Supporting Information

Total Syntheses of Tardioxopiperazine A, Isoechinulin A and Variecolorin C

Qipu Dai[†], Xingang Xie[†], Shiyan Xu[†], Donghui Ma[†], Shibing Tang[†], Xuegong She*[,†,‡]

[†]State Key Laboratory of Applied Organic Chemistry, Department of Chemistry, Lanzhou University, Lanzhou 730000, P. R. China and [‡]State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China

shexg@lzu.edu.cn

Table of Contents

1. Experimental procedures and data for the compounds

2. Tables for spectroscopic comparisons

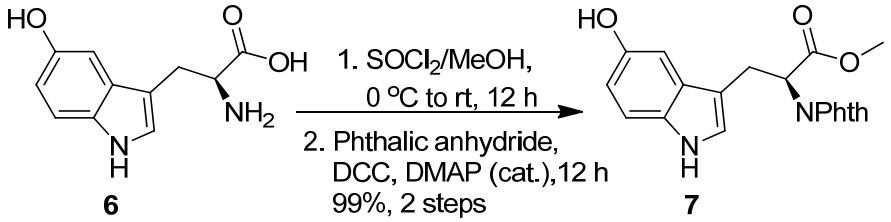
3. Spectra (^{1}H and ^{13}C NMR) of compounds

1. Experimental procedures and data for the compounds

General Experimental Details. Oxygen- and moisture-sensitive reactions were carried out under argon atmosphere. Solvents were purified and dried by standard methods prior to use. All commercially available reagents were used without further purification unless otherwise noted. Column chromatography was performed on silica gel (200-300 mesh). Optical rotations were measured on a precision automated polarimeter. Infrared spectra were recorded on a FT-IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometers. Chemical shifts are reported as δ values relative to internal chloroform (δ 7.27 ppm for ^{1}H NMR and 77.0 for ^{13}C NMR), internal DMSO-d_6 (δ 2.50 ppm for ^{1}H NMR and 39.95 for ^{13}C NMR), and internal CD_3COCD_3 (δ 2.05 ppm for ^{1}H NMR and 29.2 for ^{13}C NMR).

Experimental Section

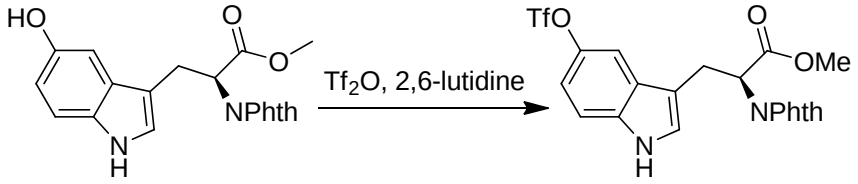
Synthesis of 7



To a stirred suspension of L-5-hydroxytryptophan **6** (440 mg, 2 mmol) in methanol (20 mL), was added thionyl dichloride (0.292 mL, 4 mmol) dropwise at 0°C. The mixture was stirred at rt for 12 h. The resulting solution was concentrated under reduced pressure to do the next step.

To a solution of the above-mentioned product in anhydrous 1,4-dioxane (20 mL) were added phthalic anhydride (592 mg, 4 mmol), DCC (824 mg, 2 mmol) and DMAP (20 mg). The mixture was stirred under reflux for 12 h. The resulting solution was concentrated under reduced pressure and diluted with ethyl acetate (10 mL), washed with saturated aqueous NH_4Cl, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 2:1) afforded **7** (721 mg, 99% yield) as a yellow cubes; m.p. = 184 – 185 °C; Rf = 0.30 (silica gel, 2:1 hexane:ethyl acetate); $[\alpha]^{20}_{D}$ = +63 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3399, 2927, 2853, 1740, 1710, 1391, 1207, 721 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.44 (s, 1 H), 8.57 (s, 1 H), 7.82 (s, 4 H), 7.04 (d, J = 8.8 Hz, 1 H), 6.91 (s, 1 H), 6.79 (s, 1 H), 6.54 (d, J = 8.8 Hz, 1 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 169.8, 167.5, 150.8, 135.4, 131.2, 131.0, 128.1, 124.3, 123.9, 112.2, 111.9, 108.7, 102.3, 53.1, 52.7, 24.6; HRMS (ESI-TOF) calcd for $C_{20}H_{20}N_3O_5^+$ $[M + NH_4]^+$ 382.1397, found 382.1386.

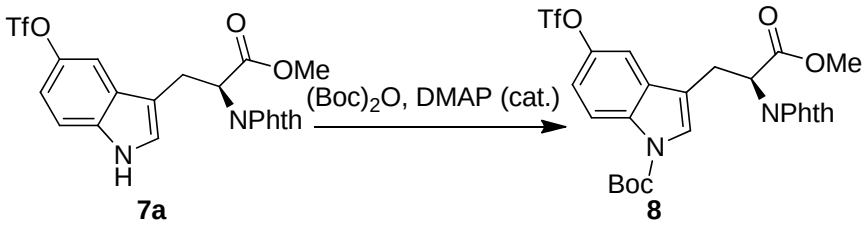
Synthesis of 7a



7 **7a**

To a solution of **7** (182 mg, 0.5 mmol) in DCM (5 mL), was added 2,6-lutidine (58.9 mg, 0.55 mmol) at 0°C within 5 min, then was added Tf_2O (105 mg, 0.5 mmol) at 0 °C. The mixture was stirred at rt for 12 h, was quenched by saturated aqueous NH_4Cl, extracted by DCM, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 3:1) afforded **7a** (236 mg, 95% yield) as a yellow cubes; m.p. = 119 – 120 °C; Rf = 0.45 (silica gel, 2:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = -97 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3390, 2985, 2956, 1775, 1743, 1713, 1417, 1390, 1243, 1210, 930, 721, 608 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.24 (s, 1 H), 7.75 (m, 2 H), 7.66 (m, 2 H),7.45 (d, J = 2.4 Hz, 1 H), 7.26 (d, J = 8.8 Hz, 1 H), 7.13 (s, 1 H), 7.00 (dd, J = 8.8, 2.4 Hz , 1 H), 5.18 (dd, J = 9.2, 6.4 Hz, 1 H), 3.80 (d, s, 1 H), 3.71 (d, J =4.4 Hz, 1 H), 3.70 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.7, 167.5, 136.0, 133.9, 131.6, 127.1, 123.3, 122.6, 122.0, 119.4, 118.4, 111.1, 111.0, 52.8, 52.6, 24.8.; HRMS (ESI-TOF) calcd for $C_{21}H_{19}F_3N_3O_7S^+$ $[M + NH_4]^+$ 514.0890, found 514.0897.

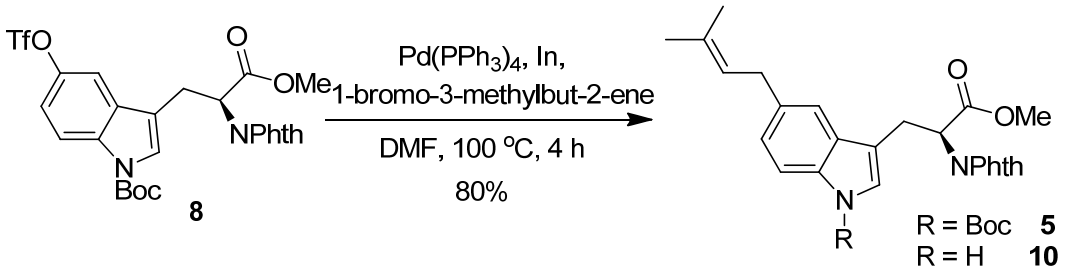
Synthesis of 8



7a **8**

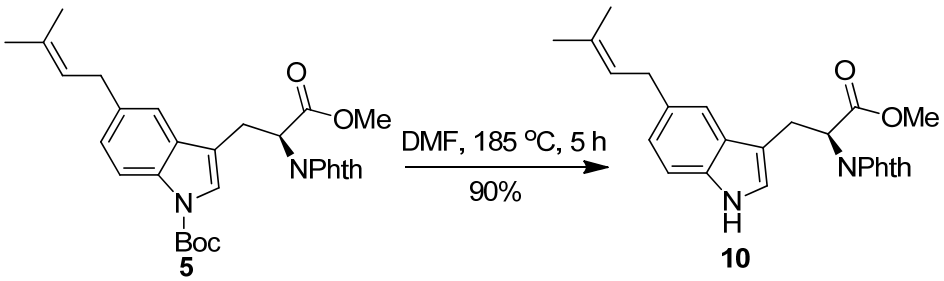
To a solution of **7a** (200 mg, 0.40 mmol) in DCM (5 mL), was added $(Boc)_2O$ (175 mg, 0.80 mmol) at 0 °C, then was added DMAP (20 mg) at 0 °C. The mixture was stirred at rt overnight, was quenched by saturated aqueous NH_4Cl and extracted by DCM, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 5:1) afforded **8** (238 mg, 99% yield) as colorless oil; Rf = 0.45 (silica gel, 5:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = -54 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 2982, 2934, 2857, 1805, 1746, 1720, 1656, 1451, 1421, 1389, 1212, 1119, 1072, 928, 721 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.13 (d, J = 8.8 Hz, 1 H), 7.81 (m, 2 H), 7.71 (m, 2 H), 7.51 (s, 1 H), 7.43 (d, J = 2.4 Hz, 1 H), 7.15 (dd, J = 8.8, 2.4 Hz , 1 H), 5.19 (m, 1 H), 3.80 (s, 3 H), 3.66 (d, J = 8 Hz, 2 H), 1.60 (s, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.0, 167.5, 148.9, 145.2, 134.2, 131.6, 131.0, 126.2, 123.6, 117.4,116.5, 115.8, 111.4, 84.4, 53.0, 51.8, 28.0, 24.5.; HRMS (ESI-TOF) calcd for $C_{26}H_{27}F_3N_3O_9S^+$ $[M + NH_4]^+$ 614.1415, found 614.1427.

Synthesis of 5



To a suspension of $Pd(PPh_3)_4$ (57.0 mg, 5 mol %) and lithium chloride (64 mg, 1.5 mmol) in DMF (1 mL) was added **8** (298 mg, 0.5 mmol) at room temperature under a nitrogen atmosphere. After 15 min, allyl indium, which is generated from 3,3-Dimethylallyl bromide (112 mg, 0.75 mmol) and indium (57.0 mg, 0.5 mmol) in DMF (1 mL), was added and the mixture was stirred at 100 °C for 3 h. The reaction mixture was quenched with $NaHCO_3$ (saturated aqueous). The aqueous layer was extracted with ethyl acetate and the combined organics were washed with water and brine, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash chromatography (hexane/ethyl acetate = 5:1) afforded **5** and **10** (197 mg, 80% over yield) as colorless oil; Rf = 0.50 (silica gel, 5:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = -74 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3476, 2978, 2930, 2855, 1776, 1719, 1452, 1388, 1252, 1158, 1105, 721 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.93 (s, 1 H), 7.81 (m, 2 H), 7.71 (m, 2 H), 7.37 (s, 1 H), 7.29 (s, 1 H), 7.08 (dd, J = 8.4, 1.2 Hz, 1 H), 5.30 (m, 2 H), 3.81 (s, 3 H), 3.67 (d, J = 8 Hz, 2 H), 1.76 (s, 3 H), 1.75 (s, 3 H), 1.59 (s, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ169.3, 167.4, 149.5, 136.1, 134.1, 133.7, 132.1, 131.7, 130.3, 125.1, 123.8, 123.7, 123.5, 117.8, 115.7, 115.0, 83.2, 52.9, 51.9, 34.2, 28.1, 25.7, 24.6, 17.8; HRMS (ESI-TOF) calcd for $C_{30}H_{36}N_3O_6^+$ [M + NH_4]$^+$ 534.2599, found 534.2606.

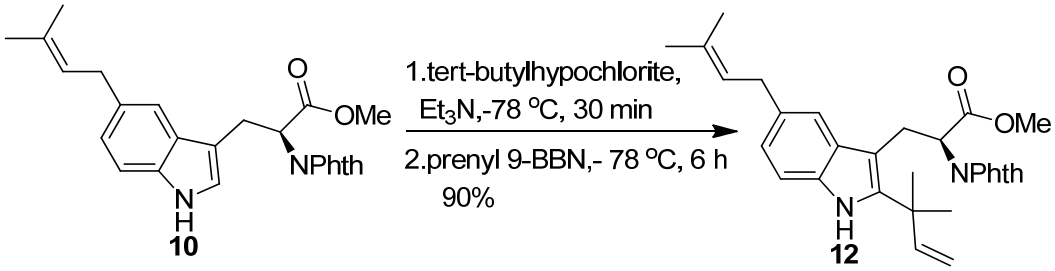
Synthesis of 10



A solution of **5** (258 mg, 0.5 mmol) in DMF (2 mL), was heated to 185 °C. The mixture was stirred at 185 °C for 4 h, was cooled and quenched by saturated aqueous $NaHCO_3$ and extracted by ethyl acetate, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 3:1) afforded **10** (187 mg, 90% yield) as colorless oil; Rf = 0.45 (silica gel, 2:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = -82 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3410, 2960, 2924, 2857, 1775, 1745, 1713, 1436, 1390, 1259, 1105, 721 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.07 (s, 1 H), 7.73 (m, 2 H), 7.64 (m, 2 H), 7.35 (s, 1 H), 7.14 (d, J = 8.4 Hz , 1 H), 6.95 (s, 1 H), 6.94 (d, J = 8.4 Hz , 1 H), 5.29 (m, 2 H), 3.81

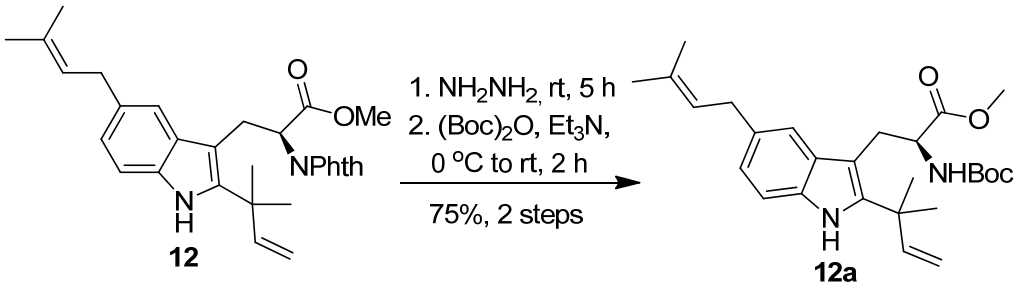
(s, 3 H), 3.76 (m, 2 H), 3.36 (d, J = 7.2 Hz , 1 H) , 1.77(s, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.8, 167.6, 134.6, 134.0, 132.8, 131.7, 131.5, 127.5, 124.5, 123.4, 130.0, 122.8, 117.4, 111.1, 110.6, 52.9, 52.8, 34.5, 25.8, 24.8, 17.9; HRMS (ESI-TOF) calcd for $C_{25}H_{28}N_3O_4^+$ $[M + NH_4]^+$ 434.2074, found 434.2086.

Synthesis of 12



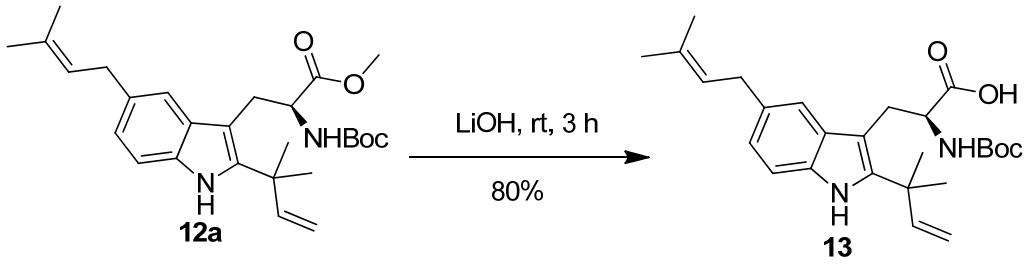
To a cold (-78 °C) solution of **10** (2.37 g, 5.70 mmol) and Et_3N (0.95 mL, 6.84 mmol) in 20 mL of THF was added *tert*-butyl hypochlorite (0.83 mL, 6.84 mmol). After the solution was stirred for 0.5 h at -78°C, a 1.0 M solution of prenyl-9-BBN (11.4 mL, 11.4 mmol) in THF was added dropwise. The solution was allowed to warm slowly over 6 h to ambient temperature, after which 5 mL of a saturated solution of K_2CO_3(aq.) was added. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3x10 mL). The organics were combined, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 5:1) afforded **12** (2.48 g, 90% yield) as colorless oil; Rf = 0.45 (silica gel, 4:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = -10 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3388, 2924, 2854, 1741, 1716, 1461, 1389, 1251, 1210, 1105, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (s, 1 H), 7.70 (m, 2 H), 7.63 (m, 2 H), 7.04 (d, J = 8.4 Hz , 1 H), 7.00 (s, 1 H), 6.70 (dd, J = 8.4, 1.6 Hz, 1 H), 6.21 (dd, J = 17.2, 10.4 Hz, 1 H), 5.20 (m, 3 H), 4.98 (t, J = 6.4 Hz , 1 H), 3.84 (dd, J = 15.2, 3.6 Hz , 1 H), 3.80 (s, 3 H) , 3.64 (dd, J = 15.2, 11.6 Hz, 1 H), 3.07 (dd, J = 15.2, 7.2 Hz, 1 H), 2.96 (dd, J = 15.2, 7.2 Hz , 1 H) , 1.70 (s, 3 H) , 1.67 (s, 3 H) , 1.58 (s, 6 H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.6, 167.6, 145.8, 140.2, 133.7, 132.4, 132.3, 131.8, 131.0, 129.9, 124.4, 123.1, 121.8, 116.7, 112.0, 110.1, 105.9, 53.5, 52.7, 39.1, 34.2, 27.5, 27.4, 25.7, 24.2, 17.7; HRMS (ESI-TOF) calcd for $C_{30}H_{33}N_2O_4^+$ $[M + H]^+$ 485.2435, found 485.2443.

Synthesis of 12a



Hydrazine monohydrate (45 mg, 0.9 mmol) was added to a solution of **12** (146 mg, 0.3 mmol) in ethanol (3 mL). After the solution was stirred at ambient temperature for 5 h, after which the ethanol and hydrazine were removed in vacuo. The residue was taken up in 5 mL of H_2O/ethyl acetate (1:1), and the layers were separated. The aqueous layer was extracted with ethyl acetate, and the organics were combined, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting solution was concentrated under reduced pressure to do the next step. Di-*tert*-butyl dicarbonate (131 mg, 0.6 mmol) was added to a solution of the above-mentioned product (105 mg, 0.3 mmol) and Et_3N (61 mg, 0.6 mmol) in DCM (3 mL). After the solution was stirred at ambient temperature for 2 h, H_2O (2 mL) was added. The aqueous layer was extracted with DCM. The organics were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 5:1) afforded **12a** (102 mg, 75% yield) as a yellow oil; Rf = 0.50 (silica gel, 5:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = -16 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3373, 2923, 2854, 1713, 1451, 1368, 1252, 1164, 1023, 664 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.94 (s, 1 H), 7.27 (d, J = 2.8 Hz, 1 H), 7.20 (d, J = 8.2 Hz, 1 H), 6.97 (d, J = 8.2 Hz, 1 H), 6.15 (dd, J = 17.4, 10.6 Hz, 1 H), 5.39 (ddd, J = 7.6, 6.0, 1.2 Hz, 1 H), 5.24 – 5.15 (m, 2 H), 5.10 (d, J = 7.6 Hz, 1 H), 4.56 (dd, J = 14.8, 8.0 Hz, 1 H), 3.62 (s, 3 H), 3.44 (d, J = 7.2 Hz, 2 H), 3.32 (dd, J = 14.4, 6.4 Hz, 1 H), 3.21 (dd, J = 14.8, 8.0 Hz, 1 H), 1.78 (d, J = 8.4 Hz, 6 H), 1.57 (s, 3 H), 1.56 (s, 3 H), 1.35 (s, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ173.5, 155.1, 146.1, 142.2, 140.7, 132.9, 132.7, 131.4, 130.0, 124.7, 122.4, 117.3, 112.3, 112.2, 110.3, 105.4, 79.5, 54.7, 52.1, 39.2, 36.0, 34.7, 28.4, 28.2, 27.7, 25.8, 17.9; HRMS (ESI-TOF) calcd for $C_{27}H_{39}N_2O_4^+$ $[M + H]^+$ 455.2904, found 455.2903.

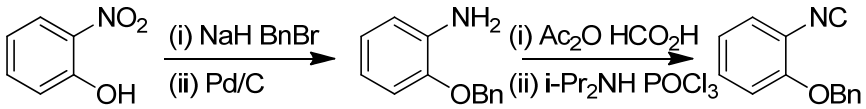
Synthesis of 13



To solid LiOH monohydrate (34 mg, 0.82 mmol) was added to a solution of **12a** (74 mg, 0.16 mmol) in THF/MeOH/H_2O (8/1/1, 2 mL). After the solution was stirred at

ambient temperature for 3 h, 1 N HCl was added to neutralize the solution. The aqueous layer was extracted with ethyl acetate, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 3:1) afforded **13** (57 mg, 80% yield) as a yellow oil; Rf = 0.45 (silica gel, 2:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = +20 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3357, 2970, 2926, 2858, 1702, 1485, 1451, 1369, 1248, 1165, 1054, 1023, 761, 650 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.88 (s, 1 H), 7.34 (s, 1 H), 7.20 (d, J = 8.2 Hz, 1 H), 6.97 (d, J = 7.6 Hz, 1 H), 6.15 (dd, J = 17.4, 10.4 Hz, 1 H), 5.37 (s, 1 H), 5.25 – 5.15 (m, 2 H), 5.07 (s, 1 H), 4.57 (s, 1 H), 3.49 – 3.37 (m, 3 H), 3.20 (dd, J = 14.8, 10.0 Hz, 1 H), 1.76 (s, 3 H), 1.75 (s, 3 H), 1.56 (s, 3 H), 1.55 (s, 3 H), 1.26 (s, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 177.6, 155.5, 146.0, 140.8, 133.1, 132.7, 131.5, 124.6, 122.5, 117.8, 117.2, 112.2, 110.3, 105.3, 79.8, 62.1, 54.7, 44.1, 39.0, 36.0, 34.6, 28.1, 25.7, 17.8; HRMS (ESI-TOF) calcd for $C_{26}H_{37}N_2O_4^+$ $[M + H]^+$ 441.2748, found 441.2749.

Synthesis of 1-Benzyloxy-2-isocyano-benzene 27



25 **26** **27**

To a stirred of **25** (1.39 g, 10.0 mmol) in THF (100 mL), was added NaH (0.8 g, 20.0 mmol) at 0 °C. The mixture was stirred at 0 °C for 0.5 h, then added BnBr (1.87 g, 11.0 mmol). The mixture was stirred at rt overnight, after which 1 N HCl was neutralized the solution. The aqueous layer was extracted with ethyl acetate, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to do the next step.

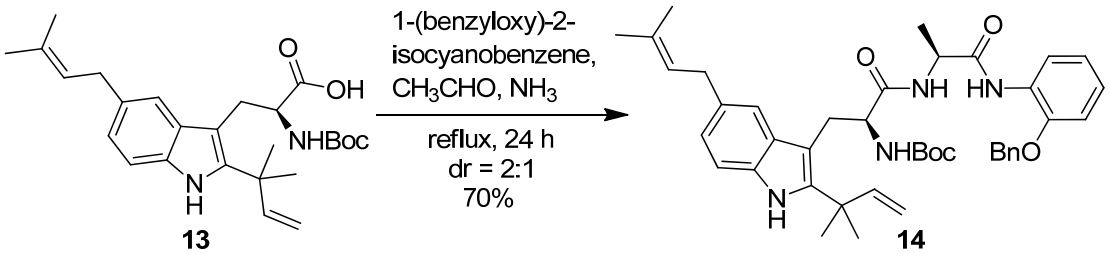
To a solution of the above-mentioned product in anhydrous MeOH (30 mL), was added Pd/C (100 mg, 10%), the mixture was stirred at rt under H_2 for 12 h, filtered and concentrated under reduced pressure to do the next step.

A 100 mL flask was charged with acetic anhydride (2.89 g, 27.0 mmol) under Ar. Formic acid (2.03 g, 33.8 mmol) was added slowly over 40 min. The mixture was heated to 60 °C within 30 min and maintained at 60 °C for 1.5 h, cooled to rt and diluted with anhydrous THF and added the above-mentioned product **26** in anhydrous THF (10 mL) slowly, the mixture was stirred at rt for 12 h, concentrated under reduced pressure to do the next step.

To a solution of the above-mentioned product in anhydrous DCM (30 mL), was added diisopropylamine (2.73 g, 27.0 mmol) at 0 °C, then added $POCl_3$ (1.66 g, 11.0 mmol). The mixture was stirred at 0 °C for 12 h, quenched by saturated aqueous Na_2CO_3, extracted by DCM, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 20:1) afforded **27** (1.57 g, 75% over yield) as a a colorless powder; Rf = 0.80 (silica gel, 6:1 hexane:ethyl acetate); IR (film) ν_{max} 3067, 3034, 2932, 2125, 1596, 1496, 1453, 1383, 1292, 1258, 1111, 1018, 749, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, J = 7.4 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.39 – 7.30 (m, 3H), 7.01 (d, J = 8.4 Hz,

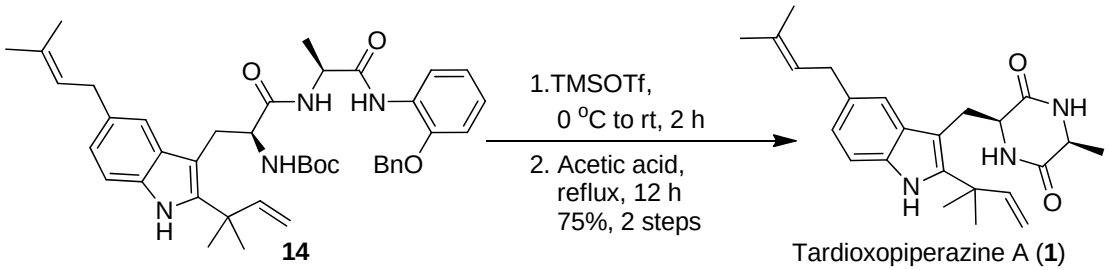
1H), 6.95 (td, J = 7.8, 1.2 Hz, 1H), 5.17 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.5, 153.6, 135.6, 130.1, 128.3, 127.9, 127.7, 127.3, 126.6, 120.5, 116.1, 113.0, 70.1; HRMS (ESI-TOF) calcd for $C_{14}H_{12}NO^+$ $[M + H]^+$ 210.0913, found 210.0915.

Synthesis of 14



To a stirred suspension of Ammonia in MeOH (15 mL), was added Acetaldehyde (30 mg, 0.68 mmol) at 0 °C. The mixture was stirred at rt for 5 h, then added 1-Benzyloxy-2-isocyano-benzene (71 mg, 0.34 mmol) and **13** (150 mg, 0.34 mmol), The resulting solution was heated under reflux for 24 h, then cooled and quenched by saturated aqueous NH_4Cl, extracted by ethyl acetate, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 2:1) afforded **14** and **14b** (165 mg, 70%, dr = 2:1) as a yellow oil; Rf = 0.45 (silica gel, 2:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = -5 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3344, 2972, 2928, 1694, 1601, 1531, 1487, 1451, 1370, 1251, 1167, 744 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.45 (s, 1 H), 8.27 (d, J = 7.8 Hz, 1 H), 7.89 (s, 1 H), 7.46 – 7.41 (m, 5 H), 7.36 (d, J = 3.4 Hz, 1 H), 7.31 (s, 1 H), 7.19 (d, J = 8.2 Hz, 1 H), 7.02 – 6.90 (m, 5 H), 6.14 (dd, J = 17.4, 10.6 Hz, 1 H), 5.78 (s, 1 H), 5.35 (d, J = 6.2 Hz, 2 H), 5.22 (d, J = 6.8 Hz, 1 H), 5.18 (s, 1 H), 5.15 (s, 2 H), 4.41 (dd, J = 15.6, 7.8 Hz, 1 H), 4.30 (s, 1 H), 3.41 (s, 2 H), 3.30 – 3.21 (m, 2 H), 1.76 (s, 3 H), 1.73 (s, 3 H), 1.59 (s, 3 H), 1.57 (s, 6 H), 1.34 (s, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.7, 169.6, 147.3, 145.9, 140.7, 136.4, 136.3, 133.3, 132.6, 131.5, 128.7, 128.2, 127.7, 127.4, 124.5, 124.0, 122.6, 121.3, 120.2, 117.4, 112.4, 111.8, 110.4, 105.7, 70.8, 60.4, 49.7, 39.1, 36.9, 34.6, 28.2, 27.6, 25.8, 21.1, 17.9, 14.2; HRMS (ESI-TOF) calcd for $C_{42}H_{53}N_4O_5^+$ $[M + H]^+$ 693.4010, found 693.4012.

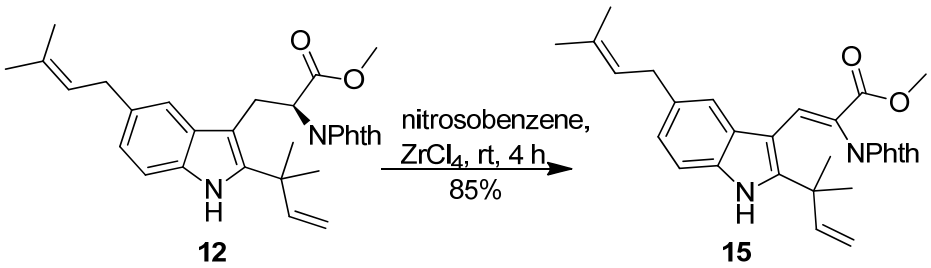
Synthesis of 1



To a stirred suspension of **14** (60 mg, 0.1 mmol) in DCM (5 mL), was added 2,6-lutidine (53.5 mg, 0.5 mmol), then was added TMSOTf (88.8 mg, 0.4 mmol) at 0 °C for 5 min. The mixture was stirred at rt for 2 h, was quenched by saturated aqueous $NaHCO_3$, extracted by ethyl acetate, washed with water and brine, dried over Na_2SO_4,

filtered, and concentrated in vacuo. Redissolved in MeOH (5 mL), was added Acetic acid (0.1 mL), then it was stirred under reflux for 12 h, concentrated and purification by flash chromatography (DCM/MeOH = 100:1) to afforded **1** (26 mg, 75% yield) as a pale yellow powder; Rf = 0.25 (silica gel, 30:1 DCM:MeOH); $[\alpha]^{20}_{D}$ = -24 (c = 0.2, $CHCl_3$); IR (film) ν_{max} 3373, 3194, 3084, 3048, 2965, 2922, 2855, 1673, 1454, 1327, 1102, 802, 648 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ 10.41 (s, 1 H), 8.16 (d, J = 2.4 Hz, 1 H), 7.40 (d, J = 2.8 Hz, 1 H), 7.22 (d, J = 8.4 Hz, 1 H), 7.21 (s, 1 H), 6.84 (d, J = 8.4 Hz, 1 H), 6.16 (dd, J = 17.2, 10.4 Hz , 1 H), 5.33 (t, J = 7.2 Hz, 1 H), 5.04 (d, J = 17.2 Hz, 1 H), 5.01 (d, J = 10.4 Hz, 1 H), 3.94 (m, 1 H), 3.80 (m, 1 H), 3.30 (m, 2 H), 3.02 (dd, J = 14.4, 9.6 Hz , 1 H), 1.71 (s, 3 H), 1.70 (s, 3 H), 1.48 (s, 3 H), 1.47 (s, 3 H), 1.31 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 167.8, 167.3, 146.5, 141.4, 133.4, 131.1, 130.3, 129.1, 124.8, 121.3, 116.9, 110.9, 110.7, 104.3, 55.54, 50.3, 39.9, 34.1, 31.0, 27.9, 25.5, 20.6, 17.6; HRMS (ESI-TOF) calcd for $C_{24}H_{32}N_3O_2^+$ $[M + H]^+$ 394.2489, found 394.2486.

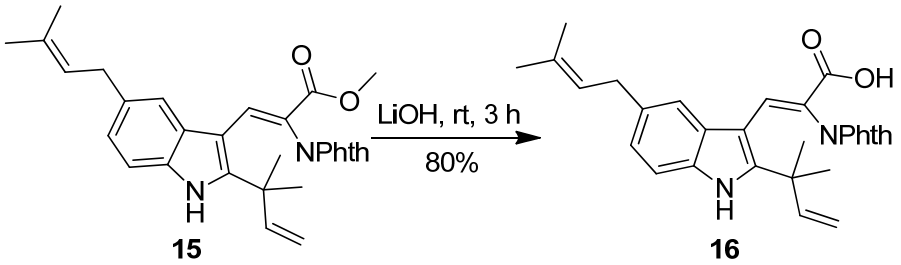
Synthesis of 15



12 **15**

To a solution of **12** (100 mg, 0.21 mmol) and nitrosobenzene (56 mg, 0.53 mmol) in toluene (2 mL) at 0 °C was added $ZrCl_4$ (48 mg, 0.21 mmol) in one portion. The cooling bath was removed and the reaction mixture was stirred for 4 h and turned from an initial green color to dark brown. Once the reaction was complete as judged by TLC, the reaction mixture was filtered through Celite and concentrated. The crude residue was purified by flash chromatography (hexane/ethyl acetate = 5:1) to afforded **15** (85 mg, 85% yield) as colorless oil; Rf = 0.45 (silica gel, 4:1 hexane:ethyl acetate); IR (film) ν_{max} 3369, 2958, 2922, 2853, 1719, 1620, 1435, 1398, 1253, 1116, 725 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.44 (s, 1 H), 8.26 (s, 1 H), 7.74 (m, 2 H), 7.64 (m, 2 H), 7.11 (d, J = 8.4 Hz, 1 H), 6.96 (s, 1 H), 6.77 (dd, J = 1.2, 8.0 Hz , 1 H), 6.18 (dd, J = 17.6, 10.4 Hz , 1 H), 5.33-5.29 (m, 2 H), 4.84 (m, 1 H), 3.85 (s, 1 H), 3.01 (d, J = 7.2 Hz, 2 H), 1.66 (s, 6 H), 1.64 (s, 3 H), 1.62 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.5, 164.6, 146.5, 144.2, 137.1, 134.4, 133.9, 132.6, 132.2, 131.2, 126.2, 124.0, 123.4, 122.7, 119.1, 116.6, 113.4, 110.8, 106.5, 52.5, 39.4, 34.3, 27.7, 25.7, 17.7; HRMS (ESI-TOF) calcd for $C_{30}H_{31}N_2O_4^+$ $[M + H]^+$ 483.2278, found 483.2279.

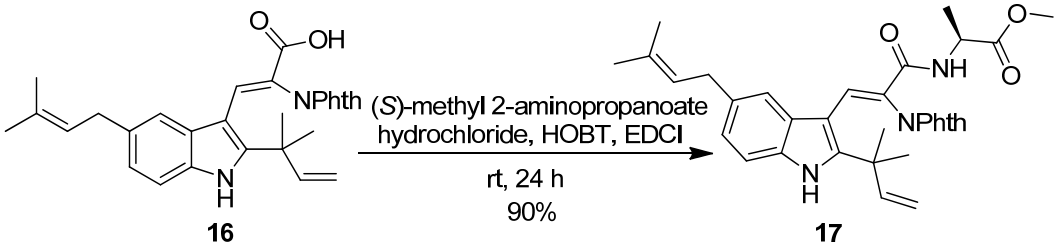
Synthesis of 16



15 16

To solid LiOH monohydrate (52 mg, 1.25 mmol) was added to a solution of **15** (120 mg, 0.25 mmol) in THF/MeOH/H_2O (8/1/1, 3 mL). After the solution was stirred at ambient temperature for 3 h, 1 N HCl was added to neutralize the solution. The aqueous layer was extracted with ethyl acetate, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 3:1) afforded **16** (93 mg, 80% yield) as colorless oil; Rf = 0.45 (silica gel, 2:1 hexane:ethyl acetate); IR (film) ν_{max} 3373, 2964, 2924, 2854, 1716, 1612, 1431, 1387, 1252, 1089, 726 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.58 (s, 1 H), 8.32 (s, 1 H), 7.75 (m, 2 H), 7.64 (m, 2 H), 7.12 (d, J = 8.0 Hz, 1 H), 6.97 (s, 1 H), 6.78 (dd, J = 8.4, 1.6 Hz, 1 H), 6.16 (dd, J = 17.6, 10.8 Hz, 1 H), 5.32 (m, 2H), 4.81 (m, 1 H), 3.00 (d, J = 7.6 Hz, 2 H), 1.66 (s, 6 H), 1.63 (s, 3 H), 1.61 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.1, 166.4, 147.5, 143.9, 139.2, 134.7, 133.9, 132.6, 132.1, 131.3, 126.1, 123.9, 123.4, 122.9, 119.2, 115.3, 113.7, 110.9, 106.6, 39.4, 34.2, 27.8, 25.7, 17.7; HRMS (ESI-TOF) calcd for $C_{29}H_{29}N_2O_4^+$ $[M + H]^+$ 469.2122, found 469.2124.

