Supporting Information

Copper(II)-Mediated *O*-Arylation of Protected Serines and Threonines

Mirna El Khatib,[§] Gary A. Molander [§]*

[§] Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 S. 34th St., Philadelphia, Pennsylvania 19104-6323, United States

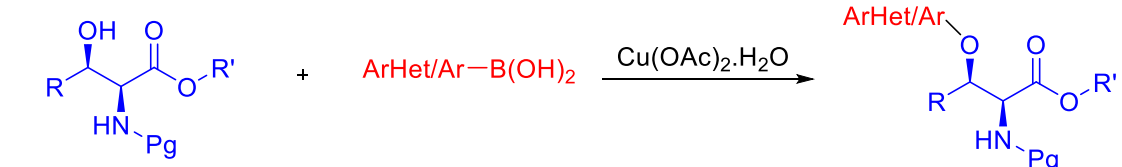
*gmolandr@sas.upenn.edu

Supporting Information-

Experimental Section

General. All known compounds were characterized by ^{1}H and ^{13}C NMR and melting point determination (for solids) and compared with literature values. All new compounds were characterized by ^{1}H, ^{13}C, ^{19}F NMR spectra, high-resolution mass spectrometry (HRMS), and melting point determination (for solids). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at 500.4, 125.8, and 470.8 MHz, respectively. Melting points (°C) are uncorrected. HRMS (CI) data were obtained in positive mode, using ethane as the ionizing gas. HRMS (ESI) data were obtained in positive or negative mode. Reactions were performed using Biotage microwave vials. Reactions were monitored by thin-layer chromatography carried out on silica plates using UV-light for visualization. Chromatography was performed on a Combiflash Rf 200 equipped with an integrated evaporative light scattering detector (ELSD) and UV-Vis using hexanes and ethyl acetate as eluent.

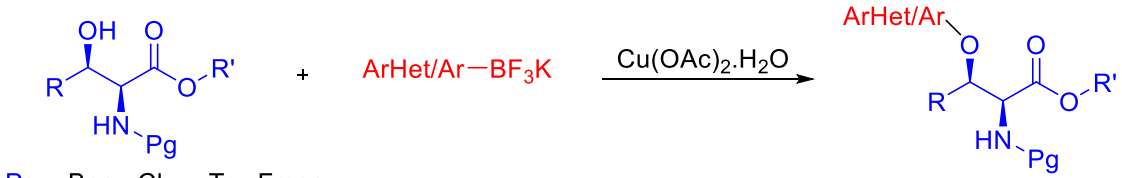
General procedure for Chan-Lam cross coupling reaction of serine and threonine with aryl- and heteroarylboronic acids.



Pg = Boc-, Cbz-, Tr-, Fmoc-
R = H (L-Ser), CH_3 (L-Thr)

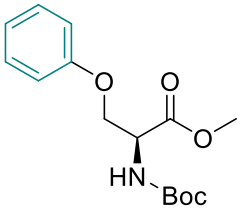
To the aryl/heteroarylboronic acid (1 mmol), Pg-Ser-OR' (or Pg-Thr-OR', 1 mmol), and DMAP (24 mg, 20 mol %) was added $Cu(OAc)_2 \cdot H_2O$ (20 mg, 10 mol %) in a glass Biotage vial equipped with a magnetic stirring bar. CH_2Cl_2 (3.5 mL, 0.275 M) was added and the reaction was stirred overnight at rt (monitored by TLC). The suspension was then concentrated under reduced pressure and purified by Combiflash column chromatography using EtOAc and hexanes to obtain the desired product. The product was characterized by spectroscopic techniques.

General procedure for Chan-Lam cross coupling reaction of serine and threonine with aryl- and heteroaryltrifluoroborates.



Pg = Boc-, Cbz-, Tr-, Fmoc-
R = H (L-Ser), CH_3 (L-Thr)

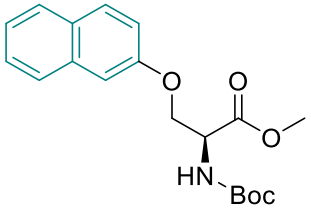
To the aryl/heteroaryltrifluoroborate (1 mmol), Pg-Ser-OR' (or Pg-Thr-OR', 1 mmol), and DMAP (24 mg, 20 mol %) was added $Cu(OAc)_2 \cdot H_2O$ (20 mg, 10 mol %) in a glass Biotage vial equipped with a magnetic stirring bar. CH_2Cl_2 (3.5 mL, 0.275 M) and H_2O (~0.1 mL, 10 mol %) was added and the reaction was stirred overnight at rt (monitored by TLC). The suspension was then concentrated under reduced pressure and purified by Combiflash column chromatography using EtOAc and hexanes to obtain the desired product. The product was characterized by spectroscopic techniques.



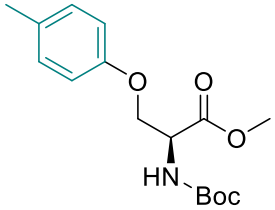
Methyl *N*-(*tert*-butoxycarbonyl)-*O*-phenyl-L-serinate (3a). Obtained from the aryl/heteroarylboronic acid [X_n = $B(OH)_2$] as a colorless oil (251 mg, 85%); $[\alpha]_D^{20}$ +7.0 (*c* 0.23, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, J = 7.8 Hz, 2H), 6.98 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 8.0 Hz, 2H), 5.51 (d, J = 8.5 Hz, 1H), 4.67 (d, J = 9.0 Hz, 1H), 4.40 (dd, J = 9.5, 3.0 Hz, 1H), 4.20 (dd, J = 9.0, 3.0 Hz, 1H), 3.77 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.7, 129.7, 121.6, 114.8, 68.4, 53.7, 52.8, 28.5; HRMS (TOF MS ES+) *m/z* calcd. for $C_{15}H_{21}NO_5Na$ $[M+Na]^+$ 318.1317, found 318.1315.

From the aryl/heteroaryltrifluoroborate [X_n = BF_3K]: (257 mg, 87%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 - 7.25 (m, 2H), 6.97 (t, J = 7.5 Hz, 1H), 6.88 (dd, J = 8.5, 1.0 Hz, 2H), 5.50 (d, J = 8.0 Hz, 1H), 4.66 (d, J = 8.5 Hz, 1H), 4.39 (dd, J = 9.5, 2.0 Hz, 1H), 4.20 (d, J

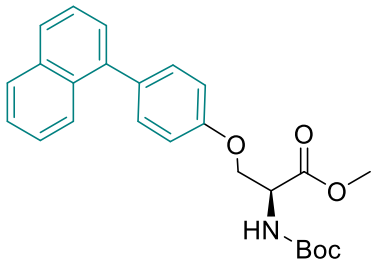
= 9.5, 3.0 Hz, 1H), 3.77 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.7, 158.4, 129.7, 121.6, 114.8, 80.4, 68.4, 53.7, 52.8, 28.5.



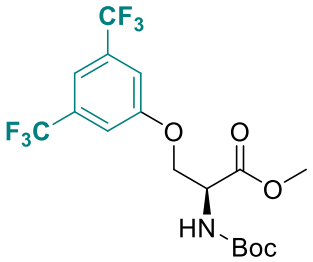
Methyl *N*-(*tert*-butoxycarbonyl)-*O*-(naphthalen-2-yl)-L-serinate (3b). Obtained from the aryl/heteroarylboronic acid [$X_n = B(OH)_2$] as a yellow oil (328 mg, 95%); $[\alpha]_D^{20}$ +35.4 (*c* 2.05, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.69 (m, 3H), 7.45 – 7.41 (m, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 2.5 Hz, 2H), 5.58 (d, *J* = 8.5 Hz, 1H), 4.73 (d, *J* = 6.0 Hz, 1H), 4.50 (d, *J* = 8.5 Hz, 1H), 4.32 (d, *J* = 8.5 Hz, 1H), 3.76 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.7, 156.2, 155.6, 134.4, 129.6, 129.4, 127.7, 126.9, 126.6, 124.1, 118.6, 107.2, 80.4, 68.4, 53.7, 52.8, 28.4; HRMS (TOF MS ES+) *m/z* calcd. for $C_{19}H_{23}NO_5Na$ $[M]^+$ 368.1474, found 368.1475



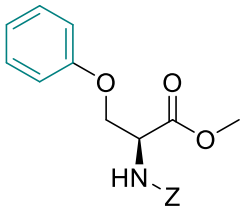
Methyl *N*-(*tert*-butoxycarbonyl)-*O*-(*p*-tolyl)-L-serinate (3c). Obtained from the aryl/heteroaryltrifluoroborate [$X_n = BF_3K$] as a colorless oil (254 mg, 82%); $[\alpha]_D^{20}$ +8.4 (*c* 2.52, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 5.51 (d, *J* = 8.0 Hz, 1H), 5.01 (s, 1H), 4.64 (d, *J* = 9.0 Hz, 1H), 4.36 (dd, *J* = 9.0, 2.0 Hz, 1H), 4.16 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.75 (s, 3H), 2.28 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.7, 156.2, 130.0, 129.9, 115.1, 114.5, 80.3, 68.4, 53.6, 52.7, 28.3, 20.5; HRMS (TOF MS ES+) *m/z* calcd. for $C_{16}H_{23}NO_5Na$ $[M+Na]^+$ 332.1474, found 332.1474.



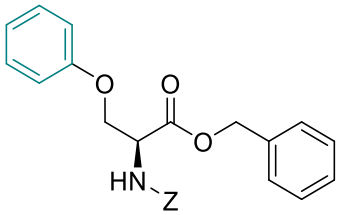
Methyl *N*-(*tert*-butoxycarbonyl)-*O*-(4-(naphthalen-1-yl)phenyl)-L-serinate (3d). Obtained from the aryl/heteroarylboronic acid [X_n = $B(OH)_2$] as a yellow transparent oil (337 mg, 80%); $[\alpha]_D^{20}$ +8.1 (*c* 1.27, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (t, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.5, 1H), 7.53 - 7.46 (m, 2H), 7.43-7.37 (m, 4H), 7.01 (d, *J* = 8.5 Hz, 2H), 5.55 (d, *J* = 8.5 Hz, 1H), 4.72 (d, *J* = 8.5 Hz, 1H), 4.49 (dd, *J* = 9.0, 2.0 Hz, 1H), 4.30 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.81 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.7, 157.8, 155.6, 139.8, 134.2, 134.0, 131.9, 131.3, 128.4, 127.6, 127.0, 126.1, 126.1, 125.9, 125.5, 125.5, 114.6, 114.5, 80.4, 68.6, 53.8, 52.9, 28.5; HRMS (TOF MS ES+) *m/z* calcd. for $C_{27}H_{27}N_2O_5Na$ $[M+Na]^+$ 444.1787, found 444.1790.



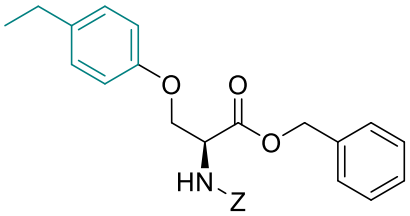
Methyl *O*-[3,5-bis(trifluoromethyl)phenyl]-*N*-(*tert*-butoxycarbonyl)-L-serinate (3e). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a transparent colorless oil (151 mg, 35%); $[\alpha]_D^{20}$ +3.5 (*c* 2.00, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 - 7.48 (m, 1H), 7.35 - 7.28 (m, 2H), 5.61 - 5.55 (m, 1H), 4.73 (d, *J* = 3.0 Hz, 1H), 4.49 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.33 (dd, *J* = 9.0, 2.0 Hz, 1H), 3.81 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.1, 158.9, 155.5, 134.2, 133.2 (q, *J* = 33.8 Hz), 131.2, 126.4, 124.2, 122.1, 119.9, 115.3, 115.2, 80.9, 69.2, 53.5, 53.1, 28.4; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ – 63.1; HRMS (TOF MS ES+) *m/z* calcd. for $C_{17}H_{19}NO_5NaF_6$ $[M+Na]^+$ 454.1065, found 454.1062.



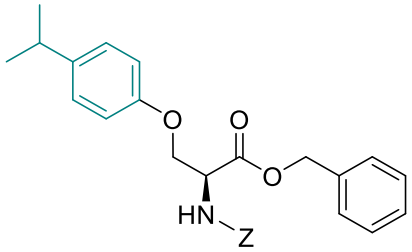
Methyl *N*-[(benzyloxy)carbonyl]-*O*-phenyl-L-serinate (3f). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a creamy white solid (247 mg, 75%). mp: 79-80 °C; $[\alpha]_D^{20}$ +7.3 (*c* 0.15, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 - 7.31 (m, 5H), 7.29 - 7.27 (m, 2H), 6.97 (t, *J* = 7.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 2H), 5.74 (d, *J* = 8.5 Hz, 1H), 5.14 (s, 2H), 4.72 (d, *J* = 9.0 Hz, 1H), 4.42 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.24 (dd, *J* = 9.5, 3.6 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.3, 158.2, 156.1, 136.2, 129.7, 128.7, 128.4, 128.3, 121.7, 114.8, 68.1, 67.4, 54.1, 53.0, 29.9; HRMS (TOF MS ES+) *m/z* calcd. for $C_{18}H_{19}NO_5Na$ $[M+Na]^+$ 352.1161, found 352.1164.



Benzyl *N*-[(benzyloxy)carbonyl]-*O*-phenyl-L-serinate (3g).[1] Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a colorless solid (365 mg, 90%). mp: 90-91 °C; $[\alpha]_D^{20}$ +0.2 (*c* 1.70, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 - 7.32 (m, 5H), 7.31 - 7.28 (m, 6H), 7.25 - 7.24 (m, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 2H), 5.77 (d, *J* = 8.5 Hz, 1H), 5.21 (d, *J* = 3.0 Hz, 2H), 5.13 (s, 2H), 4.77 (d, *J* = 8.5 Hz, 1H), 4.44 (dd, *J* = 9.5, 2.5 Hz, 1H), 4.25 (dd, *J* = 9.5, 3.0 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.8, 158.2, 156.1, 136.2, 135.3, 129.7, 128.7, 128.7, 128.5, 128.4, 128.3, 128.2, 121.7, 114.8, 68.2, 67.7, 67.4, 54.3; HRMS (TOF MS ES+) *m/z* calcd. for $C_{24}H_{23}NO_5Na$ $[M+Na]^+$ 428.1474, found 428.1476.

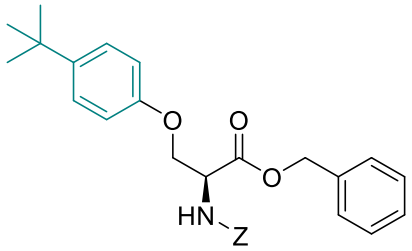


Benzyl *N*-[(benzyloxy)carbonyl]-*O*-(4-ethylphenyl)-L-serinate (3h). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a white solid (399 mg, 92%); mp: 64-65 °C; $[\alpha]_D^{20}$ +6.0 (*c* 7.56, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 - 7.20 (m, 10H), 7.09 - 7.03 (m, 2H), 6.75 - 6.68 (m, 2H), 5.80 - 5.76 (m, 1H), 5.18 (d, *J* = 15.0 Hz, 2H), 5.11 (d, *J* = 15.5 Hz, 2H), 4.74 (dd, *J* = 8.5, 3.0 Hz, 1H), 4.41 (d, *J* = 9.0 Hz, 1H), 4.22 - 4.18 (m, 1H), 2.58 (q, *J* = 7.5 Hz, 2H), 1.20 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.8, 156.3, 156.1, 137.5, 136.3, 135.3, 128.9, 128.7, 128.5, 128.3, 128.2, 128.2, 114.7, 68.4, 67.6, 67.3, 54.3, 28.1, 16.0; HRMS (TOF MS ES+) *m/z* calcd. for $C_{26}H_{27}NO_5Na$ $[M+Na]^+$ 456.1787, found 456.1791.

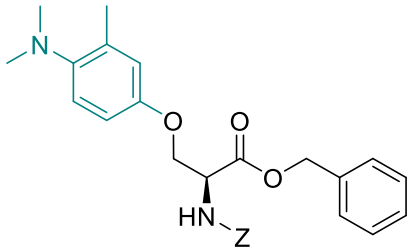


Benzyl *N*-[(benzyloxy)carbonyl]-*O*-(4-isopropylphenyl)-L-serinate (3i). Obtained from the aryl/heteroarylboronic acid [X_n = $B(OH)_2$] as a white-cream solid (380 mg, 85%); mp: 69-70 °C; $[\alpha]_D^{20}$ +5.2 (*c* 1.46, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 - 7.31 (m, 5H), 7.27 - 7.26 (m, 5H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 5.83 (d, *J* = 8.5 Hz, 2H), 5.18 (s, 2H), 5.12 - 5.10 (m, 2H), 4.74 (dd, *J* = 8.5, 3.0 Hz, 1H), 4.40 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.20 (dd, *J* = 9.0, 3.0 Hz, 1H), 2.84 (heptet, *J* = 7.0 Hz, 1H), 1.21 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.8, 156.2, 156.0, 142.1, 136.2, 135.2, 128.6, 128.4, 128.3, 128.2, 128.1, 127.4, 127.0, 114.5, 68.3, 67.5, 67.2, 54.2, 33.4, 24.3; HRMS (TOF MS ES+) *m/z* calcd. for $C_{27}H_{30}NO_5$ $[M+H]^+$ 448.2124, found 448.2136.

From the aryl/heteroaryltrifluoroborate [$X_n = BF_3K$] as a white-cream solid (394 mg, 88%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 5H), 7.31 - 7.29 (m, 5H), 7.25 (s, 1H), 7.11 (d, J = 8.5 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 5.77 (d, J = 8.5 Hz, 1H), 5.20 (s, 2H), 5.12 (s, 2H), 4.75 (d, J = 9.0 Hz, 1H), 4.42 (dd, J = 9.5, 2.5 Hz, 1H), 4.22 (dd, J = 9.5, 3.0 Hz, 1H), 2.85 (heptet, J = 7.0 Hz, 1H), 1.21 (d, J = 7.0 Hz, 6H).

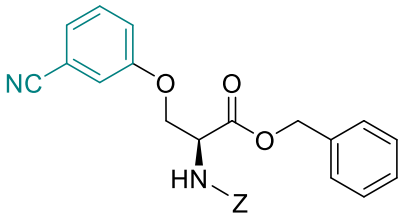


Benzyl *N*-[(benzyloxy)carbonyl]-*O*-[4-(tert-butyl)phenyl]-L-serinate (3j). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a white solid (433 mg, 94%); mp: 62-63 °C; $[\alpha]_D^{20}$ +10.6 (*c* 2.16, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 - 7.30 (m, 5H), 7.29 - 7.24 (m, 7H), 6.76 (d, J = 8.5 Hz, 2H), 5.78 (d, J = 8.5 Hz, 1H), 5.21 - 518 (m, 2H), 5.13 (s, 2H), 4.75 (dd, J = 6.0, 2.5 Hz, 1H), 4.44 - 4.21 (m, 1H), 4.22 (dd, J = 9.0, 3.0 Hz, 1H), 1.29 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.8, 156.1, 155.9, 144.4, 136.2, 135.3, 128.7, 128.5, 128.4, 128.2, 128.2, 126.4, 114.2, 68.2, 67.6, 67.3, 54.3, 34.2, 31.6; HRMS (TOF MS ES+) *m/z* calcd. for $C_{28}H_{31}NO_5Na$ $[M+Na]^+$ 484.2124, found 484.2115.

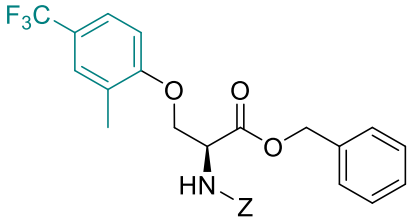


Benzyl *N*-[(benzyloxy)carbonyl]-*O*-[4-(dimethylamino)-3-methylphenyl]-L-serinate (3k). Obtained from the aryl/heteroaryltrifluoroborate [$X_n = BF_3K$] as an orange viscous oil (417 mg, 90%); $[\alpha]_D^{20}$ +1.3 (*c* 3.46, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 - 7.32 (m, 5H), 7.31 - 7.28 (m, 5H), 6.94 (dd, J = 8.5, 4.0 Hz, 1H), 6.65 (d, J = 2.5 Hz, 1H), 6.61 (dd, J = 9.0, 2.5 Hz,

1H), 5.77 (d, J = 8.0 Hz, 1H), 5.20 (br s, 2H), 5.12 (br s, 2H), 4.73 (d, J = 8.5 Hz, 1H), 4.38 (d, J = 9.0, 2.5 Hz, 1H), 4.18 (d, J = 9.0, 3.0 Hz, 1H), 2.62 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.8, 156.1, 153.8, 147.2, 136.3, 135.3, 134.2, 128.7, 128.5, 128.3, 128.2, 119.6, 117.7, 112.1, 68.5, 67.6, 67.3, 54.4, 44.9, 18.3; HRMS (TOF MS ES+) *m/z* calcd. for $C_{27}H_{31}N_2O_5$ $[M+H]^+$ 463.2233, found 463.2241.

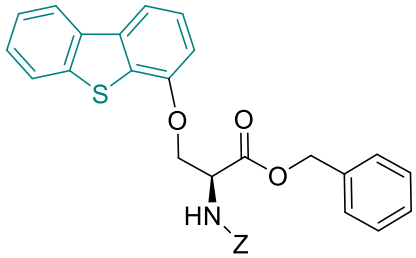


Benzyl *N*-[(benzyloxy)carbonyl]-*O*-(3-cyanophenyl)-L-serinate (3l). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a white solid (319 mg, 74%). mp: 95-96 °C; $[\alpha]_D^{20}$ +3.0 (*c* 0.99, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 - 7.32 (m, 6H), 7.30 - 7.24 (m, 5H), 7.01 (d, J = 9.0 Hz, 1H), 5.74 (d, J = 7.5 Hz, 1H), 5.28 - 5.16 (m, 2H), 5.13 (s, 2H), 4.78 (d, J = 8.0 Hz, 1H), 4.42 (dd, J = 9.0, 2.5 Hz, 1H), 4.27 (dd, J = 9.5, 3.0 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.3, 158.2, 155.9, 136.1, 135.1, 130.6, 128.8, 128.7, 128.4, 128.3, 125.5, 119.6, 118.5, 118.1, 113.5, 68.7, 67.9, 67.5, 5.0, 29.8; HRMS (TOF MS ES+) *m/z* calcd. for $C_{25}H_{22}N_2O_5Na$ $[M+Na]^+$ 453.1426, found 453.1423.

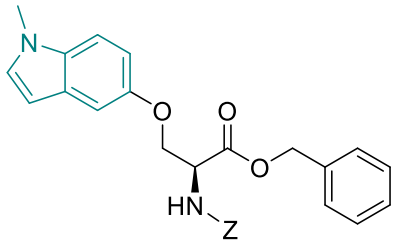


Benzyl *N*-[(benzyloxy)carbonyl]-*O*-[2-methyl-4-(trifluoromethyl)phenyl]-L-serinate (3m). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a sticky oil (263 mg, 54%). $[\alpha]_D^{20}$ +8.3 (*c* 0.64, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 - 7.33 (m, 6H), 7.26 - 7.23 (m, 6H), 6.78 - 6.75 (m, 1H), 5.73 (d, J = 6.0 Hz, 1H), 5.25 - 5.15 (m, 2H), 5.14 - 5.11 (m, 2H), 4.82 - 4.79 (m, 1H), 4.45 - 4.41 (m, 1H), 4.33 - 4.31 (m, 1H), 2.04 (d, J = 6.5 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.0, 156.1, 152.5,

136.3, 135.4, 132.7, 129.7, 128.8, 128.6, 128.6, 128.4, 128.3, 128.2, 128.2, 112.3, 110.0, 104.6, 100.6, 69.4, 67.5, 67.2, 54.5, 33.1; ^{19}F NMR (470.8 MHz, $CDCl_3$) δ -61.60; HRMS (TOF MS ES-) *m/z* calcd. for $C_{26}H_{24}NO_5F_3Cl$ $[M+Cl]^+$ 522.1295, found 522.1274.

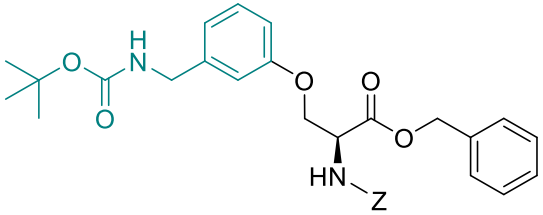


Benzyl *N*-[(benzyloxy)carbonyl]-*O*-{dibenzo[b,d]thiophen-4-yl}-L-serinate (3n). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as an orange solid (72 mg, 14%). mp: 115-116 °C; $[\alpha]_D^{20}$ +7.1 (*c* 2.20, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 - 8.12 (m, 1H), 7.85 - 7.83 (m, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.47 - 7.45 (m, 2H), 7.38 - 7.32 (m, 8H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.21 - 7.20 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 5.89 (d, *J* = 8.0 Hz, 1H), 5.25 - 5.20 (m, 2H), 5.14 (d, *J* = 8.5 Hz, 2H), 4.87 (d, *J* = 8.0 Hz, 1H), 4.64 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.51 (dd, *J* = 9.5, 3.0 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.5, 160.2, 156.1, 153.2, 140.0, 137.6, 136.2, 135.9, 135.1, 128.8, 128.7, 128.7, 128.5, 128.4, 128.3, 127.0, 125.8, 124.5, 123.1, 122.1, 115.2, 108.4, 69.1, 67.9, 67.4, 54.4, HRMS (TOF MS ES-) *m/z* calcd. for $C_{30}H_{26}NO_5S$ $[M+H]^+$ 512.1532, found 512.1528.

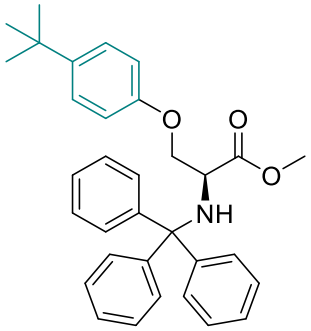


Benzyl *N*-[(benzyloxy)carbonyl]-*O*-(1-methyl-1*H*-indol-5-yl)-L-serinate (3o). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a brown solid (114.6 mg, 25%). mp: 80-82 °C; $[\alpha]_D^{20}$ +2.6 (*c* 4.73, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 - 7.29 (m, 9H), 7.16 (d, *J* = 9.0, 1H), 7.00 (d, *J* = 3.0 Hz, 2H), 6.78 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.36 (d, *J* = 2.5 Hz, 1H), 5.84 (d, *J* = 8.5 Hz, 1H), 5.25-5.18 (m, 2H), 5.13 (s, 2H), 4.76 (dd, *J* = 6.0, 2.5 Hz, 1H), 4.47 (dd, *J* = 9.5, 3.0 Hz, 1H), 4.26 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.72

(s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.0,156.1, 152.5, 136.3, 135.4, 132.7, 129.7, 128.8, 128.6, 128.6, 128.4, 128.3, 128.2, 128.2, 112.3, 110.0, 104.6, 100.6, 69.4, 67.5, 67.2, 54.5, 33.1; HRMS (TOF MS ES+) *m/z* calcd. for $C_{27}H_{26}N_2O_5Na$ $[M+Na]^+$ 481.1739, found 481.1738.

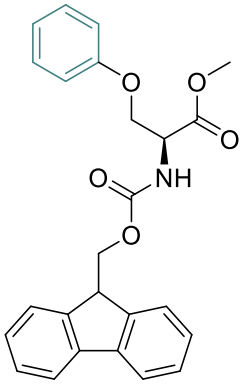


Benzyl *N*-[(benzyloxy)carbonyl]-*O*-(3-{[(*tert*-butoxycarbonyl)amino)methyl]phenyl}-L-serinate (3p). Obtained from the aryl/heteroarylboronic acid [X_n = $B(OH)_2$] as a colorless viscous oil (342 mg, 64%); $[\alpha]_D^{20}$ +20.0 (*c* 0.05, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 - 7.18 (m, 11H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.73 - 6.66 (m, 2H), 5.75 - 5.73 (m, 1H), 5.30 - 5.16 (m, 2H), 5.17 - 5.08 (m, 2H), 4.77 - 4.72 (m, 2H), 4.51 - 4.40 (m, 1H), 4.25 - 4.22 (m, 2H), 1.26 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.7,158.5, 156.1, 156.0, 140.8, 136.2, 135.3, 129.9, 128.8, 128.7, 128.6, 128.4, 128.4, 128.3, 120.7, 113.9, 113.5, 79.7, 68.3, 67.7, 67.4, 54.2, 44.7, 28.6; HRMS (TOF MS ES+) *m/z* calcd. for $C_{30}H_{34}N_2O_7Na$ $[M+Na]^+$ 557.2264, found 557.2259.

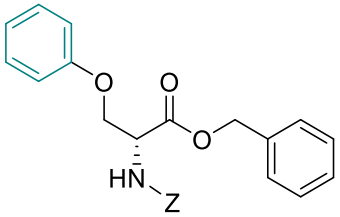


Methyl *O*-[4-(*tert*-butyl)phenyl]-*N*-trityl-L-serinate (3q). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a light clear oil (439 mg, 89%); $[\alpha]_D^{20}$ +43.7 (*c* 11.85, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.0 Hz, 5H), 7.29 (d, *J* = 8.5 Hz, 3H), 7.24 (t, *J* = 8.0 Hz, 6H), 7.17 (t, *J* = 7.5 Hz, 3H), 6.82 (d, *J* = 9.0 Hz, 2H), 4.23 (dd, *J* = 9.0, 5.0 Hz, 1H), 4.02 (dd, *J* = 9.5, 7.0

Hz, 1H), 3.75 - 3.70 (m, 1H), 3.20 (s, 3H), 2.89 (d, J = 10.5 Hz, 1H), 1.29 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 173.7, 156.4, 147.0, 145.9, 143.9, 128.9, 128.0, 127.4, 126.6, 126.3, 114.2, 71.1, 70.6, 56.4, 52.0, 34.2, 31.7; HRMS (TOF MS ES+) *m/z* calcd. for $C_{33}H_{34}NO_3$ $[M-H]^+$ 492.2539, found 492.2539.

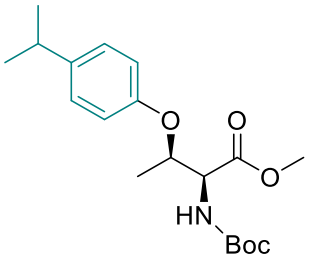


Methyl N-[(9*H*-fluoren-9-yl)methoxy)carbonyl]-*O*-phenyl-L-serinate (3r). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a white solid (153 mg, 41%). mp: 121-122 °C; $[\alpha]_D^{20}$ +12.4 (*c* 0.17, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79-7.76 (m, 2H), 7.64-7.59 (m, 2H), 7.39 (dd, J = 12.5, 6.0 Hz, 2H), 7.32 - 7.30 (m, 5H), 7.00 (t, J = 6.5 Hz, 1H), 6.91 (d, J = 7.5 Hz, 2H), 5.79 (d, J = 7.5 Hz, 1H), 4.74 (d, J = 7.0 Hz, 1H), 4.44 - 4.40 (m, 3H), 4.25 (d, J = 8.0 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.4, 158.3, 156.1, 144.0, 143.8, 141.4, 129.7, 127.9, 127.2, 125.3, 121.8, 120.1, 114.8, 68.1, 67.5, 54.1, 53.0, 47.3; HRMS (TOF MS ES+) *m/z* calcd. for $C_{25}H_{23}NO_5Na$ $[M+Na]^+$ 440.1474, found 440.1477.



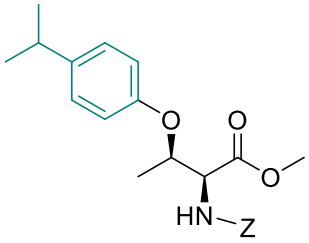
Benzyl *N*-[(benzyloxy)carbonyl]-*O*-phenyl-D-serinate (3s). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a clear oil (337 mg, 83%); $[\alpha]_D^{20}$ +4.3 (*c* 0.46, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 5H), 7.30 - 7.25 (m, 6H), 7.24 (s,

1H), 6.97 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 8.0 Hz, 2H), 5.76 (d, J = 8.5 Hz, 1H), 5.23 (d, J = 8.5 Hz, 1H), 5.20 (d, J = 12.5 Hz, 1H), 5.13 (s, 2H), 4.76 (dd, J = 6.0, 2.5 Hz, 1H), 4.44 (dd, J = 9.0, 2.5 Hz, 1H), 4.25 (dd, J = 9.0, 2.5 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.8, 158.2, 156.1, 149.9, 136.2, 135.3, 129.6, 128.7, 128.5, 128.4, 128.2, 128.2, 121.7, 114.8, 68.2, 67.6, 67.3, 54.3; HRMS (TOF MS ES+) *m/z* calcd. for $C_{24}H_{23}NO_5Na$ $[M+Na]^+$ 428.1474, found 428.1472.

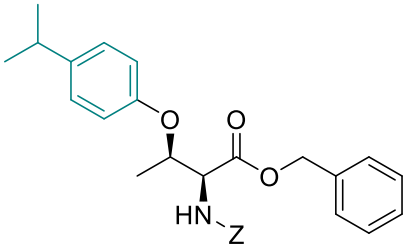


Methyl *N*-(*tert*-butoxycarbonyl)-*O*-(4-isopropylphenyl)-L-threoninate (5a). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a yellow oil (260 mg, 74%); $[\alpha]_D^{20}$ +21.6 (*c* 0.44, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, J = 8.5 Hz, 2H), 6.80 (d, J = 8.5 Hz, 2H), 5.40 (d, J = 9.5 Hz, 1H), 4.93 - 4.89 (m, 1H), 4.47 (dd, J = 9.5, 2.0 Hz, 1H), 3.66 (s, 3H), 2.85 (heptet, J = 7.0 Hz, 1H), 1.49 (s, 9H), 1.33 (d, J = 6.0 Hz, 3H), 1.21 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 171.2, 156.3, 155.2, 142.3, 127.4, 116.5, 80.2, 74.6, 58.2, 52.6, 33.4, 28.5, 24.3, 16.5; HRMS (TOF MS ES+) *m/z* calcd. for $C_{19}H_{29}NO_5Na$ $[M+Na]^+$ 374.1943, found 374.1943.

From the aryl/heteroarylboronic acid [X_n = $B(OH)_2$]: (245 mg, 70%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 8.0 Hz, 2H), 4.41 (d, J = 9.5 Hz, 1H), 4.92 - 4.90 (m, 1H), 4.72 (d, J = 10.0 Hz, 1H), 3.67 (s, 3H), 2.85 (heptet, J = 7.0 Hz, 1H), 1.49 (s, 9H), 1.33 (d, J = 6.0 Hz, 3H), 1.21 (dd, J = 7.0, 1.0 Hz, 6H).

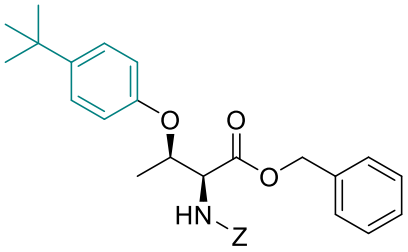


Methyl *N*-[(benzyloxy)carbonyl]-*O*-(4-isopropylphenyl)-L-threoninate (5b). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a white solid (304 mg, 79%); mp: 71-73 °C; $[\alpha]_D^{20}$ +37.6 (*c* 0.45, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 - 7.36 (m, 4H), 7.34 - 7.31 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 5.64 (d, *J* = 9.0 Hz, 1H), 5.17 (s, 2H), 4.93 - 4.90 (m, 1H), 4.53 (d, *J* = 9.5 Hz, 1H), 3.67 (s, 3H), 2.83 (dd, *J* = 13.5, 7.0 Hz, 1H), 1.32 (t, *J* = 6.0 Hz, 3H), 1.20 (t, *J* = 6.5 Hz, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.9, 156.9, 155.1, 142.5, 136.4, 128.7, 128.4, 128.2, 127.5, 116.5, 74.5, 67.4, 58.6, 52.7, 33.4, 24.3, 16.6, 16.5; HRMS (TOF MS ES+) *m/z* calcd. for $C_{22}H_{27}NO_5$ $[M+Na]^+$ 408.1787, found 408.1769.

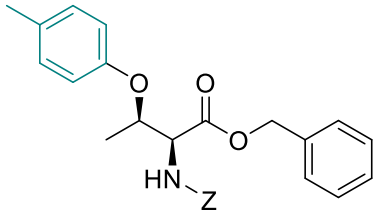


Benzyl *N*-[(benzyloxy)carbonyl]-*O*-(4-isopropylphenyl)-L-threoninate (5c). Obtained from the aryl/heteroarylboronic acid [X_n = $B(OH)_2$] as a yellow solid (342 mg, 74%). mp: 62-63 °C; $[\alpha]_D^{20}$ +4.7 (*c* 3.26, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.32 (m, 6H), 7.32-7.21 (m, 4H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 5.67 (d, *J* = 9.5 Hz, 1H), 5.16 (s, 2H), 5.14 - 5.03 (m, 2H), 4.95 - 4.91 (m, 1H), 4.58 (dd, *J* = 9.5, 2.0 Hz, 1H), 2.85 (heptet, *J* = 7.0 Hz, 1H), 1.32 (d, *J* = 6.5 Hz, 3H), 1.22 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.3, 156.9, 155.1, 142.4, 136.4, 135.3, 128.7, 128.6, 128.4, 128.4, 128.2, 127.5, 116.4, 74.5, 67.5, 67.4, 58.8, 33.5, 24.3, 16.5; HRMS (TOF MS ES-) *m/z* calcd. for $C_{28}H_{30}NO_5$ $[M-H]^-$ 460.2124, found 460.2102.

From the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a yellow solid (328 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 - 7.34 (m, 5H), 7.25 - 7.23 (m, 4H), 7.17 - 7.15 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 5.67 (d, *J* = 9.5 Hz, 1H), 5.16 (s, 2H), 5.11 (d, *J* = 12.0 Hz, 1H), 5.05 (d, *J* = 12.0 Hz, 1H), 4.94 - 4.92 (m, 1H), 4.58 (dd, *J* = 10.0, 2.5 Hz, 1H), 2.85 (heptet, *J* = 7.0 Hz, 1H), 1.33 (d, *J* = 6.5 Hz, 3H), 1.22 (d, *J* = 7.0 Hz, 6H).

