Enantioconvergent Alkylations of Amines by Alkyl Electrophiles: Copper-Catalyzed Nucleophilic Substitutions of Racemic α-Halolactams by Indoles

Agnieszka Bartoszewicz, Carson D. Matier, and Gregory C. Fu*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

Supporting Information

Table of Contents

I. General Information

Ligand (*R*)−**L***, ligand (*S*)−**L***, and mesitylcopper were purchased from Strem Chemicals. Cs_2CO_3 (99.995%) was purchased from Acros Organics. *m*-Xylene (anhydrous, ≥99%) was purchased from Sigma-Aldrich. Unless otherwise noted, materials were purchased from commercial suppliers and used as received.

Microwave-assisted syntheses were performed using a Biotage® Initiator 2.5 microwave reactor.

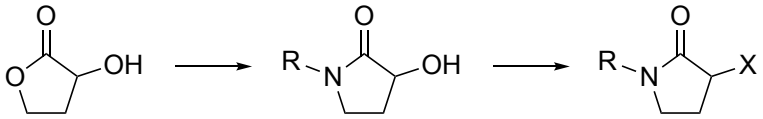
Silicycle SiliaFlash® P60 Silica gel (particle size 40–63 nm) was used for flash chromatography. Biotage® KP-C18-HS support gel (particle size 30–90 μm) was used for reverse-phase flash chromatography. Preparative thin-layer chromatography (TLC) was performed on EDM/Merck TLC Silica gel 60 F_{254} pre-coated plates (0.25 mm).

Analytical HPLC analyses were carried out using an Agilent 1100 Series system with Daicel CHIRALPAK® columns (internal diameter 4.6 mm, column length 25.0 cm, particle size 5 μm). Analytical SFC was performed with a Thar SFC supercritical CO_2 analytical chromatography system with CHIRALPAK® columns (internal diameter 4.6 mm, column length 25.0 cm, particle size 5 μm). Preparative HPLC separations were carried out using an Agilent 1100 Series system with a Daicel CHIRALPAK® IC column (internal diameter 2.0 cm, column length 25.0 cm, particle size 5 μm).

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Ascend 400 (at 400 MHz, 101 MHz, and 162 MHz, respectively), relative to $CHCl_3$ (^1H, δ 7.26; internal), $CDCl_3$ (^{13}C, δ 77.0; internal), and 85% H_3PO_4 (^{31}P, δ 0; external) references. ^{13}C NMR spectra of phosphorus-containing compounds were recorded on a Varian Inova 600 (151 MHz) with ^1H and ^{31}P decoupling. Data for ^1H NMR spectra are reported as follows: chemical shift (δ) (multiplicity, coupling constant (Hz), integration). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent.). IR spectra were recorded on a Perkin Elmer Spectrum BXII spectrometer using thin films deposited on NaCl plates and are reported in wavenumbers (cm^{-1}). Optical rotations were measured on a Jasco P-2000 polarimeter operating at the sodium D-line (589 nm), using a 100 mm path-length cell. HR-MS were acquired using an Agilent 6200 Series TOF with an Agilent G1978A multimode source in electrospray ionization (ESI) mode and a JEOL MSRoute JMS-600H mass spectrometer using fast atom bombardment (FAB).

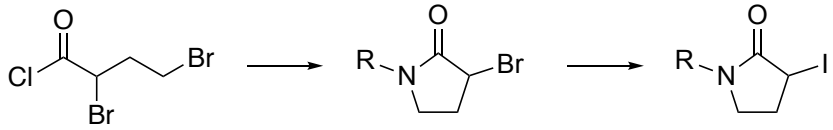
II. Preparation of Electrophiles

The yields have not been optimized.



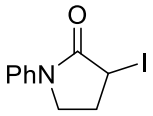
Method A. α-Hydroxy-γ-butyrolactone (10.0 mmol), the amine (12.0 mmol, 1.2 equiv), and *p*-toluenesulfonic acid (1.0 mmol, 10 mol%) were placed in a 10 mL microwave vial and stirred at 220 °C for 10 min under microwave heating. The reaction mixture was then dissolved in CH_2Cl_2 (200 mL) and washed in turn with aqueous HCl (5 M), saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over magnesium sulfate and concentrated to give the α-hydroxy-γ-lactam, which was used without further purification in the subsequent step.

A solution of PPh_3 (13.0 mmol, 1.3 equiv) in CH_2Cl_2 (100 mL) was cooled to 0 °C, and then either iodine or bromine (12.0 mmol, 1.2 equiv) was added. After 10 min of stirring, imidazole (13.0 mmol, 1.3 equiv) and the α-hydroxy-γ-lactam (10.0 mmol) were added. The reaction mixture was allowed to slowly warm to room temperature, and it was stirred at room temperature for 4 h. The reaction mixture was then washed with water, and the organic layer was dried over magnesium sulfate and concentrated. The residue was purified by column chromatography, using hexanes/Et_2O as the eluant.



Method B. 2,4-Dibromobutyryl chloride (10.0 mmol) was added over 10 min to a suspension of the amine (10.0 mmol, 1.0 equiv) and potassium phosphate tribasic (5.0 mmol, 0.5 equiv) in acetonitrile (50 mL) at 0 °C. The reaction mixture was stirred for 1 h, and then aqueous NaOH (50%; 2 mL) was added, and the reaction mixture was stirred overnight. The mixture was then filtered, the solid was washed with CH_2Cl_2 (100 mL), and the combined organic layers were concentrated. The residue was purified by column chromatography, using hexanes/Et_2O as the eluant.

Next, the α-bromo-γ-lactam (10.0 mmol) was added to a suspension of NaI (15.0 mmol, 1.5 equiv) in acetone (50 mL). After 2 h of stirring at room temperature, the reaction mixture was concentrated, and the residue was purified by column chromatography, using hexanes/Et_2O as the eluant.



3-Iodo-1-phenylpyrrolidin-2-one. The title compound was prepared according to Method B (second step) from *3*-bromo-1-phenylpyrrolidin-2-one. After purification by flash

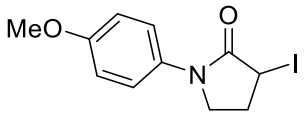
chromatography (30→60% Et_2O in hexanes), the title compound was isolated as a white solid in 85% yield.

^1H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.55 (m, 2H), 7.55 – 7.35 (m, 2H), 7.26 – 7.13 (m, 1H), 4.75 (dd, *J* = 7.1, 2.0 Hz, 1H), 3.97 (ddd, *J* = 9.9, 8.7, 6.3 Hz, 1H), 3.77 (ddd, *J* = 9.8, 7.7, 1.9 Hz, 1H), 2.83 – 2.52 (m, 1H), 2.41 (ddt, *J* = 14.4, 6.2, 1.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 139.1, 129.0, 125.3, 120.0, 47.3, 31.4, 20.9.

FT-IR (thin film): 2946, 1694, 1597, 1494, 1476, 1393, 1300, 1224, 1116, 1035, 875, 762 cm^{-1}.

HR-MS: *m*/*z* 287.9878 ($[M+H]^+$, $C_{10}H_{11}INO^+$ calcd. 287.9885).



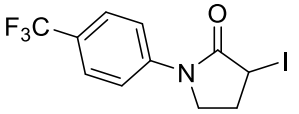
3-Iodo-1-(4-methoxyphenyl)pyrrolidin-2-one. The title compound was prepared according to Method B from 2,4-dibromobutyryl chloride and *p*-anisidine. After purification by flash chromatography (30→70% Et_2O in hexanes), the title compound was isolated as a white solid in 48% yield over 2 steps.

^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.37 (m, 2H), 7.01 – 6.84 (m, 2H), 4.71 (dd, *J* = 7.1, 2.0 Hz, 1H), 3.89 (ddd, *J* = 10.0, 8.7, 6.2 Hz, 1H), 3.81 (s, 3H), 3.69 (ddd, *J* = 9.8, 7.7, 1.9 Hz, 1H), 2.75 – 2.49 (m, 1H), 2.37 (ddt, *J* = 14.5, 6.3, 1.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 157.1, 132.3, 121.8, 114.2, 55.5, 47.8, 31.5, 21.1.

FT-IR (thin film): 2915, 1698, 1512, 1463, 1395, 1369, 1290, 1248, 1178, 1099, 1031, 828, 740 cm^{-1}.

HR-MS: *m*/*z* 317.9985 ($[M+H]^+$, $C_{11}H_{13}INO_2^+$ calcd. 317.9991).



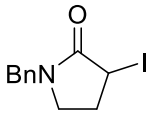
3-Iodo-1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one. The title compound was prepared according to Method B from 2,4-dibromobutyryl chloride and 4-(trifluoromethyl)aniline. After purification by flash chromatography (20→50% Et_2O in hexanes), the title compound was isolated as a yellow solid in 53% yield over 2 steps.

^1H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.73 (m, 2H), 7.77 – 7.55 (m, 2H), 4.77 (dd, *J* = 7.0, 2.1 Hz, 1H), 4.00 (td, *J* = 9.3, 6.3 Hz, 1H), 3.81 (ddd, *J* = 9.8, 7.7, 1.9 Hz, 1H), 2.87 – 2.48 (m, 1H), 2.43 (ddt, *J* = 14.5, 6.3, 2.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 142.5, 126.7 (q, *J* = 32.8 Hz), 126.2 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 271.6 Hz), 119.4, 47.0, 31.1, 20.0.

FT-IR (thin film): 2883, 1703, 1614, 1520, 1479, 1428, 1390, 1320, 1303, 1224, 1120, 1069, 1018, 879, 839 cm^{-1}.

HR-MS: *m*/*z* 355.9756 ($[M+H]^+$, $C_{11}H_{10}F_3INO^+$ calcd. 355.9759).



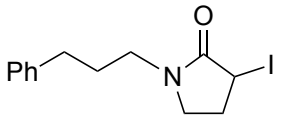
1-Benzyl-3-iodopyrrolidin-2-one. The title compound was prepared according to Method B from α-hydroxy-γ-butyrolactone and benzyl amine. After purification by flash chromatography (30→90% Et_2O in hexanes), the title compound was isolated as a yellow oil in 51% yield over 2 steps.

^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.09 (m, 5H), 4.60 (dd, *J* = 7.3, 1.9 Hz, 1H), 4.53 (d, *J* = 14.7 Hz, 1H), 4.39 (d, *J* = 14.7 Hz, 1H), 3.28 (ddd, *J* = 10.2, 8.4, 6.3 Hz, 1H), 3.11 (ddd, *J* = 9.9, 7.8, 1.8 Hz, 1H), 2.55 – 2.38 (m, 1H), 2.24 (ddt, *J* = 14.5, 6.4, 1.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 135.7, 128.8, 128.1, 127.8, 47.3, 45.2, 31.7, 19.8.

FT-IR (thin film): 3026, 2916, 1690, 1494, 1423, 1358, 1306, 1267, 1125, 1082, 1028, 878, 751 cm^{-1}.

HR-MS: *m*/*z* 302.0045 ($[M+H]^+$, $C_{11}H_{13}INO^+$ calcd. 302.0042).



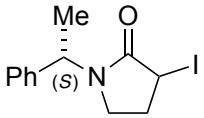
3-Iodo-1-(3-phenylpropyl)pyrrolidin-2-one. The title compound was prepared according to Method A (second step) from 3-hydroxy-1-(3-phenylpropyl)pyrrolidin-2-one. After purification by flash chromatography (40→80% Et_2O in hexanes), the title compound was isolated as a yellow oil in 65% yield.

^1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.09 (m, 5H), 4.54 (dd, *J* = 7.1, 1.8 Hz, 1H), 3.51 – 3.39 (m, 2H), 3.29 (dt, *J* = 13.8, 7.1 Hz, 1H), 3.20 (ddd, *J* = 9.8, 7.7, 1.7 Hz, 1H), 2.80 – 2.55 (m, 2H), 2.52 – 2.31 (m, 1H), 2.26 (ddt, *J* = 14.4, 6.3, 1.8 Hz, 1H), 1.93 (p, *J* = 7.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 141.3, 128.5, 128.3, 126.1, 45.7, 43.0, 33.0, 31.8, 28.6, 20.2.

FT-IR (thin film): 3056, 2929, 1691, 1590, 1483, 1435, 1308, 1279, 1194, 1118, 1070, 1028, 997, 880, 754, 722 cm^{-1}.

HR-MS: *m*/*z* 330.0354 ($[M+H]^+$, $C_{13}H_{17}INO^+$ calcd. 330.0355).



The diastereomers are formed in a 1:1 mixture, and they were used as such in the experiment described in Figure 4. For the purpose of characterization, they were separated by column chromatography.

3-Iodo-1-(1-phenylethyl)pyrrolidin-2-one. The title compound was prepared according to Method A from α-hydroxy-γ-butyrolactone and (*S*)-1-phenylethylamine. After purification by flash chromatography (30→80% Et_2O in hexanes), the title compounds were isolated as white solids in 27% and 29% yield over 2 steps.

Diastereomer 1:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.29 (m, 5H), 5.46 (q, *J* = 7.1 Hz, 1H), 4.59 (dd, *J* = 6.8, 1.8 Hz, 1H), 3.53 – 3.17 (m, 1H), 3.05 – 2.72 (m, 1H), 2.42 – 2.06 (m, 2H), 1.55 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 139.7, 128.6, 127.7, 127.1, 50.0, 41.0, 31.7, 20.9, 14.8.

FT-IR (thin film): 3025, 2969, 2934, 1670, 1478, 1440, 1425, 1344, 1309, 1282, 1227, 1178, 1129, 1053, 784, 701 cm^{-1}.

$[\alpha]^{25}_D$ (100% ee): –110° (c = 1.0, $CHCl_3$).

HR-MS: *m*/*z* 316.0196 ($[M+H]^+$, $C_{12}H_{15}INO^+$ calcd. 316.0198).

Diastereomer 2:

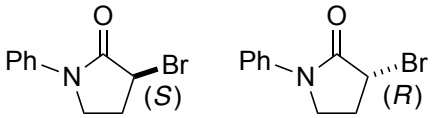
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.29 (m, 5H), 5.50 (q, *J* = 7.1 Hz, 1H), 4.61 (dd, *J* = 7.2, 1.9 Hz, 1H), 3.22 – 3.09 (m, 1H), 3.00 – 2.84 (m, 1H), 2.62 – 2.38 (m, 1H), 2.20 (ddt, *J* = 14.4, 6.3, 1.8 Hz, 1H), 1.60 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 139.1, 128.7, 127.7, 127.1, 49.5, 41.0, 31.7, 20.6, 16.2.

FT-IR (thin film): 3027, 2982, 2875, 1673, 1485, 1449, 1419, 1346, 1305, 1277, 1223, 1178, 1117, 877, 699, 657 cm^{-1}.

$[\alpha]^{25}_D$ (100% ee): –140° (c = 1.0, $CHCl_3$).

HR-MS : *m*/*z* 316.0189 ($[M+H]^+$, $C_{12}H_{15}INO^+$ calcd. 316.0198).



(*3S*)-*3*-Bromo-1-phenylpyrrolidin-2-one and (*3R*)-*3*-bromo-1-phenylpyrrolidin-2-one [77868-83-8]. A racemic mixture of the title compounds was prepared similarly to a procedure described in the literature (Method B).[1] The pure enantiomers of the title compound were obtained from the racemate by separation on a preparative Diacel CHIRALPAK® IC column; 45% *i*-PrOH in hexanes, 10.0 mL/min flow-rate; retention times: 24.9 min (*S*-enantiomer), 32.8 min (*R*-enantiomer).

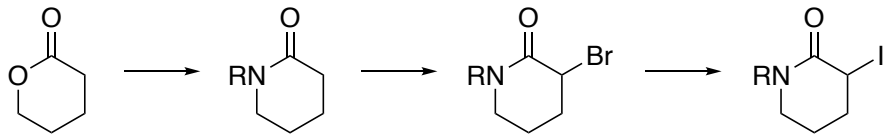
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.61 (m, 2H), 7.50 – 7.34 (m, 2H), 7.27 – 7.18 (m, 1H), 4.62 (dd, *J* = 7.0, 2.8 Hz, 1H), 4.09 (ddd, *J* = 9.8, 7.9, 6.6 Hz, 1H), 3.86 (ddd, *J* = 10.1, 7.8, 2.6 Hz, 1H), 2.88 – 2.61 (m, 1H), 2.49 (ddt, *J* = 14.3, 6.6, 2.7 Hz, 1H).

(*S*)-enantiomer $[\alpha]^{25}_D$ (100% ee): 117° (c = 1.0, $CHCl_3$).

(*R*)-enantiomer $[\alpha]^{25}_D$ (100% ee): –118° (c = 1.0, $CHCl_3$).

---

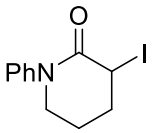
(1) Lin, X.; Chen, W.; Qiu, Z.; Guo, L.; Zhu, W.; Li, W.; Wang, Z.; Zhang, W.; Zhang, Z.; Rong, Y.; Zhang, M.; Yu, L.; Zhong, S.; Zhao, R.; Wu, X.; Wong, J. C.; Tang, G. Design and Synthesis of Orally Bioavailable Aminopyrrolidinone Histone Deacetylase 6 Inhibitors. *J. Med. Chem.* **2015,** *58*, 2809−2820.



Method C. δ-Valerolactone (10.0 mmol), the amine (12.0 mmol, 1.2 equiv), and *p*-toluenesulfonic acid (1.0 mmol, 10 mol%) were placed in a 10 mL microwave vial and stirred at 220 °C for 10 min under microwave heating. The reaction mixture was then dissolved in CH_2Cl_2 (200 mL) and washed in turn with aqueous HCl (5 M), saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over magnesium sulfate and concentrated to give a residue that was purified by column chromatography, using hexanes/Et_2O as the eluent, to give the δ-lactam.

Next, *s*-BuLi (1.0 M in hexanes; 11.0 mL) was added to a solution of the δ-lactam (10.0 mmol) in THF (200 mL) at −78 °C. The reaction mixture was stirred for 30 min, and then it was further cooled to −100 °C, and bromine (10.0 mmol, 1.0 equiv) was added dropwise over 2 min. The reaction was then immediately quenched at −100 °C by the addition of water (10 mL). The reaction mixture was allowed to slowly warm to room temperature, and then it was washed with aqueous sodium thiosulfate and then with aqueous ammonium chloride. The organic layer was dried over magnesium sulfate and concentrated, and the residue was purified by column chromatography, using hexanes/Et_2O as the eluant.

Next, the α-bromo-δ-lactam (10.0 mmol) was added to a suspension of NaI (15.0 mmol, 1.5 equiv) in acetone (50 mL). After 2 h of stirring at room temperature, the reaction was concentrated, and the residue was purified by column chromatography, using hexanes/Et_2O as the eluant.



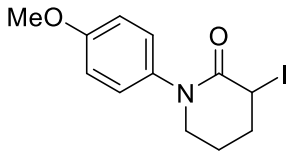
3-Iodo-1-phenylpiperidin-2-one. The title compound was prepared according to Method C from δ-valerolactone and aniline. In the first step, 1-phenylpiperidin-2-one was obtained in 58% yield. In the second step, after purification by flash chromatography (50→90% Et_2O in hexanes), 3-bromo-1-phenylpiperidin-2-one was obtained in 53% yield. In the third step, after purification by flash chromatography (50→90% Et_2O in hexanes), the title compound was obtained in 92% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 2H), 7.31 – 7.24 (m, 3H), 5.00 (ddd, *J* = 4.7, 3.2, 1.4 Hz, 1H), 3.94 (ddd, *J* = 12.1, 10.9, 5.0 Hz, 1H), 3.76 (dddd, *J* = 12.2, 5.7, 3.3, 1.4 Hz, 1H), 2.60 – 2.40 (m, 1H), 2.42 – 2.29 (m, 1H), 2.32 – 2.17 (m, 1H), 2.05 – 1.92 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 142.9, 129.1, 127.0, 125.6, 51.2, 32.7, 23.5, 21.0.

FT-IR (thin film): 2946, 1651, 1595, 1492, 1417, 1346, 1310, 1240, 1173, 763 cm^{-1}.

HR-MS: *m*/*z* 302.0051 ([M+H]$^+$, $C_{11}H_{13}INO^+$ calcd. 302.0042).



3-Iodo-1-(4-methoxyphenyl)piperidin-2-one. The title compound was prepared according to Method C from 3-bromo-1-(4-methoxyphenyl)piperidin-2-one. After purification by flash chromatography (50→100% Et_2O in hexanes), the title product was obtained in 71% yield as a white solid.

^1H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.10 (m, 2H), 7.03 – 6.78 (m, 2H), 4.99 (ddd, *J* = 4.7, 3.1, 1.4 Hz, 1H), 3.89 (ddd, *J* = 12.3, 10.9, 5.0 Hz, 1H), 3.83 (s, 3H), 3.76 – 3.67 (m, 1H), 2.55 – 2.39 (m, 1H), 2.39 – 2.29 (m, 1H), 2.29 – 2.14 (m, 1H), 2.07 – 1.92 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 158.2, 135.7, 126.8, 114.4, 55.5, 51.5, 32.7, 23.6, 21.0.

FT-IR (thin film): 2953, 2833, 1651, 1605, 1510, 1440, 1345, 1317, 1298, 1241, 1173, 1148, 1032, 830 cm^{-1}.

HR-MS: *m*/*z* 332.0160 ($[M+H]^+$, $C_{12}H_{15}INO_2^+$ calcd. 332.0147).

III. Copper-Catalyzed Enantioconvergent Alkylations

General Procedure. In a nitrogen-filled glovebox, an oven-dried 4 mL amber-glass vial was charged with the nucleophile (0.250 mmol) and a solution of mesitylcopper[2] (4.6 mg, 0.025 mmol) in *m*-xylene (500 μL). A stir bar was added, and the vial was closed with a screw cap. The mixture was stirred for 10 min, and then a solution of (*R*)–**L*** (17.7 mg, 0.050 mmol) in *m*-xylene (500 μL) was added, and the vial was re-capped. The mixture was stirred for 10 min, and then the electrophile (0.375 mmol) was added. The reaction mixture became homogeneous after ~5 min, at which time Cs_2CO_3 (0.250–0.400 mmol) was added. The vial was re-capped and wrapped thoroughly with electrical tape in order to keep the reaction in the dark. The vial was removed from the glovebox, and the reaction mixture was stirred vigorously (1500 rpm; adequate stirring is necessary in order to achieve full conversion) at ~23-26 °C (because lower ee is observed at higher temperature, the vial was suspended above the magnetic stirrer, and a fan was used to avoid heating by the magnetic stirrer (Figure S–1)). After the indicated time, the reaction mixture was directly transferred to the top of a column of silica gel; the reaction vial was washed with toluene (2 mL) and then CH_2Cl_2 (1 mL), and the washings were also applied to the top of the column. The product was purified by column chromatography, using the indicated solvent system.

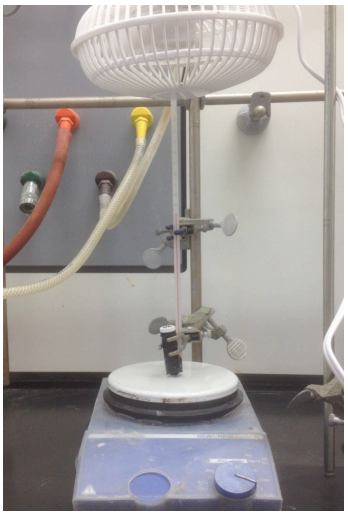
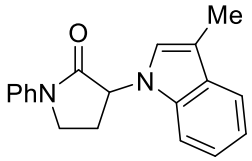


Figure S–1. Reaction setup.

(2) Mesitylcopper can be purchased from Strem Chemicals or prepared using a previously described procedure: Tsuda, T.; Yazawa, T.; Watanabe, K.; Fujii, T.; Saegusa, T. Preparation of Thermally Stable and Soluble Mesitylcopper(I) and Its Application in Organic Synthesis. *J. Org. Chem.* **1981,** *46*, 192–194.



3-(3-Methyl-1*H*-indol-1-yl)-1-phenylpyrrolidin-2-one (Table 2, entry 1). The title compound was prepared according to the General Procedure from 3-iodo-1-phenylpyrrolidin-2-one (108 mg, 0.375 mmol) and 3-methyl-1*H*-indole (32.8 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 1.8 equiv of Cs_2CO_3 (147 mg, 0.450 mmol). The reaction was run for 72 h at 23-25 °C. After purification by flash chromatography (20→50% Et_2O in hexanes) and reverse phase chromatography (0→60% MeOH in H_2O), the title compound was isolated as a white solid in 72% yield (52 mg) and 86% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 74% yield (54 mg) and 89% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IC column; 35% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 22.5 min (minor), 26.5 min (major) for (*R*)−**L***.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.67 (m, 2H), 7.62 – 7.60 (m, 1H), 7.53 – 7.35 (m, 2H), 7.30 – 7.27 (m, 1H), 7.27 – 7.21 (m, 2H), 7.18 – 7.14 (m, 1H), 6.97 (q, *J* = 1.1 Hz, 1H), 5.31 (dd, *J* = 10.1, 8.7 Hz, 1H), 4.06 – 3.96 (m, 2H), 2.88 – 2.74 (m, 1H), 2.53 – 2.37 (m, 1H), 2.36 (d, *J* = 1.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 139.1, 136.4, 129.3, 129.1, 125.2, 123.4, 121.9, 119.8, 119.4, 119.3, 112.4, 109.1, 57.9, 45.0, 26.5, 9.7.

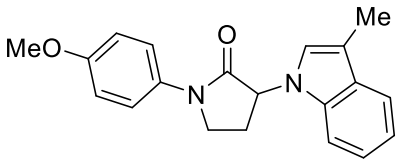
FT-IR (thin film): 3045, 2915, 1704, 1598, 1500, 1462, 1394, 1370, 1307, 1237, 1199, 758, 739, 691 cm^{-1}.

$[\alpha]^{25}_D$ = –54° (c = 1.0, $CHCl_3$); 86% ee from (*R*)−**L***.

HR-MS: *m*/*z* 291.1495 ($[M+H]^+$, $C_{19}H_{19}N_2O^+$ calcd. 291.1497).

Eq 1. The title compound was also prepared using 3-bromo-1-phenylpyrrolidin-2-one (90.0 mg, 0.375 mmol) and was isolated in 58% yield (42 mg) and 88% ee with (*R*)−**L*** and in 63% yield (46 mg) and 87% ee with (*S*)−**L***.

Eq 1. The title compound was also prepared using 3-bromo-1-phenylpyrrolidin-2-one (120 mg, 0.50 mmol) and was isolated in 83% yield (60 mg) and 88% ee with (*R*)−**L*** and in 87% yield (63 mg) and 86% ee with (*S*)−**L***.



1-(4-Methoxyphenyl)-3-(3-methyl-1*H*-indol-1-yl)pyrrolidin-2-one (Table 2, entry 2). The title compound was prepared according to the General Procedure from 3-iodo-1-(4-methoxyphenyl)pyrrolidin-2-one (119 mg, 0.375 mmol) and 3-methyl-1*H*-indole (32.8 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 2.2 equiv of Cs_2CO_3 (179 mg, 0.550 mmol). The reaction was run for 72 h at 23-25 °C. After purification by flash

chromatography (20→80% Et_2O in hexanes) and reverse phase chromatography (0→70% MeOH in H_2O), the title compound was isolated as a white solid in 83% yield (66 mg) and 90% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 72% yield (58 mg) and 92% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IA column; 30% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 27.3 min (minor), 31.4 min (major) for (*R*)−**L***.

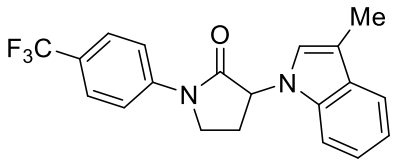
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.58 (m, 3H), 7.37 – 7.11 (m, 3H), 7.03 – 6.91 (m, 3H), 5.27 (dd, *J* = 9.9, 8.7 Hz, 1H), 4.02 – 3.89 (m, 2H), 3.85 (s, 3H), 2.85 – 2.69 (m, 1H), 2.47 – 2.29 (m, 1H), 2.36 (d, *J* = 1.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 157.0, 136.4, 132.3, 129.3, 123.4, 121.8, 121.5, 119.3, 119.2, 114.2, 112.1, 109.1, 57.7, 55.5, 45.3, 26.5, 9.7.

FT-IR (thin film): 3049, 2915, 1697, 1512, 1463, 1395, 1290, 1249, 1179, 1032, 828, 740 cm^{-1}.

$[\alpha]^{25}_D$ = –60° (c = 1.0, $CHCl_3$); 90% ee from (*R*)−**L***.

HR-MS: *m*/*z* 321.1601 ($[M+H]^+$, $C_{20}H_{21}N_2O_2^+$ calcd. 321.1603).



3-(3-Methyl-1*H*-indol-1-yl)-1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one (Table 2, entry 3). The title compound was prepared according to the General Procedure from 3-iodo-1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one (133 mg, 0.375 mmol) and 3-methyl-1*H*-indole (32.8 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 1.8 equiv of Cs_2CO_3 (147 mg, 0.450 mmol). The reaction was run for 72 h at 23-25 °C. After purification by flash chromatography (20→60% Et_2O in hexanes) and reverse phase chromatography (0→80% MeOH in H_2O), the title compound was isolated as a white solid in 75% yield (67 mg) and 90% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 71% yield (64 mg) and 91% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IA column; 20% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 16.7 min (major), 23.3 min (minor) for (*R*)−**L***.

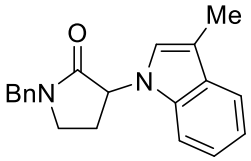
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.87 (m, 2H), 7.75 – 7.66 (m, 2H), 7.66 – 7.59 (m, 1H), 7.34 – 7.13 (m, 3H), 6.95 (q, *J* = 1.1 Hz, 1H), 5.33 (dd, *J* = 10.4, 8.8 Hz, 1H), 4.11 – 3.97 (m, 2H), 2.91 – 2.78 (m, 1H), 2.56 – 2.42 (m, 1H), 2.36 (d, *J* = 1.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 141.9, 136.4, 129.3, 126.3, 123.1, 122.0, 119.5, 119.4, 119.2, 112.4, 109.0, 57.8, 44.7, 26.2, 9.7.

FT-IR (thin film): 2920, 1712, 1614, 1520, 1463, 1389, 1322, 1237, 1197, 1165, 1120, 1069, 1015, 840, 740 cm^{-1}.

$[\alpha]^{25}_D$ = –40° (c = 1.0, $CHCl_3$); 90% ee from (*R*)−**L***.

HR-MS: *m*/*z* 359.1371 ($[M+H]^+$, $C_{20}H_{18}F_3N_2O^+$ calcd. 359.1371).



1-Benzyl-3-(3-methyl-1*H*-indol-1-yl)pyrrolidin-2-one (Table 2, entry 4). The title compound was prepared according to the General Procedure from 1-benzyl-3-iodopyrrolidin-2-one (113 mg, 0.375 mmol) and 3-methyl-1*H*-indole (32.8 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 2.2 equiv of Cs_2CO_3 (179 mg, 0.550 mmol). The reaction was run for 72 h at 23-25 °C. After purification by flash chromatography (20→80% Et_2O in hexanes) and reverse phase chromatography (0→100% MeOH in H_2O), the title compound was isolated as a white solid in 76% yield (58 mg) and 90% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 67% yield (51 mg) and 90% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IA column; hexanes:2-propanol/50:50, 1.0 mL/min flow-rate; retention times: 7.9 min (minor), 9.7 min (major) for (*R*)−**L***.

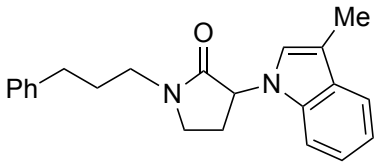
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 1H), 7.48 – 7.27 (m, 5H), 7.27 – 7.09 (m, 3H), 6.90 (q, *J* = 1.1 Hz, 1H), 5.16 (t, *J* = 9.1 Hz, 1H), 4.71 (d, *J* = 14.5 Hz, 1H), 4.55 (d, *J* = 14.5 Hz, 1H), 3.50 – 3.29 (m, 2H), 2.69 – 2.55 (m, 1H), 2.36 (d, *J* = 1.1 Hz, 3H), 2.17 (dq, *J* = 13.2, 8.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 136.4, 135.9, 129.3, 128.9, 128.5, 128.0, 123.4, 121.7, 119.3, 119.1, 112.0, 109.1, 56.8, 47.5, 43.3, 26.5, 9.7.

FT-IR (thin film): 3028, 2917, 1697, 1494, 1461, 1439, 1357, 1289, 1256, 1233, 739, 700cm^{-1}.

$[\alpha]^{25}_D$ = –4.2° (c = 1.0, $CHCl_3$); 90% ee from (*R*)−**L***.

HR-MS: *m*/*z* 305.1650 ([M+H]$^+$, $C_{20}H_{21}N_2O^+$ calcd. 305.1654).



3-(3-Methyl-1*H*-indol-1-yl)-1-(3-phenylpropyl)pyrrolidin-2-one (Table 2, entry 5). The title compound was prepared according to the General Procedure from 3-iodo-1-(3-phenylpropyl)pyrrolidin-2-one (123 mg, 0.375 mmol) and 3-methyl-1*H*-indole (32.8 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 2.2 equiv of Cs_2CO_3 (180 mg, 0.550 mmol). The reaction was run for 48 h at 23-25 °C. After purification by flash chromatography (35→100% Et_2O in hexanes) and reverse phase chromatography (0→70% MeOH in H_2O), the title compound was isolated as a yellow oil in 85% yield (71 mg) and 83% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a yellow oil in 76% yield (63 mg) and 81% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IA column; 50% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 12.5 min (minor), 13.6 min (major) for (*R*)−**L***.

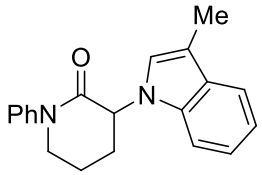
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.56 (m, 1H), 7.45 – 7.33 (m, 2H), 7.33 – 7.20 (m, 5H), 7.21 – 7.10 (m, 1H), 6.89 (q, *J* = 1.1 Hz, 1H), 5.05 (t, *J* = 9.1 Hz, 1H), 3.59 – 3.37 (m, 4H), 2.83 – 2.69 (m, 2H), 2.67 – 2.51 (m, 1H), 2.37 (d, *J* = 1.2 Hz, 3H), 2.23 – 2.06 (m, 1H), 2.09 – 1.91 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 141.2, 136.5, 129.3, 128.6, 128.4, 126.2, 123.4, 121.7, 119.3, 119.1, 111.9, 109.1, 56.8, 43.9, 43.2, 33.3, 28.8, 26.8, 9.8.

FT-IR (thin film): 3053, 3025, 2926, 2859, 1698, 1494, 1462, 1386, 1368, 1292, 1233, 1199, 739, 700 cm^{-1}.

$[\alpha]^{25}_D$ = –42° (c = 1.0, $CHCl_3$); 83% ee from (*R*)–**L***.

HR-MS: *m*/*z* 333.1965 ($[M+H]^+$, $C_{22}H_{25}N_2O^+$ calcd. 333.1967).



3-(3-Methyl-1*H*-indol-1-yl)-1-phenylpiperidin-2-one (Table 2, entry 6). The title compound was prepared according to the General Procedure from 1-phenyl-3-iodopiperidin-2-one (113 mg, 0.375 mmol) and 3-methyl-1*H*-indole (32.8 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)–**L***, and 1.8 equiv of Cs_2CO_3 (147 mg, 0.450 mmol). The reaction was run for 48 h at 23-25 °C. After purification by flash chromatography (20→80% Et_2O in hexanes) and reverse phase chromatography (0→70% MeOH in H_2O), the title compound was isolated as a white solid in 89% yield (68 mg) and 80% ee.

The second run was performed with (*S*)–**L***. The product was isolated as a white solid in 86% yield (65 mg) and 80% ee.

HPLC analysis of the product: Diacel CHIRALPAK® AD column; 30% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 13.7 min (major), 16.9 min (minor) for (*R*)–**L***.

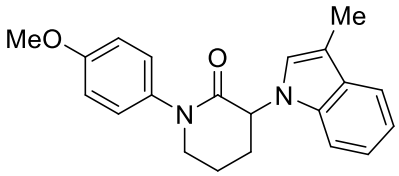
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 1H), 7.49 – 7.41 (m, 2H), 7.41 – 7.35 (m, 2H), 7.35 – 7.31 (m, 2H), 7.26 – 7.18 (m, 1H), 7.16 – 7.08 (m, 1H), 6.96 (q, *J* = 1.2 Hz, 1H), 5.17 (t, *J* = 8.2 Hz, 1H), 4.12 – 3.92 (m, 1H), 3.90 – 3.76 (m, 1H), 2.51 – 2.42 (m, 2H), 2.37 (d, *J* = 1.1 Hz, 3H), 2.30 – 2.11 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 142.6, 136.5, 129.13, 129.09, 126.9, 125.9, 124.0, 121.6, 119.2, 118.9, 111.3, 109.2, 56.7, 51.5, 28.8, 21.9, 9.7.

FT-IR (thin film): 3049, 2916, 2861, 1660, 1594, 1493, 1462, 1422, 1351, 1327, 1224, 1190, 759, 737, 694 cm^{-1}.

$[\alpha]^{25}_D$ = –3.2° (c = 1.0, $CHCl_3$); 80% ee from (*R*)–**L***.

HR-MS: *m*/*z* 305.1649 ($[M+H]^+$, $C_{20}H_{21}N_2O^+$ calcd. 305.1654).



1-(4-Methoxyphenyl)-3-(3-methyl-1*H*-indol-1-yl)piperidin-2-one (Table 2, entry 7). The title compound was prepared according to the General Procedure from 1-(4-methoxyphenyl)-3-iodopiperidin-2-one (124 mg, 0.375 mmol) and 3-methyl-1*H*-indole (32.8 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 2.2 equiv of Cs_2CO_3 (179 mg, 0.550 mmol). The reaction was run for 72 h at 23-25 °C. After purification by flash chromatography (0→10% MeOH in CH_2Cl_2) and reverse phase chromatography (0→50% MeOH in H_2O), the title compound was isolated as a white solid in 78% yield (66 mg) and 89% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 69% yield (58 mg) and 87% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IA column; 50% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 10.6 min (major), 15.7 min (minor) for (*R*)−**L***.

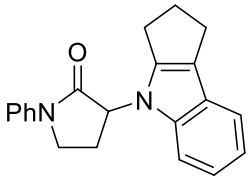
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.40 – 7.20 (m, 4H), 7.14 (d, *J* = 1.0 Hz, 1H), 7.04 – 6.88 (m, 3H), 5.12 (t, *J* = 8.1 Hz, 1H), 3.94 – 3.84 (m, 1H), 3.81 (s, 3H), 3.81 – 3.71 (m, 1H), 2.47 – 2.38 (m, 2H), 2.36 (d, *J* = 1.1 Hz, 3H), 2.23 – 2.10 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 158.2, 136.5, 135.6, 129.1, 127.1, 124.1, 121.6, 119.2, 118.9, 114.4, 111.1, 109.3, 56.7, 55.5, 51.9, 28.8, 21.9, 9.8.

FT-IR (thin film): 3046, 2933, 2835, 1660, 1607, 1510, 1462, 1326, 1296, 1240, 1189, 1032, 829, 738 cm^{-1}.

$[\alpha]^{25}_D$ = –1.8° (c = 1.0, $CHCl_3$); 89% ee from (*R*)−**L***.

HR-MS: *m*/*z* 335.1755 ($[M+H]^+$, $C_{21}H_{23}N_2O_2^+$ calcd. 335.1760).



3-(2,3-Dihydrocyclopenta[*b*]indol-4(1*H*)-yl)-1-phenylpyrrolidin-2-one (Table 3, entry 1). The title compound was prepared according to the General Procedure from 3-iodo-1-phenylpyrrolidin-2-one (108 mg, 0.375 mmol) and 1,2,3,4-tetrahydrocyclopenta[*b*]indole (39.3 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 1.8 equiv of Cs_2CO_3 (147 mg, 0.450 mmol). The reaction was run for 72 h at 23-25 °C. After purification by flash chromatography (25→55% Et_2O in hexanes) and reverse phase chromatography (0→75% MeOH in H_2O), the title compound was isolated as a white solid in 67% yield (53 mg) and 97% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 64% yield (51 mg) and 96% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IB column; 20% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 22.4 min (minor), 40.6 min (major) for (*R*)−**L***.

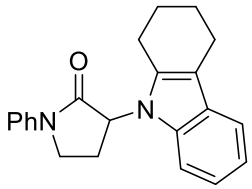
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.66 (m, 2H), 7.64 – 7.39 (m, 3H), 7.36 – 7.19 (m, 2H), 7.19 – 7.06 (m, 2H), 5.26 (dd, *J* = 10.4, 8.9 Hz, 1H), 3.98 – 3.89 (m, 2H), 3.05 – 2.78 (m, 4H), 2.76 – 2.65 (m, 1H), 2.63 – 2.50 (m, 2H), 2.39 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 144.9, 141.0, 139.2, 129.1, 125.2, 125.1, 120.4, 120.1, 119.8, 119.5, 119.0, 109.5, 57.1, 44.9, 28.6, 26.1, 26.0, 24.4.

FT-IR (thin film): 3045, 2951, 2850, 1706, 1597, 1495, 1456, 1402, 1375, 1307, 738, 690 cm^{-1}.

$[\alpha]^{25}_D$ = –86° (c = 1.0, $CHCl_3$); 97% ee from (*R*)−**L***.

HR-MS: *m*/*z* 317.1648 ([M+H]$^+$, $C_{21}H_{21}N_2O^+$ calcd. 317.1654).



3-(3,4-Dihydro-1*H*-carbazol-9(2*H*)-yl)-1-phenylpyrrolidin-2-one (Table 3, entry 2). The title compound was prepared according to the General Procedure from 3-iodo-1-phenylpyrrolidin-2-one (108 mg, 0.375 mmol) and 2,3,4,9-tetrahydro-1*H*-carbazole (42.8 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 1.8 equiv of Cs_2CO_3 (147 mg, 0.450 mmol). The reaction was run for 72 h at 23-25 °C. After purification by flash chromatography (0→5% MeOH in CH_2Cl_2) and reverse phase chromatography (0→100% MeOH in H_2O), the title compound was isolated as a white solid in 72% yield (59 mg) and 98% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 66% yield (55 mg) and 97% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IC column; 35% i-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 14.5 min (minor), 27.9 min (major) for (*R*)−**L***.

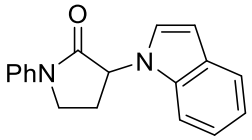
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.72 (m, 2H), 7.55 – 7.40 (m, 3H), 7.28 – 7.21 (m, 1H), 7.21 – 7.07 (m, 3H), 5.25 (s, 1H), 4.22 – 3.84 (m, 2H), 3.07 – 2.70 (m, 4H), 2.71 – 2.42 (m, 2H), 2.17 – 1.73 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 139.2, 129.1, 125.2, 121.0, 119.8, 119.2, 118.3, 56.0, 44.8, 23.3, 23.0, 21.1.

FT-IR (thin film): 3046, 2929, 2838, 1705, 1597, 1495, 1464, 1401, 1375, 1309, 1226, 758, 738, 692 cm^{-1}.

$[\alpha]^{25}_D$ = –94° (c = 1.0, $CHCl_3$); 98% ee from (*R*)−**L***.

HR-MS: *m*/*z* 331.1806 ([M+H]$^+$, $C_{22}H_{23}N_2O^+$ calcd. 331.1810).



3-(1*H*-Indol-1-yl)-1-phenylpyrrolidin-2-one (Table 3, entry 3). The title compound was prepared according to the General Procedure from 3-iodo-1-phenylpyrrolidin-2-one (108 mg, 0.375 mmol) and indole (29.3 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 1.8 equiv of Cs_2CO_3 (147 mg, 0.450 mmol). The reaction was run for 72 h at 25-26 °C. After purification by flash chromatography (35→60% Et_2O in hexanes), the title compound was isolated as a white solid in 54% yield (37 mg) and 83% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 49% yield (34 mg) and 83% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IC column; 35% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 28.4 min (minor), 35.1 min (major) for (*R*)−**L***.

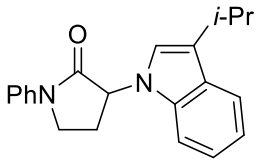
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 2H), 7.73 – 7.65 (m, 1H), 7.55 – 7.40 (m, 2H), 7.37 – 7.33 (m, 1H), 7.29 – 7.21 (m, 2H), 7.21 – 7.12 (m, 2H), 6.63 (d, *J* = 3.2 Hz, 1H), 5.33 (dd, *J* = 10.1, 8.7 Hz, 1H), 4.19 – 3.85 (m, 2H), 2.98 – 2.63 (m, 1H), 2.45 (dq, *J* = 12.9, 8.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 139.0, 136.0, 129.1, 129.0, 126.1, 125.3, 121.9, 121.3, 119.9, 119.8, 109.4, 102.9, 58.2, 45.0, 26.4.

FT-IR (thin film): 3048, 2952, 1701, 1597, 1496, 1480, 1460, 1396, 1310, 1226, 1199, 759, 741, 690 cm^{-1}.

$[\alpha]^{25}_D$ = –55° (c = 1.0, $CHCl_3$); 83% ee from (*R*)−**L***.

HR-MS: *m*/*z* 277.1339 ([M+H]$^+$, $C_{18}H_{17}N_2O^+$ calcd. 277.1341).



