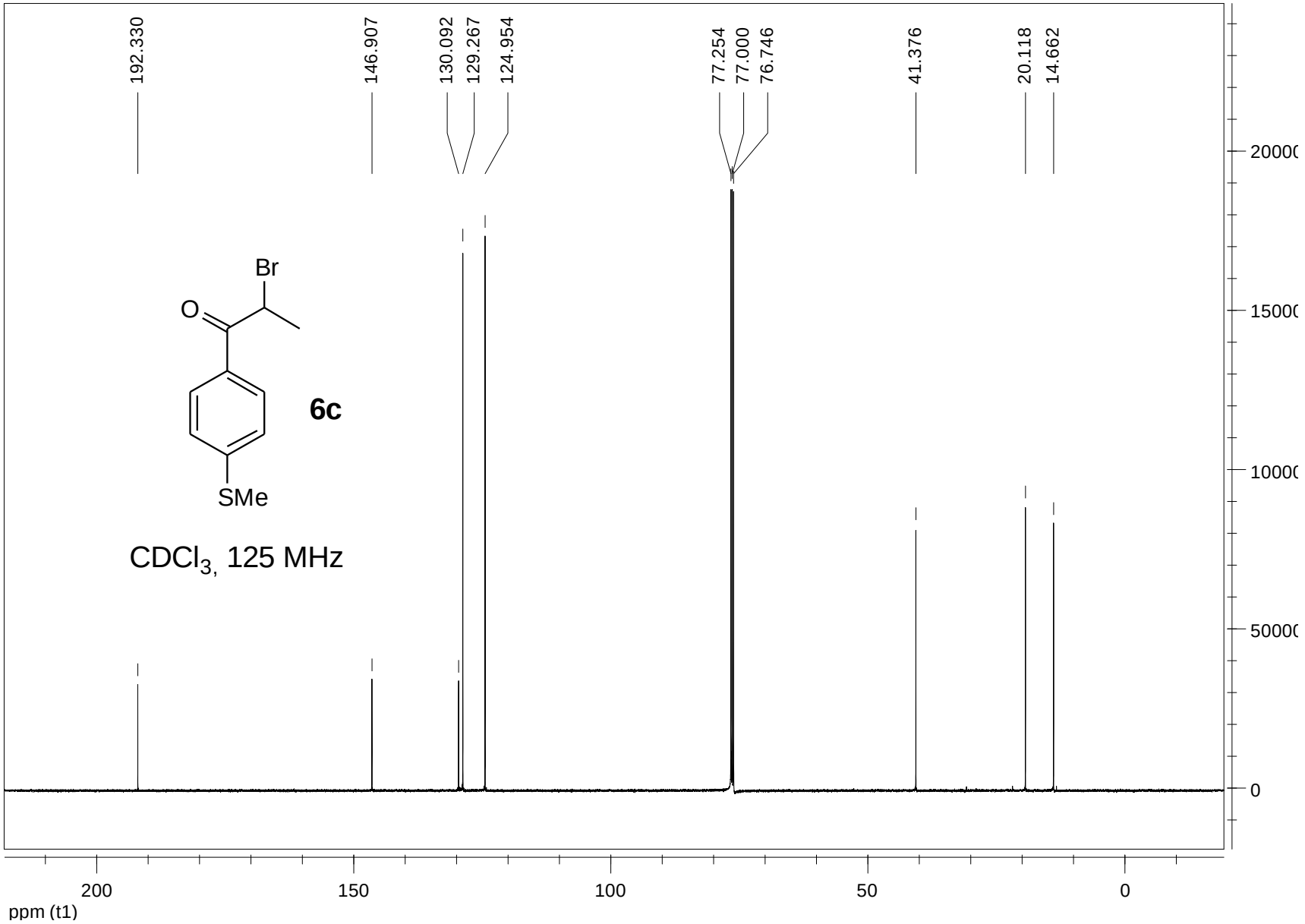

Br
O
6a
CDCl3, 500 MHz
7.936
7.919
7.294
7.278
7.260
5.300
5.287
5.274
5.260
2.427
1.903
1.890
2.00
2.01
1.05
3.13
3.18
ppm (t1)
15.0
10.0
5.0
0.0

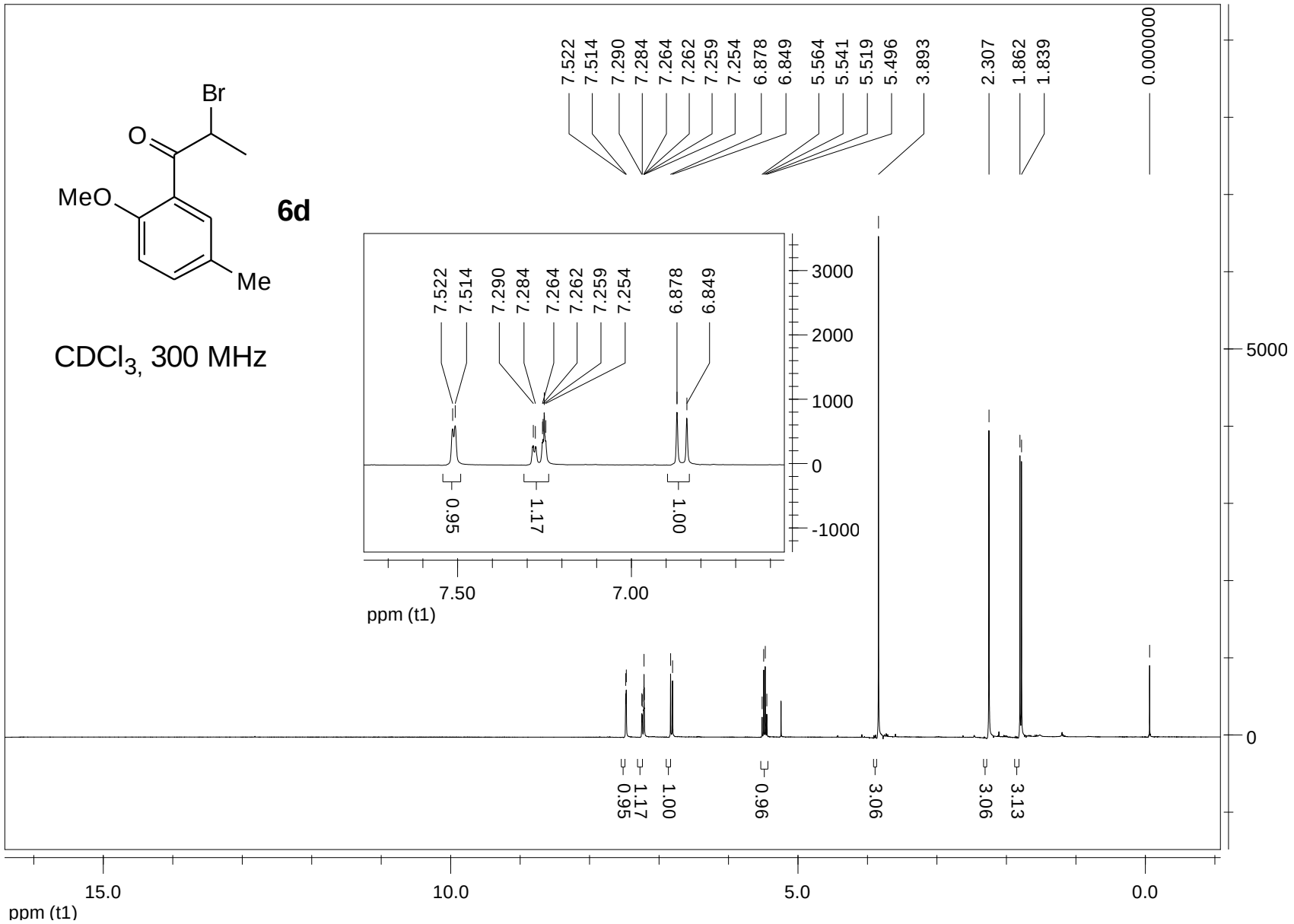

192.994
144.668
131.468
129.439
129.027
77.254
77.000
76.746
41.512
21.717
20.170
131.468
129.439
129.027
132.0
131.0
130.0
129.0
128.0
ppm (t1)
Br
O
6a
CDCl3, 125 MHz
200
150
100
50
0
ppm (t1)

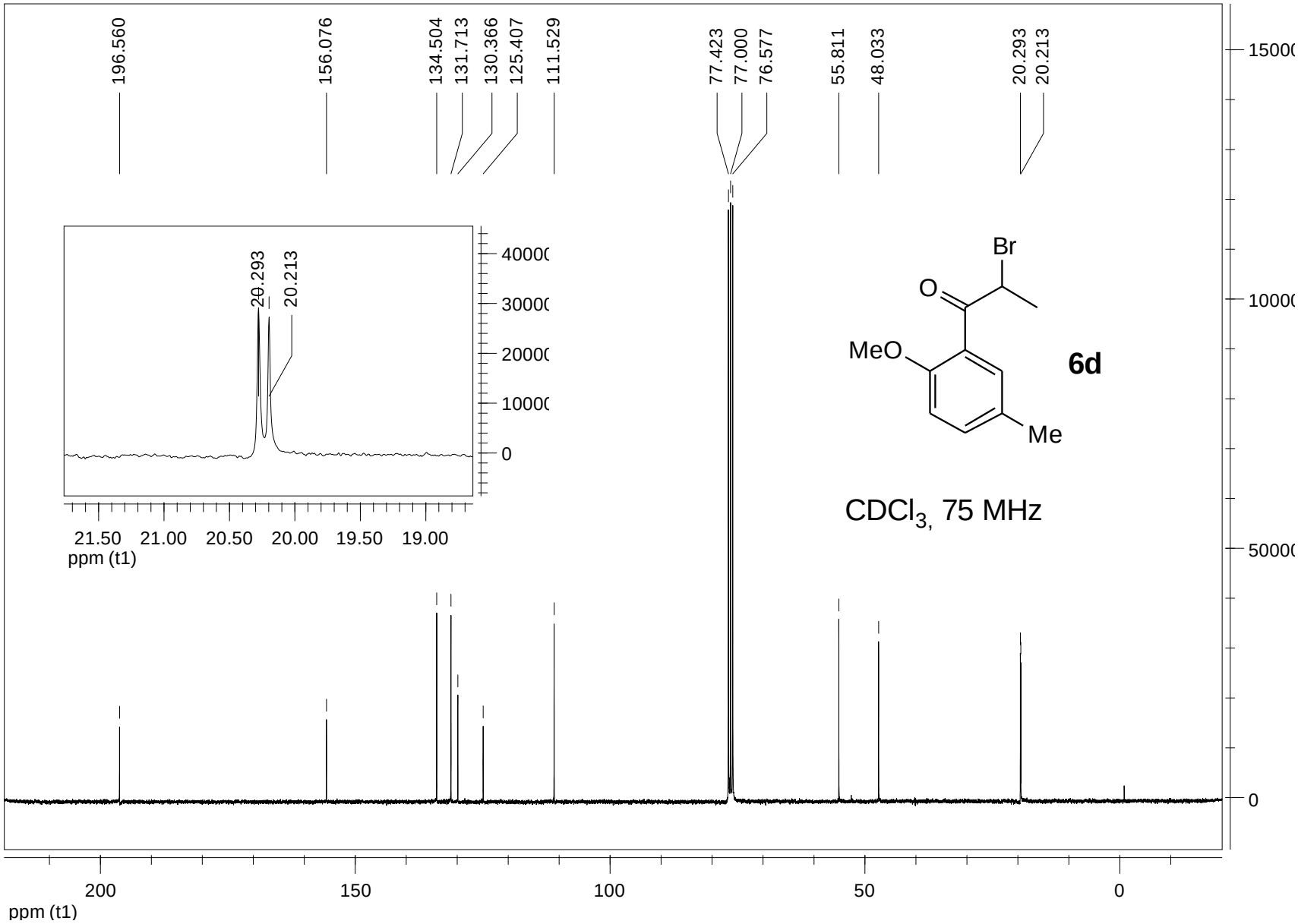

8.028
7.998
7.259
6.972
6.942
5.292
5.270
5.247
5.225
3.883
1.901
1.879
Br
O
OMe
6b
CDCl3, 300 MHz
1.99
2.05
1.00
3.03
3.11
4000
3000
2000
1000
0
15.0
10.0
5.0
0.0
ppm (t1)

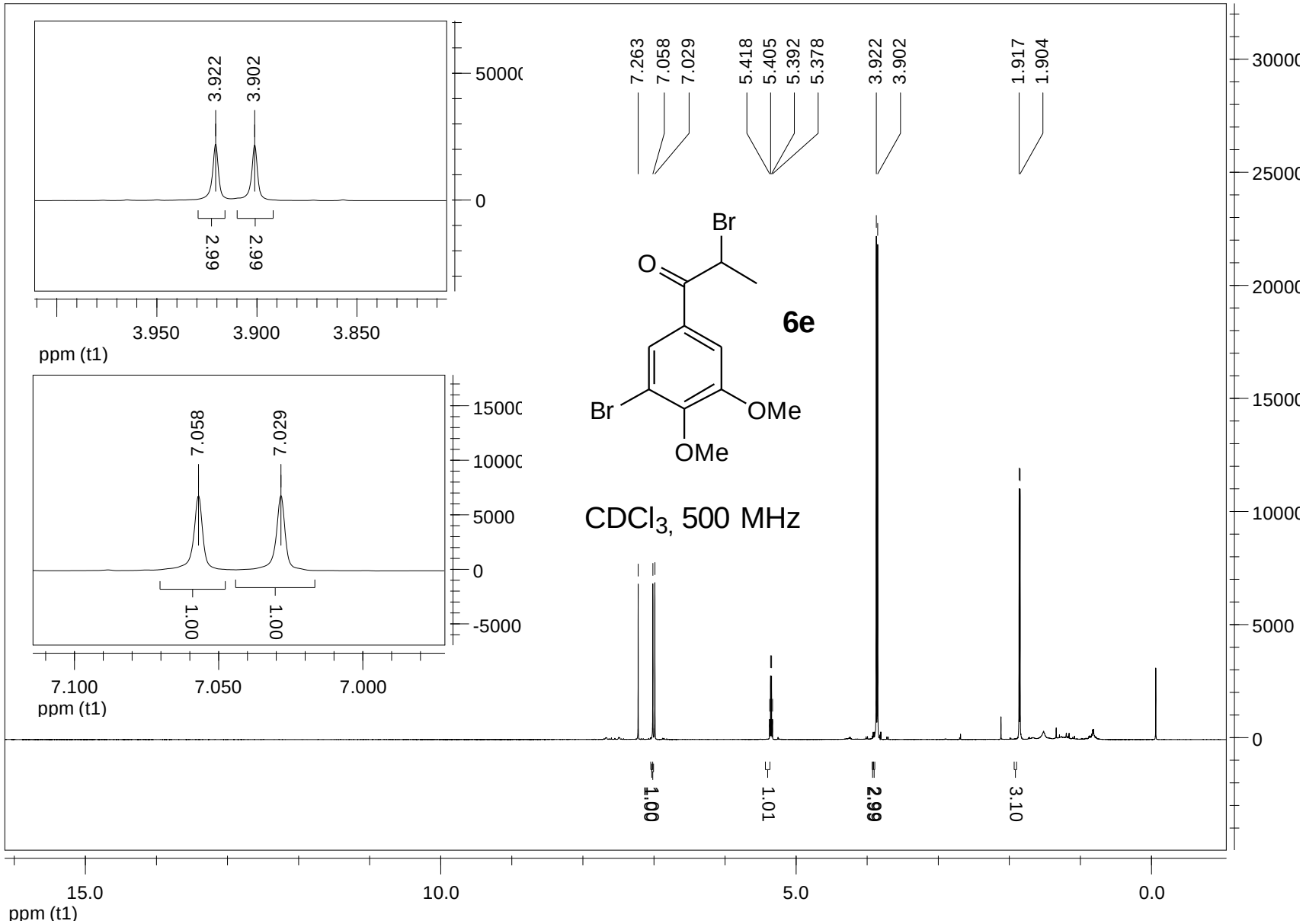

191.959
163.940
131.287
126.886
113.962
77.423
77.000
76.577
55.527
41.440
20.251
Br
O
OMe
6b
CDCl3, 75 MHz
10000
5000
0
200
150
100
50
0
ppm (t1)

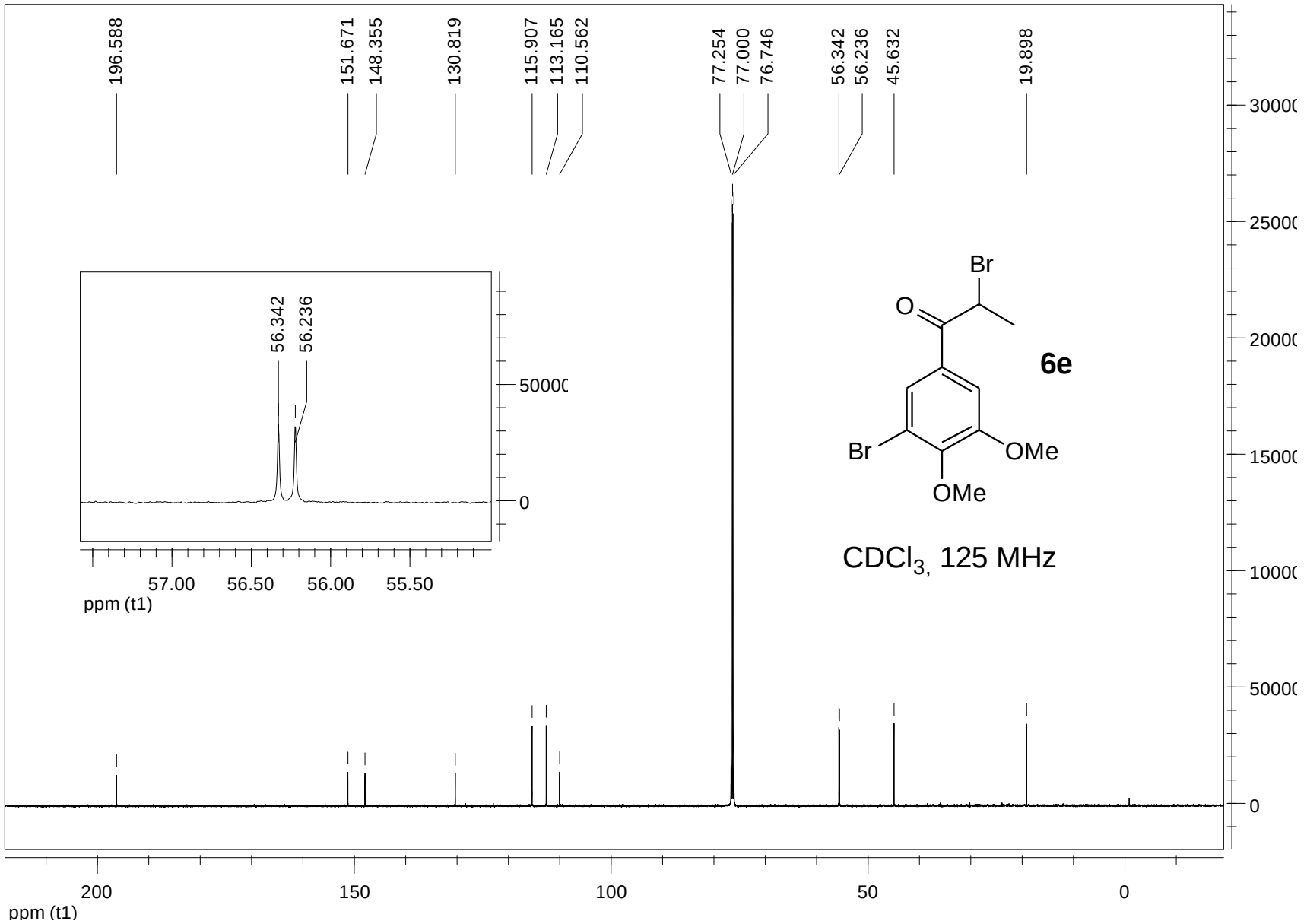

7.942
7.925
7.288
7.271
7.264
5.268
5.255
5.242
5.229
2.528
1.900
1.887
Br
O
SMe
6c
CDCl3, 500 MHz
1.94
2.04
1.00
3.01
3.00
15.0
10.0
5.0
0.0
ppm (t1)

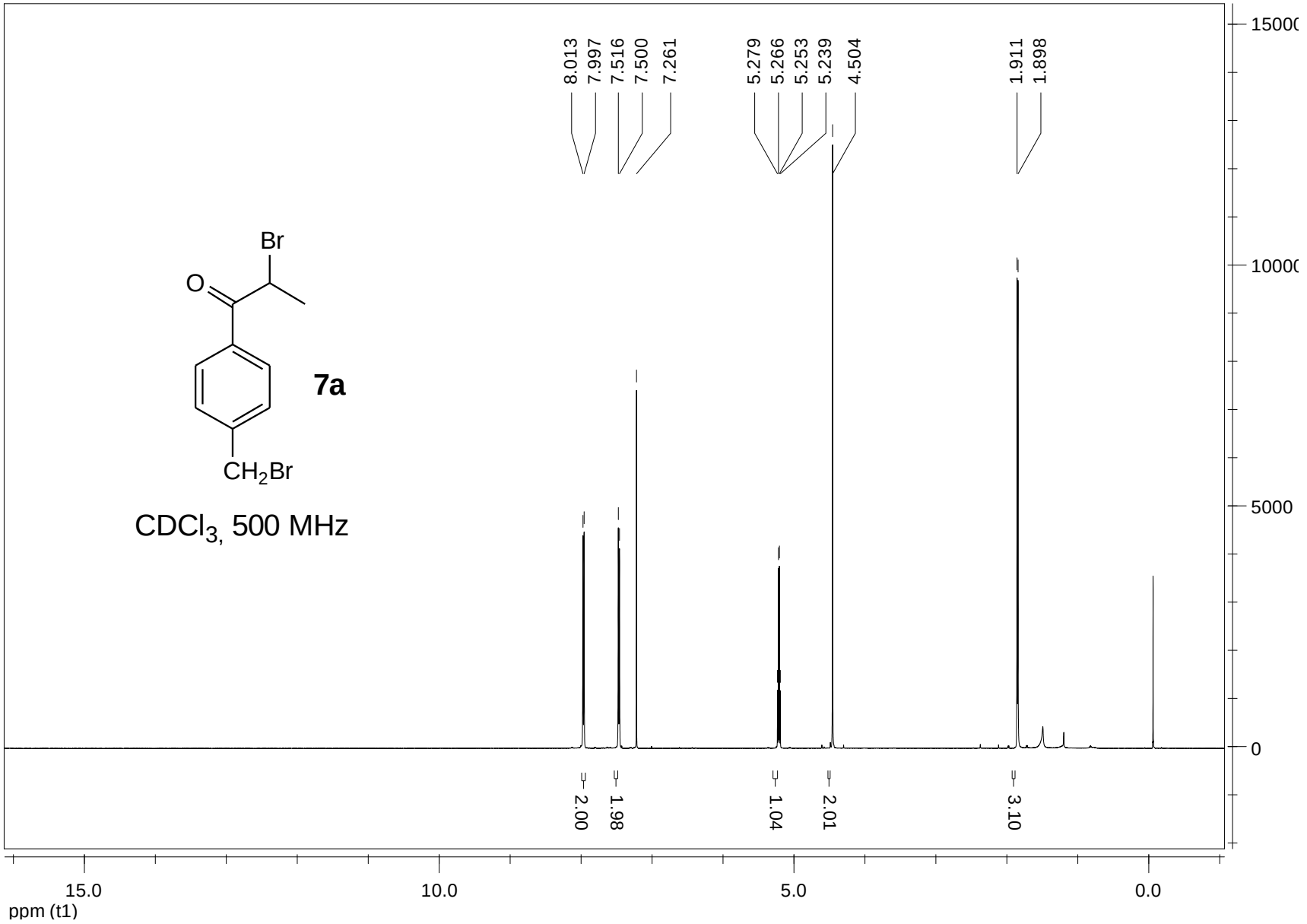

192.330
146.907
130.092
129.267
124.954
77.254
77.000
76.746
41.376
20.118
14.662
Br
O
SMe
6c
CDCl3, 125 MHz
200
150
100
50
0
ppm (t1)

