Organic LETTERS

Supporting Information

Cu-Catalyzed Asymmetric Hydroboration of a-Dehydroamino Acid Derivatives: Facile Synthesis of Chiral b-Hydroxy-a-Amino Acids

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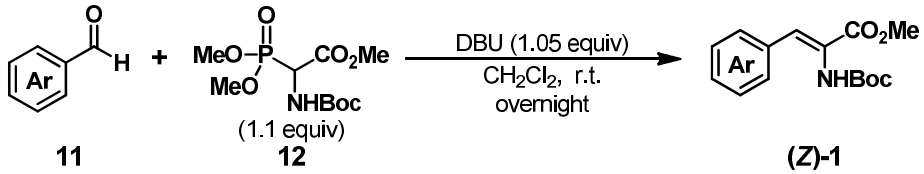
1. GENERAL INFORMATION

All solvents were dried before use following the standard procedures. Unless otherwise indicated, all starting materials purchased from commercial suppliers were used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-400 MHz in the indicated solvents. Chemical shifts are reported in δ (ppm) referenced to an internal TMS standard for ^{1}H NMR and $CDCl_3$ (δ = 77.10 ppm) for ^{13}C NMR. Coupling constants (*J*) are quoted in Hz. Optical rotations were measured on a JASCO P-1030 polarimeter. IR spectra were recorded on Nicolet iN 10 MX. ESI mass spectra were recorded on Agilent1200/G6100A. HRMS of boron-containing compounds is based on ^{10}B.

2. SUBSTRATE PREPARATION

General procedures for the preparation of (*Z*)-β-substituted α-dehydroamino acid substrates[1]

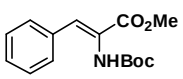


11 **12** **(*Z*)-1**

A well-stirred solution of *N*-Boc-α-phosphonoglycine trimethyl ester (**12**, 400 mg, 1.35 mmol, 1.1 equiv.) and DBU (0.2 mL, 1.05 equiv.) in 2.5 mL DCM was treated with the aldehyde **11** (1.25 mmol). After it was stirred overnight at room temperature, the reaction mixture was diluted with 10 mL sulfuric acid (1 N) and extracted with ethyl acetate (15 mL × 3). The combined organic phases were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate eluent to afford the desired product **(*Z*)-1**.

Notice: Both the (*Z*)-**1** isomer and (*E*)-**1** isomer can be obtained at the same time, but they can be isolated from the flash column chromatography. In our cases, the (*E*)-**1** isomer was minor and appeared in an upper position on TLC plate relative to the (*Z*)-**1** isomer.

(*Z*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-phenylacrylate [(*Z*)-1a][1,2]



(*Z*)-1a

White solid. 322 mg, 93% yield. mp 82.7–83.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.53 (d, J = 7.2 Hz, 2H), 7.38–7.25 (m, 4H), 6.17 (brs, 1H), 3.85 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.07, 152.70, 134.07, 130.17, 129.69, 129.12, 128.46, 124.50, 80.88, 52.50, 20.04; ESI-MS: $[M+Na]^{\oplus}$ 300.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{15}H_{19}NO_4Na^{\oplus}$ 300.1206, found 300.1215; IR (KBr) ν (cm^{-1}) 3327, 3030, 2990, 2971, 2946, 1721, 1701, 1644, 1488, 1368, 1287, 1162, 990, 761, 716.

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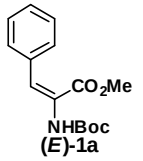
[1] (a) Ulrich S.; Helmut G.; Volker L.; Albrecht L.; Rainer M.; Regina M.; Bernd R. *Synthesis*, **1992**, 487. (b) Yasuno, Y.; Hamada, M.; Yamada, T.; Shinada, T.; Ohfune, Y. *Eur. J. Org. Chem.* **2013**, 1884.

[2] Miki K.; Kohki I.; Rumi K.; Hideki K. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 364.

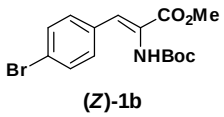
(*E*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-phenylacrylate [(*E*)-1a][1]



(*E*)-1a

Colorless oil. 24 mg, 7% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.51 (brs, 1H), 7.31–7.21 (m, 5H), 6.71 (brs, 1H), 3.63 (s, 3H), 1.50 (s, 9H); ESI-MS: $[M+Na]^{\oplus}$ 300.1.

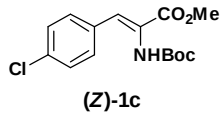
(*Z*)-Methyl 3-(4-bromophenyl)-2-((*tert*-butoxycarbonyl)amino)acrylate [(*Z*)-1b][1]



(*Z*)-1b

White solid. 390 mg, 88% yield. mp 128.3–129.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.48 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 7.19 (s, 1H), 6.24 (brs, 1H), 3.86 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.84, 152.58, 133.11, 131.57, 131.13, 128.60, 124.98, 123.15, 81.11, 52.64, 28.17, 28.06; ESI-MS: $[M-H]^{\Theta}$ 354.2; HRMS (FTMS-ESI): $[M-H]^{\Theta}$ calcd for $C_{15}H_{17}{}^{79}BrNO_4$ 354.0346, found 354.0358; IR (KBr) ν (cm^{-1}) 3325, 2992, 2948, 1724, 1698, 1497, 1483, 1369, 1292, 1193, 1070, 991, 814, 790.

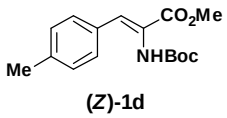
(*Z*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4-chlorophenyl)acrylate [(*Z*)-1c][2]



(*Z*)-1c

White solid. 311 mg, 80% yield. mp 112.2–113.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.46 (d, J = 8.4 Hz, 2H),7.32 (d, J = 8.4 Hz, 2H), 7.21 (s, 1H), 6.25 (brs, 1H), 3.86 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.85, 152.25, 134.79, 132.68, 130.91, 128.61, 128.45, 124.84, 81.09, 52.62, 28.05; ESI-MS: $[M+Na]^{\oplus}$ 334.0; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{15}H_{18}{}^{35}ClNO_4Na^{\oplus}$ 334.0817, found 334.0825; IR (KBr) ν (cm^{-1}) 3327, 2992, 2975, 2947, 1725, 1698, 1485, 1439, 1370, 1292, 1193, 990, 791.

(*Z*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(*p*-tolyl)acrylate [(*Z*)-1d][2]



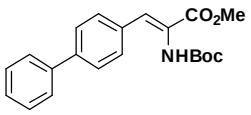
(*Z*)-1d

White solid. 349 mg, 96% yield. mp 87.3–88.7 ^{o}C.^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.44 (d, J = 8.0 Hz, 2H), 7.25 (s, 1H), 7.17 (d, J = 8.0 Hz, 2H), 6.13 (brs, 1H), 3.84 (s, 3H), 2.36 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.11, 152.91, 139.35, 131.04, 130.73, 129.76, 129.09, 123.75, 80.61, 52.28, 27.97, 21.28; ESI-MS: $[M+Na]^{\oplus}$ 314.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{21}NO_4Na^{\oplus}$ 314.1363, found 314.1376; IR (KBr) ν (cm^{-1}) 3339, 2970, 1720, 1707, 1630, 1488, 1343, 1272, 1171, 1136, 988, 819, 776.

[1] Miki K.; Kohki I.; Rumi K.; Hideki K. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 364.

[2] Blake, J. F.; Kallan, N. C.; Xiao, D.; Xu, R.; Bencsik, J. R.; Skelton, N. J.; Spencer, K. L.; Mitchell, I. S.; Woessner, R. D.; Gloor, S. L.; Risoma, T.; Gross, S. D.; Martinson, M.; Morales, T. H.; Vigers, G. P. A.; Brandhuber, B. J. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 5607.

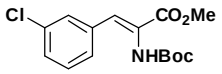
(*Z*)-Methyl 3-([1,1'-biphenyl]-4-yl)-2-((*tert*-butoxycarbonyl)amino)acrylate [(*Z*)-1e][1]



(*Z*)-1e

White solid. 348 mg, 79% yield. mp 121.2–121.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.63–7.59 (m, 6H), 7.46–7.42 (m, 2H), 7.38–7.36 (m, 1H), 7.30 (s, 1H), 6.24 (brs, 1H), 3.86 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.13, 153.08, 141.78, 140.24, 133.10, 130.35, 130.06, 128.88, 127.73, 127.05, 127.00, 124.54, 80.94, 52.54, 28.14; ESI-MS: $[M+Na]^{\oplus}$ 376.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{23}NO_4Na^{\oplus}$ 376.1519, found 376.1528; IR (KBr) ν (cm^{-1}) 3332, 2977, 2948, 1724, 1706, 1636, 1508, 1366. 1263, 1161, 1027, 836, 766.

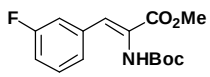
(*Z*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(3-chlorophenyl)acrylate [(*Z*)-1f][1]



(*Z*)-1f

White solid. 357 mg, 92% yield. mp 100.5–101.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.52 (s, 1H), 7.37 (d, J = 4.4 Hz, 1H), 7.28 (d, J = 5.6 Hz, 2H), 7.19 (s, 1H), 6.30 (brs, 1H), 3.66 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.72, 152.43, 136.03, 134.22, 129.55, 129.18, 128.88, 128.05, 127.90, 125.36, 81.09, 52.63, 28.01; ESI-MS: $[M+Na]^{\oplus}$ 334.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{15}H_{18}{}^{35}ClNO_4Na^{\oplus}$ 334.0817, found 334.0815; IR (KBr) ν (cm^{-1}) 3230, 3114, 3060, 2993, 2970, 1709, 1636, 1453, 1365, 1263, 1144, 1051, 994, 779, 683.

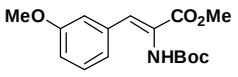
(*Z*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(3-fluorophenyl)acrylate [(*Z*)-1g][2]



(*Z*)-1g

White solid. 258 mg, 70% yield. mp 84.5–86.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.33–7.21 (m, 4H), 7.01 (t, J = 8.0 Hz, 1H), 6.27 (brs, 1H), 3.86 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.80, 162.72 (d, J_{CF} = 244.0 Hz), 152.46, 136.44 (d, J_{CF} = 8.7 Hz), 129.88 (d, J_{CF} = 7.9 Hz), 128.30 (d, J_{CF} = 2.3 Hz), 125.62 (d, J_{CF} = 3.2 Hz), 116.08 (d, J_{CF} = 4.0 Hz), 115.88, 115.84, 81.29, 52.71, 28.08; ESI-MS: $[M+Na]^{\oplus}$ 318.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{15}H_{18}FNO_4Na^{\oplus}$ 318.1112, found 318.1115; IR (KBr) ν (cm^{-1}) 3212, 3101, 3005, 2990, 2950, 1732, 1698, 1644, 1440, 1358, 1285, 1155, 955, 783.

(*Z*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(3-methoxyphenyl)acrylate [(*Z*)-1h]



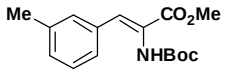
(*Z*)-1h

White solid. 357 mg, 93% yield. mp 85.7–86.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.30–7.26 (m, 2H), 7.13–7.09 (m, 2H), 6.89–6.86 (m, 1H), 6.14 (brs, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.99, 159.43, 153.00, 135.22, 130.14, 129.38, 125.12, 122.24, 115.07, 114.64, 80.75, 55.04, 52.43, 28.01; ESI-MS: $[M+Na]^{\oplus}$ 330.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{21}NO_5Na^{\oplus}$ 330.1312, found 330.1304; IR (KBr) ν (cm^{-1}) 3213, 3106, 2978, 2933, 1727, 1692, 1596, 1496, 1360, 1271, 1166, 988, 783.

[1] Blake, J. F.; Kallan, N. C.; Xiao, D.; Xu, R.; Bencsik, J. R.; Skelton, N. J.; Spencer, K. L.; Mitchell, I. S.; Woessner, R. D.; Gloor, S. L.; Risoma, T.; Gross, S. D.; Martinson, M.; Morales, T. H.; Vigers, G. P. A.; Brandhuber, B. J. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 5607.

[2] Krause, H. W.; Kreuzfeld, H.-J.; Schmidt, U.; Dobler, Ch.; Michalik, M.; Taudien, S.; Fischer, Ch. *Chirality* **1996**, *8*, 173.

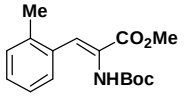
(*Z*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(*m*-tolyl)acrylate [(*Z*)-1i]



(*Z*)-1i

White solid. 254 mg, 70% yield. mp 89.0–90.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35–7.33 (m, 2H), 7.26–7.23 (m, 2H), 7.13 (d, J = 7.2 Hz, 1H), 6.16 (brs, 1H), 3.85 (s, 3H), 2.34 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.11, 152.92, 137.90, 133.97, 130.46, 130.39, 129.98, 128.32, 126.89, 124.38, 80.74, 52.44, 28.05, 21.33; ESI-MS: $[M+Na]^{\oplus}$ 314.0; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{21}NO_4Na^{\oplus}$ 314.1363, found 314.1374; IR (KBr) ν (cm^{-1}) 3232, 3111, 2989, 2941, 1718, 1697, 1636, 1432, 1366, 1275, 1231, 1159, 776.

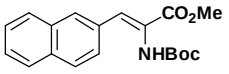
(*Z*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(*o*-tolyl)acrylate [(*Z*)-1j]



(*Z*)-1j

White solid. 320 mg, 88% yield. mp 89.3–91.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.47 (d, J = 7.2 Hz, 1H), 7.25–7.16 (m, 4H), 6.07 (brs, 1H), 3.86 (s, 3H), 2.33 (s, 3H), 2.21 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.84, 152.79, 137.10, 133.15, 130.25, 128.61, 127.98, 127.12, 125.90, 125.72, 80.62, 52.40, 27.90, 19.89; ESI-MS: $[M+Na]^{\oplus}$ 314.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{21}NO_4Na^{\oplus}$ 314.1363, found 314.1364; IR (KBr) ν (cm^{-1}) 3217, 3120, 2986, 2940, 1710, 1642, 1366, 1263, 1147, 1054, 994, 755.

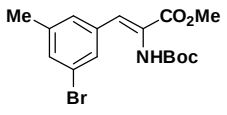
(*Z*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(naphthalen-2-yl)acrylate [(*Z*)-1k][1]



(*Z*)-1k

White solid. 298 mg, 73% yield. mp 135.1–136.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (s, 1H), 7.83–7.79 (m, 3H), 7.70 (d, J = 8.8 Hz, 1H), 7.50–7.44 (m, 3H), 6.31 (brs, 1H), 3.88 (s, 3H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.15, 152.89, 133.45, 133.11, 131.73, 130.38, 128.47, 127.94, 127.60, 126.96, 126.38, 126.29, 124.60, 124.50, 80.90, 52.55, 28.10; ESI-MS: $[M+Na]^{\oplus}$ 350.0; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{19}H_{21}NO_4Na^{\oplus}$ 350.1363, found 350.1367; IR (KBr) ν (cm^{-1}) 3312, 3018, 2970, 1736, 1703, 1638, 1526, 1439, 1348, 1253, 1155, 1047, 917, 789.

(*Z*)-Methyl 3-(3-bromo-5-methylphenyl)-2-((*tert*-butoxycarbonyl)amino)acrylate [(*Z*)-1m]

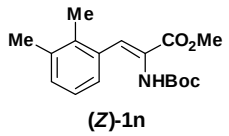


(*Z*)-1m

White solid. 332 mg, 72% yield. mp 140.1–140.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.49 (s, 1H), 7.26 (s, 1H), 7.21 (s, 1H), 7.15 (s, 1H), 6.34 (brs, 1H), 3.85 (s, 3H), 2.31 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.70, 152.22, 139.80, 136.00, 132.45, 129.17, 128.86, 128.09, 124.89, 122.15, 81.04, 52.63, 28.03, 21.01; ESI-MS: $[M+Na]^{\oplus}$ 391.9; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{20}{}^{79}BrNO_4Na^{\oplus}$ 392.0468, found 392.0469; IR (KBr) ν (cm^{-1}) 3223, 3116, 2972, 2943, 1702, 1635, 1365, 1280, 1158, 1050, 777, 684.

[1] Krause, H. W.; Kreuzfeld, H.-J.; Schmidt, U.; Dobler, Ch.; Michalik, M.; Taudien, S.; Fischer, Ch. *Chirality* **1996**, *8*, 173.

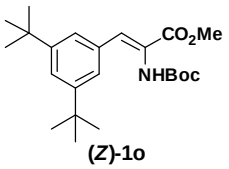
(*Z*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(2,3-dimethylphenyl)acrylate [(*Z*)-1n]



(*Z*)-1n

Colorless oil. 370 mg, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.26–7.23 (m, 2H), 7.12–7.06 (m, 2H), 6.00 (brs, 1H), 3.86 (s, 3H), 2.29 (s, 3H), 2.21 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.33, 152.85, 137.00, 135.41, 133.19, 130.11, 128.14, 126.40, 125.93, 125.39, 80.56, 52.36, 27.94, 20.38, 16.05; ESI-MS: $[M+Na]^{\oplus}$ 328.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{23}NO_4Na^{\oplus}$ 328.1519, found 328.1515; IR (KBr) ν (cm^{-1}) 3334, 2978, 2951, 1712, 1644, 1457, 1367, 1240, 1163, 1048, 772.

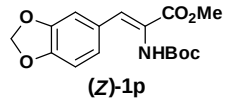
(*Z*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(3,5-*di*-*tert*-butylphenyl)acrylate [(*Z*)-1o]



(*Z*)-1o

White solid. 423 mg, 87% yield. mp 127.5–128.2 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.40 (s, 3H), 7.29 (s, 1H), 6.03 (brs, 1H), 3.85 (s, 3H), 1.42 (s, 9H), 1.32 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.04, 153.22, 150.77, 133.05, 132.20, 124.44, 123.98, 123.53, 80.43, 52.28, 34.70, 31.27, 28.07; ESI-MS: $[M+Na]^{\oplus}$ 412.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{23}H_{35}NO_4Na^{\oplus}$ 412.2458, found 412.2466; IR (KBr) ν (cm^{-1}) 3218, 3100, 2965, 1731, .1699, 1360, 1250, 1164, 1056, 994, 777.

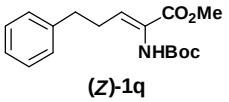
(*Z*)-Methyl 3-(benzo[d][1,3]dioxol-5-yl)-2-((*tert*-butoxycarbonyl)amino)acrylate [(*Z*)-1p]



(*Z*)-1p

White solid. 361 mg, 90% yield. mp 94.7–95.9 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.22 (s, 1H), 7.15 (s, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 6.10 (brs, 1H), 5.98 (s, 2H), 3.83 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.18, 152.88, 148.45, 147.76, 131.14, 128.02, 125.70, 122.68, 109.06, 108.20, 101.35, 80.72, 52.35, 28.06; ESI-MS: $[M+Na]^{\oplus}$ 344.0; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{19}NO_6Na^{\oplus}$ 344.1105, found 344.1108; IR (KBr) ν (cm^{-1}) 3311, 2983, 2947, 2905, 2846, 1730, 1697, 1485, 1347, 1290, 1227, 1165, 1038, 940, 790.

(*Z*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-5-phenylpent-2-enoate [(*Z*)-1q][1]



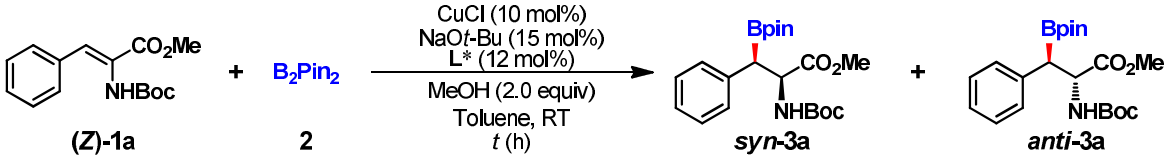
(*Z*)-1q

White solid. 343 mg, 90% yield. mp 54.2–56 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31–7.26 (m, 2H), 7.22–7.19 (m, 3H), 6.58 (t, J = 7.2 Hz, 1H), 5.85 (brs, 1H), 3.76 (s, 3H), 2.79 (t, J = 7.6 Hz, 2H), 2.53 (q, J = 7.6 Hz, 2H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 165.33, 153.31, 141.08, 135.49, 128.44, 128.36, 126.09, 116.47, 80.44, 52.24, 34.24, 30.06, 28.17; ESI-MS: $[M+Na]^{\oplus}$ 328.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{23}NO_4Na^{\oplus}$ 328.1519, found 328.1529; IR (KBr) ν (cm^{-1}) 3241, 3118, 2977, 2928, 1706, 1662, 1497, 1366, 1267, 1162, 1049, 778, 699.

[1] Miki K.; Kohki I.; Rumi K.; Hideki K. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 364.

3. Chiral Ligands Investigation

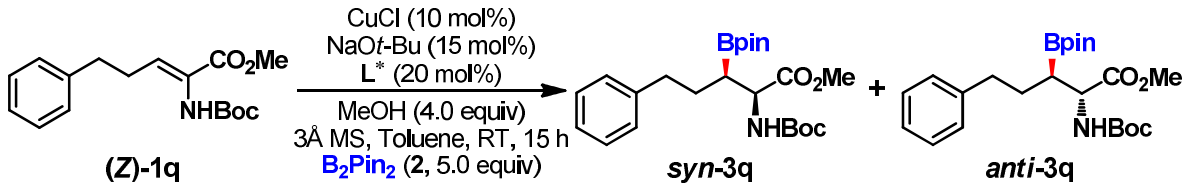
Table S1. Evaluation of Chiral Ligands for Cu-Catalyzed Asymmetric Hydroboration of a-Dehydroamino Acid Derivate (*Z*)-1a.[a]



Entry	L*	**2** (*x* mol%)	*t* (h)	Yield (%)[b]	*syn*-**3a** (%)[c]	*anti*-**3a** (%)[d]	*ee* (*syn*-**3a**)[e]	*ee* (*anti*-**3a**)[e]
1	(*R*,S_p)-Josiphos, **L1**	1.1	17	N.R.[j]	–	–	–	–
2	(2R,3R)-3-QuinoxP*, **L2**	1.1	12	51	20	31	60	62
3[f]	(2S,3S)-3-NHC, **L3**	1.1	17	74	67	7	9	–10
4	(*R*)-MonoPhos, **L4**	1.1	18	30	20	10	–22	–33
5	(*R*)-iPr-PHOX, **L5**	1.1	17	64	20	44	–50	–40
6	(*S*,S_p)-ip-FOXAP, **L6**	1.1	15	39	16	22	96	95
7[g]	(*S*,S_p)-ip-FOXAP, **L6**	2.0	15	49	22	27	95	93
8[g,h,i]	(*S*,S_p)-ip-FOXAP, **L6**	4.0	13	91	50	41	95	95
9[g,h,i]	(*S*,S_p)-ip-FOXAP, **L6**	5.0	12	>99	54	46	97	96
10	((2*R*,3*R*)-3-Ph-BPE), **L7**	1.1	17	20	20	0	0	–
11	(*R*)-BINAP, **L8**	1.1	17	N.R.[j]	–	–	–	–
12	(*R*)-MeO-BIPHEP, **L9**	1.1	40	N.R.[j]	–	–	–	–
13	(*R*)-Segphos, **L10**	1.1	40	N.R.[j]	–	–	–	–
14	(*S*)-P-PHOS, **L11**	1.1	40	trace	–	–	–	–
15	(2*R*,3*R*)-3-iPr-Duphos, **L12**	1.1	17	N.R.[j]	–	–	–	–
16	(*S*,*S*,*R*,*R*)-TangPhos, **L13**	1.1	17	N.R.[j]	–	–	–	–
17	**L14**	1.1	19	52	27	25	9	–30
18	(*R*)-SIPHOS-PE, **L15**	1.1	9	57	25	32	8	0
19[f]	(2*R*,3*R*)-3-NHC, **L16**	1.1	21	62	22	40	2	5
20	(*S*)-Ph-PHOX, **L17**	1.1	16	70	20	50	58	58
21	**L18**	1.1	15	65	30	35	2	3
22	**L19**	1.1	9	N.R.[j]	–	–	–	–
23	(2*R*,3*R*)-3-PhBOX, **L20**	1.1	9	N.R.[j]	–	–	–	–

[a]Reactions were performed under argon atmosphere. [b]Combined yield of *syn*-**3a** and *anti*-**3a**. [c]Yield of the isolated product *syn*-**3a**. [d]Yield of the isolated product *anti*-**3a**. [e]Determined by HPLC analysis using a chiral stationary phase. [f]NaO*t*-Bu (25 mol%) was used. [g]MeOH (4.0 equiv) was used. [h]Molecular sieve (3Å) was added. [i]**L6** (20 mol%) was used. [j]No reaction. B_2Pin_2 = bis(pinacolato)diboron, Boc = *tert*-butoxycarbonyl.

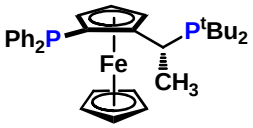
Table S2. Evaluation of Chiral Ligands for Cu-Catalyzed Asymmetric Hydroboration of a-Dehydroamino Acid Derivate (*Z*)-1q.[a]



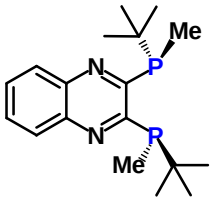
Entry	**L***	*t* (h)	Yield (%)[b]	*syn*-**3q** (%)[c]	*anti*-**3q** (%)[d]	*ee* (*syn*-**3q**)[e]	*ee* (*anti*-**3q**)[e]
1	(2R,3R)-3-QuinoxP*, **L2**	11	>99	38	62	45	–
2[f]	(2S,3S)-3-NHC, **L3**	16	>99	57	43	–11	–
3	(*R*)-MonoPhos, **L4**	13	>99	53	47	–36	–
4	(*R*)-iPr-PHOX, **L5**	13	94	43	51	–17	–
5	(S,S_p)-ip-FOXAP, **L6**	11	84	33	51	26	29
6	((2R,3R)-3-Ph-BPE), **L7**	15	>99	50	50	–82	–92
7	(*R*)-BINAP, **L8**	17	trace	–	–	–	–
8	(*S*)-P-PHOS, **L11**	12	trace	–	–	–	–
9	(2R,3R)-3-iPr-Duphos, **L12**	14	>99	38	62	–63	–
10	**L14**	15	>99	49	51	–22	–
11	(*S*)-Ph-PHOX, **L17**	10	>99	32	68	42	–
12	(*S*,*R*,*R*)-**L21**	15	trace	–	–	–	–
13	(1*R*,1'*R*,2*S*,2'*S*)-DuanPhos, **L22**	15	83	23	60	35	–
14	(2S,3S)-3-DIPAMP, **L23**	20	>99	45	55	5	–
15	**L24**	22	78	55	23	–57	–

[a]Reactions were performed under argon atmosphere. [b]Combined yield of *syn*-**3q** and *anti*-**3q**. [c]Yield of the isolated product *syn*-**3q**. [d]Yield of the isolated product *anti*-**3q**. [e]Determined by HPLC analysis using a chiral stationary phase. [f]NaO*t*-Bu (25 mol%) was used. B_2Pin_2 = bis(pinacolato)diboron, Boc = *tert*-butoxycarbonyl.

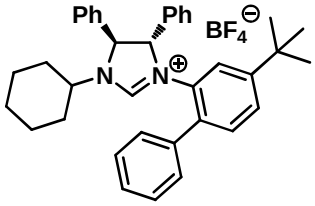
Chemical Structures of Various Chiral Ligands.



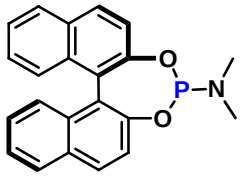
(R,S_p)-Josiphos, **L1**



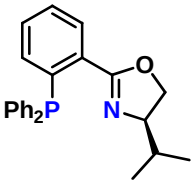
(R,R)-QuinoxP*, **L2**



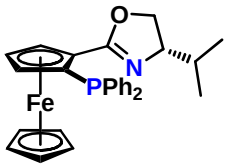
(S,S)-NHC, **L3**



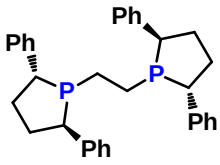
(R)-MonoPhos, **L4**



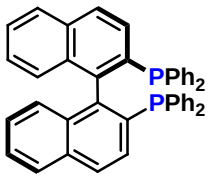
(R)-*i*Pr-PHOX, **L5**



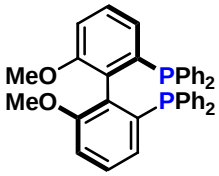
(S,S_p)-ip-FOXAP, **L6**



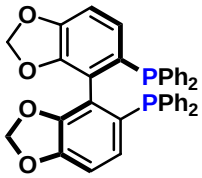
((R,R)-Ph-BPE), **L7**



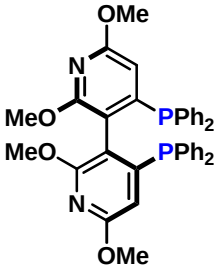
(R)-BINAP, **L8**



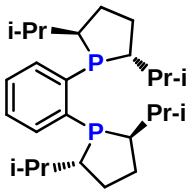
(R)-MeO-BIPHEP, **L9**



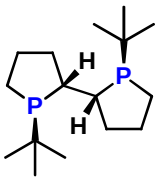
(R)-Segphos, **L10**



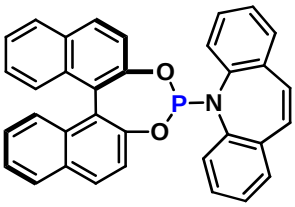
(S)-P-PHOS, **L11**



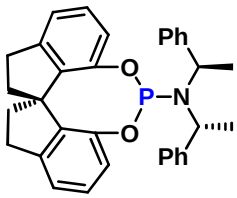
(R,R)-*i*Pr-Duphos, **L12**



(S,S,R,R)-TangPhos, **L13**

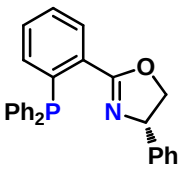


L14

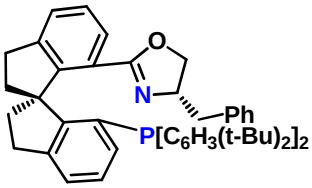


(R)-SIPHOS-PE, **L15**

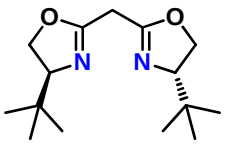
L16



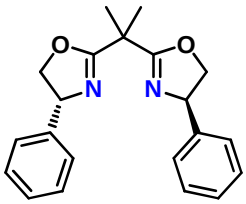
(S)-Ph-PHOX, **L17**



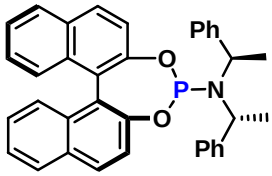
L18



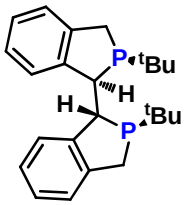
L19



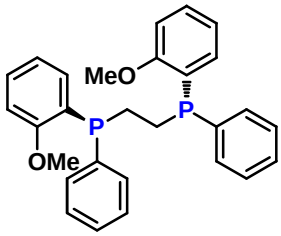
(R,R)-PhBOX, **L20**



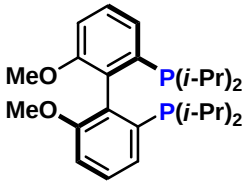
(S,R,R)-**L21**



(1R,1'R,2S,2'S)-DuanPhos, **L22**

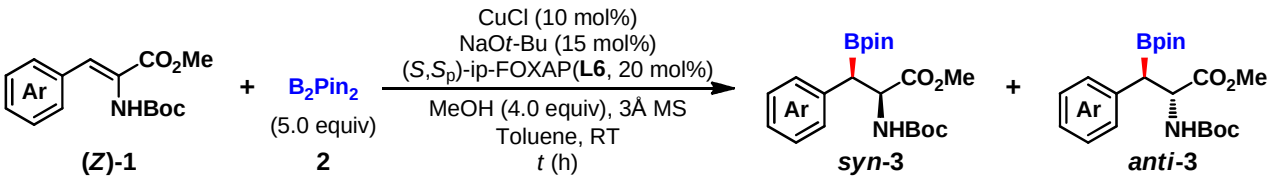


(S,S)-DIPAMP, **L23**



L24

4. SCOPE OF THE SUBSTRATES



(*Z*)-**1** **2** ***syn*-3** ***anti*-3**

(*Z*)-**1a** (Ar = C_6H_5-) (*Z*)-**1b** (Ar = 4-Br-C_6H_4-) (*Z*)-**1c** (Ar = 4-Cl-C_6H_4-) (*Z*)-**1d** (Ar = 4-Me-C_6H_4-)
(*Z*)-**1e** (Ar = 4-Ph-C_6H_4-) (*Z*)-**1f** (Ar = 3-Cl-C_6H_4-) (*Z*)-**1g** (Ar = 3-F-C_6H_4-) (*Z*)-**1h** (Ar = 3-MeO-C_6H_4-)
(*Z*)-**1i** (Ar = 3-Me-C_6H_4-) (*Z*)-**1j** (Ar = 2-Me-C_6H_4-) (*Z*)-**1k** (Ar = 2-Naphenthyl-) (*Z*)-**1m** (Ar = 3-Br-5-Me-C_6H_3-)
(*Z*)-**1n** (Ar = 2,3-(Me)$_2$-C_6H_3-) (*Z*)-**1o** (Ar = 3,5-(*t*-Bu)$_2$-C_6H_3-) (*Z*)-**1p** (Ar = 3,4-(-OCH_2O-)-C_6H_3-)

GENERAL PROCEDURE for 3a to 3p: A dried Schlenk flask was charged with CuCl (1.0 mg, 0.01 mmol), ligand (*S*,*S*$_P$)-ip-FOXAP (**L6**, 10 mg, 0.02 mmol), B_2Pin_2 (**2**, 128 mg, 0.50 mmol), NaO*t*Bu (1.5 mg, 0.015 mmol) , 3Å molecular sieves (20 mg) and anhydrous toluene (0.5 mL) under argon atmosphere. After the mixture was stirred at room temperature for 30 min, a solution of substrate **1** (0.10 mmol) in anhydrous toluene (0.5 mL) was added, followed by anhydrous MeOH (16 μL, 0.40 mmol). The resulting mixture was stirred at room temperature for 1 to 24 hours. Then the reaction mixture was quenched with water (5 mL), extracted with EtOAc (15 mL × 3) and washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash silica gel (300-400 mesh) chromatography to afford the desired products *syn*-**3** and *anti*-**3**.

(Notice: The hydroboration products were unstable, especially for *syn*-**3**, so the purification operation should be quick).

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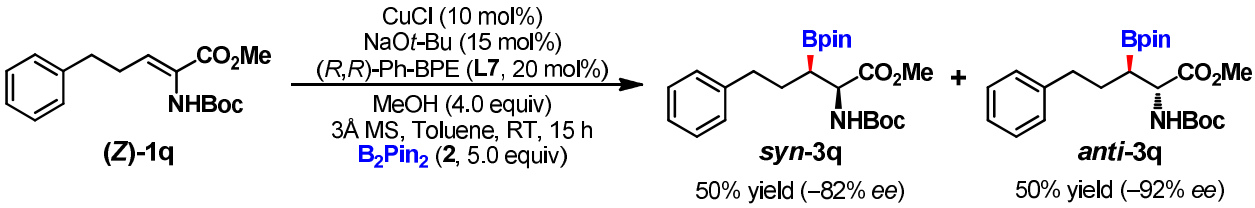
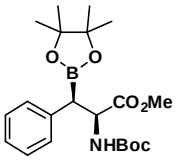


(*Z*)-**1q** ***syn*-3q** ***anti*-3q**

50% yield (–82% *ee*) 50% yield (–92% *ee*)

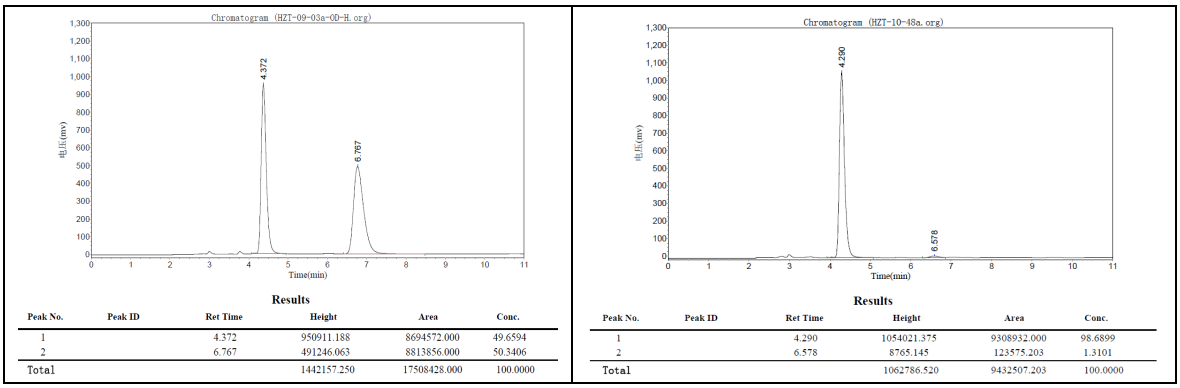
PROCEDURE for 3q: A dried Schlenk flask was charged with CuCl (1.0 mg, 0.01 mmol), ligand (2*R*,3*R*)-3-Ph-BPE (**L7**, 10 mg, 0.02 mmol), B_2Pin_2 (**2**, 128 mg, 0.50 mmol), NaO*t*Bu (1.5 mg, 0.015 mmol) , 3Å molecular sieves (20 mg) and anhydrous toluene (0.5 mL) under argon atmosphere. After the mixture was stirred at room temperature for 30 min, a solution of substrate (*Z*)-**1q** (31 mg, 0.10 mmol) in anhydrous toluene (0.5 mL) was added, followed by anhydrous MeOH (16 μL, 0.40 mmol). The resulting mixture was stirred at room temperature for 15 hours. Then the reaction mixture was quenched with water (5 mL), extracted with EtOAc (15 mL × 3) and washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash silica gel (300-400 mesh) chromatography to afford the desired products *syn*-**3q** and *anti*-**3q**.

(2*S*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*syn*-3a)

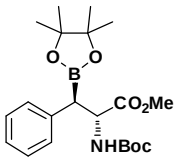


***syn*-3a**

Colorless oil. 21.9 mg, 54% yield. $[\alpha]_D^{25.7}$ +17.7 (*c* 1.11, $CHCl_3$) for 97% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.26–7.17 (m, 5H), 5.35 (brs, 1H), 4.73 (brs, 1H), 3.64 (s, 3H), 2.91 (d, *J* = 5.2 Hz, 1H), 1.40 (s, 9H), 1.26 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.96, 155.30, 137.77, 129.68, 128.51, 126.52, 84.12, 79.70, 56.34, 52.09, 28.41, 24.87, 24.59; ESI-MS: $[M+Na]^{\oplus}$ 428.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{32}{}^{10}BNO_6Na^{\oplus}$ 427.2251, found 427.2258; IR (KBr) ν (cm^{-1}) 3432, 3081, 2981, 2952, 2930, 1741, 1698, 1380, 1259, 1138, 853, 774, 700; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 4.3 min (2*S*,3*R*)-**3a**, 6.6 min (2*R*,3*S*)-**3a**.

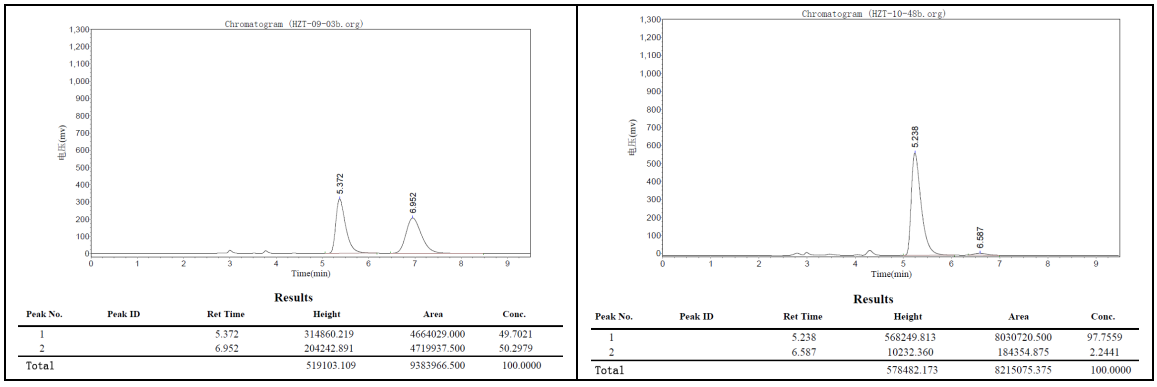


(2*R*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*anti*-3a)

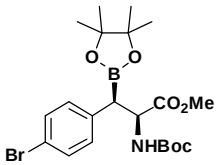


***anti*-3a**

Colorless oil. 18.6 mg, 46% yield. $[\alpha]_D^{25.7}$ +9.8 (*c* 0.94, $CHCl_3$) for 96% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.28–7.18 (m, 5H), 4.79 (brs, 2H), 3.71 (s, 3H), 2.80 (brs, 1H), 1.34 (s, 9H), 1.21 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.09, 155.35, 137.61, 129.60, 128.52, 126.42, 83.90, 79.56, 65.27, 52.21, 28.31, 24.66, 24.61; (The carbon directly attached to the boron atom was not detected, likely due to quadrupole relaxation.) ESI-MS: $[M+Na]^{\oplus}$ 428.3; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{32}{}^{10}BNO_6Na^{\oplus}$ 427.2251, found 427.2266; IR (KBr) ν (cm^{-1}) 3370, 2979, 2927, 2852, 1738, 1691, 1522, 1367, 1320, 1143, 969, 851, 701; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 5.2 min (2*R*, 3*R*)-**3a**, 6.6 min (2*S*,3*S*)-**3a**.

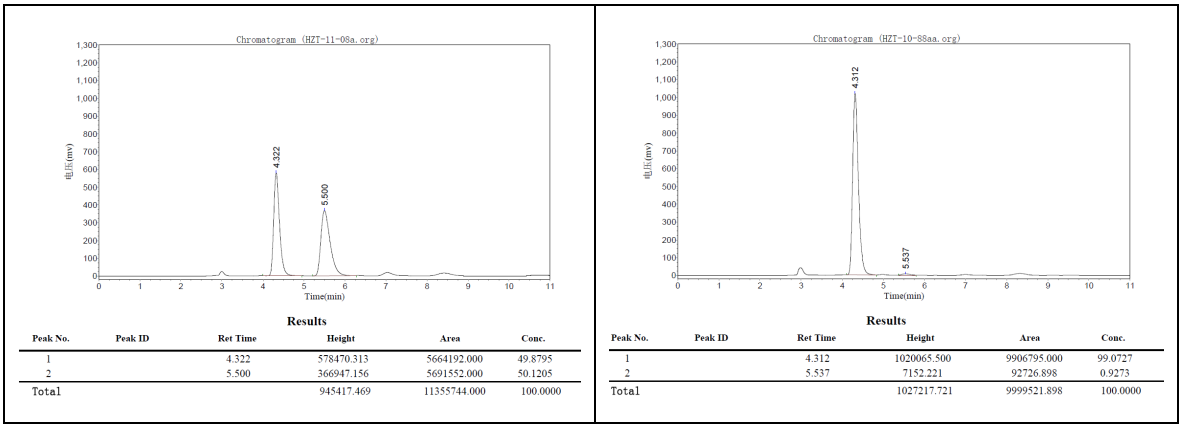


(2*S*,3*R*)-Methyl 3-(4-bromophenyl)-2-((*tert*-butoxycarbonyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*syn*-3b)



syn-3b

Colorless oil. 20.3 mg, 42% yield. $[\alpha]_D^{25.7}$ +16.7 (*c* 1.02, $CHCl_3$) for 98% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.38 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 5.29 (brs, 1H), 4.71 (brs, 1H), 3.65 (s, 3H), 2.88 (d, *J* = 5.2 Hz, 1H), 1.41 (s, 9H), 1.26 (s, 6H), 1.23 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.51, 155.21, 136.76, 131.47, 131.34, 120.51, 84.15, 79.80, 55.99, 52.09, 28.28, 24.74, 24.48; ESI-MS: $[M+Na]^{\oplus}$ 506.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{31}{}^{10}B^{79}BrNO_6Na^{\oplus}$ 505.1356, found 505.1374; IR (KBr) *v* (cm^{-1}) 3430, 3010, 2976, 2926, 1746, 1698, 1457, 1374, 1263, 1138, 853, 745; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 4.3 min (2*S*,3*R*)-**3b**, 5.5 min (2*R*,3*S*)-**3b**.



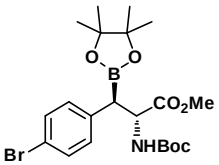
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		4.322	578470.313	5664192.000	49.8795
2		5.500	366947.156	5691552.000	50.1205
Total			945417.469	11355744.000	100.0000

Results

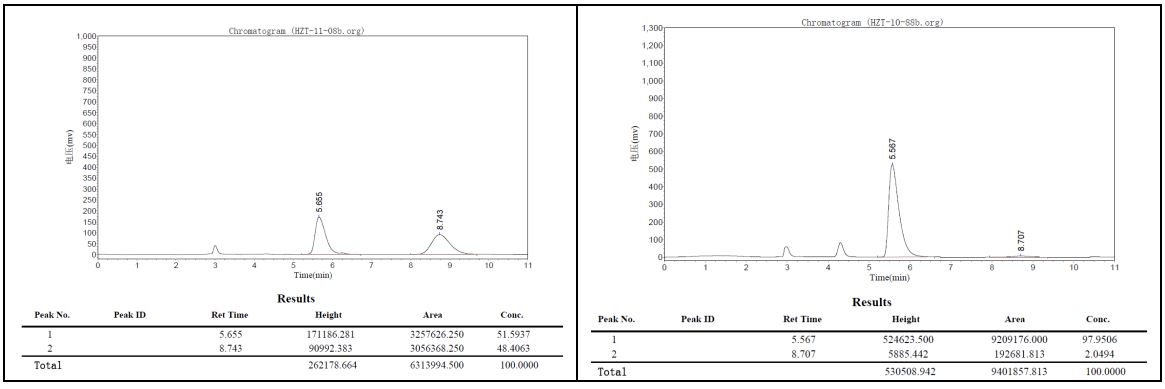
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		4.312	1020065.500	9906795.000	99.0727
2		5.537	7152.221	92726.898	0.9273
Total			1027217.721	9999521.898	100.0000

(2*R*,3*R*)-Methyl 3-(4-bromophenyl)-2-((*tert*-butoxycarbonyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*anti*-3b)



anti-3b

Colorless oil. 24.6 mg, 51% yield. $[\alpha]_D^{25.6}$ +11.5 (*c* 1.23, $CHCl_3$) for 96% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.38 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 4.78 (brs, 2H), 3.71 (s, 3H), 2.73 (brs, 1H), 1.35 (s, 9H), 1.21 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.71, 155.21, 136.71, 131.41, 131.22, 120.27, 83.91, 55.17, 52.26, 28.15, 24.55, 24.49; (The carbon directly attached to the boron atom was not detected, likely due to quadrupole relaxation.) ESI-MS: $[M+Na]^{\oplus}$ 506.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{31}{}^{10}B^{79}BrNO_6Na^{\oplus}$ 505.1356, found 505.1370; IR (KBr) *v* (cm^{-1}) 3373, 2979, 2929, 2851, 1717, 1506. 1488, 1367, 1271, 1166, 1011, 968, 850, 738; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 5.6 min (2*R*,3*R*)-**3b**, 8.7 min (2*S*,3*S*)-**3b**.



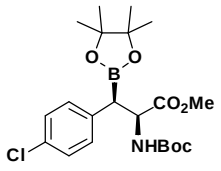
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.655	171186.281	3257626.250	51.5937
2		8.743	90992.383	3056368.250	48.4063
Total			262178.664	6313994.500	100.0000

Results

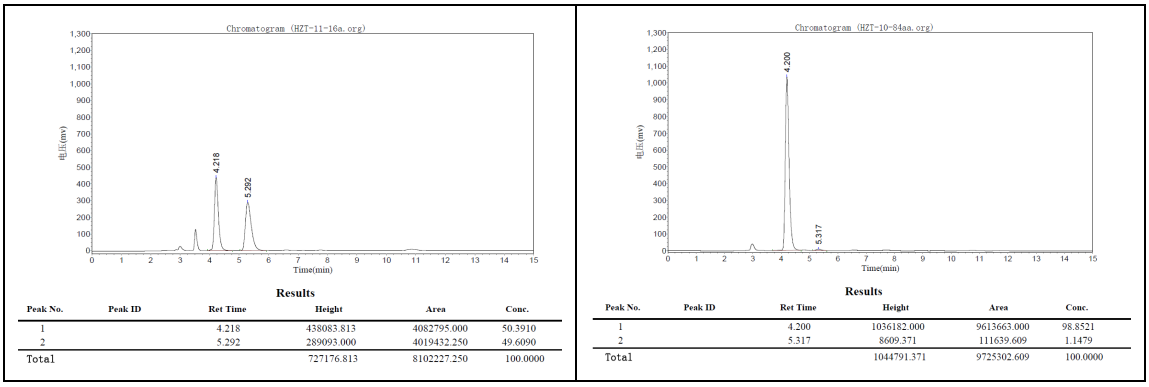
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.567	524623.500	9209176.000	97.9506
2		8.707	5885.442	192681.813	2.0494
Total			530508.942	9401857.813	100.0000

(2*S*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*syn*-3c)

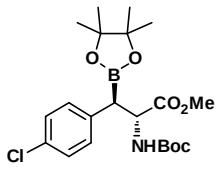


syn-3c

Colorless oil. 19.8 mg, 45% yield. $[\alpha]_D^{25.6}$ +17.1 (*c* 0.88, $CHCl_3$) for 98% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.30 (brs, 1H), 4.71 (brs, 1H), 3.65 (s, 3H), 2.89 (d, *J* = 4.8 Hz, 1H), 1.41 (s, 9H), 1.26 (s, 6H), 1.23 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.57, 136.37, 132.44, 130.98, 128.55, 127.48, 84.19, 79.83, 56.14, 52.04, 28.31, 24.76, 24.52; ESI-MS: $[M+Na]^{\oplus}$ 462.3; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{31}{}^{10}B^{35}ClNO_6Na^{\oplus}$ 461.1861, found 461.1878; IR (KBr) *v* (cm^{-1}) 3435, 2979, 2931, 1721, 1493, 1368, 1255, 1166, 1016, 851, 778; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 4.2 min (2*S*,3*R*)-**3c**, 5.3 min (2*R*,3*S*)-**3c**.

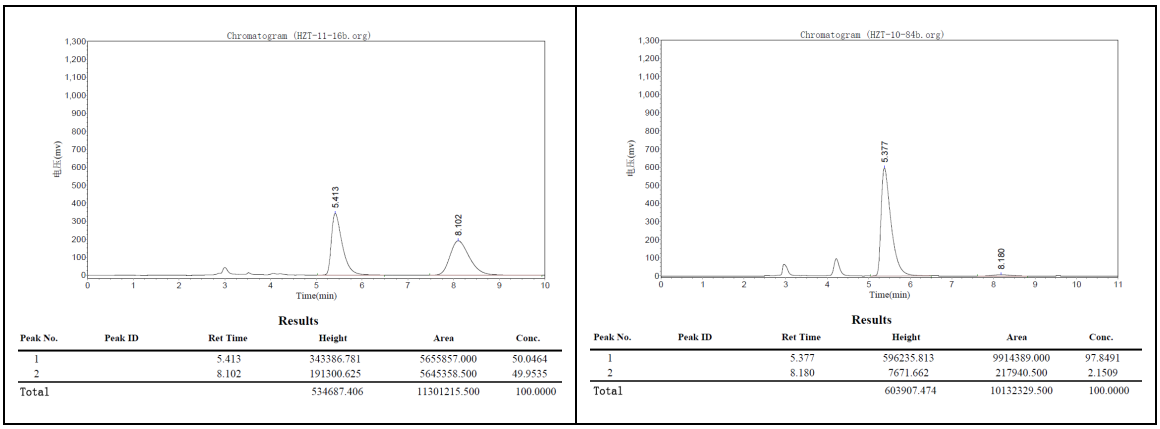


((2*R*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*anti*-3c)

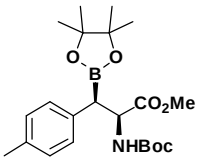


anti-3c

Colorless oil. 20.6 mg, 47% yield. $[\alpha]_D^{25.7}$ +10.6 (*c* 0.87, $CHCl_3$) for 96% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.23 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.78 (brs, 2H), 3.71 (s, 3H), 2.75 (brs, 1H)), 1.35 (s, 9H), 1.21 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.00, 155.35, 136.16, 132.13, 130.81, 128.45, 83.90, 79.69, 55.22, 52.25, 28.15, 24.53, 24.49; (The carbon directly attached to the boron atom was not detected, likely due to quadrupole relaxation.) ESI-MS: $[M+Na]^{\oplus}$ 462.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{31}{}^{10}B^{35}ClNO_6Na^{\oplus}$ 461.1861, found 461.1879; IR (KBr) *v* (cm^{-1}) 3370, 2978, 2931, 1717, 1491, 1367, 1326, 1166, 1015, 968, 851, 737; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 5.4 min (2*R*, 3*R*)-**3c**, 8.2 min (2*S*,3*S*)-**3c**.

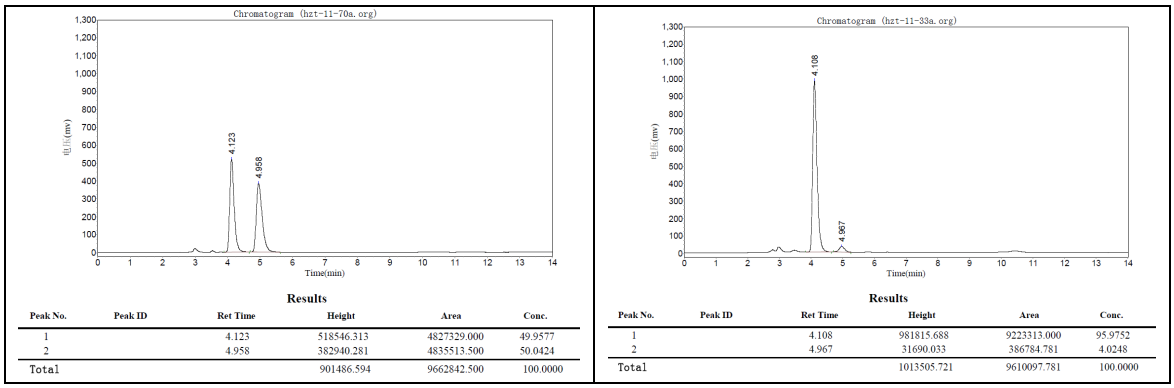


(2*S*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*p*-tolyl)propanoate (*syn*-3d)

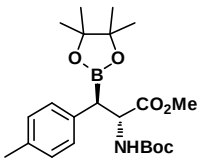


***syn*-3d**

Colorless oil. 18.4 mg, 44% yield. $[\alpha]_D^{25.0}$ +15.1 (*c* 0.93, $CHCl_3$) for 92% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.06 (d, *J* = 8.0 Hz, 4H), 5.33 (brs, 1H), 4.71 (brs, 1H), 3.64 (s, 3H), 2.86 (d, *J* = 5.2 Hz, 1H), 2.29 (s, 3H), 1.40 (s, 9H), 1.26 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.92, 155.20, 135.87, 134.42, 129.43, 129.14, 83.94, 79.55, 56.28, 51.95, 28.31, 24.75, 24.49, 20.97; ESI-MS: $[M+Na]^{\oplus}$ 442.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{34}{}^{10}BNO_6Na^{\oplus}$ 441.2408, found 441.2410; IR (KBr) *v* (cm^{-1}) 3436, 2978, 2927, 1720, 1512, 1368, 1166, 1053, 852, 779; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 4.1 min (2*S*,3*R*)-**3d**, 5.0 min (2*R*,3*S*)-**3d**.

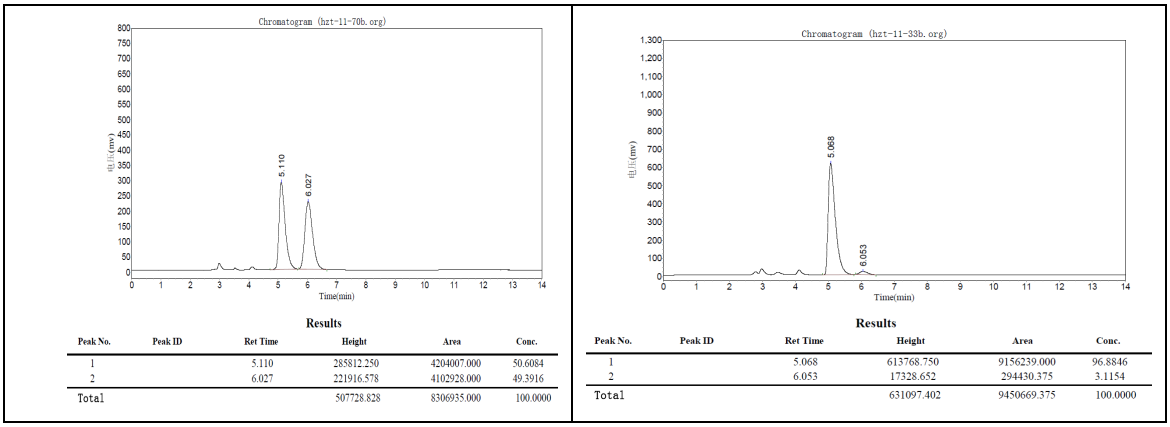


(2*R*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*p*-tolyl)propanoate (*anti*-3d)

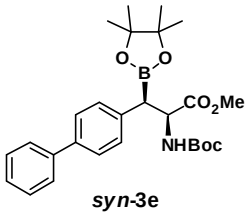


***anti*-3d**

Colorless oil. 21.8 mg, 52% yield. $[\alpha]_D^{25.1}$ +8.84 (*c* 1.1, $CHCl_3$) for 94% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.08 (dd, *J* = 15.2 Hz, *J* = 8.4 Hz, 4H), 4.77 (brs, 2H), 3.70 (s, 3H), 2.75 (brs, 1H), 2.29 (s, 3H), 1.35 (s, 9H), 1.21 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.00, 155.28, 135.78, 134.16, 129.35, 129.14, 83.72, 79.44, 55.36, 52.08, 28.18, 24.56, 24.50, 20.97; (The carbon directly attached to the boron atom was not detected, likely due to quadrupole relaxation.) ESI-MS: $[M+Na]^{\oplus}$ 442.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{34}{}^{10}BNO_6Na^{\oplus}$ 441.2408, found 441.2412; IR (KBr) *v* (cm^{-1}) 3378, 2978, 2925, 2850, 1717, 1513, 1366, 1326, 1166, 969, 851; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 5.1 min (2*R*, 3*R*)-**3d**, 6.1 min (2*S*,3*S*)-**3d**.

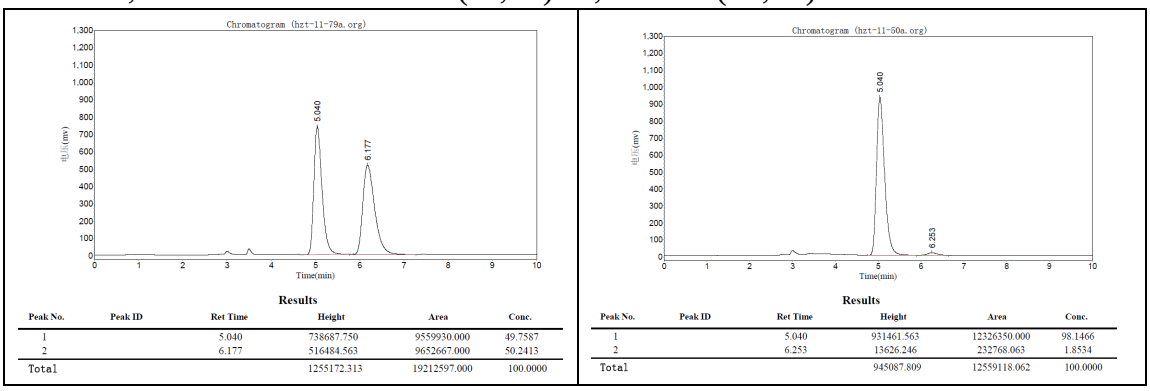


(2*S*,3*R*)-Methyl 3-([1,1'-biphenyl]-4-yl)-2-((*tert*-butoxycarbonyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*syn*-3e)



syn-3e

Colorless oil. 17.8 mg, 37% yield. $[\alpha]_D^{25.9}$ +8.3 (*c* 0.86, $CHCl_3$) for 96% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.56 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.33–7.26 (m, 3H), 5.39 (brs, 1H), 4.78 (brs, 1H), 3.66 (s, 3H), 2.96 (d, *J* = 5.2 Hz, 1H), 1.41 (s, 9H), 1.28 (s, 6H), 1.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.91, 155.34, 141.06, 139.34, 136.87, 130.09, 128.77, 127.25, 127.14, 127.06, 84.21, 79.80, 56.31, 52.16, 28.43, 24.90, 24.62; ESI-MS: $[M\text{-}Boc+H]^{\oplus}$ 382.3; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{27}H_{36}{}^{10}BNO_6Na^{\oplus}$ 503.2564, found 503.2572; IR (KBr) *v* (cm^{-1}) 3428, 3029, 2978, 2927, 1720, 1488, 1368, 1166, 1009, 852, 767; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 5.0 min (2*S*,3*R*)-**3e**, 6.3 min (2*R*,3*R*)-**3e**.



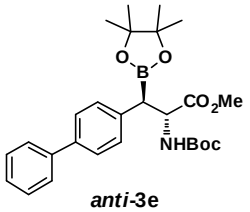
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.040	738687.750	9559930.000	49.7587
2		6.177	516484.563	9652667.000	50.2413
Total			1255172.313	19212597.000	100.0000

Results

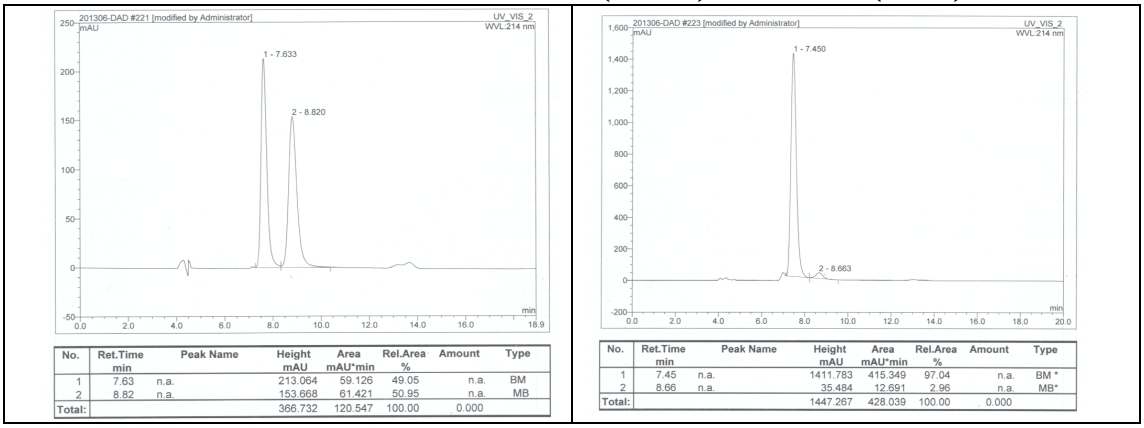
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.040	931461.563	12326350.000	98.1466
2		6.253	13626.246	232768.063	1.8534
Total			945087.809	12559118.062	100.0000

(2*R*,3*R*)-Methyl 3-([1,1'-biphenyl]-4-yl)-2-((*tert*-butoxycarbonyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*anti*-3e)



anti-3e

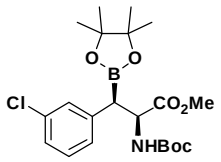
Colorless oil. 26.5 mg, 55% yield. $[\alpha]_D^{25.9}$ +16.5 (*c* 1.00, $CHCl_3$) for 94% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.57 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.33–7.29 (m, 3H), 4.84 (brs, 2H), 3.73 (s, 3H), 2.83 (brs, 1H), 1.34 (s, 9H), 1.23 (s, 6H), 1.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.96, 155.28, 140.91, 139.10, 136.58, 129.91, 128.67, 127.07, 127.03, `126.90, 83.85, 79.60, 55.20, 52.20, 28.18, 24.58, 24.52; (The carbon directly attached to the boron atom was not detected, likely due to quadrupole relaxation.) ESI-MS: $[M\text{-}Boc+H]^{\oplus}$ 382.3; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{27}H_{36}{}^{10}BNO_6Na^{\oplus}$ 503.2564, found 503.2564; IR (KBr) *v* (cm^{-1}) 3382, 2977, 2931，2850，1716, 1506, 1488, 1366, 1165, 1048, 851, 740; HPLC: Phenomenex Lux 5u Cellulose-4 (PC-4) Column; detected at 214 nm; n-hexane / *i*-propanol = 80/20; flow rate = 0.7 ml/min; Retention time: 7.5 min (2*R*, 3*R*)-**3e**, 8.7 min (2*S*,3*S*)-**3e**.



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.63	n.a.	213.064	59.126	49.05	n.a.	BM
2	8.82	n.a.	153.668	61.421	50.95	n.a.	MB
Total:			366.732	120.547	100.00	0.000	

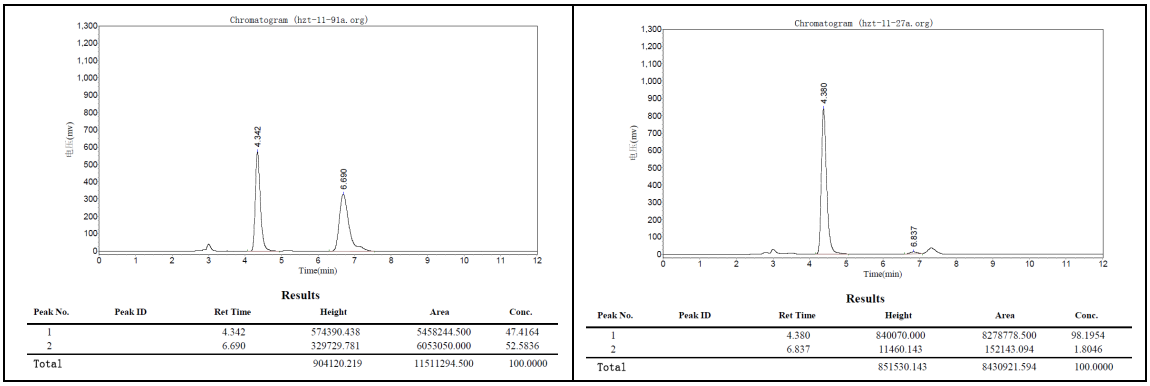
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.45	n.a.	1411.783	415.349	97.04	n.a.	BM *
2	8.66	n.a.	35.484	12.691	2.96	n.a.	MB*
Total:			1447.267	428.039	100.00	0.000	

(2*S*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(3-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*syn*-3f)

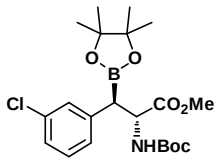


***syn*-3f**

Colorless oil. 18.0 mg, 41% yield. $[\alpha]_D^{25.1}$ +15.7 (*c* 0.86, $CHCl_3$) for 96% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.23–7.18 (m, 3H), 7.10 (d, *J* = 6.0 Hz, 1H), 5.35(brs, 1H), 4.72 (brs, 1H), 3.67 (s, 3H), 2.91 (d, *J* = 4.8 Hz, 1H), 1.41 (s, 9H), 1.26 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.60, 155.25, 140.03, 134.20, 129.83, 129.69, 127.92, 126.75, 84.34, 79.95, 56.17, 52.20, 28.38, 24.85, 24.61; ESI-MS: $[M\text{-}Boc+H]^{\oplus}$ 340.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{31}{}^{10}B^{35}ClNO_6Na^{\oplus}$ 461.1861, found 461.1876; IR (KBr) *v* (cm^{-1}) 3434, 2979, 2923, 2850, 1720, 1596, 1503, 1478, 1368, 1165, 1057, 852, 787, 698; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 4.4 min (2*S*,3*R*)-**3f**, 6.8 min (2*R*,3*S*)-**3f**.

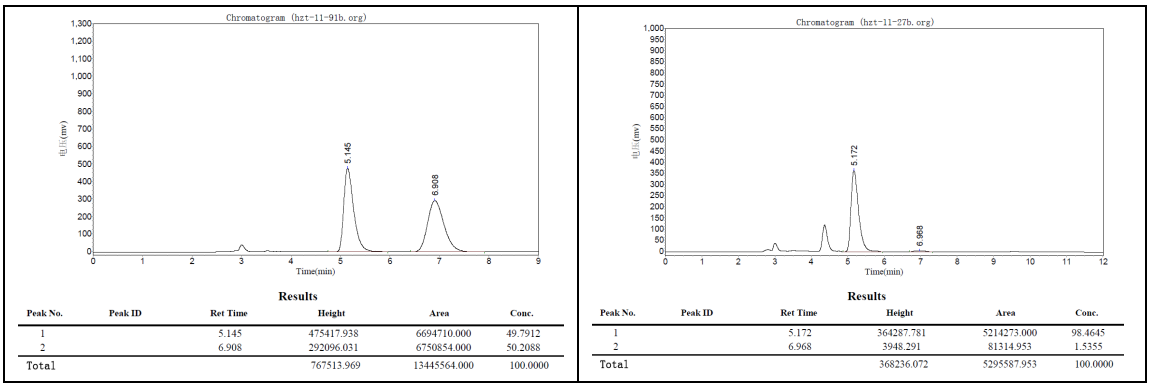


(2*R*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(3-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*anti*-3f)

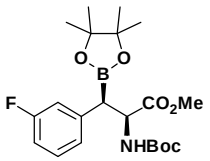


***anti*-3f**

Colorless oil. 22.0 mg, 50% yield. $[\alpha]_D^{25.2}$ +15.7 (*c* 1.00, $CHCl_3$) for 97% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.22–7.13 (m, 4H), 4.78 (brs, 2H), 3.72 (s, 3H), 2.76 (brs, 1H), 1.35 (s, 9H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.80, 155.22, 139.92, 134.16, 129.74, 129.64, 127.69, 126.60, 84.06, 83.16, 55.28, 52.40, 28.26, 24.65, 24.57; (The carbon directly attached to the boron atom was not detected, likely due to quadrupole relaxation.) ESI-MS: $[M\text{-}Boc+H]^{\oplus}$ 340.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{31}{}^{10}B^{35}ClNO_6Na^{\oplus}$ 461.1861, found 461.1857; IR (KBr) *v* (cm^{-1}) 3370, 2978, 2928, 1713, 1596, 1512, 1477, 1367, 1165, 968, 849, 786; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 5.2 min (2*R*, 3*R*)-**3f**, 7.0 min (2*S*,3*S*)-**3f**.

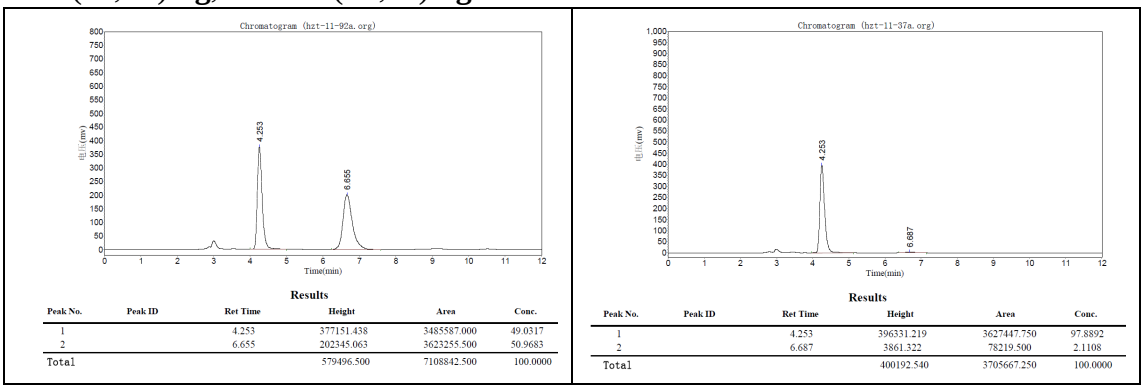


(2*S*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(3-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*syn*-3g)

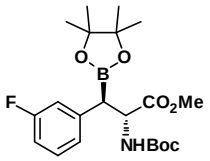


syn-3g

Colorless oil. 14.0 mg, 33% yield. $[\alpha]_D^{25.3}$ +16.4 (*c* 0.68, $CHCl_3$) for 96% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.25–7.19 (m, 1H), 6.99–6.87 (m, 3H), 5.35(brs, 1H), 4.73 (brs, 1H), 3.66 (s, 3H), 2.93 (d, *J* = 4.0 Hz, 1H), 1.41 (s, 9H), 1.27 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.66, 162.90 (d, J_{CF} = 243.6 Hz),, 155.28, 140.47 (d, J_{CF} = 7.3 Hz), 129.85 (d, J_{CF} = 8.7 Hz), 125.49 (d, J_{CF} = 2.2 Hz), 116.56 (d, J_{CF} = 11.1 Hz), 113.48 (d, J_{CF} = 21.2 Hz), 84.32, 79.92, 56.20, 52.18, 28.38, 24.86, 24.60; ESI-MS: $[M\text{-Boc}+H]^{\oplus}$ 324.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{31}{}^{10}BFNO_6Na^{\oplus}$ 445.2157, found 445.2137; IR (KBr) *v* (cm^{-1}) 3438, 2979, 2924, 2851, 1721, 1614, 1588, 1503, 1449, 1368, 1251, 1166, 869, 782; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 4.3 min (2*S*,3*R*)-**3g**, 6.7 min (2*R*,3*S*)-**3g**.