3-(3-Isopropyl-1*H*-indol-1-yl)-1-phenylpyrrolidin-2-one (Table 3, entry 4). The title compound was prepared according to the General Procedure from 3-iodo-1-phenylpyrrolidin-2-one (108 mg, 0.375 mmol) and 3-isopropyl-1*H*-indole (39.8 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 1.8 equiv of Cs_2CO_3 (147 mg, 0.450 mmol). The reaction was run for 72 h at 23-25 °C. After purification by flash chromatography (35% Et_2O in hexanes) and reverse phase chromatography (0→75% MeOH in H_2O), the title compound was isolated as a white solid in 82% yield (65 mg) and 89% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 86% yield (68 mg) and 91% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IC column; 35% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 9.5 min (minor), 12.3 min (major) for (*R*)−**L***.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 2H), 7.74 – 7.63 (m, 1H), 7.50 – 7.42 (m, 2H), 7.34 – 7.19 (m, 3H), 7.18 – 7.09 (m, 1H), 6.94 (d, *J* = 0.9 Hz, 1H), 5.31 (dd, *J* = 10.3, 8.8 Hz, 1H),

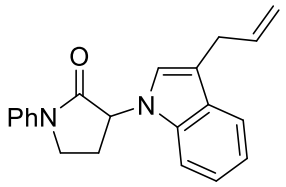
4.40 – 3.59 (m, 2H), 3.24 (septd, *J* = 6.8, 0.9 Hz, 1H), 2.80 (dddd, *J* = 13.0, 8.8, 5.6, 3.4 Hz, 1H), 2.44 (ddt, *J* = 13.0, 10.3, 9.2 Hz, 1H), 1.39 (d, *J* = 6.8, 3H),1.37 (d, *J* = 6.8, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 139.1, 136.7, 129.1, 128.0, 125.3, 124.2, 121.8, 121.2, 119.9, 119.8, 119.1, 109.3, 58.0, 45.0, 26.3, 25.6, 23.30, 23.26.

FT-IR (thin film): 3046, 2958, 2868, 1706, 1598, 1495, 1462, 1395, 1307, 1226, 1198, 758, 739, 690 cm^{-1}.

$[\alpha]^{25}_D$ = –51° (c = 1.0, $CHCl_3$); 89% ee from (*R*)−**L***.

HR-MS: *m*/*z* 319.1805 ([M+H]$^+$, $C_{21}H_{23}N_2O^+$ calcd. 319.1810).



3-(3-Allyl-1*H*-indol-1-yl)-1-phenylpyrrolidin-2-one (Table 3, entry 5). The title compound was prepared according to the General Procedure from 3-iodo-1-phenylpyrrolidin-2-one (108 mg, 0.375 mmol) and 3-allyl-1*H*-indole (39.3 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 1.8 equiv of Cs_2CO_3 (147 mg, 0.450 mmol). The reaction was run for 72 h at 23-24 °C. After purification by flash chromatography (35% Et_2O in hexanes) and reverse phase chromatography (0→75% MeOH in H_2O), the title compound was isolated as a yellow oil in 89% yield (70 mg) and 87% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a yellow oil in 98% yield (78 mg) and 87% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IC column; 35% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 14.5 min (minor), 17.0 min (major) for (*R*)−**L***.

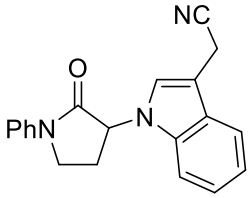
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H), 7.64 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.32 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.28 – 7.20 (m, 2H), 7.15 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.99 (s, 1H), 6.10 (ddt, *J* = 16.6, 10.0, 6.5 Hz, 1H), 5.32 (dd, *J* = 10.2, 8.7 Hz, 1H), 5.20 (dq, *J* = 17.0, 1.7 Hz, 1H), 5.14 – 5.06 (m, 1H), 4.02 (dd, *J* = 9.2, 4.6 Hz, 2H), 3.55 (dq, *J* = 6.5, 1.4 Hz, 2H), 2.81 (ddt, *J* = 13.2, 8.9, 4.5 Hz, 1H), 2.44 (ddt, *J* = 13.0, 10.3, 9.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 139.1, 137.2, 136.6, 129.1, 128.5, 125.3, 123.6, 122.0, 119.8, 119.6, 119.4, 115.4, 114.8, 109.4, 58.0, 44.9, 30.0, 26.3.

FT-IR (thin film): 3057, 2923, 1704, 1638, 1598, 1500, 1462, 1395, 1308, 1225, 1177, 1113, 995, 912, 758, 740 cm^{-1}.

$[\alpha]^{25}_D$ = –53° (c = 1.0, $CHCl_3$); 87% ee from (*R*)−**L***.

HR-MS: *m*/*z* 317.1647 ([M+H]$^+$, $C_{21}H_{21}N_2O^+$ calcd. 317.1654).



2-(1-(2-Oxo-1-phenylpyrrolidin-3-yl)-1*H*-indol-3-yl)acetonitrile (Table 3, entry 6). The title compound was prepared according to the General Procedure from 3-iodo-1-phenylpyrrolidin-2-one (108 mg, 0.375 mmol) and 2-(1*H*-indol-3-yl)acetonitrile (39.0 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 1.0 equiv of Cs_2CO_3 (81.5 mg, 0.250 mmol). The reaction was run for 48 h at 23-25 °C. After purification by flash chromatography (50→100% Et_2O in hexanes), the title compound was isolated as a yellow oil in 55% yield (43 mg) and 86% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a yellow oil in 52% yield (41 mg) and 88% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IC column; 50% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 15.4 min (minor), 48.1 min (major) for (*R*)−**L***.

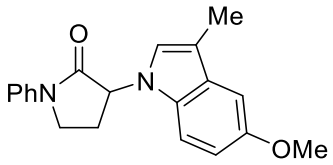
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 2H), 7.65 – 7.59 (m, 1H), 7.51 – 7.42 (m, 2H), 7.39 – 7.20 (m, 5H), 5.33 (dd, *J* = 10.4, 8.7 Hz, 1H), 4.11 – 3.94 (m, 2H), 3.86 (d, *J* = 1.1 Hz, 2H), 2.95 – 2.72 (m, 1H), 2.59 – 2.30 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 138.8, 136.5, 129.1, 127.0, 125.5, 124.6, 122.9, 120.5, 119.9, 118.7, 118.1, 109.8, 105.0, 58.1, 45.0, 26.5, 14.5.

FT-IR (thin film): 3050, 2922, 2248, 1700, 1597, 1495, 1464, 1398, 1307, 1226, 1205, 1178, 742, 692 cm^{-1}.

$[\alpha]^{25}_D$ = –44° (c = 1.0, $CHCl_3$); 86% ee from (*R*)−**L***.

HR-MS: *m*/*z* 316.1443 ($[M+H]^+$, $C_{20}H_{18}N_3O^+$ calcd. 316.1450).



3-(5-Methoxy-3-methyl-1*H*-indol-1-yl)-1-phenylpyrrolidin-2-one (Table 3, entry 7). The title compound was prepared according to the General Procedure from 3-iodo-1-phenylpyrrolidin-2-one (108 mg, 0.375 mmol) and 5-methoxy-3-methyl-1*H*-indole (40.0 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 2.2 equiv of Cs_2CO_3 (180 mg, 0.550 mmol). The reaction was run for 72 h at 24-25 °C. After purification by flash chromatography (25→85% Et_2O in hexanes), the title compound was isolated as a white solid in 86% yield (69 mg) and 91% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 83% yield (66 mg) and 90% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IA column; 50% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 10.0 min (minor), 31.0 min (major) for (*R*)−**L***.

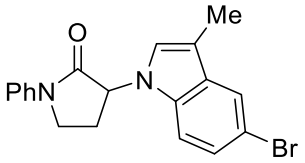
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.68 (m, 2H), 7.59 – 7.37 (m, 2H), 7.28 – 7.21 (m, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.95 (d, *J* = 1.2 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.22 (dd, *J* = 10.2, 8.7 Hz, 1H), 4.04 – 3.94 (m, 2H), 3.90 (s, 3H), 2.89 – 2.64 (m, 1H), 2.52 – 2.33 (m, 1H), 2.33 (d, *J* = 1.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 154.0, 139.1, 131.6, 129.7, 129.1, 125.2, 124.2, 119.8, 112.0, 111.6, 109.9, 101.3, 58.1, 56.0, 45.0, 26.4, 9.8.

FT-IR (thin film): 2933, 1704, 1597, 1487, 1457, 1395, 1309, 1244, 1221, 1100, 1047, 759 cm^{-1}.

$[\alpha]^{25}_D$ = –75° (c = 1.0, $CHCl_3$); 91% ee from (*R*)–**L***.

HR-MS: *m*/*z* 321.1592 ([M+H]$^+$, $C_{20}H_{21}N_2O_2^+$ calcd. 321.1603).



3-(5-Bromo-3-methyl-1*H*-indol-1-yl)-1-phenylpyrrolidin-2-one (Table 3, entry 8). The title compound was prepared according to the General Procedure from 3-iodo-1-phenylpyrrolidin-2-one (108 mg, 0.375 mmol) and 5-bromo-3-methyl-1*H*-indole (52.2 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)–**L***, and 1.8 equiv of Cs_2CO_3 (147 mg, 0.450 mmol). The reaction was run for 48 h at 24-25 °C. After purification by flash chromatography (25→75% Et_2O in hexanes), the title compound was isolated as a white solid in 74% yield (68 mg) and 87% ee.

The second run was performed with (*S*)–**L***. The product was isolated as a white solid in 65% yield (60 mg) and 90% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IC column; 35% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 15.3 min (minor), 17.1 min (major) for (*R*)–**L***.

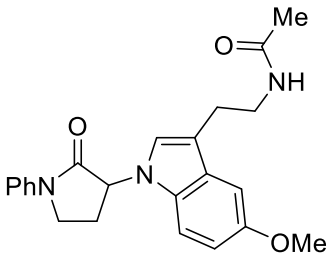
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 3H), 7.58 – 7.38 (m, 2H), 7.38 – 7.20 (m, 2H), 7.20 – 7.12 (m, 1H), 6.96 (q, *J* = 1.2 Hz, 1H), 5.21 (dd, *J* = 10.2, 8.7 Hz, 1H), 4.13 – 3.86 (m, 2H), 2.89 – 2.67 (m, 1H), 2.55 – 2.33 (m, 1H), 2.31 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 138.9, 135.1, 131.0, 129.1, 125.4, 124.7, 124.6, 122.0, 119.8, 112.6, 111.8, 110.7, 58.0, 44.9, 26.3, 9.6.

FT-IR (thin film): 2917, 1700, 1598, 1494, 1458, 1394, 1307, 1225, 1199, 786, 758, 691 cm^{-1}.

$[\alpha]^{25}_D$ = –23° (c = 1.0, $CHCl_3$); 87% ee from (*R*)–**L***.

HR-MS: *m*/*z* 369.0593 ([M+H]$^+$, $C_{19}H_{18}BrN_2O^+$ calcd. 369.0603).



N*-(2-(5-Methoxy-1-(2-oxo-1-phenylpyrrolidin-3-yl)-1*H*-indol-3-yl)ethyl)acetamide (Table 3, entry 9)**. The title compound was prepared according to the General Procedure from 3-iodo-1-phenylpyrrolidin-2-one (108 mg, 0.375 mmol) and *N*-acetyl-5-methoxytryptamine (58.1 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L, and 2.2 equiv of Cs_2CO_3 (179 mg, 0.550 mmol). The reaction was run for 72 h at 25-26 °C. After purification by flash chromatography (0→15% MeOH in CH_2Cl_2) and reverse phase chromatography (0→70% MeOH in H_2O), the title compound was isolated as a white solid in 57% yield (56 mg) and 86% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 54% yield (53 mg) and 83% ee.

SFC analysis of the product: Diacel CHIRALPAK® IC column; 50% MeOH in CO_2, 3.0 mL/min flow-rate; retention times: 5.1 min (minor), 5.9 min (major) for (*R*)−**L***.

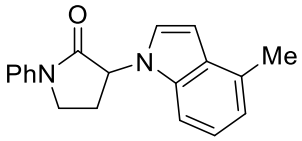
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.68 (m, 2H), 7.54 – 7.41 (m, 2H), 7.28 – 7.18 (m, 2H), 7.10 – 7.06 (d, *J* = 2.4 Hz, 1H), 7.00 (s, 1H), 6.91 (dd, *J* = 8.9, 2.5 Hz, 1H), 5.66 (br s, 1H), 5.24 (dd, *J* = 10.2, 8.7 Hz, 1H), 4.11 – 3.93 (m, 2H), 3.88 (s, 3H), 3.76 – 3.46 (m, 2H), 3.11 – 2.87 (m, 2H), 2.88 – 2.76 (m, 1H), 2.52 – 2.37 (m, 1H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 169.6, 154.3, 138.9, 131.7, 129.1, 128.9, 125.4, 124.7, 119.8, 112.9, 112.4, 110.3, 101.1, 58.3, 56.0, 45.0, 39.7, 26.4, 25.3, 23.4.

FT-IR (thin film): 3305, 3065, 2934, 1703, 1651, 1597, 1548, 1485, 1452, 1396, 1307, 1223, 1176, 1030, 760, 692 cm^{-1}.

$[\alpha]^{25}_D$ = –29° (c = 1.0, $CHCl_3$); 86% ee from (*R*)−**L***.

HR-MS: *m*/*z* 392.1973 ($[M+H]^+$, $C_{23}H_{26}N_3O_3^+$ calcd. 392.1974).



3-(4-Methyl-1*H*-indol-1-yl)-1-phenylpyrrolidin-2-one (Table 3, entry 10). The title compound was prepared according to the General Procedure from 3-iodo-1-phenylpyrrolidin-2-one (108 mg, 0.375 mmol) and 4-methyl-1*H*-indole (32.8 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 1.8 equiv of Cs_2CO_3 (147 mg, 0.450 mmol). The reaction was run for 48 h at 23-25 °C. After purification by flash chromatography (0→60% Et_2O in hexanes), the title compound was isolated as a white solid in 59% yield (43 mg) and 91% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 58% yield (42 mg) and 91% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IB column; 20% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 4.5 min (minor), 5.1 min (major) for (*R*)−**L***.

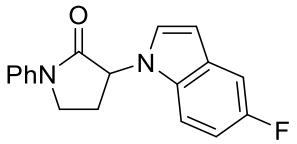
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 2H), 7.49 – 7.42 (m, 2H), 7.27 – 7.11 (m, 4H), 6.99 – 6.93 (m, 1H), 6.64 (dd, *J* = 3.3, 0.8 Hz, 1H), 5.34 (dd, *J* = 10.1, 8.7 Hz, 1H), 4.09 – 3.98 (m, 2H), 2.88 – 2.79 (m, 1H), 2.59 (s, 3H), 2.53 – 2.41 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 139.0, 135.7, 130.8, 129.1, 128.8, 125.4, 125.3, 122.1, 120.2, 119.8, 107.0, 101.4, 58.3, 45.0, 26.5, 18.7.

FT-IR (thin film): 3045, 2917, 1703, 1598, 1492, 1458, 1397, 1307, 1226, 749, 690 cm^{-1}.

$[\alpha]^{25}_D$ = –3.2° (c = 1.0, $CHCl_3$); 91% ee from (*R*)−**L***.

HR-MS: *m*/*z* 291.1487 ([M+H]$^+$, $C_{19}H_{19}N_2O^+$ calcd. 291.1497).



3-(5-Fluoro-1*H*-indol-1-yl)-1-phenylpyrrolidin-2-one (Table 3, entry 11). The title compound was prepared according to the General Procedure from 3-iodo-1-phenylpyrrolidin-2-one (108 mg, 0.375 mmol) and 5-fluoro-1*H*-indole (33.8 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 1.8 equiv of Cs_2CO_3 (147 mg, 0.450 mmol). The reaction was run for 72 h at 25-26 °C. After purification by flash chromatography (30→65% Et_2O in hexanes), the title compound was isolated as a white solid in 52% yield (38 mg) and 83% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 54% yield (35 mg) and 84% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IC column; 35% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 14.6 min (minor), 18.6 min (major) for (*R*)−**L***.

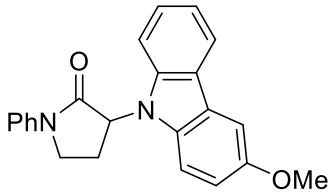
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.67 (m, 2H), 7.59 – 7.40 (m, 2H), 7.38 – 7.11 (m, 4H), 7.07 – 6.90 (m, 1H), 6.57 (d, *J* = 3.3, 1H), 5.29 (dd, *J* = 10.2, 8.7 Hz, 1H), 4.20 – 3.83 (m, 2H), 2.92 – 2.70 (m, 1H), 2.56 – 2.35 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 158.1 (d, *J* = 234.8 Hz), 138.9, 132.6, 129.4 (d, *J* = 10.2 Hz), 129.1, 127.7, 125.4, 119.8, 110.3 (d, *J* = 26.4 Hz), 110.0 (d, *J* = 9.7 Hz), 106.1 (d, *J* = 23.3 Hz), 102.9 (d, *J* = 4.7 Hz), 58.4, 45.0, 26.4.

FT-IR (thin film): 3065, 2923, 1704, 1597, 1495, 1482, 1449, 1399, 1309, 1222, 1117, 949, 758, 690 cm^{-1}.

$[\alpha]^{25}_D$ = –34° (c = 1.0, $CHCl_3$); 83% ee from (*R*)−**L***.

HR-MS: *m*/*z* 295.1241 ([M+H]$^+$, $C_{18}H_{16}FN_2O^+$ calcd. 295.1247).



3-(3-Methoxy-9*H*-carbazol-9-yl)-1-phenylpyrrolidin-2-one (Table 3, entry 12). The title compound was prepared according to the General Procedure from 3-iodo-1-phenylpyrrolidin-2-one (108 mg, 0.375 mmol) and 3-methoxy-9*H*-carbazole (49.3 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 1.8 equiv of Cs_2CO_3 (147 mg, 0.450 mmol). The reaction was run for 60 h at 23-25 °C. After purification by flash chromatography (25→80% Et_2O in hexanes), the title compound was obtained as a white solid in 79% yield (70 mg) and 96% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 84% yield (75 mg) and 97% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IA column; 50% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 13.6 min (minor), 41.6 min (major) for (*R*)−**L***.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 1H), 7.87 – 7.76 (m, 2H), 7.63 (d, *J* = 2.5 Hz, 1H), 7.57 – 7.39 (m, 3H), 7.37 – 7.18 (m, 4H), 7.08 (dd, *J* = 8.9, 2.5 Hz, 1H), 5.54 (dd, *J* = 10.8, 9.3 Hz, 1H), 4.32 – 3.97 (m, 2H), 3.95 (s, 3H), 2.74 – 2.52 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 154.1, 139.2, 129.1, 125.8, 125.3, 124.2, 123.6, 120.5, 119.7, 119.2, 114.8, 110.0, 109.3, 103.7, 56.23, 56.15, 44.9, 23.3.

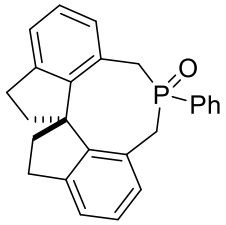
FT-IR (thin film): 3049, 2952, 2831, 1704, 1597, 1490, 1462, 1405, 1306, 1201, 1081, 1032, 744, 689 cm^{-1}.

$[\alpha]^{25}_D$ = –89° (c = 1.0, $CHCl_3$); 96% ee from (*R*)−**L***.

HR-MS: *m*/*z* 357.1593 ($[M+H]^+$, $C_{23}H_{21}N_2O_2^+$ calcd. 357.1603).

Gram-scale reaction. The title compound was prepared as above from 3-iodo-1-phenylpyrrolidin-2-one (1.51 g, 5.25 mmol) and 3-methoxy-9*H*-carbazole (690 mg, 3.50 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*S*)−**L***, and 2.5 equiv of Cs_2CO_3 (2.85 g, 8.75 mmol). The reaction was run for 90 h at 23-25 °C. The product was isolated as a white solid in 85% yield (1.06 g) and 92% ee.

If desired, **L*** can be recovered:



Recovery of (*S*)−L* oxide. Upon column chromatography of the gram-scale reaction, the fractions that contained **L*** and **L*** oxide (but not any unreacted electrophile) were collected and concentrated. The residue was dissolved in MeOH (~10 mL) and cooled to 0 °C. Next, H_2O_2 (30% w/w in H_2O; 200 μL) was added. The reaction mixture was warmed to room temperature, stirred for 1 h, and then concentrated. The residue was purified by flash

chromatography (0→15% MeOH in Et_2O), which afforded (*S*)−**L*** oxide as a yellow solid in 94% recovery (243 mg).

^1H {^{31}P} NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.46 (m, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.26 – 7.14 (m, 4H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.24 (d, *J* = 7.5 Hz, 1H), 3.81 (d, *J* = 13.8 Hz, 1H), 3.65 (d, *J* = 13.9 Hz, 1H), 3.08 (ddd, *J* = 17.7, 11.5, 6.7 Hz, 2H), 2.94 (ddd, *J* = 15.9, 10.8, 8.2 Hz, 2H), 2.81 (ddd, *J* = 28.2, 13.8, 1.7 Hz, 2H), 2.33 (dd, *J* = 12.4, 6.6 Hz, 1H), 2.25 (dd, *J* = 12.4, 6.6 Hz, 1H), 2.00 (dtdd, *J* = 36.4, 11.9, 7.3, 3.1 Hz, 2H).

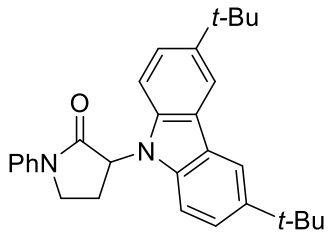
^{31}P {^1H} NMR (162 MHz, $CDCl_3$) δ 35.6.

FT-IR (thin film): 3054, 2945, 2850, 1703, 1591, 1468, 1452, 1435, 1405, 1306, 1257, 1223, 1213, 1177, 1106, 1061, 848, 822, 804, 752 cm^{-1}.

$[\alpha]^{25}_D$ = –39.8° (c = 1.0, $CHCl_3$).

HR-MS: *m*/*z* 371.1567 ($[M+H]^+$, $C_{25}H_{24}PO^+$ calcd. 371.1565).

Regeneration of (*S*)−L*.[3] In a nitrogen-filled glovebox, (*S*)−**L*** oxide was dissolved in toluene (0.03 M) in a sealed flask, and then triethylamine (7.0 equiv) was added. Next, trichlorosilane (5.0 equiv) was added to the reaction mixture dropwise over 15 min. The flask was removed from the glovebox, and the reaction mixture was stirred under nitrogen at 110 °C for 16 h. Next, the flask was taken into the glovebox, and it was capped with a septum and a needle vent. Then, the reaction was quenched by the dropwise addition over 30 min of a degassed aqueous solution of KOH (5.0 M; 10 mL). The reaction mixture was stirred for 20 min, and the organic layer was removed by pipette. The aqueous phase was extracted with benzene, and the combined organic layers were concentrated. The residue was dissolved in benzene, and the resulting solution was filtered through a pipette that contained a plug of silica gel, using benzene as the eluant. The filtrate was concentrated and isolated as a white solid (211 mg). ^1H NMR data matched previously reported data.[4]



3-(3,6-Di-tert-butyl-9*H*-carbazol-9-yl)-1-phenylpyrrolidin-2-one (Table 3, entry 13). The title compound was prepared according to the General Procedure from 3-iodo-1-

(3) This procedure is adapted from: Wu, H.-C.; Yu, J.-Q.; Spencer, J. B. Stereospecific Deoxygenation of Phosphine Oxides with Retention of Configuration Using Triphenylphosphine or Triethyl Phosphite as an Oxygen Acceptor. *Org. Lett*. **2004**, *6*, 4675−4678.

(4) Zhu, S.-F.; Yang, Y.; Wang, L.-X.; Liu, B.; Zhou, Q.-L. Synthesis and Application of Chiral Spiro Phospholane Ligand in Pd-Catalyzed Asymmetric Allylation of Aldehydes with Allylic Alcohols. *Org. Lett.* **2005**, *7*, 2333−2335.

phenylpyrrolidin-2-one (108 mg, 0.375 mmol) and 3,6-di-tert-butyl-9*H*-carbazole (69.9 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 1.8 equiv of Cs_2CO_3 (147 mg, 0.450 mmol). The reaction was run for 72 h at 23-25 °C. After purification by flash chromatography (0→50% Et_2O in hexanes) and reverse phase chromatography (0→80% MeOH in H_2O), the title compound was isolated as a white solid in 79% yield (87 mg) and 94% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 81% yield (89 mg) and 95% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IC column; 15% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 15.4 min (minor), 48.1 min (major) for (*R*)−**L***.

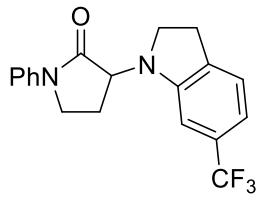
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 0.6 Hz, 2H), 7.87 – 7.79 (m, 2H), 7.56 – 7.42 (m, 4H), 7.33 – 7.17 (m, 3H), 5.58 (dd, *J* = 10.5, 9.6 Hz, 1H), 4.12 – 4.02 (m, 2H), 2.73 – 2.63 (m, 2H), 1.48 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 142.4, 139.3, 129.1, 125.2, 123.5, 119.8, 116.6, 56.1, 44.9, 34.7, 32.0, 23.4.

FT-IR (thin film): 3046, 2959, 1708, 1598, 1491, 1477, 1404, 1392, 1362, 1308, 1262, 1167, 804, 757, 691 cm^{-1}.

$[\alpha]^{25}_D$ = –84° (c = 1.0, $CHCl_3$); 94% ee from (*R*)−**L***.

HR-MS: *m*/*z* 439.2743 ($[M+H]^+$, $C_{30}H_{35}N_2O^+$ calcd. 439.2749).



1-Phenyl-3-(6-(trifluoromethyl)indolin-1-yl)pyrrolidin-2-one (Table 3, entry 14). The title compound was prepared according to the General Procedure from 3-iodo-1-phenylpyrrolidin-2-one (108 mg, 0.375 mmol) and 6-(trifluoromethyl)indoline (46.8 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)−**L***, and 1.5 equiv of Cs_2CO_3 (122 mg, 0.375 mmol). The reaction was run for 48 h at 25-26 °C. After purification by flash chromatography (10→100% Et_2O in hexanes) and reverse phase chromatography (0→75% MeOH in H_2O), the title compound was isolated as a white solid in 69% yield (60 mg) and 86% ee.

The second run was performed with (*S*)−**L***. The product was isolated as a white solid in 59% yield (51 mg) and 90% ee.

HPLC analysis of the product: Diacel CHIRALPAK® IC column; 35% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 7.9 min (minor), 10.1 min (major) for (*R*)−**L***.

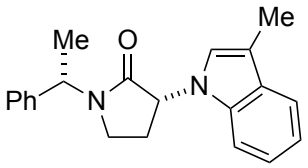
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 2H), 7.47 – 7.32 (m, 2H), 7.25 – 7.18 (m, 1H), 7.18 – 7.12 (m, 1H), 7.00 – 6.87 (m, 1H), 6.72 – 6.64 (m, 1H), 4.63 (dd, *J* = 10.5, 8.6 Hz, 1H), 4.12 – 3.79 (m, 2H), 3.79 – 3.49 (m, 2H), 3.24 – 3.00 (m, 2H), 2.63 – 2.37 (m, 1H), 2.39 – 2.11 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 151.2, 139.1, 133.9, 129.8 (q, *J* = 31.5 Hz), 129.0, 125.1, 124.6, 124.6 (q, *J* = 272.1 Hz), 119.7, 115.2 (q, *J* = 4.2 Hz), 103.1 (q, *J* = 3.9 Hz), 58.4, 48.5, 45.0, 28.2, 20.8.

FT-IR (thin film): 3045, 2954, 2853, 1698, 1614, 1598, 1497, 1450, 1402, 1316, 1286, 1160, 1115, 1059, 760, 691 cm^{-1}.

$[\alpha]^{25}_D$ = –12° (c = 1.0, $CHCl_3$); 86% ee from (*R*)–**L***.

HR-MS: *m*/*z* 347.1365 ([M+H]$^+$, $C_{19}H_{18}F_3N_2O^+$ calcd. 347.1371).



(3*R*)-3-(3-Methyl-1*H*-indol-1-yl)-1-((1*S*)-1-phenylethyl)pyrrolidin-2-one (Figure 4). The title compound was prepared according to the General Procedure from 3-iodo-1-((*S*)-1-phenylethyl)pyrrolidin-2-one (1:1 mixture of diastereomers; 118 mg, 0.375 mmol) and 3-methyl-1*H*-indole (32.8 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*R*)–**L***, and 1.8 equiv of Cs_2CO_3 (147 mg, 0.450 mmol). After purification by flash chromatography (20→60% Et_2O in hexanes) and reverse phase chromatography (0→90% MeOH in H_2O), the title compound was isolated as a white solid in 64% yield (51 mg) and 15:85 dr.

Second run: 61% yield (49 mg) and 15:85 dr.

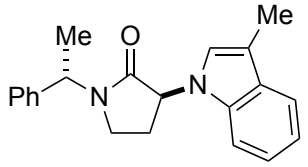
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 1H), 7.45 – 7.30 (m, 5H), 7.27 – 7.18 (m, 2H), 7.18 – 7.10 (m, 1H), 6.89 (t, *J* = 1.1 Hz, 1H), 5.69 (q, *J* = 7.1 Hz, 1H), 5.10 (t, *J* = 8.9 Hz, 1H), 3.63 – 3.37 (m, 1H), 3.06 (dt, *J* = 10.0, 7.8 Hz, 1H), 2.62 – 2.44 (m, 1H), 2.35 (d, *J* = 1.1 Hz, 3H), 2.23 – 2.08 (m, 1H), 1.71 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 139.6, 136.5, 129.4, 128.8, 128.0, 127.4, 123.5, 121.8, 119.3, 119.2, 111.8, 109.3, 57.3, 50.2, 39.4, 26.5, 16.3, 9.8.

FT-IR (thin film): 3050, 2974, 1695, 1490, 1457, 1424, 1283, 1234, 1014, 778, 739 cm^{-1}.

$[\alpha]^{25}_D$ = –171° (c = 1.0, $CHCl_3$); >99% ee from (*R*)–**L***.

HR-MS: *m*/*z* 319.1807 ([M+H]$^+$, $C_{21}H_{23}N_2O^+$ calcd. 319.1810).



(3*S*)-3-(3-Methyl-1*H*-indol-1-yl)-1-((1*S*)-1-phenylethyl)pyrrolidin-2-one (Figure 4). The title compound was prepared according to the General Procedure from 3-iodo-1-((*S*)-1-phenylethyl)pyrrolidin-2-one (118 mg, 0.375 mmol) and 3-methyl-1*H*-indole (32.8 mg, 0.250 mmol), using 10 mol% of mesitylcopper, 20 mol% of (*S*)–**L***, and 1.8 equiv of Cs_2CO_3 (147 mg, 0.450 mmol). After purification by flash chromatography (20→60% Et_2O in hexanes) and reverse phase chromatography (0→90% MeOH in H_2O), the product was isolated as a white solid in 68% yield (54 mg) and 94:6 dr.

Second run: 70% yield (56 mg) and 94:6 dr.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.52 (m, 1H), 7.52 – 7.41 (m, 4H), 7.41 – 7.32 (m, 1H), 7.22 – 7.08 (m, 3H), 6.82 (d, *J* = 1.2 Hz, 1H), 5.68 (q, *J* = 7.1 Hz, 1H), 5.16 (t, *J* = 9.1 Hz, 1H), 3.53 –

3.41 (m, 1H), 3.26 – 3.12 (m, 1H), 2.65 – 2.55 (m, 1H), 2.32 (d, J = 1.1 Hz, 3H), 2.17 – 2.00 (m, 1H), 1.64 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 139.6, 136.3, 129.3, 128.8, 127.9, 127.2, 123.5, 121.7, 119.3, 119.1, 111.8, 109.2, 57.3, 49.9, 39.1, 26.5, 16.1, 9.7.

FT-IR (thin film): 3050, 2976, 1693, 1494, 1462, 1428, 1353, 1285, 1219, 1015, 781, 739 cm^{-1}.

$[\alpha]^{25}_D$ = –175° (c = 1.0, $CHCl_3$); >99% ee from (*S*)−**L***.

HR-MS: *m*/*z* 319.1804 ($[M+H]^+$, $C_{21}H_{23}N_2O^+$ calcd. 319.1810).

IV. Time-Course Experiments (Figures 5 and 6)

Figure 5. In a nitrogen-filled glovebox, an oven-dried 4 mL amber-glass vial was charged with 3-methyl-1*H*-indole (26.2 mg, 0.200 mmol) and a solution of mesitylcopper (3.6 mg, 0.020 mmol) in *m*-xylene (200 μL). A stir bar was added, and the vial was closed with a screw cap. The mixture was stirred for 10 min, and then a solution of (*S*)–**L*** (14.1 mg, 0.040 mmol) and an internal standard (4,4′-di-*tert*-butylbiphenyl; 26.6 mg, 0.10 mmol) in *m*-xylene (680 μL) was added, and the vial was re-capped. The mixture was stirred for 10 min, and then the α-iodo-γ-lactam (86.1 mg, 0.30 mmol) was added. After the reaction mixture became homogeneous (~5 min), Cs_2CO_3 (97.7 mg, 0.300 mmol) was added. The vial was re-capped and wrapped thoroughly with electrical tape in order to keep the reaction in the dark. The reaction mixture was stirred vigorously at 24 °C in the glovebox. Aliquots (~20 μL) were taken from reaction mixture at various reaction times, and the reactions were immediately quenched by dilution with CH_2Cl_2 (2 mL) and filtration through a syringe filter. The solvent was removed by evaporation (air flow), leading to a solid yellowish-white residue. The composition of each sample was determined via analysis by ^{1}H NMR spectroscopy.

The ee's were determined via HPLC analysis: Diacel CHIRALPAK® IC column; 35% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times for the product: 22.5 min (major), 26.5 min (minor); retention times for the electrophile: 13.9 min (major) and 15.0 min (minor) for (*S*)–**L***.

Figure 6. In a nitrogen-filled glovebox, an oven-dried 4 mL amber-glass vial was charged with 3-methyl-1*H*-indole (26.2 mg, 0.200 mmol) and a solution of mesitylcopper (3.6 mg, 0.020 mmol) in *m*-xylene (200 μL). A stir bar was added, and the vial was closed with a screw cap. The mixture was stirred for 10 min, and then a solution of (*S*)–**L*** (14.1 mg, 0.040 mmol) and an internal standard (4,4′-di-*tert*-butylbiphenyl; 26.6 mg, 0.10 mmol) in *m*-xylene (680 μL) was added, and the vial was re-capped. The mixture was stirred for 10 min, and then the α-bromo-γ-lactam (72.0 mg, 0.300 mmol) was added. After the reaction mixture became homogeneous (~5 min), Cs_2CO_3 (97.7 mg, 0.300 mmol) was added. The vial was re-capped and wrapped thoroughly with electrical tape in order to keep the reaction in the dark. The reaction mixture was stirred vigorously at 24 °C in the glovebox. Aliquots (~200 μL) were taken from reaction mixture at various reaction times, and the reactions were immediately quenched by dilution with CH_2Cl_2 (2 mL) and filtration through a syringe filter. The solvent was removed by evaporation (air flow), leading to a solid yellowish-white residue. The composition of each sample was determined via analysis by ^{1}H NMR spectroscopy.

The ee's were determined via HPLC analysis: Diacel CHIRALPAK® IC column; 35% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times for the product: 22.5 min (major), 26.5 min (minor); retention times for the electrophile 12.8 min (major) and 17.0 min (minor) for (*S*)–**L***.

V. Synthesis and Reactivity of Copper Complex B (from (*R*)–L*)

Preparation of copper complex B (eq 2). In a nitrogen-filled glovebox**,** an oven-dried 4 mL amber-glass vial was charged with 3-methyl-1*H*-indole (16.4 mg, 0.125 mmol), mesitylcopper (22.8 mg, 0.125 mmol), a stir bar, and then benzene (0.5 mL). The mixture was stirred for 10 min, and then a solution of (*R*)−**L*** (88.5 mg, 0.250 mmol) in benzene (1.5 mL) was added. The mixture was stirred for 16 h, and then it was concentrated to ~0.25 mL, and pentane (2.0 mL) was added dropwise. The mixture was stirred for 1 h, and then the resulting white precipitate of copper complex **B** was filtered, rinsed with pentane (5 mL), and dried to give the desired product as a white powder in 65% yield (73 mg). X-ray quality crystals were obtained by slow evaporation of the solvent from a saturated solution in a mixture of benzene/Et_2O/pentane.

^{1}H NMR (400 MHz, C_6D_6) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.27 (m, 1H), 7.15 – 6.79 (m, 21H), 6.65 (t, *J* = 7.5 Hz, 2H), 5.70 (d, *J* = 7.5 Hz, 2H), 3.32 (d, *J* = 14.0 Hz, 2H), 3.24 (t, *J* = 11.1 Hz, 2H), 2.88 (d, *J* = 12.0 Hz, 2H), 2.78 – 2.66 (m, 4H), 2.70 (s, 3H), 2.63 – 2.51 (m, 4H), 2.38 (d, *J* = 14.0 Hz, 2H), 1.94 (ddd, *J* = 24.8, 12.2, 6.5 Hz, 4H), 1.87 – 1.69 (m, 4H).

^{13}C NMR (101 MHz, C_6D_6) δ 147.6, 147.4, 147.1, 142.9, 142.6, 135.8, 132.9 (d, *J* = 13.3 Hz), 132.1 (d, *J* = 15.3 Hz), 131.2, 130.5, 129.9, 129.6, 128.8, 128.6, 126.3, 123.2 (d, *J* = 20.3 Hz), 117.8 (d, *J* = 19.4 Hz), 115.7 (d, *J* = 19.4 Hz), 108.1, 61.4, 38.0 (d, *J* = 47.9 Hz), 30.6, 30.2 (d, *J* = 17.6 Hz), 25.3 (d, *J* = 7.4 Hz), 10.7.

^{31}P {^{1}H} NMR (162 MHz, C_6D_6) δ -13.8.

Copper complex B as a catalyst. In a nitrogen-filled glovebox, an oven-dried 4 mL amber-glass vial was charged with 3-methyl-1*H*-indole (13.1 mg, 0.100 mmol), a stir bar, and a solution of complex **B** (9.0 mg, 0.010 mmol) in *m*-xylene (200 μL). The vial was closed with a screw cap, the reaction mixture was stirred for 10 min, and then the α-iodo-γ-lactam (**A**; 43.1 mg, 0.150 mmol) and an internal standard (4,4′-di-*tert*-butylbiphenyl; 9.8 mg, 0.037 mmol) were added. After the reaction mixture became homogeneous (~5 min), Cs_2CO_3 (58.7 mg, 0.180 mmol) was added. The vial was re-capped and wrapped thoroughly with electrical tape in order to keep the reaction in the dark. The reaction mixture was stirred vigorously (1500 rpm) at 24 °C in the glovebox. After 72 h, the reaction mixture was diluted with $CDCl_3$ (1 mL). A portion of the mixture was removed for purification by preparative TLC (40% Et_2O in hexanes) and then ee analysis. The remainder of the mixture was filtered through a syringe filter, and the solvent was removed by evaporation (air flow), until a solid yellowish-white residue remained. The residue was then redissolved in $CDCl_3$ and analyzed via ^{1}H NMR spectroscopy.

The ee was determined via HPLC analysis: Diacel CHIRALPAK® IC column; 35% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times for the product: 22.5 min (minor), 26.5 min (major).

Run 1: 95% yield, 80% ee; Run 2: 98% yield, 77% ee.

Stoichiometric reaction of copper complex B with an alkyl iodide (eq 3). In a nitrogen-filled glovebox, an oven-dried 4 mL amber-glass vial was charged with copper complex **B** (9.0

mg, 0.010 mmol), a stir bar, and a solution of α-iodo-γ-lactam (**A**; 5.7 mg, 0.020 mmol) and internal standard (4,4′-di-*tert*-butylbiphenyl, 4.8 mg, 0.018 mmol) in d_8-toluene (150 μL). The vial was then closed with a screw cap, and the reaction mixture was stirred vigorously for 15 min at 24 °C in the glovebox. The vial was then removed from the glovebox, and the reaction mixture was diluted with $CDCl_3$ (1 mL) and filtered through a syringe filter. An aliquot (50 μL) of the filtrate was used for analysis via ^{1}H NMR spectroscopy. A sample of purified product was obtained via preparative TLC (40% Et_2O in hexanes).

The ee of the product was determined via HPLC analysis: Diacel CHIRALPAK® IC column; 35% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times for the product: 22.5 min (minor), 26.5 min (major). The yield was determined via ^{1}H NMR spectroscopy. 94% yield, 87% ee.

Stoichiometric reactions of copper complex B with alkyl bromides (Table 4). In a nitrogen-filled glovebox, two parallel reactions were prepared. Two oven-dried 4 mL amber-glass vials were charged with copper complex **B** (9.0 mg, 0.010 mmol) and a stir bar. A solution of (*S*)-α-bromo-γ-lactam (3.6 mg, 0.015 mmol) and an internal standard (4,4′-di-*tert*-butylbiphenyl; 4.0 mg, 0.015 mmol) in d_8-toluene (150 μL) was added to the first vial, and a solution of (*R*)-α-bromo-γ-lactam (3.6 mg, 0.015 mmol) and an internal standard (4,4′-di-*tert*-butylbiphenyl; 4.0 mg, 0.015 mmol) in d_8-toluene (150 μL) was added to the second vial. The vials were closed with a screw cap, and the reaction mixtures were stirred vigorously for 4 h at 24 °C in the glovebox. Aliquots (~100 μL) were taken from the reaction mixtures at different times, and they were immediately quenched by dilution with CH_2Cl_2 (2 mL) and filtration through a syringe filter. The composition of each sample was determined via analysis by ^{1}H NMR spectroscopy. Samples of purified product were obtained via preparative TLC (40% Et_2O in hexanes).

The ee's were determined via HPLC analysis: Diacel CHIRALPAK® IC column; 35% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times for: (*S*)-product 22.5 min, (*R*)-product 26.5 min. The stereochemical outcomes have been unambiguously determined via X-ray crystallographic characterization of the electrophile and product (see Section VII).

VI. Study of Non-Linear Effects

Non-linear effect (electrophile A, as well as its bromide analogue). In a nitrogen-filled glovebox, an oven-dried 4 mL amber-glass vial was charged with a 50 μL aliquot that contained 3-methyl-1*H*-indole (6.6 mg, 0.050 mmol), mesitylcopper (0.91 mg, 0.0050 mmol), and an internal standard (4,4′-di-*tert*-butylbiphenyl; 2.9 mg, 0.011) in *m*-xylene, taken from a stock solution. To this vial was added a 100 μL aliquot that contained **L*** of known ee (0.010 mmol) in *m*-xylene, also taken from a stock solution. The vial was charged with a stir bar and stirred for 10 min. Next, a solution of the electrophile (0.075 mmol) in *m*-xylene (150 μL) was added. The vial was re-capped and wrapped thoroughly with electrical tape in order to keep the reaction in the dark. The reaction mixture was stirred vigorously for 4 h at 24 °C in glovebox. After this time, the reaction mixture was removed from the glovebox, diluted with $CDCl_3$ (2 mL), and filtered through a syringe filter. An aliquot (50 μL) of the filtrate was analyzed via ^1H NMR spectroscopy (yield of product: ~9-10%). Pure product was obtained by preparative TLC (40% Et_2O in hexanes).

This study was performed with 24 parallel reactions containing **L*** (range of ee's) and the α-iodo-γ-lactam (12 reactions) or the α-bromo-γ-lactam (12 reactions).

The ee of the product was determined via HPLC analysis: Diacel CHIRALPAK® IC column; 35% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: 22.5 min, 26.5 min.

The ee of the **L*** used in each reaction was determined via HPLC analysis of the **L*** oxide: Diacel CHIRALPAK® AD column; 40% *i*-PrOH in hexanes, 1.0 mL/min flow-rate; retention times: (*S*)−**L*** oxide 5.0 min, (*R*)−**L*** oxide 15.4 min.

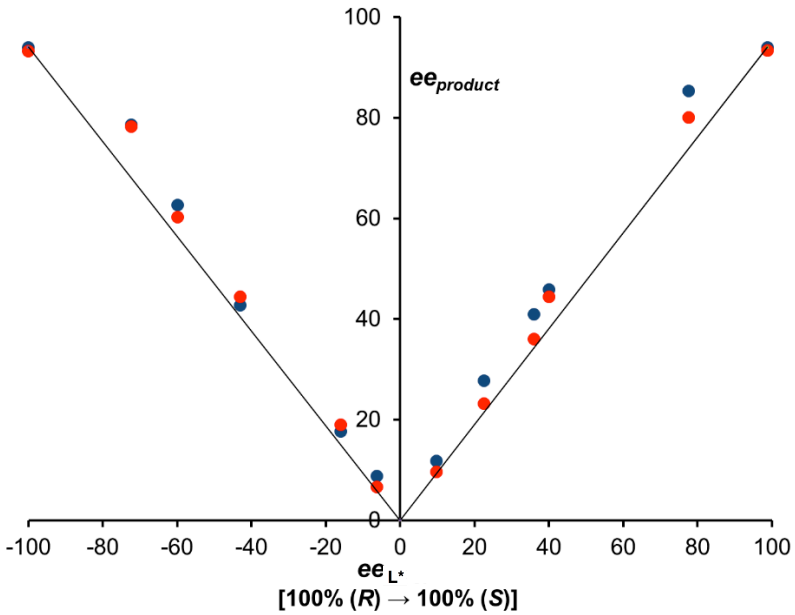


Figure S–2. Dependence of the ee of the product on the ee of **L***: Blue: alkyl iodide; b) Red: alkyl bromide.