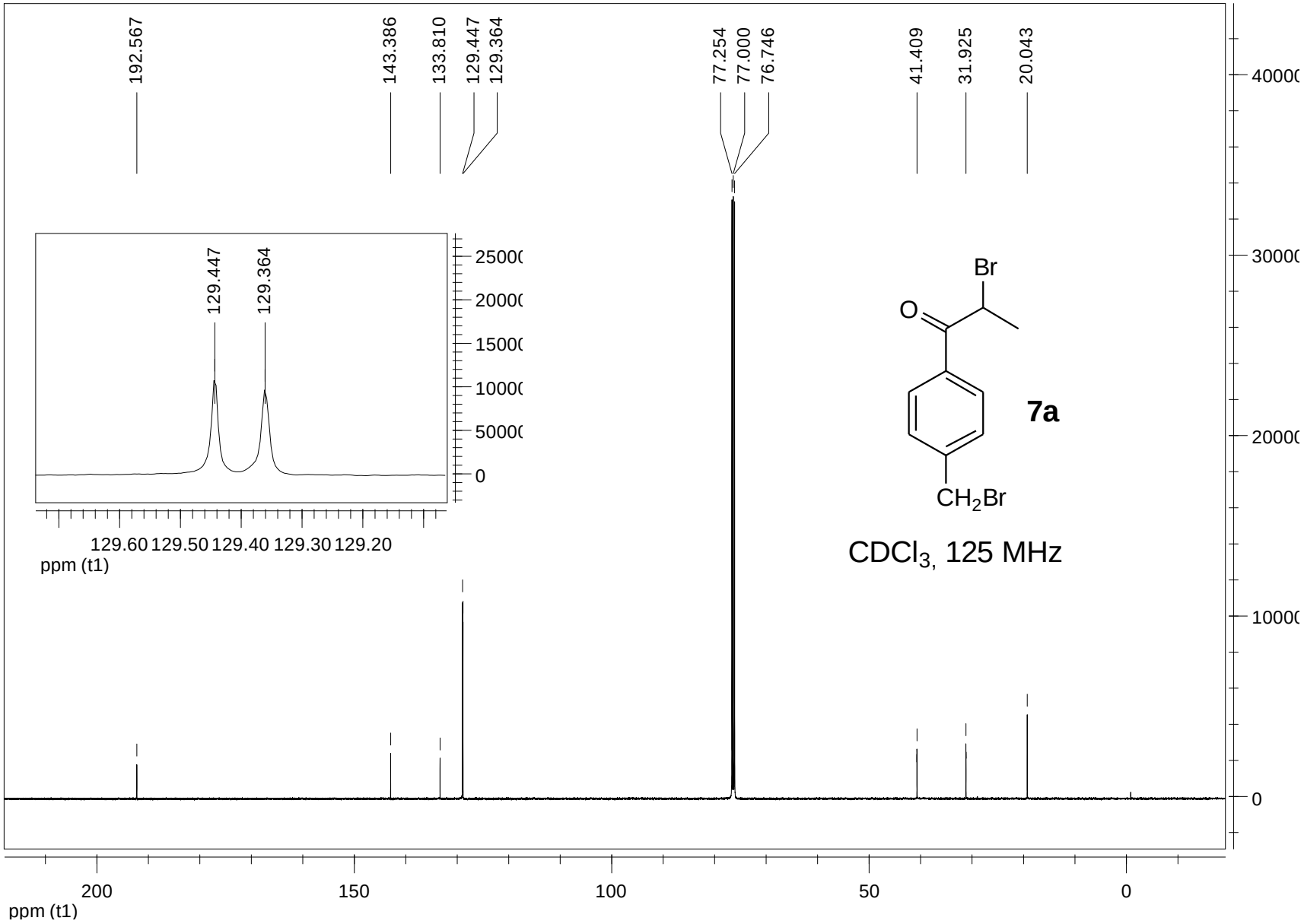

Br
O
MeO
Me
6d
CDCl3, 300 MHz
7.522
7.514
7.290
7.284
7.264
7.262
7.259
7.254
6.878
6.849
5.564
5.541
5.519
5.496
3.893
2.307
1.862
1.839
0.000000
0.95
1.17
1.00
0.96
3.06
3.06
3.13
ppm (t1)
15.0
10.0
5.0
0.0

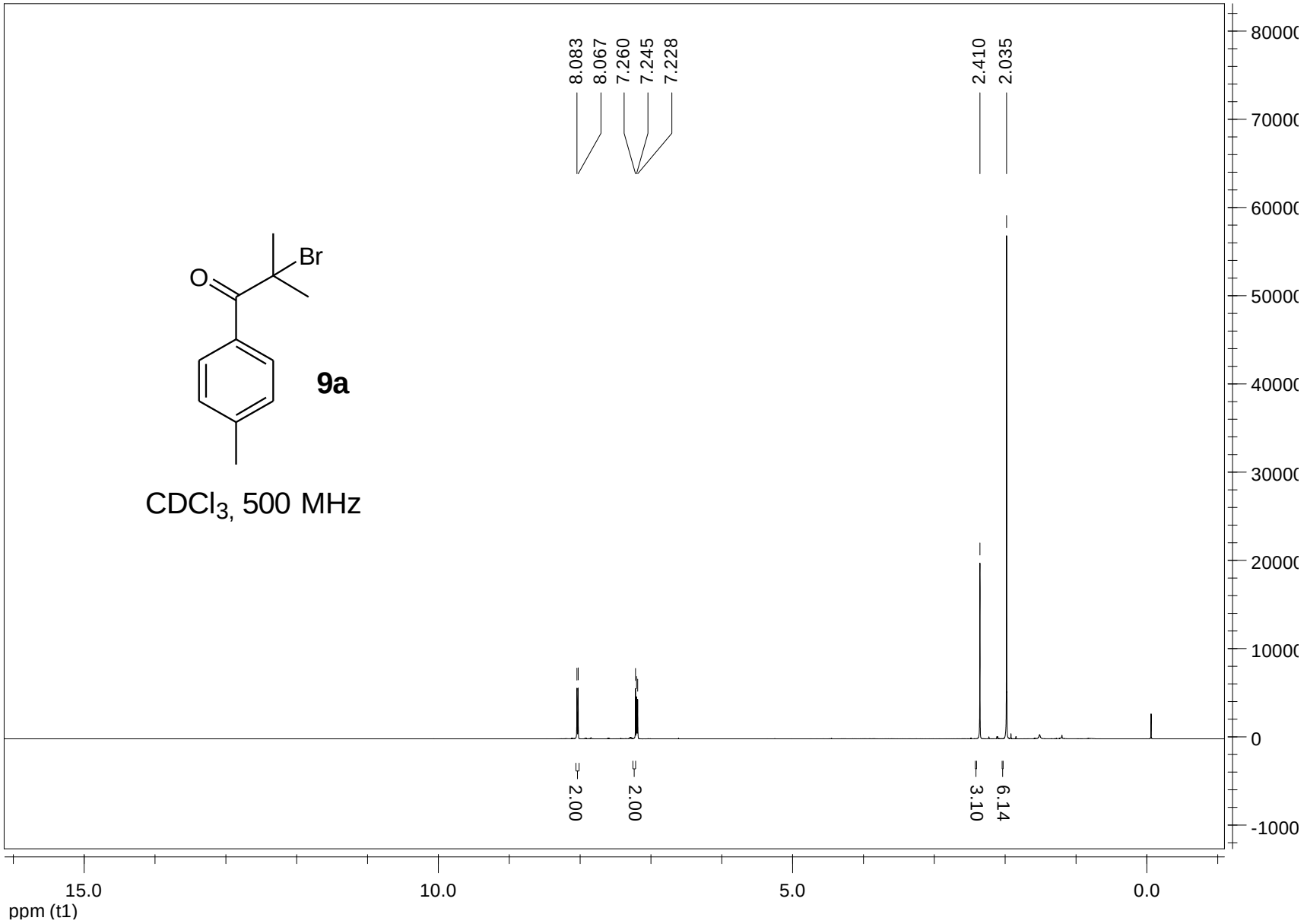

196.560
156.076
134.504
131.713
130.366
125.407
111.529
77.423
77.000
76.577
55.811
48.033
20.293
20.213
Br
O
MeO
Me
6d
CDCl3, 75 MHz
ppm (t1)
ppm (t1)

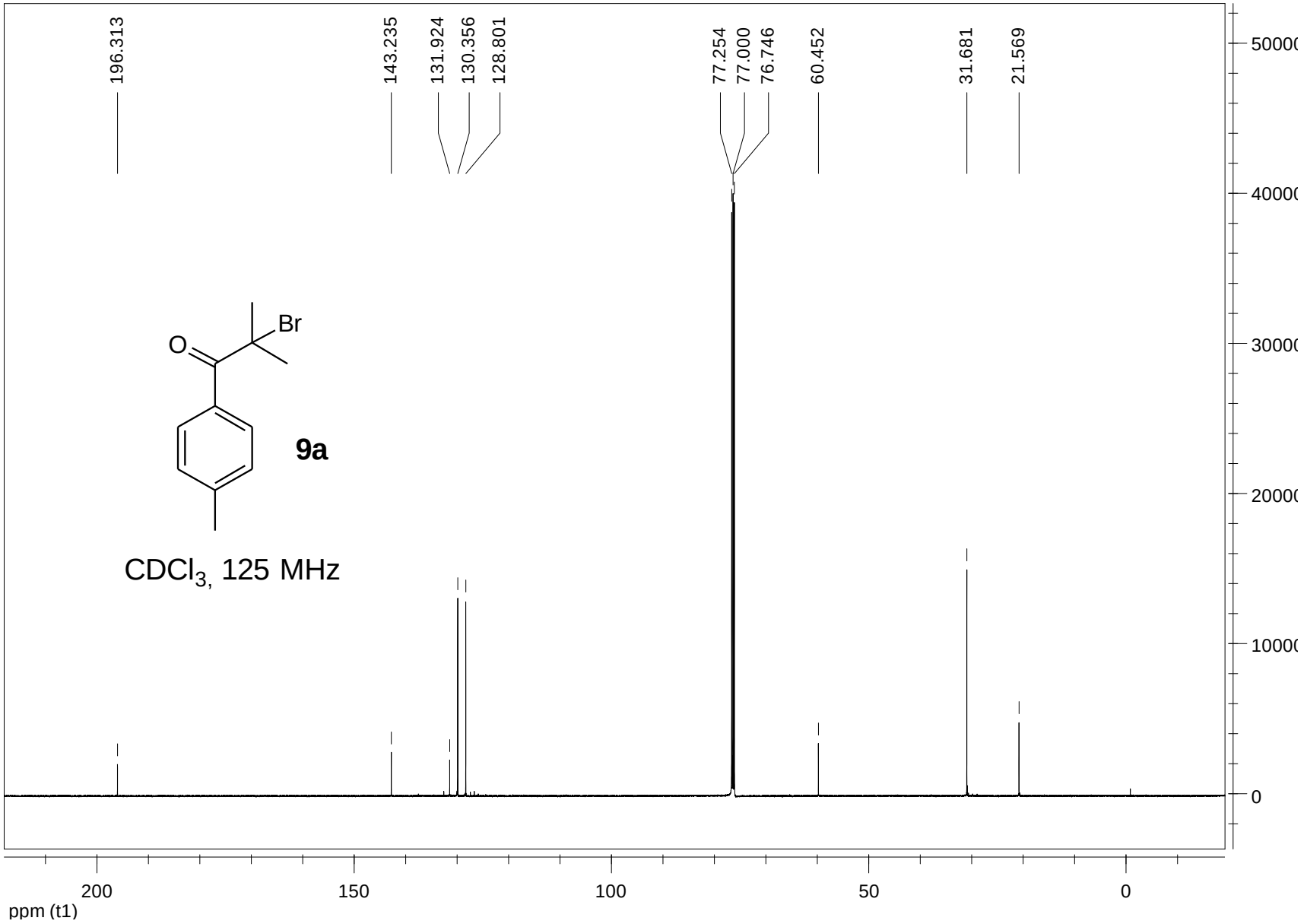

7.263
7.058
7.029
5.418
5.405
5.392
5.378
3.922
3.902
1.917
1.904
Br
O
Br
OMe
OMe
6e
CDCl3, 500 MHz
1.00
1.01
2.99
3.10
3.922
3.902
2.99
2.99
3.950
3.900
3.850
ppm (t1)
7.058
7.029
1.00
1.00
7.100
7.050
7.000
ppm (t1)
15.0
10.0
5.0
0.0
ppm (t1)

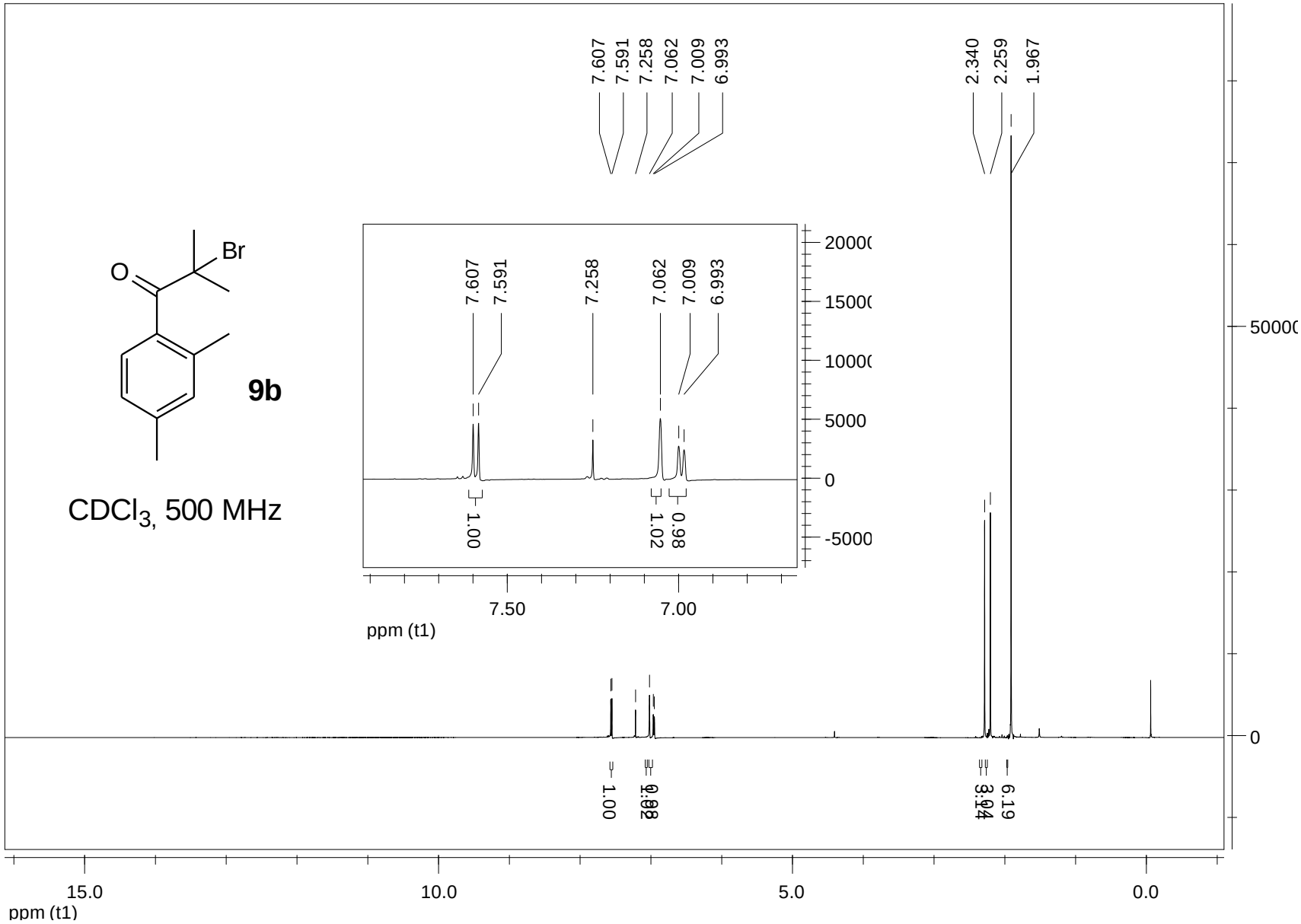

196.588
151.671
148.355
130.819
115.907
113.165
110.562
77.254
77.000
76.746
56.342
56.236
45.632
19.898
56.342
56.236
50000
0
57.00
56.50
56.00
55.50
ppm (t1)
Br
O
6e
Br
OMe
OMe
CDCl3, 125 MHz
30000
25000
20000
15000
10000
50000
0
200
150
100
50
0
ppm (t1)

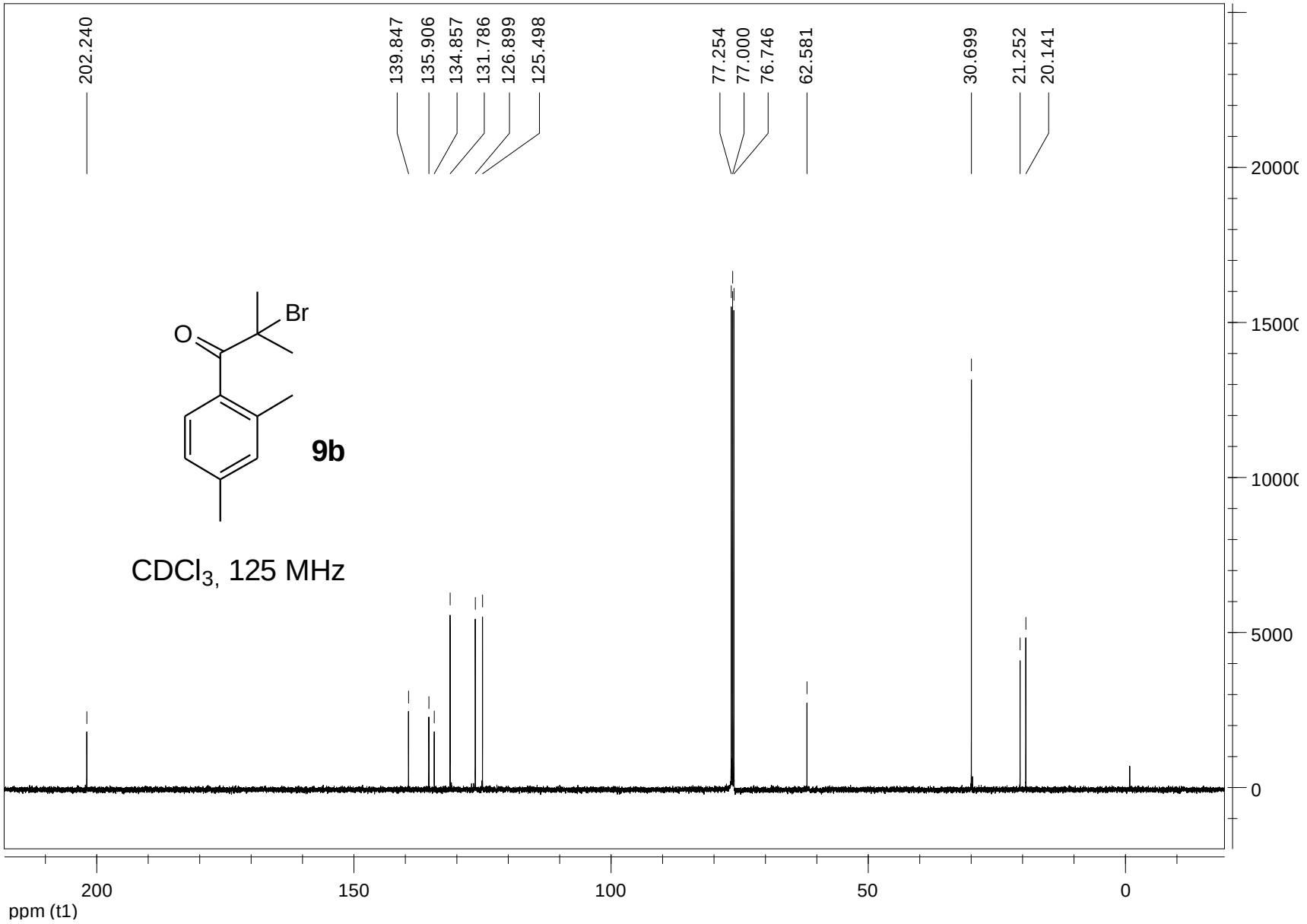

8.013
7.997
7.516
7.500
7.261
5.279
5.266
5.253
5.239
4.504
1.911
1.898
Br
O
CH2Br
7a
CDCl3, 500 MHz
2.00
1.98
1.04
2.01
3.10
15000
10000
5000
0
15.0
10.0
5.0
0.0
ppm (t1)