Synthesis of 17

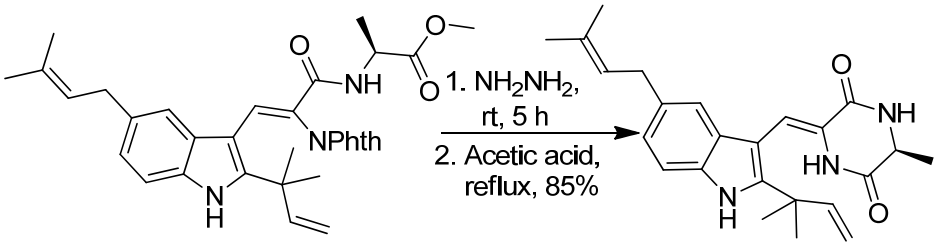


16 17

To a stirred suspension of **16** (94 mg, 0.2 mmol) in THF (2 mL), was added HOBT (40.5 mg, 0.3 mmol) at 0 °C within 10 min, then was added EDCI (54 mg, 0.28 mmol) and the suspension of L-2-Amino-propionic acid methyl ester hydrochloride in THF (0.2 mL) which adjust PH to 8-9 with 4-Methyl-morpholine and stirred at rt for 20 min. The mixture was stirred at 0 °C for 2 h and rt for 16 h, quenched by saturated aqueous $NaHCO_3$ and extracted by ethyl acetate, washed with 1 N citric acid, water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 3:1) afforded **17** (100 mg, 90% yield) as colorless oil; Rf = 0.45 (silica gel, 2:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = -2 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3351, 2955, 2920, 2851, 1727, 1602, 1462, 1377, 1238, 1044, 1023, 802, 727 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.19 (s, 1 H), 8.05 (s, 1 H), 7.69 (m, 2 H), 7.63 (m, 2 H), 7.10 (d, J = 8.4 Hz, 1 H), 6.91 (s, 1 H), 6.75 (dd, J = 8.0, 1.2 Hz, 1 H), 6.58 (d, J = 3.2 Hz, 1 H), 6.23 (dd, J = 17.6, 10.8 Hz, 1 H), 5.32 (m, 2H),

4.84 (t, J = 7.2 Hz, 1 H), 4.77 (t, J = 7.2 Hz, 1 H), 3.80 (s, 3 H), 3.00 (d, J = 7.2 Hz, 2 H), 1.66 (s, 6 H), 1.63 (s, 3 H), 1.58 (s, 3 H), 1.54 (d, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.5, 145.3, 144.3, 134.2, 133.9, 132.6, 132.0, 131.2, 131.0, 124.0, 123.4, 122.6, 121.0, 118.7, 113.1, 110.8, 106.4, 52.5, 48.7, 39.4, 34.2, 29.7, 27.6, 27.5, 25.7, 18.7, 17.7; HRMS (ESI-TOF) calcd for $C_{33}H_{36}N_3O_5^+$ $[M + H]^+$ 554.2649, found 554.2647.

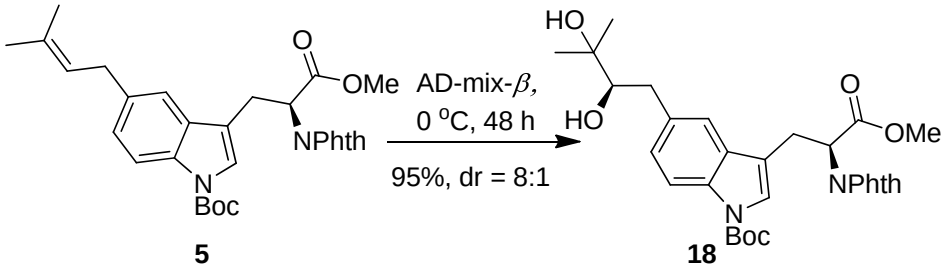
Synthesis of 2



17 Isoechinulin A (**2**)

Hydrazine monohydrate (11 mg, 0.22 mmol) was added to a solution of **17** (40 mg, 0.07 mmol) in ethanol (1 mL) and But-2-ene-(Z)-1,4-diol (0.1 mL). After the solution was stirred at ambient temperature for 5 h, ethanol and hydrazine were removed in vacuo. The residue was taken up in 5 mL of H_2O/ethyl acetate (1:1), and the layers were separated. The aqueous layer was extracted with ethyl acetate, and the organics were combined, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude compound was redissolved in EtOH/ toluene (1:1 v:v, 2 mL), added Acetic acid (0.04 mL), then the mixture was stirred under reflux for 12 h, concentrated and purified by flash chromatography (DCM/MeOH = 100:1) to afforded **2** (24 mg, 85% yield) as a pale yellow powder; Rf = 0.30 (silica gel, 20:1 DCM:MeOH); $[\alpha]^{20}_D$ = -30 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3347, 2923, 2853, 1678, 1630, 1427, 1380, 1156, 1070, 1025, 906, 802 cm^{-1}; ^{1}H NMR (CD_3COCD_3, 400 MHz): δ 10.21 (s, 1 H), 7.92 (s, 1 H), 7.38 (s, 1 H), 7.30 (d, J = 8.2 Hz, 1 H), 7.10 (s, 1 H), 7.05 (s, 1 H), 6.96 (dd, J = 8.2, 1.2 Hz,, 1 H), 6.14 (dd, J = 17.4, 10.6 Hz, 1 H), 5.35 (t, J = 7.4 Hz, 1 H), 5.09 (dd, J = 17.4, 10.6 Hz, 2 H), 4.26 (dt, J = 8.4, 5.8 Hz, 1 H), 3.39 (d, J = 7.4 Hz, 2 H), 1.71 (s, 6 H), 1.55 (s, 6 H),1.54 (d, J = 7.2 Hz, 3 H); ^{13}C NMR (CD_3COCD_3, 100 MHz): δ 166.1, 160.2, 145.3, 144.3, 143.7, 134.0, 131.3, 125.6, 124.7, 122.5, 118.2, 113.3, 111.6, 111.5, 110.2, 103.6, 51.6, 39.4, 34.5, 27.3, 25.3, 20.2, 17.2; HRMS (ESI-TOF) calcd for $C_{24}H_{30}N_3O_2^+$ $[M + H]^+$ 392.2333, found 392.2328.

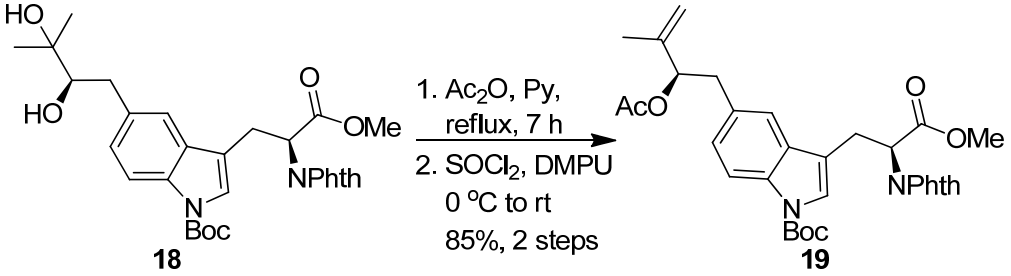
Synthesis of 18



5 **18**

A mixture of AD-mix-β (1.3 g, 1 mmol) in *t*-BuOH/H_2O (1:1 v:v, 10 mL) was stirred at room temperature for 15 min, and then cooled to 0 °C. To this solution was added **5** (516 mg, 1 mmol). The reaction mixture was stirred at 0 ºC for 48 hours and then quenched with Na_2SO_3 (7.5 g) at 0 ºC within 0.5 h. ethyl acetate was added to the reaction mixture, the aqueous layer was further extracted with ethyl acetate twice. The combined organic layers were dried over Na_2SO_4 and the solvent were evaporated. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 1:1) to give 523 mg of corresponding diol **18** (523 mg, 95% yield, dr = 8:1) as a colorless oil: $[\alpha]^{20}_D$ = -102 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3376, 2973, 2928, 2855, 1718, 1469, 1440, 1386, 1252, 1158, 722, 541 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.98 (s, 1 H), 7.78 (m, 2 H), 7.69 (m, 2 H), 7.38 (m, 2 H), 7.14 (d, J = 8.4 Hz, 1 H), 5.28 (t, J = 8.0 Hz, 1 H), 3.81 (s, 3 H), 3.69 (s, 1 H), 3.66 (s, 2 H), 2.95 (d, J = 12.8 Hz, 1 H), 2.64 (dd, J = 12.8, 10.8 Hz, 1 H), 2.34 (s, 1 H), 2.12 (s, 1 H), 1.59 (s, 9 H), 1.48 (s, 1 H), 1.32 (s, 3 H), 1.29 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.3, 167.4, 149.4, 134.1, 133.0, 131.7, 130.4, 125.9, 124.3, 123.5, 119.0, 115.6, 115.4, 83.5, 79.1, 72.5, 52.9, 51.8, 38.1, 28.1, 26.5, 24.7, 23.8; HRMS (ESI-TOF) calcd for $C_{30}H_{35}N_2O_8^+$ $[M + H]^+$ 551.2388, found 551.2389.

Synthesis of 19

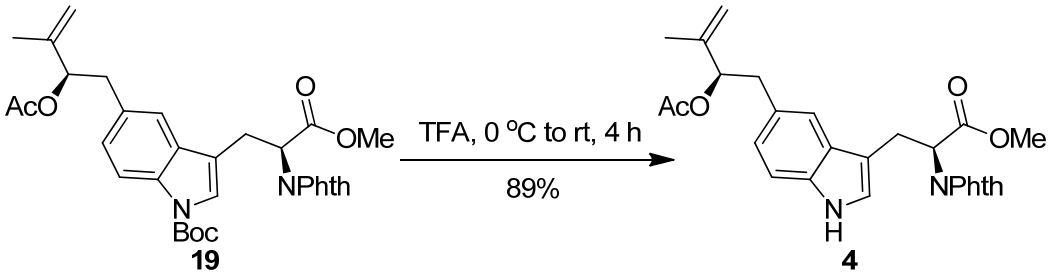


To a stirred suspension of **18** (87 mg, 0.16 mmol) in DCM (2 mL), was added pyridine (38 mg, 0.48 mmol) and acetic anhydride (48 mg, 0.48 mmol) at 0 °C, then it was stirred under reflux for 12 h, quenched by saturated aqueous NH_4Cl and extracted by DCM, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to do the next step.

To a solution of the above-mentioned product in DCM (2 mL) were added DMPU (82 mg, 0.64 mmol), then was added thionyl dichloride (38 mg, 0.32 mmol) at 0 °C. The mixture was stirred at rt for 3 h, was quenched by saturated aqueous NH_4Cl and extracted by DCM, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 5:1) afforded **19** (78 mg, 85% yield) as a colorless oil; Rf = 0.45 (silica gel, 3:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = -91 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3465, 2982, 2929, 1739, 1691, 1596, 1470, 1387, 1241, 1158, 1046, 779, 724 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.95 (d, J = 7.2 Hz, 1 H), 7.82 – 7.80 (m, 2 H), 7.72 – 7.70 (m, 2 H), 7.36 – 7.34 (m, 2 H), 7.11 (d, J = 8.4 Hz, 1 H), 5.37 (t, J = 6.4 Hz, 1 H), 5.28 – 5.24 (m, 1 H), 4.86 (s, 2 H), 3.81 (s, 3 H), 3.73 – 3.64 (m, 2 H), 3.03 – 2.91 (m, 2 H), 2.01 (s, 3 H), 1.77 (s, 3 H), 1.58 (s, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.1, 169.3, 167.5, 142.8, 134.1, 131.8, 131.6, 130.2, 125.9, 123.9, 119.2, 119.1, 115.6, 114.9,

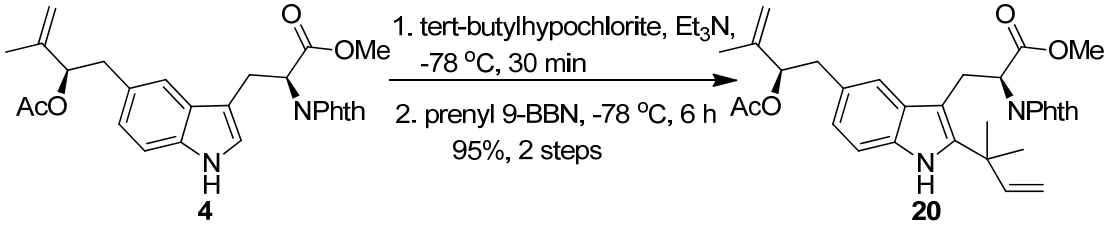
113.1, 78.1, 53.0, 51.8, 39.5, 29.7, 28.1, 24.6, 21.1, 18.5; HRMS (ESI-TOF) calcd for $C_{32}H_{35}N_2O_8^+$ $[M + H]^+$ 575.2388, found 575.2389.

Synthesis of 4



To a stirred suspension of **19** (287 mg, 0.5 mmol) in DCM (6 mL), was added TFA (2 mL) at 0°C. The mixture was stirred at rt for 4 h, quenched by Tethyl acetate and extracted by DCM, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 3:1) afforded **4** (211 mg, 89% yield) as a colorless oil; Rf = 0.40 (silica gel, 2:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = -69 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3372, 2921, 2852, 1713, 1434, 1387, 1239, 1103, 1019, 720 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.91 (s, 1 H), 7.76 (dd, J = 5.6, 3.0 Hz, 2 H), 7.67 (dd, J = 5.6, 3.0 Hz, 2 H), 7.39 (s, 1 H), 7.17 (d, J = 8.4 Hz, 1 H), 7.00 – 6.94 (m, 2 H), 5.40 – 5.31 (m, 1 H), 5.26 (dd, J = 10.6, 5.4 Hz, 1 H), 4.85 (s, 2 H), 3.81 (s, 3 H), 3.73 (dd, J = 11.6, 8.0 Hz, 2 H), 3.03 – 2.88 (m, 2 H), 2.01 (s, 3 H), 1.77 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.2, 169.7, 167.5, 143.0, 135.0, 134.0, 131.7, 128.5, 128.4, 127.3, 123.7, 123.4, 122.6, 118.9, 112.9, 110.8, 78.5, 52.9, 52.5, 39.7, 29.7, 24.7, 21.2, 21.1, 18.6, 14.2; HRMS (ESI-TOF) calcd for $C_{27}H_{27}N_2O_6^+$ $[M + H]^+$ 475.1864, found 475.1867.

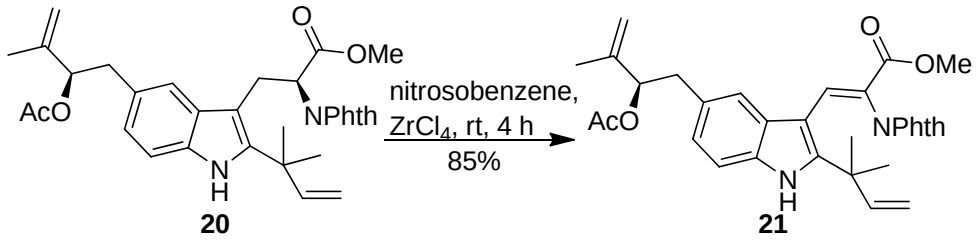
Synthesis of 20



To a cold (-78 °C) solution of **4** (545 mg, 1.15 mmol) and Et_3N (0.2 mL, 1.38 mmol) in THF (20 mL) was added *tert*-butyl hypochlorite (0.17 mL, 1.38 mmol). After the solution was stirred for 0.5 h at -78°C, a 1.0 M solution of prenyl-9-BBN (3.45 mL, 3.45 mmol) in THF was added dropwise. The solution was allowed to warm slowly to ambient temperature within 6 h, after which 5 mL of a saturated solution of K_2CO_3(aq.) was added. The layers were separated, and the aqueous layer was extracted with ethyl acetate (3x10 mL). The organics were combined, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 5:1) afforded **20** (592 mg, 95% yield) as colorless oil; Rf = 0.45 (silica gel, 4:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = -90 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3403, 2929, 1743, 1717, 1466, 1439, 1389, 1241, 1107, 1027, 721 cm^{-1}; ^1H NMR

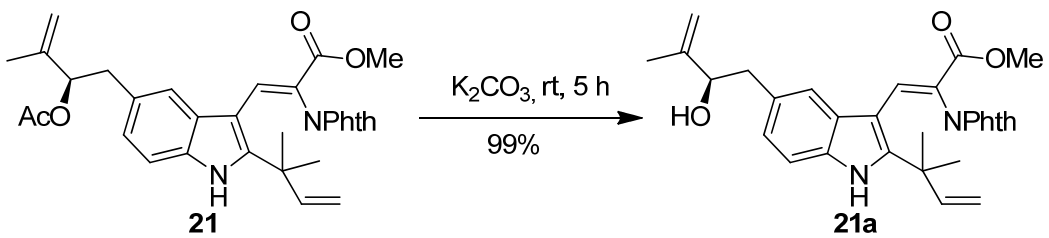
($CDCl_3$, 400 MHz): δ 7.94 (s, 1 H), 7.73 (dd, J = 5.4, 3.2 Hz, 2 H), 7.64 (dd, J = 5.4, 3.2 Hz, 2 H), 7.08 – 7.00 (m, 2 H), 6.73 (dd, J = 8.4, 1.2 Hz, 1 H), 6.19 (dd, J = 17.6, 10.6 Hz, 1 H), 5.25 – 5.11 (m, 4 H), 4.73 (s, 1 H), 4.56 (s, 1 H), 3.85 (dd, J = 15.4, 3.8 Hz, 1 H), 3.78 (s, 3 H), 3.66 (dd, J = 15.4, 11.4 Hz, 1 H), 2.72 (dd, J = 13.8, 7.0 Hz, 1H), 2.63 – 2.54 (m, 1 H), 2.01 (s, 3 H), 1.62 (s, 3 H), 1.56 (s, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.0, 169.5, 167.6, 145.7, 142.6, 140.4, 133.9, 132.7, 131.7, 129.8, 127.6, 123.2, 122.7, 118.1, 113.0, 112.0, 109.9, 105.9, 78.5, 53.4, 52.7, 39.3, 39.1, 27.5, 27.4, 24.3, 21.2, 18.3; HRMS (ESI-TOF) calcd for $C_{32}H_{35}N_2O_6^+$ $[M + H]^+$ 543.2490, found 543.2493.

Synthesis of 21



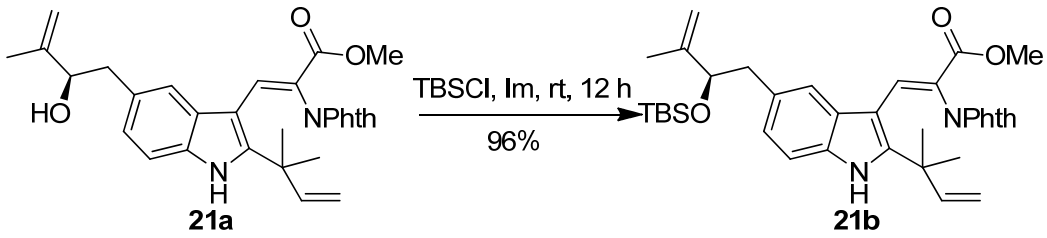
To a solution of **20** (90 mg, 0.17 mmol) and nitrosobenzene (44 mg, 0.42 mmol) in toluene (2 mL) at 0 °C was added $ZrCl_4$ (40 mg, 0.17 mmol) in one portion. The cooling bath was removed and the reaction mixture was stirred for 4 h at rt and turned from an initial green color to dark brown. Once the reaction was complete as judged by TLC, the reaction mixture was filtered through Celite, and concentrated. The crude residue was purified by flash chromatography (hexane/ethyl acetate = 5:1) afforded **21** (76 mg, 85% yield) as colorless oil; Rf = 0.45 (silica gel, 4:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = -12 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3368, 2955, 2921, 2852, 1719, 1622, 1434, 1397, 1371, 1246, 1116, 1071, 1022, 887, 727 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.69 (d, J = 10.4 Hz, 1 H), 8.47 (d, J = 4.6 Hz, 1 H), 7.80 – 7.69 (m, 2 H), 7.64 (dd, J = 8.0, 4.6 Hz, 2 H), 7.02 (dd, J = 18.4, 6.2 Hz, 2 H), 6.78 (d, J = 8.0 Hz, 1 H), 6.15 (dd, J = 17.4, 10.6 Hz, 1 H), 5.27 (m, 3 H), 5.00 (t, J = 7.0 Hz, 1 H), 4.71 (s, 1 H), 4.63 (s, 1 H), 3.83 (s, 3 H), 2.57 (d, J = 7.0 Hz, 2 H), 1.92 (s, 3 H), 1.60 (s, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.9, 166.6, 164.6, 146.9, 144.1, 142.9, 137.5, 134.1, 134.0, 133.2, 131.9, 129.7, 126.0, 123.5, 123.3, 120.3, 116.3, 113.2, 112.5, 110.8, 106.2, 78.1, 52.5, 39.3, 27.7, 21.0, 18.4; HRMS (ESI-TOF) calcd for $C_{32}H_{33}N_2O_6^+$ $[M + H]^+$ 541.2333, found 541.2335.

Synthesis of 21a



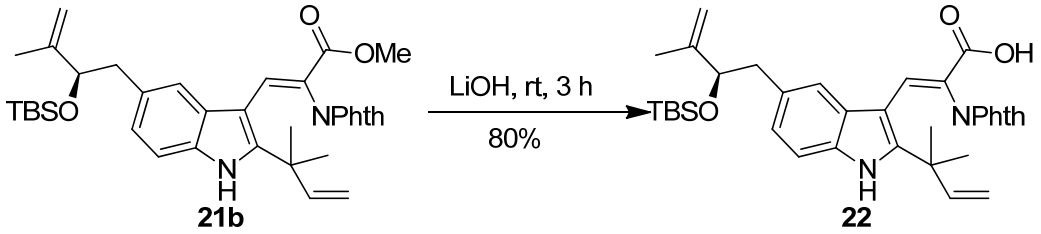
To a solution of **21** (370 mg, 0.69 mmol) in MeOH (10 mL), was added K_2CO_3 (284 mg, 2.1 mmol). The mixture was stirred for 3 h at rt. Once the reaction was complete as judged by TLC, the reaction mixture was quenched by saturated aqueous NH_4Cl and extracted by ethyl acetate (3x10 mL). The organics were combined, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 3:1) afforded **21a** (338 mg, 99% yield) as colorless oil; Rf = 0.50 (silica gel, 1:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = -5 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3372, 2922, 2852, 1785, 1717, 1620, 1435, 1399, 1253, 1118, 1072, 754, 728 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.48 (s, 1 H), 8.45 (s, 1 H), 7.71 (dd, *J* = 5.4, 3.2 Hz, 2 H), 7.62 (dd, *J* = 5.4, 3.2 Hz, 2 H), 7.07 (d, *J* = 7.8 Hz, 2 H), 6.83 – 6.77 (m, 1 H), 6.16 (dd, *J* = 17.6, 10.6 Hz, 1 H), 5.35 – 5.26 (m, 2 H), 4.82 (s, 1 H), 4.78 (s, 1 H), 3.89 (d, *J* = 8.6 Hz, 1 H), 3.84 (s, 3 H), 2.66 (dd, *J* = 13.8, 4.0 Hz, 1 H), 2.42 (dd, *J* = 13.8, 9.4 Hz, 1 H), 1.74 (s, 3 H), 1.64 (s, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.8, 166.7, 164.5, 146.8, 144.1, 137.5, 134.1, 133.2, 132.0, 131.9, 130.6, 126.4, 123.6, 123.5, 123.4, 120.0, 116.9, 113.4, 111.0, 110.8, 106.2, 76.6, 52.7, 42.3, 39.5, 27.7, 18.1; HRMS (ESI-TOF) calculated for calcd for $C_{30}H_{31}N_2O_5^+$ $[M + H]^+$ 499.2227, found 499.2228.

Synthesis of 21b



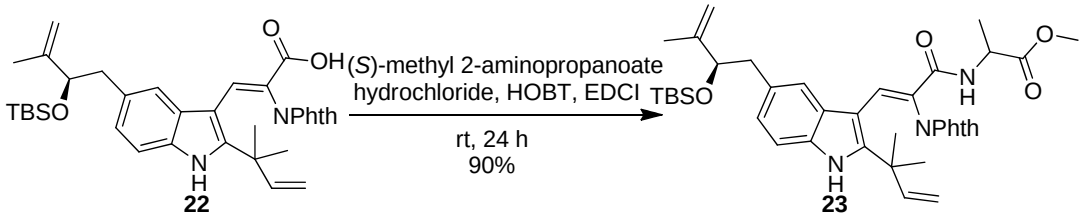
To a solution of **21a** (338 mg, 0.69 mmol) in DMF (0.7 mL), was added imidazole (280 mg, 4.1 mmol) and TBSCl (414 mg, 2.7 mmol). The mixture was stirred for 3 h at rt. Once the reaction was complete as judged by TLC, the reaction mixture was quenched by saturated aqueous NH_4Cl and extracted by ethyl acetate (3x10 mL). The organics were combined, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 6:1) afforded **21b** (398 mg, 96% yield) as colorless oil; Rf = 0.60 (silica gel, 3:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = +30 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3378, 2953, 2928, 2855, 1720, 1624, 1435, 1397, 1252, 1074, 835, 776, 725 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.45 (s, 1 H), 8.36 (s, 1 H), 7.80 – 7.70 (m, 2 H), 7.64 (dd, *J* = 5.8, 2.8 Hz, 2 H), 7.07 (d, *J* = 8.2 Hz, 1 H), 7.00 (s, 1 H), 6.84 (dd, *J* = 8.2, 1.0 Hz, 1 H), 6.18 (dd, *J* = 17.6, 10.4 Hz, 1 H), 5.37 – 5.23 (m, 2 H), 4.63 (s, 2 H), 3.83 (s, 3 H), 3.80 (t, *J* = 6.2 Hz, 1 H), 2.45 (d, *J* = 6.6 Hz, 2 H), 1.67 (s, 3 H), 1.65 (s, 6 H), 0.78 (s, 9 H), -0.29 (s, 3 H), -0.53 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.0, 166.4, 164.6, 147.5, 146.3, 144.2, 137.6, 134.0, 133.0, 132.2, 131.8, 126.1, 124.8, 123.5, 123.3, 120.0, 116.7, 113.3, 110.5, 110.1, 106.3, 78.5, 52.6, 43.4, 39.4, 27.8, 27.7, 25.8, 18.1, 17.6, -5.2, -5.7; HRMS (ESI-TOF) calcd for $C_{36}H_{45}N_2O_5Si^+$ $[M + H]^+$ 613.3092, found 613.3093.

Synthesis of 22



To solid LiOH monohydrate (51.4 mg, 1.23 mmol) was added to a solution of **21b** (150 mg, 0.25 mmol) in THF/MeOH/H2O (8/1/1, 3 mL) solution. After the solution was stirred at ambient temperature for 3 h, 1 N HCl was added to neutralize the solution. The aqueous layer was extracted with ethyl acetate, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 3:1) afforded **22** (117 mg, 80% yield) as colorless oil; Rf = 0.30 (silica gel, 2:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = +45 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3294, 3068, 2954, 2928, 2855, 1713, 1647, 1584, 1395, 1252, 1076, 834, 775, 751 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ11.08 (s, 1 H), 8.60 (s, 1 H), 8.34 (s, 1 H), 7.75 (m, 2 H), 7.40 (m, 2 H), 7.08 (d, J = 8.4 Hz, 1 H), 7.02 (s, 1 H), 6.85 (dd, J = 1.2, 8.4 Hz, 1 H), 6.17 (dd, J = 17.2, 10.4 Hz, 1 H), 5.31 (dd, J = 10.4, 17.2 Hz, 2 H), 4.63 (s, 2 H), 3.79 (t, J = 6.4 Hz, 1 H), 2.44 (d, J = 6.8 Hz, 2 H), 1.67 (s, 9 H), 0.78 (s, 9 H), -0.28 (s, 3 H), -0.51 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ169.4, 166.9, 166.3, 147.5, 147.2, 144.0, 139.7, 134.0, 133.0, 132.2, 132.1, 126.1, 125.0, 123.5, 123.4, 120.3, 115.5, 113.6, 110.5, 110.2, 106.5, 78.5, 43.3, 39.5, 27.8, 27.7, 25.8, 18.1, 17.6, -5.1, -5.6; HRMS (ESI-TOF) calcd for $C_{35}H_{43}N_2O_5Si^+$ $[M + H]^+$ 599.2936, found 599.2936.

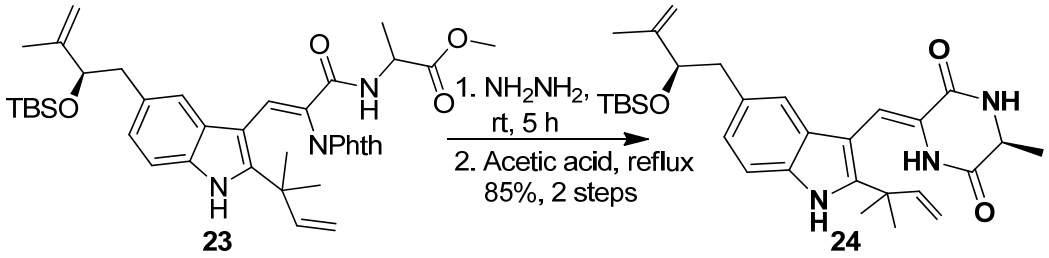
Synthesis of 23



To a stirred suspension of **22** (40 mg, 0.07 mmol) in THF (1 mL), was added HOBT (15 mg, 0.11 mmol) at 0 °C and stirred for 10 min at the temperature, then was added EDCI (18 mg, 0.09 mmol) and the suspension of L-2-Amino-propionic acid methyl ester hydrochloride (12 mg, 0.08 mmol) in THF (0.2 mL) which adjust PH to 8-9 with 4-Methyl-morpholine and stirred at rt for 20 min. The mixture was stirred at 0 °C for 2 h and rt for 16 h, quenched by saturated aqueous $NaHCO_3$ and extracted by ethyl acetate, washed with 1 N citric acid, water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (hexane/ethyl acetate = 3:1) afforded **23** (41 mg, 90% yield) as colorless oil; Rf = 0.45 (silica gel, 2:1 hexane:ethyl acetate); $[\alpha]^{20}_D$ = +20 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3336, 2922, 2852, 1722, 1648, 1531, 1445, 1384, 1307, 1252, 1211, 1072, 835, 776, 724, 670 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ11.08 (s, 1 H), 8.60 (s, 1 H), 8.34 (s, 1 H), 7.75 (m, 2 H), 7.40 (m, 2 H), 7.08 (d, J = 8.4 Hz, 1 H), 7.02 (s, 1 H), 6.85 (dd, J = 8.4, 1.2 Hz, 1 H),

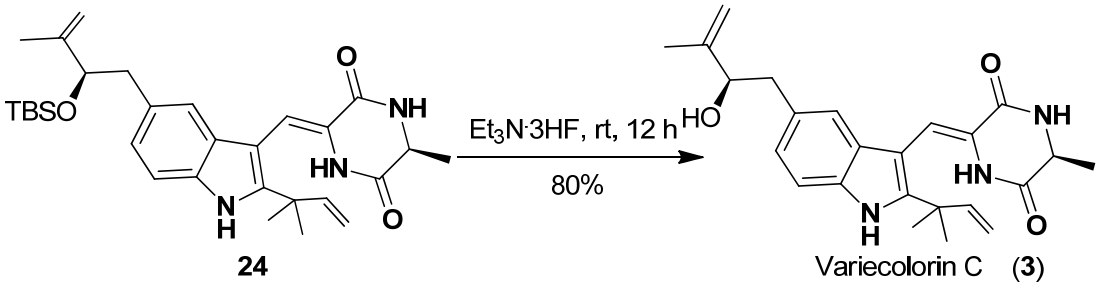
6.17 (dd, *J* = 17.2, 10.4 Hz, 1 H), 5.31 (dd, *J* = 17.2, 10.4 Hz, 2 H), 4.63 (s, 2 H), 3.79 (t, *J* = 6.4 Hz, 1 H), 2.44 (d, *J* = 6.8 Hz, 2 H), 1.67 (s, 9 H), 0.78 (s, 9 H), -0.28 (s, 3 H), -0.51 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ169.4, 166.9, 166.3, 147.5, 147.2, 144.0, 139.7, 134.0, 133.0, 132.2, 132.1, 126.1, 125.0, 123.5, 123.4, 120.3, 115.5, 113.6, 110.5, 110.2, 106.5, 78.5, 43.3, 39.5, 27.8, 27.7, 25.8, 18.1, 17.6, -5.1, -5.6; HRMS (ESI-TOF) calcd for $C_{39}H_{50}N_3O_6Si^+$ $[M + H]^+$ 684.3463, found 684.3465.

Synthesis of 24



Hydrazine monohydrate (15 mg, 0.3 mmol) was added to a solution of **23** (70 mg, 0.1 mmol) in 1 mL of ethanol and 0.1 mL of But-2-ene-(Z)-1,4-diol. The solution was stirred at ambient temperature for 5 h, after which the ethanol and hydrazine were removed in vacuo. The residue was taken up in 5 mL of H_2O/ethyl acetate (1:1), and the layers were separated. The aqueous layer was extracted with ethyl acetate, and the organics were combined, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Redissolved in EtOH/ toluene (1:1 v:v, 5 mL), was added Acetic acid (0.1 mL), then it was stirred under reflux for 12 h, concentrated and purification by flash chromatography (DCM/MeOH = 100:1) afforded **24** (45 mg, 85% yield) as a pale yellow powder; Rf = 0.40 (silica gel, 30:1 DCM:MeOH); $[\alpha]^{20}_D$ = -14 (c = 1.0, $CHCl_3$); IR (film) ν_{max} 3359, 3229, 2955, 2929, 2856, 1674, 1632, 1425, 1330, 1251, 1076, 896, 835, 776 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20 (s, 1 H), 7.41 (s, 1 H), 7.25 (d, *J* = 8.8 Hz, 1 H), 7.20 (s, 1 H), 7.04 (d, *J* = 7.0 Hz, 2 H), 6.12 (s, 1 H), 6.08 (dd, *J* = 17.4, 10.6 Hz, 1 H), 5.25 – 5.15 (m, 2 H), 4.76 (s, 1 H), 4.72 (s, 1 H), 4.36 – 4.29 (m, 1 H), 4.19 (t, *J* = 6.6 Hz, 1 H), 2.84 (d, *J* = 6.6 Hz, 2 H), 1.74 (s, 3 H), 1.60 (s, 3 H), 1.53 (s, 6 H), 0.82 (s, 9 H), -0.13 (s, 3 H), -0.25 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.6, 160.1, 147.1, 144.3, 143.5, 133.0, 126.1, 124.6, 124.5, 119.4, 113.1, 112.0, 111.2, 110.6 102.6, 78.9, 51.6, 43.6, 39.2, 27.3, 25.8, 20.8, 18.1, 17.3; HRMS (ESI-TOF) calcd for $C_{30}H_{44}N_3O_3Si^+$ $[M + H]^+$ 522.3146, found 522.3148.

Synthesis of 3



A solution of **24** (20 mg, 0.038 mmol) in THF (6 mL), was added triethylammonium fluoride (23 mg, 0.192 mmol) and the mixture was stirred for 24 h at room temperature. The reaction was diluted with ethyl acetate (10 mL), washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (DCM/MeOH = 100:1) afforded **3** (12 mg, 80% yield) as a pale yellow powder; Rf = 0.20 (silica gel, 20:1 DCM:MeOH); $[\alpha]^{20}_{D}$ = -40 (c = 0.1, MeOH); IR (KBr) ν_{max} 3354, 3084, 2923, 2855, 1677, 1631, 1434, 1324, 1157, 1069, 1025, 905, 751, 663 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ 10.95 (s, 1 H), 8.46 (s, 1 H), 8.37 (s, 1 H), 7.29 (d, J = 8.4 Hz, 1 H), 6.99 (s, 1 H), 6.95 (dd, J = 8.4, 1.2 Hz, 1 H), 6.88 (s, 1 H), 6.07 (dd, J = 17.6, 10.8 Hz, 1 H), 5.05 (d, J = 10.8 Hz, 1 H), 5.02 (d, J = 17.6 Hz, 1 H), 4.72 (s, 1 H), 4.69 (d, J = 3.2 Hz, 1 H), 4.64 (s, 1 H), 4.13 (dd, J = 6.8, 2.0 Hz, 1 H), 4.08 (d, J = 4.8 Hz, 1 H), 2.72 (m, 2 H), 1.68 (s, 3 H), 1.47 (s, 6 H), 1.40 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 166.3, 160.0, 147.7, 145.2, 143.9, 133.7, 130.1, 125.9, 124.7, 122.7, 119.1, 111.5, 110.9, 110.5, 103.0, 76.3, 50.6, 42.2, 39.0, 27.5, 19.8, 17.6; HRMS (ESIMS) calcd for $C_{24}H_{30}N_3O_3^+$ $[M + H]^+$ 408.2282, found 408.2292.

