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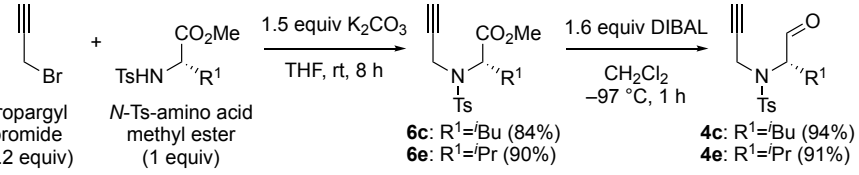
Experimental Procedures

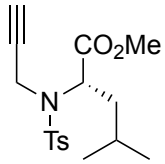
General Techniques. All commercially available reagents and anhydrous solvents including tetrahydrofuran (THF), dichloromethane (DCM), and 1,2-dimethoxyethane (DME) were purchased and used without further purification. Anhydrous methanol (MeOH), *N*,*N*-dimethylformamide (DMF), and toluene were obtained by distillation from magnesium, calcium hydride, and sodium, respectively. All reactions were monitored by thin layer chromatography (TLC) performed on 0.25 mm silica gel glass plates (60 F_{254}) using UV light and ethanolic *p*-anisaldehyde-sulfuric acid, ethanolic molybdatophosphoric acid, aqueous cerium sulfate-hexaammonium heptamolybdate-sulfuric acid, or aqueous potassium permanganate-potassium carbonate-sodium hydroxide solutions as visualizing agents. Flash column chromatography was carried out with silica gel (spherical, neutral, 100–210 μm grade). Preparative thin layer chromatography were performed on 0.75 mm Wakogel® B-5F PLC plates. Yields refer to chromatographically and spectroscopically homogenous materials. Melting points were measured on a melting point apparatus and were uncorrected. Only the strongest and/or structurally important absorptions of infrared (IR) spectra are reported in reciprocal centimeters (cm^{-1}). ^{1}H-NMR spectra (400 MHz or 600 MHz) and ^{13}C{^{1}H}NMR spectra (100 MHz or 151 MHz) were recorded in the indicated solvent. Chemical shifts (δ) are reported in delta (δ) units, parts per million (ppm). Chemical shifts for ^{1}H-NMR spectra are given relative to signals for internal tetramethylsilane (0 ppm) or residual nondeuterated solvents, i.e., chloroform (7.26 ppm). Chemical shifts for ^{13}C-NMR spectra are given relative to the signal for chloroform-*d* (77.0 ppm). Multiplicities are reported by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Coupling constants (*J*) are represented in hertz (Hz). ^{1}H and ^{13}C-NMR chemical shifts were assigned using a combination of COSY, NOESY, HMQC, and HMBC. Low and high-resolution mass spectra were measured on TOF-MS with EI, FAB, or ESI probe.

Ynals **4a**, **4b**, **4d**, **4j**, **4k**, **4m**, and **4n** were prepared according to the literature procedure [1].

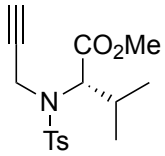
Procedure for the preparation of parent esters **6c** and **6e** for ynals **4c** and **4e**



To a suspension of *N*-tosyl amino acid methyl ester (1.0 equiv) [2] and K_2CO_3 (1.5 equiv) in anhydrous THF (1.0 M) was added propargyl bromide (1.2 equiv) at room temperature under argon. After being stirred at the same temperature for 8 h, the reaction mixture was treated with saturated aqueous NH_4Cl. The resulting mixture was extracted with EtOAc, washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography eluting with 4–8% EtOAc/hexane to give *N*-propargyl ester.

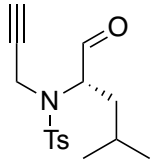


Method: Methyl *N*-(prop-2-yn-1-yl)-*N*-tosyl-L-leucinate (**6c**) (1.14 g, 84%) was obtained from the parent sulfonamide (1.20 g, 4.01 mmol), K_2CO_3 (830 mg, 6.01 mmol), and propargyl bromide (362 µL, 4.81 mmol).
Pale yellow solid. Mp 124–125 °C. Rf 0.62 (33% EtOAc/hexane). $[\alpha]_D^{22}$ –51 (*c* 1.03, $CHCl_3$). IR (neat): 3278, 2957, 2871, 2122, 1741, 1598, 1436, 1344, 1159, 1092, 1055, 994, 902, 869, 816, 744, 660 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 6.8 Hz, 2H), 7.28 (d, *J* = 6.8 Hz, 2H), 4.61–4.53 (m, 1H), 4.27 (d, *J* = 19.0 Hz, 1H), 4.12 (d, *J* = 19.0 Hz, 1H), 3.52 (s, 3H), 2.42 (s, 3H), 2.21 (s, 1H), 1.83–1.76 (m, 2H), 1.70–1.55 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.8, 143.5, 136.5, 129.3, 127.5, 79.4, 71.9, 57.4, 51.9, 38.9, 33.7, 24.3, 22.6, 21.5, 21.1. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{17}H_{23}NNaO_4S$ 360.1240, found 360.1239.

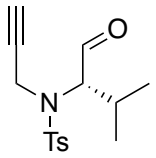


Method: Methyl *N*-(prop-2-yn-1-yl)-*N*-tosyl-L-valinate (**6e**) (938 mg, 90%) was obtained from the parent sulfonamide (920 mg, 3.22 mmol), K_2CO_3 (668 mg, 4.84 mmol), and propargyl bromide (291 µL, 3.87 mmol).
Pale yellow oil. Rf 0.55 (25% EtOAc/hexane). $[\alpha]_D^{21}$ –78 (*c* 1.04, $CHCl_3$). IR (neat): 3280, 2960, 2866, 1734, 1433, 1338, 1159, 815, 744, 667 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.38 (d, *J* = 18.8 Hz, 1H), 4.14 (d, *J* = 18.8 Hz, 1H), 4.06 (d, *J* = 10.5 Hz, 1H), 3.47 (s, 3H), 2.41 (s, 3H), 2.29–2.13 (m, 2H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 170.9, 143.5, 136.5, 129.1, 127.7, 79.2, 72.0, 64.9, 51.4, 33.5, 28.5, 21.5, 19.7, 19.1. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{16}H_{21}NNaO_4S$ 346.1084, found 346.1083.

Procedure for the synthesis of ynals **4c** and **4e**
To a solution of the above ester **6** (1 equiv) in anhydrous DCM (0.50 M) was added 1.0 M DIBAL solution in toluene (1.6 equiv) at –97 °C under argon. After being stirred at the same temperature for 1 h, the reaction mixture was treated with MeOH to consume an excess of DIBAL. The resulting mixture was diluted with ether and treated with 1 M aqueous Rochelle salt at room temperature. The mixture was vigorously stirred at the same temperature for 1 h and then extracted with Et_2O. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The crude ynals **4c** and **4e** were pure enough for analysis and used for the arylative cyclization without further purification.



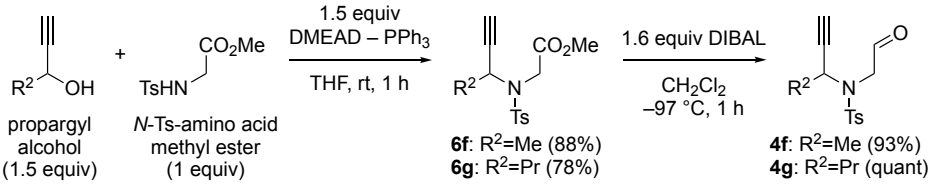
Method: (*S*)-4-Methyl-*N*-(4-methyl-1-oxopentan-2-yl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**4c**) (containing a small amount of hydrate) (146 mg, 94%) was obtained from the parent ester (170 mg, 0.504 mmol) and 1.0 M DIBAL solution in toluene (0.80 mL, 0.80 mmol).
Pale yellow oil. Rf 0.45 (33% EtOAc/hexane). IR (neat): 3277, 2959, 1733, 1335, 1160, 662 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.61 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.37 (m, 1H), 4.21 (dd, *J* = 2.4, 19.2 Hz, 1H), 4.05 (dd, *J* = 2.4, 19.2 Hz, 1H), 2.44 (s, 3H), 2.23 (dd, *J* = 2.4, 2.4 Hz, 1H), 1.75 (m, 1H), 1.57 (m, 2H), 0.89 (d, *J* = 6.4 Hz, 3H), 0.84 (d, *J* = 6.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 200.2, 144.0, 136.8, 129.7, 127.2, 78.2, 74.0, 64.0, 34.9, 34.2, 24.1, 22.7, 21.4, 21.1. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{16}H_{21}NNaO_3S$ 330.1135, found 330.1135.



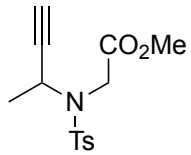
Method: (*S*)-4-Methyl-*N*-(3-methyl-1-oxobutan-2-yl)-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**4e**) (containing a small amount of hydrate) (201 mg, 91%) was obtained from the parent ester (244 mg, 0.754 mmol) and 1.0 M DIBAL solution in toluene (1.2 mL, 1.21 mmol).

Pale yellow oil. Rf 0.45 (25% EtOAc/hexane). IR (neat): 3280, 1733, 1338, 1159, 667 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.17 (d, *J* = 18.4 Hz, 1H), 4.08 (d, *J* = 18.4 Hz, 1H), 3.98 (d, *J* = 9.6 Hz, 1H), 2.43 (s, 3H), 2.31–2.18 (m, 1H), 2.20 (s, 1H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 198.3, 143.7, 136.5, 129.4, 127.2, 78.4, 73.6, 70.8, 34.4, 26.5, 21.3, 19.8, 19.4. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{15}H_{19}NNaO_3S$ 316.0978, found 316.0980.

Procedure for the preparation of parent esters **6f** and **6g** for ynals **4f** and **4g**

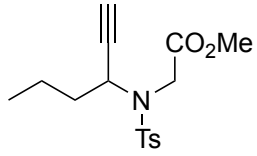


To a solution of methyl *N*-tosyl-glycinate (1.0 equiv) and PPh_3 (1.5 equiv) in anhydrous THF (0.33 M) were successively added propargyl alcohol (1.5 equiv) and bis(2-methoxyethyl) azodicarboxylate (DMEAD, 1.5 equiv) at room temperature under argon. After being stirred at the same temperature for 1 h, the reaction mixture was treated with water. The resulting mixture was extracted with Et_2O, washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography eluting with 4–8% EtOAc/hexane to give *N*-propargyl ester.



Method: Methyl *N*-(but-3-yn-2-yl)-*N*-tosylglycinate (260 mg, 88%) was obtained from methyl *N*-tosyl-glycinate (244 mg, 1.00 mmol), PPh_3 (394 mg, 1.50 mmol), but-3-yn-2-ol (105 mg, 1.50 mmol), and DMEAD (350 mg, 1.49 mmol).

Colorless oil. Rf 0.60 (33% EtOAc/hexane). IR (neat): 3273, 2986, 1760, 1342, 1159, 663 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 4.76 (dq, *J* = 2.4, 7.6 Hz, 1H), 4.10 (d, *J* = 18.4 Hz, 1H), 3.94 (d, *J* = 18.4 Hz, 1H), 3.73 (s, 3H), 2.42 (s, 3H), 2.21 (d, *J* = 2.4 Hz, 1H), 1.40 (d, *J* = 7.6 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 169.9, 143.6, 135.8, 129.4, 127.5, 80.5, 73.4, 52.1, 45.7, 44.7, 21.5, 21.3. HRMS (ESI, $[M+H]^+$) m/z calcd for $C_{14}H_{17}NNaO_4S$ 318.0771, found 318.0764.

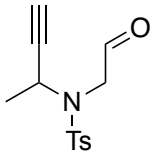


Method: Methyl *N*-(hex-1-yn-3-yl)-*N*-tosylglycinate (252 mg, 78%) was obtained from methyl *N*-tosyl-glycinate (243 mg, 1.00 mmol), PPh_3 (393 mg, 1.50 mmol), hex-1-yn-3-ol (147 mg, 1.50 mmol), and DMEAD (351 mg, 1.50 mmol).

Colorless oil. Rf 0.60 (33% EtOAc/hexane). IR (neat): 3276, 2958, 2932, 1765, 1334, 1216, 1155, 661 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.62–4.55 (m, 1H), 4.03 (d, *J* =

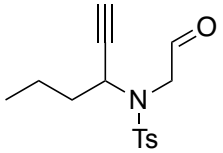
18.4 Hz, 1H), 3.88 (d, *J* = 18.4 Hz, 1H), 3.78 (s, 3H), 2.42 (s, 3H), 2.16 (d, *J* = 2.0 Hz, 1H), 1.74–1.43 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 169.9, 143.7, 135.7, 129.5, 127.7, 79.9, 73.9, 52.2, 50.4, 45.3, 37.1, 21.4, 19.0, 13.2. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{16}H_{21}NNaO_4S$ 346.1084, found 346.1077.

Procedure for *N*-(but-3-yn-2-yl)-4-methyl-*N*-(2-oxoethyl)benzenesulfonamide (**4f**)



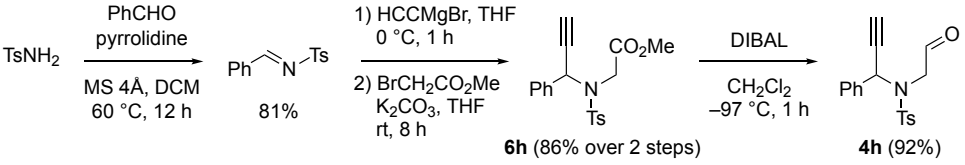
Method: Crude **4f** (156 mg, 93%) was obtained from the above ester (187 mg, 0.633 mmol) and 1.0 M DIBAL solution in toluene (1.0 mL, 1.01 mmol) according to the procedure described for **4c** and **4e**.
Colorless oil. Rf 0.45 (25% EtOAc/hexane). IR (neat): 3278, 1736, 1341, 1158, 1120, 662 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.67 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 4.94 (dq, *J* = 2.0, 6.4 Hz, 1H), 3.82 (dd, *J* = 19.0, 2.0 Hz, 1H), 3.75 (d, *J* = 19.0, 2.0 Hz, 1H), 2.44 (s, 3H), 2.17 (d, *J* = 2.0 Hz, 1H), 1.39 (d, *J* = 6.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.3, 144.2, 129.8, 127.6, 118.2, 80.4, 74.1, 52.7, 45.9, 21.6, 21.5. HRMS (ESI, $[M+Na]^+$) m/z calcd for $C_{13}H_{15}NNaO_3S$ 288.0635, found 288.0666.

Procedure for *N*-(hex-1-yn-3-yl)-4-methyl-*N*-(2-oxoethyl)benzenesulfonamide (**4g**) (containing a small amount of hydrate)



Method: Crude **4g** (150 mg, quant) was obtained from the above ester (162 mg, 0.500 mmol) and 1.0 M DIBAL solution in toluene (0.8 mL, 0.80 mmol) according to the procedure described for **4c** and **4e**.
Pale yellow oil. Rf 0.45 (25% EtOAc/hexane). IR (neat): 3278, 1735, 1340, 1162, 1121, 1092, 815, 662 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.67 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.74 (t, *J* = 8.0 Hz, 1H), 3.77 (d, *J* = 18.4 Hz, 1H), 3.71 (d, *J* = 18.4 Hz, 1H), 2.43 (s, 3H), 2.15 (s, 1H), 1.63–1.58 (m, 2H), 1.51–1.46 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.1, 144.2, 135.0, 129.7, 127.6, 79.5, 74.5, 53.0, 50.2, 37.0, 21.5, 19.9, 13.2. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{15}H_{19}NNaO_3S$ 316.0978, found 316.0980.

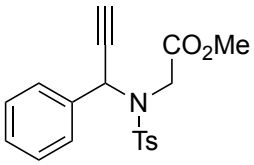
Procedure for the preparation of parent ester **6h** for ynal **4h**



To a test tube containing *p*-toluenesulfonamide (171 mg, 1.00 mmol) and molecular sieves 4Å (1.0 g) in DCM (3.2 mL) were added benzaldehyde (121 μL, 1.20 mmol) and pyrrolidine (8.3 μL, 0.10 mmol) under argon. The resulting mixture was sealed with a screw cap and stirred at 60 ºC for 12 h. The reaction mixture was cooled down to room temperature and filtered through a short pad of Celite, which was thoroughly rinsed with DCM. The filtrate was concentrated in vacuo and the residue was recrystallized with 9% EtOAc/Hexane to give *N*-benzylidene-*p*-toluenesulfonamide [3] (210 mg, 81%).
To a solution of *N*-benzylidene-*p*-toluenesulfonamide (70.0 mg, 0.270 mmol) in anhydrous THF (0.27 mL) was added 0.5 M ethynylmagnesium bromide solution in THF (1.2 mL, 0.60 mmol) at 0 ºC under argon. After being stirred at the same temperature for 1 h, the reaction mixture was treated with saturated aqueous NH_4Cl. The resulting mixture was extracted with EtOAc, washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo to give *N*-propargyl sulfonamide, which was used for the next step without further purification.
To a suspension of the crude *N*-propargyl sulfonamide (77.0 mg, 0.270 mmol) and K_2CO_3 (56.0 mg, 0.405 mmol) in anhydrous THF (0.6 mL) was added methyl bromoacetate (30.7 μL, 0.324 mmol) at room temperature under argon. After being stirred at the same temperature for 8 h, the reaction mixture was treated with saturated

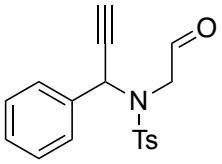
aqueous NH_4Cl. The resulting mixture was extracted with EtOAc, washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography eluting with 4–7% EtOAc/hexane to give *N*-propargyl ester (82.3 mg, 86% over 2 steps).

Methyl *N*-(1-phenylprop-2-yn-1-yl)-*N*-tosylglycinate (**6h**)



Pale yellow oil. Rf 0.50 (25% EtOAc/hexane). IR (neat): 3269, 1762, 1740, 1349, 1165, 667 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 6.0 Hz, 2H), 7.37–7.30 (m, 5H), 5.90 (d, *J* = 2.4 Hz, 1H), 3.96 (d, *J* = 17.6 Hz, 1H), 3.80 (d, *J* = 17.6 Hz, 1H), 3.40 (s, 3H), 2.45 (s, 3H), 2.39 (d, *J* = 2.4 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 169.0, 143.9, 135.8, 134.4, 129.5, 128.6, 128.3, 128.2, 127.9, 77.5, 76.4, 53.3, 51.8, 45.5, 21.5. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{19}H_{19}NNaO_4S$ 380.0937, found 380.0919.

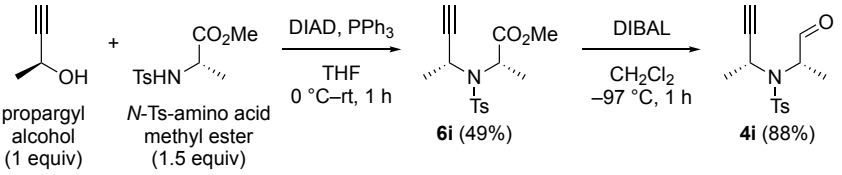
4-Methyl-*N*-(2-oxoethyl)-*N*-(1-phenylprop-2-yn-1-yl)benzenesulfonamide (**4h**) (containing a small amount of hydrate)



Method: **4h** (60.2 mg, 92%) was obtained from the above ester (77.1 mg, 0.200 mmol) and 1.0 M DIBAL solution in toluene (0.32 mL, 0.32 mmol) according to the procedure described for **4c** and **4e** and isolated by silica gel column chromatography eluting with 3–5% EtOAc/hexane.

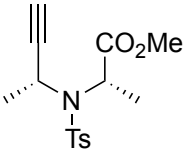
Pale yellow oil. Rf 0.5 (25% EtOAc/hexane). IR (neat): 3277, 1734, 1598, 1494, 1453, 1351, 1165, 1094, 667 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.11 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 6.8 Hz, 2H), 7.42–7.32 (m, 5H), 6.11 (s, 1H), 3.67 (d, *J* = 18.8 Hz, 1H), 3.54 (d, *J* = 18.8 Hz, 1H), 2.46 (s, 3H), 2.38 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 198.6, 144.4, 135.0, 134.7, 129.8, 129.1, 128.9, 128.1, 127.9, 77.3, 77.1, 53.5, 53.0, 21.6. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{18}H_{17}NNaO_3S$ 350.0821, found 350.0821.

Procedure for the preparation of parent ester **6i** for ynal **4i**



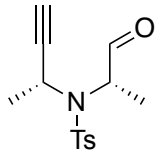
To a solution of methyl *N*-tosyl-L-alaninate (772 mg, 3.00 mmol), PPh_3 (787 mg, 3.00 mmol), and (*S*)-3-butyn-2-ol (157 μL, 2.00 mmol) in anhydrous THF (8.0 mL) was added DIAD (580 μL, 3.00 mmol) at 0 °C under argon. After being stirred at room temperature for 1 h, the reaction mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography eluting with 6–12% EtOAc/hexane and again purified by silica gel column chromatography eluting with 0.4–0.6 % EtOAc/toluene to give *N*-propargyl ester (453 mg, 49%).

Methyl *N*-((*R*)-but-3-yn-2-yl)-*N*-tosyl-*L*-alaninate (**6i**)



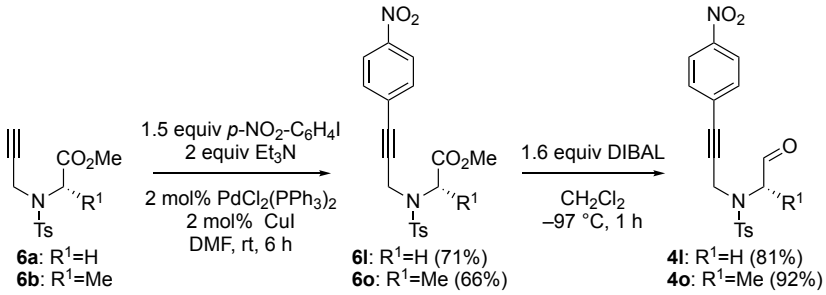
Pale brown oil. Rf 0.60 (33% EtOAc/hexane). $[\alpha]_D^{23}$ +59 (*c* 0.95, $CHCl_3$). IR (neat): 3270, 2992, 2951, 1744, 1597, 1449, 1338, 1229, 1158, 1092, 768, 663 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 4.51 (dq, *J* = 2.8, 7.2 Hz, 1H), 4.19 (q, *J* = 6.8 Hz, 1H), 3.65 (s, 3H), 2.32 (s, 3H), 2.26 (d, *J* = 2.8 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H), 1.43 (d, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 172.0, 143.3, 138.0, 129.3, 127.3, 81.6, 72.9, 53.8, 52.2, 45.5, 21.9, 21.3, 16.5. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{15}H_{19}NNaO_4S$ 332.0927, found 332.0919.

N-((*R*)-But-3-yn-2-yl)-4-methyl-*N*-((*S*)-1-oxopropan-2-yl)benzenesulfonamide (**4i**) (containing a small amount of hydrate)



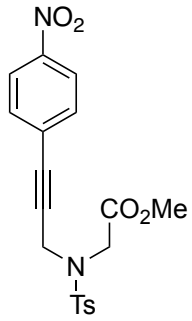
Method: Crude **4i** (158 mg, 88%) was obtained from the above ester (200 mg, 0.647 mmol) and 1.0 M DIBAL solution in toluene (1.0 mL, 1.0 mmol) according to the procedure described for **4c** and **4e**.
Pale yellow oil. Rf 0.60 (33% EtOAc/hexane). IR (neat): 3277, 1739, 1335, 1158, 662 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.75 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.88 (dq, *J* = 2.4, 7.2 Hz, 1H,), 3.99 (q, *J* = 7.2 Hz, 1H), 2.43 (s, 3H), 2.34 (d, *J* = 2.4 Hz, 1H), 1.54 (d, *J* = 7.2 Hz, 3H), 1.44 (d, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.8, 143.8, 138.0, 129.7, 127.0, 81.1, 73.0, 60.3, 45.9, 22.6, 21.5, 13.8. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{14}H_{17}NNaO_3S$ 302.0821, found 302.0823.

Procedure for the preparation of parent esters **6l** and **6o** for ynals **4l** and **4o**



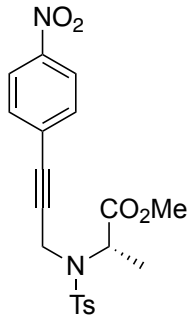
6a: R^1=H
6b: R^1=Me
6l: R^1=H (71%)
6o: R^1=Me (66%)
4l: R^1=H (81%)
4o: R^1=Me (92%)

To a solution of *N*-propargyl ester (1.0 equiv) in anhydrous DMF (0.5 M) were successively added iodobenzene or 1-iodo-4-nitrobenzene (1.5 equiv), $PdCl_2(PPh_3)_2$ (2 mol%), CuI (2 mol%), and Et_3N (2.0 equiv) at room temperature under argon. After being stirred at the same temperature for 6 h, the reaction mixture was treated with saturated aqueous NH_4Cl. The resulting mixture was extracted with Et_2O, washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel column chromatography eluting with 6–12% EtOAc/hexane to give internal alkyne-ester.



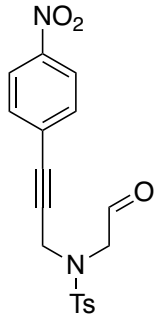
Method: Methyl *N*-(3-(4-nitrophenyl)prop-2-yn-1-yl)-*N*-tosylglycinate (**6l**) (315 mg, 71%) was obtained from methyl *N*-(prop-2-yn-1-yl)-*N*-tosylglycinate (**6a**) (310 mg, 1.10 mmol)

Pale yellow oil. Rf 0.47 (33% EtOAc/hexane). IR (neat): 2952, 1752, 1595, 1520, 1344, 1216, 1163, 1094, 918, 854, 751, 663 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.33–7.27 (m, 4H), 4.52 (s, 2H), 4.17 (s, 2H), 3.72 (s, 3H), 2.39 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 168.7, 147.2, 144.0, 135.8, 132.3, 129.6, 128.7, 127.6, 123.4, 87.1, 84.0, 52.4, 47.1, 38.2, 21.5. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{19}H_{18}N_2NaO_6S$ 425.0778, found 425.0777.



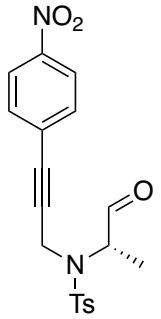
Method: Methyl *N*-(3-(4-nitrophenyl)prop-2-yn-1-yl)-*N*-tosyl-L-alaninate (**6o**) (346 mg, 66%) was obtained from methyl *N*-(prop-2-yn-1-yl)-*N*-tosyl-L-alaninate (**6b**) (372 mg, 1.26 mmol).
Pale yellow oil. Rf 0.50 (33% EtOAc/hexane). $[\alpha]_D^{23}$ −13 (*c* 1.0, $CHCl_3$). IR (neat): 1743, 1594, 1519, 1344, 1159, 854, 751, 661 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 4.76 (q, *J* = 7.2 Hz, 1H), 4.53 (d, *J* = 18.8 Hz, 1H), 4.37 (d, *J* = 18.8 Hz, 1H), 3.61 (s, 3H), 2.40 (s, 3H), 1.54 (d, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.3, 146.8, 143.5, 136.7, 132.0, 129.3, 129.0, 127.2, 123.2, 90.0, 82.3, 54.6, 52.1, 34.4, 21.2, 16.0. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{20}H_{20}N_2NaO_6S$ 439.0934, found 439.0933.

4-Methyl-*N*-(3-(4-nitrophenyl)prop-2-yn-1-yl)-*N*-(2-oxoethyl)benzenesulfonamide (**4l**) (containing a small amount of hydrate)



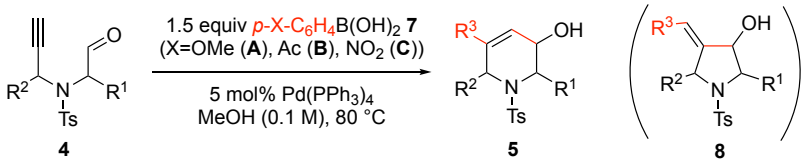
Method: Crude **4l** (62.9 mg, 81%) was obtained from the above ester (83.6 mg, 0.208 mmol) and 1.0 M DIBAL solution in toluene (0.32 mL, 0.32 mmol) according to the procedure described for **4c** and **4e**.
Pale yellow oil. Rf 0.53 (50% EtOAc/hexane). IR (neat): 3640–3200 (br), 2925, 2854, 1734, 1595, 1519, 1344, 1162, 855, 751, 664 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.72 (s, 1H), 8.14 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.39–7.22 (m, 4H), 4.43 (s, 2H), 4.02 (s, 2H), 2.40 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 197.0, 147.4, 144.4, 134.9, 132.3, 129.9, 128.4, 127.8, 123.5, 86.5, 84.5, 56.2, 39.5, 21.5. LRMS (EI) *m/z* (relative intensity) 372 ($[M]^+$, 3), 343 (100), 155 (42), 91 (44). HRMS (EI, $[M]^+$): *m/z* calcd for $C_{18}H_{16}N_2O_5S$, 372.0780; found, 372.0805.

(*S*)-4-Methyl-*N*-(3-(4-nitrophenyl)prop-2-yn-1-yl)-*N*-(1-oxopropan-2-yl)benzenesulfonamide (**4o**) (containing a small amount of hydrate)



Method: Crude **4o** (77.9 mg, 92%) was obtained from the above ester (91.3 mg, 0.219 mmol) and 1.0 M DIBAL solution in toluene (0.32 mL, 0.32 mmol) according to the procedure described for **4c** and **4e**.
Pale yellow oil. Rf 0.40 (33% EtOAc/hexane). IR (neat): 1595, 1522, 1343, 1159, 1092, 854, 750, 663 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.76 (s, 1H), 8.16 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.55 (d, *J* = 18.0 Hz, 1H), 4.46 (q, *J* = 6.8 Hz, 1H), 4.19 (d, *J* = 18.0 Hz, 1H), 2.43 (s, 3H), 1.30 (d, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.8, 147.4, 144.3, 136.3, 132.2, 130.0, 128.4, 127.3, 123.5, 88.1, 84.2, 61.3, 35.2, 21.5, 11.3. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{19}H_{18}N_2NaO_5S$ 409.0829, found 409.0826.

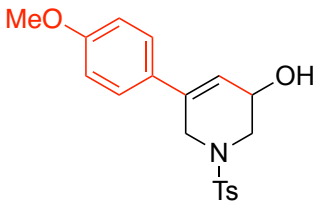
General Procedure for the $Pd(PPh_3)_4$-Catalyzed Arylative Cyclizations of Terminal Alkyne-Aldehyde **4a–i** with Arylboronic Acid **7A–C** (Scheme 3)



4 **5** **8**

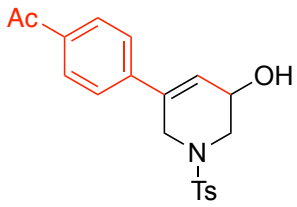
To a test tube containing **4a–i** (1 equiv), arylboronic acid **7A–C** (1.5 equiv), and $Pd(PPh_3)_4$ (5 mol%) was added anhydrous MeOH (0.1 M) under argon. The resulting mixture was sealed with a screw cap and agitated at 80 °C for the time described in Scheme 3. The reaction mixture was cooled down to room temperature and then treated with polymer supported diethanolamine (PL-DEAM^{TM}, 1.72 mmol/g, 3 equiv, X g) and THF (10 × X mL) to remove an excess of **7A–C**. The mixture was agitated at room temperature for 2 h. The mixture was filtered and the resin was thoroughly rinsed with $CHCl_3$. The filtrate was concentrated in vacuo and the residue was purified by preparative TLC or silica gel column chromatography to give endocyclic products **5(a–i)(A–C)** in the yield described in Scheme 3.

Procedure for 5-(4-methoxyphenyl)-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5aA**)



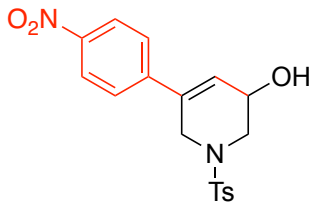
Method: **5aA** (16.6 mg, 90%) was obtained from **4a** (12.9 mg, 0.0513 mmol), **7A** (11.4 mg), and $Pd(PPh_3)_4$ (2.9 mg) and isolated by silica gel column chromatography eluting with 15% EtOAc/hexane. Spectra data of **5aA** were in agreement with those reported in the literature [4].

Procedure for 1-(4-(5-hydroxy-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)phenyl)ethan-1-one (**5aB**)



Method: **5aB** (12.3 mg, 70%) was obtained from **4a** (11.9 mg, 0.0474 mmol), **7B** (12.3 mg), and $Pd(PPh_3)_4$ (2.9 mg) and isolated by preparative TLC eluting with 20% EtOAc/toluene. Spectra data of **5aB** were in agreement with those reported in the literature [5].

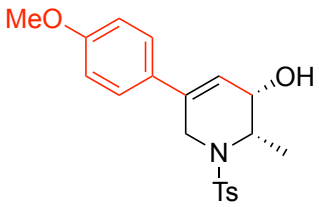
Procedure for 5-(4-nitrophenyl)-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5aC**)



Method: **5aC** (28.2 mg, 51%) was obtained from **4a** (37.7 mg, 0.150 mmol), **7C** (37.6 mg), and $Pd(PPh_3)_4$ (8.6 mg) and isolated by preparative TLC eluting with 20% EtOAc/toluene.

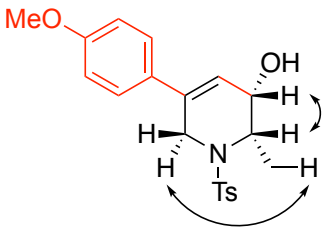
Pale brown oil. IR (neat): 3620–3200, 1681, 1604, 1344, 1271, 1167, 1094, 819, 755, 660 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.35 (s, 1H), 4.45 (ddd, *J* = 4.8, 4.0, 5.6 Hz, 1H), 4.09 (d, *J* = 16.0 Hz, 1H), 3.76 (d, *J* = 16.0 Hz, 1H), 3.37 (dd, *J* = 12.0, 4.8 Hz, 1H), 3.24 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.60 (d, *J* = 5.6 Hz, 1H), 2.44 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 147.7, 144.3, 143.7, 135.0, 132.9, 130.0, 128.1, 127.7, 126.3, 124.0, 63.7, 49.7, 46.2, 21.6. LRMS (EI) *m/z* (relative intensity) 374 ([M]$^+$, 2), 356 (3), 184 (100), 155 (61). HRMS (EI, [M]$^+$): *m/z* calcd for $C_{18}H_{18}N_2O_5S$, 374.0936; found, 374.0956.

Procedure for (2*S*,3*S*)-5-(4-methoxyphenyl)-2-methyl-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5bA**)



Method: **5bA** (33.1 mg, 87%, dr >95 : <5) was obtained from **4b** (27.1 mg, 0.102 mmol), **7A** (22.8 mg), and $Pd(PPh_3)_4$ (5.8 mg) and isolated by preparative TLC eluting with 10% EtOAc/toluene.

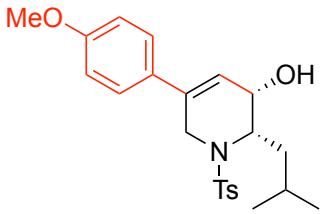
Colorless oil. Rf 0.40 (50% EtOAc/hexane). $[\alpha]_D^{23}$ −5.8 (*c* 0.60, $CHCl_3$). IR (neat): 3497, 1608, 1335, 1515, 1160, 1030, 816, 752, 659 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 2H) 7.32–7.28 (m, 4H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.82 (s, 1H), 4.49 (m, 1H), 4.47 (d, *J* = 16.0 Hz, 1H), 4.34 (m, 1H), 3.81 (s, 3H), 3.74 (d, *J* = 16.0 Hz, 1H), 2.42 (s, 3H), 1.88 (br-s, 1H), 0.91 (d, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.9, 143.5, 137.0, 133.5, 129.8, 129.5, 127.0, 126.3, 123.2, 114.0, 67.0, 55.3, 50.8, 41.5, 21.5, 9.4. HRMS (ESI, [M+Na]$^+$) *m/z* calcd for $C_{20}H_{23}NNaO_4S$ 396.1240, found 396.1242.



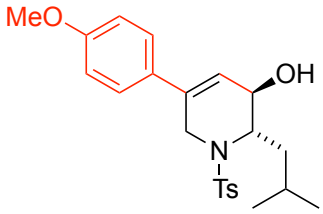
NOESY analysis

Procedure for 2-isobutyl-5-(4-methoxyphenyl)-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5cA**)

Method: **5cA** (19.1 mg, 92%, dr 91 : 9) was obtained from **4c** (15.4 mg, 0.0501 mmol), **7A** (11.5 mg), and $Pd(PPh_3)_4$ (3.0 mg) and isolated by preparative TLC eluting with 10% EtOAc/toluene.

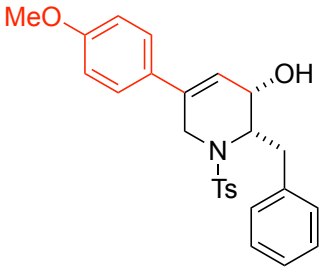


For (2*S*,3*S*)-**5cA** as a major diastereomer: Colorless oil. Rf 0.38 (10% EtOAc/toluene). $[\alpha]_D^{22}$ −131 (*c* 0.52, $CHCl_3$). IR (neat): 3505, 2955, 1608, 1514, 1331, 1158, 817, 745, 660 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.76 (s, 1H), 4.52 (d, *J* = 18.0 Hz, 1H), 4.33–4.20 (m, 2H), 3.83 (d, *J* = 18.0 Hz, 1H), 3.82 (s, 3H), 2.34 (s, 3H), 1.80–1.64 (m, 2H), 1.36 (m, 2H), 0.94 (d, *J* = 6.4 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.6, 143.3, 138.0, 129.7, 129.3, 126.8, 126.5, 126.2, 123.4, 114.0, 65.7, 55.3, 52.7, 41.5, 33.0, 24.3, 23.9, 21.5 (one signal missing due to an overlap). HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{23}H_{29}NNaO_4S$ 438.1710, found 438.1707.



For (2*S*,3*R*)-**5cA** as a minor diastereomer: Colorless oil. Rf 0.42 (10% EtOAc/toluene). IR (neat): 3600–3200, 2926, 2869, 1607, 1515, 1335, 1247, 1158, 1093, 1031, 827, 754, 655 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.33–7.28 (m, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.12 (d, *J* = 6.1 Hz, 1H), 4.51 (d, *J* = 17.5 Hz, 1H), 4.19 (t, *J* = 7.2 Hz, 1H), 3.99 (dd, *J* = 10.5, 6.1 Hz, 1H), 3.82 (s, 3H), 3.76 (d, *J* = 17.5 Hz, 1H), 2.43 (s, 3H), 1.96 (d, *J* = 10.5, 1H), 1.61–1.51 (m, 1H), 1.20–1.14 (m, 2H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 160.0, 143.6, 137.2, 136.4, 129.74, 129.70, 127.4, 126.5, 120.6, 114.1, 66.7, 56.8, 55.4, 41.7, 37.6, 25.1, 22.7, 22.6, 21.5. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{23}H_{29}NNaO_4S$ 438.1710, found 438.1707.

Procedure for (2*R**, 3*R**)-2-benzyl-5-(4-methoxyphenyl)-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5dA**)

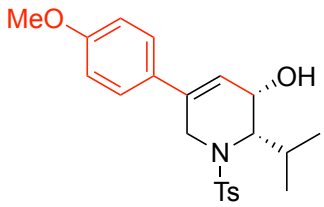


Method: **5dA** (42.5 mg, 95%, dr >95 : <5) was obtained from **4d** (33.0 mg, 0.100 mmol), **7A** (22.8 mg), and $Pd(PPh_3)_4$ (5.8 mg) and isolated by preparative TLC eluting with 50% EtOAc/hexane.

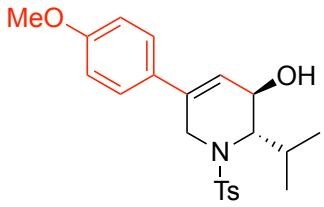
Pale yellow oil. Rf 0.50 (50% EtOAc/hexane). IR (neat): 3492, 1607, 1514, 1248, 1157, 1096, 752, 660 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 6.8 Hz, 2H), 7.27–7.13 (m, 7H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 5.94 (s, 1H), 4.64 (dd, *J* = 5.4, 6.0 Hz, 1H), 4.57 (ddd, *J* = 4.8, 5.4, 9.6 Hz, 1H), 4.47 (d, *J* = 18.0 Hz, 1H), 3.86 (d, *J* = 18.0 Hz, 1H), 3.11 (dd, *J* = 4.8, 14.2 Hz, 1H), 2.56 (dd, *J* = 9.6, 14.2 Hz, 1H), 2.36 (s, 3H), 1.77 (d, *J* = 6.0 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.6, 143.0, 138.6, 137.1, 133.4, 129.5, 129.4, 129.1, 128.4, 126.9, 126.3, 126.2, 123.6, 114.0, 66.7, 56.4, 55.3, 41.6, 31.2, 21.4. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{26}H_{27}NNaO_4S$ 472.1553, found 472.1548.

Procedure for 2-isopropyl-5-(4-methoxyphenyl)-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5eA**)

Method: **5eA** (33.8 mg, 86%, dr 70 : 30) was obtained from **4e** (15.4 mg, 0.525 mmol), **7A** (11.5 mg), and $Pd(PPh_3)_4$ (3.0 mg) and isolated by preparative TLC eluting with 15% EtOAc/toluene.



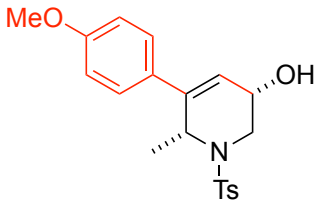
For (2*S*,3*S*)-**5eA** as a major diastereomer: Colorless oil. Rf 0.39 (15% EtOAc/toluene). $[\alpha]_D^{23}$ −82 (*c* 0.58, $CHCl_3$). IR (neat): 3509, 2962, 1608, 1515, 1464, 1333, 1251, 1159, 1090, 1046, 816, 758, 663 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.31–7.20 (m, 4H), 6.87 (d, *J* = 6.8 Hz, 2H), 5.88 (s, 1H), 4.44 (d, *J* = 18.0 Hz, 1H), 4.35 (m, 1H), 3.98–3.90 (m, 2H), 3.80 (s, 3H), 2.39 (s, 3H), 2.00 (m, 2H), 1.14 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.6, 143.2, 138.0, 133.0, 129.7, 129.4, 126.7, 126.2, 124.2, 114.0, 67.3, 60.2, 55.3, 43.5, 27.0, 21.5, 20.9 (one signal missing due to an overlap). HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{15}H_{19}NNaO_4S$ 424.1553, found 424.1551.



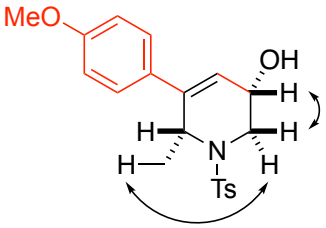
For (2*S*,3*R*)-**5eA** as a minor diastereomer: Colorless oil. Rf 0.44 (15% EtOAc/toluene). $[\alpha]_D^{23}$ −122 (*c* 2.25 in $CHCl_3$). IR (neat): 3600–3260, 2964, 1607, 1515, 1457, 1326, 1250, 1156, 1093, 1033, 826, 760, 657 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.31–7.20 (m, 4H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.11 (d, *J* = 5.5 Hz, 1H), 4.46 (d, *J* = 18.3 Hz, 1H), 4.32–4.20 (m, 1H), 3.89–3.73 (m, 5H), 2.40 (s, 3H), 1.84 (d, *J* = 9.3 Hz, 1H), 1.76–1.61 (m, 1H), 1.01 (d, *J* = 6.3 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.9, 143.4, 137.7, 136.3, 129.6, 129.5, 127.3, 126.3, 120.5, 114.0, 64.7, 64.5, 55.3, 41.9, 27.5, 21.5, 20.8, 20.3. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{15}H_{19}NNaO_4S$ 424.1553, found 424.1551.

Procedure for 5-(4-methoxyphenyl)-6-methyl-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5fA**)

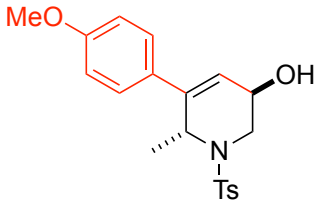
Method: **5fA** (17.0 mg, 90%, dr 94 : 6) was obtained from **4f** (13.3 mg, 0.0507 mmol), **7A** (11.4 mg), and $Pd(PPh_3)_4$ (2.9 mg) and isolated by preparative TLC eluting with 10% EtOAc/toluene (developed six times).



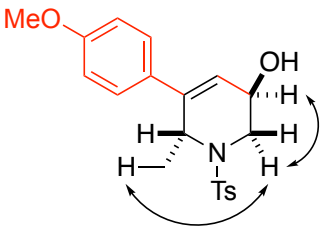
For (3*R**,6*S**)-**5fA** as a major diastereomer: Colorless oil. Rf 0.37 (17% EtOAc/toluene). IR (neat): 3492, 1607, 1514, 1248, 1157, 252, 660 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.2 Hz, 2H) 7.27–2.22 (m, 4H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.29 (s, 1H), 4.96 (q, *J* = 6.8 Hz, 1H), 4.18 (dd, *J* = 6.4, 10.0 Hz, 1H), 4.07 (dd, *J* = 6.4, 13.6 Hz, 1H), 3.81 (s, 3H), 2.90 (dd, *J* = 10.0 Hz, 13.6 Hz, 1H), 2.39 (s, 3H), 2.15 (br-s, 1H), 1.16 (d, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.5, 143.4, 142.0, 137.9, 130.4, 129.7, 127.5, 126.7, 125.2, 114.0, 63.1, 55.3, 50.6, 43.5, 21.4, 18.3. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{20}H_{23}NNaO_4S$ 396.1240, found 396.1239.



NOESY analysis

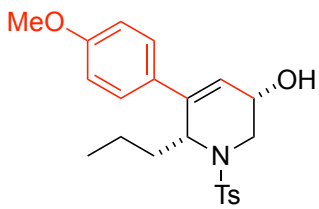


For (3*R**,6*R**)-**5fA** as a minor diastereomer: Colorless oil. Rf 0.38 (17% EtOAc/toluene). IR (neat): 3600–3160 (br), 2979, 2934, 2838, 1607, 1513, 1335, 1247, 1155, 1122, 1088, 1013, 815, 741, 654 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.6 Hz, 2H) 7.33–7.24 (m, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.93 (d, *J* = 4.1 Hz, 1H), 5.05 (q, *J* = 6.9 Hz, 1H), 4.18–4.12 (m, 1H), 3.90 (d, *J* = 14.4 Hz, 1H), 3.82 (s, 3H), 3.33 (d, *J* = 14.4 Hz, 1H), 2.42 (s, 3H), 1.95 (d, *J* = 10.3 Hz, 1H), 1.06 (d, *J* = 6.9 Hz, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 159.9, 144.1, 143.5, 137.6, 130.5, 129.8, 127.7, 127.3, 122.2, 114.1, 63.6, 55.3, 50.5, 45.1, 21.5, 16.6. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{20}H_{23}NNaO_4S$ 396.1240, found 396.1238.



NOESY analysis

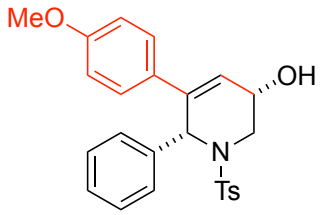
Procedure for (3*R**,6*S**)-5-(4-methoxyphenyl)-6-propyl-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5gA**)



Method: **5gA** (21.6 mg, 78%, dr >95 : <5) was obtained from **4g** (20.2 mg, 0.0689 mmol), **7A** (15.7 mg), and $Pd(PPh_3)_4$ (4.0 mg) and isolated by preparative TLC eluting with 10% EtOAc/toluene.

Pale yellow oil. Rf 0.30 (33% EtOAc/hexane). IR (neat): 3494, 2959, 2934, 1606, 1513, 1336, 1248, 825, 761, 661 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.0 Hz, 2H) 7.25 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.55 (s, 1H), 4.82 (t, *J* = 10.0 Hz, 1H), 4.08 (dd, *J* = 6.8 Hz, 14.0 Hz, 1H), 3.90 (dd, *J* = 6.8, 10.0 Hz, 1H), 3.83 (s, 3H), 2.96 (dd, *J* = 10.0 Hz, 14.0 Hz, 1H), 2.41 (s, 3H), 1.77 (br-s, 1H), 1.61–1,30 (m, 4H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.5, 143.4, 141.7, 138.1, 130.8, 129.6, 127.3, 126.8, 124.8, 114.1, 62.0, 55.3, 43.8, 43.8, 34.6, 21.5, 19.9, 13.6. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{22}H_{27}NNaO_4S$ 424.1553, found 424.1550.

Procedure for (3*R**,6*S**)-5-(4-methoxyphenyl)-6-phenyl-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5hA**)

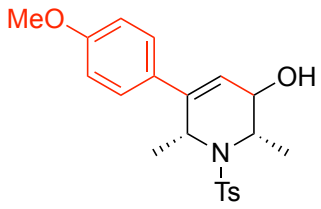


Method: **5hA** (2.9 mg, 36%, dr >95 : <5) was obtained from **4h** (16.4 mg, 0.0501 mmol), **7A** (11.4 mg), and $Pd(PPh_3)_4$ (2.9 mg) and isolated by preparative TLC eluting with 15% EtOAc/toluene.

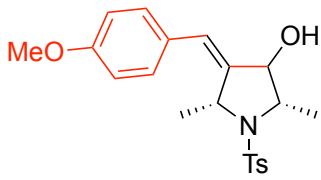
Pale yellow oil. Rf 0.40 (50% EtOAc/hexane). IR (neat): 3491, 1606, 1513, 1335, 1250, 1160, 1034, 815, 744, 704, 661 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 2H) 7.39 (d, *J* = 6.8 Hz, 2H), 7.30–7.15 (m, 7H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.05 (s, 1H), 6.02 (s, 1H), 4.18 (dd, *J* = 7.6, 10.3 Hz, 1H), 3.88 (dd, *J* = 7.6 Hz, 14.1 Hz, 1H), 3.74 (s, 3H), 2.84 (dd, *J* = 10.3, 14.1 Hz, 1H), 2.37 (s, 3H), 1.82 (br-s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.4, 143.4, 137.8, 137.68, 137.66, 130.0, 129.6, 129.0, 128.5, 128.0, 127.2, 127.0, 126.5, 113.9, 62.8, 57.5, 55.2, 43.6, 21.5. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{25}H_{25}NNaO_4S$ 458.1397, found 458.1398.

Procedure for (2*S*,6*R*)-5-(4-methoxyphenyl)-2,6-dimethyl-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5iA**) and (2*S*,5*R*)-4-((*E*)-4–methoxybenzylidene)-2,5-dimethyl-1-tosylpyrrolidin-3-ol (**8iA**)

Method: **5iA** (98 mg, 45%, dr >95 : <5) and **8iA** (44 mg, 20%, dr >95 : <5) were obtained from **4i** (158 mg, 0.566 mmol), **7A** (129 mg), and $Pd(PPh_3)_4$ (49.0 mg) and isolated by preparative TLC eluting with 40% EtOAc/hexane.

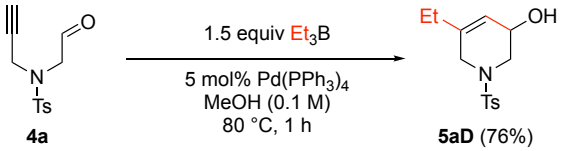


For **5iA**: Pale yellow oil. Rf 0.30 (40% EtOAc/hexane). $[\alpha]_D^{21}$ –163 (*c* 0.55, $CHCl_3$). IR (neat): 3492, 1607, 1514, 1248, 1157, 752, 660 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 2H) 7.32–7.20 (m , 4H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.56 (s, 1H), 4.97 (q, *J* = 7.2 Hz, 1H), 4.26 (m, 1H), 4.13 (m, 1H), 3.82 (s, 3H), 2.40 (s, 3H), 1.78 (br-s, 1H), 1.31 (d, *J* = 7.2 Hz, 3H), 1.23 (d, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.4, 143.3, 142.0, 138.4, 130.9, 129.8, 127.9, 126.8, 123.8, 113.9, 65.8, 55.3, 49.8, 49.7, 22.1, 21.5, 14.8. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{21}H_{25}NNaO_4S$ 410.1397, found 410.1396.



For **8iA**: Pale yellow oil. Rf 0.33 (40% EtOAc/hexane). IR (neat): 3491, 1606, 1513, 1250, 1160, 744, 661 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.35 (s, 1H), 4.77 (q, *J* = 6.9 Hz, 1H), 4.22 (dd, *J* = 5.5, 6.5 Hz, 1H), 3.84 (s, 3H), 3.66 (dq, *J* = 5.5, 6.5 Hz, 1H), 2.37 (s, 3H), 1.65 (d, *J* = 5.5 Hz, 1H), 1.56 (d, *J* = 6.5 Hz, 3H), 1.38 (d, *J* = 6.9 Hz, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 159.1, 143.3, 141.3, 135.3, 129.9, 129.6, 128.0, 127.2, 125.1, 113.9, 76.9, 58.2, 56.9, 55.3, 23.5, 21.5, 16.5. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{21}H_{25}NNaO_4S$ 410.1397, found 410.1396.

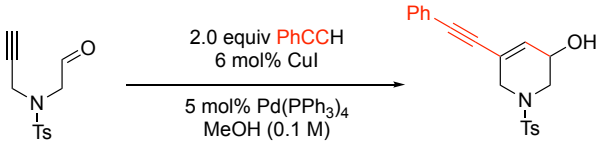
Procedure for 5-ethyl-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5aD**) (Scheme 3)



4a **5aD** (76%)

To a test tube containing **4a** (50.3 mg, 0.200 mmol) and $Pd(PPh_3)_4$ (11.6 mg, 5 mol%) were added anhydrous MeOH (2.0 mL) and 1.0 M Et_3B solution in THF (0.30 mL, 1.5 equiv) under argon. The resulting mixture was sealed with a screw cap and agitated at 80 °C for 1 h. The reaction mixture was cooled down to room temperature and then concentrated in vacuo. The residue was purified by preparative TLC eluting with 20% EtOAc/toluene to give **5aD** (42.8 mg, 76%) as a colorless oil. Spectra data of **5aD** were in agreement with those reported in the literature [4].

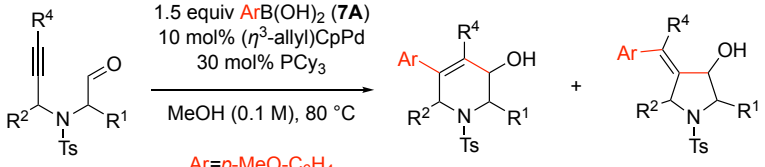
Procedure for 5-(phenylethynyl)-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5aE**) (Scheme 3)



4a **5aE** (77%)

To a test tube containing **4a** (25.1 mg, 0.100 mmol), CuI (1.2 mg, 6 mol%), PhCCH (22 μL, 2.0 equiv), and $Pd(PPh_3)_4$ (5.8 mg, 5 mol%) was added anhydrous MeOH (1.0 mL) under argon. The resulting mixture was sealed with a screw cap and agitated at 80 °C for 1.5 h. The reaction mixture was cooled down to room temperature and then concentrated in vacuo. The residue was purified by preparative TLC eluting with 20% EtOAc/toluene to give **5aE** (27.3 mg, 77%) as a pale yellow oil. Spectra data of **5aE** were in agreement with those reported in the literature [5].

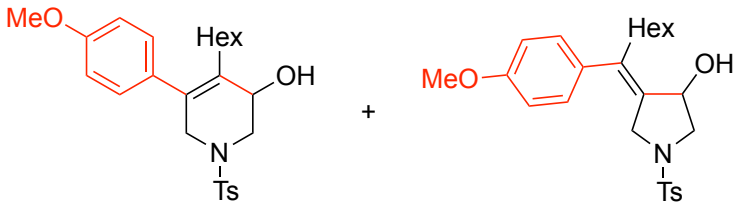
General Procedure for the Pd/PCy_3-Catalyzed Arylative Cyclizations of Internal Alkyne-Aldehyde **4j**–**o** with **7A** (Scheme 4)



4 **5** **8**

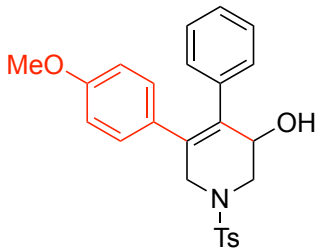
To a test tube containing **4j–o** (1 equiv), *p*-methoxyphenylboronic acid (**7A**, 1.5 equiv), (η^3-allyl)CpPd (10 mol%), and PCy_3 (30 mol%) was added anhydrous MeOH (0.10 M) under argon. The resulting mixture was sealed with a screw cap and agitated at 80 °C for the time described in Scheme 4. The reaction mixture was cooled down to room temperature and then treated with PL-DEAM^{TM} (1.72 mmol/g, 2 equiv, X g) and THF (10 × X mL) to remove an excess of **7A**. The mixture was agitated at room temperature for 2 h. The mixture was filtered and the resin was thoroughly rinsed with $CHCl_3$. The filtrate was concentrated in vacuo and the residue was purified by preparative TLC to give **5(j–o)A** along with a small amount of **8(j–o)A** in the yield described in Scheme 4.