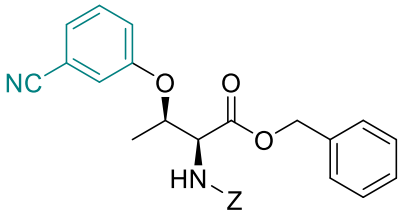


Benzyl *N*-[(benzyloxy)carbonyl]-*O*-[4-(*tert*-butyl)phenyl]-L-threoninate (5d). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a white solid (400 mg, 84%). mp: 66-67 °C; $[\alpha]_D^{20}$ +4.3 (*c* 3.96, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 - 7.31 (m, 5H), 7.25 - 7.20 (m, 5H), 7.15 (d, *J* = 6.5 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 5.71 (d, *J* = 9.5 Hz, 1H), 5.16 (s, 2H), 5.12 - 5.02 (m, 2H), 4.95 (d, *J* = 6.0 Hz, 1H), 4.59 (d, *J* = 9.5 Hz, 1H), 1.33 (d, *J* = 6.5 Hz, 3H), 1.29 (s, 9H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.2, 156.9, 154.8, 144.5, 136.3, 135.2, 128.7, 128.6, 128.4, 128.3, 128.2, 126.4, 115.8, 74.3, 67.5, 67.4, 58.7, 34.2, 31.7, 31.6, 22.8, 16.5, 14.2 ; HRMS (TOF MS ES+) *m/z* calcd. for $C_{29}H_{34}NO_5$ $[M+H]^+$ 476.2437, found 476.2435.

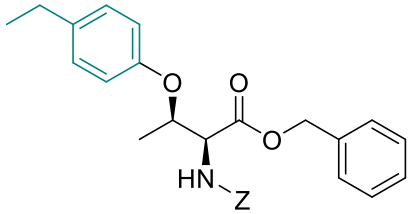


Benzyl *N*-[(benzyloxy)carbonyl]-*O*-(*p*-tolyl)-L-threoninate (5e). Obtained from the aryl/heteroarylboronic acid [X_n = $B(OH)_2$] as a white solid (347 mg, 80%). mp: 42-43 °C; $[\alpha]_D^{20}$ +5.8 (*c* 4.34, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 - 7.32 (m, 5H), 7.27 - 7.23 (m, 3H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 2H), 5.70 (d, *J* = 9.5 Hz, 1H), 5.16 (s, 2H), 5.13 - 5.04 (m, 2H), 4.92 - 4.90 (m, 2H), 4.58 (d, *J* = 9.5 Hz, 1H), 2.27 (s, 3H), 1.31 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.2, 156.9, 154.9, 136.3, 135.2, 131.2, 130.1, 128.7, 128.6, 128.4, 128.3, 128.2, 127.1, 116.5, 74.6, 67.5, 67.4, 58.7, 20.6, 16.4; HRMS (TOF MS ES+) *m/z* calcd. for $C_{26}H_{27}NO_5Na$ $[M+Na]^+$ 456.1787, found 456.1783.

From the aryl/heteroaryltrifluoroborate [X_n = BF_3K]: (355 mg, 82%). mp: 42-43 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 - 7.32 (m, 5H), 7.28 - 7.25 (m, 3H), 7.18 (d, J = 7.5 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 6.70 (d, J = 8.0 Hz, 2H), 5.69 (d, J = 9.5 Hz, 1H), 5.16 (s, 2H), 5.13 - 5.04 (m, 2H), 4.93 - 4.91 (m, 1H), 4.58 (d, J = 9.5 Hz, 1H), 2.28 (s, 3H), 1.31 (d, J = 6.0 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.3, 156.9, 154.9, 136.3, 135.2, 131.2, 130.1, 128.7, 128.6, 128.5, 128.4, 128.2, 116.5, 74.6, 67.5, 67.4, 58.7, 20.7, 16.5; HRMS (TOF MS ES+) *m/z* calcd. for $C_{26}H_{27}NO_5Na$ $[M+Na]^+$ 456.1787, found 456.1791.

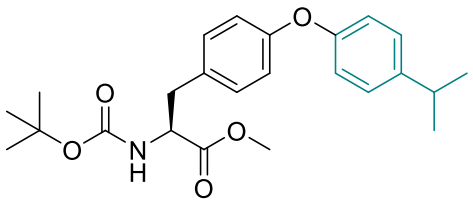


Benzyl *N*-[(benzyloxy)carbonyl]-*O*-(3-cyanophenyl)-L-threoninate (5f). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a yellow oil (311 mg, 70%). $[\alpha]_D^{20}$ +0.7 (*c* 1.98, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 7H), 7.25 – 7.22 (m, 3H), 7.18 (d, J = 7.5 Hz, 2H), 6.99 (d, J = 12.0 Hz, 2H), 5.62 (d, J = 9.5 Hz, 1H), 5.19 (d, J = 12.0 Hz, 1H), 5.17 (s, 2H), 5.04 (d, J = 12.0 Hz, 1H), 4.95 (dd, J = 6.0, 1.5 Hz, 1H), 4.63 (dd, J = 10.0, 2.0 Hz, 1H), 1.33 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 169.7, 157.1, 156.8, 136.2, 135.0, 130.6, 128.7, 128.7, 128.5, 128.5, 128.3, 125.5, 121.0, 119.3, 118.5, 113.6, 74.9, 67.7, 67.6, 58.3, 16.0; HRMS (TOF MS ES+) *m/z* calcd. for $C_{26}H_{24}N_2O_5Na$ $[M+Na]^+$ 467.1583, found 467.1594.

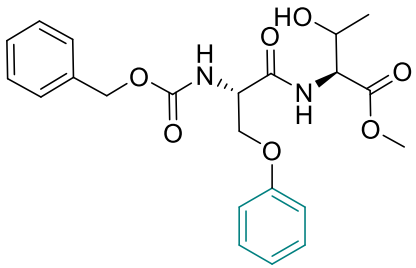


Benzyl *N*-(benzoyloxy)-*O*-(4-ethylphenyl)-L-threoninate (5g). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K] as a yellow oil (356 mg, 83%). $[\alpha]_D^{20}$ +0.6 (*c* 5.62, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 - 7.31 (m, 5H), 7.31 - 7.21 (m, 3H), 7.17 (d, J = 6.5 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 8.5 Hz, 2H), 5.68 (d, J = 9.5 Hz, 2H), 5.16 (s, 2H), 5.11 (d, J = 12.0 Hz, 1H),

5.05 (d, J = 12.5 Hz, 1H), 4.92 (dd, J = 6.5, 2.0 Hz, 1H), 4.58 (dd, J =10.0, 2.5 Hz, 1H), 2.57 (q, J = 8.0 Hz, 2H), 1.32 (d, J = 6.5 Hz, 3H), 1.20 (t, J =7.5 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 170.3, 156.9, 155.1, 137.7, 136.3, 135.3, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2, 116.6, 116.5, 74.6, 67.5, 67.4, 58.7, 28.1, 16.5, 15.9; HRMS (TOF MS ES+) *m/z* calcd. for $C_{27}H_{23}NO_5Na$ $[M+Na]^+$ 470.1943, found 470.1942.

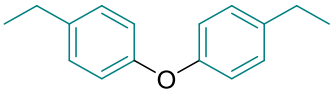


Methyl (*S*)-2-[(*tert*-butoxycarbonyl)amino]-3-[4-(4-isopropylphenoxy)phenyl]propanoate (9). Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K as a transparent yellow viscous oil (174 mg, 42%); $[\alpha]_D^{20}$ +28.8 (*c* 4.49, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, J = 8.5 Hz, 1H), 7.06 (d, J = 8.5 Hz, 1H), 6.96 (d, J = 8.5 Hz, 2H), 6.91 (dd, J= 8.5, 5.5 Hz, 2H), 6.74 (d, J = 7.5 Hz, 2H), 6.20 (s, 1H), 5.01 (d, J = 7.0 Hz, 1H), 4.55 (dd, J = 16.0, 7.5 Hz, 2H), 3.71 (s, 3H), 2.90 (heptet, J = 7.0 Hz, 1H), 1.42 (s, 9H), 1.25 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 172.5, 156.9, 155.4, 144.1, 130.6, 130.5, 127.7, 119.1, 118.6, 115.6, 80.2, 54.8, 52.3, 37.7, 33.6, 28.4, 24.2; HRMS (TOF MS ES+) *m/z* calcd. for $C_{24}H31NO_5Na$ $[M+Na]^+$ 436.2100, found 436.2102.



Methyl (2*S*)-2-[(*S*)-2-{[(benzyloxy)carbonyl]amino}-3-phenoxypropanamido]-3-hydroxybutanoate (7). Obtained from the aryl/heteroaryltrifluoroborate X_n = BF_3K, 2 equiv] as a clear yellow oil (95 mg, 22%); $[\alpha]_D^{20}$ +19.4 (*c* 1.28, CH_2Cl_2); ^{1}H NMR (500

MHz, $CDCl_3$) δ 7.39 - 7.31 (m, 5H), 7.29 - 7.25 (m, 1H), 7.17 (d, J = 9.0, 1H), 6.99 - 6.96 (m, 1H), 6.92 (d, J = 7.5 Hz, 2H), 5.81 (d, J = 6.5 Hz, 1H), 5.15 (br s, 2H), 4.65 - 4.60 (m, 2H), 4.47 - 4.45 (m, 1H), 4.37 - 4.35 (m, 1H), 4.10 - 4.07 (m, 1H), 3.69 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 171.0, 170.0, 157.9, 136.1, 129.8, 128.8, 128.5, 128.4, 121.9, 114.8, 68.2, 67.6, 57.6, 54.3, 52.8, 20.0; HRMS (TOF MS ES+) *m/z* calcd. for $C_{22}H_{26}N_2O_7Na$ $[M+Na]^+$ 453.1638, found 453.1636.

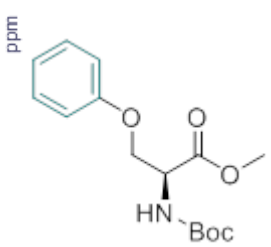


4,4'-Oxybis(ethylbenzene) (10).[2] Obtained from the aryl/heteroaryltrifluoroborate [X_n = BF_3K as a yellow clear oil (22.6 mg, 10%); The reaction in the absence of amino acid affords the same 4,4'-oxybis(ethylbenzene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, J = 8.5 Hz, 4H), 6.91 (d, J= 8.5 Hz, 4H), 2.61 (q, J = 8.0 Hz, 4H), 1.22 (t, J = 7.5 Hz, 6H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 155.6, 139.0, 129.1, 118.8, 28.3, 15.9; HRMS (TOF MS ES+) *m/z* calcd. for $C_{16}H_{18}O$ $[M]^+$ 226.1357, found 226.1374.

References

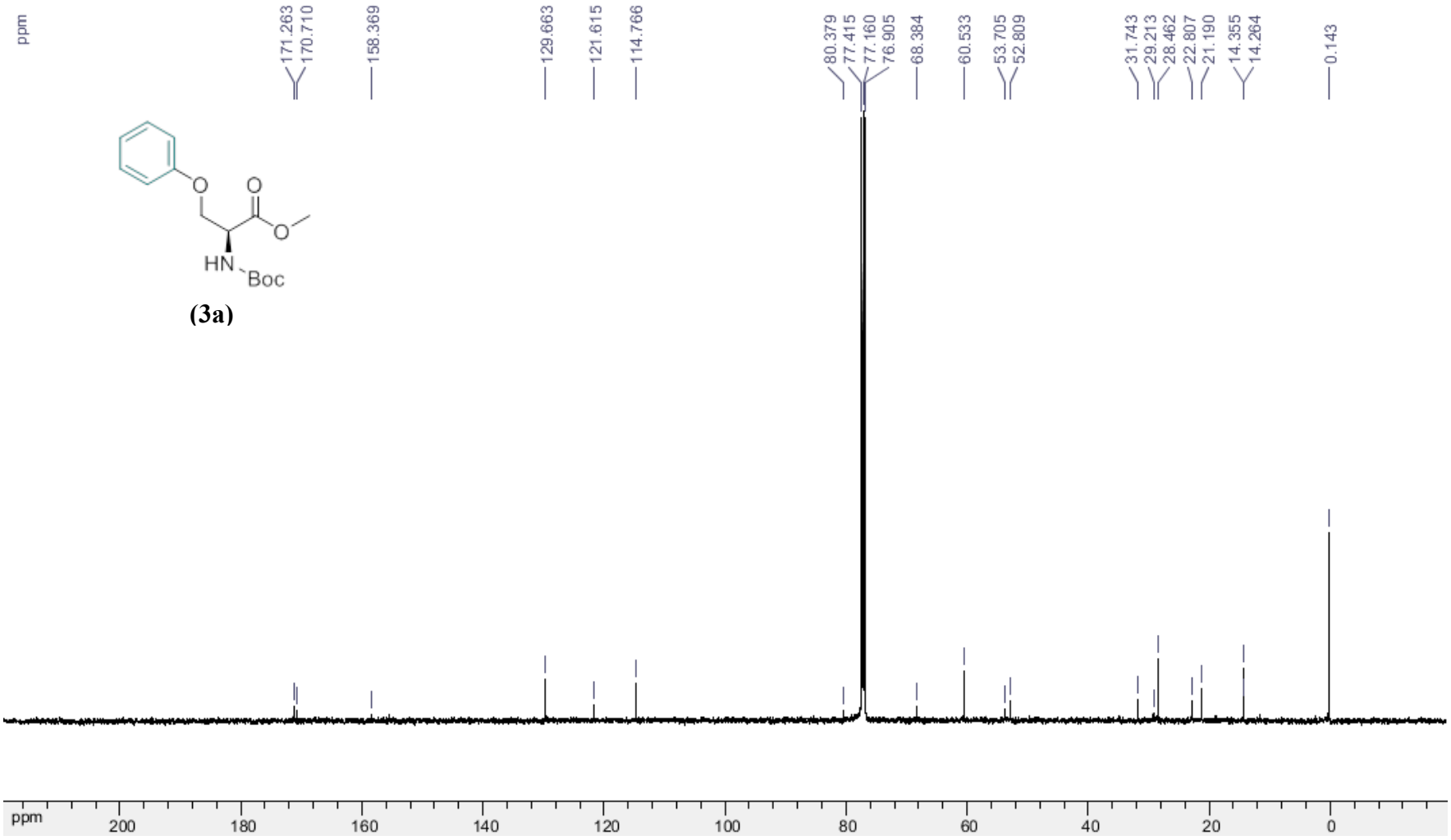
(1) Nakajima, K.; Neya, M.; Yamada, S.; Okawa, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3049.
(2) Tomita, M. *Yakugaku Zasshi* **1938**, *58*, 510.

^{1}H NMR (500 MHz, $CDCl_3$) of **Methyl *N*-(*tert*-butoxycarbonyl)-*O*-phenyl-L-serinate (3a) (from the aryl/heteroarylboronic acid [X_n = $B(OH)_2$].**



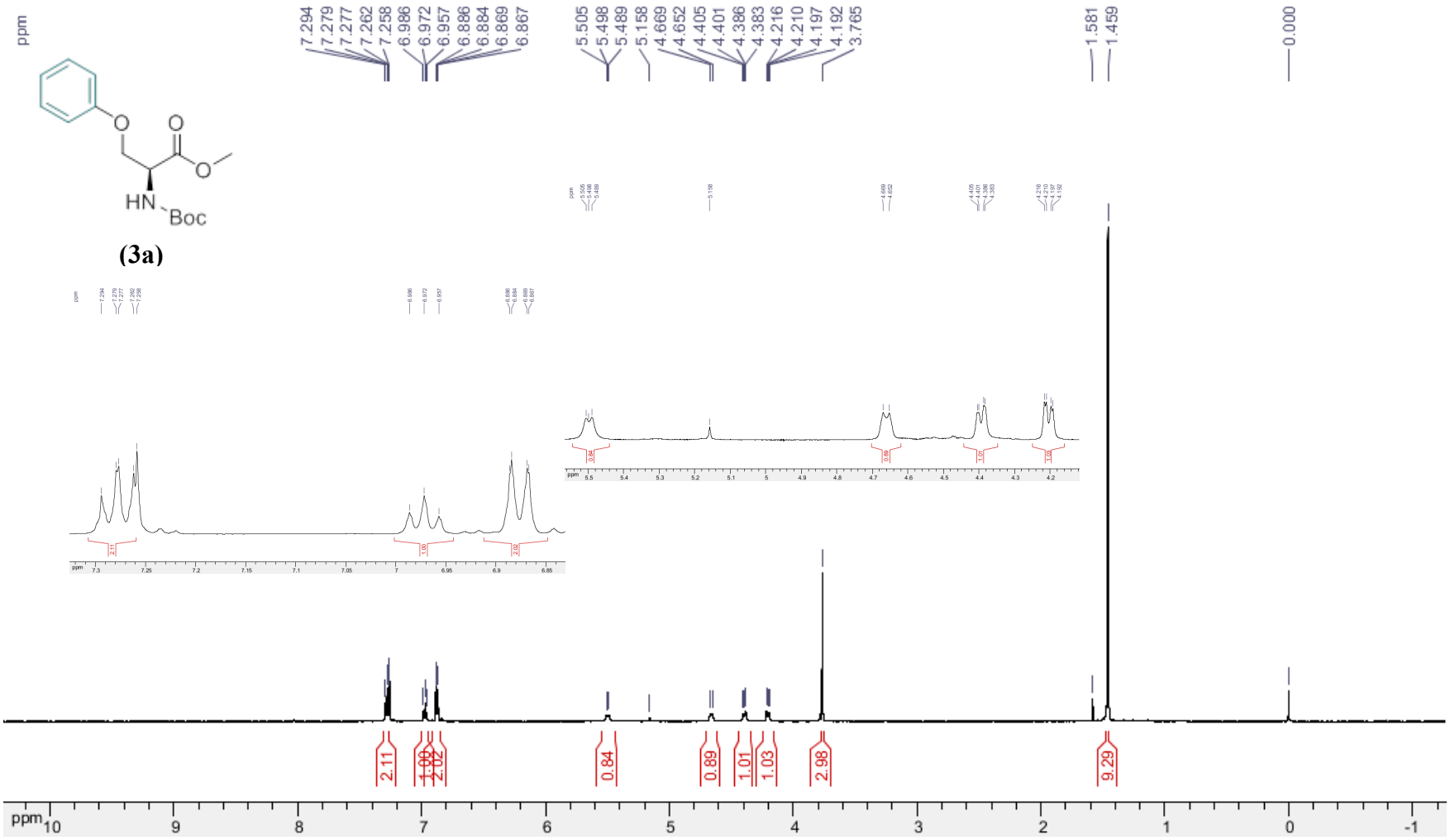
(3a)

^{13}C NMR (125.8 MHz, $CDCl_3$) of **Methyl *N*-(*tert*-butoxycarbonyl)-*O*-phenyl-L-serinate (3a) (from the aryl/heteroarylboronic acid [X_n = $B(OH)_2$].**

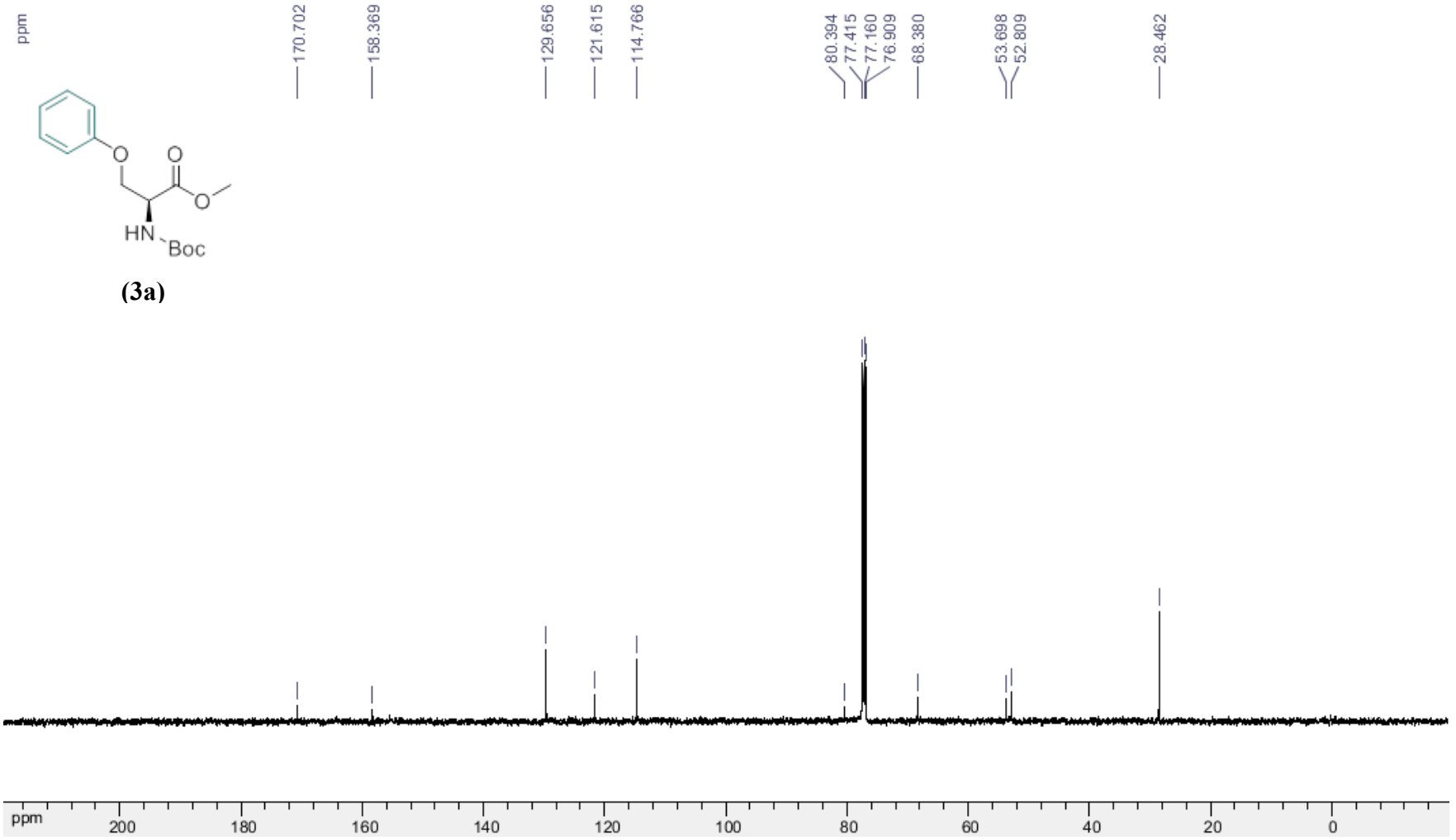


(3a)

^{1}H NMR (500 MHz, $CDCl_3$) of **Methyl *N*-(*tert*-butoxycarbonyl)-*O*-phenyl-L-serinate (3a) (from the aryl/heteroaryltrifluoroborate [$X_n = BF_3K$].**

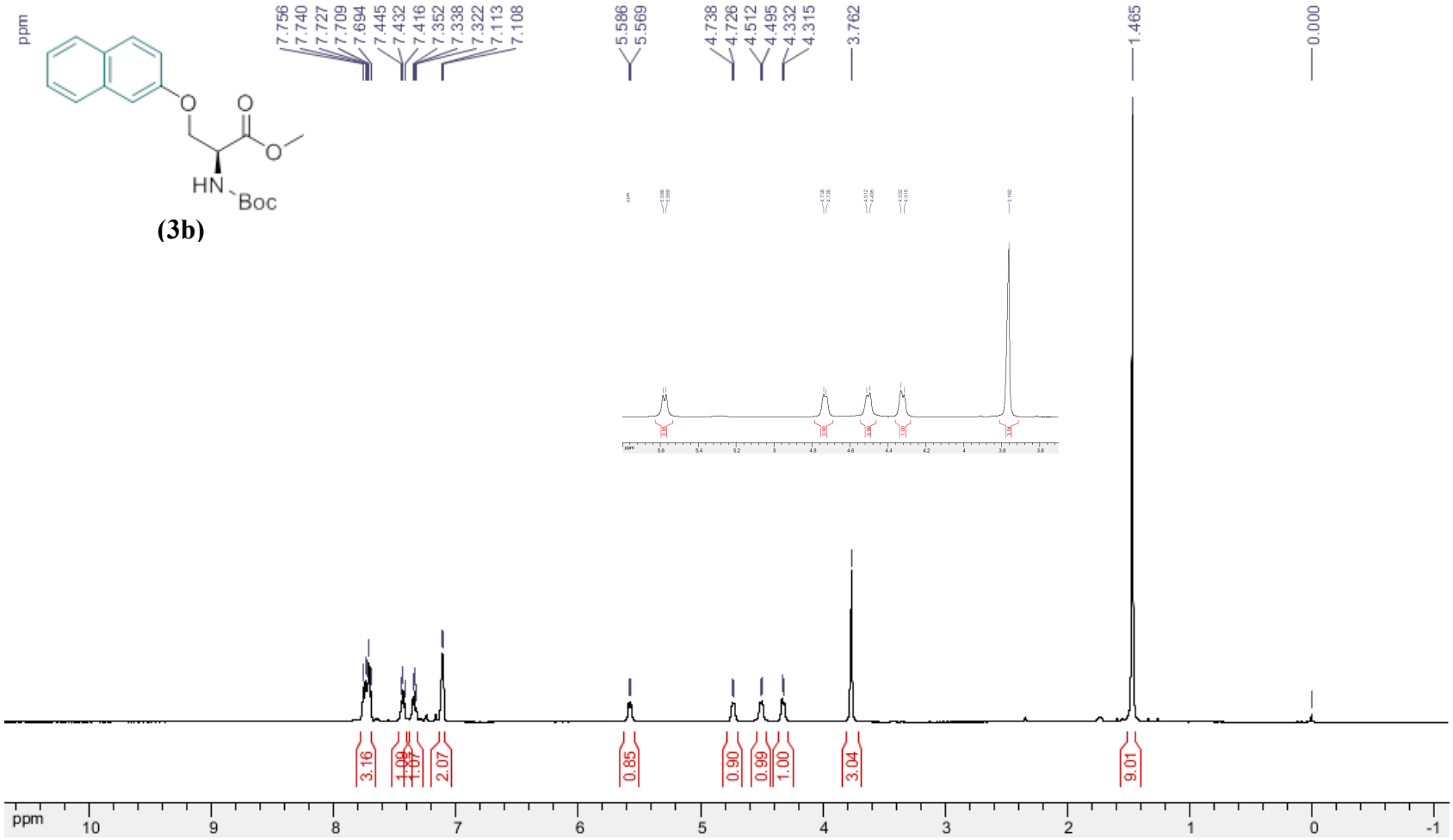


^{13}C NMR (125.8 MHz, $CDCl_3$) of **Methyl *N*-(*tert*-butoxycarbonyl)-*O*-phenyl-L-serinate (3a) (from the aryl/heteroaryltrifluoroborate [$X_n = BF_3K$].**



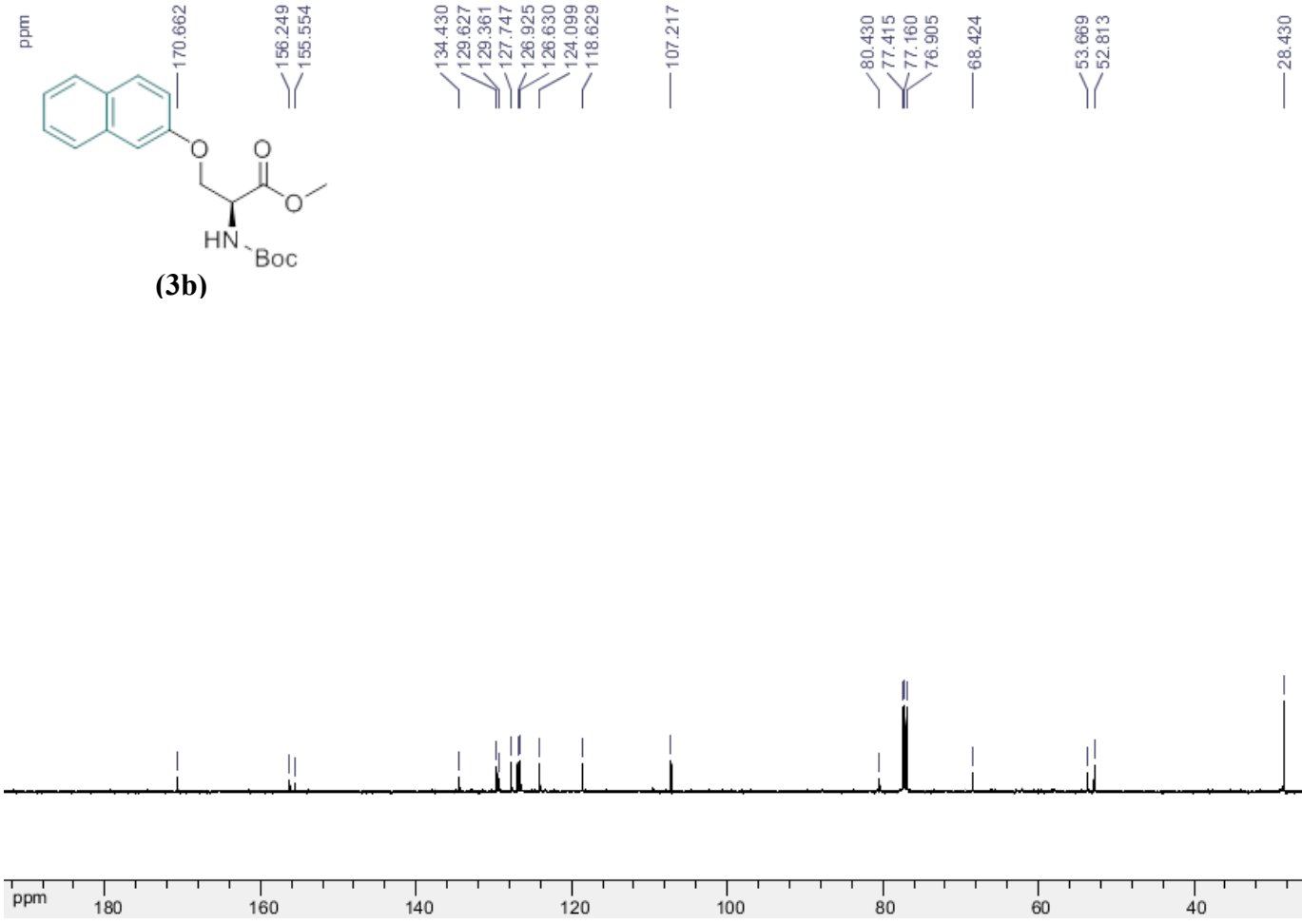
(3a)

^{1}H NMR (500 MHz, $CDCl_3$) of **Methyl *N*-(*tert*-butoxycarbonyl)-*O*-(naphthalen-2-yl)-L-serinate (3b).**



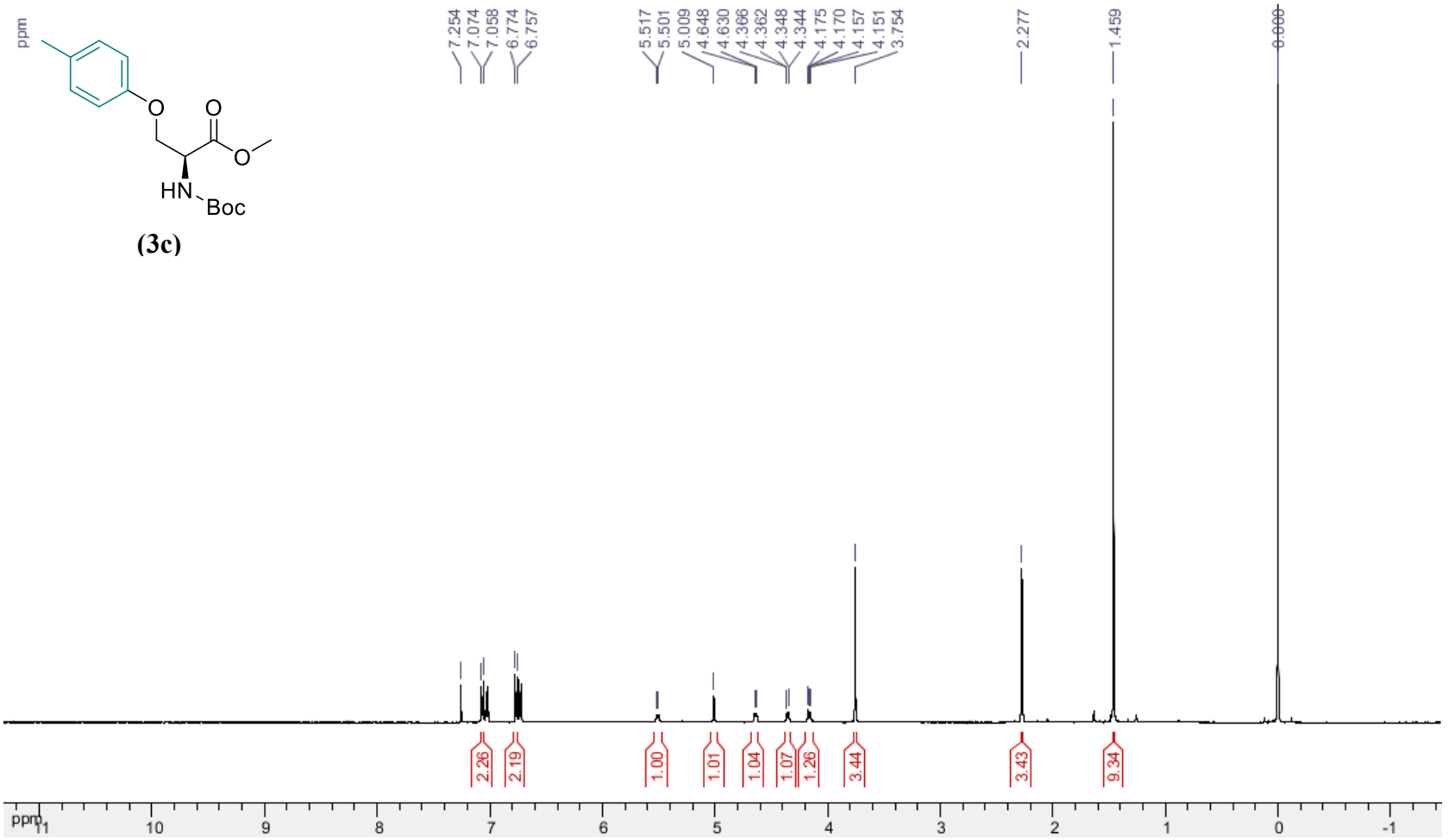
(3b)

^{13}C NMR (125.8 MHz, $CDCl_3$) of **Methyl *N*-(*tert*-butoxycarbonyl)-*O*-(naphthalen-2-yl)-L-serinate (3b).**



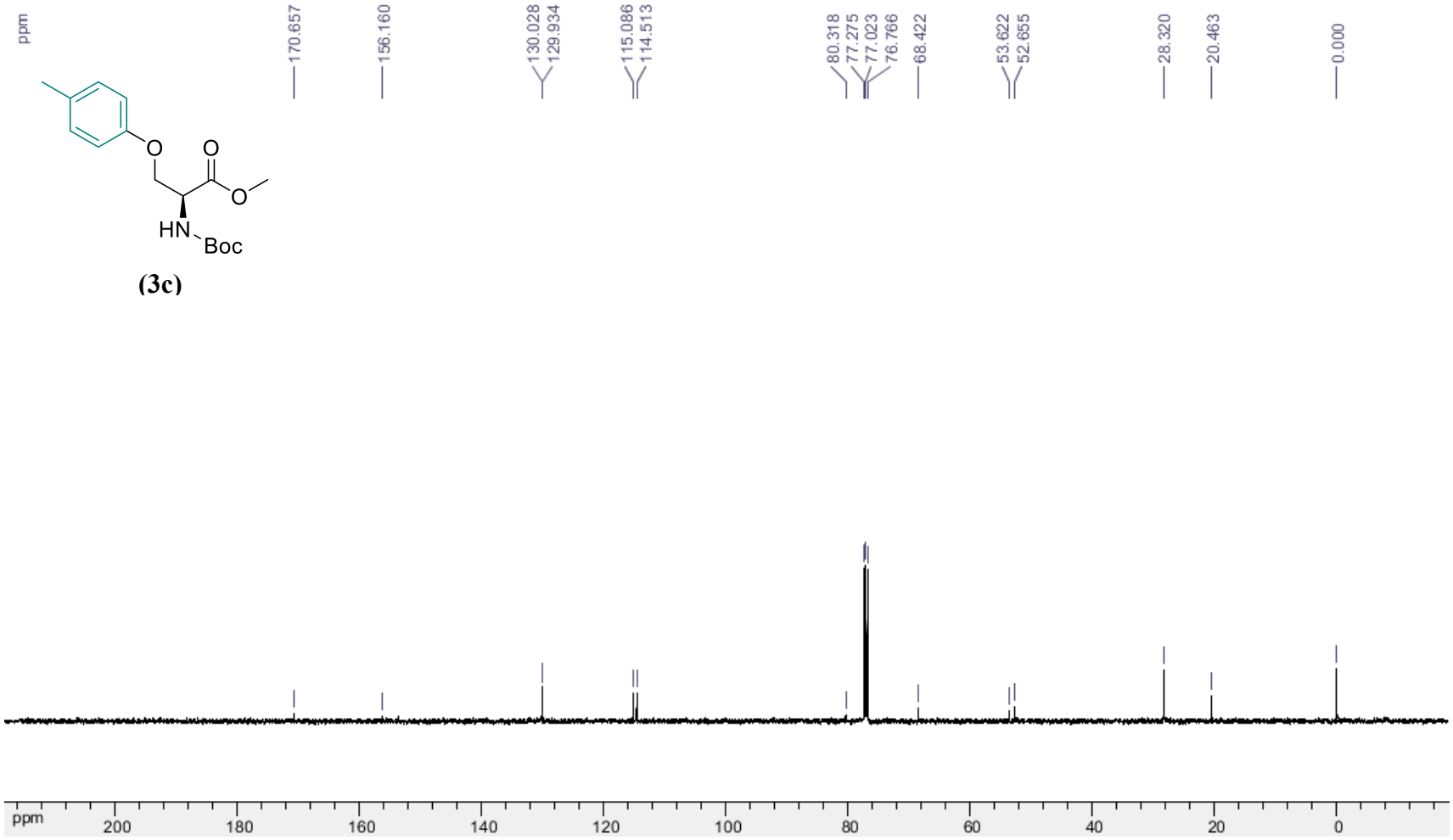
(3b)

^{1}H NMR (500 MHz, $CDCl_3$) of **Methyl *N*-(*tert*-butoxycarbonyl)-*O*-(*p*-tolyl)-L-serinate (3c).**



