Supporting Information

Cyclopropenimine-Catalyzed Enantioselective Mannich Reactions of *tert*-Butyl Glycinates with N-Boc-Imines

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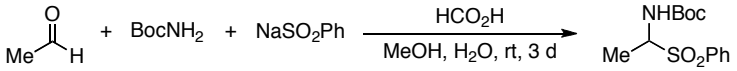
General information. All reactions were performed open to the atmosphere, unless otherwise noted. Organic solutions were concentrated using a Buchi rotary evaporator. Methylene chloride, diethyl ether, benzene and toluene were dried using a J.C. Meyer solvent purification system. All other solvents and commercial reagents were used as provided. Flash column chromatography was performed employing 40-63 μm silica gel (SiliaFlash P60 from Silicycle). Thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} plates (EMD).

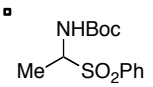
^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (except where noted) on Bruker DRX-300, DRX-400 or DRX-500 spectrometers as noted. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, m = multiplet), coupling constant (Hz), integration, and assignment. Data for ^{13}C and ^{19}F NMR are reported in terms of chemical shift. Infrared spectra were recorded on a Nicolet Avatar 370DTGS FT-IR. Optical rotations were measured using a Jasco DIP-1000 digital polarimeter. High-resolution mass spectra were obtained from the Columbia University Mass Spectrometry Facility on a JOEL JMSHX110 HF mass spectrometer using FAB+ ionization mode. Low-resolution mass spectrometry (LRMS) was performed on a JEOL JMS-LCmate liquid chromatography spectrometer system using APCl+ ionization technique. HPLC analysis was performed on an Agilent Technologies 1200 series instrument with a Daicel Chiralpak AD-H or OD-H chiral column (25 cm) using the given conditions.

Preparation of Starting Materials

Glycinate imines: Methyl, benzyl and *tert*-butyl glycinate benzophenone imines were prepared according to established procedures.[1]

N-Boc-aldimines: Most N-Boc-aldimines were prepared according to established procedures that are noted for each substrate entry below. Three new aliphatic N-Boc-aldimines were used and their preparation is described here.

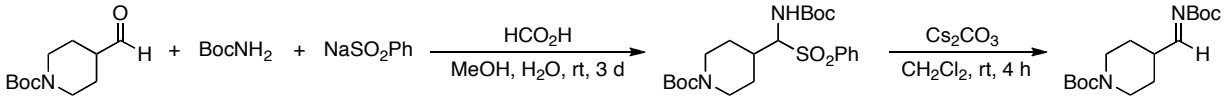


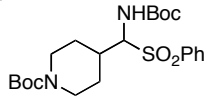


***tert*-Butyl 1-(phenylsulfonyl)ethylcarbamate:** The following chemicals were mixed and stirred at room temperature for three days: acetaldehyde (1.4 mL, 25.5

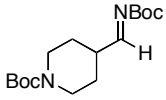
[1] (a) O'Donnell, M. J.; Polt, R. L. *J. Org. Chem.*, **1982**, *47*, 2663. (b) Danner, P.; Bauer, M.; Phukan, P.; Maier, M. E. *Eur. J. Org. Chem*. **2005**, 317**.**

mmol, 2.0 equiv), *tert*-butyl carbamate (1.50 g, 12.8 mmol, 1.0 equiv), benzenesulfinic acid sodium salt (5.20 g, 32.0 mmol, 2.5 equiv), formic acid (1.3 mL), methanol (16 mL) and water (32 mL). A white precipitate formed during the course of the reaction. The reaction mixture was extracted with dichloromethane (3 x 30 mL), the combined dichloromethane was then dried with anhydrous sodium sulfate and concentrated *in vacuo* to a white solid. This solid was triturated with hot hexanes to yield the title product as a white solid (1.91 g, 6.66 mmol, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, 7.5 Hz, 2H, Ar**H**), 7.62 (t, 7.3 Hz, 1H, Ar**H**), 7.54 (t, 7.5 Hz, 2H, Ar**H**), 5.13 (d, 10.2 Hz, 1H, N**H**Boc), 5.00 (m, 1H, C**H**NHBoc), 1.62 (d, 6.9 Hz, 3H, C**H$_3$**), 1.21 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 136.8, 134.0, 129.5, 129.2, 80.9, 66.9, 28.1, 13.1. IR (thin film, cm^{-1}) 3337, 2974, 1691, 1517, 1447, 1312, 1241, 1144, 850, 727, 690, 580. The mass spectrum of this compound showed only a peak corresponding to the *tert*-butyl ethylidenecarbamate elimination product; LRMS (APCI+) m/z = 144.07 calcd for $C_7H_{13}NO_2$ $[M+1]^+$ 144.09.



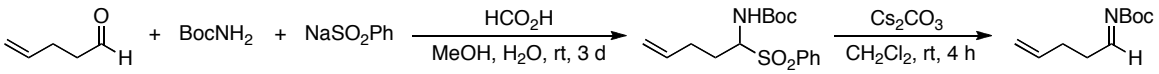


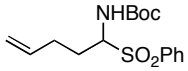
***tert*-Butyl 4-((*tert*-butoxycarbonylamino)(phenylsulfonyl)methyl)-piperidine-1-carboxylate:** The following chemicals were mixed and stirred at room temperature for three days: 1-Boc-piperidine-4-carboxaldehyde (500 mg, 2.34 mmol, 1.0 equiv), *tert*-butyl carbamate (275 mg, 2.34 mmol, 1.0 equiv), benzenesulfinic acid sodium salt (1.00 g, 5.86 mmol, 2.5 equiv), formic acid (0.2 mL), methanol (3.0 mL) and water (6.0 mL). A white precipitate formed during the course of the reaction. The reaction mixture was extracted with dichloromethane (3 x 10 mL), the combined dichloromethane was then dried with anhydrous sodium sulfate and concentrated *in vacuo* to a white solid. This solid was triturated with hot hexanes to yield the title product as a white solid (580 mg, 1.28 mmol, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, 7.8 Hz, 2H, Ar**H**), 7.63 (t, 7.2 Hz, 1H, Ar**H**), 7.53 (t, J = 7.8 Hz, 2H, Ar**H**), 5.10 (d, 11.2 Hz, 1H, N**H**Boc), 4.77 (dd, 3.4 and 11.2 Hz, 1H, C**H**NHBoc), 4.18 (br s, 2H, Cy**H**), 2.77 (m, 2H, Cy**H**), 2.61 (m, 1H, Cy**H**), 2.09 (d, J = 12.4 Hz, 1H, Cy**H**), 1.75 (d, 12.6 Hz, 1H, Cy**H**), 1.46 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.35 (m, 2H, Cy**H**), 1.21 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 153.9, 137.6, 133.9, 129.1, 129.0, 80.9, 79.6, 73.3, 43.2 (broad), 34.8, 28.4, 27.9. IR (thin film, cm^{-1}) 3364, 2977, 1713, 1684, 1510, 1428, 1311, 1160, 1134, 867, 591. The mass spectrum of this compound showed only a peak corresponding to the *N*-Boc-aldimine elimination product; see directly below for details.



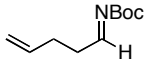
***tert*-Butyl 4-((*tert*-butoxycarbonylimino)methyl)piperidine-1-carboxylate:** A 25 mL round bottom flask, charged with cesium carbonate (1.80 g, 5.50 mmol, 10 equiv), was flame-dried for five minutes. The flask was then put under an atmosphere of argon, and a solution of the title product from the previous reaction (250 mg, 0.55 mmol, 1.0 equiv) in dichloromethane (6 mL) was added and the reaction mixture was stirred at room temperature. After four hours (hr), the reaction mixture was diluted with hexanes (10 mL), filtered through celite and the filtrate was concentrated *in vacuo* to yield the title product as a

clear oil (160 mg, 0.51 mmol, 93% yield). Note: the temperature of the rotovap was kept at 20 °C or cooler. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H, N**H**), 4.05 (br s, 2H, Cy**H**), 2.77 (t, 11.6 Hz, 2H, Cy**H**), 2.41 (m, 1H, Cy**H**), 2.20 (m, 2H, Cy**H**), 1.47 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.40 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.47-1.40 (m, 2H, Cy**H**). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 162.1, 154.7, 82.4, 79.6, 43.1 (broad), 41.8, 28.5, 27.9, 27.7. LRMS (APCI+) m/z = 312.91 calcd for $C_{16}H_{28}N_2O_4$ $[M+1]^+$ 313.20.





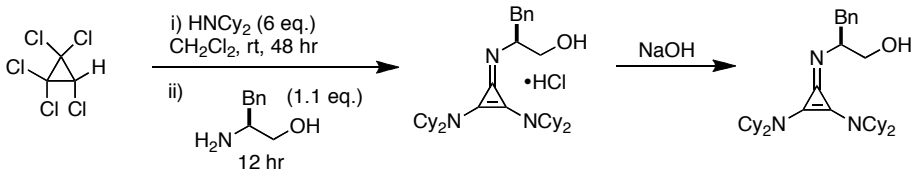
***tert*-Butyl 1-(phenylsulfonyl)pent-4-enylcarbamate:** The following chemicals were mixed and stirred at room temperature for three days: pent-4-enal[2] (1.18 g, 14.0 mmol, 1.0 equiv), *tert*-butyl carbamate (1.60 g, 14.0 mmol, 1.0 equiv), benzenesulfinic acid sodium salt (5.70 g, 35.0 mmol, 2.5 equiv), formic acid (1.0 mL), methanol (8 mL) and water (16 mL). A white precipitate formed during the course of the reaction. The reaction mixture was extracted with dichloromethane (3 x 25 mL), the combined dichloromethane was then dried with anhydrous sodium sulfate and concentrated *in vacuo* to a white solid. This solid was triturated with hot hexanes to yield the title product as a white solid (606 mg, 1.86 mmol, 13% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, 7.3 Hz, 2H, Ar**H**), 7.61 (t, 7.4 Hz, 1H, Ar**H**), 7.52 (t, 7.8 Hz, 2H, Ar**H**), 5.80 (m, 1H, H_2C=C**H**R), 5.18 (d, 10.6 Hz, 1H, N**H**Boc), 5.05 (m, 2H, $\mathbf{H_2}$C=CHR), 4.89 (td, 2.8 and 10.6 Hz, 1H, C**H**NHBoc), 2.33 (m, 2H, -C$\mathbf{H_2}$-), 2.18 (m, 1H, -C$\mathbf{H_2}$-), 1.86 (m, 1H, -C$\mathbf{H_2}$-), 1.21 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 137.0, 136.0, 133.9, 129.4, 129.1, 116.7, 80.8, 70.3, 29.4, 28.0, 25.7. IR (thin film, cm^{-1}) 3281, 2977, 1691, 1527, 1309, 1251, 1141, 683, 589. The mass spectrum of this compound showed only a peak corresponding to the N-Boc-aldimine elimination product; see directly below for details.

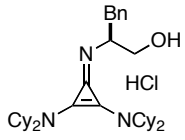


***tert*-Butyl pent-4-enylidenecarbamate:** A 25 mL round bottom flask, charged with cesium carbonate (1.50 g, 4.60 mmol, 10 equiv), was flame-dried for five minutes. The flask was then put under an atmosphere of argon, and a solution of the title product from the previous reaction (150 mg, 0.46 mmol, 1.0 equiv) in dichloromethane (5 mL) was added and the reaction mixture was stirred at room temperature. After four hr, the reaction mixture was diluted with hexanes (10 mL), filtered through celite and the filtrate was concentrated *in vacuo* to yield the title product as a clear oil (75 mg, 0.41 mmol, 89% yield). Note: the temperature of the rotovap was kept at 20 °C or cooler. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H, N**H**), 5.85 (m, 1H, H_2C=C**H**R), 5.05 (td, 1.6 and 12.4 Hz, 2H, $\mathbf{H_2}$C=CHR), 2.50 (br s, 2H, -C$\mathbf{H_2}$-), 2.39 (t, 6.3 Hz, 2H, -C$\mathbf{H_2}$-), 1.53 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 162.1, 136.5, 115.9, 82.2, 35.3, 28.8, 27.9. LRMS (APCI+) m/z = 184.12 calcd for $C_{10}H_{17}NO_2$ $[M+1]^+$ 184.13.

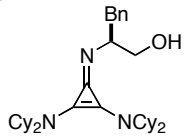
[2] Farquhar, D.; Cherif, A.; Bakina, E.; Nelson, J., A.; *J. Med. Chem.* **1998**, *41*, 965.

Cyclcopropenimine catalyst: An improved synthesis of chiral cyclopropenimine **1** is described below.[3] Our previously reported preparation uses tetrachlorocyclopropene as a starting material, the procedure below uses less expensive pentachlorocyclopropane.





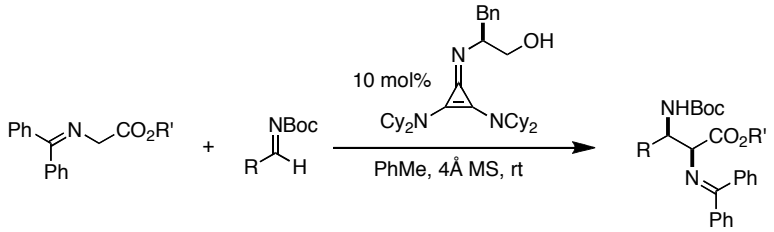
(*S*)-2-(2,3-Bis(dicyclohexylamino)cyclopropenimine)-3-phenylpropan-1-ol hydrochloride: Dicyclohexylamine (108 mL, 541 mmol, 6.0 equiv) was slowly added to a solution of pentachlorocyclopropane[4] (19.3 g, 90.2 mmol, 1.0 equiv) in CH_2Cl_2 (900 mL) in a 3L round bottom flask. A white precipitate formed as the reaction mixture was stirred for a further 48 hr at room temperature. Next, (*S*)-2-amino-3-phenylpropan-1-ol[5] (15.0 g, 99.2 mmol, 1.1 equiv) was added in one portion and the reaction mixture was stirred for an additional 12 hr. The crude reaction mixture was filtered through a celite plug, then washed with 1.0 M HCl (3 x 500 mL), dried with anhydrous sodium sulfate and concentrated *in vacuo* to yield crude cyclopropenimine hydrochloride salt as an off-white solid. Recrystallization from ethyl acetate/hexanes (approximately 1/2) yielded pure cyclopropenimine hydrochloride salt as a white solid (38.5 g, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, 9.2 Hz, 1H, N**H**), 7.0-7.15 (m, 5H, Ar**H**), 5.17 (t, 5.6 Hz, 1H, -O**H**), 3.60-3.85 (m, 3H, NC**H**BnC**H$_2$**OH), 3.10 (m, 4H, NCy**H**), 2.80-3.00 (m, 2H, -C**H$_2$**Ph), 1.00-1.70 (m, 40H, Cy**H**). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 129.2, 128.0, 126.2, 116.5, 114.5, 63.7, 61.3, 59.1, 38.4, 32.1, 31.9, 25.4, 24.4.



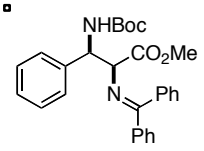
(*S*)-2-(2,3-Bis(dicyclohexylamino)cyclopropenimine)-3-phenylpropan-1-ol: Cyclopropenimine freebase was prepared and stored in a freezer on a weekly basis. Pure cyclopropenimine freebase was quantitatively obtained by dissolving the corresponding hydrochloride salt in CH_2Cl_2 and washing the solution with 1.0 M NaOH (3 x), drying with anhydrous sodium sulfate and concentrating *in vacuo*. The cyclopropenimine is obtained as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10-7.25 (m, 5H, Ar**H**), 3.79 (m, 1H, NC**H**BnCH_2OH), 3.40-3.50 (m, 2H, NCHBnC**H$_2$**OH), 3.00-3.10 (m, 4H, NCy**H**), 2.70-2.85 (m, 2H, -C**H$_2$**Ph), 1.00-1.90 (m, 40H, Cy**H**). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 129.7, 129.4, 127.8, 125.5, 65.1, 61.7, 58.3, 41.7, 34.4, 33.1, 32.8, 32.6, 26.3, 26.1, 25.3, 25.2.

[3] For full characterization of this cyclopropenimine: Bandar, J. S.; Lambert, T. H. *J. Am. Chem. Soc.* **2012**, *134*, 5552.
[4] Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1966**, *88*, 2478.
[5] Shi, L.; Chen, L.; Chen, R.; Chen, L. *J. Label Compd. Radiopharm.* **2010**, *53*, 147-151.

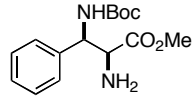
General Procedure for Glycinate Mannich Reactions



Cyclopropenimine (0.1 equiv), glycinate benzophenone Schiff base (1.0 g, 1.0 equiv) and activated ground 4Å molecular sieves (500 mg) were mixed in toluene (0.25 M). N-Boc-aldimine (2.0 equiv) was then added and the reaction solution was stirred at room temperature. Upon complete consumption of starting material, monitored by ^{1}H NMR, the reaction solution was concentrated and the crude material subjected to silica gel column chromatography (Et_2O/Hexanes eluent as noted).

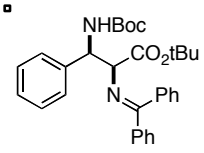


(2*S*,3*R*)-Methyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethylene-amino)-3-phenylpropanoate: [6] General procedure was followed using cyclopropenimine (215 mg, 0.395 mmol, 0.1 equiv), methyl glycinate benzophenone imine (1.00 g, 3.95 mmol, 1.0 equiv) and *tert*-butyl benzylidenecarbamate [7] (1.62 g, 7.9 mmol, 2.0 equiv). The reaction was complete after 15 min. Benzyl ether (188 µl, 0.987 mmol, 0.25 equiv) was added to the reaction solution to use as an internal standard (80% ^{1}H NMR yield was determined, see spectrum below). HPLC analysis: Chiralpak AD-H (Hex/IPA = 96/4, 1.0 mL/min, 254 nm, 23 °C), 13.9 min (major), 15.1 min (minor), 16.0 min (anti), 17.1 (anti), 94:6 dr (syn:anti), 95% ee (syn). This product was characterized after hydrolysis of the benzophenone imine (see below).

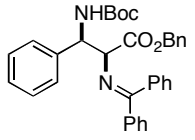


(2*S*,3*R*)-Methyl 2-amino-3-(*tert*-butoxycarbonylamino)-3-phenyl-propanoate: The reaction mixture from entry 1 (R = Me) of Table 2 was concentrated *in vacuo*, dissolved in THF (112 mL) and added to a 0.5 M citric acid aqueous solution (8.80 g citric acid in 80 mL H_2O). The reaction mixture was stirred for 1 hr, then washed with Et_2O (3 x 100 mL), basified with sat. Na_2CO_3(aq), and extracted with ethyl acetate (3 x 100 mL). The collected ethyl acetate solution was concentrated *in vacuo* to a crude solid that was recrystallized from hexanes to yield the pure title product as white crystals (0.940 g, 3.19 mmol, 80% two-step yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.25 (m, 5H, Ar**H**), 5.85 (d, 9.0 Hz, 1H, PhC**H**NHBoc), 5.20 (s, 1H, C**H**NH_2CO_2Me), 3.89 (s, 1H, N**H**Boc), 3.75 (s, 3H, $CO_2C\mathbf{H_3}$), 1.42 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 155.3, 139.9, 128.6, 127.5, 126.4, 79.5, 58.6, 56.4, 52.4, 28.3. IR (thin film, cm^{-1}) 3400, 3371, 2973, 1732, 1684, 1512, 1364, 1244, 1156, 882, 765, 706, 553. $[\alpha]^{20}_D$ = +21.1 (1.0 c, $CHCl_3$). LRMS (FAB+) m/z = 295.16 calcd for $C_{15}H_{22}N_2O_4$ $[M+1]^+$ 295.16.

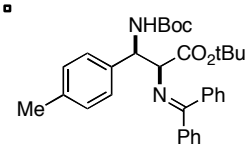
[6] Zhang, H.; Syed, S.; Barbas, III, C. F. *Org. Lett.* **2010**, *12*, 708.
[7] Tsai, A. S.; Tauchert, M. E.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2011**, *133*, 1248.



(2*S*,3*R*)-*tert*-Butyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethyleneamino)-3-phenylpropanoate: [8] General procedure was followed using cyclopropenimine (185 mg, 0.339 mmol, 0.1 equiv), *tert*-butyl glycinate benzophenone imine (1.00 g, 3.39 mmol, 1.0 equiv) and *tert*-butyl benzylidenecarbamate (1.39 g, 6.78 mmol, 2.0 equiv). After 24 hr, the reaction mixture was purified by silica gel column chromatography (1/4 Et_2O/Hexanes) to yield the title product as a white solid (1.65 g, 3.29 mmol, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, 7.2 Hz, 2H, Ar**H**), 7.30-7.08 (m, 11H, Ar**H**), 6.43 (d, 6.4 Hz, 2H, Ar**H**), 6.30 (d, 8.8 Hz, 1H, ArC**H**NHBoc), 5.37 (d, 8.4 Hz, 1H, C**H**CO_2tBu), 4.07 (s, 1H, N**H**Boc), 1.41 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.39 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 169.2, 155.2, 140.8, 139.0, 136.2, 130.5, 128.9, 128.5, 128.3, 128.2, 128.0, 127.2, 127.0, 126.7, 81.9, 79.3, 70.3, 56.8, 28.5, 28.0. IR (thin film, cm^{-1}) 3435, 2977, 2932, 1715, 1629, 1486, 1449, 1366, 1277, 1151, 847, 696. $[\alpha]^{20}_D$ = -96.1 (1.0 c, $CHCl_3$). LRMS (FAB+) m/z = 501.18 calcd for $C_{31}H_{36}N_2O_4$ $[M+1]^+$ 501.27. HPLC analysis: Chiralpak AD-H (Hex/IPA = 97.5/2.5, 1.0 mL/min, 254 nm, 23 °C), 9.9 min (minor), 11.2 min (anti), 13.8 min (anti), 19.9 (major), 99:1 dr (syn:anti), 94% ee (syn).



(2*S*,3*R*)-Benzyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethyleneamino)-3-phenylpropanoate: General procedure was followed using cyclopropenimine (166 mg, 0.304 mmol, 0.1 equiv), benzyl glycinate benzophenone imine (1.00 g, 3.04 mmol, 1.0 equiv) and *tert*-butyl benzylidenecarbamate (1.25 g, 6.08 mmol, 2.0 equiv). After 10 min, the reaction mixture was purified by silica gel column chromatography (1/4 Et_2O/Hexanes) to yield the title product as a white solid (1.60 g, 3.00 mmol, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, 7.3 Hz, 2H, Ar**H**), 7.41-7.16 (m, 16H, Ar**H**), 6.40 (m, 3H, Ar**H** + ArC**H**NHBoc), 5.5 (d, 8.8 Hz, 1H, C**H**CO_2Bn), 5.22 (s, 2H, -O$C\mathbf{H_2}$Ph), 4.31 (s, 1H, N**H**Boc), 1.48 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 169.9, 155.3, 140.5, 138.9, 135.8, 135.8, 130.8, 129.0, 128.6, 128.3, 128.1, 127.2, 126.7, 79.6, 69.8, 67.1, 56.8, 28.5. IR (thin film, cm^{-1}) 3431, 3061, 2976, 1713, 1627, 1484, 1453, 1365, 1162, 1084, 746, 695, 563. $[\alpha]^{20}_D$ = -100.9 (1.0 c, $CHCl_3$). LRMS (FAB+) m/z = 535.16 calcd for $C_{34}H_{34}N_2O_4$ $[M+1]^+$ 535.25. HPLC analysis: Chiralpak OD-H (Hex/IPA = 98/2, 1.0 mL/min, 254 nm, 23 °C), 7.0 min (minor), 8.6 min (anti), 9.2 min (major), 10.6 (anti), 95:5 dr (syn:anti), 96% ee (syn).

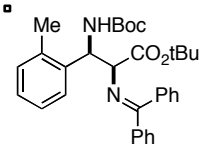


(2*S*,3*R*)-*tert*-Butyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethyleneamino)-3-*p*-tolylpropanoate: [7] General procedure was followed using cyclopropenimine (185 mg, 0.339 mmol, 0.1 equiv), *tert*-butyl glycinate benzophenone imine (1.00 g, 3.39 mmol, 1.0 equiv) and *tert*-butyl 4-methylbenzylidenecarbamate [9] (1.48 g, 6.78 mmol, 2.0 equiv). After 36 hr, the reaction mixture was purified by silica gel column chromatography (1/4 Et_2O/Hexanes) to yield the title product as a white solid (1.47 g, 2.86 mmol, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, 7.2 Hz, 2H, Ar**H**), 7.41-7.30 (m, 6H, Ar**H**), 7.08 (m, 4H, Ar**H**), 6.58 (d, 6.4

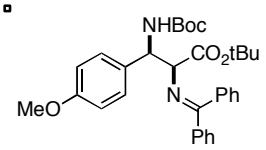
[8] Okada, A.; Shibuguchi, T.; Ohshima, T.; Masu, H.; Yamaguchi, K.; Shibasaki, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 4564.

[9] Wenzel, A. G.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 12964.

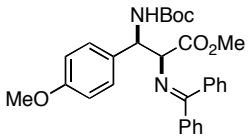
Hz, 2H, Ar**H**), 6.37 (d, 8.8 Hz, 1H, ArC**H**NHBoc), 5.43 (d, 8.8 Hz, 1H, C**H**CO_2tBu), 4.17 (s, 1H, N**H**Boc), 2.32 (s, 3H, Ar$C\mathbf{H_3}$), 1.51 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.49 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 169.3, 155.2, 139.1, 137.9, 136.5, 136.3, 130.5, 128.9, 128.8, 128.5, 128.3, 128.1, 127.8, 127.3, 126.7, 81.9, 79.3, 70.3, 56.6, 28.6, 28.2, 21.1. IR (thin film, cm^{-1}) 3436, 3342, 2976, 2930, 1716, 1629, 1485, 1315, 1277, 1149, 1050, 779, 696, 558. $[\alpha]^{20}_D$ = -78.6 (1.0 c, $CHCl_3$). LRMS (FAB+) m/z = 515.20 calcd for $C_{32}H_{38}N_2O_4$ $[M+1]^+$ 515.28. HPLC analysis: Chiralpak AD-H (Hex/IPA = 97.5/2.5, 1.0 mL/min, 254 nm, 23 °C), 10.7 min (minor), 11.7 min (anti), 12.9 min (anti), 19.7 (major), 99:1 dr (syn:anti), 97% ee (syn).



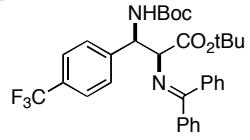
(2*S*,3*R*)-*tert*-Butyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethyleneamino)-3-*o*-tolylpropanoate:[7] General procedure was followed using cyclopropenimine (185 mg, 0.339 mmol, 0.1 equiv), *tert*-butyl glycinate benzophenone imine (1.00 g, 3.39 mmol, 1.0 equiv) and *tert*-butyl 2-methylbenzylidenecarbamate[8] (1.48 g, 6.78 mmol, 2.0 equiv). After 48 hr, the reaction mixture was purified by silica gel column chromatography (1/4 Et_2O/Hexanes) to yield the title product as a white solid (1.10 g, 2.14 mmol, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, 7.2 Hz, 2H, Ar**H**), 7.40-7.05 (m, 10H, Ar**H**), 6.43 (d, 8.6 Hz, 1H, ArC**H**NHBoc), 6.33 (m, 2H, Ar**H**), 5.66 (d, 8.6 Hz, 1H, C**H**CO_2tBu), 4.05 (s, 1H, N**H**Boc), 2.11 (s, 3H, Ar$C\mathbf{H_3}$), 1.50 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.46 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 169.4, 155.2, 138.8, 136.1, 134.8, 130.6, 130.3, 128.9, 128.5, 128.2, 128.1, 127.1, 127.0, 126.6, 125.7, 81.8, 79.3, 67.8, 53.8, 28.6, 28.3, 18.5. IR (thin film, cm^{-1}) 2976, 1714, 1624, 1484, 1366, 1222, 1150, 1048, 1026, 749, 696. $[\alpha]^{20}_D$ = -107.9 (1.0 c, $CHCl_3$). LRMS (FAB+) m/z = 515.19 calcd for $C_{32}H_{38}N_2O_4$ $[M+1]^+$ 515.28. HPLC analysis: Chiralpak AD-H (Hex/IPA = 97.5/2.5, 1.0 mL/min, 254 nm, 23 °C), 5.0 min (minor), 7.0 min (anti), 7.7 min (anti), 13.3 (major), 91:9 dr (syn:anti), 94% ee (syn).



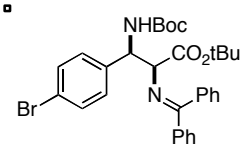
(2*S*,3*R*)-*tert*-Butyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethyleneamino)-3-(4-methoxyphenyl)propanoate:[7] General procedure was followed using cyclopropenimine (185 mg, 0.339 mmol, 0.1 equiv), *tert*-butyl glycinate benzophenone imine (1.00 g, 3.39 mmol, 1.0 equiv) and *tert*-butyl 4-methoxybenzylidenecarbamate[8] (1.59 g, 6.78 mmol, 2.0 equiv). After 60 hr, the reaction mixture was purified by silica gel column chromatography (1/4 Et_2O/Hexanes) to yield the title product as a white solid (1.56 g, 2.94 mmol, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, 7.6 Hz, 2H, Ar**H**), 7.40-7.30 (m, 7H, Ar**H**), 7.12 (d, 8.2 Hz, 2H, Ar**H**), 6.80 (d, 8.6 Hz, 2H, Ar**H**), 6.61 (m, 2H, Ar**H**), 6.35 (d, 8.6 Hz, 1H, ArC**H**NHBoc), 5.41 (d, 8.4 Hz, 1H, C**H**CO_2tBu), 4.15 (s, 1H, N**H**Boc), 3.78 (s, 3H, ArOC$\mathbf{H_3}$), 1.51 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.49 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 169.2, 158.7, 155.2, 139.1, 136.2, 133.1, 130.6, 128.9, 128.5, 128.3, 128.2, 128.1, 127.8, 127.3, 113.6, 81.9, 79.3, 70.3, 56.3, 55.3, 28.5, 28.0. IR (thin film, cm^{-1}) 3436, 2977, 2933, 1714, 1613, 1486, 1366, 1247, 1152, 1031, 834, 779, 696, 560. $[\alpha]^{20}_D$ = -77.8 (1.0 c, $CHCl_3$). LRMS (FAB+) m/z = 531.18 calcd for $C_{32}H_{38}N_2O_5$ $[M+1]^+$ 531.28. HPLC analysis: Chiralpak AD-H (Hex/IPA = 97.5/2.5, 1.0 mL/min, 254 nm, 23 °C), 12.1 min (minor), 15.4 min (anti), 16.8 min (anti), 39.3 (major), 99:1 dr (syn:anti), 95% ee (syn).



(2*S*,3*R*)-Methyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethyleneamino)-3-(4-methoxyphenyl)propanoate:[5] General procedure was followed using cyclopropenimine (215 mg, 0.395 mmol, 0.1 equiv), methyl glycinate benzophenone imine (1.00 g, 3.95 mmol, 1.0 equiv) and *tert*-butyl 4-methoxybenzylidenecarbamate[8] (1.86 g, 7.90 mmol, 2.0 equiv). After 1.5 hr, the reaction mixture was purified by silica gel column chromatography (1/4 Et_2O/Hexanes, two columns were necessary) to yield the title product as a white solid (1.83 g, 3.75 mmol, 95% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, 7.3 Hz, 2H, Ar**H**), 7.36-7.20 (m, 6H, Ar**H**), 7.07 (d, 8.3 Hz, 2H, Ar**H**), 6.75 (d, 8.3 Hz, 2H, Ar**H**), 6.52 (d, 5.6 Hz, 2H, Ar**H**), 6.30 (d, 8.0 Hz, 1H, ArC**H**NHBoc), 5.43 (d, 7.7 Hz, 1H, C**H**CO_2tBu), 4.26 (s, 1H, N**H**Boc), 3.71 (s, 3H, $CO_2C\mathbf{H_3}$), 3.70 (s, 3H, ArOC$\mathbf{H_3}$), 1.45 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 170.3, 158.6, 155.1, 138.7, 135.7, 132.5, 130.6, 128.7, 128.5, 128.2, 128.0, 127.6, 127.0, 113.5, 79.2, 69.6, 56.1, 55.0, 52.1, 28.2. IR (thin film, cm^{-1}) 3431, 2976, 1713, 1613, 1486, 1365, 1247, 1165, 1029, 699. $[\alpha]^{20}_D$ = -108.4 (1.0 c, $CHCl_3$). HPLC analysis: Chiralpak AD-H (Hex/IPA = 93/7, 1.0 mL/min, 254 nm, 23 °C), 14.6 min (minor + anti), 17.7 min (anti), 19.7 (major), 99:1 dr (syn:anti), 97% ee (syn).



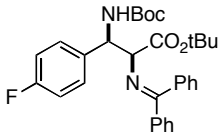
(2*S*,3*R*)-*tert*-Butyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethyleneamino)-3-(4-(trifluoromethyl)phenyl)propanoate: General procedure was followed using cyclopropenimine (185 mg, 0.339 mmol, 0.1 equiv), *tert*-butyl glycinate benzophenone imine (1.00 g, 3.39 mmol, 1.0 equiv) and *tert*-butyl 4-(trifluoromethyl)benzylidenecarbamate[10] (1.85 g, 6.78 mmol, 2.0 equiv). After 96 hr, the reaction mixture was purified by silica gel column chromatography (1/9 Et_2O/Hexanes) to yield the title product as a white solid (1.68 g, 2.95 mmol, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, 7.2 Hz, 2H, Ar**H**), 7.53 (d, 7.2 Hz, 2H, Ar**H**), 7.37-7.30 (m, 8H, Ar**H**), 6.56 (m, 2H, Ar**H**), 6.46 (d, 8.4 Hz, 1H, ArC**H**NHBoc), 5.52 (d, 8.4 Hz, 1H C**H**CO_2tBu), 4.21 (s, 1H, N**H**Boc), 1.53 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.51 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 168.8, 155.3, 145.2, 138.7, 135.9, 130.8, 128.9, 128.8, 128.7, 128.4, 128.3, 128.2, 127.1, 125.2, 82.3, 79.8, 69.9, 56.7, 28.5, 28.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -61.4 (s, 3F). IR (thin film, cm^{-1}) 3436, 2979, 2933, 1716, 1621, 1485, 1485, 1367, 1323, 1155, 1122, 1066, 845, 697. $[\alpha]^{20}_D$ = -32.4 (1.0 c, $CHCl_3$). LRMS (FAB+) m/z = 569.14 calcd for $C_{32}H_{35}F_3N_2O_4$ $[M+1]^+$ 569.25. HPLC analysis: Chiralpak AD-H (Hex/IPA = 97/3, 1.0 mL/min, 254 nm, 23 °C), 6.1 min (minor), 8.2 min (anti), 8.8 min (anti), 14.6 (major), 97:3 dr (syn:anti), 38% ee (syn).



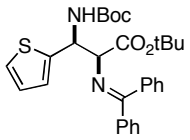
(2*S*,3*R*)-*tert*-Butyl 3-(4-bromophenyl)-3-(*tert*-butoxycarbonylamino)-2-(diphenylmethyleneamino)propanoate: General procedure was followed using cyclopropenimine (185 mg, 0.339 mmol, 0.1 equiv), *tert*-butyl glycinate benzophenone imine (1.00 g, 3.39 mmol, 1.0 equiv) and *tert*-butyl 4-bromobenzylidenecarbamate[8] (1.92 g, 6.78 mmol, 2.0 equiv). After 24 hr, the reaction mixture was purified by silica gel column chromatography (1/9 Et_2O/Hexanes) to yield the title product as a white solid (1.95 g, 3.37 mmol, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, 6.1 Hz, 2H, Ar**H**), 7.44-7.30 (m, 8H, Ar**H**), 7.08 (d, 6.4 Hz, 2H, Ar**H**), 6.61

[10] Huang, L.; Wulff, W. D. *J. Am. Chem. Soc.* **2011**, *133*, 8892.

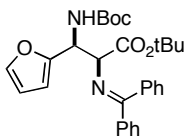
(m, 2H, Ar**H**), 6.36 (d, 6.6 Hz, 1H, ArC**H**NHBoc), 5.40 (d, 6.6 Hz, 1H, C**H**CO_2tBu), 4.15 (s, 1H, N**H**Boc), 1.50 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.49 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 168.9, 155.2, 140.1, 138.8, 136.0, 131.3, 130.7, 128.9, 128.7, 128.5, 128.4, 128.1, 127.2, 120.9, 82.2, 79.6, 69.9, 56.4, 28.5, 28.0. IR (thin film, cm^{-1}) 3431, 2977, 1715, 1628, 1485, 1366, 1284, 1151, 774, 696, 553. $[\alpha]^{20}_D$ = -50.6 (1.0 c, $CHCl_3$). LRMS (FAB+) m/z = 579.03 and 581.03 calcd for $C_{31}H_{35}BrN_2O_4$ $[M+1]^+$ 579.18 and 581.18. HPLC analysis: Chiralpak AD-H (Hex/IPA = 97.5/2.5, 1.0 mL/min, 254 nm, 23 °C), 8.3 min (minor), 10.8 min (anti), 12.6 min (anti), 20.5 (major), 97:3 dr (syn:anti), 86% ee (syn).



(2*S*,3*R*)-*tert*-Butyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethylene-amino)-3-(4-fluorophenyl)propanoate:[7] General procedure was followed using cyclopropenimine (185 mg, 0.339 mmol, 0.1 equiv), *tert*-butyl glycinate benzophenone imine (1.00 g, 3.39 mmol, 1.0 equiv) and *tert*-butyl 4-fluorobenzylidenecarbamate[8] (1.51 g, 6.78 mmol, 2.0 equiv). After 20 hr, the reaction mixture was purified by silica gel column chromatography (1/4 Et_2O/Hexanes) to yield the title product as a white solid (1.75 g, 3.37 mmol, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, 6.2 Hz, 2H, Ar**H**), 7.43-7.16 (m, 8H, Ar**H**), 6.95 (t, 6.8 Hz, 2H, Ar**H**), 6.60 (m, 2H, Ar**H**), 6.37 (d, 6.6 Hz, 1H, ArC**H**NHBoc), 5.43 (d, 6.6 Hz, 1H, C**H**CO_2tBu), 4.14 (s, 1H, N**H**Boc), 1.50 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.49 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 169.0, 163.2, 160.7, 155.2, 138.9, 136.7, 136.1, 130.7, 128.9, 128.7, 128.6, 128.4, 128.3, 128.1, 127.2, 115.1, 114.9, 82.1, 79.5, 70.2, 56.3, 28.5, 28.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -115.1 (s, 1F). IR (thin film, cm^{-1}) 3435, 2977, 1715, 1629, 1485, 1366, 1219, 1152, 1050, 696. $[\alpha]^{20}_D$ = -87.2 (1.0 c, $CHCl_3$). LRMS (FAB+) m/z = 519.16 calcd for $C_{31}H_{35}FN_2O_4$ $[M+1]^+$ 519.26. HPLC analysis: Chiralpak AD-H (Hex/IPA = 97/3, 1.0 mL/min, 254 nm, 23 °C), 7.1 min (minor), 8.0 min (anti), 9.3 min (anti), 13.6 (major), 99:1 dr (syn:anti), 92% ee (syn).

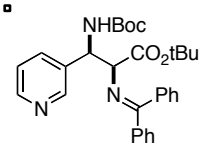


(2*S*,3*S*)-*tert*-Butyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethylene-amino)-3-(thiophen-2-yl)propanoate:[7] General procedure was followed using cyclopropenimine (185 mg, 0.339 mmol, 0.1 equiv), *tert*-butyl glycinate benzophenone imine (1.00 g, 3.39 mmol, 1.0 equiv) and *tert*-butyl thiophen-2-ylmethylenecarbamate[6] (1.43 g, 6.78 mmol, 2.0 equiv). After 24 hr, benzyl ether (161 µl, 0.846 mmol, 0.20 equiv) was added to the reaction solution to use as an internal standard (93% ^{1}H NMR yield was determined, see spectrum below). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.1 Hz, 2H, Ar**H**), 7.50-7.40 (m, 6H, Ar**H**), 7.12 (m, 1H, Ar**H**), 6.29 (d, J = 9.2 Hz, 1H, ArC**H**NHBoc), 5.71 (d, J = 9.2 Hz, 1H, C**H**CO_2tBu), 4.22 (s, 1H, N**H**Boc), 1.46 (s, 18H, 2 x $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 168.6, 154.9, 144.9, 139.0, 130.6, 129.0, 128.7, 128.4, 128.0, 127.2, 126.5, 124.5, 124.4, 82.0, 79.4, 70.0, 53.1, 28.4, 27.9. HPLC analysis: Chiralpak AD-H (Hex/IPA = 98/2, 1.0 mL/min, 254 nm, 23 °C), 11.7 min (minor), 15.2 min (anti), 30.2 (major), 97:3 dr (syn:anti), 94% ee (syn).

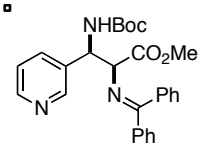


(2*S*,3*S*)-*tert*-Butyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethylene-amino)-3-(furan-2-yl)propanoate: General procedure was followed using cyclopropenimine (185 mg, 0.339 mmol, 0.1 equiv), *tert*-butyl glycinate benzophenone imine (1.00 g, 3.39 mmol, 1.0 equiv) and *tert*-butyl furan-2-

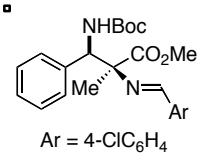
ylmethylenecarbamate[8] (1.32 g, 6.78 mmol, 2.0 equiv). After 20 hr, the reaction mixture was purified by silica gel column chromatography (1/4 Et_2O/Hexanes) to yield the title product as a white solid (1.63 g, 3.32 mmol, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, 7.2 Hz, 2H, Ar**H**), 7.40-7.20 (m, 7H, Ar**H**), 6.90 (m, 2H, Ar**H**), 6.24 (s, 1H, Ar**H**), 6.13 (m, 1H, Ar**H**), 6.10 (d, 9.2 Hz, 1H, ArC**H**NHBoc), 5.50 (d, 9.2 Hz, 1H, C**H**CO_2tBu), 4.36 (s, 1H, N**H**Boc), 1.46 (s, 18H, 2 x $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 168.8, 155.2, 154.0, 141.5, 139.3, 136.4, 130.6, 129.0, 128.8, 128.4, 128.0, 127.5, 110.4, 106.4, 82.0, 79.5, 67.9, 51.9, 28.5, 28.0. IR (thin film, cm^{-1}) 3441, 2978, 2932, 1722, 1622, 1485, 1367, 1284, 1155, 774, 729, 694, 510. $[\alpha]^{20}_D$ = -71.1 (1.0 c, $CHCl_3$). LRMS (FAB+) m/z = 491.15 calcd for $C_{29}H_{34}N_2O_5$ $[M+1]^+$ 491.25. HPLC analysis: Chiralpak AD-H (Hex/IPA = 97.5/2.5, 1.0 mL/min, 254 nm, 23 °C), 9.7 min (anti), 11.2 min (minor), 13.4 min (anti), 17.5 (major), 98:2 dr (syn:anti), 89% ee (syn).



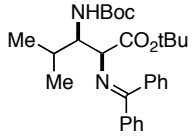
(2*S*,3*R*)-*tert*-Butyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethylene-amino)-3-(pyridin-3-yl)propanoate: General procedure was followed using cyclopropenimine (185 mg, 0.339 mmol, 0.1 equiv), *tert*-butyl glycinate benzophenone imine (1.00 g, 3.39 mmol, 1.0 equiv) and *tert*-butyl pyridin-3-ylmethylenecarbamate[8] (1.40 g, 6.78 mmol, 2.0 equiv). After 20 hr, the reaction mixture was purified by silica gel column chromatography (4/1 Et_2O/Hexanes) to yield the title product as a white solid (1.68 g, 3.35 mmol, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (m, 2H, Ar**H**), 7.55-7.48 (m, 3H, Ar**H**), 7.37-7.27 (m, 6H, Ar**H**), 7.15 (m, 1H, Ar**H**), 6.58 (d, 6.5 Hz, 2H, Ar**H**), 6.35 (d, 8.6 Hz, 1H, ArC**H**NHBoc), 5.43 (d, 8.3 Hz, 1H, C**H**CO_2tBu), 4.13 (s, 1H, N**H**Boc), 1.45 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.43 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 168.6, 155.1, 148.5, 138.6, 136.3, 135.9, 134.4, 130.8, 128.8, 128.5, 128.1, 126.9, 123.1, 82.3, 79.7, 69.7, 54.9, 28.4, 28.3. IR (thin film, cm^{-1}) 3433, 2977, 2932, 1713, 1626, 1485, 1366, 1284, 1251, 1151, 1051, 776, 697, 565. $[\alpha]^{20}_D$ = -47.8 (1.0 c, $CHCl_3$). HPLC analysis: Chiralpak AD-H (Hex/IPA = 90/10, 1.0 mL/min, 254 nm, 23 °C), 6.1 min (minor), 7.2 min (anti), 9.5 min (anti), 10.1 (major), 98:2 dr (syn:anti), 51% ee (syn).