VII. X-Ray Crystallography, Including Absolute Configuration

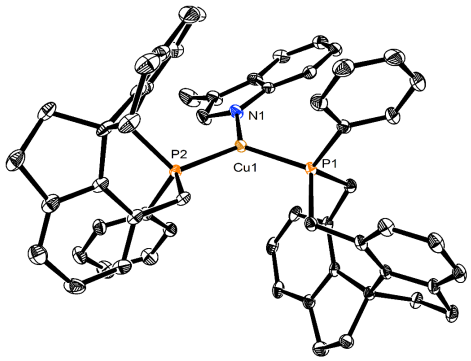


Figure S–3. Structure of copper complex **B**. Disordered solvent is omitted for clarity.

Copper complex B. A crystal suitable for X-ray crystallography was grown by slow evaporation of solvent from a saturated solution of copper complex **B** in a benzene/pentane mixture.

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON 100 CMOS detector with Mo K_α radiation (λ = 0.71073 Å) from an IμS micro-source. The structure was solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-2014 using established refinement techniques.[5] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). All disordered atoms were refined with the help of similarity restraints on the 1,2- and 1,3-distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters.

Copper complex **B** crystallized in the tetragonal space group $P4_3$ with one molecule in the asymmetric unit along with half a molecule of pentane. The pentane molecule is located near a crystallographic 4_3-screw axis. It was modeled as a disorder with two unique components in addition to the components generated by the 4_3-screw axis.

(5) Sheldrick, G. M. A Short History of SHELX. *Acta. Crystallogr. A*. **2008**, *64*, 112–122.

Table S–1. Crystal data and structure refinement for crystal_02.

Identification code	crystal_02
Empirical formula	$C_{61.50}H_{60}CuNP_2$
Formula weight	938.58
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	$P4_3$
Unit cell dimensions	a = 21.5667(6) Å α = 90°. b = 21.5667(6) Å β = 90°. c = 10.3865(3) Å γ = 90°.
Volume	4831.0(3) $Å^3$
Z	4
Density (calculated)	1.290 Mg/m^3
Absorption coefficient	0.560 mm^{-1}
F(000)	1980
Crystal size	0.300 x 0.100 x 0.100 mm^3
Theta range for data collection	2.372 to 36.351°
Index ranges	-35<=h<=35, -35<=k<=35, -15<=l<=17
Reflections collected	86761
Independent reflections	23032 [R(int) = 0.0533]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7471 and 0.6762
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	23032 / 172 / 660
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0461, wR2 = 0.0853
R indices (all data)	R1 = 0.0773, wR2 = 0.0942
Absolute structure parameter	-0.007(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.464 and -0.435 $e/Å^{-3}$

Table S–2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for crystal_02. U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	2491(1)	7377(1)	7838(1)	13(1)
P(1)	2006(1)	8278(1)	8125(1)	13(1)
C(1)	1864(1)	8476(1)	9837(2)	14(1)
C(2)	1918(1)	9648(1)	10118(2)	14(1)
C(3)	1571(1)	9100(1)	10036(2)	14(1)
C(4)	925(1)	9149(1)	10051(2)	19(1)
C(5)	629(1)	9718(1)	10183(2)	22(1)
C(6)	977(1)	10257(1)	10279(2)	21(1)
C(7)	1616(1)	10222(1)	10225(2)	17(1)
C(8)	2076(1)	10746(1)	10232(2)	20(1)
C(9)	2660(1)	10435(1)	9690(2)	18(1)
C(10)	2617(1)	9752(1)	10164(2)	14(1)
C(11)	2859(1)	9715(1)	11571(2)	18(1)
C(12)	3563(1)	9622(1)	11440(2)	23(1)
C(13)	3617(1)	9271(1)	10189(2)	16(1)
C(14)	4124(1)	8930(1)	9744(2)	19(1)
C(15)	4071(1)	8626(1)	8562(2)	19(1)
C(16)	3524(1)	8656(1)	7859(2)	17(1)
C(17)	3014(1)	9009(1)	8294(2)	14(1)
C(18)	3071(1)	9322(1)	9466(2)	14(1)
C(19)	2412(1)	8980(1)	7556(2)	14(1)
C(21)	1228(1)	8314(1)	7455(2)	16(1)
C(22)	1001(1)	8824(1)	6765(2)	23(1)
C(23)	395(1)	8820(1)	6305(3)	31(1)
C(24)	10(1)	8320(1)	6537(3)	32(1)
C(25)	234(1)	7808(1)	7209(3)	30(1)
C(26)	842(1)	7805(1)	7646(2)	23(1)
P(2)	2516(1)	6684(1)	9432(1)	12(1)
C(31)	1934(1)	6813(1)	10719(2)	15(1)
C(32)	1650(1)	5757(1)	11676(2)	16(1)
C(33)	1937(1)	6338(1)	11781(2)	15(1)
C(34)	2287(1)	6463(1)	12884(2)	20(1)
C(35)	2366(1)	6023(1)	13841(2)	26(1)
C(36)	2104(1)	5437(1)	13704(2)	29(1)
C(37)	1749(1)	5310(1)	12626(2)	22(1)
C(38)	1430(1)	4707(1)	12279(3)	27(1)
C(39)	1291(1)	4797(1)	10840(2)	23(1)
C(40)	1196(1)	5507(1)	10670(2)	17(1)
C(41)	515(1)	5677(1)	11028(3)	24(1)
C(42)	140(1)	5571(1)	9794(3)	30(1)
C(43)	607(1)	5710(1)	8756(3)	23(1)
C(44)	503(1)	5840(1)	7468(3)	30(1)

C(45)	1001(1)	5959(1)	6663(3)	32(1)
C(46)	1602(1)	5954(1)	7156(2)	25(1)
C(47)	1717(1)	5823(1)	8453(2)	17(1)
C(48)	1213(1)	5697(1)	9253(2)	17(1)
C(49)	2365(1)	5871(1)	8968(2)	15(1)
C(51)	3277(1)	6633(1)	10194(2)	14(1)
C(52)	3453(1)	6145(1)	10995(2)	18(1)
C(53)	4053(1)	6110(1)	11467(2)	24(1)
C(54)	4485(1)	6563(1)	11147(3)	26(1)
C(55)	4315(1)	7051(1)	10346(3)	24(1)
C(56)	3715(1)	7086(1)	9874(2)	17(1)
N(1)	2963(1)	7240(1)	6297(2)	18(1)
C(61)	3526(1)	6928(1)	6239(2)	24(1)
C(62)	3832(1)	7019(1)	5093(2)	24(1)
C(69)	4450(1)	6761(2)	4686(3)	38(1)
C(63)	3443(1)	7415(1)	4356(2)	18(1)
C(64)	3486(1)	7674(1)	3119(2)	20(1)
C(65)	3018(1)	8056(1)	2681(2)	21(1)
C(66)	2494(1)	8176(1)	3450(2)	19(1)
C(67)	2435(1)	7922(1)	4672(2)	17(1)
C(68)	2915(1)	7541(1)	5132(2)	14(1)
C(1S)	5187(14)	5199(9)	9570(20)	63(6)
C(2S)	5351(13)	5747(8)	8880(20)	68(4)
C(3S)	4998(13)	5940(9)	7765(19)	82(4)
C(4S)	4764(14)	5440(10)	6890(20)	83(4)
C(5S)	4149(13)	5367(13)	6540(30)	86(5)
C(1T)	5220(9)	6268(9)	8020(20)	83(5)
C(2T)	4746(10)	5803(7)	7976(16)	66(3)
C(3T)	4766(14)	5280(11)	7120(30)	81(4)
C(4T)	4493(12)	5149(10)	5944(18)	95(4)
C(5T)	4034(15)	4679(13)	5730(30)	129(8)

Table S–3. Bond lengths [Å] and angles [°] for crystal_02.

Bond length [Å]		Bond angle [°]	
Cu(1)-N(1)	1.9202(19)	N(1)-Cu(1)-P(1)	119.70(6)
Cu(1)-P(1)	2.2277(6)	N(1)-Cu(1)-P(2)	120.17(6)
Cu(1)-P(2)	2.2318(6)	P(1)-Cu(1)-P(2)	119.75(2)
P(1)-C(21)	1.817(2)	C(21)-P(1)-C(19)	106.29(10)
P(1)-C(19)	1.844(2)	C(21)-P(1)-C(1)	101.87(10)
P(1)-C(1)	1.854(2)	C(19)-P(1)-C(1)	101.37(10)
C(1)-C(3)	1.501(3)	C(21)-P(1)-Cu(1)	114.81(7)
C(1)-H(1A)	0.9900	C(19)-P(1)-Cu(1)	116.68(7)
C(1)-H(1B)	0.9900	C(1)-P(1)-Cu(1)	113.97(7)
C(2)-C(3)	1.401(3)	C(3)-C(1)-P(1)	114.06(14)
C(2)-C(7)	1.403(3)	C(3)-C(1)-H(1A)	108.7
C(2)-C(10)	1.526(3)	P(1)-C(1)-H(1A)	108.7
C(3)-C(4)	1.399(3)	C(3)-C(1)-H(1B)	108.7
C(4)-C(5)	1.390(3)	P(1)-C(1)-H(1B)	108.7
C(4)-H(4)	0.9500	H(1A)-C(1)-H(1B)	107.6
C(5)-C(6)	1.386(3)	C(3)-C(2)-C(7)	120.10(19)
C(5)-H(5)	0.9500	C(3)-C(2)-C(10)	130.71(18)
C(6)-C(7)	1.380(3)	C(7)-C(2)-C(10)	109.14(18)
C(6)-H(6)	0.9500	C(4)-C(3)-C(2)	117.83(19)
C(7)-C(8)	1.504(3)	C(4)-C(3)-C(1)	119.25(19)
C(8)-C(9)	1.535(3)	C(2)-C(3)-C(1)	122.75(18)
C(8)-H(8A)	0.9900	C(5)-C(4)-C(3)	121.7(2)
C(8)-H(8B)	0.9900	C(5)-C(4)-H(4)	119.2
C(9)-C(10)	1.557(3)	C(3)-C(4)-H(4)	119.2
C(9)-H(9A)	0.9900	C(6)-C(5)-C(4)	119.9(2)
C(9)-H(9B)	0.9900	C(6)-C(5)-H(5)	120.1
C(10)-C(18)	1.530(3)	C(4)-C(5)-H(5)	120.1
C(10)-C(11)	1.554(3)	C(7)-C(6)-C(5)	119.5(2)
C(11)-C(12)	1.538(3)	C(7)-C(6)-H(6)	120.3
C(11)-H(11A)	0.9900	C(5)-C(6)-H(6)	120.3
C(11)-H(11B)	0.9900	C(6)-C(7)-C(2)	121.0(2)
C(12)-C(13)	1.508(3)	C(6)-C(7)-C(8)	128.13(19)
C(12)-H(12A)	0.9900	C(2)-C(7)-C(8)	110.89(18)
C(12)-H(12B)	0.9900	C(7)-C(8)-C(9)	102.25(17)
C(13)-C(14)	1.398(3)	C(7)-C(8)-H(8A)	111.3
C(13)-C(18)	1.401(3)	C(9)-C(8)-H(8A)	111.3
C(14)-C(15)	1.396(3)	C(7)-C(8)-H(8B)	111.3
C(14)-H(14)	0.9500	C(9)-C(8)-H(8B)	111.3
C(15)-C(16)	1.388(3)	H(8A)-C(8)-H(8B)	109.2
C(15)-H(15)	0.9500	C(8)-C(9)-C(10)	104.39(17)
C(16)-C(17)	1.412(3)	C(8)-C(9)-H(9A)	110.9
C(16)-H(16)	0.9500	C(10)-C(9)-H(9A)	110.9

C(17)-C(18)	1.397(3)	C(8)-C(9)-H(9B)	110.9
C(17)-C(19)	1.509(3)	C(10)-C(9)-H(9B)	110.9
C(19)-H(19A)	0.9900	H(9A)-C(9)-H(9B)	108.9
C(19)-H(19B)	0.9900	C(2)-C(10)-C(18)	121.87(17)
C(21)-C(26)	1.394(3)	C(2)-C(10)-C(11)	110.71(17)
C(21)-C(22)	1.401(3)	C(18)-C(10)-C(11)	101.58(16)
C(22)-C(23)	1.392(3)	C(2)-C(10)-C(9)	100.79(16)
C(22)-H(22)	0.9500	C(18)-C(10)-C(9)	112.70(17)
C(23)-C(24)	1.382(4)	C(11)-C(10)-C(9)	109.04(18)
C(23)-H(23)	0.9500	C(12)-C(11)-C(10)	104.76(17)
C(24)-C(25)	1.393(4)	C(12)-C(11)-H(11A)	110.8
C(24)-H(24)	0.9500	C(10)-C(11)-H(11A)	110.8
C(25)-C(26)	1.386(3)	C(12)-C(11)-H(11B)	110.8
C(25)-H(25)	0.9500	C(10)-C(11)-H(11B)	110.8
C(26)-H(26)	0.9500	H(11A)-C(11)-H(11B)	108.9
P(2)-C(51)	1.825(2)	C(13)-C(12)-C(11)	102.53(18)
P(2)-C(49)	1.848(2)	C(13)-C(12)-H(12A)	111.3
P(2)-C(31)	1.854(2)	C(11)-C(12)-H(12A)	111.3
C(31)-C(33)	1.505(3)	C(13)-C(12)-H(12B)	111.3
C(31)-H(31A)	0.9900	C(11)-C(12)-H(12B)	111.3
C(31)-H(31B)	0.9900	H(12A)-C(12)-H(12B)	109.2
C(32)-C(37)	1.396(3)	C(14)-C(13)-C(18)	121.4(2)
C(32)-C(33)	1.403(3)	C(14)-C(13)-C(12)	127.6(2)
C(32)-C(40)	1.530(3)	C(18)-C(13)-C(12)	111.04(18)
C(33)-C(34)	1.397(3)	C(15)-C(14)-C(13)	118.3(2)
C(34)-C(35)	1.385(3)	C(15)-C(14)-H(14)	120.8
C(34)-H(34)	0.9500	C(13)-C(14)-H(14)	120.8
C(35)-C(36)	1.390(4)	C(16)-C(15)-C(14)	120.67(19)
C(35)-H(35)	0.9500	C(16)-C(15)-H(15)	119.7
C(36)-C(37)	1.384(4)	C(14)-C(15)-H(15)	119.7
C(36)-H(36)	0.9500	C(15)-C(16)-C(17)	121.3(2)
C(37)-C(38)	1.516(3)	C(15)-C(16)-H(16)	119.4
C(38)-C(39)	1.537(4)	C(17)-C(16)-H(16)	119.4
C(38)-H(38A)	0.9900	C(18)-C(17)-C(16)	118.00(19)
C(38)-H(38B)	0.9900	C(18)-C(17)-C(19)	122.62(18)
C(39)-C(40)	1.555(3)	C(16)-C(17)-C(19)	119.05(19)
C(39)-H(39A)	0.9900	C(17)-C(18)-C(13)	120.28(19)
C(39)-H(39B)	0.9900	C(17)-C(18)-C(10)	130.48(18)
C(40)-C(48)	1.528(3)	C(13)-C(18)-C(10)	109.24(18)
C(40)-C(41)	1.559(3)	C(17)-C(19)-P(1)	106.29(14)
C(41)-C(42)	1.533(4)	C(17)-C(19)-H(19A)	110.5
C(41)-H(41A)	0.9900	P(1)-C(19)-H(19A)	110.5
C(41)-H(41B)	0.9900	C(17)-C(19)-H(19B)	110.5
C(42)-C(43)	1.506(4)	P(1)-C(19)-H(19B)	110.5
C(42)-H(42A)	0.9900	H(19A)-C(19)-H(19B)	108.7

C(42)-H(42B)	0.9900	C(26)-C(21)-C(22)	118.9(2)
C(43)-C(44)	1.386(4)	C(26)-C(21)-P(1)	117.63(17)
C(43)-C(48)	1.405(3)	C(22)-C(21)-P(1)	123.50(18)
C(44)-C(45)	1.384(4)	C(23)-C(22)-C(21)	119.9(2)
C(44)-H(44)	0.9500	C(23)-C(22)-H(22)	120.0
C(45)-C(46)	1.395(4)	C(21)-C(22)-H(22)	120.0
C(45)-H(45)	0.9500	C(24)-C(23)-C(22)	120.7(2)
C(46)-C(47)	1.398(3)	C(24)-C(23)-H(23)	119.7
C(46)-H(46)	0.9500	C(22)-C(23)-H(23)	119.7
C(47)-C(48)	1.394(3)	C(23)-C(24)-C(25)	119.7(2)
C(47)-C(49)	1.501(3)	C(23)-C(24)-H(24)	120.1
C(49)-H(49A)	0.9900	C(25)-C(24)-H(24)	120.1
C(49)-H(49B)	0.9900	C(26)-C(25)-C(24)	119.8(2)
C(51)-C(52)	1.394(3)	C(26)-C(25)-H(25)	120.1
C(51)-C(56)	1.399(3)	C(24)-C(25)-H(25)	120.1
C(52)-C(53)	1.386(3)	C(25)-C(26)-C(21)	120.9(2)
C(52)-H(52)	0.9500	C(25)-C(26)-H(26)	119.5
C(53)-C(54)	1.391(4)	C(21)-C(26)-H(26)	119.5
C(53)-H(53)	0.9500	C(51)-P(2)-C(49)	102.36(9)
C(54)-C(55)	1.389(4)	C(51)-P(2)-C(31)	107.78(10)
C(54)-H(54)	0.9500	C(49)-P(2)-C(31)	102.19(9)
C(55)-C(56)	1.387(3)	C(51)-P(2)-Cu(1)	112.57(7)
C(55)-H(55)	0.9500	C(49)-P(2)-Cu(1)	115.95(7)
C(56)-H(56)	0.9500	C(31)-P(2)-Cu(1)	114.73(7)
N(1)-C(68)	1.377(3)	C(33)-C(31)-P(2)	115.06(14)
N(1)-C(61)	1.388(3)	C(33)-C(31)-H(31A)	108.5
C(61)-C(62)	1.376(3)	P(2)-C(31)-H(31A)	108.5
C(61)-H(61)	0.9500	C(33)-C(31)-H(31B)	108.5
C(62)-C(63)	1.422(3)	P(2)-C(31)-H(31B)	108.5
C(62)-C(69)	1.503(3)	H(31A)-C(31)-H(31B)	107.5
C(69)-H(69A)	0.9800	C(37)-C(32)-C(33)	119.6(2)
C(69)-H(69B)	0.9800	C(37)-C(32)-C(40)	109.72(18)
C(69)-H(69C)	0.9800	C(33)-C(32)-C(40)	130.6(2)
C(63)-C(64)	1.404(3)	C(34)-C(33)-C(32)	118.3(2)
C(63)-C(68)	1.421(3)	C(34)-C(33)-C(31)	118.20(18)
C(64)-C(65)	1.380(3)	C(32)-C(33)-C(31)	123.27(19)
C(64)-H(64)	0.9500	C(35)-C(34)-C(33)	121.5(2)
C(65)-C(66)	1.408(3)	C(35)-C(34)-H(34)	119.3
C(65)-H(65)	0.9500	C(33)-C(34)-H(34)	119.3
C(66)-C(67)	1.389(3)	C(34)-C(35)-C(36)	120.0(2)
C(66)-H(66)	0.9500	C(34)-C(35)-H(35)	120.0
C(67)-C(68)	1.405(3)	C(36)-C(35)-H(35)	120.0
C(67)-H(67)	0.9500	C(37)-C(36)-C(35)	119.1(2)
C(1S)-C(2S)	1.422(18)	C(37)-C(36)-H(36)	120.4
C(1S)-H(1S1)	0.9800	C(35)-C(36)-H(36)	120.4

C(1S)-H(1S2)	0.9800
C(1S)-H(1S3)	0.9800
C(2S)-C(3S)	1.451(19)
C(2S)-H(2S1)	0.9900
C(2S)-H(2S2)	0.9900
C(3S)-C(4S)	1.501(18)
C(3S)-H(3S1)	0.9900
C(3S)-H(3S2)	0.9900
C(4S)-C(5S)	1.383(19)
C(4S)-H(4S1)	0.9900
C(4S)-H(4S2)	0.9900
C(5S)-H(5S1)	0.9800
C(5S)-H(5S2)	0.9800
C(5S)-H(5S3)	0.9800
C(1T)-C(2T)	1.432(18)
C(1T)-H(1T1)	0.9800
C(1T)-H(1T2)	0.9800
C(1T)-H(1T3)	0.9800
C(2T)-C(3T)	1.436(18)
C(2T)-H(2T1)	0.9900
C(2T)-H(2T2)	0.9900
C(3T)-C(4T)	1.386(18)
C(3T)-H(3T1)	0.9900
C(3T)-H(3T2)	0.9900
C(4T)-C(5T)	1.434(18)
C(4T)-H(4T1)	0.9900
C(4T)-H(4T2)	0.9900
C(5T)-H(5T1)	0.9800
C(5T)-H(5T2)	0.9800
C(5T)-H(5T3)	0.9800

C(36)-C(37)-C(32)	121.3(2)
C(36)-C(37)-C(38)	127.8(2)
C(32)-C(37)-C(38)	110.8(2)
C(37)-C(38)-C(39)	102.16(19)
C(37)-C(38)-H(38A)	111.3
C(39)-C(38)-H(38A)	111.3
C(37)-C(38)-H(38B)	111.3
C(39)-C(38)-H(38B)	111.3
H(38A)-C(38)-H(38B)	109.2
C(38)-C(39)-C(40)	105.18(18)
C(38)-C(39)-H(39A)	110.7
C(40)-C(39)-H(39A)	110.7
C(38)-C(39)-H(39B)	110.7
C(40)-C(39)-H(39B)	110.7
H(39A)-C(39)-H(39B)	108.8
C(48)-C(40)-C(32)	123.21(18)
C(48)-C(40)-C(39)	111.76(17)
C(32)-C(40)-C(39)	100.67(18)
C(48)-C(40)-C(41)	100.93(19)
C(32)-C(40)-C(41)	110.93(18)
C(39)-C(40)-C(41)	109.14(18)
C(42)-C(41)-C(40)	105.27(19)
C(42)-C(41)-H(41A)	110.7
C(40)-C(41)-H(41A)	110.7
C(42)-C(41)-H(41B)	110.7
C(40)-C(41)-H(41B)	110.7
H(41A)-C(41)-H(41B)	108.8
C(43)-C(42)-C(41)	102.39(19)
C(43)-C(42)-H(42A)	111.3
C(41)-C(42)-H(42A)	111.3
C(43)-C(42)-H(42B)	111.3
C(41)-C(42)-H(42B)	111.3
H(42A)-C(42)-H(42B)	109.2
C(44)-C(43)-C(48)	120.6(2)
C(44)-C(43)-C(42)	128.5(2)
C(48)-C(43)-C(42)	110.9(2)
C(45)-C(44)-C(43)	119.7(2)
C(45)-C(44)-H(44)	120.2
C(43)-C(44)-H(44)	120.2
C(44)-C(45)-C(46)	119.9(3)
C(44)-C(45)-H(45)	120.1
C(46)-C(45)-H(45)	120.1
C(45)-C(46)-C(47)	121.3(2)
C(45)-C(46)-H(46)	119.3
C(47)-C(46)-H(46)	119.3

C(48)-C(47)-C(46)	118.4(2)
C(48)-C(47)-C(49)	121.8(2)
C(46)-C(47)-C(49)	119.6(2)
C(47)-C(48)-C(43)	120.1(2)
C(47)-C(48)-C(40)	130.2(2)
C(43)-C(48)-C(40)	109.6(2)
C(47)-C(49)-P(2)	108.78(14)
C(47)-C(49)-H(49A)	109.9
P(2)-C(49)-H(49A)	109.9
C(47)-C(49)-H(49B)	109.9
P(2)-C(49)-H(49B)	109.9
H(49A)-C(49)-H(49B)	108.3
C(52)-C(51)-C(56)	119.01(19)
C(52)-C(51)-P(2)	123.29(16)
C(56)-C(51)-P(2)	117.52(16)
C(53)-C(52)-C(51)	120.4(2)
C(53)-C(52)-H(52)	119.8
C(51)-C(52)-H(52)	119.8
C(52)-C(53)-C(54)	120.1(2)
C(52)-C(53)-H(53)	119.9
C(54)-C(53)-H(53)	119.9
C(55)-C(54)-C(53)	120.0(2)
C(55)-C(54)-H(54)	120.0
C(53)-C(54)-H(54)	120.0
C(56)-C(55)-C(54)	119.9(2)
C(56)-C(55)-H(55)	120.1
C(54)-C(55)-H(55)	120.1
C(55)-C(56)-C(51)	120.6(2)
C(55)-C(56)-H(56)	119.7
C(51)-C(56)-H(56)	119.7
C(68)-N(1)-C(61)	104.91(18)
C(68)-N(1)-Cu(1)	128.27(14)
C(61)-N(1)-Cu(1)	125.01(15)
C(62)-C(61)-N(1)	112.8(2)
C(62)-C(61)-H(61)	123.6
N(1)-C(61)-H(61)	123.6
C(61)-C(62)-C(63)	105.5(2)
C(61)-C(62)-C(69)	128.1(2)
C(63)-C(62)-C(69)	126.5(2)
C(62)-C(69)-H(69A)	109.5
C(62)-C(69)-H(69B)	109.5
H(69A)-C(69)-H(69B)	109.5
C(62)-C(69)-H(69C)	109.5
H(69A)-C(69)-H(69C)	109.5
H(69B)-C(69)-H(69C)	109.5

C(64)-C(63)-C(68)	119.7(2)
C(64)-C(63)-C(62)	133.8(2)
C(68)-C(63)-C(62)	106.47(19)
C(65)-C(64)-C(63)	119.4(2)
C(65)-C(64)-H(64)	120.3
C(63)-C(64)-H(64)	120.3
C(64)-C(65)-C(66)	120.7(2)
C(64)-C(65)-H(65)	119.7
C(66)-C(65)-H(65)	119.7
C(67)-C(66)-C(65)	121.3(2)
C(67)-C(66)-H(66)	119.4
C(65)-C(66)-H(66)	119.4
C(66)-C(67)-C(68)	118.3(2)
C(66)-C(67)-H(67)	120.9
C(68)-C(67)-H(67)	120.9
N(1)-C(68)-C(67)	129.02(19)
N(1)-C(68)-C(63)	110.32(18)
C(67)-C(68)-C(63)	120.65(19)
C(2S)-C(1S)-H(1S1)	109.5
C(2S)-C(1S)-H(1S2)	109.5
H(1S1)-C(1S)-H(1S2)	109.5
C(2S)-C(1S)-H(1S3)	109.5
H(1S1)-C(1S)-H(1S3)	109.5
H(1S2)-C(1S)-H(1S3)	109.5
C(1S)-C(2S)-C(3S)	120.5(18)
C(1S)-C(2S)-H(2S1)	107.2
C(3S)-C(2S)-H(2S1)	107.2
C(1S)-C(2S)-H(2S2)	107.2
C(3S)-C(2S)-H(2S2)	107.2
H(2S1)-C(2S)-H(2S2)	106.8
C(2S)-C(3S)-C(4S)	117.2(14)
C(2S)-C(3S)-H(3S1)	108.0
C(4S)-C(3S)-H(3S1)	108.0
C(2S)-C(3S)-H(3S2)	108.0
C(4S)-C(3S)-H(3S2)	108.0
H(3S1)-C(3S)-H(3S2)	107.2
C(5S)-C(4S)-C(3S)	124(2)
C(5S)-C(4S)-H(4S1)	106.3
C(3S)-C(4S)-H(4S1)	106.3
C(5S)-C(4S)-H(4S2)	106.3
C(3S)-C(4S)-H(4S2)	106.3
H(4S1)-C(4S)-H(4S2)	106.4
C(4S)-C(5S)-H(5S1)	109.5
C(4S)-C(5S)-H(5S2)	109.5
H(5S1)-C(5S)-H(5S2)	109.5

C(4S)-C(5S)-H(5S3)	109.5
H(5S1)-C(5S)-H(5S3)	109.5
H(5S2)-C(5S)-H(5S3)	109.5
C(2T)-C(1T)-H(1T1)	109.5
C(2T)-C(1T)-H(1T2)	109.5
H(1T1)-C(1T)-H(1T2)	109.5
C(2T)-C(1T)-H(1T3)	109.5
H(1T1)-C(1T)-H(1T3)	109.5
H(1T2)-C(1T)-H(1T3)	109.5
C(1T)-C(2T)-C(3T)	123.2(17)
C(1T)-C(2T)-H(2T1)	106.5
C(3T)-C(2T)-H(2T1)	106.5
C(1T)-C(2T)-H(2T2)	106.5
C(3T)-C(2T)-H(2T2)	106.5
H(2T1)-C(2T)-H(2T2)	106.5
C(4T)-C(3T)-C(2T)	134(2)
C(4T)-C(3T)-H(3T1)	103.7
C(2T)-C(3T)-H(3T1)	103.7
C(4T)-C(3T)-H(3T2)	103.7
C(2T)-C(3T)-H(3T2)	103.7
H(3T1)-C(3T)-H(3T2)	105.4
C(3T)-C(4T)-C(5T)	125(2)
C(3T)-C(4T)-H(4T1)	106.1
C(5T)-C(4T)-H(4T1)	106.1
C(3T)-C(4T)-H(4T2)	106.1
C(5T)-C(4T)-H(4T2)	106.1
H(4T1)-C(4T)-H(4T2)	106.3
C(4T)-C(5T)-H(5T1)	109.5
C(4T)-C(5T)-H(5T2)	109.5
H(5T1)-C(5T)-H(5T2)	109.5
C(4T)-C(5T)-H(5T3)	109.5
H(5T1)-C(5T)-H(5T3)	109.5
H(5T2)-C(5T)-H(5T3)	109.5

Table S–4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for crystal_02. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	13(1)	14(1)	12(1)	1(1)	0(1)	1(1)
P(1)	12(1)	14(1)	13(1)	2(1)	0(1)	2(1)
C(1)	15(1)	15(1)	13(1)	2(1)	1(1)	2(1)
C(2)	14(1)	17(1)	12(1)	2(1)	1(1)	5(1)
C(3)	14(1)	18(1)	12(1)	4(1)	3(1)	4(1)
C(4)	15(1)	25(1)	18(1)	3(1)	4(1)	2(1)
C(5)	14(1)	31(1)	20(1)	5(1)	4(1)	8(1)
C(6)	19(1)	26(1)	17(1)	3(1)	5(1)	12(1)
C(7)	19(1)	18(1)	14(1)	2(1)	2(1)	7(1)
C(8)	22(1)	16(1)	21(1)	2(1)	3(1)	7(1)
C(9)	20(1)	14(1)	21(1)	1(1)	4(1)	3(1)
C(10)	13(1)	14(1)	14(1)	0(1)	2(1)	3(1)
C(11)	17(1)	21(1)	16(1)	-1(1)	-1(1)	4(1)
C(12)	18(1)	28(1)	22(1)	-5(1)	-3(1)	5(1)
C(13)	12(1)	15(1)	20(1)	0(1)	-1(1)	2(1)
C(14)	13(1)	15(1)	29(1)	2(1)	1(1)	3(1)
C(15)	13(1)	15(1)	30(1)	1(1)	6(1)	4(1)
C(16)	15(1)	14(1)	21(1)	-1(1)	7(1)	1(1)
C(17)	12(1)	12(1)	18(1)	3(1)	4(1)	1(1)
C(18)	12(1)	12(1)	17(1)	2(1)	2(1)	3(1)
C(19)	15(1)	15(1)	14(1)	2(1)	2(1)	1(1)
C(21)	14(1)	20(1)	15(1)	-3(1)	-2(1)	5(1)
C(22)	21(1)	22(1)	26(1)	1(1)	-7(1)	4(1)
C(23)	26(1)	29(1)	38(2)	-1(1)	-14(1)	10(1)
C(24)	18(1)	37(2)	42(2)	-13(1)	-14(1)	6(1)
C(25)	20(1)	30(1)	38(2)	-9(1)	-4(1)	-4(1)
C(26)	19(1)	23(1)	26(1)	0(1)	-4(1)	-1(1)
P(2)	12(1)	11(1)	13(1)	0(1)	1(1)	0(1)
C(31)	16(1)	12(1)	16(1)	-4(1)	2(1)	-2(1)
C(32)	17(1)	14(1)	17(1)	-4(1)	6(1)	-4(1)
C(33)	17(1)	14(1)	16(1)	-2(1)	6(1)	-4(1)
C(34)	23(1)	20(1)	16(1)	-2(1)	4(1)	-9(1)
C(35)	34(1)	31(1)	13(1)	1(1)	1(1)	-11(1)
C(36)	42(2)	27(1)	17(1)	7(1)	5(1)	-8(1)
C(37)	27(1)	18(1)	21(1)	0(1)	8(1)	-7(1)
C(38)	34(1)	16(1)	29(1)	0(1)	9(1)	-8(1)
C(39)	28(1)	13(1)	28(1)	-5(1)	6(1)	-6(1)
C(40)	15(1)	13(1)	24(1)	-6(1)	4(1)	-4(1)
C(41)	16(1)	22(1)	34(1)	-9(1)	7(1)	-4(1)
C(42)	14(1)	30(1)	44(2)	-12(1)	2(1)	-4(1)
C(43)	16(1)	20(1)	34(1)	-9(1)	-4(1)	0(1)
C(44)	22(1)	30(1)	39(2)	-6(1)	-12(1)	0(1)

C(45)	32(1)	36(1)	27(1)	-2(1)	-13(1)	-3(1)
C(46)	24(1)	27(1)	23(1)	-5(1)	-3(1)	-1(1)
C(47)	18(1)	13(1)	20(1)	-5(1)	0(1)	1(1)
C(48)	15(1)	12(1)	24(1)	-7(1)	0(1)	-1(1)
C(49)	14(1)	12(1)	17(1)	-2(1)	3(1)	1(1)
C(51)	13(1)	15(1)	15(1)	1(1)	1(1)	-1(1)
C(52)	18(1)	17(1)	20(1)	5(1)	-2(1)	-1(1)
C(53)	22(1)	25(1)	26(1)	6(1)	-5(1)	2(1)
C(54)	15(1)	34(1)	30(1)	3(1)	-4(1)	0(1)
C(55)	17(1)	27(1)	27(1)	3(1)	0(1)	-6(1)
C(56)	17(1)	17(1)	17(1)	3(1)	0(1)	-3(1)
N(1)	18(1)	22(1)	14(1)	0(1)	0(1)	6(1)
C(61)	23(1)	31(1)	17(1)	-1(1)	-2(1)	13(1)
C(62)	18(1)	34(1)	19(1)	-3(1)	-1(1)	8(1)
C(69)	24(1)	65(2)	26(1)	-5(1)	1(1)	19(1)
C(63)	13(1)	26(1)	15(1)	-2(1)	0(1)	-1(1)
C(64)	16(1)	28(1)	17(1)	-1(1)	3(1)	-6(1)
C(65)	24(1)	22(1)	15(1)	3(1)	0(1)	-7(1)
C(66)	22(1)	18(1)	18(1)	2(1)	-4(1)	-1(1)
C(67)	17(1)	16(1)	16(1)	-2(1)	1(1)	0(1)
C(68)	15(1)	16(1)	12(1)	-2(1)	-1(1)	-1(1)
C(1S)	100(17)	34(7)	54(9)	-26(5)	15(10)	13(8)
C(2S)	104(10)	35(6)	64(7)	-25(6)	40(6)	17(6)
C(3S)	128(10)	48(7)	71(7)	-6(6)	34(6)	17(7)
C(4S)	137(10)	52(8)	61(7)	7(6)	21(7)	8(7)
C(5S)	137(11)	42(9)	80(12)	21(8)	17(11)	8(10)
C(1T)	105(11)	78(10)	66(10)	-15(8)	28(9)	4(7)
C(2T)	102(9)	41(6)	56(6)	7(5)	54(6)	23(5)
C(3T)	132(10)	49(7)	62(7)	-1(6)	38(7)	7(7)
C(4T)	149(11)	67(8)	70(7)	6(6)	23(8)	-1(8)
C(5T)	171(18)	102(14)	115(16)	-38(12)	30(12)	-22(12)

Table S–5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for crystal_02.

	x	y	z	U(eq)
H(1A)	1592	8156	10218	17
H(1B)	2264	8464	10304	17
H(4)	682	8784	9968	23
H(5)	189	9739	10208	26
H(6)	778	10647	10380	25
H(8A)	2146	10903	11115	24
H(8B)	1937	11092	9676	24
H(9A)	3039	10638	10024	22
H(9B)	2665	10455	8737	22
H(11A)	2765	10103	12044	22
H(11B)	2667	9362	12033	22
H(12A)	3783	10025	11395	27
H(12B)	3731	9378	12168	27
H(14)	4495	8904	10233	23
H(15)	4412	8396	8236	23
H(16)	3493	8436	7070	20
H(19A)	2493	8952	6619	17
H(19B)	2158	9354	7725	17
H(22)	1261	9172	6611	28
H(23)	245	9164	5827	37
H(24)	-407	8326	6239	39
H(25)	-28	7463	7368	35
H(26)	997	7450	8082	27
H(31A)	2007	7227	11102	18
H(31B)	1517	6818	10322	18
H(34)	2474	6859	12980	24
H(35)	2599	6121	14590	31
H(36)	2169	5128	14341	35
H(38A)	1044	4649	12781	32
H(38B)	1707	4347	12423	32
H(39A)	912	4568	10589	28
H(39B)	1641	4650	10307	28
H(41A)	362	5408	11731	29
H(41B)	486	6115	11306	29
H(42A)	-10	5138	9737	35
H(42B)	-219	5856	9745	35
H(44)	92	5846	7138	37
H(45)	932	6044	5777	38
H(46)	1941	6041	6599	30
H(49A)	2666	5739	8301	18
H(49B)	2414	5597	9725	18

H(52)	3159	5834	11218	22
H(53)	4169	5775	12010	29
H(54)	4895	6539	11475	32
H(55)	4610	7360	10123	28
H(56)	3600	7420	9328	21
H(61)	3682	6678	6920	28
H(69A)	4687	6640	5450	57
H(69B)	4680	7078	4207	57
H(69C)	4385	6398	4135	57
H(64)	3834	7587	2589	24
H(65)	3049	8239	1852	25
H(66)	2174	8437	3127	23
H(67)	2079	8003	5185	20
H(1S1)	5473	5139	10289	94
H(1S2)	4762	5238	9892	94
H(1S3)	5212	4841	8985	94
H(2S1)	5788	5699	8608	81
H(2S2)	5341	6093	9509	81
H(3S1)	5261	6224	7251	99
H(3S2)	4637	6183	8069	99
H(4S1)	4999	5482	6072	100
H(4S2)	4894	5041	7274	100
H(5S1)	4109	5011	5960	130
H(5S2)	3898	5297	7312	130
H(5S3)	4004	5742	6099	130
H(1T1)	5113	6580	8666	124
H(1T2)	5617	6075	8241	124
H(1T3)	5254	6467	7171	124
H(2T1)	4352	6022	7798	79
H(2T2)	4712	5633	8858	79
H(3T1)	5214	5219	6959	97
H(3T2)	4639	4928	7673	97
H(4T1)	4838	5056	5345	114
H(4T2)	4307	5543	5643	114
H(5T1)	3915	4678	4817	194
H(5T2)	4206	4273	5959	194
H(5T3)	3669	4765	6259	194

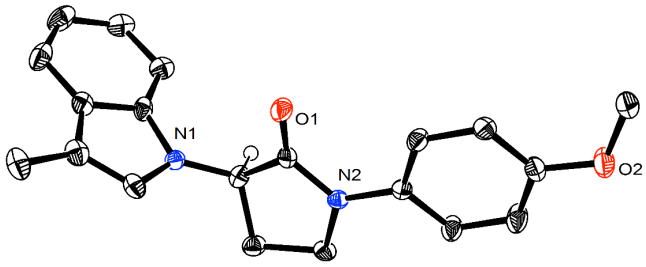


Figure S–4. Structure of (3*R*)-1-(4-methoxyphenyl)-3-(3-methyl-1*H*-indol-1-yl)pyrrolidin-2-one. One of two molecules in the asymmetric unit is shown.

(3*R*)-1-(4-Methoxyphenyl)-3-(3-methyl-1*H*-indol-1-yl)pyrrolidin-2-one (Table 2, entry 2; synthesized using (*R*)–L*). A suitable crystal for X-ray crystallography was grown by vapor diffusion with Et_2O and hexane.

A crystal of $C_{20}H_{20}N_2O_2$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Photon diffractometer with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2,[6] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package[5] using least squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

(6) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

Table S–6. Crystal data and structure refinement for crystal_03.

Identification code	crystal_03
Empirical formula	$C_{20}H_{20}N_2O_2$
Formula weight	320.38
Temperature	100 K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 8.0191(4) Å α = 90°. b = 11.0299(6) Å β = 90° c = 36.6492(19) Å γ = 90°.
Volume	3241.6(3) $Å^3$
Z	8
Density (calculated)	1.313 Mg/m^3
Absorption coefficient	0.682 mm^{-1}
F(000)	1360
Crystal size	0.20 x 0.15 x 0.05 mm^3
Theta range for data collection	2.411 to 74.548°.
Index ranges	-9<=h<=10, -6<=k<=13, -44<=l<=45
Reflections collected	22350
Independent reflections	6493 [R(int) = 0.0655]
Completeness to theta = 67.679°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7468 and 0.6802
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6493 / 0 / 437
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0573, wR2 = 0.1417
R indices (all data)	R1 = 0.0708, wR2 = 0.1507
Absolute structure parameter	0.0(2)
Largest diff. peak and hole	0.551 and -0.209 $e/Å^{-3}$

Table S–7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for crystal_03. U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-8642(4)	-192(3)	761(1)	28(1)
O(2)	-6222(4)	-1004(3)	-928(1)	31(1)
N(1)	-7939(4)	-930(3)	1497(1)	19(1)
N(2)	-6330(4)	-1317(3)	596(1)	16(1)
C(1)	-7547(5)	-919(3)	827(1)	19(1)
C(2)	-7354(5)	-1606(3)	1190(1)	21(1)
C(3)	-5534(5)	-1993(3)	1187(1)	23(1)
C(4)	-5151(5)	-2143(3)	779(1)	20(1)
C(5)	-6325(4)	-1182(3)	210(1)	17(1)
C(6)	-7379(5)	-379(3)	30(1)	21(1)
C(7)	-7394(5)	-305(3)	-348(1)	21(1)
C(8)	-6316(5)	-1019(3)	-554(1)	22(1)
C(9)	-5245(6)	-1803(4)	-377(1)	32(1)
C(10)	-5236(5)	-1888(4)	3(1)	26(1)
C(11)	-7412(5)	-278(3)	-1120(1)	25(1)
C(12)	-7261(5)	135(3)	1639(1)	24(1)
C(13)	-8255(5)	623(3)	1902(1)	25(1)
C(14)	-9646(5)	-174(3)	1933(1)	22(1)
C(15)	-11071(6)	-171(4)	2160(1)	31(1)
C(16)	-12234(6)	-1073(4)	2120(1)	34(1)
C(17)	-12022(5)	-1988(4)	1857(1)	28(1)
C(18)	-10658(5)	-2009(3)	1630(1)	25(1)
C(19)	-9448(5)	-1103(3)	1675(1)	21(1)
C(20)	-7997(6)	1767(4)	2106(1)	30(1)
O(3)	-6409(5)	-4912(3)	740(1)	40(1)
O(4)	-8515(4)	-5985(3)	-963(1)	31(1)
N(3)	-6663(5)	-6007(3)	1452(1)	29(1)
N(4)	-8293(4)	-6376(3)	558(1)	18(1)
C(21)	-7437(5)	-5692(3)	804(1)	24(1)
C(22)	-8009(5)	-6069(4)	1186(1)	29(1)
C(23)	-8756(6)	-7305(4)	1127(1)	34(1)
C(24)	-9402(5)	-7259(3)	739(1)	23(1)
C(25)	-8298(5)	-6238(3)	172(1)	19(1)
C(26)	-7203(5)	-5477(3)	-9(1)	21(1)
C(27)	-7229(5)	-5372(3)	-388(1)	21(1)
C(28)	-8380(5)	-6028(3)	-591(1)	21(1)
C(29)	-9476(6)	-6788(4)	-410(1)	29(1)
C(30)	-9447(5)	-6897(3)	-33(1)	25(1)
C(31)	-7280(5)	-5296(3)	-1153(1)	25(1)
C(32)	-5229(6)	-6750(4)	1462(1)	30(1)
C(33)	-4247(6)	-6392(4)	1739(1)	32(1)

C(34)	-5035(5)	-5362(3)	1915(1)	22(1)
C(35)	-4596(6)	-4634(4)	2203(1)	35(1)
C(36)	-5649(7)	-3663(5)	2291(1)	39(1)
C(37)	-7096(6)	-3460(4)	2100(1)	35(1)
C(38)	-7591(5)	-4233(4)	1810(1)	28(1)
C(39)	-6546(6)	-5165(4)	1720(1)	28(1)
C(40)	-2603(6)	-6929(4)	1847(1)	37(1)

Table S–8. Bond lengths [Å] and angles [°] for crystal_03.