Procedure for 4-hexyl-5-(4-methoxyphenyl)-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5jA**) and (*E*)-4-(1-(4-methoxyphenyl)heptyli–dene)-1-tosylpyrrolidin-3-ol (**8jA**)



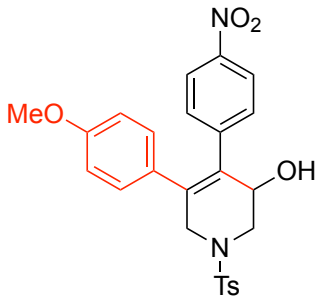
Method: **5jA** (28.4 mg, 65%) and **8jA** (3.6 mg, 8%) were obtained from **4j** (33.5 mg, 0.0999 mmol), **7A** (23.0 mg), (η^3-allyl)CpPd (1.1 mg), and PCy_3 (4.2 mg) and isolated by preparative TLC eluting with 15% EtOAc/toluene (developed four times). Spectra data of **5jA** and **8jA** were in agreement with those reported in the literature [5].

Procedure for 5-(4-methoxyphenyl)-4-phenyl-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5kA**)



Method: **5kA** (32.5 mg, 98%) was obtained from **4k** (24.6 mg, 0.0751 mmol), **7A** (17.1 mg), (η^3-allyl)CpPd (1.5 mg), and PCy_3 (5.7 mg) and isolated by preparative TLC eluting with 20% EtOAc/toluene. Spectra data of **5kA** were in agreement with those reported in the literature [5].

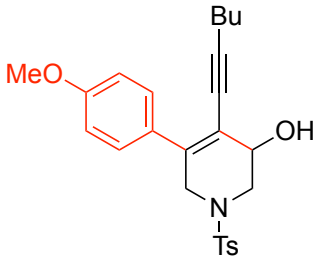
Procedure for 5-(4-methoxyphenyl)-4-(4-nitrophenyl)-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5lA**)



Method: **5lA** (15.8 mg, 80%) was obtained from **4l** (15.3 mg, 0.0411 mmol), **7A** (11.4 mg), (η^3-allyl)CpPd (1.0 mg), and PCy_3 (3.8 mg) and isolated by preparative TLC eluting with 20% EtOAc/toluene.

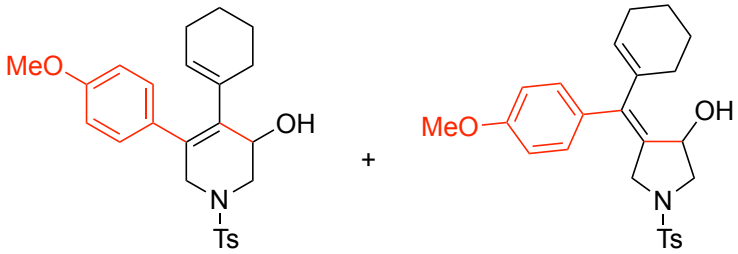
Pale yellow oil. Rf 0.40 (50% EtOAc/hexane). IR (neat): 3600–3160 (br), 2925, 1598, 1514, 1449, 1344, 1250, 1166, 1092, 1032, 760, 661 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.8 Hz, 2H) 7.73 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 4.59–4.51 (m, 1H), 4.39 (d, *J* = 17.1 Hz, 1H), 3.97 (dd, *J* = 12.1, 2.4 Hz, 1H), 3.74 (s, 3H), 3.37 (d, *J* = 17.1 Hz, 1H), 2.92 (dd, *J* = 12.1, 2.7 Hz, 1H), 2.45 (s, 3H), 2.46–2.36 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.4, 146.48, 146.45, 144.3, 136.8, 133.7, 132.4, 130.2, 130.1, 130.0, 129.1, 127.9, 123.3, 114.0, 67.1, 55.2, 50.8, 49.6, 21.5. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{25}H_{24}N_2NaO_6S$ 503.1247, found 503.1246.

Procedure for 4-(hex-1-ynyl)-5-(4-methoxyphenyl)-1-(toluene-4-sulfonyl)-1,2,3,6-tetrahydropyridin-3-ol (**5mA**)



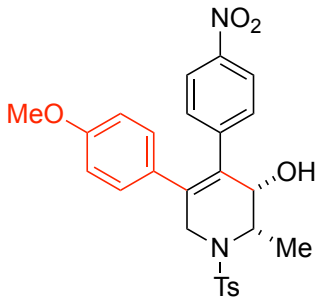
Method: **5mA** (12.0 mg, 70%) was obtained from **4m** (14.0 mg, 0.0422 mmol), **7A** (9.6 mg), (η^3-allyl)CpPd (0.8 mg), and PCy_3 (3.2 mg) and isolated by preparative TLC eluting with 25% EtOAc/toluene. Spectra data of **5mA** were in agreement with those reported in the literature [5].

Procedure for 4-(cyclohex-1-en-1-yl)-5-(4-methoxyphenyl)-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5nA**) and (*E*)-4-(cyclohex-1–en-1-yl(4-methoxyphenyl)methylene)-1-tosylpyrrolidin-3-ol (**8nA**)



Method: **5nA** (13.0 mg, 53%) and **8nA** (1.6 mg, 7%) were obtained from **4n** (18.5 mg, 0.0558 mmol), **7A** (12.7 mg), (η^3-allyl)CpPd (1.2 mg), and PCy_3 (4.7 mg) and isolated by preparative TLC eluting with 40% EtOAc/hexane. Spectra data of **5nA** and **8nA** were in agreement with those reported in the literature [5].

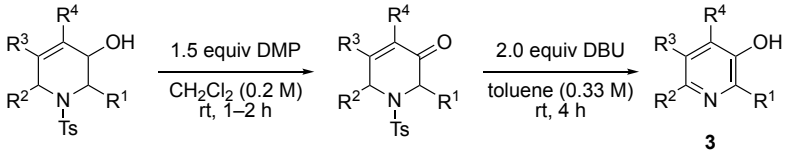
Procedure for (2*S*,3*S*)-5-(4-methoxyphenyl)-2-methyl-4-(4-nitrophenyl)-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (**5oA**)



Method: **5oA** (21.0 mg, 90%, dr >95 : <5) was obtained from **4o** (18.2 mg, 0.0471 mmol), **7A** (11.4 mg), (η^3-allyl)CpPd (1.0 mg), and PCy_3 (3.8 mg) and isolated by preparative TLC eluting with 20% EtOAc/toluene.

Pale yellow oil. Rf 0.40 (50% EtOAc/hexane). $[\alpha]_D^{22}$ −29 (*c* 0.22, $CHCl_3$). IR (neat): 2932, 1607, 1596, 1512, 1344, 1248, 1160, 1031, 757, 662 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.8 Hz, 2H) 7.74 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 7.6 Hz, 2H), 4.79 (m, 1H), 4.46 (m, 1H), 4.28 (d, *J* = 18.0 Hz, 1H), 3.89 (d, *J* = 18.0 Hz, 1H), 3.72 (s, 3H), 2.45 (3H, s), 1.09 (d, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.9, 146.3, 144.9, 143.6, 143.6, 136.8, 134.5, 133.7, 130.9, 129.9, 129.5, 127.1, 122.9, 113.8, 68.1, 55.1, 51.0, 45.2, 21.5, 9.8. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{26}H_{26}N_2NaO_6S$ 517.1404, found 517.1401.

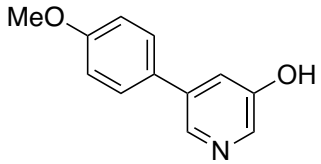
General Procedure for the Transformations of Tetrahydropyridine **5** into 3-Hydroxypyridine **3** (Scheme 5)



To a solution of tetrahydropyridine **5** (1 equiv) in anhydrous DCM (0.2 M) was added Dess-Martin periodinane (1.5 equiv) at room temperature. In the oxidation of **5eA**, sodium bicarbonate (2 equiv) was added prior to Dess-Martin periodinane to prevent acid-mediated dehydration. After being stirred at the same temperature for 1–2 h, the reaction mixture was diluted with Et_2O and treated with saturated aqueous sodium thiosulfate and saturated aqueous $NaHCO_3$. The resulting mixture was stirred for 1 h and then extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo to give enone, which was used for the next step without further purification.

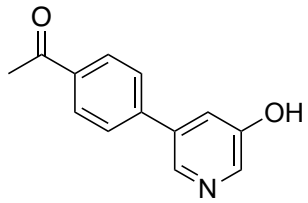
To a solution of the crude enone (1 equiv) in anhydrous toluene (0.33 M) was added DBU (2.0 equiv) at room temperature under argon. After being stirred at the same temperature for 4 h, the reaction mixture was concentrated in vacuo. The residue was purified by preparative TLC eluting with 10% MeOH/$CHCl_3$ to give 3-hydroxypyridine **3**.

Procedure for 5-(4-methoxyphenyl)pyridin-3-ol (**3aA**)



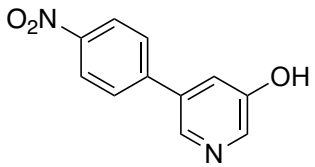
Method: **3aA** (2.3 mg, 80%) was obtained from **5aA** (5.0 mg, 0.0139 mmol), DMPI (8.3 mg), and DBU (4.2 μL).
Pale yellow oil. Rf 0.61 (10% MeOH/$CHCl_3$). IR (neat): 2929, 2853, 1609, 1583, 1518, 1440, 1290, 1251, 1221, 1180, 1149, 1031, 828, 755 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$:CD_3OD = 3:1): δ 8.24 (s, 1H), 8.06 (s, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.37 (s, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$:CD_3OD = 3:1): δ 159.6, 153.9, 138.0, 135.1, 129.6, 128.0, 120.9, 114.3, 109.2, 55.1. HRMS (ESI, $[M+H]^+$) *m/z* calcd for $C_{12}H_{12}NO_2$ 202.0863, found 202.0862.

Procedure for 1-(4-(5-hydroxypyridin-3-yl)phenyl)ethan-1-one (**3aB**)



Method: **3aB** (10.2 mg, 73%) was obtained from **5aB** (25.0 mg, 0.0673 mmol), DMPI (40.0 mg), and DBU (20.0 μL).
Pale yellow oil. Rf 0.55 (10% MeOH/$CHCl_3$). IR (neat): 2925, 1684, 1604, 1267, 1162, 755, 668 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$:CD_3OD = 3:1): δ 8.33 (s, 1H), 8.17 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.42 (s, 1H), 2.66 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$:CD_3OD = 3:1): δ 198.4, 154.0, 142.1, 138.5, 136.9, 136.5, 136.3, 128.9, 127.2, 121.5, 26.4. HRMS (ESI, $[M+H]^+$) *m/z* calcd for $C_{13}H_{12}NO_2$ 214.0863, found 214.0858.

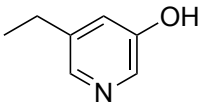
Procedure for 5-(4-nitrophenyl)pyridin-3-ol (**3aC**)



Method: **3aC** (6.5 mg, 65%) was obtained from **5aC** (17.3 mg, 0.0462 mmol), DMPI (27.5 mg), and DBU (14.0 μL).

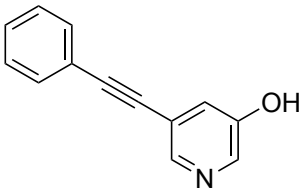
Pale yellow oil. Rf 0.53 (10% MeOH/$CHCl_3$). IR (neat): 2923, 1598, 1521, 1345, 1159, 795 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$:CD_3OD = 3:1): δ 8.34 (s, 1H), 8.33 (d, *J* = 8.0 Hz, 2H), 8.21 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.42 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$:CD_3OD = 3:1): δ 154.1, 147.5, 143.9, 138.4, 137.6, 135.4, 127.8, 124.1, 121.5. HRMS (ESI, $[M+H]^+$) *m/z* calcd for $C_{11}H_9N_2O_3$ 217.0608, found 217.0607.

Procedure for 5-ethylpyridin-3-ol (**3aD**)



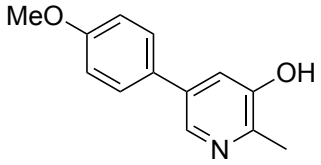
Method: **3aD** (15.2 mg, 86%) was obtained from **5aD** (40.5 mg, 0.144 mmol), DMPI (91.6 mg), and DBU (43.0 μL). Pale yellow oil. Rf 0.55 (10% MeOH/$CHCl_3$). IR (neat): 2968, 1585, 1438, 1225, 756, 707 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.94 (s, 1H), 7.16 (s, 1H), 2.63 (q, *J* = 7.8 Hz, 2H), 1.24 (t, *J* = 7.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.2, 141.6, 138.8, 133.6, 124.6, 25.9, 15.0. LRMS (EI) *m/z* (relative intensity) 123 ($[M]^+$, 100), 108 (70), 95 (12). HRMS (EI, $[M]^+$): *m/z* calcd for C_7H_9NO, 123.0684; found, 123.0684.

Procedure for 5-(phenylethynyl)pyridin-3-ol (**3aE**)



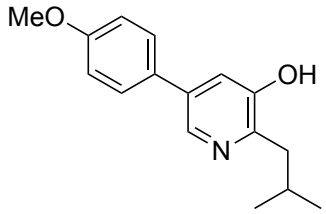
Method: **3aE** (4.2 mg, 50%) was obtained from **5aE** (14.5 mg, 0.0410 mmol), DMPI (24.2 mg), and DBU (12.8 μL). Pale yellow oil. Rf 0.57 (10% MeOH/$CHCl_3$). IR (neat): 2924, 2644, 2568, 2216, 1579, 1425, 1325, 1248, 1150, 1124, 1022, 868, 754, 688 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$:CD_3OD = 3:1): δ 8.19 (s, 1H), 8.08 (s, 1H), 7.57–7.48 (m, 2H), 7.44–7.35 (m, 3H), 7.33 (s, 1H). ^{13}C-NMR (151 MHz, $CDCl_3$:CD_3OD = 3:1): δ 153.2, 142.1, 136.5, 131.2, 128.4, 128.0, 124.8, 122.0, 120.8, 91.9, 85.5. LRMS (EI) *m/z* (relative intensity) 195 ($[M]^+$, 100), 139 (25), 69 (11). HRMS (EI, $[M]^+$): *m/z* calcd for $C_{13}H_9NO$, 195.0684; found, 195.0700.

Procedure for 5-(4-methoxyphenyl)-2-methylpyridin-3-ol (**3bA**)



Method: **3bA** (8.7 mg, 67%) was obtained from **5bA** (22.6 mg, 0.0605 mmol), DMPI (35.9 mg), and DBU (18.1 μL).
Pale yellow oil. Rf 0.50 (10% MeOH/$CHCl_3$). IR (neat): 2922, 1604, 1515, 1444, 1287, 1220, 1163, 773 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$:CD_3OD = 3:1): δ 8.03 (s, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.24 (s, 1H), 6.93 (d, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 2.40 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$:CD_3OD = 3:1): δ 159.3, 144.5, 136.7, 135.3, 129.9, 127.7, 126.7, 119.7, 114.2, 55.1, 17.1. HRMS (ESI, $[M+H]^+$) *m/z* calcd for $C_{13}H_{14}NO_2$ 216.1019, found 216.1015.

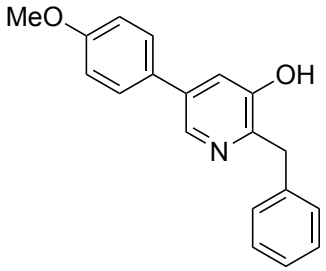
Procedure for 2-isobutyl-5-(4-methoxyphenyl)pyridin-3-ol (**3cA**)



Method: **3cA** (7.8 mg, 59%) was obtained from **5cA** (21.5 mg, 0.0517 mmol), DMPI (30.7 mg), and DBU (15.5 μL).

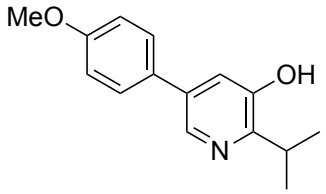
Pale yellow oil. Rf 0.55 (10% MeOH/$CHCl_3$). IR (neat): 2955, 1608, 1608, 1521, 1393, 1252, 1165, 1033, 830, 772 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$:CD_3OD = 3:1): δ 8.14 (s, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.30 (s, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.71 (d, *J* = 7.8 Hz, 2H), 2.15 (t–sept, *J* = 7.8, 6.8 Hz, 1H), 0.96 (d, *J* = 6.8 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$:CD_3OD = 3:1): δ 159.3, 151.7, 147.7, 136.6, 135.0, 129.9, 127.7, 119.9, 114.1, 55.0, 40.4, 27.9, 22.1. HRMS (ESI, $[M+H]^+$) *m/z* calcd for $C_{16}H_{20}NO_2$ 258.1489, found 258.1487.

Procedure for 2-benzyl-5-(4-methoxyphenyl)pyridin-3-ol (**3dA**)



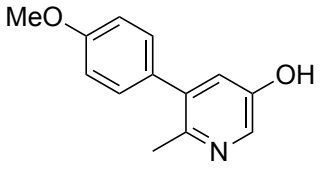
Method: **3dA** (82.2 mg, 95%) was obtained from **5dA** (133 mg, 0.296 mmol), DMPI (176 mg), and DBU (88.4 μL). Pale yellow oil. Rf 0.55 (10% MeOH/$CHCl_3$). IR (neat): 1600, 1522, 1433, 1392, 1257, 1176, 1027, 827 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$:CD_3OD = 3:1): δ 8.16 (d, *J* = 2.0 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 2.0 Hz, 1H), 7.25 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 4.19 (s, 2H), 3.85 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$:CD_3OD = 3:1): δ 159.3, 151.5, 146.7, 139.3, 137.1, 135.7, 129.8, 128.6, 128.0, 127.8, 125.7, 120.4, 114.2, 55.0, 37.7. LRMS (EI) *m/z* (relative intensity) 291 ($[M]^+$, 100), 274 (12). HRMS (EI, $[M]^+$): *m/z* calcd for $C_{19}H_{17}NO_2$, 291.1259; found, 291.1248.

Procedure for 2-isopropyl-5-(4-methoxyphenyl)pyridin-3-ol (**3eA**)



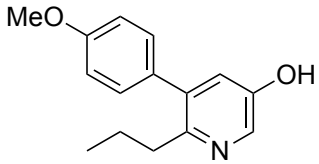
Method: **3eA** (6.8 mg, 64%) was obtained from **5eA** (16.3 mg, 0.0406 mmol), DMPI (26.3 mg), $NaHCO_3$ (6.9 mg), and DBU (12.4 μL).
Pale yellow oil. Rf 0.55 (10% MeOH/$CHCl_3$). IR (neat): 2969, 2932, 1610, 1518, 1290, 1251, 1229, 1176, 1033, 830, 756 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$:CD_3OD = 3:1): δ 8.33 (s, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.26 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3,47 (sept, *J* = 7.2 Hz, 1H), 1.35 (d, *J* = 7.2 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$:CD_3OD = 3:1): δ 159.6, 152.6, 149.8, 138.5, 135.1, 130.0, 128.0, 120.5, 114.4, 53.3, 29.1, 21.1. HRMS (ESI, $[M+H]^+$) *m/z* calcd for $C_{15}H_{18}NO_2$ 244.1332, found 244.1330.

Procedure for 5-(4-methoxyphenyl)-6-methylpyridin-3-ol (**3fA**)



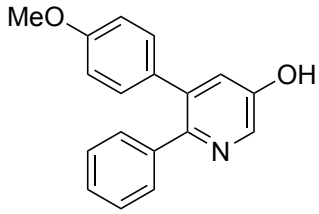
Method: **3fA** (9.3 mg, 67%) was obtained from **5fA** (24.2 mg, 0.0648 mmol), DMPI (38.5 mg), and DBU (19.4 μL). Pale yellow oil. Rf 0.55 (10% MeOH/$CHCl_3$). IR (neat): 2931, 1610, 1515, 1453, 1290, 1248, 1176, 1031, 834, 771, 707 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$:CD_3OD = 3:1): δ 7.97 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H), 2.38 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$:CD_3OD = 3:1): δ 158.8, 151.7, 145.9, 137.5, 134.4, 131.7, 129.8, 124.7, 113.6, 55.0, 21.2. HRMS (ESI, $[M+H]^+$) *m/z* calcd for $C_{13}H_{14}NO_2$ 216.1019, found 216.1015.

Procedure for 5-(4-methoxyphenyl)-6-propylpyridin-3-ol (**3gA**)



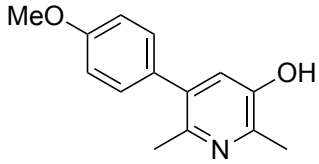
Method: **3gA** (7.2 mg, 74%) was obtained from **5gA** (16.0 mg, 0.0398 mmol), DMPI (23.7 mg), and DBU (12.0 μL).
Pale yellow oil. Rf 0.55 (10% MeOH/$CHCl_3$). IR (neat): 2960, 2931, 1610, 1516, 1452, 1288, 1248, 1175, 1032, 835, 755, 705 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$:CD_3OD = 3:1): δ 8.27 (d, *J* = 2.4 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 2.4 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.68 (s, 3H), 2.71 (t, *J* = 7.8 Hz, 2H), 1.57 (tq, *J* = 7.8, 7.2 Hz, 2H), 0.81 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$:CD_3OD = 3:1): δ 159.0, 152.6, 150.6, 138.4, 134.5, 131.8, 130.1, 126.9, 113.8, 55.3, 35.6, 23.7, 14.0. HRMS (ESI, $[M+Na]^+$) *m/z* calcd for $C_{15}H_{17}NNaO_2$ 266.1152, found 266.1151.

Procedure for 5-(4-methoxyphenyl)-6-phenylpyridin-3-ol (**3hA**)



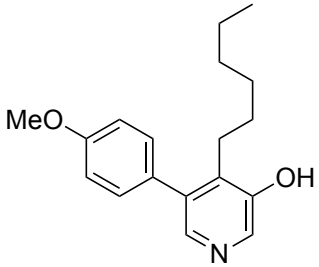
Method: **3hA** (6.6 mg, 80%) was obtained from **5hA** (12.8 mg, 0.0294 mmol), DMPI (17.5 mg), and DBU (8.8 μL).
Pale yellow oil. Rf 0.55 (10% MeOH/$CHCl_3$). IR (neat): 2917, 1610, 1514, 1447, 1290, 1249, 1177, 1030, 833, 752, 702 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$:CD_3OD = 3:1): δ 8.14 (s, 1H), 7.44 (s, 1H), 7.25–7.18 (m, 5H), 7.06 (d, *J* = 6.8 Hz, 2H), 6.79 (d, *J* = 6.8 Hz, 2H), 3.78 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$:CD_3OD = 3:1): δ 158.8, 151.5, 141.3, 137.2, 135.7, 135.4, 133.6, 130.9, 130.3, 129.4, 128.5, 127.9, 113.4, 54.8. HRMS (ESI, $[M+H]^+$) *m/z* calcd for $C_{18}H_{16}NO_2$ 278.1176, found 278.1170.

Procedure for 5-(4-methoxyphenyl)-2,6-dimethylpyridin-3-ol (**3iA**)



Method: **3iA** (23.8 mg, 73%) was obtained from **5iA** (55.2 mg, 0.142 mmol), DMPI (90.7 mg), and DBU (44.5 μL).
Pale yellow oil. Rf 0.55 (10% MeOH/$CHCl_3$). IR (neat): 2924, 1516, 1289, 1249, 1161, 1033, 840, 812, 719, 668 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$:CD_3OD = 3:1): δ 7.36 (s, 1H), 7.22 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 2.46 (s, 3H), 2.38 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$:CD_3OD = 3:1): δ 158.7, 149.2, 144.8, 144.0, 135.0, 132.0, 129.9, 123.7, 113.6, 55.1, 21.1, 17.6. HRMS (ESI, $[M+H]^+$) *m/z* calcd for $C_{14}H_{16}NO_2$ 230.1176, found 230.1171.

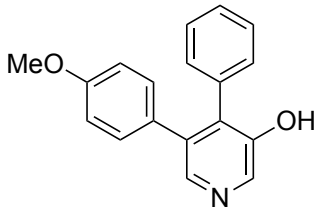
Procedure for 4-hexyl-5-(4-methoxyphenyl)pyridin-3-ol (**3jA**)



Method: **3jA** (9.3 mg, 48%) was obtained from **5jA** (30.8 mg, 0.0694 mmol), DMPI (41.2 mg), and DBU (20.7 μL).

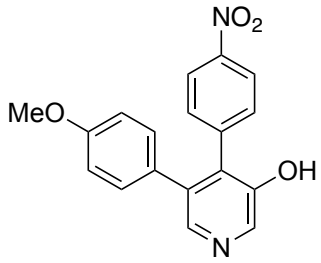
Pale yellow oil. Rf 0.50 (10% MeOH/$CHCl_3$). IR (neat): 2955, 1611, 1517, 1501, 1425, 1289, 1244, 1176, 1036, 831 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.96 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H), 2.64 (t, *J* = 2.8 Hz, 2H), 1.60–1.48 (m, 2H), 1.30–1.10 (m, 6H), 0.81 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.1, 153.8, 140.1, 139.0, 138.9, 134.1, 130.4, 130.1, 113.7, 55.3, 31.4, 29.4, 28.8, 26.8, 22.5, 14.0. HRMS (ESI, $[M+H]^+$) *m/z* calcd for $C_{18}H_{24}NO_2$ 286.1802, found 286.1801.

Procedure for 5-(4-methoxyphenyl)-4-phenylpyridin-3-ol (**3kA**)



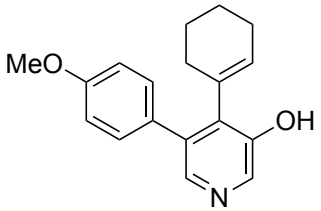
Method: **3kA** (22.3 mg, 80%) was obtained from **5kA** (43.6 mg, 0.100 mmol), DMPI (59.4 mg), and DBU (29.9 µL). Pale yellow oil. Rf 0.55 (10% MeOH/$CHCl_3$). IR (neat): 2933, 1609, 1425, 1290, 1249, 1178, 1033, 831, 750, 699 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.16 (s, 1H), 7.35–7.25 (m, 3H), 7.20 (d, *J* = 6.8 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 3.75 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.8, 151.5, 141.3, 137.2, 135.7, 135.4, 133.6, 130.9, 130.3, 129.4, 128.5, 127.9, 113.5, 55.1. HRMS (ESI, $[M+H]^+$) *m/z* calcd for $C_{18}H_{16}NO_2$ 278.1176, found 278.1173.

Procedure for 5-(4-methoxyphenyl)-4-(4-nitrophenyl)pyridin-3-ol (**3lA**)



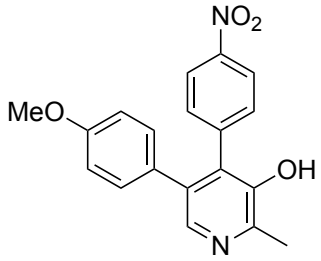
Method: **3lA** (25.9 mg, 77%) was obtained from **5lA** (50.2 mg, 0.104 mmol), DMPI (62.1 mg), and DBU (33.1 µL). Pale yellow oil. Rf 0.51 (10% MeOH/$CHCl_3$). IR (neat): 2933, 1515, 1247, 1176, 1110, 1033, 830, 753 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$:CD_3OD = 1:1): δ 8.21 (s, 1H), 8.16–8.09 (m, 3H), 7.39 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H). ^{13}C-NMR (151 MHz, $CDCl_3$:CD_3OD = 1:1): δ 158.7, 146.5, 141.4, 140.7, 135.5, 132.6, 131.3, 130.4, 128.4, 122.4, 113.3, 54.5. (two signals missing due to an overlap). HRMS (ESI, $[M+H]^+$) *m/z* calcd for $C_{18}H_{15}N_2O_4$ 323.1026, found 323.1025.

Procedure for 4-(cyclohex-1-en-1-yl)-5-(4-methoxyphenyl)pyridin-3-ol (**3nA**)



Method: **3nA** (26.4 mg, 58%) was obtained from **5nA** (71.2 mg, 0.162 mmol), DMPI (96.2 mg), and DBU (49.0 µL).
Pale yellow oil. Rf 0.55 (10% MeOH/$CHCl_3$). IR (neat): 2931, 1610, 1511, 1452, 1246, 1170, 1032, 832, 758, 664 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.30 (s, 1H), 8.12 (s, 1H), 7.34 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 5.98–5.94 (m, 1H), 3.85 (s, 3H), 2.24–2.19 (m, 2H), 2.73–2.69 (m, 2H), 2.61–2.54 (m, 2H), 2.52–2.44 (m, 2H). ^{13}C-NMR (151 MHz, $CDCl_3$): δ 159.3, 148.7, 142.1, 136.2, 135.4, 135.0, 132.6, 131.5, 130.0, 129.9, 113.7, 55.3, 28.1, 25.4, 22.5, 21.6. HRMS (ESI, $[M+H]^+$) *m/z* calcd for $C_{18}H_{20}NO_2$ 282.1489, found 282.1486.

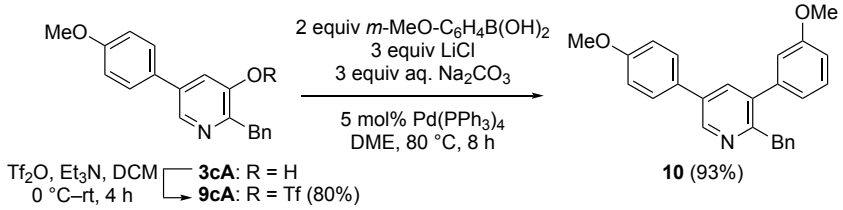
Procedure for 5-(4-methoxyphenyl)-2-methyl-4-(4-nitrophenyl)pyridin-3-ol (**3oA**)



Method: **3oA** (9.3 mg, 72%) was obtained from **5oA** (20.5 mg, 0.0415 mmol), DMPI (24.6 mg), and DBU (12.4 μL).

Pale yellow oil. Rf 0.55 (10% MeOH/$CHCl_3$). IR (neat): 2923, 1513, 1343, 1241, 1219, 1176, 1128, 1106, 1033, 829, 755 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.8 Hz, 2H), 8.03 (s, 1H), 7.35 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 2.56 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.7, 146.8, 145.8, 141.9, 134.9, 131.47, 131.45, 130.59, 130.56, 128.8, 123.02, 122.99, 113.6, 54.9, 18.5. HRMS (ESI, $[M+H]^+$) *m/z* calcd for $C_{19}H_{17}N_2O_4$ 337.1183, found 337.1179.

Procedure for 2-benzyl-3-(3-methoxyphenyl)-5-(4-methoxyphenyl)pyridine (**10**)



To a solution of **3cA** (40.0 mg, 0.137 mmol) and Et_3N (38.2 μL, 0.274 mmol) in anhydrous DCM (1.0 mL) was added Tf_2O (38.2 μL, 0.164 mmol) at 0 °C under argon. After being stirred at the same temperature for 4 h, the reaction mixture was treated with saturated aqueous $NaHCO_3$. The resulting mixture was extracted with EtOAc, washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by preparative TLC eluting with 10% EtOAc/toluene to give triflate (46.6 mg, 80%).

To a test tube containing the above triflate (8.7 mg, 0.021 mmol), *m*–methoxyphenylboronic acid (6.2 mg, 2 equiv), $Pd(PPh_3)_4$ (1.2 mg, 5 mol%), and LiCl (2.6 mg, 3 equiv) in DME (0.3 mL) was added 2.0 M aqueous Na_2CO_3 (31 μL) under argon. The resulting mixture was sealed with a screw cap and stirred at 80 °C for 8 h. The reaction mixture was cooled down to room temperature, diluted with EtOAc, washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by preparative TLC eluting with 20% EtOAc/toluene to give **10** (7.2 mg, 93%) as a brown solid.

Rf 0.70 (20% EtOAc/toluene). IR (neat): 1609, 1516, 1455, 1440, 1288, 1248, 1179, 1148, 1035, 830, 701 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 1H), 7.71 (s, 1H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.32 (t, *J* = 8.4 Hz, 1H), 7.24–7.10 (m, 3H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.75 (s, 1H), 4.18 (s, 2H), 3.85 (s, 3H), 3.72 (s, 3H).; ^{13}C-NME (100 MHz, $CDCl_3$): δ 159.7, 159.4, 155.8, 146.3, 140.9, 140.1, 137.3, 135.6, 133.9, 130.0, 129.8, 129.4, 128.8, 128.2, 128.1, 125.9, 121.5, 114.5, 113.6, 55.3, 55.2, 41.3. HRMS (ESI, $[M+H]^+$) *m/z* calcd for $C_{26}H_{24}NO_2$ 382.1802, found 382.1796.

References

[1] (a) Shibata, N.; Tsuchiya, T.; Hashimoto, Y.; Morita, N.; Ban, S.; Tamura, O. Thiyl radical-mediated cyclization of ω-alkynyl *O*-*tert*-butyldiphenylsilyloximes. *Org. Biomol. Chem.* **2017**, *15*, 3025–3034. (b) Takahashi, K.; Honda, T. Diastereoselective Syntheses of Functionalized Five-Membered Carbocycles and Heterocycles by a SmI_2-Promoted Intramolecular Coupling of Bromoalkynes and α,β-Unsaturated Esters. *Org. Lett.* **2010**, *12*, 3026–3029. (c) Padín, D.; Cambeiro, F.; Fañanás-Mastral, M.; Varela, J.; Saá, A. C. [2 + 1] Cycloaddition of Catalytic Ruthenium Vinyl Carbenes: A Stereoselective Controlled Access to (*Z*)- and (*E*)-Vinyl Epoxypyrrolidines. *ACS Catal.* **2017**, *7*, 992–996.

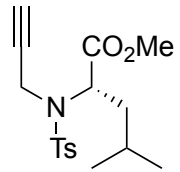
[2] Ordóñez, M.; De la Cruz-Cordero, R.; Fernández-Zertuche, M.; Muñoz-Hernández, M. A.; García-Barradas, O. Diastereoselective reduction of dimethyl γ-[(*N*-*p*-toluenesulfonyl)amino]-β-ketophosphonates derived from amino acids. *Tetrahedron: Asymmetry* **2004**, *15*, 3035–3043.

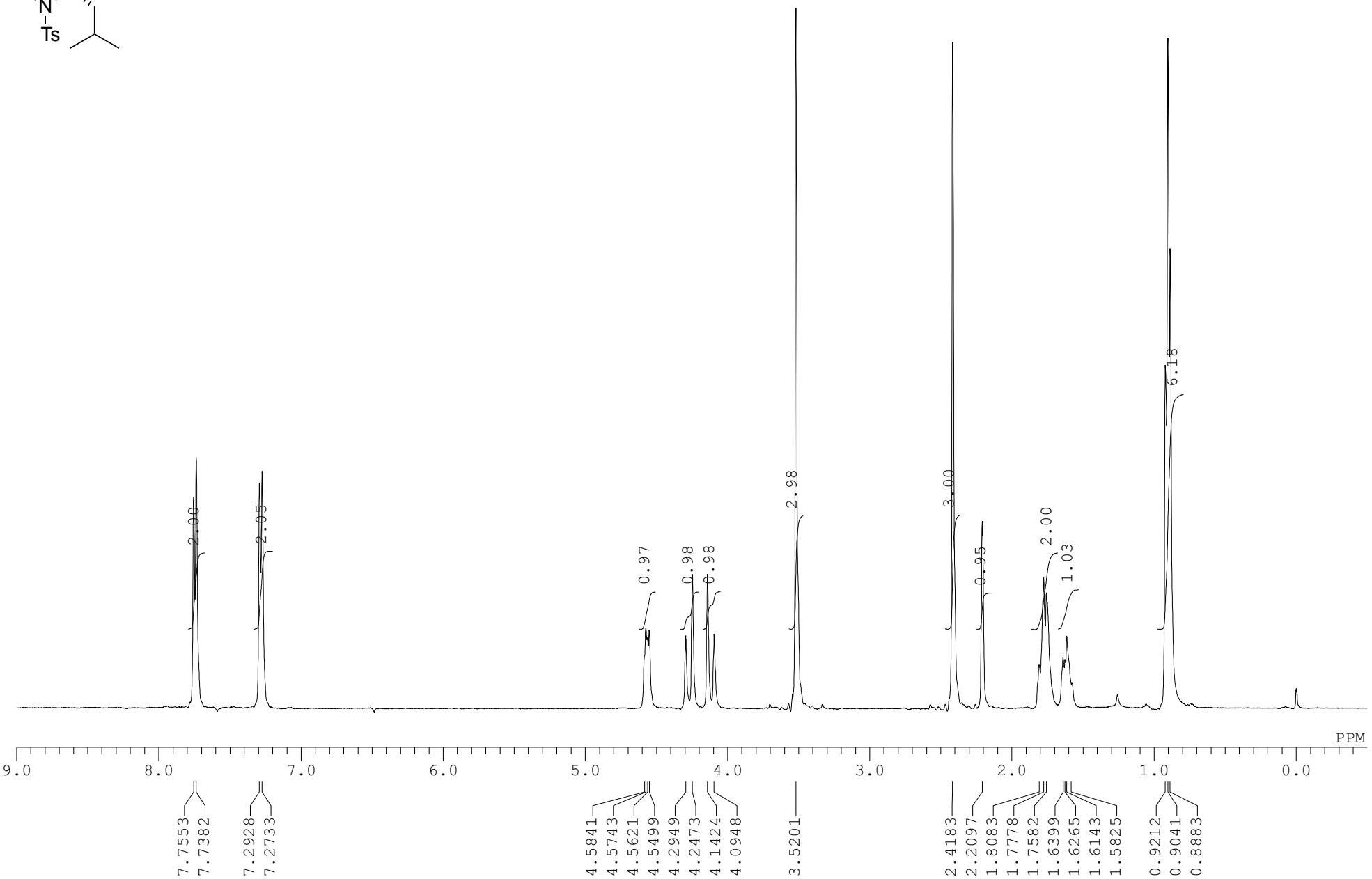
[3] Morales, S.; Guijarro, F. G.; Ruano, J. L. G.; Cid, M. B. A General Aminocatalytic Method for the Synthesis of Aldimines. *J. Am. Chem. Soc.* **2014**, *136*, 1082–1089.

[4] Tsukamoto, H.; Ueno, T.; Kondo, Y. *J. Am. Chem. Soc.* **2006**, *128*, 1406–1407.

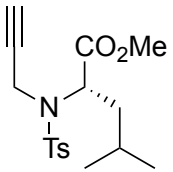
[5] Tsukamoto, H.; Ito, K.; Ueno, T.; Shiraishi, M.; Kondo, Y.; Doi, T. Palladium(0)-Catalyzed *Anti*-Selective Addition-Cyclizations of Alkynyl Electrophiles. *Chem. Eur. J.* DOI: 10.1002/chem.202203068.

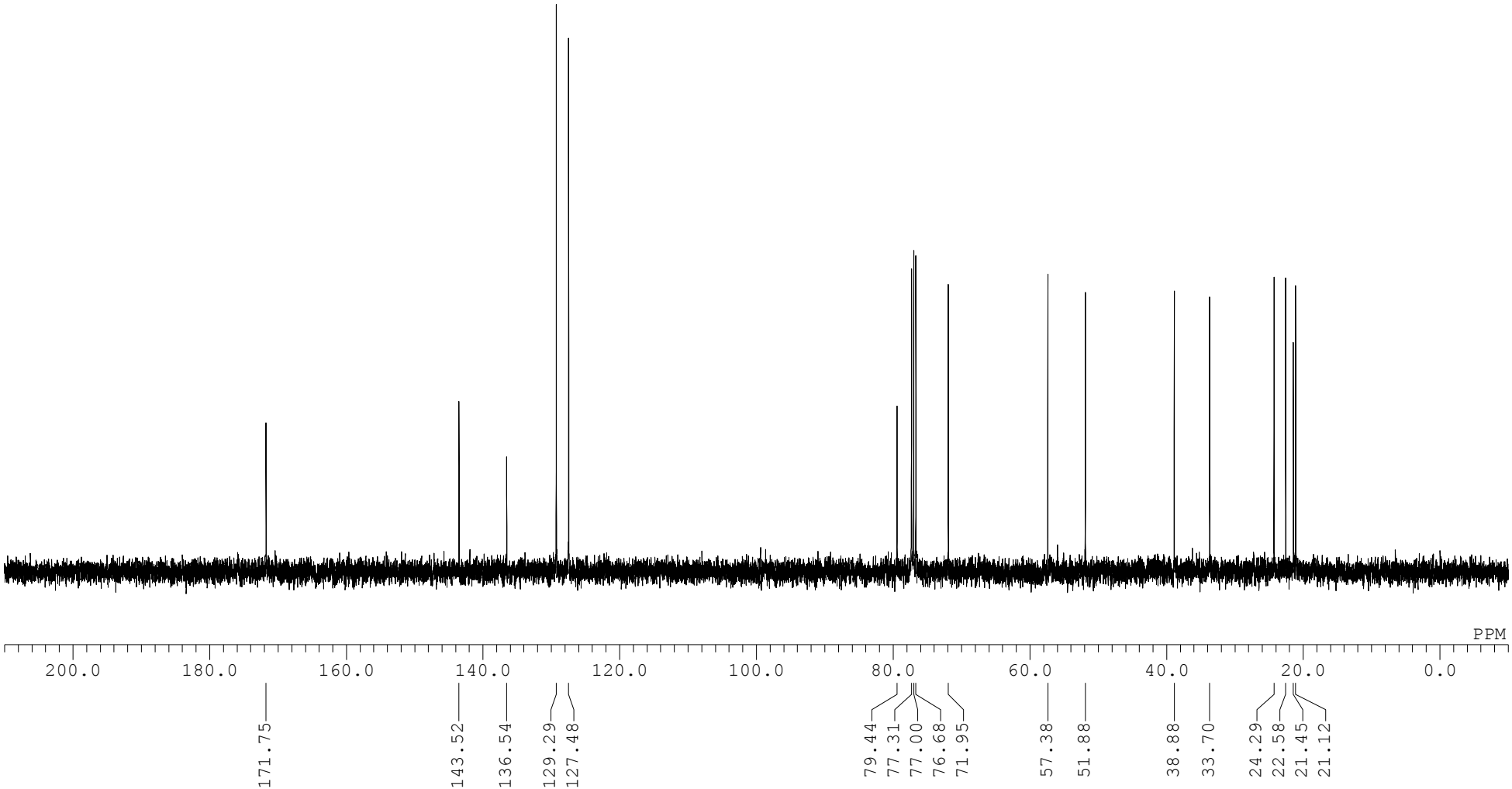
^{1}H NMR spectrum of methyl *N*-(prop-2-yn-1-yl)-*N*-tosyl-L-leucinate (**6c**)



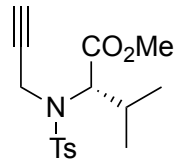


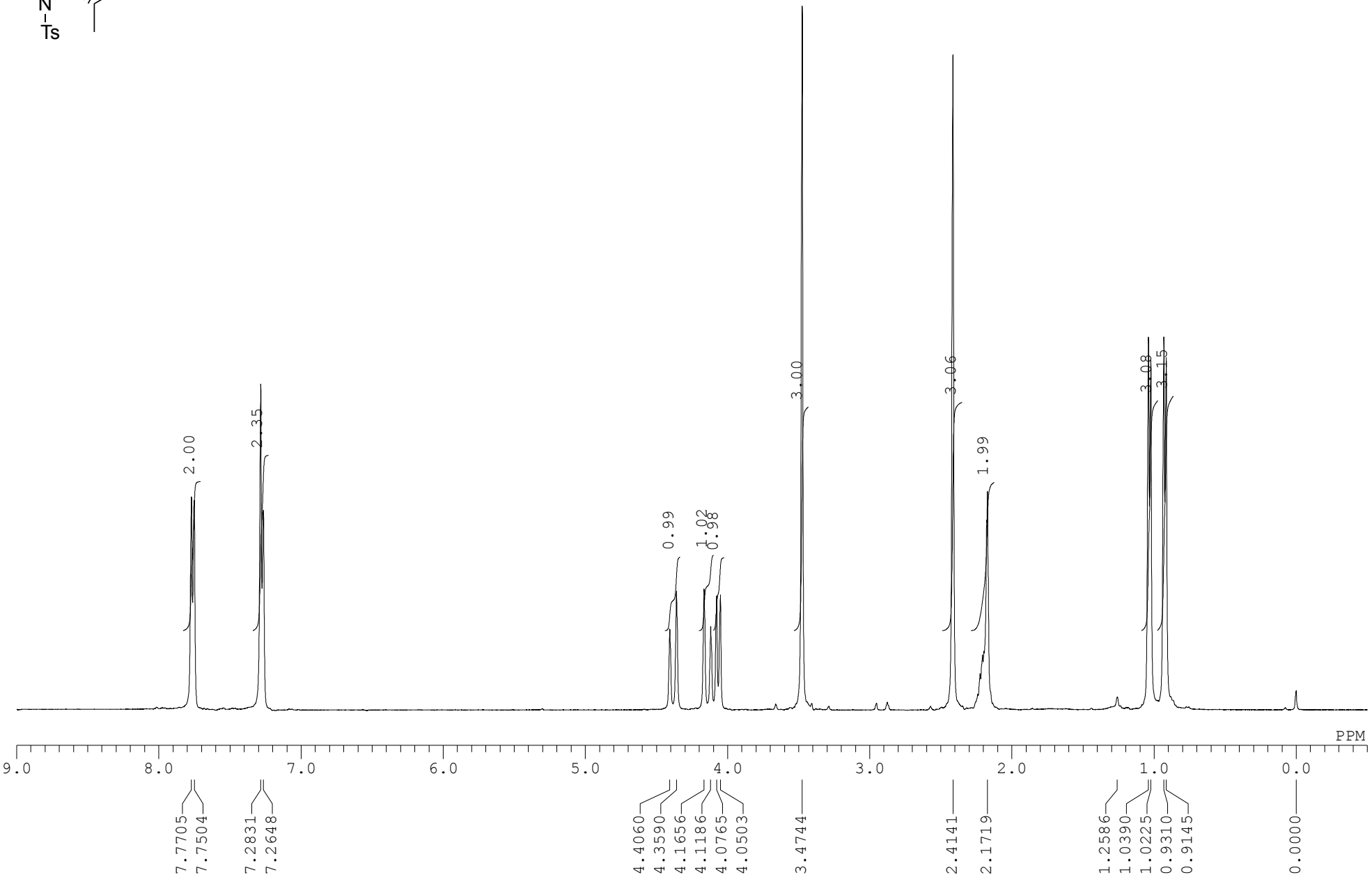
^{13}C NMR spectrum of methyl *N*-(prop-2-yn-1-yl)-*N*-tosyl-L-leucinate (**6c**)



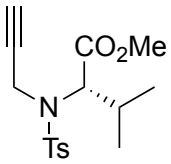


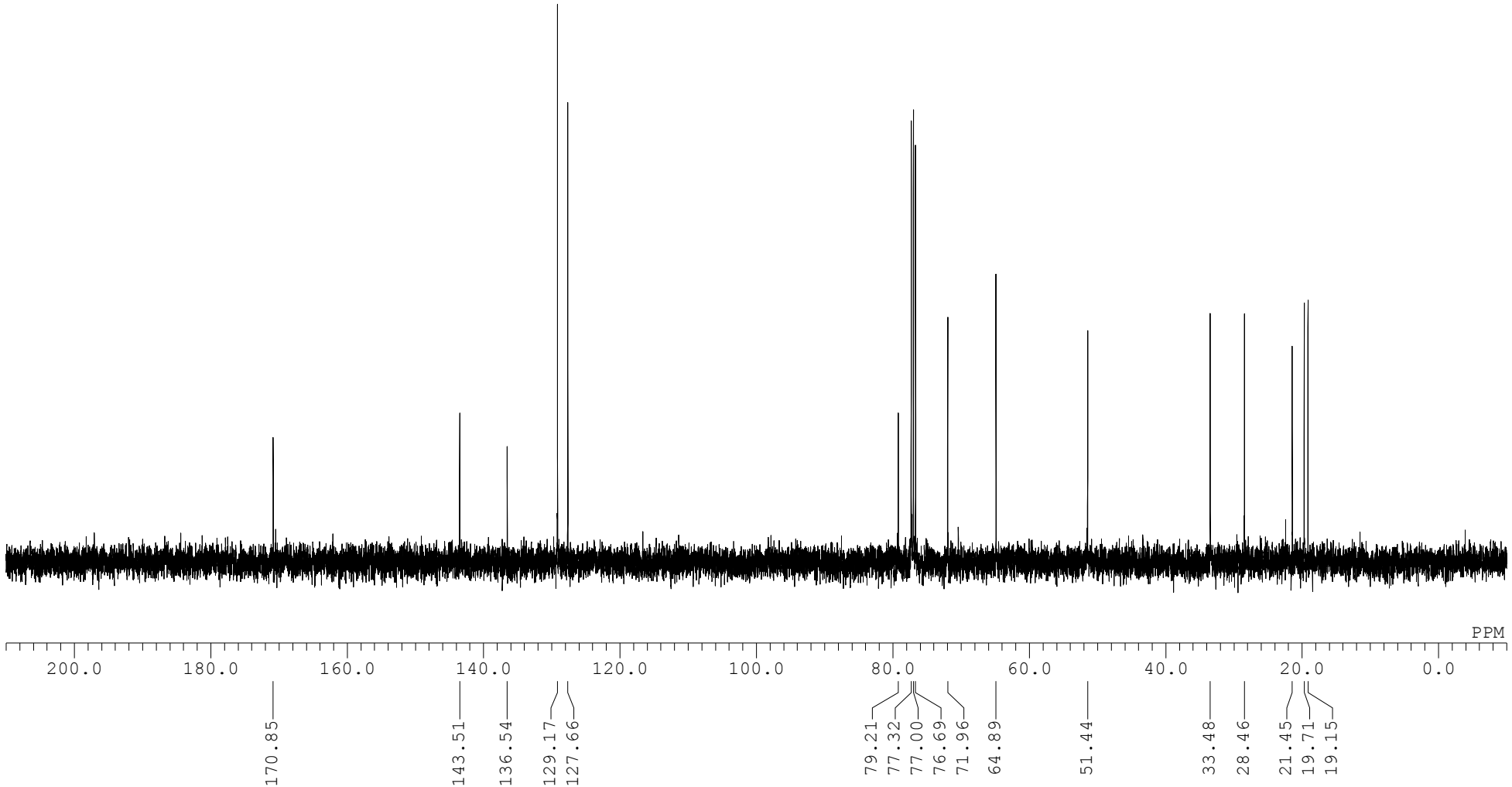
^{1}H NMR spectrum of methyl *N*-(prop-2-yn-1-yl)-*N*-tosyl-L-valinate (**6e**)



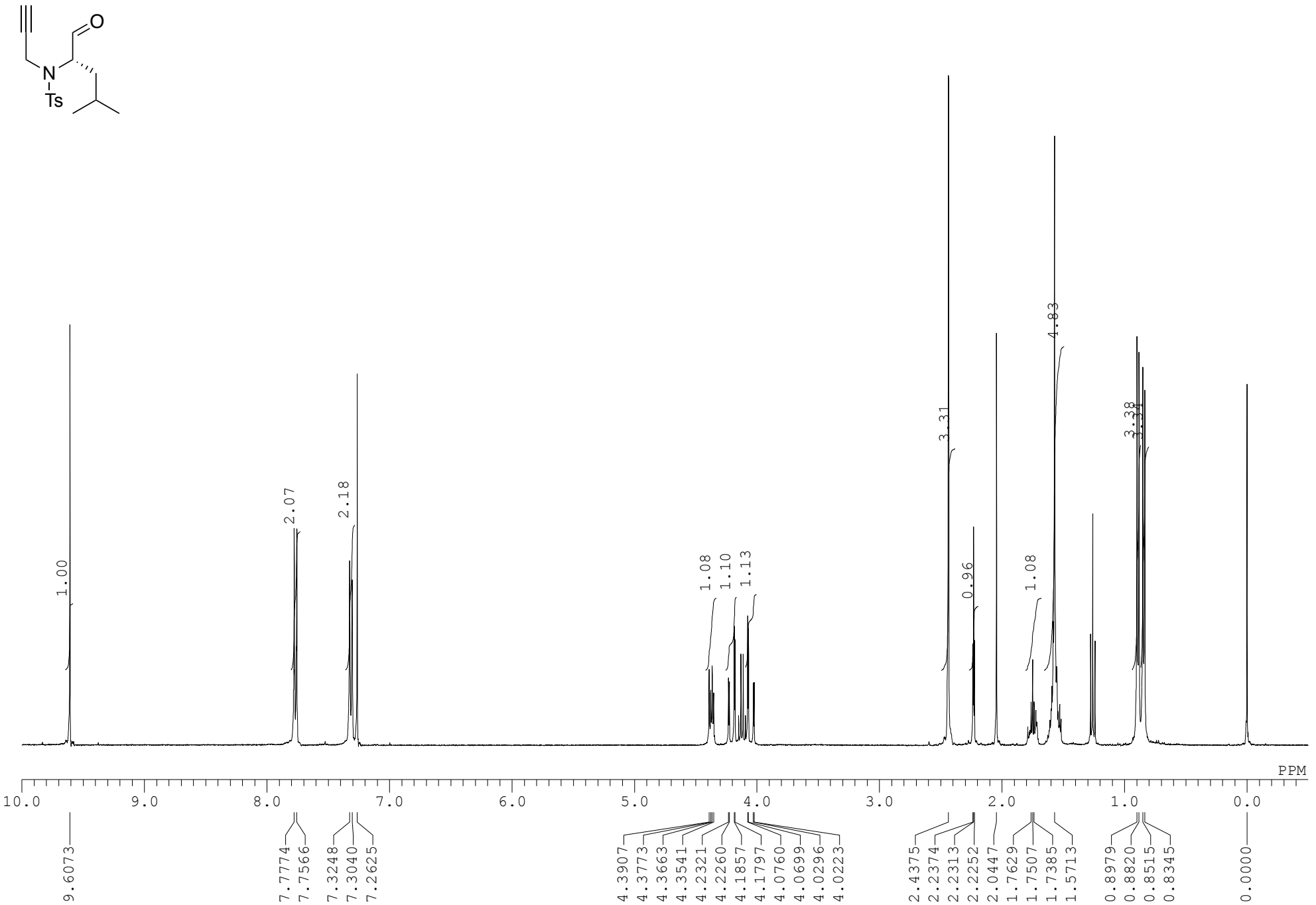


^{13}C NMR spectrum of methyl *N*-(prop-2-yn-1-yl)-*N*-tosyl-L-valinate (**6e**)