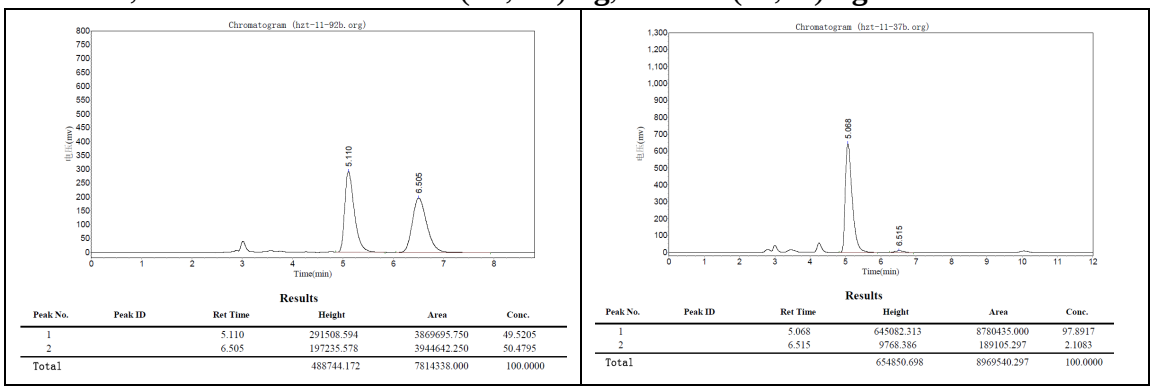


(2*R*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(3-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*anti*-3g)

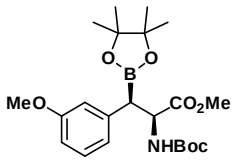


anti-3g

Colorless oil. 21.2 mg, 50% yield. $[\alpha]_D^{25.3}$ +15.6 (*c* 1.06, $CHCl_3$) for 96% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.22 (dd, *J* = 14.4 Hz,, *J* = 8.0 Hz,1H), 7.00–6.96 (m, 2H), 6.88 (t, *J* = 8.4 Hz, 1H), 4.79 (brs, *J* = 7.6 Hz, 1H), 3.72 (s, 3H), 2.79 (brs, *J* = 7.6 Hz, 1H), 1.35 (s, 9H), 1.22 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.70, 162.75 (d, J_{CF} = 244.5 Hz), 155.12, 140.22 (d, J_{CF} = 7.6 Hz), 129.68 (d, J_{CF} = 7.6 Hz), 125.16 (d, J_{CF} = 1.6 Hz), 116.34 (d, J_{CF} = 22.0 Hz), 113.21 (d, J_{CF} = 22.0 Hz), 83.93, 79.73, 55.24, 52.26, 28.15, 24.52, 24.47; (The carbon directly attached to the boron atom was not detected, likely due to quadrupole relaxation.) ESI-MS: $[M\text{-Boc}+H]^{\oplus}$ 324.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{31}{}^{10}BFNO_6Na^{\oplus}$ 445.2157, found 445.2137; IR (KBr) *v* (cm^{-1}) 3340, 2980, 2924, 2851, 1732, 1687, 1588, 1532, 1368, 1296, 1146, 971, 870, 784; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 5.1 min (2*R*, 3*R*)-**3g**, 6.5 min (2*S*,3*S*)-**3g**.

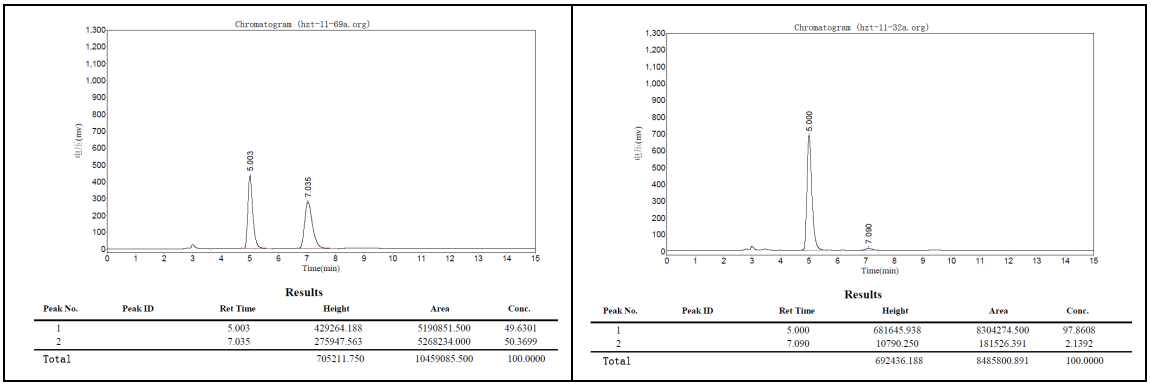


(2*S*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(3-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*syn*-3h)

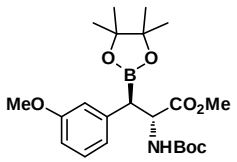


syn-3h

Colorless oil. 19.6 mg, 45% yield. $[\alpha]_D^{24.8}$ +15.0 (*c* 0.99, $CHCl_3$) for 95% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.17(t, *J* = 8.0 Hz, 1H), 6.80–6.73 (m, 3H), 5.38(brs, 1H), 4.73 (brs, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 2.88 (d, *J* = 4.8 Hz, 1H), 1.41 (s, 9H), 1.27 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.87, 159.51, 155.27, 139.13, 129.30, 121.96, 115.03, 112.08, 84.02, 79.61, 56.12, 55.01, 52.01, 28.28, 24.75, 24.49; ESI-MS: $[M+Na]^{\oplus}$ 458.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{34}{}^{10}BNO_7Na^{\oplus}$ 457.2357, found 457.2365; IR (KBr) ν (cm^{-1}) 3428, 2978, 2930, 2850, 1720, 1601, 1492, 1456, 1368, 1258, 1165, 1051, 852, 781; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 5.0 min (2*S*,3*R*)-**3h**, 7.1 min (2*R*,3*S*)-**3h**.

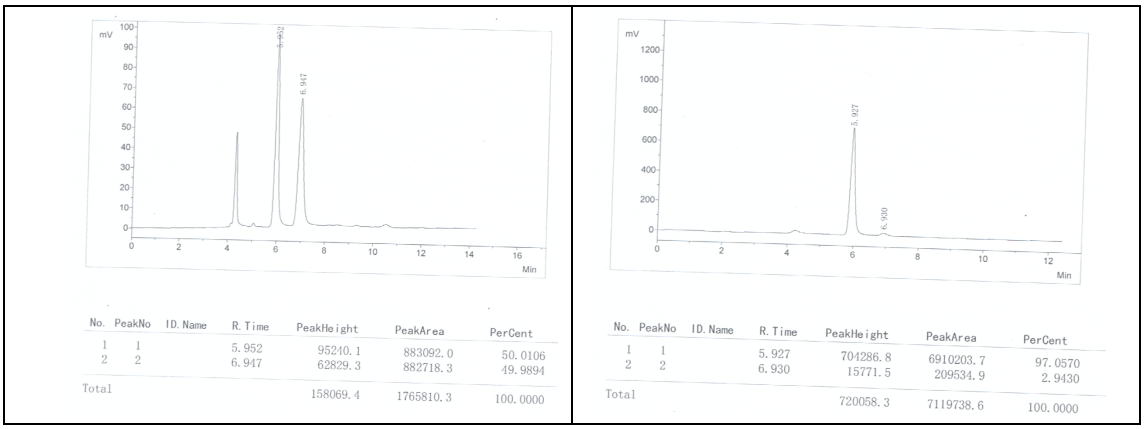


(2*R*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(3-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*anti*-3h)

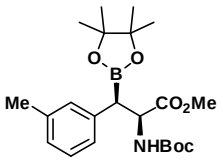


anti-3h

Colorless oil. 21.3 mg, 49% yield. $[\alpha]_D^{24.9}$ +10.0 (*c* 1.04, $CHCl_3$) for 94% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.17(t, *J* = 8.0 Hz, 1H), 6.81–6.72 (m, 3H), 4.78 (brs, 2H), 3.78 (s, 3H), 3.71 (s, 3H), 2.77 (brs, 1H), 1.35 (s, 9H), 1.21 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.94, 159.54, 155.25, 138.96, 129.30, 121.85, 114.78, 112.11, 83.78, 79.53, 55.06, 52.15, 28.18, 24.56, 24.48; (The carbon directly attached to the boron atom was not detected, likely due to quadrupole relaxation.) ESI-MS: $[M+Na]^{\oplus}$ 458.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{34}{}^{10}BNO_7Na^{\oplus}$ 457.2357, found 457.2360; IR (KBr) ν (cm^{-1}) 3370, 2978, 2930, 2850, 1717, 1600, 1491, 1456, 1367, 1260, 1048, 969, 850, 783; HPLC: Phenomenex Lux 5u Cellulose-4 (PC-4) Column; detected at 214 nm; n-hexane / *i*-propanol = 70/30; flow rate = 0.7 ml/min; Retention time: 5.9 min (2*R*, 3*R*)-**3h**, 6.9 min (2*S*,3*S*)-**3h**.

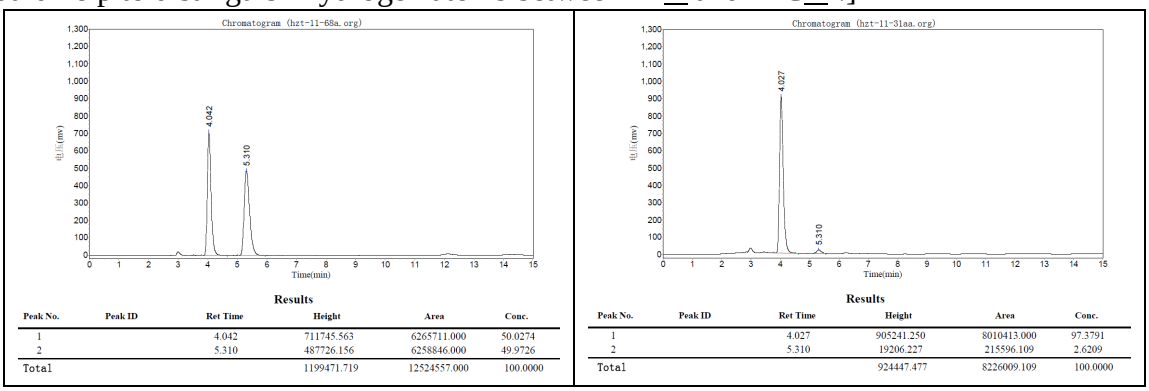


(2*S*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*m*-tolyl)propanoate (*syn*-3i)

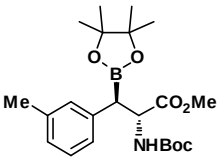


syn-3i

Colorless oil. 21.0 mg, 50% yield. $[\alpha]_D^{25.6}$ +16.2 (*c* 1.05, $CHCl_3$) for 95% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.14 (t, *J* = 8.0 Hz, 1H), 7.05–6.97 (m, 3H), 5.37(brs, 1H, N-H), 4.71 (brs, 1H, N-CH-), 3.64 (s, 3H), 2.87 (d, *J* = 4.8 Hz, 1H), 2.30 (s, 3H), 1.41 (s, 9H), 1.26 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.00, 155.30, 137.83, 137.60, 130.39, 128.23, 127.17, 126.40, 83.98, 79.49, 56.18, 51.96, 28.30, 24.74, 24.46, 21.28; ESI-MS: $[M+Na]^{\oplus}$ 442.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{34}{}^{10}BNO_6Na^{\oplus}$ 441.2408, found 441.2422; IR (KBr) ν (cm^{-1}) 3436, 2978, 2926, 2850, 1721, 1606, 1503, 1368, 1166, 1054, 1014, 850, 707; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 4.0 min (2*S*,3*R*)-**3i**, 5.3 min (2*R*,3*S*)-**3i**. [Notice: The HSQC spectra (see page S101) could help to distinguish hydrogen atoms between N-H and N-CH-.]

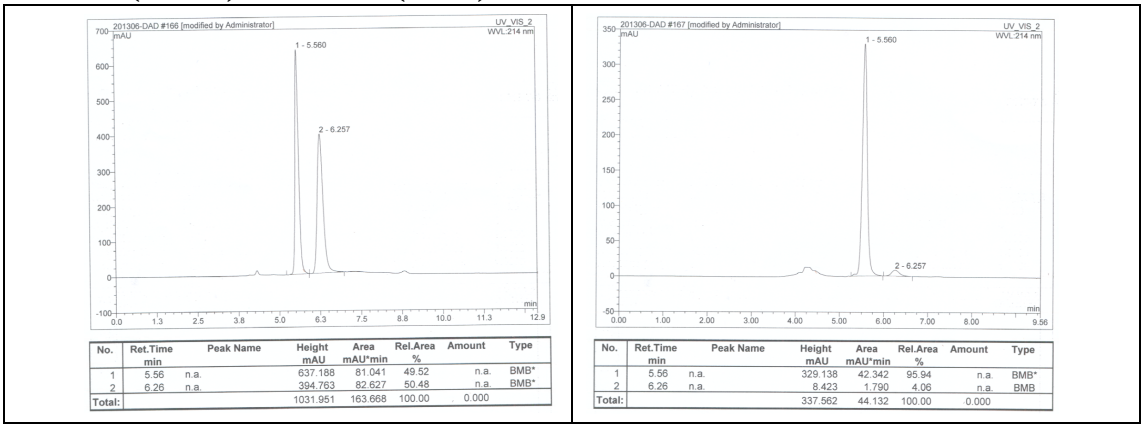


(2*R*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*m*-tolyl)propanoate (*anti*-3i)

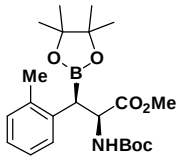


anti-3i

Colorless oil. 21.0 mg, 50% yield. $[\alpha]_D^{25.6}$ +9.7 (*c* 1.05, $CHCl_3$) for 92% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.15(t, *J* = 7.6 Hz, 1H), 7.03–6.98 (m, 3H), 4.77 (brs, 2H), 3.71 (s, 3H), 2.74 (brs, 1H), 2.30 (s, 3H), 1.34 (s, 9H), 1.21 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.04, 155.33, 137.87, 137.27, 130.27, 128.25, 127.06, 126.34, 83.72, 79.61, 55.29, 52.11, 28.18, 24.53, 24.46, 21.37; (The carbon directly attached to the boron atom was not detected, likely due to quadrupole relaxation.) ESI-MS: $[M+Na]^{\oplus}$ 442.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{34}{}^{10}BNO_6Na^{\oplus}$ 441.2408, found 441.2417; IR (KBr) ν (cm^{-1}) 3377, 2977, 2923, 2850, 1717, 1606, 1505, 1366, 1324, 1167, 1049, 969, 849, 786, 715; HPLC: Phenomenex Lux 5u Cellulose-4 (PC-4) Column; detected at 214 nm; n-hexane / *i*-propanol = 70/30; flow rate = 0.7 ml/min; Retention time: 5.6 min (2*R*, 3*R*)-**3i**, 6.3 min (2*S*,3*S*)-**3i**.

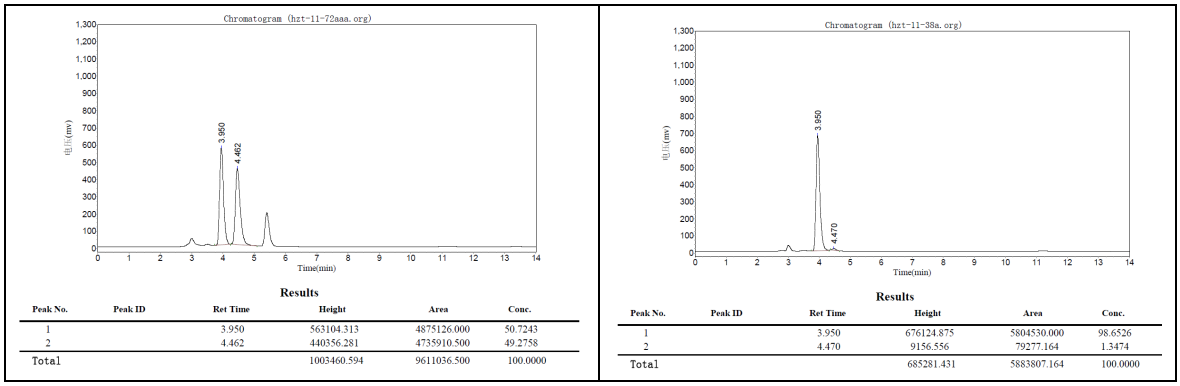


(2*S*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*o*-tolyl)propanoate (*syn*-3j)

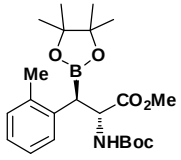


syn-3j

Colorless oil. 14.7 mg, 35% yield. $[\alpha]_D^{25.3}$ –6.7 (*c* 0.74, $CHCl_3$) for 97% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.15–7.08 (m, 4H), 5.47 (brs, 1H), 4.63 (brs, 1H), 3.66 (s, 3H), 3.19 (d, *J* = 5.2 Hz, 1H), 2.36 (s, 3H), 1.36 (s, 9H), 1.27 (s, 6H), 1.23 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.11, 155.28, 136.80, 136.18, 130.59, 129.33, 126.38, 125.71, 83.99, 79.48, 55.27, 52.08, 28.28, 24.81, 24.40, 19.87; ESI-MS: $[M+Na]^{\oplus}$ 442.3; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{34}{}^{10}BNO_6Na^{\oplus}$ 441.2408, found 441.2407; IR (KBr) ν (cm^{-1}) 3436, 2978, 2930, 1721, 1506, 1457, 1372, 1330, 1167, 1053, 851, 733; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 4.0 min (2*S*,3*R*)-**3j**, 4.5 min (2*R*,3*S*)-**3j**.

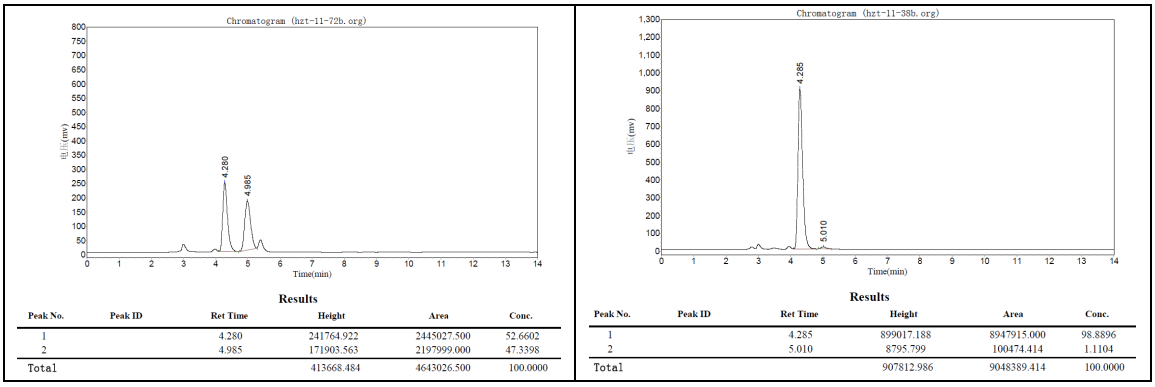


(2*R*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*o*-tolyl)propanoate (*anti*-3j)

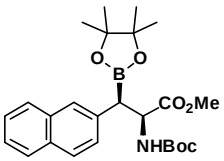


anti-3j

Colorless oil. 27.2 mg, 65% yield. $[\alpha]_D^{25.5}$+11.2 (*c*1.30, $CHCl_3$) for 98% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.26 (d, *J* = 7.6 Hz, 1H), 7.13–7.04 (m, 3H), 4.79 (brs, 2H), 3.71 (s, 3H), 3.01 (brs, 1H), 2.32 (s, 3H), 1.34 (s, 9H), 1.18 (s, 6H), 1.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.35, 155.24, 139.76, 136.78, 135.80, 130.31, 128.72, 125.91, 83.63, 79.59, 54.92, 52.15, 28.28, 24.59, 24.53, 20.11; (The carbon directly attached to the boron atom was not detected, likely due to quadrupole relaxation.) ESI-MS: $[M+Na]^{\oplus}$ 442.3; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{34}{}^{10}BNO_6Na^{\oplus}$ 441.2408, found 441.2418; IR (KBr) ν (cm^{-1}) 3391, 2977, 2929, 1717, 1506, 1390, 1323, 1165, 1142, 1052, 969, 850, 733; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 4.3 min (2*R*, 3*R*)-**3j**, 5.0 min (2*S*,3*S*)-**3j**.

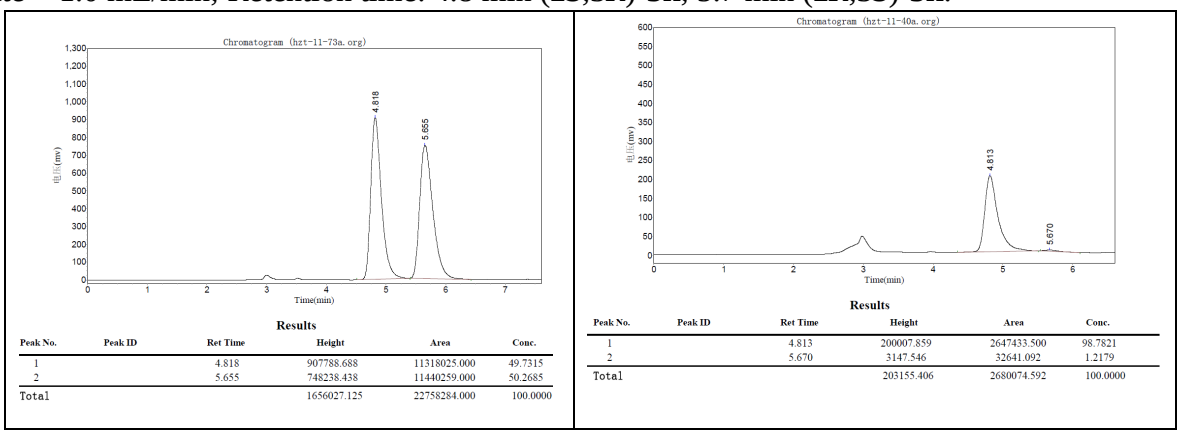


(2*S*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(naphthalen-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*syn*-3k)



***syn*-3k**

Colorless oil. 22.3 mg, 49% yield. $[\alpha]_D^{26.0}$ +9.6 (*c* 0.75, $CHCl_3$) for 98% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79–7.73 (m, 3H), 7.65 (s, 1H), 7.45–7.36 (m, 3H), 5.39 (brs, 1H), 4.84 (brs, 1H), 3.63 (s, 3H), 3.08 (d, *J* = 5.6 Hz, 1H), 1.38 (s, 9H), 1.27 (s, 6H), 1.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.89, 155.21, 135.24, 133.56, 132.21, 128.07, 127.94, 127.91, 127.66, 127.48, 125.76, 125.38, 84.11, 79.68, 56.09, 52.02, 28.27, 24.76, 24.62; ESI-MS: $[M+Na]^{\oplus}$ 478.0; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{25}H_{34}{}^{10}BNO_6Na^{\oplus}$ 477.2408, found 477.2400; IR (KBr) *v* (cm^{-1}) 3428, 3056, 2978, 2927, 2851, 1717, 1506, 1368, 1332, 1166, 1055, 1013, 858, 749; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 4.8 min (2*S*,3*R*)-**3k**, 5.7 min (2*R*,3*S*)-**3k**.



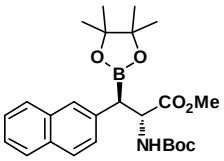
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		4.818	907788.688	11318025.000	49.7315
2		5.655	748238.438	11440259.000	50.2685
Total			1656027.125	22758284.000	100.0000

Results

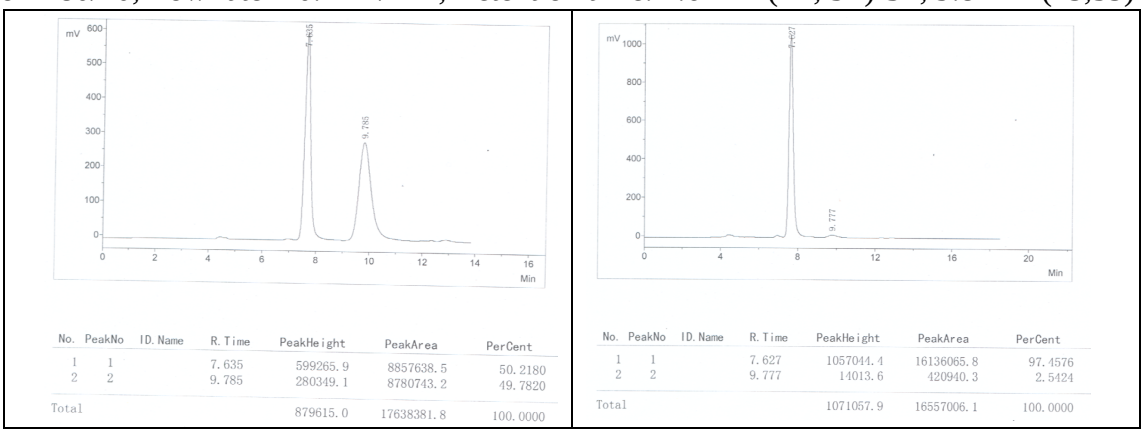
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		4.813	200007.859	2647433.500	98.7821
2		5.670	3147.546	32641.092	1.2179
Total			203155.406	2680074.592	100.0000

(2*R*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(naphthalen-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*anti*-3k)



***anti*-3k**

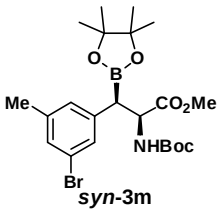
Colorless oil. 22.8 mg, 50% yield. $[\alpha]_D^{25.8}$ +18.2 (*c* 1.13, $CHCl_3$) for 95% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79–7.74 (m, 3H), 7.66 (s, 1H), 7.45–7.38 (m, 3H), 4.89 (brs, 1H), 4.79 (brs, 1H), 3.73 (s, 3H), 2.95 (d, *J* = 9.2 Hz, 1H), 1.28 (s, 9H), 1.21 (s, 6H), 1.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.03, 155.24, 135.36, 133.59, 132.21, 128.06, 127.93, 127.60, 127.53, 127.50, 125.79, 125.34, 83.85, 79.61, 85.27, 55.27, 52.24, 28.11, 24.56, 24.49; (The carbon directly attached to the boron atom was not detected, likely due to quadrupole relaxation.) ESI-MS: $[M+Na]^{\oplus}$ 478.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{25}H_{34}{}^{10}BNO_6Na^{\oplus}$ 477.2408, found 477.2403; IR (KBr) *v* (cm^{-1}) 3444, 2976, 2927, 2851, 1755, 1719, 1480, 1365, 1270, 1156, 970, 860, 760; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; n-hexane / *i*-propanol = 80/20; flow rate = 0.7 ml/min; Retention time: 7.6 min (2*R*, 3*R*)-**3k**, 9.8 min (2*S*,3*S*)-**3k**.



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		7.635	599265.9	8857638.5	50.2180
2	2		9.785	280349.1	8780743.2	49.7820
Total				879615.0	17638381.8	100.0000

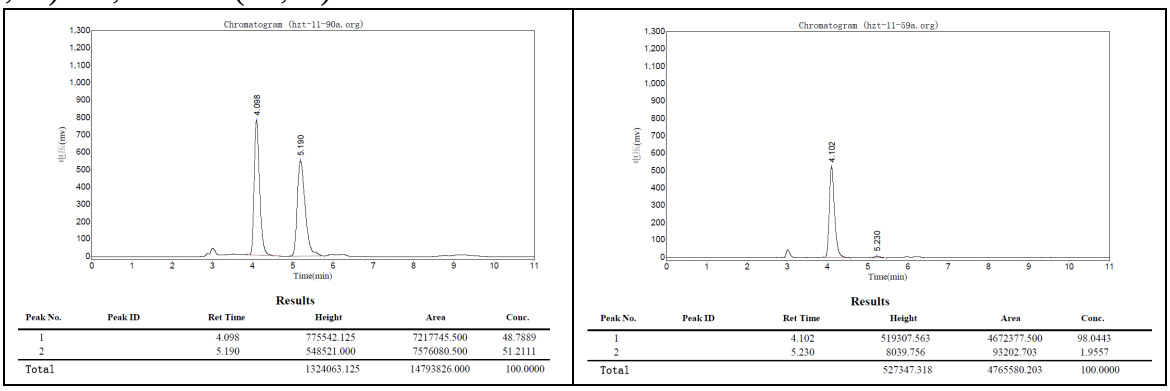
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		7.627	1057044.4	16136065.8	97.4576
2	2		9.777	14013.6	420940.3	2.5424
Total				1071057.9	16557006.1	100.0000

(2*S*,3*R*)-Methyl 3-(3-bromo-5-methylphenyl)-2-((*tert*-butoxycarbonyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*syn*-3m)



syn-3m

Colorless oil. 21.4 mg, 43% yield. $[\alpha]_D^{25.4}$ +17.7 (*c* 1.01, $CHCl_3$) for 96% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.16 (s, 2H), 6.94 (s, 1H), 5.36 (brs, 1H), 4.69 (brs, 1H), 3.67 (s, 3H), 2.86 (d, *J* = 4.8 Hz, 1H), 2.27 (s, 3H), 1.42 (s, 9H), 1.26 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.58, 155.22, 139.94, 139.77, 130.18, 129.46, 129.17, 122.10, 84.18, 79.73, 55.96, 52.09, 28.28, 24.98, 24.69, 24.44; ESI-MS: $[M\text{-Boc+H}]^{\oplus}$ 398.1; HRMS (FTMS-ESI): $[M\text{-Boc+H}]^{\oplus}$ calcd for $C_{17}H_{26}{}^{10}B^{79}BrNO_4^{\oplus}$ 397.1169, found 397.1154; IR (KBr) *v* (cm^{-1}) 3426, 2978, 2925, 1721, 1601, 1503, 1445, 1367, 1166, 1057, 1021, 852; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 4.1 min (2*S*,3*R*)-**3m**, 5.2 min (2*R*,3*S*)-**3m**.



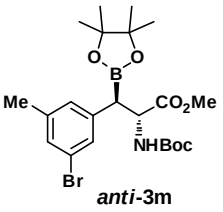
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		4.098	775542.125	7217745.500	48.7889
2		5.190	548521.000	7576080.500	51.2111
Total			1324063.125	14793826.000	100.0000

Results

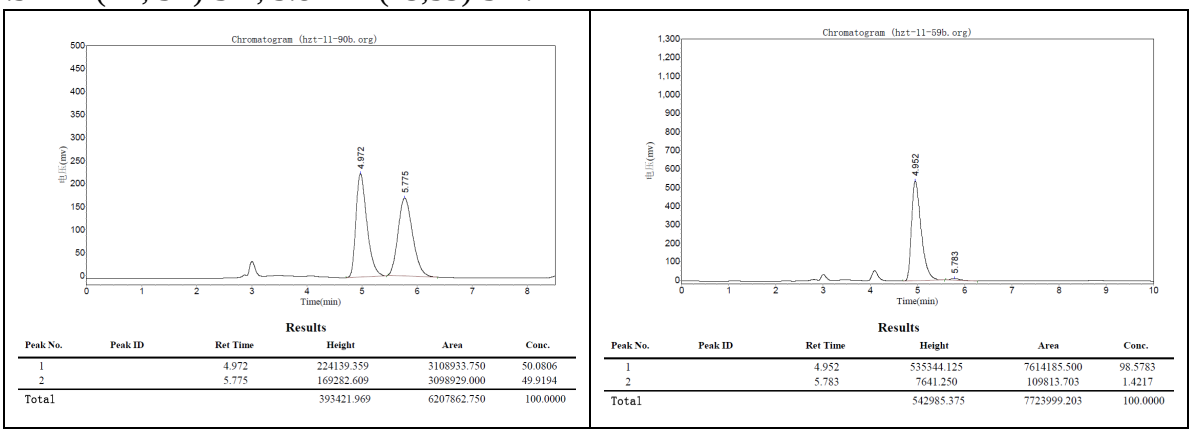
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		4.102	519307.563	4672377.500	98.0443
2		5.230	8039.756	93202.703	1.9557
Total			527347.318	4765580.203	100.0000

(2*R*,3*R*)-Methyl 3-(3-bromo-5-methylphenyl)-2-((*tert*-butoxycarbonyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*anti*-3m)



anti-3m

Colorless oil. 25.4 mg, 51% yield. $[\alpha]_D^{25.5}$ +15.6 (*c* 1.21, $CHCl_3$) for 97% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.16 (d, *J* = 10.8 Hz, 2H), 6.96 (s, 1H), 4.75 (brs, 2H), 3.72 (s, 3H), 2.72 (brs, *J* = 8.4Hz, 1H), 2.28 (s, 3H), 1.36 (s, 9H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.73, 155.22, 139.90, 139.74, 130.04, 129.41, 128.90, 122.09, 83.89, 79.70, 55.25, 52.25, 28.25, 24.65, 24.41, 21.07; (The carbon directly attached to the boron atom was not detected, likely due to quadrupole relaxation.) ESI-MS: $[M\text{-Boc+H}]^{\oplus}$ 398.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{33}{}^{10}B^{79}BrNO_6Na^{\oplus}$ 519.1513, found 519.1505; IR (KBr) *v* (cm^{-1}) 3382, 2977, 2924, 2851, 1713, 1568, 1505, 1445, 1367, 1166, 1049, 852, 669; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 4.9 min (2*R*, 3*R*)-**3m**, 5.8 min (2*S*,3*S*)-**3m**.



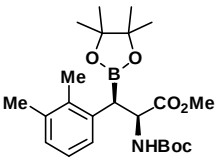
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		4.972	224139.359	3108933.750	50.0806
2		5.775	169282.609	3098929.000	49.9194
Total			393421.969	6207862.750	100.0000

Results

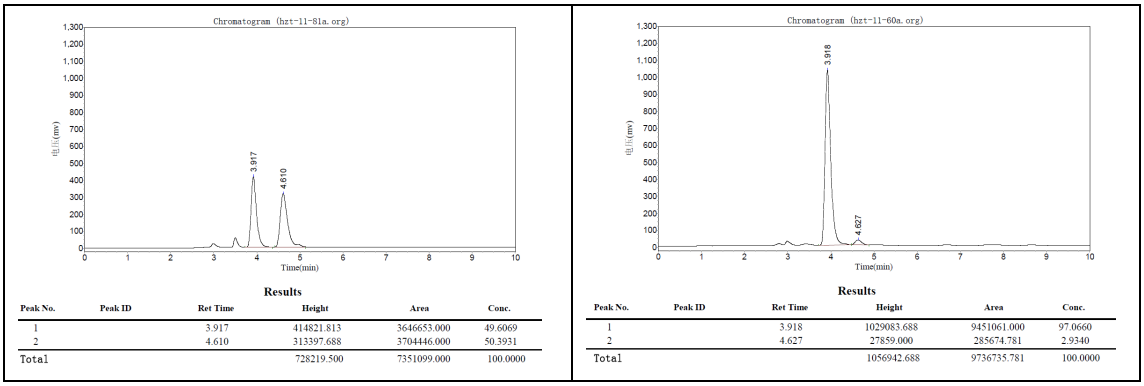
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		4.952	535344.125	7614185.500	98.5783
2		5.783	7641.250	109813.703	1.4217
Total			542985.375	7723999.203	100.0000

(2*S*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(2,3-dimethylphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*syn*-3n)

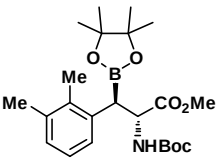


syn-3n

Colorless oil. 21.7 mg, 50% yield. $[\alpha]_D^{26.0}$ –6.1 (*c* 0.98, $CHCl_3$) for 94% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.99–6.98(m, 3H), 5.50 (brs, 1H), 4.60 (brs, 1H), 3.67 (s, 3H), 3.29 (d, *J* = 4.8 Hz, 1H), 2.26 (s, 3H), 2.25 (s, 3H), 1.36 (s, 9H), 1.28 (s, 6H), 1.23 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.11, 155.48, 137.05, 136.05, 135.49, 128.29, 127.36, 124.96, 83.96, 79.42, 55.58, 52.07, 28.29, 24.84, 24.37, 21.19, 15.26; ESI-MS: $[M+Na]^{\oplus}$ 456.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{23}H_{36}{}^{10}BNO_6Na^{\oplus}$ 455.2564, found 455.2565; IR (KBr) *v* (cm^{-1}) 3413, 2978, 2925, 2852, 1760, 1710, 1503, 1374, 1166, 1052, 964, 856, 789; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 3.9 min (2*S*,3*R*)-**3n**, 4.6 min (2*R*,3*S*)-**3n**.

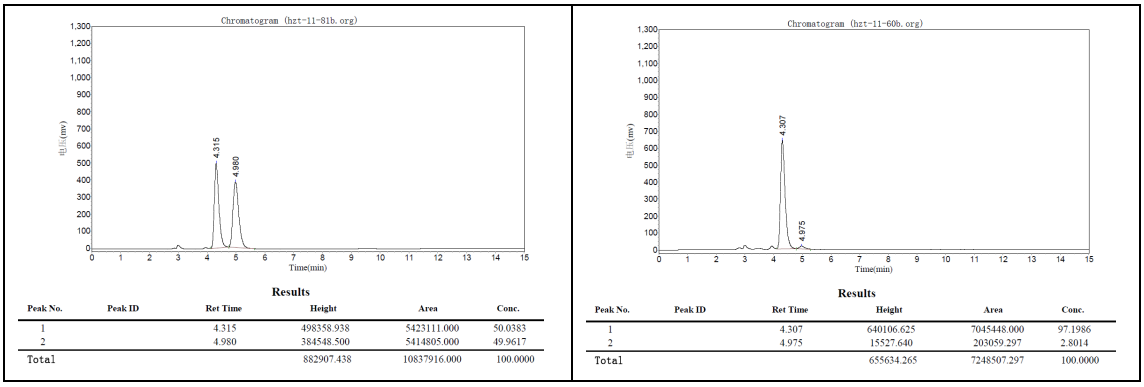


(2*R*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(2,3-dimethylphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*anti*-3n)

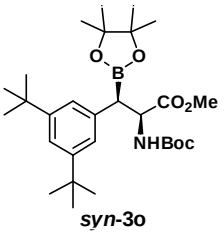


anti-3n

Colorless oil. 21.7 mg, 50% yield. $[\alpha]_D^{26.0}$ +10.4 (*c* 1.09, $CHCl_3$) for 94% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.11 (d, *J* = 7.6 Hz, 1H), 7.03–6.96 (m, 2H), 4.77 (brs, 2H), 3.71 (s, 3H), 3.09 (brs, 1H), 2.26 (s, 3H), 2.21 (s, 3H), 1.34 (s, 9H), 1.19 (s, 6H), 1.17 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.35, 155.19, 135.17, 135.42, 127.91, 127.85, 126.90, 125.21, 83.63, 79.53, 55.17, 52.08, 28.18, 24.52, 24.45, 21.18, 15.56; (The carbon directly attached to the boron atom was not detected, likely due to quadrupole relaxation.) ESI-MS: $[M-Boc+H]^{\oplus}$ 334.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{23}H_{36}{}^{10}BNO_6Na^{\oplus}$ 455.2564, found 455.2570; IR (KBr) *v* (cm^{-1}) 3403, 2980, 2924, 2852, 1739, 1717, 1510, 1478, 1361, 1320, 1274, 1149, 1020, 969, 847, 792; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 4.3 min (2*R*, 3*R*)-**3n**, 5.0 min (2*S*,3*S*)-**3n**.

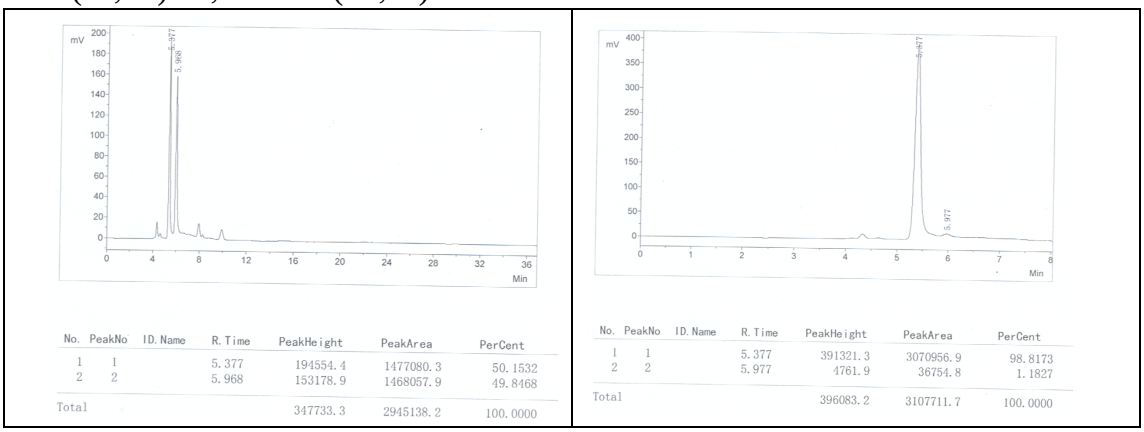


(2*S*,3*R*)-methyl 2-((*tert*-butoxycarbonyl)amino)-3-(3,5-*di*-*tert*-butylphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*syn*-3o)

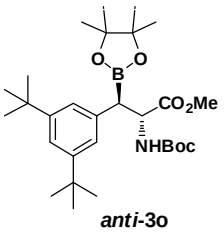


syn-3o

Colorless oil. 25.9 mg, 50% yield. $[\alpha]_D^{25.8}$ +17.6 (*c* 1.29, $CHCl_3$) for 98% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.22 (s, 1H), 7.04 (s, 2H), 5.37 (brs, 1H), 4.75 (brs, 1H), 3.62 (s, 3H), 2.88 (d, *J* = 5.2 Hz, 1H), 2.27 (s, 3H), 1.41 (s, 9H), 1.29 (s, 18H), 1.28 (s, 6H), 1.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.00, 155.11, 150.27, 136.20, 123.94, 120.11, 83.86, 79.42, 56.15, 51.91, 34.72, 31.45, 28.33, 24.83, 24.56; ESI-MS: $[M\text{-}Boc+H]^{\oplus}$ 418.4; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{29}H_{48}{}^{10}BNO_6Na^{\oplus}$ 539.3503, found 539.3499; IR (KBr) *v* (cm^{-1}) 3441, 2966, 2868, 1721, 1598, 1506, 1366, 1166, 1056, 871, 851, 715; HPLC: Phenomenex Lux 5u Cellulose-4 (PC-4) Column; detected at 214 nm; n-hexane / *i*-propanol = 90/10; flow rate = 0.7 ml/min; Retention time: 5.4 min (2*S*,3*R*)-**3o**, 6.0 min (2*R*,3*S*)-**3o**.

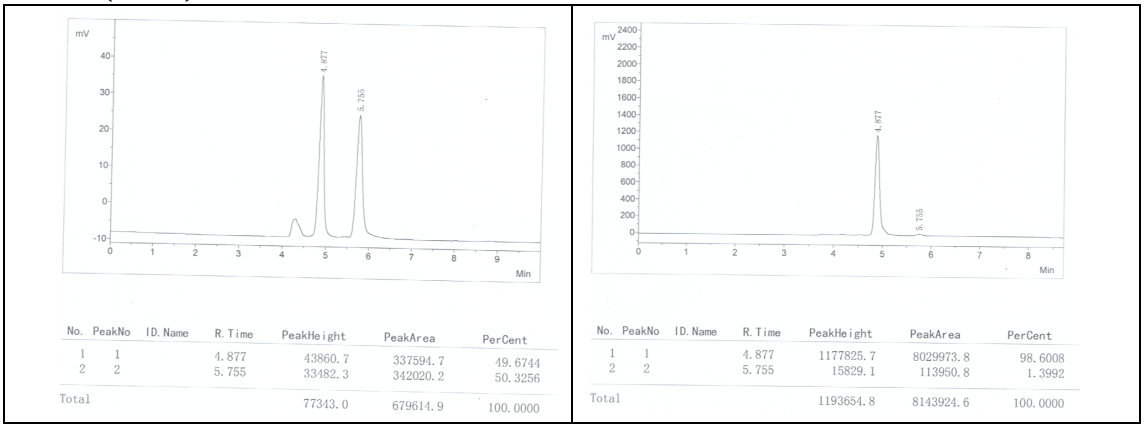


(2*R*,3*R*)-methyl 2-((*tert*-butoxycarbonyl)amino)-3-(3,5-*di*-*tert*-butylphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*anti*-3o)

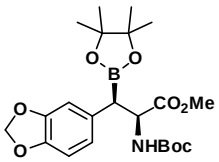


anti-3o

Colorless oil. 23.3 mg, 45% yield. $[\alpha]_D^{25.7}$ +5.5 (*c* 1.14, $CHCl_3$) for 97% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.22 (s, 1H), 7.03 (s, 2H), 4.75 (brs, 2H), 3.71 (s, 3H), 2.79 (brs, 1H), 2.27 (s, 3H), 1.34 (s, 9H), 1.29 (s, 18H), 1.22 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.11, 155.07, 150.46, 135.94, 123.94, 120.03, 83.62, 79.16, 55.14, 52.08, 34.72, 31.43, 28.21, 24.62, 24.53; (The carbon directly attached to the boron atom was not detected, likely due to quadrupole relaxation.) ESI-MS: $[M\text{-}Boc+H]^{\oplus}$ 418.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{29}H_{48}{}^{10}BNO_6Na^{\oplus}$ 539.3503, found 539.3515; IR (KBr) *v* (cm^{-1}) 3398, 2965, 2925, 2867, 1731, 1713, 1597, 1477, 1363, 1248, 1146, 1012, 876, 850; HPLC: Phenomenex Lux 5u Amylose-2 (PA-2) Column; detected at 214 nm; n-hexane / *i*-propanol = 80/20; flow rate = 0.7 ml/min; Retention time: 4.9 min (2*R*, 3*R*)-**3o**, 5.8 min (2*S*,3*S*)-**3o**.

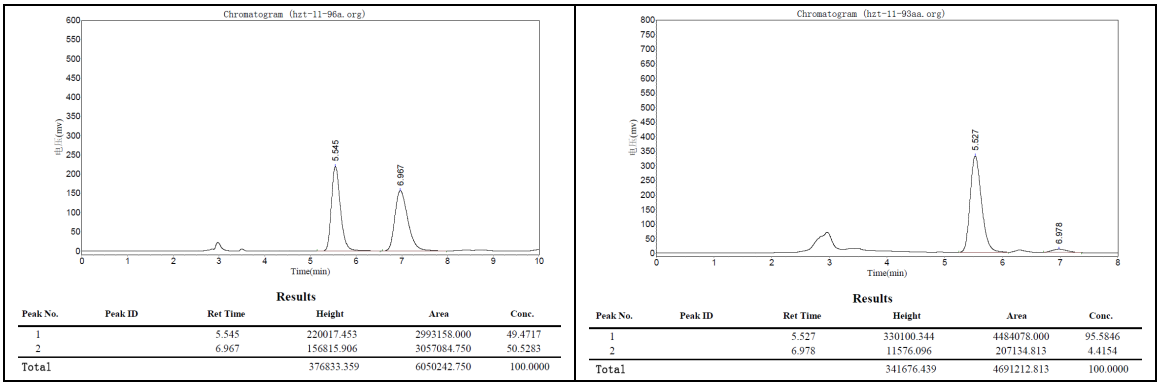


(2*S*,3*R*)-Methyl 3-(benzo[d][1,3]dioxol-5-yl)-2-((*tert* -butoxycarbonyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*syn*-3p)

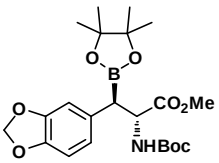


***syn*-3p**

Colorless oil. 21.1 mg, 47% yield. $[\alpha]_D^{25.3}$ +12.9 (*c* 0.70, $CHCl_3$) for 91% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.71 (d, *J* = 10.8 Hz, 2H), 6.64 (d, *J* = 7.6 Hz, 1H), 5.90 (d, *J* = 6.8 Hz, 2H), 5.32 (brs, 1H), 4.68 (brs, 1H), 3.66 (s, 3H), 2.82 (d, *J* = 4.4 Hz, 1H), 1.41 (s, 9H), 1.26 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.77, 155.38, 147.62, 146.20, 131.29, 122.83, 110.01, 108.24, 100.76, 84.03, 79.61, 56.43, 52.02, 28.28, 24.75, 24.49; ESI-MS: $[M+Na]^{\oplus}$ 472.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{32}{}^{10}BNO_8Na^{\oplus}$ 471.2150, found 471.2157; IR (KBr) *v* (cm^{-1}) 3389, 2979, 2924, 1745, 1694, 1493, 1445, 1368, 1251, 1163, 1039, 930, 854; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 5.5 min (2*S*,3*R*)-**3p**, 7.0 min (2*R*,3*S*)-**3p**.

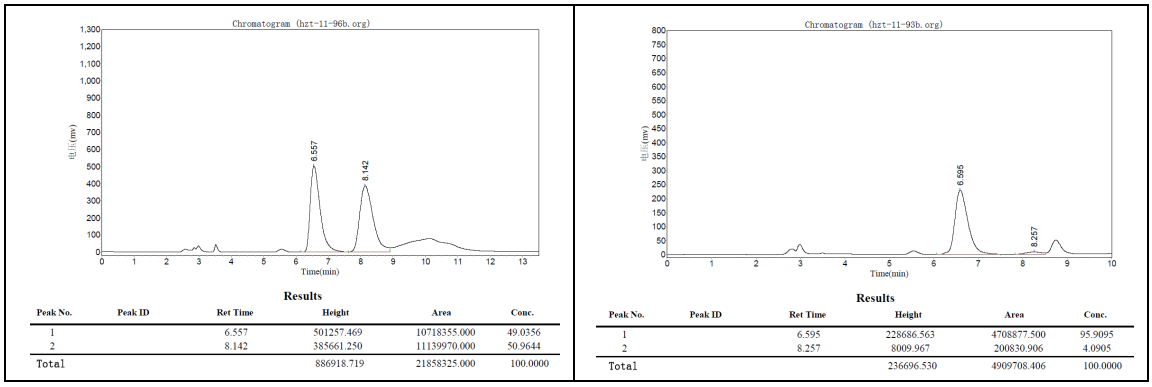


(2*R*,3*R*)-Methyl 3-(benzo[d][1,3]dioxol-5-yl)-2-((*tert*-butoxycarbonyl)amino)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (*anti*-3p)

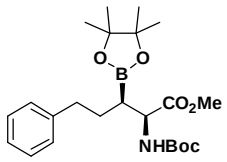


***anti*-3p**

Colorless oil. 22.0 mg, 49% yield. $[\alpha]_D^{25.5}$ –16.5 (*c* 1.10, $CHCl_3$) for 92% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.76–6.64 (m, 3H), 5.91 (d, *J* = 4.0 Hz, 1H), 4.81 (brs, 1H), 4.70 (brs, 1H), 3.71 (s, 3H), 2.72 (4.81 (brs, 1H), 1H), 1.37 (s, 9H), 1.22 (s, 6H), 1.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 172.84, 155.21, 147.56, 146.17, 131.01, 122.71, 109.89, 108.24, 100.78, 83.83, 79.56, 55.52, 52.14, 28.20, 24.57, 24.52; (The carbon directly attached to the boron atom was not detected, likely due to quadrupole relaxation.) ESI-MS: $[M-Boc+H]^{\oplus}$ 350.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{32}{}^{10}BNO_8Na^{\oplus}$ 471.2150, found 471.2157; IR (KBr) *v* (cm^{-1}) 3389, 2979, 2925, 2853, 1698, 1506, 1446, 1369, 1249, 1165, 1039, 983, 932, 852; HPLC: Chiracel OD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 6.6 min (2*R*,3*R*)-**3p**, 8.3 min (2*S*,3*S*)-**3p**.

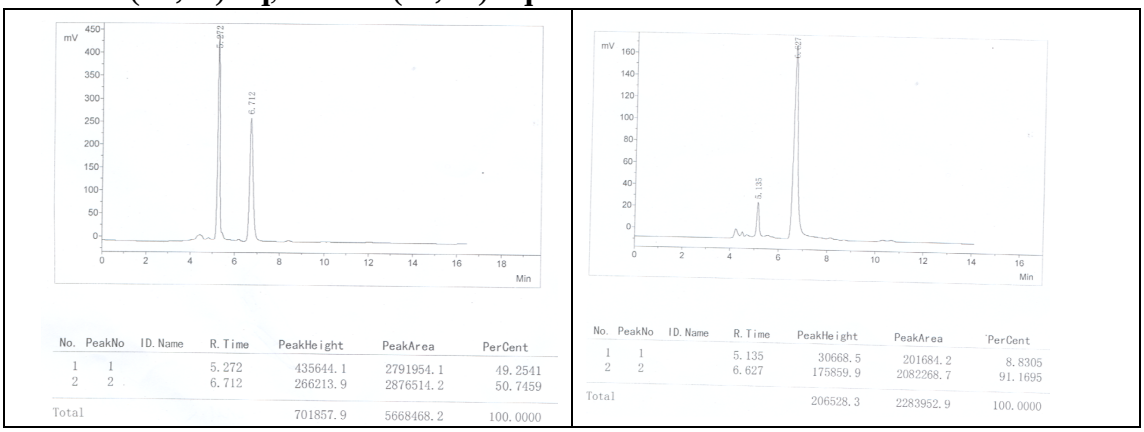


(2*S*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-5-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (*syn*-3q)

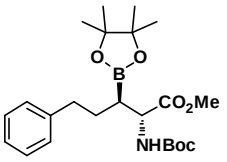


syn-3q

Colorless oil. 21.7 mg, 50% yield. $[\alpha]_D^{21.7}$ –3.7 (*c* 1.07, $CHCl_3$) for –82% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.26 (t, *J* = 7.6 Hz, 2H), 7.18–7.15 (m, 3H), 5.38 (brs, 1H), 4.51 (brs, 1H), 3.69 (s, 3H), 2.69–2.63 (m, 2H), 1.79–1.65 (m, 3H), 1.45 (s, 9H), 1.25 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.47, 155.77, 142.15, 128.42, 128.27, 125.75, 83.73, 79.58, 54.26, 52.05, 34.99, 29.66, 28.34, 24.84, 24.56; ESI-MS: $[M+Na]^{\oplus}$ 456.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{23}H_{36}{}^{10}BNO_6Na^{\oplus}$ 455.2564, found 455.2568; IR (KBr) *v* (cm^{-1}) 3432, 2978, 2928, 2856, 1718, 1498, 1456, 1371, 1284, 1168, 850, 701; HPLC: Phenomenex Lux 5u Cellulose-4 (PC-4) Column; detected at 214 nm; n-hexane / *i*-propanol = 70/30; flow rate = 0.7 ml/min; Retention time: 5.1 min (2*R*,3*S*)-**3q**, 6.6 min (2*S*,3*R*)-**3q**.

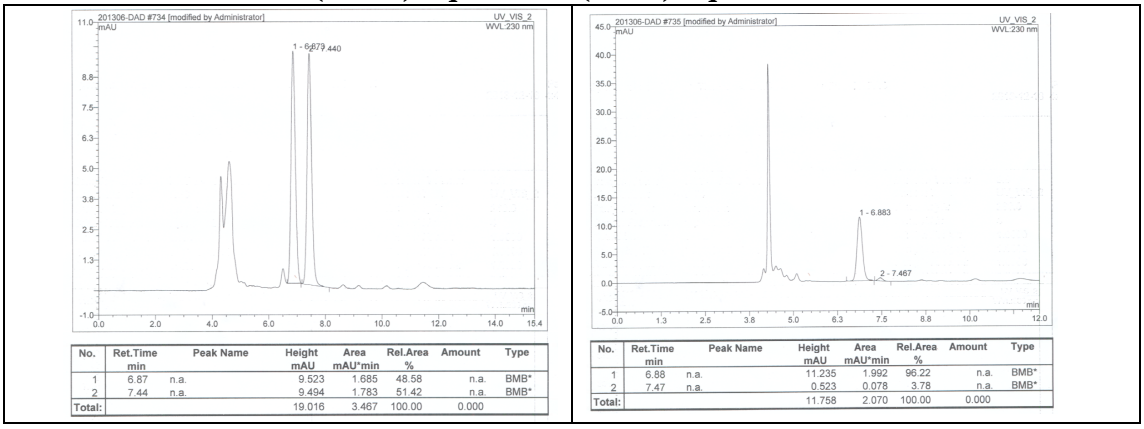


(2*R*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-5-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (*anti*-3q)



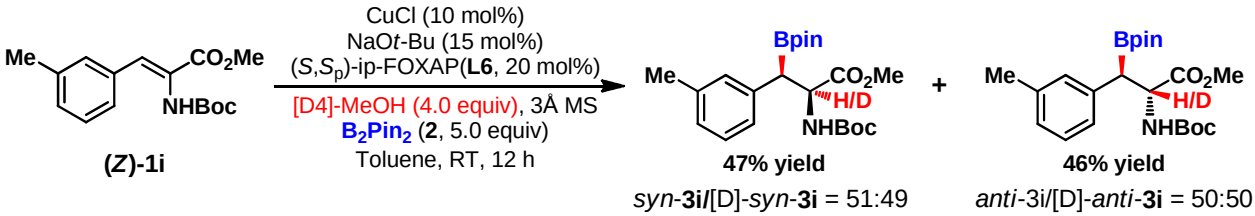
anti-3q

Colorless oil. 21.7 mg, 50% yield. $[\alpha]_D^{21.7}$ –4.9 (*c* 0.92, $CHCl_3$) for –92% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.26 (t, *J* = 7.6 Hz, 2H), 7.18–7.15 (m, 3H), 5.25 (brs, 1H), 4.47 (brs, 1H), 3.68 (s, 3H), 2.76–2.69 (m, 1H), 2.61–2.54 (m, 1H), 1.89–1.79 (m, 1H), 1.62 (brs, 2H), 1.43 (s, 9H), 1.27 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 173.46, 155.43, 142.25, 128.54, 128.37, 125.86, 83.77, 79.72, 54.68, 52.11, 35.09, 29.30, 28.43, 25.09, 24.76; ESI-MS: $[M+Na]^{\oplus}$ 456.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{23}H_{36}{}^{10}BNO_6Na^{\oplus}$ 455.2564, found 455.2565; IR (KBr) *v* (cm^{-1}) 3427, 2979, 2927, 2854, 1716, 1498, 1381, 1266, 1167, 739, 702; HPLC: Phenomenex Lux 5u Cellulose-4 (PC-4) Column; detected at 230 nm; n-hexane / *i*-propanol = 90/10; flow rate = 0.7 ml/min; Retention time: 6.9 min (2*R*,3*R*)-**3q**, 7.5 min (2*S*,3*S*)-**3q**.



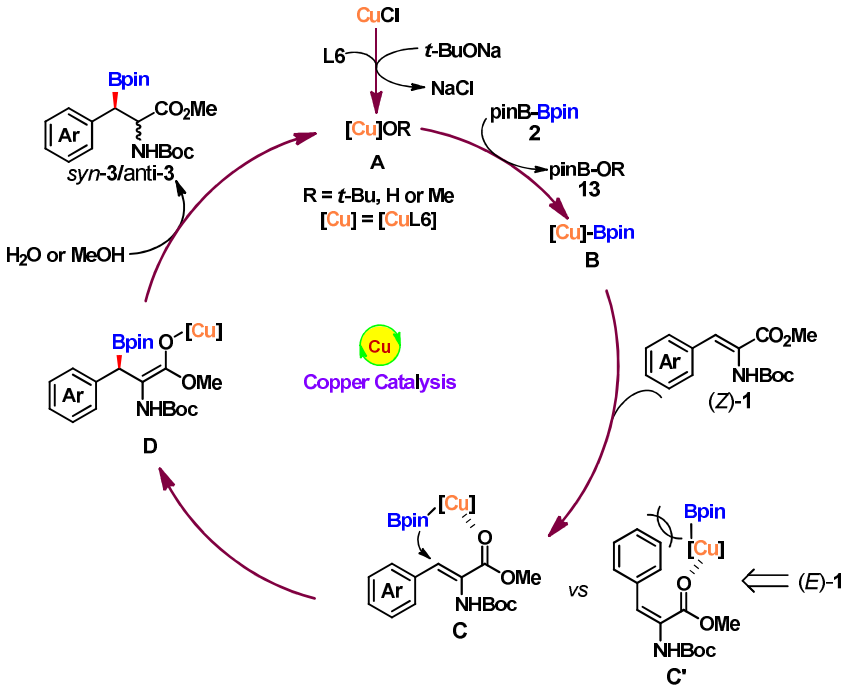
5. MECHANISM PRELIMINARY INVESTIGATION

To probe the '*hydrogen*' source of this conjugate hydroboration reaction, [D4]-methanol experiment was investigated.

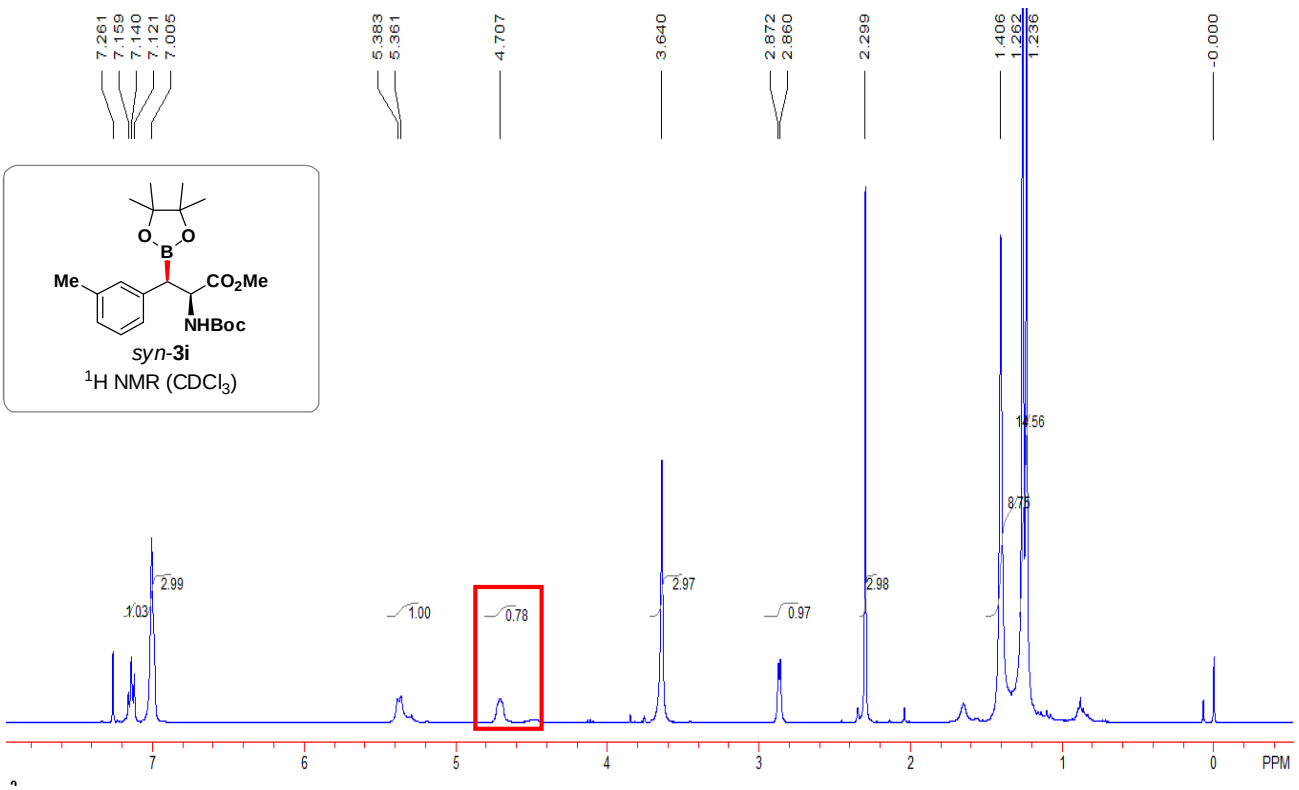


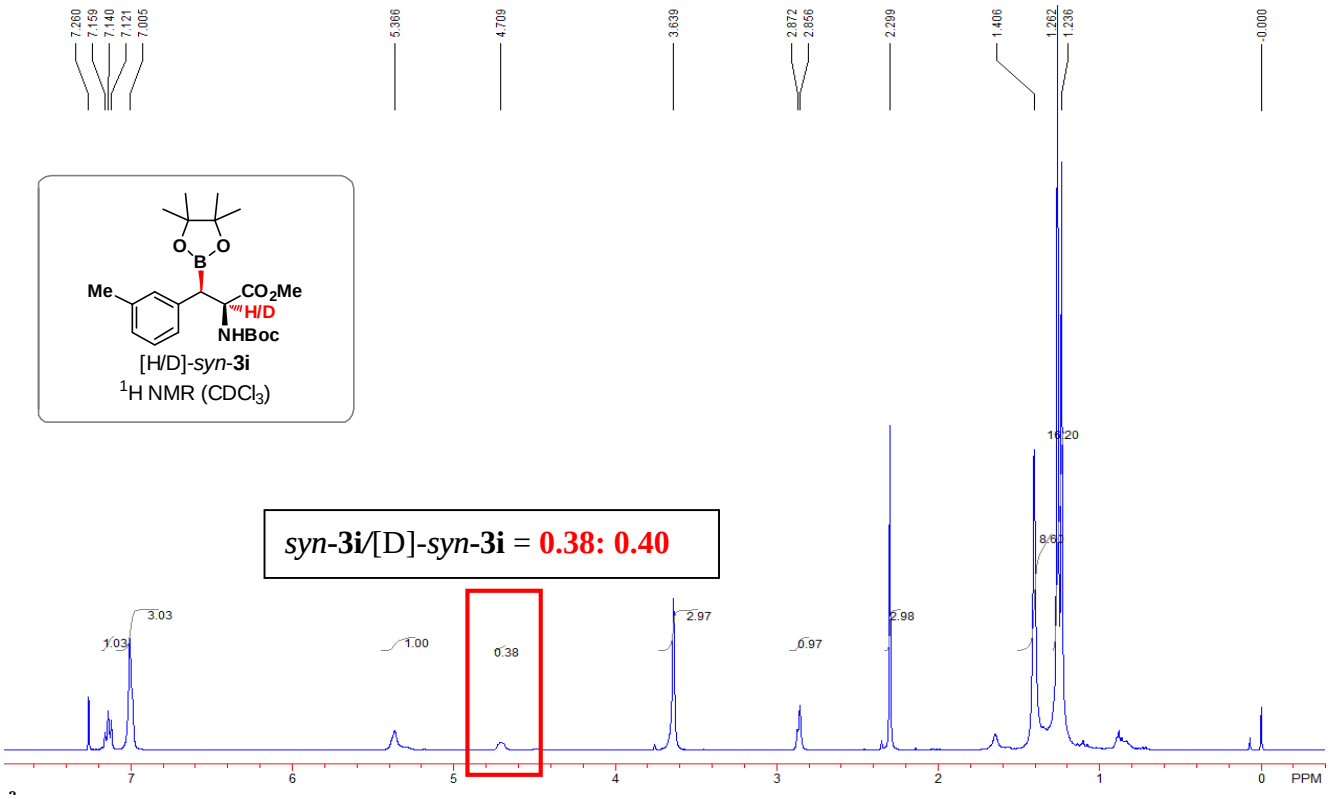
PROCEDURE: A dried Schlenk flask was charged with CuCl (1.0 mg, 0.01 mmol), ligand (*S*,*S*$_P$)-ip-FOXAP (**L6**, 10 mg, 0.02 mmol), B_2Pin_2 (**2**, 128 mg, 0.50 mmol), NaO*t*Bu (1.5 mg, 0.015 mmol) , 3Å molecular sieves (20 mg) and anhydrous toluene (0.5 mL) under argon atmosphere. After the mixture was stirred at room temperature for 30 min, a solution of substrate (*Z*)-**1i** (29 mg, 0.10 mmol) in anhydrous toluene (0.5 mL) was added, followed by anhydrous [D4]-MeOH (16 μL, 0.40 mmol). The resulting mixture was stirred at room temperature for 1 to 24 hours. Then the reaction mixture was quenched with water (5 mL), extracted with EtOAc (15 mL × 3) and washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash silica gel (300-400 mesh) chromatography to afford the desired products *syn*-**3i** and *anti*-**3i**. [Only 50% of deuterated product was observed with [D4]-MeOH (4 equiv) as additive, which showed that the trace water in reaction system also could provide the protons. The HSQC spectra (see page S101) of *syn*-**3i** could help to distinguish its hydrogen atoms between N-H and N-CH-.]

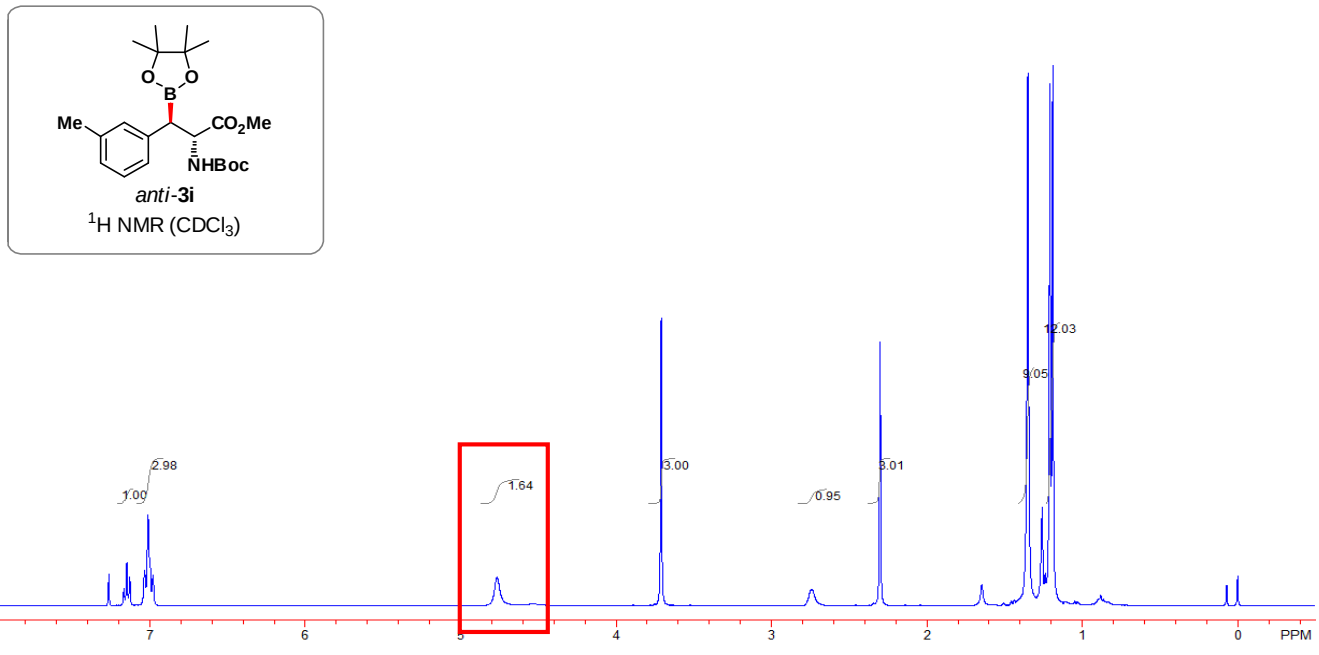
PROPOSED MECHANISM: Initiation of the reaction through the transmetallation of a (pinacolato)boron group (Bpin) from boron to copper species **A** generated the borylated copper **B**, which was coordinated with substrate (*Z*)-**1** and subsequently underwent conjugate addition to α,β-unsaturated double bond in the substrate (*Z*)-**1** to afford borylated enloate-copper intermediate **D**. [Due to the steric hindrance (see **C'**), the conjugate addition of (*E*)-**1** was difficult to occur.] The intermediate **D** was readily protonated by trace water or methanol to regenerate **A** and liberate the product **3**.