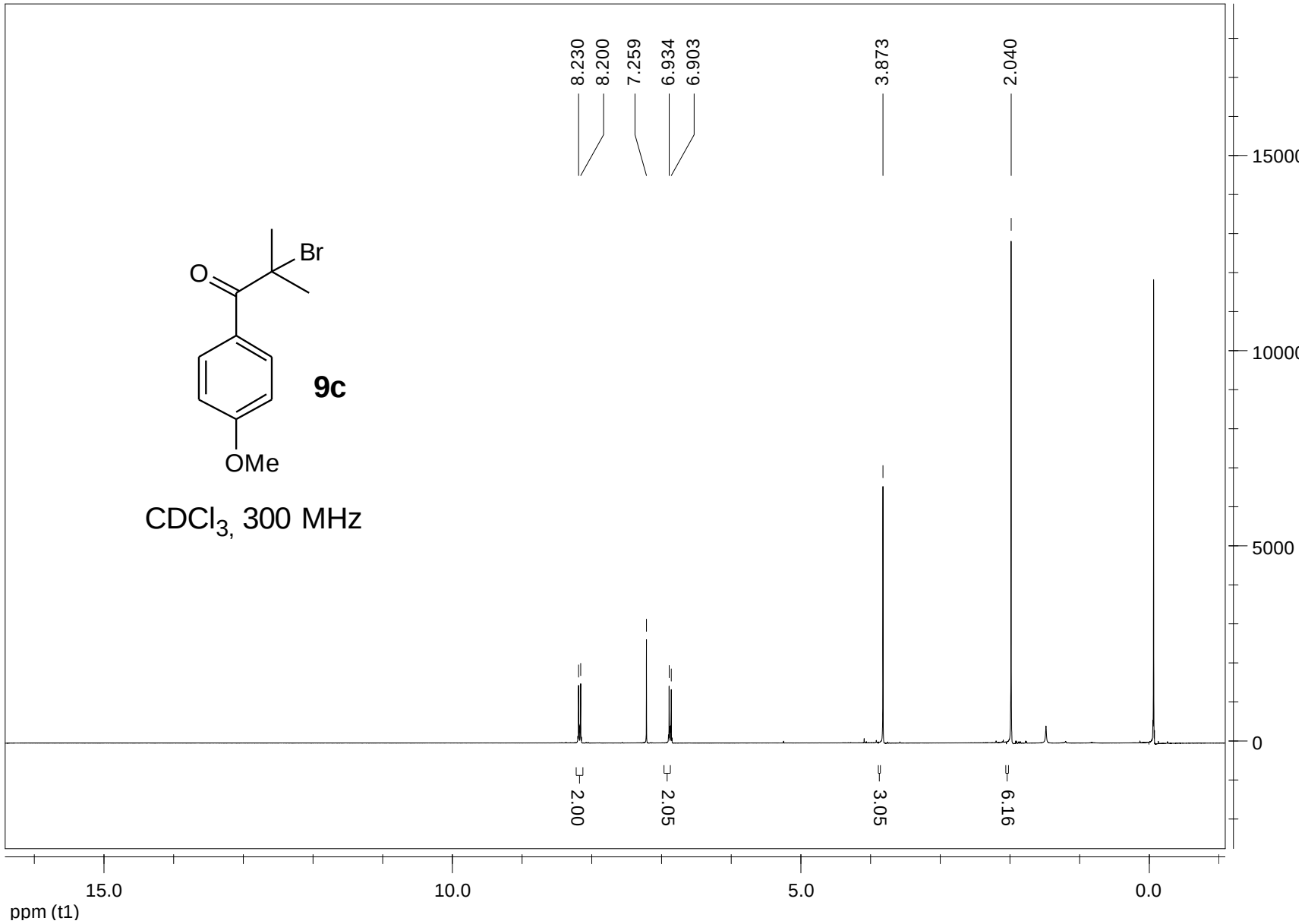

192.567
143.386
133.810
129.447
129.364
77.254
77.000
76.746
41.409
31.925
20.043
129.447
129.364
129.60 129.50 129.40 129.30 129.20
ppm (t1)
Br
O
7a
CH2Br
CDCl3, 125 MHz
200
150
100
50
0
ppm (t1)

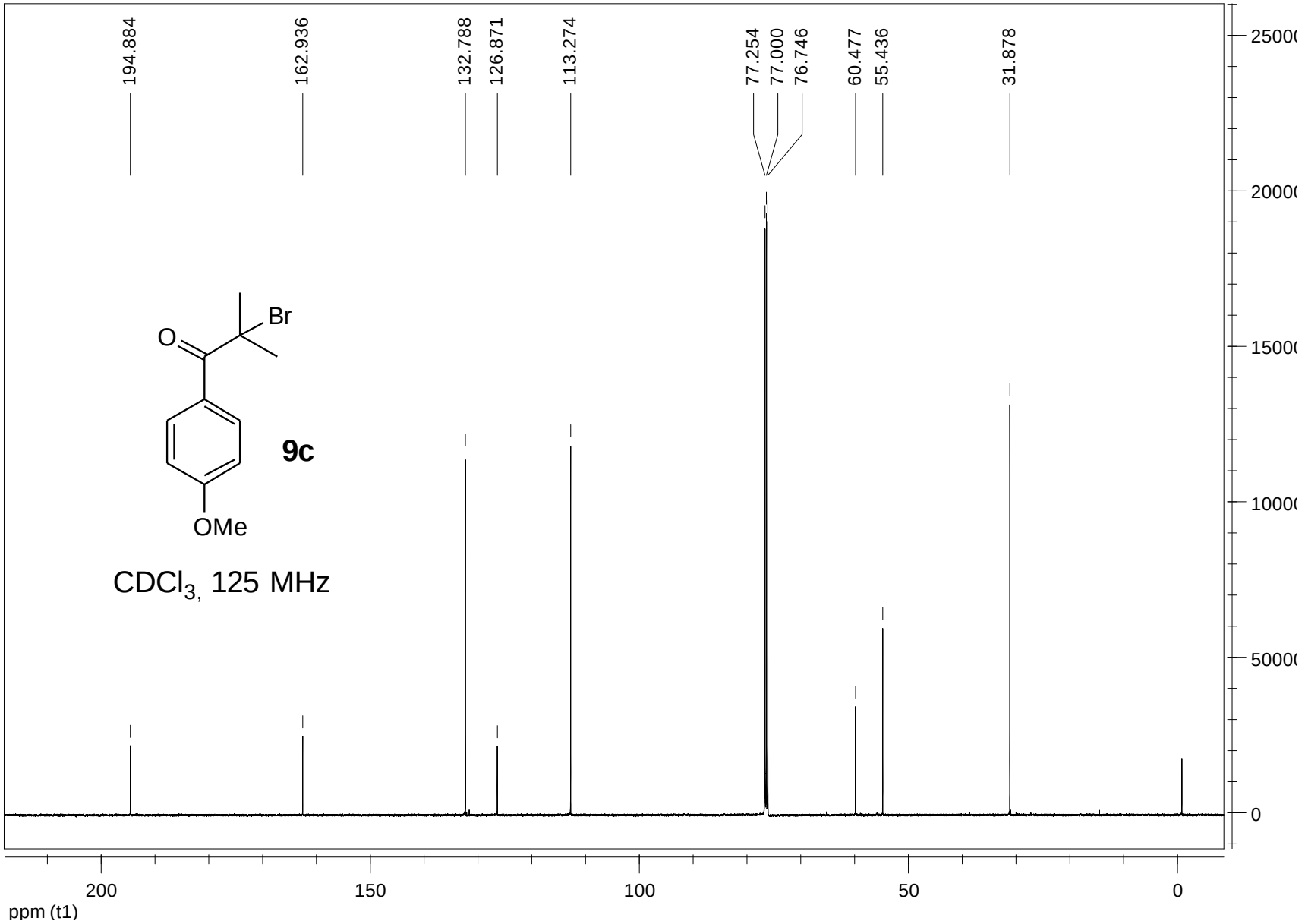

8.083
8.067
7.260
7.245
7.228
2.410
2.035
Br
O
9a
CDCl3, 500 MHz
2.00
2.00
3.10
6.14
80000
70000
60000
50000
40000
30000
20000
10000
0
-1000
15.0
10.0
5.0
0.0
ppm (t1)

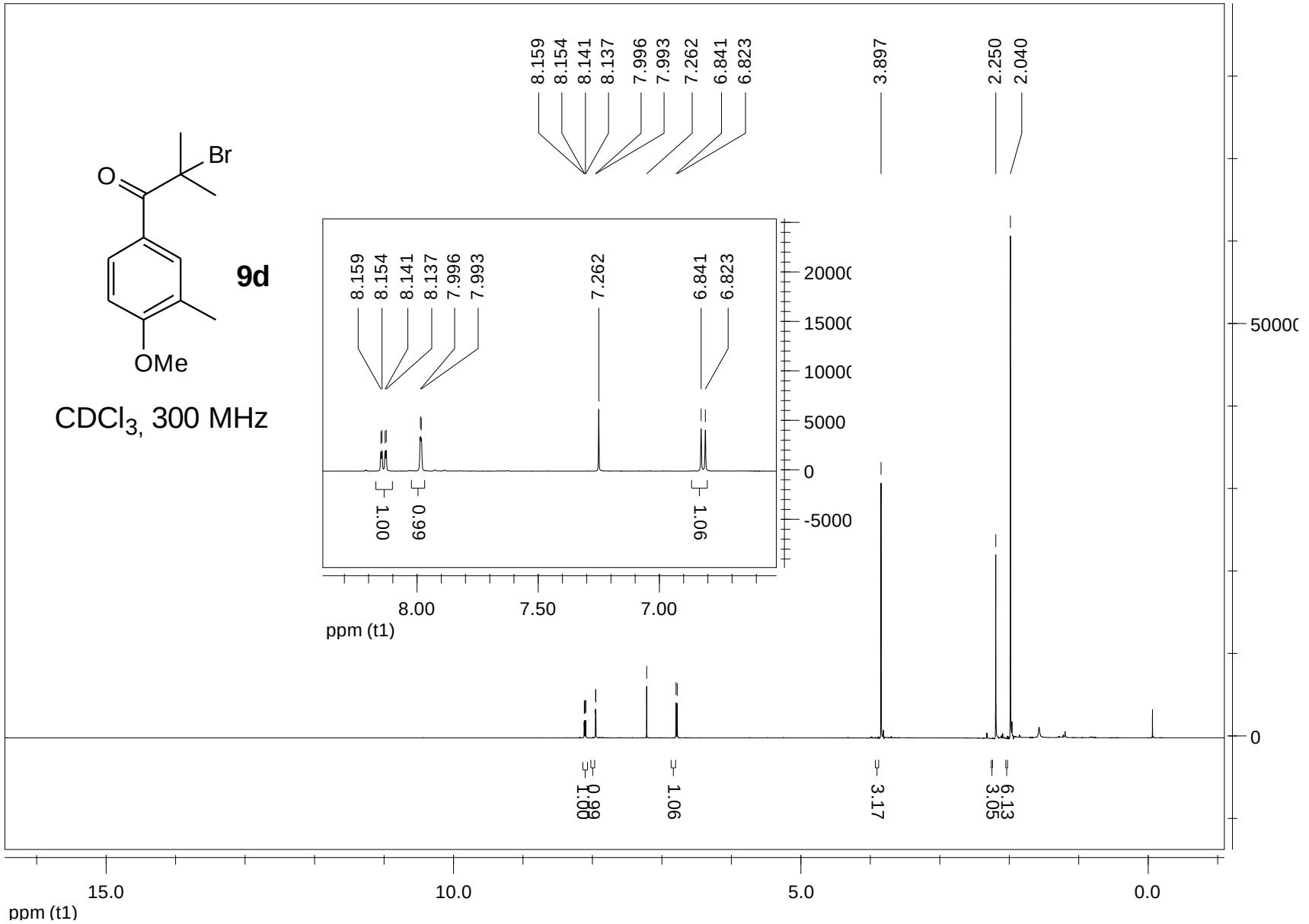

196.313
143.235
131.924
130.356
128.801
77.254
77.000
76.746
60.452
31.681
21.569
Br
O
9a
CDCl3, 125 MHz
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)

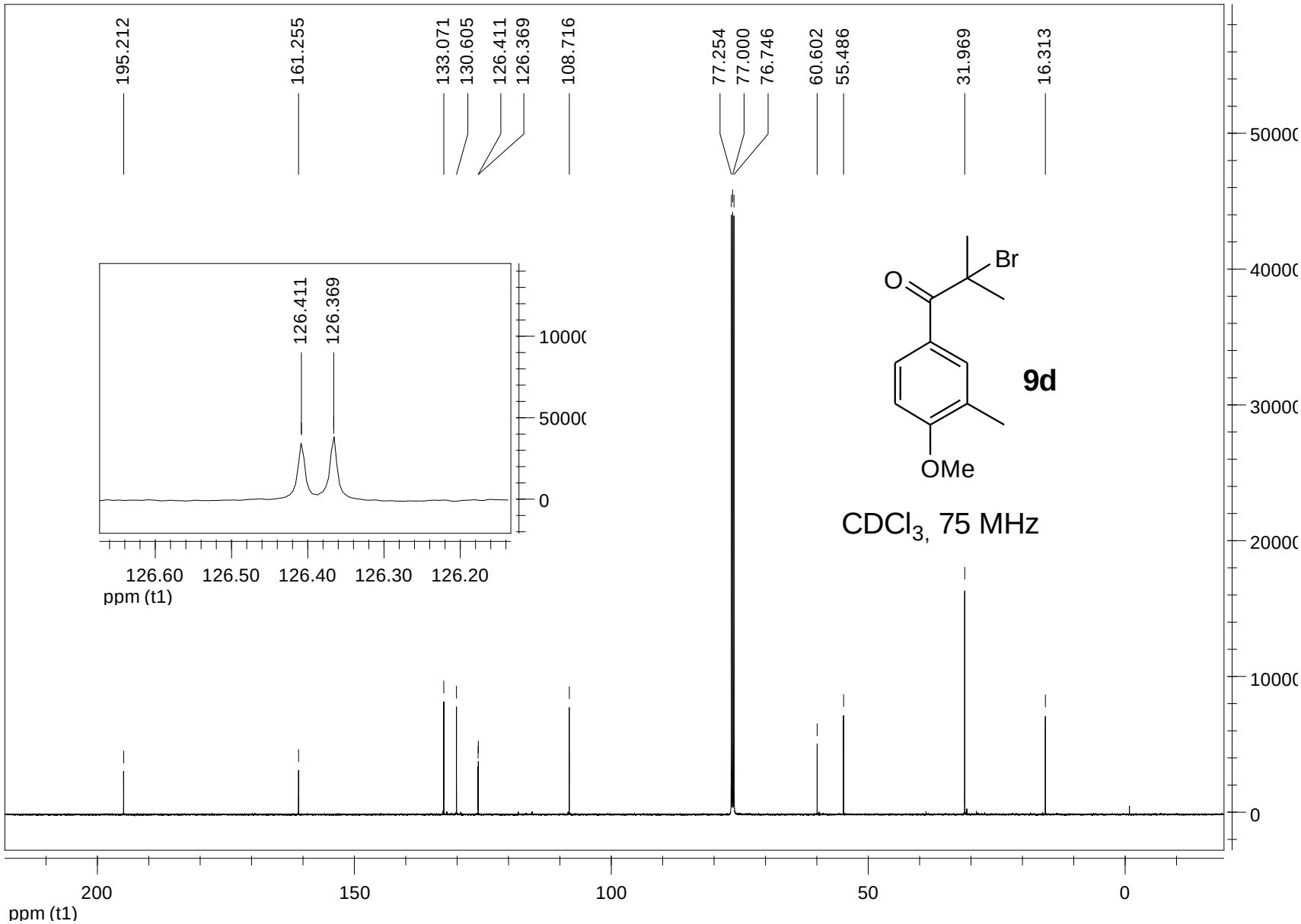

7.607
7.591
7.258
7.062
7.009
6.993
2.340
2.259
1.967
O
Br
9b
CDCl3, 500 MHz
1.00
1.02
0.98
ppm (t1)
7.50
7.00
20000
15000
10000
5000
0
-5000
50000
0
1.00
0.98
3.04
6.19
15.0
10.0
5.0
0.0
ppm (t1)

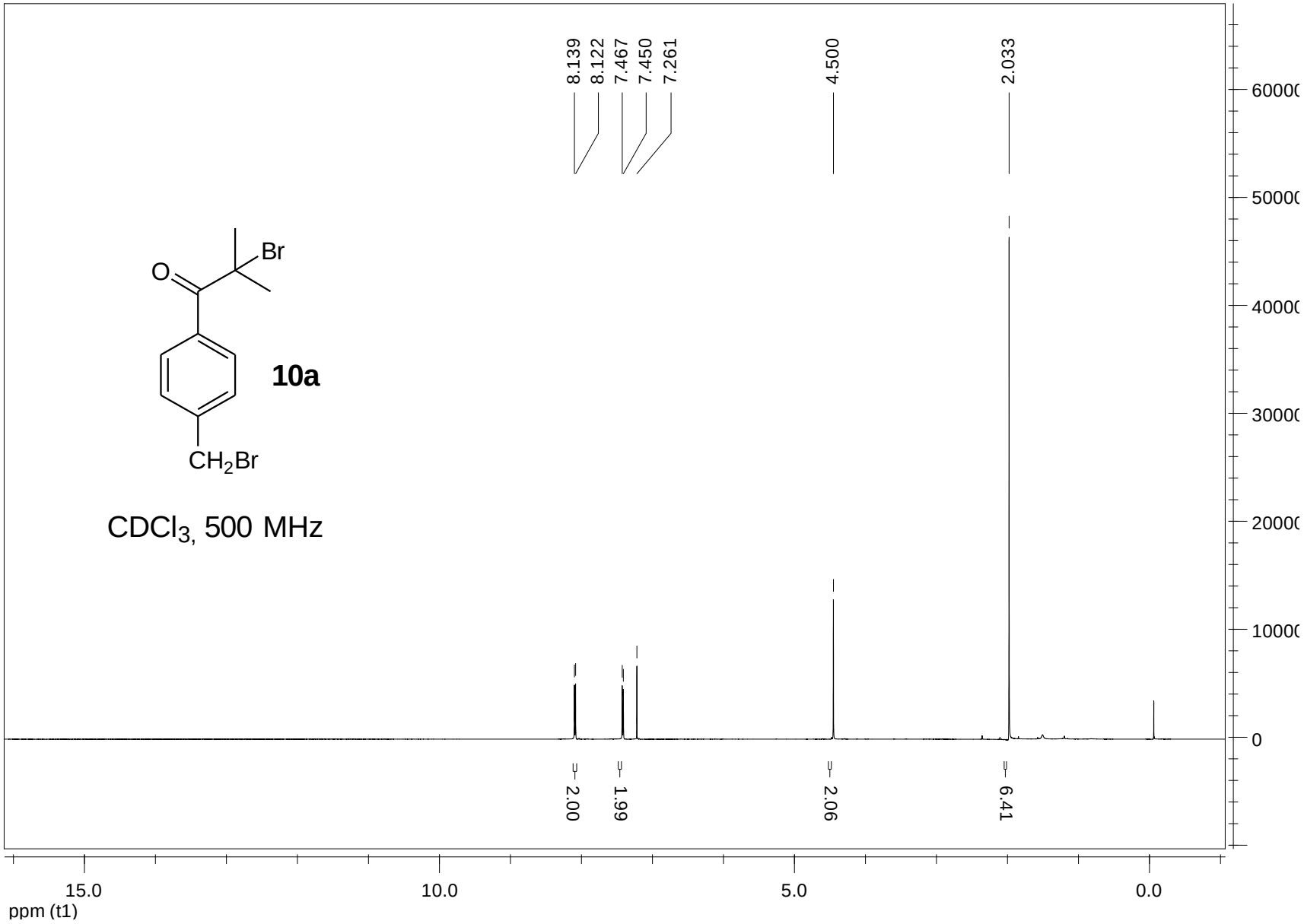

202.240
139.847
135.906
134.857
131.786
126.899
125.498
77.254
77.000
76.746
62.581
30.699
21.252
20.141
Br
O
9b
CDCl3, 125 MHz
20000
15000
10000
5000
0
200
150
100
50
0
ppm (t1)