(2*S*,3*R*)-Methyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethylene-amino)-3-(pyridin-3-yl)propanoate: General procedure was followed using cyclopropenimine (215 mg, 0.395 mmol, 0.1 equiv), methyl glycinate benzophenone imine (1.00 g, 3.95 mmol, 1.0 equiv) and *tert*-butyl pyridin-3-ylmethylenecarbamate[8] (1.40 g, 7.90 mmol, 2.0 equiv). The reaction solution was diluted to 0.07 M in toluene. After 2.5 hr, the reaction mixture was purified by silica gel column chromatography (4/1 Et_2O/Hexanes) to yield the title product as a white solid (1.77 g, 3.44 mmol, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (m, 2H, Ar**H**), 7.60 (d, 7.4 Hz, 2H, Ar**H**), 7.50 (d, 7.7 Hz, 1H, Ar**H**), 7.35-7.18 (m, 7H, Ar**H**), 6.56 (d, 5.9 Hz, 2H, Ar**H**), 6.36 (d, 8.2 Hz, 1H, ArC**H**NHBoc), 5.50 (d, 8.2 Hz, 1H, C**H**CO_2Me), 4.30 (s, 1H, N**H**Boc), 3.79 (s, 3H, $CO_2C\mathbf{H_3}$), 1.49 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 169.9, 155.1, 148.5, 148.4, 138.3, 135.9, 135.4, 134.2, 130.9, 128.7, 128.4, 128.1, 126.7, 123.0, 79.8, 69.0, 54.8, 52.4, 28.2. IR (thin film, cm^{-1}) 2978, 1739, 1710, 1484, 1366, 1162, 768, 697. $[\alpha]^{20}_D$ = -125.1 (1.0 c, $CHCl_3$). LRMS (FAB+) m/z = 460.16 calcd for $C_{27}H_{29}N_3O_4$ $[M+1]^+$ 460.22. HPLC analysis: Chiralpak AD-H (Hex/IPA = 92/8, 1.0 mL/min, 254 nm, 23 °C), 20.0 min (minor), 21.2 min (anti), 23.7 min (major), 29.4 (anti), 96:4 dr (syn:anti), 94% ee (syn).

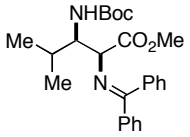


(2*S*,3*R*)-Methyl 3-(*tert*-butoxycarbonylamino)-2-((*E*)-4-chlorobenzylidene-amino)-2-methyl-3-phenylpropanoate: General procedure was followed using cyclopropenimine (97.0 mg, 0.177 mmol, 0.2 equiv), methyl alanine *p*-chlorobenzaldimine (200 mg, 0.886 mmol, 1.0 equiv) and *tert*-butyl benzylidenecarbamate (364 mg, 1.77 mmol, 2.0 equiv). After 34 hr, the reaction mixture was purified by silica gel column chromatography (1/4 Et_2O/Hexanes) to yield the title product as an off-white solid (357 mg, 0.828 mmol, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ *8.29 (s, 1H, **H**C=N), 8.06 (s, 1H, **H**C=N), 7.47 (d, 8.4 Hz, 2H, Ar**H**), 7.50-7.15 (m, 7H, Ar**H**), 6.20 (d, 9.0 Hz, 1H, C**H**NHBoc), *5.89 (d, 9.8 Hz, 1H, C**H**NHBoc), 5.30 (d, 9.0 Hz, 1H, N**H**Boc), *5.20 (d, 9.8 Hz, 1H, N**H**Boc), 3.77 (s, 3H, $CO_2C\mathbf{H_3}$), *3.57 (s, 3H, $CO_2C\mathbf{H_3}$), 1.40 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), *1.38 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.30 (m, 3H, C**H**$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, *172.7, *161.6, 161.3, 155.4, *154.9, 139.4, 138.5, 137.3, 137.2, 134.8, 134.4, 129.7, 129.6, 129.0, 128.9, 128.8, 128.3, 128.0, 127.8, 127.6, 127.5, 79.5, *79.4, *71.6, 70.9, 60.9, 52.7, 52.0, 28.3, *23.7, 21.3. Note: * denotes chemical shift corresponding to the minor diastereomer where discernable. IR (thin film, cm^{-1}) 3428, 2978, 2932, 1735, 1708, 1647, 1486, 1454, 1365, 1240, 1162, 1112, 1087, 1013, 701, 501. $[\alpha]^{20}_D$ = -72.6 (1.0 c, $CHCl_3$). LRMS (FAB+) m/z = 431.11 calcd for $C_{23}H_{27}ClN_2O_4$ $[M+1]^+$ 431.17. HPLC analysis: Chiralpak AD-H (Hex/IPA = 92/8, 1.0 mL/min, 254 nm, 23 °C), 7.8 min (minor, anti), 7.2 min (minor, syn), 9.5 min (major, anti), 10.1 (major, syn), 64:36 dr (syn:anti), 63% ee (syn) and 43% ee (anti).

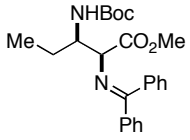


(2*S*,3*R*)-*tert*-Butyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethylene-amino)-4-methylpentanoate: General procedure was followed using cyclopropenimine (185 mg, 0.339 mmol, 0.1 equiv), *tert*-butyl glycinate benzophenone imine (1.00 g, 3.39 mmol, 1.0 equiv) and *tert*-butyl 2-methylpropylidenecarbamate[11] (1.16 g, 6.78 mmol, 2.0 equiv). After 24 hr, another 0.1 equiv. of cyclopropenimine **1** (185 mg, 0.339 mmol) was added to the reaction solution. After 72 hr, the reaction mixture was purified by silica gel column chromatography (1/9 Et_2O/Hexanes) to yield the title product as a white solid (1.42 g, 3.04 mmol, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, 7.0 Hz, 2H, Ar**H**), 7.43-7.14 (m, 8H, Ar**H**), 5.68 (d, 10.0 Hz, 1H, C**H**CO_2tBu), 4.04 (s, 1H, N**H**Boc), 3.86 (t, 10.0 Hz, 1H, iPrC**H**NHBoc), 1.48 (m, 1H, C**H**Me_2), 1.44 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.42 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 0.97 (d, 6.7 Hz, 3H, C**H**$_3$), 0.70 (d, 6.7 Hz, 3H, C**H**$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8, 170.5, 155.8, 139.3, 136.7, 130.6, 129.0, 128.6, 128.1, 127.6, 81.6, 78.7, 66.5, 59.0, 31.6, 28.6, 28.0, 19.6, 19.3. IR (thin film, cm^{-1}) 3429, 2975, 1724, 1625, 1486, 1449, 1159, 692. $[\alpha]^{20}_D$ = -25.3 (1.0 c, $CHCl_3$). LRMS (FAB+) m/z = 467.18 calcd for $C_{28}H_{38}N_2O_4$ $[M+1]^+$ 467.28. HPLC analysis: Chiralpak AD-H (Hex/IPA = 97.5/2.5, 1.0 mL/min, 254 nm, 23 °C), 8.1 min (minor), 9.8 min (major), 99:1 dr (syn:anti), 89% ee (syn).

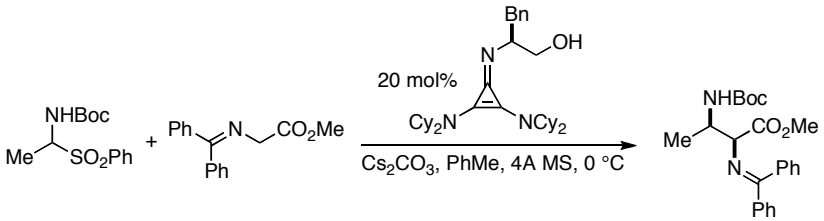
[11] Probst, N.; Madarász, A.; Valkonen, A.; Pápai, I.; Rissanen, K.; Neuvonen, A.; Pihko, P. M. *Angew. Chem. Int. Ed.* **2012**, *51*, 8495.

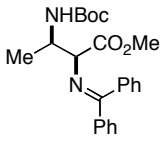


(2*S*,3*R*)-Methyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethylene-amino)-4-methylpentanoate: General procedure was followed using cyclopropenimine (215 mg, 0.395 mmol, 0.1 equiv), methyl glycinate benzophenone imine (1.00 g, 3.95 mmol, 1.0 equiv) and *tert*-butyl 2-methylpropylidenecarbamate[11] (1.35 g, 7.90 mmol, 2.0 equiv). After 36 hr, the reaction mixture was purified by silica gel column chromatography (1/9 Et_2O/Hexanes) to yield the title product as a white solid (1.46 g, 3.44 mmol, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, 7.3 Hz, 2H, Ar**H**), **7**.43-7.33 (m, 6H, Ar**H**), 7.12 (m, 2H, Ar**H**), 5.65 (d, 10.0 Hz, 1H, C**H**CO_2Me), 4.20 (s, 1H, N**H**Boc), 3.93 (t, 10.0 Hz, 1H, iPrC**H**NHBoc), 3.68 (s, 3H, $CO_2C\mathbf{H_3}$), 1.55 (m, 1H, C**H**Me_2), 1.45 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 0.97 (d, 6.8 Hz, 3H, C$\mathbf{H_3}$), 0.72 (d, 6.8 Hz, 3H, C$\mathbf{H_3}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 171.7, 155.7, 138.9, 136.2, 130.6, 128.9, 128.8, 128.5, 128.0, 127.3, 78.8, 65.8, 58.9, 52.0, 30.8, 28.3, 30.8, 28.3, 19.4, 19.1, 17.2. IR (thin film, cm^{-1}) 3433, 2969, 1736, 1712, 1626, 1487, 1365, 1166, 772, 695, 566. $[\alpha]^{20}_D$ = -28.7 (1.0 c, $CHCl_3$). LRMS (FAB+) m/z = 425.17 calcd for $C_{25}H_{32}N_2O_4$ $[M+1]^+$ 425.24. HPLC analysis: Chiralpak OD-H (Hex/IPA = 98.5/1.5, 1.0 mL/min, 254 nm, 23 °C), 9.7 min (minor), 10.4 min (major), 13.5 min (anti), 99:1 dr (syn:anti), 94% ee (syn).

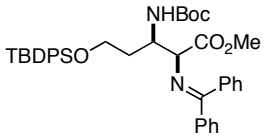


(2*S*,3*R*)-Methyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethylene-amino)pentanoate: General procedure was followed using cyclopropenimine (22.0 mg, 0.040 mmol, 0.1 equiv), methyl glycinate benzophenone imine (101 mg, 0.399 mmol, 1.0 equiv), *tert*-butyl propylidenecarbamate[11] (250 mg, 1.59 mmol, 4.0 equiv) and 4Å molecular sieves (125 mg) in toluene (1.6 mL). After 8 hr, the reaction mixture was purified by silica gel column chromatography (1/9 Et_2O/Hexanes) to yield the title product as a white solid (156 mg, 0.380 mmol, 95% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, 7.3 Hz, 2H, Ar**H**), 7.44 (m, 4H, Ar**H**), 7.33 (t, 7.8 Hz, 2H, Ar**H**), 7.11 (m, 2H, Ar**H**), 5.53 (d, 9.8 Hz, 1H, C**H**CO_2Me), 4.15 (m, 1H, EtC**H**NHBoc), 4.09 (d, 2.2 Hz, 1H, N**H**Boc), 3.69 (s, 3H, $CO_2C\mathbf{H_3}$), 1.44 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.50-1.45 (m, 2H, $CH_3C\mathbf{H_2}$CHNHBoc), 0.81 (t, 7.4 Hz, 3H, C$\mathbf{H_3}CH_2$CHNHBoc). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 171.5, 155.7, 139.1, 136.3, 130.8, 129.0, 128.7, 128.2, 127.5, 79.1, 67.2, 54.7, 52.2, 28.4, 26.6, 10.6. IR (thin film, cm^{-1}) 3435, 2971, 2933, 1741, 1713, 1490, 1365, 1161, 778, 697. $[\alpha]^{20}_D$ = -27.6 (1.0 c, $CHCl_3$). LRMS (APCI+) m/z = 410.86 calcd for $C_{24}H_{30}N_2O_4$ $[M+1]^+$ 411.22. HPLC analysis: for diastereoselectivity: Chiralpak AD-H (Hex/EtOH = 95/5, 0.6 mL/min, 254 nm, 23 °C), 6.4 min (anti), 6.8 min (syn), 7.6 min (anti), 93:7 dr (syn:anti); for enantioselectivity: Chiralpak OD-H (Hex/EtOH = 99/1, 0.6 mL/min, 254 nm, 23 °C), 5.2 min (minor), 6.0 min (major syn and anti), 7.1 min (anti), 98% ee (syn).

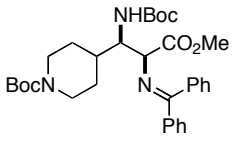




(2*S*,3*R*)-Methyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethyleneamino)butanoate: Methyl glycinate benzophenone imine (30.0 mg, 0.117 mmol, 1.0 equiv), cesium carbonate (1.37 g, 4.20 mmol, 12 equiv) and 4Å molecular sieves (50 mg) were mixed in a vial containing toluene (2.3 mL). The reaction mixture was cooled to 0 °C in an ice bath, at which point *tert*-butyl 1-(phenylsulfonyl)ethylcarbamate (100 mg, 0.350 mmol, 3.0 equiv) and cyclopropenimine (13.0 mg, 0.023 mmol, 0.2 equiv) were added. After 12 hr, the reaction was filtered and concentrated *in vacuo* to a crude oil. The crude oil was purified by silica gel column chromatography (2/3 Et_2O/Hexanes) to yield the title product as a white solid (39.4 mg, 0.099 mmol, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, 6.9 Hz, 2H, Ar**H**), 7.50-7.34 (m, 6H, Ar**H**), 7.10 (m, 2H, Ar**H**), 5.52 (d, 9.0 Hz, 1H, C**H**CO_2Me), 4.33 (m, 1H, MeC**H**NHBoc), 4.00 (d, 2.5 Hz, 1H, N**H**Boc), 3.69 (s, 3H, $CO_2C\mathbf{H_3}$), 1.44 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.08 (d, 6.8 Hz, 3H, CHC**H**$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 171.3, 155.4, 139.2, 136.3, 130.8, 129.0, 128.9, 128.8, 128.2, 127.6, 79.2, 28.9, 52.3, 49.0, 28.5, 19.2. IR (thin film, cm^{-1}) 3434, 2976, 1740, 1711, 1626, 1490, 1447, 1366, 1162, 1056, 779, 698. $[\alpha]^{20}_D$ = -4.0 (0.5 c, $CHCl_3$). LRMS (APCI+) m/z = 396.86 calcd for $C_{23}H_{28}N_2O_4$ $[M+1]^+$ 397.20. HPLC analysis: Chiralpak AD-H (Hex/IPA = 97.5/2.5, 1.0 mL/min, 254 nm, 23 °C), 10.4 min (anti), 11.7 min (anti), 12.6 min (minor), 14.3 min (major) 97:3 dr (syn:anti), 44% ee (syn).

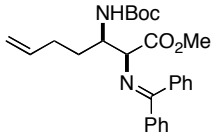


(2*S*,3*R*)-Methyl 3-(*tert*-butoxycarbonylamino)-5-(*tert*-butyldiphenylsilyloxy)-2-(diphenylmethyleneamino)pentanoate: General procedure was followed at -25 °C using cyclopropenimine (7.5 mg, 0.013 mmol, 0.1 equiv), methyl glycinate benzophenone imine (34.0 mg, 0.133 mmol, 1.0 equiv), *tert*-butyl 3-(*tert*-butyldiphenylsilyloxy)propylidenecarbamate[11] (220 mg, 0.534 mmol, 4.0 equiv) and 4Å molecular sieves (110 mg) in toluene (0.54 mL). After 5 hr, the reaction mixture was purified by silica gel column chromatography (1/4 Et_2O/Hexanes) to yield the title product as a white solid (89.0 mg, 0.133 mmol, 99% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (m, 6H, Ar**H**), 7.50-7.30 (m, 12H, Ar**H**), 7.00 (m, 2H, Ar**H**), 5.41 (d, 9.8 Hz, 1H, C**H**CO_2Me), 4.35 (broad q, 7.5 Hz, 1H, RC**H**NHBoc), 4.02 (s, 1H, N**H**Boc), 3.66 (s, 3H, $CO_2C\mathbf{H_3}$), 3.65 (m, 2H, SiOC$\mathbf{H_2}$CH$_2$), 1.68 (quintet, 6.3 Hz, 2H, SiOCH$_2$C$\mathbf{H_2}$CHNHBoc), 1.41 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.00 (s, 9H, $SiC(C\mathbf{H_3})_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 171.4, 155.4, 139.2, 136.3, 135.7, 135.6, 133.9, 132.5, 130.8, 130.2, 129.7, 129.1, 129.0, 128.8, 128.4, 128.2, 127.9, 127.8, 127.7, 127.6, 79.1, 68.0, 61.2, 52.2, 50.6, 36.4, 28.5, 27.0, 19.3. IR (thin film, cm^{-1}) 2931, 2858, 1742, 1714, 1490, 1169, 1108, 739, 699, 504. $[\alpha]^{20}_D$ = -8.5 (0.3 c, $CHCl_3$). LRMS (APCI+) m/z = 665.37 calcd for $C_{40}H_{48}N_2O_5Si$ $[M+1]^+$ 665.33. HPLC analysis: Chiralpak AD-H (Hex/IPA = 97.5/2.5, 1.0 mL/min, 254 nm, 23 °C), 5.3 min (minor), 5.8 min (anti), 7.0 min (anti), 8.9 min (major) 99:1 dr (syn:anti), 84% ee (syn).



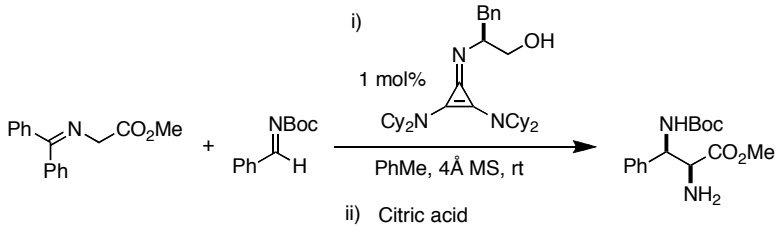
***tert*-Butyl 4-((1*R*,2*S*)-1-(*tert*-butoxycarbonylamino)-2-(diphenylmethyleneamino)-3-methoxy-3-oxopropyl)piperidine-1-carboxylate:** General procedure was followed using cyclopropenimine (7.0 mg, 0.013 mmol, 0.1 equiv), methyl glycinate benzophenone imine (32.0 mg, 0.128 mmol, 1.0 equiv), *tert*-butyl 4-((*tert*-butoxycarbonylimino)methyl)piperidine-1-carboxylate (100

mg, 0.320 mmol, 2.5 equiv) and 4Å molecular sieves (50 mg) in toluene (0.5 mL). After 6 hr, the reaction mixture was purified by silica gel column chromatography (1/4 Et_2O/Hexanes) to yield the title product as a white solid (70.0 mg, 0.124 mmol, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, 7.5 Hz, 2H, Ar**H**), 7.42 (m, 4H, Ar**H**), 7.35 (t, 7.6 Hz, 2H, Ar**H**), 7.09 (m, 2H, Ar**H**), 5.62 (d, 9.4 Hz, 1H, C**H**CO_2Me), 4.18 (s, 1H, N**H**Boc), 4.10 (br s, 2H, Cy**H**), 4.00 (t, 9.4 Hz, 1H, C**H**NHBoc), 3.66 (s, 3H, $CO_2C\mathbf{H_3}$), 2.55 (m, 2H, Cy**H**), 1.77 (m, 1H, Cy**H**), 1.20 (m, 4H, Cy**H**), 1.43 (s, 9H, $CO_2C(C\mathbf{H_3})_3$), 1.41 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 171.5, 155.8, 154.8, 139.0, 136.2, 131.0, 129.3, 129.0, 128.8, 128.3, 127.4, 79.4, 79.3, 65.3, 57.2, 52.3, 42.3 (broad), 39.0, 28.5, 28.4. IR (thin film, cm^{-1}) 3421, 2938, 1746, 1715, 1688, 1486, 1160, 769, 698. $[\alpha]^{20}_D$ = -8.9 (0.35 c, $CHCl_3$). LRMS (APCI+) m/z = 565.82 calcd for $C_{32}H_{43}N_3O_6$ $[M+1]^+$ 566.32. HPLC analysis: Chiralpak OD-H (Hex/EtOH = 99/1, 0.6 mL/min, 254 nm, 23 °C), 10.9 min (anti), 11.6 min (minor), 13.3 min (major), 15.1 min (anti), 94:6 dr (syn:anti), 91% ee (syn).



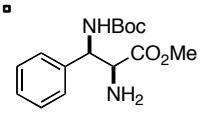
(2*S*,3*R*)-Methyl 3-(*tert*-butoxycarbonylamino)-2-(diphenylmethylene-amino)hept-6-enoate: General procedure was followed at -25 °C using cyclopropenimine (7.0 mg, 0.012 mmol, 0.1 equiv), methyl glycinate benzophenone imine (31.0 mg, 0.122 mmol, 1.0 equiv), *tert*-butyl pent-4-enylidenecarbamate (90 mg, 0.490 mmol, 4.0 equiv) and 4Å molecular sieves (45 mg) in toluene (0.50 mL). After 2 hr, the reaction mixture was purified by silica gel column chromatography (1/4 Et_2O/Hexanes) to yield the title product as a white solid (45.0 mg, 0.103 mmol, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, 7.0 Hz, 2H, Ar**H**), 7.43 (m, 4H, Ar**H**), 7.26 (t, 7.3 Hz, 2H, Ar**H**), 7.11 (m, 2H, Ar**H**), 5.78 (m, 1H, H_2C=C**H**R), 5.54 (d, 9.8 Hz, 1H, C**H**CO_2Me), 4.96 (m, 2H, $\mathbf{H_2}$C=CHR), 4.24 (m, 1H, C**H**NHBoc), 4.06 (d, 2.2 Hz, 1H, N**H**Boc), 3.68 (s, 3H, $CO_2C\mathbf{H_3}$), 2.02 (m, 2H, -C$\mathbf{H_2}$-), 1.60-1.45 (m, 2H, -C$\mathbf{H_2}$-), 1.45 (s, 9H, $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.7, 171.4, 155.6, 139.1, 137.9, 136.3, 130.9, 129.1, 128.8, 128.3, 127.6, 115.1, 79.3, 67.6, 52.8, 52.3, 32.9, 30.3, 28.5. IR (thin film, cm^{-1}) 3433, 3061, 2976, 1740, 1712, 1490, 1446, 1167, 913, 773, 696. $[\alpha]^{20}_D$ = -23.9 (0.45 c, $CHCl_3$). LRMS (APCI+) m/z = 436.86 calcd for $C_{26}H_{32}N_2O_4$ $[M+1]^+$ 437.24. HPLC analysis: Chiralpak AD-H (Hex/iPrOH = 90/10, 1.0 mL/min, 254 nm, 23 °C), 5.0 min (minor), 5.2 min (anti), 6.3 min (major), 7.1min (anti), 96:4 dr (syn:anti), 91% ee (syn).

Large-scale Mannich reaction:



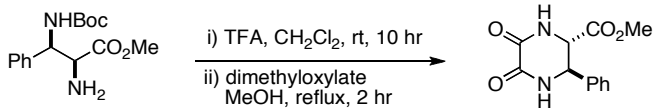
Cyclopropenimine (0.674 g, 1.23 mmol, 0.01 equiv), methyl glycinate benzophenone Schiff base (31.3 g, 123 mmol, 1.0 equiv) and 4Å molecular sieves (15 g) were mixed in toluene (310 mL, 0.4 M). *tert*-Butyl benzylidenecarbamate (38.0 g, 185 mmol, 1.5 equiv) was then added and the

reaction solution was stirred at room temperature. The reaction was complete after 8 hr, as determined by ^{1}H NMR. A small aliquot (0.25 mL) was removed to perform chiral HPLC analysis on. HPLC analysis: Chiralpak AD-H (Hex/IPA = 96/4, 1.0 mL/min, 254 nm, 23 °C), 13.9 min (major), 15.1 min (minor), 16.0 min (anti), 17.1 (anti), 96:4 dr (syn:anti), 93% ee (syn).

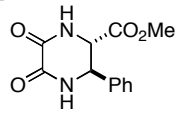


(2*S*,3*R*)-Methyl 2-amino-3-(*tert*-butoxycarbonylamino)-3-phenyl-propanoate: The remaining reaction mixture was concentrated *in vacuo*, dissolved in THF (985 mL) and added to a 0.5 M citric acid aqueous solution (103 g citric acid in 985 mL H_2O) in a 5L round bottom flask. The reaction mixture was stirred for 4 hr. The approximate 2L of reaction mixture was divided into four fractions to be worked up separately. Each fraction of the reaction mixture was washed with Et_2O (3 x 300 mL), basified with sat. Na_2CO_3(aq), and extracted with ethyl acetate (3 x 300 mL). The collected ethyl acetate solution was concentrated *in vacuo* to a crude solid that was recrystallized from hexanes to yield the pure title product as white crystals (26.7 g, 90.6 mmol, 73% two-step yield).

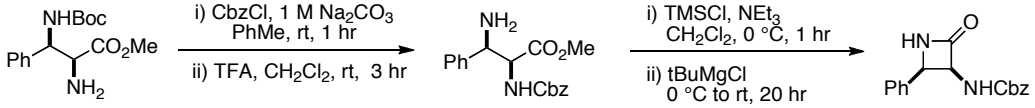
Product derivatizations:



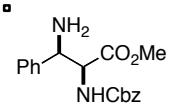
Trifluoroacetic acid (12.5 mL) was added to a solution of (2*S*,3*R*)-methyl 2-amino-3-(*tert*-butoxycarbonylamino)-3-phenylpropanoate (2.50 g, 8.49 mmol) in dichloromethane (200 mL). The reaction solution was stirred for 10 hr at room temperature. The reaction was quenched with saturated aqueous Na_2CO_3 (300 mL) and was then extracted with ethyl acetate (3 x 200 mL), dried with anhydrous sodium sulfate and concentrated *in vacuo* to yield crude (2*S*,3*R*)-methyl 2,3-diamino-3-phenylpropanoate as an off-white solid.



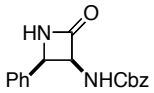
(2*S*,3*R*)-Methyl 5,6-dioxo-3-phenylpiperazine-2-carboxylate: Crude (2*S*,3*R*)-methyl 2,3-diamino-3-phenylpropanoate (assumed to be 8.49 mmol, 1.0 equiv) and dimethyl oxalate (1.00 g, 8.49 mmol, 1.0 equiv) were dissolved in dry methanol (85 mL, 0.1 M) in an oven-dried 250 mL round bottom flask fitted with a reflux condenser. After refluxing the reaction solution for 2 hr, the reaction solution was concentrated *in vacuo* to a crude brown solid. Washing of the crude solid with a hot mixture of hexanes and dichloromethane (1/1, 3 x 30 mL) yielded the pure title product as a white solid (1.53 g, 6.15 mmol, 72% two-step yield). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 9.07 (d, 3.6 Hz, 1H, N**H**), 8.72 (d, 4.1 Hz, 1H, N**H**), 7.50-7.25 (m, 5H, Ar**H**), 4.97 (d, 2.8 Hz, 1H, C**H**CO_2Me), 4.45 (d, 4.0 Hz, 1H, C**H**Ph), 3.79 (s, 3H, $CO_2C\mathbf{H_3}$). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 170.9, 158.1, 157.7, 139.2, 128.7, 128.0, 126.1, 58.0, 54.7, 53.1. IR (thin film, cm^{-1}) 3207, 2956, 1744, 1679, 1437, 1253, 1201, 1177, 1130, 1055, 720, 698, 518. $[\alpha]^{20}_D$ = -66.4 (1.0 c, MeOH). LRMS (APCI+) m/z = 248.92 calcd for $C_{12}H_{12}N_2O_4$ $[M+1]^+$ 249.08.



Benzyl chloroformate (1.90 mL, 13.2 mmol, 1.3 equiv) was added to a stirred solution of (2*S*,3*R*)-methyl 2-amino-3-(*tert*-butoxycarbonylamino)-3-phenylpropanoate (3.00 g, 10.2 mmol, 1.0 equiv) in toluene (10 mL, 1.0 M). Next, 1 M aqueous Na_2CO_3 (16 mL, 1.5 equiv of Na_2CO_3) was added to the reaction mixture. The reaction mixture became cloudy with an off-white precipitate over the course of an hour. The reaction mixture was then extracted with ethyl acetate (3 x 50 mL), dried with anhydrous sodium sulfate and concentrated *in vacuo* to yield a crude white solid that was used without further purification.

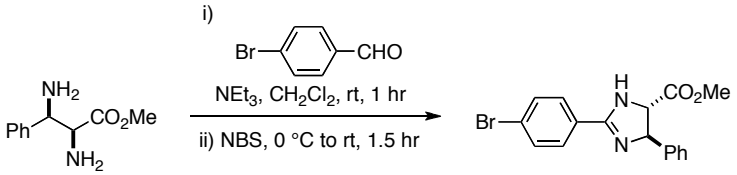


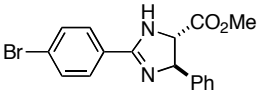
(2*S*,3*R*)-Methyl 3-amino-2-(benzyloxycarbonylamino)-3-phenylpropanoate: The crude solid from above was dissolved in dichloromethane (400 mL) and then trifluoroacetic acid (15 mL) was added to the reaction solution. After stirring the reaction solution at room temperature for 3 hr, the reaction was quenched with 1 M NaOH (200 mL), extracted with ethyl acetate (3 x 200 mL), dried with anhydrous sodium sulfate and concentrated *in vacuo* to give a crude white solid. The crude material was semi-purified by silica gel column chromatography (3% MeOH in DCM) to yield the title product as a white solid. This material was not completely pure, although the yield was estimated to be 95%; both ^{1}H NMR and ^{13}C NMR spectra for this material are provided below for reference.



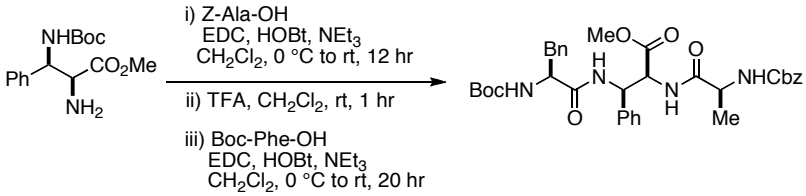
Benzyl (3*S*,4*R*)-2-oxo-4-phenylazetidin-3-ylcarbamate: This compound was prepared in a similar manner to the previously reported trans diastereomer.[12] The material obtained above containing (2*S*,3*R*)-methyl 3-amino-2-(benzyloxycarbonylamino)-3-phenylpropanoate (estimated to be 9.43 mmol, 1.0 equiv) was dissolved in dichloromethane (50 mL, 0.2 M) under an atmosphere of argon and cooled to 0 °C in an ice bath. Chlorotrimethylsilane (3.60 mL, 28.3 mmol, 3.0 equiv) and triethylamine (4.00 mL, 28.3 mmol, 3.0 equiv) were added and the reaction solution was stirred for 1 hr. At this time, tBuMgCl (94 mL of a 1.0 M solution in THF, 94.0 mmol, 10 equiv) was added slowly and the resulting reaction mixture was allowed to warm to room temperature as it stirred for 20 hr. The reaction was quenched by adding water (200 mL) and the resulting slurry was filtered through celite. The collected filtrate was then extracted with dichloromethane (3 x 100 mL), dried with anhydrous sodium sulfate and concentrated *in vacuo* to a crude oil. The crude material was purified by silica gel column chromatography (1/3 EtOAc/Hexanes) to yield the title product as a white solid (440 mg, 1.49 mmol, 15% three-step yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.12 (m, 10H, Ar**H**), 6.30 (s, 1H, lactam N**H**), 5.40 (dd, 5.1 and 9.4 Hz, 1H, C**H**NHCbz), 5.01 (d, 5.1 Hz, 1H, Cbz N**H**), 4.96 (d, 2.0 Hz, 2H, $CO_2C\mathbf{H_2}Ph$), 4.87 (d, 9.4 Hz, 1H, C**H**Ph). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 155.4, 136.0, 135.8, 129.0, 128.6, 128.3, 128.0, 126.6, 67.2, 63.2, 57.9. IR (thin film, cm^{-1}) 3335, 3218, 3062, 3037, 2961, 1770, 1721, 1693, 1527, 1382, 1251, 1208, 1057, 737, 695, 626. $[\alpha]^{20}_D$ = +29.3 (1.0 c, $CHCl_3$). LRMS (APCI+) m/z = 296.64 calcd for $C_{17}H_{16}N_2O_3$ $[M+1]^+$ 297.12.

[12] Kano, T.; Sakamoto, R.; Akakura, M.; Maruoka, K. *J. Am. Chem. Soc.* **2012**, *134*, 7516.





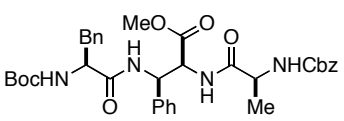
(4*R*,5*S*)-Methyl 2-(4-bromophenyl)-4-phenyl-4,5-dihydro-1*H*-imidazole-5-carboxylate: Crude (2*S*,3*R*)-methyl 2,3-diamino-3-phenylpropanoate (obtained from same procedure as above, assumed to be 6.79 mmol, 1.0 equiv) and triethylamine (4.70 mL, 34.0 mmol, 5 equiv) were dissolved in dichloromethane (68 mL, 0.1 M). 4-Bromobenzaldehyde (1.23 g, 6.66 mmol, 1.0 equiv) was then added and the reaction solution was stirred at room temperature for 1 hr. At this time, the reaction solution was cooled to 0 °C in an ice bath and N-bromosuccinimide (1.27 g, 7.13 mmol, 1.1 equiv) was added. The reaction solution was allowed to warm to room temperature over 1.5 hr, at which time the reaction was quenched with 5% aqueous NaOH (200 mL) and extracted with dichloromethane (3 x 100 mL), dried with anhydrous sodium sulfate and concentrated *in vacuo* to a crude yellow solid. The crude material was purified by silica gel column chromatography (1/2/17 NEt_3/EtOAc/Hexanes) to yield the title product as a yellow solid (1.75 g, 4.87 mmol, 72% two-step yield). ^{1}H NMR (400 MHz, CD_3OH) δ 7.80 (d, 7.9 Hz, 2H, BrAr**H**), 7.62 (d, 7.9 Hz, 2H, BrAr**H**), 7.34-7.30 (m, 5H, Ar**H**), 5.26 (d, 6.8 Hz, 1H, C**H**CO_2Me), 4.43 (d, 6.8 Hz, 1H, C**H**Ph), 3.80 (s, 1H, $CO_2C\mathbf{H_3}$). ^{13}C NMR (100 MHz, CD_3OH) δ 174.2, 165.7, 144.1, 132.9, 130.5, 129.9, 129.5, 128.9, 127.4, 126.8, 53.0. IR (thin film, cm^{-1}) 3158, 3030, 2950, 1736, 1608, 1560, 1494, 1452, 1217, 1123, 1009, 836, 698. $[\alpha]^{20}_D$ = +30.0 (1.0 c, $CHCl_3$). LRMS (APCI+) m/z = 358.57 and 360.58 calcd for $C_{17}H_{15}BrN_2O_2$ $[M+1]^+$ 359.03 and 361.03.



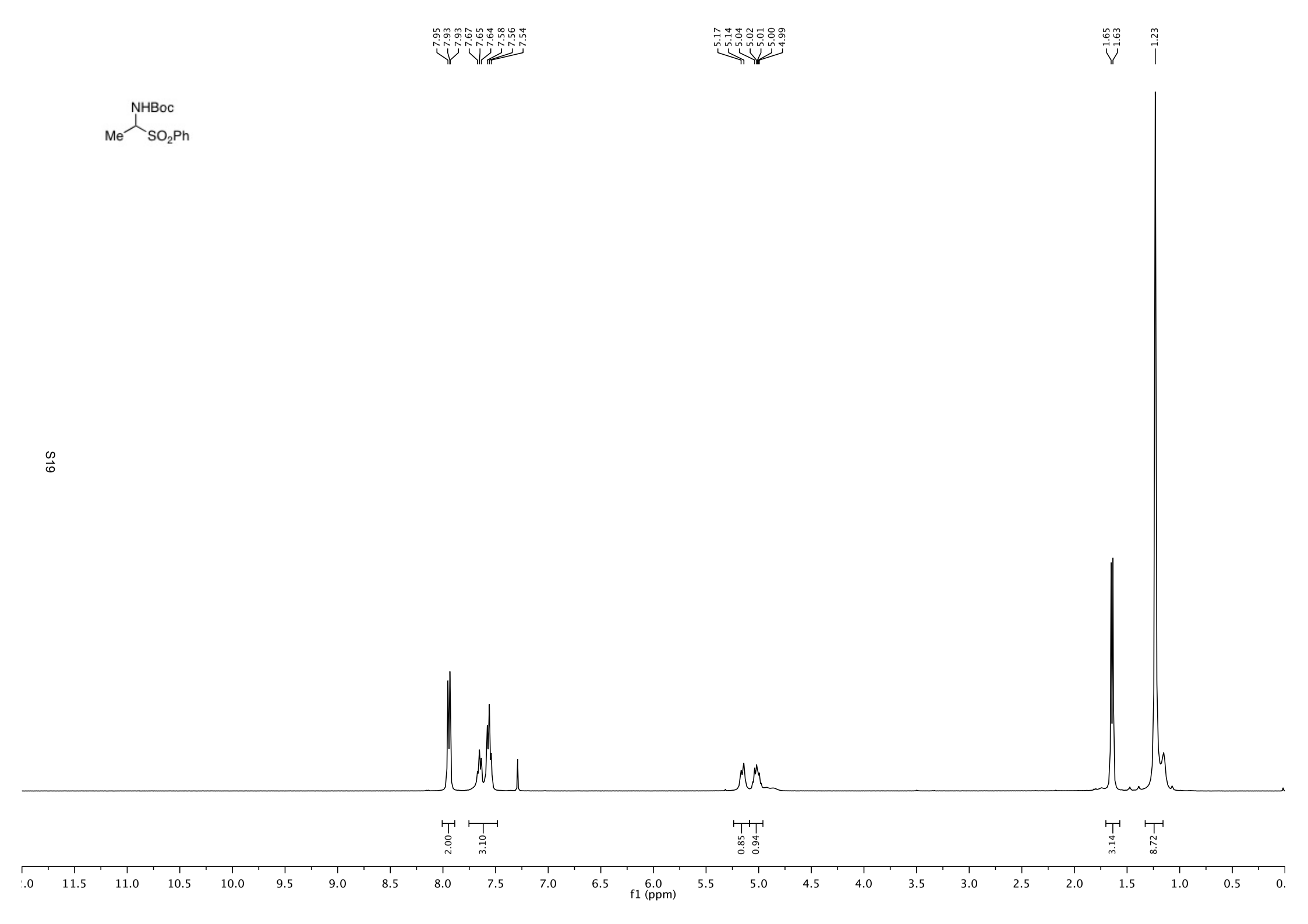
Triethylamine (2.10 mL, 15.3 mmol, 3.0 equiv) and 1-hydroxybenzotriazole (1.03 g, 7.64 mmol, 1.5 equiv) were added to a 0 °C solution of (2*S*,3*R*)-methyl 2-amino-3-(*tert*-butoxycarbonylamino)-3-phenylpropanoate (1.50 g, 5.10 mmol, 1.0 equiv) and carbobenzyloxy-L-alanine (1.05 g, 5.10 mmol, 1.0 equiv) in dichloromethane (25 mL, 0.2 M). The reaction solution was stirred for 15 min, then N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (1.22 g, 6.37 mmol, 1.25 equiv) was added. After 12 hr, the reaction solution was washed with water (1 x 25 mL) and brine (1 x 25 mL), then dried with anhydrous sodium sulfate and concentrated *in vacuo* to yield a white solid. This material was carried forward without any further purification.