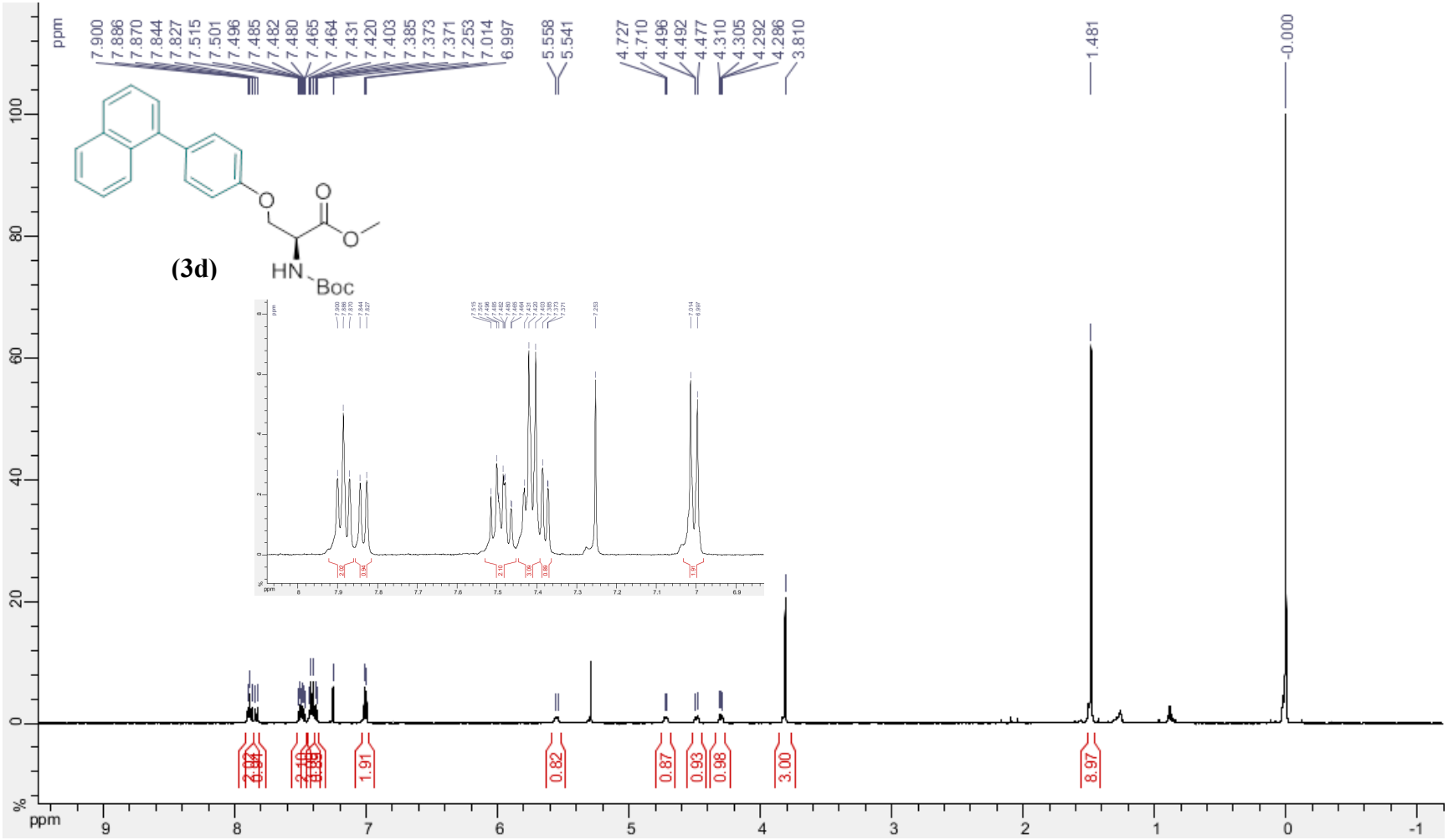
(3c)

^{13}C NMR (125.8 MHz, $CDCl_3$) of **Methyl *N*-(*tert*-butoxycarbonyl)-*O*-(*p*-tolyl)-L-serinate (3c).**

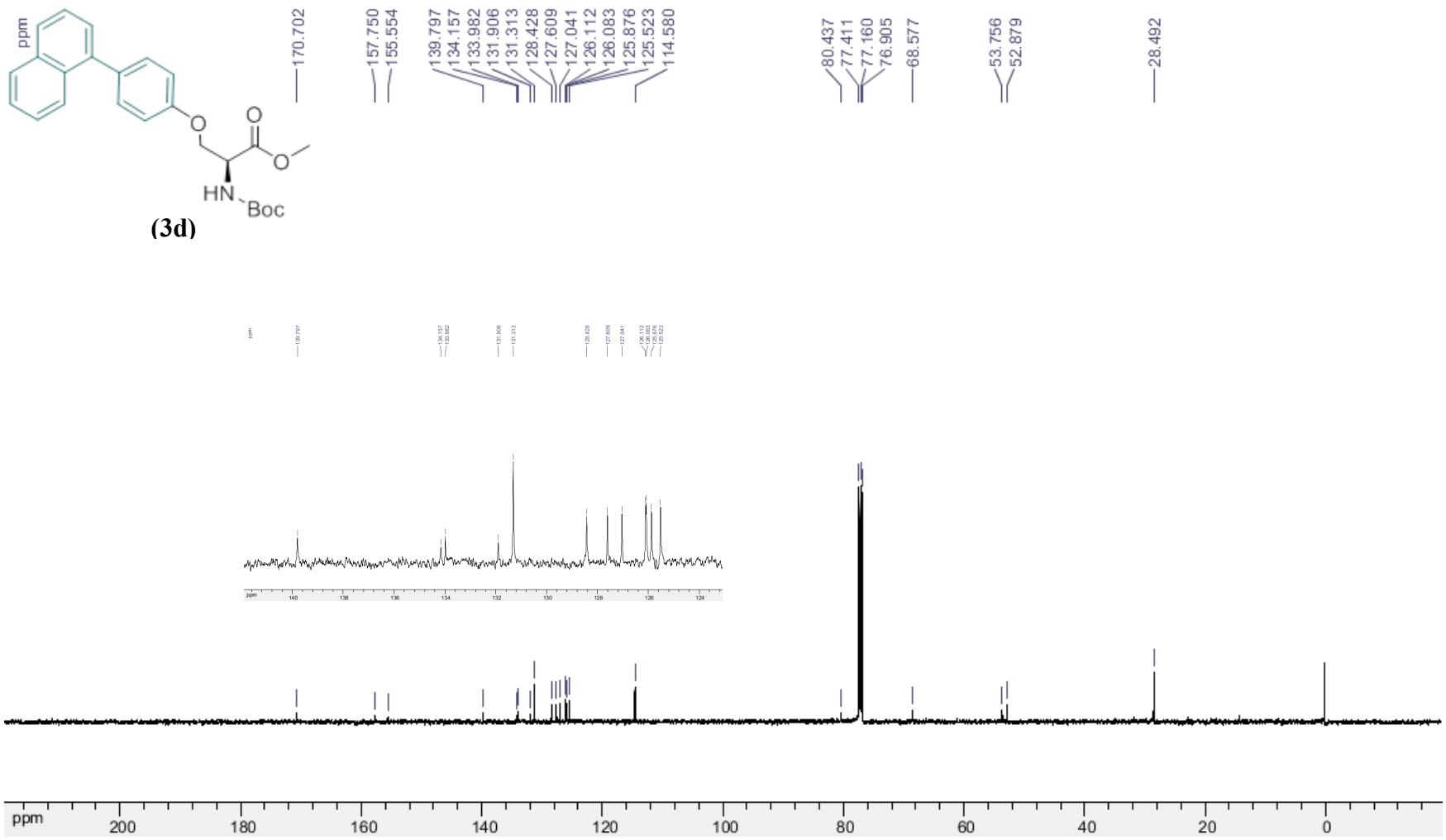


(3c)

^{1}H NMR (500 MHz, $CDCl_3$) of **Methyl *N*-(*tert*-butoxycarbonyl)-*O*-(4-(naphthalen-1-yl)phenyl)-L-serinate (3d).**

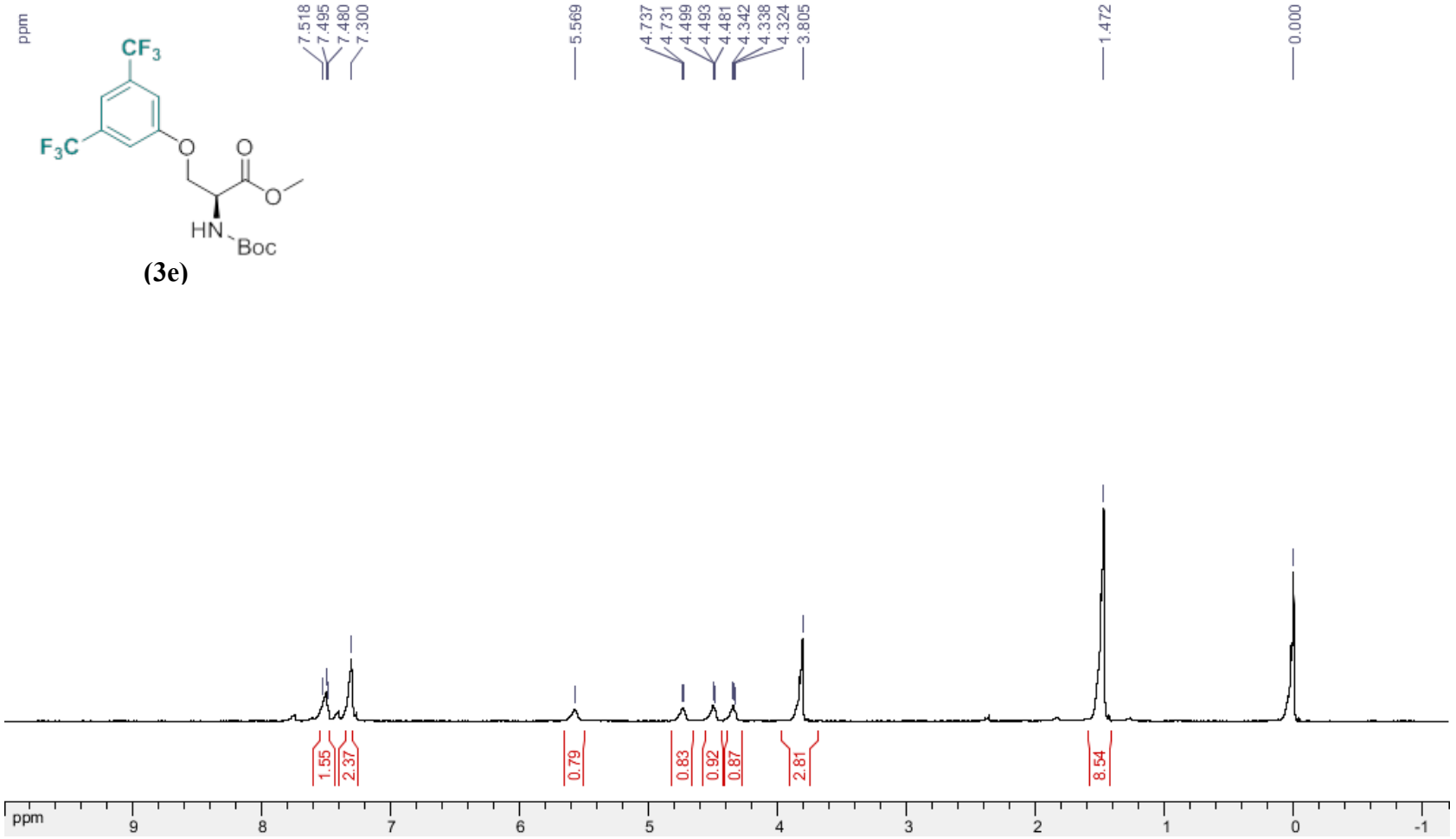


^{13}C NMR (125.8 MHz, $CDCl_3$) of **Methyl *N*-(*tert*-butoxycarbonyl)-*O*-(4-(naphthalen-1-yl)phenyl)-L-serinate (3d).**



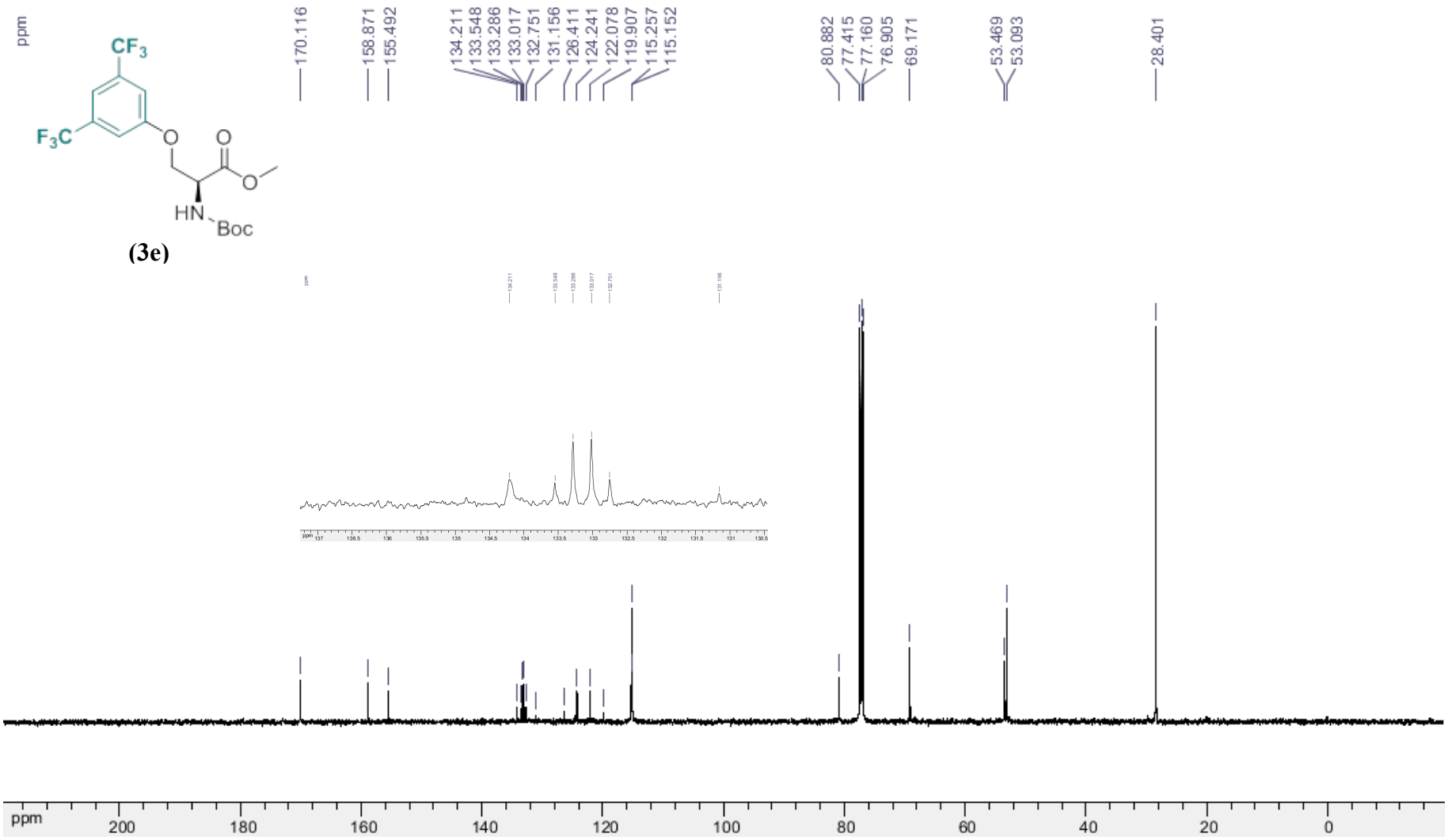
(3d)

^{1}H NMR (500 MHz, $CDCl_3$) of **Methyl *O*-(3,5-bis(trifluoromethyl)phenyl)-*N*-(*tert*-butoxycarbonyl)-L-serinate (3e).**



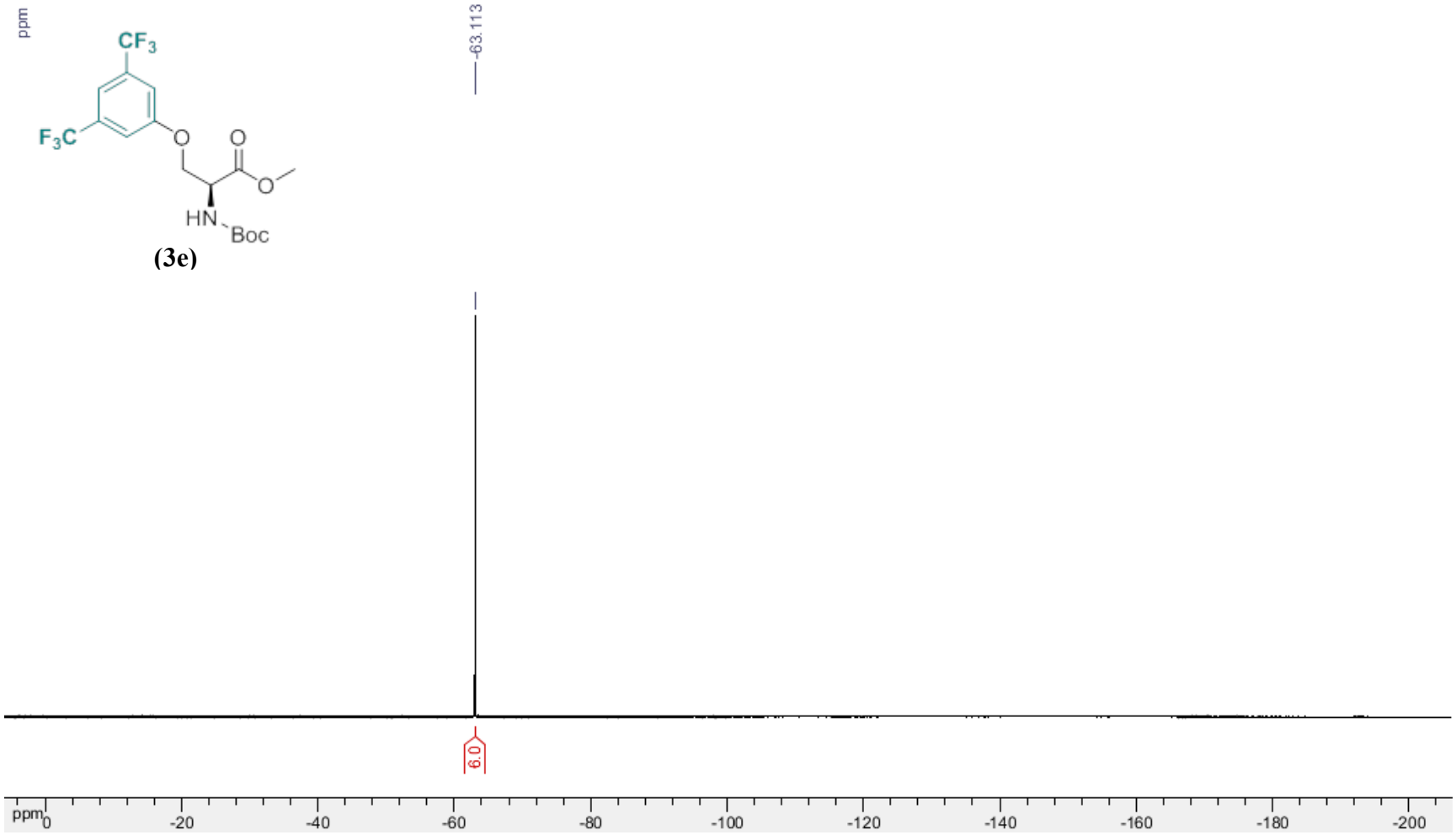
(3e)

^{13}C NMR (125.8 MHz, $CDCl_3$) of **Methyl *O*-(3,5-bis(trifluoromethyl)phenyl)-*N*-(*tert*-butoxycarbonyl)-L-serinate (3e).**



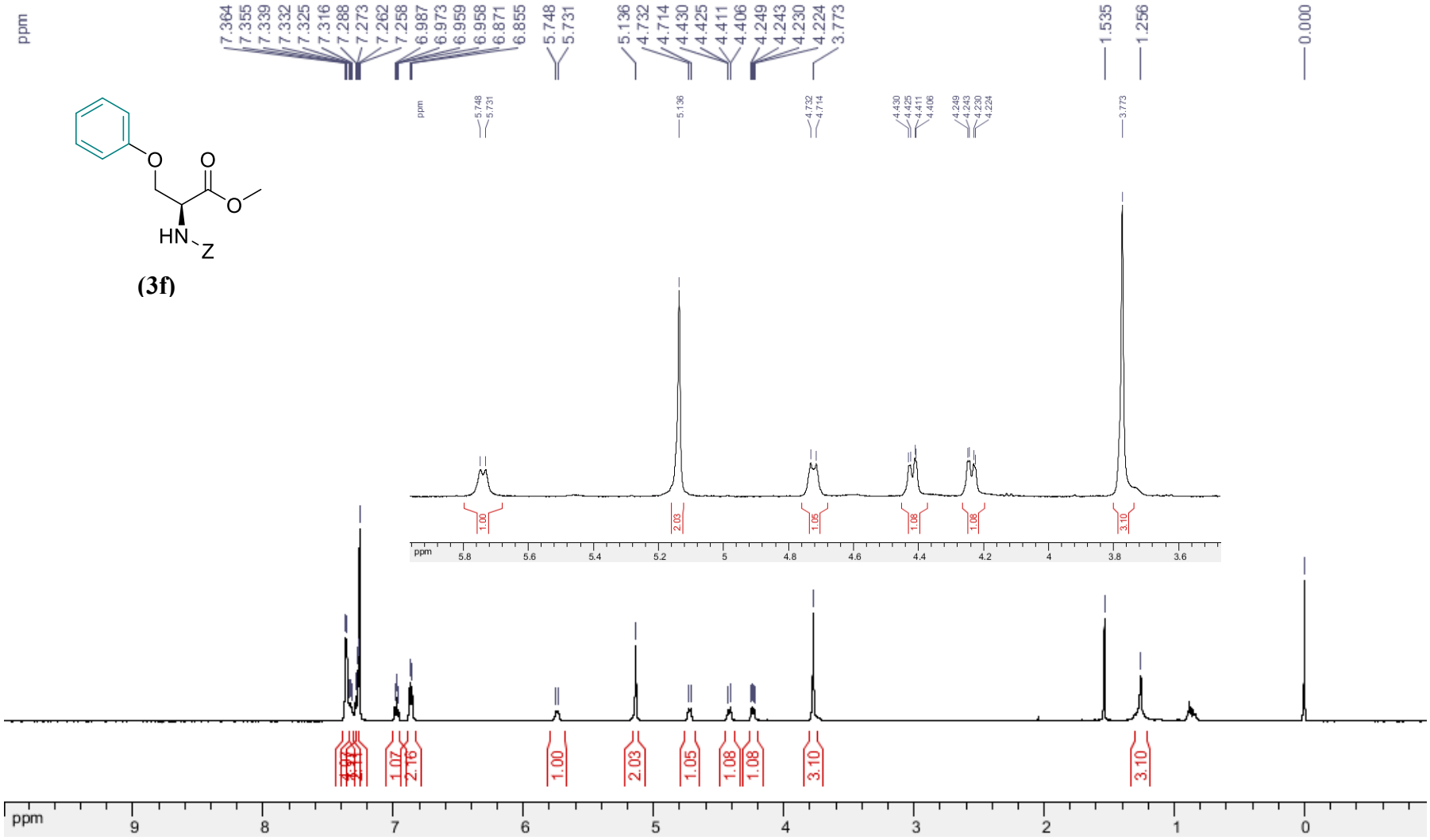
(3e)

^{19}F NMR (470.8 MHz, $CDCl_3$) of **Methyl *O*-(3,5-bis(trifluoromethyl)phenyl)-*N*-(*tert*-butoxycarbonyl)-L-serinate (3e).**



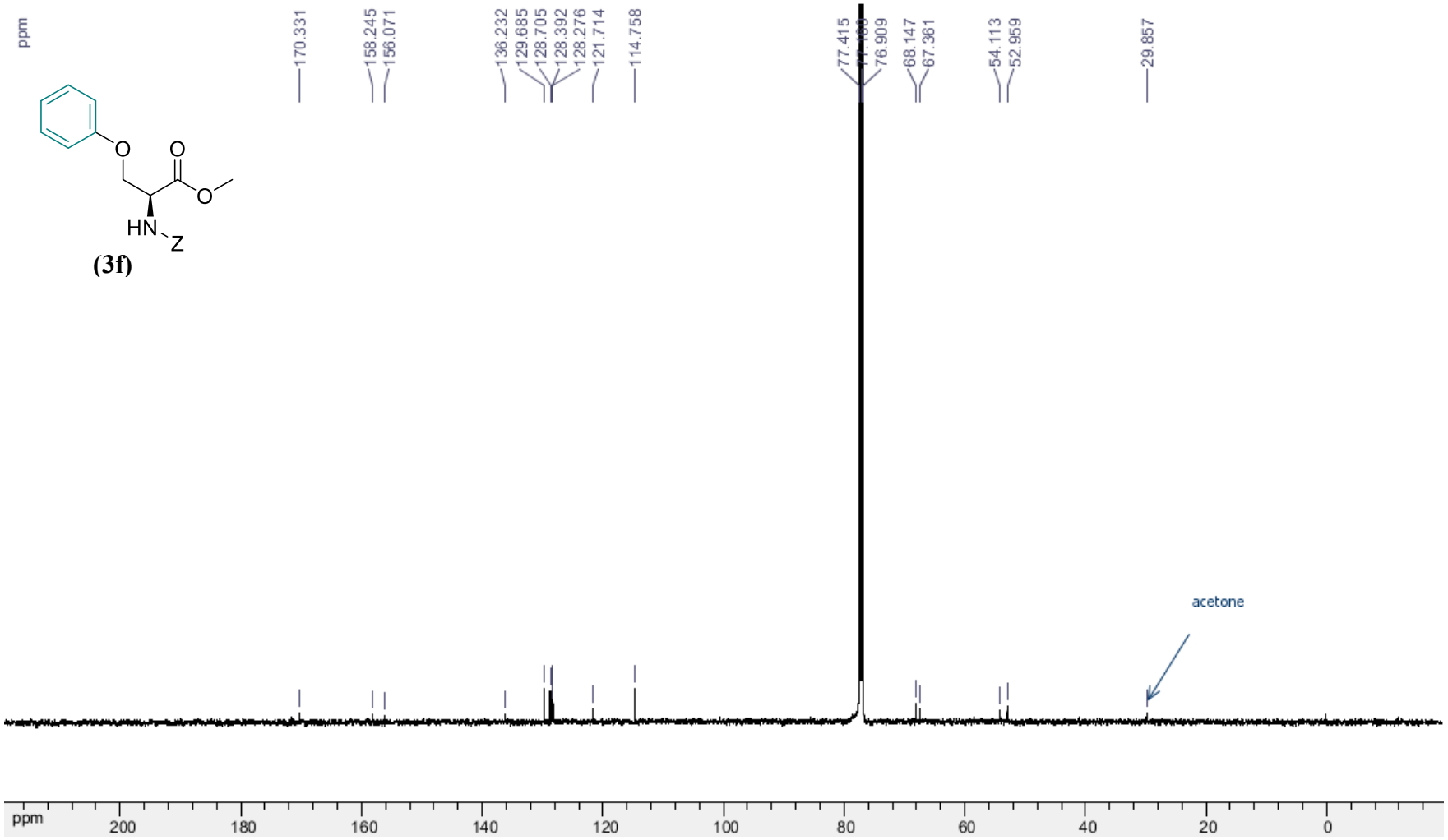
(3e)

^{1}H NMR (500 MHz, $CDCl_3$) of **Methyl *N*-((benzyloxy)carbonyl)-O-phenyl-L-serinate (3f).**

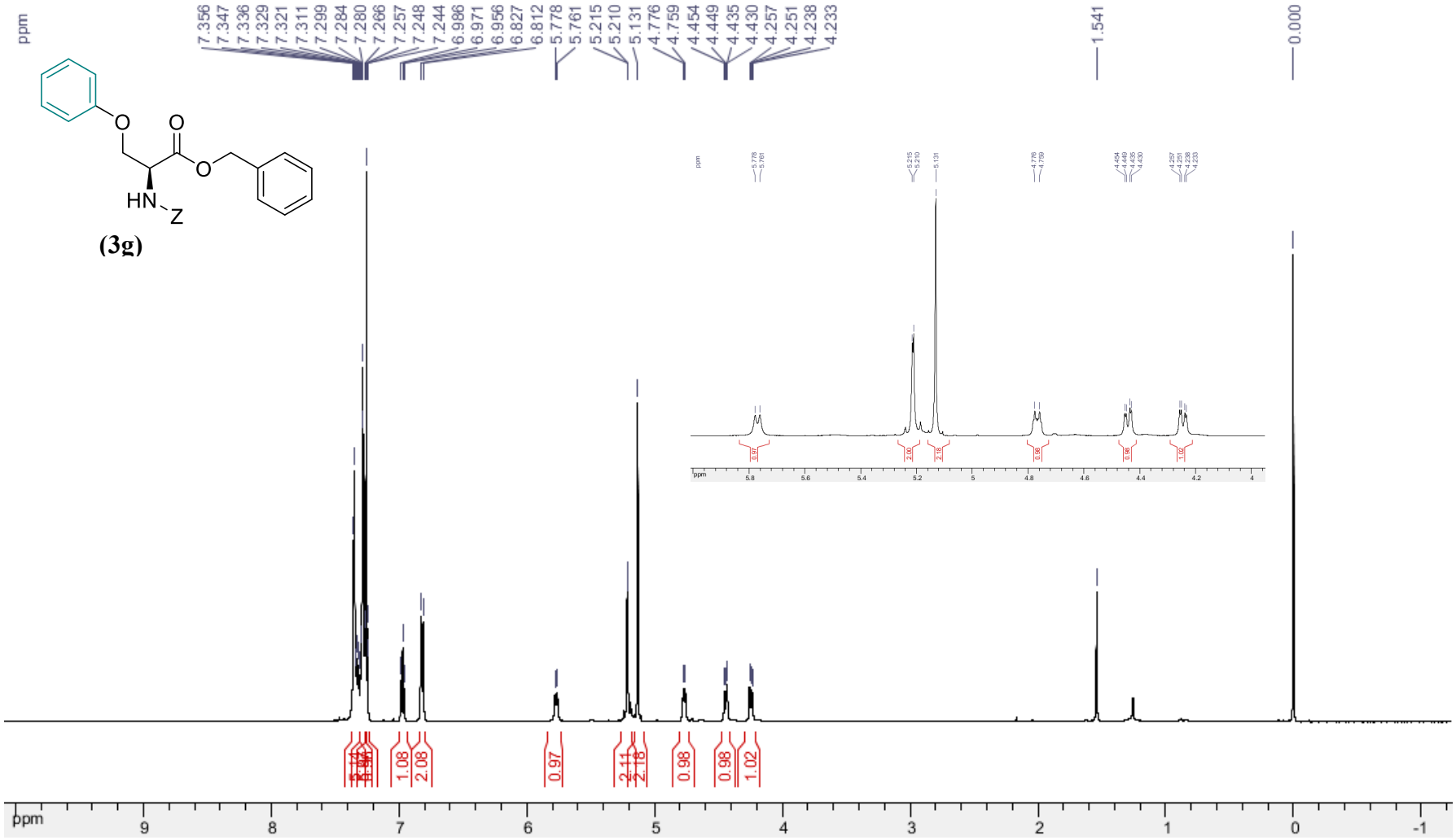


(3f)

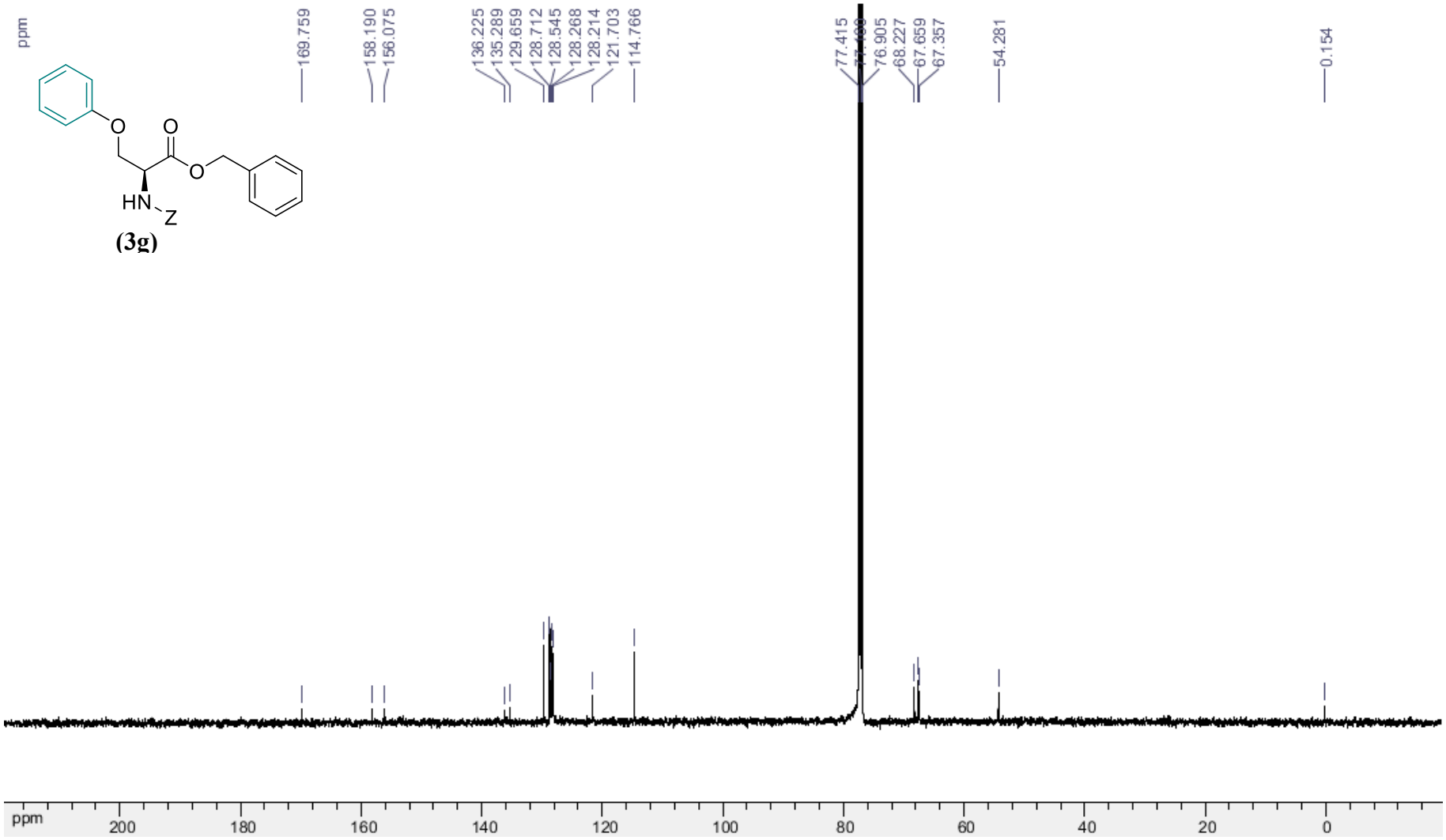
^{13}C NMR (125.8 MHz, $CDCl_3$) of **Methyl *N*-((benzyloxy)carbonyl)-*O*-phenyl-L-serinate (3f).**



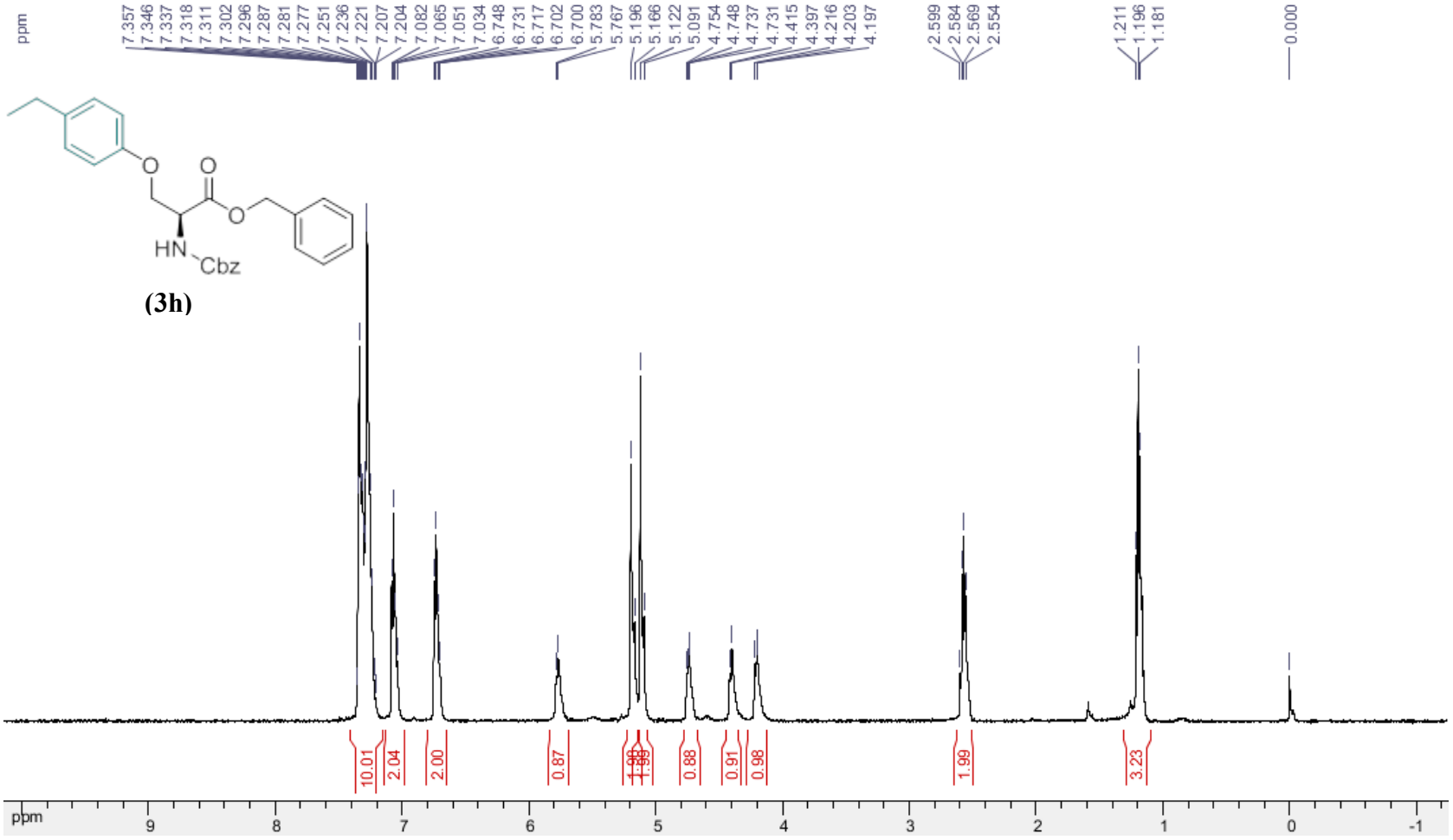
^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-phenyl-L-serinate (3g).**