Bond length [Å]			Bond angle [°]
O(1)-C(1)	1.213(5)	C(8)-O(2)-C(11)	117.4(3)
O(2)-C(8)	1.374(5)	C(12)-N(1)-C(2)	127.2(3)
O(2)-C(11)	1.431(5)	C(19)-N(1)-C(2)	125.7(3)
N(1)-C(2)	1.428(5)	C(19)-N(1)-C(12)	106.3(3)
N(1)-C(12)	1.394(5)	C(1)-N(2)-C(4)	112.0(3)
N(1)-C(19)	1.387(5)	C(1)-N(2)-C(5)	125.9(3)
N(2)-C(1)	1.364(5)	C(5)-N(2)-C(4)	121.0(3)
N(2)-C(4)	1.476(4)	O(1)-C(1)-N(2)	127.3(4)
N(2)-C(5)	1.420(5)	O(1)-C(1)-C(2)	124.7(3)
C(1)-C(2)	1.541(5)	N(2)-C(1)-C(2)	107.9(3)
C(2)-C(3)	1.521(5)	N(1)-C(2)-C(1)	113.0(3)
C(3)-C(4)	1.535(5)	N(1)-C(2)-C(3)	118.0(3)
C(5)-C(6)	1.391(5)	C(3)-C(2)-C(1)	103.1(3)
C(5)-C(10)	1.396(5)	C(2)-C(3)-C(4)	103.4(3)
C(6)-C(7)	1.388(5)	N(2)-C(4)-C(3)	104.4(3)
C(7)-C(8)	1.391(5)	C(6)-C(5)-N(2)	122.4(3)
C(8)-C(9)	1.381(6)	C(6)-C(5)-C(10)	118.5(4)
C(9)-C(10)	1.394(6)	C(10)-C(5)-N(2)	119.1(3)
C(12)-C(13)	1.361(6)	C(7)-C(6)-C(5)	121.1(3)
C(13)-C(14)	1.425(6)	C(6)-C(7)-C(8)	120.2(3)
C(13)-C(20)	1.483(6)	O(2)-C(8)-C(7)	124.7(4)
C(14)-C(15)	1.412(6)	O(2)-C(8)-C(9)	116.2(4)
C(14)-C(19)	1.404(5)	C(9)-C(8)-C(7)	119.1(4)
C(15)-C(16)	1.371(7)	C(8)-C(9)-C(10)	120.9(4)
C(16)-C(17)	1.407(7)	C(9)-C(10)-C(5)	120.2(4)
C(17)-C(18)	1.372(6)	C(13)-C(12)-N(1)	111.6(4)
C(18)-C(19)	1.403(6)	C(12)-C(13)-C(14)	105.8(3)
O(3)-C(21)	1.215(5)	C(12)-C(13)-C(20)	127.8(4)
O(4)-C(28)	1.371(5)	C(14)-C(13)-C(20)	126.4(4)
O(4)-C(31)	1.428(5)	C(15)-C(14)-C(13)	132.8(4)
N(3)-C(22)	1.457(5)	C(19)-C(14)-C(13)	107.9(4)
N(3)-C(32)	1.413(6)	C(19)-C(14)-C(15)	119.3(4)
N(3)-C(39)	1.355(6)	C(16)-C(15)-C(14)	119.1(4)
N(4)-C(21)	1.359(5)	C(15)-C(16)-C(17)	120.7(4)
N(4)-C(24)	1.476(4)	C(18)-C(17)-C(16)	121.6(4)
N(4)-C(25)	1.423(5)	C(17)-C(18)-C(19)	118.0(4)
C(21)-C(22)	1.531(6)	N(1)-C(19)-C(14)	108.4(3)
C(22)-C(23)	1.505(6)	N(1)-C(19)-C(18)	130.4(4)
C(23)-C(24)	1.514(6)	C(18)-C(19)-C(14)	121.3(4)
C(25)-C(26)	1.383(5)	C(28)-O(4)-C(31)	116.6(3)
C(25)-C(30)	1.395(5)	C(32)-N(3)-C(22)	126.4(4)
C(26)-C(27)	1.396(6)	C(39)-N(3)-C(22)	124.7(4)

C(27)-C(28)	1.388(5)	C(39)-N(3)-C(32)	108.8(4)
C(28)-C(29)	1.384(5)	C(21)-N(4)-C(24)	112.0(3)
C(29)-C(30)	1.387(6)	C(21)-N(4)-C(25)	126.9(3)
C(32)-C(33)	1.343(7)	C(25)-N(4)-C(24)	120.9(3)
C(33)-C(34)	1.451(6)	O(3)-C(21)-N(4)	127.4(4)
C(33)-C(40)	1.499(6)	O(3)-C(21)-C(22)	124.9(4)
C(34)-C(35)	1.373(6)	N(4)-C(21)-C(22)	107.6(3)
C(34)-C(39)	1.423(6)	N(3)-C(22)-C(21)	112.2(3)
C(35)-C(36)	1.401(7)	N(3)-C(22)-C(23)	115.7(4)
C(36)-C(37)	1.373(7)	C(23)-C(22)-C(21)	103.5(4)
C(37)-C(38)	1.420(7)	C(22)-C(23)-C(24)	103.9(3)
C(38)-C(39)	1.366(6)	N(4)-C(24)-C(23)	103.7(3)
		C(26)-C(25)-N(4)	122.7(3)
		C(26)-C(25)-C(30)	118.5(4)
		C(30)-C(25)-N(4)	118.9(3)
		C(25)-C(26)-C(27)	121.3(4)
		C(28)-C(27)-C(26)	119.9(3)
		O(4)-C(28)-C(27)	124.6(4)
		O(4)-C(28)-C(29)	116.6(3)
		C(29)-C(28)-C(27)	118.8(4)
		C(28)-C(29)-C(30)	121.3(4)
		C(29)-C(30)-C(25)	120.2(4)
		C(33)-C(32)-N(3)	109.1(4)
		C(32)-C(33)-C(34)	108.1(4)
		C(32)-C(33)-C(40)	126.8(4)
		C(34)-C(33)-C(40)	125.1(4)
		C(35)-C(34)-C(33)	133.5(4)
		C(35)-C(34)-C(39)	121.0(4)
		C(39)-C(34)-C(33)	105.5(4)
		C(34)-C(35)-C(36)	117.9(4)
		C(37)-C(36)-C(35)	121.2(4)
		C(36)-C(37)-C(38)	121.3(4)
		C(39)-C(38)-C(37)	117.4(4)
		N(3)-C(39)-C(34)	108.5(4)
		N(3)-C(39)-C(38)	130.3(4)
		C(38)-C(39)-C(34)	121.1(4)

Table S–9. Anisotropic displacement parameters ($Å^2 \times 10^3$) for crystal_03. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	28(1)	37(2)	21(2)	-2(1)	-1(1)	16(1)
O(2)	39(2)	38(2)	17(2)	-1(1)	0(1)	13(1)
N(1)	17(1)	22(2)	17(2)	2(1)	1(1)	1(1)
N(2)	15(1)	16(1)	18(2)	2(1)	-1(1)	1(1)
C(1)	20(2)	21(2)	18(2)	-3(1)	-1(2)	2(1)
C(2)	22(2)	20(2)	20(2)	0(1)	4(2)	0(1)
C(3)	20(2)	26(2)	24(2)	5(2)	1(2)	2(2)
C(4)	20(2)	19(2)	22(2)	3(1)	-4(2)	5(1)
C(5)	17(2)	15(2)	18(2)	0(1)	0(1)	-2(1)
C(6)	22(2)	22(2)	20(2)	0(1)	3(2)	5(2)
C(7)	21(2)	21(2)	20(2)	5(1)	-1(2)	4(2)
C(8)	25(2)	23(2)	17(2)	-1(2)	-2(2)	-3(2)
C(9)	39(2)	34(2)	21(2)	-4(2)	3(2)	18(2)
C(10)	30(2)	30(2)	19(2)	-1(2)	1(2)	12(2)
C(11)	28(2)	28(2)	19(2)	0(2)	-1(2)	0(2)
C(12)	28(2)	23(2)	20(2)	0(1)	-5(2)	0(2)
C(13)	32(2)	22(2)	22(2)	4(2)	-4(2)	3(2)
C(14)	28(2)	24(2)	15(2)	6(1)	-2(2)	6(2)
C(15)	38(2)	35(2)	21(2)	5(2)	7(2)	15(2)
C(16)	31(2)	42(2)	29(2)	13(2)	13(2)	9(2)
C(17)	24(2)	27(2)	32(2)	11(2)	1(2)	0(2)
C(18)	25(2)	23(2)	26(2)	7(2)	0(2)	3(2)
C(19)	28(2)	22(2)	14(2)	3(1)	1(2)	5(2)
C(20)	44(3)	25(2)	22(2)	-1(2)	-6(2)	1(2)
O(3)	50(2)	42(2)	28(2)	12(1)	-13(2)	-29(2)
O(4)	34(2)	38(2)	21(2)	-1(1)	2(1)	-12(1)
N(3)	28(2)	32(2)	26(2)	3(2)	-3(2)	-2(1)
N(4)	17(2)	15(1)	23(2)	3(1)	3(1)	-1(1)
C(21)	24(2)	28(2)	22(2)	9(2)	-6(2)	-4(2)
C(22)	26(2)	35(2)	25(2)	6(2)	-5(2)	-8(2)
C(23)	37(2)	37(2)	29(2)	13(2)	4(2)	-11(2)
C(24)	23(2)	23(2)	23(2)	3(2)	5(2)	-4(2)
C(25)	21(2)	15(2)	21(2)	2(1)	-1(2)	4(1)
C(26)	16(2)	19(2)	27(2)	5(1)	-3(2)	0(1)
C(27)	18(2)	20(2)	24(2)	4(1)	1(2)	0(1)
C(28)	22(2)	21(2)	20(2)	-1(2)	0(2)	3(2)
C(29)	33(2)	30(2)	23(2)	-6(2)	2(2)	-13(2)
C(30)	25(2)	23(2)	26(2)	-1(2)	4(2)	-8(2)
C(31)	23(2)	27(2)	24(2)	5(2)	1(2)	0(2)
C(32)	40(2)	24(2)	27(2)	-1(2)	7(2)	1(2)
C(33)	30(2)	35(2)	32(2)	6(2)	4(2)	0(2)
C(34)	18(2)	28(2)	19(2)	8(2)	2(1)	-3(1)

C(35)	32(2)	40(2)	33(3)	1(2)	0(2)	-6(2)
C(36)	42(3)	49(3)	26(2)	-5(2)	3(2)	-15(2)
C(37)	42(3)	31(2)	33(3)	2(2)	13(2)	0(2)
C(38)	24(2)	32(2)	27(2)	9(2)	0(2)	-2(2)
C(39)	31(2)	30(2)	23(2)	6(2)	5(2)	-2(2)
C(40)	27(2)	43(2)	41(3)	17(2)	6(2)	4(2)

Table S–10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for crystal_03.

	x	y	z	U(eq)
H(2)	-8046	-2358	1174	25
H(3A)	-5377	-2767	1319	28
H(3B)	-4813	-1365	1298	28
H(4A)	-3983	-1913	725	24
H(4B)	-5333	-2992	700	24
H(6)	-8101	126	168	26
H(7)	-8141	235	-466	25
H(9)	-4504	-2291	-516	38
H(10)	-4486	-2428	120	32
H(11A)	-7279	-402	-1383	38
H(11B)	-7231	579	-1062	38
H(11C)	-8542	-514	-1047	38
H(12)	-6234	477	1561	28
H(15)	-11221	448	2337	38
H(16)	-13193	-1080	2272	41
H(17)	-12842	-2605	1835	33
H(18)	-10538	-2619	1449	30
H(20A)	-8794	2378	2021	45
H(20B)	-6858	2060	2066	45
H(20C)	-8168	1620	2367	45
H(22)	-8917	-5506	1265	34
H(23A)	-9675	-7458	1301	41
H(23B)	-7903	-7947	1155	41
H(24A)	-9323	-8065	621	28
H(24B)	-10576	-6983	732	28
H(26)	-6419	-5018	128	25
H(27)	-6459	-4852	-508	25
H(29)	-10263	-7244	-547	34
H(30)	-10213	-7423	86	30
H(31A)	-7499	-5328	-1416	37
H(31B)	-6173	-5634	-1102	37
H(31C)	-7319	-4451	-1070	37
H(32)	-4996	-7398	1300	36
H(35)	-3608	-4784	2339	42
H(36)	-5356	-3136	2485	47
H(37)	-7780	-2790	2164	42
H(38)	-8609	-4107	1683	33
H(40A)	-1748	-6293	1848	56
H(40B)	-2291	-7562	1673	56
H(40C)	-2694	-7282	2092	56

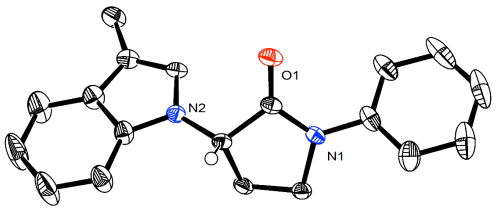


Figure S–5. Structure of (3*S*)-3-(3-methyl-1*H*-indol-1-yl)-1-phenylpyrrolidin-2-one. The more-ordered of two molecules in the asymmetric unit is shown.

(3*S*)-3-(3-Methyl-1*H*-indol-1-yl)-1-phenylpyrrolidin-2-one (Table 2, entry 1; synthesized using (*S*)–L*). A suitable crystal for X-ray crystallography was grown by vapor diffusion with Et_2O and hexane.

A crystal of $C_{19}H_{18}N_2O$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Photon diffractometer with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2,[6] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package[5] using least squares minimization. All disordered atoms were refined with the help of similarity restraints on the 1,2- and 1,3-distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S–11. Crystal data and structure refinement for crystal_04.

Identification code	crystal_04
Empirical formula	$C_{19}H_{18}N_2O$
Formula weight	290.35
Temperature	100.15 K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 6.4841(3) Å α = 90°. b = 21.5067(11) Å β = 90°. c = 22.0917(12) Å γ = 90°.
Volume	3080.7(3) $Å^3$
Z	8
Density (calculated)	1.252 Mg/m^3
Absorption coefficient	0.615 mm^{-1}
F(000)	1232
Crystal size	0.4 x 0.1 x 0.05 mm^3
Theta range for data collection	2.867 to 79.181°.
Index ranges	-7<=h<=7, -19<=k<=27, -23<=l<=27
Reflections collected	19550
Independent reflections	6052 [R(int) = 0.0668]
Completeness to theta = 67.679°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7542 and 0.5932
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6052 / 381 / 491
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0596, wR2 = 0.1386
R indices (all data)	R1 = 0.0709, wR2 = 0.1452
Absolute structure parameter	0.08(18)
Largest diff. peak and hole	0.200 and -0.273 $e/Å^{-3}$

Table S–12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for crystal_04. U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5805(4)	7923(1)	326(1)	28(1)
N(1)	2651(5)	8424(1)	356(1)	21(1)
N(2)	4192(5)	7244(1)	1381(1)	22(1)
C(1)	4018(6)	7972(2)	503(2)	22(1)
C(2)	2900(5)	7514(2)	917(2)	21(1)
C(3)	1052(6)	7885(2)	1145(2)	25(1)
C(4)	593(6)	8319(2)	616(2)	24(1)
C(5)	3004(7)	8893(2)	-84(2)	28(1)
C(6)	4853(8)	9213(2)	-96(2)	36(1)
C(7)	5106(10)	9697(2)	-517(2)	52(2)
C(8)	3560(10)	9843(2)	-916(2)	55(2)
C(9)	1739(10)	9513(2)	-909(2)	48(1)
C(10)	1437(8)	9041(2)	-491(2)	37(1)
C(11)	5902(6)	7510(2)	1649(2)	23(1)
C(12)	3746(7)	6698(2)	1681(2)	28(1)
C(13)	2130(8)	6283(2)	1605(2)	40(1)
C(14)	2045(10)	5776(2)	1985(2)	60(2)
C(15)	3577(11)	5676(3)	2420(3)	69(2)
C(16)	5184(9)	6084(2)	2496(2)	51(1)
C(17)	5283(7)	6617(2)	2131(2)	31(1)
C(18)	8452(7)	7264(2)	2511(2)	37(1)
C(19)	6624(6)	7142(2)	2106(2)	28(1)
O(2)	8787(4)	9828(1)	1055(2)	40(1)
N(4)	12242(5)	9986(2)	1265(2)	26(1)
N(5)	9211(9)	11004(3)	478(3)	23(1)
N(5A)	9285(15)	10945(5)	191(5)	21(2)
C(1O)	10453(6)	10079(2)	962(2)	31(1)
C(20)	10882(6)	10545(2)	462(2)	34(1)
C(21)	12967(6)	10828(2)	619(2)	33(1)
C(22)	14001(6)	10330(2)	1002(2)	28(1)
C(23)	12540(6)	9557(2)	1745(2)	27(1)
C(24)	10942(8)	9423(2)	2144(2)	41(1)
C(25)	11290(10)	9020(2)	2622(2)	52(1)
C(26)	13226(10)	8756(2)	2711(2)	50(1)
C(27)	14801(8)	8892(2)	2309(2)	43(1)
C(28)	14459(7)	9291(2)	1831(2)	32(1)
C(29)	8446(12)	11352(4)	963(4)	24(2)
C(29A)	8640(20)	11095(7)	-392(7)	26(3)
C(30)	8347(9)	11235(3)	-42(3)	22(1)
C(30A)	8361(17)	11352(6)	577(6)	24(2)
C(31)	8640(13)	11053(4)	-650(3)	29(2)
C(31A)	8490(20)	11417(7)	1211(6)	23(2)
C(32)	7513(10)	11371(3)	-1082(3)	32(1)
C(32A)	7283(17)	11867(5)	1476(6)	32(2)
C(33)	6030(30)	11866(8)	-895(7)	36(3)

C(33A)	5900(70)	12260(20)	1089(11)	32(4)
C(34)	5883(10)	12034(3)	-328(3)	33(1)
C(34A)	5870(18)	12200(5)	500(6)	32(2)
C(35)	6990(20)	11722(6)	111(5)	24(2)
C(35A)	7070(40)	11748(11)	243(8)	23(2)
C(36)	6020(40)	12257(11)	1169(6)	38(3)
C(36A)	6270(50)	11778(15)	-978(11)	29(5)
C(38)	7239(17)	11553(5)	-388(5)	29(2)
C(39)	7129(9)	11786(3)	768(3)	28(1)

Table S–13. Bond lengths [Å] and angles [°] for crystal_04.

Bond length [Å]		Bond angle [°]	
O(1)-C(1)	1.228(4)	C(1)-N(1)-C(4)	112.8(3)
N(1)-C(1)	1.356(5)	C(1)-N(1)-C(5)	124.7(3)
N(1)-C(4)	1.471(5)	C(5)-N(1)-C(4)	121.6(3)
N(1)-C(5)	1.419(5)	C(11)-N(2)-C(2)	127.1(3)
N(2)-C(2)	1.445(5)	C(12)-N(2)-C(2)	124.1(3)
N(2)-C(11)	1.381(5)	C(12)-N(2)-C(11)	108.4(3)
N(2)-C(12)	1.379(5)	O(1)-C(1)-N(1)	127.0(3)
C(1)-C(2)	1.526(5)	O(1)-C(1)-C(2)	125.8(3)
C(2)-C(3)	1.526(5)	N(1)-C(1)-C(2)	107.2(3)
C(3)-C(4)	1.523(5)	N(2)-C(2)-C(1)	114.1(3)
C(5)-C(6)	1.383(6)	N(2)-C(2)-C(3)	115.5(3)
C(5)-C(10)	1.394(6)	C(3)-C(2)-C(1)	103.5(3)
C(6)-C(7)	1.406(6)	C(4)-C(3)-C(2)	102.7(3)
C(7)-C(8)	1.370(8)	N(1)-C(4)-C(3)	102.5(3)
C(8)-C(9)	1.378(8)	C(6)-C(5)-N(1)	120.5(4)
C(9)-C(10)	1.387(6)	C(6)-C(5)-C(10)	120.4(4)
C(11)-C(19)	1.366(6)	C(10)-C(5)-N(1)	119.1(4)
C(12)-C(13)	1.386(6)	C(5)-C(6)-C(7)	118.8(5)
C(12)-C(17)	1.419(6)	C(8)-C(7)-C(6)	120.7(5)
C(13)-C(14)	1.378(6)	C(7)-C(8)-C(9)	120.1(4)
C(14)-C(15)	1.398(7)	C(8)-C(9)-C(10)	120.4(5)
C(15)-C(16)	1.373(7)	C(9)-C(10)-C(5)	119.6(5)
C(16)-C(17)	1.403(6)	C(19)-C(11)-N(2)	110.6(3)
C(17)-C(19)	1.425(6)	N(2)-C(12)-C(13)	130.4(4)
C(18)-C(19)	1.508(6)	N(2)-C(12)-C(17)	107.1(3)
O(2)-C(1O)	1.225(5)	C(13)-C(12)-C(17)	122.5(4)
N(4)-C(1O)	1.354(5)	C(14)-C(13)-C(12)	117.8(4)
N(4)-C(22)	1.478(5)	C(13)-C(14)-C(15)	120.8(5)
N(4)-C(23)	1.419(5)	C(16)-C(15)-C(14)	121.7(4)
N(5)-C(20)	1.466(6)	C(15)-C(16)-C(17)	119.1(4)
N(5)-C(29)	1.398(8)	C(12)-C(17)-C(19)	107.8(3)
N(5)-C(30)	1.372(8)	C(16)-C(17)-C(12)	118.1(4)
N(5A)-C(20)	1.474(9)	C(16)-C(17)-C(19)	134.2(4)
N(5A)-C(29A)	1.393(12)	C(11)-C(19)-C(17)	106.2(3)
N(5A)-C(30A)	1.360(17)	C(11)-C(19)-C(18)	127.4(4)
C(1O)-C(20)	1.515(6)	C(17)-C(19)-C(18)	126.5(4)
C(20)-C(21)	1.522(6)	C(1O)-N(4)-C(22)	113.1(3)
C(21)-C(22)	1.521(6)	C(1O)-N(4)-C(23)	125.7(3)
C(23)-C(24)	1.390(6)	C(23)-N(4)-C(22)	120.9(3)
C(23)-C(28)	1.383(6)	C(29)-N(5)-C(20)	129.9(6)
C(24)-C(25)	1.383(7)	C(30)-N(5)-C(20)	121.8(5)
C(25)-C(26)	1.392(8)	C(30)-N(5)-C(29)	107.6(6)
C(26)-C(27)	1.384(7)	C(29A)-N(5A)-C(20)	136.3(11)
C(27)-C(28)	1.380(6)	C(30A)-N(5A)-C(20)	115.6(9)
C(29)-C(39)	1.336(9)	C(30A)-N(5A)-C(29A)	107.2(10)
C(29A)-C(38)	1.339(13)	O(2)-C(1O)-N(4)	127.3(4)

C(30)-C(31)	1.413(8)
C(30)-C(35)	1.406(8)
C(30A)-C(31A)	1.411(12)
C(30A)-C(35A)	1.403(12)
C(31)-C(32)	1.382(10)
C(31A)-C(32A)	1.376(13)
C(32)-C(33)	1.493(17)
C(32A)-C(33A)	1.49(2)
C(33)-C(34)	1.308(17)
C(33A)-C(34A)	1.31(2)
C(34)-C(35)	1.382(10)
C(34A)-C(35A)	1.368(13)
C(35)-C(39)	1.462(12)
C(35A)-C(38)	1.461(16)
C(36)-C(39)	1.525(16)
C(36A)-C(38)	1.53(2)

O(2)-C(1O)-C(20)	125.1(4)
N(4)-C(1O)-C(20)	107.5(3)
N(5)-C(20)-C(1O)	106.9(4)
N(5)-C(20)-C(21)	112.4(4)
N(5A)-C(20)-C(1O)	123.5(5)
N(5A)-C(20)-C(21)	118.9(5)
C(1O)-C(20)-C(21)	105.1(4)
C(22)-C(21)-C(20)	103.7(3)
N(4)-C(22)-C(21)	103.3(3)
C(24)-C(23)-N(4)	120.5(4)
C(28)-C(23)-N(4)	119.6(4)
C(28)-C(23)-C(24)	119.9(4)
C(25)-C(24)-C(23)	119.5(5)
C(24)-C(25)-C(26)	120.7(5)
C(27)-C(26)-C(25)	119.2(5)
C(28)-C(27)-C(26)	120.3(5)
C(27)-C(28)-C(23)	120.4(4)
C(39)-C(29)-N(5)	110.8(7)
C(38)-C(29A)-N(5A)	111.7(13)
N(5)-C(30)-C(31)	129.8(6)
N(5)-C(30)-C(35)	108.9(6)
C(35)-C(30)-C(31)	121.3(7)
N(5A)-C(30A)-C(31A)	131.2(11)
N(5A)-C(30A)-C(35A)	109.0(11)
C(35A)-C(30A)-C(31A)	119.8(13)
C(32)-C(31)-C(30)	116.6(7)
C(32A)-C(31A)-C(30A)	117.3(13)
C(31)-C(32)-C(33)	120.2(8)
C(31A)-C(32A)-C(33A)	119.5(17)
C(34)-C(33)-C(32)	120.5(12)
C(34A)-C(33A)-C(32A)	122(2)
C(33)-C(34)-C(35)	120.0(9)
C(33A)-C(34A)-C(35A)	118.1(18)
C(30)-C(35)-C(39)	105.8(6)
C(34)-C(35)-C(30)	121.2(8)
C(34)-C(35)-C(39)	133.0(7)
C(30A)-C(35A)-C(38)	106.4(11)
C(34A)-C(35A)-C(30A)	123.5(15)
C(34A)-C(35A)-C(38)	130.0(12)
C(29A)-C(38)-C(35A)	105.5(11)
C(29A)-C(38)-C(36A)	120.5(15)
C(35A)-C(38)-C(36A)	133.9(14)
C(29)-C(39)-C(35)	107.0(6)
C(29)-C(39)-C(36)	125.3(8)
C(35)-C(39)-C(36)	127.7(7)

Table S–14. Anisotropic displacement parameters ($Å^2 \times 10^3$) for crystal_04. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	21(1)	38(2)	26(1)	-1(1)	5(1)	-4(1)
N(1)	22(2)	19(1)	23(2)	-2(1)	3(1)	-5(1)
N(2)	20(2)	22(2)	24(2)	-1(1)	-2(1)	-2(1)
C(1)	20(2)	26(2)	19(2)	-5(2)	0(2)	-5(2)
C(2)	17(2)	24(2)	23(2)	-2(2)	-2(2)	-4(2)
C(3)	20(2)	25(2)	31(2)	3(2)	6(2)	-3(2)
C(4)	19(2)	22(2)	30(2)	0(2)	3(2)	0(2)
C(5)	42(2)	18(2)	24(2)	-4(2)	11(2)	-4(2)
C(6)	47(3)	26(2)	34(2)	-3(2)	18(2)	-7(2)
C(7)	76(4)	26(2)	54(3)	-6(2)	43(3)	-13(2)
C(8)	98(5)	25(2)	41(3)	12(2)	38(3)	16(3)
C(9)	84(4)	29(2)	31(2)	6(2)	11(2)	14(3)
C(10)	56(3)	26(2)	31(2)	-1(2)	-1(2)	3(2)
C(11)	17(2)	31(2)	22(2)	-2(2)	2(2)	-4(2)
C(12)	37(2)	26(2)	21(2)	1(2)	-5(2)	-4(2)
C(13)	50(3)	38(2)	31(2)	11(2)	-15(2)	-17(2)
C(14)	82(4)	46(3)	53(3)	22(3)	-31(3)	-40(3)
C(15)	97(5)	56(3)	53(3)	35(3)	-42(3)	-42(3)
C(16)	69(4)	49(3)	34(3)	12(2)	-30(2)	-19(3)
C(17)	39(2)	35(2)	21(2)	0(2)	-6(2)	-5(2)
C(18)	32(2)	53(3)	24(2)	6(2)	-7(2)	-12(2)
C(19)	26(2)	34(2)	23(2)	-4(2)	2(2)	-2(2)
O(2)	16(1)	24(1)	82(2)	6(2)	2(2)	-2(1)
N(4)	19(2)	24(2)	36(2)	-4(1)	4(1)	-1(1)
N(5)	24(2)	22(2)	23(3)	-13(3)	2(3)	4(2)
N(5A)	18(4)	20(4)	26(5)	12(4)	-2(4)	-6(4)
C(1O)	16(2)	20(2)	57(3)	-7(2)	1(2)	4(2)
C(20)	19(2)	23(2)	59(3)	3(2)	-4(2)	-1(2)
C(21)	23(2)	27(2)	49(3)	-1(2)	5(2)	-3(2)
C(22)	16(2)	31(2)	36(2)	-7(2)	5(2)	-6(2)
C(23)	28(2)	26(2)	29(2)	-10(2)	6(2)	-7(2)
C(24)	42(3)	37(2)	43(3)	-14(2)	15(2)	-11(2)
C(25)	67(4)	47(3)	42(3)	-7(2)	17(3)	-23(3)
C(26)	74(4)	43(3)	32(2)	1(2)	-3(2)	-20(3)
C(27)	49(3)	37(2)	43(3)	-4(2)	-8(2)	0(2)
C(28)	32(2)	33(2)	32(2)	-8(2)	-2(2)	-4(2)
C(29)	24(3)	23(3)	26(4)	-12(4)	5(4)	-1(2)
C(29A)	21(5)	29(5)	28(6)	9(6)	0(6)	-5(4)
C(30)	16(2)	21(3)	31(3)	-6(2)	1(2)	-3(2)
C(30A)	19(4)	21(4)	30(4)	12(4)	2(4)	-4(3)
C(31)	25(3)	32(3)	31(4)	-11(3)	-1(3)	-3(2)
C(31A)	22(4)	21(5)	28(5)	7(5)	5(5)	-2(4)
C(32)	26(3)	38(3)	33(3)	0(3)	-4(3)	-10(3)
C(32A)	22(5)	31(5)	42(5)	-1(4)	5(4)	-4(4)
C(33)	27(5)	40(5)	42(5)	20(4)	-4(4)	2(4)

C(33A)	20(6)	25(7)	50(6)	-10(6)	3(6)	-5(6)
C(34)	21(3)	28(3)	50(3)	6(3)	-2(3)	-3(2)
C(34A)	23(4)	23(4)	51(5)	15(4)	-5(4)	-2(4)
C(35)	16(3)	16(3)	41(4)	3(3)	-3(3)	-5(2)
C(35A)	15(4)	21(4)	34(5)	18(4)	-6(4)	-3(4)
C(36)	31(6)	25(4)	58(6)	-14(5)	13(6)	2(4)
C(36A)	16(8)	39(9)	32(8)	1(7)	-11(7)	3(7)
C(38)	25(4)	30(4)	34(4)	18(4)	-3(4)	-5(3)
C(39)	23(2)	19(2)	41(3)	-9(2)	4(2)	-2(2)

Table S–15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for crystal_04.

	x	y	z	U(eq)
H(2)	2364	7167	659	26
H(3A)	-136	7610	1231	30
H(3B)	1403	8123	1515	30
H(4A)	-340	8120	319	28
H(4B)	-32	8713	757	28
H(6)	5934	9108	176	43
H(7)	6360	9925	-526	62
H(8)	3744	10173	-1197	66
H(9)	685	9610	-1193	58
H(10)	171	8819	-483	45
H(11)	6494	7895	1531	28
H(13)	1115	6346	1301	48
H(14)	932	5490	1951	72
H(15)	3504	5316	2669	82
H(16)	6217	6007	2791	61
H(18A)	8013	7247	2935	55
H(18B)	9018	7676	2422	55
H(18C)	9511	6947	2439	55
H(20)	10936	10333	60	40
H(20A)	11245	10266	116	40
H(21A)	13777	10915	249	40
H(21B)	12798	11218	851	40
H(22A)	14867	10053	749	33
H(22B)	14867	10517	1322	33
H(24)	9621	9605	2089	49
H(25)	10196	8924	2892	62
H(26)	13463	8486	3044	59
H(27)	16122	8709	2363	51
H(28)	15551	9384	1559	39
H(29)	8812	11289	1375	29
H(29A)	9126	10897	-748	31
H(31)	9565	10728	-757	35
H(31A)	9377	11161	1446	28
H(32)	7683	11274	-1498	39
H(32A)	7327	11930	1901	38
H(33)	5185	12060	-1191	44
H(33A)	5024	12553	1276	38
H(34)	5011	12370	-217	39
H(34A)	5037	12464	258	39
H(36A)	6410	12679	1047	57
H(36B)	6411	12189	1592	57
H(36C)	4526	12205	1125	57
H(36D)	7062	11618	-1322	44
H(36E)	6275	12234	-988	44

H(36F)	4844	11628	-1004	44

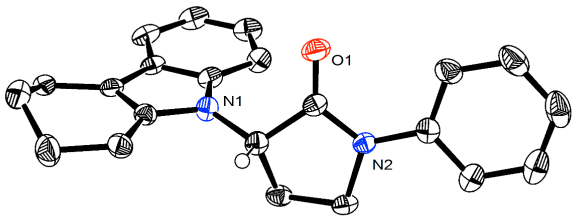


Figure S–6. Structure of (3*S*)-3-(3,4-dihydro-1*H*-carbazol-9(2*H*)-yl)-1-phenylpyrrolidin-2-one.

(3*S*)-3-(3,4-dihydro-1*H*-carbazol-9(2*H*)-yl)-1-phenylpyrrolidin-2-one (Table 3, entry 2; synthesized using (*S*)–L*). A suitable crystal for X-ray crystallography was grown by vapor diffusion with Et_2O and hexane.

A crystal of $C_{22}H_{22}N_2O$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker Photon diffractometer with filtered Cu-Kα radiation at a temperature of 100 K. Using Olex2,[6] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package[5] using least squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S–16. Crystal data and structure refinement for crystal_05.

Identification code	crystal_05
Empirical formula	$C_{22}H_{22}N_2O$
Formula weight	330.41
Temperature	100 K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 9.0886(6) Å α = 90°. b = 10.7170(7) Å β = 90°. c = 17.6036(11) Å γ = 90°.
Volume	1714.64(19) $Å^3$
Z	4
Density (calculated)	1.280 Mg/m^3
Absorption coefficient	0.616 mm^{-1}
F(000)	704
Crystal size	0.27 x 0.22 x 0.09 mm^3
Theta range for data collection	4.831 to 79.321°.
Index ranges	-11<=h<=11, -13<=k<=13, -22<=l<=22
Reflections collected	82723
Independent reflections	3706 [R(int) = 0.0489]
Completeness to theta = 67.679°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7542 and 0.6622
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3706 / 0 / 226
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.1012
R indices (all data)	R1 = 0.0401, wR2 = 0.1027
Absolute structure parameter	0.01(6)
Largest diff. peak and hole	0.317 and -0.250 $e/Å^{-3}$

Table S–17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for crystal_05. U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-8695(2)	-6943(2)	-2555(1)	35(1)
N(1)	-11681(2)	-7667(2)	-2174(1)	26(1)
N(2)	-8872(2)	-8428(2)	-3509(1)	23(1)
C(1)	-9290(2)	-7826(2)	-2860(1)	24(1)
C(2)	-10670(2)	-8484(2)	-2566(1)	25(1)
C(3)	-11280(2)	-9157(2)	-3261(1)	29(1)
C(4)	-9900(2)	-9436(2)	-3723(1)	26(1)
C(5)	-7518(2)	-8280(2)	-3898(1)	26(1)
C(6)	-6489(2)	-7366(2)	-3686(1)	33(1)
C(7)	-5156(3)	-7280(2)	-4071(2)	42(1)
C(8)	-4828(3)	-8081(2)	-4669(2)	45(1)
C(9)	-5848(3)	-8960(2)	-4882(1)	39(1)
C(10)	-7191(3)	-9079(2)	-4502(1)	31(1)
C(11)	-12426(2)	-7971(2)	-1509(1)	24(1)
C(12)	-12014(2)	-9025(2)	-999(1)	29(1)
C(13)	-13159(3)	-9174(2)	-374(2)	44(1)
C(14)	-13762(3)	-7966(2)	-78(1)	42(1)
C(15)	-14516(2)	-7206(2)	-705(1)	31(1)
C(16)	-13540(2)	-7139(2)	-1385(1)	25(1)
C(17)	-13513(2)	-6268(2)	-2004(1)	25(1)
C(18)	-14339(3)	-5199(2)	-2183(1)	32(1)
C(19)	-13949(3)	-4506(2)	-2823(1)	36(1)
C(20)	-12778(3)	-4859(2)	-3282(1)	35(1)
C(21)	-11953(3)	-5928(2)	-3131(1)	31(1)
C(22)	-12338(2)	-6616(2)	-2482(1)	26(1)

Table S–18. Bond lengths [Å] and angles [°] for crystal_05.

Bond length [Å]		Bond angle [°]	
O(1)-C(1)	1.215(3)	C(11)-N(1)-C(2)	124.72(17)
N(1)-C(2)	1.444(3)	C(22)-N(1)-C(2)	125.49(17)
N(1)-C(11)	1.392(3)	C(22)-N(1)-C(11)	108.04(17)
N(1)-C(22)	1.386(2)	C(1)-N(2)-C(4)	112.51(16)
N(2)-C(1)	1.367(2)	C(1)-N(2)-C(5)	126.29(17)
N(2)-C(4)	1.477(2)	C(5)-N(2)-C(4)	120.59(16)
N(2)-C(5)	1.417(3)	O(1)-C(1)-N(2)	127.9(2)
C(1)-C(2)	1.530(3)	O(1)-C(1)-C(2)	125.10(19)
C(2)-C(3)	1.524(3)	N(2)-C(1)-C(2)	107.00(17)
C(3)-C(4)	1.525(3)	N(1)-C(2)-C(1)	113.78(17)
C(5)-C(6)	1.404(3)	N(1)-C(2)-C(3)	116.01(17)
C(5)-C(10)	1.398(3)	C(3)-C(2)-C(1)	104.22(16)
C(6)-C(7)	1.391(3)	C(2)-C(3)-C(4)	102.81(16)
C(7)-C(8)	1.390(4)	N(2)-C(4)-C(3)	103.98(15)
C(8)-C(9)	1.374(4)	C(6)-C(5)-N(2)	121.93(18)
C(9)-C(10)	1.398(3)	C(10)-C(5)-N(2)	118.89(19)
C(11)-C(12)	1.491(3)	C(10)-C(5)-C(6)	119.2(2)
C(11)-C(16)	1.366(3)	C(7)-C(6)-C(5)	119.8(2)
C(12)-C(13)	1.523(3)	C(8)-C(7)-C(6)	121.0(2)
C(13)-C(14)	1.499(4)	C(9)-C(8)-C(7)	119.0(2)
C(14)-C(15)	1.533(4)	C(8)-C(9)-C(10)	121.4(2)
C(15)-C(16)	1.492(3)	C(9)-C(10)-C(5)	119.6(2)
C(16)-C(17)	1.433(3)	N(1)-C(11)-C(12)	124.17(17)
C(17)-C(18)	1.406(3)	C(16)-C(11)-N(1)	109.99(17)
C(17)-C(22)	1.410(3)	C(16)-C(11)-C(12)	125.81(18)
C(18)-C(19)	1.395(3)	C(11)-C(12)-C(13)	109.99(18)
C(19)-C(20)	1.388(4)	C(14)-C(13)-C(12)	114.3(2)
C(20)-C(21)	1.395(3)	C(13)-C(14)-C(15)	111.8(2)
C(21)-C(22)	1.404(3)	C(16)-C(15)-C(14)	109.75(19)
		C(11)-C(16)-C(15)	122.44(19)
		C(11)-C(16)-C(17)	106.93(17)
		C(17)-C(16)-C(15)	130.63(18)
		C(18)-C(17)-C(16)	133.8(2)
		C(18)-C(17)-C(22)	119.0(2)
		C(22)-C(17)-C(16)	107.15(17)
		C(19)-C(18)-C(17)	118.7(2)
		C(20)-C(19)-C(18)	121.3(2)
		C(19)-C(20)-C(21)	121.7(2)
		C(20)-C(21)-C(22)	116.8(2)
		N(1)-C(22)-C(17)	107.89(18)
		N(1)-C(22)-C(21)	129.6(2)
		C(21)-C(22)-C(17)	122.47(19)

Table S–19. Anisotropic displacement parameters ($Å^2 \times 10^3$) for crystal_05. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	32(1)	32(1)	41(1)	-14(1)	-2(1)	-2(1)
N(1)	27(1)	25(1)	26(1)	4(1)	1(1)	7(1)
N(2)	24(1)	21(1)	24(1)	-1(1)	-1(1)	2(1)
C(1)	24(1)	23(1)	26(1)	-1(1)	-3(1)	5(1)
C(2)	25(1)	23(1)	28(1)	2(1)	0(1)	6(1)
C(3)	26(1)	22(1)	38(1)	-1(1)	-4(1)	1(1)
C(4)	27(1)	22(1)	31(1)	-6(1)	-6(1)	1(1)
C(5)	27(1)	24(1)	26(1)	7(1)	-1(1)	6(1)
C(6)	34(1)	23(1)	42(1)	5(1)	2(1)	0(1)
C(7)	35(1)	31(1)	61(2)	15(1)	5(1)	-3(1)
C(8)	40(1)	42(1)	52(2)	24(1)	17(1)	8(1)
C(9)	47(1)	42(1)	28(1)	12(1)	9(1)	20(1)
C(10)	35(1)	32(1)	25(1)	4(1)	0(1)	9(1)
C(11)	23(1)	24(1)	26(1)	-1(1)	-1(1)	-1(1)
C(12)	34(1)	24(1)	30(1)	4(1)	2(1)	1(1)
C(13)	54(2)	36(1)	42(1)	11(1)	18(1)	4(1)
C(14)	52(2)	40(1)	33(1)	-3(1)	10(1)	-2(1)
C(15)	32(1)	25(1)	37(1)	-9(1)	10(1)	-4(1)
C(16)	24(1)	21(1)	30(1)	-7(1)	-1(1)	-2(1)
C(17)	26(1)	23(1)	27(1)	-7(1)	-6(1)	2(1)
C(18)	34(1)	28(1)	34(1)	-10(1)	-10(1)	8(1)
C(19)	45(1)	28(1)	35(1)	-2(1)	-14(1)	9(1)
C(20)	45(1)	27(1)	32(1)	4(1)	-11(1)	3(1)
C(21)	36(1)	29(1)	27(1)	3(1)	-1(1)	6(1)
C(22)	28(1)	23(1)	27(1)	-1(1)	-6(1)	5(1)

Table S–20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for crystal_05.

	x	y	z	U(eq)
H(2)	-10345	-9136	-2196	30
H(3A)	-11968	-8617	-3547	34
H(3B)	-11794	-9935	-3114	34
H(4A)	-9492	-10264	-3590	32
H(4B)	-10114	-9415	-4274	32
H(6)	-6702	-6809	-3282	40
H(7)	-4459	-6666	-3923	51
H(8)	-3912	-8021	-4927	54
H(9)	-5636	-9499	-5297	47
H(10)	-7878	-9699	-4654	37
H(12A)	-11038	-8862	-770	35
H(12B)	-11948	-9806	-1298	35
H(13A)	-13984	-9681	-573	53
H(13B)	-12712	-9639	53	53
H(14A)	-12950	-7468	143	50
H(14B)	-14480	-8141	331	50
H(15A)	-15460	-7605	-845	38
H(15B)	-14727	-6354	-518	38
H(18)	-15147	-4953	-1875	38
H(19)	-14494	-3778	-2947	43
H(20)	-12534	-4360	-3710	42
H(21)	-11167	-6180	-3453	37

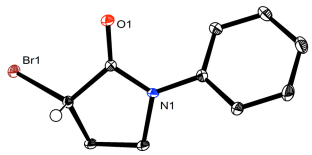


Figure S–7. Structure of (3*S*)-3-Bromo-1-phenylpyrrolidin-2-one.

(3*S*)-3-Bromo-1-phenylpyrrolidin-2-one. A suitable crystal for X-ray crystallography was grown by vapor diffusion with isopropanol and hexane.

A crystal of $C_{10}H_{10}BrNO$ was selected and mounted in a nylon loop in immersion oil. All measurements were made on a Bruker APEX2 diffractometer with filtered Mo-Kα radiation at a temperature of 100 K. Using Olex2,[6] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package[5] using least squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table S–21. Crystal data and structure refinement for crystal_06.