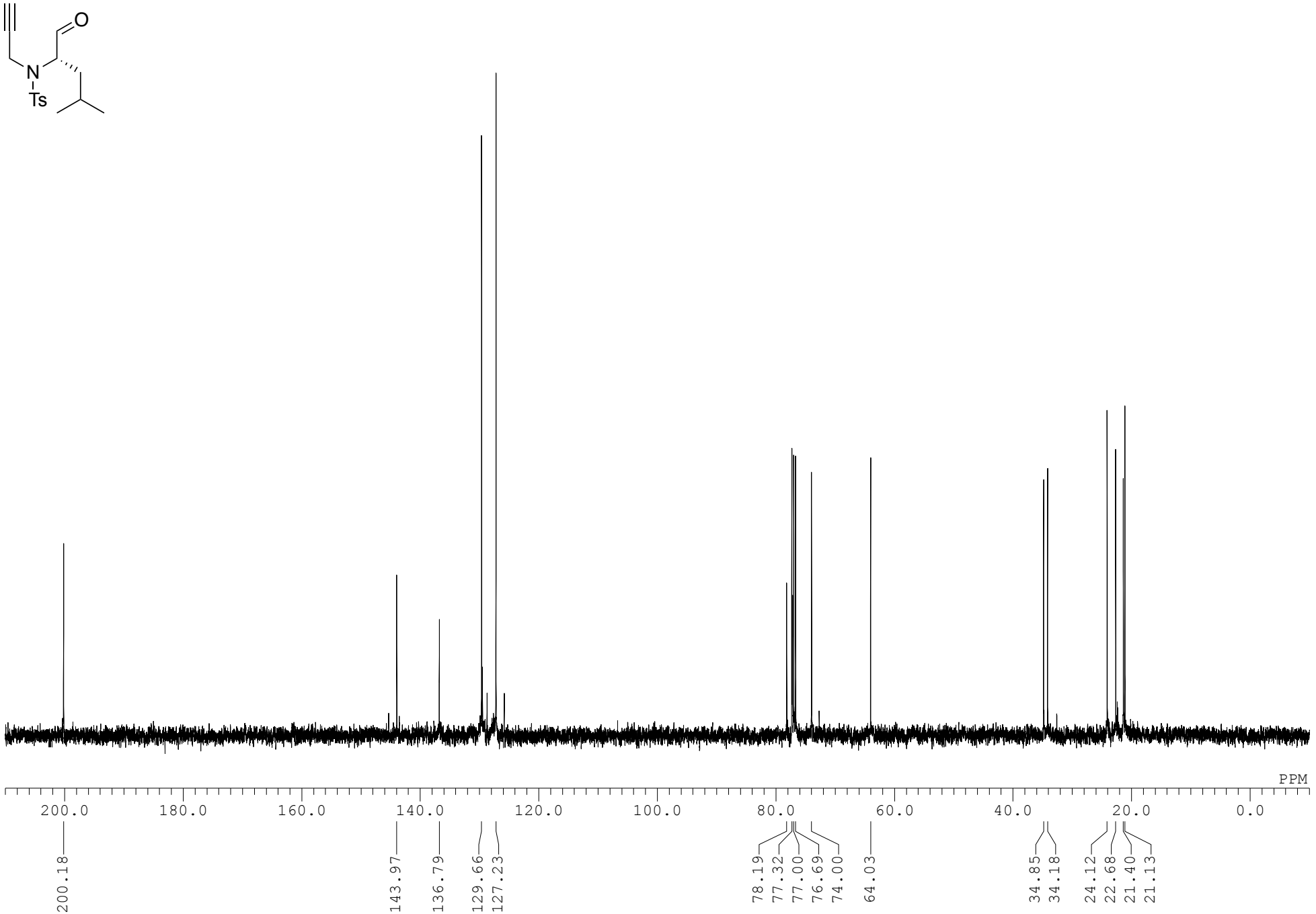




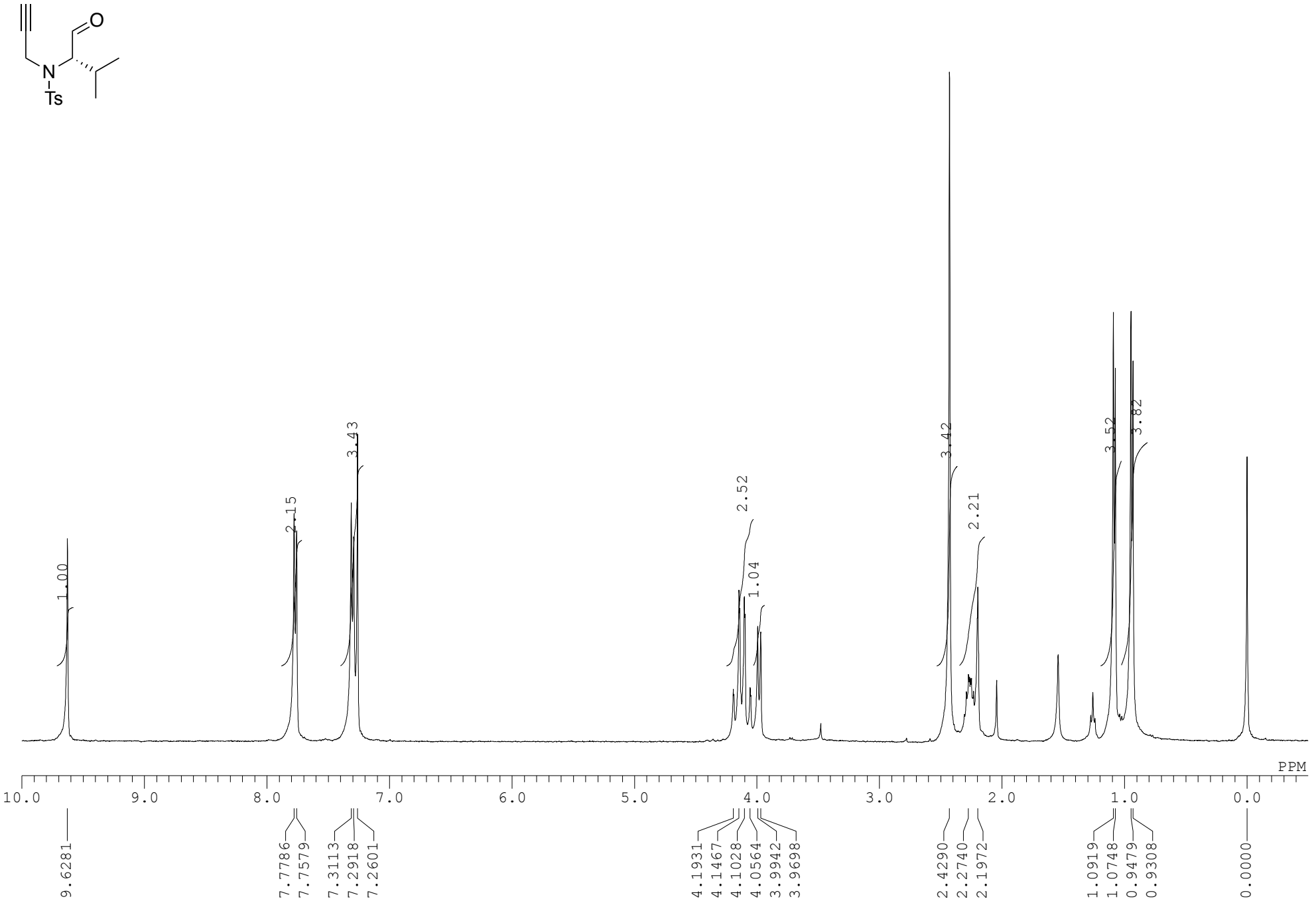
^{1}H NMR spectrum of **4c**



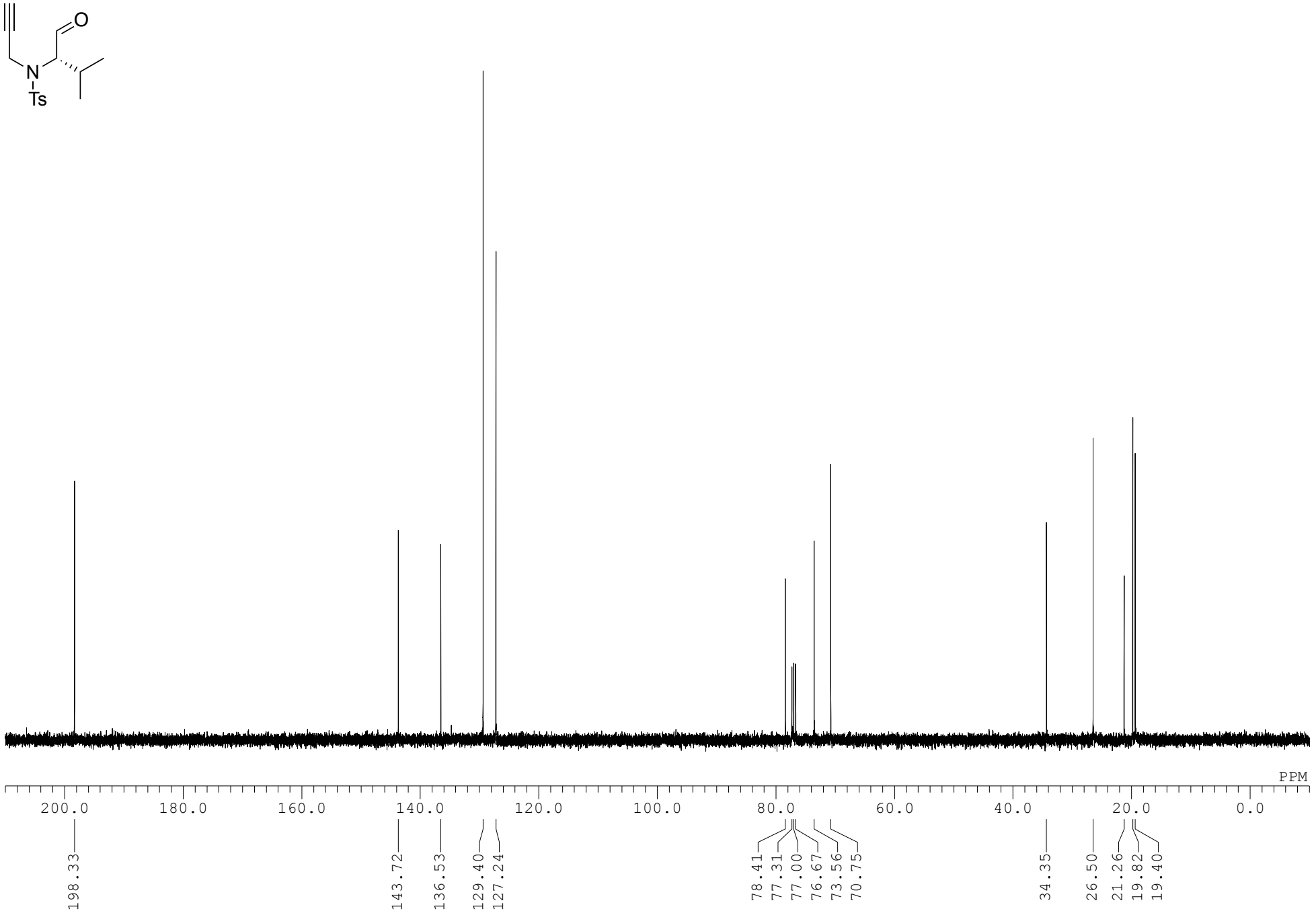
^{13}C NMR spectrum of **4c**



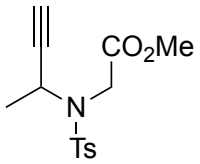
^{1}H NMR spectrum of **4e**

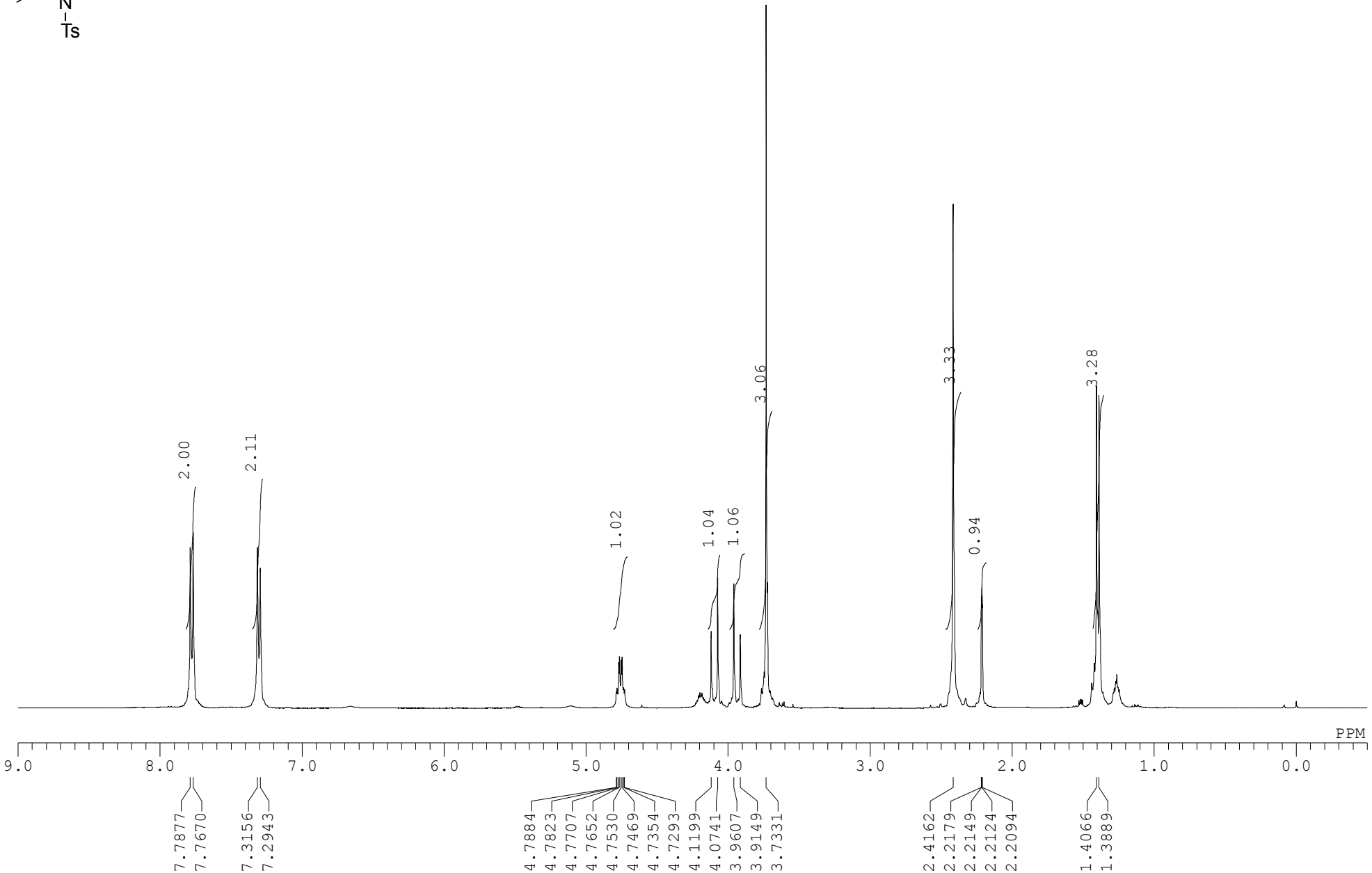


^{13}C NMR spectrum of **4e**

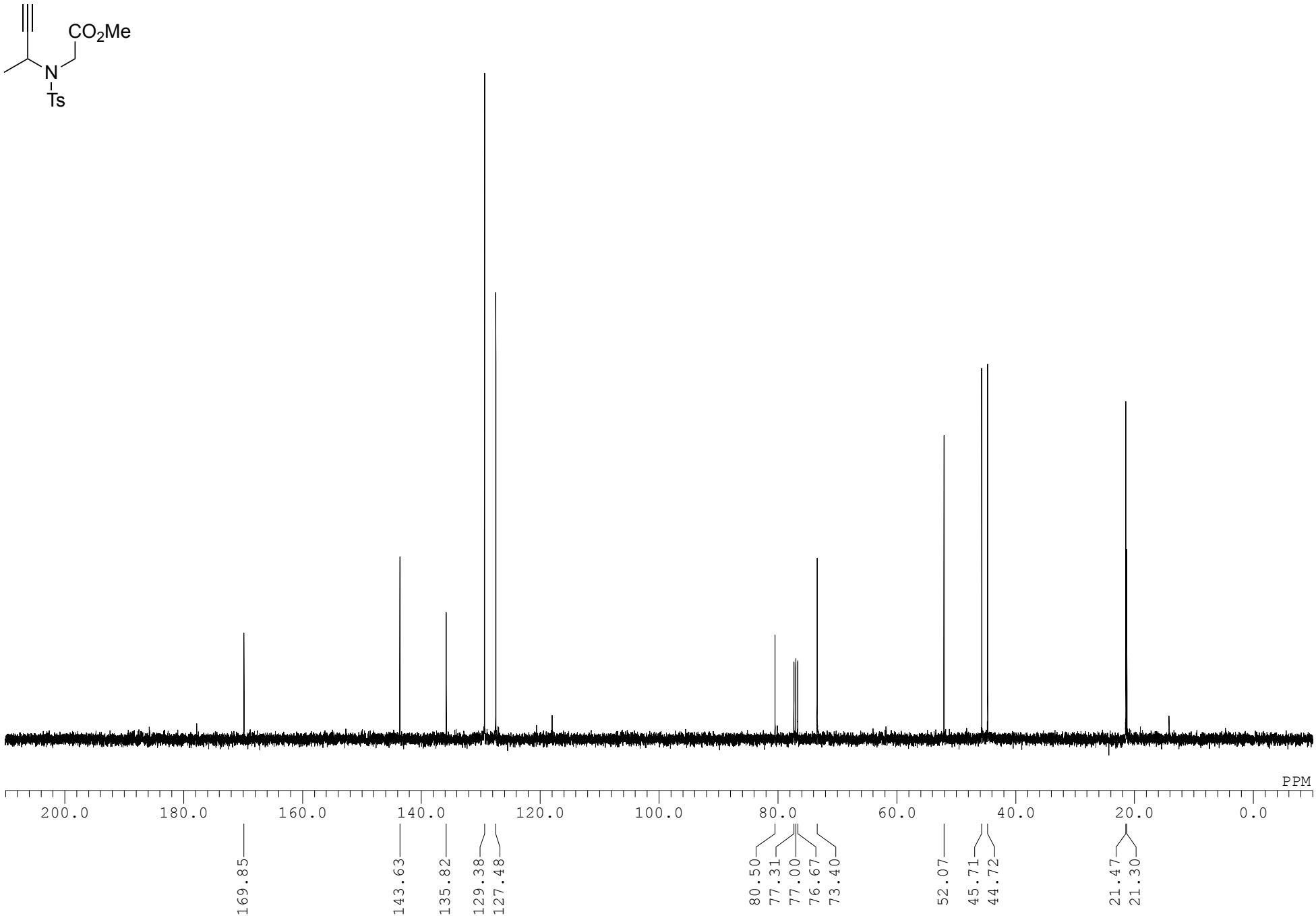


^{1}H NMR spectrum of methyl *N*-(but-3-yn-2-yl)-*N*-tosylglycinate (**6f**)

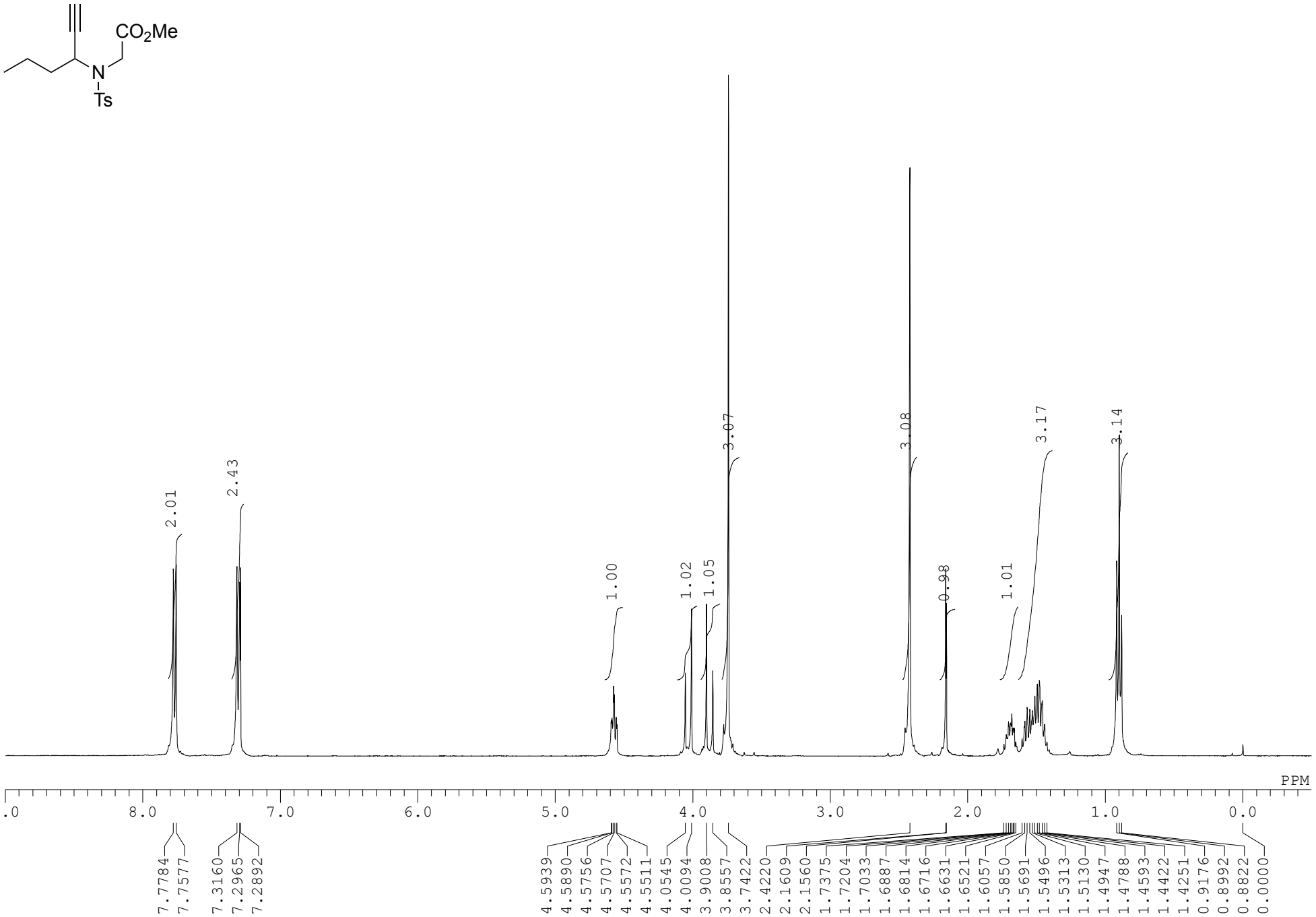




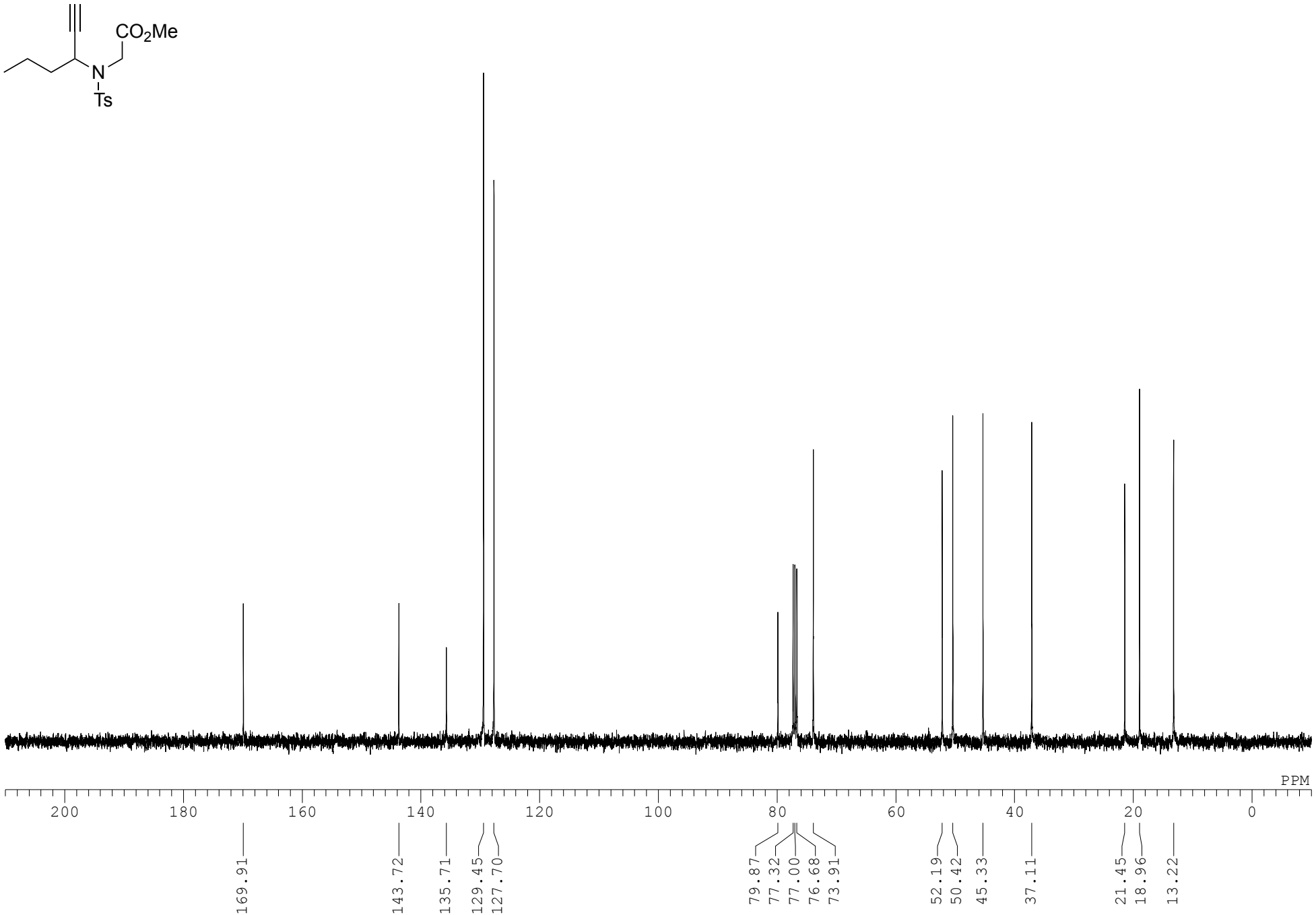
^{13}C NMR spectrum of methyl *N*-(but-3-yn-2-yl)-*N*-tosylglycinate (**6f**)



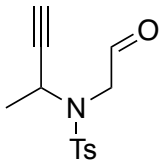
^{1}H NMR spectrum of methyl *N*-(hex-1-yn-3-yl)-*N*-tosylglycinate (**6g**)

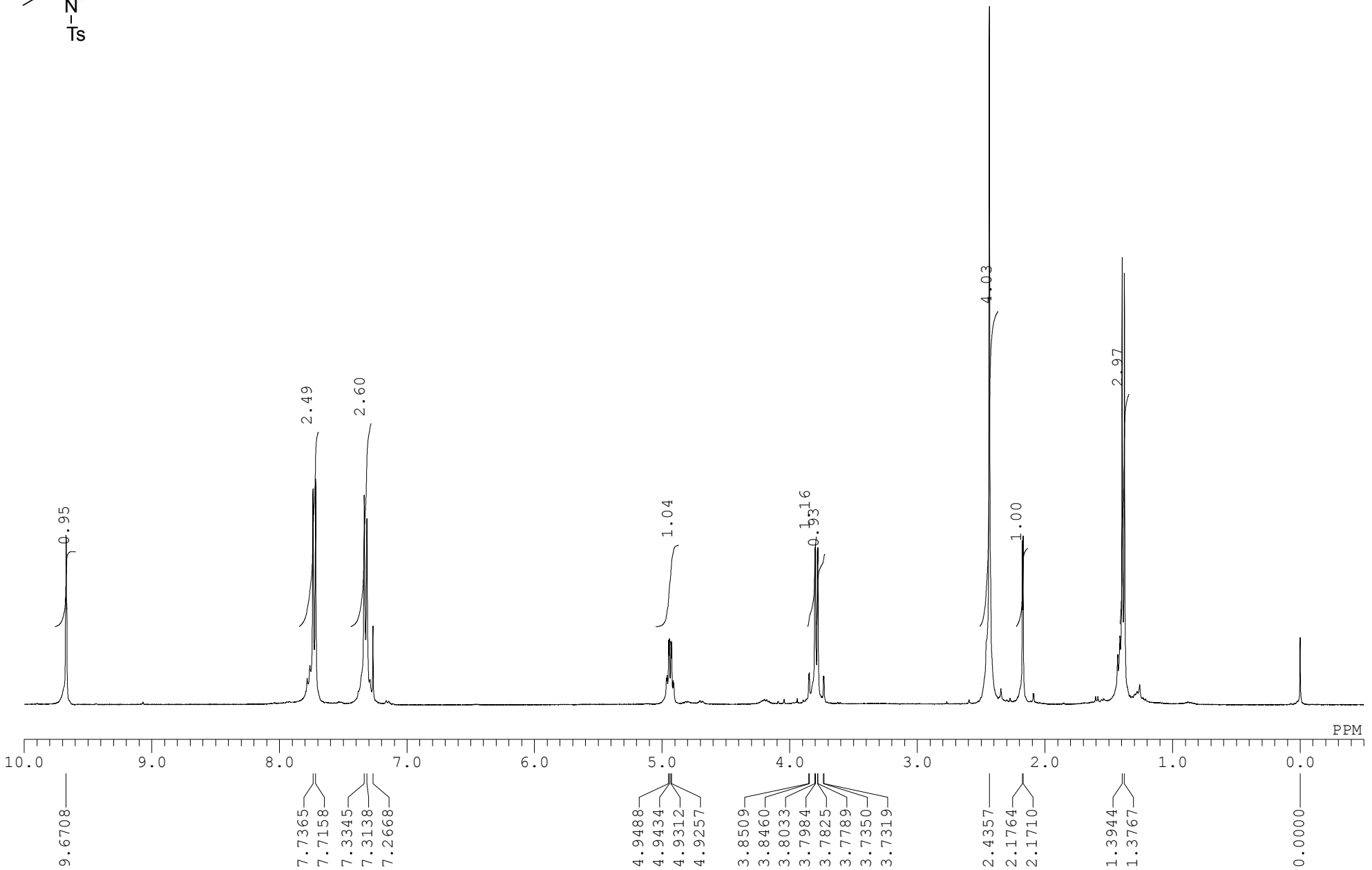


^{13}C NMR spectrum of methyl *N*-(hex-1-yn-3-yl)-*N*-tosylglycinate (**6g**)

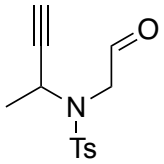


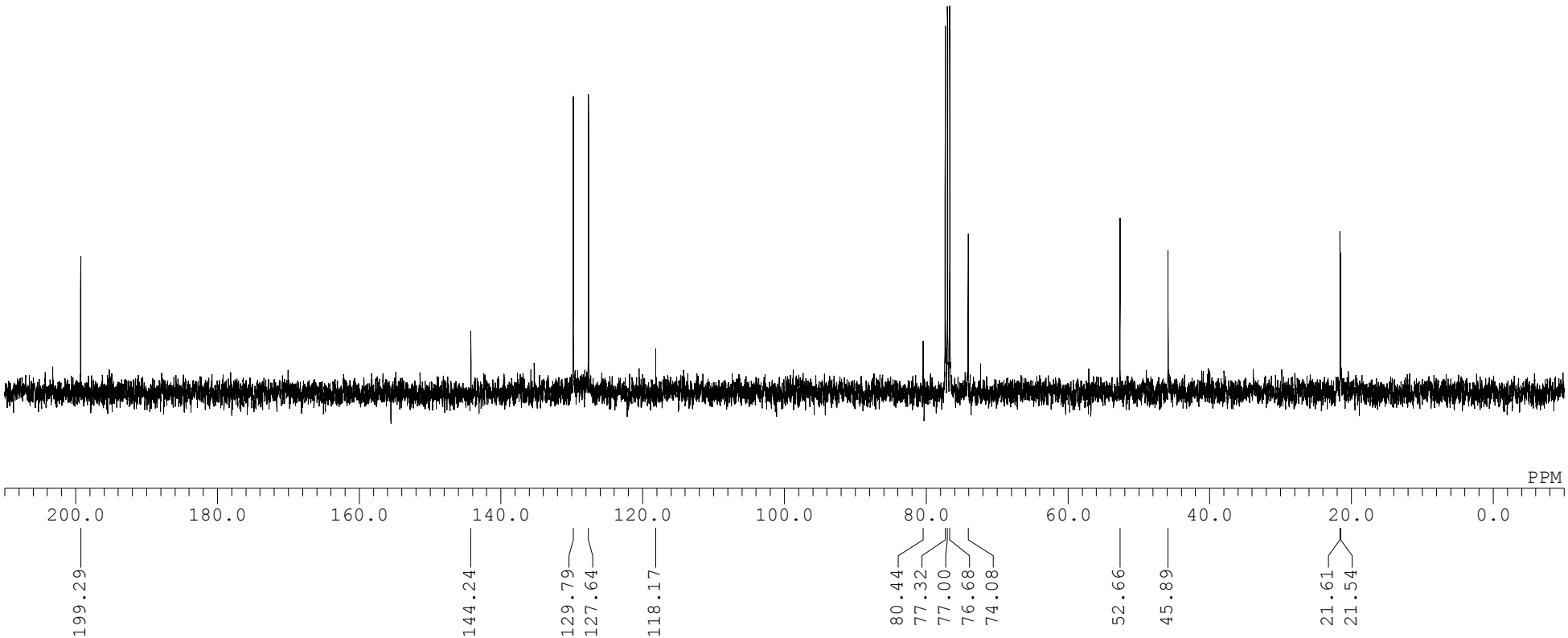
^{1}H NMR spectrum of **4f**



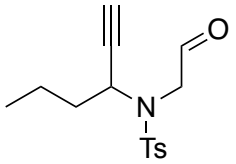


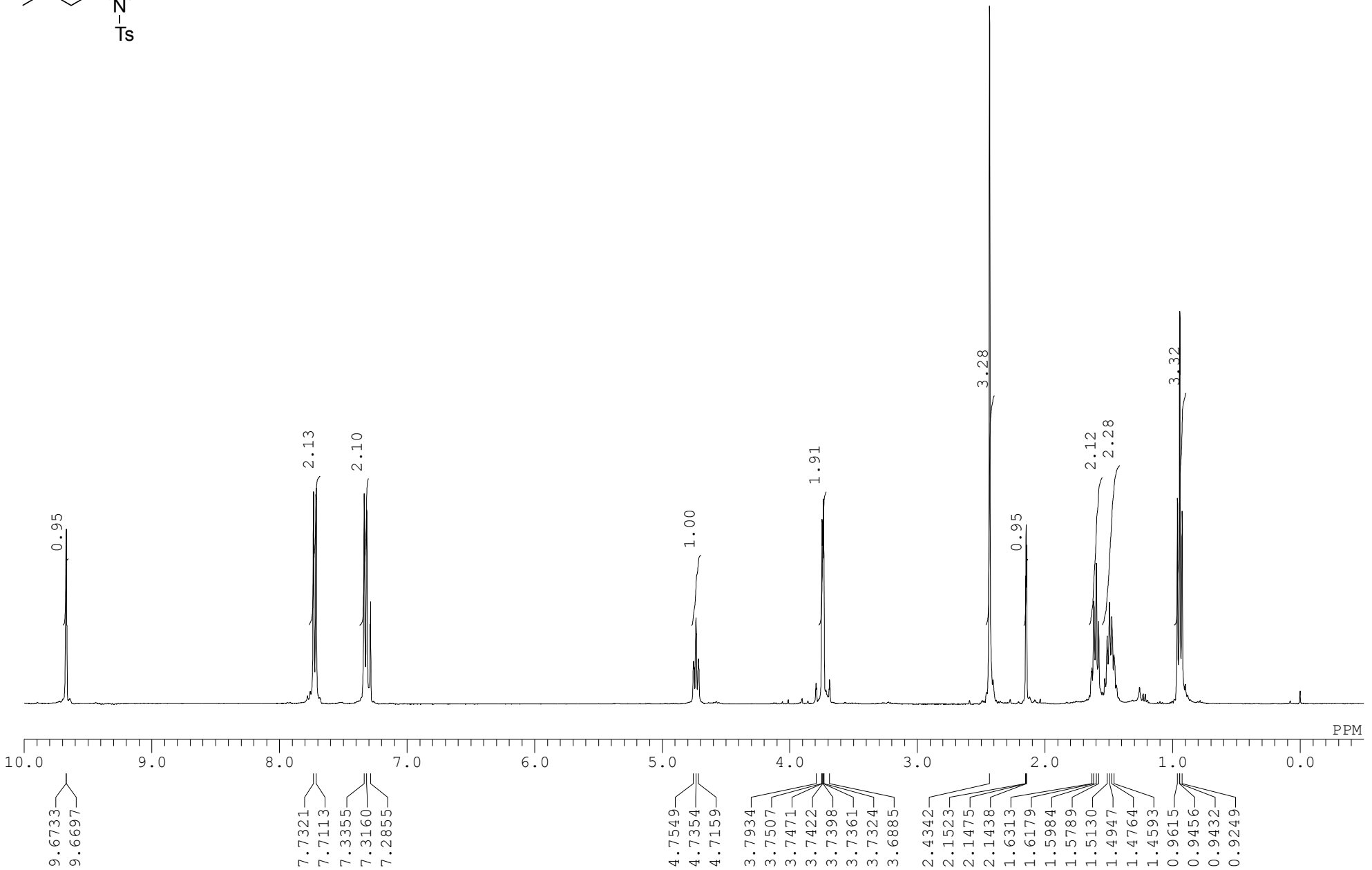
^{13}C NMR spectrum of **4f**



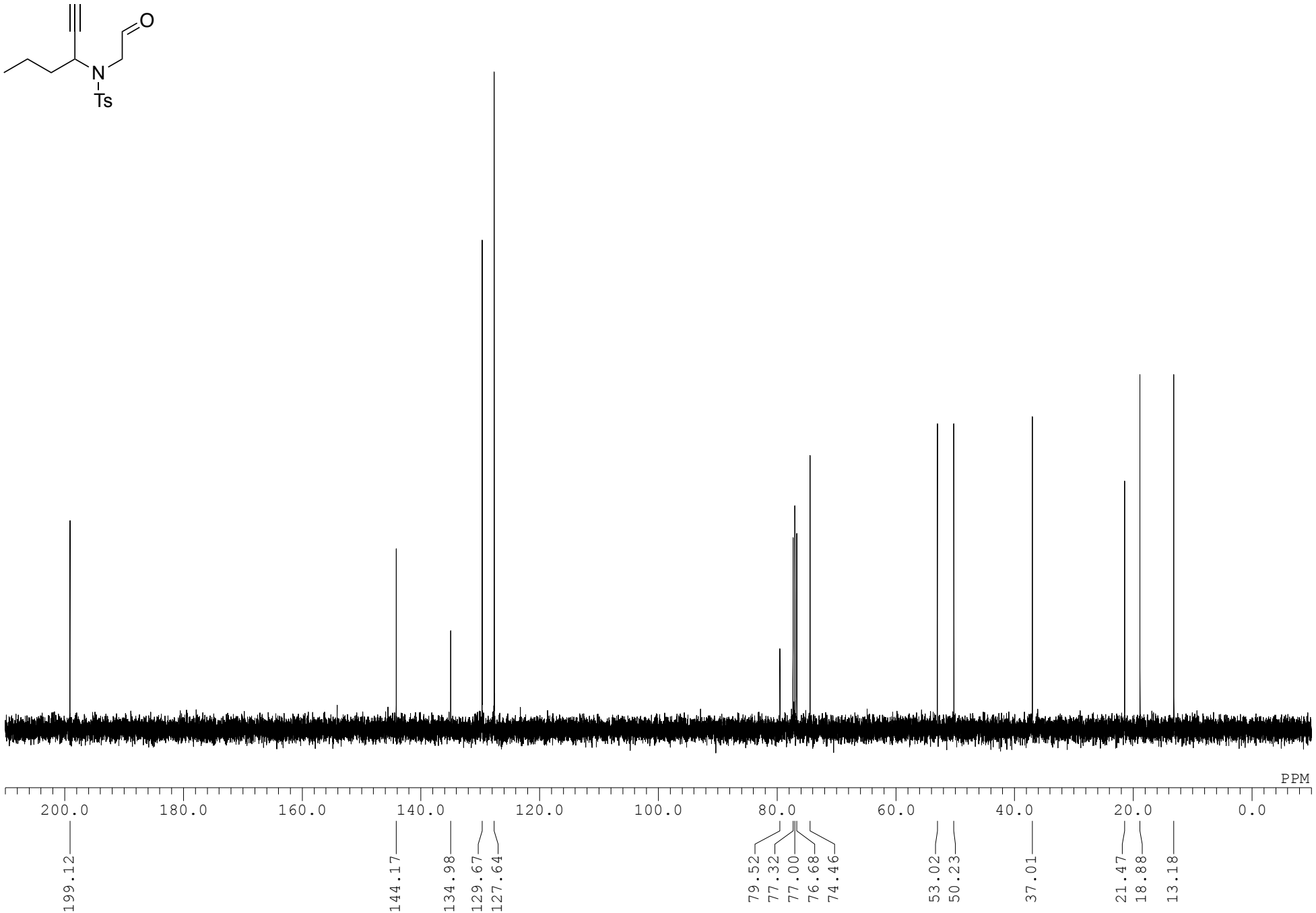


^{1}H NMR spectrum of **4g**

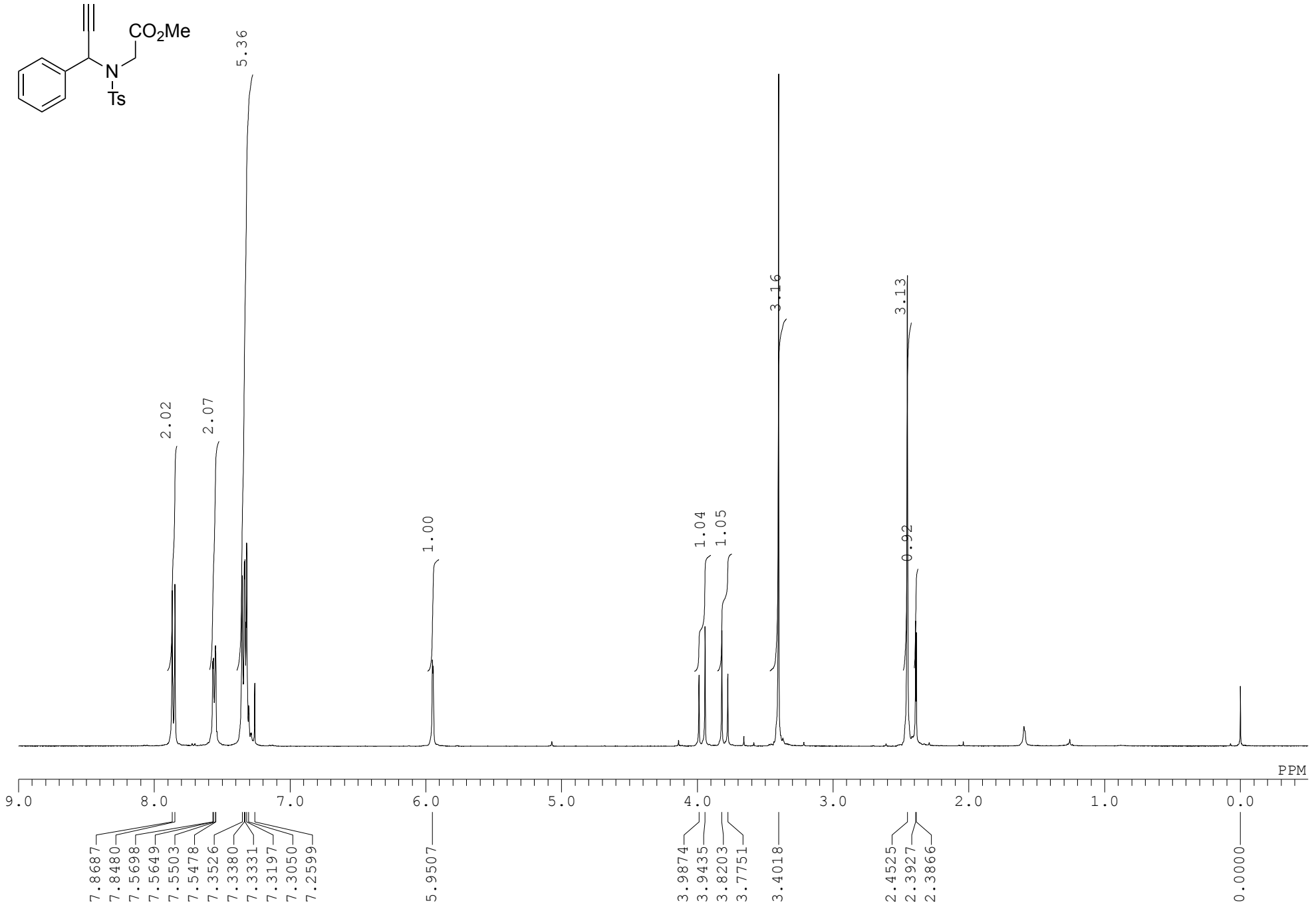




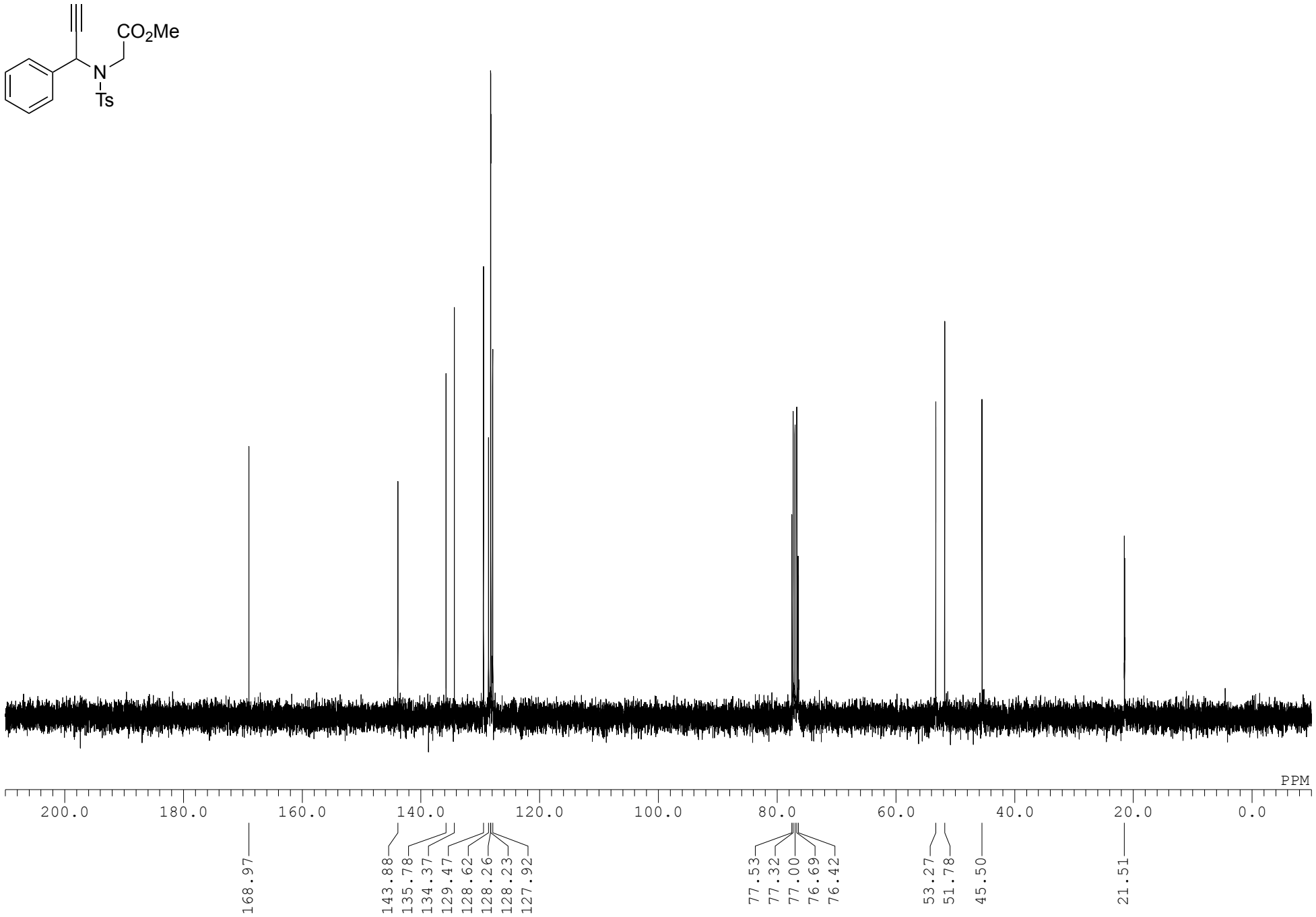
^{13}C NMR spectrum of **4g**



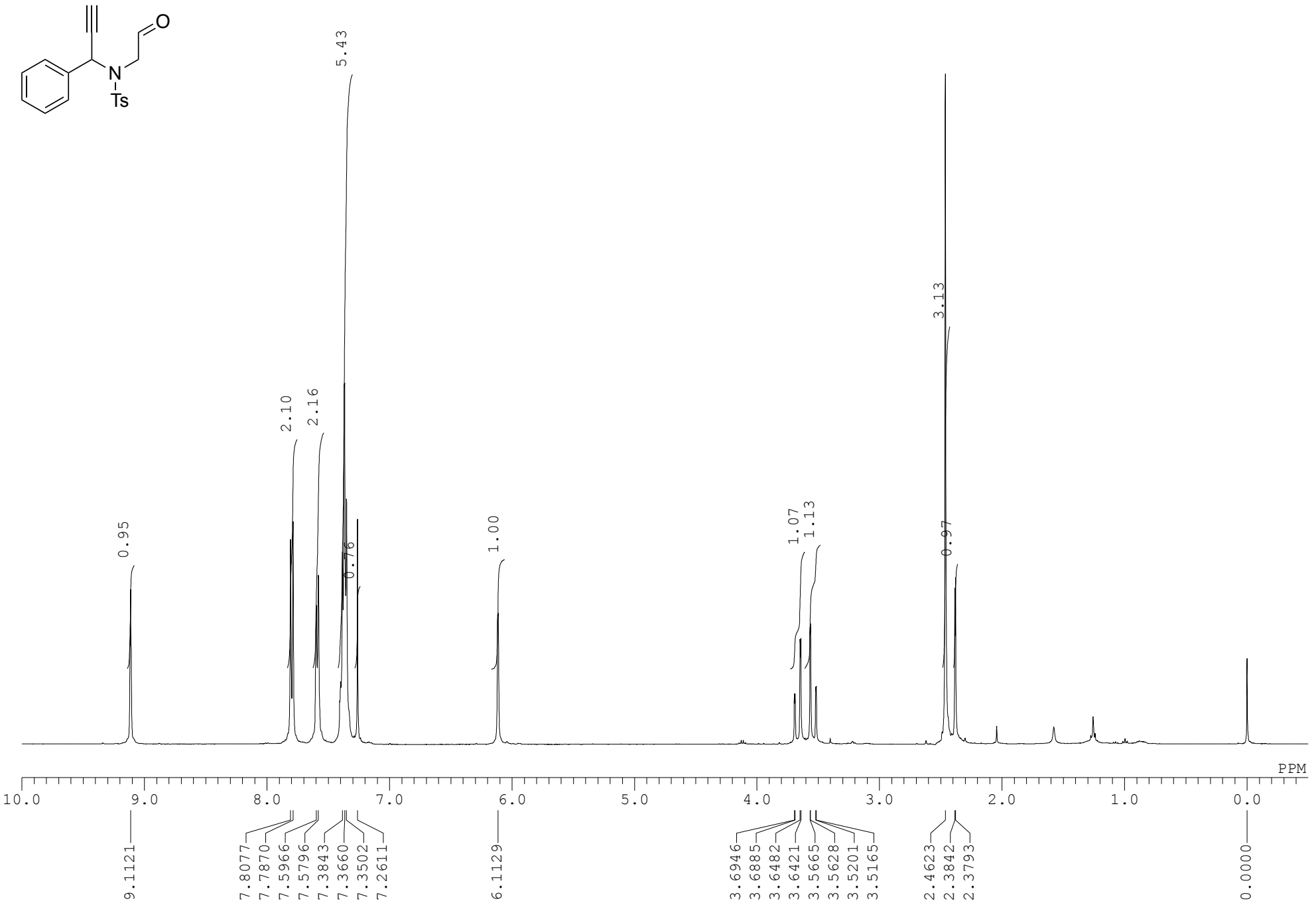
^{1}H NMR spectrum of methyl *N*-(1-phenylprop-2-yn-1-yl)-*N*-tosylglycinate (**6h**)



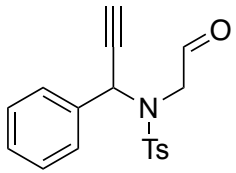
^{13}C NMR spectrum of methyl *N*-(1-phenylprop-2-yn-1-yl)-*N*-tosylglycinate (**6h**)

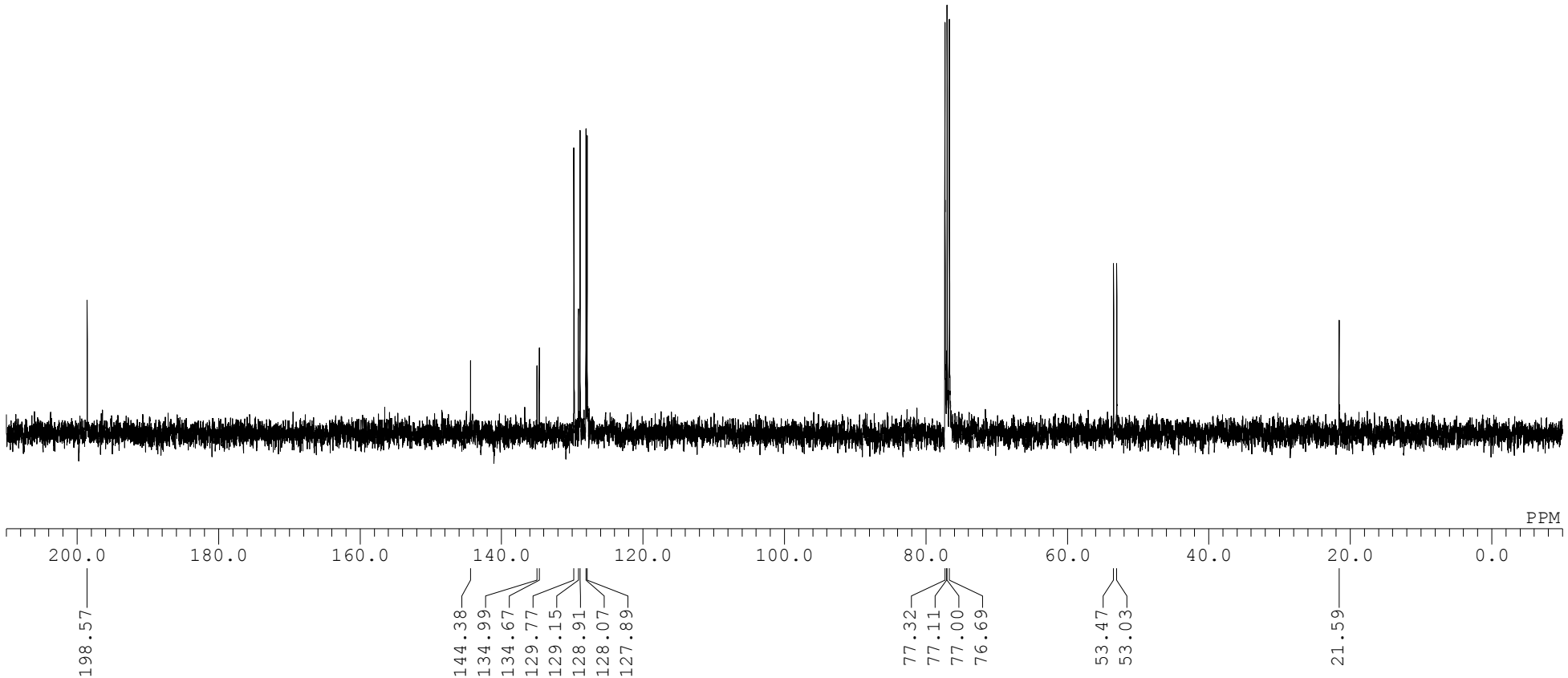


^{1}H NMR spectrum of **4h**

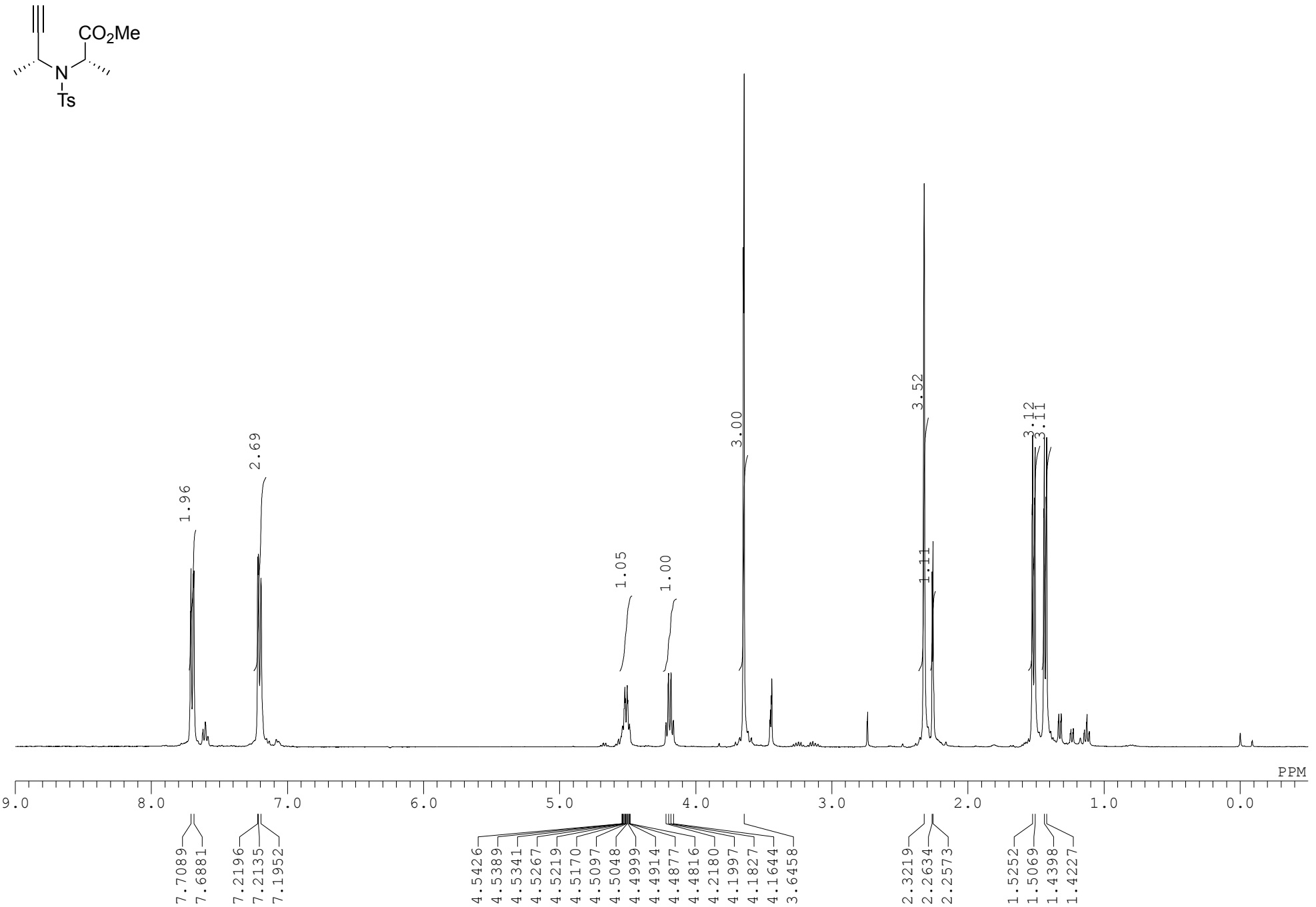


^{13}C NMR spectrum of **4h**

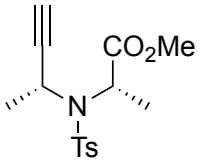


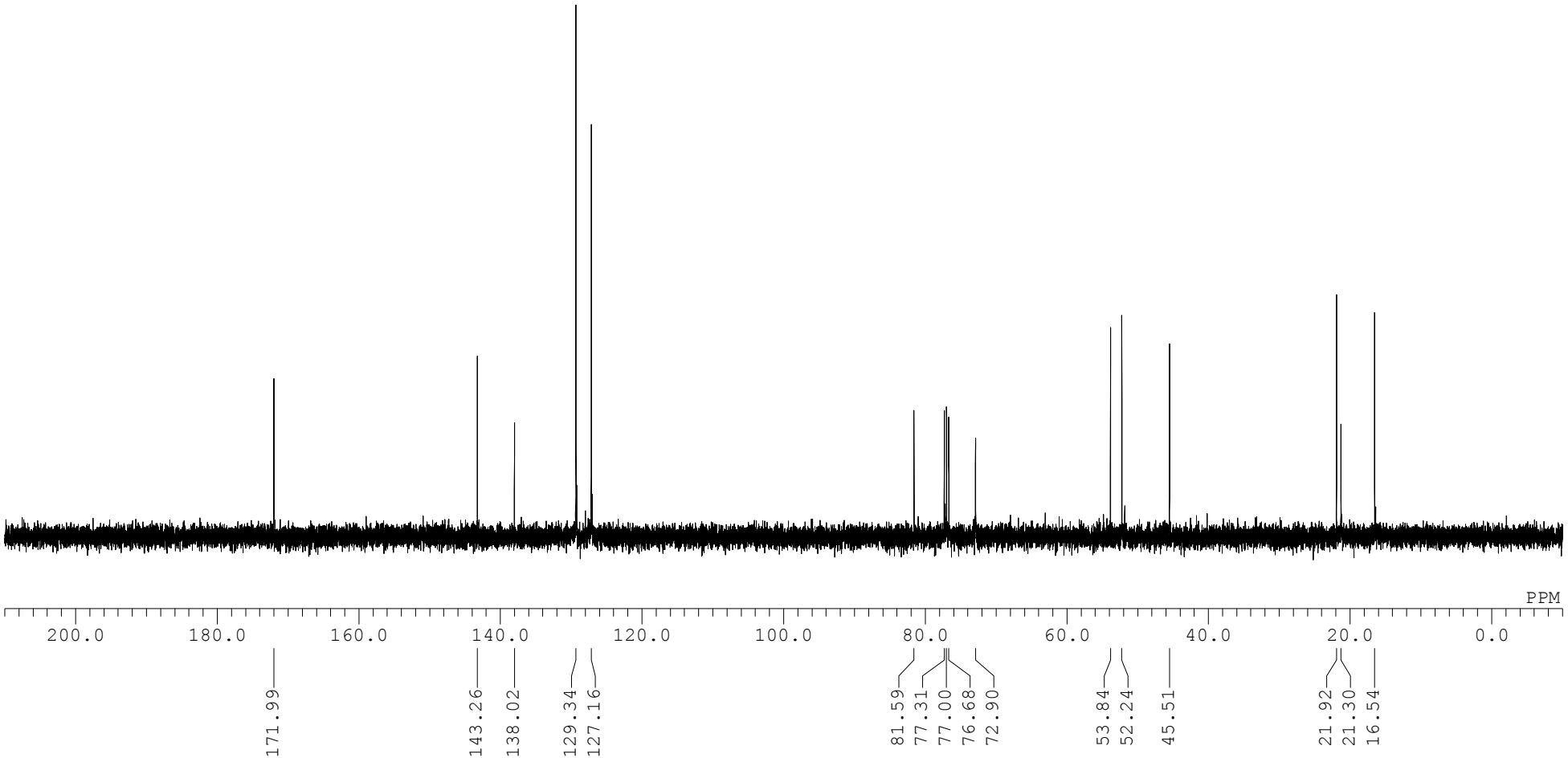


^{1}H NMR spectrum of methyl *N*-((*R*)-but-3-yn-2-yl)-*N*-tosyl-L-alaninate (**6i**)