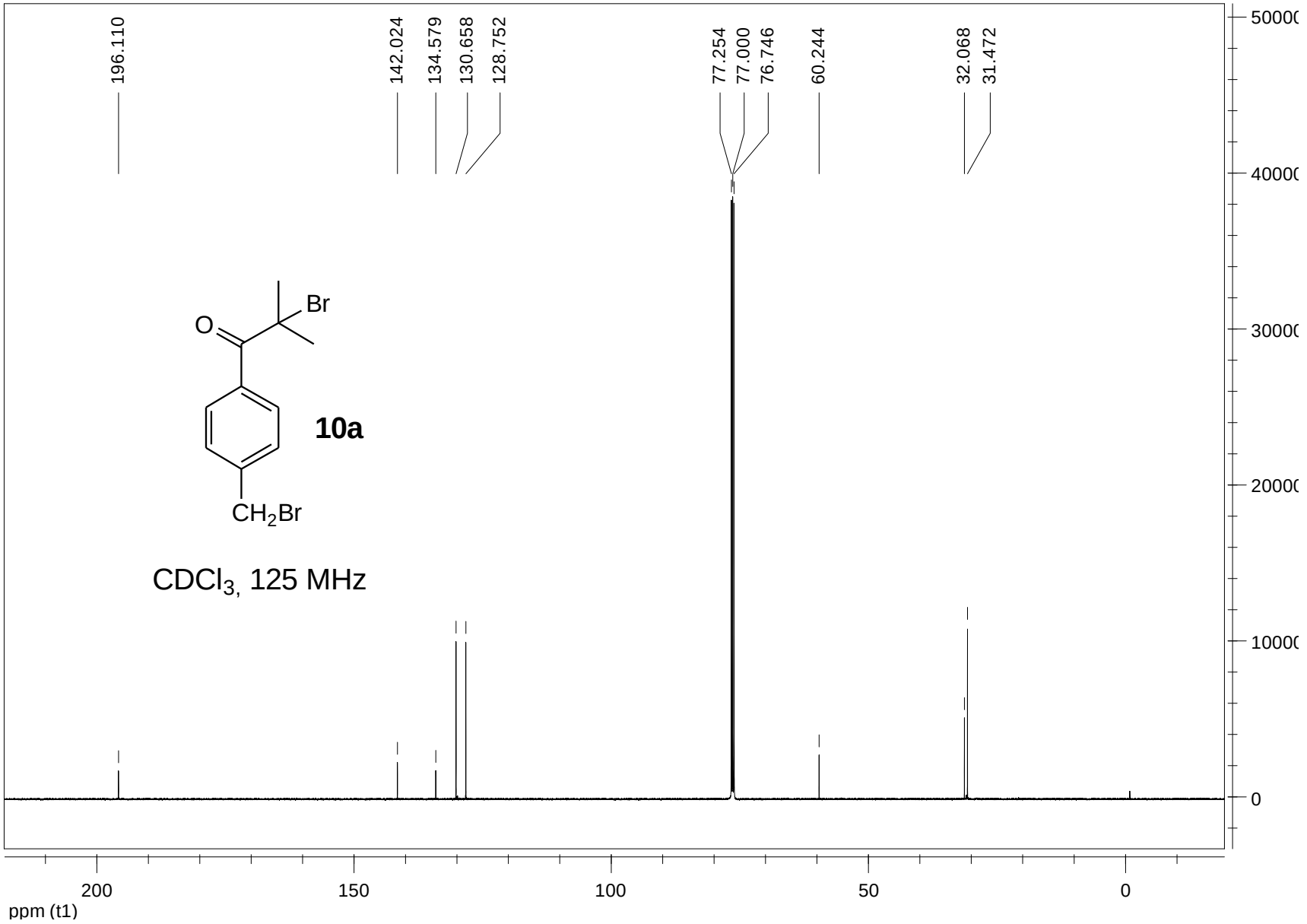

8.230
8.200
7.259
6.934
6.903
3.873
2.040
O
Br
OMe
9c
CDCl3, 300 MHz
2.00
2.05
3.05
6.16
15000
10000
5000
0
15.0
10.0
5.0
0.0
ppm (t1)

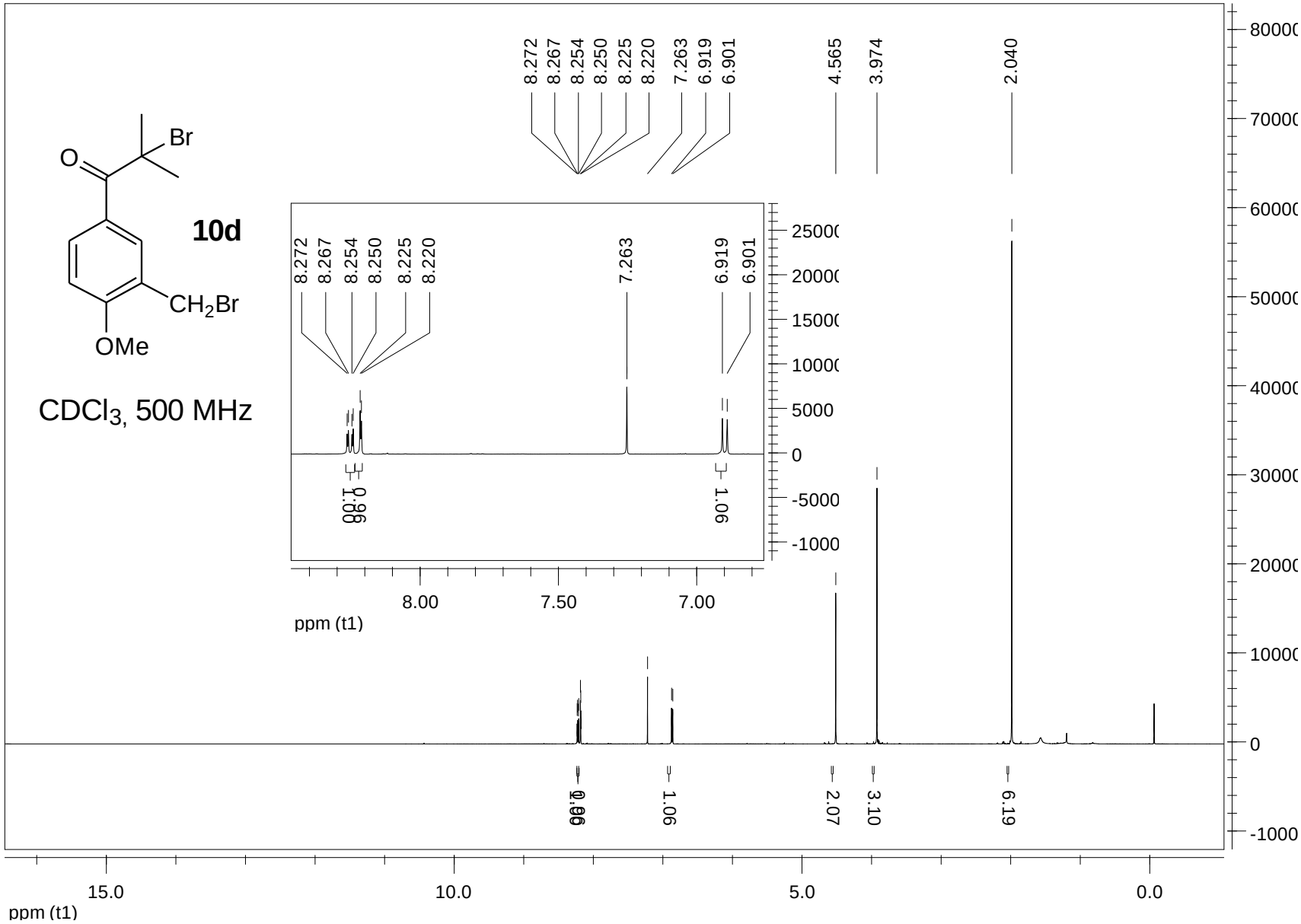

194.884
162.936
132.788
126.871
113.274
77.254
77.000
76.746
60.477
55.436
31.878
Br
O
OMe
9c
CDCl3, 125 MHz
2500
2000
1500
1000
5000
0
200
150
100
50
0
ppm (t1)

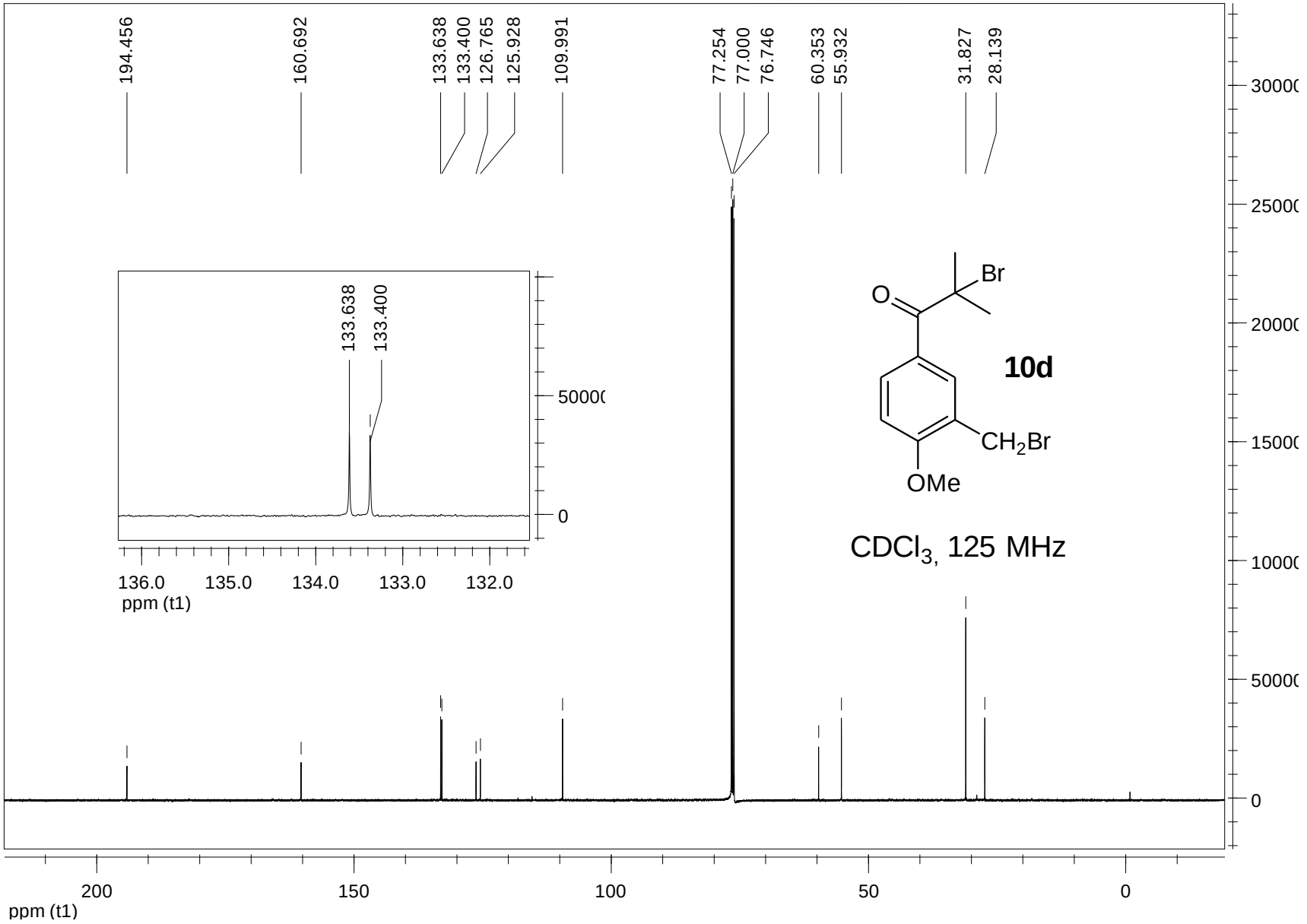

Br
O
OMe
9d
CDCl3, 300 MHz
8.159
8.154
8.141
8.137
7.996
7.993
7.262
6.841
6.823
3.897
2.250
2.040
1.00
0.99
1.06
3.17
6.13
3.05
ppm (t1)

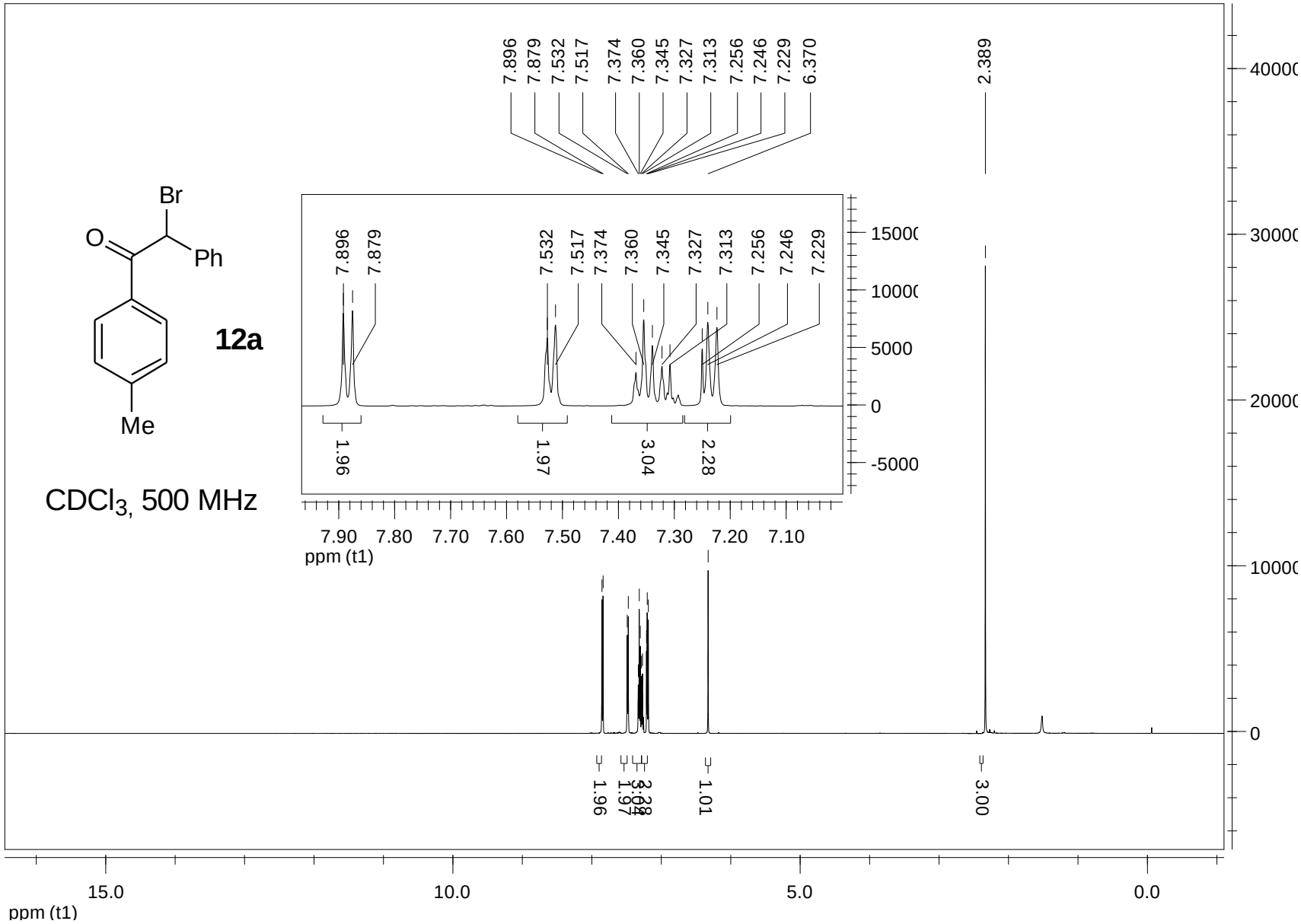

195.212
161.255
133.071
130.605
126.411
126.369
108.716
77.254
77.000
76.746
60.602
55.486
31.969
16.313
126.411
126.369
126.60
126.50
126.40
126.30
126.20
ppm (t1)
Br
O
OMe
9d
CDCl3, 75 MHz
200
150
100
50
0
ppm (t1)

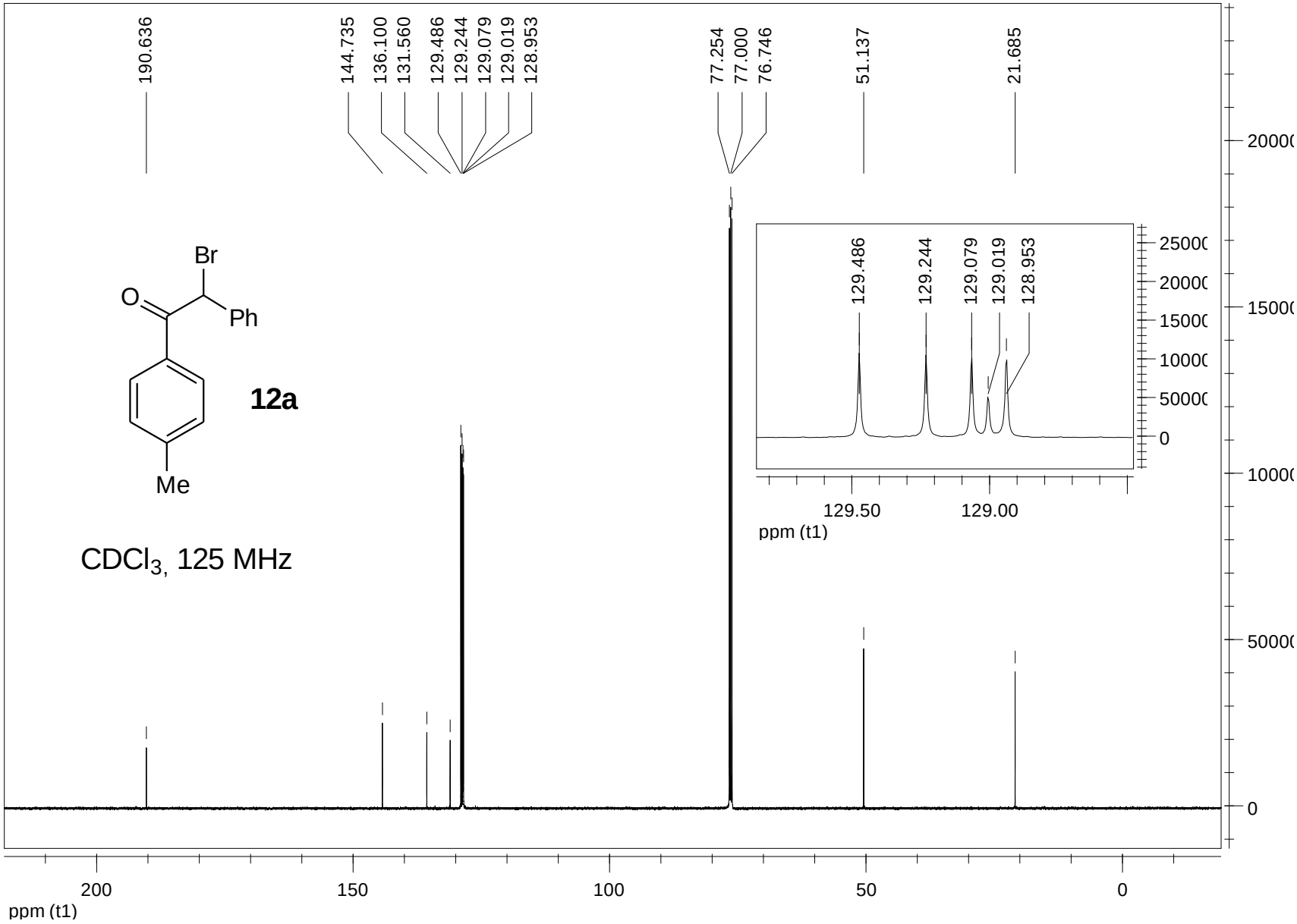

8.139
8.122
7.467
7.450
7.261
4.500
2.033
O
Br
CH2Br
10a
CDCl3, 500 MHz
2.00
1.99
2.06
6.41
60000
50000
40000
30000
20000
10000
0
15.0
10.0
5.0
0.0
ppm (t1)

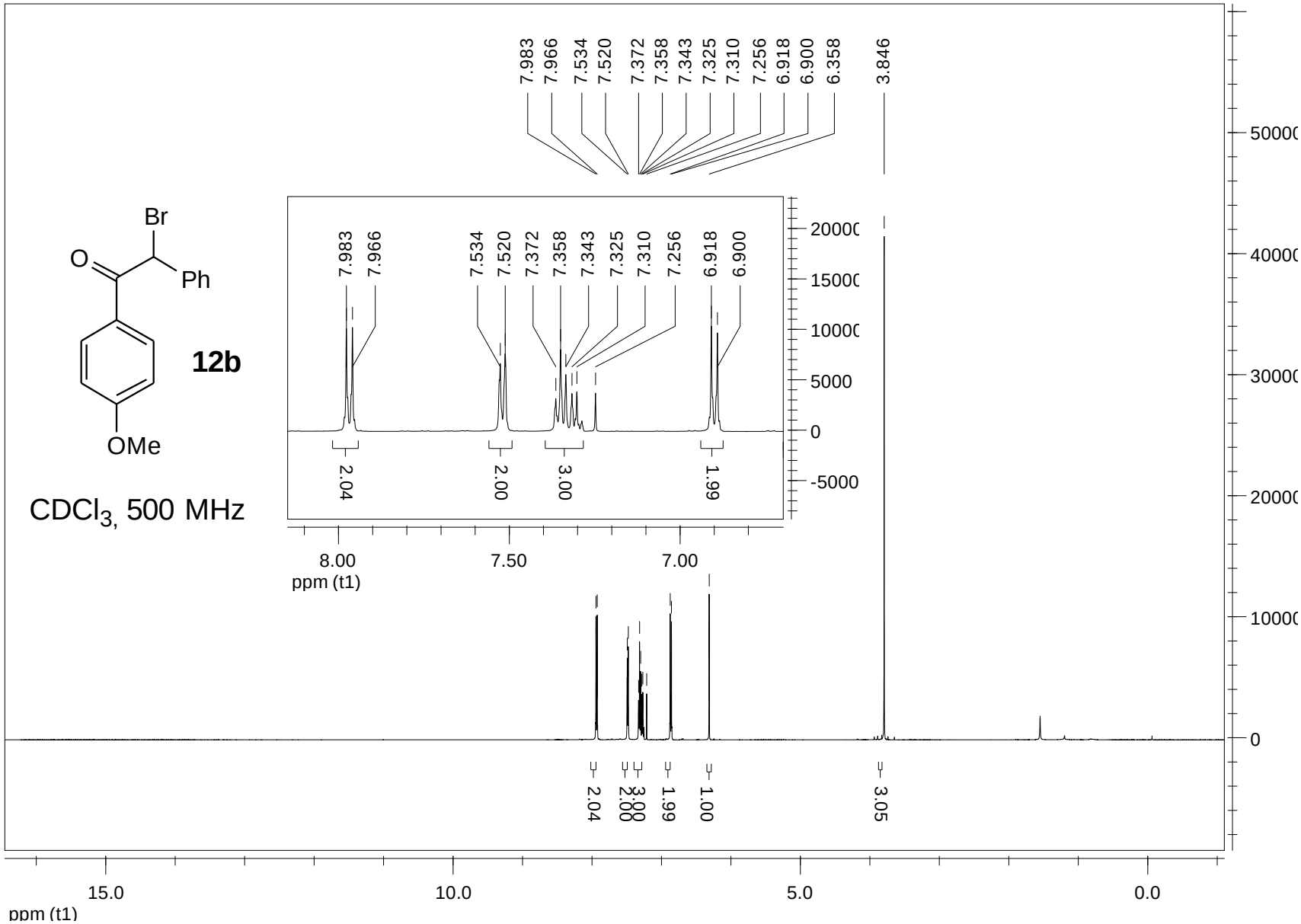

196.110
142.024
134.579
130.658
128.752
77.254
77.000
76.746
60.244
32.068
31.472
Br
O
CH2Br
10a
CDCl3, 125 MHz
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)

