Supporting Information

Direct amination of α-substituted nitroacetates using di-*tert*-butyl azodicarboxylate catalyzed by Hatakeyama's catalyst β-ICD

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General information:

Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX-300 or Bruker DPX-400 spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

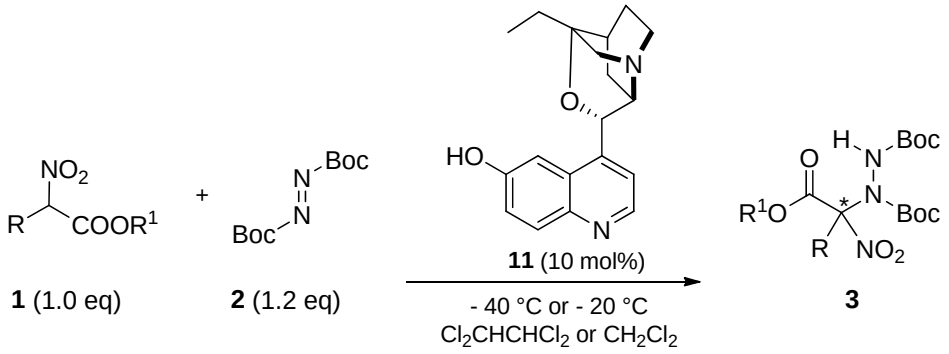
All reactions were run under atmosphere except noted. $MeOBu^{t}$, toluene and THF were prepared by distillation over sodium-benzophenone ketyl prior to use. Anhydrous acetone and $CH_3CO_2{}^{i}Pr$ was distilled over anhydrous $CaSO_4$ and stored over MS 4 Å. Anhydrous CH_2Cl_2 and $Cl_2CHCHCl_2$ were prepared by first distillation over P_2O_5 and then from CaH_2. α-Monosubstituted nitroacetates were easily prepared using literature procedures[1]. Catalysts **4**, **5, 7** and **8** were purchased from Aldrich, β-ICD **11** was purchased from TCI. Catalysts **6**[2] and **9-10**[3] were prepared using a literature method.

[1] (a) J. P. Berry, A. F. Isbell and G. E. Hunt, *J. Org. Chem.*, 1972, **37,** 4396; (b) N. Kornblum, R. K.Blackwood and J. W. Powers, *J. Am. Chem. Soc.*, 1957, **79**, 2507; (c) S. Nakamura, H. Sugimoto and T. Ohwada, *J. Am. Chem. Soc.*, 2007, **129**, 1724; (d) P. G. Mattingly and M. J. Miller, *J. Org. Chem.*, 1981, **46,** 1557.

[2] N. F. Dummer, R. Jenkins, X. Li, S. M. Bawaked, P. McMorn, A. Burrows, C. J. Kiely, R. P. K. Wells, D. J. Willock and G. J. Hutchings, *J. Catal.* 2006, **243**, 165.

[3] X. Liu, H. Li and L. Deng, *Org. Lett.*, 2005, **7**, 167.

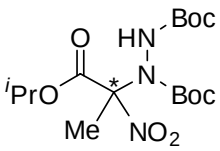
General procedure for the organocatalytic asymmetric amination reaction.



To a 5 mL vial were added catalyst **11** (7.7 mg, 0.025 mmol), nitroacetate **1** (0.25 mmol) and 2.5 mL of anhydrous CH_2Cl_2 or $Cl_2CHCHCl_2$. After the reaction mixture was stirred at -20 °C or -40 °C for half an hour, DTAD **2** (0.3 mmol) was added. The resulting mixture was stirred at the indicated temperature till almost full conversion of **1** by TLC analysis. The reaction mixture was directly subjected to column chromatography (petroleum ether/ethyl acetate, 30/1 to 15/1) to afford the desired product **3**.

It should be noted that due to the distinct presence of rotameric isomers, the ^{1}H NMR and ^{13}C NMR contained extra peaks, as reported in the related work.[4]

Di-*tert*-butyl 1-(1-isopropoxy-2-nitro-1-oxopropan-2-yl)hydrazine-1,2-dicarboxylate (3a)

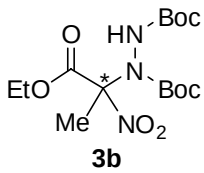


3a

Reaction was run in $CHCl_2CHCl_2$ at -40 °C for 5 days. R_f = 0.3 (petroleum ether/ethyl acetate, 10/1), The product **3a** was obtained in 93% yield as colorless oil. HPLC analysis (Chiralcel IC-H, hexane/^{i}PrOH = 95/5, 1.0 mL/min, 205 nm; t_r (minor) = 13.91 min, t_r (major) = 22.49 min) gave the isomeric composition of the product: 92% ee, $[\alpha]_D^{20}$ = -94.2 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.14 (s, br, 1H), 5.20-5.03 (m, 1H), 2.03 (s, 3H), 1.50-1.45 (m, 18H), 1.32-1.24 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.85, 154.81, 153.23, 84.54, 81.94, 71.94, 71.21, 27.99, 27.80, 27.73, 21.37, 21.25, 21.06; IR (neat): 3329, 2982, 1754, 1564, 1147, 917, 845, 766, 689; HRMS (ESI): exact mass calculated for $C_{16}H_{29}N_3O_8Na$ $[M+Na]^+$: 414.1847, found: 414.1845.

[4] (a) R. Matsubara and S. Kobayashi, *Angew. Chem. Int. Ed.*, 2006, **45**, 7993; (b) T. B. Poulsen, C. Alemparte and K. A. Jørgensen, *J. Am. Chem. Soc.*, 2005, **127**, 11614; (c) S. Saaby, M. Bella and K. A. Jørgensen, *J. Am. Chem. Soc.,* 2004, **126**, 8120; (d) M, Terada, M. Nagano and H. Ube, *J. Am. Chem. Soc.*, 2006, **128**, 16044; (e) S. Mouri, Z. Chen, H. Mitsunuma, M. Furutachi, S. Matsunaga and M. Shibasaki, *J. Am. Chem. Soc.*, 2010, **132**, 1255; (f) T. Bui, M. Borregan, C. Milite and C. F. Barbas III, *Org. Lett.*, 2010, **12**, 5696.

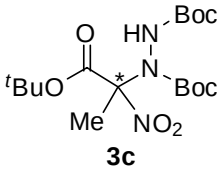
Di-*tert*-butyl 1-(1-ethoxy-2-nitro-1-oxopropan-2-yl)hydrazine-1,2-dicarboxylate (3b)



3b

Reaction was run in $CHCl_2CHCl_2$ at -40 °C for 3 days. The product **3b** was obtained in 98% yield as colorless oil. R_f = 0.4 (petroleum ether/ethyl acetate, 10/1). HPLC analysis (Chiralcel IC-H, hexane/^{i}PrOH = 95/5, 1.0 mL/min, 205 nm; t_r (minor) = 17.79 min, t_r (major) = 25.58 min) gave the isomeric composition of the product: 91% ee, $[\alpha]_D^{20}$ = -84.8 (*c* = 0.77, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.26 (s, br, 1H), 4.33-4.27 (m, 2H), 2.05 (s, 3H), 1.49 (s, 9H), 1.46 (s, 9H), 1.32-1.29 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.50, 153.27, 84.70, 82.08, 63.57, 63.16, 27.98, 27.81, 27.75, 13.79, 13.64; IR (neat): 3329, 2981, 1736, 1567, 1368, 1241, 1151, 1017, 874, 730; HRMS (ESI): exact mass calculated for $C_{15}H_{27}N_3O_8Na$ $[M+Na]^+$: 400.1690, found: 400.1688.

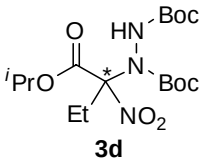
Di-*tert*-butyl 1-(1-*tert*-butoxy-2-nitro-1-oxopropan-2-yl)hydrazine-1,2-dicarboxylate (3c)



3c

Reaction was run in $CHCl_2CHCl_2$ at -40 °C for 7 days. The product **3c** was obtained in 65% yield as colorless oil. R_f = 0.2 (petroleum ether/ethyl acetate, 10/1). HPLC analysis (Chiralcel IC-H, hexane/^{i}PrOH = 95/5, 1.0 mL/min, 205 nm; t_r (minor) = 9.31 min, t_r (major) = 17.25 min) gave the isomeric composition of the product: 92% ee, $[\alpha]_D^{20}$ = -58.2 (*c* = 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.19 (s, br, 1H), 1.99 (s, 3H), 1.49 (s, 18H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.84, 154.55, 153.31, 85.27, 84.49, 81.84, 60.30, 28.05, 27.85, 27.81, 27.61, 27.37, 14.11; IR (neat): 3337, 2980, 1737, 1566, 1369, 1253, 1138, 1017, 845, 799, 777, 729; HRMS (ESI): exact mass calculated for $C_{17}H_{31}N_3O_8Na$ $[M+Na]^+$: 428.2003, found: 428.1993.

Di-*tert*-butyl 1-(1-isopropoxy-2-nitro-1-oxobutan-2-yl)hydrazine-1, 2-dicarboxylate (3d)

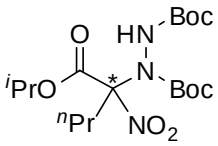


3d

Reaction was run in CH_2Cl_2 at -40 °C for 5 days. The product **3d** was obtained in 87% yield as colorless oil. R_f = 0.3 (petroleum ether/ethyl acetate, 10/1). HPLC analysis (Chiralcel IC-H, hexane/^{i}PrOH = 95/5, 1.0 mL/min, 205 nm; t_r (minor) = 11.65 min, t_r (major) = 15.94 min) gave the isomeric composition of the product: 88% ee, $[\alpha]_D^{20}$ = -46.4 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.19 (s, br, 1H), 5.19-5.03 (m, 1H), 2.61-2.22 (m, 2H), 1.48-1.44 (m, 18H), 1.32-1.22 (m, 6H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.36, 161.75, 153.78, 84.56, 81.84, 71.88, 71.19, 29.60, 28.03, 27.77, 27.73, 21.58, 21.32, 8.74; IR

(neat): 3332, 2981, 1737, 1565, 1458, 1369, 1238, 1152, 1101, 931, 877, 831, 765; HRMS (ESI): exact mass calculated for $C_{17}H_{31}N_3O_8Na$ $[M+Na]^+$: 428.2003, found: 428.2005.

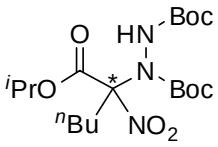
Di-*tert*-butyl 1-(1-isopropoxy-2-nitro-1-oxopentan-2-yl)hydrazine-1, 2-dicarboxylate (3e)



3e

Reaction was run in $CHCl_2CHCl_2$ at -40 °C for 5 days. The product **3e** was obtained in 60% yield as colorless oil. R_f = 0.3 (petroleum ether/ethyl acetate, 10/1). HPLC analysis (Chiralcel IC-H, hexane/^{i}PrOH = 95/5, 1.0 mL/min, 205 nm; t_r (minor) = 11.24 min, t_r (major) = 14.94 min) gave the isomeric composition of the product: 89% ee, $[\alpha]_D^{20}$ = -32.9 (*c* = 0.65, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.18 (s, br, 1H), 5.18-5.01 (m, 1H), 2.51-2.11 (m, 2H), 1.98-1.65 (m, 2H), 1.48-1.45 (m, 18H), 1.31-1.22 (m, 6H), 0.98-0.89 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.37, 161.85, 153.77, 84.58, 81.80, 71.86, 71.18, 37.68, 28.03, 27.79, 27.74, 21.56, 21.31, 17.45, 14.13; IR (neat): 3332, 2979, 1737, 1566, 1368, 1309, 1235, 1153, 1102, 1051, 847, 827, 772; HRMS (ESI): exact mass calculated for $C_{18}H_{33}N_3O_8Na$ $[M+Na]^+$: 442.2160, found: 442.2156.

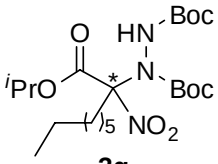
Di-*tert*-butyl 1-(1-isopropoxy-2-nitro-1-oxohexan-2-yl)hydrazine-1, 2-dicarboxylate (3f)



3f

Reaction was run in $CHCl_2CHCl_2$ at -40 °C for 5 days. The product **3f** was obtained in 60% yield as colorless oil. R_f = 0.2 (petroleum ether/ethyl acetate, 10/1). HPLC analysis (Chiralcel IC-H, hexane/^{i}PrOH = 95/5, 1.0 mL/min, 205 nm; t_r (minor) = 11.15 min, t_r (major) = 14.34 min) gave the isomeric composition of the product: 90% ee, $[\alpha]_D^{20}$ = -37.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.19 (s, br, 1H), 5.18-5.01 (m, 1H), 2.52-2.13 (m, 2H), 1.89-1.65 (m, 2H), 1.44 (s, 18H), 1.37-1.22 (m, 8H), 0.93-0.83 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.38, 161.88, 153.77, 84.52, 81.76, 71.82, 71.14, 35.40, 27.99, 27.76, 27.71, 25.85, 22.70, 21.52, 21.28, 13.48; IR (neat): 3234, 2979, 2874, 1747, 1719, 1565, 1467, 1367, 1311, 1255, 1154, 1051, 960, 829, 788; HRMS (ESI): exact mass calculated for $C_{19}H_{35}N_3O_8Na$ $[M+Na]^+$: 456.2316, found: 456.2310.

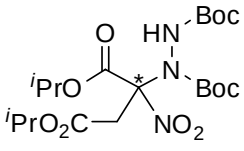
Di-*tert*-butyl 1-(1-isopropoxy-2-nitro-1-oxononan-2-yl)hydrazine-1, 2-dicarboxylate (3g)



3g

Reaction was run in CH_2Cl_2 at -40 °C for 6 days. The product **3g** was obtained in 54% yield as colorless oil. R_f = 0.3 (petroleum ether/ethyl acetate, 10/1). HPLC analysis (Chiralcel IC-H, hexane/^{i}PrOH = 95/5, 1.0 mL/min, 205 nm; t_r (minor) = 11.54 min, t_r (major) = 15.05 min) gave the isomeric composition of the product: 85% ee, $[\alpha]_D^{20}$ = -37.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.19 (s, br, 1H), 5.18-5.01 (m, 1H), 2.51-2.11 (m, 2H), 1.93-1.65 (m, 2H), 1.47-1.44 (m, 18H), 1.30-1.22 (m, 14H), 0.85-0.81 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.39, 161.89, 153.77, 84.52, 81.78, 71.82, 71.14, 35.74, 31.52, 29.55, 28.66, 28.01, 27.78, 27.72, 23.80, 23.80, 22.45, 21.54, 21.31, 13.93; IR (neat): 3330, 2980, 1739, 1566, 1460, 1369, 1315, 1238, 1151, 1051, 849, 829, 725; HRMS (ESI): exact mass calculated for $C_{22}H_{41}N_3O_8Na$ $[M+Na]^+$: 498.2786, found: 498.2783.

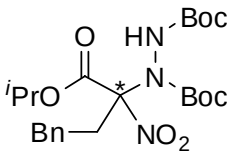
Di-*tert*-butyl 1-(1,4-diisopropoxy-2-nitro-1,4-dioxobutan-2-yl)hydrazine-1, 2-dicarboxylate (3h)



3h

Reaction was run in $CHCl_2CHCl_2$ at -40 °C for 6 days. The product **3h** was obtained in 72% yield as colorless oil. R_f = 0.3 (petroleum ether/ethyl acetate, 10/1). HPLC analysis (Chiralcel AS-H + AS-H, hexane/^{i}PrOH = 95/5, 0.6 mL/min, 205 nm; t_r (minor) = 34.17 min, t_r (major) = 23.66 min) gave the isomeric composition of the product: 93% ee, $[\alpha]_D^{20}$ = -34.6 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.37 (s, br, 1H), 5.16-5.05 (m, 1H), 5.04-4.96 (m, 1H), 3.47 (ABd, *J* = 16.8 Hz, 1H), 3.21 (ABd, *J* = 16.4 Hz, 1H), 1.47 (s, 9H), 1.46 (s, 9H), 1.32-1.27 (m, 6H), 1.26-1.20 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.58, 161.36, 154.22, 152.72, 84.40, 81.97, 72.38, 71.93, 69.24, 39.25, 28.07, 27.77, 21.58, 21.49, 21.38, 21.19; IR (neat): 3321, 2982, 1737, 1577, 1468, 1370, 1314, 1235, 1147, 1103, 996, 848, 734; HRMS (ESI): exact mass calculated for $C_{20}H_{35}N_3O_{10}Na$ $[M+Na]^+$: 500.2215, found: 500.2208.

Di-*tert*-butyl 1-(1-isopropoxy-2-nitro-1-oxo-4-phenylbutan-2-yl)hydrazine-1, 2-dicarboxylate (3i)

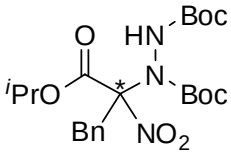


3i

Reaction was run in $CHCl_2CHCl_2$ at -40 °C for 6 days. The product **3i** was obtained

in 68% yield as colorless oil. R_f = 0.2 (petroleum ether/ethyl acetate, 10/1). HPLC analysis (Chiralcel AS-H + AS-H, hexane/^{i}PrOH = 95/5, 0.5 mL/min, 205 nm; t_r (minor) = 35.72 min, t_r (major) = 24.13 min) gave the isomeric composition of the product: 90% ee, $[\alpha]_D^{20}$ = -36.2 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.14 (m, 5H), 6.19 (s, br, 1H), 5.26-5.11 (m, 1H), 3.34-2.46 (m, 4H), 1.50 (s, 9H), 1.49 (s, 9H), 1.37 (d, *J* = 6.4Hz, 3H), 1.34-1.29 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.30, 161.77, 153.90, 140.81, 128.60, 128.40, 126.41, 126.24, 84.86, 82.17, 72.23, 71.55, 31.44, 30.37, 28.12, 27.89, 27.83, 21.72, 21.47; IR (neat): 3329, 2981, 1737, 1566, 1456, 1369, 1310, 1239, 1148, 1100, 1045, 930, 849, 828, 700; HRMS (ESI): exact mass calculated for $C_{23}H_{35}N_3O_8Na$ $[M+Na]^+$: 504.2316, found: 504.2312.

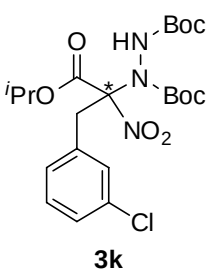
Di-*tert*-butyl 1-(1-isopropoxy-2-nitro-1-oxo-3-phenylpropan-2-yl)hydrazine-1, 2-dicarboxylate (3j)



3j

Reaction was run in $CHCl_2CHCl_2$ at -20 °C for 6 days. The product **3j** was obtained in 59% yield as colorless oil. R_f = 0.2 (petroleum ether/ethyl acetate, 10/1). HPLC analysis (Chiralcel IC-H, hexane/^{i}PrOH = 90/10, 1.0 mL/min, 205 nm; t_r (minor) = 8.37 min, t_r (major) = 11.21 min) gave the isomeric composition of the product: 84% ee, $[\alpha]_D^{20}$ = -6.6 (*c* = 0.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43-7.27 (m, 5H), 6.22 (s, br, 1H), 5.01-4.94 (m, 1H), 3.85-3.58 (m, 2H), 1.51-1.47 (m, 18H), 1.16-1.04 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.16, 154.76, 153.71, 132.64, 131.07, 128.11, 128.07, 127.76, 127.31, 84.74, 82.00, 72.24, 71.66, 41.39, 28.15, 27.90, 27.84, 21.26, 20.97; IR (neat): 3326, 2983, 1717, 1567, 1370, 1250, 1144, 1050, 914, 831, 768, 699; HRMS (ESI): exact mass calculated for $C_{22}H_{33}N_3O_8Na$ $[M+Na]^+$: 490.2160, found: 490.2155.

Di-*tert*-butyl 1-(3-(3-chlorophenyl)-1-isopropoxy-2-nitro-1-oxopropan-2-yl)hydrazine-1, 2-dicarboxylate (3k)

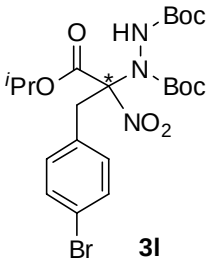


3k

Reaction was run in $CHCl_2CHCl_2$ at -20 °C for 5 days. The product **3k** was obtained in 84% yield as colorless oil. R_f = 0.2 (petroleum ether/ethyl acetate, 10/1). HPLC analysis (Chiralcel IC-H, hexane/^{i}PrOH = 90/10, 1.0 mL/min, 230 nm; t_r (minor) = 9.63 min, t_r (major) = 14.19 min) gave the isomeric composition of the product: 80%

ee, $[\alpha]_D^{20}$ = -9.7 (*c* = 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.21 (m, 4H), 6.22 (s, br, 1H), 5.02-4.76 (m, 1H), 4.21-3.55 (m, 2H), 1.64-1.41 (m, 18H), 1.18-1.08 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.98, 154.81, 153.59, 134.63, 133.82, 131.29, 129.35, 127.97, 127.50, 85.18, 82.24, 72.57, 71.99, 40.84, 28.13, 27.89, 27.83, 21.29; IR (neat): 3328, 2985, 1730, 1569, 1476, 1370, 1321, 1251, 1145, 1079, 1050, 910, 830, 771, 685; HRMS (ESI): exact mass calculated for $C_{22}H_{32}ClN_3O_8Na$ $[M+Na]^+$: 524.1770, found: 524.1760.

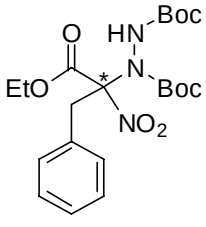
Di-*tert*-butyl 1-(3-(4-bromophenyl)-1-isopropoxy-2-nitro-1-oxopropan-2-yl)hydrazine-1, 2-dicarboxylate (3l)



3l

Reaction was run in CH_2Cl_2 at -40 °C for 5 days. The product **3l** was obtained in 77% yield as colorless oil. R_f = 0.2 (petroleum ether/ethyl acetate, 10/1). HPLC analysis (Chiralcel IC-H, hexane/^{i}PrOH = 95/5, 1.0 mL/min, 205 nm; t_r (minor) = 9.46 min, t_r (major) = 10.49 min) gave the isomeric composition of the product: 80% ee, $[\alpha]_D^{20}$ = -11.9 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.16 (m, 4H), 6.22 (s, br, 1H), 5.04-4.76 (m, 1H), 4.22-3.54 (m, 2H), 1.51-1.46 (m, 18H), 1.17-1.07 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.99, 154.77, 153.61, 132.82, 132.43, 131.69, 131.22, 131.11, 122.04, 85.17, 82.20, 72.49, 71.88, 40.72, 29.66, 28.14, 28.01, 27.90, 27.88, 27.82, 21.28, 20.98; IR (neat): 3338, 2981, 1736, 1566, 1489, 1368, 1312, 1240, 1148, 1103, 1013, 847, 823, 766, 736, 710; HRMS (ESI): exact mass calculated for $C_{22}H_{32}BrN_3O_8Na$ $[M+Na]^+$: 568.1265, found: 568.1253.

Di-*tert*-butyl 1-(1-ethoxy-2-nitro-1-oxo-3-phenylpropan-2-yl)hydrazine-1, 2-dicarboxylate (3m)

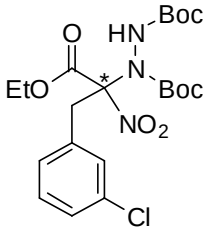


3m

Reaction was run in $CHCl_2CHCl_2$ at -20 °C for 5 days. The product **3m** was obtained in 55% yield as colorless oil. R_f = 0.2 (petroleum ether/ethyl acetate, 10/1). HPLC analysis (Chiralcel AD-H, hexane/^{i}PrOH = 95/5, 1.0 mL/min, 205 nm; t_r (minor) = 26.69 min, t_r (major) = 43.45 min) gave the isomeric composition of the product: 87% ee, $[\alpha]_D^{20}$ = -31.1 (*c* = 0.55, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44-7.26 (m, 5H), 6.27 (s, br, 1H), 4.26-4.19 (m, 1H), 4.07-4.02 (m, 1H), 3.80-3.58 (m, 2H), 1.52-1.46 (m, 18H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.70, 154.84, 153.67, 132.54, 131.05,

131.00, 128.12, 128.04, 127.46, 85.06, 82.16, 63.18, 62.98, 41.49, 28.11, 28.00, 27.88, 27.80, 13.65; IR (neat): 3322, 2981, 1736, 1566, 1456, 1368, 1313, 1242, 1148, 1095, 1021, 968, 847, 777, 741, 700; HRMS (ESI): exact mass calculated for $C_{21}H_{31}N_3O_8Na$ $[M+Na]^+$: 476.2003, found: 476.2003.

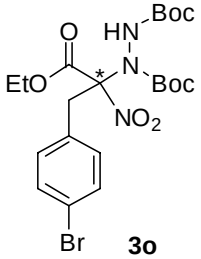
Di-*tert*-butyl 1-(3-(3-chlorophenyl)-1-ethoxy-2-nitro-1-oxopropan-2-yl)hydrazine-1, 2-dicarboxylate (3n)



3n

Reaction was run in $CHCl_2CHCl_2$ at -20 °C for 5 days. The product **3n** was obtained in 63% yield as colorless oil. R_f = 0.2 (petroleum ether/ethyl acetate, 10/1). HPLC analysis (Chiralcel IC-H, hexane/^{i}PrOH = 95/5, 1.0 mL/min, 230 nm; t_r (minor) = 12.28 min, t_r (major) = 19.87 min) gave the isomeric composition of the product: 80% ee, $[\alpha]_D^{20}$ = -25.6 (*c* = 0.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.10 (m, 4H), 6.27 (s, br, 1H), 4.35-4.10 (m, 2H), 3.93-3.50 (m, 2H), 1.60-1.36 (m, 18H), 1.26-1.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.53, 154.98, 153.56, 134.56, 133.85, 131.31, 129.35, 129.27, 128.04, 85.20, 82.42, 63.45, 63.20, 40.95, 28.25, 28.10, 27.98, 27.87, 27.79, 13.66; IR (neat): 3368, 2982, 1675, 1568, 1457, 1370, 1315, 1201, 1145, 1011, 846, 800, 716, 685; HRMS (ESI): exact mass calculated for $C_{21}H_{30}ClN_3O_8Na$ $[M+Na]^+$: 510.1614, found: 510.1601.

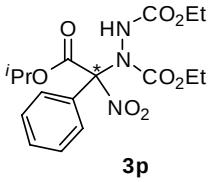
Di-*tert*-butyl 1-(3-(4-bromophenyl)-1-ethoxy-2-nitro-1-oxopropan-2-yl)hydrazine-1, 2-dicarboxylate (3o)



3o

Reaction was run in $CHCl_2CHCl_2$ at -20 °C for 5 days. The product **3o** was obtained in 61% yield as colorless oil. R_f = 0.2 (petroleum ether/ethyl acetate, 10/1). HPLC analysis (Chiralcel AD-H, hexane/^{i}PrOH = 90/10, 1.0 mL/min, 230 nm; t_r (minor) = 16.85 min, t_r (major) = 25.51 min) gave the isomeric composition of the product: 85% ee, $[\alpha]_D^{20}$ = -25.4 (*c* = 0.55, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.14 (m, 4H), 6.25 (s, br, 1H), 4.31-4.07 (m, 2H), 3.92-3.54 (m, 2H), 1.51-1.44 (m, 18H), 1.25-1.17 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.53, 154.90, 153.58, 132.75, 131.89, 131.58, 131.25, 131.13, 122.13, 85.20, 82.37, 63.40, 63.15, 40.82, 28.11, 27.99, 27.86, 27.79, 13.68; IR (neat): 3368, 2981, 1735, 1567, 1488, 1394, 1369, 1316, 1250, 1147, 1109, 1013, 911, 846, 763, 731, 648; HRMS (ESI): exact mass calculated for $C_{21}H_{30}BrN_3O_8Na$ $[M+Na]^+$: 554.1108, found: 554.1093.

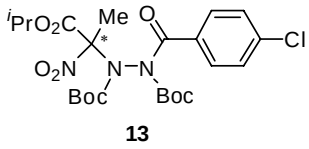
Diethyl 1-(2-isopropoxy-1-nitro-2-oxo-1-phenylethyl)hydrazine-1, 2-dicarboxylate (3p)



3p

Reaction was run in THF at -40 °C for 7 days. The product **3p** was obtained in 61% yield as colorless oil. R_f = 0.3 (petroleum ether/ethyl acetate, 5/1). HPLC analysis (Chiralcel IC-H, hexane/^{i}PrOH = 85/15, 0.8 mL/min, 230 nm; t_r (minor) = 18.54 min, t_r (major) = 29.60 min) gave the isomeric composition of the product: 22% ee, $[\alpha]_D^{20}$ = -4.0 (*c* = 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84-7.27 (m, 5H), 6.52 (s, br, 1H), 5.20-5.04 (m, 1H), 4.31-4.18 (m, 2H), 4.09-3.95 (m, 2H), 1.43-1.23 (m, 6H), 1.21-1.02 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.16, 160.46, 155.37, 129.92, 128.84, 128.87, 127.93, 127.84, 127.72, 72.82, 72.34, 64.46, 64.21, 21.32, 20.95, 14.35, 14.18; IR (neat): 3307, 2925, 1733, 1571, 1450, 1375, 1231, 1100, 1066, 1017，989, 828, 767, 733, 695; HRMS (ESI): exact mass calculated for $C_{17}H_{23}N_3O_8Na$ $[M+Na]^+$: 420.1377, found: 420.1368.