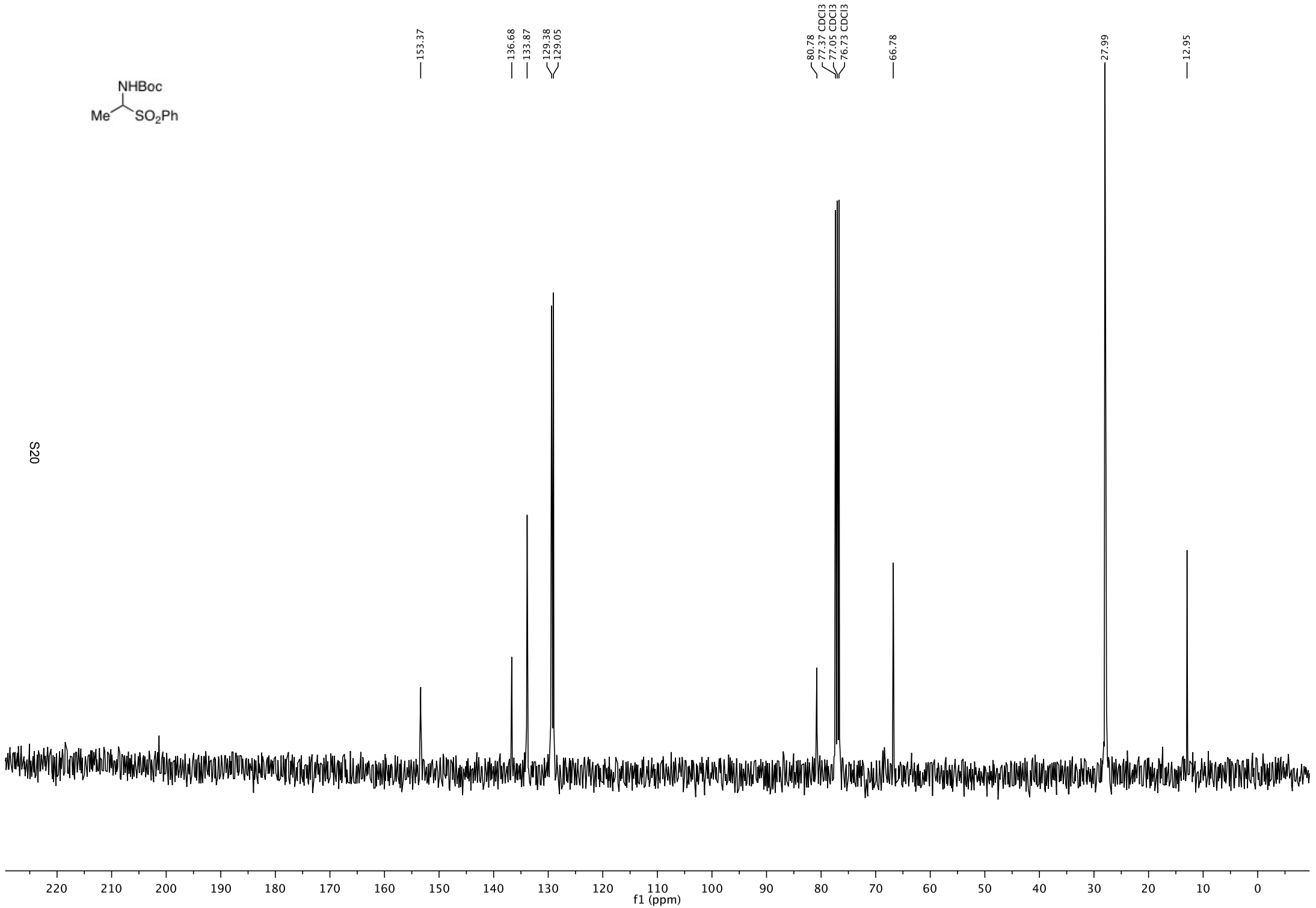
Trifluoroacetic acid (5.25 mL) was added to a solution of the crude material obtained above (assumed to be 5.10 mmol) in dichloromethane (20.4 mL, 0.25 M). After stirring for 1 hr at room

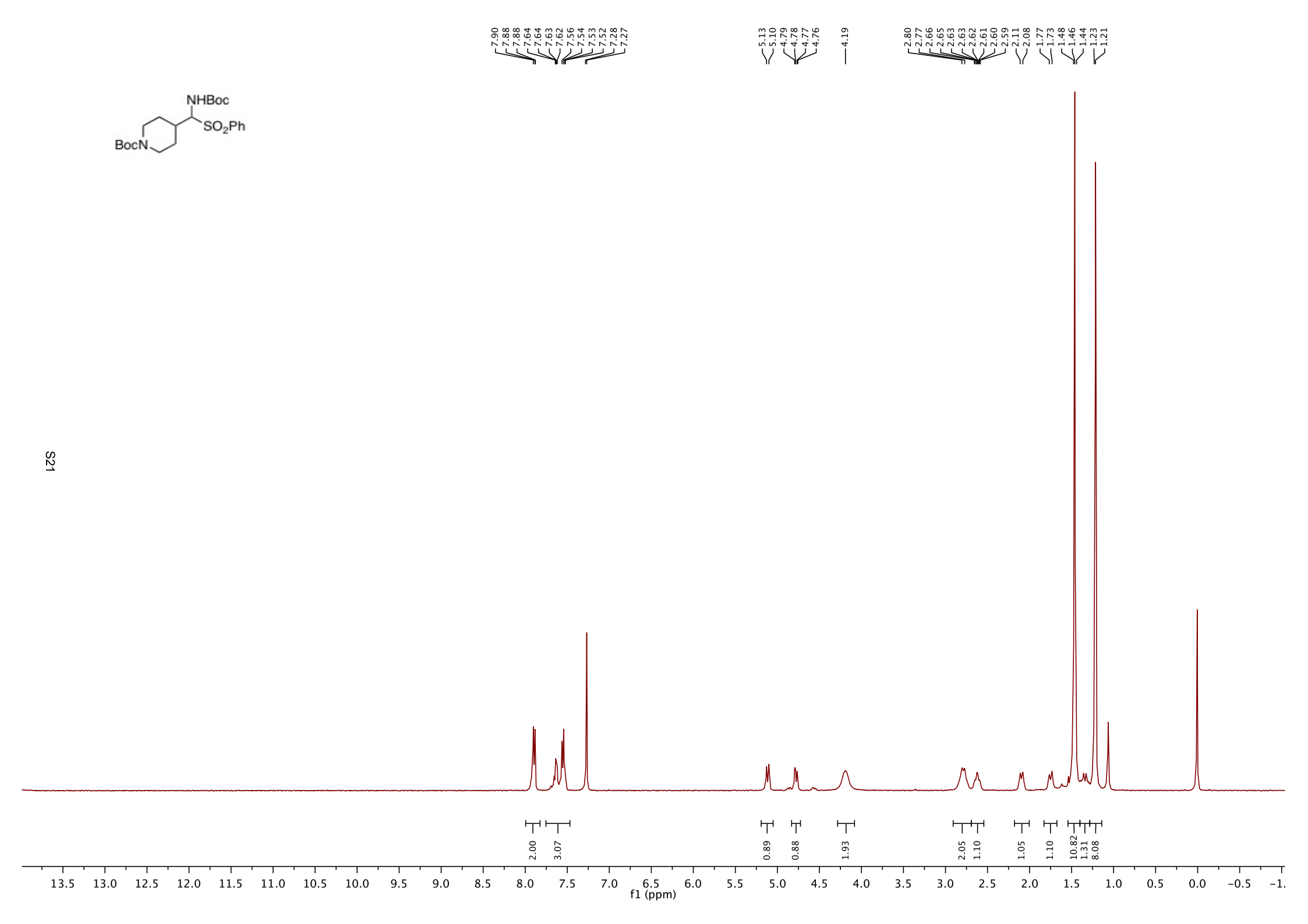
temperature, the reaction solution was concentrated *in vacuo* to yield a white solid. This material was carried forward without any further purification.

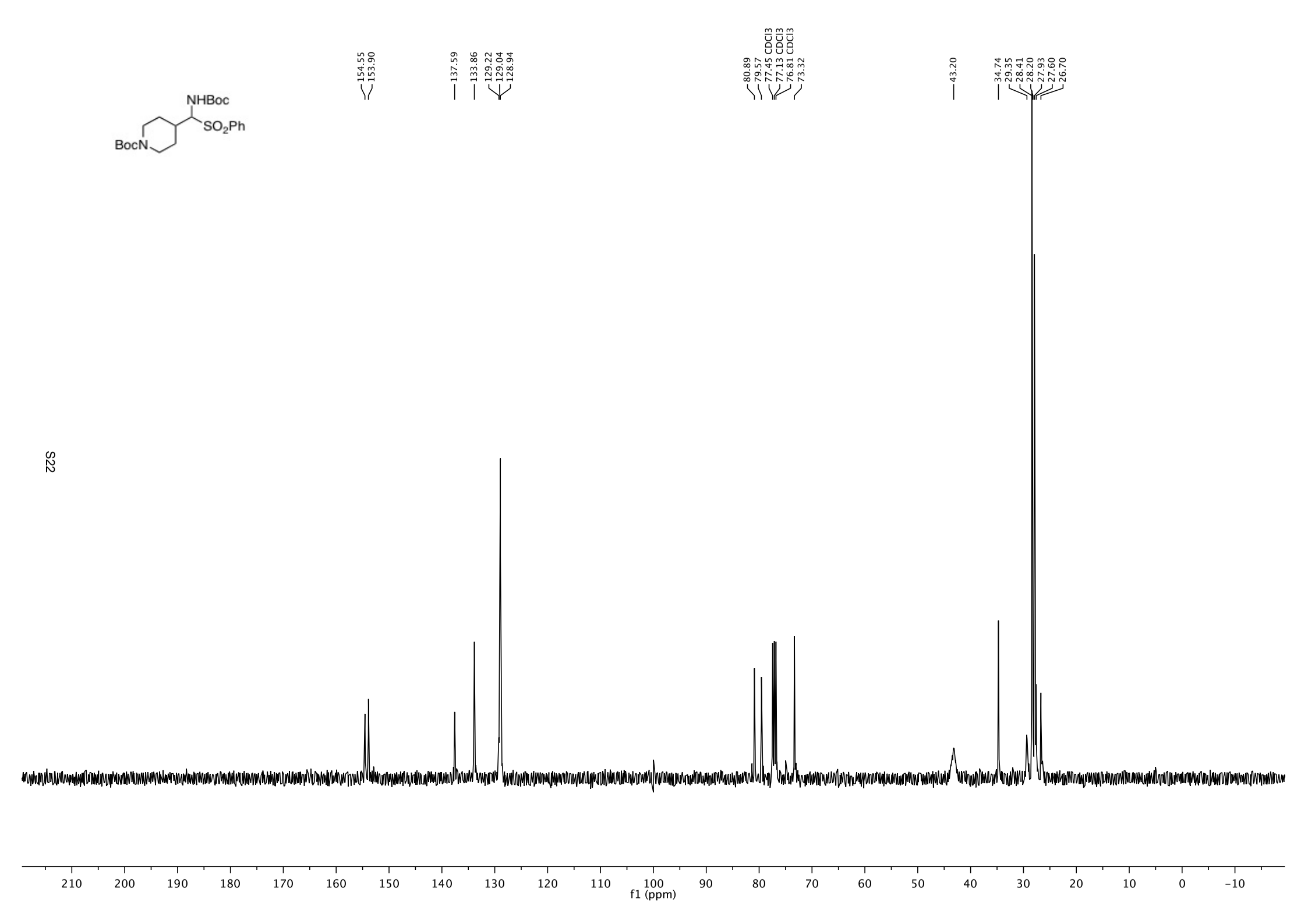


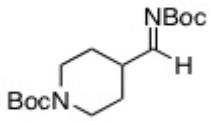
(5*S*,8*S*,9*R*,12*S*)-Methyl 12-benzyl-5,16,16-trimethyl-3,6,11,14-tetraoxo-1,9-diphenyl-2,15-dioxa-4,7,10,13-tetraazaheptadecane-8-carboxylate: Triethylamine (2.10 mL, 15.3 mmol, 3.0 equiv) and 1-hydroxybenzotriazole (1.03 g, 7.64 mmol, 1.5 equiv) were added to a 0 °C solution of the crude material obtained above (assumed to be 5.10 mmol, 1.0 equiv) and *N*-(*tert*-butoxycarbonyl)-L-phenylalanine (1.35 g, 5.10 mmol, 1.0 equiv) in dichloromethane (25 mL, 0.2 M). The reaction solution was stirred for 15 min, then N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (1.22 g, 6.37 mmol, 1.25 equiv) was added. After 20 hr, the reaction solution was washed with water (1 x 25 mL) and brine (1 x 25 mL), then dried with anhydrous sodium sulfate and concentrated *in vacuo* to yield a white solid. The crude material was purified by silica gel column chromatography (2/3 EtOAc/Hexanes) to yield the title product as a white solid (2.45 g, 3.79 mmol, 74% three-step yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.05 (m, 16H, Ar**H** and N**H**), 6.99 (s, 1H, N**H**), 5.57 (s, 1H, N**H**), 5.38 (s, 1H, N**H**), 5.31 (t, 6.2 Hz, 1H, C**H**CO_2Me) 5.20-5.00 (dd, 9.7 and 63.0 Hz, 2H, $CO_2C\mathbf{H_2}$Ph), 4.90 (t, 6.5 Hz, 1H, NC**H**RPh), 4.27 (m, 2H, C**H**CH_2Ph and C**H**CH_3), 3.53 (s, 3H, $CO_2C\mathbf{H_3}$), 3.05-2.90 (m, 2H, CHC$\mathbf{H_2}$Ph), 1.35 (br s, 12 H, CHC$\mathbf{H_3}$ and $CO_2C(C\mathbf{H_3})_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 172.0, 170.1, 156.4, 155.9, 137.3, 136.7, 136.2, 129.3, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2, 127.1, 126.9, 80.4, 67.3, 57.0, 56.3, 55.6, 52.5, 50.6, 38.0, 28.4, 18.1. IR (thin film, cm^{-1}) 3303, 2979, 1737, 1689, 1652, 1526, 1453, 1367, 1239, 1166, 1047, 738, 697, 641. $[\alpha]^{20}_{D}$ = -17.1 (1.0 c, $CHCl_3$). LRMS (APCI+) m/z = 647.00 calcd for $C_{35}H_{42}N_4O_8$ $[M+1]^+$ 647.30.


7.95
7.93
7.93
7.67
7.65
7.64
7.58
7.56
7.54
5.17
5.14
5.04
5.02
5.01
5.00
4.99
1.65
1.63
1.23
NHBoc
Me
SO2Ph
2.00
3.10
0.85
0.94
3.14
8.72
f1 (ppm)

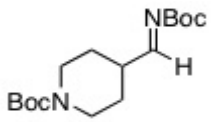

NHBoc
Me
SO2Ph
153.37
136.68
133.87
129.38
129.05
80.78
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
66.78
27.99
12.95
f1 (ppm)


7.90
7.88
7.88
7.64
7.64
7.63
7.62
7.56
7.54
7.53
7.52
7.28
7.27
5.13
5.10
4.79
4.78
4.77
4.76
4.19
2.80
2.77
2.66
2.65
2.63
2.63
2.62
2.61
2.60
2.59
2.11
2.08
1.77
1.73
1.48
1.46
1.44
1.23
1.21
NHBoc
SO2Ph
BocN
S21
2.00
3.07
0.89
0.88
1.93
2.05
1.10
1.05
1.10
10.82
1.31
8.08
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)


NHBoc
SO2Ph
BocN
154.55
153.90
137.59
133.86
129.22
129.04
128.94
80.89
79.57
77.45 CDCl3
77.13 CDCl3
76.81 CDCl3
73.32
43.20
34.74
29.35
28.41
28.20
27.93
27.60
26.70
S22
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

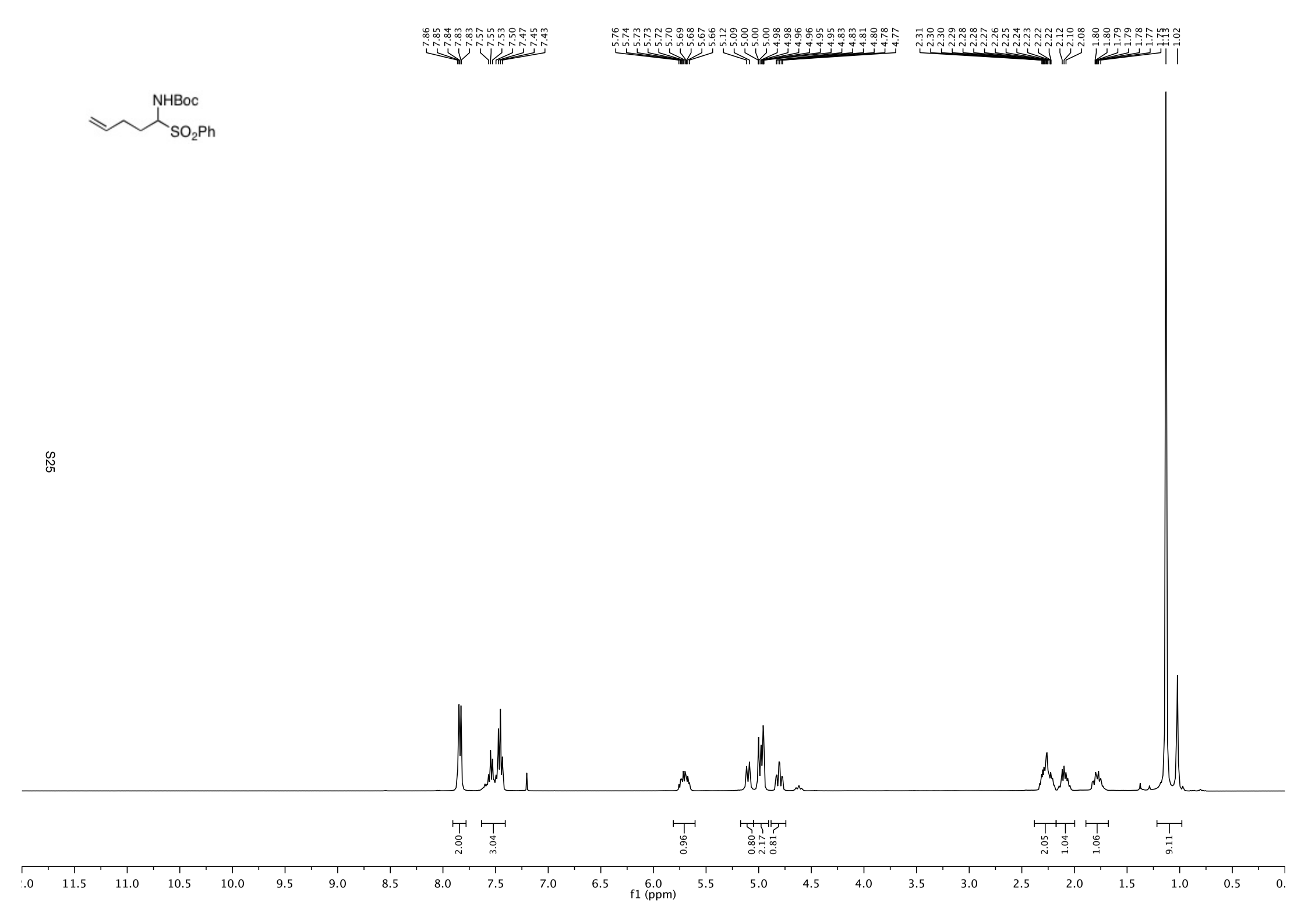

NBoc
H
BocN

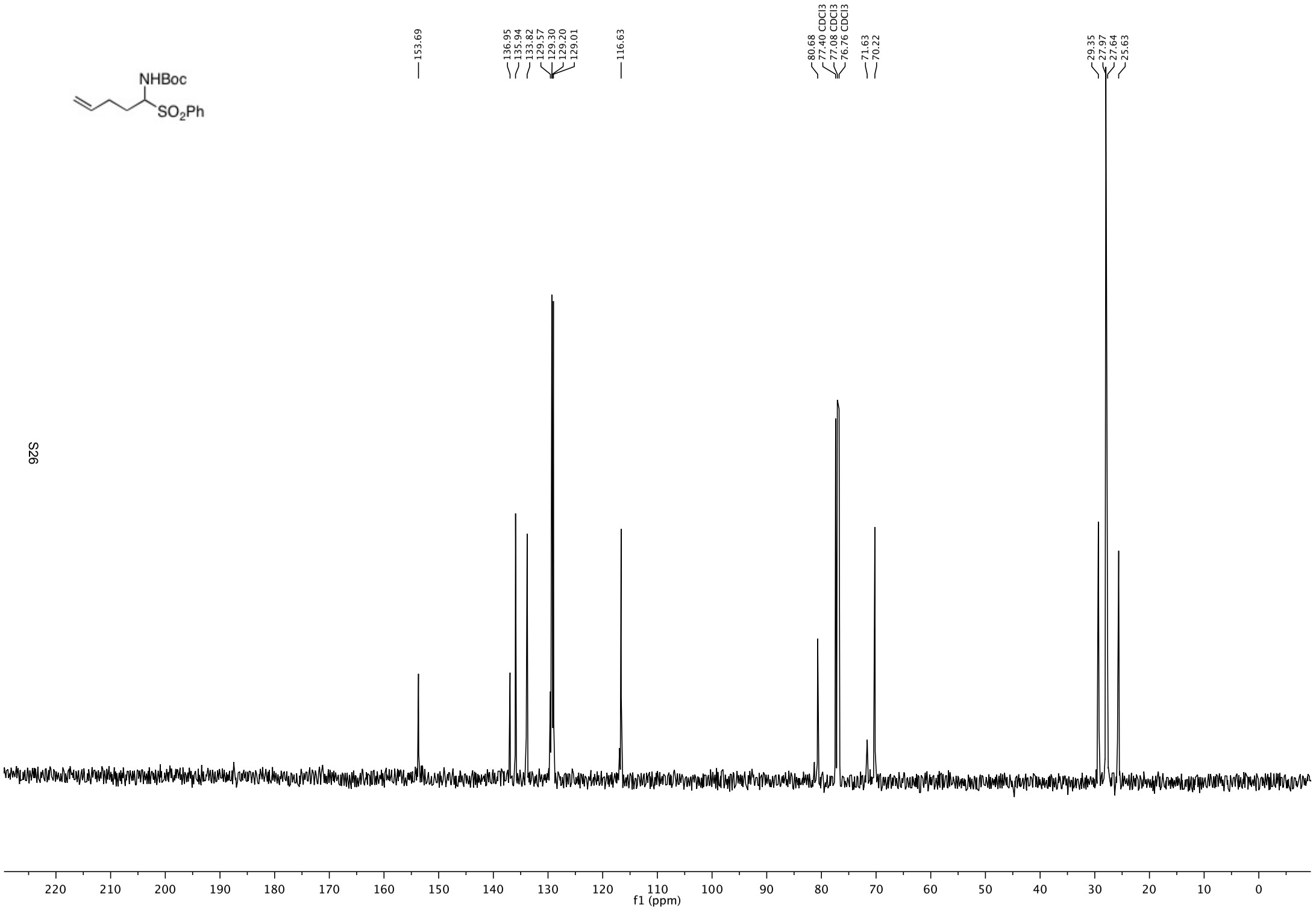
8.14
4.10
4.09
4.08
4.05
2.83
2.80
2.77
2.44
2.43
2.43
2.42
2.41
1.85
1.84
1.82
1.81
1.50
1.49
1.42
1.41
1.00
2.24
2.13
1.10
2.19
11.69
11.08
f1 (ppm)

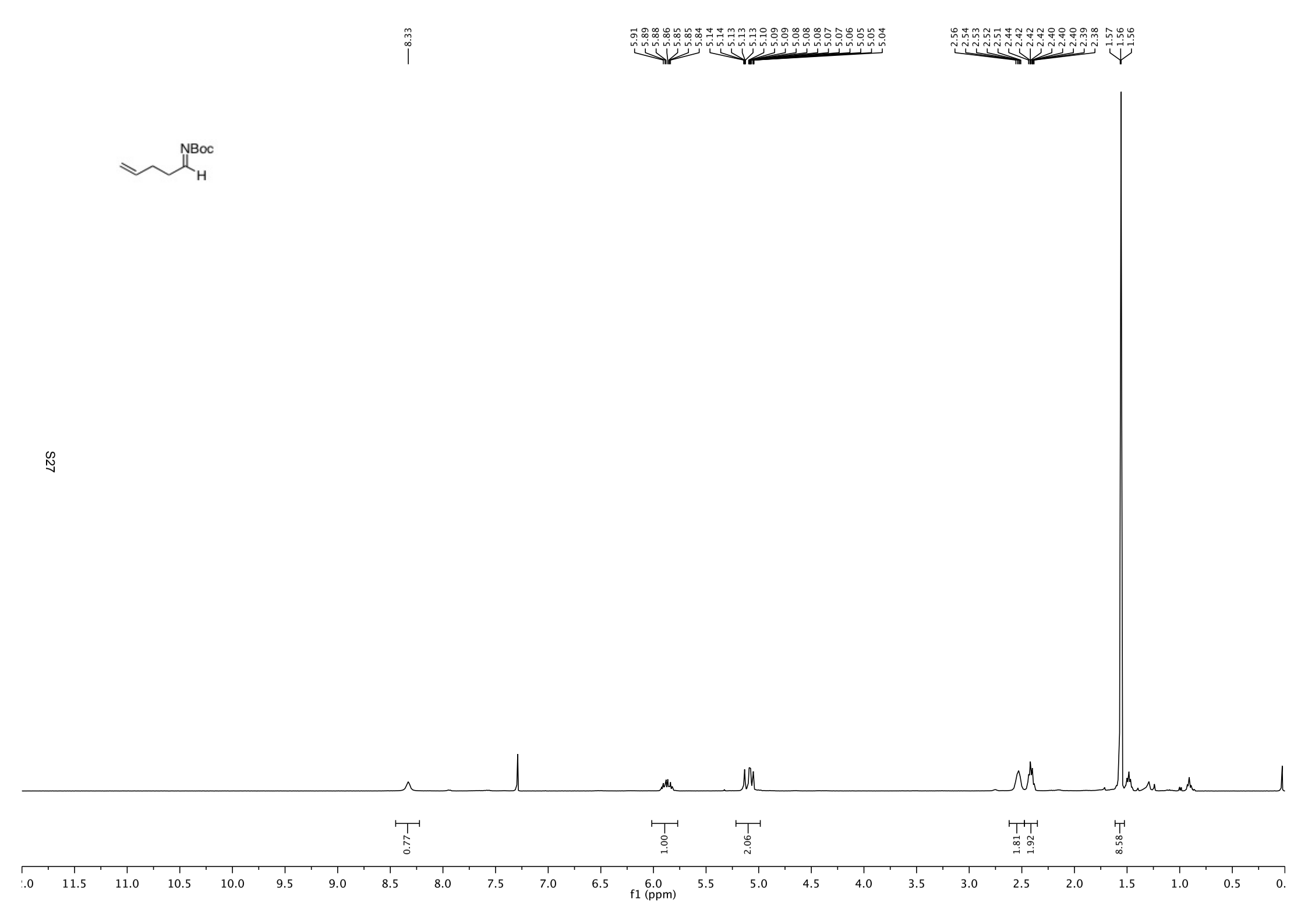


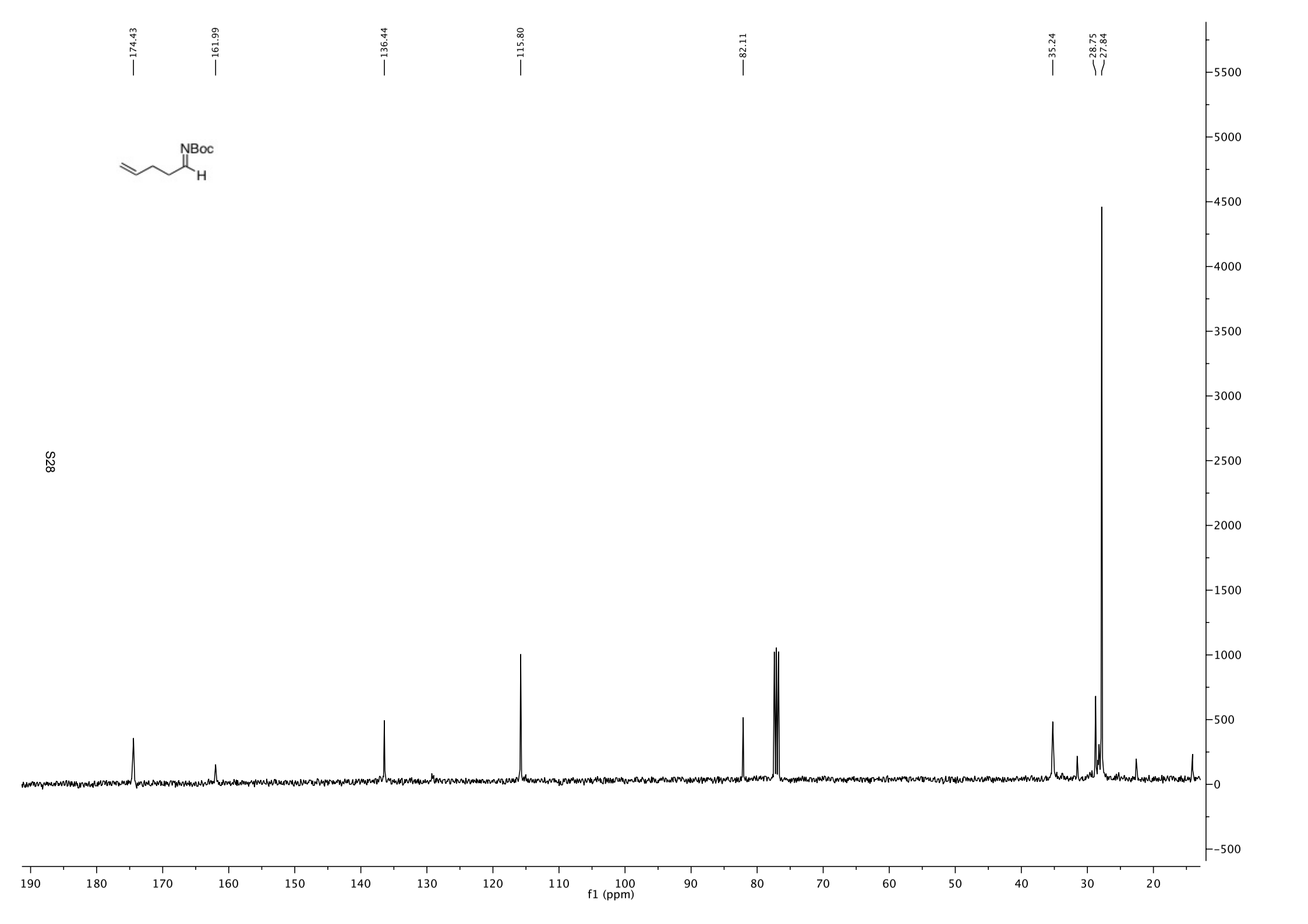
175.88
162.06
154.58
82.32
79.53
77.40 CDCl3
77.08 CDCl3
76.76 CDCl3
43.03
41.74
28.38
28.30
27.81
27.60

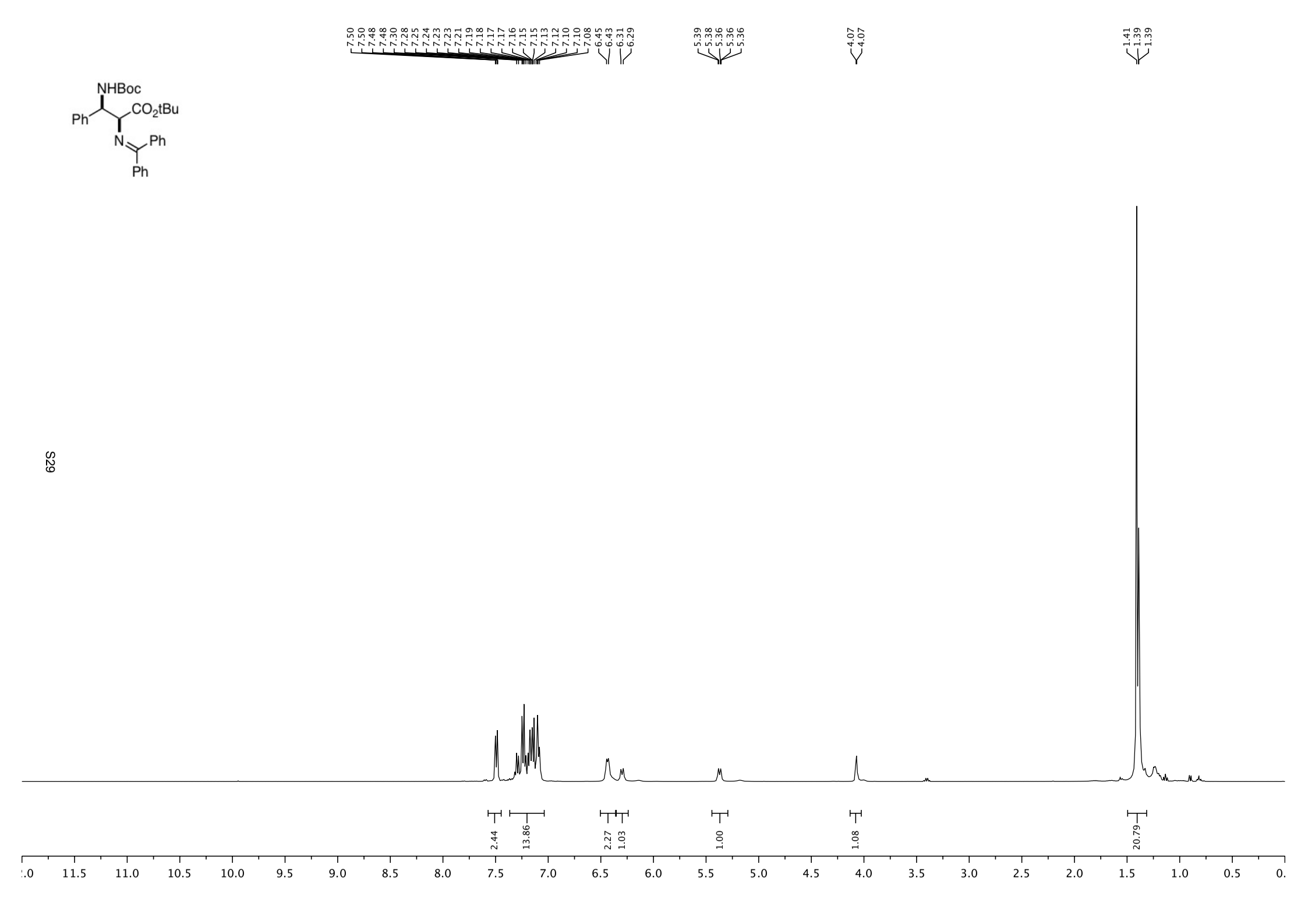
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

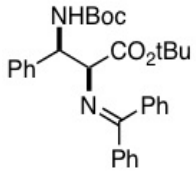

NHBoc
SO2Ph
7.86
7.85
7.84
7.83
7.83
7.57
7.55
7.53
7.50
7.47
7.45
7.43
5.76
5.74
5.73
5.73
5.72
5.70
5.69
5.68
5.67
5.66
5.12
5.09
5.00
5.00
5.00
4.98
4.98
4.96
4.96
4.95
4.95
4.83
4.81
4.80
4.78
4.77
2.31
2.30
2.30
2.29
2.28
2.28
2.27
2.26
2.25
2.24
2.23
2.22
2.22
2.12
2.10
2.08
1.80
1.80
1.79
1.79
1.78
1.77
1.02
2.00
3.04
0.96
0.80
2.17
0.81
2.05
1.04
1.06
9.11
f1 (ppm)


NHBoc
SO2Ph
153.69
136.95
135.94
133.82
129.57
129.30
129.20
129.01
116.63
80.68
77.40 CDCl3
77.08 CDCl3
76.76 CDCl3
71.63
70.22
29.35
27.97
27.64
25.63
S26
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.33
5.91
5.89
5.88
5.86
5.85
5.85
5.84
5.14
5.13
5.13
5.13
5.10
5.09
5.09
5.08
5.08
5.08
5.07
5.07
5.06
5.05
5.05
5.04
2.56
2.54
2.53
2.52
2.51
2.44
2.42
2.42
2.42
2.40
2.40
2.40
2.39
2.38
1.57
1.56
1.56
NBoc
H
S27
0.77
1.00
2.06
1.81
1.92
8.58
f1 (ppm)

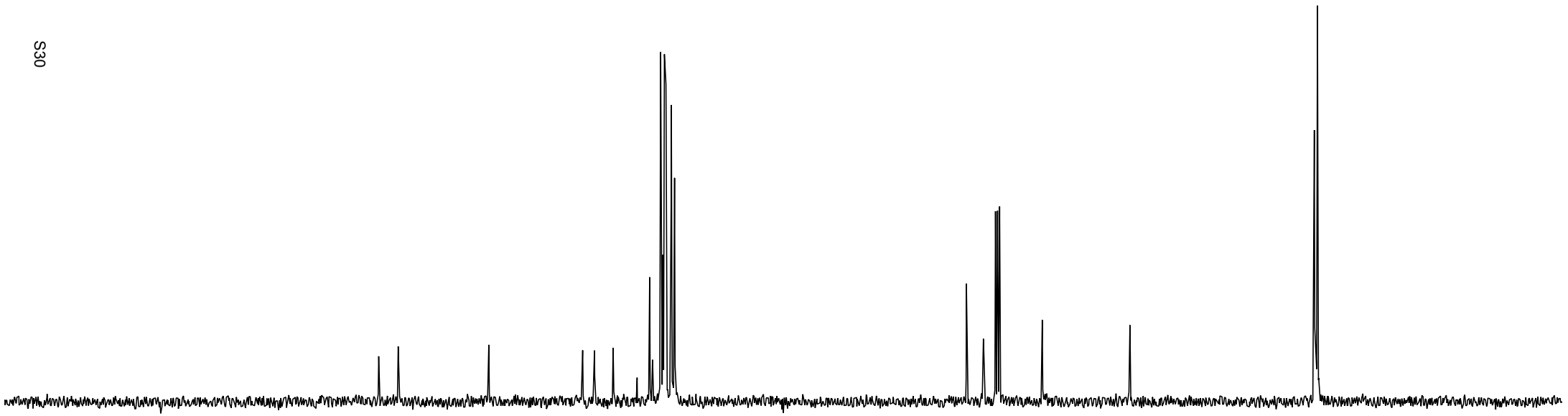

174.43
161.99
136.44
115.80
82.11
35.24
28.75
27.84
NBoc
H
S28
f1 (ppm)


7.50
7.50
7.48
7.48
7.30
7.28
7.25
7.24
7.23
7.23
7.21
7.19
7.18
7.17
7.17
7.16
7.15
7.15
7.13
7.12
7.10
7.10
7.08
6.45
6.43
6.31
6.29
5.39
5.38
5.36
5.36
5.36
4.07
4.07
1.41
1.39
1.39
NHBoc
CO2tBu
Ph
N
Ph
Ph
S29
2.44
13.86
2.27
1.03
1.00
1.08
20.79
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



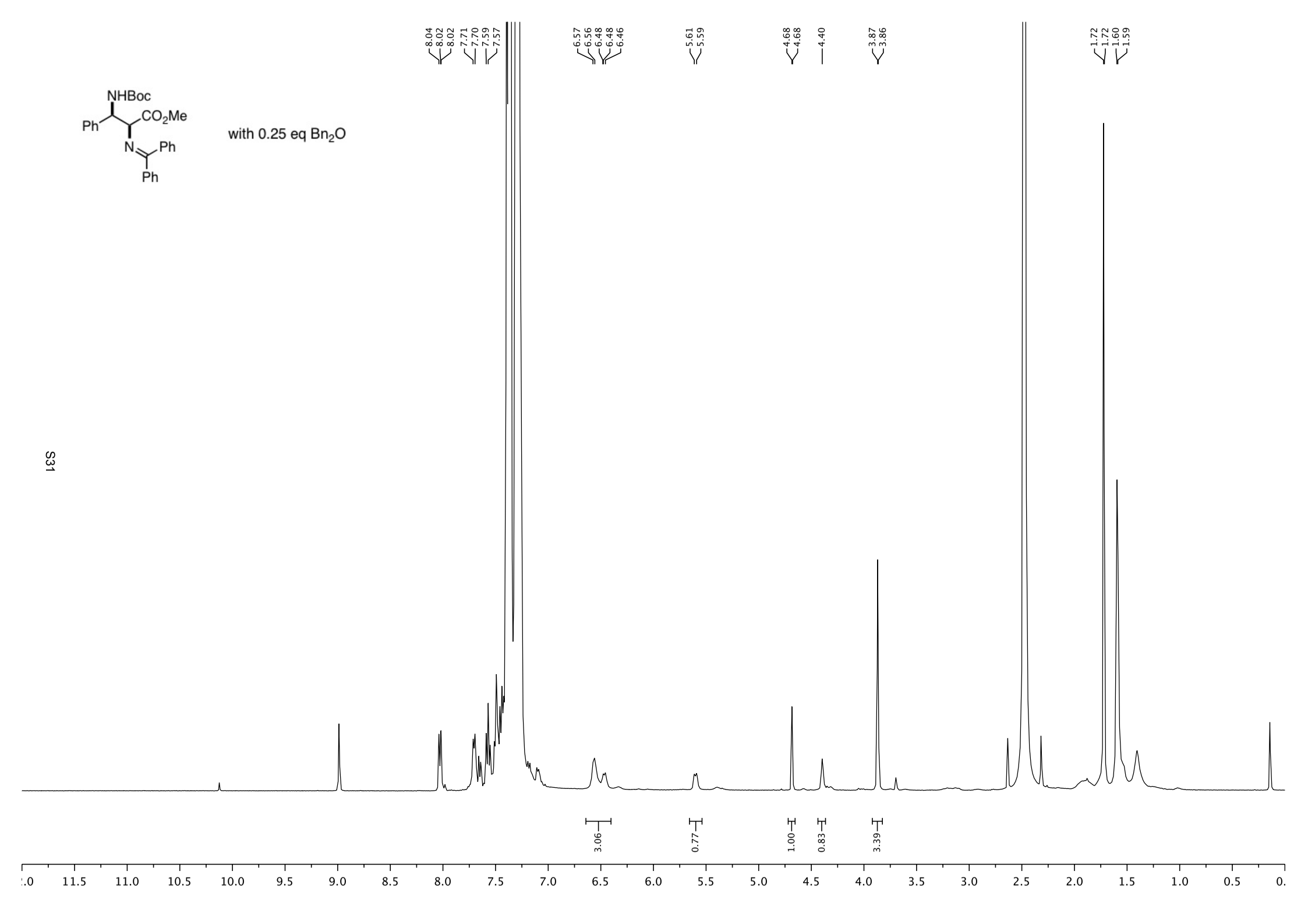
172.15
169.16
155.25
140.84
139.02
136.17
130.55
130.12
128.87
128.53
128.35
128.30
128.21
128.06
127.23
127.02
126.73
81.94
79.32
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
70.29
56.83
28.53
28.43
28.05

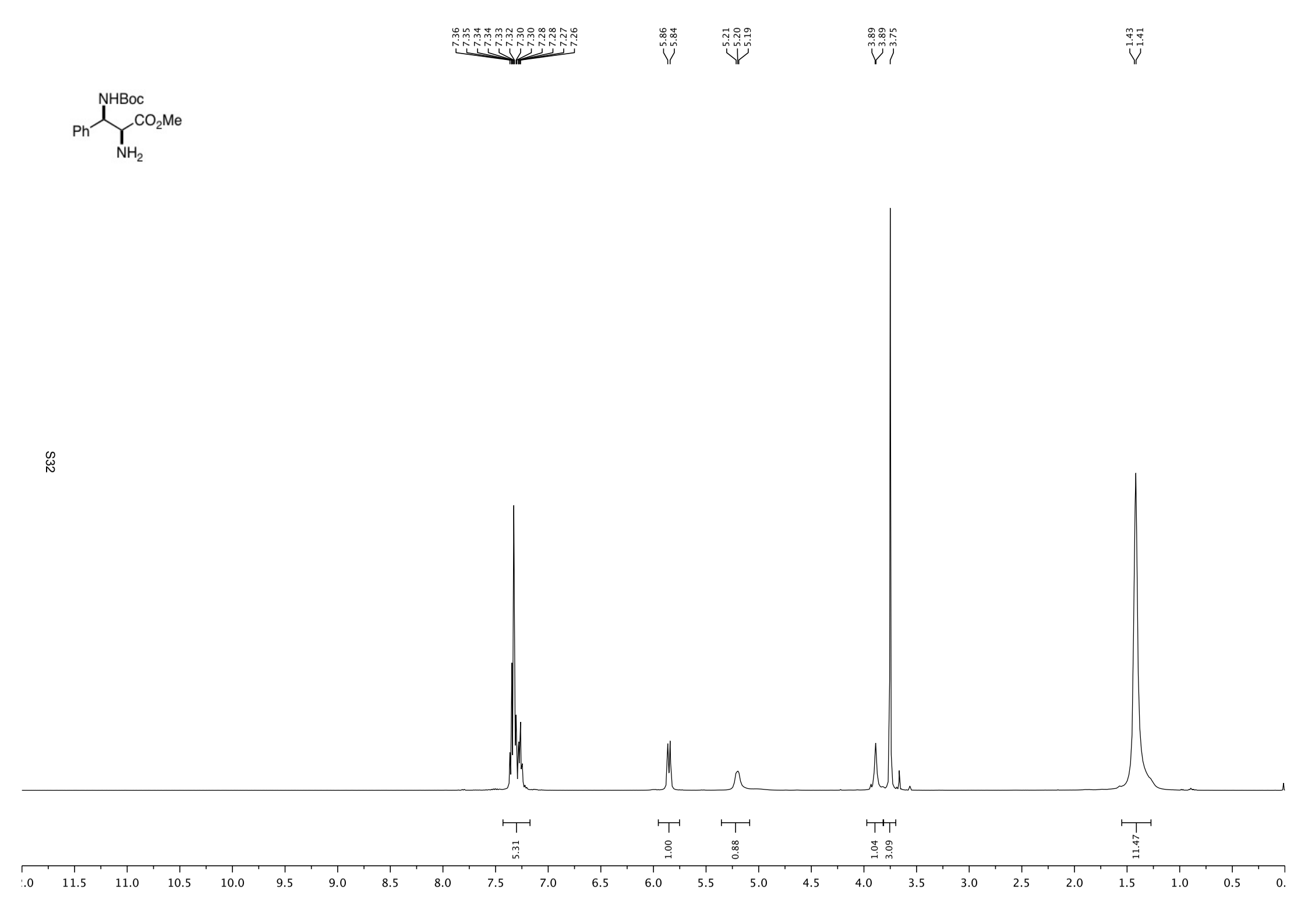
S30

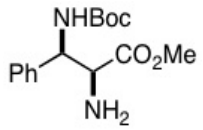


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

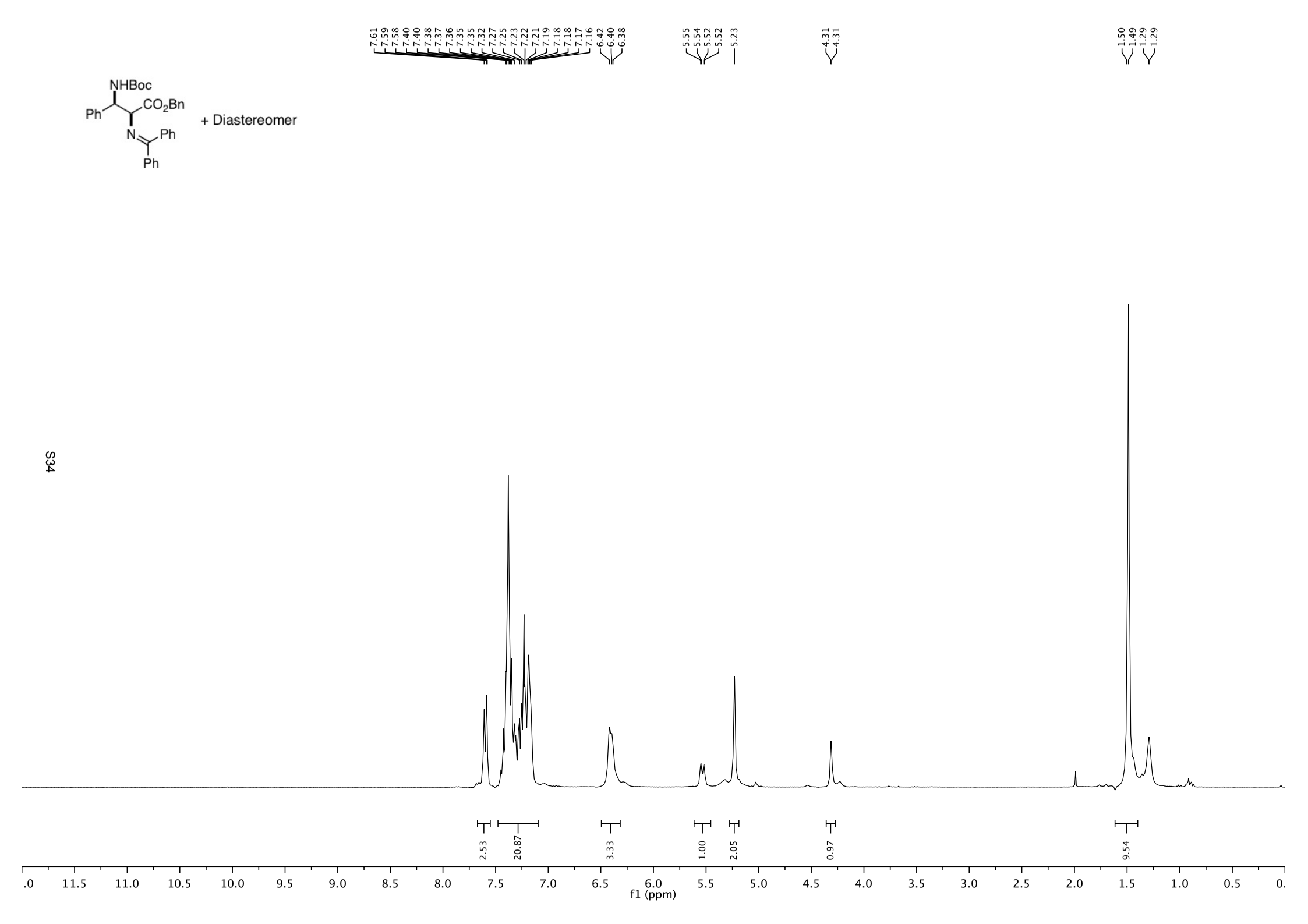

NHBoc
Ph
CO2Me
N
Ph
Ph
with 0.25 eq Bn2O
8.04
8.02
8.02
7.71
7.70
7.59
7.57
6.57
6.56
6.48
6.48
6.46
5.61
5.59
4.68
4.68
4.40
3.87
3.86
1.72
1.72
1.60
1.59
3.06
0.77
1.00
0.83
3.39
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