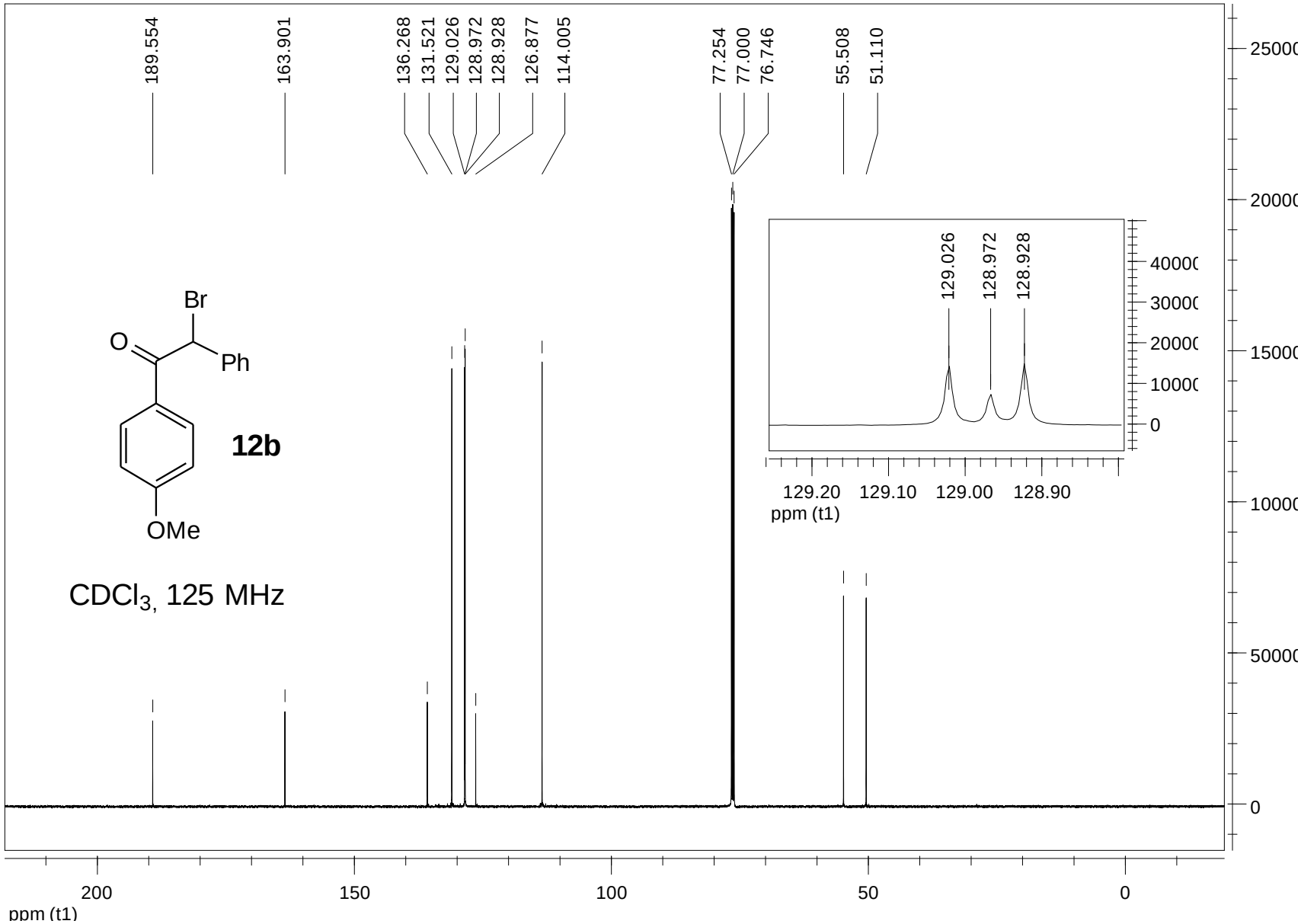

Br
O
10d
CH2Br
OMe
CDCl3, 500 MHz
8.272
8.267
8.254
8.250
8.225
8.220
7.263
6.919
6.901
4.565
3.974
2.040
1.06
1.06
1.06
2.07
3.10
6.19
ppm (t1)
15.0
10.0
5.0
0.0

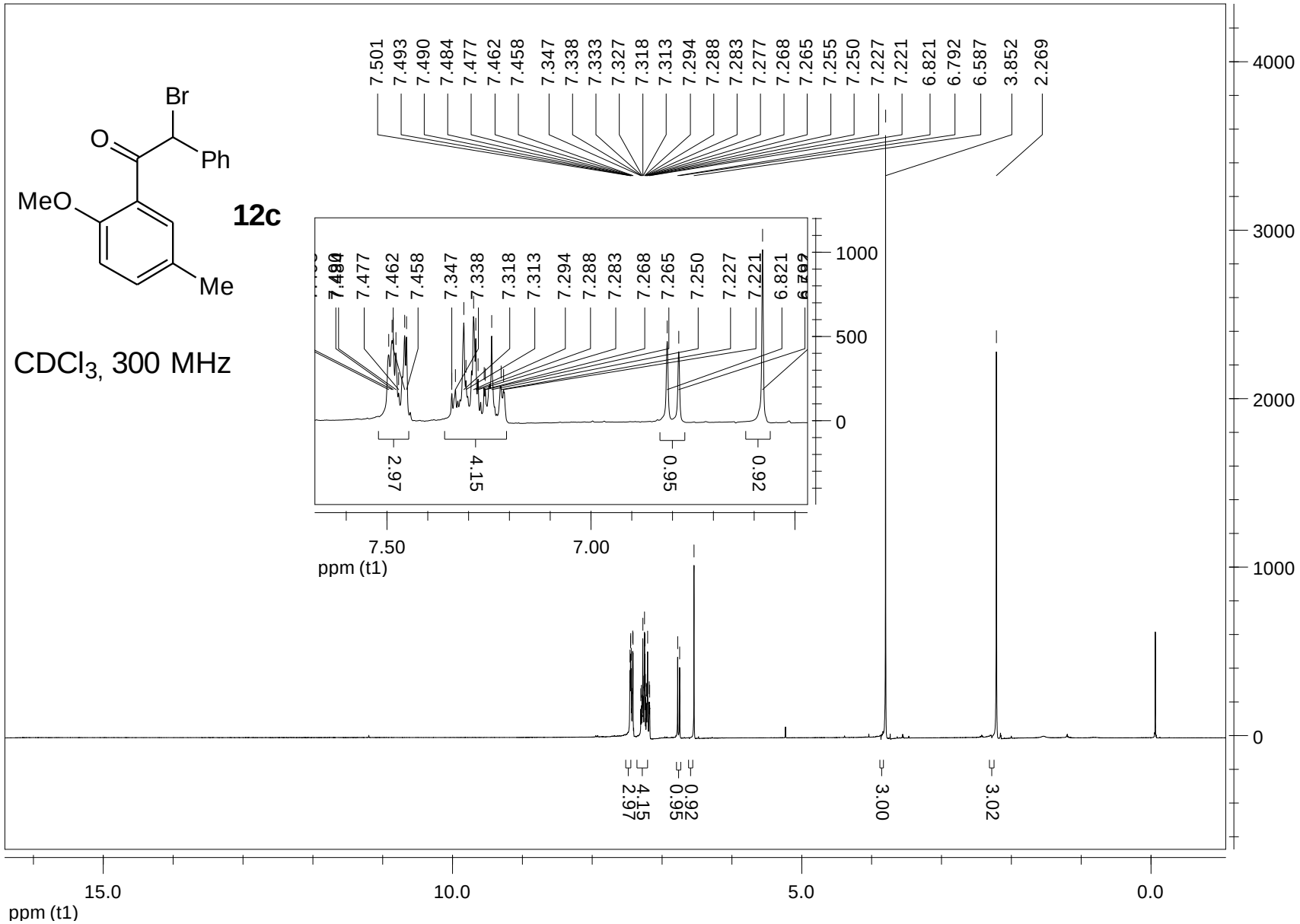

194.456
160.692
133.638
133.400
126.765
125.928
109.991
77.254
77.000
76.746
60.353
55.932
31.827
28.139
133.638
133.400
5000(
0
136.0
135.0
134.0
133.0
132.0
ppm (t1)
O
Br
10d
CH2Br
OMe
CDCl3, 125 MHz
30000
25000
20000
15000
10000
5000(
0
200
150
100
50
0
ppm (t1)

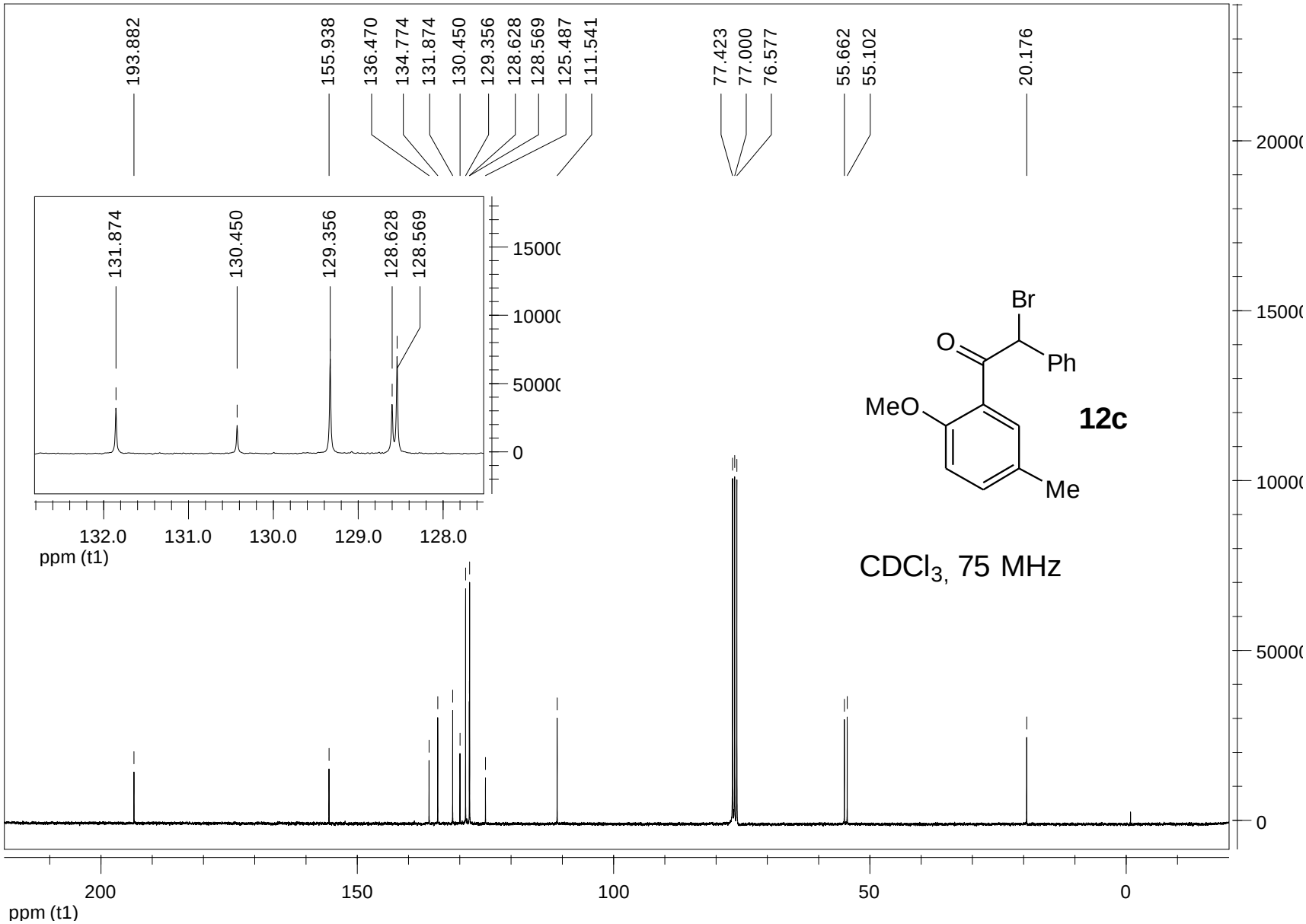

Br
O
Ph
Me
12a
CDCl3, 500 MHz
7.896
7.879
7.532
7.517
7.374
7.360
7.345
7.327
7.313
7.256
7.246
7.229
6.370
2.389
1.96
1.97
3.04
2.28
1.01
3.00
ppm (t1)
15.0
10.0
5.0
0.0

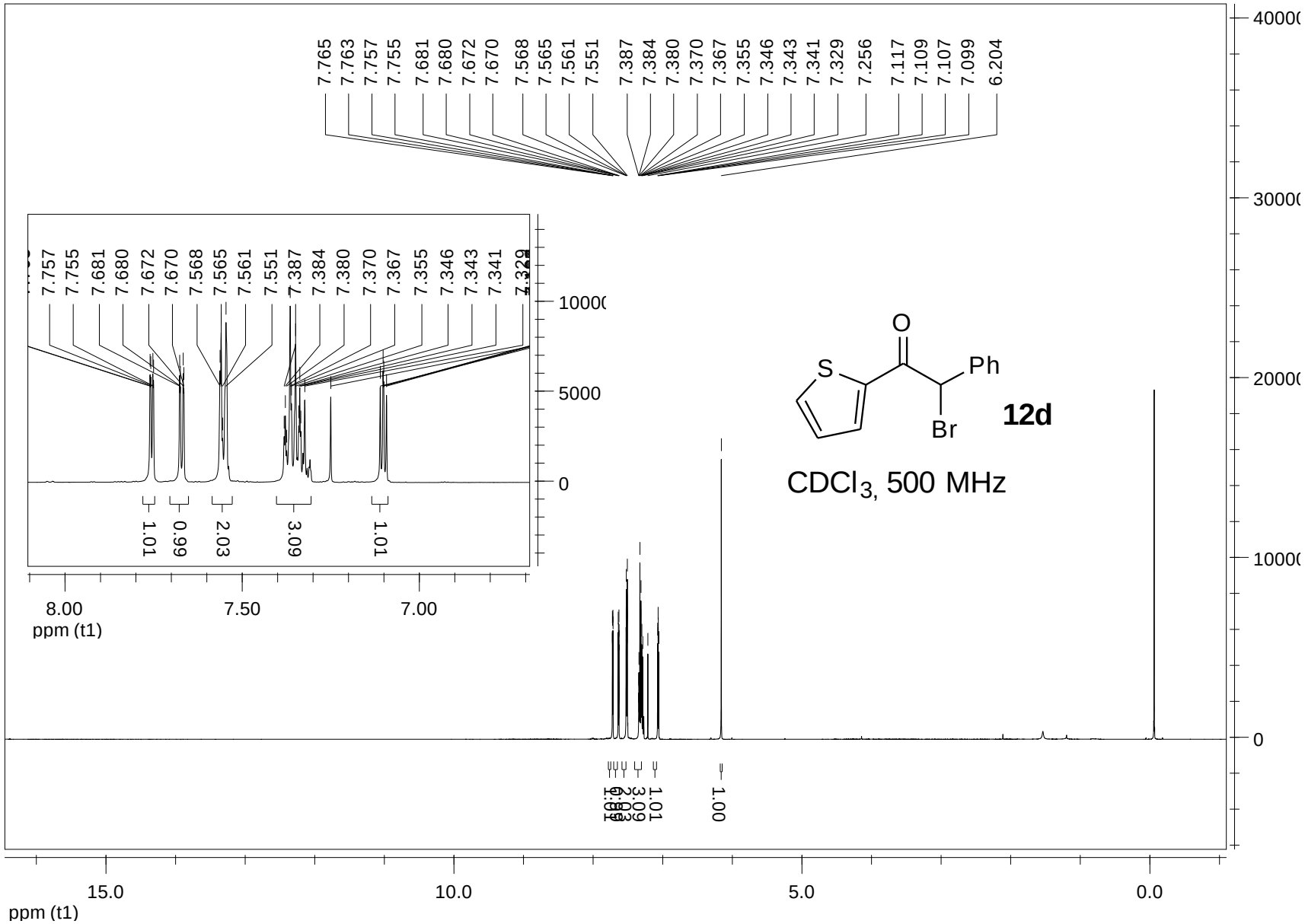

190.636
144.735
136.100
131.560
129.486
129.244
129.079
129.019
128.953
77.254
77.000
76.746
51.137
21.685
Br
O
Ph
Me
12a
CDCl3, 125 MHz
129.486
129.244
129.079
129.019
128.953
129.50
129.00
ppm (t1)
200
150
100
50
0
ppm (t1)

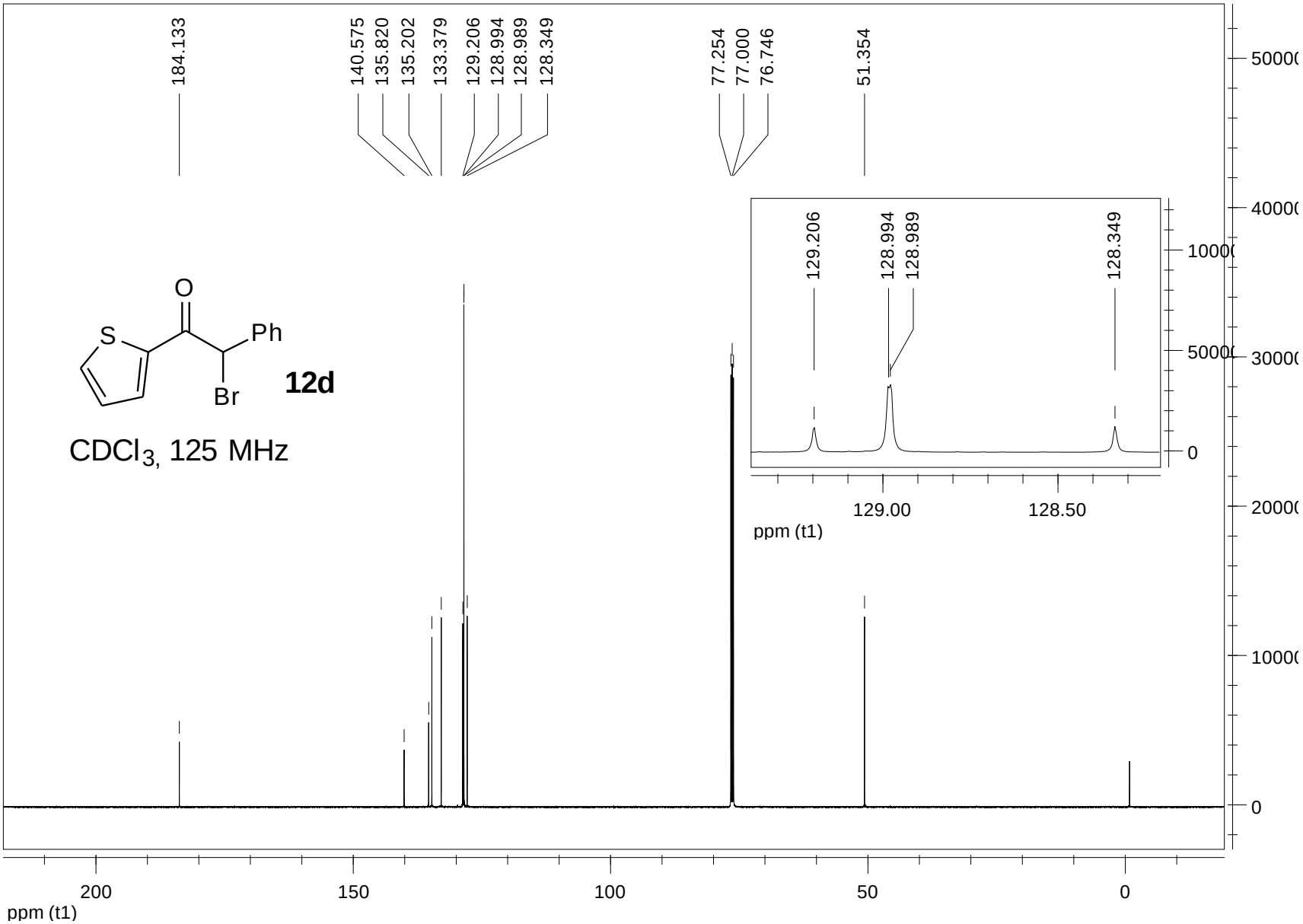

7.983
7.966
7.534
7.520
7.372
7.358
7.343
7.325
7.310
7.256
6.918
6.900
6.358
3.846
Br
O
Ph
OMe
12b
CDCl3, 500 MHz
2.04
2.00
3.00
1.99
8.00
7.50
7.00
ppm (t1)
2.04
3.00
1.99
1.00
3.05
15.0
10.0
5.0
0.0
ppm (t1)