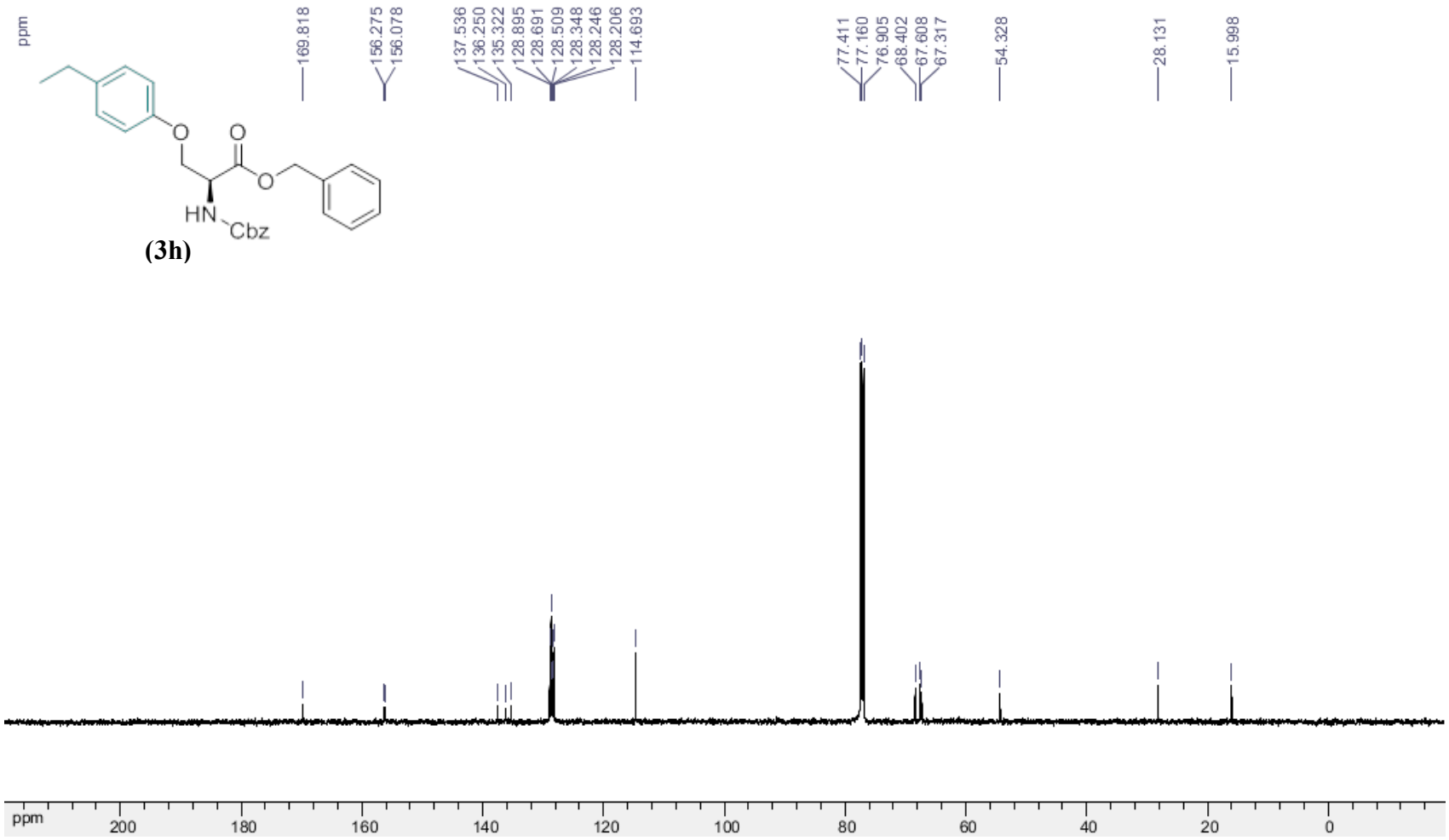
^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-phenyl-L-serinate (3g).**



^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(4-ethylphenyl)-L-serinate (3h).**

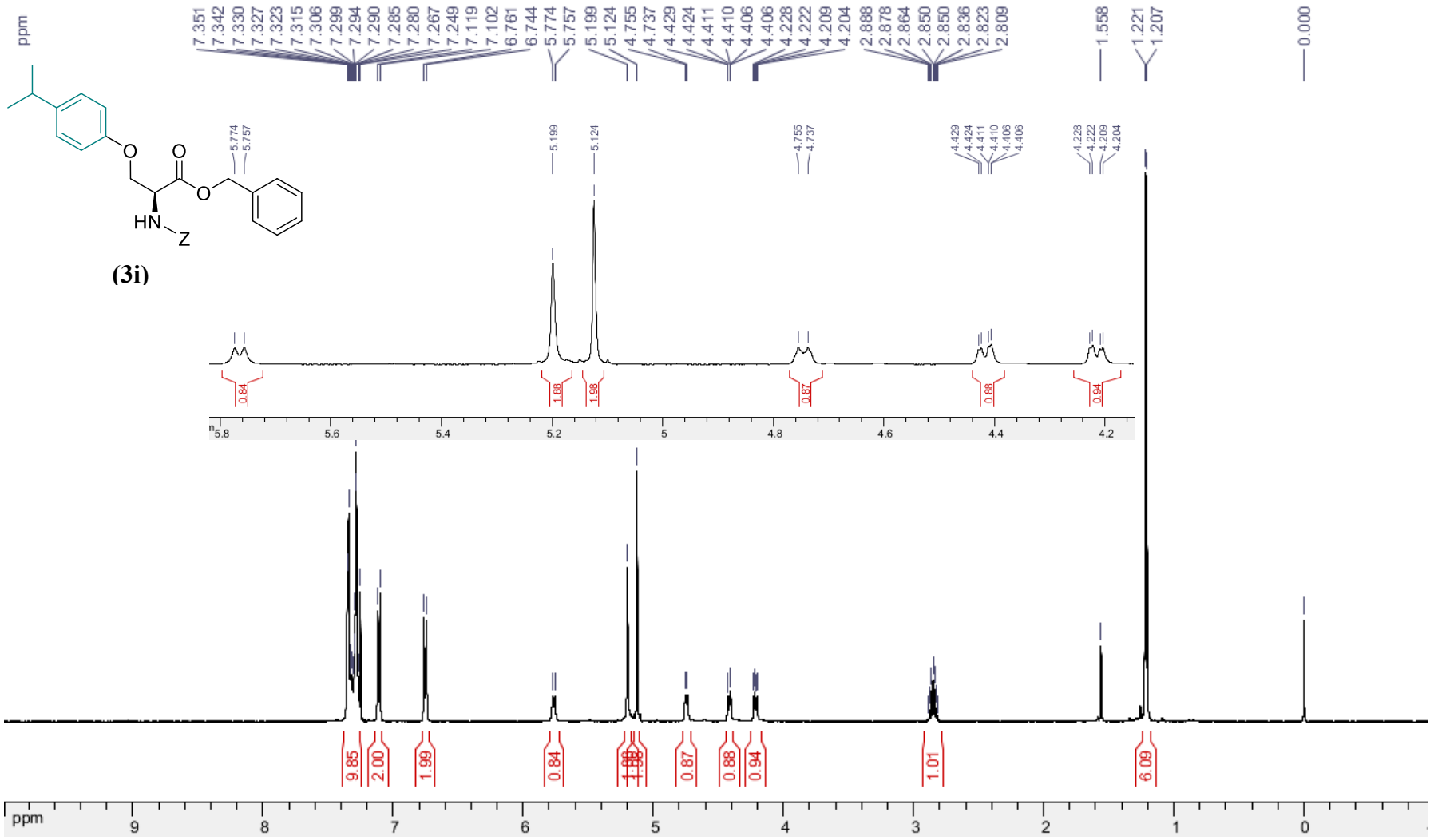


^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(4-ethylphenyl)-L-serinate (3h).**

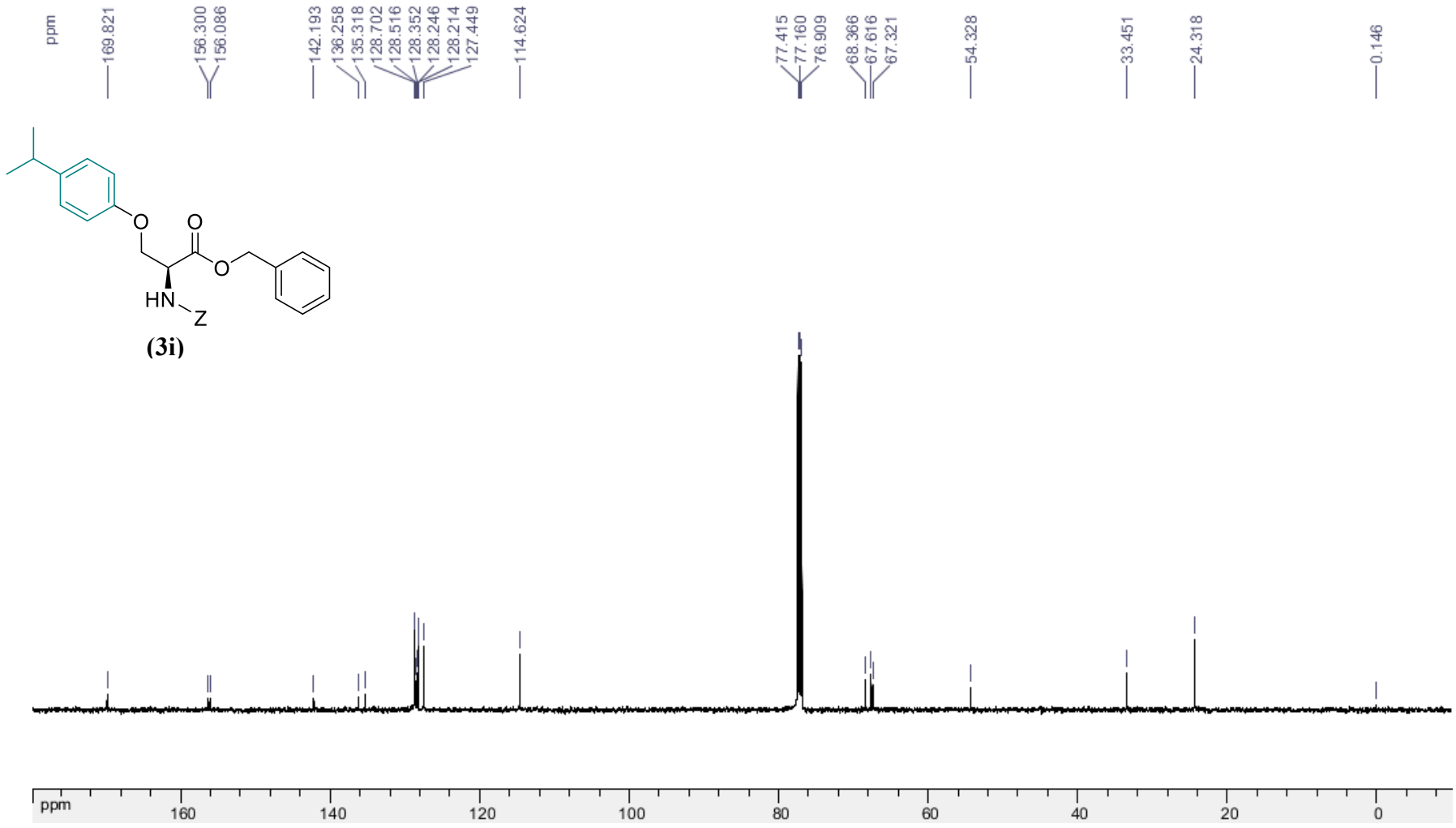


(3h)

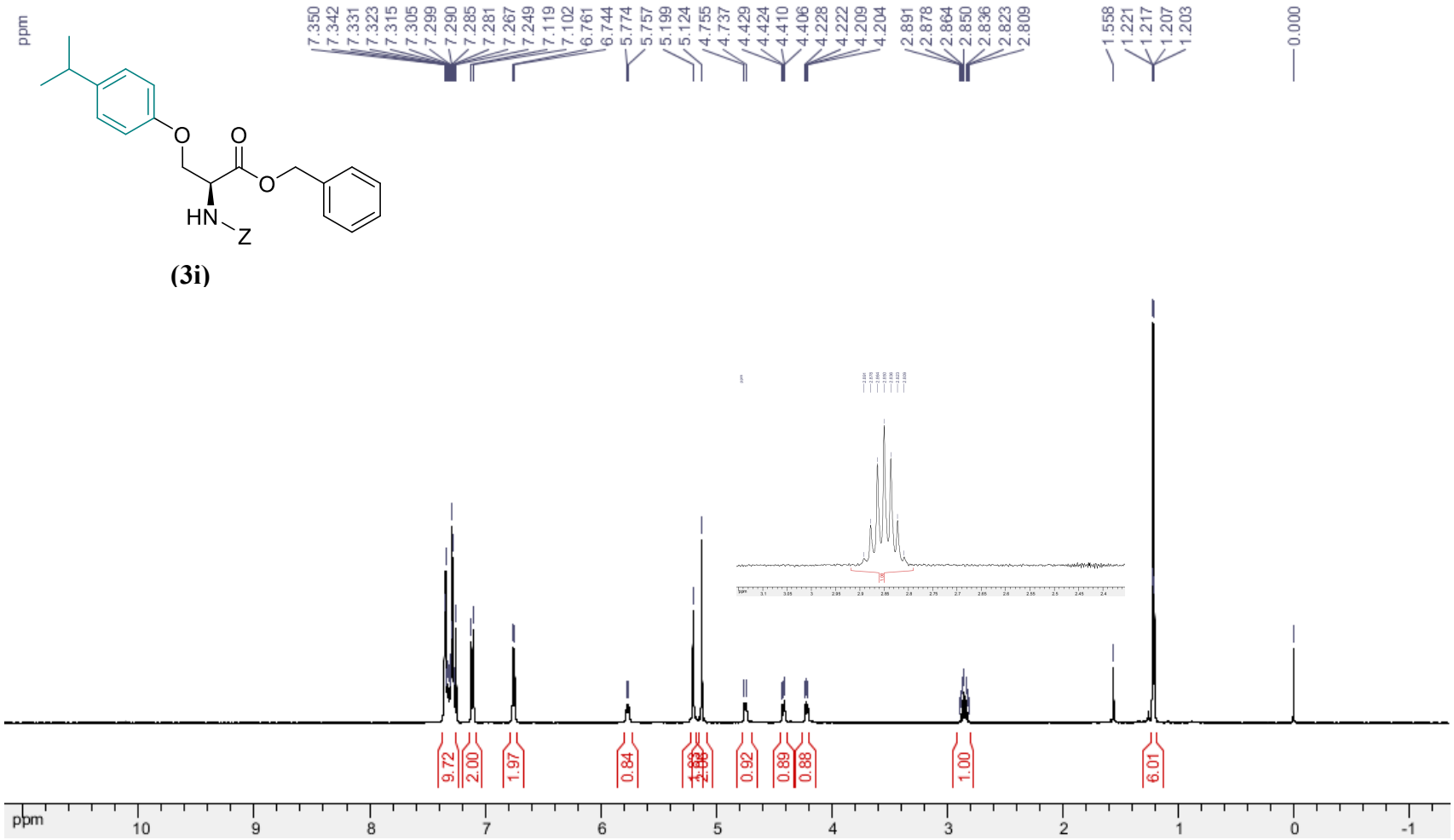
^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(4-isopropylphenyl)-L-serinate (3i) (from the aryl/heteroarylboronic acid [X_n = $B(OH)_2$].**



^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(4-isopropylphenyl)-L-serinate (from the aryl/heteroarylboronic acid (3i) [$X_n = B(OH)_2$].**

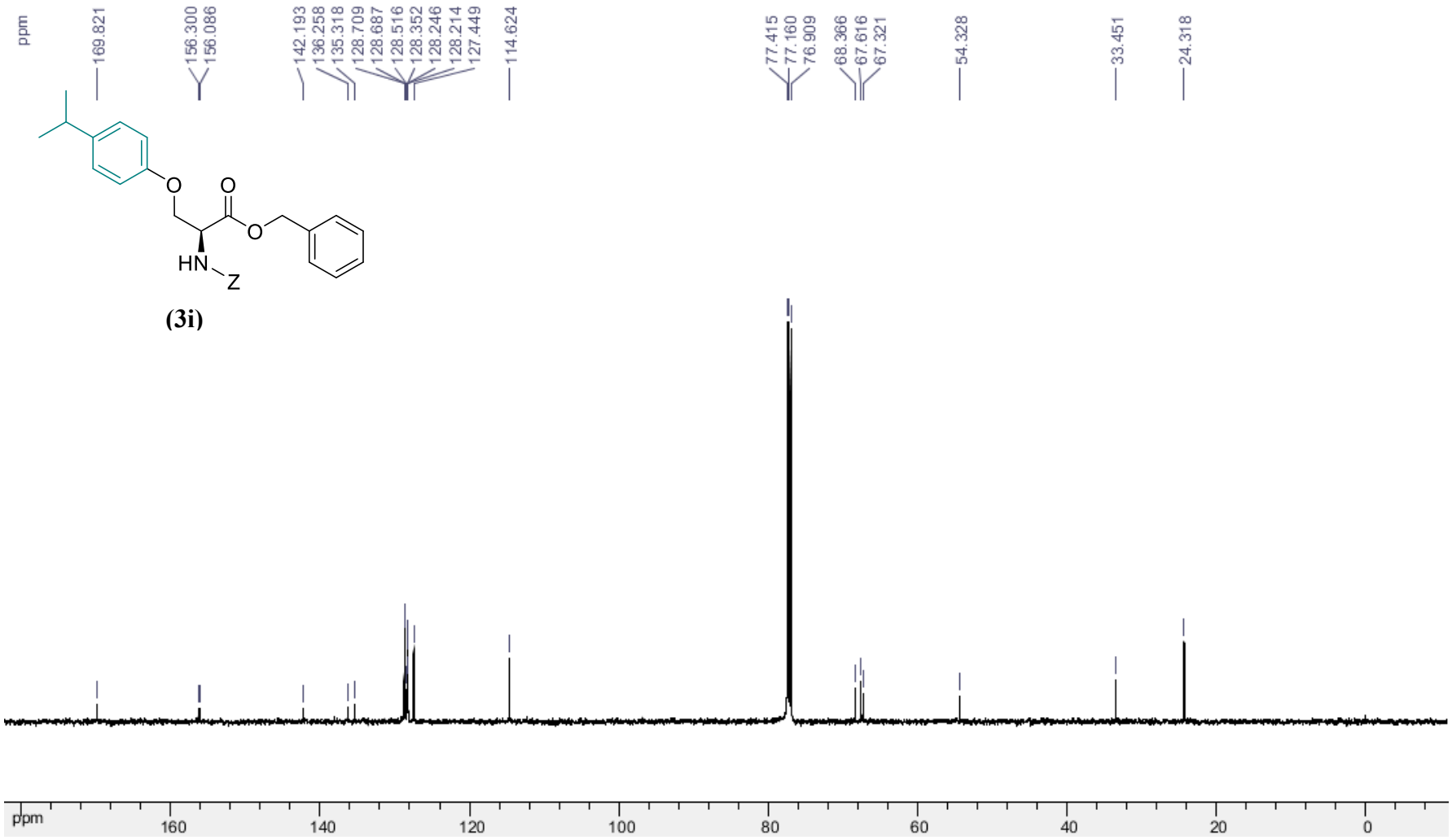


^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(4-isopropylphenyl)-L-serinate (3i) (from the aryl/heteroaryltrifluoroborate (X_n = BF_3K).**



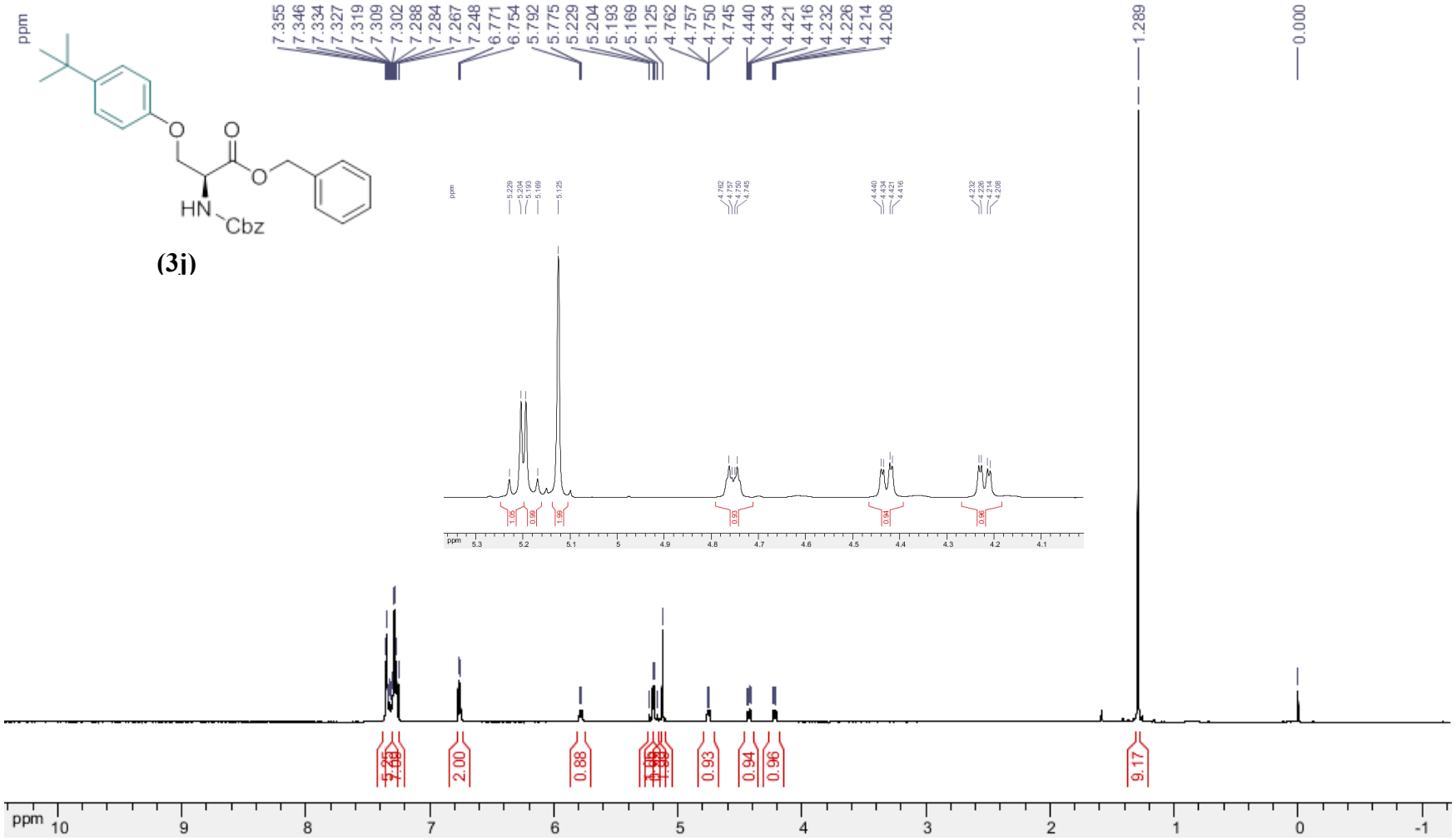
(3i)

^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(4-isopropylphenyl)-L-serinate (3i) (from the aryl/heteroaryltrifluoroborate ($X_n = BF_3K$).**

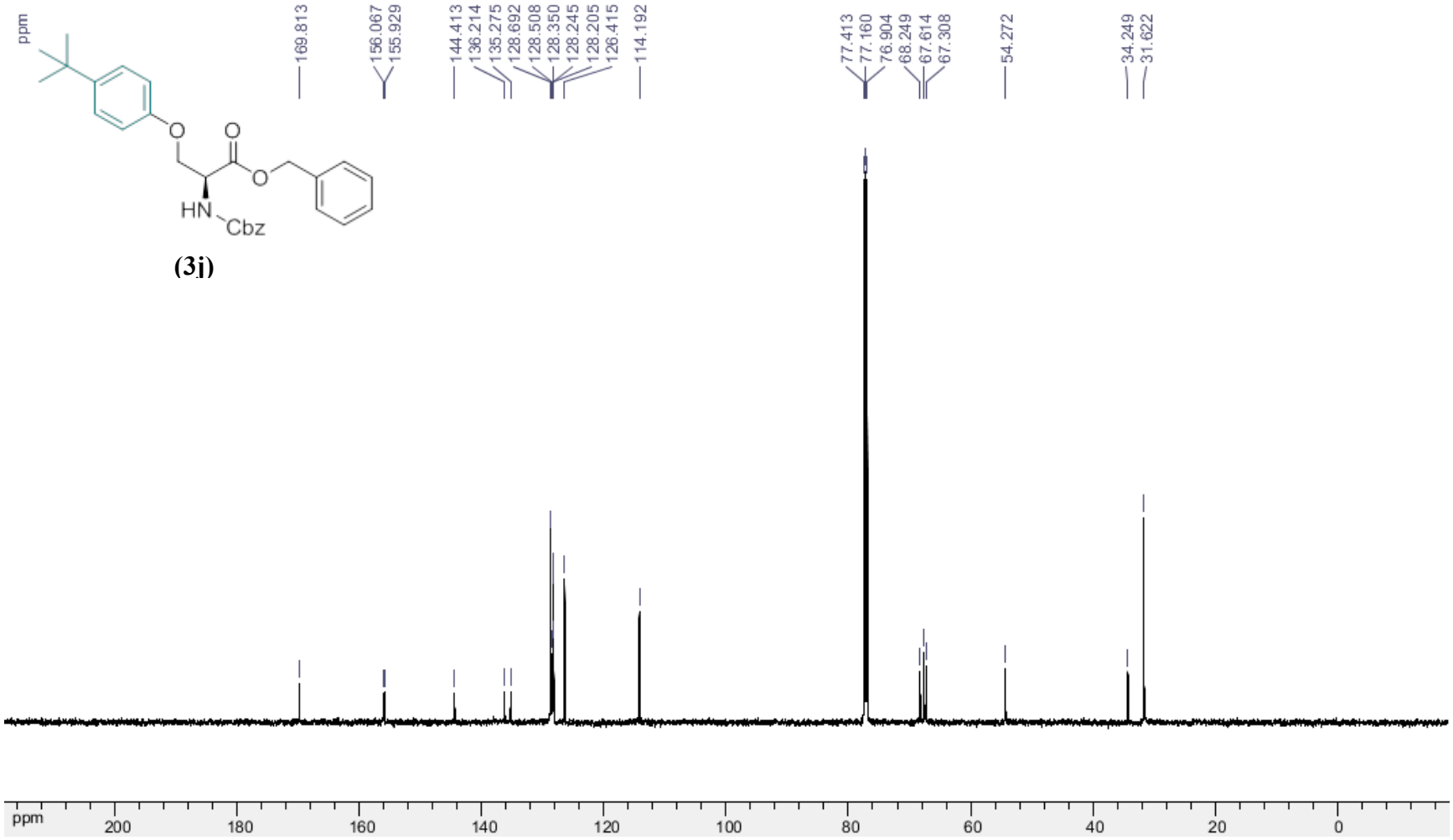


(3i)

^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(4-(*tert*-butyl)phenyl)-L-serinate (3j).**

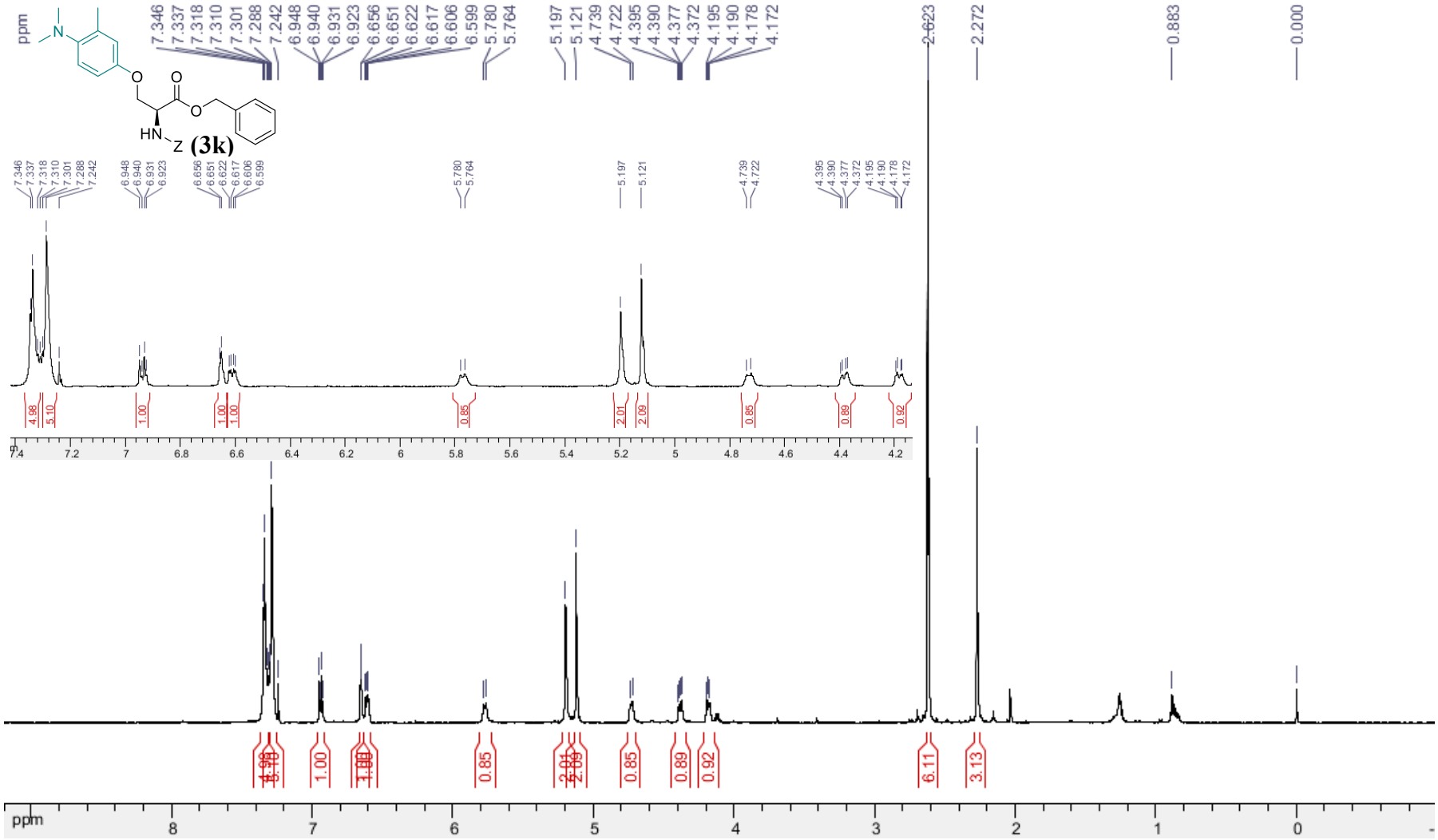


^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(4-(*tert*-butyl)phenyl)-L-serinate (3j).**

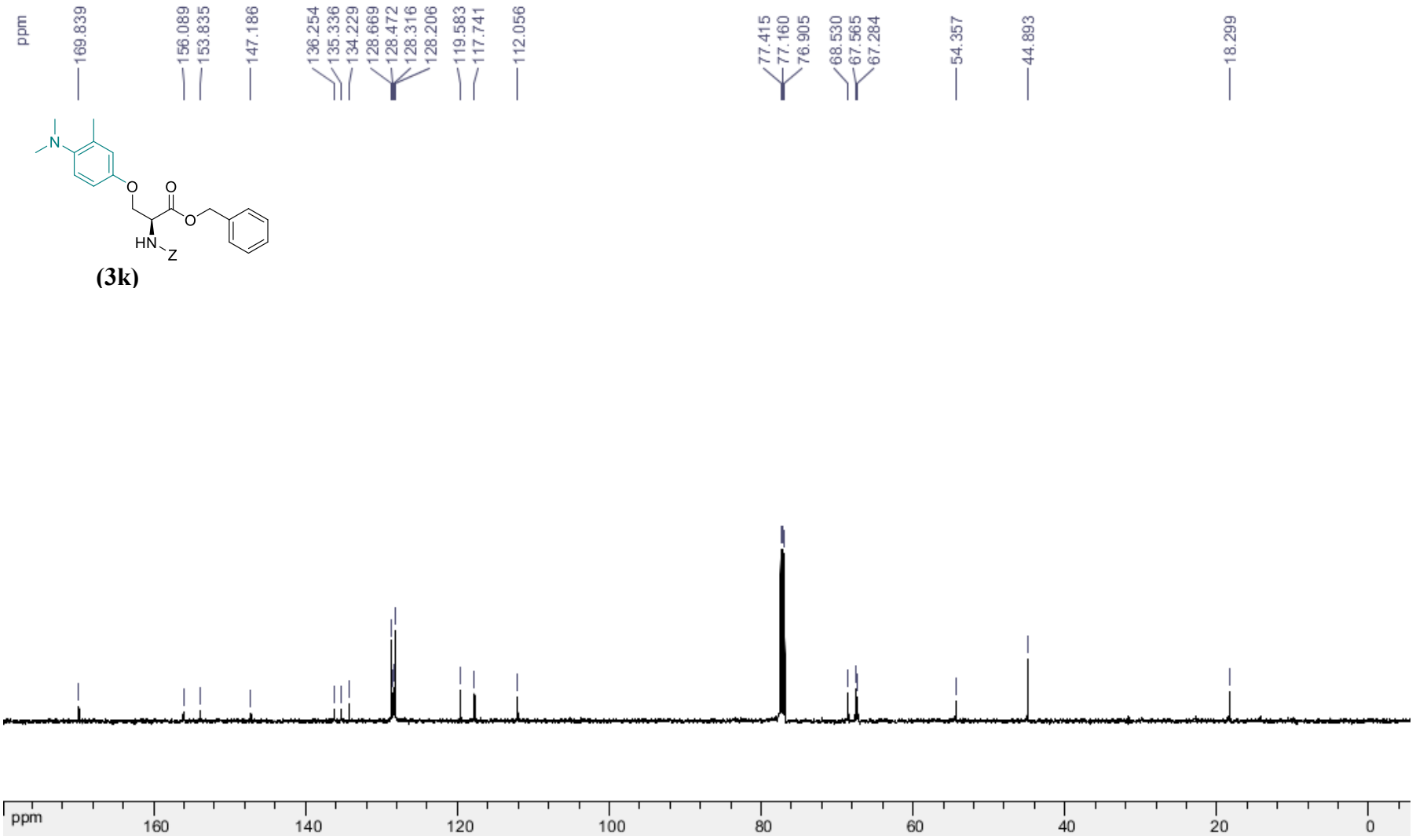


(3j)

^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(4-(dimethylamino)-3-methylphenyl)-L-serinate (3k).**

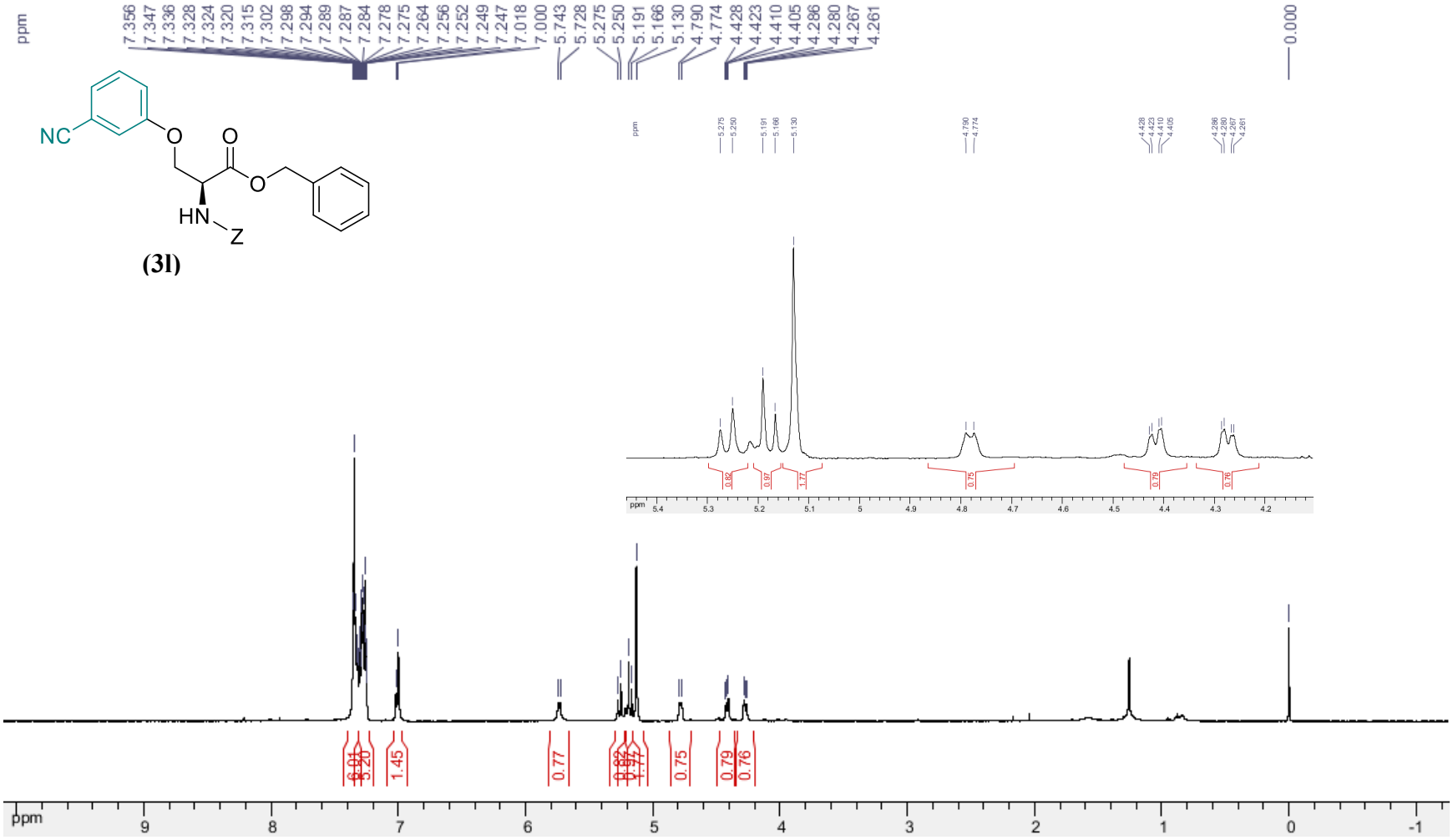


^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(4-(dimethylamino)-3-methylphenyl)-L-serinate (3k).**

