# Diastereo- and Enantioselective Conjugate Addition of α-Ketoesters to Nitroalkenes Catalyzed by Chiral $Ni(OAc)_2$ Complex under Mild Conditions

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**Supporting Information**

**(A) Recent selected papers on catalytic asymmetric conjugate addition of pronucleophiles to nitroalkenes**

1,3-Dicarbonyls: (a) Li, X.-J.; Liu, K.; Ma, H.; Nie, J.; Ma, J.-A. *Synlett* **2008**, 3242. (b) Janka, M.; He, W.; Haedicke, I. E.; Fronczek, F. R.; Frontier, A. J.; Eisenberg, R. *J. Am. Chem. Soc.* **2006**, *128*, 5312. (c) Terada, M.; Ube, H.; Yaguchi, Y. *J. Am. Chem. Soc.* **2006**, *128*, 1454. (d) Okino, T.; Hoashi, Y.; Furukawa, T.; Xu, X.; Takemoto, Y. *J. Am. Chem. Soc*. **2005**, *127*, 119. (e) Watanabe, M.; Ikagawa, A.; Wang, H.; Murata, K.; Ikariya, T. *J. Am. Chem. Soc*. **2004**, *126*, 11148. (f) Evans, D. A.; Mito, S.; Seidel, D. *J. Am. Chem. Soc.* **2007**, *129*, 11583, and references therein.

Oxindoles: (g) Kato, Y.; Furutachi, M.; Chen, Z.; Mitsunuma, H.; Matsunaga, S.; Shibasaki, M. *J. Am. Chem. Soc*. **2009**, *131*, 9168. (h) Bui, T.; Syed, S.; Barbas III, C. F. *J. Am. Chem. Soc*. **2009**, *131*, 8758. (i) He, R.; Shirakawa, S.; Maruoka, K. *J. Am. Chem. Soc.* **2009**, *131*, 16620.

Ketones and aldehydes: (j) Scroggins, S. T.; Chi, Y.; Fréchet, J. M. J. *Angew. Chem. Int. Ed.* **2009**, early view (anie.200902945). (k) RiRocco, D. A.; Oberg, K. M.; Dalton, D. M.; Rovis, T. *J. Am. Chem. Soc*. **2009**, *131*, 10872. (l) Rasappan, R.; Reiser, O. *Eur. J. Org. Chem*. **2009**, 1305. (m) Tan, B.; Zeng, X.; Lu, Y.; Chua, P. J.; Zhong, G. *Org. Lett*. **2009**, *11*, 1927. (n) Mandal, T.; Zhao, C.-G. *Angew. Chem. Int. Ed*. **2008**, *47*, 7714. (o) Wiesner, M.; Revell, J. D.; Wennemers, H. *Angew. Chem. Int. Ed*. **2008**, *47*, 1871. (p) Enders, D.; Huttl, M. R. M.; Grondal, C.; Raabe, G. *Nature* **2006**, *441*, 861. (q) Palomo, C.; Vera, S.; Mielgo, A.; Gómez-Bengoa, E. *Angew. Chem. Int. Ed*. **2006**, *45*, 5984. (r) Hayashi, Y.; Okano, T.; Aratake, S.; Hazelard, D. *Angew. Chem. Int. Ed*. **2007**, *46*, 4922. (s) Pansare, S. V.; Pandya, K. *J. Am. Chem. Soc*. **2006**, *128*, 9624. (t) Huang, H.; Jacobsen, E. N. *J. Am. Chem. Soc*. **2006**, *128*, 7170. (u) Wang, J.; Li, H.; Lou, B.; Zu, L.; Guo, H.; Wang, W. *Chem. Eur. J*. **2006**, *12*, 4321. (v) Mase, N.; Watanabe, K.; Yoda, H.; Takabe, K.; Tanaka, F.; Barbas III, C. F. *J. Am. Chem. Soc*. **2006**, *128*, 4966. (w) Ishii, T.; Fujioka, S.; Sekiguchi, Y.; Kotsuki, H. *J. Am. Chem. Soc*. **2004**, *126*, 9558. (x) Wiesner, M.; Upert, G.; Angelici, G.; Wennemers, H. *J. Am. Chem. Soc*. **2010**, *132*, 6. (y) Zeng, Z.; Perkins, B. L.; Ni, B. *J. Am. Chem. Soc*. **2010**, *132*, 50.

Nitroalkanes: (z) Yang, X.; Zhou, X.; Lin, L.; Chang, L.; Liu, X.; Feng, X. *Angew. Chem. Int. Ed*. **2008**, *47*, 7079. (aa) Rabalakos, C.; Wulff, W. D. *J. Am. Chem. Soc*. **2008**, *130*, 13524. (bb) Lu, S.-F.; Du, D.-M.; Xu, J.; Zhang, S.-W. *J. Am. Chem. Soc*. **2006**, *128*, 7418.

2-Furanone: (cc) Trost, B. M.; Hitce, J. *J. Am. Chem. Soc*. **2009**, *131*, 4572.

Heteroaromatics: (dd) Trost, B. M.; Müller, C. *J. Am. Chem. Soc*. **2008**, *130*, 2438. (ee) Arai, T.; Yokoyama, N. *Angew. Chem. Int. Ed.* **2008**, *47*, 4989.

**(B) General**

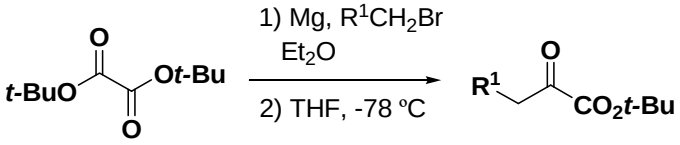
$^{1}$NMR spectra were recorded at 400 MHz for $^{1}$H-NMR, 100.4 MHz for $^{13}$C-NMR, or at 500 MHz for $^{1}$H-NMR, 125.8 MHz for $^{13}$C-NMR. Chemical shifts were reported downfield from TMS (= 0) for

$^1$H-NMR. For $^{13}$C-NMR, chemical shifts were reported in the scale relative to $CDCl_3$ or acetone as an internal reference. FAB-LRMS and HRMS were taken using *m*-nitrobenzyl alcohol (*m*NBA) or glycerol as matrix. IR was measured by attenuated total reflectance (ATR). Flash column chromatography was performed with silica gel N 60 (40-100 μm). In some case, purification was carried out using medium pressure liquid chromatography (MPLC) or precoated thin layer chromatography (TLC) plates (silica gel 60 $F_{254}$, 0.50 mm). Precoated TLC plates (silica gel 60 $F_{254}$, 0.25 mm) were used for the TLC analysis. The enantiomeric excesses (ees) were determined by chiral HPLC analysis. Dehydrated solvents used in this paper were purchased and used directly without further purification. Triethylamine was distilled from calcium hydride. $Pd(OAc)_2$, $Ni(OAc)_2{\cdot}4H_2O$, $Cu(OAc)_2{\cdot}2H_2O$, $Zn(OAc)_2{\cdot}2H_2O$, $NiBr_2$, (*R*)-BINAP and (*S*,*S*)-(-)-*tert*-Bu-BOX were obtained from commercial source and were used as received. Other reagents were purified by usual methods. Known ligands and nitroalkenes were prepared according to literature procedures.

**(C) Preparation of α-ketoesters and nitroalkenes used in this work**

**(C-1) General procedure for α-ketoesters**

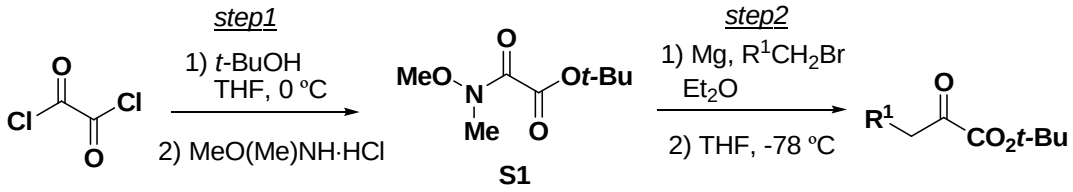
**General procedure A**[1]




Magnesium turnings (0.29 g, 11.9 mmol) were placed inside 3-necked flask. Diethyl ether (2 mL) and a piece of iodine were added, and the resulting mixture was stirred until the yellow color of iodine had faded out. The alkyl bromide (16.4 mmol) in diethyl ether (3 mL) was added dropwise over 30 min at 0 °C. The reaction mixture was stirred for 1 h. To di-*tert*-butyl-glyoxylate (2.00 g, 11.9 mmol) in dichloromethane (20 mL) was added the resulting Grignard solution by dropwise over 30 min at -78 °C. The reaction mixture was stirred for 1 h at -78 °C and quenched with saturated aqueous $NH_4Cl$ (20 mL). The aqueous layer was extracted with dichloromethane (15 mL x 3). The combined organic layers were washed with brine, then dried over $Na_2SO_4$, and concentrated under reduced pressure. Further purification by column chromatography ($SiO_2$), followed by recrystallization from *n*-hexane/diethyl ether gave the product.

[1] Weinstock, L. M.; Currie, R. B.; Lovell, A. V. *Synth. Commun*. **1981**, *11*, 943.

**General procedure B**[2]




Step1: *tert*-Butanol (24 mL, 251 mmol) was added in one batch to a solution of oxalyl chloride (distilled, 22 mL, 257 mmol) in THF (400 mL) at 0 °C under $N_2$ atmosphere. After 1 h, *N*, *O*-dimethylhydroxylamine hydrochloride (25.0 g, 256 mmol) and triethylamine (107 mL, 769 mmol) were added and the solution was stirred for 2 h. Water (200 mL) was added, and THF was evaporated under reduced pressure. The aqueous layer was extracted with ethyl acetate (100 mL x 3). The combined organic layers were washed with water (100 mL), brine (100 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography ($SiO_2$, *n*-hexane/ethyl acetate = 5:1) to give mono-*tert*-butyloxalic acid-*N*-methoxy-*N*-methylamide (**S1**) in 71% yield as a slightly yellow oil (33.7 g).

**mono-*tert*-Butyloxalic acid-*N*-methoxy-*N*-methylamide (S1)**

IR (neat) ν 2982, 2941, 1736, 1674, 1260, 1151, 1090, 993, 844 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 3.20 (s, 3H), 1.56 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 162.2, 161.7, 84.3, 62.1, 31.3, 28.0; MS (CI+) m/z 190 $[M+H]^+$; HRMS (CI+) calcd for $C_8H_{16}NO_4$ 190.1079, found 190.1066.

Step2: Magnesium turnings (972 mg, 40.0 mmol) were placed inside 3-necked flask. Diethyl ether (5 mL) and a piece of iodine were added, and the resulting mixture was stirred until the yellow color of iodine had faded out. The alkyl bromide (30.0 mmol) in diethyl ether (5 mL) was added dropwise over 30 min at 0 °C. The reaction mixture was stirred for 1 h. To **S1** (3.78 g, 20.0 mmol) in dichloromethane (75 mL) was added the Grignard solution dropwise over 30 min at -78 °C. The mixture was stirred at -78 °C for 1.5 h and quenched with saturated aqueous $NH_4Cl$ (75 mL). The aqueous layer was extracted with dichloromethane (50 mL x 3). The combined organic layers were washed with brine (100 mL), then dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography, and distillation or recrystallization gave the pure product.

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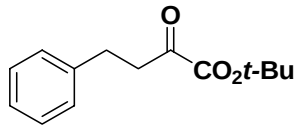
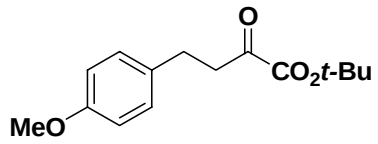
[2] (a) Nimitz, J. S.; Mosher, H. S. *J. Org. Chem*. **1981**, *46*, 211. (b) Heras, M. A; Vaquero, J. J.; Garcia-Navio, J. L.; Alvarez-Builla, J. *J. Org. Chem.* **1996**, *61*, 9009. (c) Chiu, C. C.; Jordan, F. *J. Org. Chem*. **1994**, *59*, 5763.




**_tert_-Butyl 2-oxo-4-phenylbutanoate (1a)**[3]

The title compound was prepared according to the general procedure A using 2-bromoethylbenzene as the bromide and purified by column chromatography ($SiO_2$, *n*-hexane/ethyl acetate = 10:1), followed by recrystallization from *n*-hexane/diethyl ether to give **1a** in 52% yield as colorless crystals.

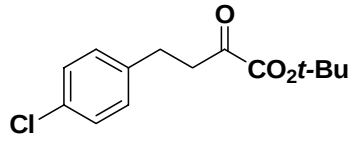
Mp 52-53 °C; IR (neat) ν 2984, 1738, 1367, 1251, 1155, 1082, 833, 753 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.34-7.13 (m, 5H), 3.11 (t, *J* = 7.6 Hz, 2H), 2.94 (t, *J* = 7.6 Hz, 2H), 1.52 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 194.5, 160.3, 140.2, 128.5, 128.3, 126.2, 84.0, 40.9, 29.2, 27.8; MS (CI+) m/z 235 $[M+H]^+$; HRMS (CI+) calcd for $C_{14}H_{19}O_3$ 235.1334, found 235.1338.




**_tert_-Butyl 4-(4'-methoxyphenyl)-2-oxobutanoate (S2)**[3]

The title compound was prepared according to the general procedure A using 4-methoxyphenethyl bromide as the bromide and purified by column chromatography ($SiO_2$, *n*-hexane/ethyl acetate = 10:1, and then $SiO_2$, dichloromethane/*n*-hexane = 1:2 to 2:1) to give the product in 57% yield as a colorless solid. Before use, the solid was recrystallized from *n*-hexane/diethyl ether to give **S2** as a microcrystalline colorless powder.

Mp 62-63 °C; IR (neat) ν 2985, 1715, 1511, 1260, 1242, 1156, 1078, 1015 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 3.07 (t, *J* = 7.6 Hz, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 1.53 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 194.6, 160.3, 158.0, 132.2, 129.3, 113.9, 84.0, 55.3, 41.1, 28.3, 27.8; MS (EI+) m/z 264 $[M]^+$; HRMS (EI+) calcd for $C_{15}H_{20}O_4$ 264.1362, found 264.1398.



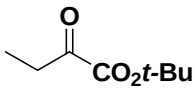

**_tert_-Butyl 4-(4'-chlorophenyl)-2-oxobutanoate (S3)**[3]

The title compound was prepared according to the general procedure B using 4-chlorophenethyl bromide as the bromide and purified by column chromatography ($SiO_2$, *n*-hexane/ethyl acetate = 8:1) to give the product in 75% yield as a pale yellow oil. The product was further purified by recrystallization from *n*-hexane/diethyl ether to give **S3** in 46% yield as colorless crystals.

Mp 50-52 °C; IR (neat) ν 2980, 1742, 1366, 1252, 1154, 1082, 1016 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 3.09 (t, *J* = 7.6 Hz, 2H), 2.91 (t, *J* = 7.6

[3] Rueppel, M. L.; Rapoport, H. *J. Am. Chem. Soc*. **1972**, *94*, 3877.

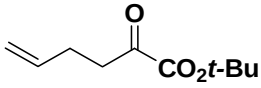
Hz, 2H), 1.53 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 194.2, 160.1, 138.6, 132.0, 129.7, 128.6, 84.1, 40.6, 28.5, 27.8; MS (CI+) m/z 269 $[M+H]^+$; HRMS (CI+) calcd for $C_{14}H_{18}ClO_3$ 269.0944, found 269.0974.




***tert*-Butyl 2-oxobutanoate (S4)**[4]

Di-*tert*-butyl-glyoxylate (2.02 g, 10.0 mmol) was dissolved in THF (6 mL) and diethyl ether (14 mL) and cooled to -78 °C. The ethyl magnesium bromide (1.0 M in THF, 10 mL) was added dropwise over 30 min with stirring. The solution was allowed to warm up to room temperature over 4.5 h and quenched with saturated aqueous $NH_4Cl$ (20 mL). The resulting mixture was extracted with diethyl ether (20 mL x 3). The combined organic layers were washed with brine (20 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography ($SiO_2$, *n*-hexane/ethyl acetate = 100:0 to 5:1) and distillation (18 mmHg, 90 °C) gave **S4** in 30% as a colorless oil (0.47 g).

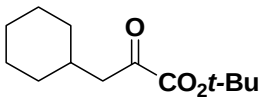
IR (neat) ν 2982, 2941, 1721, 1099 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 2.80 (q, *J* = 7.2 Hz, 2H), 1.55 (s, 9H), 1.11 (t, *J* = 7.2 Hz, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 196.0, 160.6, 83.8, 32.6, 27.9, 7.1; MS (CI+) m/z 159 $[M+H]^+$; HRMS (CI+) calcd for $C_8H_{15}O_3$ 159.1021, found 159.1047.




***tert*-Butyl 2-oxohex-5-enoate (S5)**

The title compound was prepared according to the general procedure A using 4-bromo-1-butene as the bromide and purified by column chromatography ($SiO_2$, *n*-hexane/diethyl ether = 15:1, and then $SiO_2$, *n*-hexane/dichloromethane = 2:1) to give **S5** in 51% yield as a pale yellow oil.

IR (neat) ν 3081, 2982, 1720, 1642, 1138, 1070 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 5.89-5.74 (m, 1H), 5.06 (dd, *J* = 17.1, 1.5 Hz, 1H), 5.01 (dd, *J* = 10.0 Hz, 1H), 2.88 (t, *J* = 7.3 Hz, 2H), 2.37 (apparent q, *J* = 7.1 Hz, 2H), 1.55 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 194.7, 160.4, 136.2, 115.7, 83.9, 38.3, 27.8, 27.1; MS (CI+) m/z 185 $[M+H]^+$; HRMS (CI+) calcd for $C_{10}H_{17}O_3$ 185.1178, found 185.1179.

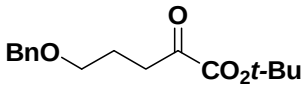



***tert*-Butyl 3-cyclohexyl-2-oxopropanoate (S6)**

The title compound was prepared according to the general procedure A using (bromomethyl)cyclohexane as the bromide and purified by column

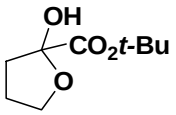
[4] Hari, Y.; Tanaka, S.; Takuma, Y.; Aoyama, T. *Synlett* **2003**, *14*, 2151.

chromatography ($SiO_2$, *n*-hexane/ethyl acetate = 20:1) to give **S6** in 31% yield as a colorless oil.
IR (neat) ν 2924, 2853, 1718, 1162, 1143, 1047 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 2.63 (d, *J* = 6.8 Hz, 2H), 1.94-1.79 (m, 1H), 1.77-1.61 (m, 5H), 1.54 (s, 9H), 1.41-1.08 (m, 3H), 1.04-0.91 (m, 2H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 195.3, 160.9, 83.8, 46.6, 33.7, 33.2, 28.0, 26.2, 26.1; MS (CI+) m/z 227 $[M+H]^+$; HRMS (CI+) calcd for $C_{13}H_{23}O_3$ 227.1647, found 227.1655.




***tert*-Butyl 5-(benzyloxy)-2-oxopentanoate (S7)**

The title compound was prepared according to the general procedure A using benzyl 3-bromopropylether as the bromide and purified by column chromatography ($SiO_2$, *n*-hexane/ethyl acetate = 10:1, and then *n*-hexane/ethyl acetate = 5:1) to give **S7** in 52% yield as a colorless oil.
IR (neat) ν 2980, 2861, 1718, 1369, 1162, 1099, 1029, 736, 698 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (m, 5H), 4.46 (s, 2H), 3.49 (t, *J* = 6.1 Hz, 2H), 2.89 (t, *J* = 7.1 Hz, 2H), 1.95 (tt, *J* = 7.1, 6.1 Hz, 2H), 1.52 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 195.0, 160.3, 138.1, 128.2, 127.5, 127.4, 83.6, 72.8, 68.8, 36.1, 27.8, 23.7; MS (CI+) m/z 279 $[M+H]^+$; HRMS (CI+) calcd for $C_{16}H_{23}O_4$ 279.1569, found 279.1586.



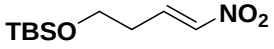

***tert*-Butyl tetrahydro-2-hydroxyfuran-2-carboxylate (S8)**

A solution of **S7** (200 mg, 0.719 mmol) in methanol (2.5 mL) with 10% Pd/C (10 wt%) was submitted to a hydrogen atmosphere for 18 h. The mixture was filtered through a pad of celite to remove Pd/C. After evaporation, the residue was purified by column chromatography ($SiO_2$, *n*-hexane/ethyl acetate = 5:1 to 0:100) to give **S8** in 66% as a colorless oil.
IR (neat) ν 3455 (br), 2980, 2884, 1729, 1143, 1053 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 4.15-4.06 (m, 1H), 4.00 (s, 1H), 4.00-3.93 (m, 1H), 2.41-2.29 (m, 1H), 2.18-2.07 (m, 1H), 2.07-1.96 (m, 2H), 1.51 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 170.1, 102.3, 83.0, 69.4, 35.0, 27.9, 25.5; MS (FAB) m/z 211 $[M+Na]^+$; HRMS (FAB) calcd for $C_9H_{16}NaO_4$ 211.0946, found 211.0943.

## (C-2) General procedure for nitro-alkenes

1-Methoxy-4-[(*E*)-2-nitrovinyl]benzene[5b], 1-bromo-4-[(*E*)-2-nitrovinyl]benzene[5b], 2-[(*E*)-2-nitrovinyl]furan[5c], and [(*E*)-2-nitrovinyl]cyclohexane[5d] were prepared according to the

reported procedure.[5a]



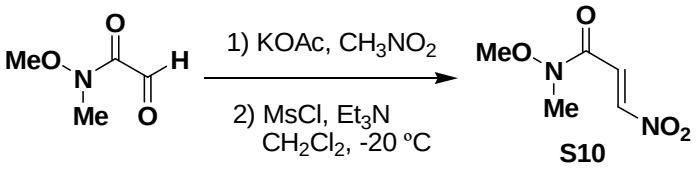

**tert-Butyldimethylsilyl [(*E*)-4-nitro-but-3-enyl]ether (S9)**

To a solution of 3-(*tert*-butyldimethylsilanoxy)propionaldehyde (1.17 g, 6.21 mmol) and nitromethane (1.7 mL, 31.1 mmol) was added triethylamine (86 μL, 0.62 mmol) dropwise at room temperature. The reaction mixture was stirred for 8 h at room temperature then filtered through a pad of $SiO_2$ (*n*-hexane/ethyl acetate = 1:1). The filtrate was concentrated under reduced pressure to yield the crude nitro-alcohol, which was used in the next step without further purification.

The crude nitro-alcohol was dissolved in dichloromethane (30 mL) at 0 ºC. Methanesulfonyl chloride (0.96 mL, 12.4 mmol) and diisopropylethylamine (3.8 mL, 21.7 mmol) were added successively and the mixture was stirred at 0 ºC for 30 min and at room temperature for 15 min. Brine (20 mL) was added and the aqueous phase was separated. The aqueous layer was extracted with dichloromethane (15 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography ($SiO_2$, *n*-hexane/ethyl acetate = 20:1) to give **S9** in 43% yield as a yellow oil (619 mg).

IR (neat) ν 2954, 2929, 2857, 1650, l529, 1472, 1351, 1254, 1096, 971, 832, 775 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.29 (dt, *J* = 13.5, 7.3 Hz, 1H), 7.05 (dt, *J* = 13.5, 1.5 Hz, 1H), 3.78 (t, *J* = 6.0 Hz, 2H), 2.47 (dtd, *J* = 7.3, 6.0, 1.5 Hz, 2H), 0.89 (s, 9H), 0.06 (s, 6H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 140.5, 139.7, 60.6, 31.8, 25.8, 18.2, -5.4; MS (FAB) m/z 254 $[M+Na]^+$; HRMS (FAB) calcd for $C_{10}H_{21}NNaO_3Si$ 254.1183, found 254.1194.

**N-Methoxy-N-methyl-3-nitroacrylamide (S10)**




**S10**

Step1. Potassium acetate (0.94 g, 9.57 mmol) was added to a solution of formyl-*N*-methoxy-*N*-methylformamide[6] (1.12 g, 9.57 mmol) in nitromethane (10 mL) under $N_2$ atmosphere. The mixture was stirred for 1.5 h and quenched with water (10 mL). The aqueous layer

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[5] (a) McNulty, J.; Steere, J. A.; Wolf, S. *Tetrahedron Lett.* **1998**, *39*, 8013. (b) Batra, S.; Sabnis, Y. A.; Rosenthal, P. J.; Avery, M. A. *Bioorg. Med. Chem.* **2003**, *11*, 2293. (c) Mahmood, S. Y.; Lallemand, M.-C.; Sader-Bakaouni, L.; Charton, O.; Vérité, P.; Dufat, H.; Tillequin, F. *Tetrahedron* **2004**, *60*, 5105. (d) Trost, B. M.; Müller, C. *J. Am. Chem. Soc*. **2008**, *130*, 2438.

[6] Parhi, A. K.; Frank, R. W. *Org. Lett.* **2004**, *6*, 3063.

was extracted with diethyl ether (20 mL x 3). The combined organic layers were washed with brine (20 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography ($SiO_2$, *n*-hexane/ethyl acetate = 1:2) to give nitro-alcohol in 55% yield as a colorless oil (0.94 g).
$^1$H-NMR (400 MHz, $CDCl_3$) δ 5.00 (ddd, *J* = 7.6, 7.1, 3.2 Hz, 1H), 4.75 (dd, *J* = 12.7, 3.2 Hz, 1H), 4.51 (dd, *J* = 12.7, 7.6 Hz, 1H), 3.81 (d, *J* = 7.1 Hz, 1H), 3.80 (s, 3H), 3.31 (s, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 169.2, 77.8, 66.6, 61.8, 32.7.

Step2. Triethylamine (2.04 mL, 14.7 mmol) was added to a solution of nitro-alcohol (0.87 g, 4.91 mmol) and methanesulfonyl chloride (1.14 mL, 14.7 mmol) in dichloromethane (12 mL) at -20 °C under $N_2$ atmosphere. The reaction mixture was stirred for 15 min at -20 °C and then quenched with water (10 mL). The aqueous layer was extracted with dichloromethane (10 mL x 3). The combined organic layers were washed with brine (10 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography ($SiO_2$, *n*-hexane/ethyl acetate = 2:1 to 1:1) to give **S10** in 84% yield as a pale yellow solid (0.66 g).
Mp 36-38 °C; IR (neat) ν 3115, 2991, 1660, 1626, 1512, 1354, 947 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 13.2 Hz, 1H), 7.68 (d, *J* = 13.2 Hz, 1H), 3.79 (s, 3H), 3.32 (s, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 161.7, 148.5, 126.0, 62.6, 32.5; MS (EI+) m/z 160 $[M]^+$; HRMS (EI+) calcd for $C_5H_8N_2O_4$ 160.0484, found for 160.0465.

**(D) Synthesis of metal catalysts**

**(D-1) Preparation of palladium complex 5**

The palladium μ-hydroxo complex **5** was prepared according to the reported procedures.[7]

**(D-2) Preparation of diamine ligands**

(*R*,*R*)-*N*,*N*'-Dibenzylcyclohexane-1,2-diamine **7**[8a] and (*R*,*R*)-*N*,*N*'-dibenzyl-1,2-diphenyl-1,2-ethane-

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[7] (a) Fujii, A.; Hagiwara, E.; Sodeoka, M. *J. Am. Chem. Soc.* **1999**, *121*, 5450. (b) Hamashima, Y.; Yagi, K.; Takano, H.; Tamás, L.; Sodeoka, M. *J. Am. Chem. Soc*. **2002**, *124*, 14530. (c) Dubs, C.; Hamashima, Y.; Sasamoto, N.; Seidel, T. M.; Suzuki, S.; Hashizume, D.; Sodeoka, M. *J. Org. Chem*. **2008**, *73*, 5859.

[8] (a) Denmark, S. E.; Stadler, H.; Dorow, R. L.; Kim, J. H. *J. Org. Chem*. **1991**, *56*, 5063. (b) Hamada, T.; Manabe, K.; Kobayashi, S. *Angew. Chem. Int. Ed*. **2003**, *42*, 3927. (c) Hamada, T.; Manabe, K.;

diamine **8**[8a-c] were prepared according to the reported procedure.[8a,d]
**7**: $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.36-7.18 (m, 10H), 3.89 (d, *J* = 13.2 Hz, 2H), 3.65 (d, *J* = 13.2 Hz, 2H), 2.32-2.21 (m, 2H), 2.20-2.08 (m, 2H), 1.84 (br s, 2H), 1.78-1.63 (m, 2H), 1.31-1.15 (m, 2H), 1.12-0.94 (m, 2H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 141.0, 128.2, 128.0, 126.6, 60.9, 50.9, 31.6, 25.1.
**8**: $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.03 (m, 20H), 3.71 (s, 2H), 3.66 (d, *J* = 13.5 Hz, 2H), 3.49 (d, *J* = 13.5 Hz, 2H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 141.0, 140.5, 128.2, 128.0, 127.9, 127.9, 126.8, 126.7, 68.3, 51.4.

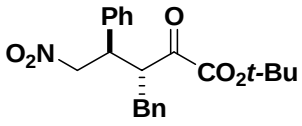
**(D-3) Preparation of isolated nickel-diamine complex**

A mixture of diamine **7** (123 mg, 0.418 mmol) and nickel acetate tetrahydrate (104 mg, 0.418 mmol) in ethanol (17 mL) was stirred for 1.5 h at room temperature. The resulting solution was filtered through a membrane filter. The filtrate was concentrated under reduced pressure. The residue was dissolved in dichloromethane and concentrated under reduced pressure to give the complex as a blue powder (197 mg).

**(E) Optimization studies**

**(E-1) Experimental procedure for optimization of the reaction of 1a with 2a.**

Metal acetate *n* hydrate (5 mol%) and corresponding ligand (5 mol%) were combined under $N_2$ atmosphere in 2-propanol (100 μL) and the mixture was stirred for 30 min at room temperature. *tert*-Butyl 2-oxo-4-phenylbutanoate (**1a**, 23.4 mg, 0.100 mmol) and *trans*-β-nitrostyrene (**2a**, 15.0 mg, 0.101 mmol) were added to the resulting solution and the mixture was stirred for the time given in the main text (Table 1). During the reaction, the product started to precipitate out, and the resulting suspension was dissolved in ethyl acetate (1 mL). The solution was passed through a pad of $SiO_2$ and concentrated under reduced pressure. $^1$H-NMR of the residue was measured to determine the diastereomeric ratio. Purification by MPLC gave pure products.



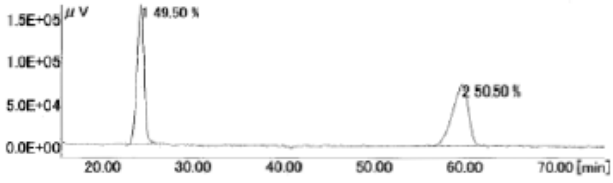

**(3*R*,4*R*)-*tert*-Butyl 3-benzyl-5-nitro-2-oxo-4-phenylpentanoate (3a)**
The title compound was prepared according to the experimental procedure and purified by MPLC (*n*-hexane/ethyl acetate = 9:1) to give **3a** as a colorless solid. Single recrystallization from IPA gave optically pure

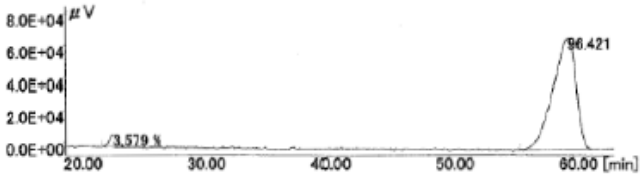
Kobayashi, S. *Chem. Eur. J*. **2006**, *12*, 1205. (d) Corey, E. J.; Jardine, P. D.; Virgil, S.; Yuen, P.; Connell, R. D. *J. Am. Chem. Soc*. **1989**, *111*, 9243.

compound in 79% (>99% ee).

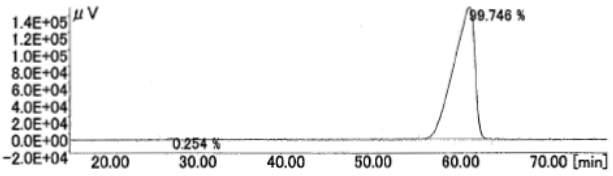
Mp 135-136 °C; IR (neat) ν 2983, 2937, 1733, 1540, 1284, 1157, 700 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.16-7.34 (m, 8H), 7.11 (d, *J* = 7.3 Hz, 2H), 4.81 (dd, *J* = 12.7, 5.4 Hz, 1H), 4.75 (dd, *J* = 12.7, 9.3 Hz, 1H), 4.22 (apparent q, *J* = 8.0 Hz, 1H), 3.93 (apparent td, *J* = 9.3, 5.4 Hz, 1H), 2.99 (d, *J* = 8.0 Hz, 2H), 1.28 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 196.2, 159.1, 137.0, 136.6, 129.0, 128.9, 128.7, 128.1, 128.1, 126.9, 84.1, 77.7, 50.8, 45.6, 35.9, 27.5; MS (CI+) m/z 384 $[M+H]^+$; HRMS (CI+) calcd for $C_{22}H_{26}NO_5$ 384.1811, found 384.1809; $[\alpha]_D^{30}$ +34.2 (*c* 1.01, $CHCl_3$) (>99% ee); HPLC (DAICEL CHIRALCEL OD-H, *n*-hexane/IPA = 9:1, 1.0 mL/min, 254 nm, $\tau_{minor}$ 22.8 min, $\tau_{major}$ 59.6 min).

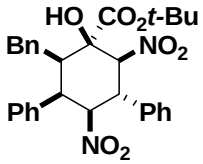
Before recrystallization (93% ee)




After recrystallization (>99% ee)

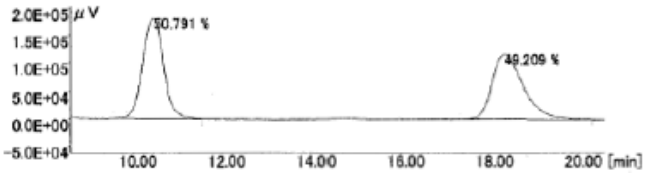


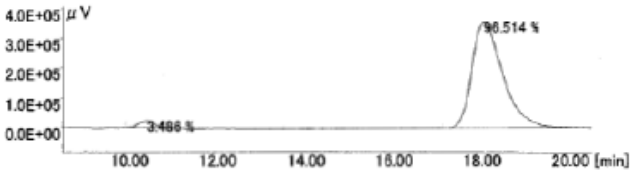




**(1*R*,2*R*,3*R*,4*S*,5*R*,6*S*)-*tert*-Butyl-2-benzyl-1-hydroxy-4,6-dinitro-3,5-diphenyl-cyclohexanecarboxylate (4a)**

The title compound was prepared according to the experimental procedure and purified by MPLC (*n*-hexane/ethyl acetate = 9:1) to give **4a** as a colorless solid.

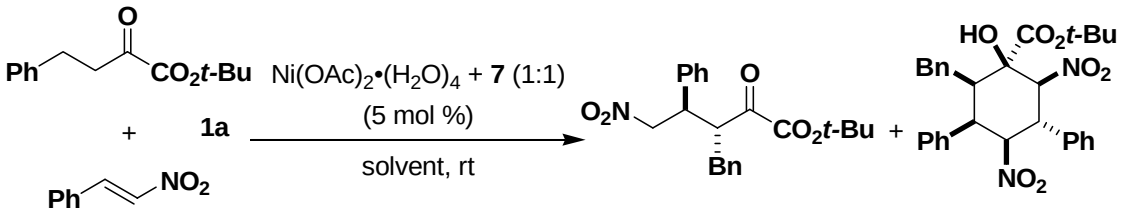
Mp 159-161 °C (*n*-hexane/ethyl acetate); IR (neat) ν 3445, 2984, 1721, 1550, 700 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.41-7.18 (m, 13H), 6.90-6.80 (m, 2H), 5.26 (d, *J* = 12.2 Hz, 1H), 5.17 (dd, *J* = 12.4, 6.4 Hz, 1H), 4.56 (t, *J* = 12.4 Hz, 1H), 4.25 (s, 1H), 3.63 (t, *J* = 6.4 Hz, 1H), 3.07-2.97 (m, 1H), 2.59-2.46 (m, 2H), 1.66 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 171.2, 137.2, 134.7, 131.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.1, 126.8, 92.6, 90.3, 86.5, 77.6, 47.2, 45.7, 40.4, 33.7, 28.0; MS (ESI-) m/z 531 $[M-H]^-$; HRMS (ESI-) calcd for $C_{30}H_{31}N_2O_7$ 531.21313, found 531.21322; $[\alpha]_D^{29}$ +41.7 (*c* 0.19, $CHCl_3$) (93% ee); HPLC (DAICEL CHIRALPAK IA, *n*-hexane/IPA = 9:1, 1.0 mL/min, 254 nm, $\tau_{minor}$ 10.5 min, $\tau_{major}$ 18.2 min).




**(E-2) Solvent effect**

The reactions in usual organic solvents basically took longer time to reach >70% yield.

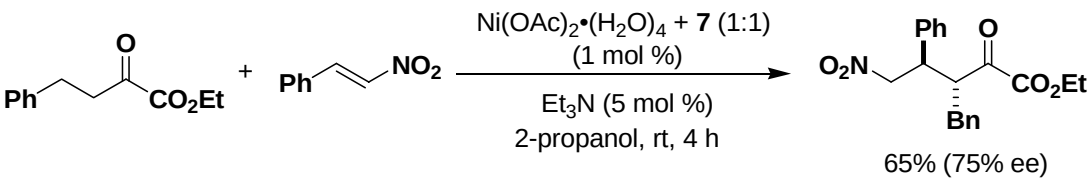



| Entry | Solvent | Time (h) | **3a** yield (%)[a] [%ee][b] | **epi-3a** yield (%)[a] | **4a** yield (%)[a] |
|---|---|---|---|---|---|
| 1 | ethanol | 12 | 58 [83] | trace | 11 |
| 2 | 2,2,2-trifluoroethanol | 48 | 78 [46] | - | 7 |
| 3 | dichloromethane | 53 | 75 [85] | 13 | not detected |
| 4 | toluene | 24 | 81 [79] | 9 | 4 |
| 5 | THF | 29 | 79 [94] | 13 | not detected |
| 6 | dimethoxyethane | 6 | 91 [92] | not detected | trace |

[a]Isolated yield based on **1a**. [b]The ee was determined by chiral HPLC analysis. [c]The catalyst was prepared in situ.

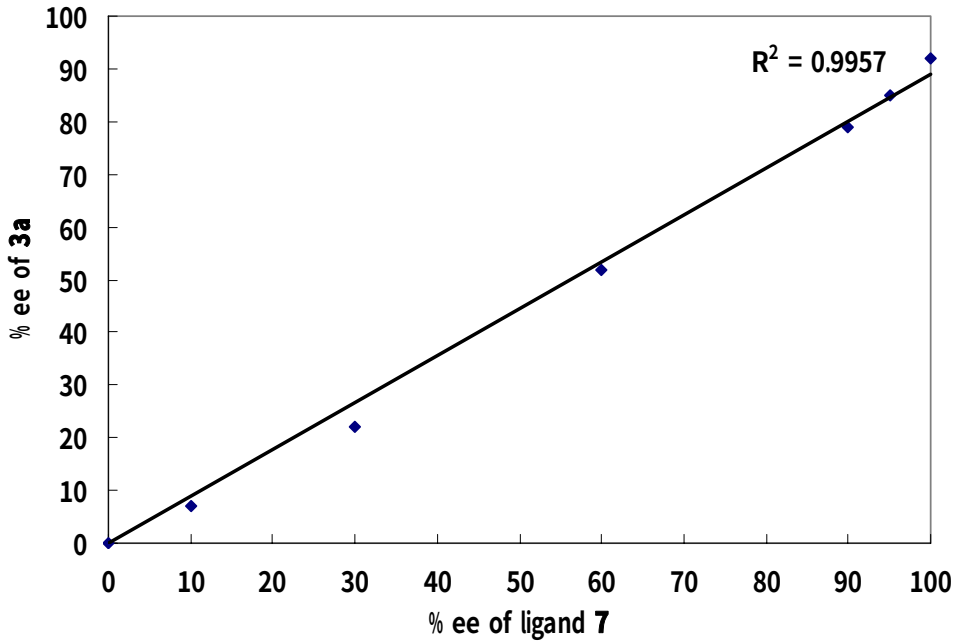
**(E-3) Ester effect**

The corresponding ethyl ester gave a lower enantioselectivity.



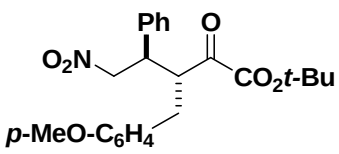

**(F) Investigation on non-linear effect**

In order to obtain insight into the mechanism of the reaction, the relationship between the enantiomeric excess values of **3a** and ligand **7** was investigated. The linear relationship ($R^2$ = 0.9957) was observed and it suggests that the active catalyst is a monomeric species.




**(G) General procedure of the conjugate addition of α-ketoesters to nitroalkenes for generality of the reaction**

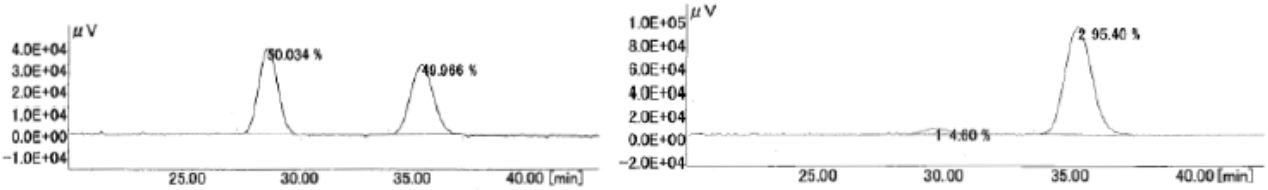
$Ni(OAc)_2 \cdot (H_2O)_4$ + **7** complex (isolated, 0.5 mg, 1 mol % or 2.5 mg, 5 mol %) and triethylamine (0.7 μL, 5 mol %) were combined under $N_2$ atmosphere in 2-propanol (100 μL) at room temperature. α-Ketoester (0.100 or 0.150 mmol) and nitroalkene (0.101 mmol) were added to the resulting mixture and the mixture was stirred for the time given in the main text (Chart 1). During the reaction, the product started to precipitate out, and the resulting suspension was dissolved in ethyl acetate (1 mL). The solution was passed through a pad of $SiO_2$. After evaporation of solvent, the residue was purified by MPLC or preparative thin layer chromatography to give the corresponding product.

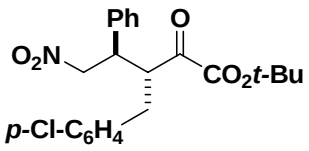



***tert*-Butyl 3-(4'-methoxybenzyl)-5-nitro-2-oxo-4-phenylpentanoate (3b)**

The title compound was prepared according to the general procedure and purified by MPLC (*n*-hexane/ethyl acetate = 9:1) to give **3b** in 82% yield as a colorless solid.

Mp 142-143 °C (*n*-hexane/ethyl acetate); IR (neat) ν 2982, 1722, 1538, 1287, 1255, 1158, 1026 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.35-7.15 (5H, m), 7.03 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 4.80 (dd, *J* = 12.9, 5.4 Hz, 1H), 4.73 (dd, *J* = 12.9, 9.3 Hz, 1H), 4.18 (td, *J* = 8.8, 6.6 Hz, 1H), 3.91 (td, *J* = 9.3, 5.4 Hz, 1H), 2.99-2.90 (m, 2H), 1.29 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 196.4, 159.1, 158.4, 136.7, 129.9, 128.9, 128.8, 128.1, 114.1, 84.1, 77.8, 55.2, 51.0, 45.6, 35.1, 27.5; MS (CI+) m/z 414 $[M+H]^+$; HRMS (CI+) calcd for $C_{23}H_{28}NO_6$ 414.1917, found for 414.1907; $[\alpha]_D^{29}$ +28.7 (*c* 1.01, $CHCl_3$) (91% ee); HPLC (DAICEL CHIRALCEL OD-H, *n*-hexane/IPA = 9:1, 1.0 mL/min, 254 nm, $\tau_{minor}$ 29.9 min, $\tau_{major}$ 35.5 min).



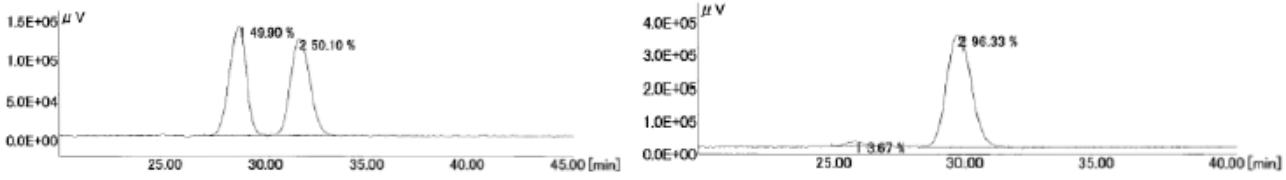




**_tert_-Butyl 3-(4'-chlorobenzyl)-5-nitro-2-oxo-4-phenylpentanoate (3c)**

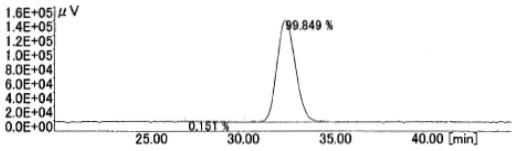
The title compound was prepared according to the general procedure and purified by MPLC (*n*-hexane/ethyl acetate = 9:1) to give **3c** in 75% yield (93% ee) as a colorless solid. Single recrystallization from IPA gave optically pure compound in 63% (>99% ee).

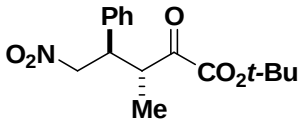
Mp 113-114 °C; IR (neat) ν 3448, 2981, 1722, 1558, 1493, 1362, 1281, 1135, 759, 699 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.35-7.16 (m, 7H), 7.04 (d, *J* = 8.3 Hz, 2H), 4.81 (dd, *J* = 12.9, 6.1 Hz, 1H), 4.77 (dd, *J* = 12.9, 8.4 Hz, 1H), 4.19 (dt, *J* = 8.1, 7.6 Hz, 1H), 3.92 (ddd, *J* = 8.4, 8.1, 6.1 Hz, 1H), 2.95 (d, *J* = 7.6 Hz, 2H), 1.30 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 195.8, 159.1, 136.3, 135.4, 132.7, 130.2, 129.0, 128.7, 128.2, 128.0, 84.4, 77.4, 50.8, 45.6, 35.0, 27.6; MS (CI+) m/z 418 $[M+H]^+$; HRMS (CI+) calcd for $C_{22}H_{25}ClNO_5$ 418.1421, found 418.1425; $[\alpha]_D^{30}$ +25.1 (*c* 1.01, $CHCl_3$) (>99% ee, after recrystallization); HPLC (93% ee, DAICEL CHIRALCEL OD-H, *n*-hexane/IPA = 9:1, 1.0 mL/min, 254 nm, $\tau_{minor}$ 26.0 min, $\tau_{major}$ 29.9 min).

Before recrystallization (93% ee)




After recrystallization (>99% ee)

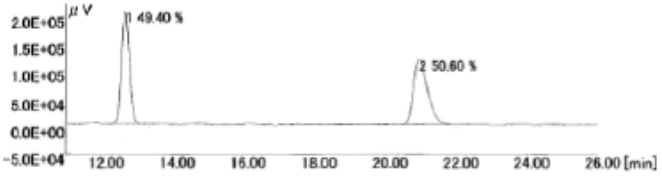


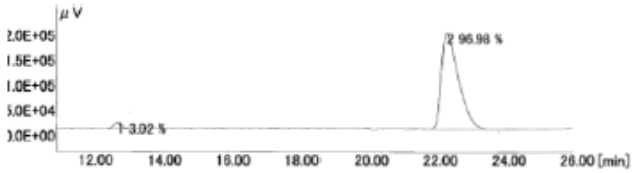



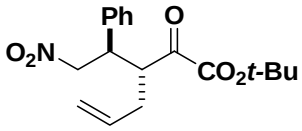

***tert*-Butyl 3-methyl-5-nitro-2-oxo-4-phenylpentanoate (3d)**

The title compound was prepared according to the general procedure and purified by MPLC (*n*-hexane/ethyl acetate = 9:1) to give **3d** in 77% yield as a colorless solid.

Mp 121-122 °C (*n*-hexane/ethyl acetate); IR (neat) ν 2987, 1716, 1541, 1306, 1160, 1013, 701 $cm^{-1}$; $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 7.34-7.18 (m, 5H), 4.76 (dd, *J* = 12.9, 5.9 Hz, 1H), 4.72 (dd, *J* = 12.9, 9.0 Hz, 1H), 3.90 (td, *J* = 9.0, 5.9 Hz, 1H), 3.79-3.70 (m, 1H), 1.45 (s, 9H), 1.23 (d, *J* = 6.8 Hz, 3H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 195.9, 159.9, 137.1, 128.9, 127.9, 127.8, 84.5, 77.3, 45.2, 44.7, 27.8, 13.5; MS (CI+) m/z 308 $[M+H]^+$; HRMS (CI+) calcd for $C_{16}H_{22}NO_5$ 308.1498, found 308.1469; $[\alpha]_D^{28}$ +9.2 (*c* 1.09, acetone) (94% ee); HPLC (DAICEL CHIRALPAK IC, *n*-hexane/ethanol = 98:2, 1.0 mL/min, 280 nm, $\tau_{minor}$ 12.8 min, $\tau_{major}$ 22.3 min).



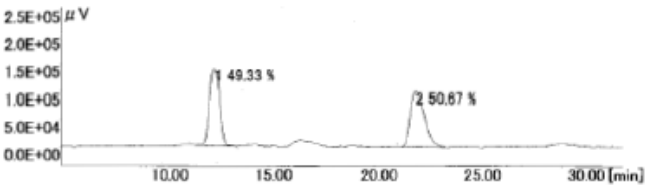



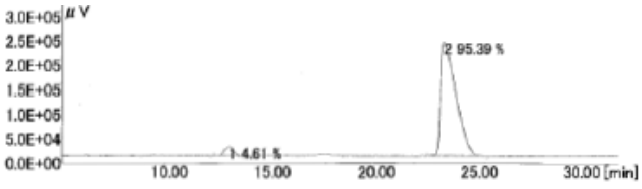



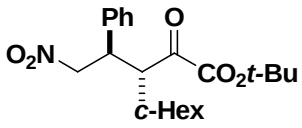

***tert*-Butyl 3-(2'-nitro-1'-phenylethyl)-2-oxohex-5-enoate (3e)**

The title compound was prepared according to the general procedure and purified by MPLC (*n*-hexane/ethyl acetate = 9:1) to give **3e** in 77% yield as a colorless solid.