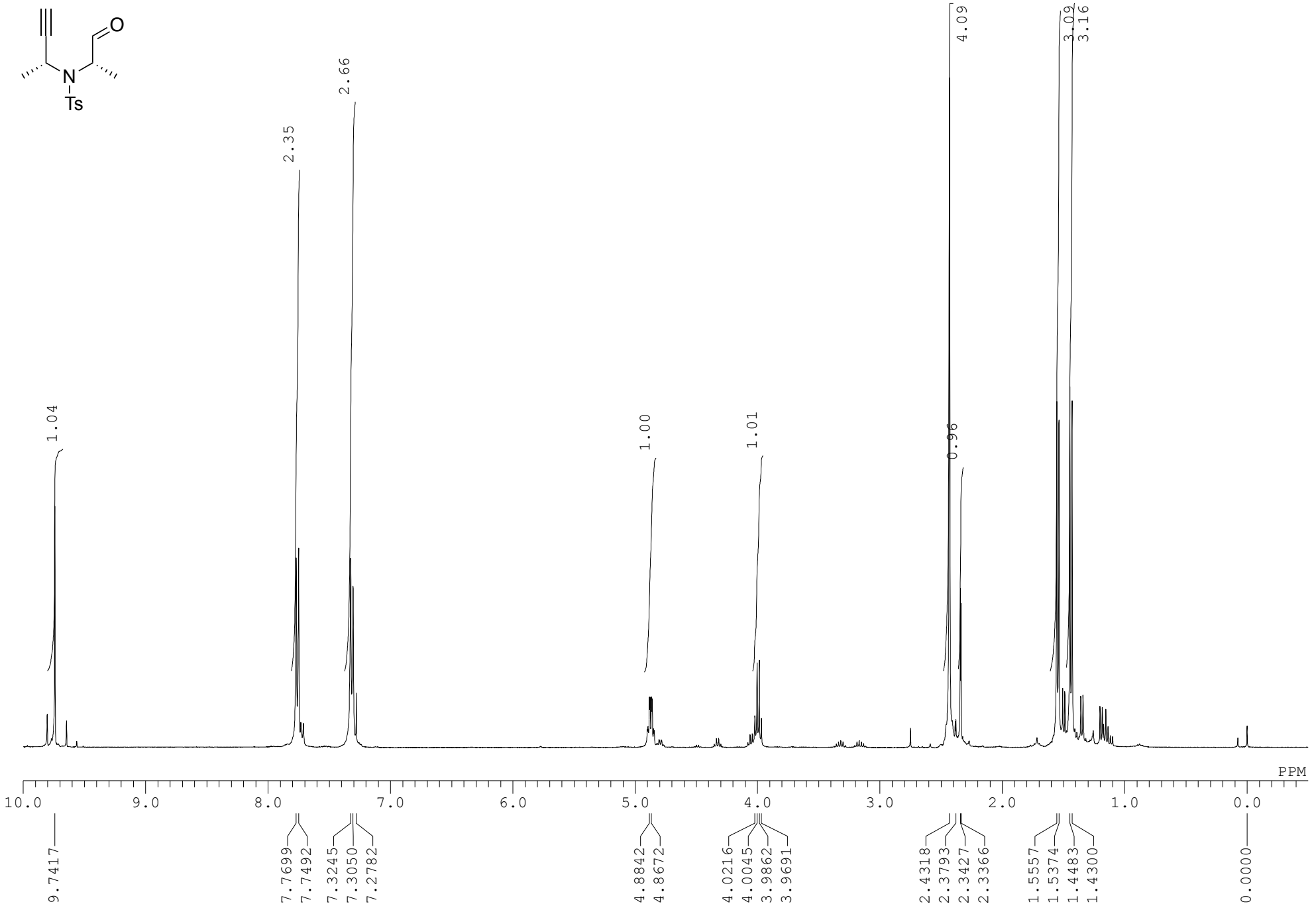


^{13}C NMR spectrum of methyl *N*-((*R*)-but-3-yn-2-yl)-*N*-tosyl-L-alaninate (**6i**)

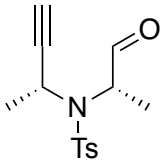


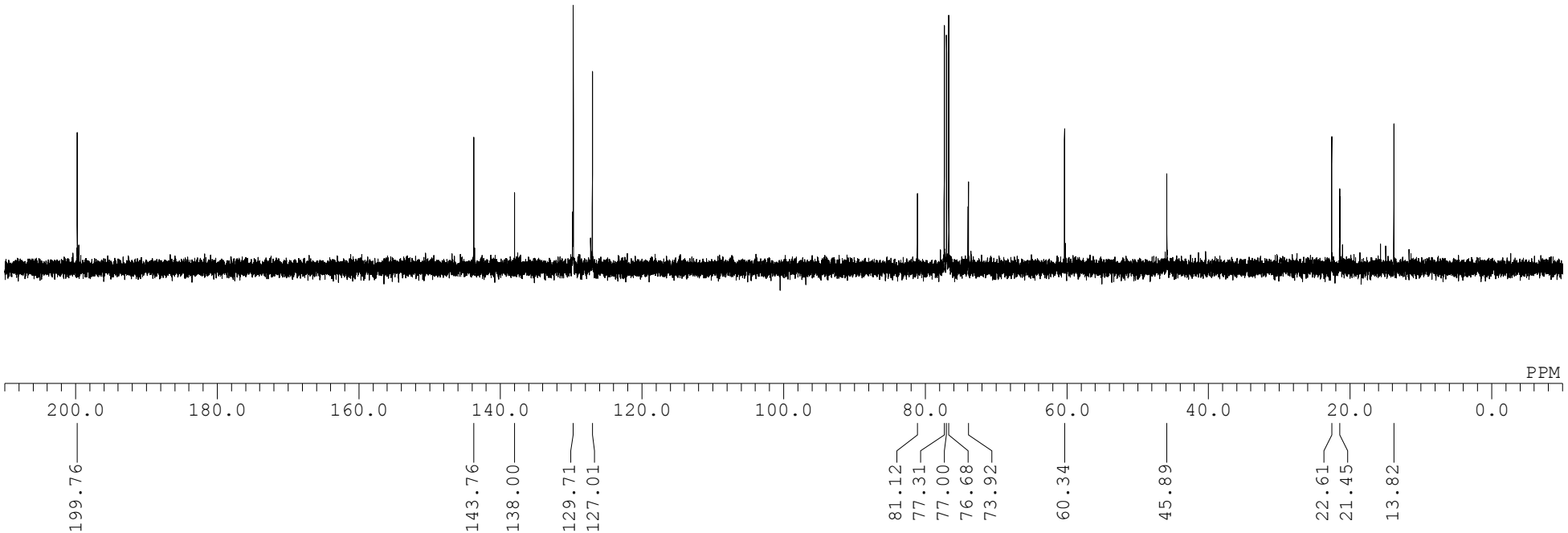


^{1}H NMR spectrum of **4i**

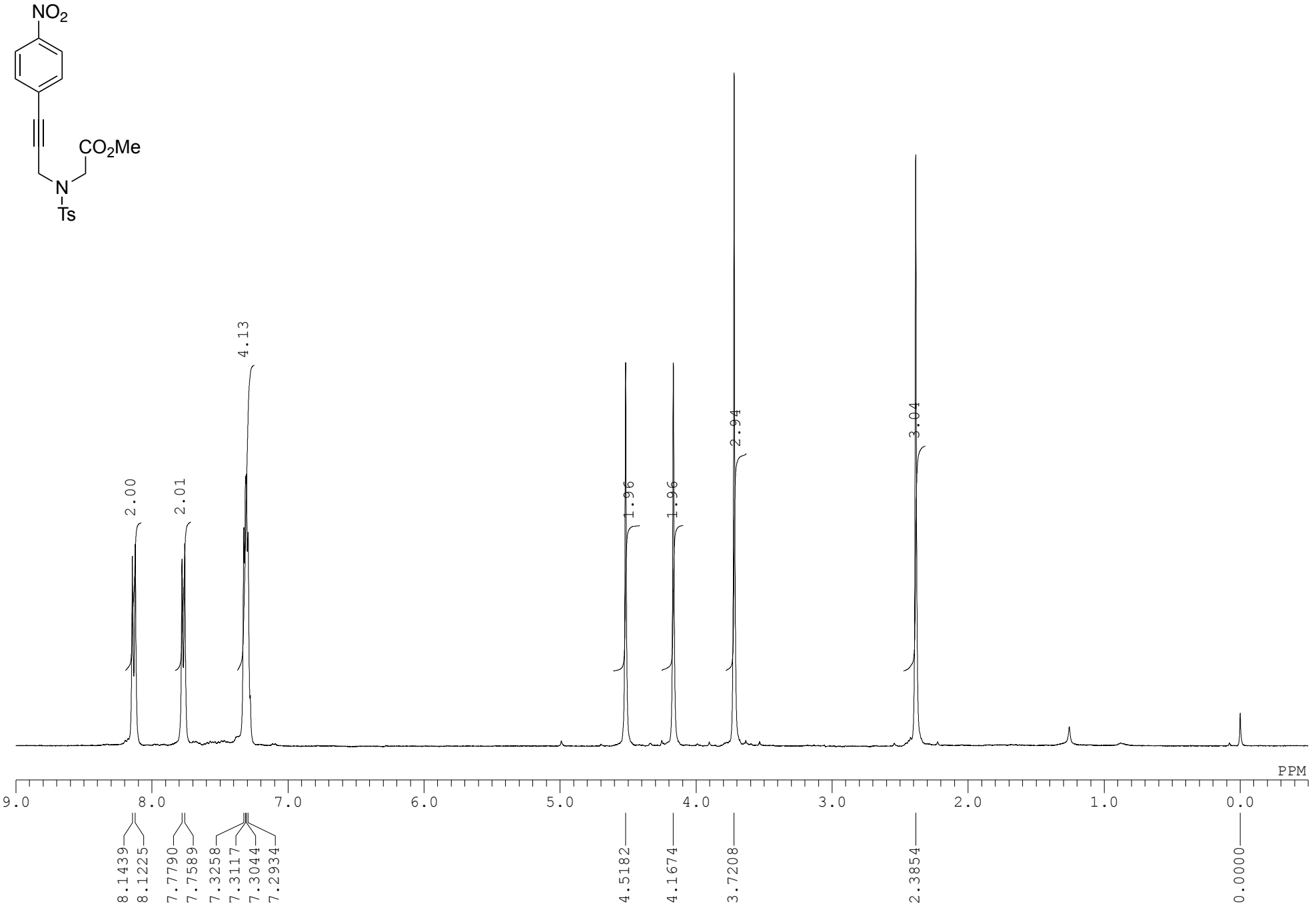


^{13}C NMR spectrum of **4i**

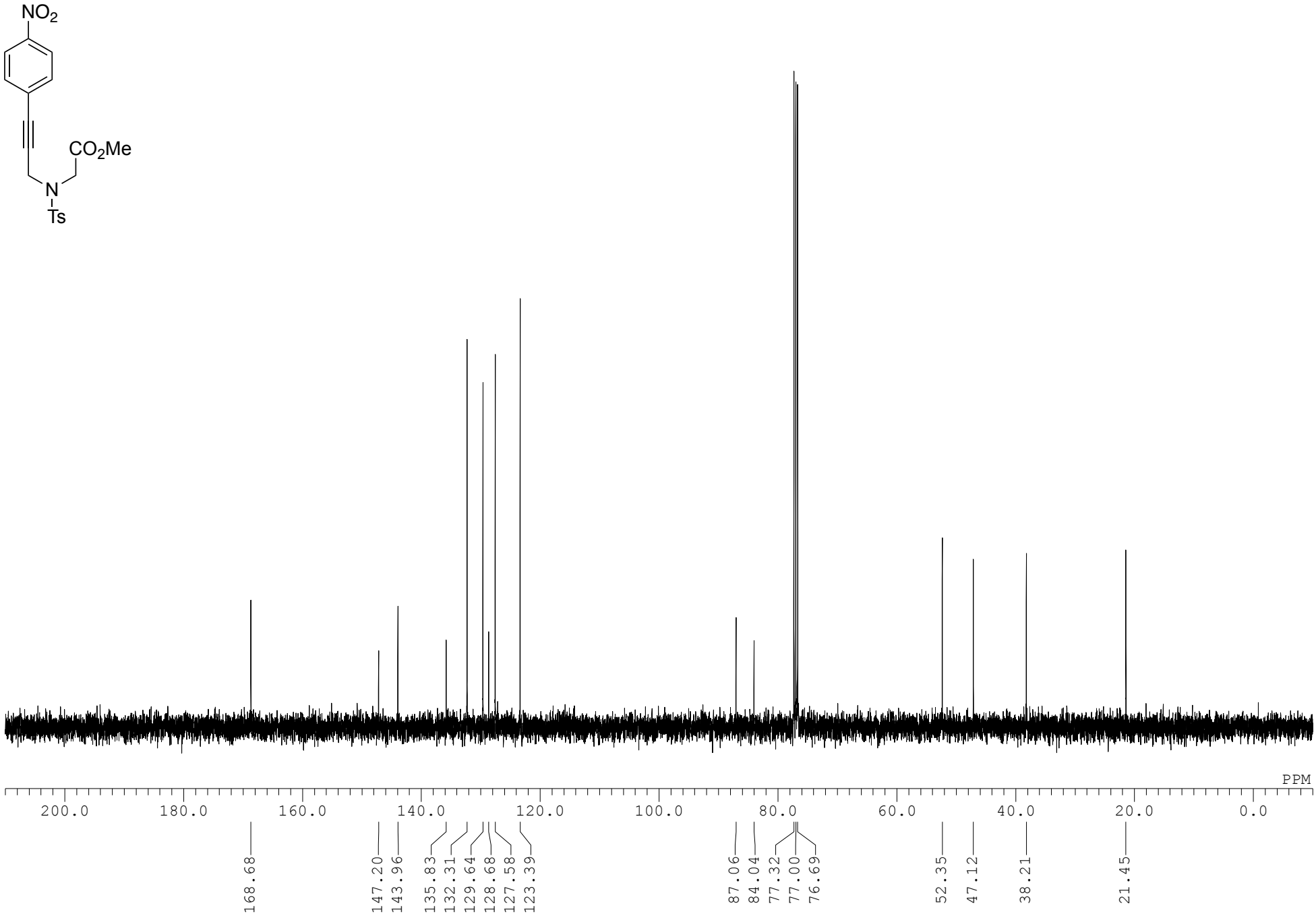




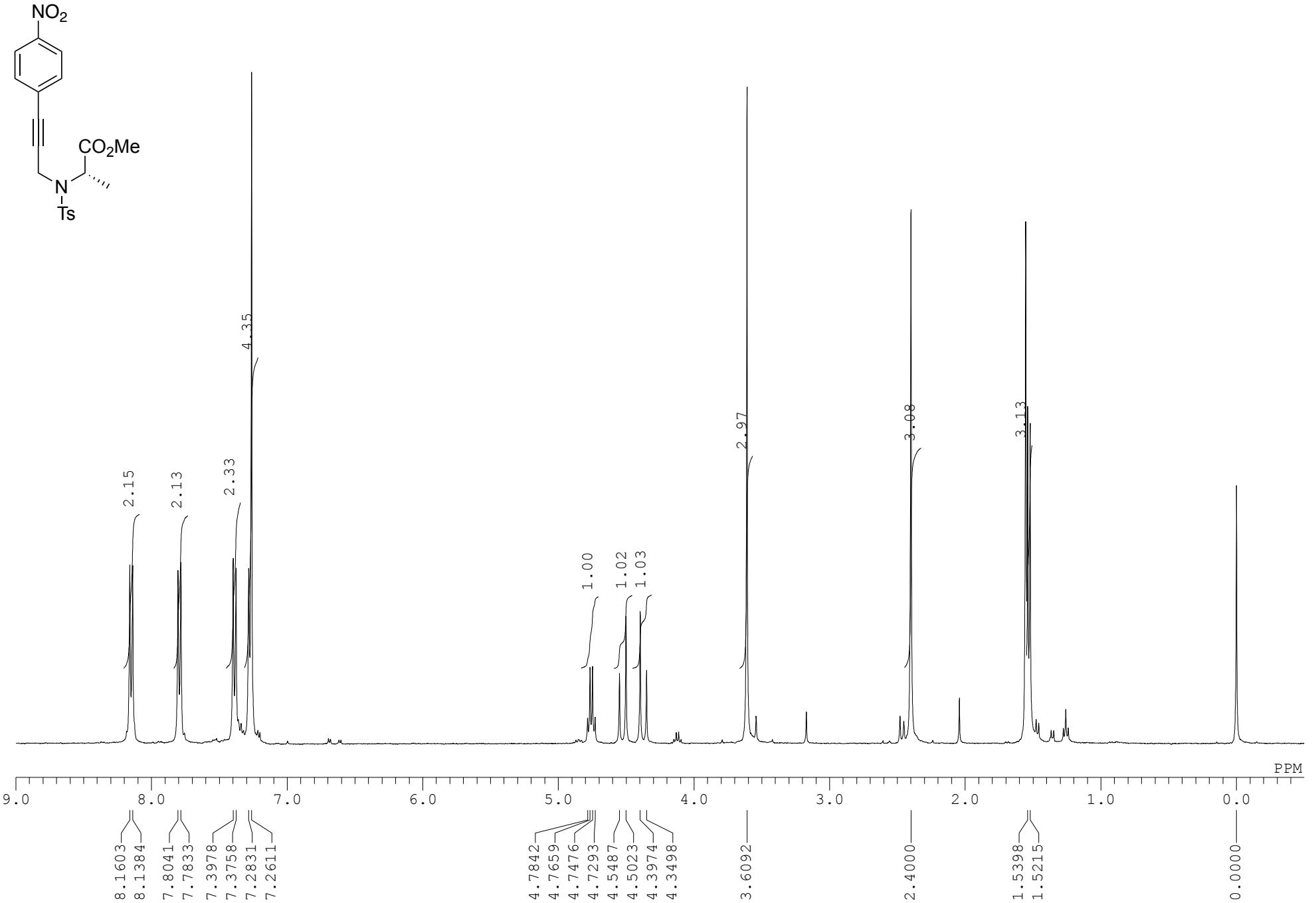
^{1}H NMR spectrum of methyl *N*-(3-(4-nitrophenyl)prop-2-yn-1-yl)-*N*-tosylglycinate (**6l**)



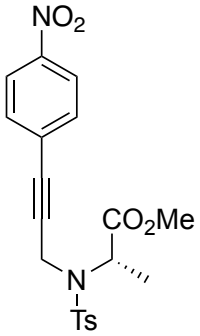
^{13}C NMR spectrum of methyl *N*-(3-(4-nitrophenyl)prop-2-yn-1-yl)-*N*-tosylglycinate (**6l**)

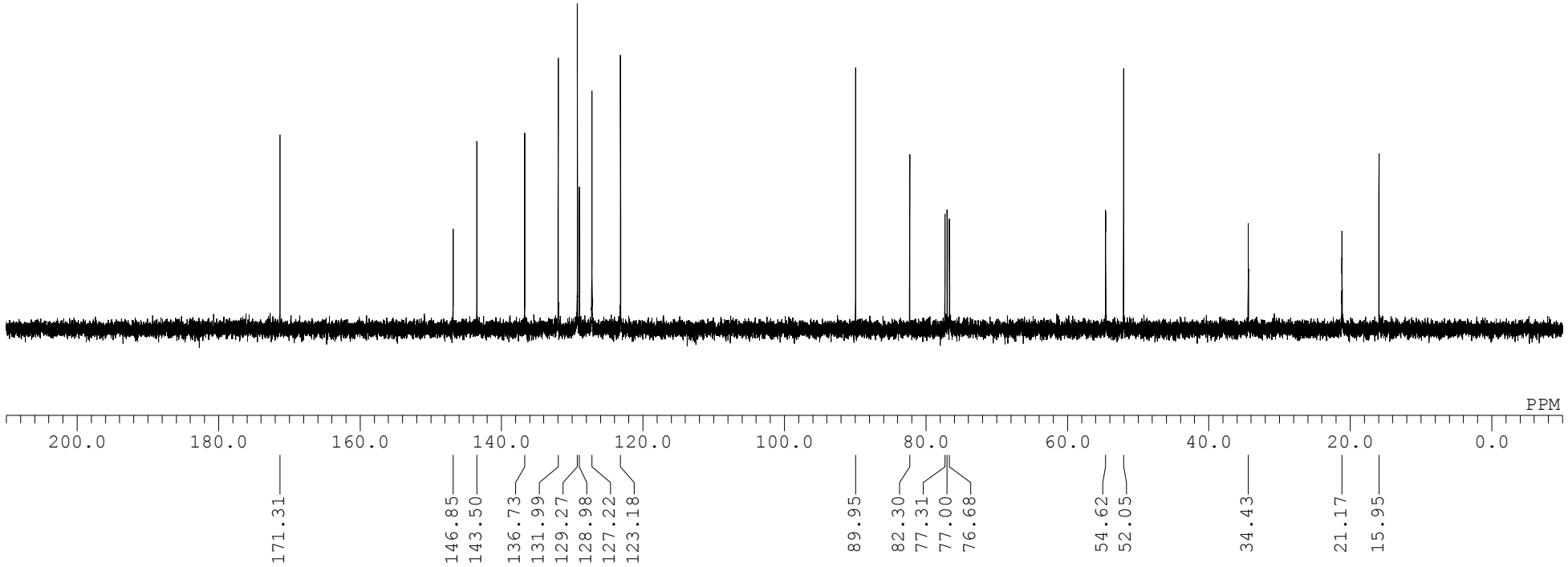


^{1}H NMR spectrum of methyl *N*-(3-(4-nitrophenyl)prop-2-yn-1-yl)-*N*-tosyl-L-alaninate (**6o**)

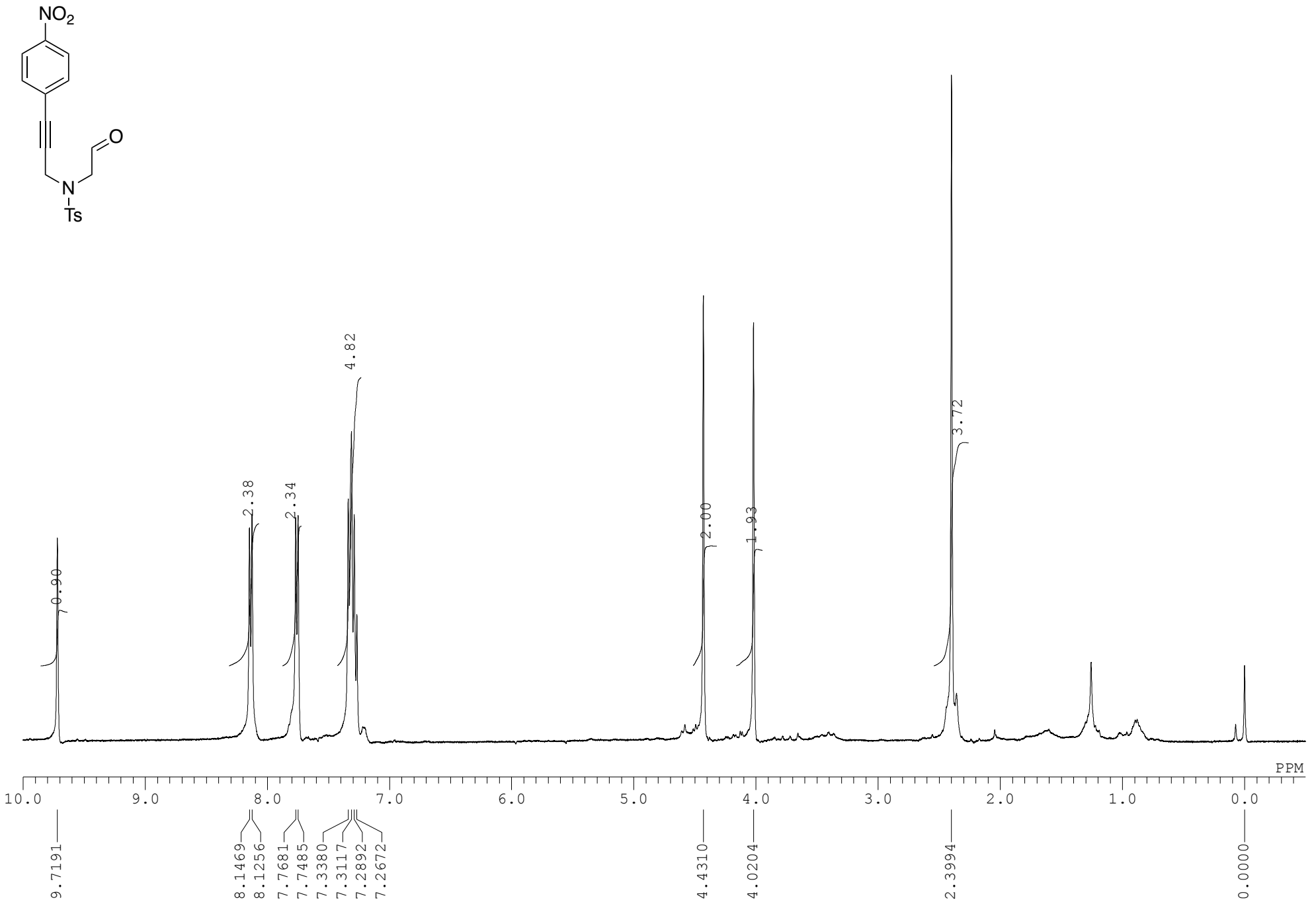


^{13}C NMR spectrum of methyl *N*-(3-(4-nitrophenyl)prop-2-yn-1-yl)-*N*-tosyl-L-alaninate (**6o**)