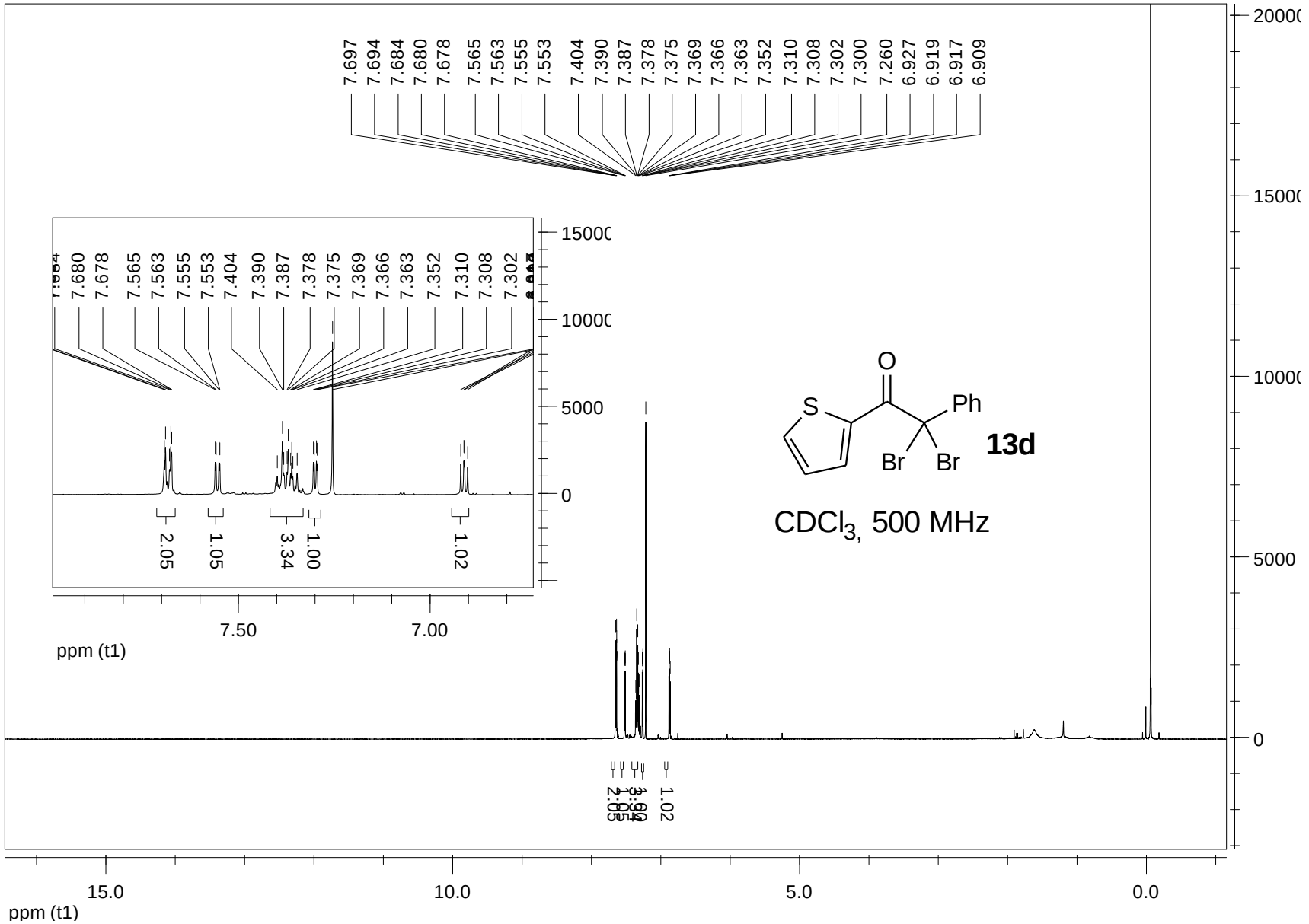

189.554
163.901
136.268
131.521
129.026
128.972
128.928
126.877
114.005
77.254
77.000
76.746
55.508
51.110
Br
O
Ph
OMe
12b
CDCl3, 125 MHz
129.026
128.972
128.928
129.20
129.10
129.00
128.90
ppm (t1)
200
150
100
50
0
ppm (t1)

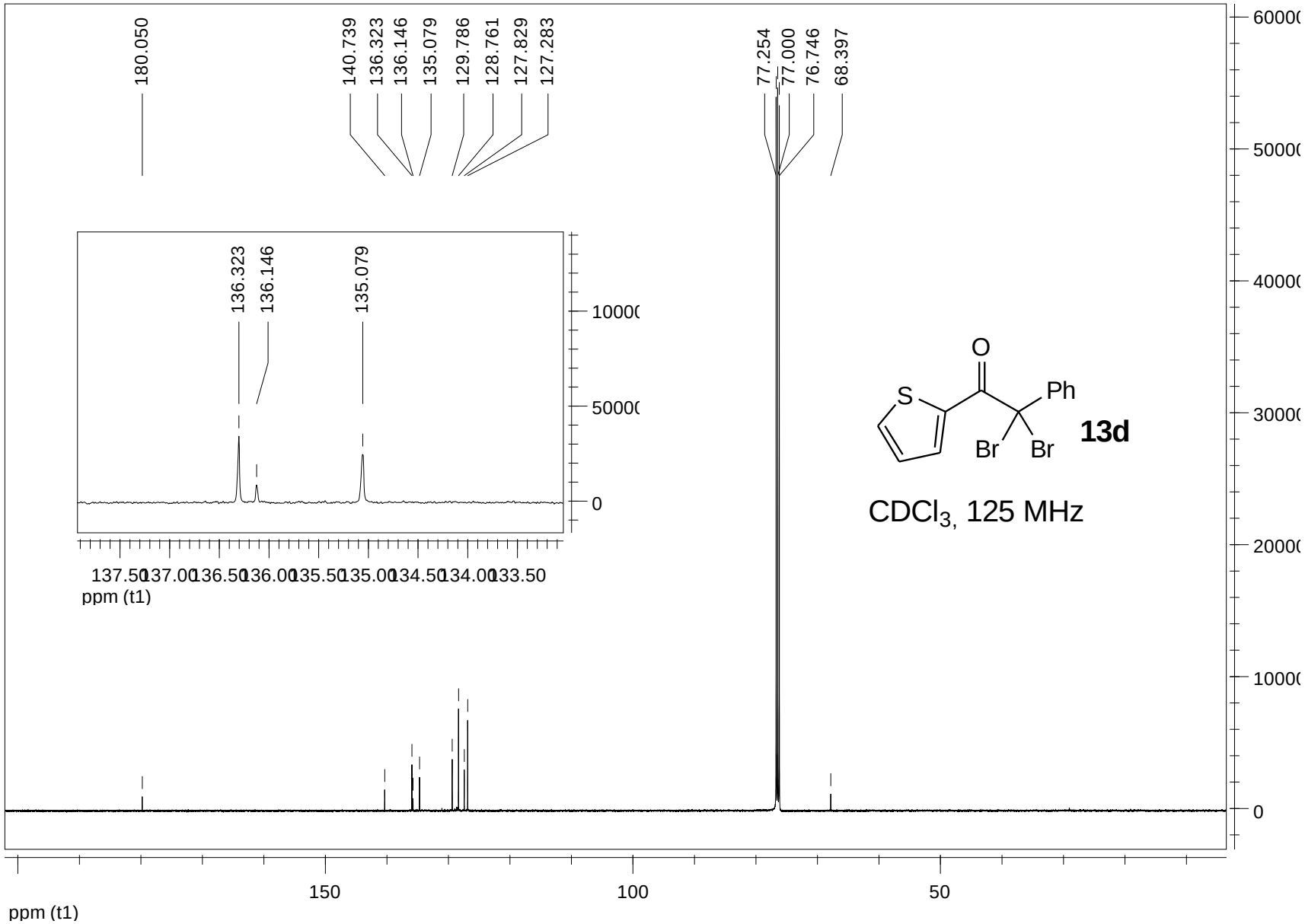

Br
O
Ph
MeO
Me
12c
CDCl3, 300 MHz
7.501
7.493
7.490
7.484
7.477
7.462
7.458
7.347
7.338
7.333
7.327
7.318
7.313
7.294
7.288
7.283
7.277
7.268
7.265
7.255
7.250
7.227
7.221
6.821
6.792
6.587
3.852
2.269
4000
3000
2000
1000
0
1000
500
0
2.97
4.15
0.95
0.92
7.50
7.00
ppm (t1)
2.97
4.15
0.95
0.92
3.00
3.02
15.0
10.0
5.0
0.0
ppm (t1)

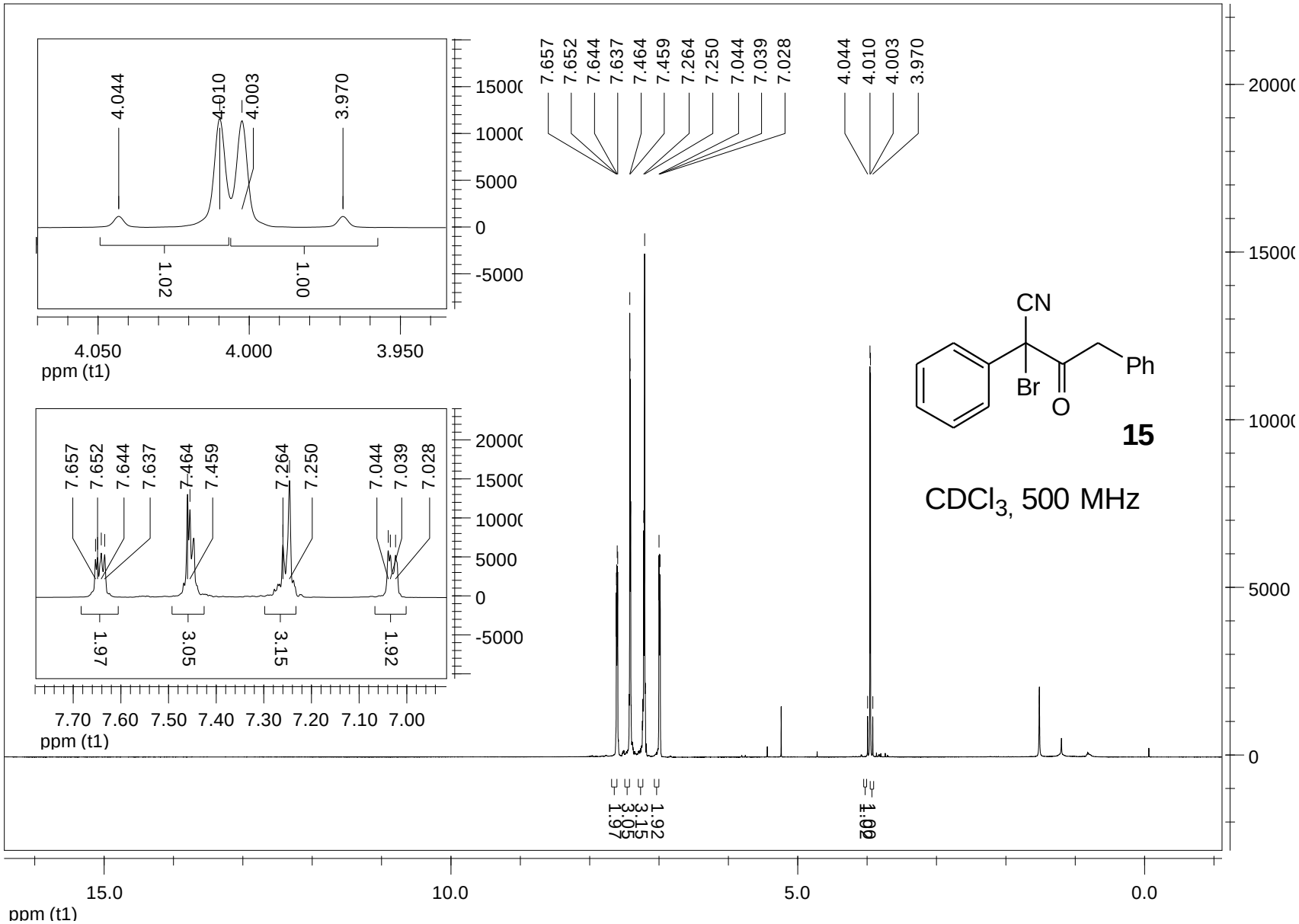

193.882
155.938
136.470
134.774
131.874
130.450
129.356
128.628
128.569
125.487
111.541
77.423
77.000
76.577
55.662
55.102
20.176
131.874
130.450
129.356
128.628
128.569
132.0
131.0
130.0
129.0
128.0
ppm (t1)
Br
O
Ph
MeO
Me
12c
CDCl3, 75 MHz
200
150
100
50
0
ppm (t1)

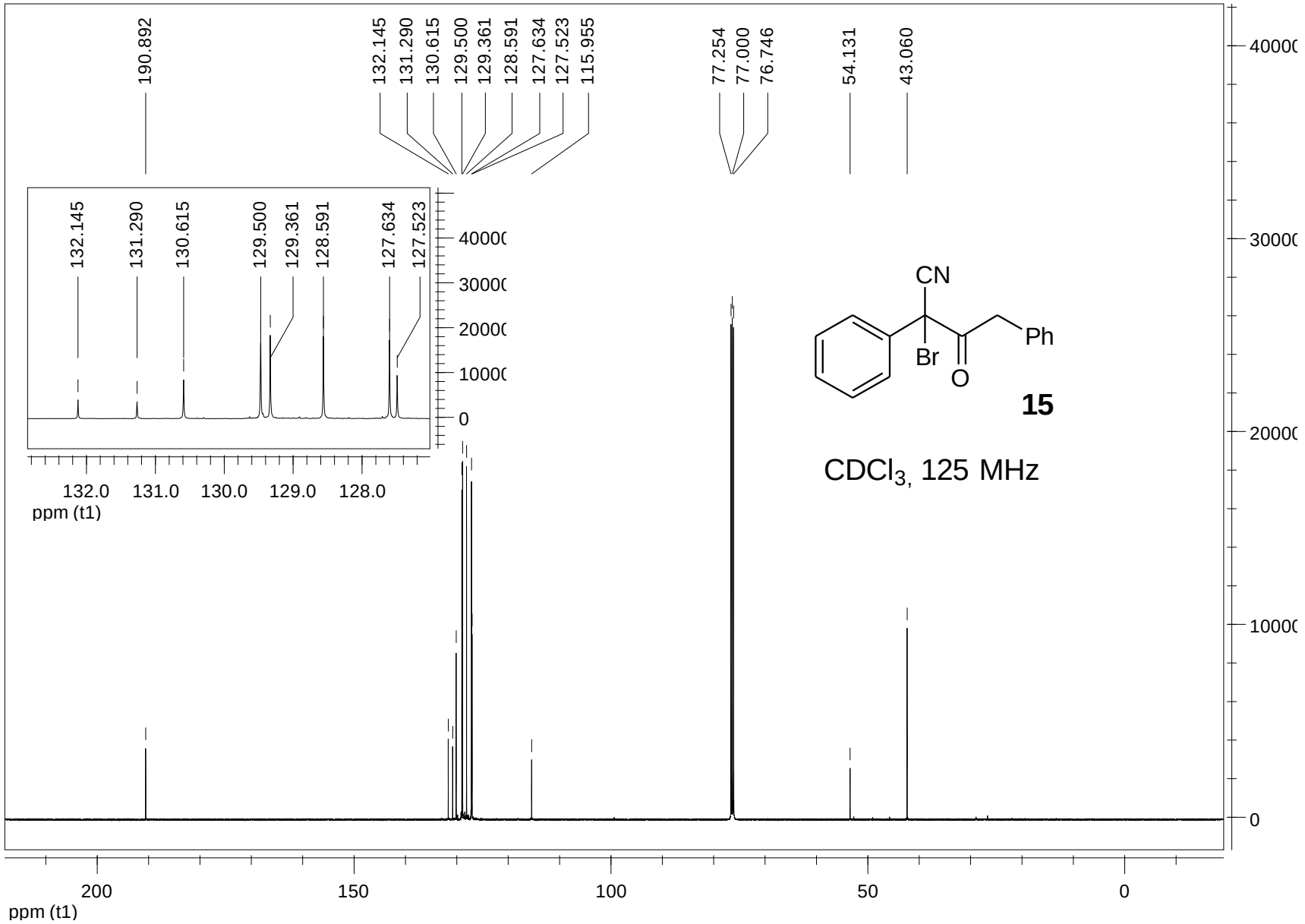

7.765
7.763
7.757
7.755
7.681
7.680
7.672
7.670
7.568
7.565
7.561
7.551
7.387
7.384
7.380
7.370
7.367
7.355
7.346
7.343
7.341
7.329
7.256
7.117
7.109
7.107
7.099
6.204
1.01
0.99
2.03
3.09
1.01
1.00
8.00
7.50
7.00
ppm (t1)
15.0
10.0
5.0
0.0
ppm (t1)
O
S
Ph
Br
12d
CDCl3, 500 MHz

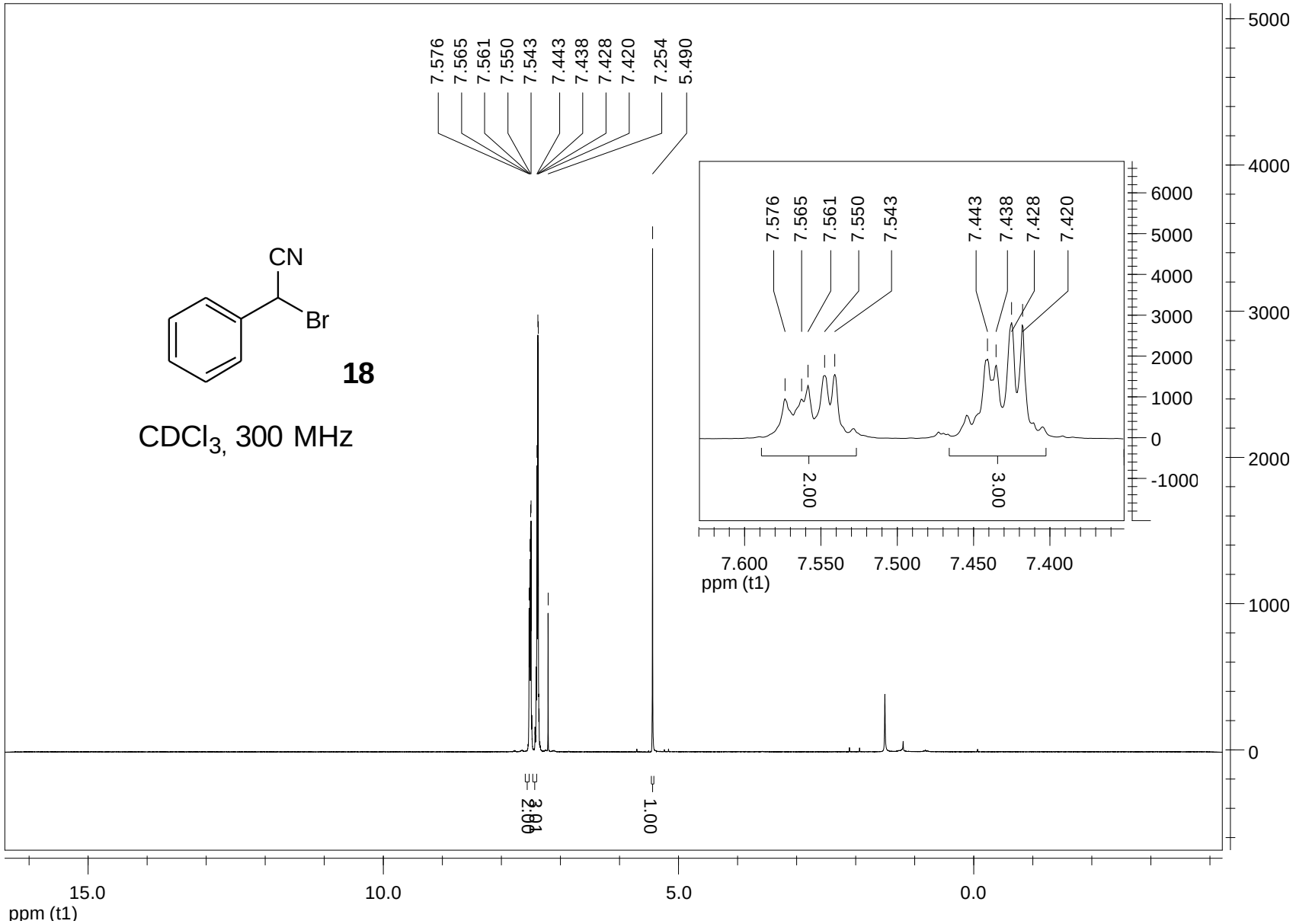

184.133
140.575
135.820
135.202
133.379
129.206
128.994
128.989
128.349
77.254
77.000
76.746
51.354
O
S
Ph
Br
12d
CDCl3, 125 MHz
129.206
128.994
128.989
128.349
129.00
128.50
ppm (t1)
200
150
100
50
0
ppm (t1)

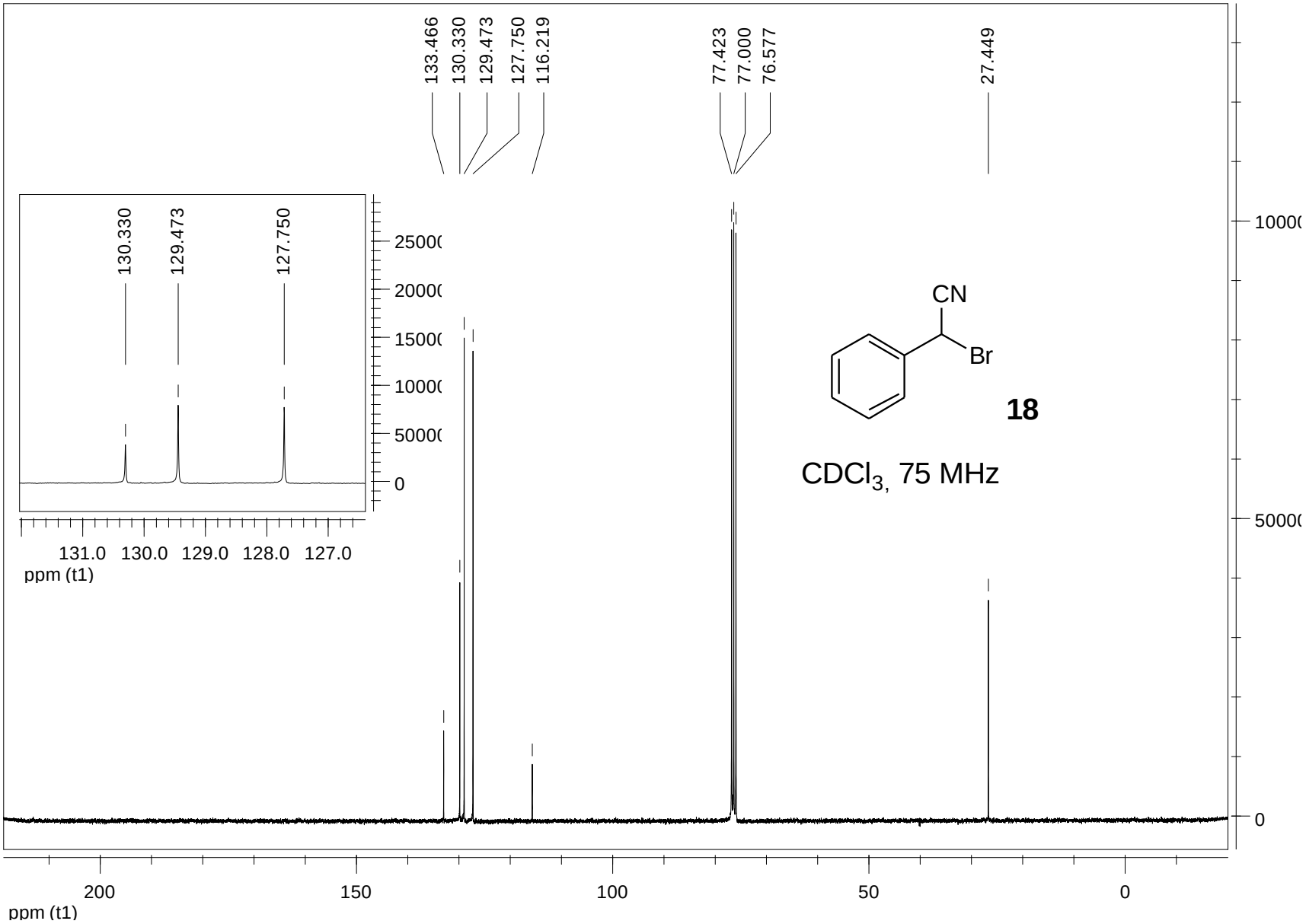

7.697
7.694
7.684
7.680
7.678
7.565
7.563
7.555
7.553
7.404
7.390
7.387
7.378
7.375
7.369
7.366
7.363
7.352
7.310
7.308
7.302
7.300
7.260
6.927
6.919
6.917
6.909
2.05
1.05
3.34
1.00
1.02
7.50
7.00
ppm (t1)
O
S
Ph
Br
Br
13d
CDCl3, 500 MHz
15.0
10.0
5.0
0.0
ppm (t1)