Mp 85-87 °C (*n*-hexane/ethyl acetate) IR (neat) ν 2982, 1709, 1550, 704 $cm^{-1}$; $^{1}$H-NMR (400 MHz, $CDCl_3$) δ 7.34-7.16 (m, 5H), 5.76-5.62 (m, 1H), 5.14-5.03 (m, 2H), 4.79 (dd, *J* = 12.7, 5.0 Hz, 1H), 4.71 (dd, *J* = 12.7, 9.0 Hz, 1H), 3.95-3.82 (m, 2H), 2.56-2.38 (m, 2H), 1.42 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 195.5, 159.8, 136.7, 133.1, 128.9, 128.1, 118.6, 84.3, 77.6, 48.9, 44.7, 33.4, 27.7; MS (CI+) m/z 334 $[M+H]^+$; HRMS (CI+) calcd for $C_{18}H_{24}NO_5$ 334.1654, found 334.1627; $[\alpha]_D^{30}$ +4.0 (*c* 1.01, $CHCl_3$) (91% ee); HPLC (DAICEL CHIRALPAK IC, *n*-hexane/IPA = 98:2, 1.0 mL/min, 254 nm, $\tau_{minor}$ 13.1 min, $\tau_{major}$ 23.6 min).



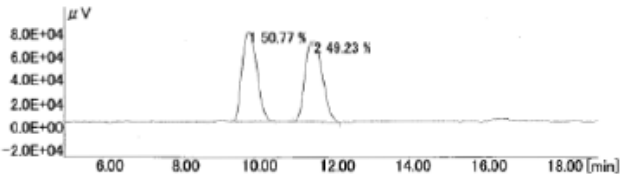



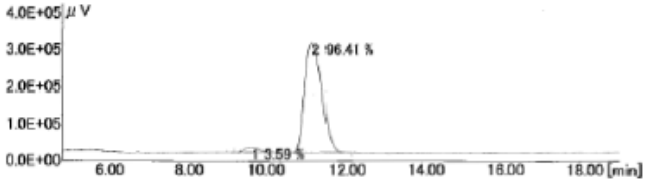



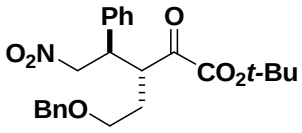

**_tert_-Butyl 3-cyclohexyl-5-nitro-2-oxo-4-phenylpentanoate (3f)**

The title compound was prepared according to the general procedure and purified by MPLC (*n*-hexane/ethyl acetate = 9:1) to give **3f** in 60% yield as a colorless solid.

Mp 139-140 °C (*n*-hexane/ethyl acetate); IR (neat) ν 2929, 2854, 1736, 1540, 1154, 701 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.29-7.15 (m, 5H), 4.73 (dd, *J* = 12.2, 4.4 Hz, 1H), 4.62 (dd, *J* = 12.2, 10.0 Hz, 1H), 4.02 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.99-3.90 (m, 1H), 1.92-1.63 (m, 6H), 1.38 (s, 9H), 1.31-1.04 (m, 4H), 0.96 (dq, *J* = 12.2, 3.2 Hz, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 196.3, 160.1, 137.1, 128.8, 128.2, 127.9, 83.9, 78.6, 52.6, 42.9, 39.1, 32.2, 27.6, 27.0, 26.9, 26.3, 26.1; MS (CI+) m/z 376 $[M+H]^+$; HRMS (CI+) calcd for $C_{21}H_{30}NO_5$ 376.2124, found 376.2102; $[\alpha]_D^{27}$ +59.1 (*c* 1.00, $CHCl_3$) (93% ee); HPLC (DAICEL CHIRALPAK IC, *n*-hexane/IPA = 98:2, 1.0 mL/min, 254 nm, $\tau_{minor}$ 9.8 min, $\tau_{major}$ 11.3 min).



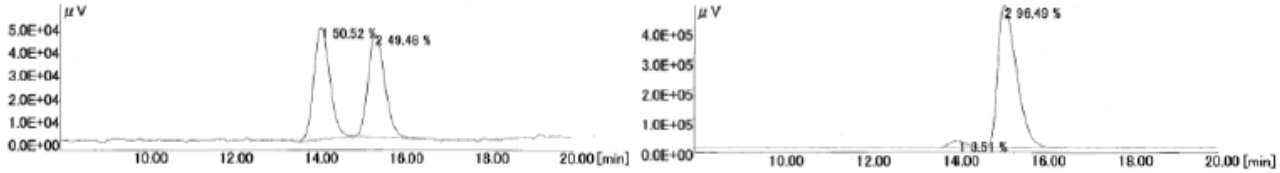



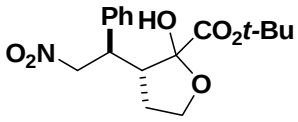

***tert*-Butyl 3-[2'-(benzyloxy)ethyl]-5-nitro-2-oxo-4-phenylpentanoate (3g)**

The title compound was prepared according to the general procedure and purified by MPLC (*n*-hexane/ethyl acetate = 9:1) to give **3g** in 93% yield as a colorless solid.

Mp 83-84 °C (*n*-hexane/ethyl acetate); IR (neat) ν 2931, 2873, 1719, 1539, 1290, 1103, 1016, 698 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.34-7.14 (m, 10H), 4.79 (dd, *J* = 12.9, 4.9 Hz, 1H), 4.70 (dd, *J* = 12.9, 9.3 Hz, 1H), 4.35 (d, *J* = 13.2 Hz, 1H), 4.32 (d, *J* = 13.2 Hz, 1H), 3.94-3.80 (m, 2H), 3.50-3.39 (m, 2H), 2.24-2.12 (m, 1H), 1.93-1.83 (m, 1H), 1.30 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 194.8, 159.3, 137.5, 136.9, 128.8, 128.2, 128.1, 127.9, 127.5, 127.4, 83.6, 77.8, 72.7, 67.8, 47.4, 45.4, 30.4, 27.5; MS (CI+) m/z 428 $[M+H]^+$; HRMS (CI+) calcd for $C_{24}H_{30}NO_6$ 428.2073, found 428.2070; $[\alpha]_D^{27}$ -13.8 (*c* 1.03, $CHCl_3$) (93% ee); HPLC (DAICEL CHIRALPAK AD-H, *n*-hexane/IPA = 90:10,

1.0 mL/min, 254 nm, $\tau_{minor}$ 14.0 min, $\tau_{major}$ 15.1 min).

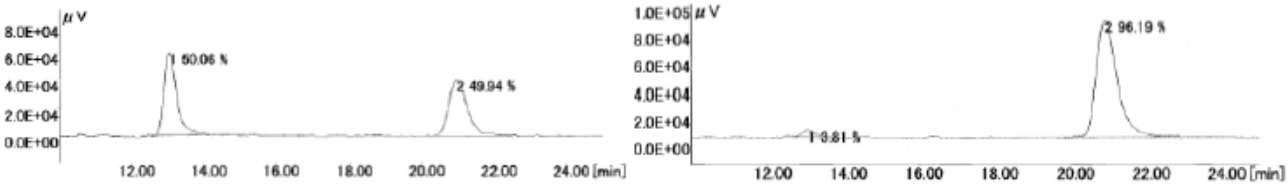


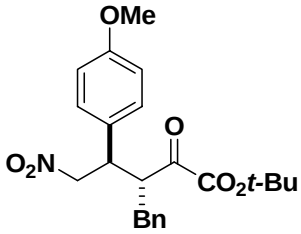




***tert*-Butyl tetrahydro-2-hydroxy-3-(2'-nitro-1'-phenylethyl)furan-2-carboxylate (3h)**

The title compound was prepared according to the general procedure and purified by MPLC (*n*-hexane/ethyl acetate = 9:1) to give **3h** in 84% yield as a colorless solid.

Mp 90-91 °C (*n*-hexane/ethyl acetate); IR (neat) ν 3551, 2976, 2898, 1733, 1552, 1251, 1056 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.15 (m, 5H), 4.75-4.63 (m, 2H), 4.24 (s, 1H), 4.19 (td, *J* = 8.5, 1.6 Hz, 1H), 3.96-3.85 (m, 1H), 3.82-3.72 (m, 1H), 2.98 (td, *J* = 11.5, 7.6 Hz, 1H), 2.28-2.16 (m, 1H), 2.14-2.00 (m, 1H), 1.20 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 168.8, 137.6, 128.6, 128.3, 127.7, 100.8, 83.5, 79.7, 67.7, 48.3, 44.1, 29.3, 27.5; MS (ESI+) m/z 355 $[M+NH_4]^+$; HRMS (ESI+) calcd for $C_{17}H_{27}N_2O_6$ 355.18691, found 355.18785; $[\alpha]_D^{28}$ +42.6 (*c* 1.02, $CHCl_3$) (92% ee); HPLC (DAICEL CHIRALPAK IC, *n*-hexane/IPA = 9:1, 1.0 mL/min, 254 nm, $\tau_{minor}$ 13.1 min, $\tau_{major}$ 20.9 min).



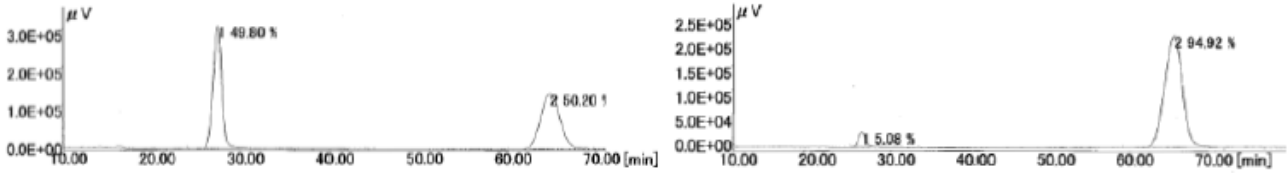



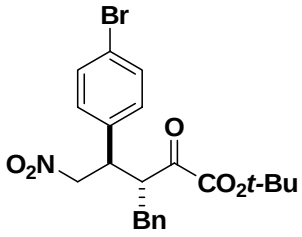

***tert*-Butyl 3-benzyl-4-(4'-methoxyphenyl)-5-nitro-2-oxopentanoate (3i)**

The title compound was prepared according to the general procedure and purified by MPLC (*n*-hexane/ethyl acetate = 4:1) to give **3i** in 81% yield as a colorless solid.

Mp 113-115 ºC; IR (neat) ν 3087, 3062, 3032, 3010, 2981, 2920, 1738, 1722, 1537, 1514, 1278, 1254, 1180, 1156, 1033, 837, 806, 748, 699 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.28-7.15 (m, 3H), 7.15-7.09 (m, 4H), 6.81 (m, 2H), 4.78 (dd, *J* = 12.6, 5.2 Hz, 1H), 4.70 (dd, *J* = 12.6, 9.5 Hz, 1H), 4.18 (dt, *J* = 9.0, 7.8 Hz, 1H), 3.86 (apparent td, *J* = 9.5, 5.2 Hz, 1H), 3.76 (s, 3H), 2.98 (d, *J* = 7.8 Hz, 2H), 1.29 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 196.3,

159.2, 159.1, 137.0, 129.2, 128.9, 128.7, 128.3, 126.9, 114.3, 84.1, 78.0, 55.2, 50.9, 45.1, 36.0, 27.5; MS (FAB) m/z 436 $[M+Na]^+$; HRMS (FAB) calcd for $C_{23}H_{27}NNaO_6$ 436.1731, found 436.1732; $[\alpha]_D^{27}$ +27.8 (*c* 0.67, $CHCl_3$) (90% ee); HPLC (DAICEL CHIRALCEL OD-H, *n*-hexane/IPA/ethyl acetate = 90:7:3, 1.0 mL/min, 254 nm, $\tau_{minor}$ 26.3 min, $\tau_{major}$ 65.7 min).

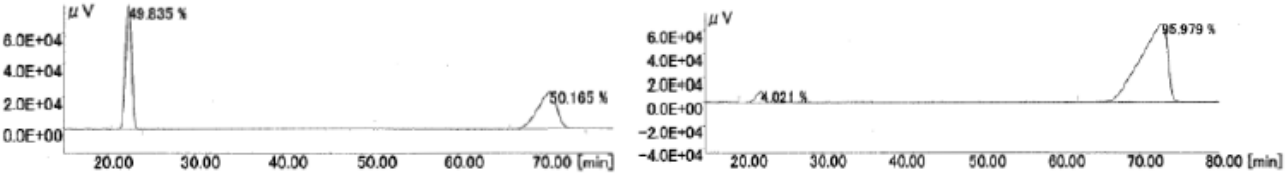


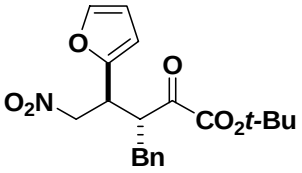




***tert*-Butyl 3-benzyl-4-(4'-bromophenyl)-5-nitro-2-oxopentanoate (3j)**

The title compound was prepared according to the general procedure and purified by MPLC (*n*-hexane/ethyl acetate = 85:15) to give **3j** in 81% yield as a colorless solid.

Mp 124-125 ºC; IR (neat) ν 3028, 2980, 2927, 2854, 1738, 1723, 1713, 1552, 1491, 1371, 1259, 1157, 1075, 1011, 832, 752, 701 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.30-7.16 (m, 3H), 7.14-7.08 (m, 4H), 4.79 (dd, *J* = 12.7, 5.1 Hz, 1H), 4.70 (dd, *J* = 12.7, 9.5 Hz, 1H), 4.19 (dt, *J* = 8.3, 7.6 Hz, 1H), 3.89 (apparent td, *J* = 9.5, 5.1 Hz, 1H), 2.97 (d, *J* = 7.6 Hz, 2H), 1.29 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 196.0, 159.2, 136.6, 135.7, 132.1, 129.8, 128.8, 128.8, 127.0, 122.2, 84.4, 77.5, 50.4, 45.1, 36.0, 27.5; MS (FAB) m/z 484 $[M+Na]^+$; HRMS (FAB) calcd for $C_{22}H_{24}BrNNaO_5$ 484.0730, found 484.0736; $[\alpha]_D^{26}$ +24.5 (*c* 1.20, $CHCl_3$) (92% ee); HPLC (DAICEL CHIRALCEL OD-H, *n*-hexane/IPA/ethyl acetate = 90:7:3, 1.0 mL/min, 280 nm, $\tau_{minor}$ 22.1 min, $\tau_{major}$ 72.7 min).



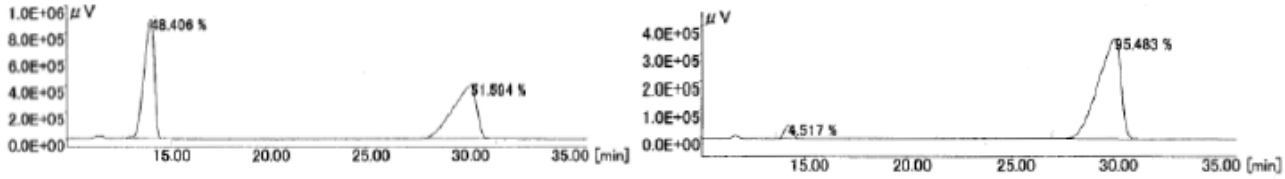



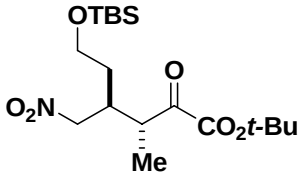

***tert*-Butyl 3-benzyl-4-(furan-2'-yl)-5-nitro-2-oxopentanoate (3k)**

The title compound was prepared according to the general procedure and purified by MPLC (*n*-hexane/ethyl acetate = 9:1) to give **3k** in 72% yield as a colorless solid.

Mp 59-60 ºC; IR (neat) ν 3318, 3087, 3064, 3030, 2981, 2935, 1741, 1722, 1713, 1552, 1507, 1371, 1256, 1156, 1066, 1015, 915, 848, 834, 740, 700 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 1H), 7.31-7.16 (m, 3H), 7.15-7.09 (m, 2H), 6.29 (dd, *J* = 3.3, 1.8 Hz, 1H),

6.22-6.08 (m, 1H), 4.78 (dd, *J* = 13.2, 8.0 Hz, 1H), 4.74 (dd, *J* = 13.2, 5.8 Hz, 1H), 4.18-4.10 (m, 1H), 4.10-4.02 (m, 1H), 2.97 (dd, *J* = 13.6, 9.2 Hz, 1H), 2.92 (dd, *J* = 13.6, 5.8 Hz, 1H), 1.39 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 195.6, 159.3, 149.8, 137.0, 128.9, 128.7, 126.9, 110.6, 108.7, 84.5, 75.4, 49.3, 38.9, 35.0, 27.6; MS (FAB) m/z 396 $[M+Na]^+$; HRMS (FAB) calcd for $C_{20}H_{23}NNaO_6$ 396.1418, found 396.1435; $[\alpha]_D^{25}$ -4.7 (*c* 0.60, THF) (90% ee); HPLC (DAICEL CHIRALCEL OD-H, *n*-hexane/IPA/ethyl acetate = 90:7:3, 1.0 mL/min, 254 nm, $\tau_{minor}$ 14.2 min, $\tau_{major}$ 30.1 min).



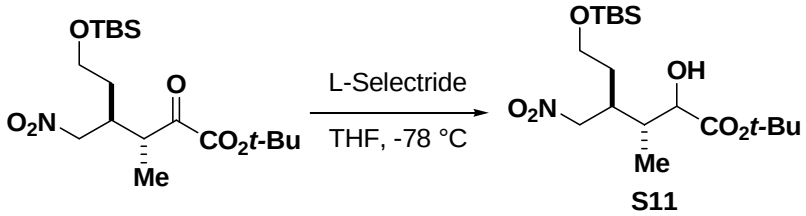

***tert*-Butyl 6-(*tert*-butyldimethylsilyloxy)-3-methyl-4-(nitromethyl)-2-oxohexanoate (3l)**

The title compound was prepared according to the general procedure and purified by MPLC (*n*-hexane/ethyl acetate = 9:1) to give **3l** in 83% yield as a colorless oil.

IR (neat) ν 2931, 2858, 1721, 1553, 1255, 1097, 835, 777 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 4.46 (dd, *J* = 13.1, 6.1 Hz, 1H), 4.42 (dd, *J* = 13.1, 6.6 Hz, 1H), 3.70 (t, *J* = 5.9 Hz, 2H), 3.48 (qd, *J* = 7.3, 4.9 Hz, 1H), 2.89-2.77 (m, 1H), 1.66 (apparent q, *J* = 5.9 Hz, 2H), 1.56 (s, 9H), 1.15 (d, *J* = 7.3 Hz, 3H), 0.88 (s, 9H), 0.05 (s, 6H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 196.9, 160.7, 84.6, 76.4, 60.8, 42.9, 36.1, 32.5, 27.9, 26.0, 18.3, 11.7, -5.3, -5.3; MS (CI+) m/z 390 $[M+H]^+$; HRMS (CI+) calcd for $C_{18}H_{36}NO_6Si$ 390.2312, found 390.2311, $[\alpha]_D^{28}$ -9.3 (*c* 0.88, $CHCl_3$) (94% ee).

**Determination of the ee of 3l**

Since **3l** was not separable on chiral HPLC, the ee of **3l** was determined after reduction below. The major isomer of alcohol **S11** was separable on chiral HPLC.

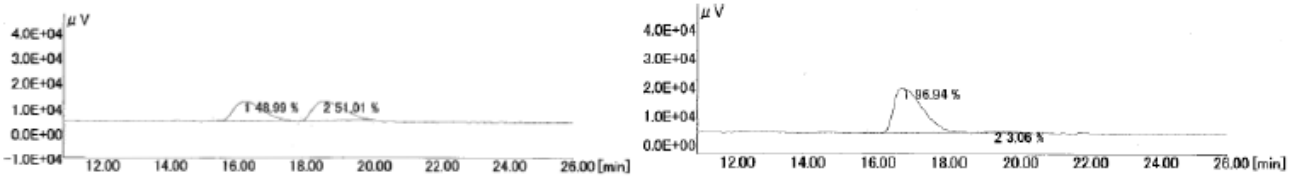


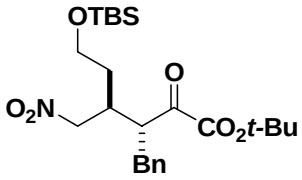

***tert*-Butyl 6-(*tert*-butyldimethylsilyloxy)-2-hydroxy-3-methyl-4-(nitromethyl)hexanoate (S11)**

To a solution of **3l** (10.0 mg, 0.0257 mmol) in THF (0.6 mL) was added L-Selectride (1.0 M in THF,

77 μL) at -78 °C. The reaction mixture was stirred for 1 h and then quenched with saturated aqueous $NH_4Cl$ (2 mL). The aqueous layer was separated and extracted with ethyl acetate (3 mL x 3). The combined organic layers were washed with brine (2 mL), dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography (*n*-hexane/ethyl acetate = 10:1) to give **S11** in 83% yield as a colorless oil.

IR (neat) ν 3505, 2930, 2858, 1722, 1551, 1253, 1150, 1091, 834, 776 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 4.82 (dd, *J* = 12.7, 4.9 Hz, 1H), 4.31 (dd, *J* = 12.7, 8.7 Hz, 1H), 4.00 (t, *J* = 4.9 Hz, 1H), 3.71-3.59 (m, 2H), 2.91 (d, *J* = 4.6 Hz, 1H), 2.58-2.45 (m, 1H), 2.17-2.04 (m, 1H), 1.73-1.58 (m, 2H), 1.52 (s, 9H), 1.01 (d, *J* = 7.3 Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 173.0, 83.3, 78.1, 74.4, 61.0, 37.8, 36.2, 33.5, 28.2, 26.0, 18.4, 12.7; MS (CI+) m/z 392 $[M+H]^+$; HRMS (CI+) calcd for $C_{18}H_{38}NO_6Si$ 392.2468, found 392.2471; $[\alpha]_D^{28}$ +3.0 (*c* 0.53, $CHCl_3$) (94% ee); HPLC (DAICEL CHIRALPAK IC, *n*-hexane/IPA = 99:1, 1.0 mL/min, 280 nm, $\tau_{major}$ 16.8 min, $\tau_{minor}$ 19.4 min).




**_tert_-Butyl 3-benzyl-6-(_tert_-butyldimethylsilyloxy)-4-(nitromethyl)-2-oxohexanoate (3m)**

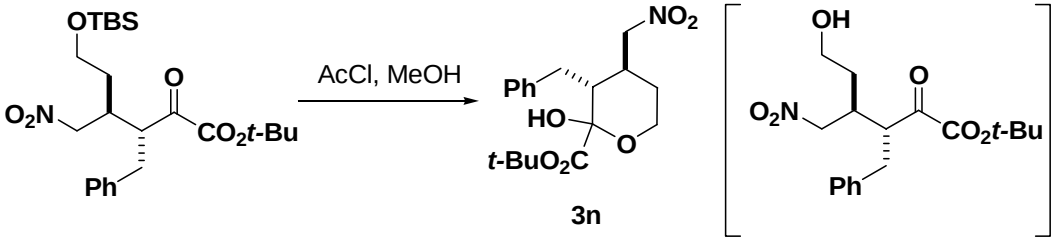
The title compound was prepared according to the general procedure and purified by preparative thin layer chromatography (toluene) to give **3m** in 77% yield as a light yellow oil.

IR (neat) ν 3030, 2954, 2930, 2858, 1738, 1722, 1552, 1370, 1254, 1159, 1098, 1048, 1031, 981, 888, 834, 776, 751, 732, 699 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.31-7.07 (m, 5H), 4.54 (dd, *J* = 13.3, 6.0 Hz, 1H), 4.48 (dd, *J* = 13.3, 6.5 Hz, 1H), 3.82 (apparent dt, *J* = 9.3, 5.6 Hz, 1H), 3.76-3.60 (m, 2H), 2.92 (dd, *J* = 13.5, 9.3 Hz, 1H), 2.82 (dd, *J* = 13.5, 5.6 Hz, 1H), 2.79-2.70 (m, 1H), 1.82-1.71 (m, 1H), 1.69-1.58 (m, 1H), 1.39 (s, 9H), 0.84 (s, 9H), 0.01 (s, 6H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 197.0, 160.3, 137.6, 128.9, 128.6, 126.7, 84.4, 76.5, 60.8, 49.6, 36.1, 34.2, 31.9, 27.7, 25.9, 18.3, -5.4, -5.4; MS (FAB) m/z 488 $[M+Na]^+$; HRMS (FAB) calcd for $C_{24}H_{39}NNaO_6Si$ 488.2439, found 488.2447; $[\alpha]_D^{26}$ +2.1 (*c* 0.48, $CHCl_3$) (92% ee).

**Determination of the ee of 3m**

Since **3m** was not separable on chiral HPLC, the ee of **3m** was determined after conversion to **3n**

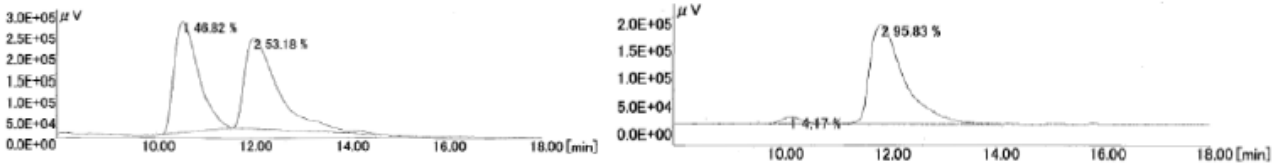
according to the following procedure.

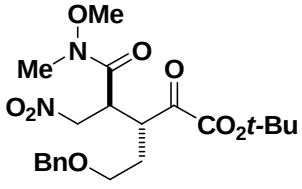



***tert*-Butyl 3-benzyl-tetrahydro-2-hydroxy-4-(nitromethyl)-2*H*-pyran-2-carboxylate (3n)**

To a solution of **3m** (72.1 mg, 0.154 mmol) in methanol (1 mL) was added acetyl chloride (2 μL, 0.028 mmol). The resulting solution was stirred at room temperature for 5 min, then the desired compound was directly purified by preparative thin layer chromatography (*n*-hexane/ethyl acetate = 85:15) to give **3n** in 94% yield as a colorless oil (50.1 mg).

IR (neat) ν 3478 (br), 3062, 3028, 2979, 2935, 1738, 1727, 1548, 1370, 1291, 1141, 1080, 1024, 841, 735, 699 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.37-7.14 (m, 5H), 4.28 (dd, *J* = 12.0, 3.9 Hz, 1H), 4.13-3.99 (m, 2H), 3.76 (dt, *J* = 11.5, 2.9 Hz, 1H), 3.71 (dd, *J* = 11.5, 11.2 Hz, 1H), 2.80-2.70 (m, 1H), 2.66 (dd, *J* = 15.9, 3.2 Hz, 1H), 2.57 (dd, *J* = 15.9, 8.4 Hz, 1H), 2.48-2.39 (m, 1H), 1.68-1.50 (m, 2H), 1.49 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 169.2, 139.8, 128.9, 128.2, 126.7, 96.1, 84.2, 79.7, 60.0, 43.0, 36.8, 36.5, 29.2, 27.8; MS (FAB) m/z 374 $[M+Na]^+$; HRMS (FAB) calcd for $C_{18}H_{25}NNaO_6$ 374.1574, found 374.1573; $[\alpha]_D^{28}$ +40.8 (*c* 1.06, $CHCl_3$) (92% ee); HPLC (DAICEL CHIRALPAK AS-H, *n*-hexane/IPA = 95:5, 1.0 mL/min, 254 nm, $\tau_{minor}$ 10.2 min, $\tau_{major}$ 11.9 min).



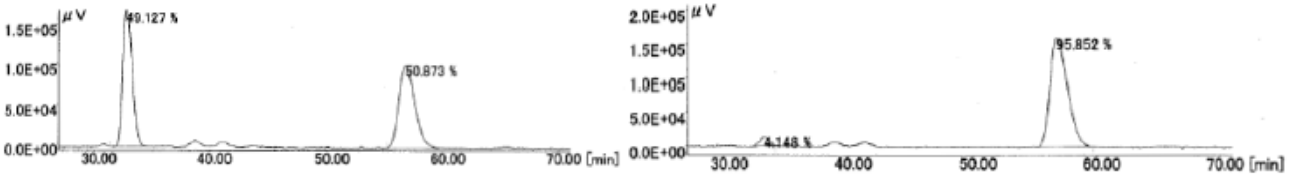




***tert*-Butyl 4-(*N*-methoxy-*N*-methylcarbamoyl)-3-[2'-(benzyloxy)ethyl]-5-nitro-2-oxopentanoate (3o)**

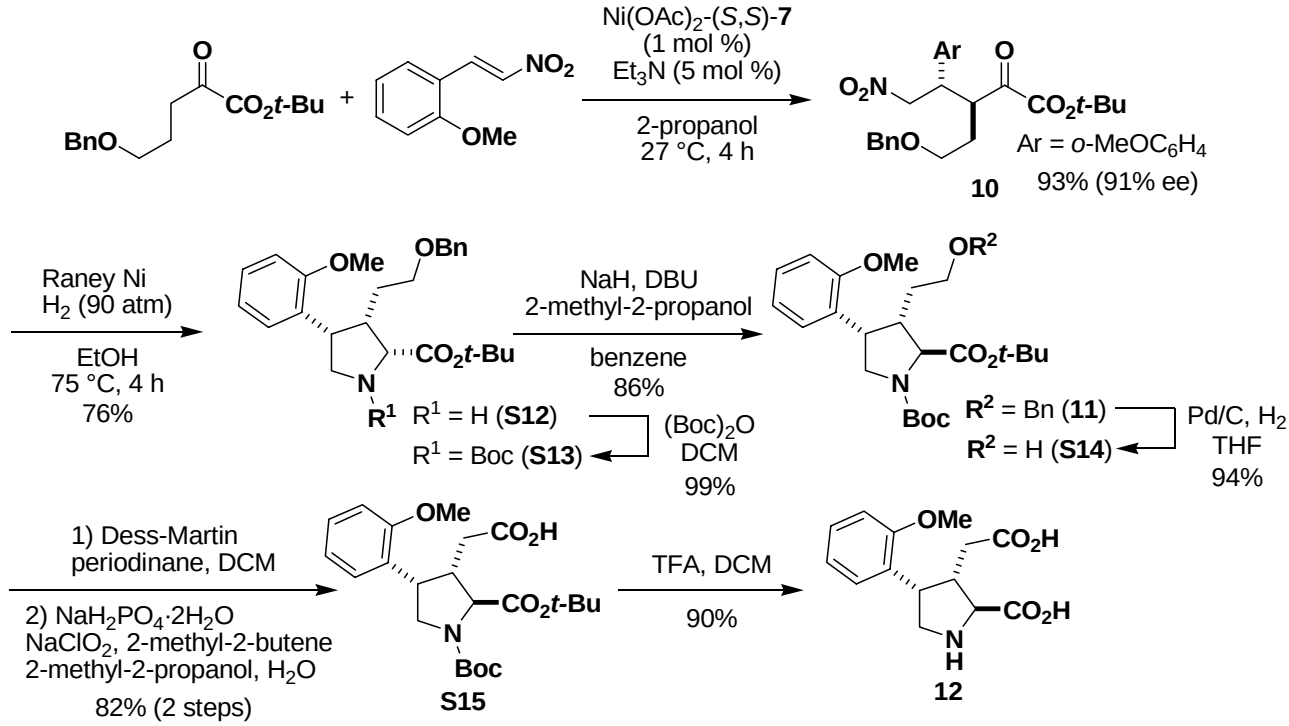
The title compound was prepared according to the general procedure and purified by MPLC (*n*-hexane/ethyl acetate = 3:1) to give **3o** in 89% yield as a colorless oil.

IR (neat) ν 2980, 2868, 1720, 1659, 1554, 1370, 1161, 1100, 1028, 750, 698 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.22 (m, 5H), 4.87 (dd, *J* = 14.4, 9.3 Hz, 1H), 4.63 (dd, *J* = 14.4, 3.4 Hz, 1H), 4.37 (s, 2H), 4.00-3.87 (m, 1H), 3.87-3.85 (m, 1H), 3.78 (s, 3H), 3.44 (t, *J* = 6.1 Hz, 2H), 3.19 (s, 3H), 2.04-1.96 (m, 2H), 1.46 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 194.4, 170.2, 159.7, 137.6, 128.2,

127.5, 127.4, 83.9, 77.2, 72.6, 67.6, 61.5, 43.1, 40.6, 32.3, 28.1, 27.7; MS (CI+) m/z 439 $[M+H]^+$; HRMS (CI+) calcd for $C_{21}H_{31}N_2O_8$ 439.2080, found 439.2041; $[\alpha]_D^{23}$ -18.9 (*c* 1.00, $CHCl_3$) (92% ee); HPLC (DAICEL CHIRALPAK IC, *n*-hexane/IPA = 9:1, 1.0 mL/min, 220 nm, $\tau_{minor}$ 33.2 min, $\tau_{major}$ 56.7 min).




**(H) Application to the synthesis of kainoid analog 12**[9]



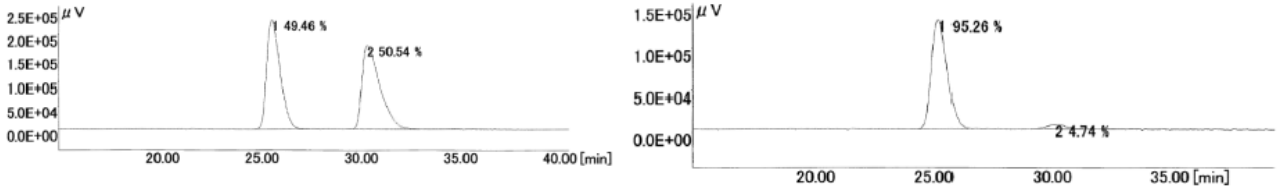

**(3*S*,4*S*)-*tert*-Butyl 3-[2'-(benzyloxy)ethyl]-5-nitro-2-oxo-4-(2'-methoxy)-phenylpentanoate (10)**

$Ni(OAc)_2·(H_2O)_4$—(S,S)-*N*,*N*'-dibenzylcyclohexane-1,2-diamine complex (isolated, 5 mg, 1 mol %) and triethylamine (7 μL, 5 mol %) were combined under $N_2$ atmosphere in 2-propanol (1 mL) at 27 °C. α-Ketoester (278 mg, 1.00 mmol) and 1-methoxy-2-[(*E*)-2-nitrovinyl]benzene (179 mg, 1.00

[9] (a) Hashimoto, K.; Horikawa, M.; Shirahama, H. *Tetrahedron Lett.* **1990**, *31*, 7047. (b) Hashimoto, K.; Shirahama, H. *Tetrahedron Lett.* **1991**, *32*, 2625. (c) Baldwin, J. E.; Fryer, A. M.; Spyvee, M. R.; Whitehead, R. C.; Wood, M. E. *Tetrahedron Lett*. **1996**, *37*, 6923. (d) Baldwin, J. E.; Bamford, S. J.; Fryer, A. M.; Rudolph, M. P. W.; Wood, M. E. *Tetrahedron* **1997**, *53*, 5255. (e) Maeda, H.; Kraus, G. A. *J. Org. Chem.* **1997**, *62*, 2314. (f) Maeda, H.; Selvakumar, N.; Kraus, G. A. *Tetrahedron* **1999**, *55*, 943. (g) Peixoto da Silva, K.; Godoi, M. N.; Correia, C. R. D. *Org. Lett*. **2007**, *9*, 2815.

mmol) were added to the resulting mixture and the mixture was stirred for 4 h. During the reaction, the product started to precipitate out, and the resulting suspension was dissolved in ethyl acetate (4 mL). The solution was passed through a pad of $SiO_2$. After evaporation of solvent, the residue was purified by MPLC ($SiO_2$, *n*-hexane/ethyl acetate = 9:1) to give **10** in 93 % yield as a colorless oil (425 mg).

IR (neat) ν 2975, 1866, 1721, 1551, 1247, 1026 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.34-7.16 (m, 6H), 7.05 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.87-6.79 (m, 2H), 4.90 (dd, *J* = 12.9, 8.3 Hz, 1H), 4.79 (dd, *J* = 12.9, 5.1 Hz, 1H), 4.35 (s, 2H), 4.11-4.05 (m, 1H), 4.05-3.97 (m, 1H), 3.81 (s, 3H), 3.47 (dd, *J* = 6.8, 4.6 Hz, 2H), 2.25-2.13 (m, 1H), 1.89 (ddd, *J* = 13.9, 8.3, 4.6 Hz, 1H), 1.31 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 194.7, 159.5, 157.0, 137.7, 130.5, 129.2, 128.2, 127.4, 127.4, 124.5, 120.7, 111.1, 83.2, 76.8, 72.6, 68.1, 55.3, 45.7, 42.7, 30.9, 27.5; MS (FAB) m/z 458 $[M+H]^+$; HRMS (FAB) calcd for $C_{25}H_{32}NO_7$ 458.2179, found 458.2180; $[\alpha]_D^{25}$ +8.3 (*c* 1.01, $CHCl_3$) (91% ee); HPLC (DAICEL CHIRALPAK IC, *n*-hexane/IPA = 95:5 1.0 mL/min, 254 nm, $\tau_{major}$ 25.2 min, $\tau_{minor}$ 30.3 min).




**(2*R*,3S,4S)-*tert*-Butyl 3-[(2'-benzyloxy)ethyl]-4-phenylpyrrolidine-2-carboxylate (S12)**

Compound **10** (410 mg, 0.897 mmol) was hydrogenated using Raney nickel (966 mg) in ethanol (10 mL) under hydrogen atmosphere (90 atm) at 75 °C for 4 h.[10] The mixture was cooled to room temperature and filtered through a pad of celite. The catalyst and the celite were washed with ethyl acetate. The combined organic solvent was concentrated under reduced pressure. The residue was purified by column chromatography ($SiO_2$, dichloromethane/methanol = 20:1) to give **S12** in 76% yield as a colorless oil (281 mg).

IR (neat) ν 2971, 2932, 2870, 1722, 1240, 1154 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.36-7.10 (m, 7H), 6.89 (td, *J* = 7.4, 0.7 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 4.21 (d, *J* = 12.0 Hz, 1H), 4.16 (d, *J* = 12.0 Hz, 1H), 4.02 (d, *J* = 6.3 Hz, 1H), 3.82 (dt, *J* = 10.3, 7.3 Hz, 1H), 3.76 (s, 3H), 3.48 (apparent t, *J* = 10.3 Hz, 1H), 3.19 (dd, *J* = 9.8, 7.3 Hz, 1H), 3.07-2.98 (m, 1H), 2.97-2.89 (m, 1H), 2.86-2.79 (m, 1H), 1.79 (br s, 1H), 1.52-1.32 (m, 11H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 172.5, 157.5, 138.4, 128.1, 127.9, 127.5, 127.4, 127.3, 127.2, 120.1, 109.9, 81.5, 72.4, 69.3, 65.8, 55.2, 48.3, 42.7, 40.8, 28.3, 26.1; MS (FAB) m/z 412 $[M+H]^+$; HRMS (FAB) calcd for $C_{25}H_{34}NO_4$ 412.2488, found 412.2490; $[\alpha]_D^{26}$ -62.2 (*c* 1.03, $CHCl_3$).

[10] Barluenga, J.; Aznar, F.; Ribas, C.; Valdés C. *J. Org. Chem*. **1998**, *63*, 10052.

**(2*R*,3*S*,4*S*)-Di-*tert*-butyl**
**3-[2-(benzyloxy)ethyl]-4-(2-methoxyphenyl)pyrrolidine-1,2-dicarboxylate (S13)**

To a solution of **S12** (358 mg, 0.869 mmol) of dichloromethane (2.7 mL) and triethylamine (242 μl, 1.74 mmol), di-*tert*-butyl dicarbonate (195 mg, 0.895 mmol) was added and stirred at room temperature for 30 min. After quenching with water, the aqueous layer was extracted with dichloromethane (8 mL x 3). The combined organic layers were washed with brine (5 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography ($SiO_2$, *n*-hexane/ethyl acetate = 5:1) to give **S13** in 99% yield as a colorless oil (440mg).

This compound exists as a mixture of rotamers in $CDCl_3$ at 23 °C, and contains the epimer **11**.

IR (neat) ν 2975, 2931, 1692, 1391, 1365, 1242, 1151 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.35-7.15 (m, 7H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.82-6.75 (m, 1H), 4.43 (d, *J* = 7.8 Hz, 0.4H [minor]), 4.37 (d, *J* = 8.3 Hz, 0.6H [major]), 4.27 (s, 2H), 3.99-3.65 (m, 6H), 3.25-2.98 (m, 3H), 1.60-1.36 (m, 20H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 167.0, 169.9, 157.2, 157.2, 154.1, 138.4, 128.6, 128.3, 128.1, 127.7, 127.7, 127.5, 127.4, 127.3, 127.3, 127.0, 126.9, 120.3, 120.2, 109.9, 109.7, 81.3, 79.9, 72.5, 69.1, 68.9, 63.9, 63.8, 55.2, 55.2, 49.9, 49.7, 41.0, 40.3, 39.7, 39.2, 28.6, 28.5, 28.2, 28.1, 26.8, 26.5; MS (FAB) m/z 512 $[M+H]^+$; HRMS (FAB) calcd for $C_{30}H_{42}NO_6$ 512.3012, found 512.2999; $[\alpha]_D^{26}$ -42.9 (*c* 1.06, $CHCl_3$).

**(2S,3*S*,4*S*)-Di-*tert*-butyl**
**3-[2-(benzyloxy)ethyl]-4-(2-methoxyphenyl)pyrrolidine-1,2-dicarboxylate (11)**

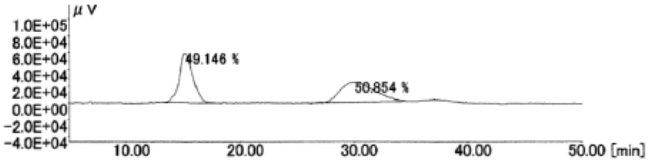
To a solution of **S13** (307 mg, 0.600 mmol) and DBU (412 μL, 3.00 mmol) in benzene (6 mL) and 2-methyl-2-propanol (307 μl, 3.23 mmol) was added sodium hydride (55%, 65.5 mg, 1.50 mmol) at room temperature and stirred for 18 h.[11] After quenching with water (3 mL), the aqueous layer was extracted with ethyl acetate (10 mL x 3). The combined organic layers were washed with brine (10 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by MPLC (*n*-hexane/ethyl acetate = 80:20) to give **11** in 86% yield as a colorless oil (246 mg).

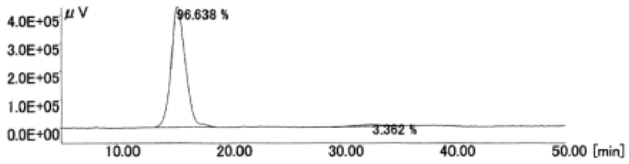
This compound exists as a mixture of rotamers in $CDCl_3$ at 22 °C.

IR (neat) ν 2976, 2927, 1693, 1392, 1365, 1244, 1154, 1121 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.33-7.19 (m, 6H), 7.09-7.02 (m, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 4.41 (s, 2H), 4.10 (d, *J* = 2.9 Hz, 0.4H [minor]), 4.08 (d, *J* = 4.2 Hz, 0.6H [major]), 4.01-3.89 (m, 1H), 3.87-3.64 (m, 5H), 3.49-3.34 (m, 2H), 2.83-2.72 (m, 1H), 1.55-1.24 (m, 20H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ

[11] Modified condition of Ogasawara's method (Takano, S.; Iwabuchi, Y.; Ogasawara, K. *J. Am. Chem. Soc.* **1987**, *109*, 1204).

171.7, 171.6, 157.1, 157.1, 154.2, 153.9, 138.3, 128.1, 127.7, 127.5, 127.4, 127.3, 127.3, 127.2, 127.1, 126.8, 120.4, 120.4, 110.2, 110.1, 80.9, 80.9, 79.8, 79.6, 72.8, 68.8, 68.5, 64.7, 64.5, 55.3, 55.2, 49.3, 48.4, 44.0, 42.8, 38.8, 38.3, 28.7, 28.6, 28.5, 28.2, 28.1, 28.1; MS (FAB) m/z 512 $[M+H]^+$; HRMS (FAB) calcd for $C_{30}H_{42}NO_6$ 512.3012, found 512.2997; $[\alpha]_D^{26}$ -40.7 (*c* 1.07, $CHCl_3$).




**(2S,3*S*,4*S*)-Di-*tert*-butyl 3-[2-(hydroxy)ethyl]-4-(2-methoxyphenyl)pyrrolidine-1,2-dicarboxylate (S14)**

Compound **11** (150.2 mg, 0.294 mmol) was hydrogenated in THF (2 mL) for 3 h in presence of 10% Pd/C (10 wt%). The mixture was filtered through a pad of celite. The catalyst and the celite were washed with ethyl acetate. The filtrate was concentrated under reduced pressure. The residue was purified by MPLC ($SiO_2$, hexane/ethyl acetate = 83:37 to 50:50) to give **S14** in 94% yield as a colorless oil (117 mg).

This compound exists as a mixture of rotamers in $CDCl_3$ at 23 °C.

IR (neat) ν 3435 (br), 2976, 1692, 1402, 1367, 1365, 1245, 1157, 1133 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.22 (apparent td, *J* = 8.1, 1.5 Hz, 1H), 7.05 (ddd, *J* = 8.1, 7.3, 1.5 Hz, 1H), 6.91 (td, *J* = 7.3, 0.7 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 4.07 (d, *J* = 4.6 Hz, 0.4H [minor]), 4.00 (d, *J* = 3.9 Hz, 0.6H [major]), 3.99-3.90 (m, 1H), 3.87-3.66 (m, 5H), 3.65-3.50 (m, 2H), 2.79-2.67 (m, 1H), 1.65-1.55 (m, 1H), 1.56-1.43 (m, 18H), 1.43-1.24 (m, 2H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 171.9, 171.8, 157.0, 156.9, 153.8, 127.8, 127.4, 127.0, 120.6, 120.6, 110.3, 110.2, 81.2, 80.0, 79.7, 64.6, 64.3, 61.3, 61.2, 55.4, 49.8, 48.9, 44.1, 43.1, 39.0, 38.4, 31.7, 28.6, 28.5, 28.1, 28.1; MS (FAB) m/z 422 $[M+H]^+$; HRMS (FAB) calcd for $C_{23}H_{36}NO_6$ 422.2543, found 422.2549; $[\alpha]_D^{27}$ -67.9 (*c* 1.03, $CHCl_3$).

**2-[(2*S*,3*S*,4*S*)-1,2-Di-(*tert*-butoxycarbonyl)-4-(2-methoxyphenyl)pyrrolidin-3-yl]acetic acid (S15)**

To a solution of **S14** (74.1 mg, 0.176 mmol) in dichloromethane (1.5 mL) was added Dess-Martin periodinane (89.5 mg, 0.211 mmol). The mixture was stirred at room temperature for 2 h. The reaction mixture was filtered and concentrated under reduced pressure. The residue was purified by column chromatography ($SiO_2$, *n*-hexane/ethyl acetate = 2:1) to give the aldehyde as a colorless oil.

To a solution of the aldehyde (43.5 mg, 0.104 mmol) in 2-methyl-2-butene (281μL, 2.65 mmol) and 2-methyl-2-propanol (3.4 mL) at 0 ºC was added a solution of $NaClO_2$ (178 mg, 1.97 mmol) and $NaH_2PO_4 \cdot 2H_2O$ (146 mg, 0.93 mmol) in $H_2O$ (0.8 mL). The reaction mixture was stirred at room

temperature for 0.5 h. The reaction was quenched by saturated aqueous $NH_4Cl$ and extracted with ethyl acetate (8 mL x 3). The combined organic layers were washed with brine (10 mL), dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by MPLC (*n*-hexane/ethyl acetate = 95:5 and then chloroform/methanol = 95:5) to give **S15** in 82% yield (2 steps) as a colorless oil (44 mg).

This compound exists as a mixture of rotamers in $CDCl_3$ at 25 °C.

IR (neat) ν 3216 (br), 2977, 2927, 1738, 1704, 1397, 1368, 1247, 1161 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) δ 7.22 (apparent td, *J* = 8.3, 1.5 Hz, 1H), 7.01 (t, *J* = 7.1 Hz, 1H), 6.90 (t, *J* = 7.1 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 4.06-3.69 (m, 7H), 3.18-3.06 (m, 1H), 2.30-2.22 (m, 1H), 2.02 (dd, *J* = 17.0, 7.2 Hz, 1H), 1.50 (s, 9H), 1.48 (s, 9H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 177.5, 177.5, 171.1, 170.9, 157.1, 157.1, 154.0, 153.9, 128.2, 127.2, 126.4, 126.0, 120.7, 120.7, 110.0, 81.3, 81.2, 80.3, 79.9, 64.1, 63.9, 55.0, 49.8, 49.0, 43.2, 42.2, 38.3, 37.7, 33.3, 33.2, 28.5, 28.4, 28.0, 28.0; MS (FAB) m/z 436 $[M+H]^+$; HRMS (FAB) calcd for $C_{23}H_{34}NO_7$ 436.2335, found 436.2345; $[\alpha]_D^{25}$ -63.4 (*c* 1.07, $CHCl_3$).

**(2*S*,3*S*,4*S*)-3-(Carboxymethyl)-4-(2-methoxyphenyl)pyrrolidine-2-carboxylic acid (12)**

To a solution of **S15** (34.8 mg, 0.080 mmol) in dichloromethane (0.5 mL) was added trifluoroacetic acid (0.3 mL) at room temperature, and the resulting mixture was stirred for 2 h. After concentration under reduced pressure, the residue was added to a column containing Dowex-50 WX8 hydrogen form (50-100 mesh). After elution with 3% aqueous $NH_3$, and the collected fractions were freeze-dried to give **12** in 90% as a white solid (20 mg).