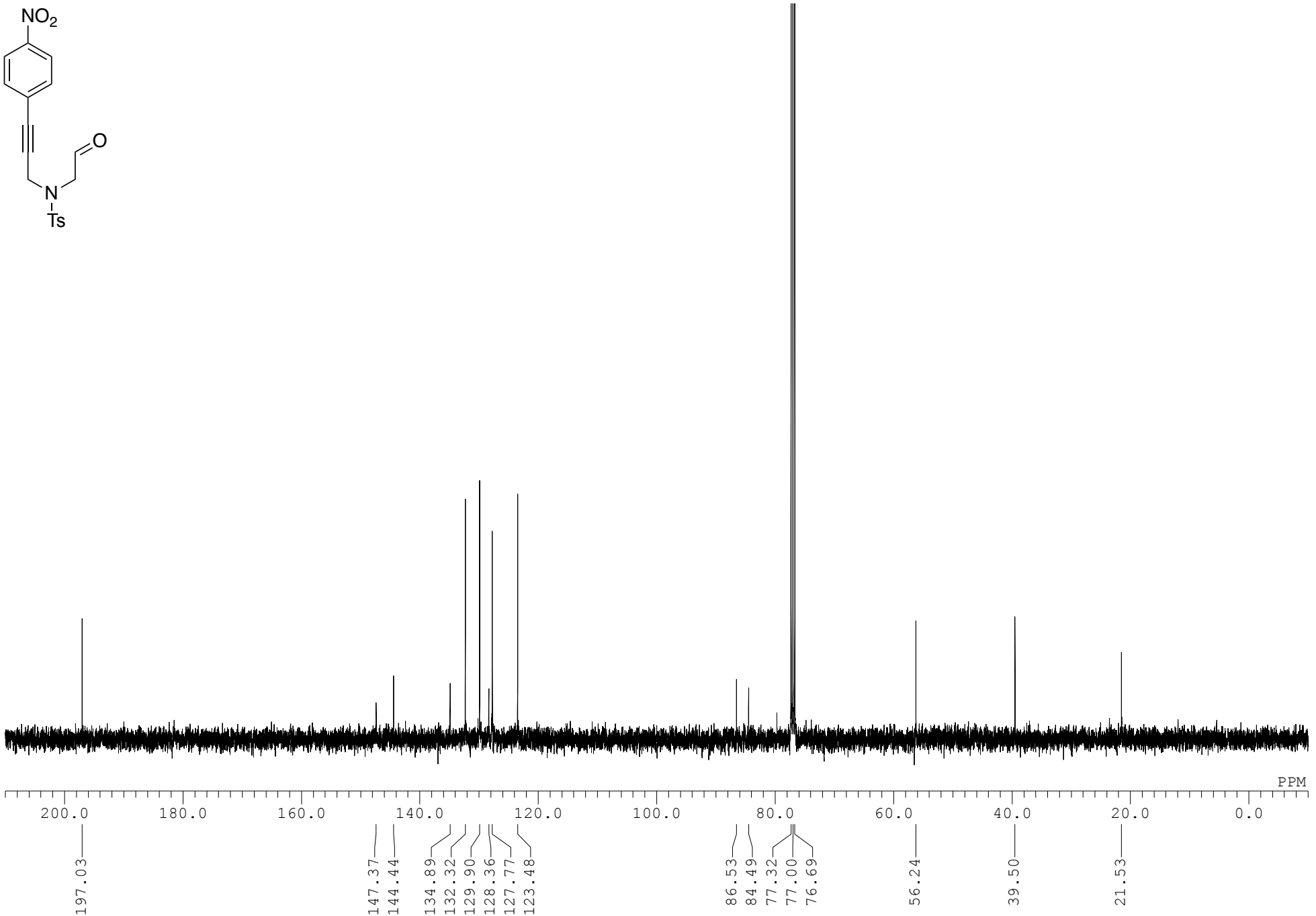




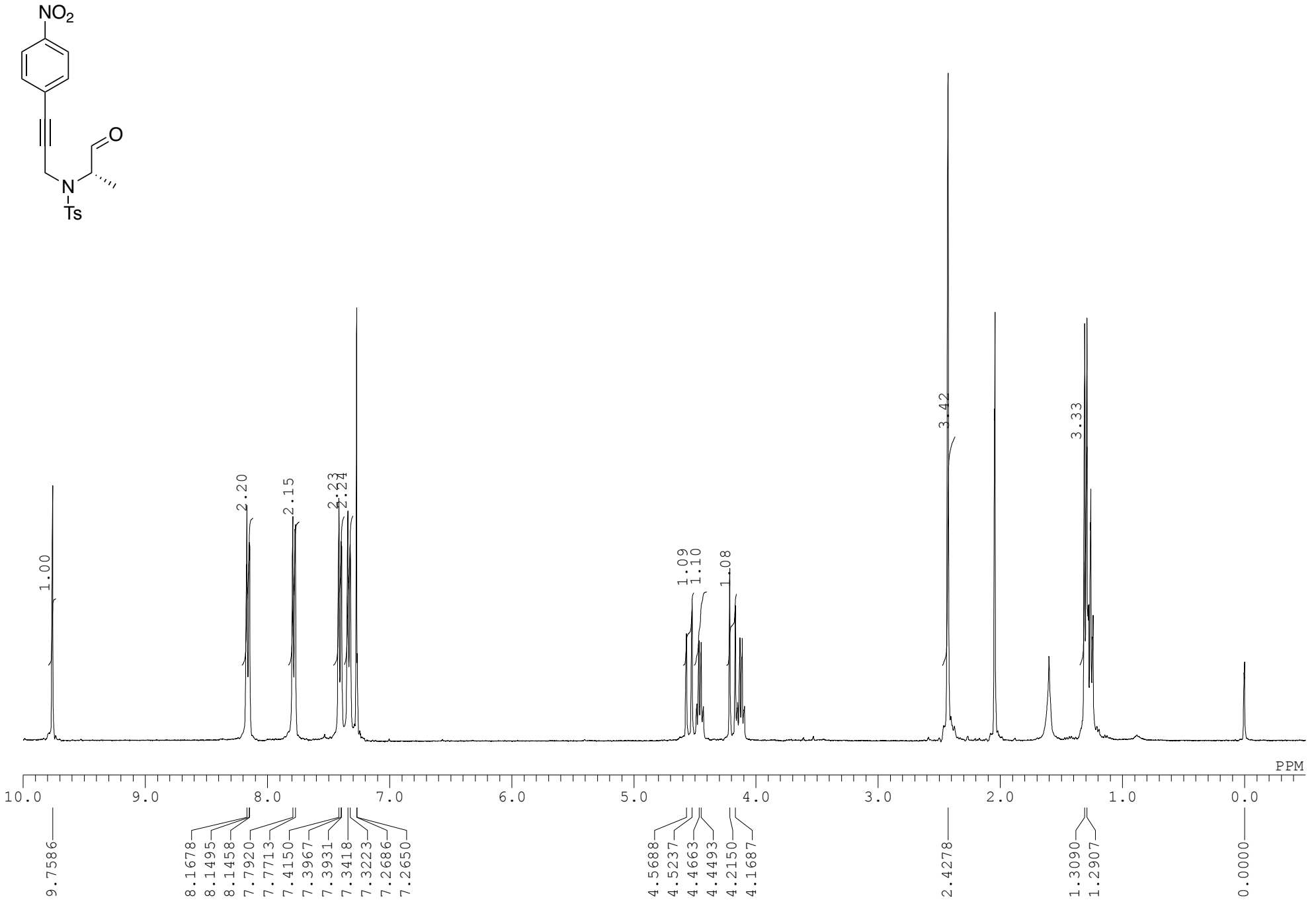
^{1}H NMR spectrum of **4l**



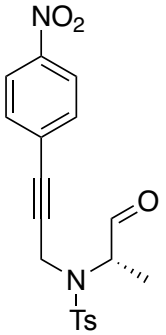
^{13}C NMR spectrum of **4l**

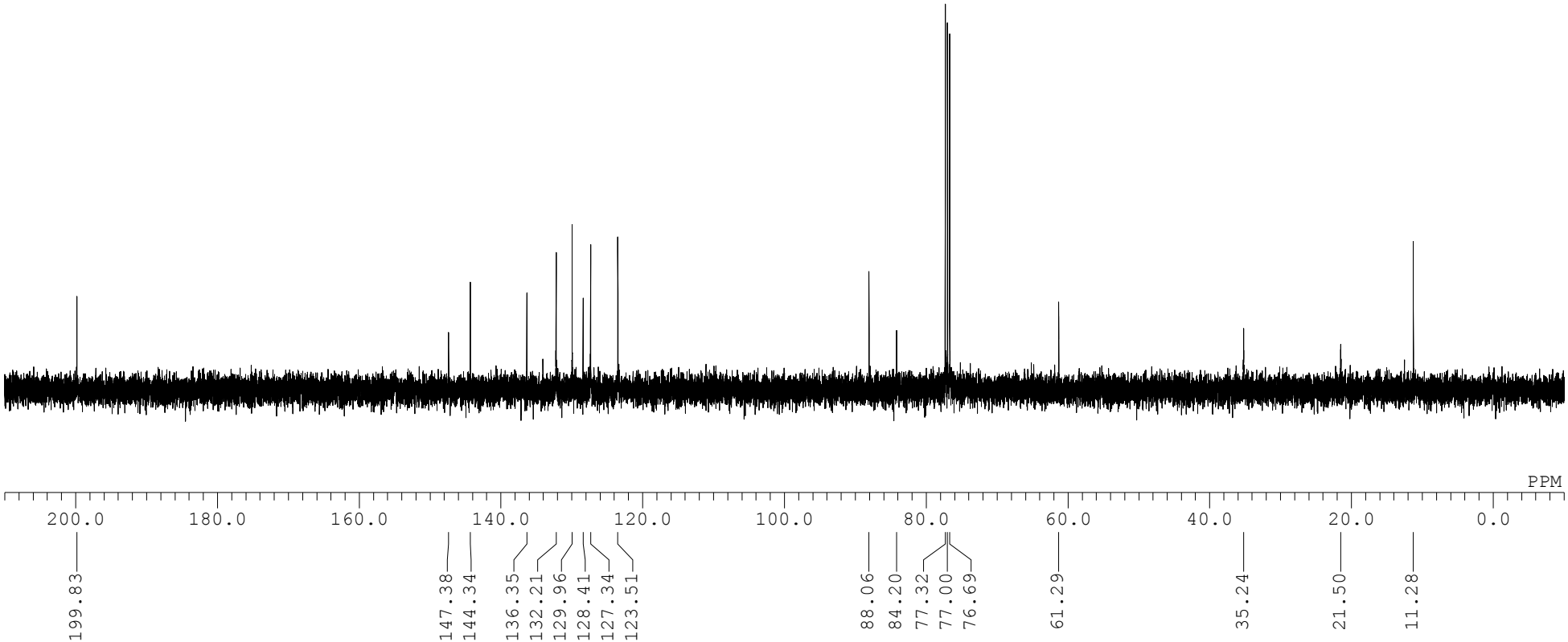


^{1}H NMR spectrum of **4o**

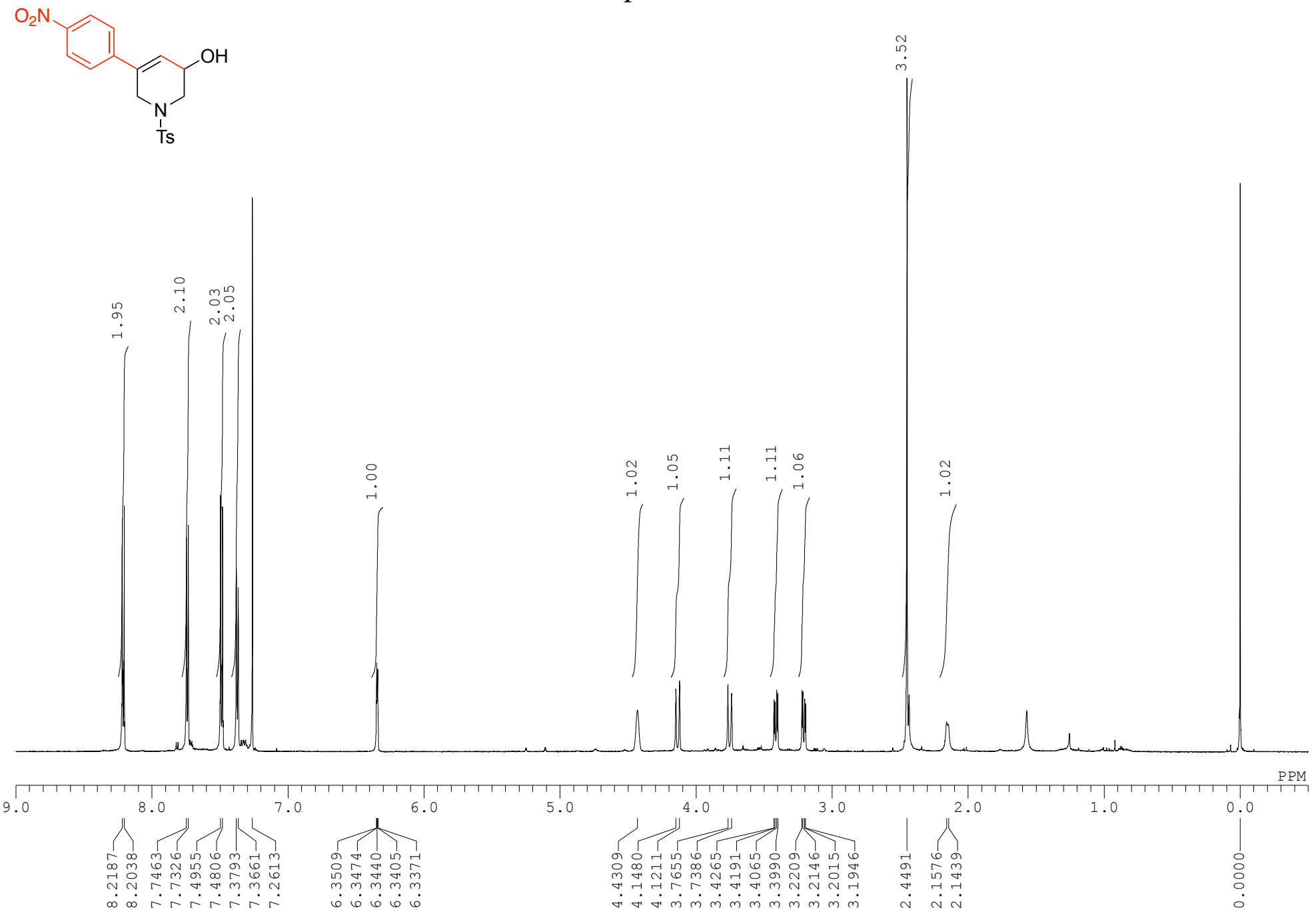


^{13}C NMR spectrum of **4o**

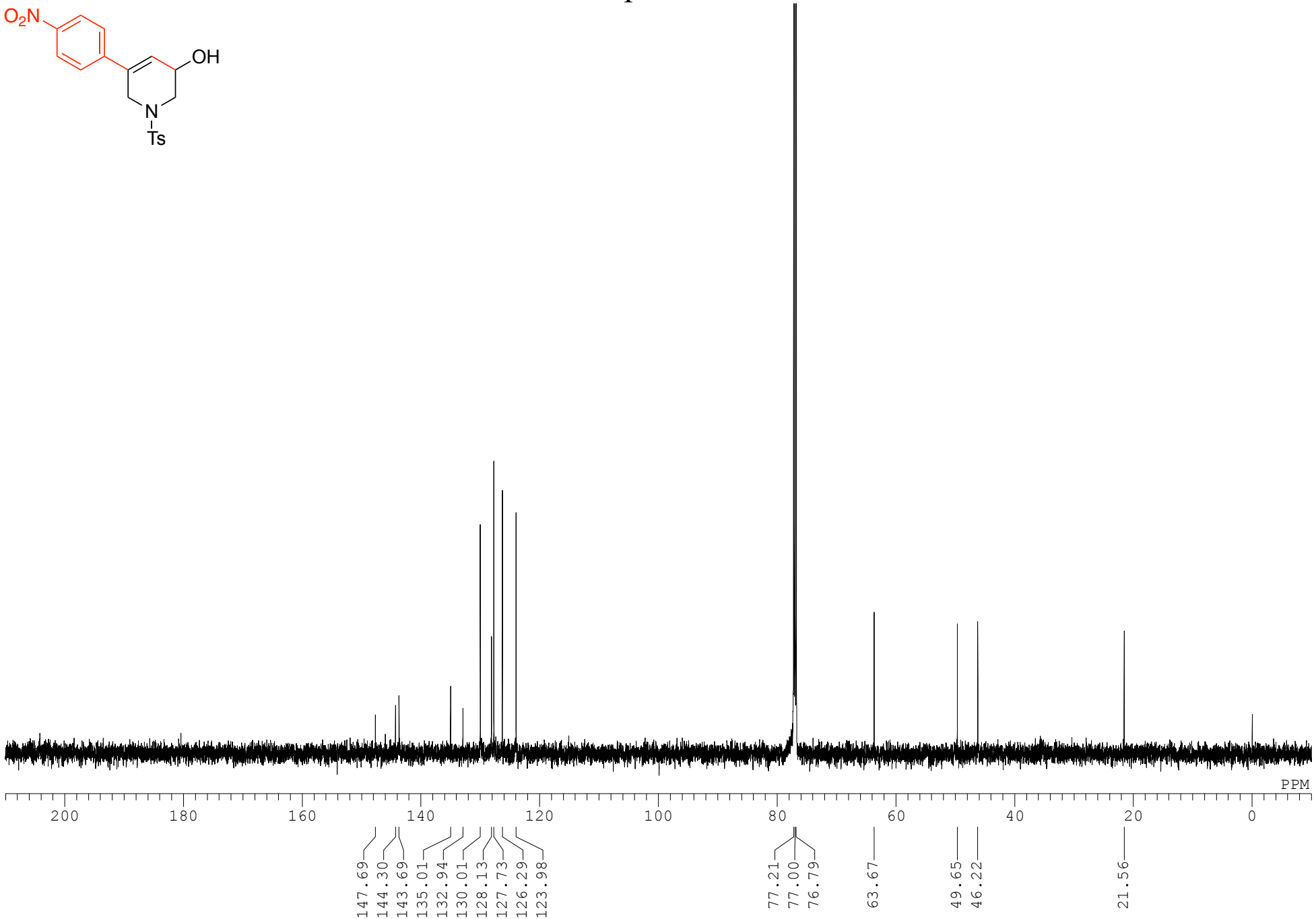




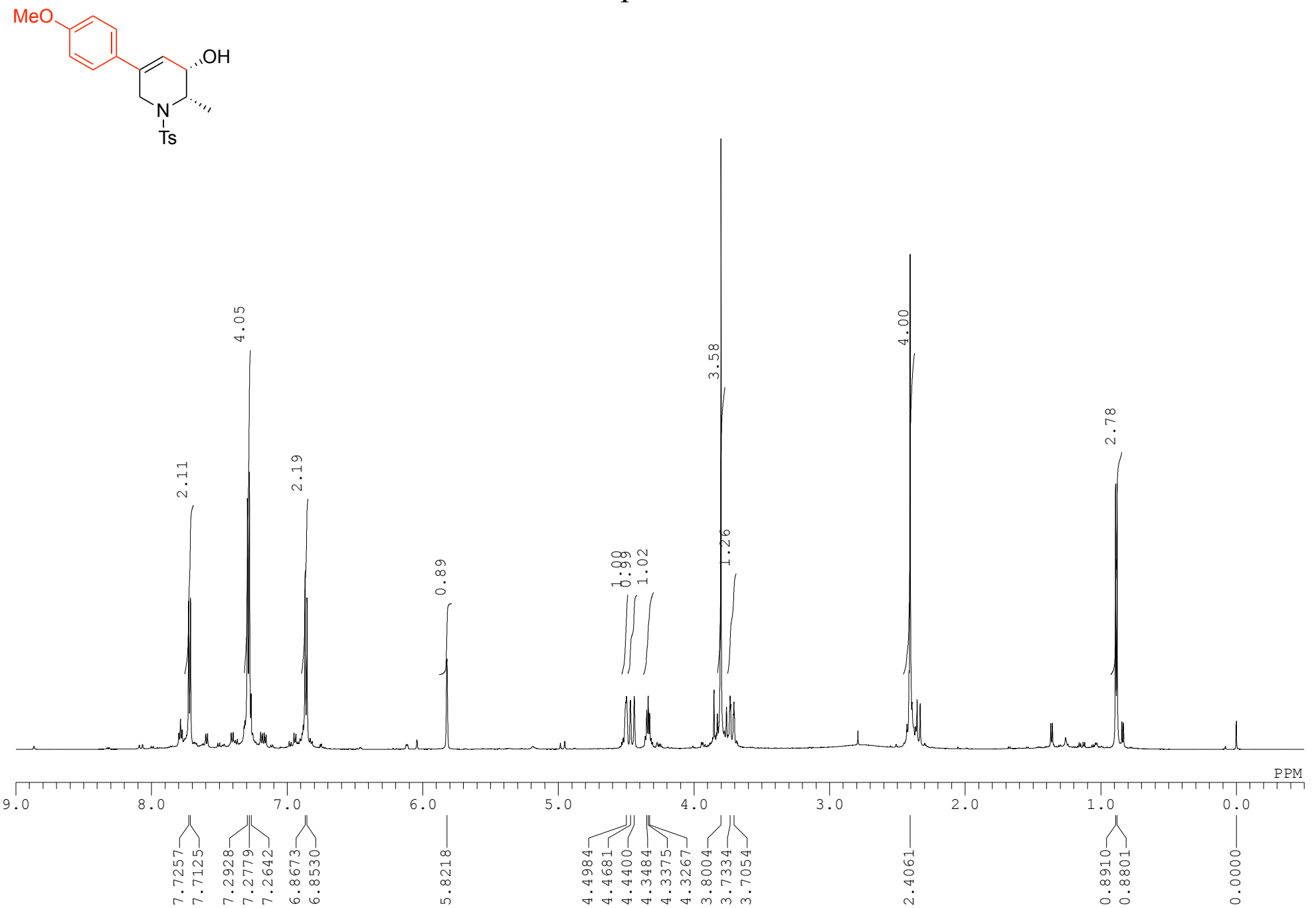
^{1}H NMR spectrum of **5aC**



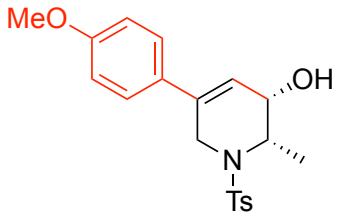
^{13}C NMR spectrum of **5aC**

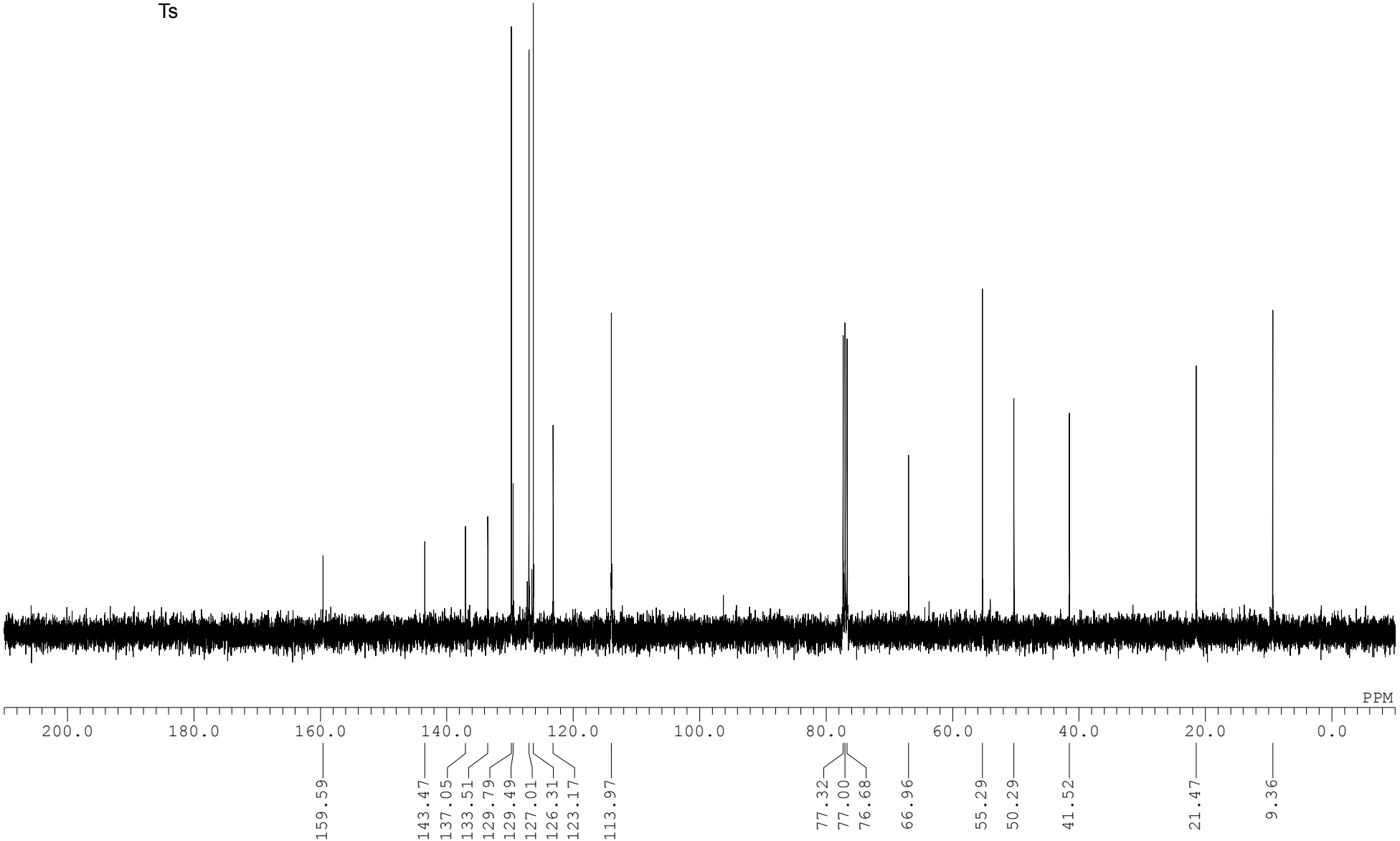


^{1}H NMR spectrum of **5bA**

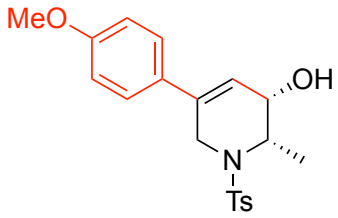


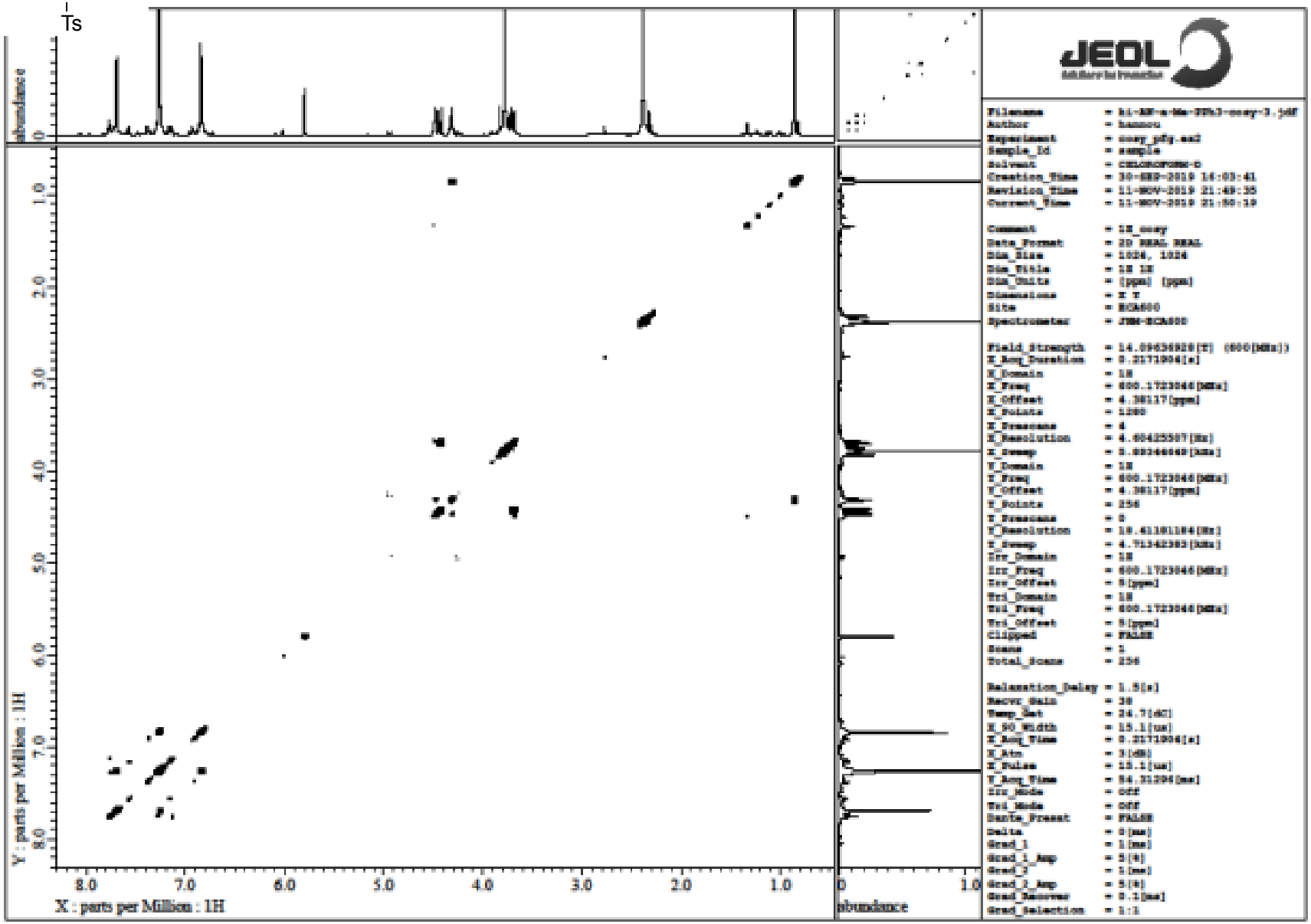
^{13}C NMR spectrum of **5bA**



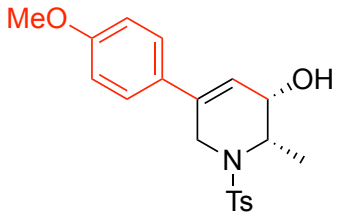


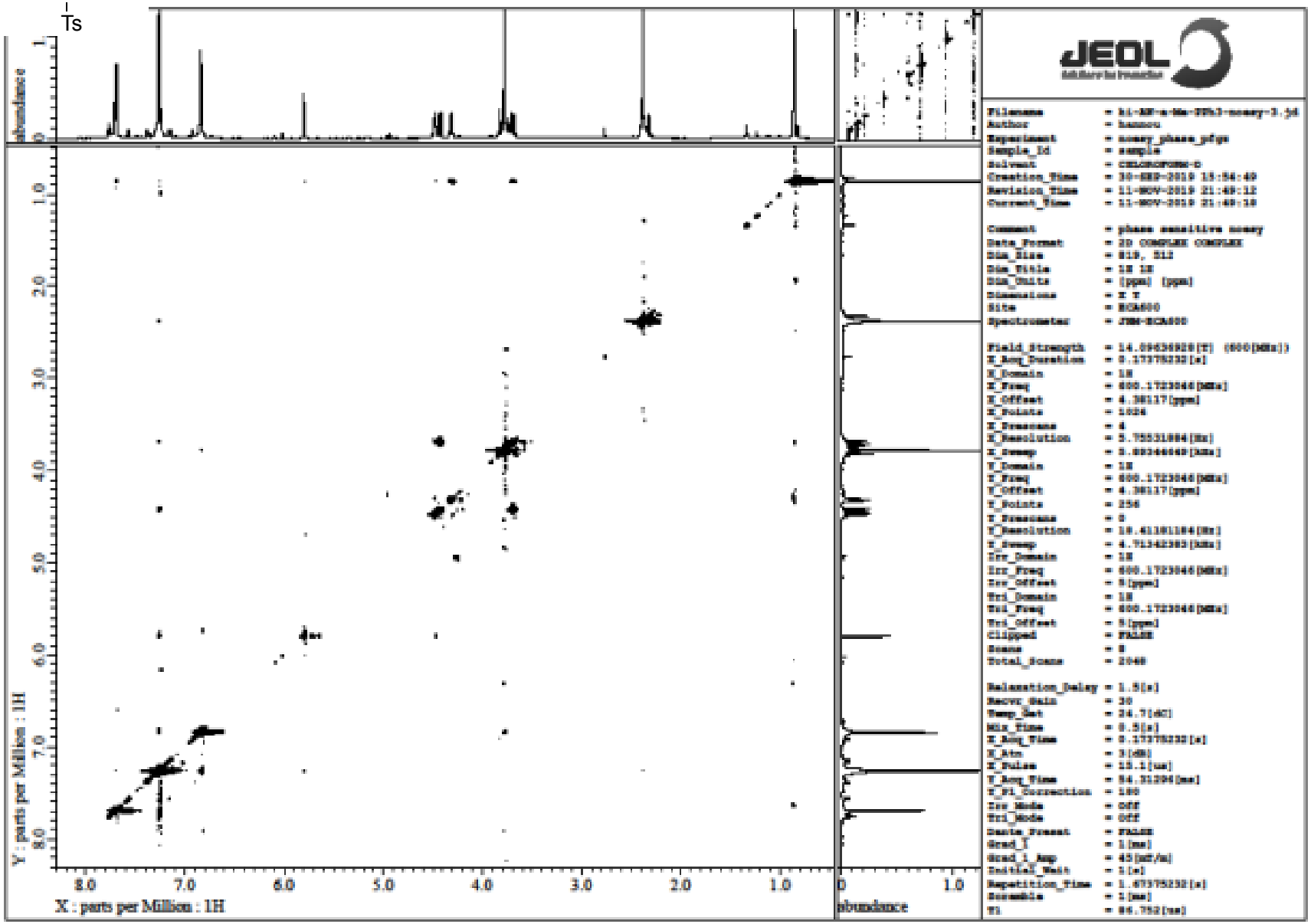
COSY spectrum of **5bA**



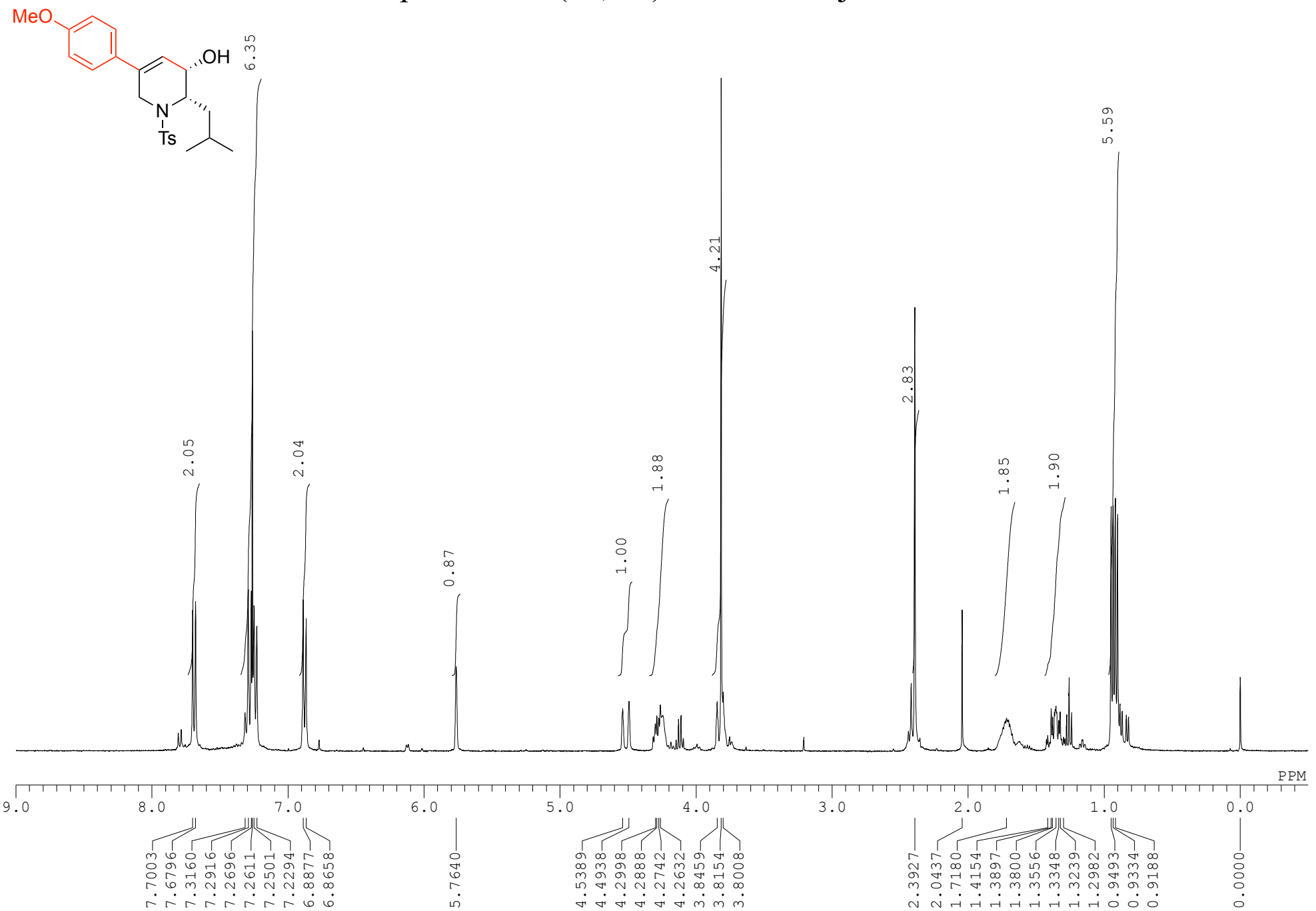


NOESY spectrum of **5bA**

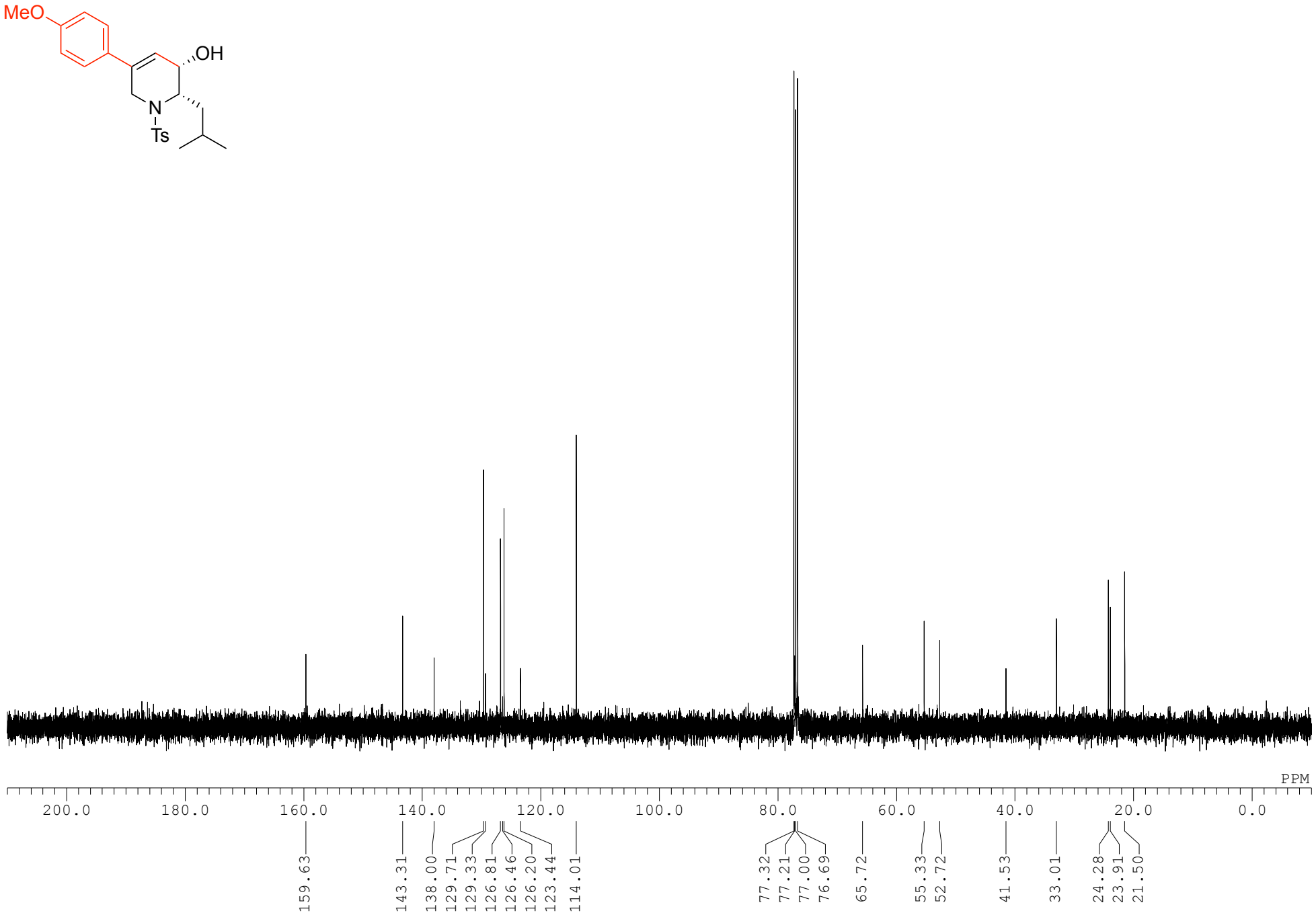




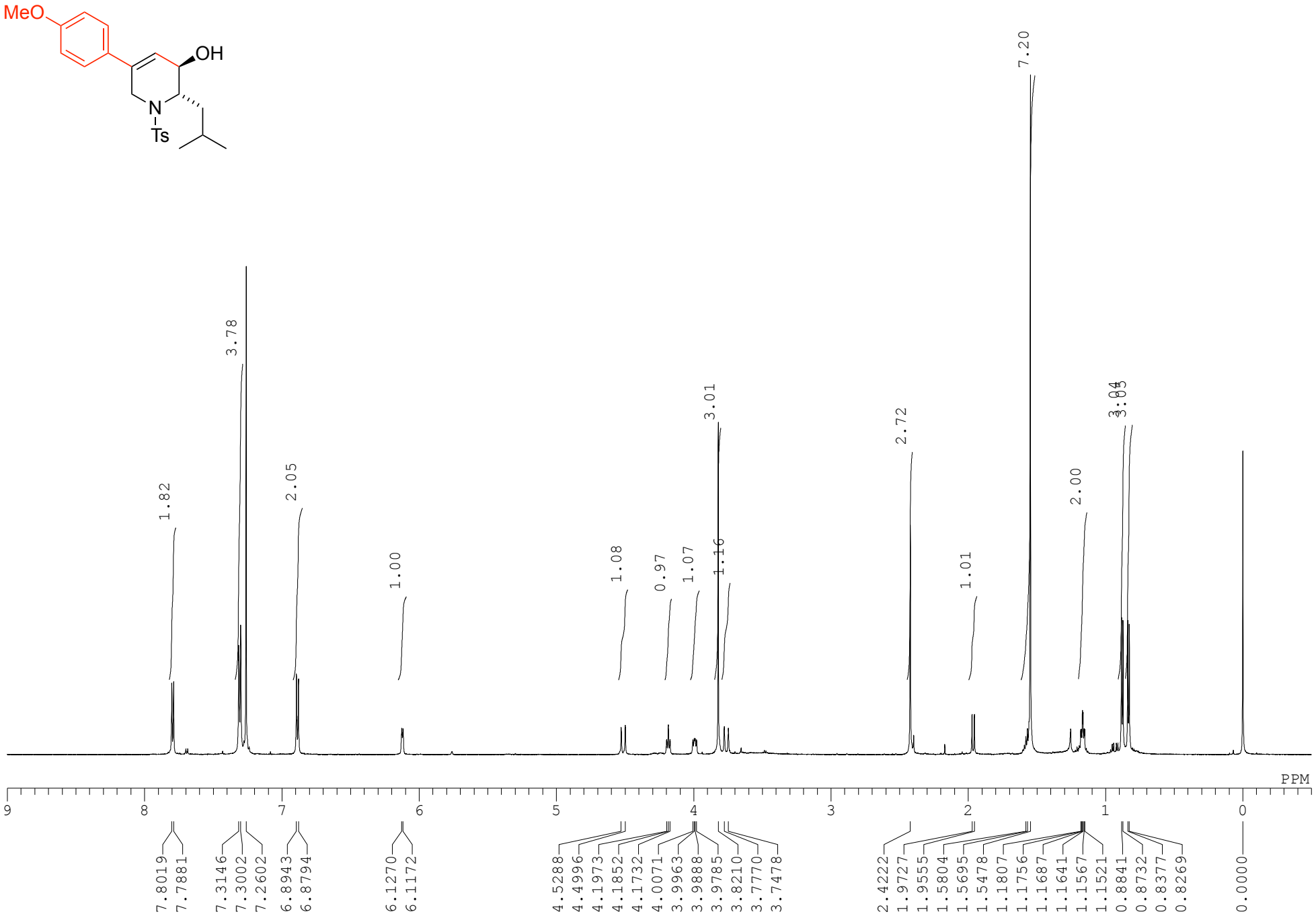
^{1}H NMR spectrum of (2*S*, 3*S*)-**5cA** as a major diastereomer



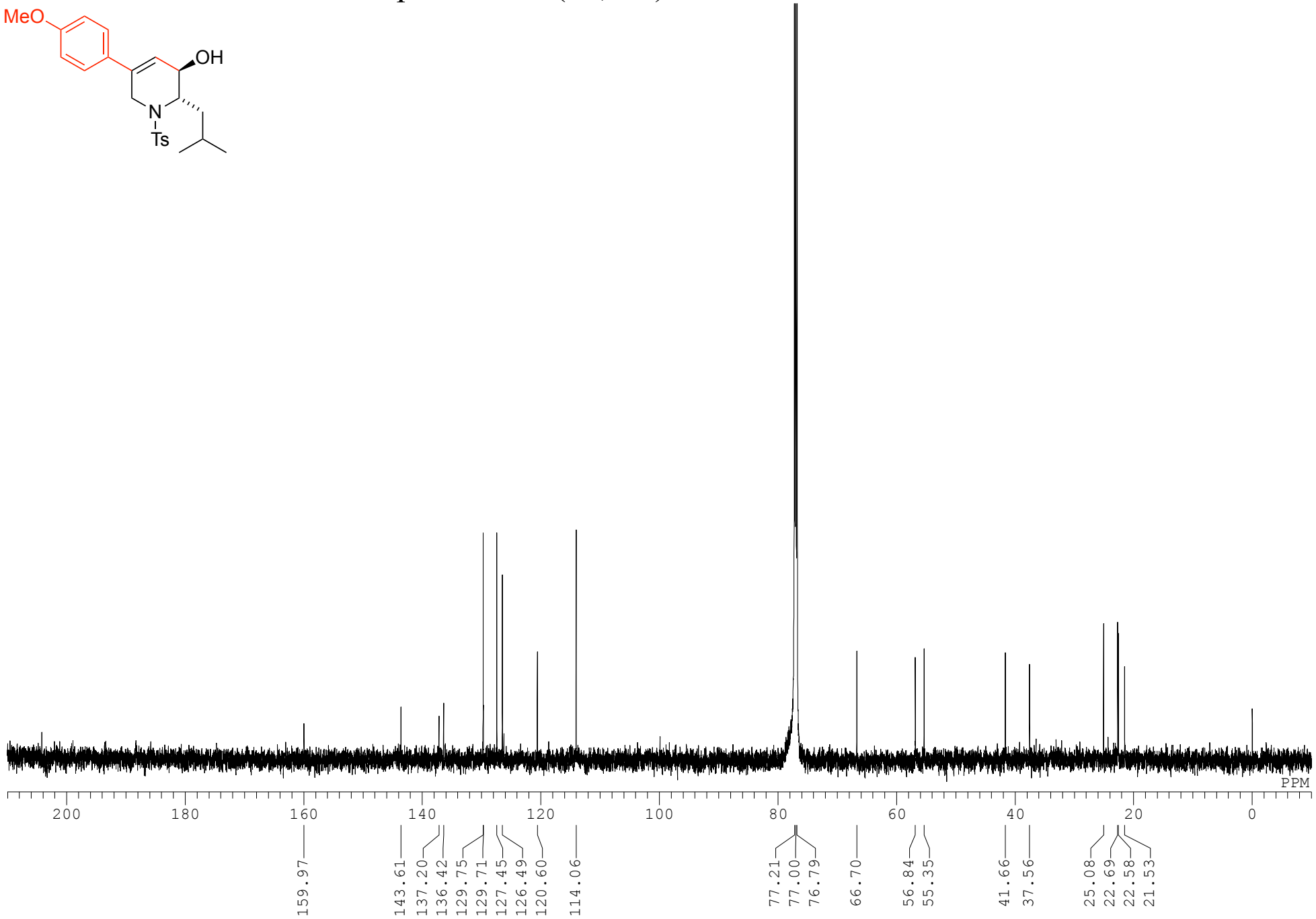
^{13}C NMR spectrum of (2*S*, 3*S*)-**5cA** as a major diastereomer



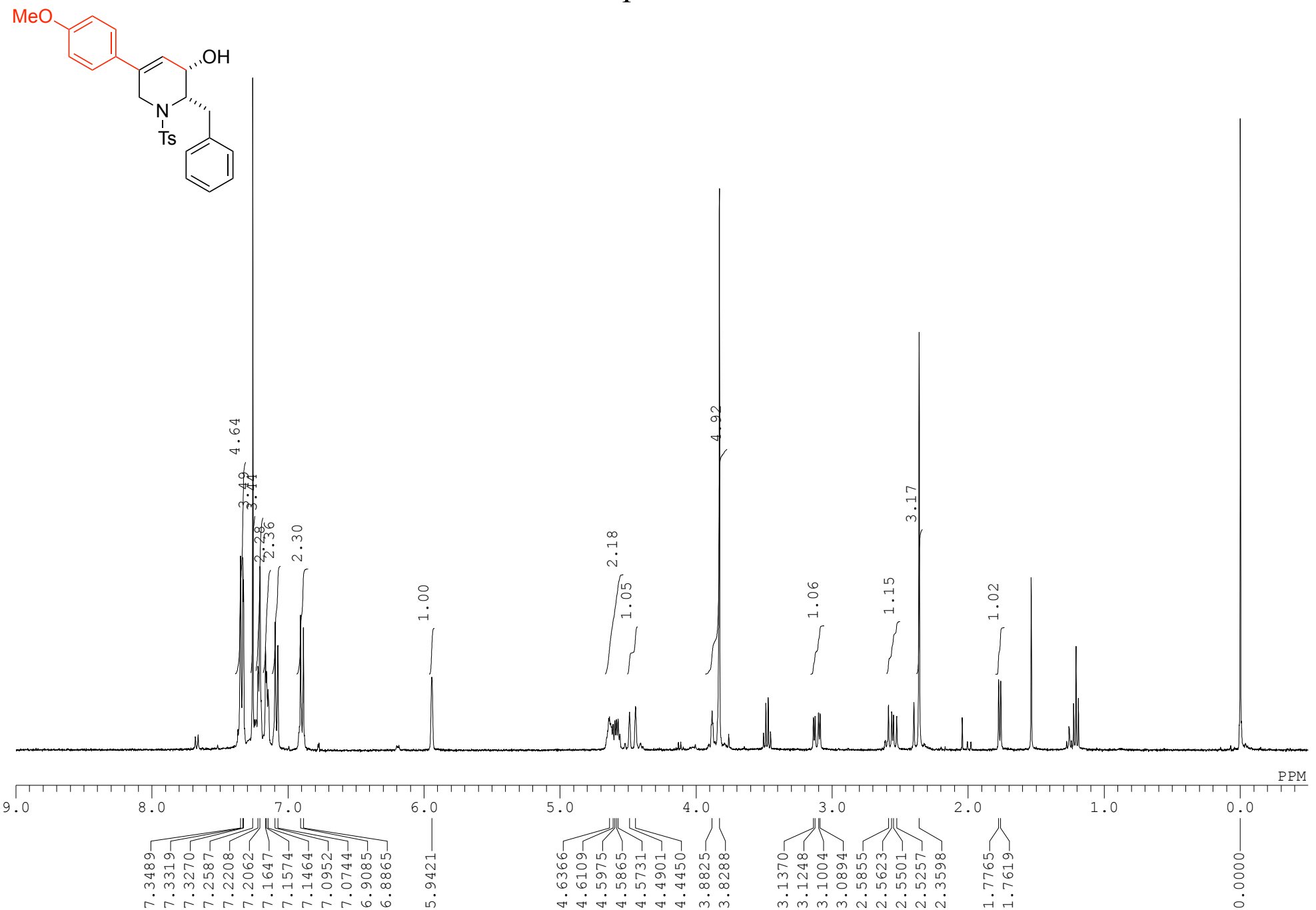
^{1}H NMR spectrum of (2*S*, 3*R*)-**5cA** as a minor diastereomer



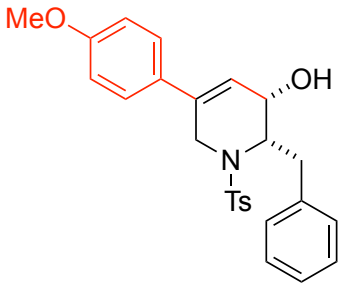
^{13}C NMR spectrum of (2*S*, 3*R*)-**5cA** as a minor diastereomer

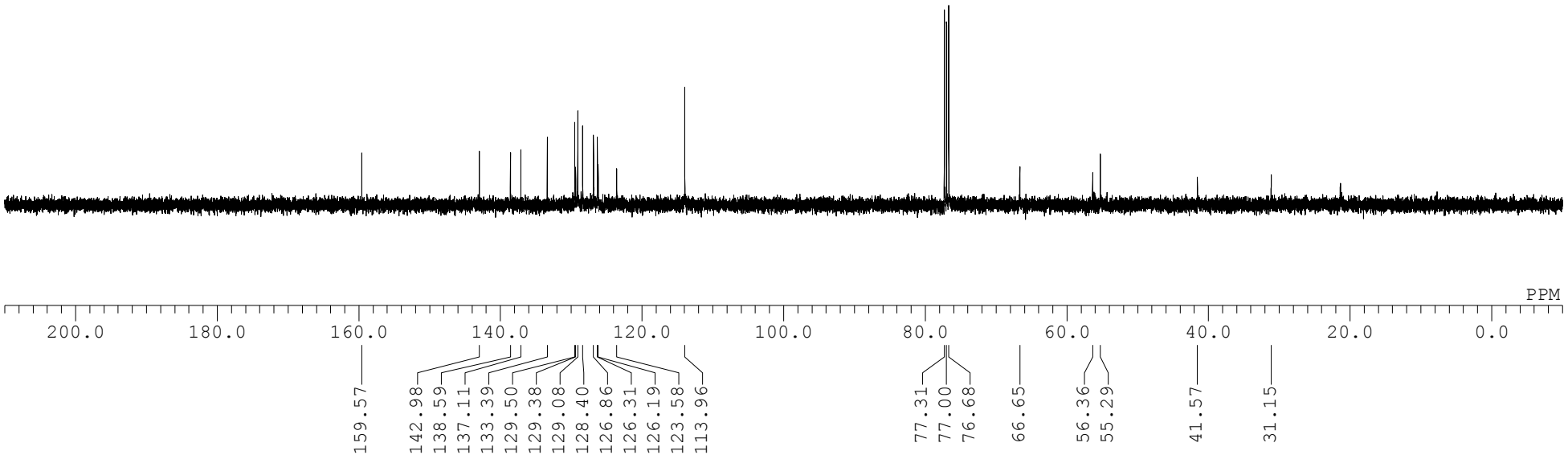


^{1}H NMR spectrum of **5dA**

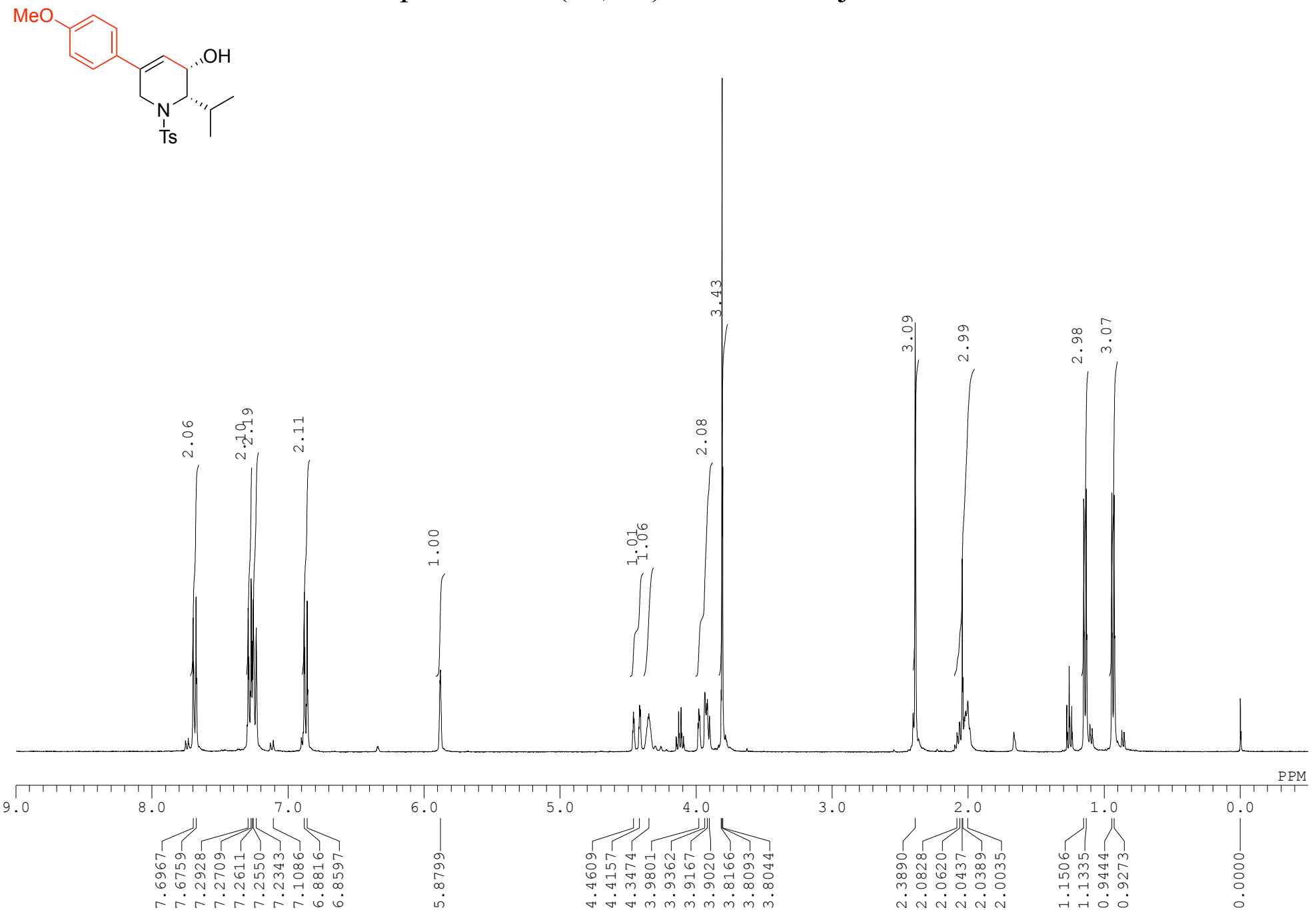


^{13}C NMR spectrum of **5dA**

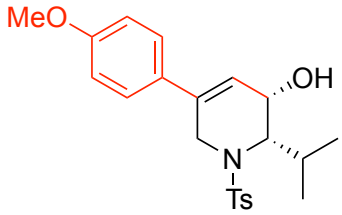


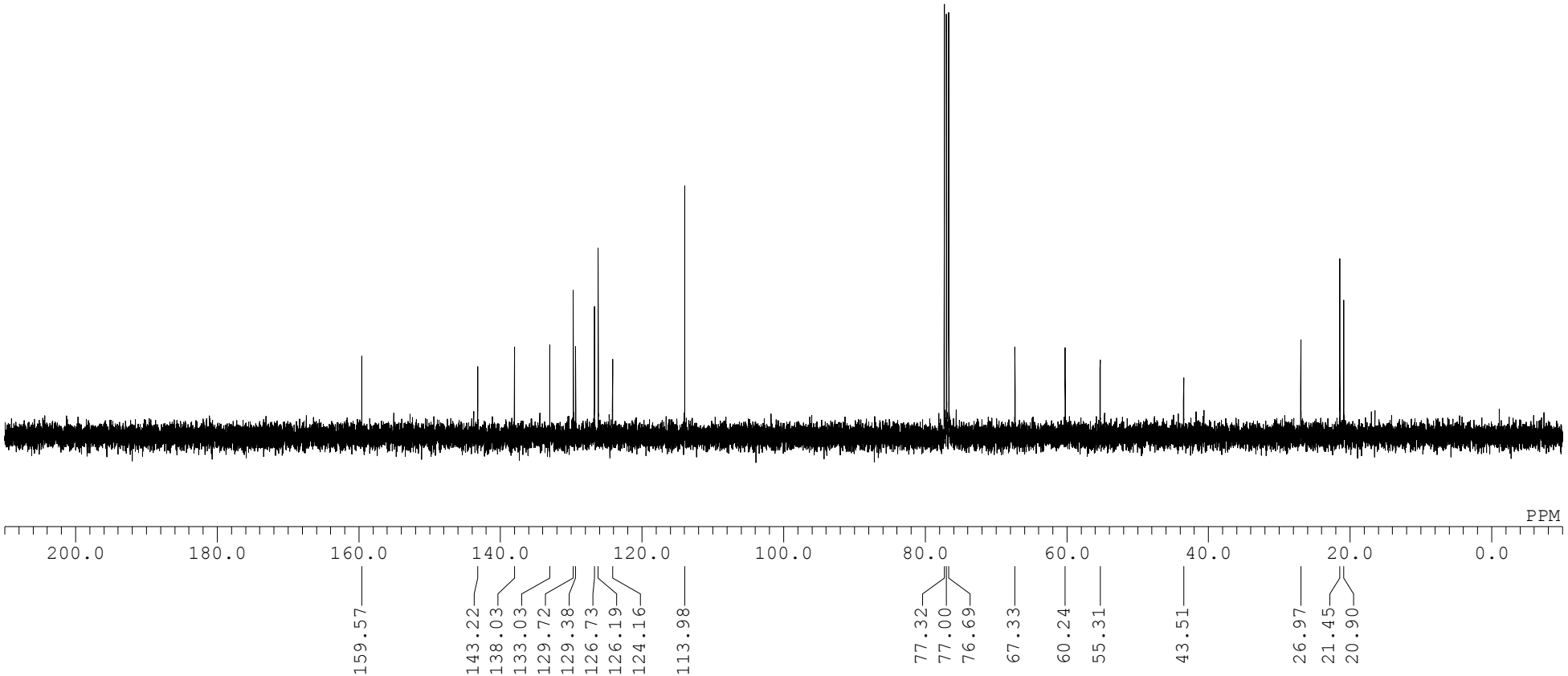


^{1}H NMR spectrum of (2*S*, 3*S*)-**5eA** as a major diastereomer

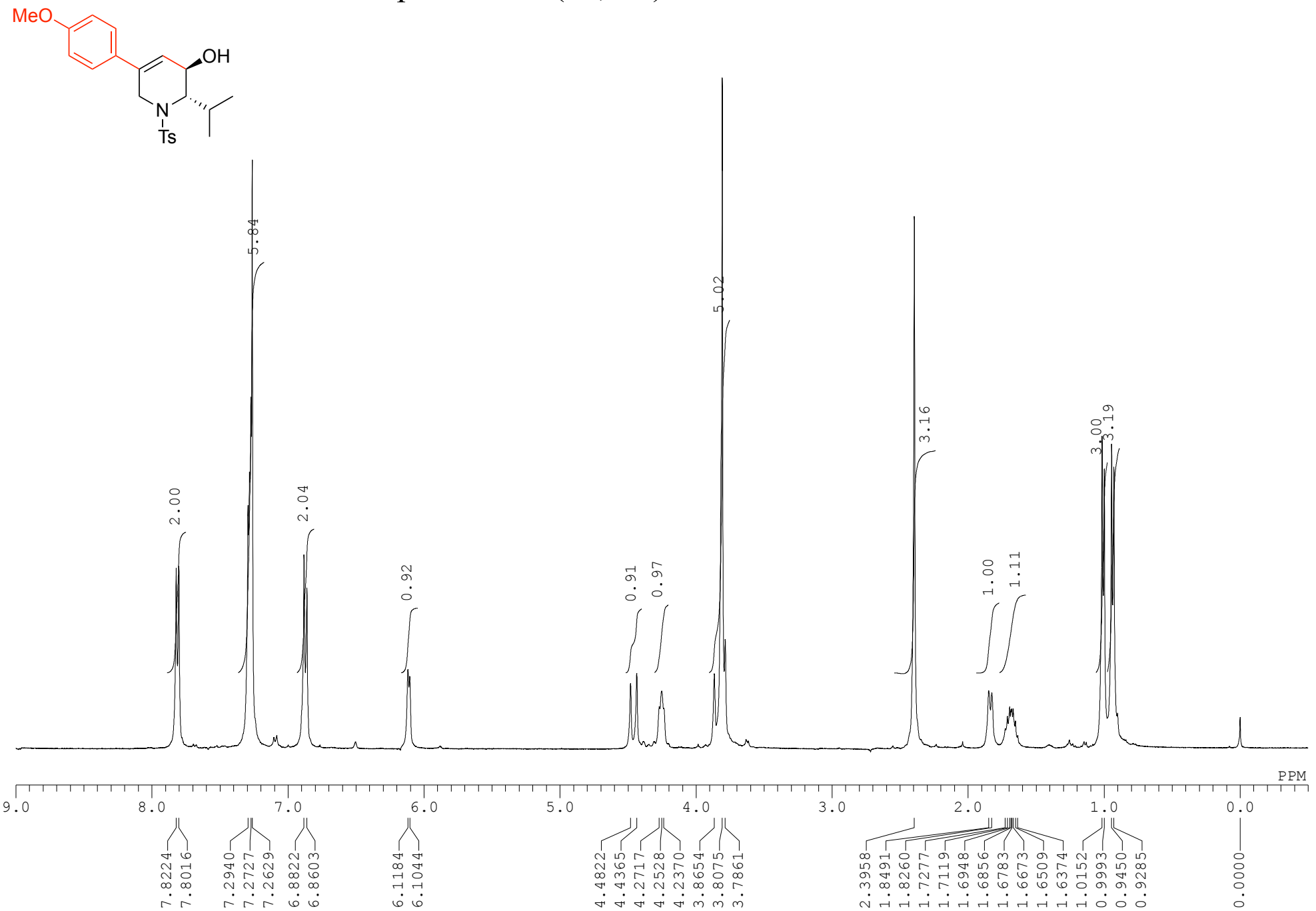


^{13}C NMR spectrum of (2*S*, 3*S*)-**5eA** as a major diastereomer

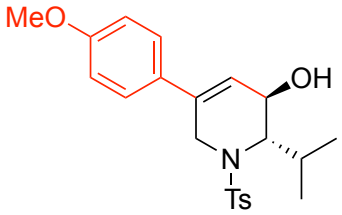


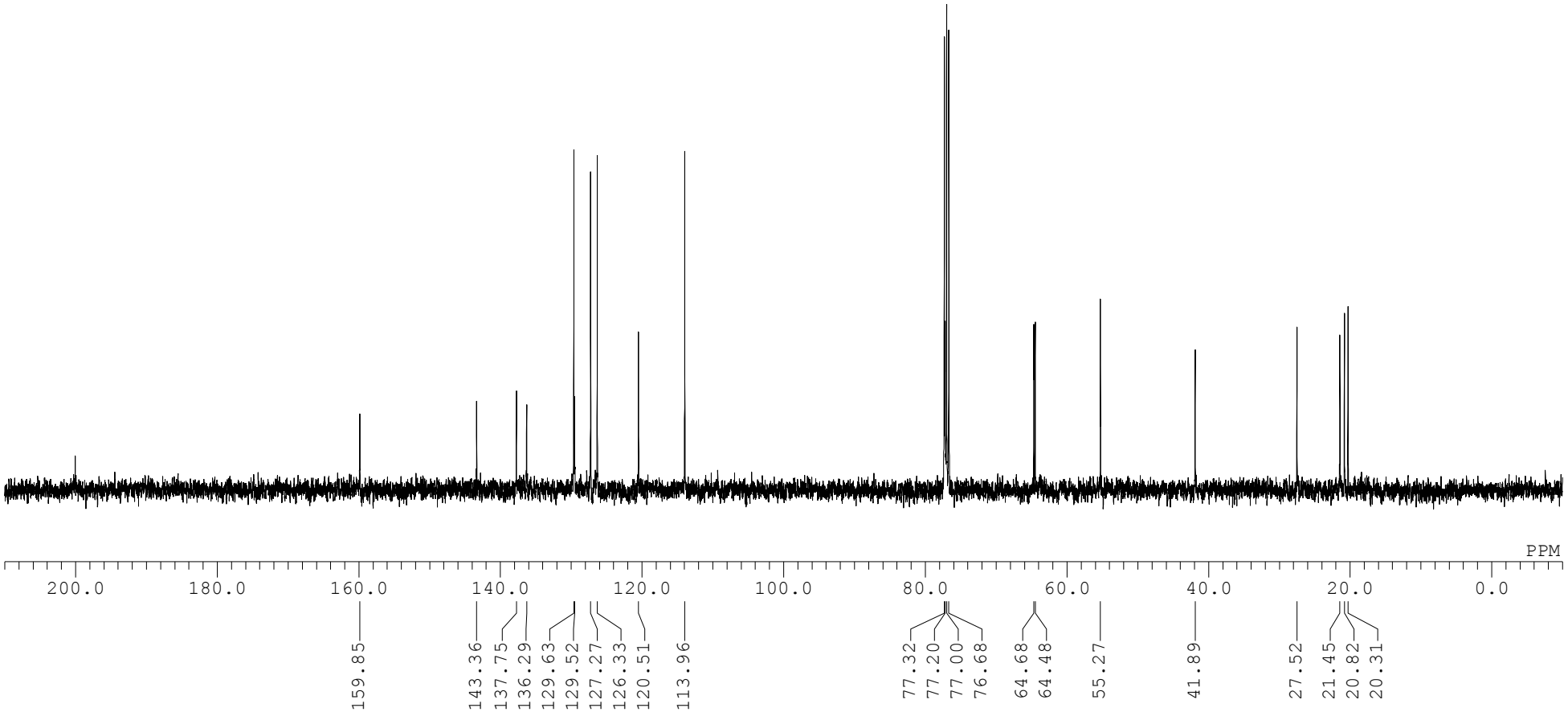


^{1}H NMR spectrum of (2*S*, 3*R*)-**5eA** as a minor diastereomer

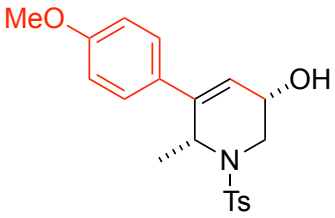


^{13}C NMR spectrum of (2*S*, 3*R*)-**5eA** as a minor diastereomer

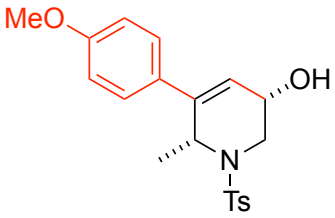




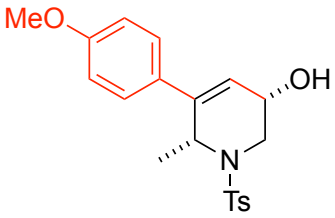
^{1}H NMR spectrum of (3*R**,6*S**)-**5fA** as a major diastereomer

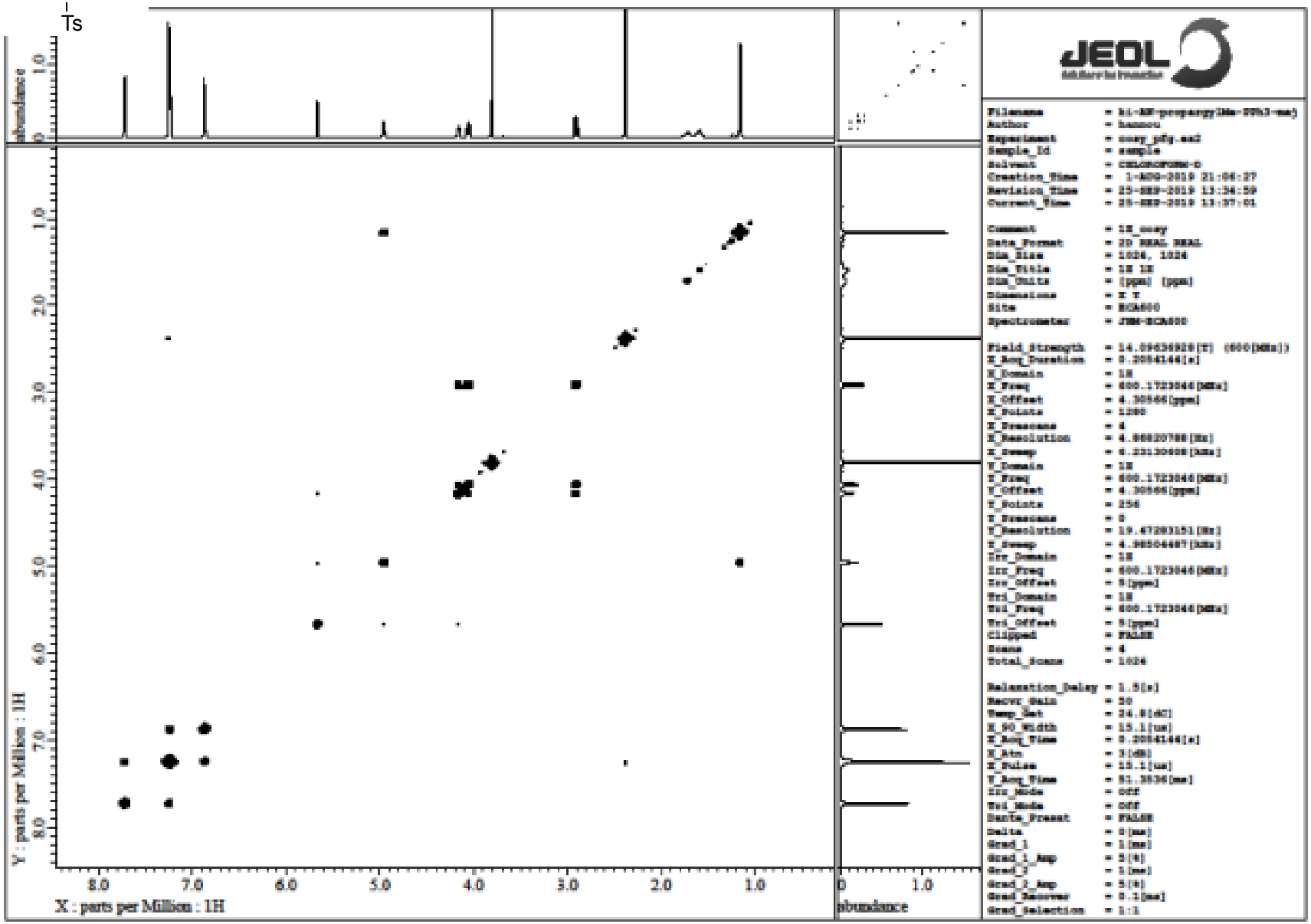


^{13}C NMR spectrum of (3*R**,6*S**)-**5fA** as a major diastereomer

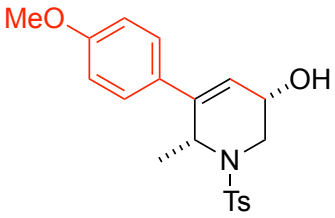


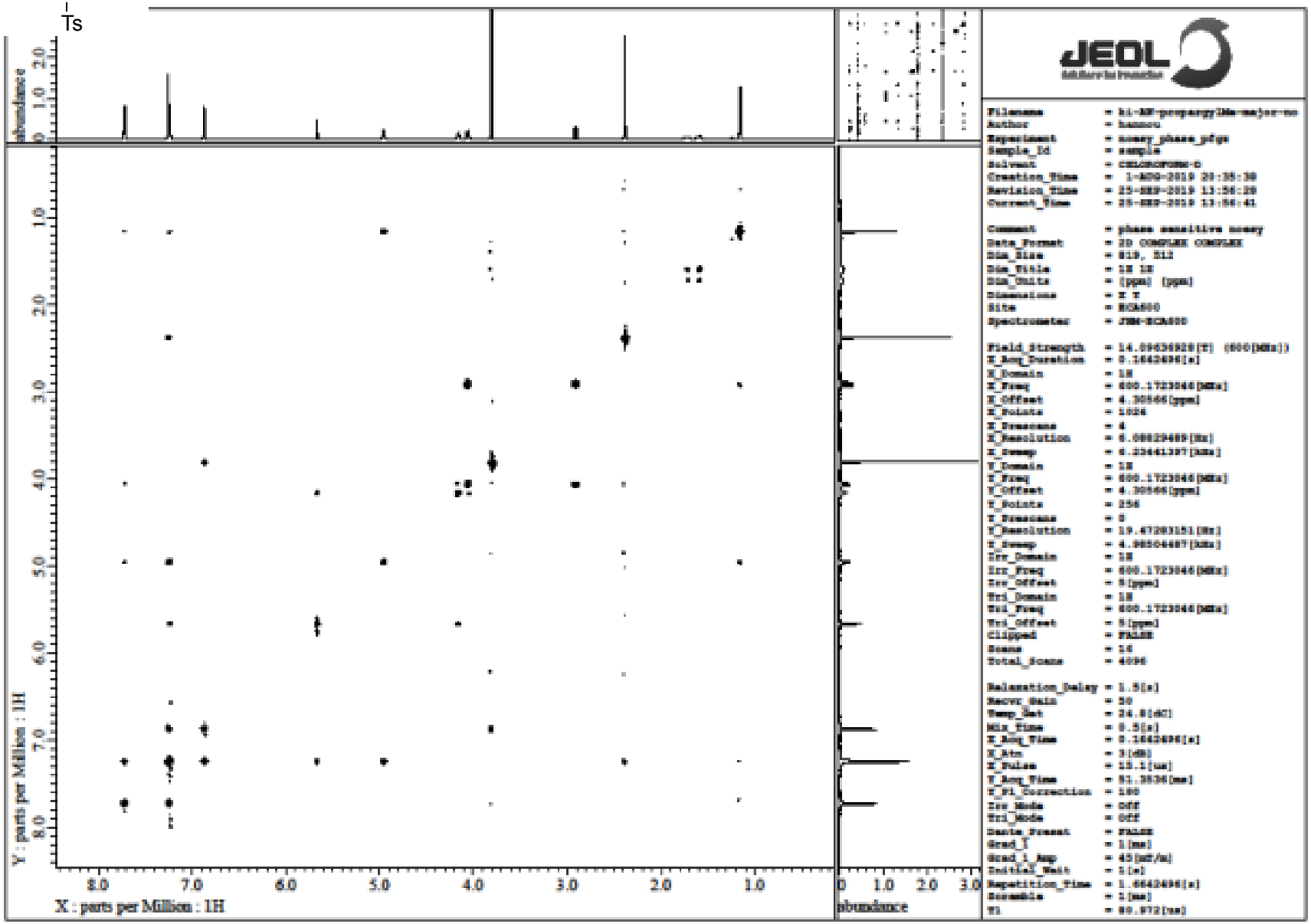
COSY spectrum of (3*R**,6*S**)-**5fA** as a major diastereomer



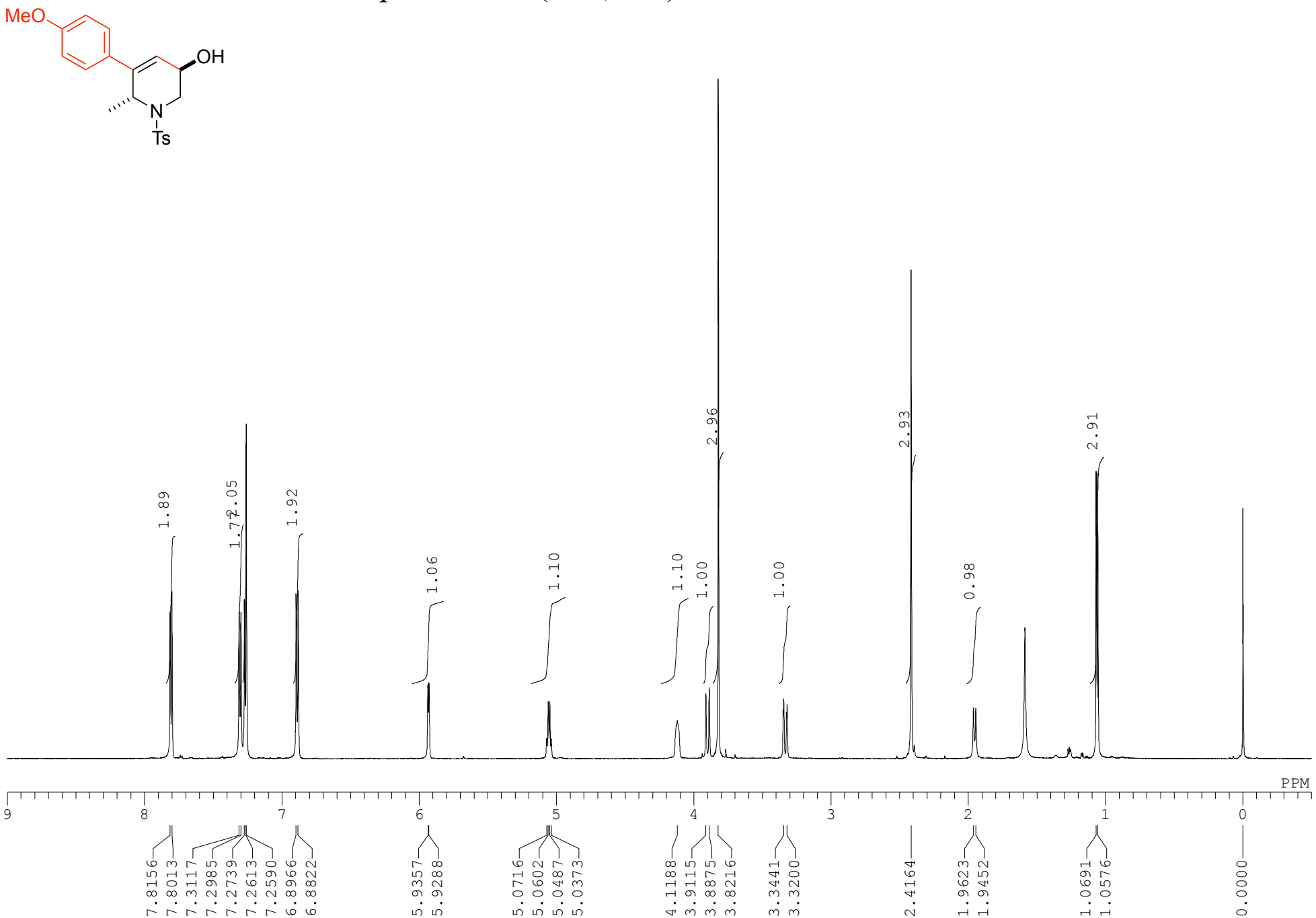


NOESY spectrum of (3*R**,6*S**)-**5fA** as a major diastereomer

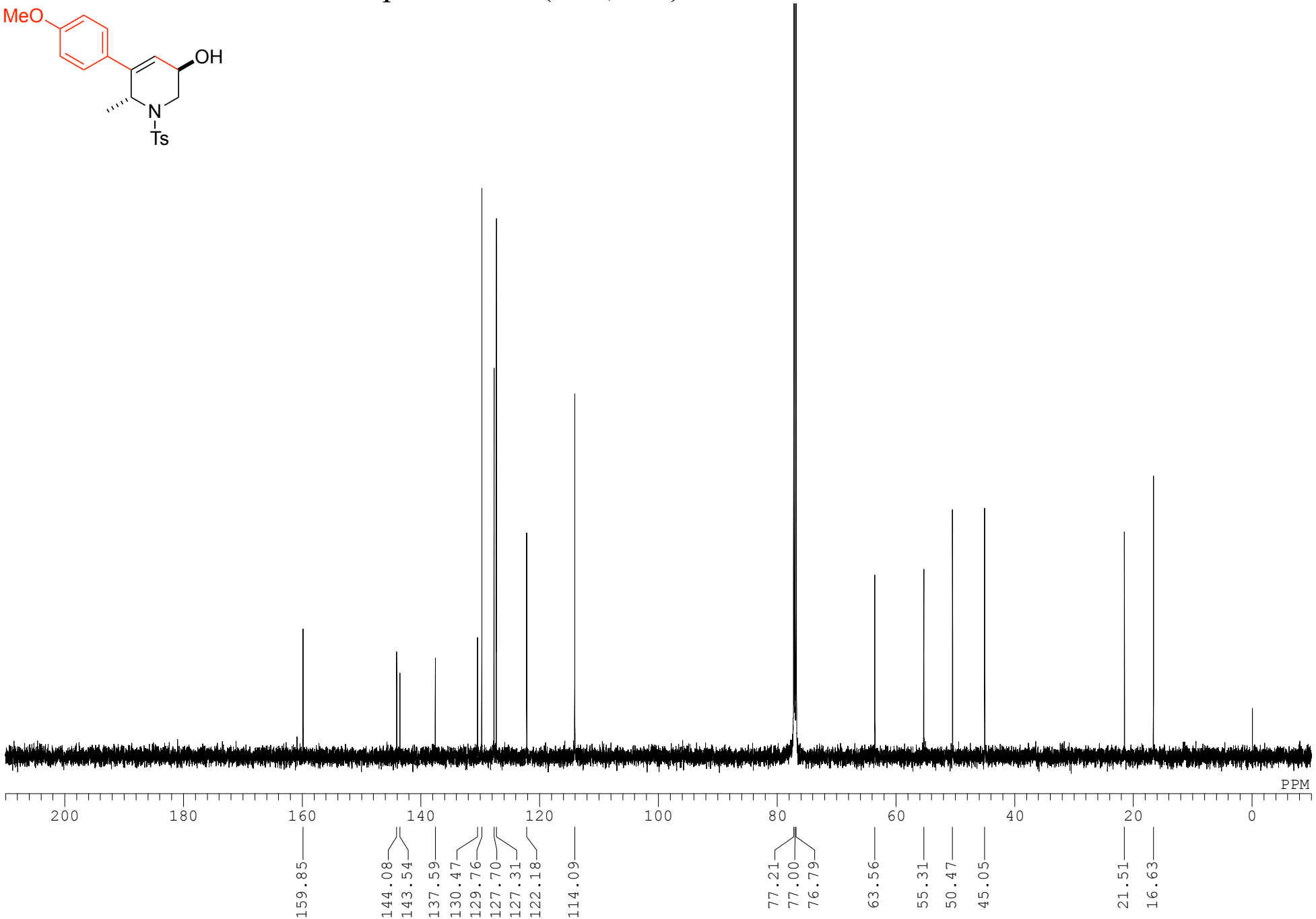




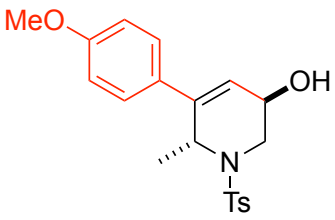
^{1}H NMR spectrum of (3*R**,6*R**)-**5fA** as a minor diastereomer