7.36
7.35
7.34
7.34
7.33
7.32
7.30
7.30
7.28
7.28
7.27
7.26
5.86
5.84
5.21
5.20
5.19
3.89
3.89
3.75
1.43
1.41
NHBoc
Ph
CO2Me
NH2
S32
5.31
1.00
0.88
1.04
3.09
11.47
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5



173.00
155.27
139.92
128.56
127.45
126.38
79.49
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
58.55
56.35
52.36
28.28

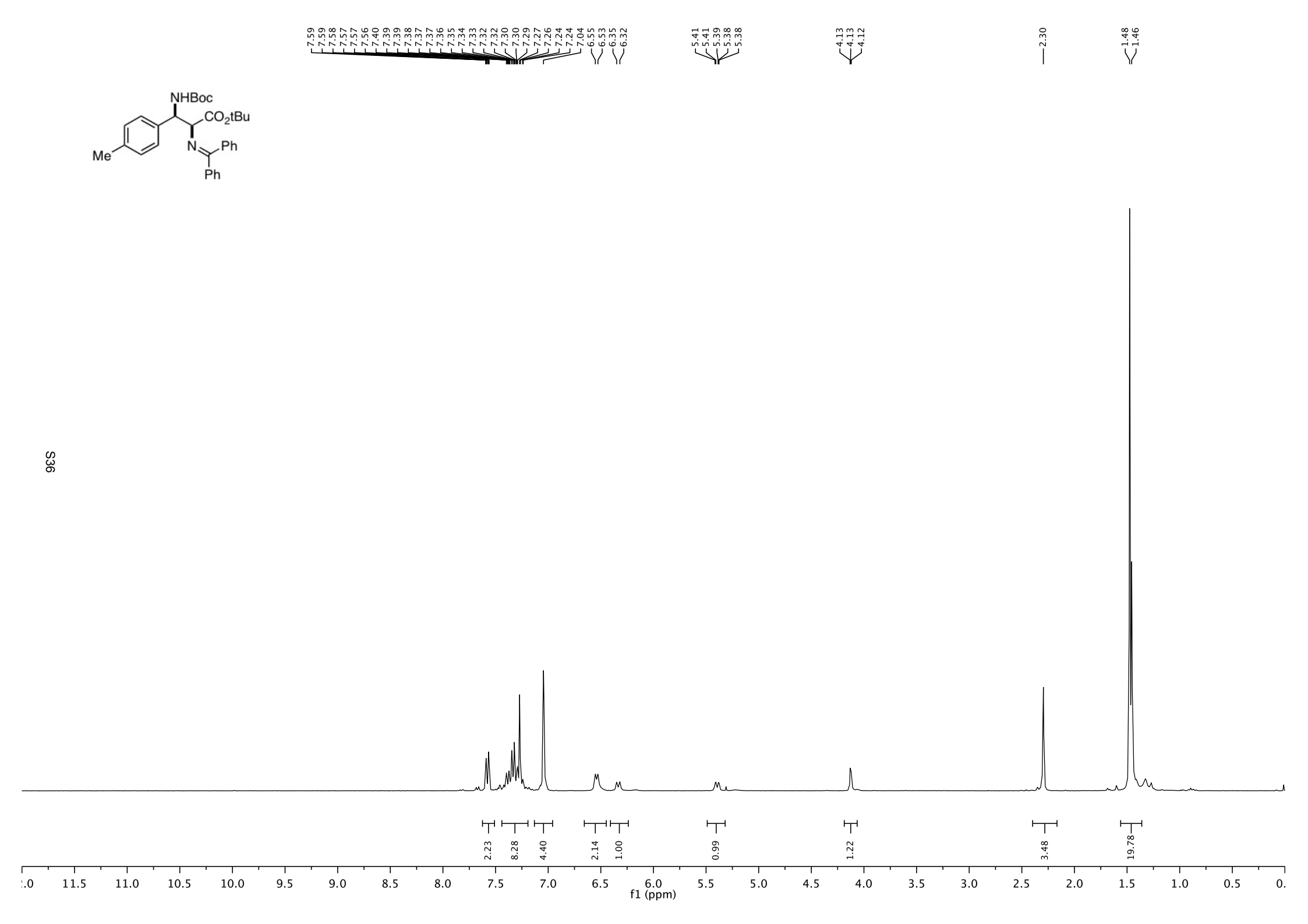
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

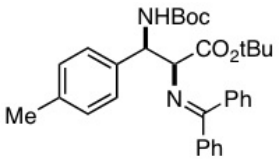

NHBoc
Ph
CO2Bn
N
Ph
Ph
+ Diastereomer
7.61
7.59
7.58
7.40
7.40
7.38
7.37
7.36
7.35
7.35
7.32
7.27
7.25
7.23
7.22
7.21
7.19
7.18
7.18
7.17
7.16
6.42
6.40
6.38
5.55
5.54
5.52
5.52
5.23
4.31
4.31
1.50
1.49
1.29
1.29
S34
2.53
20.87
3.33
1.00
2.05
0.97
9.54
f1 (ppm)

+ Diastereomer

72.82
69.89
155.32
140.54
138.88
135.84
135.76
130.75
128.96
128.65
128.62
128.34
128.31
128.16
128.14
127.18
126.71
79.57
77.44 CDCl3
77.41 CDCl3
77.18 CDCl3
77.16 CDCl3
76.93 CDCl3
76.90 CDCl3
69.81
67.08
56.76
28.52

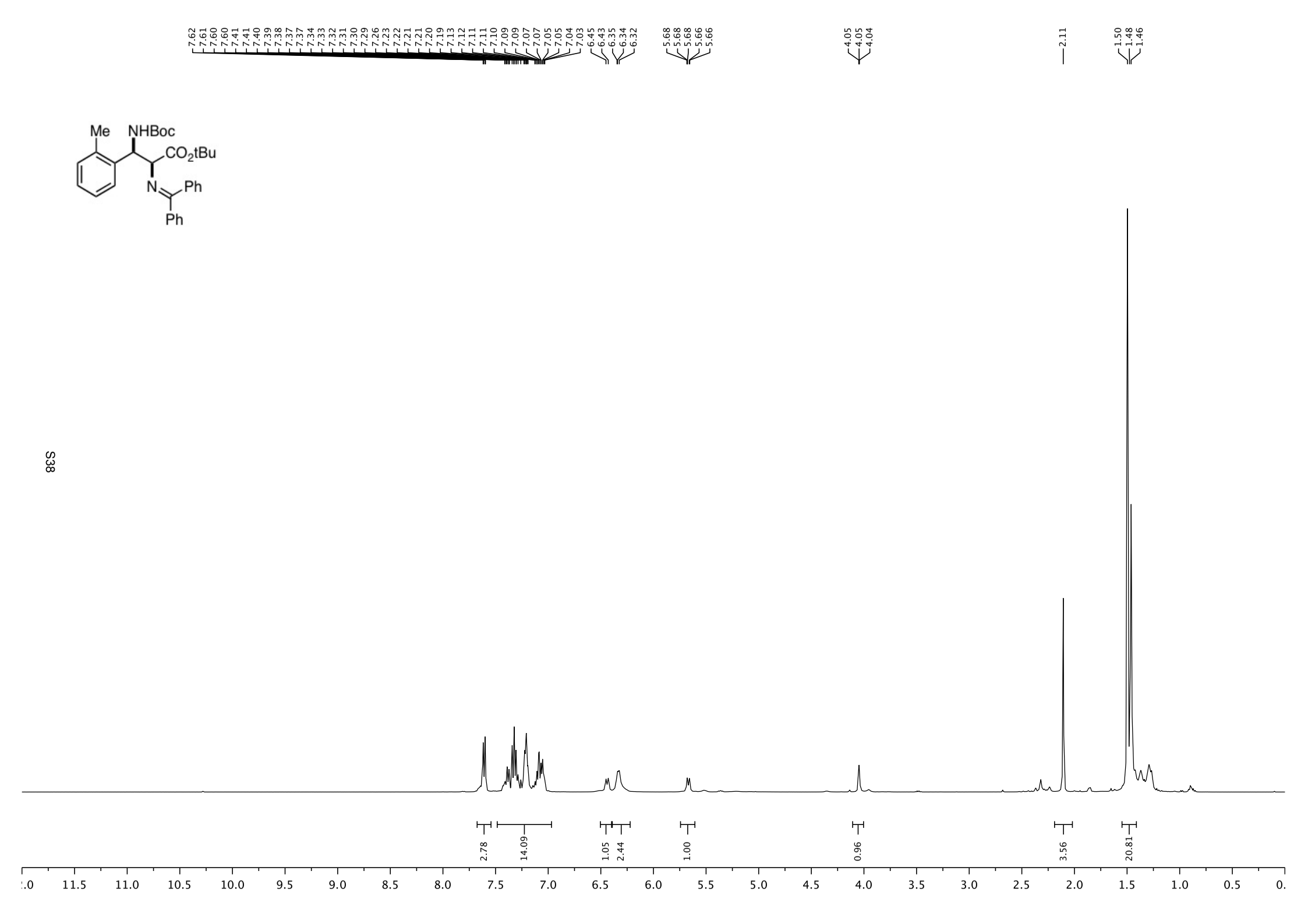
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

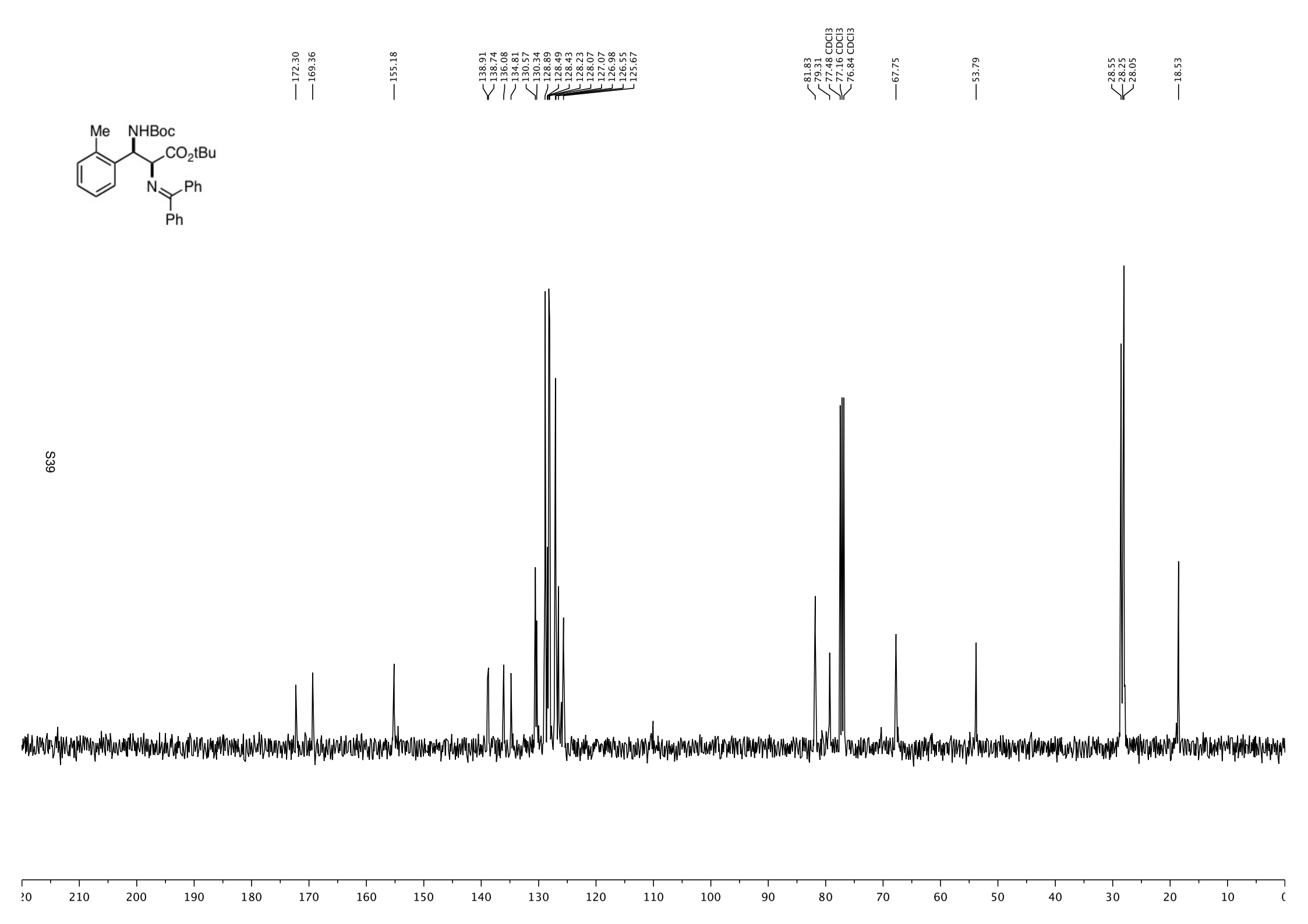

7.59
7.59
7.58
7.57
7.57
7.56
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.35
7.34
7.33
7.32
7.32
7.30
7.30
7.29
7.27
7.26
7.24
7.24
7.04
6.55
6.53
6.35
6.32
5.41
5.41
5.39
5.38
5.38
4.13
4.13
4.12
2.30
1.48
1.46
NHBoc
CO2tBu
N
Ph
Ph
Me
S36
2.23
8.28
4.40
2.14
1.00
0.99
1.22
3.48
19.78
f1 (ppm)



172.04
169.27
155.24
139.11
137.87
136.48
136.25
130.54
128.90
128.84
128.70
128.52
128.31
128.07
127.81
127.30
126.65
81.89
79.25
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
70.30
56.61
28.55
28.21
28.06
21.13

S37


7.62
7.61
7.60
7.60
7.41
7.41
7.40
7.39
7.38
7.37
7.37
7.34
7.33
7.32
7.31
7.30
7.29
7.26
7.23
7.22
7.21
7.21
7.20
7.19
7.13
7.12
7.11
7.11
7.10
7.09
7.09
7.07
7.07
7.05
7.05
7.04
7.03
6.45
6.43
6.35
6.34
6.32
5.68
5.68
5.68
5.66
5.66
4.05
4.05
4.04
2.11
1.50
1.48
1.46
Me
NHBoc
CO2tBu
N
Ph
Ph
S38
2.78
14.09
1.05
2.44
1.00
0.96
3.56
20.81
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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77.16 CDCl3
76.84 CDCl3
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18.53
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CO2tBu
N
Ph
Ph
S39
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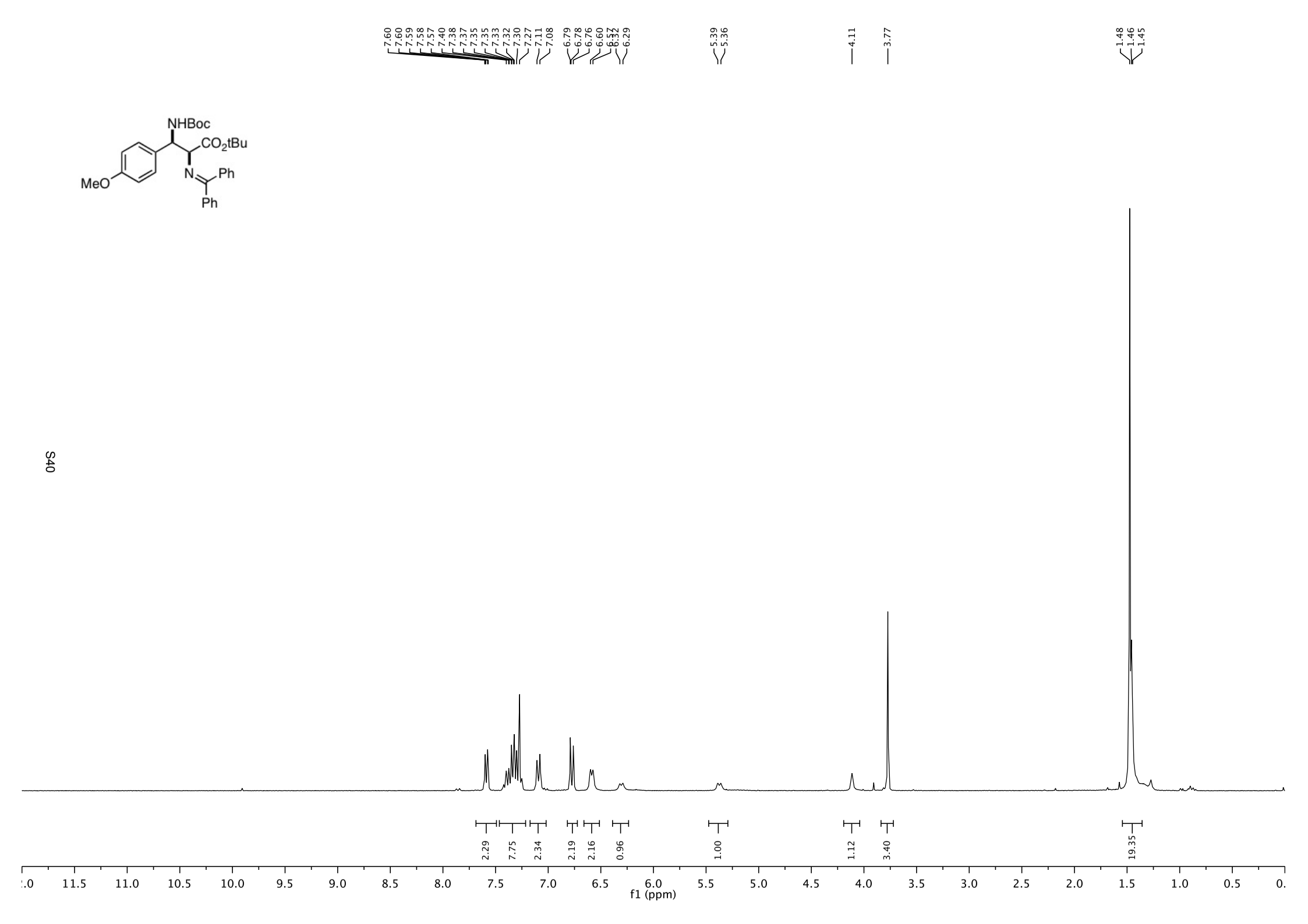
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CO2tBu
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Ph
Ph
MeO
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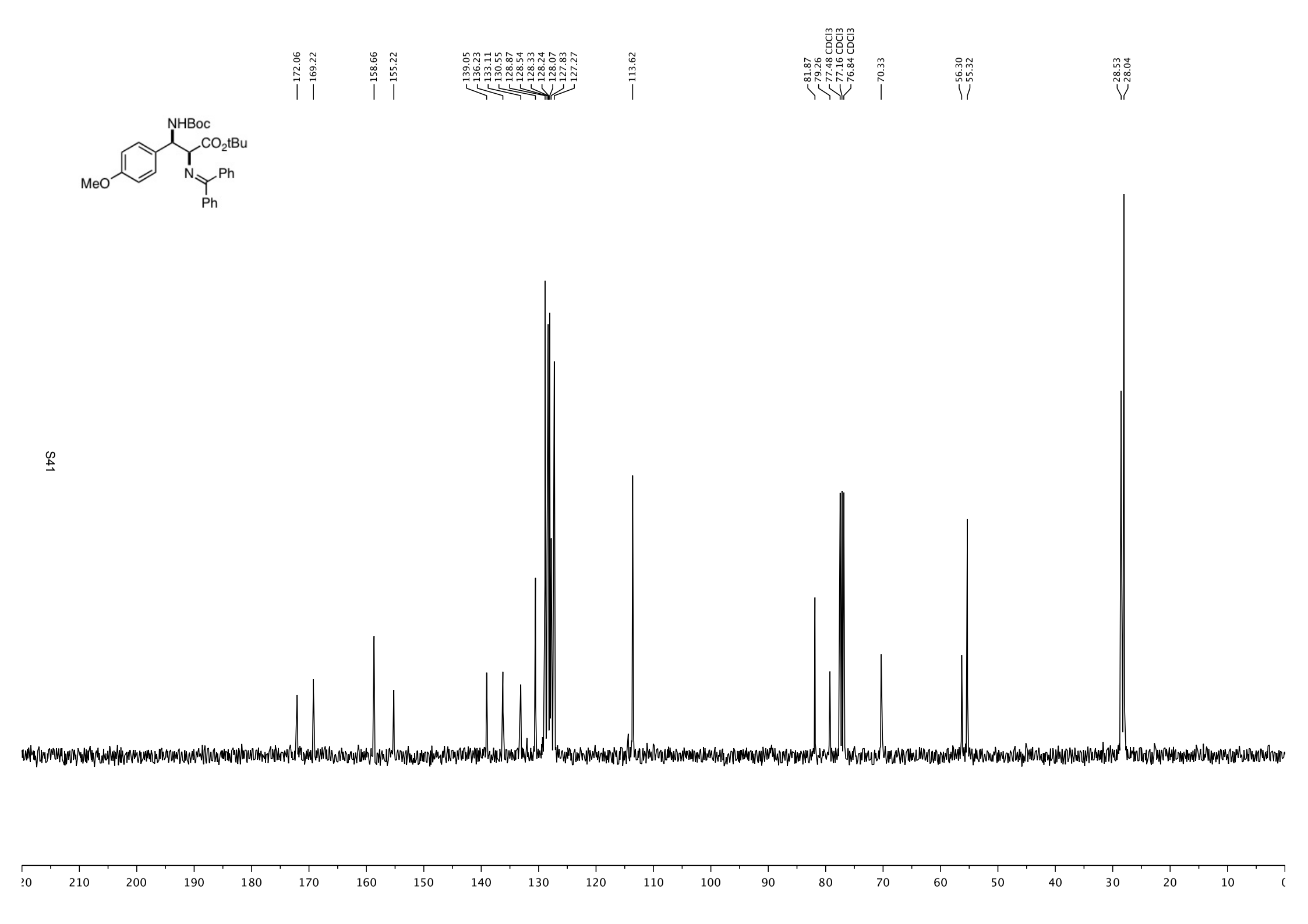
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77.16 CDCl3
76.84 CDCl3
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56.30
55.32
28.53
28.04
NHBoc
CO2tBu
N
Ph
Ph
MeO
S41
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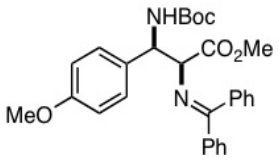
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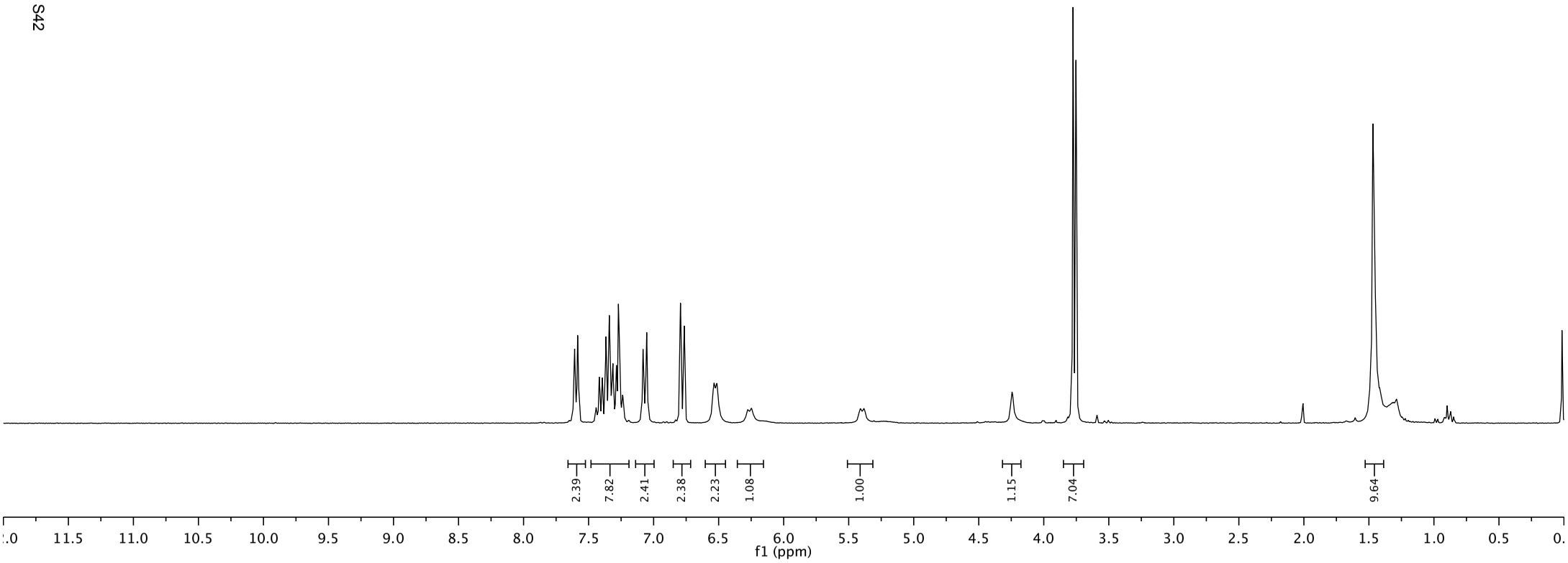
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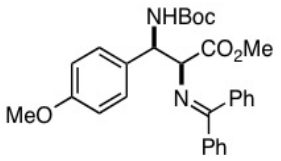