Mp 167-169 ºC; IR (neat) ν 2944 (br), 2835, 1710, 1601, 1495, 1384, 1245 $cm^{-1}$; $^1$H-NMR (400 MHz, $D_2O$) δ 7.39 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.3 Hz, 1H), 4.08 (d, *J* = 7.4 Hz, 1H), 3.98 (dd, *J* = 15.9, 7.8 Hz, 1H), 3.86 (s, 3H), 3.86-3.79 (m, 1H), 3.79-3.70 (m, 1H), 3.23-3.13 (m, 1H), 2.48 (dd, *J* = 16.4, 4.9 Hz, 1H), 2.02 (dd, *J* = 16.4, 10.3 Hz, 1H); $^{13}$C-NMR (100 MHz, $CDCl_3$) δ 177.6, 173.9, 157.6, 130.2, 129.8, 124.6, 121.1, 111.7, 66.1, 55.8, 48.4, 43.2, 41.9, 35.9; MS (FAB, negative mode) m/z 278 $[M-H]^-$; HRMS (FAB, negative mode) calcd for $C_{14}H_{16}NO_5$ 278.1028, found 278.1039; $[\alpha]_D^{25}$ +7.7 (*c* 0.58, $H_2O$).

**(I) X-ray crystal structure analysis of 3a**

CCDC-752633 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data: $C_{22}H_{25}O_5N$, $FW$ = 383.43, orthorhombic $P2_12_12_1$, $a$ = 6.14599(11), $b$ = 17.8565(3), $c$ = 19.4532(4) Å, $V$ = 2134.91(7) Å$^3$; $D_X$ = 1.193 Mg m$^{-3}$; $Z$ = 4; $\mu$(Cu $K\alpha$) = 0.691 mm$^{-1}$, $T$ = 300 K. The crystals of **3a** showed solid-to-solid phase transition below room temperature. Since the single crystal of **3a** was decomposed on the phase transition, the measurements were performed at 300 K.

Block shaped colorless crystals were grown from a *n*-hexane/chloroform solution of **3a**. A single crystal with the dimensions of 0.20 x 0.13 x 0.08 mm was mounted on a glass capillary and set on a Rigaku RAXIS-RAPID diffractomter. The diffraction data were collected using graphite-monochromated Cu $K\alpha$ radiation. The unit cell dimensions were determined using 28379 reflections with $6.8 \leq 2\theta \leq 136.6°$. The diffraction data of 38239 within $6.7 \leq 2\theta \leq 136.5°$ were collected and merged to give 3827 unique reflections with $R_{int}$ of 0.0240. The structure was solved by a direct method and refined on $F^2$ by a least-squares method by the programs SIR2004 and SHELXL97, respectively. The final $R$ values against 2620 unique reflections with $I > 2\sigma(I)$ are 0.0458 and 0.1177 for $R(F)$ and $wR(F^2)$, respectively. The phenyl and benzyl groups were disordered.

The absolute structure of the crystal was determined by comparing four Bijvoet pairs, which differed in intensities each other, significantly. The reflections were 2 1 1, 3 4 3, 3 1 2 and 1 7 6, and their Bivoet pairs. The result was confirmed by Flack parameter, which was refined using reflections of $2\theta$<120°. 1846 Friedel pairs, $\chi$ = 0.0(3).

Programs used: SIR2004: Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G., Spagna, R. *J. Appl. Cryst.* **2005**, *38*, 381-388; SHELXL97: Sheldrick, G. M. *Acta Crystallogr. Sect. A*, **2008**, *64*, 112-122.

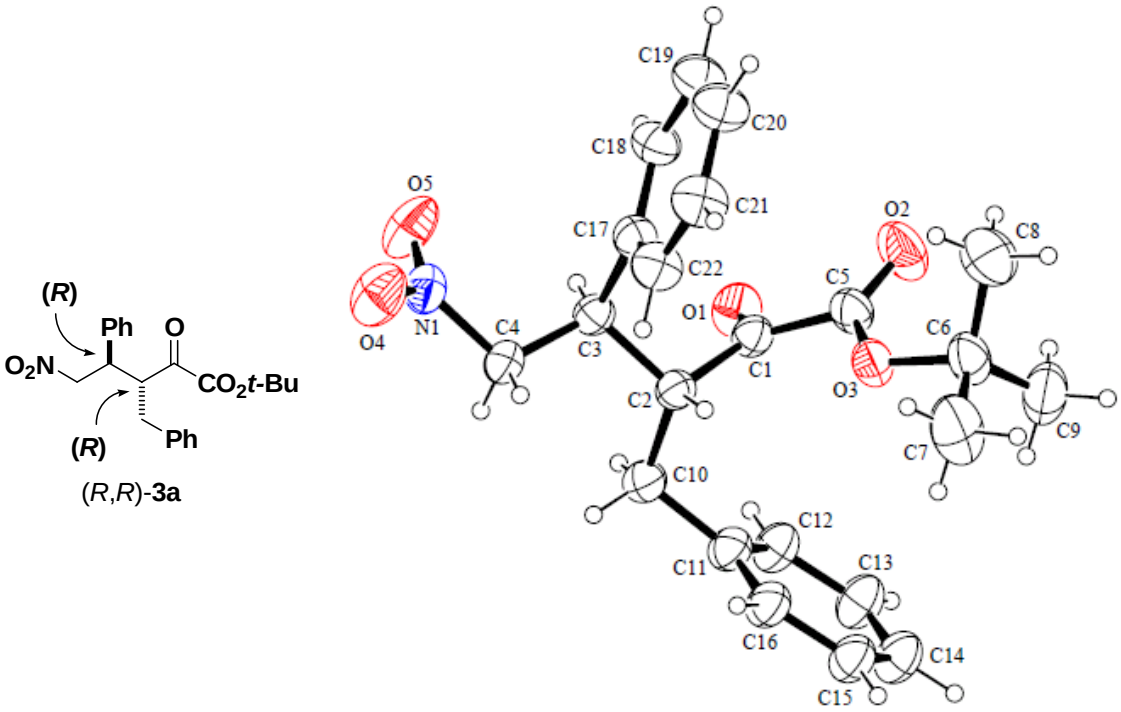
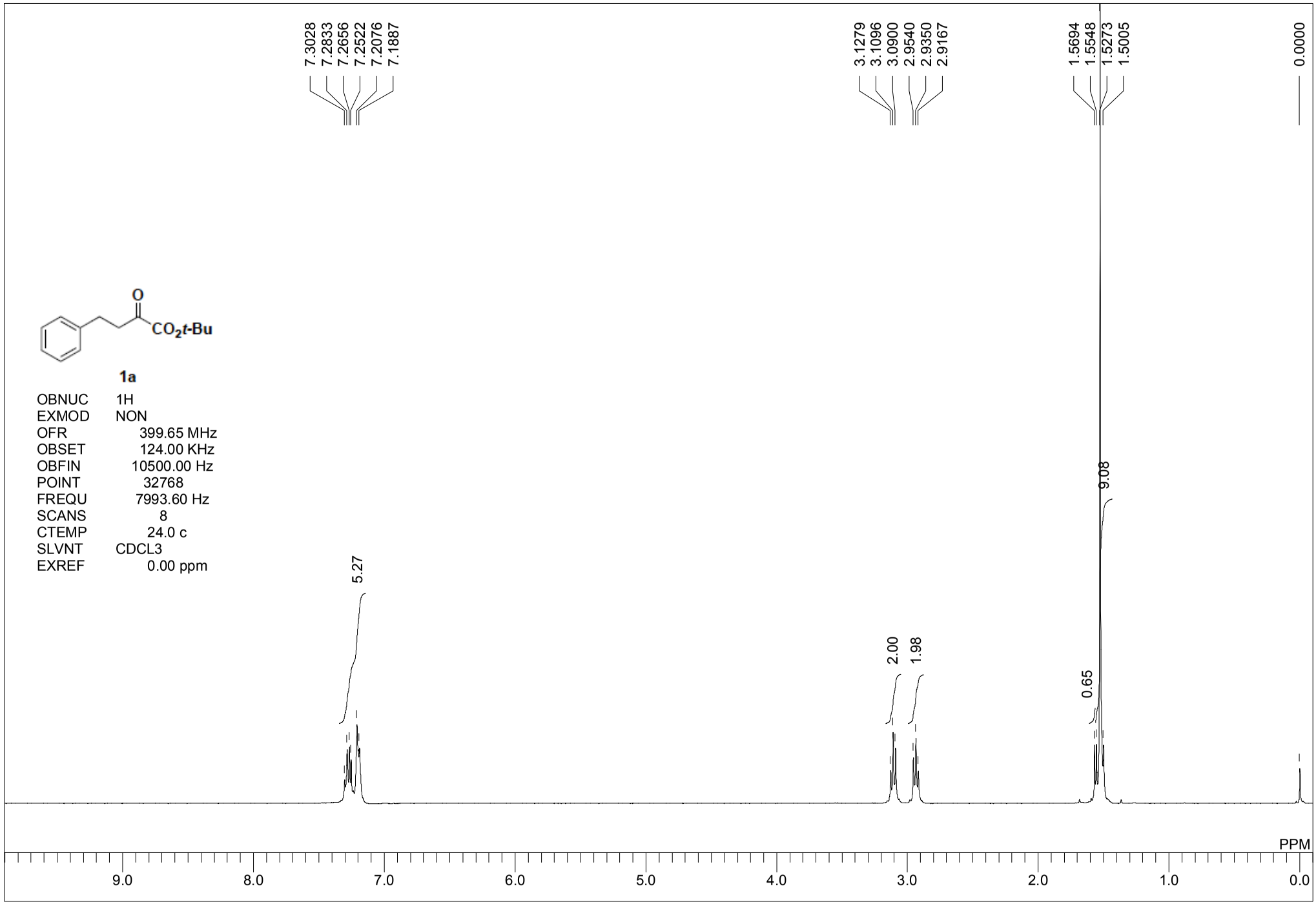



***Figure 1.*** Molecular structure of **3a**. Only the major parts of the phenyl and benzyl groups were drawn. Displacement ellipsoids are drawn at the 30 % probability level.

**(J) NMR spectra**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2.9167
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1.5273
1.5005
0.0000
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1a
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EXMOD NON
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OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
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SLVNT CDCL3
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1.98
0.65
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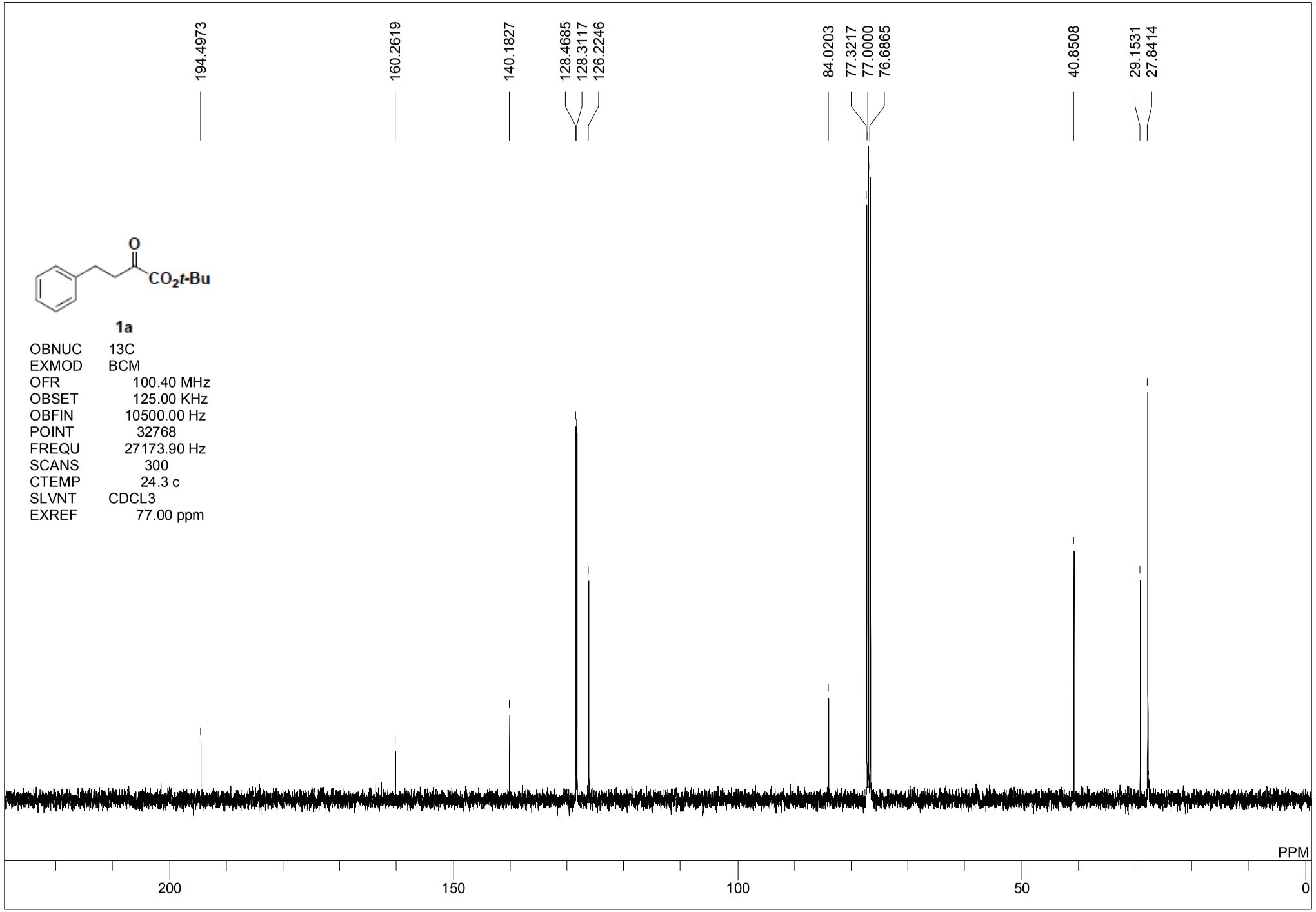
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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40.8508
29.1531
27.8414
O
CO2t-Bu
1a
OBNUC 13C
EXMOD BCM
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OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
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50
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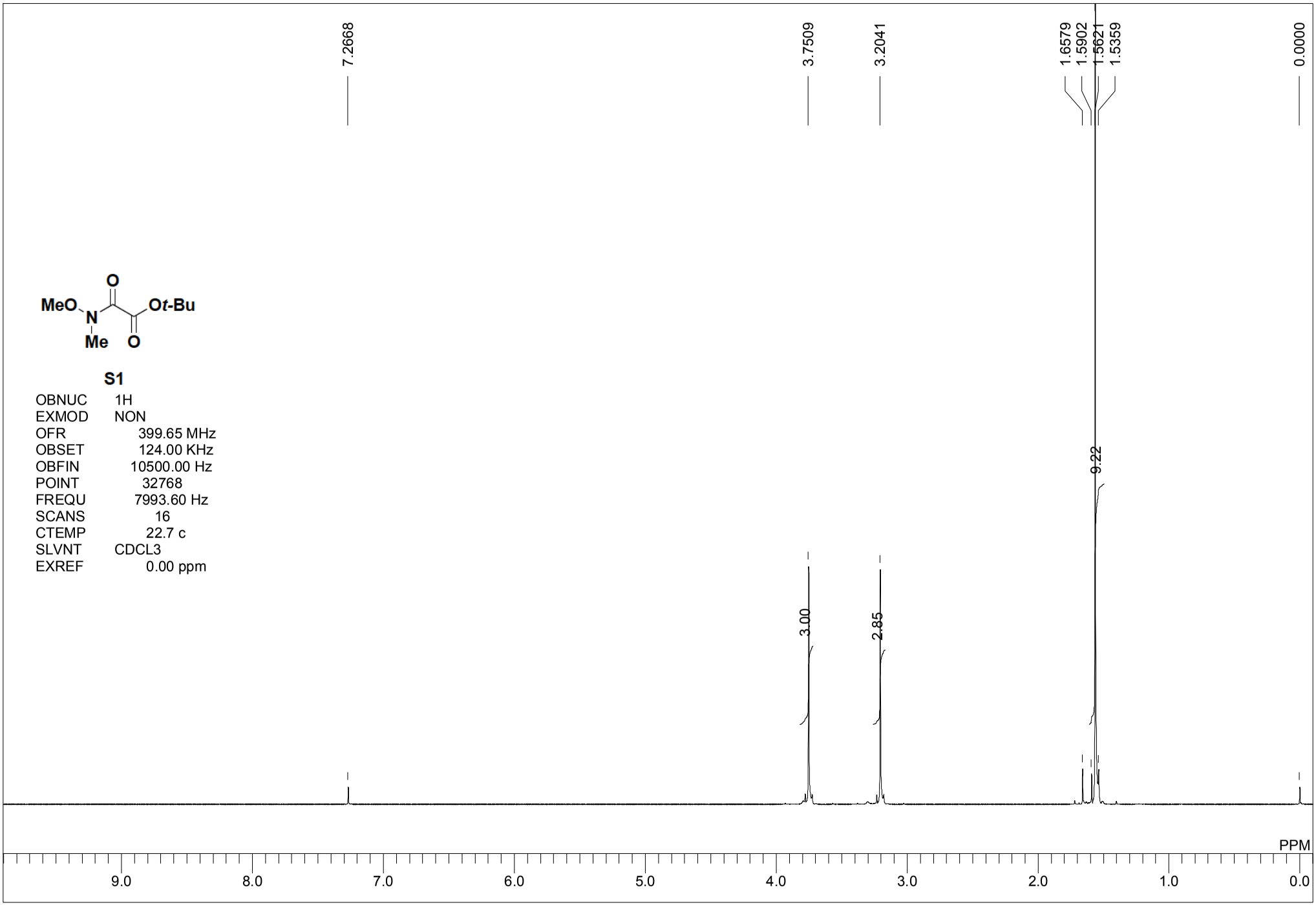
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Ot-Bu
O
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OBFIN 10500.00 Hz
POINT 32768
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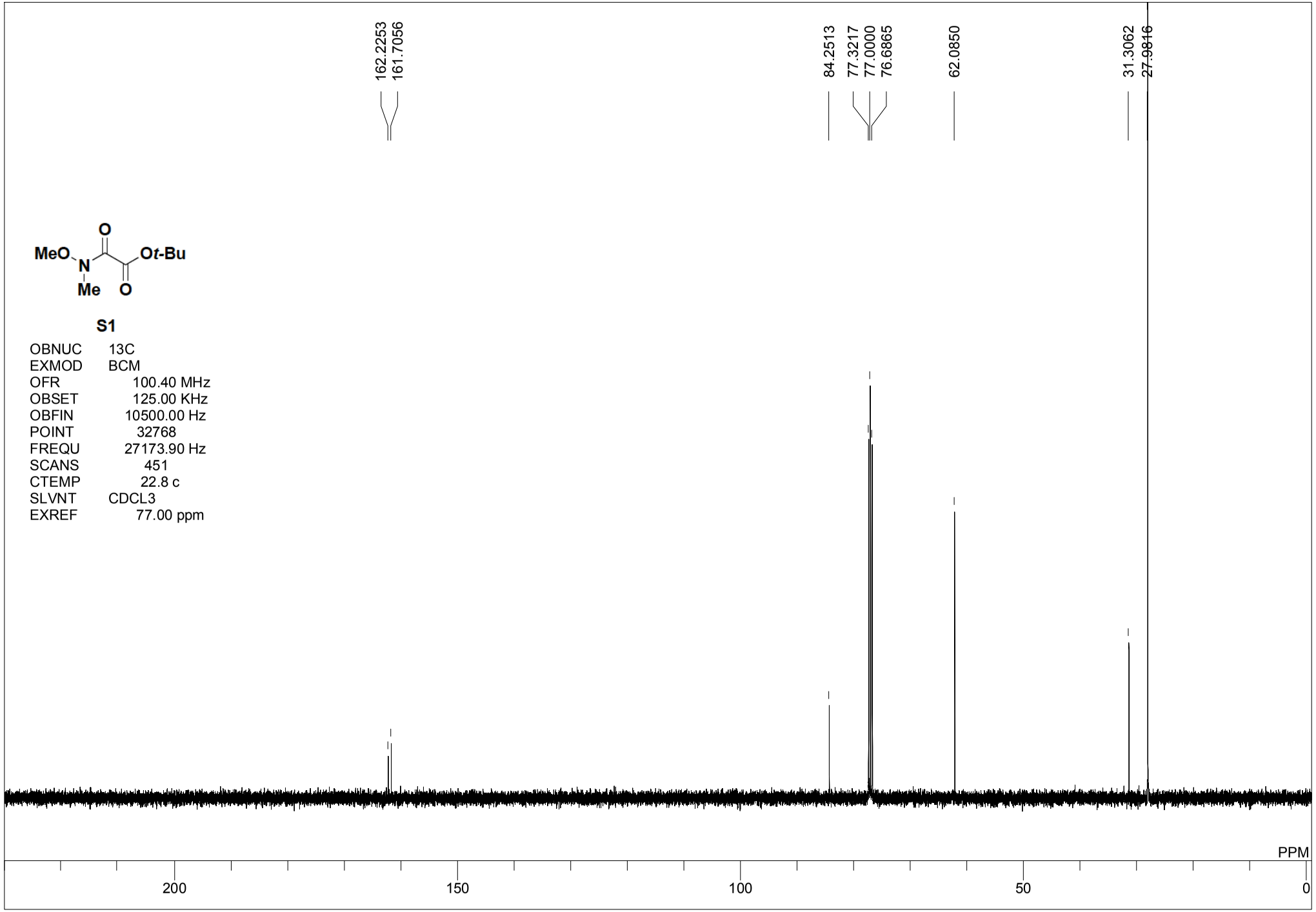
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O
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O
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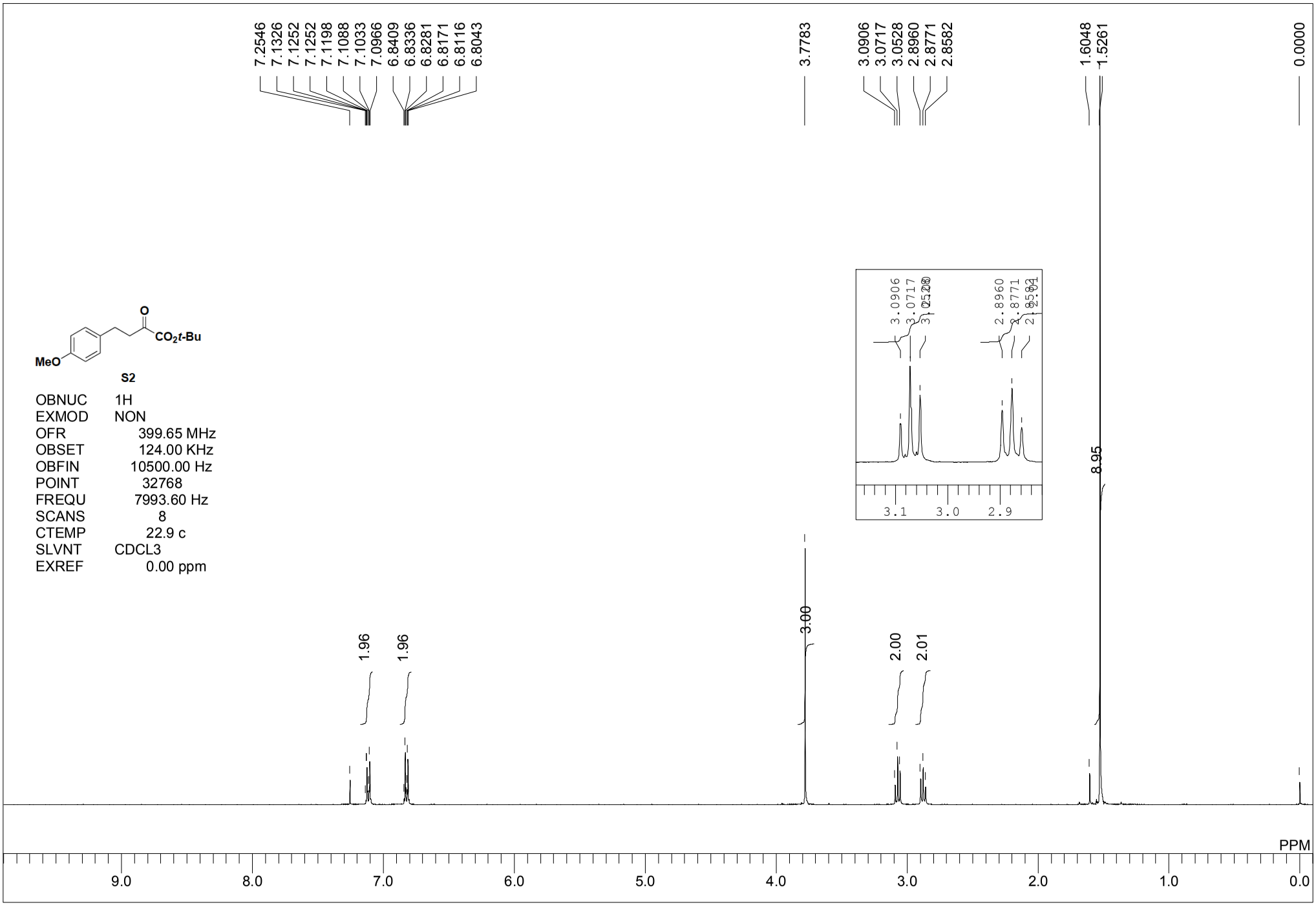
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6.8043
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2.8960
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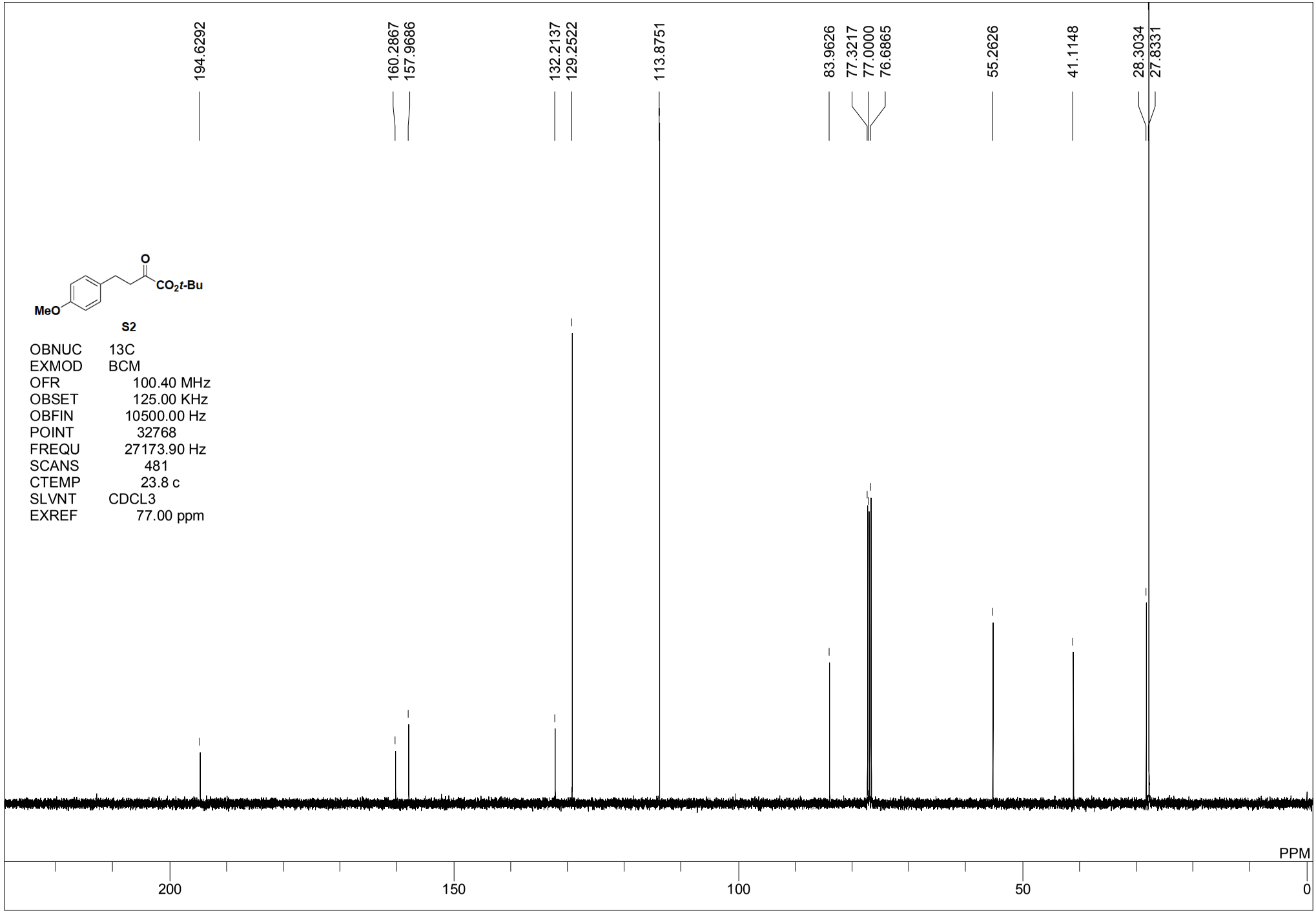
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MeO
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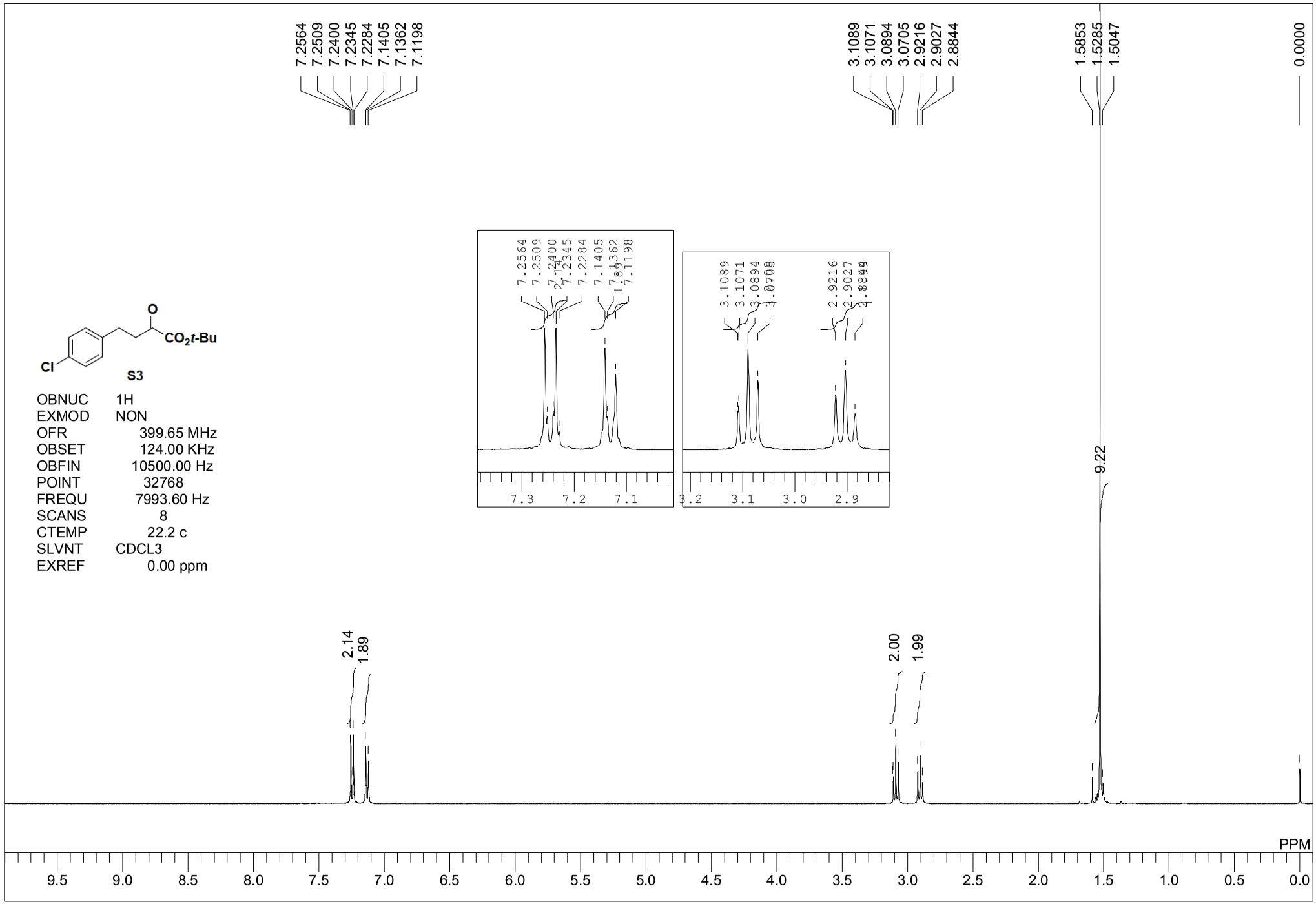
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Cl
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PPM
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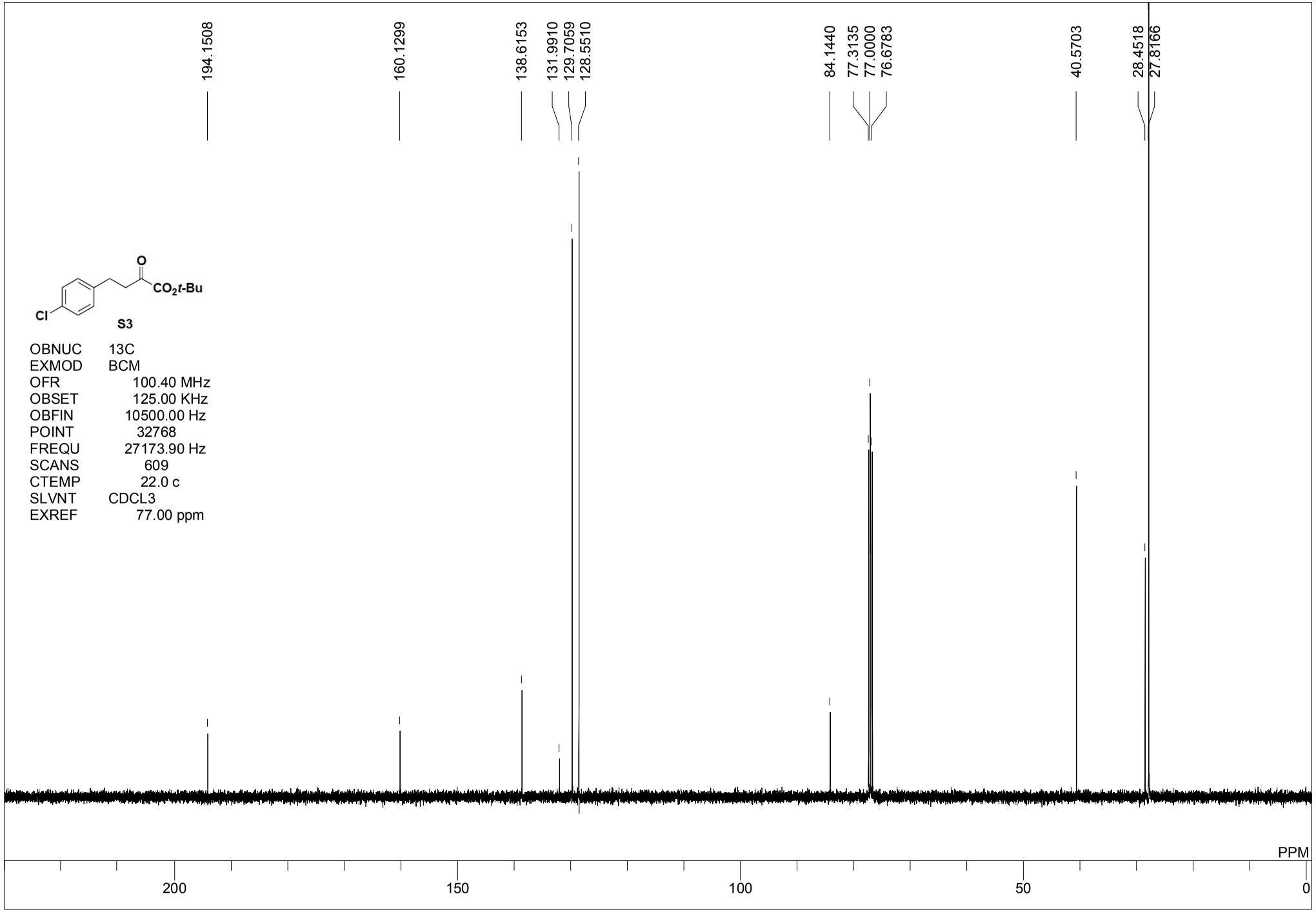
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27.8166
O
CO2t-Bu
Cl
S3
OBNUC 13C
EXMOD BCM
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OBSET 125.00 KHz
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POINT 32768
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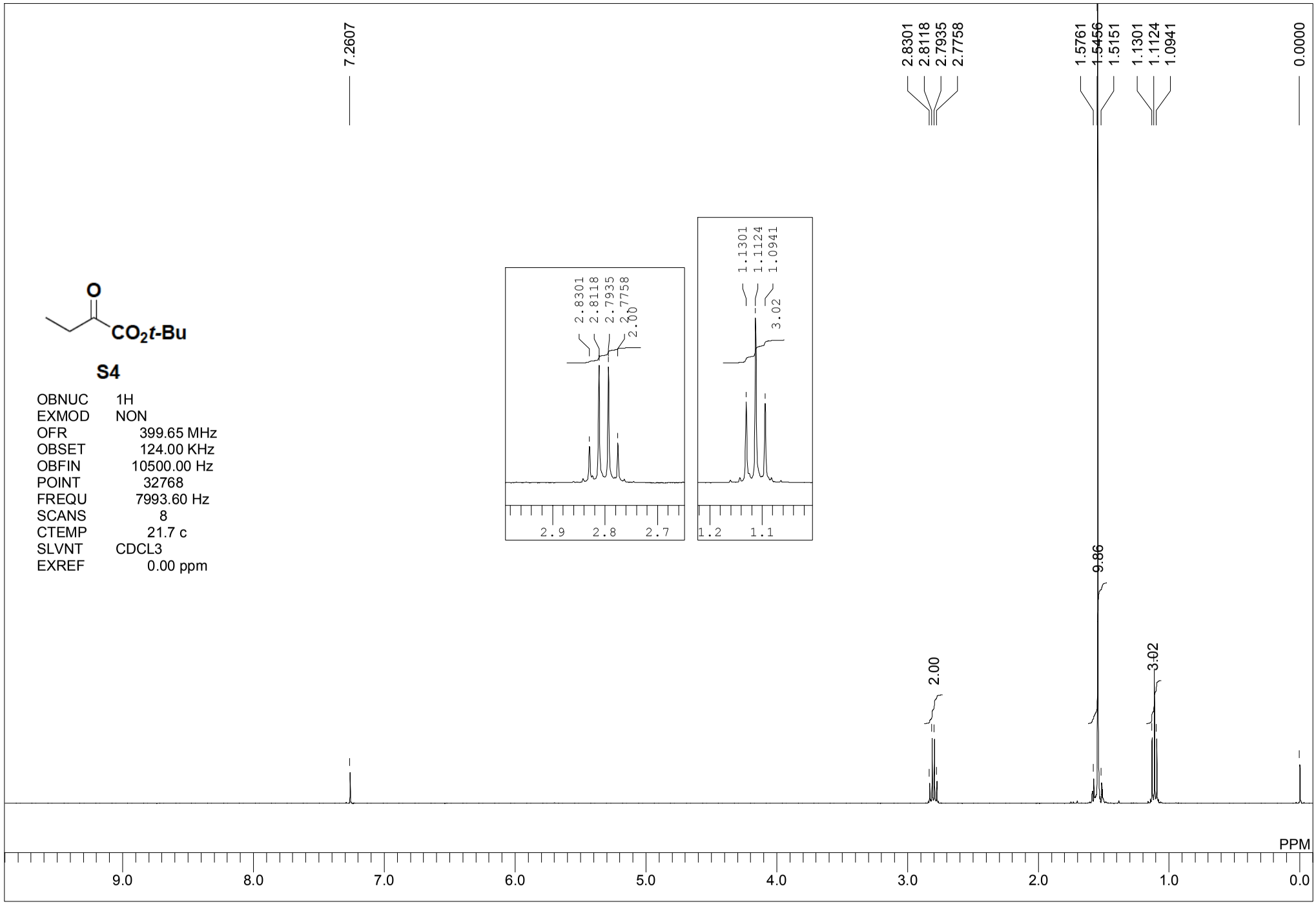
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FREQU 7993.60 Hz
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SLVNT CDCL3
EXREF 0.00 ppm
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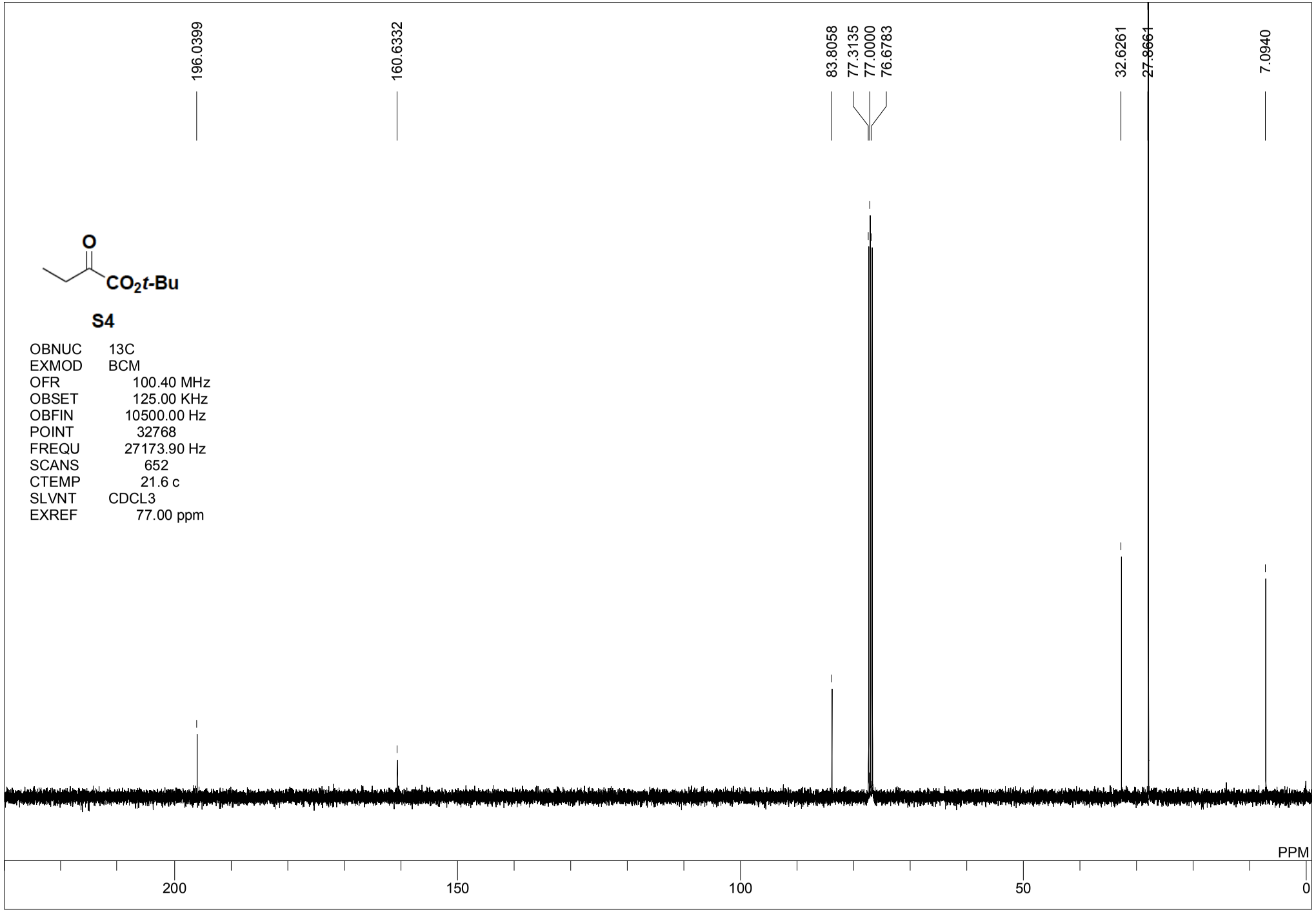
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POINT 32768
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50
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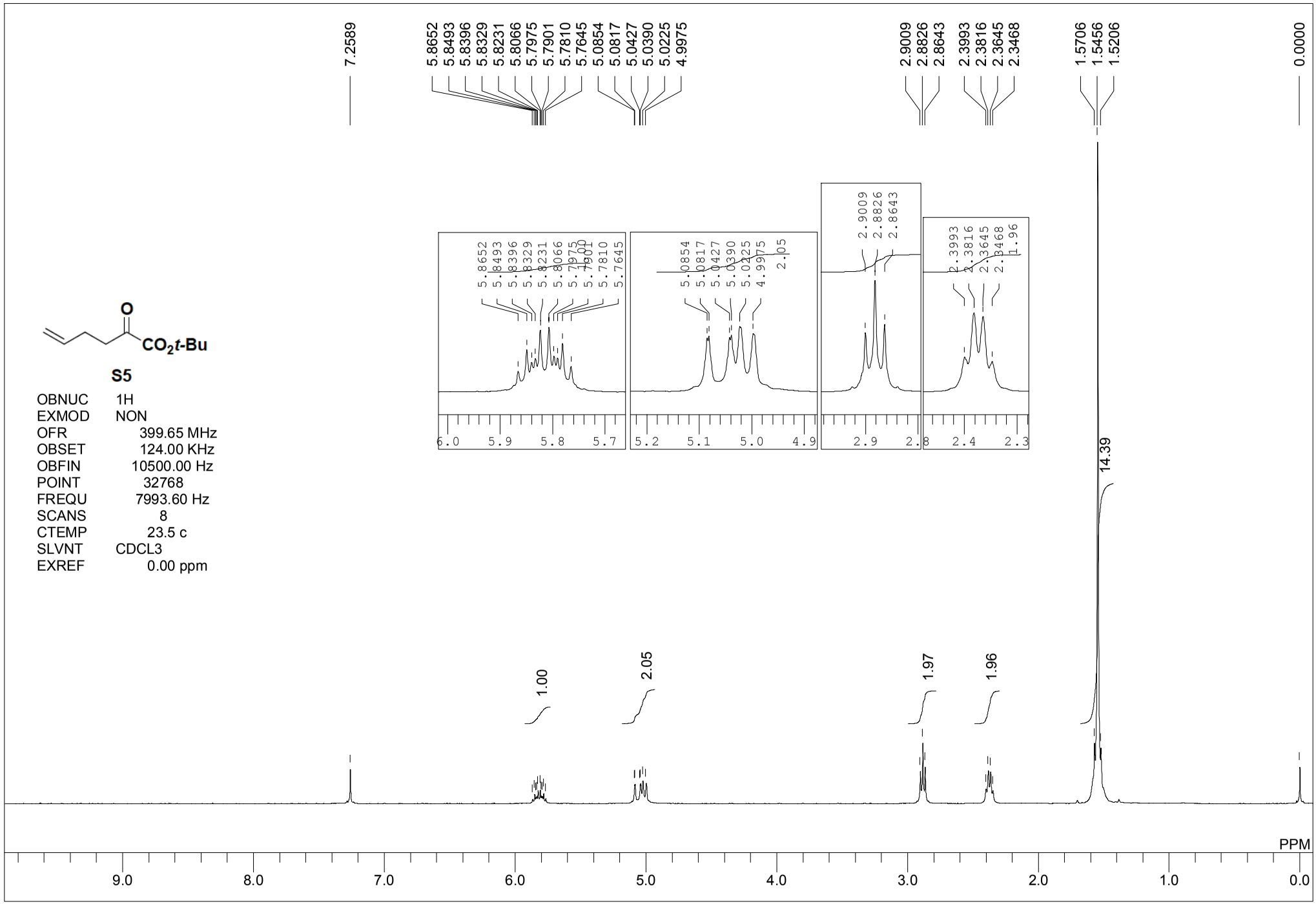
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5.7645
5.0854
5.0817
5.0427
5.0390
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4.9975
2.9009
2.8826
2.8643
2.3993
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S5
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EXMOD NON
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OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
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SLVNT CDCL3
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1.96
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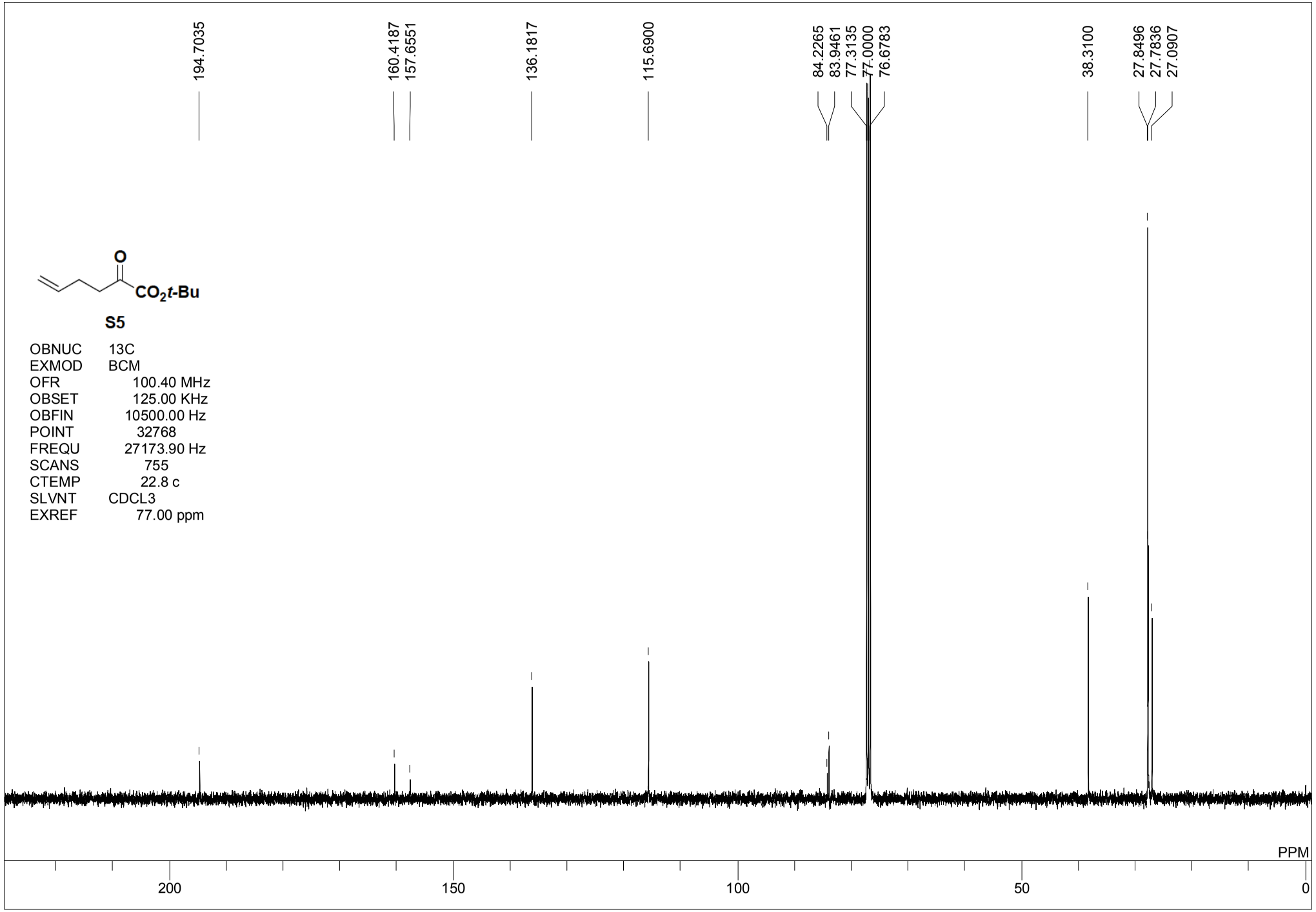
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27.0907
O
CO2t-Bu
S5
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EXMOD BCM
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OBFIN 10500.00 Hz
POINT 32768
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50
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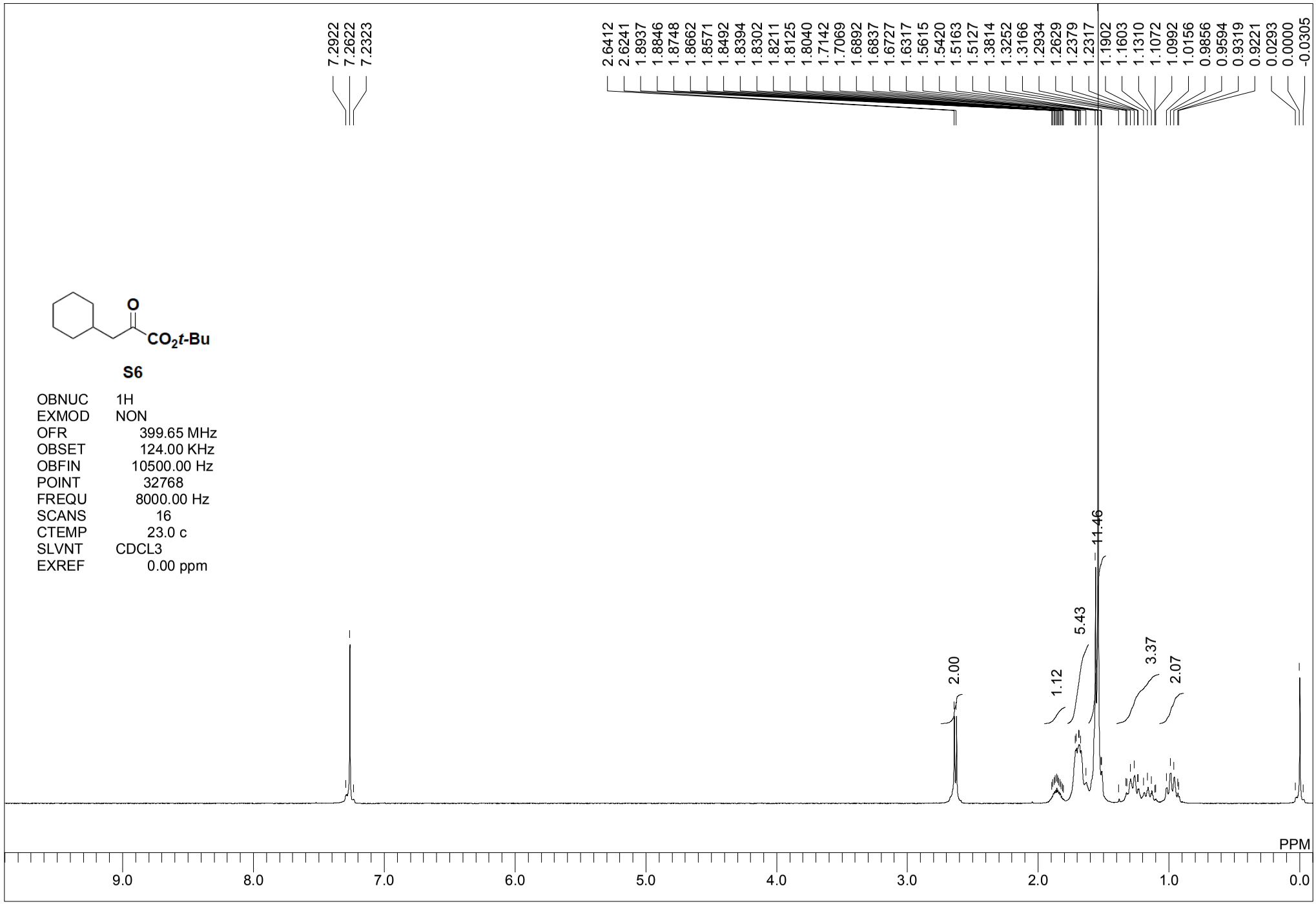
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1.7069
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1.5127
1.3814
1.3252
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1.2934
1.2629
1.2379
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1.1603
1.1310
1.1072
1.0992
1.0156
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S6
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OBFIN 10500.00 Hz
POINT 32768
FREQU 8000.00 Hz
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EXREF 0.00 ppm
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3.37
2.07
2.00
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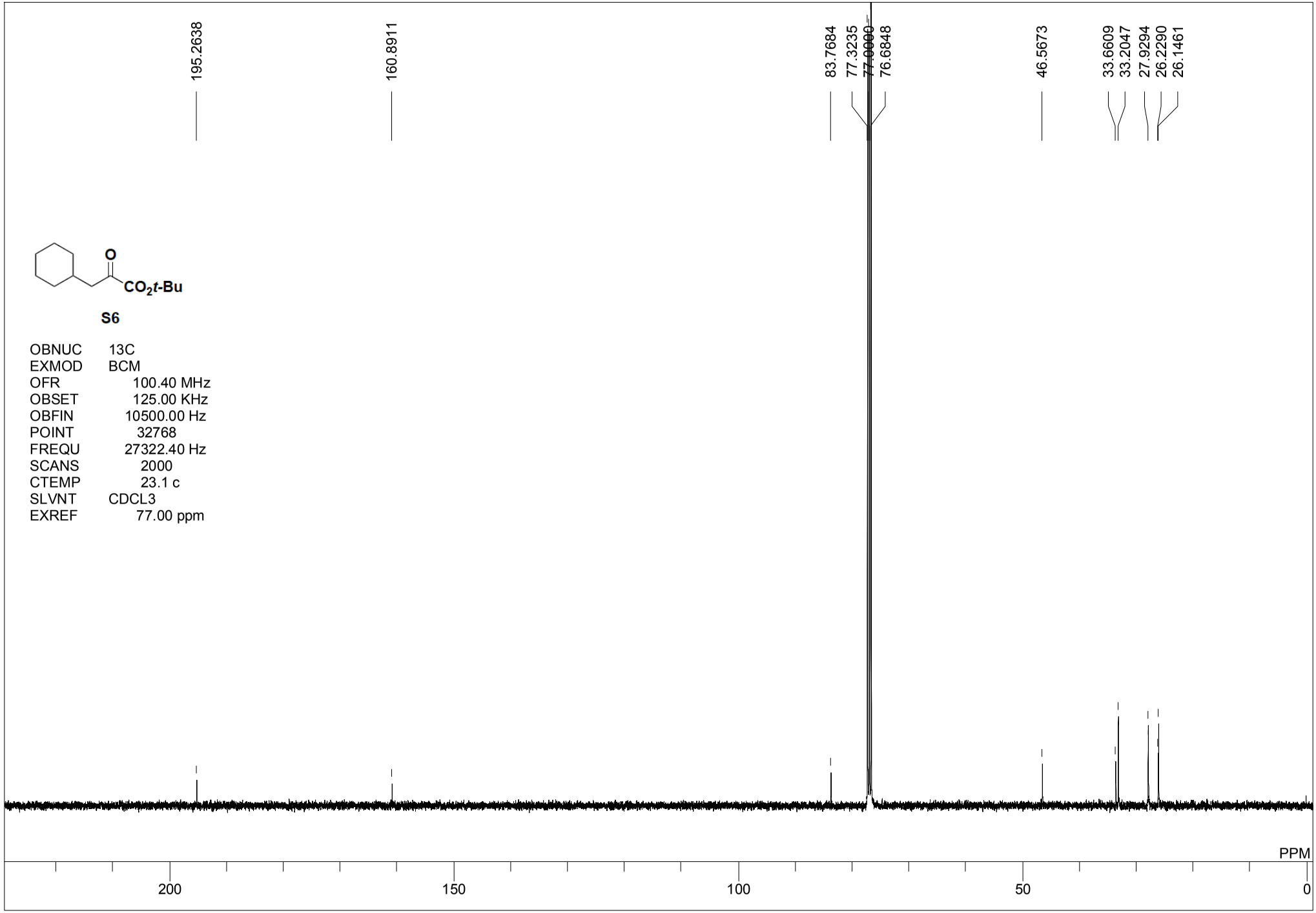
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26.1461
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CO2t-Bu
S6
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
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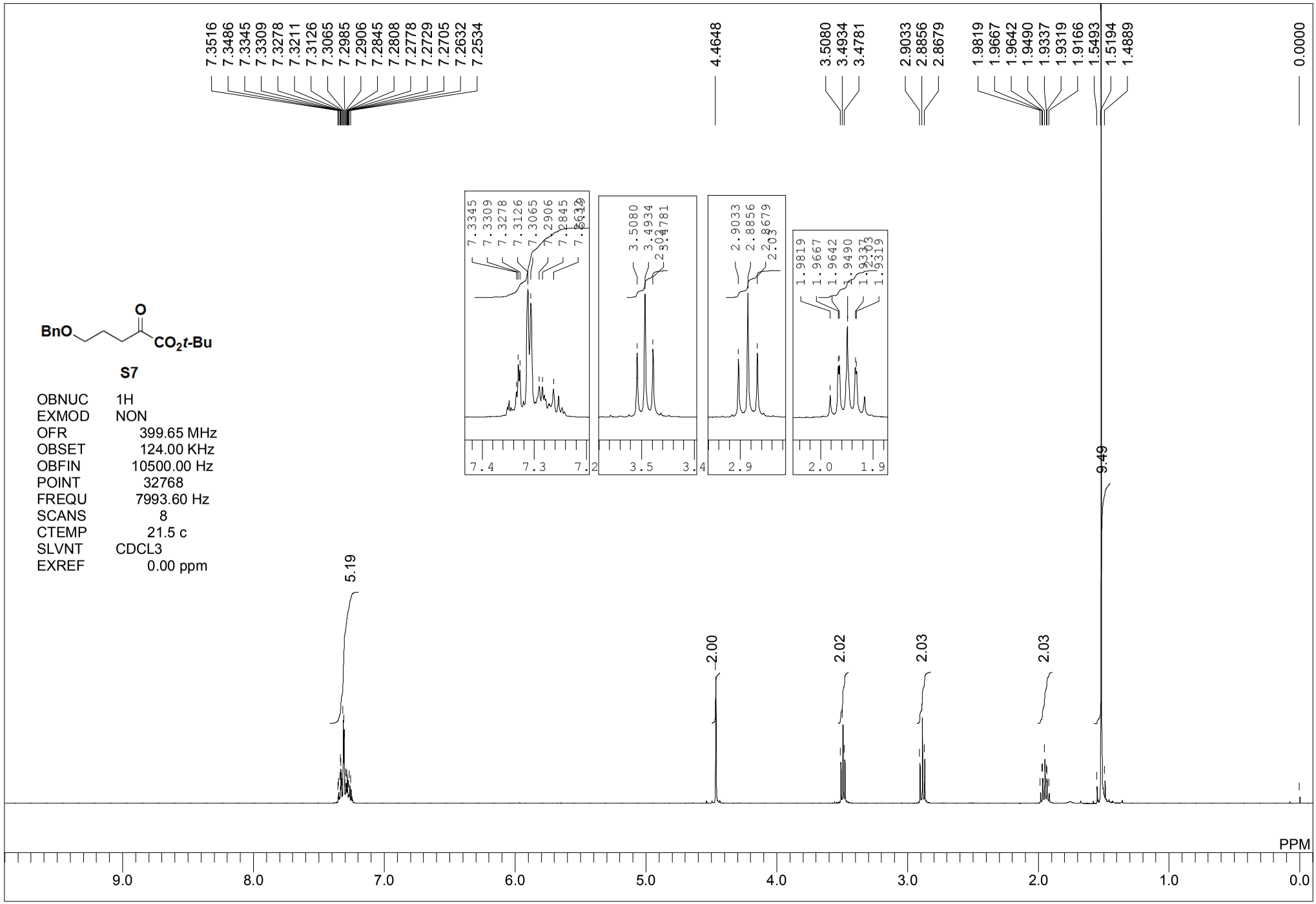
50
0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BnO
O
CO2t-Bu
S7
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EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
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2.03
2.03
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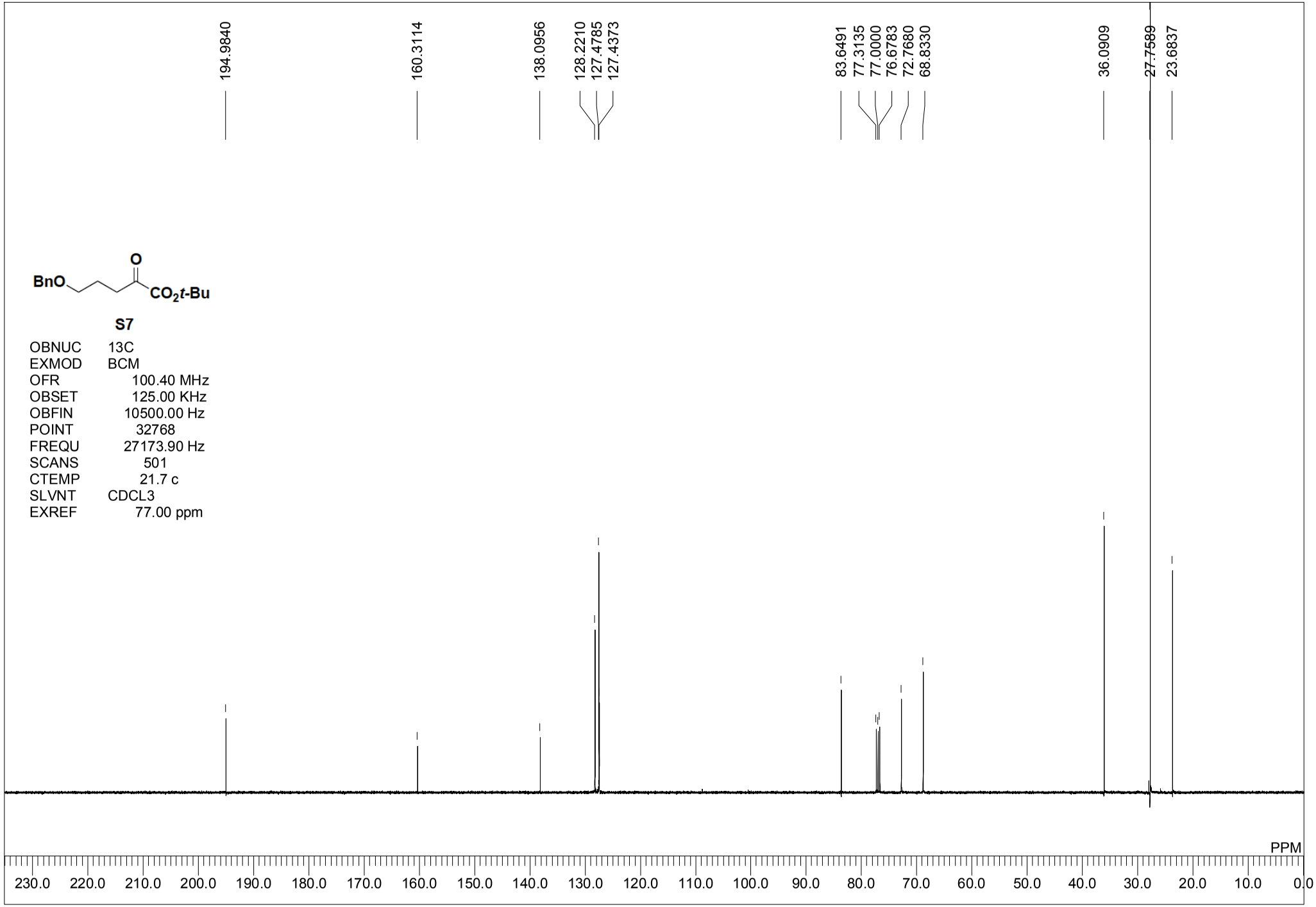
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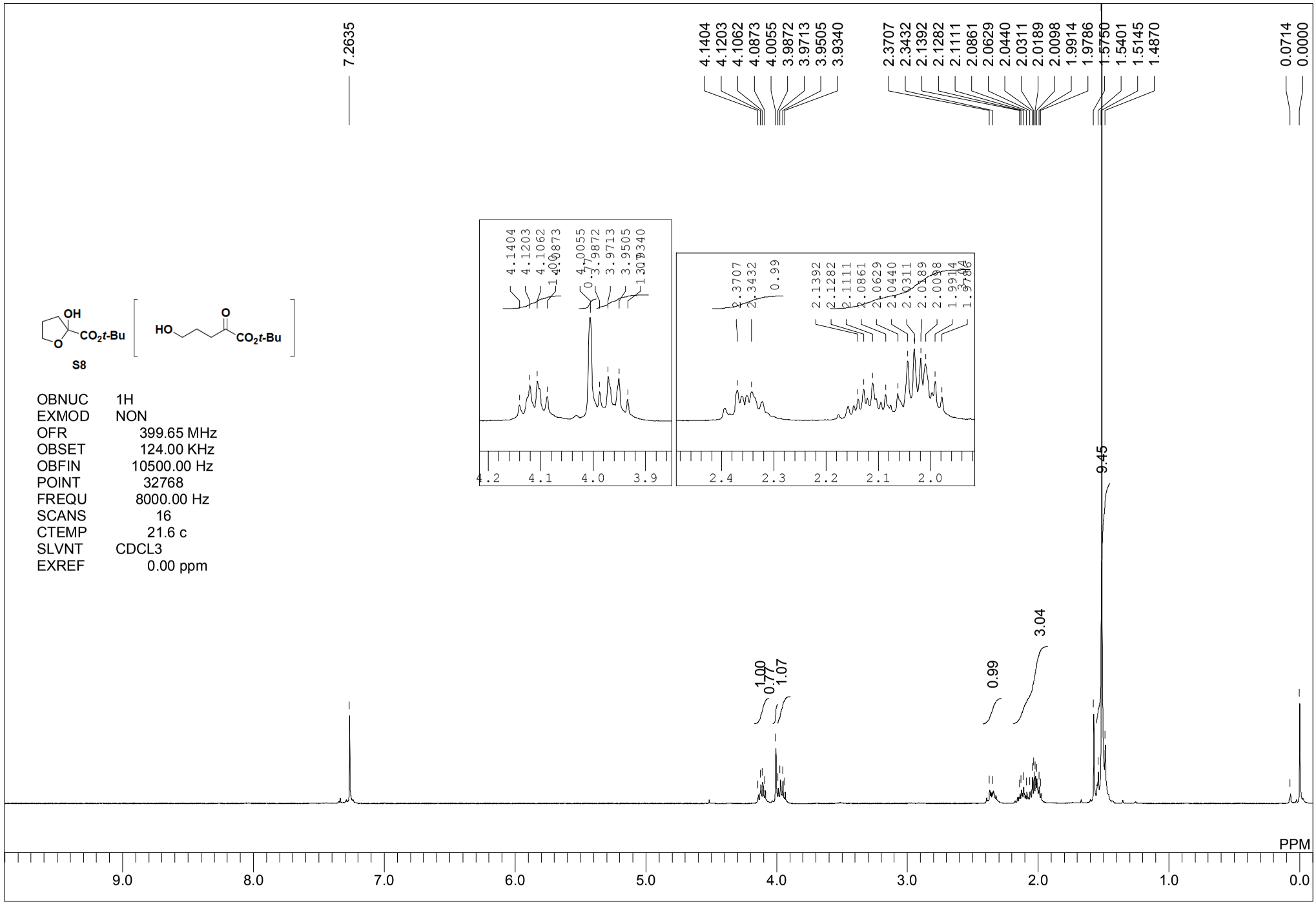
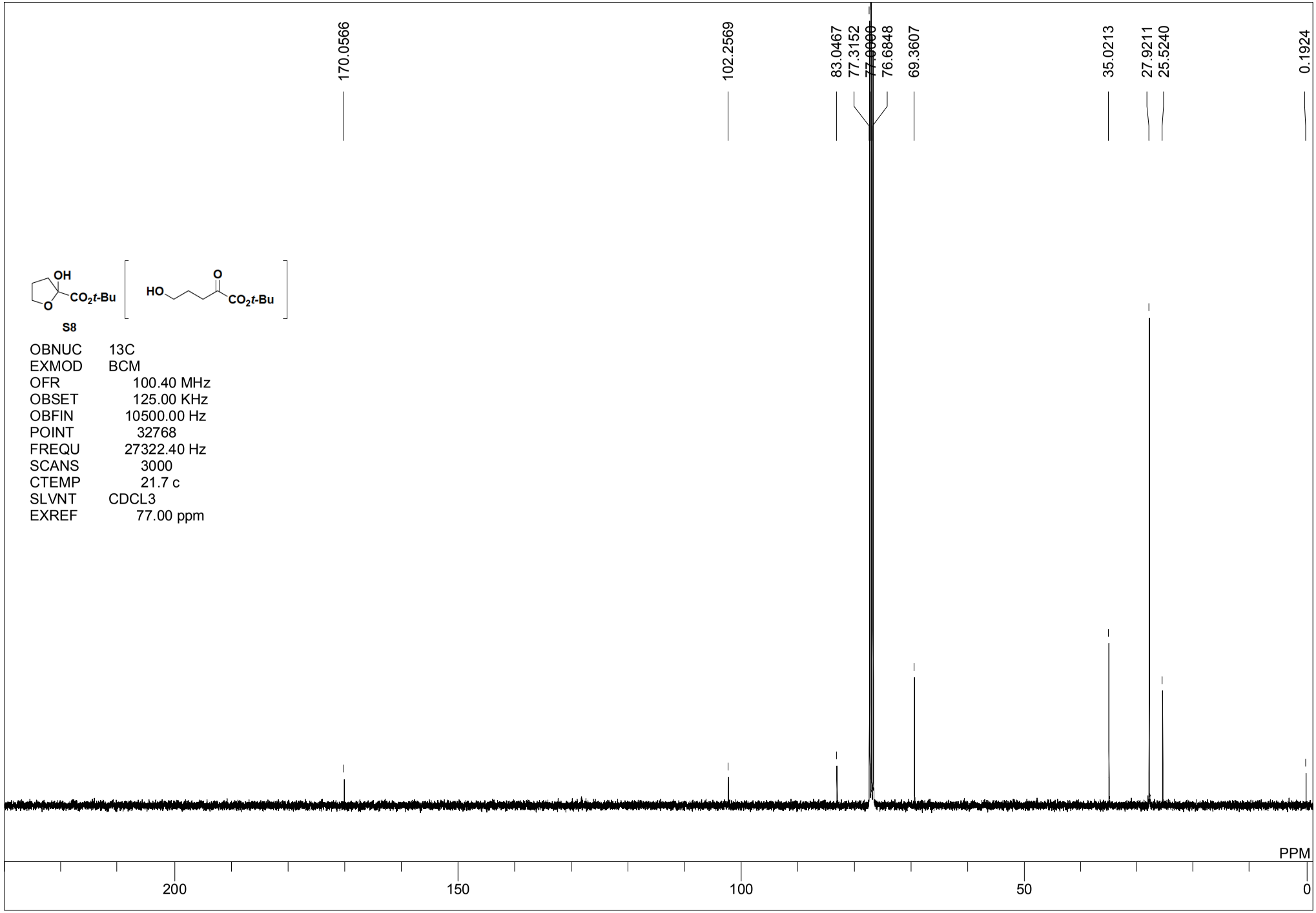
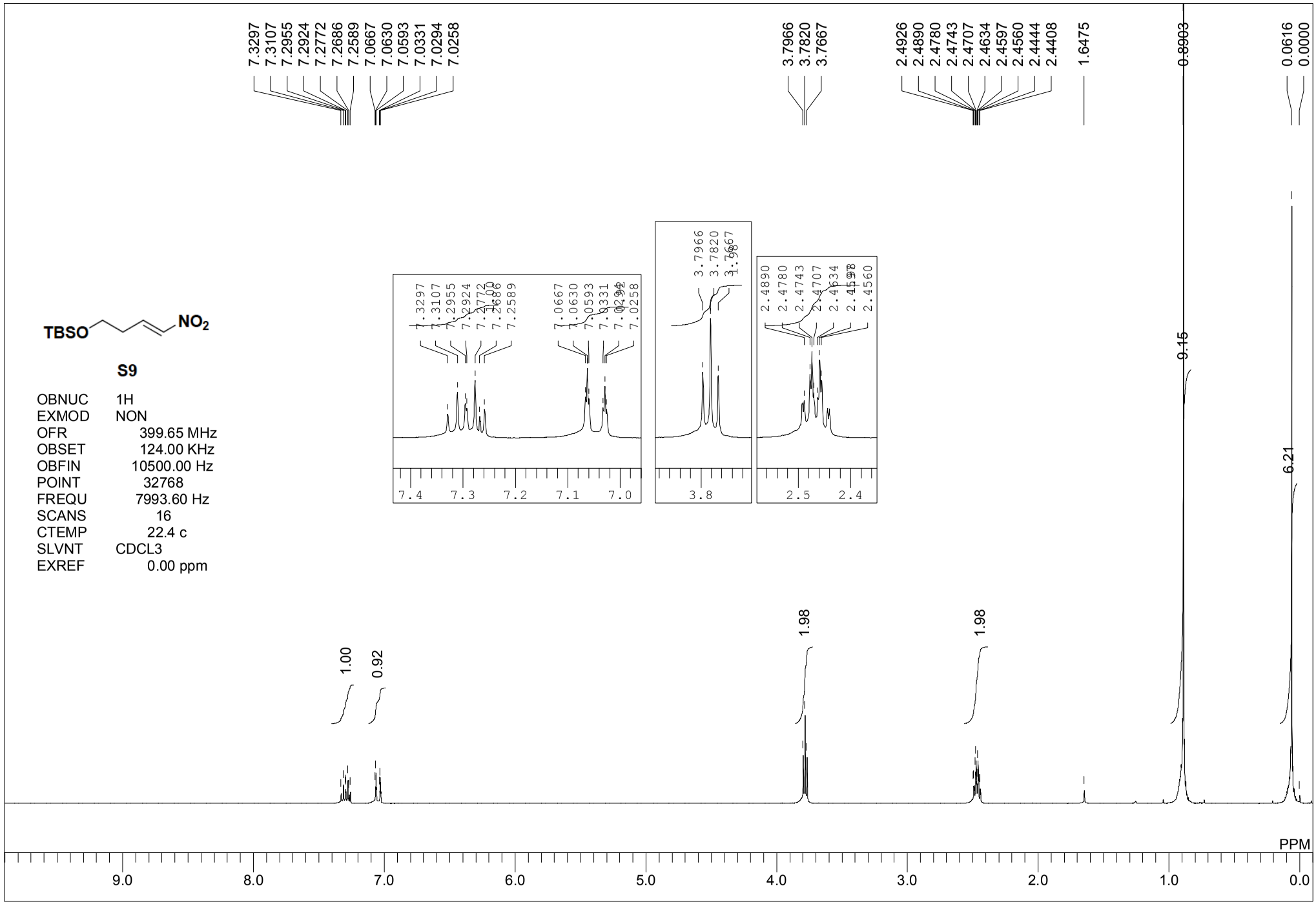
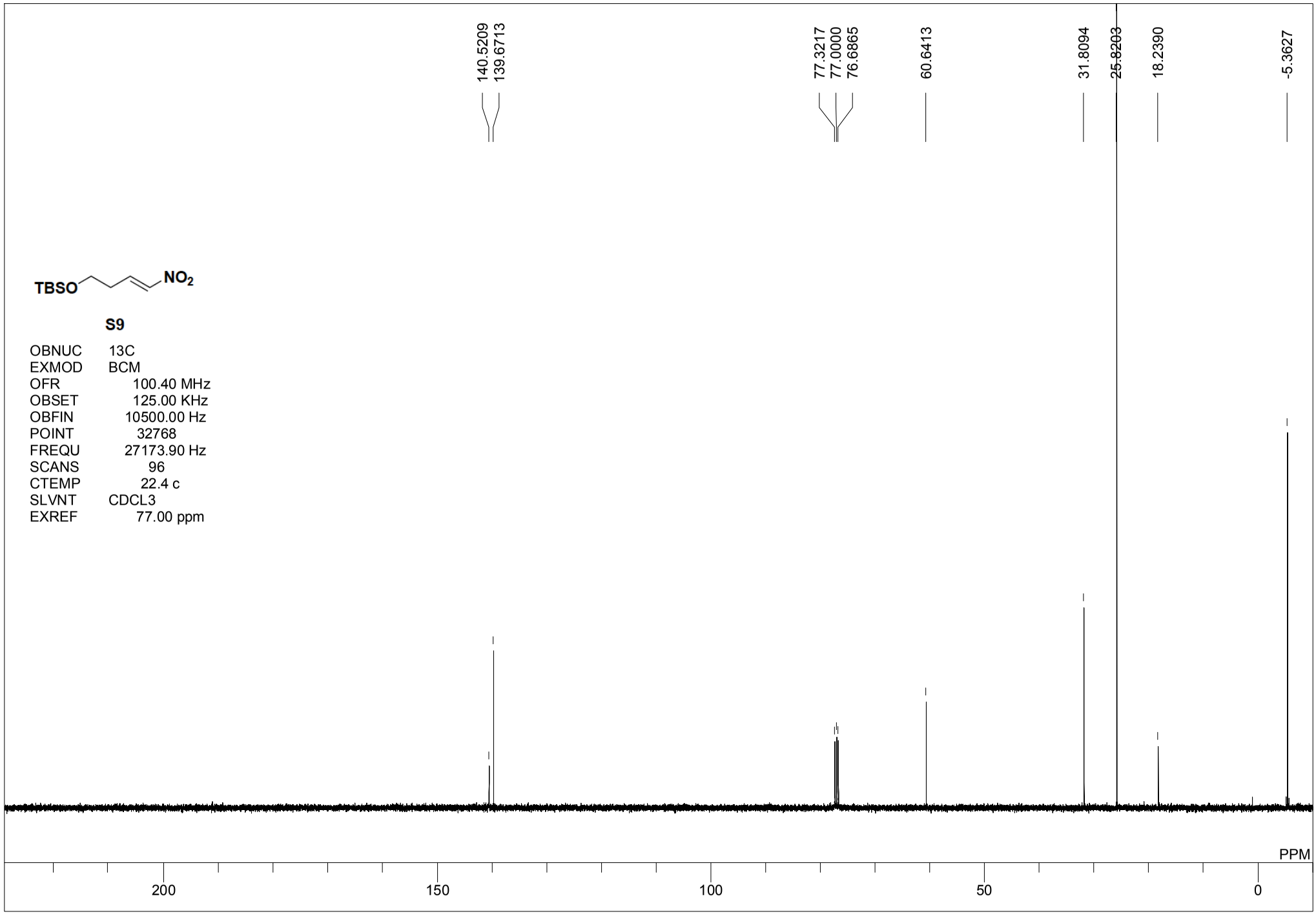
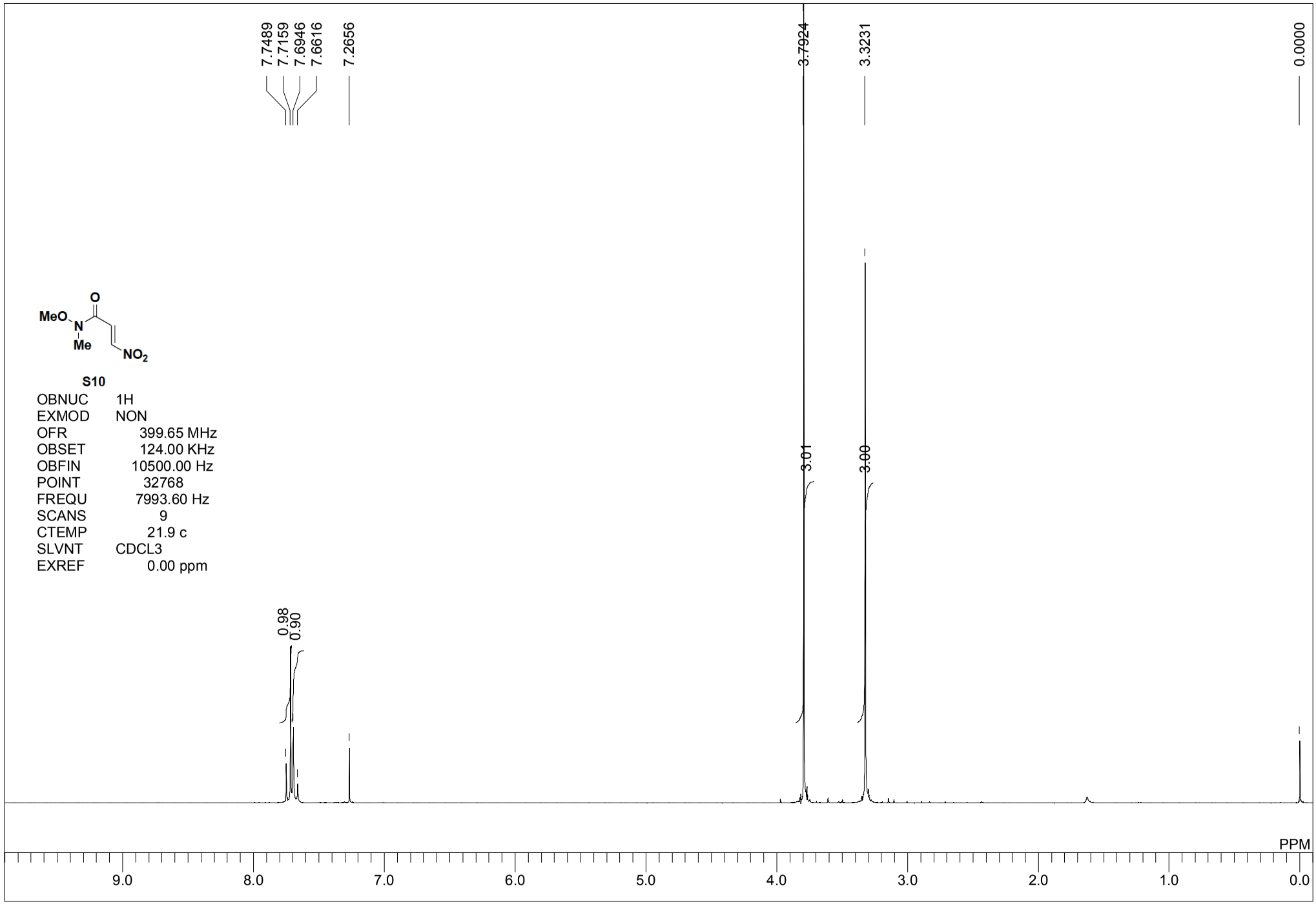
128.2210
127.4785
127.4373
83.6491
77.3135
77.0000
76.6783
72.7680
68.8330
36.0909
27.7589
23.6837
BnO
O
CO2t-Bu
S7
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 501
CTEMP 21.7 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
230.0 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0