2. **Comparison of our data for Tardioxopiperazine A with literature:**

Assignment	**Fujimoto's Report[5]** Tardioxopiperazine A ^1H NMR DMSO-d_6	**This Work** Tardioxopiperazine A ^1H NMR DMSO-d_6	**Fujimoto's Report[5]** Tardioxopiperazine A ^{13}C NMR DMSO-d_6	**This Work** Tardioxopiperazine A ^{13}C NMR DMSO-d_6, 400 MHz
N1	10.42 (s)	10.41 (s)		
C2			141.5 qC	141.4 qC
C3			104.3 qC	104.3 qC
C3a			129.2 qC	129.1 qC
C4	7.19 (s)	7.21 (s)	116.9 CH	116.9 CH
C5			131.1 qC	131.1 qC
C6	6.82 (d, 8.3)	6.84 (d, 8.4)	121.3 CH	121.3 CH
C7	7.21 (d, 8.3)	7.22 (d, 8.4)	110.7 CH	110.7 CH
C7a			133.4 qC	133.4 qC
C8	3.00 (dd, 14.5, 9.4) 3.30	3.02 (dd, 14.4, 9.6) 3.30	31.1 CH_2	31.0 CH_2

	(m)	(m)		
C9	3.93 (m)	3.94 (m)	55.6 CH	55.5 CH
C10			167.4 qC	167.3 qC
N11	8.17 (d, 2.7)	8.16 (d, 2.4)		
C12	3.79 (m)	3.80 (m)	50.3 CH	50.3 CH
C13			167.8 qC	167.8 qC
N14	7.44 (d, 3.0)	7.40 (d, 2.8)		
C15			39.9 qC	39.9 qC
C16	6.14 (dd, 17.1, 10.2)	6.16 (dd, 17.2, 10.4)	146.5 CH	146.5 CH
C17	5.01 (d, 10.2) 5.02 (d, 17.1),	5.01 (d, 10.4) 5.04 (d, 17.2),	111.0 CH_2	111.0 CH_2
C18	1.45 (3H, s)	1.47 (3H, s)	28.0 CH_3	28.0 CH_3
C19	1.46 (3H, s)	1.48 (3H, s)	28.0 CH_3	28.0 CH_3
C20	1.29 (3H, d, 7.1)	1.31 (3H, d, 6.8)	20.7 CH_3	20.6 CH_3
C21	3.3 (2H, m)	3.3 (2H, m)	34.2 CH_2	34.1 CH_2
C22	5.31 (t, 7.3)	5.33 (t, 7.2)	124.8 CH	124.8 CH
C23			130.3 qC	130.3 qC
C24	1.68 (3H, s)	1.70 (3H, s)	25.5 CH_3	25.5 CH_3
C25	1.69 (3H, s)	1.71 (3H, s)	17.7 CH_3	17.6 CH_3

3. **Comparison of our data for Isoechinulin A with literature:**

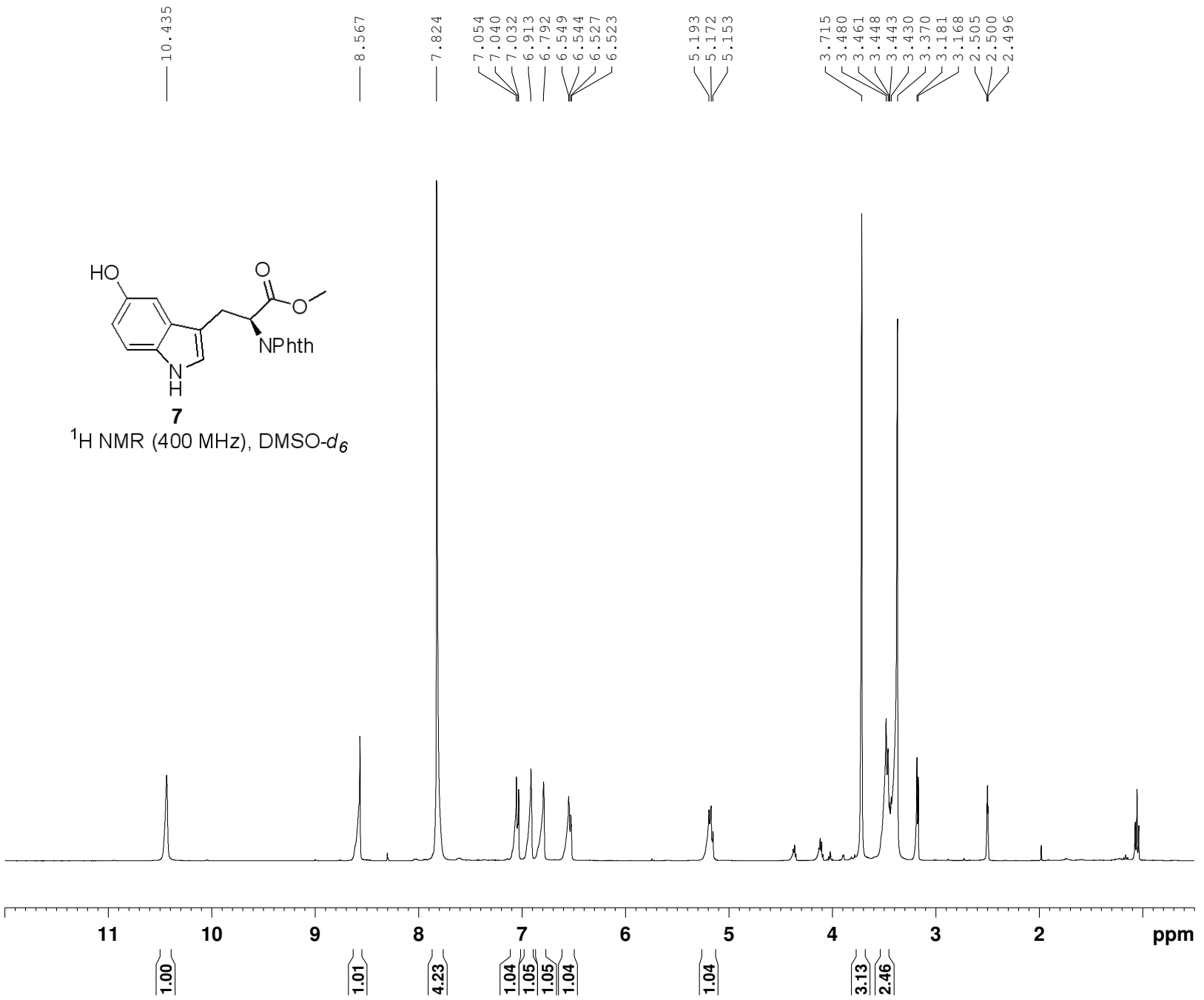
Assignment	**Nagasawa's Report**[5] Isoechinulin A ^{1}H NMR CD_3COCD_3	**This Work** Isoechinulin A ^{1}H NMR CD_3COCD_3, 400 MHz	**This Work** Isoechinulin A ^{13}C NMR CD_3COCD_3, 400 MHz
N1	10.21 (s)	10.21 (s)	
C2			143.7 qC

C3			103.6 qC
C3a			125.6 qC
C4	7.10 (d, 1.7)	7.05 (s)	118.2 CH
C5			131.3 qC
C6	6.99 (dd, 8.2, 1.7)	6.96 (dd, 8.2, 1.2)	122.5 CH
C7	7.34 (d, 8.2)	7.30 (d, 8.2)	111.6CH
C7a			134.0 qC
C8	7.15 (s)	7.10 (s)	110.2 CH
C9			124.7 qC
C10			160.2 qC
N11	7.53 (s)	7.38 (s)	
C12	4.28 (d, 7.1)	4.26 (dt, 8.4, 5.8)	51.6 CH
C13			166.1 qC
N14	7.92 (s)	7.92 (s)	
C15			39.4 qC
C16	6.16 (dd, 17.4, 10.5)	6.14 (dd, 17.4, 10.6)	145.3 CH
C17	5.13 (2H,dd,17.8,10.5)	5.09 (2H,dd,17.4,10.6)	111.5 CH_2
C18	1.55 (3H, s)	1.55 (3H, s)	27.3 CH_3
C19	1.55 (3H, s)	1.55 (3H, s)	25.3 CH_3
C20	1.55 (3H, d, 6.9)	1.54 (3H, d, 7.2)	20.2 CH_3
C21	3.40 (2H, d, 7.1)	3.39 (2H, d, 7.4)	34.5 CH_2
C22	5.38 (t, 7.1)	5.35 (t, 7.4)	113.3 CH
C23			144.3 qC
C24	1.71 (3 H, s)	1.71 (3 H, s)	17.2 CH_3
C25	1.71 (3 H, s)	1.71 (3 H, s)	17.2 CH_3

4. **Comparison of our data for Variecolorin C with literature:**

Assignment	**Zhu's Report[5]** Variecolorin C ^{1}H NMR DMSO-d_6, 400 MHz	**This Work** Variecolorin C ^{1}H NMR DMSO-d_6, 400 MHz	**Zhu's Report[5]** Variecolorin C ^{13}C NMR DMSO-d_6, 400 MHz	**This Work** Variecolorin C ^{13}C NMR DMSO-d_6, 400 MHz
N1	10.95 (s)	10.95 (s)		
C2			143.8 qC	143.9 qC
C3			103.0 qC	103.0 qC
C3a			125.9 qC	125.9 qC
C4	6.99 (br s)	6.99 (br s)	119.1 CH	119.1 CH
C5			130.3 qC	130.1 qC
C6	6.95 (br d, 8.3)	6.95 (dd, 8.4, 1.2)	122.8 CH	122.7 CH
C7	7.29 (d, 8.3)	7.29 (d, 8.0)	110.9 CH	110.9 CH
C7a			133.7 qC	133.7 qC
C8	6.88 (s)	6.88 (s)	110.4 CH	110.5 CH
C9			124.7 qC	124.7 qC
C10			159.8 qC	160.0 qC
N11	8.37 (d, 2.0)	8.37 (d, 1.2)		
C12	4.13 (qd, 6.9, 2.0)	4.13 (qd, 6.8, 2.0)	50.7 CH	50.6 CH
C13			166.3 qC	166.3 qC
N14	8.46 (s)	8.52 (s)		
C15			39.0 qC	39.0 qC
C16	6.07(dd, 17.4, 10.5)	6.07(dd, 17.6, 10.8)	145.2 CH	145.2 CH
C17	5.05 (d, 10.5) 5.02 (d, 17.4),	5.05 (d, 10.8) 5.02 (d, 17.6),	111.5 CH_2	111.5 CH_2
C18	1.47 (3H, s)	1.47 (3H, s)	27.6 CH_3	27.5 CH_3
C19	1.46 (3H, s)	1.47 (3H, s)	27.5 CH_3	27.5 CH_3
C20	1.40 (3H, d, 6.9)	1.40 (3H, d, 6.8)	20.1 CH_3	20.0 CH_3

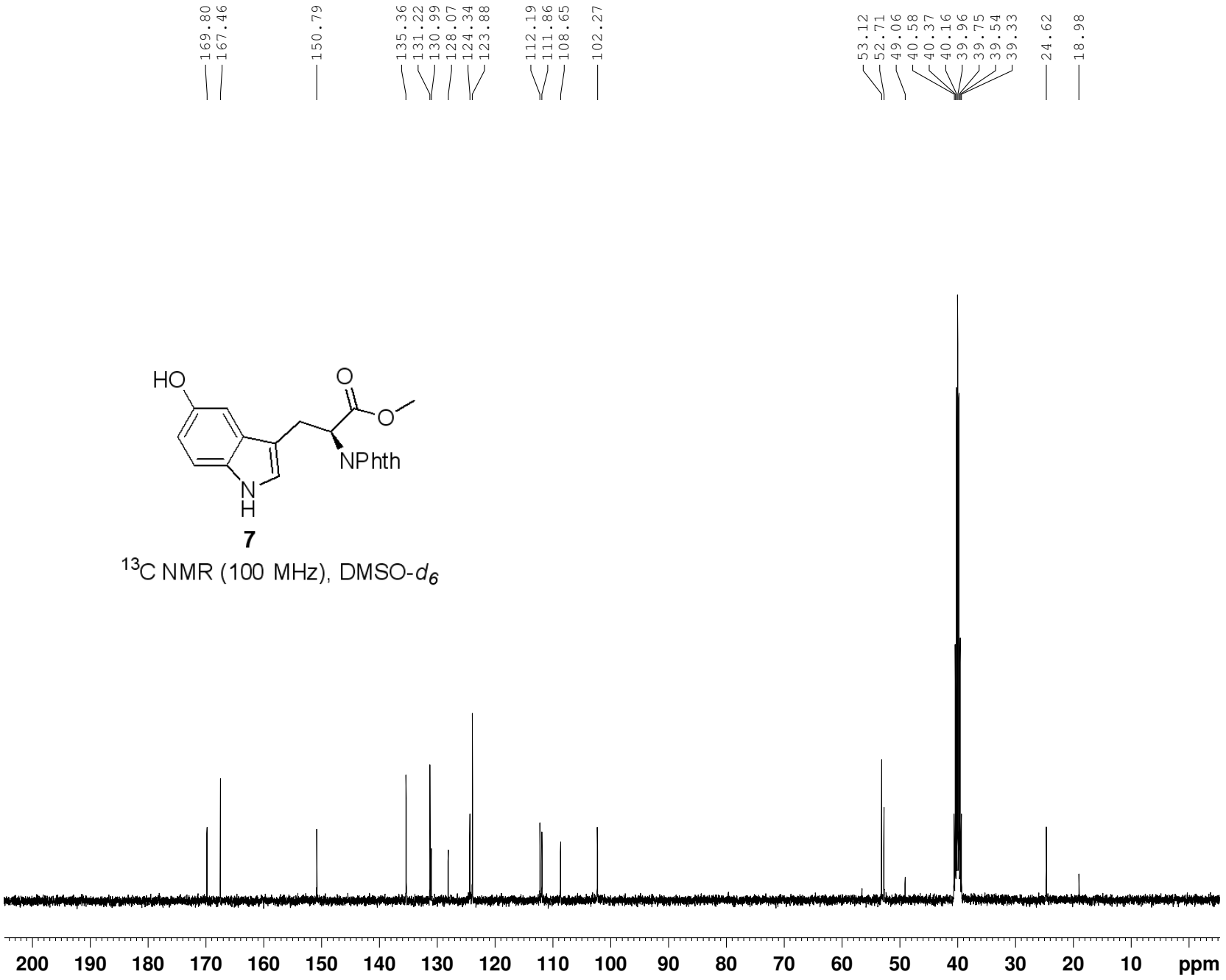
C21	2.74 (dd, 6.2, 13.6) 2.70 (dd, 13.6, 7.1)	2.72 (2H, m)	42.3 CH_2	42.2 CH_2
C22	4.08(ddd, 7.1, 6.2, 4.2)	4.08 (d, 4.8)	76.4 CH	76.3 CH
C23			147.8 qC	147.7 qC
C24	4.74 (br s) 4.64 (br s)	4.72 (br s) 4.64 (br s)	110.4 CH_2	110.5CH_2
C25	1.68 (3H, s)	1.68 (3H, s)	17.7 CH_3	17.6 CH_3
C22-OH	4.68 (d, 4.6)	4.68 (d, 3.2)		



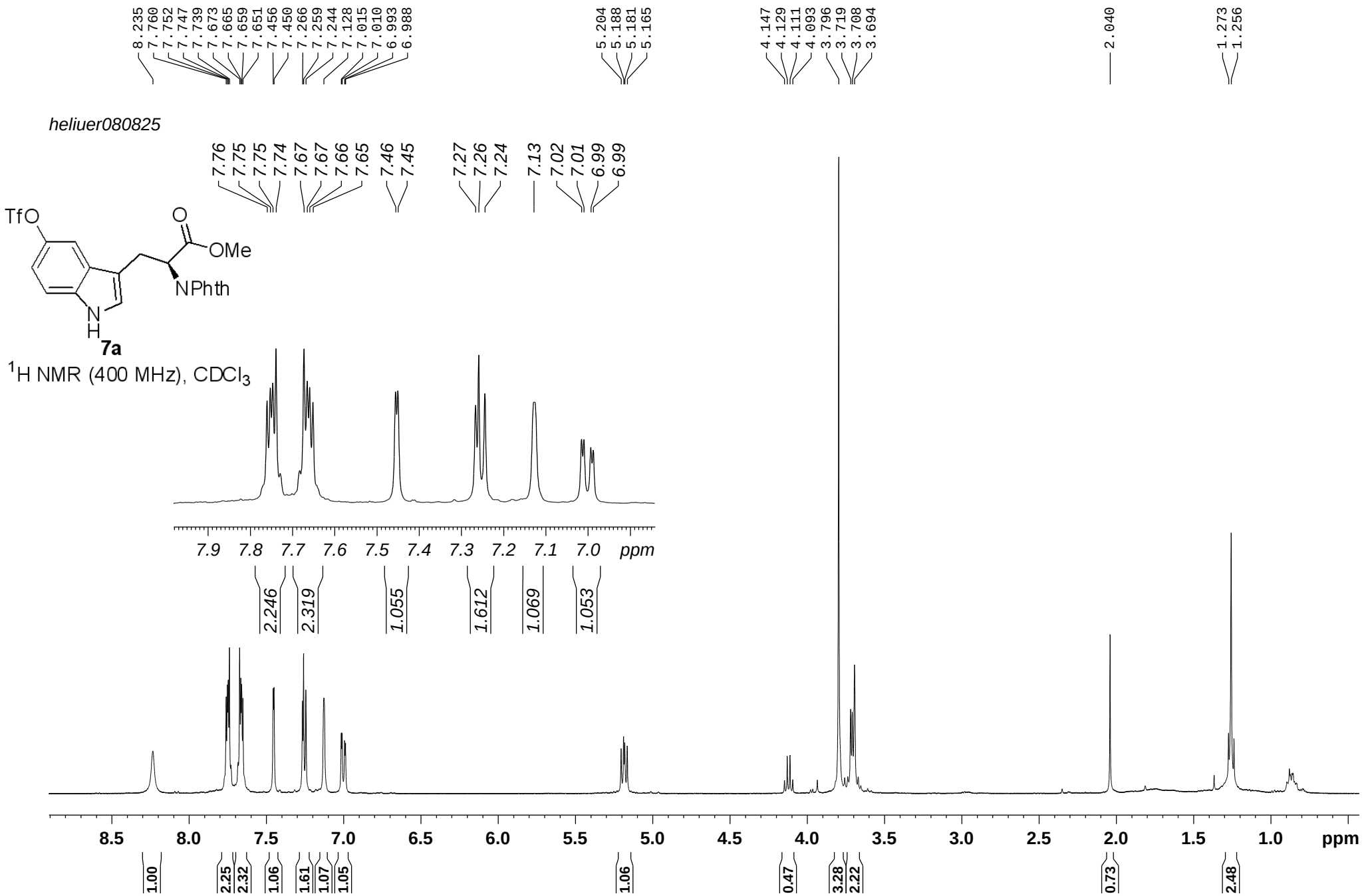
7

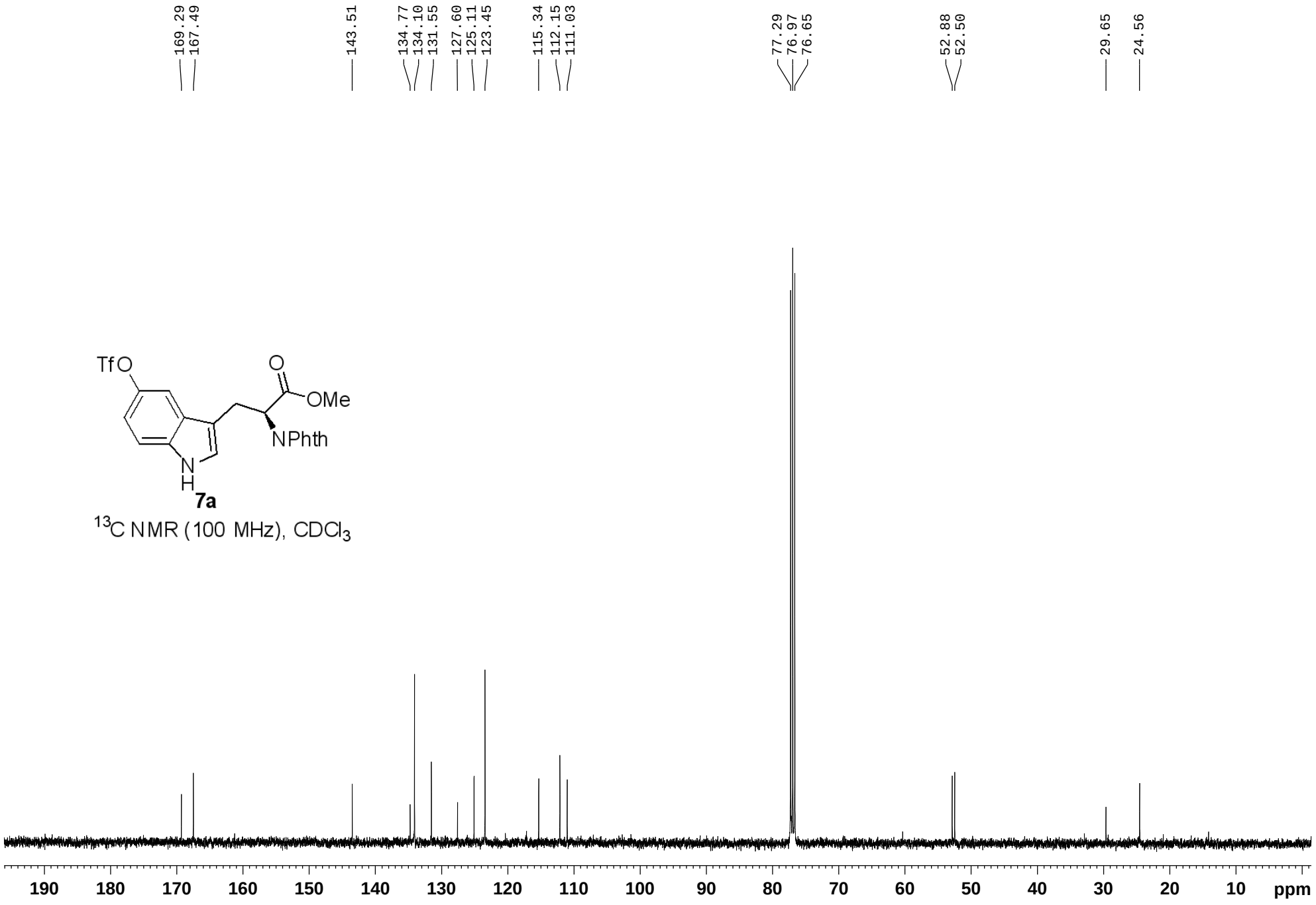
^{1}H NMR (400 MHz), DMSO-d_6

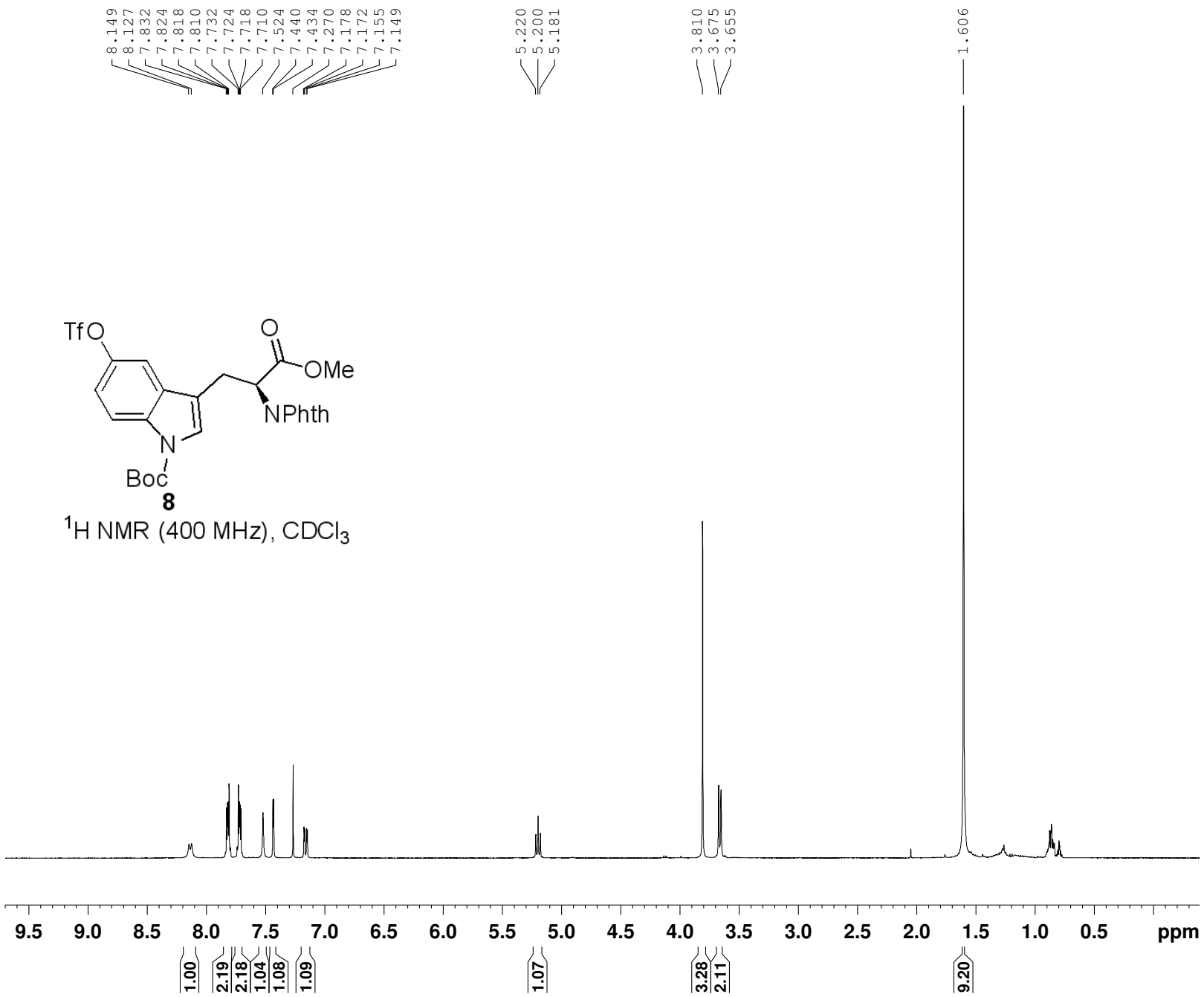
NAME	heliuer091109-1
EXPNO	10
PROCNO	1
Date_	20091111
Time	0.26
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	DMSO
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	90.5
DW	60.800 usec
DE	6.50 usec
TE	295.7 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	-1.00 dB
PL1W	13.75590801 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1299970 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



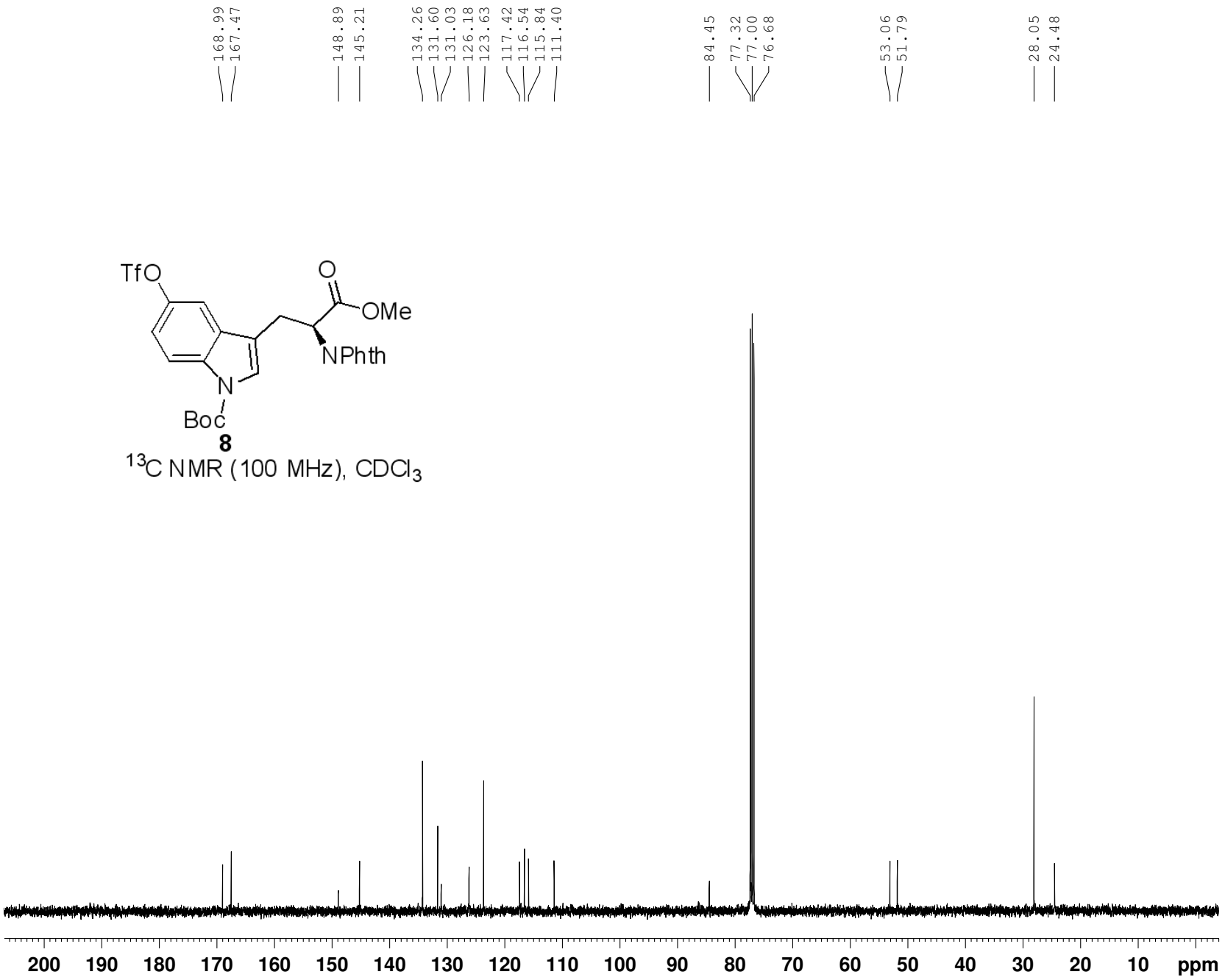

```
NAME      heliuer091109-1
EXPNO                  11
PROCNO                  1
Date_            20091111
Time                 0.34
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT              DMSO
NS                     128
DS                       4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                     645
DW                20.800 usec
DE                 6.50 usec
TE                297.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.70 usec
PL1                 -2.00 dB
PL1W         56.13311005 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                  1H
PCPD2               80.00 usec
PL2                 -2.10 dB
PL12                13.90 dB
PL13                13.90 dB
PL2W         17.72104263 W
PL12W         0.44513249 W
PL13W         0.44513249 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```


8.235
7.760
7.752
7.747
7.739
7.673
7.665
7.659
7.651
7.456
7.450
7.266
7.259
7.244
7.128
7.015
7.010
6.993
6.988
5.204
5.188
5.181
5.165
4.147
4.129
4.111
4.093
3.796
3.719
3.708
3.694
2.040
1.273
1.256
heliuer080825
7.76
7.75
7.75
7.74
7.67
7.67
7.66
7.65
7.46
7.45
7.27
7.26
7.24
7.13
7.02
7.01
6.99
6.99
TfO
O
OMe
NPhth
N
H
7a
1H NMR (400 MHz), CDCl3
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
ppm
2.246
2.319
1.055
1.612
1.069
1.053
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
ppm
1.00
2.25
2.32
1.06
1.61
1.07
1.05
1.06
0.47
3.28
2.22
0.73
2.48

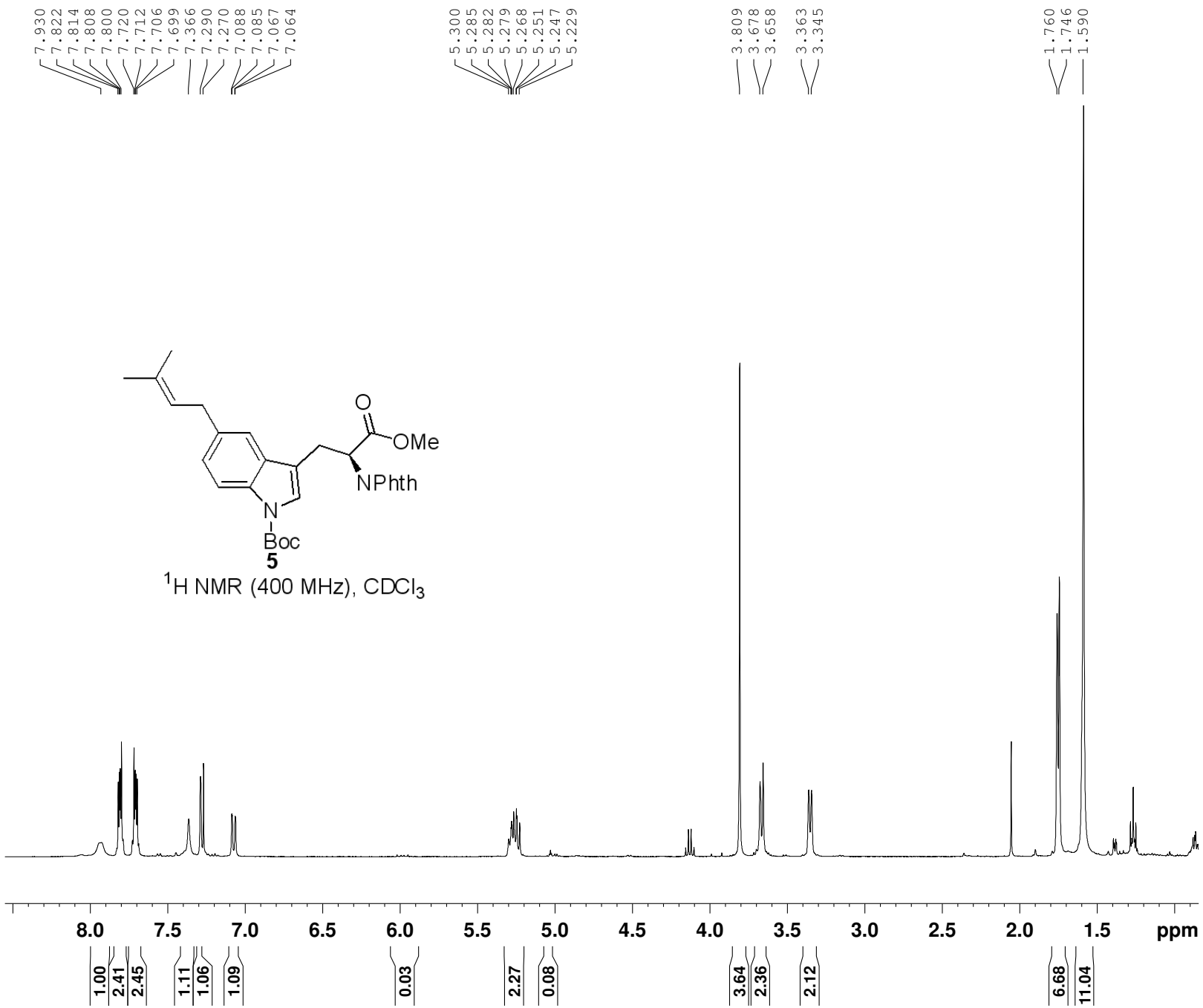

169.29
167.49
143.51
134.77
134.10
131.55
127.60
125.11
123.45
115.34
112.15
111.03
77.29
76.97
76.65
52.88
52.50
29.65
24.56
TfO
O
OMe
NPhth
N
H
7a
13C NMR (100 MHz), CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



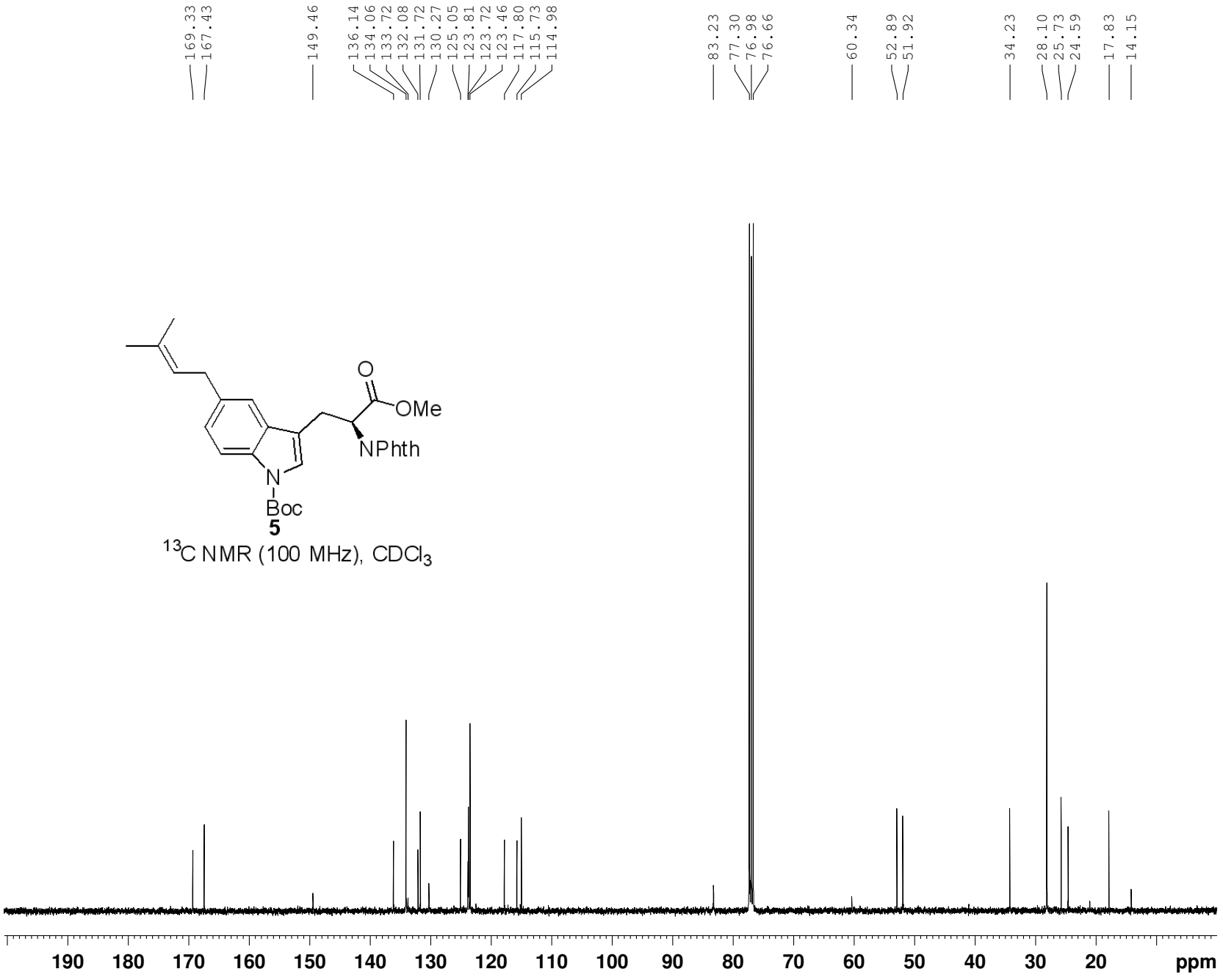