Di-*tert*-butyl 1-(4-chlorobenzoyl)-2-(1-isopropoxy-2-nitro-1-oxopropan-2-yl)hydrazine-1,2-di-Carboxylate (13)

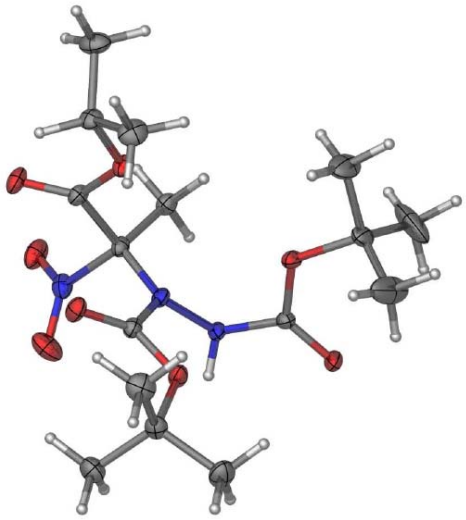


13

3a (141 mg, 0.36 mmol) was dissolved in the mixture of CH_2Cl_2 (4 mL) and Et_3N (0.7 mL), Then 4-chlorobenzoyl chloride (70 mg, 0.4 mmol) and DMAP (4.0 mg, 0.1 eq.) was added at 0 °C and the resulting mixture was gradually warmed to room temperature. The reaction was monitored by TLC. As the reaction was completed after 1.5 h. The resulting solution was concentrated under vacuum to afford the crude product. The crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 35/1) to afford the desired product **13**, 47% yield. R_f = 0.5 (petroleum ether/ethyl acetate, 10/1). HPLC analysis (Chiralcel IC-H, hexane/^{i}PrOH = 95/5, 1.0 mL/min, 230 nm; t_r (minor) = 29.15 min, t_r (major) = 33.67 min) gave the isomeric composition of the product: 92% ee, $[\alpha]_D^{20}$ = -92.3 (*c* = 0.69, $CHCl_3$); δ = 7.74 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 5.20-5.10 (m, 1H), 2.02 (s, 3H), 1.54-1.45 (m, 9H), 1.39 (s, 6H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.95, 169.50, 163.61, 163.47, 151.53, 151.24, 139.08, 132.50, 130.01, 128.53, 100.21, 85.43, 84.70, 71.79, 28.06, 27.96, 27.81, 27.53, 27.46, 27.36, 21.38, 21.30, 20.41; IR (neat): 2981, 2905, 1724, 1598, 1446, 1345, 1246, 1214, 1163, 1098, 1061, 996, 915, 731, 695; HRMS (ESI): exact mass calculated for $C_{17}H_{23}N_3O_8Na$ $[M+Na]^+$: 552.1719, found: 552.1738.

Single-Crystal X-ray Crystollgraphy[5]

Data intensity of **3a** was collected using a Bruker SMART APEX II (Mo radiation). The X-ray condition of was 50 kV × 30 mA. Data collection and reduction were done by using the Bruker ApexII software package. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for non-H atoms using SHELX-97. Hydrogen atoms were added at their geometrically idea positions and refined isotropically. Crystal data for **3a**: $C_{16}H_{29}N_3O_8$, M = 391.42, T = 173.2(2) K, λ = 0.71073 Å, Triclinic, space group P-1, a = 9.2865(5) Å, b = 10.1783(5) Å, c = 12.8619(7) Å, V = 1073.65(10) Å^3, z = 2, d_{calc} = 1.211 mg/m^3, 12281 reflections measured, 3749 unique [R_{int} = 0.0298], R_1 = 0.0390, wR_2 = 0.0952 ($I > 2\sigma(I)$), final R_1 = 0.0599, wR_2 = 0.1107 (all data), GOF = 1.027, and 248 parameters.



[5] Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center. (CCDC 833516).

Table 1. Crystal data and structure refinement for z.

Identification code	z	
Empirical formula	C16 H29 N3 O8	
Formula weight	391.42	
Temperature	173(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 9.2865(5) A	alpha = 86.696(2) deg.
	b = 10.1783(5) A	beta = 80.581(2) deg.
	c = 12.8619(7) A	gamma = 63.553(2) deg.
Volume	1073.65(10) A^3	
Z, Calculated density	2, 1.211 Mg/m^3	
Absorption coefficient	0.097 mm^-1	
F(000)	420	
Crystal size	0.38 x 0.19 x 0.17 mm	
Theta range for data collection	1.61 to 25.00 deg.	
Limiting indices	-11<=h<=10, -12<=k<=12, -15<=l<=14	
Reflections collected / unique	12281 / 3749 [R(int) = 0.0298]	
Completeness to theta = 25.00	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9837 and 0.9641	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3749 / 0 / 248	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.0952	
R indices (all data)	R1 = 0.0599, wR2 = 0.1107	
Largest diff. peak and hole	0.185 and -0.172 e.A^-3	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for z.

U(eq) is defined as one third of the trace of the orthogonalized

Uij tensor.

	x	y	z	U(eq)
O(1)	10090(2)	-1430(2)	3754(1)	61(1)
O(2)	11010(2)	124(2)	3985(1)	52(1)
O(3)	10809(2)	652(2)	1753(1)	43(1)
O(4)	8203(2)	2049(1)	1528(1)	36(1)
O(5)	6219(2)	-727(1)	2674(1)	36(1)
O(6)	8626(2)	-933(2)	1760(1)	40(1)
O(7)	3584(2)	1794(1)	4800(1)	43(1)
O(8)	4464(1)	2744(1)	3339(1)	34(1)
N(1)	10041(2)	-217(2)	3686(1)	40(1)
N(2)	7355(2)	572(2)	3199(1)	29(1)
N(3)	6245(2)	841(2)	4126(1)	29(1)
C(1)	9382(2)	1164(2)	2054(1)	32(1)
C(2)	8617(2)	1011(2)	3188(1)	30(1)
C(3)	7501(2)	-447(2)	2469(1)	31(1)
C(4)	8049(2)	2423(2)	3808(2)	36(1)
C(5)	8694(2)	2231(2)	401(1)	38(1)
C(6)	7342(3)	2327(3)	-141(2)	55(1)
C(7)	8986(3)	3570(3)	286(2)	55(1)
C(8)	6208(2)	-1989(2)	2163(2)	39(1)
C(9)	6230(3)	-1748(3)	986(2)	57(1)
C(10)	4605(3)	-1936(3)	2691(2)	57(1)
C(11)	7631(3)	-3375(2)	2437(2)	49(1)
C(12)	4644(2)	1805(2)	4120(1)	29(1)
C(13)	2831(2)	3908(2)	3213(2)	46(1)

C(14)	1786(3)	3209(4)	3005(3)	101(1)
C(15)	2166(5)	4918(3)	4156(3)	115(1)
C(16)	3204(3)	4690(3)	2258(2)	74(1)

Table 3. Bond lengths [A] and angles [deg] for z.

O(1)-N(1)	1.214(2)
O(2)-N(1)	1.218(2)
O(3)-C(1)	1.191(2)
O(4)-C(1)	1.328(2)
O(4)-C(5)	1.473(2)
O(5)-C(3)	1.327(2)
O(5)-C(8)	1.481(2)
O(6)-C(3)	1.203(2)
O(7)-C(12)	1.209(2)
O(8)-C(12)	1.323(2)
O(8)-C(13)	1.478(2)
N(1)-C(2)	1.561(2)
N(2)-C(3)	1.386(2)
N(2)-N(3)	1.3938(19)
N(2)-C(2)	1.426(2)
N(3)-C(12)	1.371(2)
N(3)-H(3A)	0.86(2)
C(1)-C(2)	1.545(2)
C(2)-C(4)	1.517(3)
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-C(6)	1.497(3)

C(5)-C(7)	1.499(3)
C(5)-H(5A)	1.0000
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-C(10)	1.510(3)
C(8)-C(11)	1.515(3)
C(8)-C(9)	1.518(3)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(13)-C(14)	1.497(3)
C(13)-C(15)	1.498(4)
C(13)-C(16)	1.502(3)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800

C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(1)-O(4)-C(5)	116.36(14)
C(3)-O(5)-C(8)	120.82(14)
C(12)-O(8)-C(13)	120.43(14)
O(1)-N(1)-O(2)	125.18(17)
O(1)-N(1)-C(2)	117.62(16)
O(2)-N(1)-C(2)	117.19(17)
C(3)-N(2)-N(3)	119.53(14)
C(3)-N(2)-C(2)	120.65(14)
N(3)-N(2)-C(2)	117.06(14)
C(12)-N(3)-N(2)	119.39(14)
C(12)-N(3)-H(3A)	113.0(13)
N(2)-N(3)-H(3A)	113.5(13)
O(3)-C(1)-O(4)	126.94(17)
O(3)-C(1)-C(2)	124.05(16)
O(4)-C(1)-C(2)	108.76(14)
N(2)-C(2)-C(4)	112.59(14)
N(2)-C(2)-C(1)	112.05(15)
C(4)-C(2)-C(1)	109.70(15)
N(2)-C(2)-N(1)	109.18(14)
C(4)-C(2)-N(1)	107.94(15)
C(1)-C(2)-N(1)	105.01(13)
O(6)-C(3)-O(5)	128.02(18)
O(6)-C(3)-N(2)	122.66(16)
O(5)-C(3)-N(2)	109.30(15)
C(2)-C(4)-H(4A)	109.5
C(2)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
C(2)-C(4)-H(4C)	109.5

H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
O(4)-C(5)-C(6)	105.83(15)
O(4)-C(5)-C(7)	108.45(16)
C(6)-C(5)-C(7)	113.99(19)
O(4)-C(5)-H(5A)	109.5
C(6)-C(5)-H(5A)	109.5
C(7)-C(5)-H(5A)	109.5
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(5)-C(7)-H(7A)	109.5
C(5)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(5)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
O(5)-C(8)-C(10)	101.85(16)
O(5)-C(8)-C(11)	108.25(16)
C(10)-C(8)-C(11)	111.26(18)
O(5)-C(8)-C(9)	110.04(16)
C(10)-C(8)-C(9)	111.23(18)
C(11)-C(8)-C(9)	113.53(18)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5

H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(7)-C(12)-O(8)	126.71(16)
O(7)-C(12)-N(3)	121.28(16)
O(8)-C(12)-N(3)	111.90(14)
O(8)-C(13)-C(14)	109.02(18)
O(8)-C(13)-C(15)	109.1(2)
C(14)-C(13)-C(15)	114.6(3)
O(8)-C(13)-C(16)	102.14(16)
C(14)-C(13)-C(16)	111.1(2)
C(15)-C(13)-C(16)	110.0(2)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5

C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(13)-C(16)-H(16A)	109.5
C(13)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for z.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	75(1)	39(1)	60(1)	7(1)	-29(1)	-12(1)
O(2)	33(1)	82(1)	41(1)	12(1)	-12(1)	-25(1)
O(3)	28(1)	63(1)	35(1)	3(1)	1(1)	-21(1)
O(4)	34(1)	46(1)	26(1)	7(1)	-4(1)	-16(1)
O(5)	29(1)	38(1)	43(1)	-8(1)	1(1)	-17(1)
O(6)	36(1)	50(1)	32(1)	-9(1)	6(1)	-21(1)
O(7)	31(1)	37(1)	46(1)	11(1)	9(1)	-7(1)
O(8)	30(1)	36(1)	37(1)	13(1)	-8(1)	-16(1)
N(1)	34(1)	48(1)	27(1)	3(1)	-3(1)	-10(1)
N(2)	27(1)	34(1)	25(1)	-2(1)	4(1)	-15(1)

N(3)	27(1)	30(1)	25(1)	4(1)	2(1)	-10(1)
C(1)	30(1)	41(1)	29(1)	2(1)	-3(1)	-19(1)
C(2)	24(1)	36(1)	27(1)	4(1)	-5(1)	-12(1)
C(3)	28(1)	34(1)	30(1)	1(1)	-2(1)	-13(1)
C(4)	34(1)	43(1)	35(1)	-2(1)	-3(1)	-21(1)
C(5)	47(1)	43(1)	24(1)	4(1)	-1(1)	-21(1)
C(6)	66(2)	69(2)	37(1)	9(1)	-17(1)	-34(1)
C(7)	80(2)	56(1)	39(1)	7(1)	-2(1)	-41(1)
C(8)	40(1)	38(1)	44(1)	-7(1)	-8(1)	-19(1)
C(9)	63(2)	65(2)	50(1)	0(1)	-22(1)	-31(1)
C(10)	47(1)	60(2)	74(2)	-8(1)	-5(1)	-34(1)
C(11)	51(1)	40(1)	52(1)	-2(1)	-9(1)	-16(1)
C(12)	30(1)	27(1)	28(1)	2(1)	-1(1)	-13(1)
C(13)	35(1)	35(1)	61(1)	18(1)	-13(1)	-10(1)
C(14)	63(2)	95(2)	176(4)	73(2)	-75(2)	-50(2)
C(15)	138(3)	44(2)	84(2)	-1(2)	-2(2)	24(2)
C(16)	63(2)	74(2)	86(2)	51(2)	-33(2)	-31(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for z.

	x	y	z	U(eq)
H(3A)	6370(20)	60(20)	4476(16)	35(5)
H(4A)	7151	3213	3509	54
H(4B)	8953	2684	3768	54
H(4C)	7676	2287	4546	54
H(5A)	9720	1350	128	46
H(6A)	7232	1412	-42	82
H(6B)	7588	2480	-896	82

H(6C)	6322	3150	159	82
H(7A)	9896	3423	648	83
H(7B)	8005	4422	599	83
H(7C)	9250	3741	-463	83
H(9A)	7284	-1794	665	85
H(9B)	5359	-783	863	85
H(9C)	6062	-2513	671	85
H(10A)	4630	-2105	3447	85
H(10B)	4426	-2699	2381	85
H(10C)	3720	-971	2586	85
H(11A)	8652	-3381	2082	74
H(11B)	7544	-4233	2205	74
H(11C)	7617	-3406	3202	74
H(14A)	2304	2570	2378	152
H(14B)	717	3974	2889	152
H(14C)	1651	2626	3614	152
H(15A)	1918	4402	4774	172
H(15B)	1170	5777	4027	172
H(15C)	2975	5236	4284	172
H(16A)	3639	4022	1645	111
H(16B)	4012	5014	2379	111
H(16C)	2205	5544	2127	111

Table 6. Torsion angles [deg] for z.

C(3)-N(2)-N(3)-C(12)	-83.2(2)
C(2)-N(2)-N(3)-C(12)	115.46(18)
C(5)-O(4)-C(1)-O(3)	10.3(3)
C(5)-O(4)-C(1)-C(2)	-175.30(14)
C(3)-N(2)-C(2)-C(4)	162.95(15)
N(3)-N(2)-C(2)-C(4)	-36.0(2)
C(3)-N(2)-C(2)-C(1)	38.7(2)
N(3)-N(2)-C(2)-C(1)	-160.21(15)
C(3)-N(2)-C(2)-N(1)	-77.18(19)
N(3)-N(2)-C(2)-N(1)	83.89(18)
O(3)-C(1)-C(2)-N(2)	-132.13(19)
O(4)-C(1)-C(2)-N(2)	53.3(2)
O(3)-C(1)-C(2)-C(4)	102.1(2)
O(4)-C(1)-C(2)-C(4)	-72.53(18)
O(3)-C(1)-C(2)-N(1)	-13.7(2)
O(4)-C(1)-C(2)-N(1)	171.70(15)
O(1)-N(1)-C(2)-N(2)	17.9(2)
O(2)-N(1)-C(2)-N(2)	-161.52(15)
O(1)-N(1)-C(2)-C(4)	140.58(17)
O(2)-N(1)-C(2)-C(4)	-38.8(2)
O(1)-N(1)-C(2)-C(1)	-102.44(18)
O(2)-N(1)-C(2)-C(1)	78.16(19)
C(8)-O(5)-C(3)-O(6)	14.6(3)
C(8)-O(5)-C(3)-N(2)	-167.33(14)
N(3)-N(2)-C(3)-O(6)	-165.54(16)
C(2)-N(2)-C(3)-O(6)	-4.9(3)
N(3)-N(2)-C(3)-O(5)	16.3(2)
C(2)-N(2)-C(3)-O(5)	176.88(14)

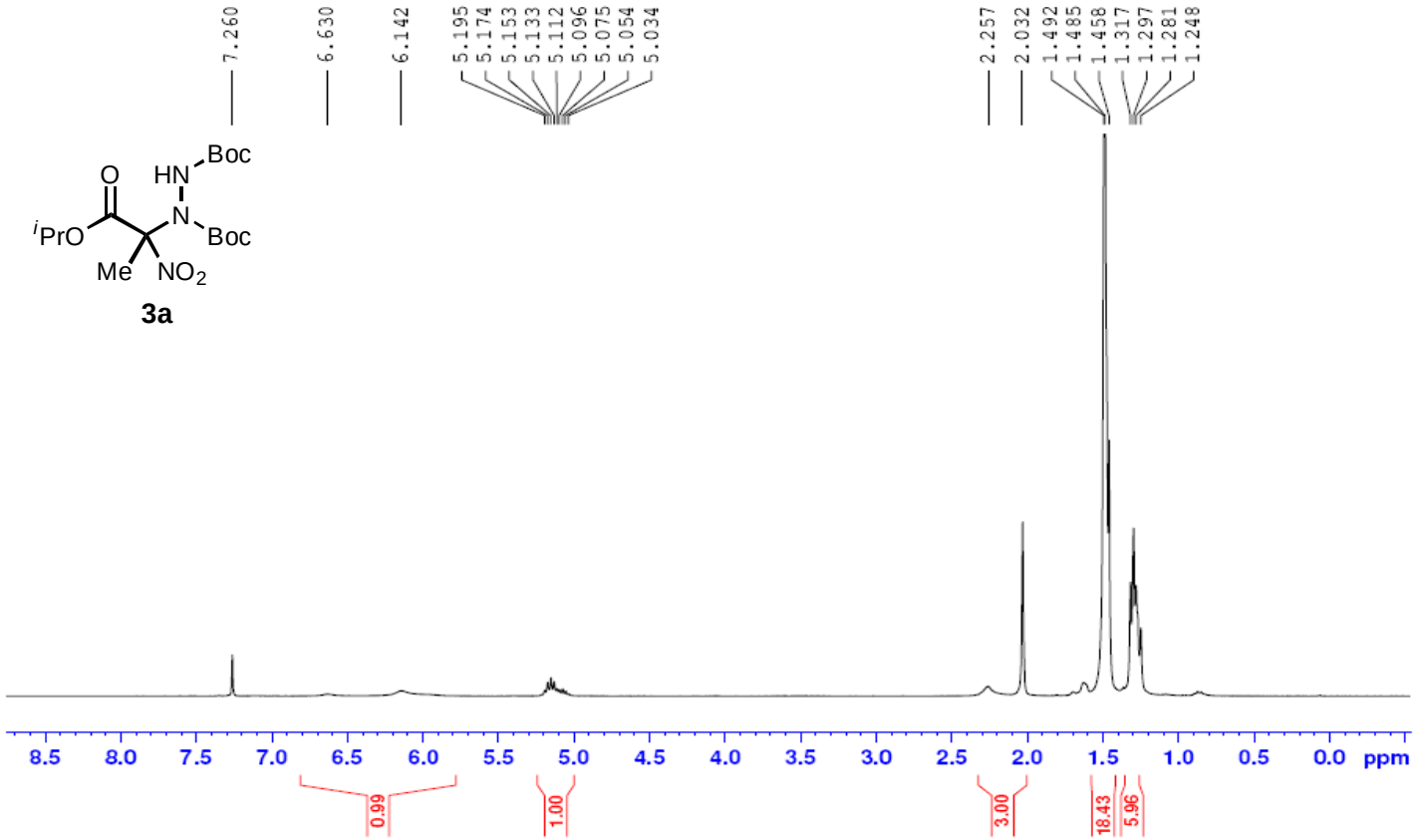
C(1)-O(4)-C(5)-C(6)	142.89(18)
C(1)-O(4)-C(5)-C(7)	-94.4(2)
C(3)-O(5)-C(8)-C(10)	175.68(17)
C(3)-O(5)-C(8)-C(11)	58.3(2)
C(3)-O(5)-C(8)-C(9)	-66.3(2)
C(13)-O(8)-C(12)-O(7)	-1.8(3)
C(13)-O(8)-C(12)-N(3)	-178.07(16)
N(2)-N(3)-C(12)-O(7)	160.63(17)
N(2)-N(3)-C(12)-O(8)	-22.9(2)
C(12)-O(8)-C(13)-C(14)	-62.6(3)
C(12)-O(8)-C(13)-C(15)	63.3(3)
C(12)-O(8)-C(13)-C(16)	179.75(19)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for z [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

^{1}H and ^{13}C NMR spectra



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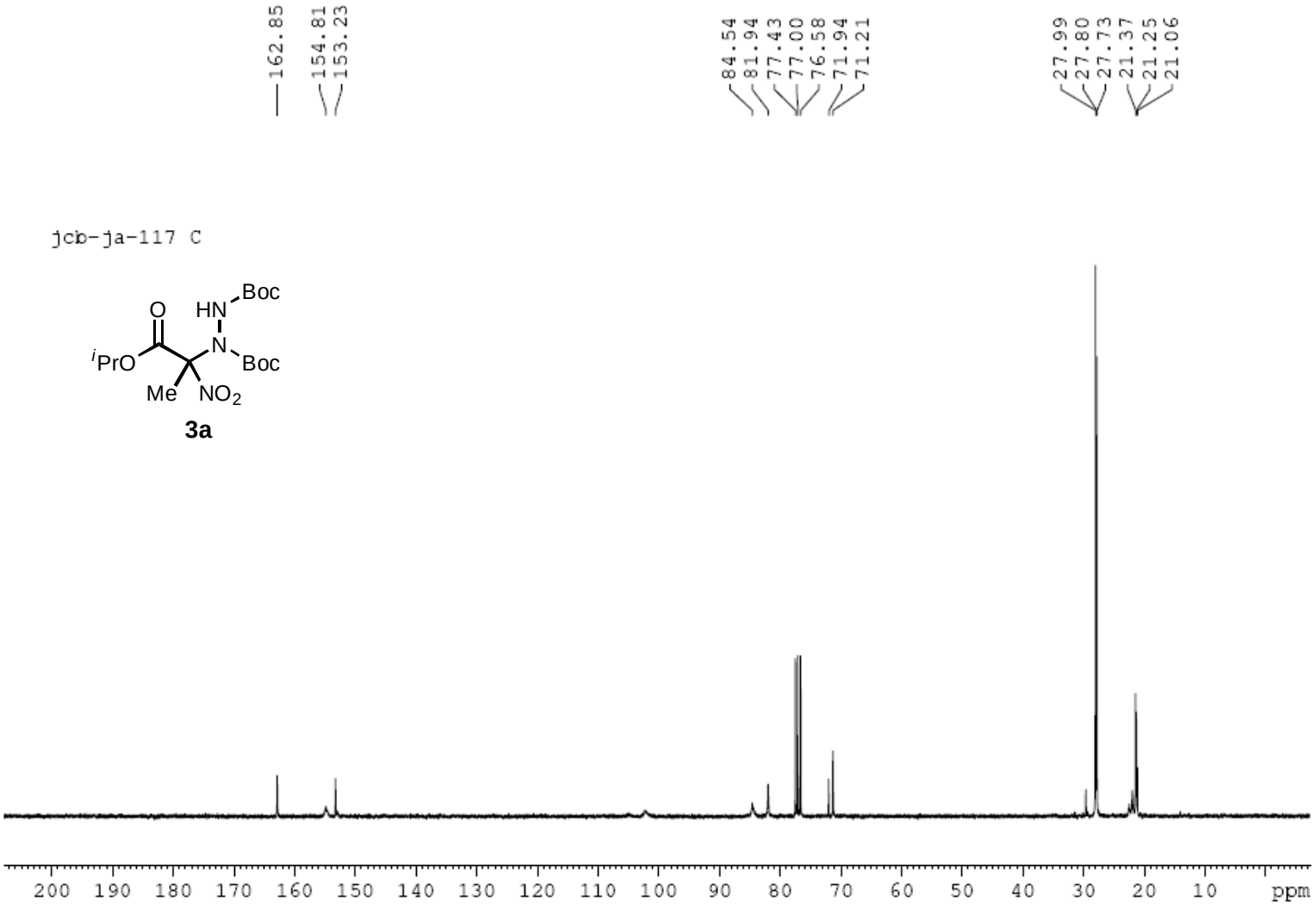