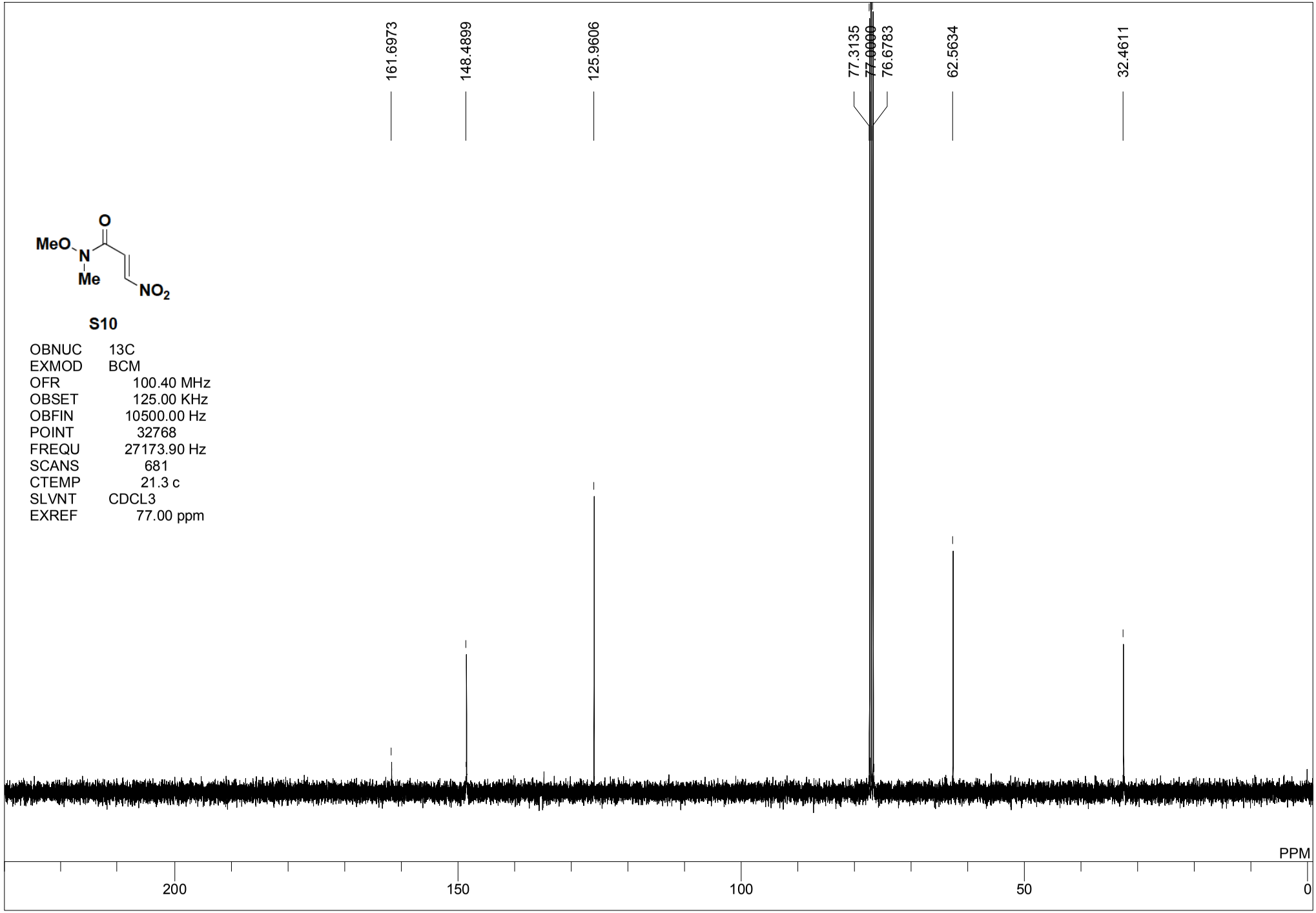

7.2635
4.1404
4.1203
4.1062
4.0873
4.0055
3.9872
3.9713
3.9505
3.9340
2.3707
2.3432
2.1392
2.1282
2.1111
2.0861
2.0629
2.0440
2.0311
2.0189
2.0098
1.9914
1.9786
1.5750
1.5401
1.5145
1.4870
0.0714
0.0000
S8
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 8000.00 Hz
SCANS 16
CTEMP 21.6 c
SLVNT CDCL3
EXREF 0.00 ppm
9.45
3.04
1.00
0.77
1.07
0.99
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

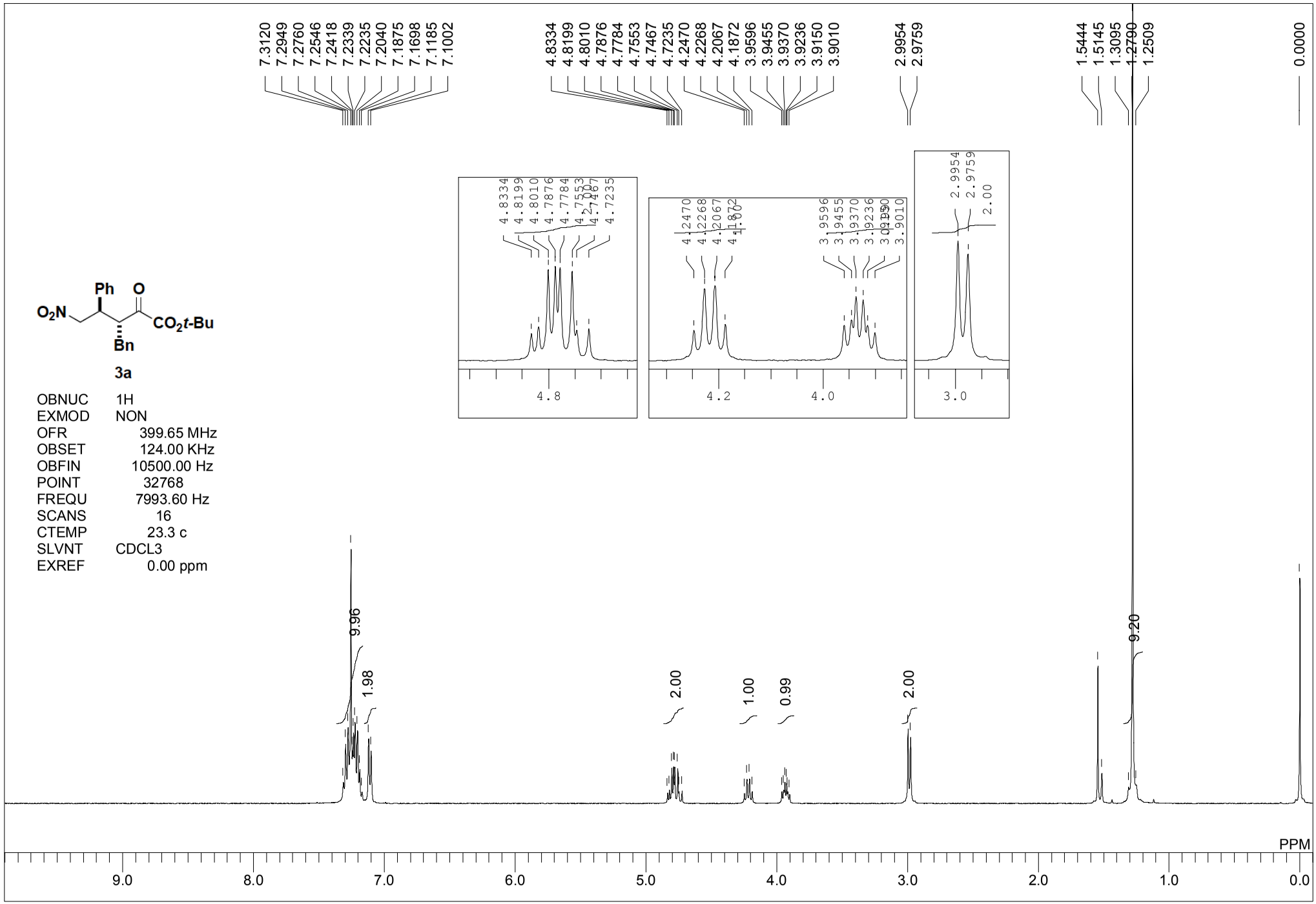

170.0566
102.2569
83.0467
77.3152
77.0000
76.6848
69.3607
35.0213
27.9211
25.5240
0.1924
OH
CO2t-Bu
O
S8
HO
O
CO2t-Bu
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27322.40 Hz
SCANS 3000
CTEMP 21.7 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0

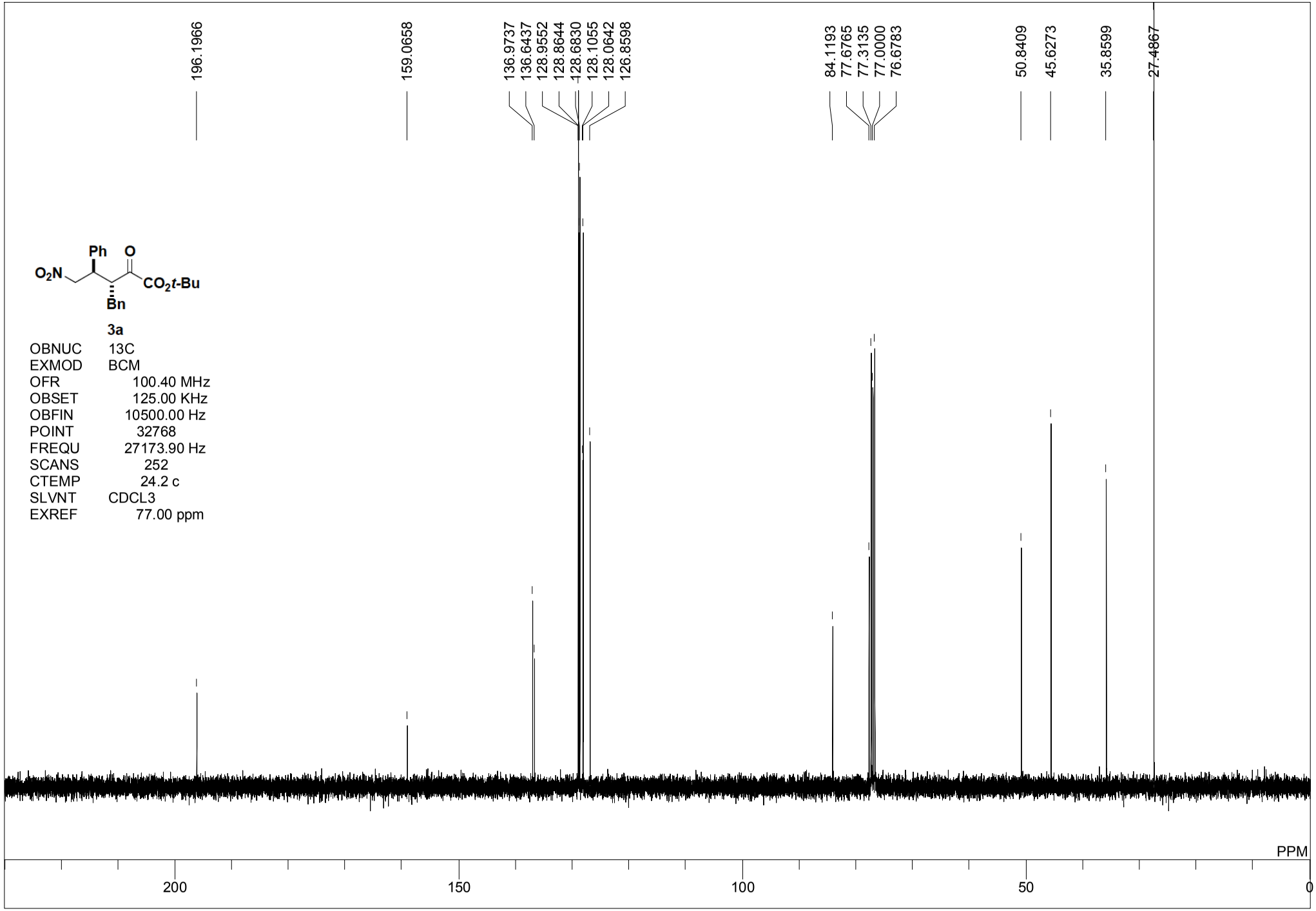

TBSO
NO2
S9
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 16
CTEMP 22.4 c
SLVNT CDCL3
EXREF 0.00 ppm
7.3297
7.3107
7.2955
7.2924
7.2772
7.2686
7.2589
7.0667
7.0630
7.0593
7.0331
7.0294
7.0258
3.7966
3.7820
3.7667
2.4926
2.4890
2.4780
2.4743
2.4707
2.4634
2.4597
2.4560
2.4444
2.4408
1.6475
0.8903
0.0616
0.0000
1.00
0.92
1.98
1.98
9.15
6.21
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

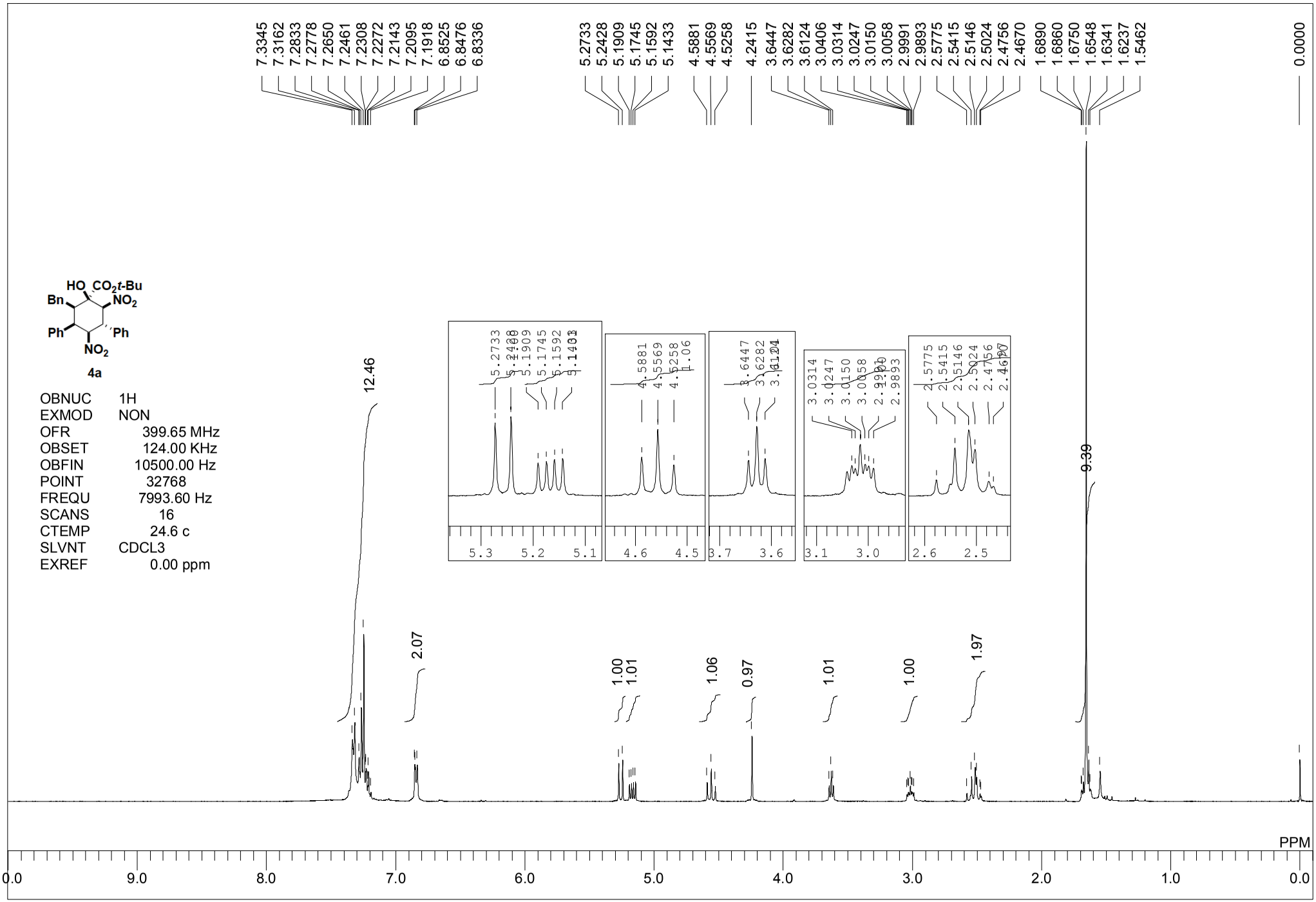

140.5209
139.6713
77.3217
77.0000
76.6865
60.6413
31.8094
25.8203
18.2390
-5.3627
TBSO
NO2
S9
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 96
CTEMP 22.4 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0