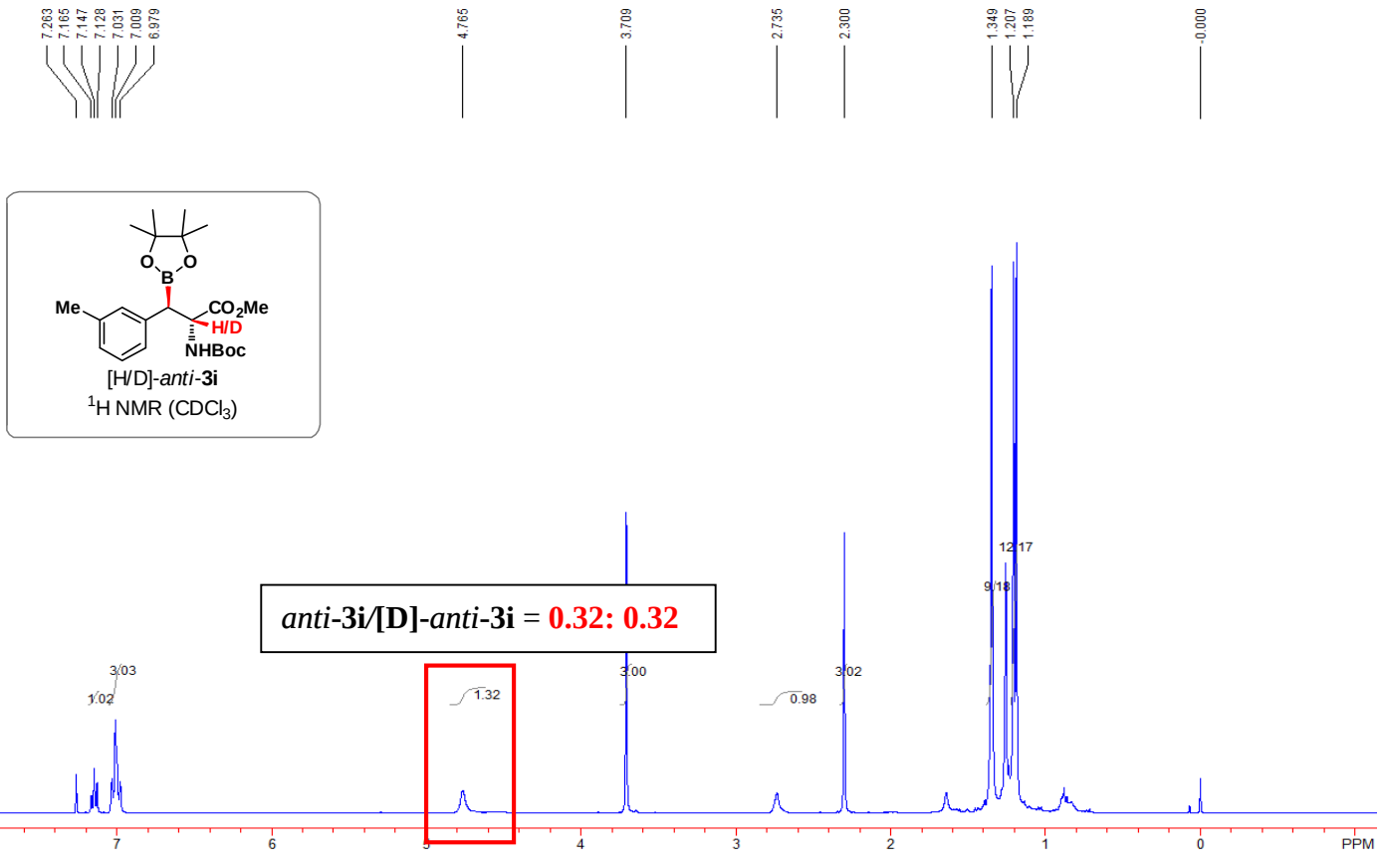


Scheme S5-1 Proposed mechanism


7.261
7.159
7.140
7.121
7.005
5.383
5.361
4.707
3.640
2.872
2.860
2.299
1.406
1.262
1.236
-0.000
Me
CO2Me
NHBoc
syn-3i
1H NMR (CDCl3)
14.56
8.75
2.99
1.03
1.00
0.78
2.97
0.97
2.98
PPM

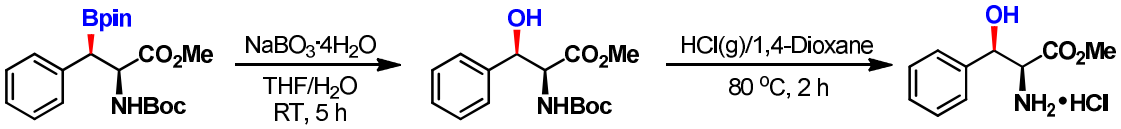

7.260
7.159
7.140
7.121
7.005
5.366
4.709
3.639
2.872
2.856
2.299
1.406
1.262
1.236
-0.000
Me
CO2Me
H/D
NHBoc
[H/D]-syn-3i
1H NMR (CDCl3)
syn-3i/[D]-syn-3i = 0.38: 0.40
16.20
8.62
3.03
1.03
1.00
0.38
2.97
0.97
2.98
PPM


7.262
7.166
7.147
7.128
7.032
7.010
6.978
4.766
3.708
2.742
2.300
1.349
1.207
1.189
0.000
Me
CO2Me
NHBoc
anti-3i
1H NMR (CDCl3)
2.98
1.00
1.64
3.00
0.95
3.01
12.03
9.05
8
7
6
5
4
3
2
1
0
PPM


7.263
7.165
7.147
7.128
7.031
7.009
6.979
4.765
3.709
2.735
2.300
1.349
1.207
1.189
0.000
Me
CO2Me
H/D
NHBoc
[H/D]-anti-3i
1H NMR (CDCl3)
anti-3i/[D]-anti-3i = 0.32: 0.32
3.03
1.02
1.32
3.00
0.98
3.02
12.17
9.18
8
7
6
5
4
3
2
1
0
PPM

6. TRANSFORMATION OF THE HYDROBORATION PRODUCTS

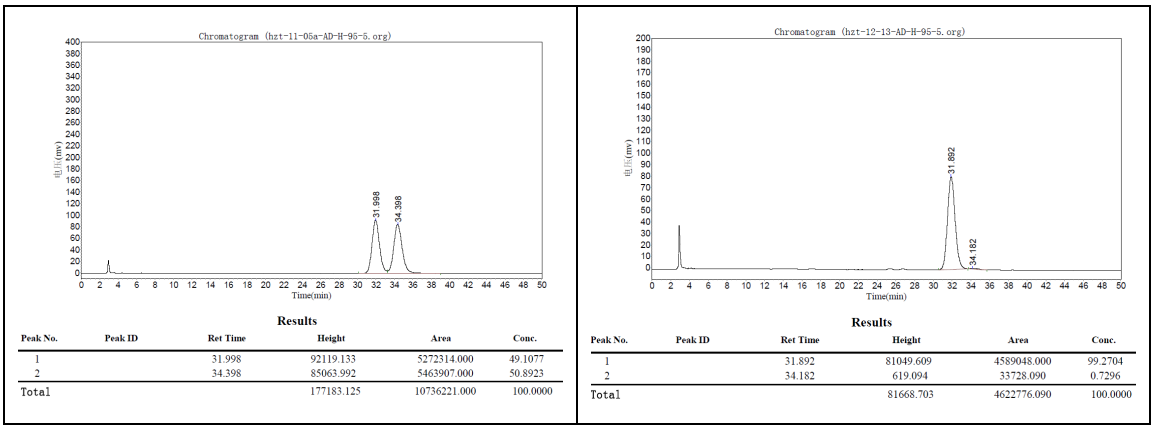
6.1 The Transformation of Hydroboration Product *syn*-3a.



***syn*-3a** (97% *ee*) **4a** (85% yield, 98% *ee*) **5a** (95% yield)

(2*S*,3*R*)-Methyl 2-((*tert*-butoxycarbonyl)amino)-3-hydroxy-3-phenylpropanoate (4a)[1]

To a solution of ***syn*-3a** (55 mg, 0.136 mmol) in THF/H_2O (1:1, 3 mL) was added $NaBO_3$•$4H_2O$ (104 mg, 5.0 equiv) and the reaction mixture was stirred at room temperature for 5 hours. Then it was diluted with H_2O (10 mL) and extracted with ethyl acetate (15 mL ×3). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate eluent (3:1) to afford the desired product **4a** (34.1 mg, 85% yield) as white solid. $[\alpha]_D^{25.3}$ –24.4 (*c* 1.45, $CHCl_3$) for 98% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37–7.28 (m, 5H), 5.35 (brs, 1H), 5.21 (s, 1H), 4.53 (brs, 1H), 3.74 (s, 3H), 3.02 (s, 1H), 1.32 (s, 9H); ESI-MS: $[M+Na]^{\oplus}$ 318.1; HPLC: Chiracel AD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 95/5; flow rate = 1.0 mL/min; Retention time: 31.9 min (2*S*, 3*R*)-**4a**, 34.2 min (2*R*,3*S*)-**4a**.



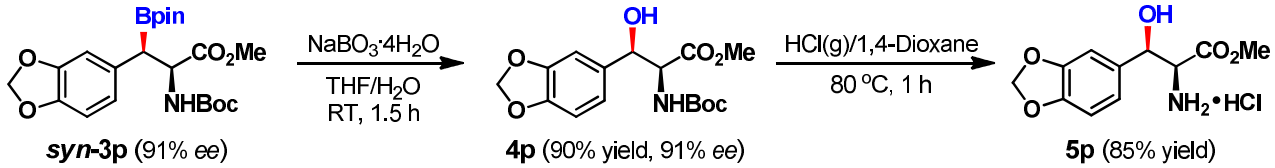
(2*S*,3*R*)-Methyl 2-amino-3-hydroxy-3-phenylpropanoate hydrochloride salt (5a)[2]

To a 1,4-dioxane (4 mL) solution of HCl (gas, 4M) was added **4a** (53.7 mg, 0.182 mmol). The resulting mixture was stirred at 80 °C for 2 h and concentrated to afford the desired product **5a** (40 mg, 95% yield) as faint yellow solid. $[\alpha]_D^{25.5}$ –31.1 (*c* 0.80, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 7.51–7.39 (m, 5H), 5.28 (d, *J* = 4.8 Hz, 1H), 4.26 (d, *J* = 4.4 Hz, 1H), 3.82 (s, 3H); ESI-MS: $[M-HCl+H]^{\oplus}$ 196.1.

[1] (a) Okiko M.; Hiroshi A.; Takeaki N. *Chem. Pharm. Bull.*, **2005**, *53*, 355. (b) Crich, D.; Banerjee, A. *J. Org. Chem.* **2006**, *71*, 7106.

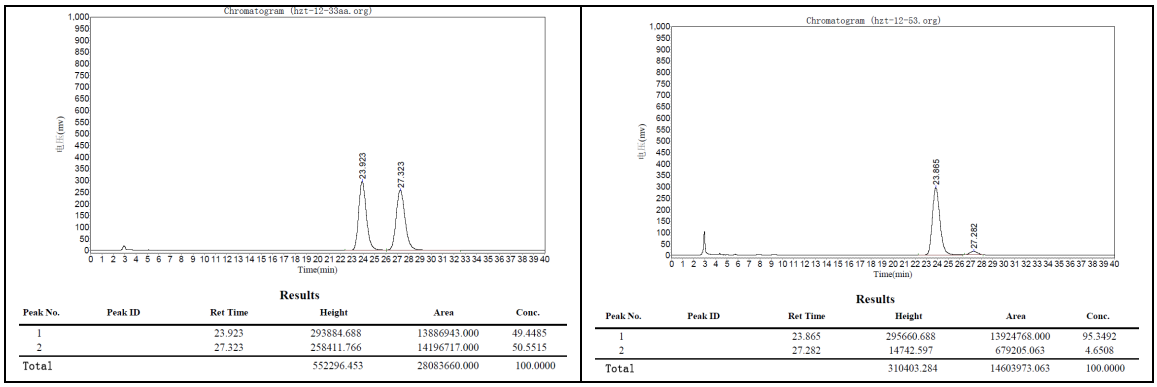
[2] Sparr, C.; Gilmour, R. *Angew. Chem. Int. Ed.* **2010,** *49*, 6520.

6.2 The Transformation of Hydroboration Product *syn*-3p.



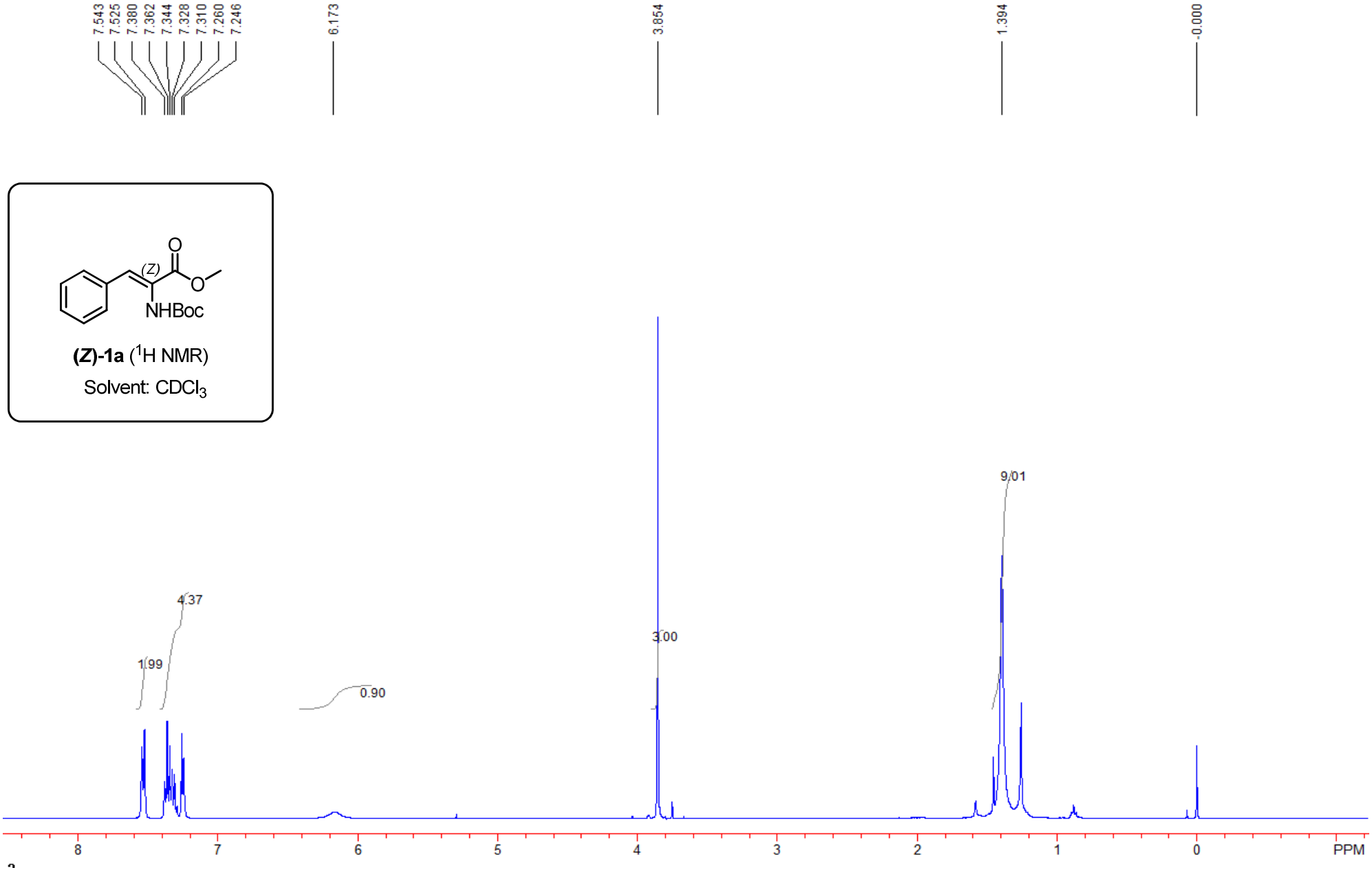
***syn*-3p** (91% *ee*) **4p** (90% yield, 91% *ee*) **5p** (85% yield)

(2*S*,3*R*)-Methyl 3-(benzo[d][1,3]dioxol-5-yl)-2-((*tert*-butoxycarbonyl)amino)-3-hydroxypropanoate (4p) To a solution of ***syn*-3p** (183 mg, 0.407 mmol) in THF/H_2O (1:1, 10mL) was added $NaBO_3$•$4H_2O$ (310 mg, 5.0 equiv) and the reaction mixture was stirred at room temperature for 1.5 hours. Then it was diluted with H_2O (20 mL) and extracted with ethyl acetate (20 mL × 3). The combined organic phases were washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using n-hexane/ethyl acetate eluent (3:1) to afford the desired product **4p** (124 mg, 90% yield) as colorless oil. $[\alpha]_D^{23.4}$ –13.2 (*c* 1.00, $CHCl_3$) for 91% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.88 (s, 1H), 6.79 (dd, *J* = 18.0 Hz, *J* = 8.0 Hz, 2H), 5.93 (d, *J* = 6.8 Hz, 2H), 5.34 (brs, 1H), 5.12 (s, 1H), 4.45 (brs, 1H), 3.75 (s, 3H), 2.85 (brs, 1H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.36, 155.69, 147.59, 147.16, 134.05, 119.43, 107.99, 106.68, 100.96, 80.06, 73.45, 59.59, 52.47, 28.11; ESI-MS: $[M+Na]^{\oplus}$ 362.0; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{21}NO_7Na^{\oplus}$ 362.1210, found 362.1210; IR (KBr) ν (cm^{-1}) 3401, 2978, 2923, 1698, 1505, 1492, 1444, 1368, 1251, 1163, 1039, 934, 855; HPLC: Chiracel AD-H Column (250 mm); detected at 210 nm; n-hexane / *i*-propanol = 90/10; flow rate = 1.0 mL/min; Retention time: 23.9 min (2*S*,3*R*)-**4p**, 27.3 min (2*R*,3*S*)-**4p**.



(2*S*,3*R*)-Methyl-2-amino-3-(benzo[d][1,3]dioxol-5-yl)-3-hydroxypropanoate hydrochloride salt (5p) To a 1,4-dioxane (4 mL) solution of HCl (gas, 4M) was added **4p** (43 mg, 0.127 mmol). The resulting mixture was stirred at 80 °C for 1 h and concentrated to afford the desired product **5p** (29.5 mg, 85% yield) as faint yellow solid. mp 80.1–82.0 °C. $[\alpha]_D^{23.8}$ –10.9 (*c* 0.65, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 6.88 (s, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.87 (s, 2H), 5.06 (d, *J* =3.6 Hz, 1H), 4.08 (d, *J* = 3.6 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 169.10, 149.60, 149.26, 134.21, 120.76, 109.31, 107.45, 102.68, 71.92, 60.59, 53.69; ESI-MS: $[M-HCl+H]^{\oplus}$ 239.9; HRMS (FTMS-ESI): $[M-HCl+H]^{\oplus}$ calcd for $C_{11}H_{14}NO_5^{\oplus}$ 240.0866, found 240.0870; IR (KBr) ν (cm^{-1}) 3383, 2920, 1746, 1505, 1488, 1444, 1244, 1035, 929, 810.

7. ^{1}H NMR, ^{13}C NMR, HSQC COPIES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7.310
7.260
7.246
6.173
3.854
1.394
-0.000
(Z)-1a (1H NMR)
Solvent: CDCl3
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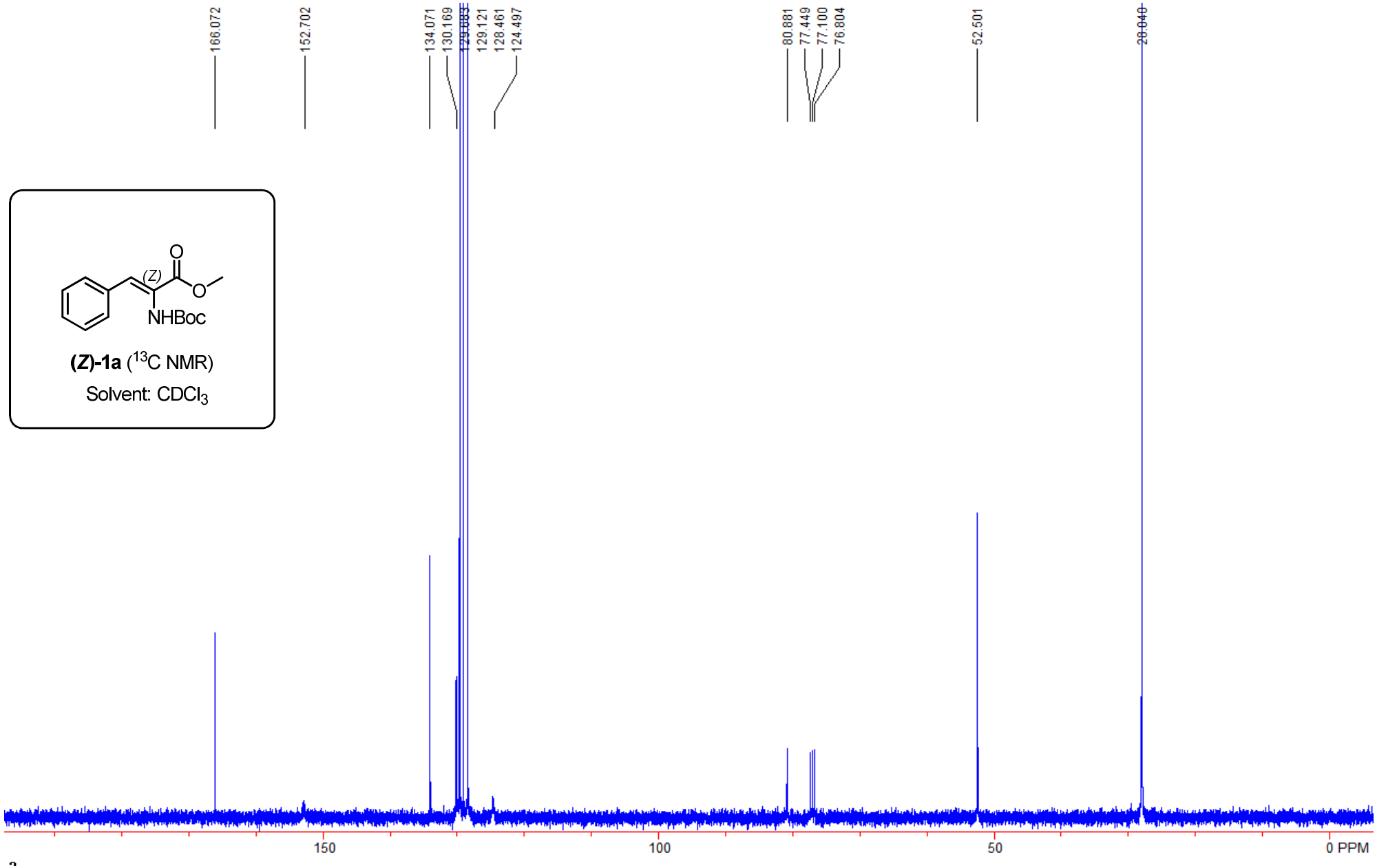
1.99
0.90
3.00
9.01
8
7
6
5
4
3
2
1
0
PPM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134.071
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129.121
128.461
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80.881
77.449
77.100
76.804
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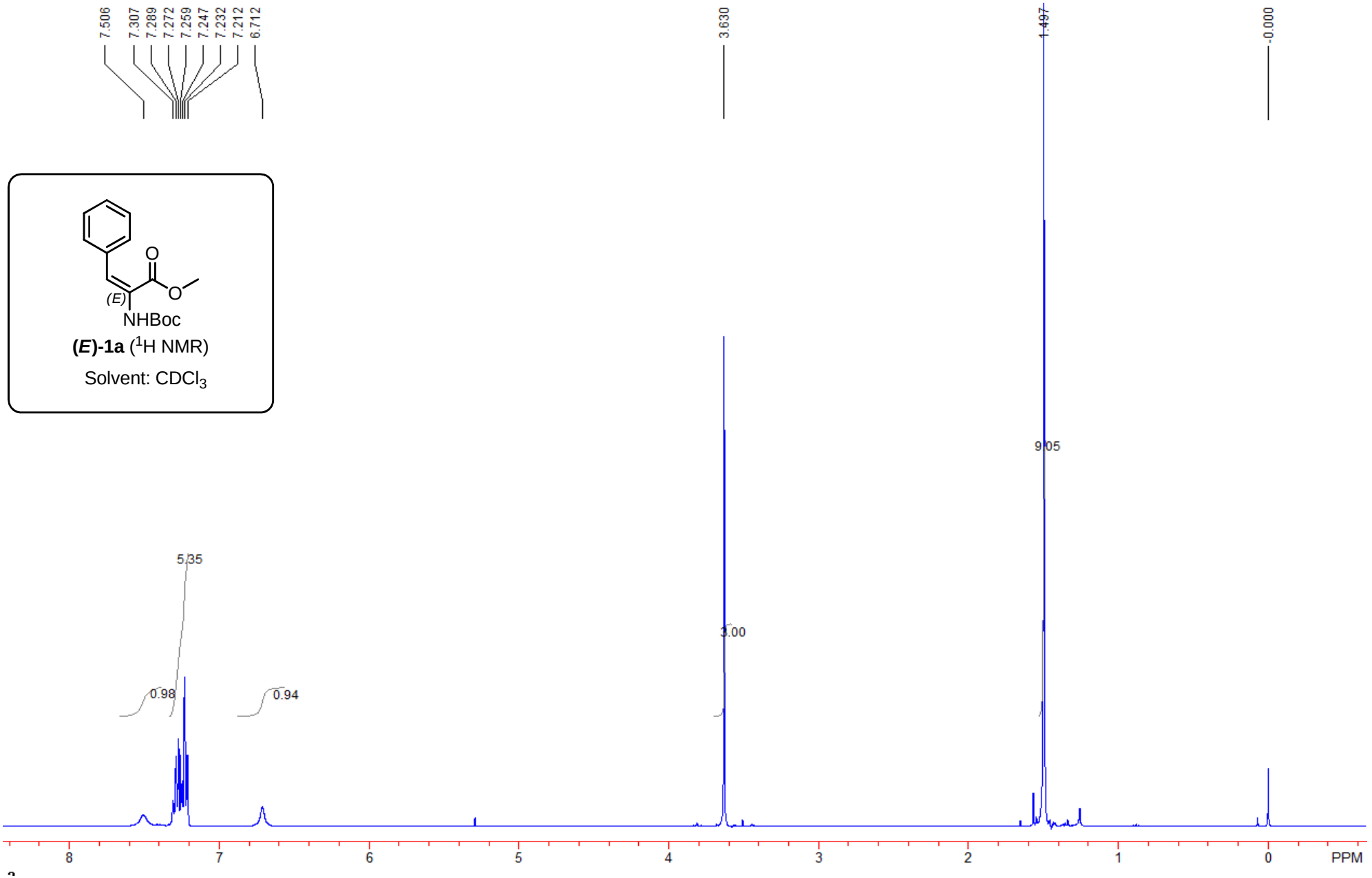
28.040
(Z)
O
O
NHBoc
(Z)-1a (13C NMR)
Solvent: CDCl3
150
100
50
0 PPM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7.272
7.259
7.247
7.232
7.212
6.712
3.630
1.497
-0.000
O
O
(E)
NHBoc
(E)-1a (1H NMR)
Solvent: CDCl3
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3.00
0.98
0.94
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7
6
5
4
3
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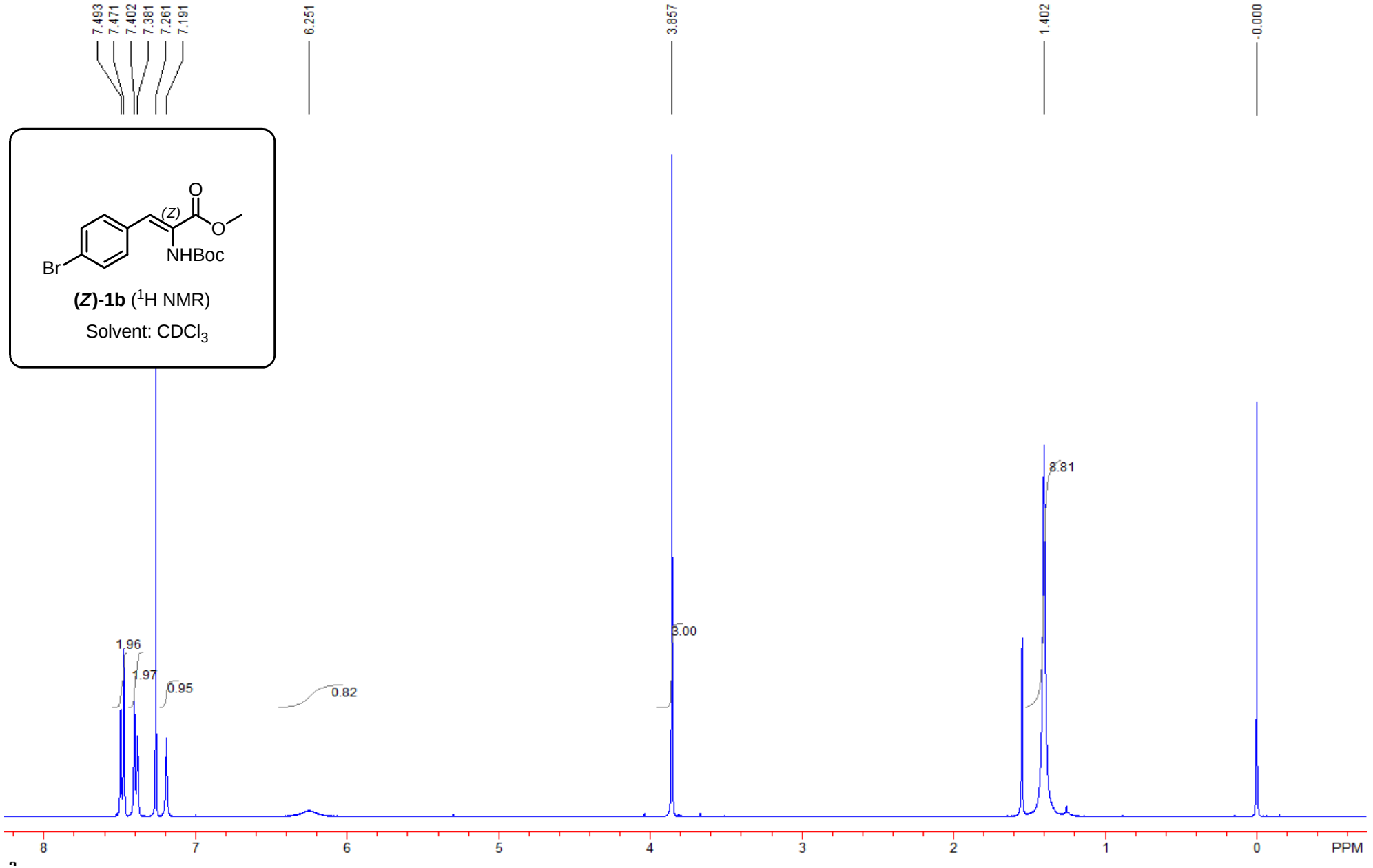
0
PPM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7.471
7.402
7.381
7.261
7.191
6.251
3.857
1.402
-0.000
(Z)
O
O
NHBoc
Br
(Z)-1b (1H NMR)
Solvent: CDCl3
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6
5
4
3
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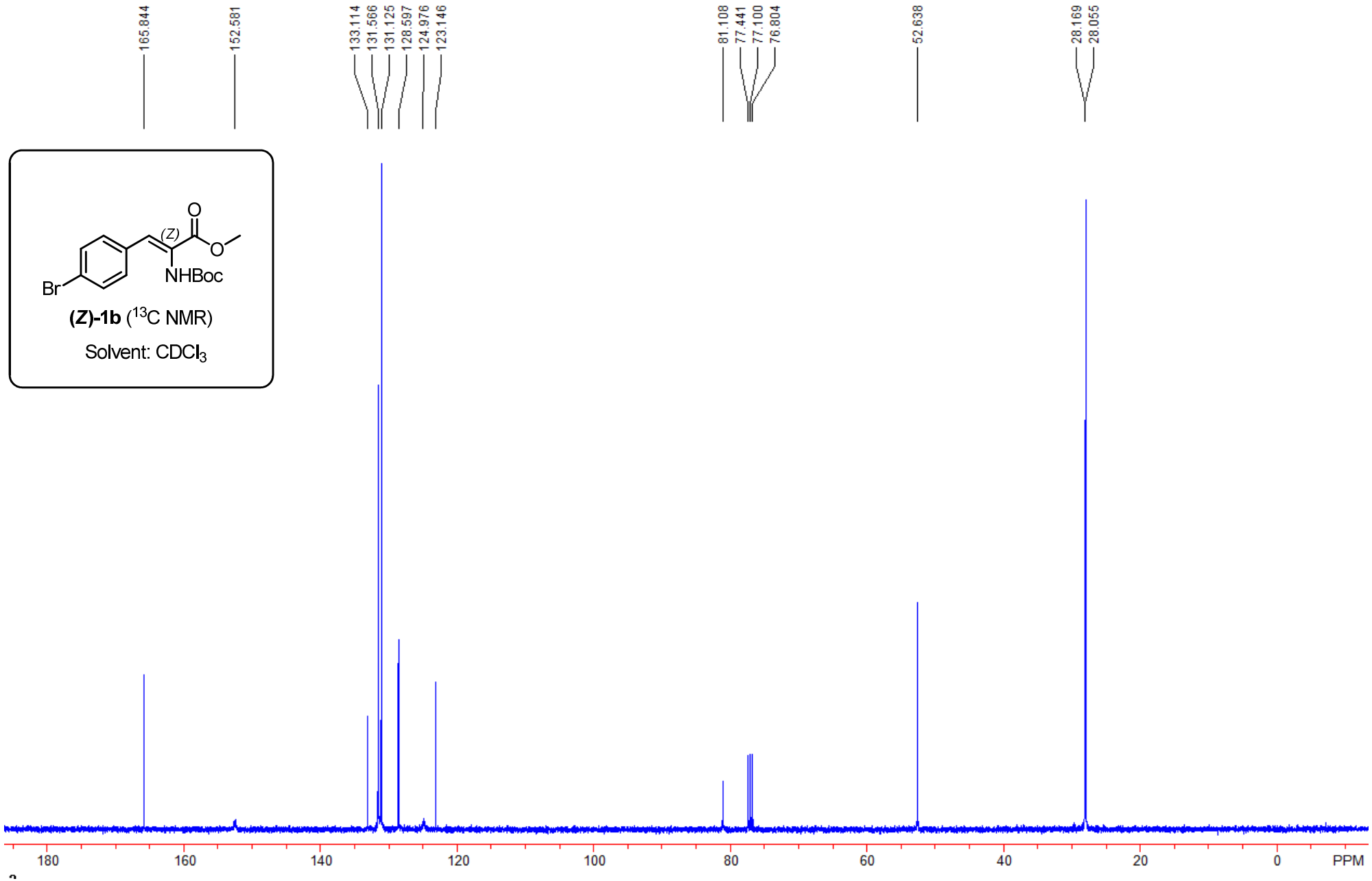
PPM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131.566
131.125
128.597
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77.100
76.804
52.638
28.169
28.055
O
(Z)
O
NHBoc
Br
(Z)-1b (13C NMR)
Solvent: CDCl3
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160
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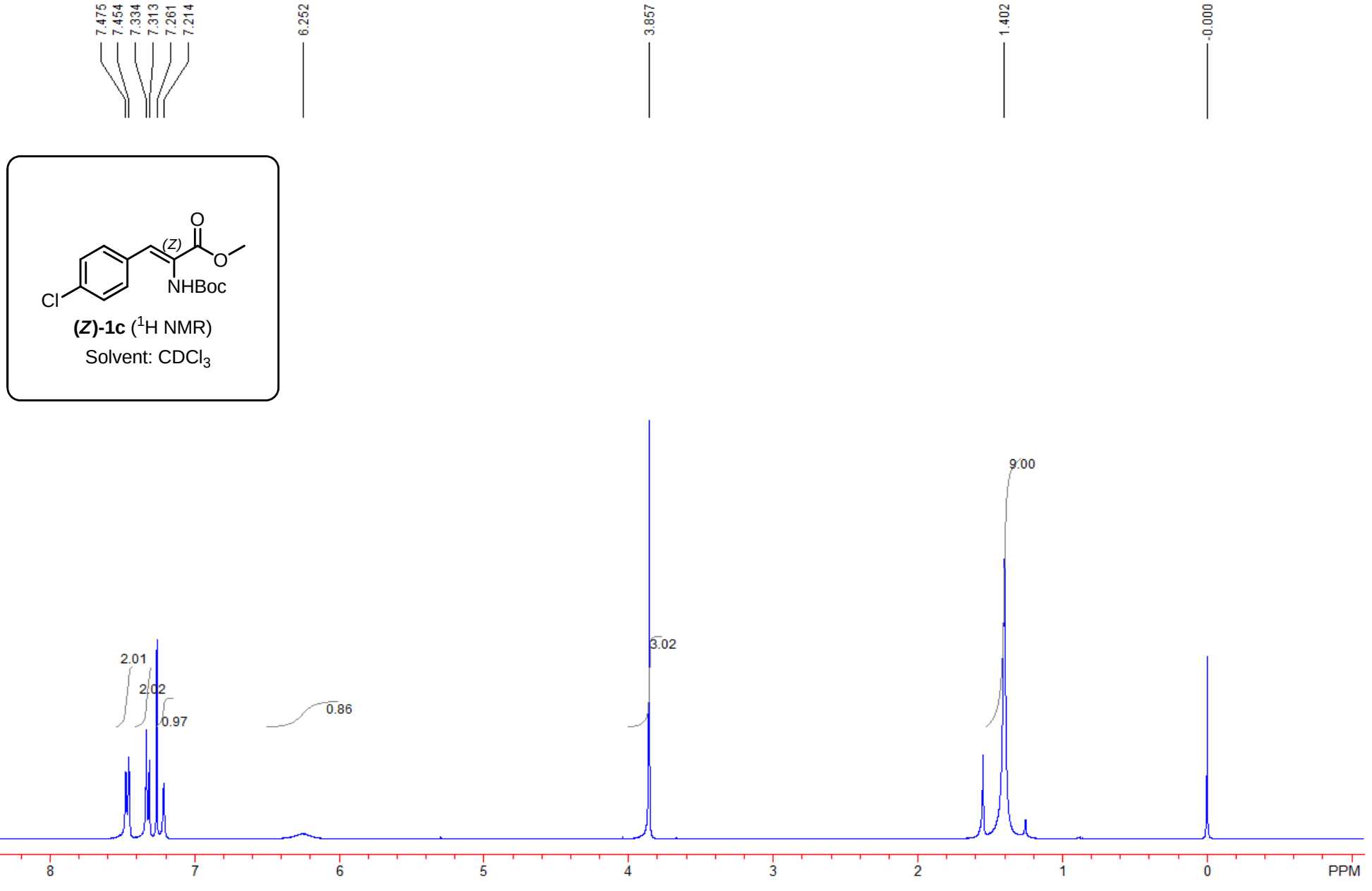
120
100
80
60
40
20
0
PPM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7.313
7.261
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6.252
3.857
1.402
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(Z)
O
NHBoc
Cl
(Z)-1c (1H NMR)
Solvent: CDCl3
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0.86
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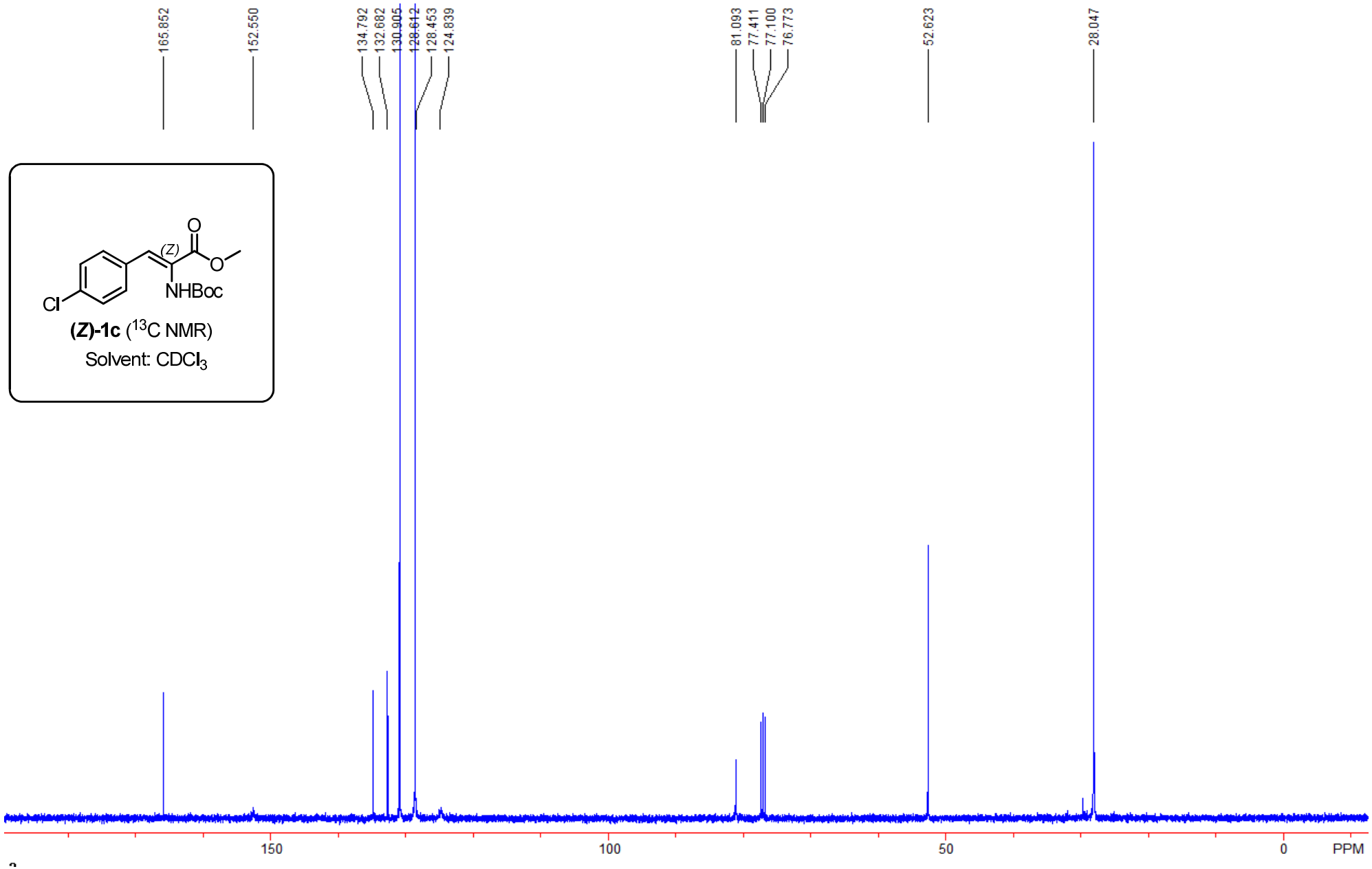
9.00
8
7
6
5
4
3
2
1
0
PPM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77.100
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52.623
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O
NHBoc
Cl
(Z)-1c (13C NMR)
Solvent: CDCl3
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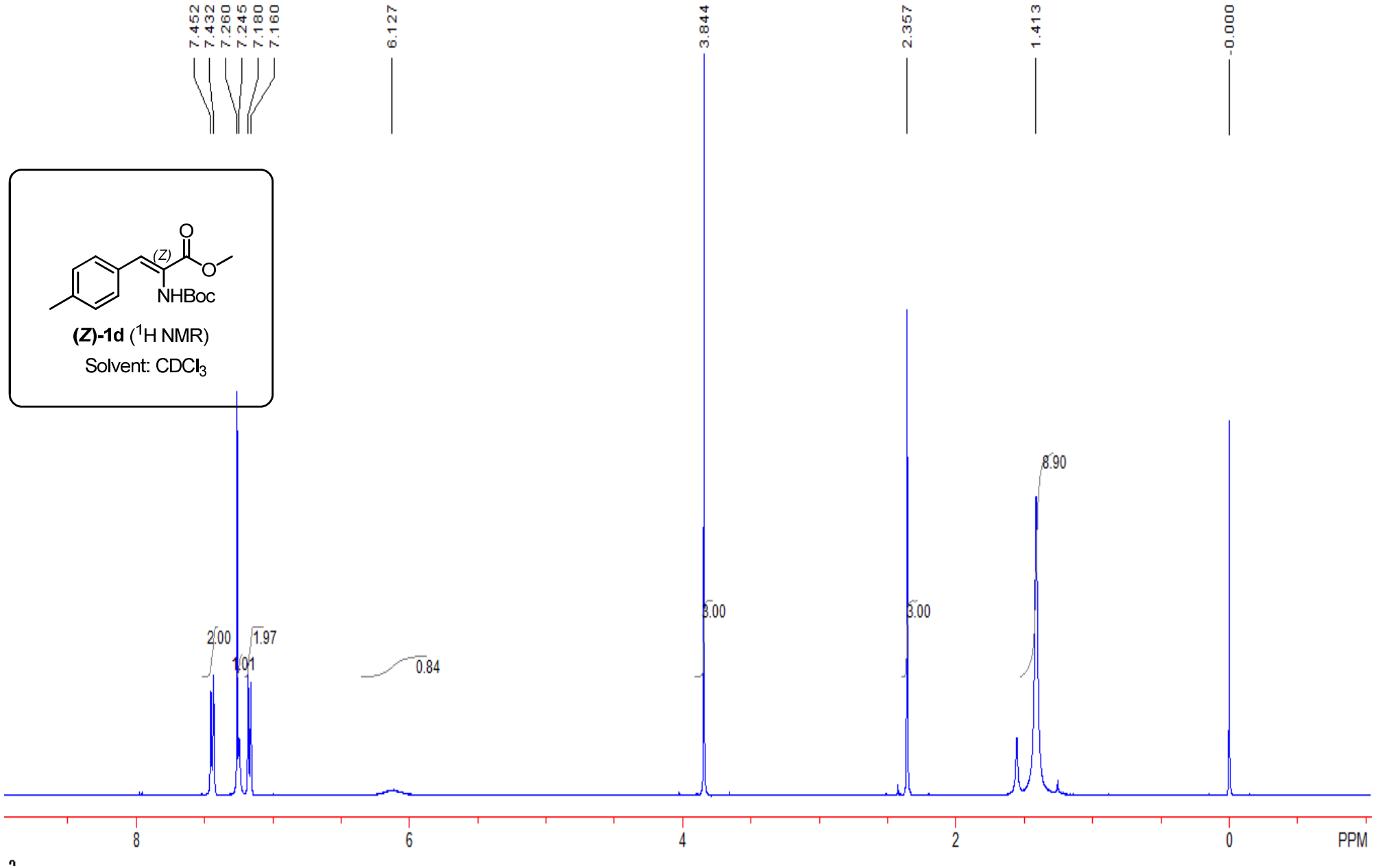
100
50
0
PPM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7.180
7.160
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3.844
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O
O
NHBoc
(Z)-1d (1H NMR)
Solvent: CDCl3
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1.01
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3.00
8.90
8
6
4
2
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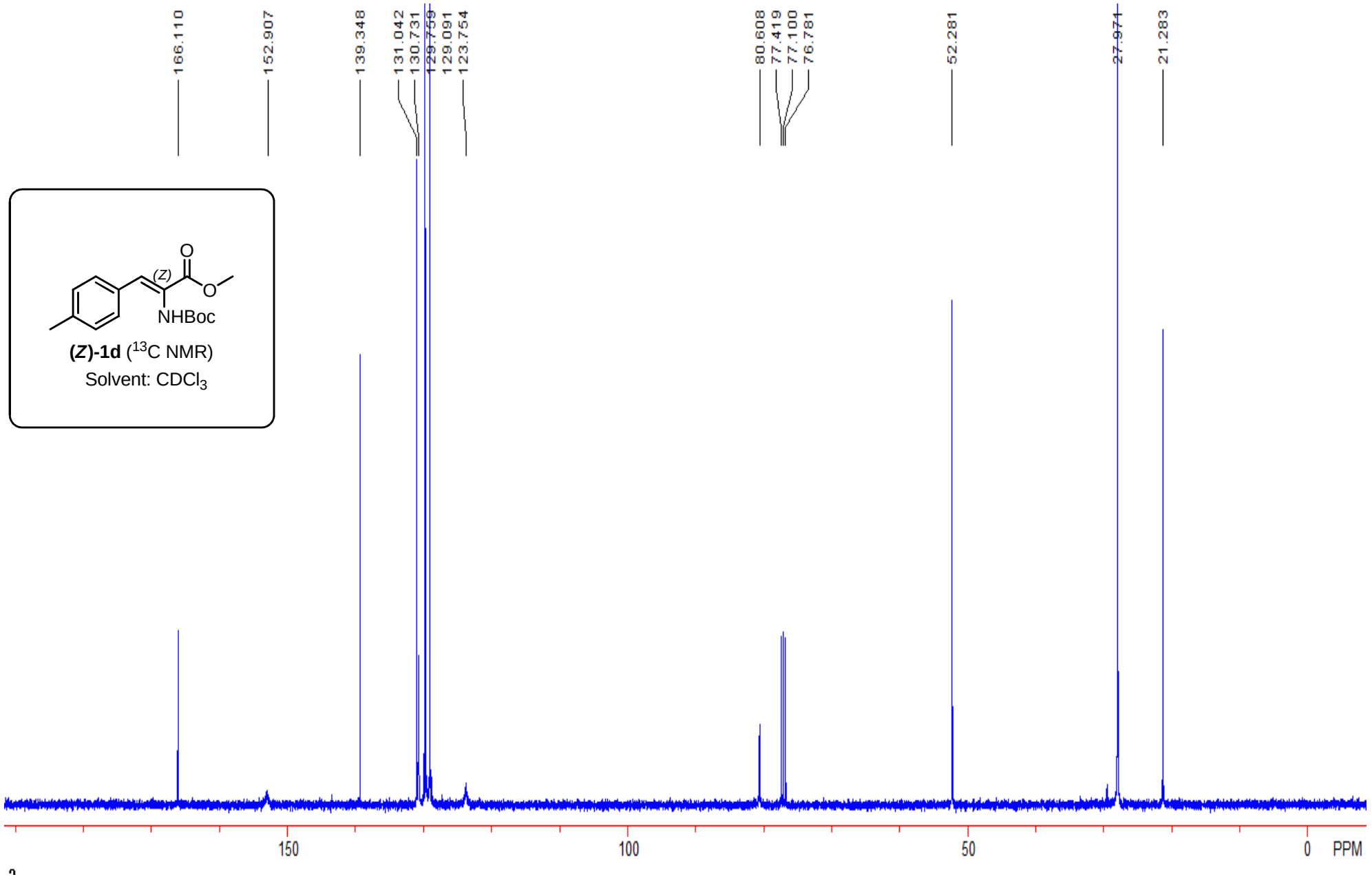
PPM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52.281
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21.283
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(Z)
O
NHBoc
(Z)-1d (13C NMR)
Solvent: CDCl3
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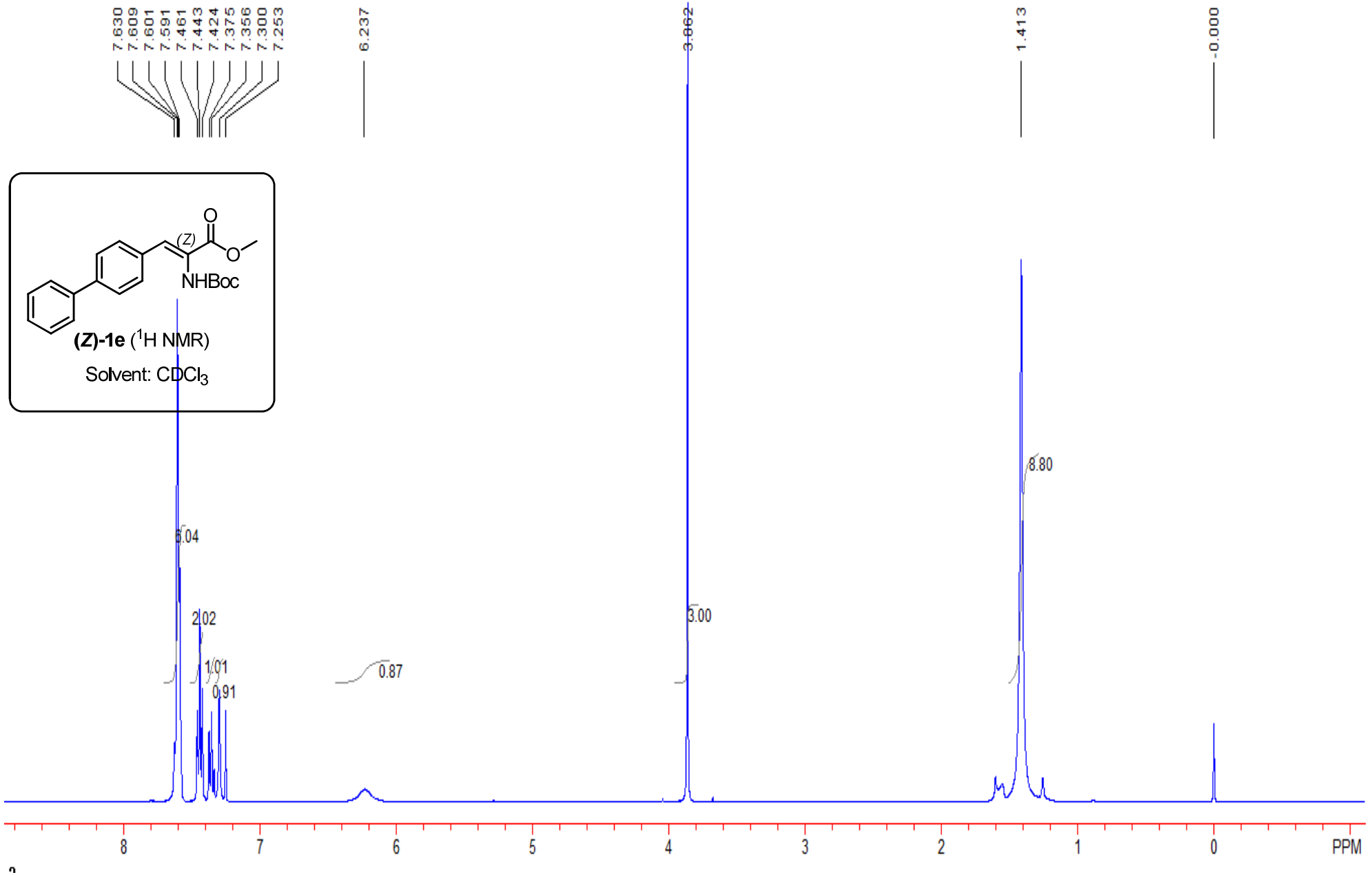
100
50
0
PPM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7.601
7.591
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7.443
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7.375
7.356
7.300
7.253
6.237
3.862
1.413
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O
NHBoc
(Z)-1e (1H NMR)
Solvent: CDCl3
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6
5
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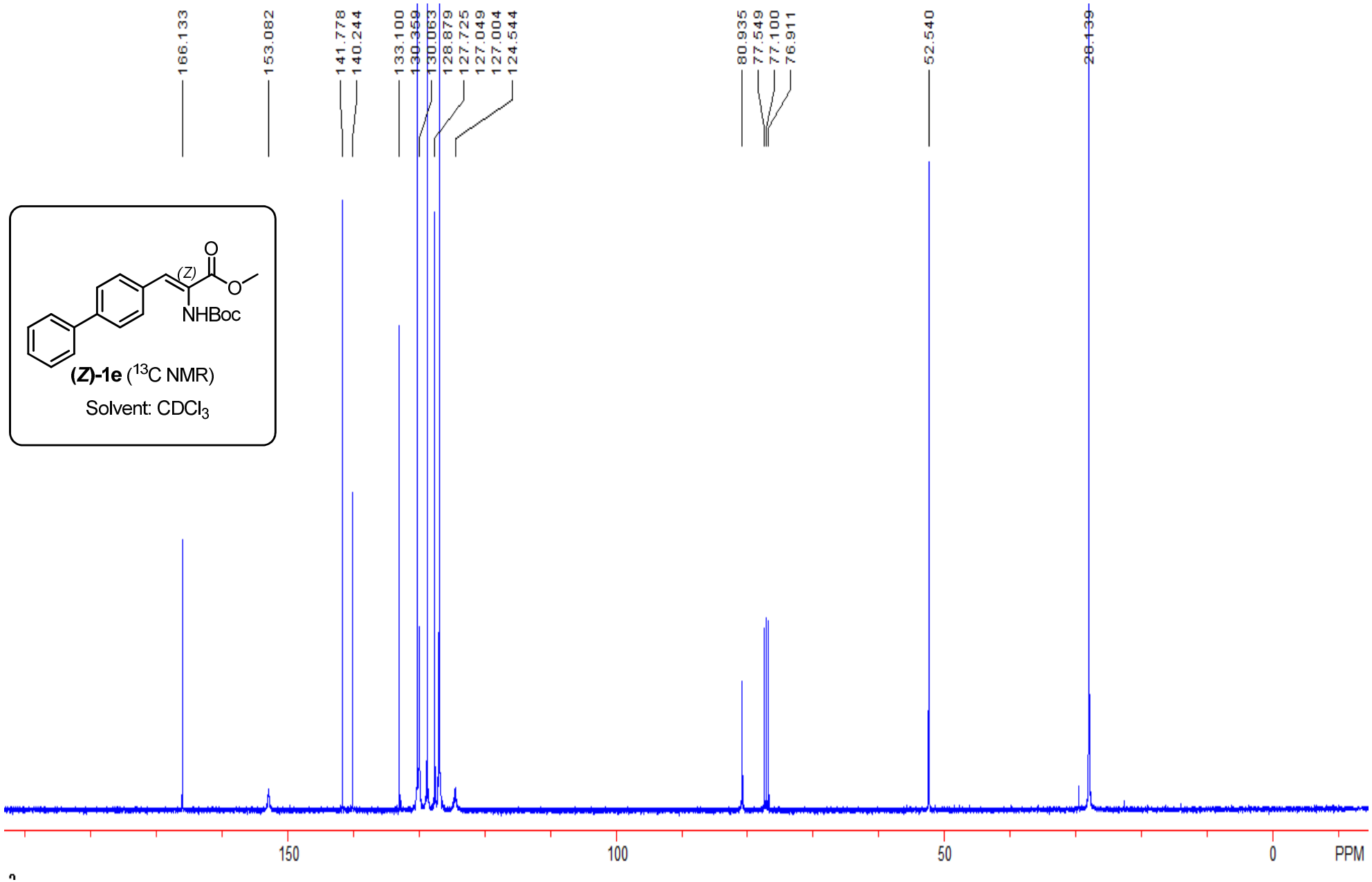
3
2
1
0
PPM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76.911
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O
O
NHBoc
(Z)-1e (13C NMR)
Solvent: CDCl3
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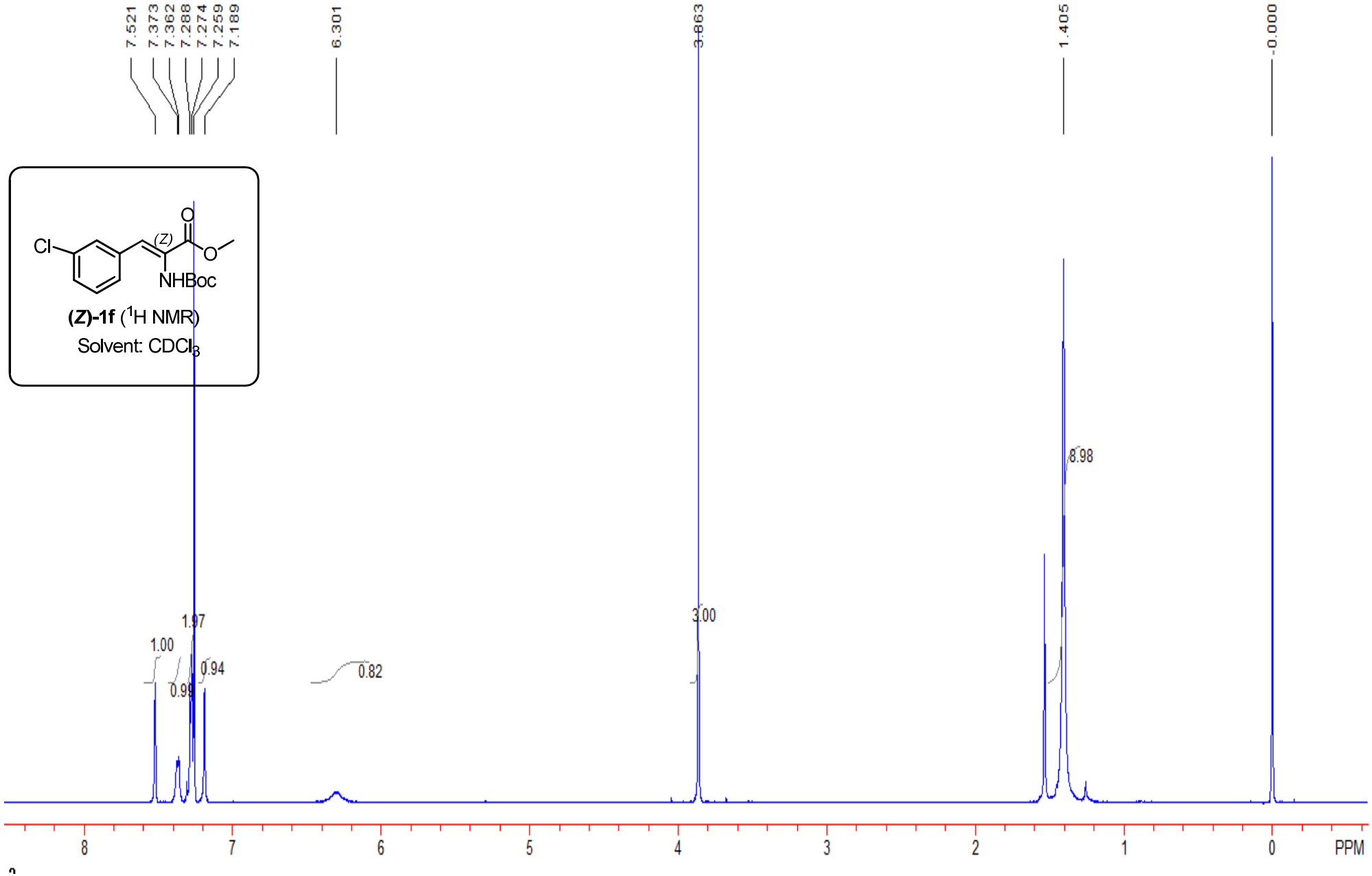
100
50
0
PPM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7.259
7.189
6.301
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-0.000
Cl
O
(Z)
O
NHBoc
(Z)-1f (1H NMR)
Solvent: CDCl3
1.00
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0.99
0.94
0.82
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8.98
8
7
6
5
4
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2
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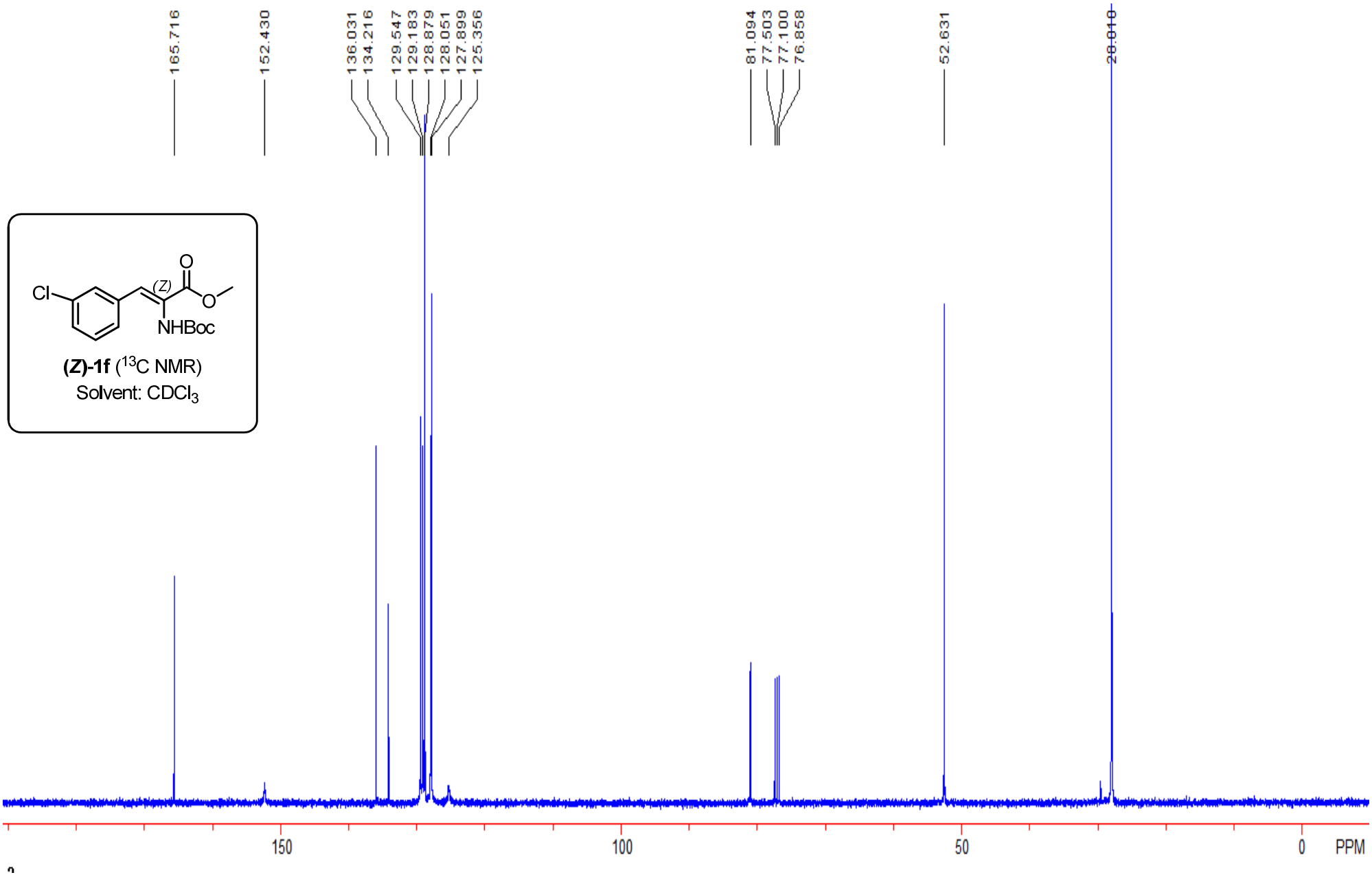
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77.100
76.858
52.631
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(Z)
O
O
NHBoc
(Z)-1f (13C NMR)
Solvent: CDCl3
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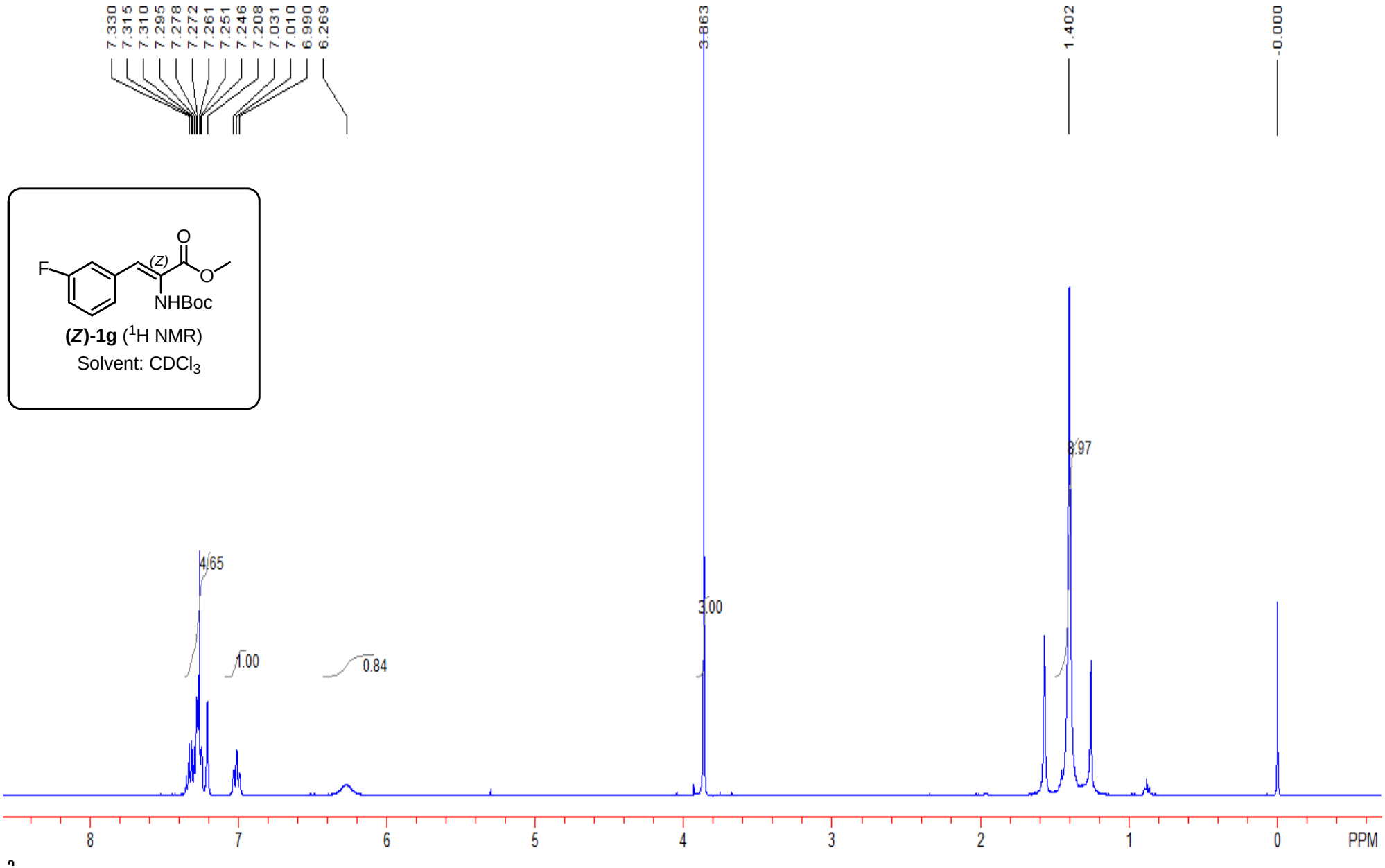
100
50
0
PPM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7.251
7.246
7.208
7.031
7.010
6.990
6.269
3.863
1.402
-0.000
F
(Z)
O
O
NHBoc
(Z)-1g (1H NMR)
Solvent: CDCl3
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6
5
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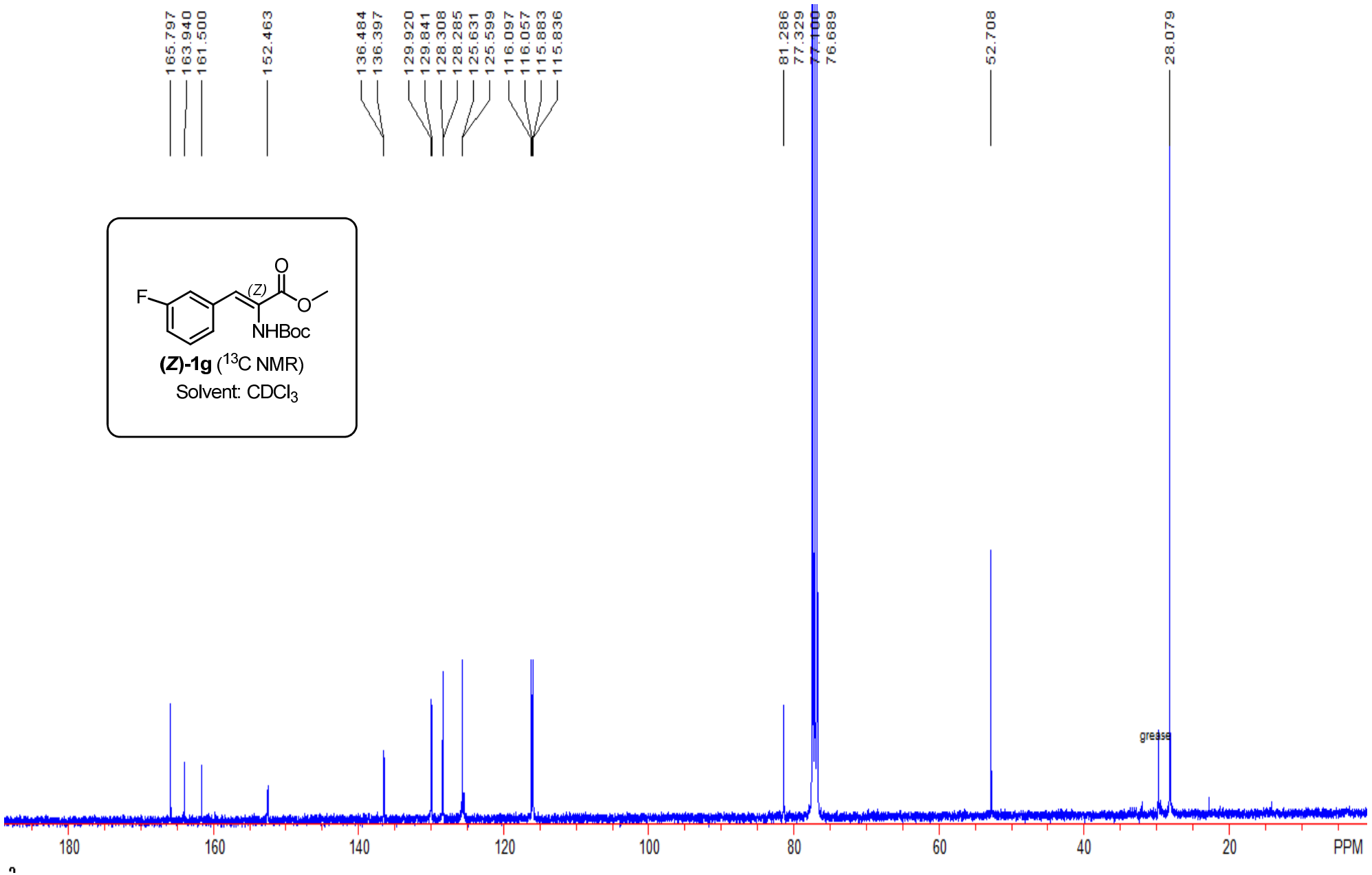
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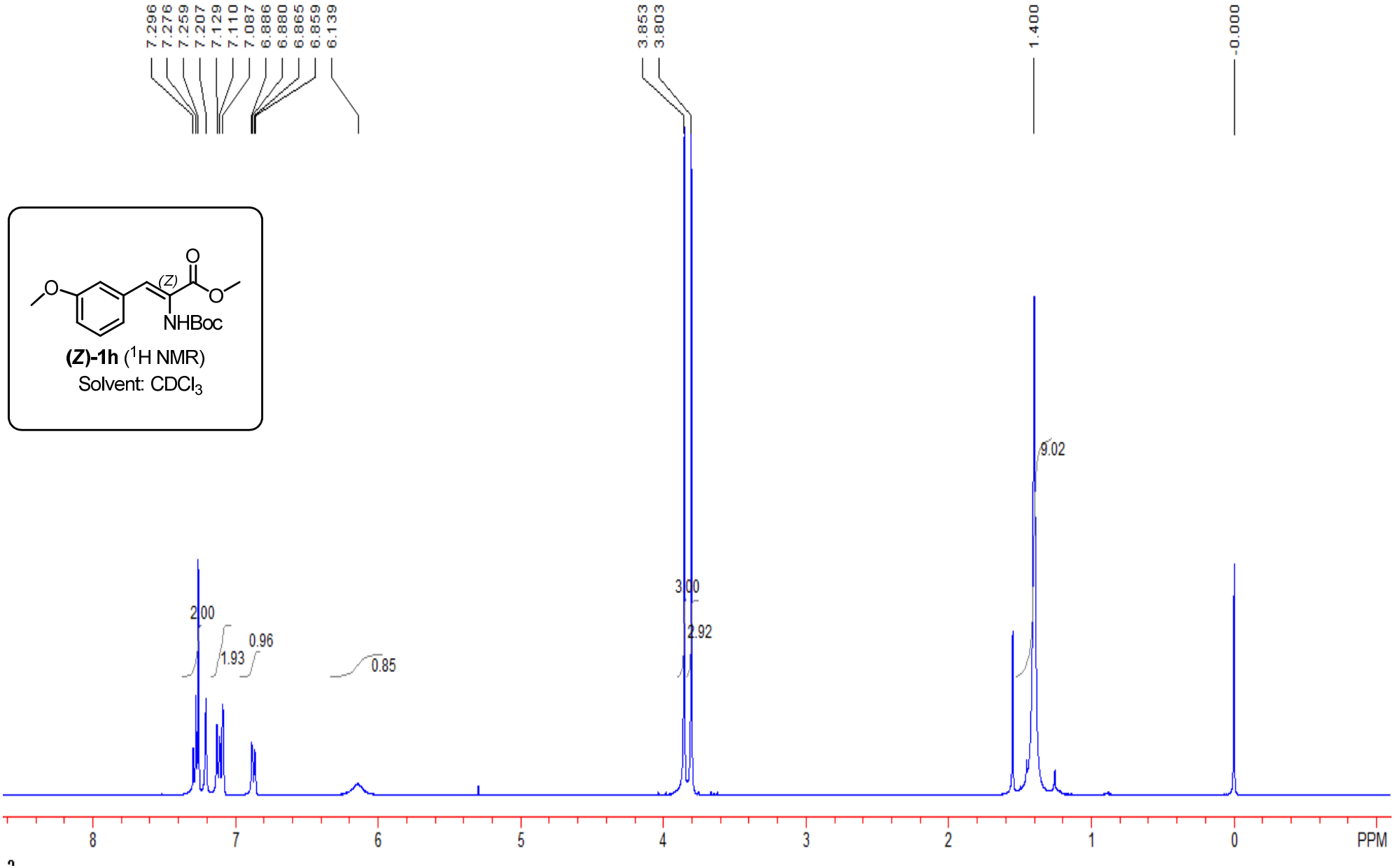
116.057
115.883
115.836
81.286
77.329
77.100
76.689
52.708
28.079
F
(Z)
O
O
NHBoc
(Z)-1g (13C NMR)
Solvent: CDCl3
grease
180
160
140
120
100
80
60
40
20
PPM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6.139
3.853
3.803
1.400
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(Z)
NHBoc
(Z)-1h (1H NMR)
Solvent: CDCl3
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3.00
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9.02
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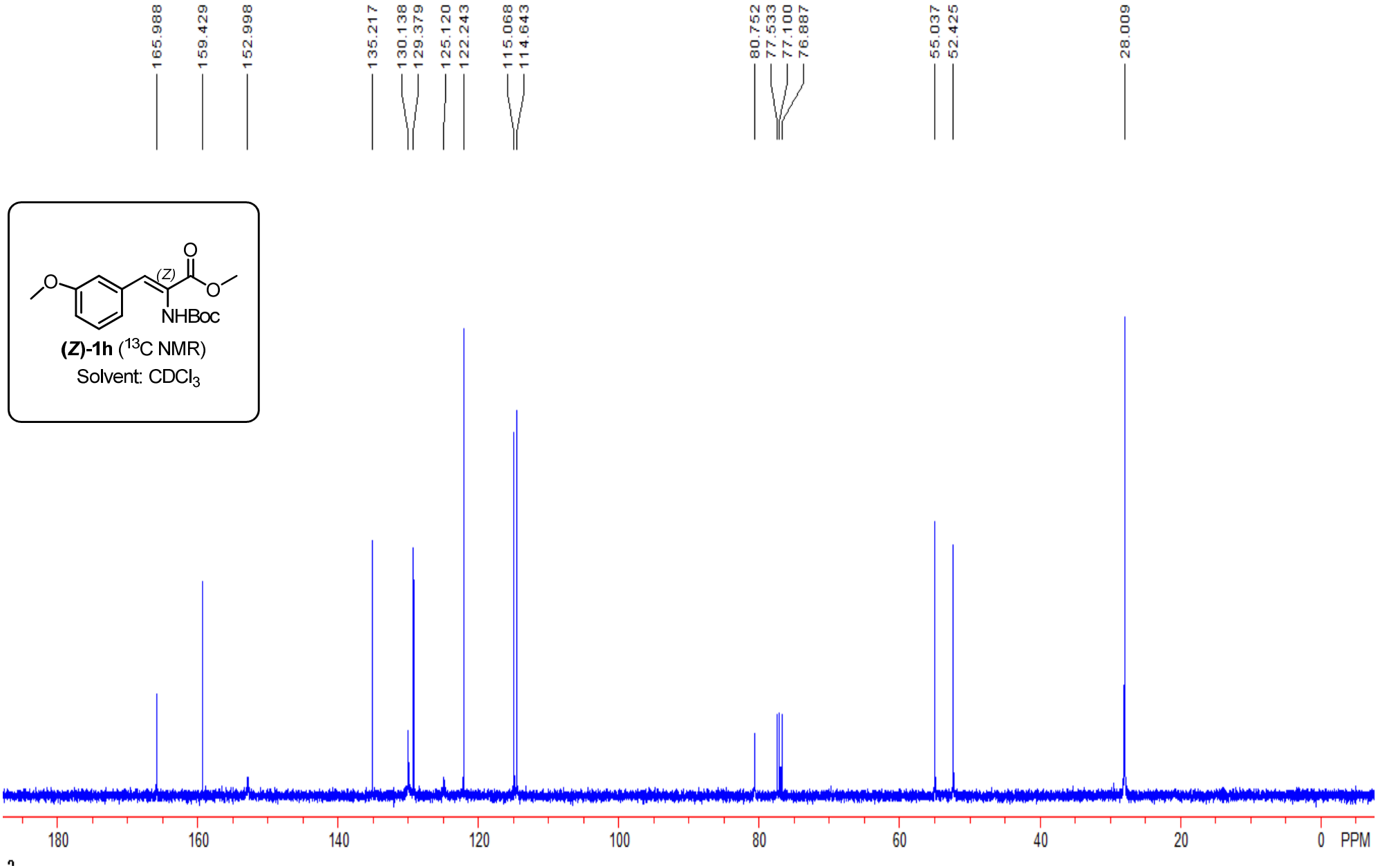
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77.100
76.887
55.037
52.425
28.009
O
(Z)
O
O
NHBoc
(Z)-1h (13C NMR)
Solvent: CDCl3
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60
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20
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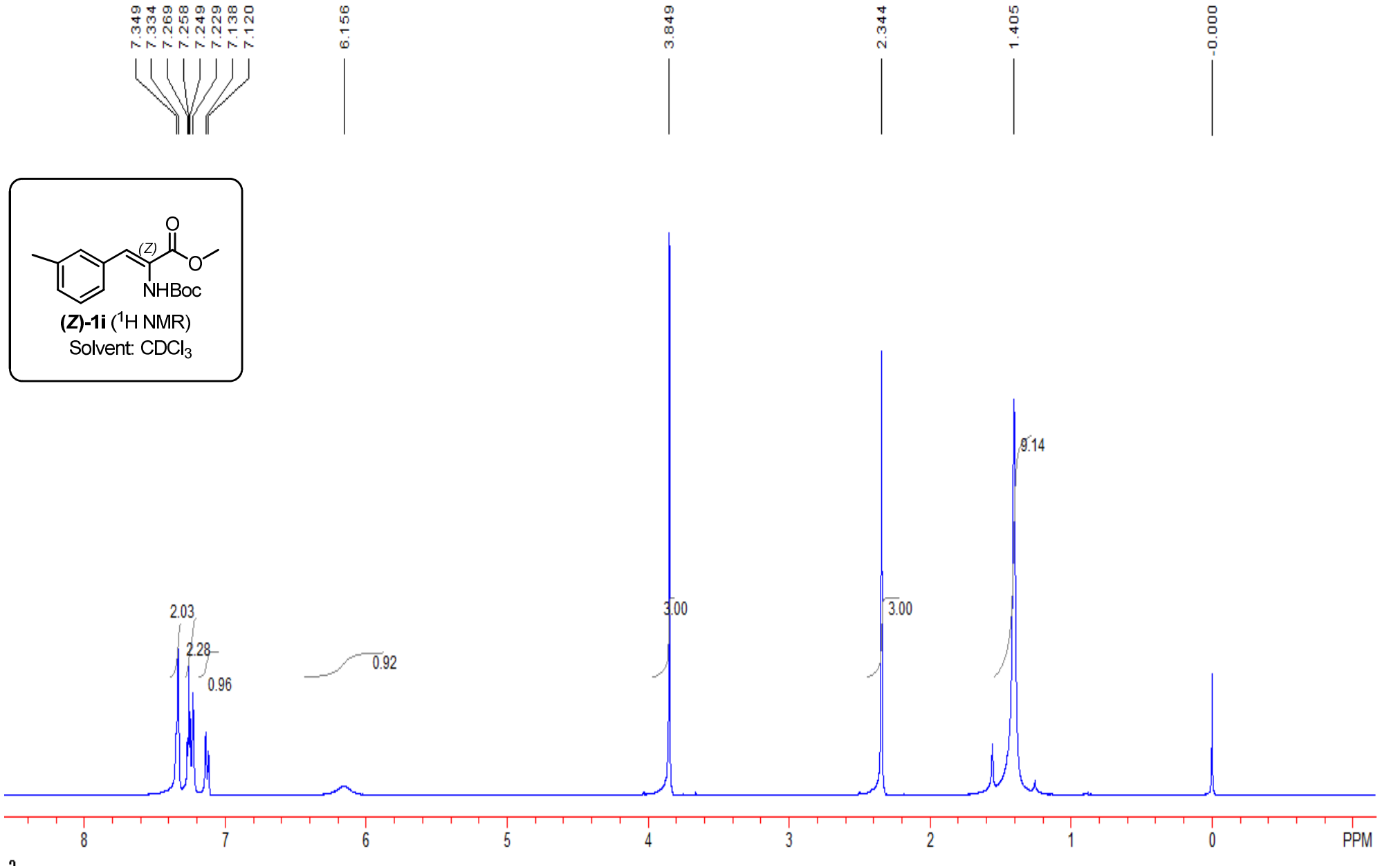
PPM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O
O
NHBoc
(Z)-1i (1H NMR)
Solvent: CDCl3
2.03
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3
2
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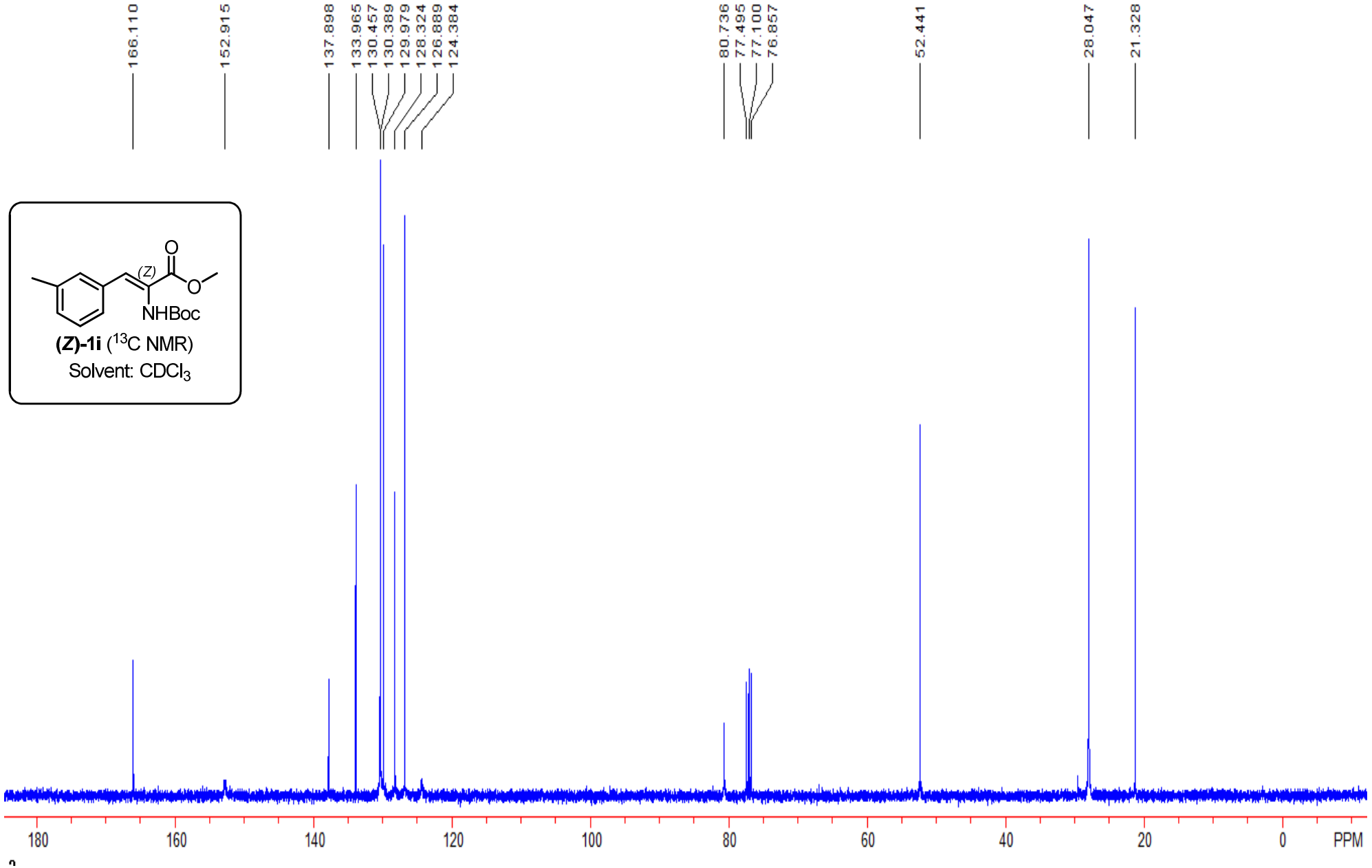
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80.736
77.495
77.100
76.857
52.441
28.047
21.328
(Z)
O
O
NHBoc
(Z)-1i (13C NMR)
Solvent: CDCl3
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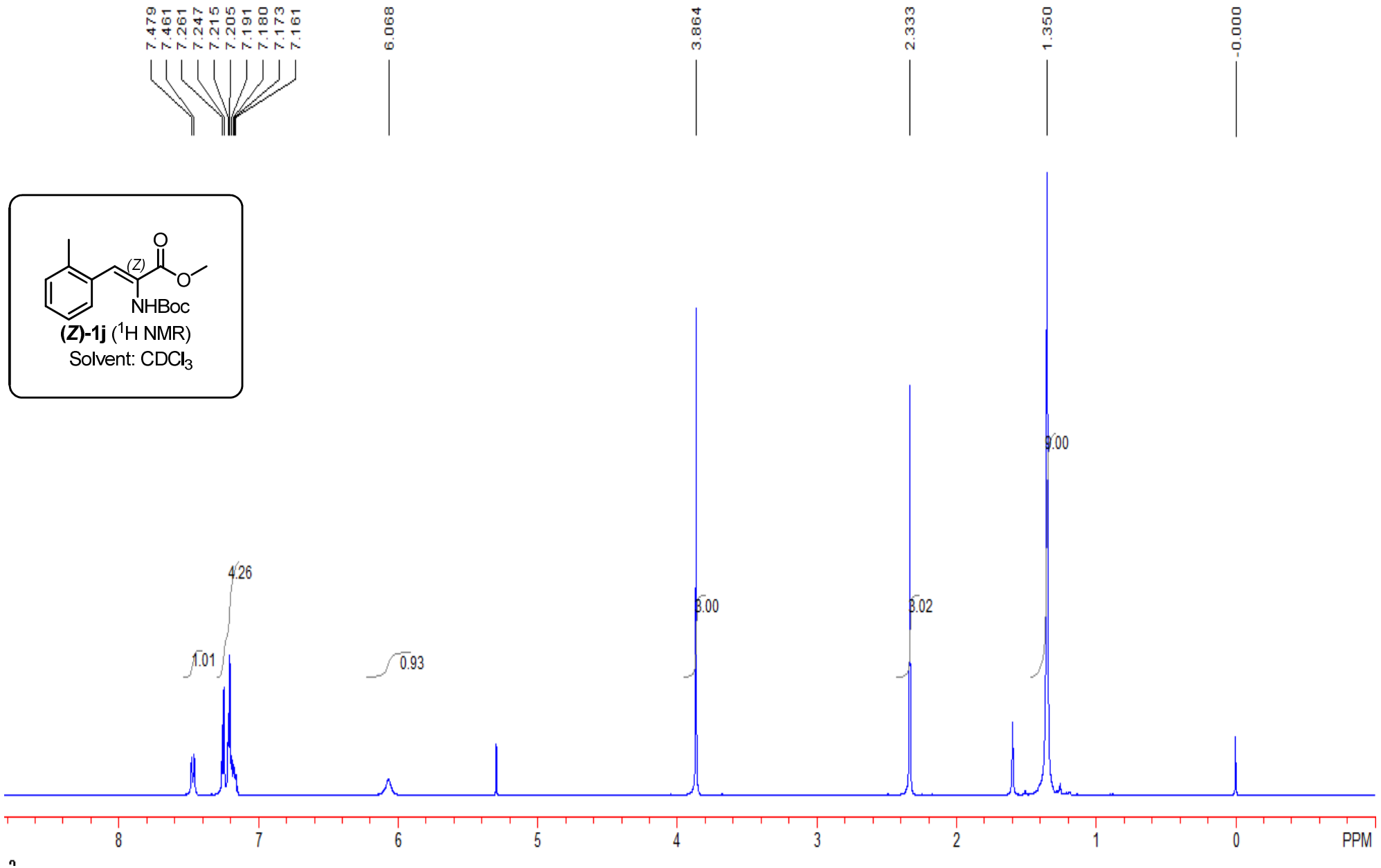
160
140
120
100
80
60
40
20
0
PPM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7.173
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6.068
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2.333
1.350
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(Z)-1j (1H NMR)
Solvent: CDCl3
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1.01
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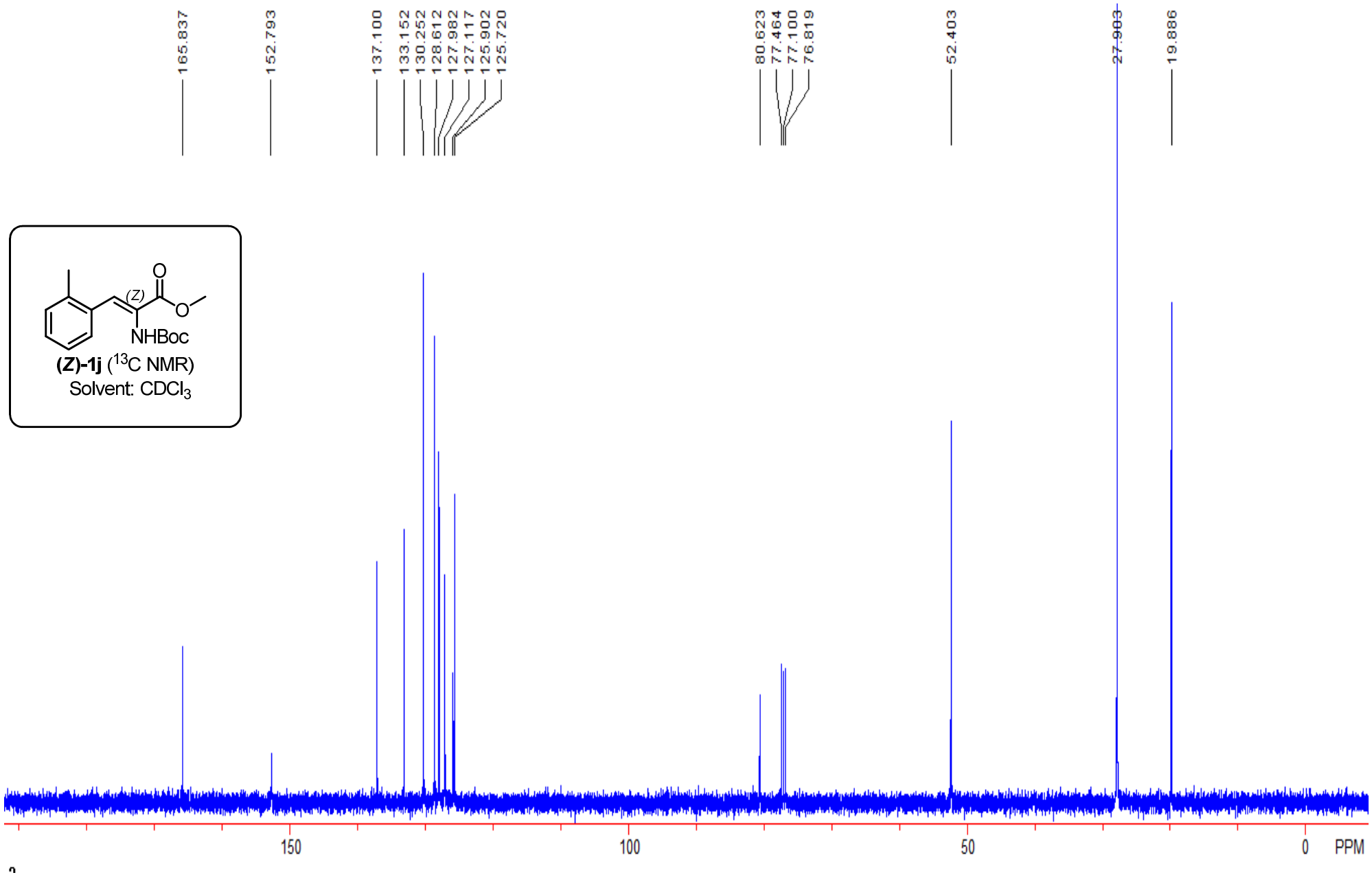
3.00
3.02
9.00
8
7
6
5
4
3
2
1
0
PPM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125.720
80.623
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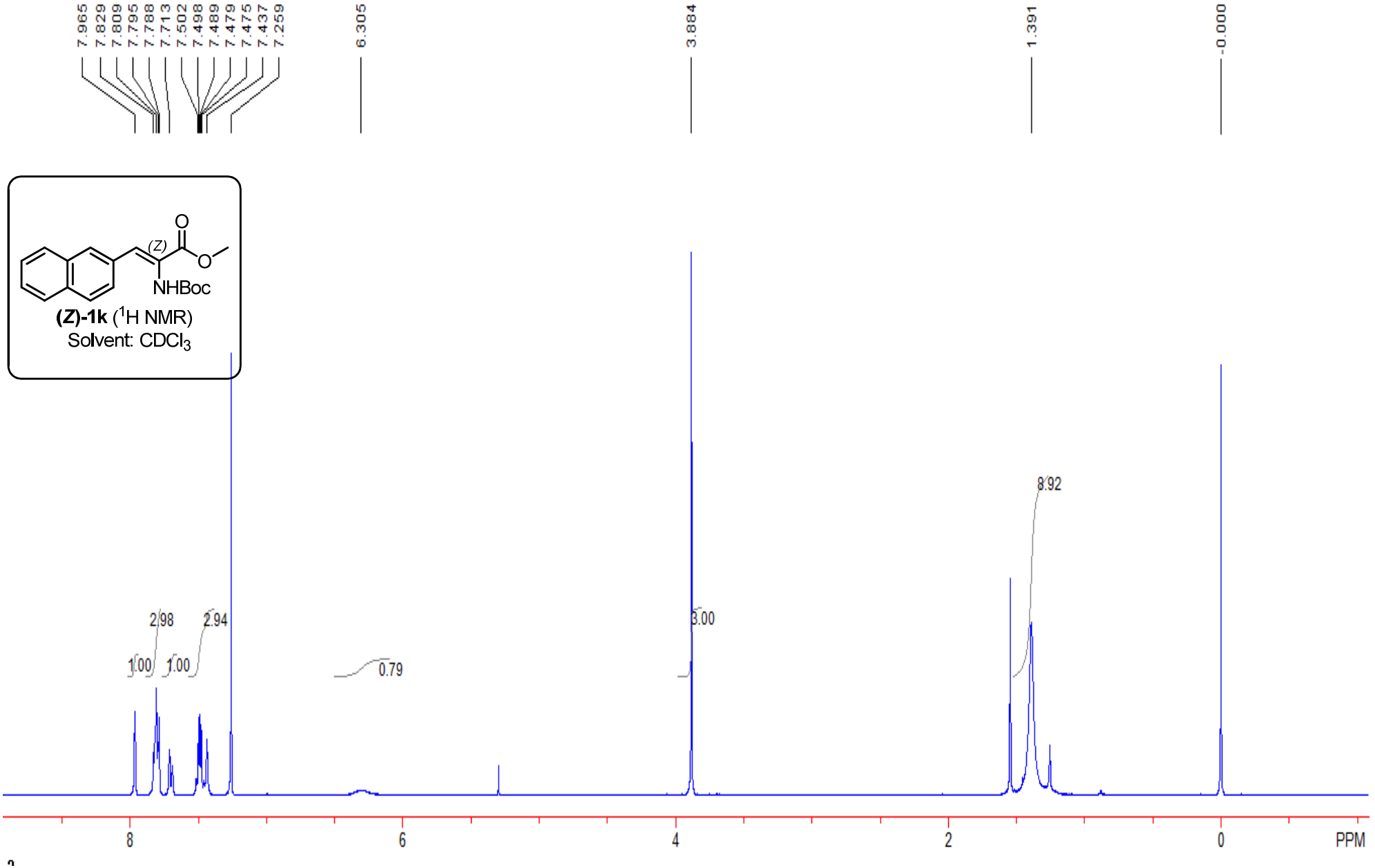
77.100
76.819
52.403
27.903
19.886
(Z)
O
O
NHBoc
(Z)-1j (13C NMR)
Solvent: CDCl3
150
100
50
0
PPM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7.788
7.713
7.502
7.498
7.489
7.479
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7.437
7.259
6.305
3.884
1.391
-0.000
(Z)-1k (1H NMR)
Solvent: CDCl3
NHBoc
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1.00
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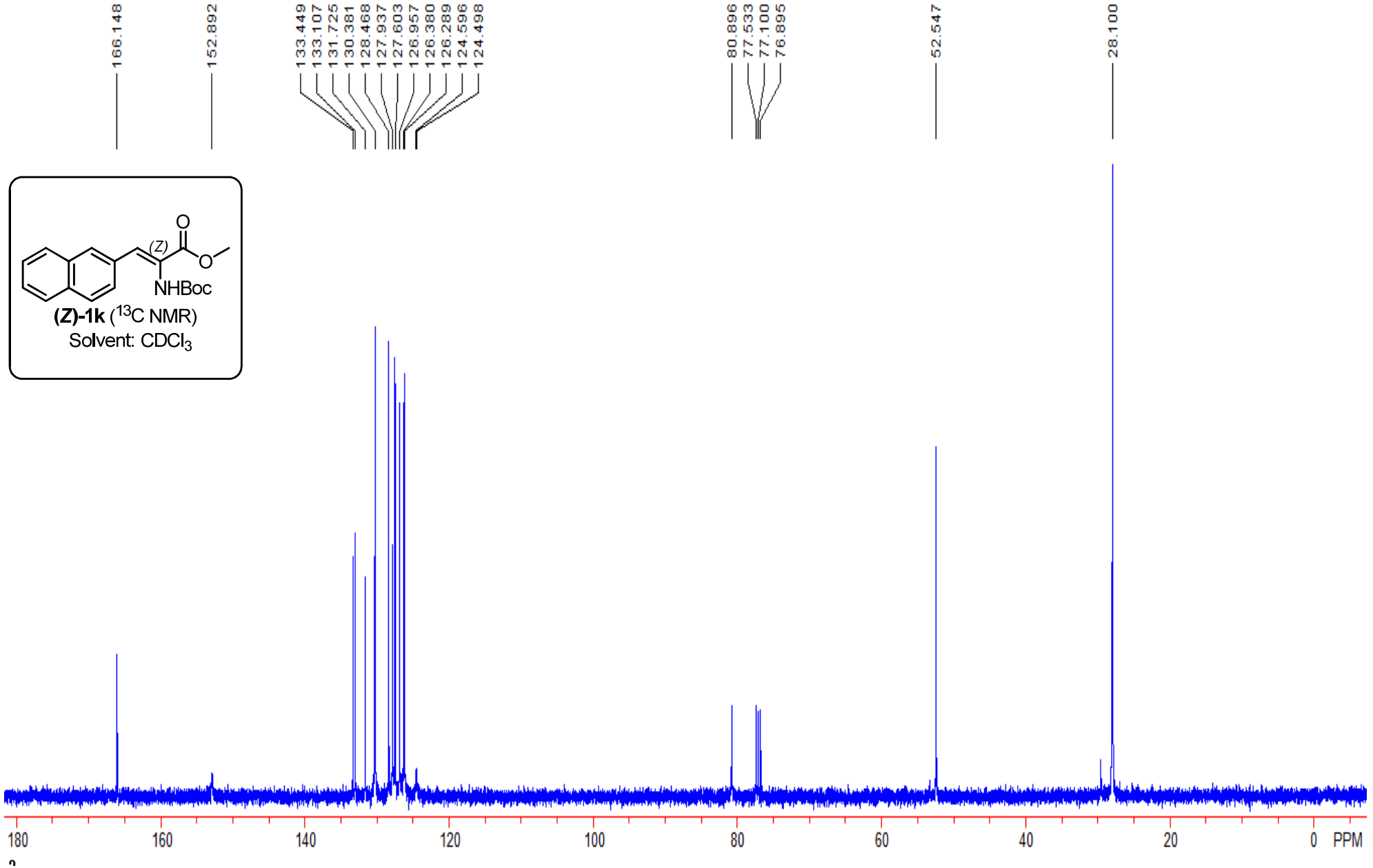
3.00
8.92
8
6
4
2
0
PPM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124.596
124.498
80.896
77.533
77.100
76.895
52.547
28.100
(Z)
O
O
NHBoc
(Z)-1k (13C NMR)
Solvent: CDCl3
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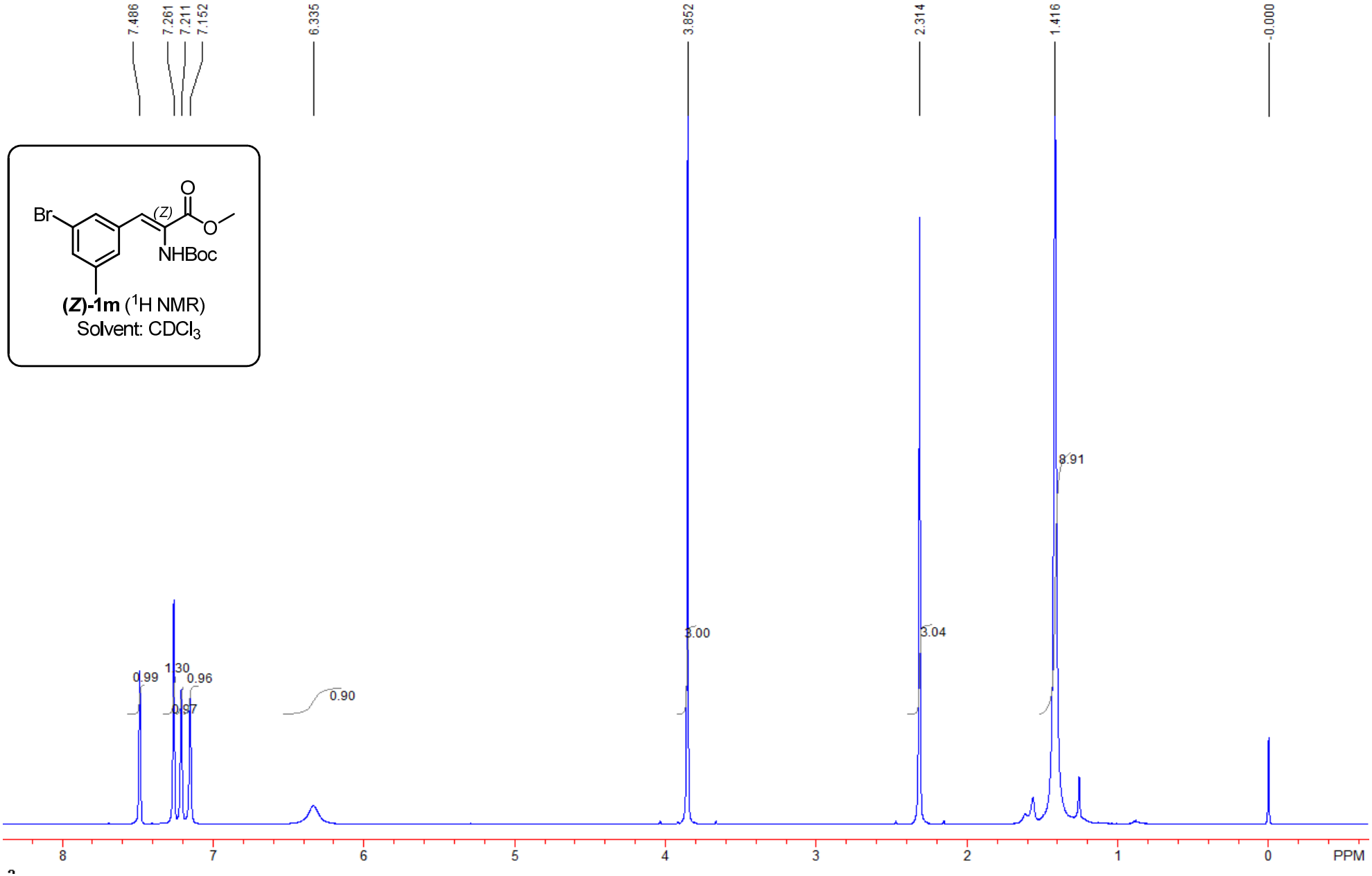
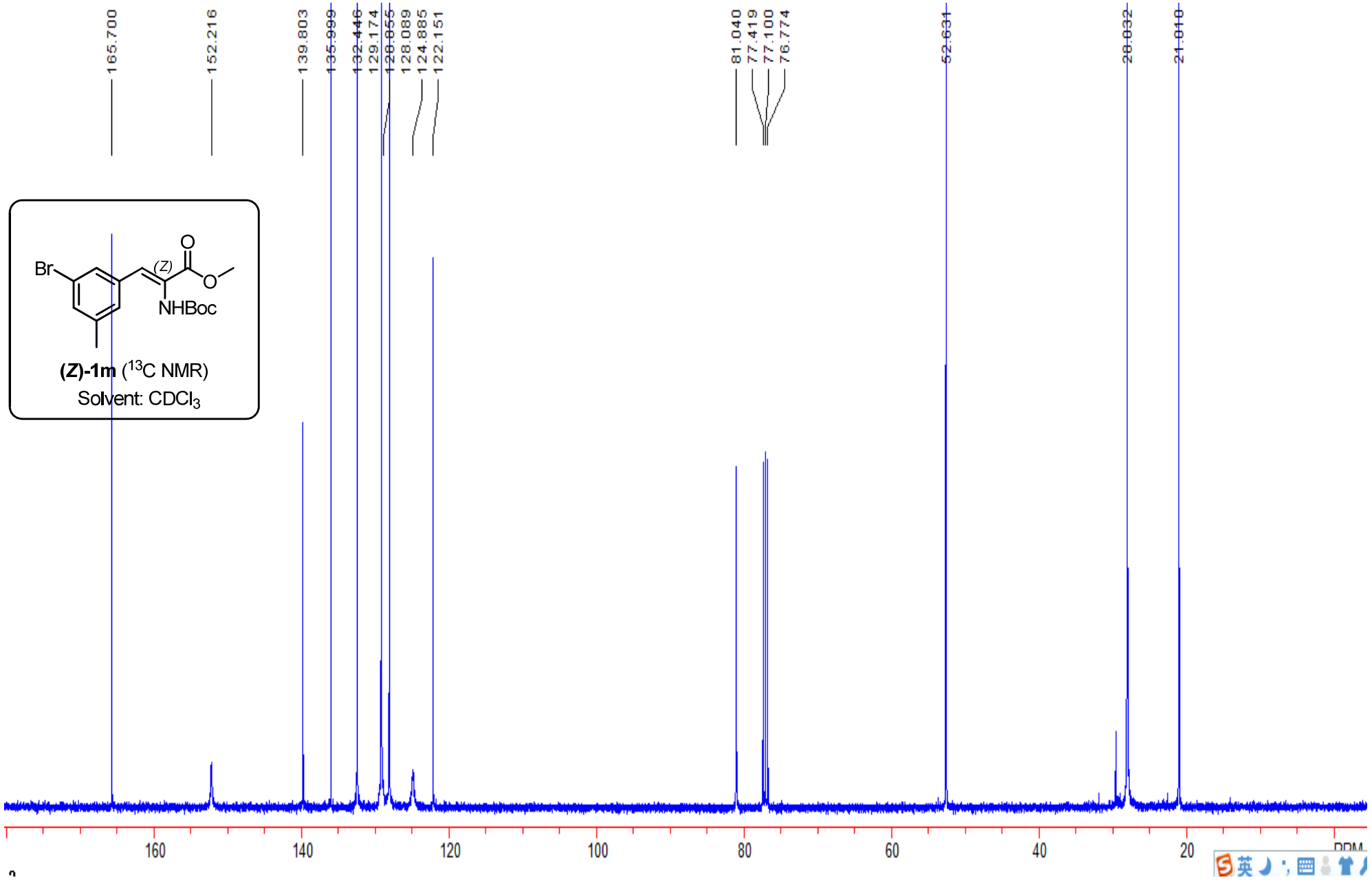
160
140
120
100
80
60
40
20
0
PPM