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28.23
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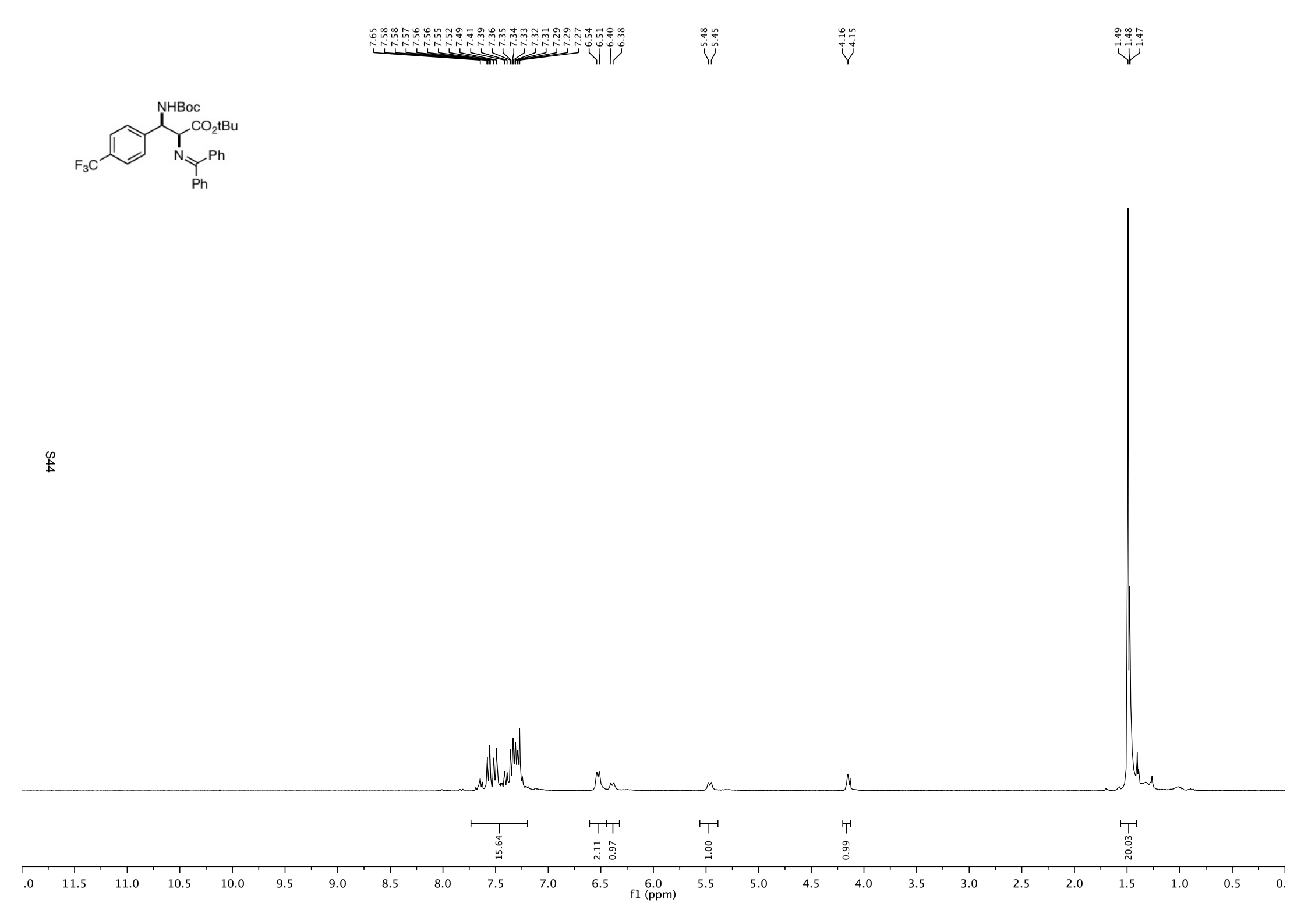
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1.49
1.48
1.47
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Ph
Ph
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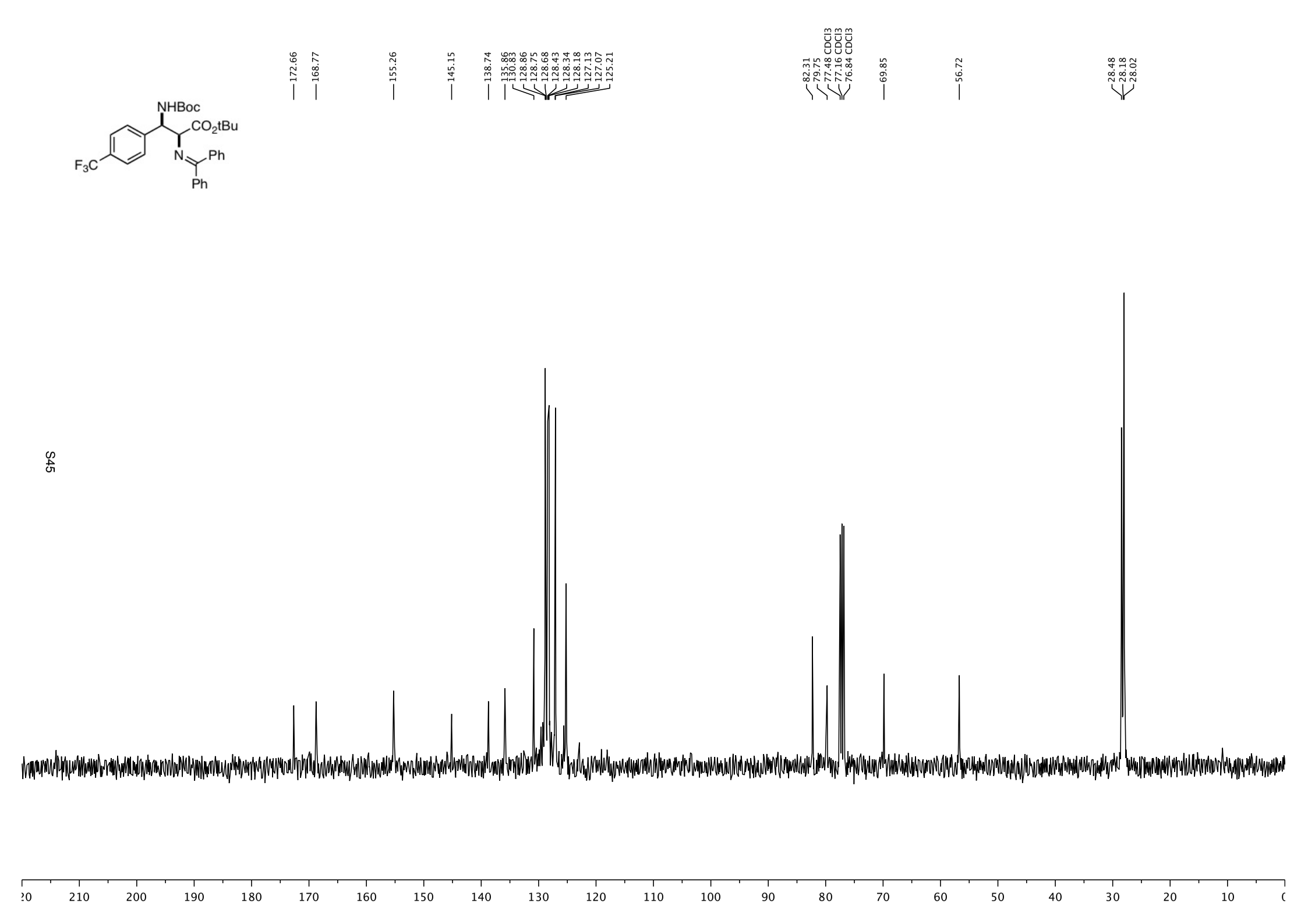
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Ph
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128.18
127.13
127.07
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79.75
77.48 CDCl3
77.16 CDCl3
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69.85
56.72
28.48
28.18
28.02
S45
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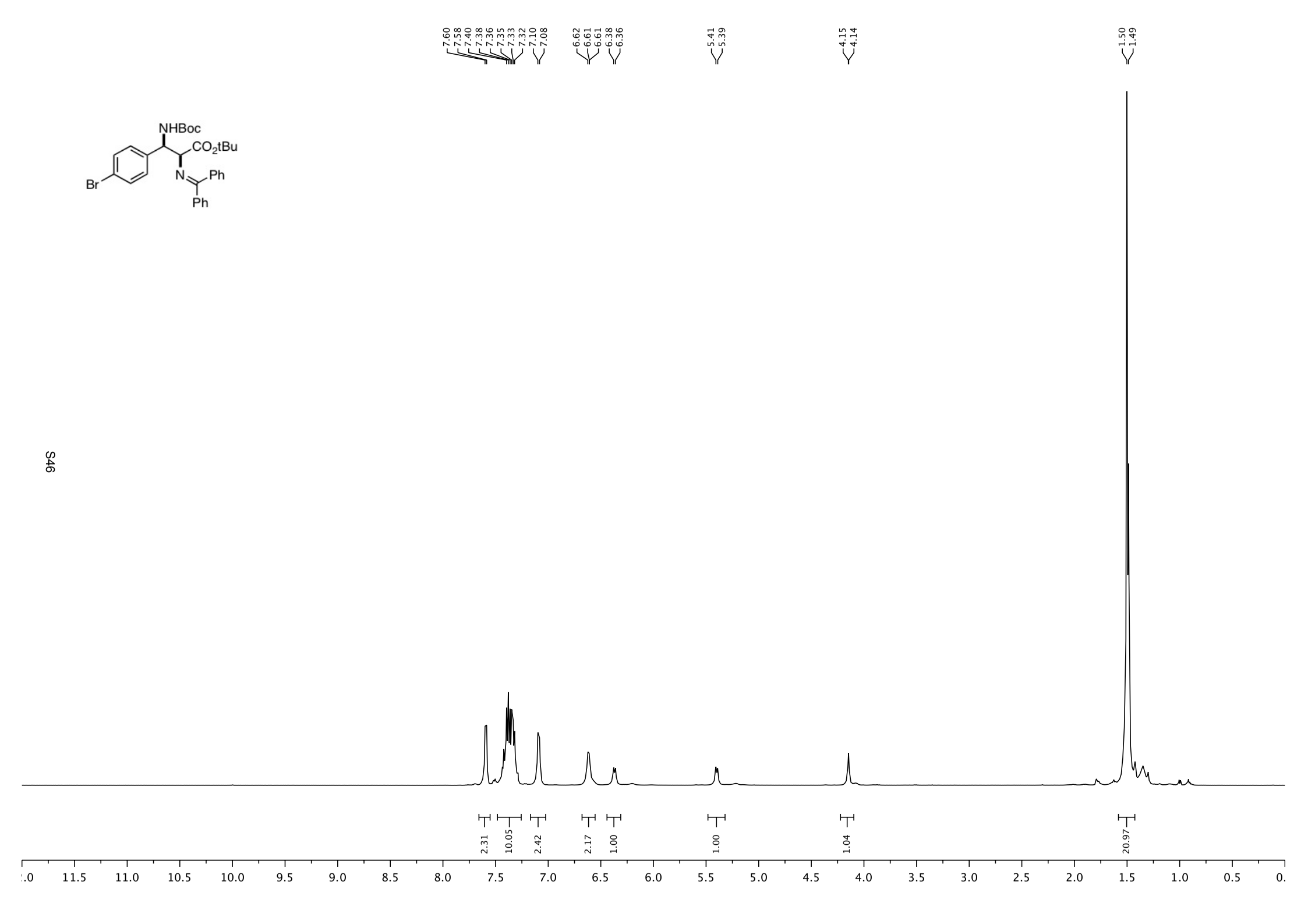
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6.36
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1.50
1.49
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CO2tBu
N
Ph
Ph
Br
2.31
10.05
2.42
2.17
1.00
1.00
1.04
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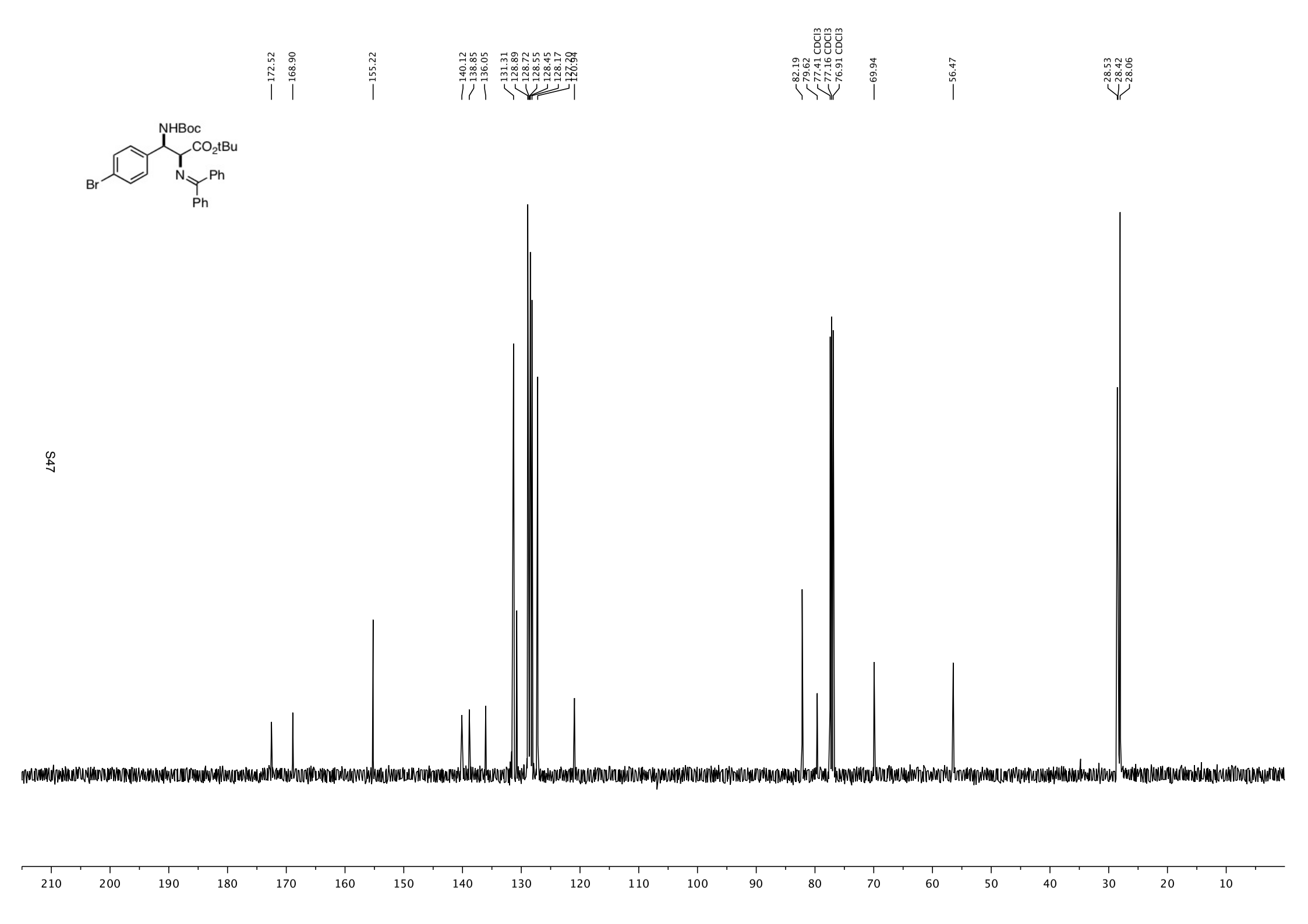
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CO2tBu
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Ph
Ph
Br
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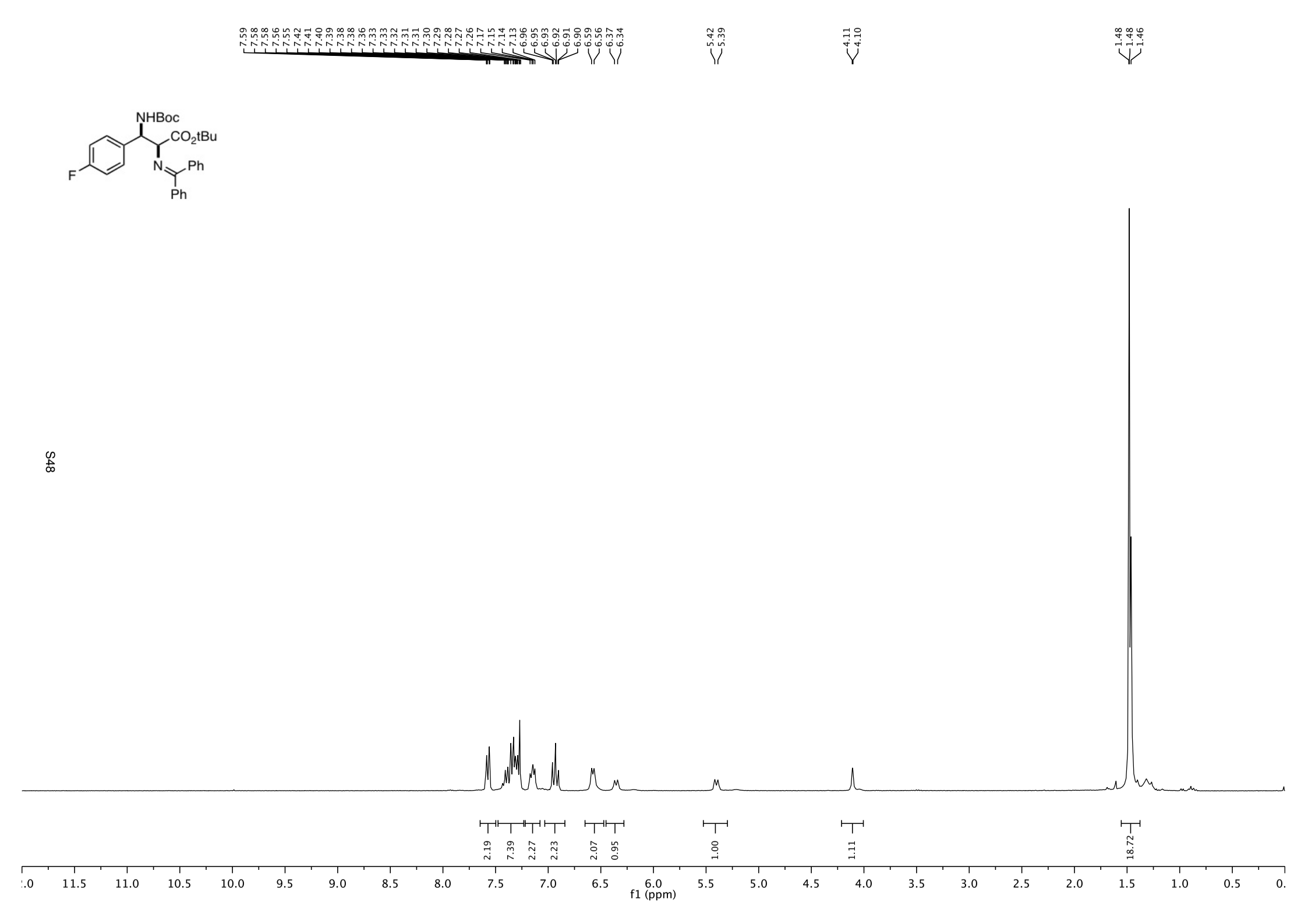
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5.42
5.39
4.11
4.10
1.48
1.48
1.46
NHBoc
CO2tBu
F
N
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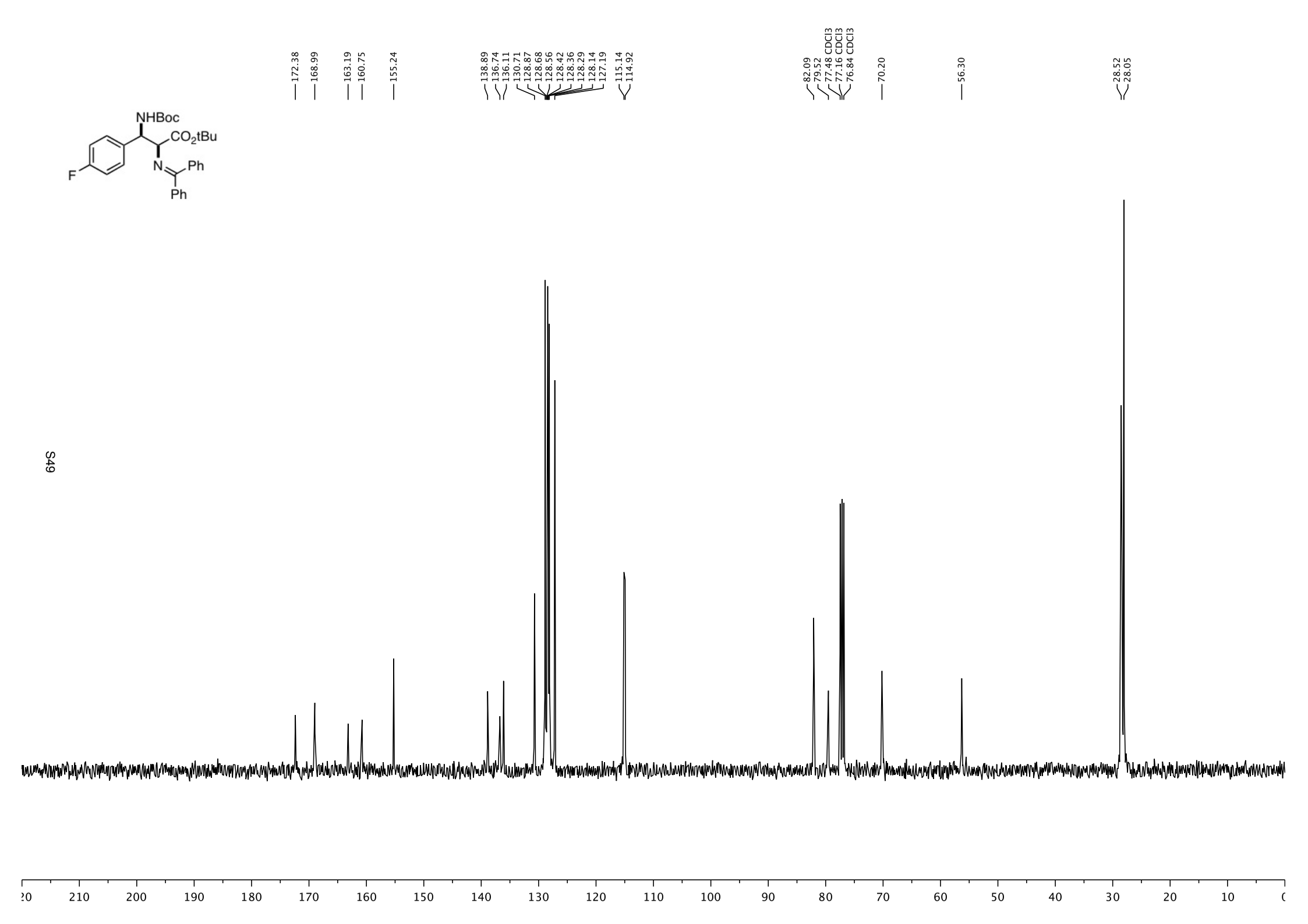
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127.19
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114.92
82.09
79.52
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77.16 CDCl3
76.84 CDCl3
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56.30
28.52
28.05
NHBoc
CO2tBu
F
N
Ph
Ph
S49
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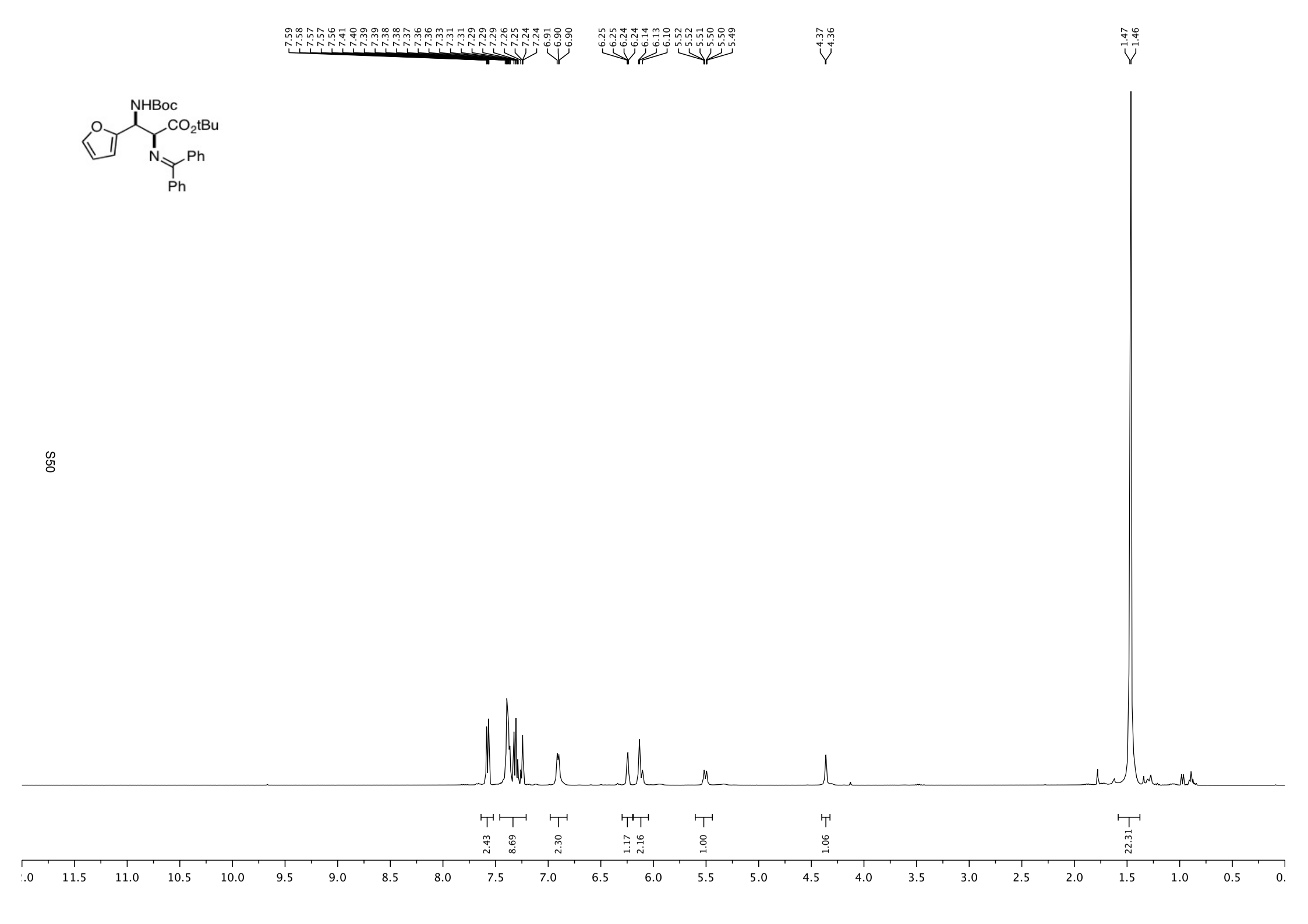
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4.36
1.47
1.46
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CO2tBu
O
N
Ph
Ph
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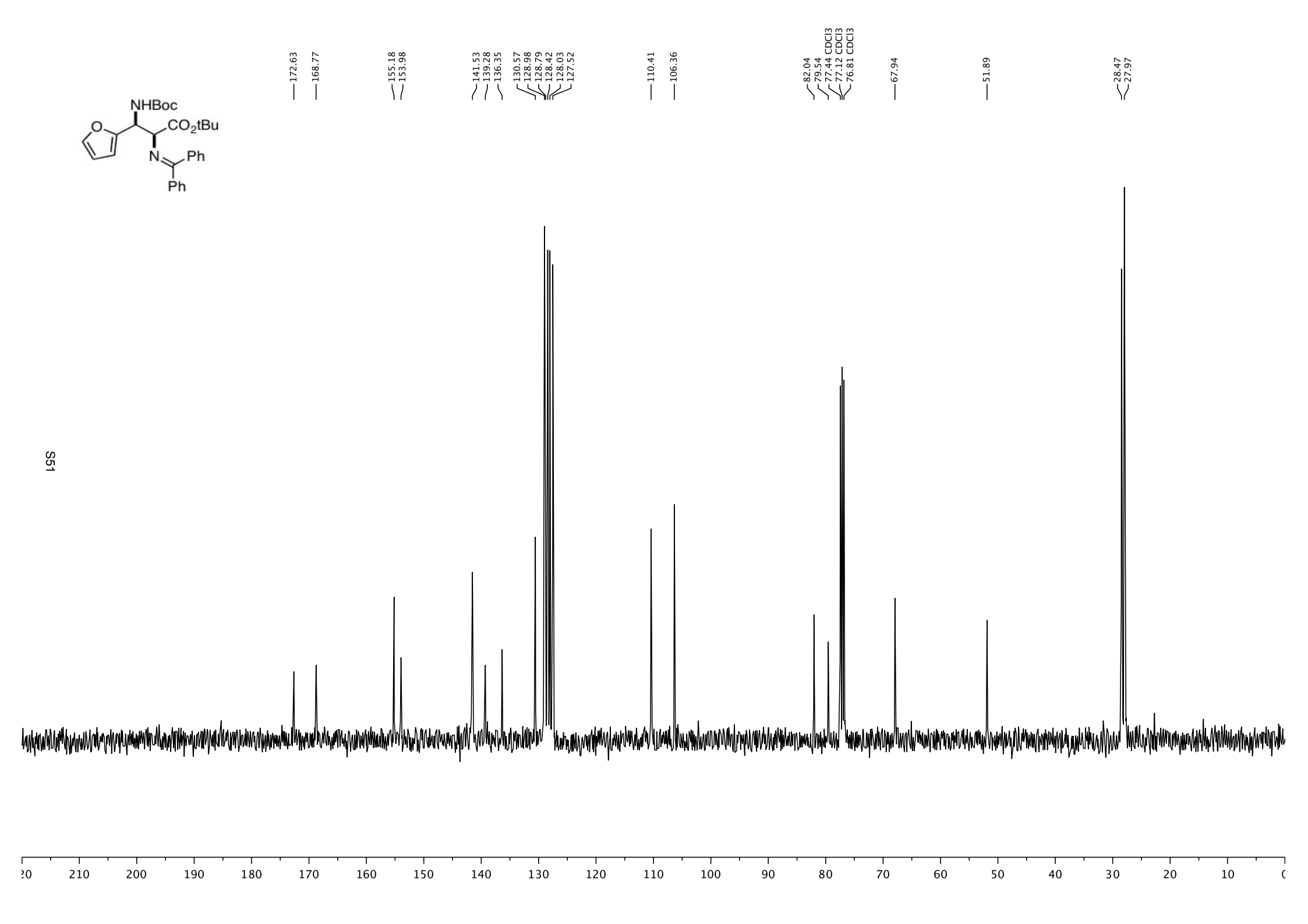
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77.12 CDCl3
76.81 CDCl3
67.94
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27.97
S51
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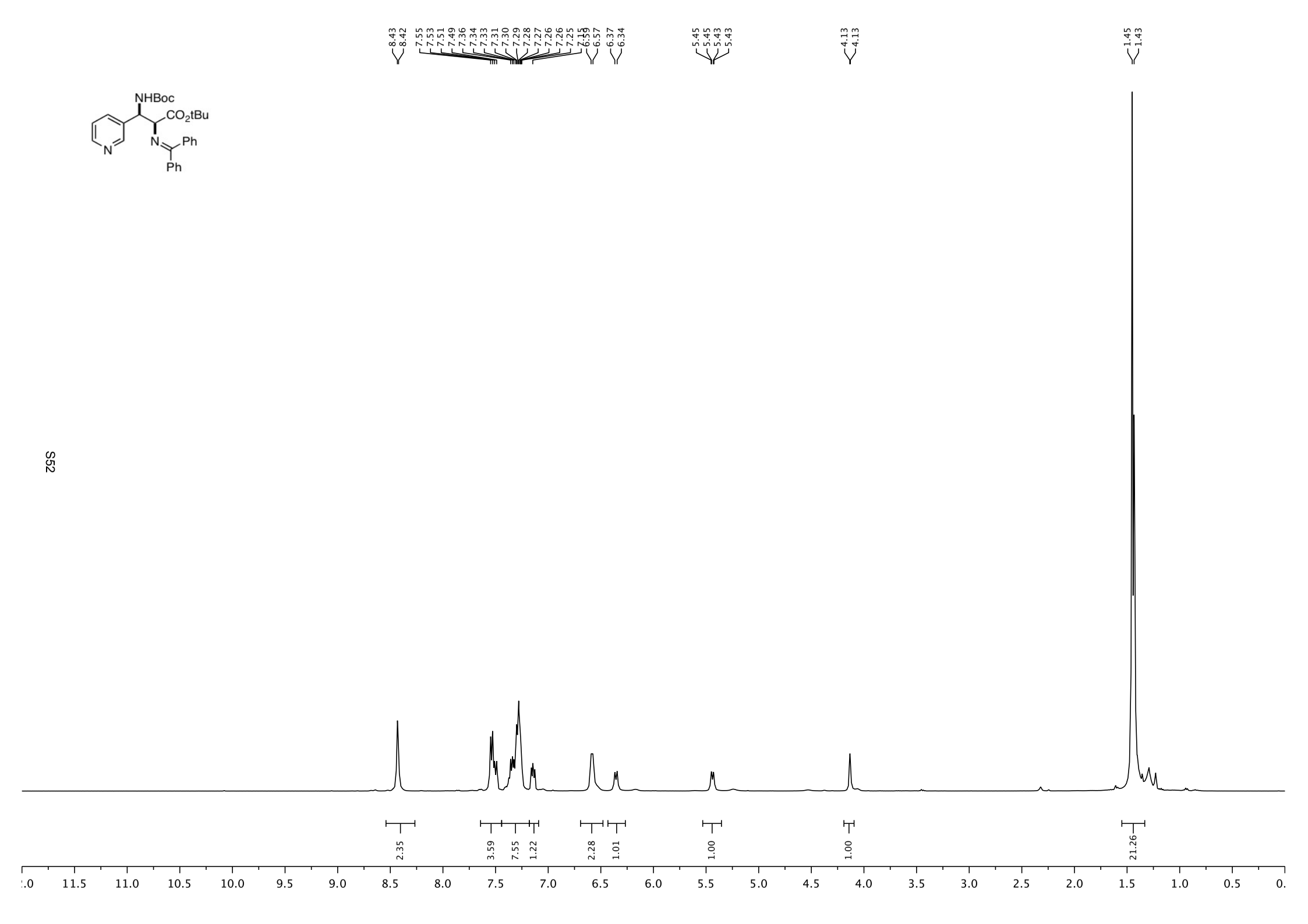
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4.13
1.45
1.43
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CO2tBu
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Ph
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Ph
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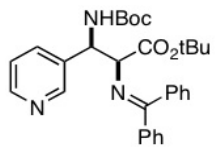

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69.69
54.95
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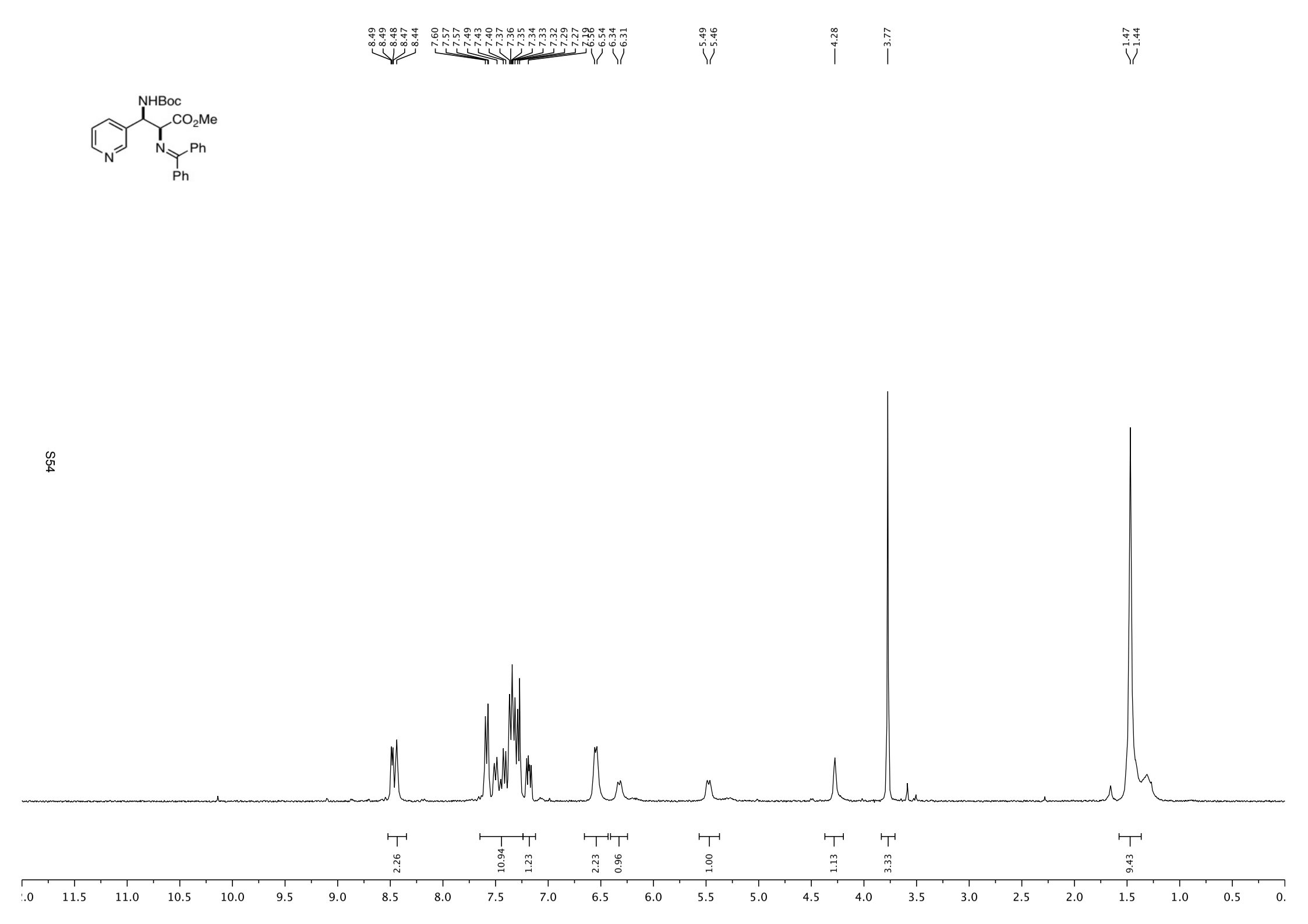
27.97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5.46
4.28
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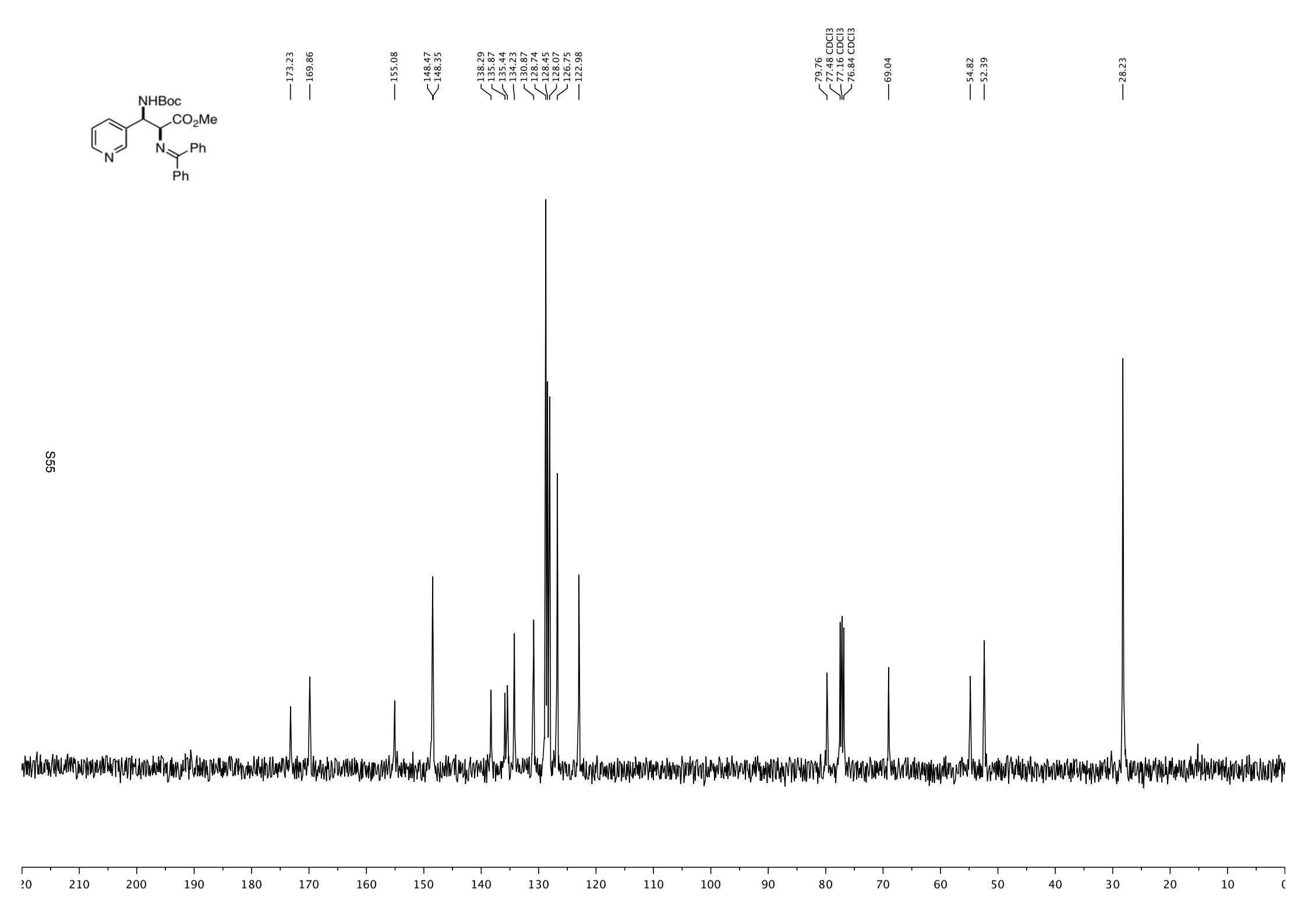
9.43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77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
69.04
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S55
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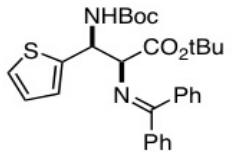
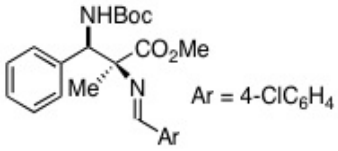


with 0.20 eq Bn_2O



+ diastereomer

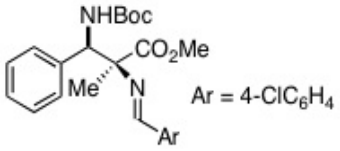
S57

8.32 8.08 7.77 7.75 7.44 7.43 7.42 7.41 7.31 7.30 7.29 7.28 7.26 7.25 7.23 7.22 6.25 6.22 5.92 5.90 5.35 5.32 5.24 5.22 3.79 3.59 1.60 1.46 1.45 1.42 1.40 1.33 1.29

1.00 1.82 5.65 22.62 1.76 0.80 1.43 0.91 6.03 3.08 3.54 36.20

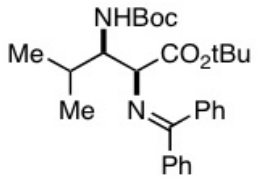
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.

f1 (ppm)



+ diastereomer

f1 (ppm)



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5.71 5.67

4.05 4.04 3.93 3.92 3.90 3.89 3.86 3.86

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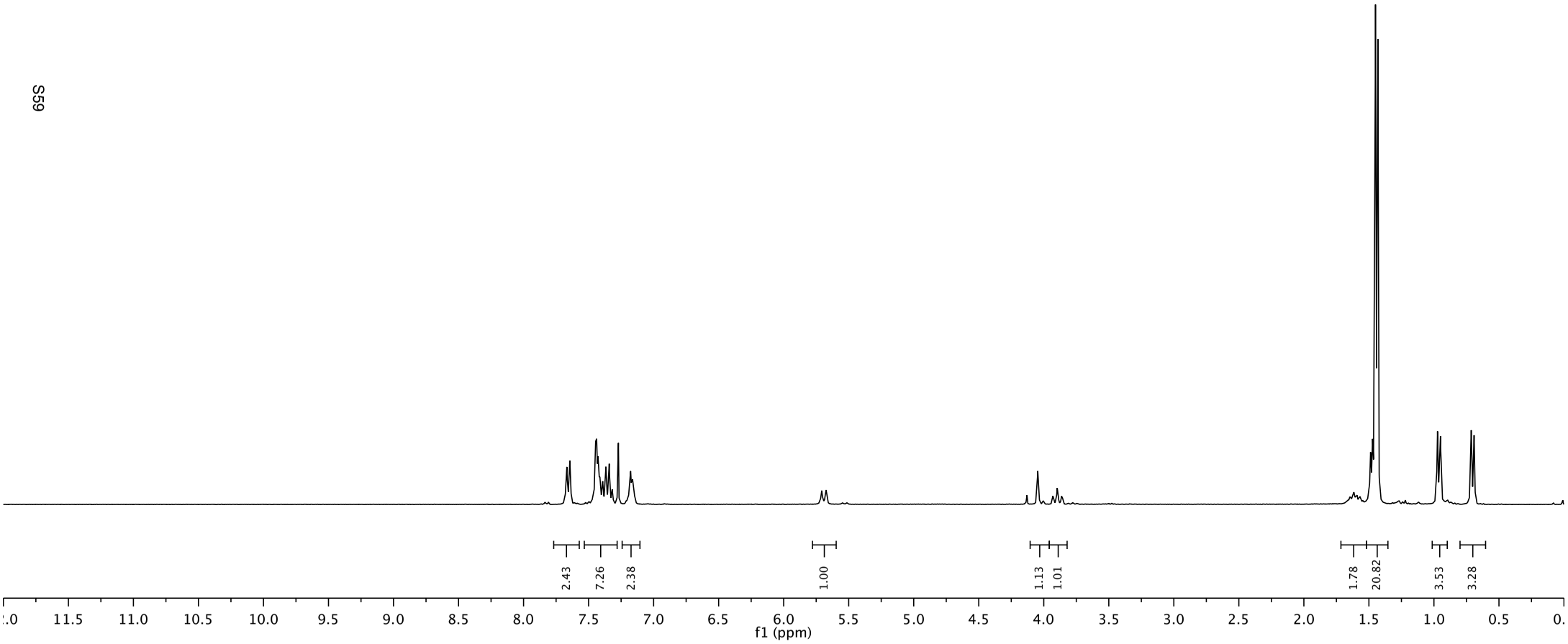

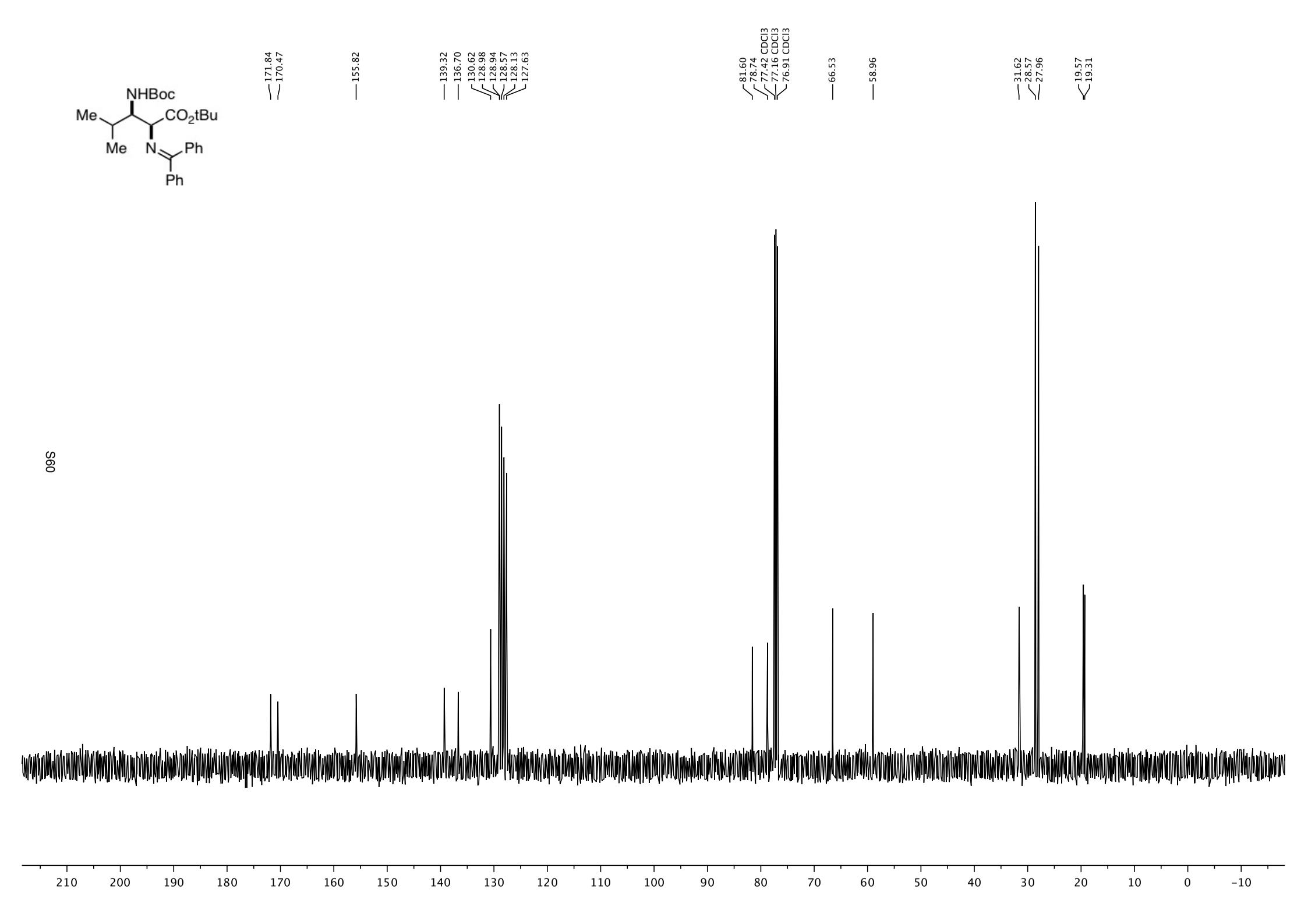
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CO2tBu
Me
N
Ph
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78.74
77.42 CDCl3
77.16 CDCl3
76.91 CDCl3
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31.62
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19.31
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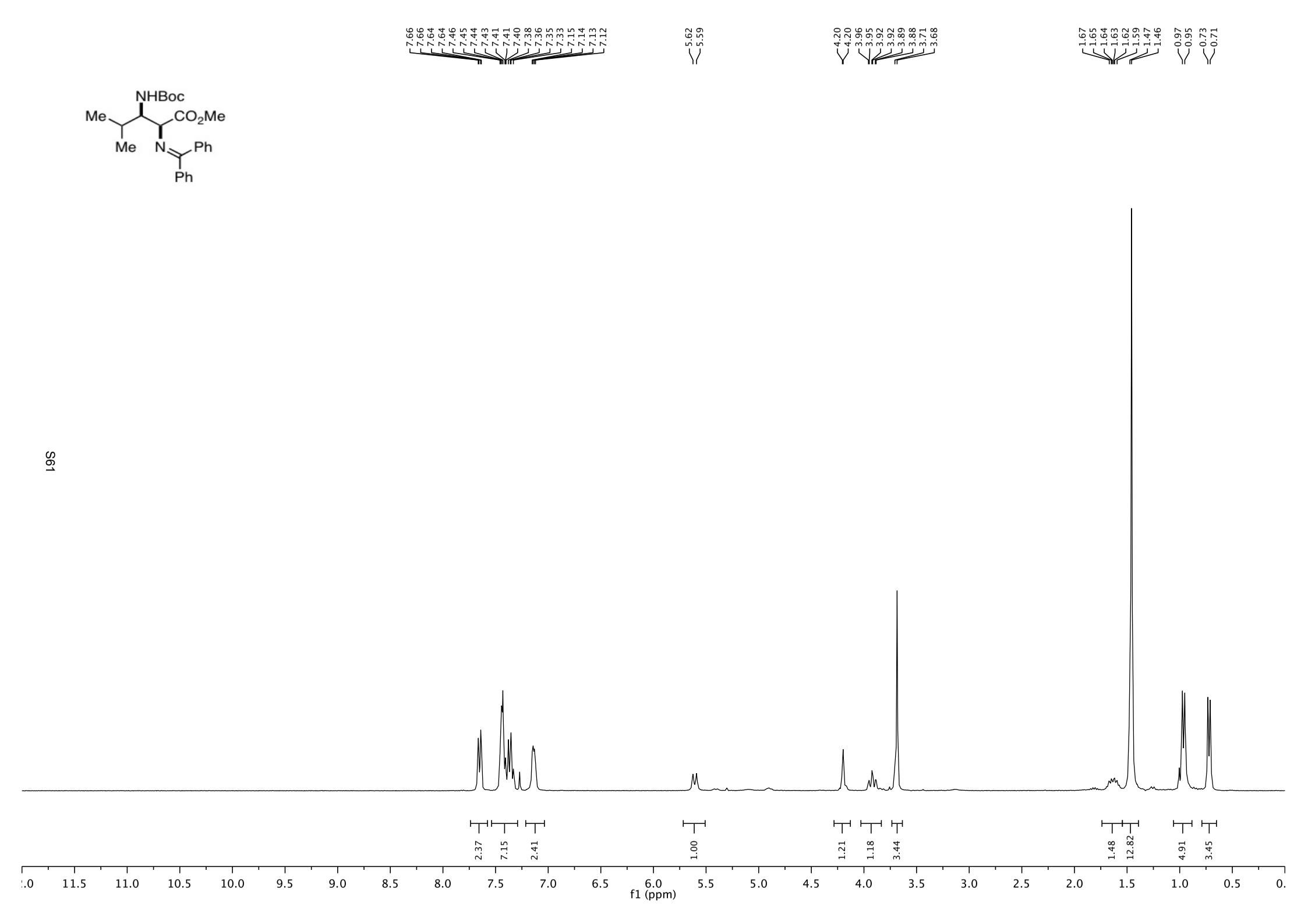
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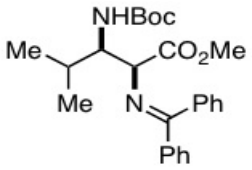
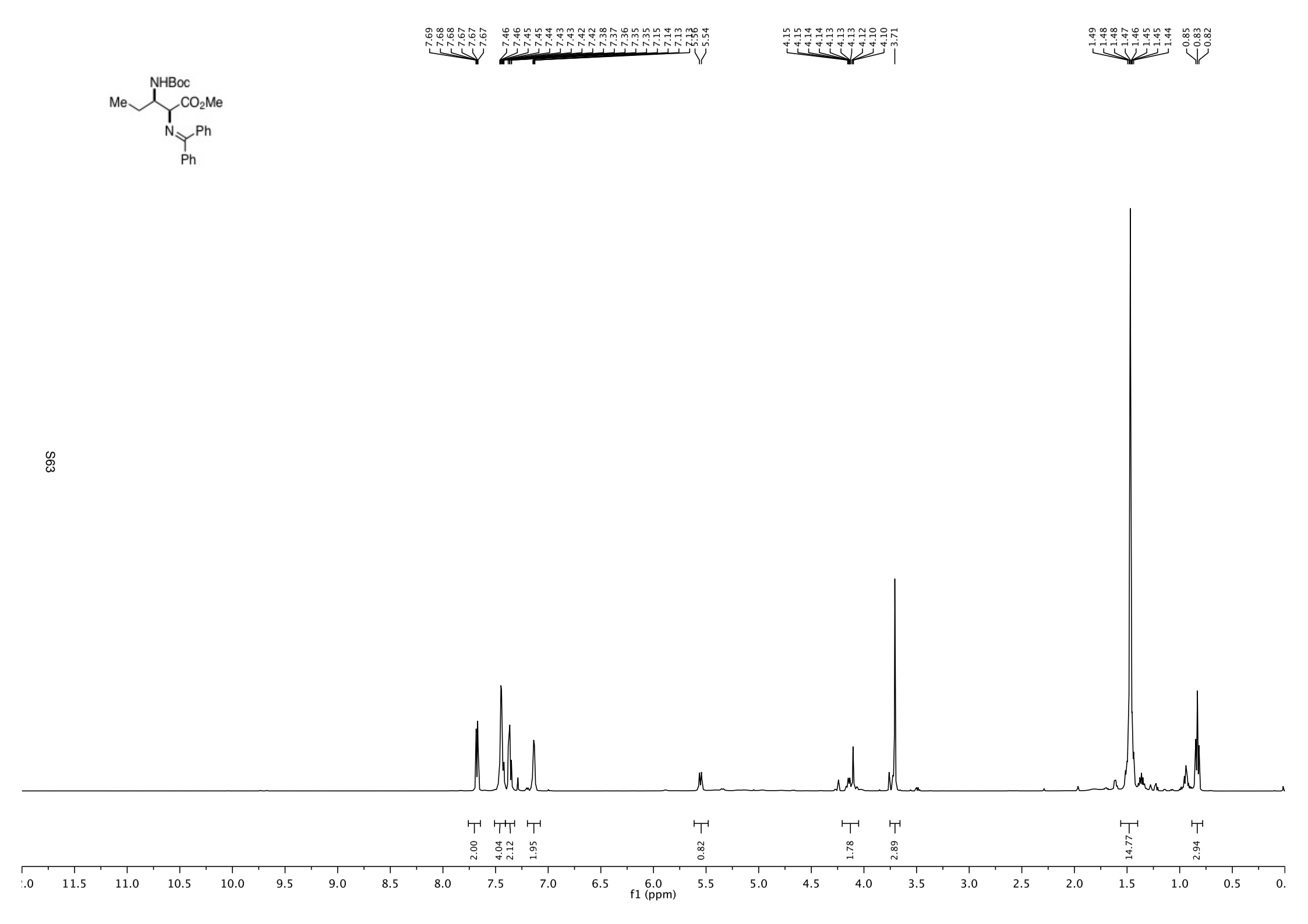
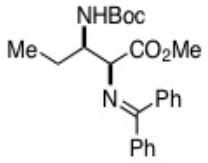
1.47
1.46
0.97
0.95
0.73
0.71
NHBoc
Me
CO2Me
Me
N
Ph
Ph
S61
2.37
7.15
2.41
1.00
1.21
1.18
3.44
1.48
12.82
4.91
3.45
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