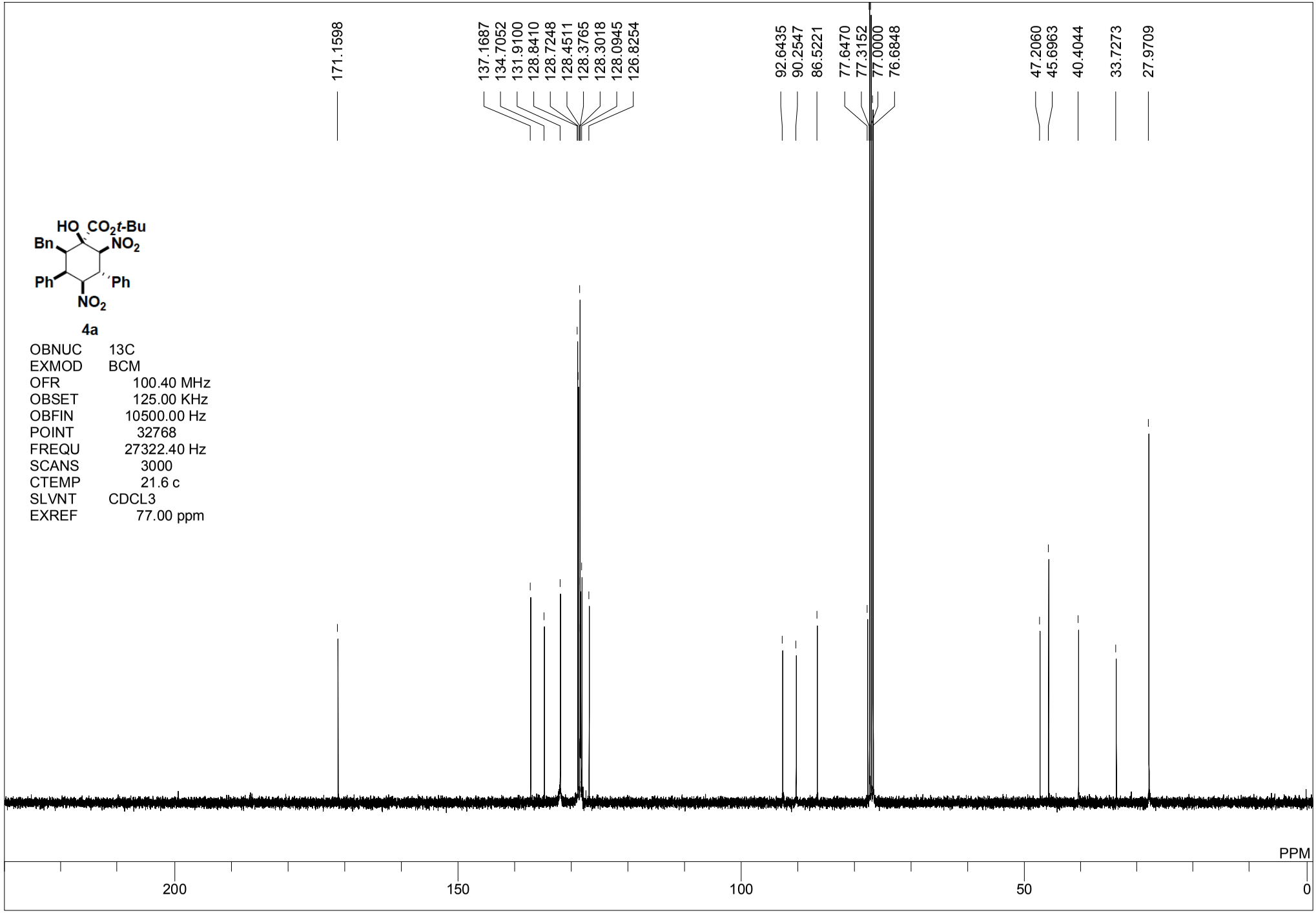

7.7489
7.7159
7.6946
7.6616
7.2656
3.7924
3.3231
0.0000
MeO
N
Me
O
NO2
S10
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 9
CTEMP 21.9 c
SLVNT CDCL3
EXREF 0.00 ppm
0.98
0.90
3.01
3.00
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

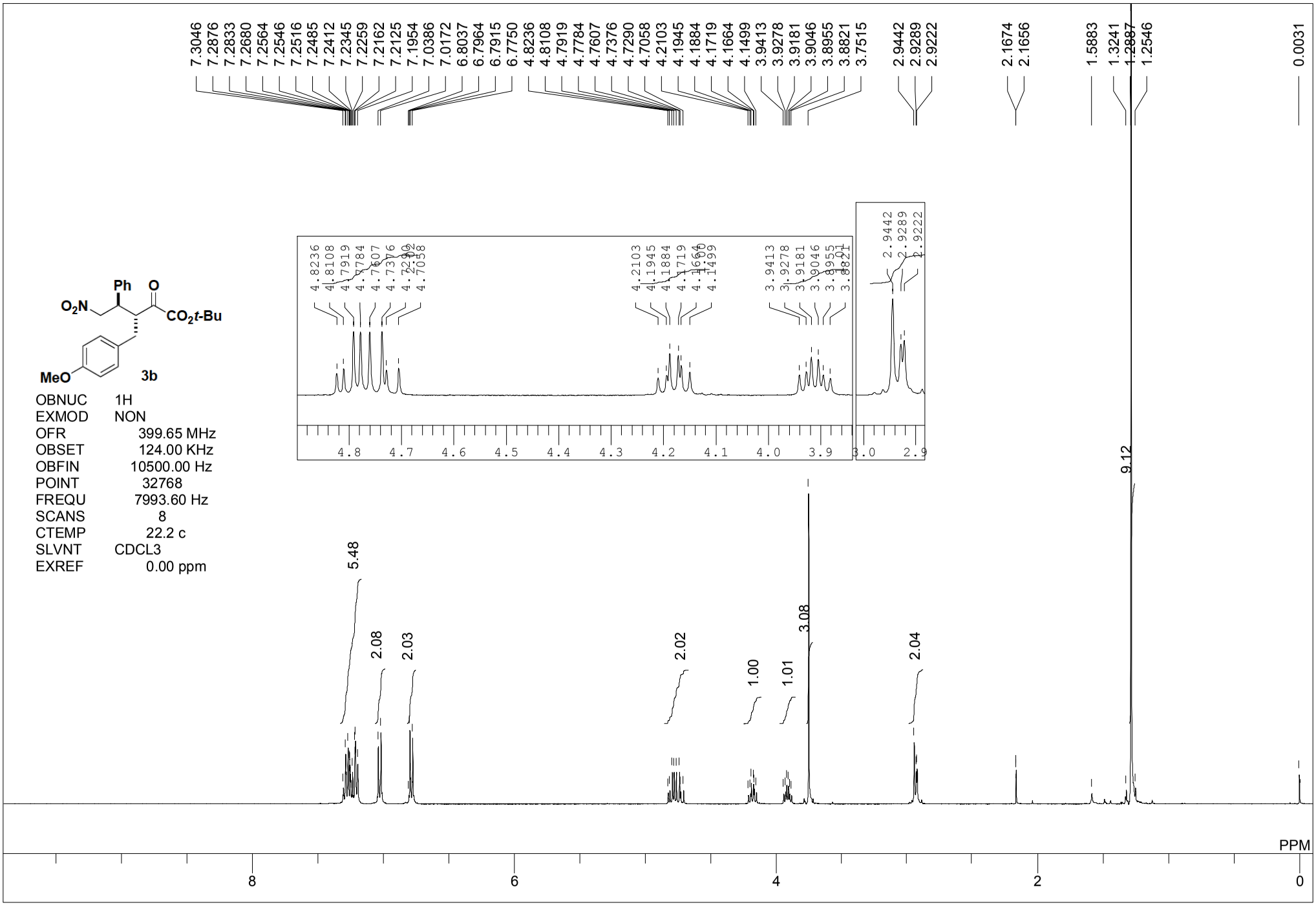

161.6973
148.4899
125.9606
77.3135
77.0000
76.6783
62.5634
32.4611
MeO
N
Me
O
NO2
S10
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 681
CTEMP 21.3 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0

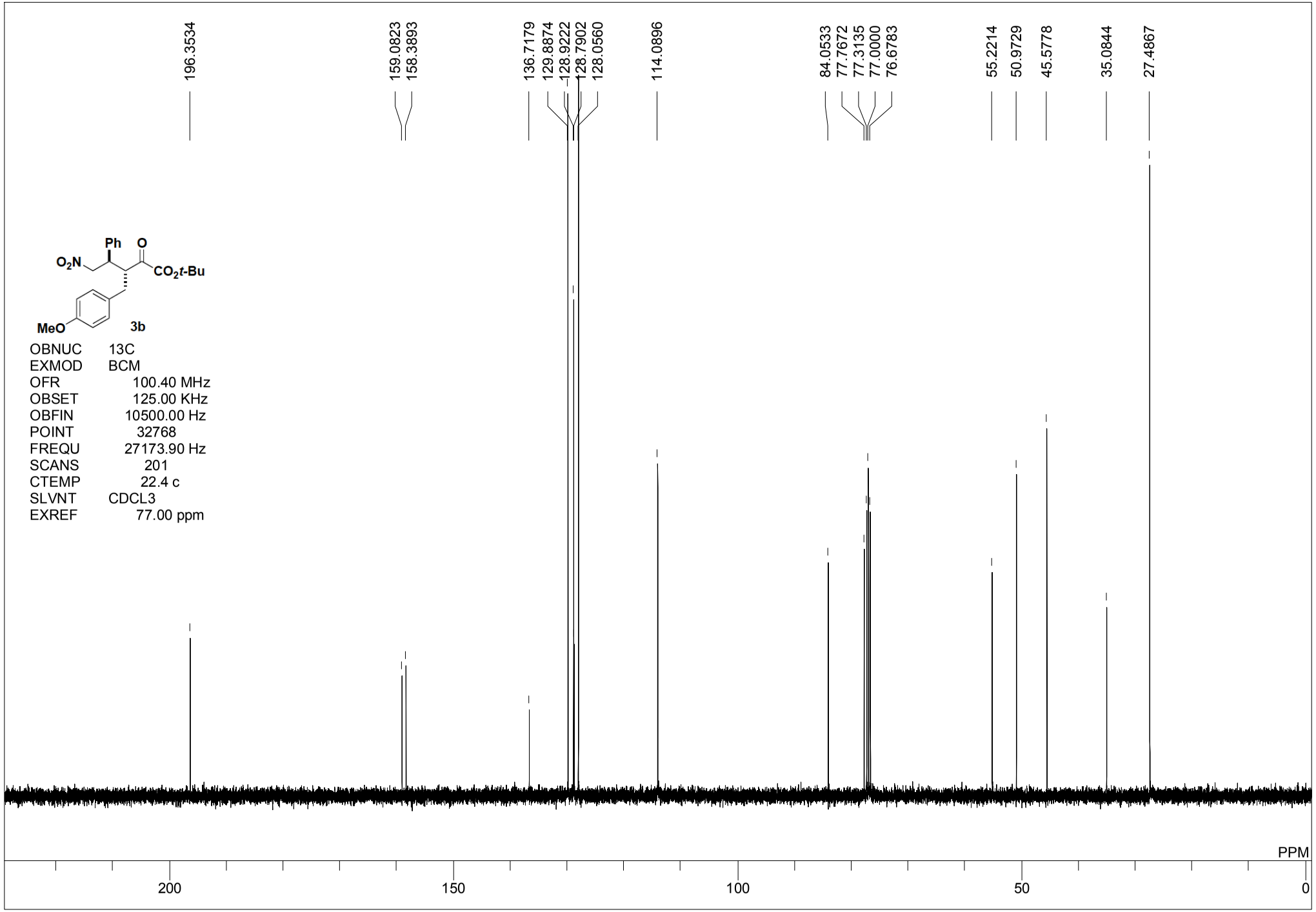

7.3120
7.2949
7.2760
7.2546
7.2418
7.2339
7.2235
7.2040
7.1875
7.1698
7.1185
7.1002
4.8334
4.8199
4.8010
4.7876
4.7784
4.7553
4.7467
4.7235
4.2470
4.2268
4.2067
4.1872
3.9596
3.9455
3.9370
3.9236
3.9150
3.9010
2.9954
2.9759
1.5444
1.5145
1.3095
1.2790
1.2509
0.0000
Ph
O
O2N
CO2t-Bu
Bn
3a
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 16
CTEMP 23.3 c
SLVNT CDCL3
EXREF 0.00 ppm
9.96
1.98
2.00
1.00
0.99
2.00
9.20
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

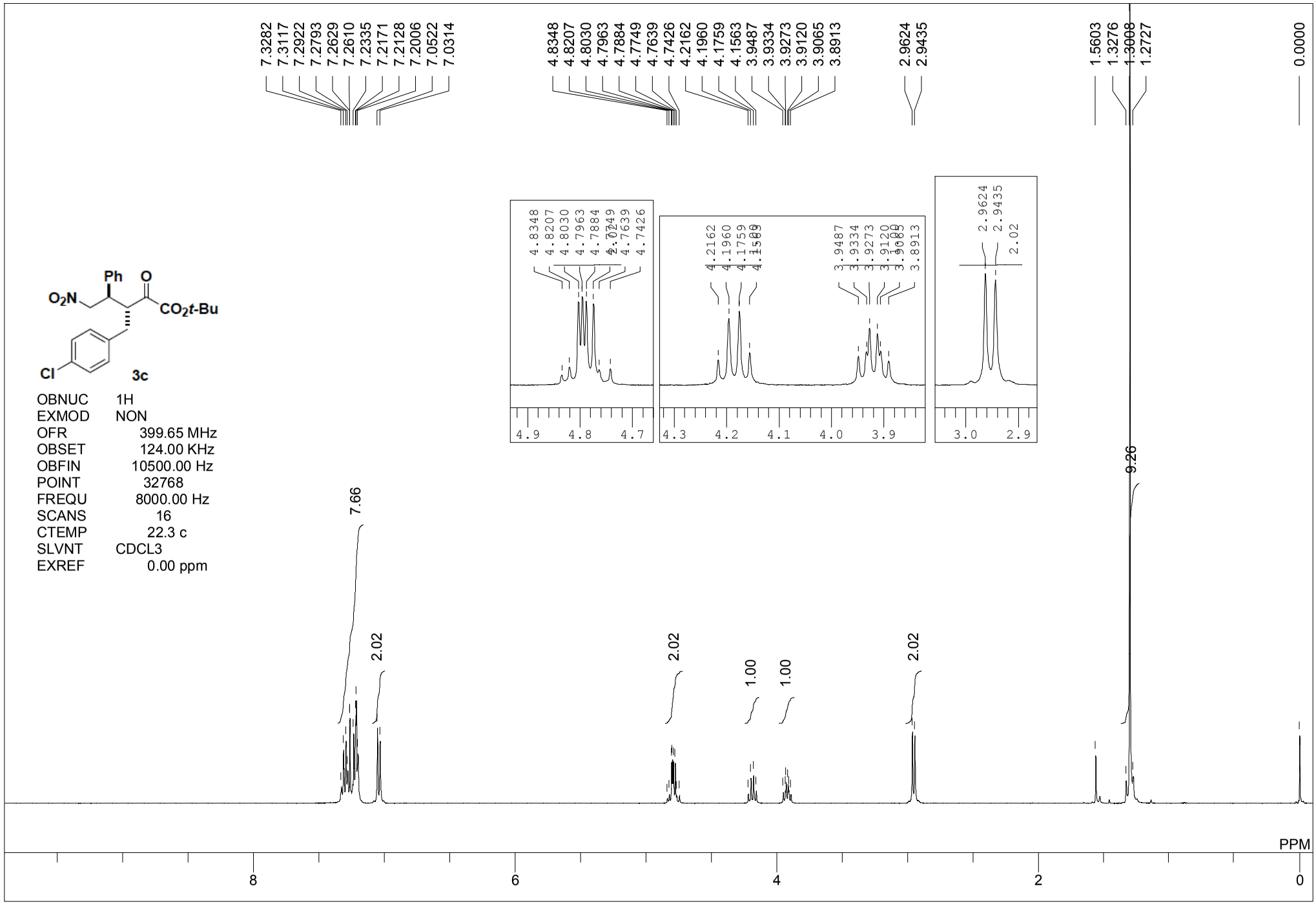

196.1966
159.0658
136.9737
136.6437
128.9552
128.8644
128.6830
128.1055
128.0642
126.8598
84.1193
77.6765
77.3135
77.0000
76.6783
50.8409
45.6273
35.8599
27.4867
Ph
O
O2N
CO2t-Bu
Bn
3a
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 252
CTEMP 24.2 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0

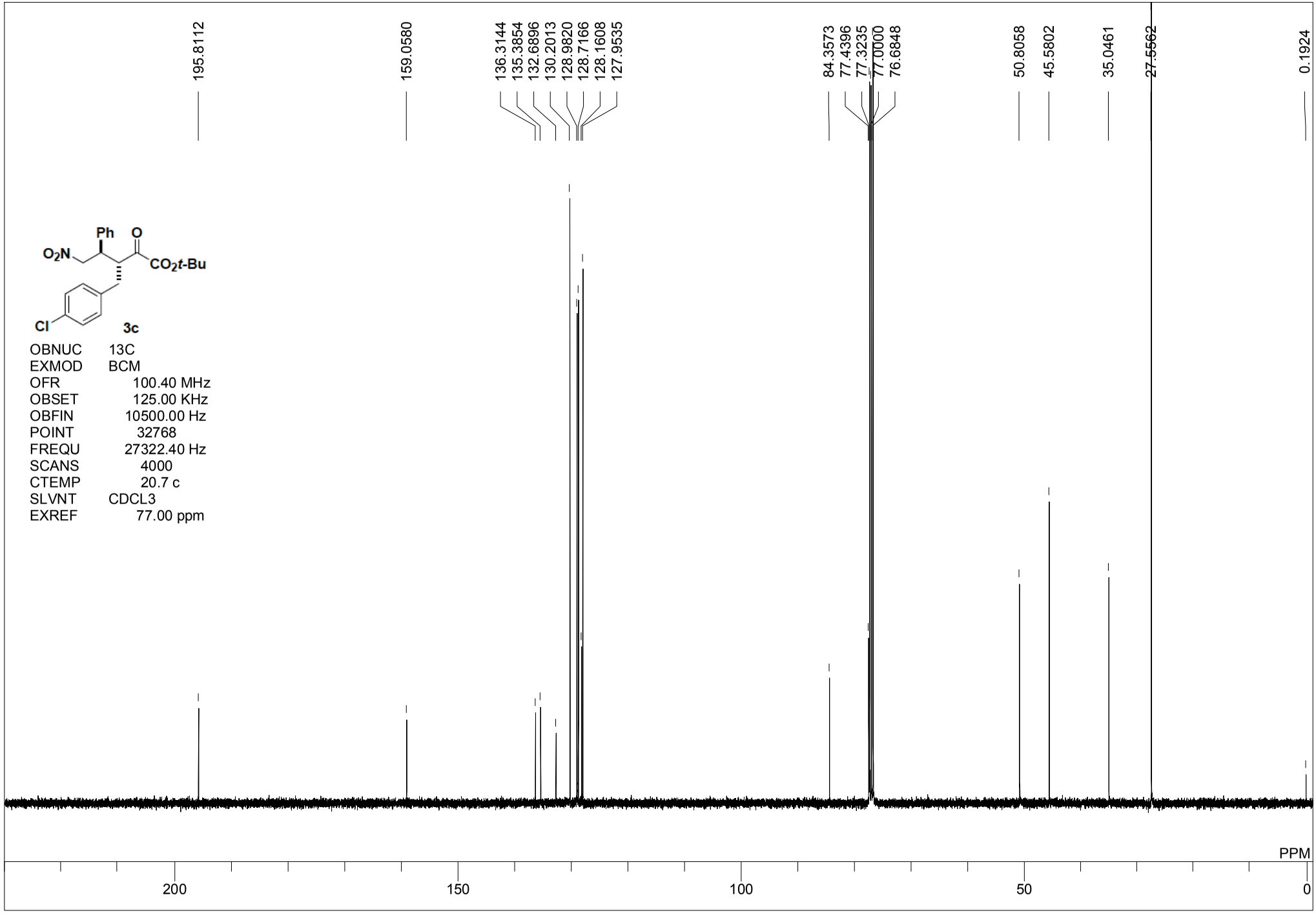

HO CO2t-Bu
Bn
NO2
Ph
Ph
NO2
4a
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 16
CTEMP 24.6 c
SLVNT CDCL3
EXREF 0.00 ppm
7.3345 7.3162 7.2833 7.2778 7.2650 7.2461 7.2308 7.2272 7.2143 7.2095 7.1918 6.8525 6.8476 6.8336
5.2733 5.2428 5.1909 5.1745 5.1592 5.1433
4.5881 4.5569 4.5258
4.2415
3.6447 3.6282 3.6124 3.0406 3.0314 3.0247 3.0150 3.0058 2.9991 2.9893
2.5775 2.5415 2.5146 2.5024 2.4756 2.4670
1.6890 1.6860 1.6750 1.6548 1.6341 1.6237 1.5462
0.0000
12.46
2.07
1.00
1.01
1.06
0.97
1.01
1.00
1.97
9.39
PPM
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0


171.1598
137.1687
134.7052
131.9100
128.8410
128.7248
128.4511
128.3765
128.3018
128.0945
126.8254
92.6435
90.2547
86.5221
77.6470
77.3152
77.0000
76.6848
47.2060
45.6963
40.4044
33.7273
27.9709
HO
CO2t-Bu
Bn
NO2
Ph
Ph
NO2
4a
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27322.40 Hz
SCANS 3000
CTEMP 21.6 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0


7.3046
7.2876
7.2833
7.2680
7.2564
7.2546
7.2516
7.2485
7.2412
7.2345
7.2259
7.2162
7.2125
7.1954
7.0386
7.0172
6.8037
6.7964
6.7915
6.7750
4.8236
4.8108
4.7919
4.7784
4.7607
4.7376
4.7290
4.7058
4.2103
4.1945
4.1884
4.1719
4.1664
4.1499
3.9413
3.9278
3.9181
3.9046
3.8955
3.8821
3.7515
2.9442
2.9289
2.9222
2.1674
2.1656
1.5883
1.3241
1.2887
1.2546
0.0031
Ph
O
O2N
CO2t-Bu
MeO
3b
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
CTEMP 22.2 c
SLVNT CDCL3
EXREF 0.00 ppm
5.48
2.08
2.03
2.02
1.00
1.01
3.08
2.04
9.12
PPM
8
6
4
2
0


196.3534
159.0823
158.3893
136.7179
129.8874
128.9222
128.7902
128.0560
114.0896
84.0533
77.7672
77.3135
77.0000
76.6783
55.2214
50.9729
45.5778
35.0844
27.4867
Ph
O
O2N
CO2t-Bu
MeO
3b
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 201
CTEMP 22.4 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0


7.3282
7.3117
7.2922
7.2793
7.2629
7.2610
7.2335
7.2171
7.2128
7.2006
7.0522
7.0314
4.8348
4.8207
4.8030
4.7963
4.7884
4.7749
4.7639
4.7426
4.2162
4.1960
4.1759
4.1563
3.9487
3.9334
3.9273
3.9120
3.9065
3.8913
2.9624
2.9435
1.5603
1.3276
1.3008
1.2727
0.0000
Ph
O
O2N
CO2t-Bu
Cl
3c
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 8000.00 Hz
SCANS 16
CTEMP 22.3 c
SLVNT CDCL3
EXREF 0.00 ppm
7.66
2.02
2.02
1.00
1.00
2.02
9.26
PPM
8
6
4
2
0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136.3144
135.3854
132.6896
130.2013
128.9820
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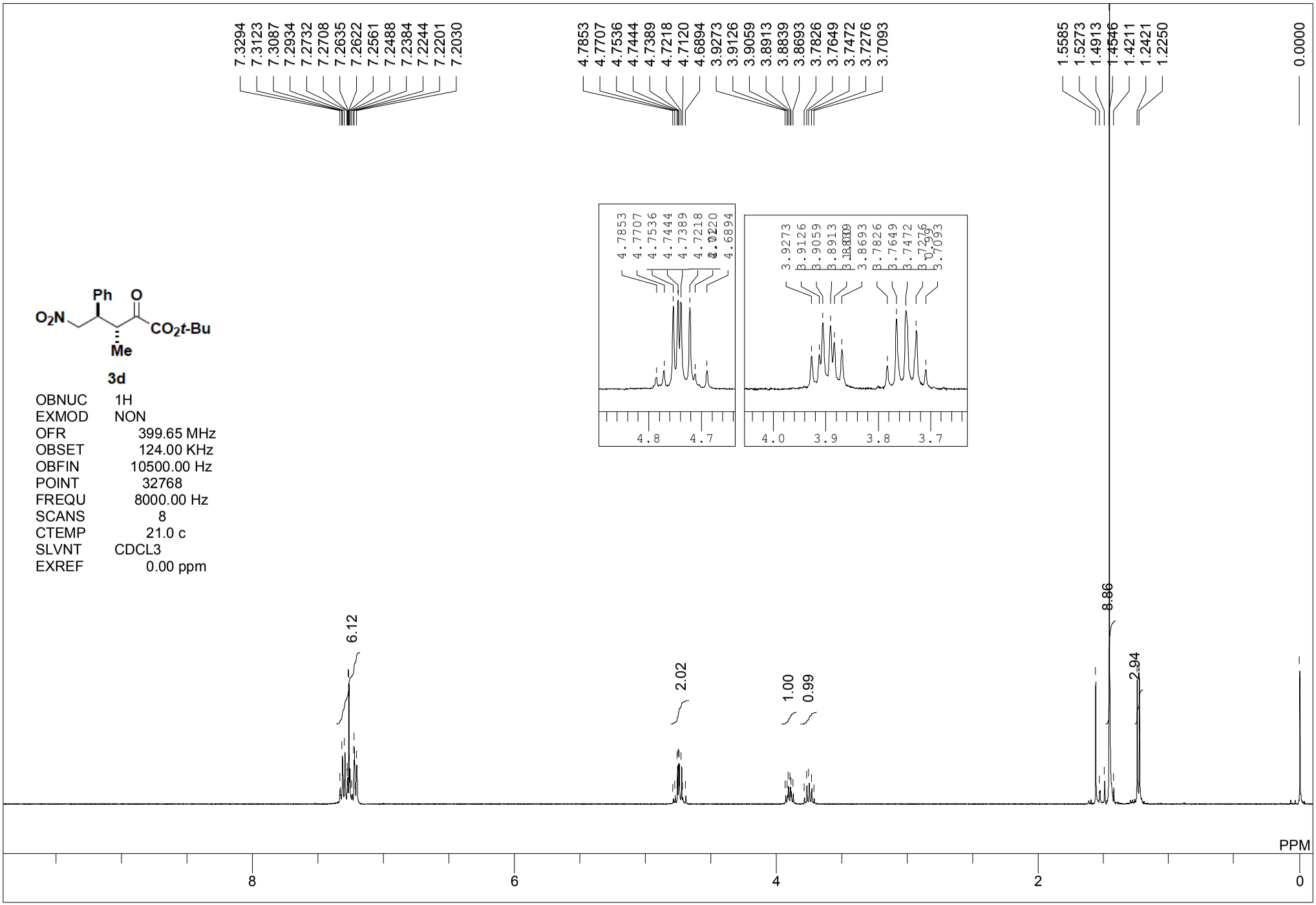
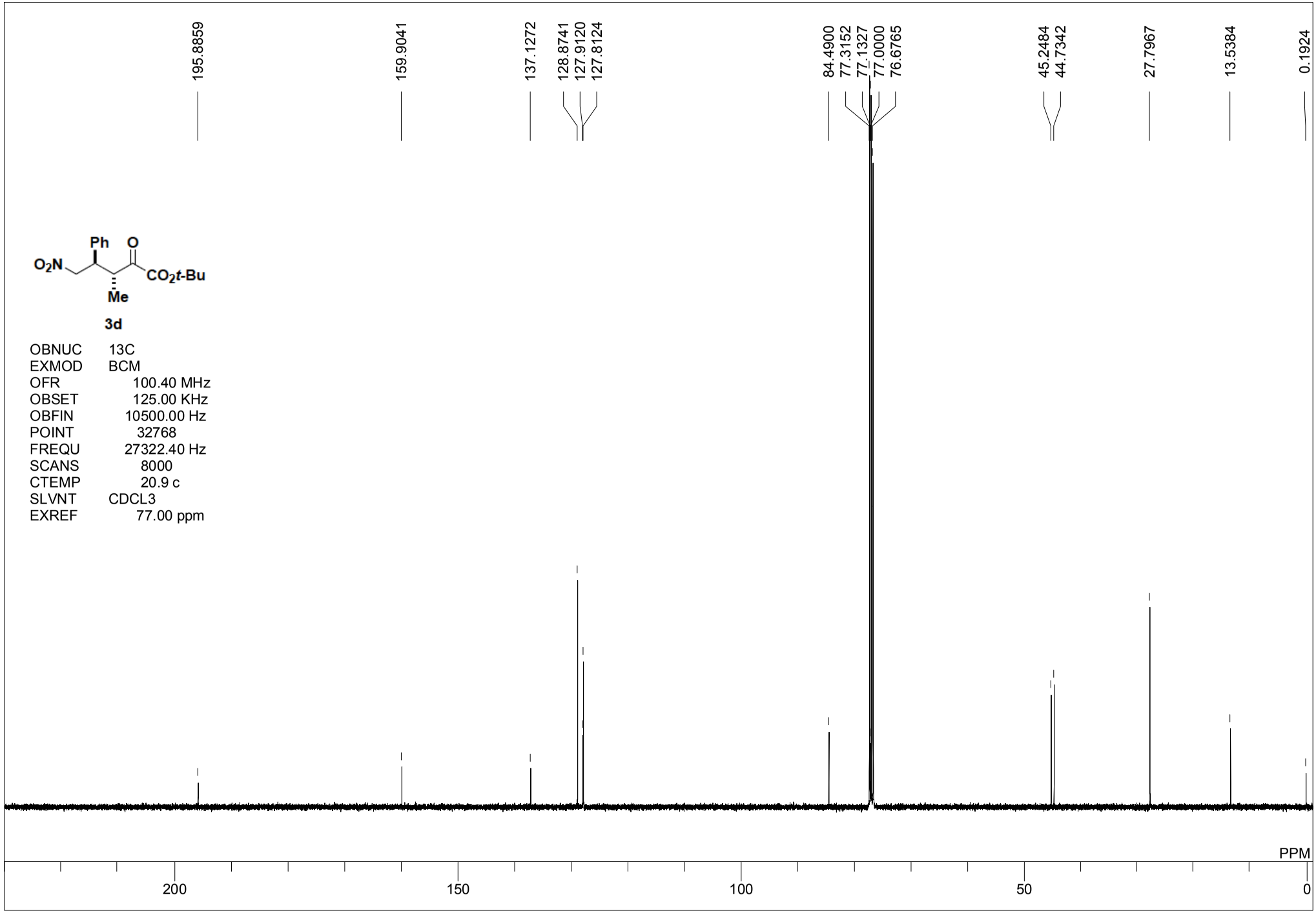
128.1608
127.9535
84.3573
77.4396
77.3235
77.0000
76.6848
50.8058
45.5802
35.0461
27.5562
0.1924
Ph
O
O2N
CO2t-Bu
Cl
3c
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27322.40 Hz
SCANS 4000
CTEMP 20.7 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0


7.3294
7.3123
7.3087
7.2934
7.2732
7.2708
7.2635
7.2622
7.2561
7.2488
7.2384
7.2244
7.2201
7.2030
4.7853
4.7707
4.7536
4.7444
4.7389
4.7218
4.7120
4.6894
3.9273
3.9126
3.9059
3.8913
3.8839
3.8693
3.7826
3.7649
3.7472
3.7276
3.7093
1.5585
1.5273
1.4913
1.4546
1.4211
1.2421
1.2250
0.0000
Ph
O
O2N
CO2t-Bu
Me
3d
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 8000.00 Hz
SCANS 8
CTEMP 21.0 c
SLVNT CDCL3
EXREF 0.00 ppm
6.12
2.02
1.00
0.99
8.86
2.94
PPM
8
6
4
2
0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127.8124
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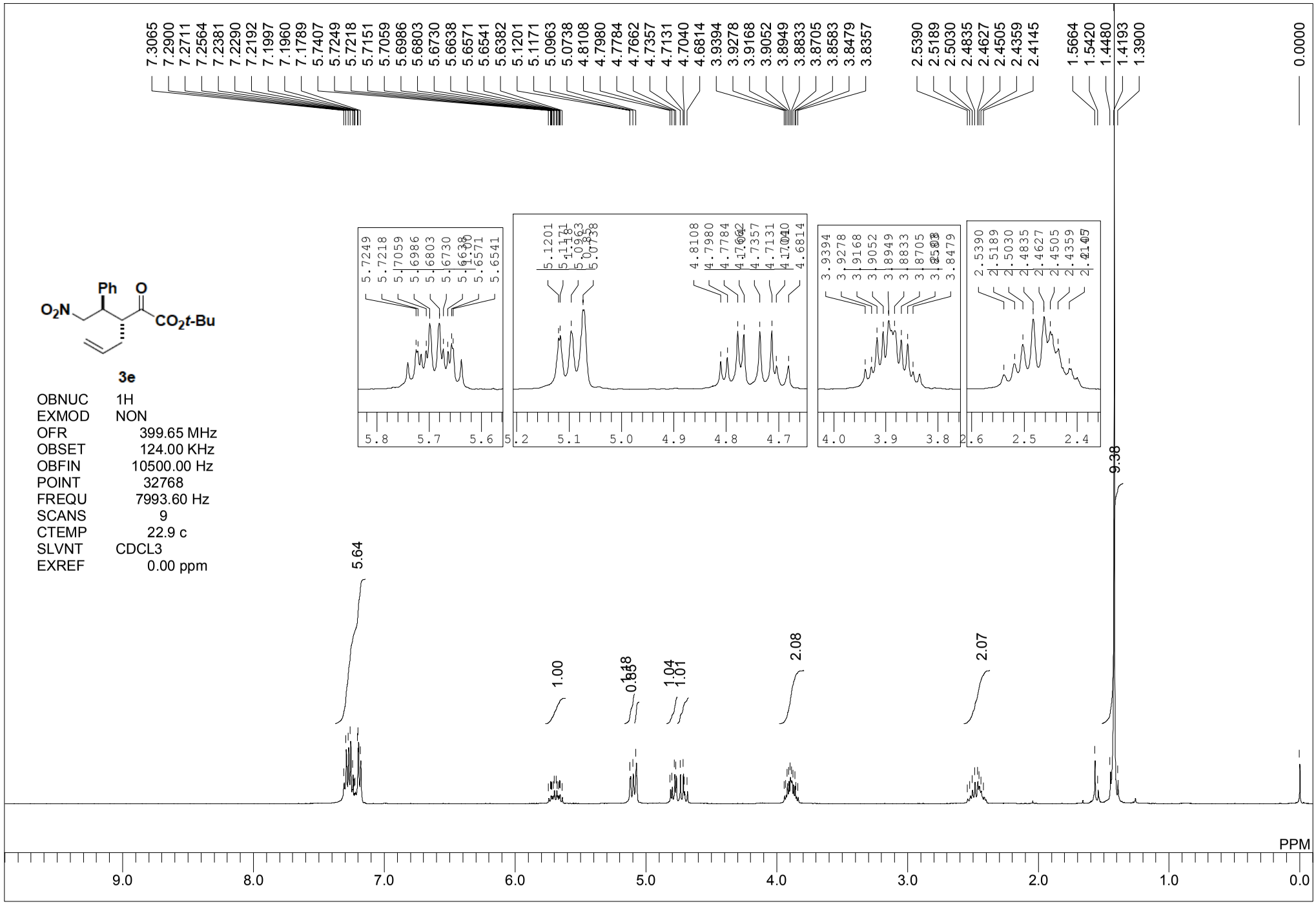
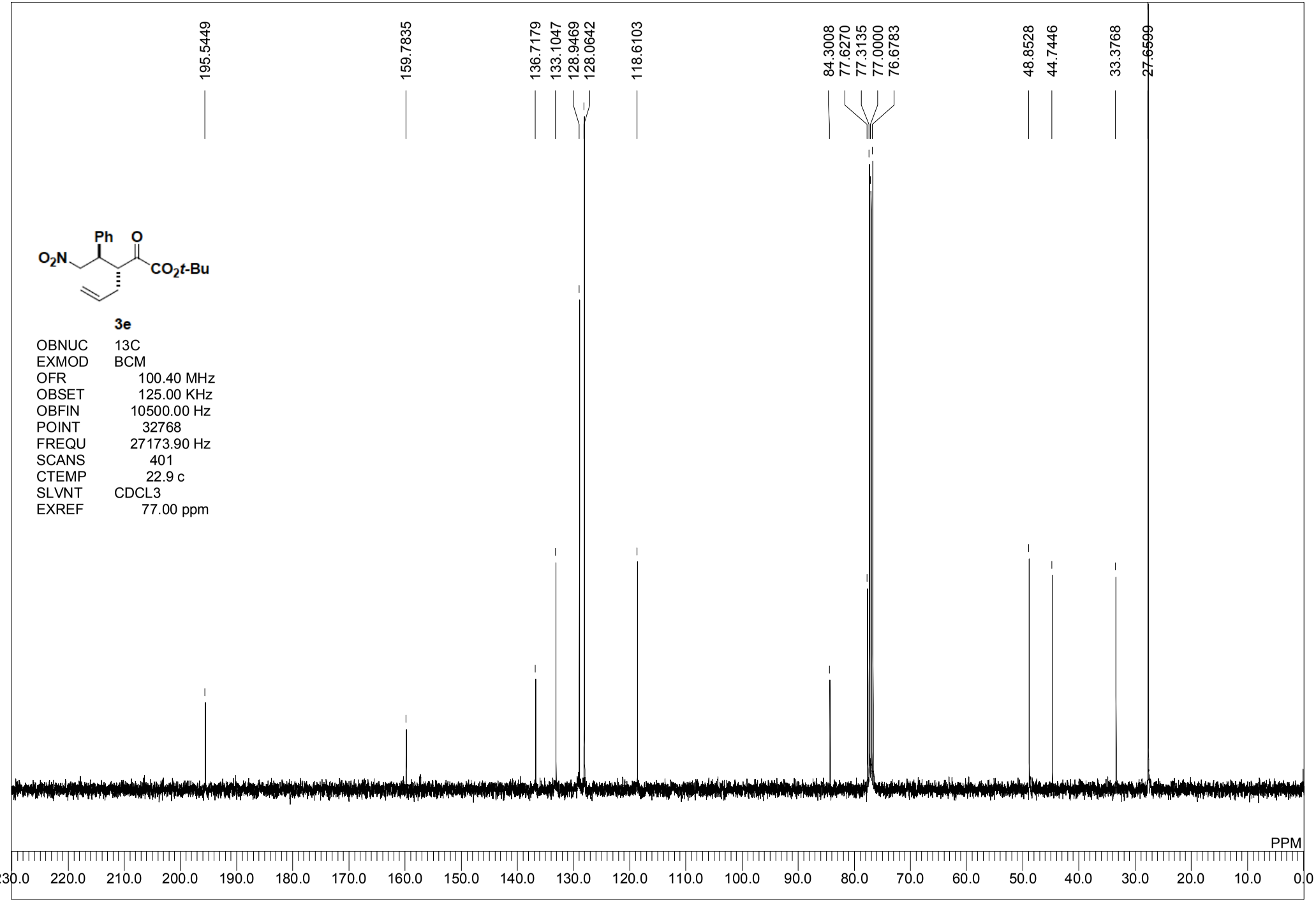
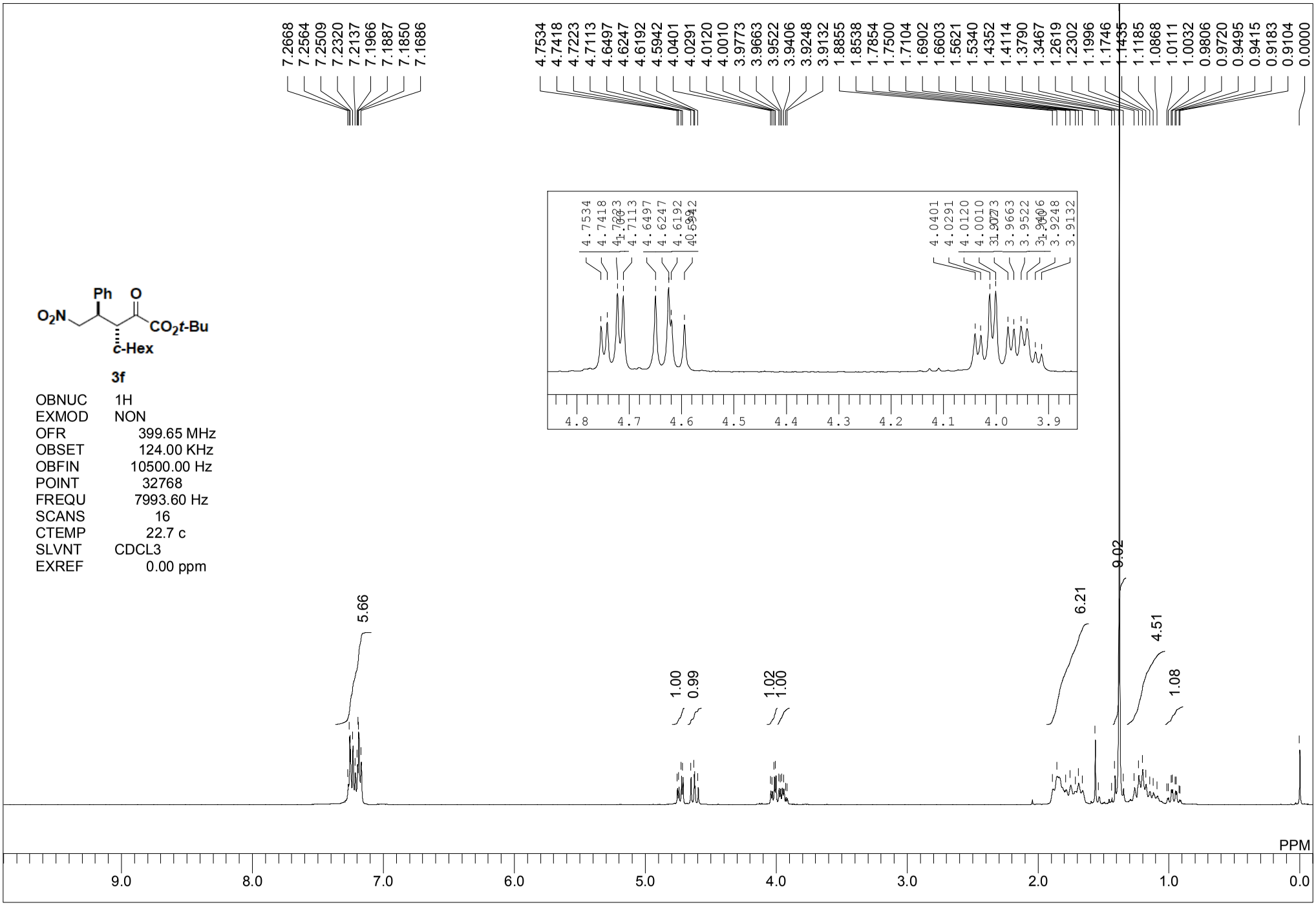
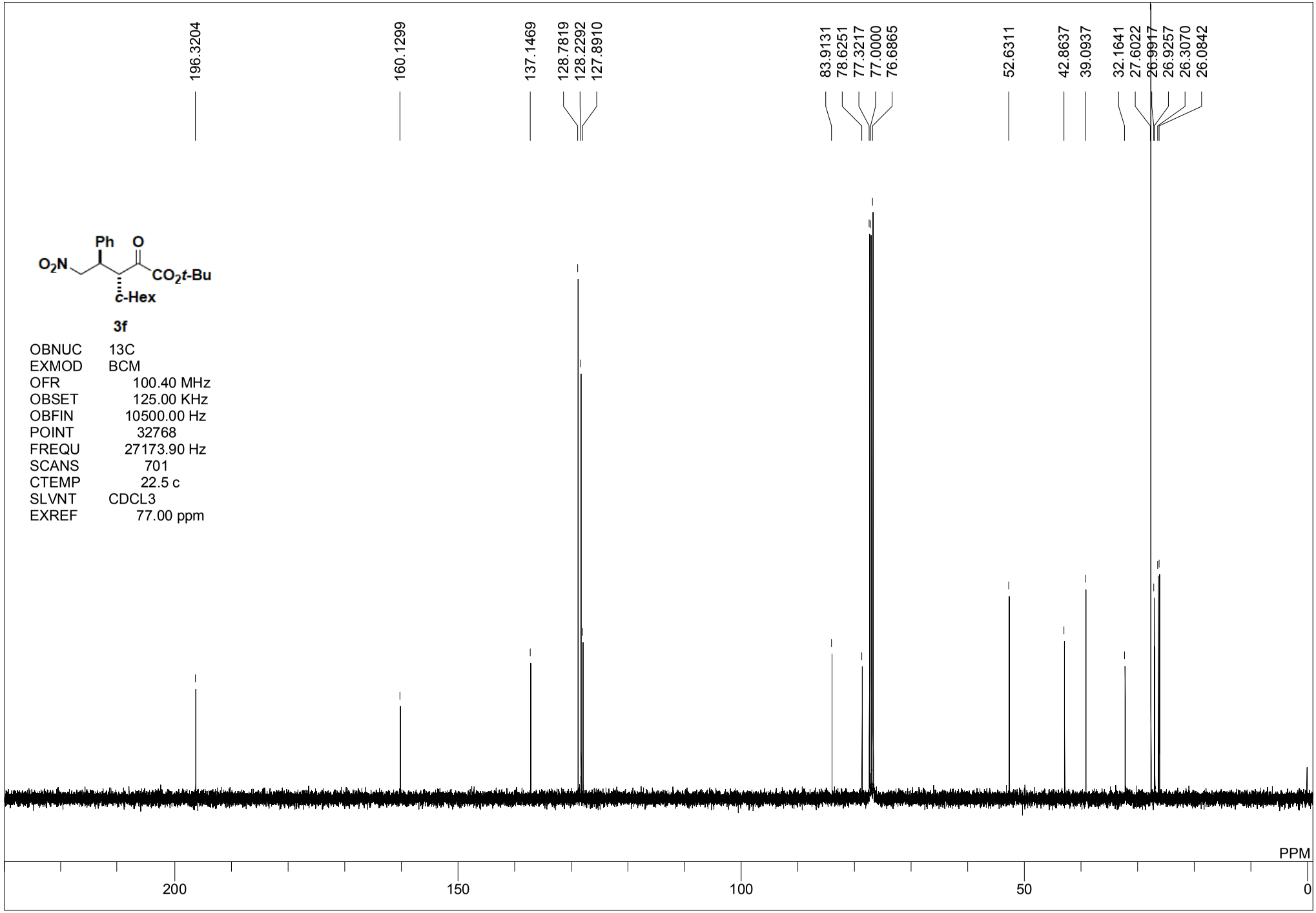
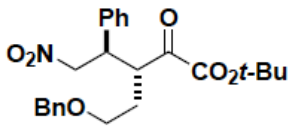
77.1327
77.0000
76.6765
45.2484
44.7342
27.7967
13.5384
0.1924
Ph
O
O2N
CO2t-Bu
Me
3d
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27322.40 Hz
SCANS 8000
CTEMP 20.9 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0


Ph
O
$O_2N$
$CO_2t$-Bu
3e
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 9
CTEMP 22.9 c
SLVNT CDCL3
EXREF 0.00 ppm
7.3065 7.2900 7.2711 7.2564 7.2381 7.2290 7.2192 7.1997 7.1960 7.1789 5.7407 5.7249 5.7218 5.7151 5.7059 5.6986 5.6803 5.6730 5.6638 5.6571 5.6541 5.6382 5.1201 5.1171 5.0963 5.0738 4.8108 4.7980 4.7784 4.7662 4.7357 4.7131 4.7040 4.6814 3.9394 3.9278 3.9168 3.9052 3.8949 3.8833 3.8705 3.8583 3.8479 3.8357
2.5390 2.5189 2.5030 2.4835 2.4627 2.4505 2.4359 2.4145
1.5664 1.5420 1.4480 1.4193 1.3900
0.0000
5.64
1.00
0.88
1.04
1.01
2.08
2.07
9.38
PPM
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0


195.5449
159.7835
136.7179
133.1047
128.9469
128.0642
118.6103
84.3008
77.6270
77.3135
77.0000
76.6783
48.8528
44.7446
33.3768
27.6599
Ph
O
O2N
CO2t-Bu
3e
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 401
CTEMP 22.9 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
230.0 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0