Identification code	crystal_06
Empirical formula	$C_{10}H_{10}BrNO$
Formula weight	240.10
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 6.3666(3) Å α = 90°. b = 7.8280(3) Å β = 90°. c = 18.4770(7) Å γ = 90°.
Volume	920.85(7) $Å^3$
Z	4
Density (calculated)	1.732 Mg/m^3
Absorption coefficient	4.419 mm^{-1}
F(000)	480
Crystal size	0.3 x 0.25 x 0.25 mm^3
Theta range for data collection	2.204 to 36.357°.
Index ranges	-10<=h<=9, -12<=k<=13, -28<=l<=30
Reflections collected	26373
Independent reflections	4469 [R(int) = 0.0353]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7471 and 0.6353
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4469 / 0 / 118
Goodness-of-fit on F^2	1.008
Final R indices [I>2sigma(I)]	R1 = 0.0211, wR2 = 0.0441
R indices (all data)	R1 = 0.0252, wR2 = 0.0449
Absolute structure parameter	0.010(4)
Largest diff. peak and hole	0.520 and -0.437 $e/Å^{-3}$

Table S–22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for crystal_06. U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	-2601(1)	3918(1)	3964(1)	13(1)
O(1)	-2221(2)	4360(1)	5681(1)	14(1)
N(1)	1088(2)	5550(2)	5554(1)	9(1)
C(1)	-628(2)	4642(2)	5335(1)	9(1)
C(2)	-129(2)	3999(2)	4575(1)	10(1)
C(3)	1571(3)	5194(2)	4304(1)	12(1)
C(4)	2748(3)	5627(2)	5002(1)	12(1)
C(5)	1435(2)	6164(2)	6269(1)	10(1)
C(6)	3444(2)	6051(2)	6564(1)	13(1)
C(7)	3828(3)	6737(2)	7249(1)	18(1)
C(8)	2233(3)	7546(2)	7627(1)	18(1)
C(9)	231(3)	7632(2)	7334(1)	15(1)
C(10)	-182(3)	6928(2)	6655(1)	12(1)

Table S–23. Bond lengths [Å] and angles [°] for crystal_06.

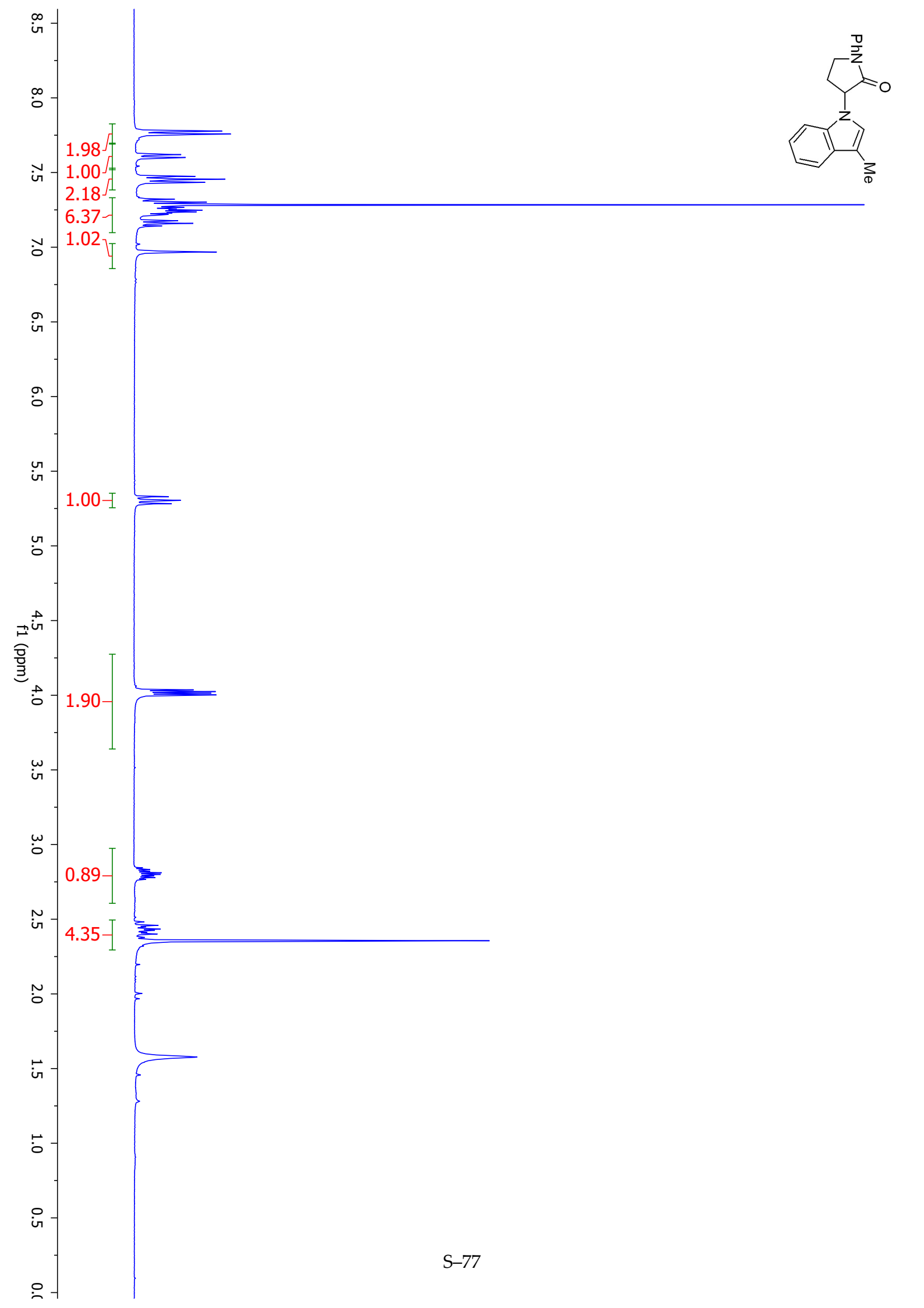
Bond length [Å]		Bond angle [°]	
Br(1)-C(2)	1.9389(14)	C(1)-N(1)-C(4)	112.99(12)
O(1)-C(1)	1.2192(19)	C(1)-N(1)-C(5)	125.19(13)
N(1)-C(1)	1.365(2)	C(5)-N(1)-C(4)	121.23(12)
N(1)-C(4)	1.4703(19)	O(1)-C(1)-N(1)	127.20(13)
N(1)-C(5)	1.4219(19)	O(1)-C(1)-C(2)	126.59(13)
C(1)-C(2)	1.524(2)	N(1)-C(1)-C(2)	106.19(13)
C(2)-C(3)	1.516(2)	C(1)-C(2)-Br(1)	112.22(10)
C(3)-C(4)	1.531(2)	C(3)-C(2)-Br(1)	114.00(10)
C(5)-C(6)	1.393(2)	C(3)-C(2)-C(1)	104.47(12)
C(5)-C(10)	1.388(2)	C(2)-C(3)-C(4)	101.94(11)
C(6)-C(7)	1.396(2)	N(1)-C(4)-C(3)	102.93(12)
C(7)-C(8)	1.386(3)	C(6)-C(5)-N(1)	118.97(14)
C(8)-C(9)	1.387(3)	C(10)-C(5)-N(1)	120.53(14)
C(9)-C(10)	1.395(2)	C(10)-C(5)-C(6)	120.46(14)
		C(5)-C(6)-C(7)	119.41(15)
		C(8)-C(7)-C(6)	120.31(16)
		C(7)-C(8)-C(9)	119.91(14)
		C(8)-C(9)-C(10)	120.34(16)
		C(5)-C(10)-C(9)	119.54(16)

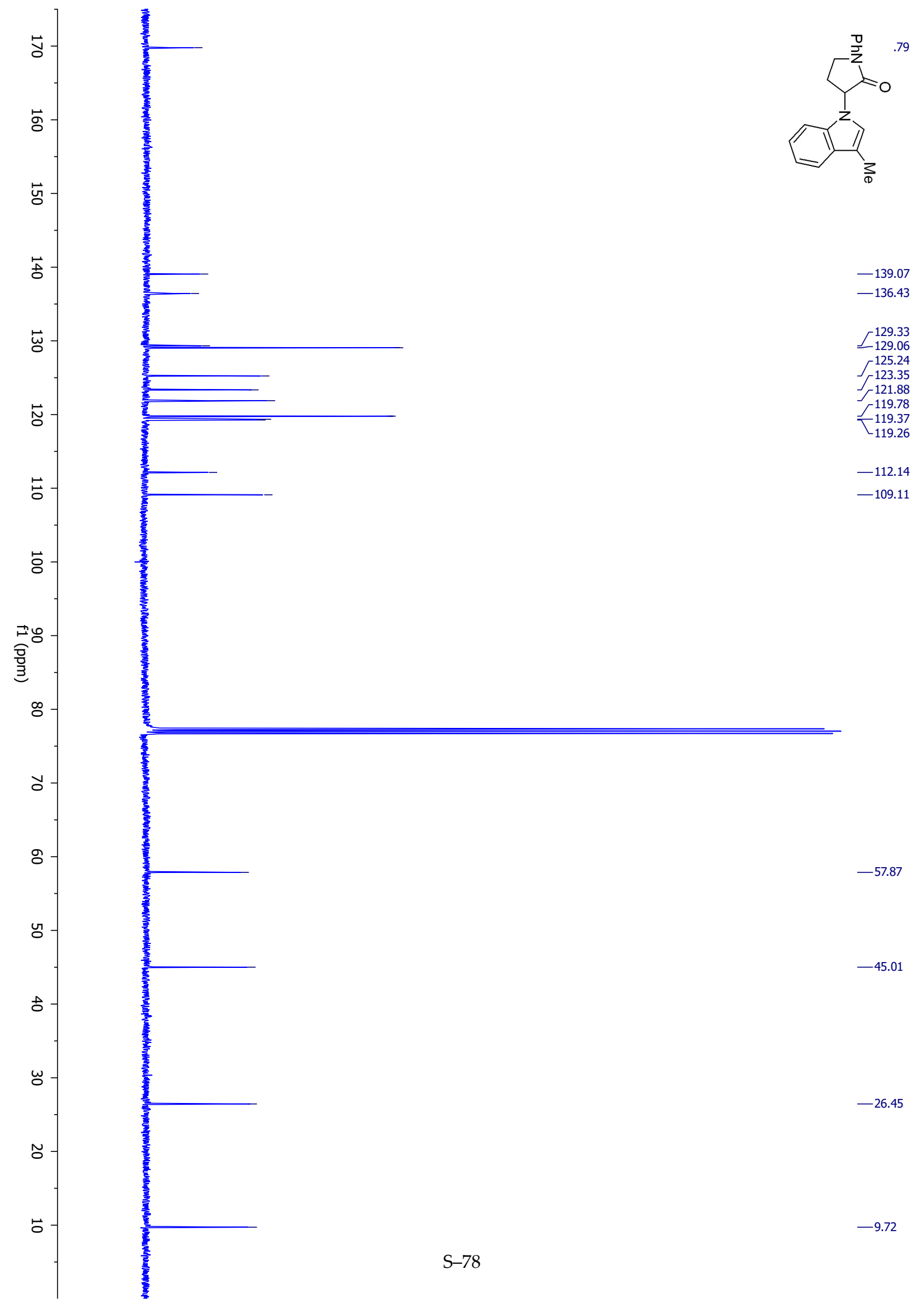
Table S–24. Anisotropic displacement parameters ($Å^2 \times 10^3$) for crystal_06. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

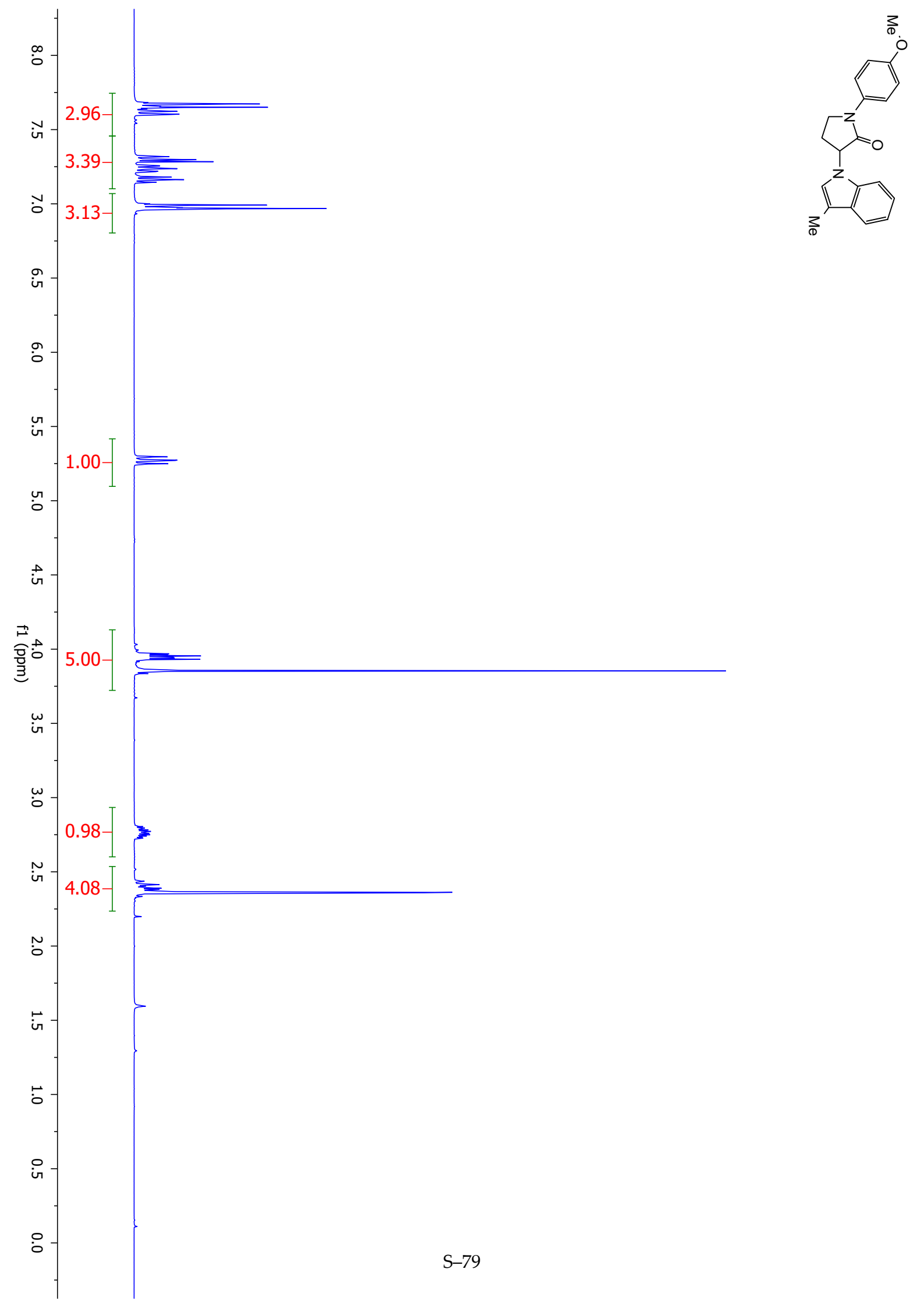
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	11(1)	20(1)	9(1)	0(1)	-2(1)	-2(1)
O(1)	11(1)	19(1)	11(1)	-1(1)	2(1)	-4(1)
N(1)	8(1)	12(1)	9(1)	0(1)	2(1)	0(1)
C(1)	9(1)	8(1)	9(1)	1(1)	0(1)	0(1)
C(2)	10(1)	10(1)	9(1)	-1(1)	-1(1)	0(1)
C(3)	9(1)	16(1)	10(1)	0(1)	2(1)	-2(1)
C(4)	9(1)	16(1)	12(1)	0(1)	2(1)	-2(1)
C(5)	12(1)	8(1)	9(1)	1(1)	0(1)	-1(1)
C(6)	10(1)	18(1)	11(1)	-1(1)	-2(1)	-1(1)
C(7)	16(1)	25(1)	13(1)	0(1)	-5(1)	-3(1)
C(8)	24(1)	19(1)	10(1)	-2(1)	0(1)	-5(1)
C(9)	21(1)	15(1)	11(1)	-1(1)	3(1)	0(1)
C(10)	13(1)	11(1)	12(1)	0(1)	2(1)	1(1)

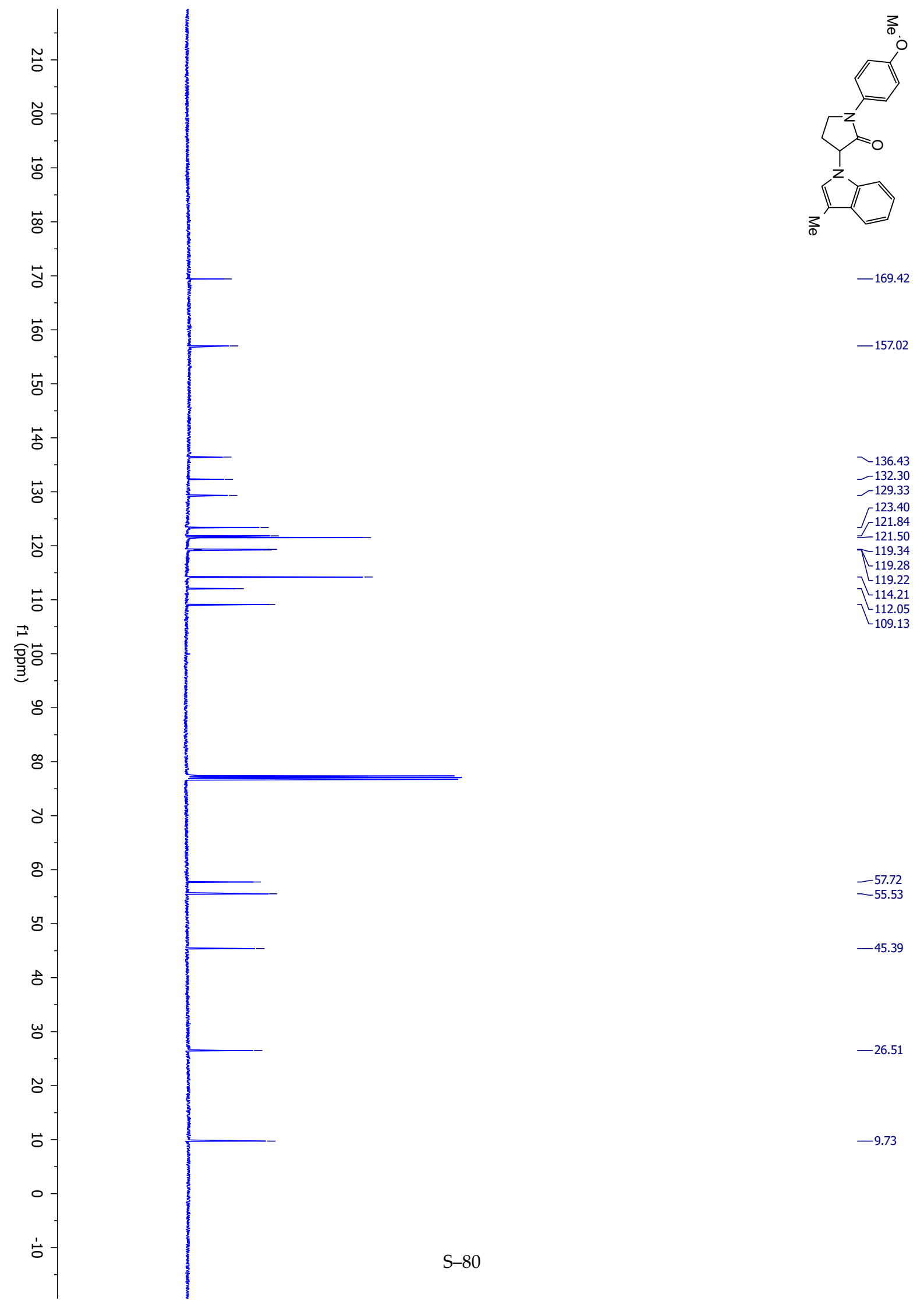
Table S–25. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for crystal_06.

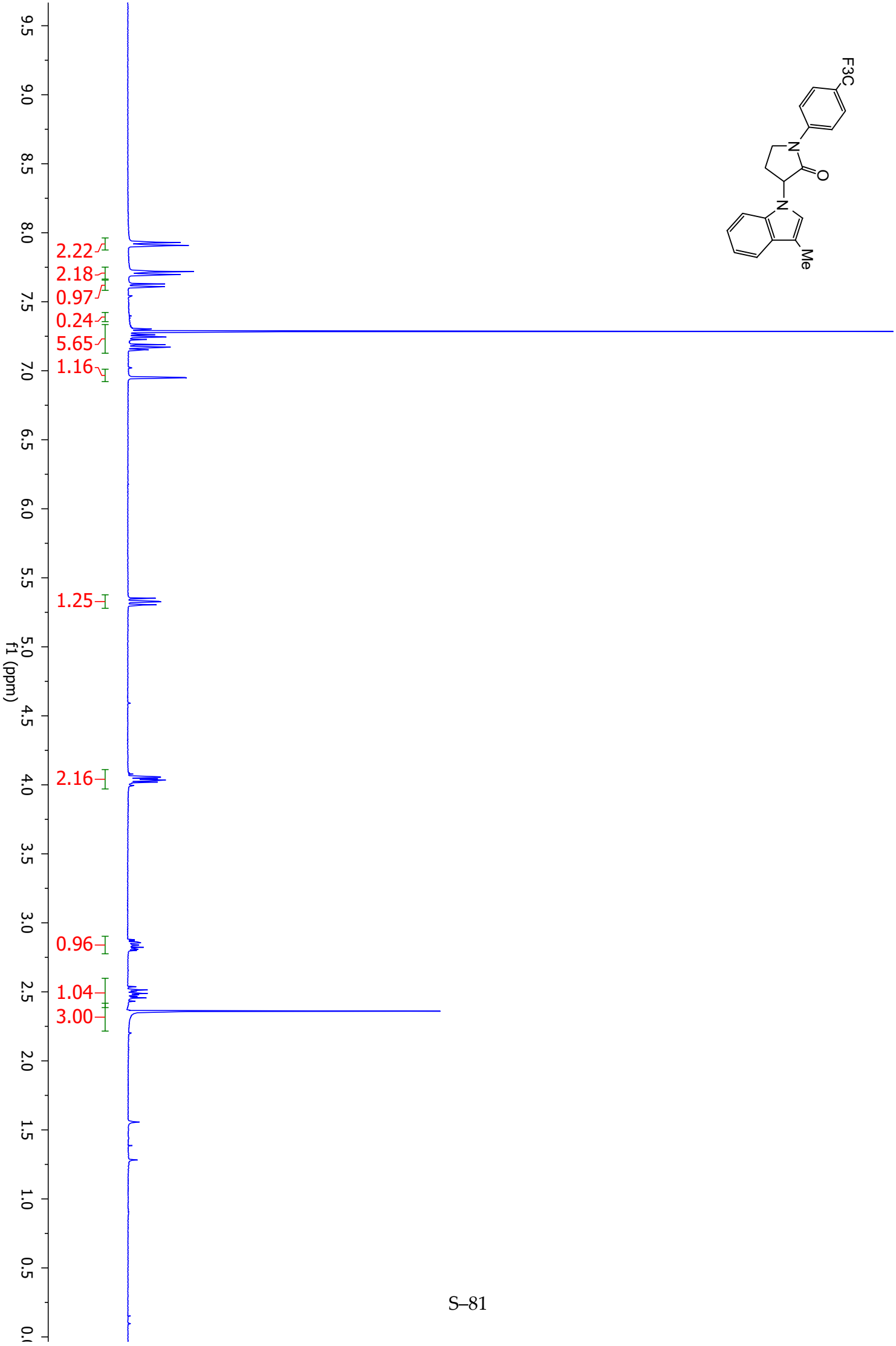
	x	y	z	U(eq)
H(2)	470	2822	4613	11
H(3A)	962	6230	4079	14
H(3B)	2501	4619	3950	14
H(4A)	3868	4781	5102	15
H(4B)	3379	6781	4977	15
H(6)	4543	5512	6301	16
H(7)	5189	6649	7456	22
H(8)	2511	8041	8087	21
H(9)	-866	8173	7597	18
H(10)	-1560	6972	6459	14

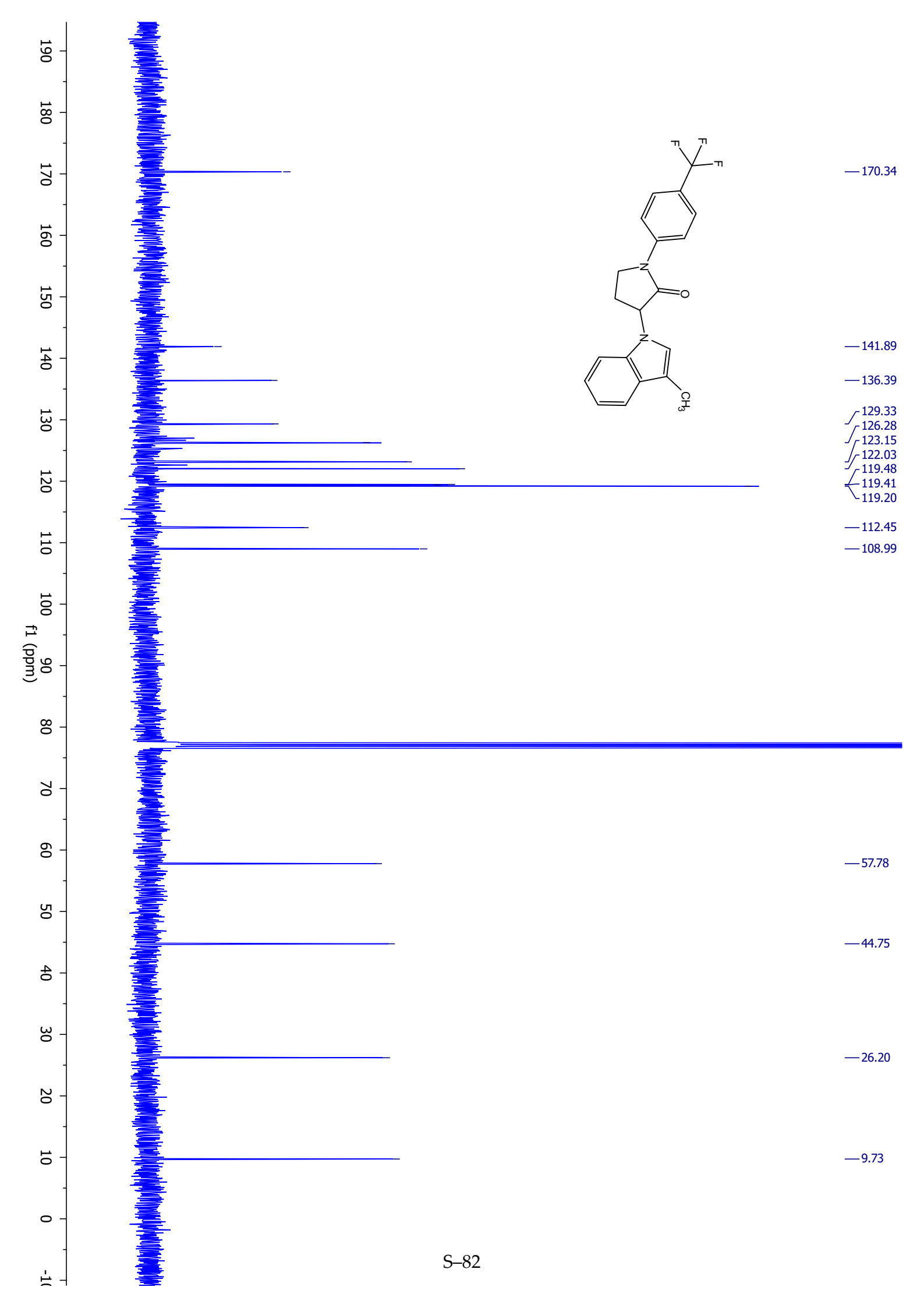

PhN
O
N
Me
1.98
1.00
2.18
6.37
1.02
1.00
1.90
0.89
4.35
f1 (ppm)

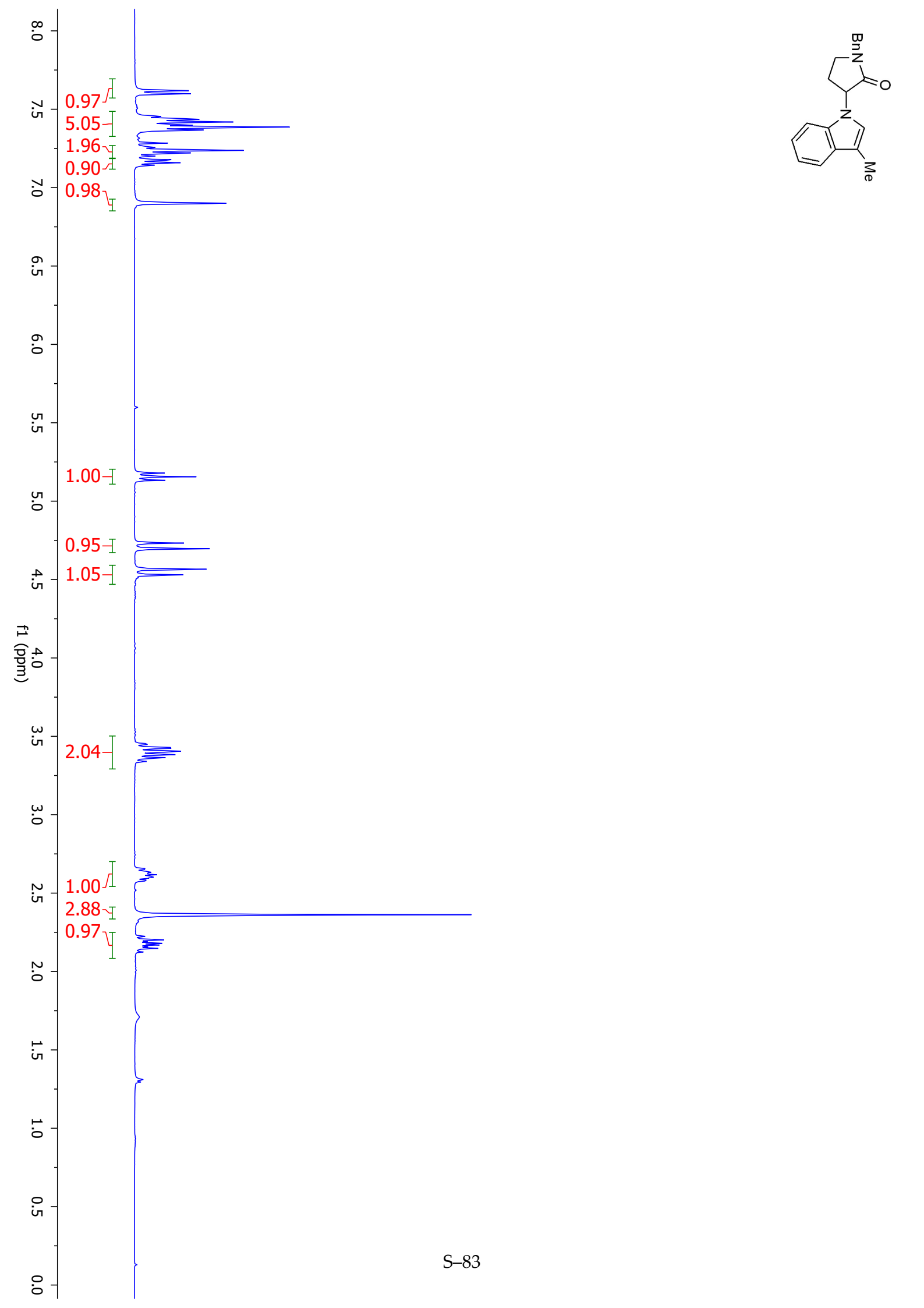

f1 (ppm)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
PhN
O
N
Me
.79
139.07
136.43
129.33
129.06
125.24
123.35
121.88
119.78
119.37
119.26
112.14
109.11
57.87
45.01
26.45
9.72

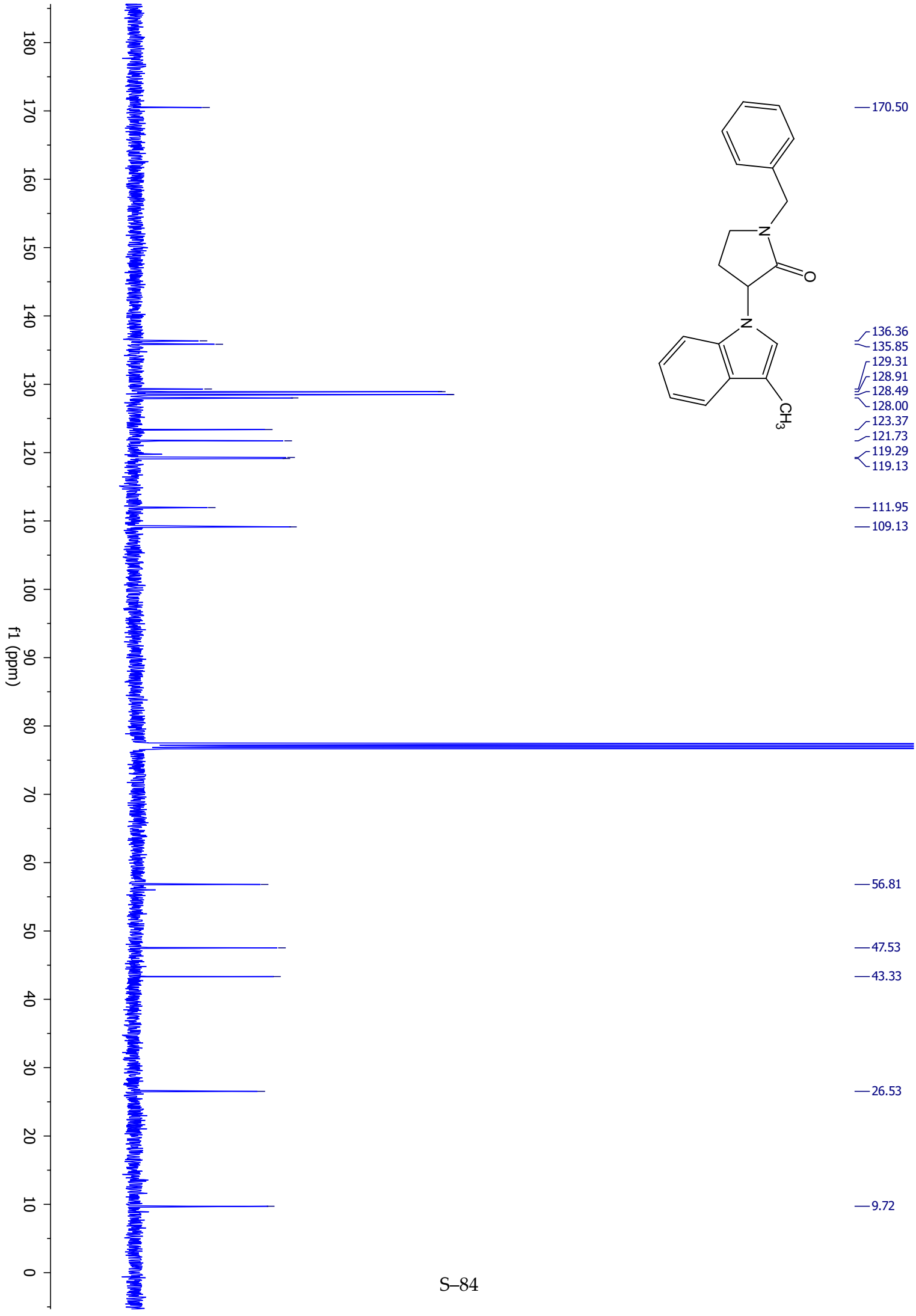

2.96
3.39
3.13
1.00
5.00
0.98
4.08
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Me
O
N
O
N
Me

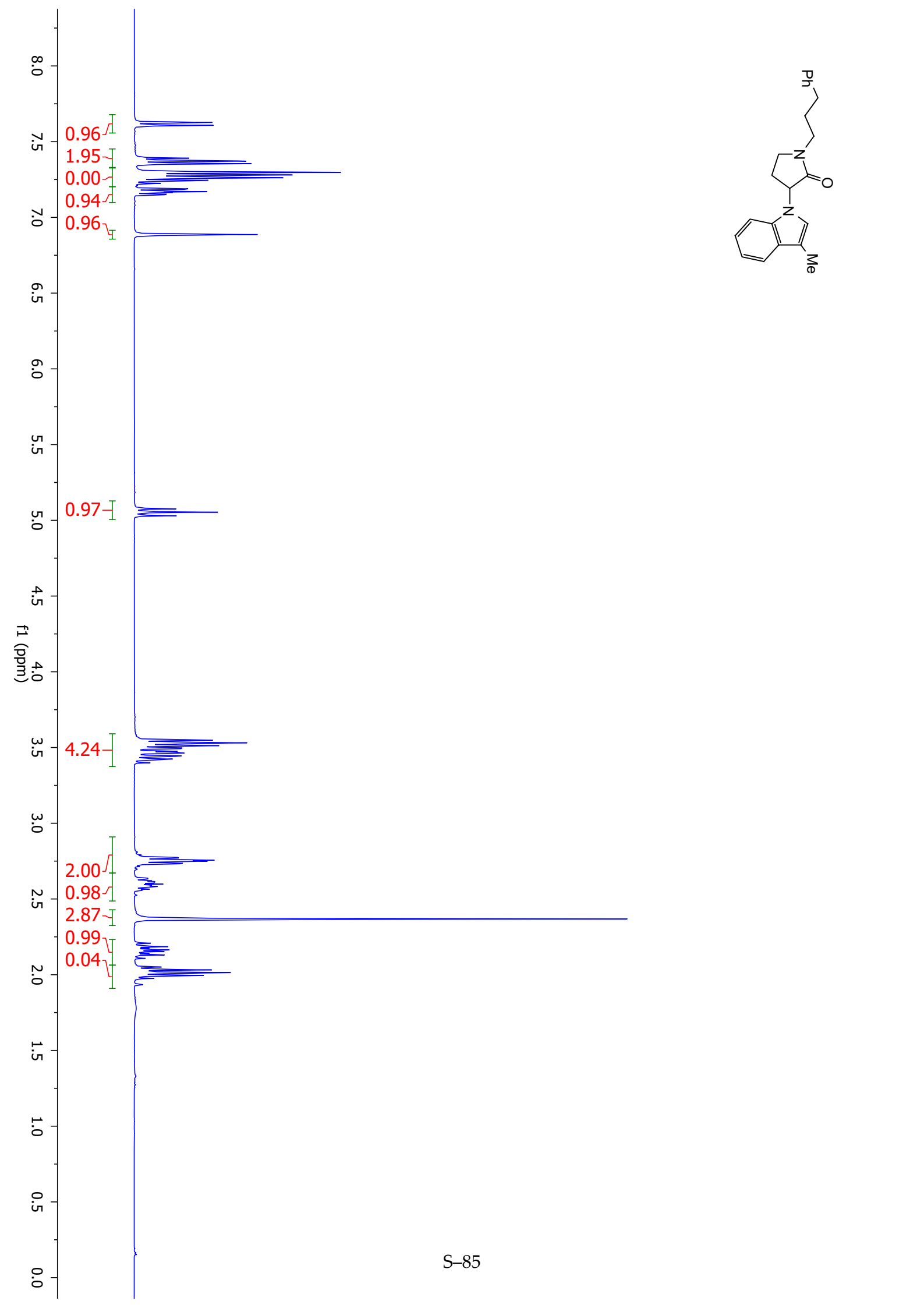

Me
O
N
O
N
Me
169.42
157.02
136.43
132.30
129.33
123.40
121.84
121.50
119.34
119.28
119.22
114.21
112.05
109.13
57.72
55.53
45.39
26.51
9.73
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

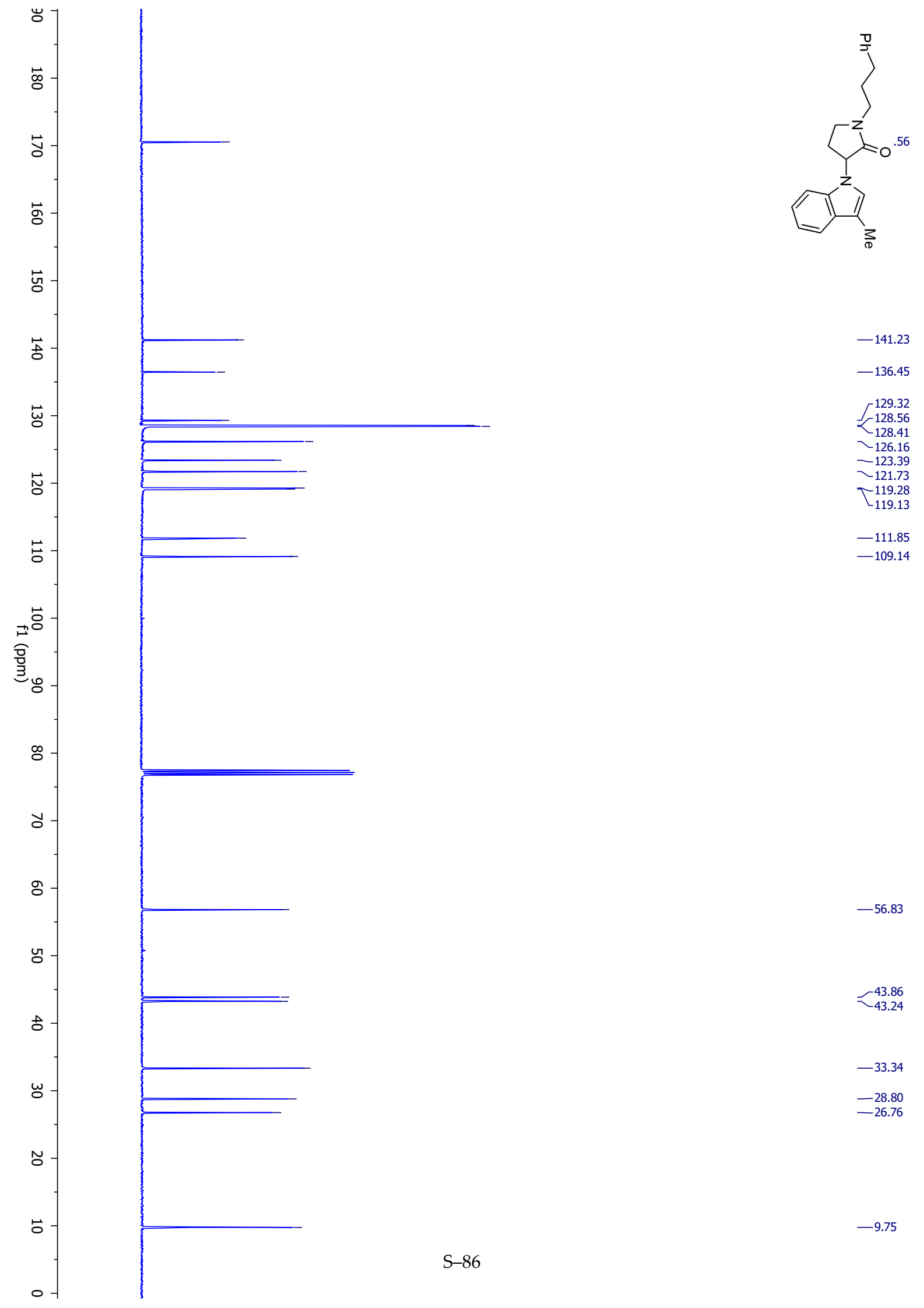

F3C
N
O
N
Me
2.22
2.18
0.97
0.24
5.65
1.16
1.25
2.16
0.96
1.04
3.00
f1 (ppm)

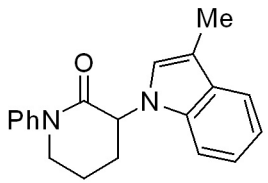

f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1(
170.34
141.89
136.39
129.33
126.28
123.15
122.03
119.48
119.41
119.20
112.45
108.99
57.78
44.75
26.20
9.73
F
F
F
N
O
N
CH3


0.97
5.05
1.96
0.90
0.98
1.00
0.95
1.05
2.04
1.00
2.88
0.97
f1 (ppm)
BnN
O
N
Me


170.50
136.36
135.85
129.31
128.91
128.49
128.00
123.37
121.73
119.29
119.13
111.95
109.13
56.81
47.53
43.33
26.53
9.72
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
N
O
N
CH3


0.96
1.95
0.00
0.94
0.96
0.97
4.24
2.00
0.98
2.87
0.99
0.04
f1 (ppm)
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
Ph
N
O
N
Me


Ph
N
O
.56
N
Me
141.23
136.45
129.32
128.56
128.41
126.16
123.39
121.73
119.28
119.13
111.85
109.14
56.83
43.86
43.24
33.34
28.80
26.76
9.75
f1 (ppm)