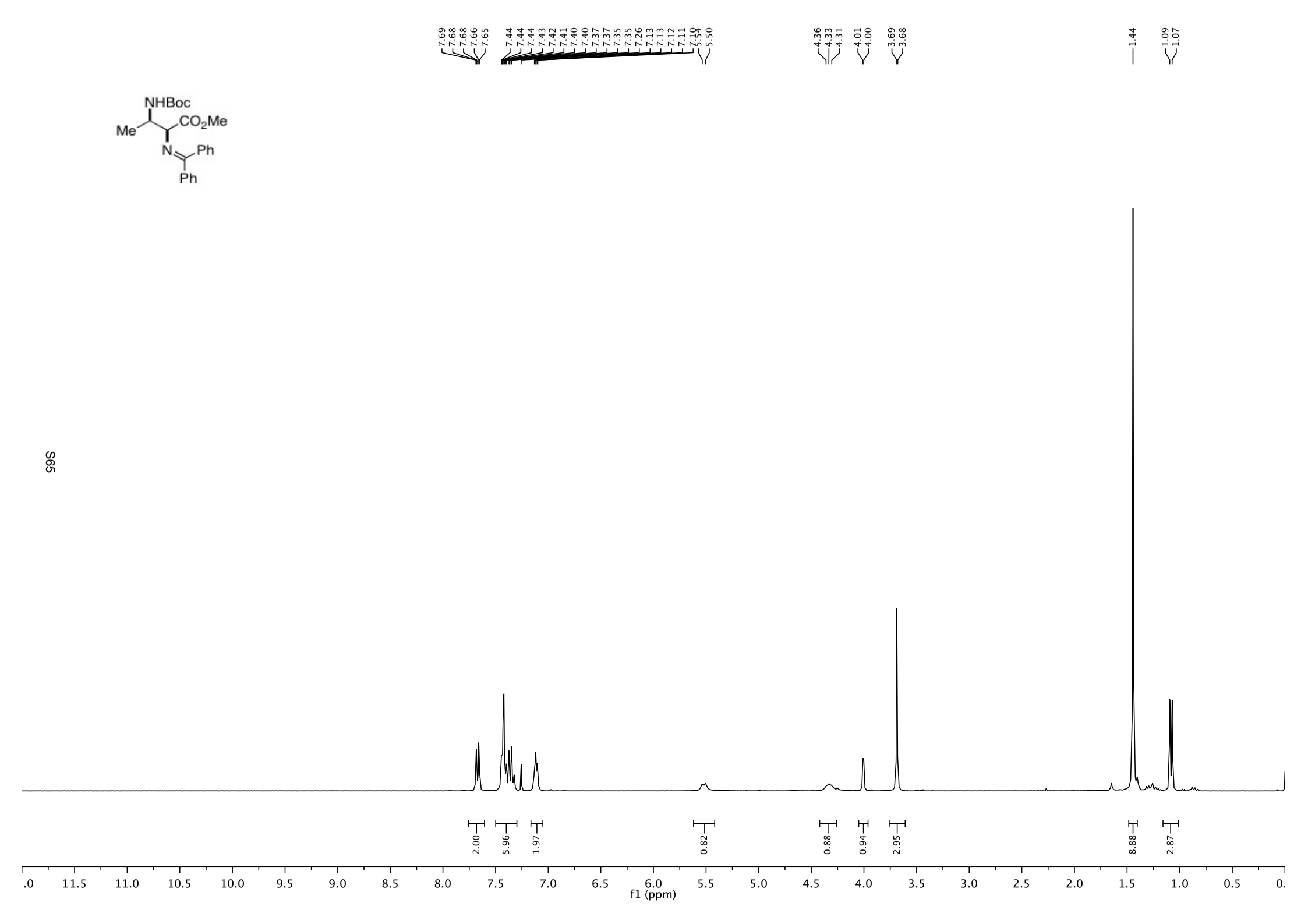
172.24
171.70
155.66
138.93
136.15
130.62
128.94
128.81
128.54
127.99
127.28
78.78 CDCl3
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
65.84
58.90
51.98
30.83
28.26
19.40
19.13

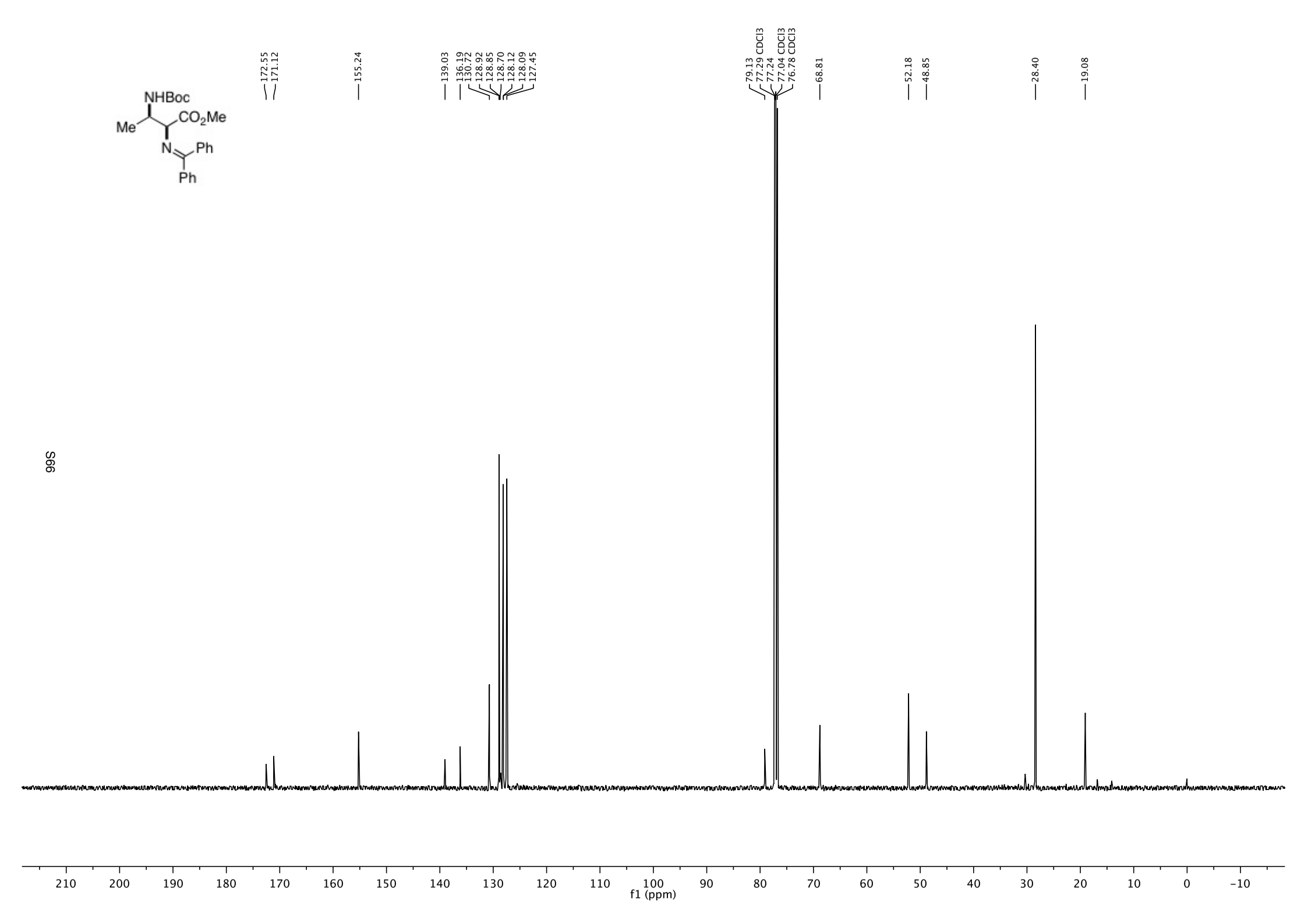

NHBoc
Me
CO2Me
N
Ph
Ph
S63
f1 (ppm)

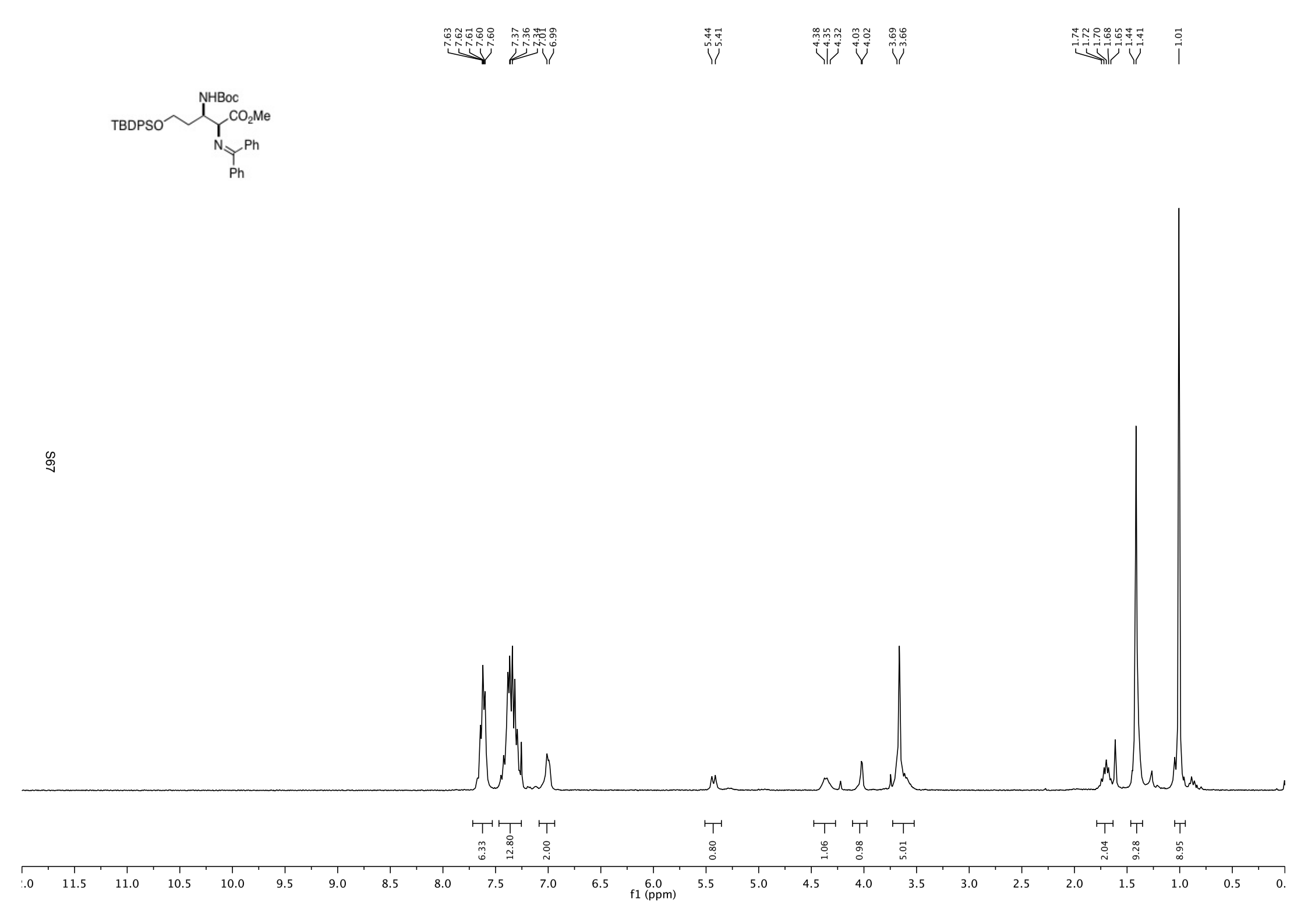


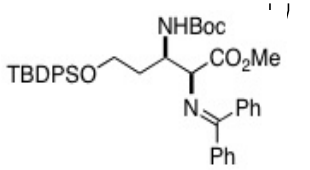
172.47
171.42
155.63
139.02
136.22
130.71
128.91
128.67
128.10
127.44
79.01
77.34 CDCl3
77.09 CDCl3
76.83 CDCl3
67.12
54.67
52.15
28.38
28.33
26.52
10.50

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

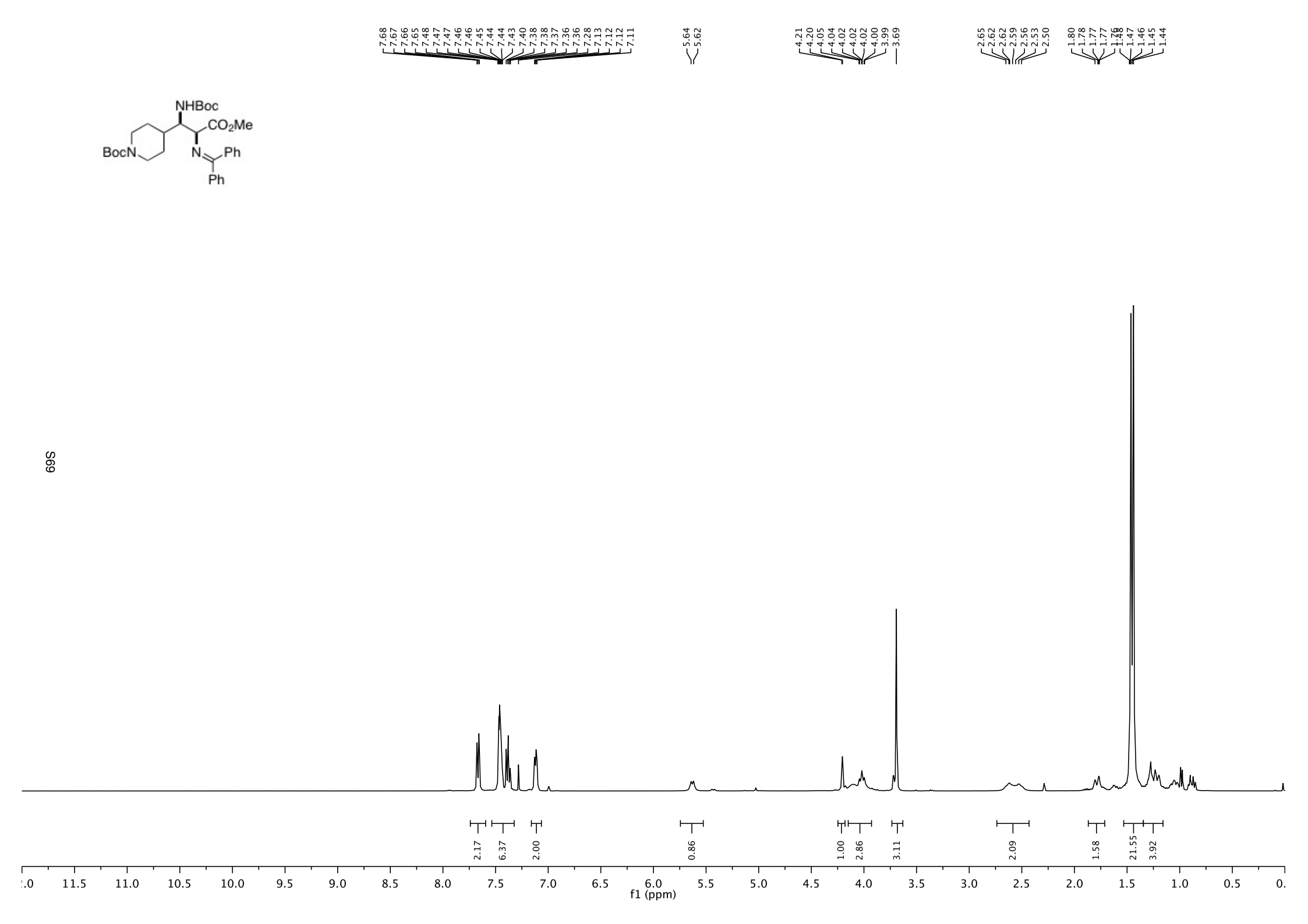

7.69
7.68
7.68
7.66
7.65
7.44
7.44
7.44
7.43
7.42
7.41
7.40
7.40
7.37
7.35
7.35
7.26
7.13
7.13
7.12
7.11
7.10
5.54
5.50
4.36
4.33
4.31
4.01
4.00
3.69
3.68
1.44
1.09
1.07
NHBoc
CO2Me
Me
N
Ph
Ph
S65
2.00
5.96
1.97
0.82
0.88
0.94
2.95
8.88
2.87
f1 (ppm)

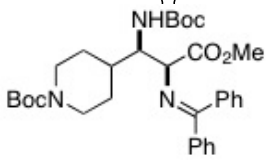

NHBoc
Me
CO2Me
N
Ph
Ph
172.55
171.12
155.24
139.03
136.19
130.72
128.92
128.85
128.70
128.12
128.09
127.45
79.13
77.29 CDCl3
77.24
77.04 CDCl3
76.78 CDCl3
68.81
52.18
48.85
28.40
19.08
S66
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.63
7.62
7.61
7.60
7.60
7.37
7.36
7.34
7.01
6.99
5.44
5.41
4.38
4.35
4.32
4.03
4.02
3.69
3.66
1.74
1.72
1.70
1.68
1.65
1.44
1.41
1.01
NHBoc
TBDPSO
CO2Me
N
Ph
Ph
S67
6.33
12.80
2.00
0.80
1.06
0.98
5.01
2.04
9.28
8.95
f1 (ppm)


NHBoc
TBDPSO
CO2Me
N
Ph
Ph

172.65
171.36
155.42
139.21
136.31
135.69
135.65
133.94
132.53
130.81
130.19
129.66
129.09
128.95
128.76
128.41
128.20
127.79
127.74
127.72
127.54
79.11
77.41 CDCl3
77.36
77.16 CDCl3
76.90 CDCl3
67.95
61.17
52.25
50.60
36.38
28.51
28.50
28.45
27.00
26.96
19.26
S68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.68
7.67
7.66
7.65
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.40
7.38
7.38
7.37
7.36
7.36
7.28
7.13
7.12
7.12
7.11
5.64
5.62
4.21
4.20
4.05
4.04
4.02
4.02
4.02
4.00
3.99
3.69
2.65
2.62
2.62
2.59
2.56
2.53
2.50
1.80
1.78
1.77
1.77
1.47
1.46
1.45
1.44
NHBoc
CO2Me
BocN
N
Ph
Ph
S69
2.17
6.37
2.00
0.86
1.00
2.86
3.11
2.09
1.58
21.55
3.92
f1 (ppm)

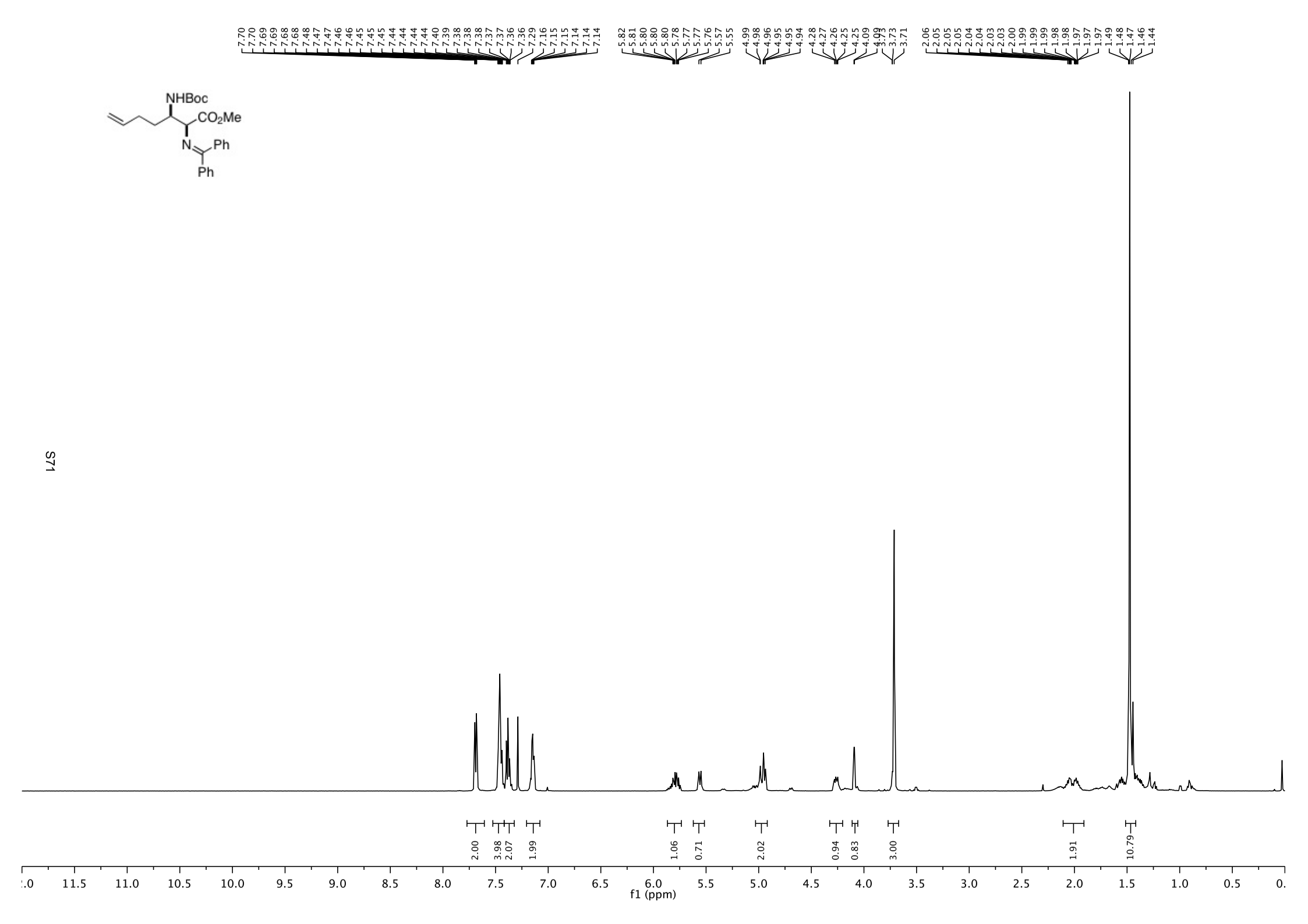


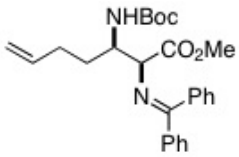
172.68
171.54
155.82
154.74
138.96
136.17
130.97
130.13
129.26
129.02
128.80
128.36
128.27
127.37
79.40
79.29
77.47 CDCl3
77.15 CDCl3
76.84 CDCl3
65.26
57.22
52.28
38.99
28.52
28.44

S70

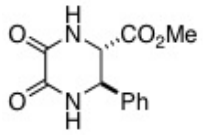
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

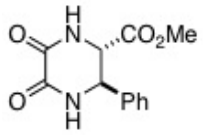

NHBoc
CO2Me
N
Ph
Ph
S71
f1 (ppm)


NHBoc
CO2Me
N
Ph
Ph

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


O
N
H
CO2Me
O
N
H
Ph

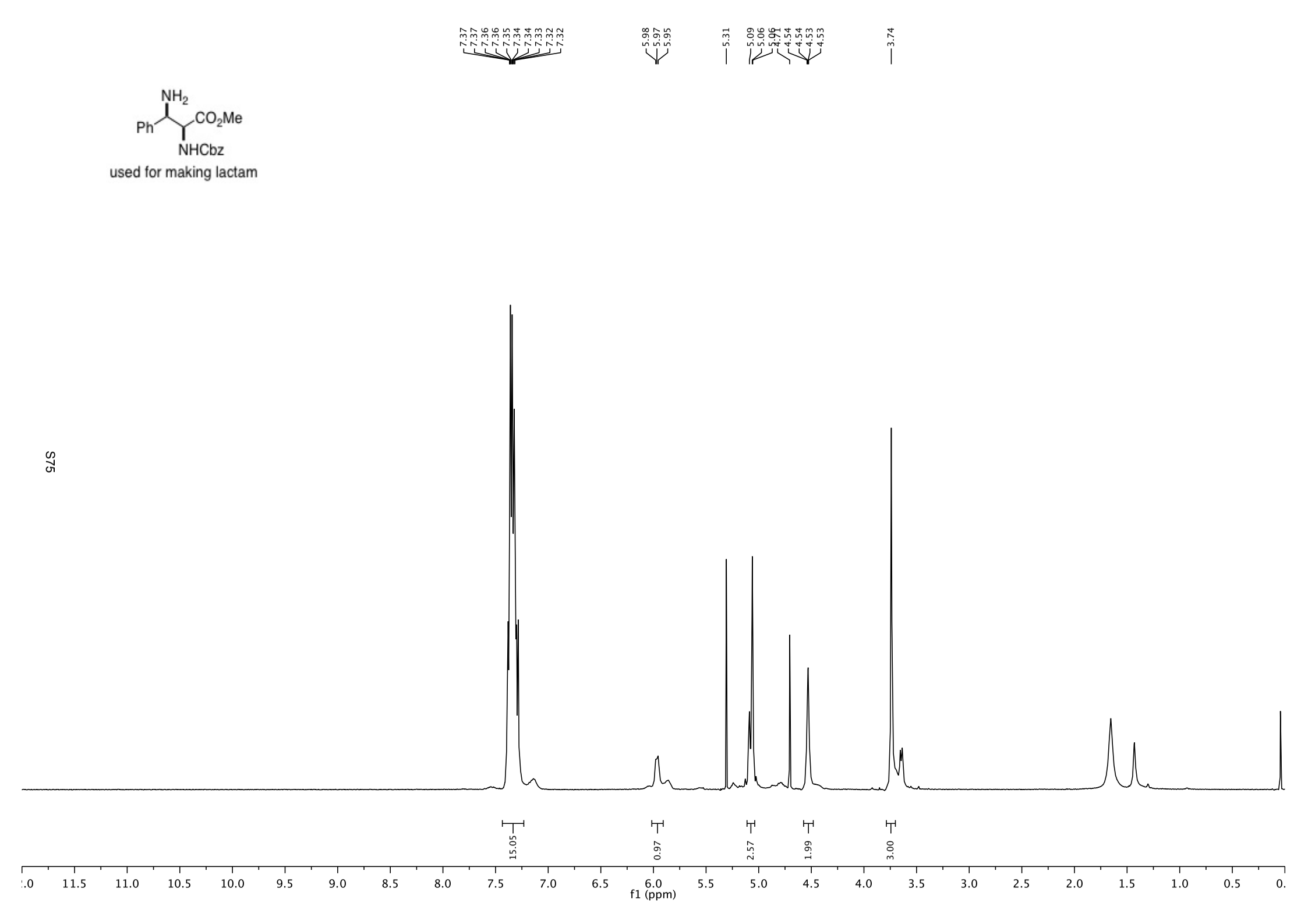
9.13
9.11
8.78
8.76
7.49
7.47
7.46
7.41
7.39
7.38
7.36
7.34
5.03
5.02
5.02
5.01
4.51
4.49
3.83
1.00
0.98
5.90
1.01
0.99
2.98
f1 (ppm)

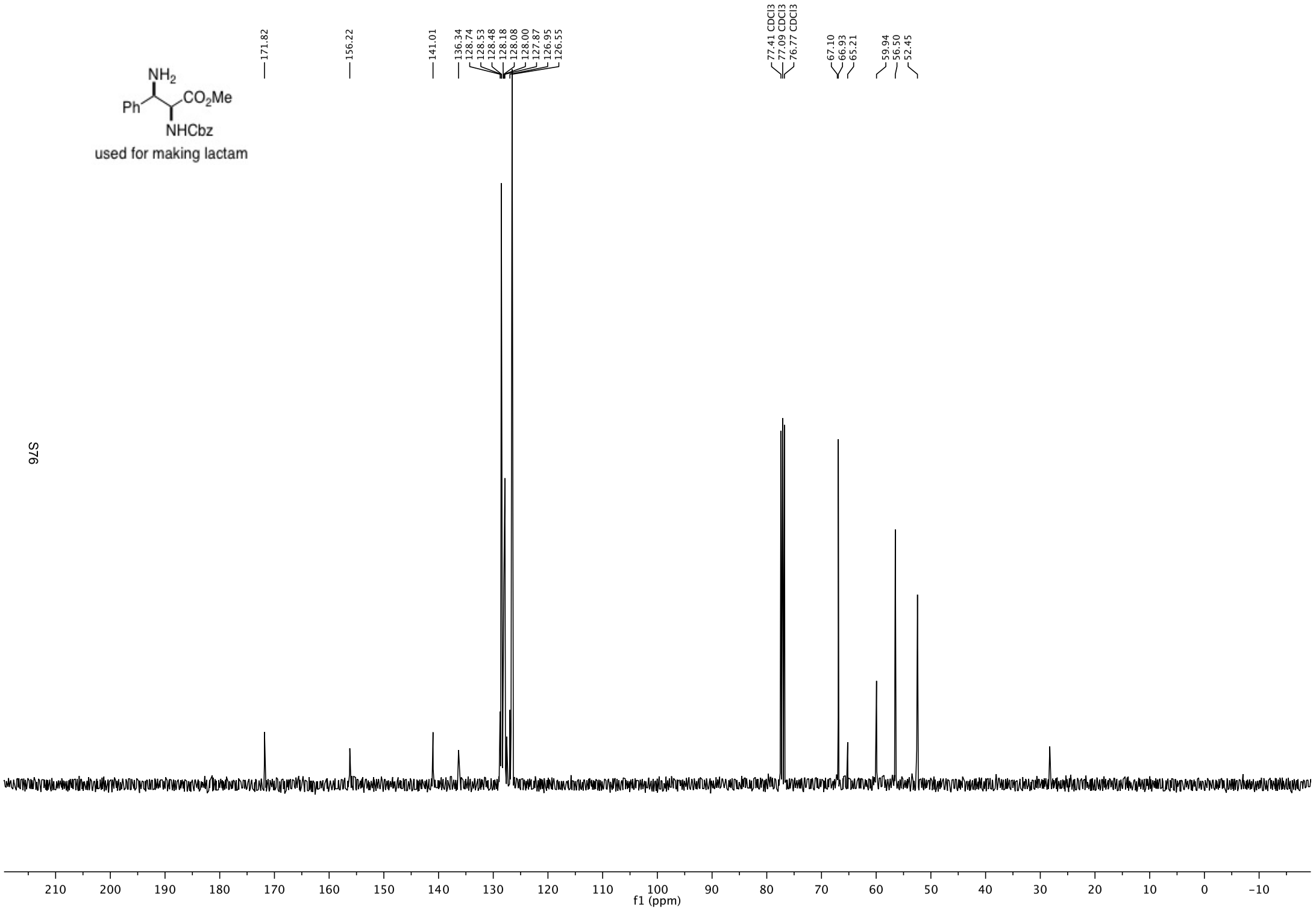


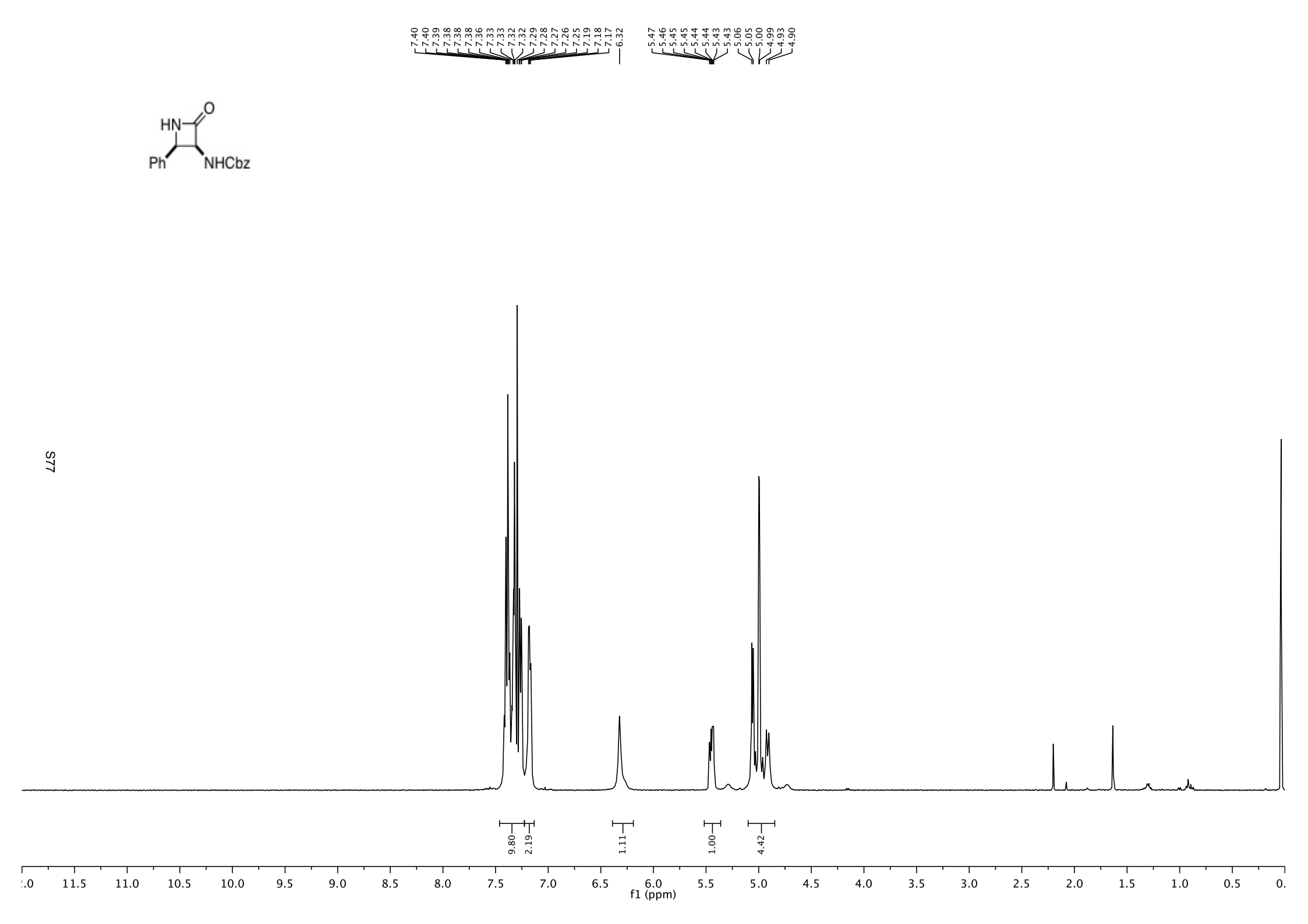
171.33
158.58
158.22
139.67
129.23
128.48
126.56
58.47
55.20
53.57

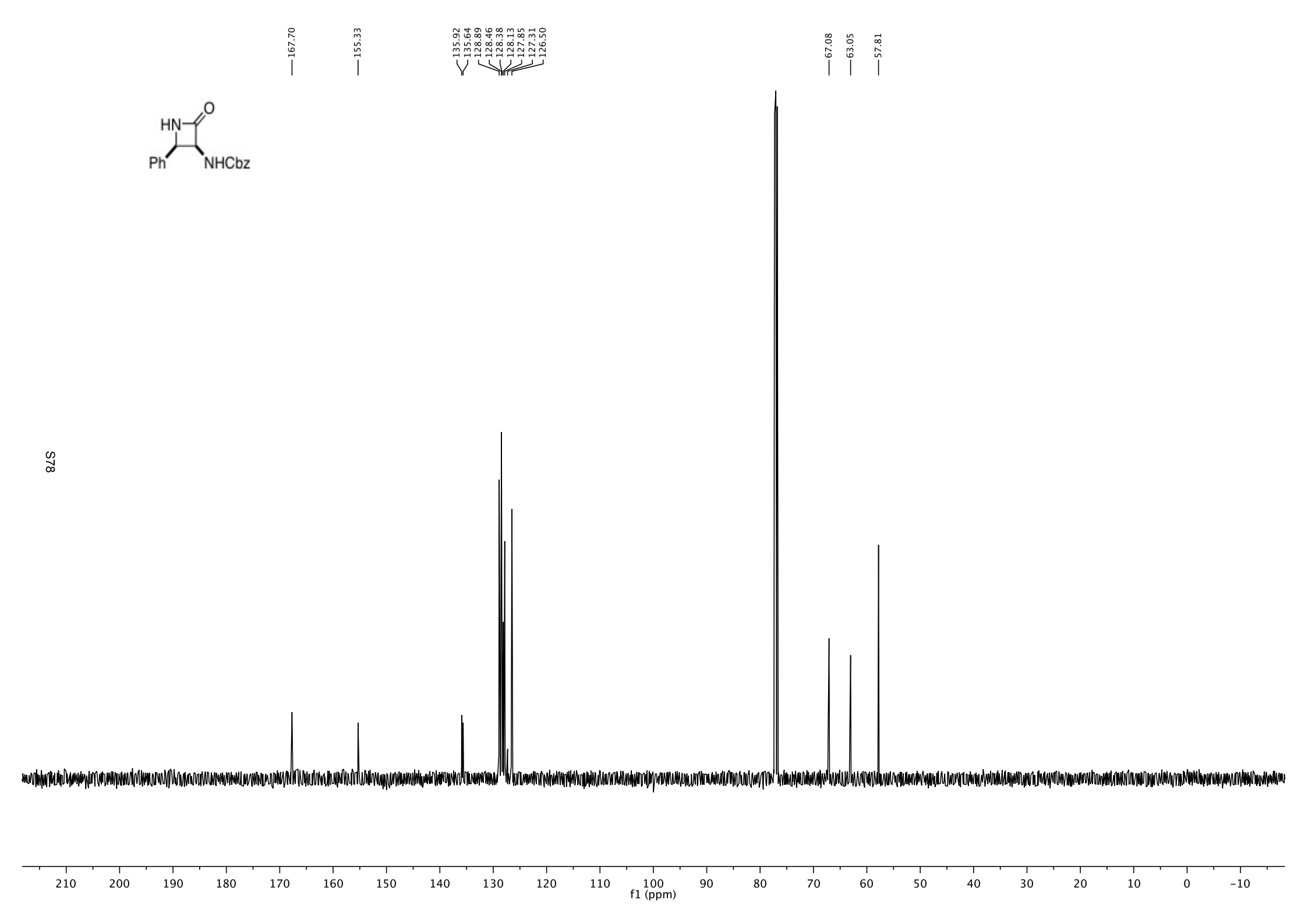
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

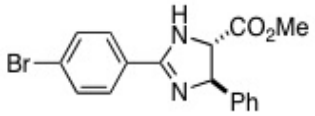
f1 (ppm)


7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
5.98
5.97
5.95
5.31
5.09
5.06
4.54
4.54
4.53
4.53
3.74
NH2
Ph
CO2Me
NHCbz
used for making lactam
S75
15.05
0.97
2.57
1.99
3.00
f1 (ppm)


171.82
156.22
141.01
136.34
128.74
128.53
128.48
128.18
128.08
128.00
127.87
126.95
126.55
77.41 CDCl3
77.09 CDCl3
76.77 CDCl3
67.10
66.93
65.21
59.94
56.50
52.45
NH2
Ph
CO2Me
NHCbz
used for making lactam
S76
f1 (ppm)


7.40
7.40
7.39
7.38
7.38
7.38
7.36
7.33
7.33
7.32
7.32
7.29
7.28
7.27
7.26
7.25
7.19
7.18
7.17
6.32
5.47
5.46
5.45
5.45
5.44
5.44
5.43
5.43
5.06
5.05
5.00
4.99
4.93
4.90
HN
O
Ph
NHCbz
S77
9.80
2.19
1.11
1.00
4.42
f1 (ppm)

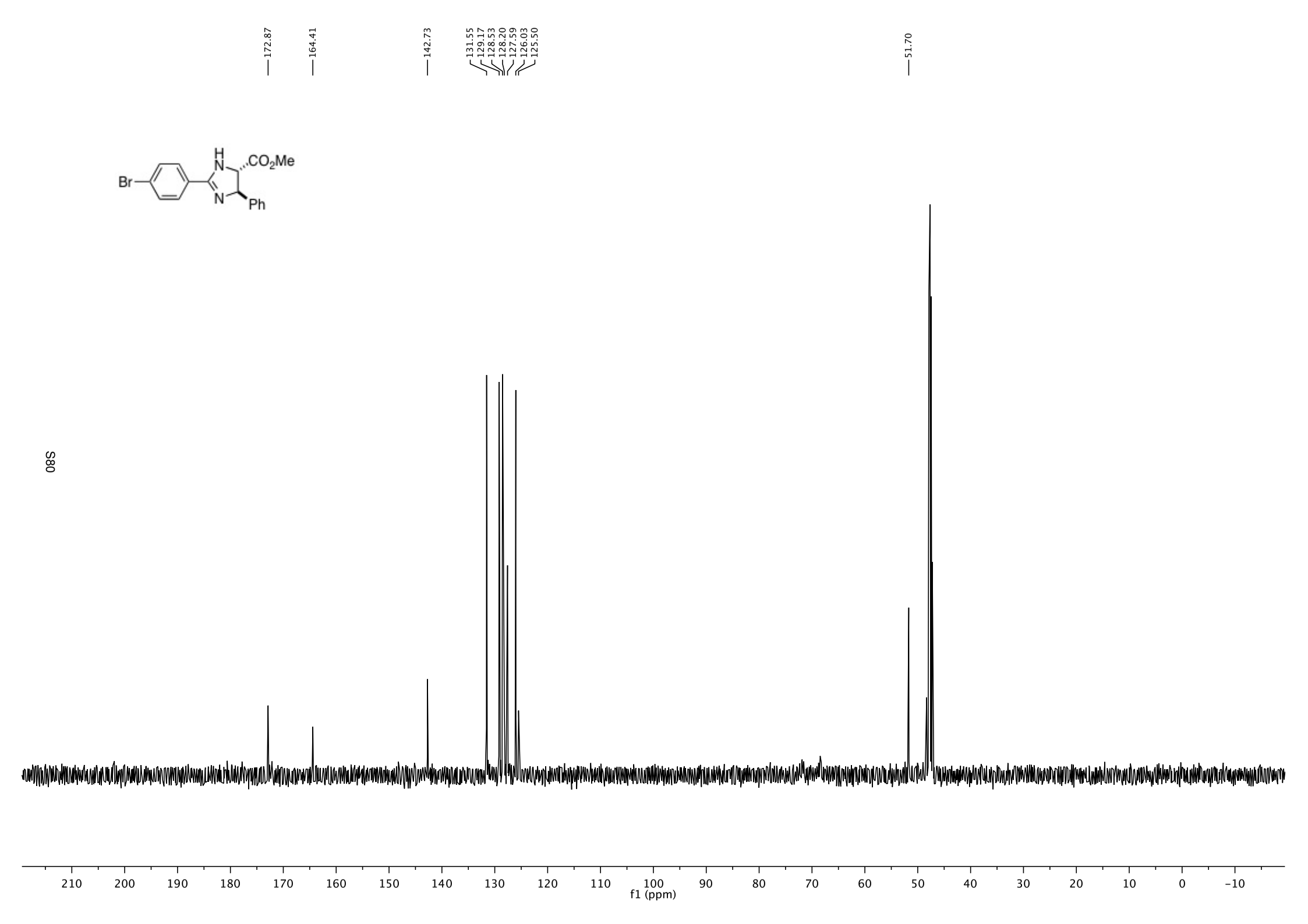

167.70
155.33
135.92
135.64
128.89
128.46
128.38
128.13
127.85
127.31
126.50
67.08
63.05
57.81
HN
O
Ph
NHCbz
S78
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