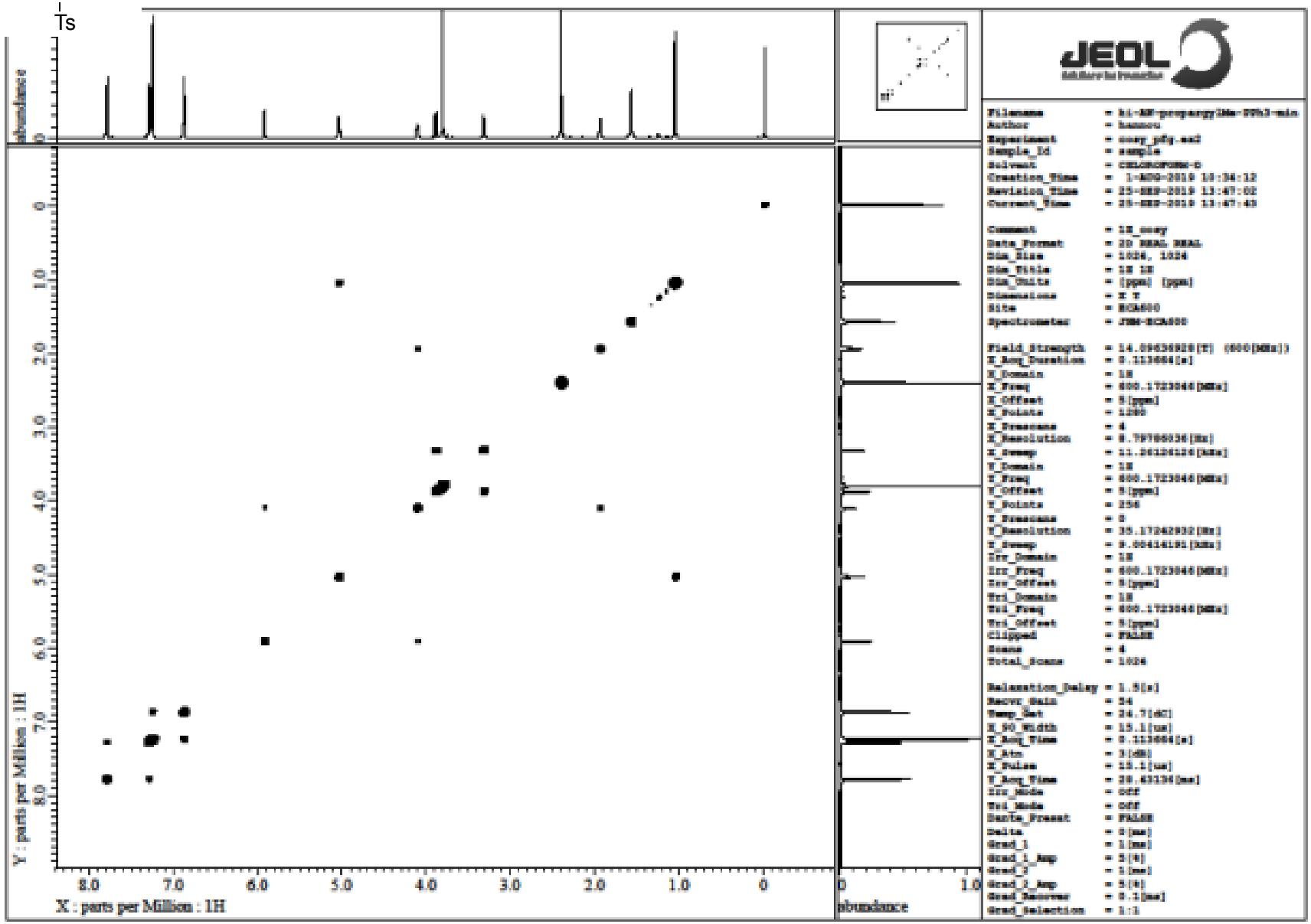


^{13}C NMR spectrum of (3*R**,6*R**)-**5fA** as a minor diastereomer

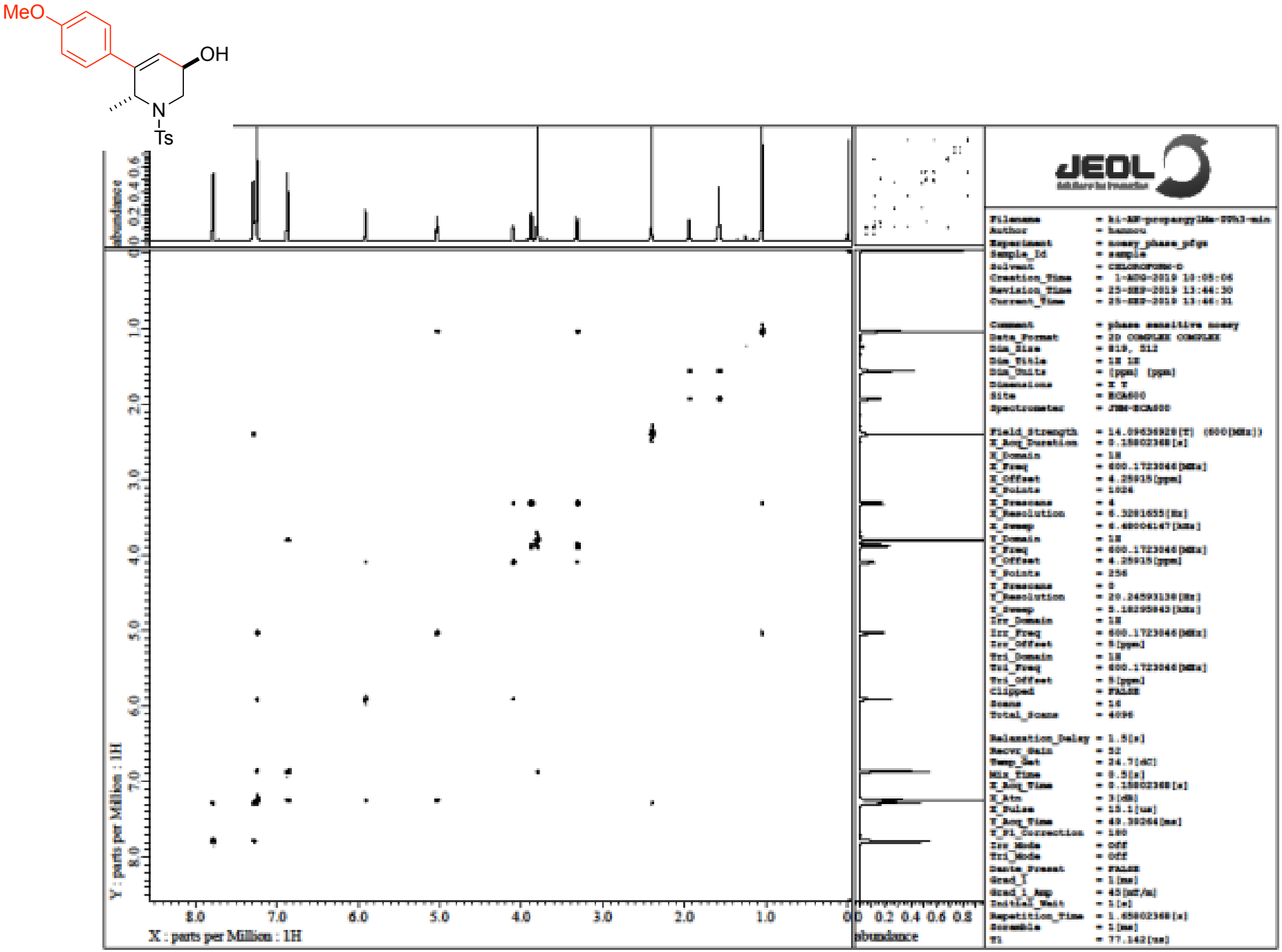


COSY spectrum of (3*R**,6*R**)-**5fA** as a minor diastereomer

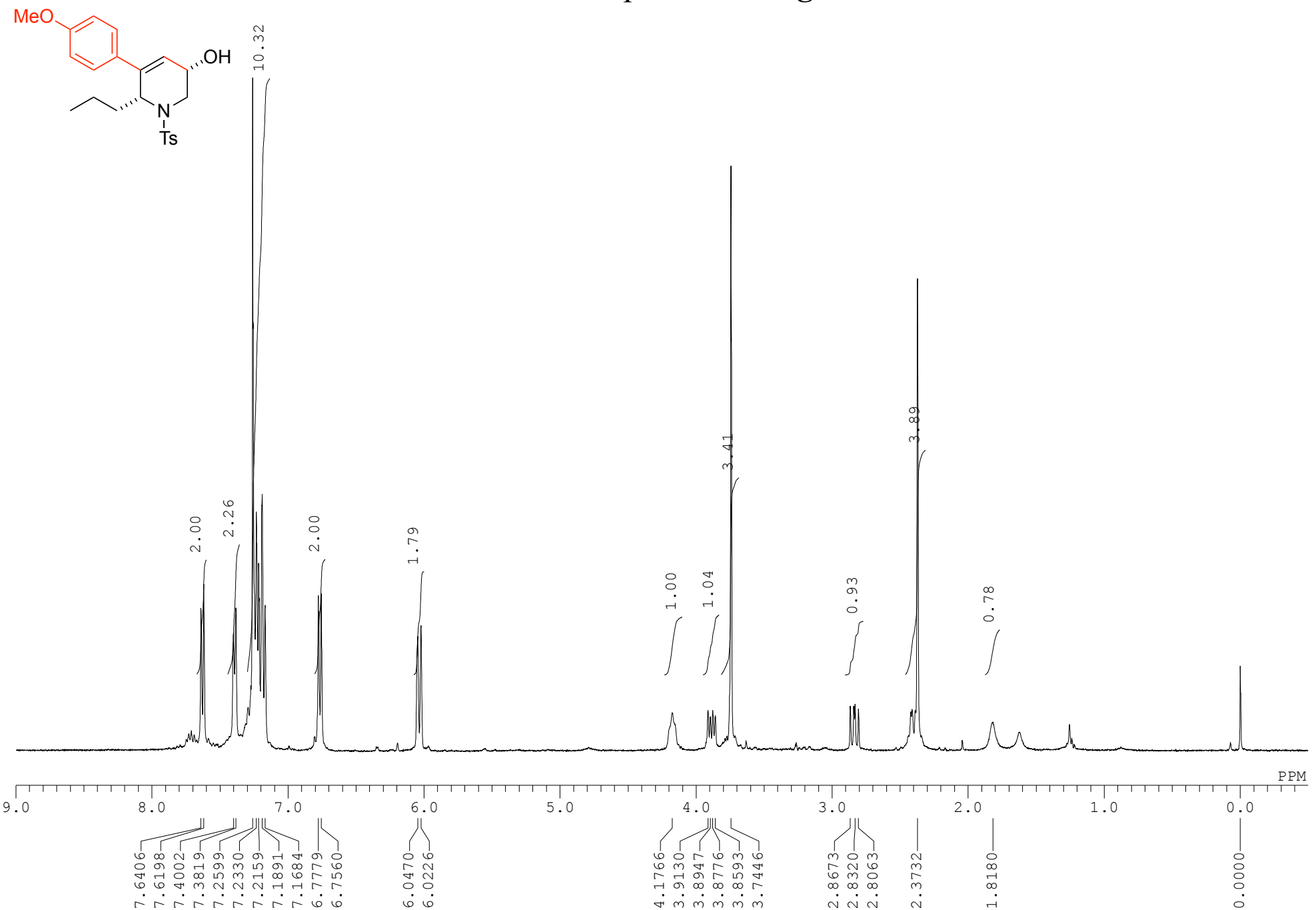




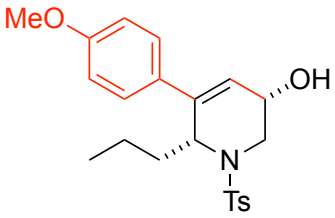
NOESY spectrum of (3*R**,6*R**)-**5fA** as a minor diastereomer