```
NAME       heliuer0926-1
EXPNO                 10
PROCNO                 1
Date_           20080926
Time               17.26
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   228
DW                60.800 usec
DE                 6.50 usec
TE                294.6 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.60 usec
PL1                0.00 dB
PL1W        11.47932053 W
SFO1        400.1324710 MHz
SI                 32768
SF          400.1300008 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```



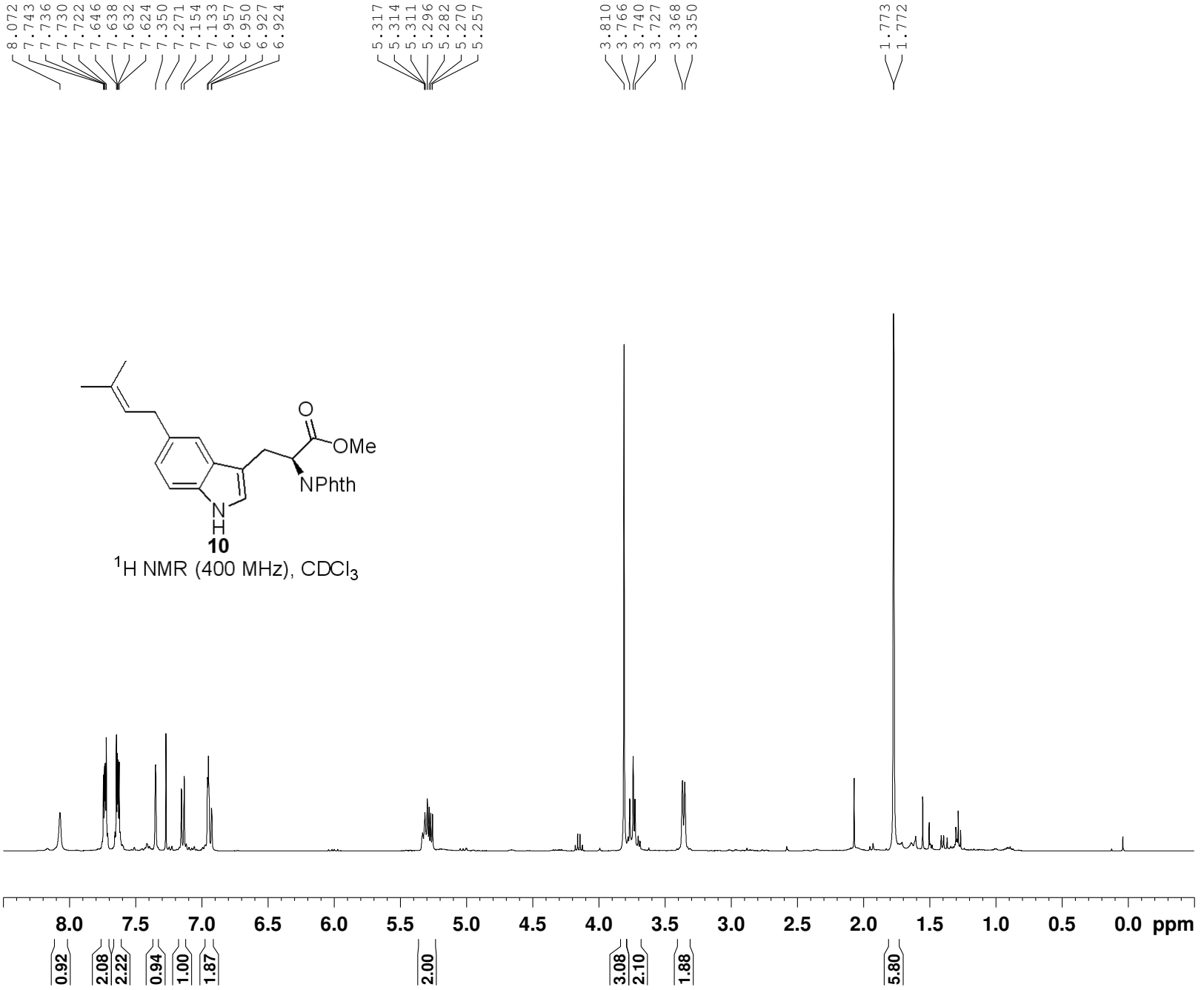

```
NAME        heliuer0926-1
EXPNO                  11
PROCNO                  1
Date_            20080926
Time                17.42
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                295.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.40 usec
PL1                -2.00 dB
PL1W         57.32743073 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                -2.00 dB
PL12               15.50 dB
PL13               15.50 dB
PL2W         18.19349861 W
PL12W         0.32353121 W
PL13W         0.32353121 W
SFO2         400.1316005 MHz
SI                 32768
SF           100.6127692 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



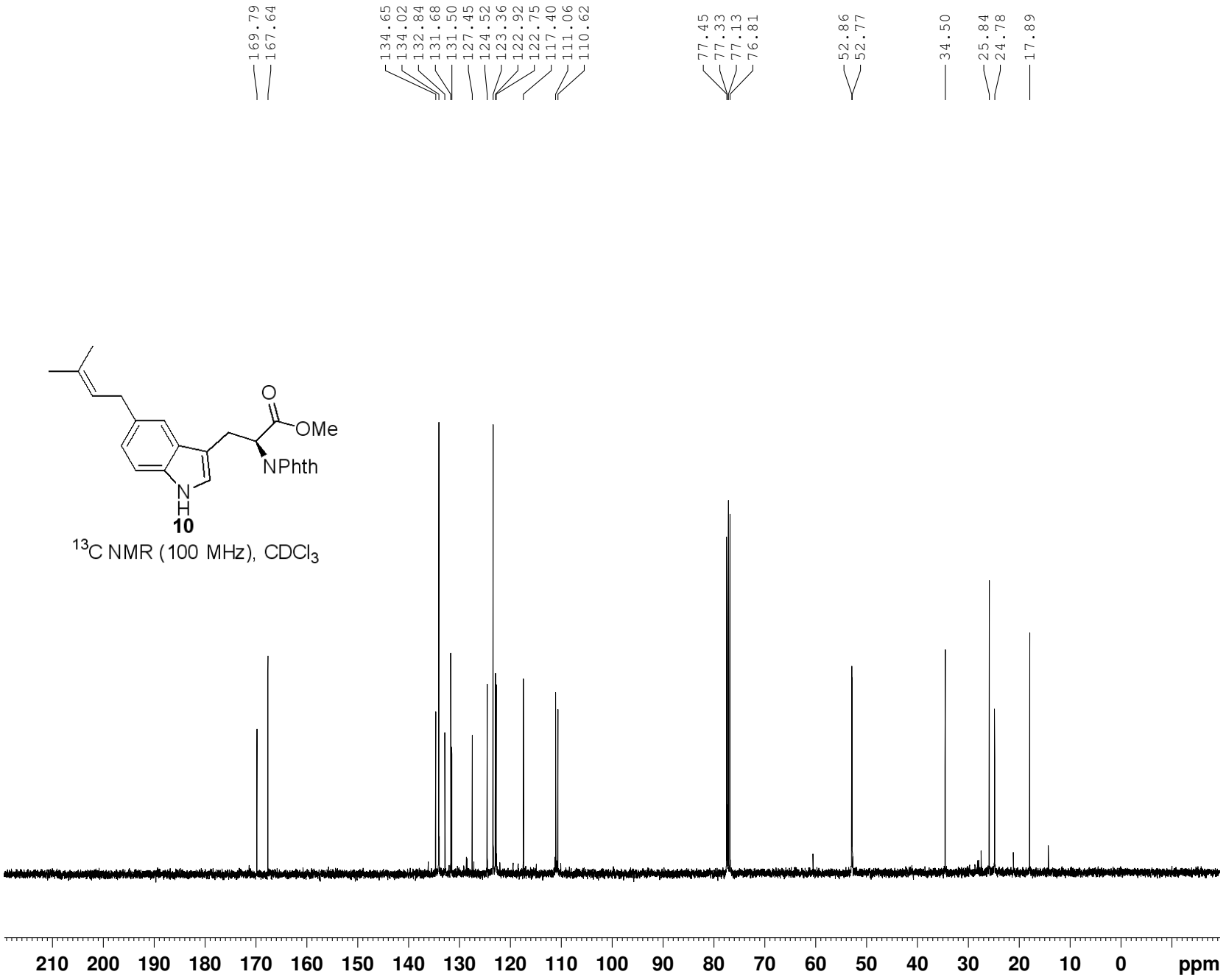

```
NAME       heliuer081216
EXPNO                 10
PROCNO                 1
Date_           20081215
Time               10.03
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   144
DW                60.800 usec
DE                 6.50 usec
TE                291.3 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.60 usec
PL1                0.00 dB
PL1W         11.47932053 W
SFO1         400.1324710 MHz
SI                 32768
SF           400.1300009 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```



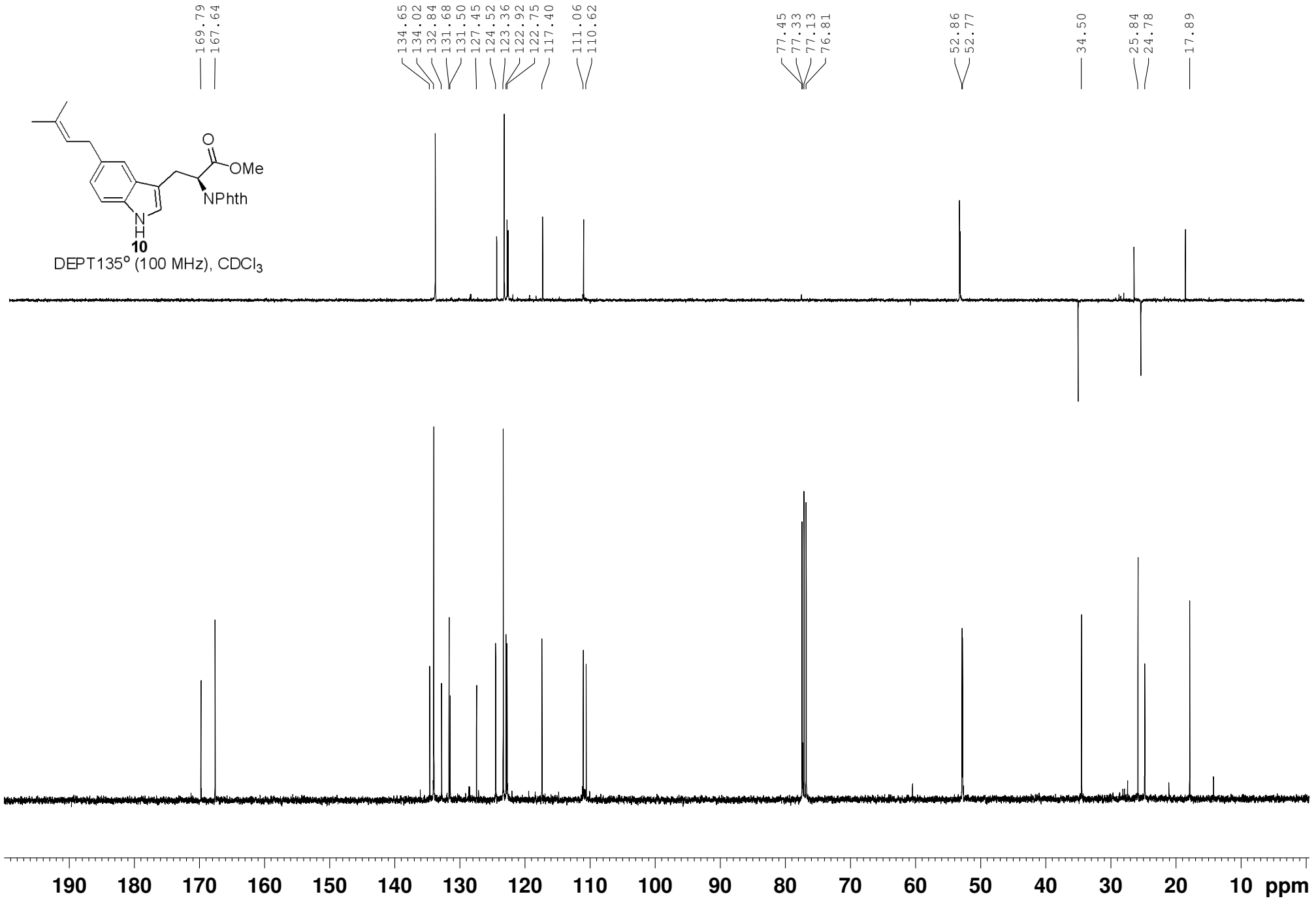
NAME	heliuer1216-1
EXPNO	10
PROCNO	1
Date_	20081215
Time	13.54
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	512
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	101
DW	20.800 usec
DE	6.50 usec
TE	294.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.70 usec
PL1	-2.00 dB
PL1W	56.13311005 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.10 dB
PL12	13.90 dB
PL13	13.90 dB
PL2W	17.72104263 W
PL12W	0.44513249 W
PL13W	0.44513249 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127732 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

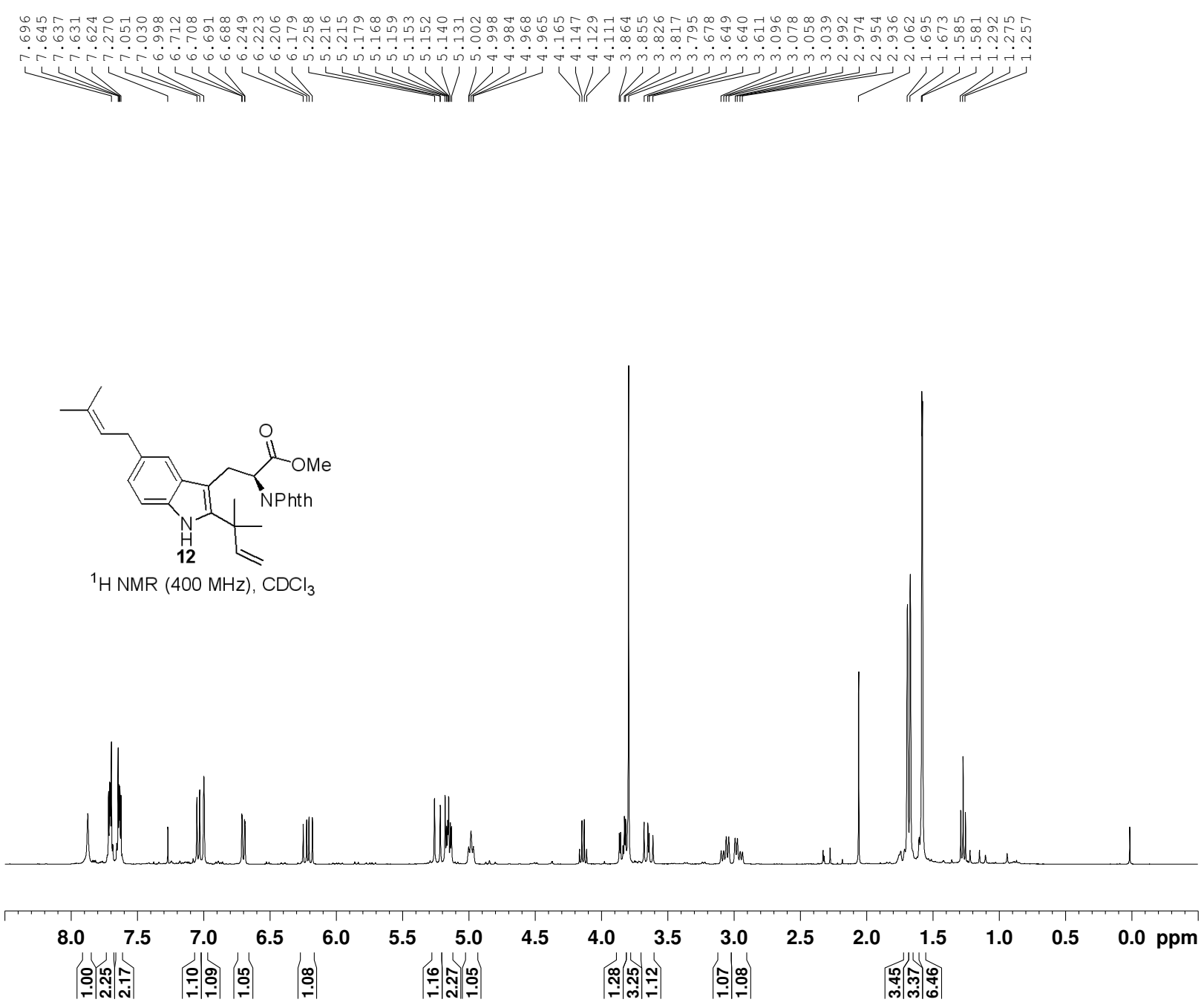



```
NAME      heliuer091124-1
EXPNO                  10
PROCNO                  1
Date_            20091125
Time                 8.15
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   80.6
DW                60.800 usec
DE                 6.50 usec
TE                291.0 K
D1           1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.00 usec
PL1                -3.00 dB
PL1W         22.90425682 W
SFO1         400.1324710 MHz
SI                  32768
SF           400.1300000 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```

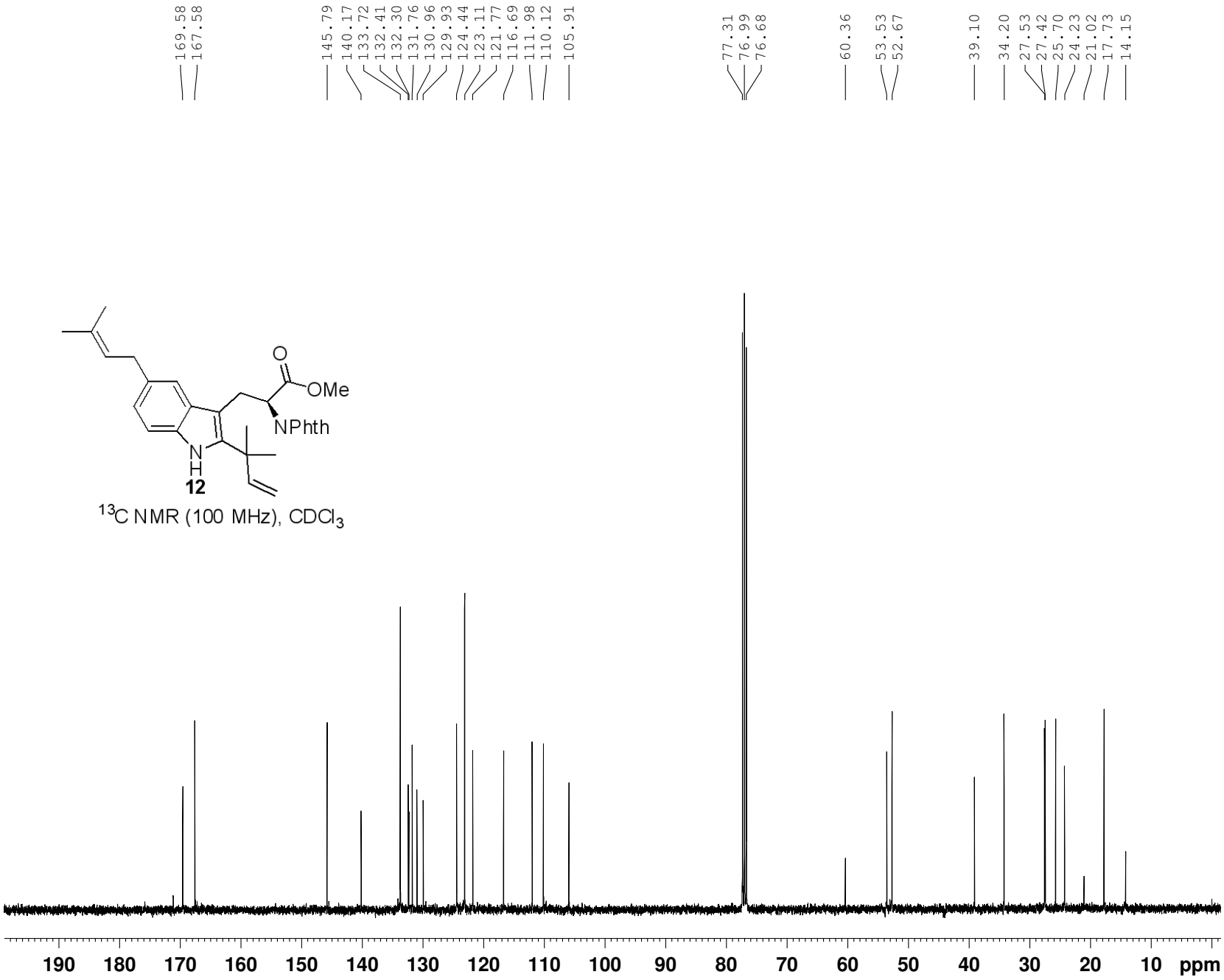



```
NAME      heliuer091124-1
EXPNO                  11
PROCNO                  1
Date_            20091125
Time                 8.23
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                    2050
DW                 20.800 usec
DE                  6.50 usec
TE                 291.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.40 usec
PL1                 -2.00 dB
PL1W         57.32743073 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2               90.00 usec
PL2                 -2.00 dB
PL12                15.50 dB
PL13                15.50 dB
PL2W         18.19349861 W
PL12W         0.32353121 W
PL13W         0.32353121 W
SFO2         400.1316005 MHz
SI                   32768
SF           100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

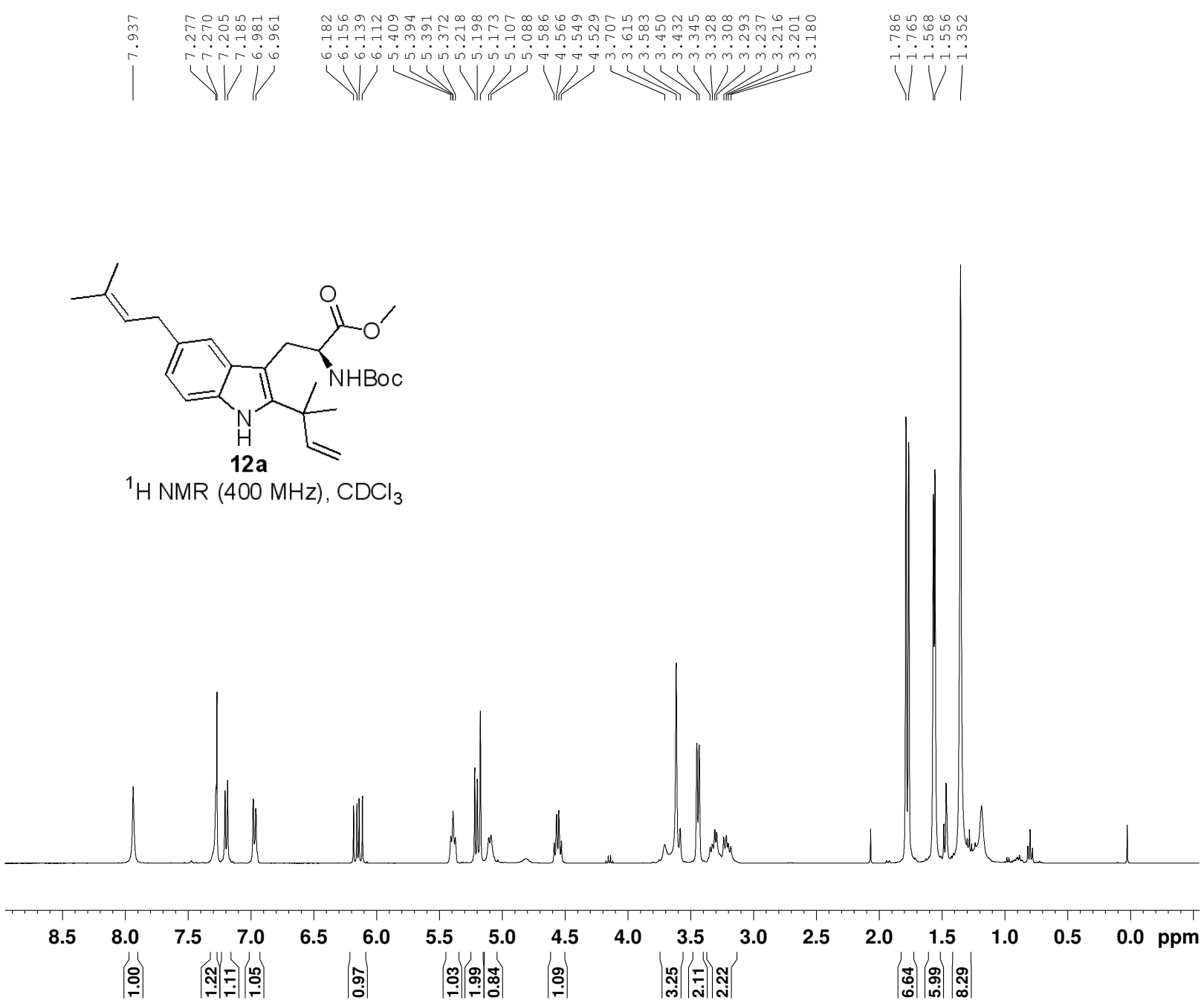

169.79
167.64
134.65
134.02
132.84
131.68
131.50
127.45
124.52
123.36
122.92
122.75
117.40
111.06
110.62
77.45
77.33
77.13
76.81
52.86
52.77
34.50
25.84
24.78
17.89
O
OMe
NPhth
N
H
10
DEPT135° (100 MHz), CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



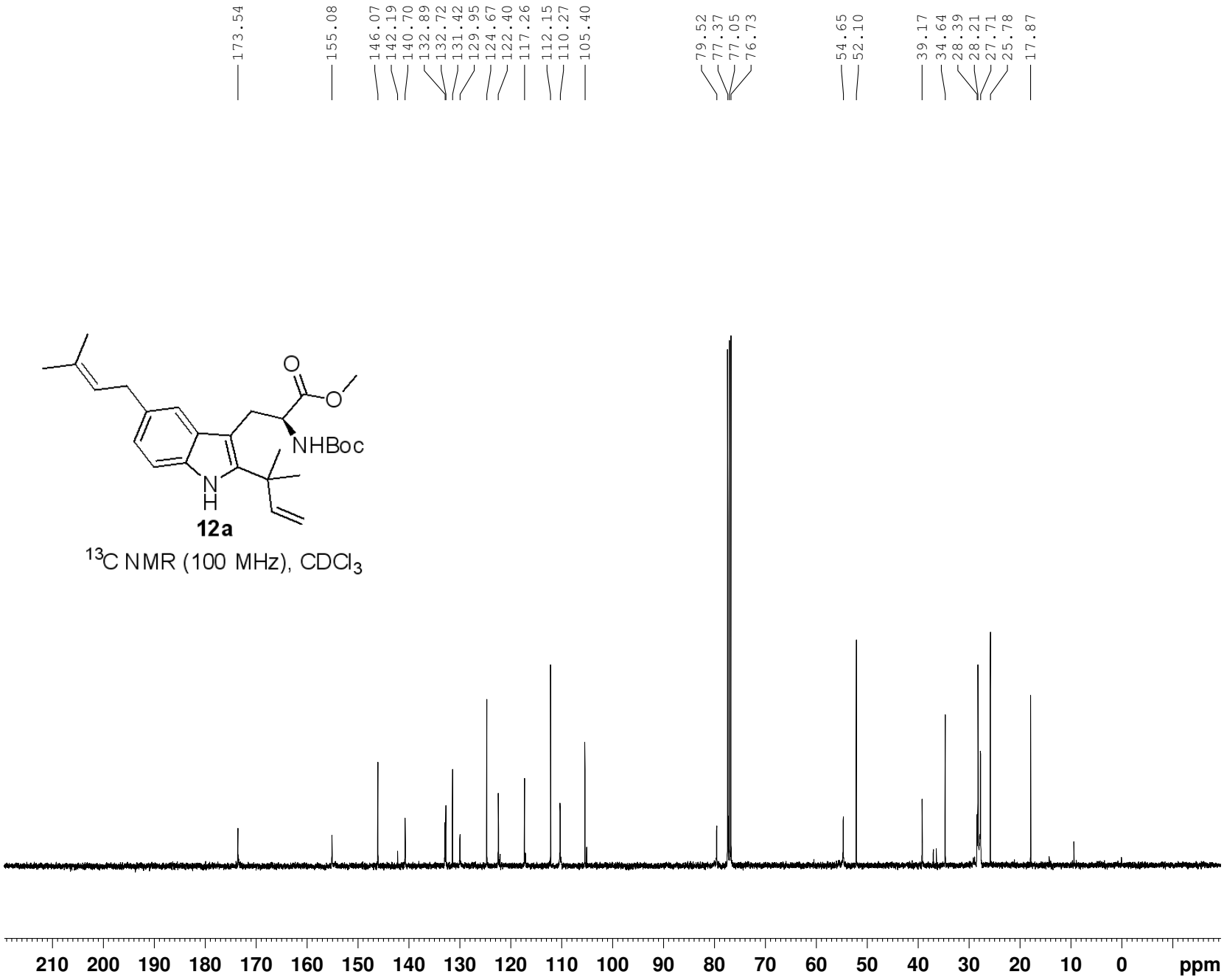
NAME	heliuer090227-1
EXPNO	10
PROCNO	1
Date_	20090227
Time	7.04
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	71.8
DW	60.800 usec
DE	6.50 usec
TE	289.1 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.70 usec
PL1	-1.00 dB
PL1W	13.75590801 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1300013 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



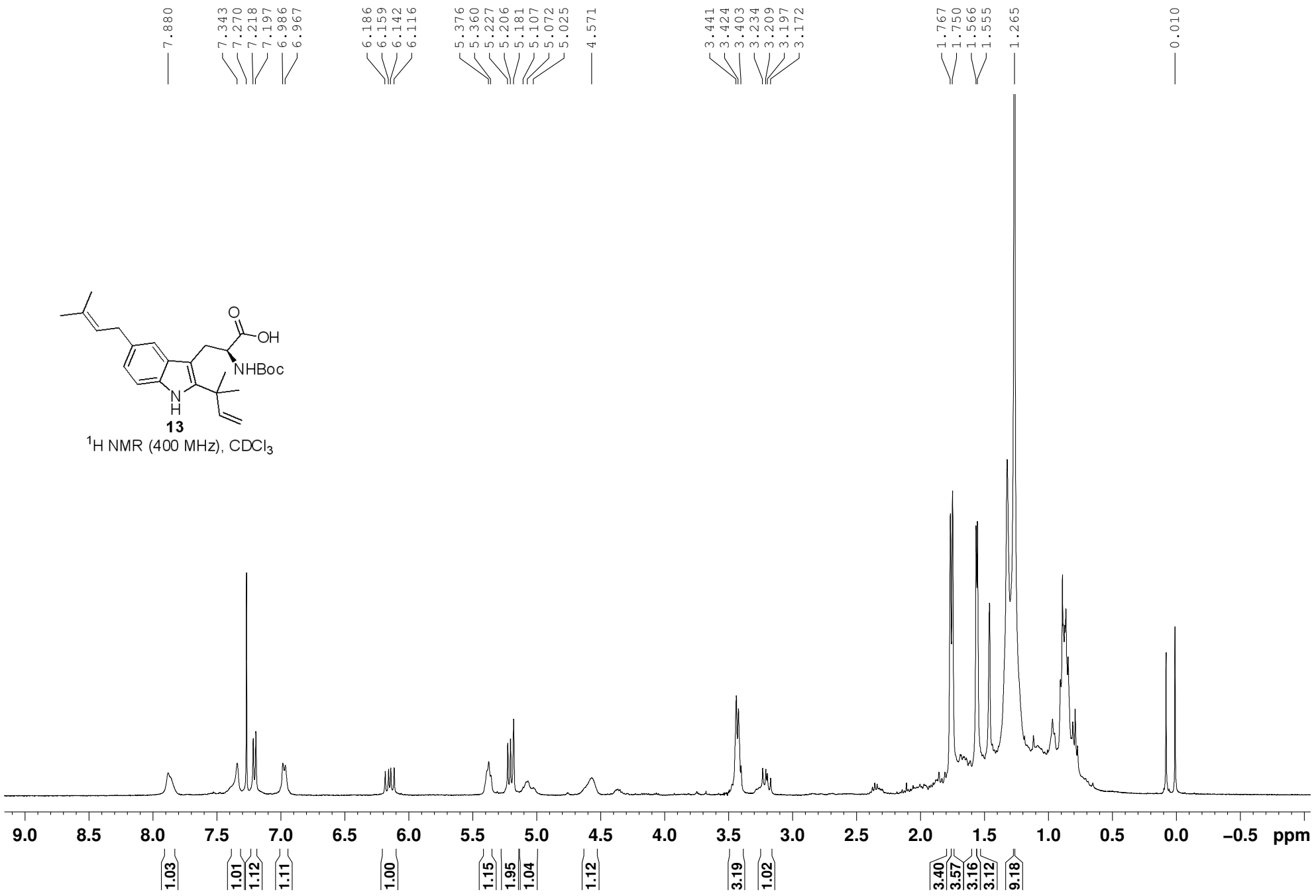
NAME	heliuer090227-1
EXPNO	11
PROCNO	1
Date_	20090227
Time	7.21
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	256
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	575
DW	20.800 usec
DE	6.50 usec
TE	290.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.70 usec
PL1	-2.00 dB
PL1W	56.13311005 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.10 dB
PL12	13.90 dB
PL13	13.90 dB
PL2W	17.72104263 W
PL12W	0.44513249 W
PL13W	0.44513249 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127750 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40




```
NAME      heliuer100306-1
EXPNO                  10
PROCNO                  1
Date_            20100306
Time                16.07
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                     57
DW                 60.800 usec
DE                  6.50 usec
TE                 293.3 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.70 usec
PL1                -1.00 dB
PL1W         13.75590801 W
SFO1         400.1324710 MHz
SI                  32768
SF           400.1300008 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

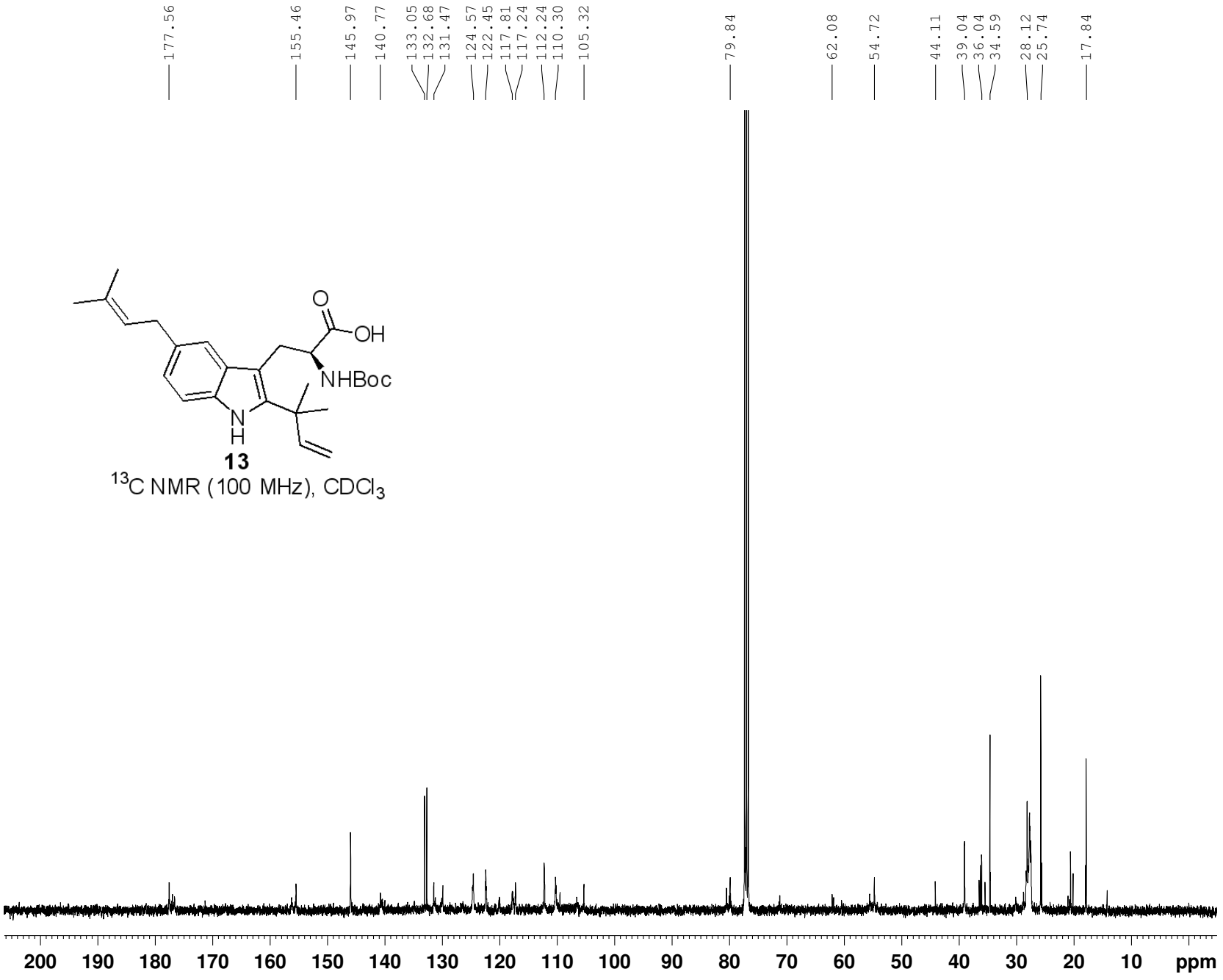