7.486
7.261
7.211
7.152
6.335
3.852
2.314
1.416
-0.000
Br
(Z)
O
O
NHBoc
(Z)-1m (1H NMR)
Solvent: CDCl3
0.99
1.30
0.96
0.97
0.90
3.00
3.04
8.91
8
7
6
5
4
3
2
1
0
PPM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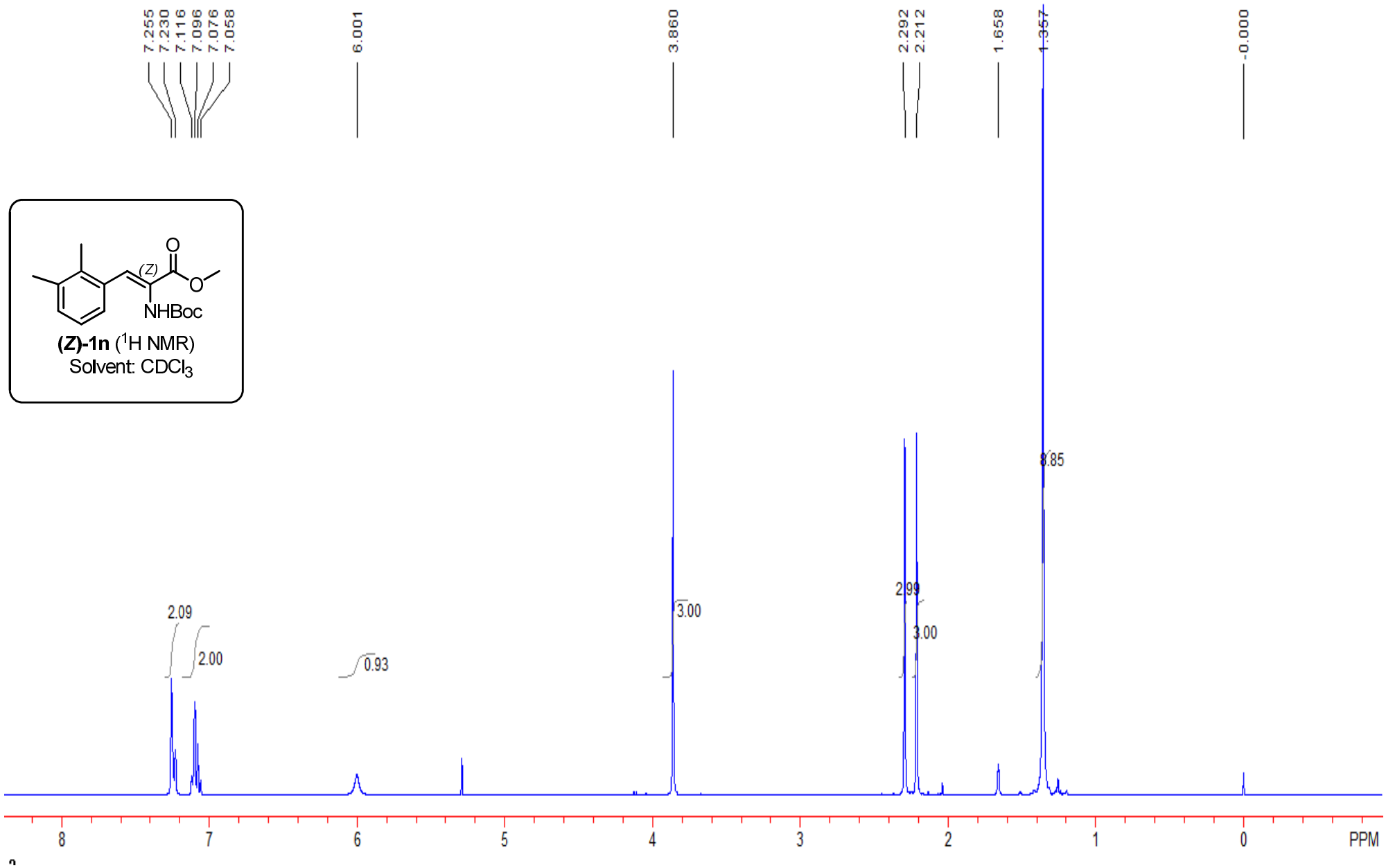
152.216
139.803
135.999
132.446
129.174
128.855
128.089
124.885
122.151
81.040
77.419
77.100
76.774
52.631
28.032
21.018
Br
(Z)
O
O
NHBoc
(Z)-1m (13C NMR)
Solvent: CDCl3
160
140
120
100
80
60
40
20
PPM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7.230
7.116
7.096
7.076
7.058
6.001
3.860
2.292
2.212
1.658
1.357
-0.000
(Z)
O
O
NHBoc
(Z)-1n (1H NMR)
Solvent: CDCl3
2.09
2.00
0.93
3.00
2.99
3.00
8.85
8
7
6
5
4
3
2
1
0
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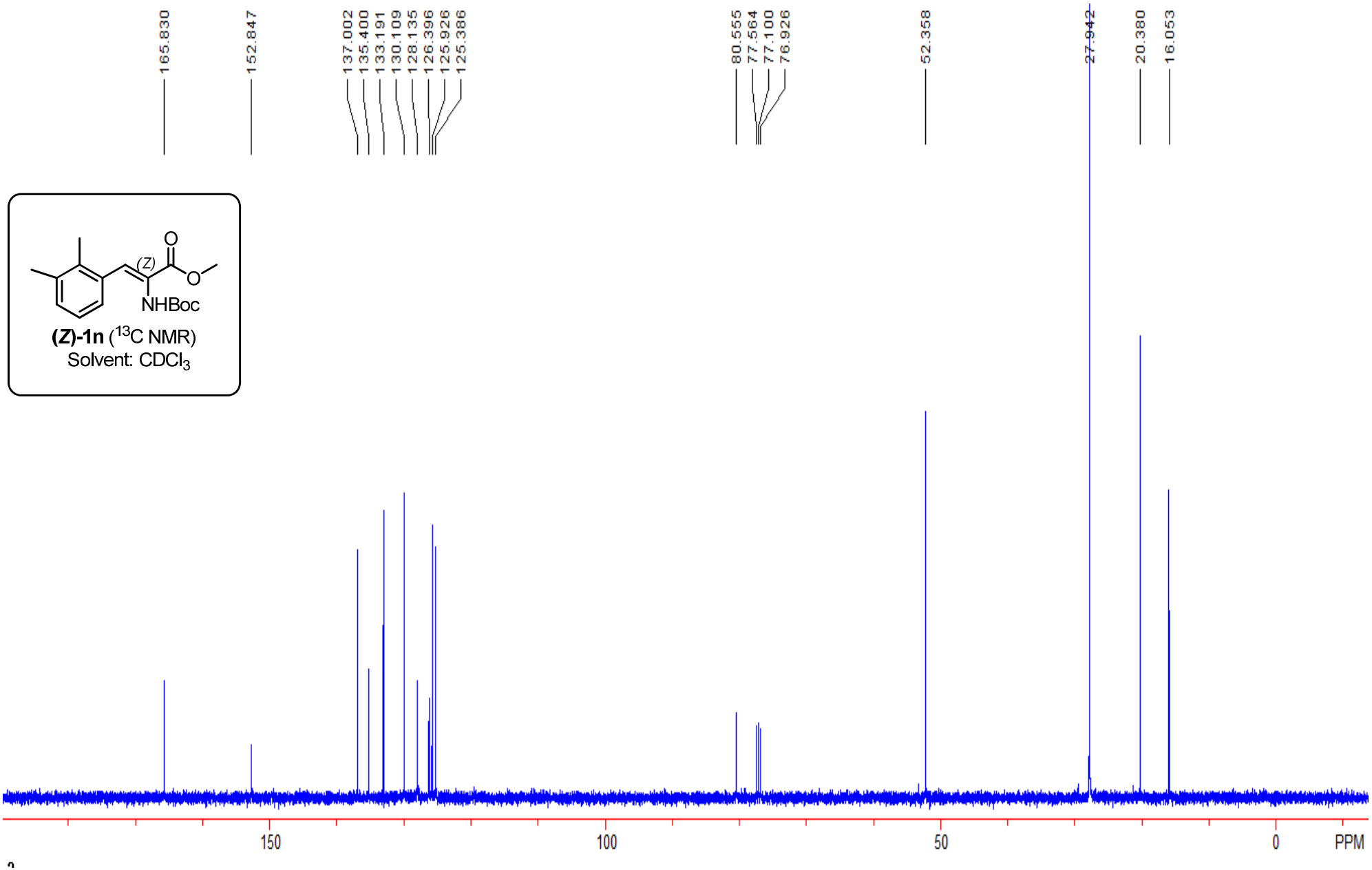
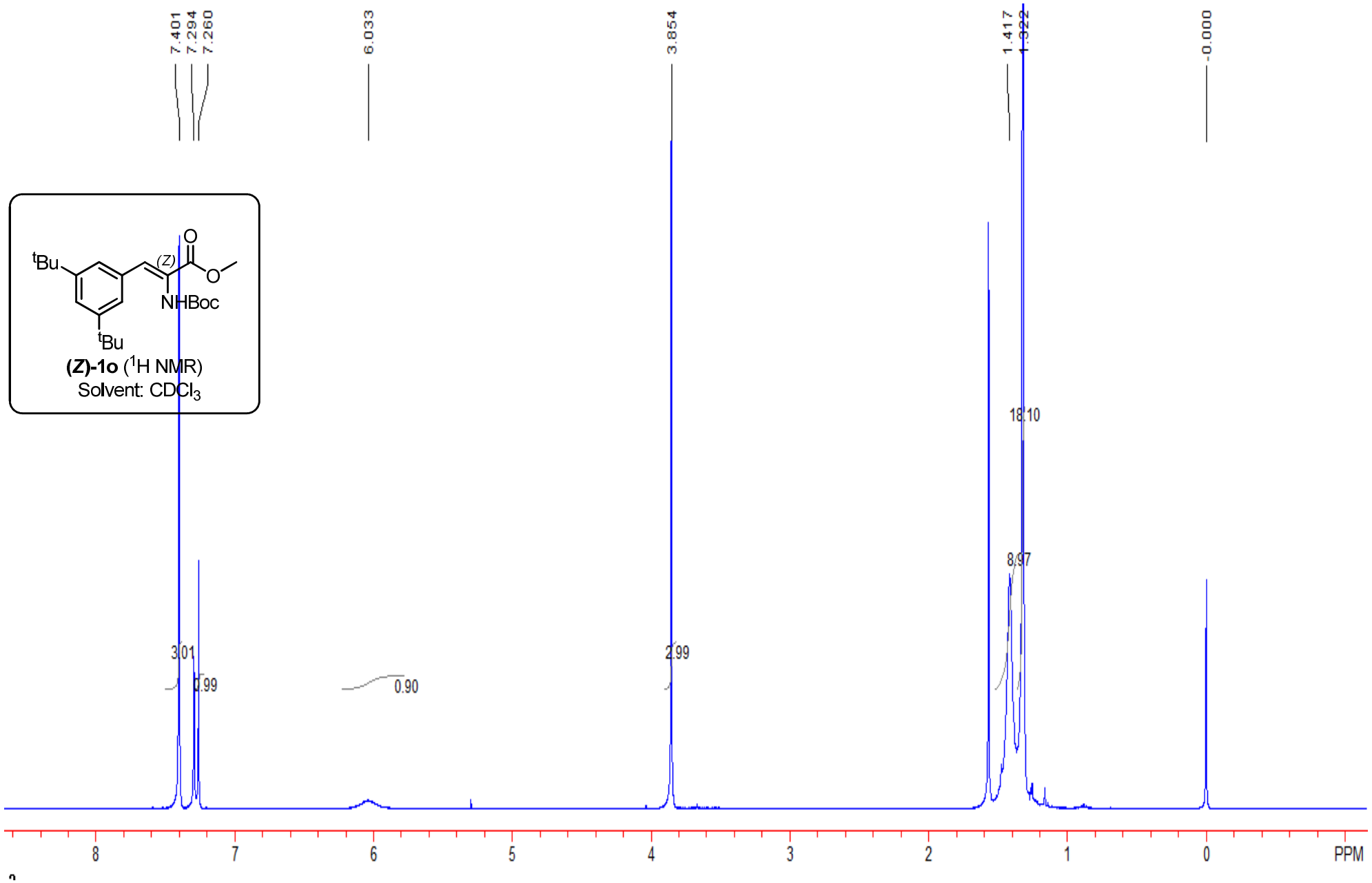
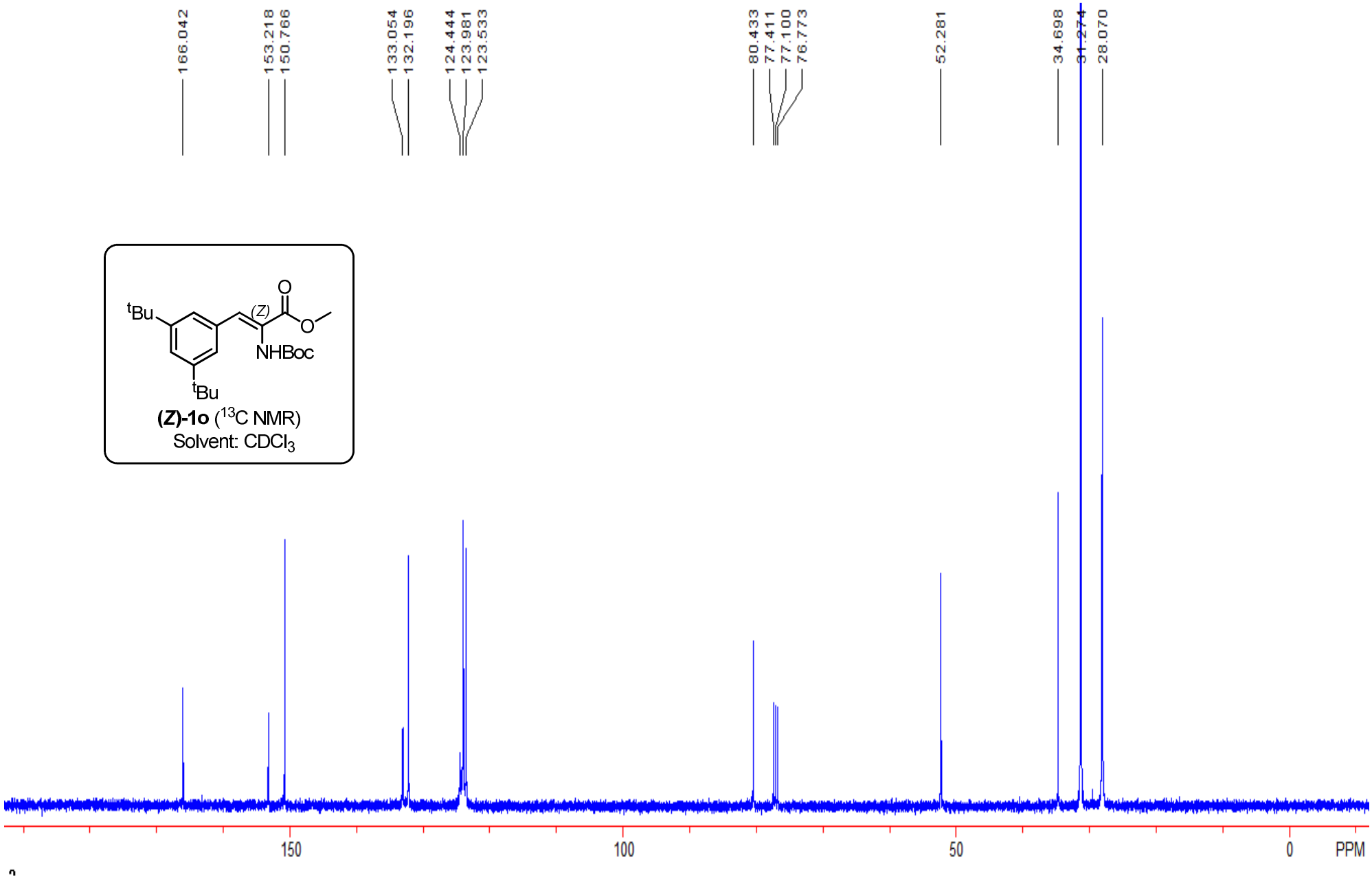
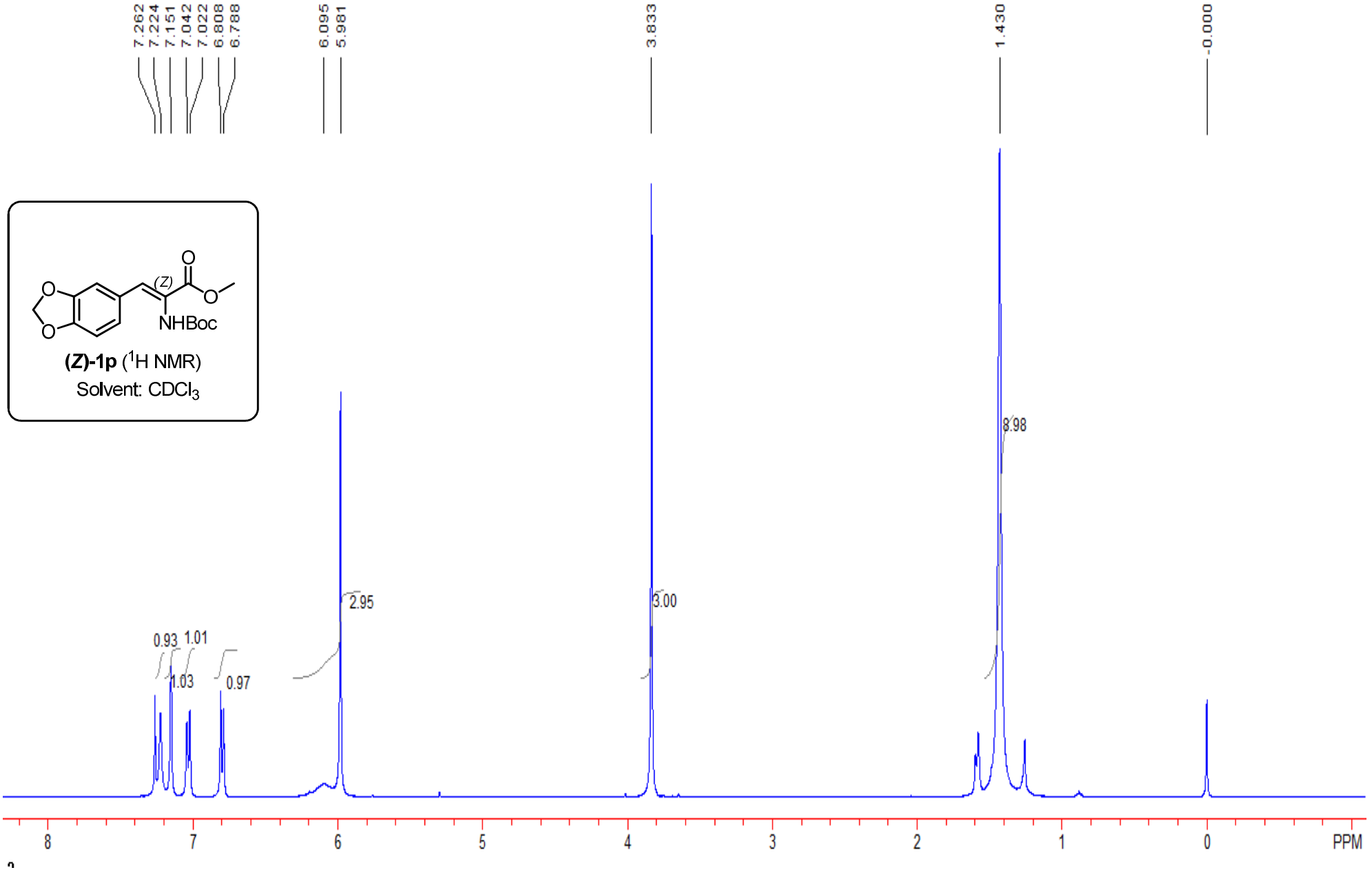
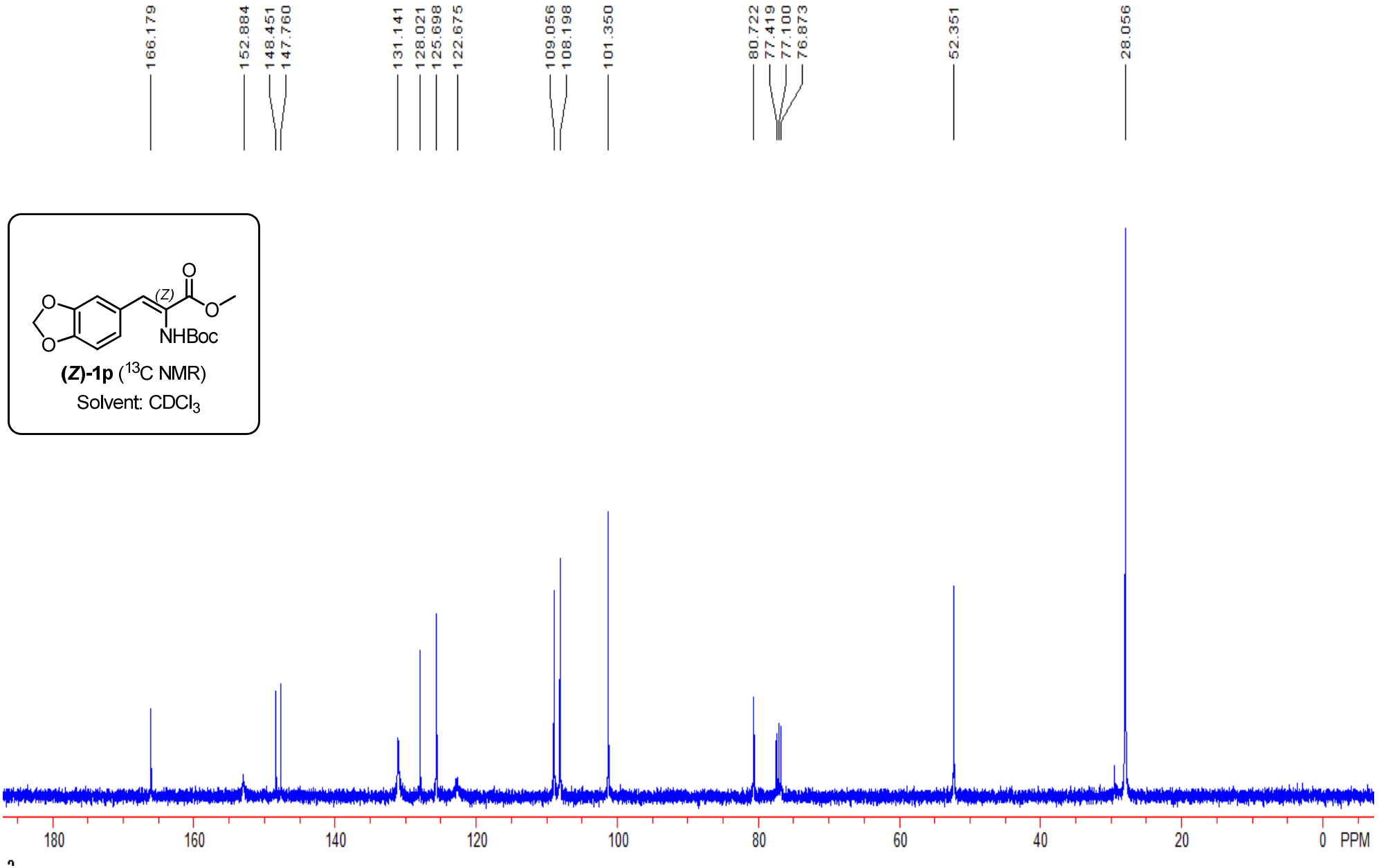

165.830
152.847
137.002
135.400
133.191
130.109
128.135
126.396
125.926
125.386
80.555
77.564
77.100
76.926
52.358
27.942
20.380
16.053
(Z)
O
O
NHBoc
(Z)-1n (13C NMR)
Solvent: CDCl3
150
100
50
0
PPM


7.401
7.294
7.260
6.033
3.854
1.417
1.322
-0.000
tBu
(Z)
O
O
NHBoc
tBu
(Z)-1o (1H NMR)
Solvent: CDCl3
18.10
8.97
3.01
0.99
0.90
2.99
8
7
6
5
4
3
2
1
0
PPM


166.042
153.218
150.766
133.054
132.196
124.444
123.981
123.533
80.433
77.411
77.100
76.773
52.281
34.698
31.274
28.070
tBu
(Z)
O
O
NHBoc
tBu
(Z)-1o (13C NMR)
Solvent: CDCl3
150
100
50
0
PPM