1.04 2.05 2.01 1.35 1.07 0.96 1.01

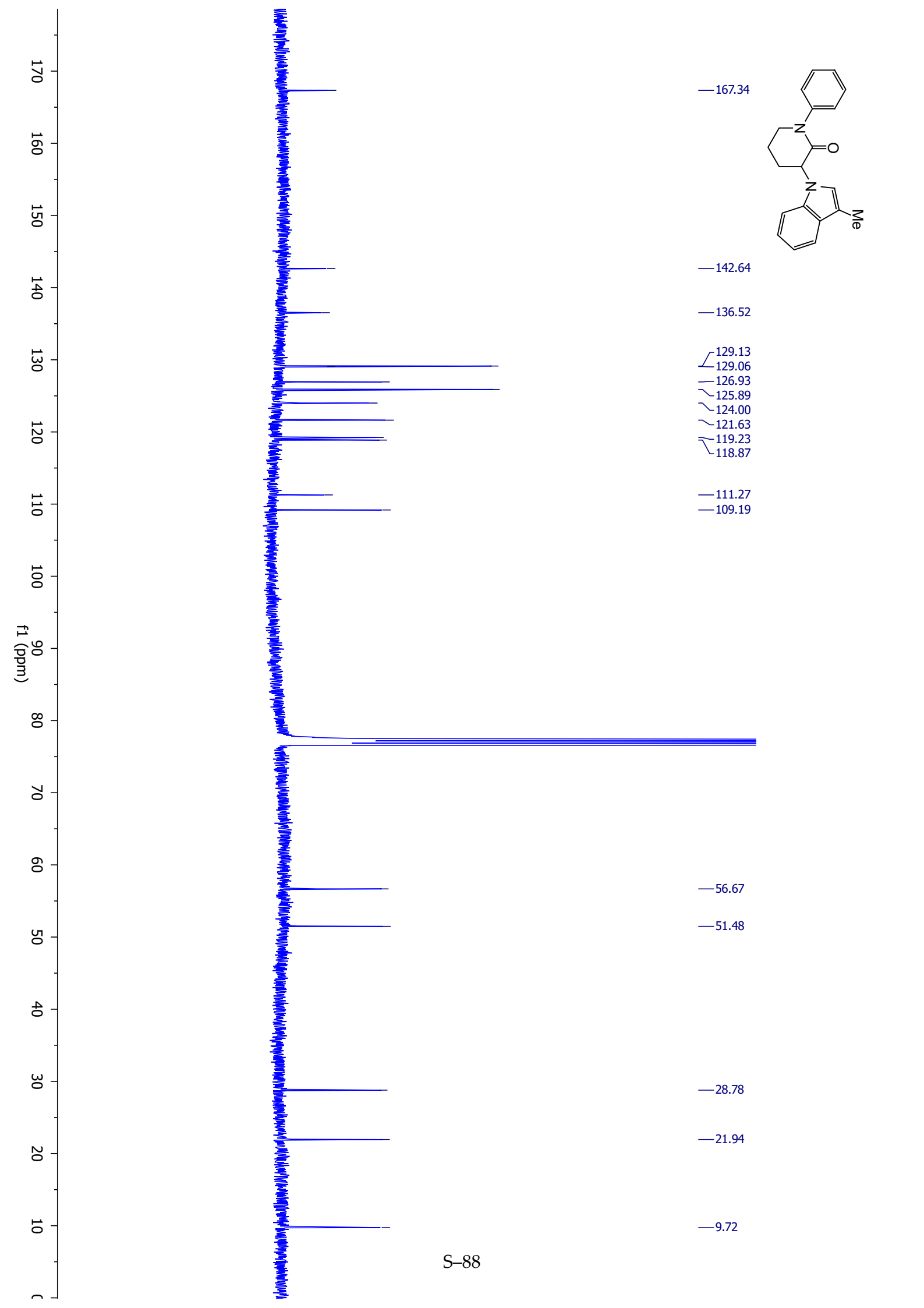
1.09

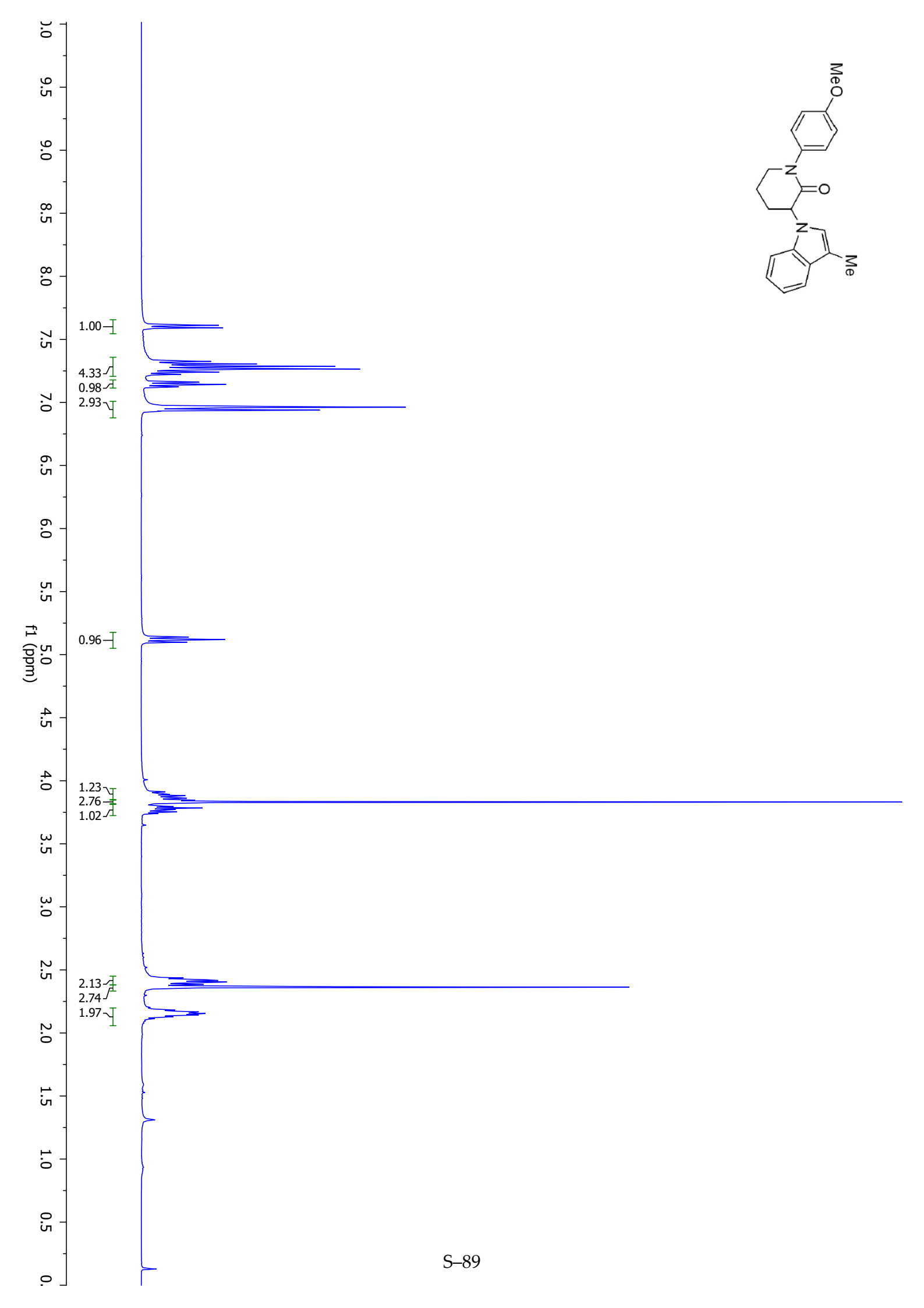
0.99 1.04

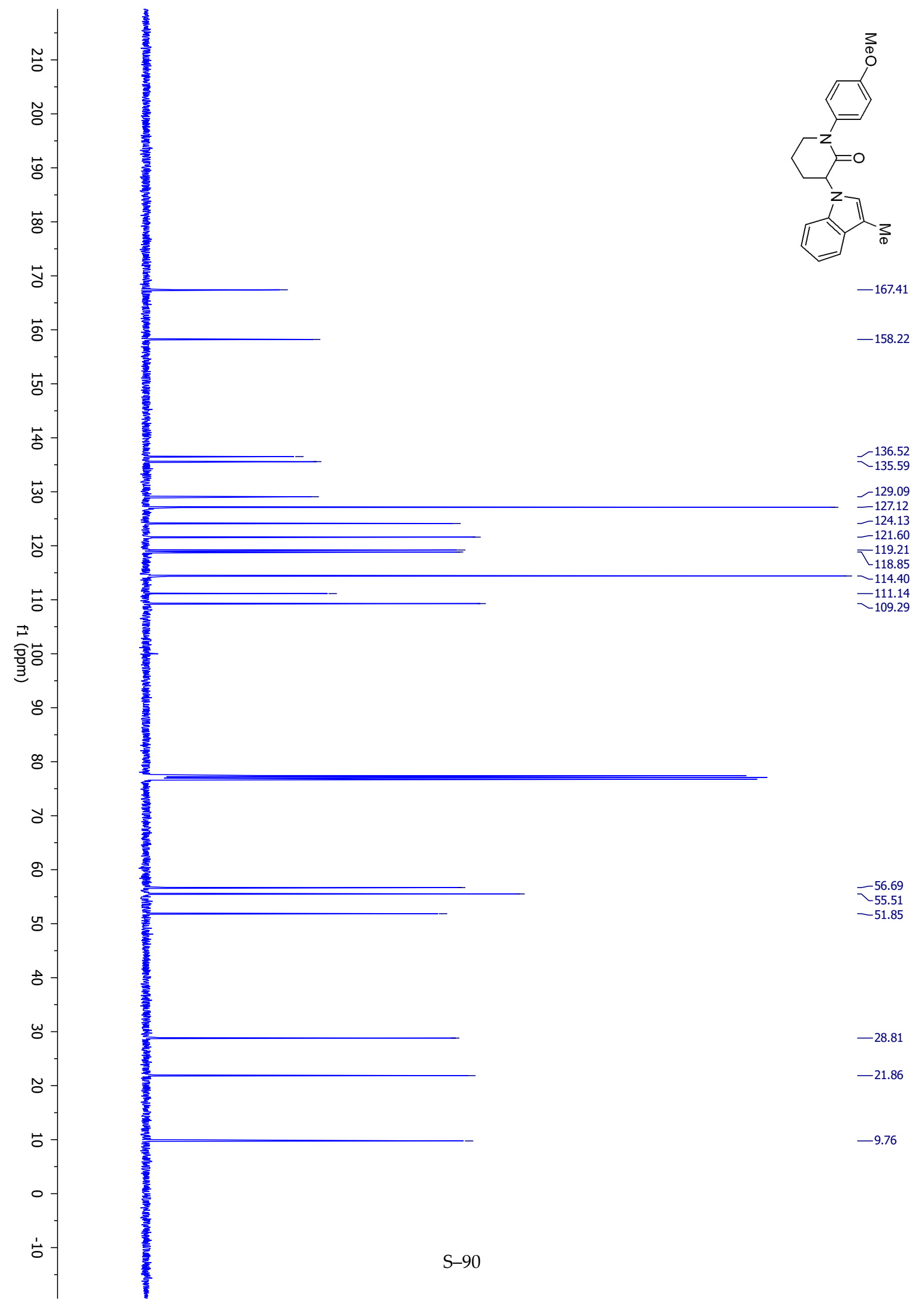
1.92 2.66 1.80

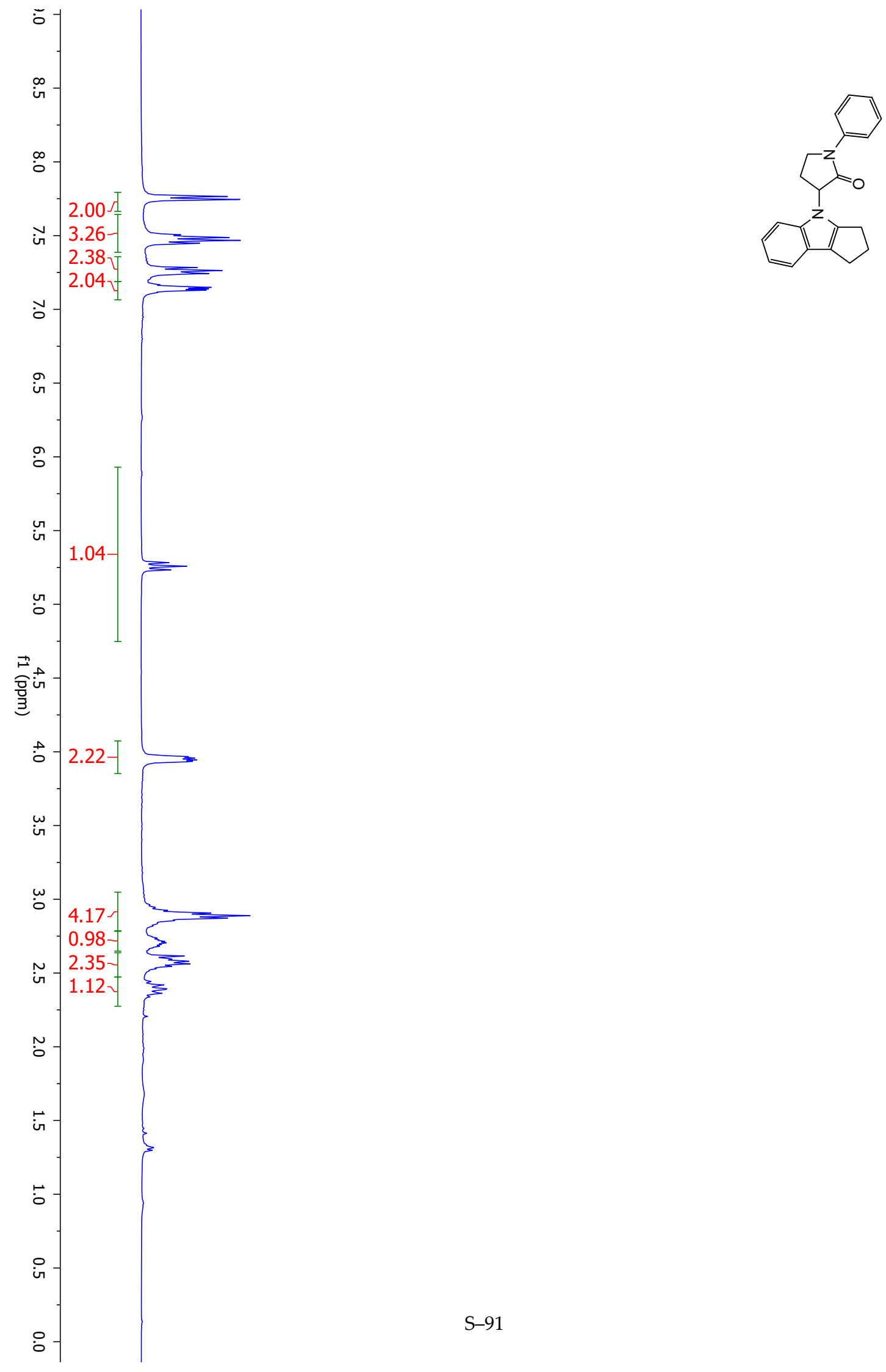
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

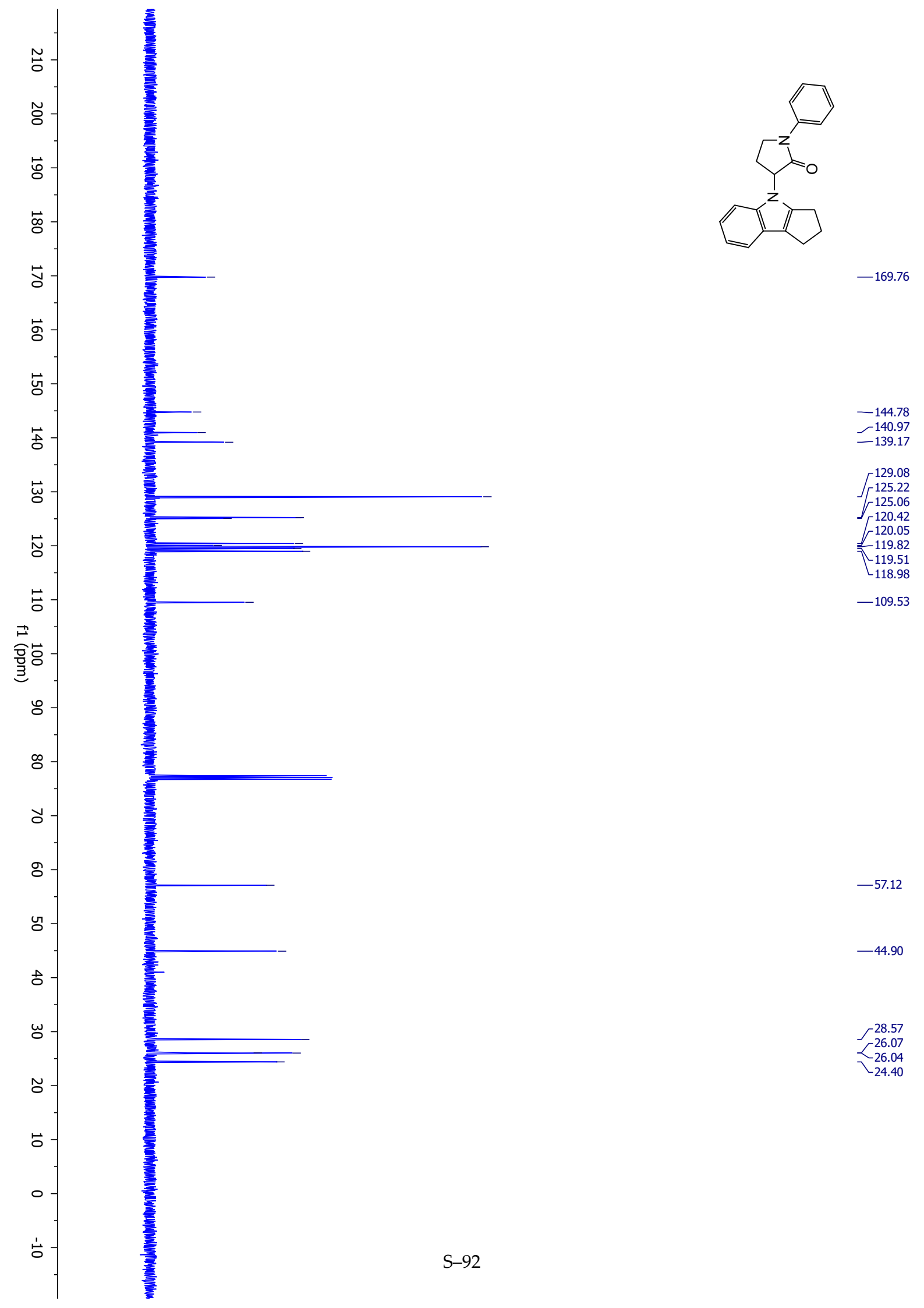
f1 (ppm)

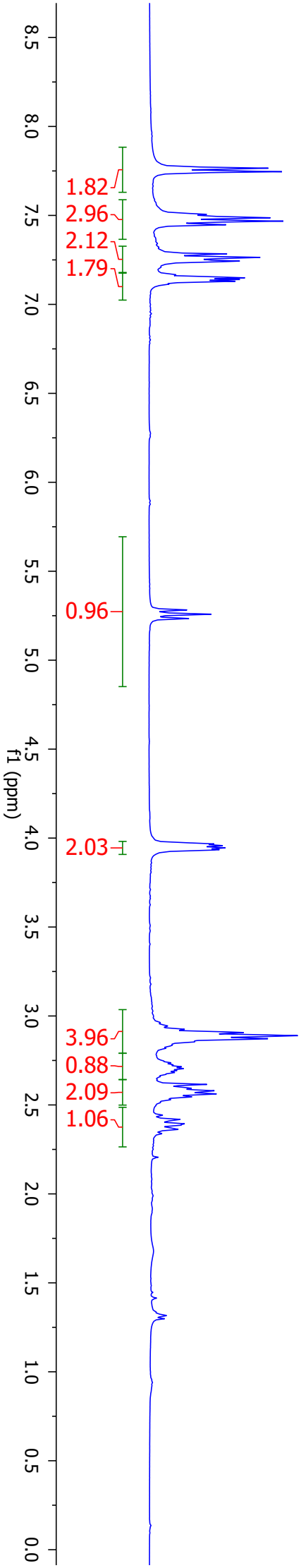

167.34
142.64
136.52
129.13
129.06
126.93
125.89
124.00
121.63
119.23
118.87
111.27
109.19
56.67
51.48
28.78
21.94
9.72
N
O
N
Me
f1 (ppm)

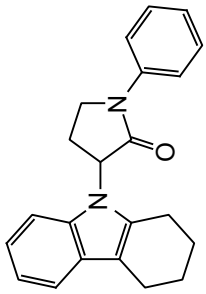

MeO
N
O
N
Me
1.00
4.33
0.98
2.93
0.96
1.23
2.76
1.02
2.13
2.74
1.97
f1 (ppm)

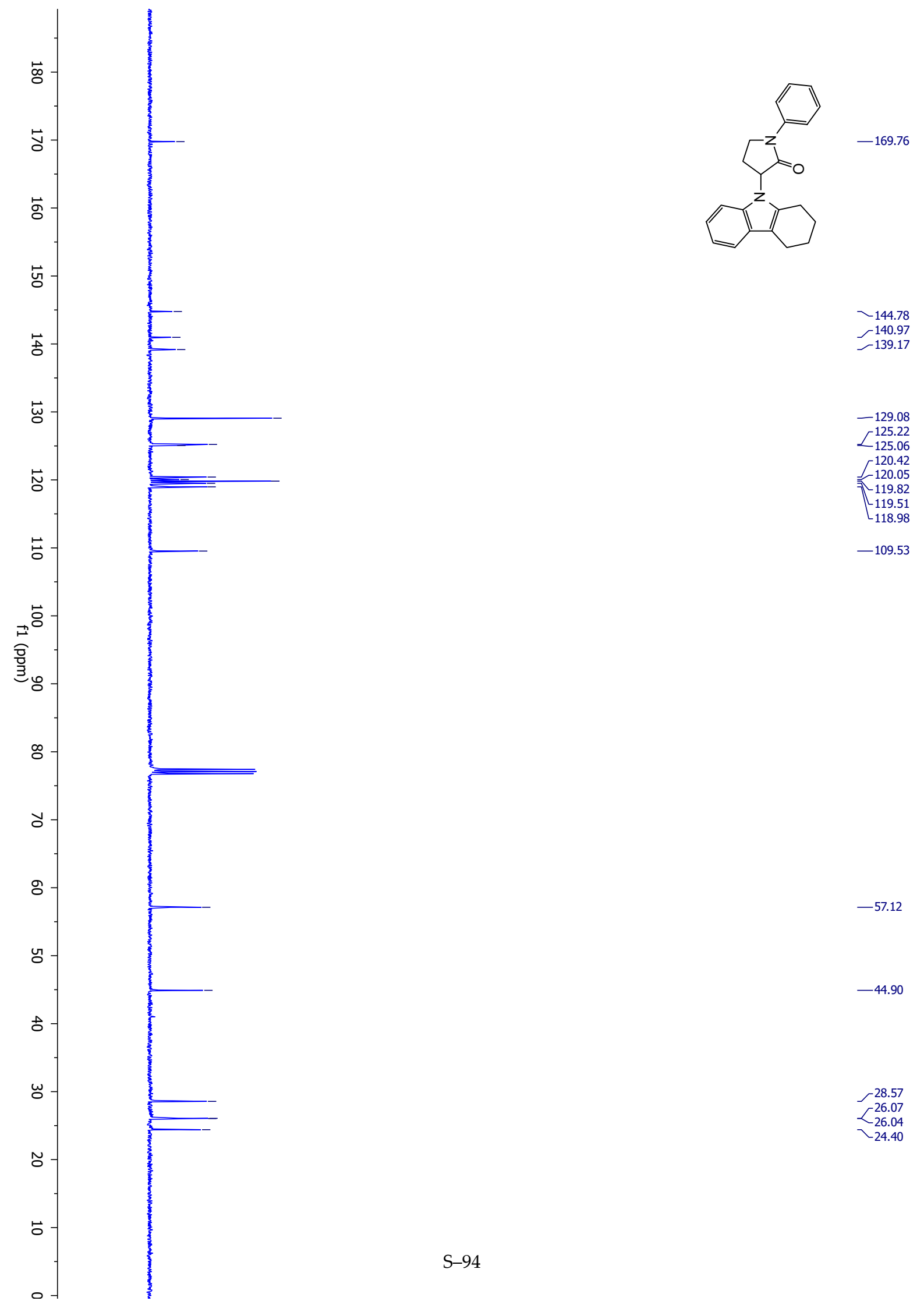

MeO
N
O
N
Me
167.41
158.22
136.52
135.59
129.09
127.12
124.13
121.60
119.21
118.85
114.40
111.14
109.29
56.69
55.51
51.85
28.81
21.86
9.76
f1 (ppm)

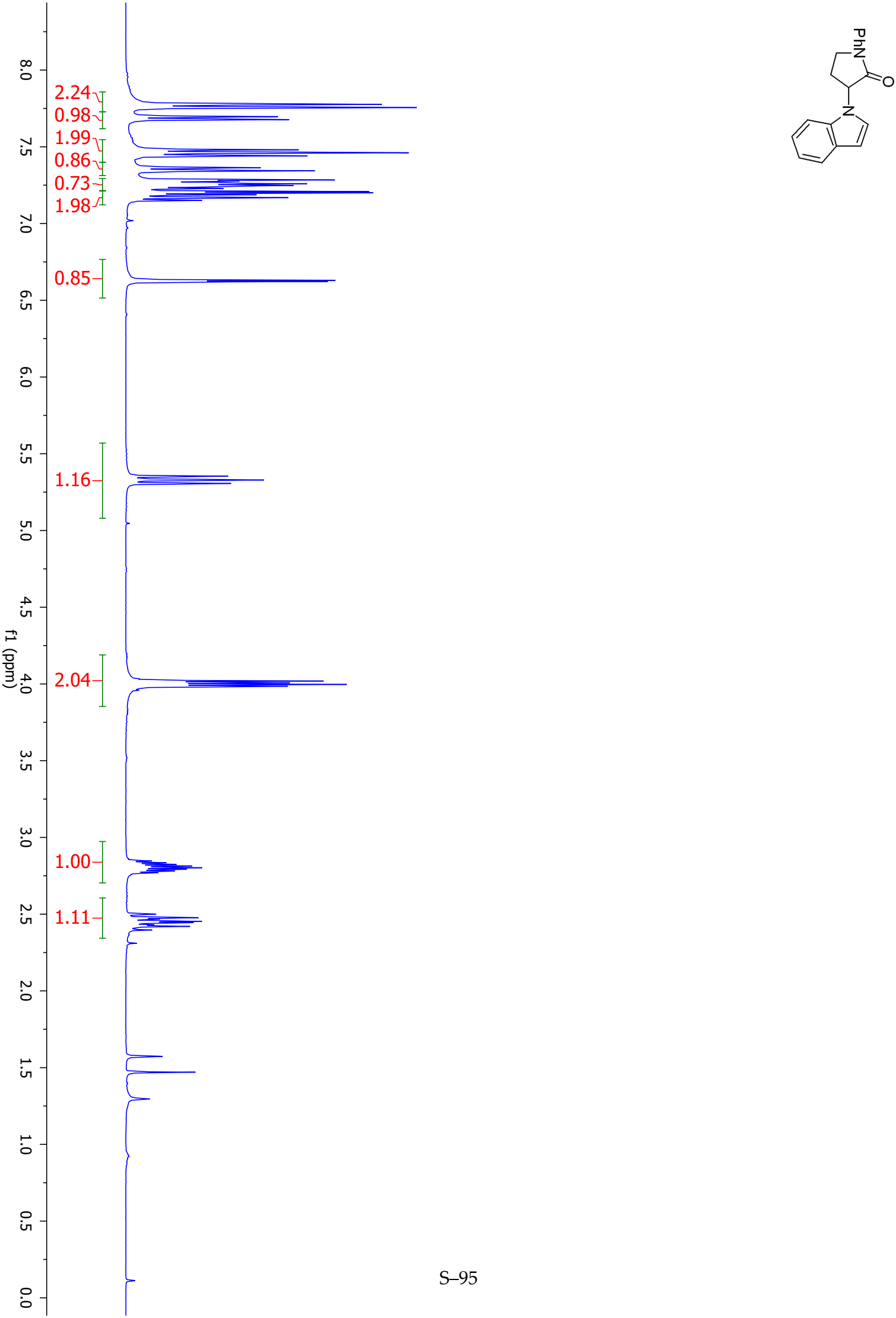

2.00
3.26
2.38
2.04
1.04
2.22
4.17
0.98
2.35
1.12
f1 (ppm)

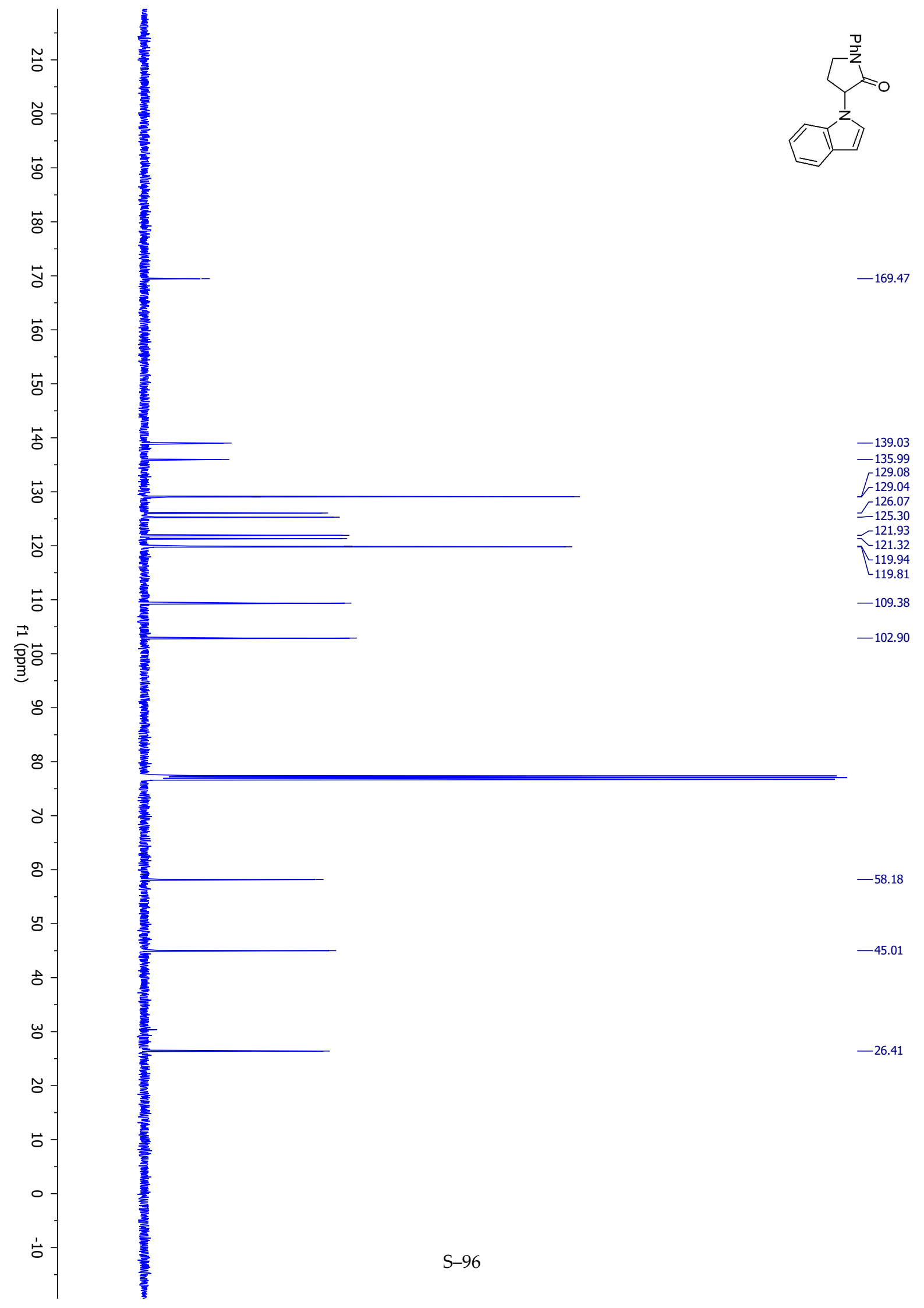

169.76
144.78
140.97
139.17
129.08
125.22
125.06
120.42
120.05
119.82
119.51
118.98
109.53
57.12
44.90
28.57
26.07
26.04
24.40
f1 (ppm)

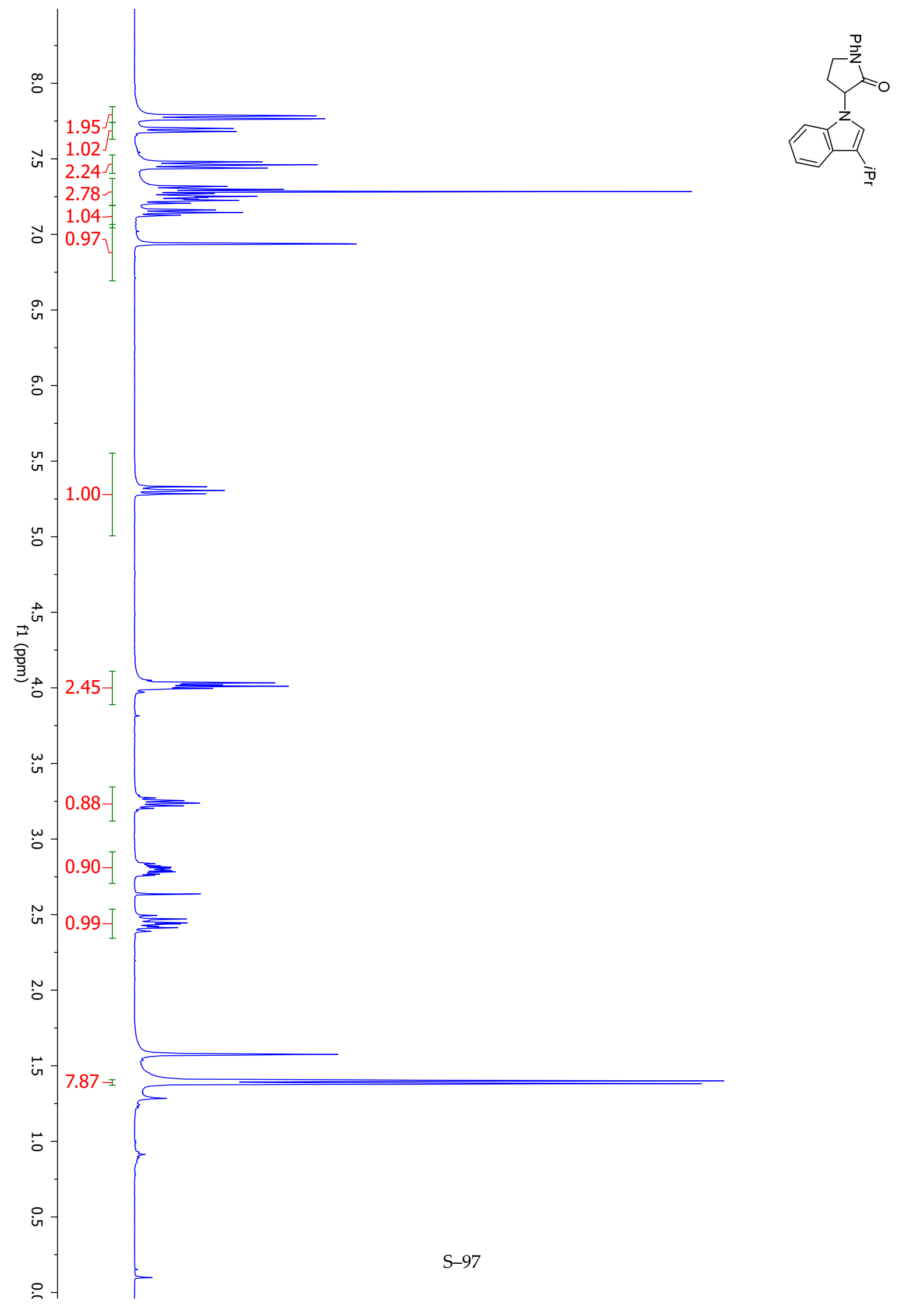

1.82
2.96
2.12
1.79
0.96
2.03
3.96
0.88
2.09
1.06
f1 (ppm)

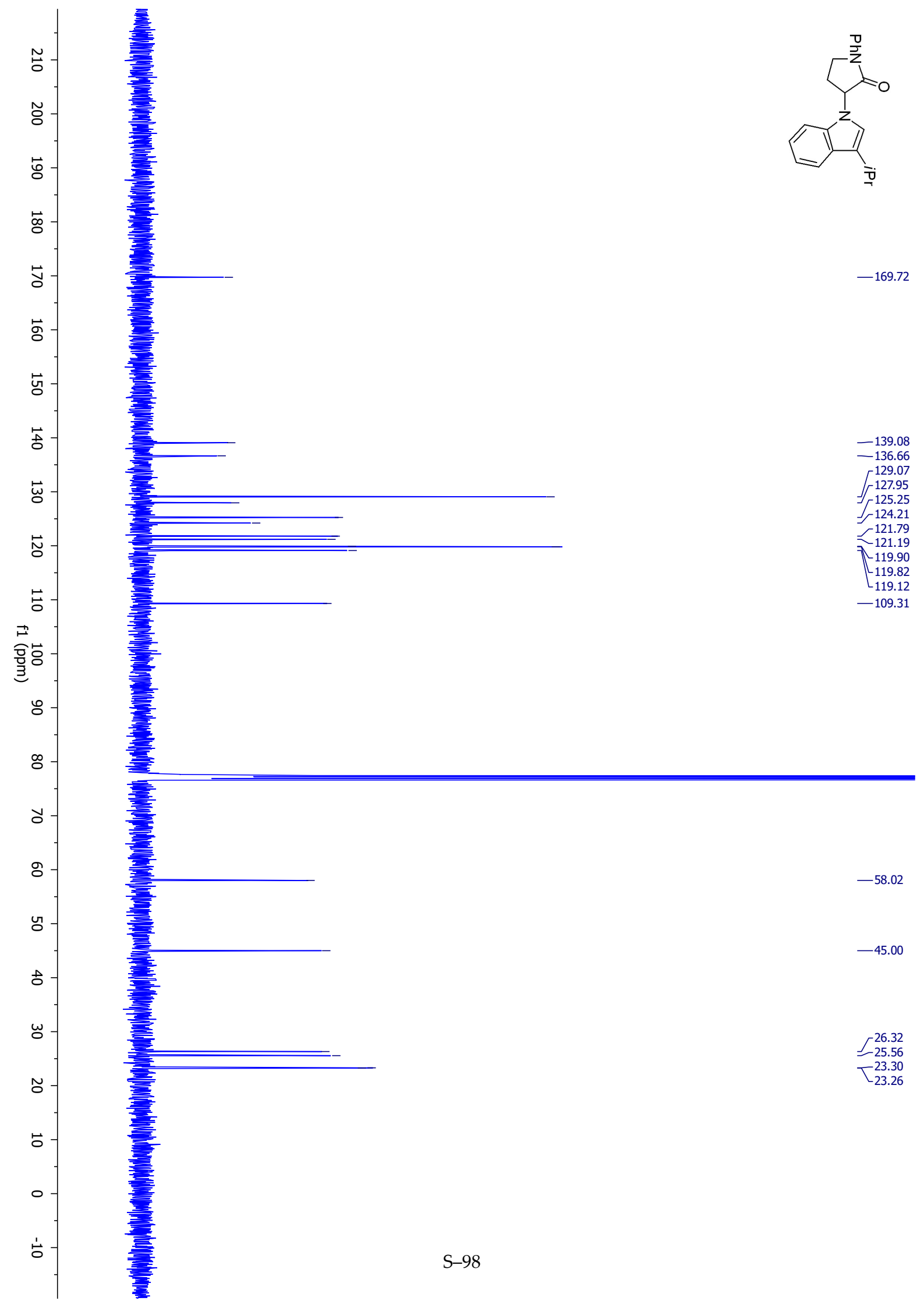


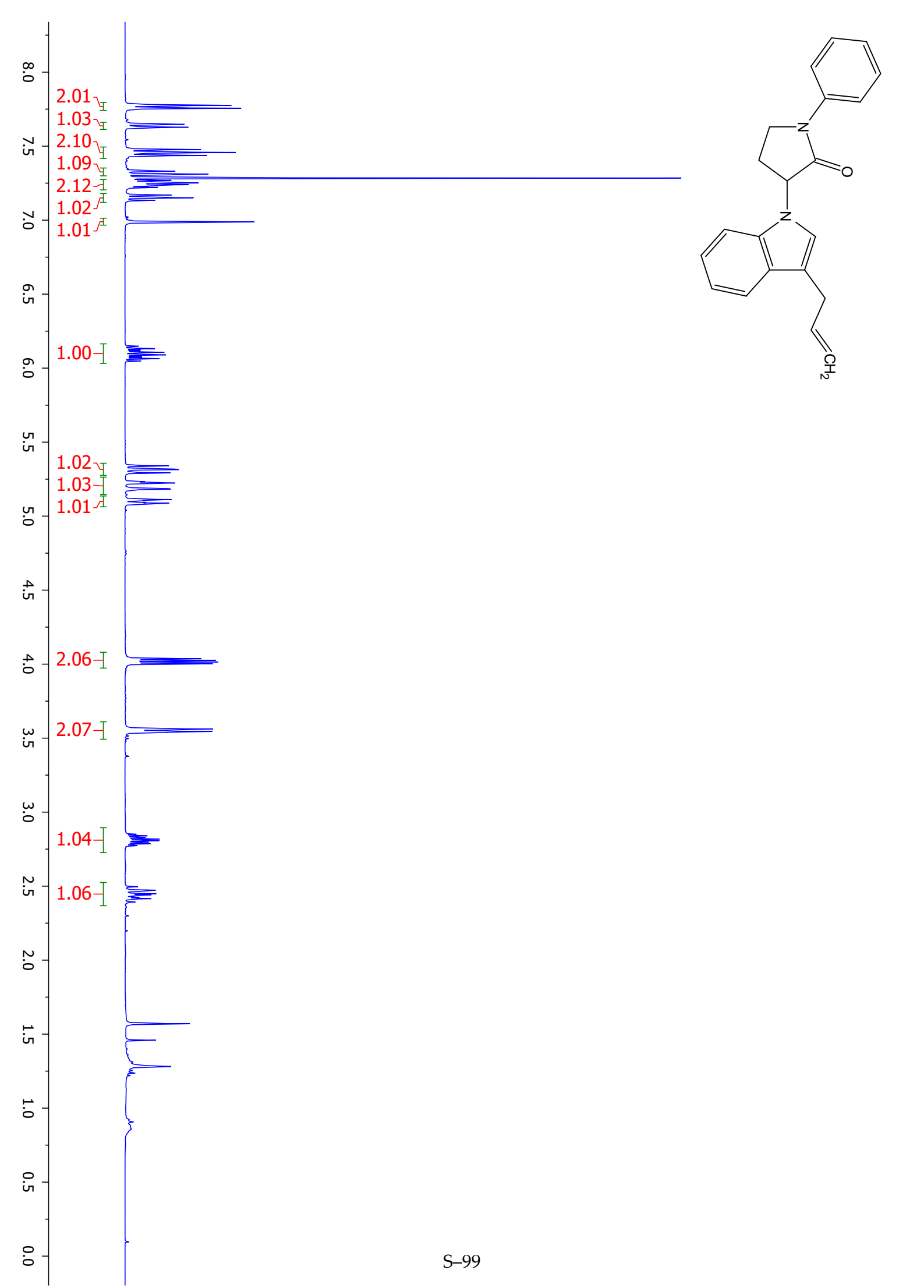

169.76
144.78
140.97
139.17
129.08
125.22
125.06
120.42
120.05
119.82
119.51
118.98
109.53
57.12
44.90
28.57
26.07
26.04
24.40
f1 (ppm)

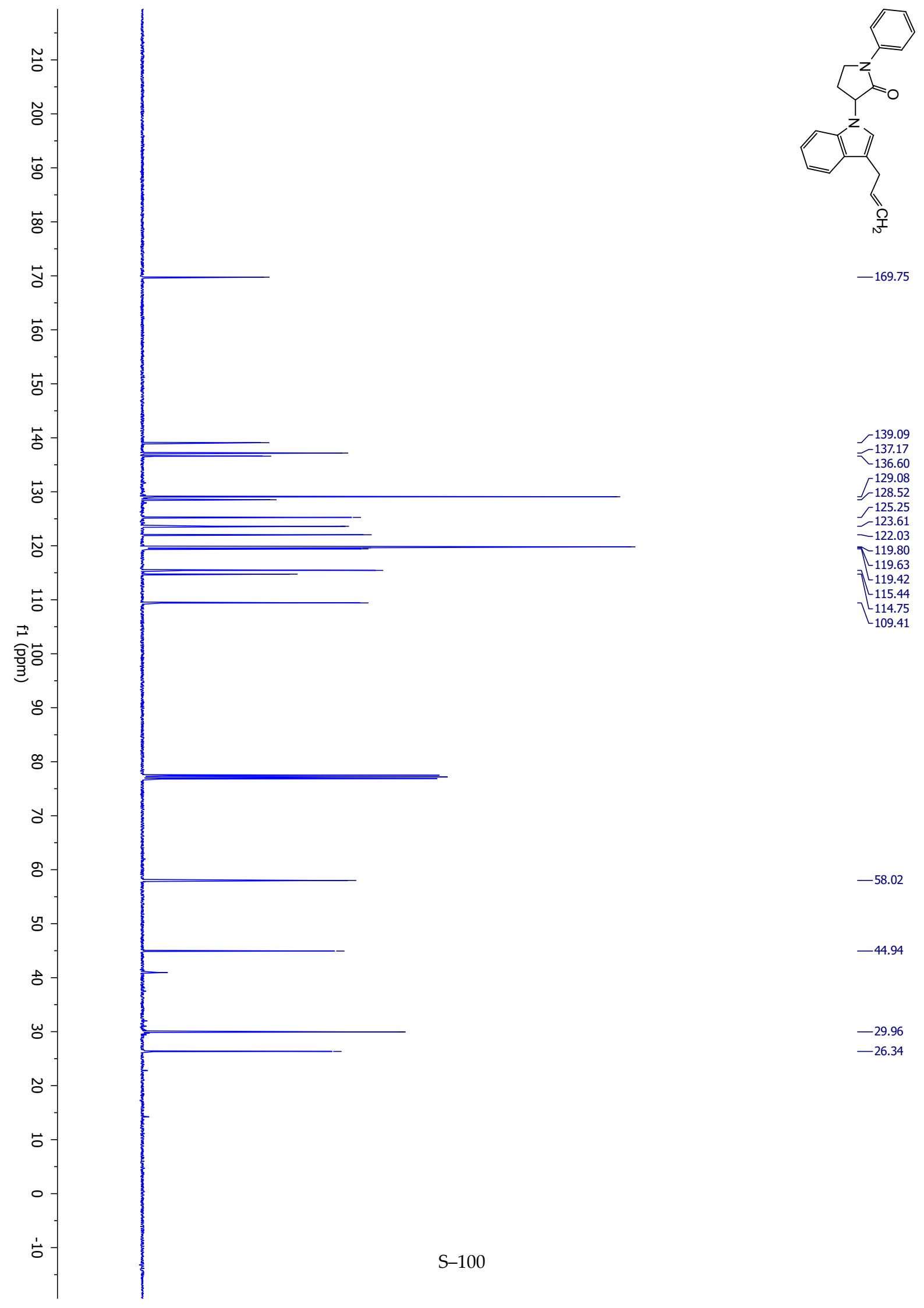

2.24
0.98
1.99
0.86
0.73
1.98
0.85
1.16
2.04
1.00
1.11
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
PhN
O
N