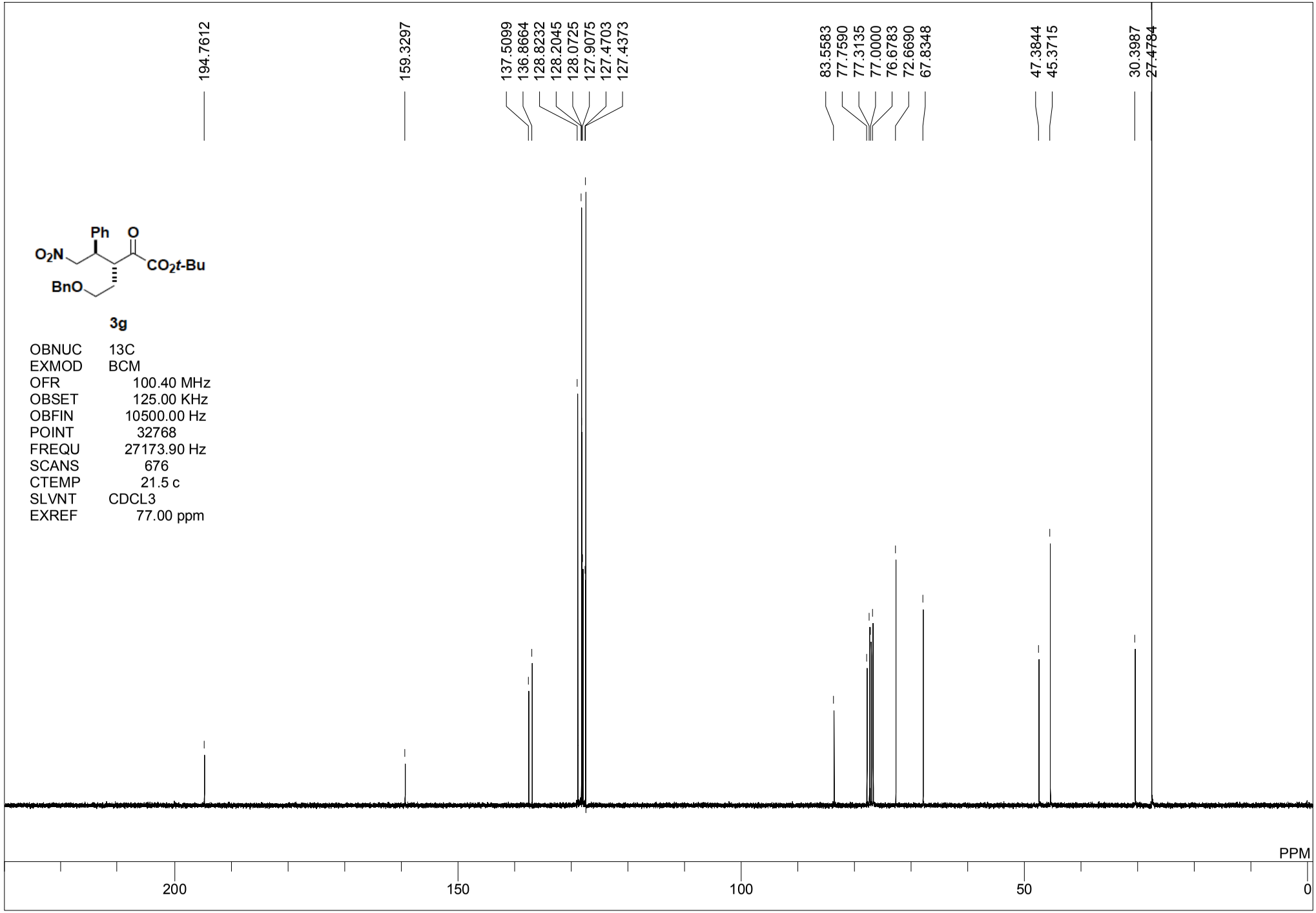

Ph
O
O2N
CO2t-Bu
c-Hex
3f
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 16
CTEMP 22.7 c
SLVNT CDCL3
EXREF 0.00 ppm
7.2668 7.2564 7.2509 7.2320 7.2137 7.1966 7.1887 7.1850 7.1686
4.7534 4.7418 4.7223 4.7113 4.6497 4.6247 4.6192 4.5942 4.0401 4.0291 4.0120 4.0010 3.9773 3.9663 3.9522 3.9406 3.9248 3.9132
1.8855 1.8538 1.7854 1.7500 1.7104 1.6902 1.6603 1.5621 1.5340 1.4352 1.4114 1.3790 1.3467 1.2619 1.2302 1.1996 1.1746 1.1435 1.1185 1.0868 1.0111 1.0032 0.9806 0.9720 0.9495 0.9415 0.9183 0.9104 0.0000
5.66
1.00
0.99
1.02
1.00
6.21
9.02
4.51
1.08
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

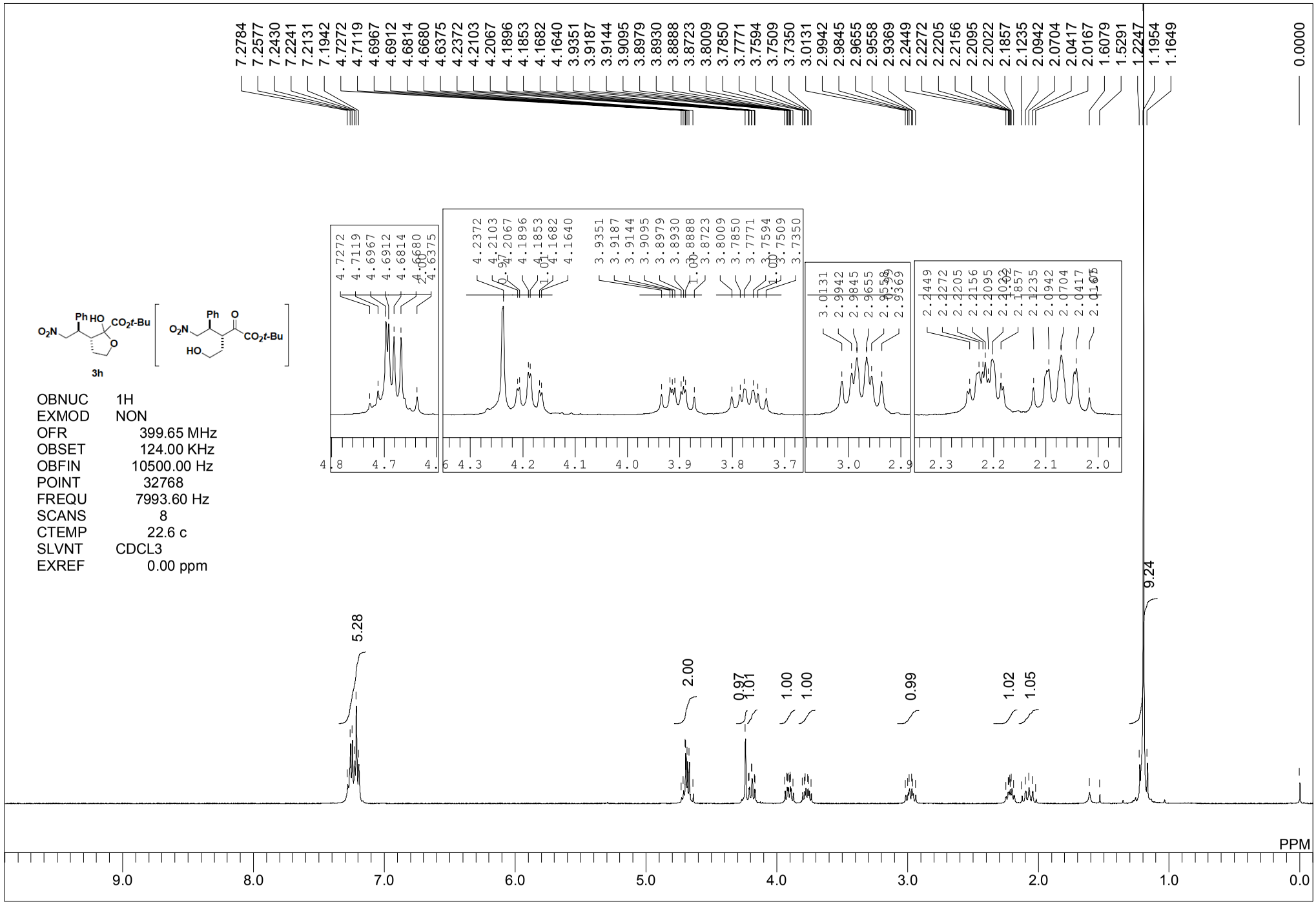

196.3204
160.1299
137.1469
128.7819
128.2292
127.8910
83.9131
78.6251
77.3217
77.0000
76.6865
52.6311
42.8637
39.0937
32.1641
27.6022
26.9917
26.9257
26.3070
26.0842
Ph
O
O2N
CO2t-Bu
c-Hex
3f
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 701
CTEMP 22.5 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0

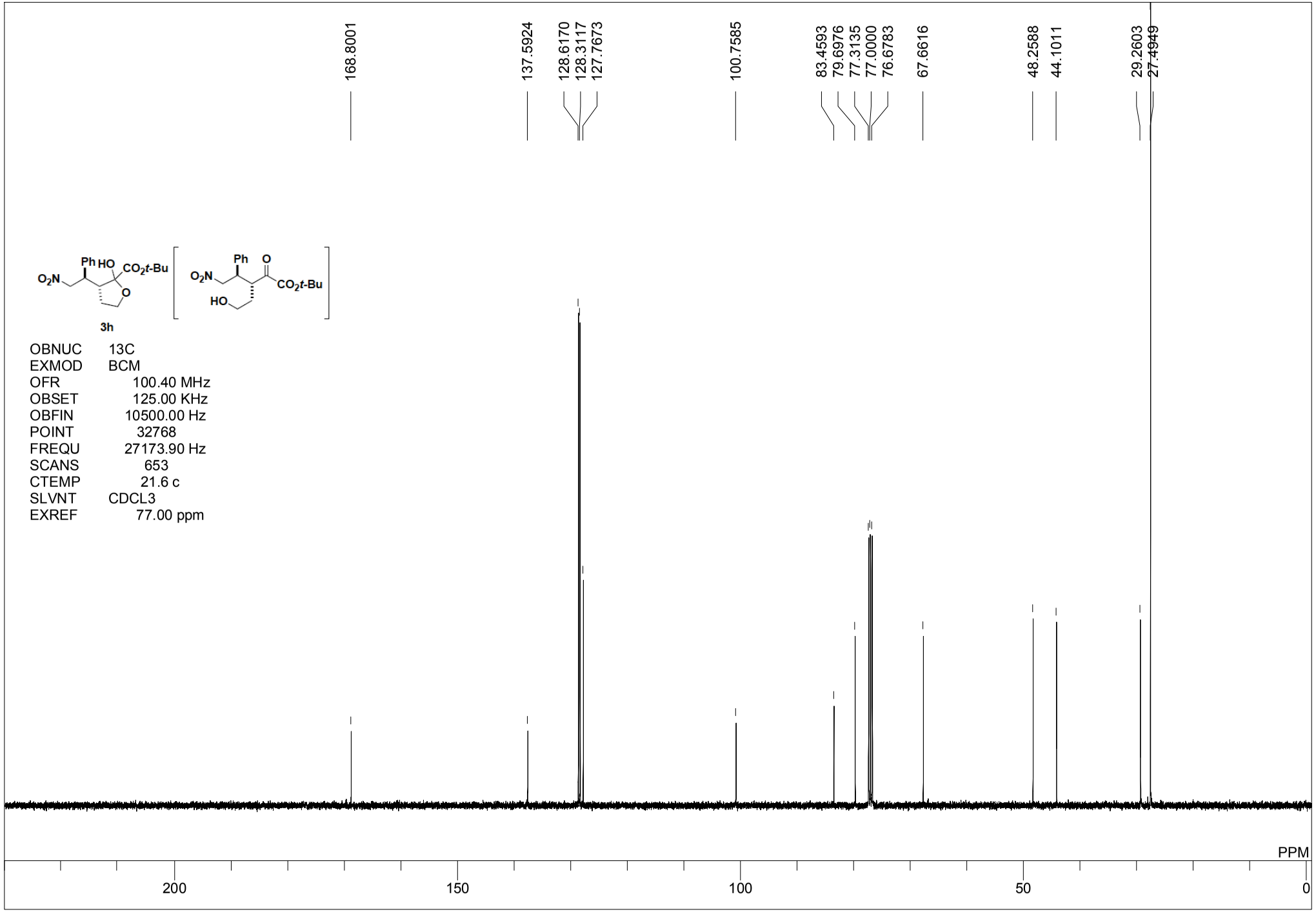


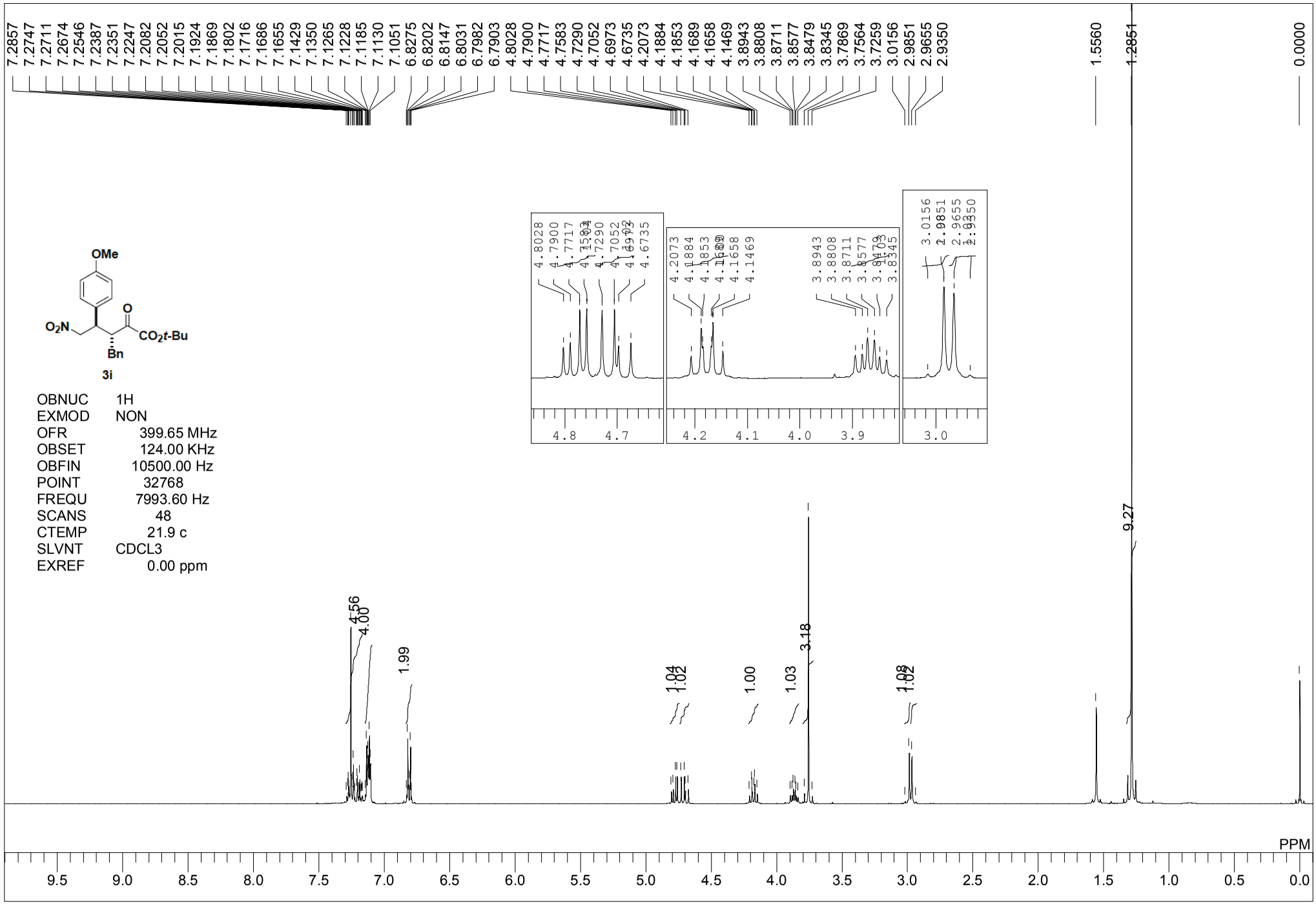

**3g**

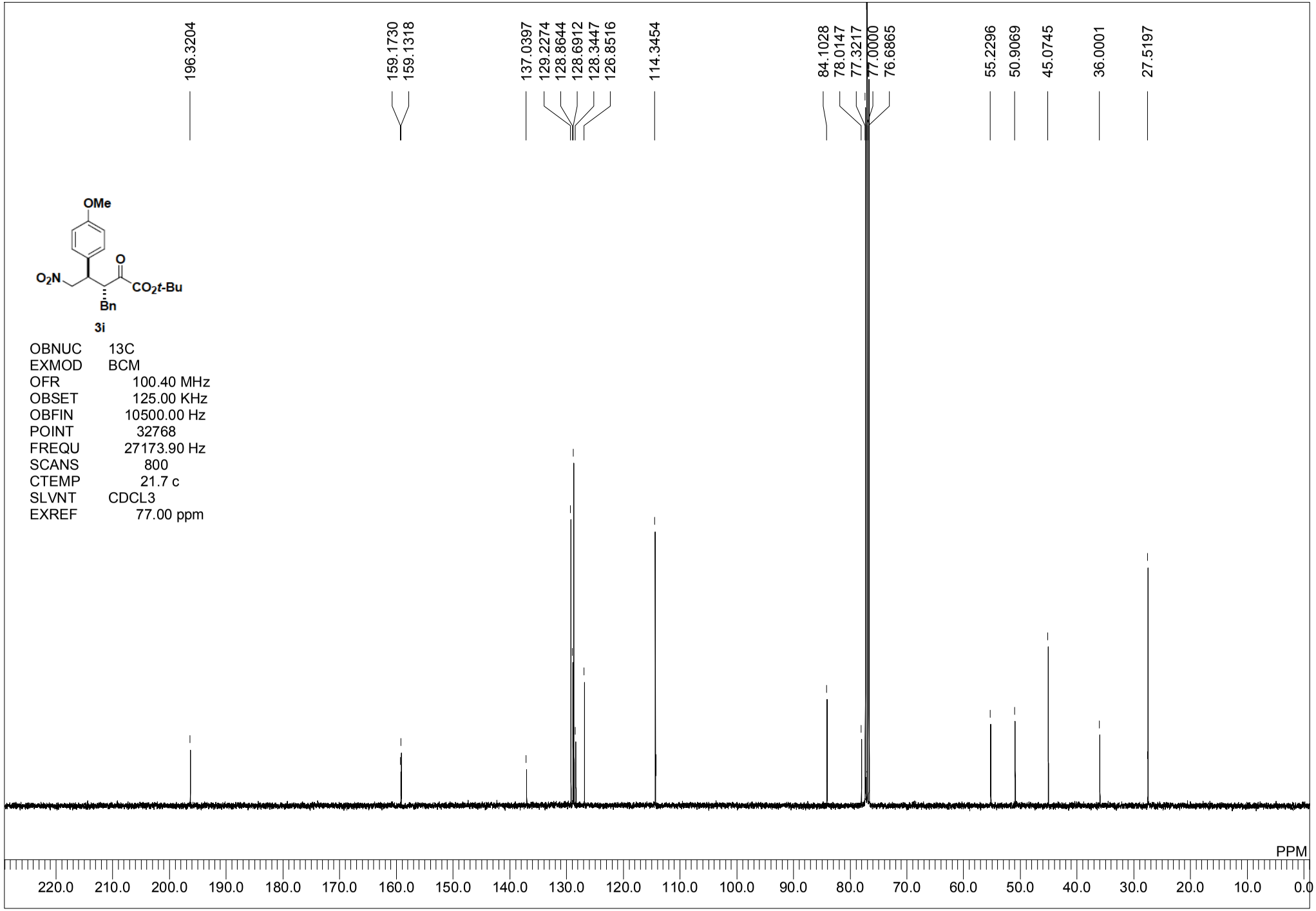
| | |
|---|---|
| OBNUC | 1H |
| EXMOD | NON |
| OFR | 399.65 MHz |
| OBSET | 124.00 KHz |
| OBFIN | 10500.00 Hz |
| POINT | 32768 |
| FREQU | 7993.60 Hz |
| SCANS | 8 |
| CTEMP | 21.4 c |
| SLVNT | CDCL3 |
| EXREF | 0.00 ppm |

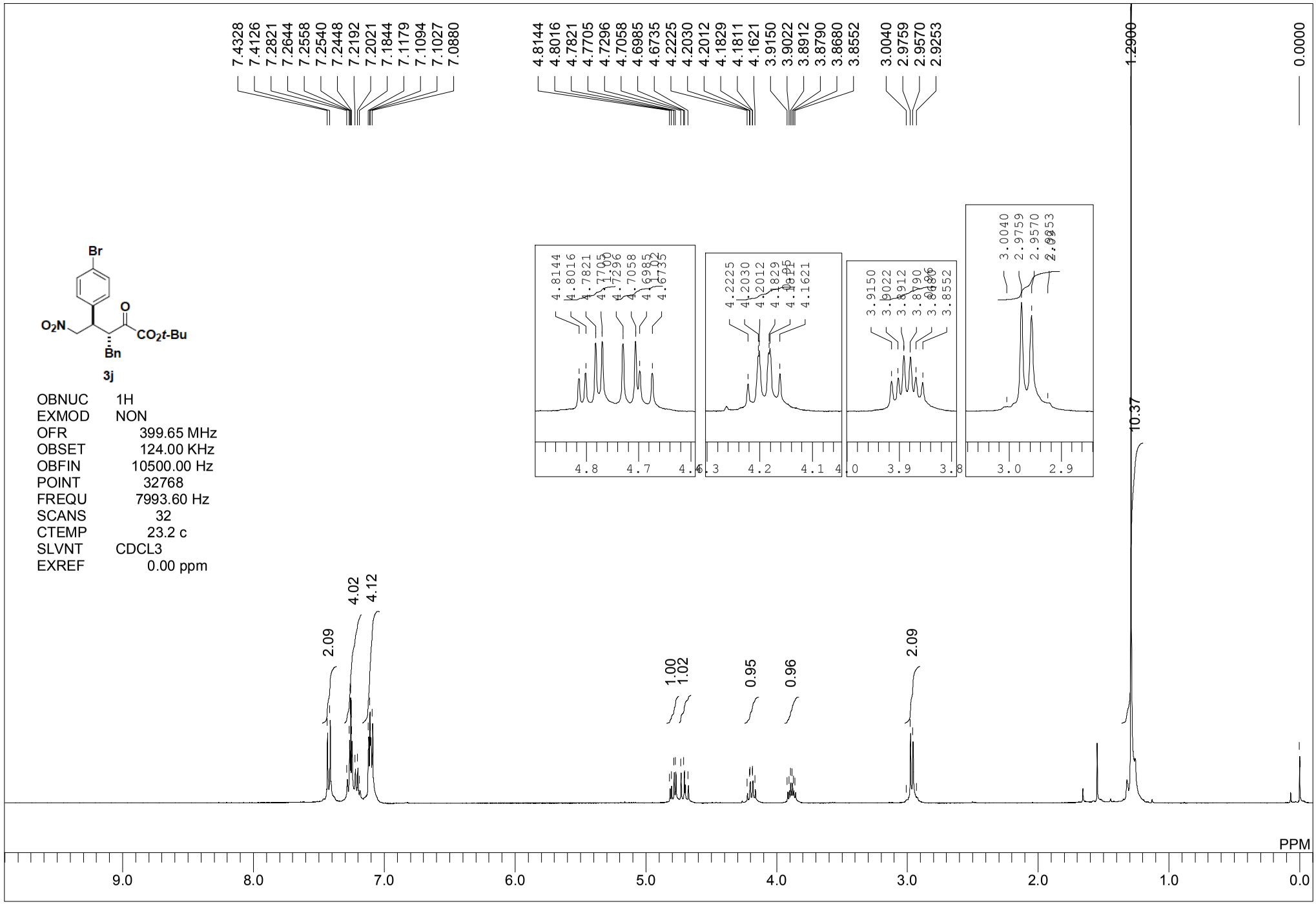

194.7612
159.3297
137.5099
136.8664
128.8232
128.2045
128.0725
127.9075
127.4703
127.4373
83.5583
77.7590
77.3135
77.0000
76.6783
72.6690
67.8348
47.3844
45.3715
30.3987
27.4784
Ph
O
O2N
CO2t-Bu
BnO
3g
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 676
CTEMP 21.5 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0

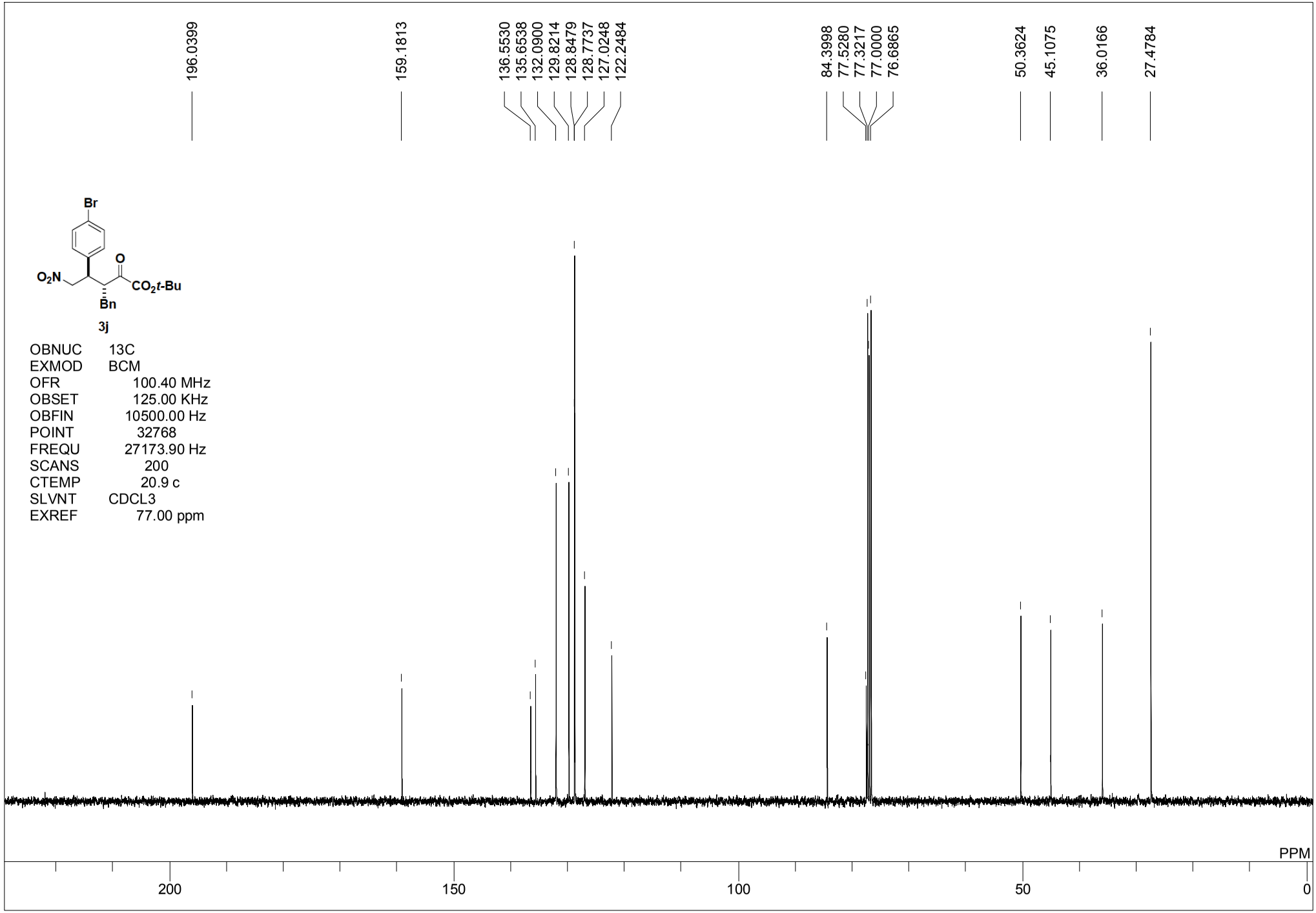

7.2784 7.2577 7.2430 7.2241 7.2131 7.1942 4.7272 4.7119 4.6967 4.6912 4.6814 4.6680 4.6375 4.2372 4.2103 4.2067 4.1896 4.1853 4.1682 4.1640 3.9351 3.9187 3.9144 3.9095 3.8979 3.8930 3.8888 3.8723 3.8009 3.7850 3.7771 3.7594 3.7509 3.7350 3.0131 2.9942 2.9845 2.9655 2.9558 2.9369 2.2449 2.2272 2.2205 2.2156 2.2095 2.2022 2.1857 2.1235 2.0942 2.0704 2.0417 2.0167 1.6079 1.5291 1.2247 1.1954 1.1649 0.0000
Ph HO CO2t-Bu O2N O
3h
Ph O O2N CO2t-Bu HO
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
CTEMP 22.6 c
SLVNT CDCL3
EXREF 0.00 ppm
5.28
2.00
0.97
1.01
1.00
1.00
0.99
1.02
1.05
9.24
PPM
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

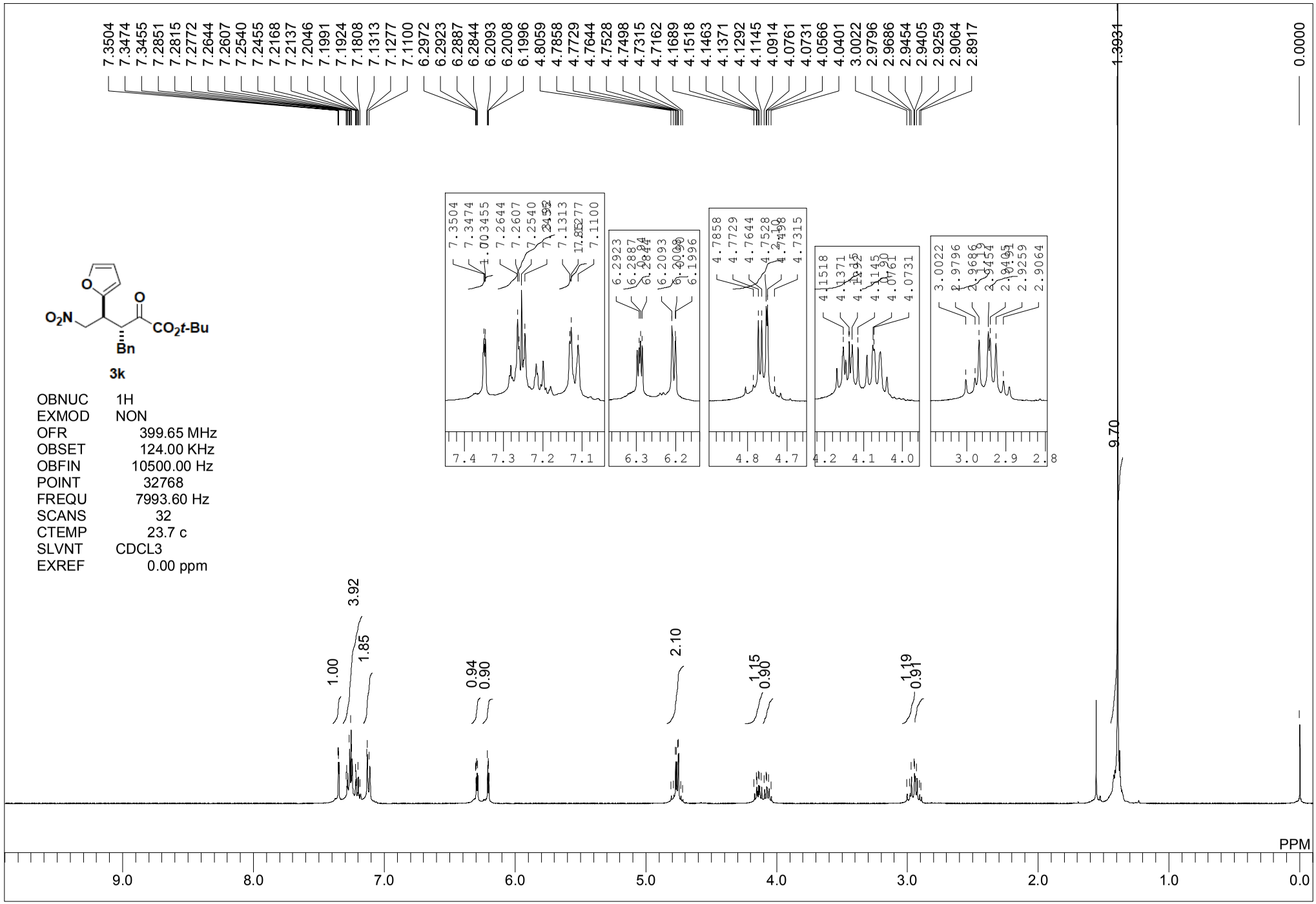

168.8001
137.5924
128.6170
128.3117
127.7673
100.7585
83.4593
79.6976
77.3135
77.0000
76.6783
67.6616
48.2588
44.1011
29.2603
27.4949
Ph
HO
CO2t-Bu
O2N
O
Ph
O
O2N
CO2t-Bu
HO
3h
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 653
CTEMP 21.6 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0

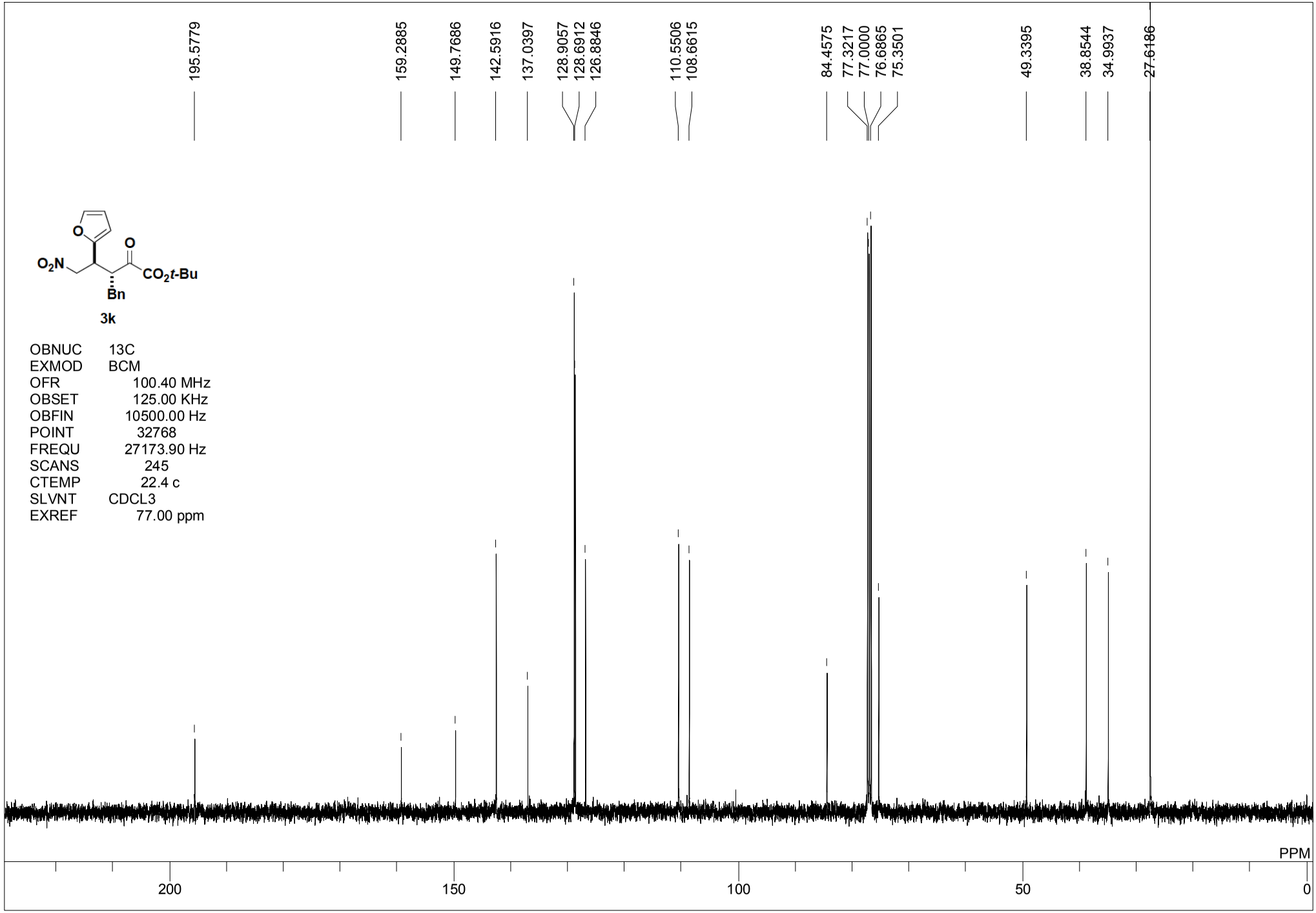

7.2857 7.2747 7.2711 7.2674 7.2546 7.2387 7.2351 7.2247 7.2082 7.2052 7.2015 7.1924 7.1869 7.1802 7.1716 7.1686 7.1655 7.1429 7.1350 7.1265 7.1228 7.1185 7.1130 7.1051 6.8275 6.8202 6.8147 6.8031 6.7982 6.7903 4.8028 4.7900 4.7717 4.7583 4.7290 4.7052 4.6973 4.6735 4.2073 4.1884 4.1853 4.1689 4.1658 4.1469 3.8943 3.8808 3.8711 3.8577 3.8479 3.8345 3.7869 3.7564 3.7259 3.0156 2.9851 2.9655 2.9350 1.5560 1.2851 0.0000
OMe
O
O2N
CO2t-Bu
Bn
3i
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 48
CTEMP 21.9 c
SLVNT CDCL3
EXREF 0.00 ppm
4.56
4.00
1.99
1.04
1.02
1.00
1.03
3.18
1.08
1.02
9.27
PPM
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

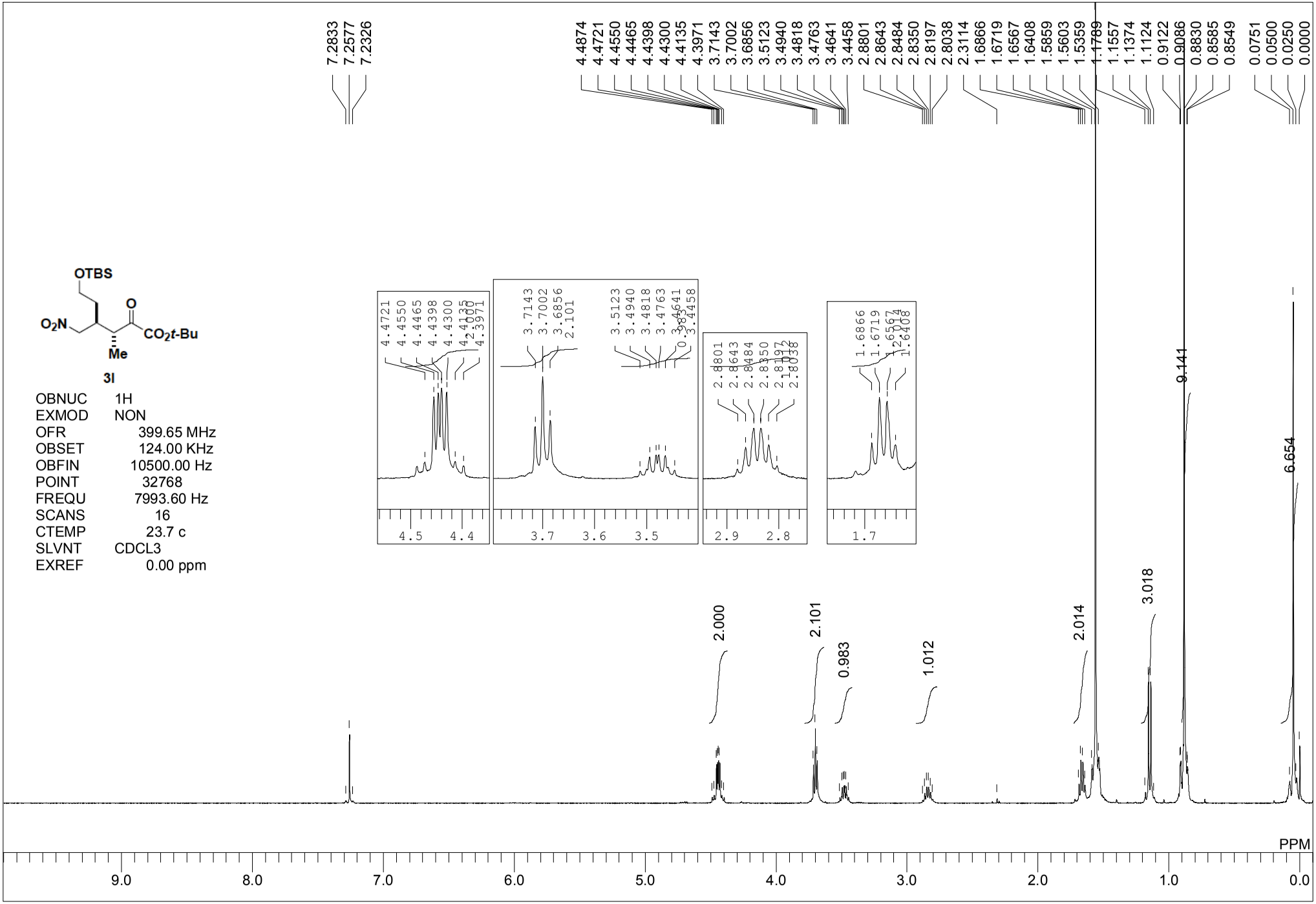

196.3204
159.1730
159.1318
137.0397
129.2274
128.8644
128.6912
128.3447
126.8516
114.3454
84.1028
78.0147
77.3217
77.0000
76.6865
55.2296
50.9069
45.0745
36.0001
27.5197
OMe
O
O2N
CO2t-Bu
Bn
3i
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 800
CTEMP 21.7 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0

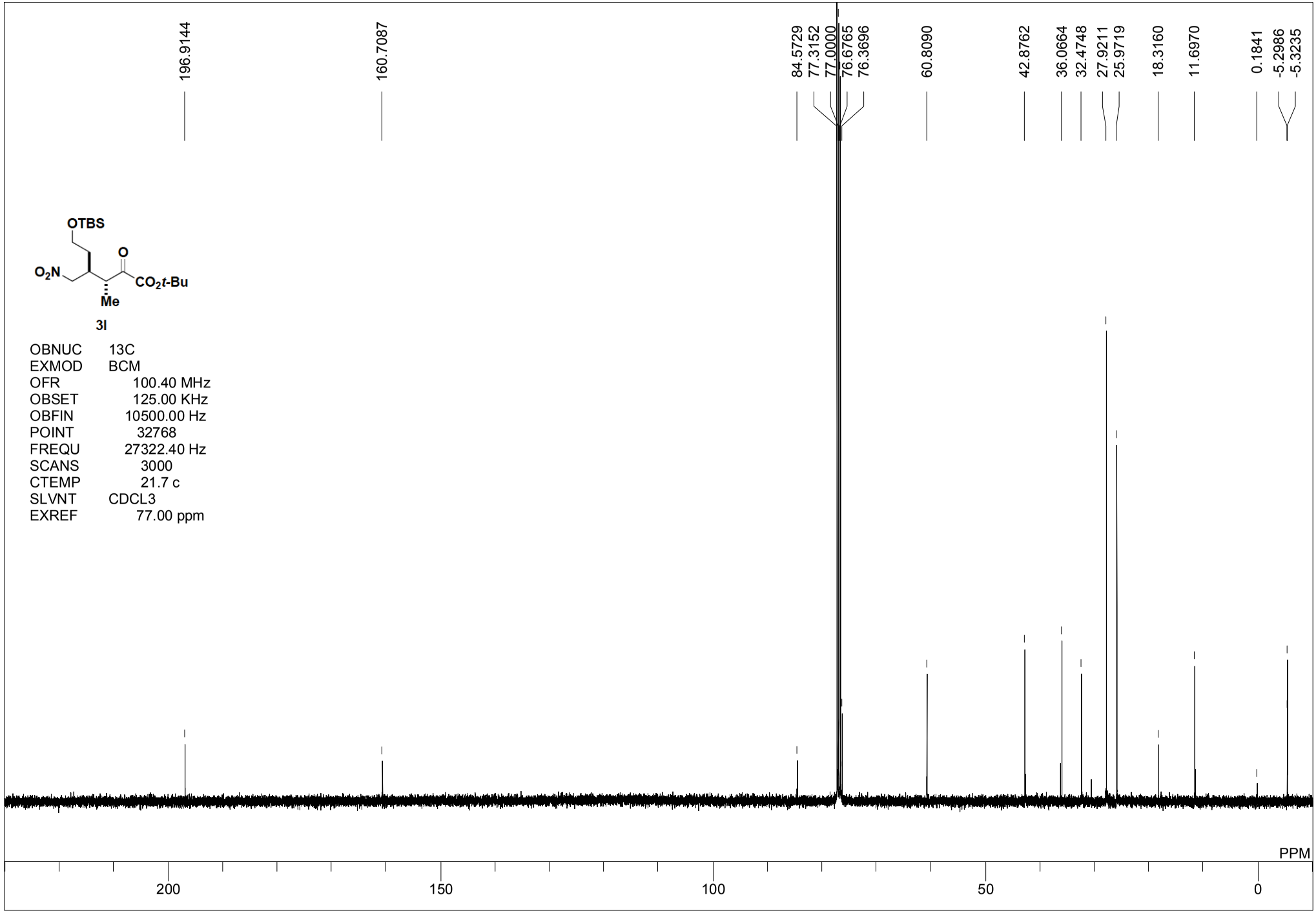

7.4328
7.4126
7.2821
7.2644
7.2558
7.2540
7.2448
7.2192
7.2021
7.1844
7.1179
7.1094
7.1027
7.0880
4.8144
4.8016
4.7821
4.7705
4.7296
4.7058
4.6985
4.6735
4.2225
4.2030
4.2012
4.1829
4.1811
4.1621
3.9150
3.9022
3.8912
3.8790
3.8680
3.8552
3.0040
2.9759
2.9570
2.9253
1.2900
0.0000
Br
O
O2N
CO2t-Bu
Bn
3j
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 32
CTEMP 23.2 c
SLVNT CDCL3
EXREF 0.00 ppm
2.09
4.02
4.12
1.00
1.02
0.95
0.96
2.09
10.37
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

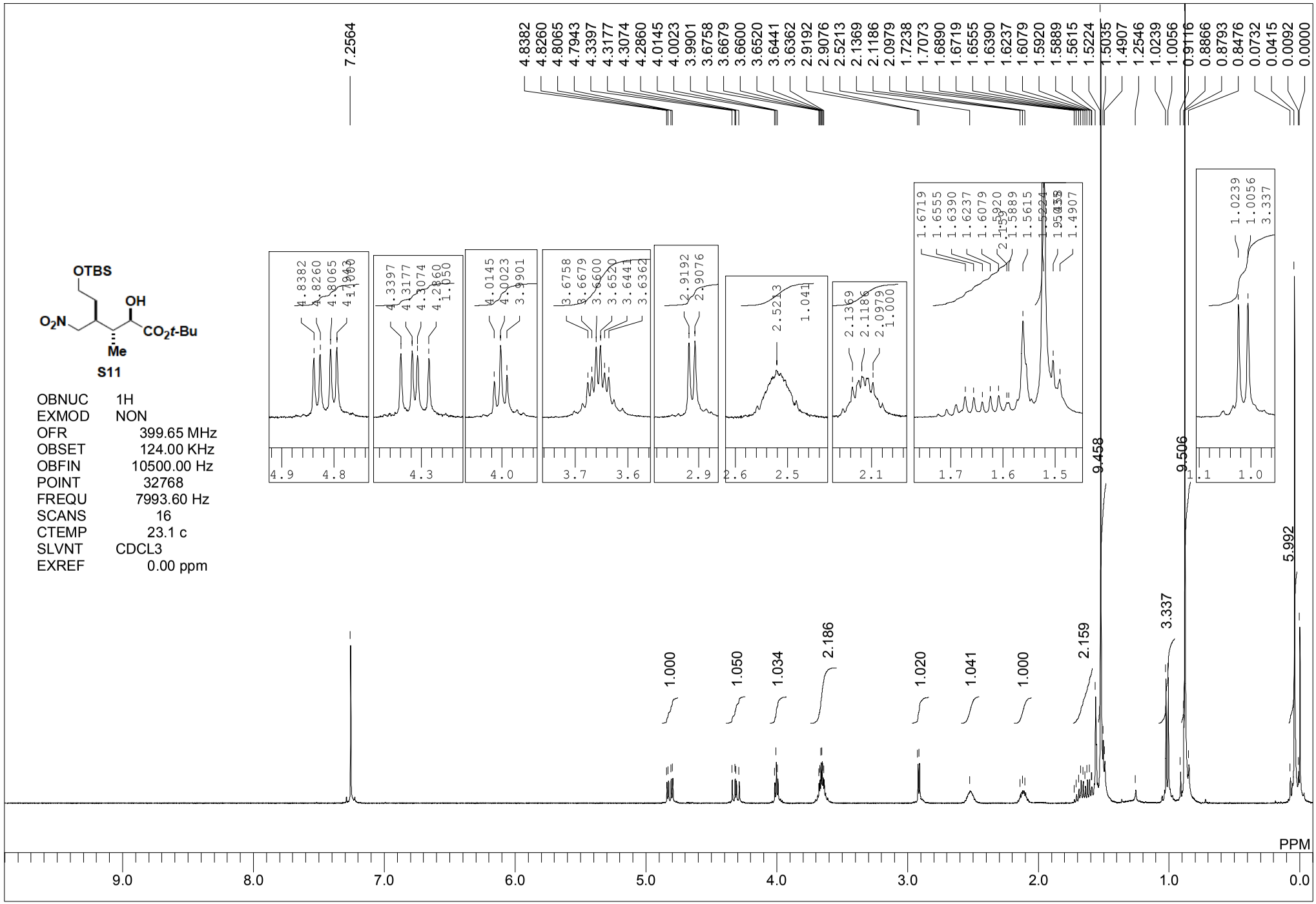

196.0399
159.1813
136.5530
135.6538
132.0900
129.8214
128.8479
128.7737
127.0248
122.2484
84.3998
77.5280
77.3217
77.0000
76.6865
50.3624
45.1075
36.0166
27.4784
Br
O
O2N
CO2t-Bu
Bn
3j
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 200
CTEMP 20.9 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0