7.262
7.224
7.151
7.042
7.022
6.808
6.788
6.095
5.981
3.833
1.430
-0.000
(Z)
NHBoc
(Z)-1p (1H NMR)
Solvent: CDCl3
0.93
1.01
1.03
0.97
2.95
3.00
8.98
8
7
6
5
4
3
2
1
0
PPM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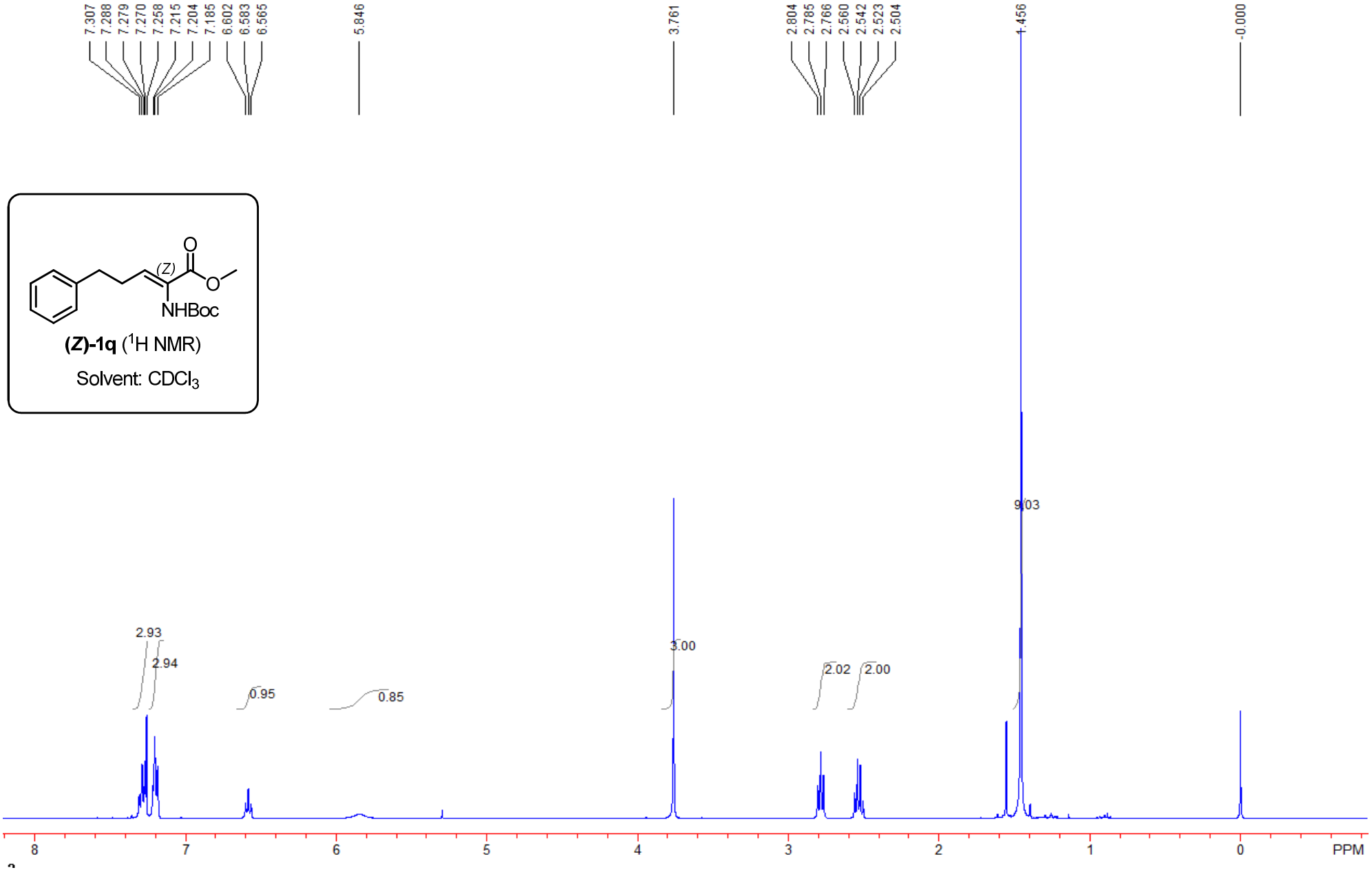
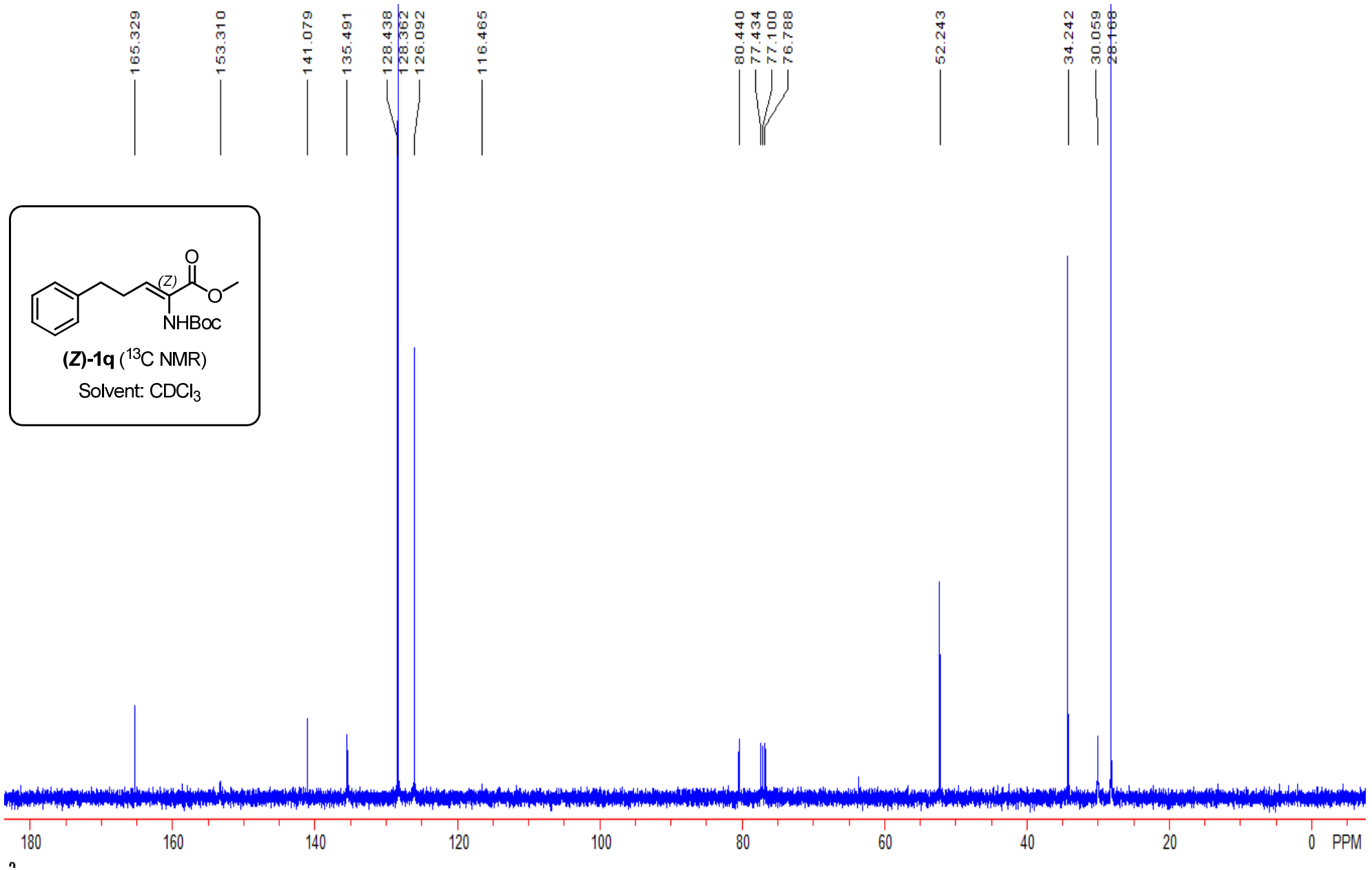
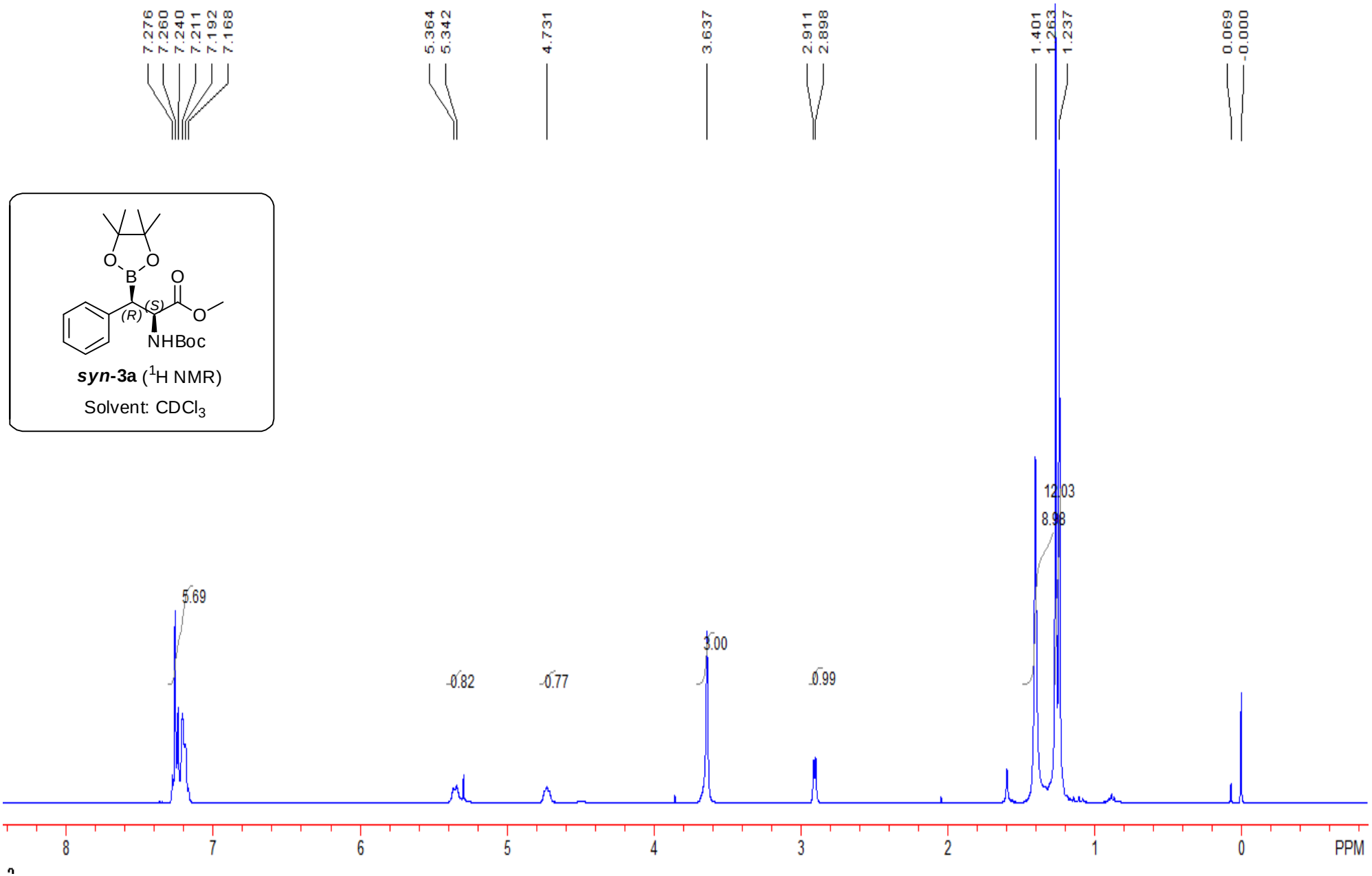
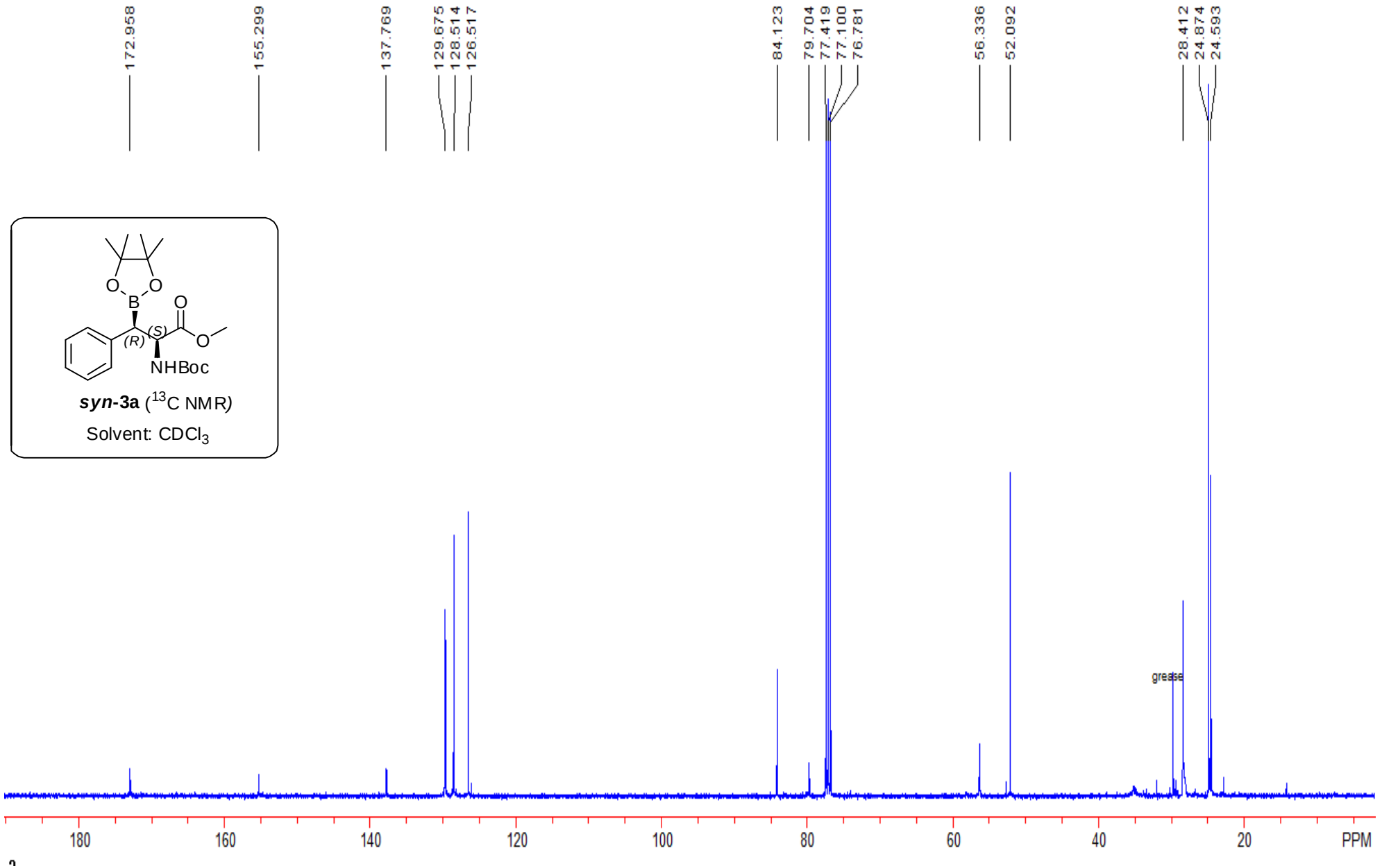
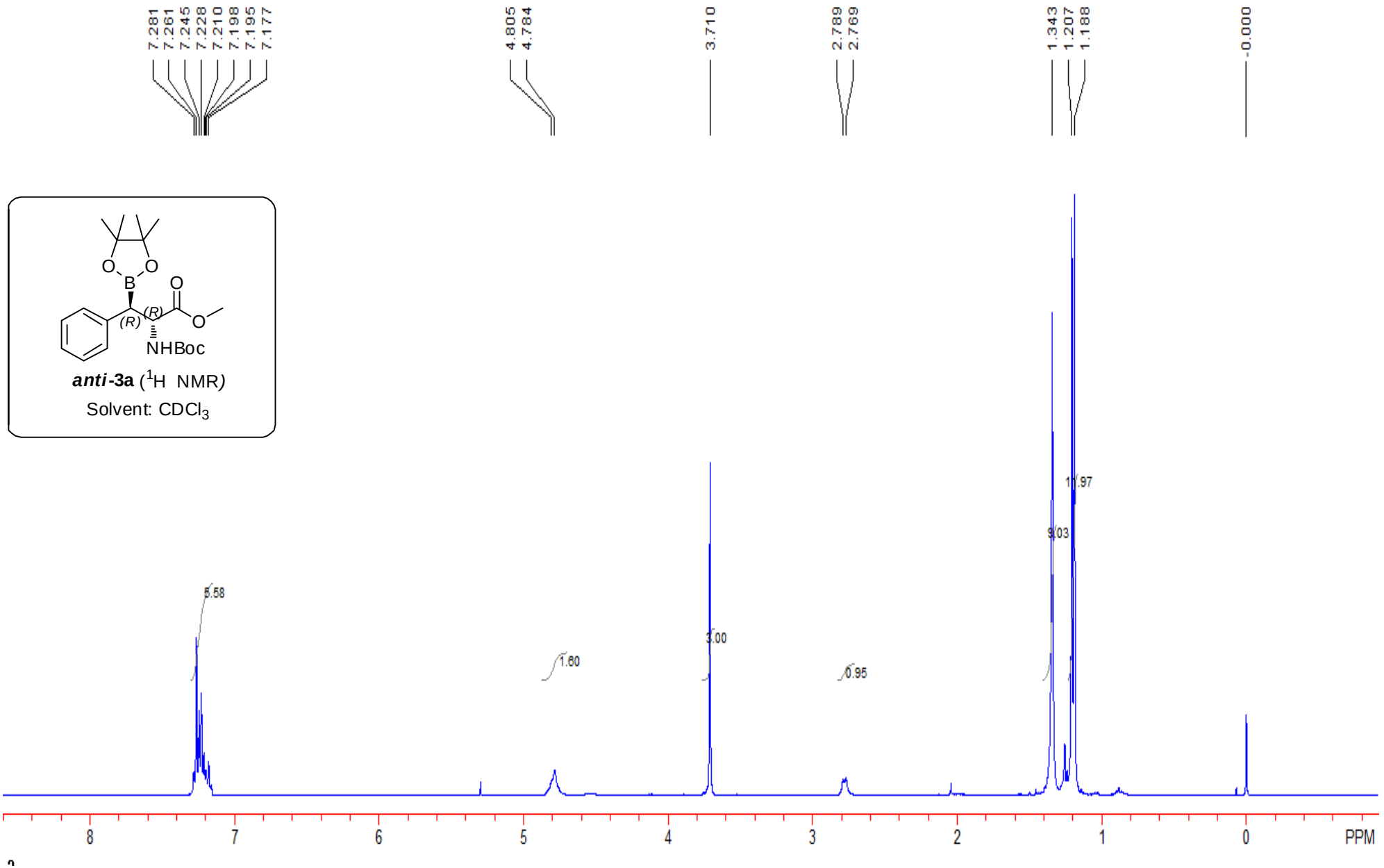
152.884
148.451
147.760
131.141
128.021
125.698
122.675
109.056
108.198
101.350
80.722
77.419
77.100
76.873
52.351
28.056
O
(Z)
O
O
O
NHBoc
(Z)-1p (13C NMR)
Solvent: CDCl3
180
160
140
120
100
80
60
40
20
0
PPM

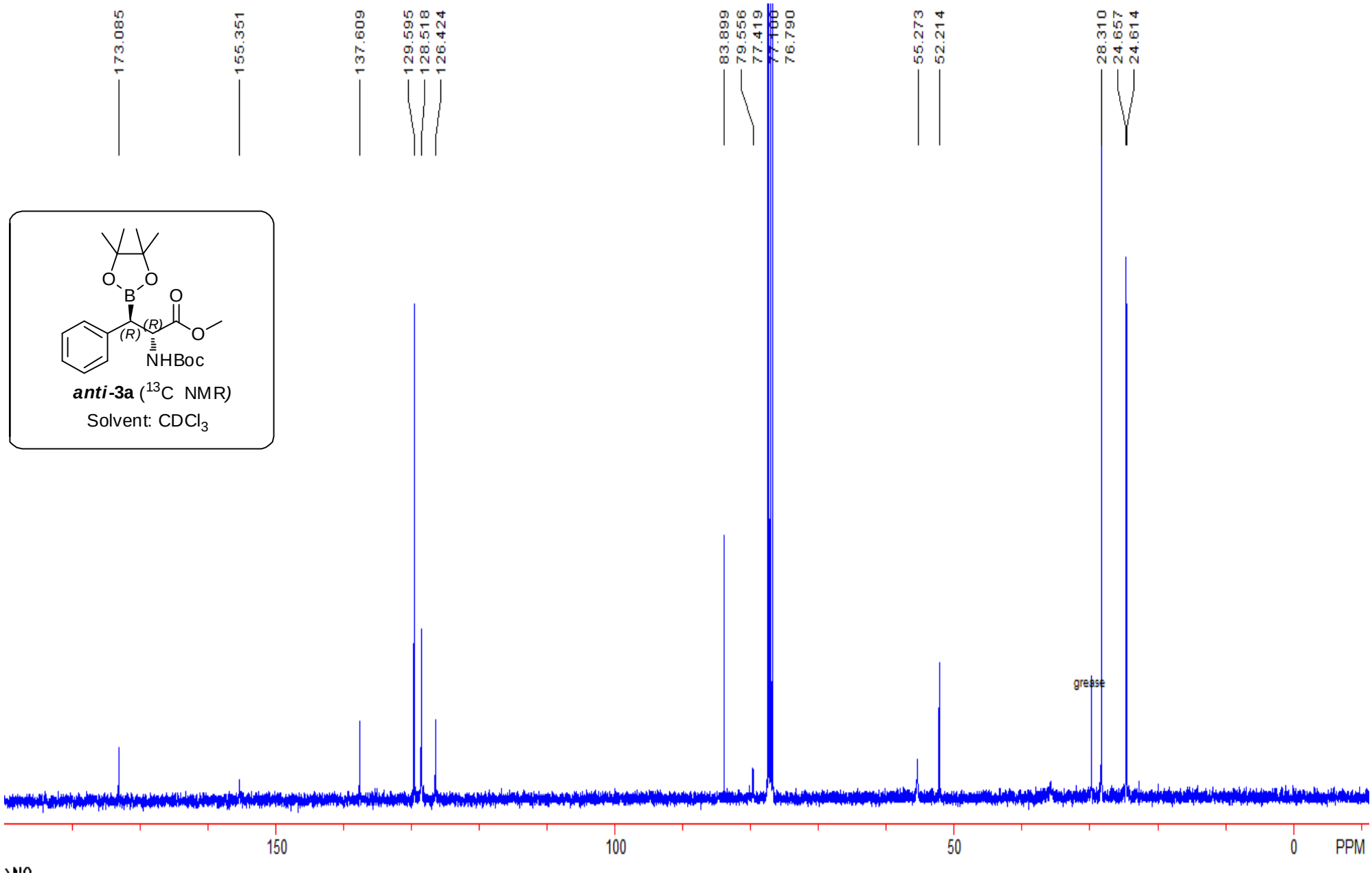

7.307
7.288
7.279
7.270
7.258
7.215
7.204
7.185
6.602
6.583
6.565
5.846
3.761
2.804
2.785
2.766
2.560
2.542
2.523
2.504
1.456
-0.000
(Z)
O
O
NHBoc
(Z)-1q (1H NMR)
Solvent: CDCl3
2.93
2.94
0.95
0.85
3.00
2.02
2.00
9.03
8
7
6
5
4
3
2
1
0
PPM

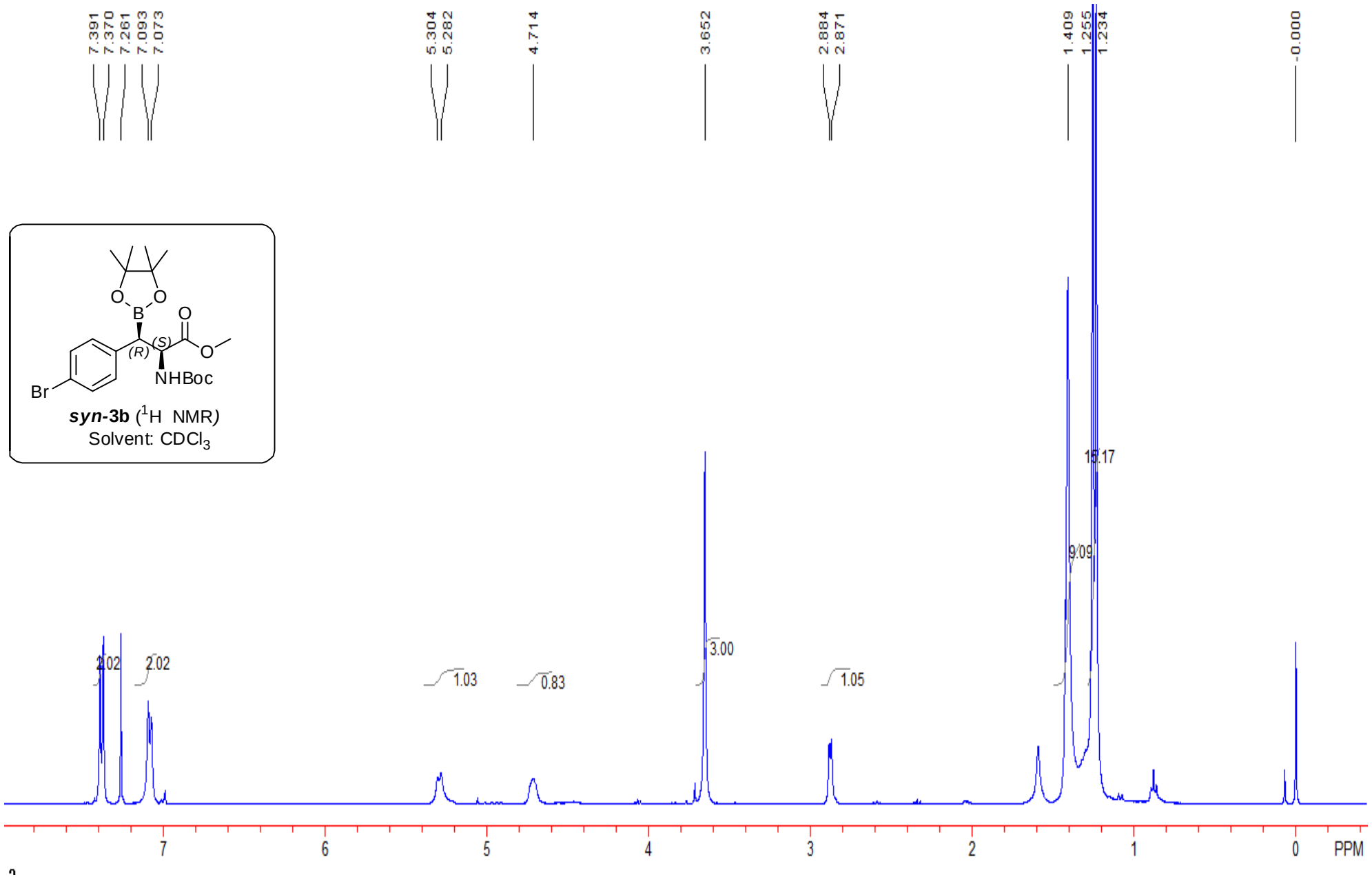

165.329
153.310
141.079
135.491
128.438
128.362
126.092
116.465
80.440
77.434
77.100
76.788
52.243
34.242
30.059
28.168
(Z)
O
O
NHBoc
(Z)-1q (13C NMR)
Solvent: CDCl3
180
160
140
120
100
80
60
40
20
0
PPM

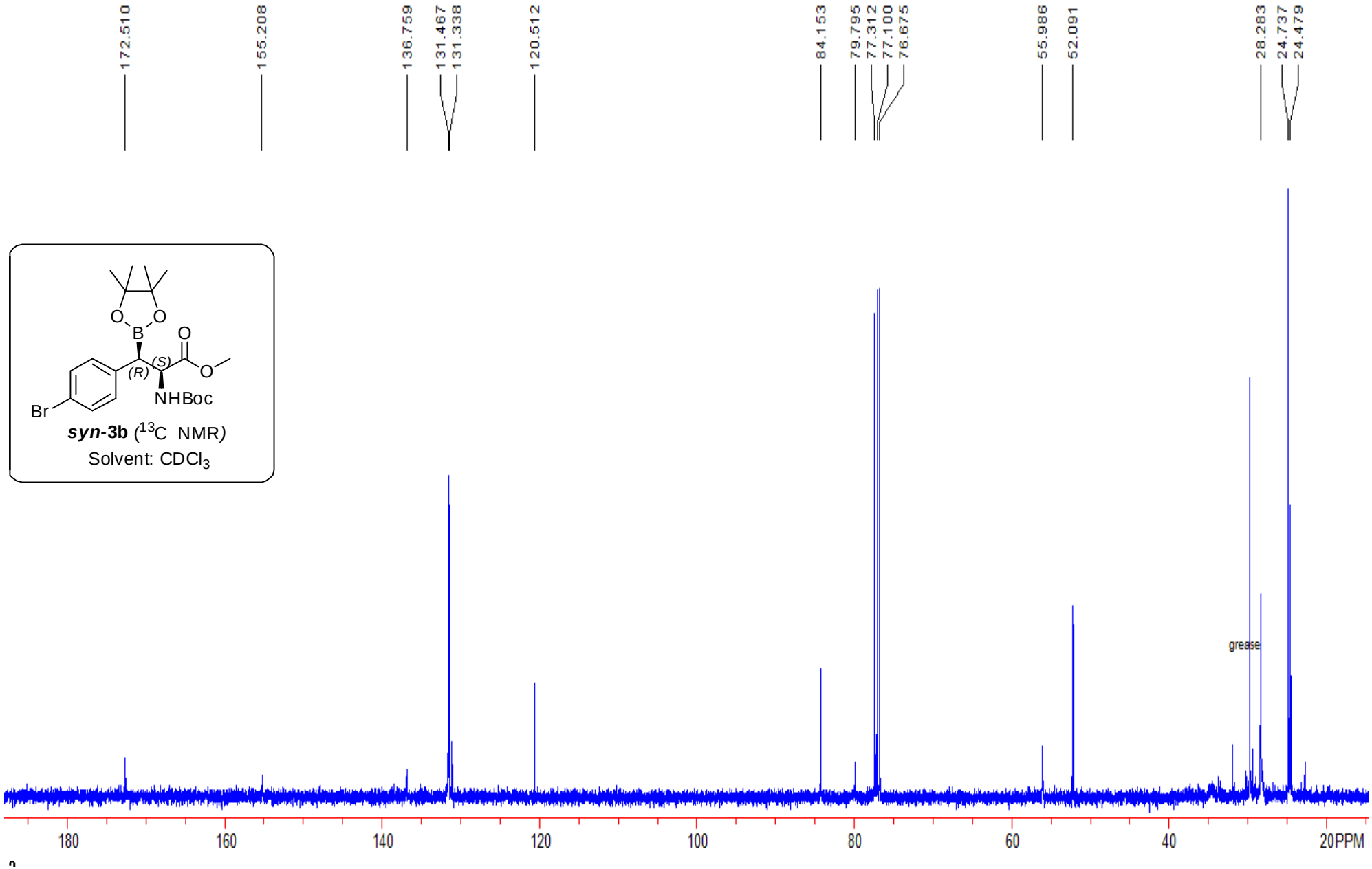

7.276
7.260
7.240
7.211
7.192
7.168
5.364
5.342
4.731
3.637
2.911
2.898
1.401
1.263
1.237
0.069
-0.000
O
O
B
O
(R)
(S)
O
NHBoc
syn-3a (1H NMR)
Solvent: CDCl3
12.03
8.98
5.69
0.82
0.77
3.00
0.99
8
7
6
5
4
3
2
1
0
PPM

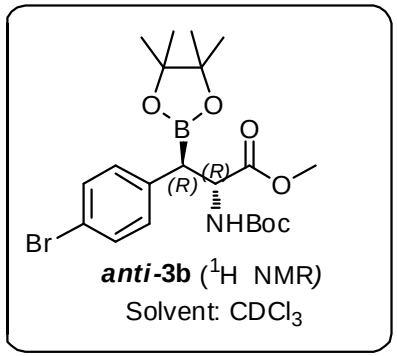

172.958
155.299
137.769
129.675
128.514
126.517
84.123
79.704
77.419
77.100
76.781
56.336
52.092
28.412
24.874
24.593
grease
180
160
140
120
100
80
60
40
20
PPM
O
O
B
O
(R)
(S)
O
NHBoc
syn-3a (13C NMR)
Solvent: CDCl3


7.281
7.261
7.245
7.228
7.210
7.198
7.195
7.177
4.805
4.784
3.710
2.789
2.769
1.343
1.207
1.188
-0.000
anti-3a (1H NMR)
Solvent: CDCl3
NHBoc
5.58
1.60
3.00
0.95
9.03
11.97
8
7
6
5
4
3
2
1
0
PPM

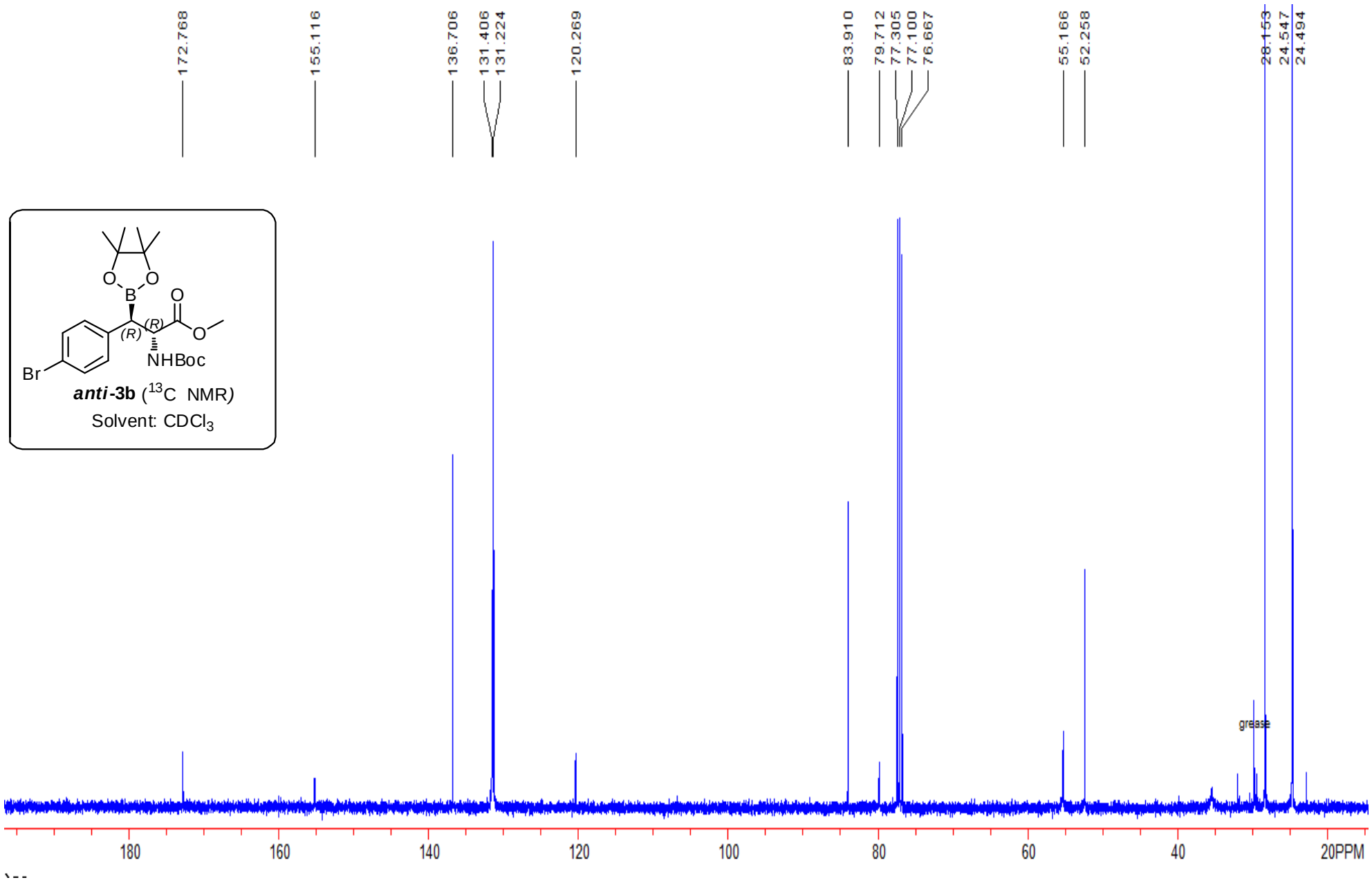

173.085
155.351
137.609
129.595
128.518
126.424
83.899
79.556
77.419
77.166
76.790
55.273
52.214
28.310
24.657
24.614
grease
150
100
50
0
PPM
anti-3a (13C NMR)
Solvent: CDCl3

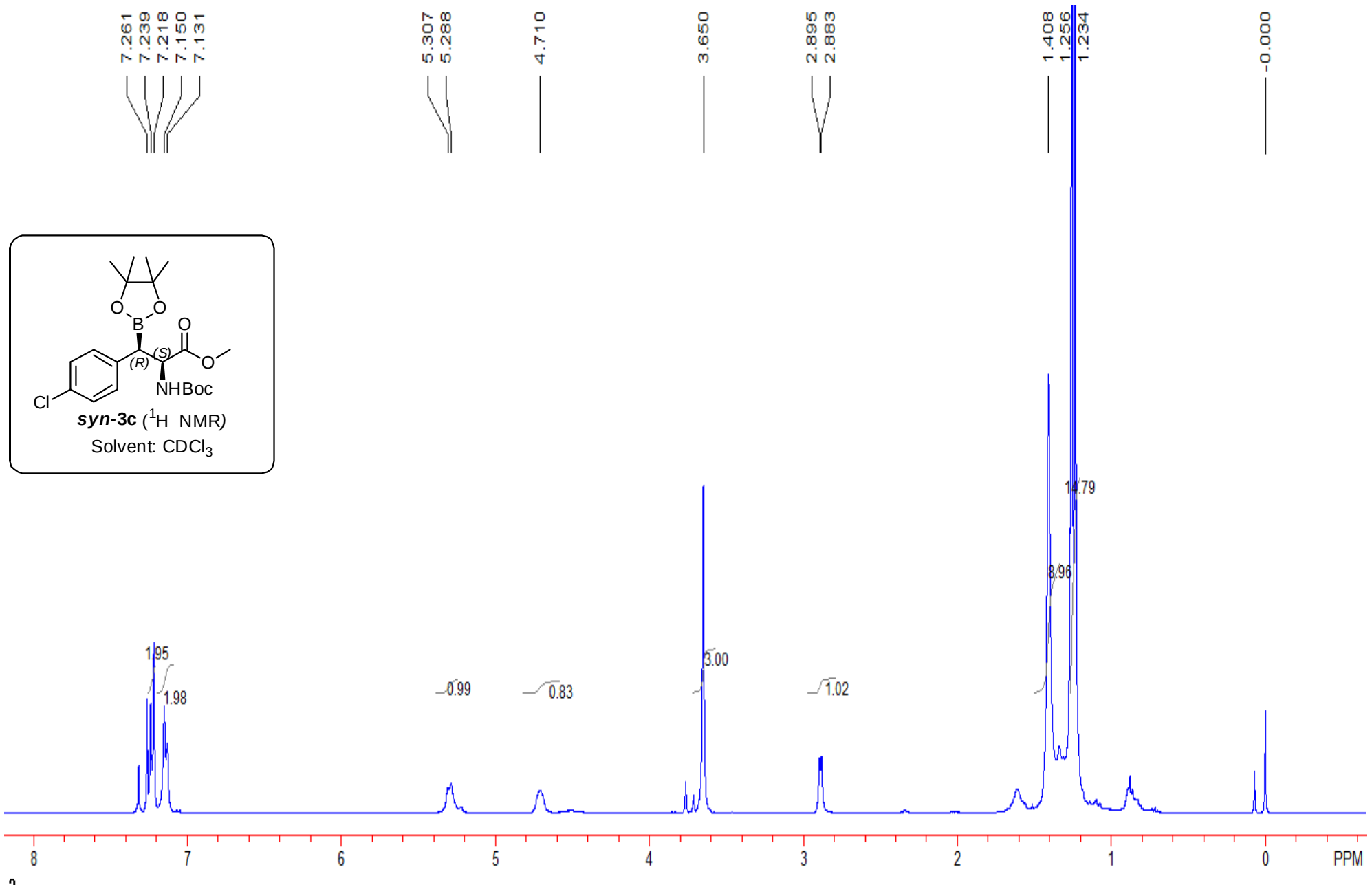

7.391
7.370
7.261
7.093
7.073
5.304
5.282
4.714
3.652
2.884
2.871
1.409
1.255
1.234
-0.000
Br
NHBoc
(R)
(S)
syn-3b (1H NMR)
Solvent: CDCl3
2.02
2.02
1.03
0.83
3.00
1.05
15.17
9.09
7
6
5
4
3
2
1
0
PPM

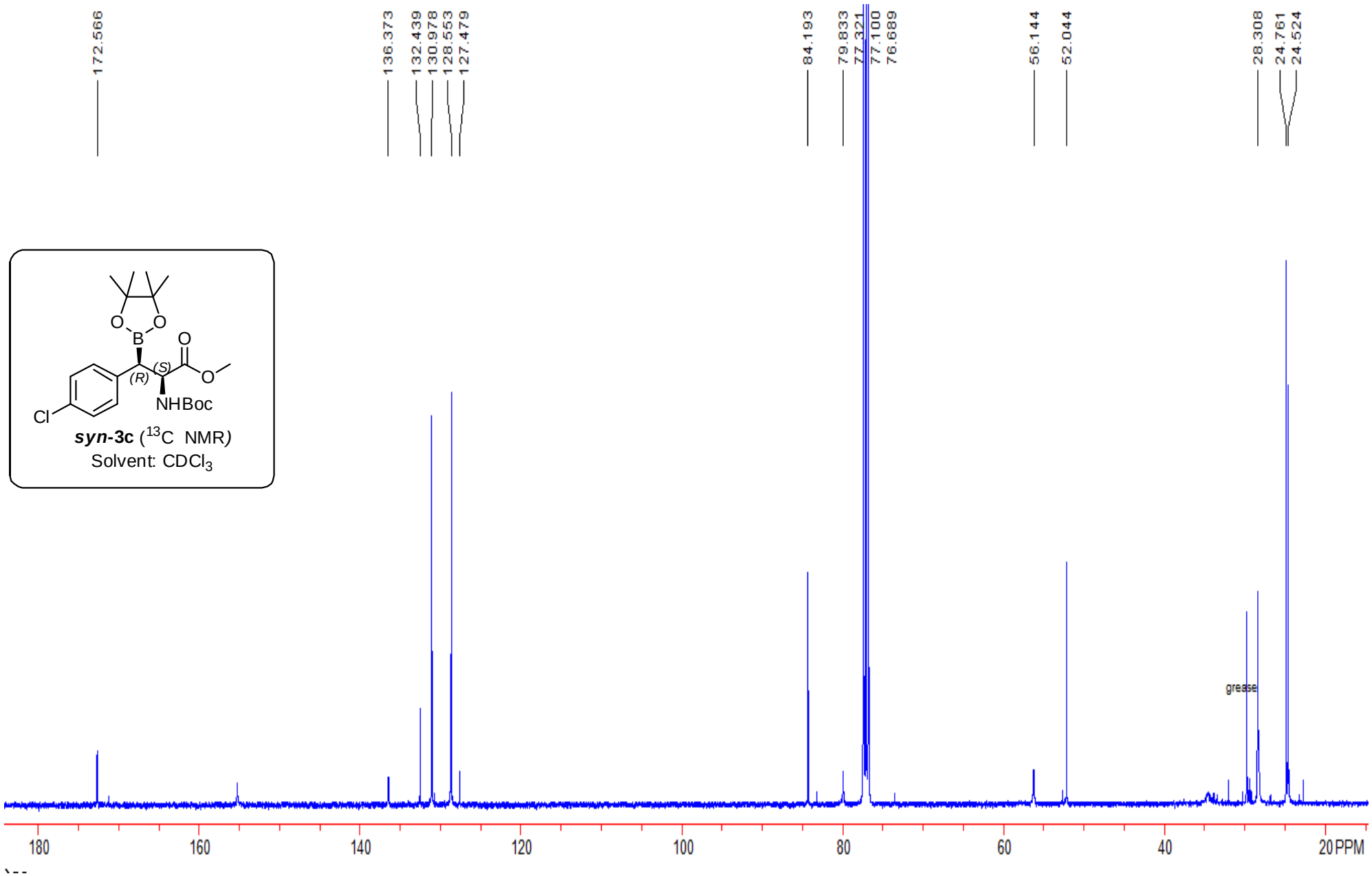

172.510
155.208
136.759
131.467
131.338
120.512
84.153
79.795
77.312
77.100
76.675
55.986
52.091
28.283
24.737
24.479
O
B
O
O
(S)
(R)
O
NHBoc
Br
syn-3b (13C NMR)
Solvent: CDCl3
grease
180
160
140
120
100
80
60
40
20PPM

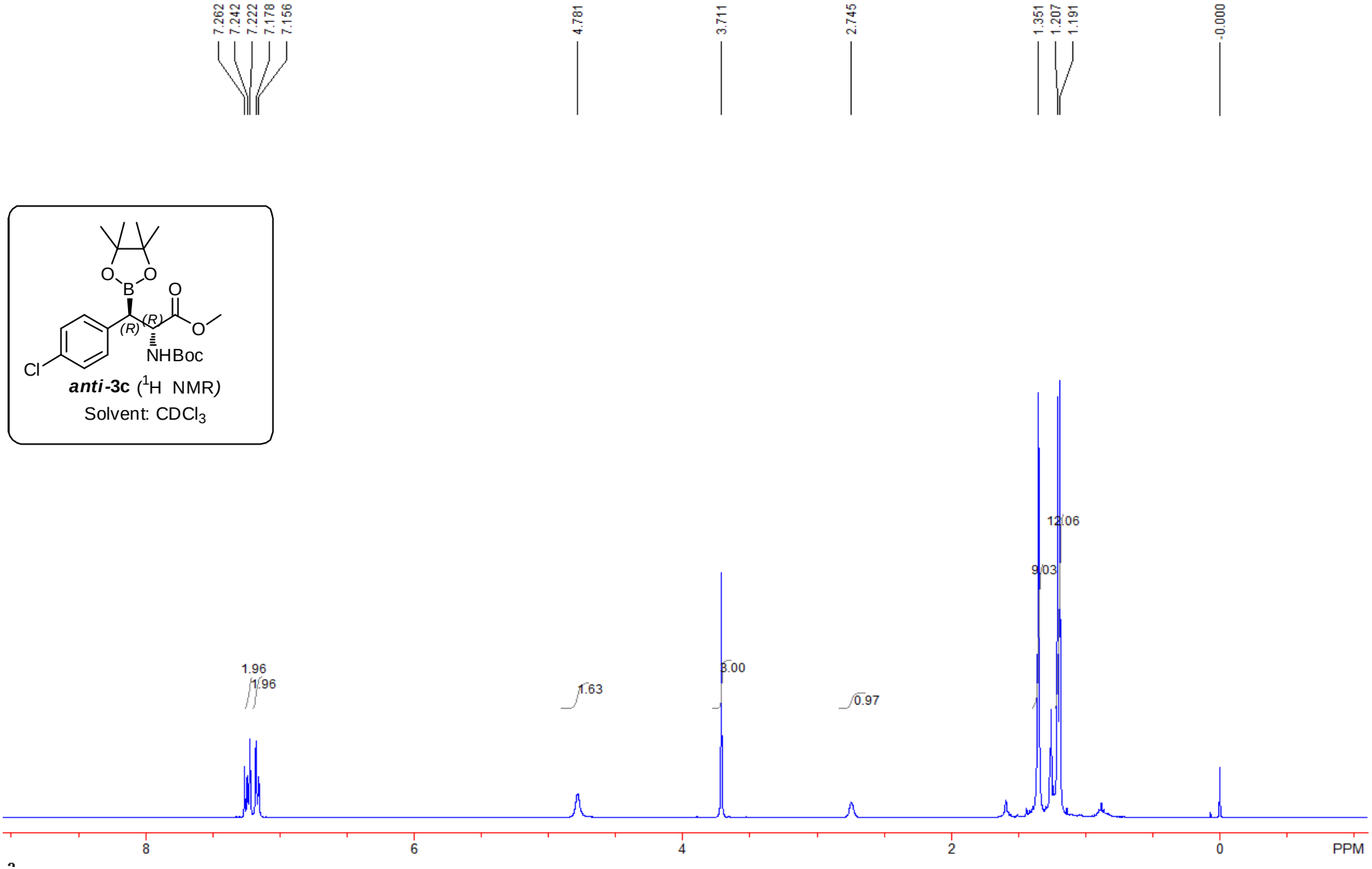


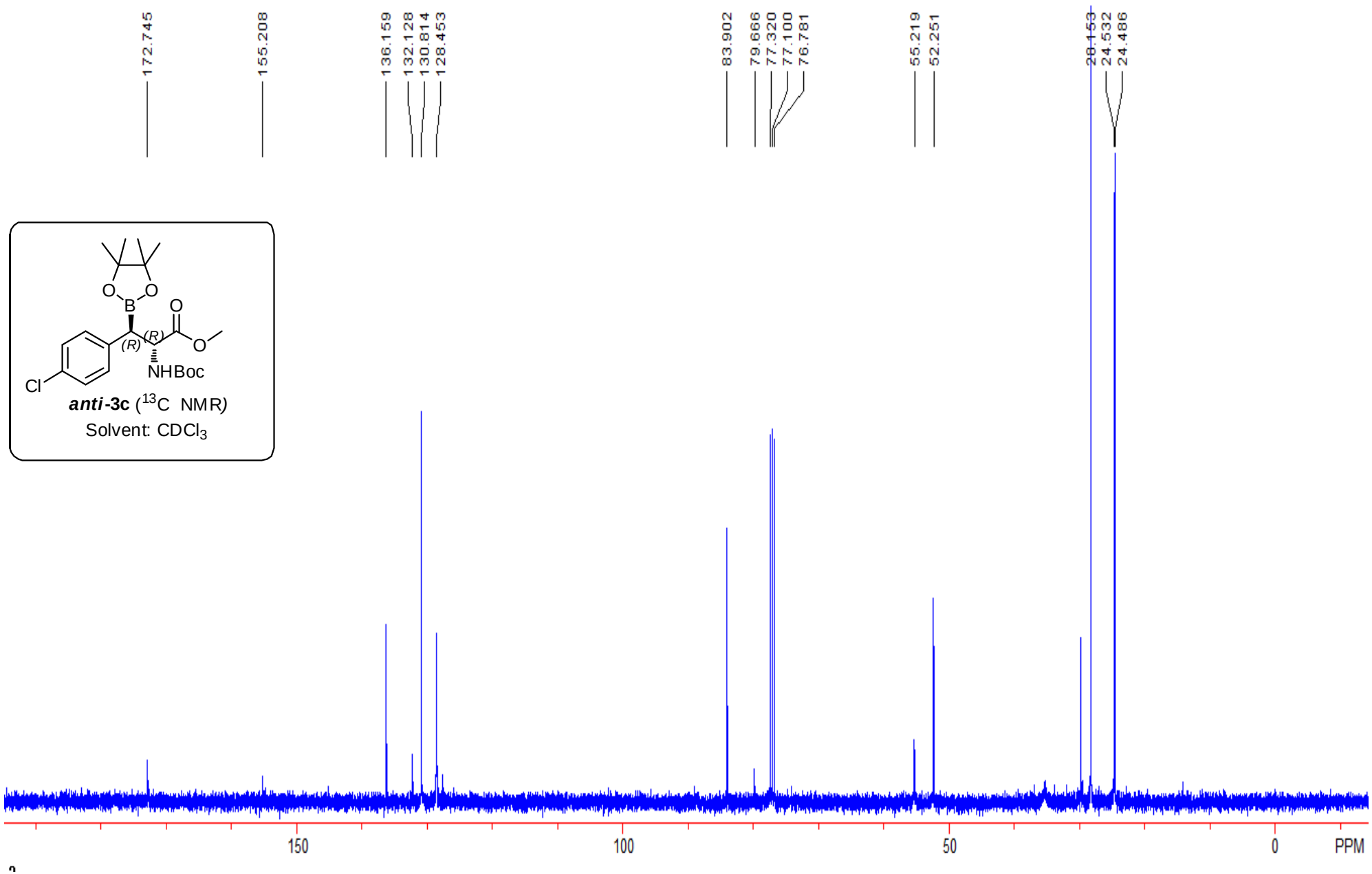
***anti*-3b** (^{1}H NMR)
Solvent: $CDCl_3$

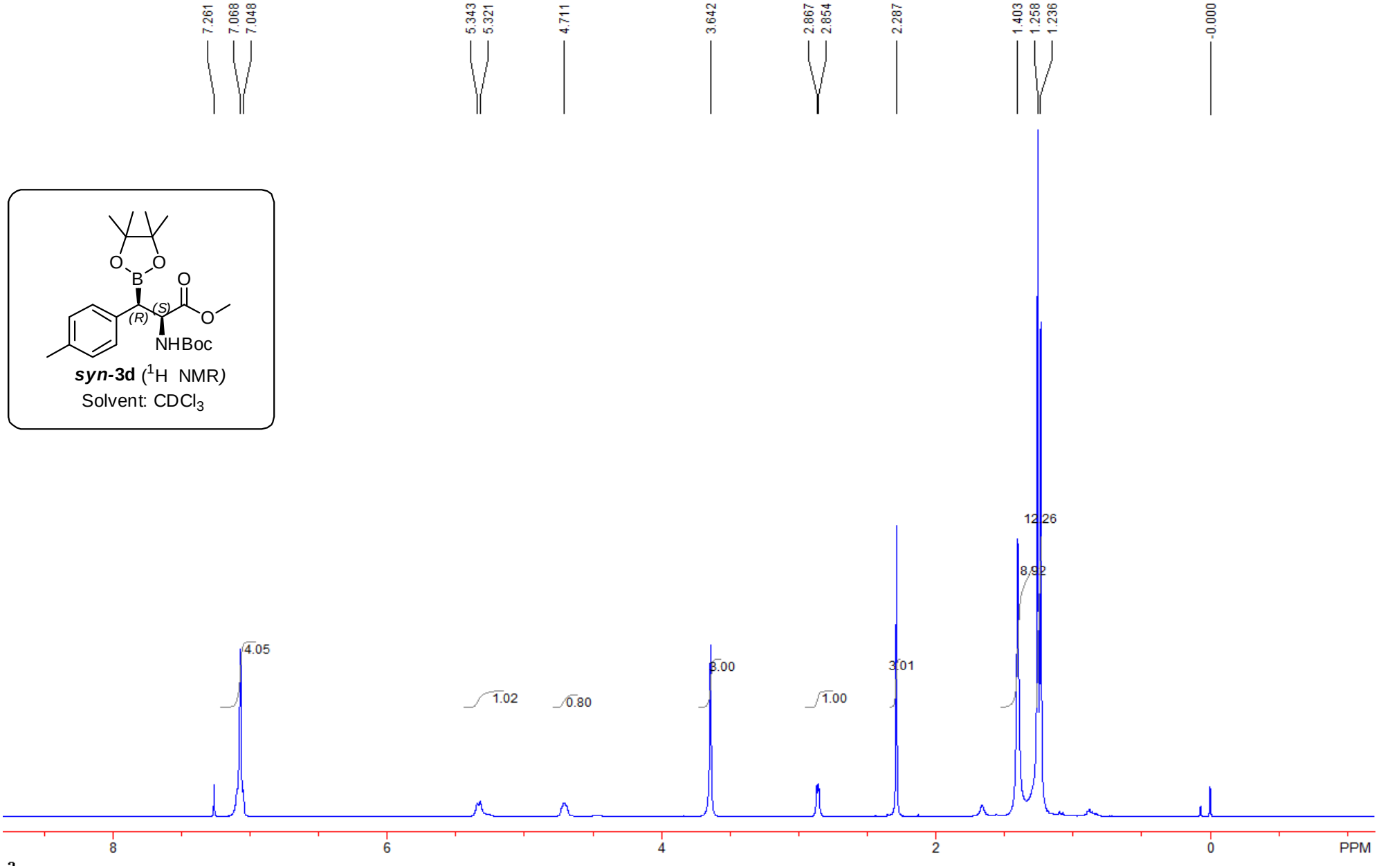

172.768
155.116
136.706
131.406
131.224
120.269
83.910
79.712
77.305
77.100
76.667
55.166
52.258
28.153
24.547
24.494
grease
180
160
140
120
100
80
60
40
20PPM
anti-3b (13C NMR)
Solvent: CDCl3

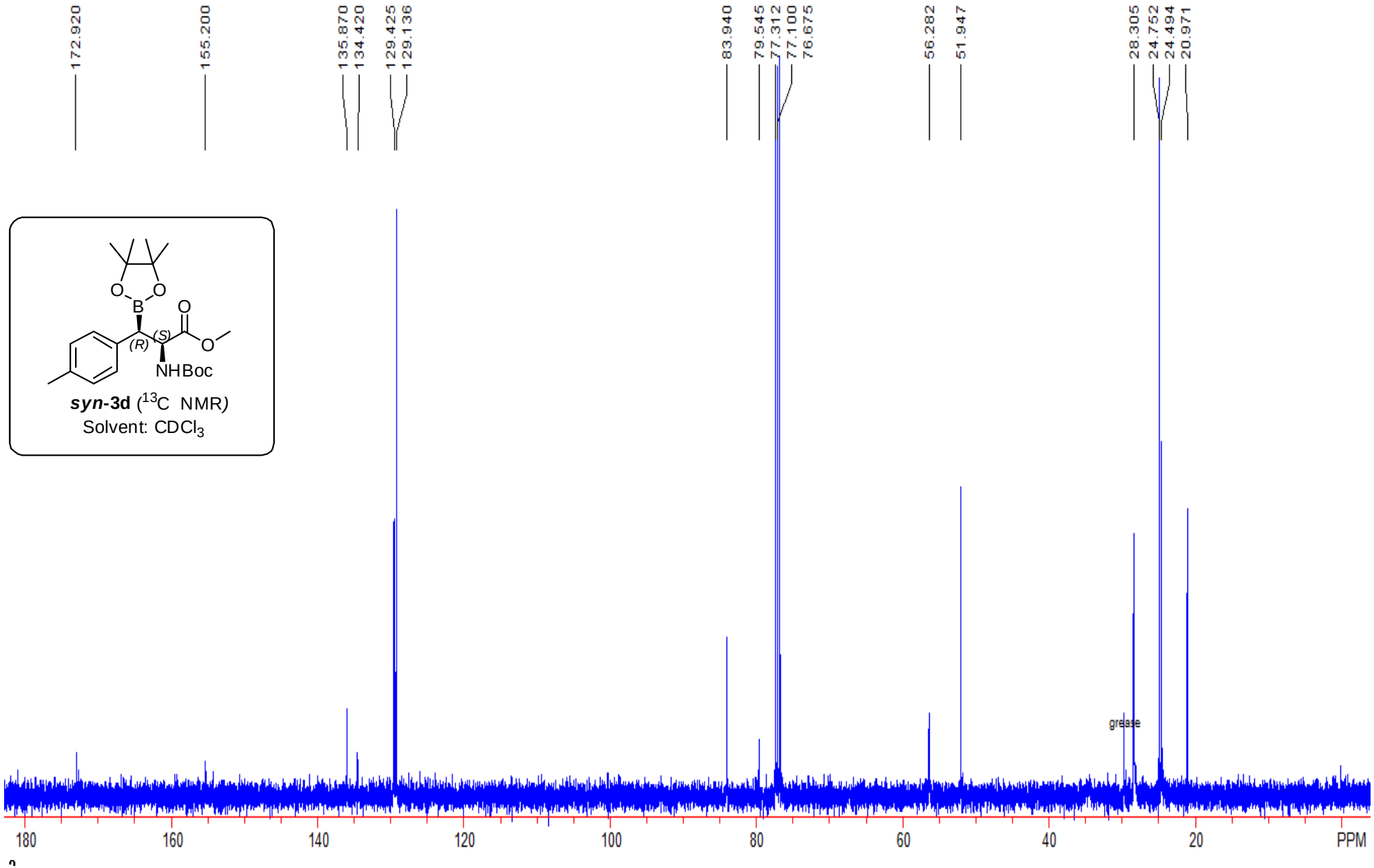

7.261
7.239
7.218
7.150
7.131
5.307
5.288
4.710
3.650
2.895
2.883
1.408
1.256
1.234
-0.000
O
B
O
O
(R)
(S)
O
NHBoc
Cl
syn-3c (1H NMR)
Solvent: CDCl3
1.95
1.98
0.99
0.83
3.00
1.02
14.79
8.96
8
7
6
5
4
3
2
1
0
PPM

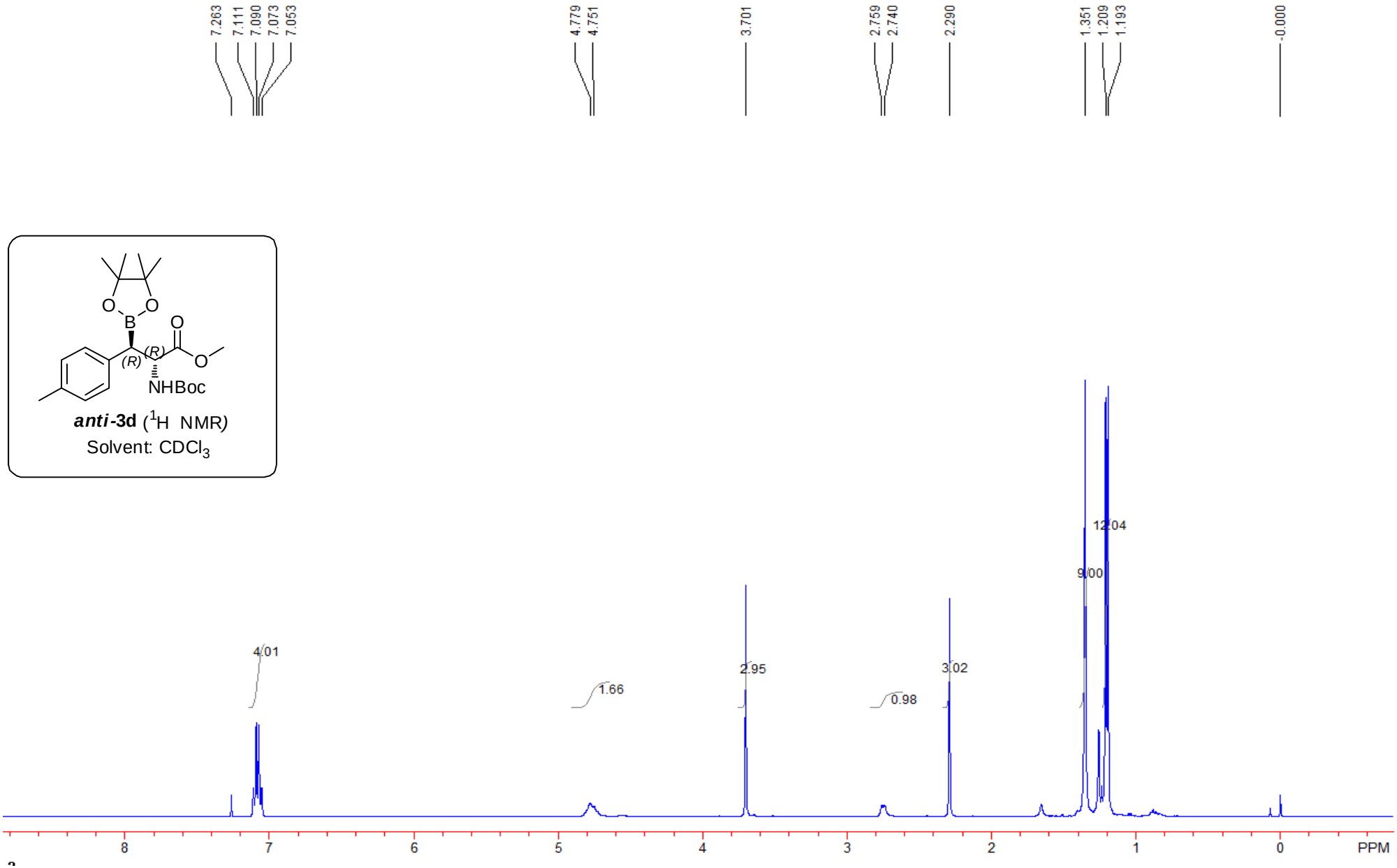

172.566
136.373
132.439
130.978
128.553
127.479
84.193
79.833
77.321
77.100
76.689
56.144
52.044
28.308
24.761
24.524
grease
180
160
140
120
100
80
60
40
20 PPM
Cl
NHBoc
(R)
(S)
syn-3c (13C NMR)
Solvent: CDCl3

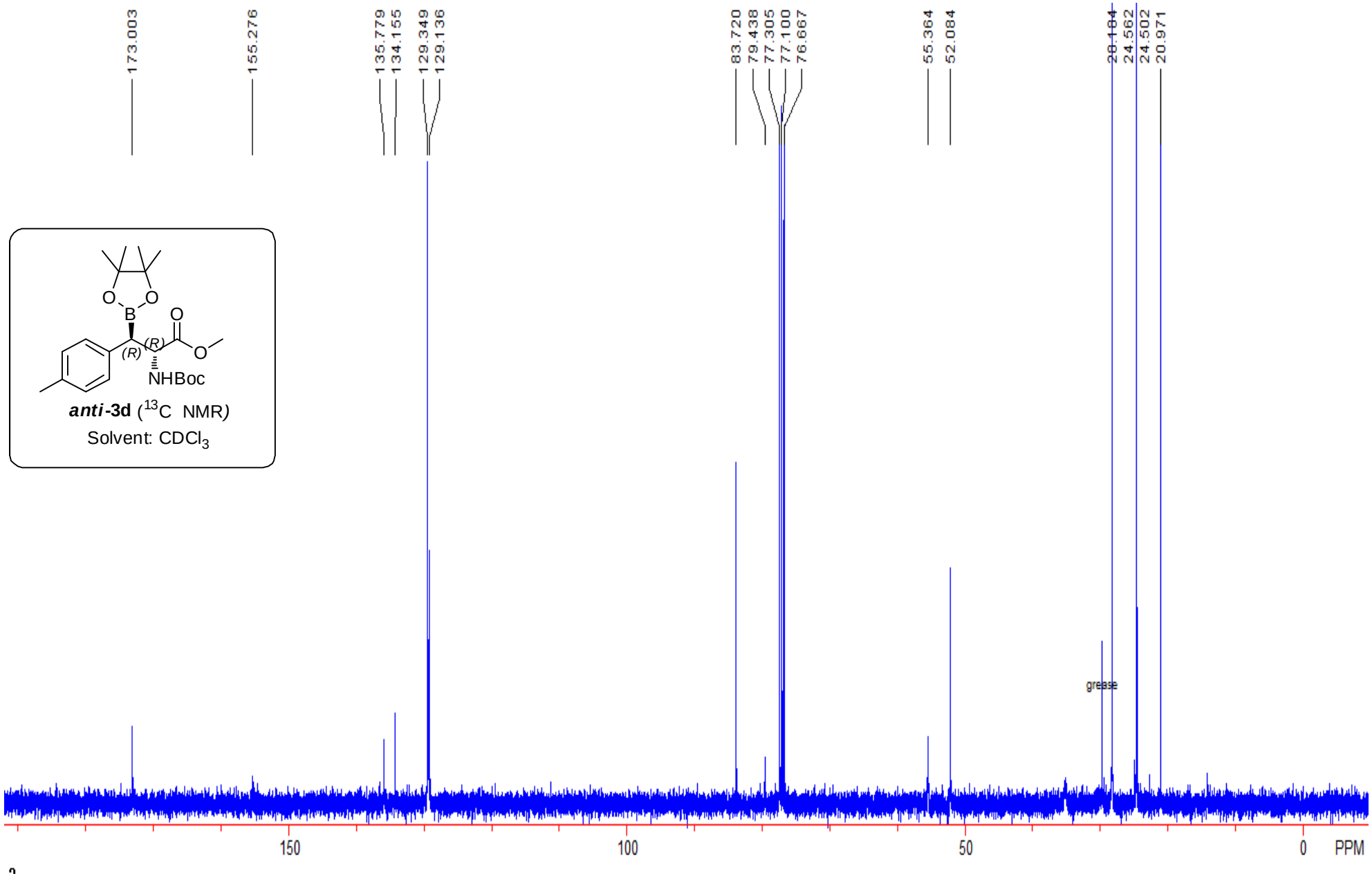

7.262
7.242
7.222
7.178
7.156
4.781
3.711
2.745
1.351
1.207
1.191
-0.000
anti-3c (1H NMR)
Solvent: CDCl3
Cl
(R)
(R)
NHBoc
1.96
1.96
1.63
3.00
0.97
9.03
12.06
8
6
4
2
0
PPM

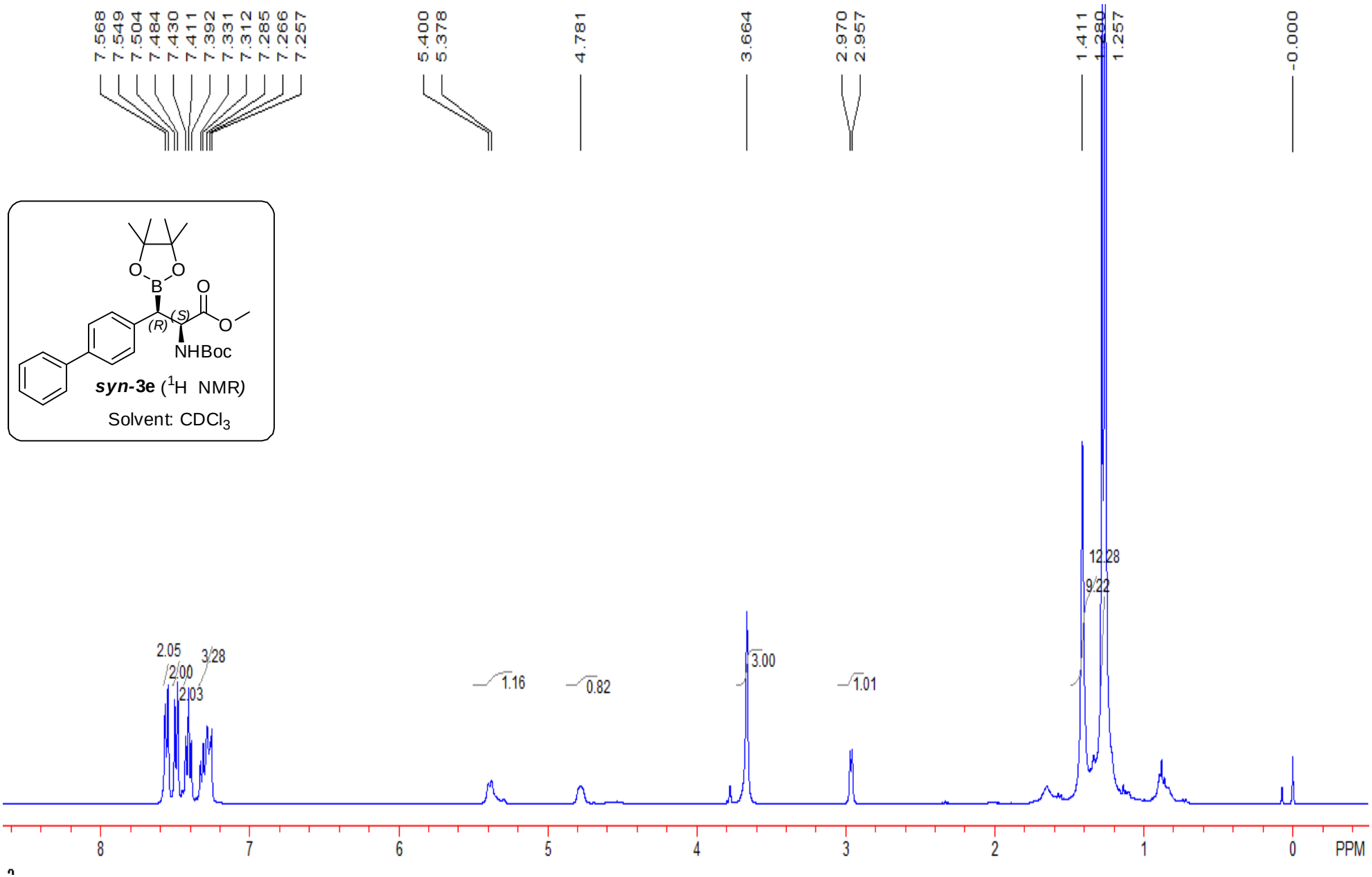

172.745
155.208
136.159
132.128
130.814
128.453
83.902
79.666
77.320
77.100
76.781
55.219
52.251
28.153
24.532
24.486
anti-3c (13C NMR)
Solvent: CDCl3
150
100
50
0
PPM

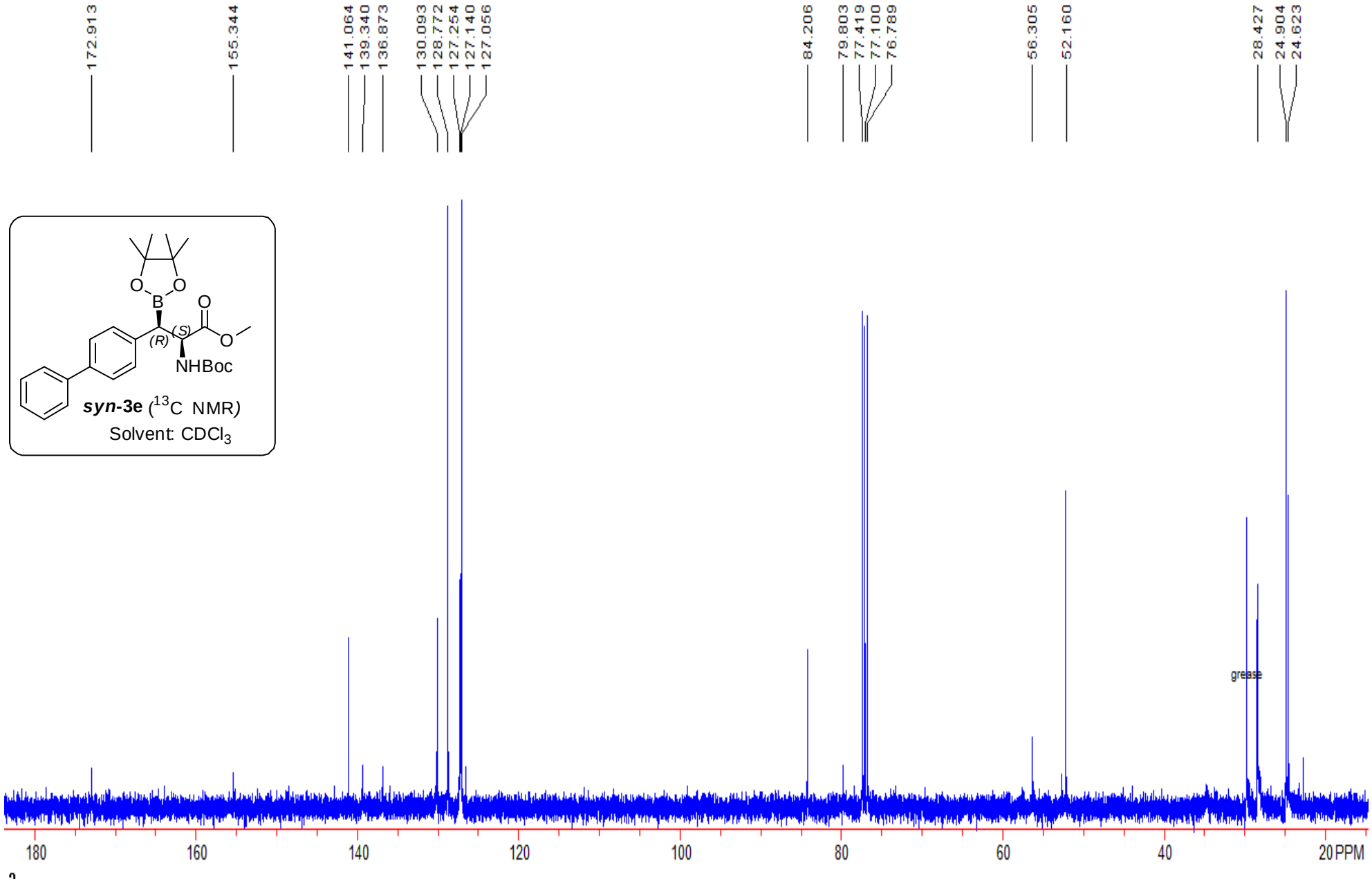

7.261
7.068
7.048
5.343
5.321
4.711
3.642
2.867
2.854
2.287
1.403
1.258
1.236
-0.000
O
B
O
O
(R)
(S)
O
NHBoc
syn-3d (1H NMR)
Solvent: CDCl3
4.05
1.02
0.80
3.00
1.00
3.01
8.92
12.26
8
6
4
2
0
PPM