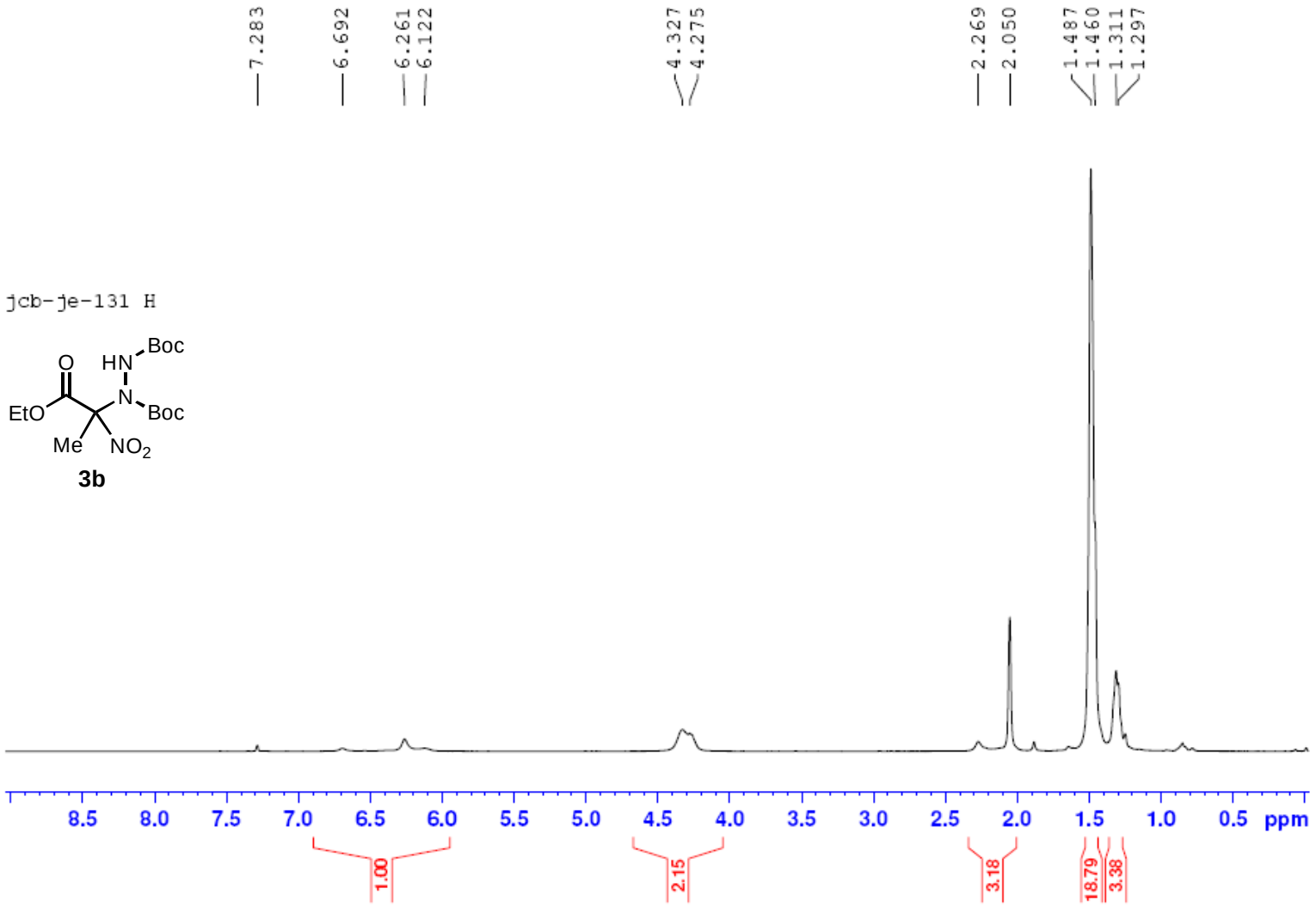

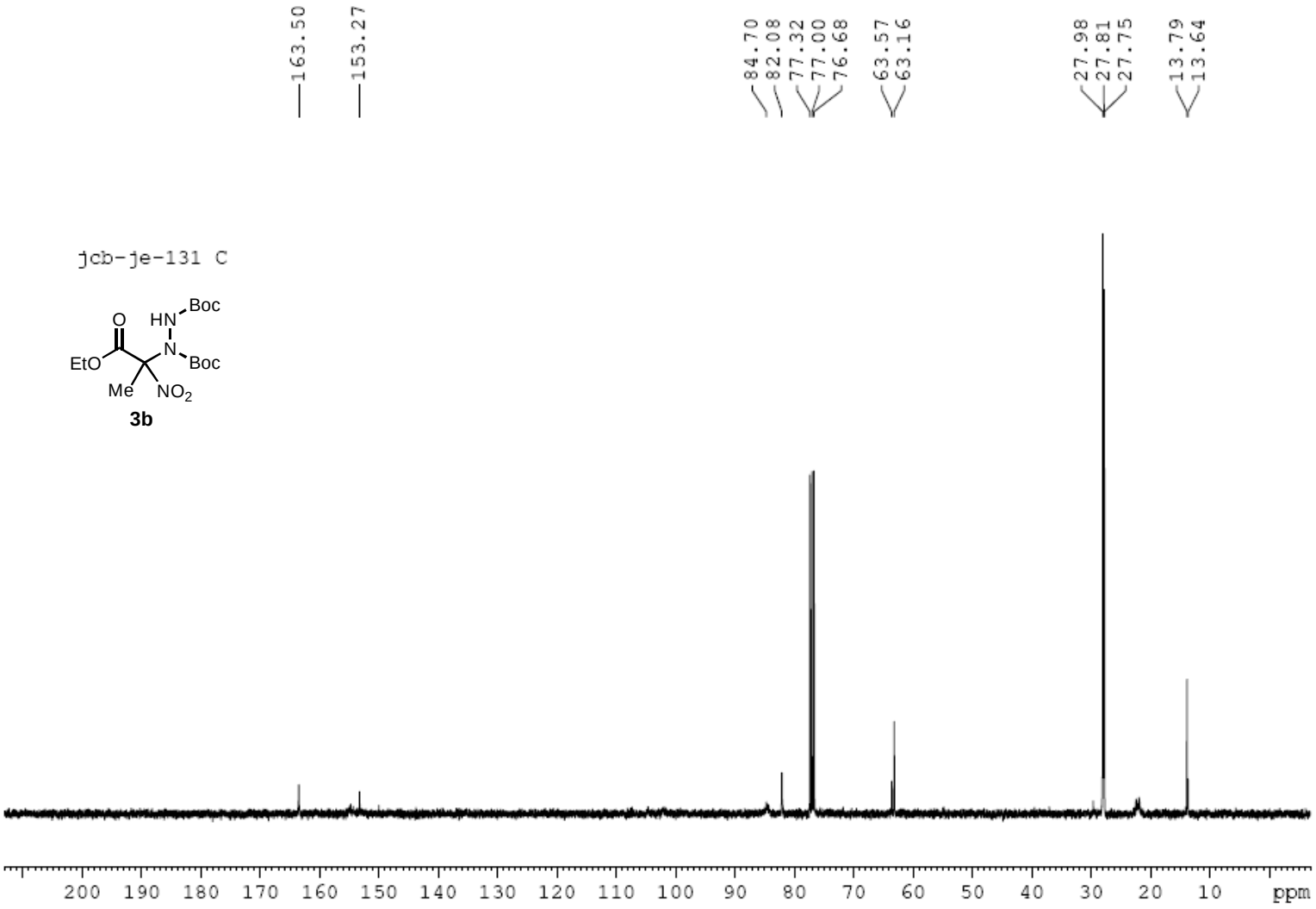

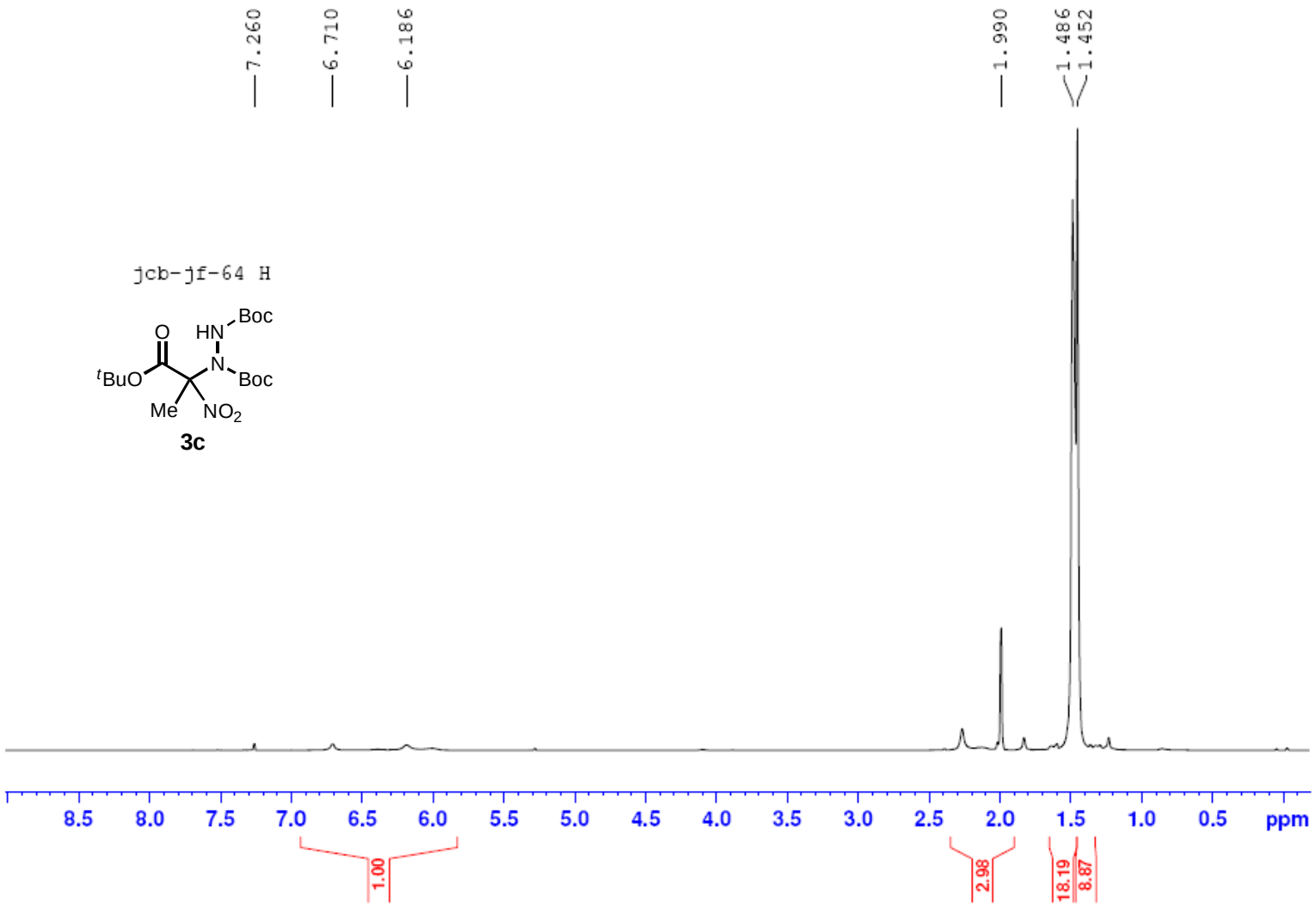

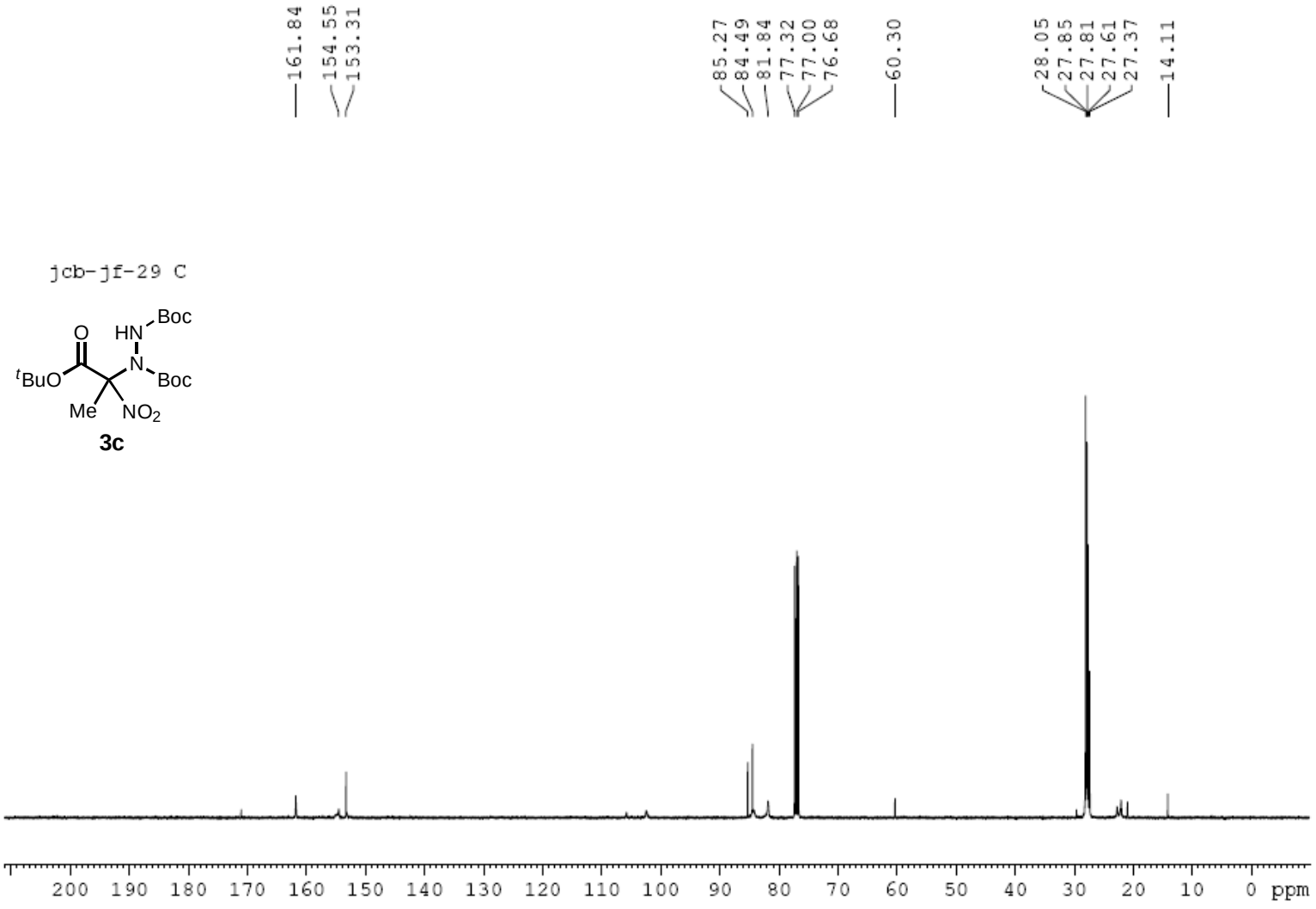

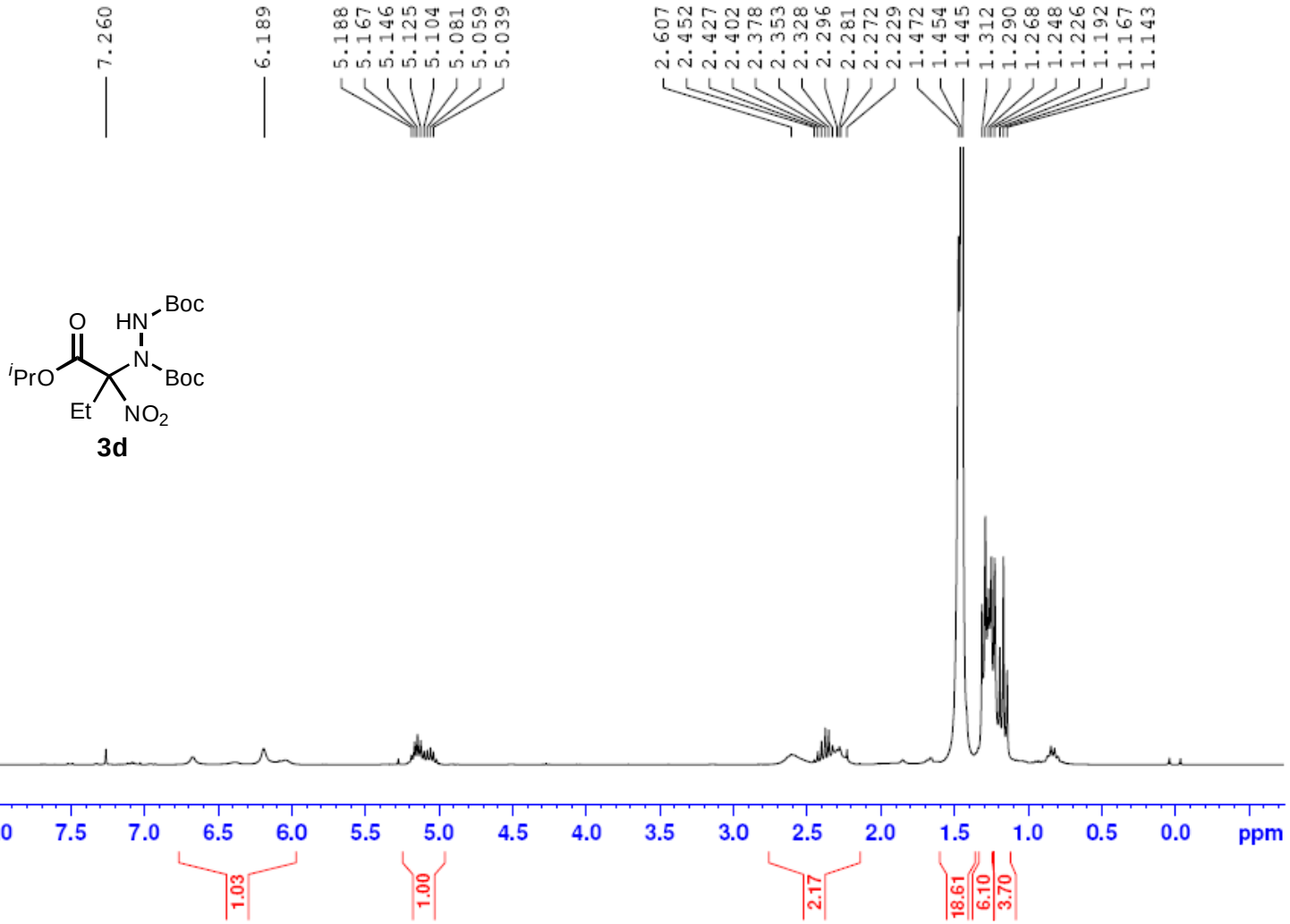

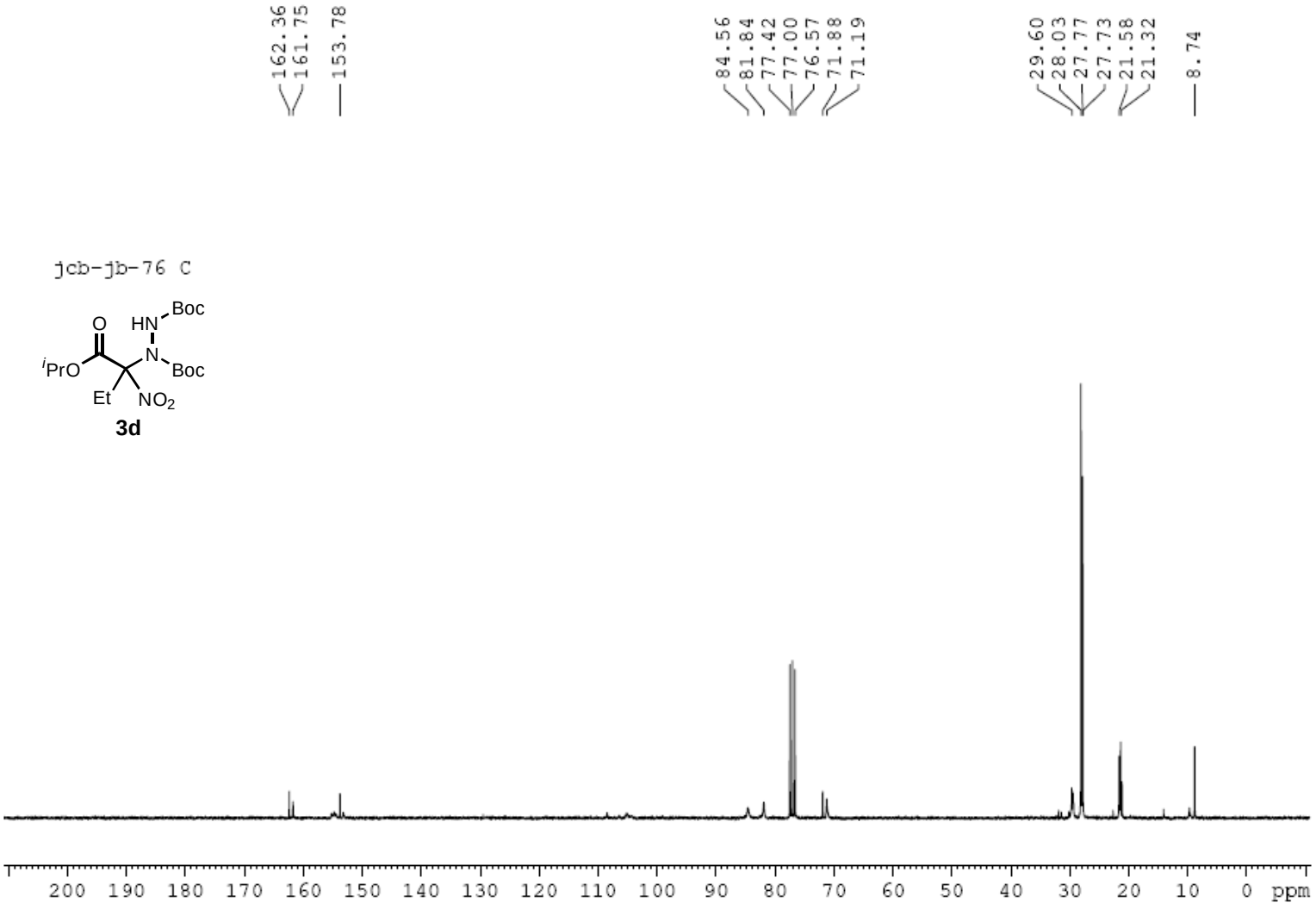

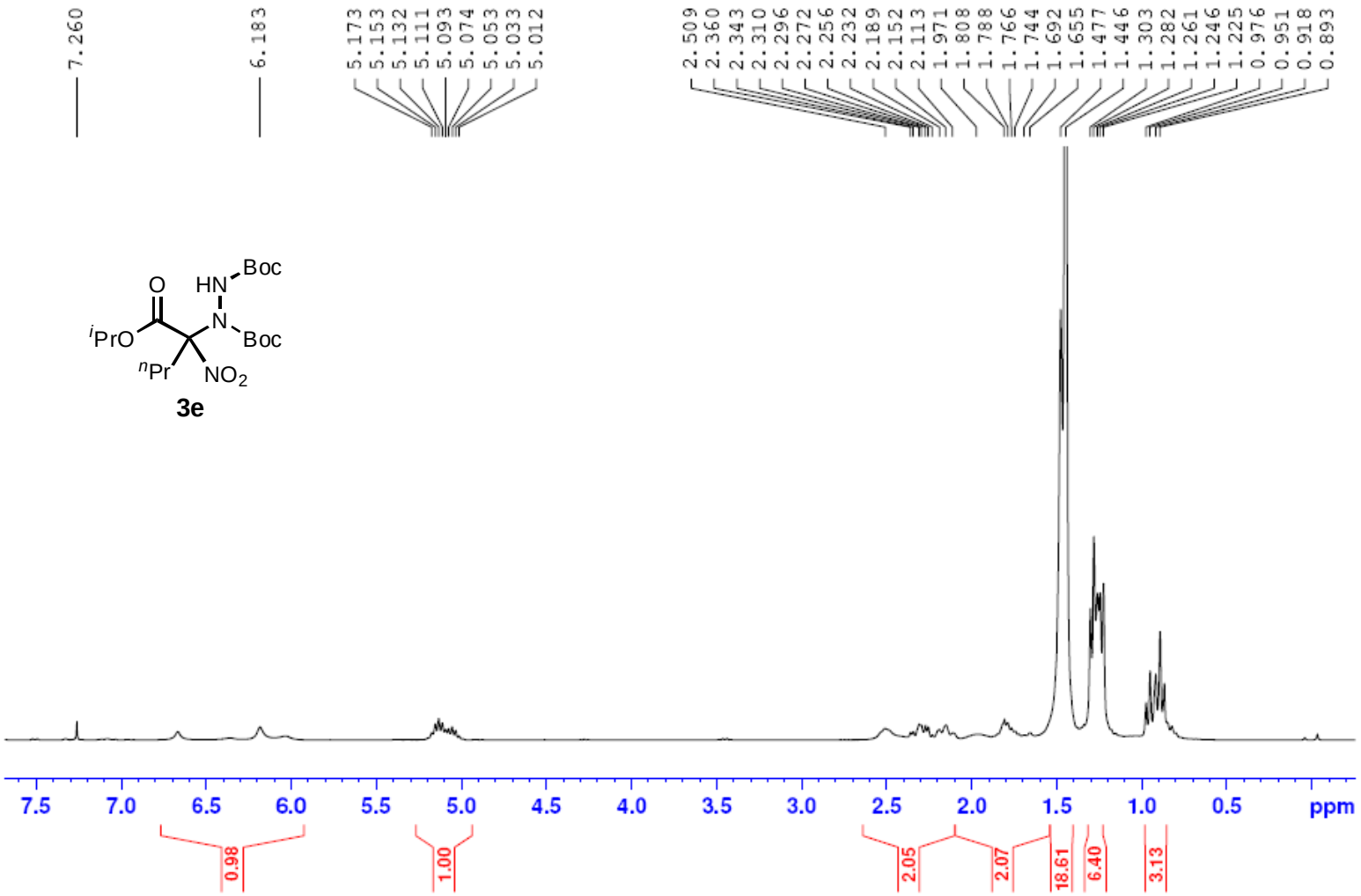

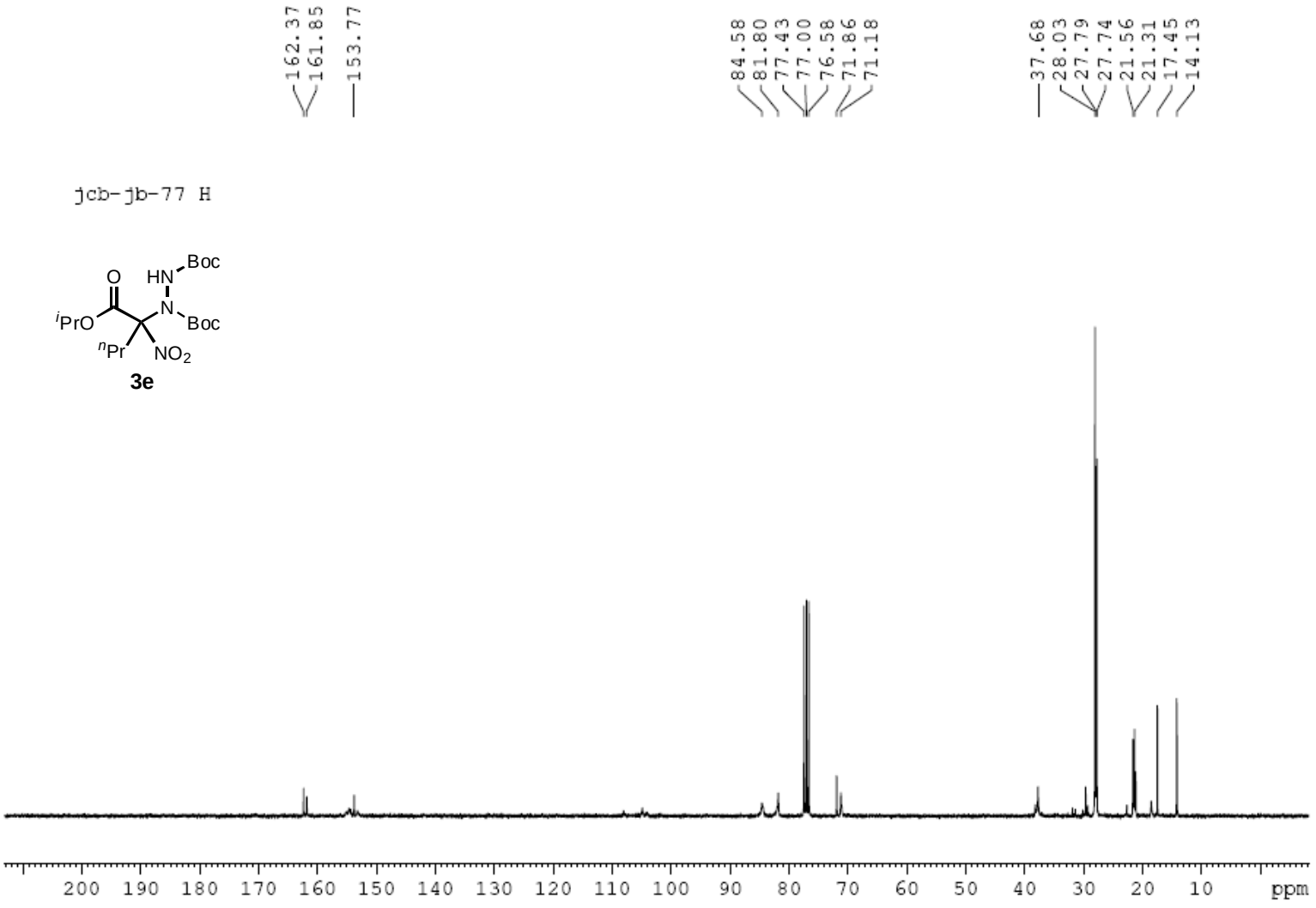

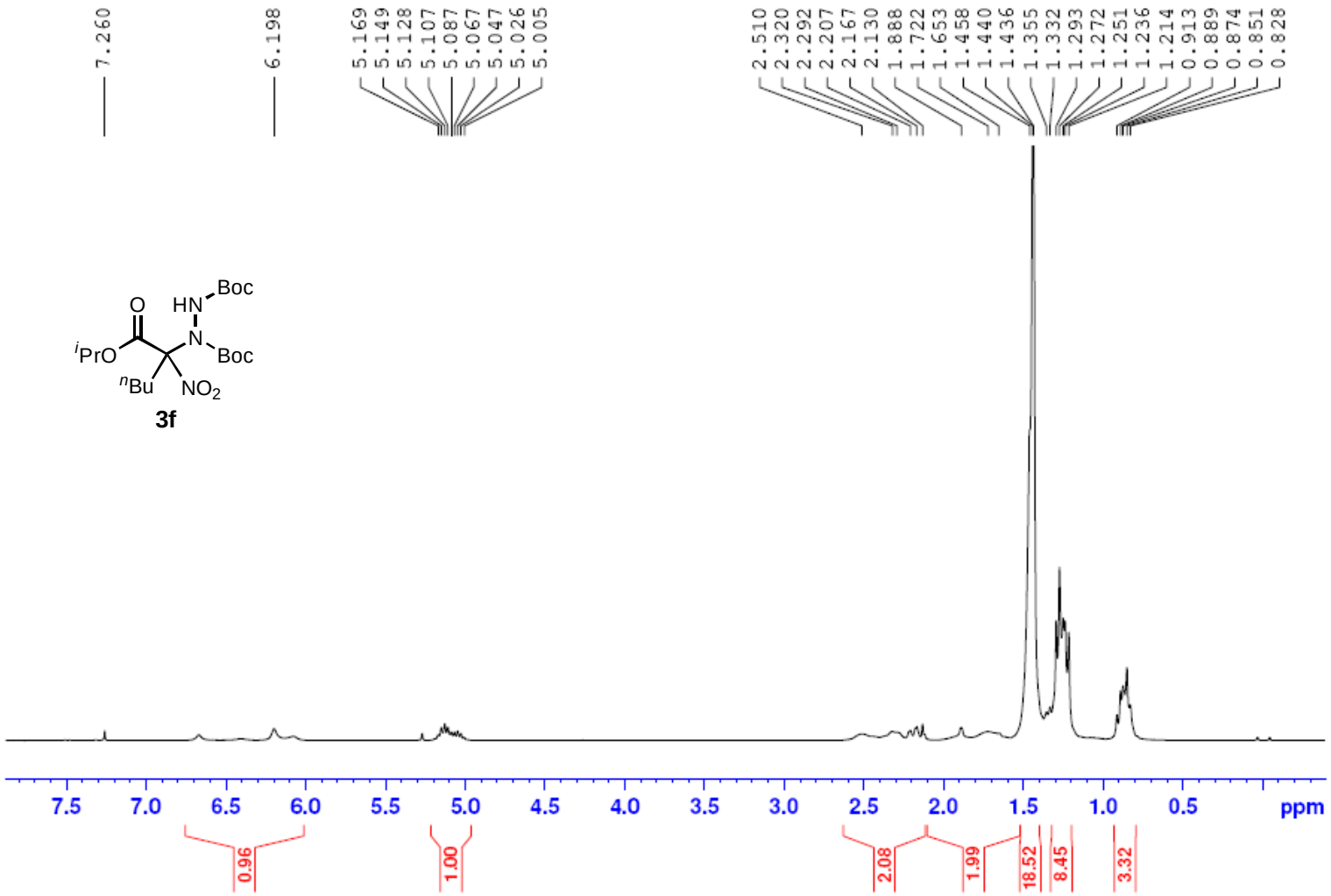

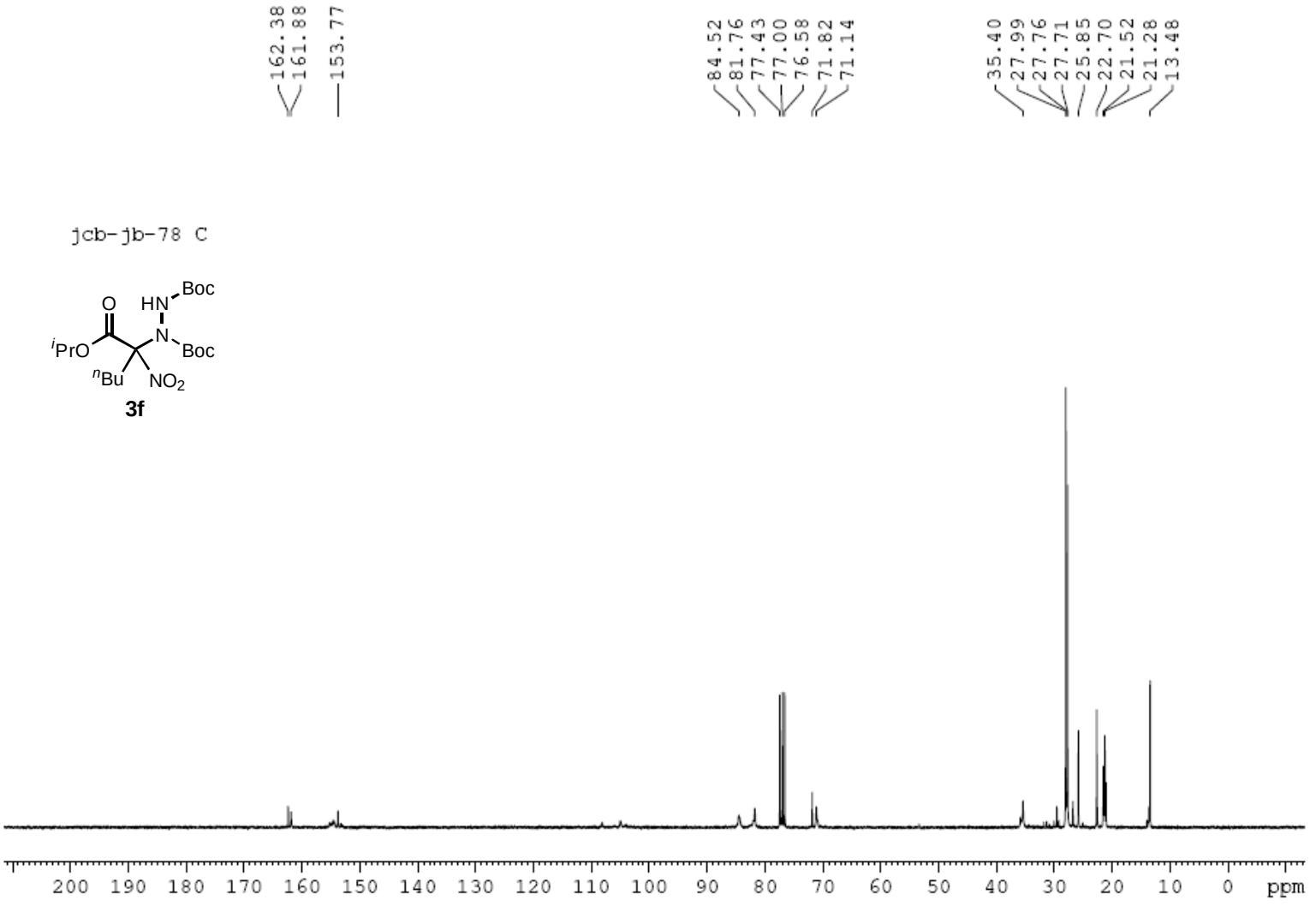

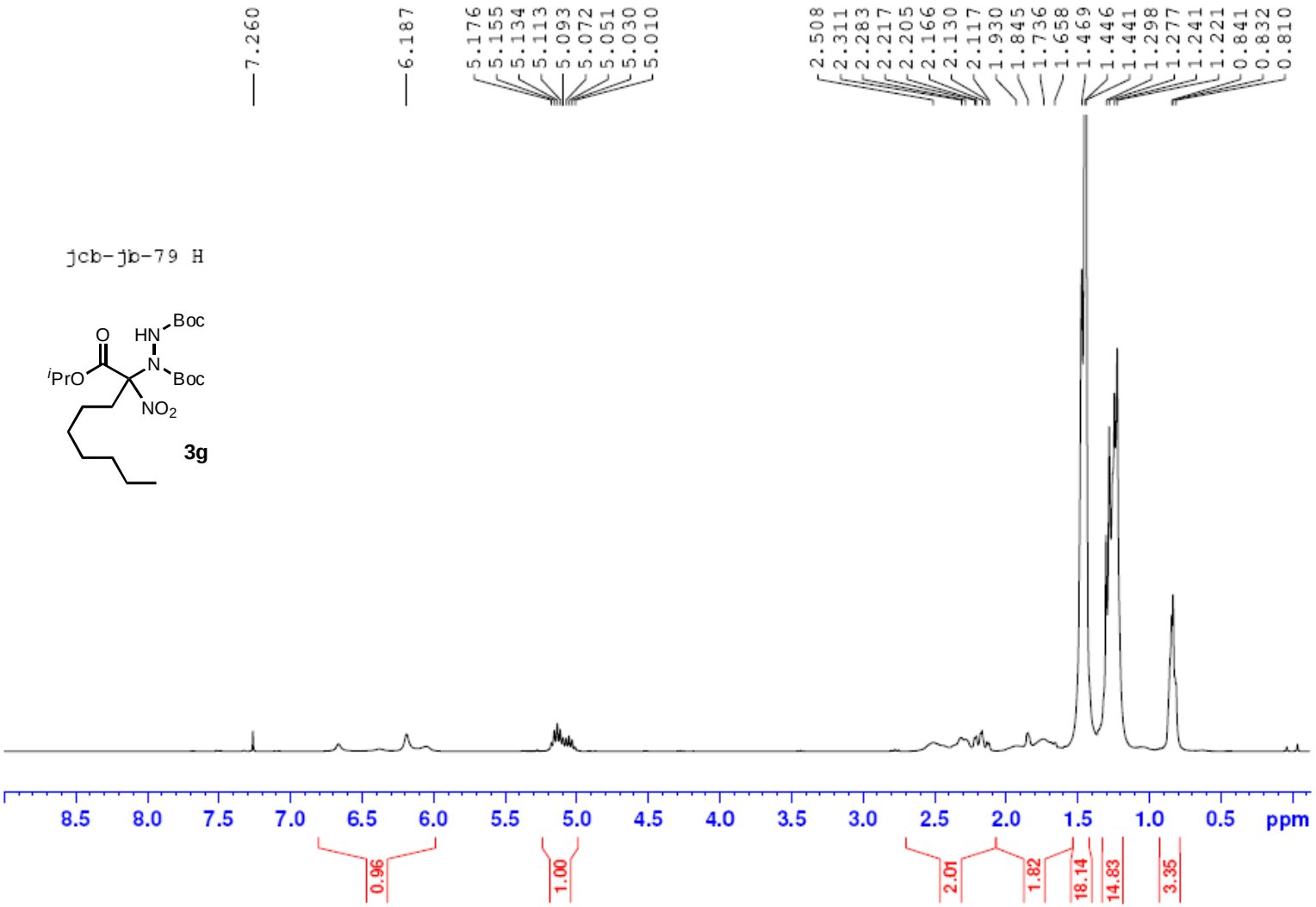

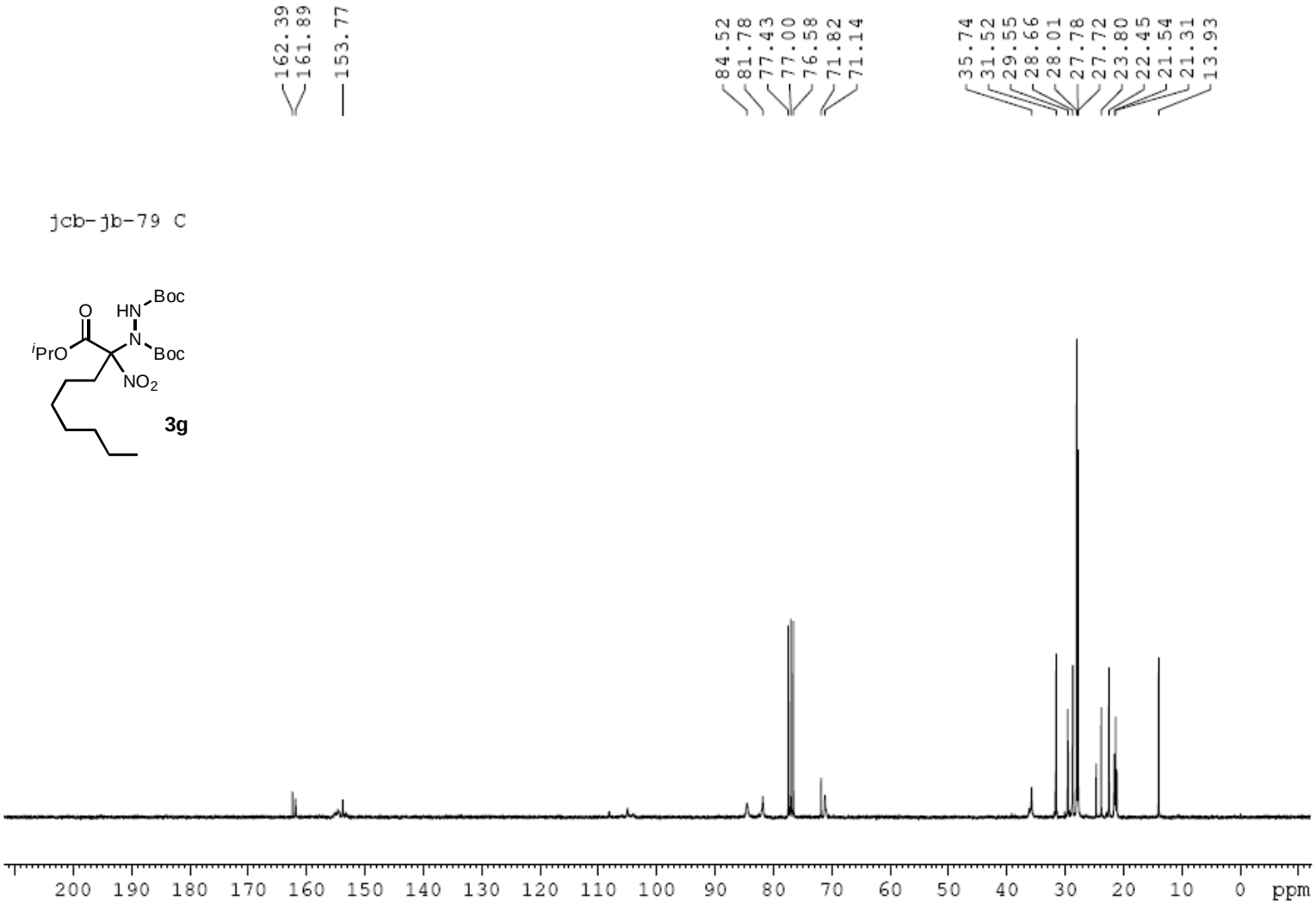

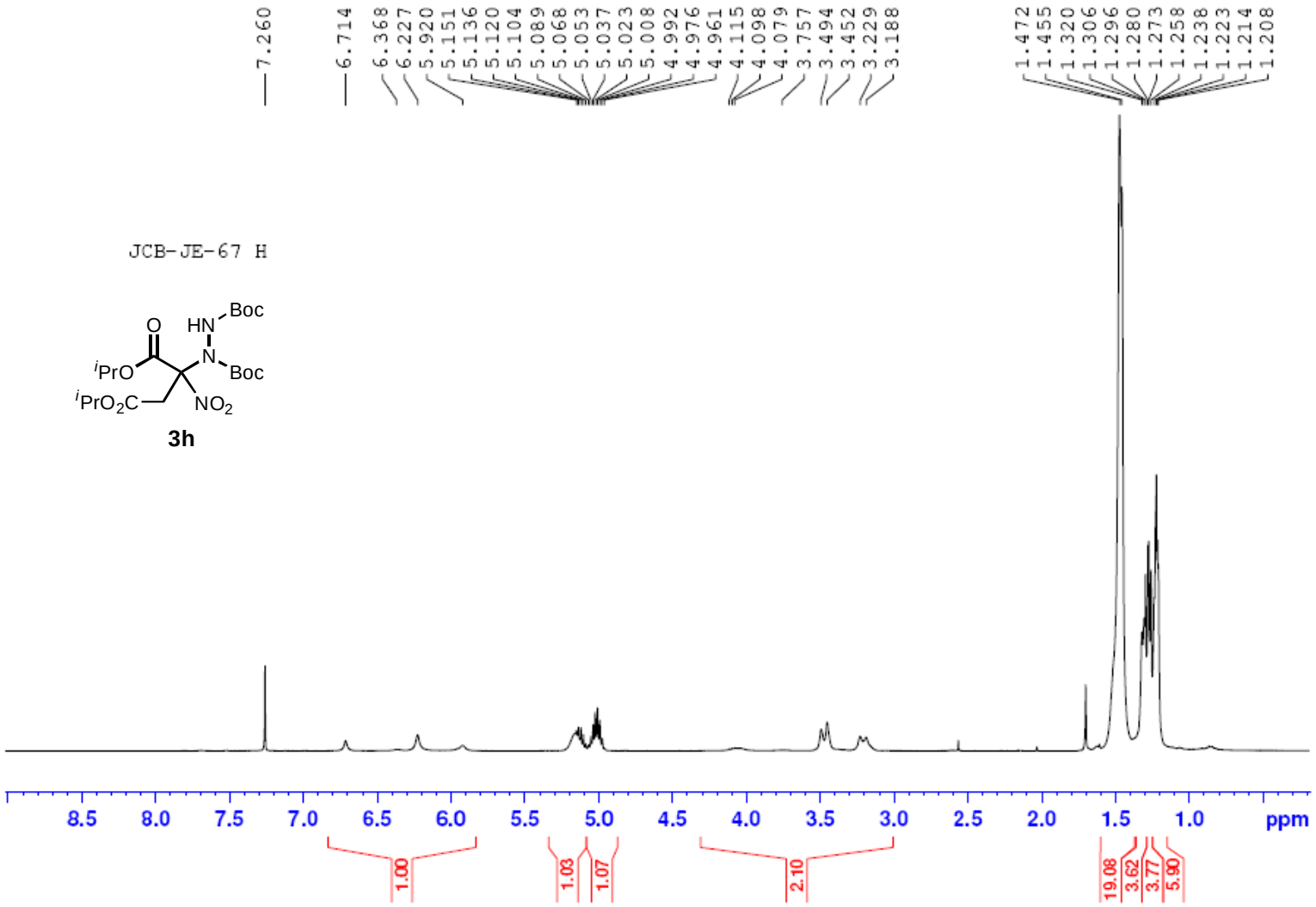

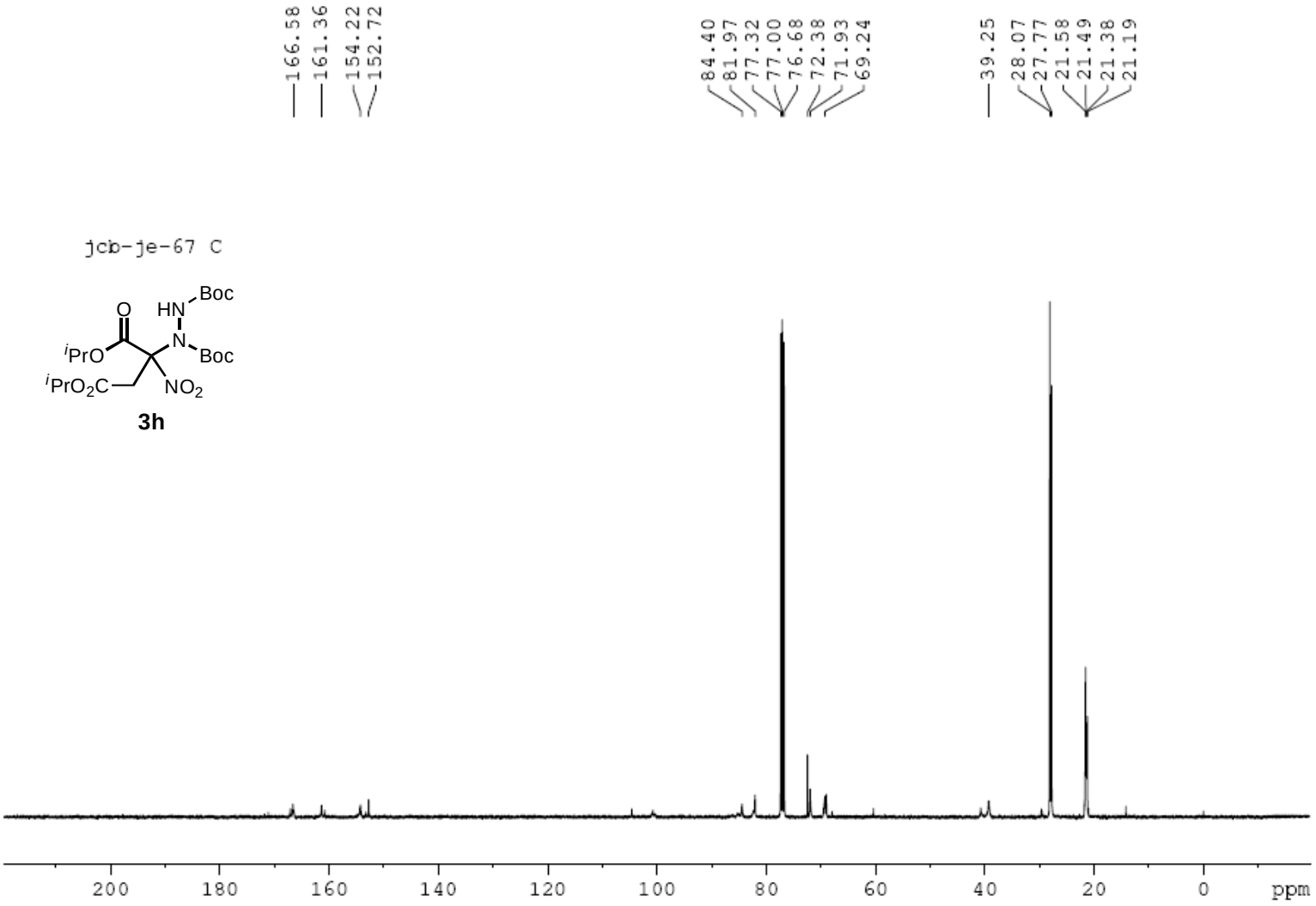