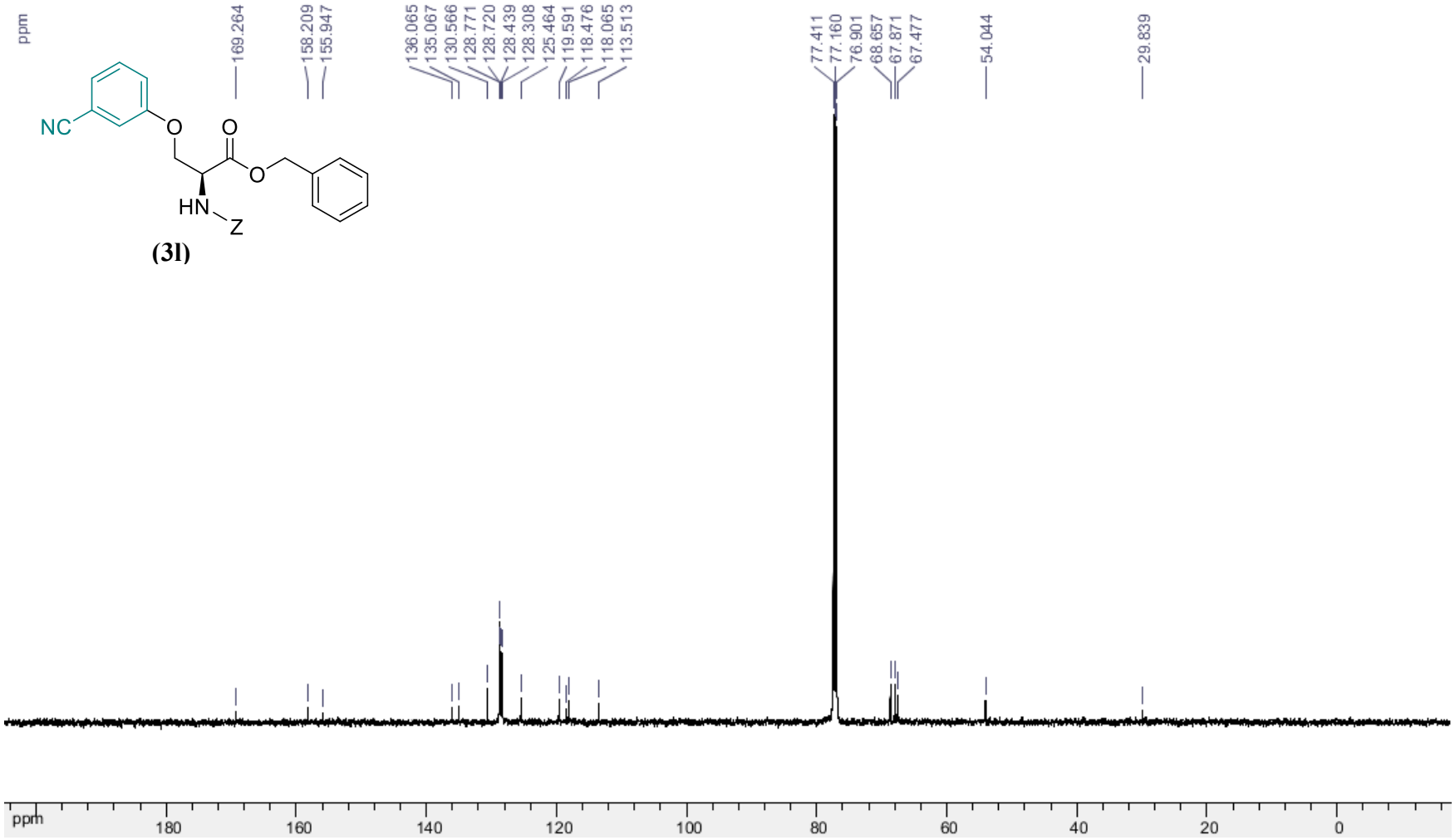


(3k)

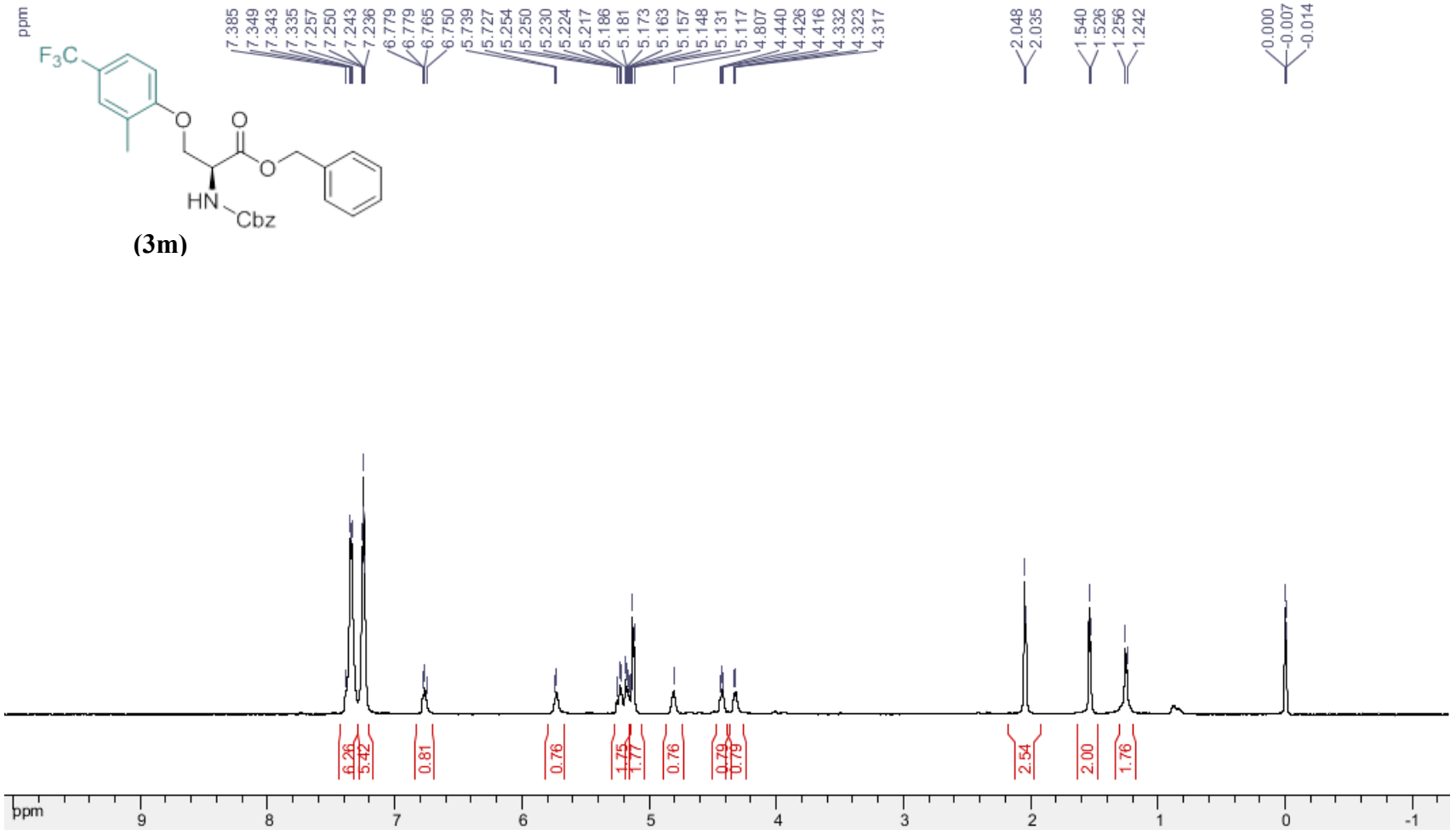
^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(3-cyanophenyl)-L-serinate (3l).**



^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(3-cyanophenyl)-L-serinate (3l).**

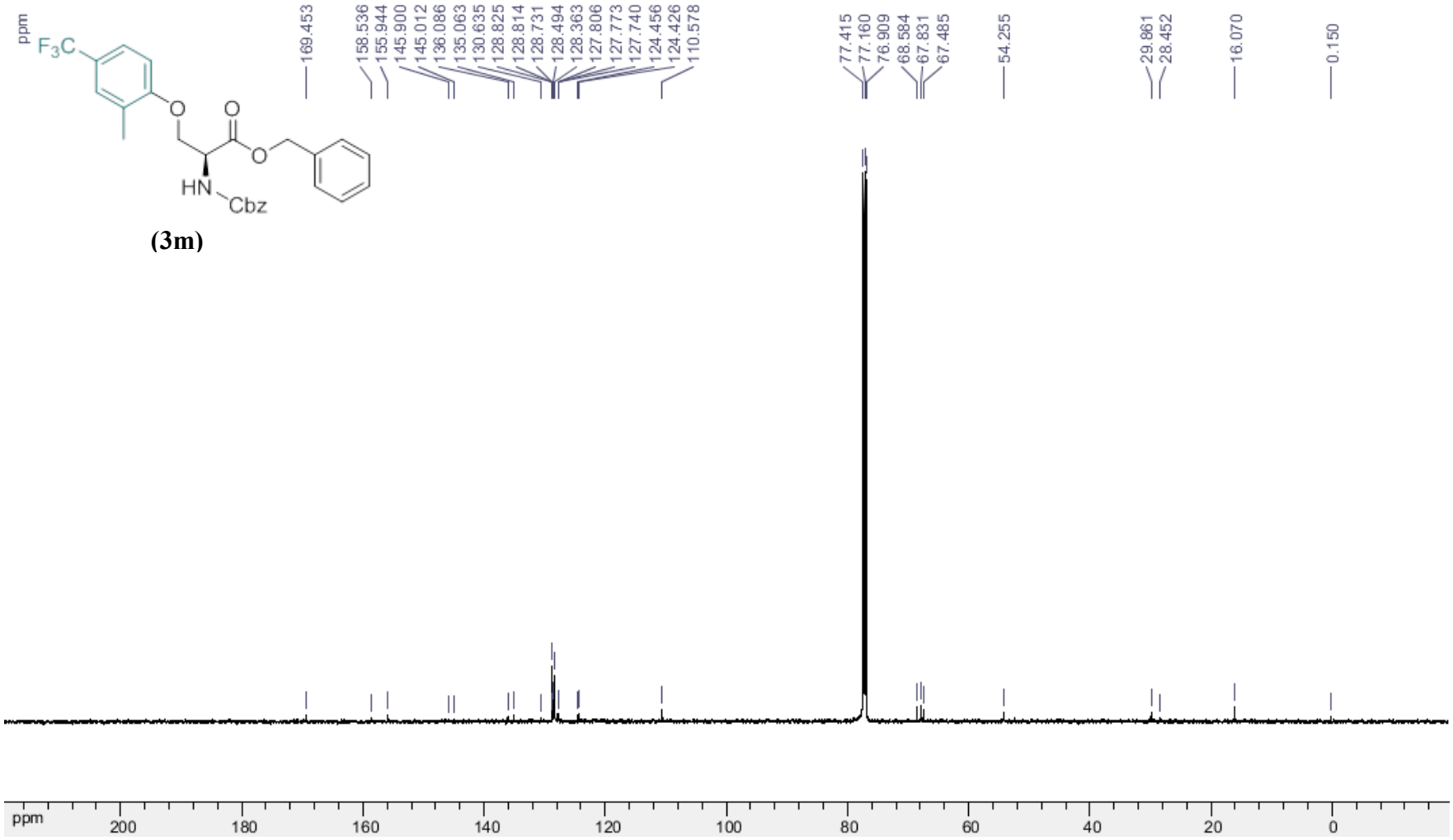


^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(2-methyl-4-(trifluoromethyl)phenyl)-L-serinate (3m).**



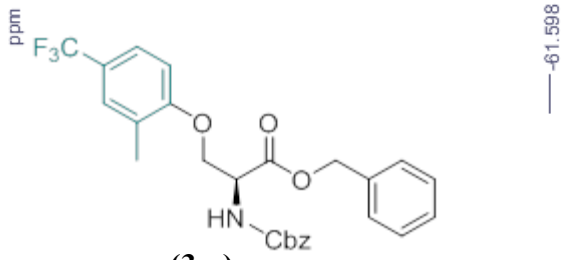
(3m)

^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(2-methyl-4-(trifluoromethyl)phenyl)-L-serinate (3m).**



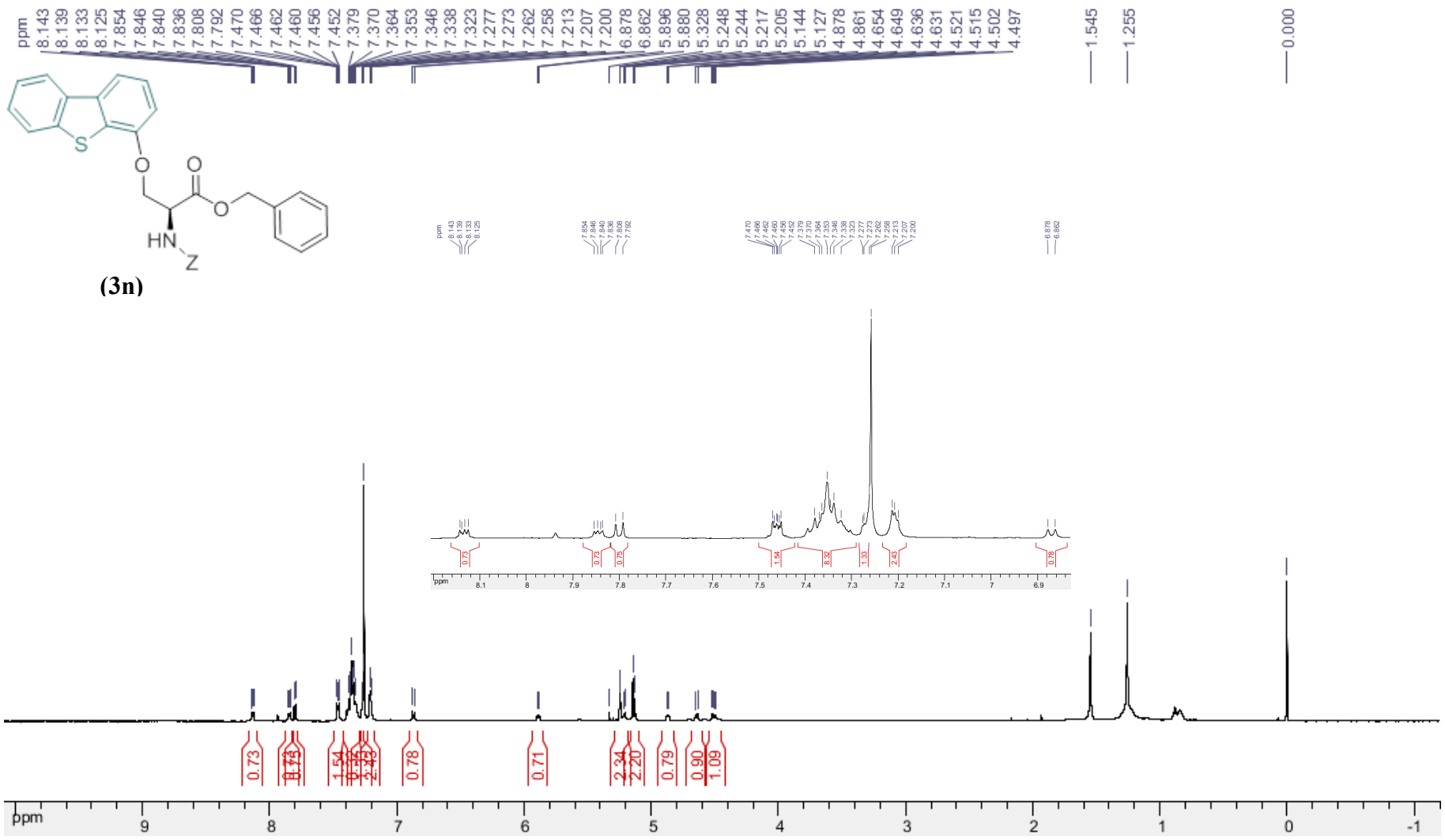
(3m)

^{19}F NMR (470.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(2-methyl-4-(trifluoromethyl)phenyl)-L-serinate (3m).**

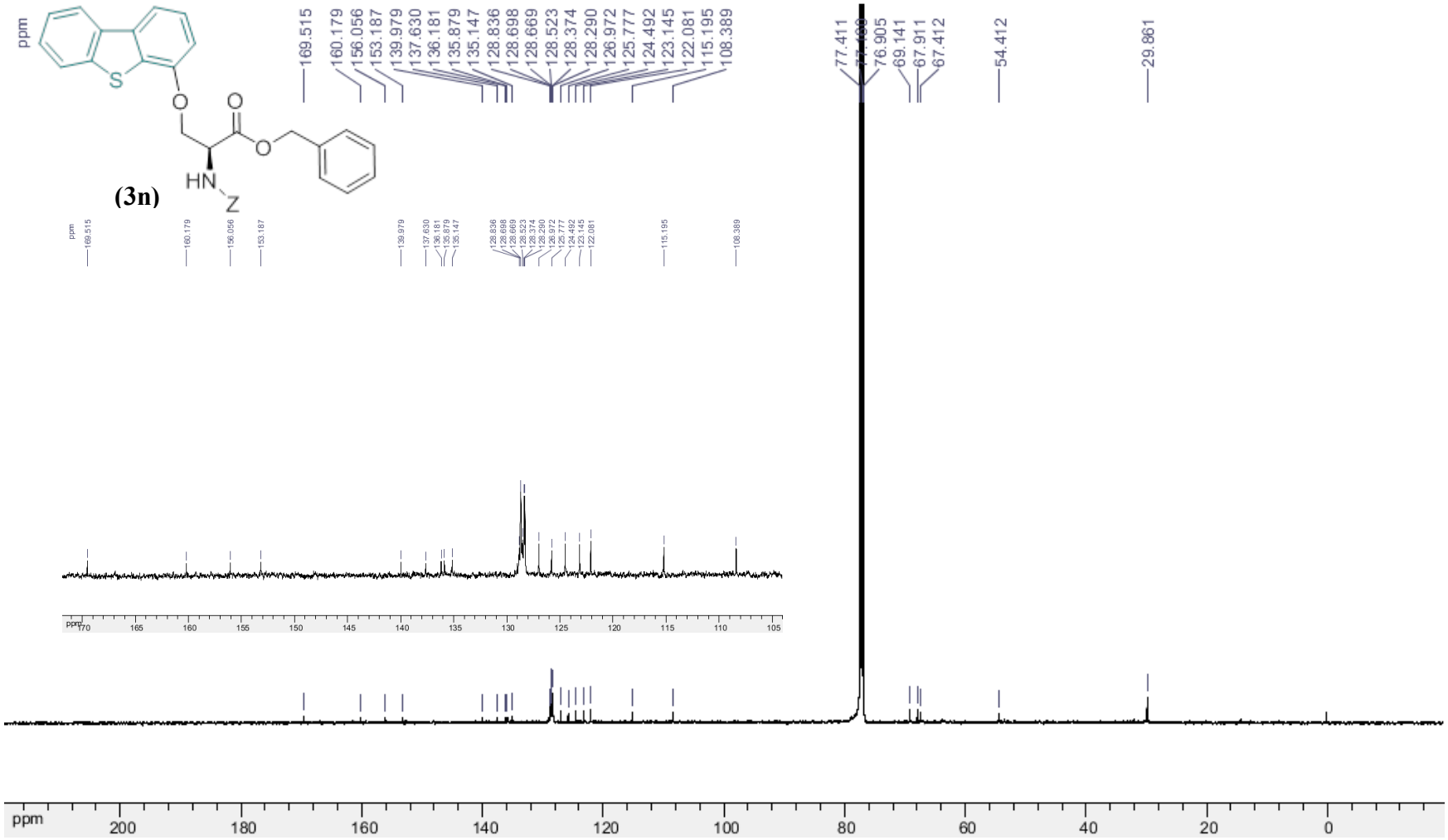


(3m)

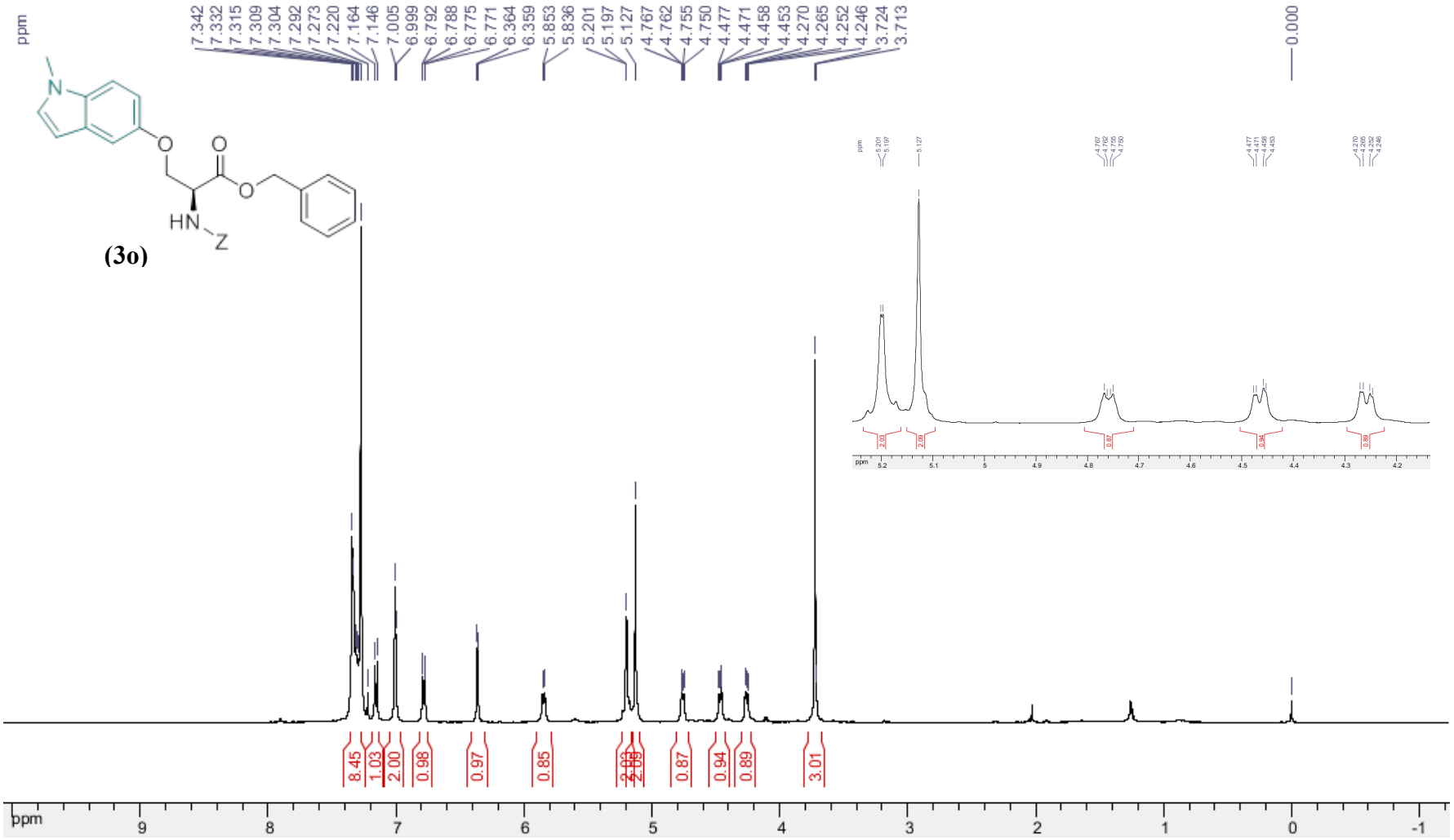
^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(dibenzo[b,d]thiophen-4-yl)-L-serinate (3n).**



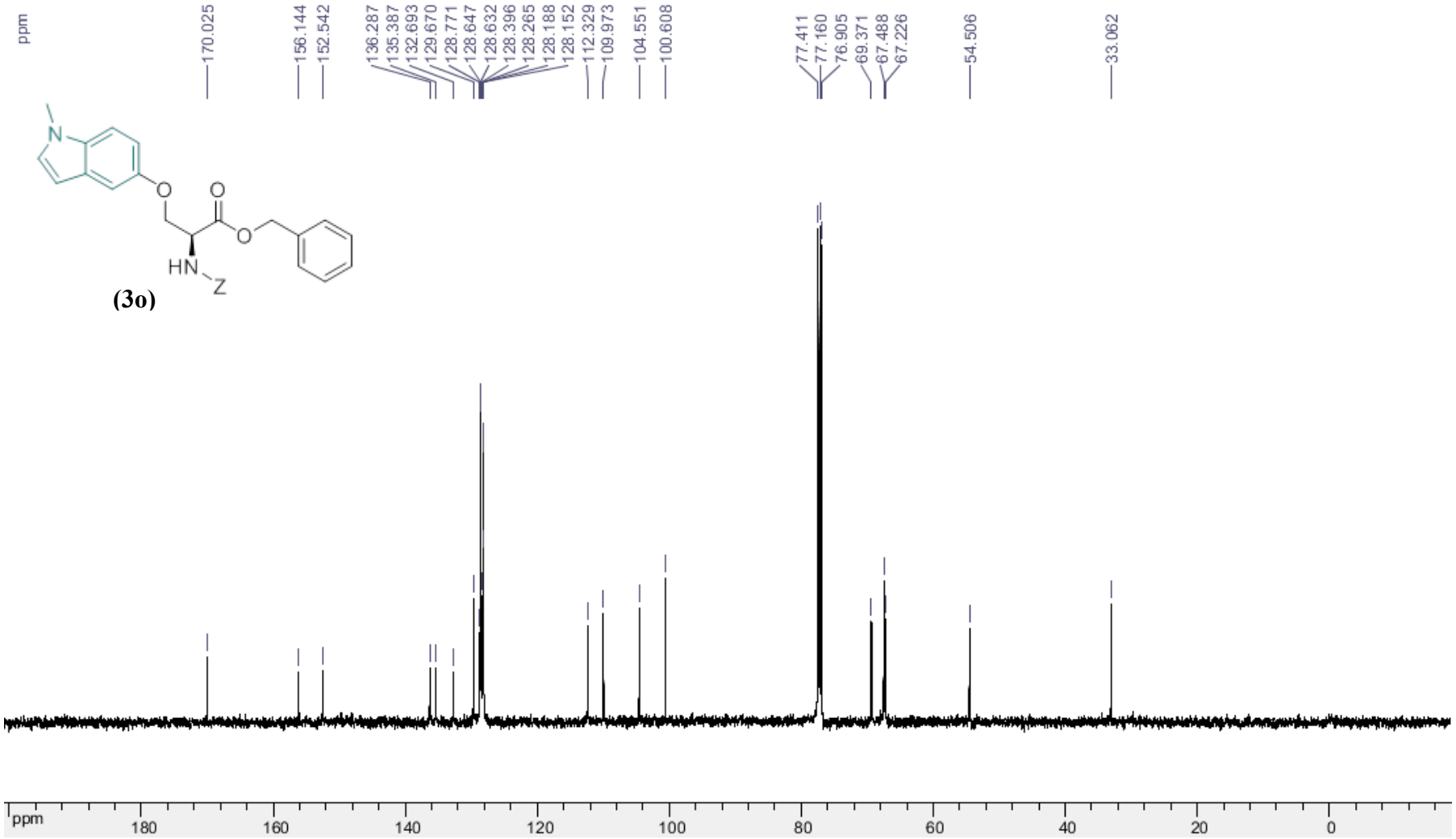
^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(dibenzo[b,d]thiophen-4-yl)-L-serinate (3n)**



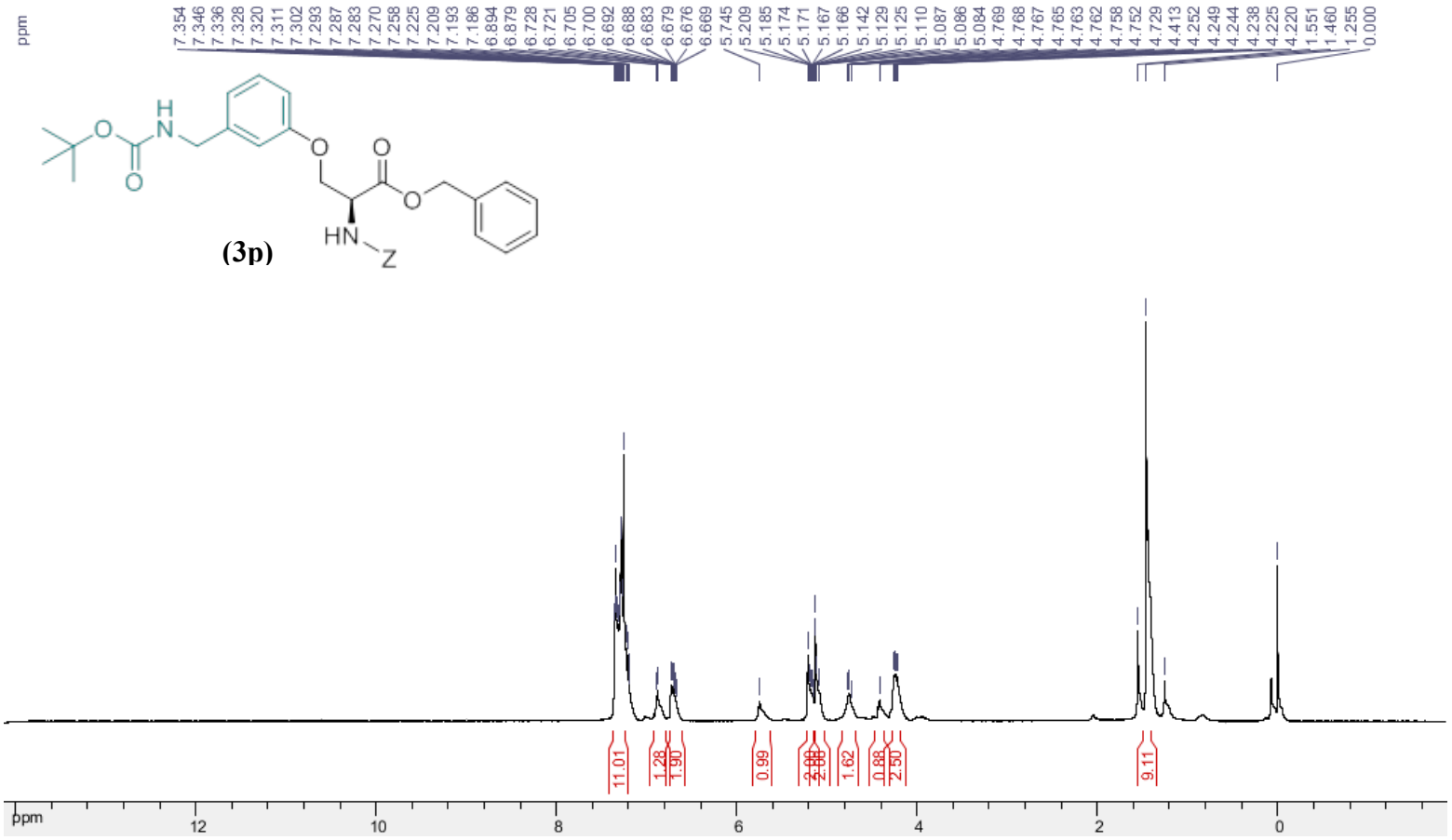
^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(1-methyl-1H-indol-5-yl)-L-serinate (3o).**



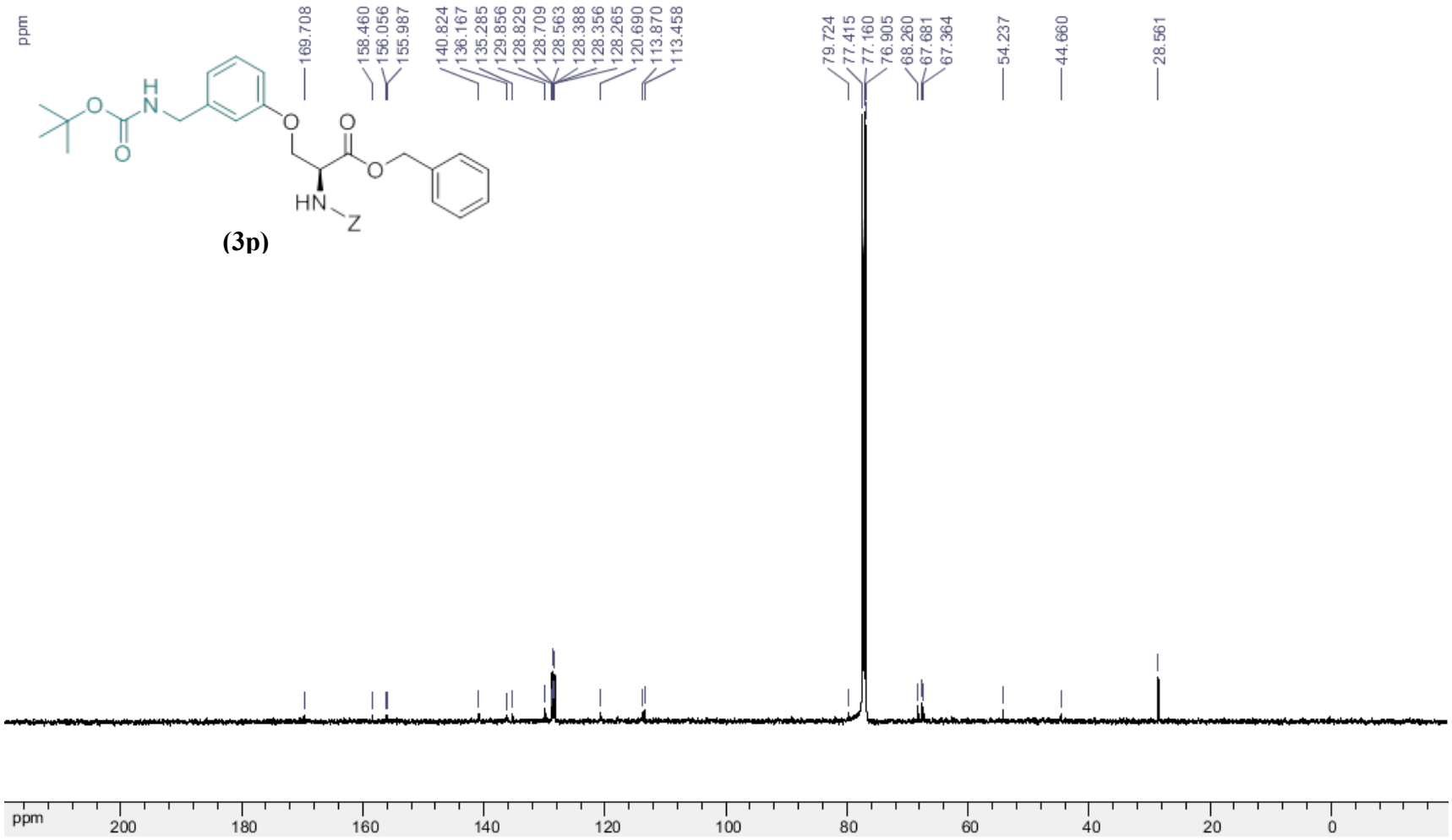
^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(1-methyl-1H-indol-5-yl)-L-serinate (3o)**



^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(3-(((*tert*-butoxycarbonyl)amino)methyl)phenyl)-L-serinate (3p).**

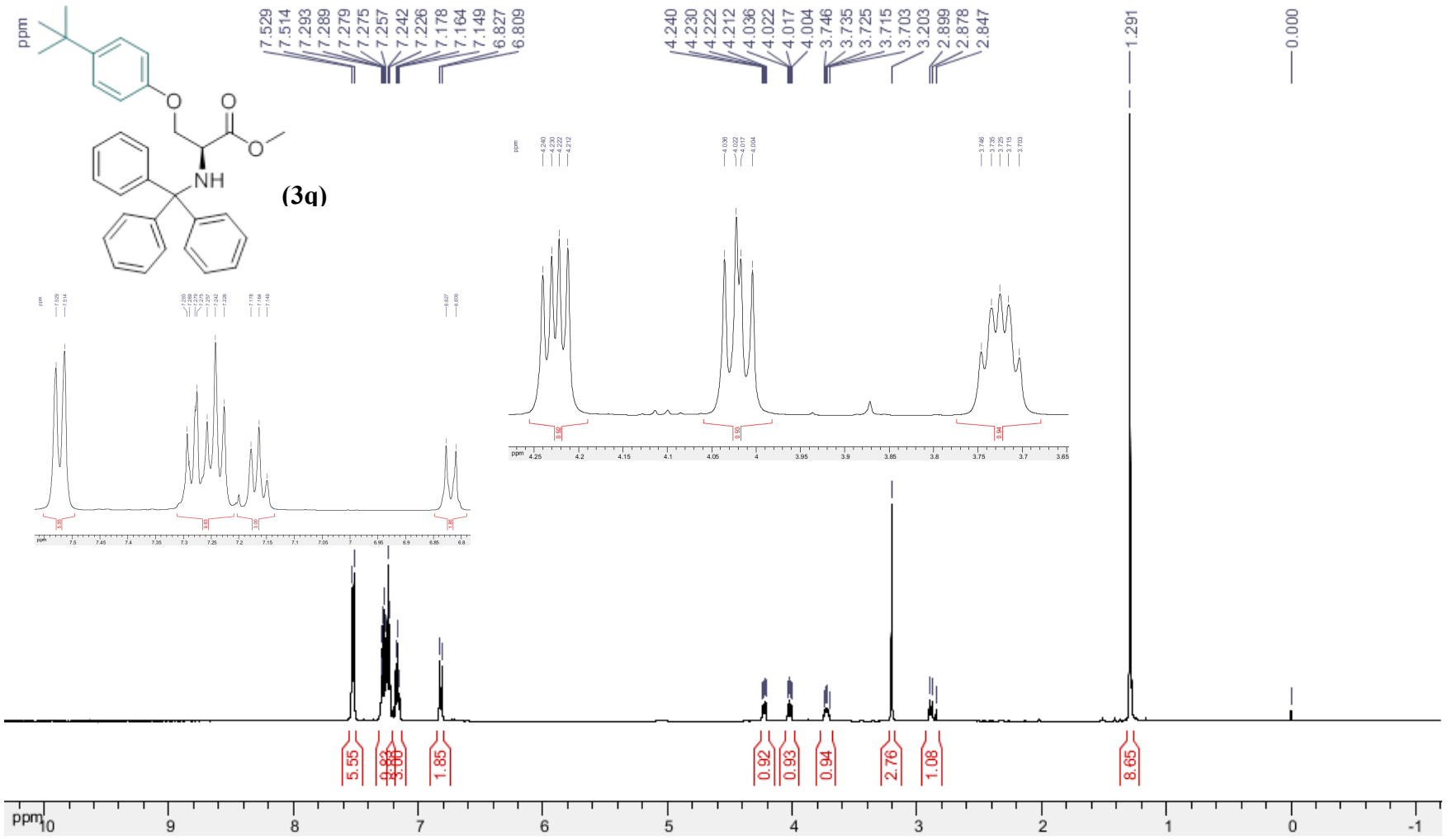


^{13}C NMR (125.8 MHz, $CDCl_3$) of of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(3-(((*tert*-butoxycarbonyl)amino)methyl)phenyl)-L-serinate (3p)**