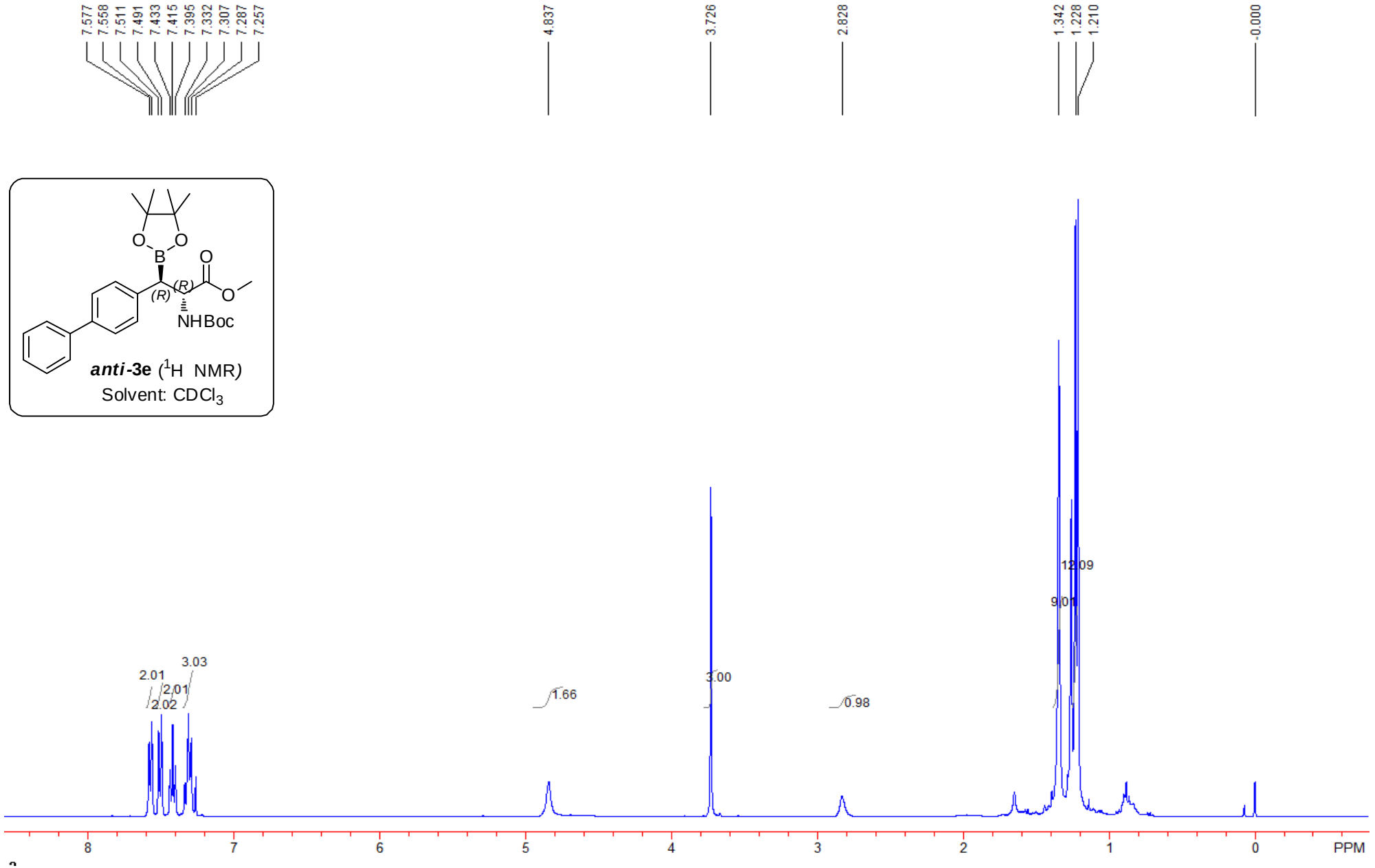

172.920
155.200
135.870
134.420
129.425
129.136
83.940
79.545
77.312
77.100
76.675
56.282
51.947
28.305
24.752
24.494
20.971
grease
180
160
140
120
100
80
60
40
20
PPM
syn-3d (13C NMR)
Solvent: CDCl3

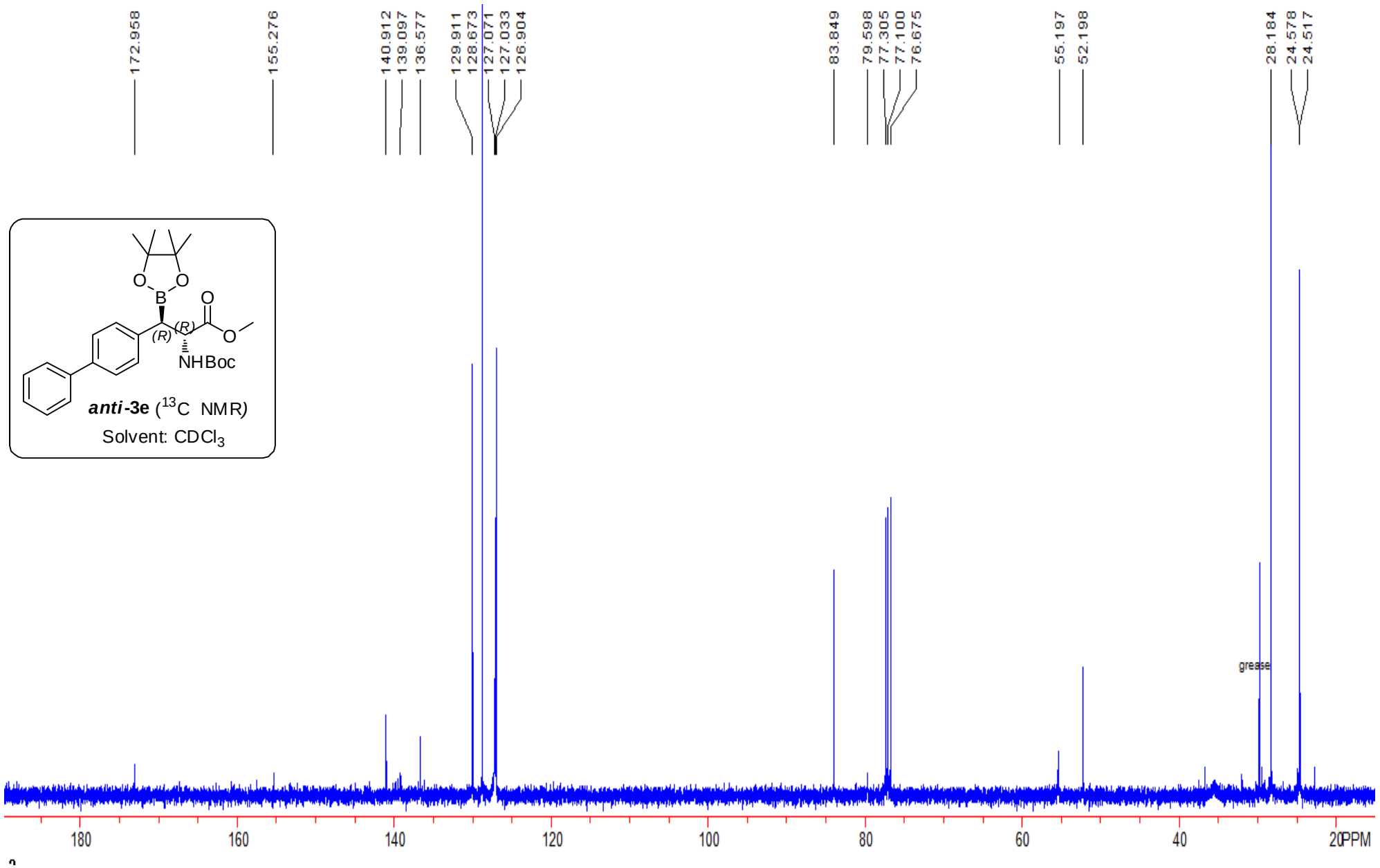

7.263
7.111
7.090
7.073
7.053
4.779
4.751
3.701
2.759
2.740
2.290
1.351
1.209
1.193
-0.000
O
B
O
O
(R)
(R)
O
NHBoc
anti-3d (1H NMR)
Solvent: CDCl3
4.01
1.66
2.95
0.98
3.02
9.00
12.04
8
7
6
5
4
3
2
1
0
PPM


173.003
155.276
135.779
134.155
129.349
129.136
83.720
79.438
77.305
77.100
76.667
55.364
52.084
28.184
24.562
24.502
20.971
grease
150
100
50
0
PPM
anti-3d (13C NMR)
Solvent: CDCl3


7.568
7.549
7.504
7.484
7.430
7.411
7.392
7.331
7.312
7.285
7.266
7.257
5.400
5.378
4.781
3.664
2.970
2.957
1.411
1.280
1.257
-0.000
O
B
O
O
(R)
(S)
O
NHBoc
syn-3e (1H NMR)
Solvent: CDCl3
2.05
2.00
2.03
3.28
1.16
0.82
3.00
1.01
12.28
9.22
8
7
6
5
4
3
2
1
0
PPM


172.913
155.344
141.064
139.340
136.873
130.093
128.772
127.254
127.140
127.056
84.206
79.803
77.419
77.100
76.789
56.305
52.160
28.427
24.904
24.623
O
B
O
O
(S)
(R)
O
NHBoc
syn-3e (13C NMR)
Solvent: CDCl3
grease
180
160
140
120
100
80
60
40
20 PPM


7.577
7.558
7.511
7.491
7.433
7.415
7.395
7.332
7.307
7.287
7.257
4.837
3.726
2.828
1.342
1.228
1.210
-0.000
O
B
O
O
(R)
(R)
O
NHBoc
anti-3e (1H NMR)
Solvent: CDCl3
2.01
2.01
2.02
3.03
1.66
3.00
0.98
12.09
9.01
8
7
6
5
4
3
2
1
0
PPM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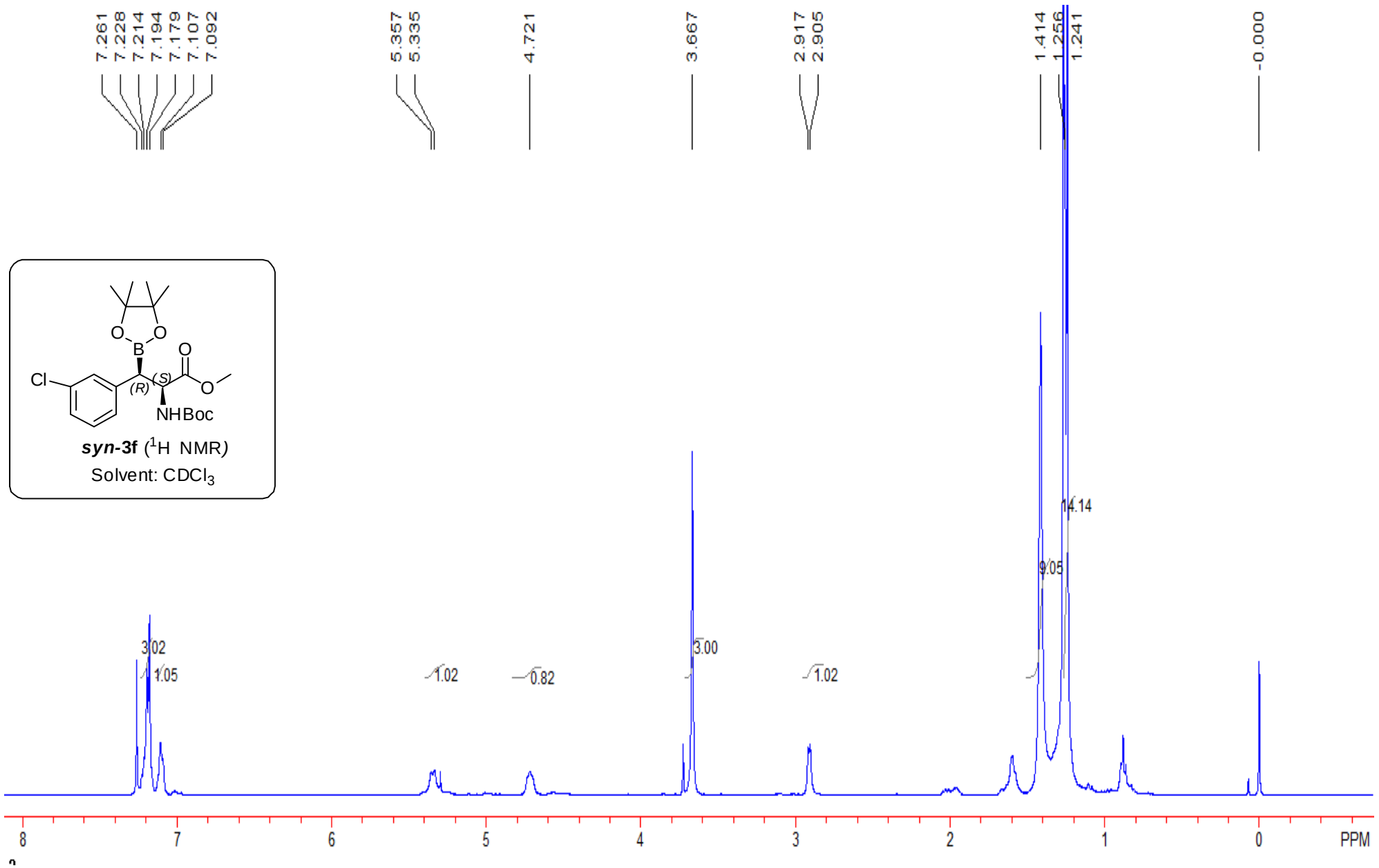
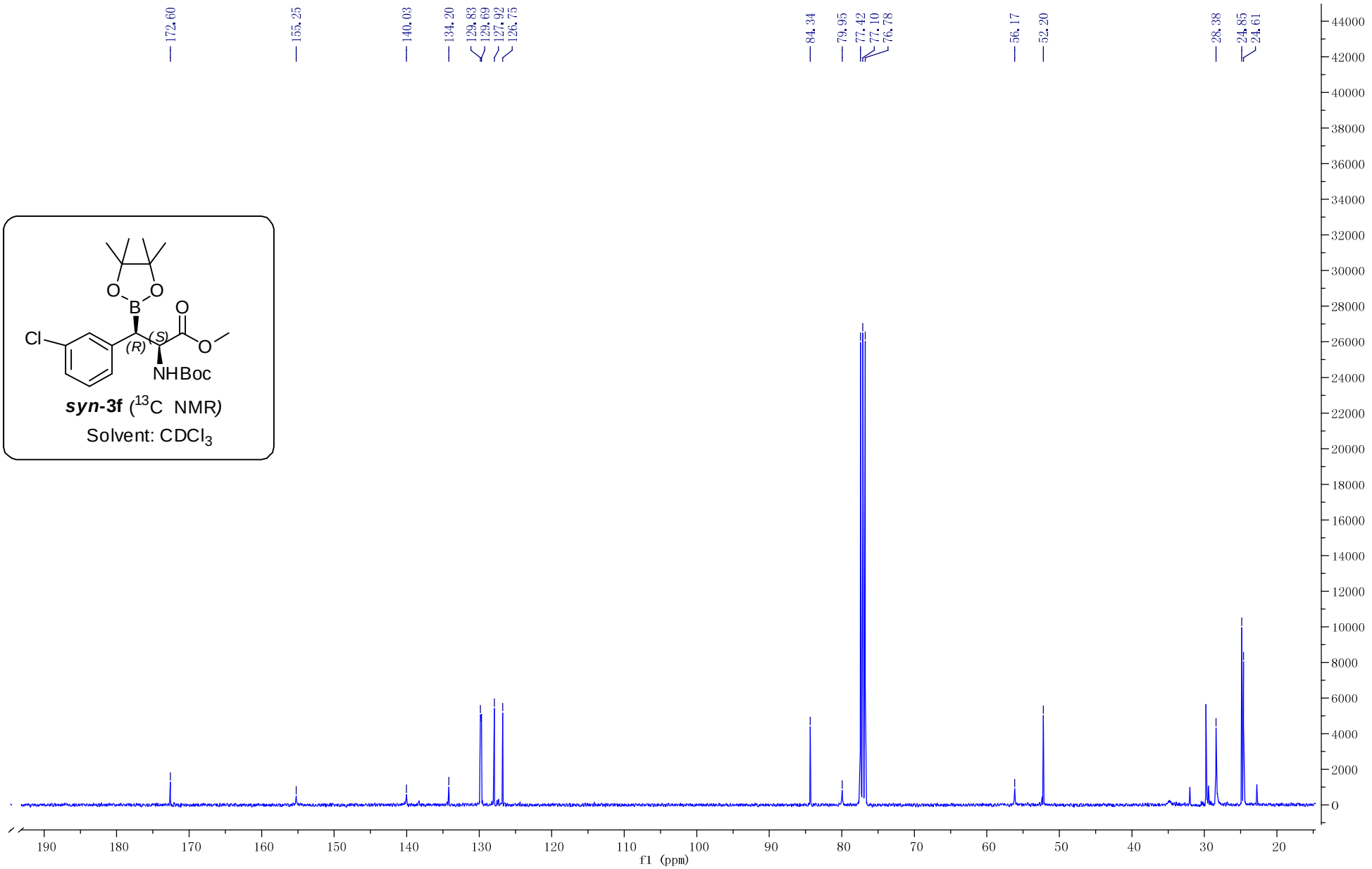
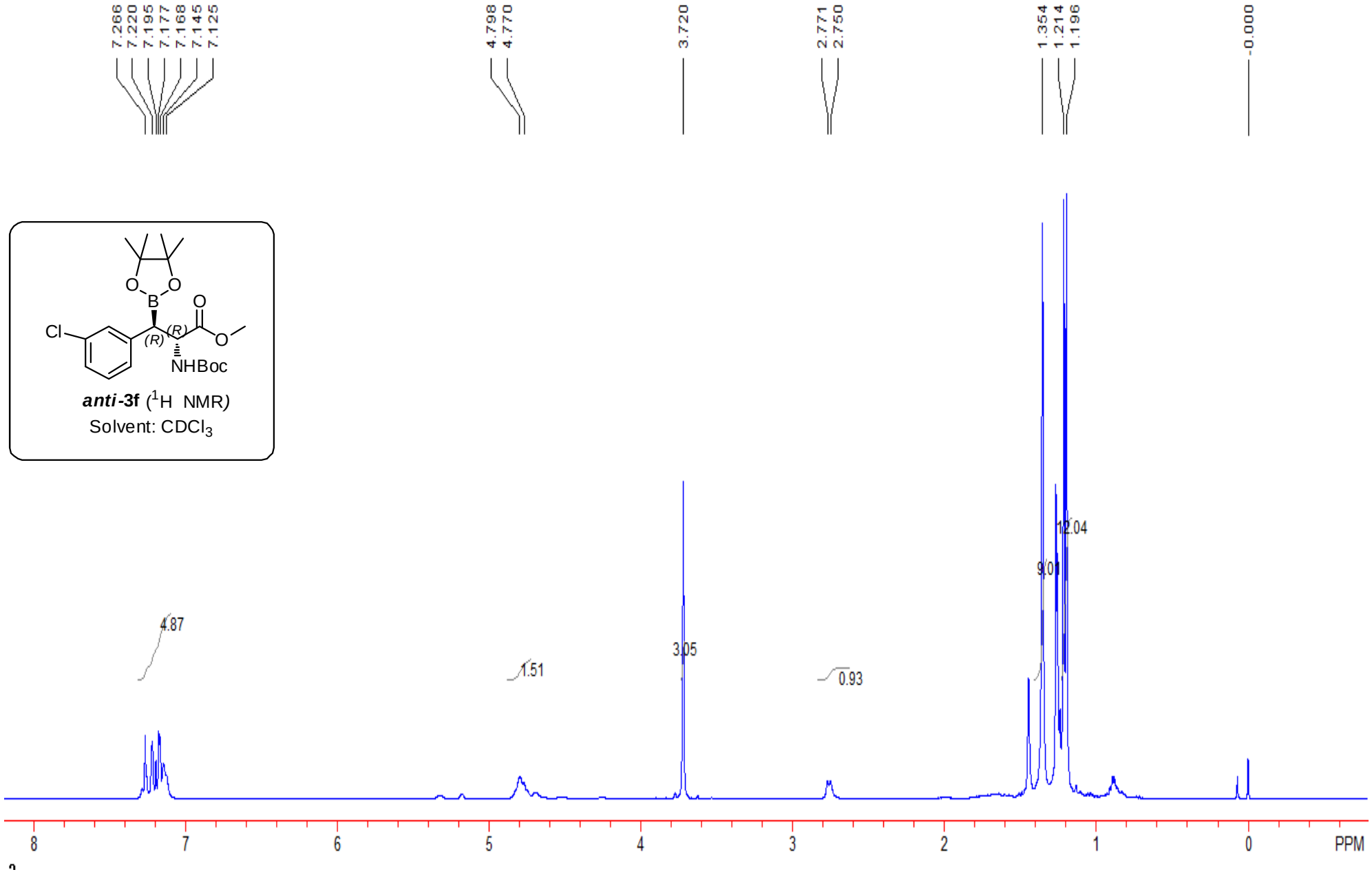
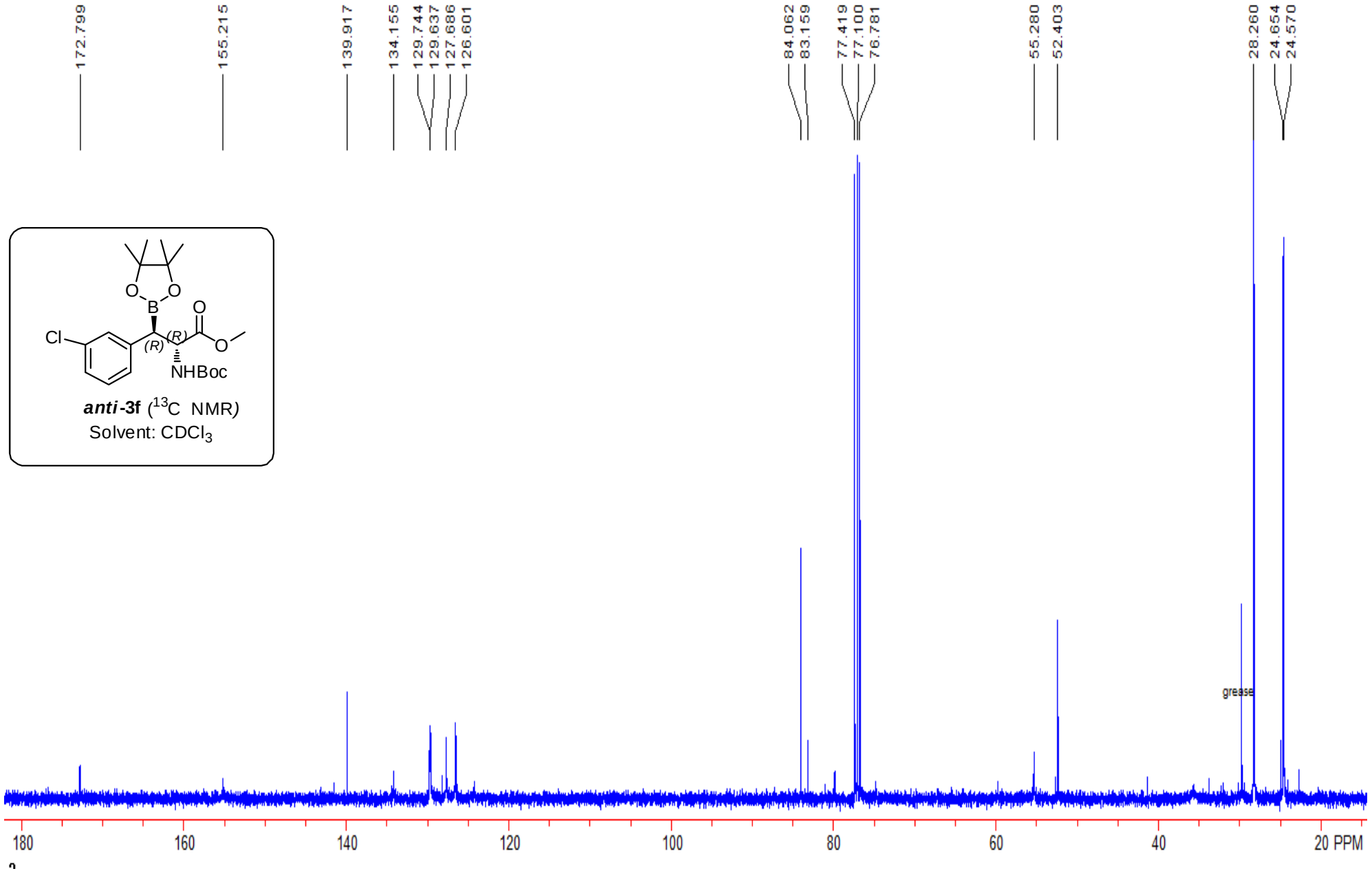
155.276
140.912
139.097
136.577
129.911
128.673
127.071
127.033
126.904
83.849
79.598
77.305
77.100
76.675
55.197
52.198
28.184
24.578
24.517
grease
180
160
140
120
100
80
60
40
20
PPM
anti-3e (13C NMR)
Solvent: CDCl3


7.261
7.228
7.214
7.194
7.179
7.107
7.092
5.357
5.335
4.721
3.667
2.917
2.905
1.414
1.256
1.241
-0.000
Cl
O
B
O
O
(R)
(S)
O
NHBoc
syn-3f (1H NMR)
Solvent: CDCl3
3.02
1.05
1.02
0.82
3.00
1.02
14.14
9.05
8
7
6
5
4
3
2
1
0
PPM


172.60
155.25
140.03
134.20
129.83
129.69
127.92
126.75
84.34
79.95
77.42
77.10
76.78
56.17
52.20
28.38
24.85
24.61
Cl
(R)
(S)
O
B
O
O
O
NHBoc
syn-3f (13C NMR)
Solvent: CDCl3
f1 (ppm)


7.266
7.220
7.195
7.177
7.168
7.145
7.125
4.798
4.770
3.720
2.771
2.750
1.354
1.214
1.196
-0.000
Cl
O
B
O
O
(R)
(R)
O
NHBoc
anti-3f (1H NMR)
Solvent: CDCl3
4.87
1.51
3.05
0.93
9.01
12.04
8
7
6
5
4
3
2
1
0
PPM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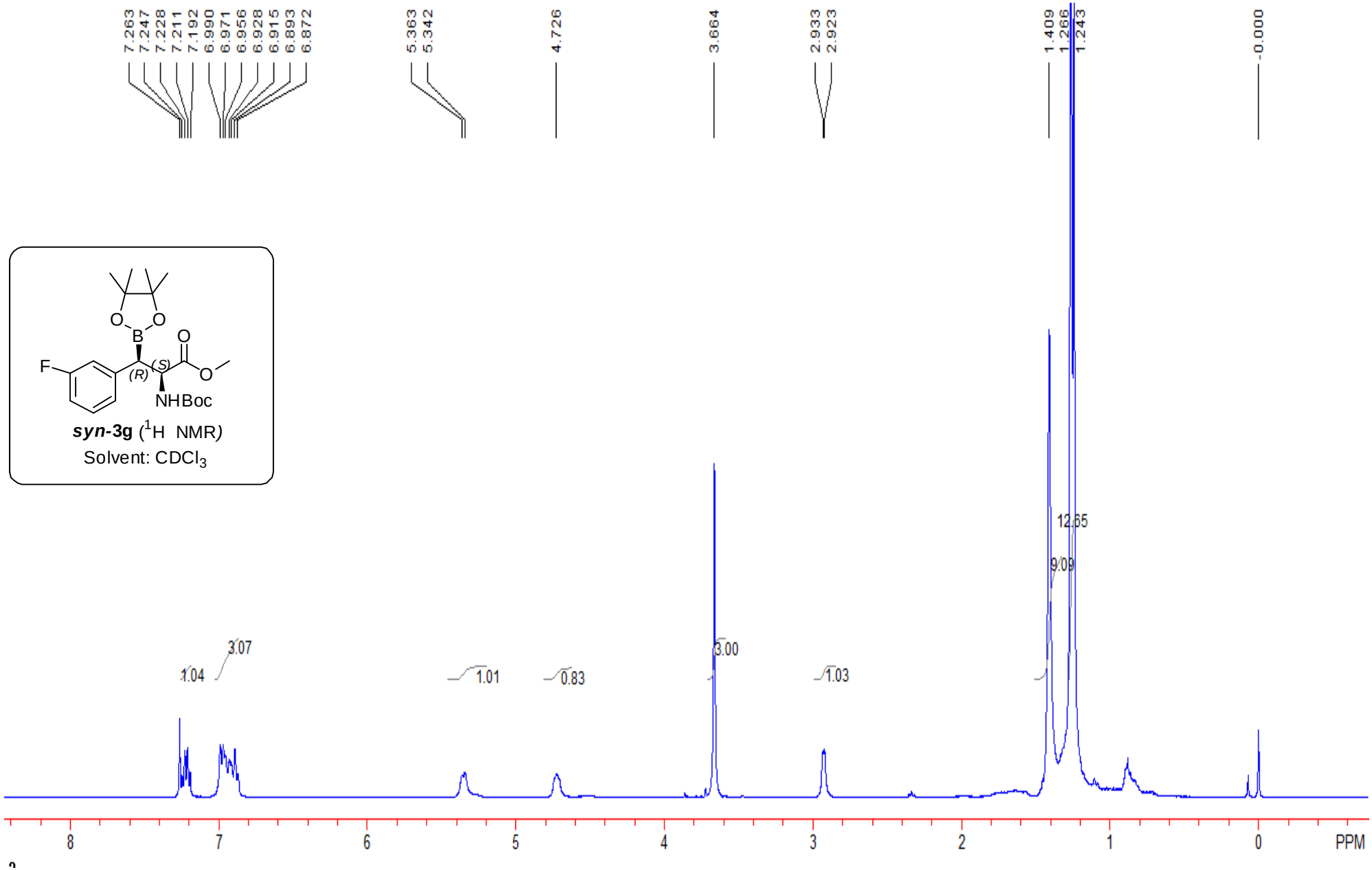
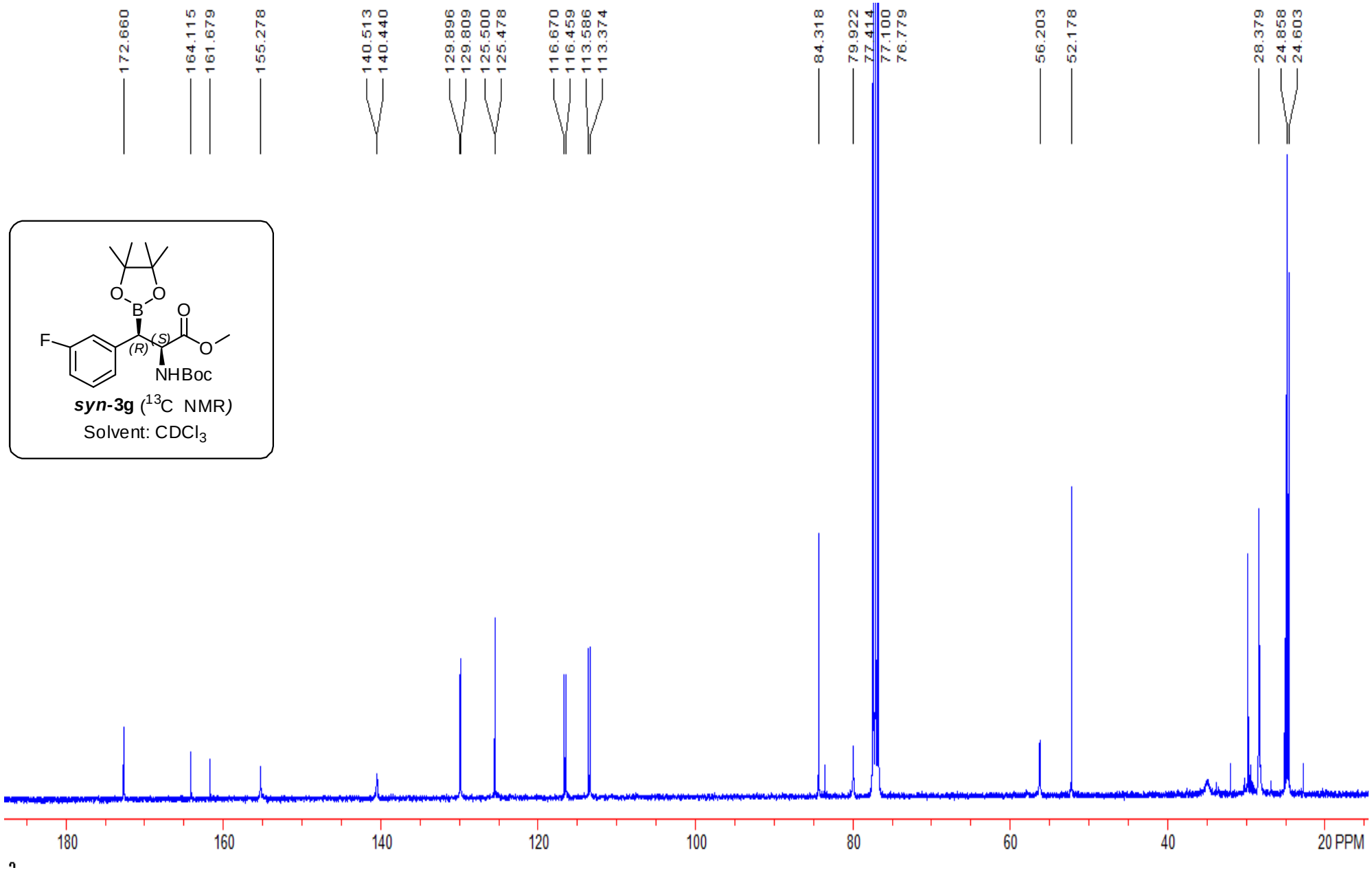
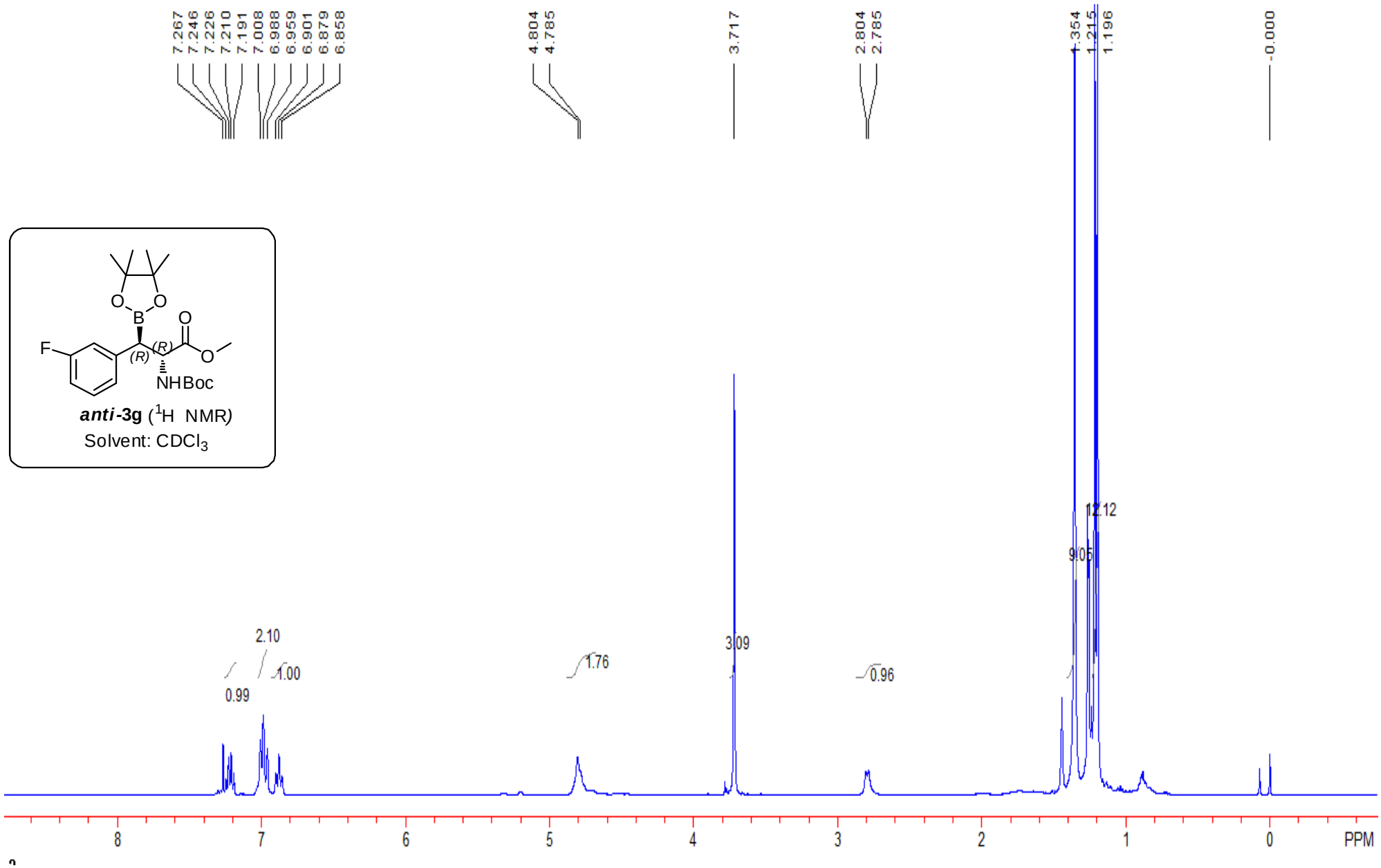
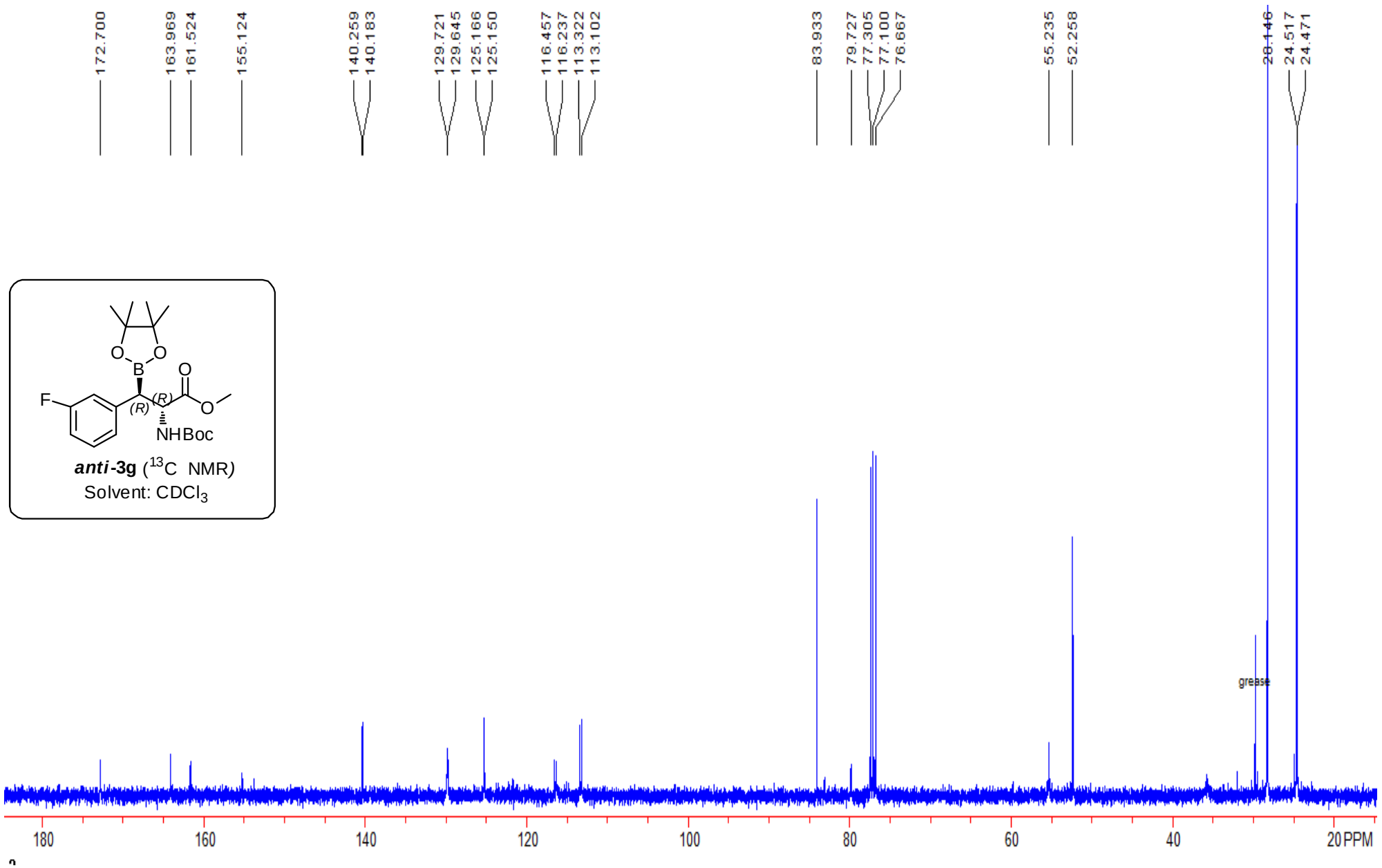
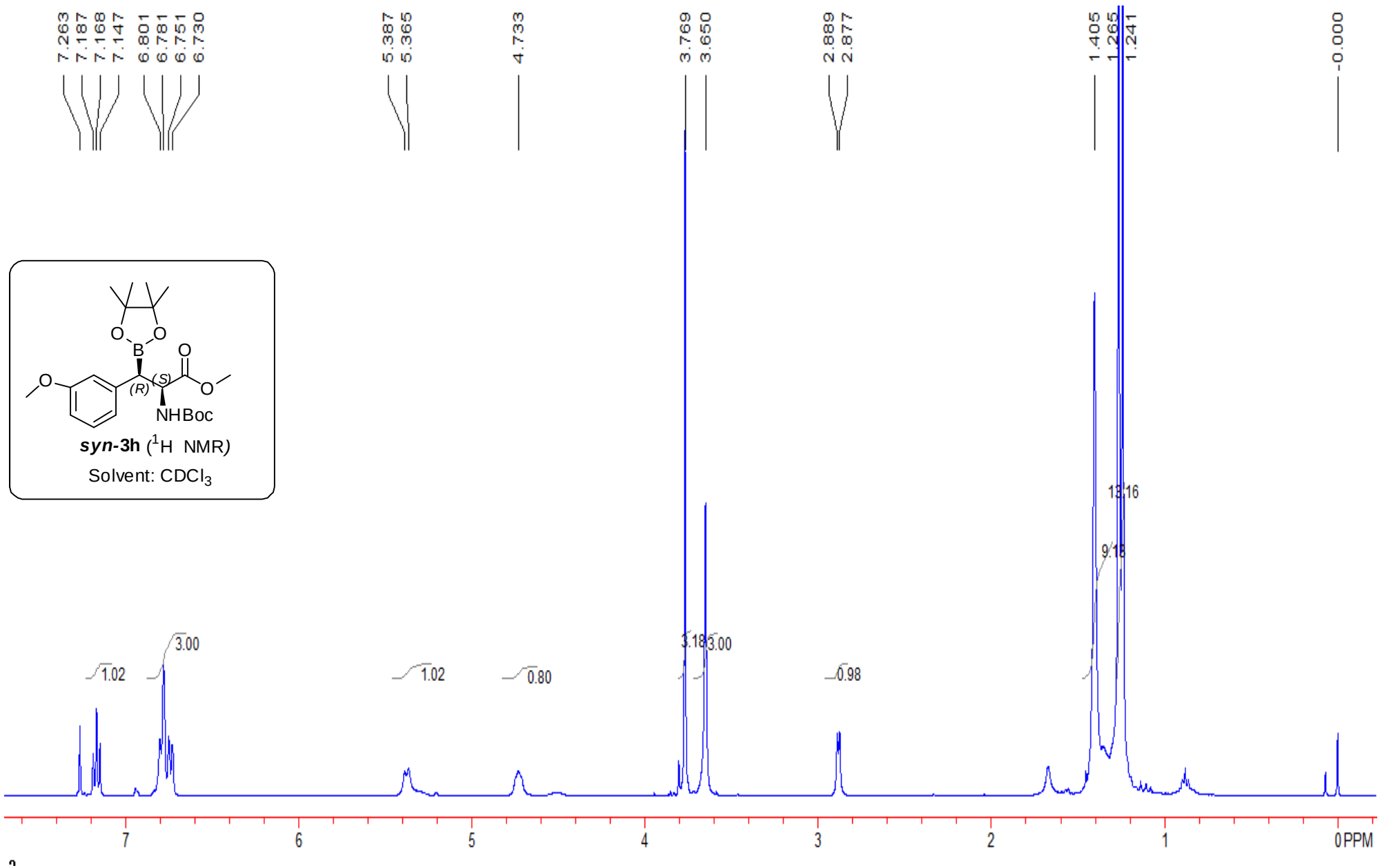
139.917
134.155
129.744
129.637
127.686
126.601
84.062
83.159
77.419
77.100
76.781
55.280
52.403
28.260
24.654
24.570
Cl
(R)
(R)
O
B
O
O
O
NHBoc
anti-3f (13C NMR)
Solvent: CDCl3
grease
180
160
140
120
100
80
60
40
20 PPM

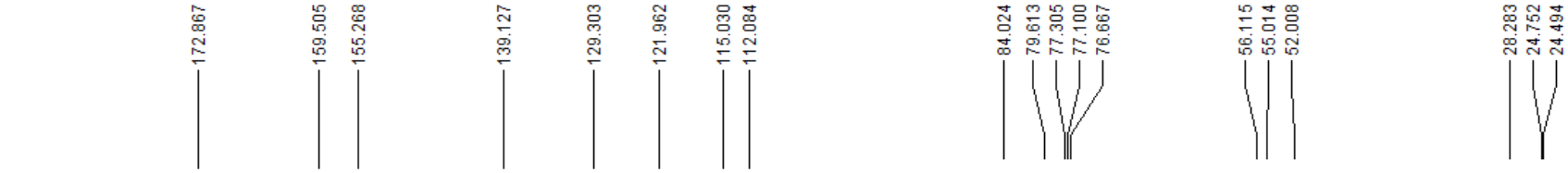

7.263
7.247
7.228
7.211
7.192
6.990
6.971
6.956
6.928
6.915
6.893
6.872
5.363
5.342
4.726
3.664
2.933
2.923
1.409
1.266
1.243
-0.000
F
O
B
O
O
(R)
(S)
O
NHBoc
syn-3g (1H NMR)
Solvent: CDCl3
1.04
3.07
1.01
0.83
3.00
1.03
12.65
9.09
8
7
6
5
4
3
2
1
0
PPM

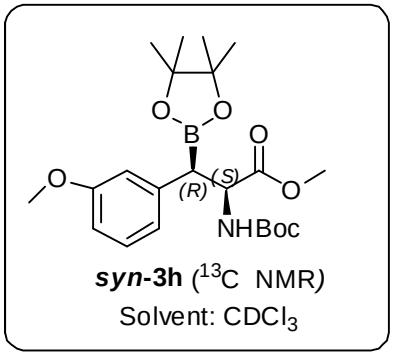

172.660
164.115
161.679
155.278
140.513
140.440
129.896
129.809
125.500
125.478
116.670
116.459
113.586
113.374
84.318
79.922
77.414
77.100
76.779
56.203
52.178
28.379
24.858
24.603
F
(R)
(S)
O
B
O
O
O
NHBoc
syn-3g (13C NMR)
Solvent: CDCl3
180
160
140
120
100
80
60
40
20 PPM


7.267
7.246
7.226
7.210
7.191
7.008
6.988
6.959
6.901
6.879
6.858
4.804
4.785
3.717
2.804
2.785
1.354
1.215
1.196
-0.000
F
O
B
O
O
(R)
(R)
O
NHBoc
anti-3g (1H NMR)
Solvent: CDCl3
2.10
1.00
0.99
1.76
3.09
0.96
12.12
9.05
8
7
6
5
4
3
2
1
0
PPM


172.700
163.969
161.524
155.124
140.259
140.183
129.721
129.645
125.166
125.150
116.457
116.237
113.322
113.102
83.933
79.727
77.305
77.100
76.667
55.235
52.258
28.146
24.517
24.471
grease
180
160
140
120
100
80
60
40
20 PPM
F
O
B
O
O
(R)
(R)
O
NHBoc
anti-3g (13C NMR)
Solvent: CDCl3

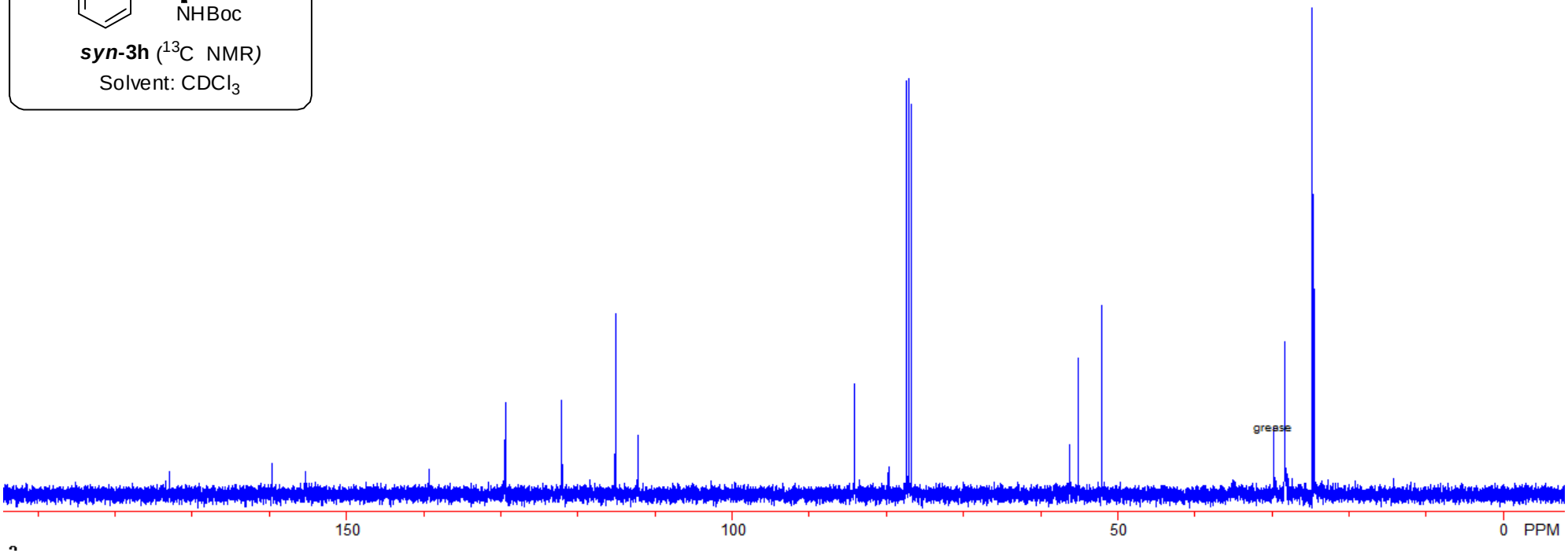

7.263
7.187
7.168
7.147
6.801
6.781
6.751
6.730
5.387
5.365
4.733
3.769
3.650
2.889
2.877
1.405
1.265
1.241
-0.000
NHBoc
syn-3h (1H NMR)
Solvent: CDCl3
1.02
3.00
1.02
0.80
3.18
3.00
0.98
13.16
9.18
7
6
5
4
3
2
1
0 PPM

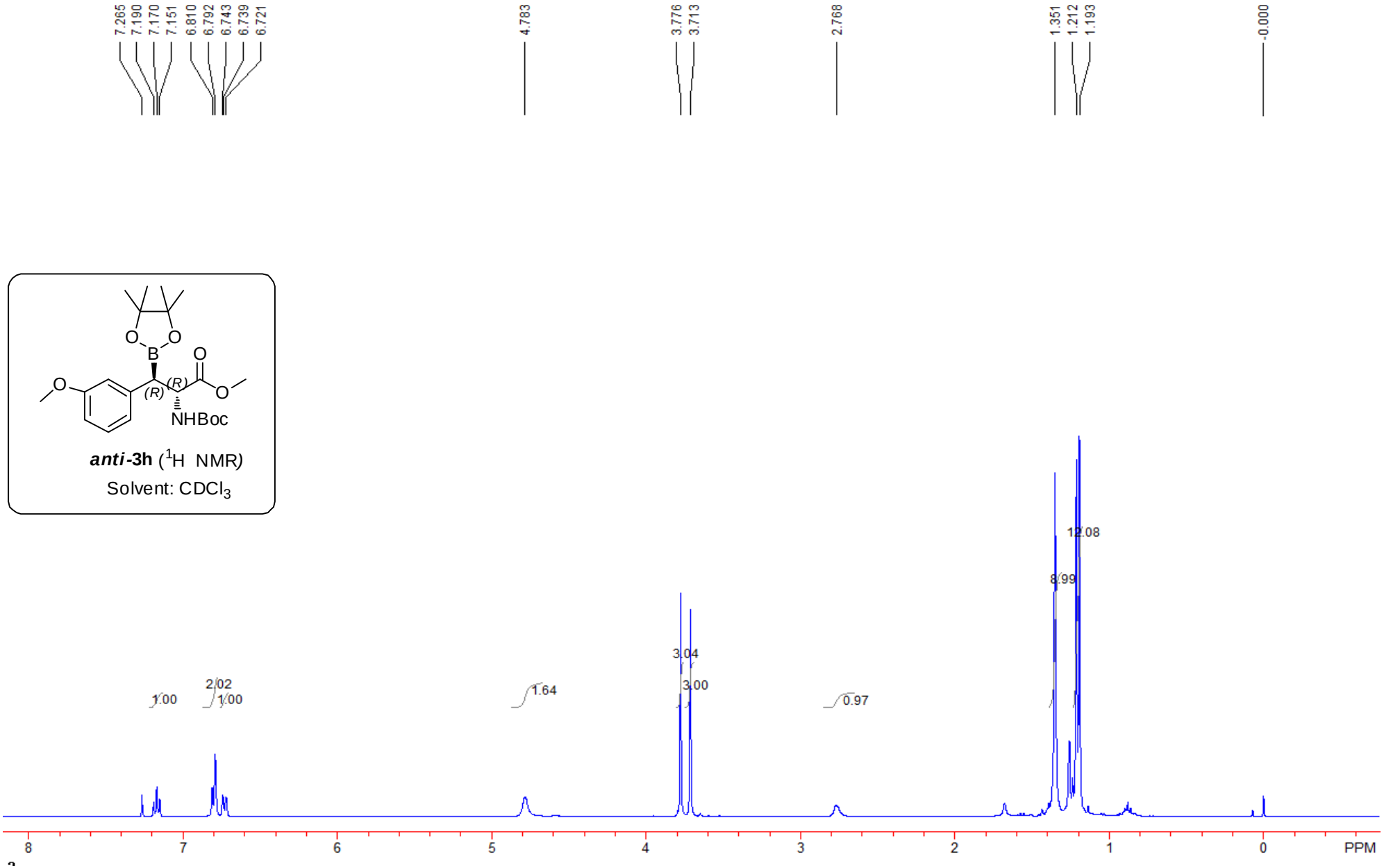


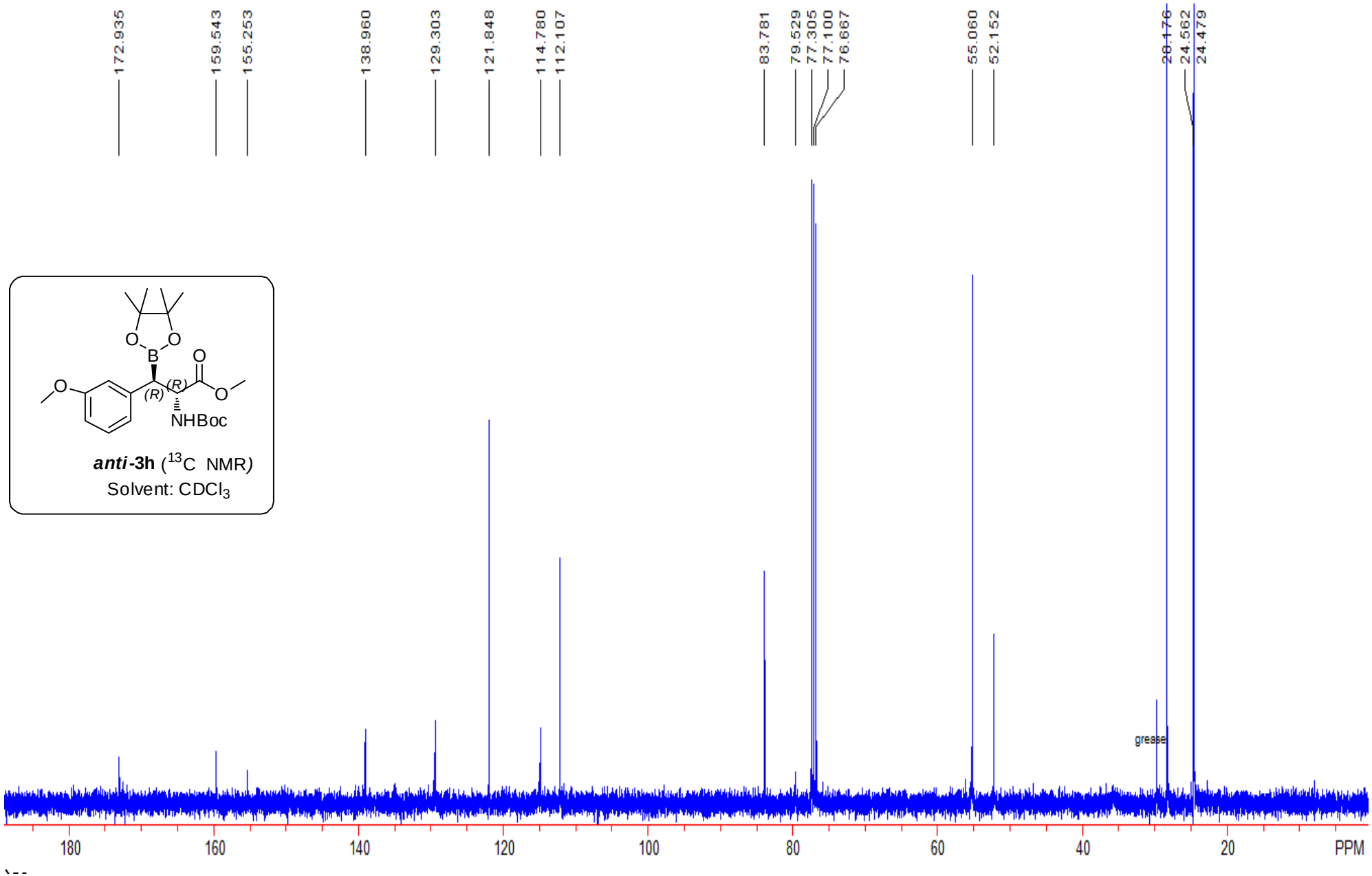


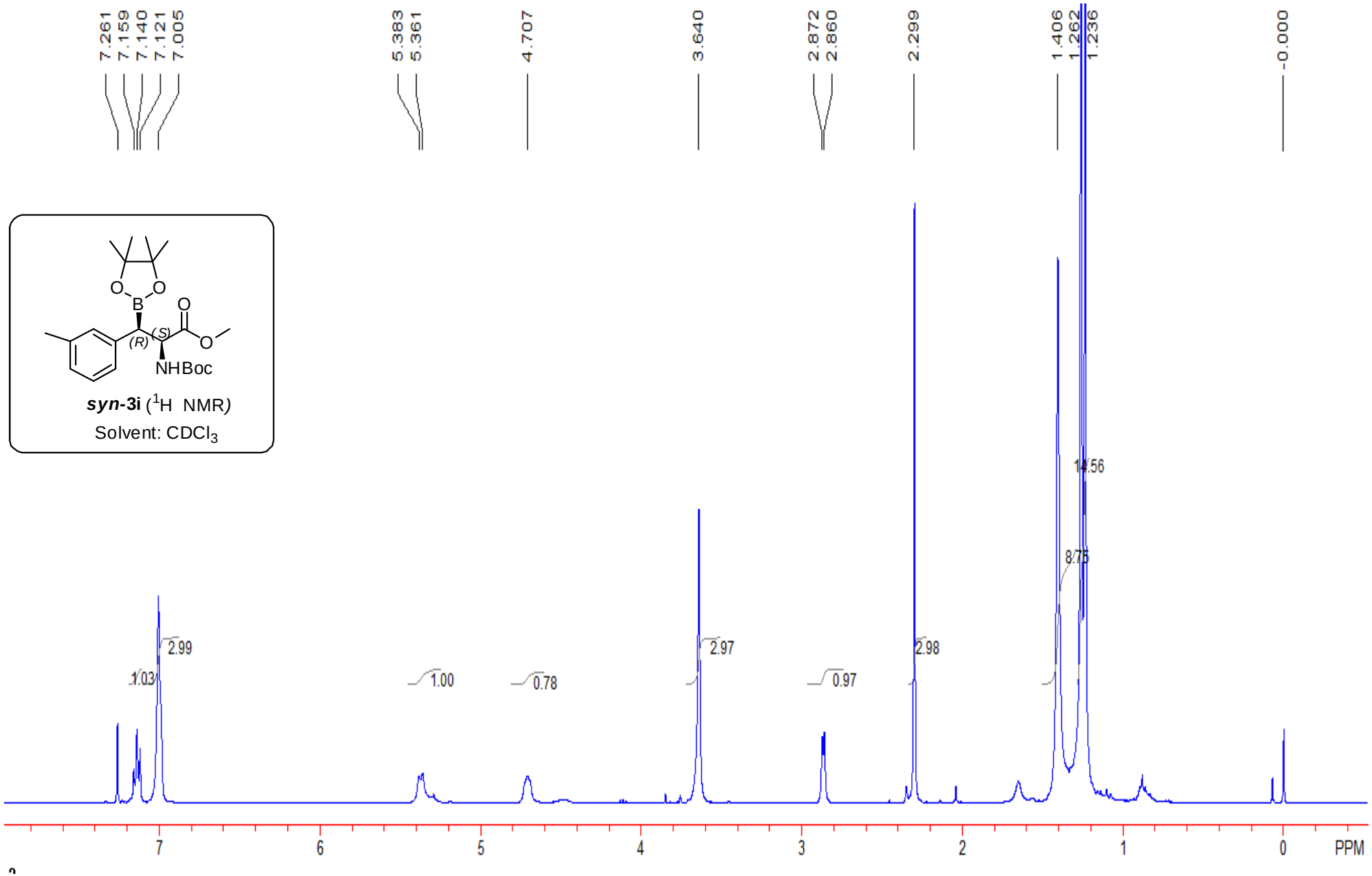
***syn*-3h** (^{13}C NMR)

Solvent: $CDCl_3$




7.265
7.190
7.170
7.151
6.810
6.792
6.743
6.739
6.721
4.783
3.776
3.713
2.768
1.351
1.212
1.193
0.000
O
B
O
O
(R)
(R)
O
NHBoc
anti-3h (1H NMR)
Solvent: CDCl3
1.00
2.02
1.00
1.64
3.04
3.00
0.97
8.99
12.08
8
7
6
5
4
3
2
1
0
PPM


172.935
159.543
155.253
138.960
129.303
121.848
114.780
112.107
83.781
79.529
77.305
77.100
76.667
55.060
52.152
28.476
24.562
24.479
grease
180
160
140
120
100
80
60
40
20
PPM
NHBoc
(R)
(R)
B
O
O
O
O
O
anti-3h (13C NMR)
Solvent: CDCl3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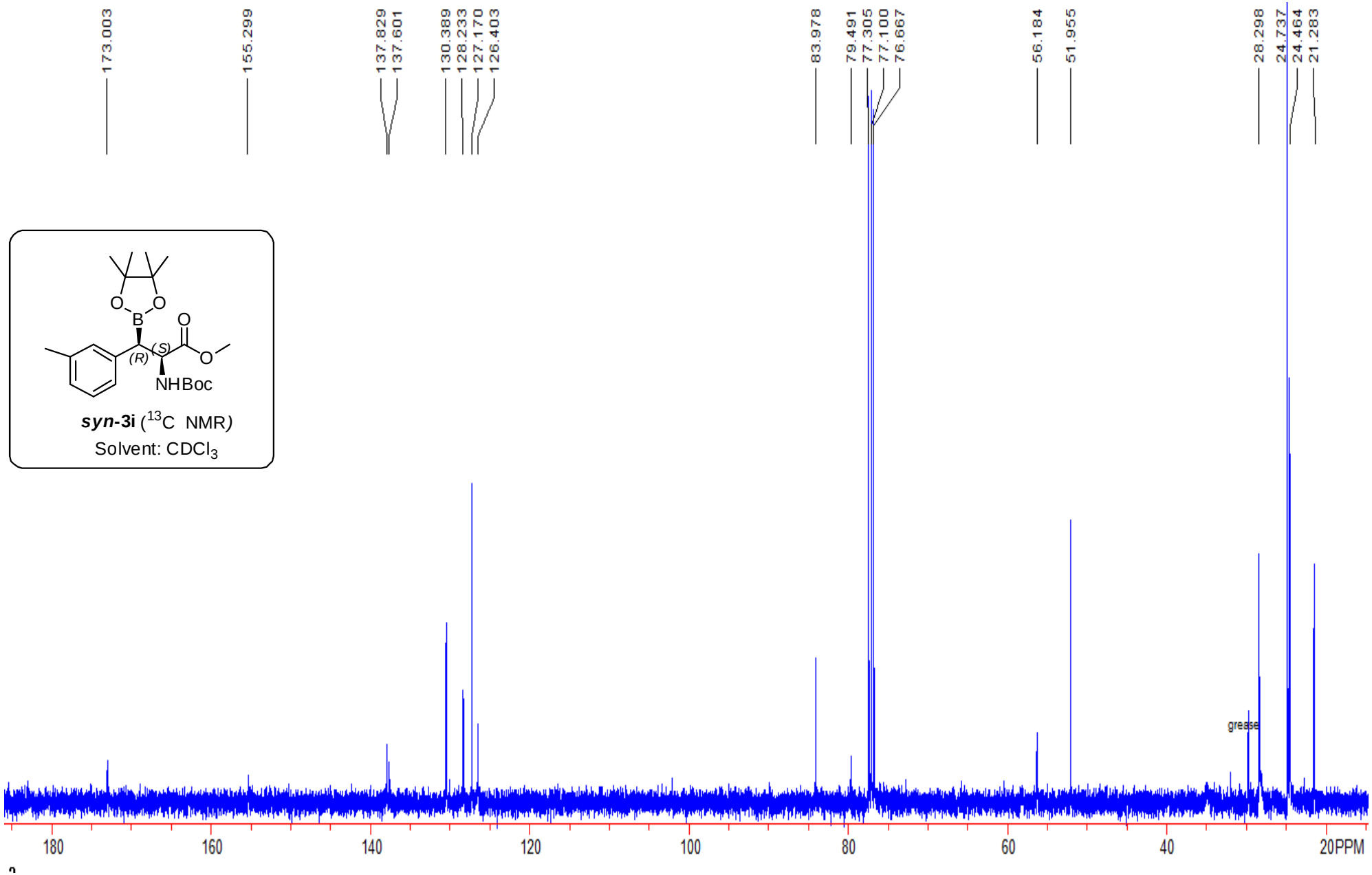
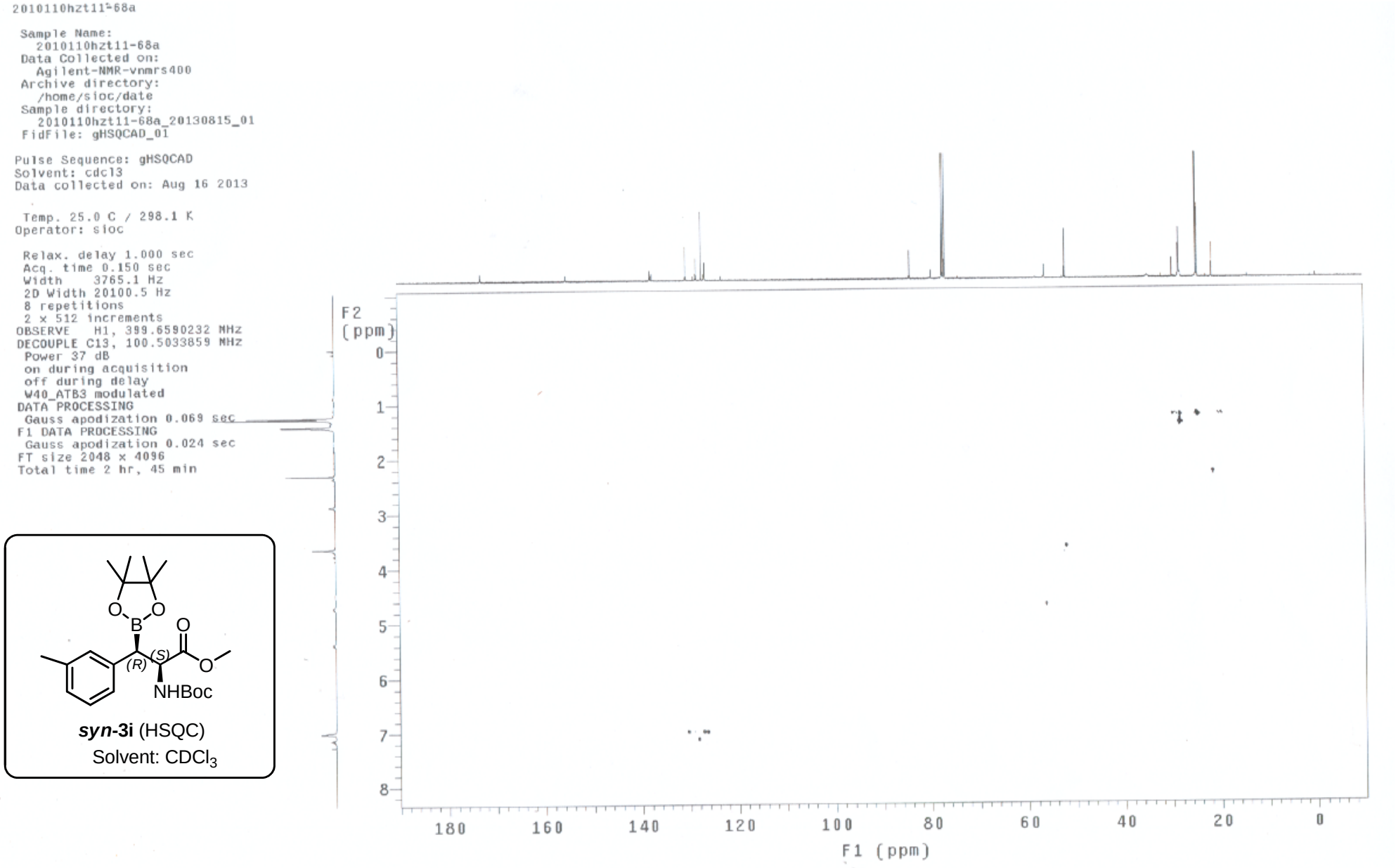
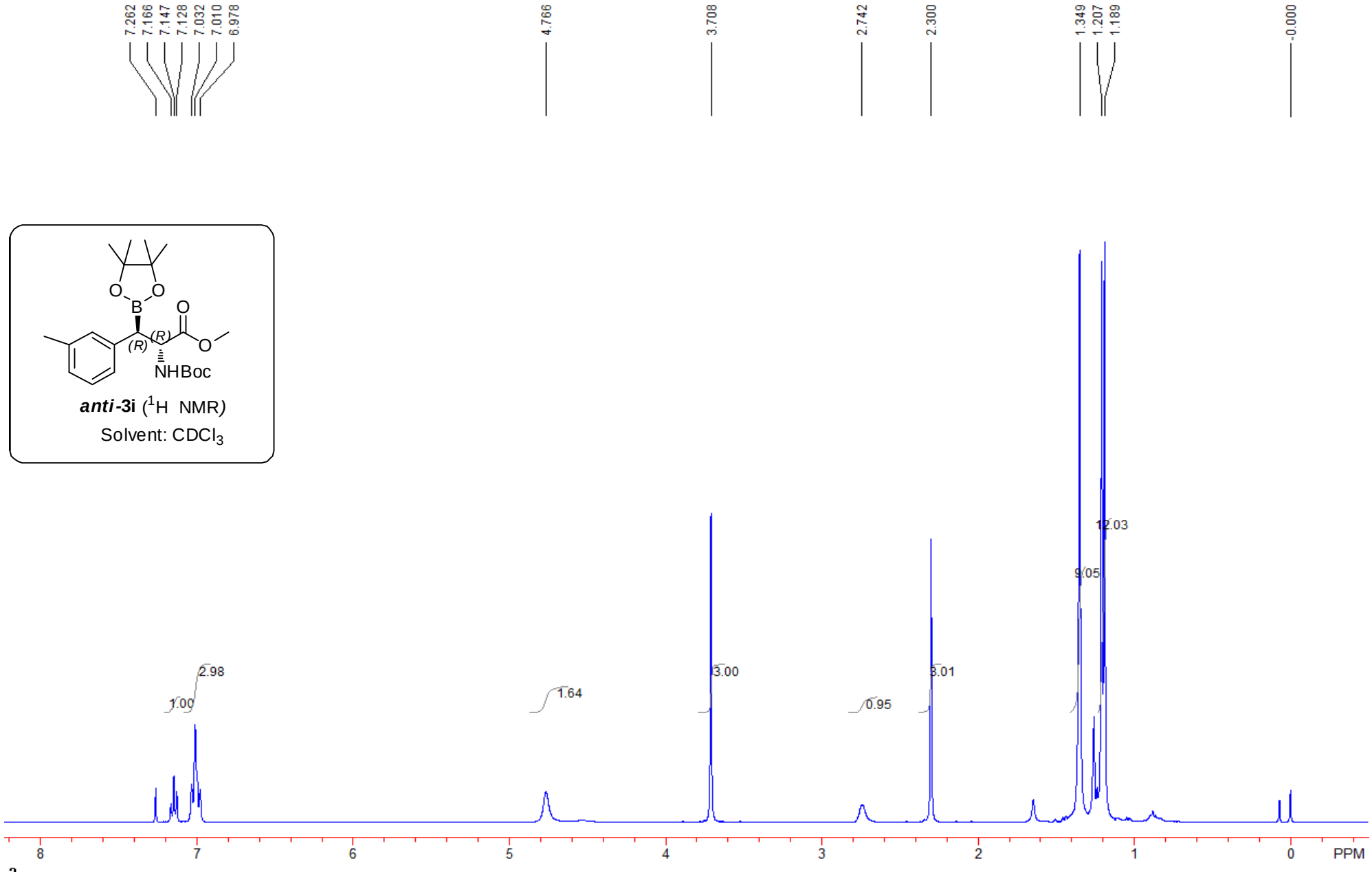
7.159
7.140
7.121
7.005
5.383
5.361
4.707
3.640
2.872
2.860
2.299
1.406
1.262
1.236
0.000
O
O
B
O
(R)
(S)
O
NHBoc
syn-3i (1H NMR)
Solvent: CDCl3
1.03
2.99
1.00
0.78
2.97
0.97
2.98
14.56
8.75
7
6
5
4
3
2
1
0
PPM