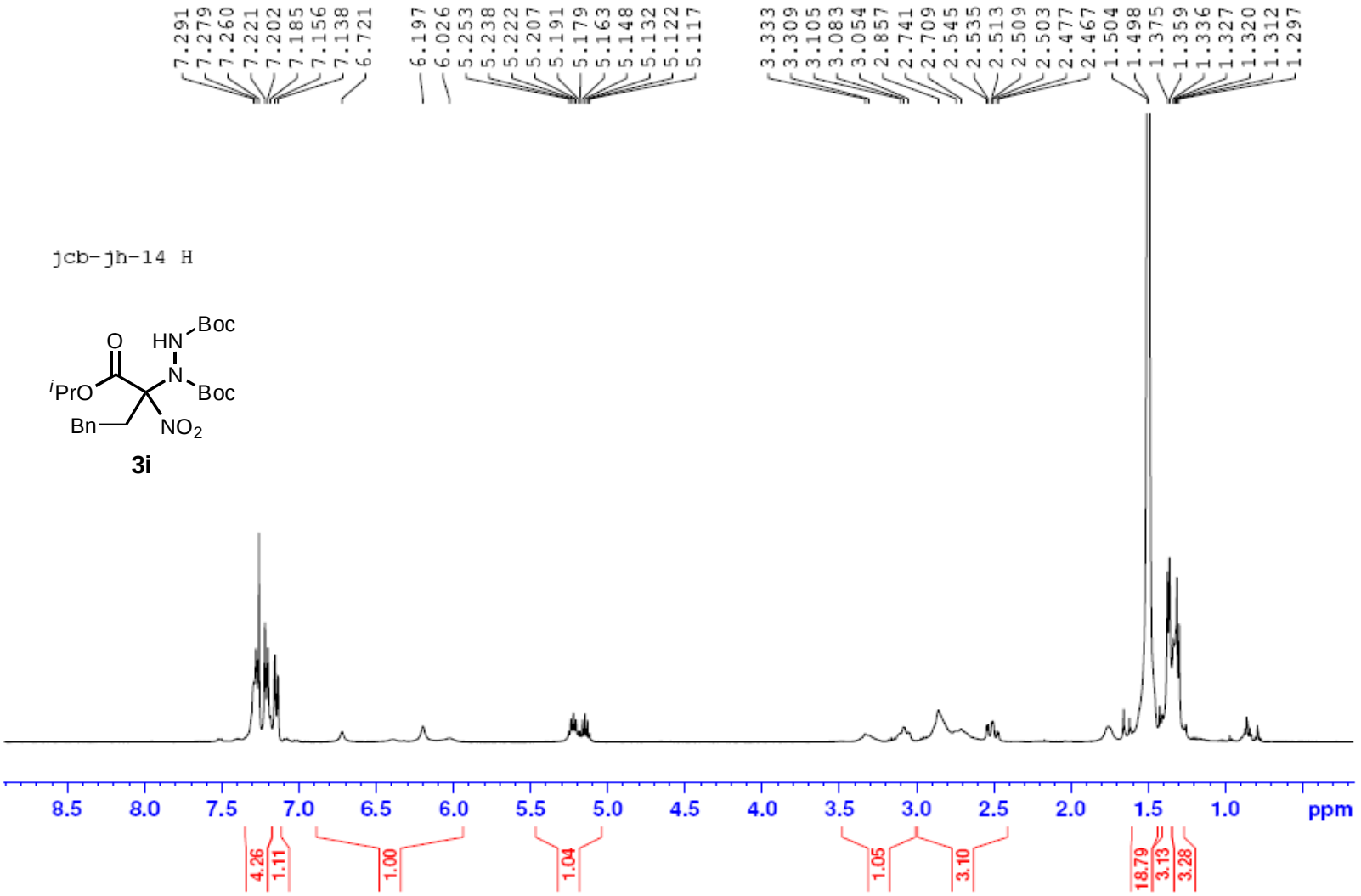

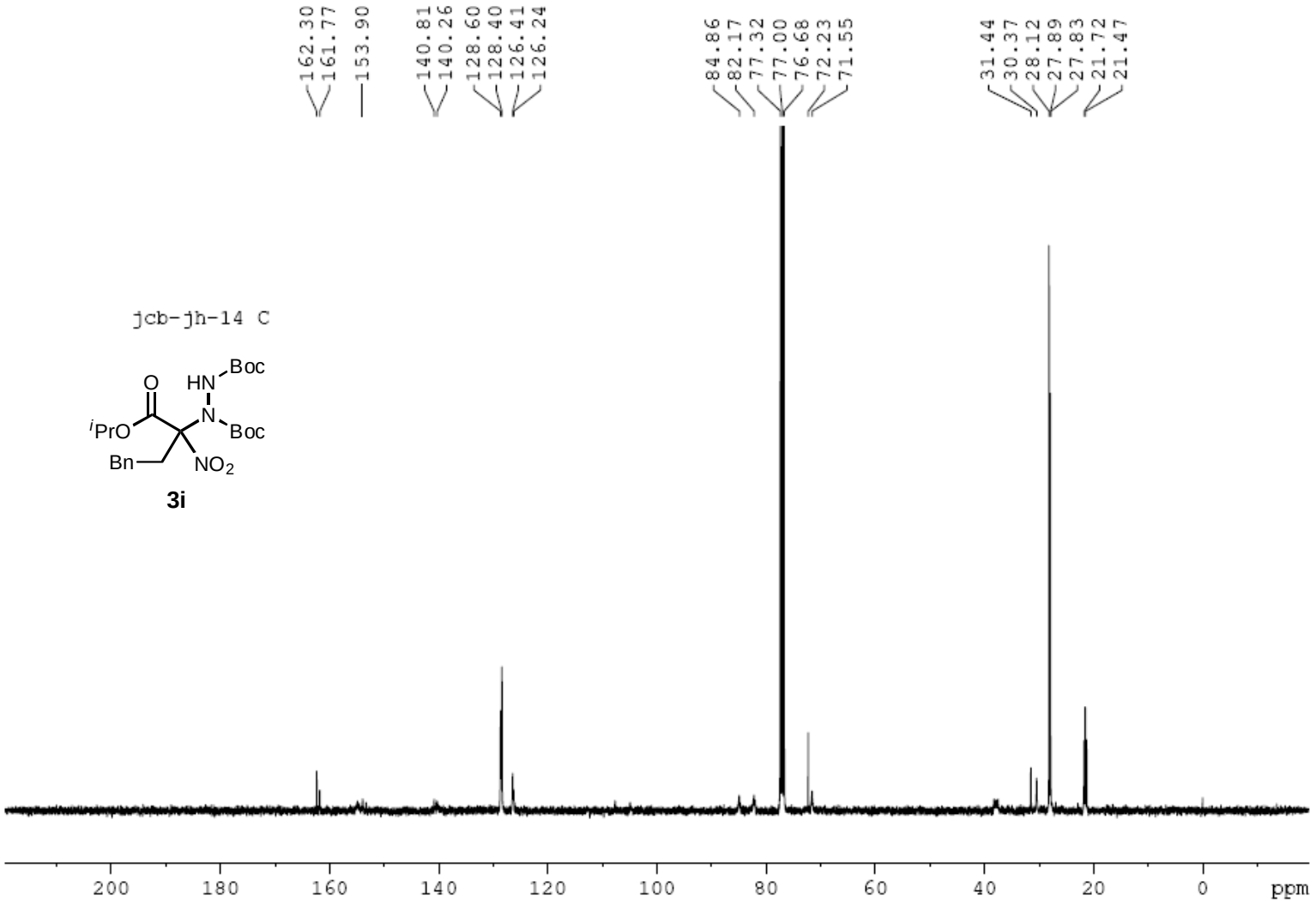

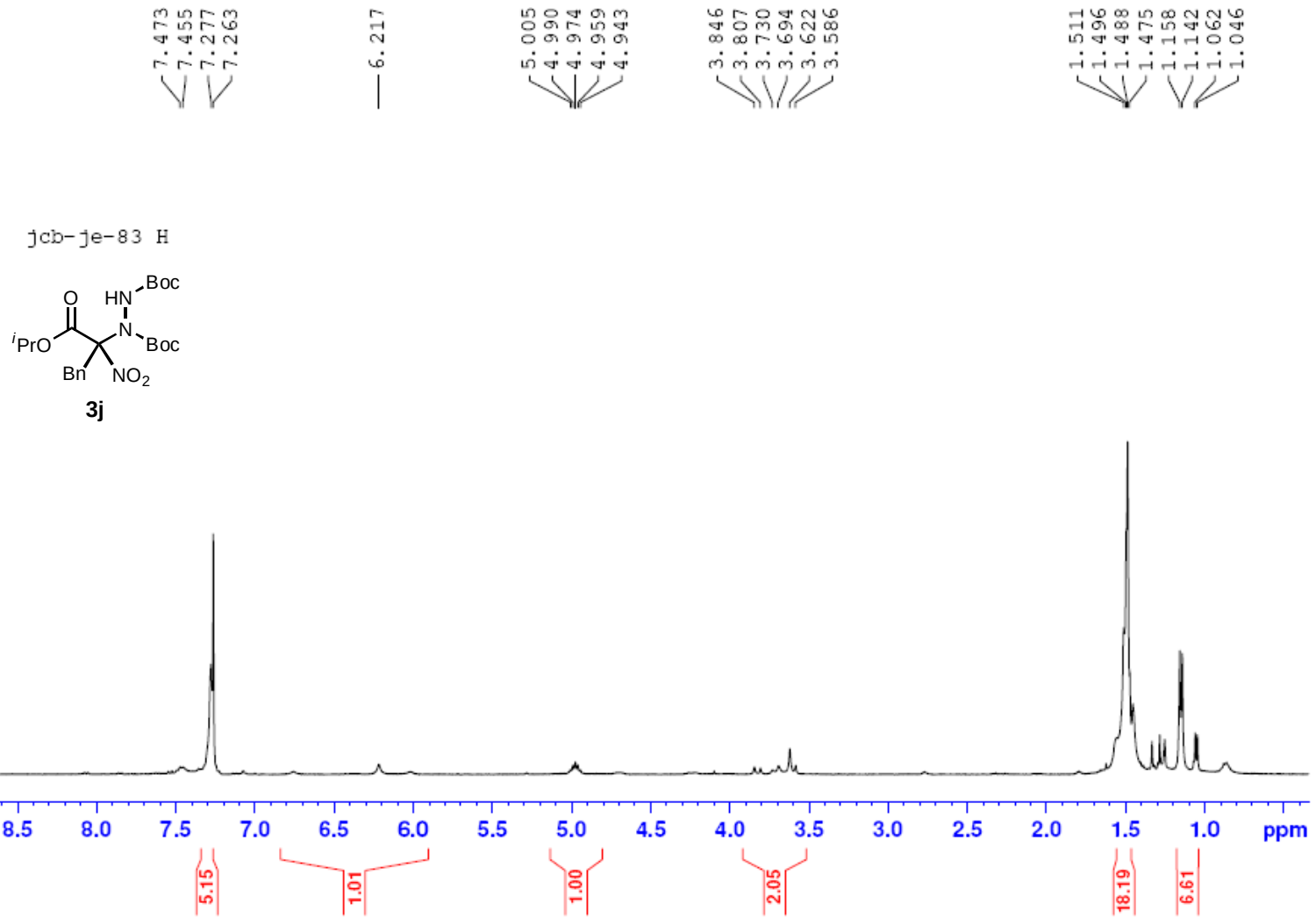

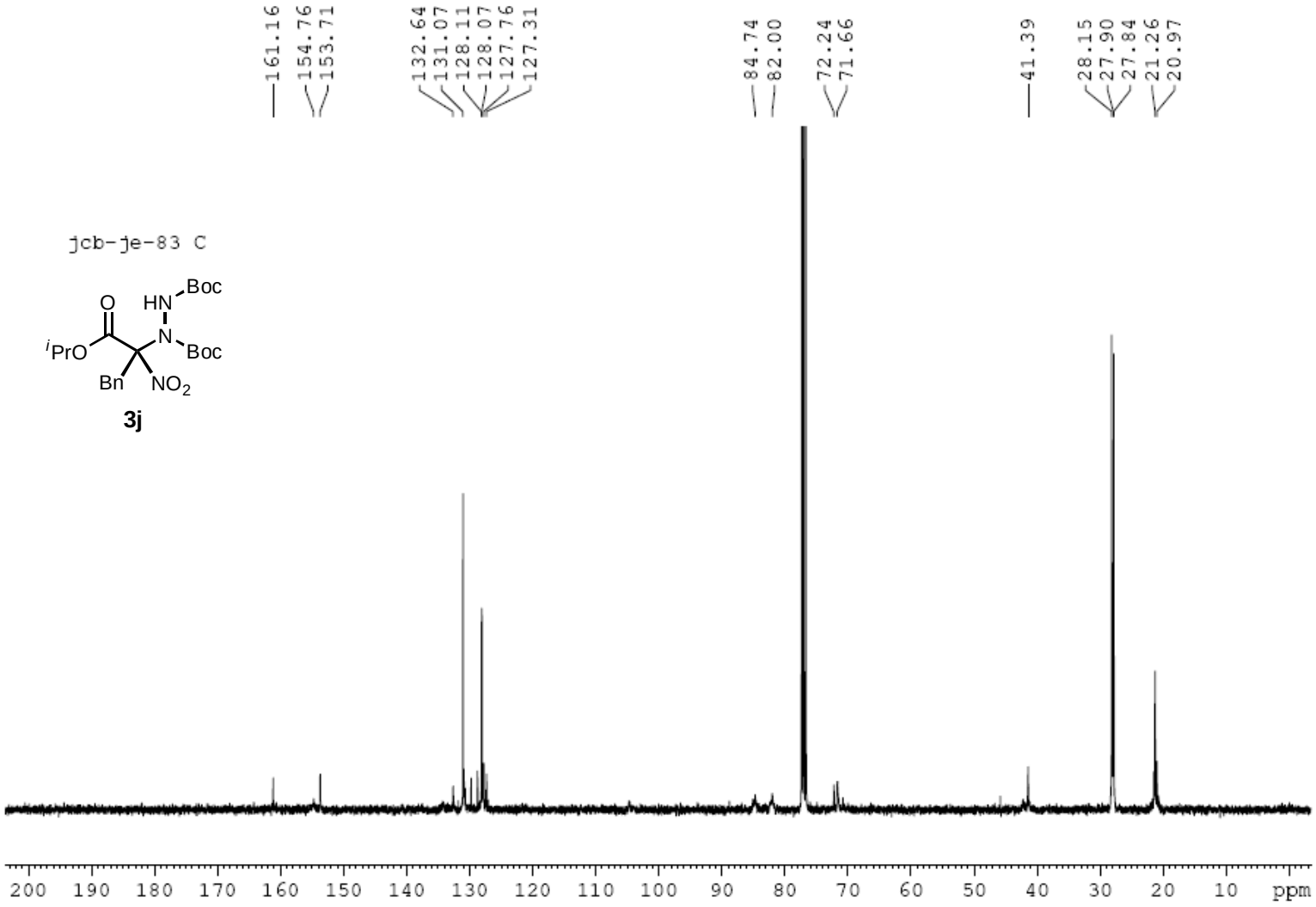

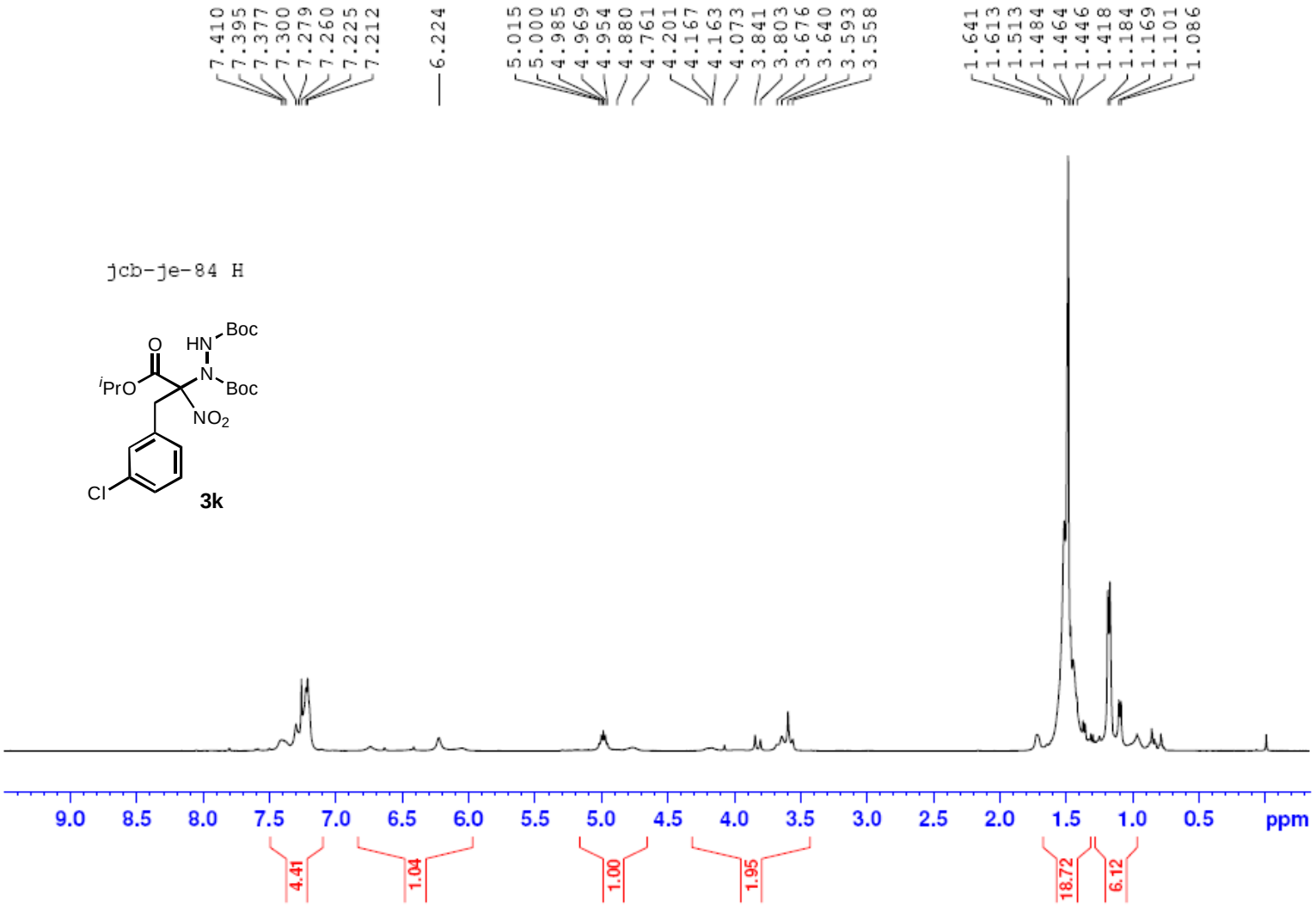

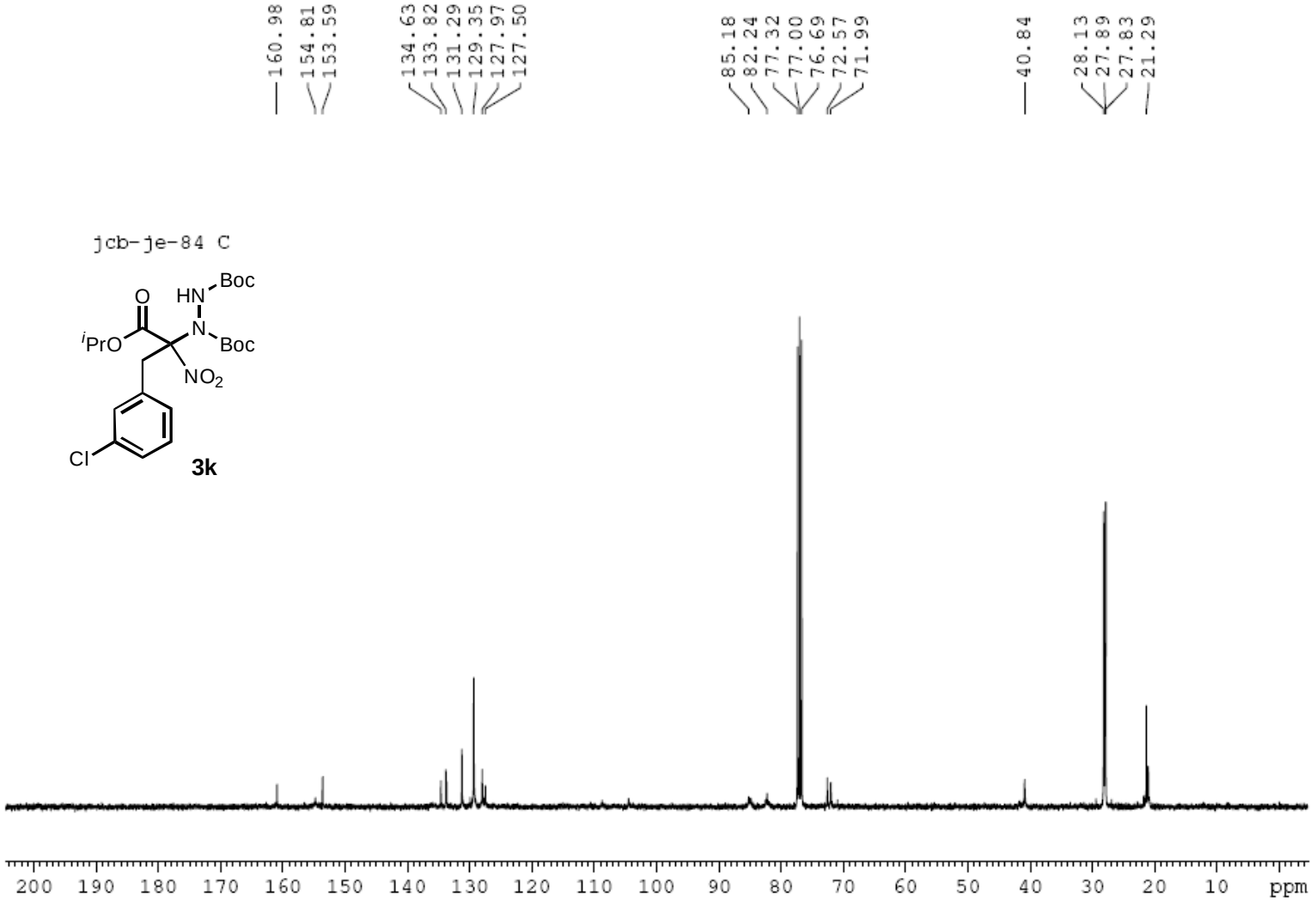

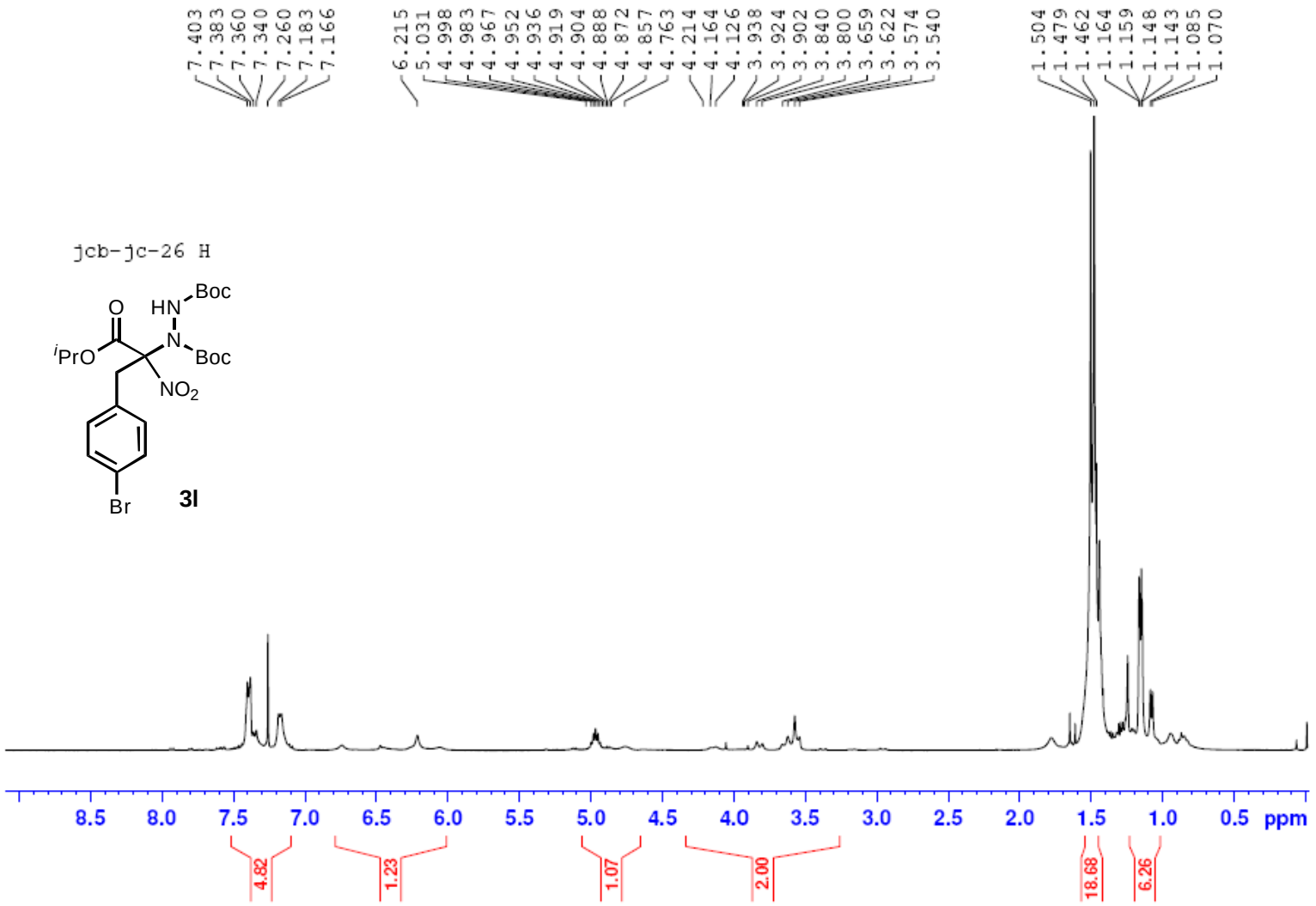

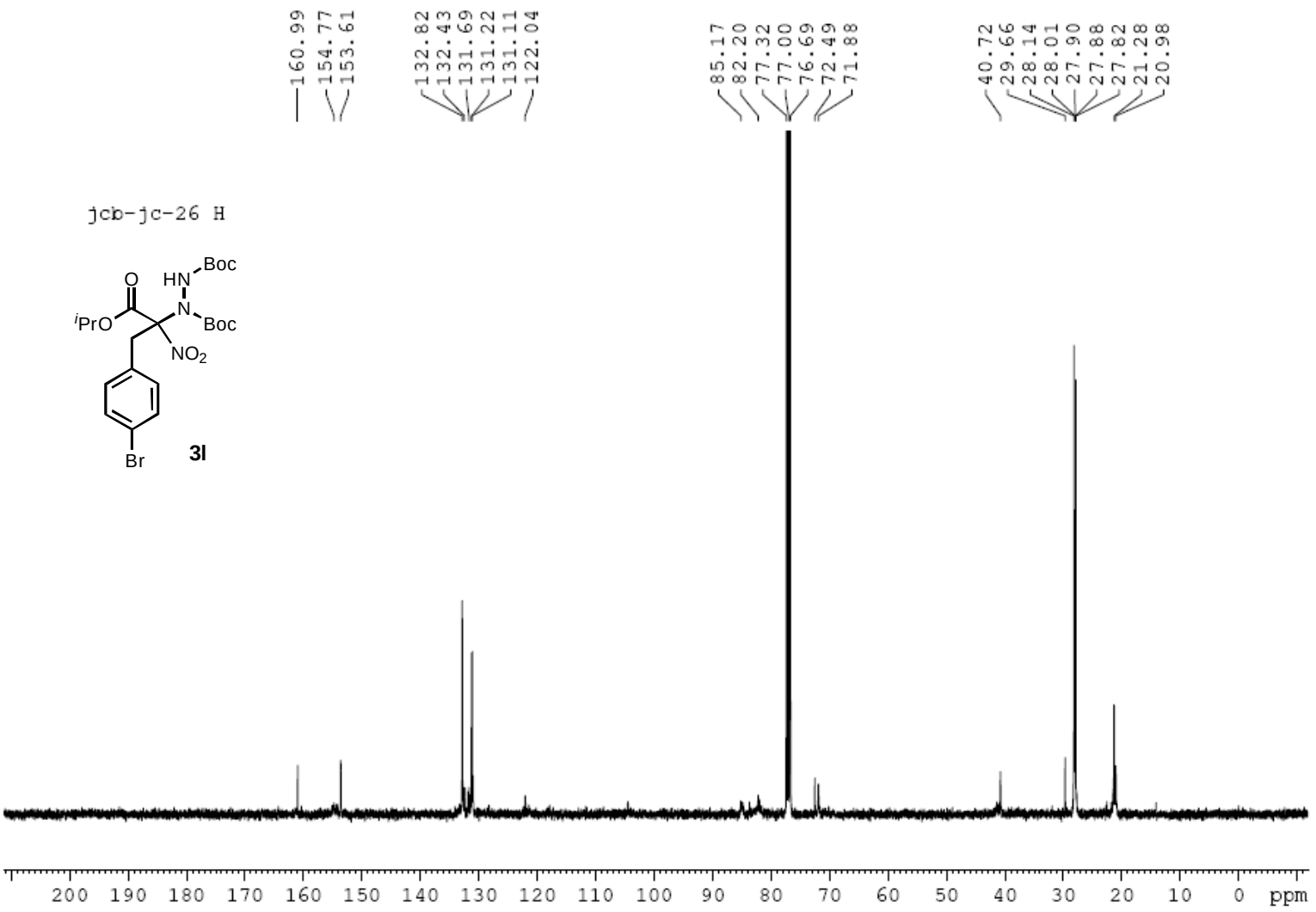

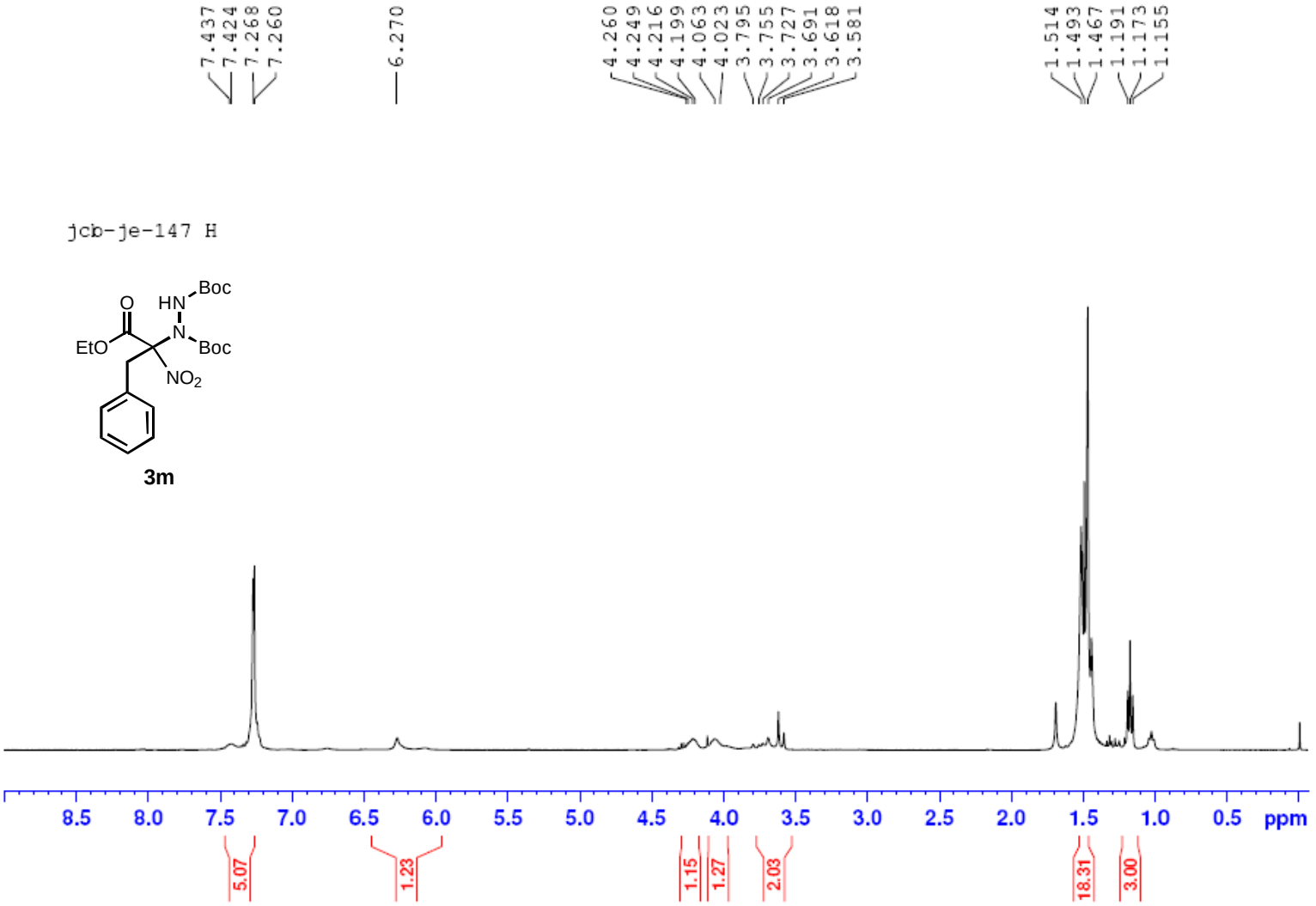

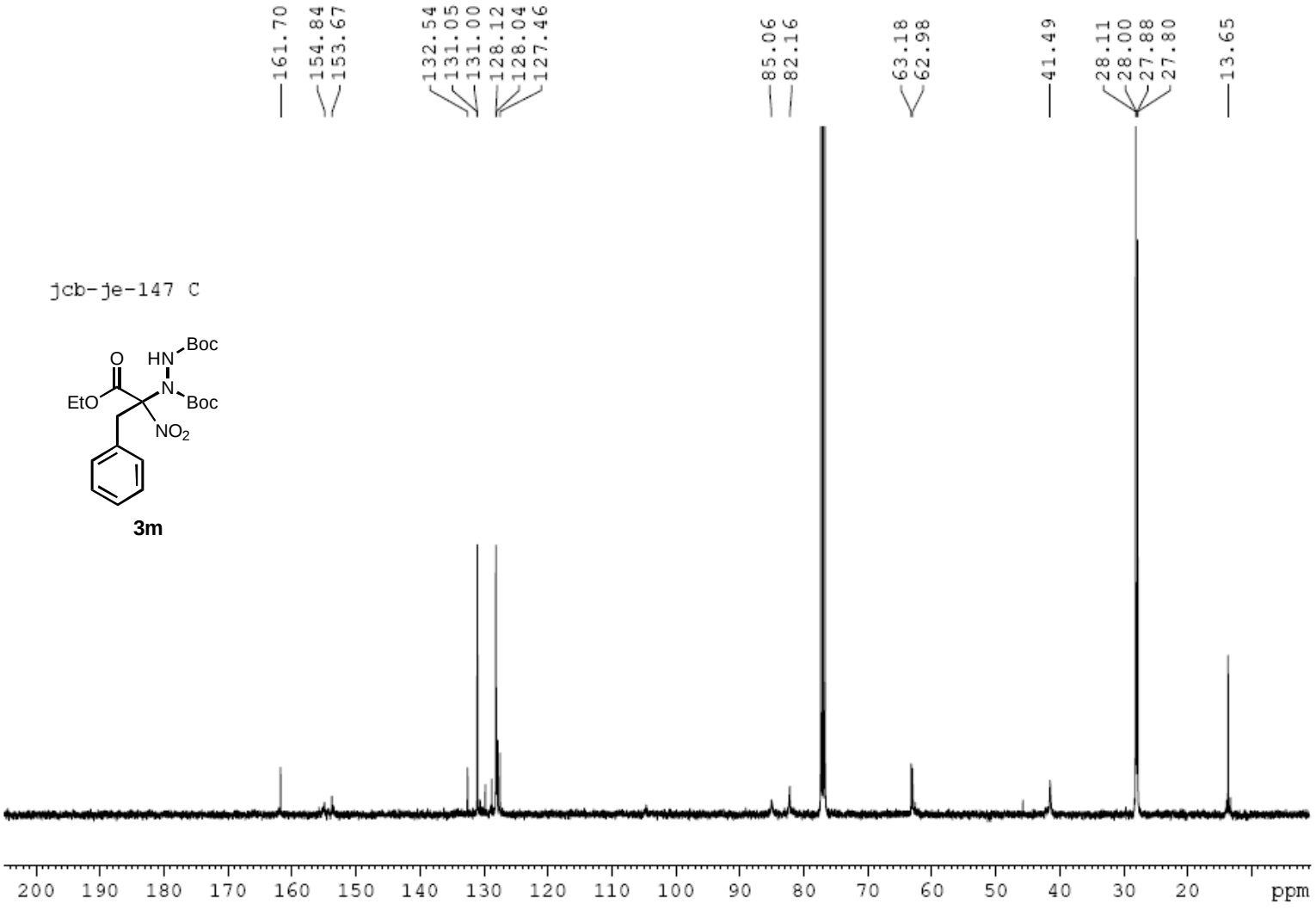

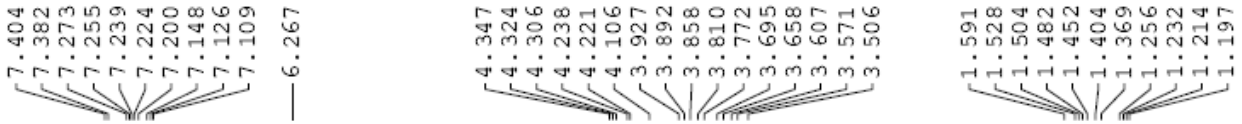

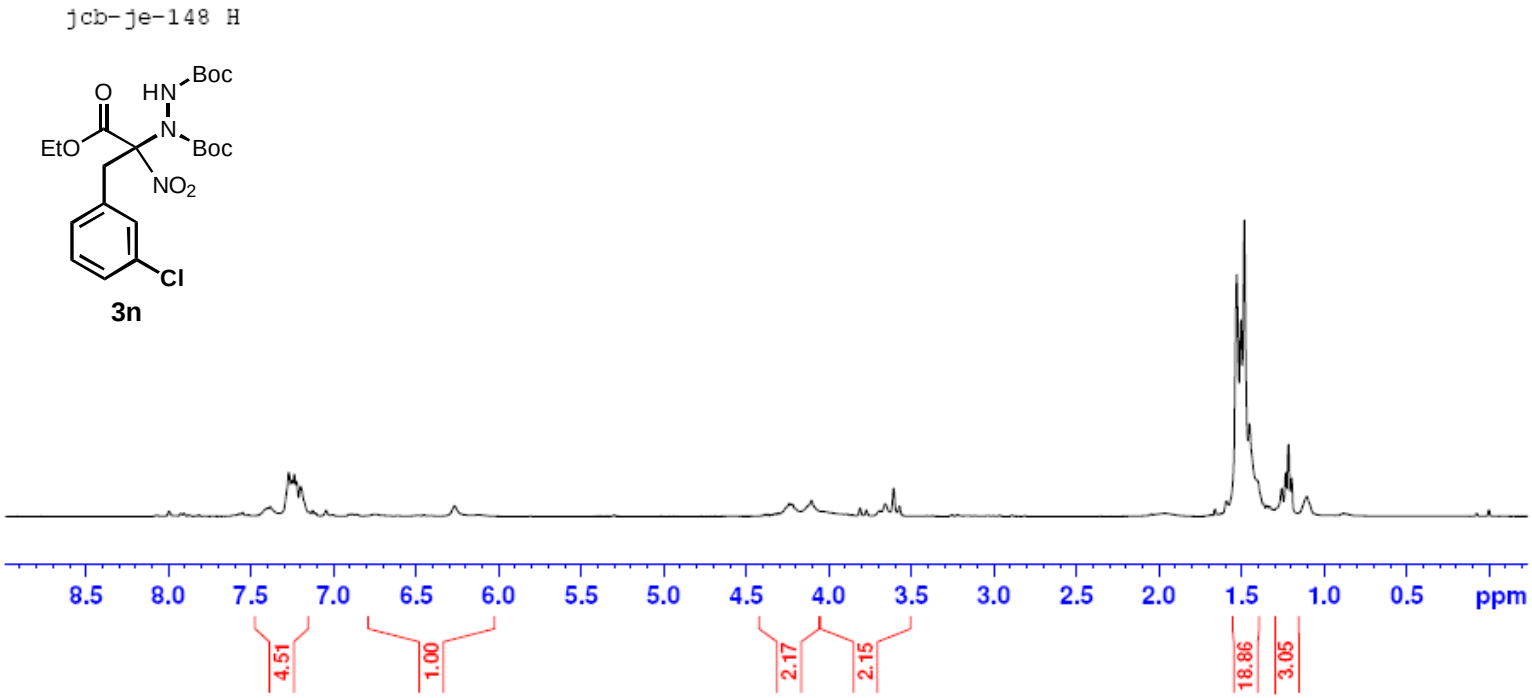

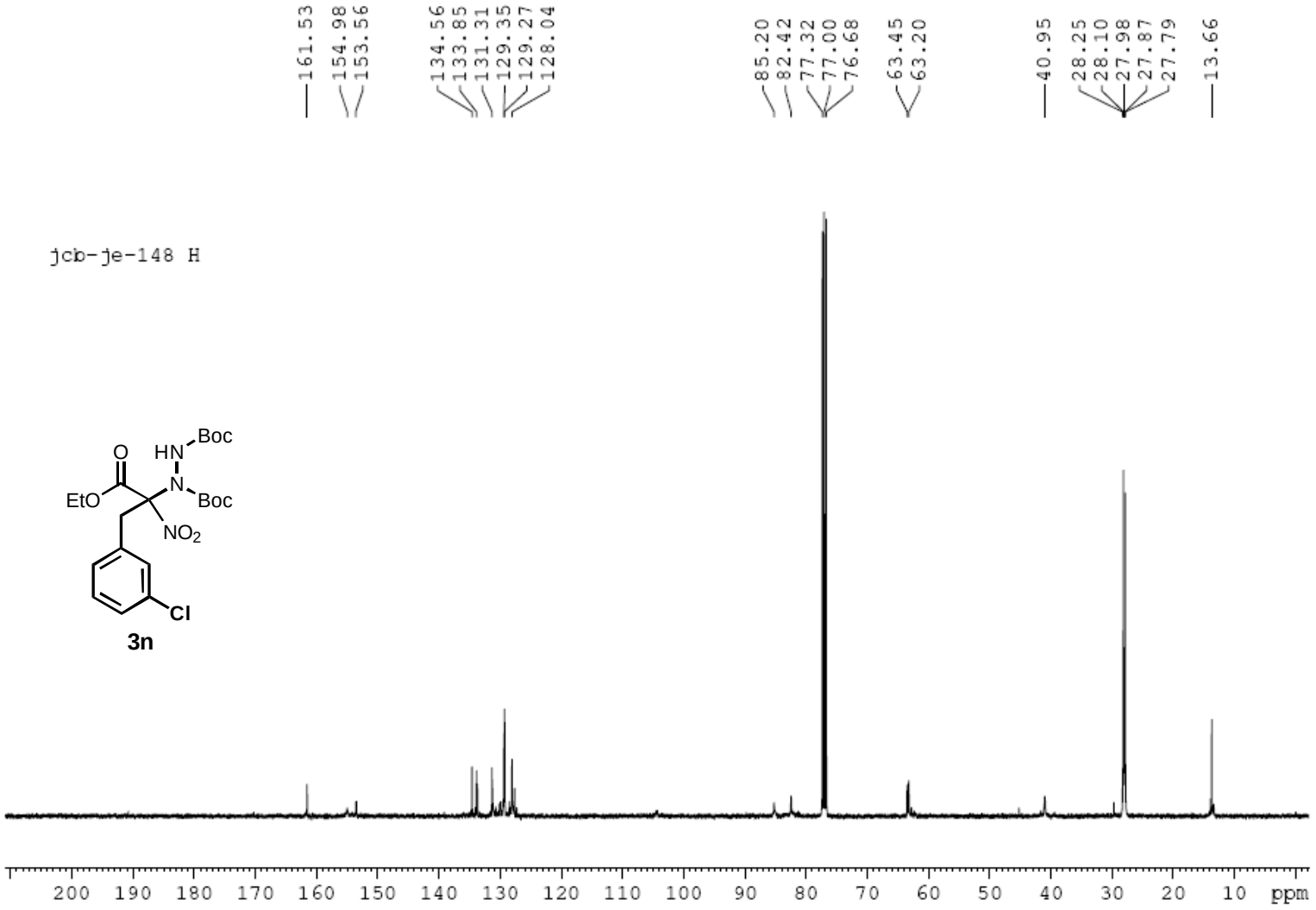

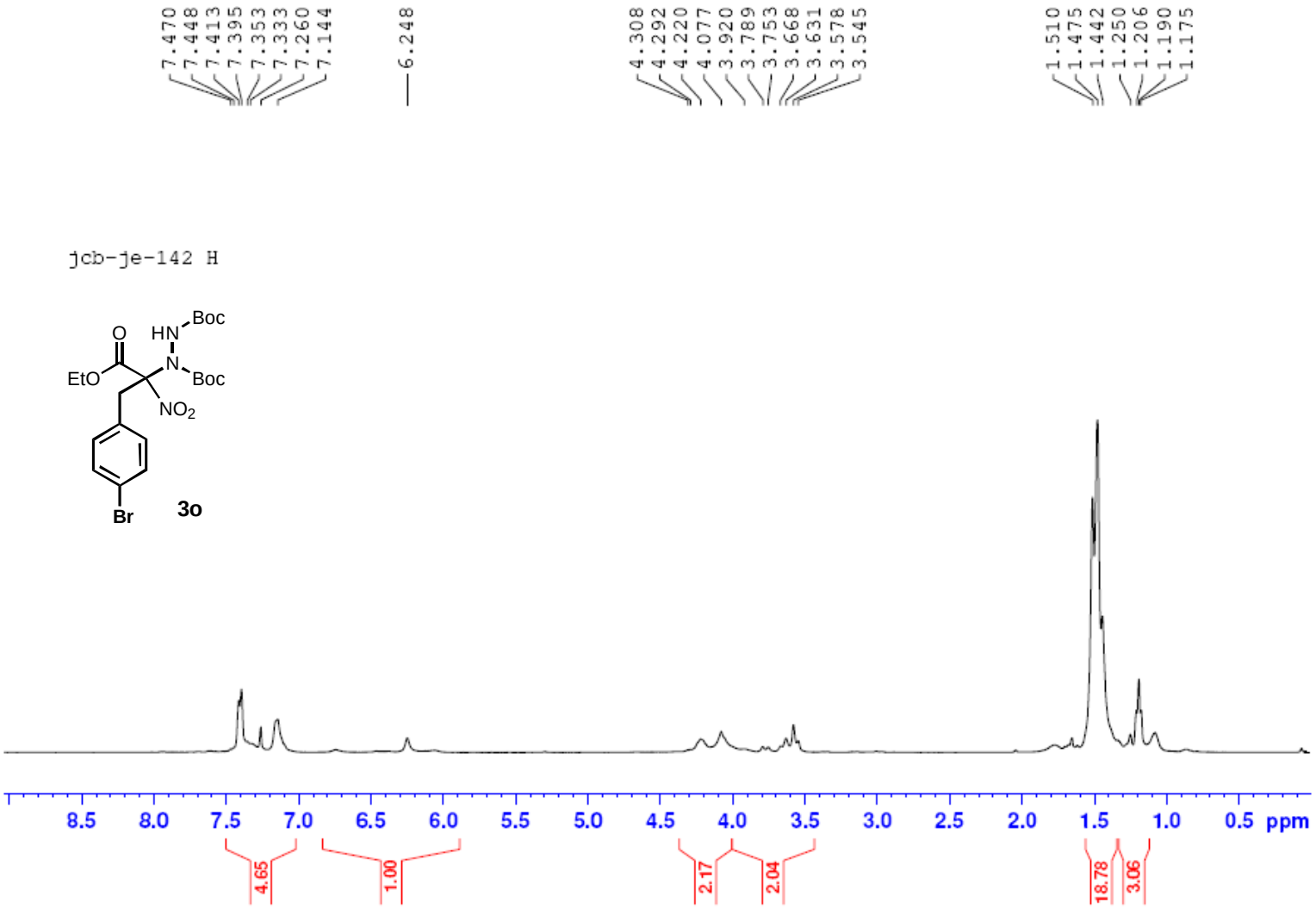