```
NAME      heliuer100306-1
EXPNO                  11
PROCNO                  1
Date_            20100306
Time                16.30
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                    368
DS                      4
SWH             24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                   90.5
DW                 20.800 usec
DE                  6.50 usec
TE                 295.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.70 usec
PL1                 -2.00 dB
PL1W         56.13311005 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2               80.00 usec
PL2                 -2.10 dB
PL12                13.90 dB
PL13                13.90 dB
PL2W         17.72104263 W
PL12W         0.44513249 W
PL13W         0.44513249 W
SFO2         400.1316005 MHz
SI                  32768
SF           100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



13

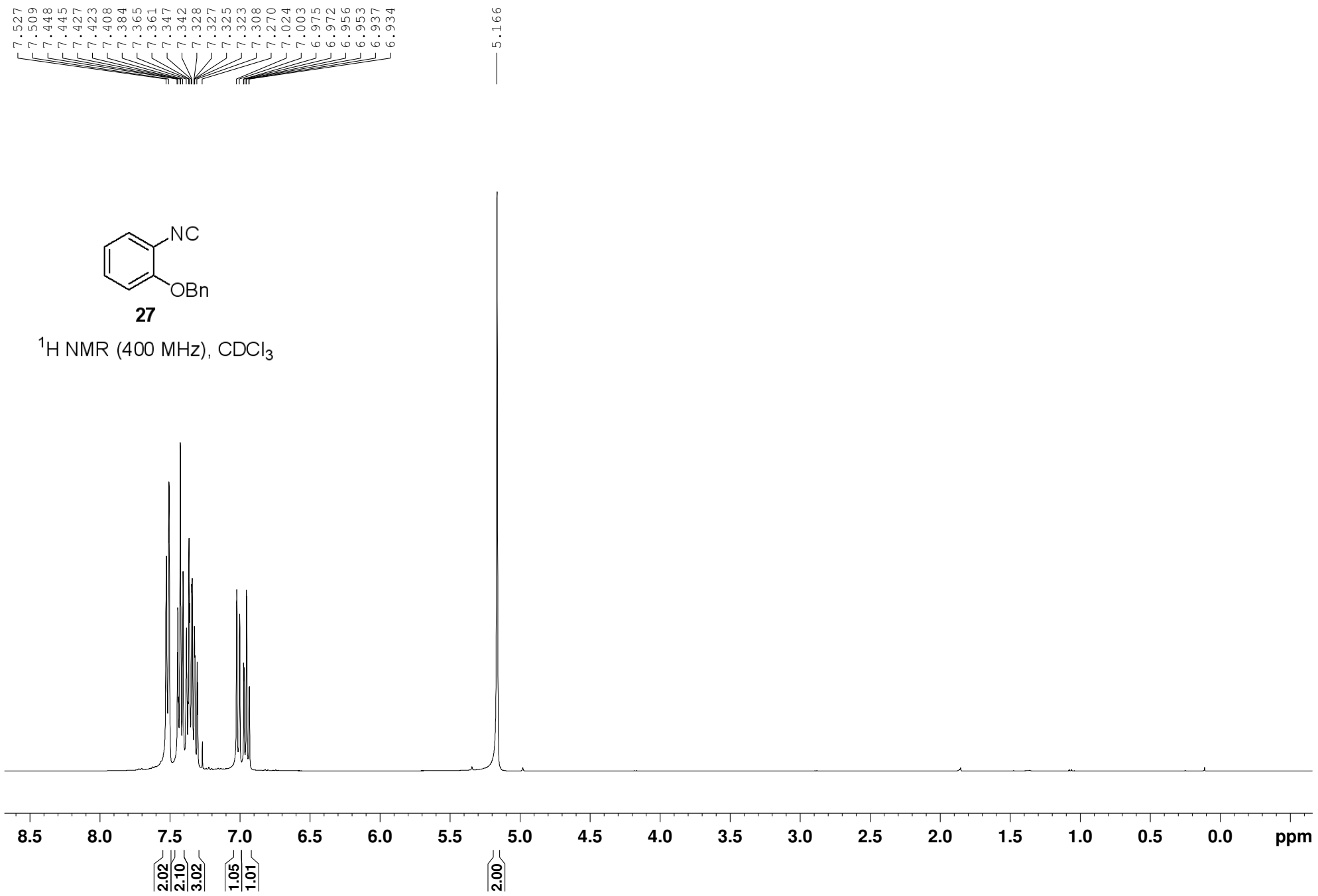
^{1}H NMR (400 MHz), $CDCl_3$

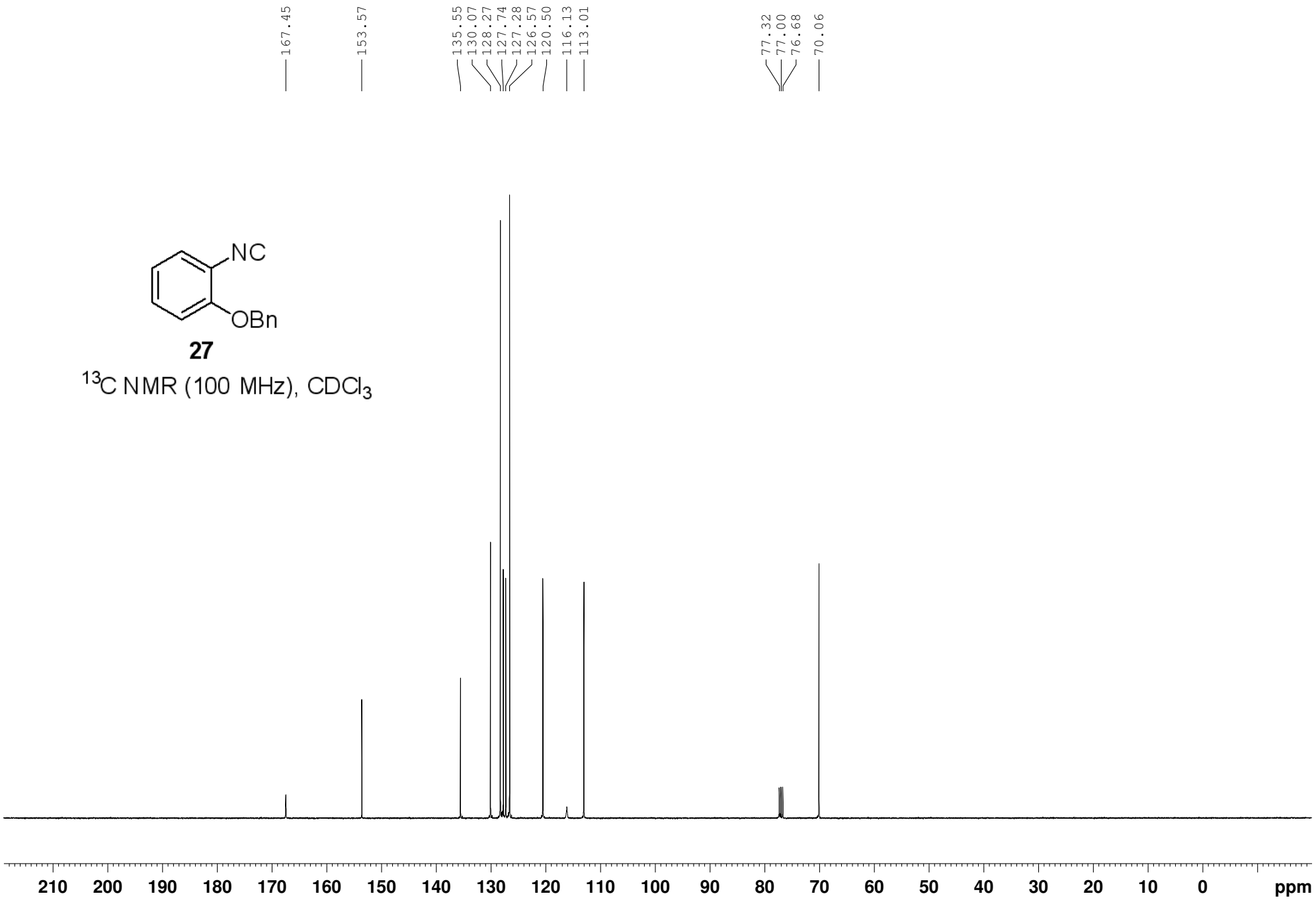


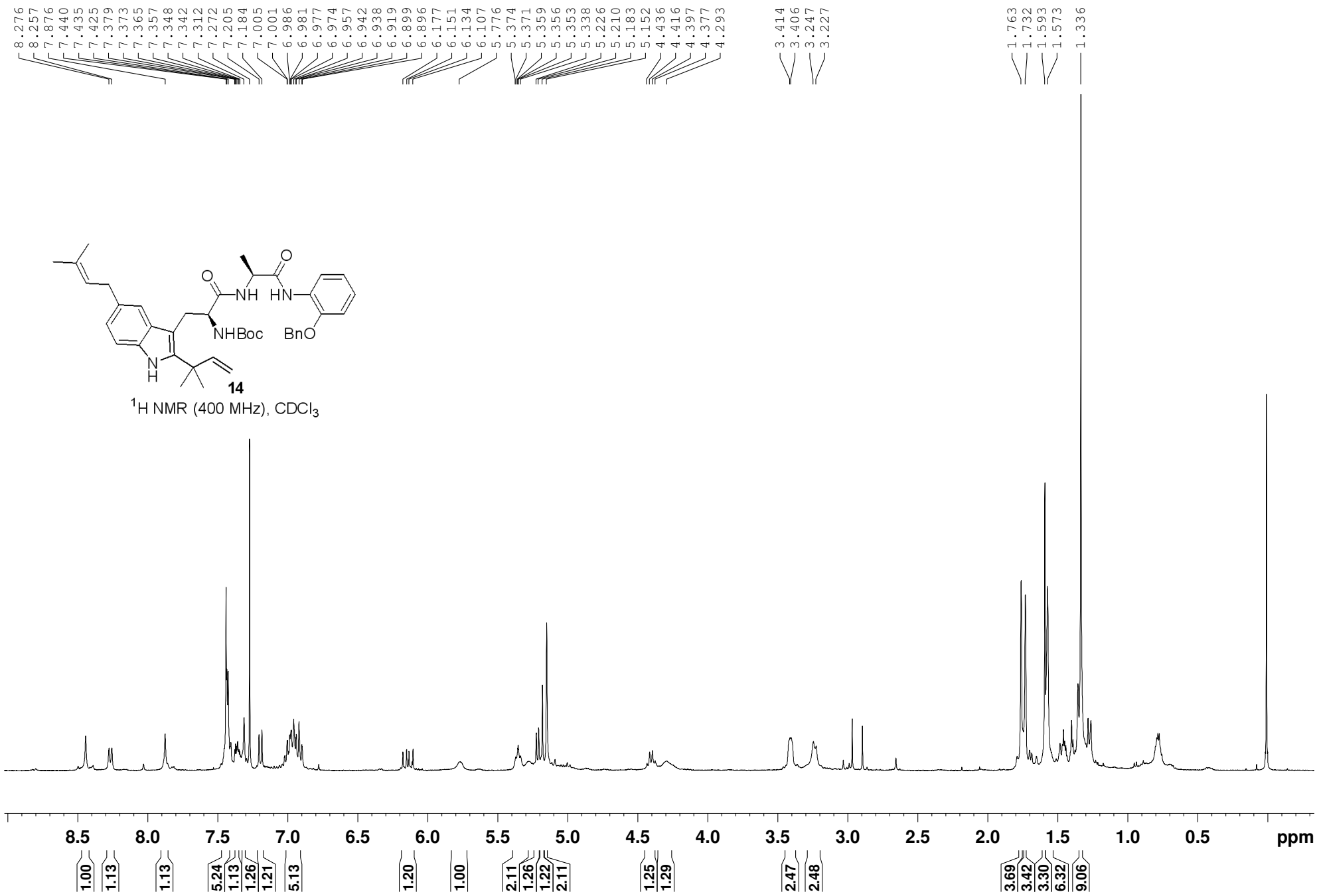
13

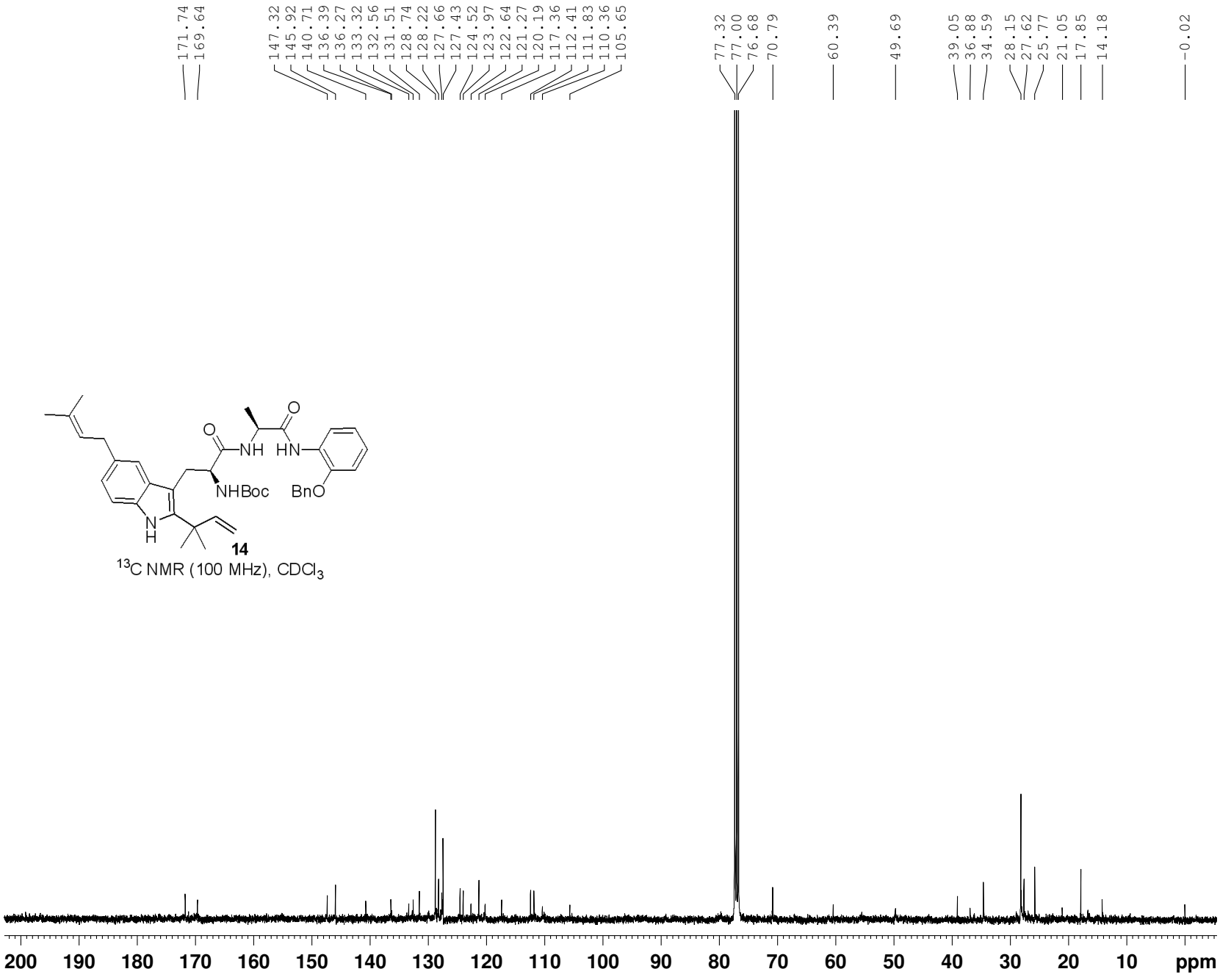
^{13}C NMR (100 MHz), $CDCl_3$

NAME	heliuer20110223-1
EXPNO	11
PROCNO	1
Date_	20110224
Time	4.31
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	293.9 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.40 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-2.00 dB
PL12	15.50 dB
PL13	15.50 dB
PL2W	18.19349861 W
PL12W	0.32353121 W
PL13W	0.32353121 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127729 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40


7.527
7.509
7.448
7.445
7.427
7.423
7.408
7.384
7.365
7.361
7.347
7.342
7.328
7.327
7.325
7.323
7.308
7.270
7.024
7.003
6.975
6.972
6.956
6.953
6.937
6.934
5.166
NC
OBn
27
1H NMR (400 MHz), CDCl3
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
ppm
2.02
2.10
3.02
1.05
1.01
2.00


167.45
153.57
135.55
130.07
128.27
127.74
127.28
126.57
120.50
116.13
113.01
77.32
77.00
76.68
70.06
NC
OBn
27
13C NMR (100 MHz), CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

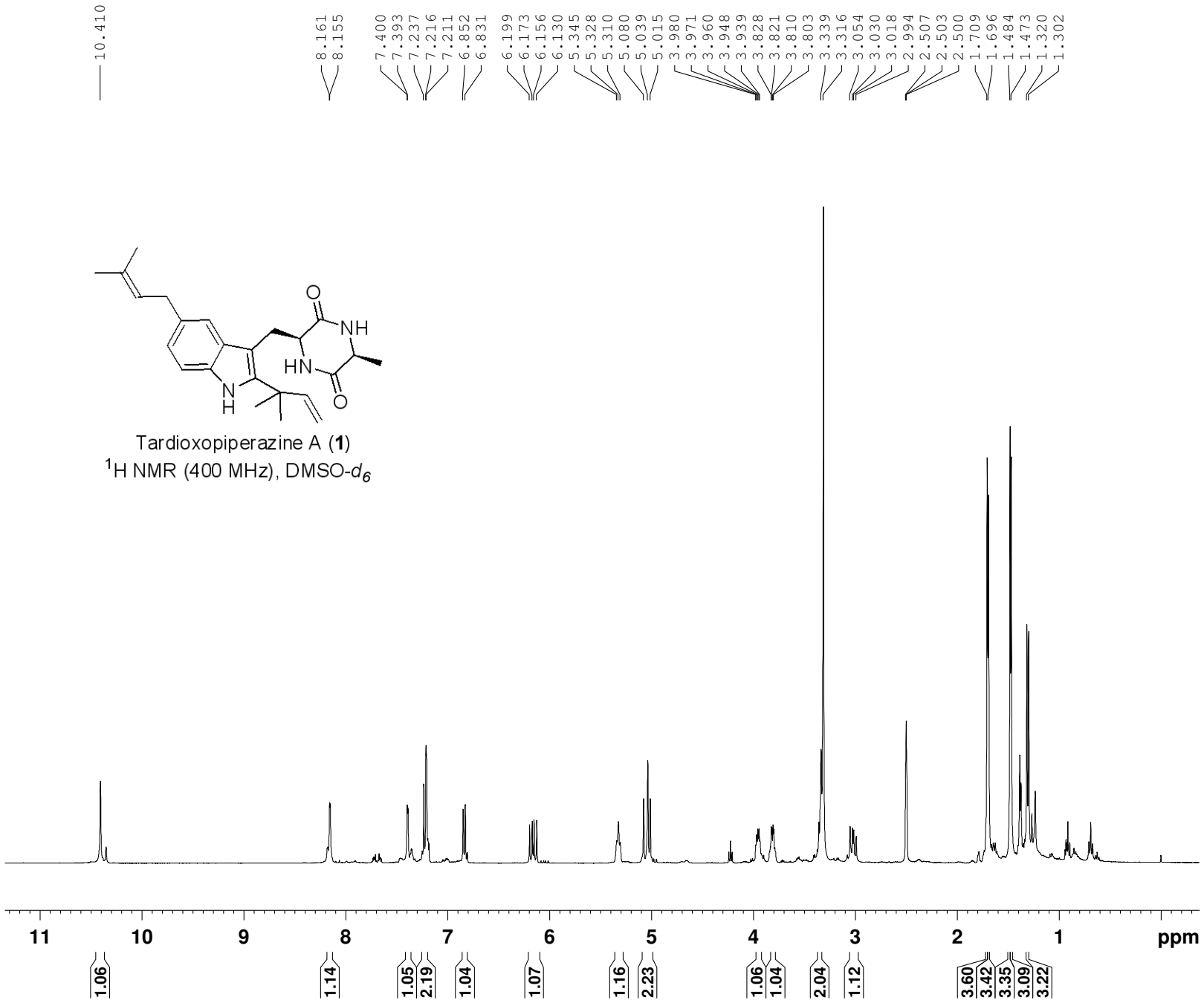

8.276
8.257
7.876
7.440
7.435
7.425
7.379
7.373
7.365
7.357
7.348
7.342
7.312
7.272
7.205
7.184
7.005
7.001
6.986
6.981
6.977
6.974
6.957
6.942
6.938
6.919
6.899
6.896
6.177
6.151
6.134
6.107
5.776
5.374
5.371
5.359
5.356
5.353
5.338
5.226
5.210
5.183
5.152
4.436
4.416
4.397
4.377
4.293
3.414
3.406
3.247
3.227
1.763
1.732
1.593
1.573
1.336
O
NH
HN
O
NHBoc
BnO
N
H
14
1H NMR (400 MHz), CDCl3
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
ppm
1.00
1.13
1.13
5.24
1.13
1.26
1.21
5.13
1.20
1.00
2.11
1.26
1.22
2.11
1.25
1.29
2.47
2.48
3.69
3.42
3.30
6.32
9.06



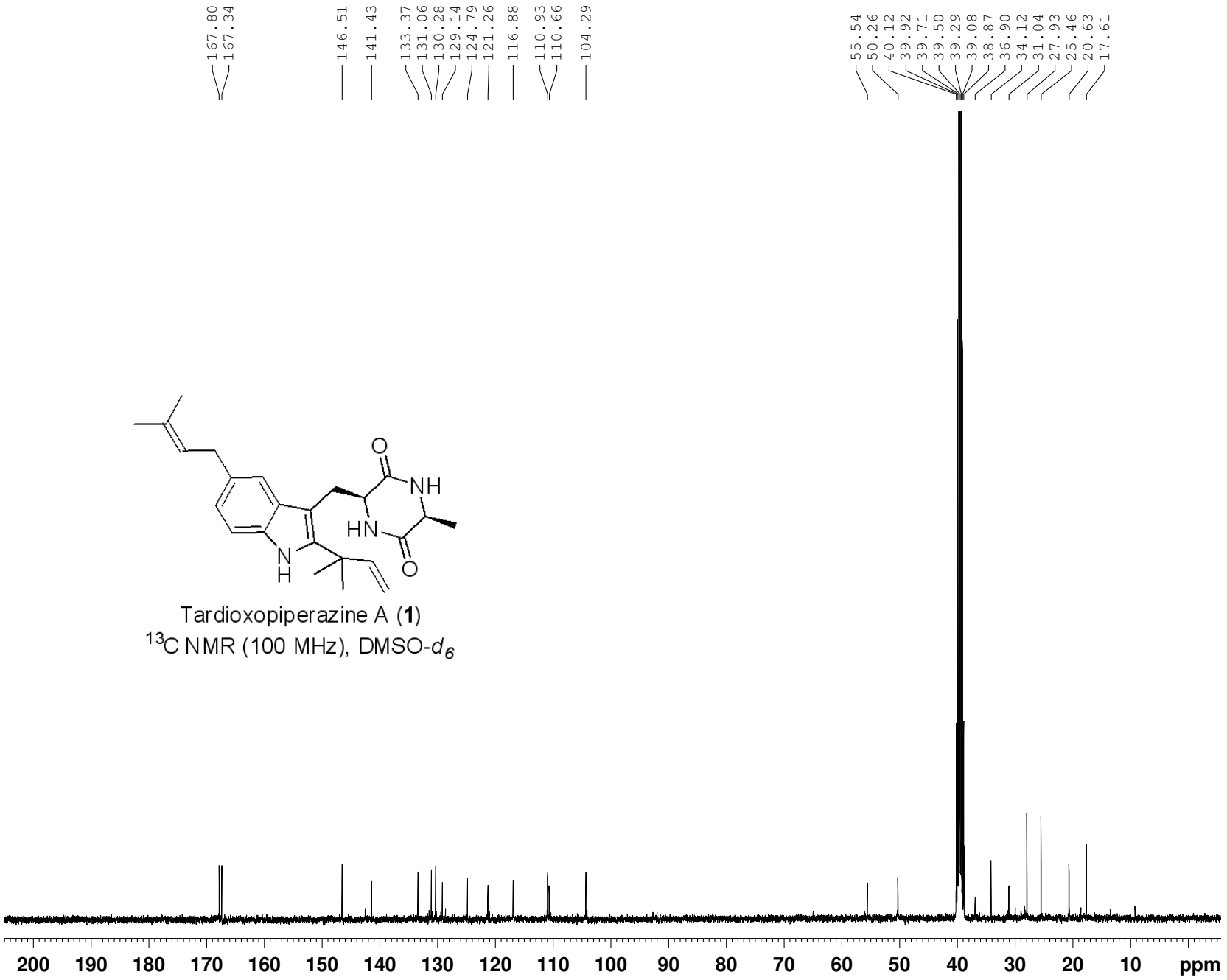
14

^{13}C NMR (100 MHz), $CDCl_3$

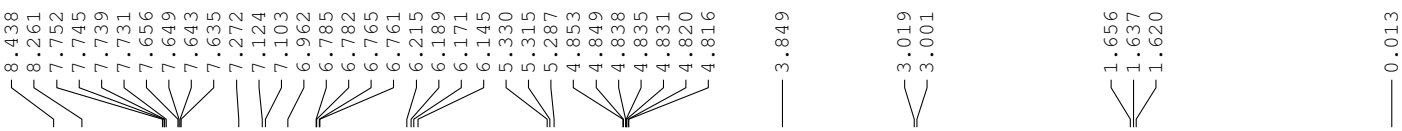
NAME	HELIUER20110228-1
EXPNO	11
PROCNO	1
Date_	20110228
Time	21.25
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	2048
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	291.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.40 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-2.00 dB
PL12	15.50 dB
PL13	15.50 dB
PL2W	18.19349861 W
PL12W	0.32353121 W
PL13W	0.32353121 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127714 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



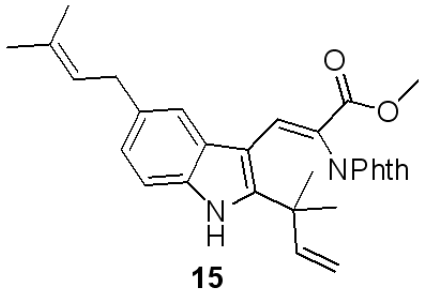
NAME	heliuer0902-2
EXPNO	10
PROCNO	1
Date_	20100903
Time	17.28
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	DMSO
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	144
DW	60.800 usec
DE	6.50 usec
TE	299.2 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	12.00 usec
PL1	-3.00 dB
PL1W	22.90425682 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1299952 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00




```
NAME        heliuer0902-2
EXPNO                  11
PROCNO                  1
Date_            20100903
Time                18.28
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT              DMSO
NS                   1024
DS                      4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                  2050
DW                20.800 usec
DE                 6.50 usec
TE                300.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.40 usec
PL1               -2.00 dB
PL1W        57.32743073 W
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             90.00 usec
PL2               -2.00 dB
PL12              15.50 dB
PL13              15.50 dB
PL2W        18.19349861 W
PL12W        0.32353121 W
PL13W        0.32353121 W
SFO2       400.1316005 MHz
SI                32768
SF         100.6128207 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

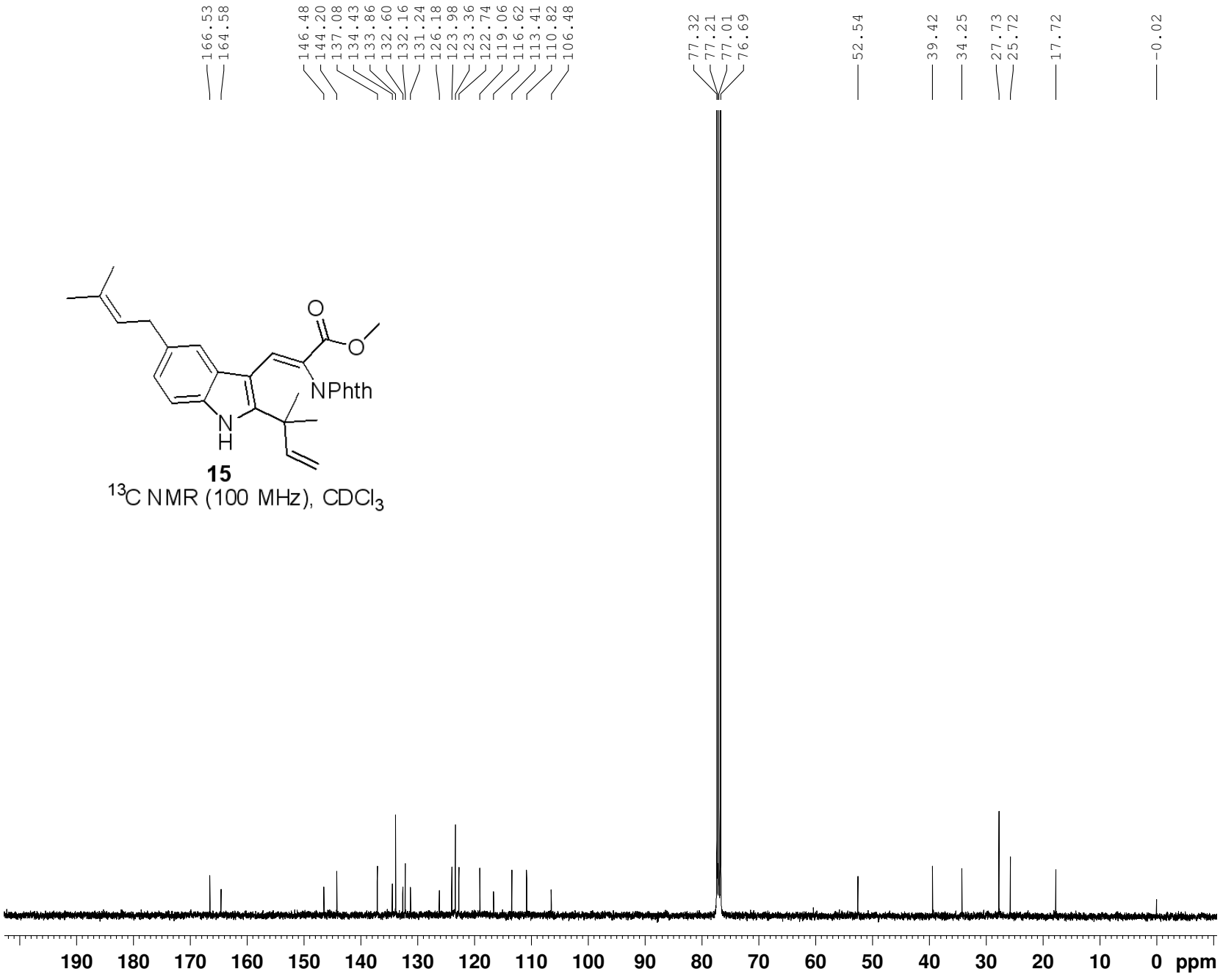



```
NAME      heliuer100531-1
EXPNO                  10
PROCNO                  1
Date_            20100601
Time                 8.36
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                    256
DW                60.800 usec
DE                 6.50 usec
TE                295.5 K
D1           1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.00 usec
PL1                -3.00 dB
PL1W         22.90425682 W
SFO1         400.1324710 MHz
SI                  32768
SF           400.1300000 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```