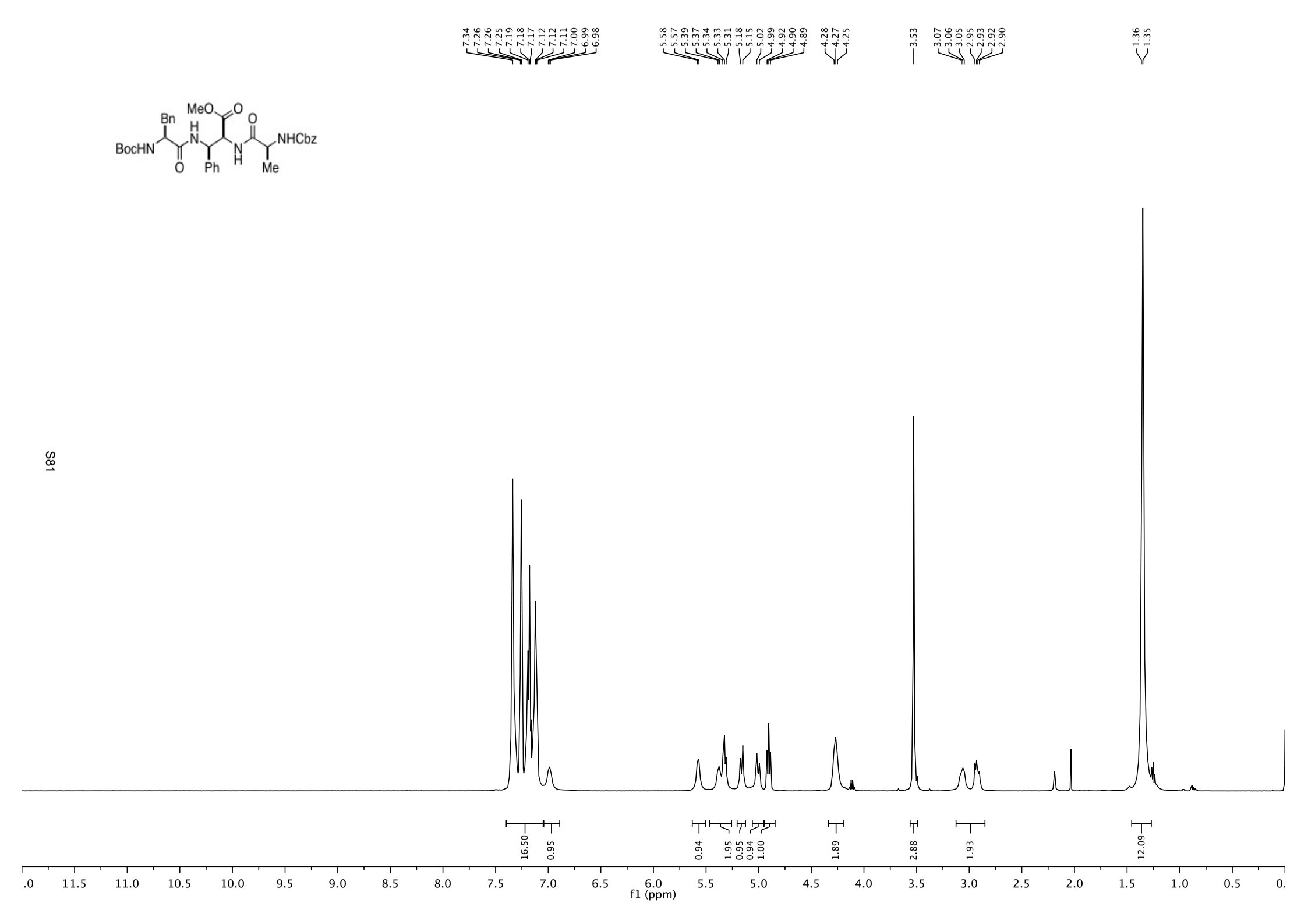


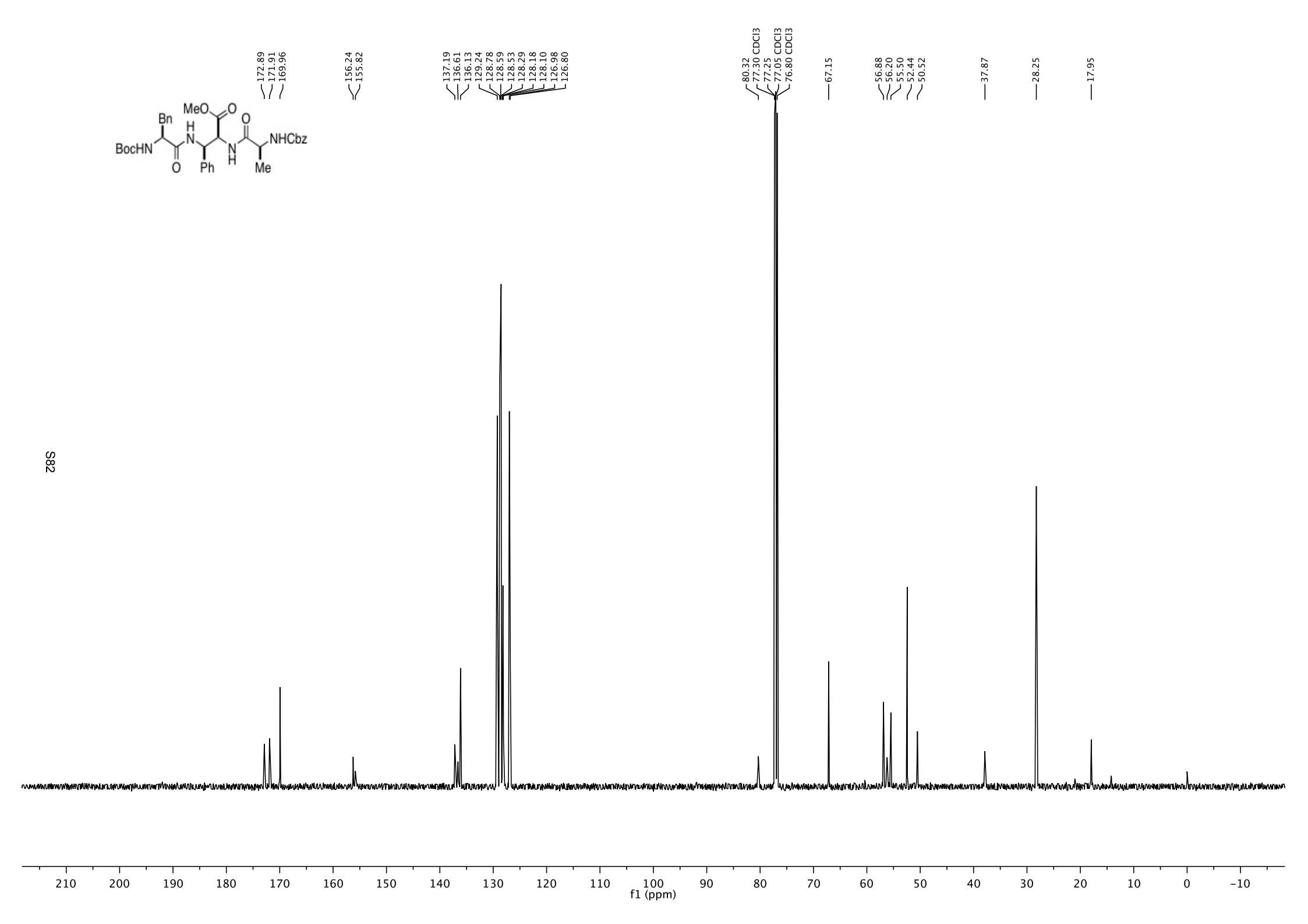
7.81
7.79
7.63
7.61
7.36
7.34
7.29
7.28
5.25
5.23
4.44
4.42
3.80

2.00
2.01
5.39
1.00
1.00
3.02

f1 (ppm)

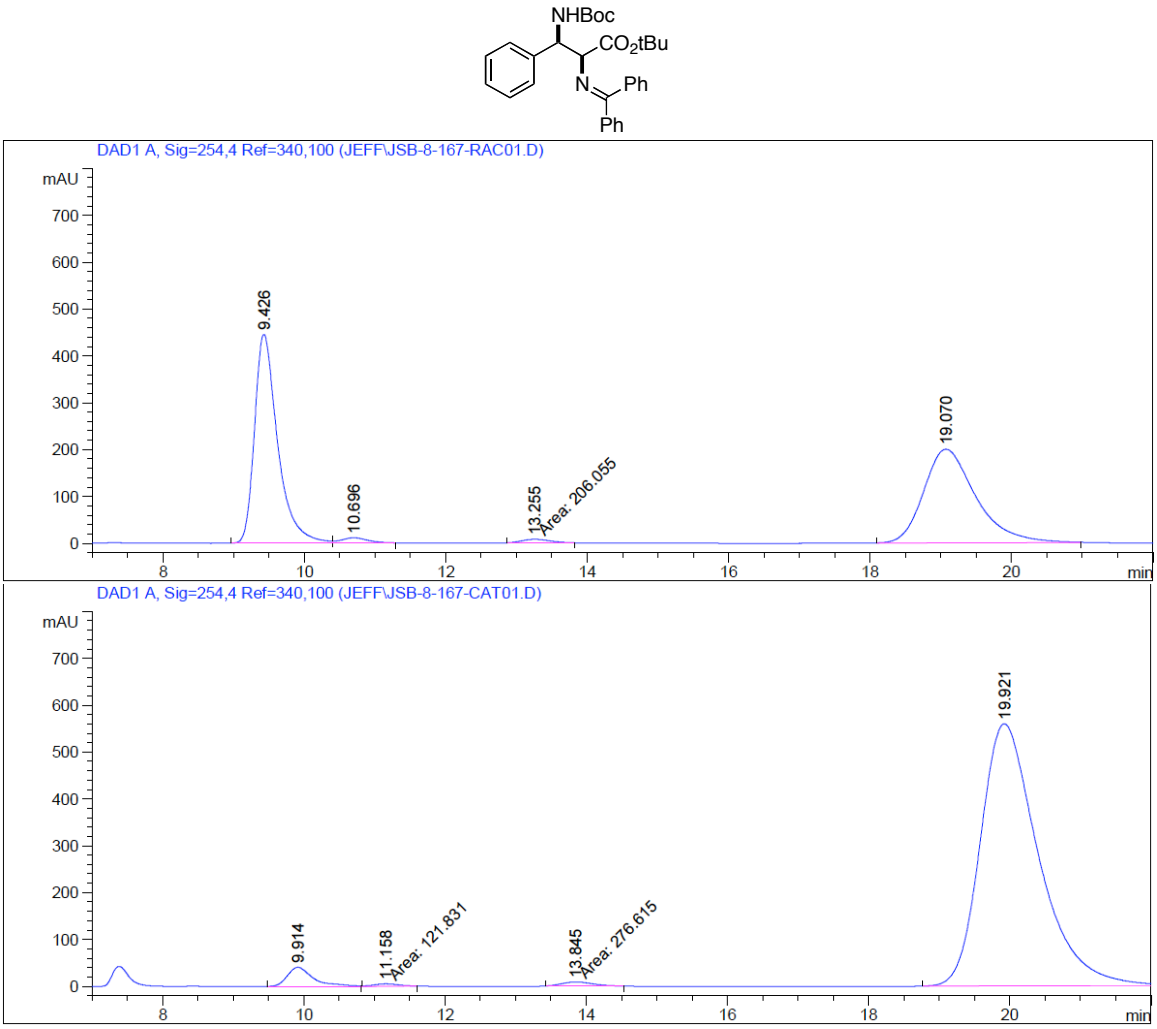

172.87
164.41
142.73
131.55
129.17
128.53
128.20
127.59
126.03
125.50
51.70
Br
H
N
N
CO2Me
Ph
S80
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.34
7.26
7.26
7.25
7.19
7.18
7.17
7.12
7.12
7.11
7.00
6.99
6.98
5.58
5.57
5.39
5.37
5.34
5.33
5.31
5.18
5.15
5.02
4.99
4.92
4.90
4.89
4.28
4.27
4.25
3.53
3.07
3.06
3.05
2.95
2.93
2.92
2.90
1.36
1.35
MeO
O
Bn
H
N
O
NHCbz
BocHN
N
H
O
Ph
Me
S81
16.50
0.95
0.94
1.95
0.95
0.94
1.00
1.89
2.88
1.93
12.09
f1 (ppm)


172.89
171.91
169.96
156.24
155.82
137.19
136.61
136.13
129.24
128.78
128.59
128.53
128.29
128.18
128.10
126.98
126.80
80.32
77.30 CDCl3
77.25
77.05 CDCl3
76.80 CDCl3
67.15
56.88
56.20
55.50
52.44
50.52
37.87
28.25
17.95
MeO
O
Bn
H
N
O
BocHN
NHCbz
O
Ph
N
H
Me
S82
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

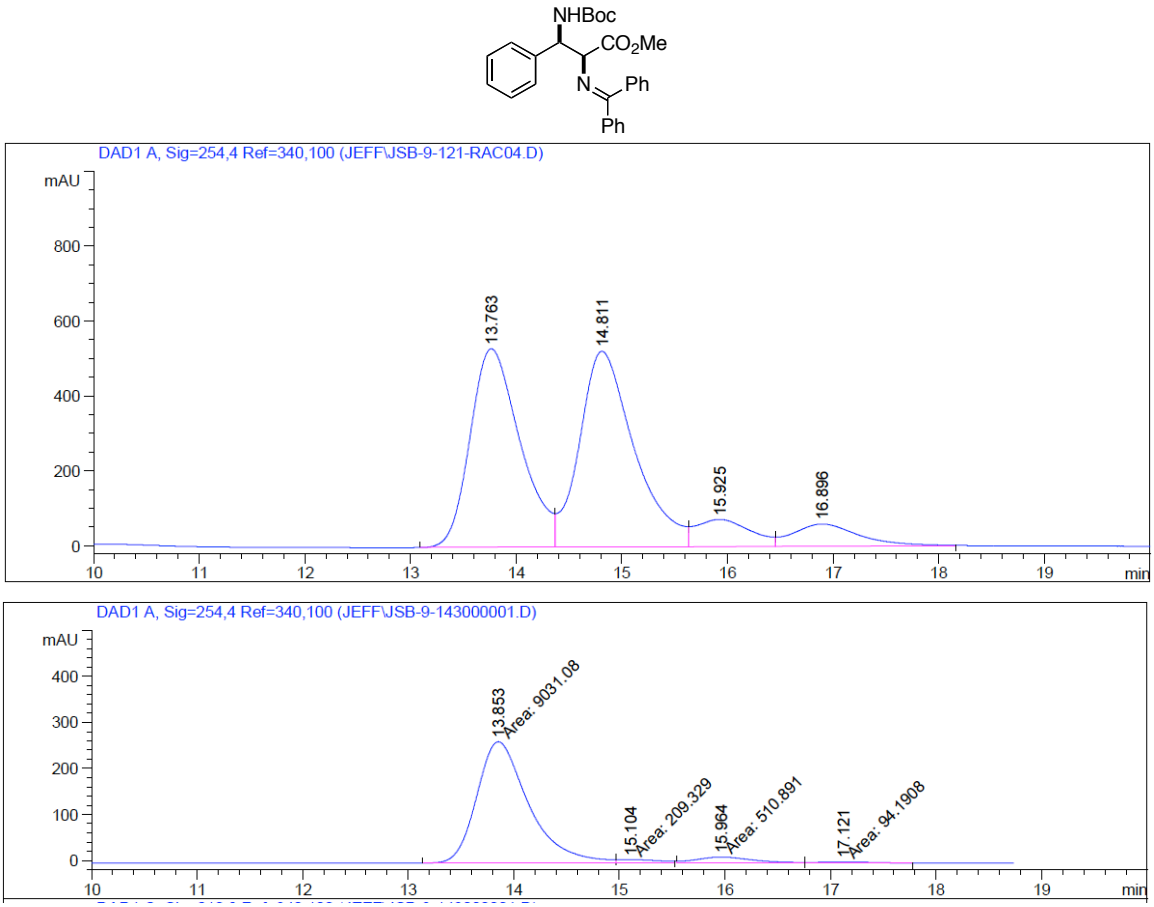
Note: For each entry, the top HPLC trace is a racemic sample that was prepared using standard conditions and a cyclopropenimine catalyst lacking a chiral substituent.

Table 2, entry 1a. Hexanes/iPrOH 97.5/2.5, 1 mL/min, 254 nm, AD-H.



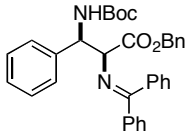
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	9.914	1	BB	1049.73889	40.70111	3.1371
2	11.158	1	MM T	121.83084	5.18297	0.3641
3	13.845	1	MM T	276.61487	9.01712	0.8266
4	19.921	1	BB	3.20143e4	559.98871	95.6722

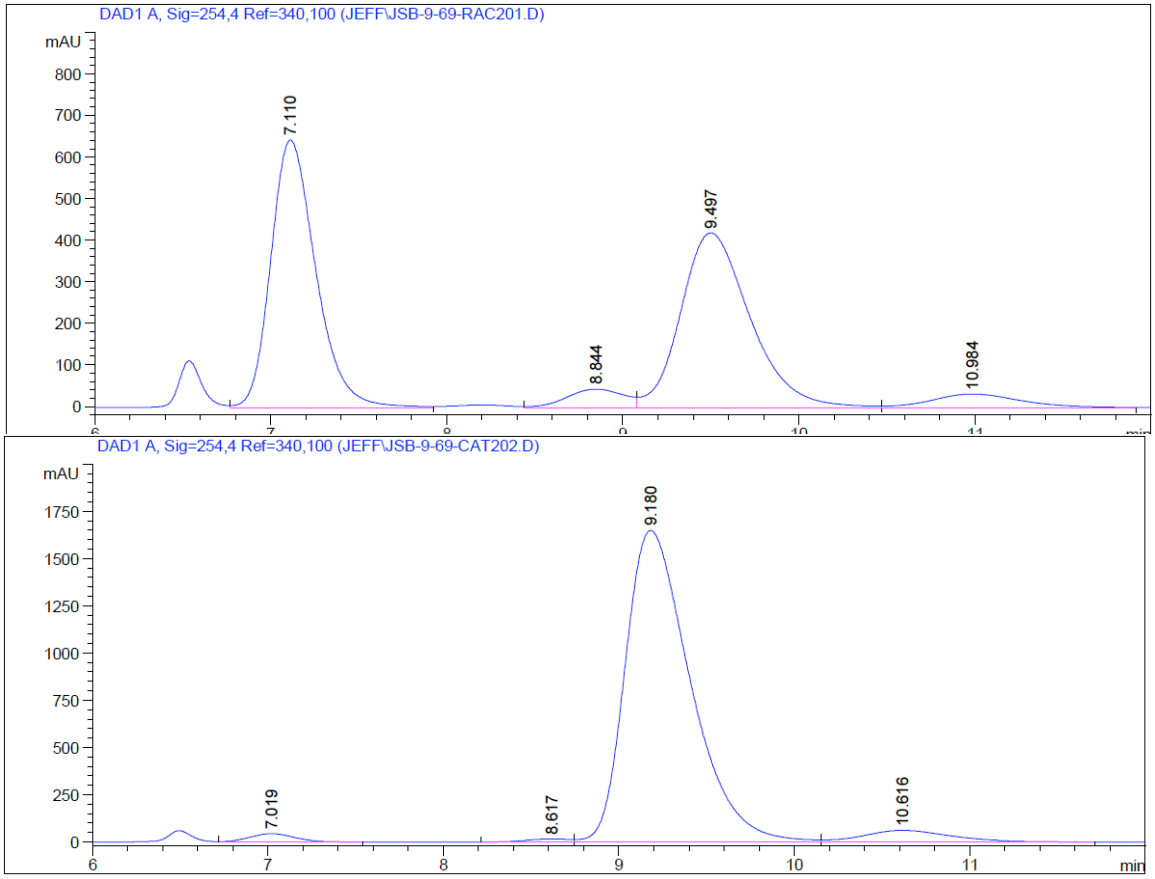
Table 2, entry 1b. Hexanes/iPrOH 96/4, 1 mL/min, 254 nm, AD-H.



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	13.853	1	MF T	9031.08105	263.42554	91.7467
2	15.104	1	MF T	209.32942	7.54479	2.1266
3	15.964	1	MF T	510.89087	13.38571	5.1901
4	17.121	1	FM T	94.19078	2.51940	0.9569

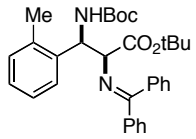
Table 2, entry 1c. Hexanes/iPrOH 98/2, 1 mL/min, 254 nm, OD-H.

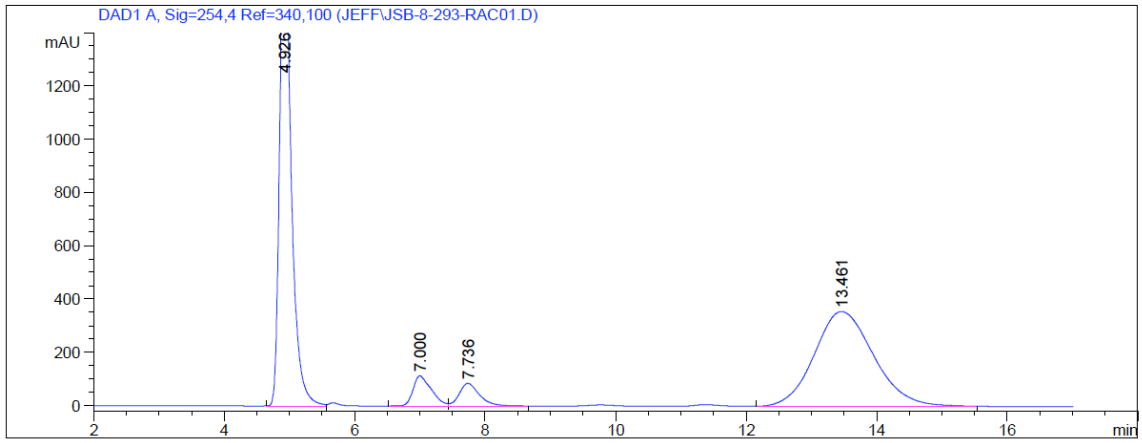


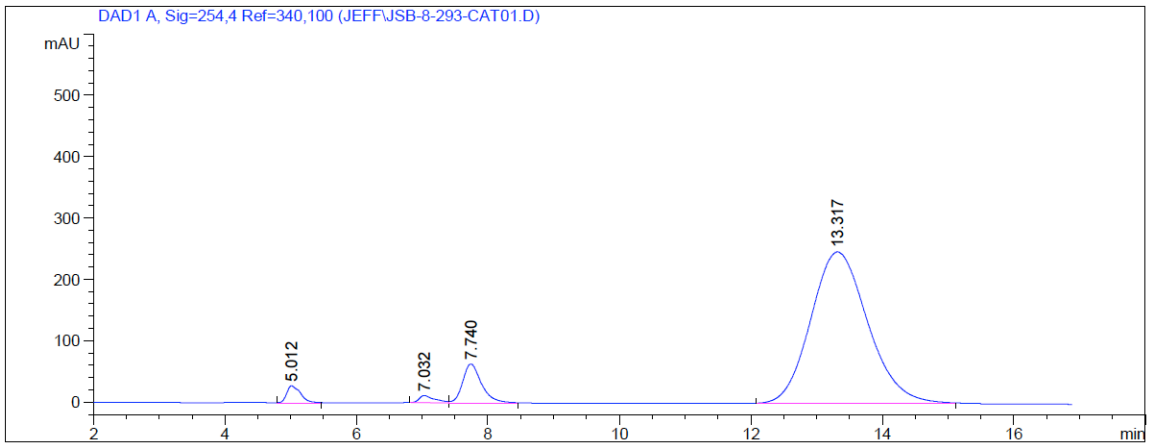


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	7.019	1	VB	814.79230	44.93319	1.7853
2	8.617	1	BV	270.24567	15.61958	0.5922
3	9.180	1	VV	4.23747e4	1649.26086	92.8497
4	10.616	1	VB	2178.20264	62.34171	4.7728

Table 2, entry 2. Hexanes/iPrOH 97.5/2.5, 1 mL/min, 254 nm, AD-H.



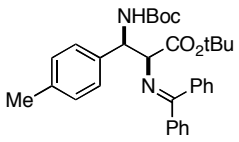


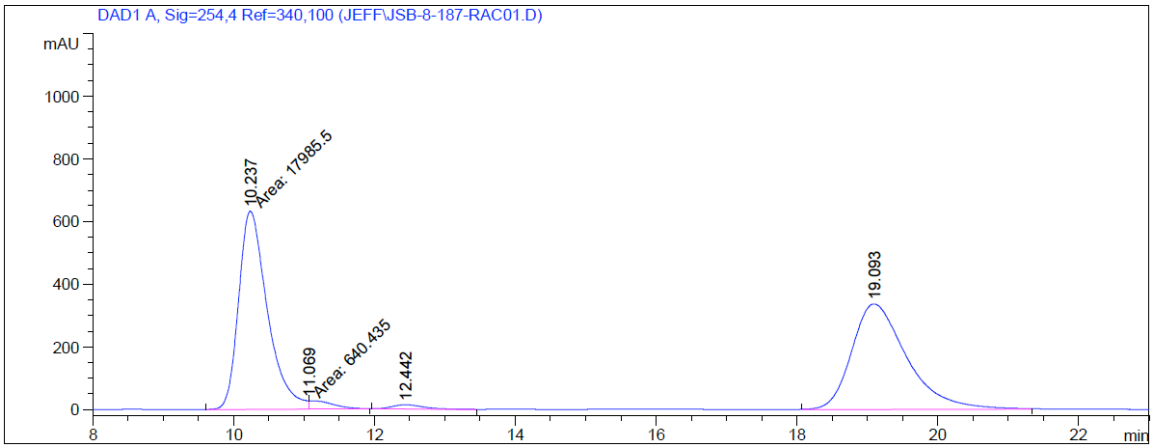


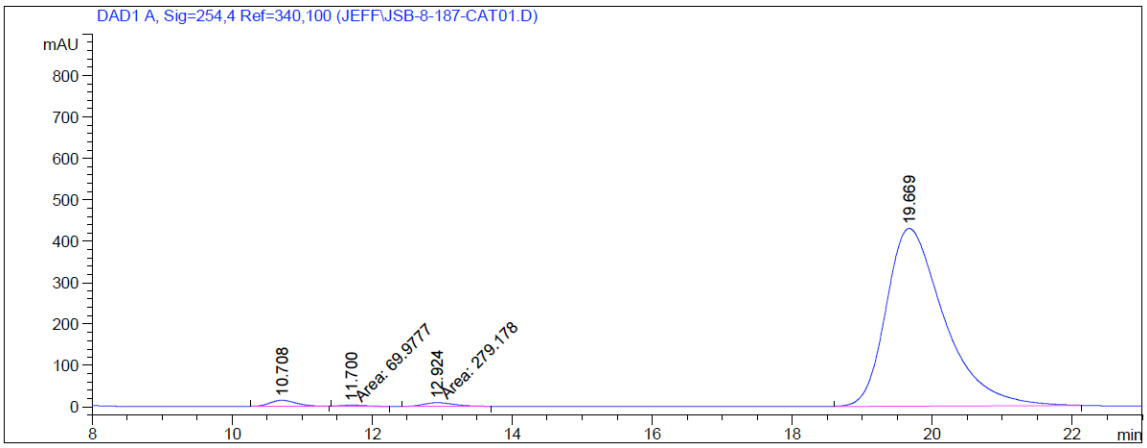
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	5.012	1	BB	397.73288	27.71351	2.3792
2	7.032	1	BV	192.69904	11.88978	1.1527

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
3	7.740	1	VB	1261.68750	63.26462	7.5471
4	13.317	1	BB	1.48653e4	246.57312	88.9210

Table 2, entry 3. Hexanes/iPrOH 97.5/2.5, 1 mL/min, 254 nm, AD-H.

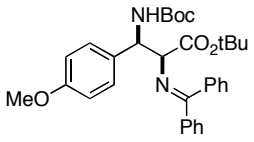


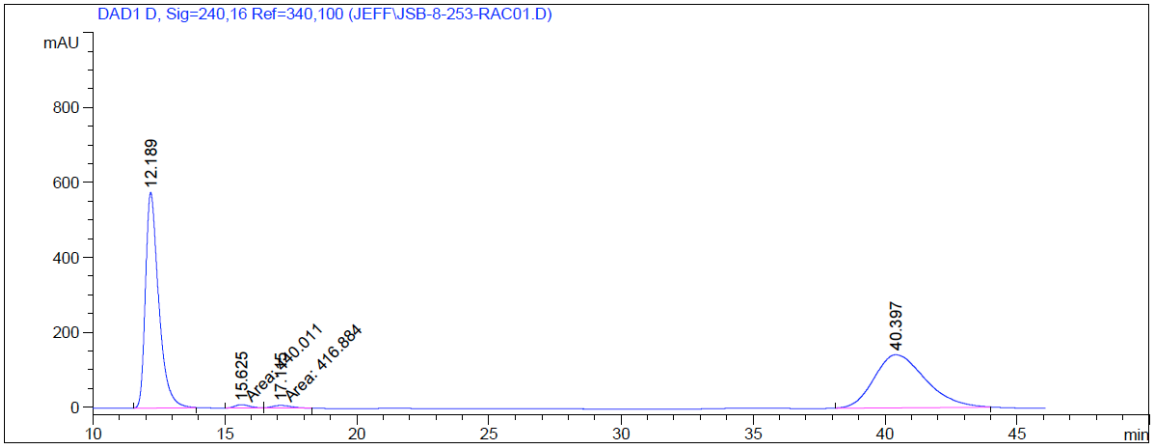


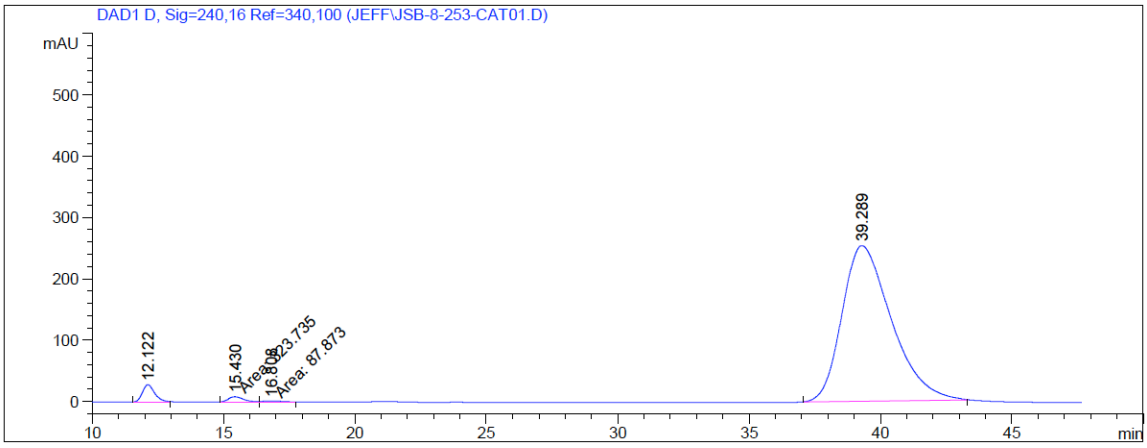


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	10.708	1	BB	391.66644	14.82517	1.5372
2	11.700	1	MM T	69.97772	2.80951	0.2746
3	12.924	1	MM T	279.17813	9.18024	1.0957
4	19.669	1	BB	2.47386e4	429.22754	97.0925

Table 2, entry 4a. Hexanes/iPrOH 97.5/2.5, 1 mL/min, 254 nm, AD-H.

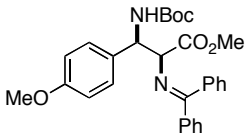


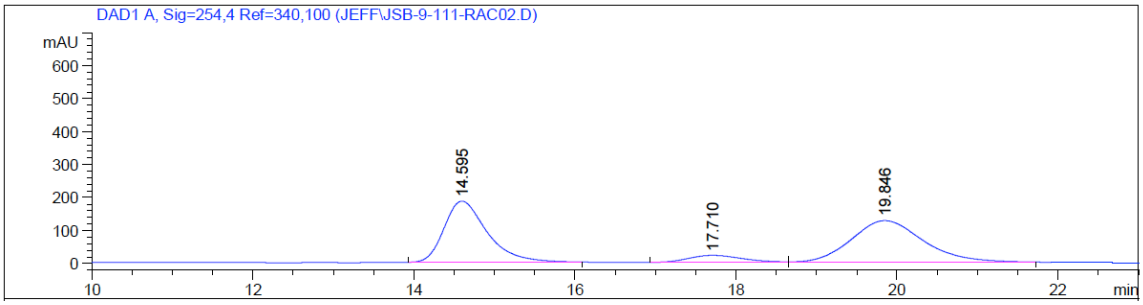


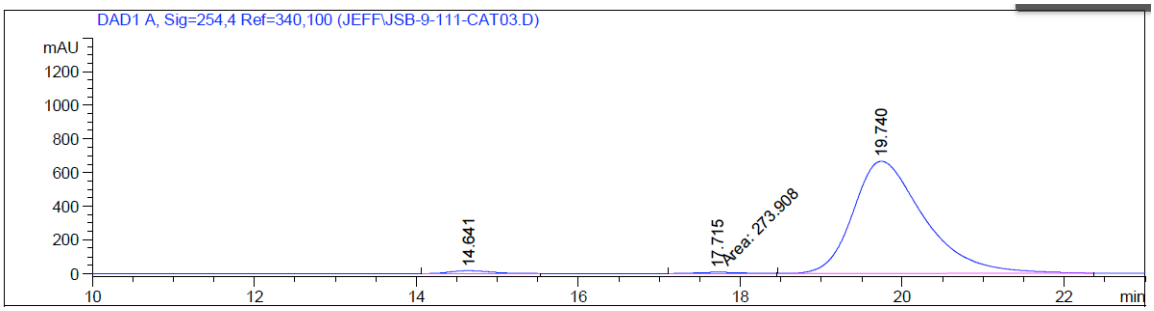


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	12.122	1	BB	899.50934	27.92510	2.6108
2	15.430	1	MF T	323.73456	8.22491	0.9396
3	16.808	1	FM T	87.87297	1.89875	0.2550
4	39.289	1	BB	3.31423e4	253.25838	96.1945

Table 2, entry 4b. Hexanes/iPrOH 93/7, 1 mL/min, 254 nm, AD-H.

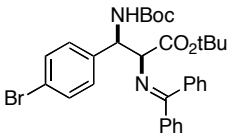


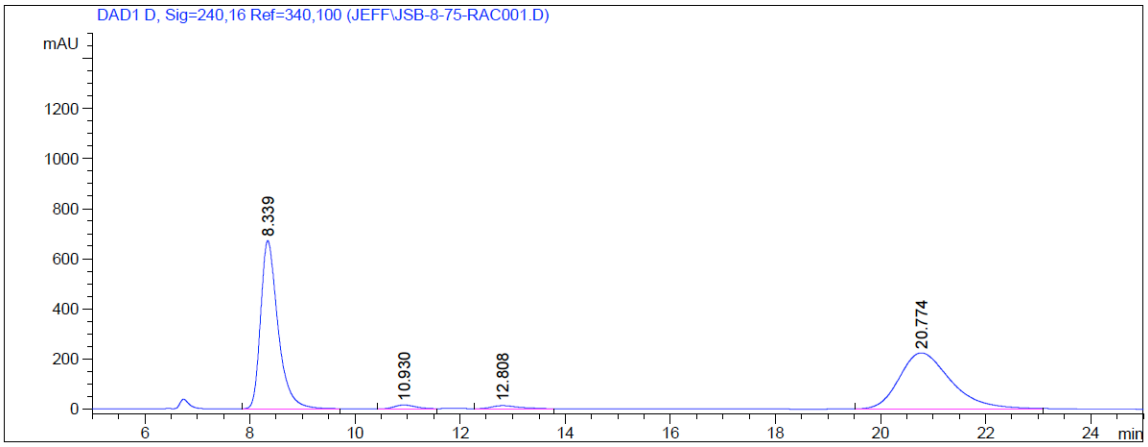


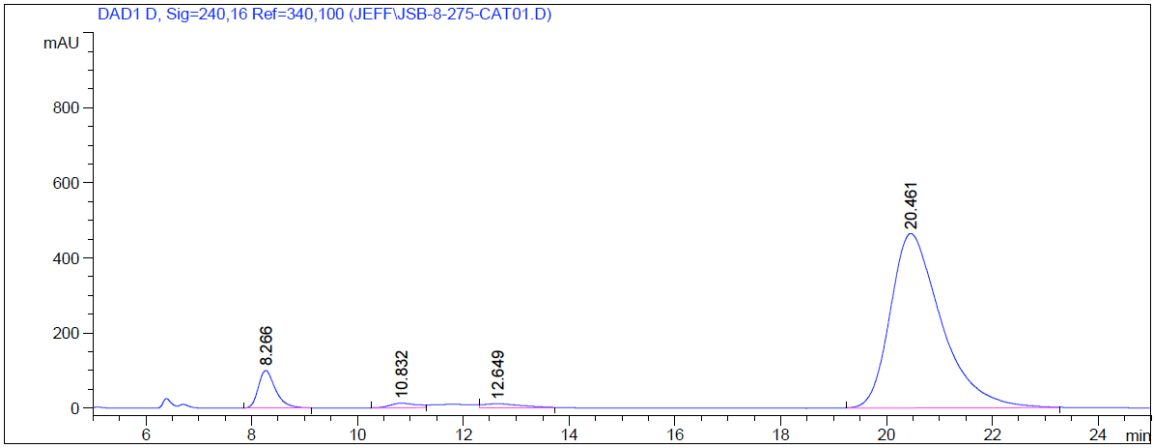


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	14.641	1	BB	550.65881	15.75667	1.3335
2	17.715	1	MM T	273.90805	6.70356	0.6633
3	19.740	1	VB	4.04713e4	665.45734	98.0080

Table 2, entry 5. Hexanes/iPrOH 97.5/2.5, 1 mL/min, 254 nm, AD-H.

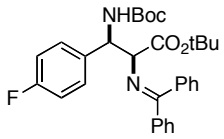


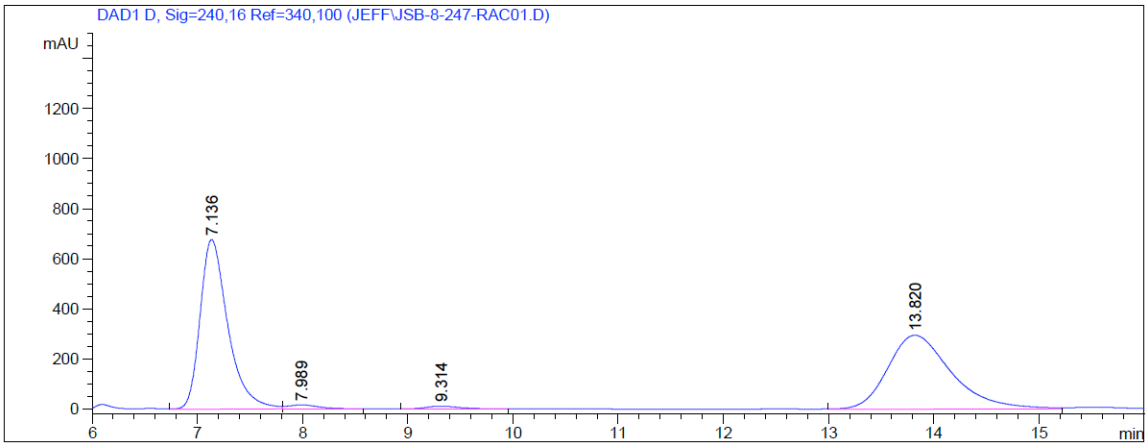


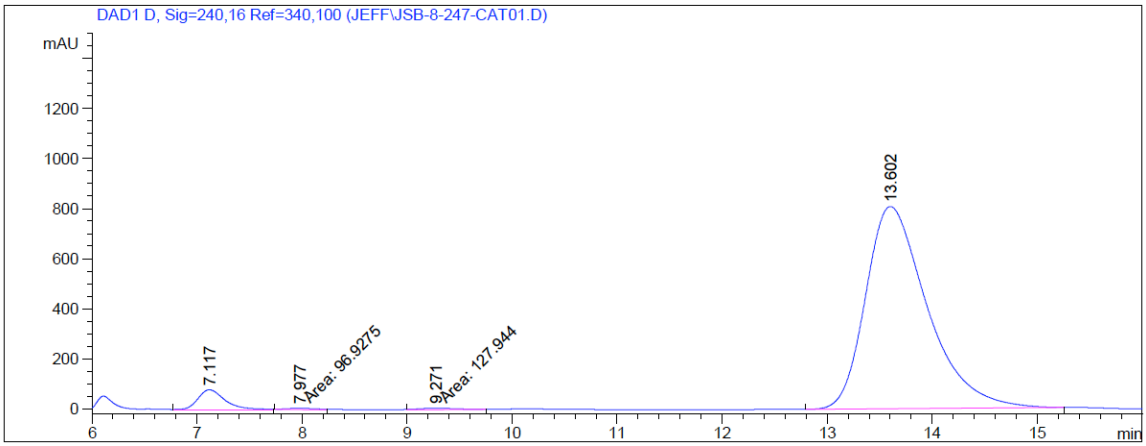


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	8.266	1	BB	2270.04810	100.22453	6.6283
2	10.832	1	BV	453.21527	12.61363	1.3233
3	12.649	1	BB	534.77118	10.79881	1.5615
4	20.461	1	BB	3.09897e4	463.69537	90.4869

Table 2, entry 6. Hexanes/iPrOH 97/3, 1 mL/min, 254 nm, AD-H.

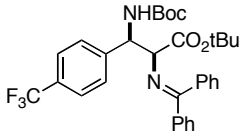


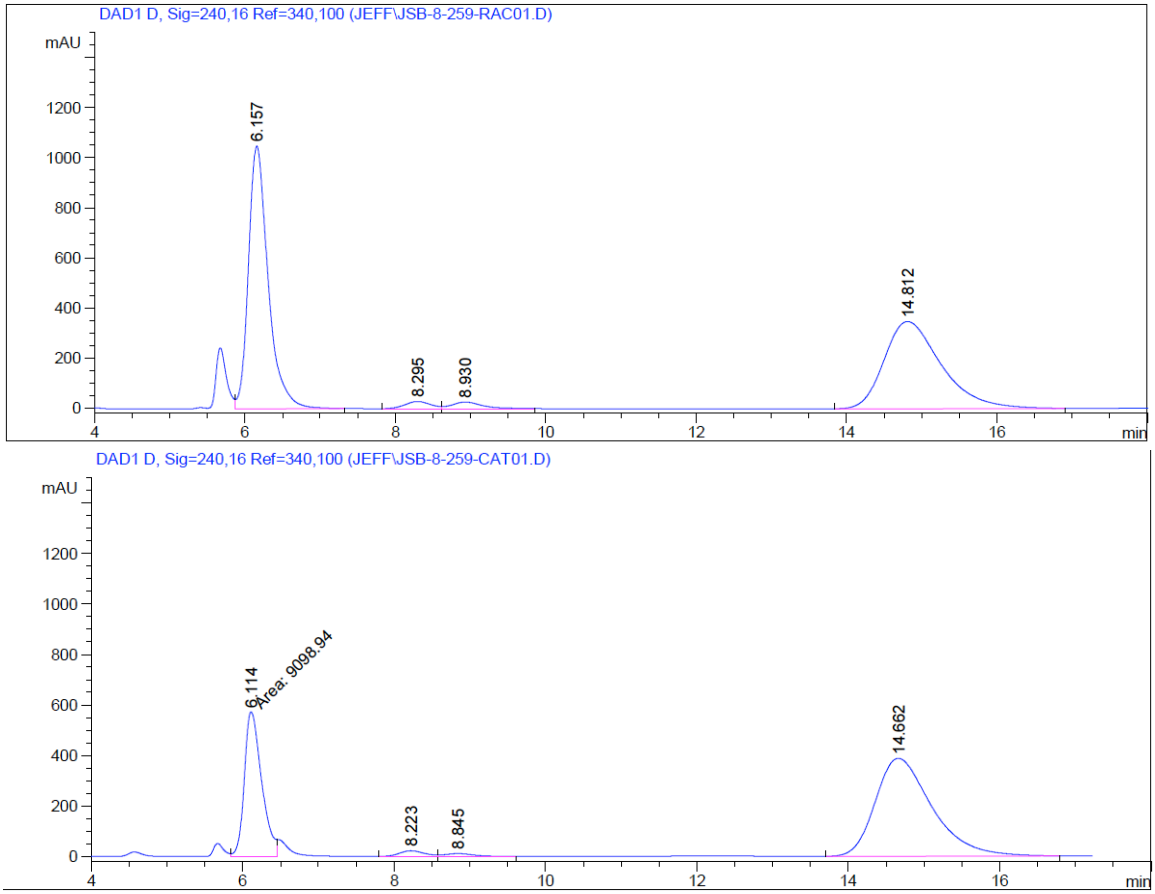




Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	7.117	1	VV	1423.62610	79.83376	4.1091
2	7.977	1	MM T	96.92754	5.31844	0.2798
3	9.271	1	MM T	127.94388	5.65441	0.3693
4	13.602	1	BB	3.29972e4	807.90698	95.2418

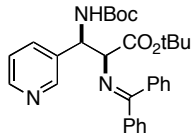
Table 2, entry 7. Hexanes/iPrOH 97/3, 1 mL/min, 254 nm, AD-H.