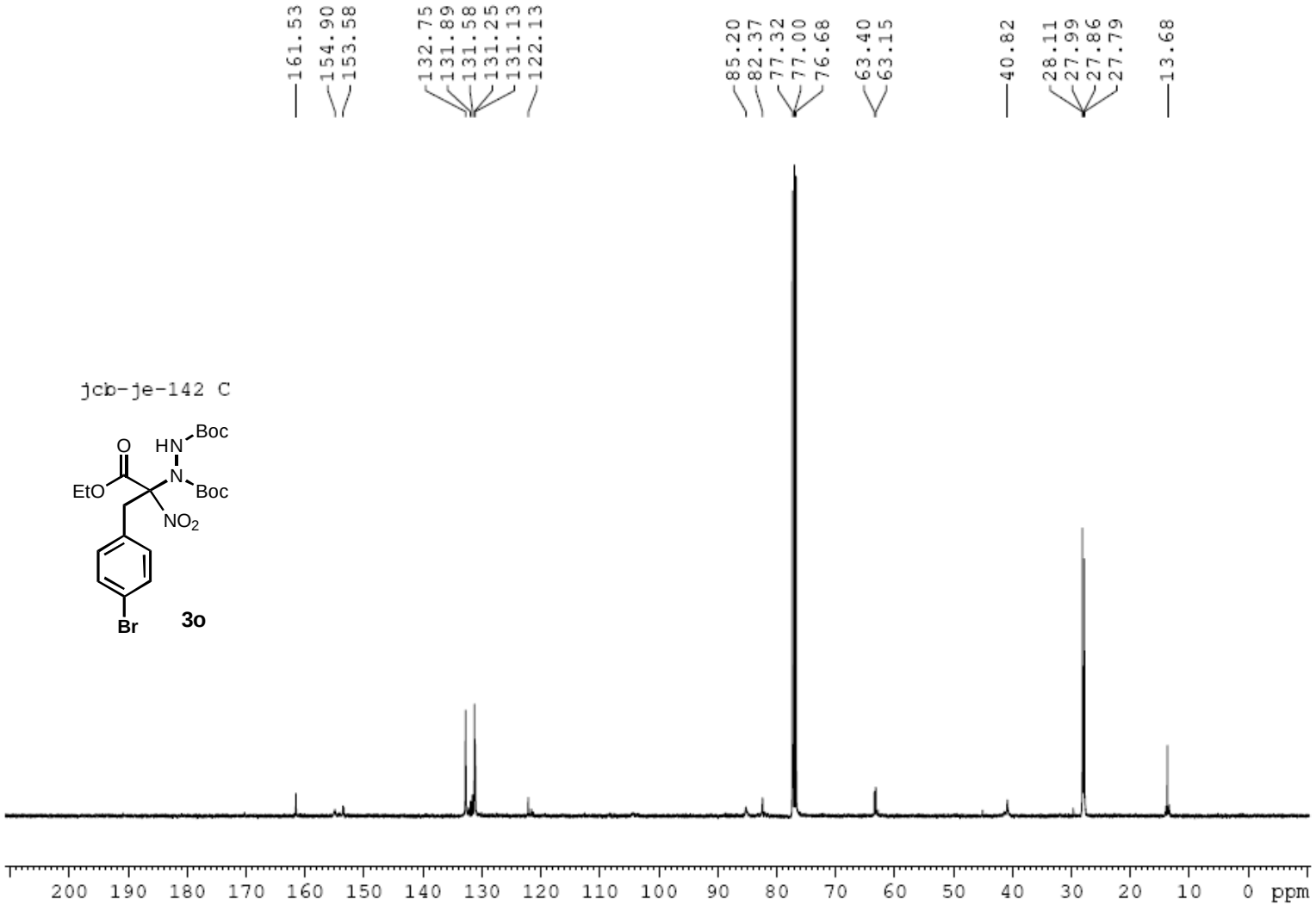

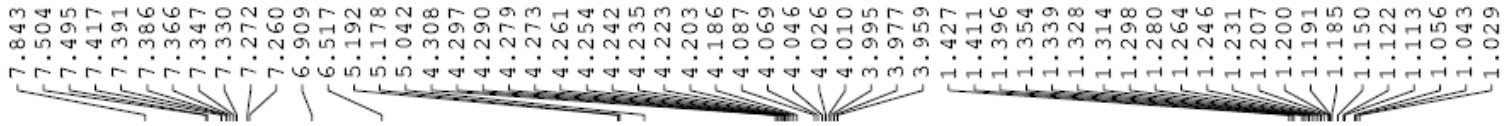

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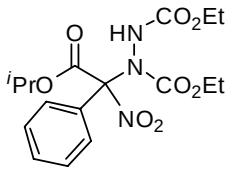
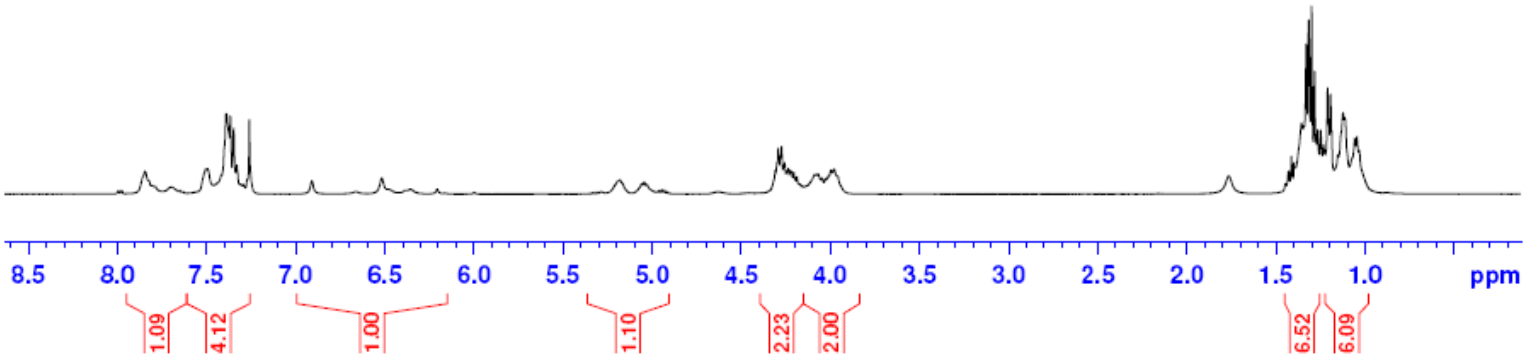
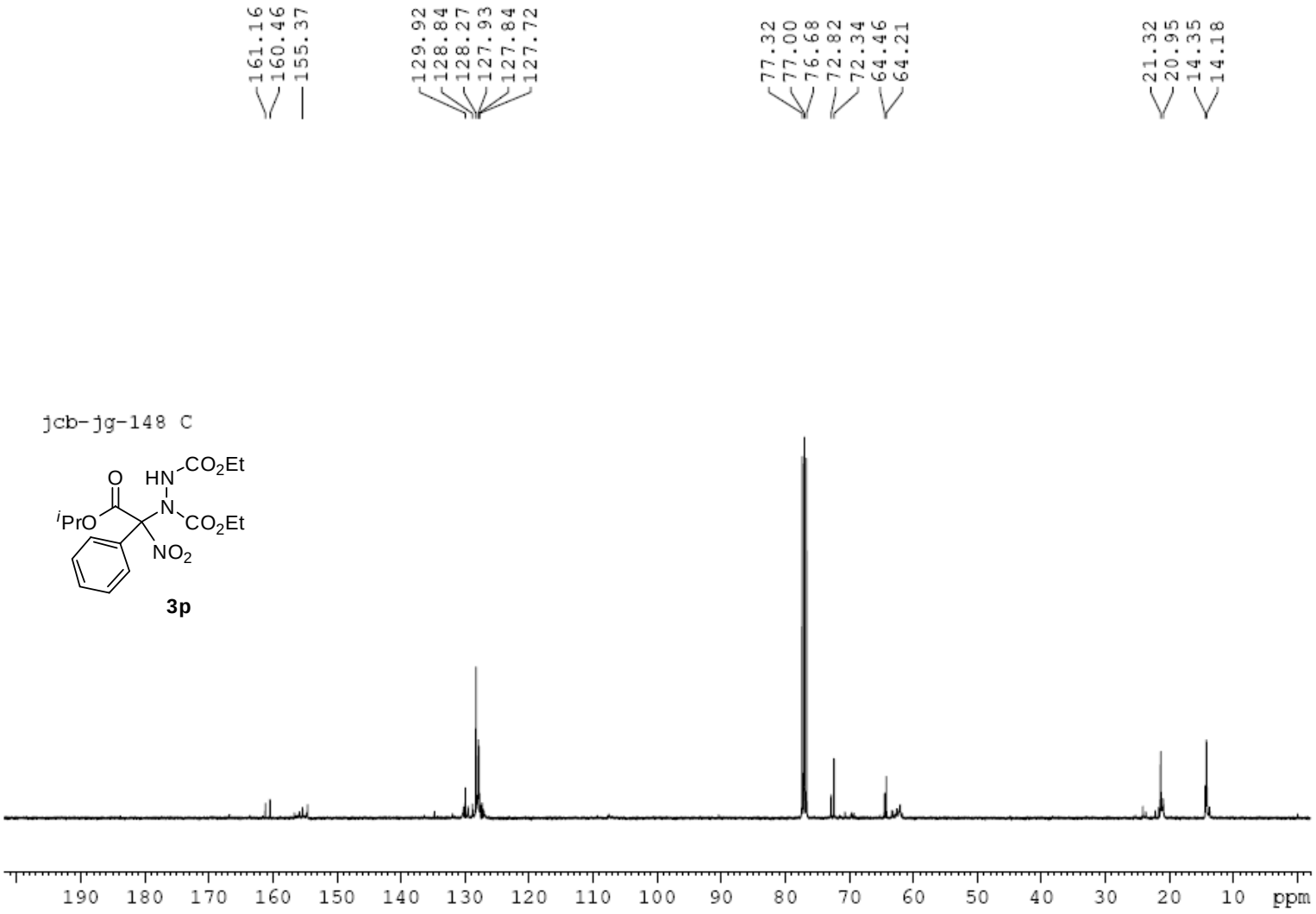
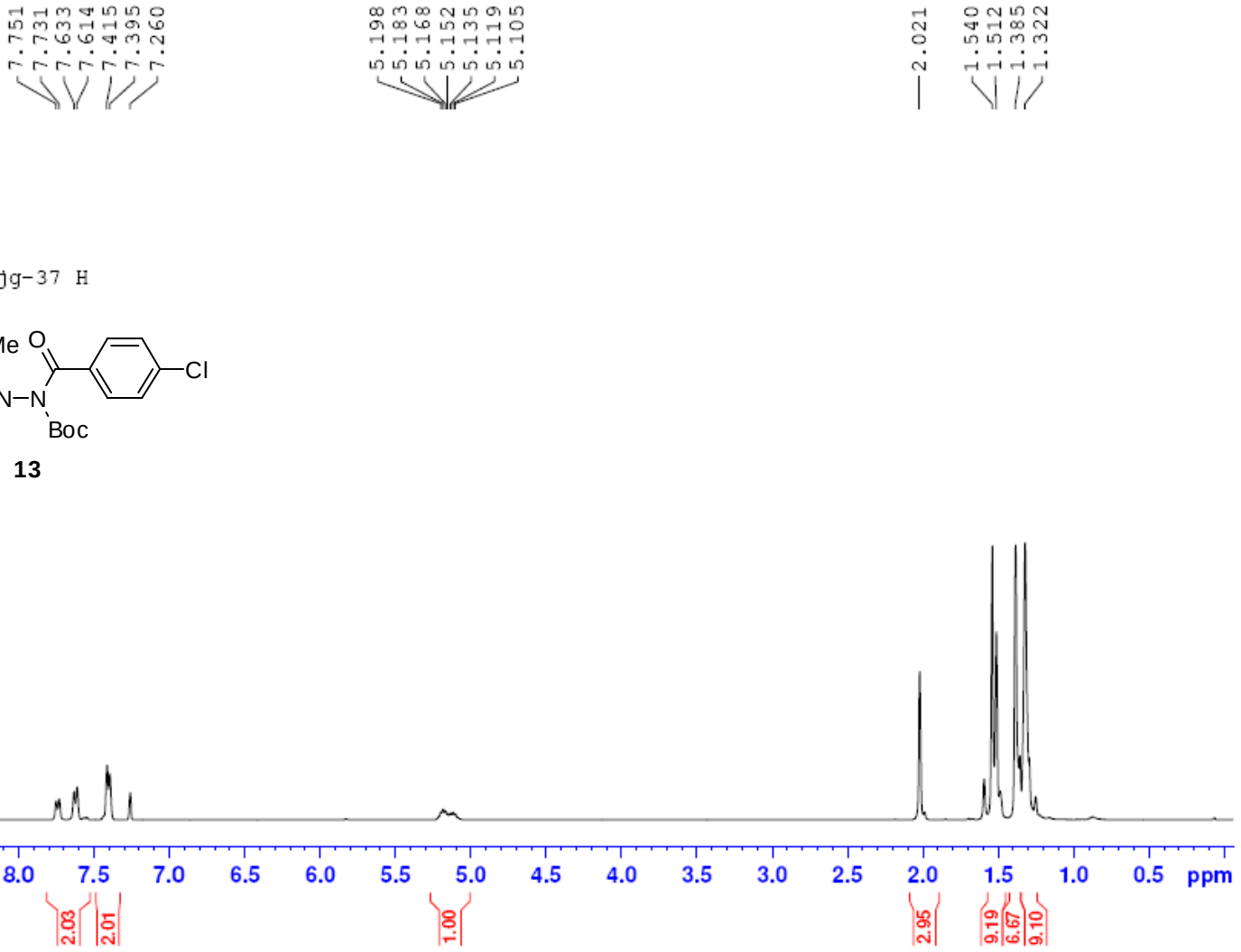
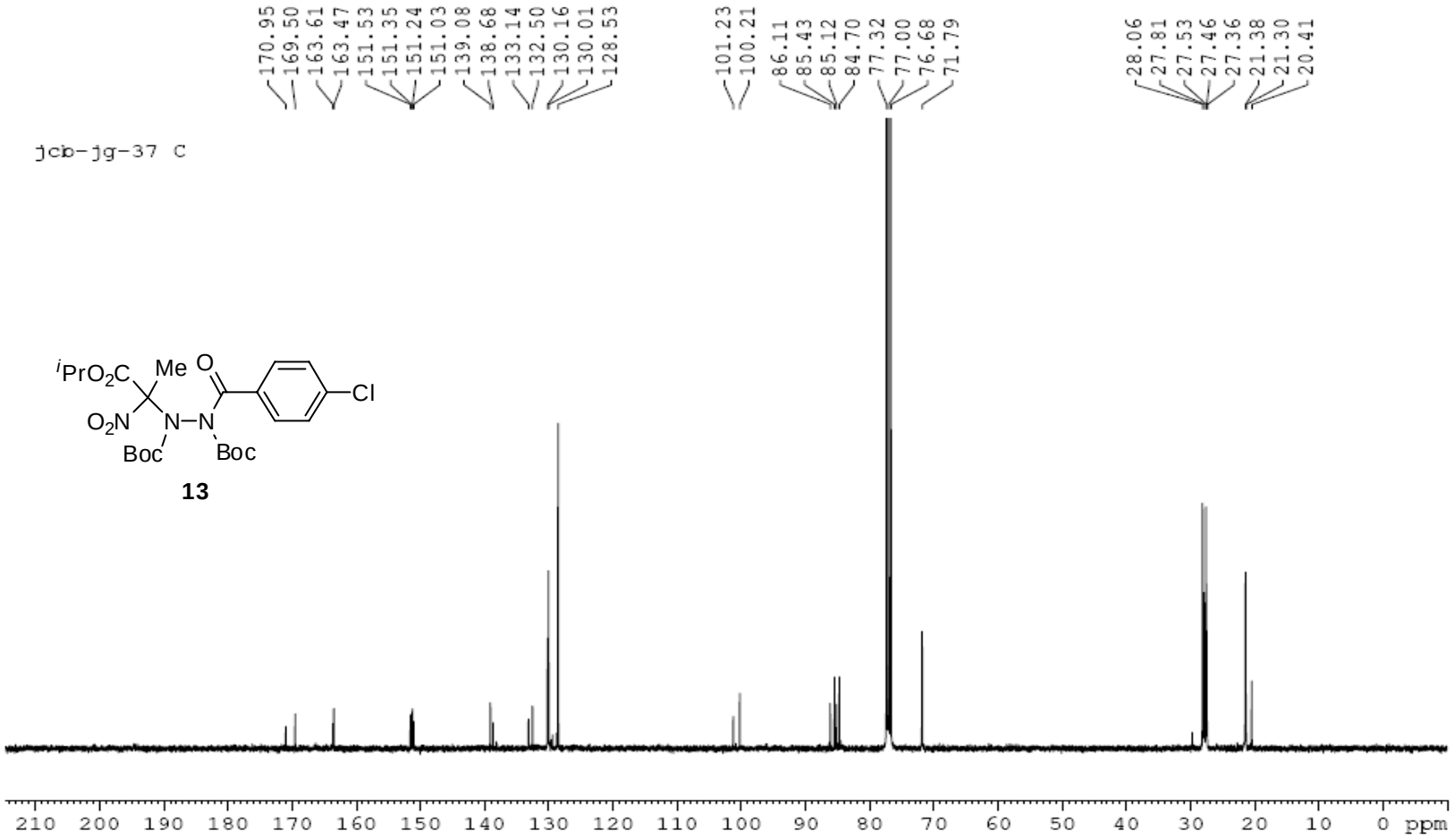


3p









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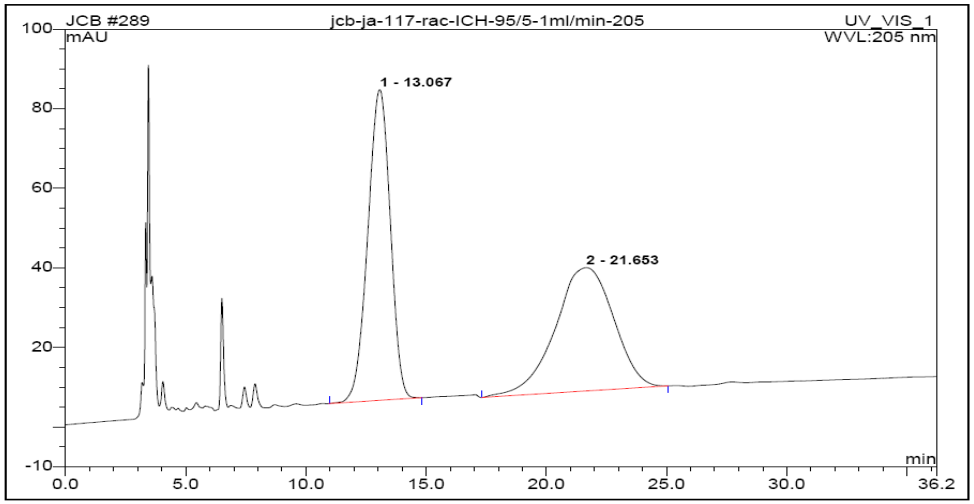
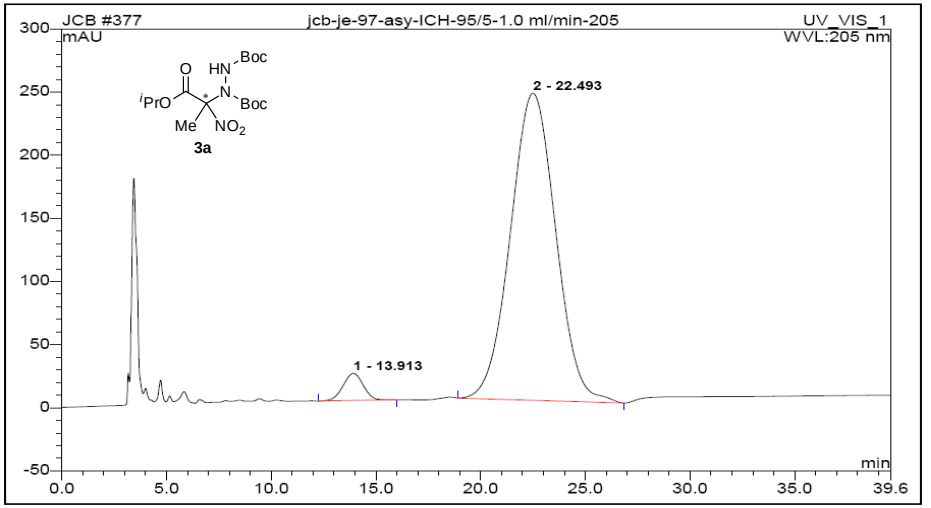
HPLC analysis of the compound 3

HPLC analysis of the mixture of racemic and chiral compound 3a obtained. (For comparison) (Table 2, entry 1)