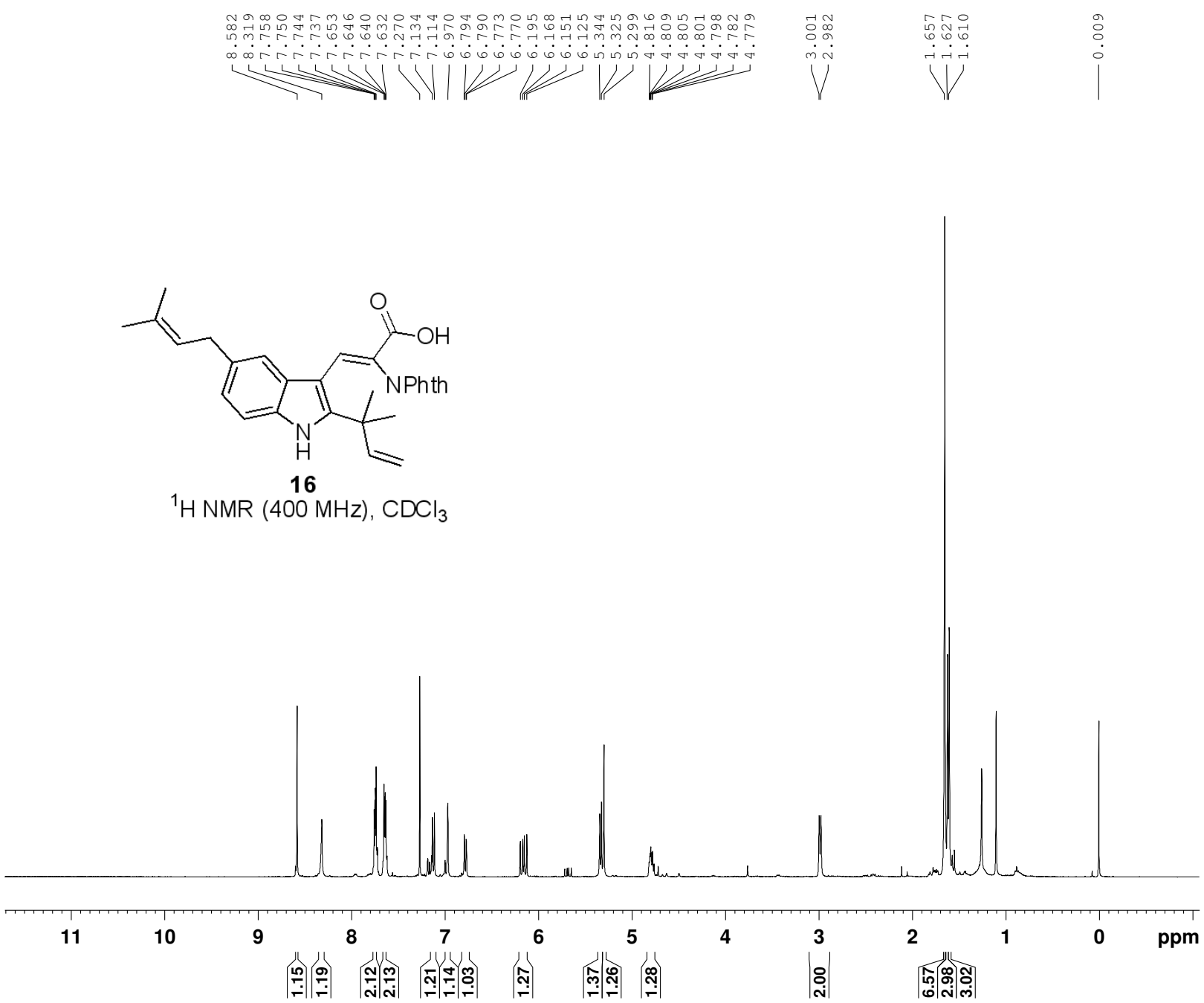


15

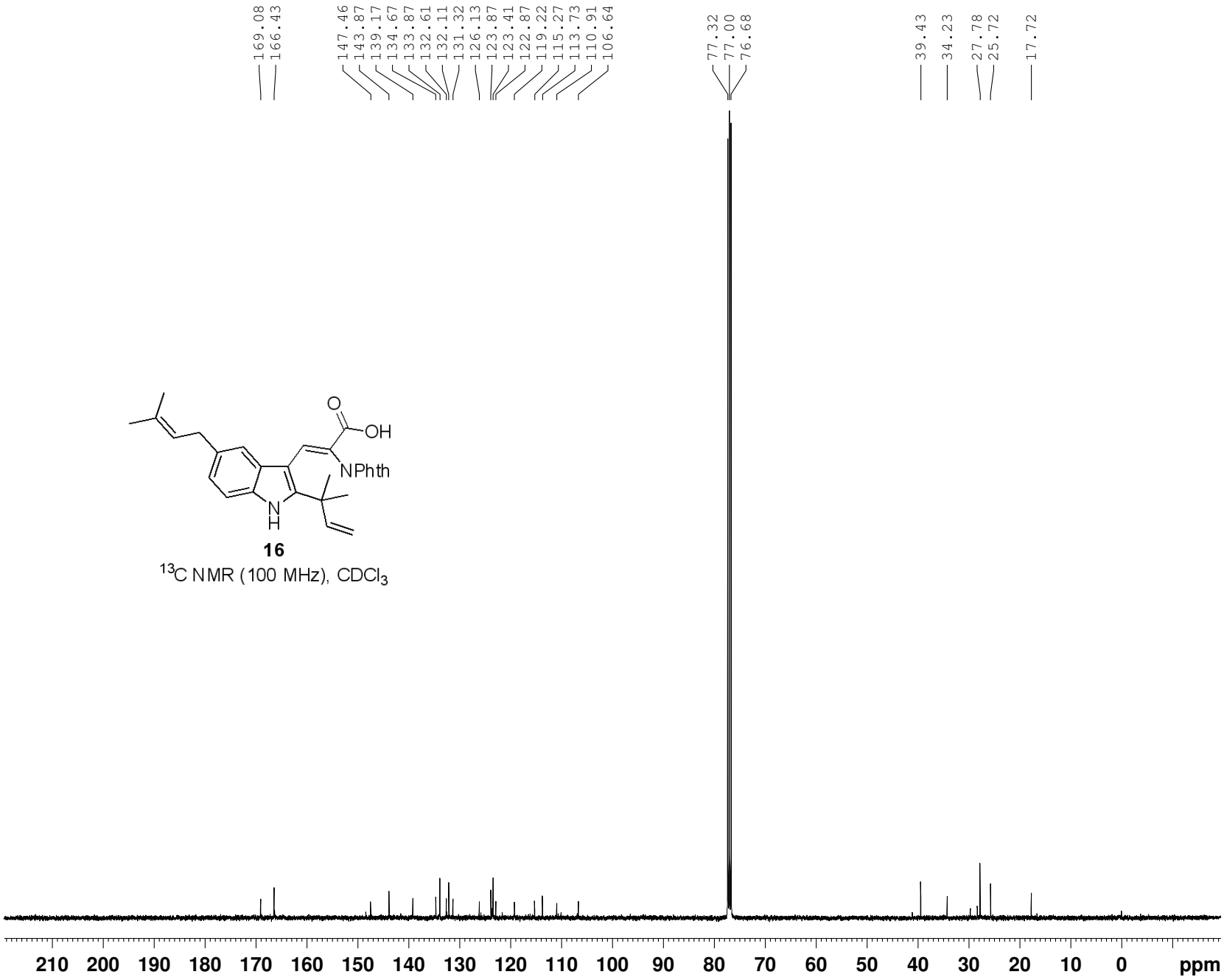
^{1}H NMR (400 MHz), $CDCl_3$



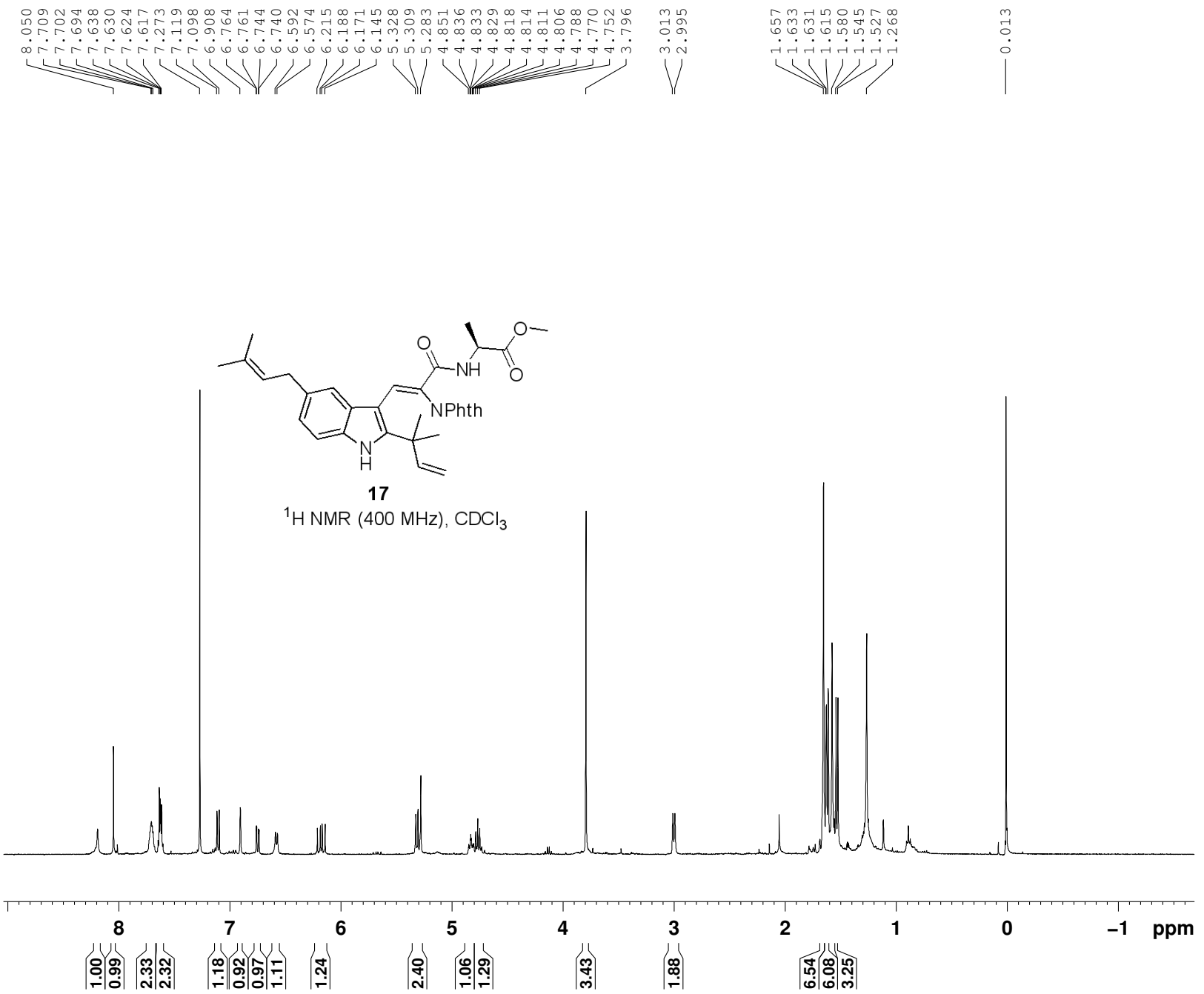
NAME	heliuer100531-1
EXPNO	11
PROCNO	1
Date_	20100601
Time	10.13
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1684
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	294.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.40 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-2.00 dB
PL12	15.50 dB
PL13	15.50 dB
PL2W	18.19349861 W
PL12W	0.32353121 W
PL13W	0.32353121 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



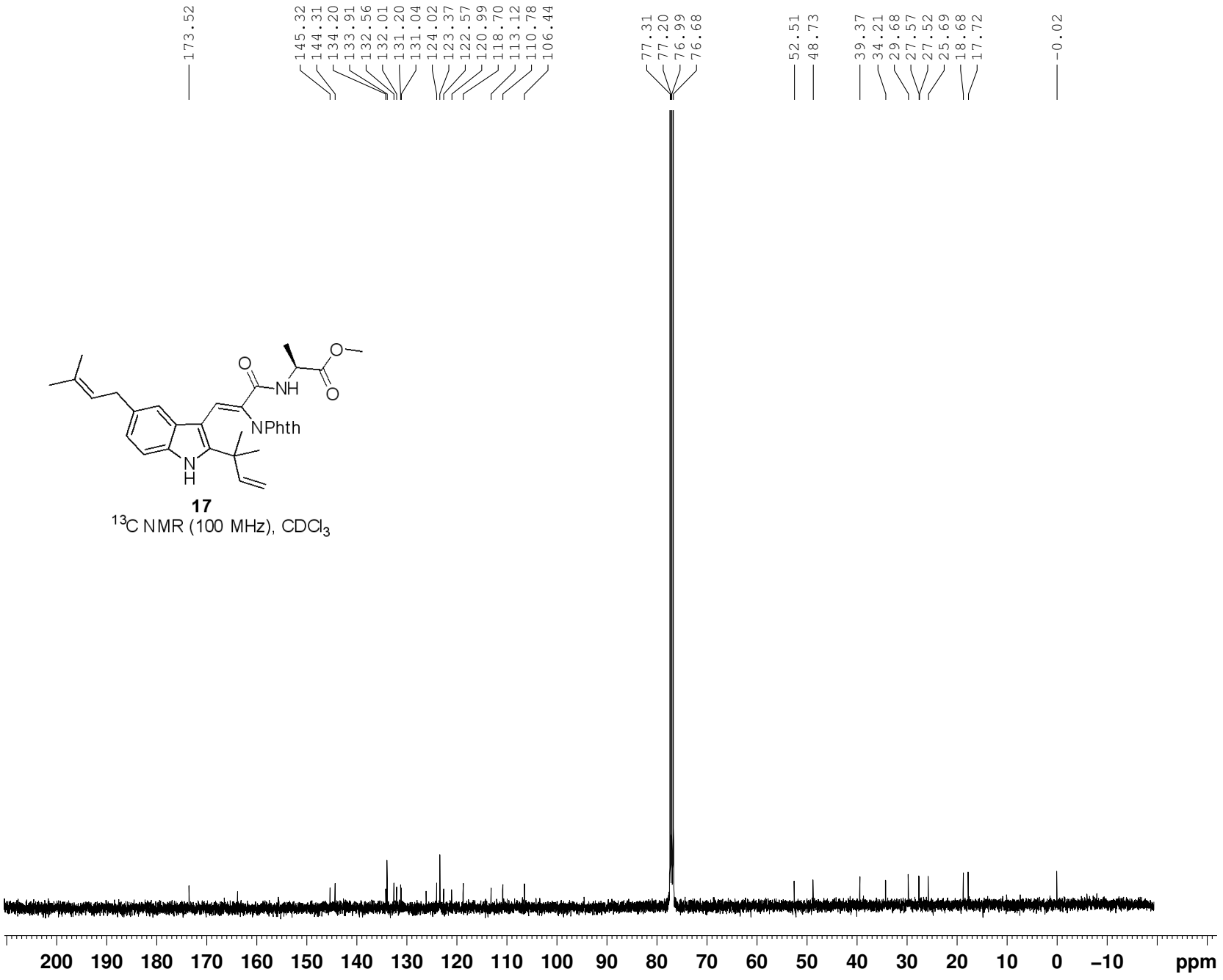

```
NAME      heliuer20110106-1
EXPNO                    10
PROCNO                    1
Date_              20110106
Time                  18.33
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                      287
DW                   60.800 usec
DE                    6.50 usec
TE                   288.9 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   12.00 usec
PL1                  -3.00 dB
PL1W            22.90425682 W
SFO1            400.1324710 MHz
SI                    32768
SF              400.1300013 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



NAME	heliuer20110106-1
EXPNO	11
PROCNO	1
Date_	20110106
Time	20.10
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1684
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	289.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.40 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-2.00 dB
PL12	15.50 dB
PL13	15.50 dB
PL2W	18.19349861 W
PL12W	0.32353121 W
PL13W	0.32353121 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127714 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



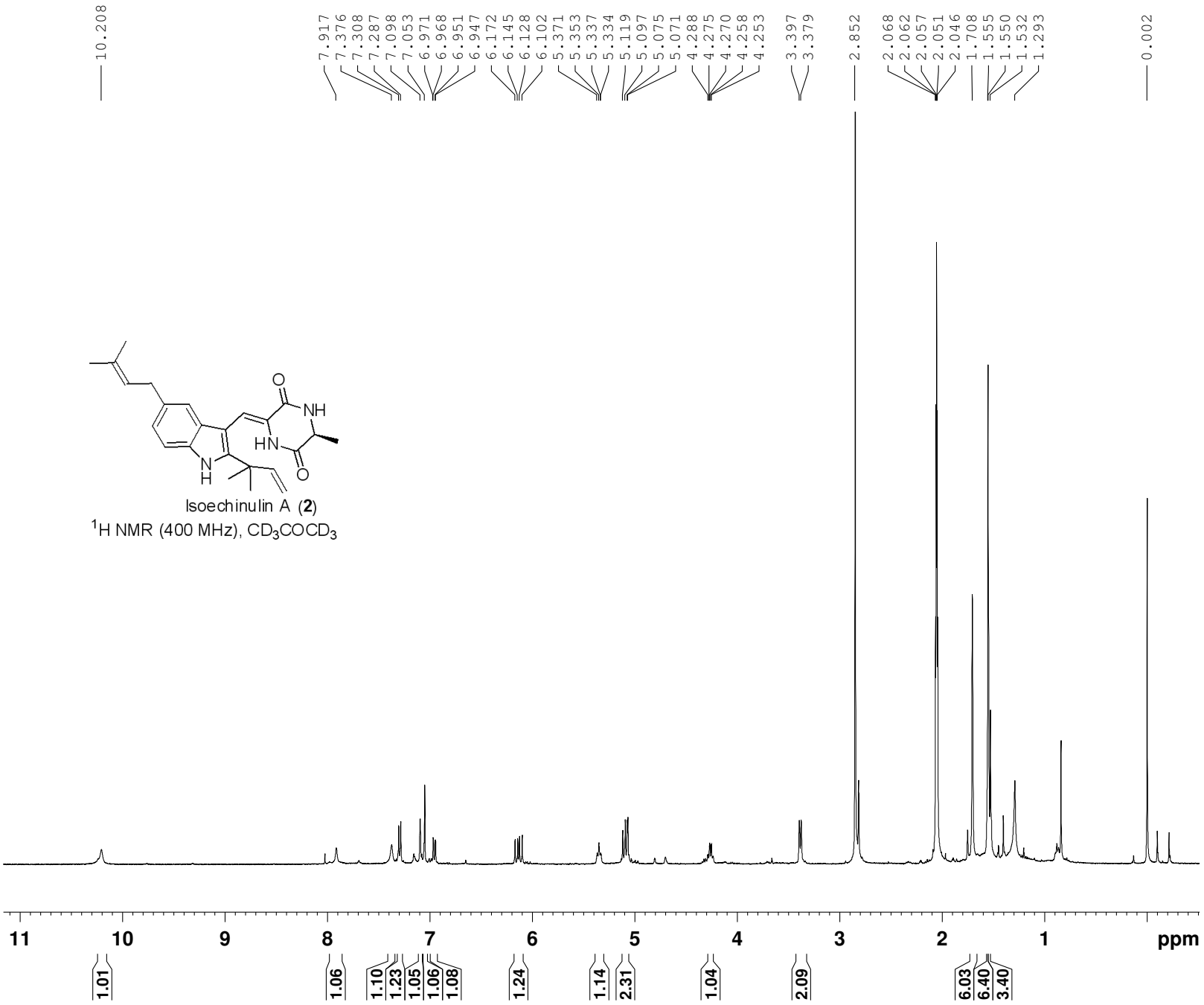

```
NAME      heliuer100727-1
EXPNO                  10
PROCNO                  1
Date_            20100728
Time                 8.42
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                    287
DW                60.800 usec
DE                 6.50 usec
TE                296.1 K
D1           1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.00 usec
PL1                -3.00 dB
PL1W         22.90425682 W
SFO1         400.1324710 MHz
SI                  32768
SF           400.1300000 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```



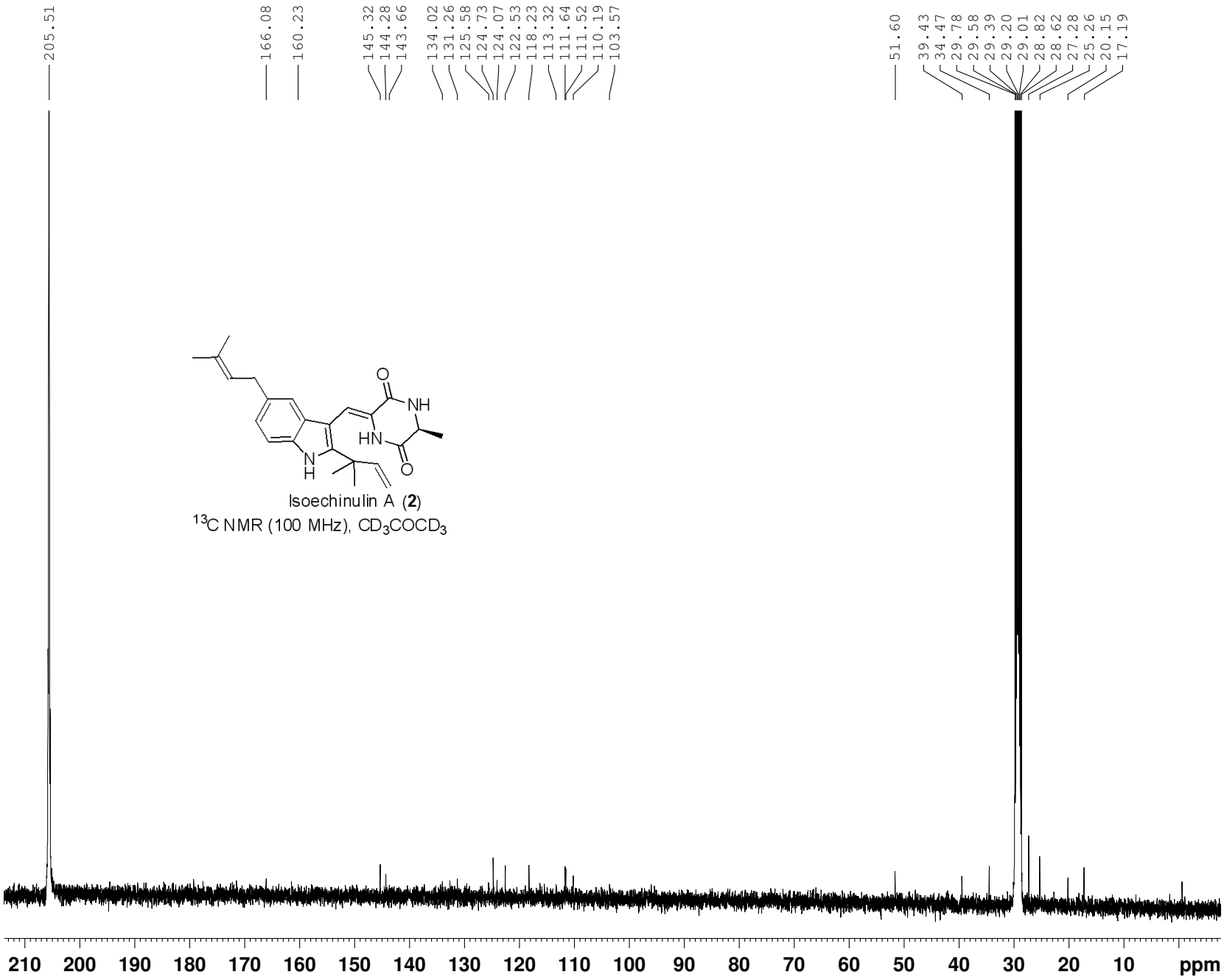
17

^{13}C NMR (100 MHz), $CDCl_3$

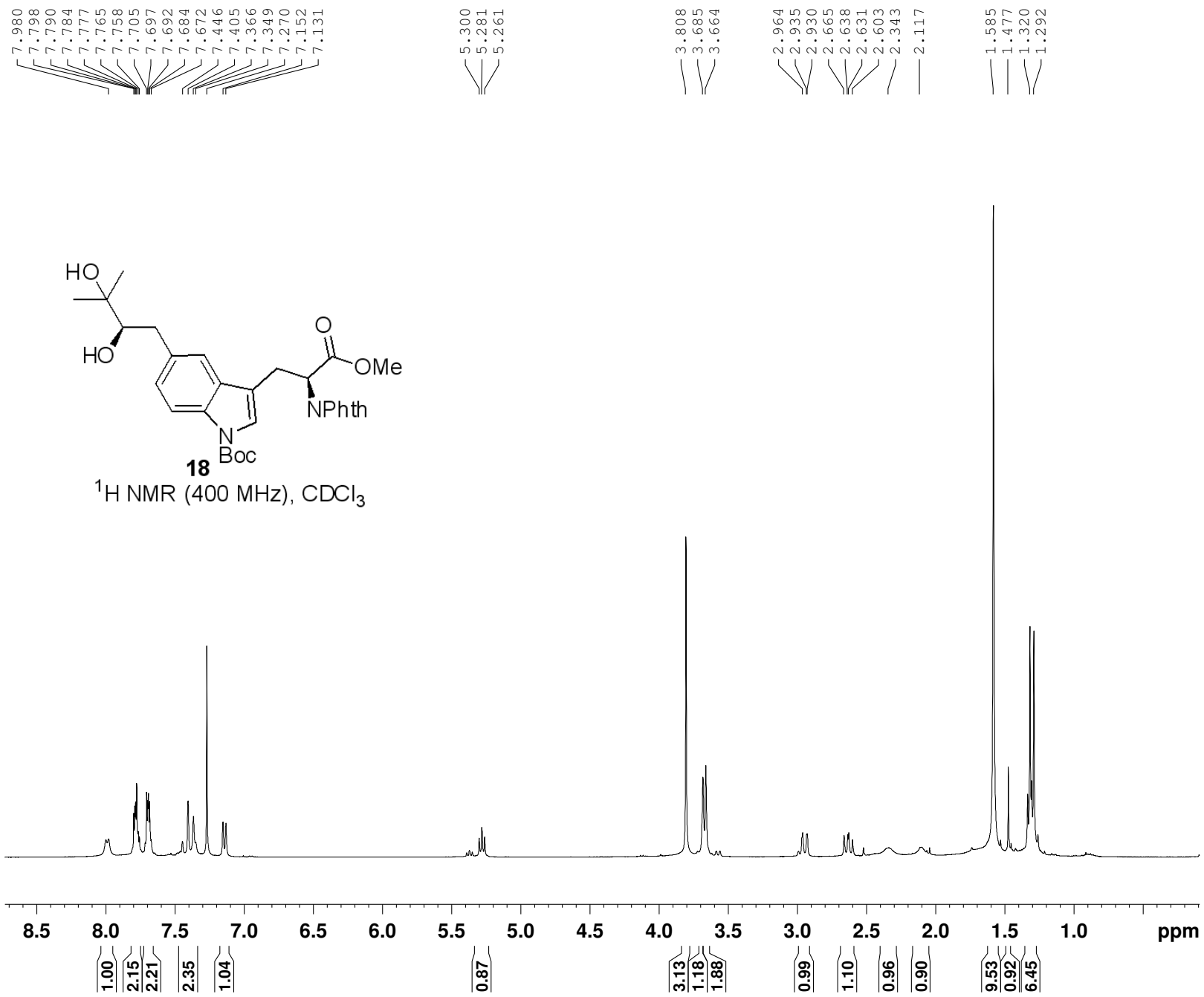
NAME	heliuer100727-1
EXPNO	11
PROCNO	1
Date_	20100728
Time	9.54
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1246
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	296.9 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.40 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-2.00 dB
PL12	15.50 dB
PL13	15.50 dB
PL2W	18.19349861 W
PL12W	0.32353121 W
PL13W	0.32353121 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



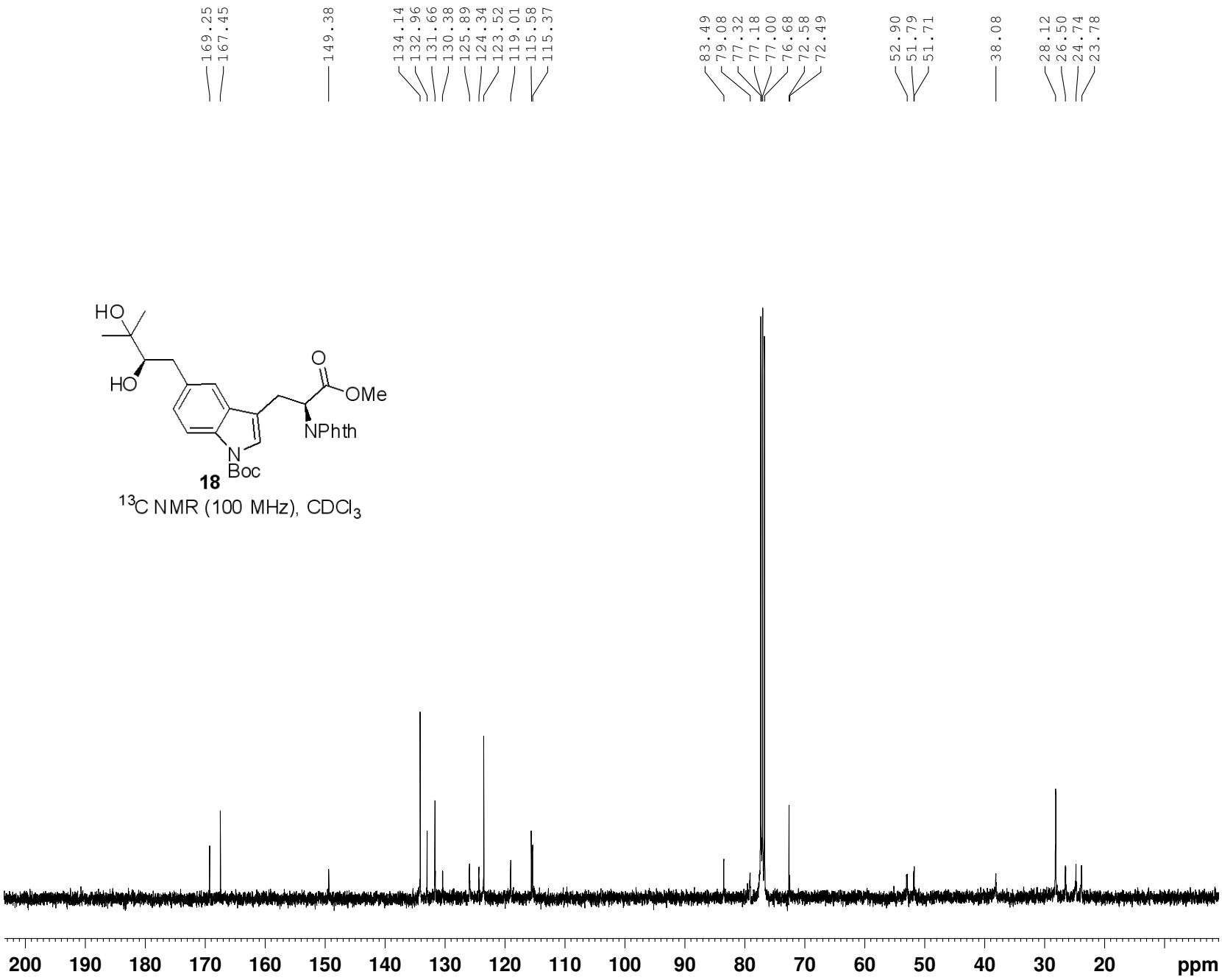

```
NAME      heliuer20110217-11a
EXPNO                  10
PROCNO                  1
Date_           20110218
Time                6.36
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT           Acetone
NS                     32
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                    512
DW                 60.800 usec
DE                  6.50 usec
TE                 290.2 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.00 usec
PL1                -3.00 dB
PL1W         22.90425682 W
SFO1         400.1324710 MHz
SI                  32768
SF           400.1300019 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



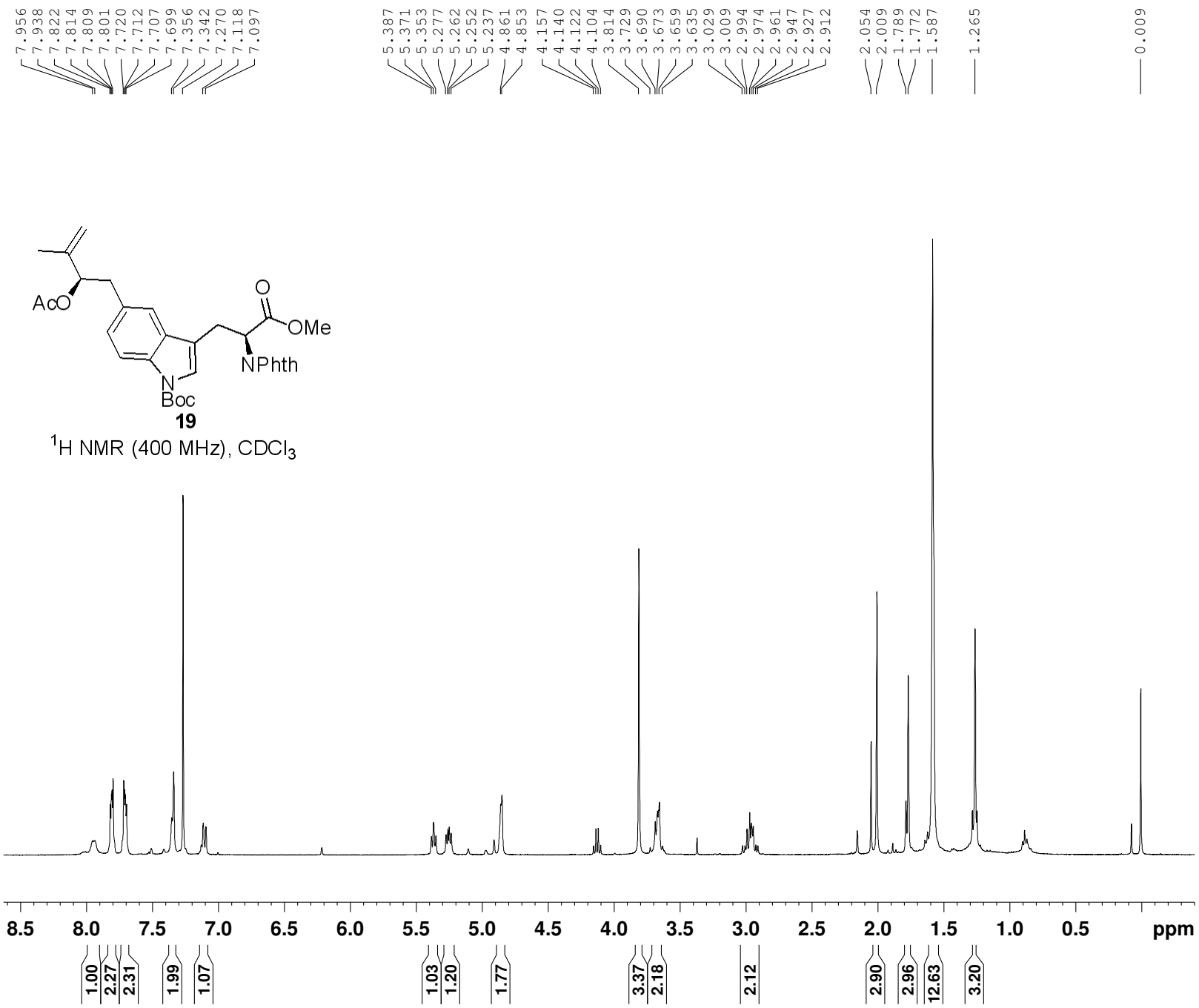
NAME	heliuer20110217-11a
EXPNO	11
PROCNO	1
Date_	20110218
Time	9.32
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	Acetone
NS	3068
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	291.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.40 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-2.00 dB
PL12	15.50 dB
PL13	15.50 dB
PL2W	18.19349861 W
PL12W	0.32353121 W
PL13W	0.32353121 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127430 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



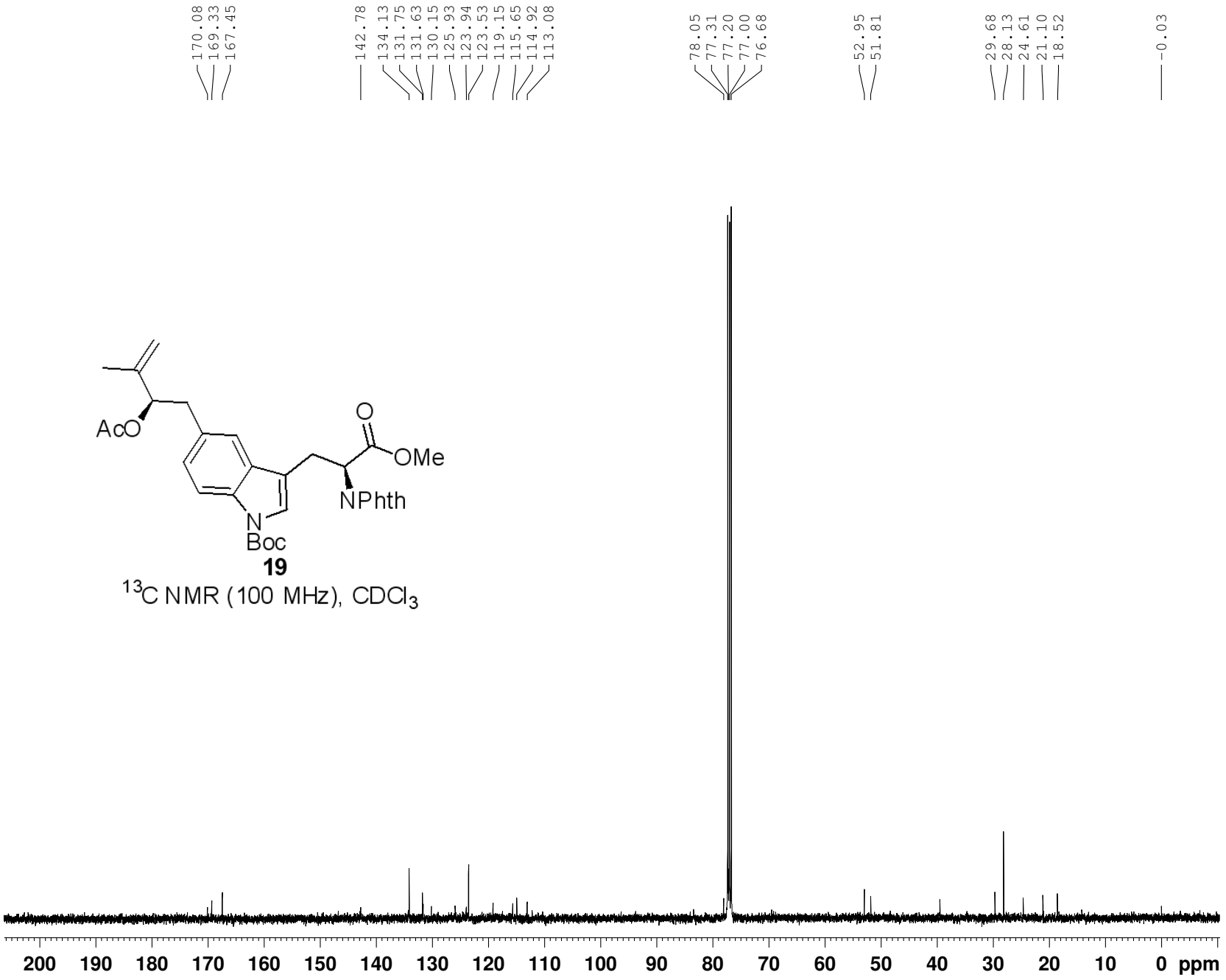

```
NAME      heliuer090620-2
EXPNO                  10
PROCNO                  1
Date_            20090620
Time                15.34
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                    228
DW                 60.800 usec
DE                  6.50 usec
TE                 297.9 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.60 usec
PL1                 0.00 dB
PL1W         11.47932053 W
SFO1         400.1324710 MHz
SI                  32768
SF           400.1300008 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