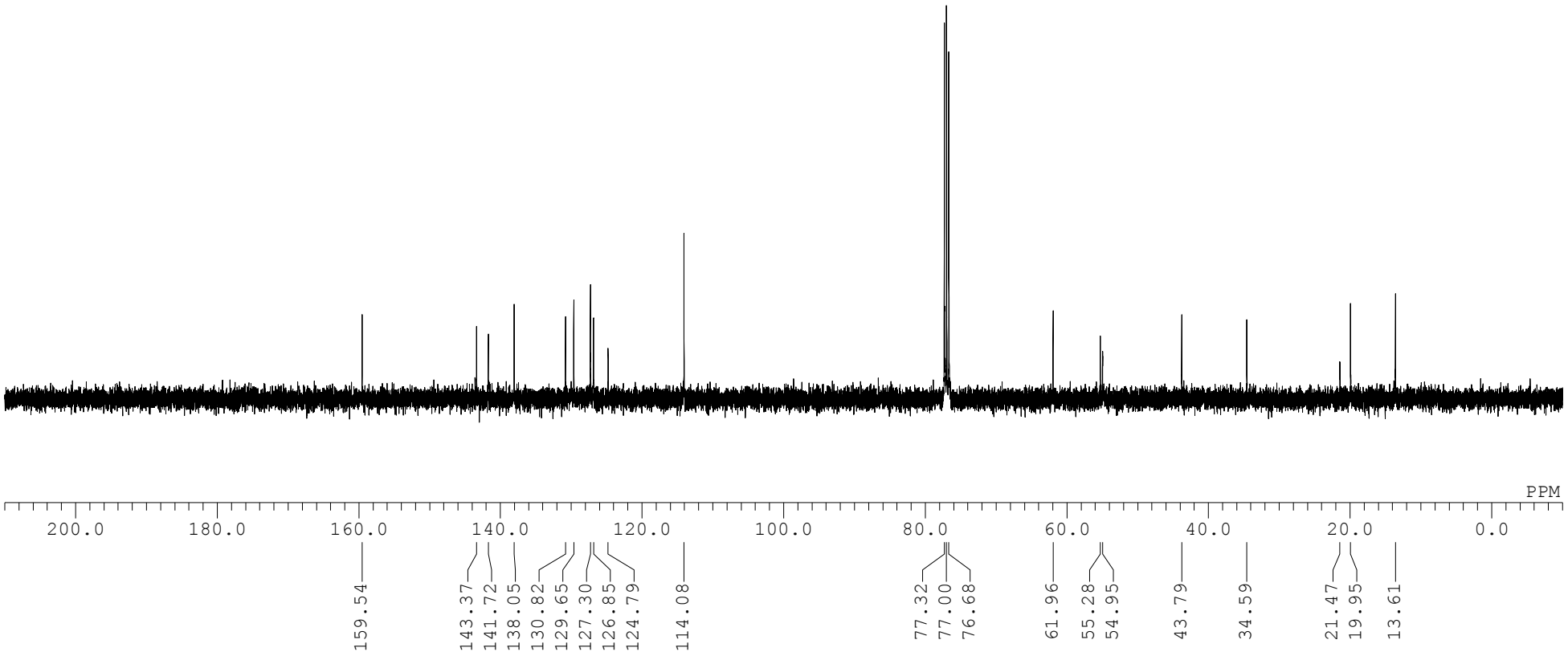


^{1}H NMR spectrum of **5gA**

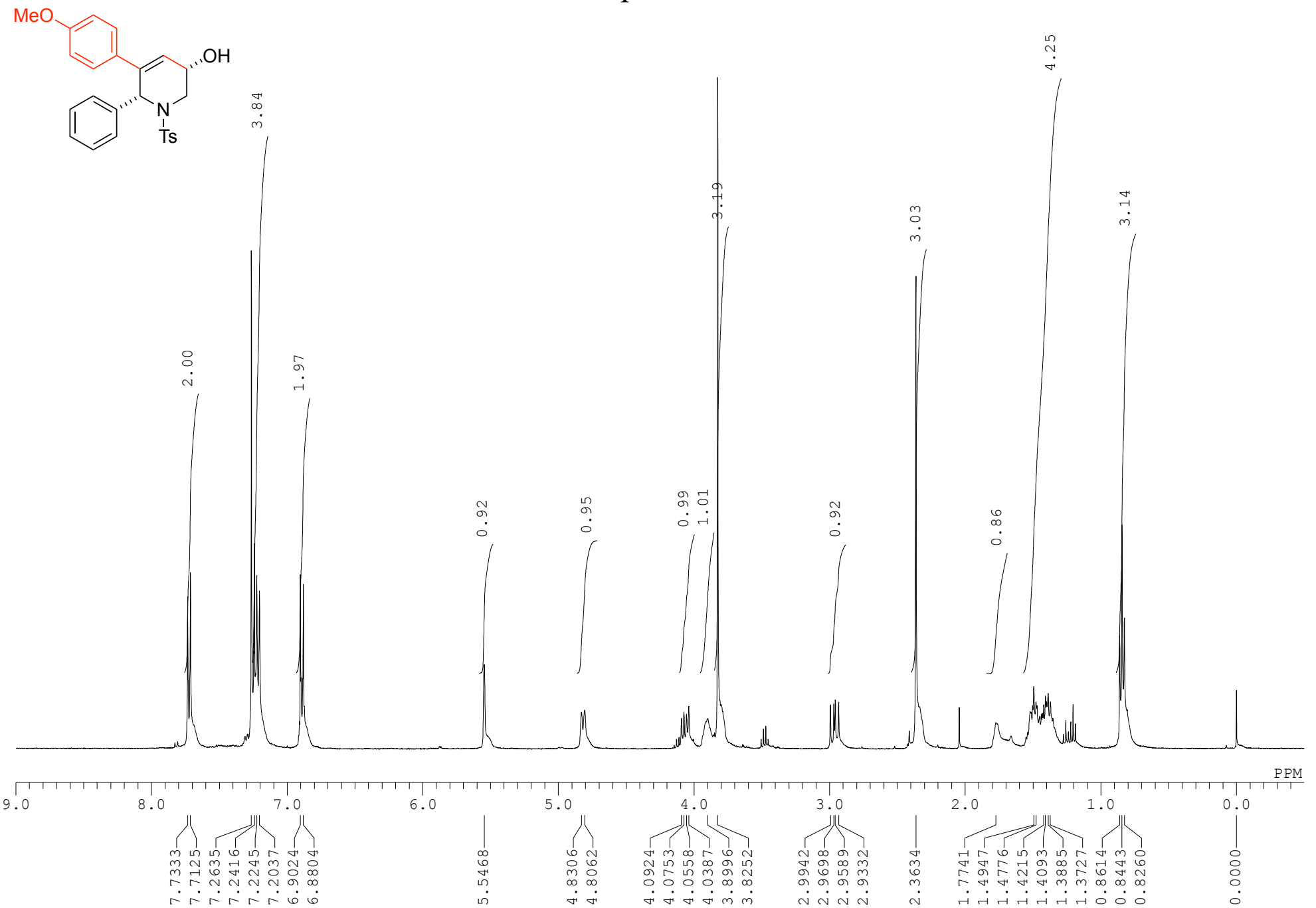


^{13}C NMR spectrum of **5gA**

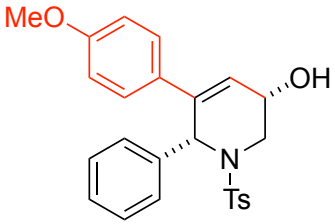


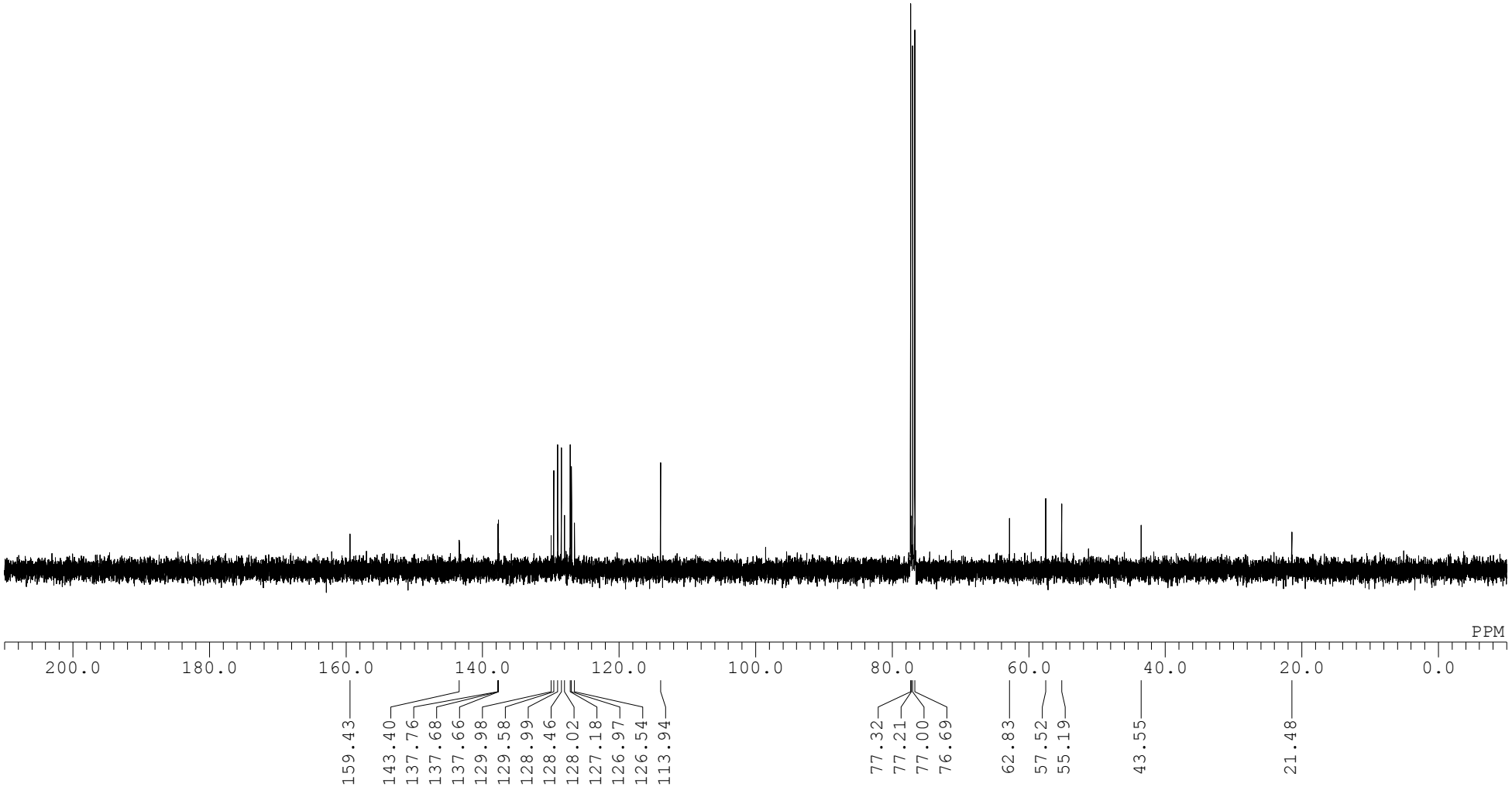


^{1}H NMR spectrum of **5hA**

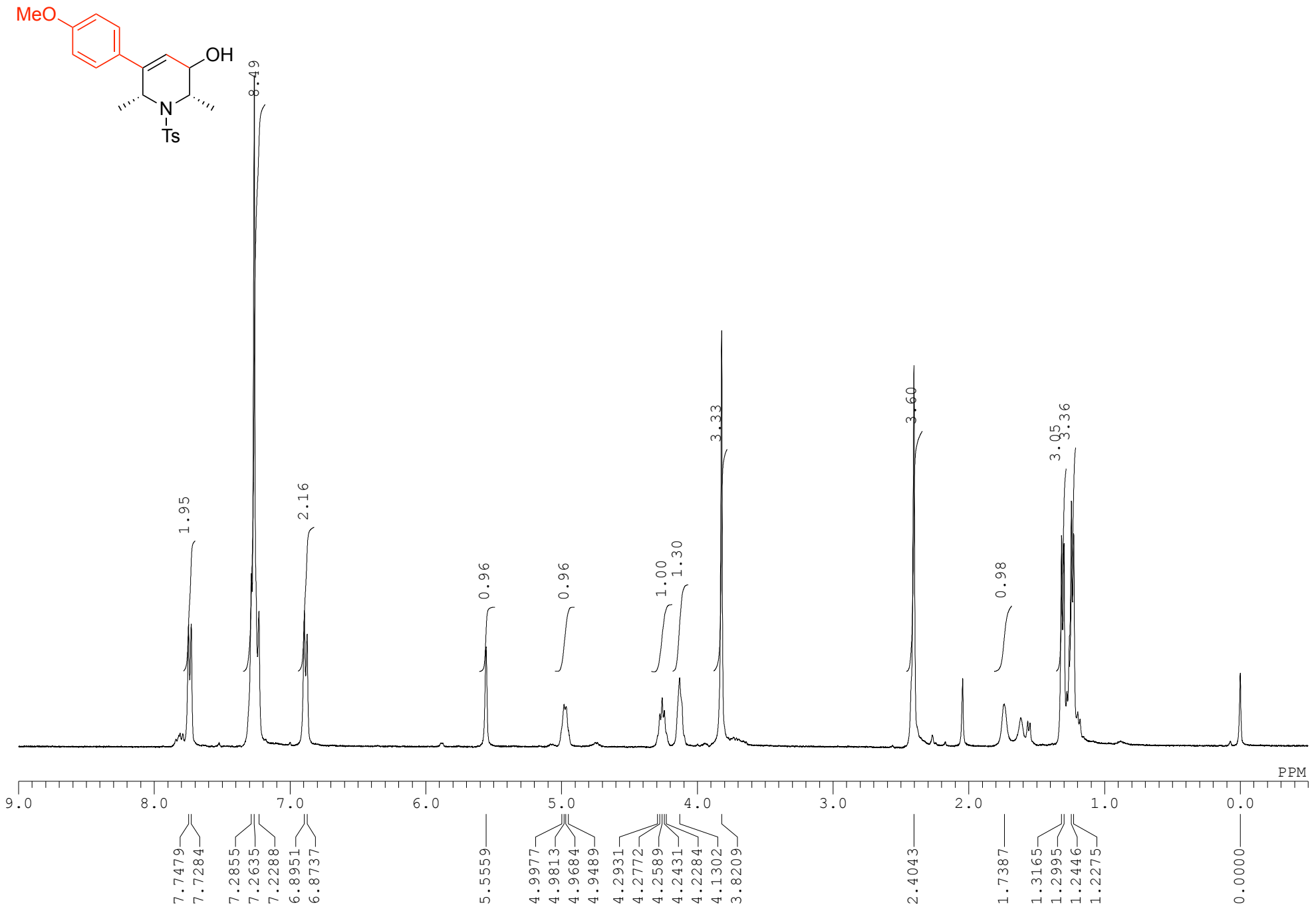


^{13}C NMR spectrum of **5hA**

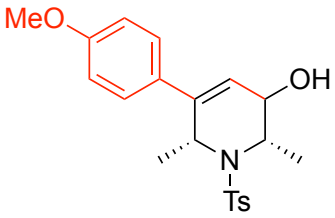


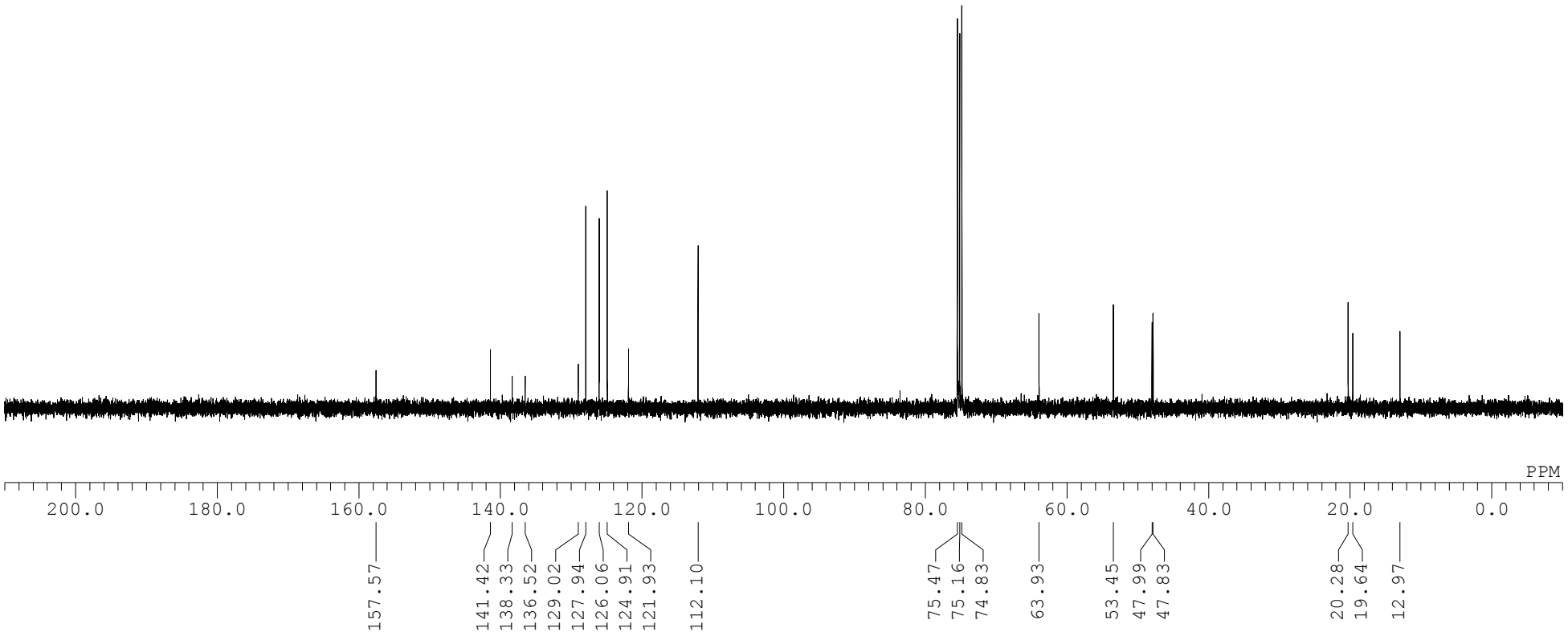


^{1}H NMR spectrum of **5iA**

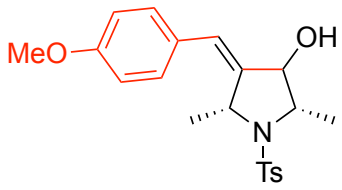


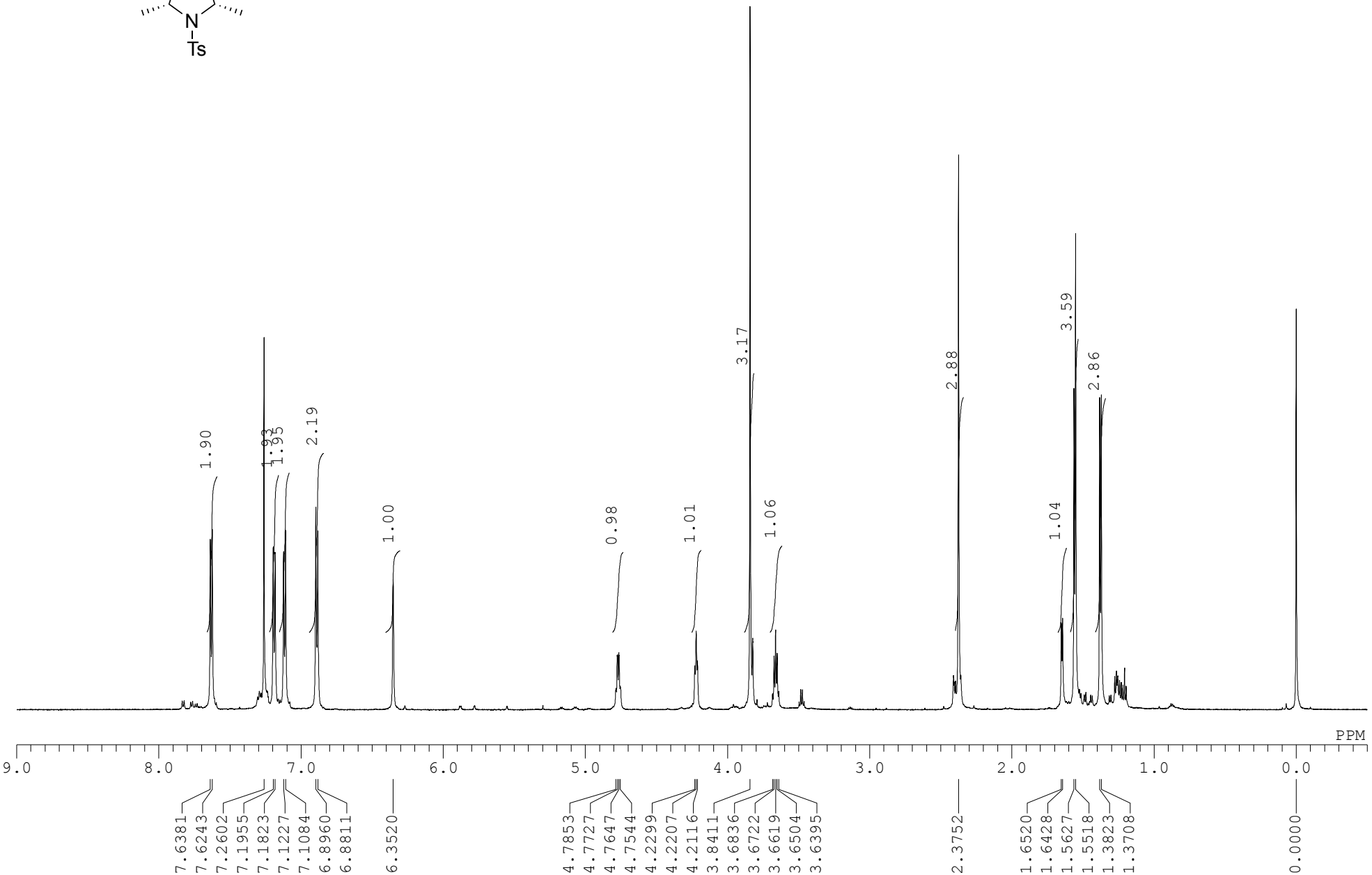
^{13}C NMR spectrum of **5iA**



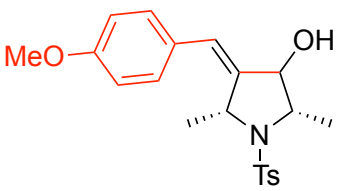


^{1}H NMR spectrum of **8iA**

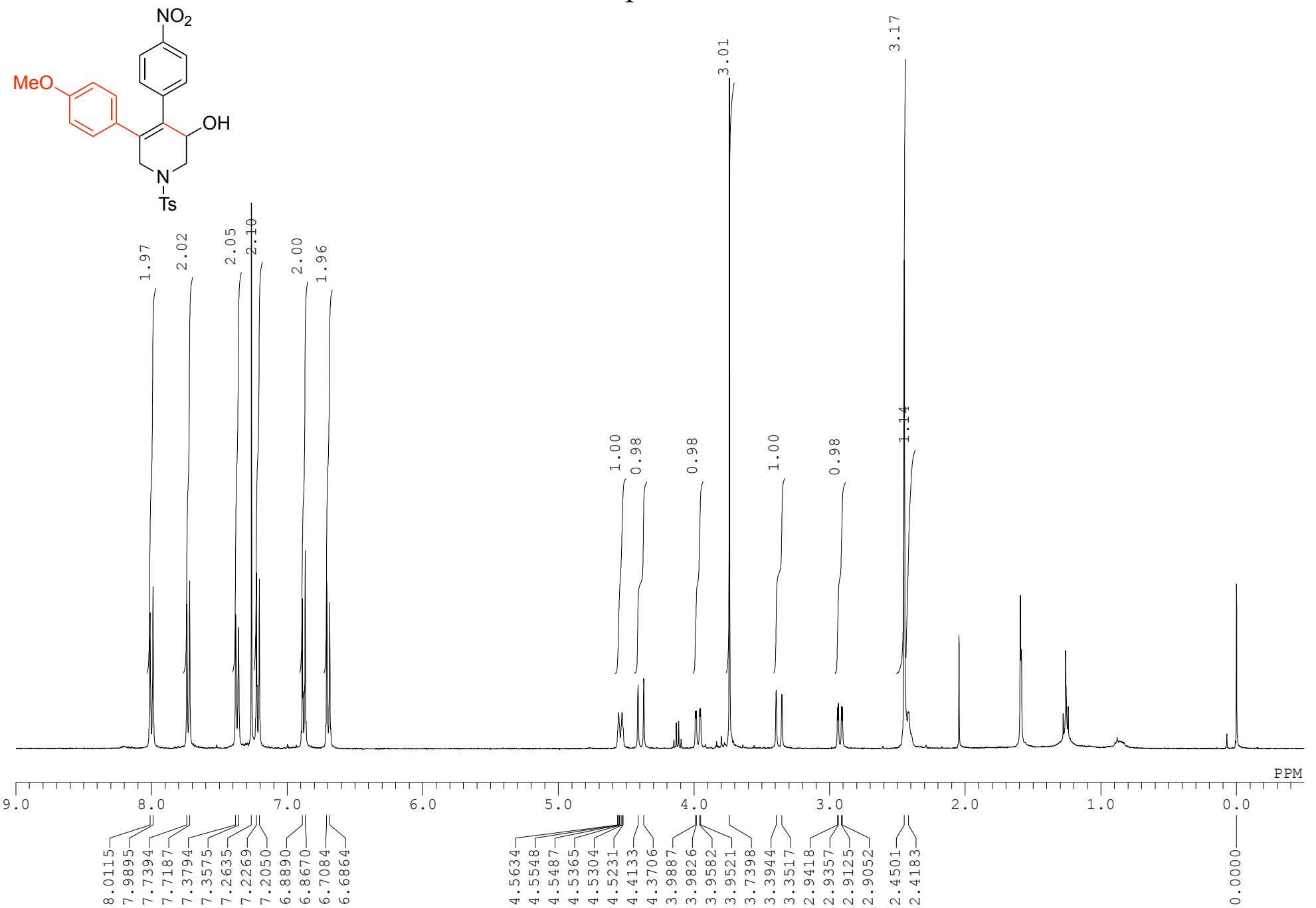




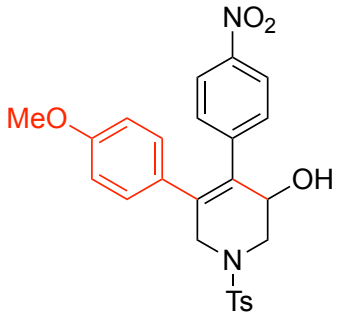
^{13}C NMR spectrum of **8iA**

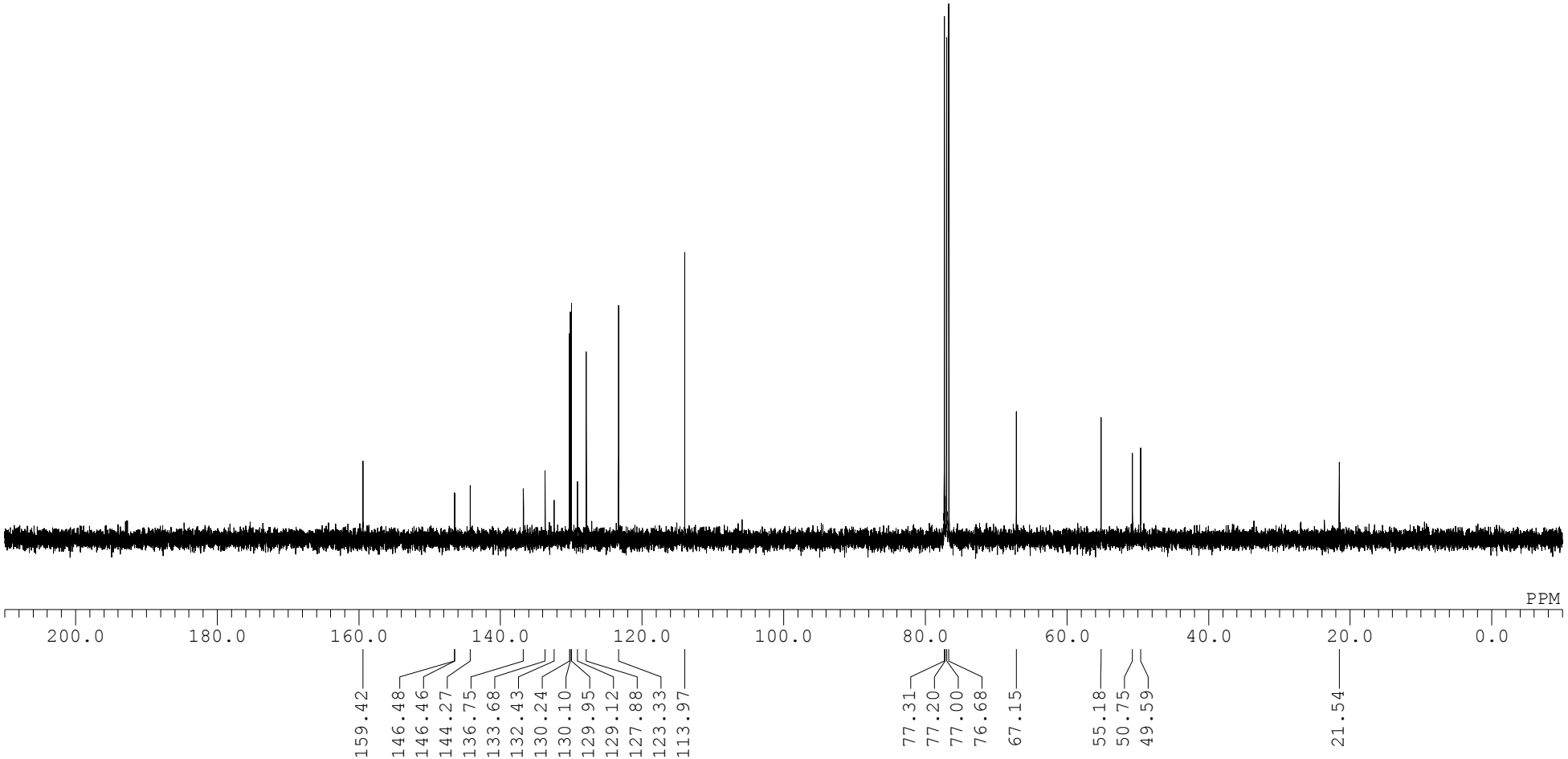


^{1}H NMR spectrum of **5lA**

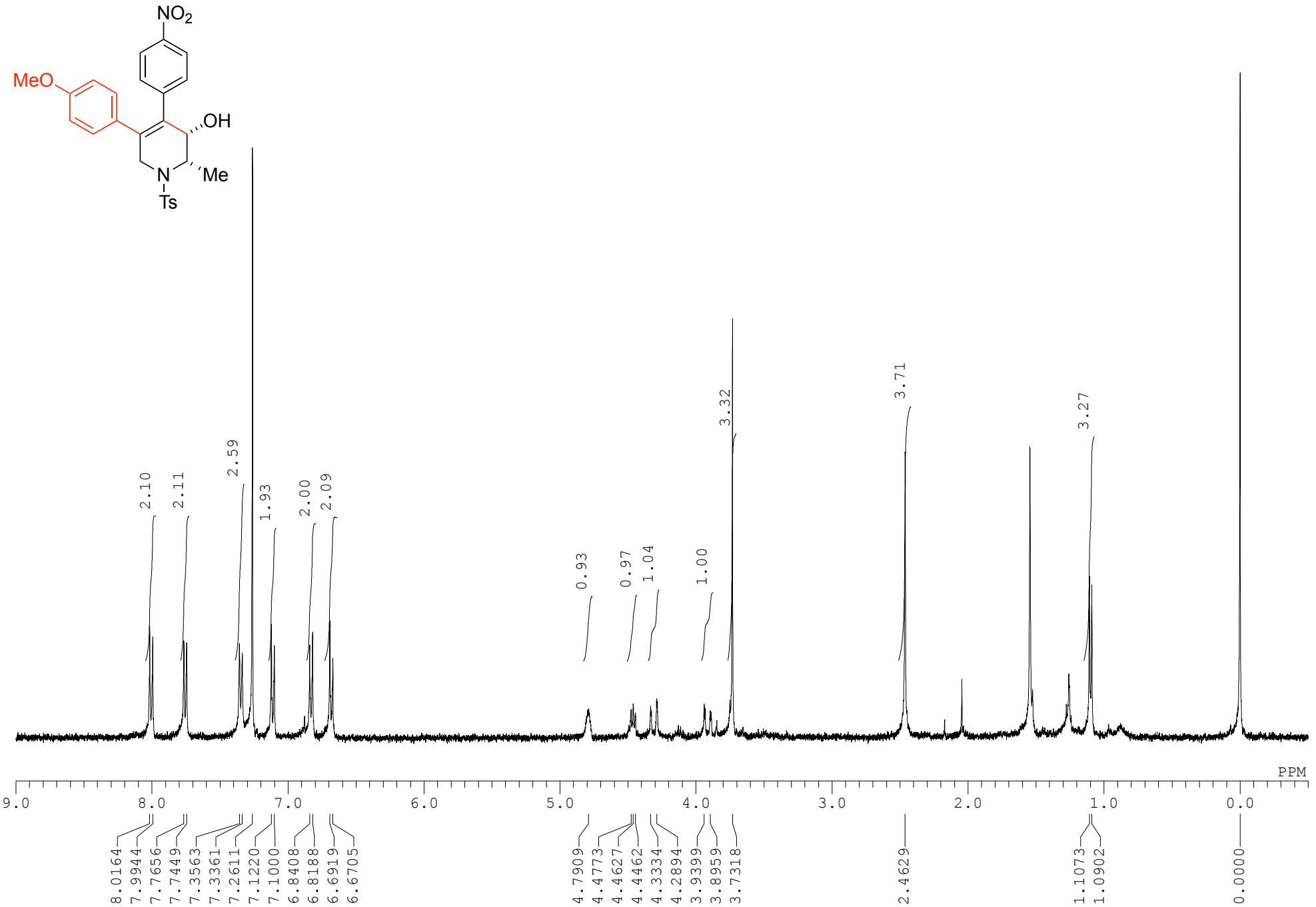


^{13}C NMR spectrum of **5lA**

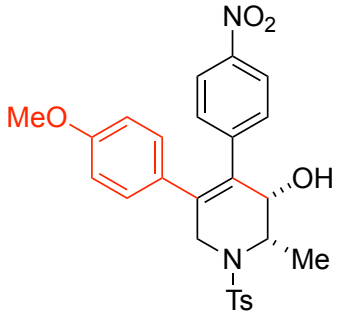


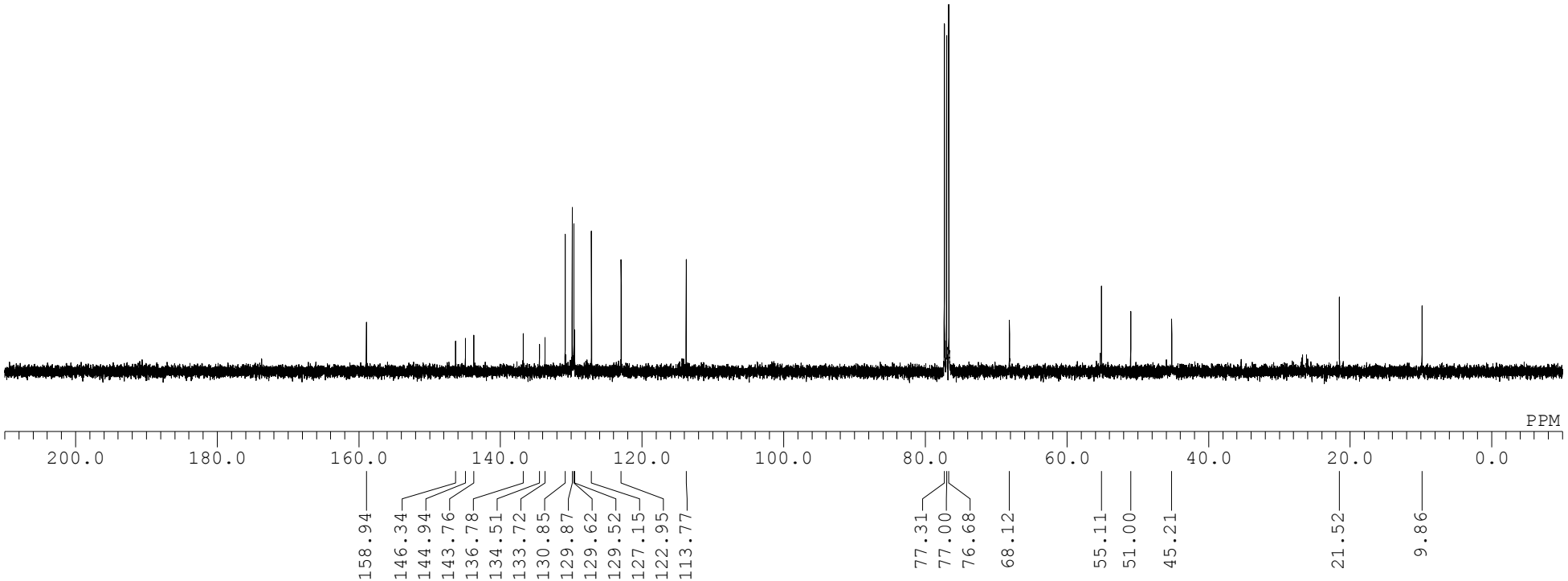


^{1}H NMR spectrum of **5oA**

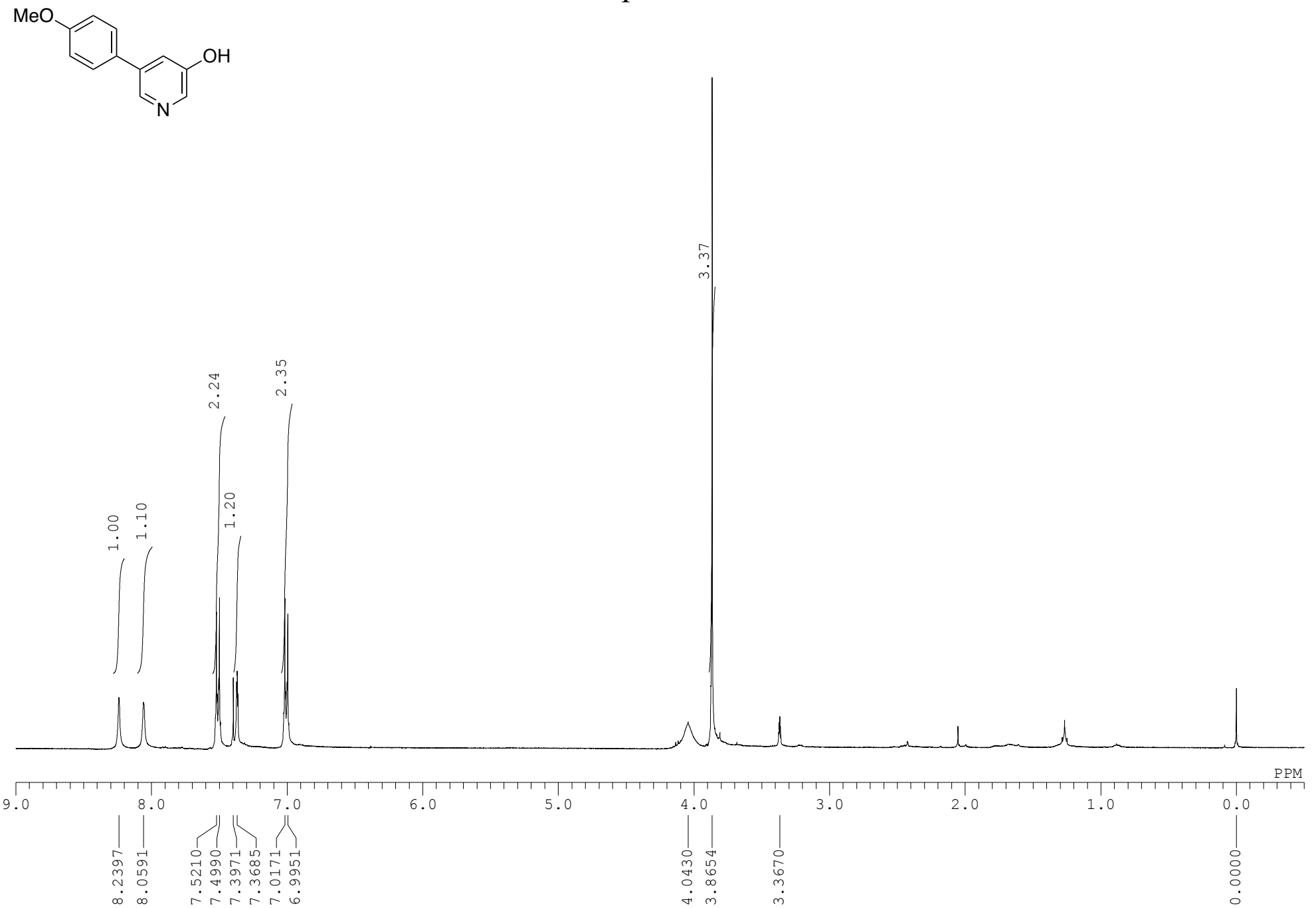


^{13}C NMR spectrum of **5oA**

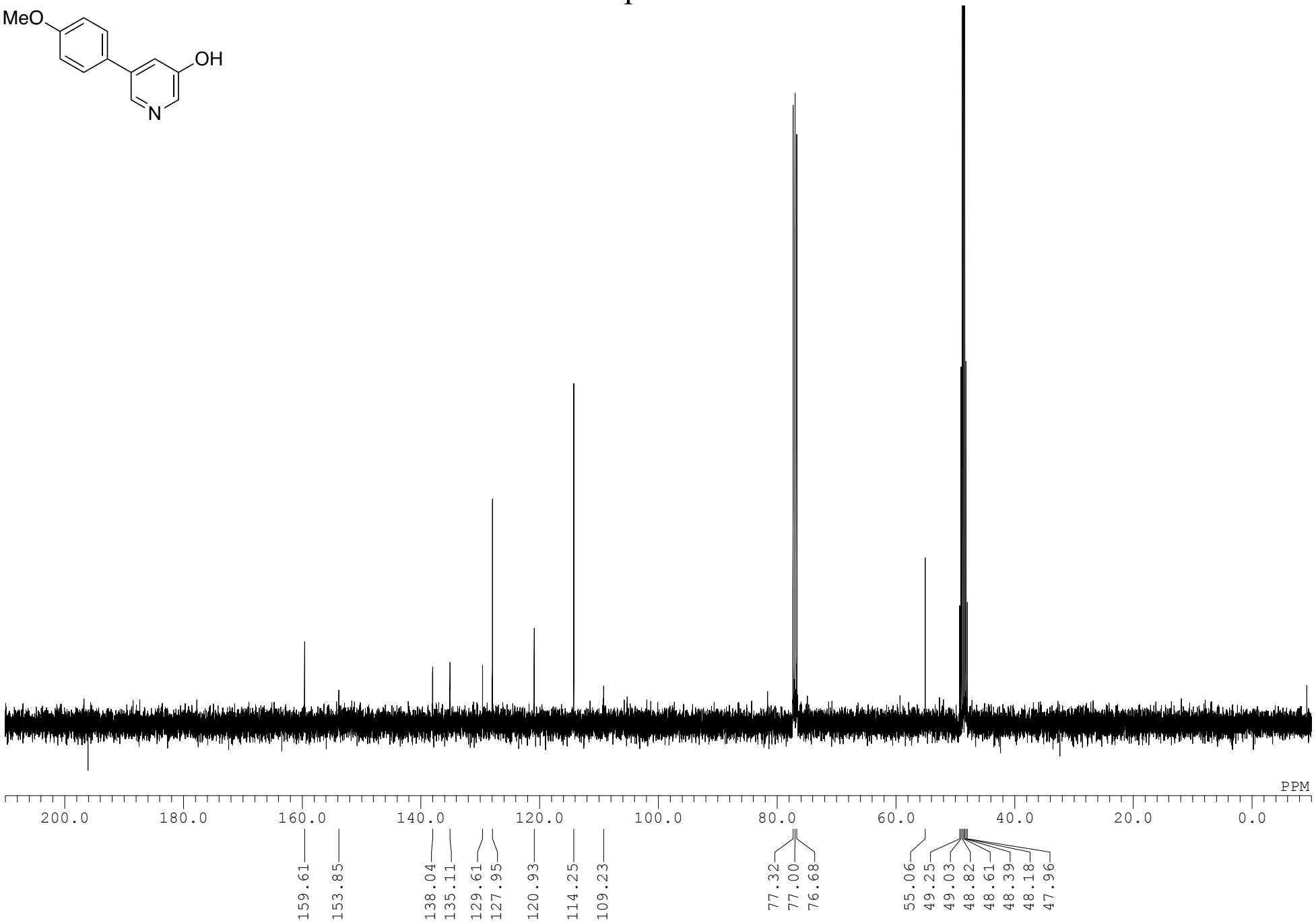




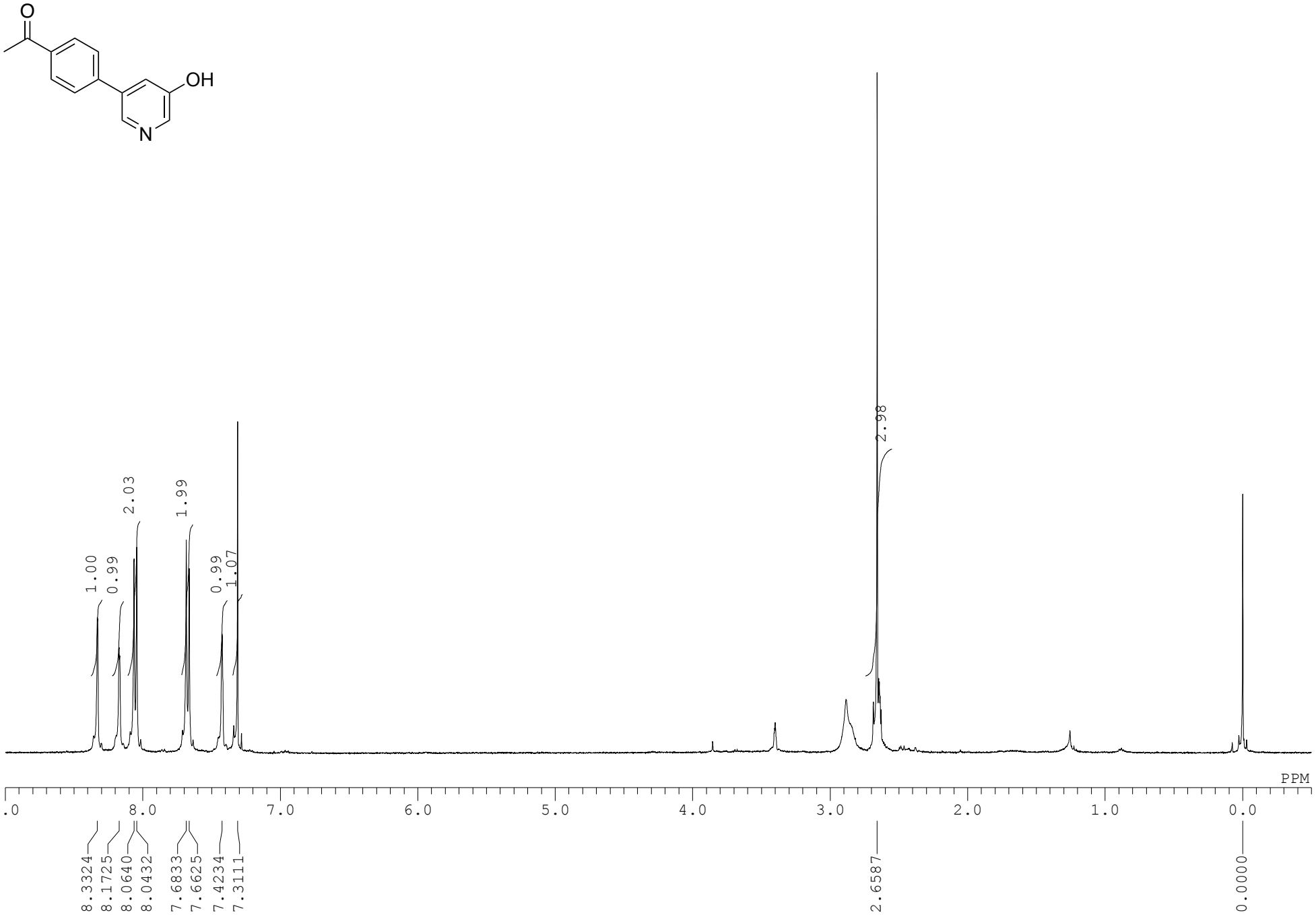
^{1}H NMR spectrum of **3aA**



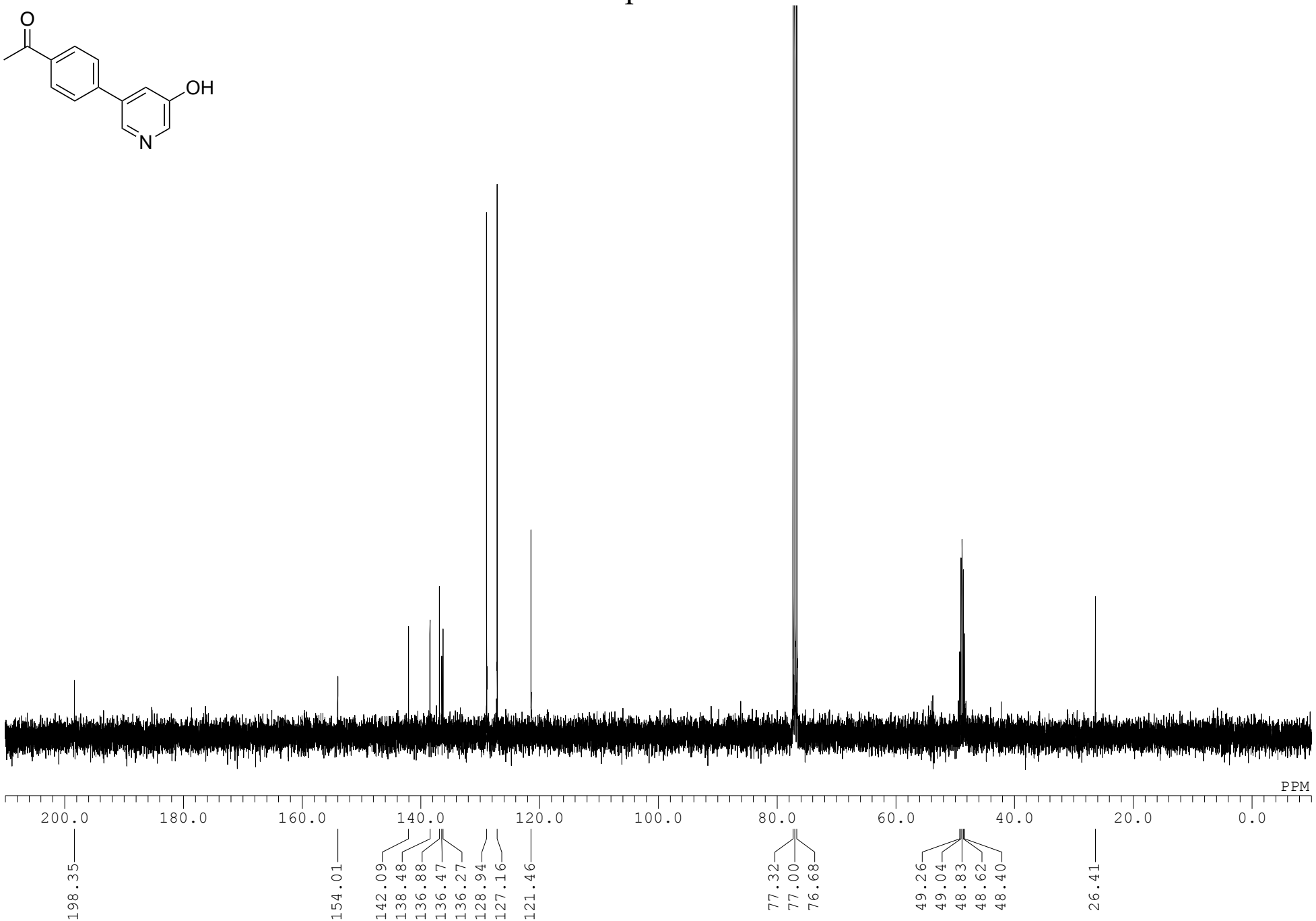
^{13}C NMR spectrum of **3aA**



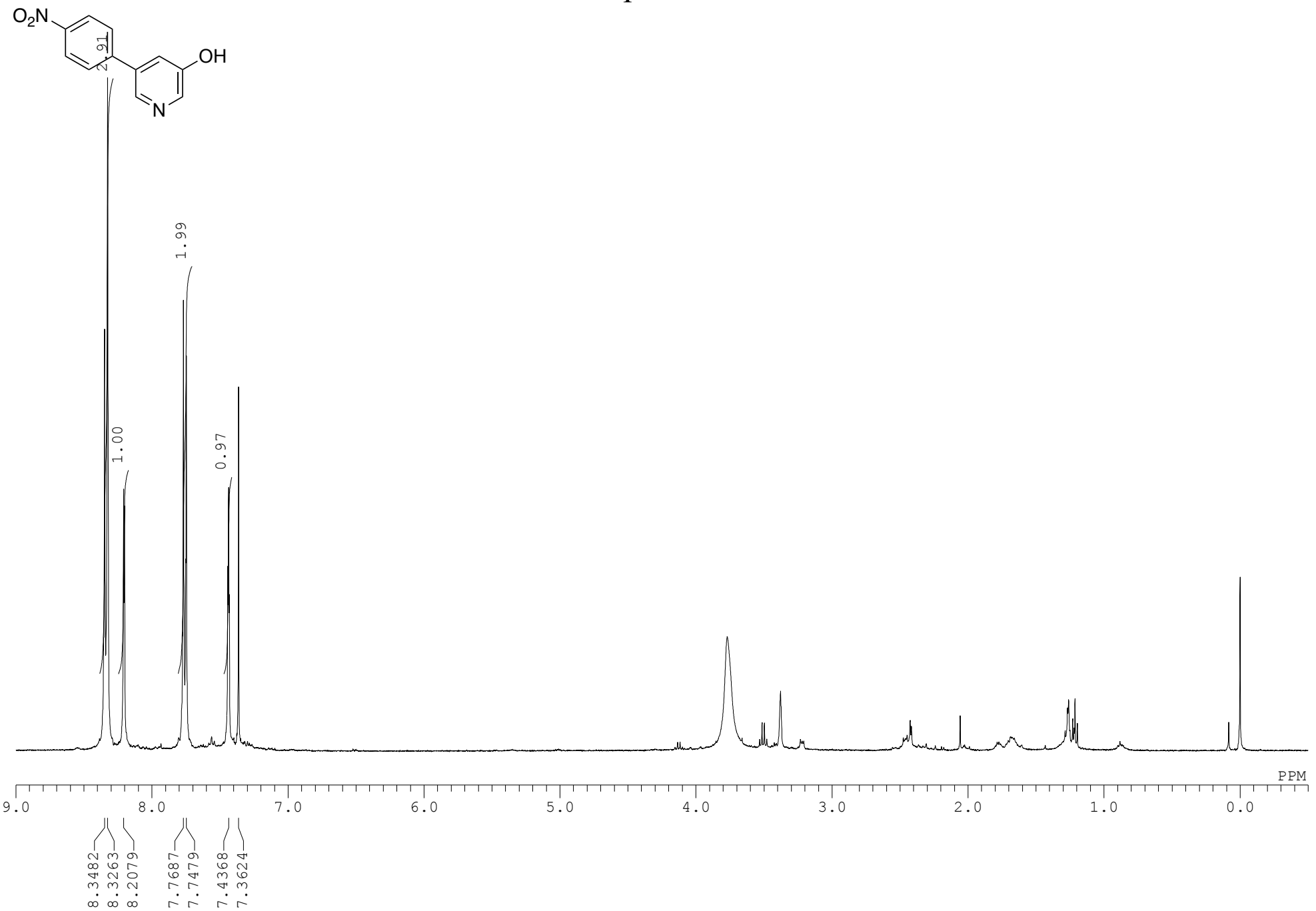
^{1}H NMR spectrum of **3aB**



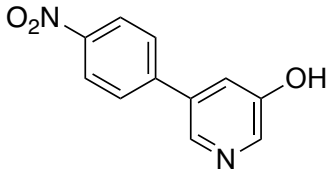
^{13}C NMR spectrum of **3aB**

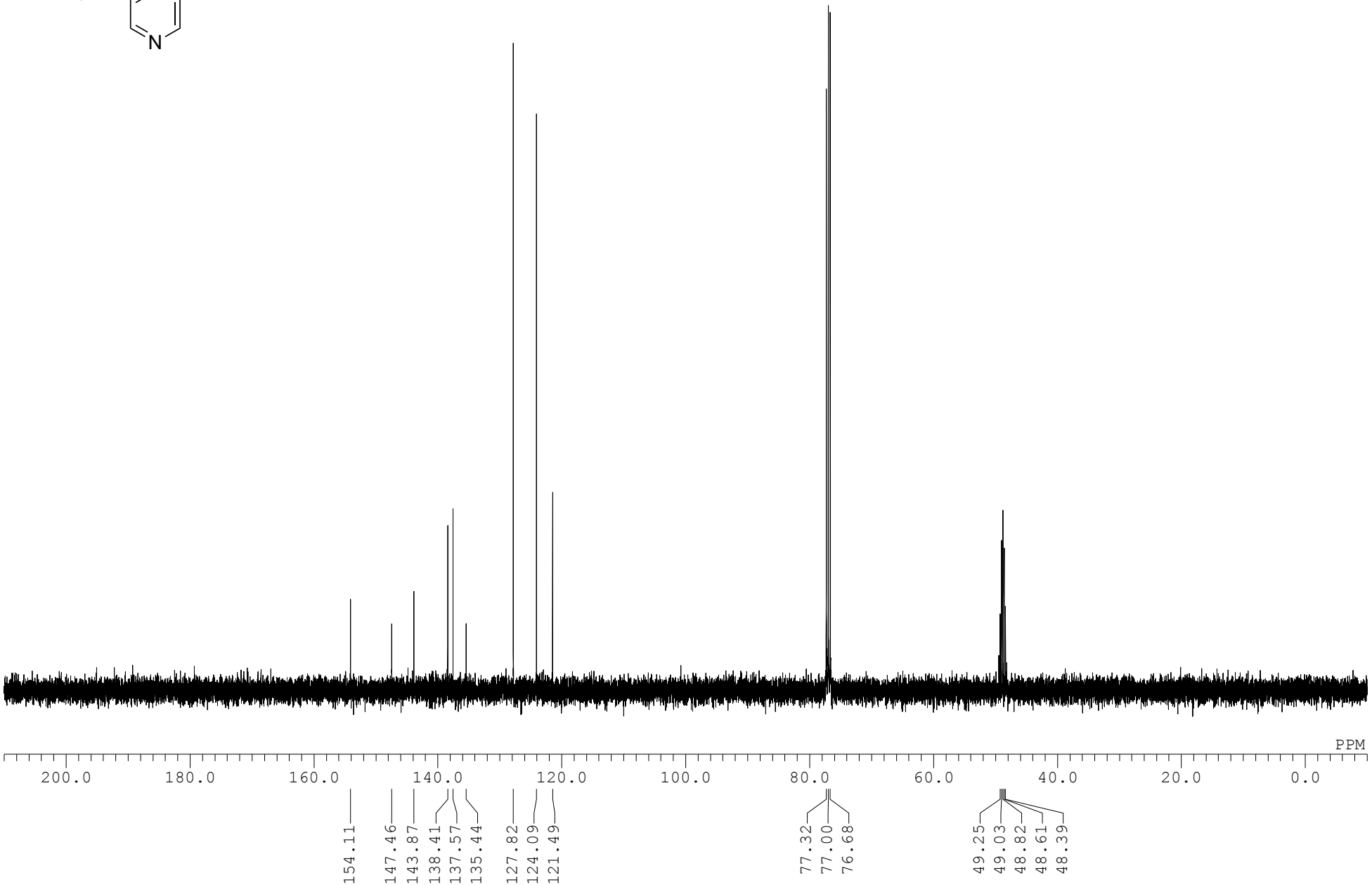


^{1}H NMR spectrum of **3aC**

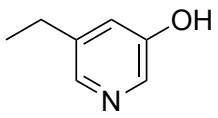


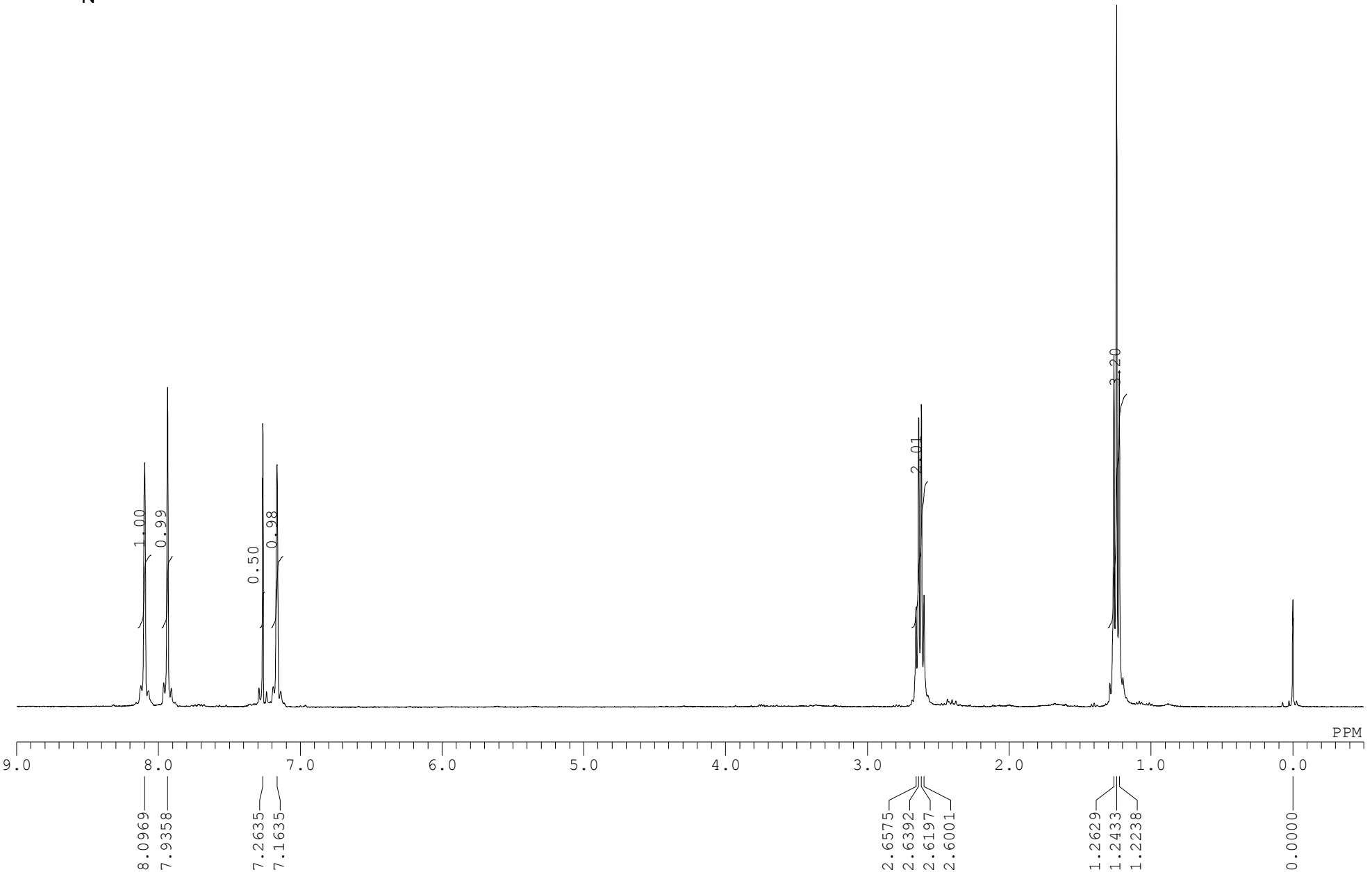
^{13}C NMR spectrum of **3aC**



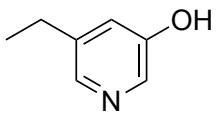


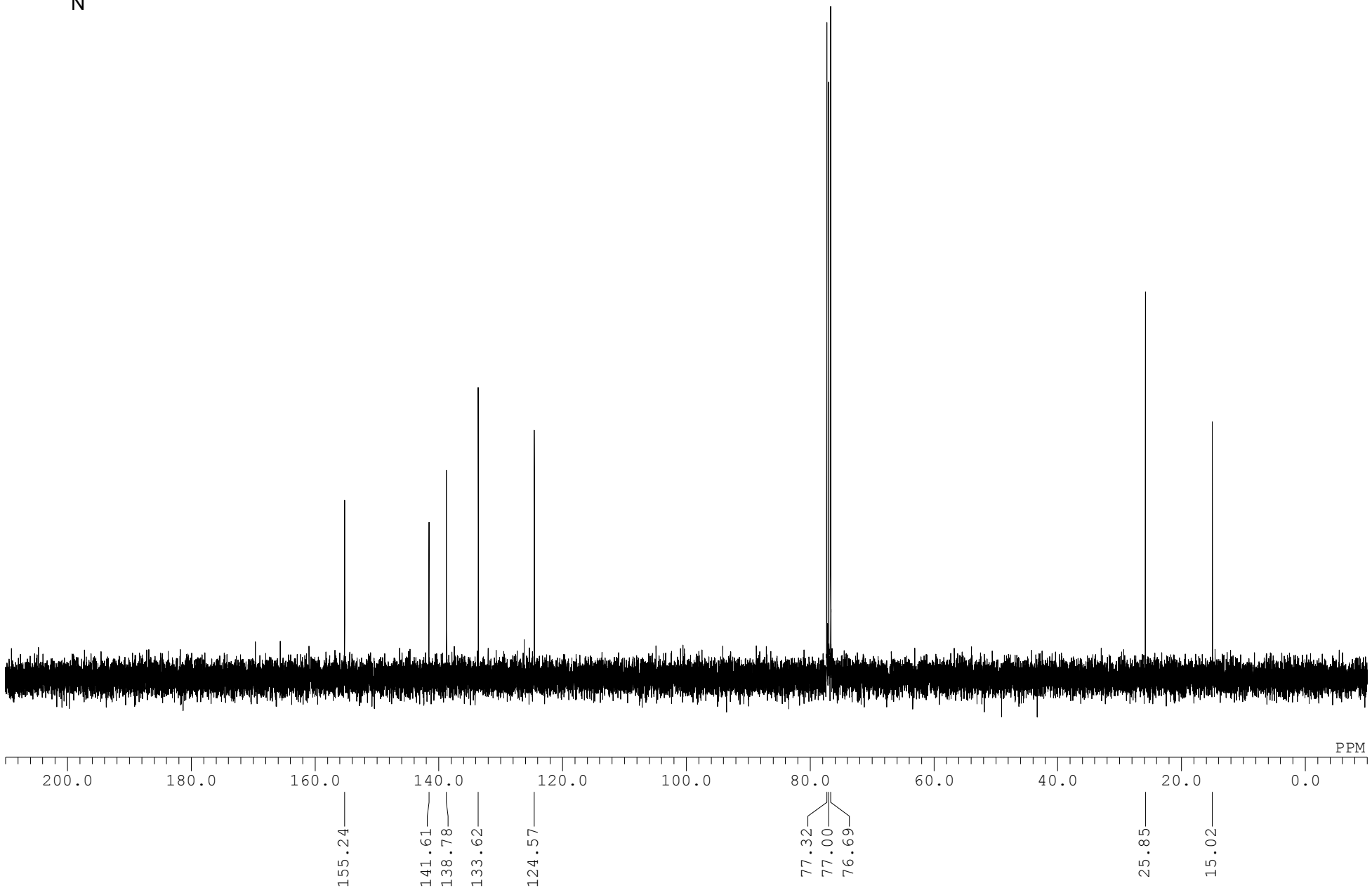
^{1}H NMR spectrum of **3aD**



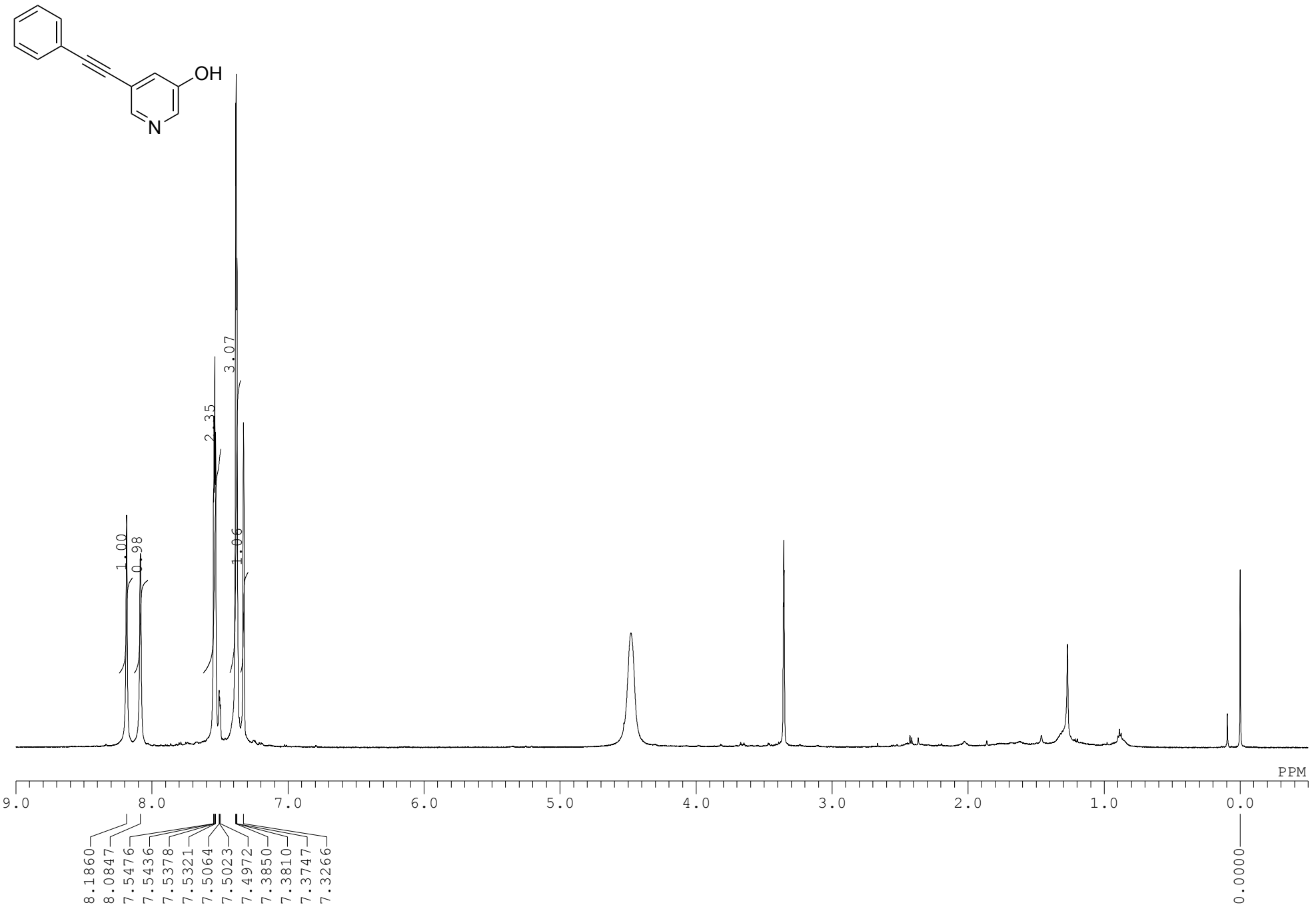


^{13}C NMR spectrum of **3aD**

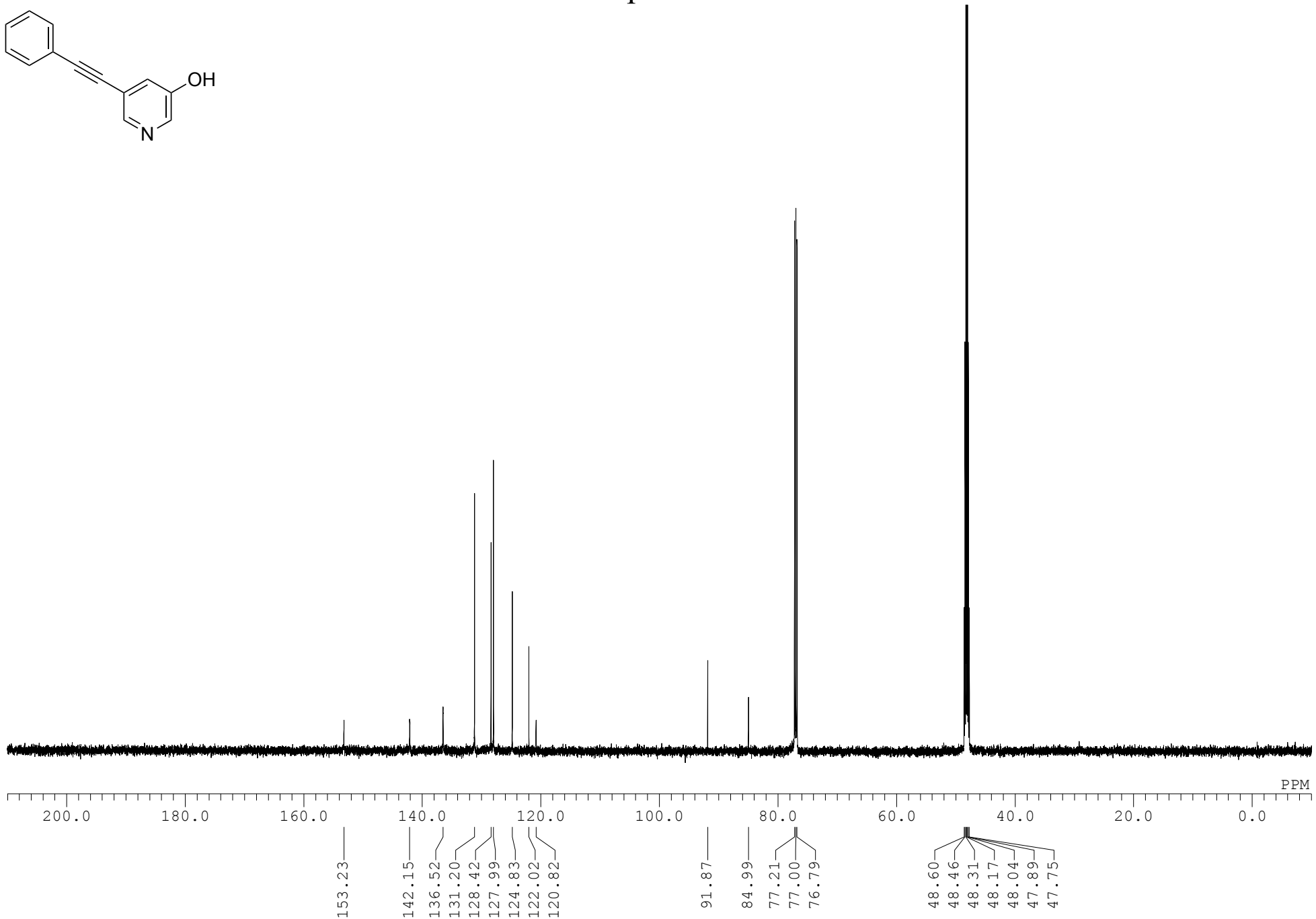




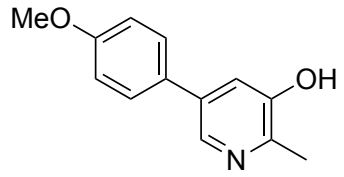
^{1}H NMR spectrum of **3eE**

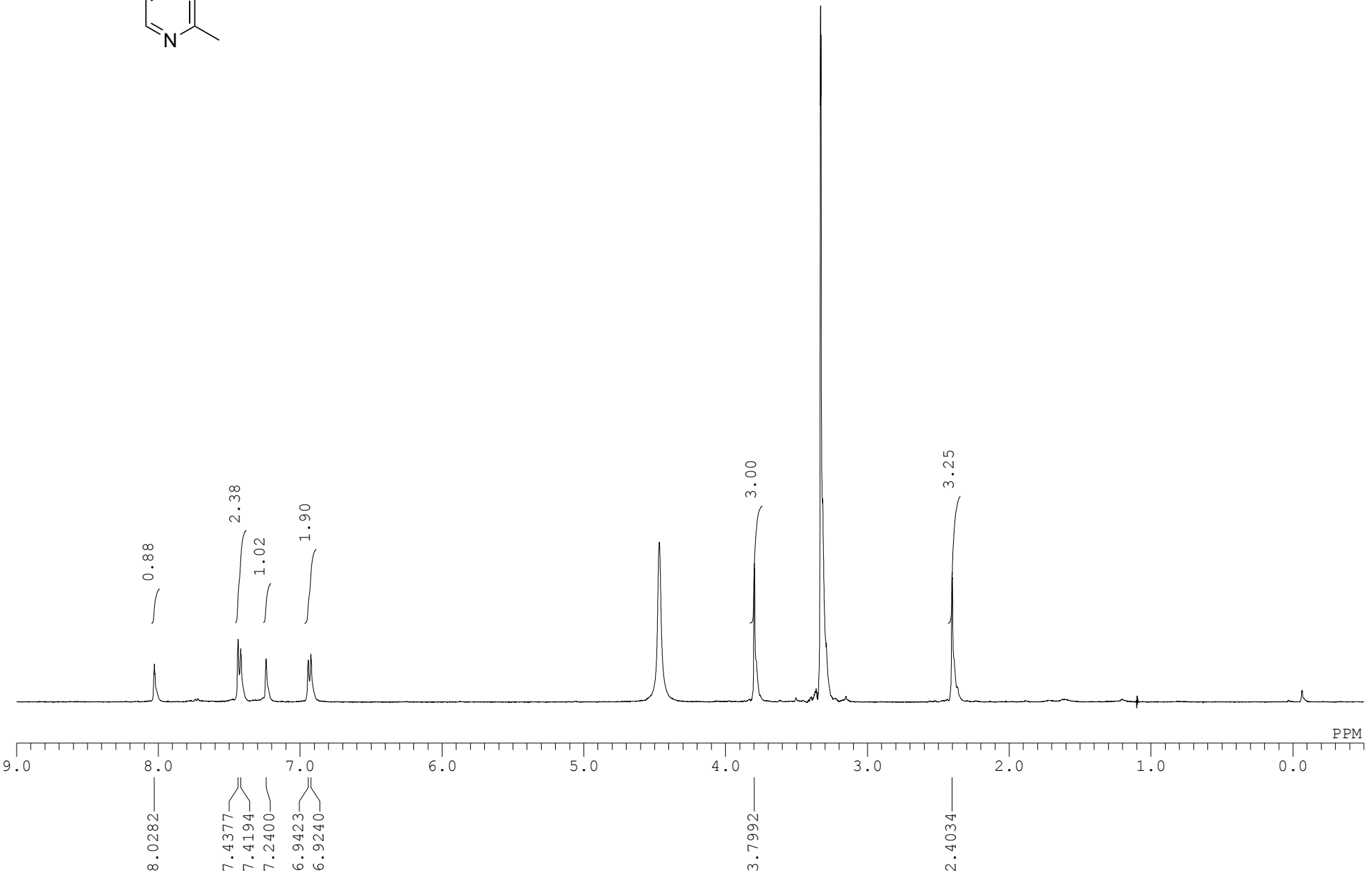


^{13}C NMR spectrum of **3eE**

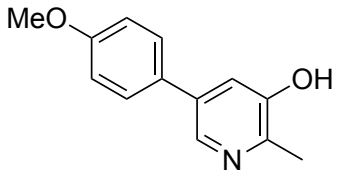


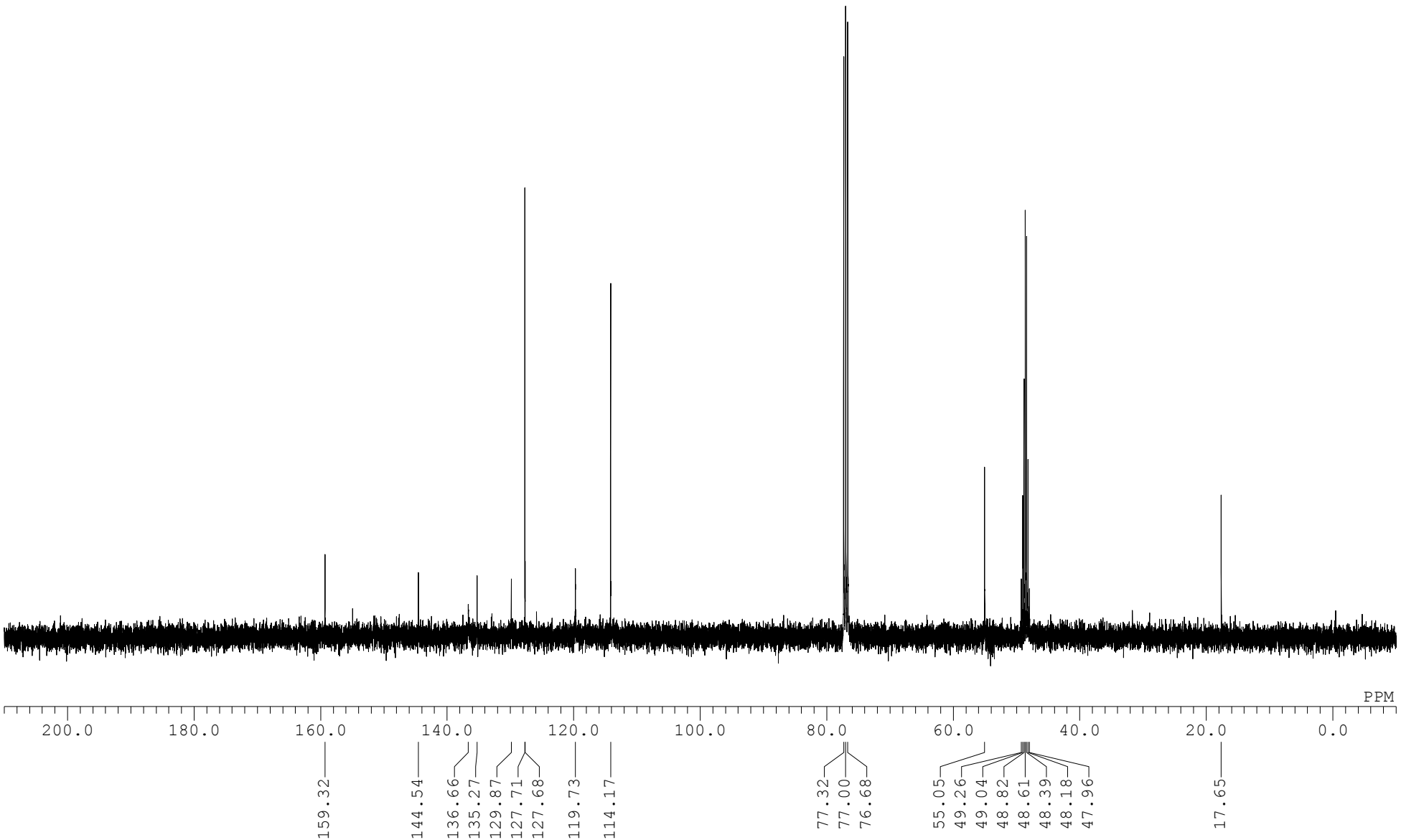
^{1}H NMR spectrum of **3bA**