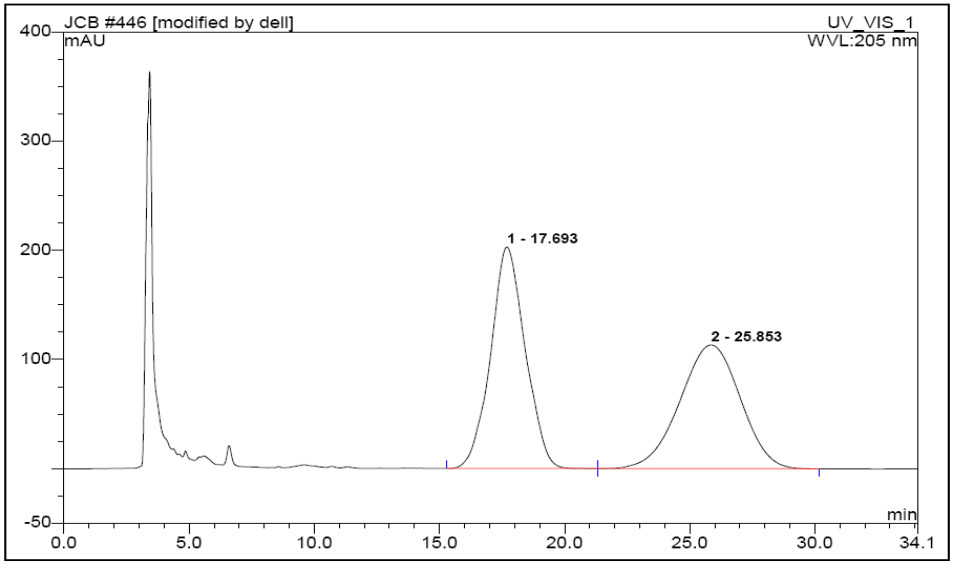


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.07	n.a.	78.075	84.653	49.22	n.a.	BMB
2	21.65	n.a.	31.015	87.330	50.78	n.a.	BMB
Total:			109.090	171.983	100.00	0.000	

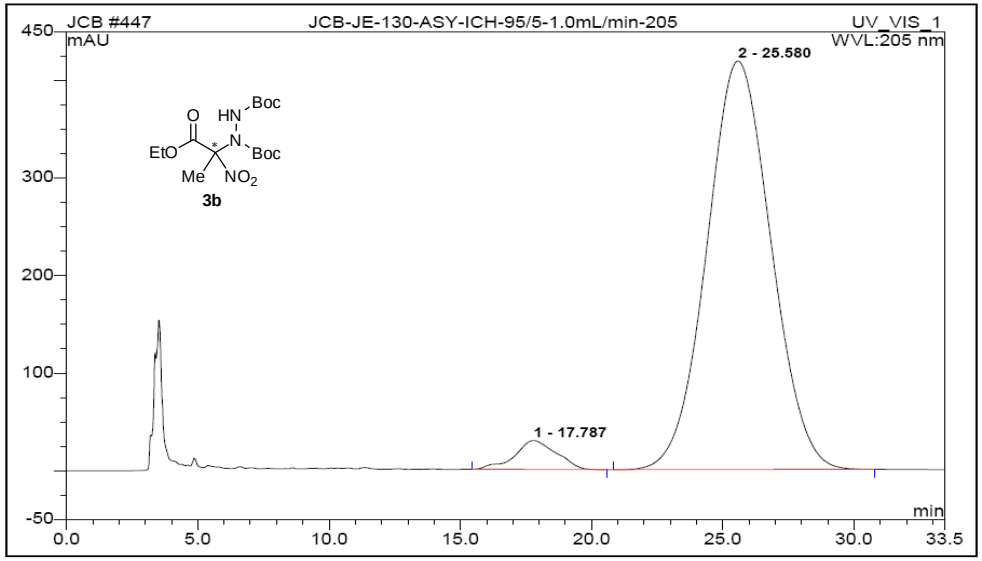


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.91	n.a.	21.334	23.811	3.76	n.a.	BMB
2	22.49	n.a.	243.077	608.938	96.24	n.a.	BMB
Total:			264.410	632.749	100.00	0.000	

HPLC analysis of the mixture of racemic and chiral compound 3b obtained. (For comparison) (Table 2, entry 2).