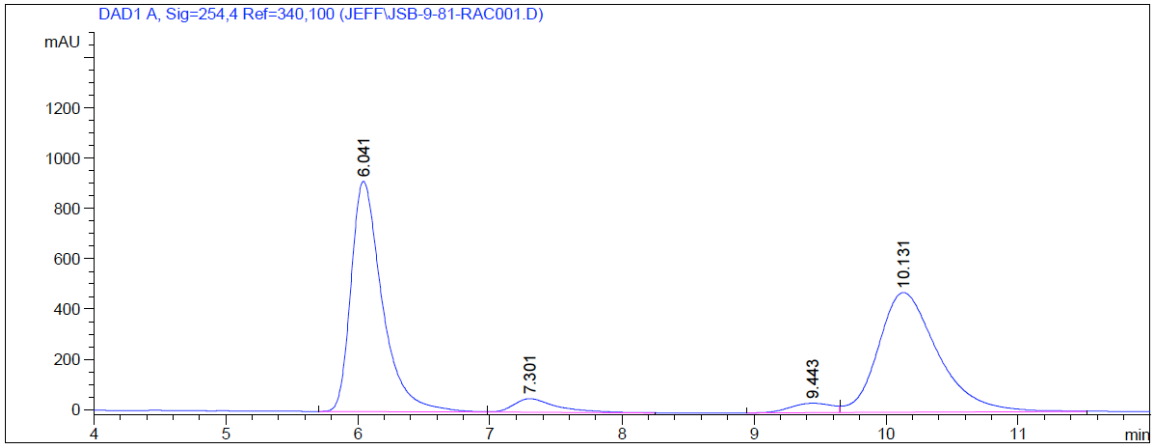


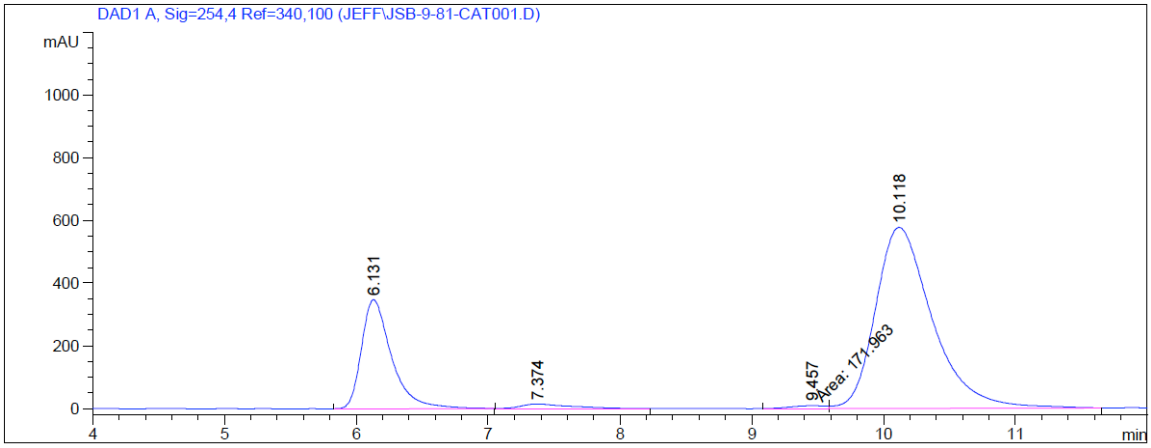


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	6.114	1	MF	9098.93555	572.16376	30.1481
2	8.223	1	BV	522.22644	22.75809	1.7303
3	8.845	1	VB	308.48053	11.64550	1.0221
4	14.662	1	BB	2.02512e4	387.98294	67.0995

Table 2, entry 8a. Hexanes/iPrOH 90/10, 1 mL/min, 254 nm, AD-H.

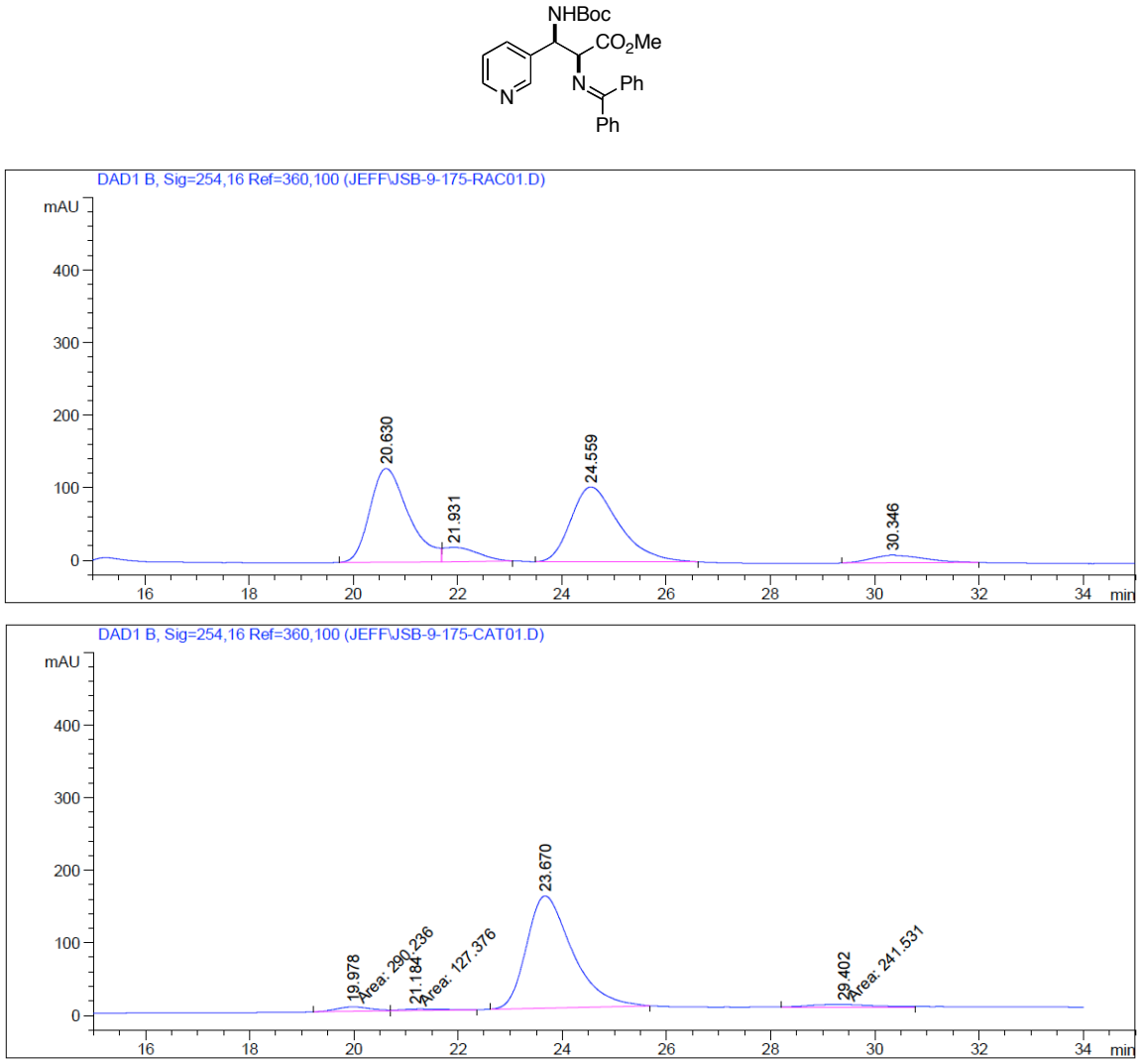






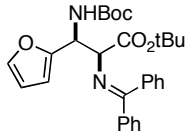
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	6.131	1	BB	5548.53369	348.10938	23.6890
2	7.374	1	BB	399.75662	15.08881	1.7067
3	9.457	1	MM T	171.96277	9.36867	0.7342
4	10.118	1	VB	1.73022e4	577.50574	73.8701

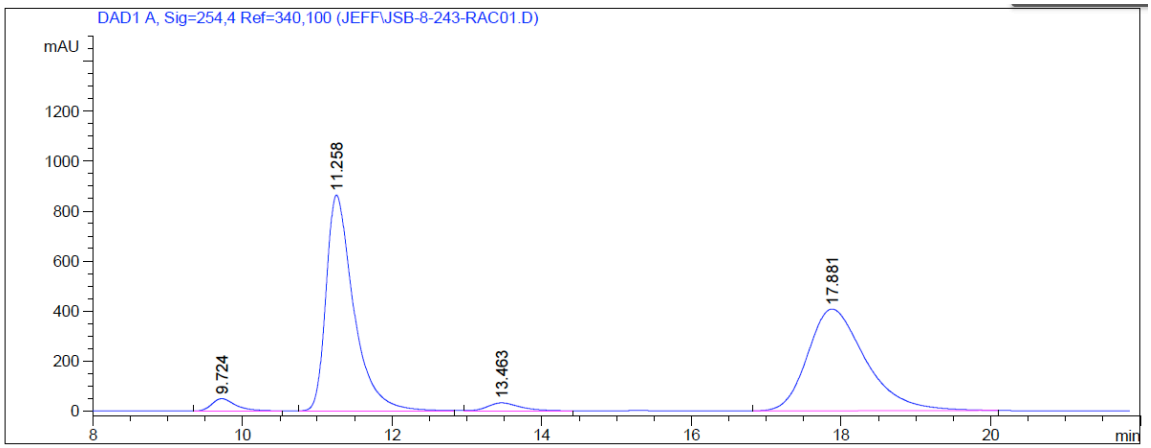
Table 2, entry 8b. Hexanes/iPrOH 92/8, 1 mL/min, 254 nm, AD-H.

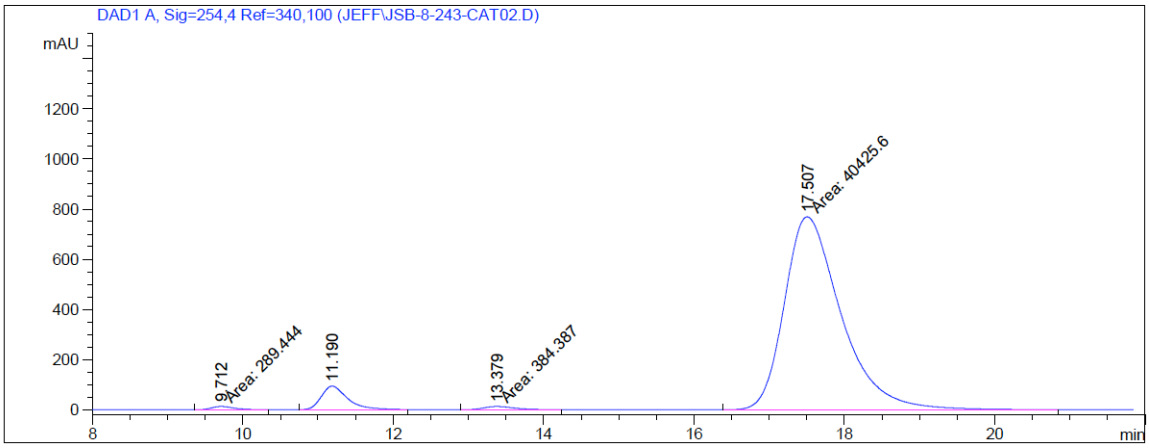


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	19.978	1	MF T	290.23572	6.30632	2.8599
2	21.184	1	FM T	127.37556	2.24767	1.2551
3	23.670	1	BB	9489.40332	154.86331	93.5051
4	29.402	1	MM T	241.53107	3.28834	2.3800

Table 2, entry 9. Hexanes/iPrOH 97.5/2.5, 1 mL/min, 254 nm, AD-H.

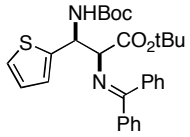


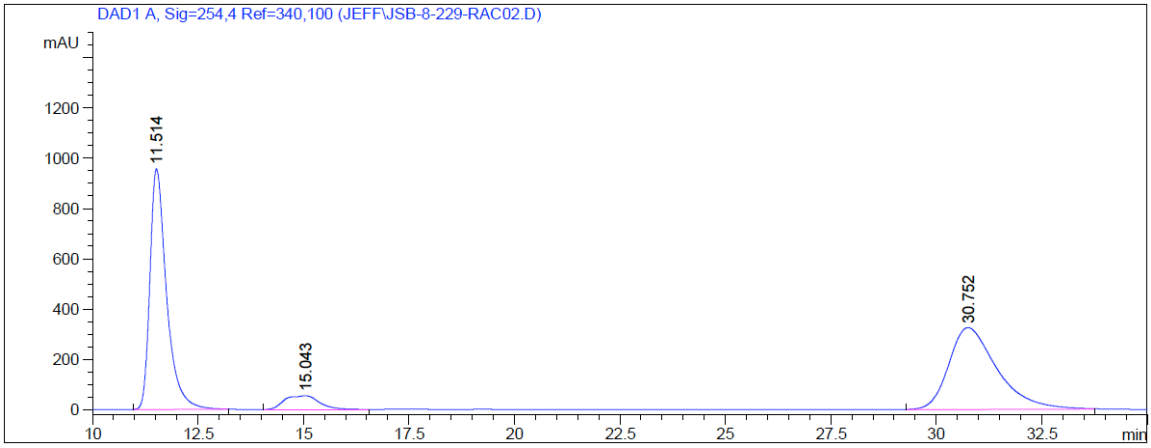


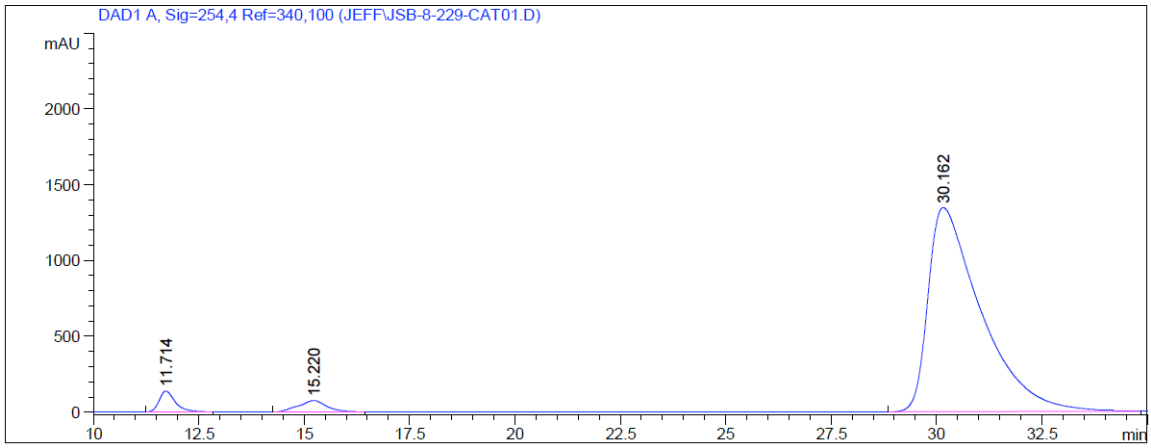


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	9.712	1	MM T	289.44388	13.67431	0.6666
2	11.190	1	BB	2322.95850	93.92095	5.3497
3	13.379	1	MM T	384.38678	13.37536	0.8852
4	17.507	1	MM T	4.04256e4	769.50018	93.0985

Table 2, entry 10. Hexanes/iPrOH 98/2, 1 mL/min, 254 nm, AD-H.

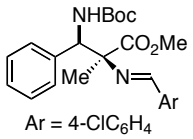


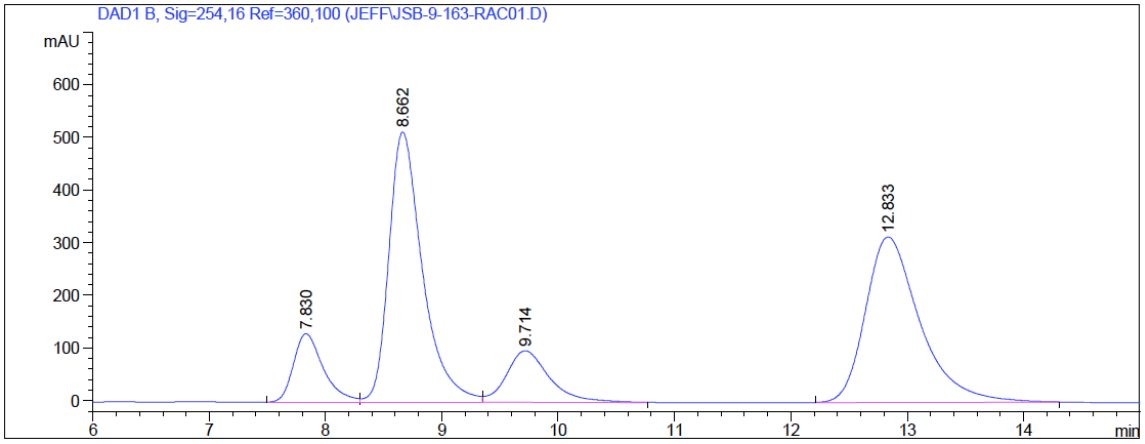


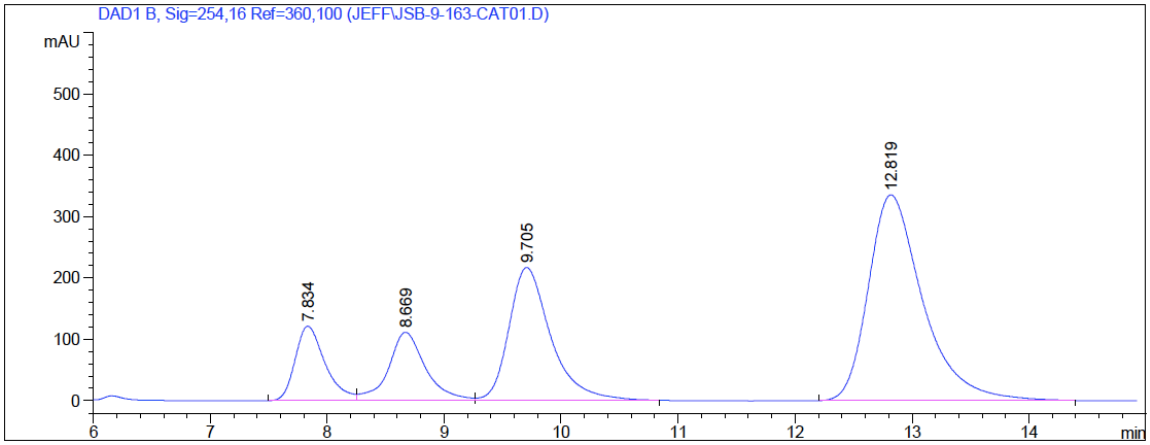


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	11.714	1	BB	3628.57251	137.62589	2.8970
2	15.220	1	BB	3485.18970	75.74220	2.7825
3	30.162	1	BB	1.18140e5	1349.26965	94.3205

Table 2, entry 11. Hexanes/iPrOH 92/8, 1 mL/min, 254 nm, AD-H.

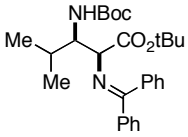


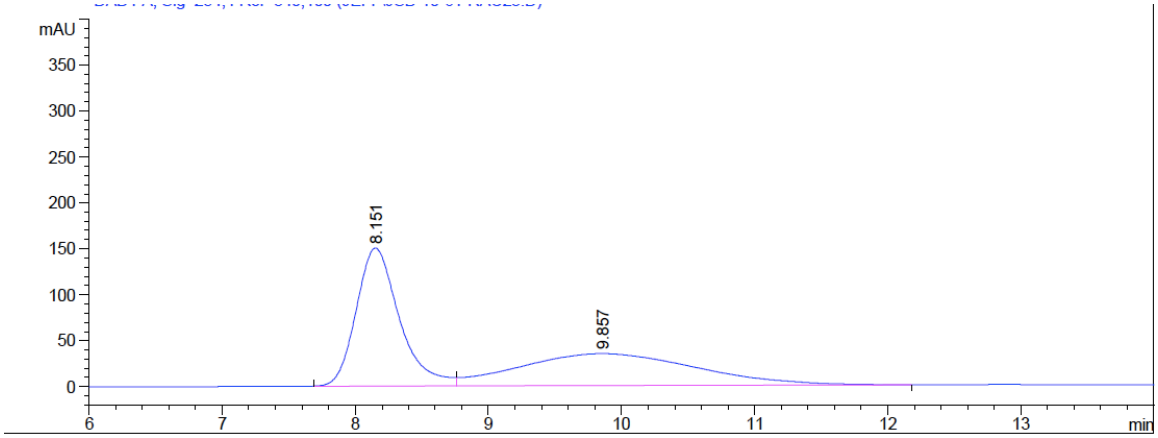


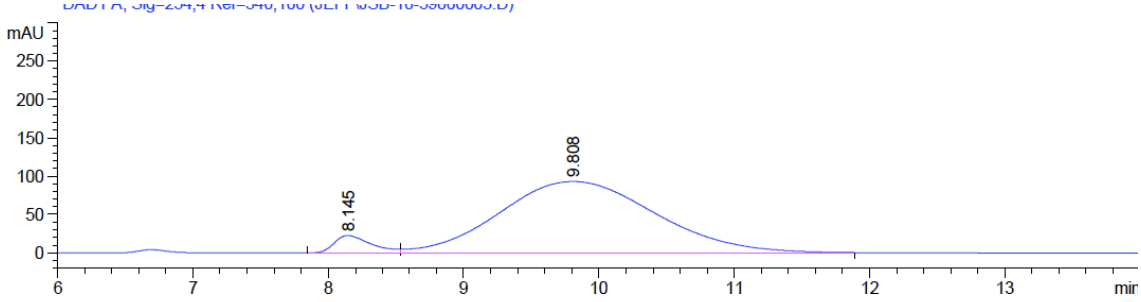


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	7.834	1	BV	2158.01855	121.27816	10.3293
2	8.669	1	VV	2454.08691	111.48518	11.7464
3	9.705	1	VB	5415.38281	216.72227	25.9205
4	12.819	1	BB	1.08648e4	335.12061	52.0039

Equation 2. Hexanes/iPrOH 97.5/2.5, 1 mL/min, 254 nm, AD-H.

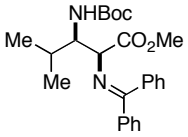


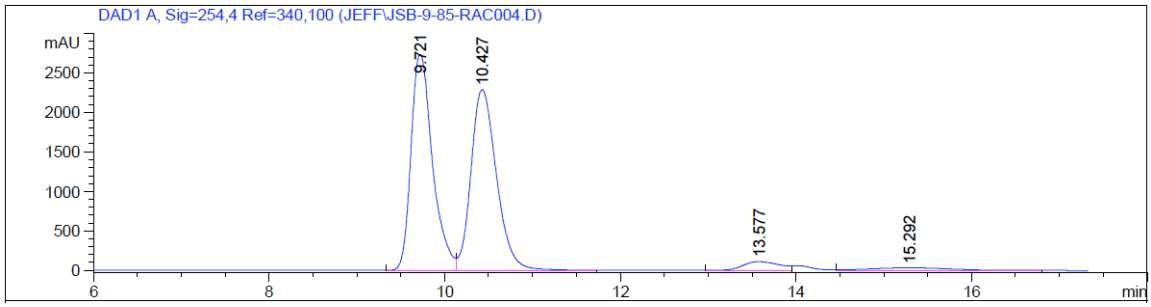


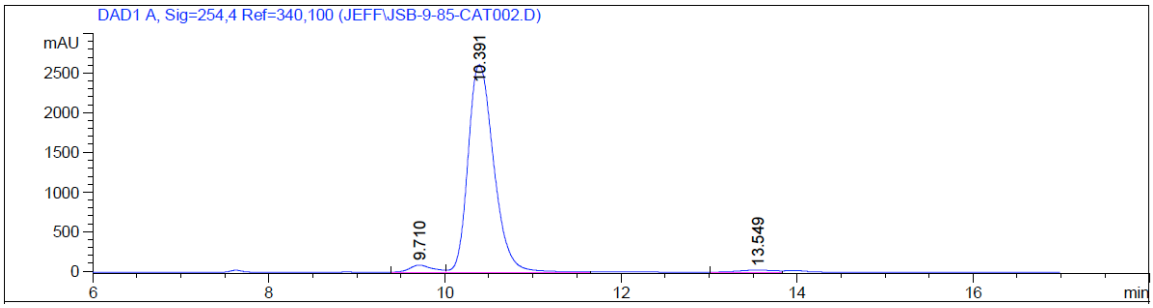


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	8.145	1	BV	426.02167	22.56806	5.4294
2	9.808	1	VB	7422.56201	92.85218	94.5961

Table 3, entry 1. Hexanes/iPrOH 98.5/1.5, 1 mL/min, 254 nm, OD-H.

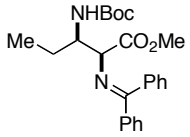




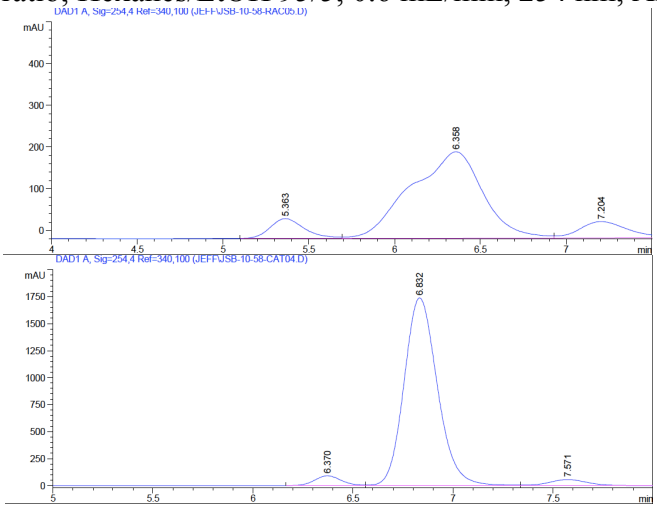


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	9.710	1	BV	1507.01746	87.08316	2.7523
2	10.391	1	VB	5.26348e4	2610.16406	96.1294
3	13.549	1	BV	614.31042	22.66205	1.1219

Table 3, entry 2. Two separate conditions were necessary to determine both dr and ee.

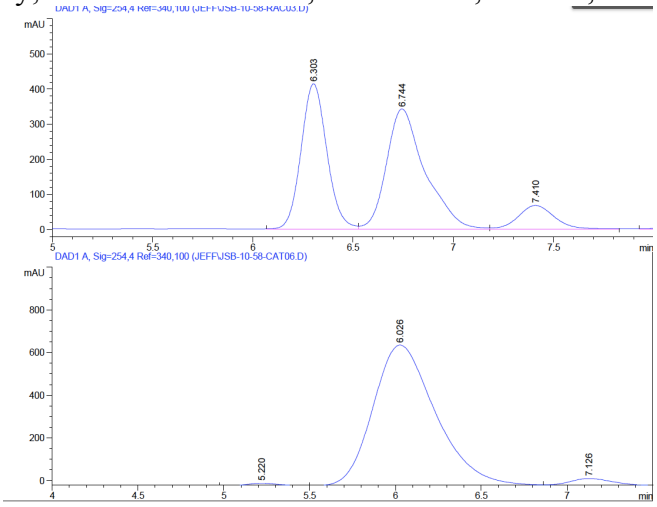


For diastereomeric ratio; Hexanes/EtOH 95/5, 0.6 mL/min, 254 nm, AD-H.



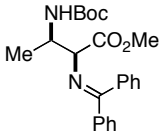
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	6.370	1	BV	832.52649	89.93372	3.8359
2	6.832	1	VV	2.01297e4	1739.02515	92.7485
3	7.571	1	VB	741.31317	55.97463	3.4156

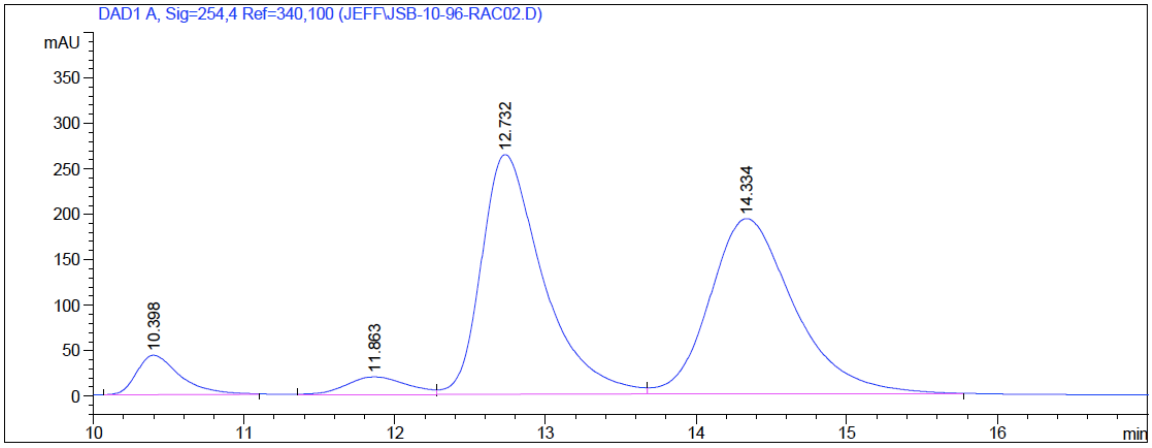
For enantioselectivity; Hexanes/EtOH 99/1, 0.8 mL/min, 254 nm, OD-H.

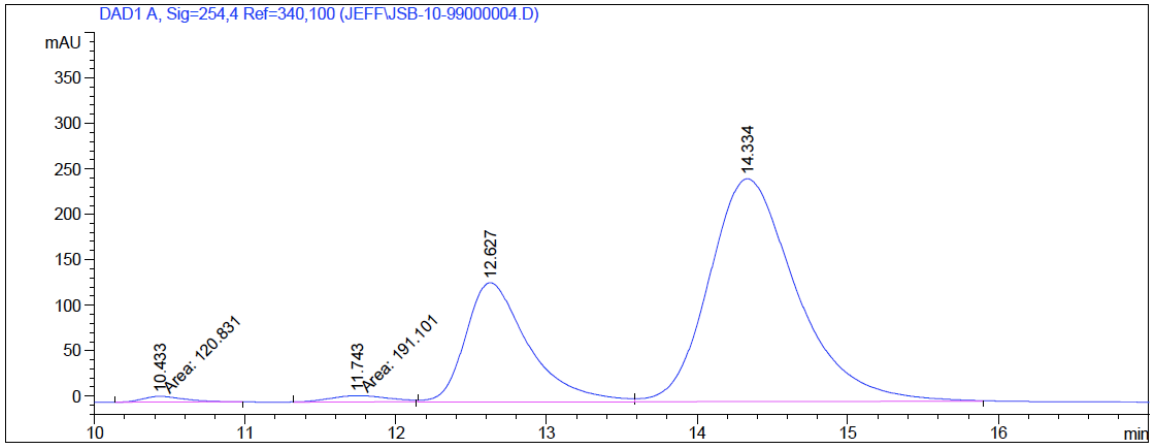


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	5.220	1	BV	171.36241	12.88332	0.9712
2	6.026	1	VV	1.68040e4	659.54633	95.2390
3	7.126	1	VB	668.67212	34.78747	3.7898

Table 3, entry 3. Hexanes/iPrOH 97.5/2.5, 1.0 mL/min, 254 nm, AD-H.

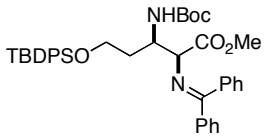


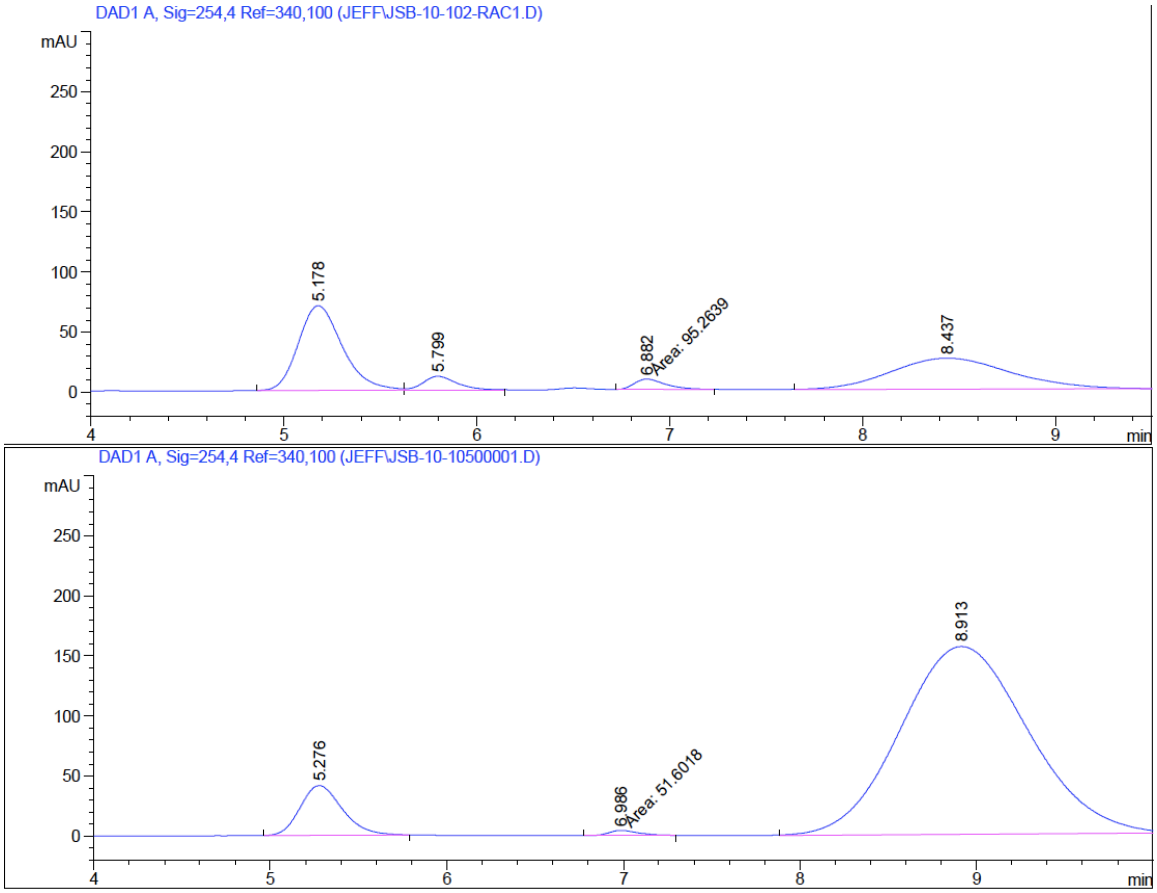




Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	10.433	1	MM T	120.83100	6.29686	0.8661
2	11.743	1	MM T	191.10083	7.00779	1.3698
3	12.627	1	VV	3778.82422	131.00935	27.0867
4	14.334	1	VB	9860.07617	244.93791	70.6773

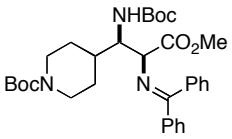
Table 3, entry 4. Hexanes/iPrOH 97.5/2.5, 1.0 mL/min, 254 nm, AD-H.

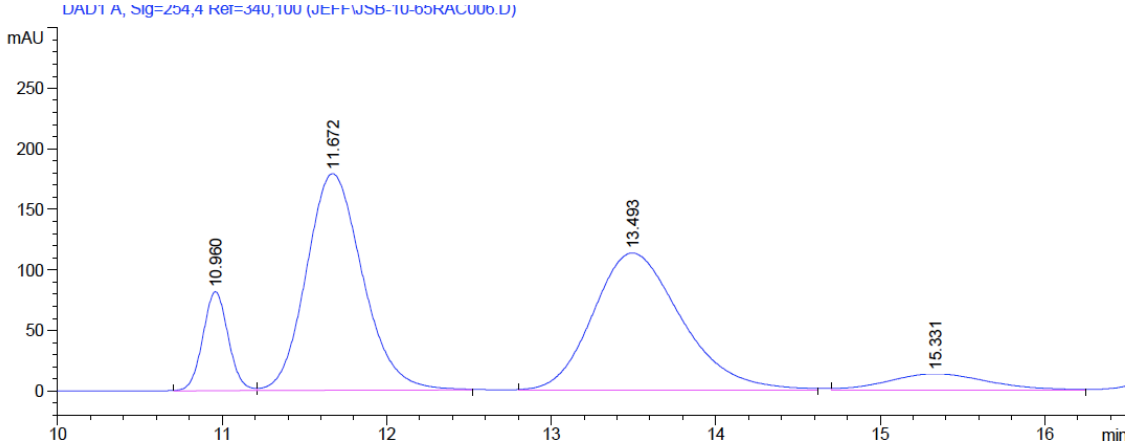


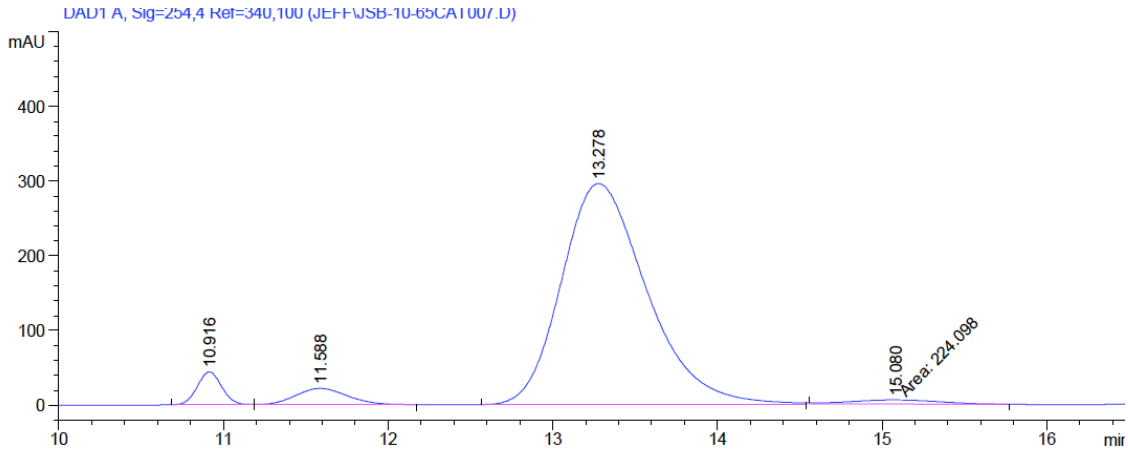


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	5.276	1	BB	696.17712	41.61232	8.0727
2	6.986	1	MM T	51.60179	4.30928	0.5984
3	8.913	1	BV	7876.03076	156.32645	91.3289

Table 3, entry 5. Hexanes/EtOH 99/1, 0.6 mL/min, 254 nm, OD-H.

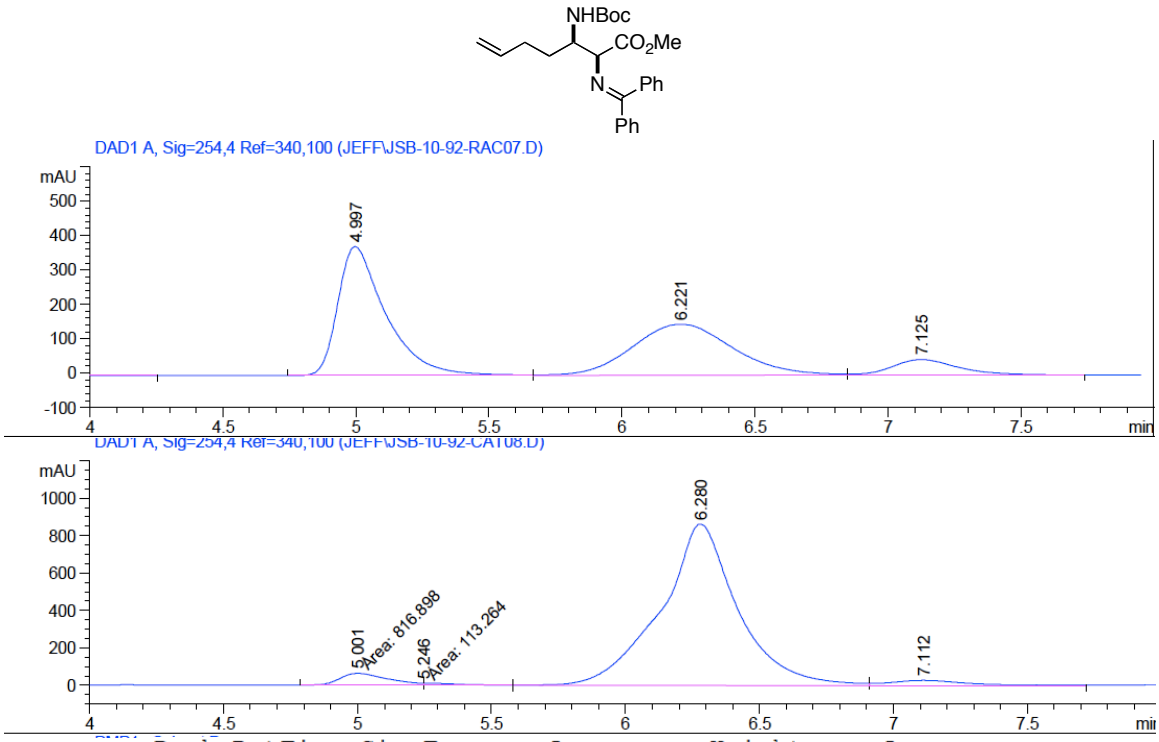






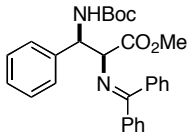
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	10.916	1	BV	466.14639	44.32785	3.9200
2	11.588	1	VB	496.88068	22.08193	4.1785
3	13.278	1	BB	1.07043e4	296.35626	90.0170
4	15.080	1	MM T	224.09766	5.69717	1.8845

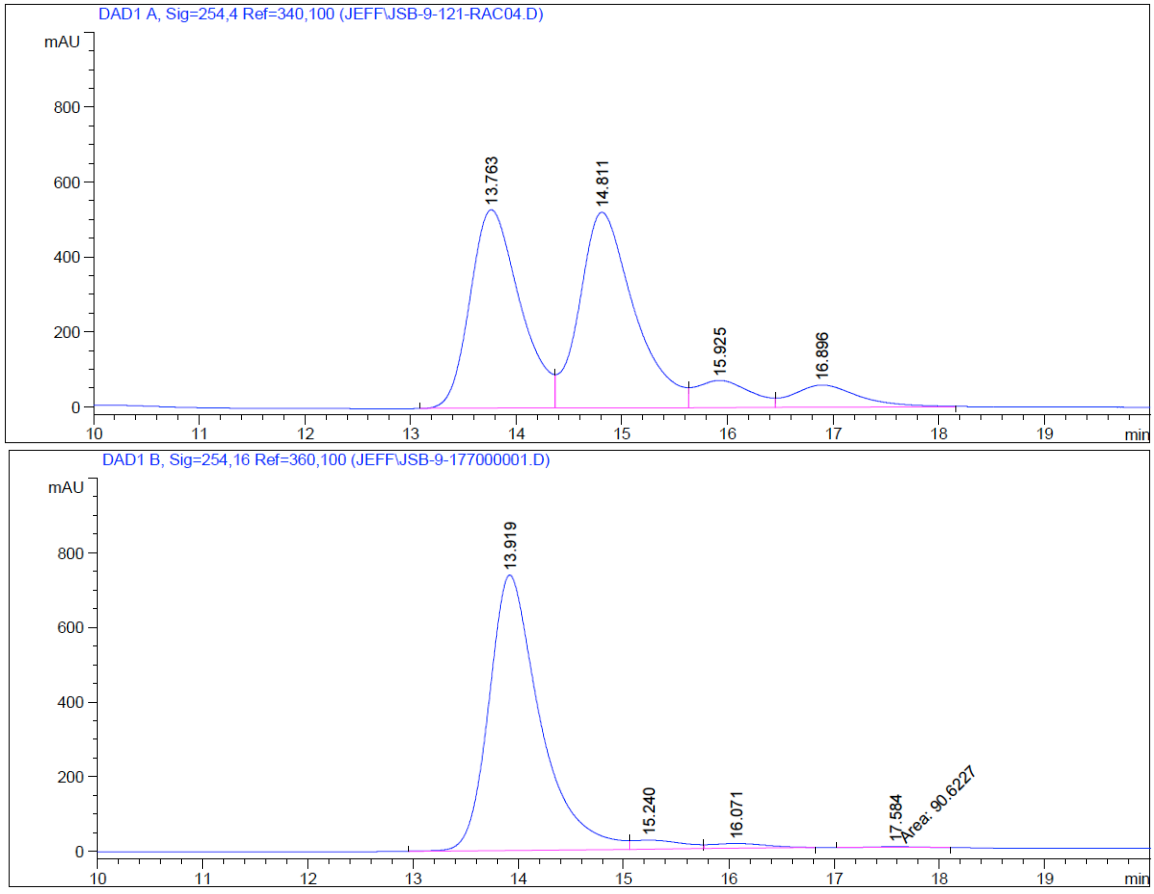
Table 3, entry 6. Hexanes/iPrOH 90/10, 1.0 mL/min, 254 nm, AD-H.



Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	5.001	1	MF	816.89807	64.79798	4.3608
2	5.246	1	FM	113.26373	11.44476	0.6046
3	6.280	1	VV	1.72445e4	861.92310	92.0543
4	7.112	1	VV	558.30371	27.11699	2.9803

Large-scale Mannich reaction. Hexanes/iPrOH 96/4, 1 mL/min, 254 nm, AD-H.





Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	13.919	1	BV	2.49027e4	736.83099	94.7670
2	15.240	1	VV	794.79401	24.02936	3.0246
3	16.071	1	VB	489.70715	12.94617	1.8636
4	17.584	1	MM T	90.62273	2.76254	0.3449