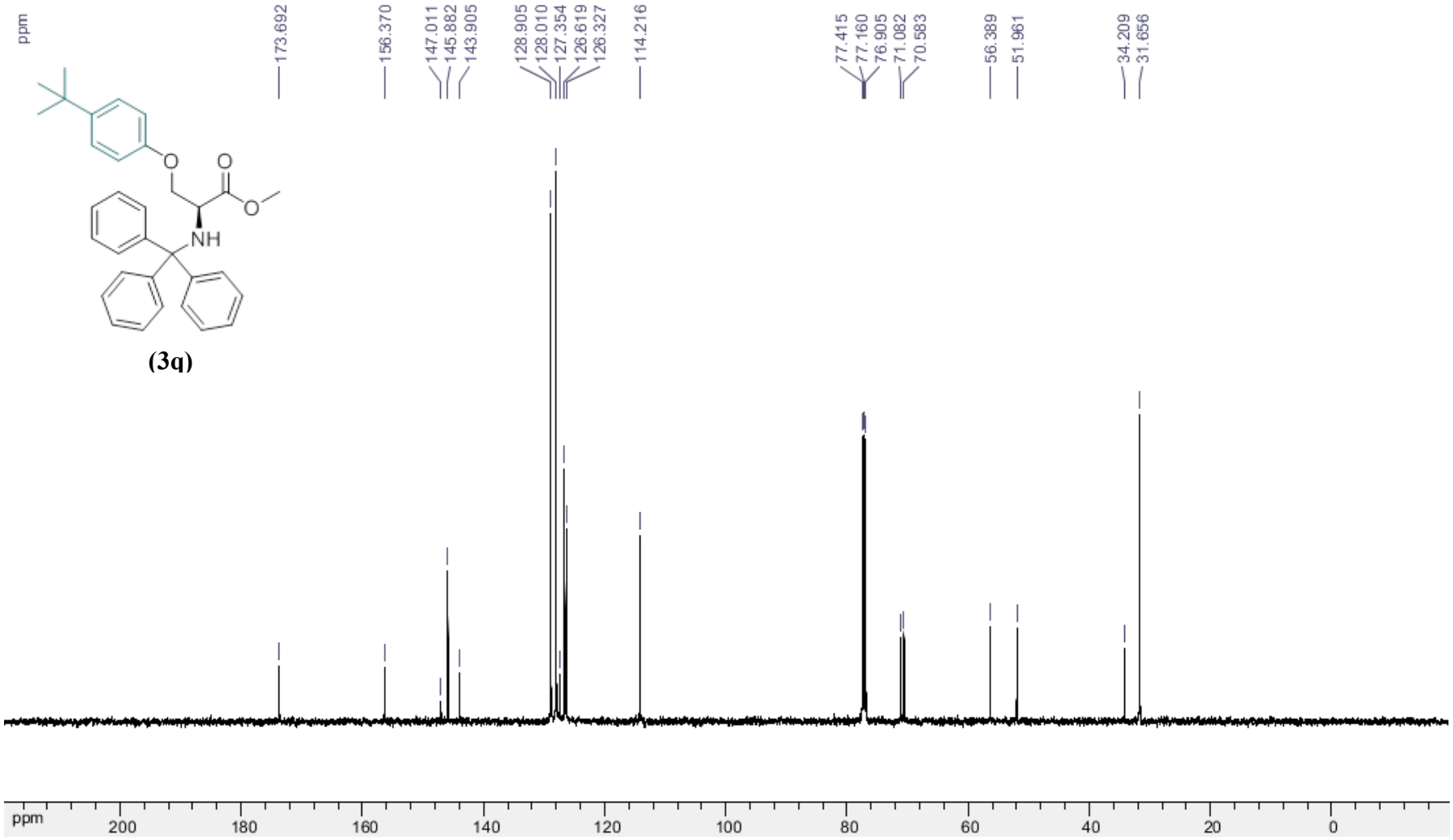


(3p)

^{1}H NMR (500 MHz, $CDCl_3$) of **Methyl *O*-(4-(*tert*-butyl)phenyl)-*N*-trityl-L-serinate (from the aryl/heteroarylboronic acid (3q).**

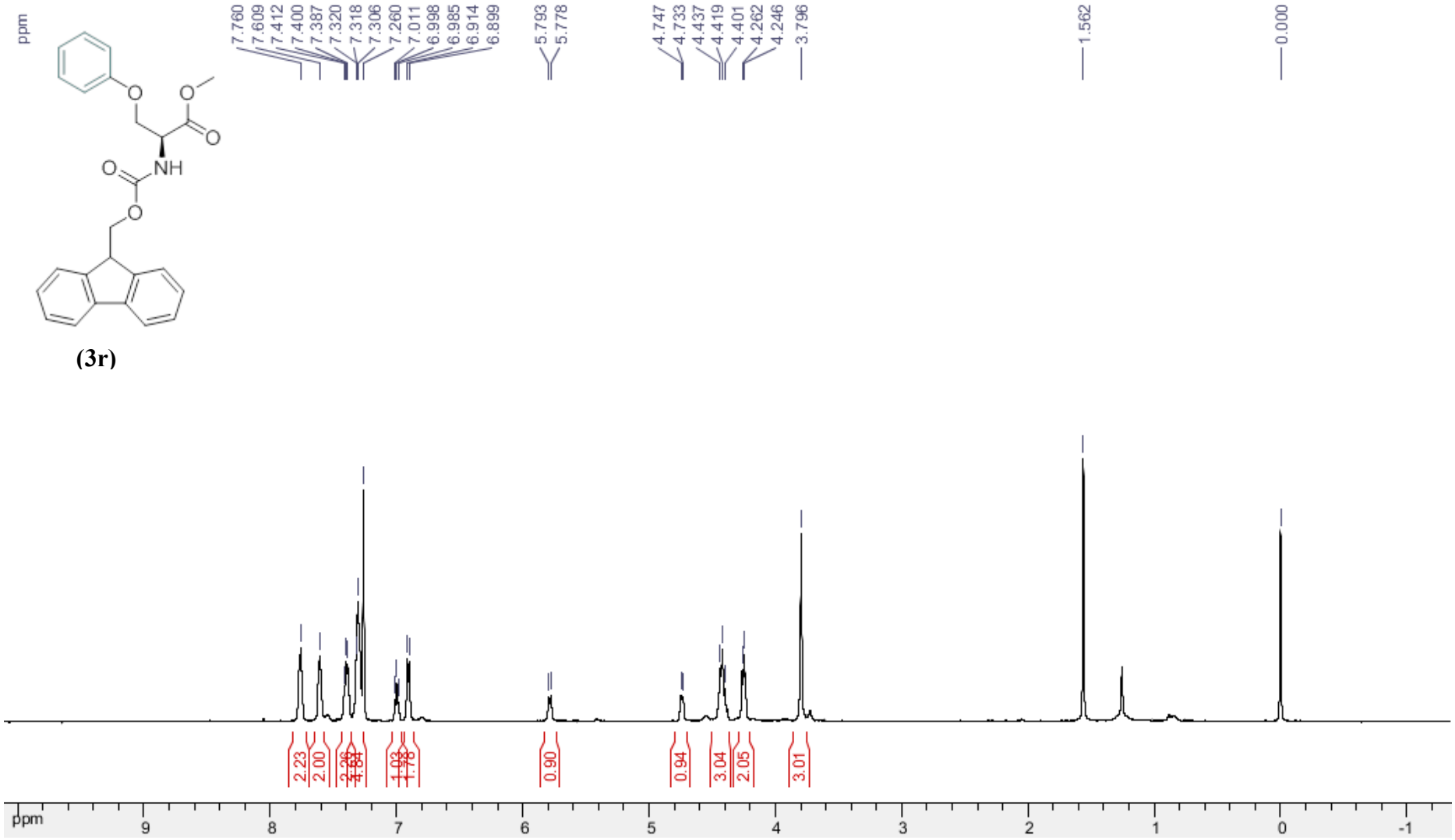


^{13}C NMR (125.8 MHz, $CDCl_3$) of **Methyl *O*-(4-(*tert*-butyl)phenyl)-*N*-trityl-L-serinate (3q)**



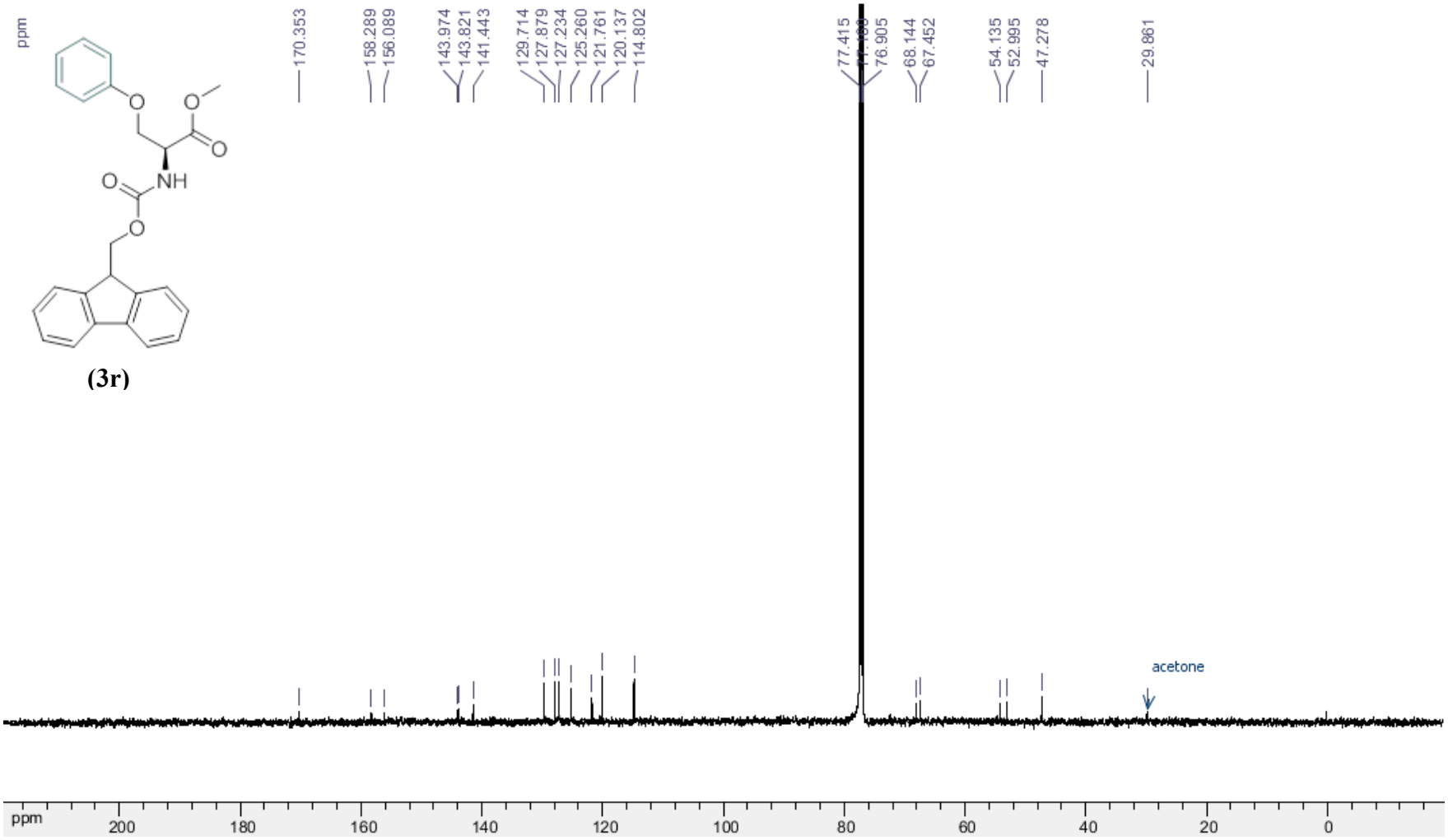
(3q)

^{1}H NMR (500 MHz, $CDCl_3$) of **Methyl *N*-((9H-fluoren-9-yl)methyl)-*O*-phenyl-L-serinate (3r).**



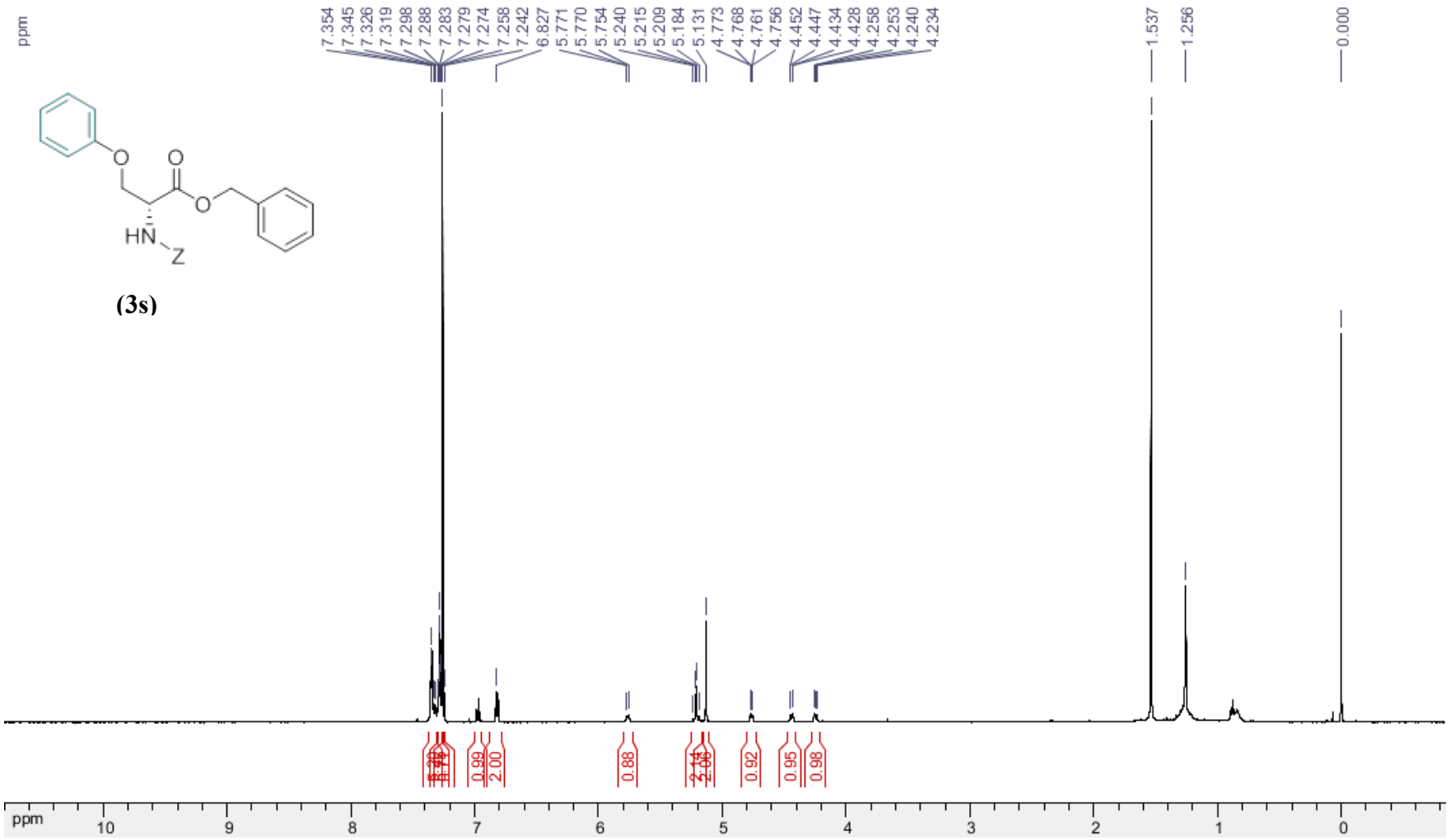
(3r)

^{13}C NMR (125.8 MHz, $CDCl_3$) of **Methyl *N*-((9H-fluoren-9-yl)methyl)-*O*-phenyl-L-serinate (3r).**



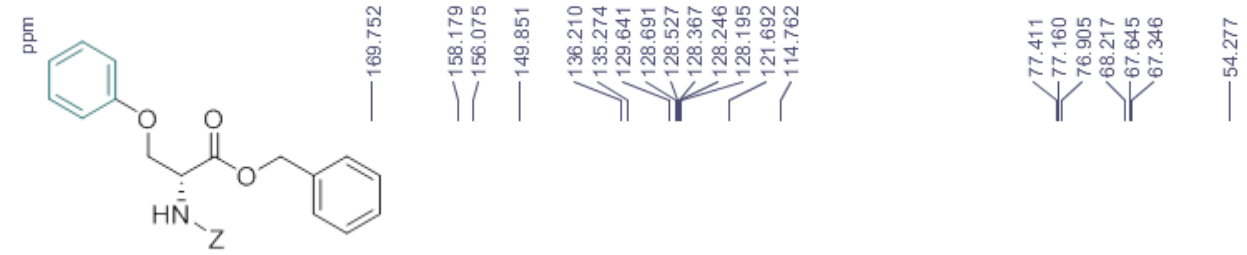
(3r)

^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-phenyl-D-serinate (3s).**

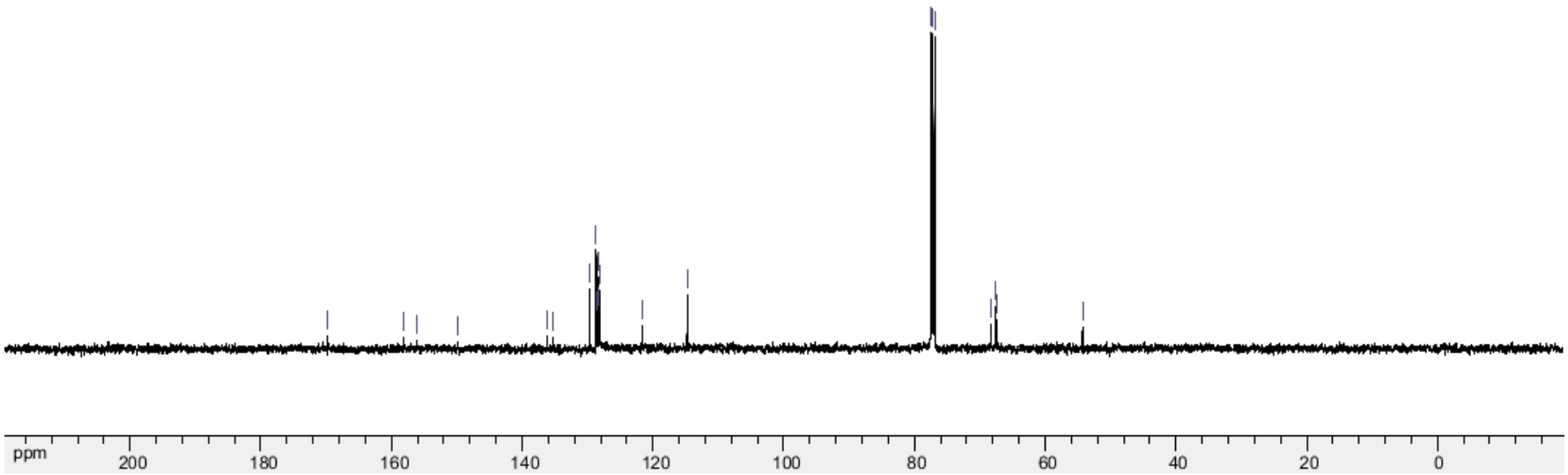


(3s)

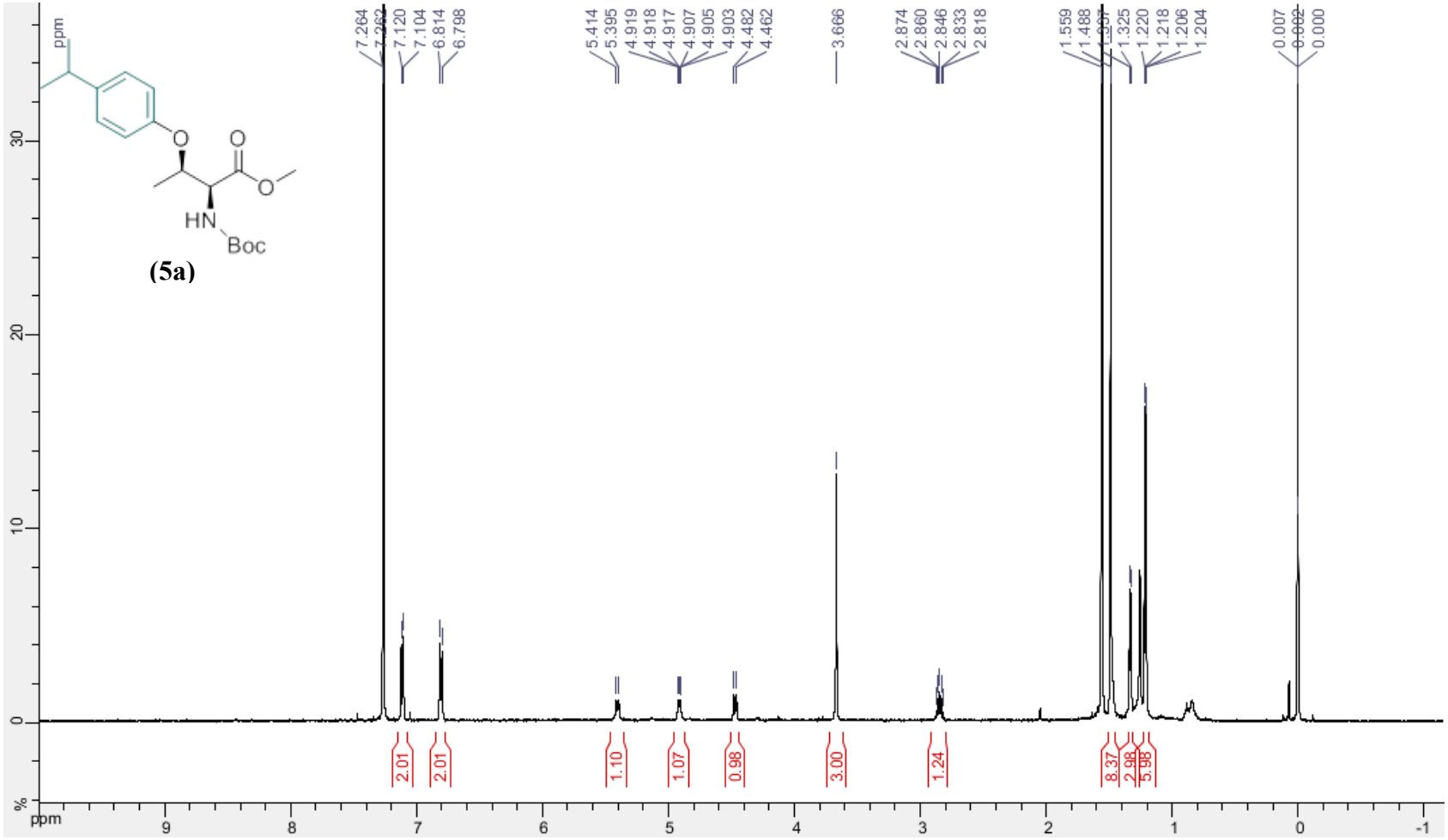
^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-phenyl-D-serinate (3s).**



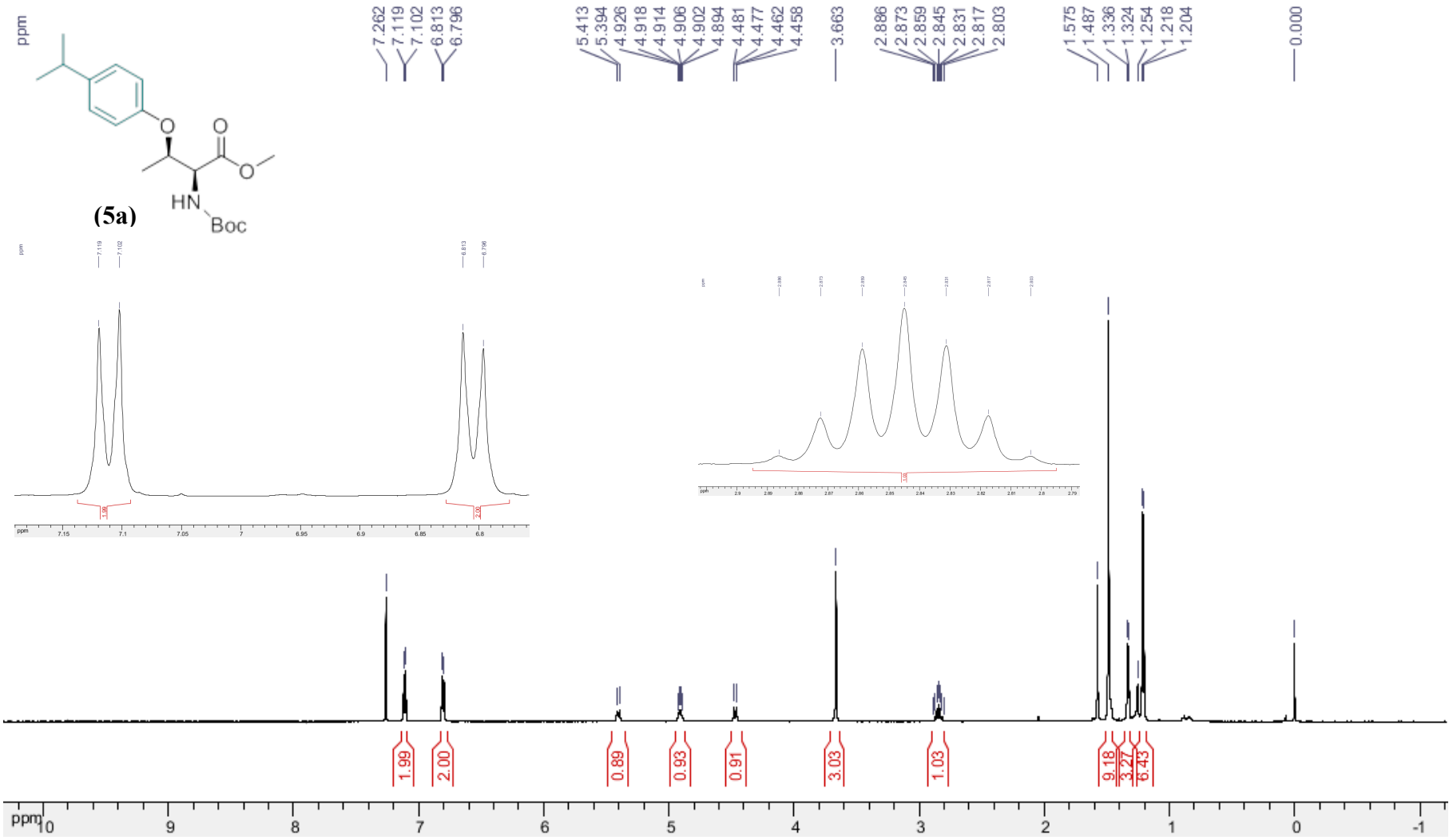
(3s)



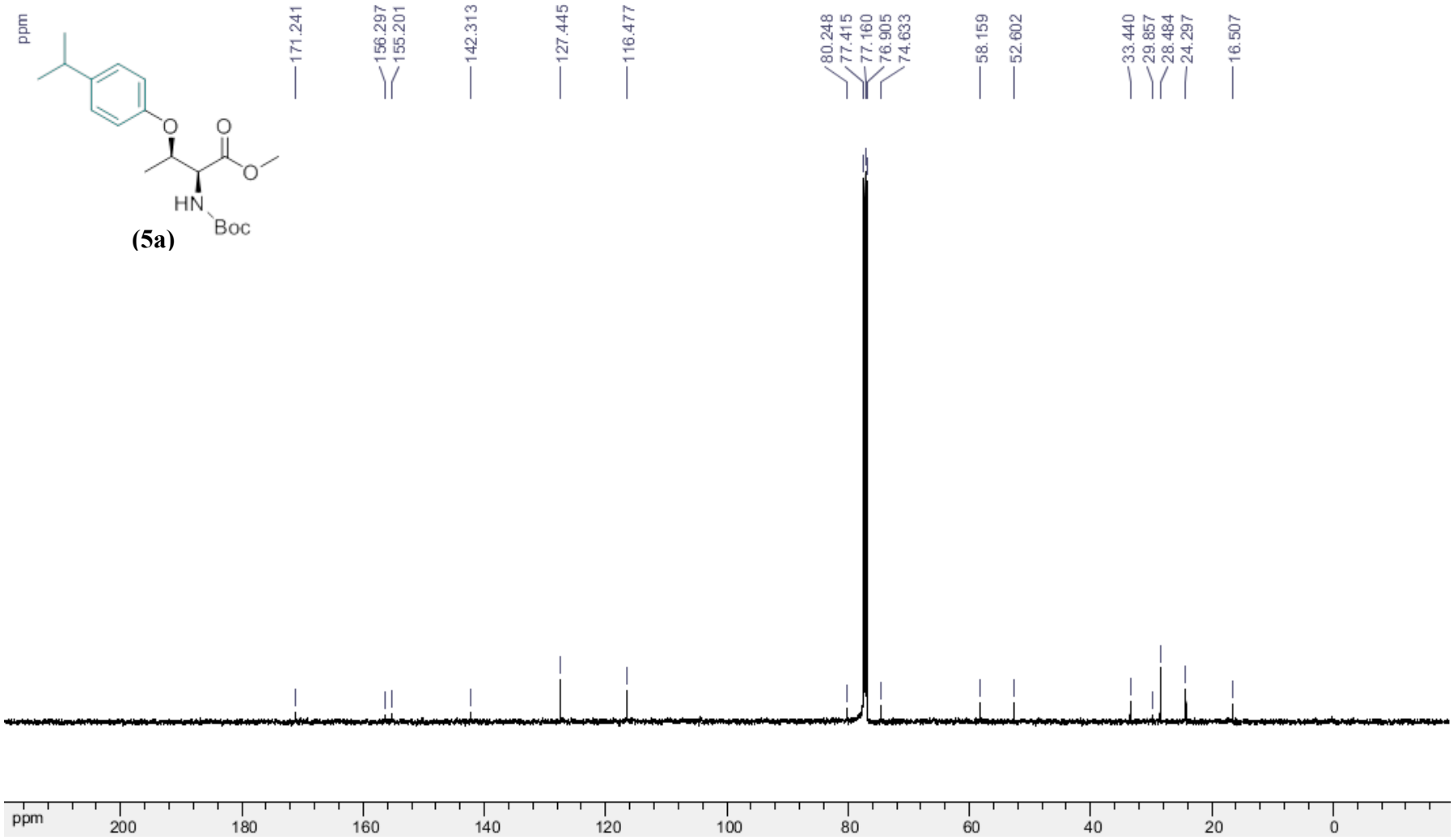
^{1}H NMR (500 MHz, $CDCl_3$) of **Methyl *N*-(*tert*-butoxycarbonyl)-*O*-(4-isopropylphenyl)-L-threoninate (5a) (from the aryl/heteroaryltrifluoroborate ($X_n = BF_3K$).**



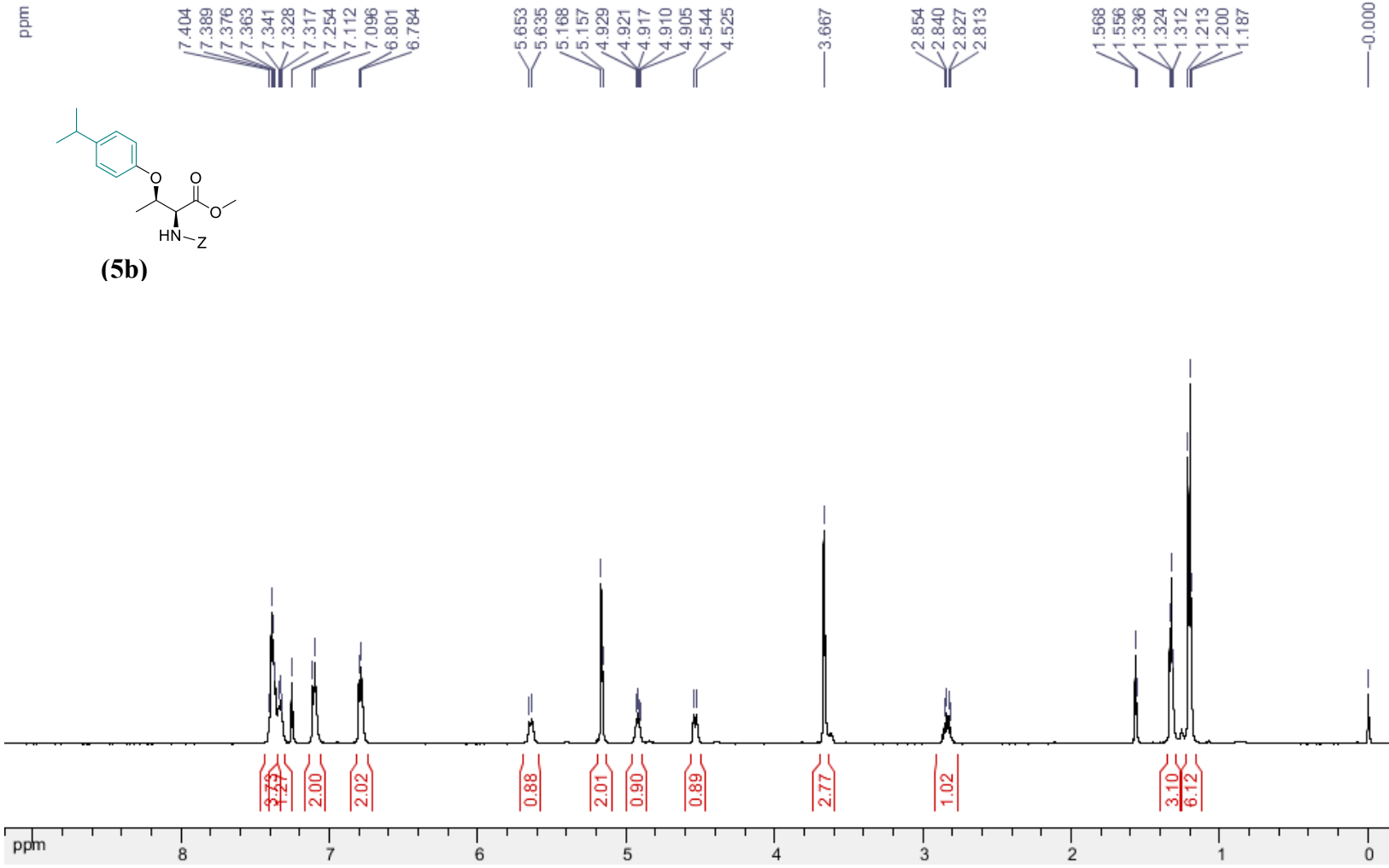
^{1}H NMR (500 MHz, $CDCl_3$) of **Methyl *N*-(*tert*-butoxycarbonyl)-*O*-(4-isopropylphenyl)-L-threoninate (5a) (from the aryl/heteroarylboronic acid [$X_n = B(OH)_2$]**



^{13}C NMR (125.8 MHz, $CDCl_3$) of **Methyl *N*-(*tert*-butoxycarbonyl)-*O*-(4-isopropylphenyl)-L-threoninate (5a).**

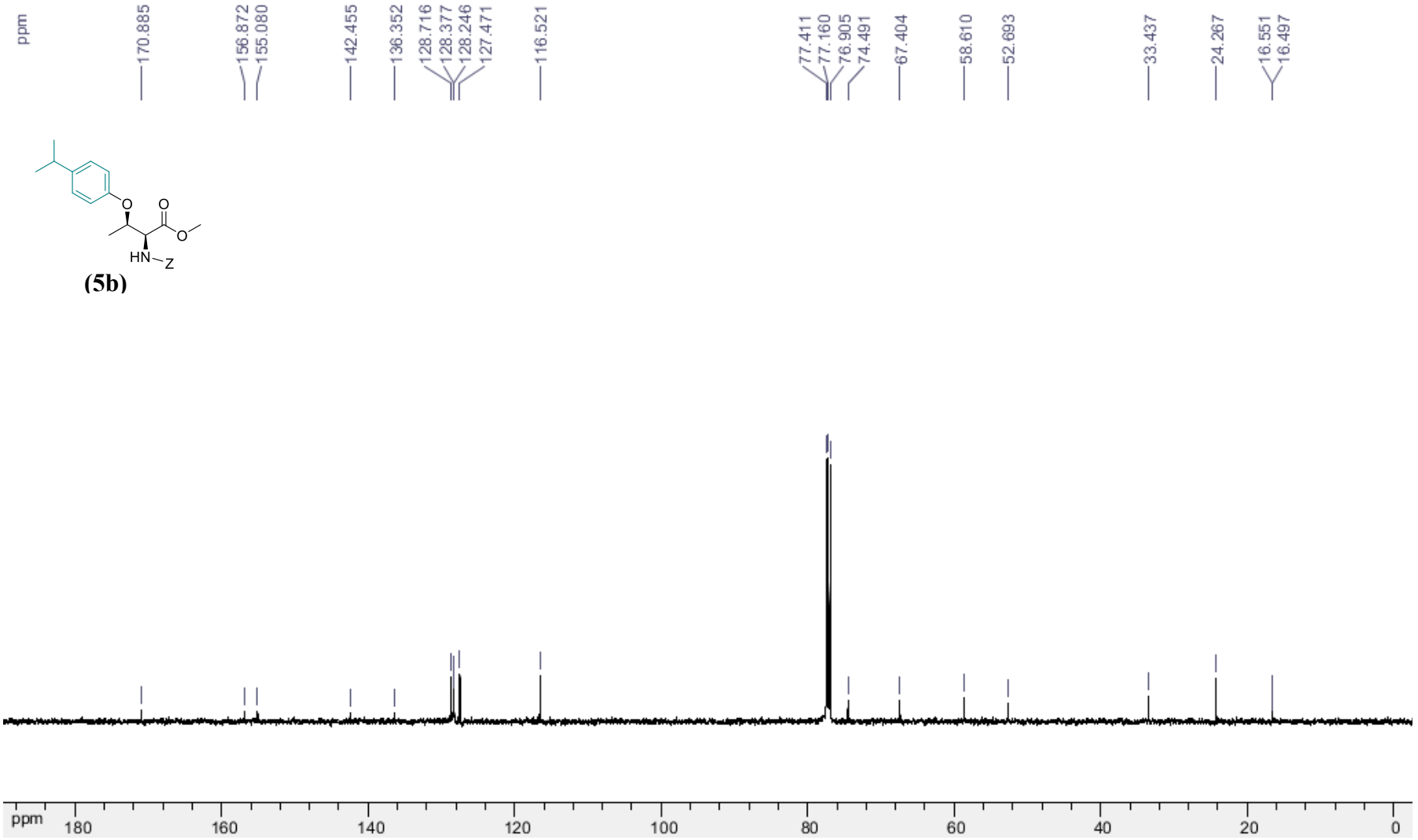


^{1}H NMR (500 MHz, $CDCl_3$) of **Methyl *N*-((benzyloxy)carbonyl)-*O*-(4-isopropylphenyl)-L-allothreoninate (5b).**