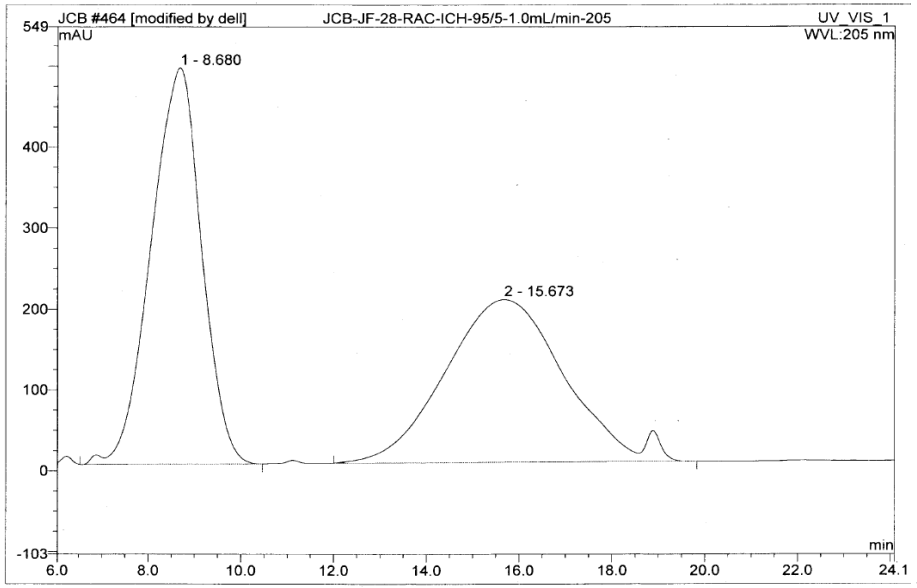


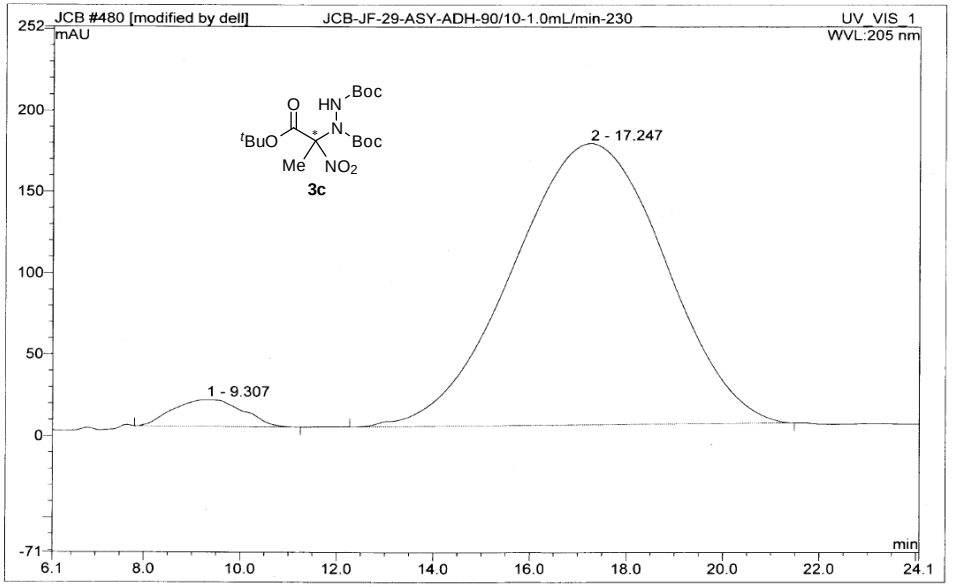
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.69	n.a.	202.734	324.512	50.54	n.a.	BM
2	25.85	n.a.	113.326	317.636	49.46	n.a.	MB
Total:			316.060	642.148	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.79	n.a.	29.646	54.569	4.40	n.a.	BMB
2	25.58	n.a.	418.271	1186.840	95.60	n.a.	BMB
Total:			447.917	1241.408	100.00	0.000	

HPLC analysis of the mixture of racemic and chiral compound 3c obtained. (For comparison) (Table 2, entry 3).

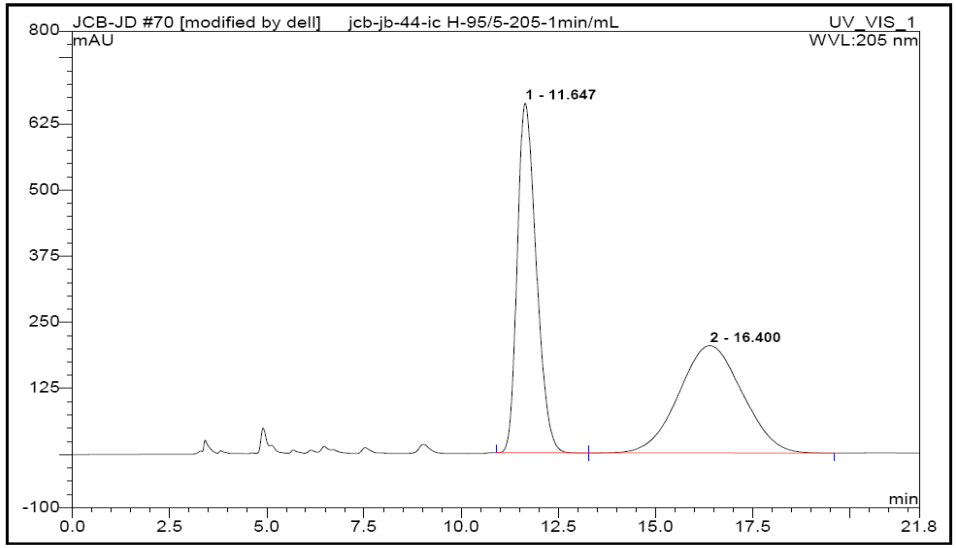




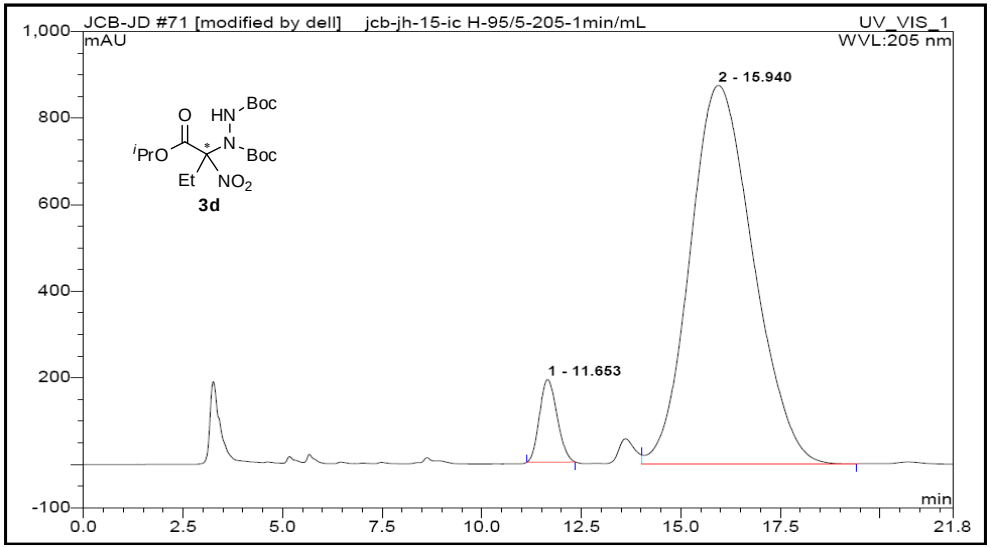
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.68	n.a.	489.429	620.209	50.75	n.a.	BMB*
2	15.67	n.a.	201.248	601.796	49.25	n.a.	BMB*
Total:			690.676	1222.006	100.00	0.000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.31	n.a.	16.308	27.266	4.15	n.a.	BMB*
2	17.25	n.a.	172.673	630.335	95.85	n.a.	BMB
Total:			188.981	657.600	100.00	0.000	

HPLC analysis of the mixture of racemic and chiral compound 3d obtained. (For comparison) (Table 2, entry 4).

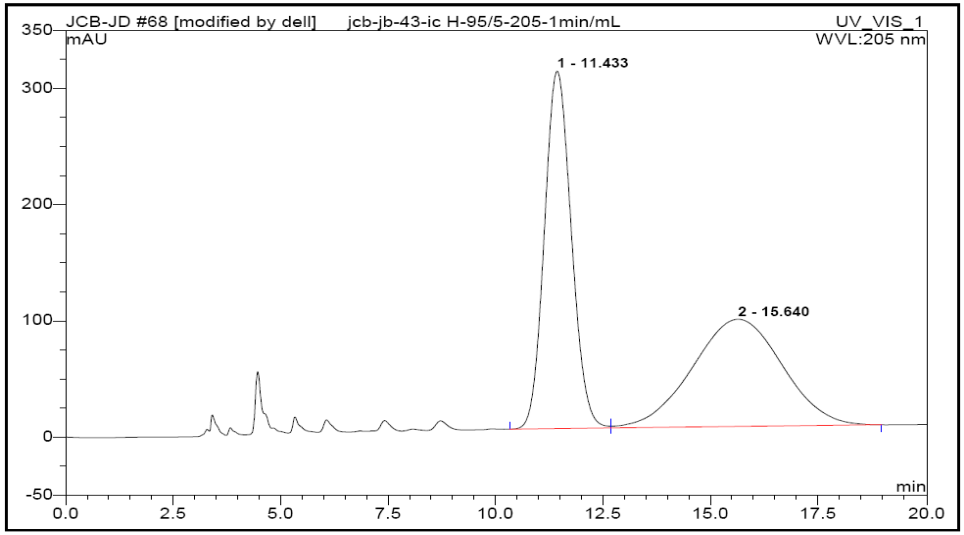


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.65	n.a.	660.031	375.408	49.47	n.a.	BM *
2	16.40	n.a.	202.634	383.464	50.53	n.a.	MB*
Total:			862.665	758.871	100.00	0.000	

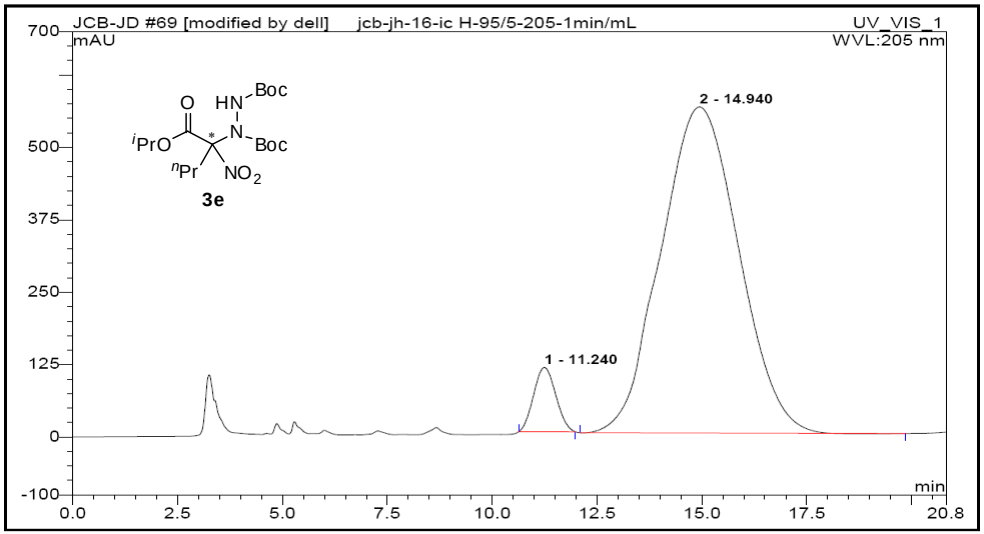


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.65	n.a.	190.724	97.754	5.75	n.a.	BMB*
2	15.94	n.a.	873.332	1601.115	94.25	n.a.	MB*
Total:			1064.056	1698.868	100.00	0.000	

HPLC analysis of the mixture of racemic and chiral compound 3e obtained. (For comparison) (Table 2, entry 5).

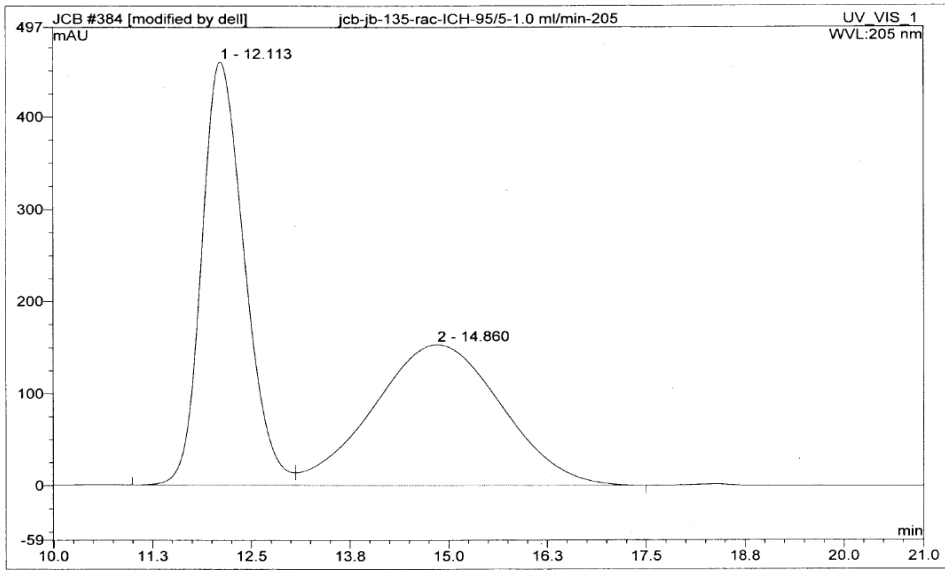


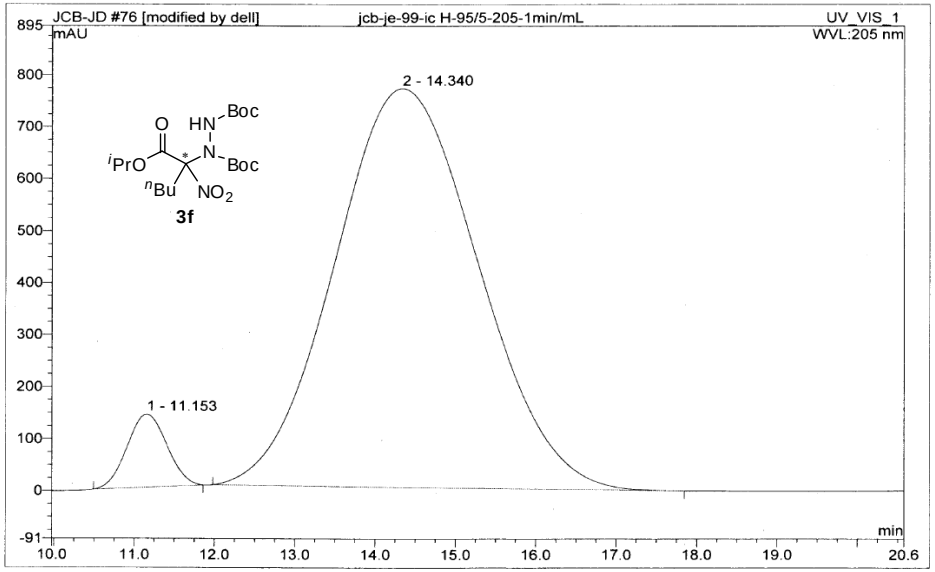
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.43	n.a.	307.614	223.698	49.92	n.a.	BM *
2	15.64	n.a.	92.250	224.456	50.08	n.a.	MB*
Total:			399.864	448.154	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.24	n.a.	110.956	67.958	5.32	n.a.	BMB*
2	14.94	n.a.	562.780	1210.483	94.68	n.a.	BMB*
Total:			673.736	1278.441	100.00	0.000	

HPLC analysis of the mixture of racemic and chiral compound 3f obtained. (For comparison) (Table 2, entry 6).

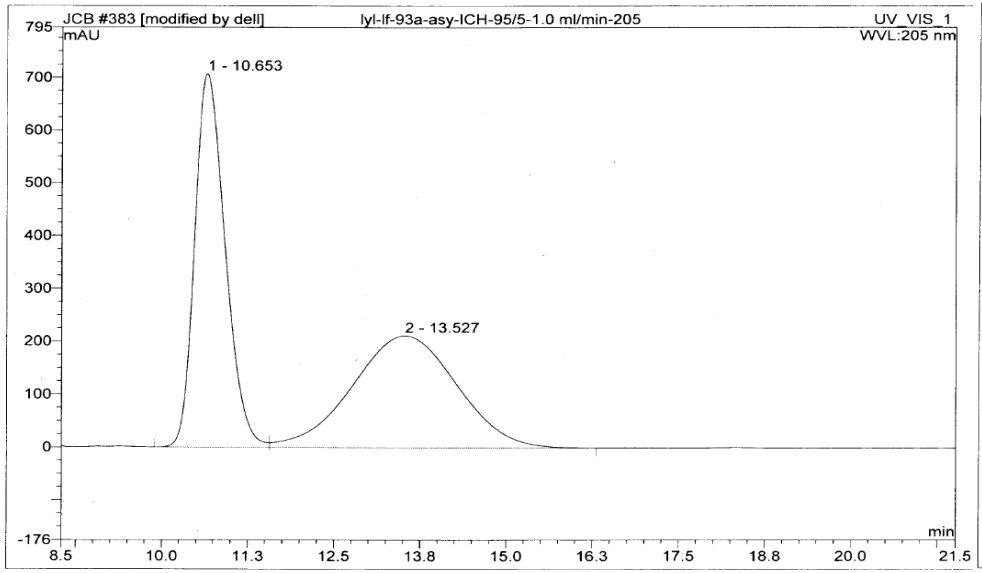


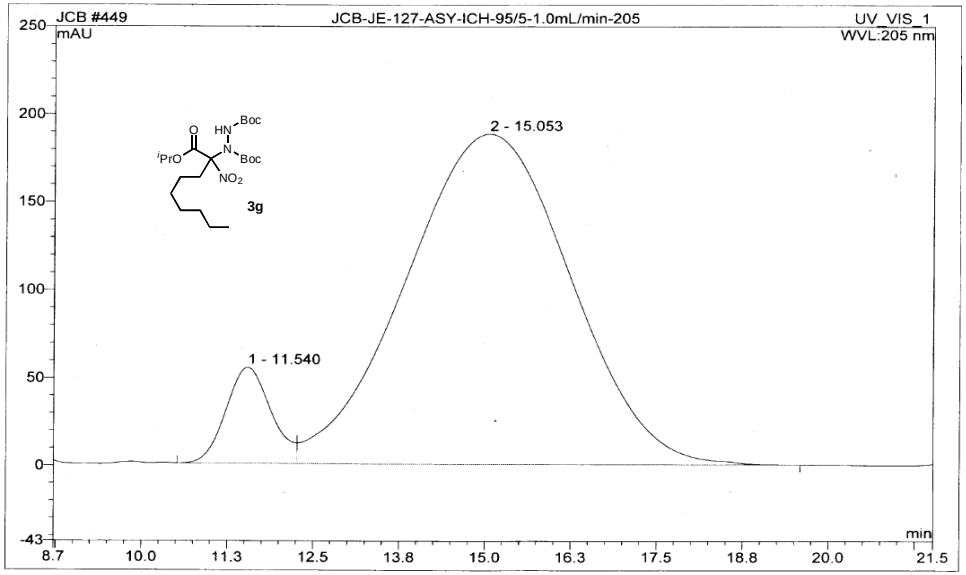


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.11	n.a.	458.948	287.487	49.91	n.a.	BM
2	14.86	n.a.	153.081	288.527	50.09	n.a.	MB
Total:			612.029	576.014	100.00	0.000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.15	n.a.	140.172	80.510	4.82	n.a.	BMB*
2	14.34	n.a.	767.644	1588.660	95.18	n.a.	BMB*
Total:			907.816	1669.170	100.00	0.000	

HPLC analysis of the mixture of racemic and chiral compound 3g obtained. (For comparison) (Table 2, entry 7).

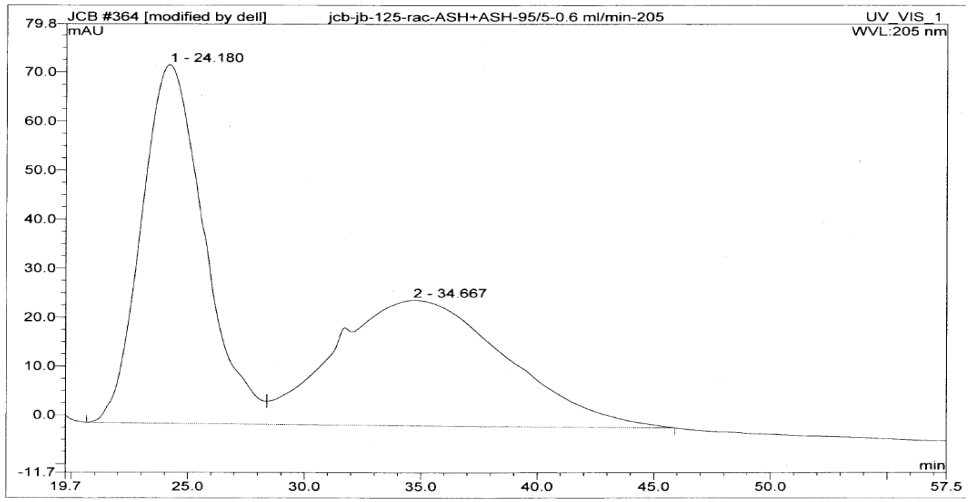




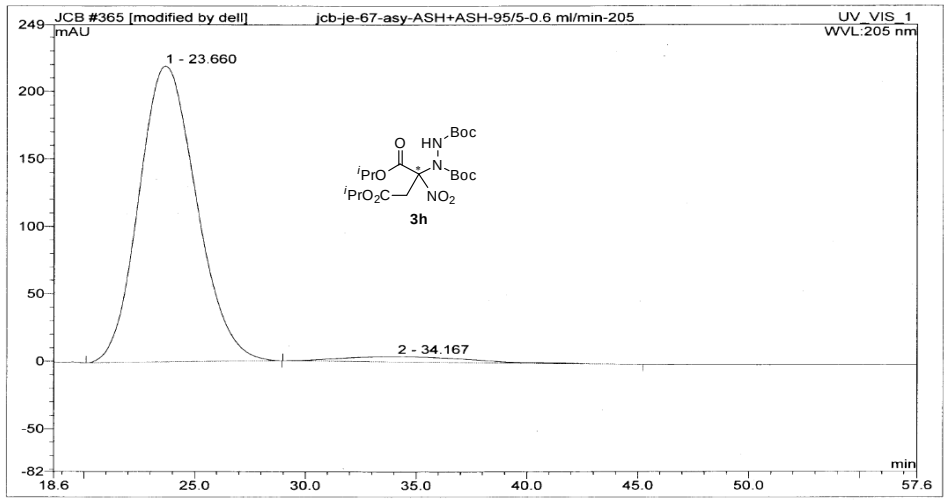
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.65	n.a.	707.119	363.880	49.45	n.a.	BM
2	13.53	n.a.	211.138	371.904	50.55	n.a.	MB
Total:			918.257	735.784	100.00	0.000	

No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.54	n.a.	54.814	41.786	7.41	n.a.	BM
2	15.05	n.a.	188.008	521.966	92.59	n.a.	MB
Total:			242.822	563.752	100.00	0.000	

HPLC analysis of the mixture of racemic and chiral compound 3h obtained. (For comparison) (Table 2, entry 8).

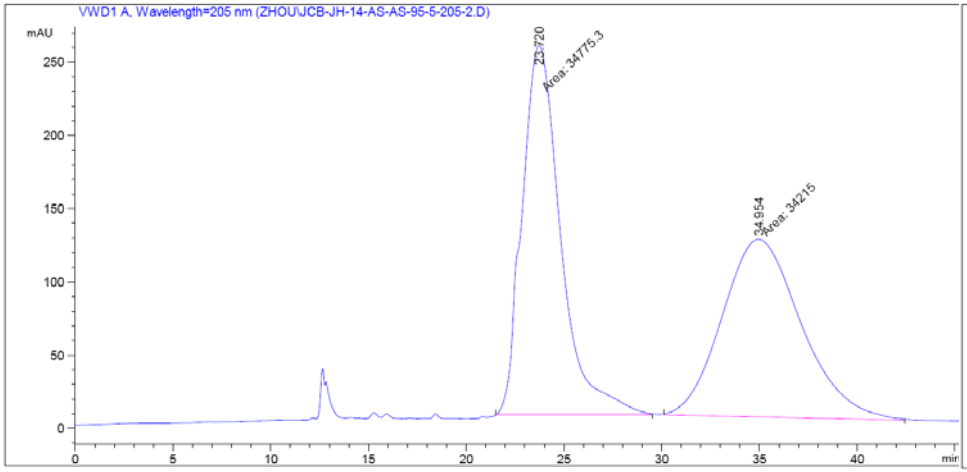


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	24.18	n.a.	73.158	228.941	50.91	n.a.	BM
2	34.67	n.a.	25.664	220.724	49.09	n.a.	MB*
Total:			98.822	449.665	100.00	0.000	

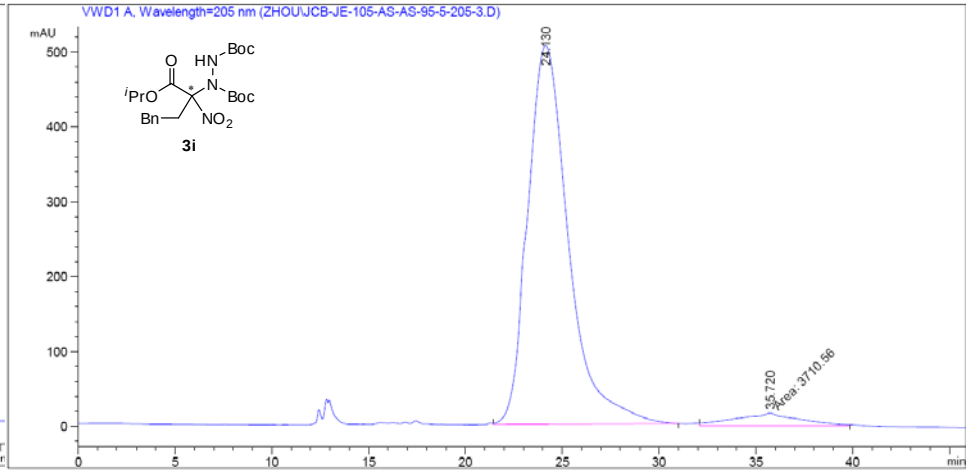


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23.66	n.a.	219.300	660.799	96.28	n.a.	BMB*
2	34.17	n.a.	3.885	25.560	3.72	n.a.	BMB*
Total:			223.185	686.359	100.00	0.000	

HPLC analysis of the mixture of racemic and chiral compound 3i obtained. (For comparison) (Table 2, entry 9).