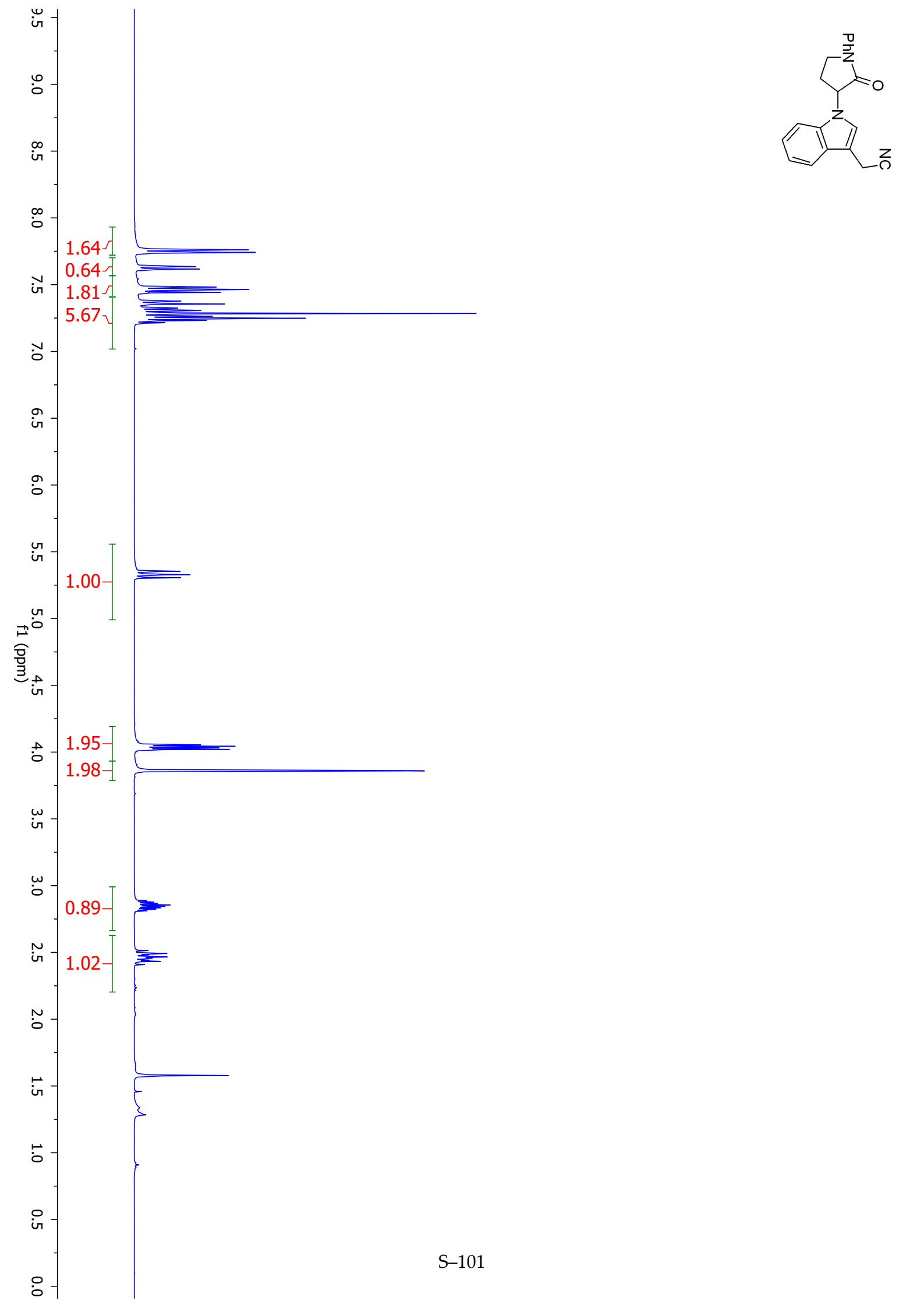

PhN
O
N
169.47
139.03
135.99
129.08
129.04
126.07
125.30
121.93
121.32
119.94
119.81
109.38
102.90
58.18
45.01
26.41
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

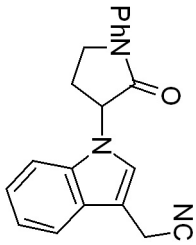

PhN
O
N
iPr
1.95
1.02
2.24
2.78
1.04
0.97
1.00
2.45
0.88
0.90
0.99
7.87
f1 (ppm)


PhN
O
N
iPr
169.72
139.08
136.66
129.07
127.95
125.25
124.21
121.79
121.19
119.90
119.82
119.12
109.31
58.02
45.00
26.32
25.56
23.30
23.26
f1 (ppm)


2.01
1.03
2.10
1.09
2.12
1.02
1.01
1.00
1.02
1.03
1.01
2.06
2.07
1.04
1.06
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
N
O
N
CH2

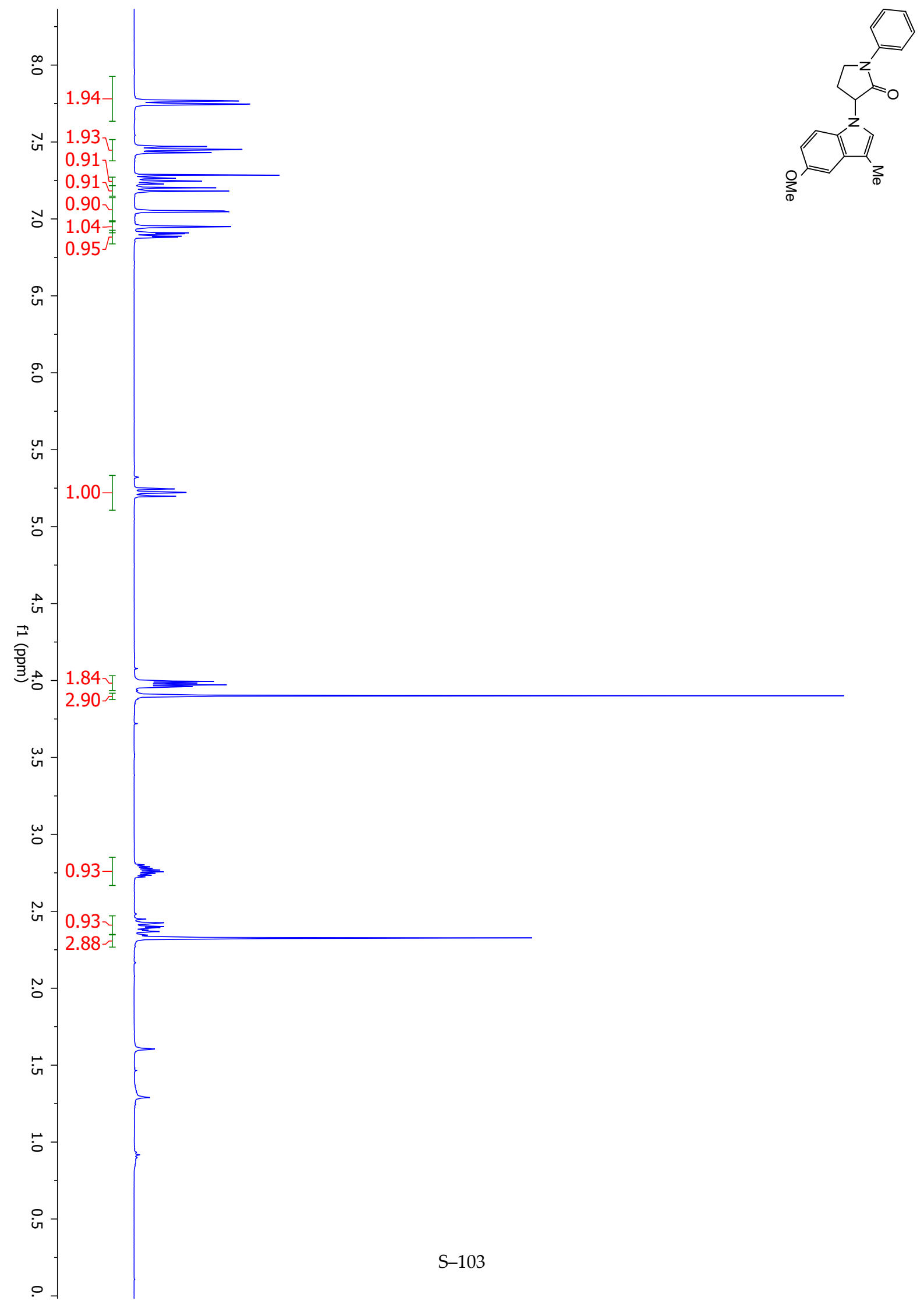

169.75
139.09
137.17
136.60
129.08
128.52
125.25
123.61
122.03
119.80
119.63
119.42
115.44
114.75
109.41
58.02
44.94
29.96
26.34
f1 (ppm)

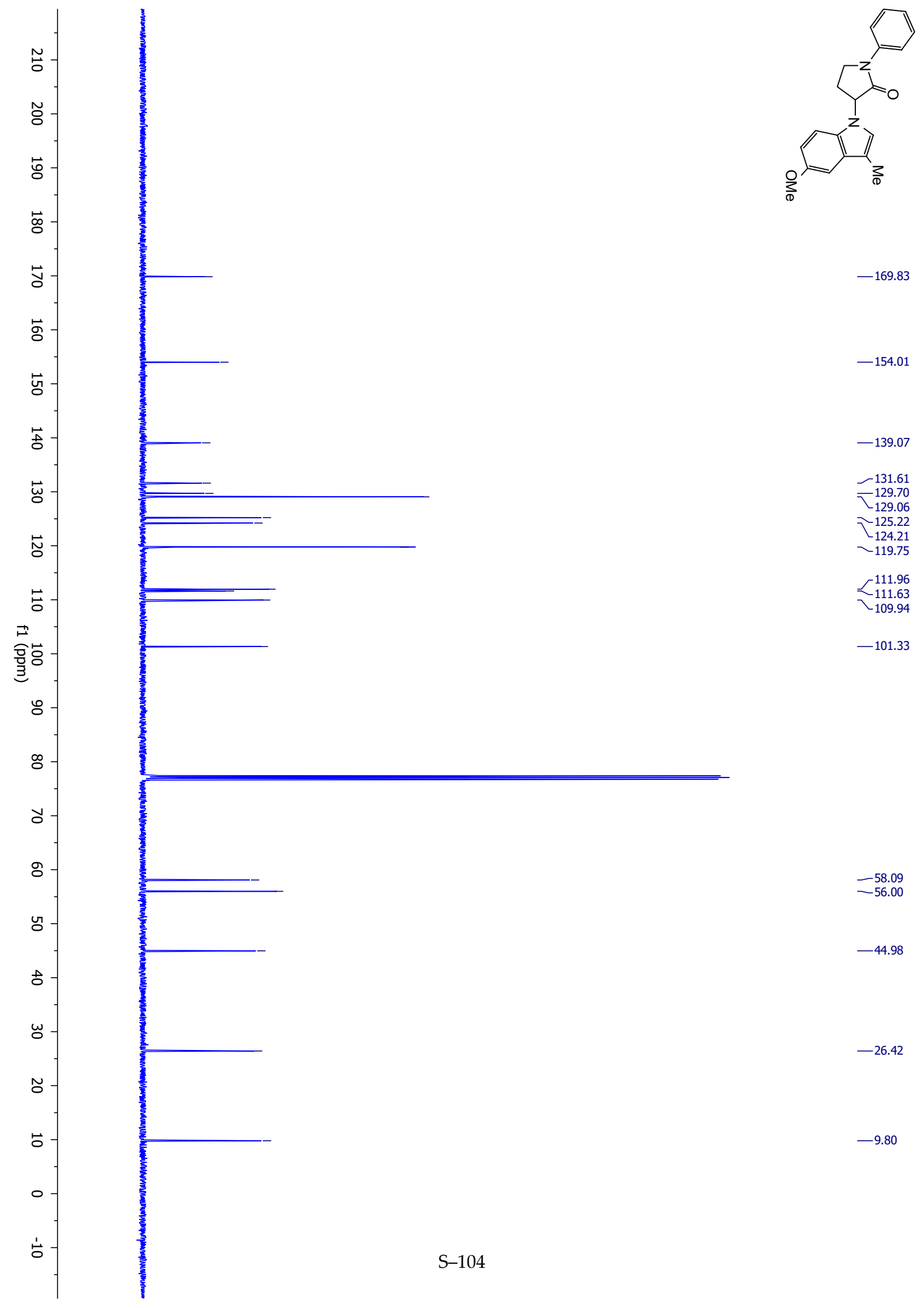

PhN
O
N
NC
1.64
0.64
1.81
5.67
1.00
1.95
1.98
0.89
1.02
f1 (ppm)

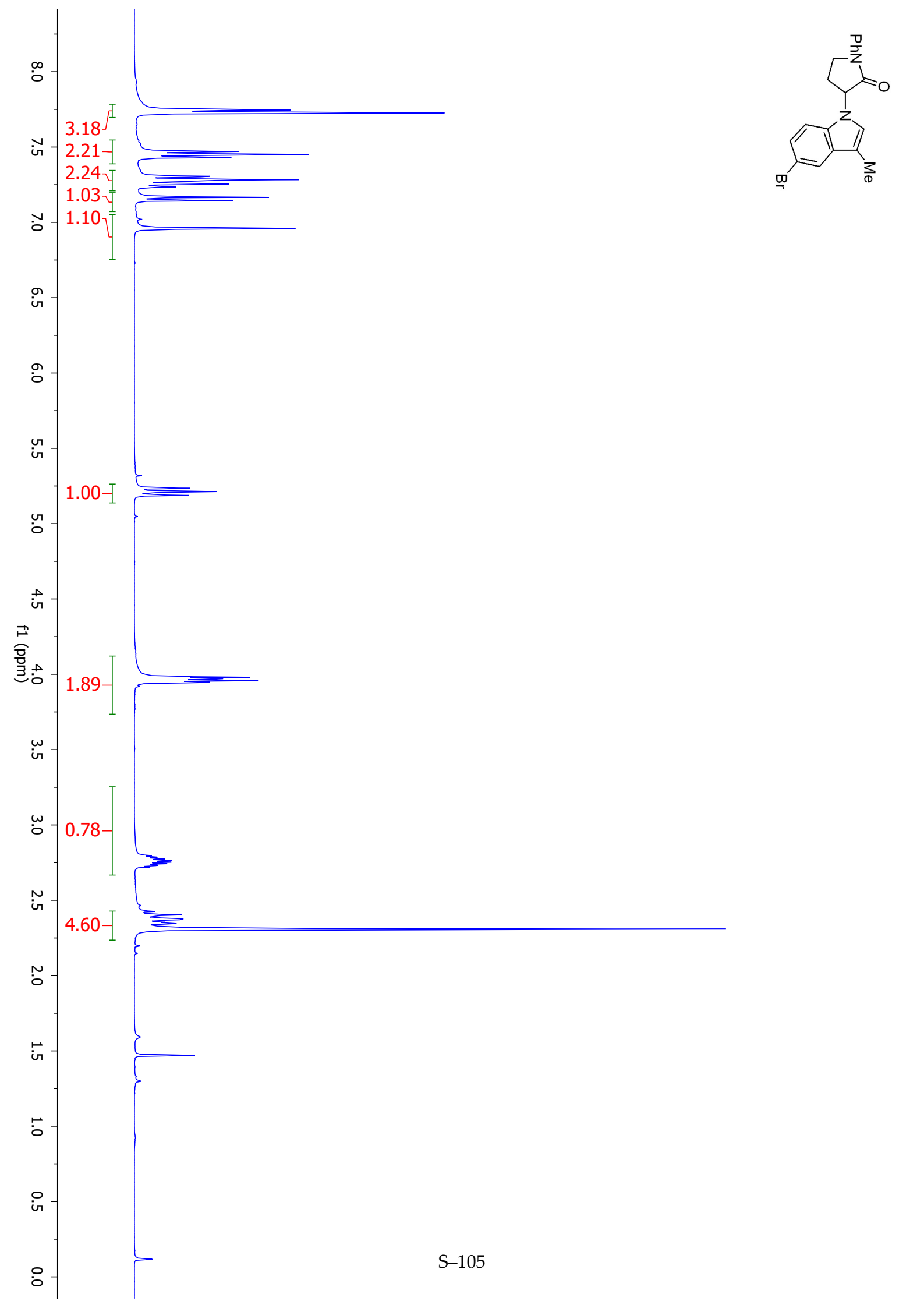


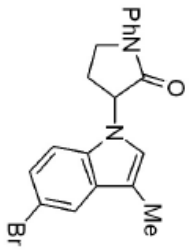
169.13
138.84
136.52
129.12
126.98
125.47
124.61
122.94
120.46
119.85
118.66
118.06
109.81
104.96
58.14
44.95
26.47
14.45

f1 (ppm)

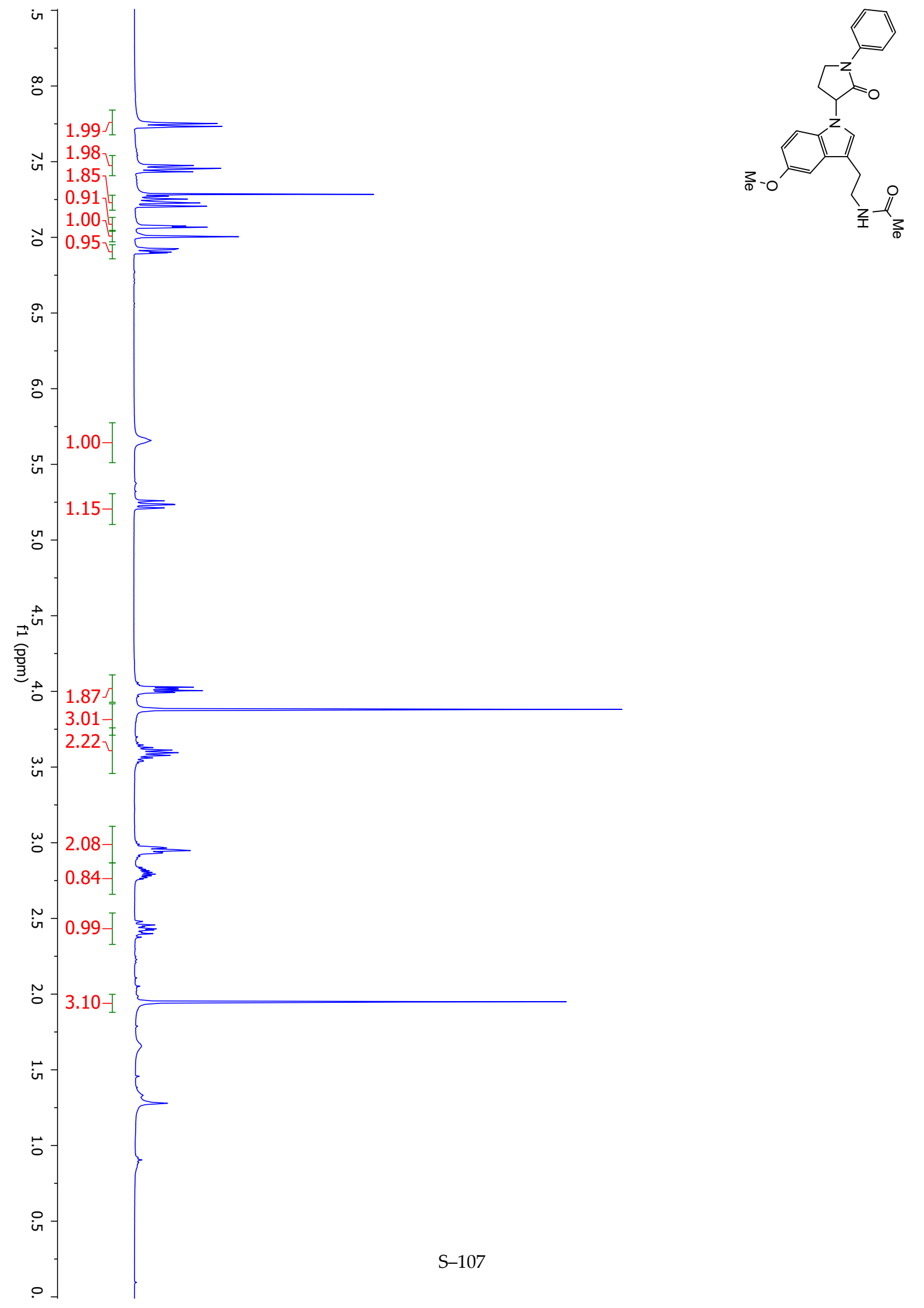

1.94
1.93
0.91
0.91
0.90
1.04
0.95
1.00
1.84
2.90
0.93
0.93
2.88
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
N
O
N
OMe
Me

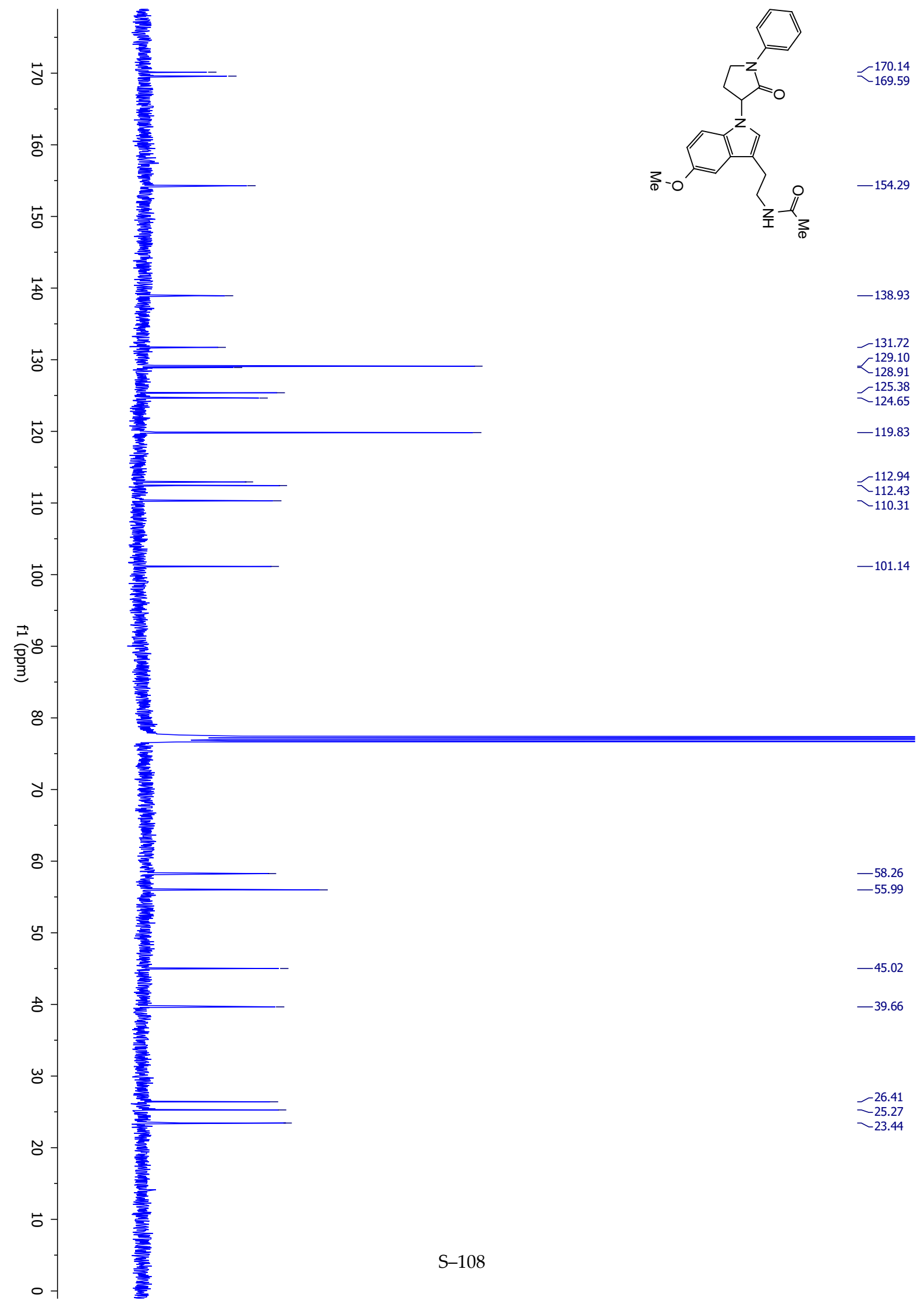

f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
169.83
154.01
139.07
131.61
129.70
129.06
125.22
124.21
119.75
111.96
111.63
109.94
101.33
58.09
56.00
44.98
26.42
9.80
N
O
N
OMe
Me

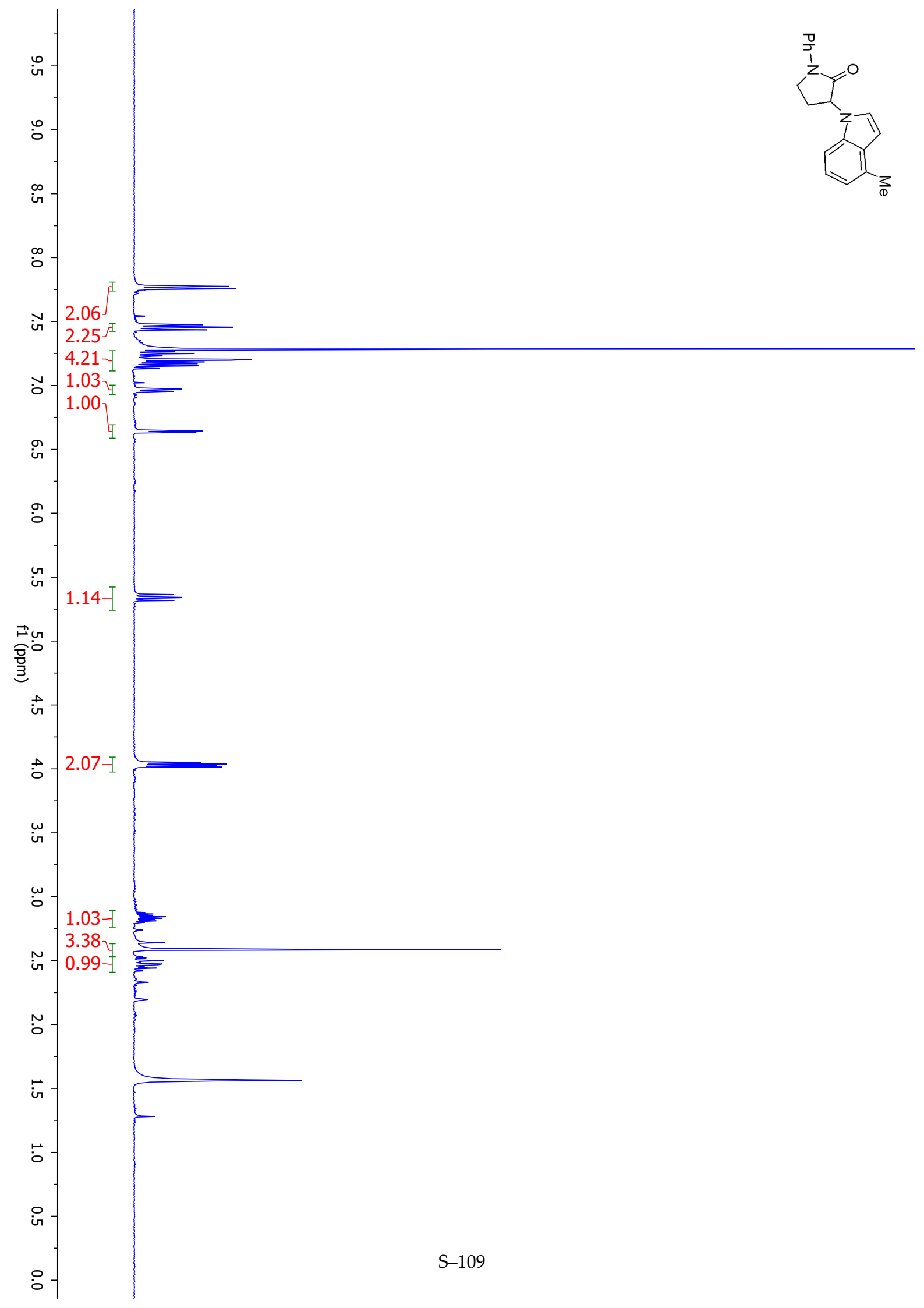

PhN
O
N
Br
Me
3.18
2.21
2.24
1.03
1.10
1.00
1.89
0.78
4.60
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

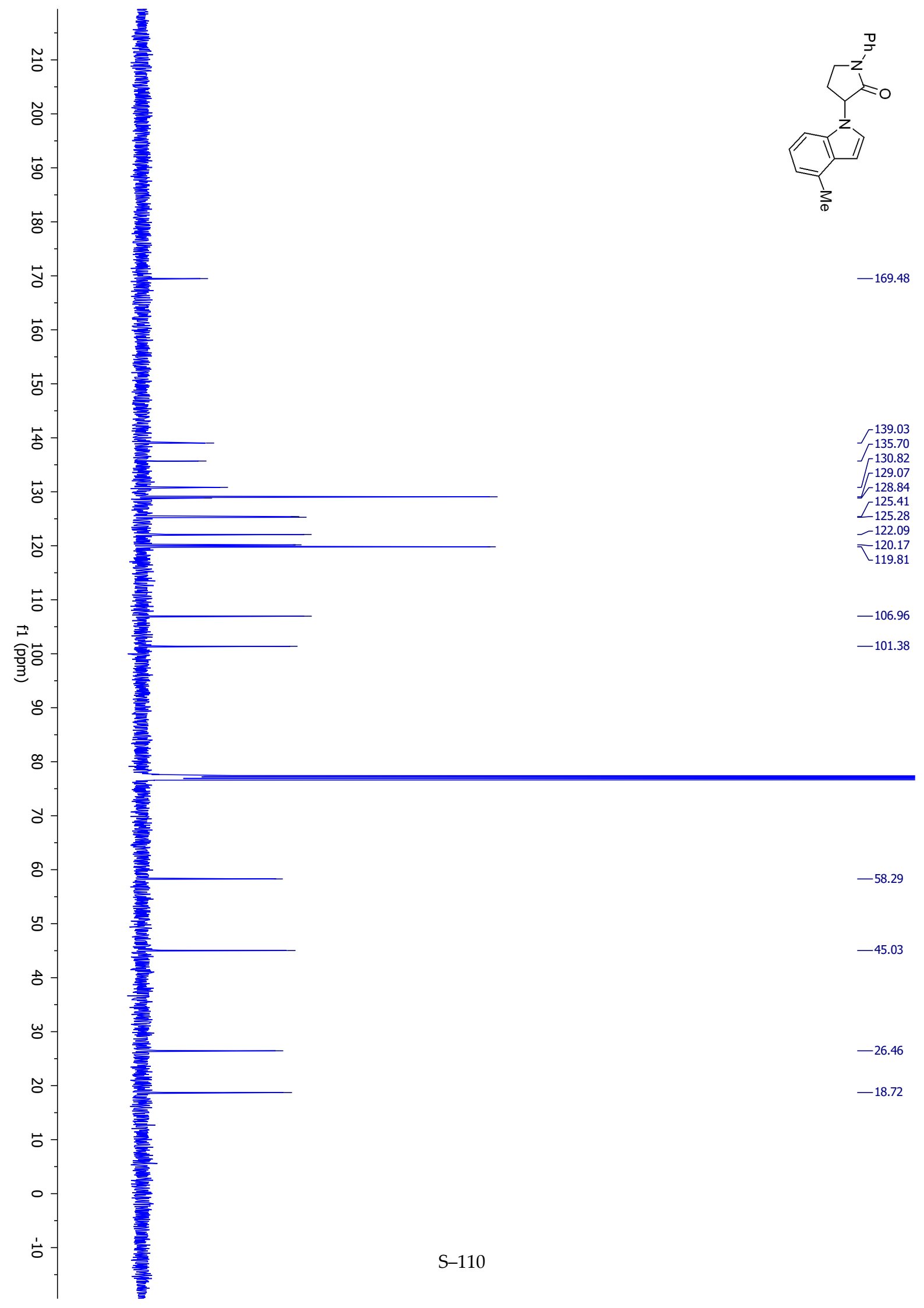

PhN
O
N
Br
Me

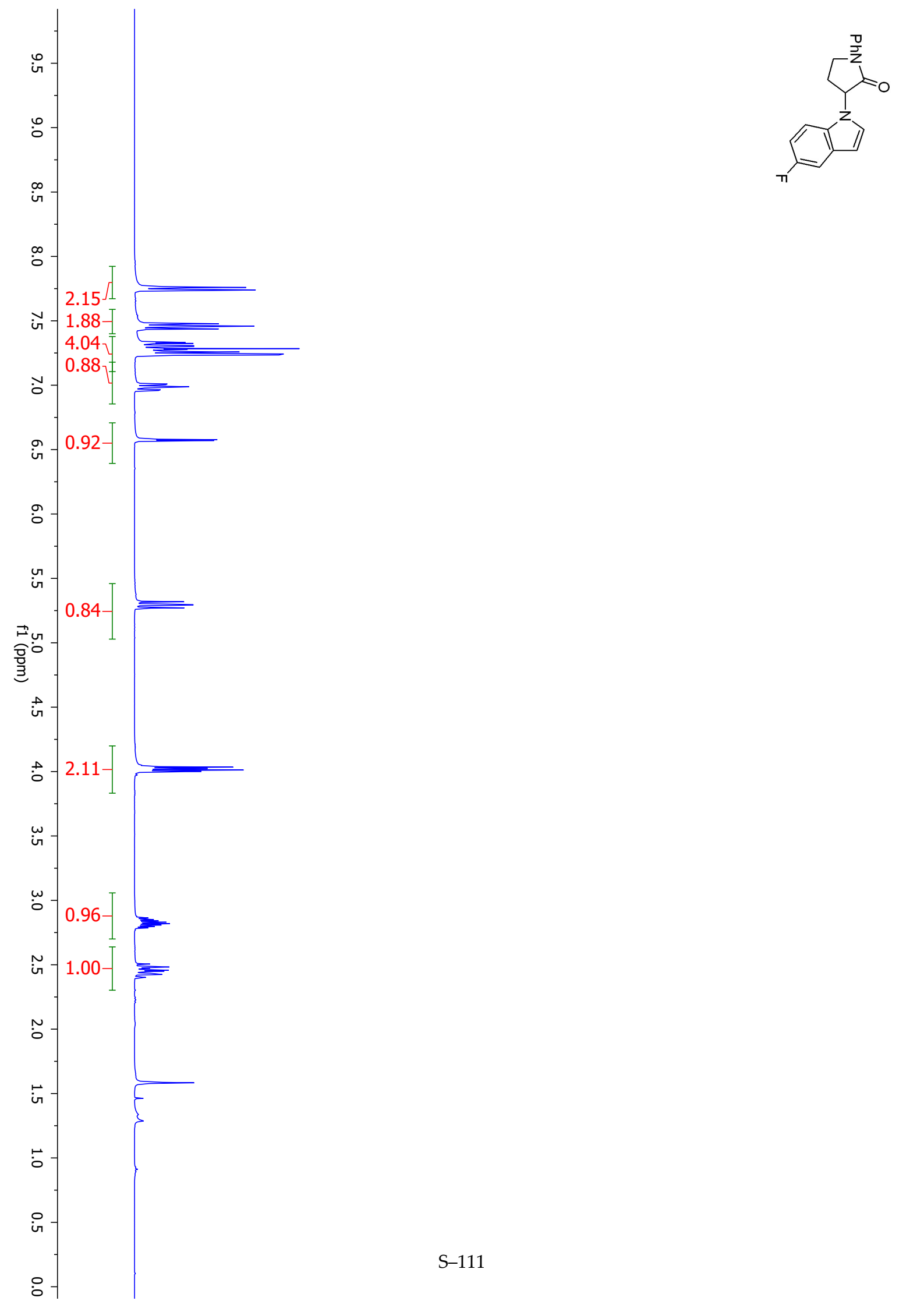
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
169.42
138.93
135.10
131.04
129.09
125.35
124.66
124.64
122.01
119.75
112.59
111.76
110.68
58.01
44.93
30.35
26.34
9.60

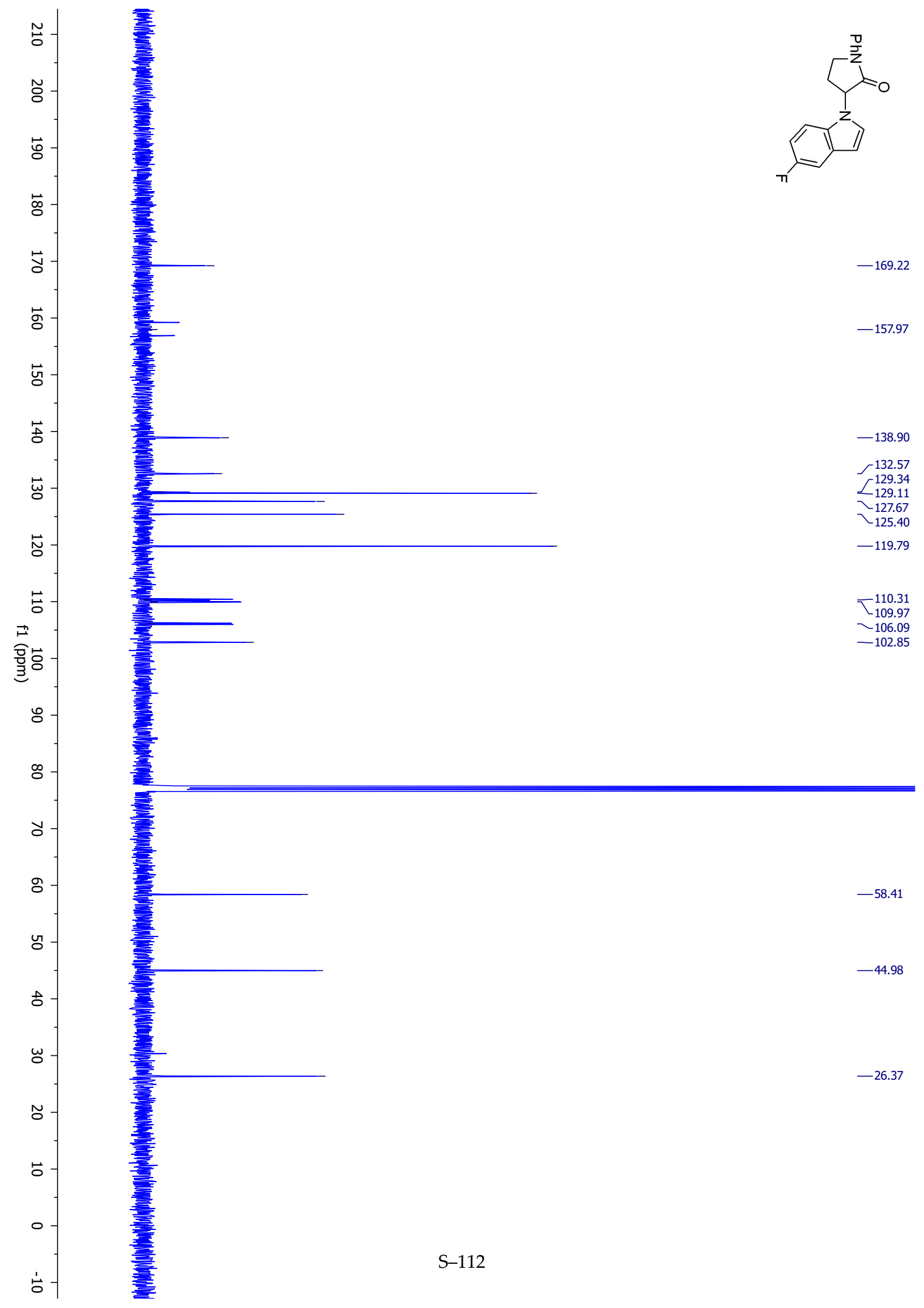

1.99
1.98
1.85
0.91
1.00
0.95
1.00
1.15
1.87
3.01
2.22
2.08
0.84
0.99
3.10
f1 (ppm)
Me
O
N
O
N
NH
O
Me

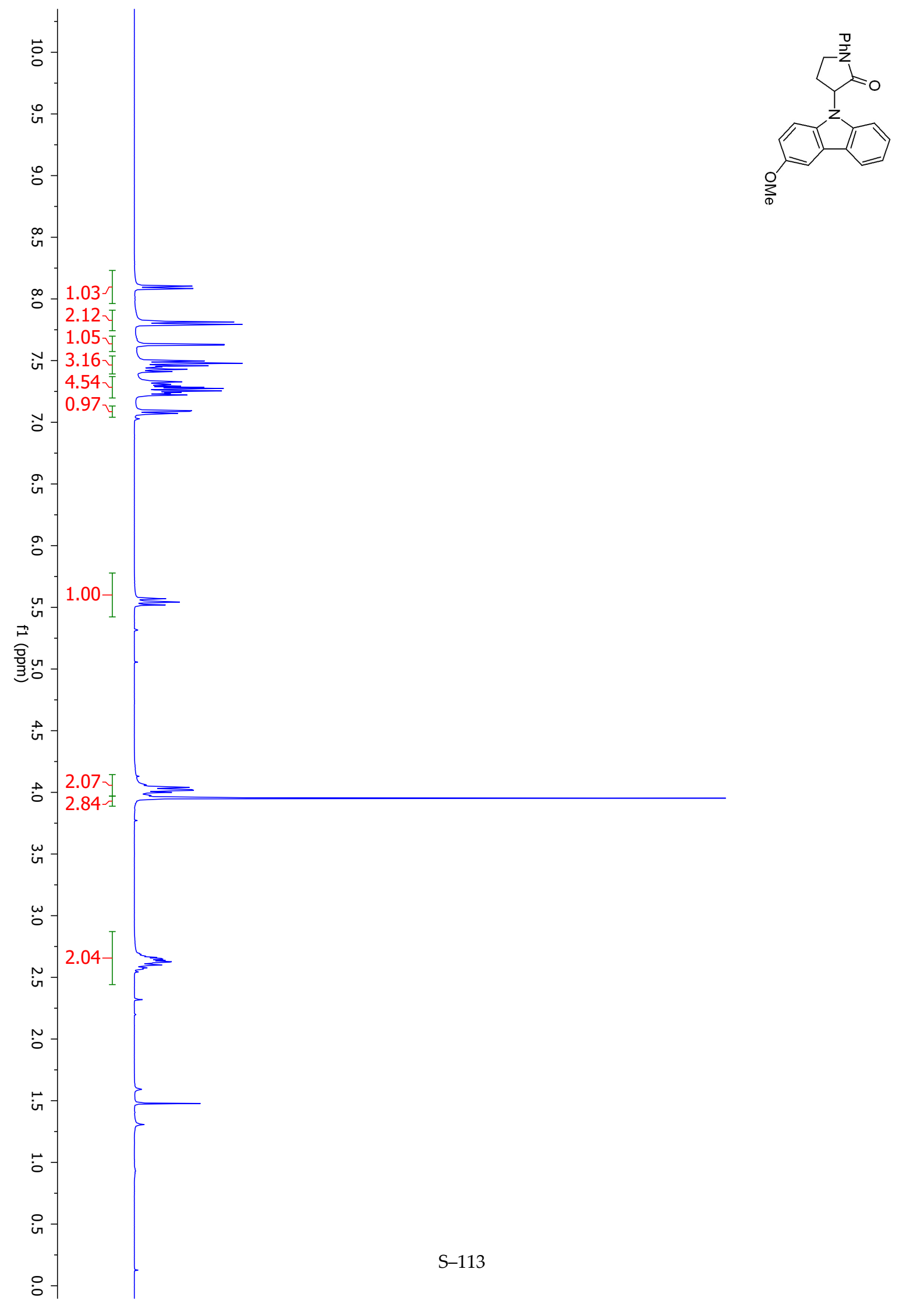

170.14
169.59
154.29
138.93
131.72
129.10
128.91
125.38
124.65
119.83
112.94
112.43
110.31
101.14
58.26
55.99
45.02
39.66
26.41
25.27
23.44
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
N
O
N
O
Me
NH
O
Me