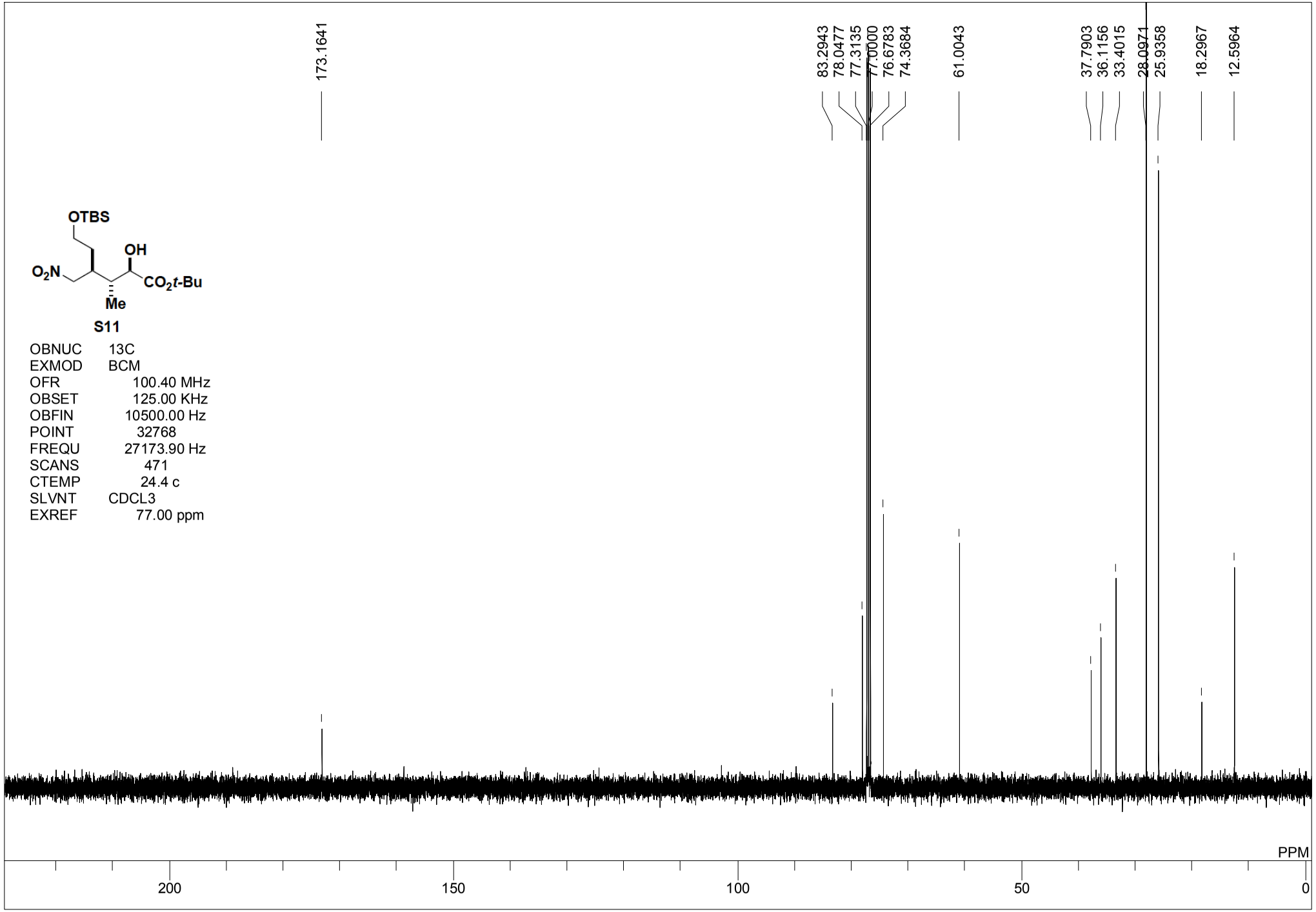

7.3504 7.3474 7.3455 7.2851 7.2815 7.2772 7.2644 7.2607 7.2540 7.2455 7.2168 7.2137 7.2046 7.1991 7.1924 7.1808 7.1313 7.1277 7.1100 6.2972 6.2923 6.2887 6.2844 6.2093 6.2008 6.1996 4.8059 4.7858 4.7729 4.7644 4.7528 4.7498 4.7315 4.7162 4.1689 4.1518 4.1463 4.1371 4.1292 4.1145 4.0914 4.0761 4.0731 4.0566 4.0401 3.0022 2.9796 2.9686 2.9454 2.9405 2.9259 2.9064 2.8917
1.3931
0.0000
O
O
O2N
CO2t-Bu
Bn
3k
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 32
CTEMP 23.7 c
SLVNT CDCL3
EXREF 0.00 ppm
1.00
3.92
1.85
0.94
0.90
2.10
1.15
0.90
1.19
0.91
9.70
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

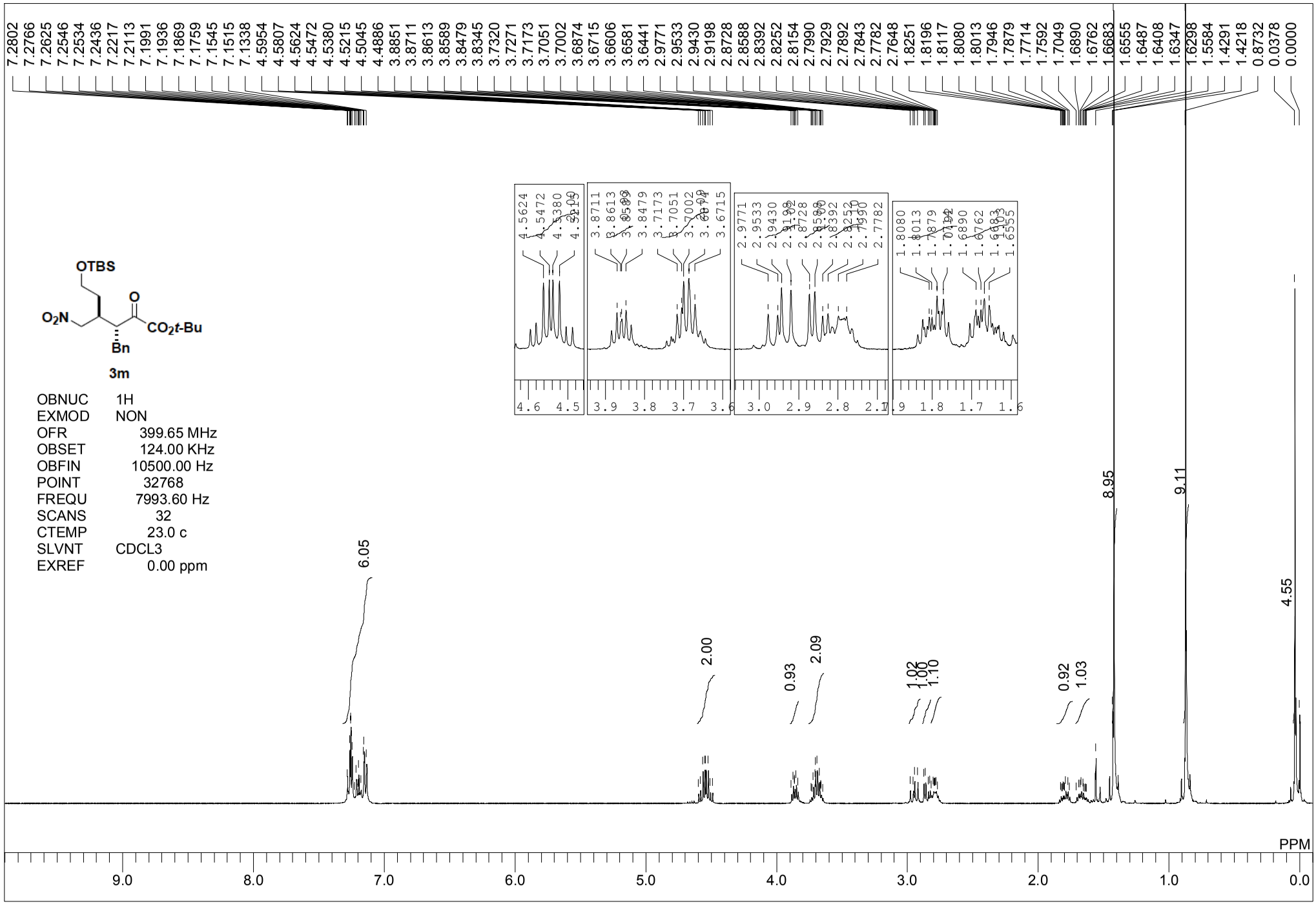

195.5779
159.2885
149.7686
142.5916
137.0397
128.9057
128.6912
126.8846
110.5506
108.6615
84.4575
77.3217
77.0000
76.6865
75.3501
49.3395
38.8544
34.9937
27.6186
O
O
O2N
O
CO2t-Bu
Bn
3k
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 245
CTEMP 22.4 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0

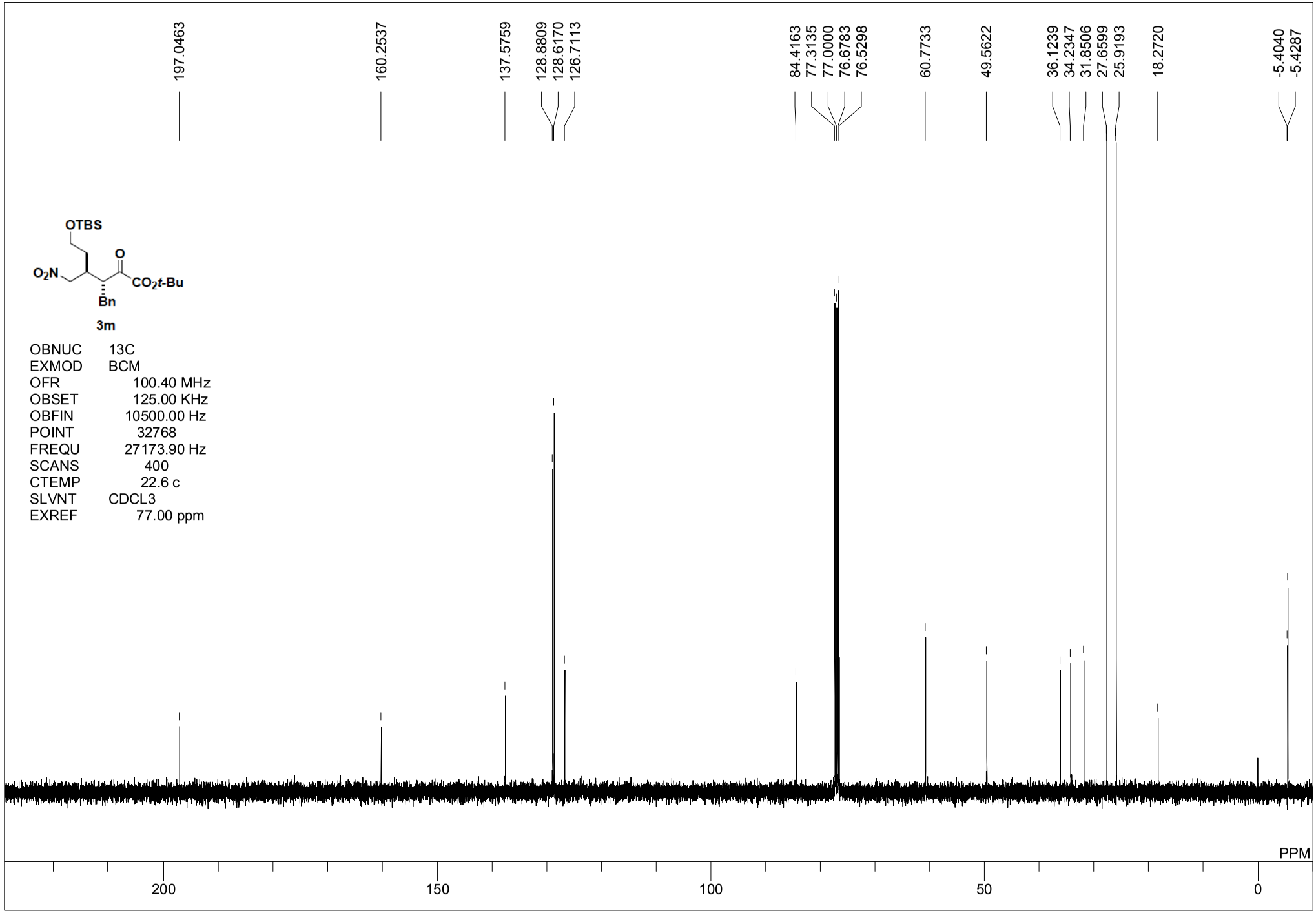

OTBS
O
O2N
CO2t-Bu
Me
3l
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 16
CTEMP 23.7 c
SLVNT CDCL3
EXREF 0.00 ppm
7.2833
7.2577
7.2326
4.4874
4.4721
4.4550
4.4465
4.4398
4.4300
4.4135
4.3971
3.7143
3.7002
3.6856
3.5123
3.4940
3.4818
3.4763
3.4641
3.4458
2.8801
2.8643
2.8484
2.8350
2.8197
2.8038
2.3114
1.6866
1.6719
1.6567
1.6408
1.5859
1.5603
1.5359
1.1789
1.1557
1.1374
1.1124
0.9122
0.9086
0.8830
0.8585
0.8549
0.0751
0.0500
0.0250
0.0000
2.000
2.101
0.983
1.012
2.014
3.018
9.141
6.654
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

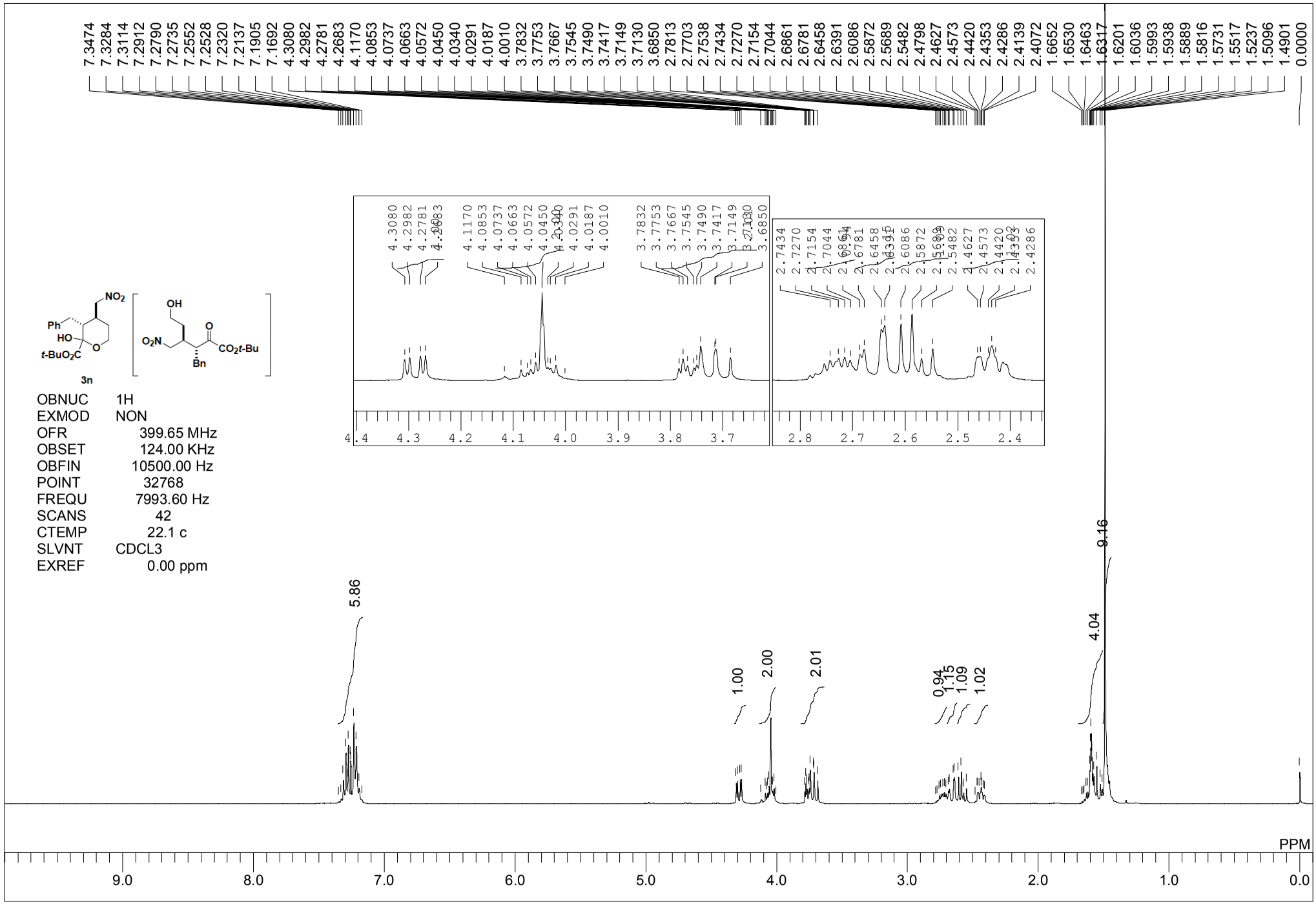

196.9144
160.7087
84.5729
77.3152
77.0000
76.6765
76.3696
60.8090
42.8762
36.0664
32.4748
27.9211
25.9719
18.3160
11.6970
0.1841
-5.2986
-5.3235
OTBS
O
O2N
CO2t-Bu
Me
3l
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27322.40 Hz
SCANS 3000
CTEMP 21.7 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0

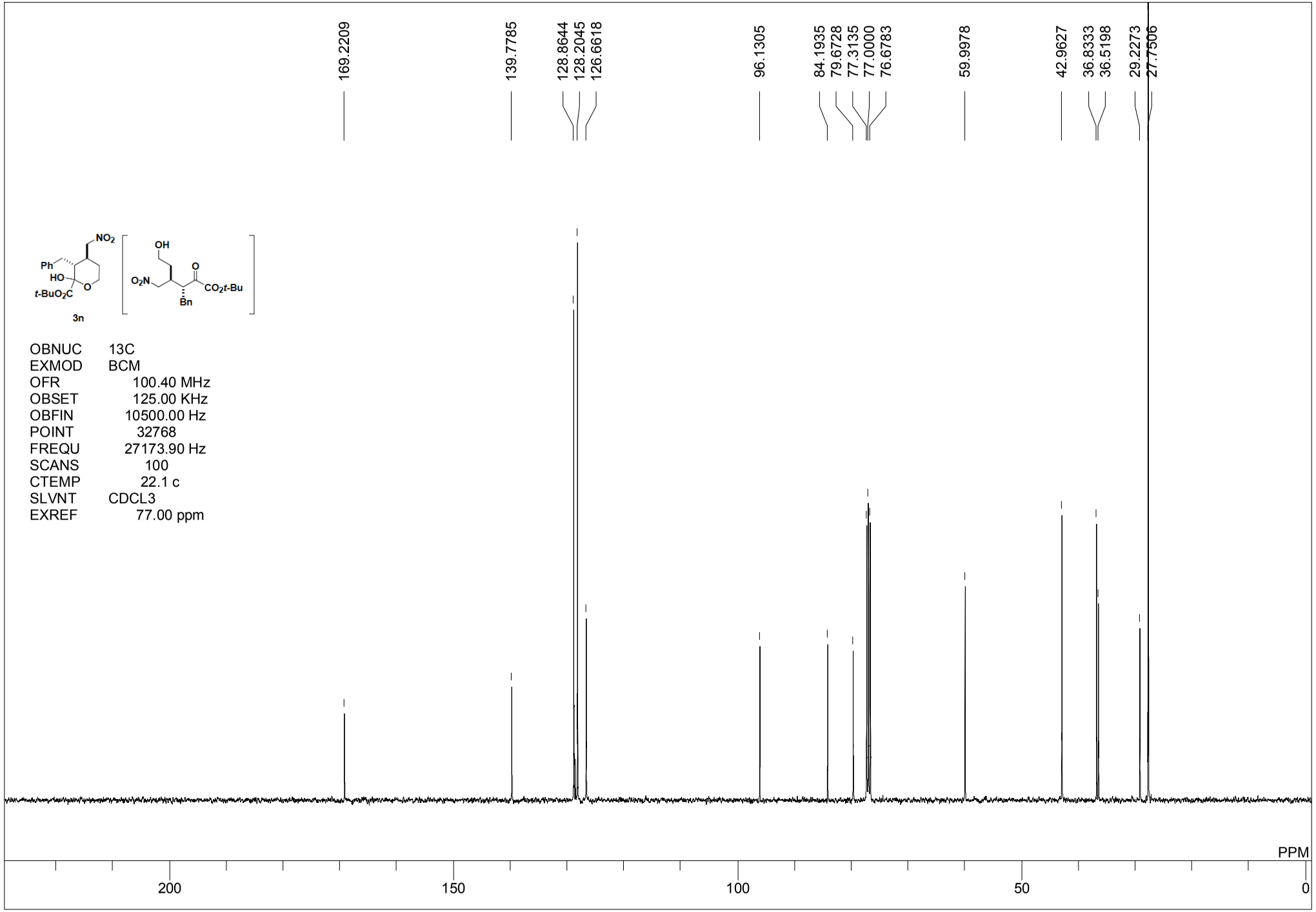

OTBS
OH
$O_2N$
$CO_2t$-Bu
Me
S11
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 16
CTEMP 23.1 c
SLVNT CDCL3
EXREF 0.00 ppm
7.2564
4.8382
4.8260
4.8065
4.7943
4.3397
4.3177
4.3074
4.2860
4.0145
4.0023
3.9901
3.6758
3.6679
3.6600
3.6520
3.6441
3.6362
2.9192
2.9076
2.5213
2.1369
2.1186
2.0979
1.7238
1.7073
1.6890
1.6719
1.6555
1.6390
1.6237
1.6079
1.5920
1.5889
1.5615
1.5224
1.5035
1.4907
1.2546
1.0239
1.0056
0.9116
0.8866
0.8793
0.8476
0.0732
0.0415
0.0092
0.0000
1.000
1.050
1.034
2.186
1.020
1.041
1.000
2.159
9.458
3.337
9.506
5.992
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

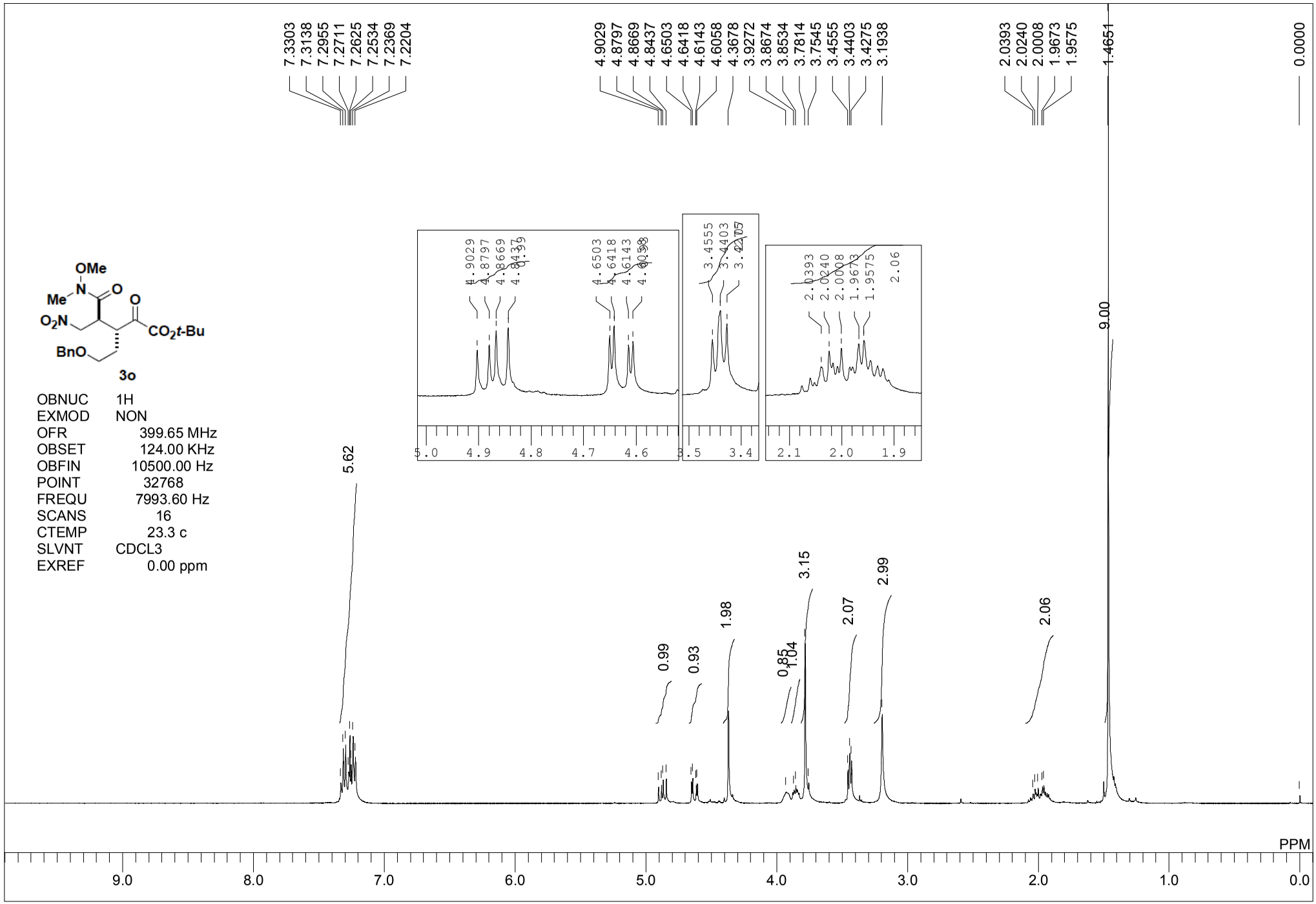

173.1641
83.2943
78.0477
77.3135
77.0000
76.6783
74.3684
61.0043
37.7903
36.1156
33.4015
28.0971
25.9358
18.2967
12.5964
OTBS
OH
$O_2N$
$CO_2t$-Bu
Me
S11
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 471
CTEMP 24.4 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0

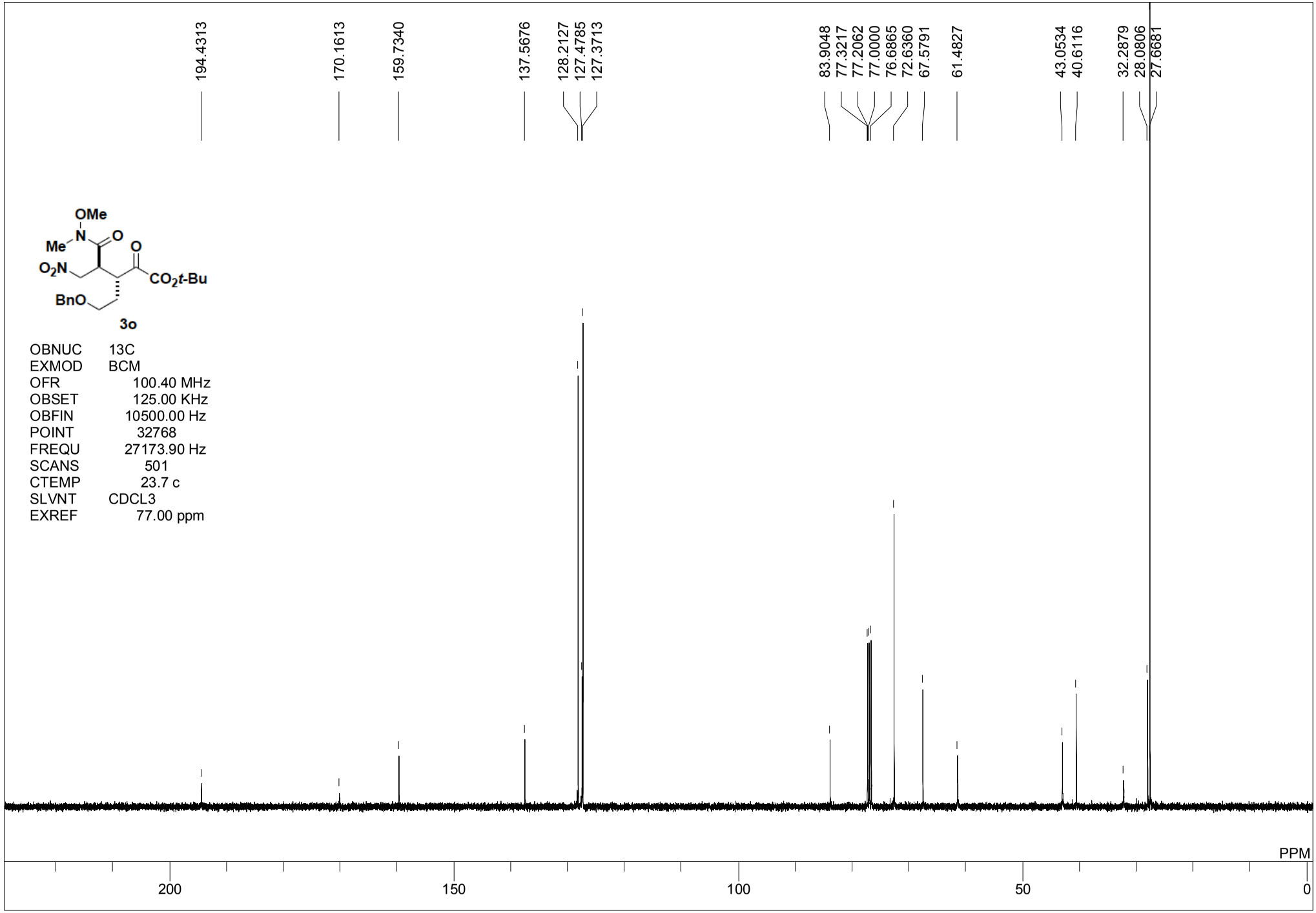

OTBS
O
O2N
CO2t-Bu
Bn
3m
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 32
CTEMP 23.0 c
SLVNT CDCL3
EXREF 0.00 ppm
6.05
2.00
0.93
2.09
1.02
1.06
1.10
0.92
1.03
8.95
9.11
4.55
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

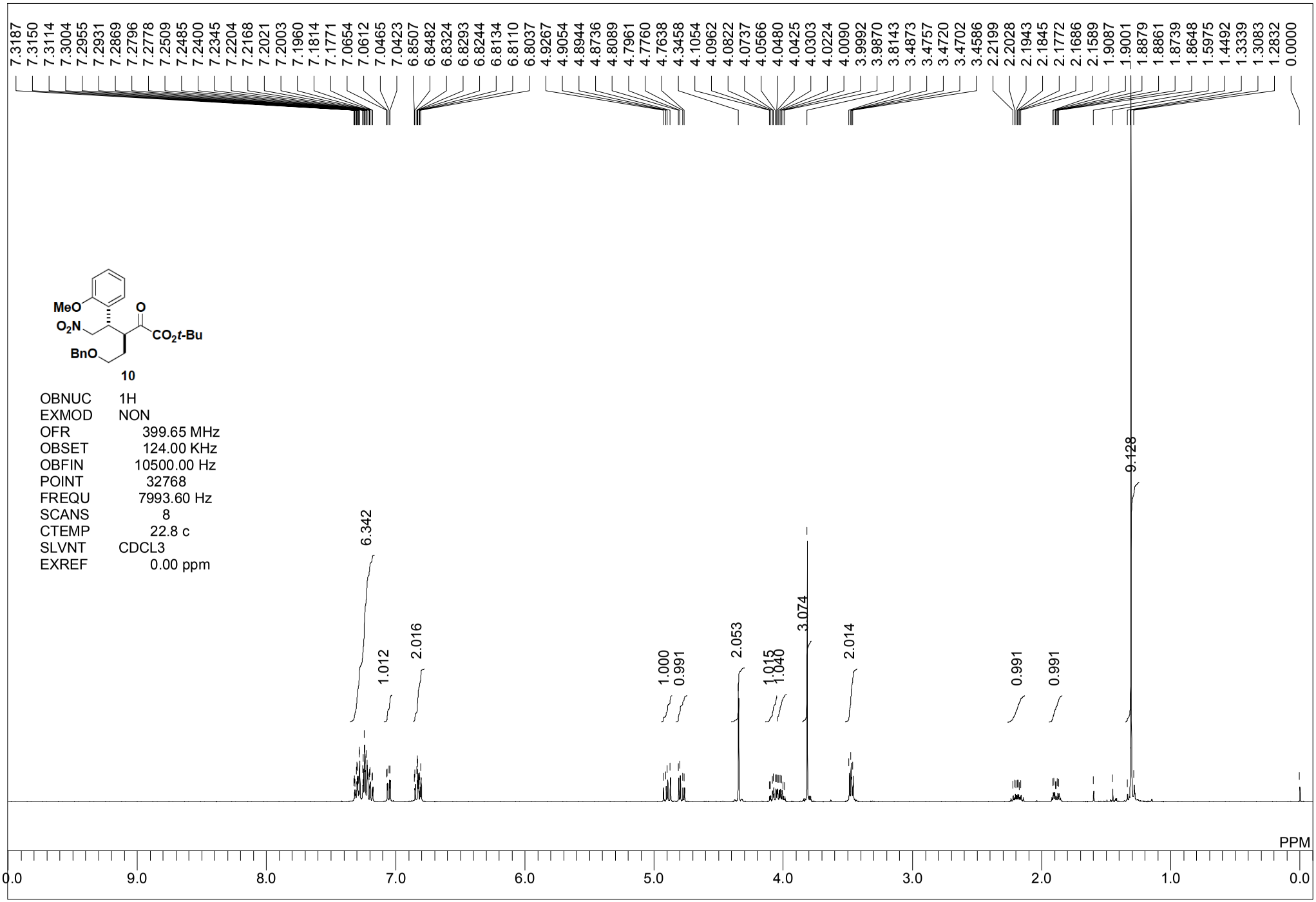

197.0463
160.2537
137.5759
128.8809
128.6170
126.7113
84.4163
77.3135
77.0000
76.6783
76.5298
60.7733
49.5622
36.1239
34.2347
31.8506
27.6599
25.9193
18.2720
-5.4040
-5.4287
OTBS
O
O2N
CO2t-Bu
Bn
3m
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 400
CTEMP 22.6 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0

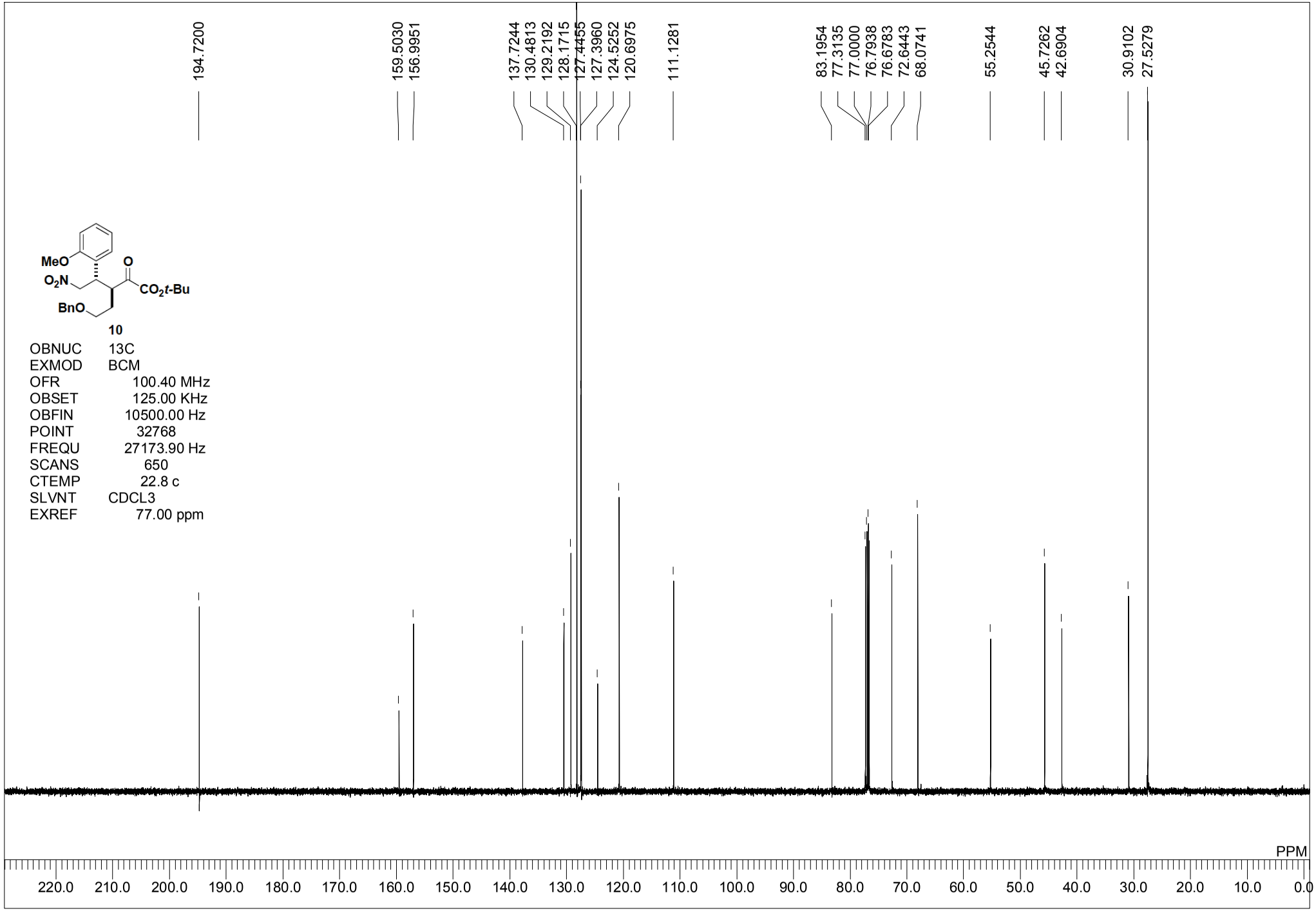

7.3474 7.3284 7.3114 7.2912 7.2790 7.2735 7.2552 7.2528 7.2320 7.2137 7.1905 7.1692 4.3080 4.2982 4.2781 4.2683 4.1170 4.0853 4.0737 4.0663 4.0572 4.0450 4.0340 4.0291 4.0187 4.0010 3.7832 3.7753 3.7667 3.7545 3.7490 3.7417 3.7149 3.7130 3.6850 2.7813 2.7703 2.7538 2.7434 2.7270 2.7154 2.7044 2.6861 2.6781 2.6458 2.6391 2.6086 2.5872 2.5689 2.5482 2.4798 2.4627 2.4573 2.4420 2.4353 2.4286 2.4139 2.4072 1.6652 1.6530 1.6463 1.6317 1.6201 1.6036 1.5993 1.5938 1.5889 1.5816 1.5731 1.5517 1.5237 1.5096 1.4901 0.0000
NO2
Ph
HO
t-BuO2C
O
OH
O2N
CO2t-Bu
Bn
3n
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 42
CTEMP 22.1 c
SLVNT CDCL3
EXREF 0.00 ppm
5.86
1.00
2.00
2.01
0.94
1.15
1.09
1.02
4.04
9.16
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

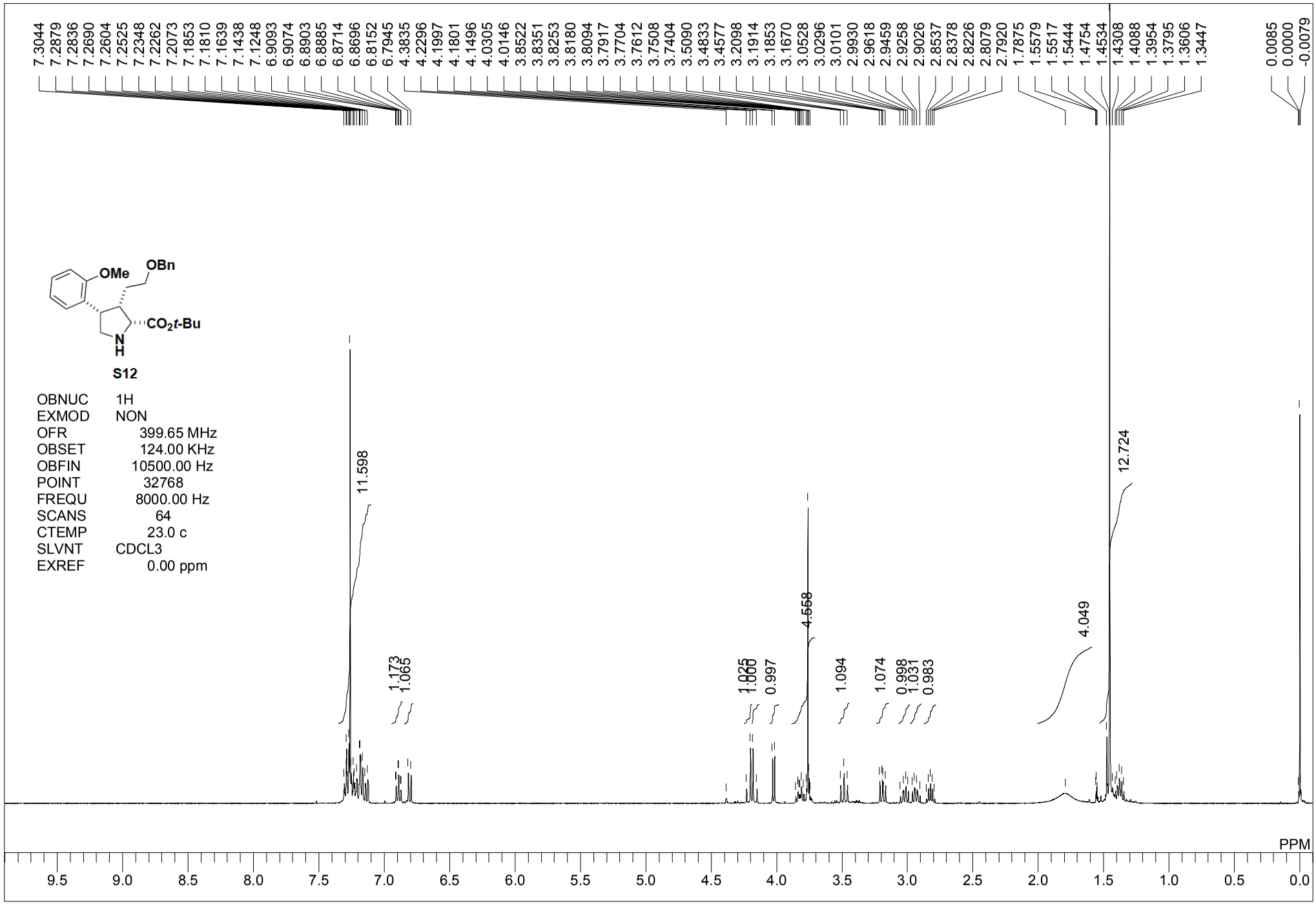

169.2209
139.7785
128.8644
128.2045
126.6618
96.1305
84.1935
79.6728
77.3135
77.0000
76.6783
59.9978
42.9627
36.8333
36.5198
29.2273
27.7506
NO2
Ph
HO
t-BuO2C
O
OH
O2N
O
CO2t-Bu
Bn
3n
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 100
CTEMP 22.1 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0

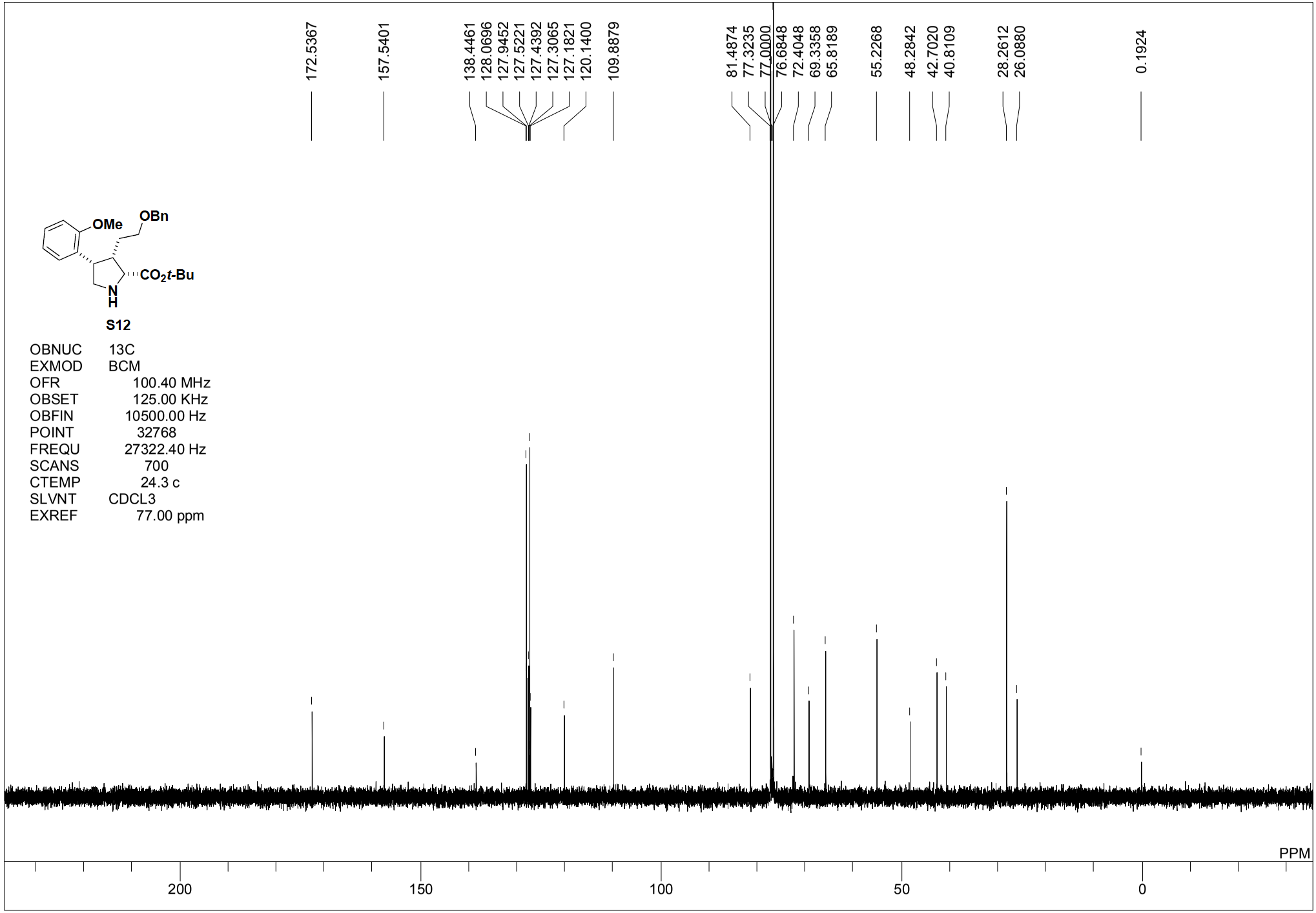

7.3303
7.3138
7.2955
7.2711
7.2625
7.2534
7.2369
7.2204
4.9029
4.8797
4.8669
4.8437
4.6503
4.6418
4.6143
4.6058
4.3678
3.9272
3.8674
3.8534
3.7814
3.7545
3.4555
3.4403
3.4275
3.1938
2.0393
2.0240
2.0008
1.9673
1.9575
1.4651
0.0000
OMe
Me
N
O
O
O2N
CO2t-Bu
BnO
3o
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 16
CTEMP 23.3 c
SLVNT CDCL3
EXREF 0.00 ppm
5.62
0.99
0.93
1.98
0.85
1.04
3.15
2.07
2.99
2.06
9.00
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

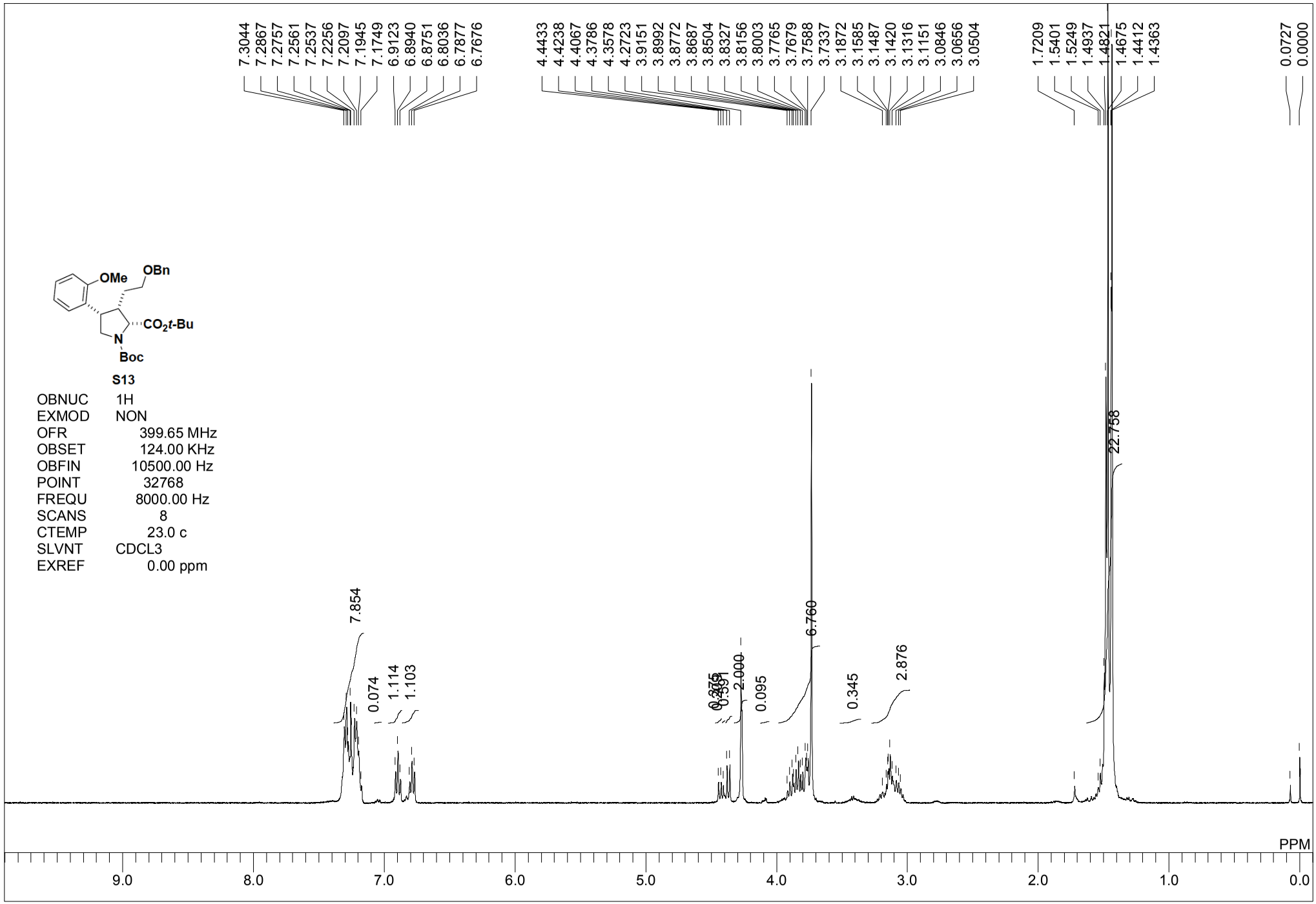

194.4313
170.1613
159.7340
137.5676
128.2127
127.4785
127.3713
83.9048
77.3217
77.2062
77.0000
76.6865
72.6360
67.5791
61.4827
43.0534
40.6116
32.2879
28.0806
27.6681
OMe
N
Me
O
O
O2N
CO2t-Bu
BnO
3o
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 501
CTEMP 23.7 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0