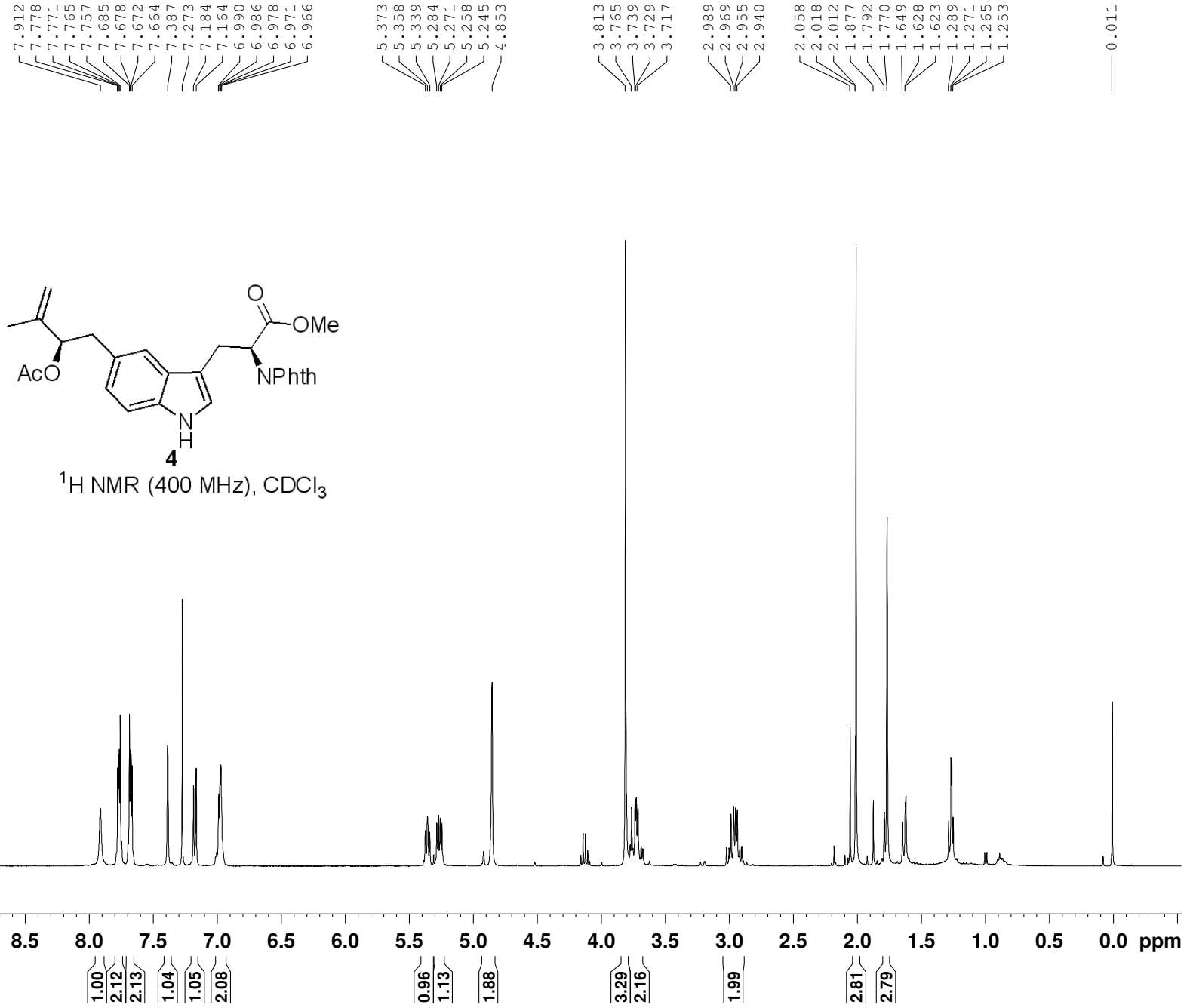

```
NAME      heliuer090620-2
EXPNO                  11
PROCNO                  1
Date_            20090620
Time                15.49
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     256
DS                       4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                    2050
DW                  20.800 usec
DE                   6.50 usec
TE                  298.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.40 usec
PL1                  -2.00 dB
PL1W          57.32743073 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                90.00 usec
PL2                  -2.00 dB
PL12                 15.50 dB
PL13                 15.50 dB
PL2W          18.19349861 W
PL12W          0.32353121 W
PL13W          0.32353121 W
SFO2          400.1316005 MHz
SI                   32768
SF            100.6127699 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



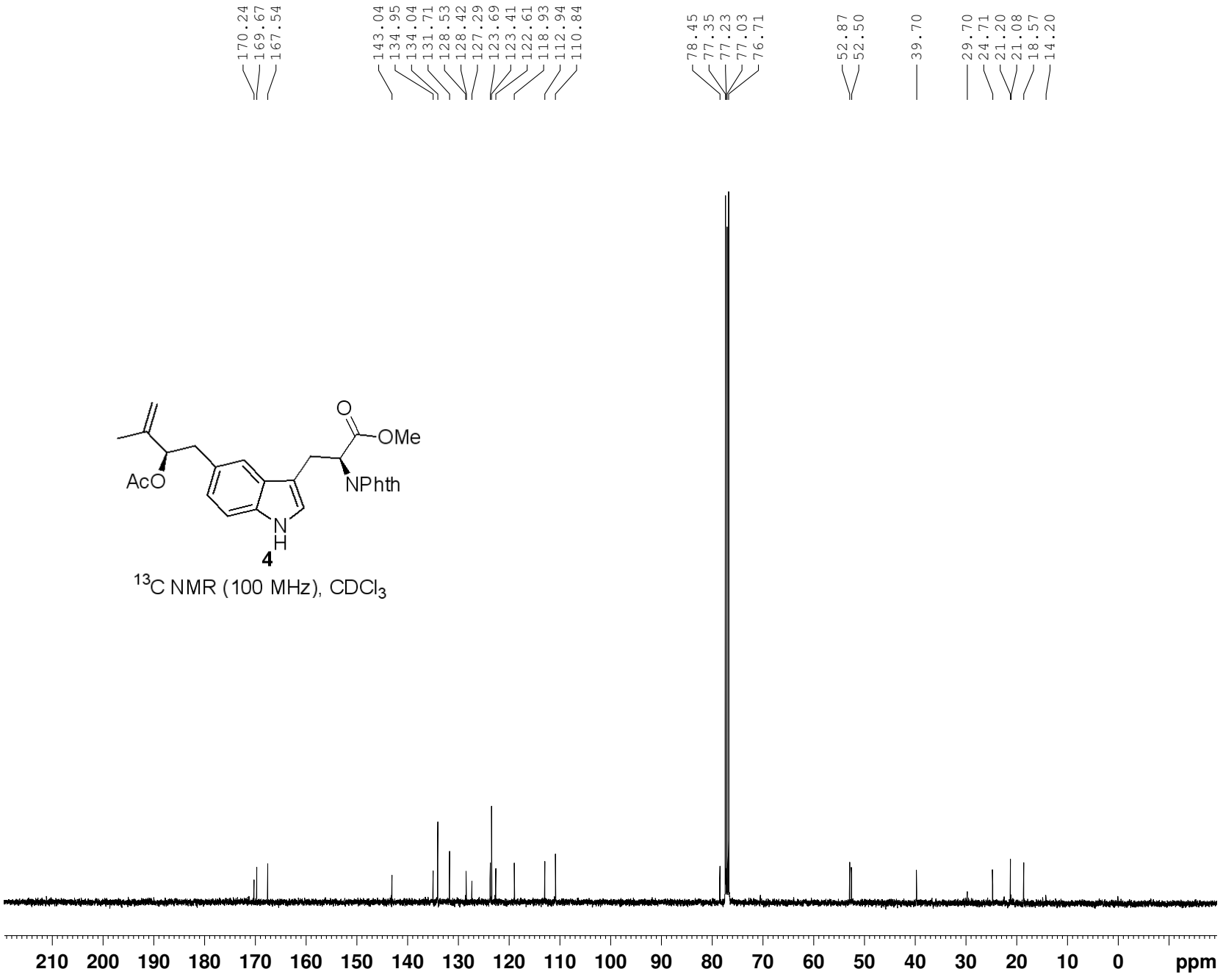

```
NAME      heliuer090712-1
EXPNO                  10
PROCNO                  1
Date_            20090712
Time                0.02
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                    203
DW                 60.800 usec
DE                  6.50 usec
TE                 295.3 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.70 usec
PL1                -1.00 dB
PL1W         13.75590801 W
SFO1         400.1324710 MHz
SI                  32768
SF           400.1300013 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



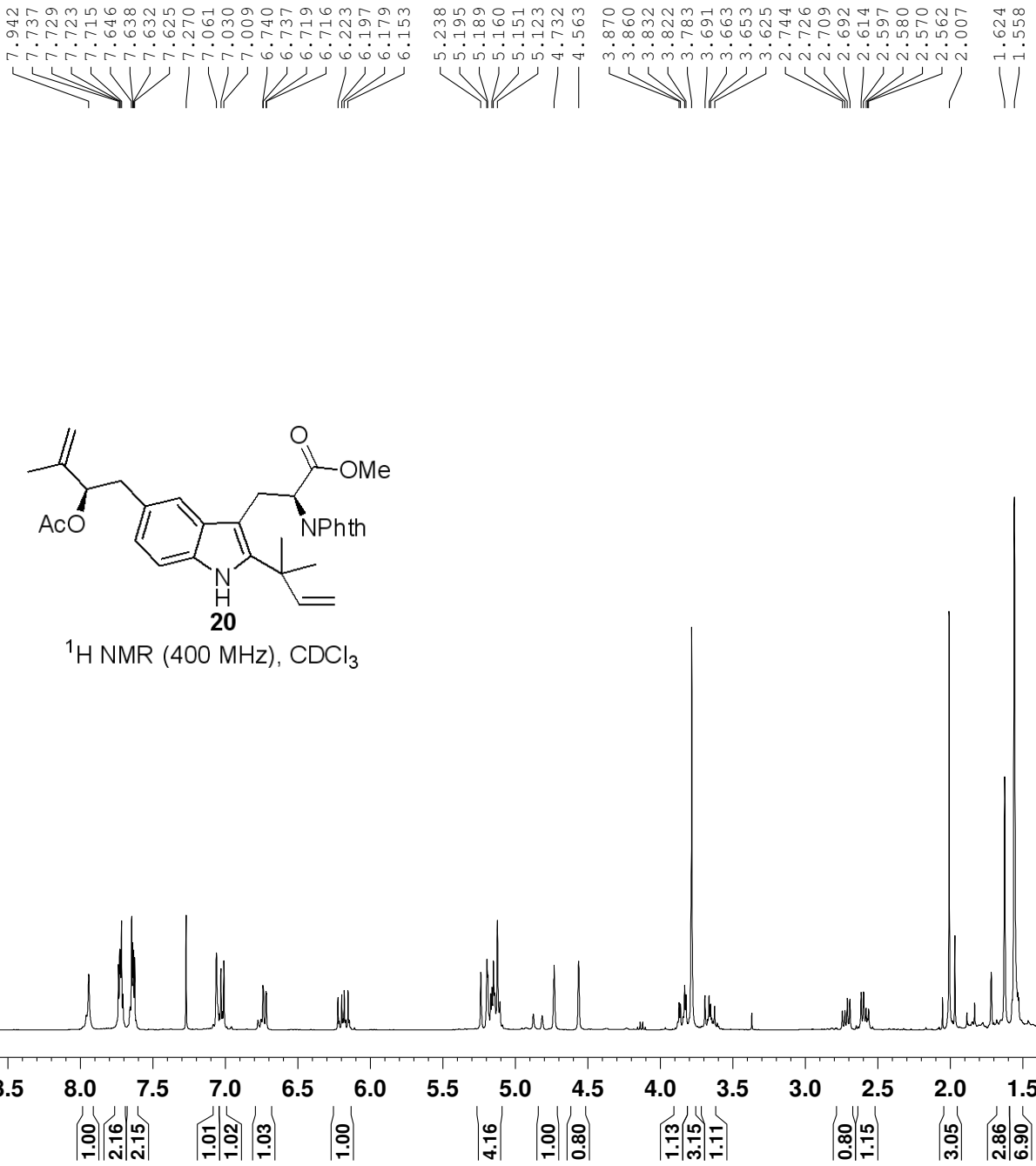

```
NAME      heliuer090712-1
EXPNO                  11
PROCNO                  1
Date_            20090712
Time                 0.33
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     512
DS                       4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                    90.5
DW                  20.800 usec
DE                   6.50 usec
TE                  297.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.70 usec
PL1                  -2.00 dB
PL1W          56.13311005 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2                  -2.10 dB
PL12                 13.90 dB
PL13                 13.90 dB
PL2W          17.72104263 W
PL12W          0.44513249 W
PL13W          0.44513249 W
SFO2          400.1316005 MHz
SI                   32768
SF            100.6127687 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



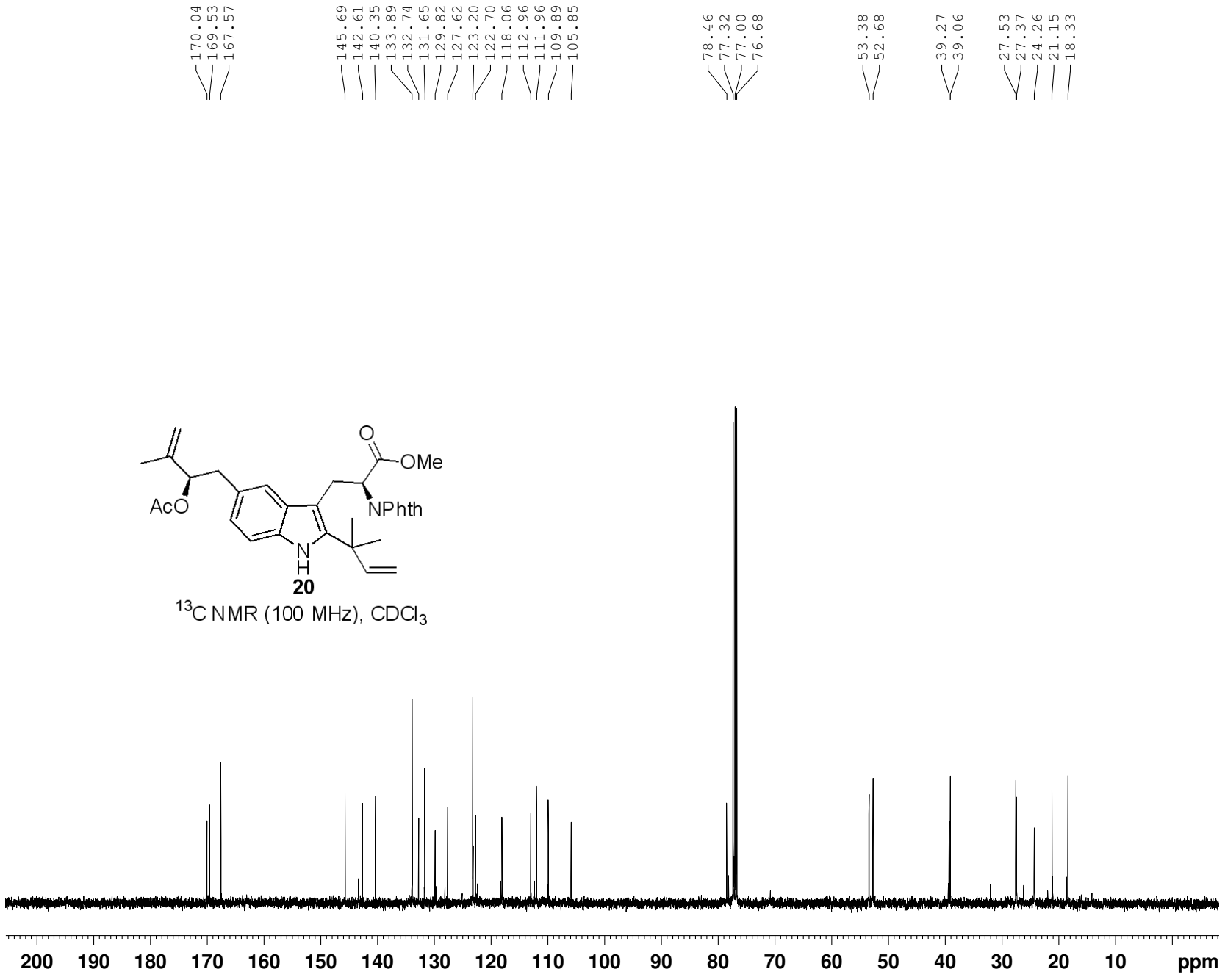

```
NAME      heliuer091222-1
EXPNO                  10
PROCNO                  1
Date_            20091222
Time                20.19
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                    181
DW                 60.800 usec
DE                  6.50 usec
TE                 289.9 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.00 usec
PL1                -3.00 dB
PL1W         22.90425682 W
SFO1         400.1324710 MHz
SI                  32768
SF           400.1300000 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                  1.00
```



NAME	heliuer091222-1
EXPNO	11
PROCNO	1
Date_	20091222
Time	20.50
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	512
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	290.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.40 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-2.00 dB
PL12	15.50 dB
PL13	15.50 dB
PL2W	18.19349861 W
PL12W	0.32353121 W
PL13W	0.32353121 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



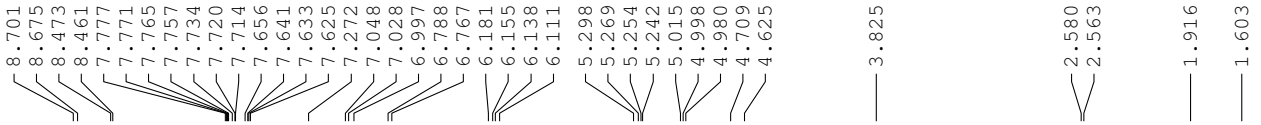

```
NAME      heliuer2011-0101-1
EXPNO                 10
PROCNO                 1
Date_           20110101
Time               10.11
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                    64
DW                60.800 usec
DE                 6.50 usec
TE                290.9 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.00 usec
PL1                -3.00 dB
PL1W         22.90425682 W
SFO1         400.1324710 MHz
SI                 32768
SF           400.1300008 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



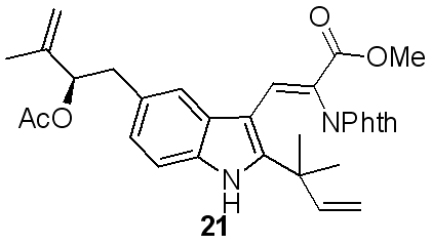
20

^{13}C NMR (100 MHz), $CDCl_3$

```
NAME      heliuer2011-0101-1
EXPNO                 11
PROCNO                 1
Date_           20110101
Time               10.19
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  124
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                 2050
DW                20.800 usec
DE                 6.50 usec
TE                291.7 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.40 usec
PL1               -2.00 dB
PL1W        57.32743073 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             90.00 usec
PL2               -2.00 dB
PL12              15.50 dB
PL13              15.50 dB
PL2W        18.19349861 W
PL12W        0.32353121 W
PL13W        0.32353121 W
SFO2        400.1316005 MHz
SI                32768
SF          100.6127773 MHz
WDW                EM
SSB                 0
LB                1.00 Hz
GB                  0
PC                1.40
```

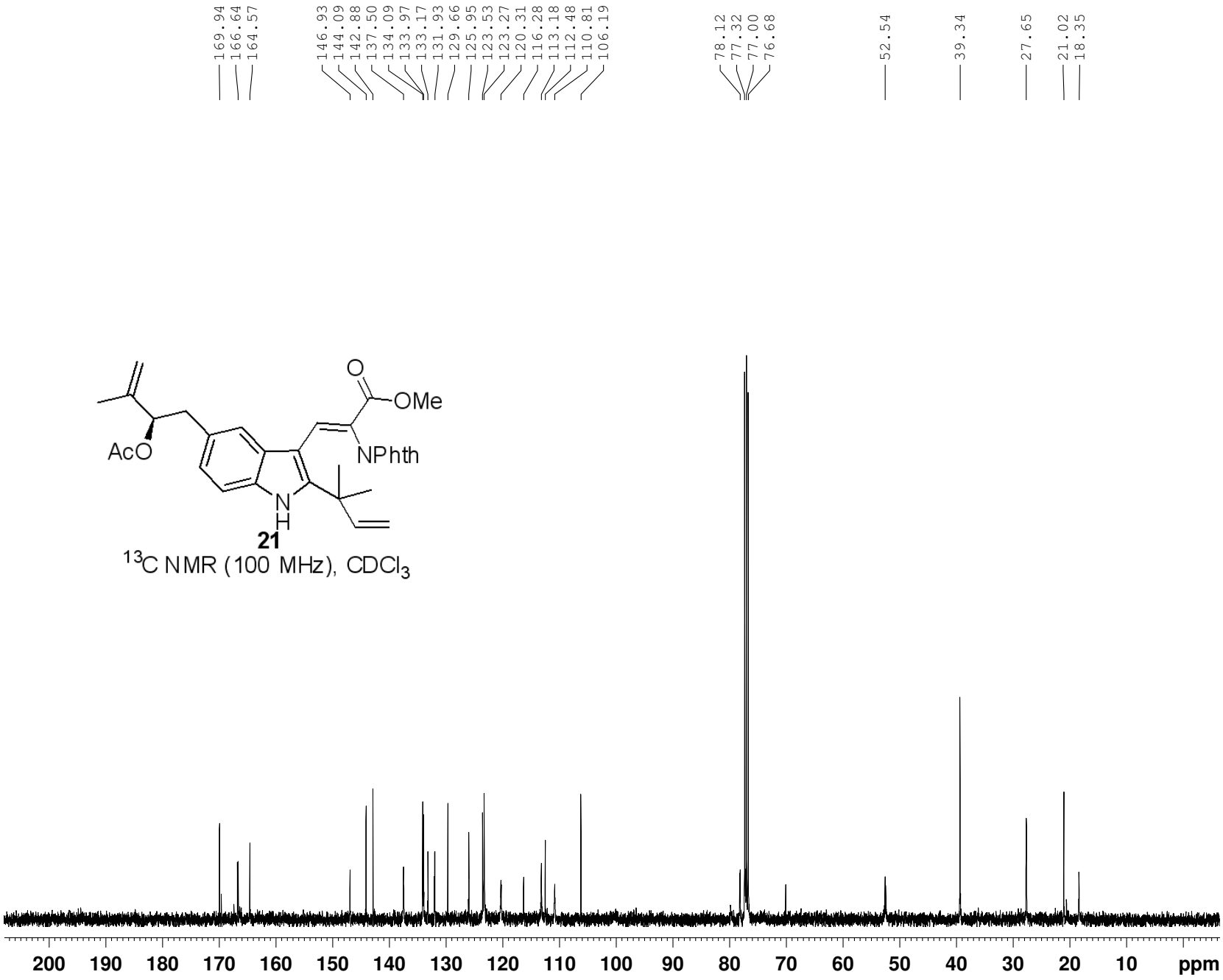



```
NAME      heliuer100629-1
EXPNO                  10
PROCNO                  1
Date_            20100628
Time                23.50
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                    101
DW                 60.800 usec
DE                  6.50 usec
TE                 294.2 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.00 usec
PL1                -3.00 dB
PL1W         22.90425682 W
SFO1         400.1324710 MHz
SI                  32768
SF           400.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

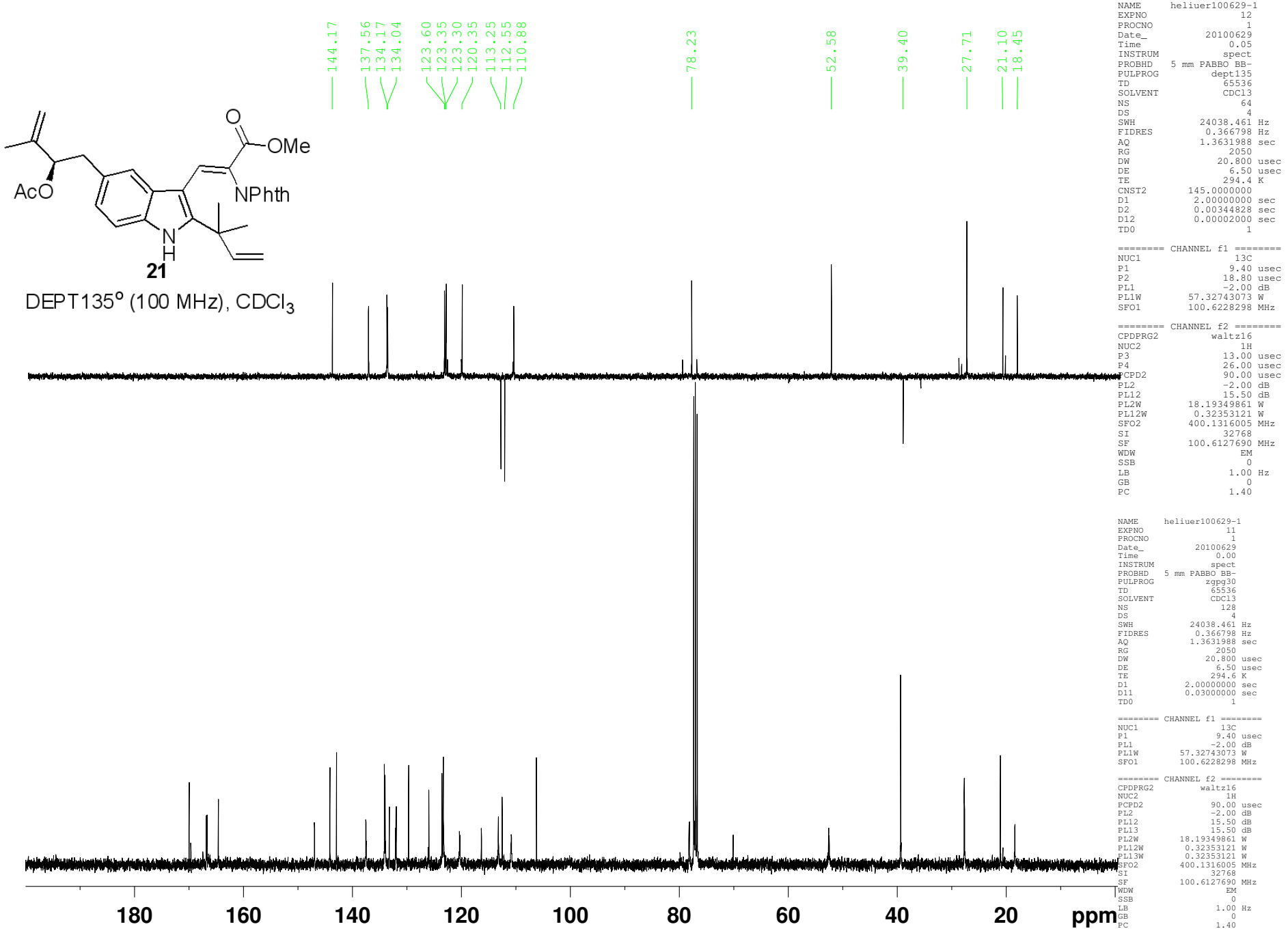


21

^{1}H NMR (400 MHz), $CDCl_3$

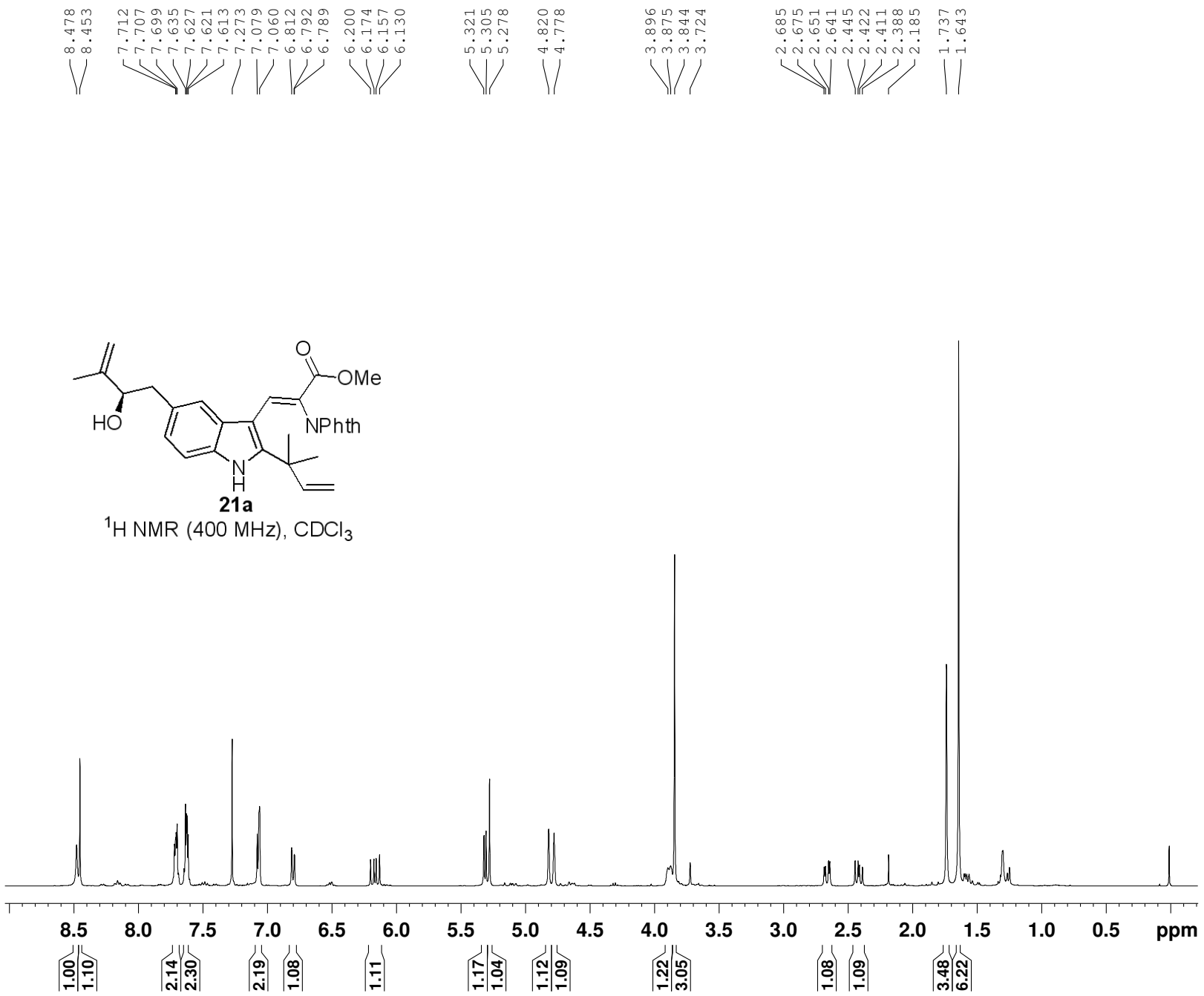


NAME	heliuer100629-1
EXPNO	11
PROCNO	1
Date_	20100629
Time	0.00
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	128
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	294.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.40 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-2.00 dB
PL12	15.50 dB
PL13	15.50 dB
PL2W	18.19349861 W
PL12W	0.32353121 W
PL13W	0.32353121 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127766 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

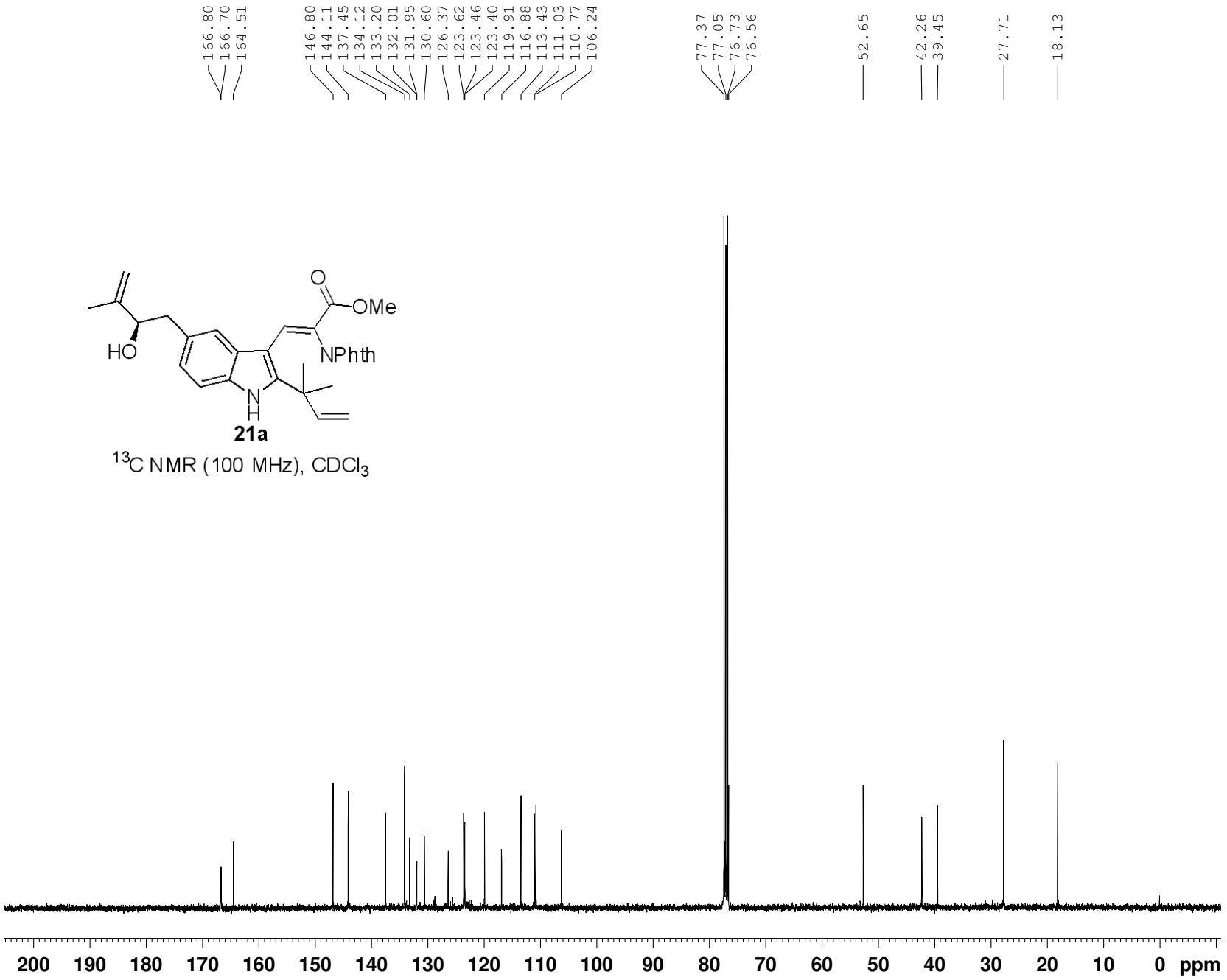



```
NAME      heliuer100629-1
EXPNO                  12
PROCNO                  1
Date_            20100629
Time                 0.05
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG           dept135
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      4
SWH             24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                   2050
DW                20.800 usec
DE                 6.50 usec
TE                294.4 K
CNST2         145.0000000
D1              2.00000000 sec
D2              0.00344828 sec
D12             0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.40 usec
P2                  18.80 usec
PL1                 -2.00 dB
PL1W         57.32743073 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
P3                  13.00 usec
P4                  26.00 usec
PCPD2               90.00 usec
PL2                 -2.00 dB
PL12                15.50 dB
PL2W         18.19349861 W
PL12W         0.32353121 W
SFO2         400.1316005 MHz
SI                  32768
SF           100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

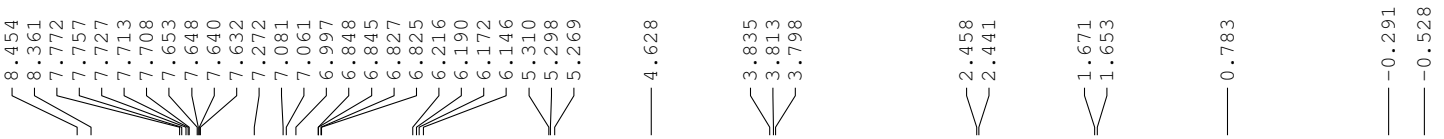
```
NAME      heliuer100629-1
EXPNO                  11
PROCNO                  1
Date_            20100629
Time                 0.00
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      4
SWH             24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                   2050
DW                20.800 usec
DE                 6.50 usec
TE                294.6 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.40 usec
PL1                 -2.00 dB
PL1W         57.32743073 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2               90.00 usec
PL2                 -2.00 dB
PL12                15.50 dB
PL13                15.50 dB
PL2W         18.19349861 W
PL12W         0.32353121 W
PL13W         0.32353121 W
SFO2         400.1316005 MHz
SI                  32768
SF           100.6127690 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



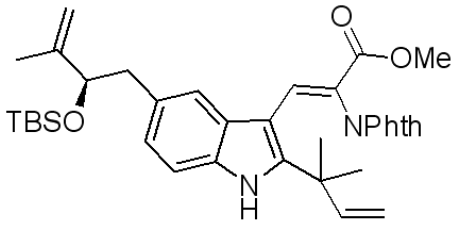

```
NAME      heliuer20101215-1a
EXPNO                 10
PROCNO                 1
Date_           20101216
Time                9.46
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   101
DW                60.800 usec
DE                 6.50 usec
TE                287.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.70 usec
PL1               -1.00 dB
PL1W         13.75590801 W
SFO1         400.1324710 MHz
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



NAME	heliuer20101215-1a
EXPNO	11
PROCNO	1
Date_	20101216
Time	10.18
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	512
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	64
DW	20.800 usec
DE	6.50 usec
TE	289.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.70 usec
PL1	-2.00 dB
PL1W	56.13311005 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.10 dB
PL12	13.90 dB
PL13	13.90 dB
PL2W	17.72104263 W
PL12W	0.44513249 W
PL13W	0.44513249 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