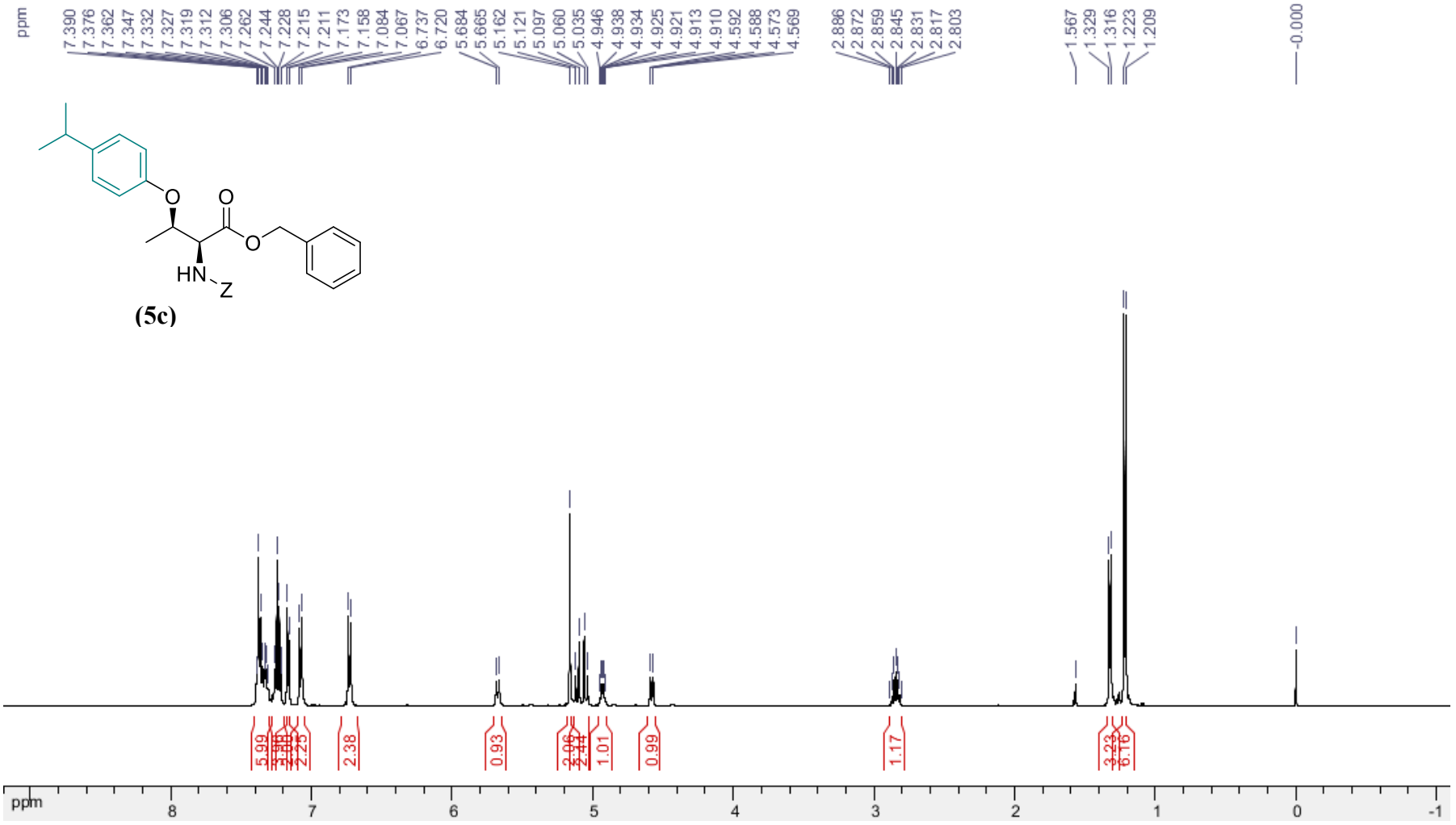
(5b)

^{13}C NMR (125.8 MHz, $CDCl_3$) of **Methyl *N*-((benzyloxy)carbonyl)-*O*-(4-isopropylphenyl)-L-allothreoninate (5b).**

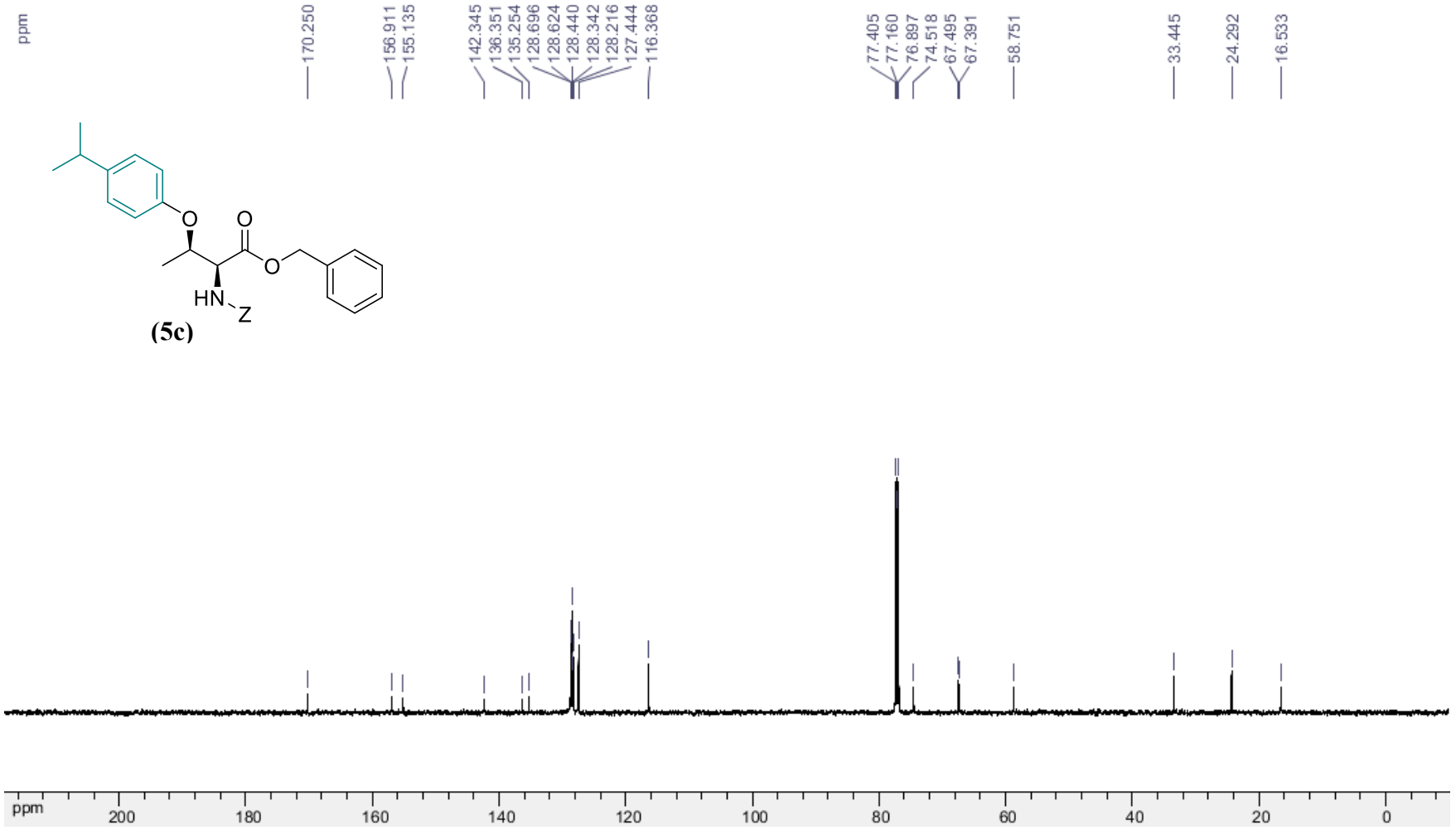


(5b)

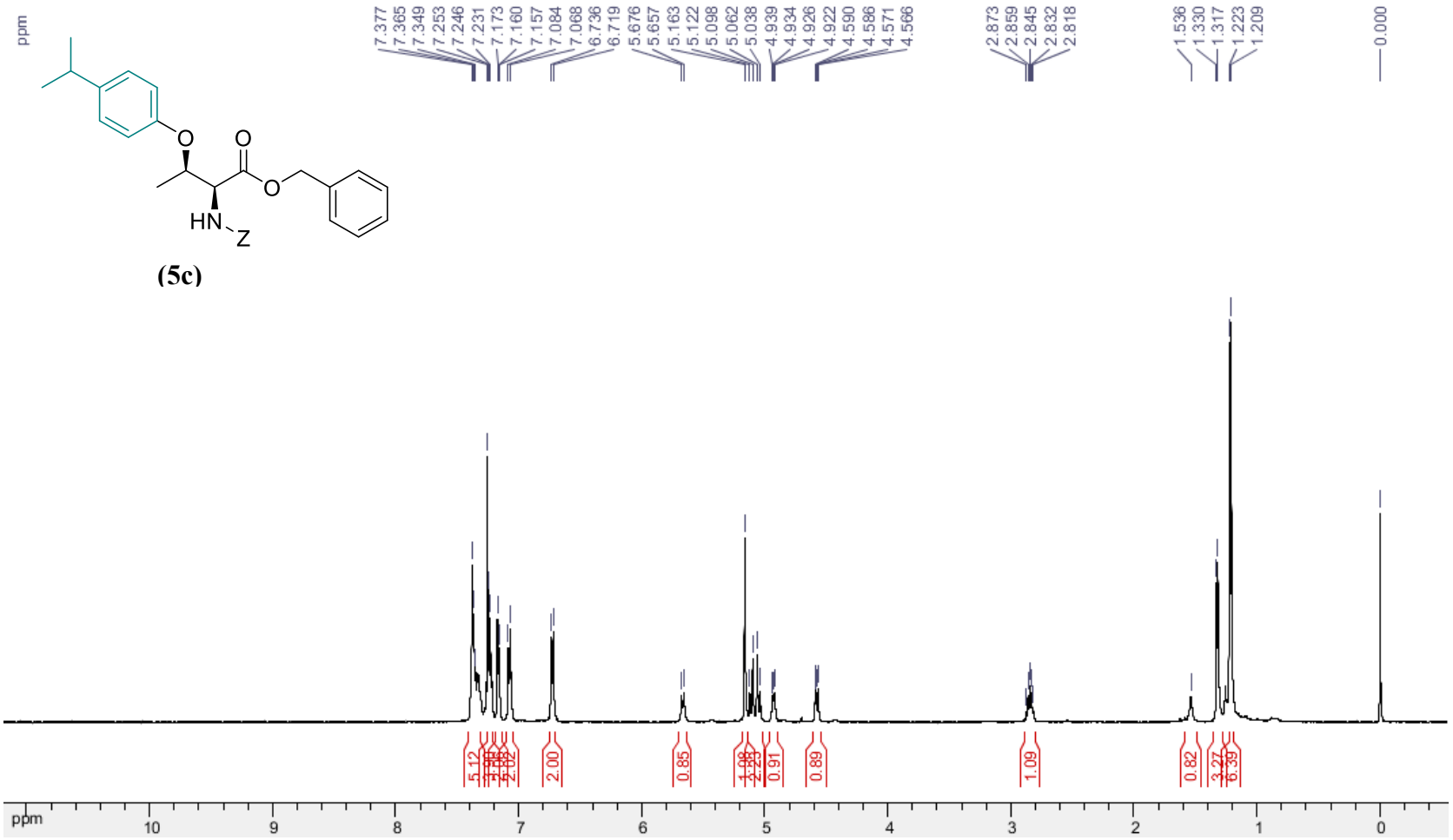
^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(4-isopropylphenyl)-L-allothreoninate (5c) (from the aryl/heteroarylboronic acid [X_n = $B(OH)_2$].**



^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(4-isopropylphenyl)-L-allothreoninate (5c).**

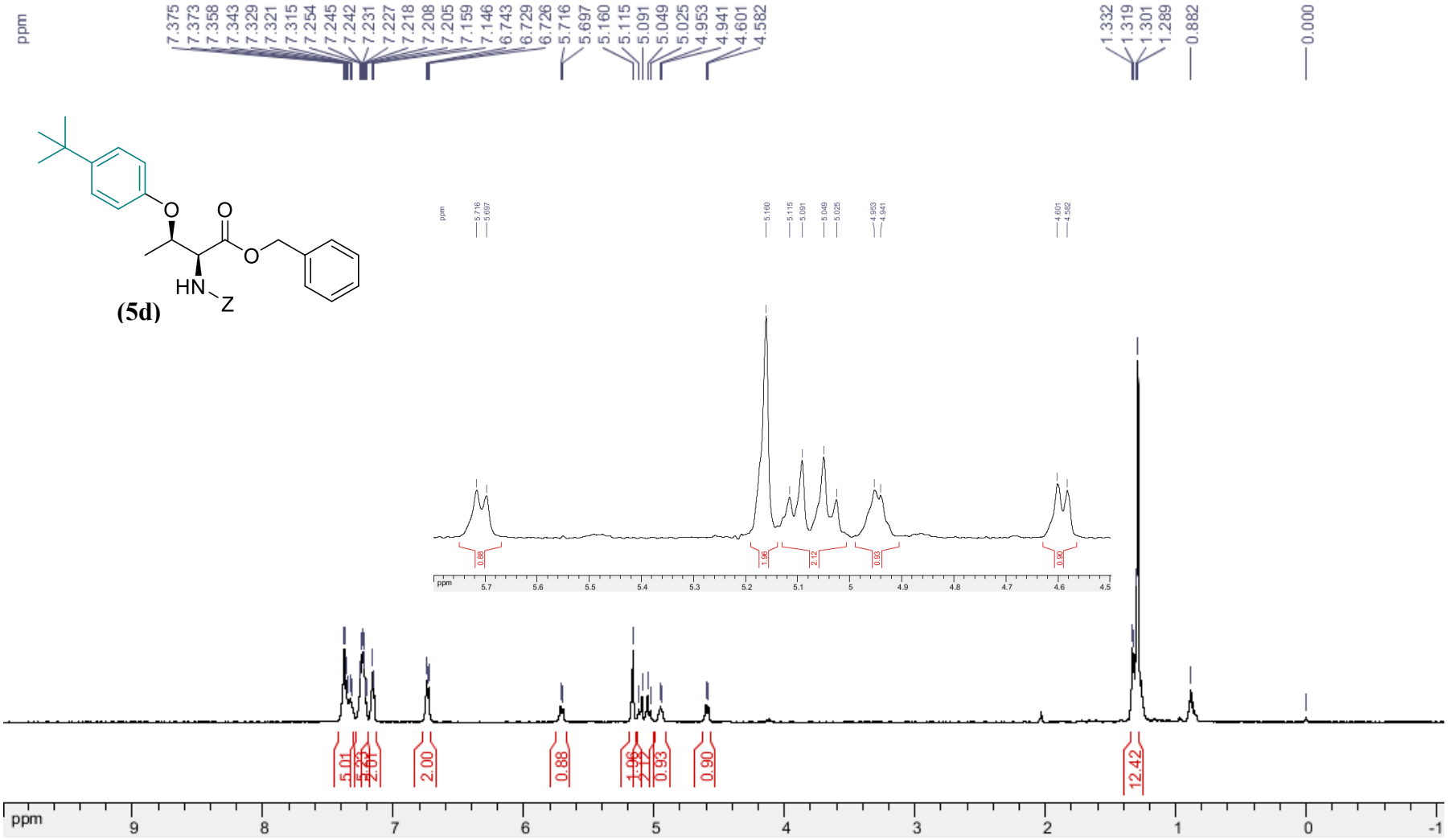


^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(4-isopropylphenyl)-L-allothreoninate (5c) (from the aryl/heteroaryltrifluoroborate (X_n = BF_3K).**

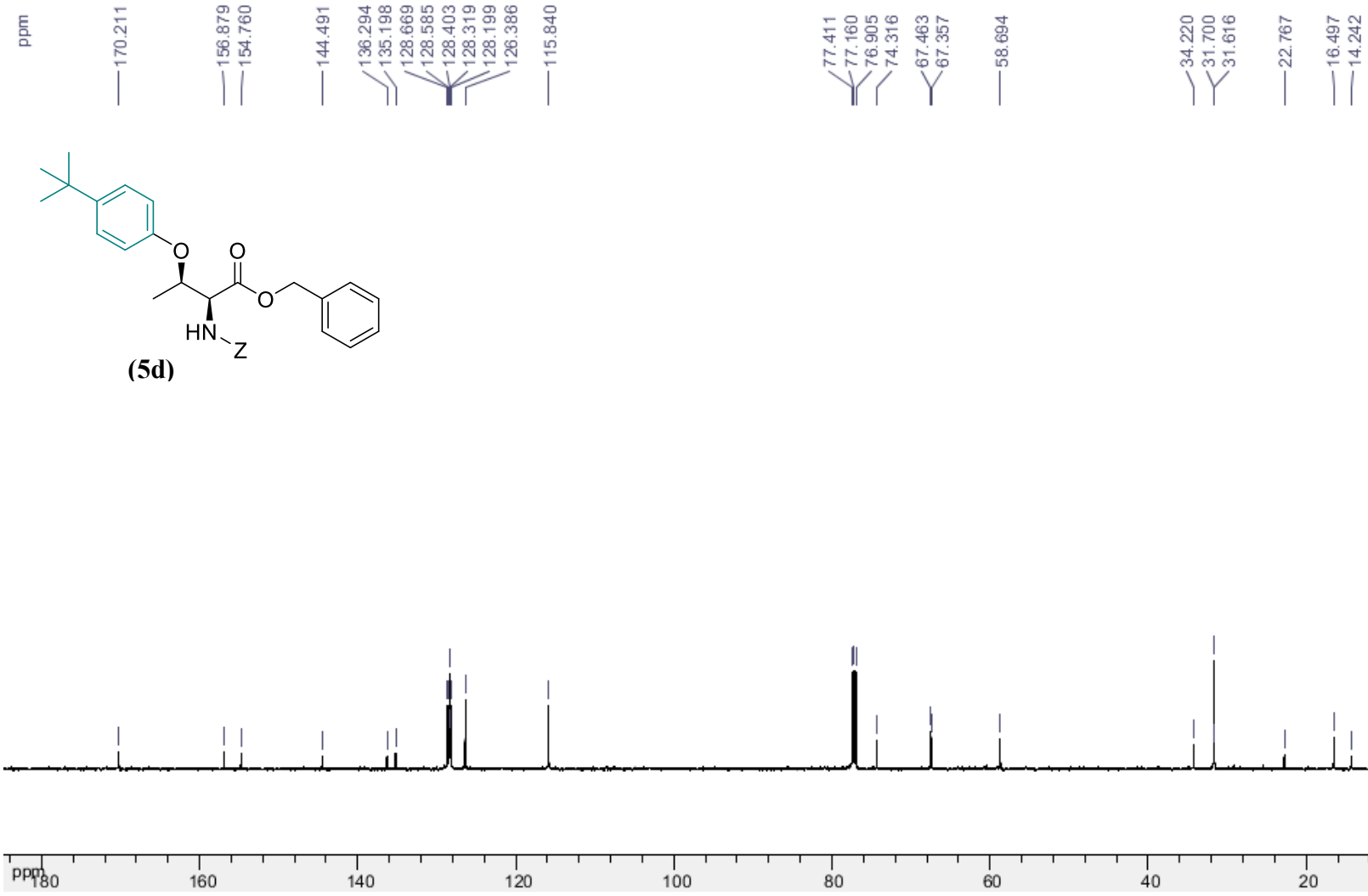


(5c)

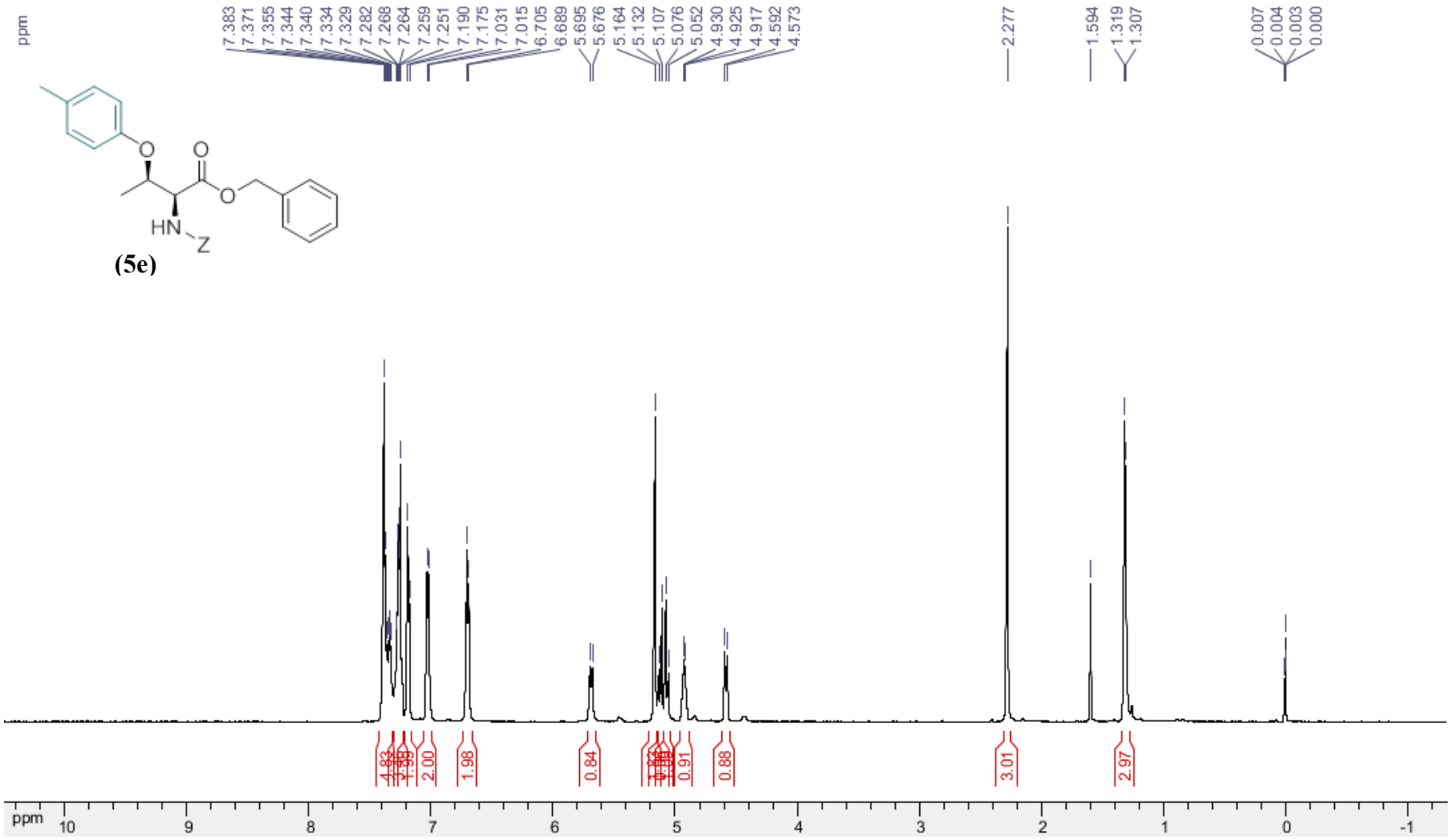
^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(4-(*tert*-butyl)phenyl)-L-allothreoninate (5d).**



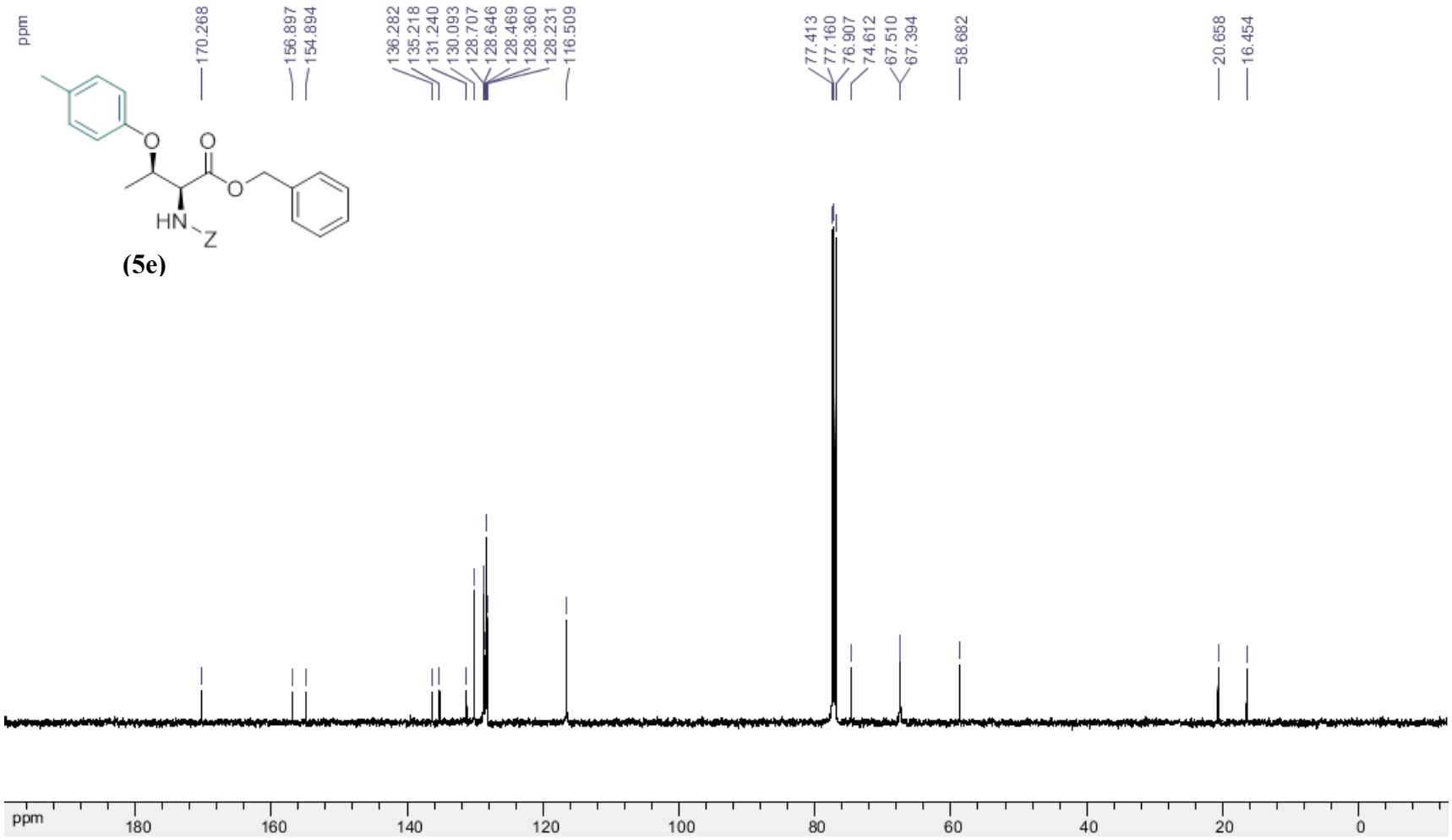
^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(4-(*tert*-butyl)phenyl)-L-allothreoninate (5d).**



^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(*p*-tolyl)-L-threoninate (5e) (from the aryl/heteroarylboronic acid [X_n = $B(OH)_2$].**

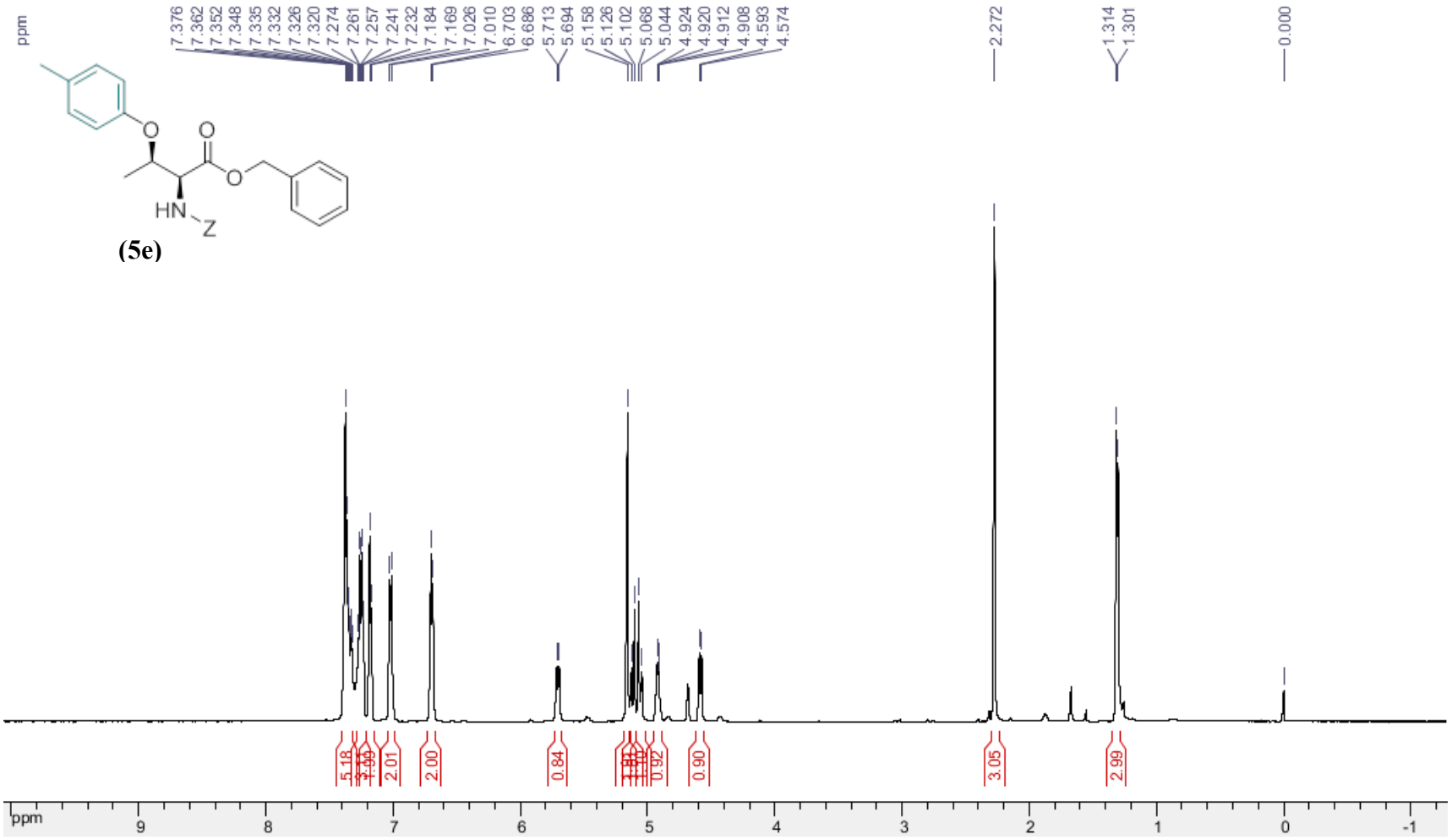


^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(*p*-tolyl)-L-threoninate (5e) (from the aryl/heteroarylboronic acid [$X_n = B(OH)_2$].**



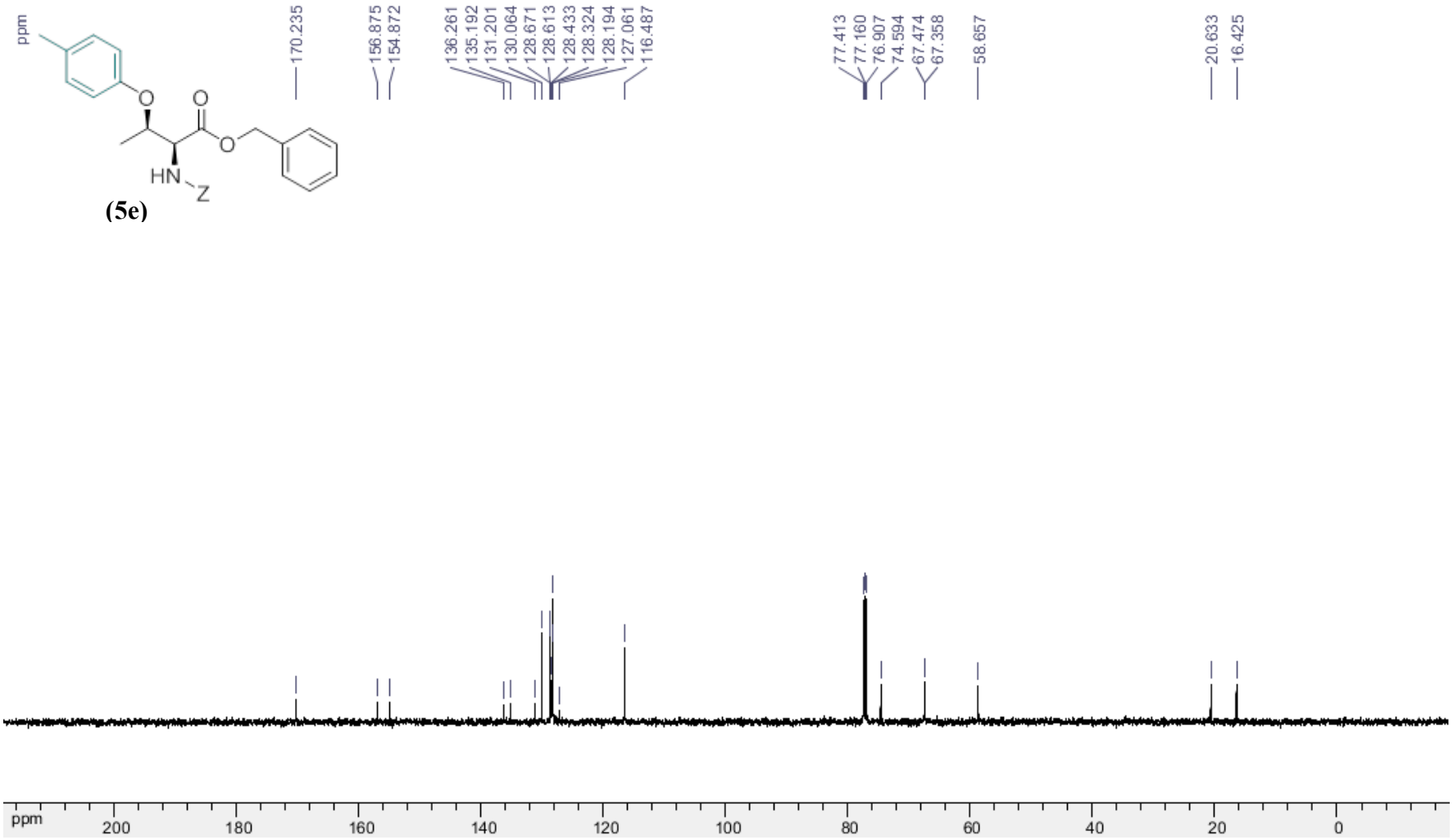
(5e)

^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(*p*-tolyl)-L-threoninate (5e) (from the aryl/heteroaryltrifluoroborate (X_n = BF_3K).**



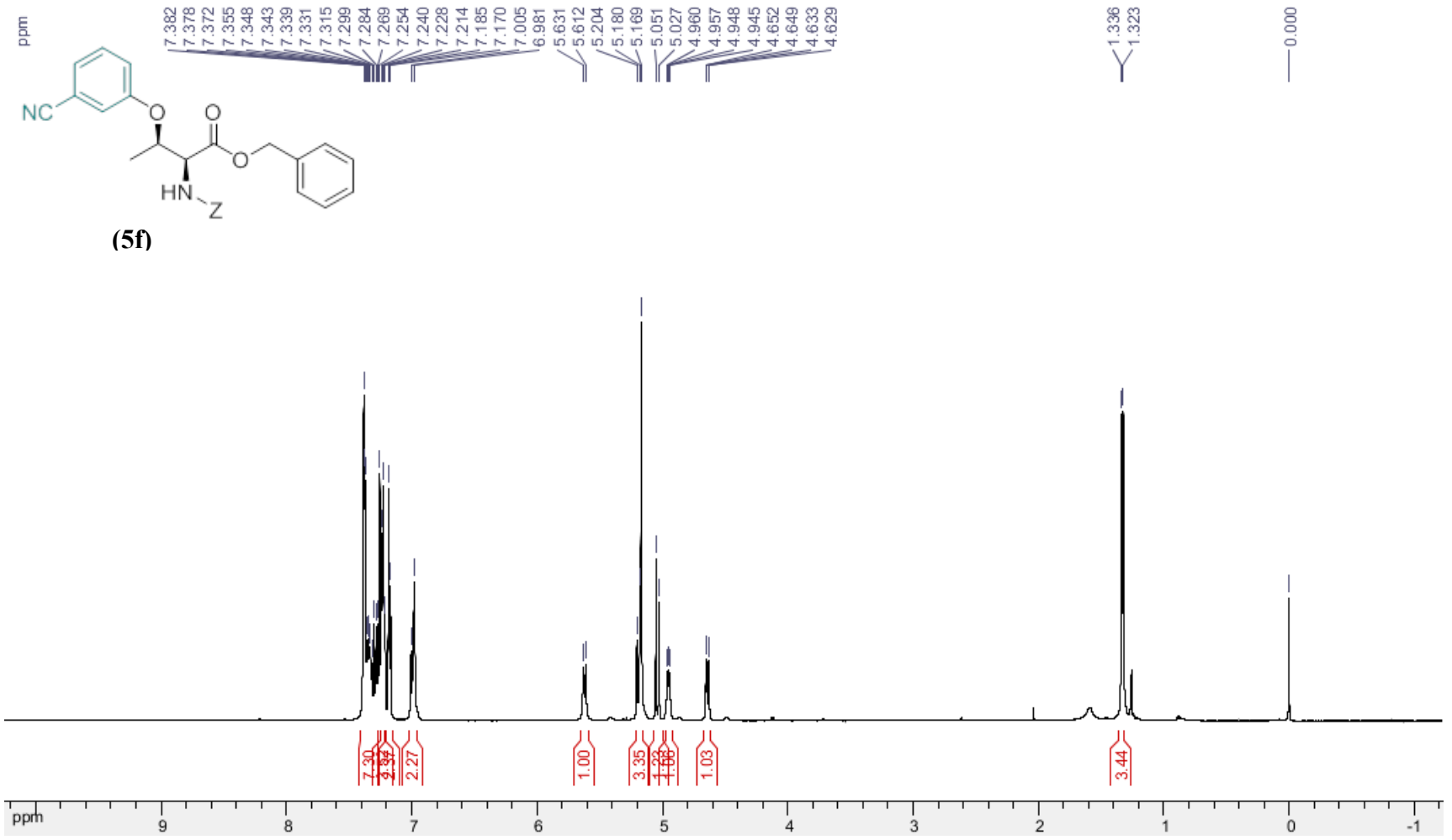
(5e)