173.003
155.299
137.829
137.601
130.389
128.233
127.170
126.403
83.978
79.491
77.305
77.100
76.667
56.184
51.955
28.298
24.737
24.464
21.283
grease
180
160
140
120
100
80
60
40
20PPM
syn-3i (13C NMR)
Solvent: CDCl3



***syn*-3i** (HSQC)
Solvent: $CDCl_3$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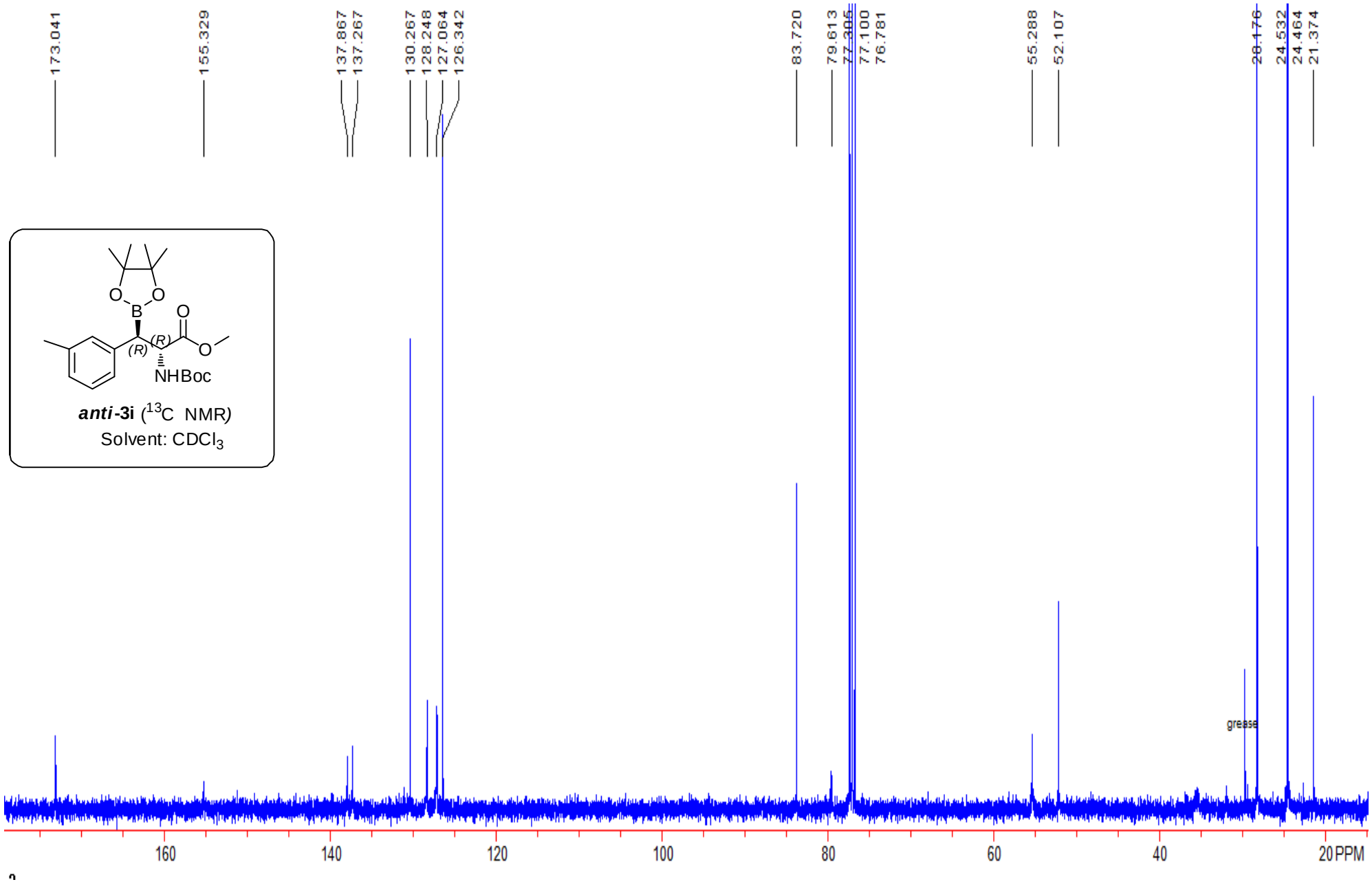
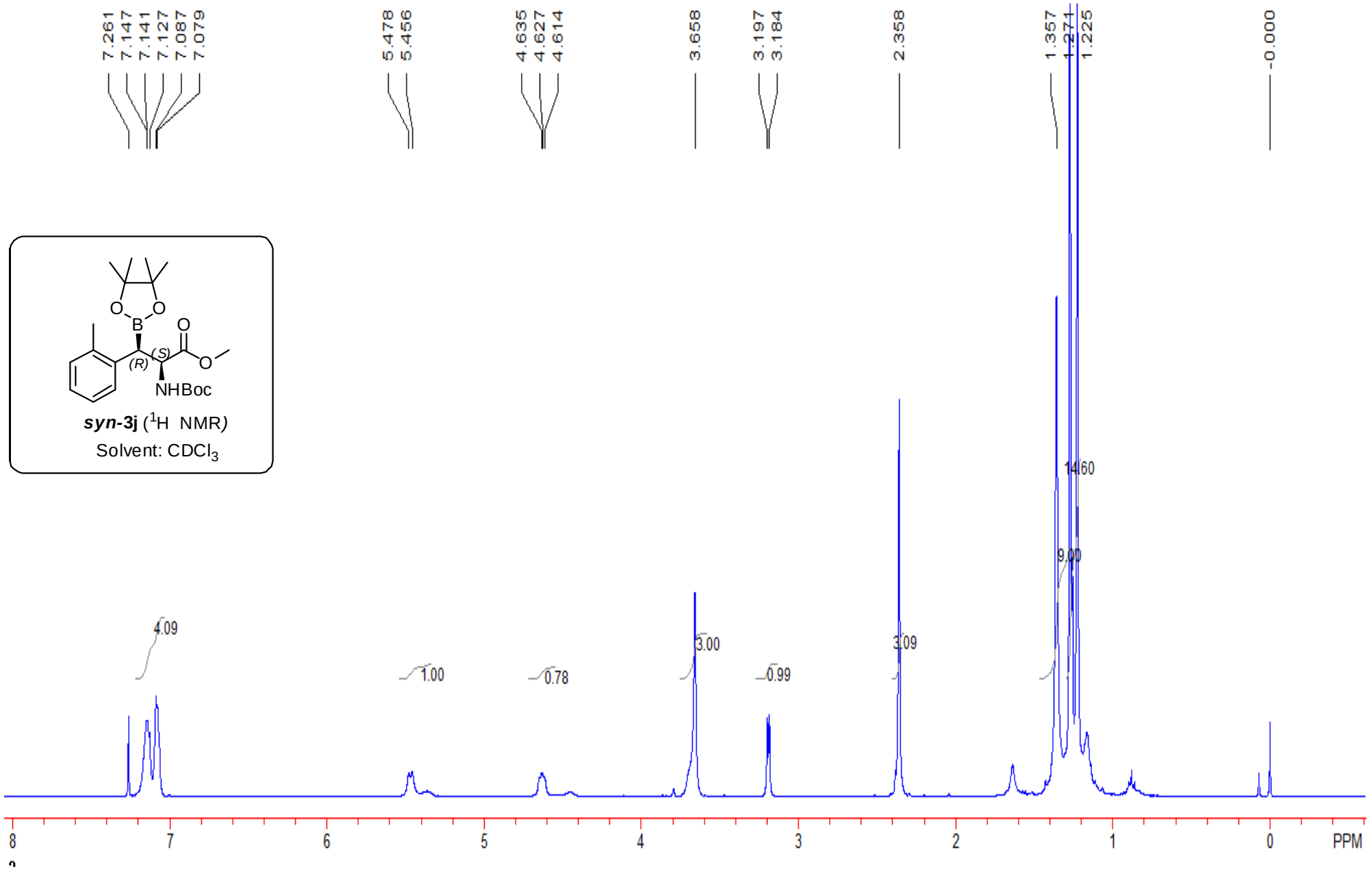
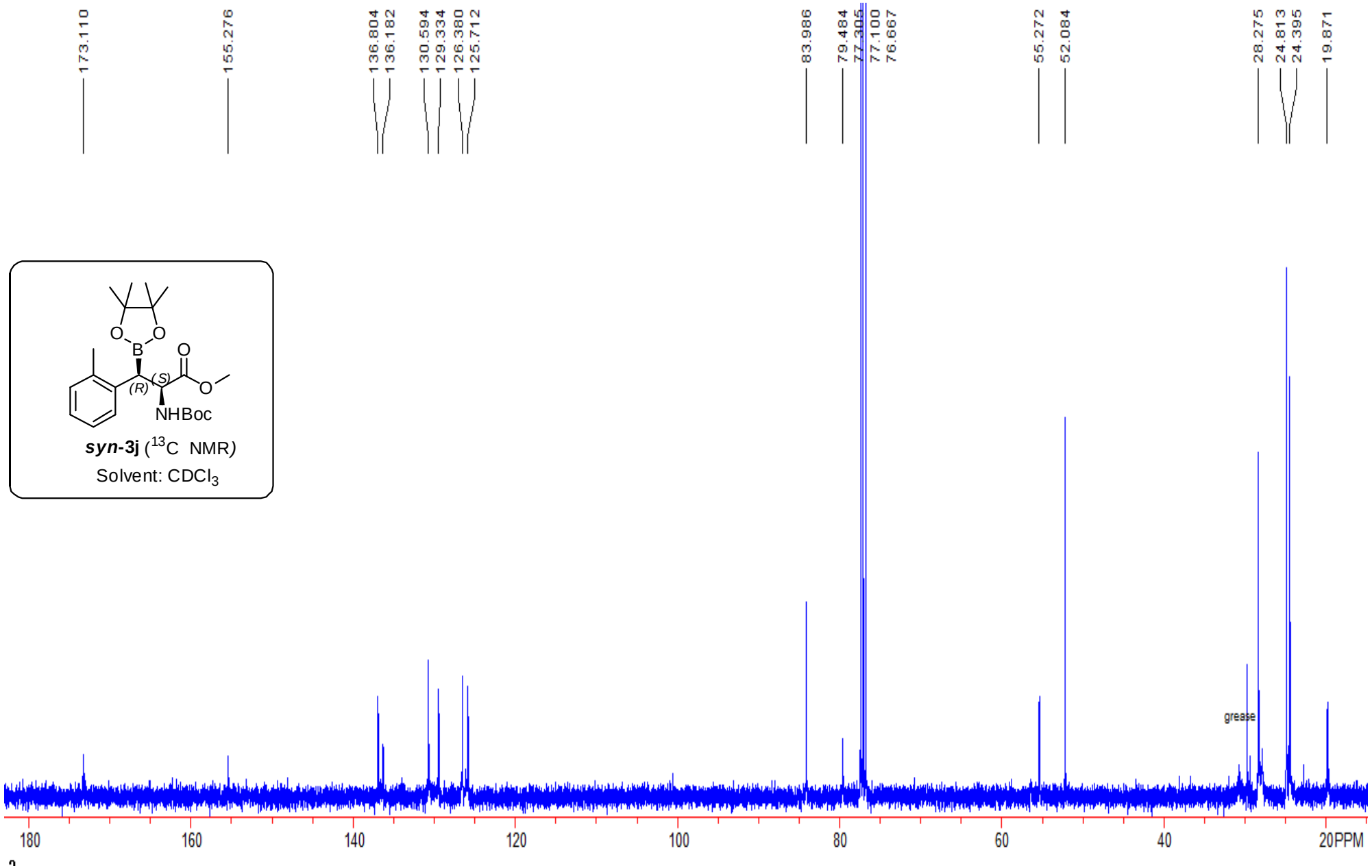
7.166
7.147
7.128
7.032
7.010
6.978
4.766
3.708
2.742
2.300
1.349
1.207
1.189
-0.000
O
O
B
O
(R)
(R)
O
NHBoc
anti-3i (1H NMR)
Solvent: CDCl3
2.98
1.00
1.64
3.00
0.95
3.01
9.05
12.03
8
7
6
5
4
3
2
1
0
PPM

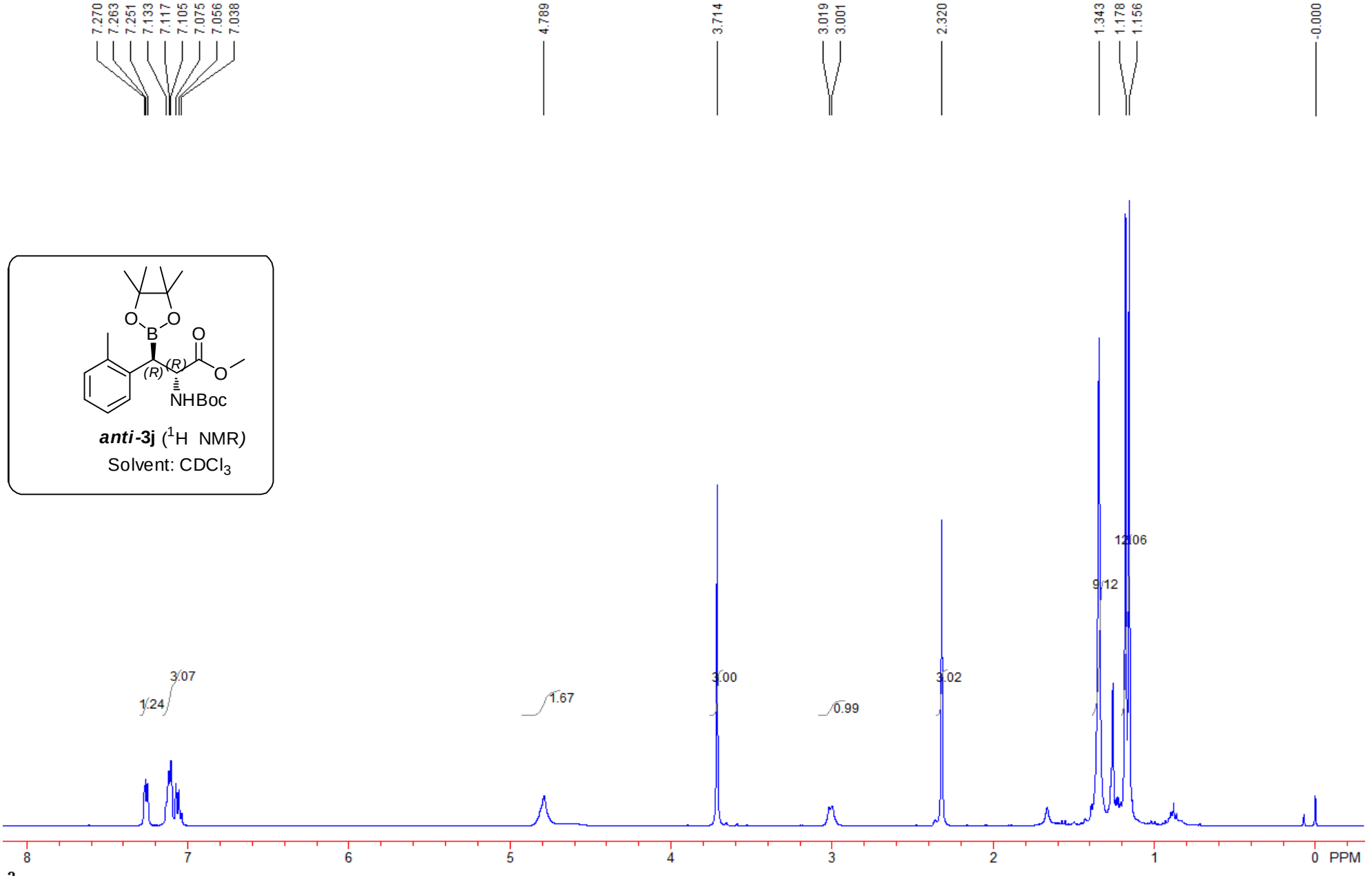

173.041
155.329
137.867
137.267
130.267
128.248
127.064
126.342
83.720
79.613
77.306
77.100
76.781
55.288
52.107
28.476
24.532
24.464
21.374
grease
160
140
120
100
80
60
40
20 PPM
anti-3i (13C NMR)
Solvent: CDCl3

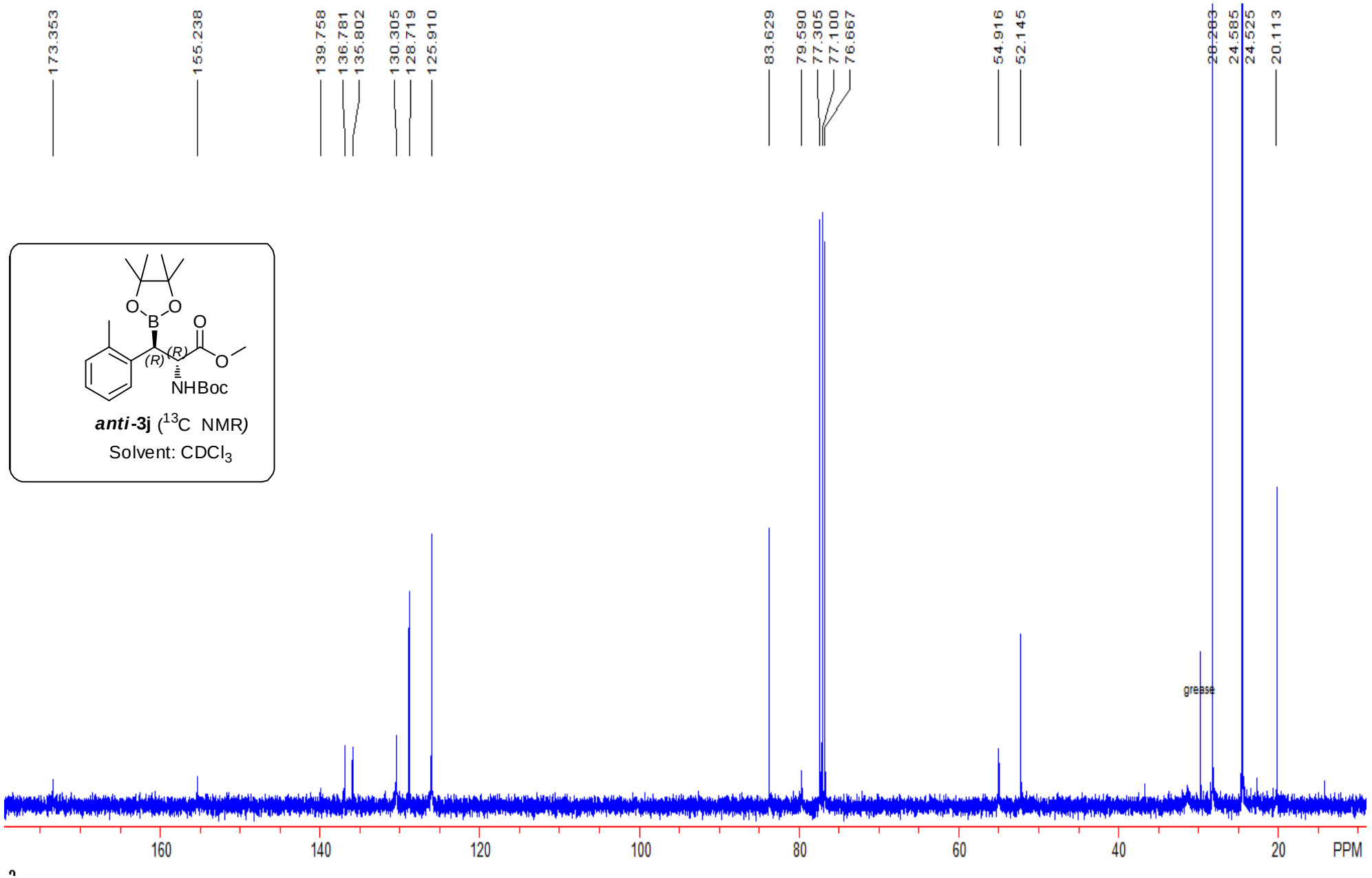

7.261
7.147
7.141
7.127
7.087
7.079
5.478
5.456
4.635
4.627
4.614
3.658
3.197
3.184
2.358
1.357
1.271
1.225
-0.000
NHBoc
syn-3j (1H NMR)
Solvent: CDCl3
4.09
1.00
0.78
3.00
0.99
3.09
14.60
9.00
8
7
6
5
4
3
2
1
0
PPM

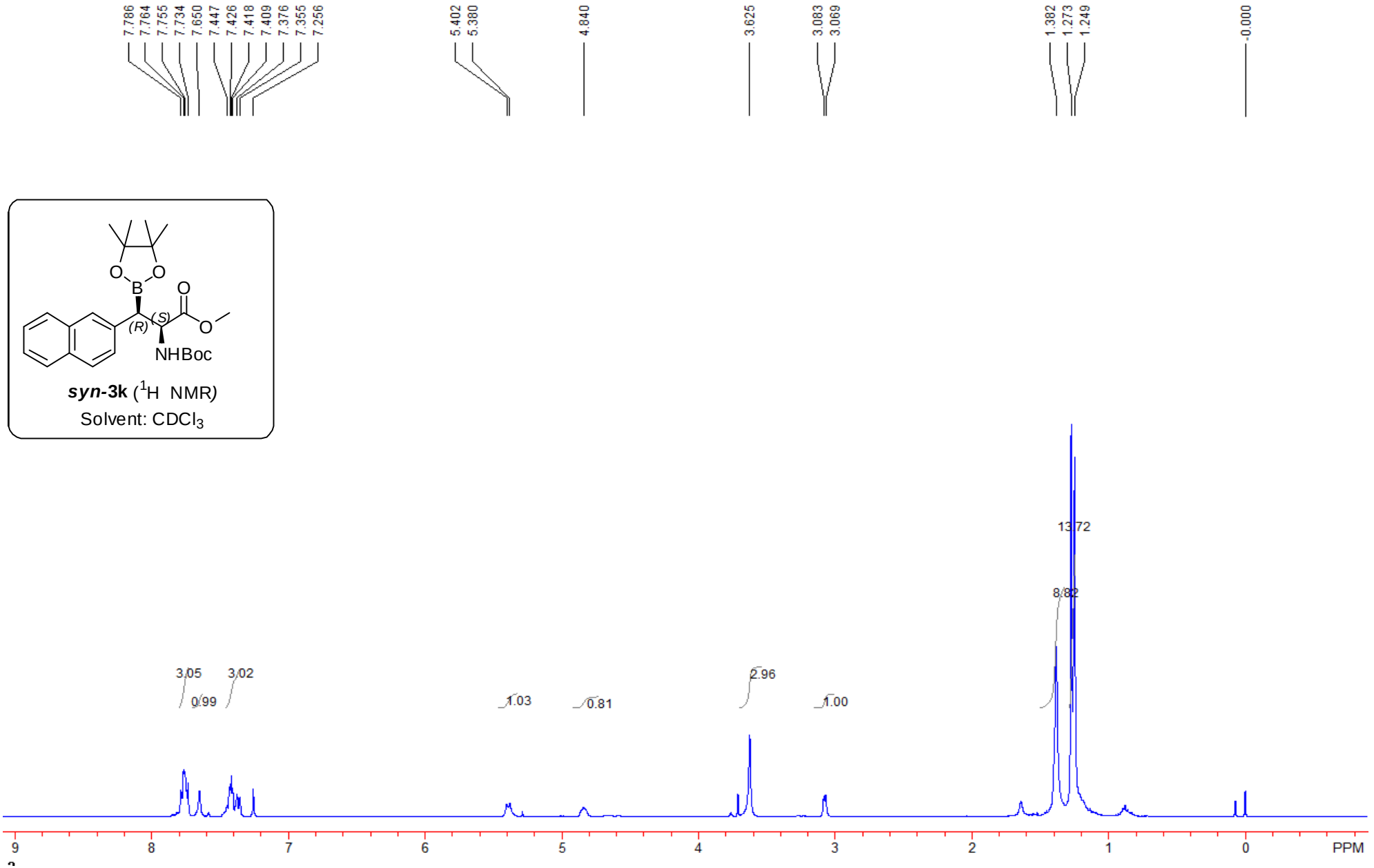


***syn*-3j** (^{13}C NMR)

Solvent: $CDCl_3$


7.270
7.263
7.251
7.133
7.117
7.105
7.075
7.056
7.038
4.789
3.714
3.019
3.001
2.320
1.343
1.178
1.156
-0.000
anti-3j (1H NMR)
Solvent: CDCl3
3.07
1.24
1.67
3.00
0.99
3.02
9.12
12.06
8
7
6
5
4
3
2
1
0
PPM


173.353
155.238
139.758
136.781
135.802
130.305
128.719
125.910
83.629
79.590
77.305
77.100
76.667
54.916
52.145
28.283
24.585
24.525
20.113
grease
160
140
120
100
80
60
40
20
PPM
anti-3j (13C NMR)
Solvent: CDCl3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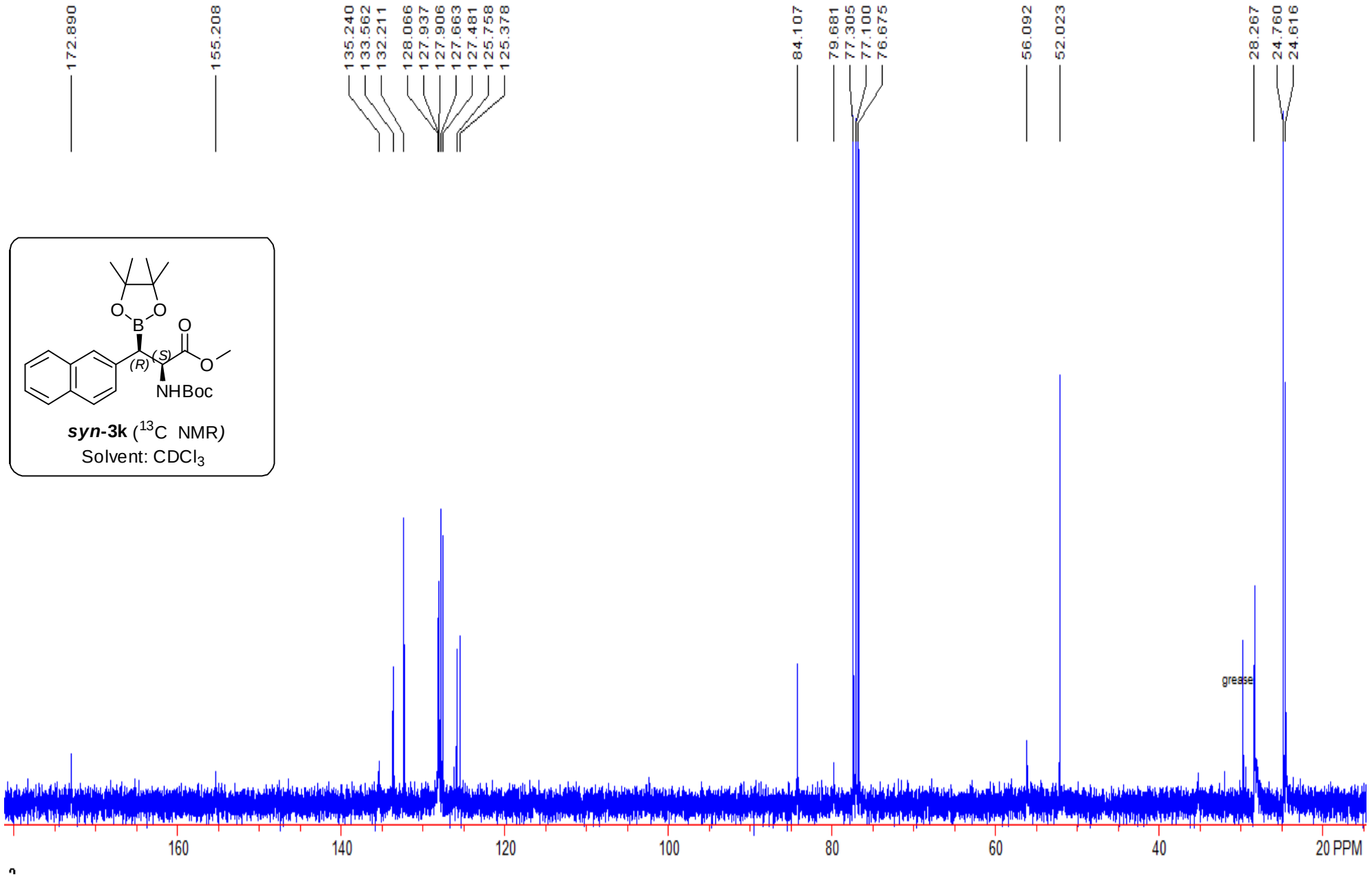
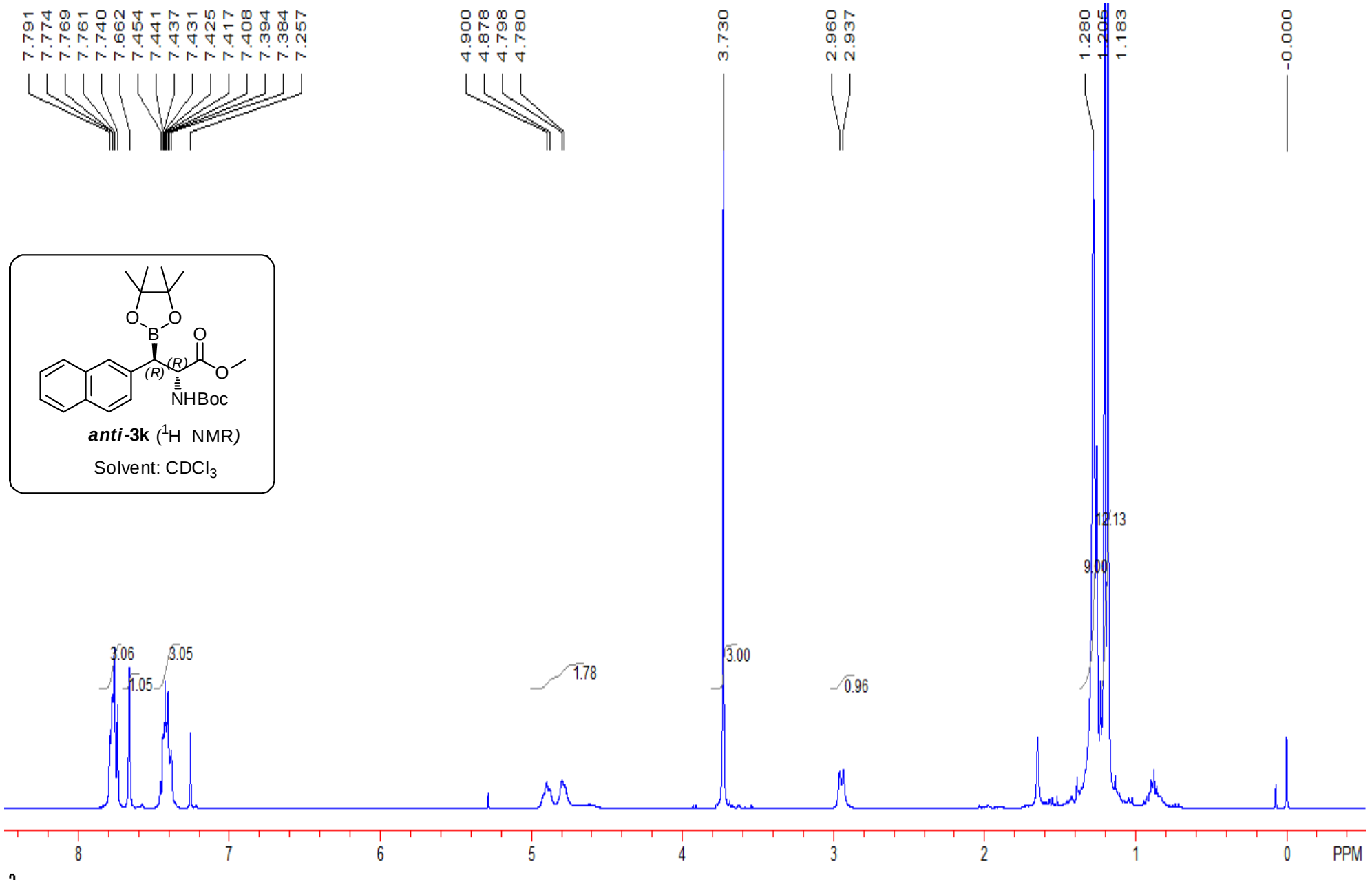
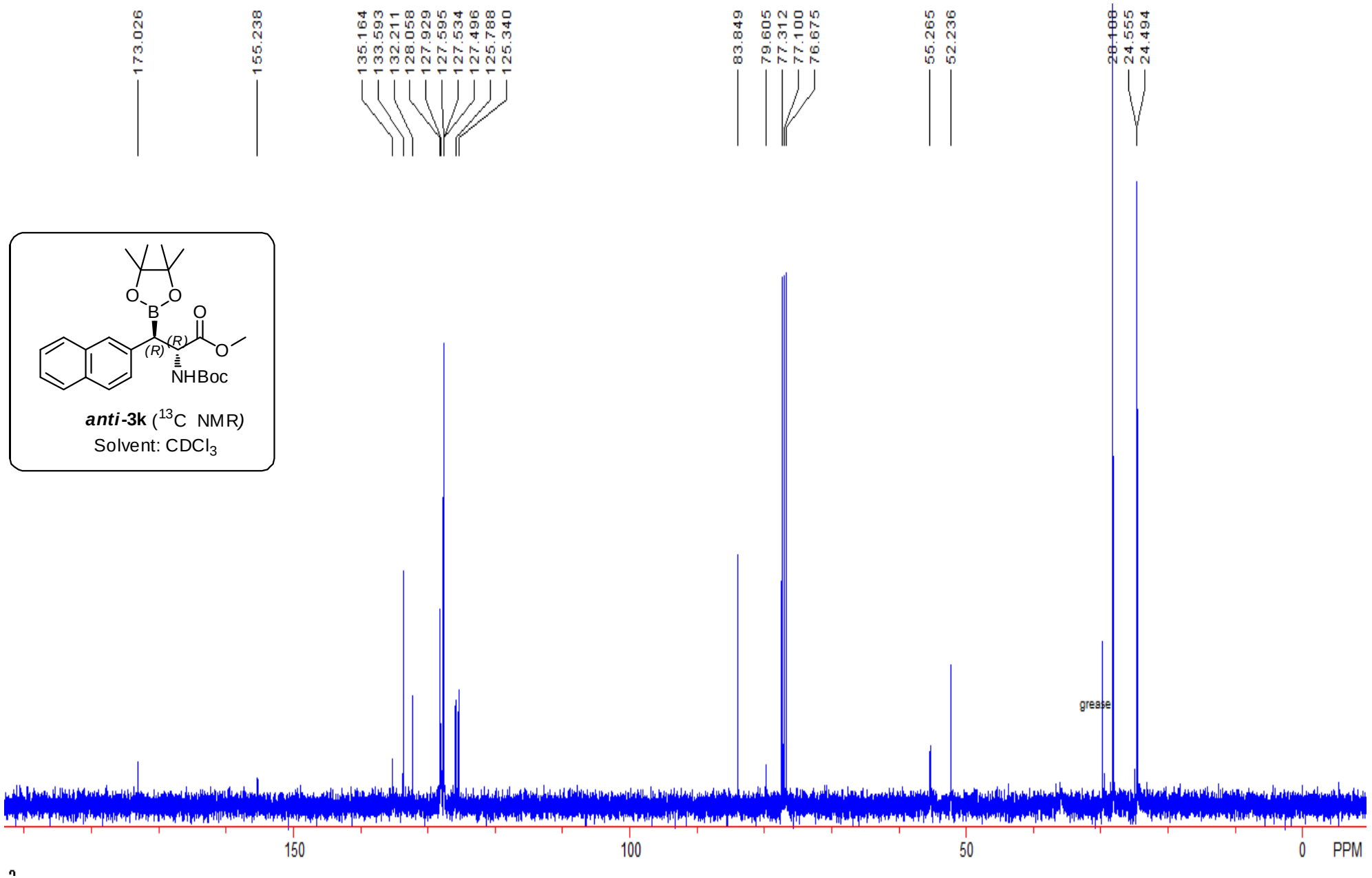
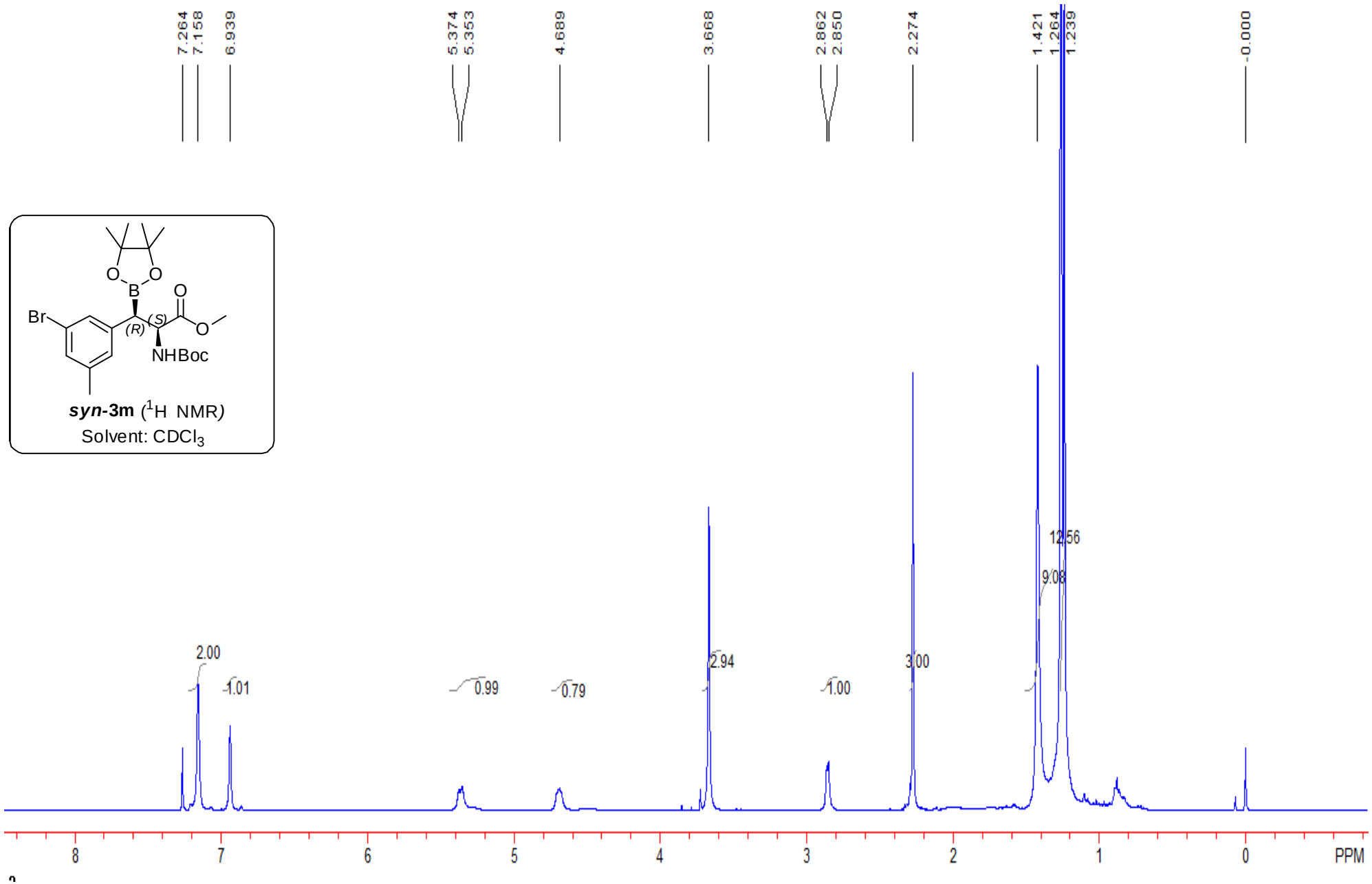
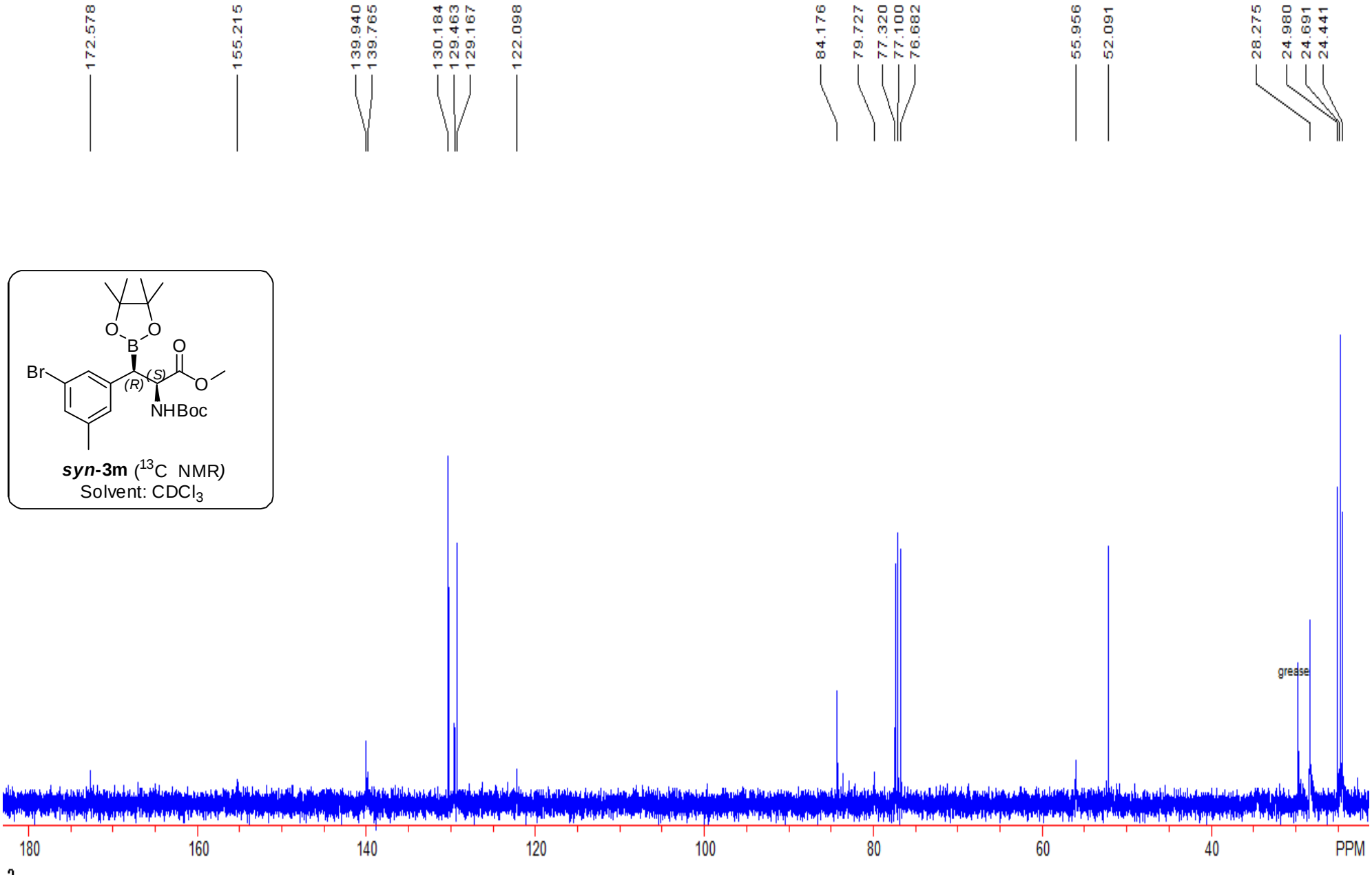
7.764
7.755
7.734
7.650
7.447
7.426
7.418
7.409
7.376
7.355
7.256
5.402
5.380
4.840
3.625
3.083
3.069
1.382
1.273
1.249
0.000
B
O
O
O
O
(R)
(S)
NHBoc
syn-3k (1H NMR)
Solvent: CDCl3
3.05
3.02
0.99
1.03
0.81
2.96
1.00
13.72
8.82
9
8
7
6
5
4
3
2
1
0
PPM


172.890
155.208
135.240
133.562
132.211
128.066
127.937
127.906
127.663
127.481
125.758
125.378
84.107
79.681
77.305
77.100
76.675
56.092
52.023
28.267
24.760
24.616
O
B
O
O
(R)
(S)
O
NHBoc
syn-3k (13C NMR)
Solvent: CDCl3
grease
160
140
120
100
80
60
40
20 PPM

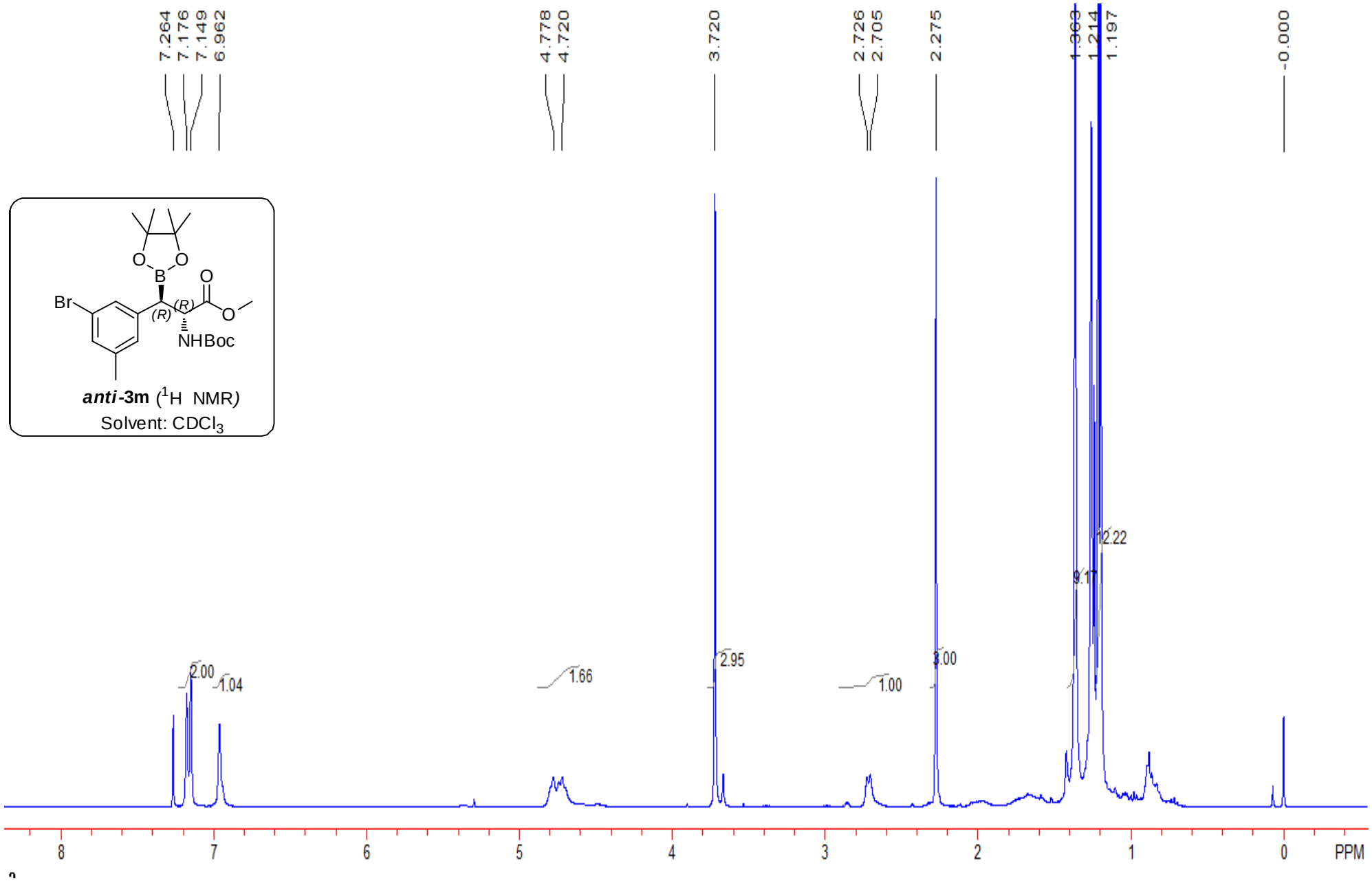

7.791
7.774
7.769
7.761
7.740
7.662
7.454
7.441
7.437
7.431
7.425
7.417
7.408
7.394
7.384
7.257
4.900
4.878
4.798
4.780
3.730
2.960
2.937
1.280
1.205
1.183
-0.000
anti-3k (1H NMR)
Solvent: CDCl3
3.06
1.05
3.05
1.78
3.00
0.96
12.13
9.00
8
7
6
5
4
3
2
1
0
PPM

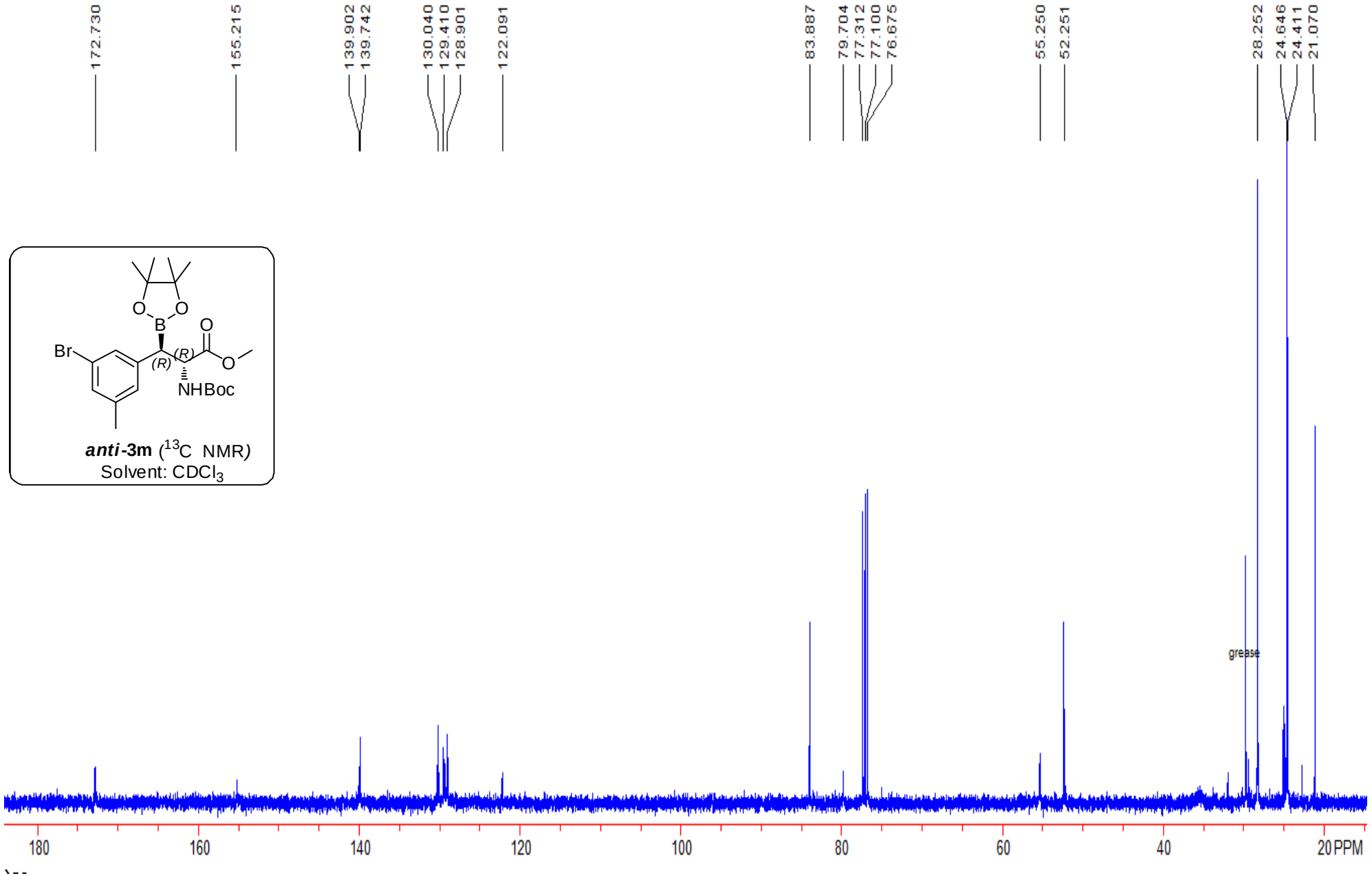

173.026
155.238
135.164
133.593
132.211
128.058
127.929
127.595
127.534
127.496
125.788
125.340
83.849
79.605
77.312
77.100
76.675
55.265
52.236
28.188
24.555
24.494
O
O
B
O
(R)
(R)
O
NHBoc
anti-3k (13C NMR)
Solvent: CDCl3
grease
150
100
50
0
PPM

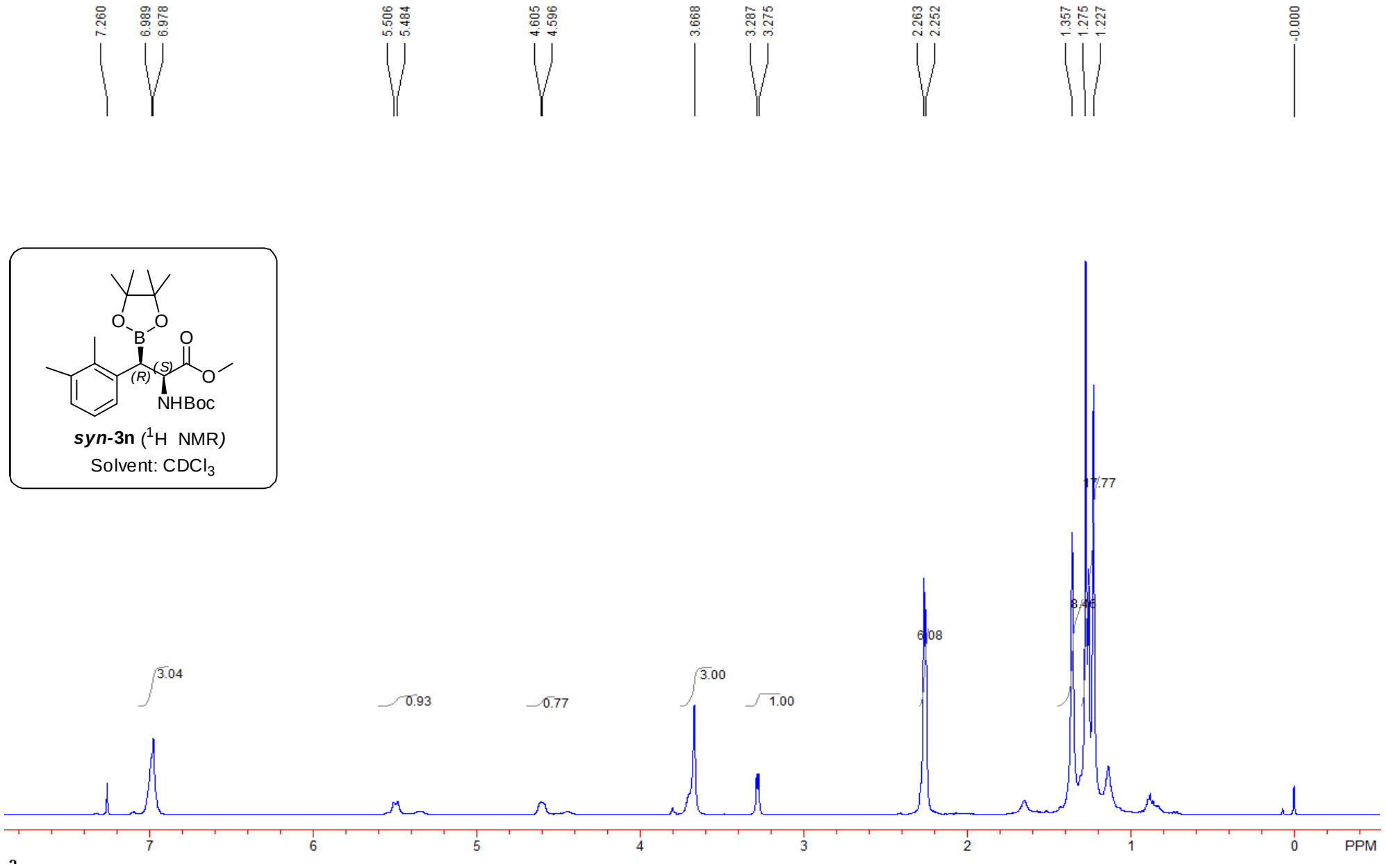

7.264
7.158
6.939
5.374
5.353
4.689
3.668
2.862
2.850
2.274
1.421
1.264
1.239
-0.000
Br
O
B
O
O
(R)
(S)
O
NHBoc
syn-3m (1H NMR)
Solvent: CDCl3
2.00
1.01
0.99
0.79
2.94
1.00
3.00
9.08
12.56
8
7
6
5
4
3
2
1
0
PPM

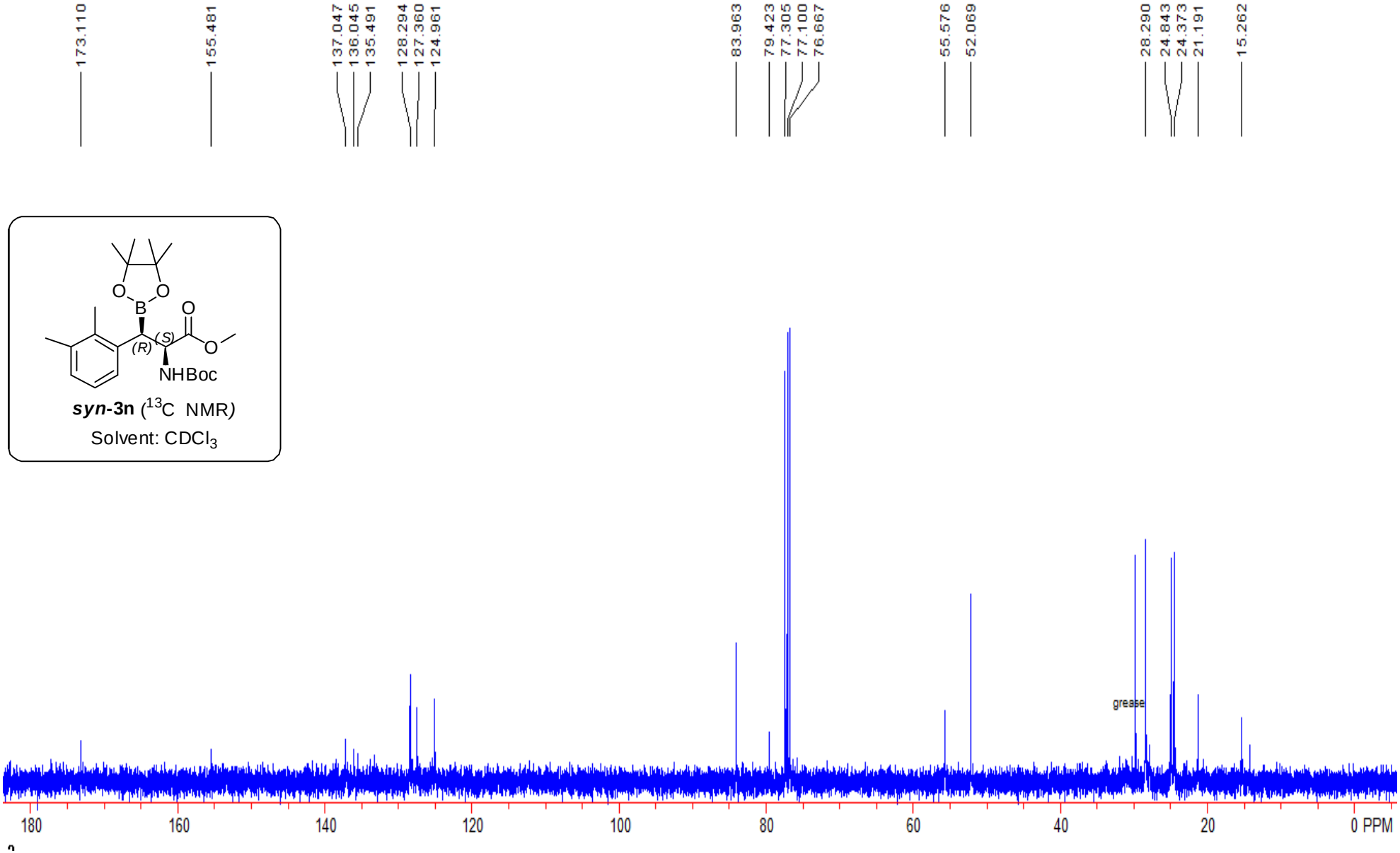


***syn*-3m** (^{13}C NMR)
Solvent: $CDCl_3$


7.264
7.176
7.149
6.962
4.778
4.720
3.720
2.726
2.705
2.275
1.363
1.214
1.197
-0.000
Br
(R)
(R)
O
B
O
O
O
NHBoc
anti-3m (1H NMR)
Solvent: CDCl3
2.00
1.04
1.66
2.95
1.00
3.00
12.22
9.17
8
7
6
5
4
3
2
1
0
PPM

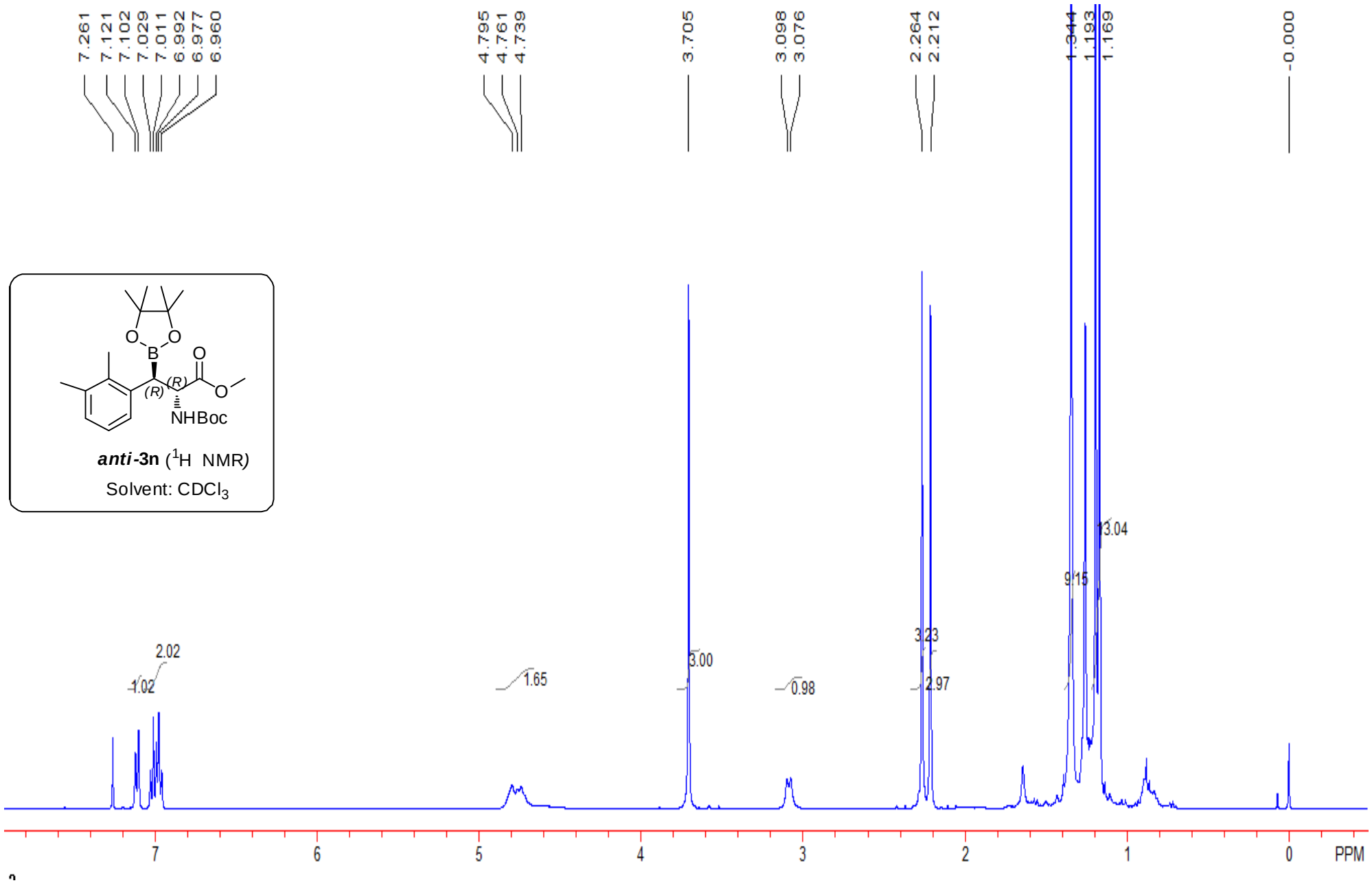

172.730
155.215
139.902
139.742
130.040
129.410
128.901
122.091
83.887
79.704
77.312
77.100
76.675
55.250
52.251
28.252
24.646
24.411
21.070
Br
O
B
O
O
(R)
(R)
O
NHBoc
anti-3m (13C NMR)
Solvent: CDCl3
grease
180
160
140
120
100
80
60
40
20
PPM

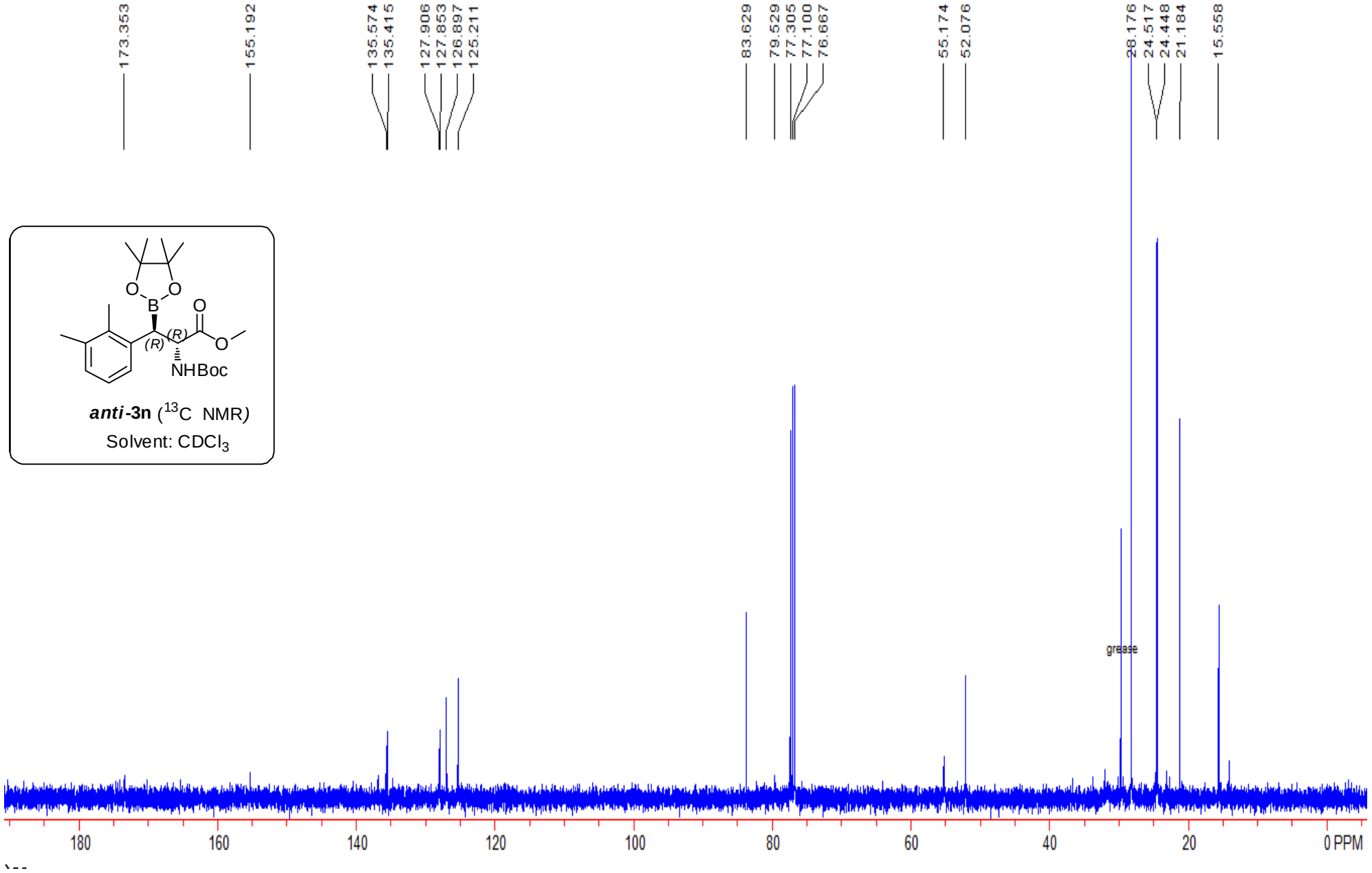

7.260
6.989
6.978
5.506
5.484
4.605
4.596
3.668
3.287
3.275
2.263
2.252
1.357
1.275
1.227
0.000
O
O
B
O
(S)
(R)
O
NHBoc
syn-3n (1H NMR)
Solvent: CDCl3
17.77
8.46
6.08
3.04
0.93
0.77
3.00
1.00
7
6
5
4
3
2
1
0
PPM