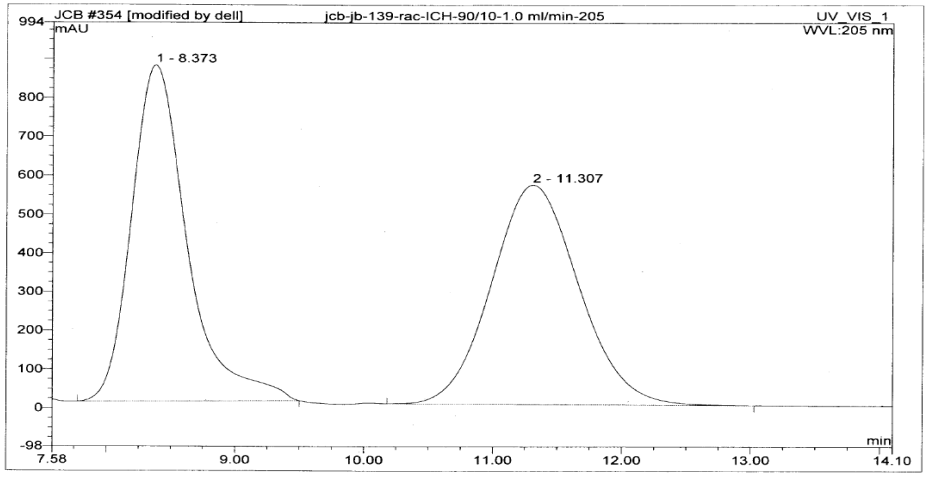


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.720	MM	2.2952	3.47753e4	252.52071	50.4061
2	34.954	MM	4.6944	3.42150e4	121.47393	49.5939
Totals :				6.89902e4	373.99464	

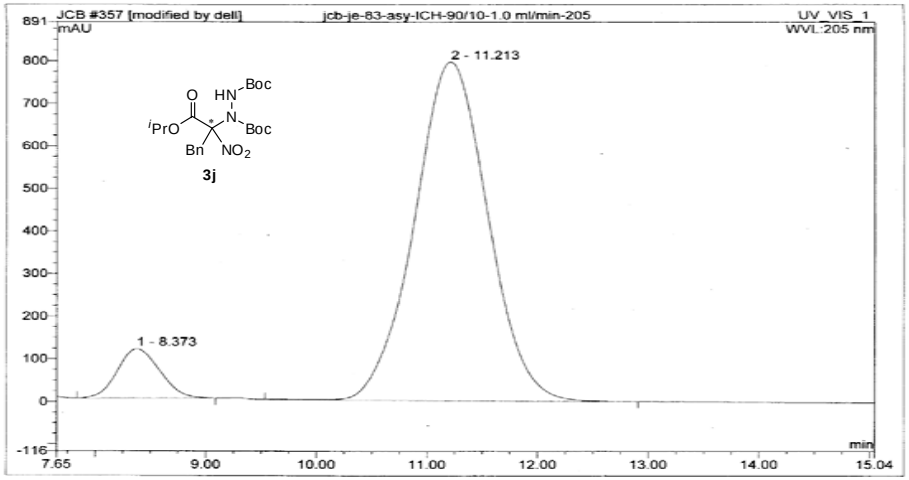


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.130	VB	2.1792	7.43101e4	506.01276	95.2441
2	35.720	MM	3.7315	3710.55713	16.57326	4.7559
Totals :				7.80207e4	522.58602	

HPLC analysis of the mixture of racemic and chiral compound 3j obtained. (For comparison) (Table 2, entry 10).

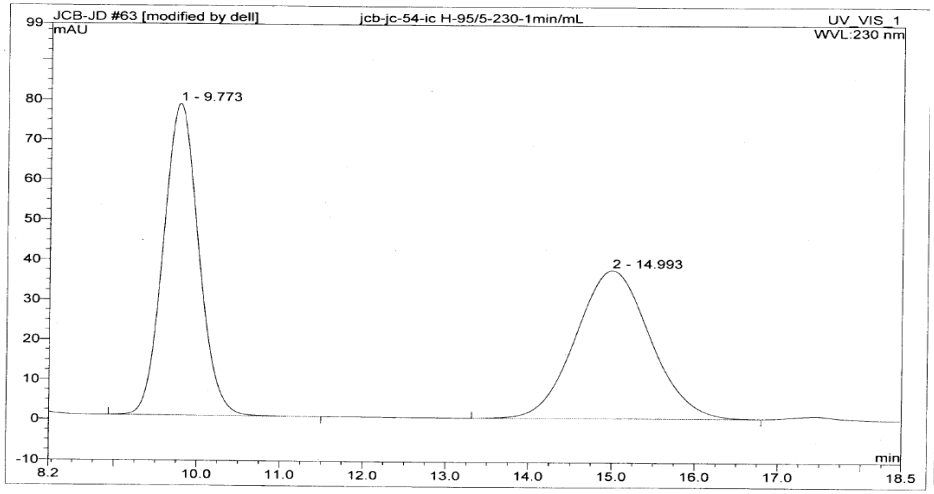


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.37	n.a.	866.582	434.877	49.43	n.a.	BMB*
2	11.31	n.a.	566.082	444.964	50.57	n.a.	BMB
Total:			1432.664	879.841	100.00	0.000	

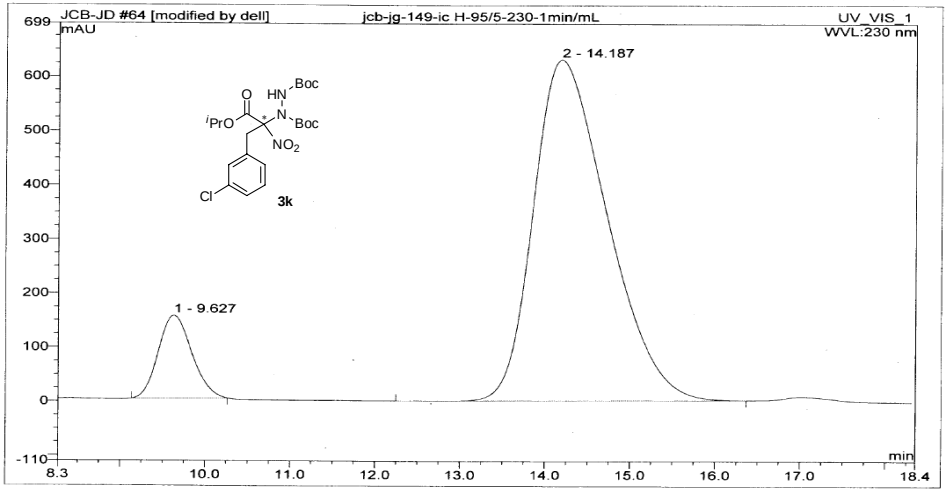


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.37	n.a.	116.592	51.423	7.76	n.a.	BMB*
2	11.21	n.a.	795.628	611.220	92.24	n.a.	BMB
Total:			912.220	662.643	100.00	0.000	

HPLC analysis of the mixture of racemic and chiral compound 3k obtained. (For comparison) (Table 2, entry 11).

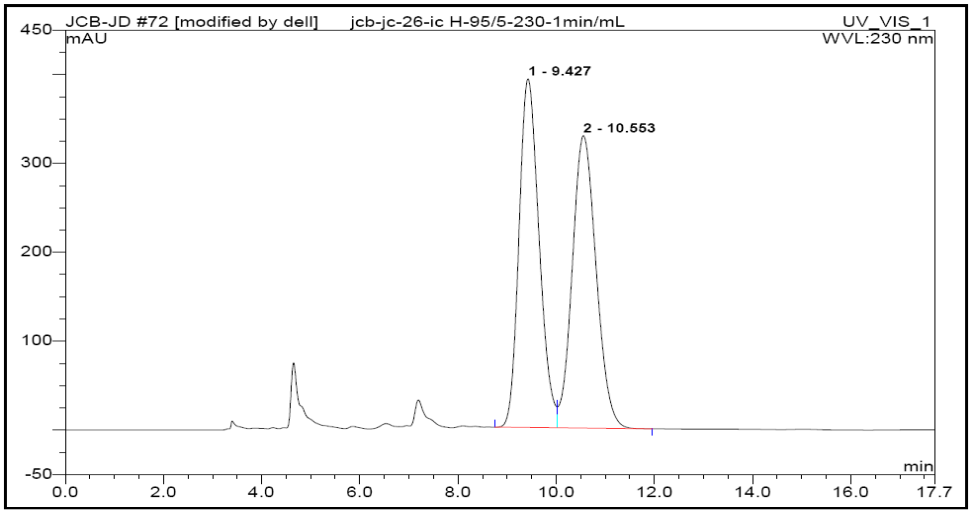


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.77	n.a.	77.977	38.638	50.00	n.a.	BMB*
2	14.99	n.a.	37.022	38.635	50.00	n.a.	BMB*
Total:			114.999	77.273	100.00	0.000	

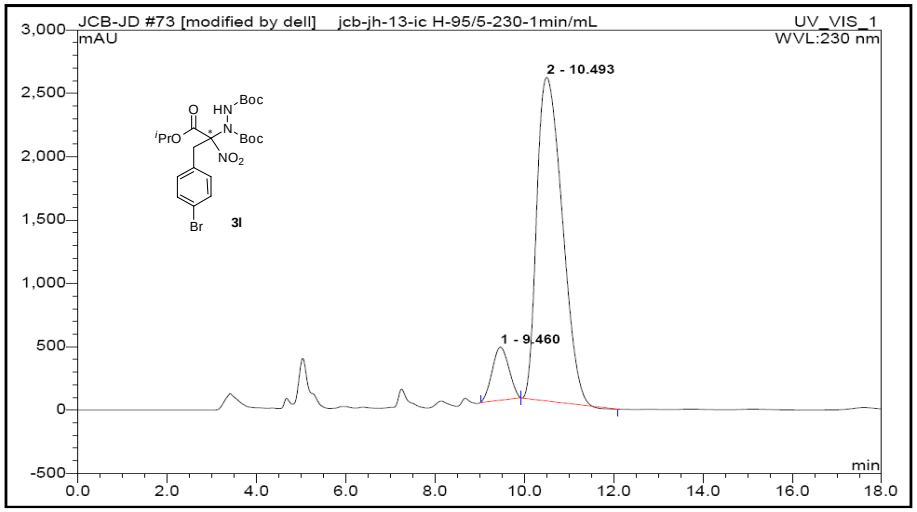


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.63	n.a.	152.926	69.898	9.93	n.a.	BMB*
2	14.19	n.a.	629.121	634.220	90.07	n.a.	BMB*
Total:			782.048	704.118	100.00	0.000	

HPLC analysis of the mixture of racemic and chiral compound 3l obtained. (For comparison) (Table 2, entry 12).

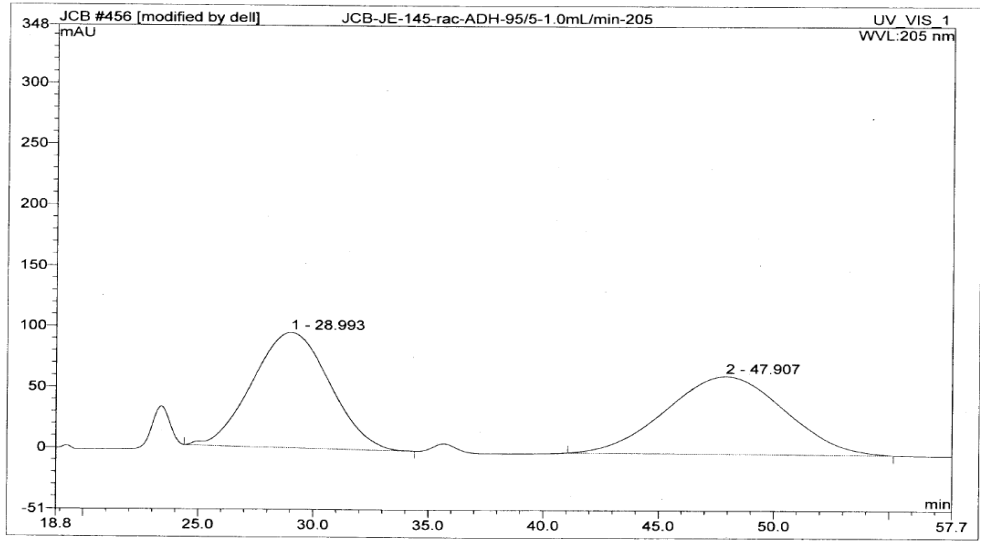


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.43	n.a.	392.152	186.170	50.08	n.a.	BM
2	10.55	n.a.	328.834	185.607	49.92	n.a.	MB
Total:			720.986	371.778	100.00	0.000	

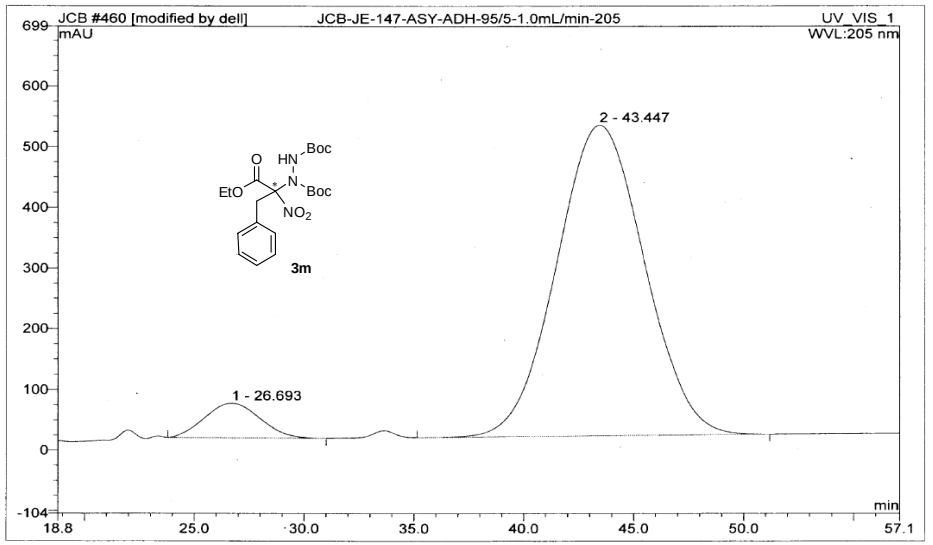


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.46	n.a.	419.211	181.485	9.73	n.a.	BMB*
2	10.49	n.a.	2554.812	1683.613	90.27	n.a.	BMB*
Total:			2974.023	1865.098	100.00	0.000	

HPLC analysis of the mixture of racemic and chiral compound 3m obtained. (For comparison) (Table 2, entry 13).

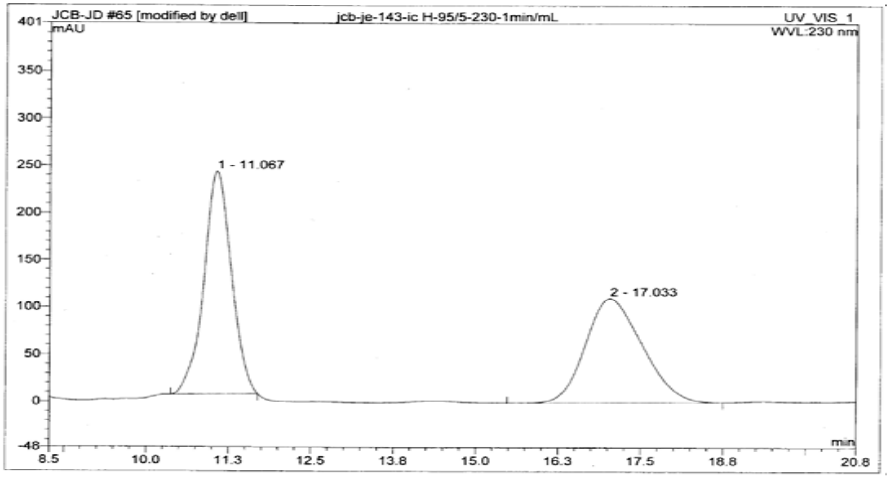


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	28.99	n.a.	94.854	369.854	49.20	n.a.	BMB*
2	47.91	n.a.	63.906	381.895	50.80	n.a.	BMB*
Total:			158.760	751.749	100.00	0.000	

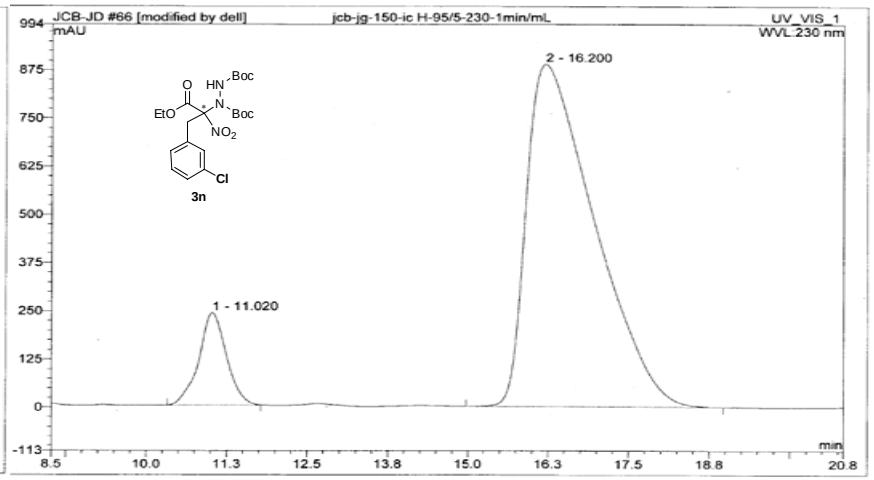


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	26.69	n.a.	57.237	166.671	6.57	n.a.	BMB*
2	43.45	n.a.	511.754	2369.436	93.43	n.a.	BMB*
Total:			568.991	2536.107	100.00	0.000	

HPLC analysis of the mixture of racemic and chiral compound 3n obtained. (For comparison) (Table 2, entry 14).

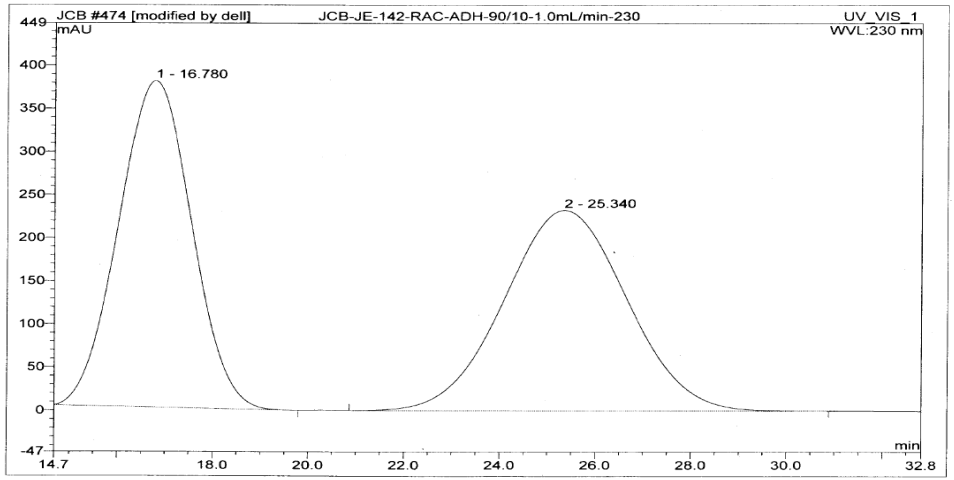


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.07	n.a.	235.859	114.197	50.96	n.a.	BMB*
2	17.03	n.a.	110.167	109.878	49.04	n.a.	BMB
Total:			346.026	224.075	100.00	0.000	

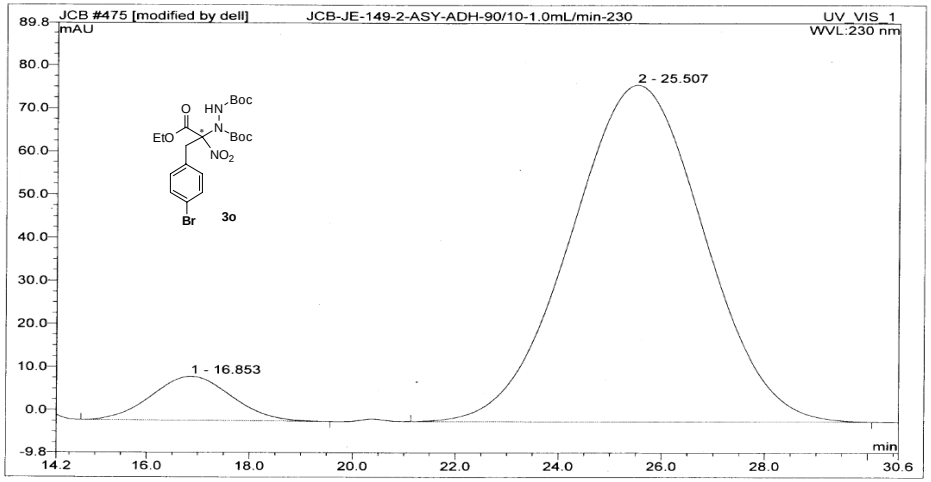


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.02	n.a.	239.668	119.431	9.90	n.a.	BMB*
2	16.20	n.a.	887.160	1086.548	90.10	n.a.	BMB*
Total:			1126.828	1205.979	100.00	0.000	

HPLC analysis of the mixture of racemic and chiral compound 3o obtained. (For comparison) (Table 2, entry 15).

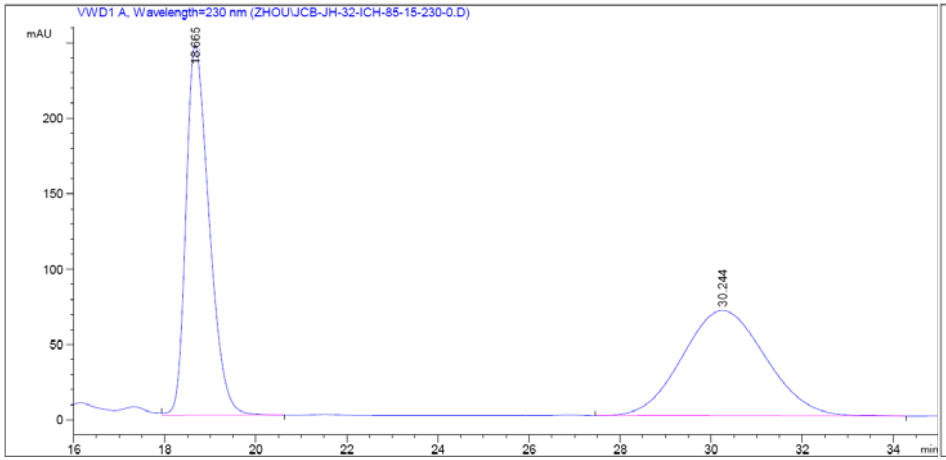


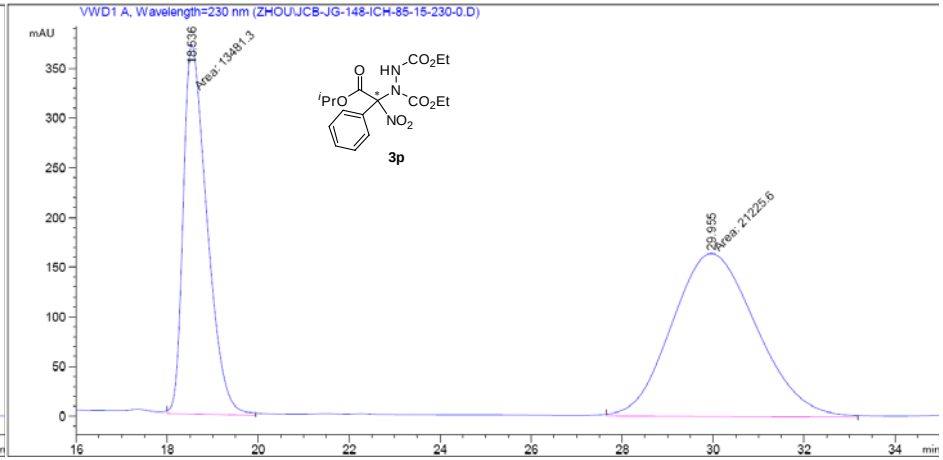
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.78	n.a.	378.453	670.462	49.28	n.a.	BMB*
2	25.34	n.a.	232.305	690.144	50.72	n.a.	BMB
Total:			610.758	1360.605	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.85	n.a.	10.211	18.353	7.28	n.a.	BMB*
2	25.51	n.a.	78.061	233.765	92.72	n.a.	BMB
Total:			88.272	252.118	100.00	0.000	

HPLC analysis of the mixture of racemic and chiral compound 3p obtained. (For comparison).

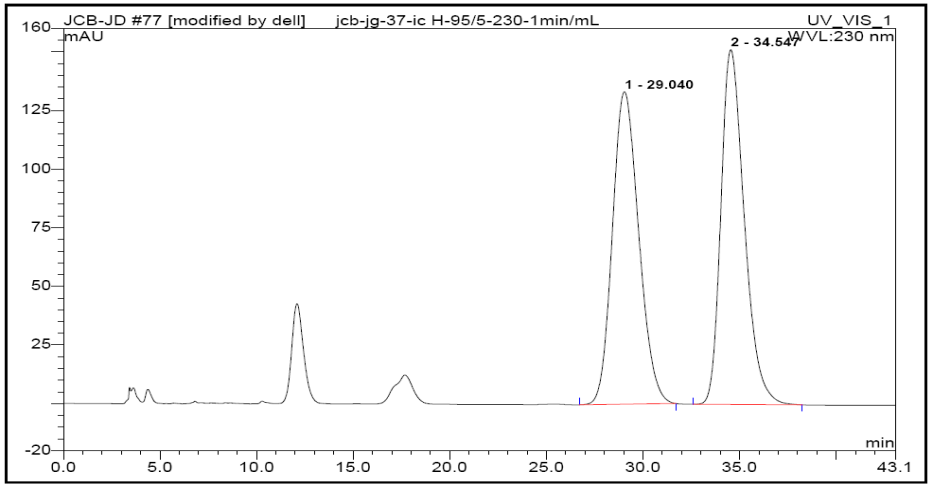




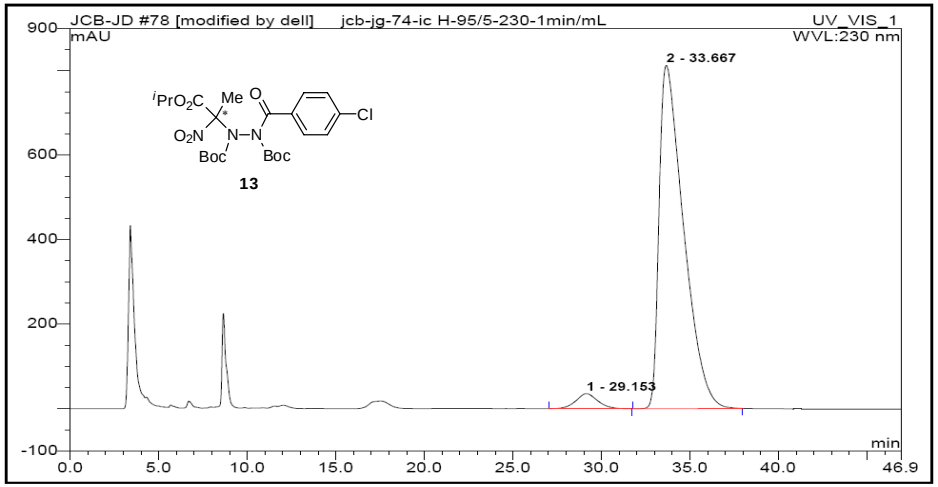
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.665	VB	0.5450	8699.14648	245.17503	49.4284
2	30.244	VB	1.9693	8900.35938	69.88151	50.5716
Totals :				1.75995e4	315.05654	

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.536	MM	0.6055	1.34813e4	371.08737	38.8432
2	29.955	MM	2.1586	2.12256e4	163.88052	61.1568
Totals :				3.47069e4	534.96790	

HPLC analysis of the mixture of racemic and chiral compound 5 obtained. (For comparison).



No.	Ret.Time min		Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	29.04	n.a.		133.176	210.468	49.79	n.a.	BMB*
2	34.55	n.a.		151.240	212.225	50.21	n.a.	BMB*
Total:				284.416	422.692	100.00	0.000	



No.	Ret.Time min		Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	29.15	n.a.		35.483	50.060	3.71	n.a.	BMB*
2	33.67	n.a.		812.545	1299.178	96.29	n.a.	BMB*
Total:				848.029	1349.238	100.00	0.000	