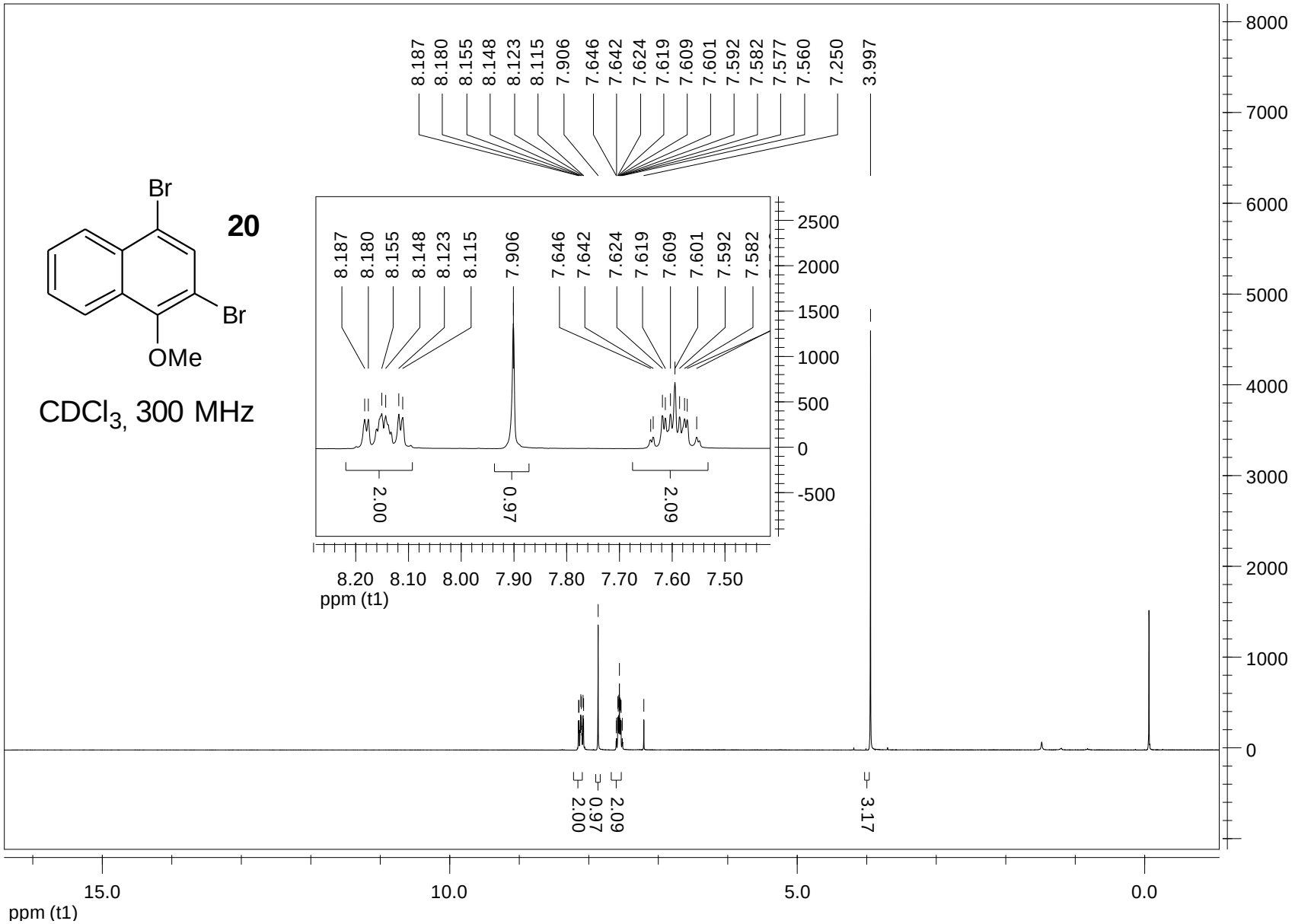

180.050
140.739
136.323
136.146
135.079
129.786
128.761
127.829
127.283
77.254
77.000
76.746
68.397
136.323
136.146
135.079
137.50
137.00
136.50
136.00
135.50
135.00
134.50
134.00
133.50
ppm (t1)
O
S
Ph
Br
Br
13d
CDCl3, 125 MHz
150
100
50
ppm (t1)

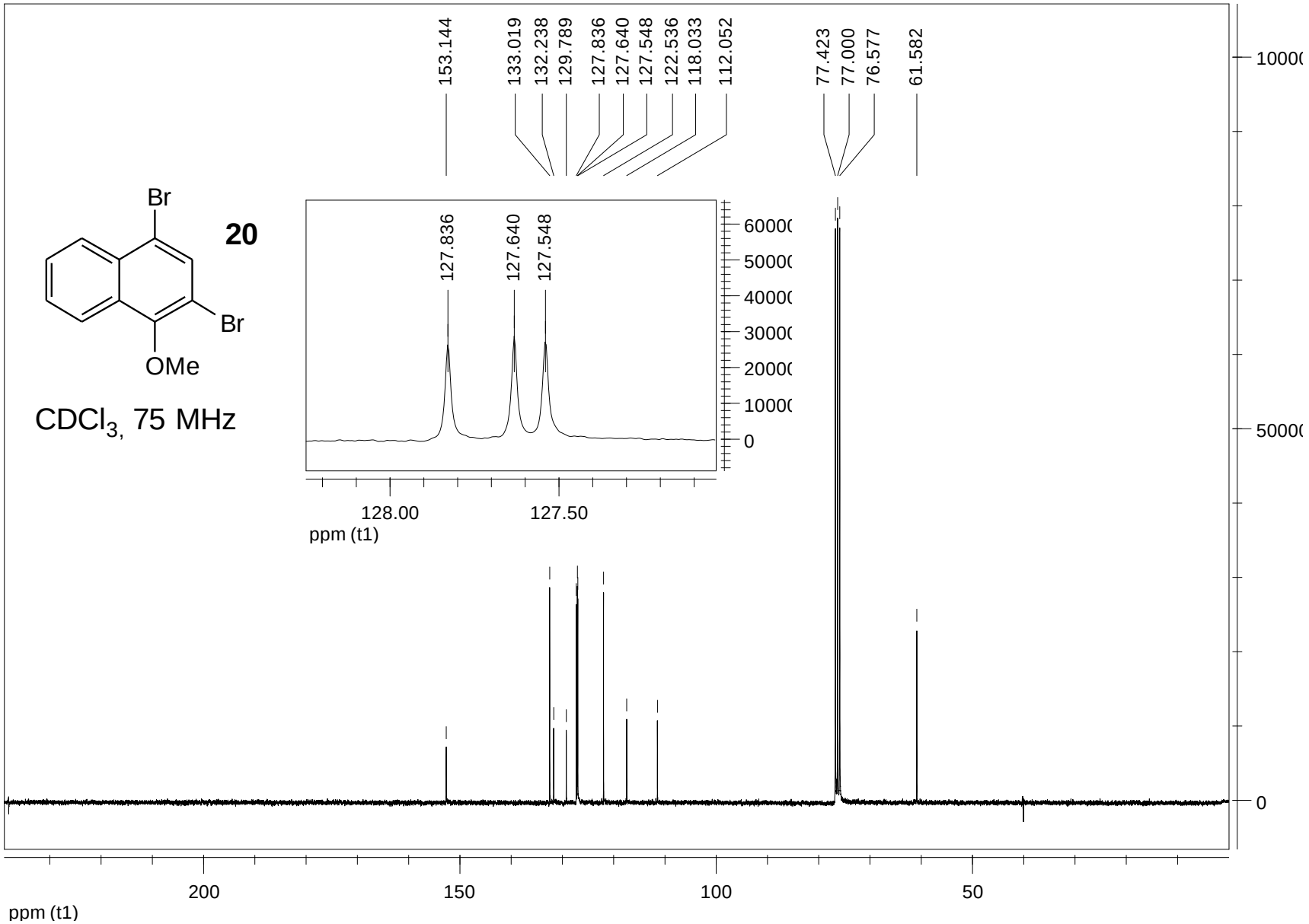

4.044
4.010
4.003
3.970
1.02
1.00
4.050
4.000
3.950
ppm (t1)
7.657
7.652
7.644
7.637
7.464
7.459
7.264
7.250
7.044
7.039
7.028
1.97
3.05
3.15
1.92
7.70 7.60 7.50 7.40 7.30 7.20 7.10 7.00
ppm (t1)
CN
Br
O
Ph
15
CDCl3, 500 MHz
15.0
10.0
5.0
0.0
ppm (t1)

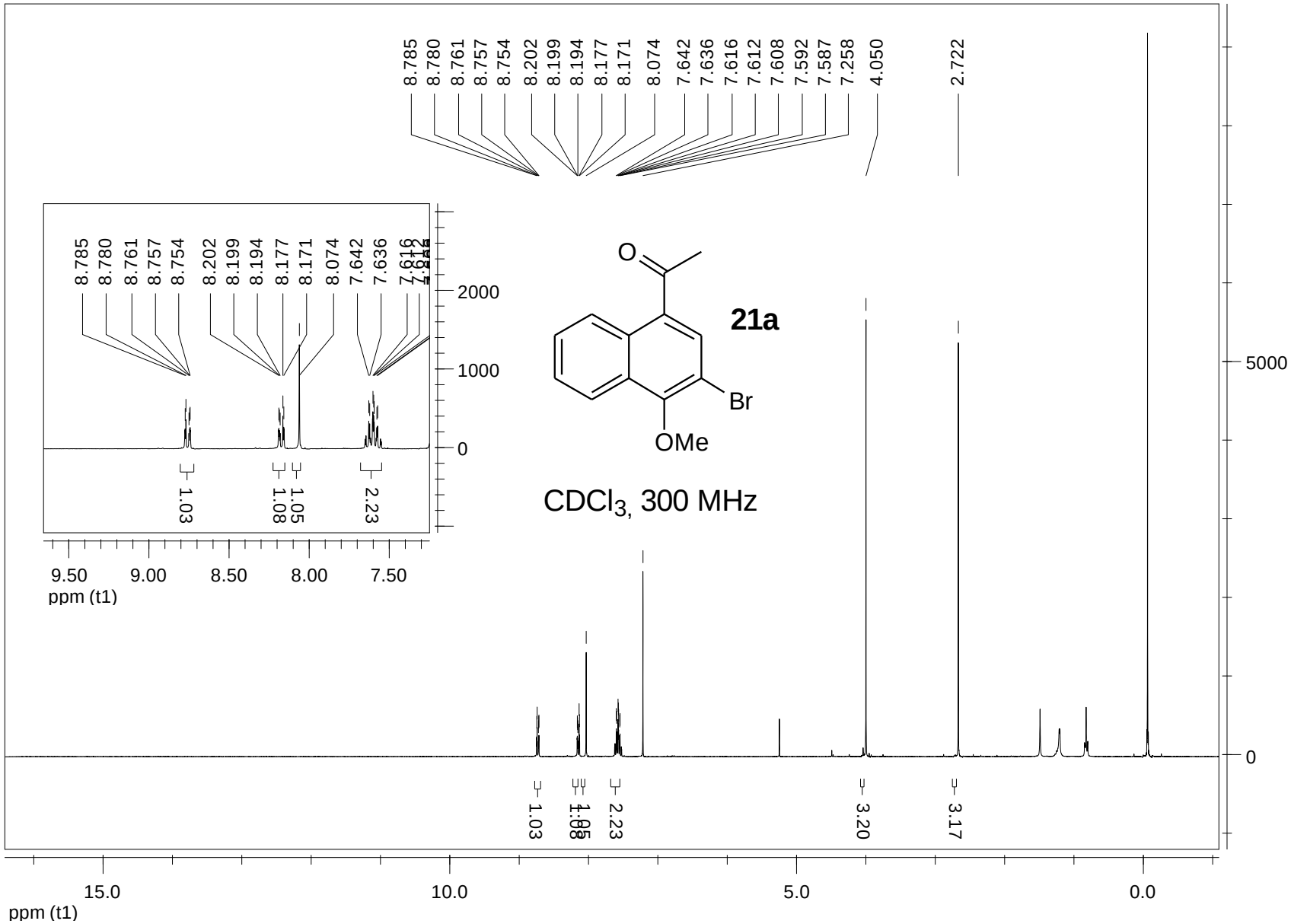

190.892
132.145
131.290
130.615
129.500
129.361
128.591
127.634
127.523
115.955
77.254
77.000
76.746
54.131
43.060
CN
Br
O
Ph
15
CDCl3, 125 MHz
ppm (t1)
ppm (t1)

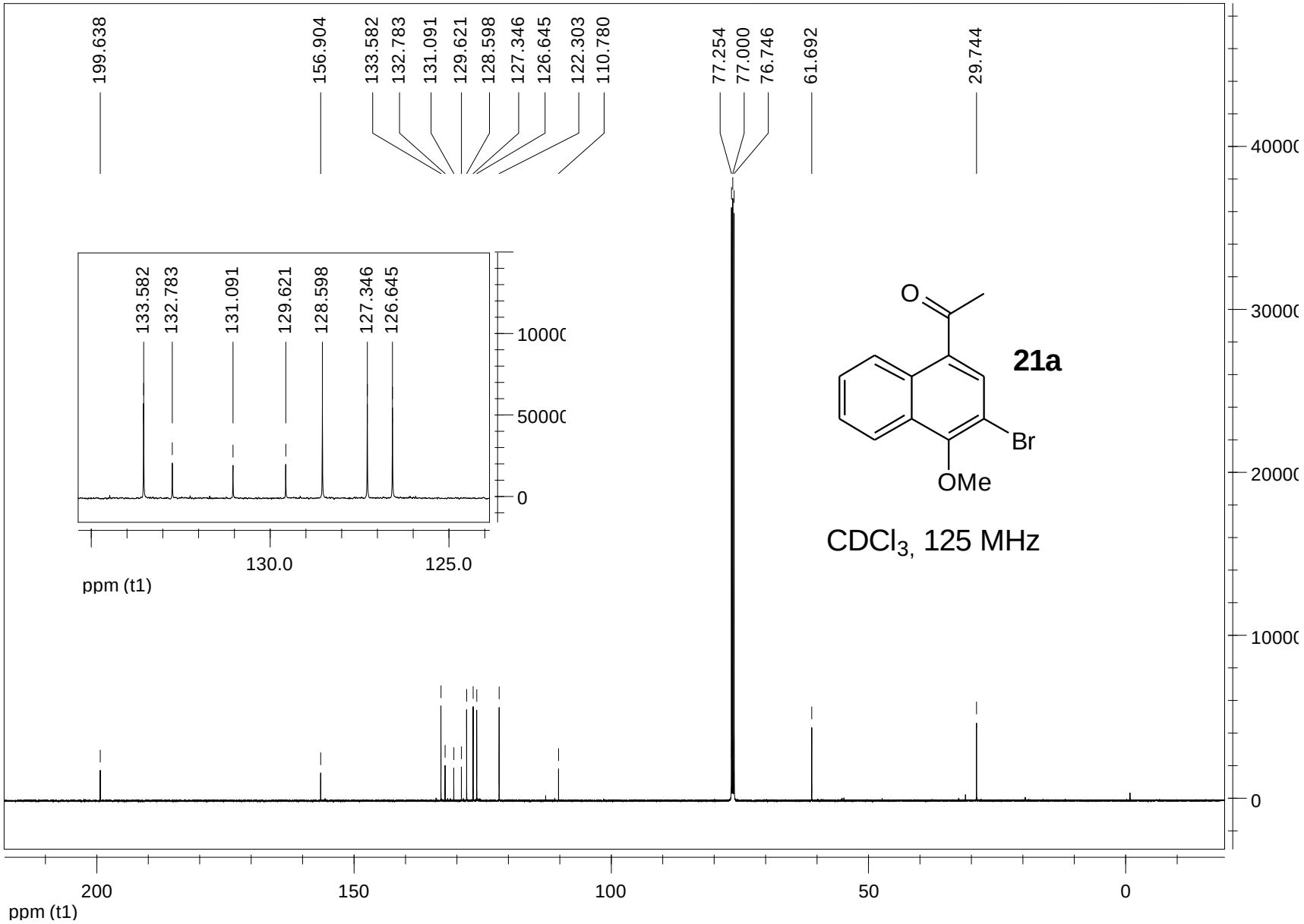

7.576
7.565
7.561
7.550
7.543
7.443
7.438
7.428
7.420
7.254
5.490
CN
Br
18
CDCl3, 300 MHz
2.00
3.01
1.00
7.600
7.550
7.500
7.450
7.400
ppm (t1)
15.0
10.0
5.0
0.0
ppm (t1)

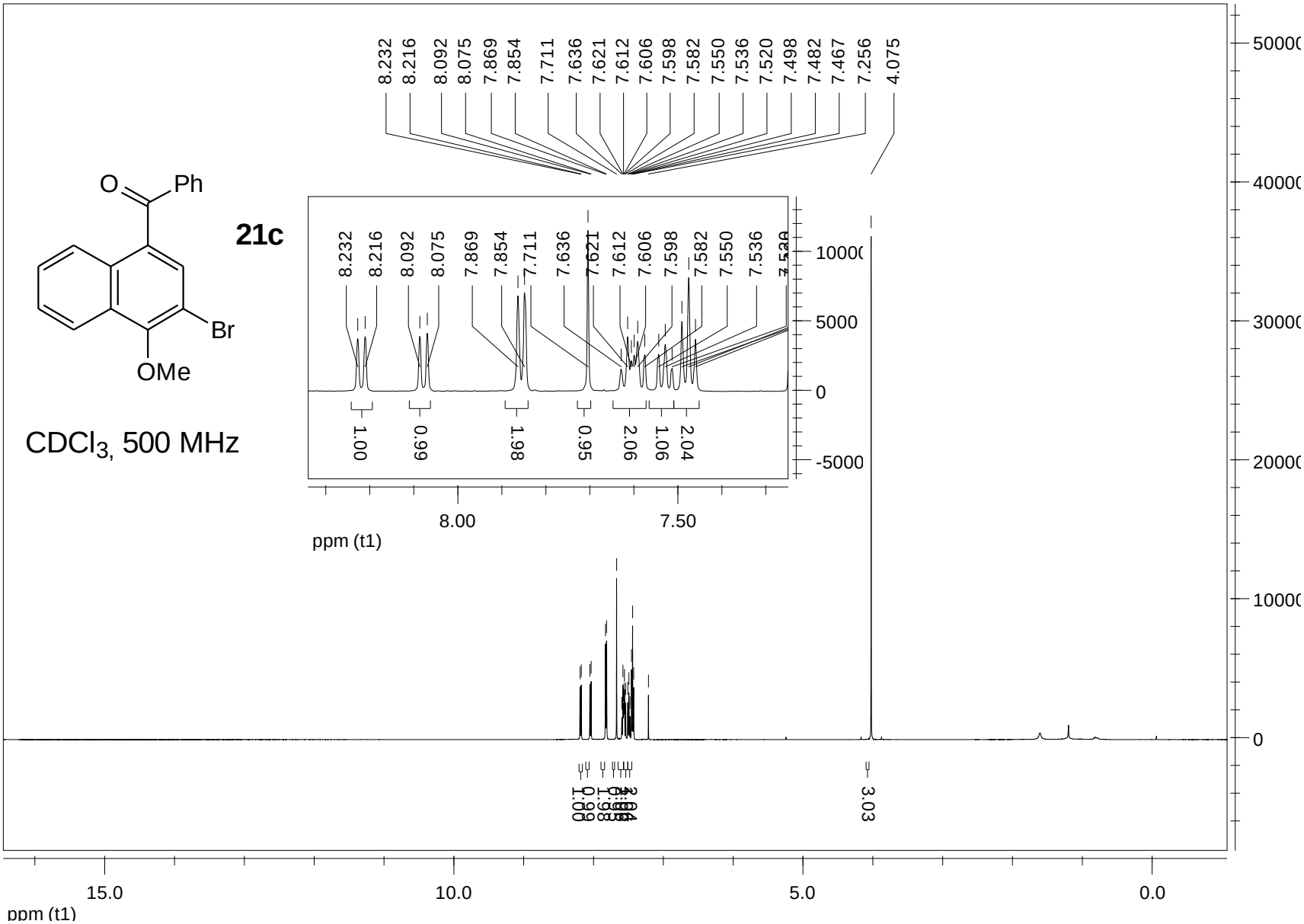

133.466
130.330
129.473
127.750
116.219
77.423
77.000
76.577
27.449
130.330
129.473
127.750
131.0 130.0 129.0 128.0 127.0
ppm (t1)
CN
Br
18
CDCl3, 75 MHz
200 150 100 50 0
ppm (t1)