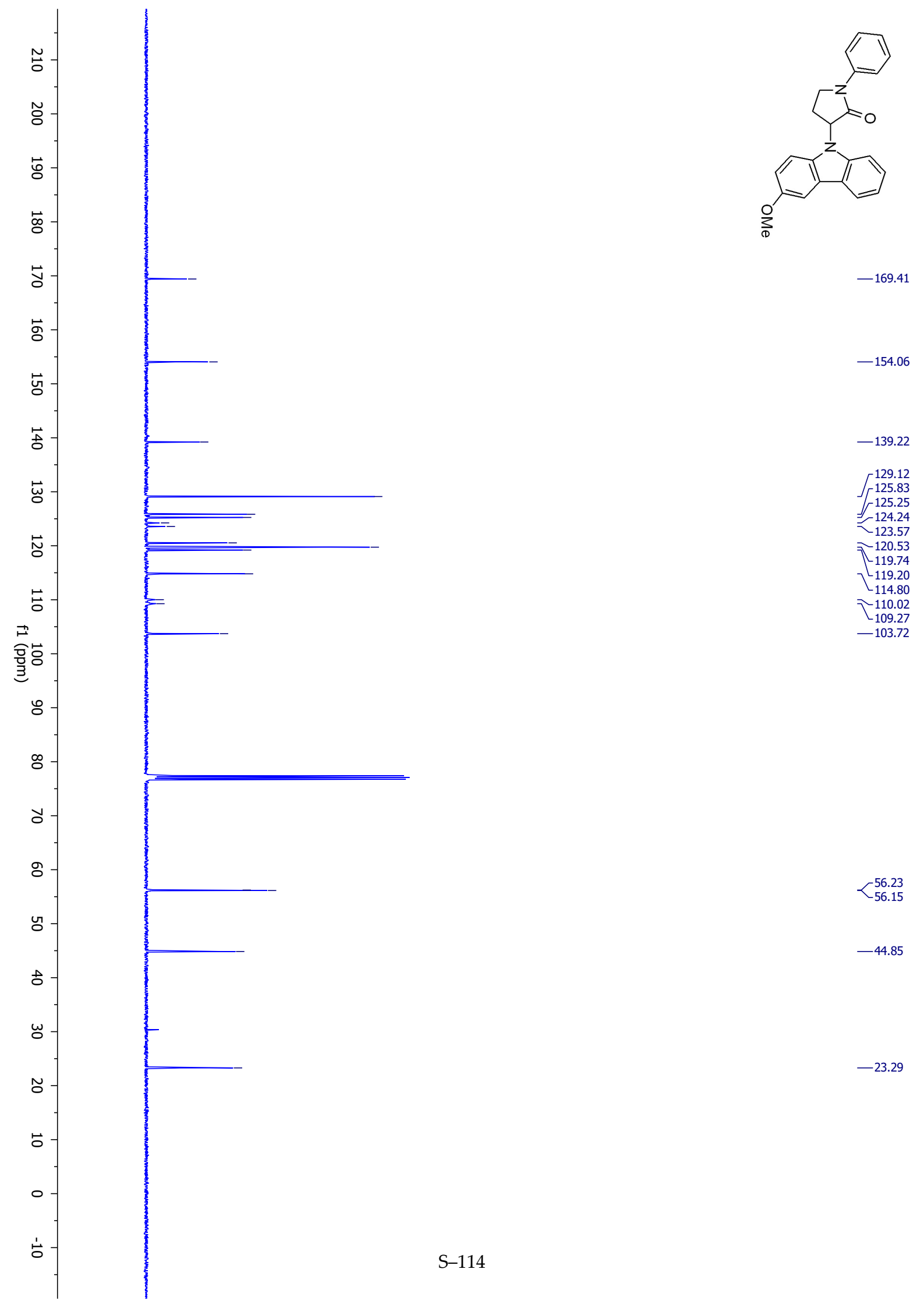

Ph–N
O
N
Me
2.06
2.25
4.21
1.03
1.00
1.14
2.07
1.03
3.38
0.99
f1 (ppm)

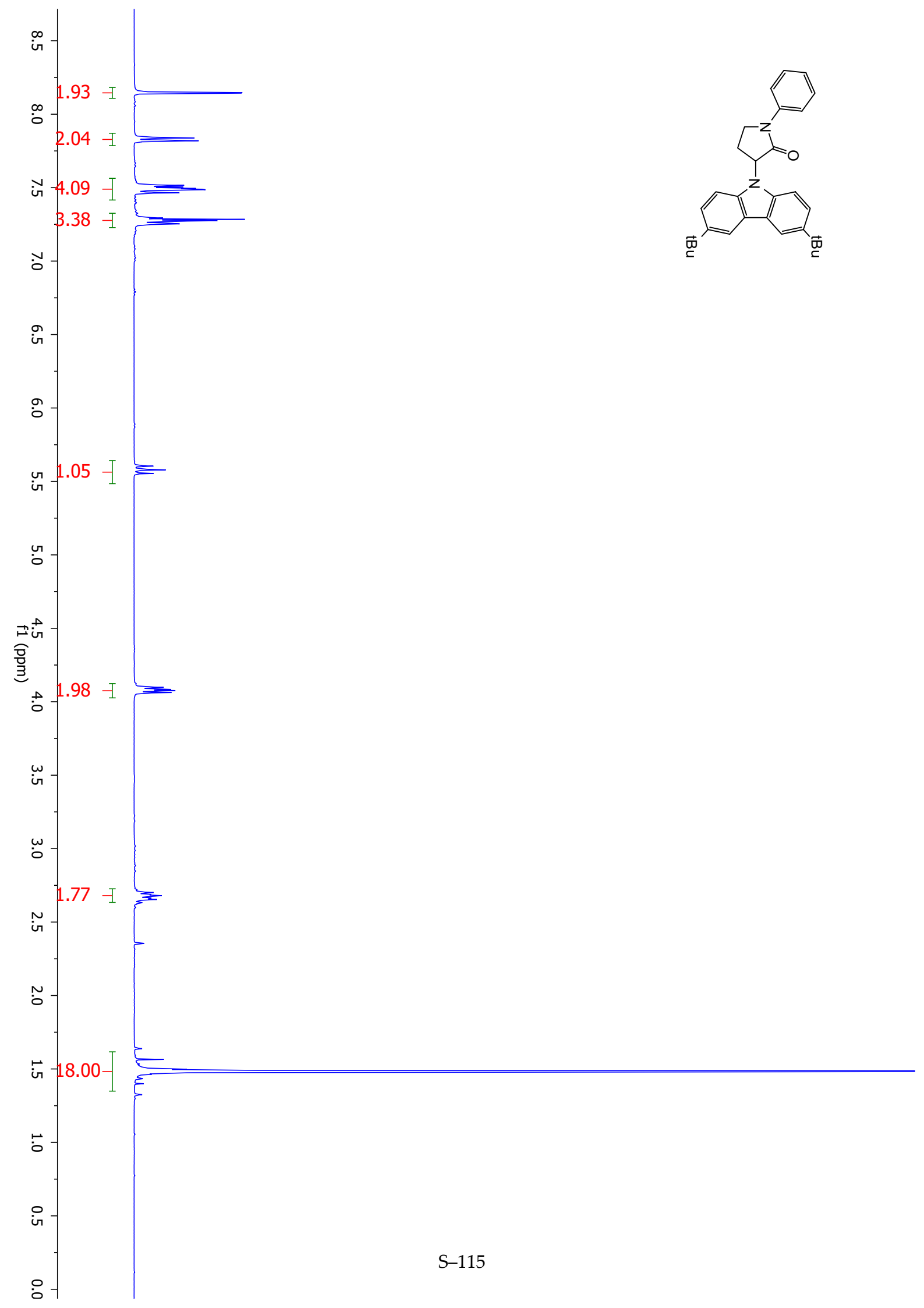

Ph
N
O
N
Me
169.48
139.03
135.70
130.82
129.07
128.84
125.41
125.28
122.09
120.17
119.81
106.96
101.38
58.29
45.03
26.46
18.72
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

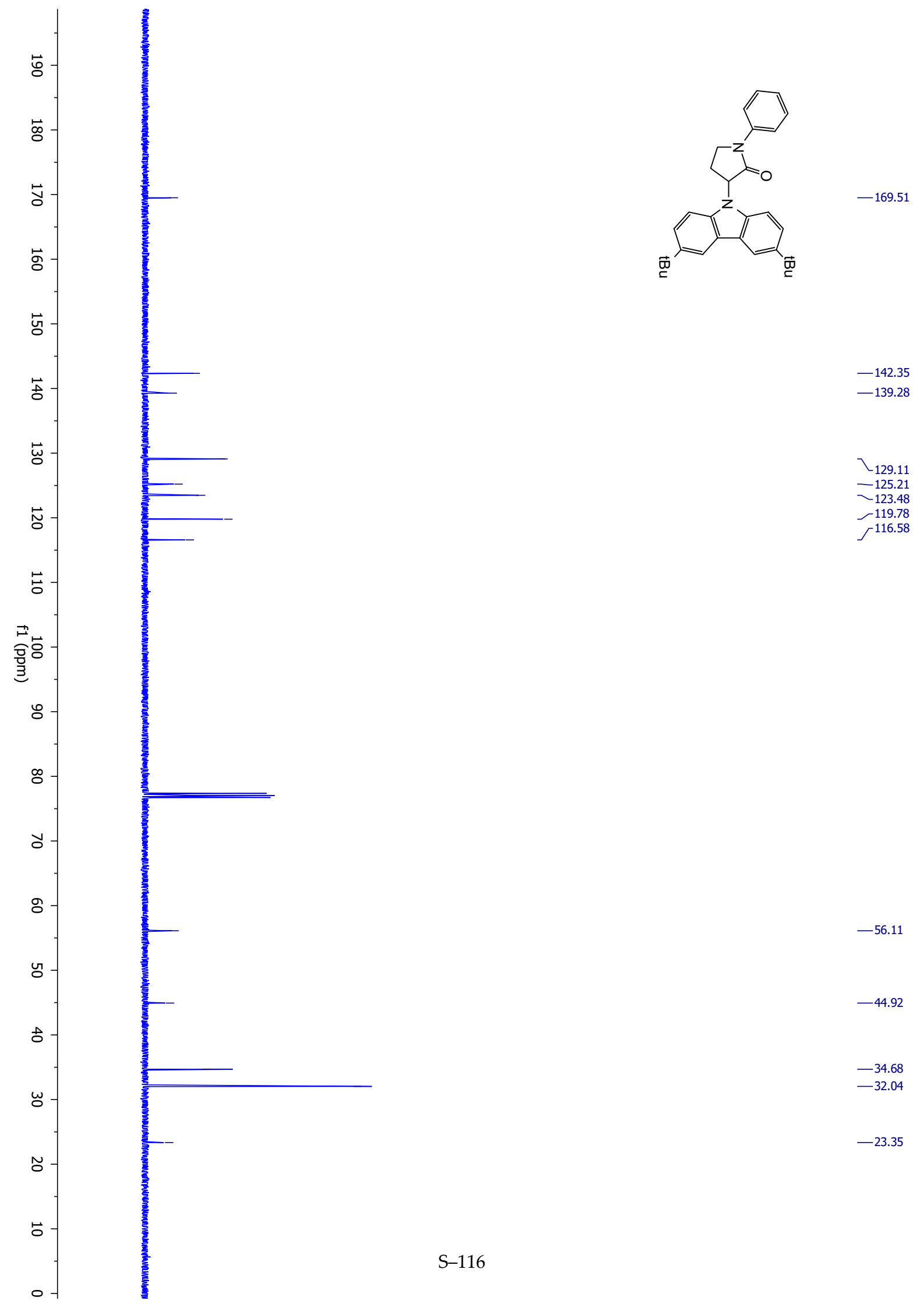

PhN
O
N
F
2.15
1.88
4.04
0.88
0.92
0.84
2.11
0.96
1.00
f1 (ppm)

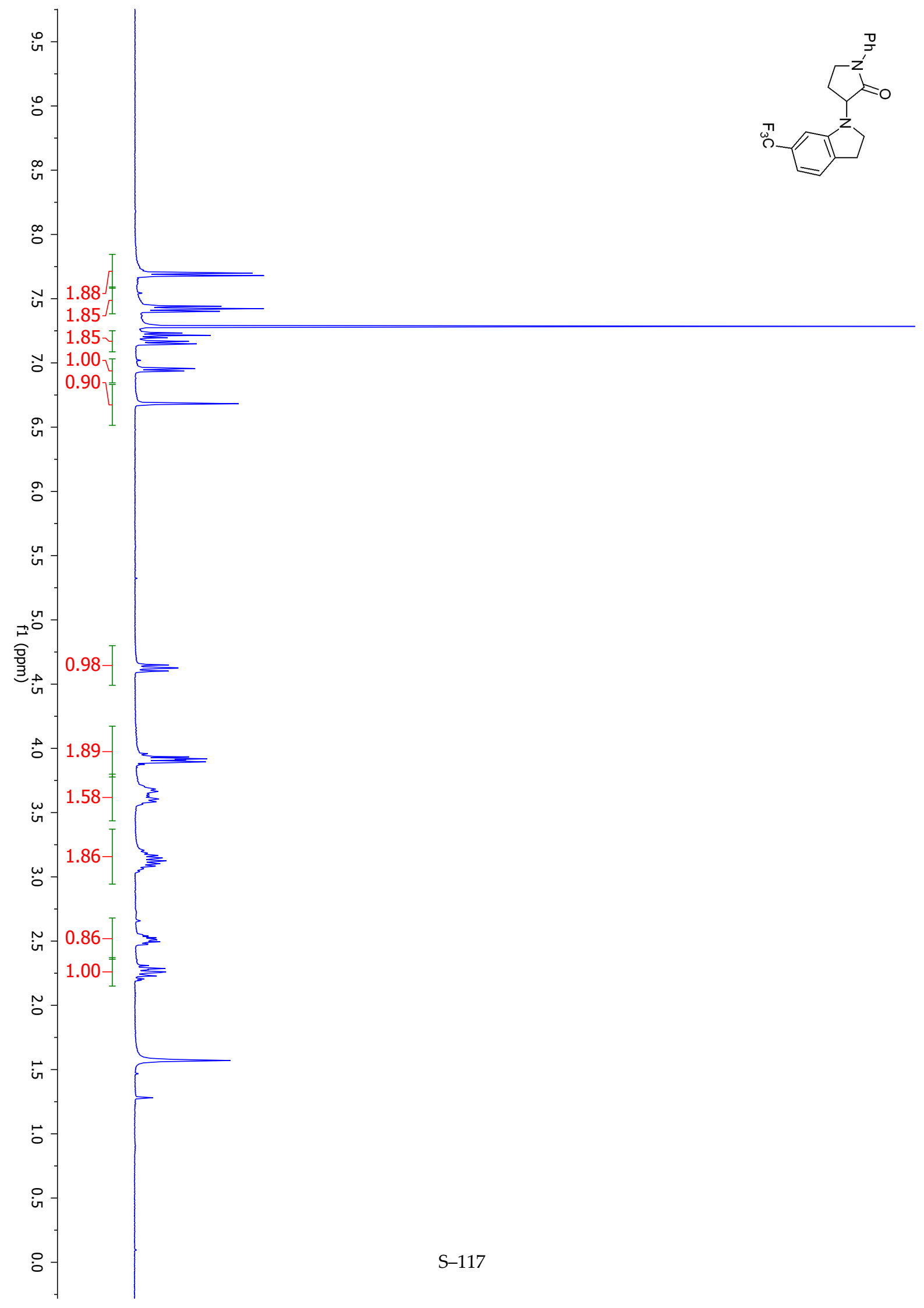

PhN
O
N
F
169.22
157.97
138.90
132.57
129.34
129.11
127.67
125.40
119.79
110.31
109.97
106.09
102.85
58.41
44.98
26.37
f1 (ppm)

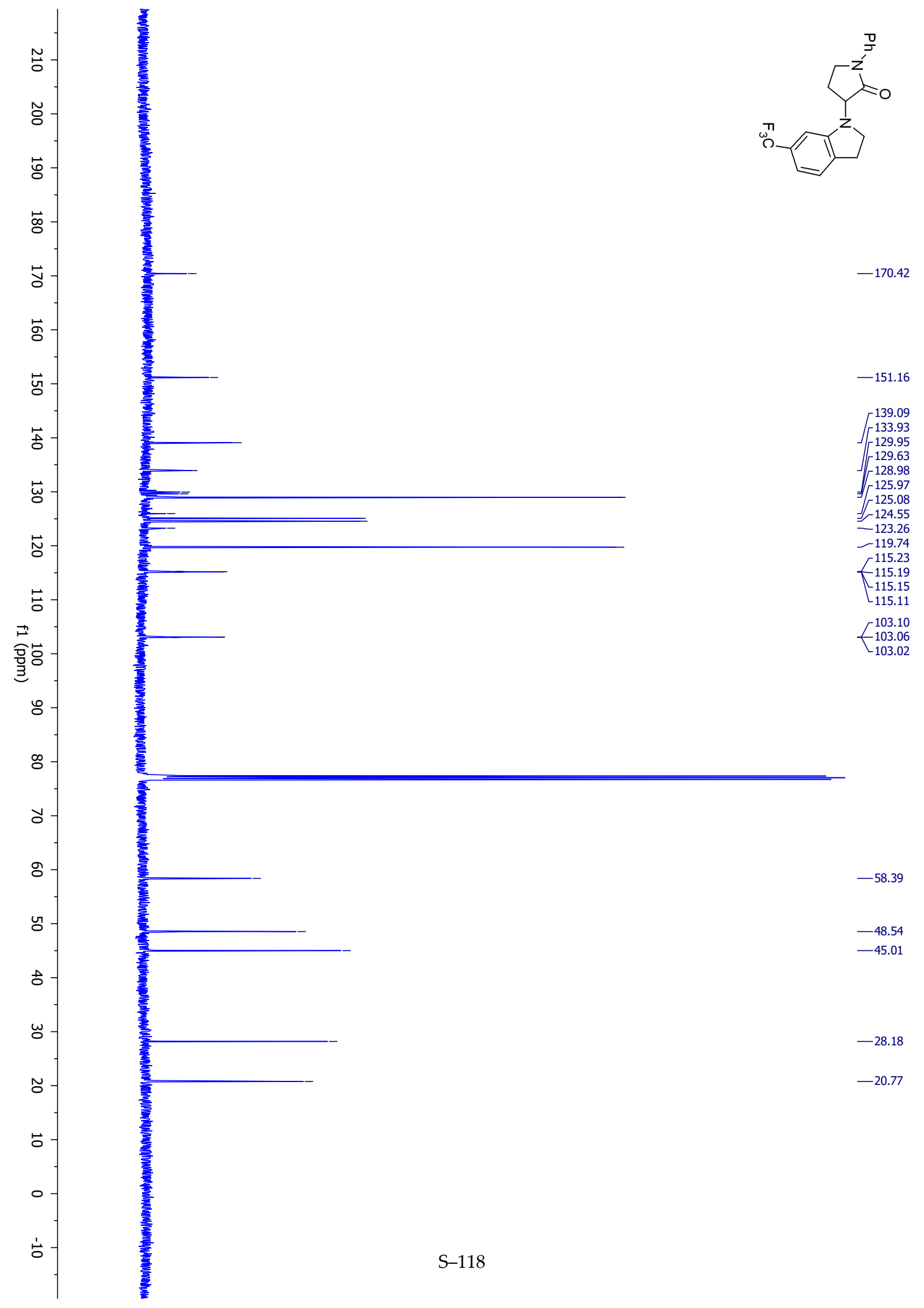

PhN
O
N
OMe
1.03
2.12
1.05
3.16
4.54
0.97
1.00
2.07
2.84
2.04
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

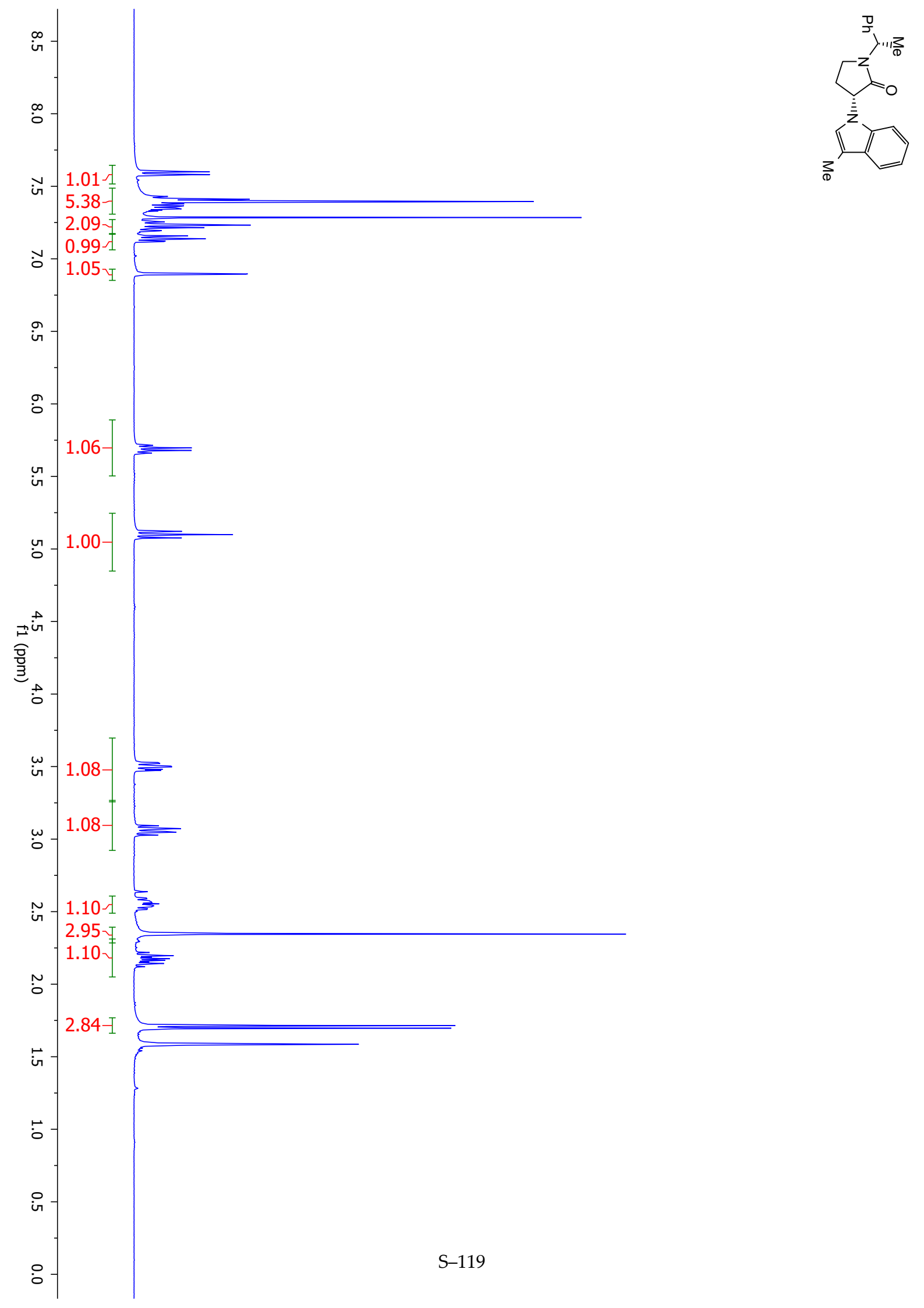

N
O
N
OMe
169.41
154.06
139.22
129.12
125.83
125.25
124.24
123.57
120.53
119.74
119.20
114.80
110.02
109.27
103.72
56.23
56.15
44.85
23.29
f1 (ppm)

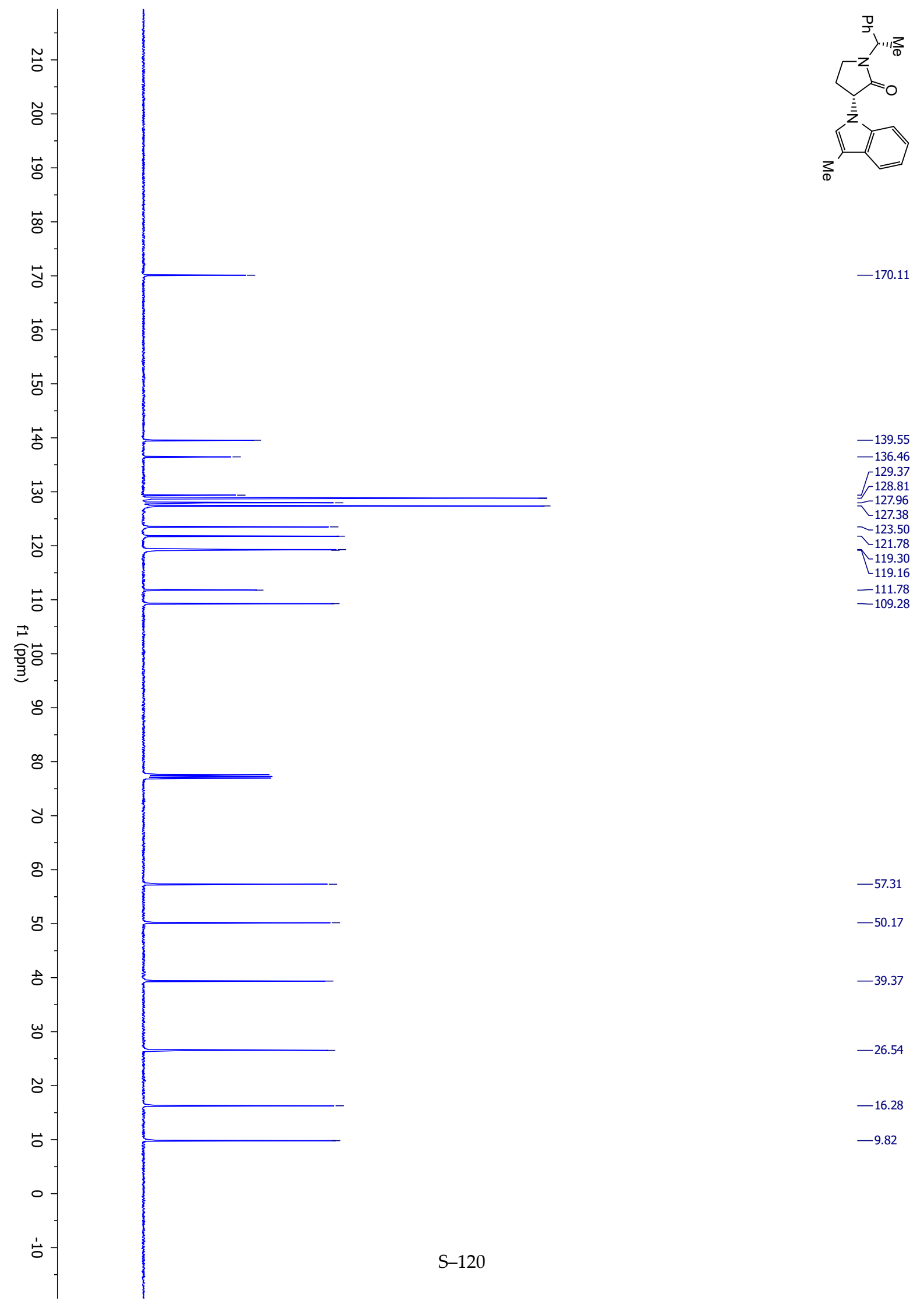

1.93
2.04
4.09
3.38
1.05
1.98
1.77
18.00
f1 (ppm)
tBu
tBu
N
O
N

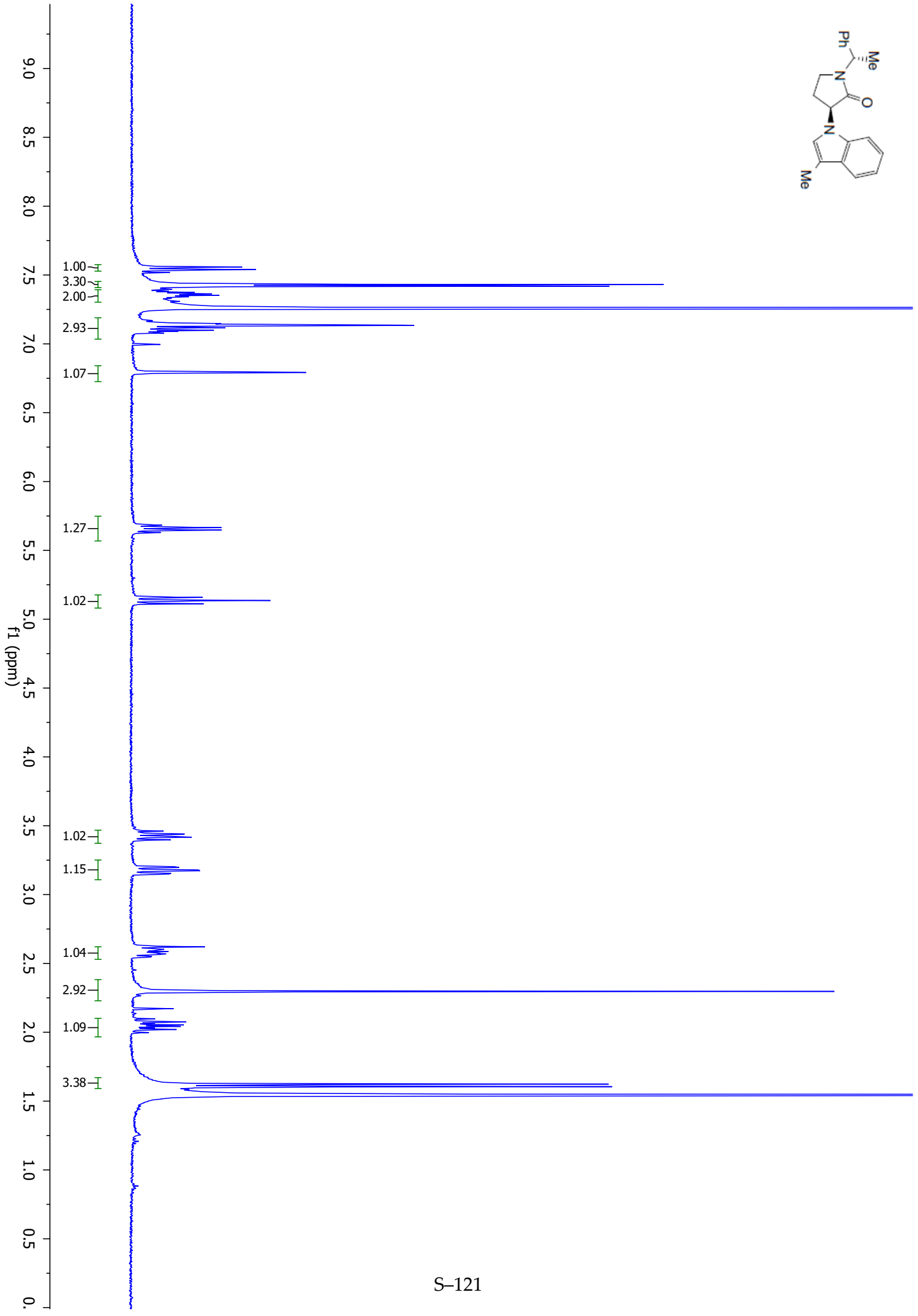

f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
N
O
N
tBu
tBu
169.51
142.35
139.28
129.11
125.21
123.48
119.78
116.58
56.11
44.92
34.68
32.04
23.35

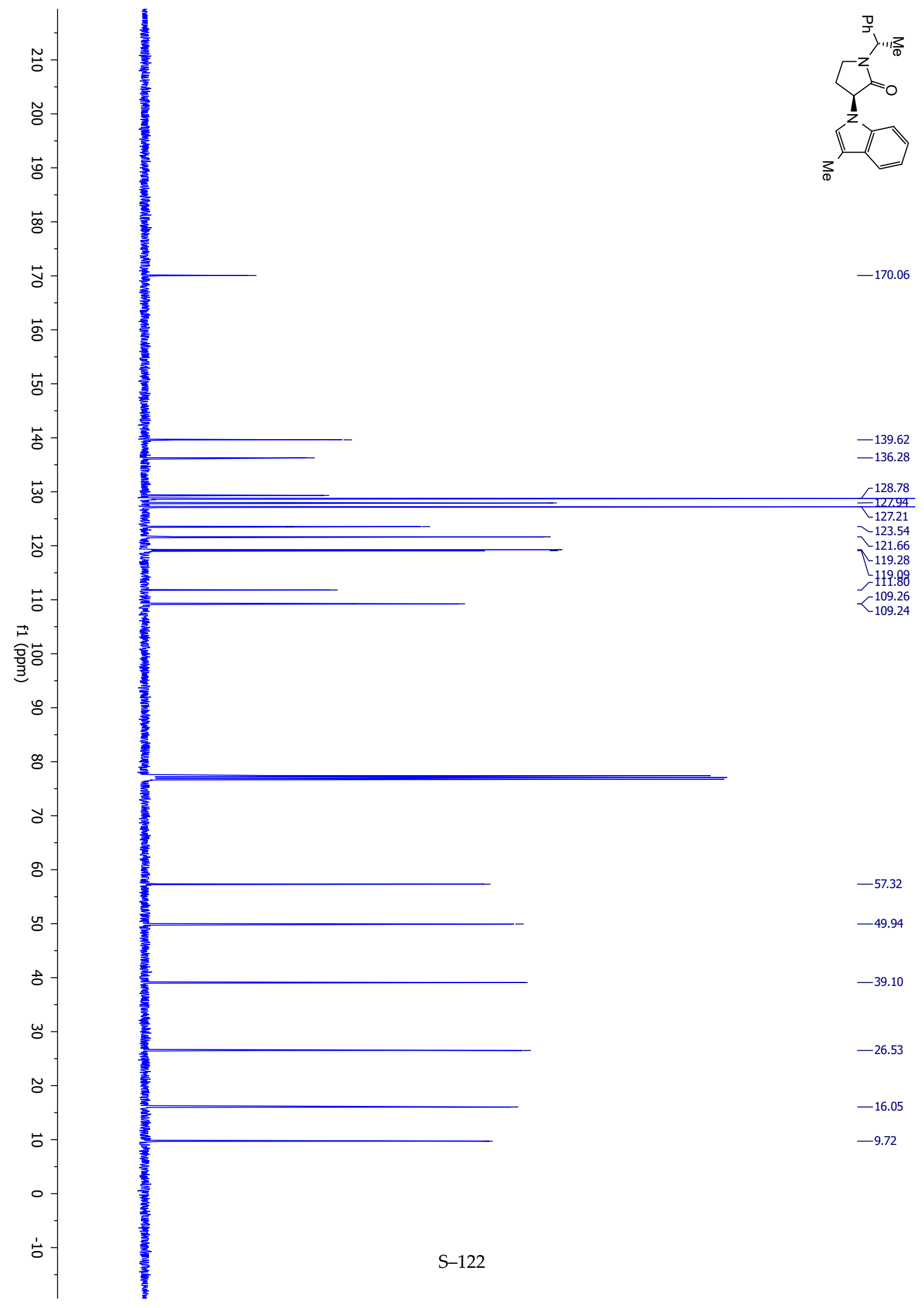

Ph
N
O
N
F3C
1.88
1.85
1.85
1.00
0.90
0.98
1.89
1.58
1.86
0.86
1.00
f1 (ppm)

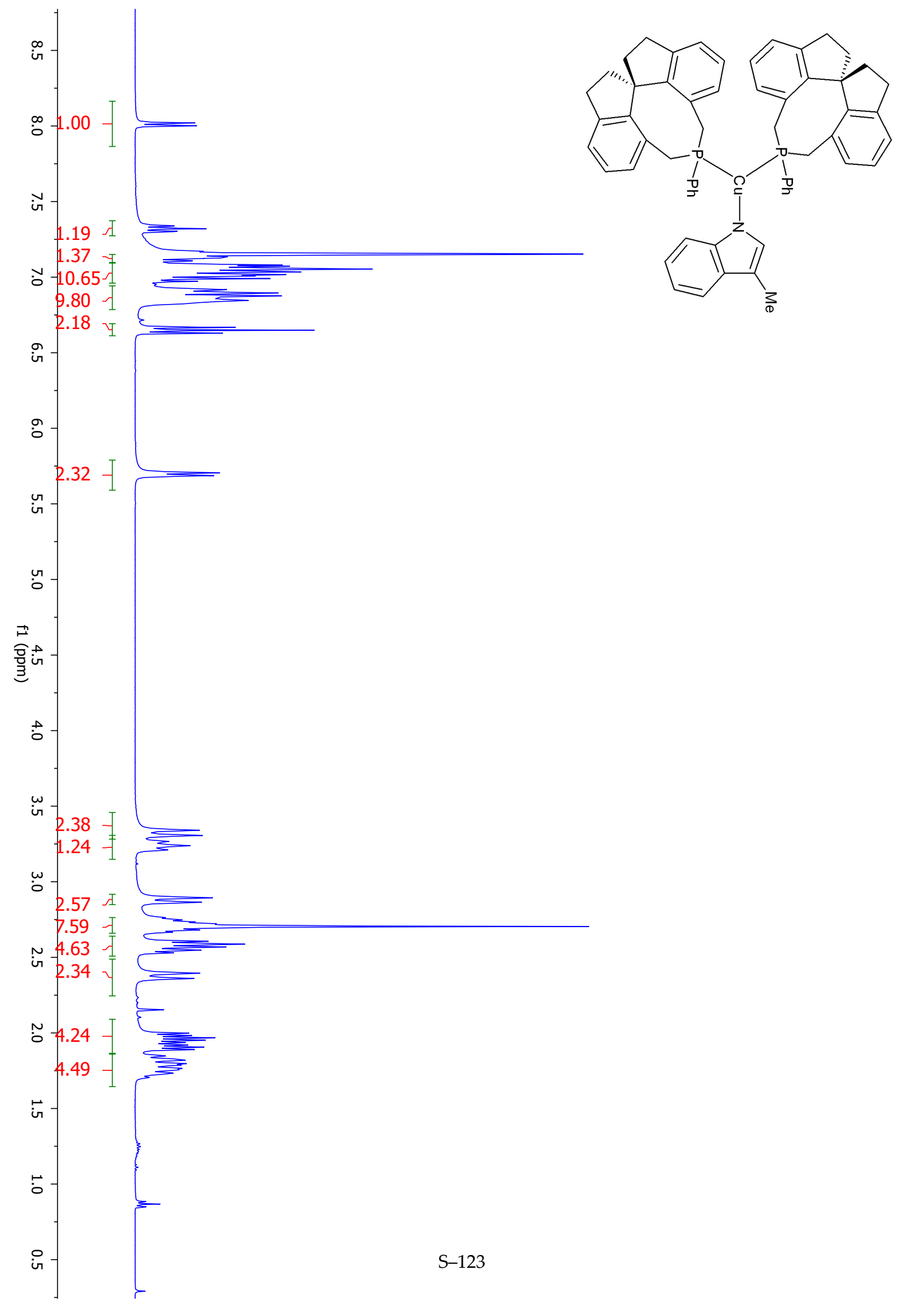

Ph
N
O
N
F3C
170.42
151.16
139.09
133.93
129.95
129.63
128.98
125.97
125.08
124.55
123.26
119.74
115.23
115.19
115.15
115.11
103.10
103.06
103.02
58.39
48.54
45.01
28.18
20.77
f1 (ppm)

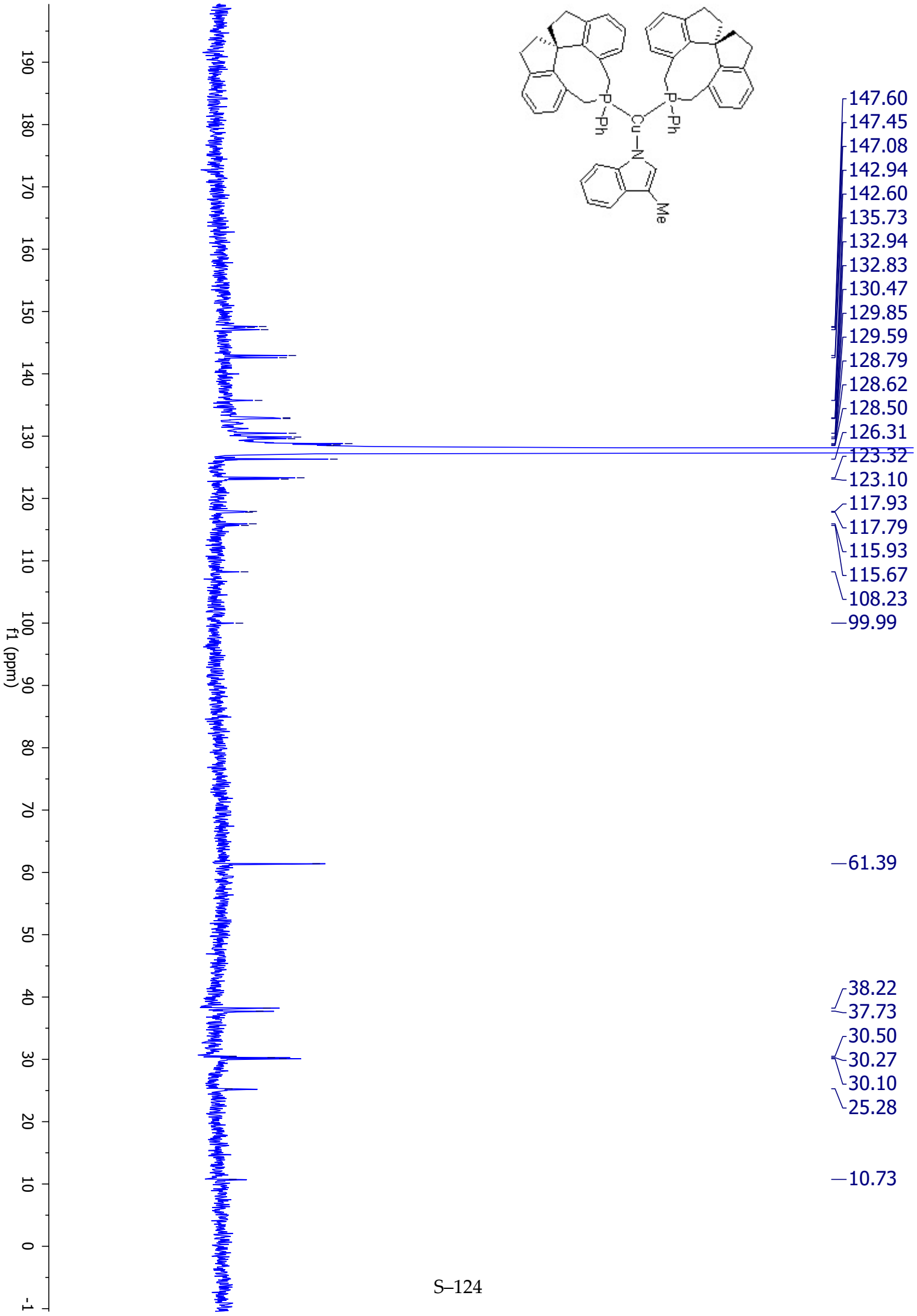

1.01
5.38
2.09
0.99
1.05
1.06
1.00
1.08
1.08
1.10
2.95
1.10
2.84
f1 (ppm)
Ph
Me
N
O
N
Me

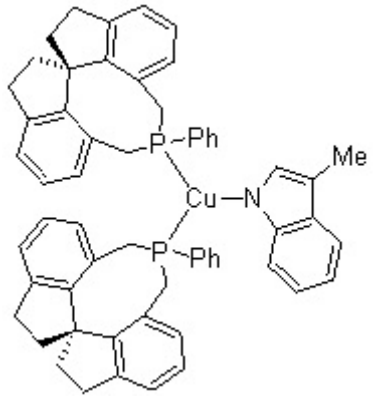

Ph
Me
N
O
N
Me
170.11
139.55
136.46
129.37
128.81
127.96
127.38
123.50
121.78
119.30
119.16
111.78
109.28
57.31
50.17
39.37
26.54
16.28
9.82
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


Ph
Me
N
O
N
Me
1.00
3.30
2.00
2.93
1.07
1.27
1.02
1.02
1.15
1.04
2.92
1.09
3.38
f1 (ppm)
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.


Ph
Me
N
O
N
Me
170.06
139.62
136.28
128.78
127.94
127.21
123.54
121.66
119.28
119.09
111.80
109.26
109.24
57.32
49.94
39.10
26.53
16.05
9.72
f1 (ppm)


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)
1.00
1.19
1.37
10.65
9.80
2.18
2.32
2.38
1.24
2.57
7.59
4.63
2.34
4.24
4.49
P
Ph
Cu
N
Me


147.60
147.45
147.08
142.94
142.60
135.73
132.94
132.83
130.47
129.85
129.59
128.79
128.62
128.50
126.31
123.32
123.10
117.93
117.79
115.93
115.67
108.23
99.99
61.39
38.22
37.73
30.50
30.27
30.10
25.28
10.73
f1 (ppm)
P
Ph
Cu
N
Me


P
Ph
Cu
N
Me
P
Ph

-13.81
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)