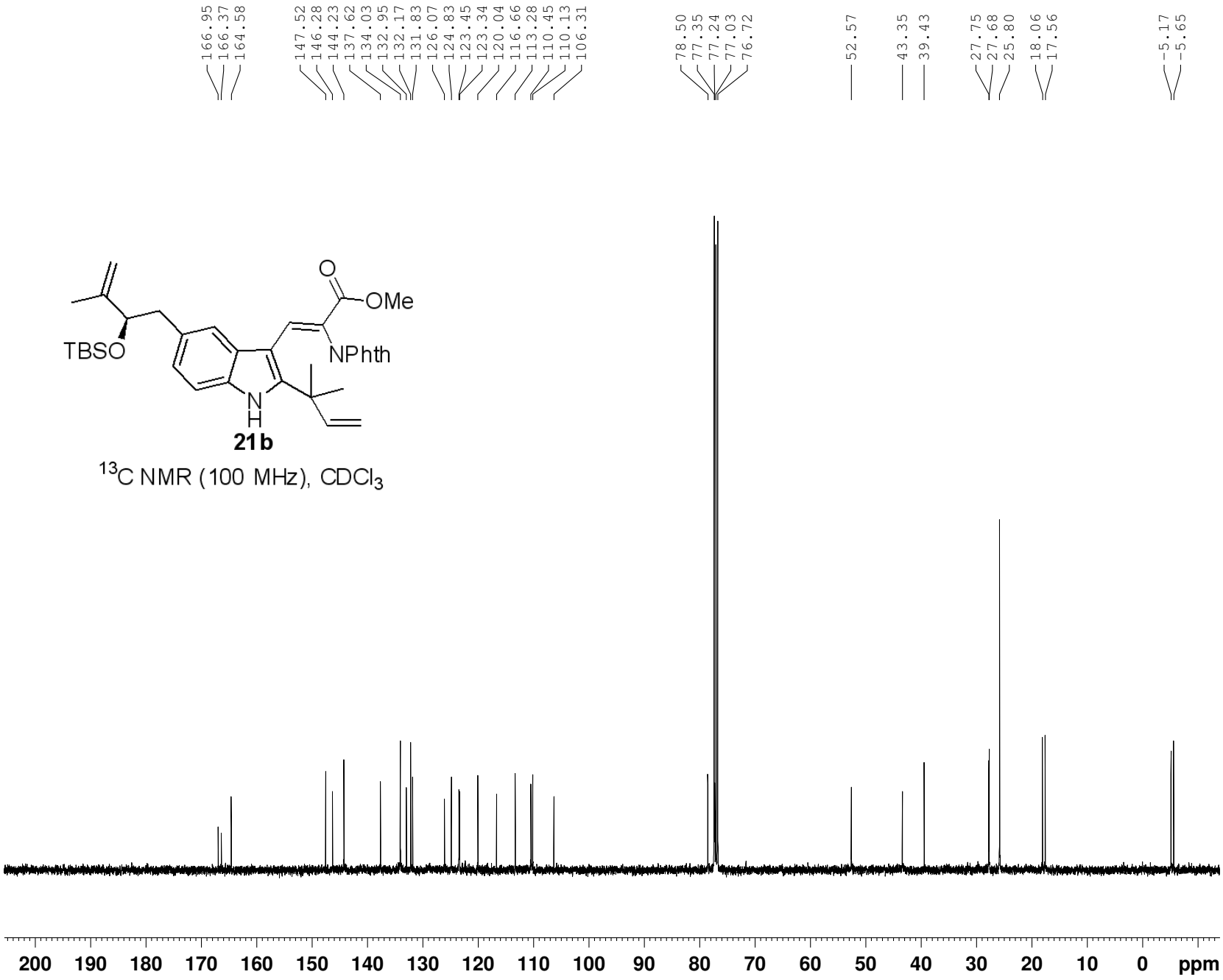



```
NAME      heliuer20101204-2
EXPNO                    10
PROCNO                    1
Date_              20101205
Time                  12.44
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                     71.8
DW                  60.800 usec
DE                   6.50 usec
TE                  228.2 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    12.00 usec
PL1                   -3.00 dB
PL1W           22.90425682 W
SFO1           400.1324710 MHz
SI                     32768
SF             400.1300000 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                     1.00
```

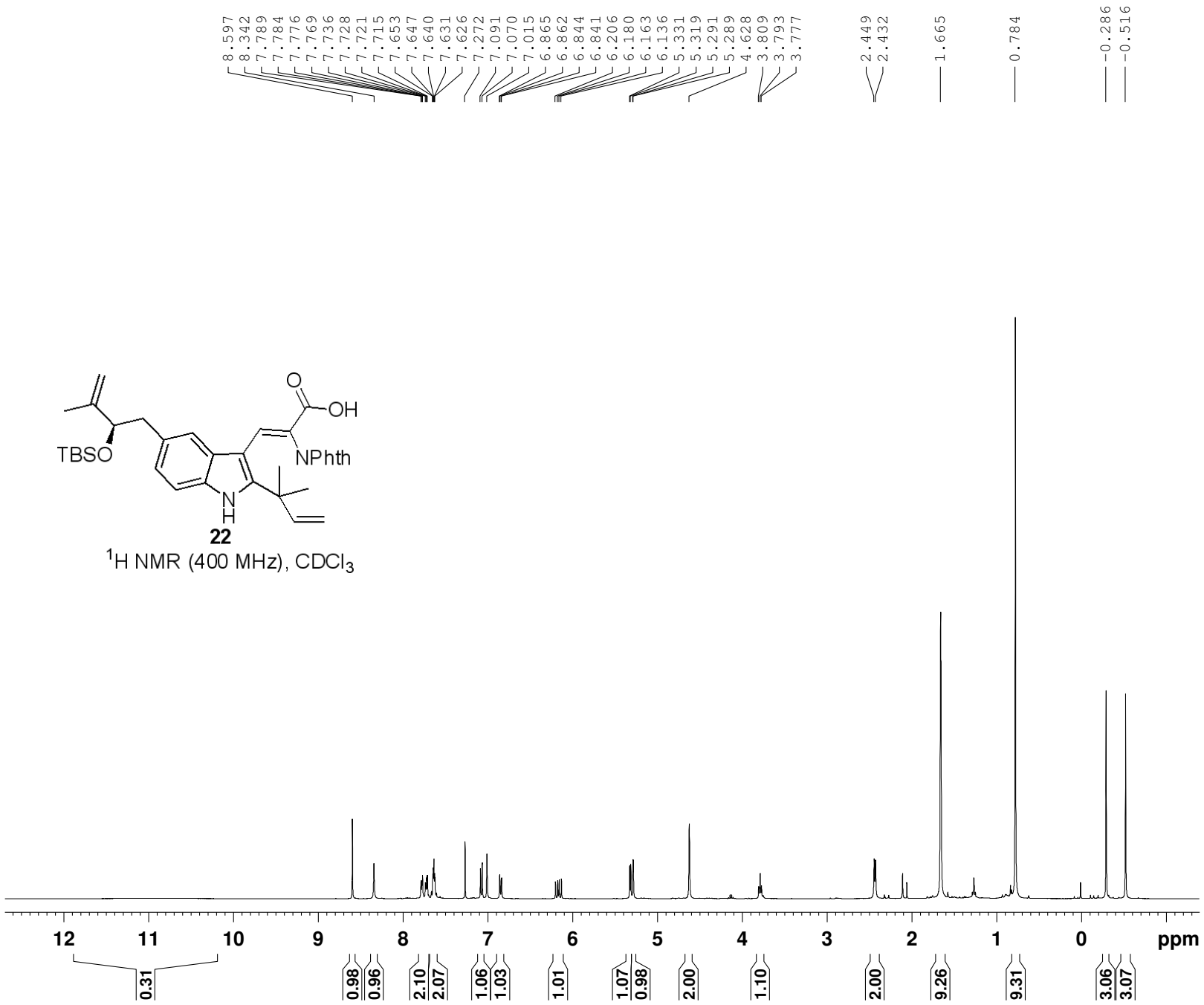


21b

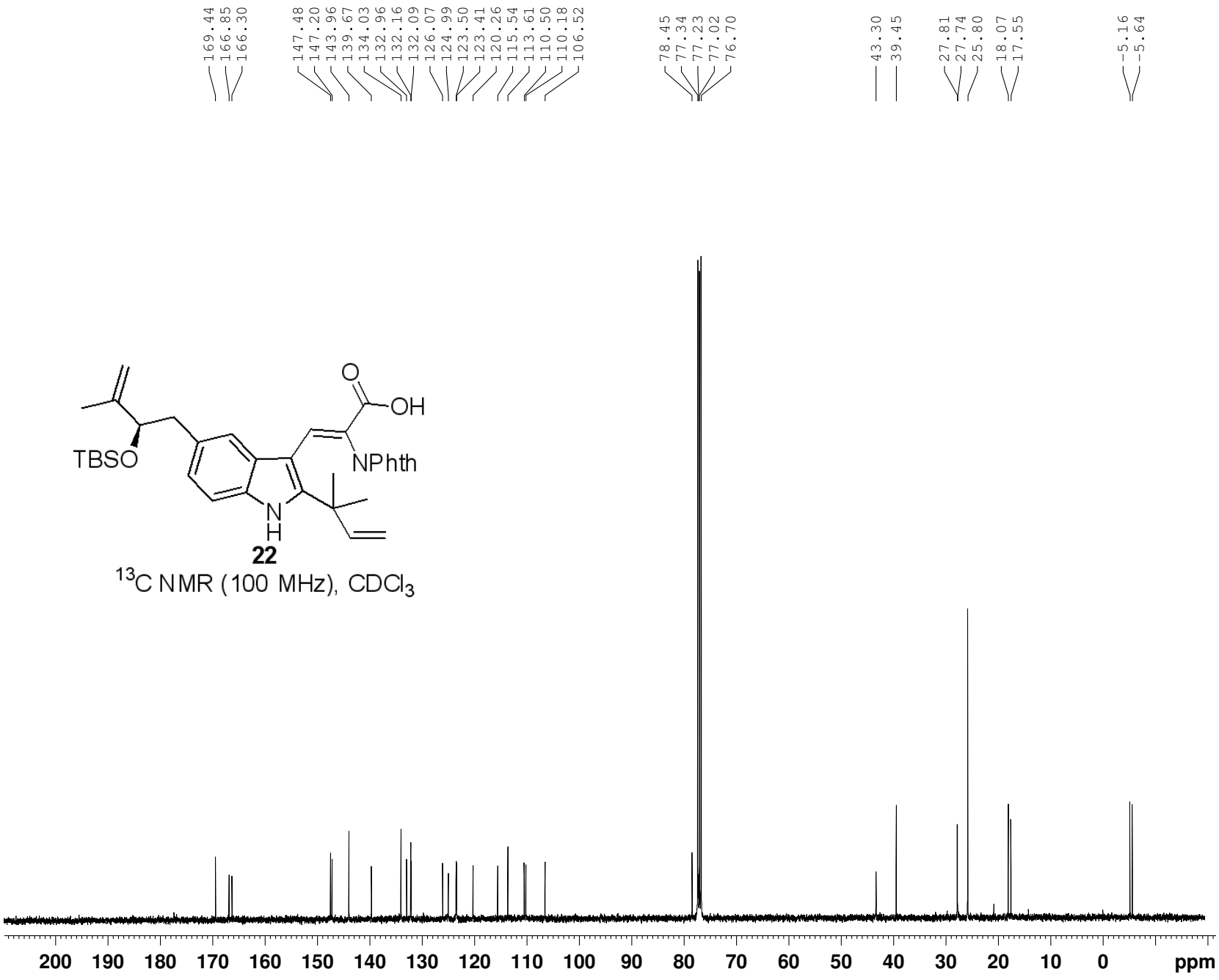
^{1}H NMR (400 MHz), $CDCl_3$



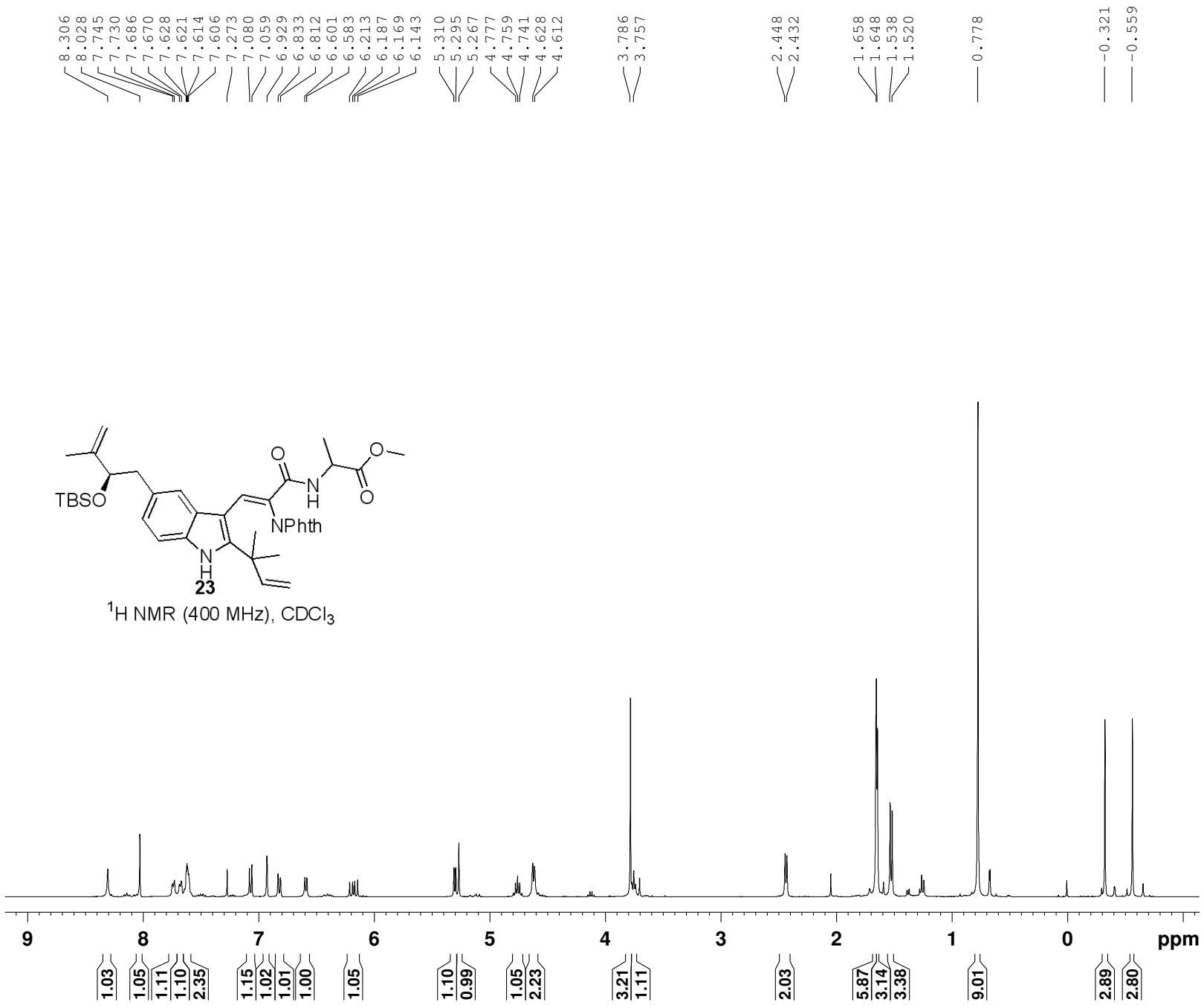
NAME	heliuer20101204-2
EXPNO	11
PROCNO	1
Date_	20101205
Time	13.00
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	256
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	229.4 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.40 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-2.00 dB
PL12	15.50 dB
PL13	15.50 dB
PL2W	18.19349861 W
PL12W	0.32353121 W
PL13W	0.32353121 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



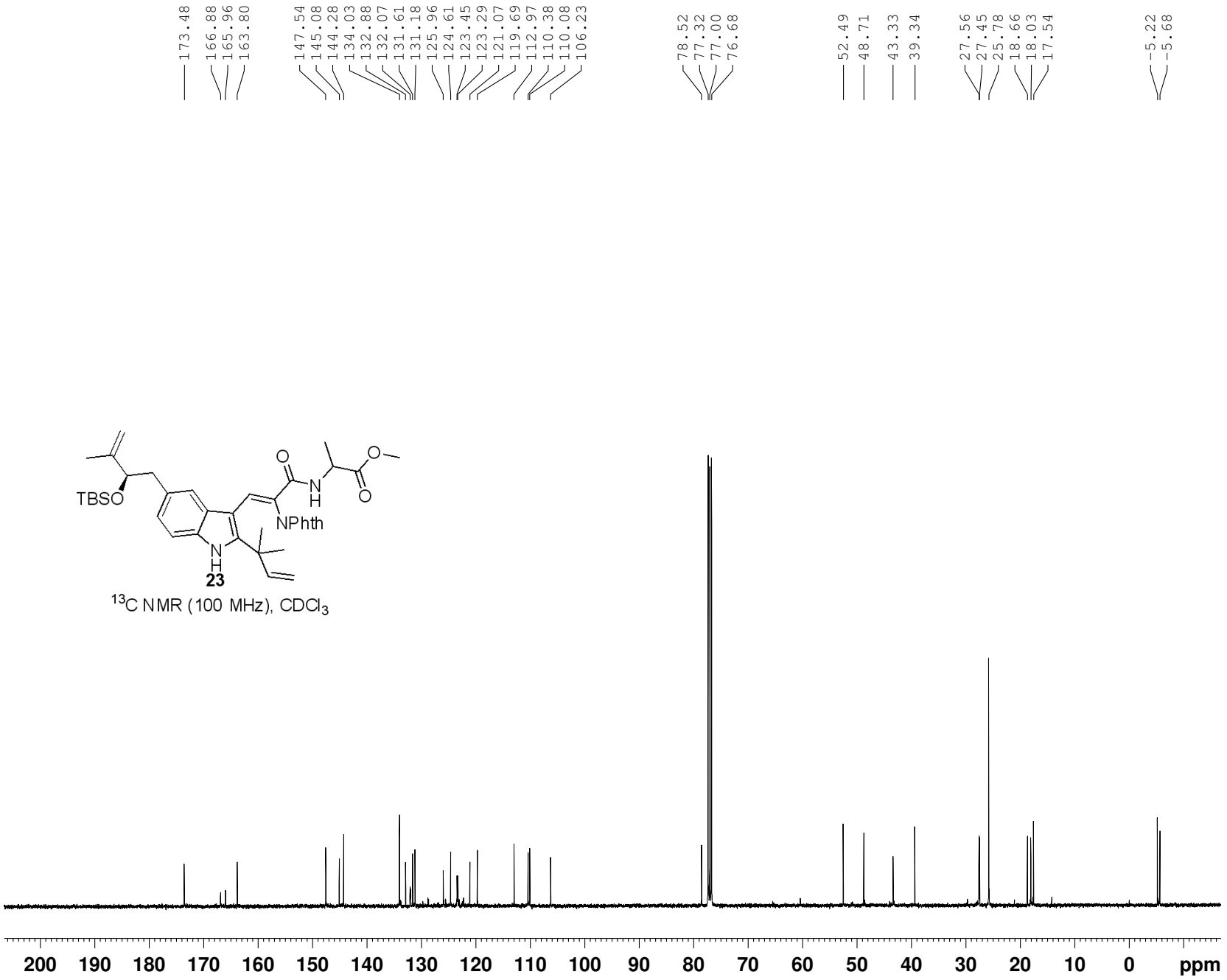

```
NAME      heliuer20101223-1
EXPNO                    10
PROCNO                    1
Date_              20101222
Time                  13.20
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                      101
DW                   60.800 usec
DE                    6.50 usec
TE                   292.2 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   12.00 usec
PL1                  -3.00 dB
PL1W            22.90425682 W
SFO1            400.1324710 MHz
SI                    32768
SF              400.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



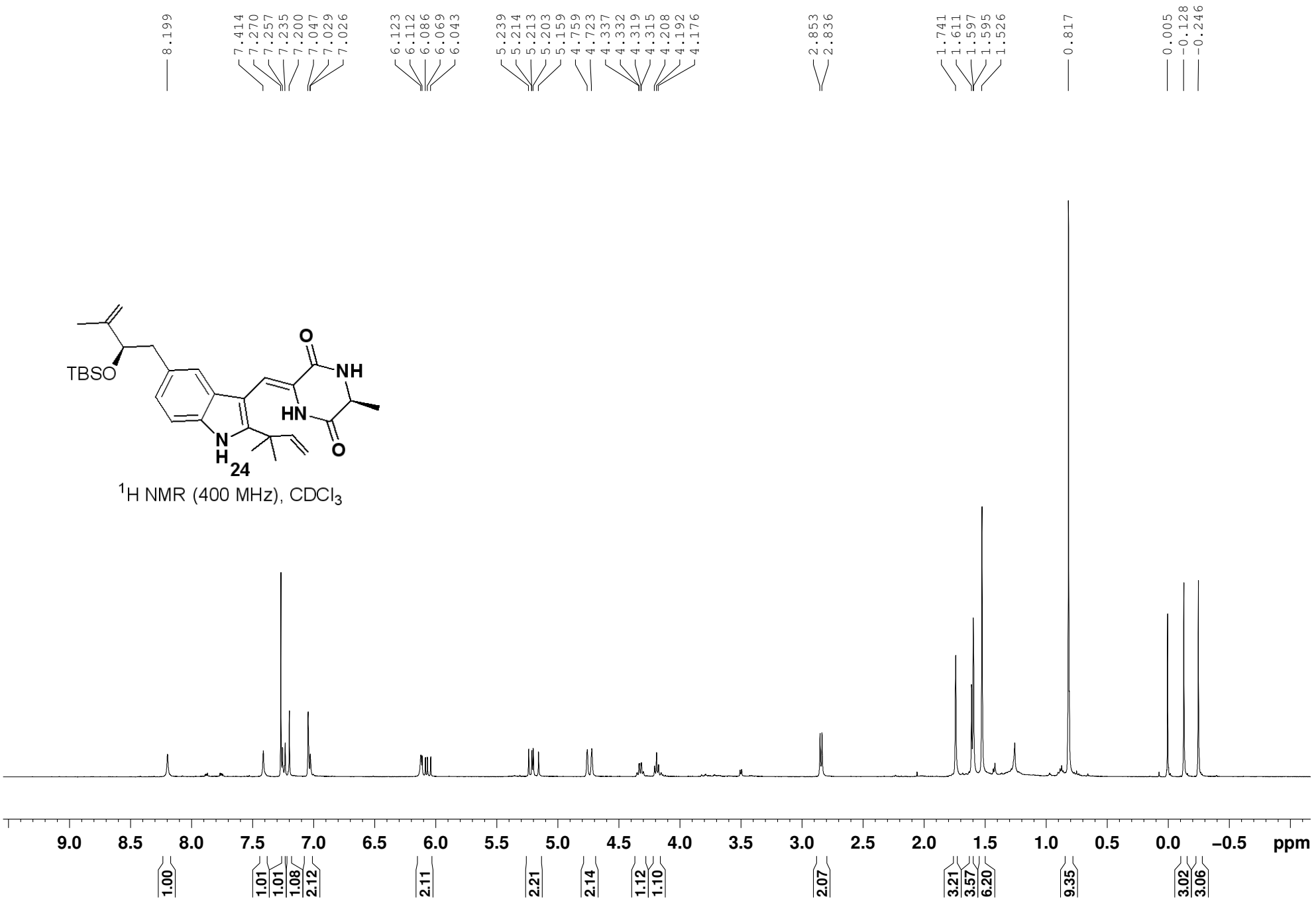

```
NAME      heliuer20101223-1
EXPNO                    11
PROCNO                    1
Date_              20101222
Time                  14.01
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      684
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                     2050
DW                   20.800 usec
DE                    6.50 usec
TE                   293.8 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     9.40 usec
PL1                   -2.00 dB
PL1W             57.32743073 W
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
PCPD2                 90.00 usec
PL2                   -2.00 dB
PL12                  15.50 dB
PL13                  15.50 dB
PL2W             18.19349861 W
PL12W             0.32353121 W
PL13W             0.32353121 W
SFO2            400.1316005 MHz
SI                     32768
SF              100.6127690 MHz
WDW                       EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

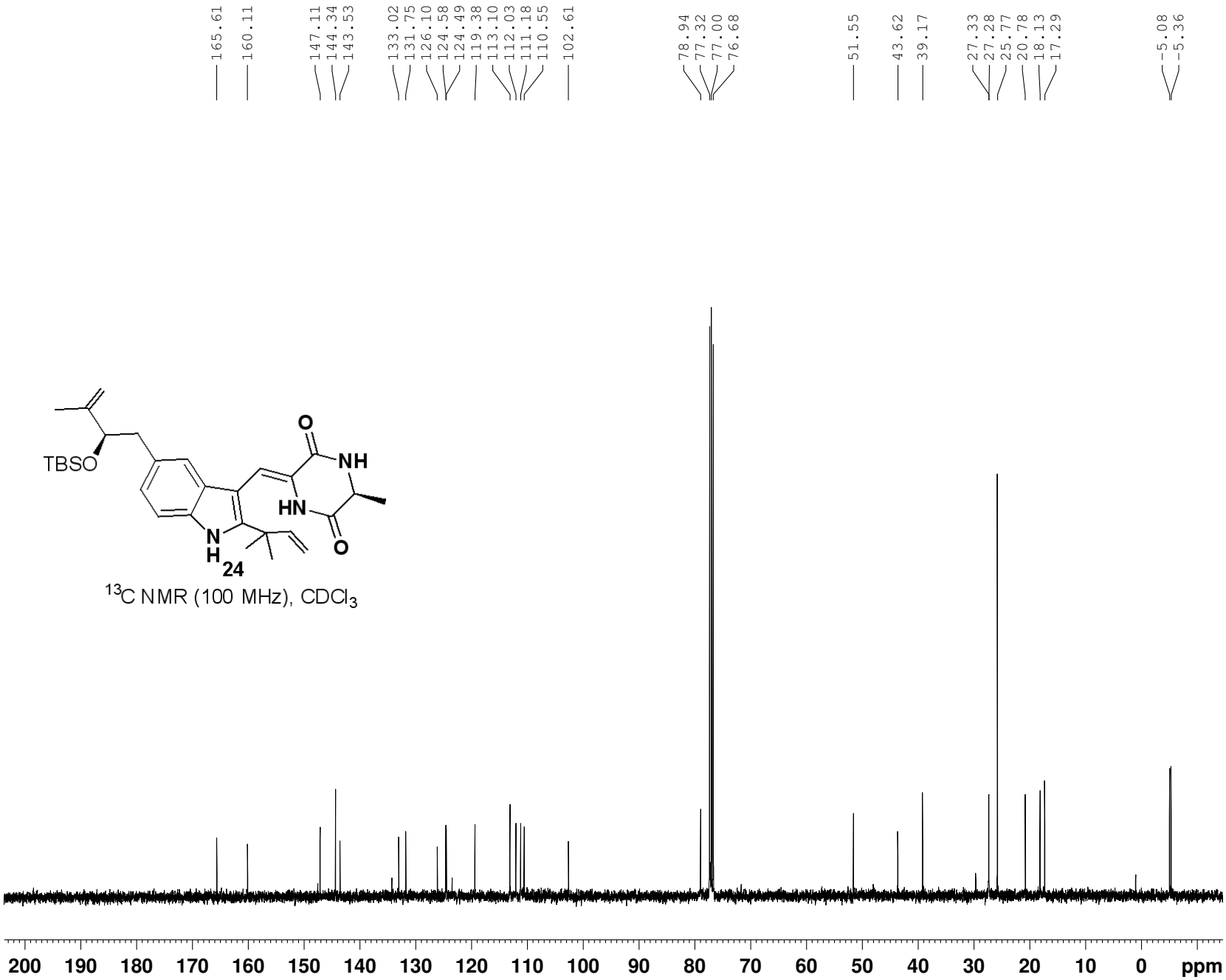



```
NAME      heliuer20101224-1
EXPNO                    20
PROCNO                    1
Date_              20101224
Time                   9.08
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                     90.5
DW                   60.800 usec
DE                    6.50 usec
TE                   291.9 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    14.70 usec
PL1                   -1.00 dB
PL1W           13.75590801 W
SFO1           400.1324710 MHz
SI                    32768
SF             400.1300000 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



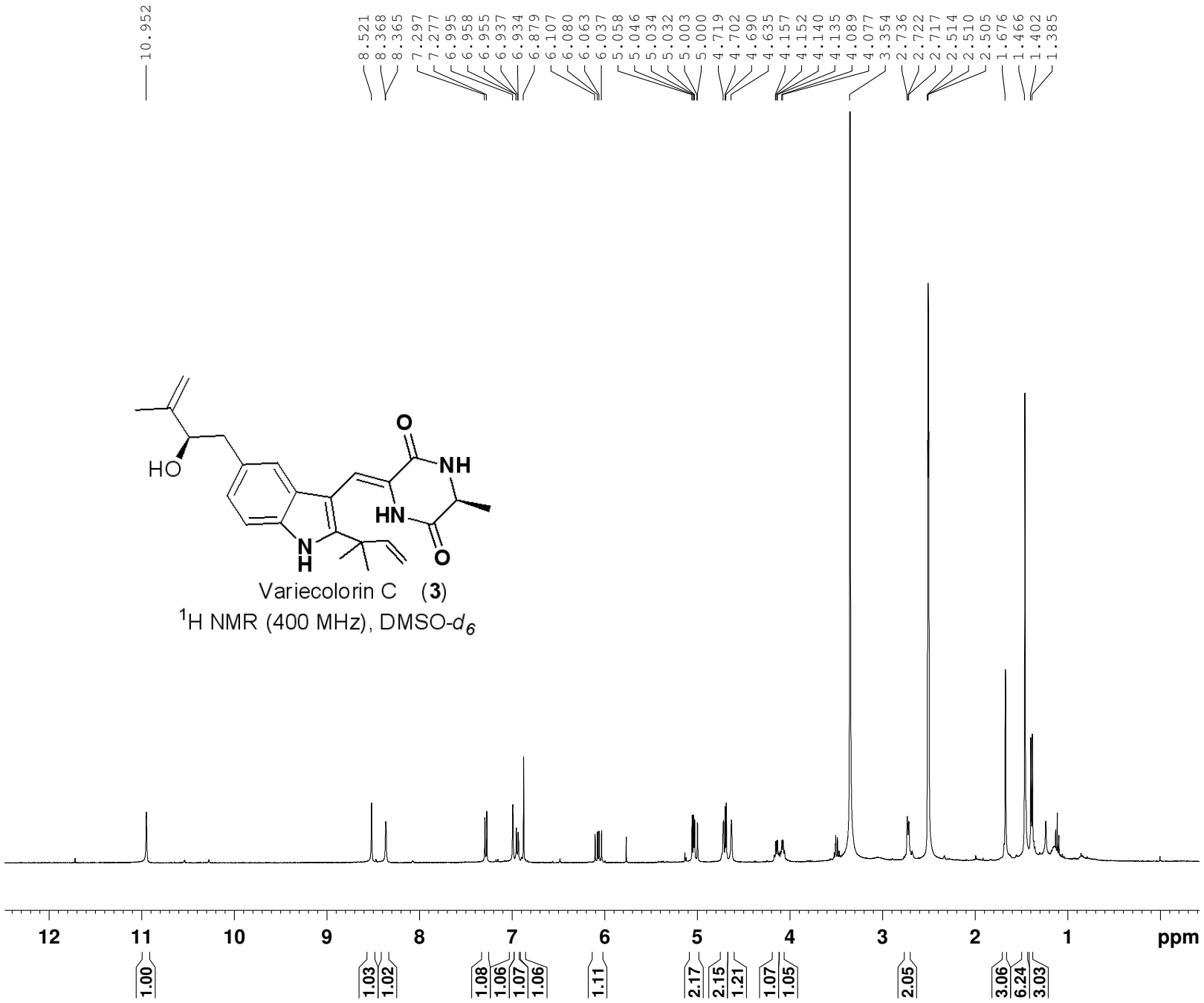
NAME	heliuer20101224-1
EXPNO	21
PROCNO	1
Date_	20101224
Time	10.08
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	1024
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	512
DW	20.800 usec
DE	6.50 usec
TE	293.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.70 usec
PL1	-2.00 dB
PL1W	56.13311005 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.10 dB
PL12	13.90 dB
PL13	13.90 dB
PL2W	17.72104263 W
PL12W	0.44513249 W
PL13W	0.44513249 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127718 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40


8.199
7.414
7.270
7.257
7.235
7.200
7.047
7.029
7.026
6.123
6.112
6.086
6.069
6.043
5.239
5.214
5.213
5.203
5.159
4.759
4.723
4.337
4.332
4.319
4.315
4.208
4.192
4.176
2.853
2.836
1.741
1.611
1.597
1.595
1.526
0.817
0.005
-0.128
-0.246
TBSO
O
NH
HN
O
N
H
24
1H NMR (400 MHz), CDCl3
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
–0.5
ppm
1.00
1.01
1.01
1.08
2.12
2.11
2.21
2.14
1.12
1.10
2.07
3.21
3.57
6.20
9.35
3.02
3.06

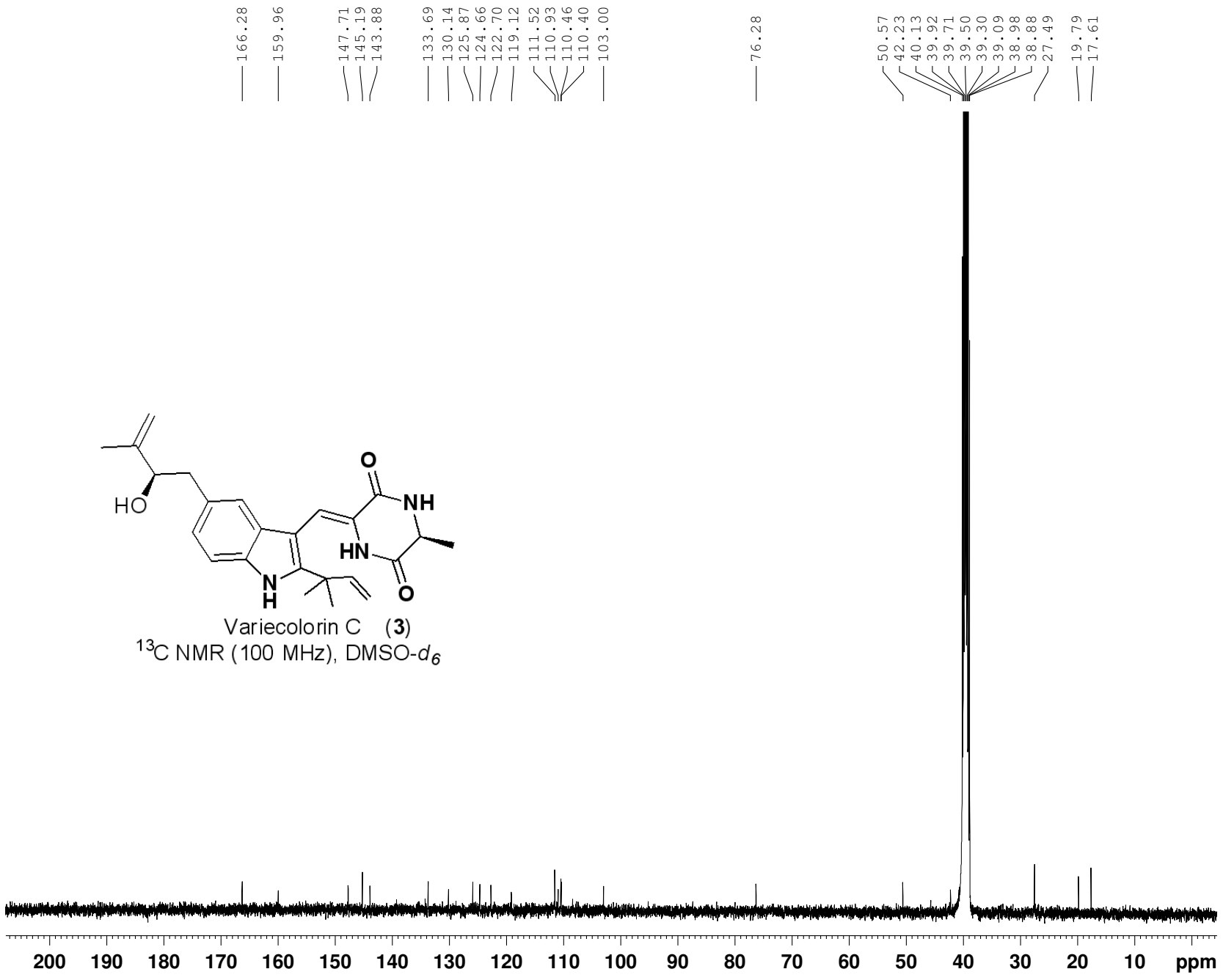


^{13}C NMR (100 MHz), $CDCl_3$

NAME	heliuer20110119-2
EXPNO	11
PROCNO	1
Date_	20110119
Time	18.37
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	128
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	71.8
DW	20.800 usec
DE	6.50 usec
TE	290.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.70 usec
PL1	-2.00 dB
PL1W	56.13311005 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-2.10 dB
PL12	13.90 dB
PL13	13.90 dB
PL2W	17.72104263 W
PL12W	0.44513249 W
PL13W	0.44513249 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127736 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40




```
NAME      heliuer20110218-2
EXPNO                    10
PROCNO                    1
Date_              20110218
Time                  17.43
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       32
DS                        2
SWH                8223.685 Hz
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                       362
DW                  60.800 usec
DE                   6.50 usec
TE                   289.7 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   14.70 usec
PL1                  -1.00 dB
PL1W            13.75590801 W
SFO1            400.1324710 MHz
SI                    32768
SF              400.1299930 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



Variecolorin C (**3**)

^{13}C NMR (100 MHz), DMSO-d_6

```
NAME      heliuer20110218-2
EXPNO                    11
PROCNO                    1
Date_              20110218
Time                  20.40
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT                DMSO
NS                     3068
DS                        4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                      575
DW                   20.800 usec
DE                    6.50 usec
TE                   291.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    9.70 usec
PL1                  -2.00 dB
PL1W          56.13311005 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -2.10 dB
PL12                 13.90 dB
PL13                 13.90 dB
PL2W          17.72104263 W
PL12W          0.44513249 W
PL13W          0.44513249 W
SFO2          400.1316005 MHz
SI                   32768
SF            100.6128148 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```