^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(*p*-tolyl)-L-threoninate (5e) (from the aryl/heteroaryltrifluoroborate ($X_n = BF_3K$).**



(5e)

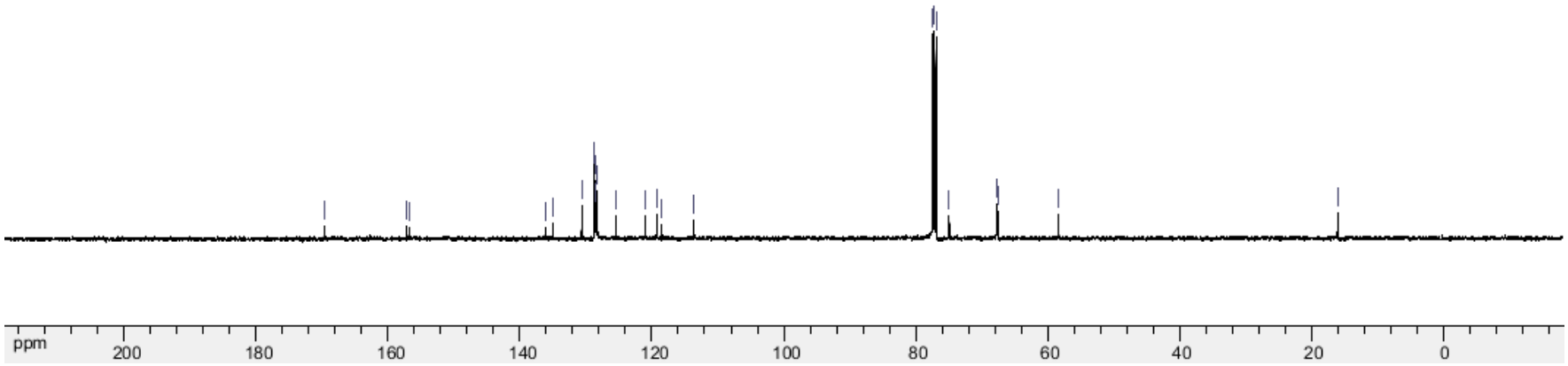
^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(3-cyanophenyl)-L-threoninate (5f).**



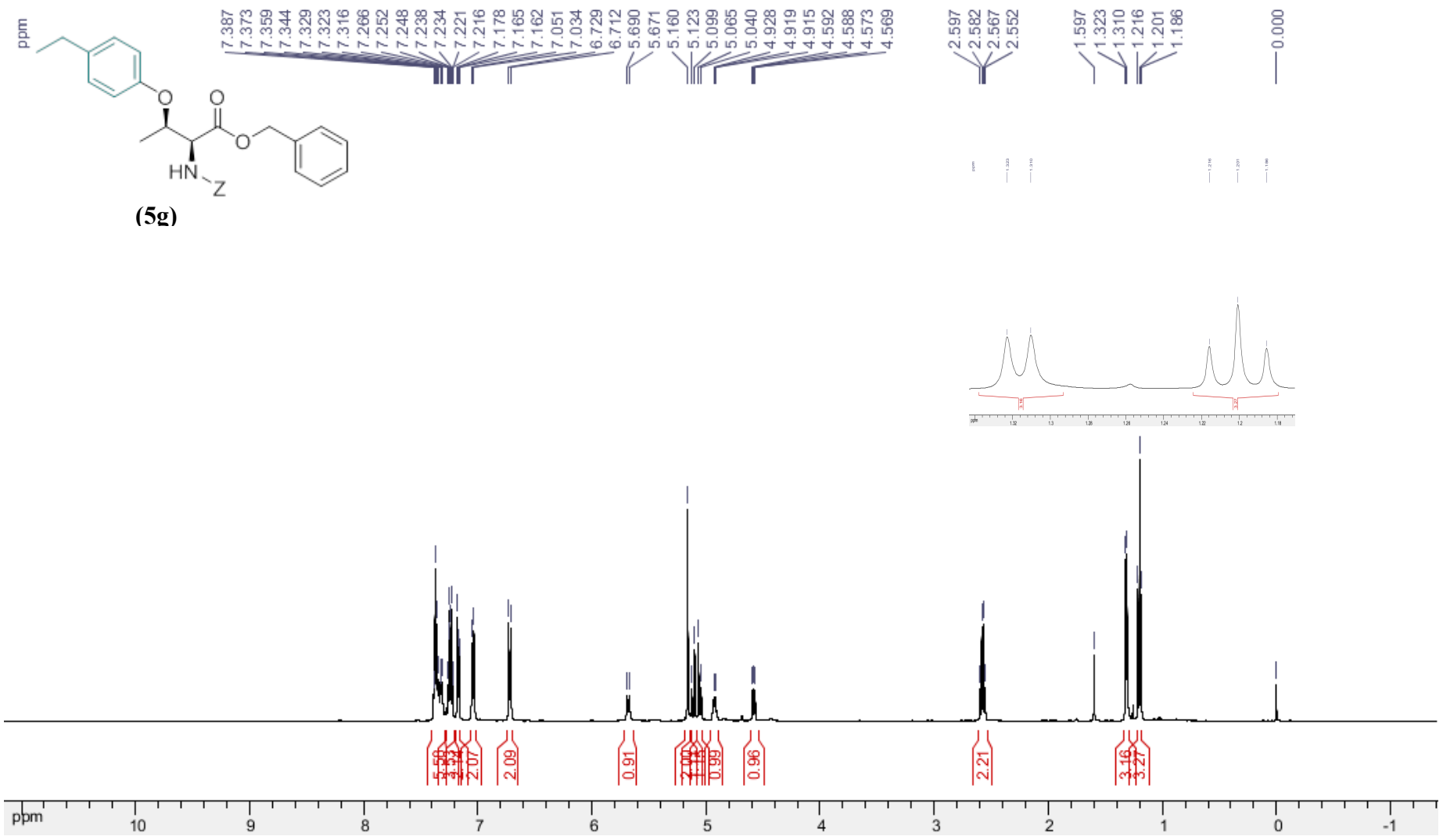
(5f)

^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *N*-((benzyloxy)carbonyl)-*O*-(3-cyanophenyl)-L-threoninate (5f).**

(5f)

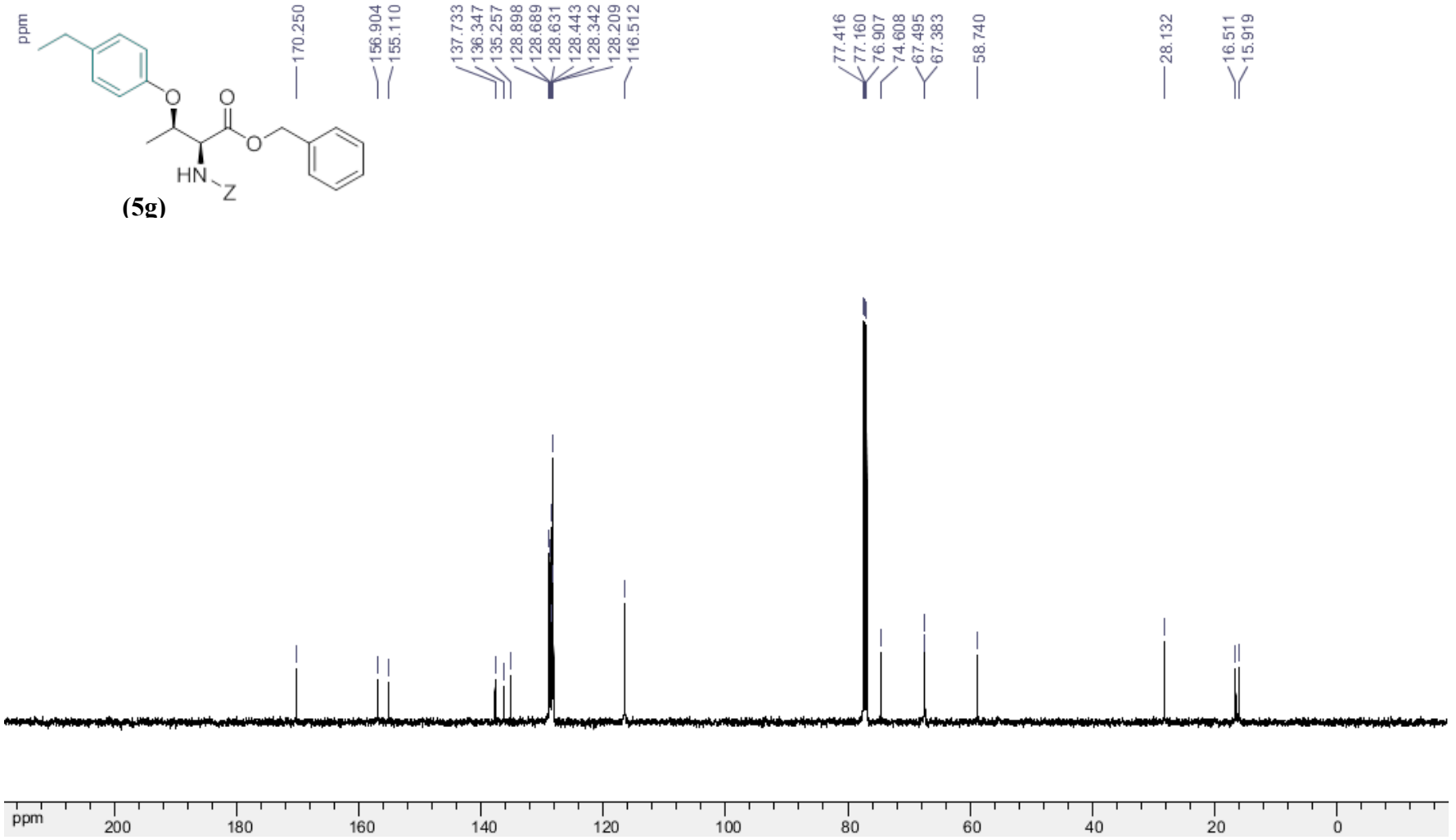


^{1}H NMR (500 MHz, $CDCl_3$) of **Benzyl *O*-(4-ethylphenyl)-*N*-(2-oxo-2-phenyl-1l2-ethyl)-L-threoninate (5g).**

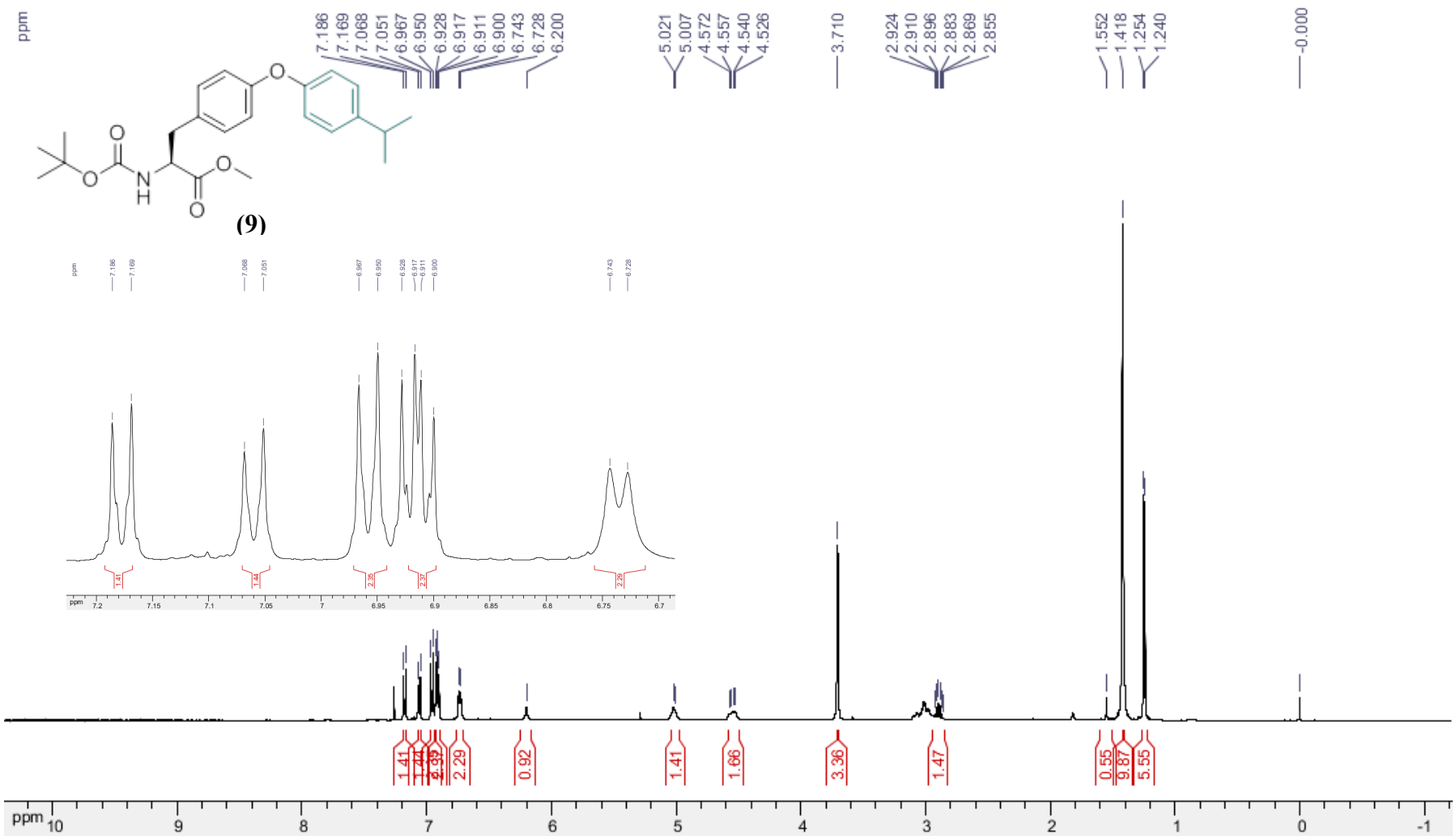


(5g)

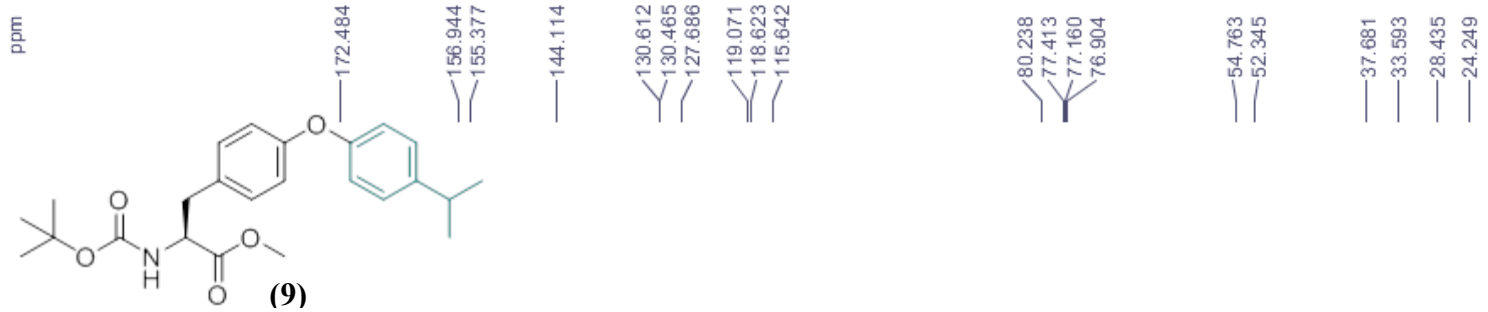
^{13}C NMR (125.8 MHz, $CDCl_3$) of **Benzyl *O*-(4-ethylphenyl)-*N*-(2-oxo-2-phenyl-1l2-ethyl)-L-threoninate (5g).**



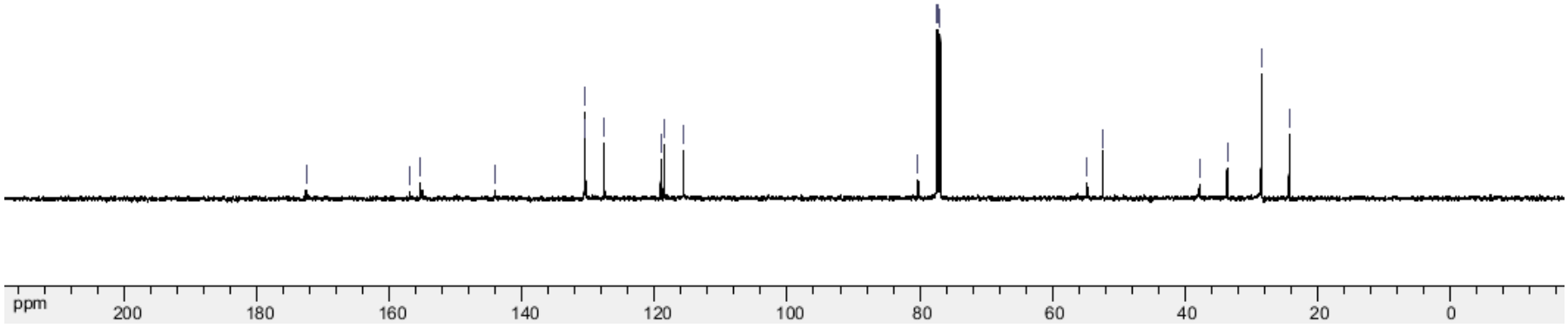
^{1}H NMR (500 MHz, $CDCl_3$) of **Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-(4-isopropylphenoxy)phenyl)propanoate (9).**



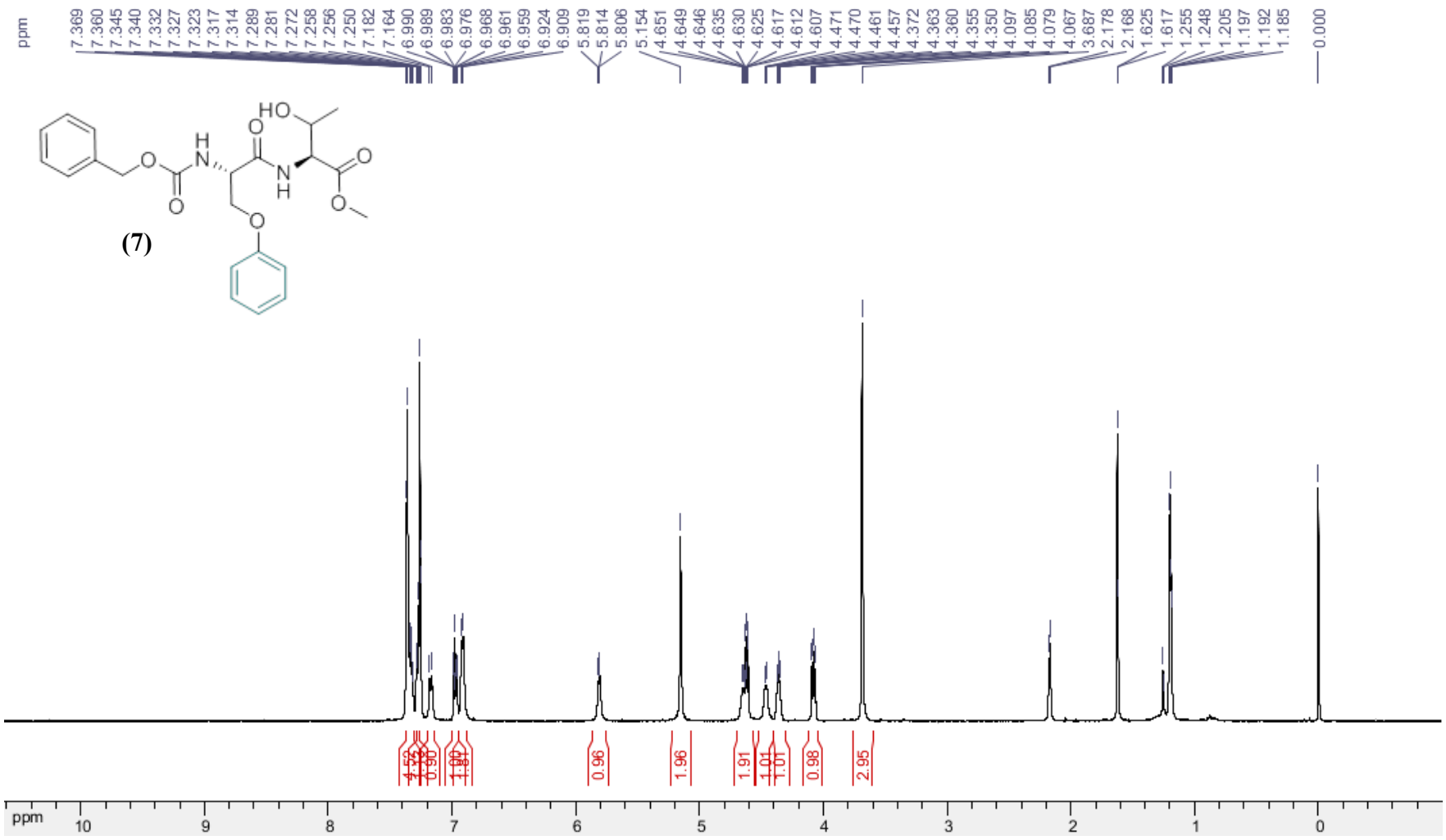
^{13}C NMR (125.8 MHz, $CDCl_3$) of **Methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(4-(4-isopropylphenoxy)phenyl)propanoate (9).**



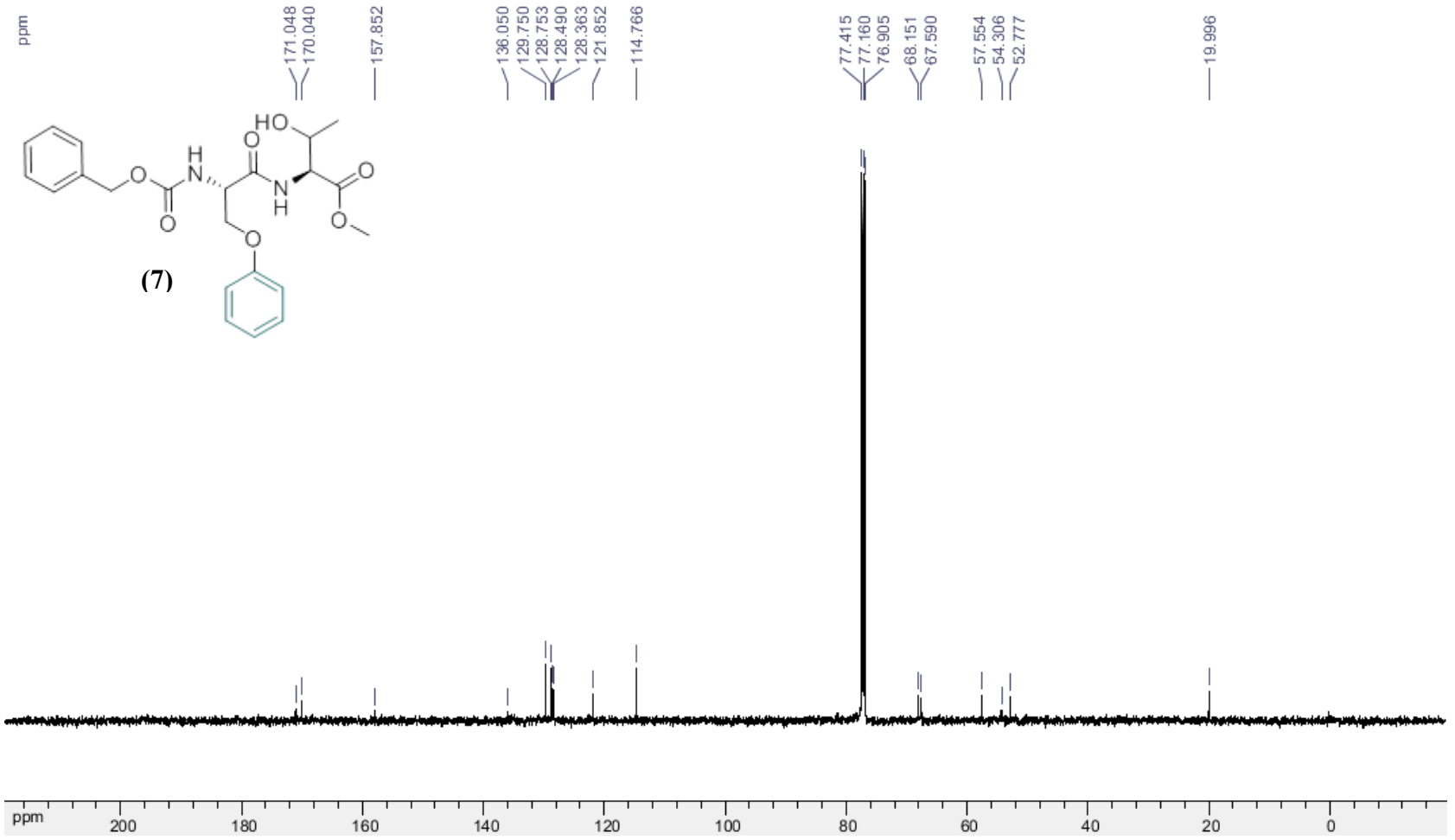
(9)



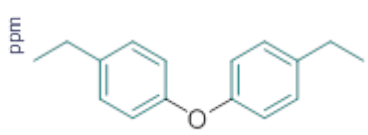
^{1}H NMR (500 MHz, $CDCl_3$) of **Methyl (2*S*)-2-((*S*)-2-(((benzyloxy)carbonyl)amino)-3-phenoxypropanamido)-3-hydroxybutanoate (7).**



^{13}C NMR (125.8 MHz, $CDCl_3$) of **Methyl (2*S*)-2-((*S*)-2-(((benzyloxy)carbonyl)amino)-3-phenoxypropanamido)-3-hydroxybutanoate (7).**



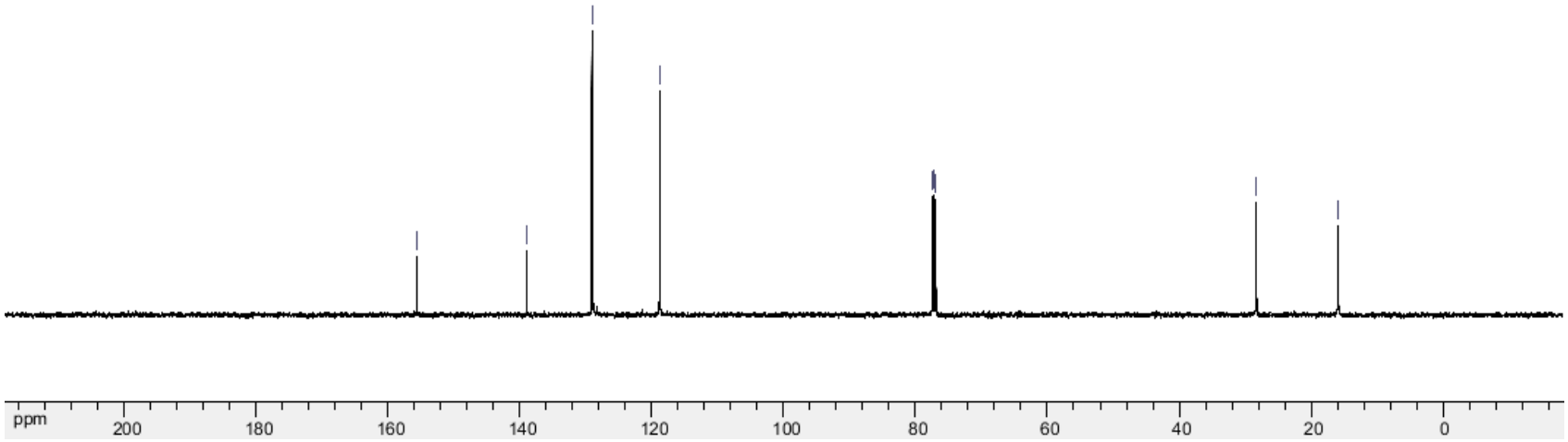
^{1}H NMR (500 MHz, $CDCl_3$) of **4,4'-Oxybis(ethylbenzene) (10).**



(10)

^{13}C NMR (125.8 MHz, $CDCl_3$) of **4,4'-Oxybis(ethylbenzene) (10)**

(10)



Mass spectral fragmentation of **Methyl (2*S*)-2-((*S*)-2-(((benzyloxy)carbonyl)amino)-3-phenoxypropanamido)-3-hydroxybutanoate**

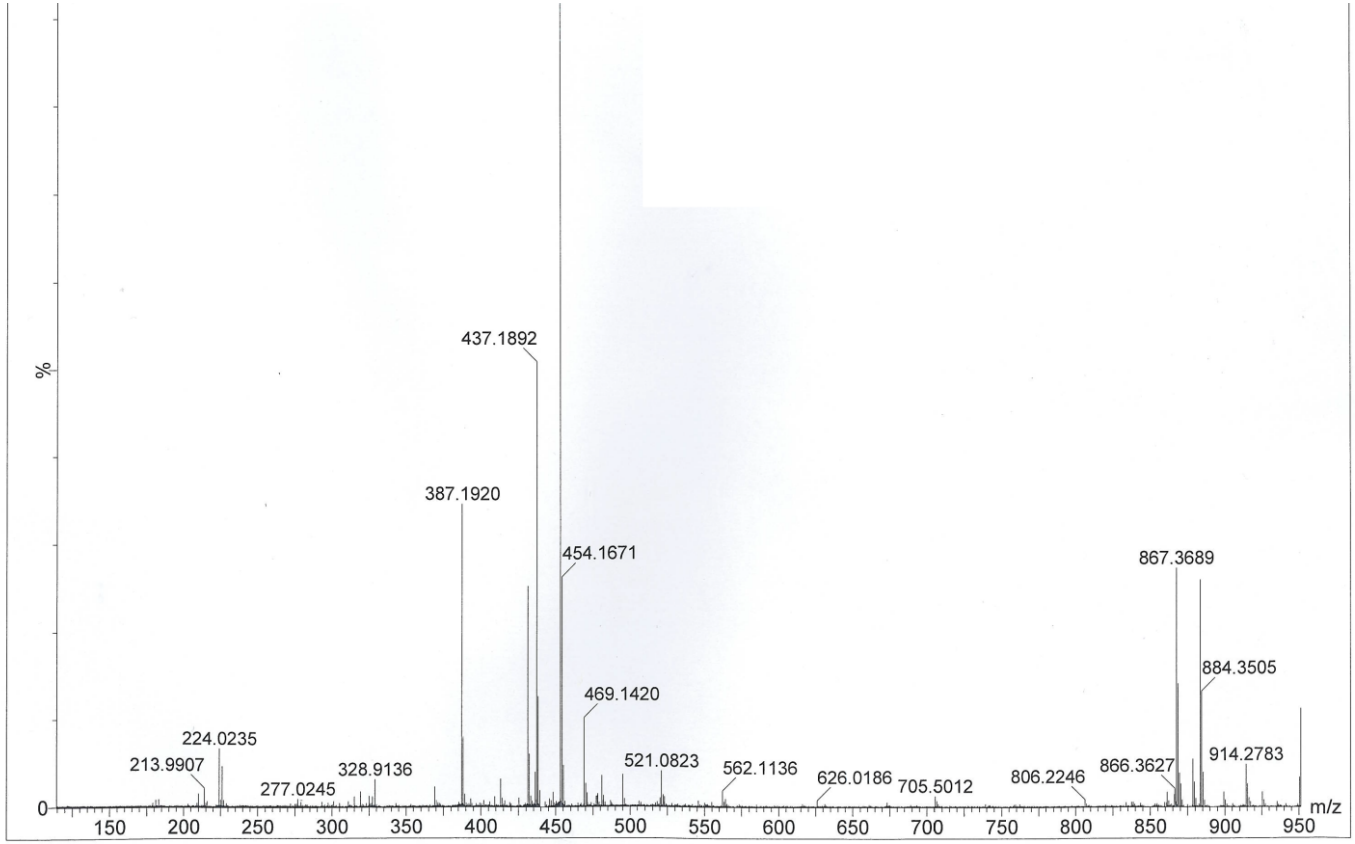
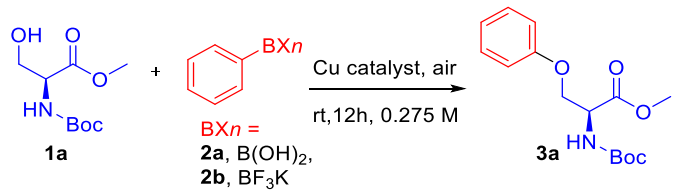


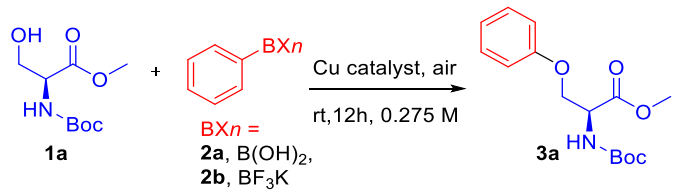
Table S1. Optimization of Reaction Conditions with Phenylboronic Acid and Potassium Phenyltrifluoroborate.



entry	catalyst (10 mol %)	base /ligand	solvent	yields of 3a (%)	
				$BX_n = B(OH)_2$	BF_3K
1	CuI	Cs_2CO_3 (3.0), 1,10-phen (0.2)	CH_3CN	n.r	n.r.
2[1]	CuI	Cs_2CO_3 (3.0), 1,10-phen (0.1)	toluene	n.r	n.r.
3	CuI	1,10-phen (0.2)	toluene	n.r.	n.r.
4	$CuSO_4{\cdot}5H_2O$	Cs_2CO_3 (3.0)	CH_3CN	n.r.	n.r.
5[a]	$CuSO_4{\cdot}5H_2O$	Cs_2CO_3 (3.0)	CH_2Cl_2	n.r.	n.r.
6	$CuSO_4{\cdot}5H_2O$	-	CH_3CN	n.r.	n.r.
7	$Cu(OAc)_2$	DMAP (0.2)	CH_2Cl_2	75%	n.r.
8	$Cu(OAc)_2$	DMAP (1.0)	CH_2Cl_2	traces	n.r.
9[2, b, c]	$Cu(OAc)_2$	py (3.0)	DMF[c]	n.r.	n.r.
10	$Cu(OAc)_2{\cdot}H_2O$	DMAP (0.2)	CH_2Cl_2	85%	80%
11[3, d]	$Cu(OAc)_2{\cdot}H_2O$	DMAP (0.2)	CH_2Cl_2	-	traces [d]
12	$Cu(OAc)_2{\cdot}H_2O$	DMAP (0.2)	CH_2Cl_2	65%	-
13[e]	$Cu(OAc)_2{\cdot}H_2O$	DMAP (0.2)	CH_2Cl_2	81%	-
14	$Cu(OAc)_2{\cdot}H_2O$	Tetramethylguanidine (0.2)	CH_2Cl_2	homocoupling	homocoupling
15	$Cu(OAc)_2{\cdot}H_2O$	DBU (0.2)	CH_2Cl_2	homocoupling	homocoupling
16	$Cu(OAc)_2{\cdot}H_2O$	DIPEA (0.2)	CH_2Cl_2	79%	70%
17	$Cu(OAc)_2.H_2O$	DABCO (0.2)	CH_2Cl_2	70%	-
18	$Cu(OAc)_2.H_2O$	1,10-phenanthroline (0.2)	CH_2Cl_2	45%	-
19[f]	$Cu(OAc)_2{\cdot}H_2O$	DMAP (0.2)	DCE (60 °C)	homocoupling	homocoupling
20	$Cu(OAc)_2{\cdot}H_2O$	-	DCE (60 °C)	n.r.	n.r.
21	$Cu(OAc)_2{\cdot}H_2O$	DMAP (0.2)	CH_3CN	n.r.	n.r.
22	$Cu(OAc)_2{\cdot}H_2O$	DMAP (0.2)	dioxane	60%	55%
23[g]	$Cu(OAc)_2{\cdot}H_2O$	DMAP (0.2)	CH_2Cl_2	84%[g]	81%[g]
24[h]	$Cu(OAc)_2{\cdot}H_2O$	DMAP (0.2)	CH_2Cl_2	85%[h]	87%[h]
25	$Cu(OAc)_2{\cdot}H_2O$	-	CH_2Cl_2	n.r.	n.r.
26	$Cu(OH)_2$	DMAP (0.2)	CH_2Cl_2	n.r.	n.r.

[a]$CuSO_4{\cdot}5H_2O$ (20 mol %); [b]$Cu(OAc)_2$ (150 mol %); [c]Under reflux; [d]$PhBF_3K$ (2 equiv);[3] [e]$Cu(OAc)_2{\cdot}H_2O$ (20 mol %); [f] $Cu(OAc)_2{\cdot}H_2O$ (5 mol %); [g]O_2 balloon; [h]O_2 balloon, H_2O (0.01 equiv).

(continued)Table S1. Optimization of Reaction Conditions with Phenylboronic Acid and Potassium Phenyltrifluoroborate.



entry	catalyst (10 mol %)	base /ligand	solvent	yields of 3a (%)	
				$BX_n = B(OH)_2$	BF_3K
27	$Cu(OH)_2$	-	CH_2Cl_2	n.r.	n.r.
28	$Cu(OH)_2$	DIPEA (0.2)	CH_2Cl_2	n.r.	n.r.
29	$CuCO_3$	DMAP (0.2)	CH_2Cl_2	n.r.	n.r.
30	$CuCO_3$	-	CH_2Cl_2	n.r.	n.r.
31	$CuCO_3$	DIPEA (0.2)	CH_2Cl_2	n.r.	n.r.
32	Copper (II) perchlorate hexahydrate	DMAP (0.2)	CH_2Cl_2	n.r.	n.r.
33	$Cu(acac)_2$	DMAP (0.2)	CH_2Cl_2	traces	traces
34	$Cu(NO_3)_2$hydrate	DMAP (0.2)	CH_2Cl_2	n.r.	n.r.
35	$Cu(SO_3CF_3)_2$	DMAP (0.2)	CH_2Cl_2	traces	traces
36	Copper (II) acetatebis(diphenylphosphino)ethane	DMAP (0.2)	CH_2Cl_2	n.r.	n.r.
37	(1,10-phenanthroline)bis(triphenylphosphine)copper(I)nitrate	DMAP (0.2)	CH_2Cl_2	n.r.	n.r.
38	$CuCl_2$hydrate	DMAP (0.2)	CH_2Cl_2	n.r.	n.r.
39	CuO	DMAP (0.2)	CH_2Cl_2	n.r.	n.r.

[a]$CuSO_4 \cdot 5H_2O$ (20 mol %); [b]$Cu(OAc)_2$ (150 mol %); [c]Under reflux; [d]$PhBF_3K$ (2 equiv);[3] [e]$Cu(OAc)_2 \cdot H_2O$ (20 mol %); [f] $Cu(OAc)_2 \cdot H_2O$ (5 mol %); [g]O_2 balloon; [h]O_2 balloon, H_2O (0.01 equiv).

Reaction performed in the glovebox (in the absence of air/oxygen and under argon)