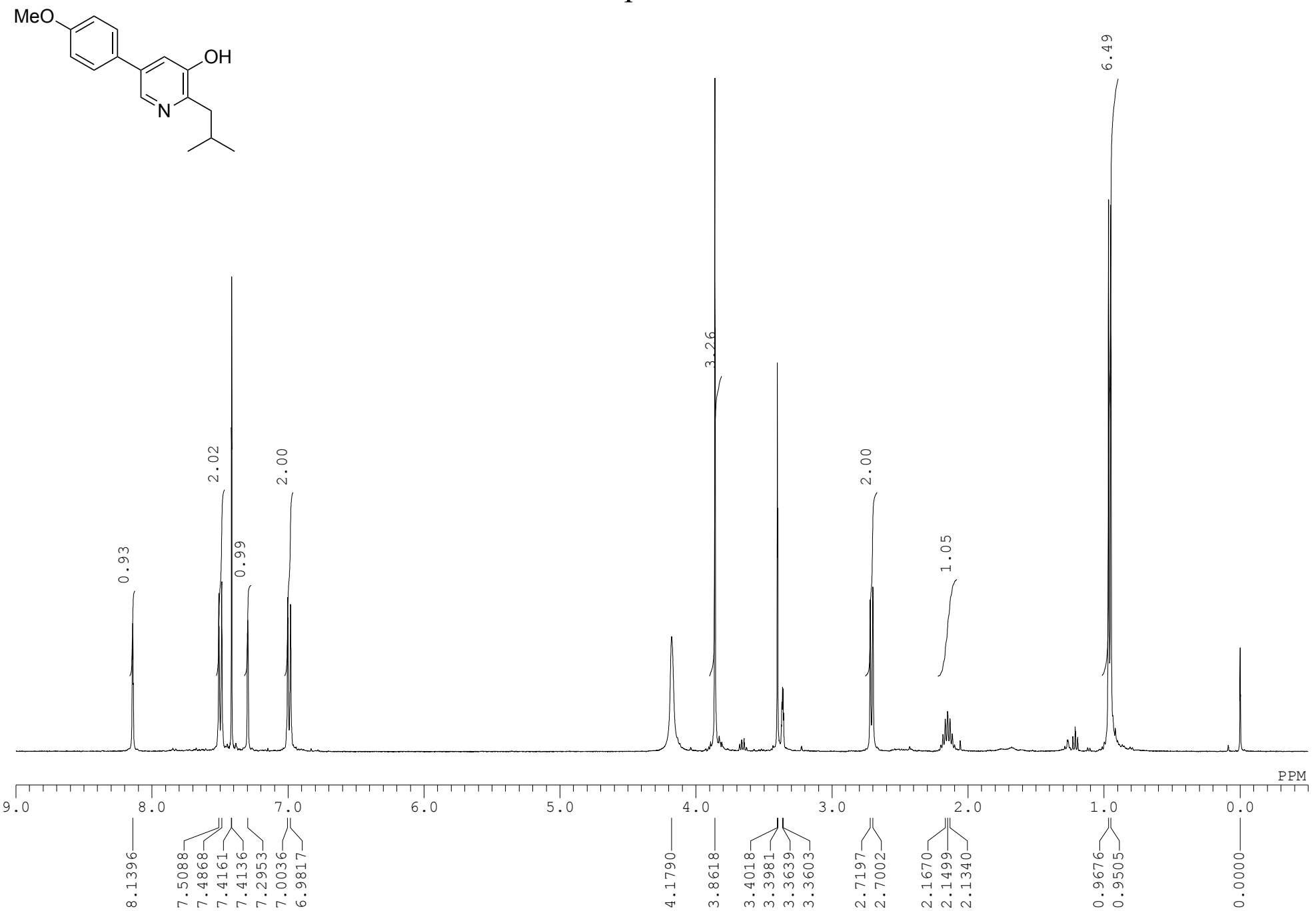


^{13}C NMR spectrum of **3bA**

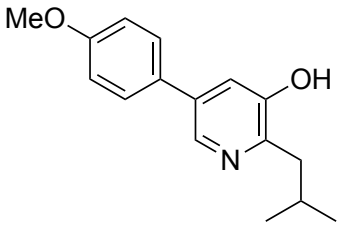




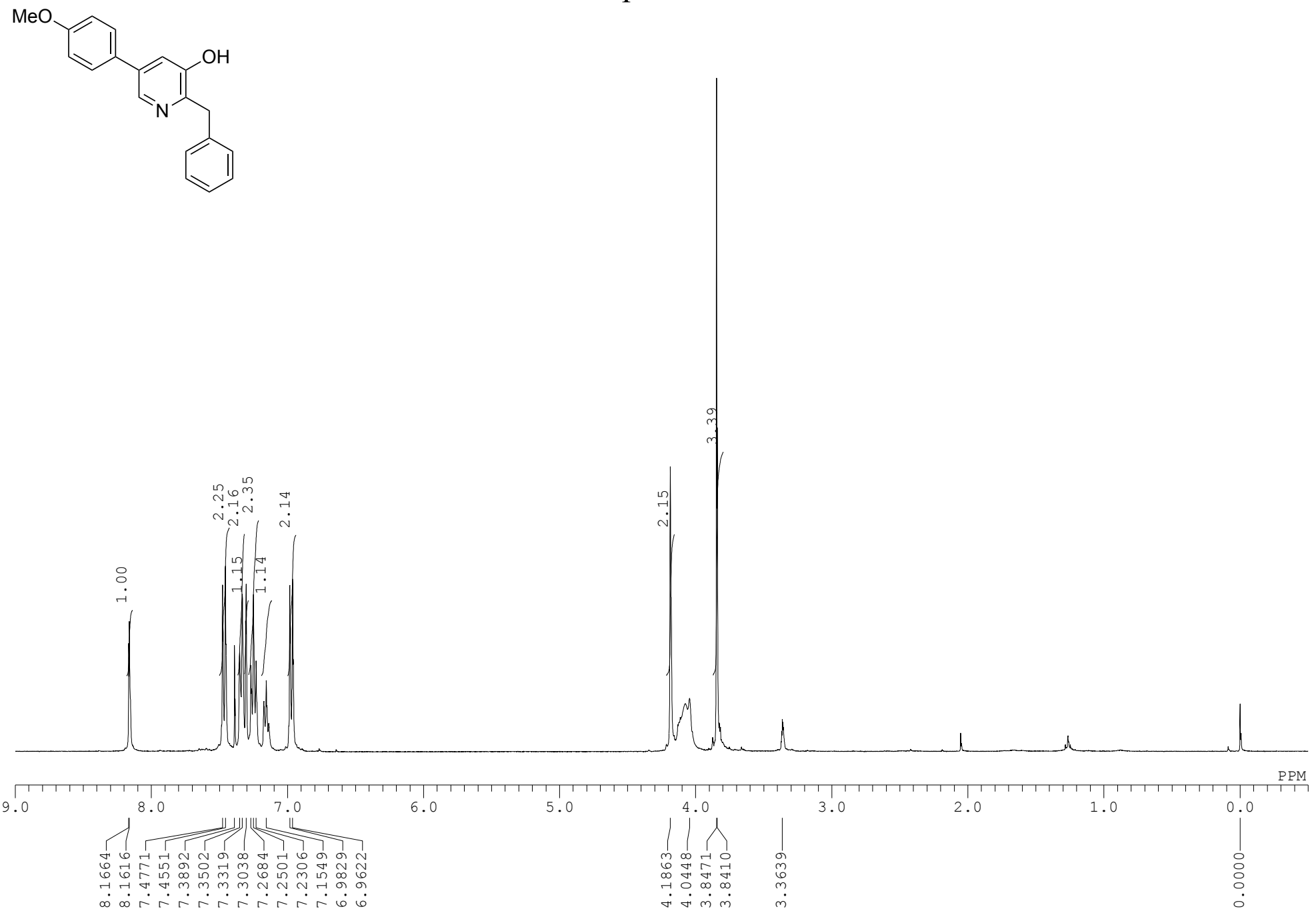
^{1}H NMR spectrum of **3cA**



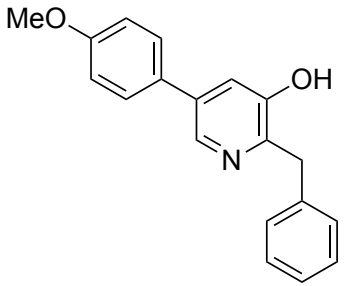
^{13}C NMR spectrum of **3cA**

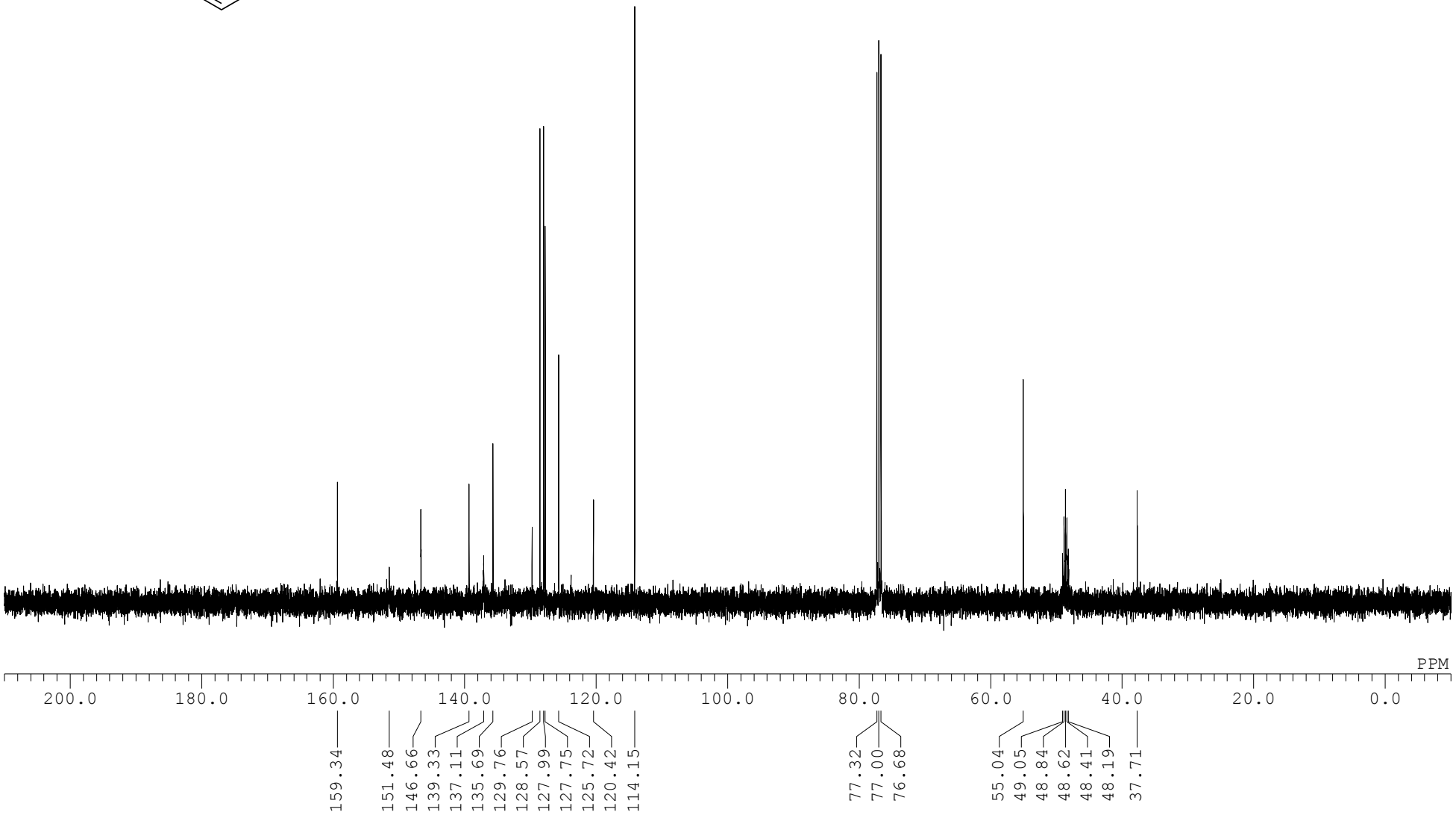


^{1}H NMR spectrum of **3dA**

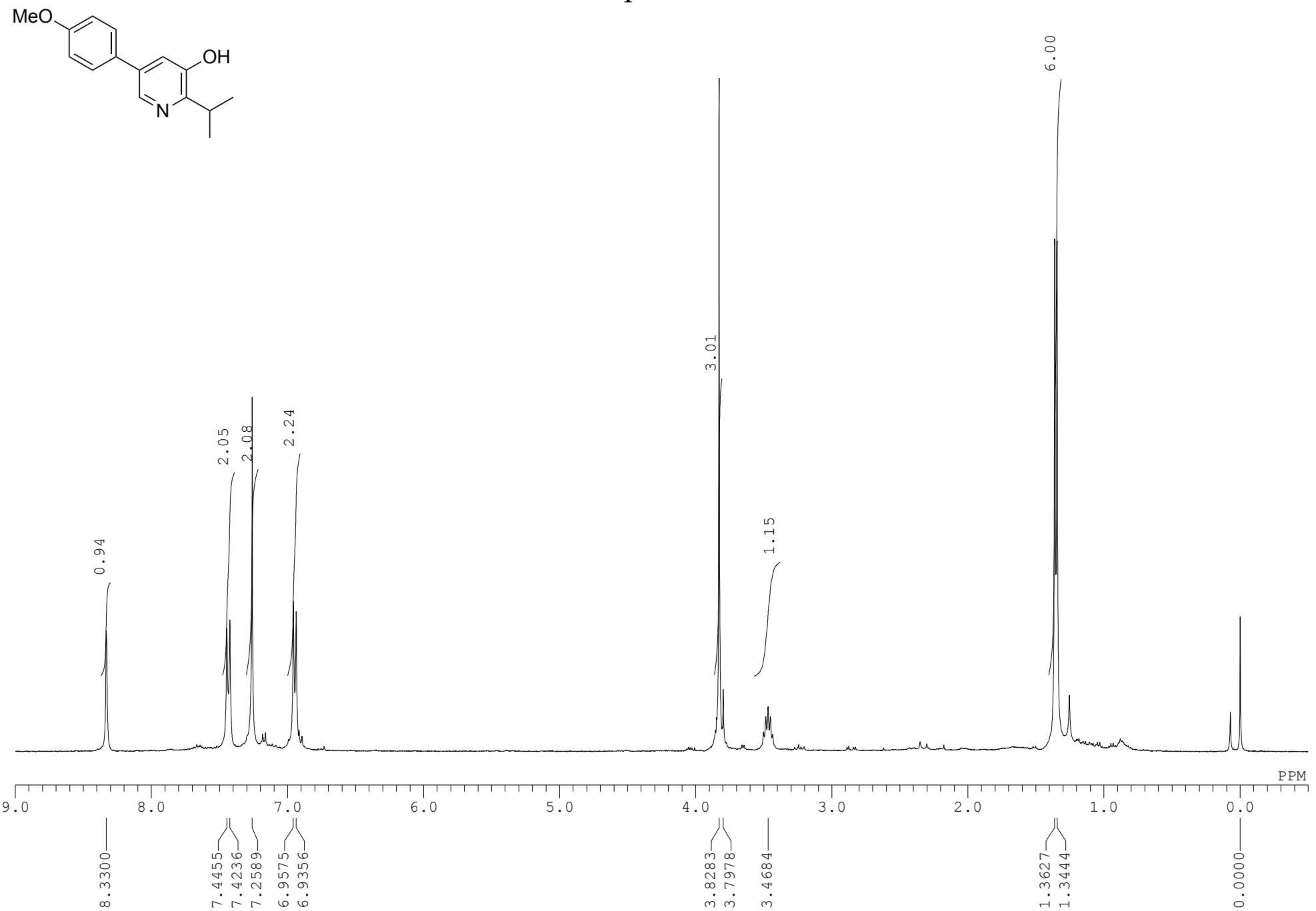


^{13}C NMR spectrum of **3dA**

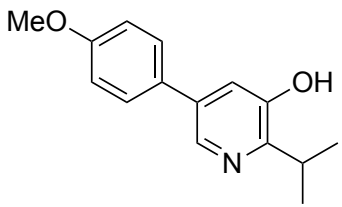




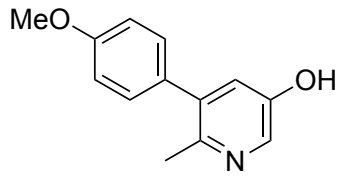
^{1}H NMR spectrum of **3eA**

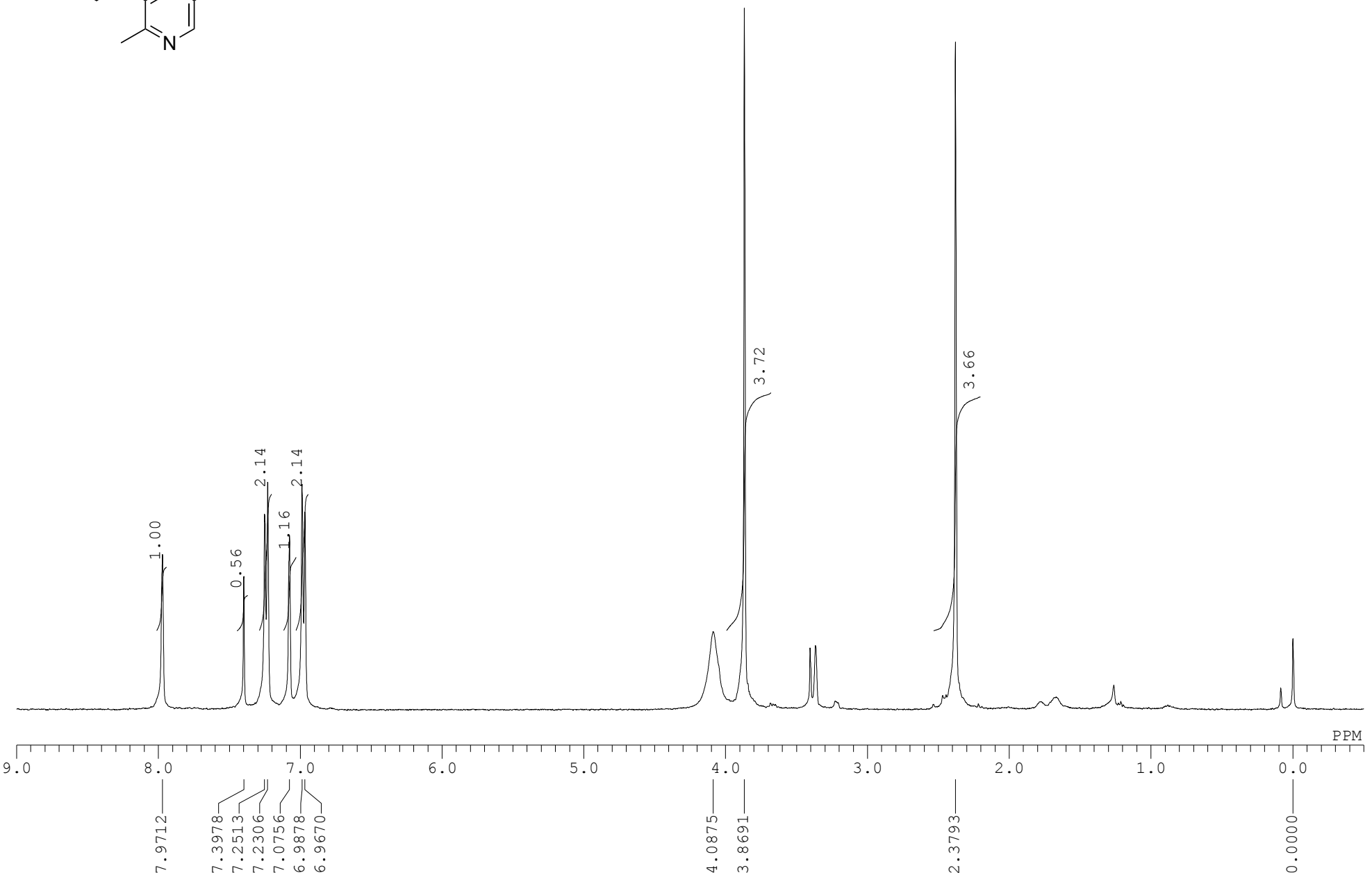


^{13}C NMR spectrum of **3eA**

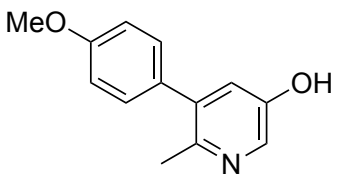


^{1}H NMR spectrum of **3fA**

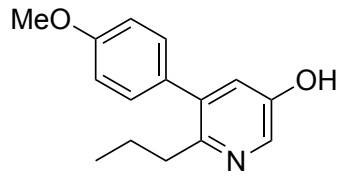


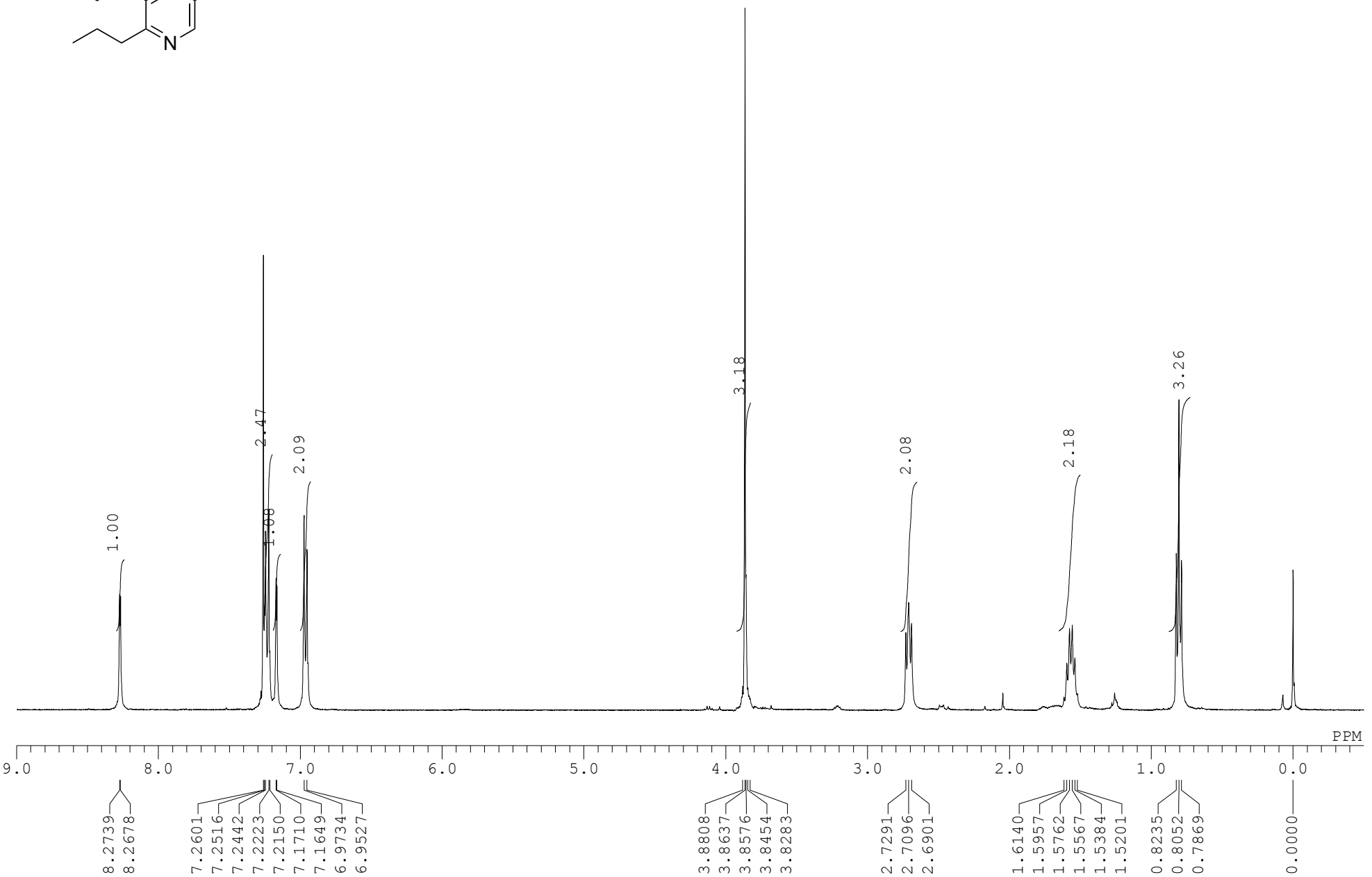


^{13}C NMR spectrum of **3fA**

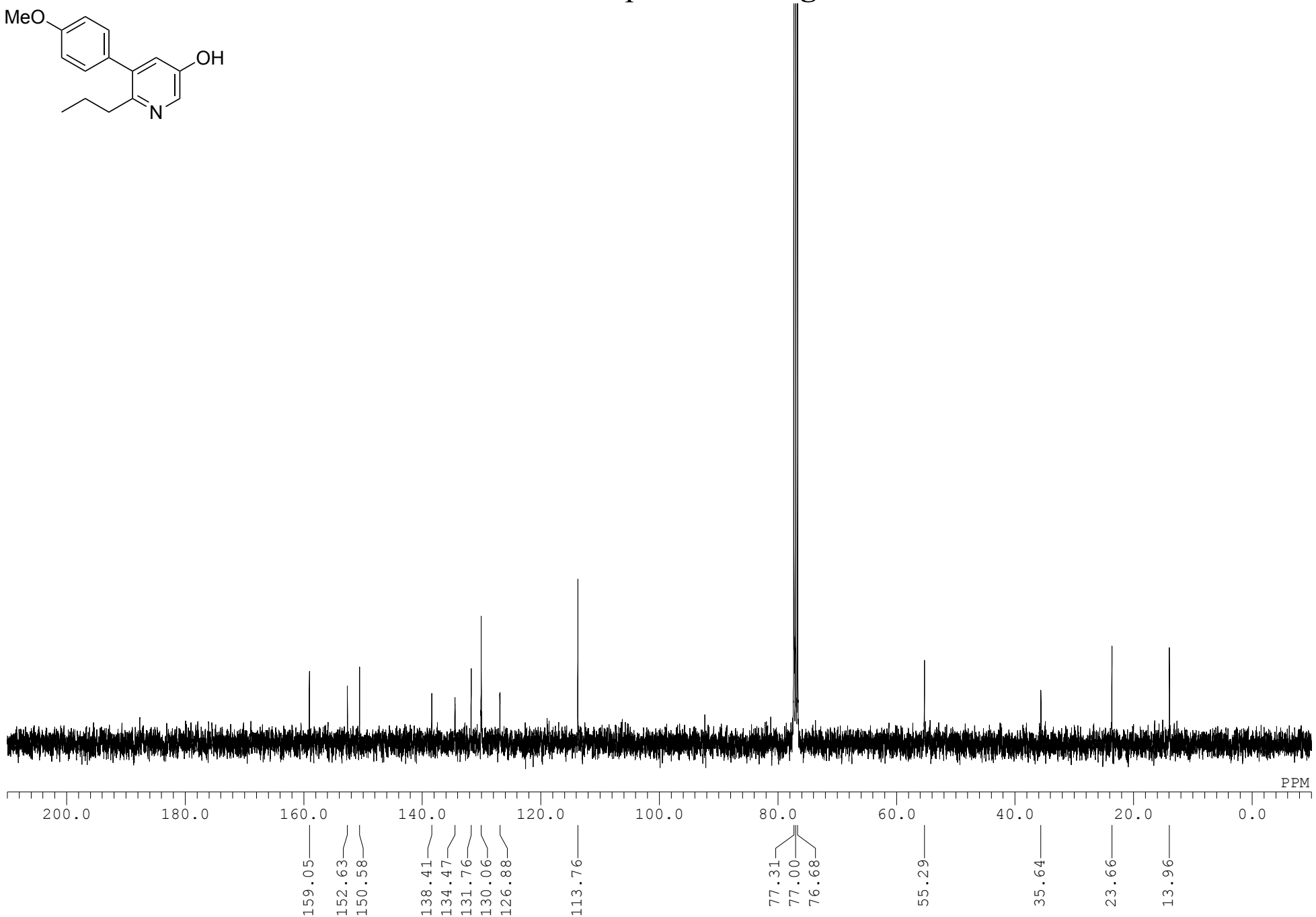


^{1}H NMR spectrum of **3gA**

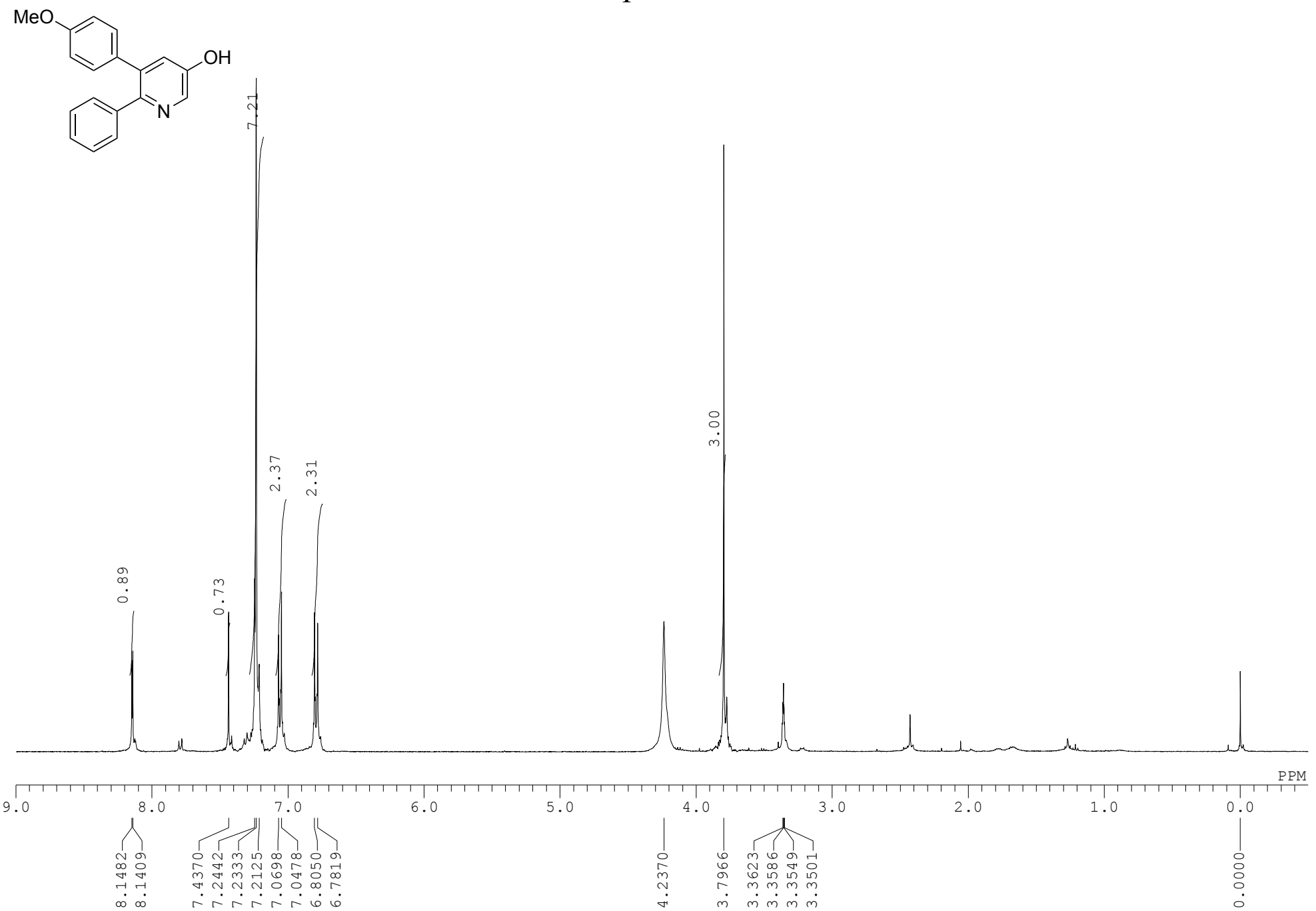




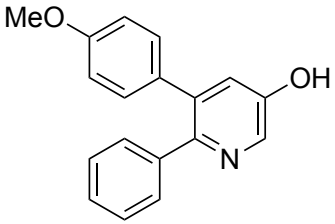
^{13}C NMR spectrum of **3gA**



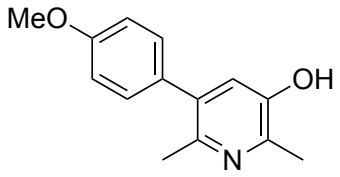
^{1}H NMR spectrum of **3hA**

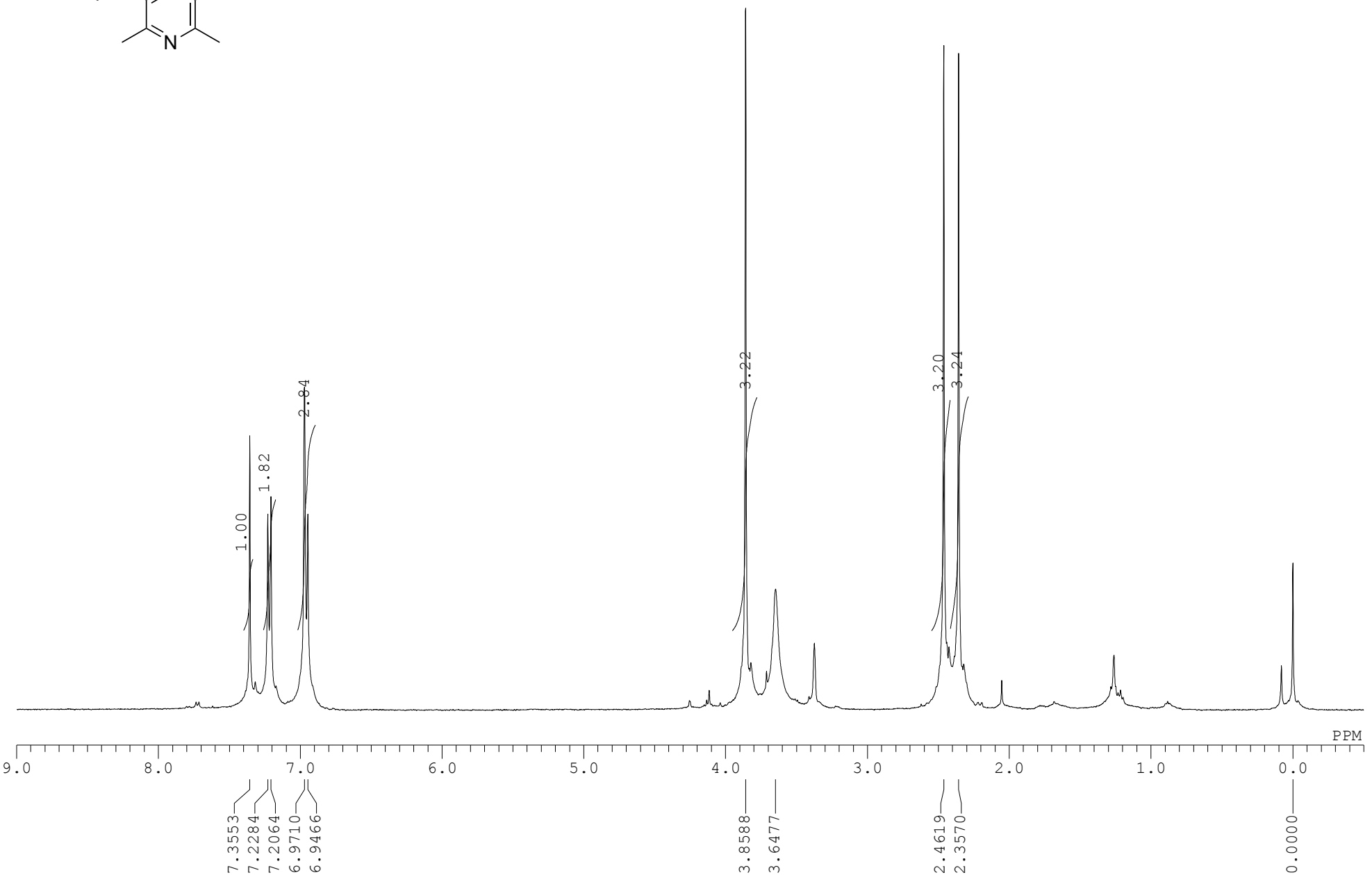


^{13}C NMR spectrum of **3hA**

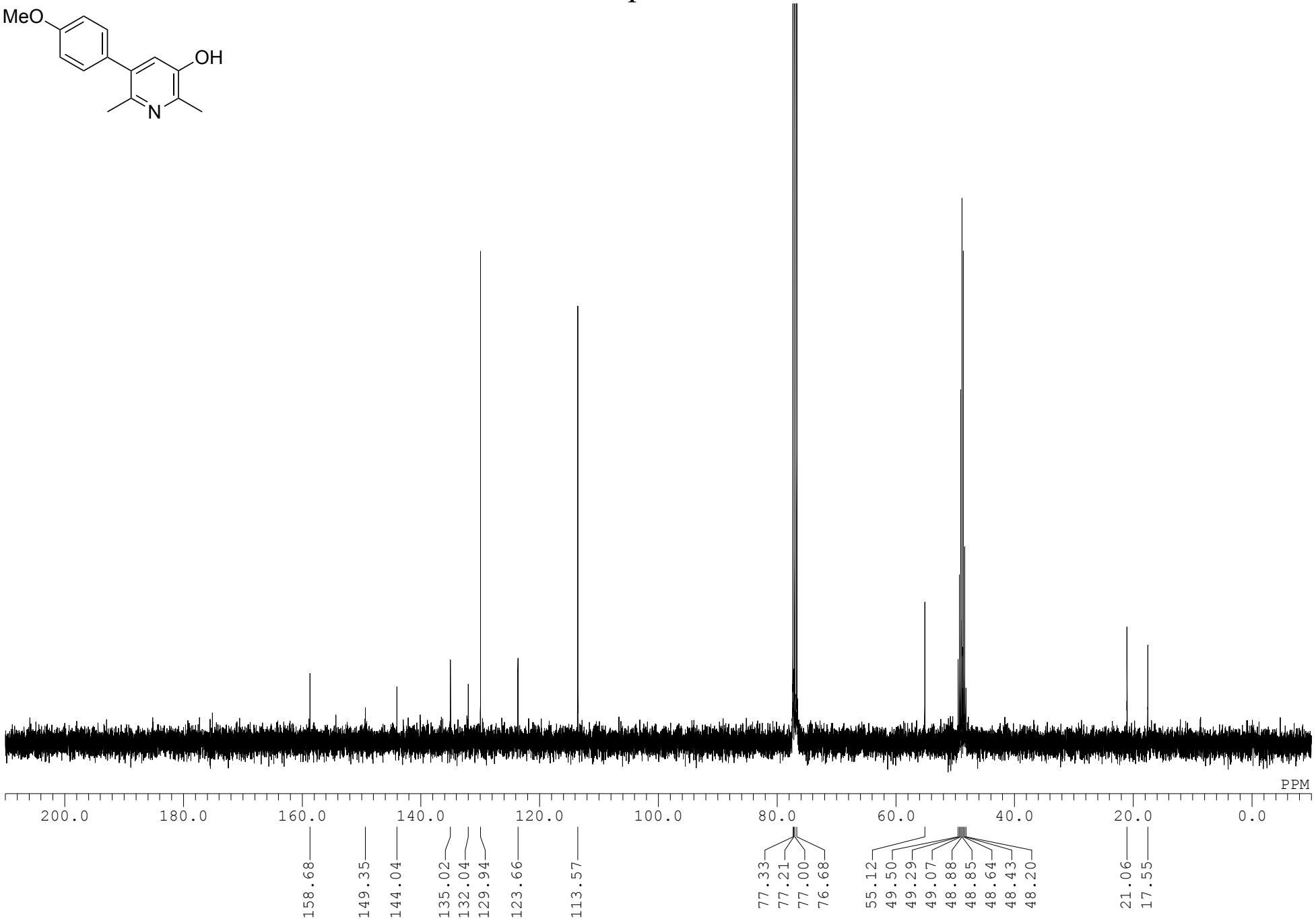


^{1}H NMR spectrum of **3iA**

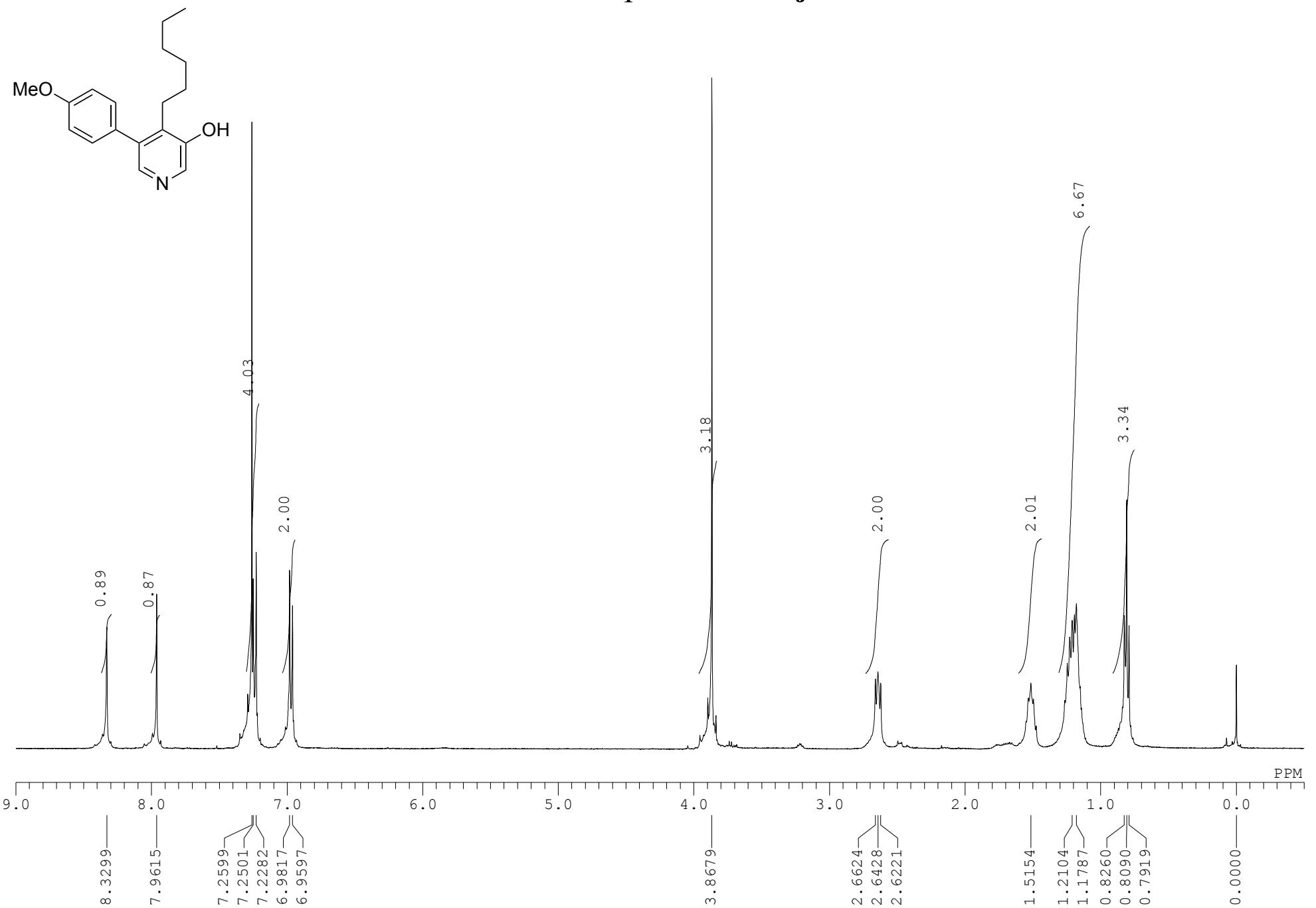




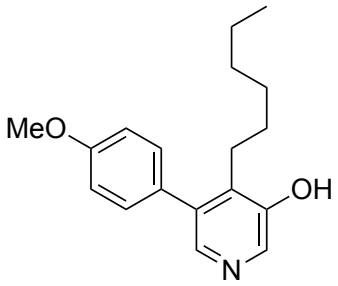
^{13}C NMR spectrum of **3iA**

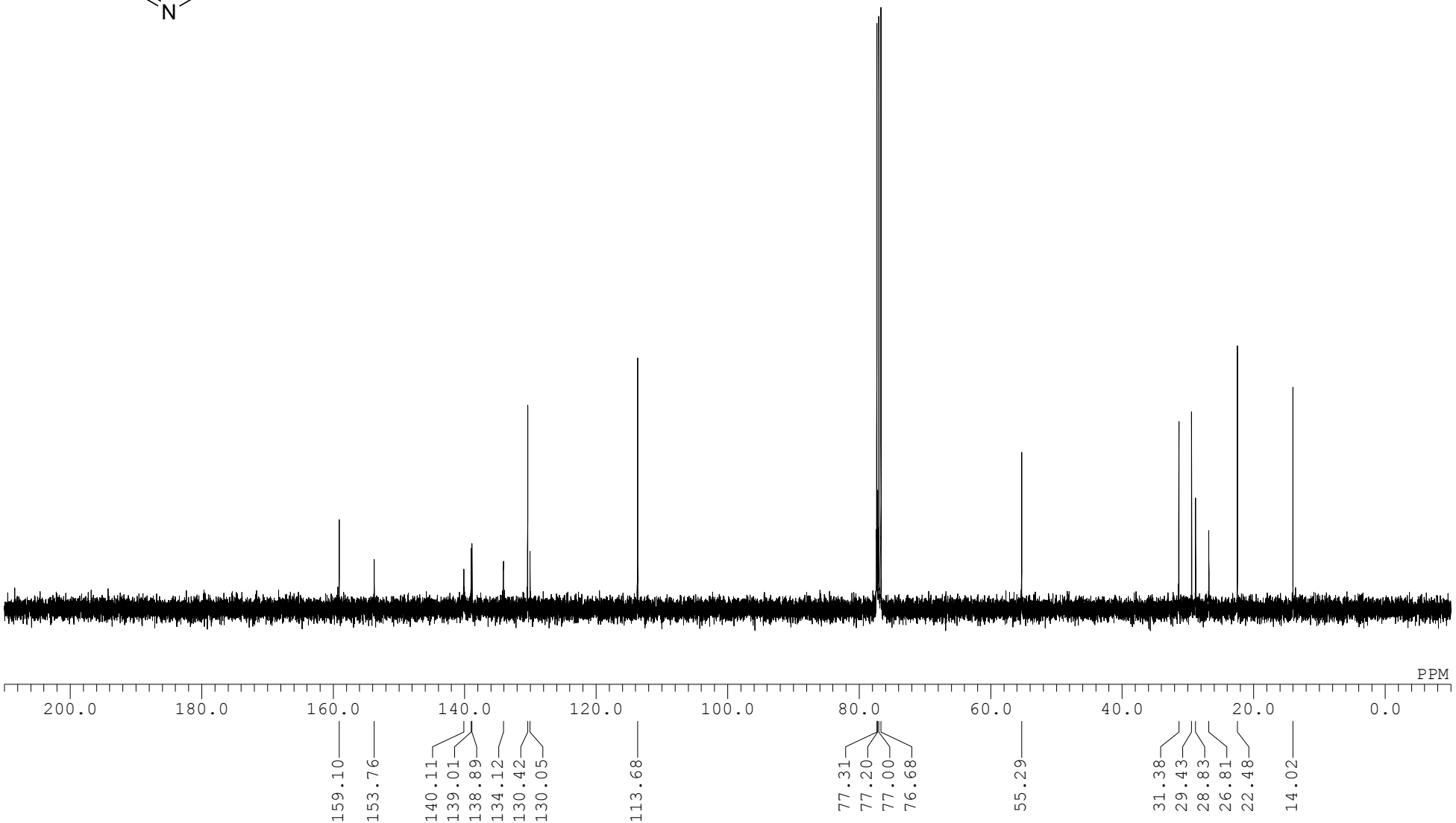


^{1}H NMR spectrum of **3jA**

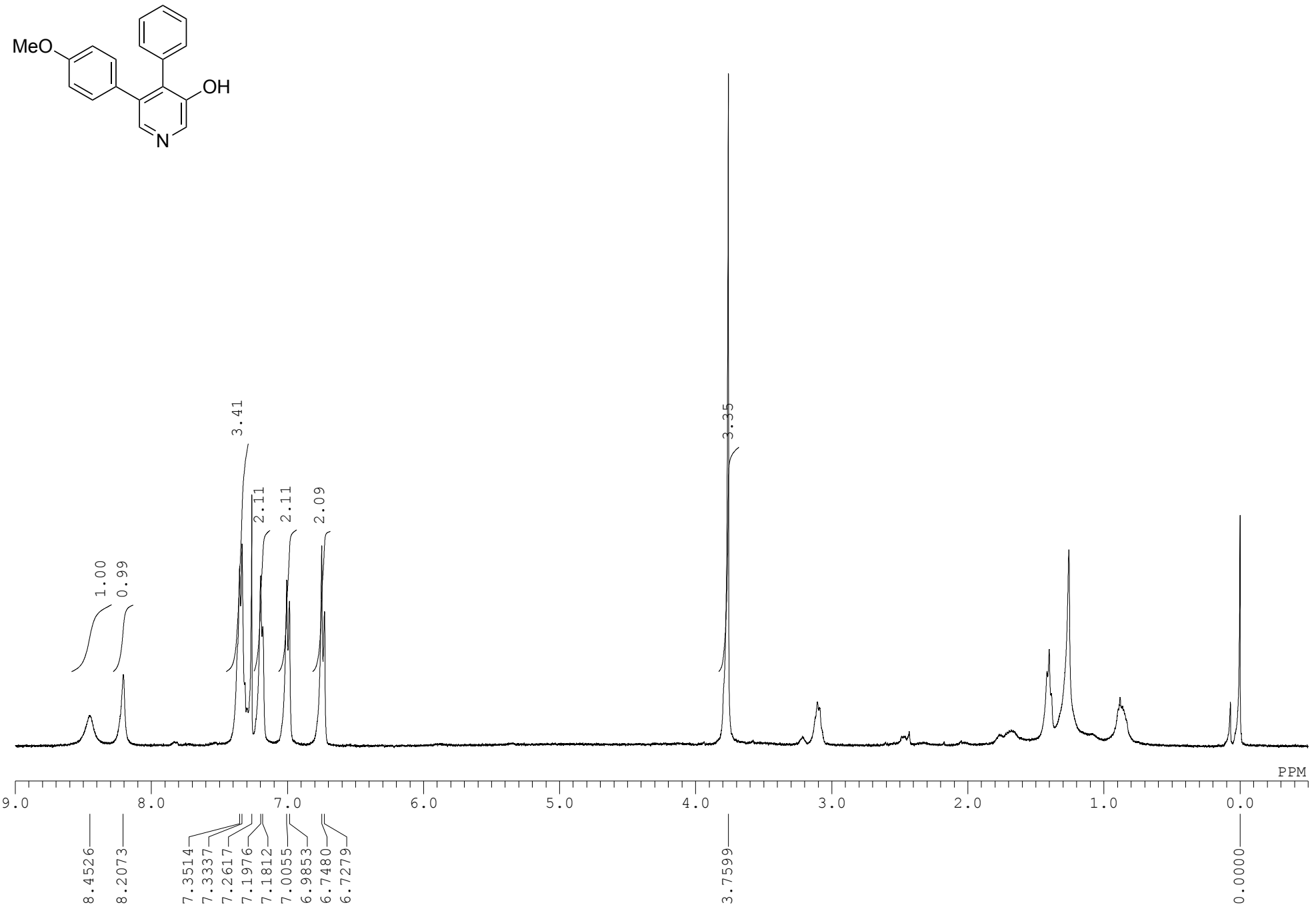


^{13}C NMR spectrum of **3jA**

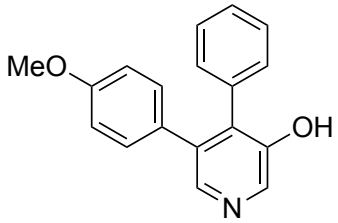


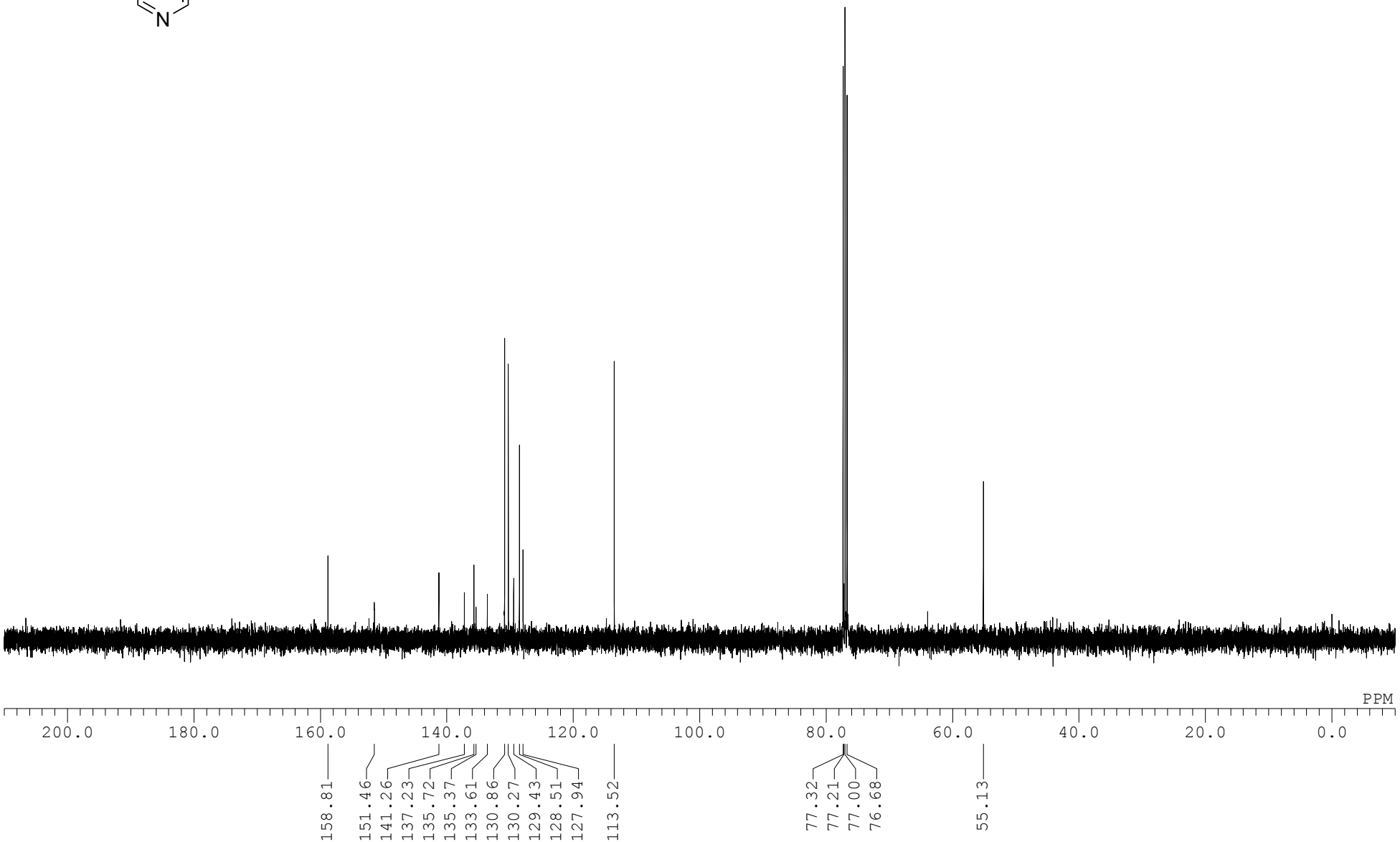


^{1}H NMR spectrum of **3kA**

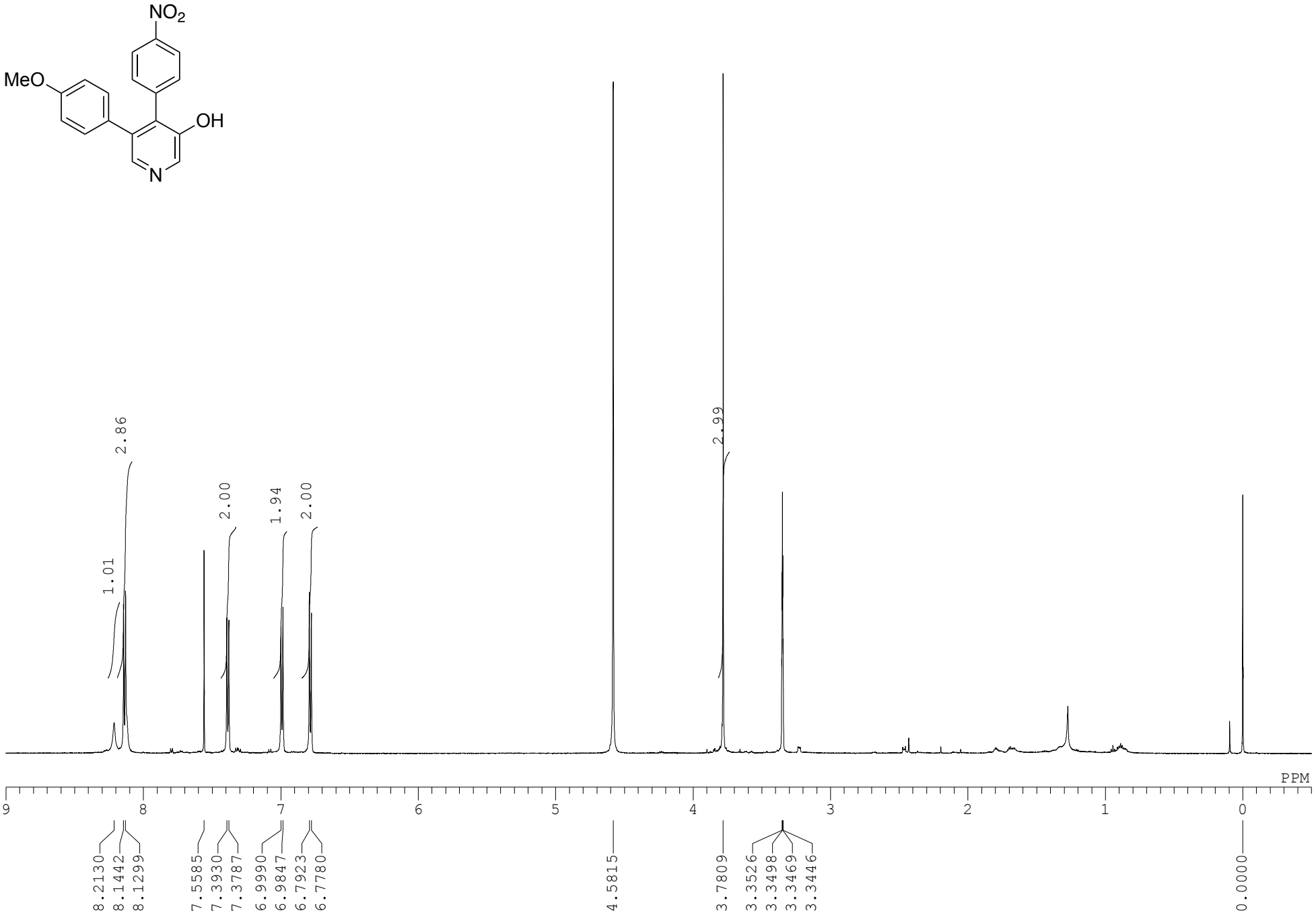


^{13}C NMR spectrum of **3kA**

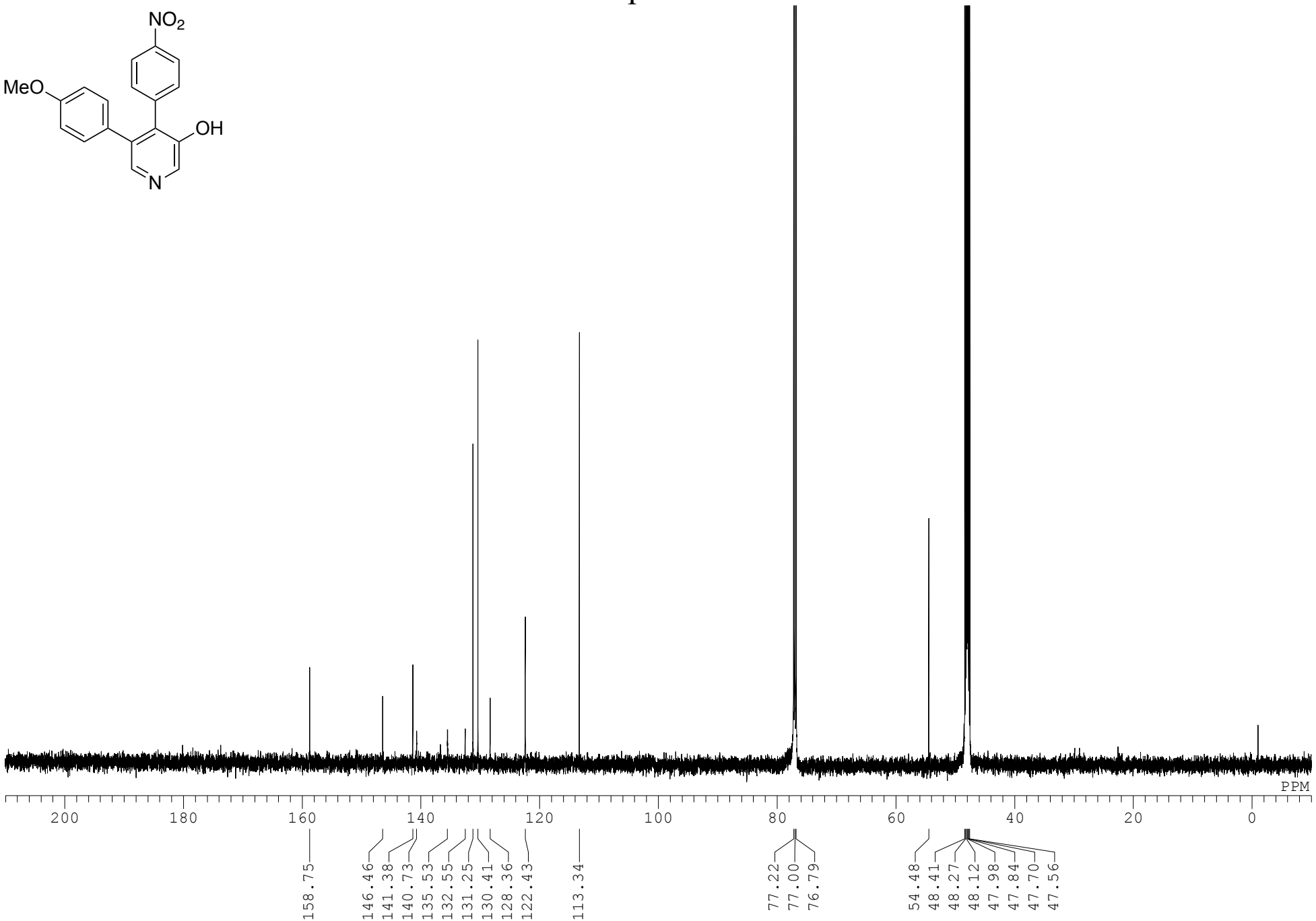




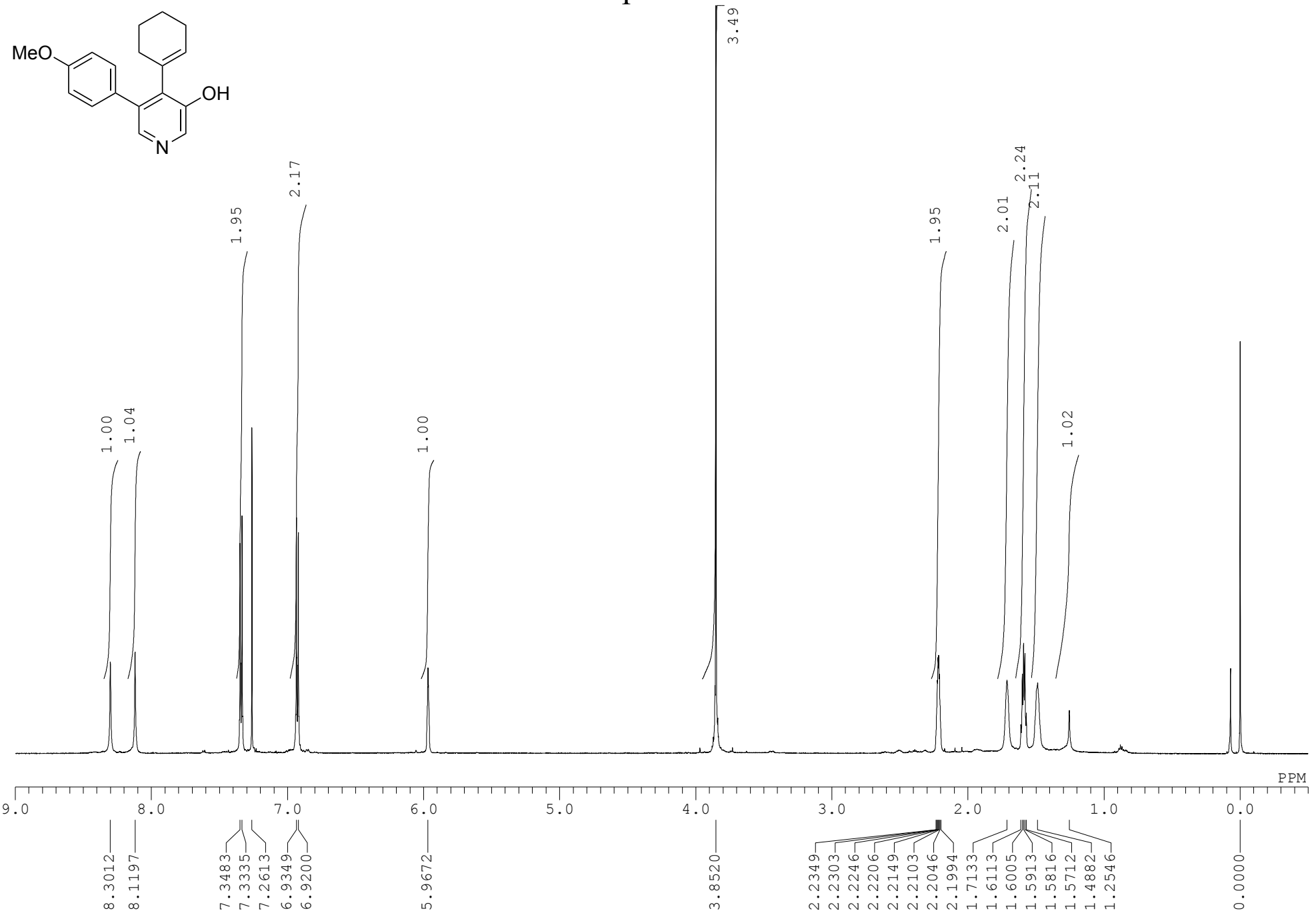
^{1}H NMR spectrum of **3lA**



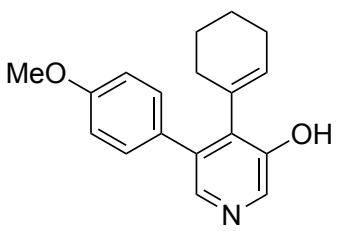
^{13}C NMR spectrum of **3lA**



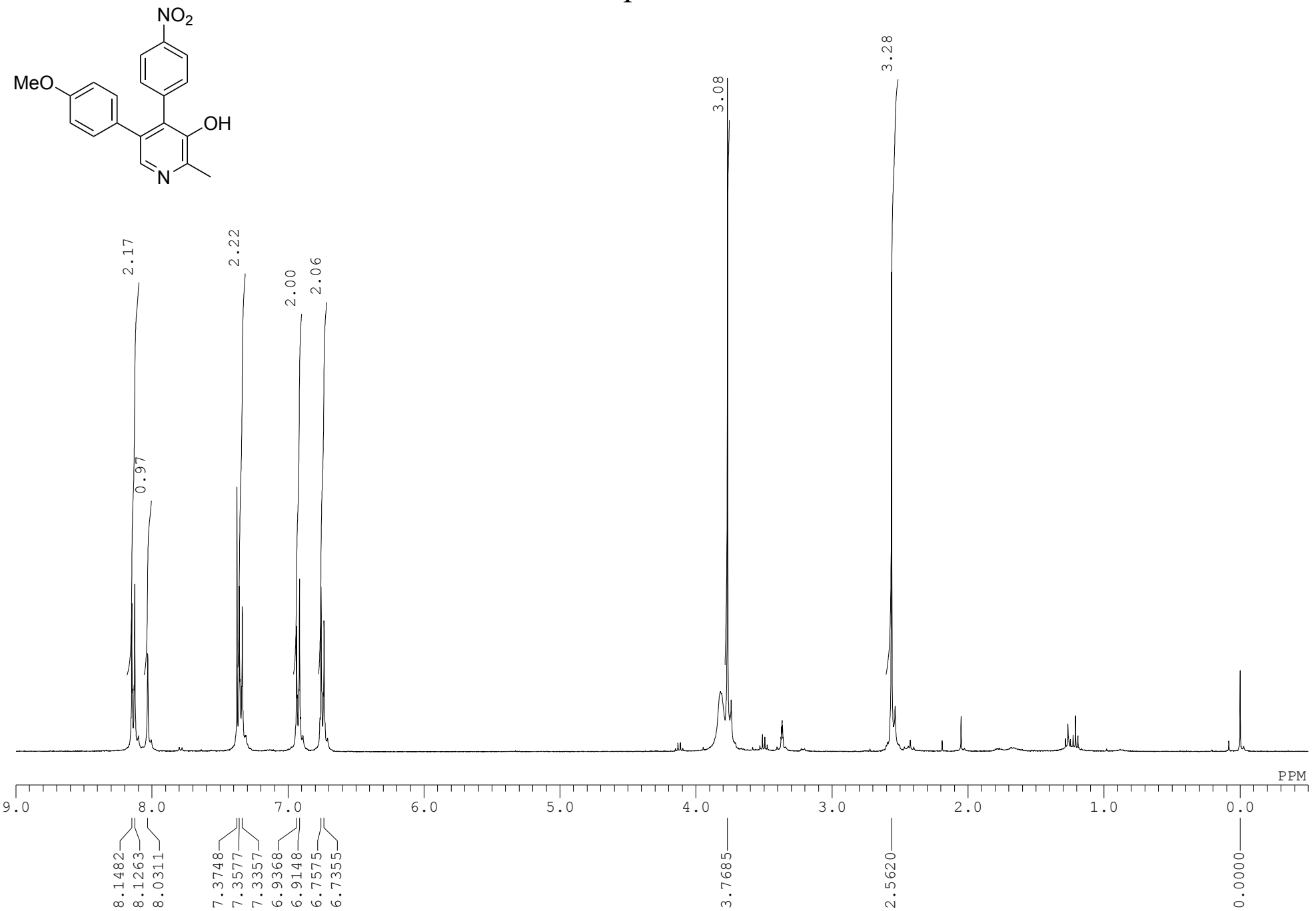
^{1}H NMR spectrum of **3nA**



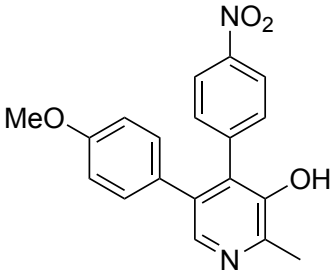
^{13}C NMR spectrum of **3nA**



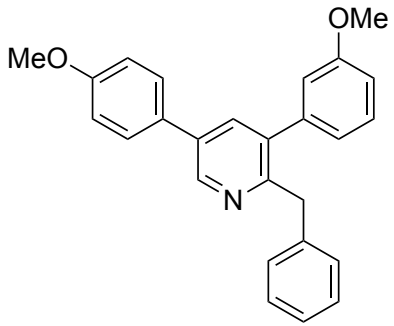
^{1}H NMR spectrum of **3oA**



^{13}C NMR spectrum of **3oA**



^{1}H NMR spectrum of **10**



^{13}C NMR spectrum of **10**