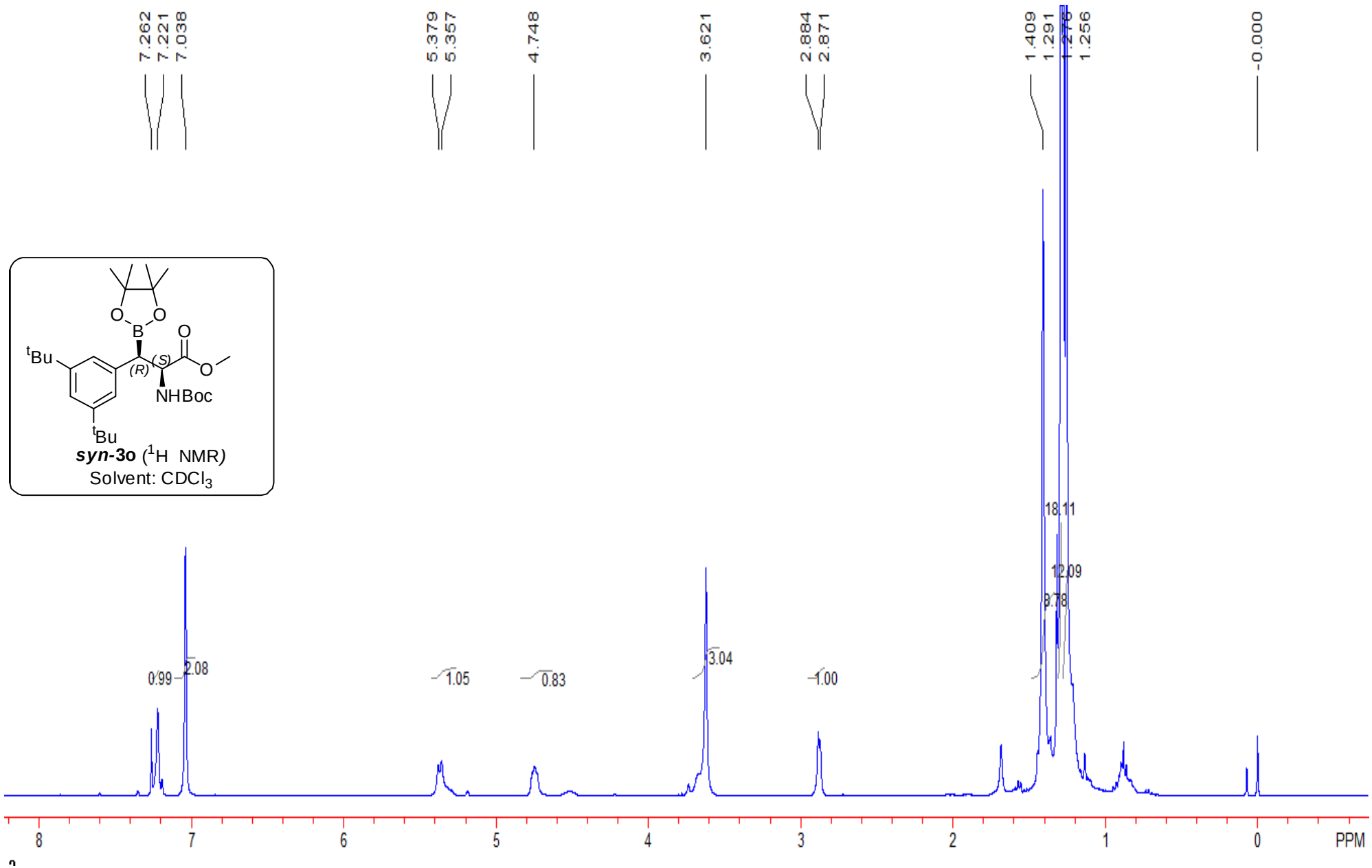


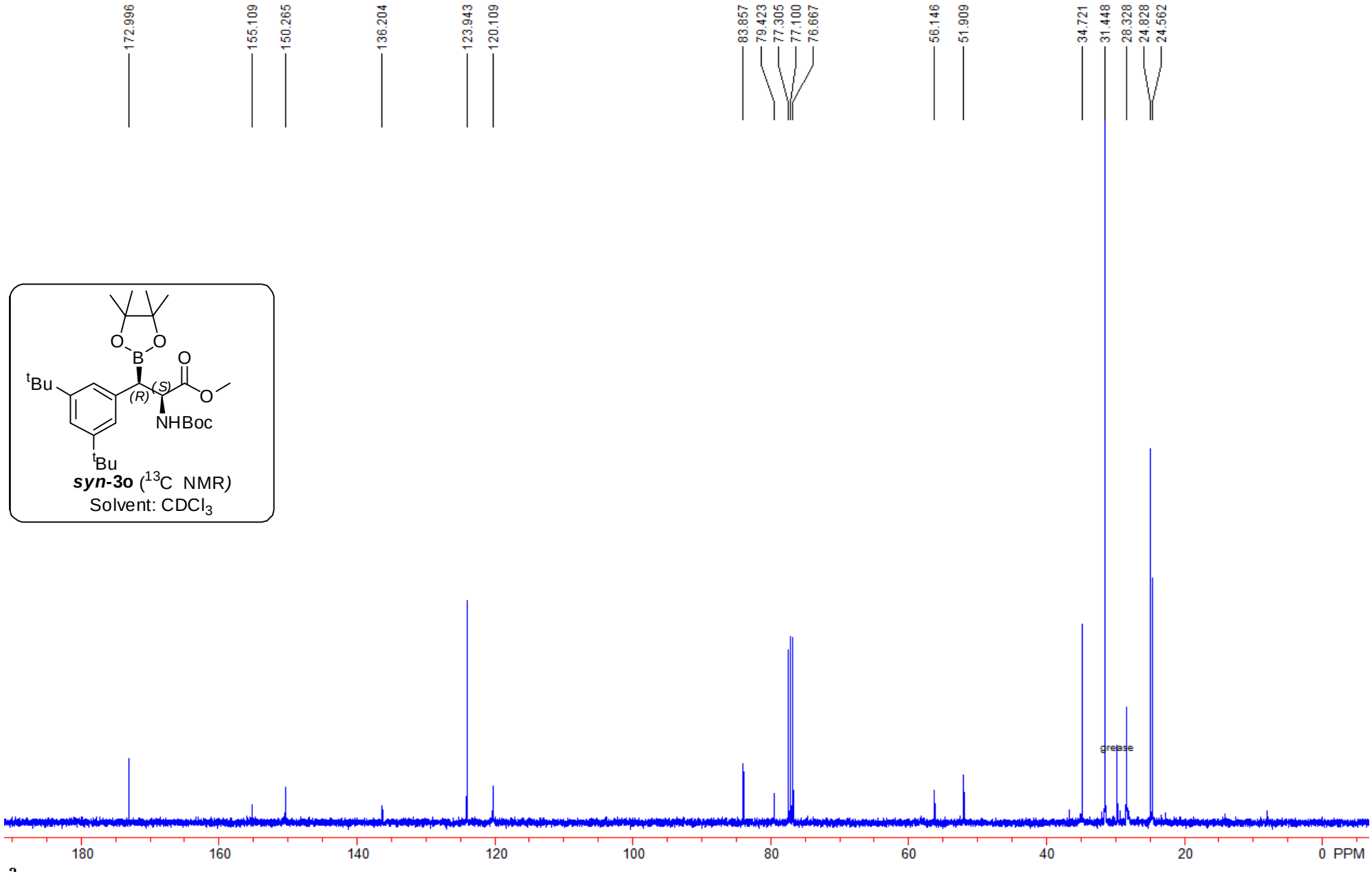
***syn*-3n** (^{13}C NMR)

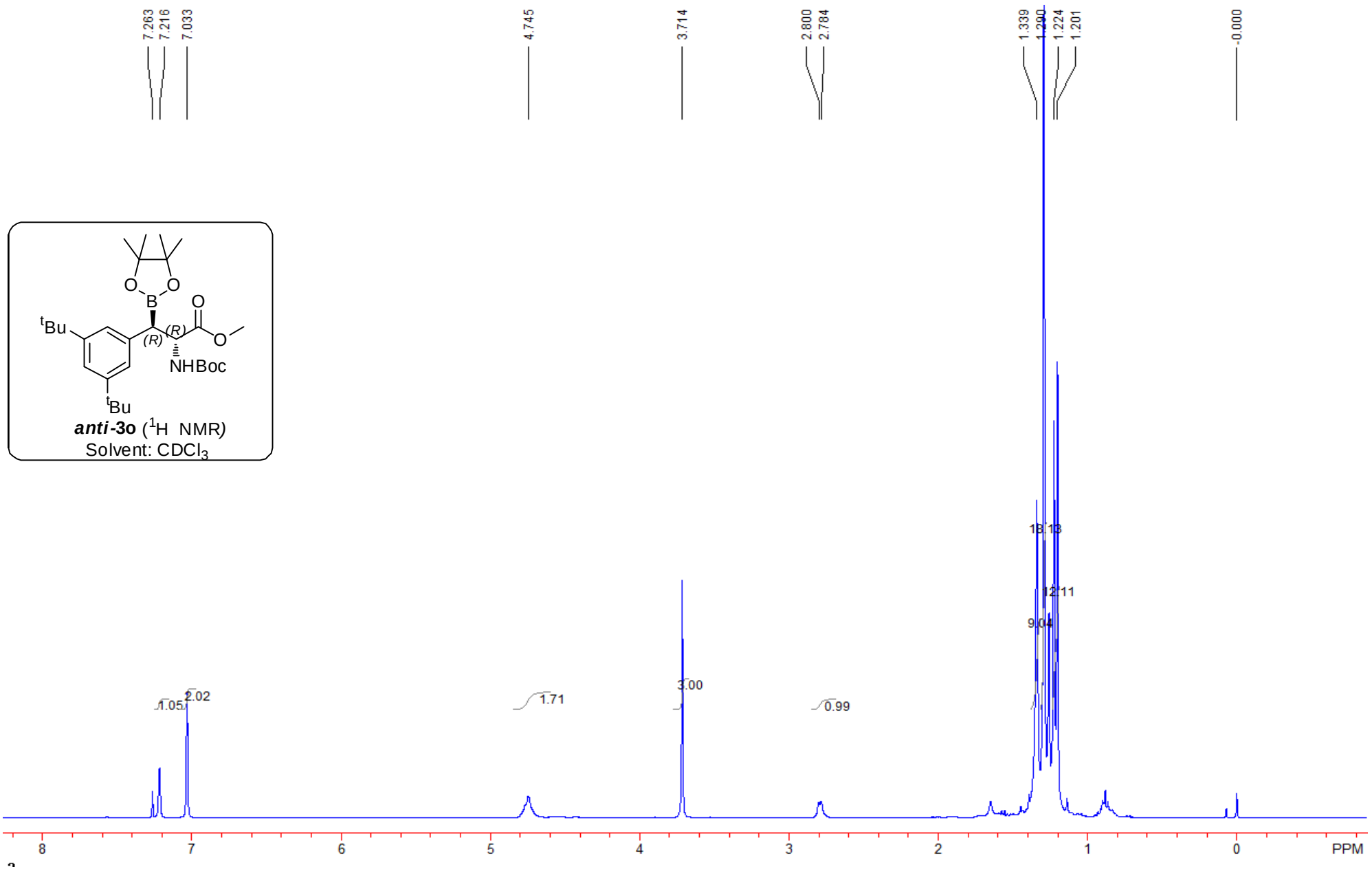
Solvent: $CDCl_3$

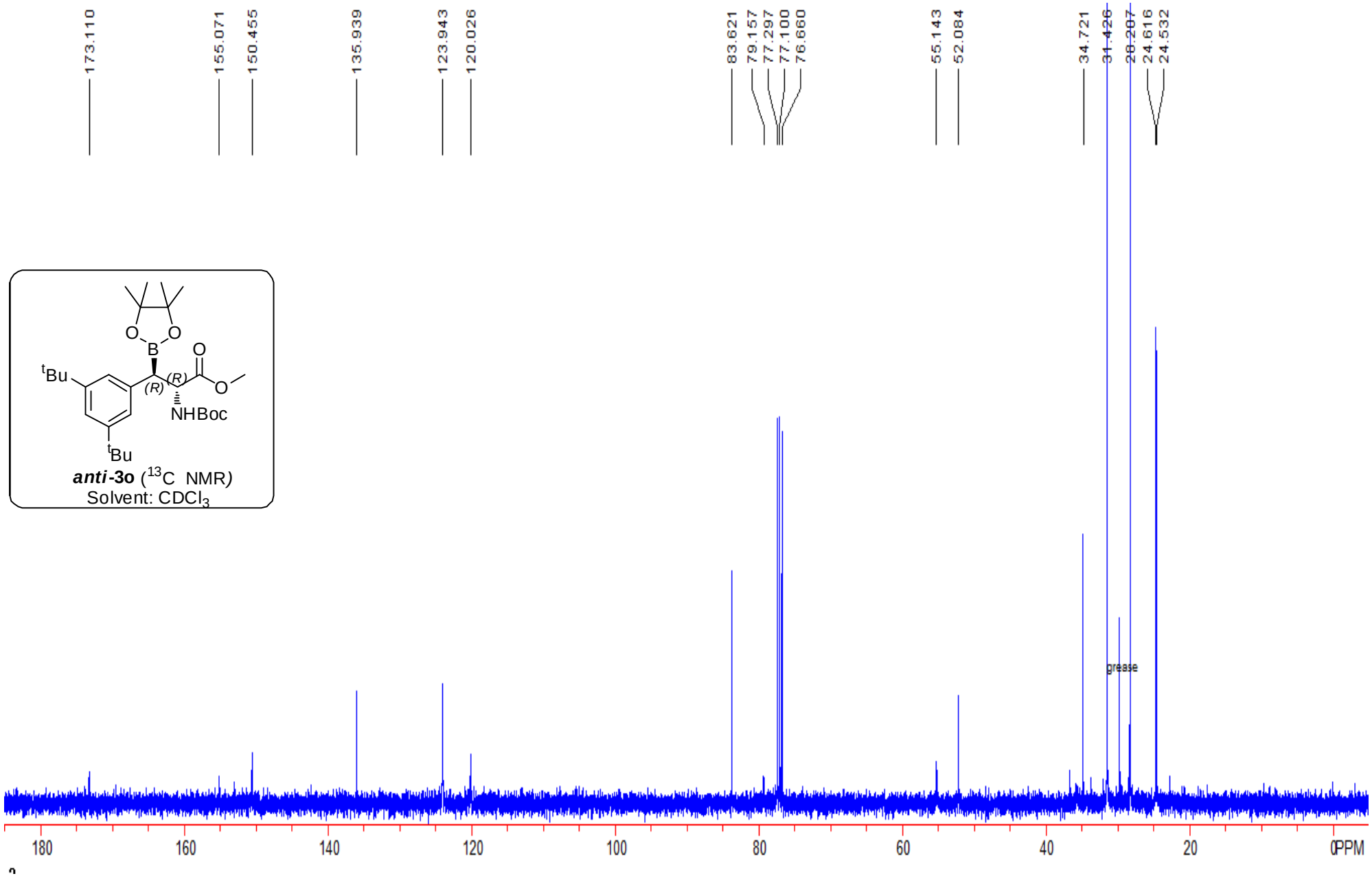

7.261
7.121
7.102
7.029
7.011
6.992
6.977
6.960
4.795
4.761
4.739
3.705
3.098
3.076
2.264
2.212
1.344
1.193
1.169
-0.000
O
O
B
O
(R)
(R)
O
NHBoc
anti-3n (1H NMR)
Solvent: CDCl3
2.02
1.02
1.65
3.00
0.98
3.23
2.97
9.15
13.04
7
6
5
4
3
2
1
0
PPM

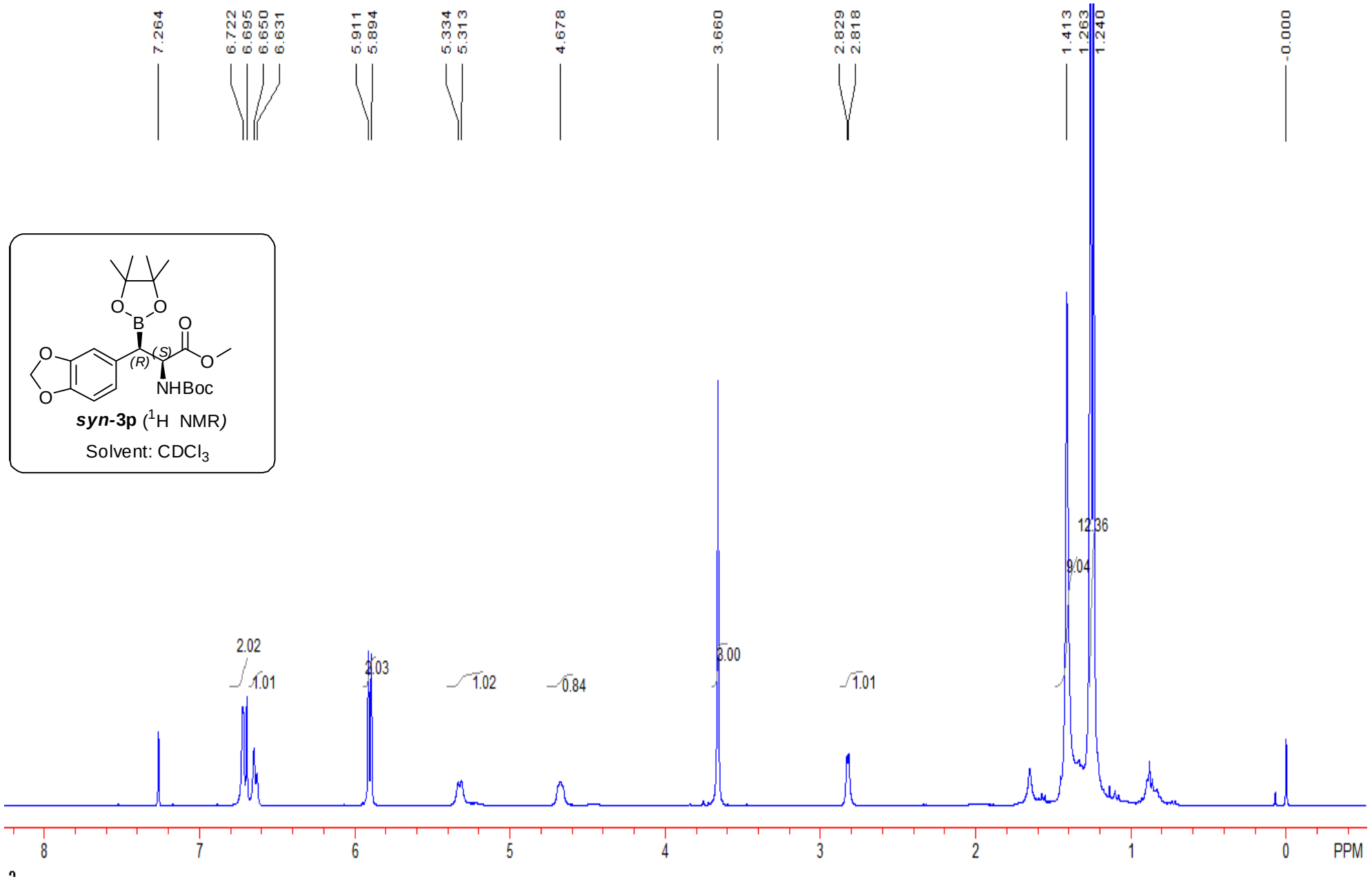

173.353
155.192
135.574
135.415
127.906
127.853
126.897
125.211
83.629
79.529
77.305
77.100
76.667
55.174
52.076
28.176
24.517
24.448
21.184
15.558
grease
180
160
140
120
100
80
60
40
20
0 PPM
anti-3n (13C NMR)
Solvent: CDCl3

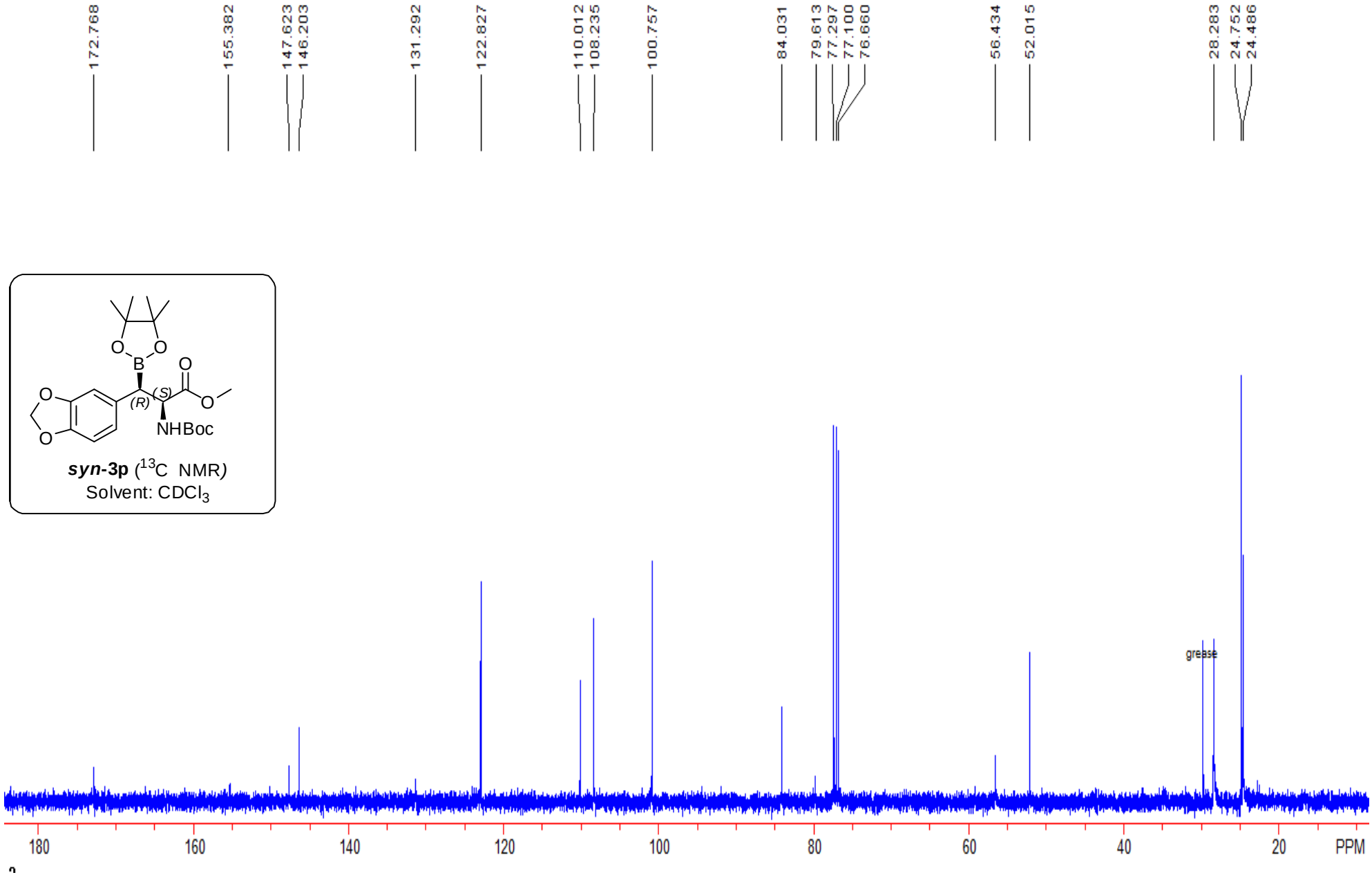

7.262
7.221
7.038
5.379
5.357
4.748
3.621
2.884
2.871
1.409
1.291
1.276
1.256
-0.000
tBu
(R)
(S)
O
B
O
O
O
NHBoc
tBu
syn-3o (1H NMR)
Solvent: CDCl3
0.99
2.08
1.05
0.83
3.04
1.00
18.11
12.09
8.78
8
7
6
5
4
3
2
1
0
PPM


172.996
155.109
150.265
136.204
123.943
120.109
83.857
79.423
77.305
77.100
76.667
56.146
51.909
34.721
31.448
28.328
24.828
24.562
tBu
(R)
(S)
O
O
B
O
O
NHBoc
tBu
syn-3o (13C NMR)
Solvent: CDCl3
grease
180
160
140
120
100
80
60
40
20
0 PPM

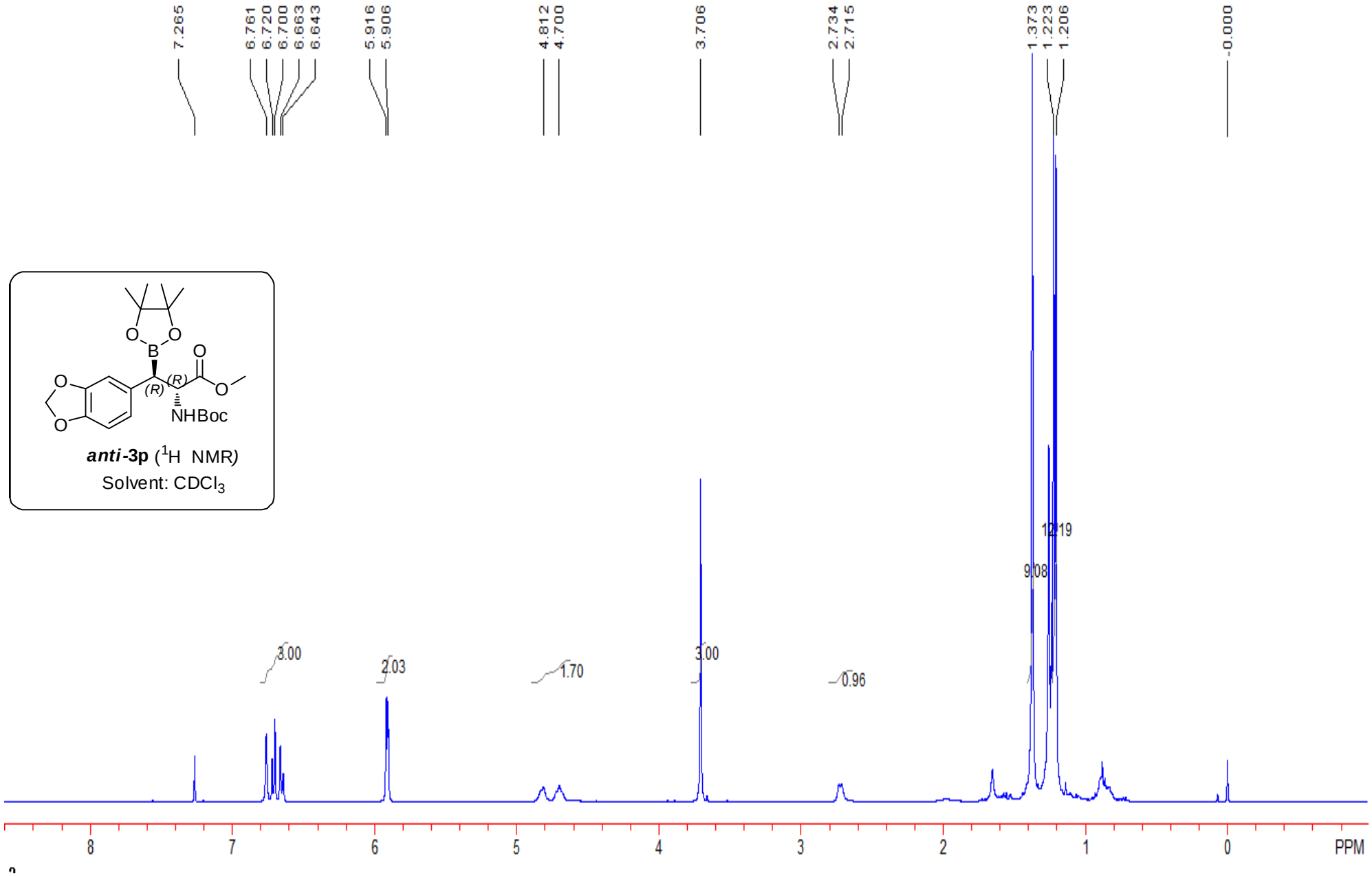

7.263
7.216
7.033
4.745
3.714
2.800
2.784
1.339
1.290
1.224
1.201
-0.000
tBu
(R)
(R)
O
O
B
O
O
NHBoc
tBu
anti-3o (1H NMR)
Solvent: CDCl3
1.05
2.02
1.71
3.00
0.99
18.13
12.11
9.04
8
7
6
5
4
3
2
1
0
PPM

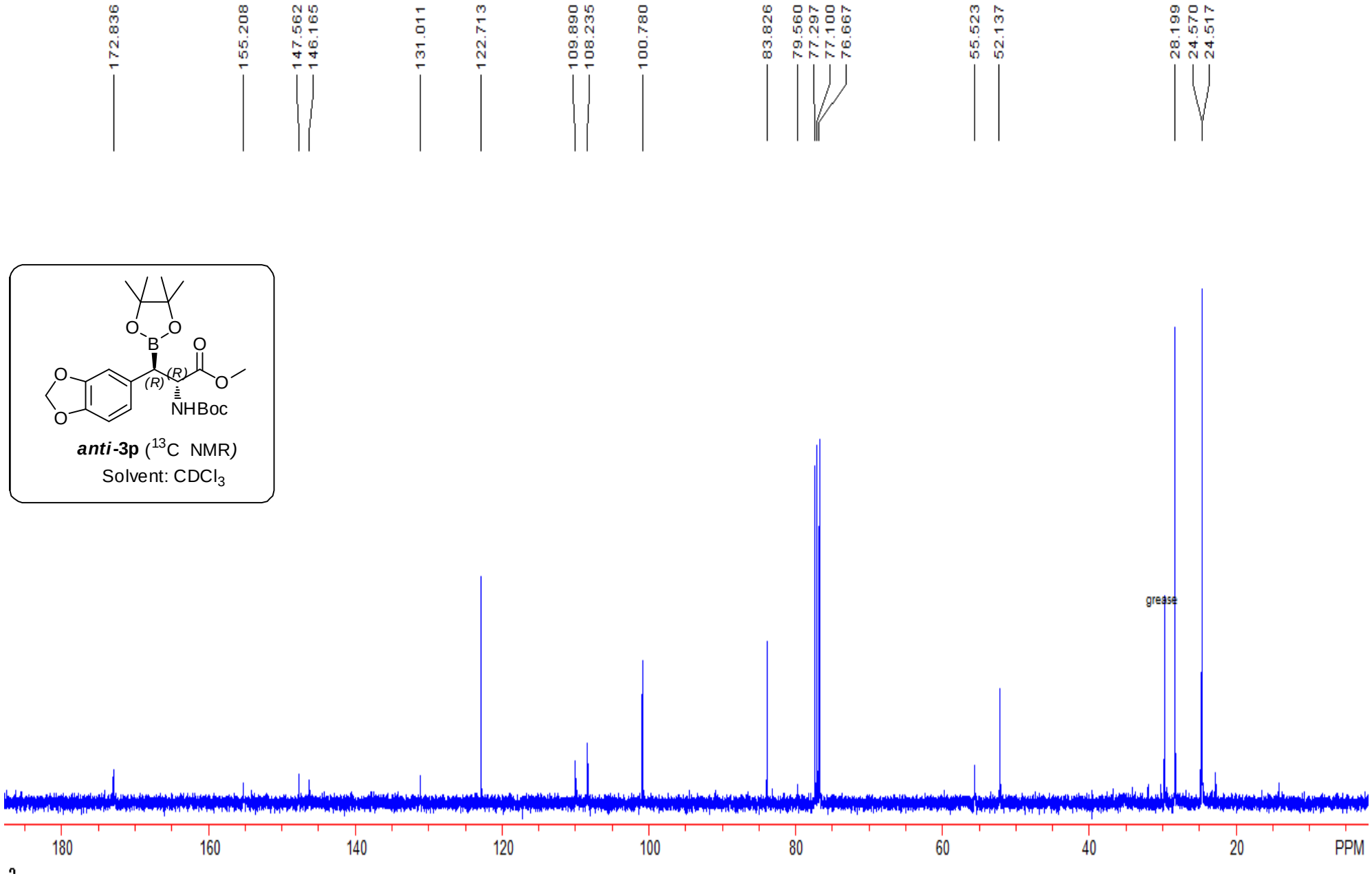

173.110
155.071
150.455
135.939
123.943
120.026
83.621
79.157
77.297
77.100
76.660
55.143
52.084
34.721
31.426
28.287
24.616
24.532
tBu
(R)
(R)
O
B
O
O
O
NHBoc
tBu
anti-3o (13C NMR)
Solvent: CDCl3
grease
180
160
140
120
100
80
60
40
20
0
PPM

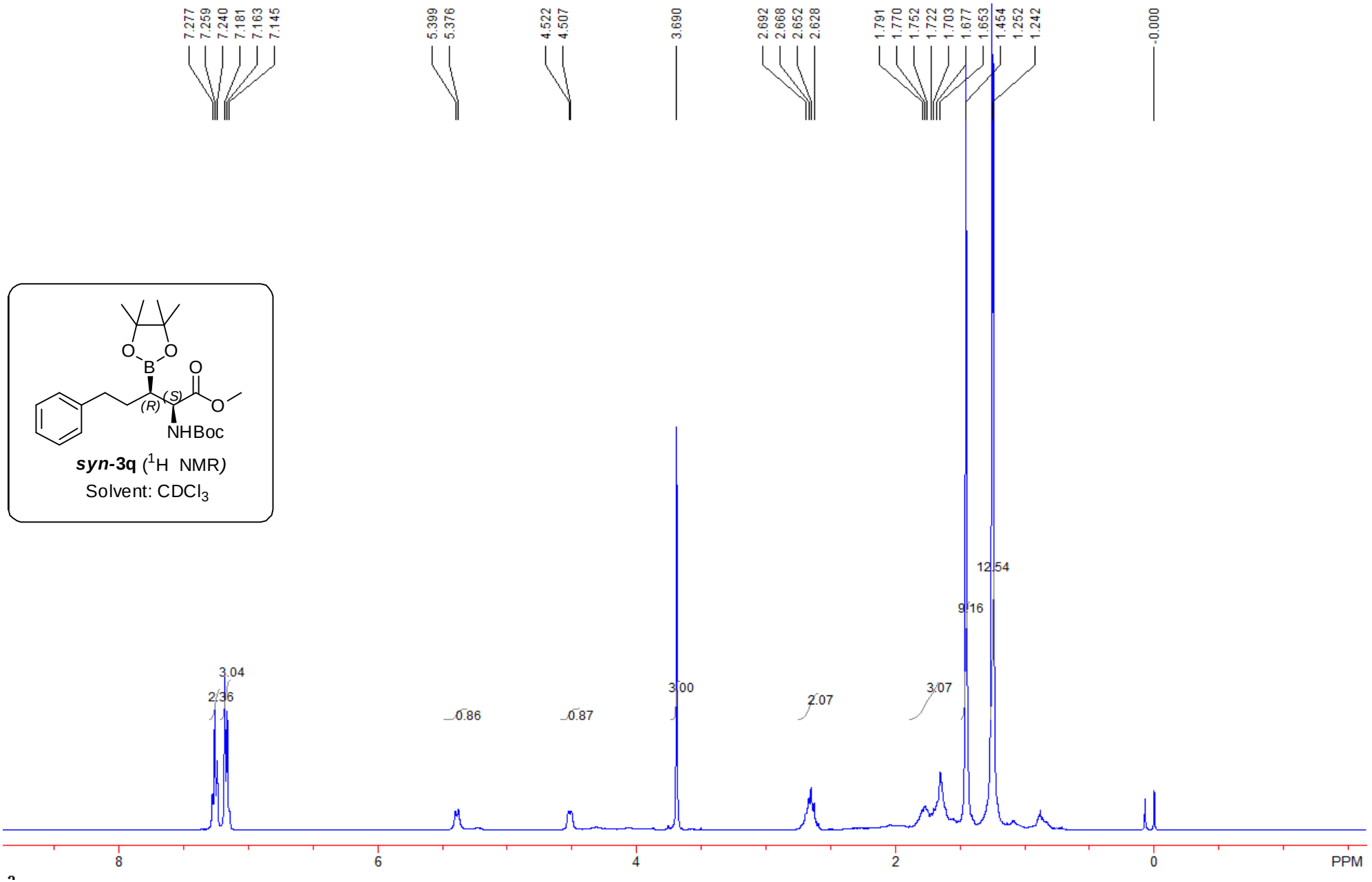

7.264
6.722
6.695
6.650
6.631
5.911
5.894
5.334
5.313
4.678
3.660
2.829
2.818
1.413
1.263
1.240
-0.000
NHBoc
syn-3p (1H NMR)
Solvent: CDCl3
2.02
1.01
2.03
1.02
0.84
3.00
1.01
12.36
9.04
8
7
6
5
4
3
2
1
0
PPM

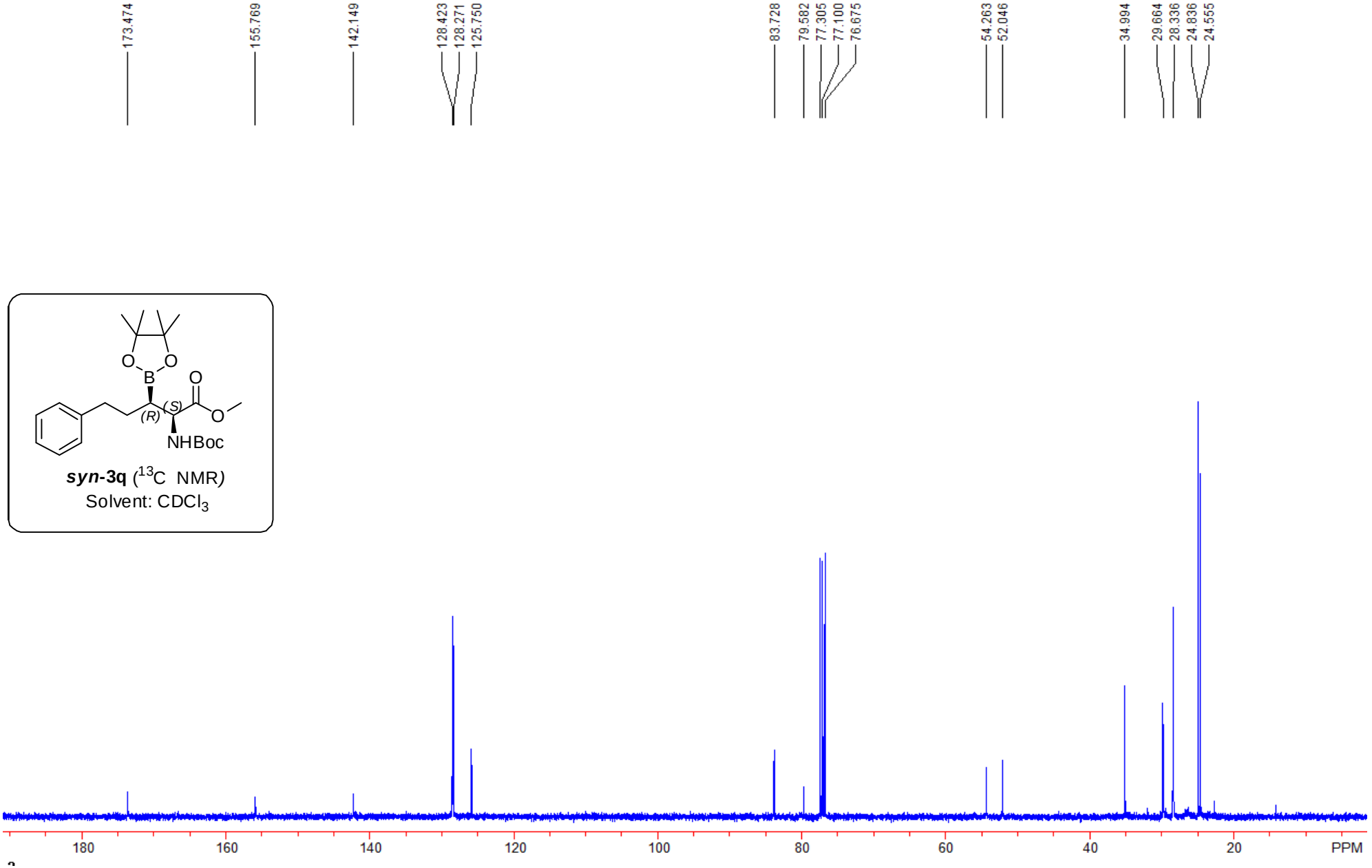


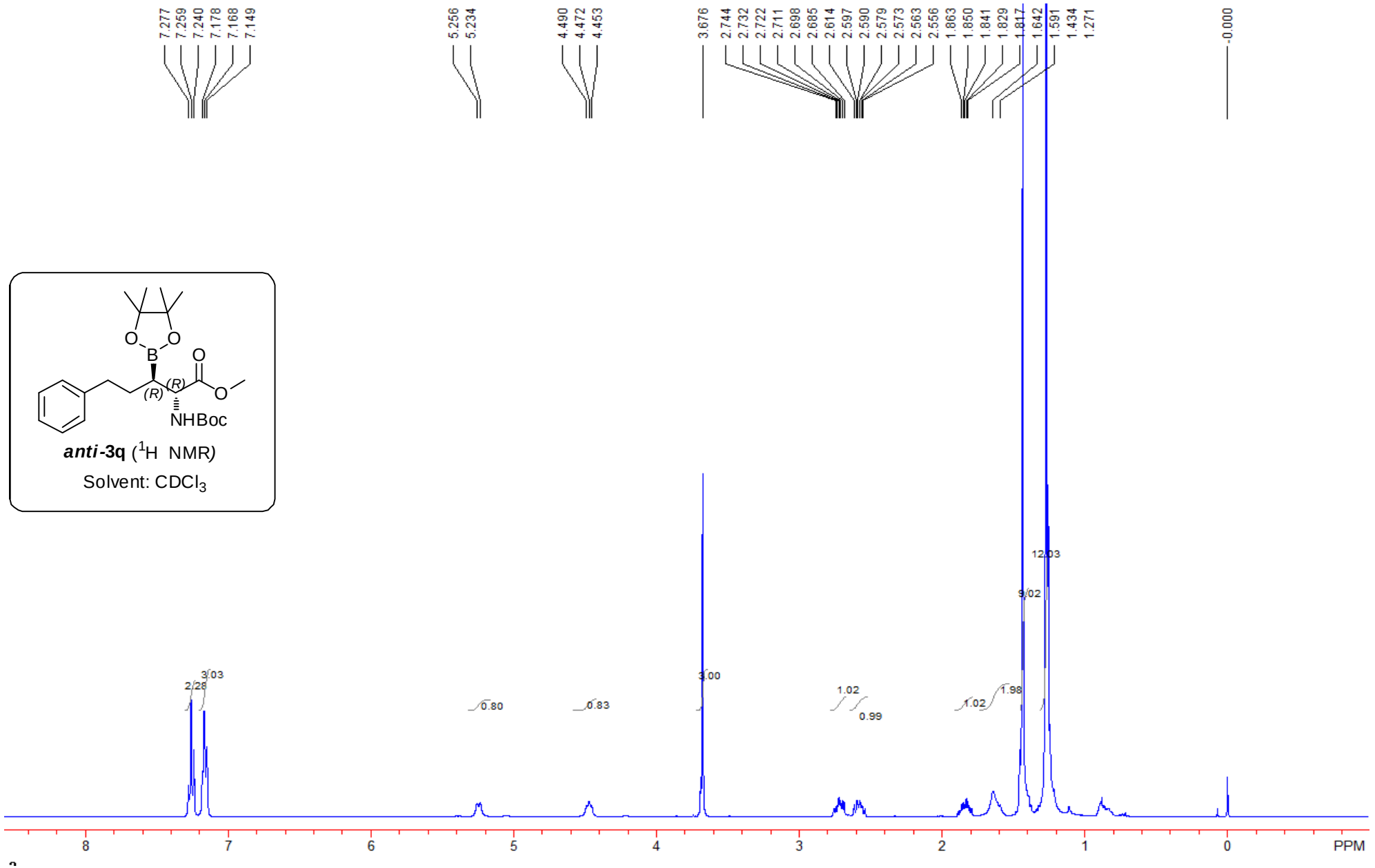
***syn*-3p** (^{13}C NMR)
Solvent: $CDCl_3$

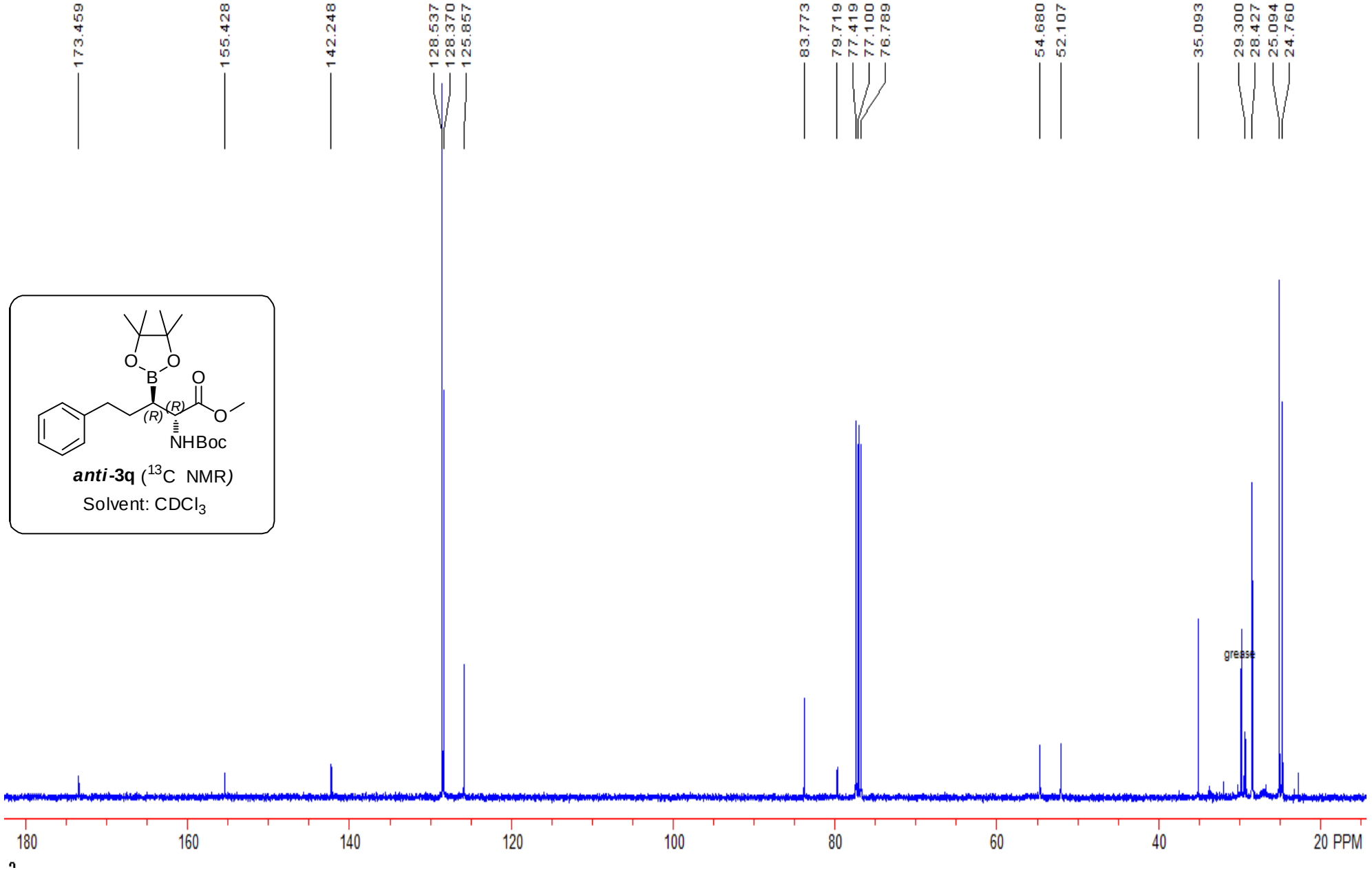

7.265
6.761
6.720
6.700
6.663
6.643
5.916
5.906
4.812
4.700
3.706
2.734
2.715
1.373
1.223
1.206
-0.000
NHBoc
anti-3p (1H NMR)
Solvent: CDCl3
3.00
2.03
1.70
3.00
0.96
12.19
9.08
8
7
6
5
4
3
2
1
0
PPM


172.836
155.208
147.562
146.165
131.011
122.713
109.890
108.235
100.780
83.826
79.560
77.297
77.100
76.667
55.523
52.137
28.199
24.570
24.517
O
B
O
O
(R)
(R)
O
O
O
NHBoc
anti-3p (13C NMR)
Solvent: CDCl3
grease
180
160
140
120
100
80
60
40
20
PPM


7.277
7.259
7.240
7.181
7.163
7.145
5.399
5.376
4.522
4.507
3.690
2.692
2.668
2.652
2.628
1.791
1.770
1.752
1.722
1.703
1.677
1.653
1.454
1.252
1.242
-0.000
O
B
O
O
(S)
(R)
O
NHBoc
syn-3q (1H NMR)
Solvent: CDCl3
3.04
2.36
0.86
0.87
3.00
2.07
3.07
9.16
12.54
8
6
4
2
0
PPM

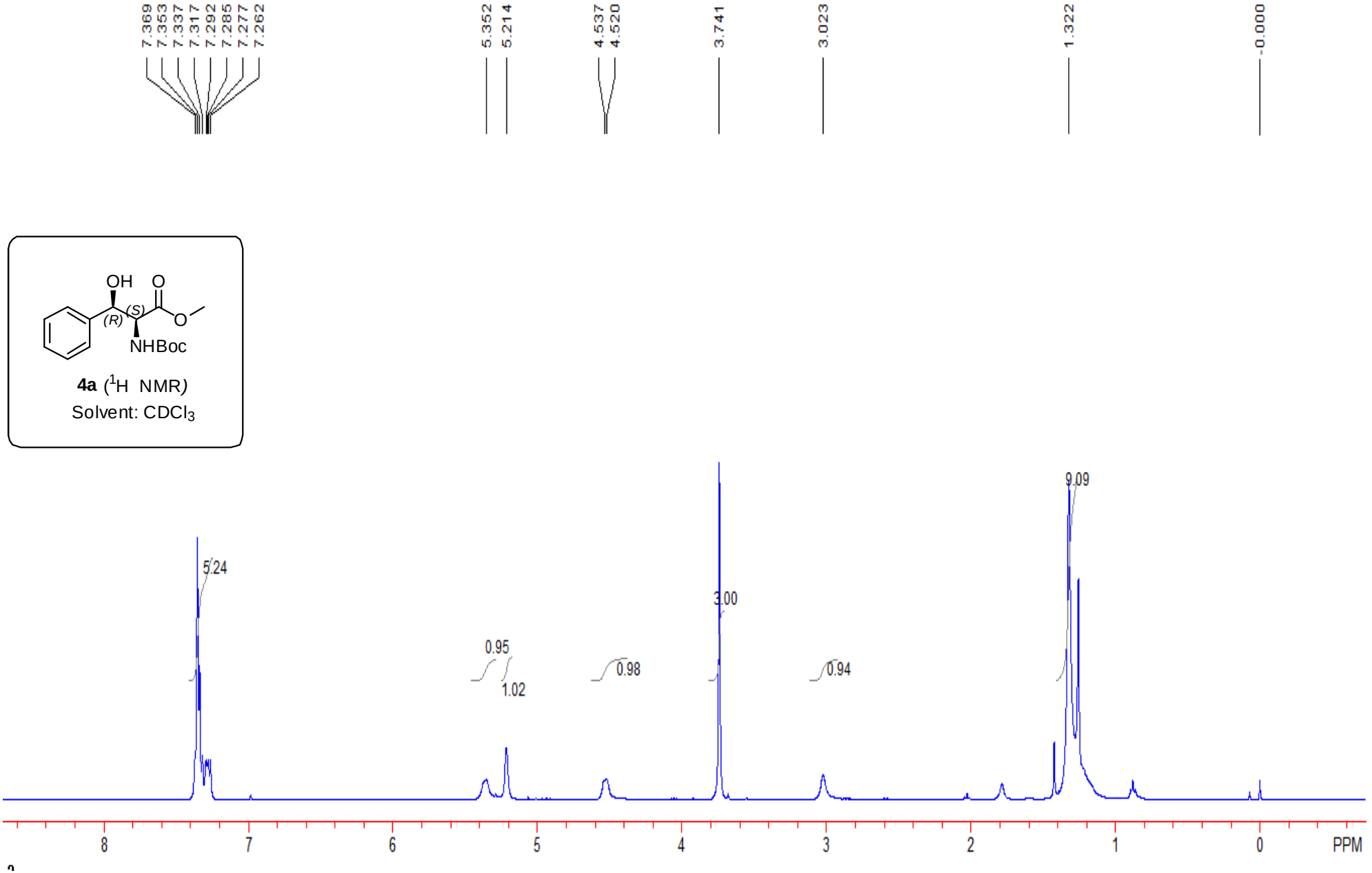

173.474
155.769
142.149
128.423
128.271
125.750
83.728
79.582
77.305
77.100
76.675
54.263
52.046
34.994
29.664
28.336
24.836
24.555
O
O
B
O
(R)
(S)
O
NHBoc
syn-3q (13C NMR)
Solvent: CDCl3
180
160
140
120
100
80
60
40
20
PPM

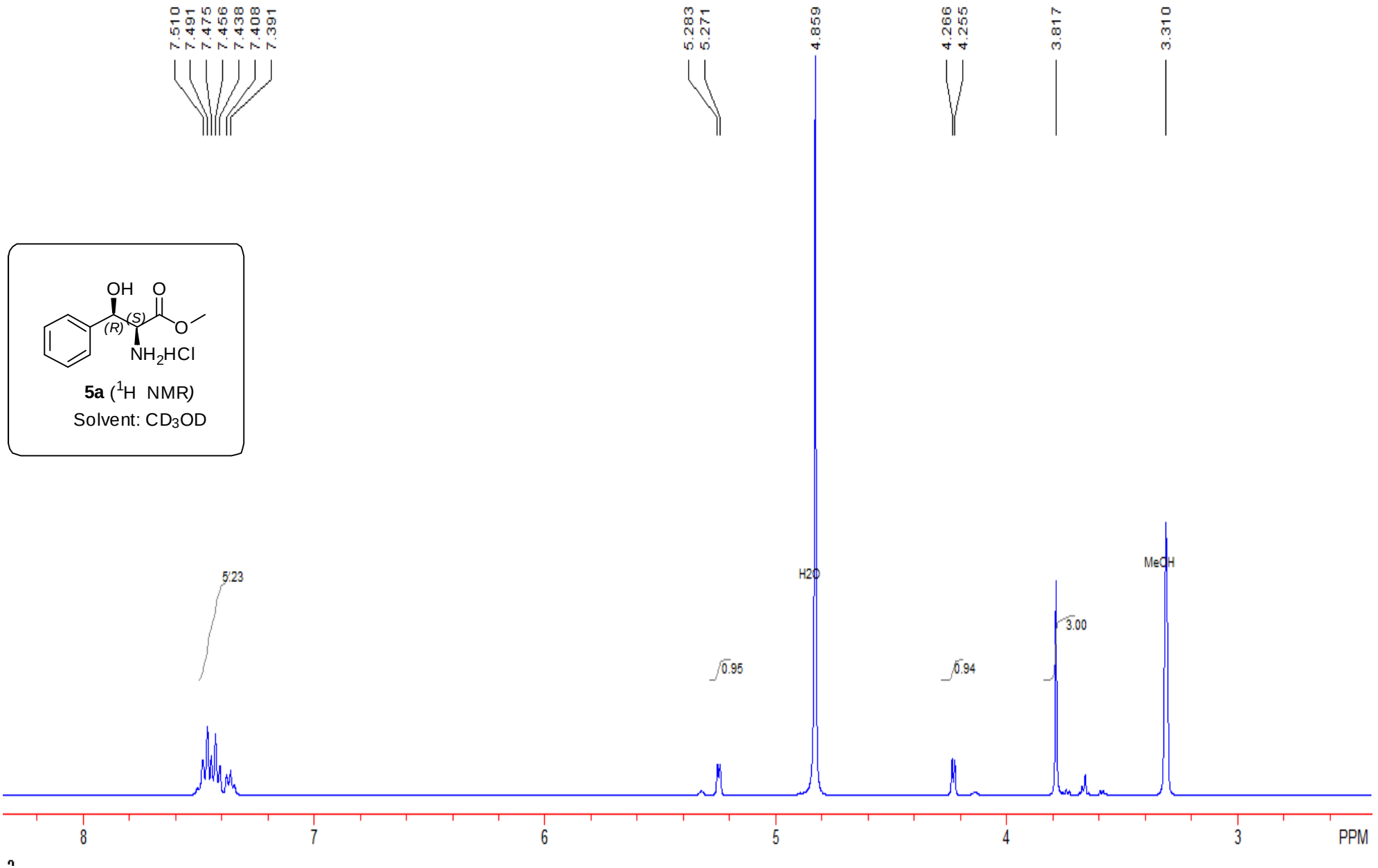

7.277
7.259
7.240
7.178
7.168
7.149
5.256
5.234
4.490
4.472
4.453
3.676
2.744
2.732
2.722
2.711
2.698
2.685
2.614
2.597
2.590
2.579
2.573
2.563
2.556
1.863
1.850
1.841
1.829
1.817
1.642
1.591
1.434
1.271
0.000
O
B
O
O
(R)
(R)
O
NHBoc
anti-3q (1H NMR)
Solvent: CDCl3
2.28
3.03
0.80
0.83
3.00
1.02
0.99
1.02
1.98
9.02
12.03
8
7
6
5
4
3
2
1
0
PPM

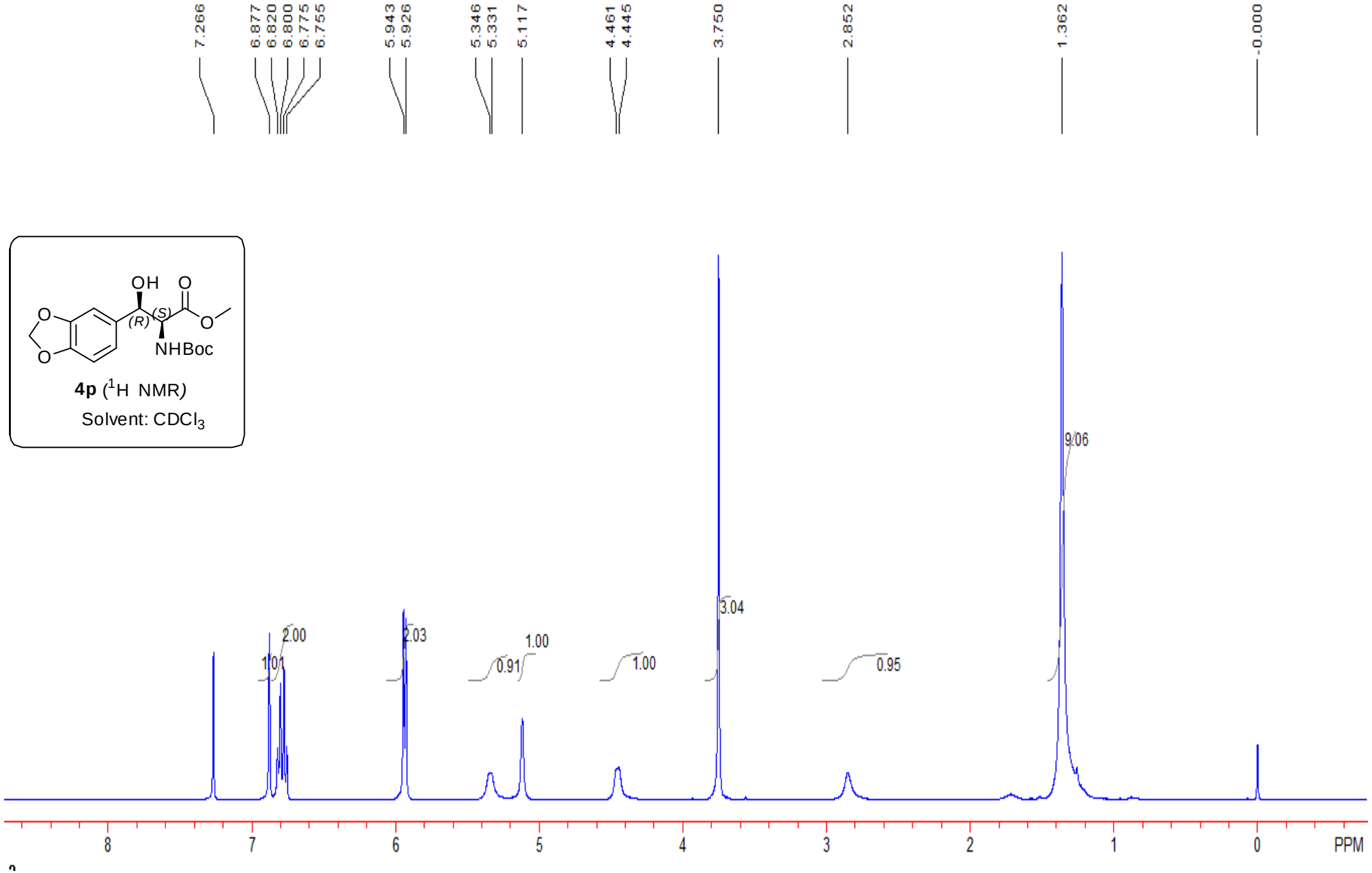


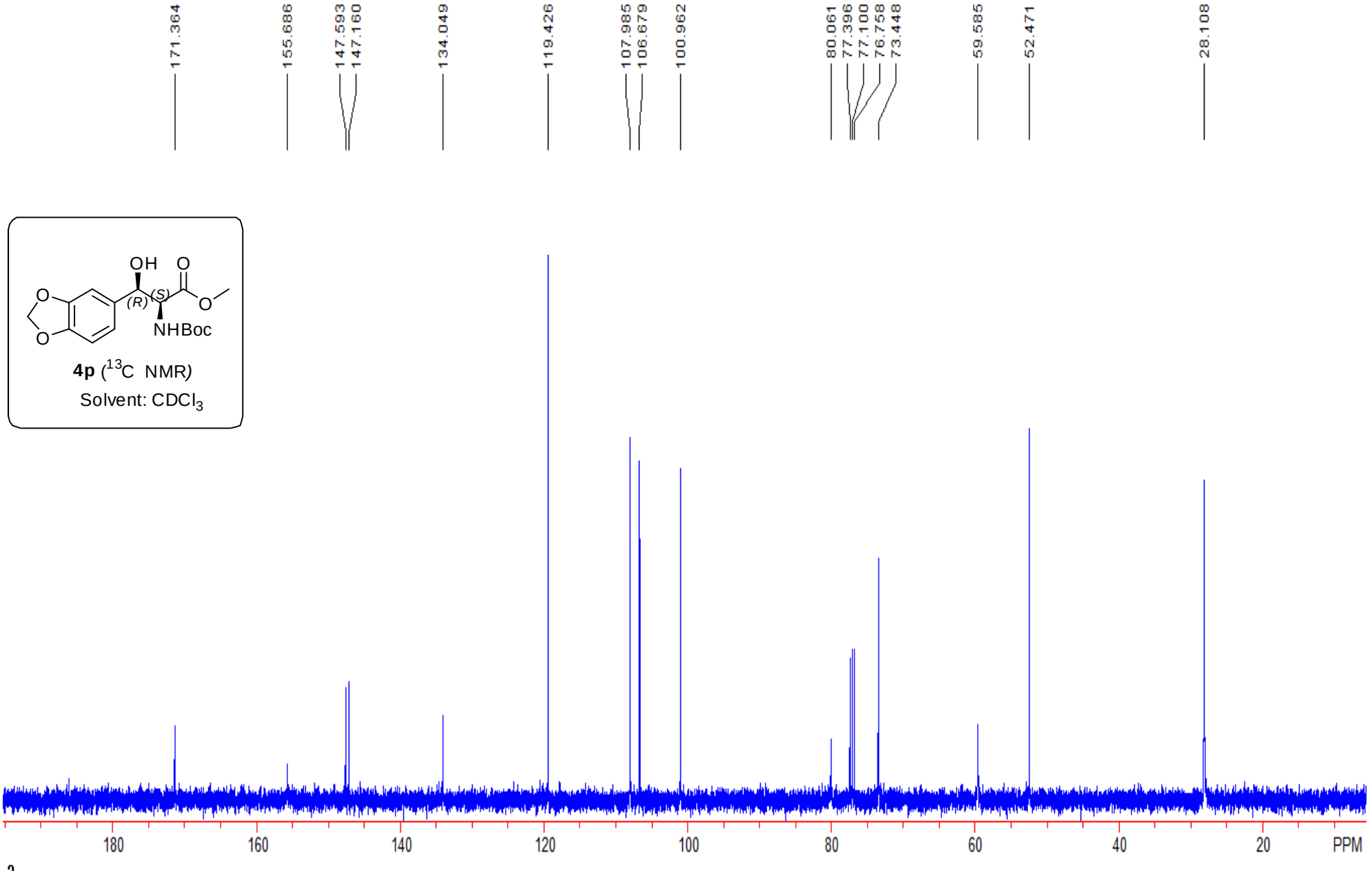
***anti*-3q** (^{13}C NMR)

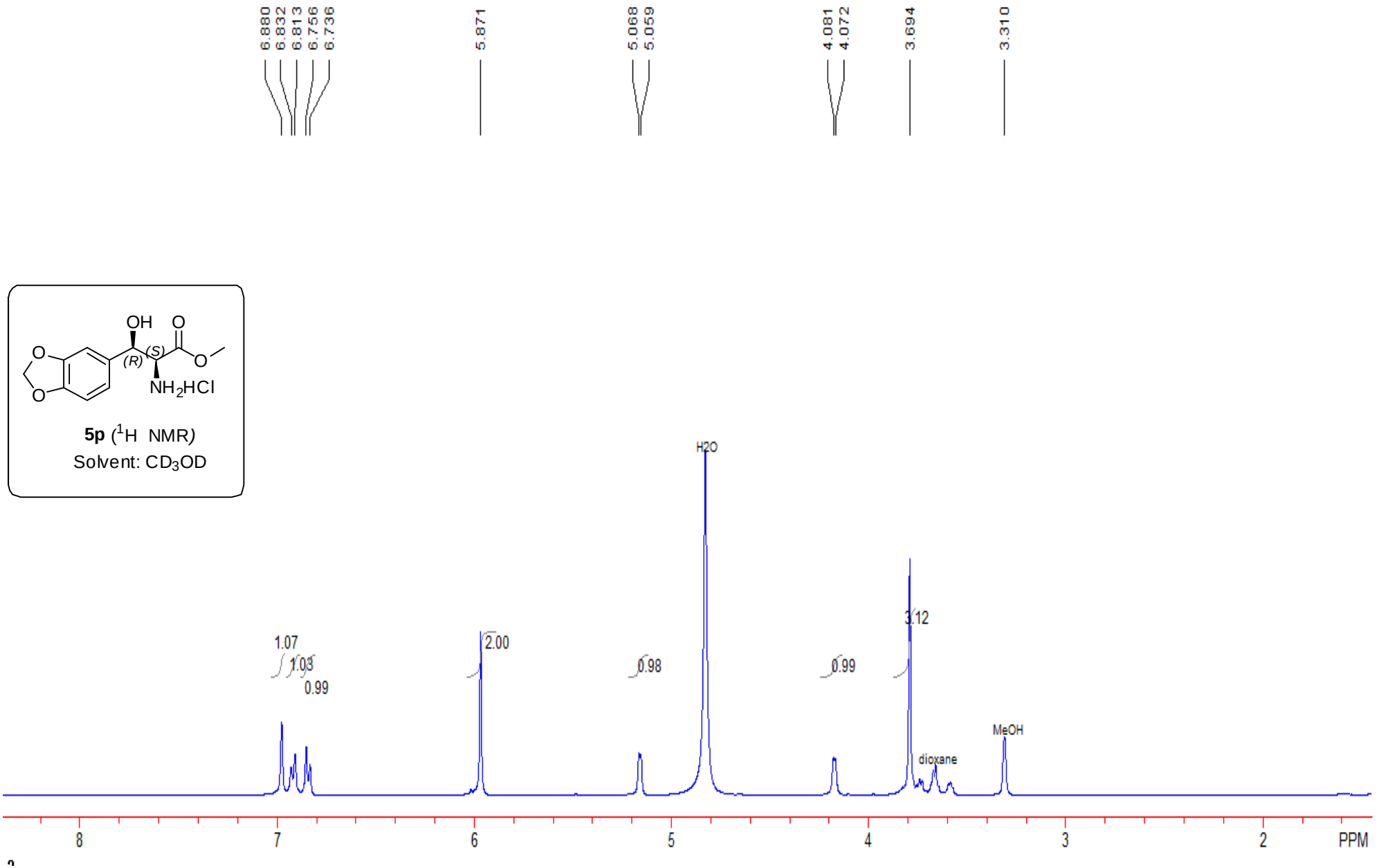
Solvent: $CDCl_3$

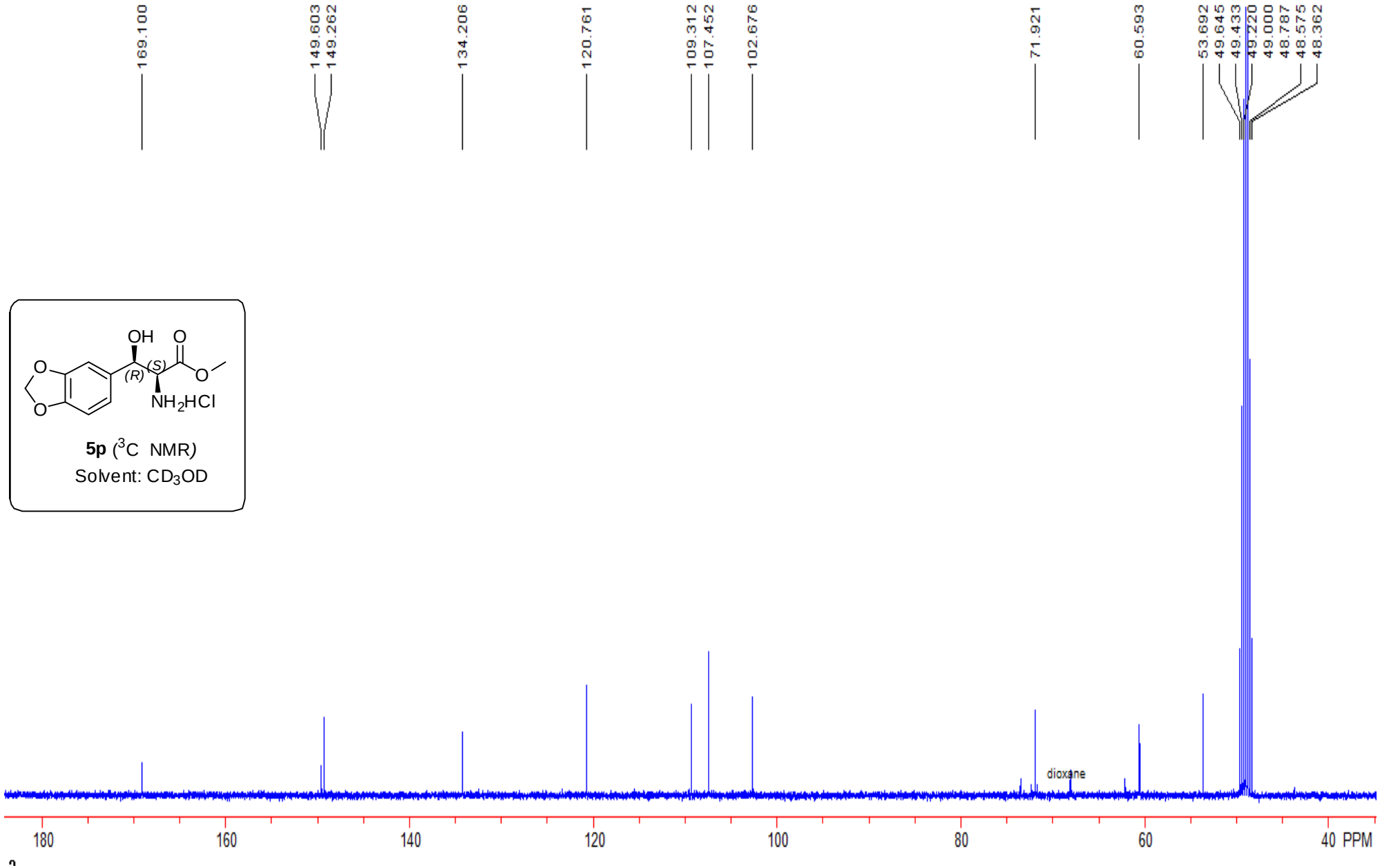

7.369
7.353
7.337
7.317
7.292
7.285
7.277
7.262
5.352
5.214
4.537
4.520
3.741
3.023
1.322
-0.000
OH
O
(S)
(R)
O
NHBoc
4a (1H NMR)
Solvent: CDCl3
5.24
0.95
1.02
0.98
3.00
0.94
9.09
8
7
6
5
4
3
2
1
0
PPM


7.510
7.491
7.475
7.456
7.438
7.408
7.391
5.283
5.271
4.859
4.266
4.255
3.817
3.310
OH
O
(R)
(S)
O
NH2HCl
5a (1H NMR)
Solvent: CD3OD
5.23
0.95
H2O
0.94
3.00
MeOH
8
7
6
5
4
3
PPM


7.266
6.877
6.820
6.800
6.775
6.755
5.943
5.926
5.346
5.331
5.117
4.461
4.445
3.750
2.852
1.362
-0.000
OH
O
(R)
(S)
O
O
O
NHBoc
4p (1H NMR)
Solvent: CDCl3
2.00
1.01
2.03
1.00
0.91
1.00
3.04
0.95
9.06
8
7
6
5
4
3
2
1
0
PPM


171.364
155.686
147.593
147.160
134.049
119.426
107.985
106.679
100.962
80.061
77.396
77.100
76.758
73.448
59.585
52.471
28.108
OH
O
(R)
(S)
O
O
O
NHBoc
4p (13C NMR)
Solvent: CDCl3
180
160
140
120
100
80
60
40
20
PPM


6.880
6.832
6.813
6.756
6.736
5.871
5.068
5.059
4.081
4.072
3.694
3.310
OH
O
(R)
(S)
O
O
O
NH2HCl
5p (1H NMR)
Solvent: CD3OD
H2O
1.07
1.03
0.99
2.00
0.98
0.99
3.12
MeOH
dioxane
8
7
6
5
4
3
2
PPM


169.100
149.603
149.262
134.206
120.761
109.312
107.452
102.676
71.921
60.593
53.692
49.645
49.433
49.220
49.000
48.787
48.575
48.362
OH
O
(R)
(S)
O
O
O
NH2HCl
5p (3C NMR)
Solvent: CD3OD
dioxane
180
160
140
120
100
80
60
40 PPM