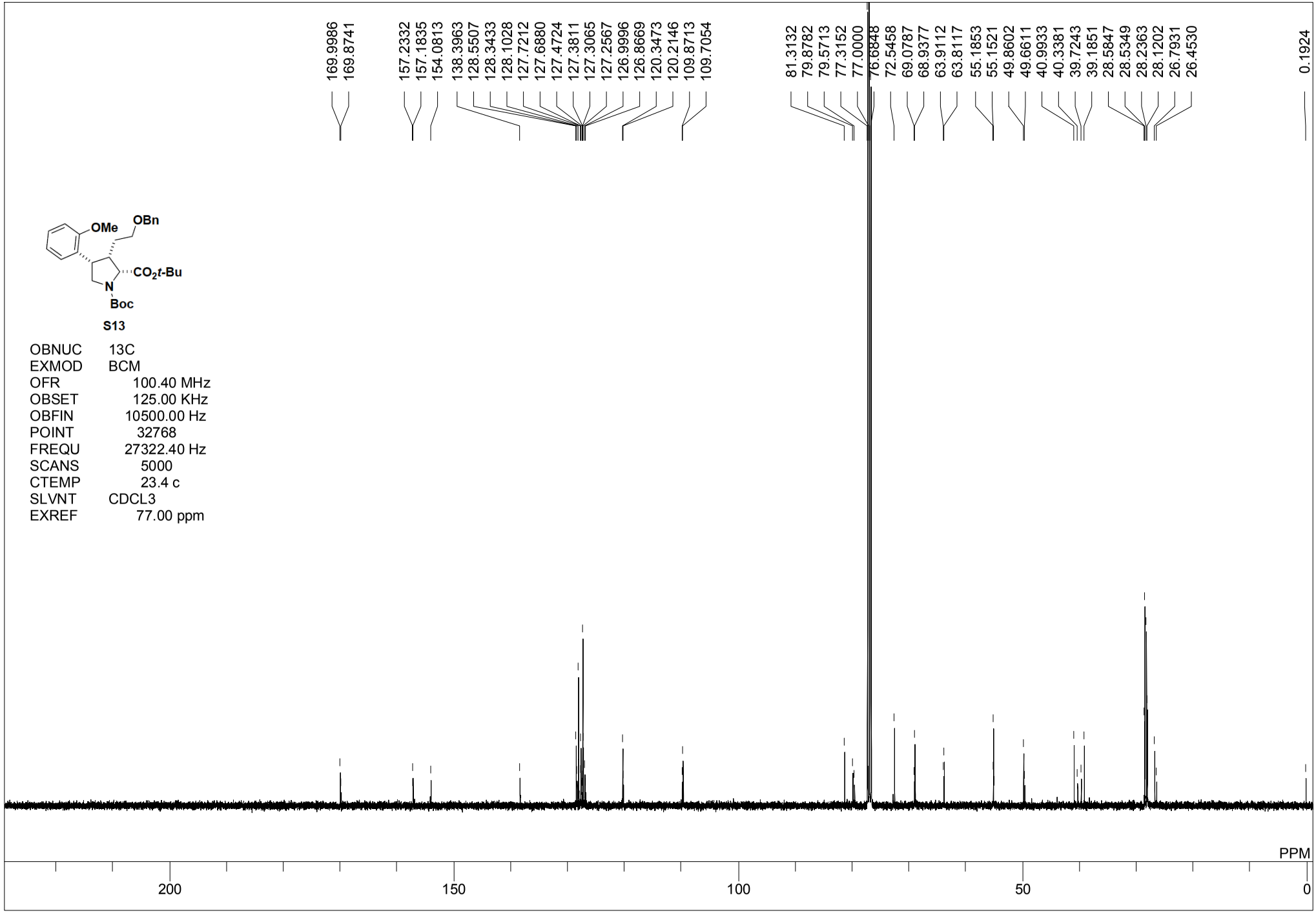

7.3187 7.3150 7.3114 7.3004 7.2955 7.2931 7.2869 7.2796 7.2778 7.2509 7.2485 7.2400 7.2345 7.2204 7.2168 7.2021 7.2003 7.1960 7.1814 7.1771 7.0654 7.0612 7.0465 7.0423 6.8507 6.8482 6.8324 6.8293 6.8244 6.8134 6.8110 6.8037 4.9267 4.9054 4.8944 4.8736 4.8089 4.7961 4.7760 4.7638 4.3458 4.1054 4.0962 4.0822 4.0737 4.0566 4.0480 4.0425 4.0303 4.0224 4.0090 3.9992 3.9870 3.8143 3.4873 3.4757 3.4720 3.4702 3.4586 2.2199 2.2028 2.1943 2.1845 2.1772 2.1686 2.1589 1.9087 1.9001 1.8879 1.8861 1.8739 1.8648 1.5975 1.4492 1.3339 1.3083 1.2832 0.0000
MeO
O
O2N
CO2t-Bu
BnO
10
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
CTEMP 22.8 c
SLVNT CDCL3
EXREF 0.00 ppm
6.342
1.012
2.016
1.000
0.991
2.053
1.015
1.040
3.074
2.014
0.991
0.991
9.128
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

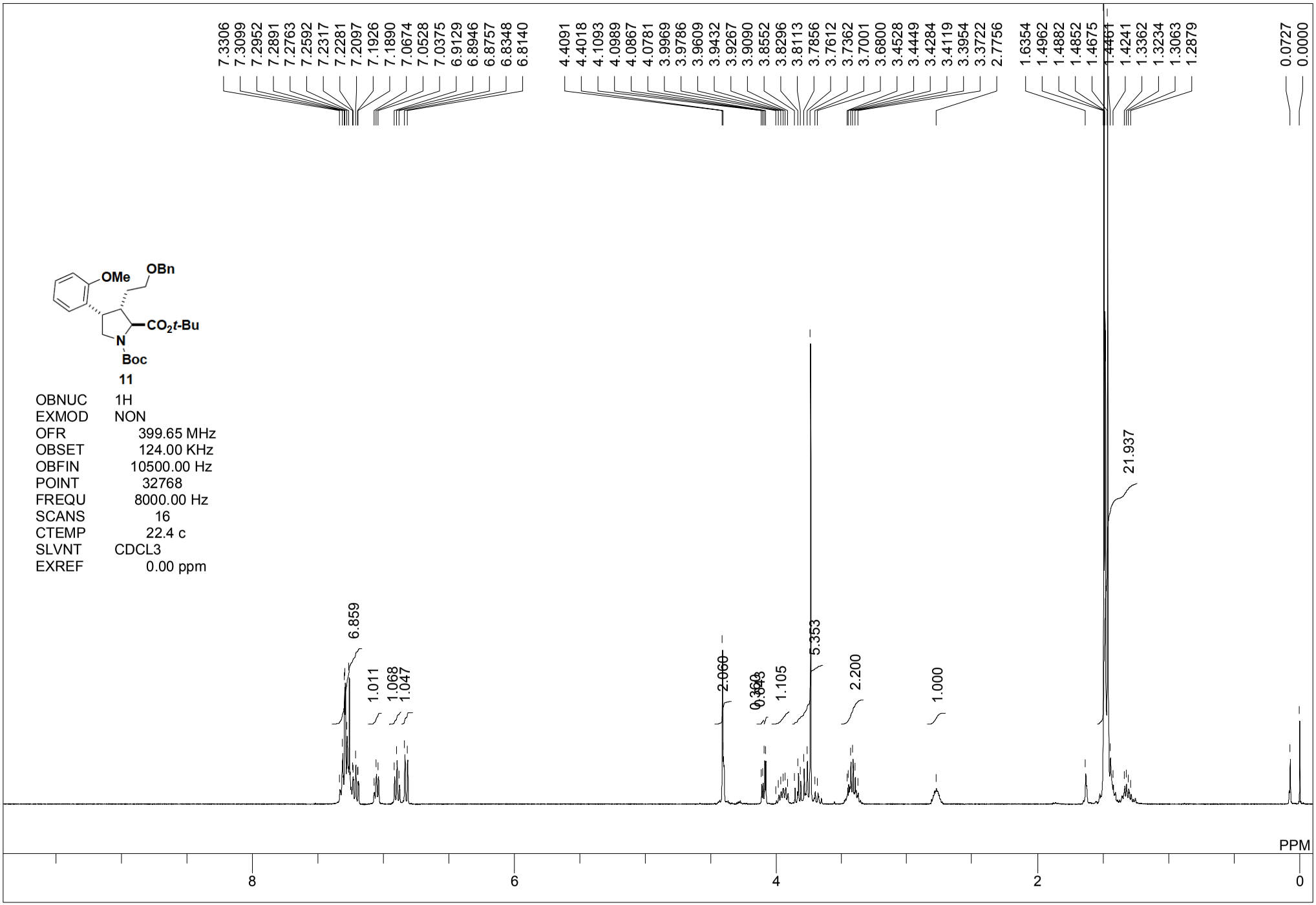

194.7200
159.5030
156.9951
137.7244
130.4813
129.2192
128.1715
127.4455
127.3960
124.5252
120.6975
111.1281
83.1954
77.3135
77.0000
76.7938
76.6783
72.6443
68.0741
55.2544
45.7262
42.6904
30.9102
27.5279
MeO
O
O2N
CO2t-Bu
BnO
10
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 650
CTEMP 22.8 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0

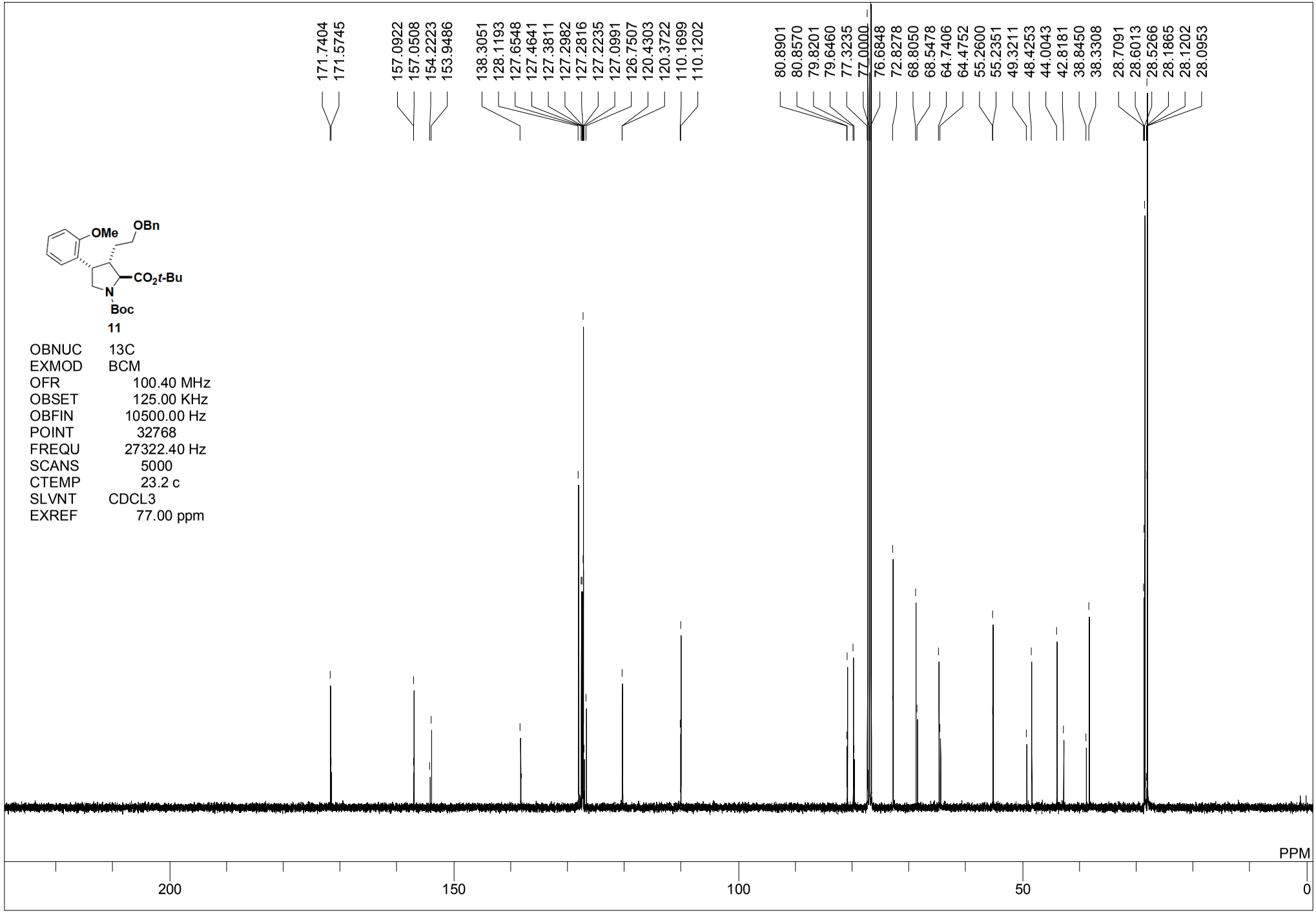

7.3044
7.2879
7.2836
7.2690
7.2604
7.2525
7.2348
7.2262
7.2073
7.1853
7.1810
7.1639
7.1438
7.1248
6.9093
6.9074
6.8903
6.8885
6.8714
6.8696
6.8152
6.7945
4.3835
4.2296
4.1997
4.1801
4.1496
4.0305
4.0146
3.8522
3.8351
3.8253
3.8180
3.8094
3.7917
3.7704
3.7612
3.7508
3.7404
3.5090
3.4833
3.4577
3.2098
3.1914
3.1853
3.1670
3.0528
3.0296
3.0101
2.9930
2.9618
2.9459
2.9258
2.9026
2.8537
2.8378
2.8226
2.8079
2.7920
1.7875
1.5579
1.5517
1.5444
1.4754
1.4534
1.4308
1.4088
1.3954
1.3795
1.3606
1.3447
0.0085
0.0000
-0.0079
OMe
OBn
CO2t-Bu
N
H
S12
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 8000.00 Hz
SCANS 64
CTEMP 23.0 c
SLVNT CDCL3
EXREF 0.00 ppm
11.598
1.173
1.065
1.025
1.000
0.997
4.558
1.094
1.074
0.998
1.031
0.983
4.049
12.724
PPM
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

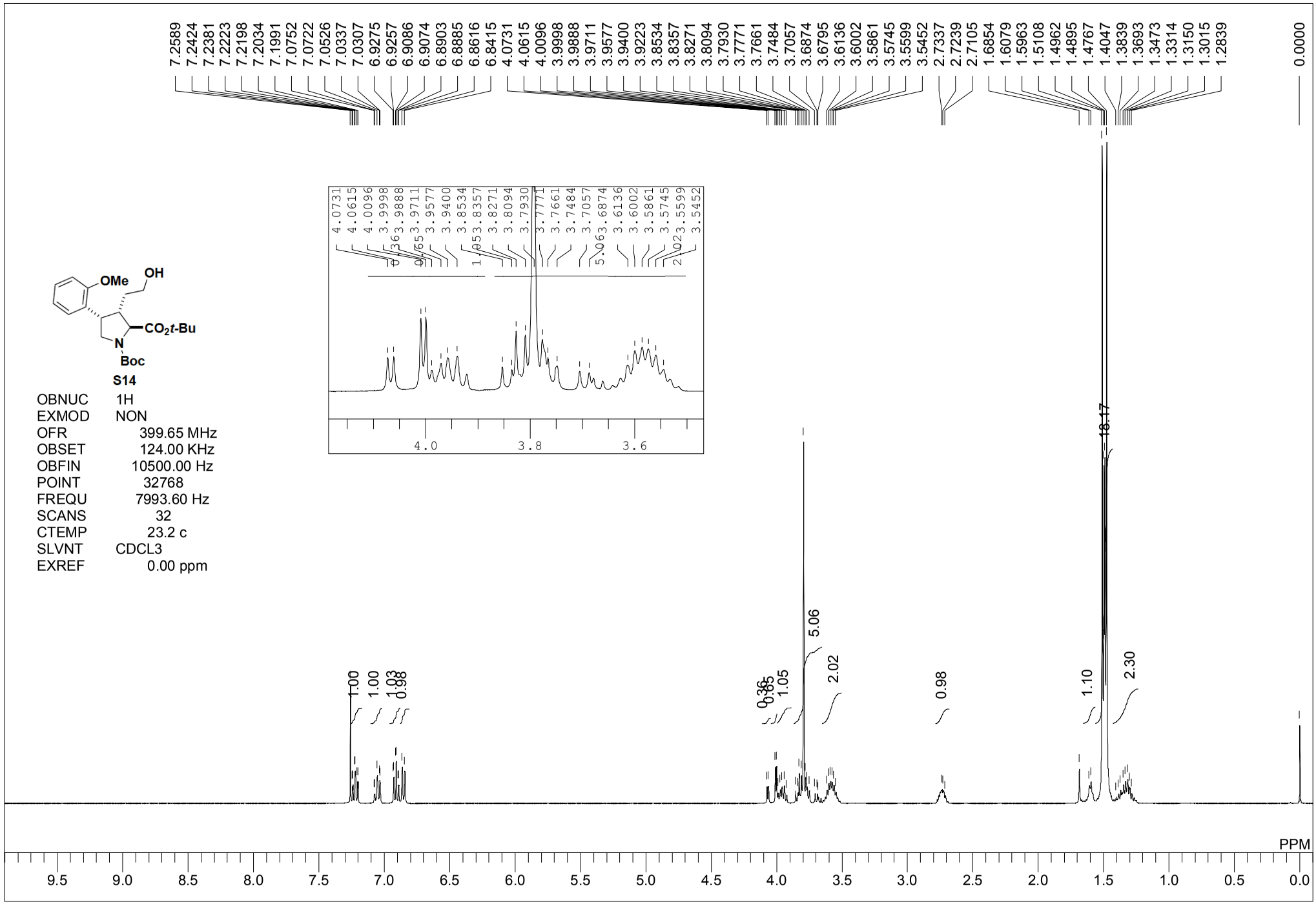

172.5367
157.5401
138.4461
128.0696
127.9452
127.5221
127.4392
127.3065
127.1821
120.1400
109.8879
81.4874
77.3235
77.0000
76.6848
72.4048
69.3358
65.8189
55.2268
48.2842
42.7020
40.8109
28.2612
26.0880
0.1924
OMe
OBn
CO2t-Bu
N
H
S12
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27322.40 Hz
SCANS 700
CTEMP 24.3 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0

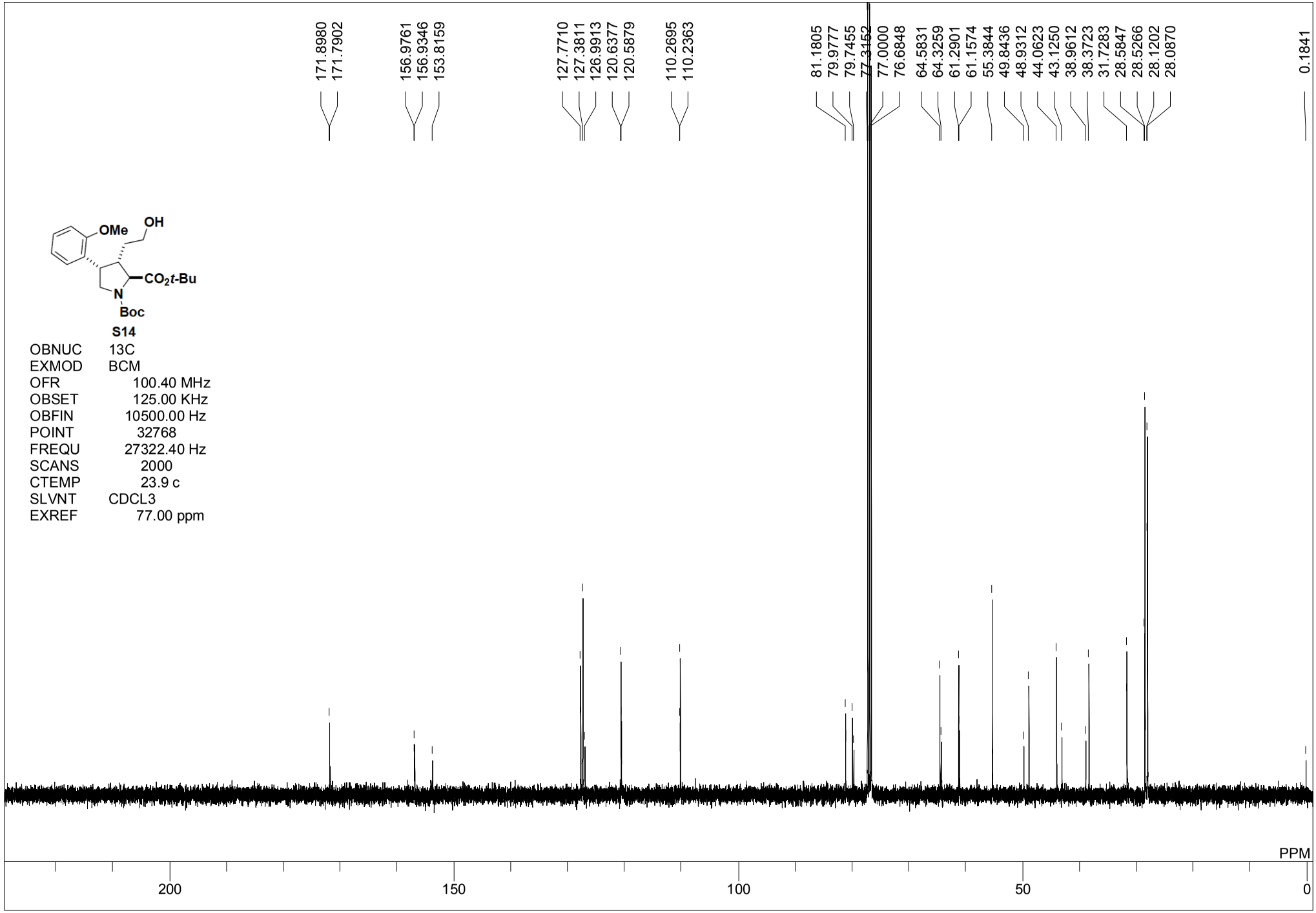

OMe
OBn
CO2t-Bu
N
Boc
S13
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 8000.00 Hz
SCANS 8
CTEMP 23.0 c
SLVNT CDCL3
EXREF 0.00 ppm
7.3044 7.2867 7.2757 7.2561 7.2537 7.2256 7.2097 7.1945 7.1749 6.9123 6.8940 6.8751 6.8036 6.7877 6.7676
4.4433 4.4238 4.4067 4.3786 4.3578 4.2723 3.9151 3.8992 3.8772 3.8687 3.8504 3.8327 3.8156 3.8003 3.7765 3.7679 3.7588 3.7337 3.1872 3.1585 3.1487 3.1420 3.1316 3.1151 3.0846 3.0656 3.0504
1.7209 1.5401 1.5249 1.4937 1.4821 1.4675 1.4412 1.4363
0.0727 0.0000
7.854
0.074
1.114
1.103
2.000
0.095
6.760
0.345
2.876
22.758
PPM
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0


169.9986
169.8741
157.2332
157.1835
154.0813
138.3963
128.5507
128.3433
128.1028
127.7212
127.6880
127.4724
127.3811
127.3065
127.2567
126.9996
126.8669
120.3473
120.2146
109.8713
109.7054
81.3132
79.8782
79.5713
77.3152
77.0000
76.6848
72.5458
69.0787
68.9377
63.9112
63.8117
55.1853
55.1521
49.8602
49.6611
40.9933
40.3381
39.7243
39.1851
28.5847
28.5349
28.2363
28.1202
26.7931
26.4530
0.1924
OMe
OBn
CO2t-Bu
N
Boc
S13
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27322.40 Hz
SCANS 5000
CTEMP 23.4 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0


7.3306
7.3099
7.2952
7.2891
7.2763
7.2592
7.2317
7.2281
7.2097
7.1926
7.1890
7.0674
7.0528
7.0375
6.9129
6.8946
6.8757
6.8348
6.8140
4.4091
4.4018
4.1093
4.0989
4.0867
4.0781
3.9969
3.9786
3.9609
3.9432
3.9267
3.9090
3.8552
3.8296
3.8113
3.7856
3.7612
3.7362
3.7001
3.6800
3.4528
3.4449
3.4284
3.4119
3.3954
3.3722
2.7756
1.6354
1.4962
1.4882
1.4852
1.4675
1.4461
1.4241
1.3362
1.3234
1.3063
1.2879
0.0727
0.0000
OMe
OBn
CO2t-Bu
N
Boc
11
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 8000.00 Hz
SCANS 16
CTEMP 22.4 c
SLVNT CDCL3
EXREF 0.00 ppm
6.859
1.011
1.068
1.047
2.060
1.105
5.353
2.200
1.000
21.937
PPM
8
6
4
2
0


171.7404
171.5745
157.0922
157.0508
154.2223
153.9486
138.3051
128.1193
127.6548
127.4641
127.3811
127.2982
127.2816
127.2235
127.0991
126.7507
120.4303
120.3722
110.1699
110.1202
80.8901
80.8570
79.8201
79.6460
77.3235
77.0000
76.6848
72.8278
68.8050
68.5478
64.7406
64.4752
55.2600
55.2351
49.3211
48.4253
44.0043
42.8181
38.8450
38.3308
28.7091
28.6013
28.5266
28.1865
28.1202
28.0953
OMe
OBn
CO2t-Bu
N
Boc
11
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27322.40 Hz
SCANS 5000
CTEMP 23.2 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0


OMe
OH
CO2t-Bu
N
Boc
S14
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 32
CTEMP 23.2 c
SLVNT CDCL3
EXREF 0.00 ppm
7.2589 7.2424 7.2381 7.2223 7.2198 7.2034 7.1991 7.0752 7.0722 7.0526 7.0337 7.0307 6.9275 6.9257 6.9086 6.9074 6.8903 6.8885 6.8616 6.8415 4.0731 4.0615 4.0096 3.9998 3.9888 3.9711 3.9577 3.9400 3.9223 3.8534 3.8357 3.8271 3.8094 3.7930 3.7771 3.7661 3.7484 3.7057 3.6874 3.6795 3.6136 3.6002 3.5861 3.5745 3.5599 3.5452 2.7337 2.7239 2.7105 1.6854 1.6079 1.5963 1.5108 1.4962 1.4895 1.4767 1.4047 1.3839 1.3693 1.3473 1.3314 1.3150 1.3015 1.2839 0.0000
1.00 1.00 1.03 0.98 0.36 0.85 1.05 5.06 2.02 0.98 1.10 18.17 2.30
4.0 3.8 3.6
PPM
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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153.8159
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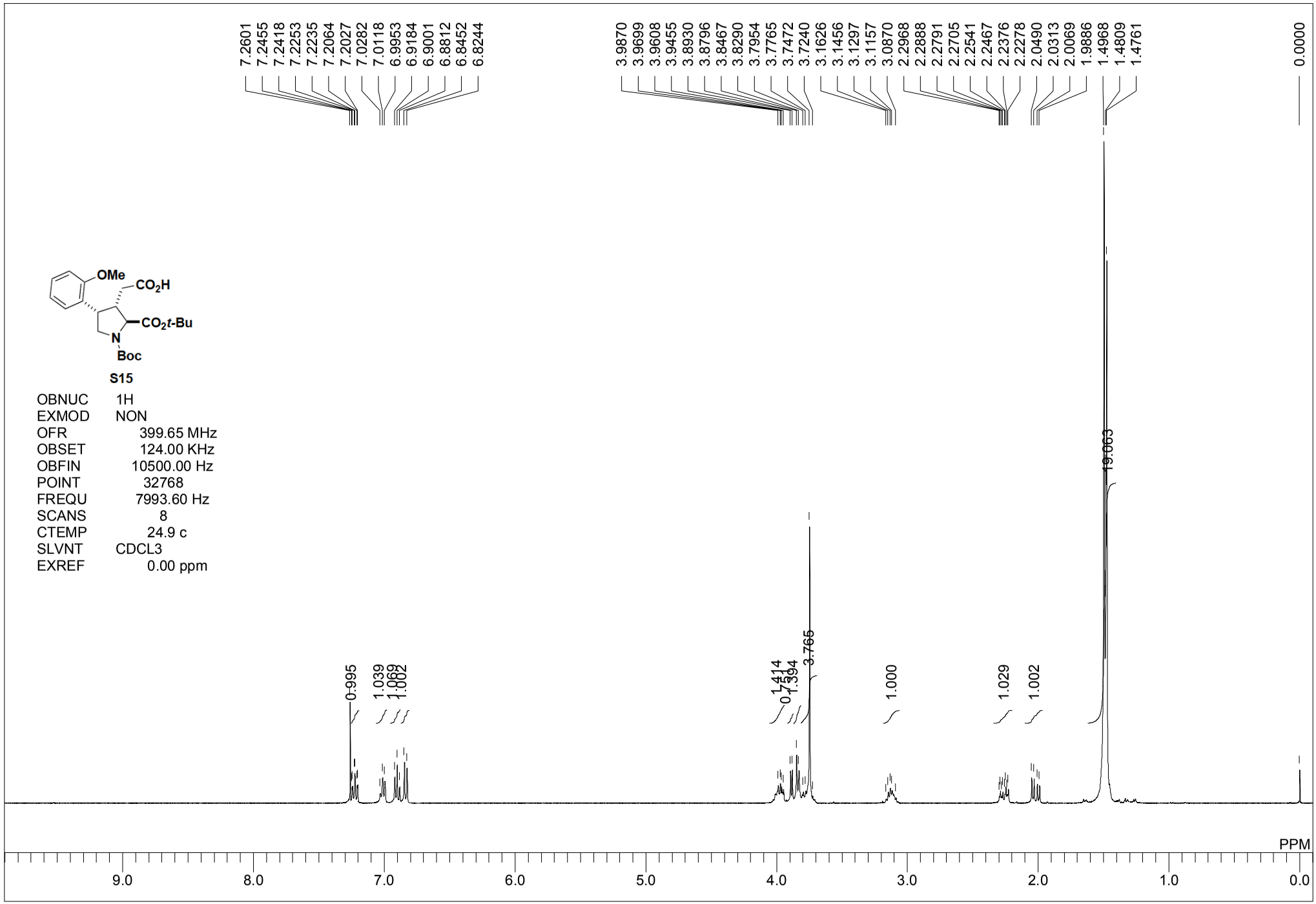
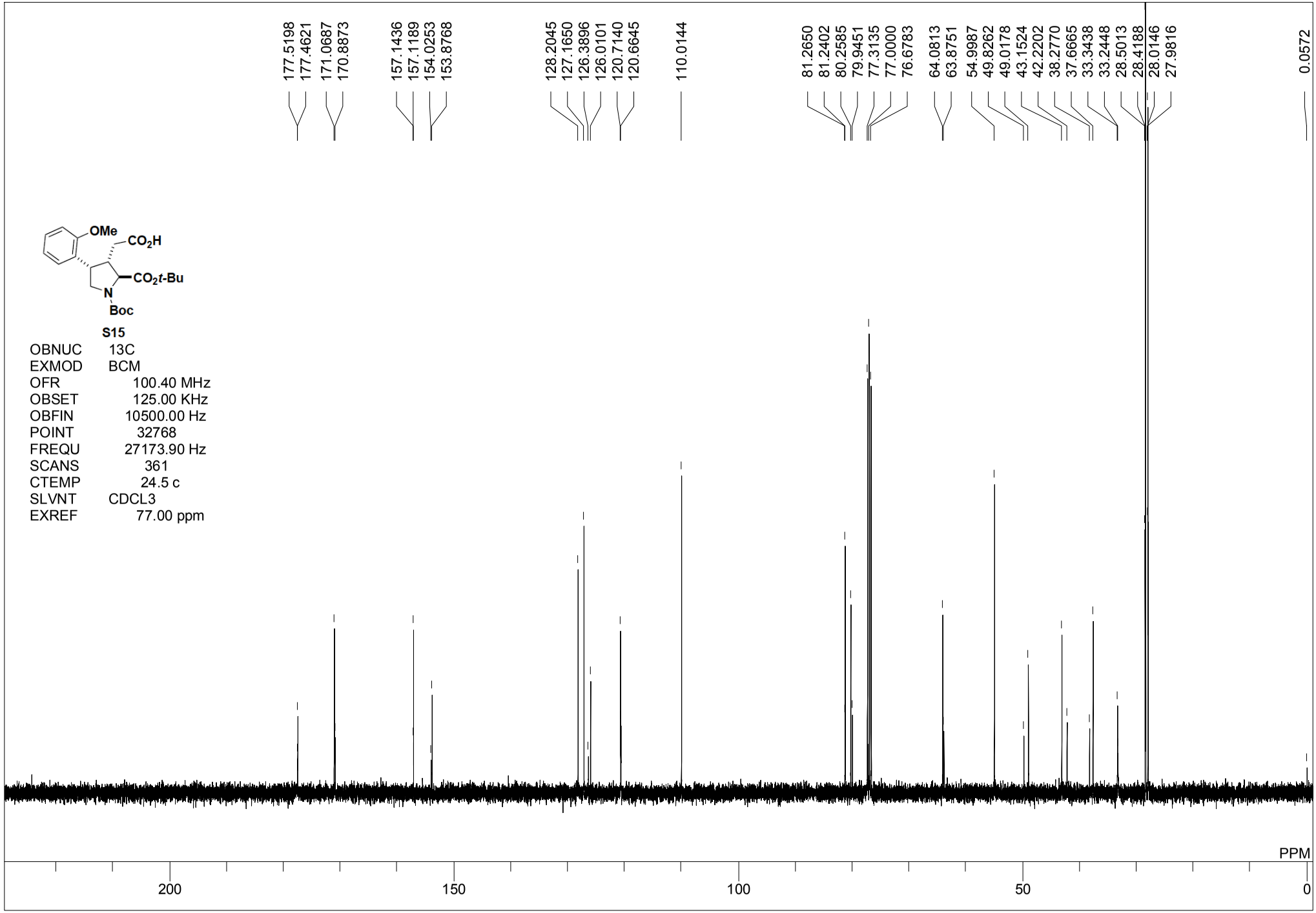
127.3811
126.9913
120.6377
120.5879
110.2695
110.2363
81.1805
79.9777
79.7455
77.3152
77.0000
76.6848
64.5831
64.3259
61.2901
61.1574
55.3844
49.8436
48.9312
44.0623
43.1250
38.9612
38.3723
31.7283
28.5847
28.5266
28.1202
28.0870
0.1841
OMe
OH
CO2t-Bu
N
Boc
S14
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27322.40 Hz
SCANS 2000
CTEMP 23.9 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0


7.2601
7.2455
7.2418
7.2253
7.2235
7.2064
7.2027
7.0282
7.0118
6.9953
6.9184
6.9001
6.8812
6.8452
6.8244
3.9870
3.9699
3.9608
3.9455
3.8930
3.8796
3.8467
3.8290
3.7954
3.7765
3.7472
3.7240
3.1626
3.1456
3.1297
3.1157
3.0870
2.2968
2.2888
2.2791
2.2705
2.2541
2.2467
2.2376
2.2278
2.0490
2.0313
2.0069
1.9886
1.4968
1.4809
1.4761
0.0000
OMe
CO2H
CO2t-Bu
N
Boc
S15
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 7993.60 Hz
SCANS 8
CTEMP 24.9 c
SLVNT CDCL3
EXREF 0.00 ppm
0.995
1.039
1.069
1.082
1.414
0.751
1.394
3.766
1.000
1.029
1.002
19.063
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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177.4621
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170.8873
157.1436
157.1189
154.0253
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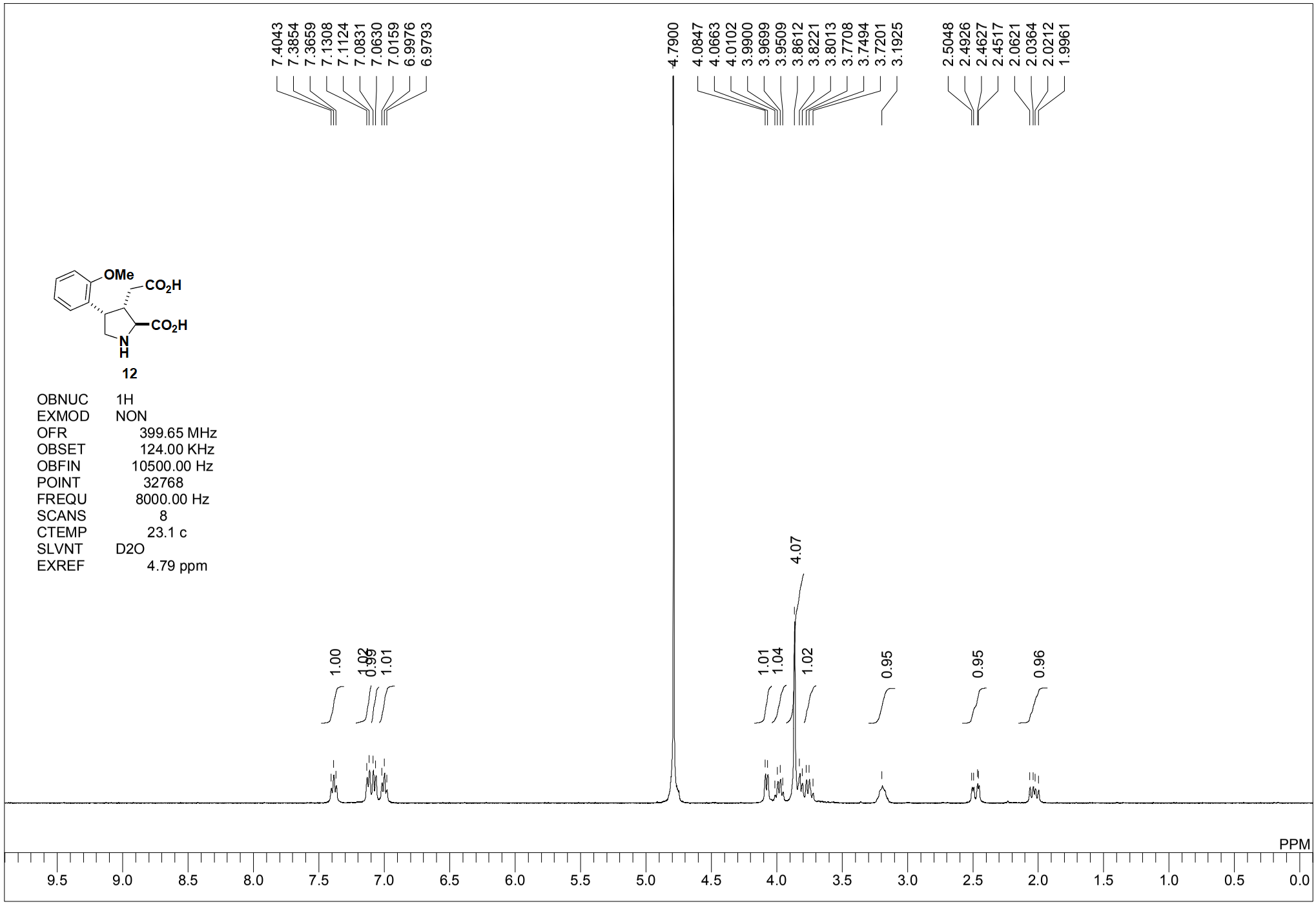
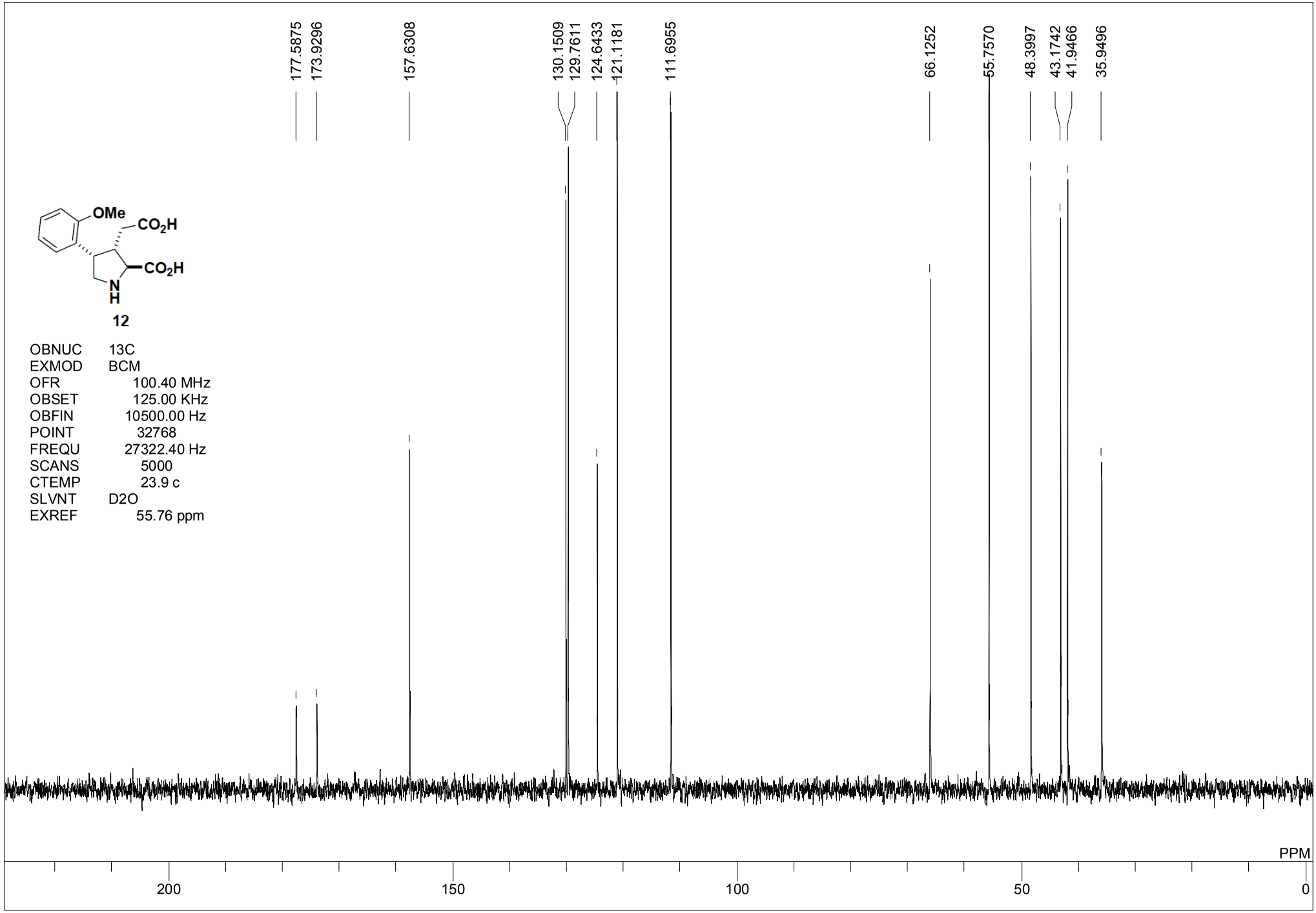
128.2045
127.1650
126.3896
126.0101
120.7140
120.6645
110.0144
81.2650
81.2402
80.2585
79.9451
77.3135
77.0000
76.6783
64.0813
63.8751
54.9987
49.8262
49.0178
43.1524
42.2202
38.2770
37.6665
33.3438
33.2448
28.5013
28.4188
28.0146
27.9816
0.0572
OMe
CO2H
CO2t-Bu
N
Boc
S15
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27173.90 Hz
SCANS 361
CTEMP 24.5 c
SLVNT CDCL3
EXREF 77.00 ppm
PPM
200
150
100
50
0


7.4043
7.3854
7.3659
7.1308
7.1124
7.0831
7.0630
7.0159
6.9976
6.9793
4.7900
4.0847
4.0663
4.0102
3.9900
3.9699
3.9509
3.8612
3.8221
3.8013
3.7708
3.7494
3.7201
3.1925
2.5048
2.4926
2.4627
2.4517
2.0621
2.0364
2.0212
1.9961
OMe
CO2H
CO2H
N
H
12
OBNUC 1H
EXMOD NON
OFR 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 8000.00 Hz
SCANS 8
CTEMP 23.1 c
SLVNT D2O
EXREF 4.79 ppm
1.00
1.02
0.99
1.01
1.01
1.04
4.07
1.02
0.95
0.95
0.96
PPM
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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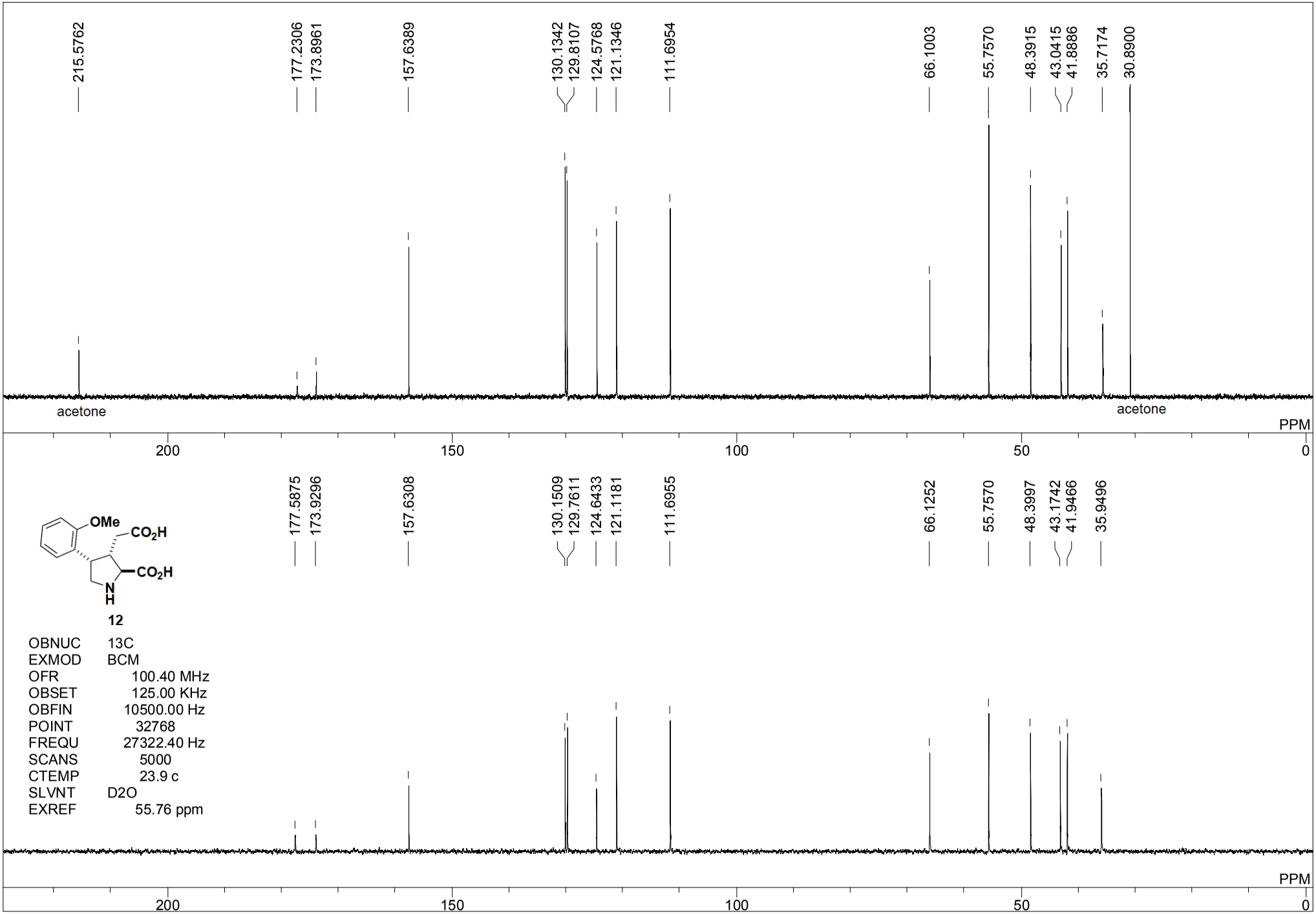
173.9296
157.6308
130.1509
129.7611
124.6433
121.1181
111.6955
66.1252
55.7570
48.3997
43.1742
41.9466
35.9496
OMe
CO2H
CO2H
N
H
12
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27322.40 Hz
SCANS 5000
CTEMP 23.9 c
SLVNT D2O
EXREF 55.76 ppm
PPM
200
150
100
50
0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173.8961
157.6389
130.1342
129.8107
124.5768
121.1346
111.6954
66.1003
55.7570
48.3915
43.0415
41.8886
35.7174
30.8900
acetone
acetone
PPM
200
150
100
50
0
177.5875
173.9296
157.6308
130.1509
129.7611
124.6433
121.1181
111.6955
66.1252
55.7570
48.3997
43.1742
41.9466
35.9496
OMe
CO2H
CO2H
N
H
12
OBNUC 13C
EXMOD BCM
OFR 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27322.40 Hz
SCANS 5000
CTEMP 23.9 c
SLVNT D2O
EXREF 55.76 ppm
PPM
200
150
100
50
0