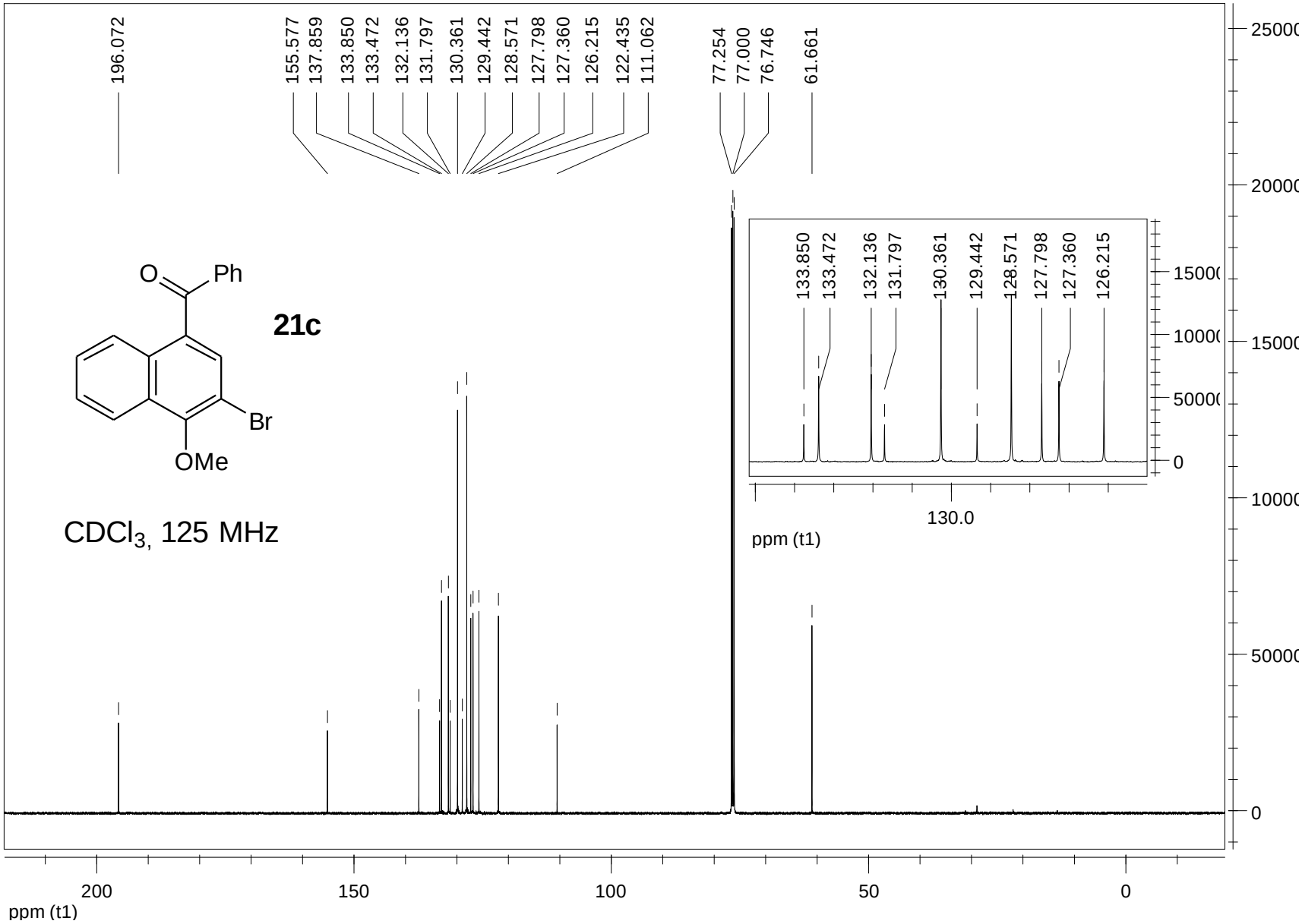

Br
Br
OMe
20
CDCl3, 300 MHz
8.187
8.180
8.155
8.148
8.123
8.115
7.906
7.646
7.642
7.624
7.619
7.609
7.601
7.592
7.582
7.577
7.560
7.250
3.997
2.00
0.97
2.09
3.17
ppm (t1)
15.0
10.0
5.0
0.0

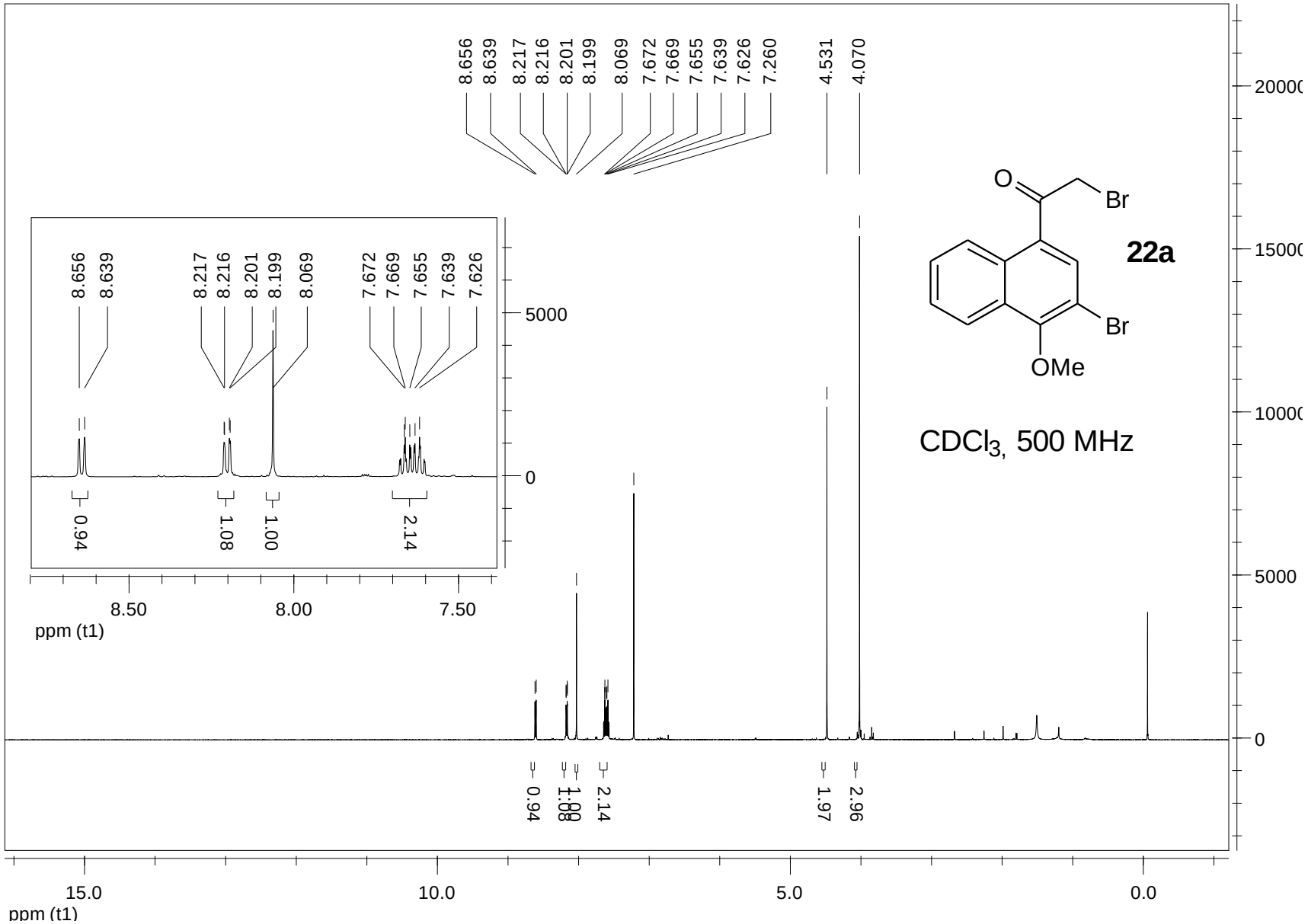

153.144
133.019
132.238
129.789
127.836
127.640
127.548
122.536
118.033
112.052
77.423
77.000
76.577
61.582
Br
Br
OMe
20
CDCl3, 75 MHz
127.836
127.640
127.548
128.00
127.50
ppm (t1)
200
150
100
50
ppm (t1)

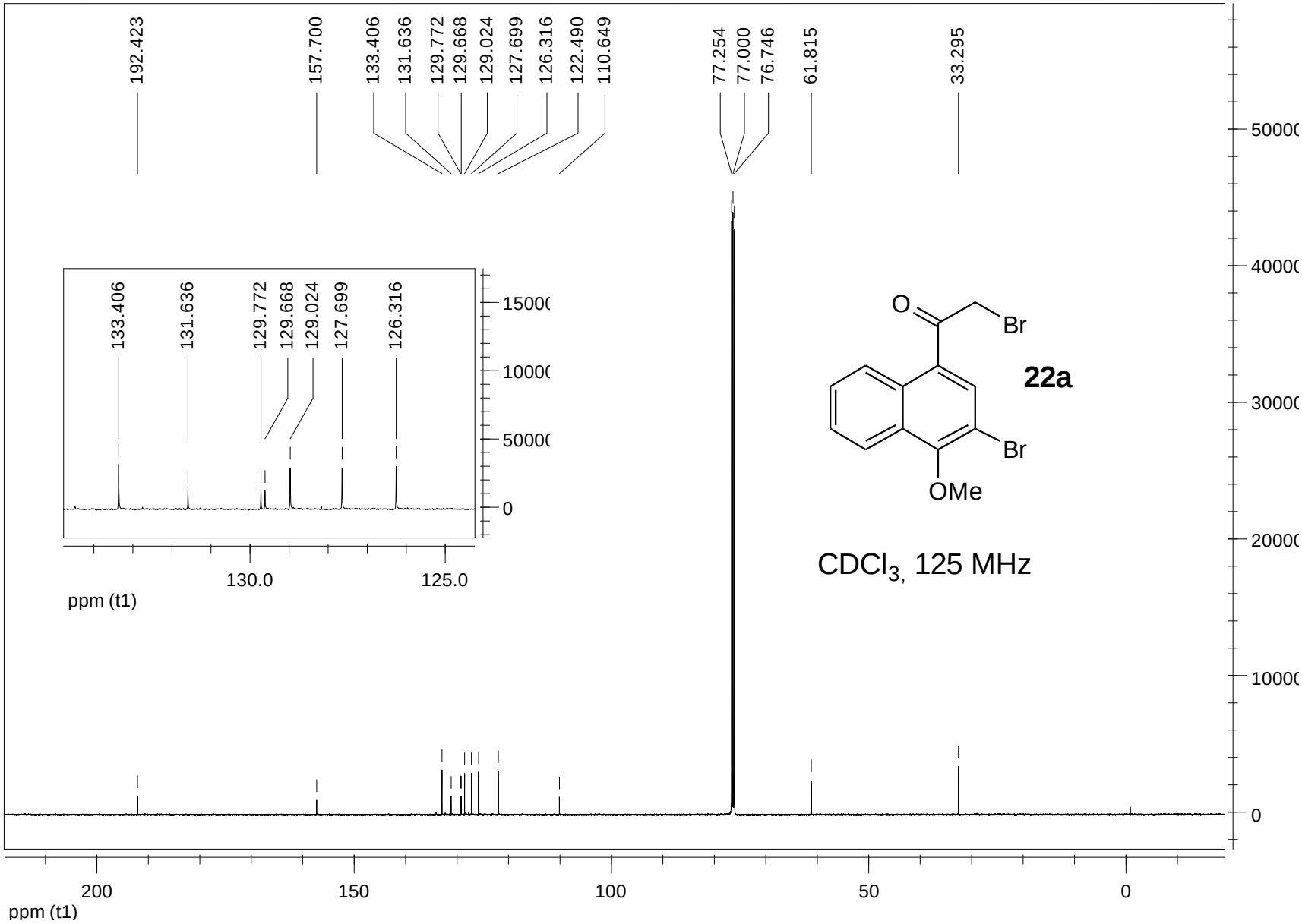

8.785
8.780
8.761
8.757
8.754
8.202
8.199
8.194
8.177
8.171
8.074
7.642
7.636
7.616
7.612
7.608
7.592
7.587
7.258
4.050
2.722
O
Br
OMe
21a
CDCl3, 300 MHz
1.03
1.05
1.08
2.23
3.20
3.17
ppm (t1)
15.0
10.0
5.0
0.0
9.50
9.00
8.50
8.00
7.50
2000
1000
0
5000

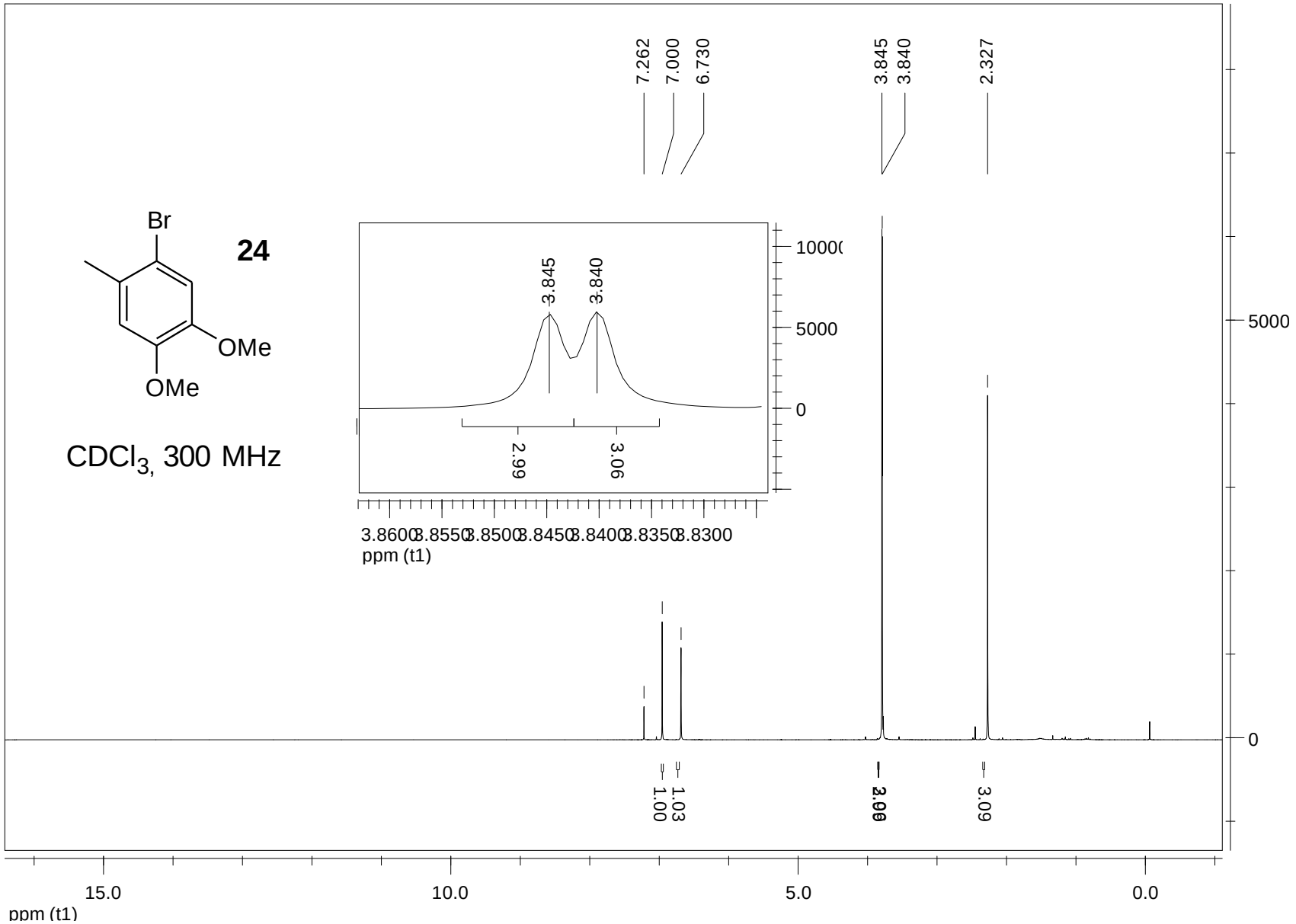

199.638
156.904
133.582
132.783
131.091
129.621
128.598
127.346
126.645
122.303
110.780
77.254
77.000
76.746
61.692
29.744
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)
133.582
132.783
131.091
129.621
128.598
127.346
126.645
10000
5000
0
130.0
125.0
ppm (t1)
O
Br
OMe
21a
CDCl3, 125 MHz

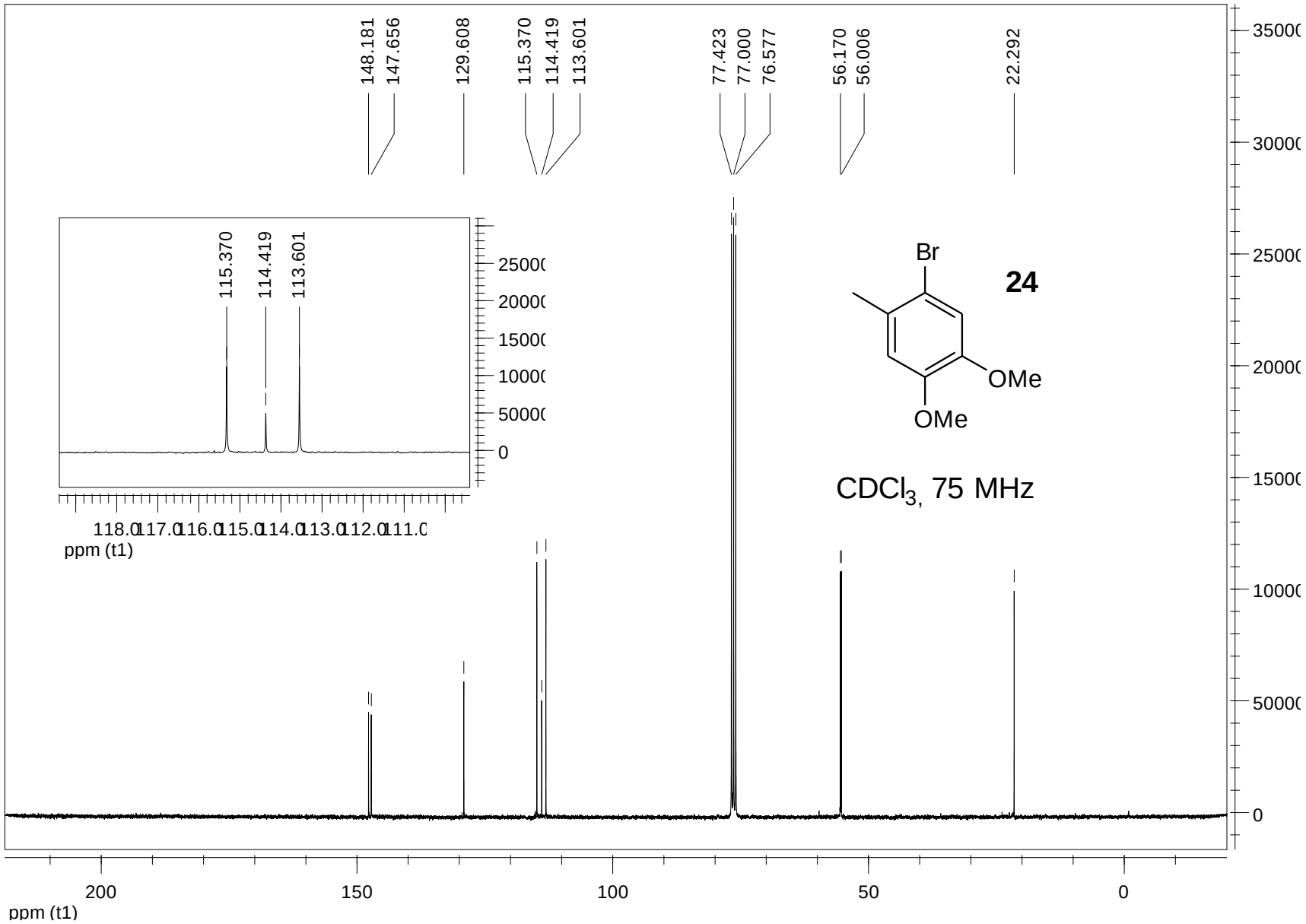

8.232
8.216
8.092
8.075
7.869
7.854
7.711
7.636
7.621
7.612
7.606
7.598
7.582
7.550
7.536
7.520
7.498
7.482
7.467
7.256
4.075
O
Ph
Br
OMe
21c
CDCl3, 500 MHz
1.00
0.99
1.98
0.95
2.06
1.06
2.04
3.03
8.00
7.50
ppm (t1)
15.0
10.0
5.0
0.0
ppm (t1)


196.072
155.577
137.859
133.850
133.472
132.136
131.797
130.361
129.442
128.571
127.798
127.360
126.215
122.435
111.062
77.254
77.000
76.746
61.661
O
Ph
Br
OMe
21c
CDCl3, 125 MHz
ppm (t1)
130.0
200
150
100
50
0


8.656
8.639
8.217
8.216
8.201
8.199
8.069
7.672
7.669
7.655
7.639
7.626
7.260
4.531
4.070
O
Br
22a
Br
OMe
CDCl3, 500 MHz
0.94
1.08
1.00
2.14
1.97
2.96
ppm (t1)
15.0
10.0
5.0
0.0
8.50
8.00
7.50
20000
15000
10000
5000
0


192.423
157.700
133.406
131.636
129.772
129.668
129.024
127.699
126.316
122.490
110.649
77.254
77.000
76.746
61.815
33.295
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)
15000
10000
5000
0
130.0
125.0
ppm (t1)
O
Br
Br
OMe
22a
CDCl3, 125 MHz


Br
OMe
OMe
24
CDCl3, 300 MHz
7.262
7.000
6.730
3.845
3.840
2.327
3.845
3.840
2.99
3.06
3.8600 3.8550 3.8500 3.8450 3.8400 3.8350 3.8300
ppm (t1)
1.00
1.03
3.09
3.09
15.0
10.0
5.0
0.0
ppm (t1)


148.181
147.656
129.608
115.370
114.419
113.601
77.423
77.000
76.577
56.170
56.006
22.292
115.370
114.419
113.601
Br
24
OMe
OMe
CDCl3, 75 MHz
ppm (t1)
ppm (t1)

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